

Supporting Information

Brønsted acid promoted substrate-dependent regiodivergent alkynylcyclopropane-cyclopentadiene rearrangement assisted by the internal carbonyl group

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1. General information

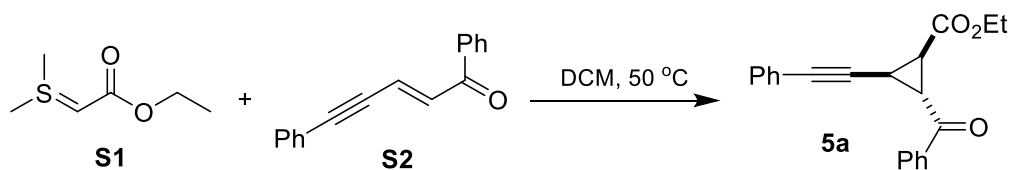
All reactions were carried out under dry argon atmosphere. All solvents and reagents were obtained from commercial sources and were purified according to standard procedures. All glassware was oven-dried before use.

NMR spectra were recorded on a Bruker 500 MHz (^1H : 500 MHz, $^{13}\text{C}\{^1\text{H}\}$: 125 MHz and ^{19}F : 470 MHz) or Bruker 600 MHz (^1H : 600 MHz, $^{13}\text{C}\{^1\text{H}\}$: 150 MHz) in CDCl_3 at 298 K. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra in CDCl_3 were internally referenced to the residual proton (^1H) of the solvent signal at 7.26 ppm and the residual carbon nuclei (^{13}C) of the solvent signal at 77.16 ppm, respectively. ^{19}F NMR spectra were referenced to external standard CFCl_3 at 0.00 ppm. The data are reported in ppm as (s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet or unresolved, br s = broad singlet, coupling constant(s) in Hz, integration). High resolution mass spectra were determined on a Bruker MAXIS impact mass spectrometer (ESI). Melting points were obtained by SGW X4 Micro Melting Point Apparatus.

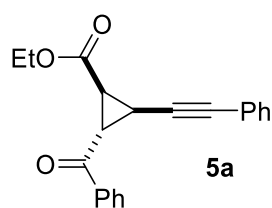
Substituted α -keto esters¹ and alkynyl cyclopropanes² were prepared according to the procedures reported in the literatures. *N*-methyl and *N*-benzyl isatins were obtained by methylation/benzylation of the commercial isatins.

2. Synthesis of alkynyl cyclopropanes

Method A:



Sulfur ylide **S1** (229.8 mg, 1.551 mmol, 1.6 equiv) and enone **S2** (233.0 mg, 1.003 mmol, 1.0 equiv) were dissolved in DCM (4.0 mL) and refluxed at 50 °C in an oil bath. After completion of the reaction, the reaction mixture was cooled to room temperature and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel eluted with EA/PE (1/50 to 1/20, v/v) to afford **5a** (213.0 mg, 67%) and *trans*-**5a** (98.5 mg, 31%).



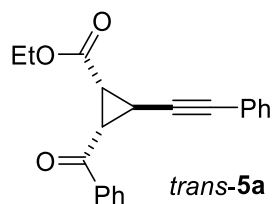
Yield: 213.0 mg, 67% (based on enone **S2**: 233.0 mg, 1.003 mmol).

Colorless solid. M.p. 56.9-58.2 °C. EA/PE = 1/50-1/20.

¹H NMR (500 MHz, CDCl₃): δ 8.07 (d, *J* = 8.0 Hz, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.42-7.41 (m, 2H), 7.30-7.29 (m, 3H), 4.26 (q, *J* = 7.0 Hz, 2H), 3.66 (t, *J* = 5.0 Hz, 1H), 2.78 (dd, *J* = 9.0, 5.0 Hz, 1H), 2.68 (dd, *J* = 9.0, 5.0 Hz, 1H), 1.31 (t, *J* = 7.0 Hz, 3H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 195.2, 168.3, 136.7, 133.9, 131.9, 128.9, 128.6, 128.4, 123.0, 85.0, 81.4, 61.5, 32.1, 31.4, 19.9, 14.5 ppm.

HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₁H₁₈O₃Na 341.1148; Found 341.1141.



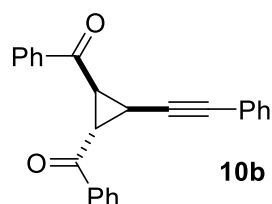
Yield: 98.5 mg, 31% (based on enone **S2**: 233.0 mg, 1.003 mmol).

Colorless solid. M.p. 59.8-61.0 °C. EA/PE = 1/50-1/20.

¹H NMR (500 MHz, CDCl₃): δ 8.05 (d, *J* = 7.5 Hz, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.42-7.41 (m, 2H), 7.31-7.30 (m, 3H), 4.07 (q, *J* = 7.0 Hz, 2H), 3.16 (dd, *J* = 9.5, 6.0 Hz, 2H), 2.94 (t, *J* = 6.0 Hz, 1H), 2.65 (dd, *J* = 9.5, 5.5 Hz, 1H), 1.31 (t, *J* = 7.0 Hz, 3H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 192.7, 168.2, 136.6, 133.7, 131.9, 128.8, 128.5, 128.4, 122.8, 87.5, 79.4, 61.5, 34.6, 31.6, 15.3, 14.1 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₁H₁₈O₃Na 341.1148; Found 341.1145.



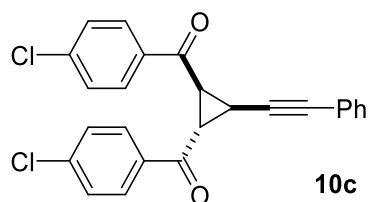
Yield: 128.0 mg, 73% (based on enone **S2**: 116.1 mg, 0.4998 mmol).

Colorless solid. M.p. 107.0-107.9 °C. EA/PE = 1/50-1/20.

¹H NMR (500 MHz, CDCl₃): δ 8.14-8.11 (m, 4H), 7.64-7.60 (m, 2H), 7.54-7.51 (m, 4H), 7.31 (d, *J* = 7.5 Hz, 2H), 7.26-7.23 (m, 3H), 4.01 (t, *J* = 5.0 Hz, 1H), 3.70 (dd, *J* = 9.0, 5.0 Hz, 1H), 2.96 (dd, *J* = 9.0, 5.5 Hz, 1H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 195.8, 192.9, 137.2, 136.7, 133.8, 133.6, 132.0, 128.9, 128.8, 128.7, 128.6, 128.3, 128.2, 122.7, 84.9, 81.8, 35.6, 31.9, 22.0 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₅H₁₈O₂Na 373.1199; Found 373.1198.



Yield: 105.2 mg, 48% (based on enone: 138.3 mg, 0.5185 mmol).

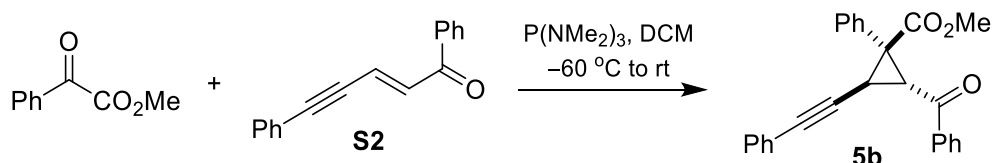
Colorless solid. M.p. 185.1-186.0 °C. EA/PE = 1/50-1/20.

¹H NMR (500 MHz, CDCl₃): δ 8.07-8.04 (m, 4H), 7.51-7.49 (m, 4H), 7.7.30-7.23 (m, 5H), 3.93 (t, *J* = 5.5 Hz, 1H), 3.64 (dd, *J* = 9.0, 5.0 Hz, 1H), 2.93 (dd, *J* = 9.0, 5.5 Hz, 1H) ppm.

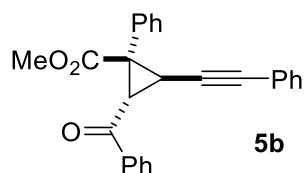
¹³C{¹H} NMR (125 MHz, CDCl₃): δ 194.6, 191.7, 140.6, 140.2, 135.4, 135.0, 132.0, 130.1, 130.0, 129.30, 129.25, 128.5, 128.3, 122.5, 84.4, 82.1, 35.6, 31.8, 22.2 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₅H₁₆Cl₂O₂Na 441.0420; Found 441.0421.

Method B:



To a stirred solution of enone **S2** (233.4 mg, 1.005 mmol, 1.0 equiv) and methyl benzoformate (199.2 mg, 1.213 mmol, 1.2 equiv) in DCM (3.0 mL) cooled at $-60\text{ }^{\circ}\text{C}$, was added dropwise $\text{P}(\text{NMe}_2)_3$ (195.8 mg, 1.200 mmol, 1.2 equiv) via syringe. Upon complete addition of $\text{P}(\text{NMe}_2)_3$, the solution was slowly warmed to rt and vigorously stirred at rt. After completion of the reaction as monitored by TLC, the reaction mixture was concentrated under vacuum and purified by flash column chromatography on silica gel eluted with $\text{Et}_2\text{O}/\text{DCM}/\text{PE}$ (1/4/10 to 3/6/20, v/v/v) to afford **5b** (187.3 mg, 49%).



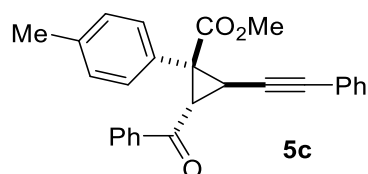
Yield: 187.3 mg, 49% (based on enone **S2**: 233.4 mg, 1.005 mmol).

Colorless solid. M.p. $104.5\text{--}105.7\text{ }^{\circ}\text{C}$. $\text{Et}_2\text{O}/\text{DCM}/\text{PE} = 1/4/10\text{--}3/6/20$.

^1H NMR (600 MHz, CDCl_3): δ 8.06 (d, $J = 7.2$ Hz, 2H), 7.61 (t, $J = 7.2$ Hz, 1H), 7.51 (t, $J = 7.2$ Hz, 2H), 7.43–7.41 (m, 2H), 7.31–7.30 (m, 3H), 7.23–7.20 (m, 3H), 7.18–7.17 (m, 2H), 4.26 (d, $J = 6.6$ Hz, 1H), 3.78 (s, 3H), 3.43 (d, $J = 6.6$ Hz, 1H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 192.6, 169.8, 137.6, 133.7, 133.3, 131.9, 130.0, 129.0, 128.63, 128.57, 128.44, 128.39, 128.3, 123.0, 85.4, 81.4, 53.4, 48.4, 38.1, 20.6 ppm.

HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{26}\text{H}_{22}\text{O}_3\text{Na}$ 403.1305; Found 403.1305.



Yield: 173.3 mg, 44% (based on enone **S2**: 233.0 mg, 1.003 mmol).

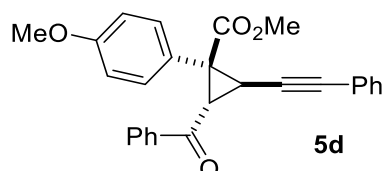
Colorless solid. M.p. $118.0\text{--}119.2\text{ }^{\circ}\text{C}$. $\text{Et}_2\text{O}/\text{DCM}/\text{PE} = 1/4/10\text{--}3/6/20$.

^1H NMR (600 MHz, CDCl_3): δ 8.07 (d, $J = 7.2$ Hz, 2H), 7.61 (t, $J = 7.2$ Hz, 1H), 7.51 (t, $J = 7.8$ Hz, 2H), 7.43–7.41 (m, 2H), 7.31–7.30 (m, 3H), 7.06 (d, $J = 7.8$ Hz, 2H), 7.02

(d, $J = 7.8$ Hz, 2H), 4.24 (d, $J = 6.6$ Hz, 1H), 3.78 (s, 3H), 3.41 (d, $J = 6.6$ Hz, 1H), 2.27 (s, 3H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 192.7, 169.9, 138.0, 137.6, 133.6, 131.9, 130.3, 129.8, 129.3, 128.9, 128.6, 128.4, 128.3, 123.0, 85.6, 81.3, 53.4, 48.1, 38.1, 21.3, 20.6 ppm.

HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{27}\text{H}_{22}\text{O}_3\text{Na}$ 417.1461; Found 417.1460.



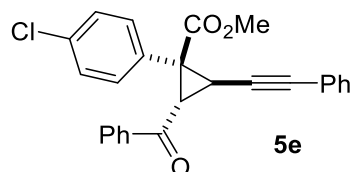
Yield: 186.7 mg, 45% (based on enone **S2**: 232.4 mg, 1.001 mmol).

Colorless solid. M.p. 113.5-114.6 °C. $\text{Et}_2\text{O}/\text{DCM}/\text{PE} = 1/4/10$ -3/6/20.

^1H NMR (500 MHz, CDCl_3): δ 8.07 (d, $J = 7.5$ Hz, 2H), 7.61 (t, $J = 7.0$ Hz, 1H), 7.51 (t, $J = 7.5$ Hz, 2H), 7.41 (br s, 2H), 7.30 (br s, 3H), 7.08 (d, $J = 8.0$ Hz, 2H), 6.73 (d, $J = 8.0$ Hz, 2H), 4.23 (d, $J = 6.5$ Hz, 1H), 3.78 (s, 3H), 3.73 (s, 3H), 3.39 (d, $J = 6.0$ Hz, 1H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 192.7, 170.0, 159.4, 137.6, 133.7, 131.9, 131.1, 128.9, 128.6, 128.4, 128.3, 125.3, 123.0, 114.0, 85.6, 81.3, 55.2, 53.4, 47.8, 38.2, 20.7 ppm.

HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{27}\text{H}_{22}\text{O}_4\text{Na}$ 433.1410; Found 433.1404.



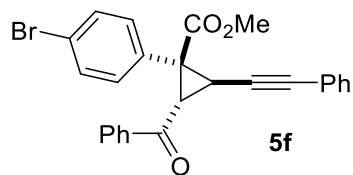
Yield: 173.2 mg, 42% (based on enone **S2**: 231.9 mg, 0.9984 mmol).

Colorless solid. M.p. 116.3-117.5°C. $\text{Et}_2\text{O}/\text{DCM}/\text{PE} = 1/4/10$ -3/6/20.

^1H NMR (500 MHz, CDCl_3): δ 8.05 (d, $J = 7.5$ Hz, 2H), 7.62 (t, $J = 7.5$ Hz, 2H), 7.52 (t, $J = 7.5$ Hz, 2H), 7.42-7.41 (m, 2H), 7.31-7.30 (m, 3H), 7.19 (d, $J = 8.5$ Hz, 2H), 7.10 (d, $J = 8.0$ Hz, 2H), 4.26 (d, $J = 6.5$ Hz, 1H), 3.78 (s, 3H), 3.38 (d, $J = 6.5$ Hz, 1H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 192.5, 169.3, 137.4, 134.3, 133.9, 132.0, 131.9, 131.4, 129.0, 128.8, 128.6, 128.4, 122.8, 85.0, 81.6, 53.5, 47.6, 38.0, 21.0 ppm.

HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{26}\text{H}_{19}\text{ClO}_3\text{Na}$ 437.0915; Found 437.0913.



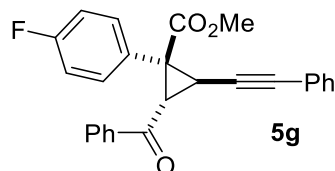
Yield: 200.2 mg, 45% (based on enone **S2**: 230.1 mg, 0.9906 mmol).

Colorless solid. M.p. 121.8-123.0 °C. Et₂O/DCM/PE = 1/4/10-3/6/20.

¹H NMR (500 MHz, CDCl₃): δ 8.05 (d, *J* = 7.5 Hz, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.42-7.41 (m, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.31 (br s, 3H), 7.04 (d, *J* = 8.0 Hz, 2H), 4.26 (d, *J* = 6.5 Hz, 1H), 3.78 (s, 3H), 3.38 (d, *J* = 6.5 Hz, 1H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 192.5, 169.2, 137.4, 133.9, 132.5, 131.9, 131.8, 131.7, 129.0, 128.6, 128.48, 128.45, 122.8, 122.6, 85.0, 81.7, 53.5, 47.6, 37.9, 21.0 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₆H₁₉BrO₃Na 481.0410; Found 481.0402.



Yield: 181.1 mg, 45% (based on enone **S2**: 233.3 mg, 1.004 mmol).

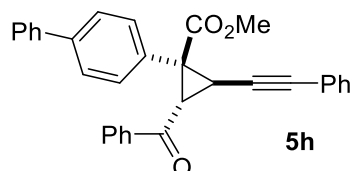
Colorless solid. M.p. 114.8-115.6 °C. Et₂O/DCM/PE = 1/4/10-3/6/20.

¹H NMR (500 MHz, CDCl₃): δ 8.06 (d, *J* = 7.5 Hz, 2H), 7.62 (t, *J* = 7.0 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.42-7.41 (m, 2H), 7.31 (br s, 3H), 7.14 (t, *J* = 7.5 Hz, 2H), 6.91 (t, *J* = 8.5 Hz, 2H), 4.25 (d, *J* = 6.5 Hz, 1H), 3.78 (s, 3H), 3.39 (d, *J* = 6.0 Hz, 1H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 192.6, 169.5, 162.5 (C-F, ¹*J*_{C-F} = 246.4 Hz), 137.4, 133.8, 131.9, 131.8 (C-F, ³*J*_{C-F} = 9.0 Hz), 129.3 (C-F, ⁴*J*_{C-F} = 3.5 Hz), 129.0, 128.6, 128.4, 122.9, 115.6 (C-F, ²*J*_{C-F} = 21.8 Hz), 85.1, 81.6, 53.4, 47.5, 38.0, 21.1 ppm.

¹⁹F NMR (470 MHz, CDCl₃): δ -113.3 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₆H₁₉FO₃Na 421.1210; Found 421.1219.



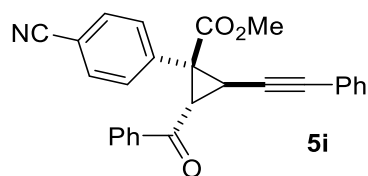
Yield: 191.1 mg, 42% (based on enone **S2**: 232.4 mg, 1.001 mmol).

Colorless solid. M.p. 123.2-124.6 °C. Et₂O/DCM/PE = 1/4/10-3/6/20.

¹H NMR (500 MHz, CDCl₃): δ 8.09 (d, *J* = 7.5 Hz, 2H), 7.62 (t, *J* = 7.0 Hz, 1H), 7.53-7.51 (m, 4H), 7.45-7.44 (m, 4H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.32-7.31 (m, 4H), 7.24 (d, *J* = 7.5 Hz, 2H), 4.29 (d, *J* = 6.0 Hz, 2H), 3.81 (s, 3H), 3.47 (d, *J* = 6.0 Hz, 1H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 192.7, 169.8, 141.1, 140.5, 137.6, 133.7, 132.3, 131.9, 130.4, 129.0, 128.8, 128.7, 128.5, 128.4, 127.5, 127.3, 127.2, 123.0, 85.4, 81.5, 53.5, 48.1, 38.2, 20.7 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₃₂H₂₄O₃Na 479.1618; Found 479.1614.



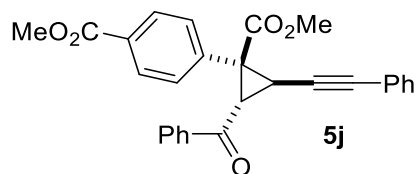
Yield: 174.1 mg, 43% (based on enone **S2**: 232.4 mg, 1.001 mmol).

Colorless solid. M.p. 125.8-127.0 °C. Et₂O/DCM/PE = 1/4/10-3/6/20.

¹H NMR (500 MHz, CDCl₃): δ 8.03 (d, *J* = 7.5 Hz, 2H), 7.64 (t, *J* = 7.0 Hz, 1H), 7.54-7.52 (m, 4H), 7.43-7.41 (m, 2H), 7.32-7.31 (m, 3H), 7.28 (d, *J* = 8.0 Hz, 2H), 4.31 (d, *J* = 6.5 Hz, 1H), 3.78 (s, 3H), 3.40 (d, *J* = 6.5 Hz, 1H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 192.3, 168.6, 138.9, 137.2, 134.1, 132.3, 131.9, 131.0, 129.1, 128.60, 128.56, 128.5, 122.6, 118.5, 112.3, 84.4, 82.1, 53.6, 47.8, 37.9, 21.4 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₇H₁₉NO₃Na 428.1257; Found 428.1265.



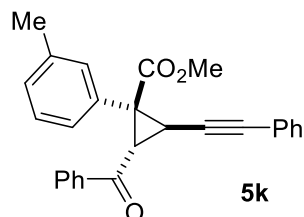
Yield: 188.3 mg, 43% (based on enone **S2**: 232.6 mg, 1.001 mmol).

Colorless solid. M.p. 138.9-139.9 °C. Et₂O/DCM/PE = 1/4/10-3/6/20.

¹H NMR (500 MHz, CDCl₃): δ 8.06 (d, *J* = 7.5 Hz, 2H), 7.92 (d, *J* = 8.0 Hz, 2H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 2H), 7.45-7.44 (m, 2H), 7.34-7.33 (m, 3H), 7.28 (d, *J* = 9.0 Hz, 2H), 4.32 (d, *J* = 6.5 Hz, 2H), 3.89 (s, 3H), 3.80 (s, 3H), 3.47 (d, *J* = 6.0 Hz, 1H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 192.4, 169.1, 166.7, 138.5, 137.3, 133.9, 131.9, 130.2, 130.1, 129.9, 129.0, 128.6, 128.49, 128.45, 122.8, 84.9, 81.7, 53.5, 52.3, 47.9, 38.0, 21.0 ppm.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{28}H_{22}O_5Na$ 461.1359; Found 461.1359.



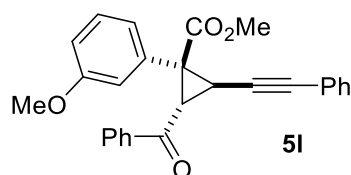
Yield: 195.3 mg, 50% (based on enone **S2**: 232.2 mg, 0.9996 mmol).

Colorless solid. M.p. 121.4-122.8 °C. Et₂O/DCM/PE = 1/4/10-3/6/20.

¹H NMR (500 MHz, CDCl₃): δ 8.07 (d, J = 7.0 Hz, 2H), 7.61 (t, J = 7.0 Hz, 1H), 7.51 (t, J = 7.5 Hz, 2H), 7.32 (d, J = 7.5 Hz, 2H), 7.23-7.18 (m, 5H), 7.11 (d, J = 7.5 Hz, 2H), 4.25 (d, J = 5.5 Hz, 1H), 3.78 (s, 3H), 3.43 (d, J = 6.0 Hz, 1H), 2.35 (s, 3H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 192.7, 169.8, 138.5, 137.6, 133.6, 133.4, 131.8, 130.0, 129.2, 128.9, 128.6, 128.5, 128.3, 119.9, 84.7, 81.5, 53.4, 48.4, 38.1, 21.6, 20.7 ppm.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{22}O_3Na$ 417.1461; Found 417.1470.



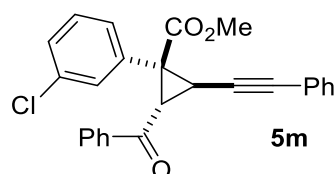
Yield: 142.8 mg, 35% (based on enone **S2**: 232.6 mg, 1.001 mmol).

Colorless solid. M.p. 123.5-124.8 °C. Et₂O/DCM/PE = 1/4/10-3/6/20.

¹H NMR (500 MHz, CDCl₃): δ 8.08 (d, J = 8.0 Hz, 2H), 7.61 (t, J = 7.5 Hz, 1H), 7.51 (t, J = 8.0 Hz, 2H), 7.43-7.42 (m, 2H), 7.31-7.30 (m, 3H), 7.12 (d, J = 8.0 Hz, 1H), 6.77-6.76 (m, 2H), 6.68 (s, 1H), 4.24 (d, J = 6.0 Hz, 1H), 3.79 (s, 3H), 3.60 (s, 3H), 3.43 (d, J = 6.0 Hz, 1H) ppm.

¹³C{¹H} NMR (150 MHz, CDCl₃): δ 192.5, 169.7, 159.5, 137.5, 134.7, 133.7, 131.9, 129.5, 128.9, 128.6, 128.43, 128.38, 123.0, 122.4, 115.5, 114.2, 85.4, 81.3, 55.1, 53.4, 48.2, 38.1, 20.5 ppm.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{22}O_4Na$ 433.1410; Found 433.1422.



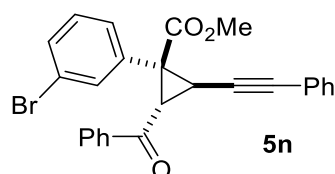
Yield: 226.5 mg, 54% (based on enone **S2**: 232.2 mg, 0.9996 mmol).

Colorless solid. M.p. 128.4-129.5 °C. Et₂O/DCM/PE = 1/4/10-3/6/20.

¹H NMR (500 MHz, CDCl₃): δ 8.05 (d, *J* = 8.0 Hz, 2H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.43-7.41 (m, 2H), 7.31-7.30 (m, 3H), 7.21-7.20 (m, 2H), 7.13 (t, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 7.5 Hz, 1H), 4.26 (d, *J* = 6.5 Hz, 1H), 3.78 (s, 3H), 3.39 (d, *J* = 6.5 Hz, 1H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 192.4, 169.1, 137.4, 135.4, 134.4, 133.9, 131.9, 130.5, 129.7, 129.0, 128.62, 128.57, 128.5, 128.4, 128.2, 122.8, 84.9, 81.7, 53.5, 47.6, 37.9, 21.0 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₆H₁₉ClO₃Na 437.0915; Found 437.0912.



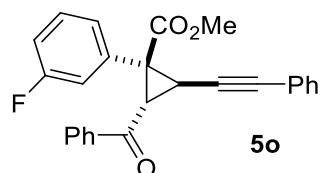
Yield: 196.6 mg, 43% (based on enone **S2**: 233.6 mg, 1.006 mmol).

Colorless solid. M.p. 108.0-108.9 °C. Et₂O/DCM/PE = 1/4/10-3/6/20.

¹H NMR (500 MHz, CDCl₃): δ 8.05 (d, *J* = 7.5 Hz, 2H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 8.0 Hz, 2H), 7.43-7.41 (m, 2H), 7.37-7.36 (m, 2H), 7.31-7.30 (m, 3H), 7.07 (d, *J* = 7.5 Hz, 1H), 7.03 (d, *J* = 7.5 Hz, 1H), 4.26 (d, *J* = 6.0 Hz, 1H), 3.78 (s, 3H), 3.38 (d, *J* = 6.5 Hz, 1H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 192.5, 169.1, 137.4, 135.6, 133.9, 133.4, 131.9, 131.5, 130.0, 129.0, 128.63, 128.58, 128.48, 128.45, 122.8, 122.5, 84.9, 81.7, 53.5, 47.6, 37.9, 21.1 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₆H₁₉BrO₃Na 481.0410; Found 481.0405.



Yield: 179.5 mg, 42% (based on enone **S2**: 233.3 mg, 1.004 mmol).

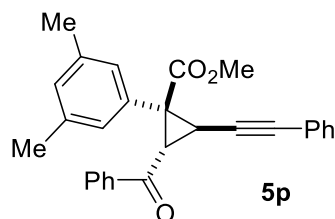
Colorless solid. M.p. 100.2-100.9 °C. Et₂O/DCM/PE = 1/4/10-3/6/20.

¹H NMR (500 MHz, CDCl₃): δ 8.05 (d, *J* = 7.5 Hz, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.43-7.41 (m, 2H), 7.31-7.30 (m, 3H), 7.20-7.16 (m, 1H), 6.94-6.90 (m, 3H), 4.26 (d, *J* = 6.5 Hz, 1H), 3.79 (s, 3H), 3.41 (d, *J* = 6.0 Hz, 1H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 192.4, 169.2, 162.6 (C-F, $^1J_{\text{C-F}} = 245.5$ Hz), 137.4, 135.8 (C-F, $^3J_{\text{C-F}} = 8.1$ Hz), 133.9, 131.9, 130.1 (C-F, $^3J_{\text{C-F}} = 8.1$ Hz), 129.0, 128.6, 128.4, 125.7 (C-F, $^4J_{\text{C-F}} = 2.8$ Hz), 122.8, 117.3 (C-F, $^2J_{\text{C-F}} = 21.6$ Hz), 115.5 (C-F, $^2J_{\text{C-F}} = 20.8$ Hz), 85.0, 81.6, 53.5, 47.7, 38.0, 21.0 ppm.

^{19}F NMR (470 MHz, CDCl_3): δ -112.6 ppm.

HRMS (ESI) m/z: $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{26}\text{H}_{19}\text{FO}_3\text{Na}$ 421.1210; Found 421.1219.



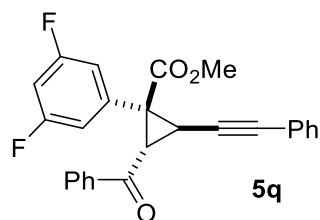
Yield: 203.0 mg, 50% (based on enone **S2**: 232.4 mg, 1.001 mmol).

Colorless solid. M.p. 128.4-129.8 °C. $\text{Et}_2\text{O}/\text{DCM}/\text{PE} = 1/4/10$ -3/6/20.

^1H NMR (500 MHz, CDCl_3): δ 8.06 (d, $J = 7.5$ Hz, 2H), 7.61 (t, $J = 7.5$ Hz, 1H), 7.51 (t, $J = 7.5$ Hz, 2H), 7.42-7.41 (m, 2H), 7.31-7.30 (m, 3H), 6.84 (s, 1H), 6.77 (s, 2H), 4.22 (d, $J = 6.5$ Hz, 1H), 3.78 (s, 3H), 3.40 (d, $J = 6.0$ Hz, 1H), 2.16 (s, 6H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 192.8, 170.0, 137.9, 137.7, 133.6, 133.0, 131.9, 130.2, 128.9, 128.6, 128.4, 128.3, 127.9, 123.1, 85.7, 81.2, 53.4, 48.3, 38.1, 21.3, 20.4 ppm.

HRMS (ESI) m/z: $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{28}\text{H}_{24}\text{O}_3\text{Na}$ 431.1618; Found 431.1616.



Yield: 195.5 mg, 47% (based on enone **S2**: 232.5 mg, 1.001 mmol).

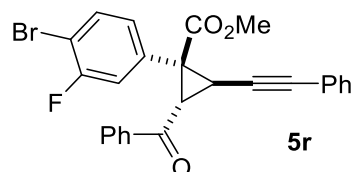
Colorless solid. M.p. 120.5-121.2 °C. $\text{Et}_2\text{O}/\text{DCM}/\text{PE} = 1/4/10$ -3/6/20.

^1H NMR (500 MHz, CDCl_3): δ 8.04 (d, $J = 7.5$ Hz, 2H), 7.64 (t, $J = 7.0$ Hz, 1H), 7.53 (t, $J = 7.5$ Hz, 2H), 7.42-7.41 (m, 2H), 7.32-7.31 (m, 3H), 6.71-6.67 (m, 3H), 4.26 (d, $J = 6.0$ Hz, 1H), 3.79 (s, 3H), 3.38 (d, $J = 6.0$ Hz, 1H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 192.3, 168.7, 162.7 (C-F, $^1J_{\text{C-F}} = 248.3$ Hz, $^3J_{\text{C-F}} = 13.6$ Hz), 137.3, 137.1 (C-F, $^3J_{\text{C-F}} = 9.9$ Hz), 134.1, 131.9, 129.1, 128.6, 128.5, 122.7, 113.3 (C-F, $^2J_{\text{C-F}} = 19.8$ Hz, $^4J_{\text{C-F}} = 6.3$ Hz), 104.2 (C-F, $^2J_{\text{C-F}} = 25.4$ Hz), 84.5, 81.9, 53.6, 47.4, 37.9, 21.3 ppm.

¹⁹F NMR (470 MHz, CDCl₃): δ -109.2 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₆H₁₈F₂O₃Na 439.1116; Found 439.1111.



Yield: 275.4 mg, 53% (based on enone **S2**: 232.9 mg, 1.003 mmol).

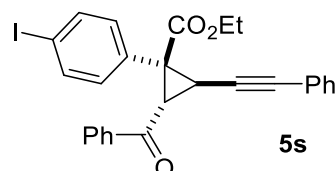
Colorless solid. M.p. 121.8-123.0 °C. Et₂O/DCM/PE = 1/4/10-3/6/20.

¹H NMR (500 MHz, CDCl₃): δ 8.05 (d, *J* = 7.5 Hz, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.42-7.41 (m, 3H), 7.32-7.31 (m, 3H), 7.01-7.00 (m, 1H), 6.94 (t, *J* = 8.0 Hz, 1H), 4.26 (d, *J* = 6.5 Hz, 1H), 3.79 (s, 3H), 3.35 (d, *J* = 6.0 Hz, 1H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 192.5, 169.0, 158.9 (C-F, ¹*J*_{C-F} = 247.3 Hz), 137.4, 135.5, 134.0, 131.9, 131.0 (C-F, ⁴*J*_{C-F} = 3.6 Hz), 130.6 (C-F, ³*J*_{C-F} = 7.1 Hz), 129.1, 128.6, 128.54, 128.47, 122.7, 116.5 (C-F, ²*J*_{C-F} = 22.5 Hz), 109.3 (C-F, ²*J*_{C-F} = 20.8 Hz), 84.6, 81.9, 53.6, 46.9, 37.8, 21.5 ppm.

¹⁹F NMR (470 MHz, CDCl₃): δ -107.4 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₆H₁₈BrFO₃Na 499.0316; Found 499.0312.



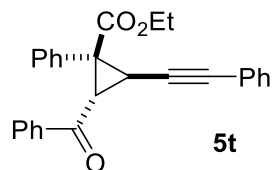
Yield: 252.5 mg, 50% (based on enone **S2**: 232.0 mg, 0.9988 mmol).

Colorless solid. M.p. 126.3-127.0 °C. Et₂O/DCM/PE = 1/4/10-3/6/20.

¹H NMR (500 MHz, CDCl₃): δ 8.05 (d, *J* = 7.5 Hz, 2H), 7.62 (d, *J* = 7.5 Hz, 1H), 7.55-7.50 (m, 4H), 7.41-7.40 (m, 2H), 7.31-7.30 (m, 3H), 6.91 (d, *J* = 8.5 Hz, 2H), 4.34-4.28 (m, 1H), 4.24 (d, *J* = 6.0 Hz, 1H), 4.20-4.14 (m, 1H), 3.37 (d, *J* = 6.0 Hz, 1H), 1.22 (t, *J* = 7.0 Hz, 3H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 192.6, 168.7, 137.6, 137.4, 133.8, 133.3, 131.9, 129.0, 128.6, 128.4, 122.9, 94.3, 85.1, 81.6, 62.5, 47.8, 37.8, 20.7, 14.5 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₆H₁₉BrO₃Na 481.0410; Found 481.0402.



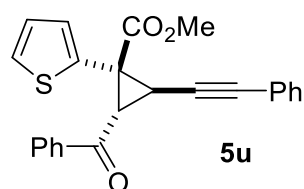
Yield: 175.3 mg, 44% (based on enone **S2**: 234.5 mg, 1.010 mmol).

Colorless solid. M.p. 108.0-109.2 °C. Et₂O/DCM/PE = 1/4/10-3/6/20.

¹H NMR (500 MHz, CDCl₃): δ 8.07 (d, *J* = 7.5 Hz, 2H), 7.61 (d, *J* = 7.0 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.42-7.41 (m, 2H), 7.31-7.30 (m, 3H), 7.22-7.17 (m, 5H), 4.35-4.29 (m, 1H), 4.24 (d, *J* = 6.5 Hz, 1H), 4.20-4.14 (m, 1H), 3.43 (d, *J* = 6.0 Hz, 1H), 1.22 (t, *J* = 7.0 Hz, 3H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 192.8, 169.2, 137.6, 133.6, 133.4, 131.9, 130.0, 128.9, 128.6, 128.5, 128.4, 128.3, 128.2, 123.0, 85.5, 81.3, 62.3, 48.4, 20.4, 14.5 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₇H₂₂O₃Na 417.1461; Found 417.1469.



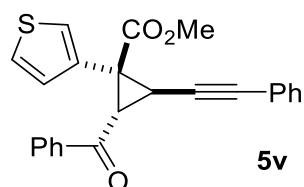
Yield: 191.6 mg, 50% (based on enone **S2**: 232.4 mg, 1.001 mmol).

Colorless solid. M.p. 111.8-113.0 °C. Et₂O/DCM/PE = 1/4/10-3/6/20.

¹H NMR (600 MHz, CDCl₃): δ 8.03 (d, *J* = 3.6 Hz, 1H), 7.69 (d, *J* = 5.4 Hz, 1H), 7.44-7.43 (m, 2H), 7.32-7.31 (m, 3H), 7.26-7.25 (m, 3H), 7.22-7.19 (m, 3H), 4.16 (d, *J* = 6.6 Hz, 1H), 3.76 (s, 3H), 3.39 (d, *J* = 6.0 Hz, 1H) ppm.

¹³C{¹H} NMR (150 MHz, CDCl₃): δ 185.0, 169.6, 145.0, 134.7, 133.3, 133.0, 131.9, 130.0, 128.6, 128.5, 128.43, 128.41, 128.38, 122.9, 85.3, 81.5, 53.4, 48.0, 38.4, 20.8 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₄H₁₈O₃SNa 409.0869; Found 409.0862.



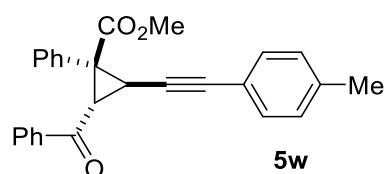
Yield: 183.3 mg, 48% (based on enone **S2**: 232.0 mg, 0.9988 mmol).

Colorless solid. M.p. 124.2-125.3 °C. Et₂O/DCM/PE = 1/4/10-3/6/20.

¹H NMR (500 MHz, CDCl₃): δ 8.05 (d, *J* = 8.0 Hz, 2H), 7.61 (t, *J* = 7.0 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.42-7.41 (m, 2H), 7.31 (br s, 3H), 7.14 (br s, 1H), 7.08 (s, 1H), 6.81 (d, *J* = 4.5 Hz, 1H), 4.18 (d, *J* = 6.5 Hz, 1H), 3.81 (s, 3H), 3.40 (d, *J* = 6.5 Hz, 1H) ppm.

¹³C{¹H} NMR (150 MHz, CDCl₃): δ 192.3, 169.4, 137.2, 133.7, 133.4, 131.9, 129.0, 128.6, 128.5, 128.43, 128.40, 125.9, 125.4, 122.9, 85.1, 81.5, 53.4, 43.0, 38.5, 20.8 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₄H₁₈O₃SNa 409.0869; Found 409.0871.



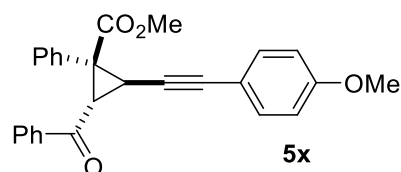
Yield: 163.1 mg, 41% (based on enone: 256.7 mg, 1.042 mmol).

Colorless solid. M.p. 120.3-121.5 °C. Et₂O/DCM/PE = 1/4/10-3/6/20.

¹H NMR (500 MHz, CDCl₃): δ 8.06 (d, *J* = 8.0 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.22 -7.18 (m, 5H), 7.11 (d, *J* = 7.5 Hz, 2H), 4.24 (d, *J* = 6.0 Hz, 1H), 3.77 (s, 3H), 3.42 (d, *J* = 6.5 Hz, 1H), 2.35 (s, 3H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 192.7, 169.8, 138.5, 137.6, 133.6, 133.4, 131.8, 130.0, 129.2, 128.9, 128.6, 128.5, 128.3, 119.9, 84.7, 81.5, 53.4, 48.4, 38.1, 21.6, 20.7 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₇H₂₂O₃Na 417.1461; Found 417.1471.



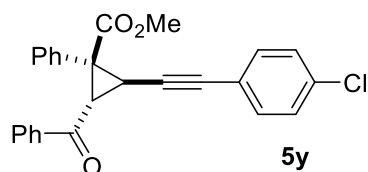
Yield: 164.9 mg, 40% (based on enone: 266.7 mg, 1.017 mmol).

Colorless solid. M.p. 108.9-110.3 °C. Et₂O/DCM/PE = 1/4/10-3/6/20.

¹H NMR (500 MHz, CDCl₃): δ 8.06 (d, *J* = 7.5 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.22 -7.18 (m, 5H), 6.83 (d, *J* = 8.5 Hz, 2H), 4.23 (d, *J* = 6.0 Hz, 1H), 3.81 (s, 3H), 3.77 (s, 3H), 3.41 (d, *J* = 6.5 Hz, 1H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 192.7, 169.8, 159.7, 137.6, 133.6, 133.4, 133.3, 130.0, 128.9, 128.6, 128.5, 128.3, 115.1, 114.1, 83.9, 81.2, 55.4, 53.4, 48.4, 38.1, 20.8 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₇H₂₂O₄Na 433.1410; Found 433.1423.



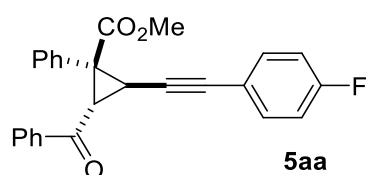
Yield: 164.9 mg, 40% (based on enone: 187.0 mg, 0.7011 mmol).

Colorless solid. M.p. 130.2-131.3 °C. Et₂O/DCM/PE = 1/4/10-3/6/20.

¹H NMR (500 MHz, CDCl₃): δ 8.06 (d, *J* = 7.5 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 7.23-7.21 (m, 3H), 7.16-7.15 (m, 2H), 4.25 (d, *J* = 6.5 Hz, 1H), 3.77 (s, 3H), 3.42 (d, *J* = 6.0 Hz, 1H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 192.5, 169.7, 137.5, 134.4, 133.7, 133.2, 133.1, 130.0, 129.0, 128.8, 128.61, 128.57, 128.4, 121.5, 86.6, 80.3, 53.4, 48.3, 38.1, 20.6 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₆H₁₉ClO₃Na 437.0915; Found 437.0916.



Yield: 183.3 mg, 51% (based on enone: 225.6 mg, 0.9014 mmol).

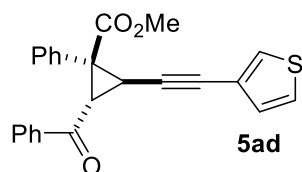
Colorless solid. M.p. 126.5-127.8 °C. Et₂O/DCM/PE = 1/4/10-3/6/20.

¹H NMR (500 MHz, CDCl₃): δ 8.06 (d, *J* = 7.5 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.41-7.38 (m, 2H), 7.23-7.17 (m, 5H), 7.00 (t, *J* = 8.5 Hz, 2H), 4.24 (d, *J* = 6.0 Hz, 1H), 3.77 (s, 3H), 3.41 (d, *J* = 6.0 Hz, 1H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 192.5, 169.7, 162.6 (C-F, ¹*J*_{C-F} = 247.4 Hz), 137.5, 133.8 (C-F, ³*J*_{C-F} = 8.1 Hz), 133.7, 133.3, 130.0, 128.9, 128.60, 128.56, 128.4, 119.1 (C-F, ⁴*J*_{C-F} = 2.8 Hz), 115.7 (C-F, ²*J*_{C-F} = 22.5 Hz), 85.1, 80.3, 53.4, 48.3, 38.0, 20.6 ppm.

¹⁹F NMR (470 MHz, CDCl₃): δ -110.9 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₆H₁₉FO₃Na 421.1210; Found 421.1214.



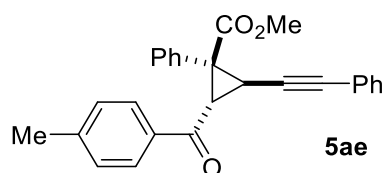
Yield: 251.0 mg, 42% (based on enone: 357.7 mg, 1.499 mmol).

Colorless solid. M.p. 149.3-150.2 °C. Et₂O/DCM/PE = 1/4/10-3/6/20.

¹H NMR (500 MHz, CDCl₃): δ 8.10 (d, *J* = 7.5 Hz, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.59 (d, *J* = 7.5 Hz, 2H), 7.54 (t, *J* = 7.5 Hz, 2H), 7.43-7.37 (m, 3H), 7.16-7.14 (m, 2H), 6.80 (d, *J* = 4.5 Hz, 1H), 3.64 (s, 3H), 3.55 (d, *J* = 6.0 Hz, 1H), 3.33 (d, *J* = 5.5 Hz, 1H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 192.6, 169.7, 137.5, 133.7, 133.3, 130.1, 130.0, 129.0, 128.9, 128.60, 128.55, 128.3, 125.4, 122.0, 84.9, 76.5, 53.3, 48.3, 38.0, 20.7 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₄H₁₈O₃Na 409.0869; Found 409.0867.



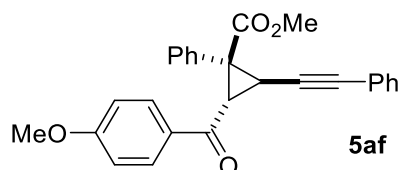
Yield: 163.6 mg, 41% (based on enone: 246.3 mg, 1.000 mmol).

Colorless solid. M.p. 103.4-104.5 °C. Et₂O/DCM/PE = 1/4/10-3/6/20.

¹H NMR (500 MHz, CDCl₃): δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.43-7.41 (m, 2H), 7.31-7.29 (m, 5H), 7.22-7.17 (m, 5H), 4.23 (d, *J* = 6.5 Hz, 1H), 3.77 (s, 3H), 3.42 (d, *J* = 6.5 Hz, 1H), 2.44 (s, 3H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 192.1, 169.8, 144.6, 135.1, 133.4, 131.9, 130.0, 129.6, 128.7, 128.5, 128.4, 128.33, 128.27, 123.0, 85.6, 81.3, 53.4, 48.1, 38.0, 21.9, 20.5 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₇H₂₂O₃Na 417.1461; Found 417.1466.



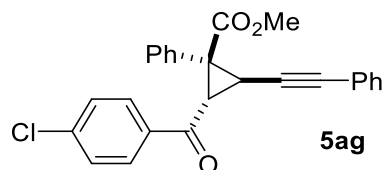
Yield: 295.0 mg, 47% (based on enone: 400.0 mg, 1.525 mmol).

Colorless solid. M.p. 110.8-112.0 °C. Et₂O/DCM/PE = 1/4/10-3/6/20.

¹H NMR (600 MHz, CDCl₃): δ 8.05 (d, *J* = 9.0 Hz, 2H), 7.43-7.41 (m, 2H), 7.31-7.29 (m, 3H), 7.23-7.19 (m, 2H), 7.17-7.15 (m, 2H), 6.97 (d, *J* = 9.0 Hz, 2H), 4.20 (d, *J* = 6.6 Hz, 2H), 3.89 (s, 3H), 3.77 (s, 3H), 3.41 (d, *J* = 6.0 Hz, 1H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 190.8, 169.8, 164.0, 133.4, 131.9, 130.9, 130.7, 130.0, 128.5, 128.4, 128.3, 128.2, 123.0, 114.1, 85.7, 81.2, 55.6, 53.3, 47.9, 37.8, 20.3 ppm.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{22}O_4Na$ 433.1410; Found 433.1420.



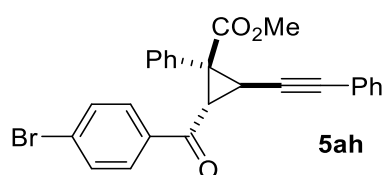
Yield: 203.4 mg, 49% (based on enone: 266.0 mg, 0.9973 mmol).

Colorless solid. M.p. 121.8-123.4 °C. Et₂O/DCM/PE = 1/4/10-3/6/20.

¹H NMR (500 MHz, CDCl₃): δ 8.00 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.42-7.41 (m, 2H), 7.31 (br s, 3H), 7.23-7.22 (m, 3H), 7.15-7.13 (m, 2H), 4.19 (d, *J* = 6.0 Hz, 1H), 3.78 (s, 3H), 3.43 (d, *J* = 5.5 Hz, 1H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 191.4, 169.7, 140.2, 135.8, 133.1, 131.9, 130.0, 129.9, 129.3, 128.6, 128.4, 122.9, 85.2, 81.5, 53.5, 48.5, 38.0, 20.6 ppm.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{19}ClO_3Na$ 437.0915; Found 437.0912.



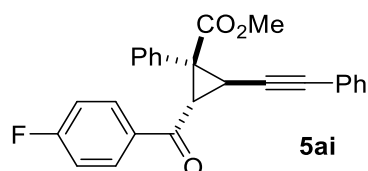
Yield: 263.2 mg, 47% (based on enone: 311.0 mg, 0.9994 mmol).

Colorless. M.p. 101.5-102.8 °C. Et₂O/DCM/PE = 1/4/10-3/6/20.

¹H NMR (500 MHz, CDCl₃): δ 7.92 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.42 (br s, 2H), 7.31-7.30 (m, 3H), 7.23-7.22 (m, 3H), 7.15 (br s, 2H), 4.19 (d, *J* = 6.0 Hz, 1H), 3.78 (s, 3H), 3.43 (d, *J* = 6.0 Hz, 1H) ppm.

¹³C NMR (125 MHz, CDCl₃): δ 191.6, 169.7, 136.2, 133.1, 132.3, 131.9, 130.1, 129.9, 129.0, 128.6, 128.5, 122.9, 85.2, 81.5, 53.5, 48.6, 38.0, 20.6 ppm.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{19}BrO_3Na$ 481.0410; Found 480.0414.



Yield: 199.2 mg, 50% (based on enone: 250.0 mg, 0.9989 mmol).

Colorless solid. M.p. 106.3-107.2 °C. Et₂O/DCM/PE = 1/4/10-3/6/20.

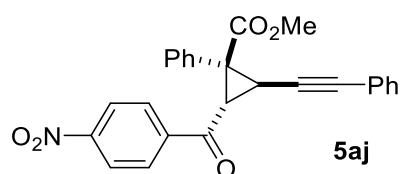
¹H NMR (500 MHz, CDCl₃): δ 8.09 (dd, *J* = 8.0, 5.5 Hz, 2H), 7.42-7.41 (m, 2H), 7.31-

7.30 (m, 3H), 7.23-7.22 (m, 3H), 7.19-7.16 (m, 4H), 4.20 (d, $J = 6.5$ Hz, 1H), 3.78 (s, 3H), 3.43 (d, $J = 6.0$ Hz, 1H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 191.0, 169.7, 166.2 (C-F, $^1J_{\text{C-F}} = 254.5$ Hz), 134.0 (C-F, $^4J_{\text{C-F}} = 2.8$ Hz), 133.2, 131.9, 131.3 (C-F, $^3J_{\text{C-F}} = 9.0$ Hz), 129.9, 128.6, 128.4, 122.9, 116.1 (C-F, $^2J_{\text{C-F}} = 21.6$ Hz), 85.3, 81.4, 53.4, 48.4, 38.0, 20.5 ppm.

^{19}F NMR (470 MHz, CDCl_3): δ -104.2 ppm.

HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{26}\text{H}_{19}\text{FO}_3\text{Na}$ 421.1210; Found 421.1219.



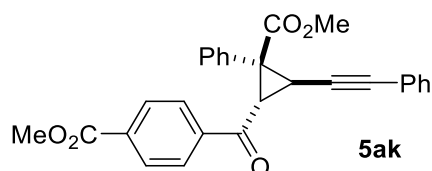
Yield: 140.6 mg, 33% (based on enone: 277.0 mg, 1.077 mmol).

Colorless solid. M.p. 129.0-130.4 °C. $\text{Et}_2\text{O}/\text{DCM}/\text{PE} = 1/4/10\text{-}3/6/20$.

^1H NMR (500 MHz, CDCl_3): δ 8.35 (d, $J = 8.5$ Hz, 2H), 8.21 (d, $J = 8.5$ Hz, 2H), 7.43-7.41 (m, 2H), 7.32-7.31 (m, 3H), 7.26-7.24 (m, 3H), 7.16-7.15 (m, 2H), 4.24 (d, $J = 6.0$ Hz, 1H), 3.79 (s, 3H), 3.47 (d, $J = 6.5$ Hz, 1H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 191.4, 169.4, 150.7, 141.6, 132.7, 131.9, 129.8, 129.6, 128.8, 128.63, 128.59, 128.5, 124.2, 122.7, 84.7, 81.9, 53.6, 49.3, 38.4, 20.9 ppm.

HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{26}\text{H}_{19}\text{NO}_5\text{Na}$ 448.1155; Found 448.1155.



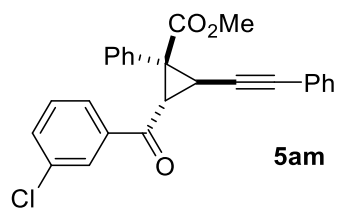
Yield: 165.6 mg, 45% (based on enone: 244.0 mg, 0.8405 mmol).

Colorless solid. M.p. 161.2-162.9 °C. $\text{Et}_2\text{O}/\text{DCM}/\text{PE} = 1/4/10\text{-}3/6/20$.

^1H NMR (600 MHz, CDCl_3): δ 8.16 (d, $J = 8.4$ Hz, 2H), 8.10 (d, $J = 7.8$ Hz, 2H), 7.42-7.41 (m, 3H), 7.31-7.30 (m, 3H), 7.24-7.21 (m, 3H), 7.16-7.15 (m, 2H), 4.26 (d, $J = 6.0$ Hz, 1H), 3.97 (s, 3H), 3.78 (s, 3H), 3.45 (d, $J = 6.0$ Hz, 1H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 192.3, 169.6, 166.3, 140.5, 134.4, 133.0, 131.9, 130.2, 130.0, 128.6, 128.51, 128.47, 128.45, 122.9, 85.1, 81.6, 53.5, 52.7, 48.8, 38.3, 20.8 ppm.

HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{28}\text{H}_{22}\text{O}_5\text{Na}$ 461.1359; Found 461.1353.



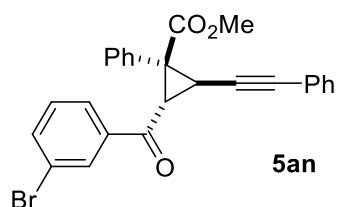
Yield: 148.2 mg, 60% (based on enone: 266.7 mg, 1.000 mmol).

Colorless solid. M.p. 114.9-115.6 °C. Et₂O/DCM/PE = 1/4/10-3/6/20.

¹H NMR (500 MHz, CDCl₃): δ 7.99-7.98 (m, 2H), 7.58 (d, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 1H), 7.43-7.42 (m, 2H), 7.31 (br s, 3H), 7.25-7.24 (m, 3H), 7.17-7.16 (m, 2H), 4.20 (d, *J* = 6.0 Hz, 1H), 3.78 (s, 3H), 3.43 (d, *J* = 6.0 Hz, 1H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 191.5, 169.5, 139.0, 135.3, 133.6, 133.0, 131.9, 130.3, 130.0, 128.6, 128.5, 128.4, 126.8, 122.8, 85.1, 81.6, 53.5, 48.7, 38.0, 20.8 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₆H₁₉ClO₃Na 437.0915; Found 437.0909.



Yield: 133.3 mg, 45% (based on enone: 200.0 mg, 0.6427 mmol).

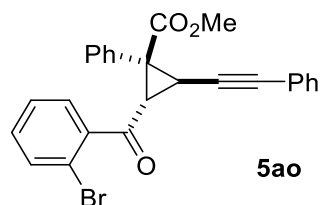
White crystals, obtained by slow evaporation of the PE and EA solution at rt.

M.p. 128.5-129.6 °C. Et₂O/DCM/PE = 1/4/10-3/6/20.

¹H NMR (500 MHz, CDCl₃): δ 8.13 (s, 1H), 8.03 (d, *J* = 7.5 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.43-7.39 (m, 3H), 7.31-7.30 (m, 3H), 7.25-7.24 (m, 3H), 7.17-7.16 (m, 2H), 4.19 (d, *J* = 6.0 Hz, 1H), 3.78 (s, 3H), 3.42 (d, *J* = 6.0 Hz, 1H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 191.4, 169.5, 139.2, 136.6, 133.0, 131.9, 131.5, 130.6, 130.0, 128.6, 128.5, 127.2, 123.4, 122.9, 85.1, 81.6, 53.5, 48.8, 37.9, 20.9 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₆H₁₉BrO₃Na 481.0410; Found 481.0405.



Yield: 197.5 mg, 43% (based on enone: 312.0 mg, 1.003 mmol).

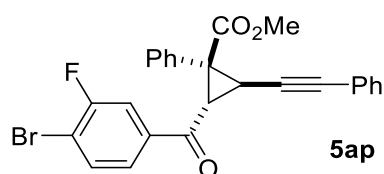
Colorless solid. M.p. 107.3-108.5 °C. Et₂O/DCM/PE = 1/4/10-3/6/20.

¹H NMR (500 MHz, CDCl₃): δ 7.66 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 7.5 Hz, 1H), 7.42-7.39 (m, 3H), 7.36-7.28 (m, 9H), 4.18 (d, *J* = 6.5 Hz, 1H), 3.75 (s, 3H), 3.38 (d, *J* = 6.5

Hz, 1H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 194.9, 169.4, 140.3, 134.3, 133.3, 132.8, 131.9, 130.6, 130.4, 128.6, 128.4, 128.3, 127.7, 122.9, 120.4, 85.2, 81.9, 53.3, 49.5, 41.0, 23.3 ppm.

HRMS (ESI) m/z: $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{26}\text{H}_{19}\text{BrO}_3\text{Na}$ 481.0410; Found 481.0411.



Yield: 210.4 mg, 49% (based on enone: 296.4 mg, 0.9005 mmol).

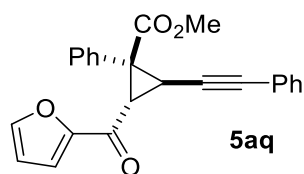
Colorless solid. M.p. 140.2-141.0 °C. $\text{Et}_2\text{O}/\text{DCM}/\text{PE} = 1/4/10\text{-}3/6/20$.

^1H NMR (500 MHz, CDCl_3): δ 8.24-8.23 (m, 1H), 8.07-8.05 (m, 1H), 7.42-7.41 (m, 2H), 7.31-7.30 (m, 3H), 7.27-7.24 (m, 4H), 7.15-7.14 (m, 2H), 4.15 (d, $J = 6.0$ Hz, 1H), 3.78 (s, 3H), 3.42 (d, $J = 6.0$ Hz, 1H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 190.1, 169.6, 162.5 (C-F, $^1J_{\text{C-F}} = 255.5$ Hz), 135.0 (C-F, $^3J_{\text{C-F}} = 2.8$ Hz), 134.4, 132.9, 131.9, 129.9, 129.8, 128.7, 128.5 (C-F, $^3J_{\text{C-F}} = 2.8$ Hz), 128.5, 122.8, 117.0 (C-F, $^2J_{\text{C-F}} = 22.6$ Hz), 110.3 (C-F, $^2J_{\text{C-F}} = 21.8$ Hz), 85.0, 81.7, 53.5, 48.8, 37.8, 20.8 ppm.

^{19}F NMR (470 MHz, CDCl_3): δ -94.4 ppm.

HRMS (ESI) m/z: $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{26}\text{H}_{18}\text{BrFO}_3\text{Na}$ 499.0316; Found 499.0315.



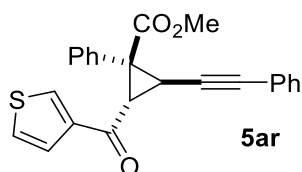
Yield: 383.1 mg, 52% (based on enone: 443.2 mg, 1.994 mmol).

Colorless solid. M.p. 137.6-139.2 °C. $\text{Et}_2\text{O}/\text{DCM}/\text{PE} = 1/4/10\text{-}3/6/20$.

^1H NMR (500 MHz, CDCl_3): δ 8.02 (d, $J = 3.0$ Hz, 1H), 7.69 (d, $J = 4.5$ Hz, 1H), 7.43-7.42 (m, 2H), 7.31 (br s, 3H), 7.25 (br s, 3H), 7.22-7.18 (m, 3H), 4.15 (d, $J = 6.0$ Hz, 1H), 3.76 (s, 3H), 3.39 (d, $J = 6.0$ Hz, 1H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 185.0, 181.0, 169.6, 169.5, 153.4, 147.2, 145.0, 134.7, 133.3, 133.0, 131.9, 130.1, 130.0, 128.7, 128.6, 128.5, 128.4, 128.3, 127.9, 127.7, 123.0, 118.3, 112.7, 85.3, 81.5, 53.4, 48.1, 38.5, 37.6, 20.8 ppm.

HRMS (ESI) m/z: $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{24}\text{H}_{18}\text{O}_4\text{Na}$ 393.1097; Found 393.1096.



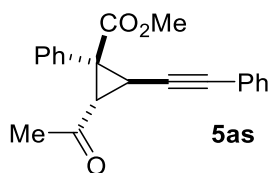
Yield: 203.8 mg, 44% (based on enone: 288.3 mg, 1.210 mmol).

Colorless solid. M.p. 153.2-154.0 °C. Et₂O/DCM/PE = 1/4/10-3/6/20.

¹H NMR (600 MHz, CDCl₃): δ 8.31 (dd, *J* = 3.0, 1.2 Hz 1H), 7.54 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.43-7.41 (m, 2H), 7.34 (dd, *J* = 5.4, 3.0 Hz, 1H), 7.31-7.29 (m, 3H), 7.26-7.23 (m, 3H), 7.18-7.16 (m, 2H), 4.11 (d, *J* = 6.0 Hz, 1H), 3.76 (s, 3H), 3.37 (d, *J* = 6.6 Hz, 1H) ppm.

¹³C{¹H} NMR (150 MHz, CDCl₃): δ 186.5, 170.0, 143.0, 133.3, 133.2, 131.9, 130.1, 128.6, 128.44, 128.40, 128.35, 127.1, 126.9, 123.0, 85.4, 81.4, 53.4, 48.1, 38.9, 20.6 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₄H₁₈O₃SNa 409.0869; Found 409.0868.



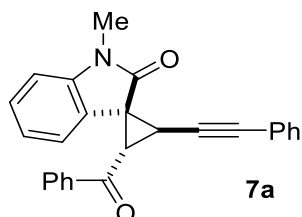
Yield: 116.5 mg, 37% (based on enone: 144.2 mg, 0.8472 mmol).

Colorless solid. M.p. 91.9-93.0 °C. Et₂O/DCM/PE = 1/4/10-3/6/20.

¹H NMR (500 MHz, CDCl₃): δ 7.52 (d, *J* = 7.0 Hz, 2H), 7.41-7.34 (m, 3H), 7.23-7.18 (m, 3H), 7.07 (d, *J* = 7.0 Hz, 2H), 3.65 (s, 3H), 3.14 (d, *J* = 5.5 Hz, 1H), 2.89 (d, *J* = 5.5 Hz, 1H), 2.47 (s, 3H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 200.7, 169.5, 133.5, 131.9, 129.9, 128.7, 128.42, 128.40, 128.36, 122.9, 85.1, 81.4, 53.3, 47.9, 40.9, 31.9, 30.0 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₁H₁₈O₃Na 341.1148; Found 341.1140.



Yield: 110.3 mg, 29% (based on enone **S2**: 233.8 mg, 1.007 mmol).

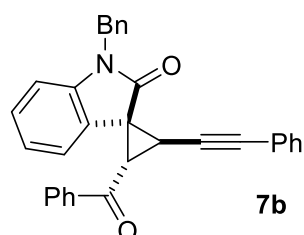
Red crystals, obtained by slow evaporation of the PE and EA solution at rt.

M.p. 149.9-150.0 °C. Et₂O/DCM/PE = 1/2/25-1/2/5.

¹H NMR (500 MHz, CDCl₃): δ 7.94 (d, *J* = 8.0 Hz, 2H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.48-7.47 (m, 2H), 7.42 (t, *J* = 8.0 Hz, 1H), 7.29-7.28 (m, 3H), 7.23 (d, *J* = 7.5 Hz, 2H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 7.5 Hz, 1H), 4.09 (d, *J* = 7.5 Hz, 1H), 3.58 (d, *J* = 7.5 Hz, 1H), 3.35 (s, 3H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 192.1, 171.2, 144.2, 136.8, 134.0, 132.1, 128.9, 128.7, 128.3, 128.2, 124.7, 123.1, 122.6, 108.2, 83.7, 83.3, 42.3, 41.2, 27.0, 24.6 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₆H₁₉NO₂Na 400.1308; Found 400.1319.



Yield: 150.1 mg, 33% (based on enone **S2**: 234.1 mg, 1.008 mmol).

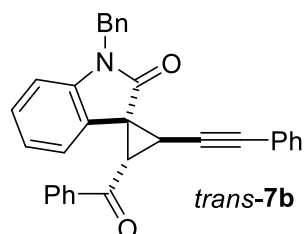
Red crystals, obtained by slow evaporation of the PE and EA solution at rt.

M.p. 175.1-176.4 °C. Et₂O/DCM/PE = 1/2/25-1/2/5.

¹H NMR (600 MHz, CDCl₃): δ 7.94 (d, *J* = 7.8 Hz, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.49-7.47 (m, 2H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.34-7.25 (m, 8H), 7.19 (d, *J* = 7.8 Hz, 1H), 7.12 (t, *J* = 7.8 Hz, 1H), 6.93 (t, *J* = 7.8 Hz, 1H), 6.77 (d, *J* = 7.8 Hz, 1H), 5.09 (d, *J* = 15.6 Hz, 1H), 5.04 (d, *J* = 15.6 Hz, 1H), 4.15 (d, *J* = 7.2 Hz, 1H), 3.61 (d, *J* = 7.8 Hz, 1H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 192.0, 171.4, 143.2, 136.8, 136.0, 134.0, 132.1, 128.95, 128.92, 128.7, 128.4, 128.1, 127.8, 127.4, 124.7, 123.1, 122.6, 122.5, 109.2, 83.6, 83.4, 44.4, 42.7, 41.1, 24.7 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₃₂H₂₃NO₂Na 476.1621; Found 476.1633.



Yield: 293.5 mg, 65% (based on enone **S2**: 234.1 mg, 1.008 mmol).

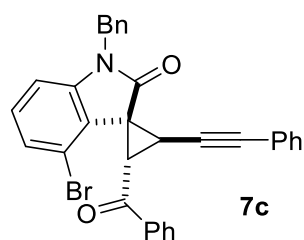
Red crystals, obtained by slow evaporation of the PE and EA solution at rt.

M.p. 178.0-179.3 °C. Et₂O/DCM/PE = 1/2/25-1/2/5.

^1H NMR (600 MHz, CDCl_3): δ 7.82 (d, J = 7.5 Hz, 2H), 7.56 (t, J = 7.0 Hz, 1H), 7.47-7.43 (m, 3H), 7.39 (t, J = 7.5 Hz, 2H), 7.33-7.27 (m, 4H), 7.20-7.13 (m, 4H), 7.02 (d, J = 7.0 Hz, 2H), 6.83 (d, J = 7.5 Hz, 1H), 5.06 (d, J = 15.5 Hz, 1H), 4.60 (d, J = 16.0 Hz, 1H), 3.59 (d, J = 7.5 Hz, 1H), 3.49 (d, J = 7.5 Hz, 1H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 190.3, 171.5, 143.6, 136.2, 135.8, 133.7, 132.0, 128.9, 128.8, 128.7, 128.6, 127.7, 127.4, 124.8, 122.7, 122.4, 121.7, 109.5, 84.3, 83.9, 44.1, 43.6, 39.1, 23.4 ppm.

HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{32}\text{H}_{23}\text{NO}_2\text{Na}$ 476.1621; Found 476.1633.



Yield: 161.2 mg, 30% (based on enone **S2**: 232.8 mg, 1.002 mmol).

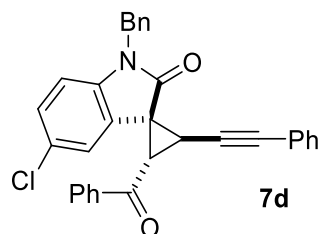
Red crystals, obtained by slow evaporation of the PE and EA solution at rt.

M.p. 150.8-152.0 °C. $\text{Et}_2\text{O}/\text{DCM}/\text{PE}$ = 1/2/25-1/2/5.

^1H NMR (500 MHz, CDCl_3): δ 8.06 (d, J = 8.0 Hz, 2H), 7.60-7.53 (m, 3H), 7.46 (t, J = 7.5 Hz, 2H), 7.34-7.28 (m, 8H), 7.04 (d, J = 8.0 Hz, 1H), 6.99 (t, J = 8.0 Hz, 1H), 6.78 (d, J = 8.0 Hz, 1H), 5.10-5.03 (m, 2H), 4.37 (d, J = 9.0 Hz, 1H), 3.60 (d, J = 9.0 Hz, 1H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 192.3, 171.3, 145.4, 136.1, 135.6, 134.0, 132.2, 129.22, 129.17, 129.0, 128.9, 128.44, 128.39, 127.9, 127.44, 127.38, 123.04, 122.95, 117.2, 108.7, 83.8, 83.1, 44.6, 43.6, 39.7, 20.5 ppm.

HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{32}\text{H}_{22}\text{BrO}_2\text{Na}$ 544.0726; Found 544.0731.



Yield: 161.2 mg, 30% (based on enone **S2**: 232.8 mg, 1.002 mmol).

Red crystals, obtained by slow evaporation of the PE and EA solution at rt.

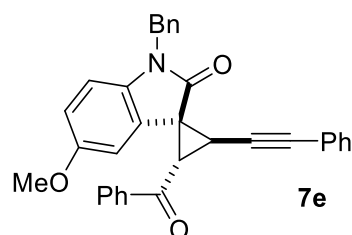
M.p. 153.8-154.9 °C. $\text{Et}_2\text{O}/\text{DCM}/\text{PE}$ = 1/2/25-1/2/5.

^1H NMR (500 MHz, CDCl_3): δ 7.96 (d, J = 7.5 Hz, 2H), 7.58 (t, J = 7.5 Hz, 1H), 7.48-7.43 (m, 4H), 7.30 (br s, 8H), 7.24 (d, J = 1.0 Hz, 1H), 7.09 (dd, J = 8.5, 1.5 Hz, 1H),

6.66 (d, $J = 8.5$ Hz, 1H), 5.08-5.00 (m, 2H), 4.17 (d, $J = 7.5$ Hz, 1H), 3.59 (d, $J = 7.5$ Hz, 1H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 191.7, 171.0, 141.7, 136.6, 135.6, 134.2, 132.1, 129.02, 128.98, 128.7, 128.5, 128.4, 128.2, 128.1, 128.0, 127.4, 126.4, 123.1, 122.9, 110.1, 83.8, 83.1, 44.5, 42.7, 41.0, 27.1, 25.4 ppm.

HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{32}\text{H}_{22}\text{ClO}_2\text{Na}$ 510.1231; Found 510.1235.



Yield: 161.2 mg, 30% (based on enone **S2**: 232.8 mg, 1.002 mmol).

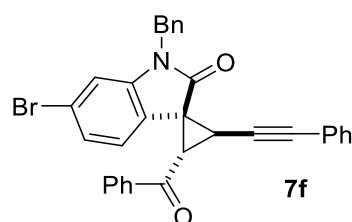
Red crystals, obtained by slow evaporation of the PE and EA solution at rt.

M.p. 150.2-151.8 °C. $\text{Et}_2\text{O}/\text{DCM}/\text{PE} = 1/2/25-1/2/5$.

^1H NMR (500 MHz, CDCl_3): δ 7.94 (d, $J = 8.0$ Hz, 2H), 7.56 (t, $J = 7.0$ Hz, 1H), 7.48 (br s, 2H), 7.42 (t, $J = 7.5$ Hz, 2H), 7.31-7.25 (m, 8H), 6.84 (s, 1H), 6.64 (s, 2H), 5.06 (d, $J = 15.5$ Hz, 1H), 5.00 (d, $J = 15.5$ Hz, 1H), 4.14 (d, $J = 7.0$ Hz, 1H), 3.71 (s, 3H), 3.57 (d, $J = 7.5$ Hz, 1H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 192.0, 171.2, 155.9, 136.8, 136.7, 136.1, 134.0, 132.1, 128.9, 128.7, 128.3, 127.8, 127.4, 125.9, 123.1, 113.2, 109.6, 109.4, 83.6, 83.4, 55.9, 44.5, 42.7, 41.4, 24.9 ppm.

HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{33}\text{H}_{25}\text{NO}_3\text{Na}$ 506.1727; Found 506.1739.



Yield: 142.3 mg, 35% (based on enone **S2**: 176.5 mg, 0.7599 mmol).

Red crystals, obtained by slow evaporation of the PE and EA solution at rt.

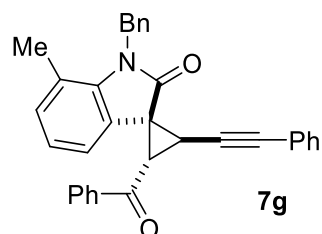
M.p. 173.1-173.8 °C. $\text{Et}_2\text{O}/\text{DCM}/\text{PE} = 1/2/25-1/4/25$.

^1H NMR (500 MHz, CDCl_3): δ 7.92 (d, $J = 8.0$ Hz, 2H), 7.57 (t, $J = 7.0$ Hz, 1H), 7.48-7.42 (m, 4H), 7.31-7.32 (m, 8H), 7.06 (s, 2H), 6.90 (s, 1H), 5.05 (d, $J = 16.0$ Hz, 1H), 5.00 (d, $J = 16.0$ Hz, 1H), 4.14 (d, $J = 7.0$ Hz, 1H), 3.59 (d, $J = 7.5$ Hz, 1H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 191.7, 171.1, 144.4, 136.5, 135.4, 134.1, 132.0,

129.0, 128.9, 128.5, 128.4, 128.3, 127.9, 127.3, 125.4, 123.7, 123.5, 122.8, 121.8, 112.4, 83.7, 83.1, 44.3, 42.6, 40.7, 24.8 ppm.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{32}H_{22}BrNO_2Na$ 554.0726; Found 554.0736.



Yield: 190.3 mg, 41% (based on enone **S2**: 233.1 mg, 1.003 mmol).

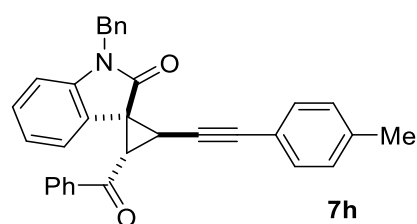
Red crystals, obtained by slow evaporation of the PE and EA solution at rt.

M.p. 128.5-129.6 °C. Et₂O/DCM/PE = 1/2/25-1/4/25.

¹H NMR (500 MHz, CDCl₃): δ 7.95 (d, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.46-7.41 (m, 4H), 7.30-7.23 (m, 6H), 7.17 (d, *J* = 7.5 Hz, 2H), 7.02 (d, *J* = 7.0 Hz, 1H), 6.89-6.82 (m, 2H), 5.40 (d, *J* = 17.0 Hz, 1H), 5.32 (d, *J* = 17.0 Hz, 1H), 4.15 (d, *J* = 7.5 Hz, 1H), 3.60 (d, *J* = 7.5 Hz, 1H), 2.29 (s, 3H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 191.8, 172.5, 141.3, 137.8, 136.7, 134.0, 132.15, 132.11, 129.0, 128.9, 128.7, 128.3, 127.4, 125.9, 125.3, 123.1, 122.7, 120.1, 120.0, 83.6, 83.3, 45.8, 43.5, 40.7, 27.1, 24.9, 19.1 ppm.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{33}H_{25}NO_2Na$ 490.1777; Found 490.1780.



Yield: 155.9 mg, 33% (based on enone: 247.1 mg, 1.003 mmol).

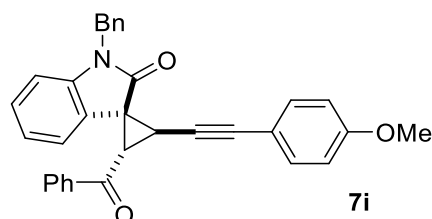
Red crystals, obtained by slow evaporation of the PE and EA solution at rt.

M.p. 130.2-131.0 °C. Et₂O/DCM/PE = 1/2/50-1/4/25.

¹H NMR (500 MHz, CDCl₃): δ 7.93 (d, *J* = 7.5 Hz, 2H), 7.53 (t, *J* = 7.0 Hz, 1H), 7.42-7.37 (m, 4H), 7.33-7.25 (m, 5H), 7.19 (d, *J* = 8.0 Hz, 1H), 7.12-7.09 (m, 3H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.75 (d, *J* = 7.5 Hz, 1H), 5.08 (d, *J* = 16.0 Hz, 1H), 5.02 (d, *J* = 16.0 Hz, 1H), 4.14 (d, *J* = 7.0 Hz, 1H), 3.60 (d, *J* = 7.5 Hz, 1H), 2.33 (s, 3H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 191.9, 171.3, 143.1, 138.4, 136.7, 136.0, 133.9, 131.9, 129.1, 128.9, 128.8, 128.5, 128.0, 127.7, 127.4, 124.6, 122.5, 122.4, 119.9, 109.1, 83.5, 82.8, 44.3, 42.7, 41.0, 24.8, 21.6 ppm.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{33}H_{25}NO_2Na$ 499.1777; Found 499.1782.



Yield: 136.9 mg, 28% (based on enone: 265.8 mg, 1.013 mmol).

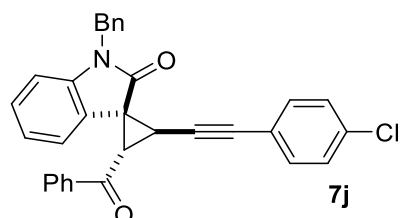
Red crystals, obtained by slow evaporation of the PE and EA solution at rt.

M.p. 142.8-143.5 °C. Et₂O/DCM/PE = 1/2/50-1/4/25.

¹H NMR (500 MHz, CDCl₃): δ 7.92 (d, *J* = 8.0 Hz, 2H), 7.53 (t, *J* = 7.0 Hz, 1H), 7.42-7.39 (m, 4H), 7.33-7.28 (m, 4H), 7.25 (s, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 8.5 Hz, 2H), 6.75 (d, *J* = 8.0 Hz, 1H), 5.08 (d, *J* = 15.5 Hz, 1H), 5.02 (d, *J* = 15.5 Hz, 1H), 4.13 (d, *J* = 8.0 Hz, 1H), 3.78 (s, 3H), 3.60 (d, *J* = 7.5 Hz, 1H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 192.1, 171.4, 159.7, 143.1, 136.7, 136.0, 133.9, 133.5, 128.91, 128.87, 128.6, 128.0, 127.8, 127.4, 124.7, 122.6, 122.4, 115.2, 114.0, 109.2, 83.3, 82.0, 55.4, 44.3, 42.8, 41.1, 24.9 ppm.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{33}H_{25}NO_3Na$ 506.1727; Found 506.1740.



Yield: 186.1 mg, 38% (based on enone: 268.1 mg, 1.005 mmol).

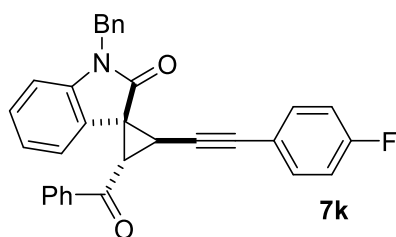
Red crystals, obtained by slow evaporation of the PE and EA solution at rt.

M.p. 173.5-174.1 °C. Et₂O/DCM/PE = 1/2/50-1/2/10.

¹H NMR (500 MHz, CDCl₃): δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.43-7.39 (m, 4H), 7.33-7.28 (m, 7H), 7.18 (d, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 5.09 (d, *J* = 15.5 Hz, 1H), 5.03 (d, *J* = 15.5 Hz, 1H), 4.13 (d, *J* = 7.5 Hz, 1H), 3.59 (d, *J* = 8.0 Hz, 1H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 191.9, 171.3, 143.2, 136.7, 136.0, 134.3, 134.0, 133.3, 128.9, 128.7, 128.6, 128.2, 127.8, 127.4, 124.5, 122.7, 122.4, 121.6, 109.3, 84.7, 82.2, 44.4, 42.6, 41.0, 24.5 ppm.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{32}H_{22}ClO_2Na$ 510.1231; Found 510.1229.



Yield: 132.7 mg, 28% (based on enone: 252.7 mg, 1.010 mmol).

Red crystals, obtained by slow evaporation of the PE and EA solution at rt.

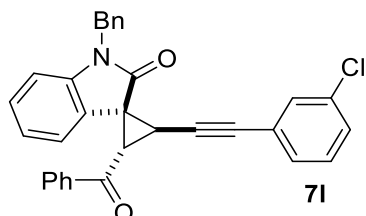
M.p. 185.1-186.1 °C. Et₂O/DCM/PE = 1/2/50-1/2/10.

¹H NMR (500 MHz, CDCl₃): δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.47-7.40 (m, 4H), 7.32-7.27 (m, 5H), 7.18 (d, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 8.0 Hz, 1H), 6.98 (t, *J* = 8.5 Hz, 2H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 5.09 (d, *J* = 15.5 Hz, 1H), 5.03 (d, *J* = 15.5 Hz, 1H), 4.12 (d, *J* = 7.5 Hz, 1H), 3.59 (d, *J* = 7.5 Hz, 1H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 191.9, 171.4, 162.6 (C-F, ¹*J*_{C-F} = 247.1 Hz), 143.2, 136.7, 136.0, 134.03, 133.96, 128.9, 128.6, 128.2, 127.8, 127.4, 124.6, 122.7, 122.5, 119.2, 115.6 (C-F, ²*J*_{C-F} = 21.6 Hz), 109.3, 83.3, 82.3, 44.4, 42.7, 41.0, 24.5 ppm.

¹⁹F NMR (470 MHz, CDCl₃): δ -111.1 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₃₂H₂₂FO₂Na 494.1527; Found 494.1524.



Yield: 123.0 mg, 25% (based on enone: 268.1 mg, 1.005 mmol).

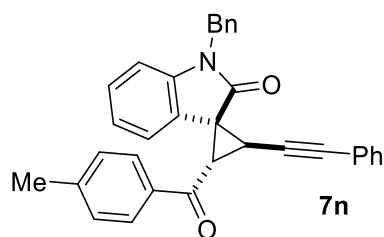
Red crystals, obtained by slow evaporation of the PE and EA solution at rt.

M.p. 141.9-143.0°C. Et₂O/DCM/PE = 1/2/50-1/2/10.

¹H NMR (500 MHz, CDCl₃): δ 7.93 (d, *J* = 7.5 Hz, 2H), 7.55 (t, *J* = 7.0 Hz, 1H), 7.46 (s, 1H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.36-7.25 (m, 7H), 7.23-7.18 (m, 2H), 7.13 (t, *J* = 7.5 Hz, 1H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.77 (d, *J* = 7.5 Hz, 1H), 5.09 (d, *J* = 15.5 Hz, 1H), 5.03 (d, *J* = 15.5 Hz, 1H), 4.13 (d, *J* = 7.5 Hz, 1H), 3.59 (d, *J* = 7.0 Hz, 1H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 191.8, 171.3, 143.2, 136.7, 136.0, 134.2, 134.1, 131.9, 130.3, 129.6, 128.95, 128.93, 128.6, 128.2, 127.8, 127.4, 124.8, 124.5, 122.7, 122.5, 109.3, 85.0, 81.9, 44.4, 42.6, 41.0, 24.3 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₃₂H₂₂ClO₂Na 510.1231; Found 510.1229.



Yield: 155.4 mg, 34% (based on enone: 239.8 mg, 0.9736 mmol).

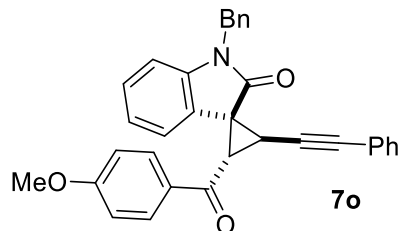
Red crystals, obtained by slow evaporation of the PE and EA solution at rt.

M.p. 159.0-160.1 °C. Et₂O/DCM/PE = 1/2/25-2/4/25.

¹H NMR (500 MHz, CDCl₃): δ 7.84 (d, *J* = 8.0 Hz, 2H), 7.48 (br s, 2H), 7.34-7.27 (m, 8H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 7.5 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.75 (d, *J* = 7.5 Hz, 1H), 5.09 (d, *J* = 16.0 Hz, 1H), 5.03 (d, *J* = 15.5 Hz, 1H), 4.13 (d, *J* = 7.5 Hz, 1H), 3.60 (d, *J* = 7.5 Hz, 1H), 2.38 (s, 3H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 191.5, 171.5, 145.1, 143.2, 136.0, 134.3, 132.1, 129.6, 128.9, 128.8, 128.33, 128.29, 128.0, 127.8, 127.41, 127.35, 124.8, 123.1, 122.6, 122.4, 109.2, 108.8, 83.7, 83.3, 44.4, 42.7, 40.9, 24.6, 21.9 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₃₃H₂₅NO₂Na 490.1777; Found 490.1788.



Yield: 136.9 mg, 28% (based on enone: 265.8 mg, 1.013 mmol).

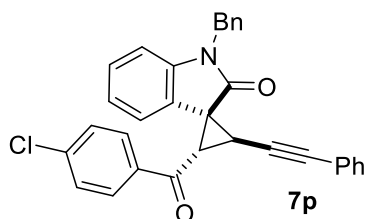
Red crystals, obtained by slow evaporation of the PE and EA solution at rt.

M.p. 146.0-146.9 °C. Et₂O/DCM/PE = 1/2/25-2/4/25.

¹H NMR (500 MHz, CDCl₃): δ 7.92 (d, *J* = 8.5 Hz, 2H), 7.48 (br s, 2H), 7.32-7.28 (m, 8H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 8.5 Hz, 2H), 6.75 (d, *J* = 7.5 Hz, 1H), 5.07 (d, *J* = 15.5 Hz, 1H), 5.02 (d, *J* = 15.5 Hz, 1H), 4.10 (d, *J* = 6.5 Hz, 1H), 3.81 (s, 3H), 3.59 (d, *J* = 6.5 Hz, 1H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 190.1, 171.5, 164.2, 143.1, 136.0, 132.1, 131.0, 129.9, 128.9, 128.30, 128.26, 128.0, 127.7, 127.4, 124.8, 123.1, 122.5, 122.4, 114.1, 109.1, 83.8, 83.2, 55.6, 44.3, 42.5, 40.8, 24.6 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₃₃H₂₅NO₃Na 506.1727; Found 506.1726.



Yield: 102.8 mg, 21% (based on enone: 268.1 mg, 1.005 mmol).

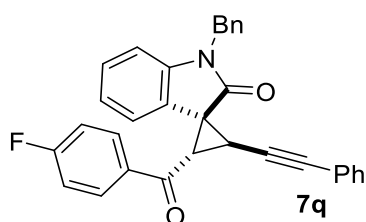
Red crystals, obtained by slow evaporation of the PE and EA solution at rt.

M.p. 168.1-168.9 °C. Et₂O/DCM/PE = 1/2/25-1/2/10.

¹H NMR (500 MHz, CDCl₃): δ 7.87 (d, *J* = 7.5 Hz, 2H), 7.48 (br s, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.33-7.27 (m, 8H), 7.17-7.12 (m, 2H), 6.93 (t, *J* = 7.0 Hz, 1H), 6.78 (d, *J* = 7.5 Hz, 1H), 5.10-5.02 (m, 2H), 4.09 (d, *J* = 7.5 Hz, 1H), 3.60 (d, *J* = 7.0 Hz, 1H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 190.9, 171.2, 143.2, 140.6, 136.0, 135.0, 132.1, 130.0, 129.3, 128.9, 128.39, 128.35, 128.2, 127.9, 127.4, 124.4, 123.0, 122.6, 122.4, 109.3, 83.5, 83.3, 44.4, 42.5, 41.1, 24.7 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₃₂H₂₂ClO₂Na 510.1231; Found 510.1231.



Yield: 155.9 mg, 33% (based on enone: 252.1 mg, 1.007 mmol).

Red crystals, obtained by slow evaporation of the PE and EA solution at rt.

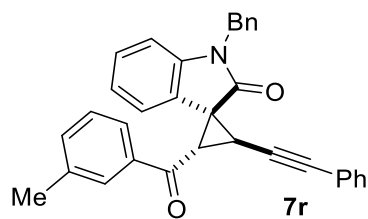
M.p. 168.9-170.3 °C. Et₂O/DCM/PE = 1/2/25-1/2/10.

¹H NMR (500 MHz, CDCl₃): δ 7.97-7.95 (m, 2H), 7.48 (br s, 2H), 7.33-7.30 (m, 8H), 7.17 (d, *J* = 7.5 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.08 (t, *J* = 8.5 Hz, 2H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 5.09-5.02 (m, 2H), 4.09 (d, *J* = 7.0 Hz, 1H), 3.59 (d, *J* = 7.5 Hz, 1H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 190.5, 171.3, 166.3 (C-F, ¹*J*_{C-F} = 254.3 Hz), 143.2, 136.0, 133.2, 131.4 (C-F, ³*J*_{C-F} = 10.3 Hz), 129.0, 128.4, 128.2, 127.9, 127.5, 124.5, 123.0, 122.7, 122.4, 116.1 (C-F, ²*J*_{C-F} = 21.8 Hz), 109.3, 83.5, 83.4, 44.4, 42.6, 41.0, 24.8 ppm.

¹⁹F NMR (470 MHz, CDCl₃): δ -103.4 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₃₂H₂₂FNO₂Na 494.1527; Found 494.1540.



Yield: 150.5 mg, 32% (based on enone: 248.0 mg, 1.007 mmol).

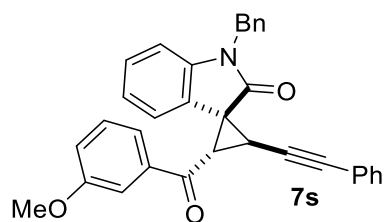
Red crystals, obtained by slow evaporation of the PE and EA solution at rt.

M.p. 149.9-150.1 °C. Et₂O/DCM/PE = 1/2/25-1/2/10.

¹H NMR (500 MHz, CDCl₃): δ 7.73 (d, *J* = 7.5 Hz, 2H), 7.48 (br s, 2H), 7.33 (d, *J* = 6.5 Hz, 3H), 7.31-7.29 (m, 6H), 7.24 (s, 1H), 7.20 (d, *J* = 7.0 Hz, 1H), 6.92 (t, *J* = 8.0 Hz, 1H), 6.76 (d, *J* = 7.5 Hz, 1H), 5.11 (d, *J* = 15.5 Hz, 1H), 5.00 (d, *J* = 16.0 Hz, 1H), 4.14 (d, *J* = 7.5 Hz, 1H), 3.61 (d, *J* = 7.5 Hz, 1H), 2.35 (s, 3H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 192.1, 171.4, 143.2, 138.8, 136.8, 136.0, 134.8, 132.1, 129.1, 128.9, 128.3, 128.1, 127.8, 127.4, 125.9, 124.7, 123.1, 122.6, 122.5, 109.2, 83.7, 83.3, 44.4, 42.7, 41.0, 24.7, 21.4 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₃₃H₂₅NO₂Na 490.1777; Found 490.1786.



Yield: 139.9 mg, 29% (based on enone: 263.9 mg, 1.006 mmol).

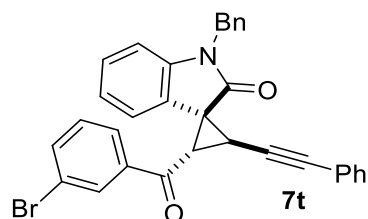
Red crystals, obtained by slow evaporation of the PE and EA solution at rt.

M.p. 137.4-138.3 °C. Et₂O/DCM/PE = 1/4/10-3/6/20.

¹H NMR (500 MHz, CDCl₃): δ 7.52-7.46 (m, 4H), 7.34-7.25 (m, 9H), 7.18 (d, *J* = 7.5 Hz, 1H), 7.14-7.09 (m, 2H), 6.93 (t, *J* = 8.0 Hz, 1H), 6.77 (d, *J* = 7.5 Hz, 1H), 5.11 (d, *J* = 15.5 Hz, 1H), 5.01 (d, *J* = 15.5 Hz, 1H), 4.13 (d, *J* = 7.5 Hz, 1H), 3.81 (s, 3H), 3.60 (d, *J* = 7.5 Hz, 1H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 191.8, 171.3, 160.0, 143.2, 138.1, 136.0, 132.1, 129.9, 128.9, 128.3, 128.1, 127.8, 127.4, 124.6, 123.1, 122.6, 122.4, 121.4, 120.7, 112.5, 109.2, 83.6, 83.4, 55.6, 44.4, 42.8, 41.1, 24.7 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₃₃H₂₅NO₃Na 506.1727; Found 506.1739.



Yield: 82.3 mg, 22% (based on enone: 222.1 mg, 0.7137 mmol).

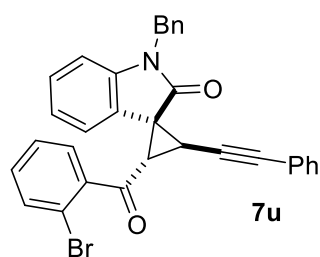
Red crystals, obtained by slow evaporation of the PE and EA solution at rt.

M.p. 148.0-149.2 °C. Et₂O/DCM/PE = 1/4/10-1/2/10.

¹H NMR (500 MHz, CDCl₃): δ 8.07 (s, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 7.5 Hz, 1H), 7.48 (br s, 2H), 7.33-7.27 (m, 9H), 7.18-7.12 (m, 2H), 6.94 (t, *J* = 8.0 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 5.12 (d, *J* = 16.0 Hz, 1H), 5.00 (d, *J* = 16.0 Hz, 1H), 4.08 (d, *J* = 7.5 Hz, 1H), 3.60 (d, *J* = 7.0 Hz, 1H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 190.8, 171.2, 143.2, 138.4, 136.9, 135.9, 132.1, 131.5, 130.5, 129.0, 128.41, 128.36, 128.3, 127.8, 127.43, 127.35, 127.2, 124.4, 123.3, 123.0, 122.7, 122.4, 109.3, 83.6, 83.3, 44.5, 42.7, 41.3, 24.8 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₃₂H₂₂BrNO₂Na 554.0726; Found 554.0723.



Yield: 255.2 mg, 48% (based on enone: 312.6 mg, 1.005 mmol).

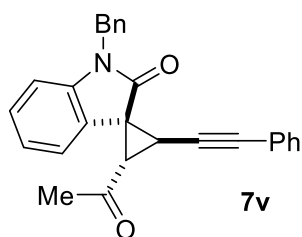
Red crystals, obtained by slow evaporation of the PE and EA solution at rt.

M.p. 133.5-135.1 °C. Et₂O/DCM/PE = 1/4/10-1/2/10.

¹H NMR (500 MHz, CDCl₃): δ 7.55 (d, *J* = 7.0 Hz, 1H), 7.48-7.46 (m, 2H), 7.43-7.40 (m, 2H), 7.37 (d, *J* = 7.5 Hz, 1H), 7.33-7.29 (m, 8H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.00 (t, *J* = 7.0 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 5.17 (d, *J* = 15.5 Hz, 1H), 4.89 (d, *J* = 15.5 Hz, 1H), 3.95 (d, *J* = 7.5 Hz, 1H), 3.65 (d, *J* = 7.5 Hz, 1H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 195.1, 171.1, 143.3, 140.3, 136.2, 134.1, 132.9, 132.1, 130.4, 128.9, 128.34, 128.30, 127.9, 127.8, 127.7, 124.7, 123.3, 123.0, 122.6, 120.3, 109.1, 83.8, 83.4, 46.2, 44.4, 43.1, 26.1 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₃₂H₂₂BrNO₂Na 554.0726; Found 554.0719.



Yield: 202.1 mg, 46% (based on enone: 191.0 mg, 1.122 mmol).

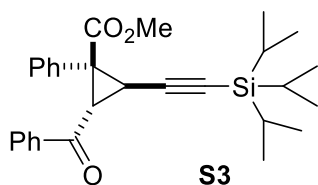
Red crystals, obtained by slow evaporation of the PE and EA solution at rt.

M.p. 102.9-103.8 °C. Et₂O/DCM/PE = 1/4/10-1/2/10.

¹H NMR (500 MHz, CDCl₃): δ 7.46 (d, *J* = 8.5 Hz, 2H), 7.35-7.29 (m, 8H), 7.24 (s, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 5.06 (d, *J* = 16.0 Hz, 1H), 4.98 (d, *J* = 15.5 Hz, 1H), 3.49 (d, *J* = 8.0 Hz, 1H), 3.35 (d, *J* = 7.5 Hz, 1H), 2.30 (s, 3H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 200.6, 171.3, 143.3, 136.0, 132.1, 128.9, 128.3, 128.2, 127.8, 127.5, 124.6, 123.0, 122.8, 122.6, 109.2, 83.38, 83.35, 45.2, 44.5, 40.9, 32.0, 25.1 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₇H₂₁NO₂Na 414.1464; Found 414.1475.



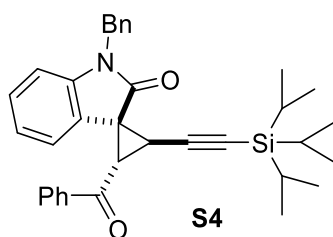
Yield: 454.6 mg, 49% (based on enone: 627.8 mg, 2.009 mmol).

Colorless oil. Et₂O/DCM/PE = 1/4/10-3/6/20.

¹H NMR (500 MHz, CDCl₃): δ 8.08 (d, *J* = 7.0 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.21-7.17 (m, 5H), 4.18 (d, *J* = 5.5 Hz, 1H), 3.75 (s, 3H), 3.33 (d, *J* = 5.5 Hz, 1H), 1.11 (s, 21H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 192.6, 169.4, 137.5, 133.6, 133.4, 129.9, 128.9, 128.6, 128.5, 128.2, 103.1, 82.3, 53.2, 48.3, 38.1, 20.5, 18.7, 11.3 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₉H₃₆SiO₃Na 483.2326; Found 483.2337.



Yield: 145.1 mg, 27% (based on enone: 314.0 mg, 1.005 mmol).

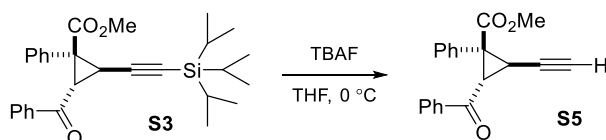
Colorless oil. Et₂O/DCM/PE = 1/4/10-3/6/20.

¹H NMR (500 MHz, CDCl₃): δ 7.94 (d, *J* = 7.5 Hz, 2H), 7.55 (t, *J* = 7.0 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.33-7.27 (m, 5H), 7.14 (d, *J* = 7.5 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.90 (t, *J* = 7.5 Hz, 1H), 6.74 (d, *J* = 7.5 Hz, 1H), 5.22 (d, *J* = 15.5 Hz, 1H), 4.85 (d, *J* = 15.5 Hz, 1H), 4.05 (d, *J* = 7.5 Hz, 1H), 3.45 (d, *J* = 8.0 Hz, 1H), 1.09 (s, 21H) ppm.

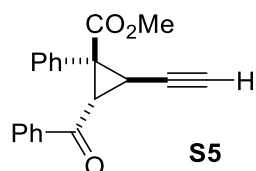
¹³C{¹H} NMR (125 MHz, CDCl₃): δ 192.1, 170.9, 143.3, 136.8, 136.1, 134.0, 128.9, 128.7, 128.0, 127.8, 127.7, 127.5, 124.8, 122.5, 122.4, 109.1, 100.7, 84.7, 44.3, 42.8, 41.0, 25.1, 18.7, 11.4 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₃₅H₃₉NSiO₂Na 556.2642; Found 556.2651.

Method C:



To the solution of **S3** (521.8 mg, 1.133 mmol) in THF (4.5 mL) at 0 °C, was added dropwise TBAF (4.5 mL, 4.5 mmol, 1.0 M) with stirring. After the completion of the reaction as monitored by TLC, the reaction was quenched with saturated aqueous NH₄Cl, and extracted with EA. The combined organics were washed with brine, dried over anhydrous Na₂SO₄, filtered, and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel eluted with EA/PE (1/20 to 1/10, v/v) to give **S5** (315.1 mg, 92%).



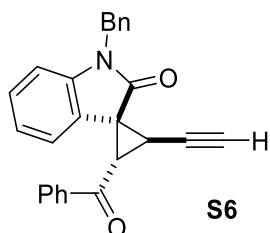
Yield: 315.1 mg, 91% (based on alkynylcyclopropane **S3**: 521.8 mg, 1.133 mmol).

Colorless crystals, obtained by slow evaporation of the PE and EA solution at rt.

M.p. 126.8-128.0 °C. EA/PE = 1/20-1/10.

¹H NMR (500 MHz, CDCl₃): δ 8.03 (d, *J* = 7.5 Hz, 2H), 7.61 (t, *J* = 7.0 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.21-7.20 (m, 3H), 7.12-7.11 (m, 2H), 4.17 (d, *J* = 6.5 Hz, 1H), 3.77 (s, 3H), 3.24 (d, *J* = 5.0 Hz, 1H), 2.12 (s, 1H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 192.3, 169.6, 137.4, 133.8, 133.1, 129.9, 129.0, 128.59, 128.55, 128.4, 79.8, 69.5, 53.5, 47.7, 37.6, 19.5 ppm.

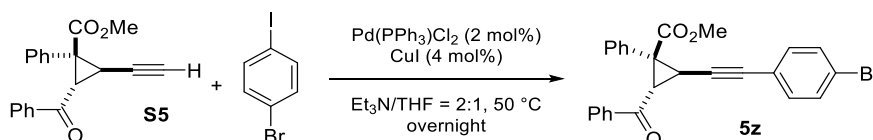


Yield: 290.5 mg, 82% (based on alkynylcyclopropane **S4**: 500.6 mg, 0.9378 mmol).

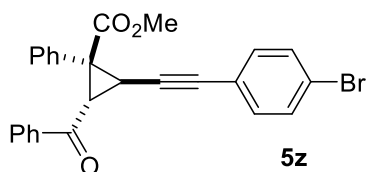
Colorless solid. M.p. 162.8-163.9 °C. EA/PE = 1/10-1/5.

¹H NMR (500 MHz, CDCl₃): δ 7.90 (d, *J* = 7.5 Hz, 2H), 7.55 (t, *J* = 7.0 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.34-7.27 (m, 5H), 7.14-7.10 (m, 2H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.75 (d, *J* = 7.5 Hz, 1H), 5.10 (d, *J* = 15.5 Hz, 1H), 5.02 (d, *J* = 15.5 Hz, 1H), 4.04 (d, *J* = 7.5 Hz, 1H), 3.41 (d, *J* = 7.5 Hz, 1H), 2.31 (s, 1H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 191.6, 171.4, 143.1, 136.6, 135.8, 134.0, 128.95, 128.91, 128.6, 128.2, 127.8, 127.4, 124.3, 122.7, 122.4, 109.4, 77.7, 71.4, 44.4, 42.3, 40.3, 23.2 ppm.



A mixture of **S5** (152.1 mg, 0.4998 mmol), 1-bromo-4-iodobenzene (213.2 mg, 0.75 mmol), Pd(PPh₃)₂Cl₂ (3.7 mg, 0.005 mmol), and CuI (2.0 mg, 0.105 mmol) in Et₃N (3.0 mL) and THF (1.5 mL) was stirred at 50 °C in an oil bath overnight. After cooling to room temperature, the solvent was evaporated. The residue was purified by flash column chromatography on silica gel eluted with Et₂O/DCM/PE (1/4/10 to 3/6/20, v/v/v) to afford **5z** (210.5 mg, 92%).

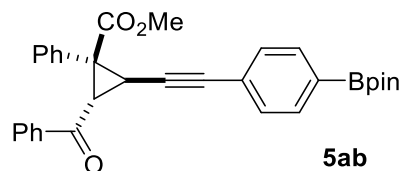


Yield: 210.5 mg, 92% (based on alkynylcyclopropane **S5**: 152.1 mg, 0.4998 mmol).

Colorless solid. M.p. 118.2-119.3 °C. Et₂O/DCM/PE = 1/4/10-3/6/20.

¹H NMR (500 MHz, CDCl₃): δ 8.06 (d, *J* = 7.5 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.23-7.21 (m, 3H), 7.17-7.16 (m, 2H), 4.25 (d, *J* = 6.0 Hz, 1H), 3.77 (s, 3H), 3.42 (d, *J* = 6.0 Hz, 1H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 192.5, 169.7, 137.5, 134.4, 133.7, 133.3, 133.2, 131.7, 130.0, 129.0, 128.61, 128.58, 128.4, 121.5, 86.8, 80.4, 53.4, 48.3, 38.0, 20.6 ppm.
HRMS (ESI) m/z: $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{26}\text{H}_{19}\text{BrO}_3\text{Na}$ 481.0410; Found 481.0420.

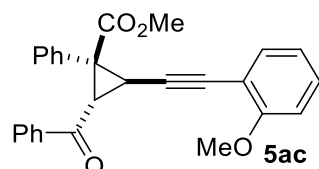


Yield: 144.7 mg, 49% (based on alkynylcyclopropane **S5**: 177.1 mg, 0.5819 mmol).
 Colorless solid. M.p. 105.6-106.8 °C. $\text{Et}_2\text{O}/\text{DCM}/\text{PE} = 1/4/10\text{-}3/6/20$.

^1H NMR (500 MHz, CDCl_3): δ 8.06 (d, $J = 8.0$ Hz, 2H), 7.74 (d, $J = 8.0$ Hz, 2H), 7.61 (t, $J = 7.5$ Hz, 1H), 7.51 (t, $J = 7.5$ Hz, 2H), 7.41 (d, $J = 7.5$ Hz, 2H), 7.22-7.21 (m, 3H), 7.17 (br s, 2H), 4.26 (d, $J = 6.0$ Hz, 1H), 3.77 (s, 3H), 3.43 (d, $J = 6.0$ Hz, 1H), 1.34 (s, 12H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 192.6, 169.7, 137.5, 137.1, 136.4, 134.7, 133.7, 133.3, 131.1, 130.0, 128.9, 128.62, 128.56, 128.3, 125.7, 86.9, 84.1, 81.5, 53.4, 48.4, 38.1, 25.0, 20.7 ppm.

HRMS (ESI) m/z: $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{32}\text{H}_{31}\text{BO}_5\text{Na}$ 529.2162; Found 529.2169.

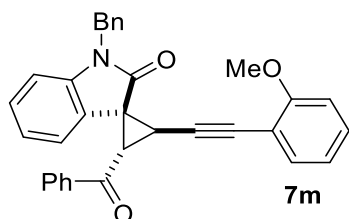


Yield: 204.6 mg, 66% (based on alkynylcyclopropane **S5**: 228.9 mg, 0.7521 mmol).
 Colorless solid. M.p. 137.8-139.2 °C. $\text{Et}_2\text{O}/\text{DCM}/\text{PE} = 1/4/10\text{-}3/6/20$.

^1H NMR (500 MHz, CDCl_3): δ 8.06 (d, $J = 7.5$ Hz, 2H), 7.60 (t, $J = 7.5$ Hz, 1H), 7.50 (t, $J = 7.5$ Hz, 2H), 7.38 (d, $J = 7.0$ Hz, 1H), 7.29-7.26 (m, 1H), 7.22-7.18 (m, 5H), 6.91-6.86 (m, 2H), 4.28 (d, $J = 6.0$ Hz, 1H), 3.89 (s, 3H), 3.79 (s, 3H), 3.49 (d, $J = 6.0$ Hz, 1H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 192.7, 169.8, 160.3, 137.6, 134.1, 133.6, 133.4, 130.0, 129.8, 128.9, 128.6, 128.5, 128.3, 120.6, 112.2, 110.8, 89.4, 77.6, 55.9, 53.3, 48.5, 38.2, 21.0 ppm.

HRMS (ESI) m/z: $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{27}\text{H}_{22}\text{O}_4\text{Na}$ 433.1410; Found 433.1422.



Yield: 123.0 mg, 25% (based on alkynylcyclopropane **S6**: 268.1 mg, 1.005 mmol).

Red crystals, obtained by slow evaporation of the PE and EA solution at rt.

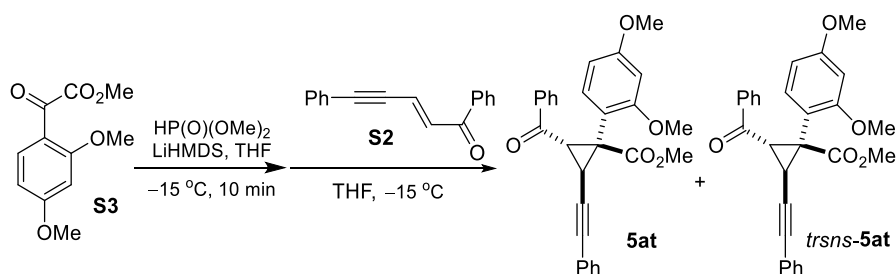
M.p. 128.1-129.7 °C. Et₂O/DCM/PE = 1/2/50-1/2/10.

¹H NMR (600 MHz, CDCl₃): δ 7.93 (d, *J* = 7.8 Hz, 2H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.48 (d, *J* = 7.2 Hz, 1H), 7.41 (d, *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 7.2 Hz, 2H), 7.31-7.24 (m, 4H), 7.19 (d, *J* = 7.2 Hz, 1H), 7.11 (t, *J* = 7.8 Hz, 1H), 6.93-6.88 (m, 2H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.74 (d, *J* = 7.8 Hz, 1H), 5.08 (d, *J* = 15.6 Hz, 1H), 5.03 (d, *J* = 15.6 Hz, 1H), 4.18 (d, *J* = 7.2 Hz, 1H), 3.87 (s, 3H), 3.68 (d, *J* = 7.2 Hz, 1H) ppm.

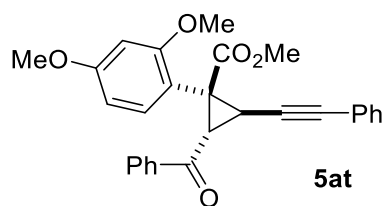
¹³C{¹H} NMR (150 MHz, CDCl₃): δ 192.0, 171.4, 160.4, 143.2, 136.8, 136.1, 134.5, 133.9, 129.8, 128.91, 128.88, 128.6, 128.0, 127.8, 127.4, 124.8, 122.6, 122.5, 120.6, 112.3, 110.7, 109.1, 87.6, 79.7, 56.0, 44.4, 42.8, 41.2, 25.2 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₃₃H₂₅NO₃Na 506.1727; Found 506.1732.

Method D:



To a solution of α-ketoester **S3** (449.0 mg, 2.0 mmol, 2.0 equiv) and dimethyl phosphite (0.18 mL, 2.0 mmol, 2.0 equiv) in THF (4.0 mL) cooled at −15 °C, was added dropwise 1.0 M LiHMDS in THF (2.0 mL, 2.0 mmol, 2.0 equiv) at −15 °C. After additional 10 min, a solution of chalcone **S2** (232.4 mg, 1.001 mmol, 1.0 equiv) in THF (5.0 mL) was added dropwise. The reaction was stirred at the same temperature and was monitored by TLC. Once **S2** was fully consumed, the reaction mixture was quenched with saturated aqueous NH₄Cl. After being warmed to rt, the mixture was extracted with EA. The combined organics were washed with brine, dried over anhydrous Na₂SO₄, filtered, and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel eluted with Et₂O/DCM/PE (1/4/10 to 1/2/10, v/v/v) to give **5at** (114.1 mg, 26%) and *trans*-**5at** (58.2 mg, 13%).



Yield: 114.1 mg, 26% (based on enone **S2**: 232.4 mg, 1.001 mmol).

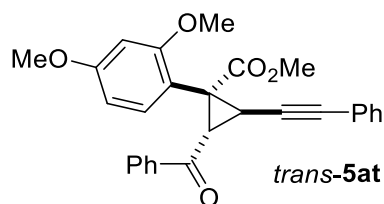
Colorless crystals, obtained by slow evaporation of the PE and EA solution at rt.

M.p. 99.4-100.6 °C. Et₂O/DCM/PE = 1/4/10-1/2/10.

¹H NMR (500 MHz, CDCl₃): δ 8.05 (d, *J* = 8.0 Hz, 2H), 7.55 (t, *J* = 7.0 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.42 (br s, 2H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.29 (br s, 3H), 6.50 (d, *J* = 8.0 Hz, 1H), 6.17 (s, 1H), 4.35 (d, *J* = 6.5 Hz, 1H), 3.76 (s, 3H), 3.75 (s, 3H), 3.34 (d, *J* = 6.5 Hz, 1H), 3.17 (s, 3H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 192.5, 169.9, 160.9, 158.4, 137.4, 133.0, 132.6, 131.9, 128.8, 128.4, 128.2, 123.2, 114.8, 104.2, 98.1, 85.8, 81.2, 55.3, 54.6, 53.2, 44.3, 37.8, 21.6 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₈H₂₄O₅Na 463.1516; Found 463.1528.



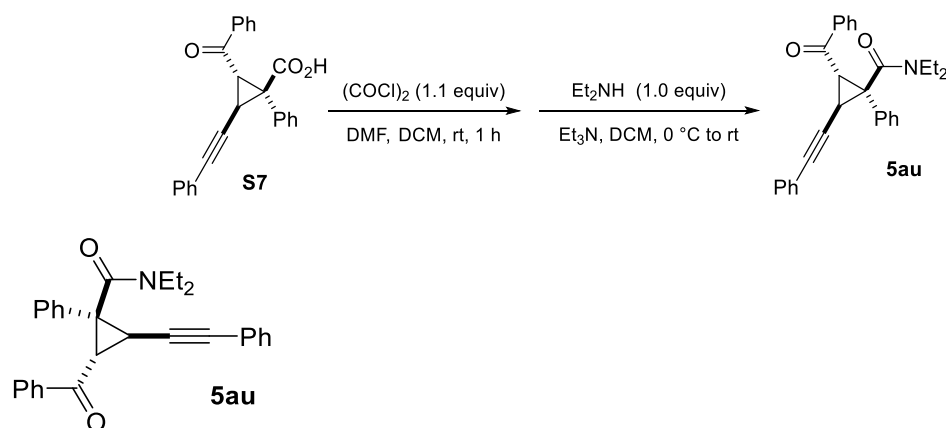
Yield: 58.2 mg, 13% (based on enone **S2**: 232.4 mg, 1.001 mmol).

Yellow oil. Et₂O/DCM/PE = 1/4/10-1/2/10.

¹H NMR (600 MHz, CDCl₃): δ 8.13 (d, *J* = 7.8 Hz, 2H), 7.61 (t, *J* = 7.2 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.23-7.19 (m, 3H), 7.10 (d, *J* = 6.6 Hz, 2H), 6.56-6.53 (m, 2H), 3.84 (s, 3H), 3.82 (s, 3H), 3.60 (s, 3H), 3.45 (d, *J* = 6.6 Hz, 1H), 3.41 (d, *J* = 6.0 Hz, 1H) ppm.

¹³C{¹H} NMR (150 MHz, CDCl₃): δ 194.2, 170.0, 161.2, 160.2, 137.1, 133.6, 131.9, 131.7, 128.8, 128.7, 128.3, 128.0, 123.3, 116.6, 104.4, 99.1, 86.8, 81.7, 55.9, 55.6, 52.8, 41.6, 40.1, 22.9 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₈H₂₄O₅Na 463.1516; Found 463.1528.



Synthesized from **S7** according to the procedure reported in the literature.³

Yield: 155.5 mg, 74% (based on **S7**: 175.8 mg, 0.4798 mmol).

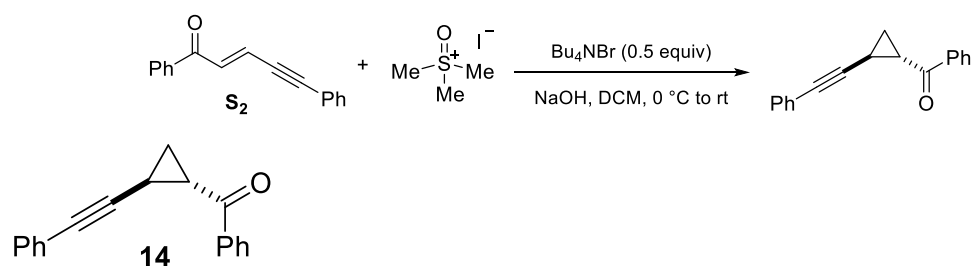
Colorless crystals, obtained by slow evaporation of the PE and EA solution at rt.

M.p. 115.2-116.0 °C. EA/PE = 1/20-1/5.

¹H NMR (500 MHz, CDCl₃): δ 8.19 (d, *J* = 7.5 Hz, 2H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.37-7.36 (m, 2H), 7.30-7.29 (m, 5H), 7.21-7.13 (m, 3H), 4.22 (d, *J* = 6.0 Hz, 1H), 3.75-3.66 (m, 3H), 3.20-3.16 (m, 1H), 3.11-3.06 (m, 1H), 1.09 (t, *J* = 7.0 Hz, 3H), 0.46 (t, *J* = 7.0 Hz, 3H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 193.4, 168.2, 137.5, 133.3, 133.2, 131.8, 128.9, 128.7, 128.6, 128.4, 128.3, 127.9, 123.0, 85.9, 80.9, 48.9, 41.6, 40.6, 40.0, 17.6, 12.5, 12.4 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₉H₂₇NO₂Na 444.1934; Found 444.1942.



Known compound. Synthesized according to the procedure reported in the literature.⁴

Yield: 97.0 mg, 39% (based on chalcone **S2**: 234.1 mg, 1.008 mmol).

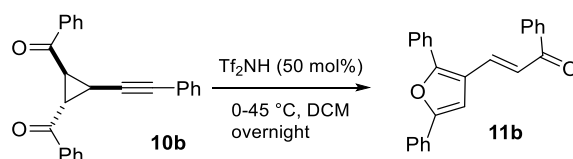
Yellow oil. EA/PE = 1/50-1/20.

¹H NMR (500 MHz, CDCl₃): δ 8.02 (d, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.0 Hz, 1H), 7.46 (t, *J* = 7.0 Hz, 1H), 7.40-7.39 (m, 2H), 7.26 (m, 3H), 3.05-3.02 (m, 1H), 2.24-2.22 (m, 1H), 1.74-1.71 (m, 1H), 1.46-1.43 (m, 1H) ppm.

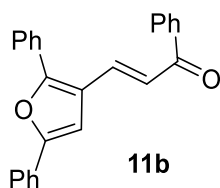
¹³C{¹H} NMR (125 MHz, CDCl₃): δ 197.7, 137.5, 133.3, 131.8, 128.8, 128.41, 128.36, 128.2, 123.3, 90.3, 78.1, 27.3, 19.9, 14.2 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₁₈H₁₄ONa 269.0937; Found 269.0934.

3. Tf₂NH-promoted reaction of **10b** and **10c**



To a dry Schlenk tube equipped with a high vacuum valve, **10b** (70.5 mg, 0.201 mmol) was dissolved in dry DCM (2.0 mL) with a stir bar. Tf₂NH (1.0 mL, 0.1 M in DCM, 0.10 mmol, 50 mol%) was added dropwise via microsyringe to the solution at 0 °C. The reaction mixture was then stirred at 45 °C in an oil bath overnight, which was then neutralized with saturated NaHCO₃. The mixture was extracted with DCM (20 mL × 3). The combined organics were washed with brine, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluted with EA/PE (1/30 to 1/10, v/v) to afford the product **11b** (63.4 mg, 90%) as yellow oil.



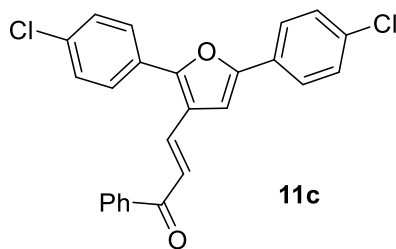
Yield: 63.4 mg, 90% (based on **10b**: 70.5 mg, 0.201 mmol).

Yellow oil. EA/PE = 1/30-1/10.

¹H NMR (500 MHz, CDCl₃): δ 8.09–8.05 (m, 3H), 7.79 (d, *J* = 7.0 Hz, 2H), 7.76 (d, *J* = 7.5 Hz, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.54–7.49 (m, 4H), 7.46–7.41 (m, 4H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.06 (s, 1H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 190.2, 155.2, 153.9, 138.4, 135.9, 132.9, 130.1, 130.0, 129.1, 129.0, 128.8, 128.6, 128.3, 127.6, 124.3, 122.7, 120.7, 104.3 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₅H₁₈O₂Na 373.1199; Found 373.1210.



Yield: 60.7 mg, 72% (based on **10c**: 84.2 mg, 0.201 mmol).

Colorless crystals, obtained by slow evaporation of the PE and DCM solution at rt.

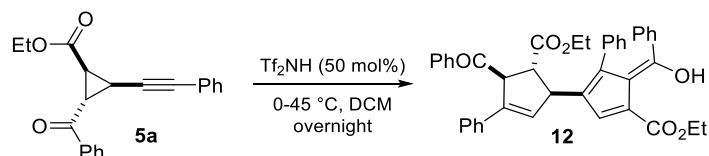
M.p. 141.9-143.0 °C. EA/PE = 1/30-1/10.

¹H NMR (500 MHz, CDCl₃): δ 8.04 (d, *J* = 7.5 Hz, 2H), 7.99 (d, *J* = 15.0 Hz, 1H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.67 (d, *J* = 8.5 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.45-7.41 (m, 3H), 7.05 (s, 1H) ppm.

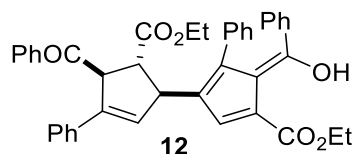
¹³C{¹H} NMR (125 MHz, CDCl₃): δ 189.9, 153.9, 153.0, 138.2, 135.2, 135.0, 134.2, 133.0, 129.4, 129.3, 128.8, 128.6, 128.3, 128.2, 125.5, 123.2, 121.1, 104.9 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₅H₁₆Cl₂NaO₂ 441.0420; Found 441.0417.

4. Tf₂NH-promoted reaction of **5a**



To a dry Schlenk tube equipped with a high vacuum valve, **5a** (63.5 mg, 0.199 mmol, 1.0 equiv) was dissolved in dry DCM (2.0 mL) with a stir bar. Tf₂NH (1.0 mL, 0.1 M in DCM, 0.10 mmol, 50 mol%) was added dropwise via microsyringe to the solution at 0 °C. The reaction mixture was stirred at 25 °C overnight, which was then neutralized with saturated NaHCO₃. The mixture was extracted with DCM (20 mL × 3). The combined organics were washed with brine, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluted with EA/PE (1/30 to 1/5, v/v) to afford the crude product **12** (44.1 mg) as red foam. Red crystals of **12** (32.4 mg, 51%) were obtained by slow evaporation of the PE and EA solution at rt.



Yield: 32.4 mg, 51% (based on **5a**: 63.5 mg, 0.199 mmol).

Red crystals, obtained by slow evaporation of the PE and EA solution at rt.

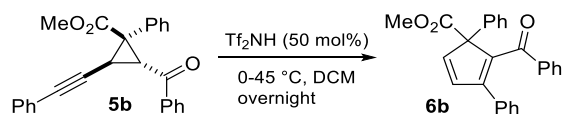
M.p. 151.7-153.1 °C. EA/PE = 1/30-1/5.

¹H NMR (500 MHz, CDCl₃): δ 16.2 (s, 1H), 8.06 (d, *J* = 7.5 Hz, 2H), 7.71 (s, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.26-7.24 (m, 2H), 7.20-7.16 (m, 5H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.95-6.89 (m, 5H), 6.83 (t, *J* = 7.5 Hz, 1H), 6.74 (d, *J* = 7.0 Hz, 1H), 6.07 (s, 1H), 5.43 (d, *J* = 6.5 Hz, 1H), 4.45 (q, *J* = 7.0 Hz, 2H), 4.24-4.22 (m, 1H), 3.96-3.86 (m, 2H), 3.29 (t, *J* = 6.5 Hz, 1H), 1.47 (t, *J* = 7.0 Hz, 3H), 0.97 (t, *J* = 7.0 Hz, 3H) ppm.

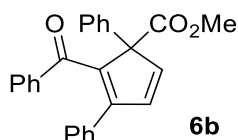
¹³C{¹H} NMR (125 MHz, CDCl₃): δ 201.1, 175.8, 173.7, 170.0, 143.2, 141.0, 137.5, 137.0, 136.8, 136.7, 135.9, 134.9, 133.6, 131.6, 131.2, 130.9, 130.0, 129.7, 128.91, 128.89, 128.5, 127.6, 127.3, 127.2, 127.1, 126.2, 126.0, 120.3, 118.3, 62.3, 61.1, 56.1, 55.9, 47.7, 14.6, 14.1 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₄₂H₃₆O₆Na 659.2404; Found 659.2412.

5. Alkynylcyclopropane-cyclopentadiene rearrangement of **5**



Representative procedure: To a dry Schlenk tube equipped with a high vacuum valve, **5b** (76.4 mg, 0.194 mmol, 1.0 equiv) was dissolved in dry DCM (2.0 mL) with a stir bar. $\text{ Tf}_2\text{NH}$ (1.0 mL, 0.1 M in DCM, 0.10 mmol, 50 mol%) was added dropwise via microsyringe to the solution at 0 °C. The reaction mixture was stirred at 45 °C in an oil bath overnight, which was then neutralized with saturated NaHCO_3 . The mixture was extracted with DCM (20 mL $\times$ 3). The combined organics were washed with brine, dried over anhydrous $\text{ Na}_2\text{SO}_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluted with EA/DCM/PE (1/4/40 to 1/4/20, v/v/v) to afford the cyclopentadiene product **6b** (57.2 mg, 75%) as yellow oil.



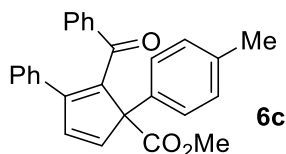
Yield: 57.2 mg, 75% (based on **5b**: 76.4 mg, 0.194 mmol).

Yellow oil. EA/DCM/PE = 1/4/40–1/4/20.

^1H NMR (500 MHz, CDCl_3): δ 7.41 (d, $J = 8.0$ Hz, 2H), 7.36 (d, $J = 8.5$ Hz, 2H), 7.26–7.20 (m, 4H), 7.17–7.13 (m, 3H), 7.06–7.03 (m, 3H), 6.99 (t, $J = 8.0$ Hz, 2H), 6.89 (d, $J = 5.5$ Hz, 1H), 6.84 (d, $J = 5.5$ Hz, 1H), 3.69 (s, 3H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 193.5, 170.4, 151.7, 143.8, 142.4, 137.8, 135.8, 135.1, 134.2, 132.0, 129.3, 128.83, 128.78, 128.5, 128.1, 127.8, 127.6, 74.8, 53.0 ppm.

HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{ C}_{26}\text{H}_{20}\text{O}_3\text{Na}$ 403.1305; Found 403.1314.



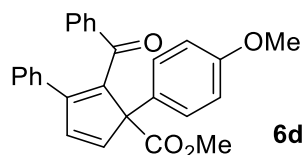
Yield: 66.4 mg, 87% (based on **5c**: 76.4 mg, 0.194 mmol).

Yellow oil. EA/PE = 1/8. EA/DCM/PE = 1/4/40–1/4/20.

^1H NMR (500 MHz, CDCl_3): δ 7.46 (d, $J = 7.5$ Hz, 2H), 7.28 (d, $J = 7.5$ Hz, 2H), 7.21–7.20 (m, 3H), 7.11–7.08 (m, 5H), 7.05 (t, $J = 7.5$ Hz, 2H), 6.91 (d, $J = 4.5$ Hz, 1H), 6.86 (d, $J = 5.0$ Hz, 1H), 3.73 (s, 3H), 2.30 (s, 3H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 193.6, 170.5, 151.6, 143.9, 142.5, 137.9, 137.4, 135.6, 134.3, 132.0, 131.9, 129.4, 129.2, 128.8, 128.7, 128.1, 127.8, 127.4, 74.6, 52.9, 21.2 ppm.

HRMS (ESI) m/z: $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{27}\text{H}_{22}\text{O}_3\text{Na}$ 417.1461; Found 417.1471.



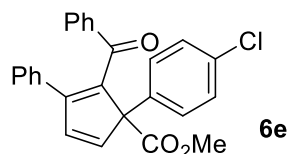
Yield: 50.1 mg, 61% (based on **5d**: 81.7 mg, 0.199 mmol).

Yellow oil. EA/DCM/PE = 1/4/40-1/4/20.

^1H NMR (500 MHz, CDCl_3): δ 7.46 (d, J = 7.5 Hz, 2H), 7.38 (d, J = 7.5 Hz, 2H), 7.29-7.20 (m, 4H), 7.14 (d, J = 8.5 Hz, 2H), 7.06 (t, J = 7.5 Hz, 2H), 6.90 (d, J = 5.0 Hz, 1H), 6.86 (d, J = 5.5 Hz, 1H), 6.61 (d, J = 8.5 Hz, 2H), 3.72 (s, 3H), 3.69 (s, 3H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 193.7, 170.6, 160.1, 151.4, 143.7, 140.9, 137.9, 135.8, 135.4, 131.9, 130.4, 129.4, 128.4, 127.9, 127.7, 127.6, 126.7, 113.6, 74.8, 55.3, 53.0 ppm.

HRMS (ESI) m/z: $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{27}\text{H}_{23}\text{O}_4$ 411.1591; Found 411.1595.



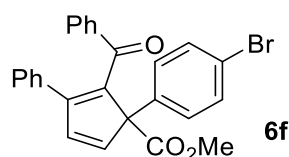
Yield: 71.1 mg, 89% (based on **5e**: 79.7 mg, 0.192 mmol).

Yellow oil. EA/DCM/PE = 1/4/40-1/4/20.

^1H NMR (500 MHz, CDCl_3): δ 7.42 (d, J = 7.0 Hz, 2H), 7.34 (d, J = 8.5 Hz, 2H), 7.26-7.24 (m, 2H), 7.21-7.18 (m, 3H), 7.12-7.07 (m, 3H), 7.04 (t, J = 7.0 Hz, 2H), 6.90 (d, J = 5.0 Hz, 1H), 6.88 (d, J = 5.0 Hz, 1H), 3.73 (s, 3H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 193.3, 170.1, 152.2, 143.5, 142.4, 137.7, 136.5, 134.0, 133.7, 133.6, 132.1, 129.3, 129.1, 129.0, 128.9, 128.6, 128.2, 127.9, 74.0, 53.1 ppm.

HRMS (ESI) m/z: $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{26}\text{H}_{20}\text{ClO}_3$ 415.1095; Found 415.1106.



Yield: 80.5 mg, 88% (based on **5f**: 91.8 mg, 0.200 mmol).

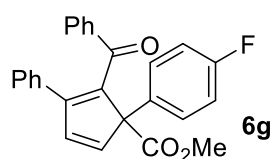
Yellow crystals, obtained by slow evaporation of the PE and EA solution at rt.

M.p. 182.5-183.5 °C. EA/DCM/PE = 1/4/40-1/4/20.

¹H NMR (500 MHz, CDCl₃): δ 7.42-7.39 (m, 4H), 7.29-7.27 (m, 2H), 7.21-7.17 (m, 3H), 7.12-7.07 (m, 3H), 7.04 (t, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 5.5 Hz, 1H), 6.87 (d, *J* = 5.0 Hz, 1H), 3.73 (s, 3H) ppm.

¹³C{¹H} NMR (150 MHz, CDCl₃): δ 193.3, 170.1, 152.2, 143.4, 142.3, 137.7, 136.5, 134.2, 134.0, 132.1, 131.5, 129.4, 129.3, 129.0, 128.9, 128.2, 127.9, 121.8, 74.0, 53.1 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₆H₁₉BrO₃Na 481.0410; Found 481.0409.



Yield: 72.3 mg, 91% (based on **5g**: 79.3 mg, 0.199 mmol).

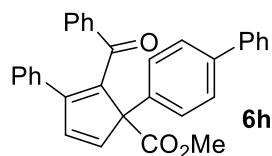
Yellow oil. EA/DCM/PE = 1/4/40-1/4/20.

¹H NMR (500 MHz, CDCl₃): δ 7.42 (d, *J* = 7.0 Hz, 2H), 7.40-7.37 (m, 2H), 7.21-7.18 (m, 3H), 7.13-7.05 (m, 3H), 7.03 (t, *J* = 8.0 Hz, 2H), 6.96 (t, *J* = 9.0 Hz, 2H), 6.89 (s, 2H), 3.73 (s, 3H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 193.4, 170.4, 162.3 (C-F, ¹*J*_{C-F} = 245.0 Hz), 152.0, 143.6, 142.6, 137.8, 136.3, 134.1, 132.1, 130.8, 129.4 (C-F, ³*J*_{C-F} = 9.3 Hz), 129.3, 128.9, 128.2, 127.9, 127.6, 115.3 (C-F, ²*J*_{C-F} = 21.6 Hz), 74.0, 53.1 ppm.

¹⁹F NMR (470 MHz, CDCl₃): δ -114.8 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₆H₁₉FO₃Na 421.1210; Found 421.1221.



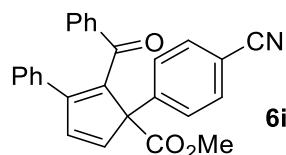
Yield: 76.3 mg, 83% (based on **5h**: 91.8 mg, 0.201 mmol).

Yellow oil. EA/DCM/PE = 1/4/40-1/4/20.

¹H NMR (500 MHz, CDCl₃): δ 7.56 (d, *J* = 7.0 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 4H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.0 Hz, 1H), 7.23-7.19 (m, 3H), 7.12-7.10 (m, 3H), 7.05 (t, *J* = 7.5 Hz, 2H), 6.96 (d, *J* = 5.0 Hz, 1H), 6.91 (d, *J* = 5.5 Hz, 1H), 3.76 (s, 3H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 193.6, 170.4, 152.0, 143.8, 142.4, 140.9, 140.6, 137.9, 136.0, 134.23, 134.18, 132.0, 129.4, 128.91, 128.87, 128.8, 128.2, 128.0, 127.8, 127.3, 127.24, 127.19, 74.6, 53.1 ppm.

HRMS (ESI) m/z: $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{32}\text{H}_{24}\text{O}_3\text{Na}$ 479.1618; Found 479.1628.



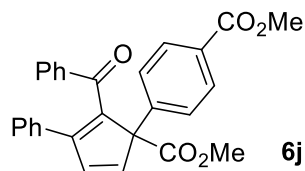
Yield: 66.3 mg, 82% (based on **5i**: 81.5 mg, 0.201 mmol).

Yellow oil. EA/DCM/PE = 1/4/40-1/4/20.

^1H NMR (500 MHz, CDCl_3): δ 7.57 (d, J = 8.5 Hz, 2H), δ 7.51 (d, J = 8.5 Hz, 2H), δ 7.40 (d, J = 7.5 Hz, 2H), 7.22-7.17 (m, 3H), 7.15-7.08 (m, 3H), 7.04 (t, J = 7.5 Hz, 2H), 6.95 (d, J = 5.0 Hz, 1H), 6.88 (d, J = 5.0 Hz, 1H), 3.75 (s, 3H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 193.1, 169.6, 152.8, 143.0, 141.9, 140.8, 137.4, 137.3, 133.7, 132.3, 132.2, 129.3, 129.2, 128.9, 128.5, 128.3, 127.9, 118.8, 111.6, 74.3, 53.3 ppm.

HRMS (ESI) m/z: $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{27}\text{H}_{19}\text{NO}_3\text{Na}$ 428.1527; Found 428.1266.



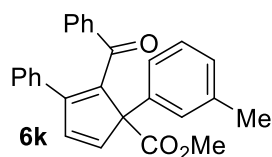
Yield: 75.1 mg, 86% (based on **5j**: 87.0 mg, 0.198 mmol).

Yellow oil. EA/DCM/PE = 1/4/40-1/4/20.

^1H NMR (500 MHz, CDCl_3): δ 7.95 (d, J = 8.5 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 7.5 Hz, 2H), 7.20-7.18 (m, 3H), 7.12-7.09 (m, 3H), 7.03 (t, J = 8.0 Hz, 2H), 6.93 (d, J = 5.5 Hz, 1H), 6.91 (d, J = 5.0 Hz, 1H), 3.87 (s, 3H), 3.75 (s, 3H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 193.2, 170.0, 166.9, 152.3, 143.4, 142.2, 140.5, 137.6, 136.7, 134.0, 132.1, 129.8, 129.5, 129.3, 129.0, 128.9, 128.2, 127.9, 127.6, 74.6, 53.2, 52.2 ppm.

HRMS (ESI) m/z: $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{28}\text{H}_{22}\text{O}_5\text{Na}$ 461.1359; Found 461.1365.



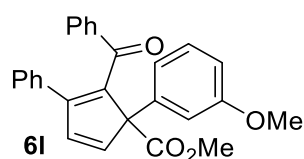
Yield: 64.4 mg, 82% (based on **5k**: 78.4 mg, 0.199 mmol).

Yellow oil. EA/DCM/PE = 1/4/40-1/4/20.

¹H NMR (500 MHz, CDCl₃): δ 7.46 (d, *J* = 7.5 Hz, 2H), 7.21-7.18 (m, 6H), 7.10-7.03 (m, 6H), 6.91 (d, *J* = 5.0 Hz, 1H), 6.86 (d, *J* = 5.0 Hz, 1H), 3.72 (s, 3H), 2.31 (s, 3H) ppm.

¹³C{¹H} NMR (150 MHz, CDCl₃): δ 193.7, 170.5, 151.6, 143.9, 142.3, 138.0, 137.9, 135.5, 135.0, 134.3, 132.0, 129.4, 128.84, 128.76, 128.6, 128.3, 128.1, 127.8, 124.6, 74.9, 52.9, 21.7 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₇H₂₂O₃Na 417.1461; Found 417.1464.



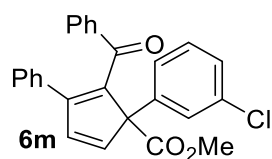
Yield: 68.9 mg, 85% (based on **5l**: 81.5 mg, 0.199 mmol).

Yellow oil. EA/DCM/PE = 1/4/40-1/4/20.

¹H NMR (500 MHz, CDCl₃): δ 7.46 (d, *J* = 8.0 Hz, 2H), 7.22-7.19 (m, 4H), 7.10-7.08 (m, 3H), 7.04 (t, *J* = 7.5 Hz, 2H), 7.01-6.97 (m, 2H), 6.91 (d, *J* = 5.0 Hz, 1H), 6.87 (d, *J* = 5.5 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 3.74 (s, 3H), 3.72 (s, 3H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 193.5, 170.3, 159.5, 151.6, 143.6, 142.2, 137.8, 136.5, 135.7, 134.2, 132.0, 129.4, 129.3, 128.82, 128.78, 128.1, 127.8, 120.1, 113.7, 113.0, 74.7, 55.3, 53.0 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₇H₂₂O₃Na 417.1461; Found 417.1467.



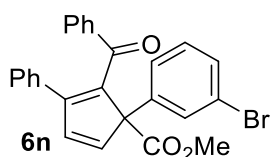
Yield: 61.2 mg, 74% (based on **5m**: 82.3 mg, 0.198 mmol).

Yellow oil. EA/DCM/PE = 1/4/40-1/4/20.

¹H NMR (500 MHz, CDCl₃): δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.38 (s, 1H), 7.33-7.32 (m, 1H), 7.22-7.19 (m, 5H), 7.12-7.08 (m, 3H), 7.05 (t, *J* = 7.5 Hz, 2H), 6.91 (d, *J* = 5.0 Hz, 1H), 6.88 (d, *J* = 5.0 Hz, 1H), 3.74 (s, 3H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 193.2, 169.9, 152.2, 143.3, 142.1, 137.7, 137.1, 136.6, 134.1, 134.0, 132.1, 129.6, 129.3, 129.0, 128.9, 128.2, 128.0, 127.9, 127.5, 126.2, 74.2, 53.1 ppm.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₆H₂₀ClO₃ 415.1095; Found 415.1101.



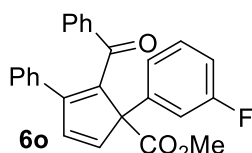
Yield: 81.2 mg, 88% (based on **5n**: 92.0 mg, 0.200 mmol).

Yellow oil. EA/DCM/PE = 1/4/40-1/4/20.

¹H NMR (500 MHz, CDCl₃): δ 7.50 (s, 1H), 7.43 (d, *J* = 7.5 Hz, 2H), 7.38-7.36 (m, 2H), 7.22-7.15 (m, 4H), 7.12-7.08 (m, 3H), 7.05 (t, *J* = 7.5 Hz, 2H), 6.92 (d, *J* = 5.0 Hz, 1H), 6.88 (d, *J* = 5.5 Hz, 1H), 3.74 (s, 3H) ppm.

¹³C{¹H} NMR (150 MHz, CDCl₃): δ 193.3, 169.9, 152.3, 143.3, 142.1, 137.7, 137.4, 136.6, 134.0, 132.1, 130.9, 130.2, 130.0, 129.3, 129.0, 128.9, 128.2, 127.9, 126.8, 122.3, 74.1, 53.2 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₆H₁₉BrO₃Na 481.0410; Found 417.0413.



Yield: 68.4 mg, 86% (based on **5o**: 80.0 mg, 0.201 mmol).

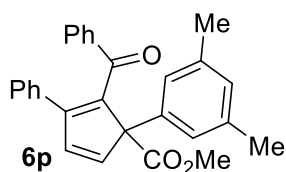
Yellow oil. EA/DCM/PE = 1/4/40-1/4/20.

¹H NMR (500 MHz, CDCl₃): δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.27-7.19 (m, 5H), 7.15-7.07 (m, 4H), 7.04 (t, *J* = 7.5 Hz, 2H), 6.96-6.92 (m, 1H), 6.91 (d, *J* = 5.0 Hz, 1H), 6.89 (d, *J* = 5.0 Hz, 1H), 3.74 (s, 3H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 193.3, 170.0, 162.7 (C-F, ¹*J*_{C-F} = 243.0 Hz), 152.1, 143.4, 142.2, 137.7, 137.5 (C-F, ³*J*_{C-F} = 8.3 Hz), 136.5, 134.0, 132.1, 129.8 (C-F, ³*J*_{C-F} = 7.1 Hz), 129.3, 129.0, 128.9, 128.2, 127.9, 123.4 (C-F, ⁴*J*_{C-F} = 3.1 Hz), 114.82, 114.77 (C-F, ²*J*_{C-F} = 23.9 Hz), 74.2, 53.1 ppm.

¹⁹F NMR (470 MHz, CDCl₃): δ -112.8 ppm.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₆H₂₀FO₃ 399.1391; Found 399.1392.



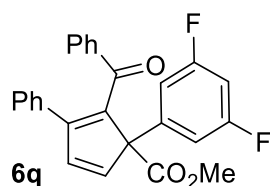
Yield: 68.4 mg, 83% (based on **5p**: 82.0 mg, 0.201 mmol).

Yellow oil. EA/DCM/PE = 1/4/40-1/4/20.

¹H NMR (500 MHz, CDCl₃): δ 7.47 (d, *J* = 7.0 Hz, 2H), 7.21-7.19 (m, 3H), 7.10-7.04 (m, 5H), 6.96 (s, 2H), 6.88 (br s, 2H), 6.84 (d, *J* = 5.5 Hz, 1H), 3.71 (s, 3H), 2.26 (s, 6H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 193.8, 170.5, 151.4, 144.0, 142.2, 138.0, 137.8, 135.2, 134.8, 134.3, 131.9, 129.6, 129.4, 128.8, 128.7, 128.2, 127.8, 125.3, 75.0, 52.9, 21.6 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₈H₂₄NaO₃ 431.1618; Found 431.1618.



Yield: 67.2 mg, 80% (based on **5q**: 83.5 mg, 0.200 mmol).

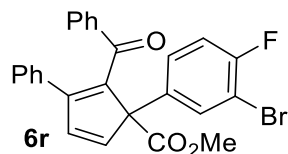
Yellow oil. EA/DCM/PE = 1/4/40-1/4/20.

¹H NMR (500 MHz, CDCl₃): δ 7.42 (d, *J* = 7.0 Hz, 2H), 7.22-7.18 (m, 3H), 7.13-7.08 (m, 3H), 7.05 (t, *J* = 7.5 Hz, 2H), 6.97 (d, *J* = 7.5 Hz, 2H), 6.92 (d, *J* = 5.0 Hz, 1H), 6.85 (d, *J* = 5.0 Hz, 1H), 6.69 (t, *J* = 8.5 Hz, 1H), 3.74 (s, 3H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 193.0, 169.6, 162.8 (C-F, ¹*J*_{C-F} = 246 Hz, ³*J*_{C-F} = 12.4 Hz), 152.6, 143.0, 142.0, 138.9 (C-F, ³*J*_{C-F} = 9.3 Hz), 137.6, 137.1, 133.8, 132.2, 129.3, 129.1, 128.9, 128.2, 127.9, 110.9 (C-F, ²*J*_{C-F} = 20.8 Hz, ⁴*J*_{C-F} = 6.3 Hz), 103.4 (C-F, ²*J*_{C-F} = 24.9 Hz), 73.7, 53.3 ppm.

¹⁹F NMR (470 MHz, CDCl₃): δ -109.7 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₆H₁₈F₂O₃Na 439.1116; Found 439.1121.



Yield: 77.5 mg, 81% (based on **5r**: 95.8 mg, 0.201 mmol).

Yellow oil. EA/DCM/PE = 1/4/40-1/4/20.

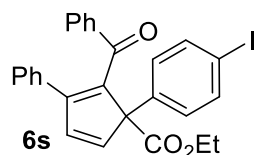
¹H NMR (500 MHz, CDCl₃): δ 7.59 (dd, *J* = 6.5, 2.0 Hz, 1H), δ 7.42 (d, *J* = 8.0 Hz, 2H), 7.39-7.36 (m, 1H), 7.22-7.18 (m, 3H), 7.14-7.07 (m, 3H), 7.06-7.01 (m, 3H), 6.93 (d, *J* = 5.0 Hz, 1H), 6.87 (d, *J* = 5.5 Hz, 1H), 3.74 (s, 3H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 193.1, 169.9, 158.5 (C-F, ¹*J*_{C-F} = 246.1 Hz), 152.5, 143.1, 142.3, 137.6, 136.9, 133.8, 132.5 (C-F, ⁴*J*_{C-F} = 3.1 Hz), 132.4, 132.2, 129.3,

129.1, 128.9 (C-F, $^3J_{\text{C-F}} = 7.3$ Hz), 128.2, 127.9, 116.3 (C-F, $^2J_{\text{C-F}} = 21.6$ Hz), 108.7 (C-F, $^2J_{\text{C-F}} = 20.6$ Hz), 73.3, 53.2 ppm.

^{19}F NMR (470 MHz, CDCl_3): δ -108.8 ppm.

HRMS (ESI) m/z: $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{26}\text{H}_{18}\text{BrFO}_3\text{Na}$ 499.0316; Found 499.0329.



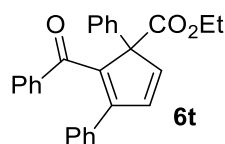
Yield: 77.5 mg, 81% (based on **5s**: 95.8 mg, 0.201 mmol).

Yellow oil. EA/DCM/PE = 1/4/40-1/4/20.

^1H NMR (500 MHz, CDCl_3): δ 7.60 (d, $J = 8.5$ Hz, 2H), 7.44 (d, $J = 7.5$ Hz, 2H), 7.22-7.07 (m, 8H), 7.04 (t, $J = 7.5$ Hz, 2H), 6.88-6.86 (m, 2H), 4.26-4.13 (m, 2H), 1.13 (t, $J = 7.5$ Hz, 3H) ppm.

^{13}C NMR (125 MHz, CDCl_3): δ 193.4, 169.4, 152.1, 143.6, 142.1, 137.7, 137.5, 136.2, 135.2, 134.1, 132.1, 129.6, 129.4, 128.9, 128.8, 128.2, 127.8, 93.4, 74.4, 62.2, 14.0 ppm.

HRMS (ESI) m/z: $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{27}\text{H}_{21}\text{IO}_3\text{Na}$ 543.0428; Found 543.0431.



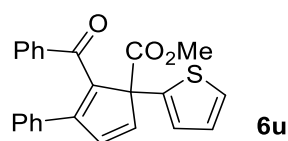
Yield: 63.1 mg, 81% (based on **5t**: 78.0 mg, 0.201 mmol).

Yellow oil. EA/DCM/PE = 1/4/40-1/4/20.

^1H NMR (500 MHz, CDCl_3): δ 7.47 (d, $J = 7.5$ Hz, 2H), δ 7.40 (d, $J = 7.5$ Hz, 2H), 7.37-7.24 (m, 3H), 7.21-7.18 (m, 3H), 7.10-7.09 (m, 3H), 7.04 (t, $J = 8.0$ Hz, 2H), 6.92 (d, $J = 4.5$ Hz, 1H), 6.86 (d, $J = 5.0$ Hz, 1H), 4.27-4.14 (m, 2H), 1.14 (t, $J = 7.0$ Hz, 3H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 193.6, 169.8, 151.6, 144.0, 142.4, 137.9, 135.4, 135.3, 134.4, 132.0, 129.4, 128.80, 128.76, 128.5, 128.2, 127.8, 127.7, 127.5, 75.1, 62.0, 14.0 ppm.

HRMS (ESI) m/z: $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{27}\text{H}_{23}\text{O}_3$ 395.1642; Found 395.1648.



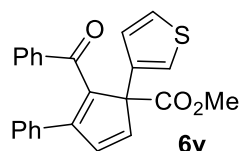
Yield: 59.6 mg, 77% (based on **5u**: 77.2 mg, 0.200 mmol).

Yellow oil. EA/DCM/PE = 1/4/40-1/4/20.

¹H NMR (500 MHz, CDCl₃): δ 7.36-7.31 (m, 5H), 7.28-7.21 (m, 3H), 7.18 (br s, 3H), 7.02-7.01 (m, 1H), 6.87-6.85 (m, 2H), 6.63 (s, 1H), 3.69 (s, 3H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 185.9, 170.2, 150.2, 144.5, 143.2, 142.1, 135.2, 135.0, 134.4, 133.7, 133.3, 128.9, 128.6, 128.5, 128.4, 127.8, 127.4, 75.0, 52.9 ppm.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₄H₁₉O₃S 387.1049; Found 387.1056.



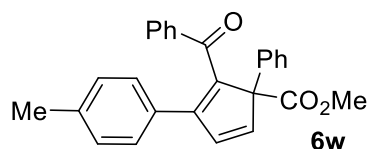
Yield: 64.1 mg, 83% (based on **5v**: 77.5 mg, 0.199 mmol).

Yellow oil. EA/DCM/PE = 1/4/40-1/4/20.

¹H NMR (500 MHz, CDCl₃): δ 7.44 (d, *J* = 7.5 Hz, 2H), 7.36 (br s, 1H), 7.22-7.17 (m, 4H), 7.11-7.03 (m, 6H), 6.90 (d, *J* = 5.5 Hz, 1H), 6.87 (d, *J* = 5.0 Hz, 1H), 3.74 (s, 3H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 193.4, 170.1, 152.0, 143.0, 142.3, 137.7, 136.1, 134.2, 134.1, 132.1, 129.4, 128.9, 128.8, 128.1, 127.8, 127.7, 124.9, 122.5, 71.0, 53.1 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₄H₁₈O₃SNa 409.0869; Found 409.0880.



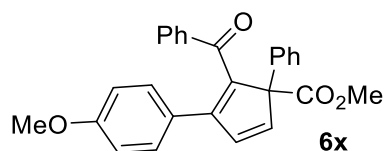
Yield: 59.3 mg, 76% (based on **5w**: 78.5 mg, 0.199 mmol).

Yellow oil. EA/DCM/PE = 1/4/40-1/4/20.

¹H NMR (500 MHz, CDCl₃): δ 7.46 (d, *J* = 7.0 Hz, 2H), 7.39 (d, *J* = 7.5 Hz, 2H), 7.29-7.19 (m, 4H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.05 (t, *J* = 7.5 Hz, 2H), 6.90-6.86 (m, 4H), 3.72 (s, 3H), 2.20 (s, 3H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 193.8, 170.5, 151.6, 143.6, 141.6, 138.9, 137.9, 135.8, 135.3, 131.9, 131.3, 129.4, 128.8, 128.5, 127.8, 127.7, 127.6, 74.9, 52.9, 21.3 ppm.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₇H₂₃O₃ 395.1642; Found 395.1650.



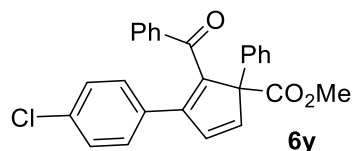
Yield: 66.6 mg, 81% (based on **5x**: 82.0 mg, 0.200 mmol).

Yellow oil. EA/DCM/PE = 1/4/40-1/4/20.

¹H NMR (500 MHz, CDCl₃): δ 7.47 (d, *J* = 7.5 Hz, 2H), 7.39 (d, *J* = 7.0 Hz, 2H), 7.28-7.21 (m, 4H), 7.14 (d, *J* = 8.5 Hz, 2H), 7.06 (t, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 5.5 Hz, 1H), 6.86 (d, *J* = 5.0 Hz, 1H), 6.61 (d, *J* = 8.5 Hz, 2H), 3.72 (s, 3H), 3.69 (s, 3H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 193.7, 170.6, 160.0, 151.4, 143.7, 140.9, 137.9, 135.8, 135.4, 131.9, 130.4, 129.4, 128.4, 127.9, 127.7, 127.6, 126.6, 113.6, 74.8, 55.3, 52.9 ppm.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₇H₂₃O₄ 411.1591; Found 411.1592.



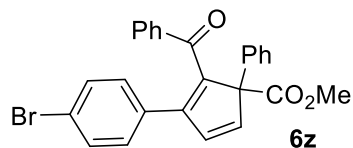
Yield: 72.5 mg, 87% (based on **5y**: 82.9 mg, 0.200 mmol).

Yellow oil. EA/DCM/PE = 1/4/40-1/4/20.

¹H NMR (500 MHz, CDCl₃): δ 7.43 (d, *J* = 7.5 Hz, 2H), 7.36 (d, *J* = 7.5 Hz, 2H), 7.30-7.24 (m, 4H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.09-7.05 (m, 4H), 6.93 (d, *J* = 5.0 Hz, 1H), 6.84 (d, *J* = 5.0 Hz, 1H), 3.72 (s, 3H) ppm.

¹³C NMR (125 MHz, CDCl₃): δ 193.4, 170.2, 150.2, 144.0, 142.9, 137.6, 135.4, 134.84, 134.78, 132.7, 132.3, 130.1, 129.3, 128.5, 128.4, 128.0, 127.9, 127.5, 75.0, 53.1 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₇H₂₂O₃Na 417.1461; Found 417.1467.



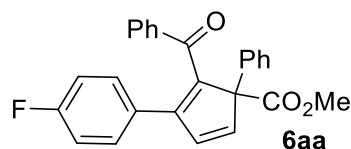
Yield: 74.2 mg, 81% (based on **5z**: 92.1 mg, 0.201 mmol).

Yellow oil. EA/DCM/PE = 1/4/40-1/4/20.

¹H NMR (500 MHz, CDCl₃): δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 7.0 Hz, 2H), 7.30-7.19 (m, 6H), 7.10-7.05 (m, 4H), 6.93 (d, *J* = 5.0 Hz, 1H), 6.83 (d, *J* = 5.0 Hz, 1H), 3.72 (s, 3H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 193.4, 170.1, 150.1, 144.0, 142.9, 137.6, 135.2, 134.8, 133.1, 132.3, 131.4, 130.3, 129.3, 128.5, 128.0, 127.9, 127.5, 123.1, 75.1, 53.0 ppm.

HRMS (ESI) m/z: $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{26}\text{H}_{20}\text{BrO}_3$ 459.0590; Found 459.0594.



Yield: 61.2 mg, 76% (based on **5aa**: 80.2 mg, 0.201 mmol).

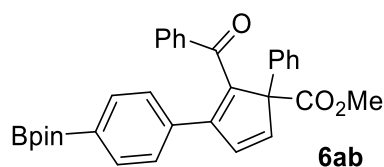
Yellow oil. EA/DCM/PE = 1/4/40-1/4/20.

^1H NMR (500 MHz, CDCl_3): δ 7.43 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 7.5 Hz, 2H), 7.30-7.22 (m, 4H), 7.18-7.16 (m, 2H), 7.06 (t, J = 7.5 Hz, 2H), 6.93 (d, J = 5.0 Hz, 1H), 6.84 (d, J = 5.0 Hz, 1H), 6.78 (t, J = 8.5 Hz, 2H), 3.73 (s, 3H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 193.4, 170.3, 163.8, 161.8, 150.5, 144.0, 142.5, 137.7, 135.6, 135.0, 132.2, 130.7, 130.6, 130.40, 130.38, 129.3, 128.5, 127.94, 127.86, 127.6, 115.3, 115.2, 74.9, 53.0 ppm.

^{19}F NMR (470 MHz, CDCl_3): δ -111.7 ppm.

HRMS (ESI) m/z: $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{26}\text{H}_{20}\text{FO}_3$ 399.1391; Found 399.1395.



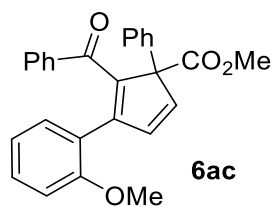
Yield: 76.1 mg, 75% (based on **5ab**: 101.0 mg, 0.199 mmol).

Yellow oil. EA/DCM/PE = 1/4/40-1/4/20.

^1H NMR (500 MHz, CDCl_3): δ 7.53 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 7.5 Hz, 2H), 7.37 (d, J = 7.5 Hz, 2H), 7.30-7.27 (m, 2H), 7.24-7.18 (m, 4H), 7.05 (t, J = 7.5 Hz, 2H), 6.91 (d, J = 5.0 Hz, 1H), 6.87 (d, J = 5.5 Hz, 1H), 3.71 (s, 3H), 1.30 (m, 12H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 193.8, 170.4, 151.0, 143.6, 142.6, 137.7, 136.8, 135.6, 135.1, 134.6, 132.2, 129.4, 128.5, 128.1, 128.0, 127.8, 127.5, 84.0, 75.1, 53.0, 25.0 ppm.

HRMS (ESI) m/z: $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{32}\text{H}_{31}\text{BO}_5\text{Na}$ 529.2162; Found 529.2174.



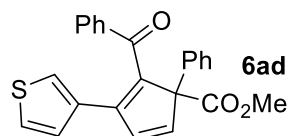
Yield: 66.0 mg, 80% (based on **5ac**: 82.0 mg, 0.200 mmol).

Yellow oil. EA/DCM/PE = 1/4/40-1/4/20.

¹H NMR (500 MHz, CDCl₃): δ 7.43-7.42 (m, 4H), 7.29-7.23 (m, 3H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.06-6.98 (m, 4H), 6.85 (d, *J* = 5.0 Hz, 1H), 6.81 (d, *J* = 5.0 Hz, 1H), 6.66 (t, *J* = 7.5 Hz, 1H), 6.57 (d, *J* = 8.0 Hz, 1H), 3.75 (s, 3H), 3.68 (s, 3H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 192.6, 170.7, 156.6, 149.8, 143.5, 142.7, 138.2, 137.0, 135.5, 131.5, 130.6, 130.3, 128.9, 128.3, 127.7, 127.6, 127.4, 124.1, 120.2, 110.3, 73.6, 55.1, 52.9 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₇H₂₂O₄Na 433.1410; Found 433.1420.



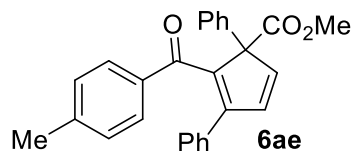
Yield: 66.4 mg, 85% (based on **5ad**: 77.5 mg, 0.201 mmol).

Yellow oil. EA/DCM/PE = 1/4/40-1/4/20.

¹H NMR (500 MHz, CDCl₃): δ 7.54 (d, *J* = 7.5 Hz, 2H), 7.36 (d, *J* = 7.0 Hz, 2H), 7.32-7.23 (m, 4H), 7.20 (s, 1H), 7.15 (t, *J* = 7.0 Hz, 2H), 7.02 (br s, 1H), 6.90 (d, *J* = 5.0 Hz, 2H), 6.85 (t, *J* = 5.5 Hz, 2H), 3.69 (s, 3H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 193.7, 170.4, 145.0, 143.5, 140.9, 137.9, 135.3, 135.2, 135.1, 132.3, 129.3, 128.5, 128.1, 128.0, 127.8, 127.5, 126.2, 125.7, 74.9, 52.9 ppm.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₄H₁₉O₃S 387.1049; Found 387.1053.



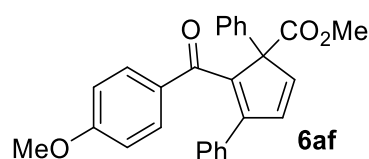
Yield: 65.1 mg, 83% (based on **5ae**: 77.4 mg, 0.199 mmol).

Yellow oil. EA/DCM/PE = 1/4/40-1/4/20.

¹H NMR (500 MHz, CDCl₃): δ 7.38-7.36 (m, 4H), 7.29-7.22 (m, 5H), 7.12-7.10 (m, 3H), 6.90 (d, *J* = 5.5 Hz, 1H), 6.87 (d, *J* = 5.0 Hz, 1H), 6.84 (d, *J* = 7.5 Hz, 2H), 3.71 (s, 3H), 2.18 (s, 3H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 193.5, 170.5, 150.8, 143.4, 142.7, 142.4, 135.6, 135.21, 135.18, 134.3, 129.6, 128.8, 128.7, 128.6, 128.5, 128.2, 127.8, 127.6, 75.0, 52.9, 21.6 ppm.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₇H₂₃O₃ 392.1642; Found 395.1652.



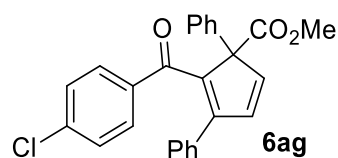
Yield: 67.6 mg, 82% (based on **5af**: 82.2 mg, 0.202 mmol).

Yellow oil. EA/DCM/PE = 1/4/40-1/4/20.

¹H NMR (500 MHz, CDCl₃): δ 7.47 (d, *J* = 7.5 Hz, 2H), 7.39 (d, *J* = 7.5 Hz, 2H), 7.29-7.20 (m, 4H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.06 (t, *J* = 7.5 Hz, 2H), 6.90 (d, *J* = 5.0 Hz, 1H), 6.86 (d, *J* = 5.5 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 2H), 3.72 (s, 3H), 3.69 (s, 3H) ppm.

¹³C{¹H} NMR (150 MHz, CDCl₃): δ 193.7, 170.6, 160.0, 151.4, 143.7, 140.9, 137.9, 135.8, 135.4, 131.9, 130.4, 129.4, 128.4, 127.9, 127.7, 127.6, 126.6, 113.6, 74.7, 55.3, 52.9 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₇H₂₂O₄Na 433.1410; Found 433.1421.



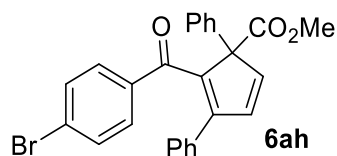
Yield: 75.3 mg, 91% (based on **5ag**: 82.3 mg, 0.198 mmol).

Yellow oil. EA/DCM/PE = 1/4/40-1/4/20.

¹H NMR (500 MHz, CDCl₃): δ 7.43 (d, *J* = 7.5 Hz, 2H), 7.36 (d, *J* = 7.5 Hz, 2H), 7.30-7.24 (m, 4H), 7.12 (d, *J* = 9.0 Hz, 2H), 7.09-7.05 (m, 4H), 6.93 (d, *J* = 5.0 Hz, 1H), 6.83 (d, *J* = 5.0 Hz, 1H), 3.72 (s, 3H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 193.4, 170.2, 150.1, 144.0, 142.9, 137.7, 135.3, 134.9, 134.8, 132.7, 132.3, 130.1, 129.3, 128.5, 128.4, 128.0, 127.9, 127.5, 75.0, 53.0 ppm.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₆H₂₀ClO₃ 415.1095; Found 415.1099.



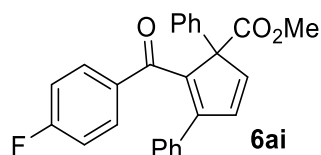
Yield: 73.5mg, 80% (based on **5ah**: 91.7 mg, 0.200 mmol).

Yellow oil. EA/DCM/PE = 1/4/40-1/4/20.

¹H NMR (500 MHz, CDCl₃): δ 7.35-7.28 (m, 7H), 7.18-7.11 (m, 7H), 6.94 (d, *J* = 5.0 Hz, 1H), 6.88 (d, *J* = 5.5 Hz, 1H), 3.74 (s, 3H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 192.5, 170.2, 151.9, 144.0, 142.0, 136.7, 135.6, 134.9, 134.0, 131.1, 130.8, 129.1, 128.8, 128.5, 128.4, 127.9, 127.4, 127.0, 75.0, 53.0 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₆H₁₉BrO₃Na 481.0410; Found 481.0416.



Yield: 74.2 mg, 81% (based on **5ai**: 92.1 mg, 0.201 mmol).

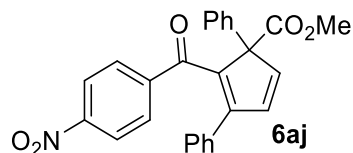
Yellow oil. EA/DCM/PE = 1/4/40-1/4/20.

¹H NMR (500 MHz, CDCl₃): δ 7.46 (dd, *J* = 8.5, 6.0 Hz, 2H), 7.35 (d, *J* = 7.0 Hz, 2H), 7.30-7.24 (m, 3H), δ 7.19 (d, *J* = 7.0 Hz, 2H), 7.15-7.11 (m, 3H), 6.92 (d, *J* = 5.0 Hz, 1H), 6.87 (d, *J* = 5.0 Hz, 1H), 6.71 (t, *J* = 8.5 Hz, 2H), 3.74 (s, 3H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 192.1, 170.3, 165.0 (C-F, ¹*J*_{C-F} = 252.3 Hz), 151.6, 143.8, 142.2, 135.7, 135.0, 134.2 (C-F, ⁴*J*_{C-F} = 3.1 Hz), 134.1, 131.9 (C-F, ³*J*_{C-F} = 9.3 Hz), 129.0, 128.8, 128.5, 128.3, 127.8, 127.5, 114.9 (C-F, ²*J*_{C-F} = 21.6 Hz), 74.9, 53.0 ppm.

¹⁹F NMR (470 MHz, CDCl₃): δ -106.8 ppm.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₆H₂₀FO₃ 399.1391; Found 399.1393.



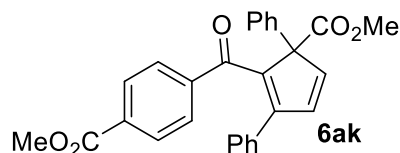
Yield: 76.7 mg, 90% (based on **5aj**: 85.1 mg, 0.200 mmol).

Yellow oil. EA/DCM/PE = 1/4/40-1/4/20.

¹H NMR (500 MHz, CDCl₃): δ 7.87 (d, *J* = 8.5 Hz, 2H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 7.0 Hz, 2H), 7.33-7.28 (m, 3H), 7.17 (d, *J* = 7.0 Hz, 2H), 7.13-7.08 (m, 3H), 6.99 (d, *J* = 4.5 Hz, 1H), 6.90 (d, *J* = 5.0 Hz, 1H), 3.78 (s, 3H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 191.3, 170.1, 153.8, 149.3, 145.0, 143.2, 142.1, 135.8, 134.6, 133.8, 130.1, 129.6, 128.8, 128.6, 128.5, 128.1, 127.4, 123.0, 75.0, 53.2 ppm.

HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{26}\text{H}_{19}\text{NO}_5\text{Na}$ 448.1155; Found 448.1165.



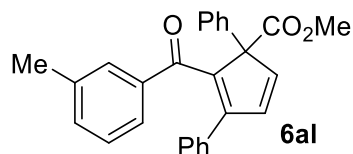
Yield: 69.5 mg, 81% (based on **5ak**: 73.2 mg, 0.167 mmol).

Yellow oil. EA/DCM/PE = 1/4/40-1/4/20.

^1H NMR (500 MHz, CDCl_3): δ 7.70 (d, J = 8.0 Hz, 2H), 7.48 (d, J = 7.5 Hz, 2H), 7.38 (d, J = 7.0 Hz, 2H), 7.29-7.26 (m, 3H), 7.18 (d, J = 6.5 Hz, 2H), 7.09-7.08 (m, 3H), 6.95 (d, J = 5.0 Hz, 1H), 6.88 (d, J = 4.5 Hz, 1H), 3.84 (s, 3H), 3.75 (s, 3H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 192.7, 170.2, 166.4, 152.7, 144.3, 142.2, 141.6, 135.8, 134.9, 133.9, 132.5, 129.2, 129.1, 129.0, 128.8, 128.5, 128.3, 127.9, 127.4, 74.9, 53.0, 52.3 ppm.

HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{28}\text{H}_{22}\text{O}_5\text{Na}$ 461.1359; Found 461.1364.



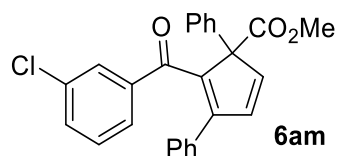
Yield: 61.8 mg, 78% (based on **5al**: 78.9 mg, 0.200 mmol).

Yellow oil. EA/DCM/PE = 1/4/40-1/4/20.

^1H NMR (500 MHz, CDCl_3): δ 7.39 (d, J = 7.5 Hz, 2H), 7.30-7.26 (m, 2H), 7.26-7.23 (m, 3H), 7.19 (d, J = 6.5 Hz, 2H), 7.10-7.09 (m, 3H), 7.00 (d, J = 7.0 Hz, 1H), 6.93-6.91 (m, 2H), 6.87 (d, J = 5.0 Hz, 1H), 3.73 (s, 3H), 2.10 (s, 3H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 193.5, 170.5, 151.9, 143.8, 142.7, 137.7, 137.4, 136.0, 135.2, 134.5, 132.7, 130.1, 128.8, 128.5, 128.1, 127.8, 127.73, 127.67, 126.7, 74.7, 53.0, 21.1 ppm.

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{27}\text{H}_{23}\text{O}_3$ 395.1642; Found 395.1650.



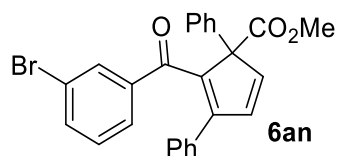
Yield: 71.0 mg, 85% (based on **5am**: 83.1 mg, 0.200 mmol).

Yellow oil. EA/DCM/PE = 1/4/40-1/4/20.

¹H NMR (500 MHz, CDCl₃): δ 7.38-7.36 (m, 3H), 7.31-7.26 (m, 4H), 7.19-7.13 (m, 6H), 6.98-6.94 (m 2H), 6.87 (d, *J* = 5.0 Hz, 1H), 3.76 (s, 3H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 191.8, 170.2, 152.9, 144.4, 142.2, 139.5, 135.9, 134.9, 134.1, 134.0, 131.8, 129.5, 129.1, 128.7, 128.6, 128.3, 127.9, 127.5, 127.4, 74.8, 53.1 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₆H₁₉ClO₃Na 437.0915; Found 437.0923.



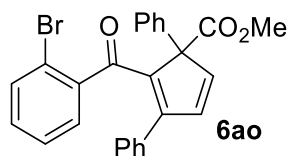
Yield: 87.9 mg, 95% (based on **5an**: 92.1 mg, 0.201 mmol).

Yellow oil. EA/DCM/PE = 1/4/40-1/4/20.

¹H NMR (500 MHz, CDCl₃): δ 7.54 (s, 1H), 7.38-7.26 (m, 7H), 7.19-7.13 (m, 5H), 6.95-6.87 (m, 3H), 3.76 (s, 3H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 191.6, 170.2, 153.0, 144.4, 142.2, 139.6, 135.9, 134.9, 134.7, 134.1, 132.4, 129.4, 129.2, 128.7, 128.5, 128.3, 127.9, 127.8, 127.5, 122.0, 74.8, 53.1 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₆H₁₉BrO₃Na 481.0410; Found 481.0406.



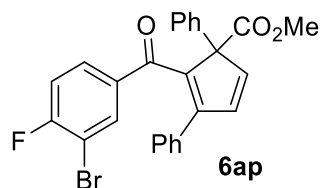
Yield: 72.6 mg, 80% (based on **5ao**: 91.0 mg, 0.198 mmol).

Yellow oil. EA/DCM/PE = 1/4/40-1/4/20.

¹H NMR (500 MHz, CDCl₃): δ 7.49 (d, *J* = 8.0 Hz, 2H), 7.32-7.26 (m, 3H), 7.21-7.17 (m, 3H), 7.08 (br s, 3H), 6.98 (d, *J* = 5.5 Hz, 2H), 6.86-6.83 (m, 3H), 6.79 (d, *J* = 5.0 Hz, 1H), 3.81 (s, 3H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 190.0, 170.3, 156.6, 145.9, 143.9, 140.6, 137.5, 135.0, 134.2, 133.1, 130.8, 130.1, 128.7, 128.5, 128.3, 128.1, 127.84, 127.79, 126.4, 120.8, 73.4, 53.1 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₆H₁₉BrO₃Na 481.0410; Found 481.0423.



Yield: 90.5 mg, 95% (based on **5ap**: 95.0 mg, 0.199 mmol).

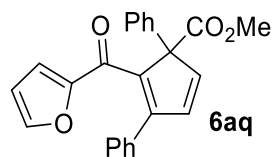
Yellow oil. EA/DCM/PE = 1/4/40-1/4/20.

¹H NMR (500 MHz, CDCl₃): δ 7.63 (d, *J* = 5.5 Hz, 1H), 7.38-7.27 (m, 6H), 7.18-7.15 (m, 5H), 6.95 (d, *J* = 5.5 Hz, 1H), 6.87 (d, *J* = 5.0 Hz, 1H), 6.77 (t, *J* = 8.0 Hz, 1H), 3.76 (s, 3H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 190.5, 170.2, 161.1 (C-F, ¹*J*_{C-F} = 253.3 Hz), 152.8, 144.4, 142.0, 135.8, 135.2 (C-F, ³*J*_{C-F} = 6.1 Hz), 134.8, 134.0, 130.4 (C-F, ³*J*_{C-F} = 9.3 Hz), 129.3, 128.7, 128.6, 128.4, 128.0, 127.4, 115.9 (C-F, ²*J*_{C-F} = 21.8 Hz), 108.7 (C-F, ²*J*_{C-F} = 21.8 Hz), 74.9, 53.1 ppm.

¹⁹F NMR (470 MHz, CDCl₃): δ -101.4 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₆H₁₈BrFO₃Na 499.0316; Found 499.0321.



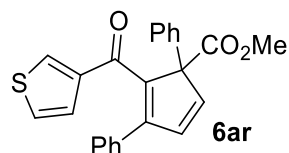
Yield: 62.1 mg, 83% (based on **5aq**: 74.5 mg, 0.201 mmol).

Yellow oil. EA/DCM/PE = 1/4/40-1/4/20.

¹H NMR (500 MHz, CDCl₃): δ 7.37 (d, *J* = 7.0 Hz, 2H), 7.34-7.33 (m, 2H), 7.29-7.23 (m, 5H), 7.11 (s, 1H), 6.89 (d, *J* = 5.0 Hz, 1H), 6.86 (d, *J* = 5.0 Hz, 1H), 6.63 (d, *J* = 3.0 Hz, 1H), 6.13 (br s, 1H), 3.74 (s, 3H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 180.4, 170.2, 152.6, 151.7, 145.9, 143.7, 141.7, 135.6, 135.0, 134.8, 128.8, 128.48, 128.45, 128.3, 127.8, 127.6, 118.7, 111.9, 74.6, 53.0 ppm.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₄H₁₉O₄ 371.1278; Found 371.1286.



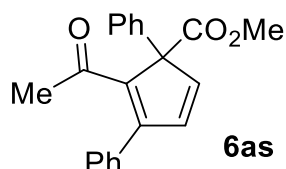
Yield: 65.3 mg, 84% (based on **5ar**: 78.0 mg, 0.202 mmol).

Yellow oil. EA/DCM/PE = 1/4/40-1/4/20.

¹H NMR (500 MHz, CDCl₃): δ 7.37-7.33 (m, 5H), 7.30-7.23 (m, 3H), 7.21-7.20 (m, 3H), 7.03 (d, *J* = 3.5 Hz, 1H), 6.89 (d, *J* = 5.0 Hz, 1H), 6.87 (d, *J* = 5.0 Hz, 1H), 6.65 (t, *J* = 4.5 Hz, 1H), 3.71 (s, 3H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 185.9, 170.2, 150.2, 144.5, 143.2, 142.1, 135.2, 135.0, 134.4, 133.8, 133.3, 128.9, 128.6, 128.52, 128.45, 127.8, 127.4, 75.1, 52.9 ppm.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₄H₁₉O₃S 387.1049; Found 387.1058.



Yield: 35.6 mg, 56% (based on **5as**: 63.7 mg, 0.200 mmol).

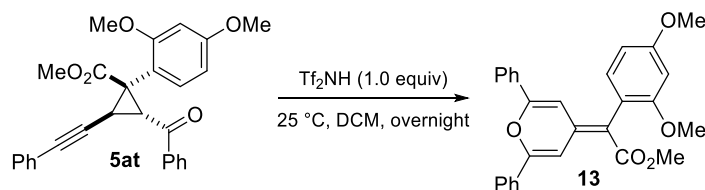
Yellow oil. EA/DCM/PE = 1/4/40-1/4/20.

¹H NMR (500 MHz, CDCl₃): δ 7.46-7.41 (m, 5H), 7.36 (d, *J* = 7.5 Hz, 2H), 7.30-7.26 (m, 3H), 6.79 (d, *J* = 5.0 Hz, 1H), 6.66 (d, *J* = 4.5 Hz, 1H), 3.76 (s, 3H), 1.89 (s, 3H) ppm.

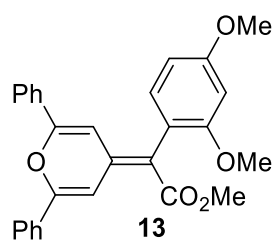
¹³C{¹H} NMR (125 MHz, CDCl₃): δ 195.5, 170.3, 153.8, 145.8, 144.6, 137.0, 135.6, 135.1, 129.2, 128.8, 128.38, 128.35, 127.8, 127.7, 73.0, 53.0, 30.1 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₁H₁₈O₃Na 341.1148; Found 341.1153.

6. Tf₂NH-promoted rearrangement of **5at**



To a dry Schlenk tube equipped with a high vacuum valve, **5at** (88.6 mg, 0.201 mmol, 1.0 equiv) was dissolved in dry DCM (2.0 mL) with a stir bar. Tf₂NH (2.0 mL, 0.1 M in DCM, 0.20 mmol, 1.0 equiv) was added dropwise via microsyringe to the solution at 0 °C. The reaction mixture was stirred at 25 °C overnight, which was then neutralized with saturated NaHCO₃. The mixture was extracted with DCM (20 mL × 3). The combined organics were washed with brine, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluted with EA/DCM/PE (1/4/40 to 1/4/20, v/v/v) to afford the product **13** (63.5 mg, 72%) as yellow-green crystals.



Yield: 63.5 mg, 72% (based on **5at**: 88.6 mg, 0.201 mmol).

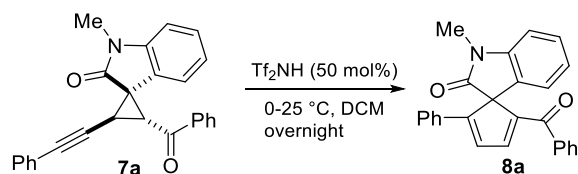
Yellow-green crystals, obtained by slow evaporation of the PE and DCM solution at rt. M.p. 155.8-157.1 °C. EA/DCM/PE = 1/4/40-1/4/20.

¹H NMR (500 MHz, CDCl₃): δ 8.46 (s, 1H), 7.91 (d, *J* = 7.0 Hz, 2H), 7.62 (d, *J* = 2.5 Hz, 2H), 7.47-7.39 (m, 6H), 7.11 (d, *J* = 8.5 Hz, 1H), 6.58-6.57 (m, 2H), 6.36 (s, 1H), 3.88 (s, 3H), 3.78 (s, 3H), 3.68 (s, 3H) ppm.

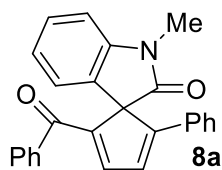
¹³C{¹H} NMR (125 MHz, CDCl₃): δ 169.2, 160.3, 159.1, 154.8, 154.6, 140.7, 133.2, 133.0, 132.5, 129.9, 128.8, 125.6, 125.3, 119.8, 108.5, 105.5, 105.1, 104.6, 99.1, 55.8, 55.5, 51.4 ppm.

HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₈H₂₄O₅Na 463.1516; Found 463.1521.

7. Alkynylcyclopropane-cyclopentadiene rearrangement of 7



Representative procedure: To a dry Schlenk tube equipped with a high vacuum valve, **7a** (75.5 mg, 0.200 mmol, 1.0 equiv) was dissolved in dry DCM (2.0 mL) with a stir bar. Tf_2NH (1.0 mL, 0.1 M in DCM, 0.10 mmol, 50 mol%) was added dropwise via microsyringe to the solution at 0 °C. The reaction mixture was stirred at 25 °C overnight, which was then neutralized with saturated NaHCO_3 . The mixture was extracted with DCM (20 mL $\times$ 3). The combined organics were washed with brine, dried over anhydrous Na_2SO_4 , filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluted with EA/DCM/PE (1/4/20 to 1/4/10, v/v/v) to afford the spiro cyclopentadiene product **8a** (65.1 mg, 86%) as yellow-red crystals.



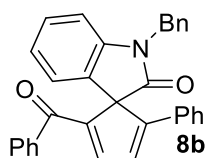
Yield: 65.1 mg, 86% (based on **7a**: 75.5 mg, 0.200 mmol).

Yellow-red crystals, obtained by slow evaporation of the PE and DCM solution at rt. M.p. 159.2-161.5 °C. EA/DCM/PE = 1/4/20-1/4/10.

^1H NMR (500 MHz, CDCl_3): δ 7.69 (d, J = 7.5 Hz, 2H), 7.51 (t, J = 7.0 Hz, 1H), 7.43-7.41 (m, 3H), 7.30 (t, J = 7.5 Hz, 1H), 7.19-7.14 (m, 6H), 7.02 (d, J = 7.5 Hz, 1H), 6.92 (t, J = 7.0 Hz, 1H), 6.86 (d, J = 7.0 Hz, 1H), 3.45 (s, 3H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 188.8, 173.1, 156.1, 148.2, 147.3, 145.6, 138.6, 133.1, 132.0, 130.7, 129.1, 129.03, 128.96, 128.9, 128.4, 126.8, 126.2, 122.9, 122.5, 109.3, 68.4, 27.6 ppm.

HRMS (ESI) m/z: $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{26}\text{H}_{19}\text{NO}_2\text{Na}$ 400.1308; Found 400.1311.



Yield: 83.9 mg, 93% (based on **7b**: 90.5 mg, 0.200 mmol).

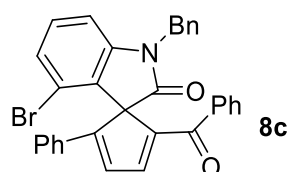
Yellow-red crystals, obtained by slow evaporation of the PE and DCM solution at rt.

M.p. 149.6-150.8 °C. EA/DCM/PE = 1/4/20-3/12/40.

¹H NMR (500 MHz, CDCl₃): δ 7.73 (d, *J* = 7.0 Hz, 2H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.45-7.43 (m, 5H), 7.35-7.28 (m, 3H), 7.20-7.10 (m, 7H), 6.88 (br s, 3H), 5.36 (d, *J* = 15.5 Hz, 1H), 4.90 (d, *J* = 16.0 Hz, 1H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 188.7, 173.0, 156.5, 148.2, 147.5, 144.9, 138.7, 136.0, 133.1, 132.0, 130.7, 129.03, 128.99, 128.8, 128.4, 128.0, 127.7, 126.7, 126.5, 122.9, 122.6, 110.4, 68.5, 45.2 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₃₂H₂₃NO₂Na 476.1621; Found 476.1623.



Yield: 83.7 mg, 78% (based on **7c**: 106.8 mg, 0.201 mmol).

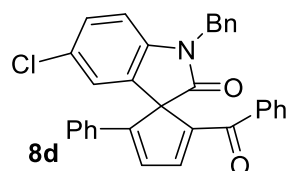
Yellow-red crystals, obtained by slow evaporation of the PE and DCM solution at rt.

M.p. 203.6-205.0 °C. EA/DCM/PE = 1/4/20-3/12/40.

¹H NMR (500 MHz, CDCl₃): δ 7.84 (d, *J* = 7.5 Hz, 2H), 7.56-7.50 (m, 2H), 7.45 (t, *J* = 7.0 Hz, 2H), 7.34-7.30 (m, 5H), 7.25-7.21 (m, 2H), 7.15-7.09 (m, 4H), 7.05 (t, *J* = 7.5 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.79 (d, *J* = 7.5 Hz, 1H), 5.32 (d, *J* = 15.5 Hz, 1H), 4.86 (d, *J* = 16.0 Hz, 1H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 189.2, 171.9, 154.3, 148.7, 146.4, 145.9, 138.5, 135.5, 133.4, 132.5, 132.2, 130.4, 129.4, 129.1, 128.90, 128.86, 128.4, 127.8, 126.8, 126.59, 126.57, 119.1, 108.8, 69.7, 45.4 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₃₂H₂₂BrNO₂Na 554.0726; Found 554.0734.



Yield: 85.2 mg, 88% (based on **7d**: 97.0 mg, 0.199 mmol).

Yellow-red crystals, obtained by slow evaporation of the PE and DCM solution at rt.

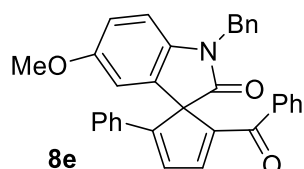
M.p. 158.8-159.6 °C. EA/DCM/PE = 1/4/20-3/12/40.

¹H NMR (500 MHz, CDCl₃): δ 7.73-7.72 (m, 2H), 7.54 (t, *J* = 7.0 Hz, 1H), 7.46-7.40 (m, 5H), 7.36-7.31 (m, 3H), 7.23 (t, *J* = 7.0 Hz, 1H), 7.16-7.11 (m, 4H), 7.08 (d, *J* = 8.0

Hz, 2H), 6.85 (d, $J = 2.0$ Hz, 1H), 6.80 (d, $J = 8.0$ Hz, 2H), 5.32 (d, $J = 15.5$ Hz, 1H), 4.87 (d, $J = 15.5$ Hz, 1H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 188.7, 172.6, 156.1, 147.9, 147.8, 143.5, 138.5, 135.5, 132.7, 132.2, 131.0, 129.3, 129.0, 128.9, 128.7, 128.5, 128.1, 128.0, 127.9, 126.5, 123.0, 111.2, 68.2, 45.3 ppm.

HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{32}\text{H}_{22}\text{ClNO}_2\text{Na}$ 510.1231; Found 510.1246.



Yield: 82.5 mg, 86% (based on **7e**: 95.8 mg, 0.198 mmol).

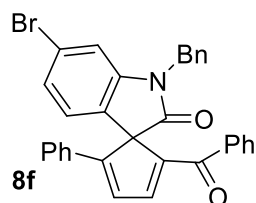
Yellow-red crystals, obtained by slow evaporation of the PE and DCM solution at rt.

M.p. 163.5-164.1 °C. EA/DCM/PE = 1/4/40-1/4/20.

^1H NMR (500 MHz, CDCl_3): δ 7.74 (d, $J = 7.5$ Hz, 2H), 7.53 (t, $J = 7.5$ Hz, 1H), 7.45-7.43 (m, 5H), 7.35-7.29 (m, 3H), 7.23-7.20 (m, 1H), 7.15-7.12 (m, 5H), 6.79 (d, $J = 9.0$ Hz, 1H), 6.70 (dd, $J = 8.5, 2.0$ Hz, 1H), 6.51 (s, 1H), 5.33 (d, $J = 15.5$ Hz, 1H), 4.88 (d, $J = 15.5$ Hz, 1H), 3.63 (s, 3H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 188.7, 172.8, 156.5, 156.0, 148.1, 147.5, 138.7, 138.3, 136.0, 133.0, 132.0, 130.6, 129.03, 128.98, 128.82, 128.80, 128.4, 128.2, 128.0, 127.7, 126.6, 112.8, 110.6, 110.2, 68.7, 55.6, 45.2 ppm.

HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{33}\text{H}_{25}\text{NNaO}_3$ 506.1727; Found 506.1730.



Yield: 86.3 mg, 81% (based on **7f**: 106.2 mg, 0.199 mmol).

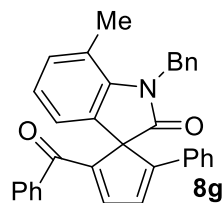
Yellow-red crystals, obtained by slow evaporation of the PE and DCM solution at rt.

M.p. 192.1-193.2 °C. EA/DCM/PE = 1/4/40-1/4/20.

^1H NMR (500 MHz, CDCl_3): δ 7.71 (d, $J = 7.5$ Hz, 2H), 7.53 (t, $J = 7.5$ Hz, 1H), 7.45-7.40 (m, 5H), 7.36-7.31 (m, 3H), 7.23 (t, $J = 7.0$ Hz, 1H), 7.13-7.12 (m, 3H), 7.07 (d, $J = 7.5$ Hz, 2H), 7.02 (d, $J = 6.5$ Hz, 2H), 6.73 (d, $J = 8.0$ Hz, 1H), 5.32 (d, $J = 15.5$ Hz, 1H), 4.84 (d, $J = 15.5$ Hz, 1H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 188.7, 172.9, 156.1, 147.9, 147.7, 146.2, 138.5, 135.4, 132.8, 132.2, 131.0, 129.3, 129.02, 128.97, 128.5, 128.0, 126.5, 125.9, 123.8, 122.5, 113.7, 68.0, 45.3 ppm.

HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{32}\text{H}_{22}\text{BrNO}_2\text{Na}$ 554.0726; Found 554.0727.



Yield: 80.7 mg, 87% (based on **7g**; 93.1 mg, 0.199 mmol).

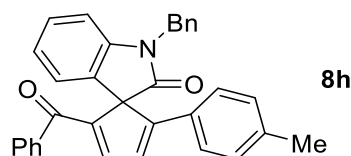
Yellow-red crystals, obtained by slow evaporation of the PE and DCM solution at rt.

M.p. 182.0-183.2 °C. EA/DCM/PE = 1/4/20-3/12/40.

^1H NMR (500 MHz, CDCl_3): δ 7.70 (d, J = 8.0 Hz, 2H), 7.49 (t, J = 7.5 Hz, 1H), 7.42-7.39 (m, 3H), 7.26-7.17 (m, 8H), 7.14 (d, J = 7.5 Hz, 2H), 7.05 (d, J = 2.5 Hz, 1H), 6.95 (d, J = 7.5 Hz, 1H), 6.80 (t, J = 7.5 Hz, 1H), 6.75 (d, J = 7.0 Hz, 1H), 5.42 (d, J = 17.0 Hz, 1H), 5.20 (d, J = 17.0 Hz, 1H), 2.33 (s, 3H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 188.8, 174.0, 157.0, 148.5, 147.5, 143.2, 138.8, 138.2, 133.4, 133.1, 132.0, 130.9, 129.1, 129.0, 128.8, 128.4, 127.1, 126.8, 126.7, 126.4, 122.9, 120.8, 120.5, 68.4, 46.4, 19.1 ppm.

HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{33}\text{H}_{25}\text{NO}_2\text{Na}$ 490.1777; Found 490.1772.



Yield: 75.6 mg, 81% (based on **7h**; 93.8 mg, 0.201 mmol).

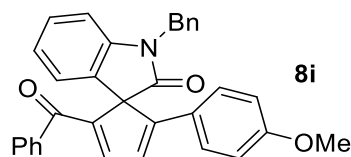
Yellow-red crystals, obtained by slow evaporation of the PE and DCM solution at rt.

M.p. 167.8-169.0 °C. EA/DCM/PE = 1/4/20-3/12/40.

^1H NMR (500 MHz, CDCl_3): δ 7.71 (d, J = 8.5 Hz, 2H), 7.51 (t, J = 8.0 Hz, 1H), 7.45-7.41 (m, 5H), 7.35-7.28 (m, 3H), 7.19-7.15 (m, 1H), 7.10 (d, J = 7.5 Hz, 1H), 6.99 (d, J = 7.5 Hz, 2H), 6.91 (d, J = 8.5 Hz, 2H), 6.88-6.85 (m, 3H), 5.34 (d, J = 15.5 Hz, 1H), 4.90 (d, J = 15.5 Hz, 1H), 2.26 (s, 3H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 188.7, 173.2, 156.7, 147.8, 144.9, 139.2, 138.8, 136.1, 132.0, 130.3, 129.8, 129.6, 129.0, 128.9, 128.8, 128.4, 128.0, 127.7, 127.0, 126.5, 122.9, 122.6, 110.3, 68.4, 45.2, 21.4 ppm.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{33}H_{25}NO_2Na$ 490.1777; Found 490.1786.



Yield: 95.4 mg, 98% (based on **7i**: 97.3 mg, 0.201 mmol).

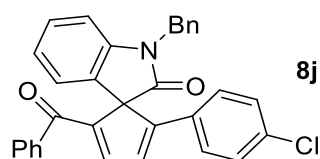
Yellow-red crystals, obtained by slow evaporation of the PE and DCM solution at rt.

M.p. 169.7-170.9 °C. EA/DCM/PE = 1/4/20-3/12/40.

¹H NMR (500 MHz, CDCl₃): δ 7.72 (d, J = 7.5 Hz, 2H), 7.51 (t, J = 7.5 Hz, 1H), 7.46-7.41 (m, 5H), 7.36-7.29 (m, 3H), 7.19 (t, J = 6.5 Hz, 1H), 7.04-7.02 (m, 3H), 6.91-6.88 (m, 3H), 6.62 (d, J = 8.5 Hz, 2H), 5.36 (d, J = 16.0 Hz, 1H), 4.89 (d, J = 15.5 Hz, 1H), 3.73 (s, 3H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 188.6, 173.3, 160.3, 156.5, 148.1, 147.3, 144.8, 138.8, 136.1, 131.9, 129.0, 128.9, 128.8, 128.3, 128.1, 128.0, 127.7, 127.3, 125.8, 122.9, 122.6, 114.3, 110.3, 68.2, 55.3, 45.1 ppm.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{33}H_{25}NO_3Na$ 506.1727; Found 506.1740.



Yield: 72.4 mg, 74% (based on **7j**: 98.0 mg, 0.201 mmol).

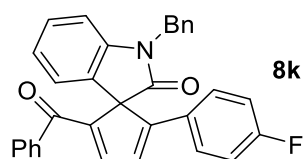
Yellow-red crystals, obtained by slow evaporation of the PE and DCM solution at rt.

M.p. 158.4-159.3 °C. EA/DCM/PE = 1/4/20-3/12/40.

¹H NMR (500 MHz, CDCl₃): δ 7.72 (d, J = 7.5 Hz, 2H), 7.53 (t, J = 7.5 Hz, 1H), 7.45-7.40 (m, 5H), 7.36-7.32 (m, 3H), 7.20 (t, J = 7.5 Hz, 1H), 7.11 (d, J = 2.0 Hz, 1H), 7.05 (d, J = 8.5 Hz, 2H), 6.98 (d, J = 8.5 Hz, 2H), 6.92-6.85 (m, 3H), 5.34 (d, J = 16.0 Hz, 1H), 4.86 (d, J = 15.5 Hz, 1H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 188.7, 172.7, 155.0, 148.3, 147.2, 144.8, 138.5, 135.9, 134.9, 132.1, 131.5, 131.2, 129.2, 129.04, 128.99, 128.9, 128.4, 128.0, 127.9, 127.8, 126.3, 123.0, 122.6, 110.4, 68.5, 45.2 ppm.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{32}H_{22}ClNO_2Na$ 510.1231; Found 510.1241.



Yield: 78.2 mg, 82% (based on **7k**: 94.8 mg, 0.201 mmol).

Yellow-red crystals, obtained by slow evaporation of the PE and DCM solution at rt.

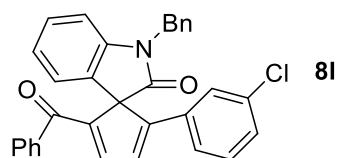
M.p. 190.1-191.3 °C. EA/DCM/PE = 1/4/20-3/12/40.

¹H NMR (500 MHz, CDCl₃): δ 7.72 (d, *J* = 7.0 Hz, 2H), 7.53 (t, *J* = 7.0 Hz, 1H), 7.45-7.39 (m, 5H), 7.35-7.30 (m, 3H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.06-7.01 (m, 3H), 6.92-6.86 (m, 3H), 6.77 (t, *J* = 8.5 Hz, 2H), 5.34 (d, *J* = 15.5 Hz, 1H), 4.86 (d, *J* = 15.5 Hz, 1H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 188.7, 172.9, 163.1 (C-F, ¹*J*_{C-F} = 249.1 Hz), 155.3, 148.1, 147.4, 144.8, 138.6, 135.9, 132.1, 130.6, 129.4 (C-F, ⁴*J*_{C-F} = 3.0 Hz), 129.1, 129.0, 128.9, 128.5, 128.4, 128.1, 127.8, 126.5, 123.0, 122.6, 115.9 (C-F, ²*J*_{C-F} = 21.8 Hz), 110.4, 68.6, 45.2 ppm.

¹⁹F NMR (470 MHz, CDCl₃): δ -111.7 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₃₂H₂₂FNO₂Na 494.1527; Found 494.1537.



Yield: 74.2 mg, 77% (based on **7l**: 96.8 mg, 0.198 mmol).

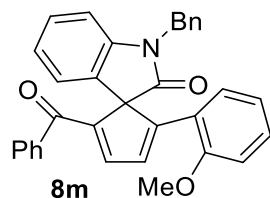
Yellow-red crystals, obtained by slow evaporation of the PE and DCM solution at rt.

M.p. 162.0-163.4 °C. EA/DCM/PE = 1/4/20-3/12/40.

¹H NMR (500 MHz, CDCl₃): δ 7.73 (d, *J* = 7.5 Hz, 2H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.45-7.43 (m, 5H), 7.36-7.28 (m, 3H), 7.21-7.15 (m, 4H), 7.00 (t, *J* = 8.0 Hz, 1H), 6.93-6.88 (m, 4H), 5.34 (d, *J* = 15.5 Hz, 1H), 4.93 (d, *J* = 15.5 Hz, 1H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 188.8, 172.7, 154.6, 148.7, 146.9, 144.9, 138.5, 135.8, 134.82, 134.79, 132.2, 131.9, 130.1, 129.2, 129.0, 128.9, 128.4, 127.8, 127.7, 126.5, 126.1, 124.5, 123.1, 122.6, 110.6, 68.5, 45.3 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₃₂H₂₂ClNO₂Na 510.1231; Found 510.1225.



Yield: 80.2mg, 84% (based on **7m**: 95.8 mg, 0.198 mmol).

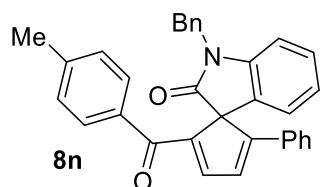
Yellow-red crystals, obtained by slow evaporation of the PE and DCM solution at rt.

M.p. 150.2-152.0 °C. EA/DCM/PE = 1/4/20-3/12/40.

¹H NMR (600 MHz, CDCl₃): δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.52-7.50 (m, 2H), 7.45 (d, *J* = 2.4 Hz, 1H), 7.43-7.41 (m, 4H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.30-7.27 (m, 1H), 7.17-7.11 (m, 2H), 6.88-6.82 (m, 4H), 6.70-6.69 (m, 1H), 6.52 (t, *J* = 7.2 Hz, 1H), 5.39 (d, *J* = 15.6 Hz, 1H), 4.86 (d, *J* = 15.6 Hz, 1H), 3.82 (s, 3H) ppm.

¹³C{¹H} NMR (150 MHz, CDCl₃): δ 188.8, 173.6, 158.2, 152.3, 148.5, 147.3, 144.8, 138.9, 136.2, 135.4, 131.9, 129.7, 129.0, 128.8, 128.7, 128.5, 128.3, 128.0, 127.6, 127.3, 122.7, 122.6, 122.2, 120.6, 111.4, 110.2, 69.6, 55.5, 45.2 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₃₃H₂₅NO₃Na 506.1727; Found 506.1737.



Yield: 67.9 mg, 73% (based on **7n**: 93.4 mg, 0.200 mmol).

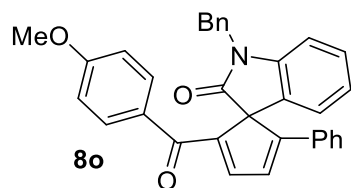
Yellow-red crystals, obtained by slow evaporation of the PE and DCM solution at rt.

M.p. 156.3-157.4 °C. EA/DCM/PE = 1/4/40-1/4/20.

¹H NMR (500 MHz, CDCl₃): δ 7.65 (d, *J* = 7.5 Hz, 2H), 7.43-7.42 (m, 3H), 7.35-7.31 (m, 3H), 7.24-7.10 (m, 9H), 6.89-6.88 (m, 3H), 5.37 (d, *J* = 15.5 Hz, 1H), 4.89 (d, *J* = 16.0 Hz, 1H), 2.41 (s, 3H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 188.5, 173.1, 156.1, 148.3, 146.9, 144.9, 142.7, 136.0, 133.1, 130.7, 129.15, 129.06, 128.94, 128.91, 128.81, 128.79, 128.0, 127.7, 126.7, 126.5, 122.9, 122.6, 110.3, 68.5, 45.1, 21.7 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₃₃H₂₅NO₂Na 490.1777; Found 490.1786.



Yield: 62.1 mg, 64% (based on **7o**: 97.1 mg, 0.201 mmol).

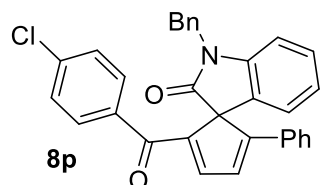
Yellow-red crystals, obtained by slow evaporation of the PE and DCM solution at rt.

M.p. 191.6-192.4 °C. EA/DCM/PE = 1/4/40-1/4/10.

¹H NMR (500 MHz, CDCl₃): δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.41-7.40 (m, 3H), 7.33-7.29 (m, 3H), 7.19-7.14 (m, 3H), 7.11-7.08 (m, 4H), 6.92 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 5.0 Hz, 3H), 5.36 (d, *J* = 15.5 Hz, 1H), 4.86 (d, *J* = 15.5 Hz, 1H), 3.85 (s, 3H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 187.6, 173.2, 162.9, 155.8, 148.4, 146.3, 144.9, 136.0, 133.2, 131.4, 131.3, 130.7, 128.94, 128.91, 128.82, 128.80, 128.0, 127.7, 126.7, 126.5, 122.9, 122.7, 113.7, 110.3, 68.7, 55.6, 45.2 ppm.

HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{33}\text{H}_{25}\text{NO}_3\text{Na}$ 506.1727; Found 506.1719.



Yield: 79.3 mg, 81% (based on **7p**: 98.3 mg, 0.201 mmol).

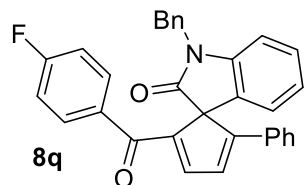
Yellow-red crystals, obtained by slow evaporation of the PE and DCM solution at rt.

M.p. 170.1-170.8 °C. EA/DCM/PE = 1/4/40-1/4/20.

^1H NMR (500 MHz, CDCl_3): δ 7.68 (d, J = 7.5 Hz, 2H), 7.43-7.41 (m, 5H), 7.34-7.30 (m, 3H), 7.21-7.18 (m, 2H), 7.15 (s, 1H), 7.13-7.10 (m, 4H), 6.91-6.88 (m, 3H), 5.34 (d, J = 15.5 Hz, 1H), 4.90 (d, J = 15.5 Hz, 1H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 187.4, 172.9, 156.9, 147.8, 147.7, 144.8, 138.3, 137.0, 135.9, 132.9, 130.6, 130.3, 129.2, 129.1, 128.8, 128.7, 128.0, 127.7, 126.5, 123.0, 122.6, 110.4, 68.5, 45.2 ppm.

HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{32}\text{H}_{22}\text{ClNO}_2\text{Na}$ 510.1231; Found 510.1245.



Yield: 70.3 mg, 88% (based on **7q**: 80.0 mg, 0.170 mmol).

Yellow-red crystals, obtained by slow evaporation of the PE and DCM solution at rt.

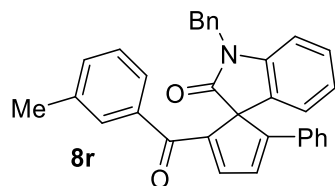
M.p. 160.9-162.1 °C. EA/DCM/PE = 1/4/40-1/4/20.

^1H NMR (500 MHz, CDCl_3): δ 7.77-7.75 (m, 2H), 7.44-7.42 (m, 3H), 7.35-7.30 (m, 3H), 7.21-7.10 (m, 9H), 6.90-6.88 (m, 3H), 5.34 (d, J = 15.5 Hz, 1H), 4.90 (d, J = 15.5 Hz, 1H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 187.2, 172.9, 165.2 (C-F, $^1J_{\text{C-F}}$ = 252.3 Hz), 156.7, 147.9, 147.4, 144.8, 135.9, 134.9 (C-F, $^4J_{\text{C-F}}$ = 2.1 Hz), 133.0, 131.4 (C-F, $^3J_{\text{C-F}}$ = 9.4 Hz), 130.6, 129.1, 129.0, 128.8, 128.6, 128.0, 127.7, 126.6, 126.5, 122.9, 122.6, 115.5 (C-F, $^2J_{\text{C-F}}$ = 20.8 Hz), 110.4, 68.6, 45.2 ppm.

^{19}F NMR (470 MHz, CDCl_3): δ -106.9 ppm.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{32}H_{22}FNO_2Na$ 494.1527; Found 494.1519.



Yield: 73.4 mg, 78% (based on **7r**: 93.6 mg, 0.200 mmol).

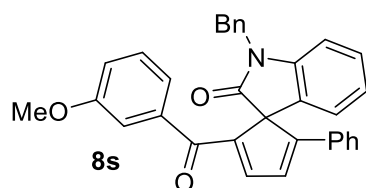
Yellow-red crystals, obtained by slow evaporation of the PE and DCM solution at rt.

M.p. 126.9-128.1 °C. EA/DCM/PE = 1/4/40-1/4/20.

1H NMR (500 MHz, $CDCl_3$): δ 7.53 (br s, 2H), 7.44-7.42 (m, 3H), 7.33-7.28 (m, 5H), 7.20-7.17 (m, 2H), 7.15 (br s, 1H), 7.10 (br s, 4H), 7.08 (s, 4H), 6.89-6.88 (m, 3H), 5.36 (d, J = 16.0 Hz, 1H), 4.89 (d, J = 15.5 Hz, 1H), 2.40 (s, 3H) ppm.

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 188.9, 173.1, 156.4, 148.3, 147.4, 144.9, 138.7, 138.2, 136.0, 133.1, 132.8, 130.7, 129.5, 129.0, 128.9, 128.8, 128.2, 128.0, 127.7, 126.8, 126.5, 126.2, 122.9, 122.6, 110.3, 68.5, 45.2, 21.5 ppm.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{33}H_{25}NO_2Na$ 490.1777; Found 490.1789.



Yield: 73.4 mg, 78% (based on **7s**: 93.6 mg, 0.200 mmol).

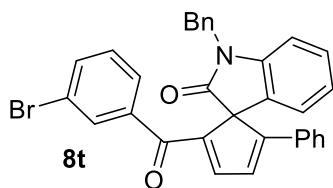
Yellow-red crystals, obtained by slow evaporation of the PE and DCM solution at rt.

M.p. 164.3-165.0 °C. EA/DCM/PE = 1/4/40-1/4/20.

1H NMR (500 MHz, $CDCl_3$): δ 7.47 (d, J = 2.0 Hz, 1H), 7.41 (d, J = 7.0 Hz, 2H), 7.35-7.29 (m, 5H), 7.23 (br s, 1H), 7.21-7.16 (m, 2H), 7.14 (d, J = 2.0 Hz, 1H), 7.12-7.06 (m, 5H), 6.90-6.87 (m, 3H), 5.35 (d, J = 15.5 Hz, 1H), 4.87 (d, J = 15.5 Hz, 1H), 3.82 (s, 3H) ppm.

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 188.5, 173.1, 159.7, 156.5, 148.1, 147.6, 144.9, 140.0, 136.0, 133.1, 130.7, 129.3, 129.1, 129.0, 128.8, 128.0, 127.7, 126.7, 126.5, 122.9, 122.6, 121.6, 118.6, 113.5, 110.4, 68.5, 55.6, 45.2 ppm.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{33}H_{25}NO_3Na$ 506.1727; Found 506.1739.



Yield: 80.5 mg, 76% (based on **7t**: 105.6 mg, 0.198 mmol).

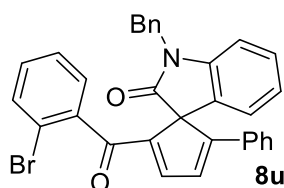
Yellow-red crystals, obtained by slow evaporation of the PE and DCM solution at rt.

M.p. 145.9-147.2 °C. EA/DCM/PE = 1/4/40-1/4/20.

¹H NMR (500 MHz, CDCl₃): δ 7.85 (s, 1H), 7.65 (d, *J* = 7.5 Hz, 2H), 7.46 (d, *J* = 2.0 Hz, 1H), 7.43 (d, *J* = 7.0 Hz, 2H), 7.35-7.29 (m, 4H), 7.22-7.18 (m, 2H), 7.16 (d, *J* = 1.5 Hz, 1H), 7.13-7.10 (m, 4H), 6.91-6.87 (m, 3H), 5.33 (d, *J* = 15.5 Hz, 1H), 4.90 (d, *J* = 15.5 Hz, 1H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 186.9, 172.8, 157.1, 148.2, 147.6, 144.8, 140.5, 135.9, 134.9, 132.9, 131.8, 130.6, 130.1, 129.2, 129.1, 128.8, 128.0, 127.7, 127.5, 126.6, 123.0, 122.6, 122.5, 110.4, 68.5, 45.2 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₃₂H₂₂BrNO₂Na 554.0726; Found 554.0741.



Yield: 93.1 mg, 88% (based on **7u**: 106.0 mg, 0.199 mmol).

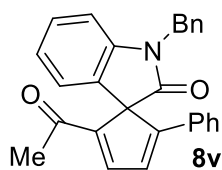
Yellow-red crystals, obtained by slow evaporation of the PE and DCM solution at rt.

M.p. 168.5-169.7 °C. EA/DCM/PE = 1/4/40-1/4/20.

¹H NMR (500 MHz, CDCl₃): δ 7.58 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 7.0 Hz, 2H), 7.36-7.28 (m, 6H), 7.22-7.19 (m, 3H), 7.13-7.10 (m, 5H), 6.94-6.90 (m, 3H), 5.27 (d, *J* = 16.0 Hz, 1H), 4.96 (d, *J* = 15.5 Hz, 1H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 188.1, 172.6, 157.6, 149.8, 147.9, 144.7, 140.6, 135.8, 133.1, 132.9, 131.0, 130.7, 129.2, 128.9, 128.82, 128.80, 127.9, 127.7, 127.2, 126.7, 126.6, 123.1, 122.9, 119.5, 110.3, 67.6, 45.0 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₃₂H₂₂BrNO₂Na 554.0726; Found 554.0739.



Yield: 25.3 mg, 32% (based on **7v**: 78.5 mg, 0.201 mmol).

Yellow-red crystals, obtained by slow evaporation of the PE and DCM solution at rt.

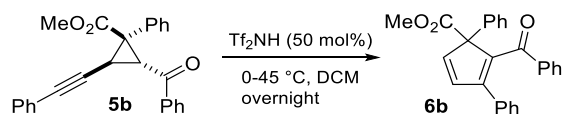
M.p. 81.3-81.5 °C. EA/DCM/PE = 1/4/40-1/4/20.

¹H NMR (500 MHz, CDCl₃): δ 7.57 (d, *J* = 2.0 Hz, 1H), 7.39 (d, *J* = 7.0 Hz, 2H), 7.33-7.28 (m, 3H), 7.20-7.16 (m, 2H), 7.10-7.03 (m, 5H), 6.89-6.84 (m, 2H), 6.75 (d, *J* = 7.0 Hz, 1H), 5.21 (d, *J* = 15.5 Hz, 1H), 4.87 (d, *J* = 15.5 Hz, 1H), 2.31 (s, 3H) ppm.

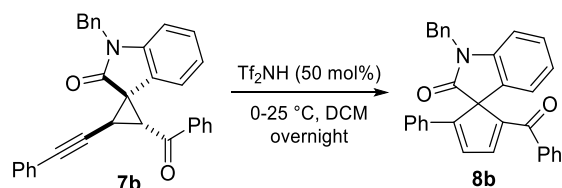
¹³C{¹H} NMR (125 MHz, CDCl₃): δ 191.2, 173.1, 156.6, 149.4, 145.3, 144.7, 135.9, 133.1, 130.3, 129.0, 128.8, 127.9, 127.7, 127.2, 126.5, 122.9, 122.4, 110.3, 67.6, 45.0, 26.3 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₇H₂₁NO₂Na 414.1464; Found 414.1468.

8. Scale-up alkynylcyclopropane-cyclopentadiene rearrangement

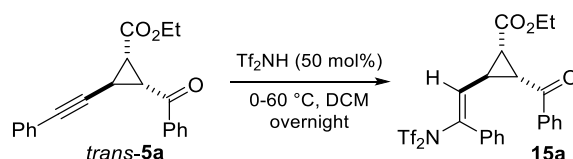


Procedure for 2.0 mmol scale reaction of 5b: To a dry Schlenk tube equipped with a high vacuum valve, **5b** (760.2 mg, 1.998 mmol, 1.0 equiv) was dissolved in DCM (10.0 mL) with a stir bar. Tf₂NH (10.0 mL, 0.1 M in DCM, 1.00 mmol, 50 mol%) was added dropwise via microsyringe to the solution at 0 °C. The reaction mixture was stirred at 45 °C in an oil bath overnight, which was then neutralized with saturated NaHCO₃. The mixture was extracted with DCM (40 mL × 3). The combined organics were washed with brine, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluted with EA/DCM/PE (1/4/40 to 1/4/20, v/v/v) to afford the product **6b** (532.8 mg, 70%) as yellow oil.

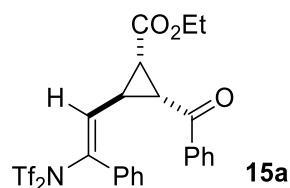


Procedure for 1.0 mmol scale reaction of 7b: To a dry Schlenk tube equipped with a high vacuum valve, **7b** (452.7 mg, 0.998 mmol, 1.0 equiv) was dissolved in dry DCM (10.0 mL) with a stir bar. Tf₂NH (5.0 mL, 0.1 M in DCM, 0.50 mmol, 50 mol%) was added dropwise via microsyringe to the solution at 0 °C. The reaction mixture was stirred at 25 °C overnight, which was then neutralized with saturated NaHCO₃. The mixture was extracted with DCM (40 mL × 3). The combined organics were washed with brine, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluted with EA/DCM/PE (1/4/20 to 1/4/10, v/v/v) to afford the spiro cyclopentadiene product **8b** (391.2 mg, 86%) as yellow-red crystals.

9. Addition of Tf₂NH on alkynylcyclopropanes



To a dry Schlenk tube equipped with a high vacuum valve, *trans*-**5a** (64.0 mg, 0.201 mmol, 1.0 equiv) was dissolved in dry DCM (2.0 mL) with a stir bar. Tf₂NH (1.0 mL, 0.1 M in DCM, 0.10 mmol, 50 mol%) was added dropwise via microsyringe to the solution at 0 °C. The reaction mixture was stirred at 60 °C in an oil bath overnight, which was then neutralized with saturated NaHCO₃. The mixture was extracted with DCM (20 mL $\times$ 3). The combined organics were washed with brine, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluted with EA/PE (1/30 to 1/10, v/v) to afford the adduct **15a** (42.9 mg, 72%) as colorless crystals.



Yield: 62.5 mg, 72% (based on Tf₂NH: 1.0 mL, 0.1 M in DCM, 0.10 mmol).

Colorless crystals, obtained by slow evaporation of the PE and DCM solution at rt.

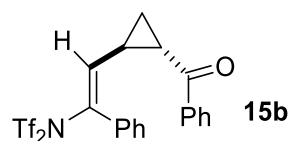
M.p. 113.3-114.2 °C. EA/ PE = 1/30-1/10.

¹H NMR (500 MHz, CDCl₃): δ 7.94 (d, J = 7.5 Hz, 2H), 7.60-7.58 (m, 3H), 7.49-7.43 (m, 5H), 5.78 (d, J = 9.0 Hz, 1H), 4.02 (q, J = 7.0 Hz, 2H), 3.02-2.95 (m, 2H), 2.49 (dd, J = 9.0, 6.0 Hz, 1H), 1.09 (t, J = 7.0 Hz, 3H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 192.2, 167.8, 140.2, 136.5, 135.1, 133.8, 132.0, 130.5, 130.0, 129.0, 128.9, 128.4, 119.2 (C-F, ¹J_{C-F} = 324.5 Hz), 61.6, 33.9, 31.1, 29.8, 25.6, 14.1 ppm.

¹⁹F NMR (470 MHz, CDCl₃): δ -69.68, -69.72 ppm.

HRMS (ESI) m/z : [M+Na]⁺ Calcd for C₂₁H₁₈O₃Na 341.1148; Found 341.1138.



Yield: 33.4 mg, 62% (based on Tf₂NH: 1.0 mL, 0.1 M in DCM, 0.100 mmol).

Yellow oil. EA/ PE = 1/30-1/10.

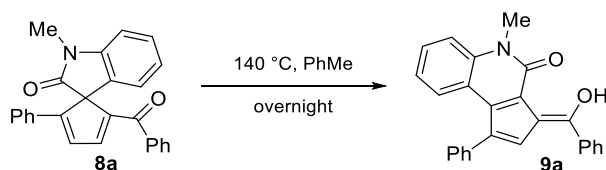
¹H NMR (500 MHz, CDCl₃): δ 7.95 (d, *J* = 7.5 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.52-7.47 (m, 4H), 7.38 (br s, 3H), 5.76 (d, *J* = 10.0 Hz, 1H), 2.93-2.89 (m, 1H), 2.33-2.28 (m, 1H), 1.86-1.82 (m, 1H), 1.36-1.33 (m, 1H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 196.9, 143.5, 137.3, 133.5, 133.0, 132.4, 130.1, 129.8, 129.0, 128.9, 128.2, 119.3 (C-F, ¹*J*_{C-F} = 323.6 Hz), 27.2, 25.3, 18.8 ppm.

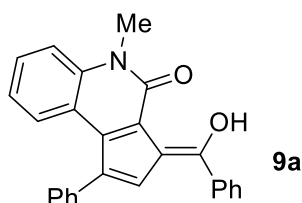
¹⁹F NMR (470 MHz, CDCl₃): δ -69.68, -69.73 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₁₈H₁₄ONa 269.0937; Found 269.0927.

10. Thermal rearrangement of **8**



Representative procedure: To a dry Schlenk tube equipped with a high vacuum valve, **8a** (36.1 mg, 0.0956 mmol) was dissolved in dry PhMe (2.0 mL) with a stir bar. The reaction mixture was heated at 140 °C overnight. After cooled to room temperature, the mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluted with EA/PE (1/10 to 1/5, v/v) to afford the product **9a** (30.1 mg, 83%) as yellow-green crystals.



Yield: 30.1 mg, 83% (based on **8a**: 36.1 mg, 0.0956 mmol).

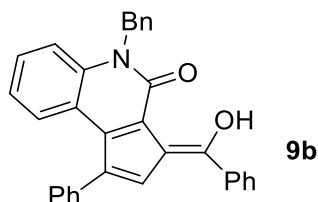
Yellow-green crystals, obtained by slow evaporation of the PE and EA solution at rt.

M.p. 186.4-187.3°C. EA/PE = 1/10-1/5.

¹H NMR (500 MHz, CDCl₃): δ 7.84-7.81 (m, 3H), 7.53-7.37 (m, 10H), 7.08 (t, *J* = 7.5 Hz, 1H), 7.03 (s, 1H), 3.95 (s, 3H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 177.4, 161.0, 138.9, 138.7, 137.3, 137.1, 135.2, 133.2, 130.8, 129.8, 129.7, 128.5, 128.3, 128.2, 127.2, 125.6, 122.9, 120.6, 118.0, 116.7, 115.6, 30.7 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₆H₁₉NO₂Na 400.1308; Found 400.1307.



Yield: 31.9 mg, 93% (based on **8b**: 34.3mg, 0.0756 mmol).

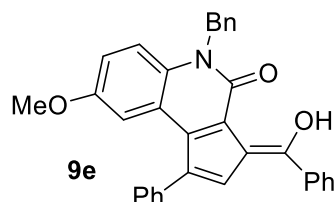
Yellow-green crystals, obtained by slow evaporation of the PE and EA solution at rt.

M.p. 198.6-199.4 °C. EA/PE = 1/10-1/5.

¹H NMR (500 MHz, CDCl₃): δ 7.85-7.81 (m, 3H), 7.52-7.38 (m, 9H), 7.36-7.28 (m, 6H), 7.08 (s, 1H), 7.02 (t, *J* = 8.0 Hz, 1H), 5.79 (br s, 2H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 177.3, 161.3, 139.3, 138.9, 137.0, 136.8, 136.3, 135.6, 133.4, 130.9, 129.9, 129.7, 129.1, 128.5, 128.3, 127.6, 127.3, 126.6, 125.6, 122.9, 120.8, 117.8, 116.8, 116.5, 47.1 ppm.

HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{32}\text{H}_{23}\text{NO}_2\text{Na}$ 476.1621; Found 476.1627.



Yield: 28.8 mg, 80% (based on **8e**: 35.9 mg, 0.0742mmol).

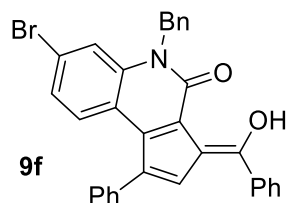
Yellow-green crystals, obtained by slow evaporation of the PE and EA solution at rt.

M.p. 187.6-188.3 °C. EA/PE = 1/10-1/5.

^1H NMR (500 MHz, CDCl_3): δ 7.84 (d, J = 7.0 Hz, 2H), 7.52-7.43 (m, 8H), 7.38-7.30 (m, 5H), 7.21 (d, J = 8.0 Hz, 1H), 7.08 (s, 1H), 6.91-6.89 (m, 1H), 5.76 (br s, 2H), 3.38 (s, 3H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 178.0, 160.5, 155.1, 138.9, 138.6, 137.2, 136.3, 134.9, 133.0, 131.0, 130.9, 130.0, 129.8, 129.1, 128.4, 128.3, 127.6, 127.3, 126.5, 121.7, 117.8, 116.9, 106.8, 55.1, 47.1 ppm.

HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{33}\text{H}_{25}\text{NO}_3\text{Na}$ 506.1727; Found 506.1738.



Yield: 53.8 mg, quant. (based on **8f**: 54.0 mg, 0.101 mmol).

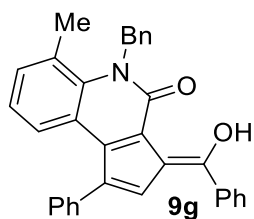
Yellow-green crystals, obtained by slow evaporation of the PE and EA solution at rt.

M.p. 223.1-224.0 °C. EA/PE = 1/10-1/5.

^1H NMR (500 MHz, CDCl_3): δ 7.83 (d, J = 7.0 Hz, 2H), 7.64 (d, J = 9.0 Hz, 1H), 7.57 (s, 1H), 7.54-7.35 (m, 10H), 7.30-7.29 (m, 3H), 7.12 (d, J = 8.5 Hz, 1H), 7.07 (s, 1H), 5.72 (br s, 2H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 177.6, 161.3, 138.6, 138.4, 137.7, 136.7, 135.8, 135.7, 133.3, 131.1, 129.9, 129.6, 129.2, 128.7, 128.3, 127.8, 127.5, 126.7, 126.6, 126.1, 122.2, 119.6, 119.3, 117.9, 116.9, 47.1 ppm.

HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{32}\text{H}_{22}\text{BrNO}_2\text{Na}$ 554.0726; Found 554.0720.



Yield: 43.4 mg, 92% (based on **8g**: 47.0 mg, 0.101 mmol).

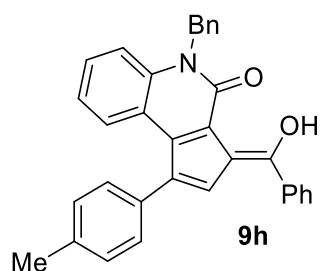
Yellow-green crystals, obtained by slow evaporation of the PE and EA solution at rt.

M.p. 160.1-161.0 °C. EA/PE = 1/10-1/5.

¹H NMR (500 MHz, CDCl₃): δ 7.82 (d, *J* = 7.0 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.51-7.32 (m, 10H), 7.26-7.24 (m, 1H), 7.19-7.16 (m, 3H), 7.04 (s, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 5.81 (br s, 2H), 2.59 (s, 3H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 177.0, 163.4, 139.9, 139.1, 138.43, 138.40, 136.9, 135.8, 133.5, 130.9, 129.9, 129.7, 128.8, 128.5, 128.3, 127.2, 127.0, 126.1, 125.8, 124.3, 123.1, 122.6, 117.9, 116.6, 51.7, 24.8 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₃₃H₂₅NO₂Na 490.1777; Found 490.1788.



Yield: 46.5 mg, quant. (based on **8h**: 47.0 mg, 0.101 mmol).

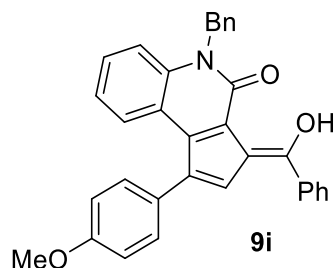
Yellow-green crystals, obtained by slow evaporation of the PE and EA solution at rt.

M.p. 178.5-179.6 °C. EA/PE = 1/10-1/5.

¹H NMR (500 MHz, CDCl₃): δ 7.87-7.83 (m, 3H), 7.51-7.24 (m, 14H), 7.05-7.02 (m, 2H), 5.79 (s, 2H), 2.44 (s, 3H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 177.0, 161.3, 139.4, 137.0, 136.7, 136.3, 135.8, 135.5, 133.5, 130.8, 129.9, 129.5, 129.2, 129.0, 128.3, 127.5, 126.5, 125.7, 122.8, 120.9, 117.8, 116.8, 116.5, 47.0, 21.4 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₃₃H₂₅NO₂Na 490.1777; Found 490.1786.



Yield: 38.5 mg, 80% (based on **8i**: 48.2 mg, 0.0997 mmol).

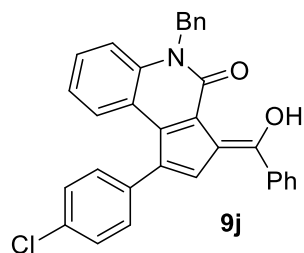
Yellow-green crystals, obtained by slow evaporation of the PE and EA solution at rt.

M.p. 189.2-191.5 °C. EA/PE = 1/10-1/5.

¹H NMR (500 MHz, CDCl₃): δ 7.84-7.83 (m, 3H), 7.51-7.46 (m, 3H), 7.41-7.39 (m, 3H), 7.35-7.27 (m, 6H), 7.04-7.02 (m, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 5.78 (br s, 2H), 3.88 (s, 3H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 176.9, 161.3, 159.0, 139.6, 137.1, 136.8, 136.3, 135.4, 133.2, 131.1, 130.82, 130.78, 129.9, 129.0, 128.3, 127.5, 126.5, 125.6, 122.9, 120.9, 117.8, 116.7, 116.5, 114.0, 55.5, 47.0 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₃₃H₂₅NO₃Na 506.1727; Found 506.1735.



Yield: 30.9 mg, 95% (based on **8j**: 32.5 mg, 0.0666 mmol).

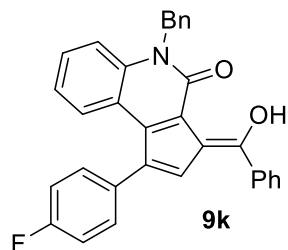
Yellow-green crystals, obtained by slow evaporation of the PE and EA solution at rt.

M.p. 237.1-238.5 °C. EA/PE = 1/10-1/5.

¹H NMR (500 MHz, CDCl₃): δ 7.83 (d, *J* = 7.0 Hz, 2H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.53-7.48 (m, 3H), 7.43-7.40 (m, 5H), 7.35-7.31 (m, 3H), 7.28-7.26 (m, 3H), 7.07-7.05 (m, 2H), 5.79 (br s, 2H) ppm.

¹³C{¹H} NMR (150 MHz, CDCl₃): δ 178.0, 161.2, 138.8, 137.4, 137.0, 136.7, 136.2, 135.7, 133.2, 131.9, 131.0, 129.9, 129.1, 128.7, 128.40, 128.35, 127.6, 126.6, 125.4, 123.1, 120.7, 117.9, 116.9, 116.6, 47.1 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₃₂H₂₂ClNO₂Na 510.1231; Found 510.1231.



Yield: 41.0 mg, 87% (based on **8k**: 47.0 mg, 0.0997 mmol).

Yellow-green crystals, obtained by slow evaporation of the PE and EA solution at rt.

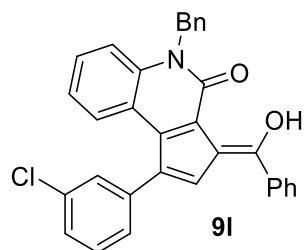
M.p. 239.7-240.7 °C. EA/PE = 1/10-1/5.

¹H NMR (500 MHz, CDCl₃): δ 7.83 (d, *J* = 7.0 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.53-7.41 (m, 6H), 7.35-7.32 (m, 3H), 7.29-7.27 (m, 3H), 7.13 (t, *J* = 8.0 Hz, 2H), 7.04-7.03 (m, 2H), 5.79 (s, 2H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 177.6, 161.3, 138.1 (C-F, ¹*J*_{C-F} = 265.7 Hz), 136.7, 136.2, 135.6, 134.8, 132.2, 131.3 (C-F, ³*J*_{C-F} = 8.3 Hz), 131.0, 129.9, 129.1, 128.3, 127.6, 126.6, 125.4, 123.0, 120.8, 117.8, 116.8, 116.6, 115.5 (C-F, ²*J*_{C-F} = 21.8 Hz), 47.1 ppm.

¹⁹F NMR (470 MHz, CDCl₃): δ -115.3 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₃₂H₂₂FNO₂Na 494.1527; Found 494.1539.



Yield: 28.4 mg, 96% (based on **8l**: 29.6mg, 0.0607 mmol).

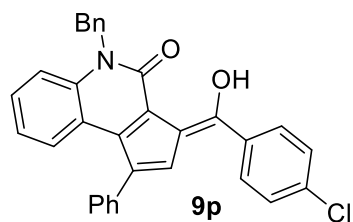
Yellow-green crystals, obtained by slow evaporation of the PE and EA solution at rt.

M.p. 207.5-208.3 °C. EA/PE = 1/10-1/5.

¹H NMR (500 MHz, CDCl₃): δ 7.83 (d, *J* = 7.5 Hz, 2H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.54-7.50 (m, 4H), 7.43 (d, *J* = 8.5 Hz, 1H), 7.37-7.31 (m, 6H), 7.29-7.26 (m, 3H), 7.08-7.05 (m, 2H), 5.79 (s, 2H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 178.2, 161.2, 140.8, 138.7, 136.9, 136.7, 136.2, 135.8, 134.4, 131.6, 131.0, 129.8, 129.71, 129.68, 129.1, 128.4, 128.0, 127.6, 127.4, 126.5, 125.4, 123.1, 120.6, 117.8, 116.9, 116.7, 47.1 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₃₂H₂₂ClNO₂Na 510.1231; Found 510.1239.



Yield: 46.2 mg, 95% (based on **8p**: 48.8 mg, 0.100 mmol).

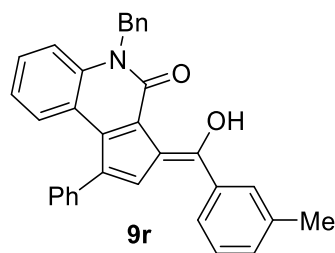
Yellow-green crystals, obtained by slow evaporation of the PE and EA solution at rt.

M.p. 213.9-215.3 °C. EA/PE = 1/10-1/5.

¹H NMR (500 MHz, CDCl₃): δ 7.82-7.77 (m, 3H), 7.49-7.38 (m, 8H), 7.35-7.27 (m, 6H), 7.04-7.02 (m, 2H), 5.78 (s, 2H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 175.7, 161.2, 139.5, 138.7, 137.1, 136.7, 136.2, 135.5, 135.1, 133.8, 131.2, 129.6, 129.1, 128.60, 128.57, 128.5, 127.6, 127.4, 126.5, 125.7, 123.0, 120.8, 117.8, 116.9, 116.5, 47.1 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₃₂H₂₂ClNO₂Na 510.1231; Found 510.1237.



Yield: 41.5 mg, 90% (based on **8r**: 46.1 mg, 0.0986 mmol).

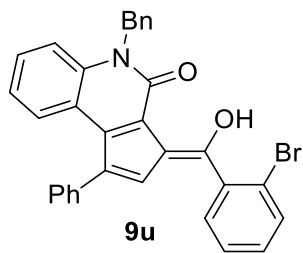
Yellow-green crystals, obtained by slow evaporation of the PE and EA solution at rt.

M.p. 180.2-181.4 °C. EA/PE = 1/10-1/5.

¹H NMR (500 MHz, CDCl₃): δ 7.80 (d, *J* = 8.0 Hz, 1H), 7.64-7.61 (m, 2H), 7.49 (d, *J* = 7.0 Hz, 2H), 7.44-7.28 (m, 12H), 7.24 (m, 1H), 7.07 (s, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 5.77 (s, 2H), 2.43 (s, 3H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 177.6, 161.3, 139.2, 138.9, 138.1, 137.0, 136.7, 136.3, 135.6, 133.3, 131.7, 130.2, 129.7, 129.0, 128.5, 128.2, 128.1, 127.5, 127.3, 127.2, 126.5, 125.6, 122.8, 120.8, 117.8, 116.8, 116.5, 47.0, 21.6 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₃₃H₂₅NO₂Na 490.1777; Found 490.1791.



Yield: 26.9 mg, 82% (based on **8u**: 33.0 mg, 0.0620 mmol).

Yellow-green crystals, obtained by slow evaporation of the PE and EA solution at rt.

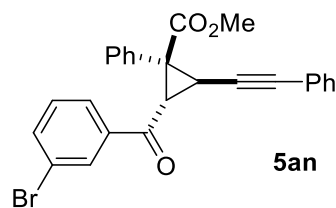
M.p. 182.8-183.9 °C. EA/PE = 1/10-1/5.

¹H NMR (500 MHz, CDCl₃): δ 7.81 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 7.5 Hz, 1H), 7.47 (d, *J* = 7.0 Hz, 2H), 7.44-7.28 (m, 12H), 7.03 (t, *J* = 8.0 Hz, 1H), 6.63 (s, 1H), 5.79 (s, 2H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 175.8, 161.1, 140.3, 138.5, 138.1, 136.9, 136.1, 135.0, 133.8, 133.3, 130.92, 130.86, 129.6, 129.1, 128.54, 128.50, 127.6, 127.4, 126.9, 126.6, 125.7, 123.0, 121.6, 120.9, 117.94, 117.88, 116.6, 47.2 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₃₂H₂₂BrNO₂Na 554.0726; Found 554.0738.

11. X-ray crystallographic data



Crystal data and structure refinement for 5an:

Empirical formula	C ₅₂ H ₃₈ Br ₂ O ₆
Formula weight	918.68
Temperature	99.99(10) K
Wavelength	1.54184 Å
Crystal system	monoclinic
Space group	P2 ₁ /c
Unit cell dimensions	a = 11.52440(10) Å, α = 90° b = 14.4273(2) Å, β = 99.8350(10)° c = 25.8302(4) Å, γ = 90°
Volume	4231.57(10) Å ³
Z	4
Density (calculated)	1.4419 mg/m ³
Absorption coefficient	2.847 mm ⁻¹
F(000)	1871.7
Crystal size	0.38 × 0.26 × 0.18 mm ³
Theta range for data collection	3.89 to 67.07°
Index ranges	-14 ≤ h ≤ 14, -17 ≤ k ≤ 17, -28 ≤ l ≤ 30
Reflections collected	121216
Independent reflections	7490 [R(int) = 0.0724]
Data / restraints / parameters	7490/0/543
Goodness-of-fit on F ²	1.045
Final R indices [I > 2σ(I)]	R ₁ = 0.0486, wR ₂ = 0.1098
R indices (all data)	R ₁ = 0.0509, wR ₂ = 0.1109
Largest diff. peak and hole	0.88 and -0.92 eÅ ⁻³

The single crystals of **5an** were grown by slow evaporation of the solution of **5an** (several milligrams) in the co-solvent of petroleum ether (3 mL) and ethyl acetate (1 mL) in a small glass vial at rt over 2-3 days. X-ray diffraction data of a suitable crystal kept at 99.99(10) K was collected on a XtaLAB AFC12 (RINC): Kappa dual home/near diffractometer.

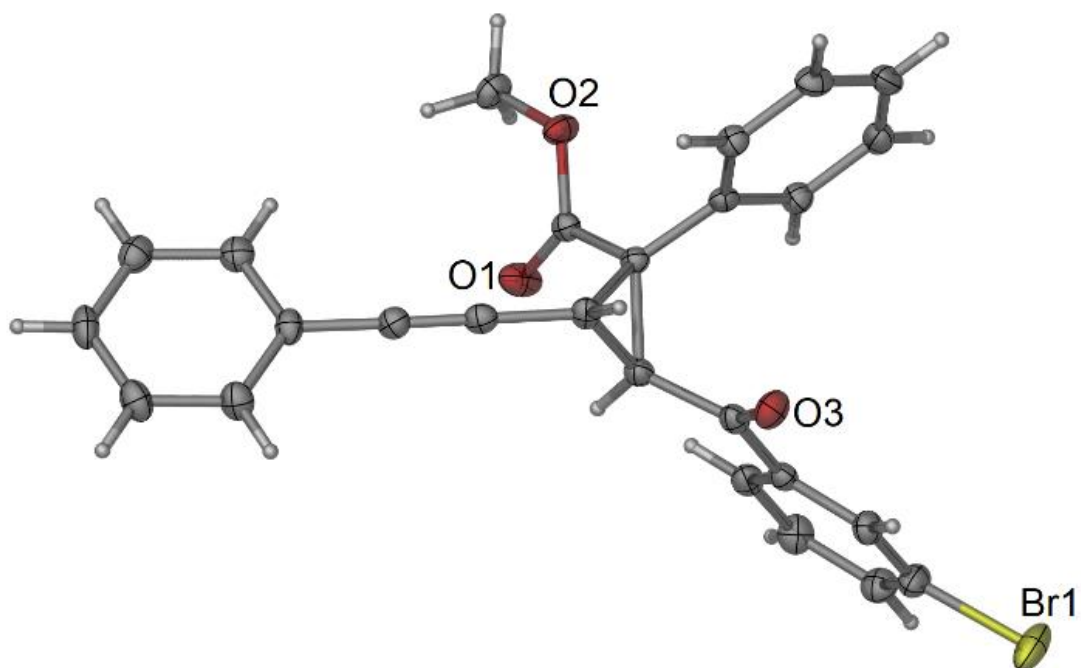
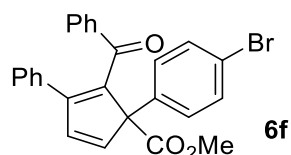


Figure S1 X-ray structure of **5an**. Thermal ellipsoid is set at 50% probability.



Crystal data and structure refinement for 6f:

Empirical formula	C ₂₆ H ₁₉ BrO ₃
Formula weight	459.32
Temperature	170(1) K
Wavelength	1.54184 Å
Crystal system	monoclinic
Space group	P2 ₁ /c
Unit cell dimensions	a = 15.2783(2) Å, α = 90° b = 10.33270(10) Å, β = 118.164(2)° c = 15.5266(2) Å, γ = 90°
Volume	2160.91(6) Å ³
Z	4
Density (calculated)	1.412 mg/m ³
Absorption coefficient	2.788 mm ⁻¹
F(000)	936.0
Crystal size	0.36 × 0.32 × 0.29 mm ³
Theta range for data collection	5.364 to 67.073°
Index ranges	-18 ≤ h ≤ 18, -11 ≤ k ≤ 12, -14 ≤ l ≤ 18
Reflections collected	21837
Independent reflections	3851 [R(int) = 0.0447]
Data / restraints / parameters	3851/0/272
Goodness-of-fit on F ²	1.078
Final R indices [I > 2σ(I)]	R ₁ = 0.0343, wR ₂ = 0.0878
R indices (all data)	R ₁ = 0.0356, wR ₂ = 0.0887
Largest diff. peak and hole	0.24 and -0.70 eÅ ⁻³

The single crystals of **6f** were grown by slow evaporation of the solution of **6f** (several milligrams) in the co-solvent of petroleum ether (3 mL) and ethyl acetate (1 mL) in a small glass vial at rt over 2-3 days. X-ray diffraction data of a suitable crystal kept at 173(1) K was collected on a XtaLAB AFC12 (RINC): Kappa dual home/near diffractometer.

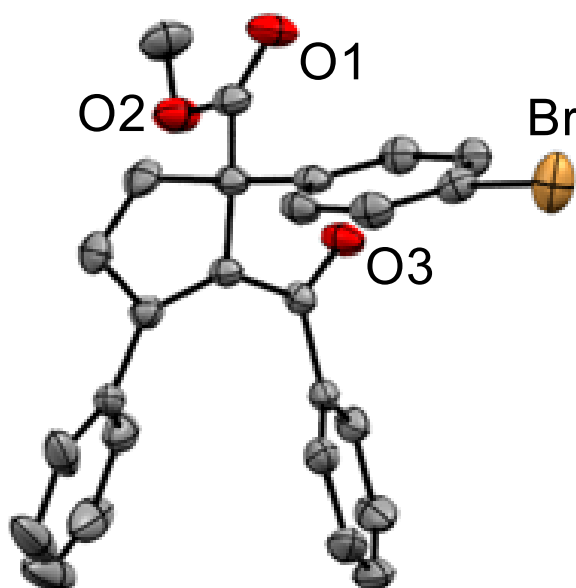
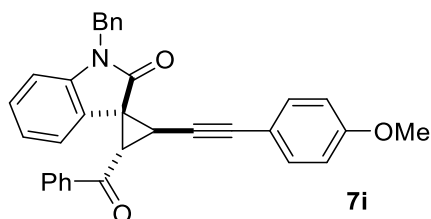


Figure S2 X-ray structure of **6f**. Thermal ellipsoid is set at 50% probability.



Crystal data and structure refinement for 7i:

Empirical formula	C ₃₃ H ₂₅ NO ₃
Formula weight	483.54
Temperature	173.00(10) K
Wavelength	1.54184 Å
Crystal system	triclinic
Space group	P-1
Unit cell dimensions	a = 10.1720(3) Å, α = 91.906(3)° b = 10.8609(4) Å, β = 103.416(3)° c = 11.9780(4) Å, γ = 102.090(3)°
Volume	1253.96(8) Å ³
Z	2
Density (calculated)	1.281 mg/m ³
Absorption coefficient	0.649 mm ⁻¹
F(000)	508.0
Crystal size	0.32 × 0.31 × 0.19 mm ³
Theta range for data collection	3.808 to 67.078°
Index ranges	−11 ≤ h ≤ 10, −12 ≤ k ≤ 12, −13 ≤ l ≤ 14
Reflections collected	11615
Independent reflections	4436 [R(int) = 0.0303]
Data / restraints / parameters	4436/0/336
Goodness-of-fit on F ²	1.061
Final R indices [I > 2σ(I)]	R ₁ = 0.0330, wR ₂ = 0.0883
R indices (all data)	R ₁ = 0.0354, wR ₂ = 0.0900
Largest diff. peak and hole	0.21 and −0.17 eÅ ⁻³

The single crystals of **7i** were grown by slow evaporation of the solution of **7i** (several milligrams) in the co-solvent of petroleum ether (3 mL) and ethyl acetate (1 mL) in a small glass vial at rt over 2-3 days. X-ray diffraction data of a suitable crystal kept at 173.00(10) K was collected on a XtaLAB AFC12 (RINC); Kappa dual home/near diffractometer.

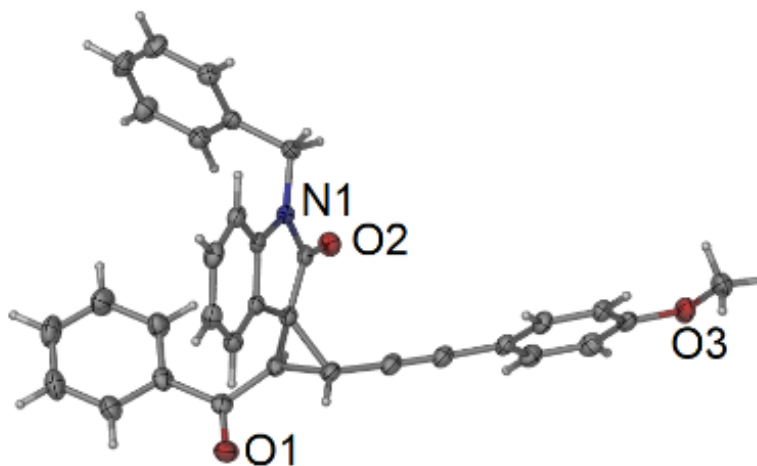
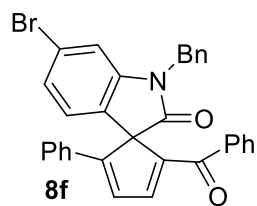


Figure S3 X-ray structure of **7i**. Thermal ellipsoid is set at 50% probability.



Crystal data and structure refinement for 8f:

Empirical formula	C ₃₂ H ₂₂ BrNO ₂
Formula weight	532.41
Temperature	169.99(10) K
Wavelength	1.54184 Å
Crystal system	triclinic
Space group	P-1
Unit cell dimensions	a = 9.2610(4) Å, α = 85.549(4)° b = 11.3469(6) Å, β = 74.375(5)° c = 12.8776(7) Å, γ = 76.275(4)°
Volume	1265.87(12) Å ³
Z	2
Density (calculated)	1.397 mg/m ³
Absorption coefficient	2.445 mm ⁻¹
F(000)	544.0
Crystal size	0.38 × 0.36 × 0.24 mm ³
Theta range for data collection	3.564 to 67.069°
Index ranges	-10 ≤ h ≤ 11, -11 ≤ k ≤ 13, -14 ≤ l ≤ 15
Reflections collected	12731
Independent reflections	4506 [R(int) = 0.0345]
Data / restraints / parameters	4506/0/325
Goodness-of-fit on F ²	1.040
Final R indices [I > 2σ(I)]	R ₁ = 0.0320, wR ₂ = 0.0821
R indices (all data)	R ₁ = 0.0336, wR ₂ = 0.0831
Largest diff. peak and hole	0.61 and -0.49 eÅ ⁻³

The single crystals of **8f** were grown by slow evaporation of the solution of **8f** (several milligrams) in the co-solvent of petroleum ether (3 mL) and ethyl acetate (1 mL) in a small glass vial at rt over 2-3 days. X-ray diffraction data of a suitable crystal kept at 169.99(10) K was collected on a XtaLAB AFC12 (RINC); Kappa dual home/near diffractometer.

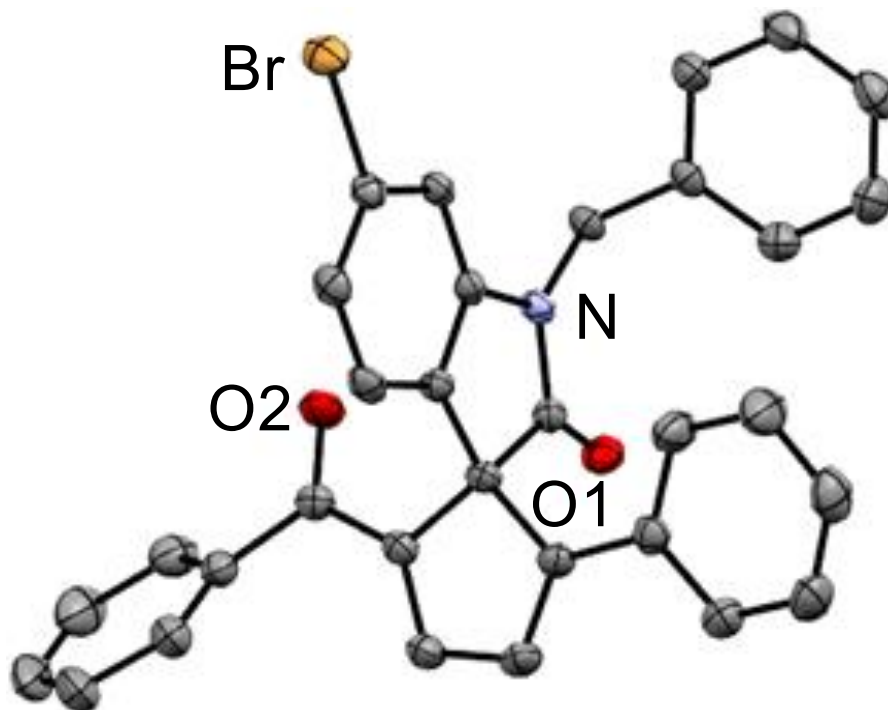
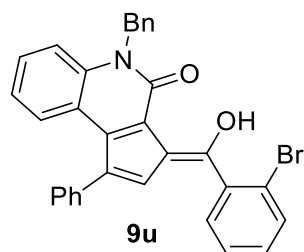


Figure S4 X-ray structure of **8f**. Thermal ellipsoid is set at 50% probability.



Crystal data and structure refinement for **9u**:

Empirical formula	C ₃₂ H ₂₂ BrNO ₂
Formula weight	532.41
Temperature	173.00(10) K
Wavelength	1.54184 Å
Crystal system	monoclinic
Space group	P2 ₁ /c
Unit cell dimensions	a = 9.70430(10) Å, α = 90° b = 17.15680(10) Å, β = 98.3360(10)° c = 14.49380(10) Å, γ = 90°
Volume	2387.65(3) Å ³
Z	4
Density (calculated)	1.481 mg/m ³
Absorption coefficient	2.592 mm ⁻¹
F(000)	1088.0
Crystal size	0.28 × 0.24 × 0.16 mm ³
Theta range for data collection	4.018 to 67.069°
Index ranges	-11 ≤ h ≤ 11, -18 ≤ k ≤ 20, -17 ≤ l ≤ 17
Reflections collected	24261
Independent reflections	4262 [R(int) = 0.0348]
Data / restraints / parameters	4262/0/326
Goodness-of-fit on F ²	1.058
Final R indices [I > 2σ(I)]	R ₁ = 0.0261, wR ₂ = 0.0693
R indices (all data)	R ₁ = 0.0278, wR ₂ = 0.0702
Largest diff. peak and hole	0.25 and -0.53 eÅ ⁻³

The single crystals of **9u** were grown by slow evaporation of the solution of **9u** (several milligrams) in the co-solvent of petroleum ether (3 mL) and ethyl acetate (1 mL) in a small glass vial at rt over 2-3 days. X-ray diffraction data of a suitable crystal kept at 173.00(10) K was collected on a XtaLAB AFC12 (RINC); Kappa dual home/near diffractometer.

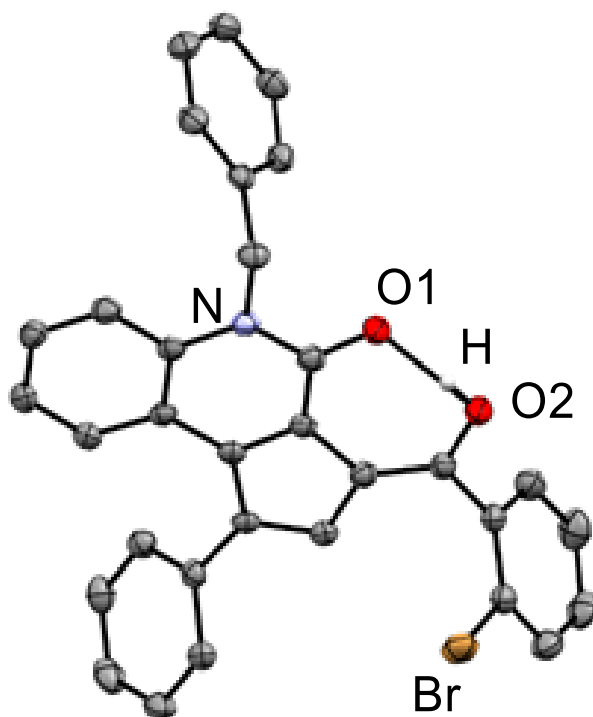
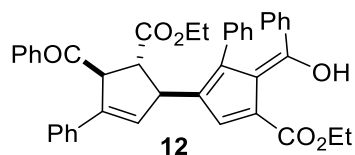


Figure S5 X-ray structure of **9u**. Thermal ellipsoid is set at 50% probability.



Crystal data and structure refinement for 12:

Empirical formula	C ₄₂ H ₃₆ O ₆
Formula weight	636.71
Temperature	173.00(10) K
Wavelength	1.54184 Å
Crystal system	monoclinic
Space group	P2 ₁ /c
Unit cell dimensions	a = 14.4529(2) Å, α = 90° b = 14.2698(3) Å, β = 108.845(2)° c = 17.1004(3) Å, γ = 90°
Volume	3337.74(11) Å ³
Z	4
Density (calculated)	1.267 mg/m ³
Absorption coefficient	0.674 mm ⁻¹
F(000)	1344.0
Crystal size	0.36 × 0.24 × 0.22 mm ³
Theta range for data collection	3.231 to 67.08°
Index ranges	-17 ≤ h ≤ 16, -17 ≤ k ≤ 16, -20 ≤ l ≤ 20
Reflections collected	18112
Independent reflections	5872 [R(int) = 0.0329]
Data / restraints / parameters	5872/116/424
Goodness-of-fit on F ²	0.885
Final R indices [I > 2σ(I)]	R ₁ = 0.1495, wR ₂ = 0.2763
R indices (all data)	R ₁ = 0.1653, wR ₂ = 0.2840
Largest diff. peak and hole	1.42 and -1.09 eÅ ⁻³

The single crystals of **12** were grown by slow evaporation of the solution of **12** (several milligrams) in the co-solvent of petroleum ether (3 mL) and ethyl acetate (1 mL) in a small glass vial at rt over 2-3 days. X-ray diffraction data of a suitable crystal kept at 173.00(10) K was collected on a XtaLAB AFC12 (RINC); Kappa dual home/near diffractometer.

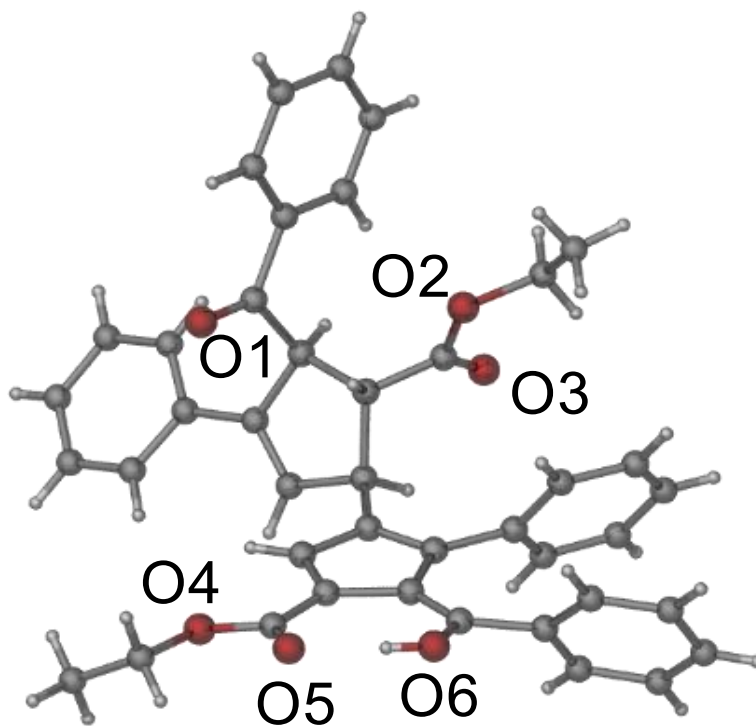
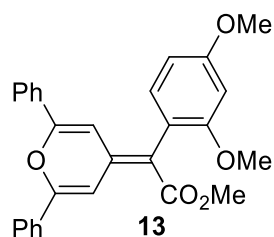


Figure S6 X-ray structure of **12**. Thermal ellipsoid is set at 50% probability.



Crystal data and structure refinement for 12:

Empirical formula	C ₂₈ H ₂₄ O ₅
Formula weight	440.47
Temperature	170.00(10) K
Wavelength	1.54184 Å
Crystal system	monoclinic
Space group	P2 ₁ /c
Unit cell dimensions	a = 11.6432(4) Å, α = 90° b = 26.6464(11) Å, β = 102.172(4)° c = 7.3107(3) Å, γ = 90°
Volume	2217.15(15) Å ³
Z	4
Density (calculated)	1.320 mg/m ³
Absorption coefficient	0.731 mm ⁻¹
F(000)	928.0
Crystal size	0.42 × 0.29 × 0.26 mm ³
Theta range for data collection	3.317 to 67.077°
Index ranges	−13 ≤ h ≤ 9, −26 ≤ k ≤ 31, −8 ≤ l ≤ 8
Reflections collected	11384
Independent reflections	3946 [R(int) = 0.0464]
Data / restraints / parameters	3946/0/302
Goodness-of-fit on F ²	1.074
Final R indices [I > 2σ(I)]	R ₁ = 0.0433, wR ₂ = 0.1144
R indices (all data)	R ₁ = 0.0498, wR ₂ = 0.1181
Largest diff. peak and hole	0.21 and −0.20 eÅ ⁻³

The single crystals of **13** were grown by slow evaporation of the solution of **13** (several milligrams) in the co-solvent of petroleum ether (3 mL) and ethyl acetate (1 mL) in a small glass vial at rt over 2-3 days. X-ray diffraction data of a suitable crystal kept at 170.00(10) K was collected on a XtaLAB AFC12 (RINC); Kappa dual home/near diffractometer.

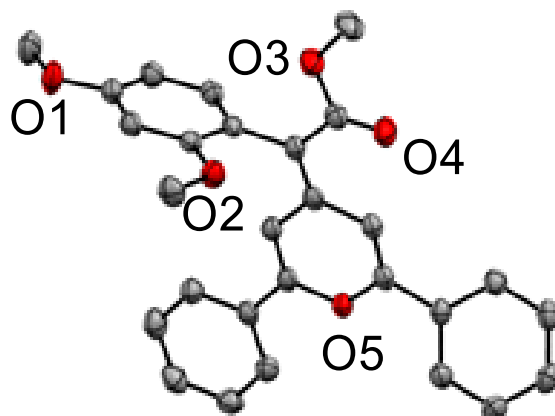


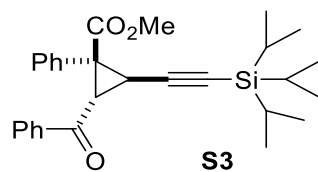
Figure S7 X-ray structure of **13**. Thermal ellipsoid is set at 50% probability.

CCDC 2180629 (**5an**), 2180630 (**6f**), 2180631 (**7i**), 2180632 (**8f**), 2180633 (**9u**), 2180634 (**12**), and 2180635 (**13**) contain the supplementary crystallographic data, which can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

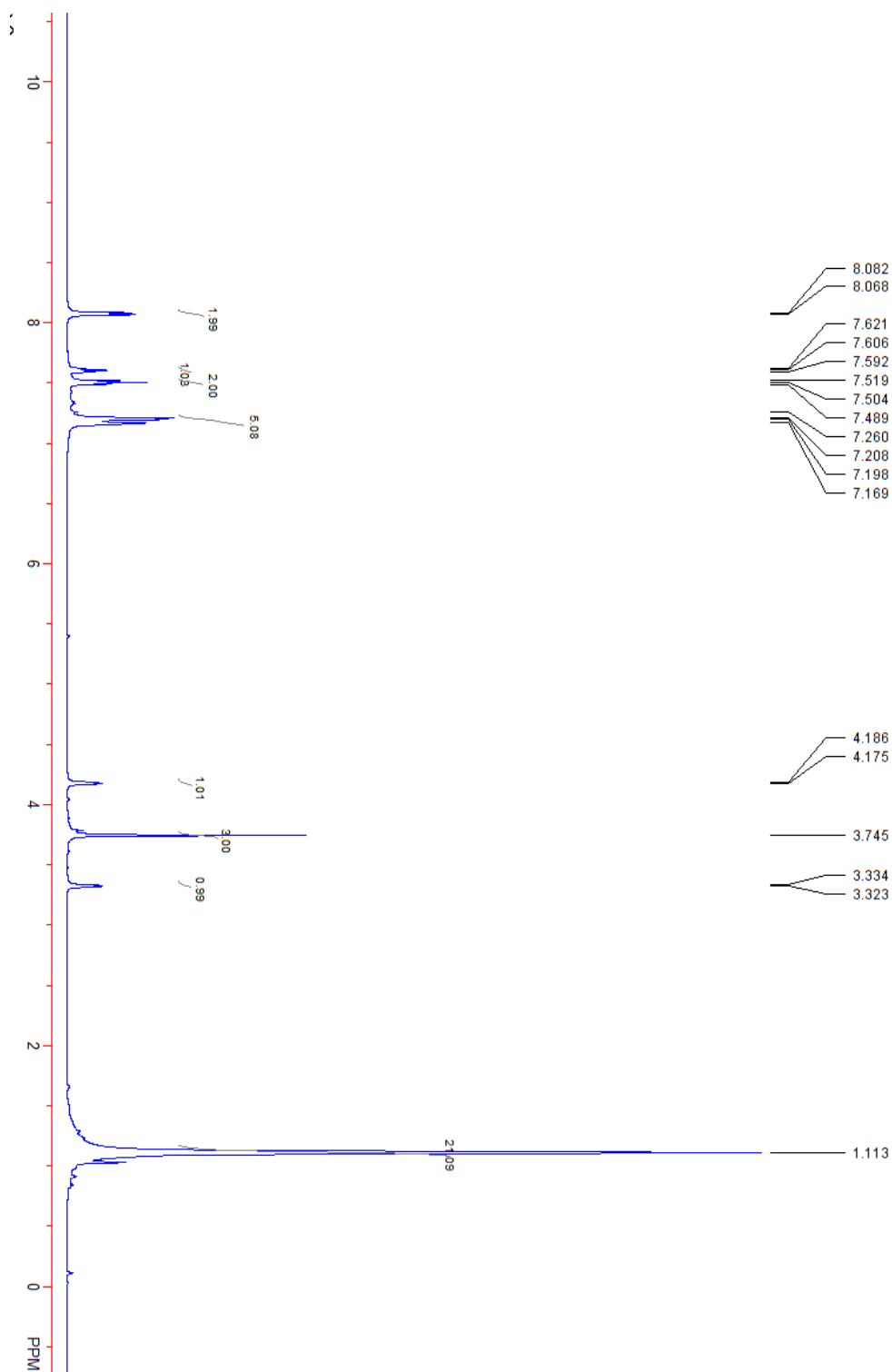
12. References

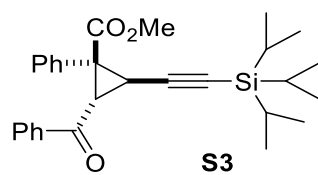
- (1) Wu, W.; Zou, S.; Lin, L.; Ji, J.; Zhang, Y.; Ma, B.; Liu, X.; Feng, X. *Chem. Commun.* **2017**, 53, 3232.
- (2) Shao, J.; Luo, Q.; Bi, H.; Wang, S. R. *Org. Lett.* **2021**, 23, 459.
- (3) Padwa, A.; Snyder, J. P.; Curtis, E. A.; Sheehan, S. M.; Worsencroft, K. J.; Kappe, C. O. *J. Am. Chem. Soc.* **2000**, 122, 8155.
- (4) Liu, J.; Liu, X.-P.; Wu, H.; Wei, Y.; Lu, F.-D.; Guo, K.-R.; Cheng, Y.; Xiao, W.-J. *Chem. Commun.* **2020**, 56, 11508.

13. NMR spectra of key compounds

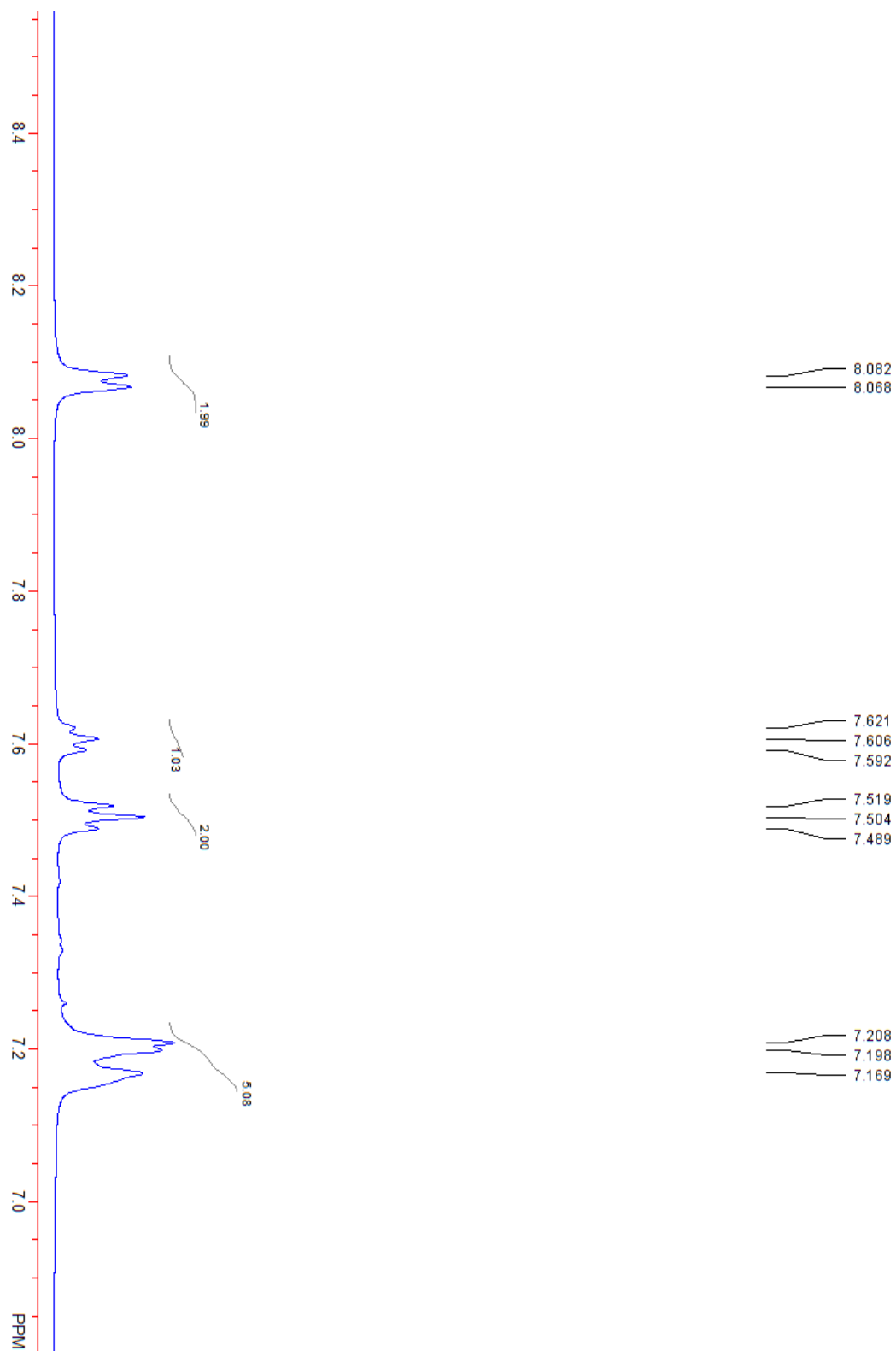


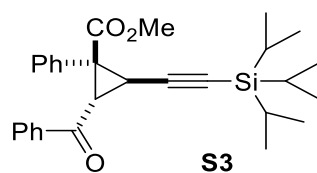
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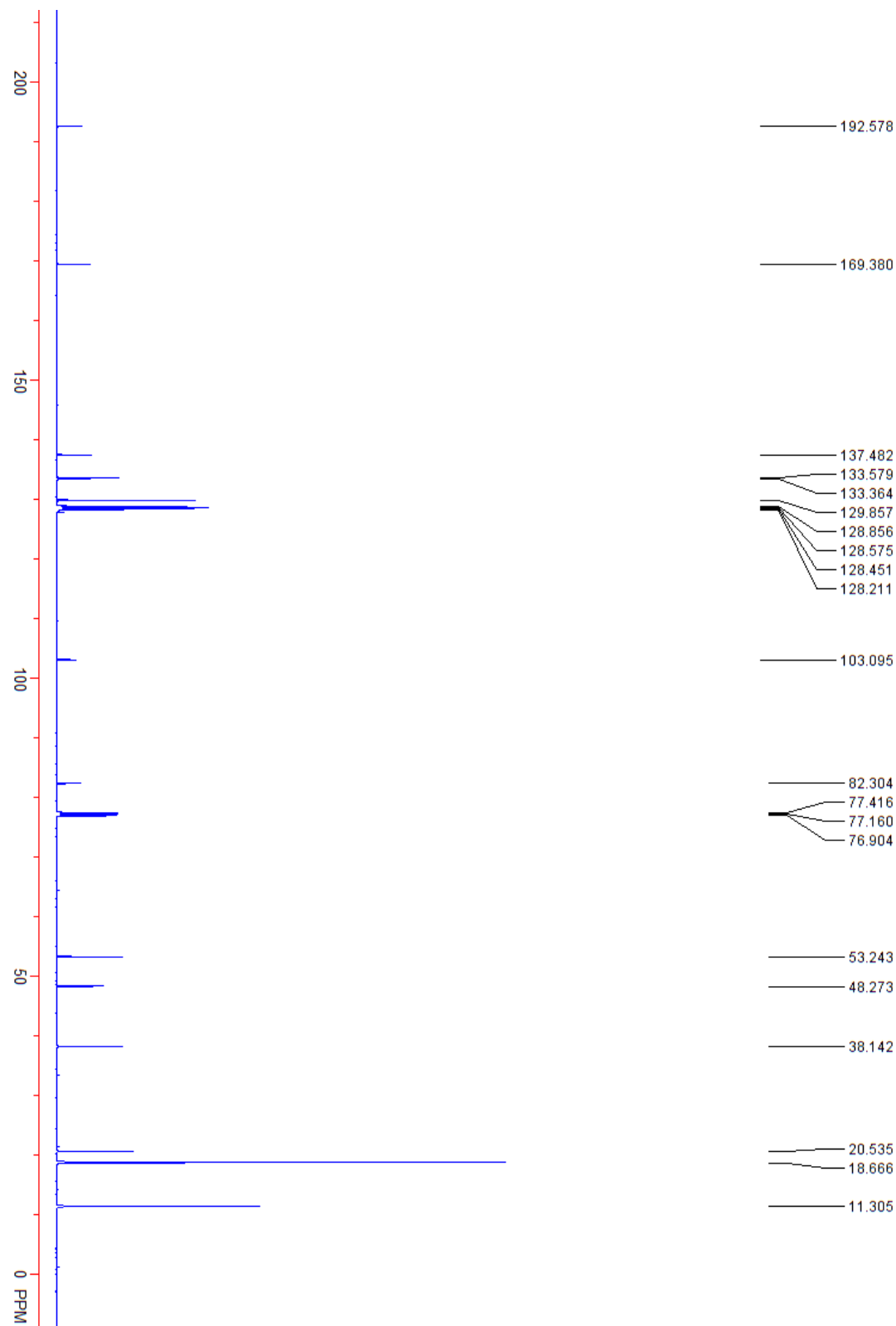


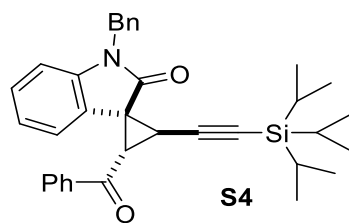
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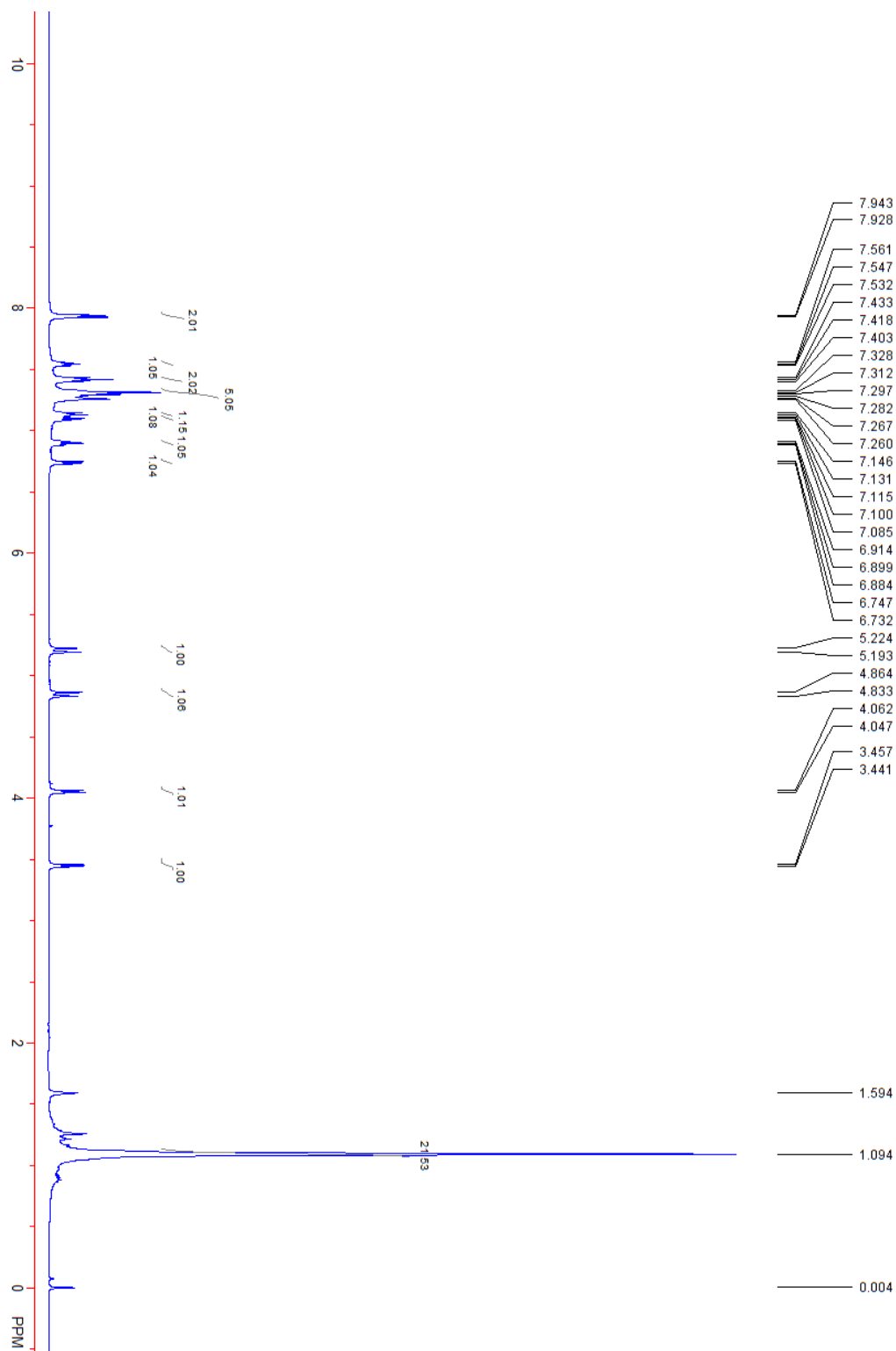


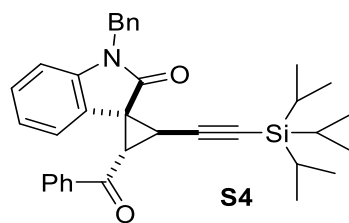
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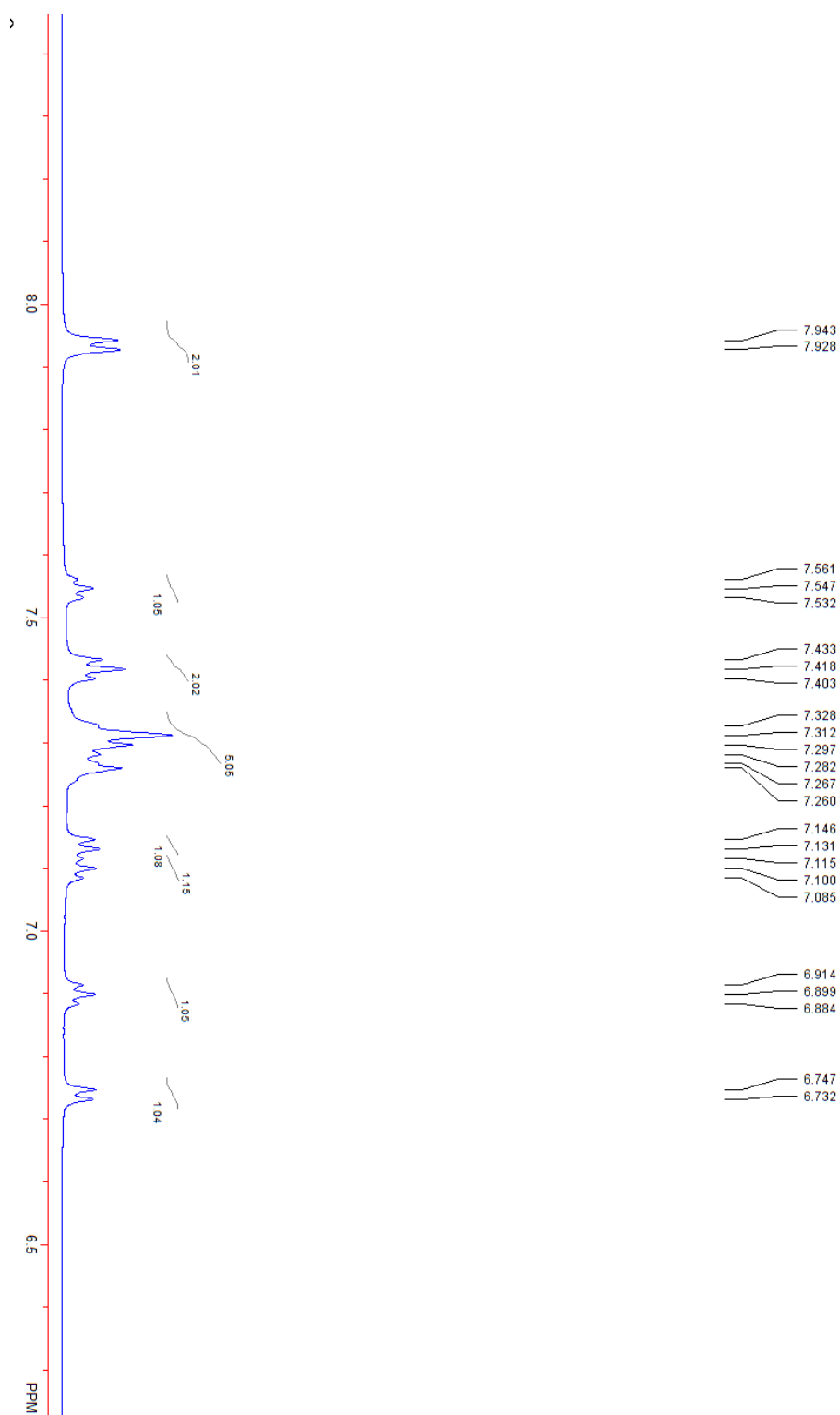


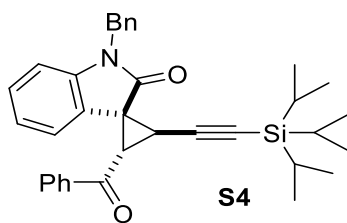
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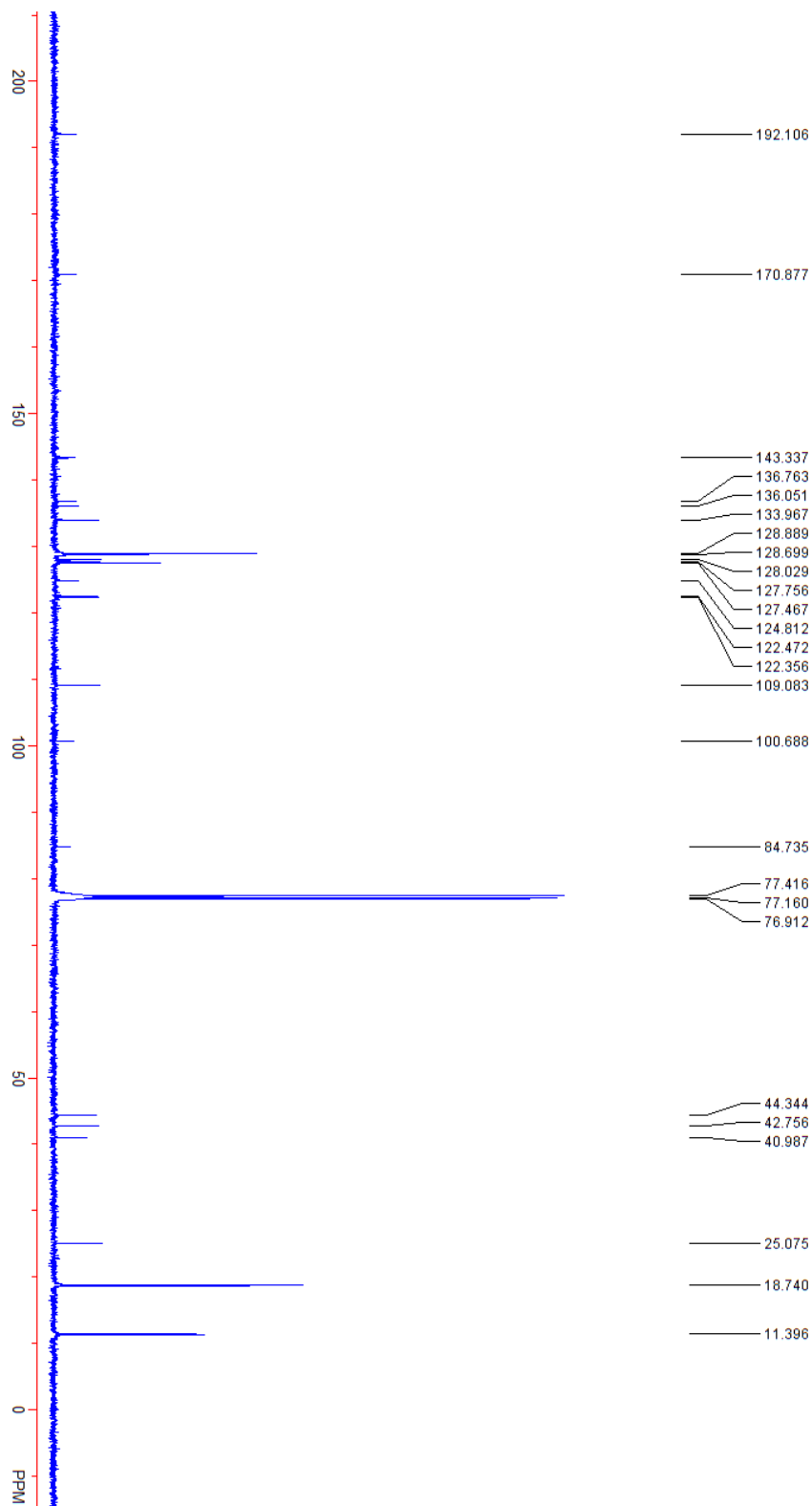


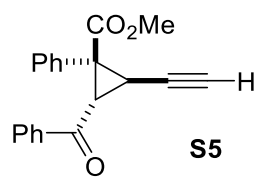
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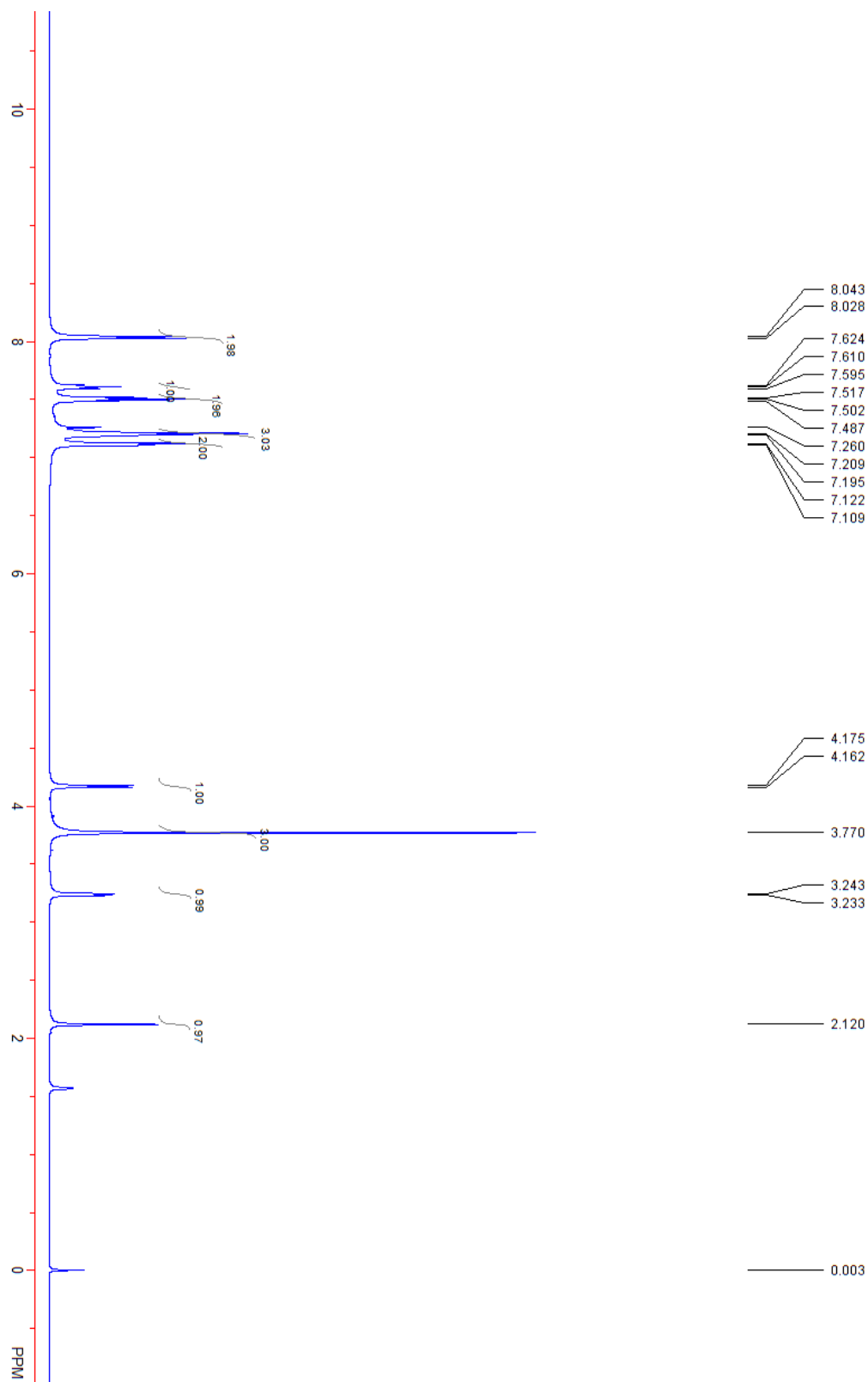


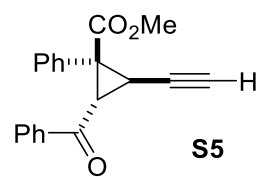
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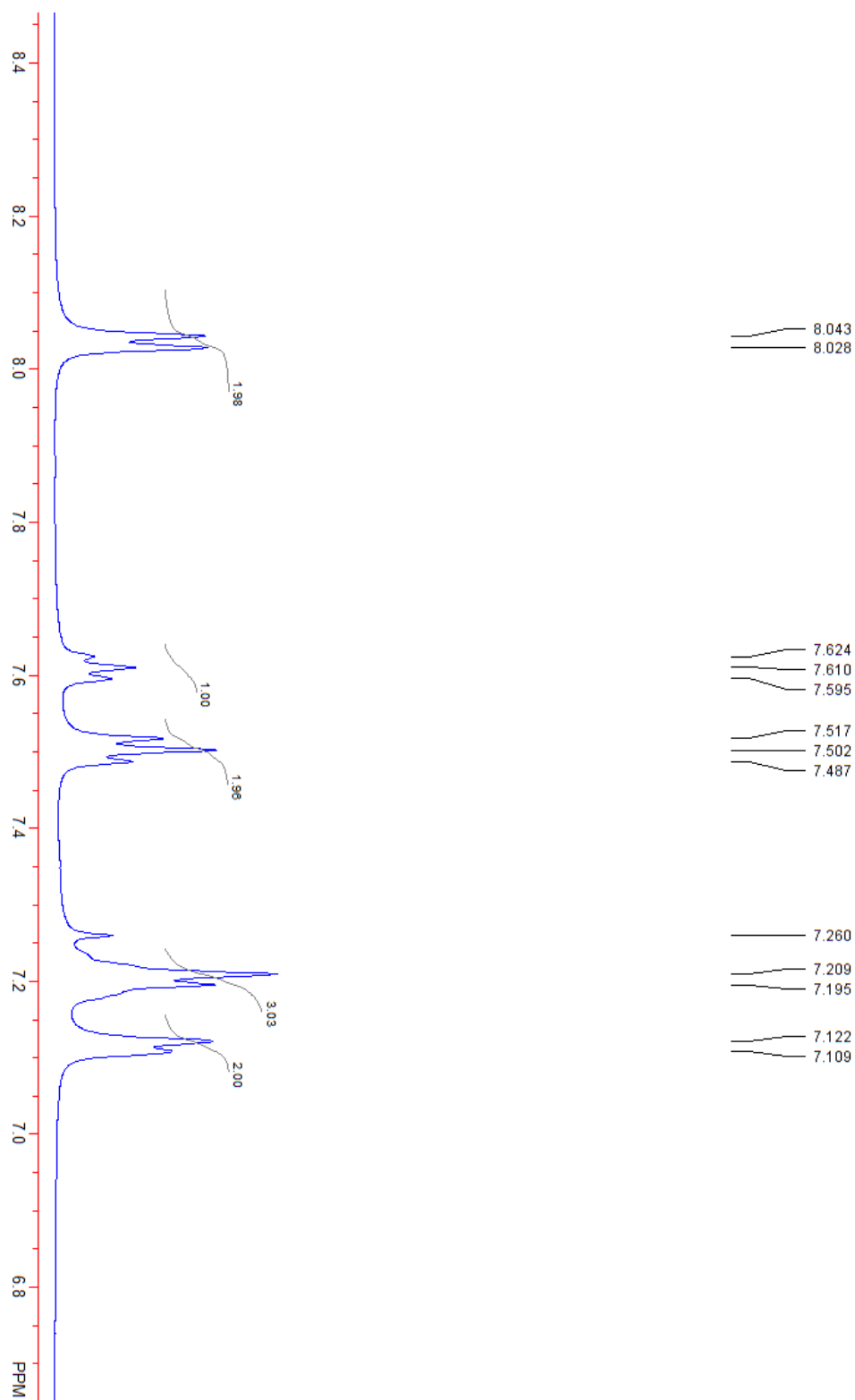


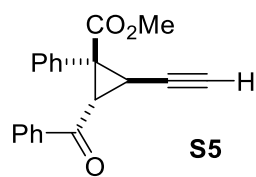
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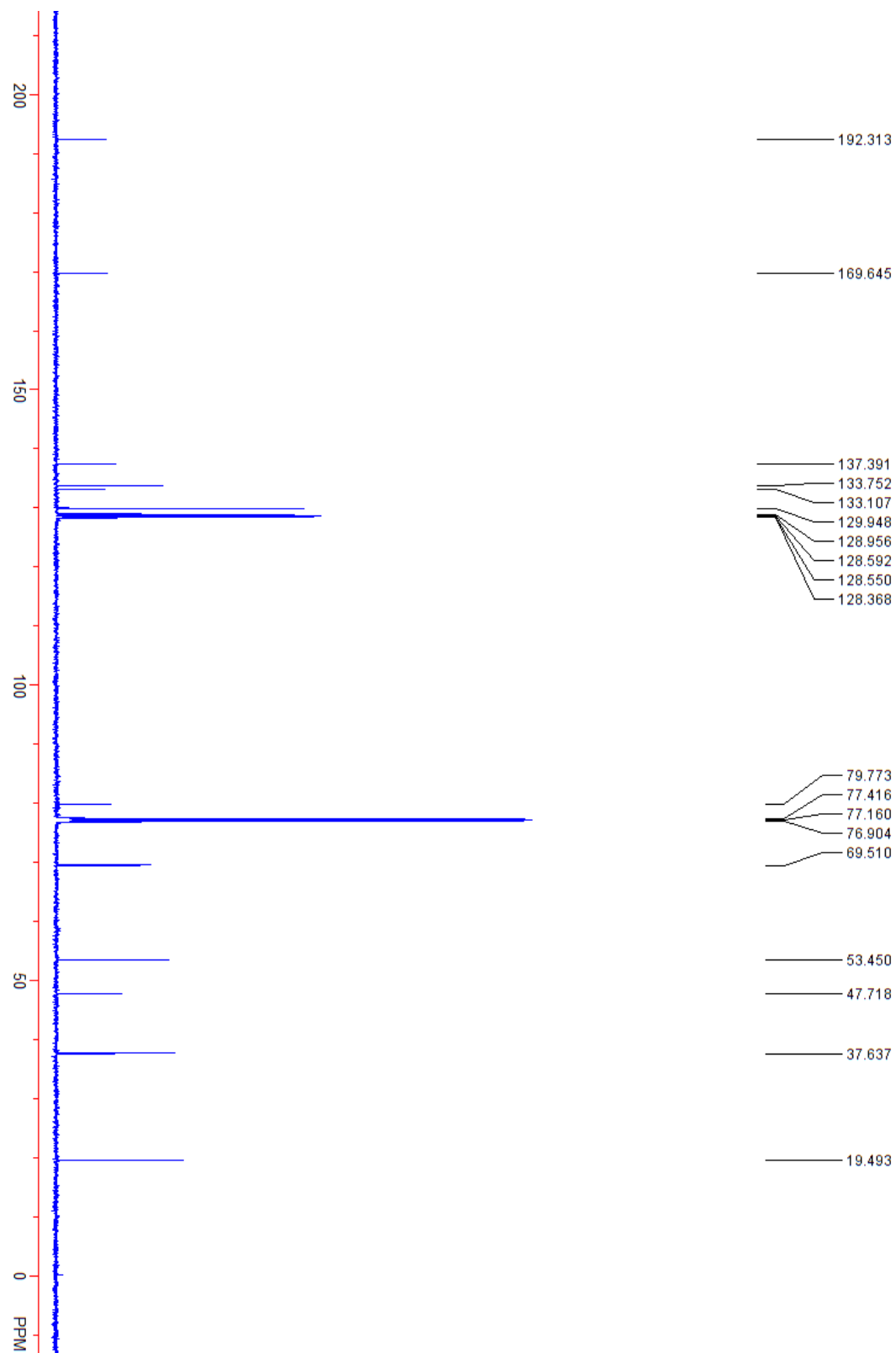


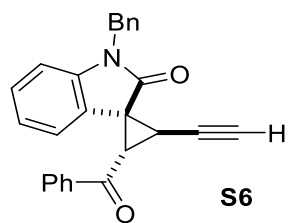
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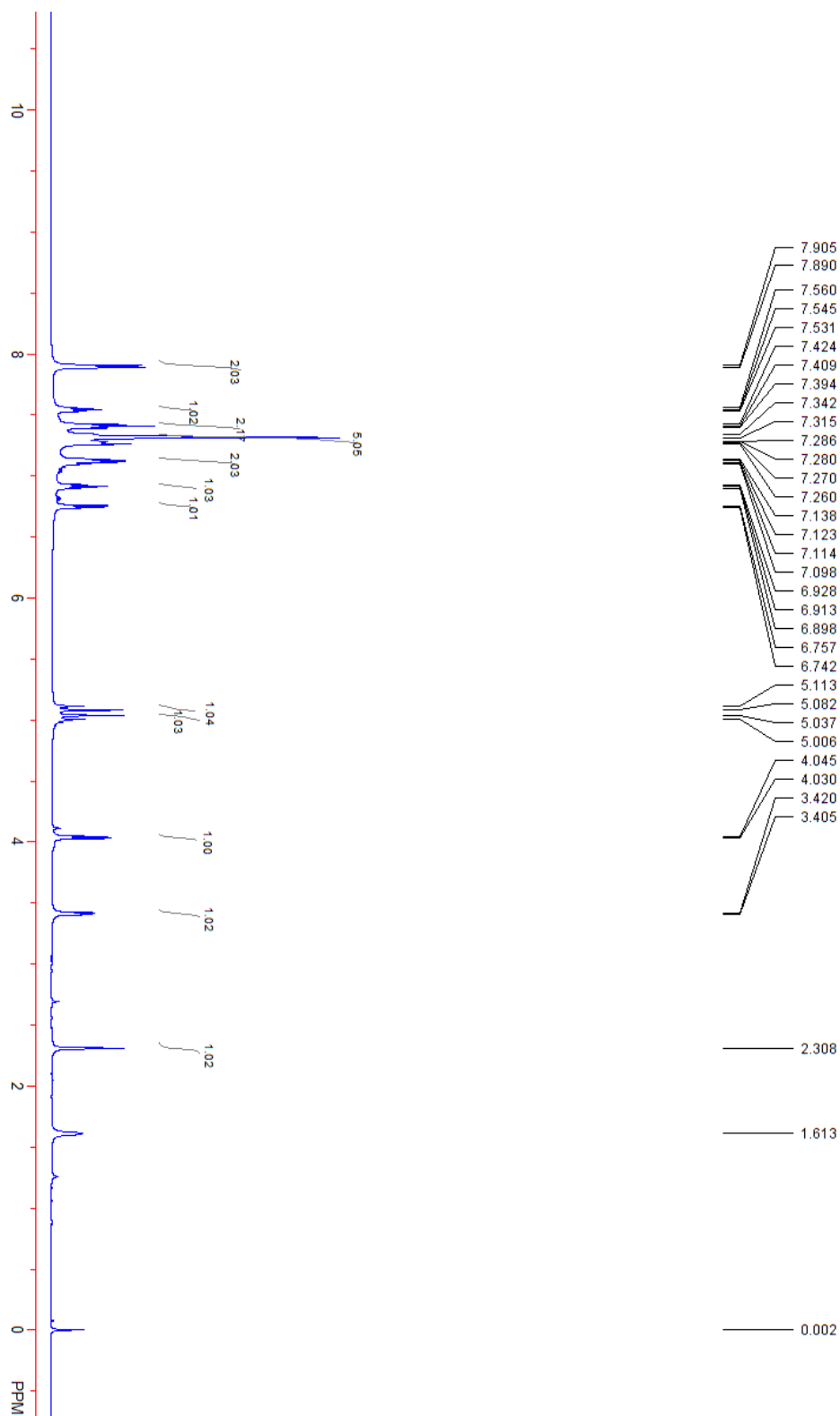


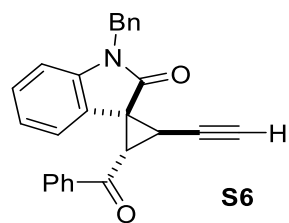
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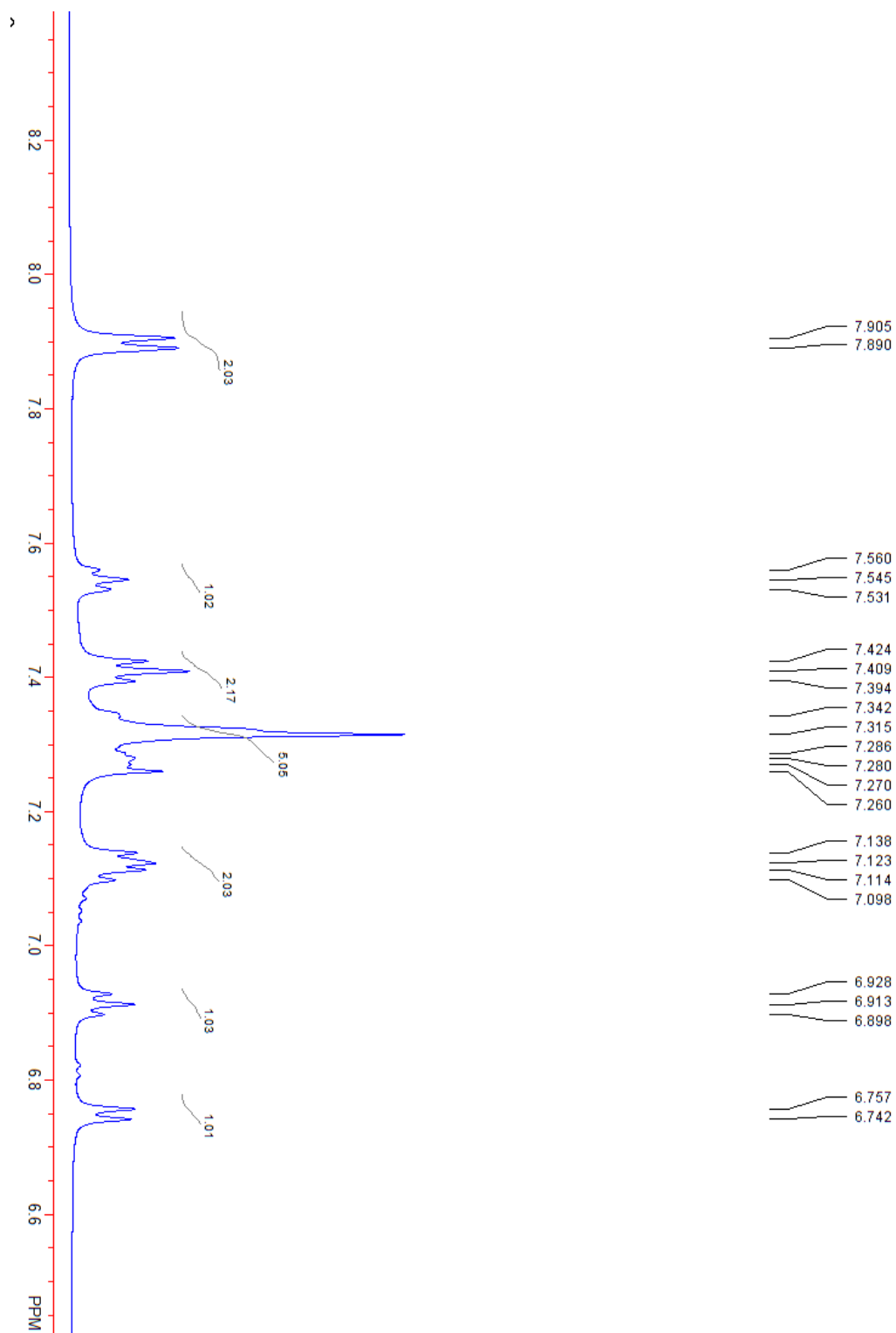


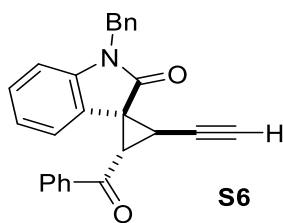
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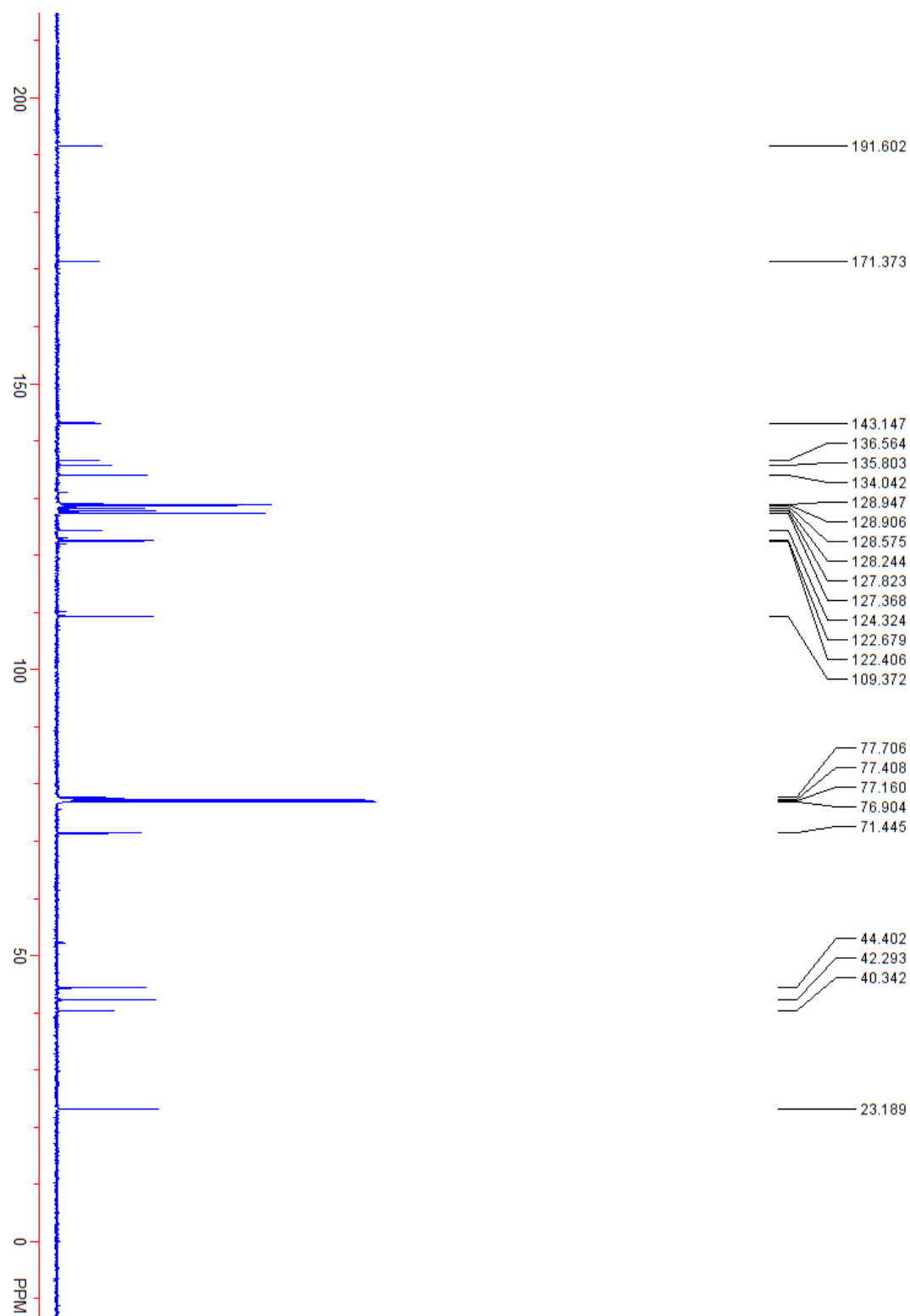


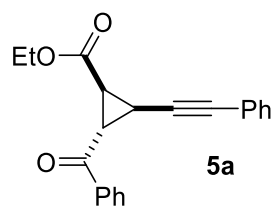
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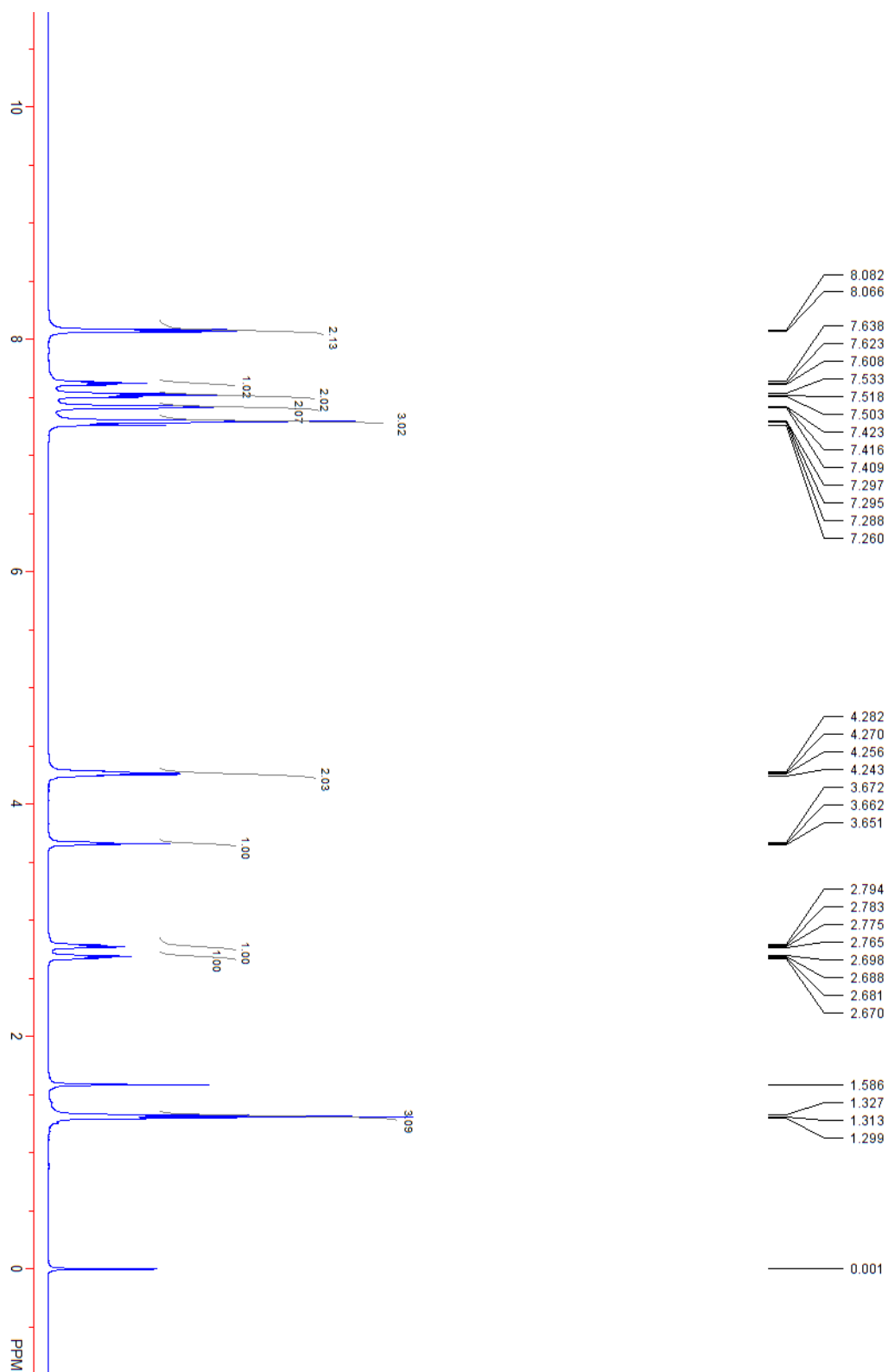


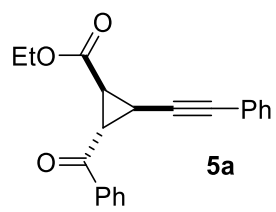
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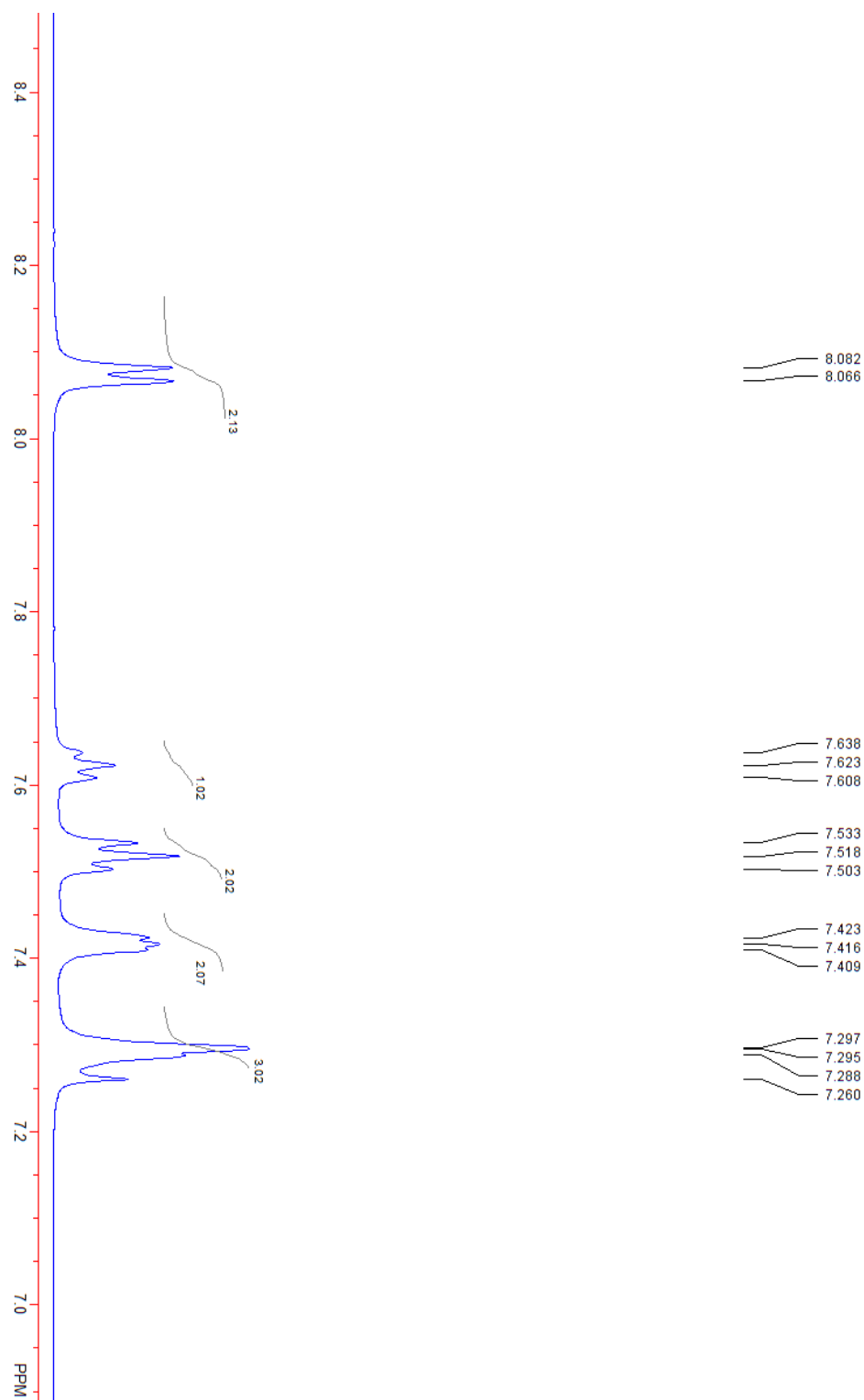


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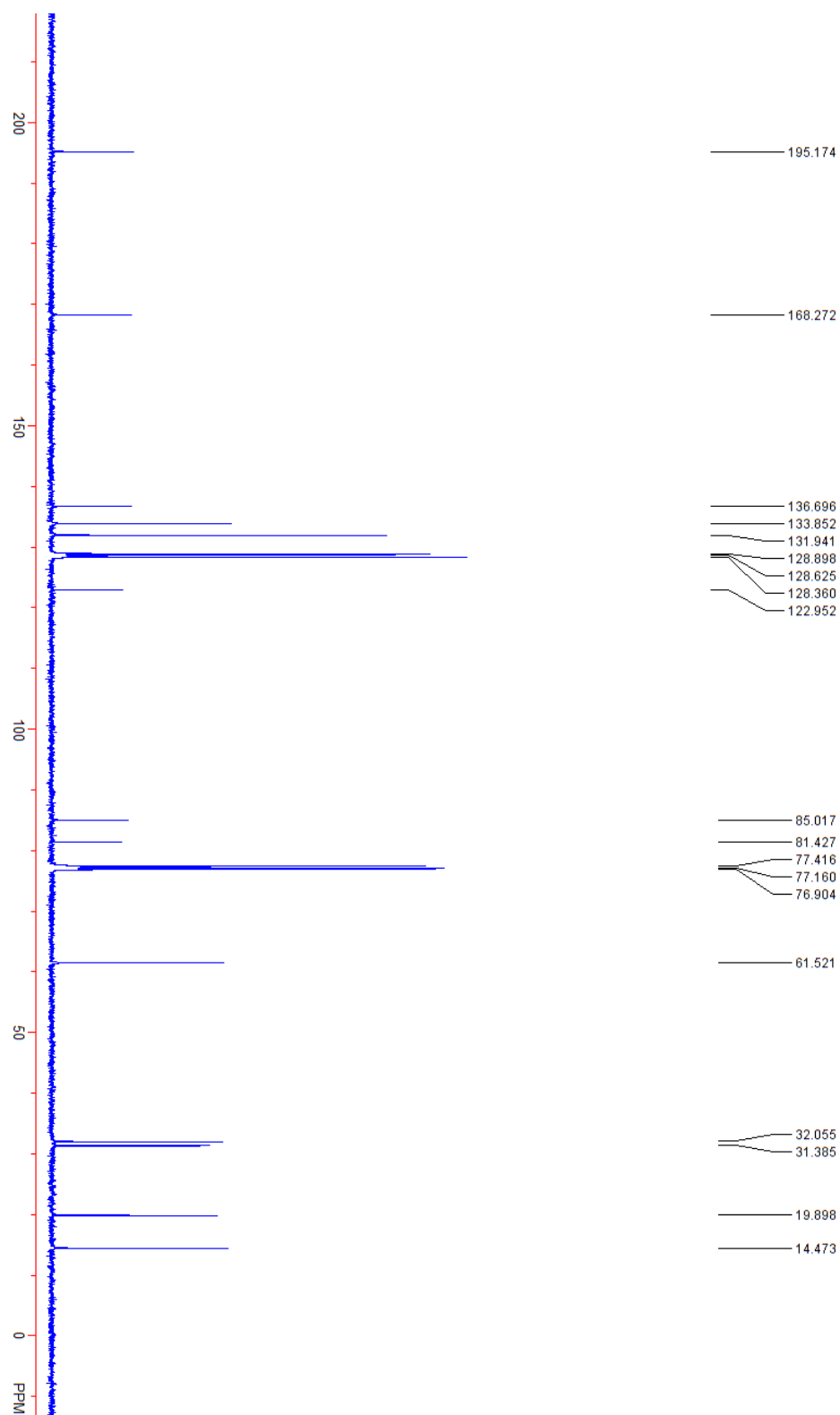
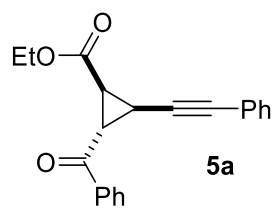




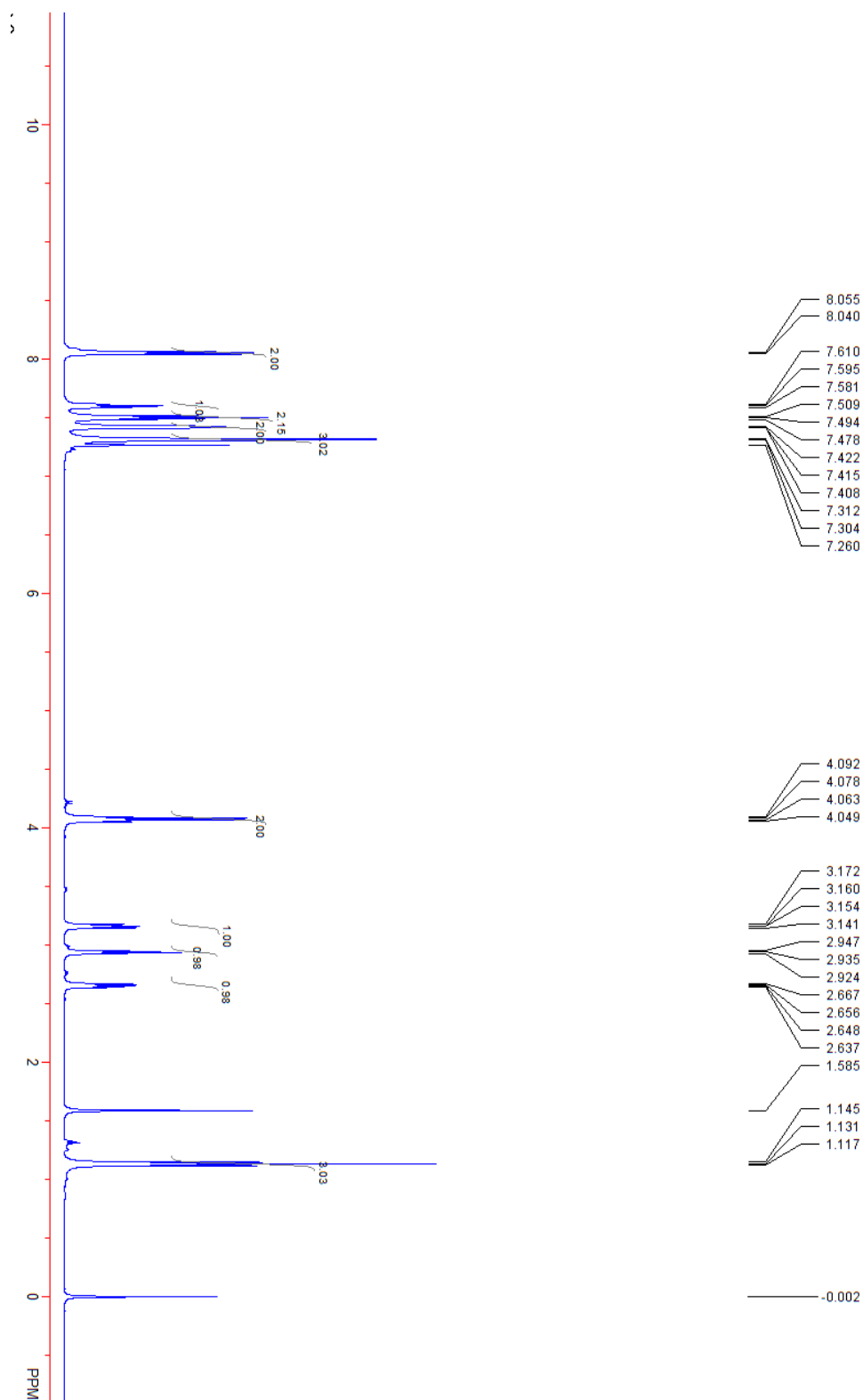
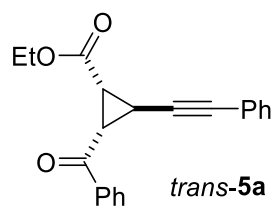
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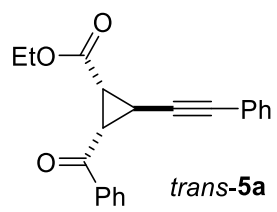


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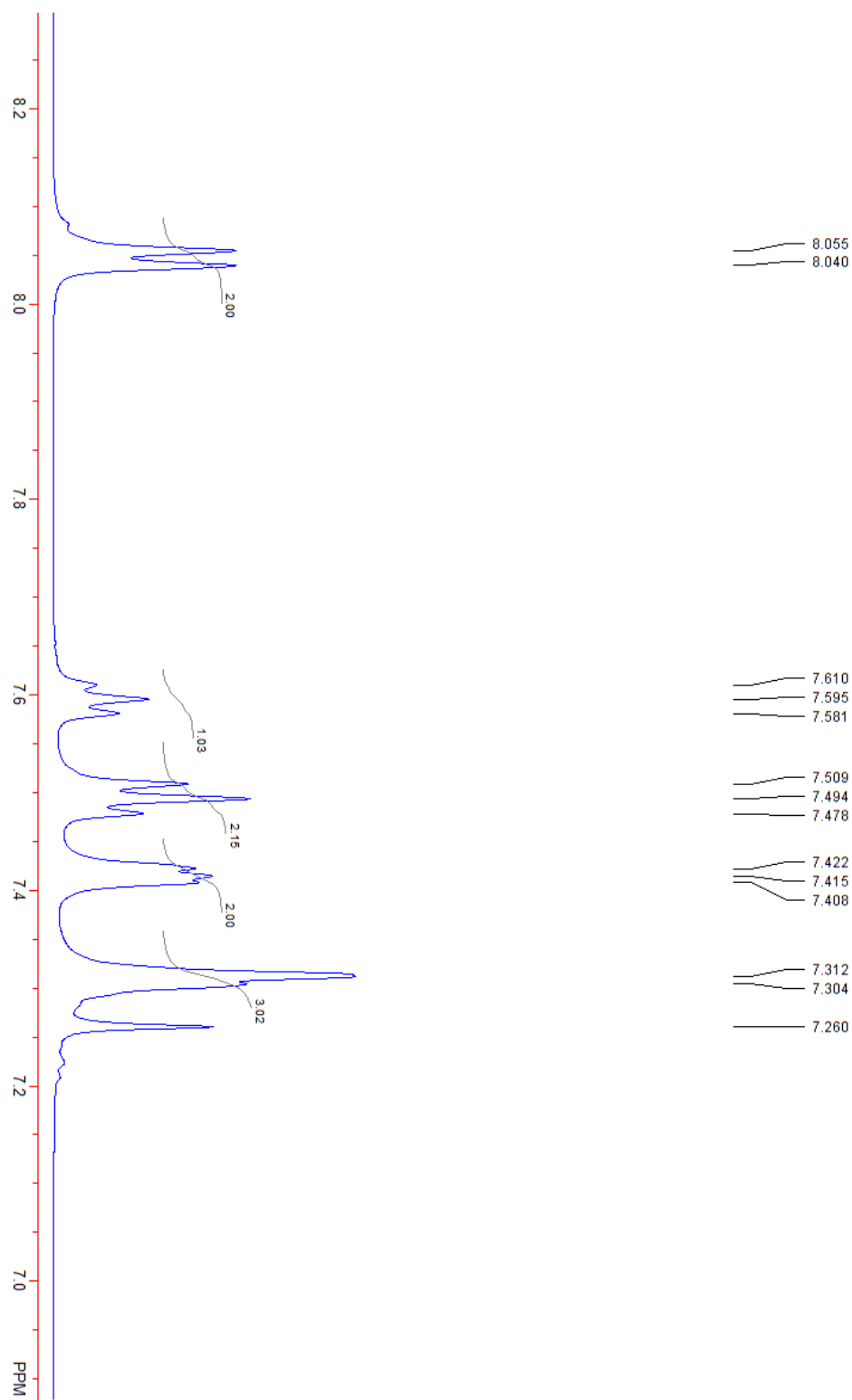


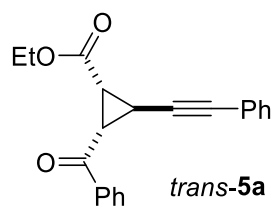
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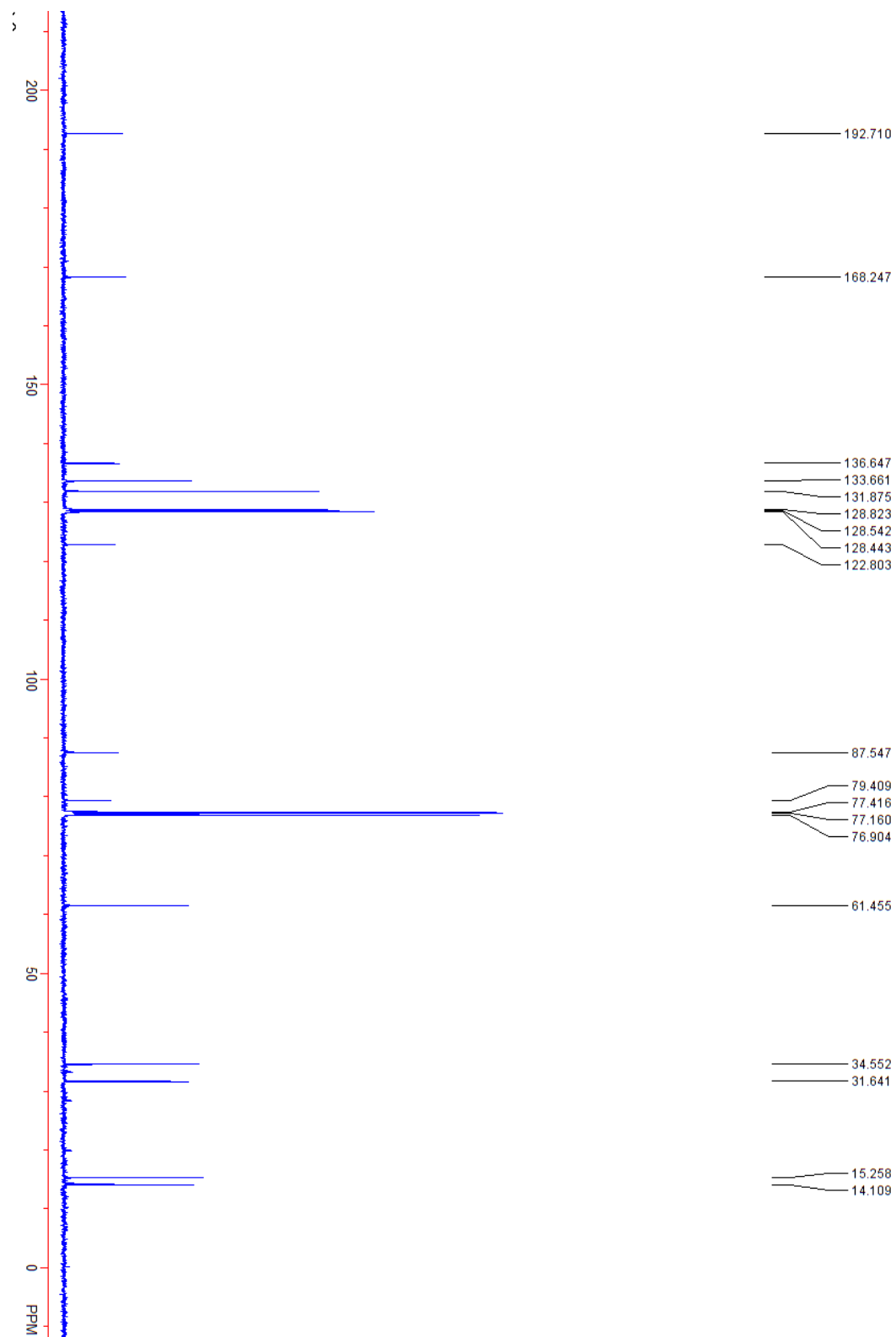


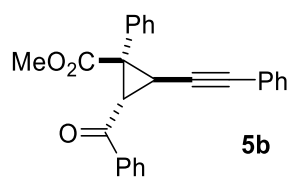
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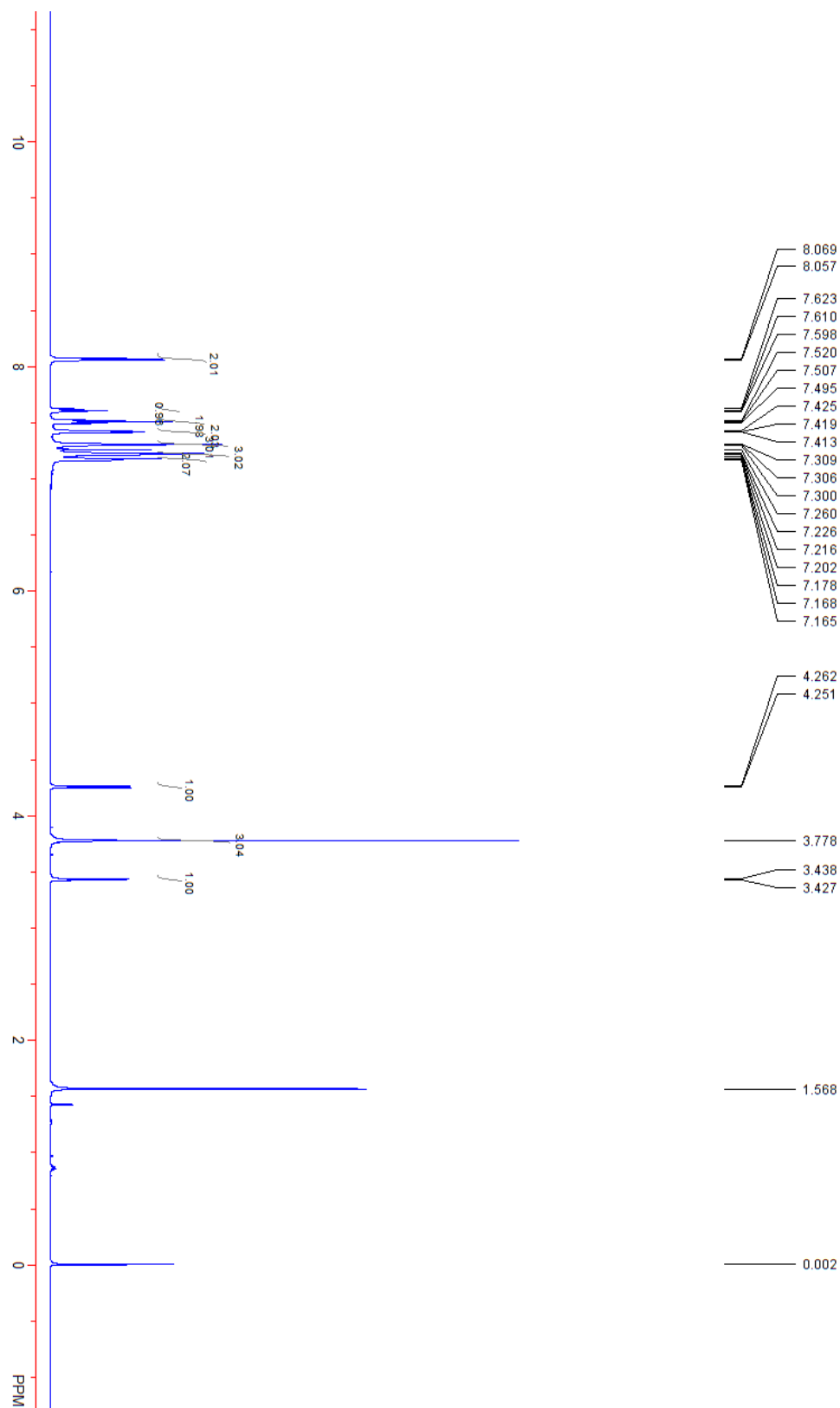


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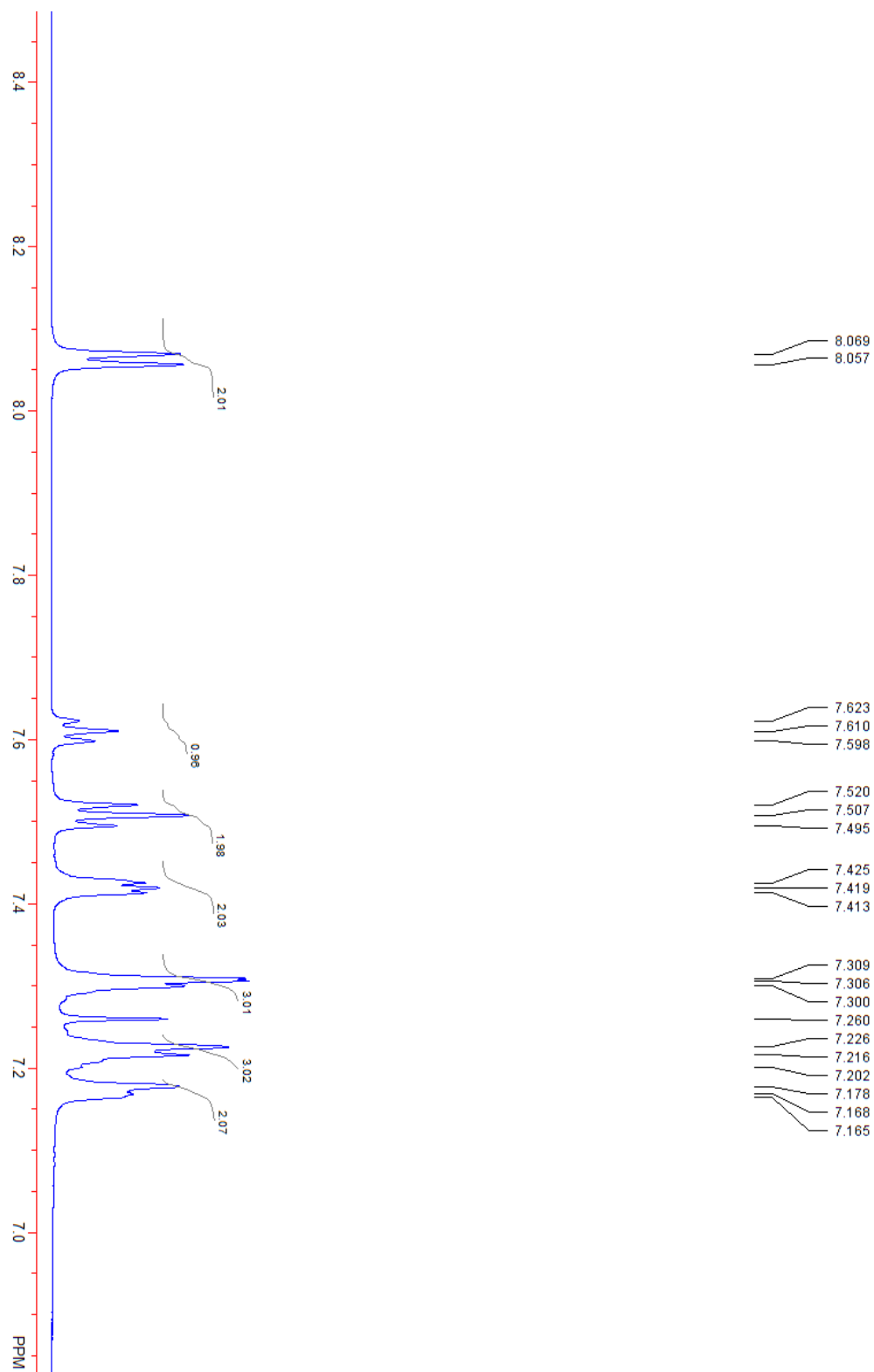
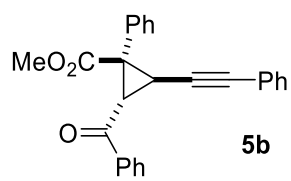


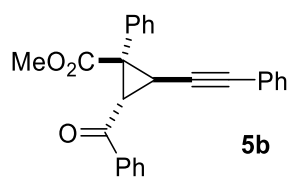


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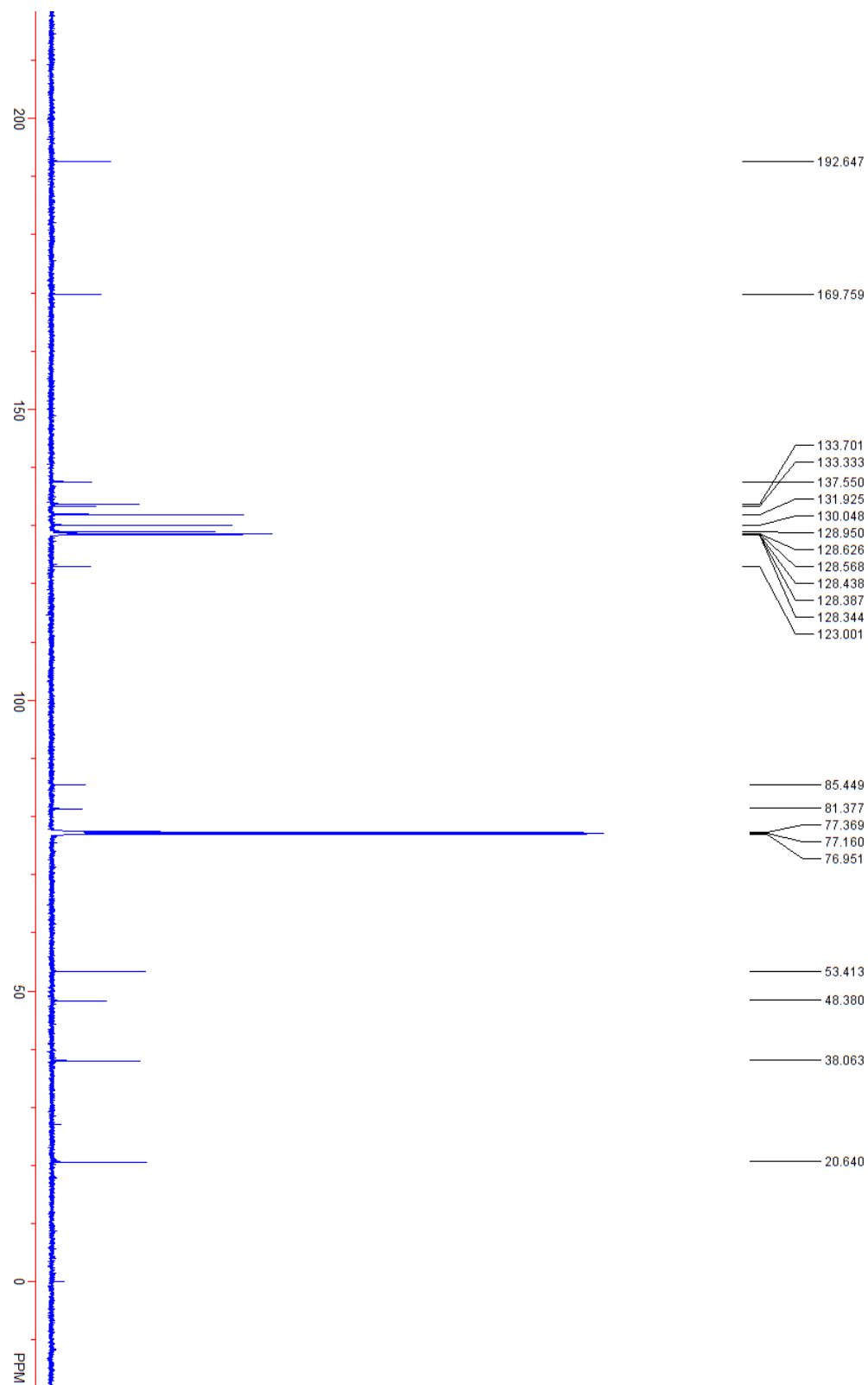


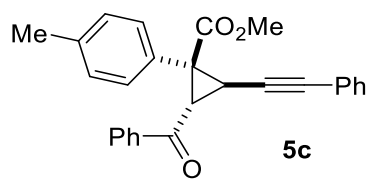
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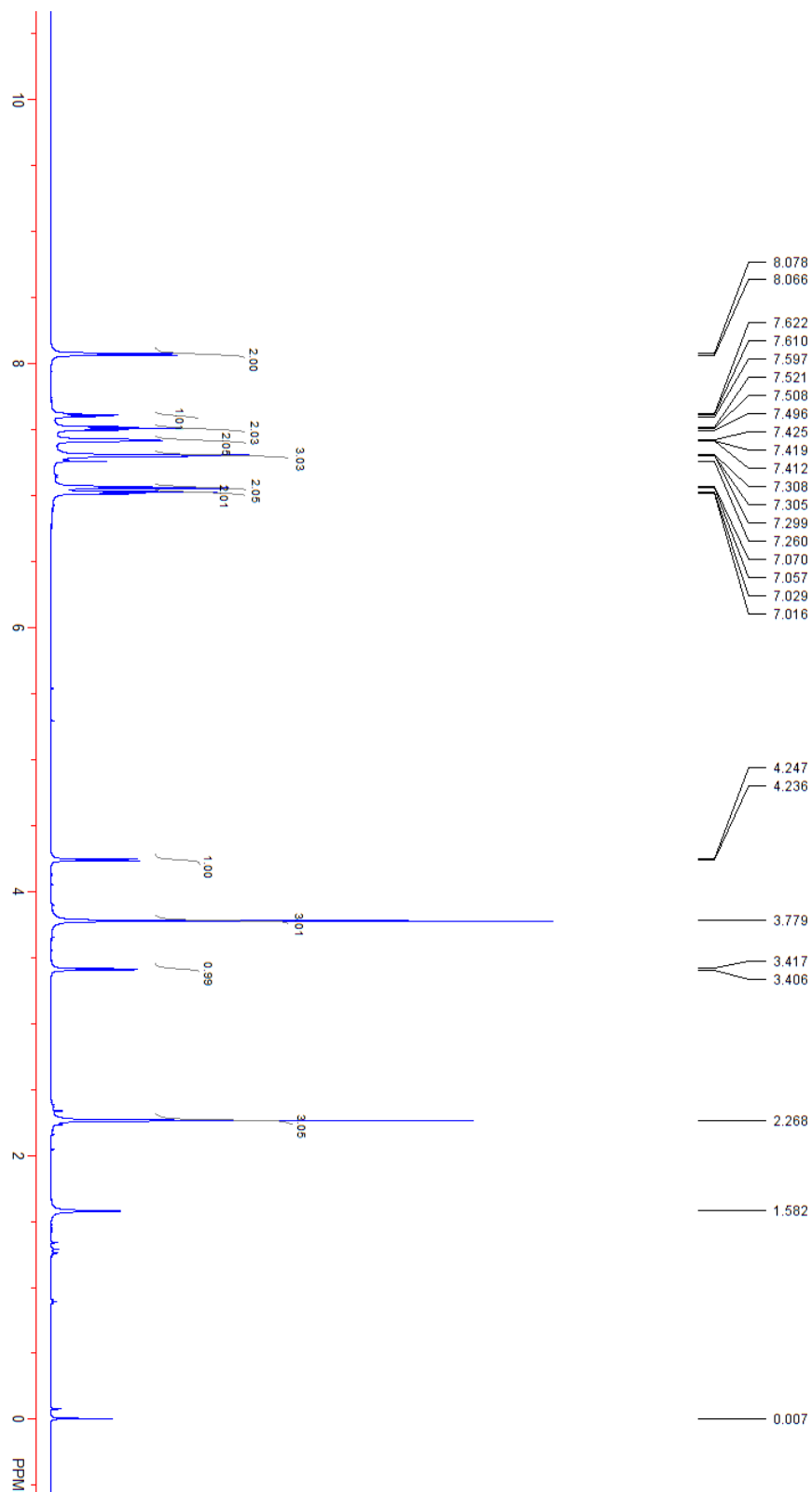


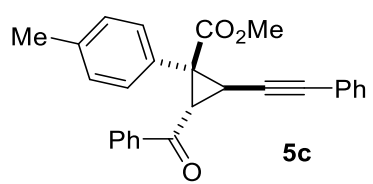
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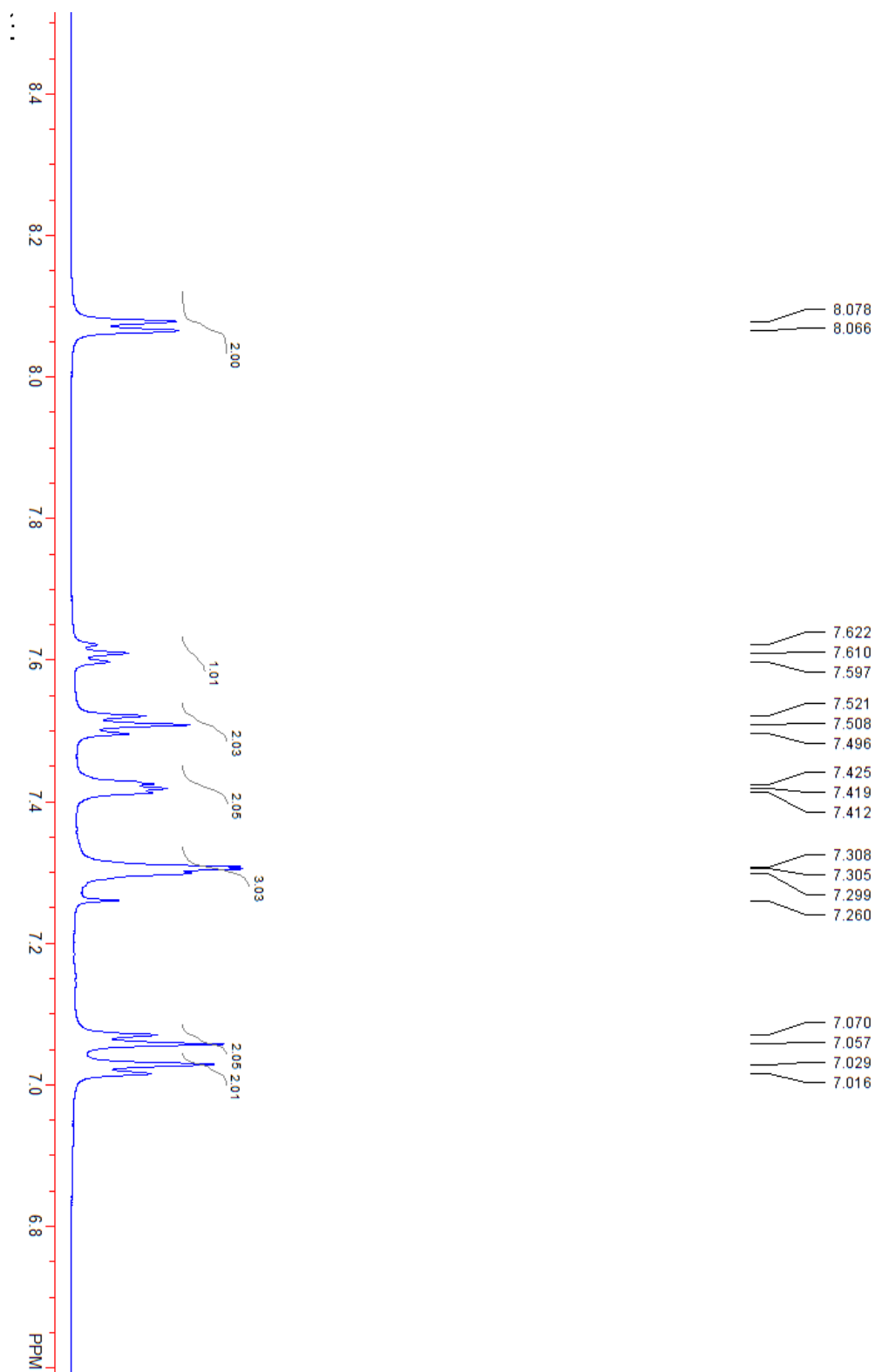


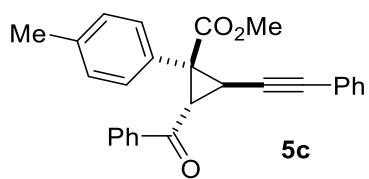
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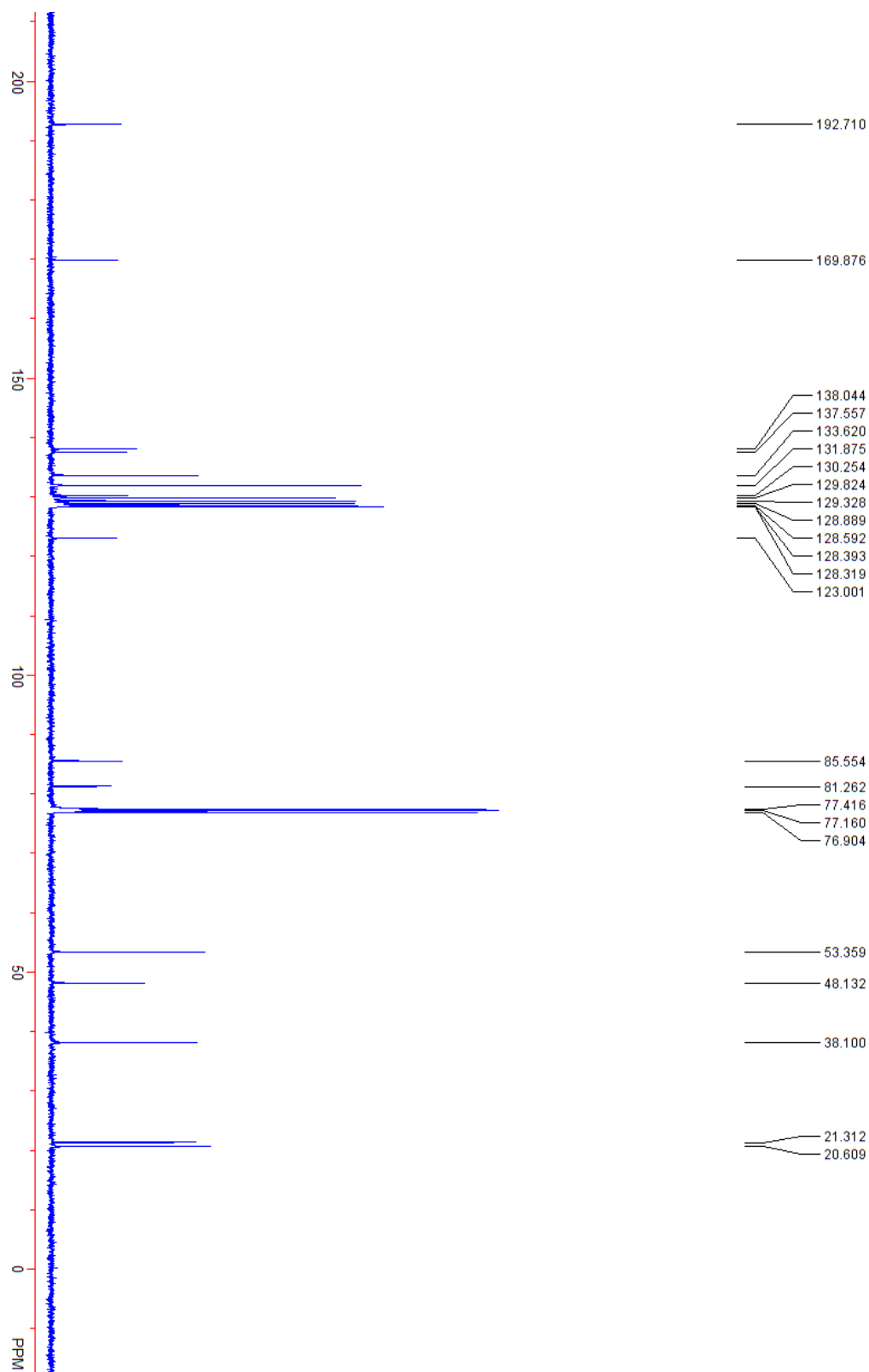


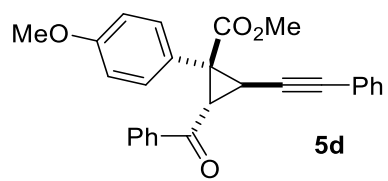
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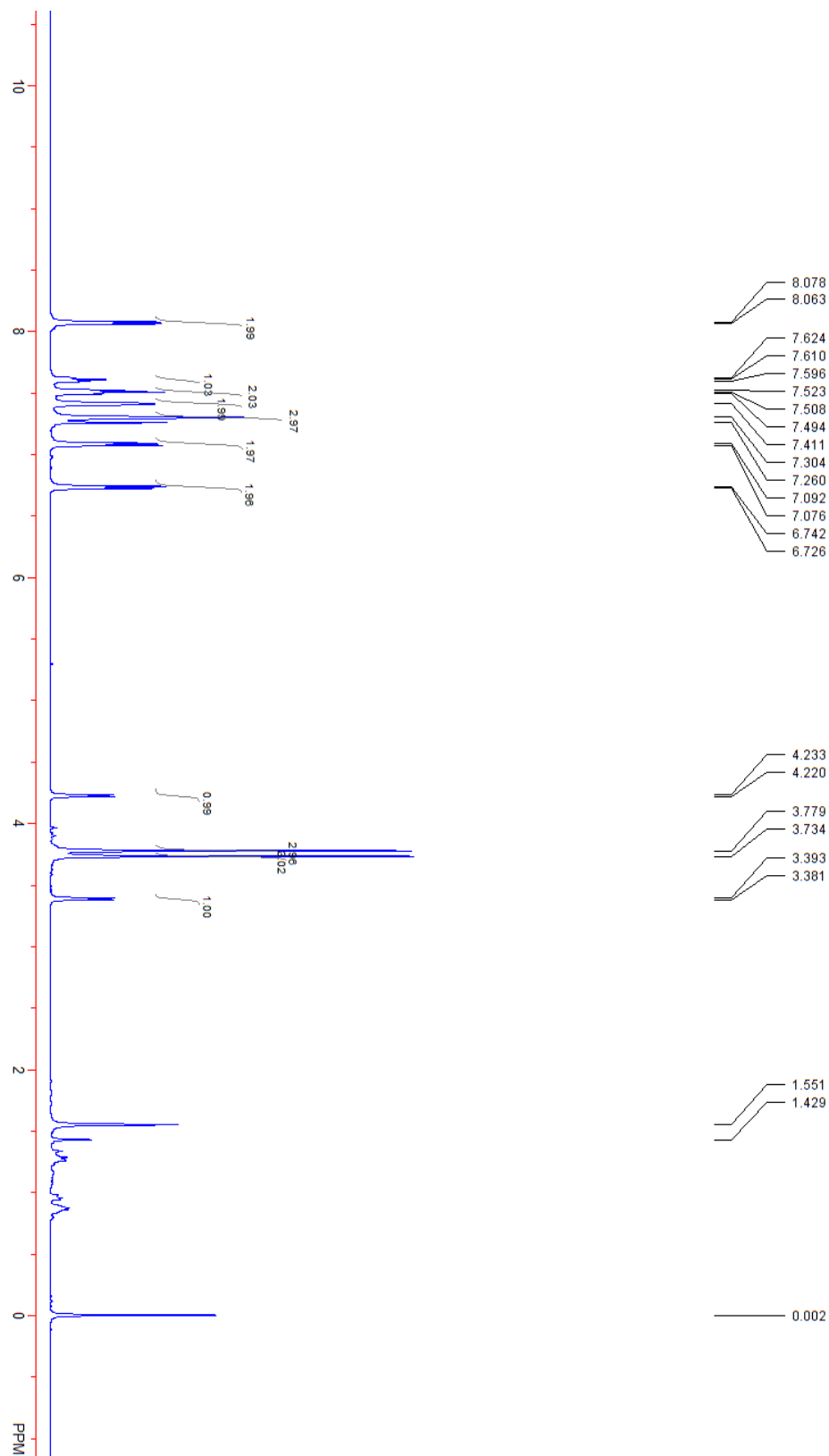


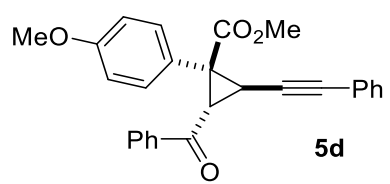
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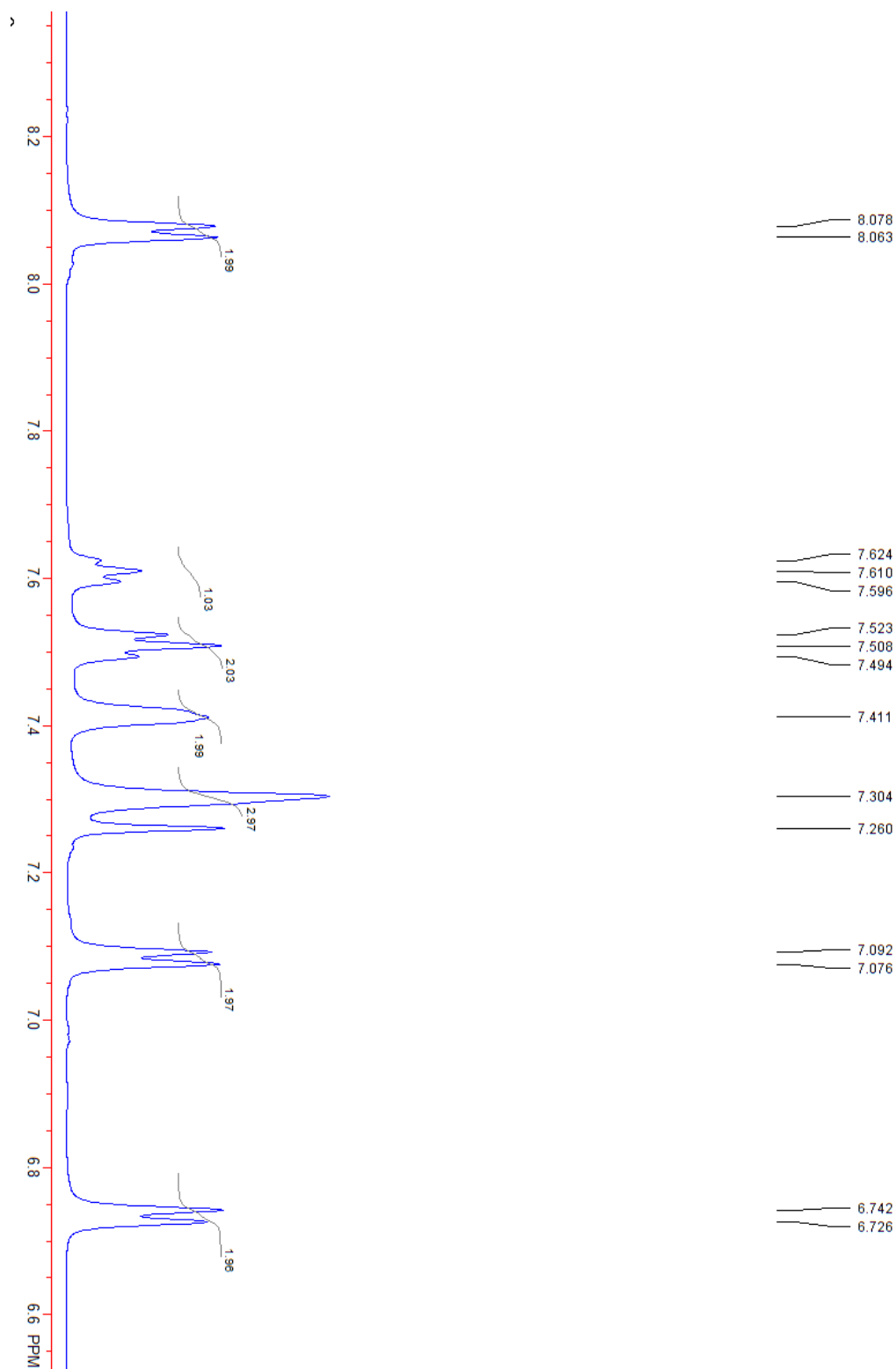


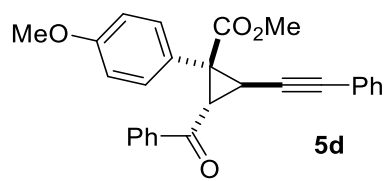
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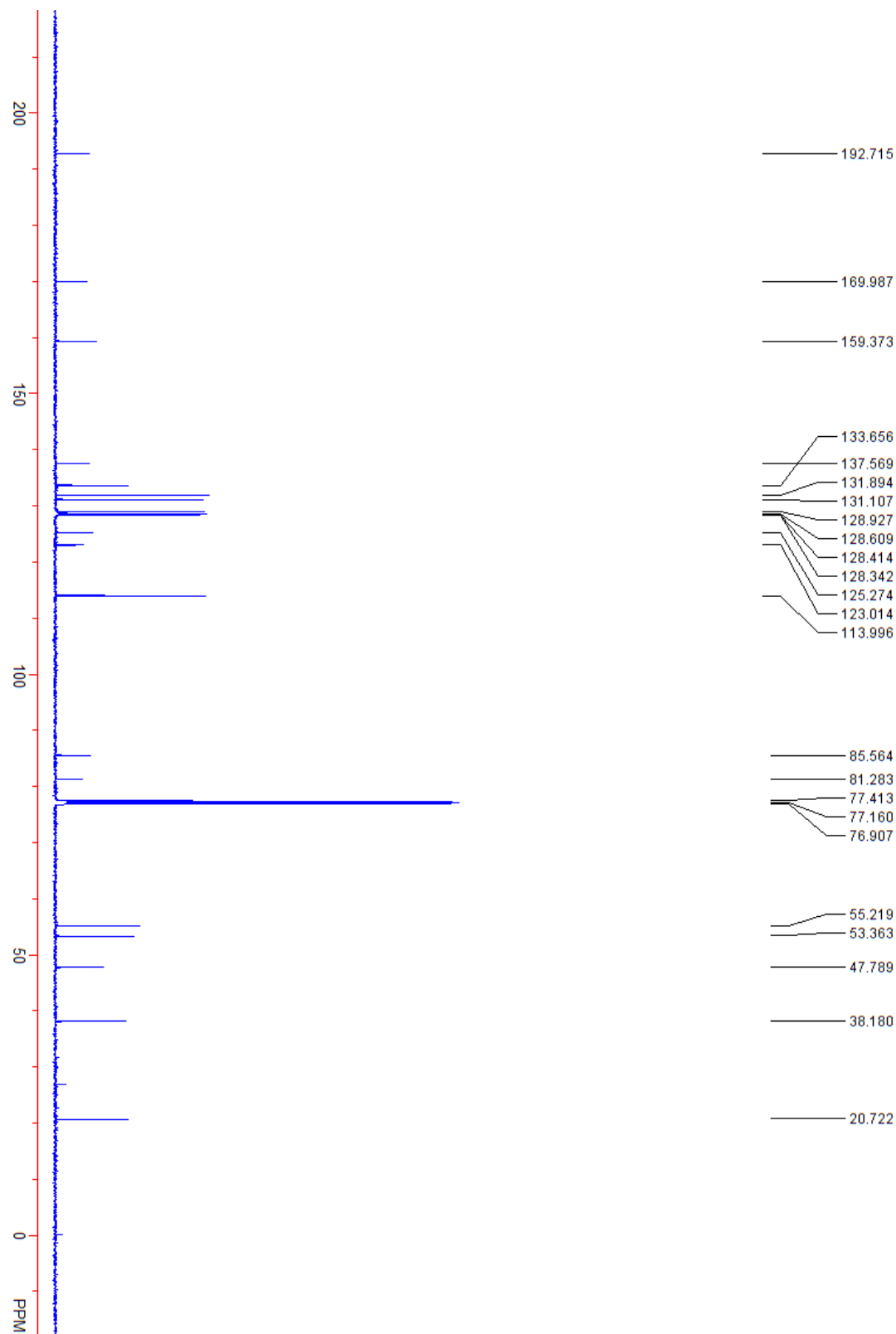


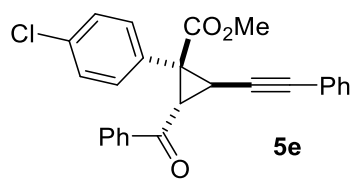
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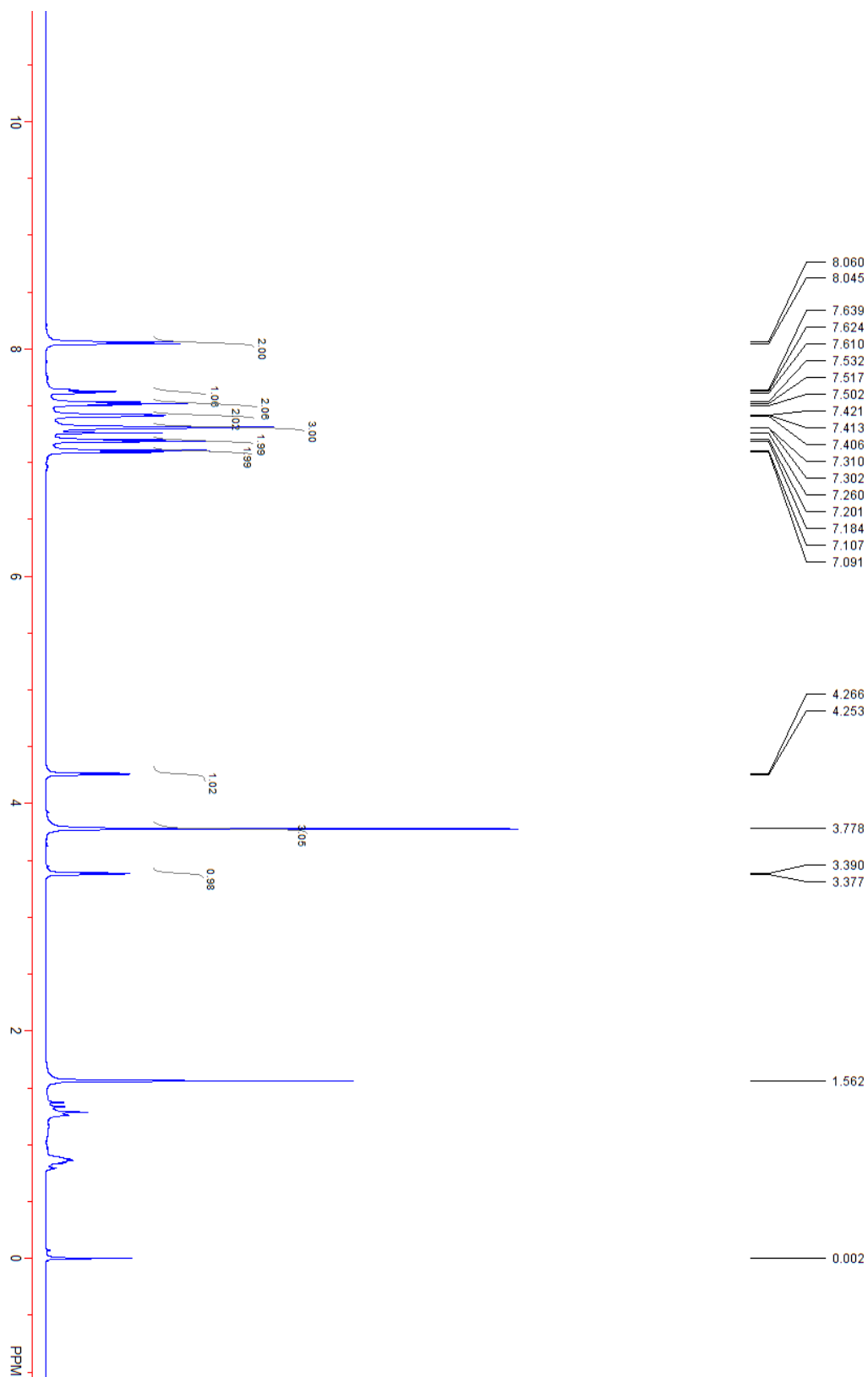


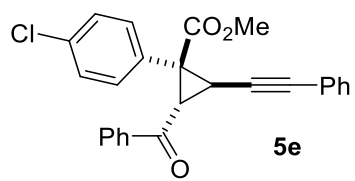
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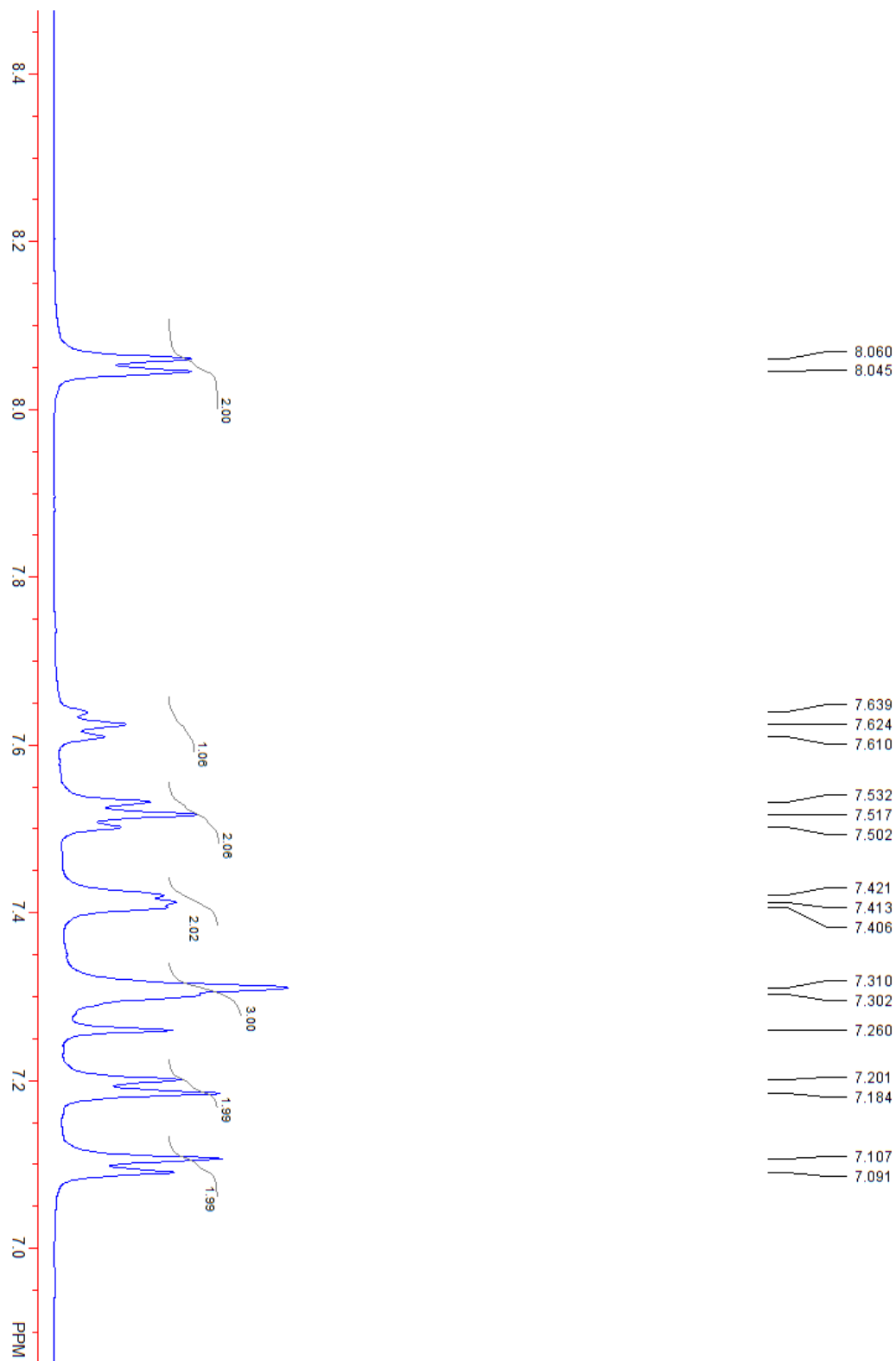


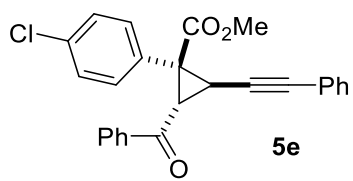
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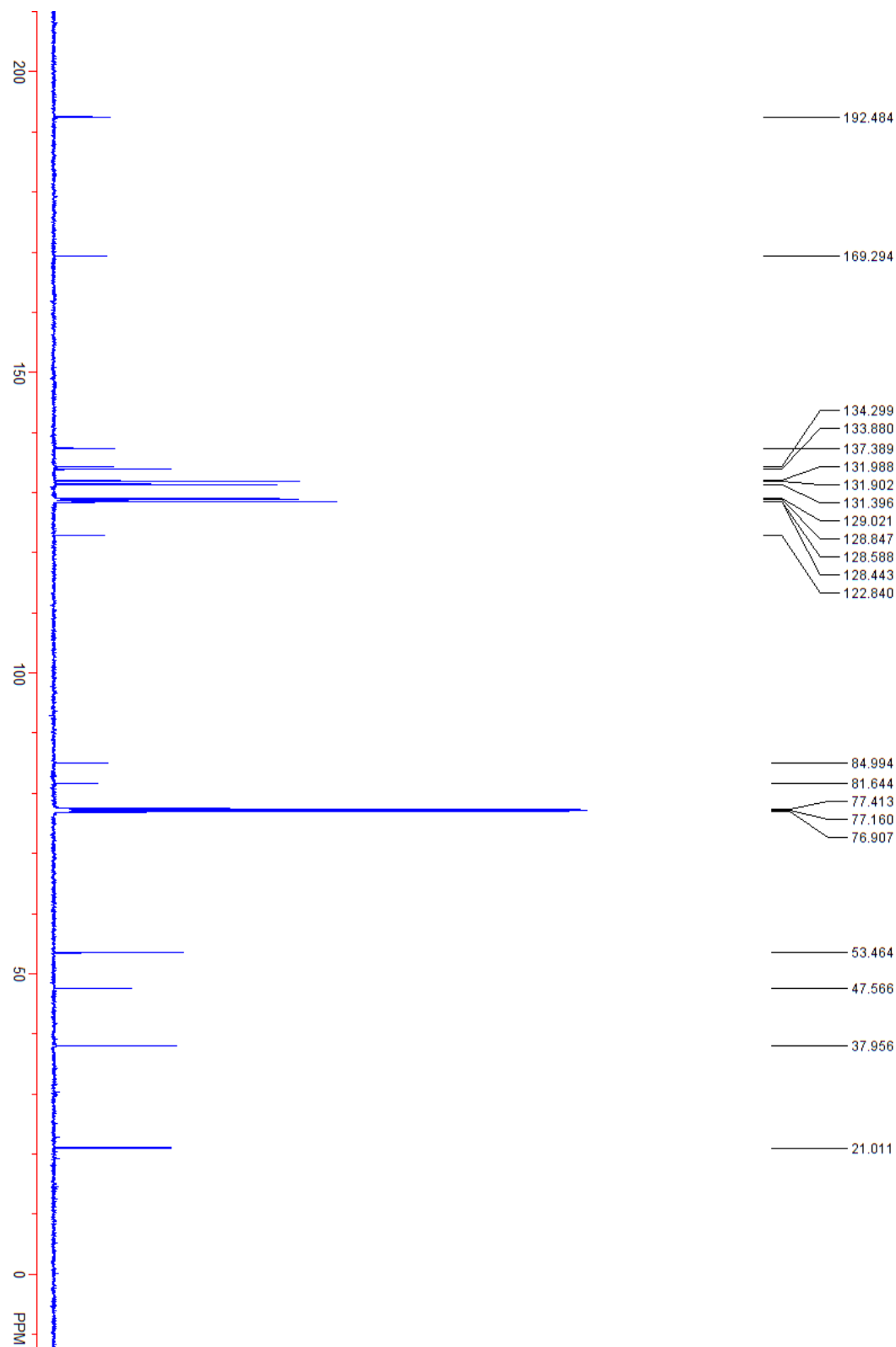


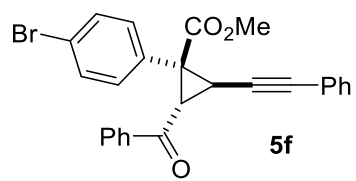
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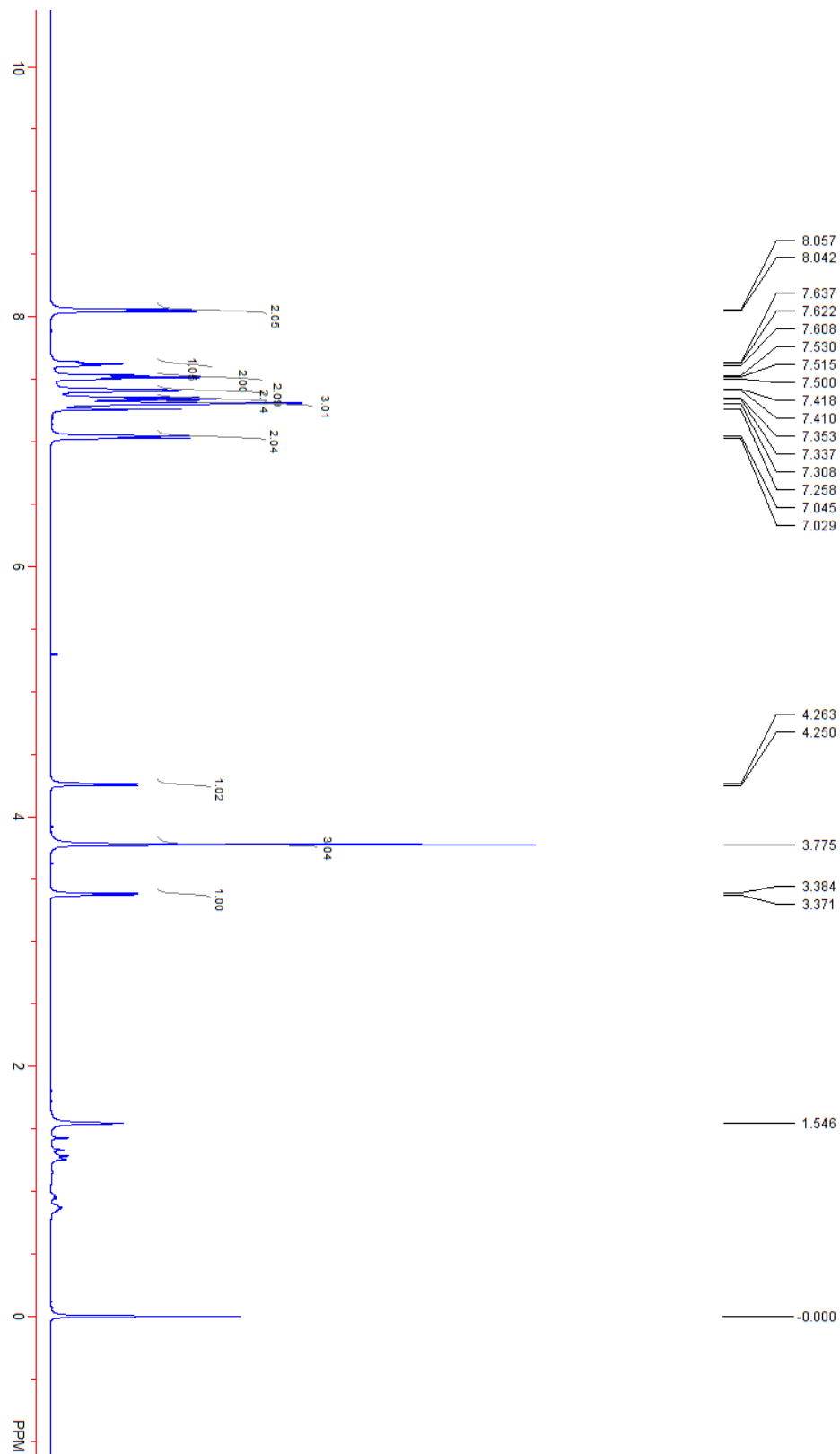


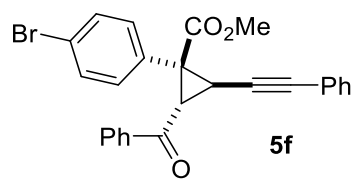
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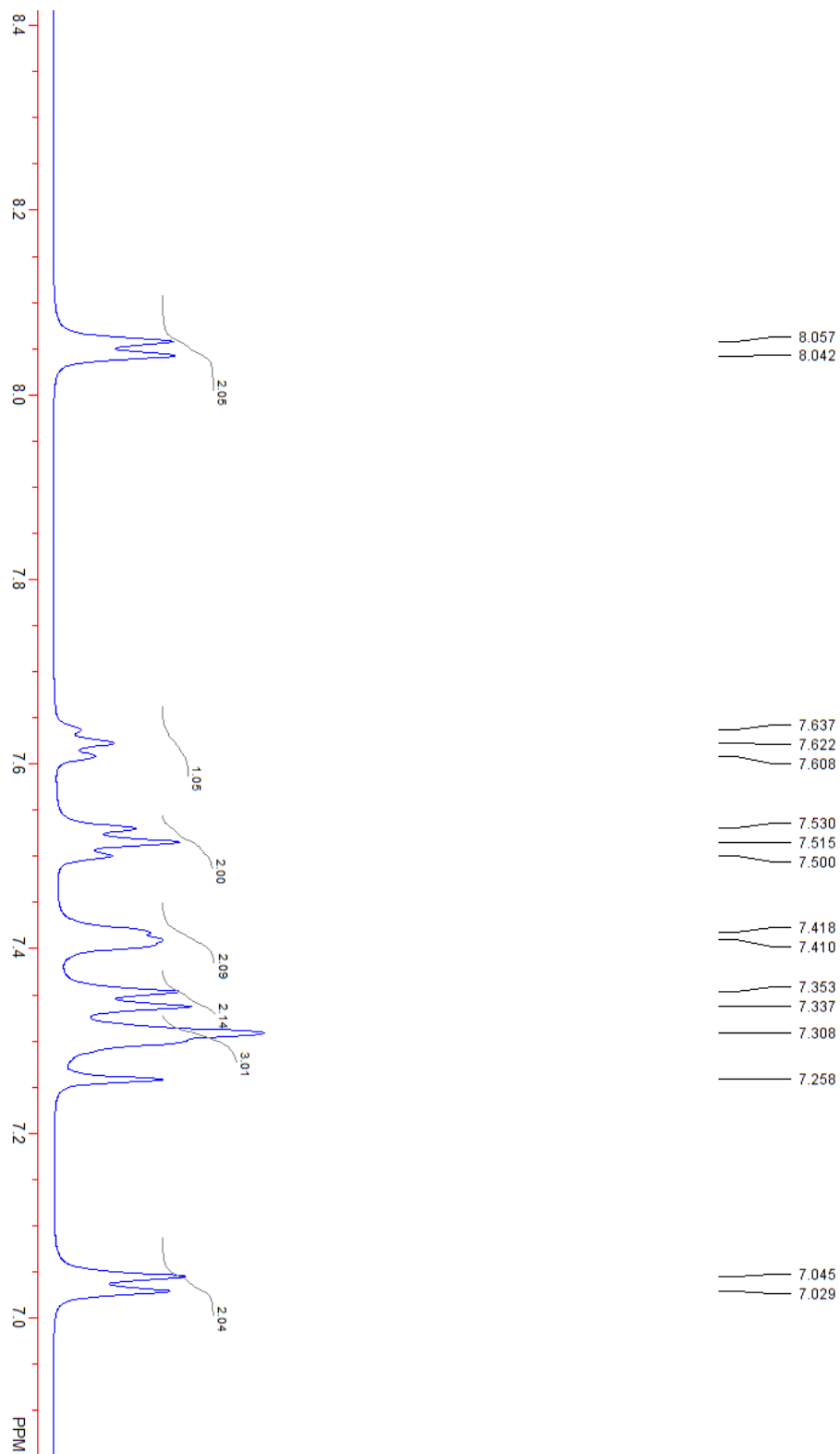


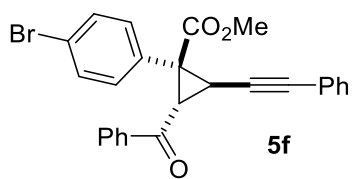
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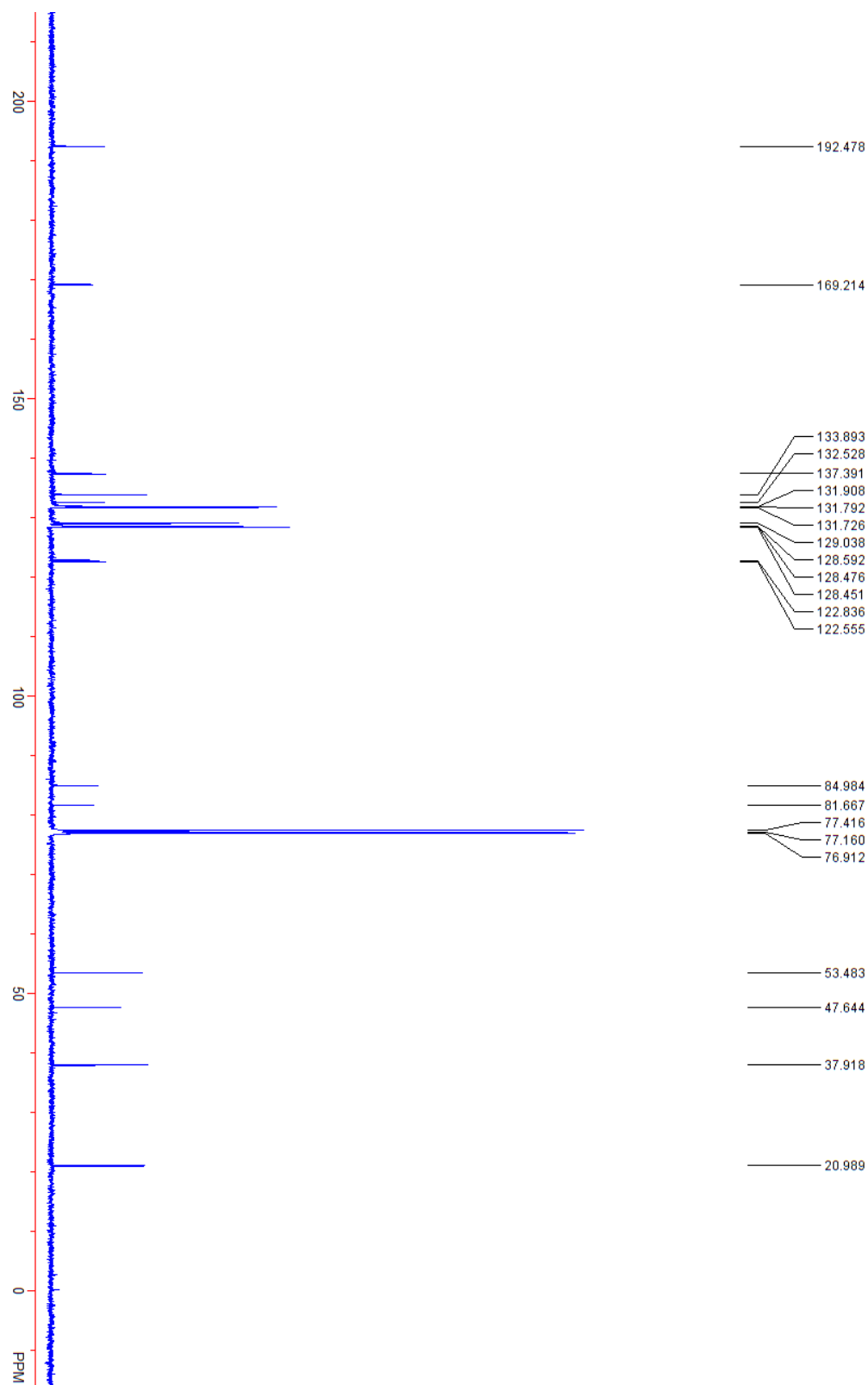


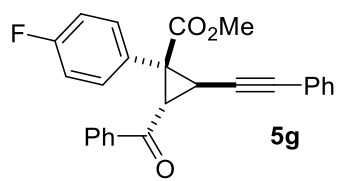
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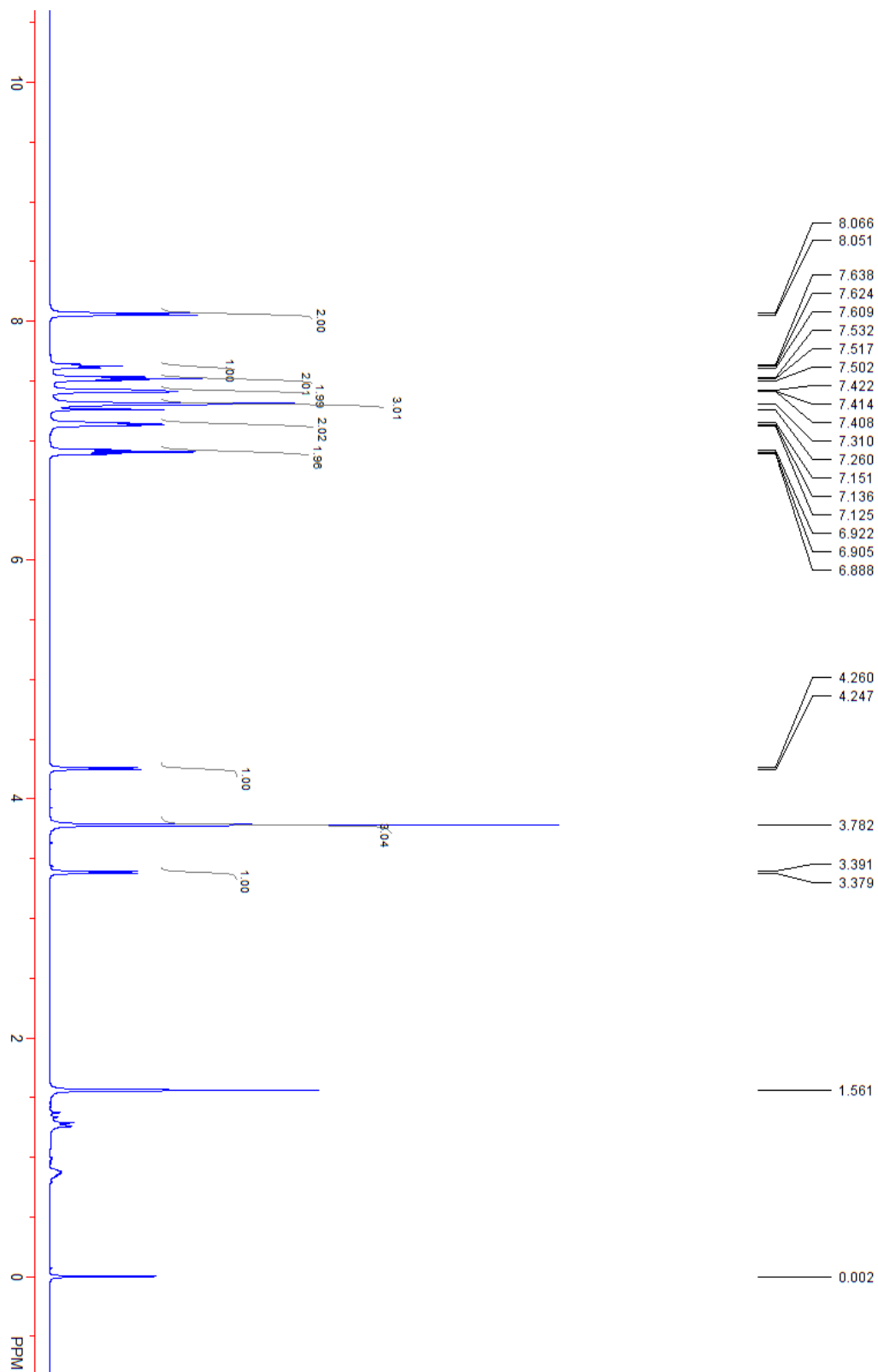


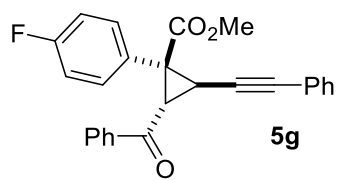
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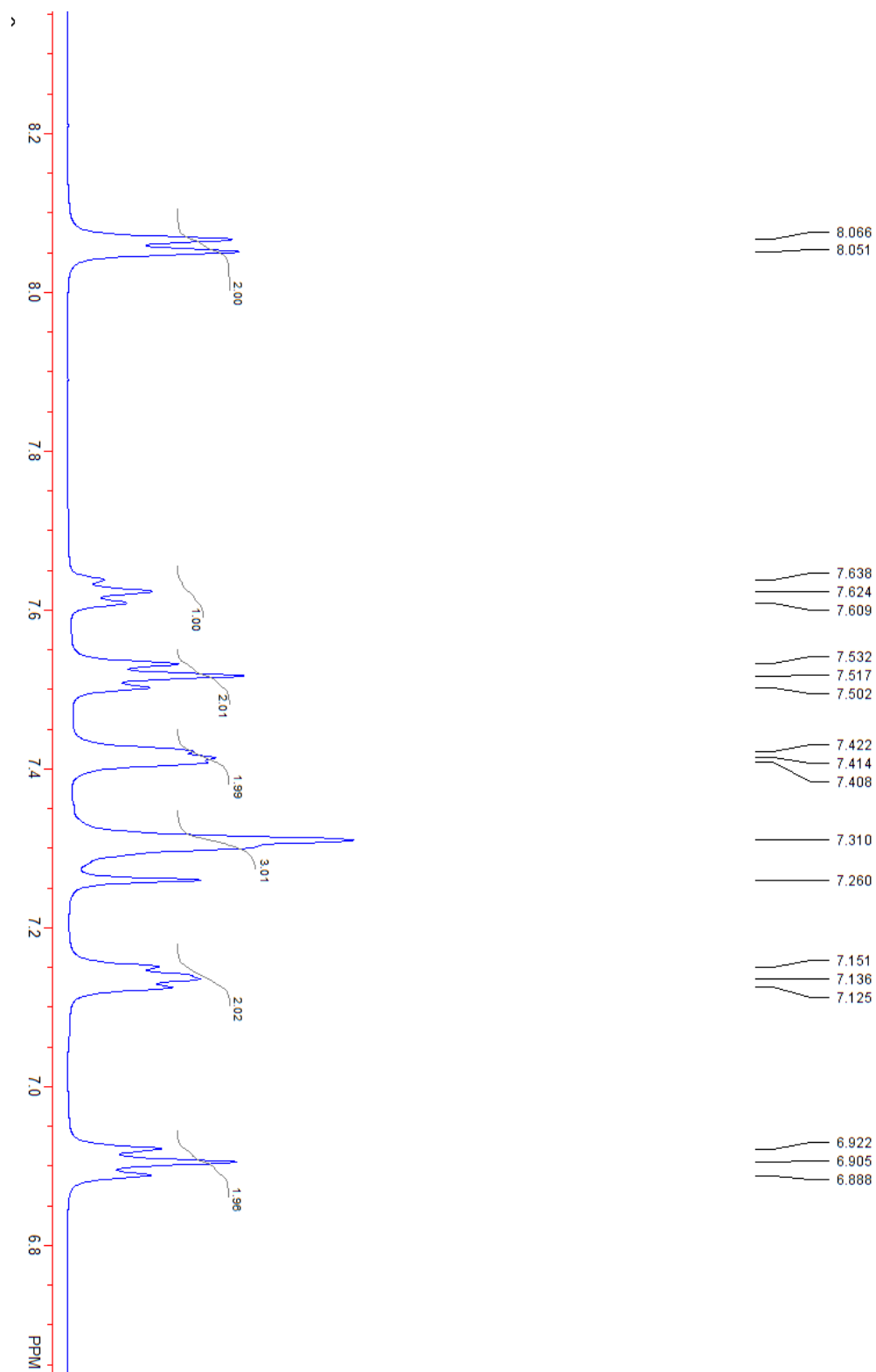


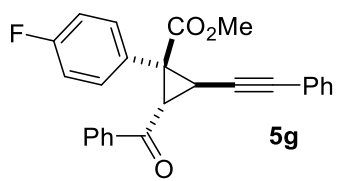
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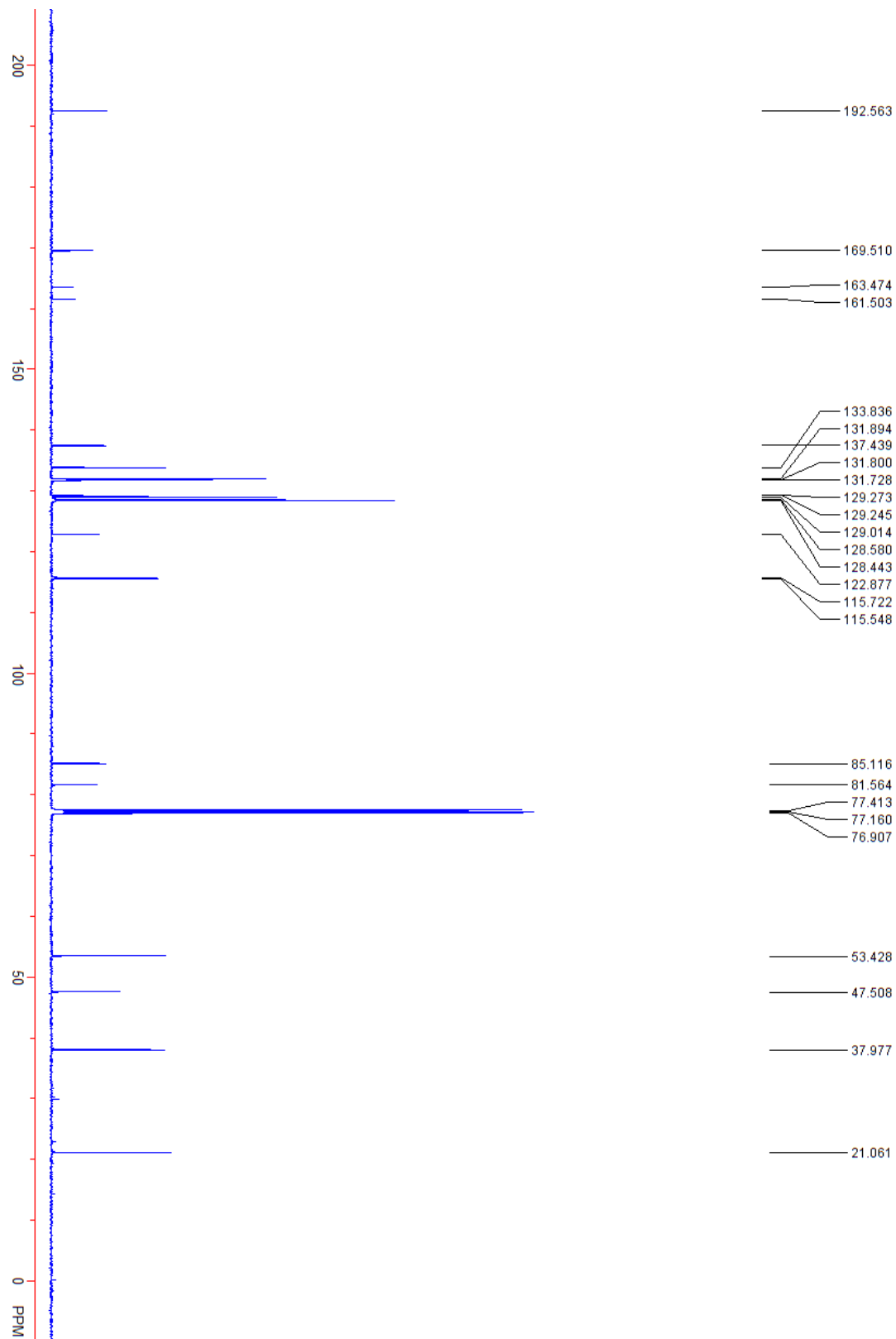


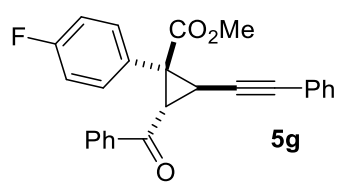
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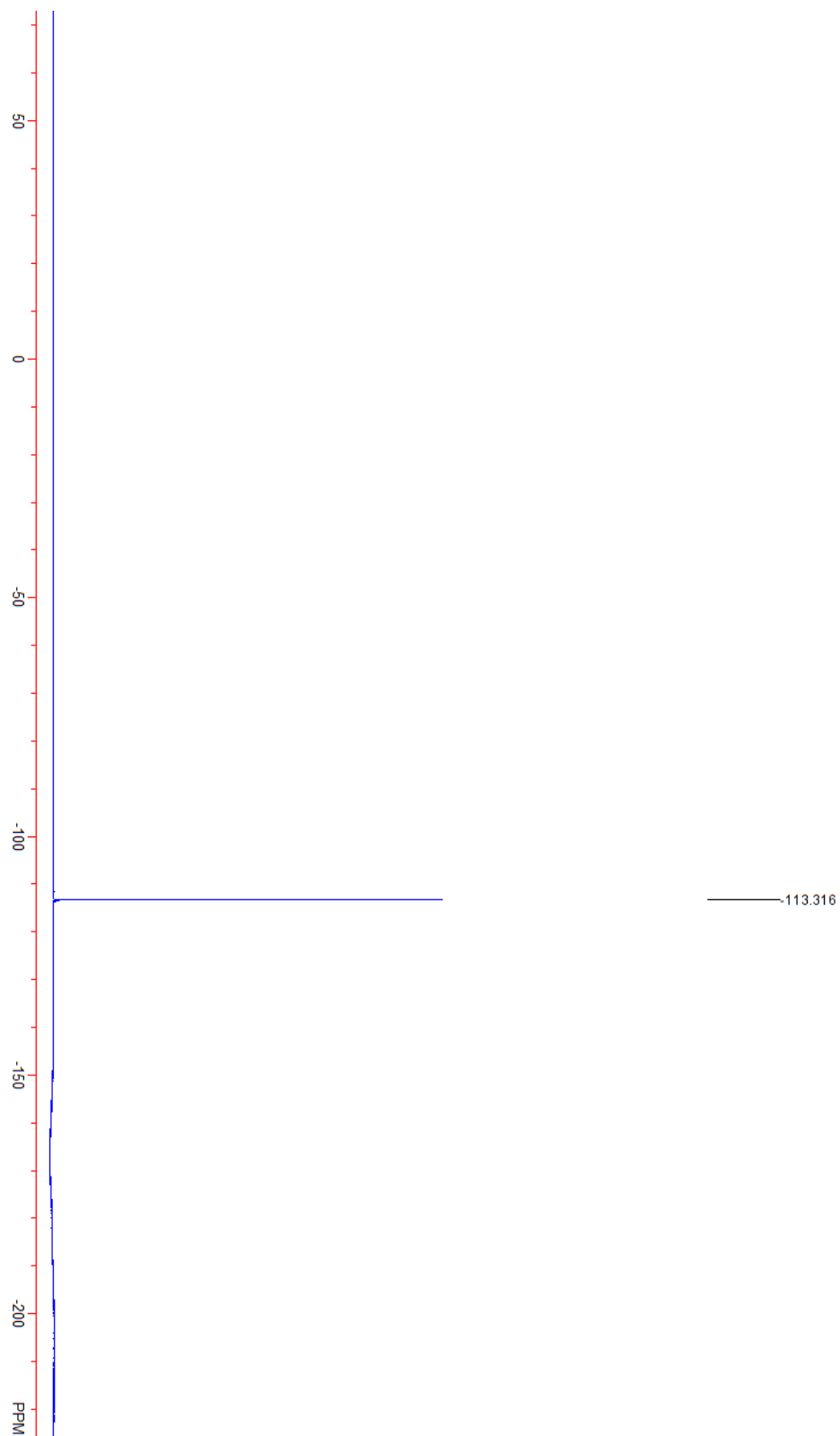


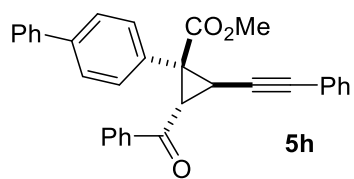
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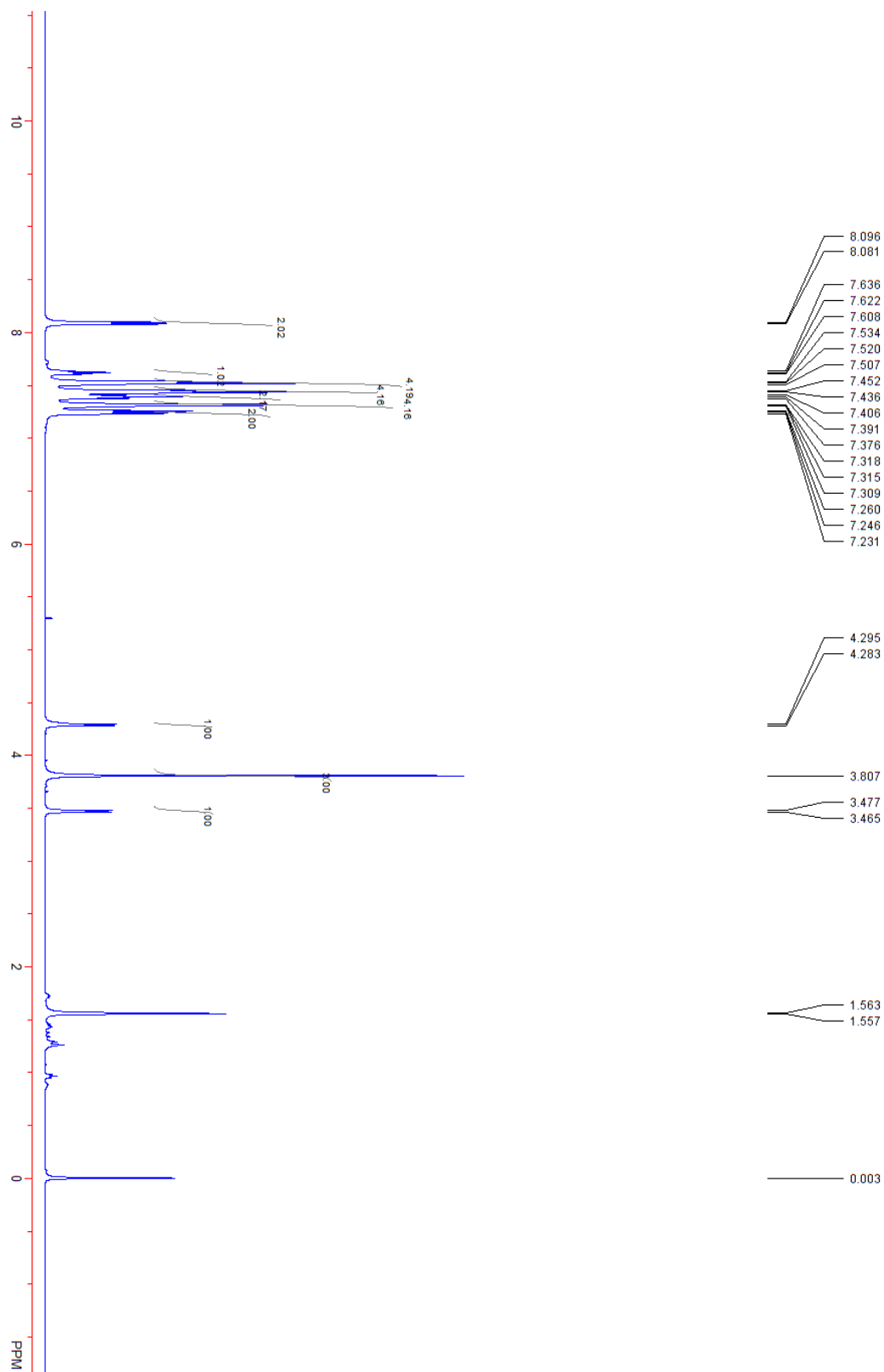


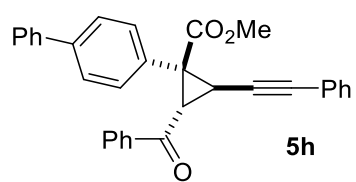
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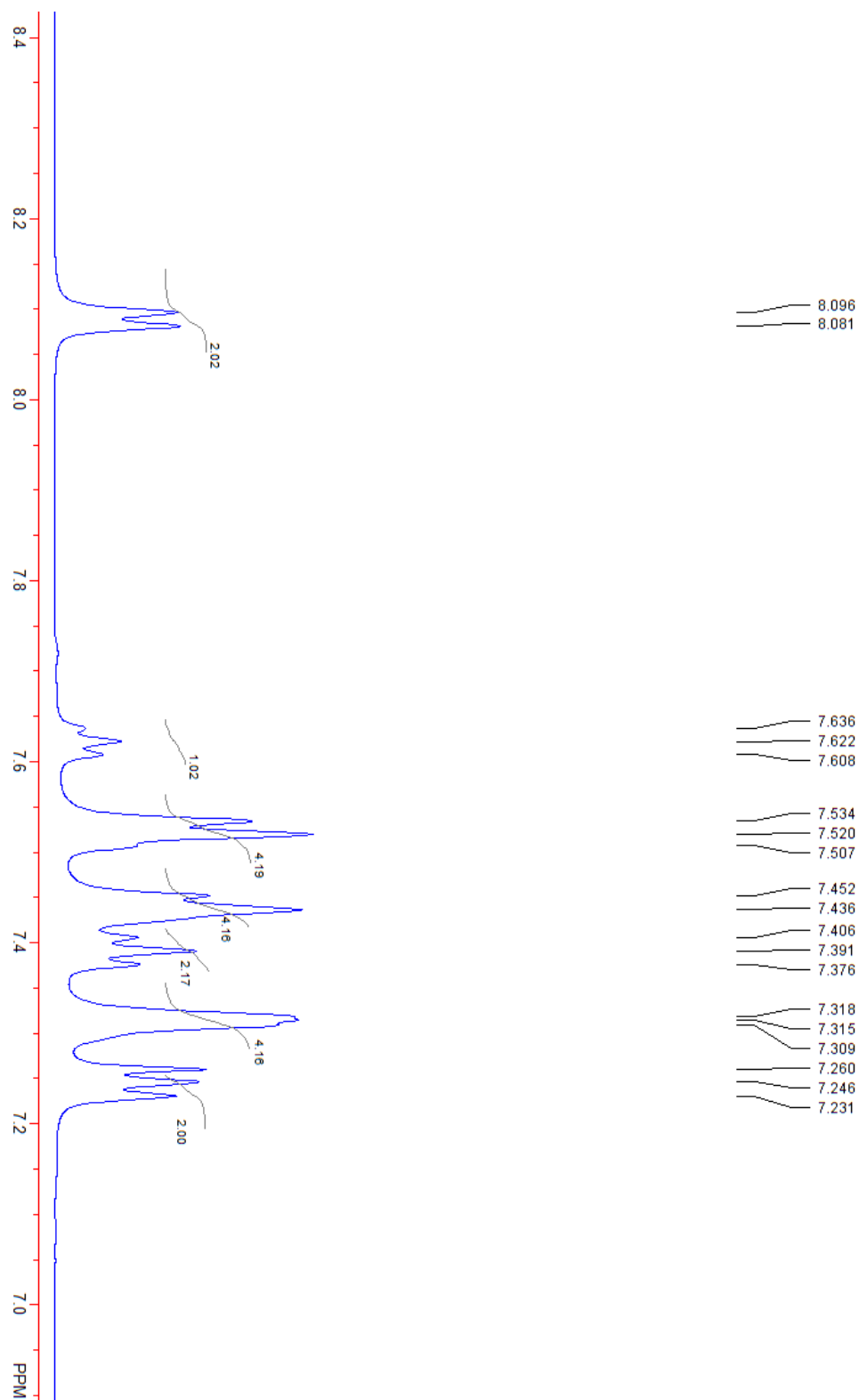


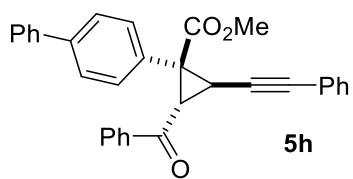
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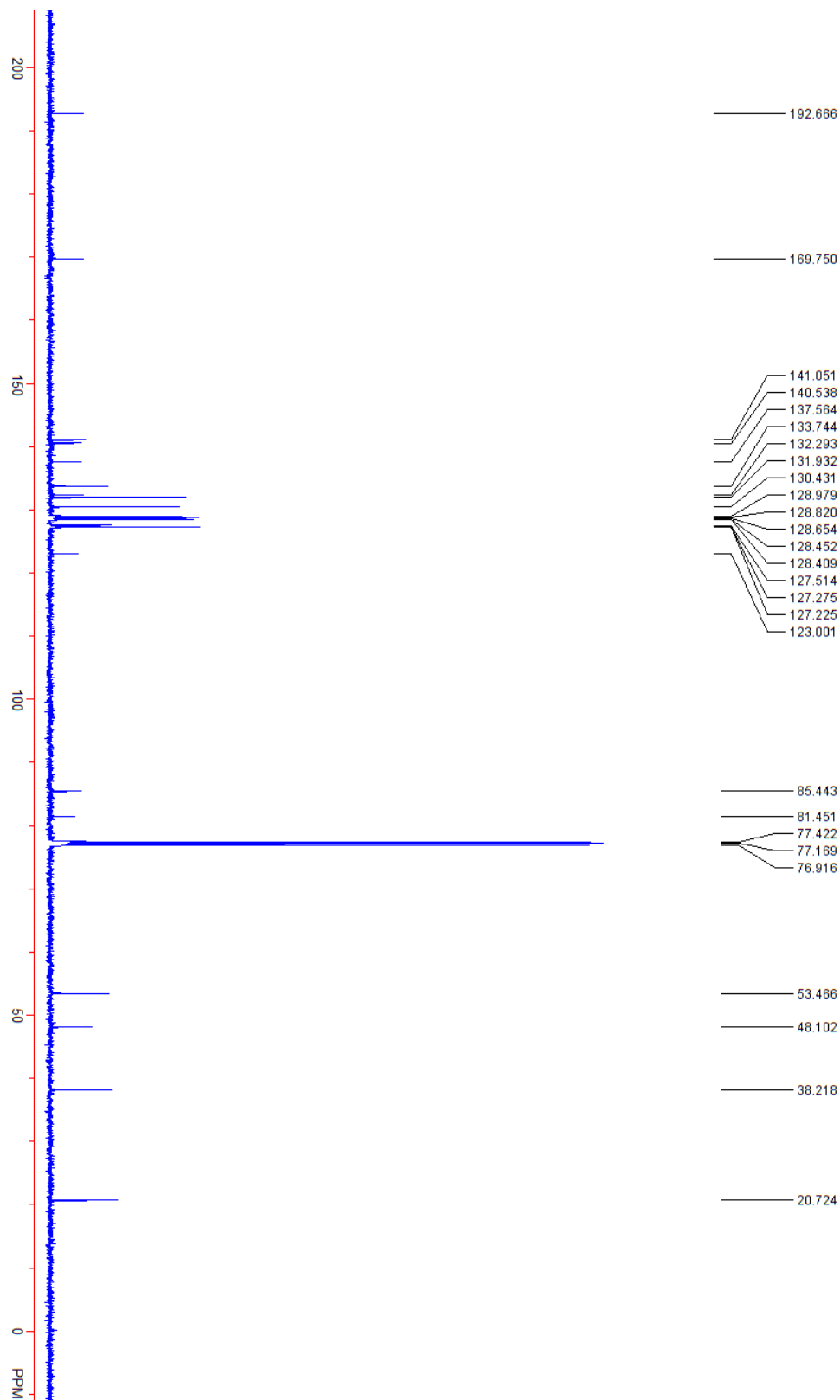


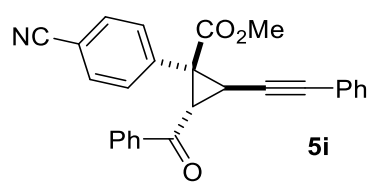
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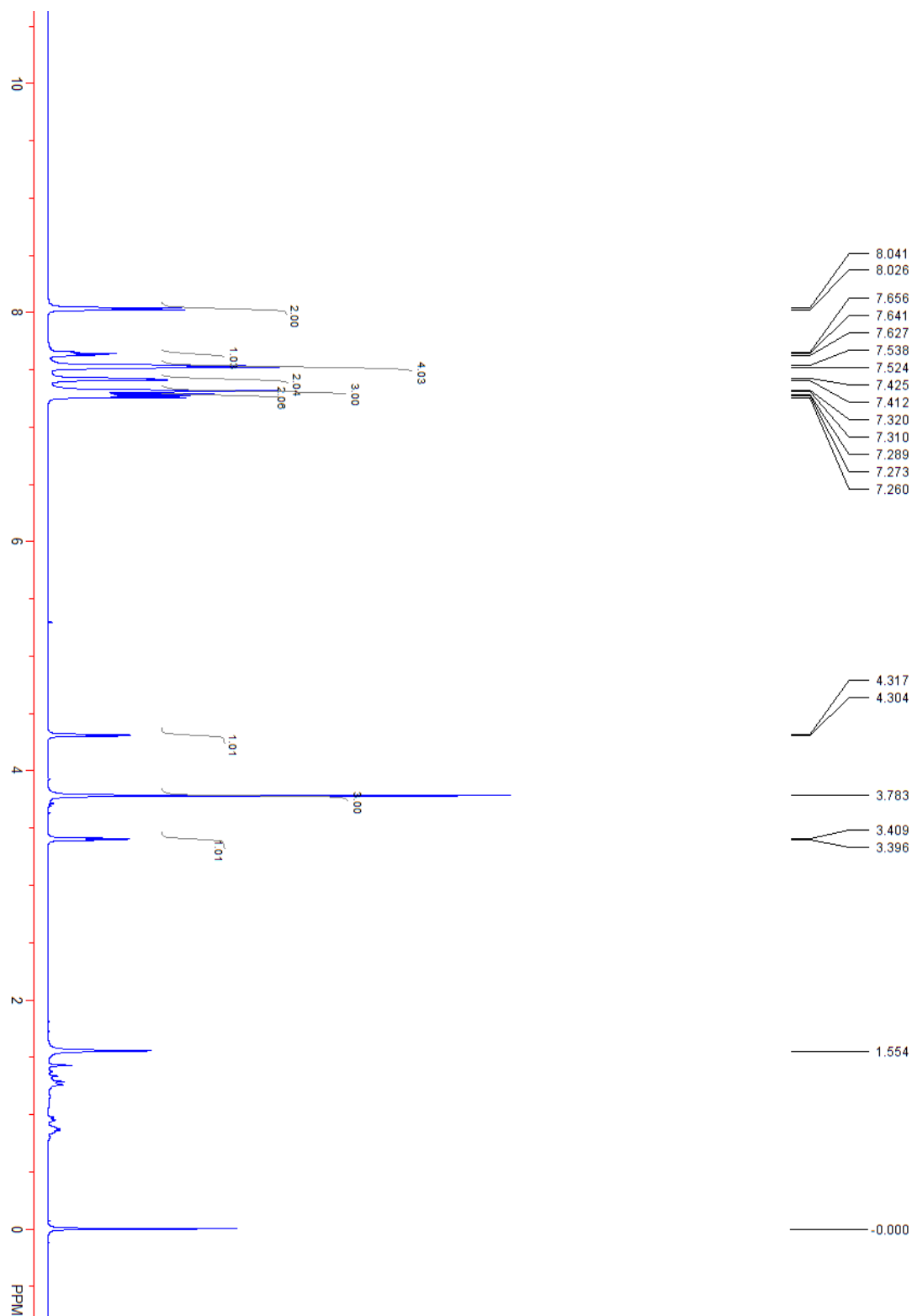


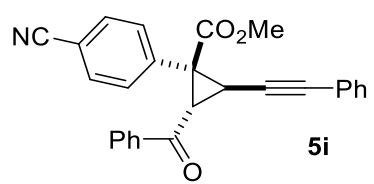
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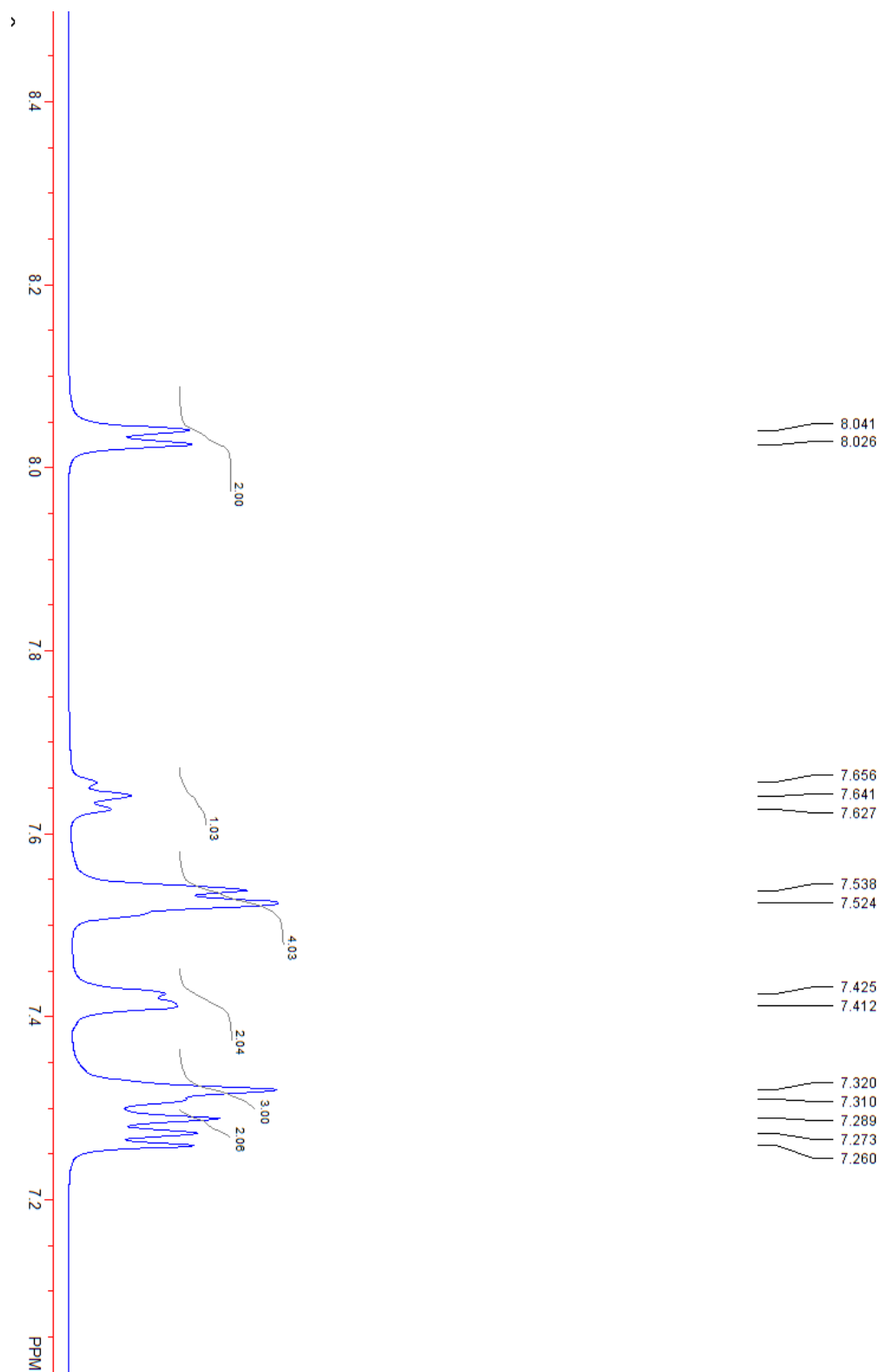


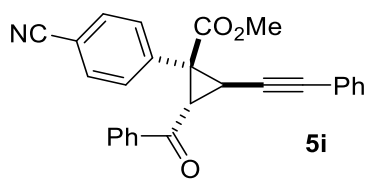
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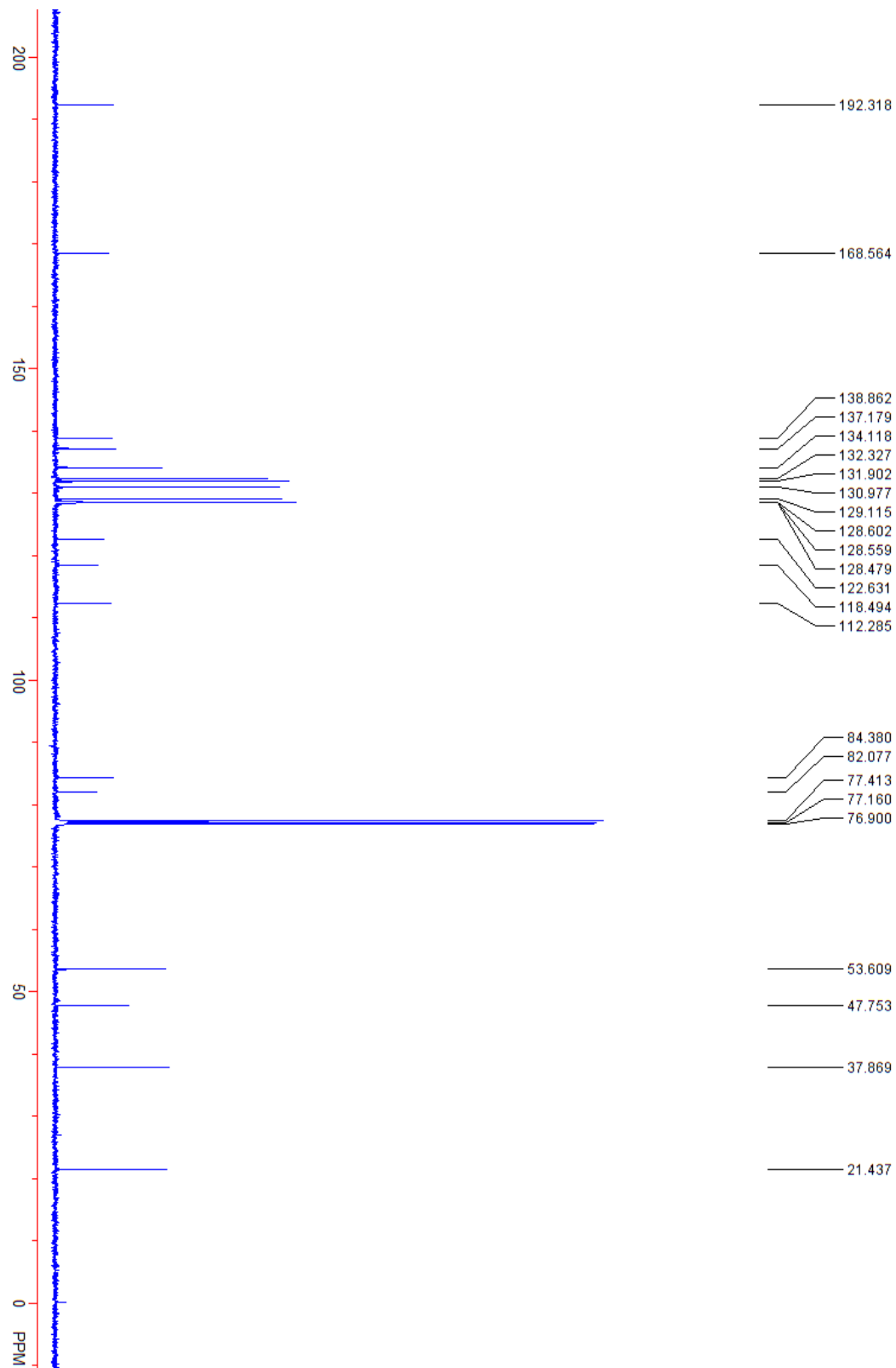


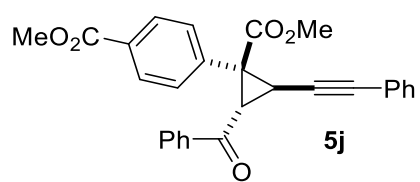
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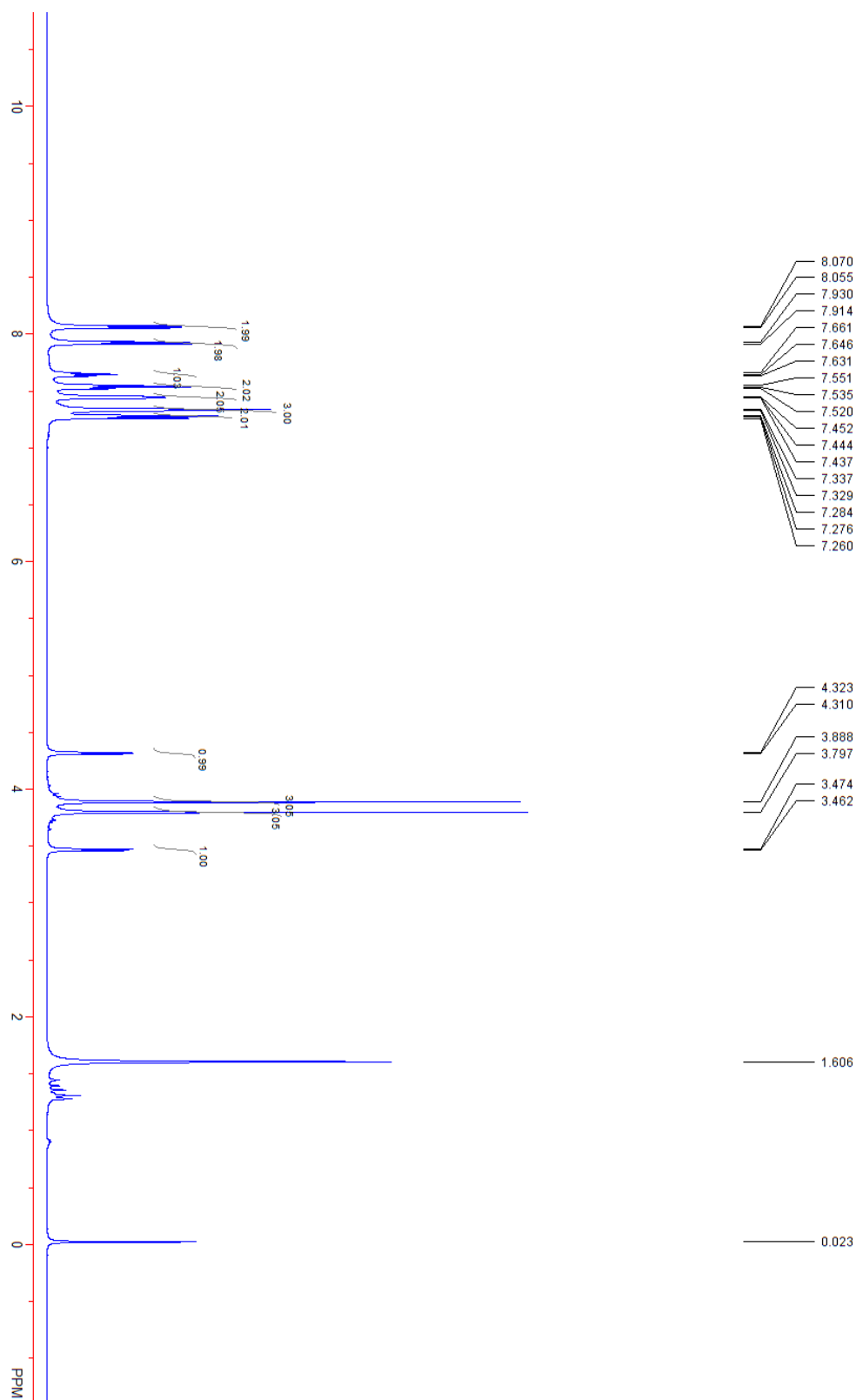


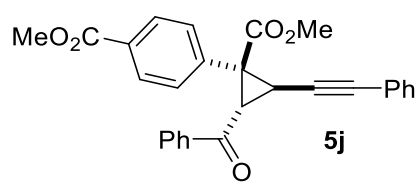
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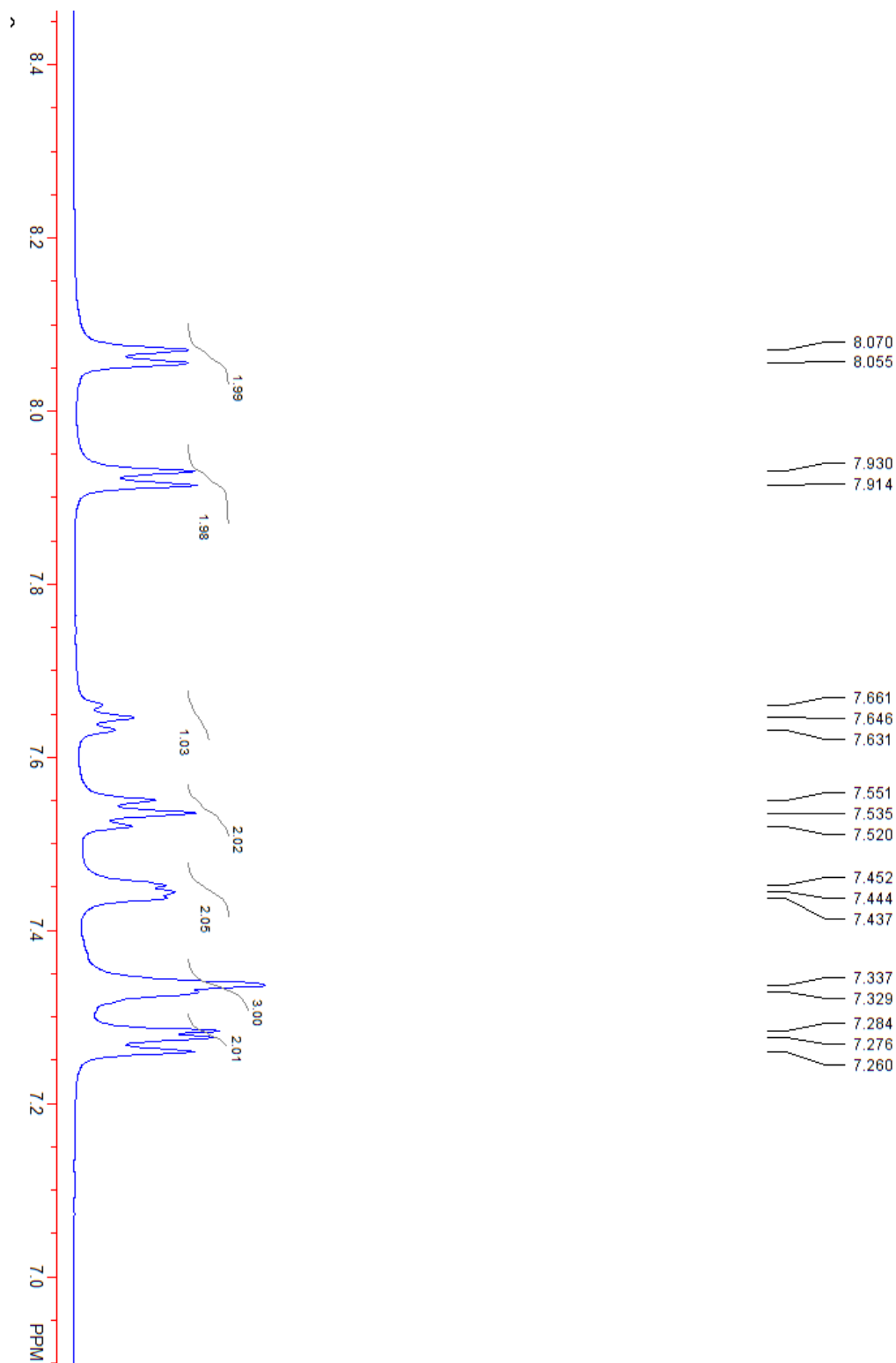


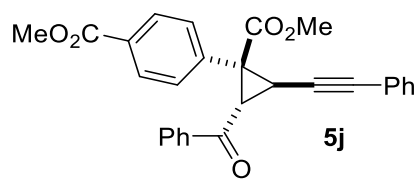
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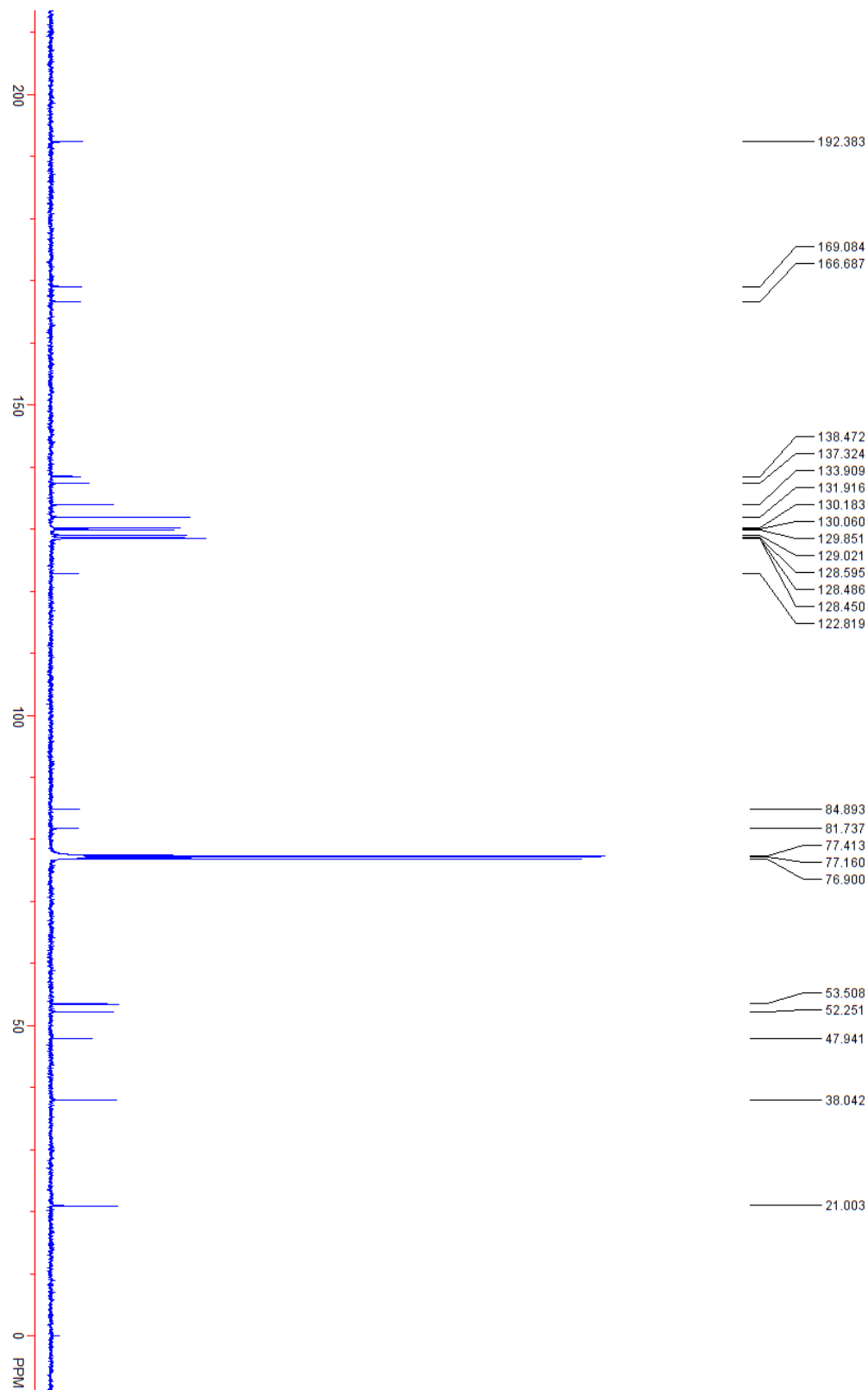


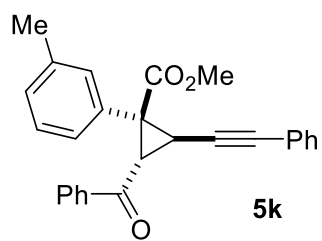
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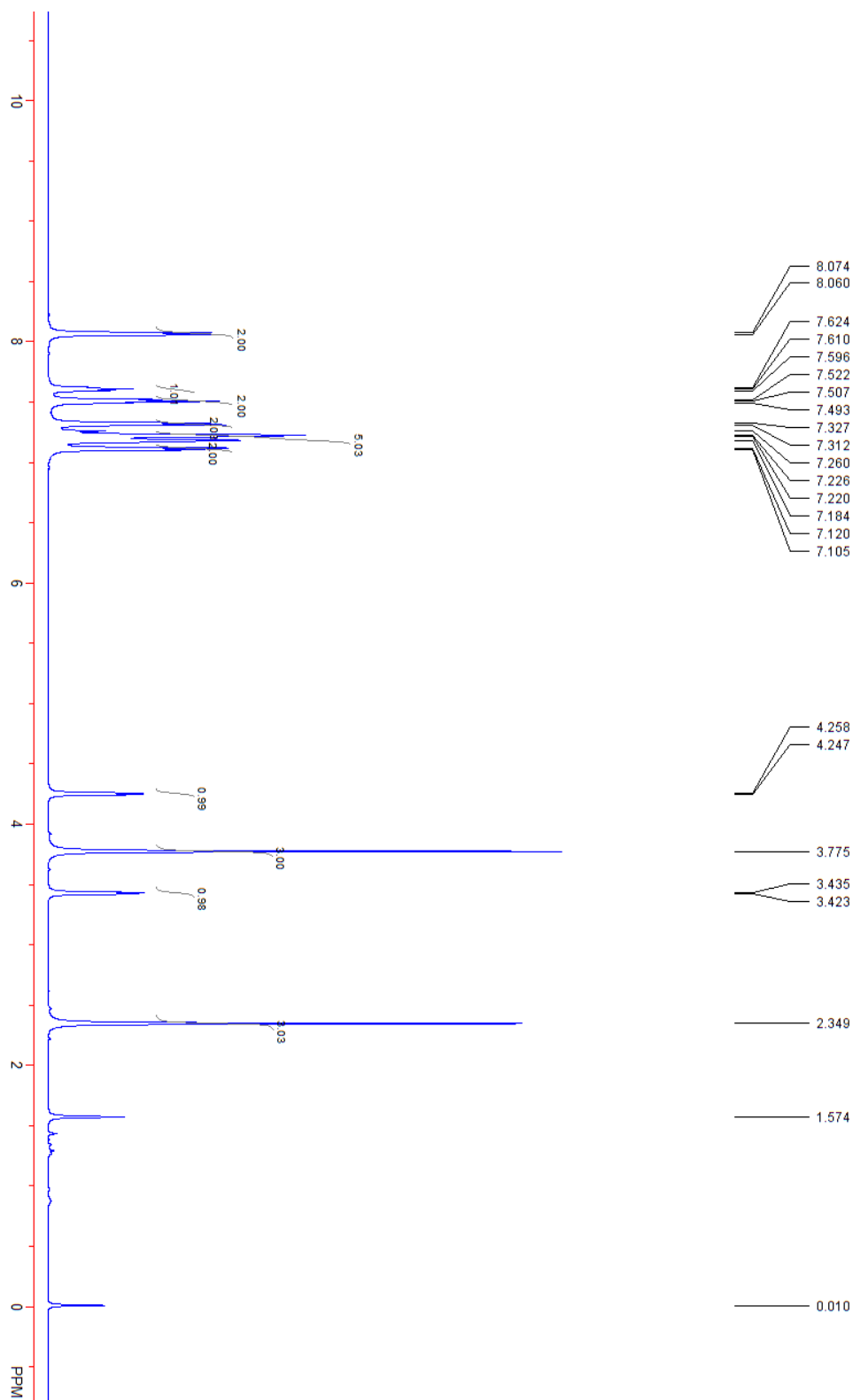


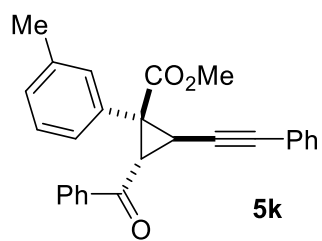
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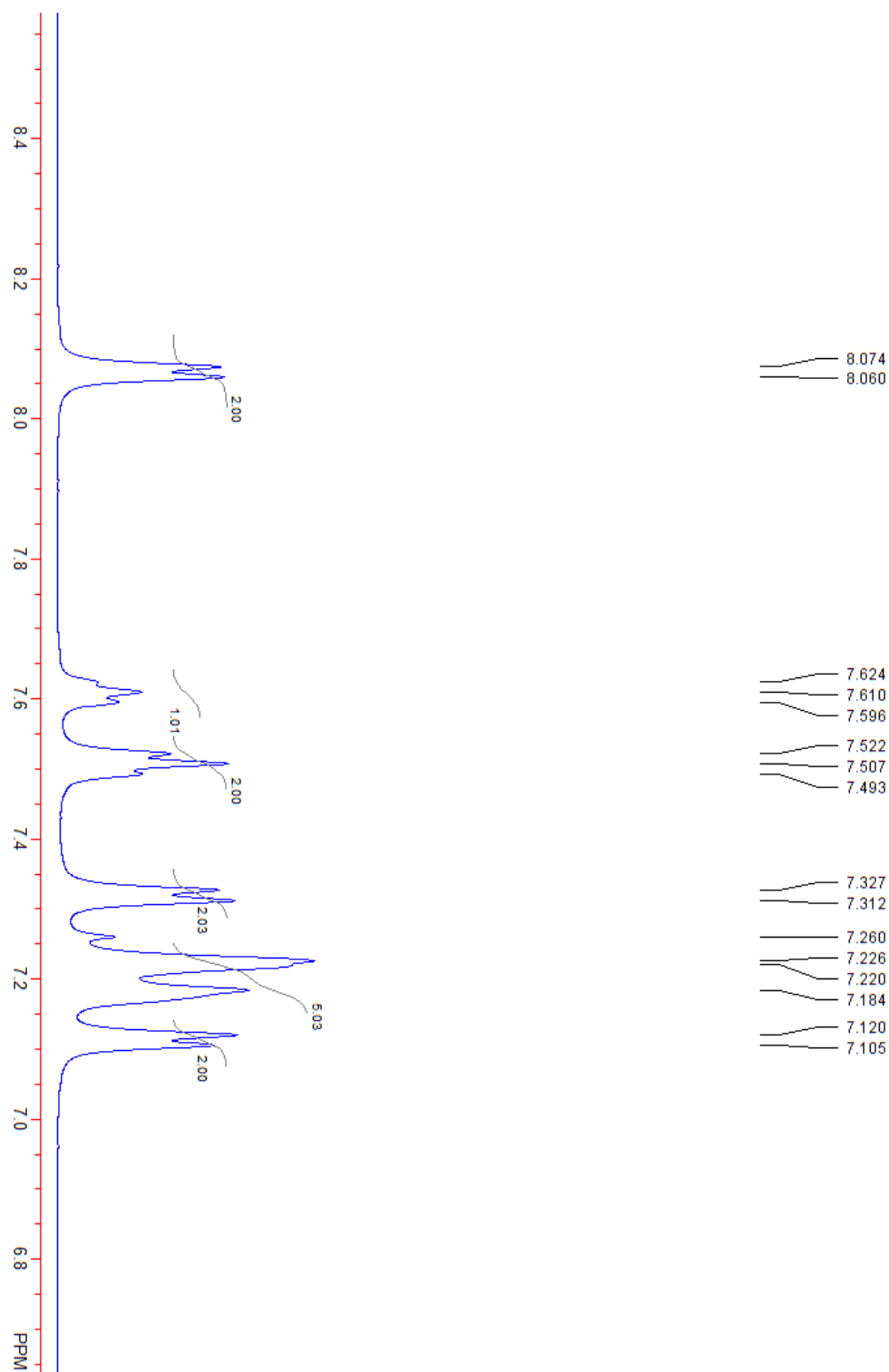


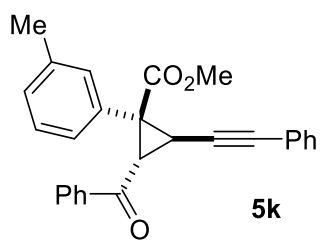
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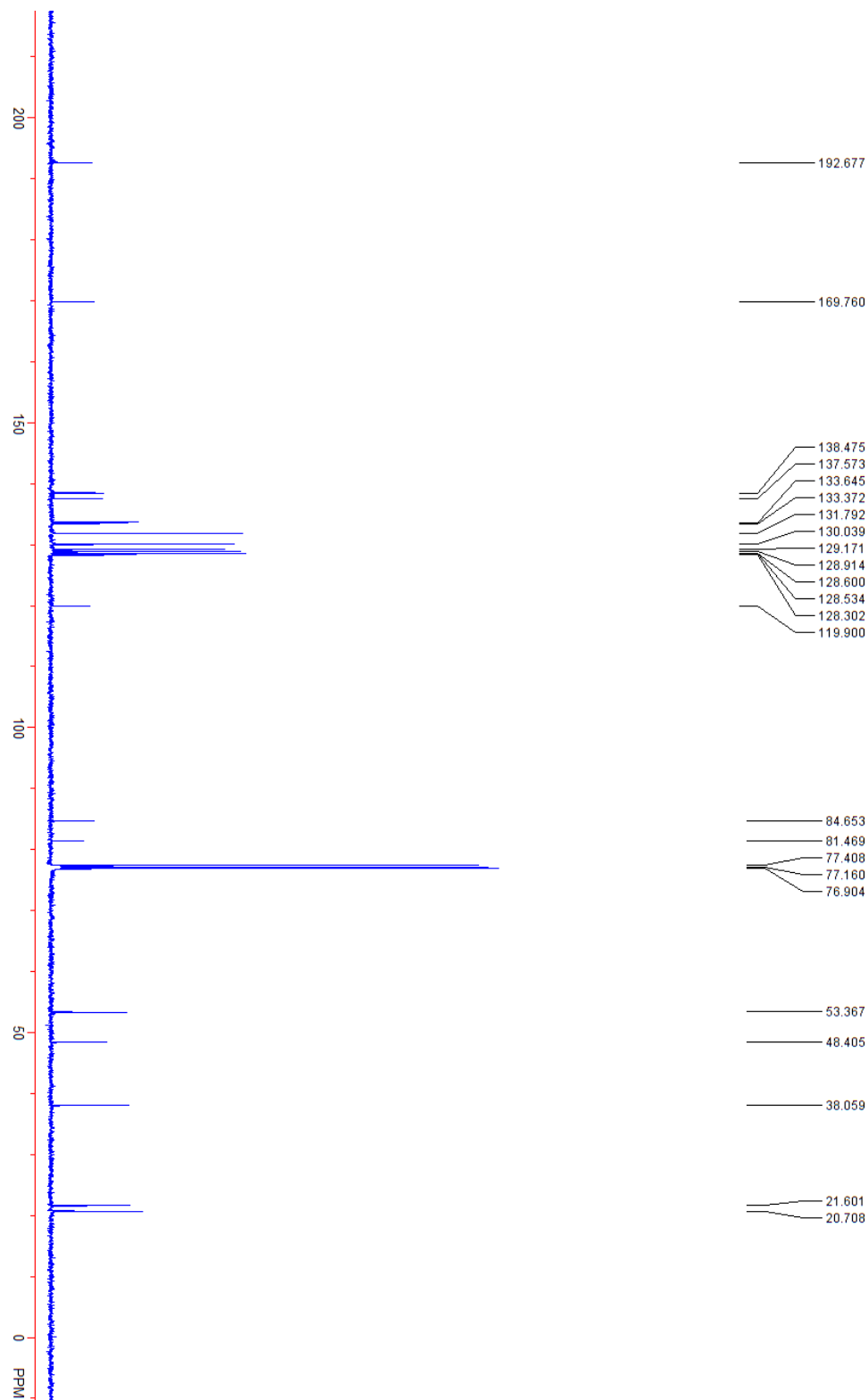


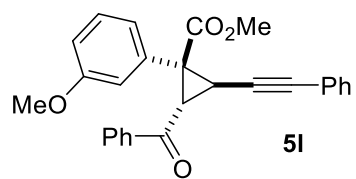
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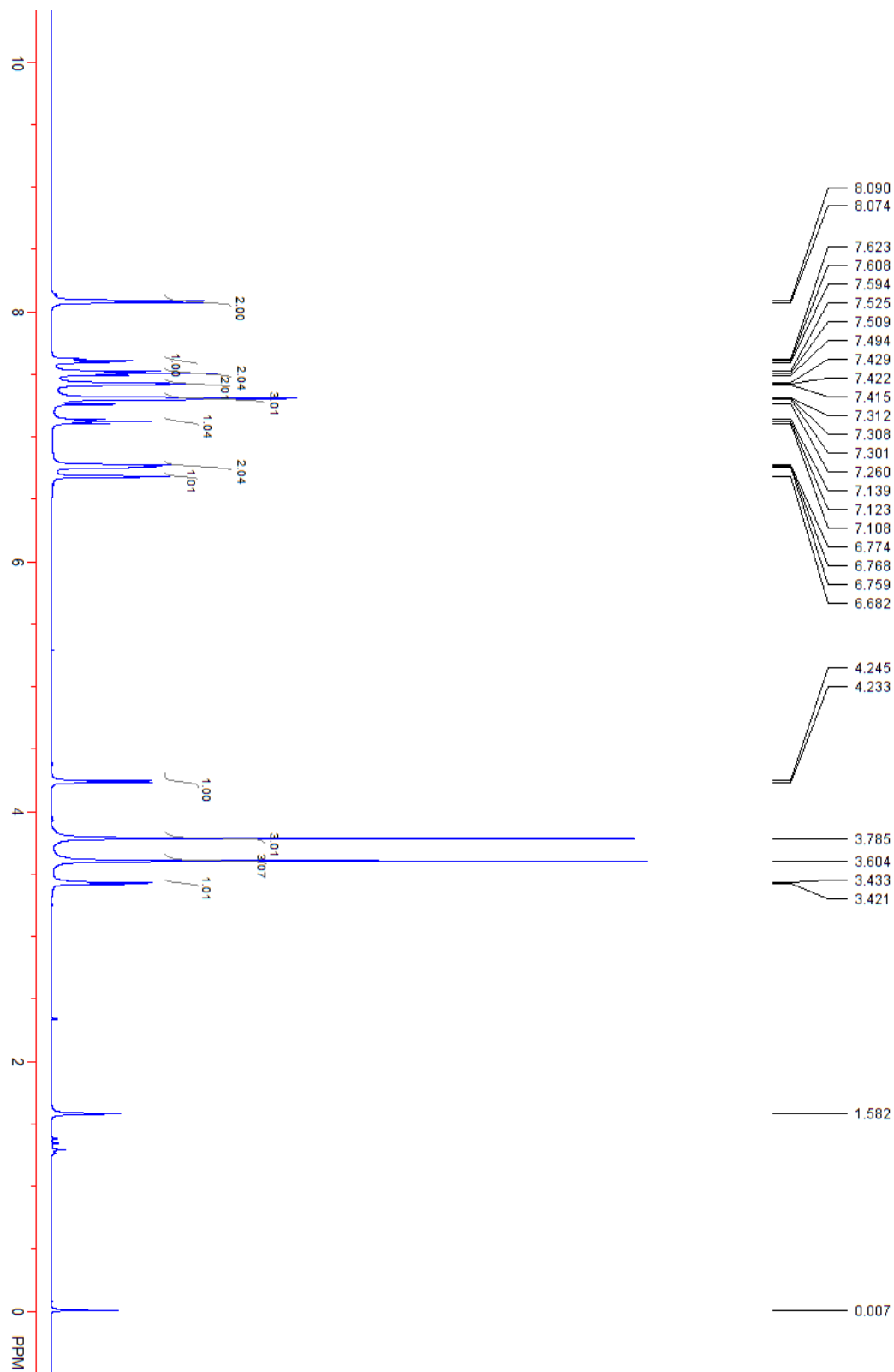


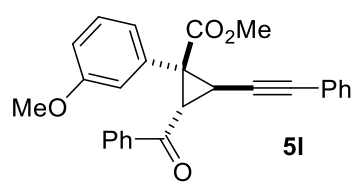
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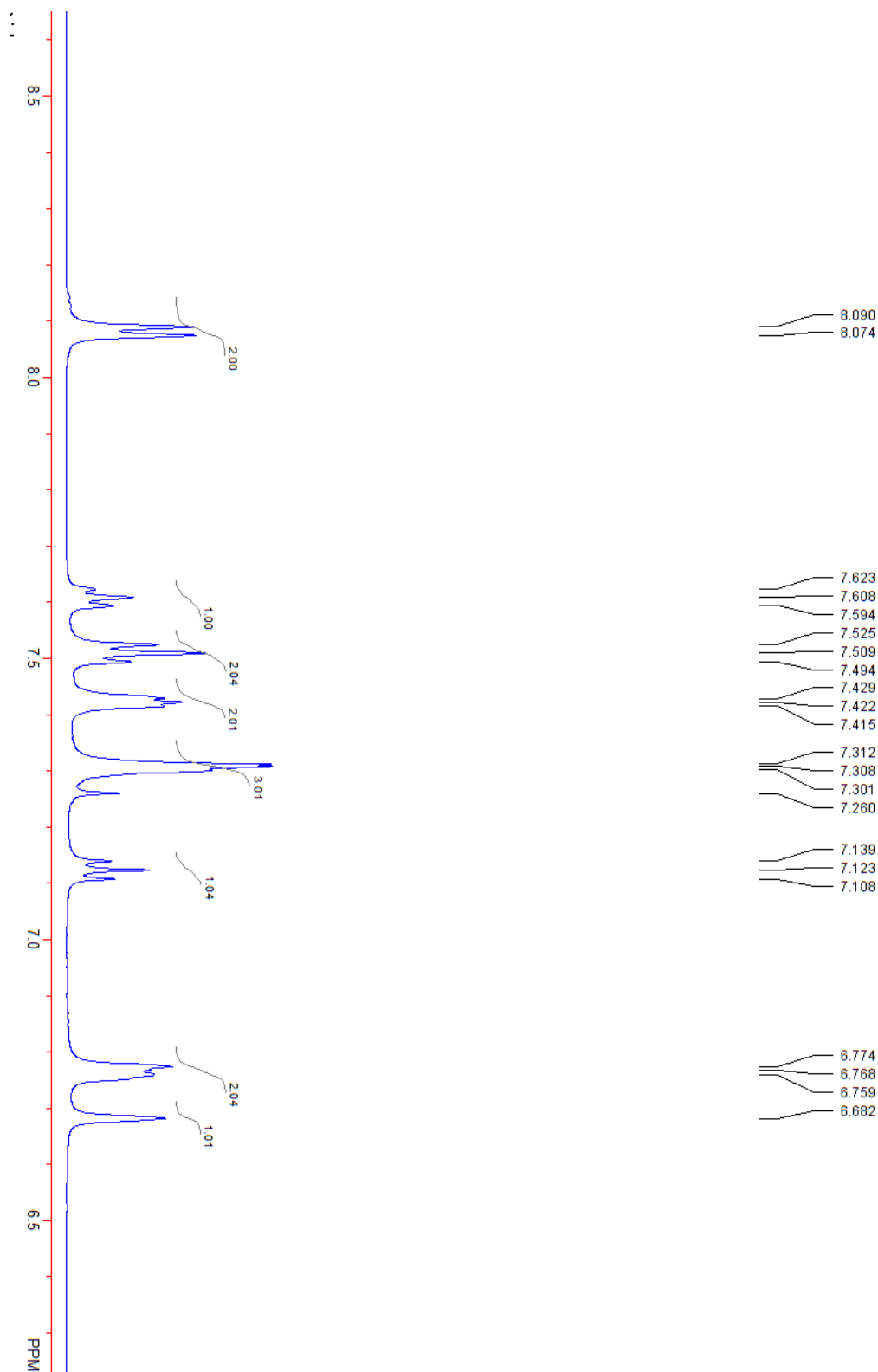


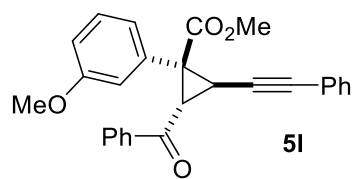
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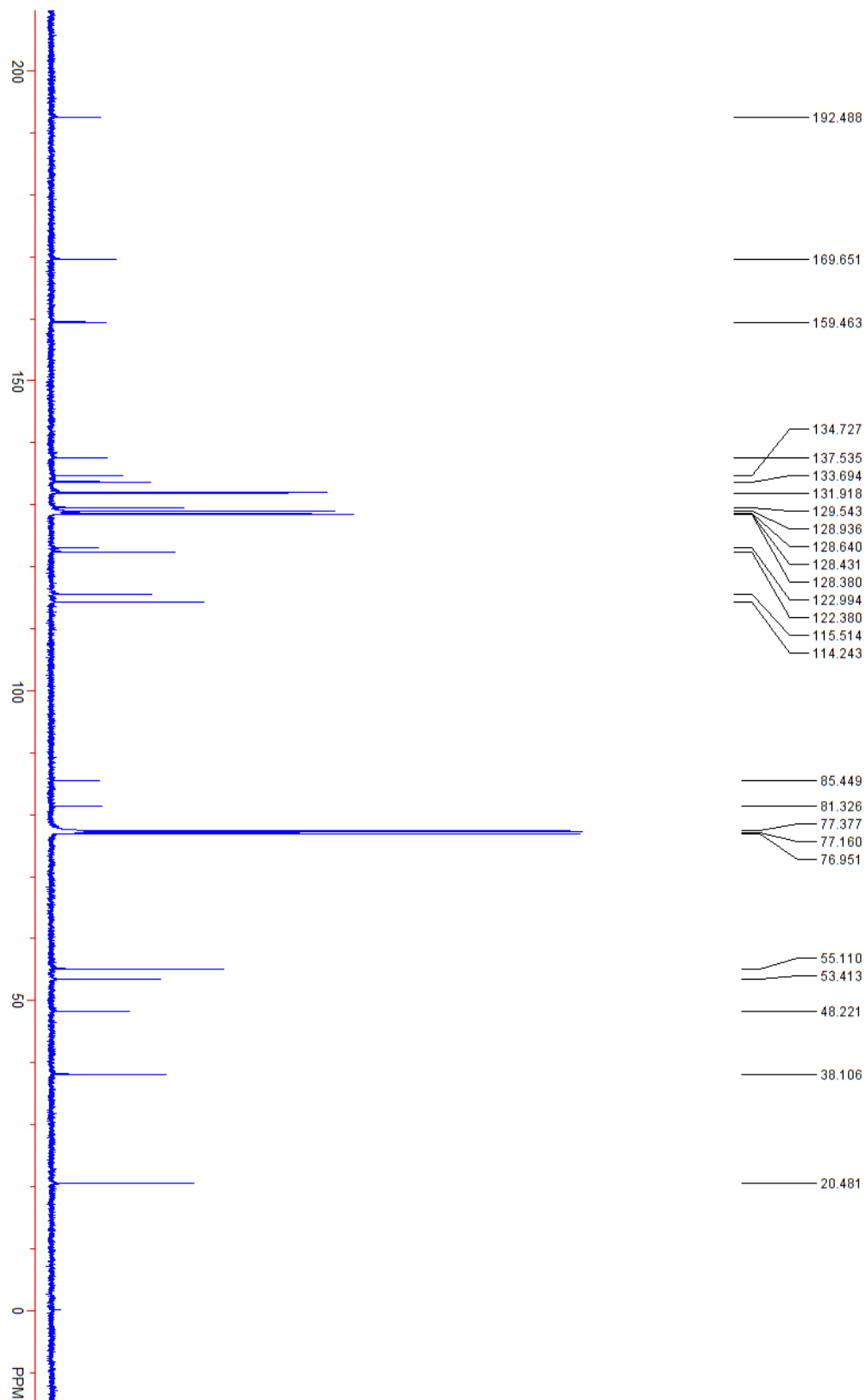


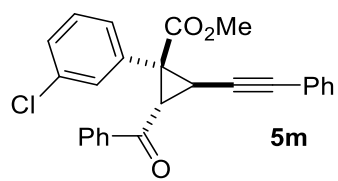
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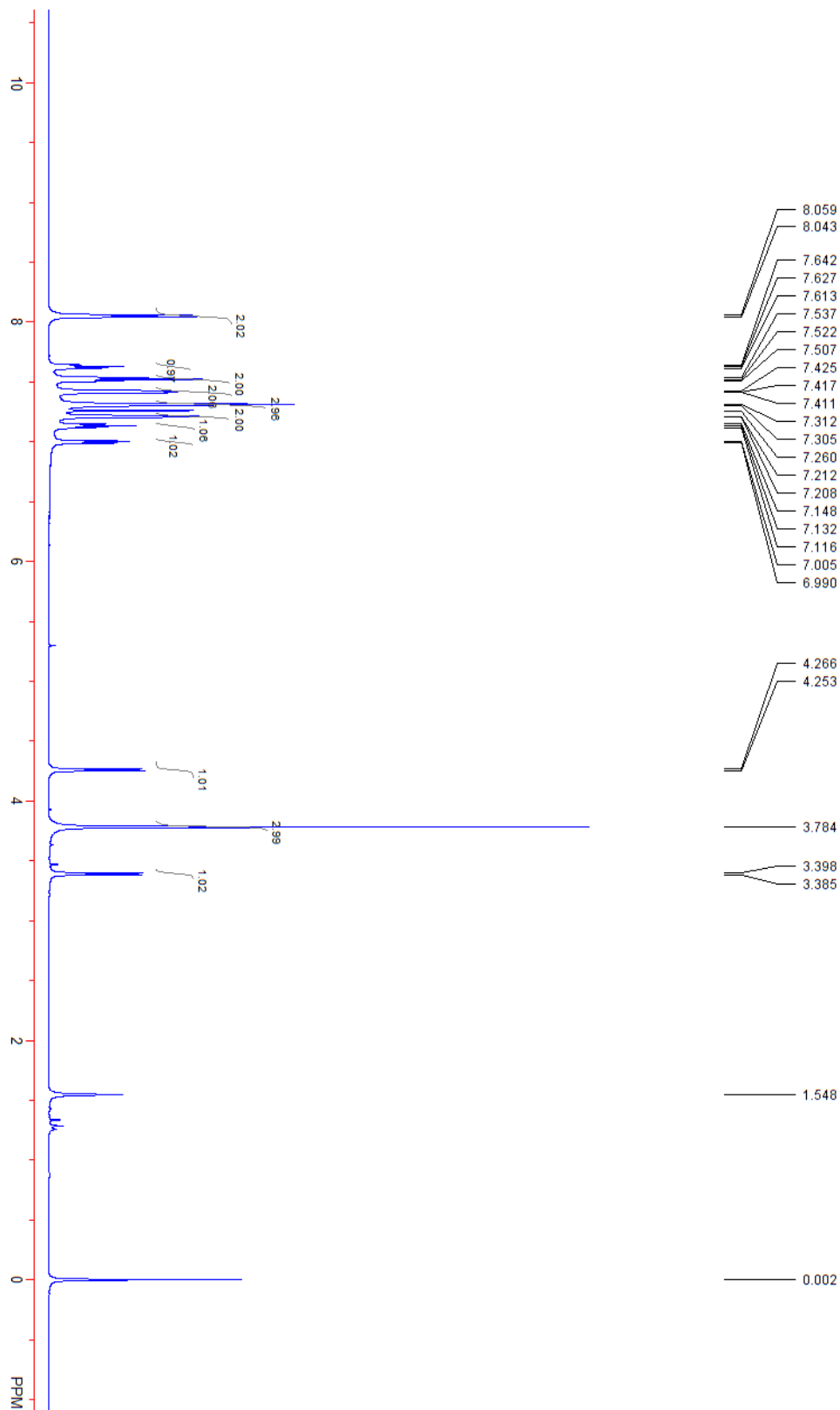


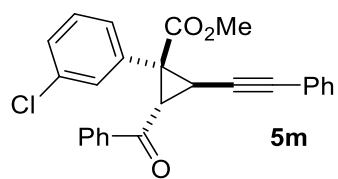
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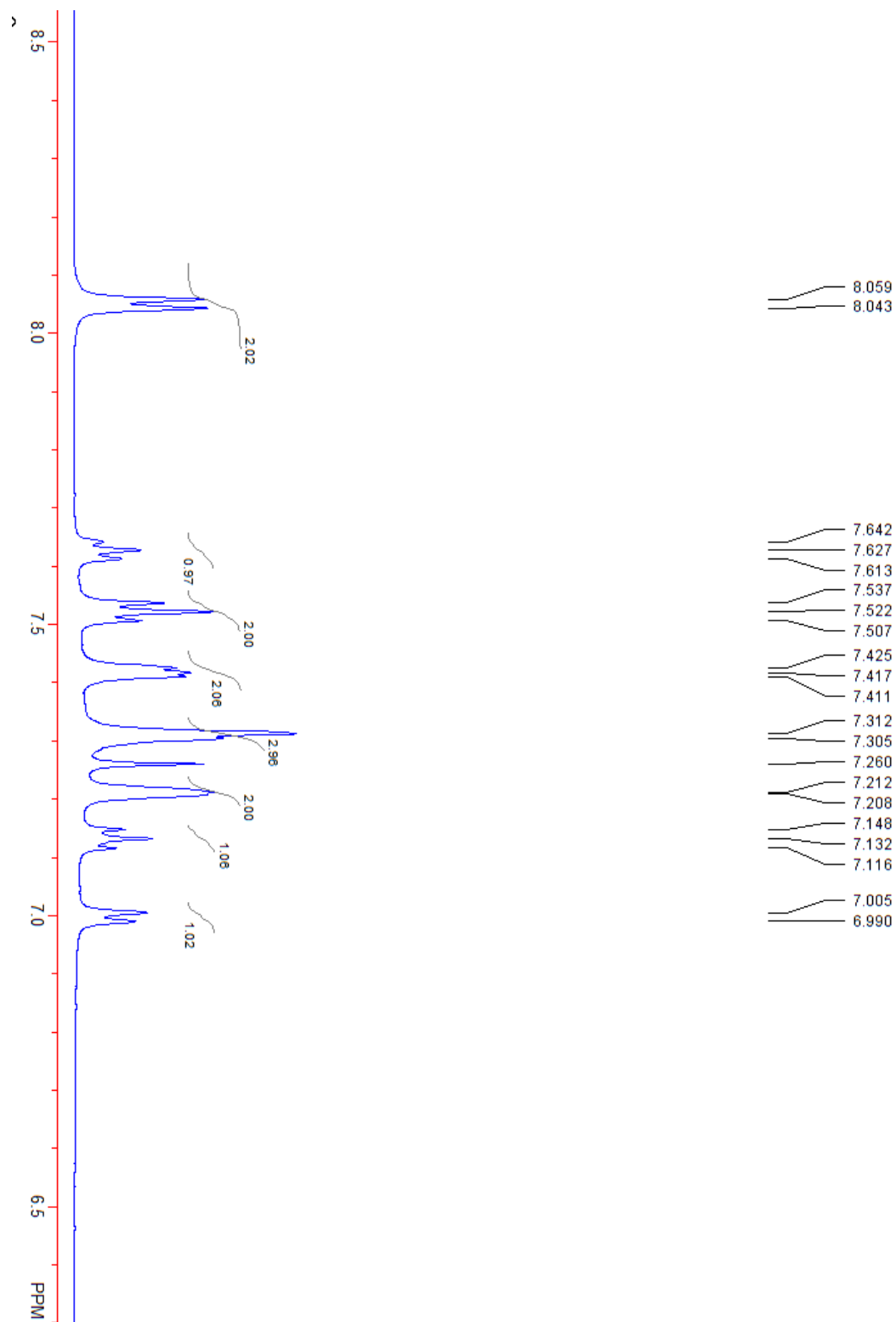


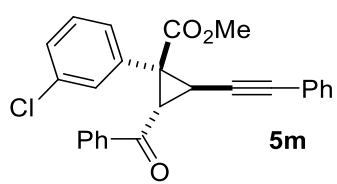
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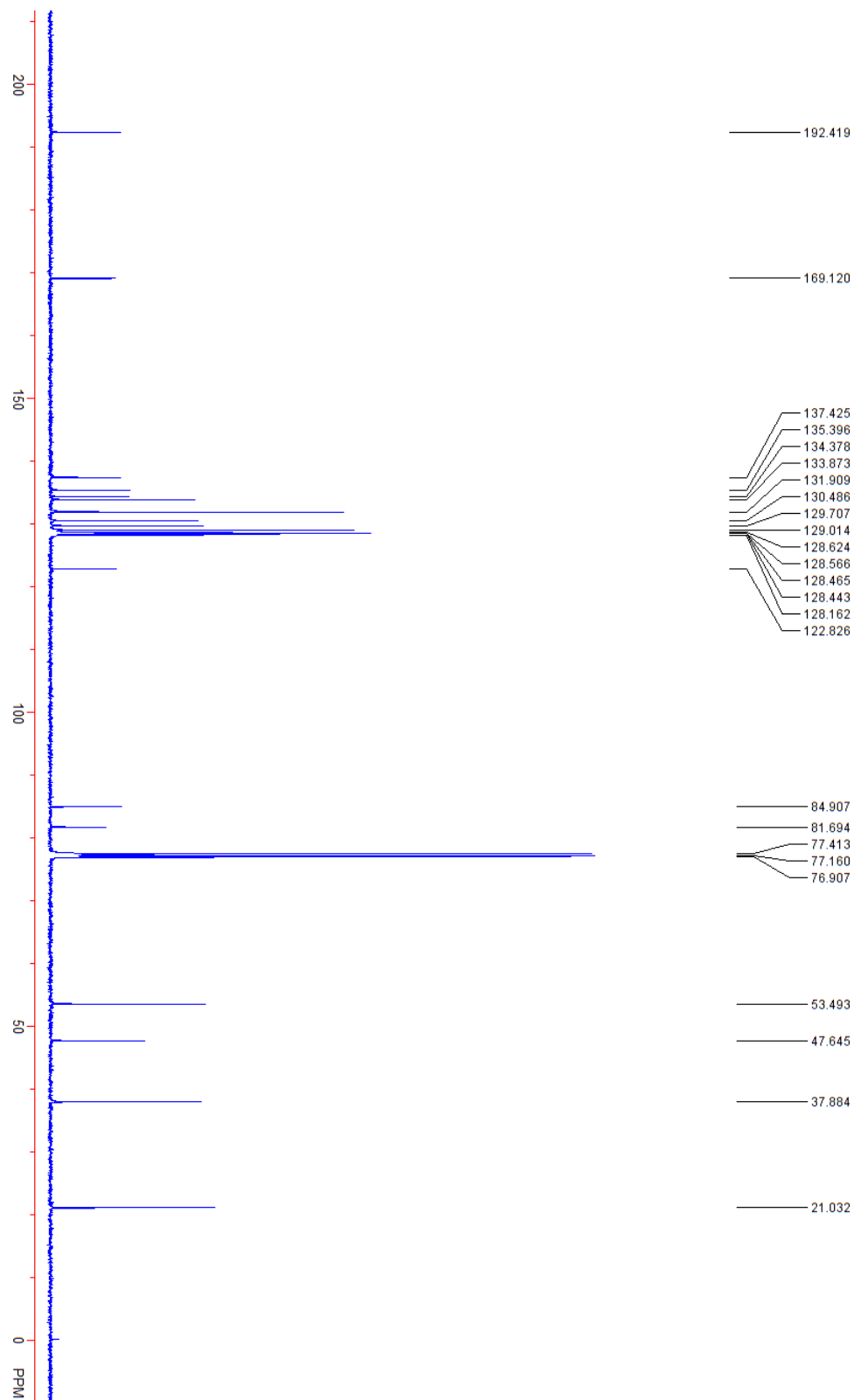


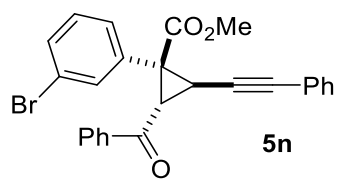
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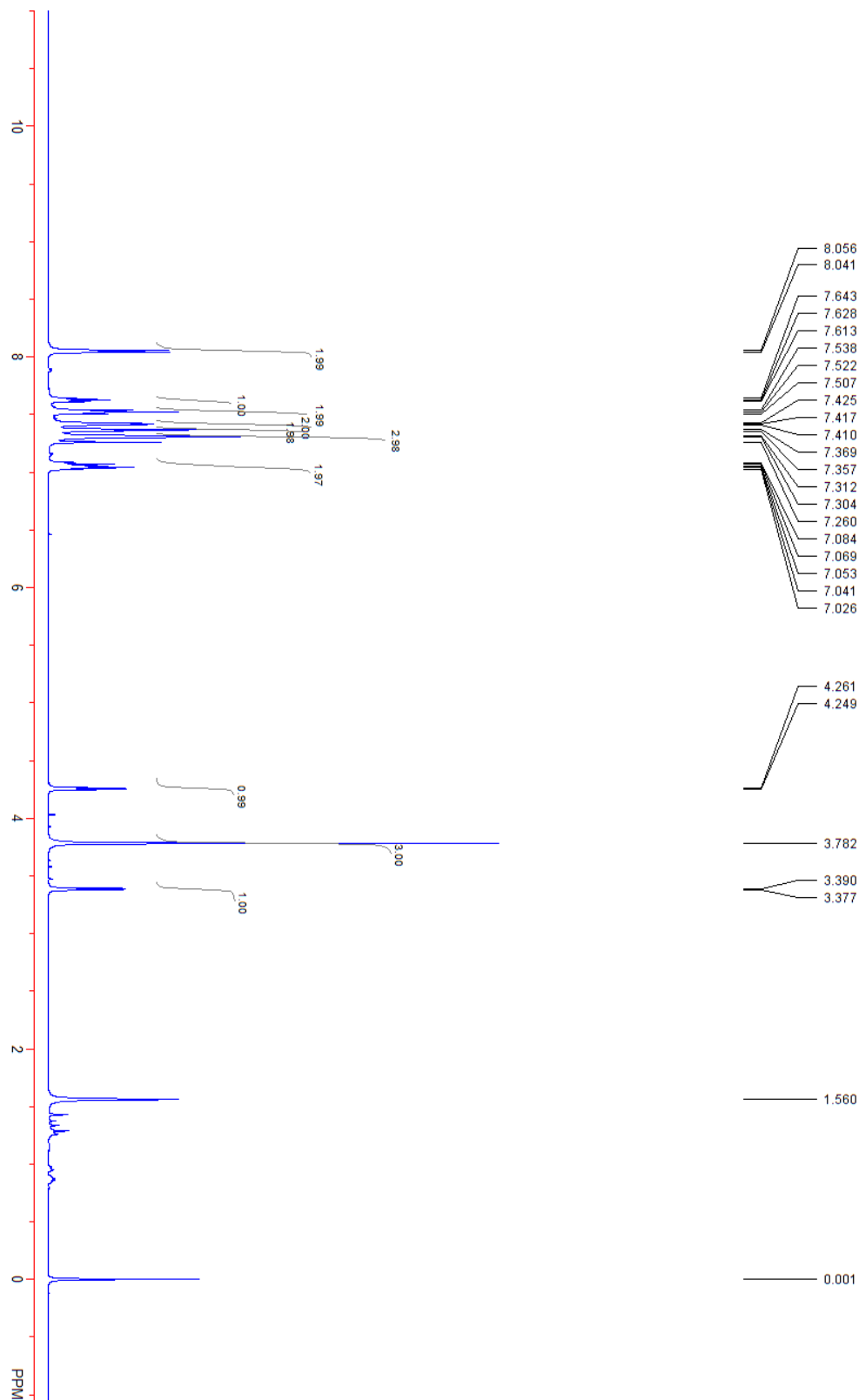


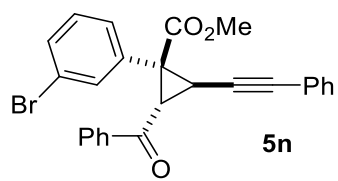
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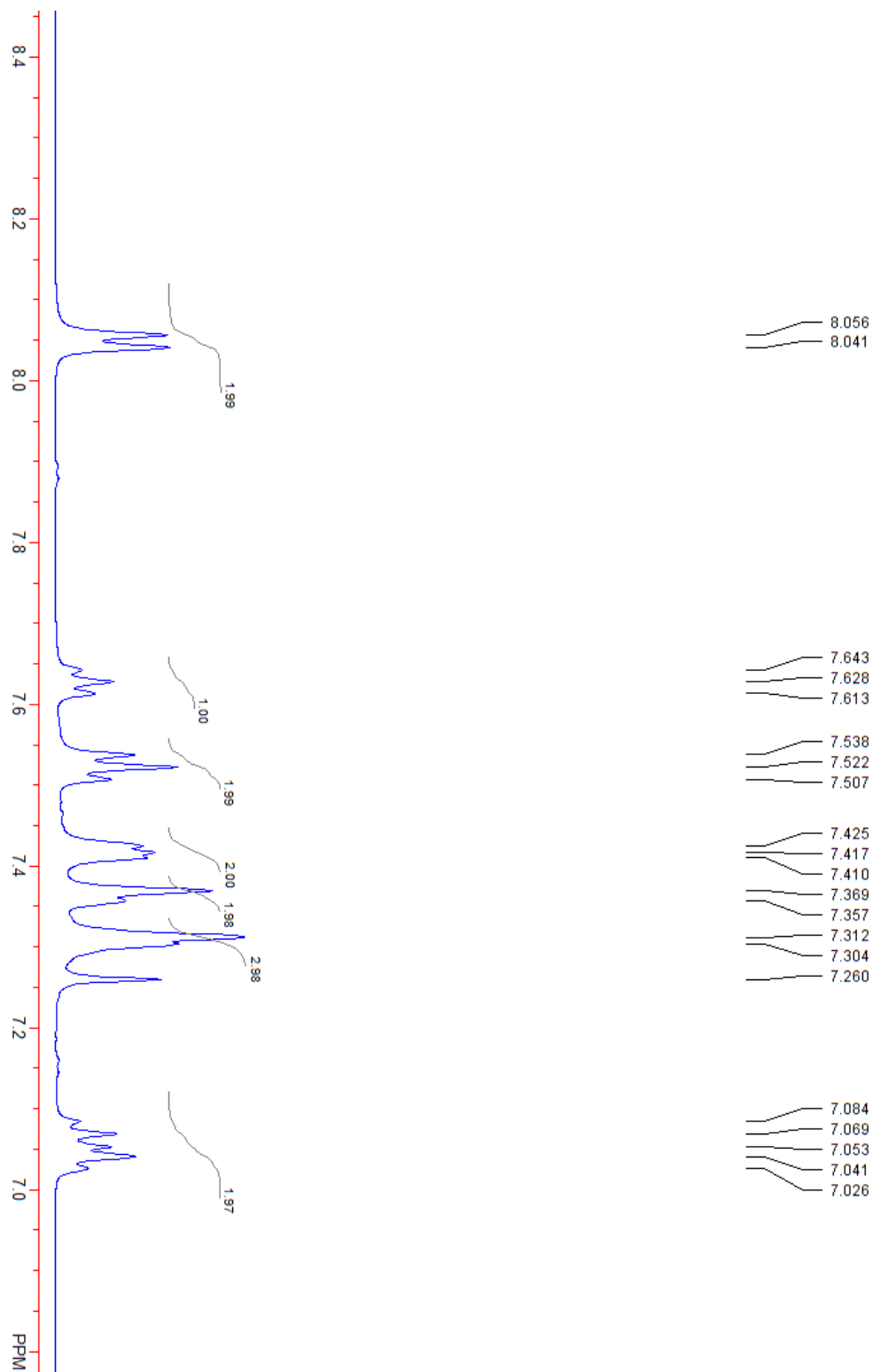


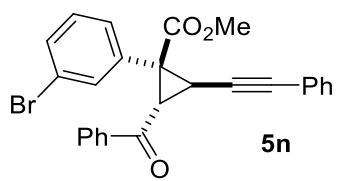
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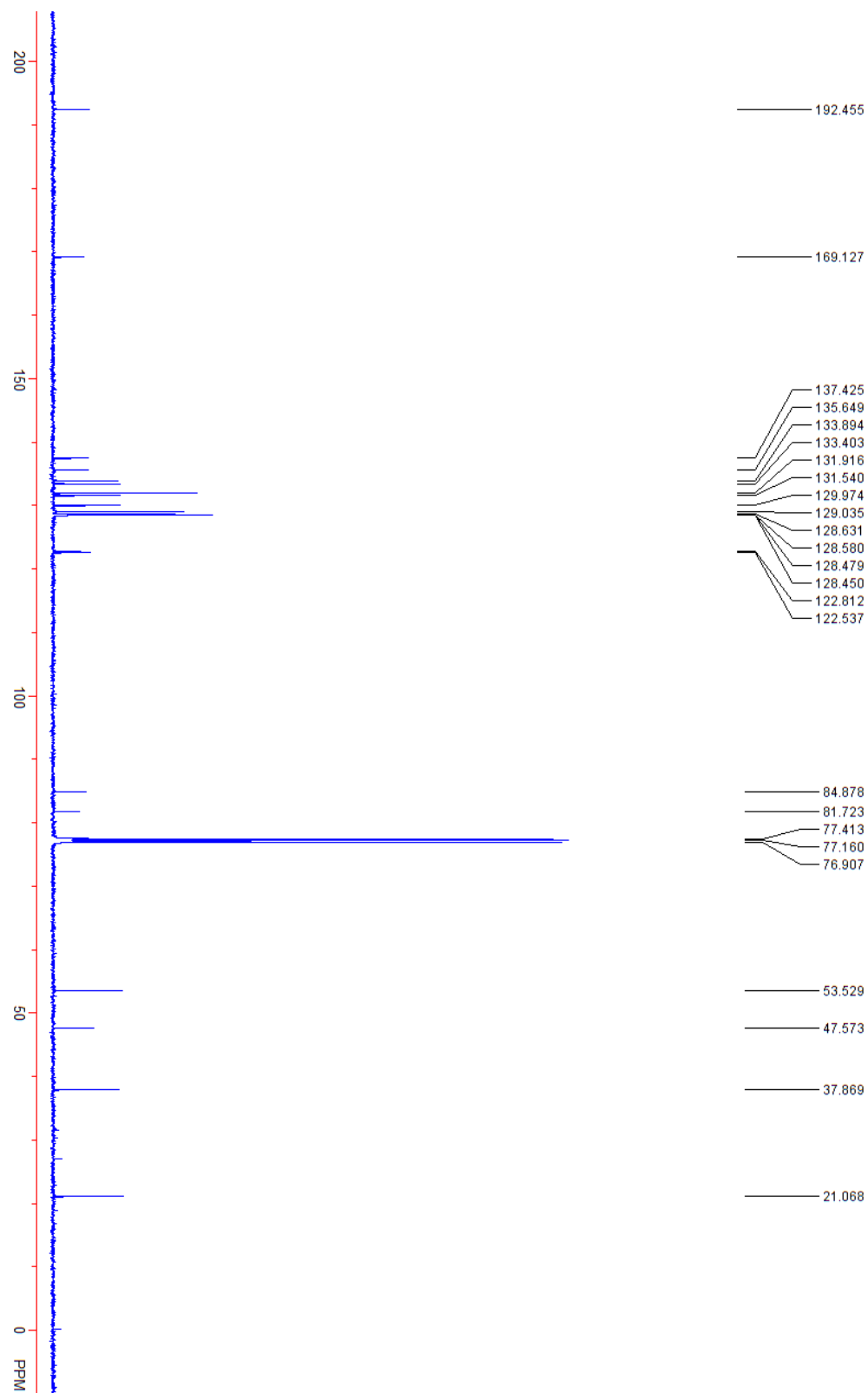


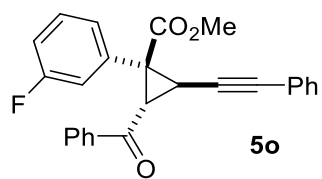
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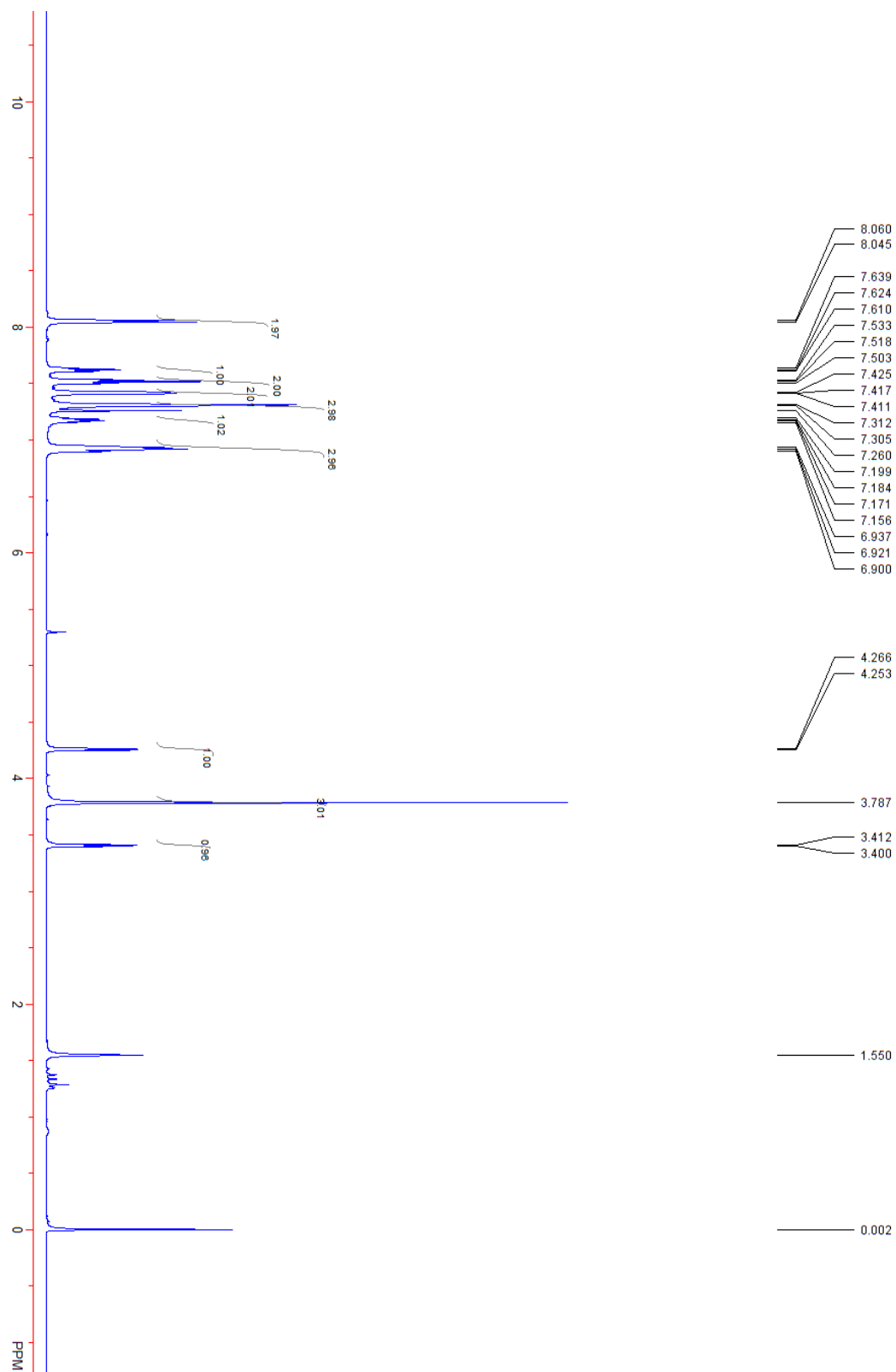


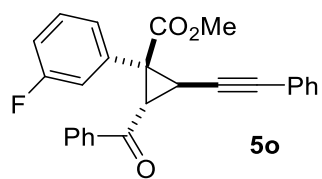
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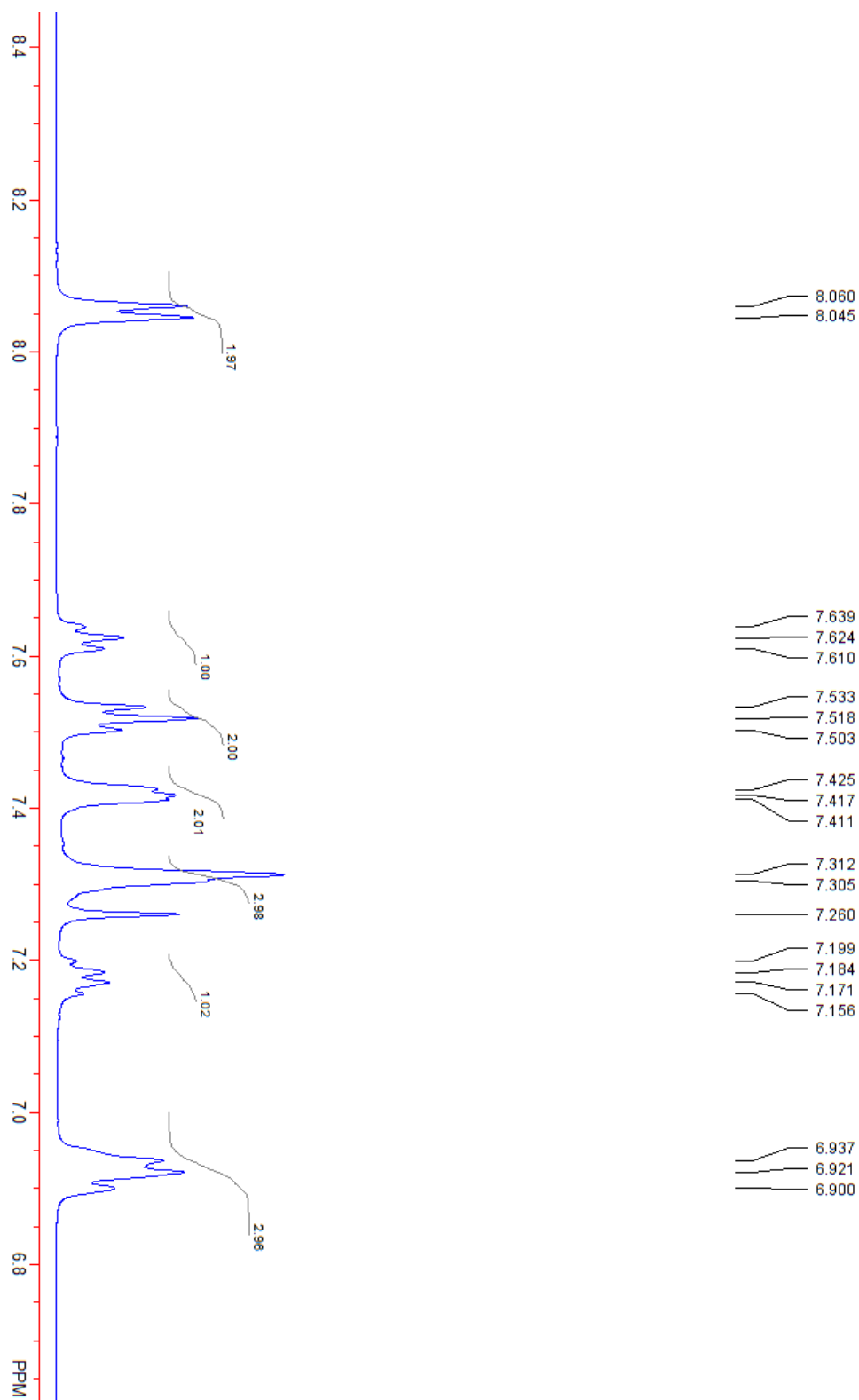


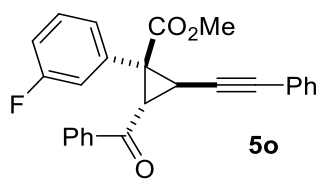
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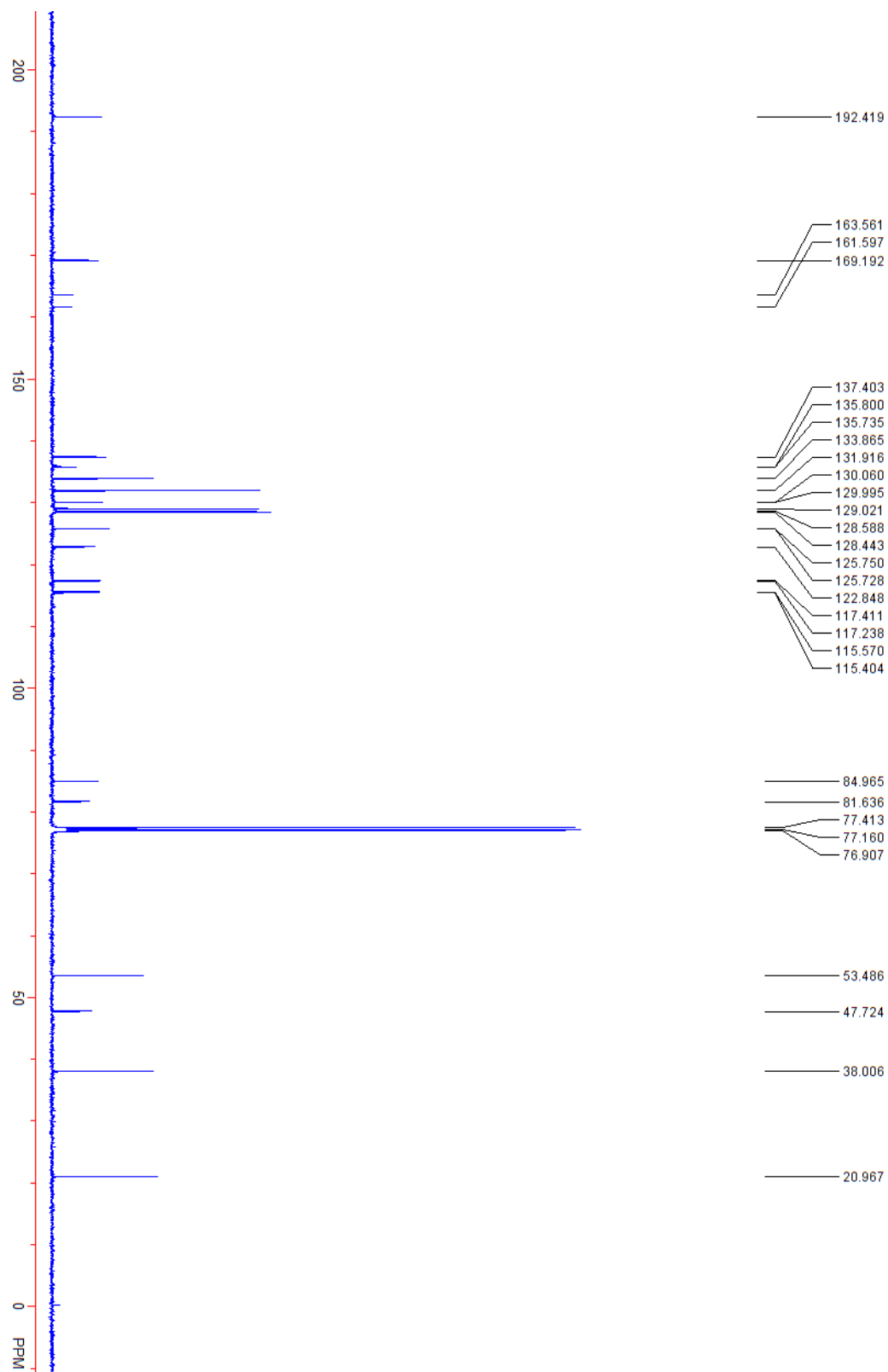


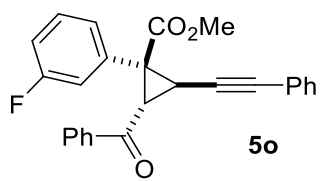
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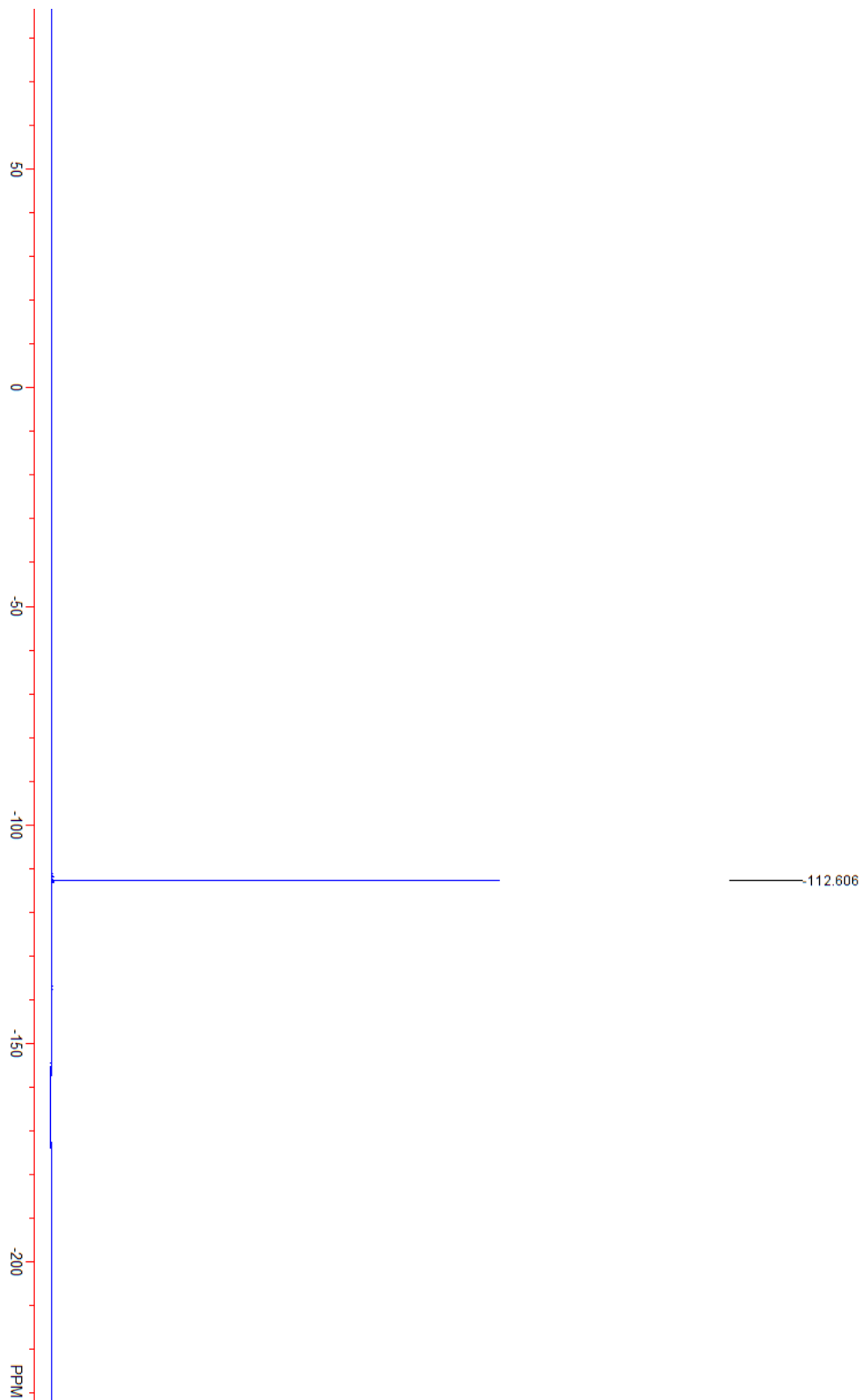


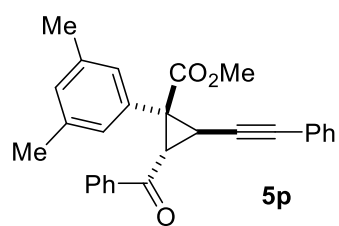
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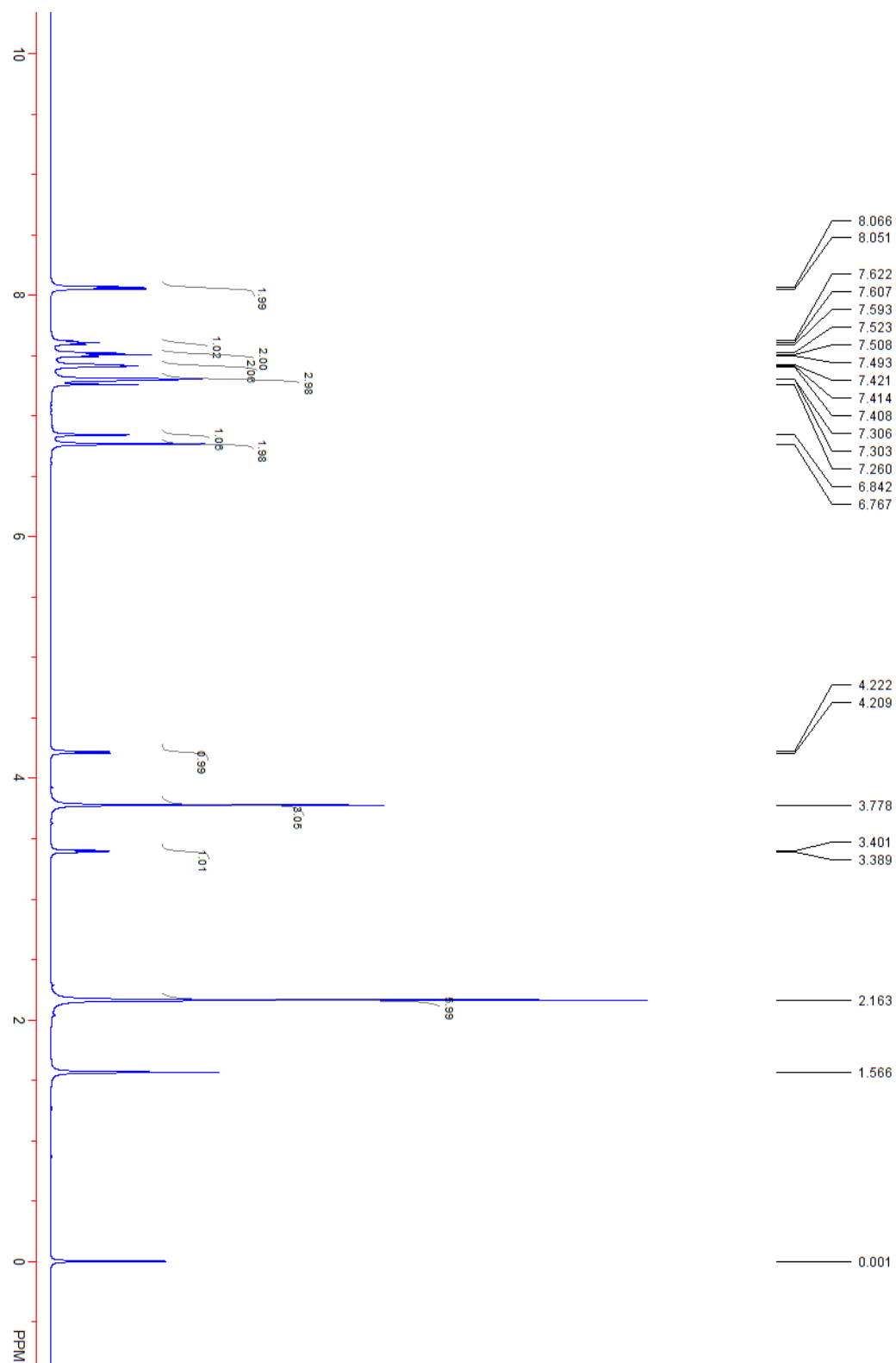


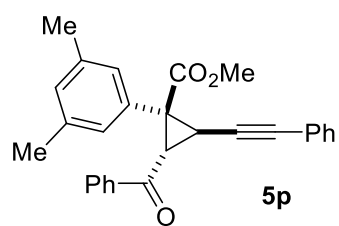
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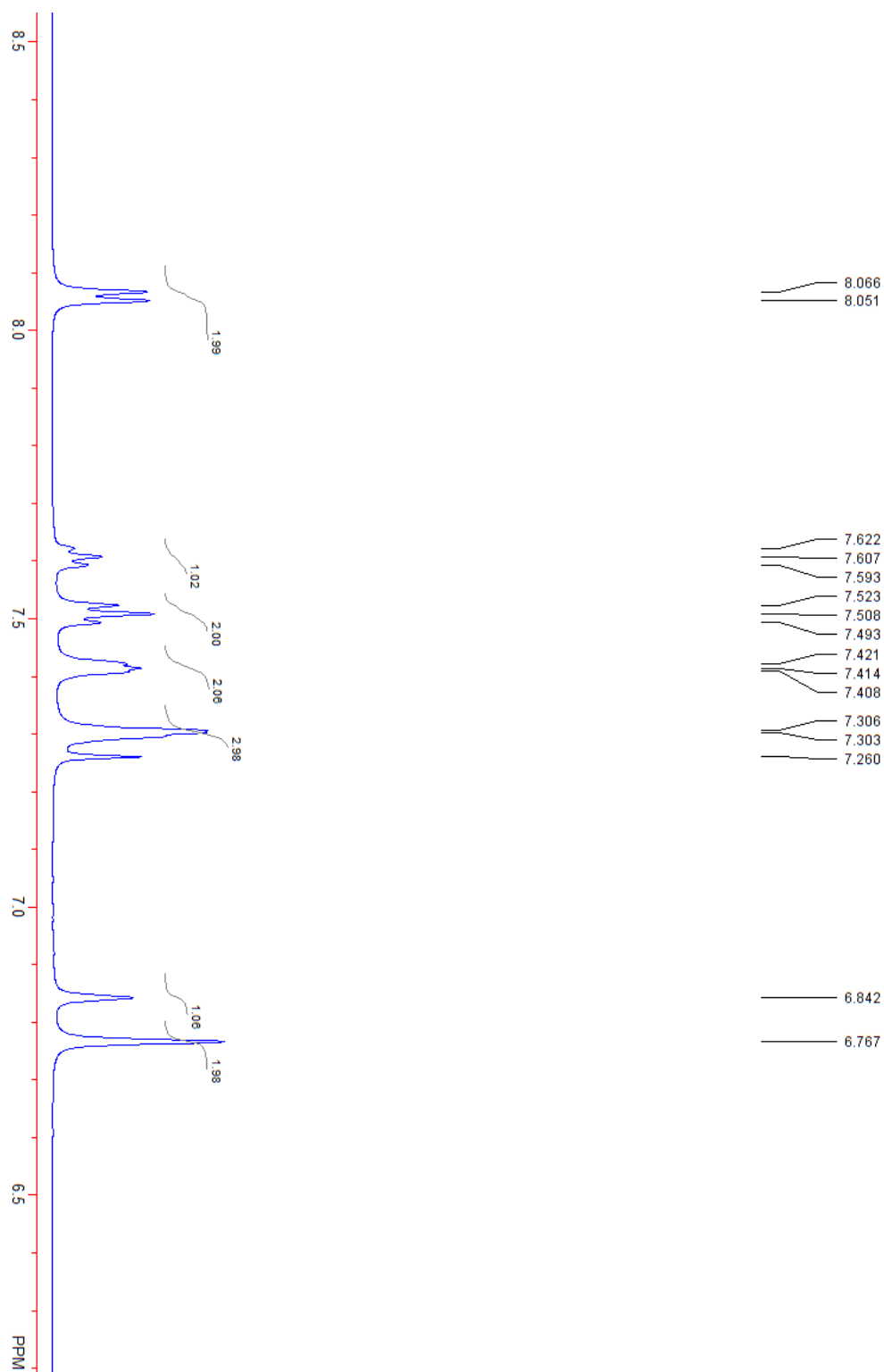


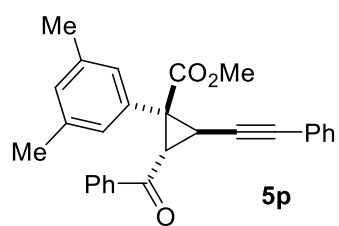
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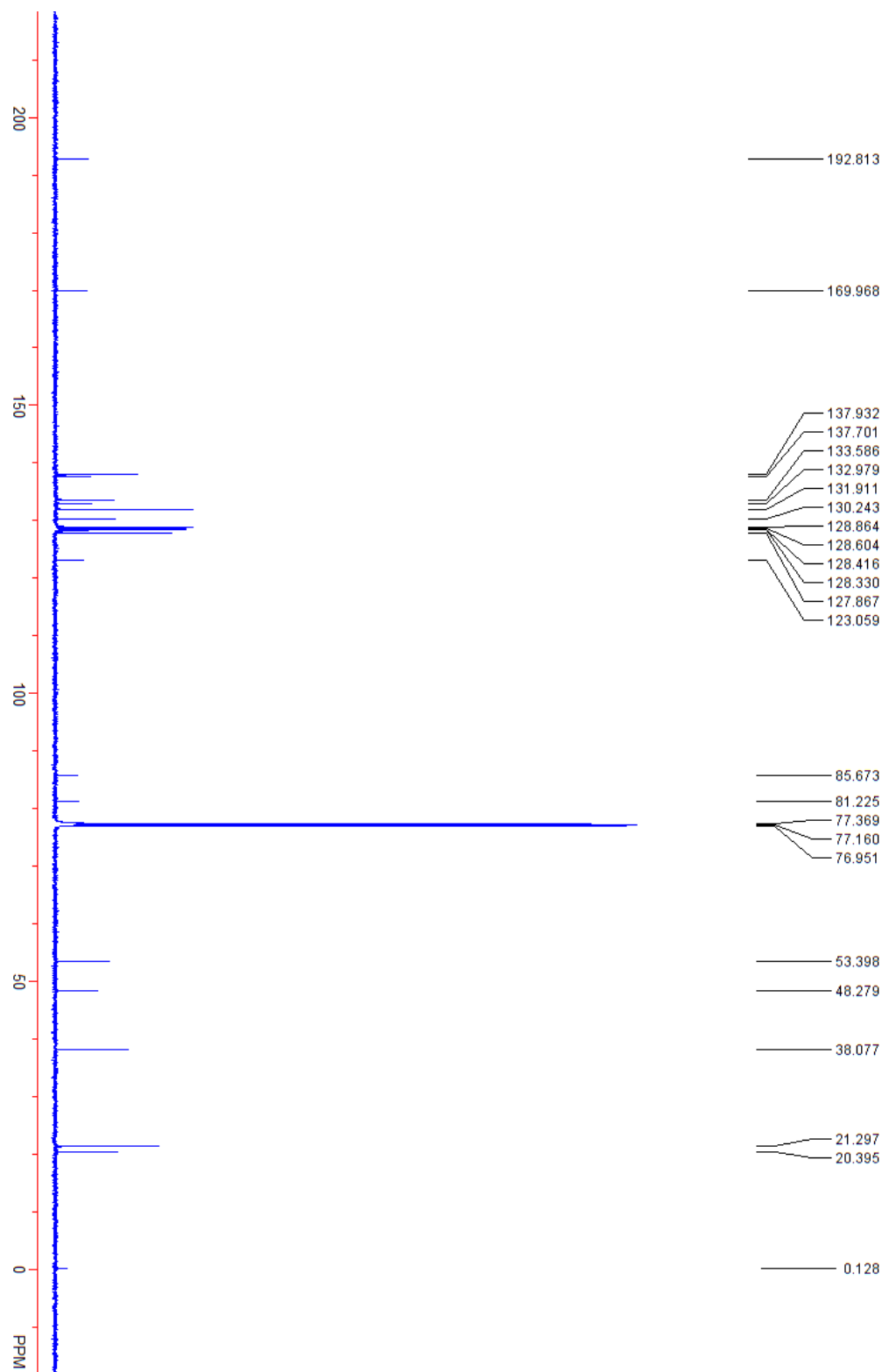


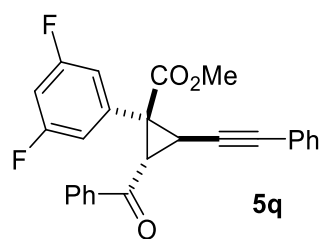
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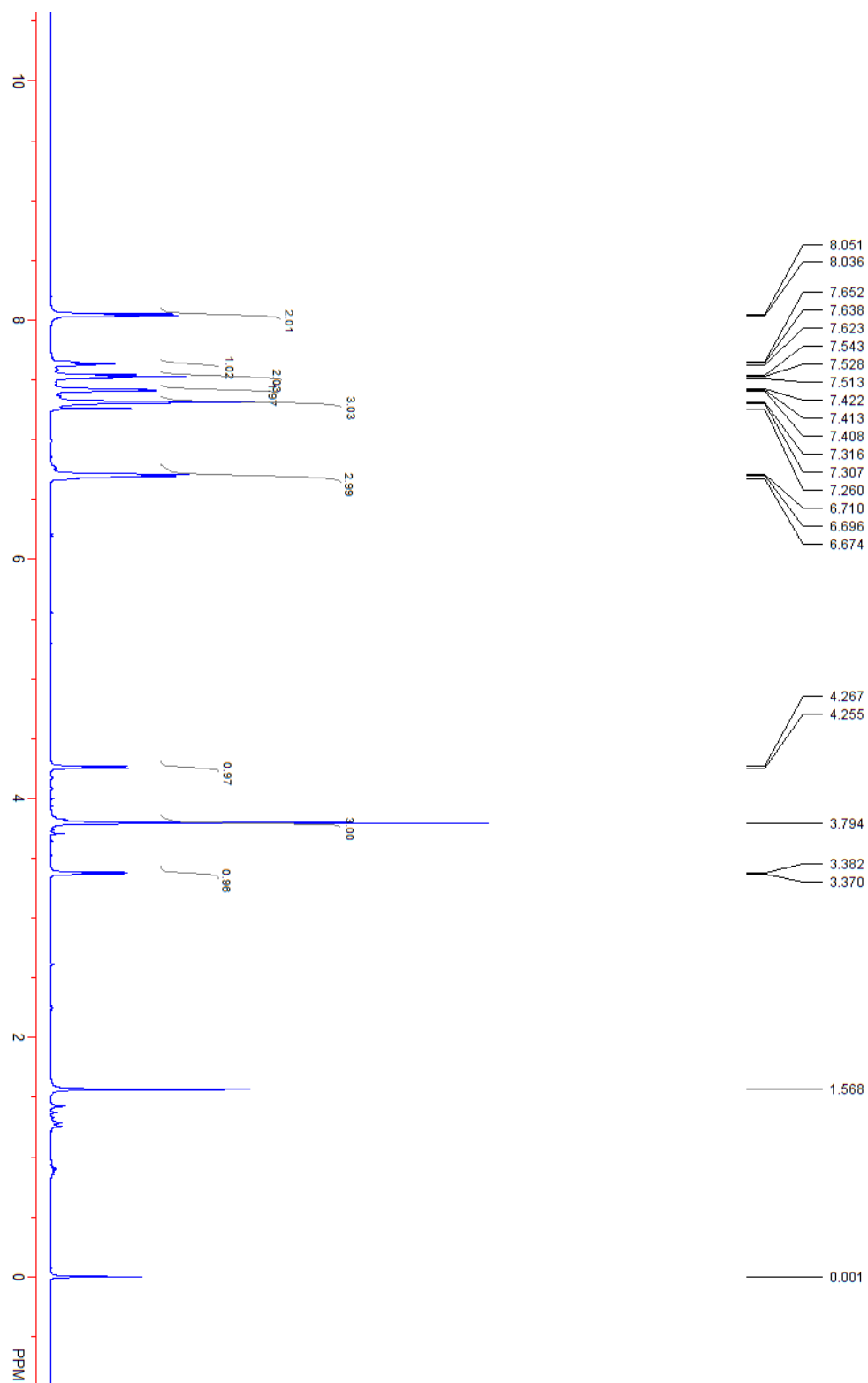


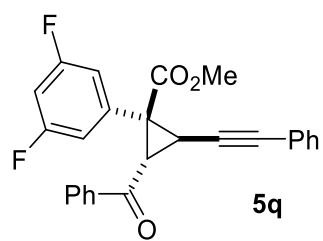
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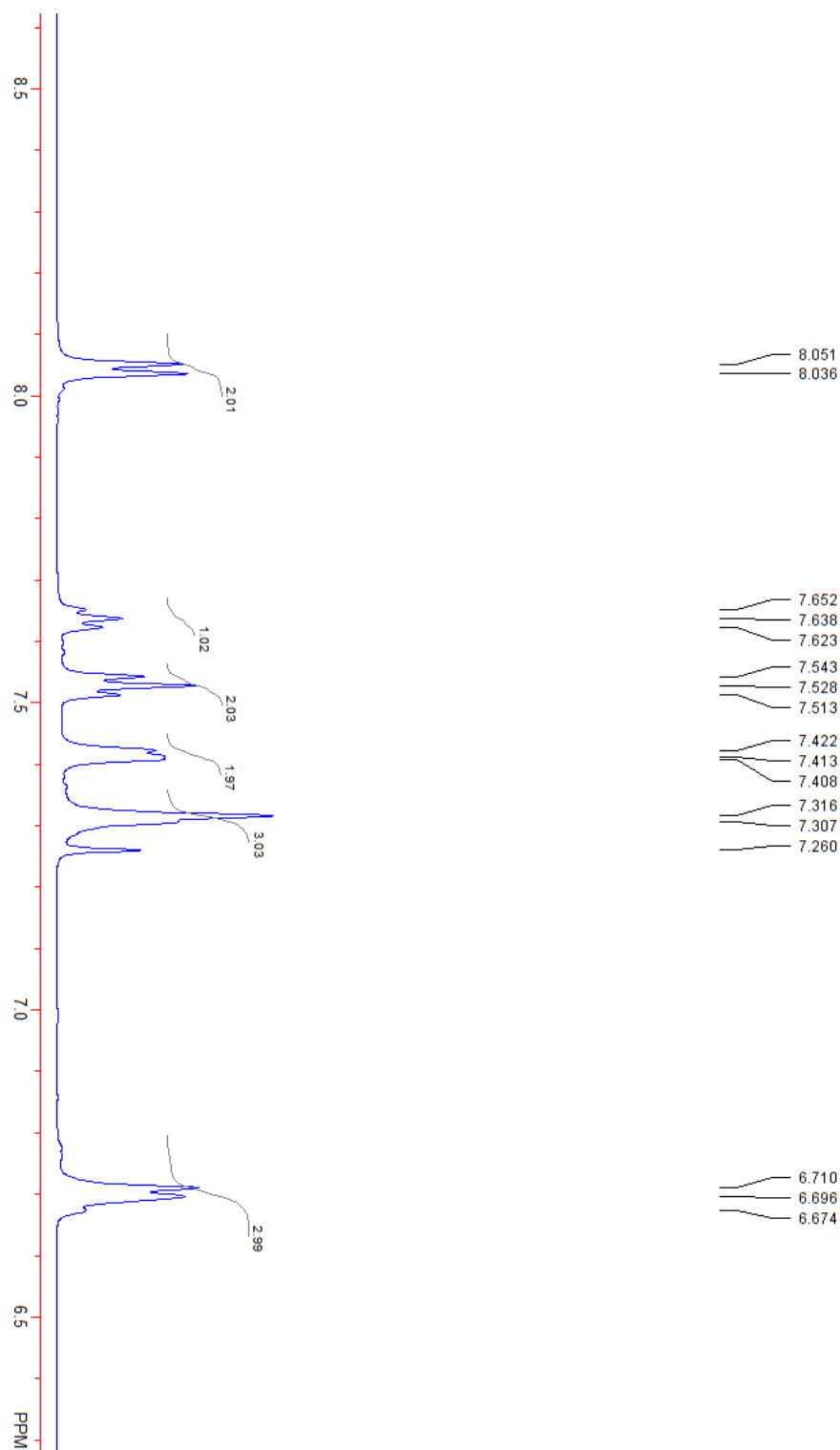


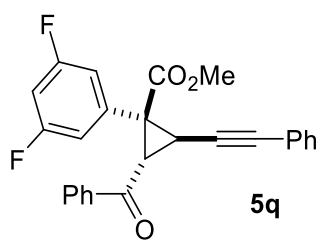
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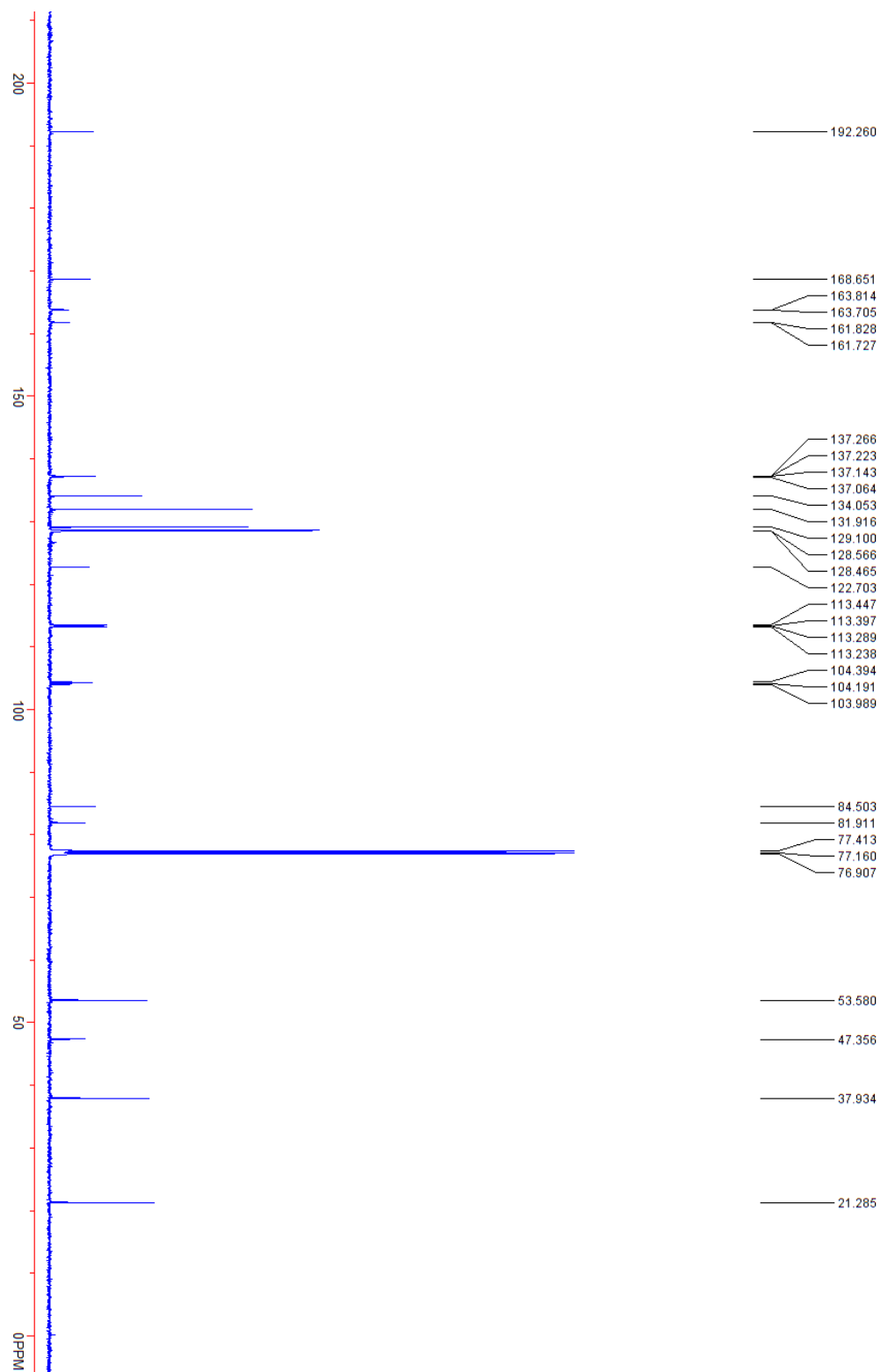


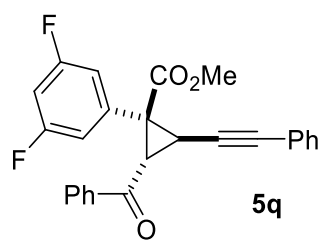
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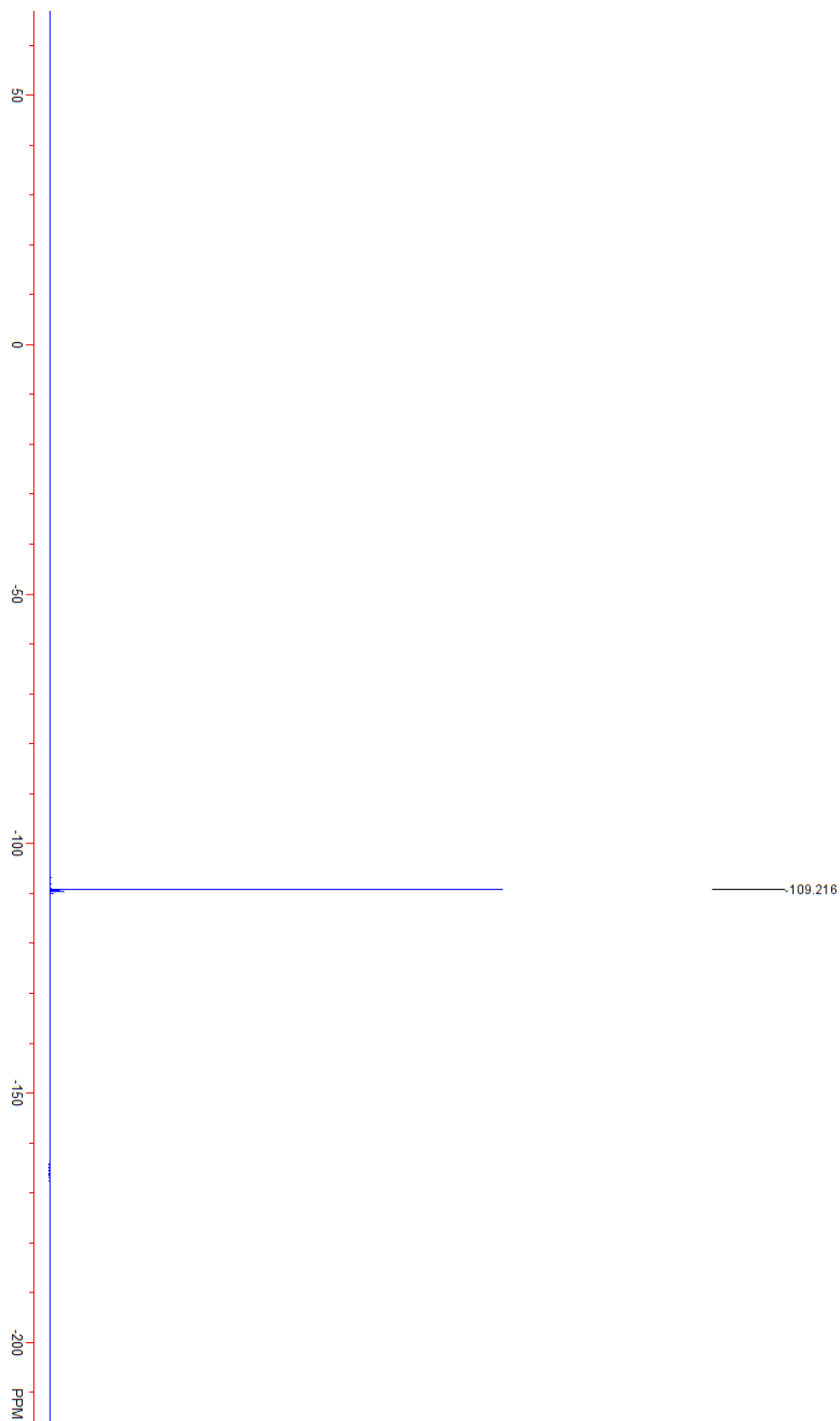


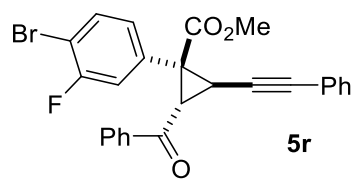
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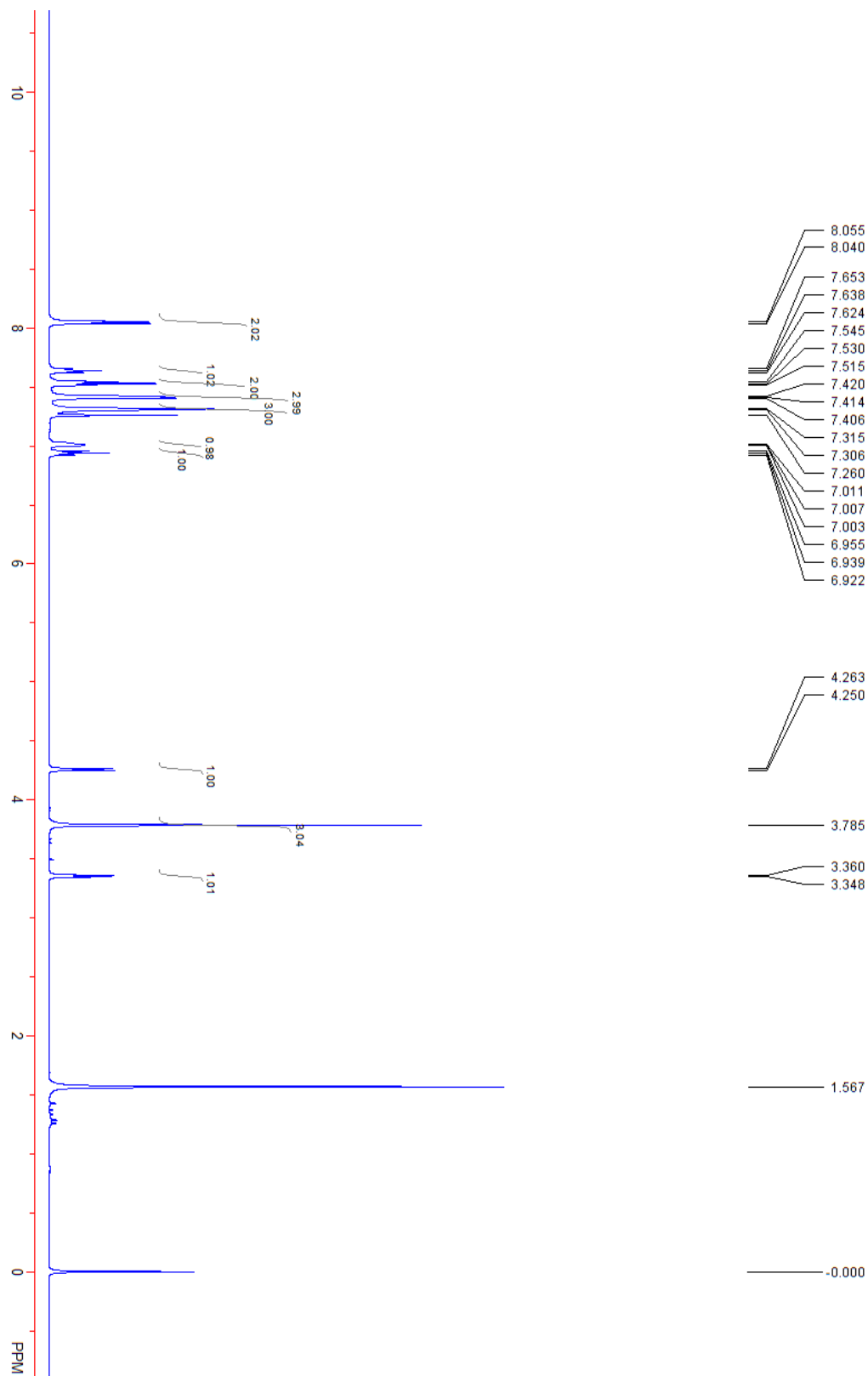


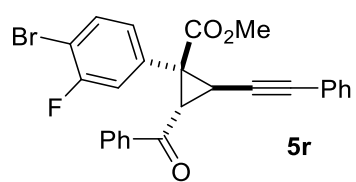
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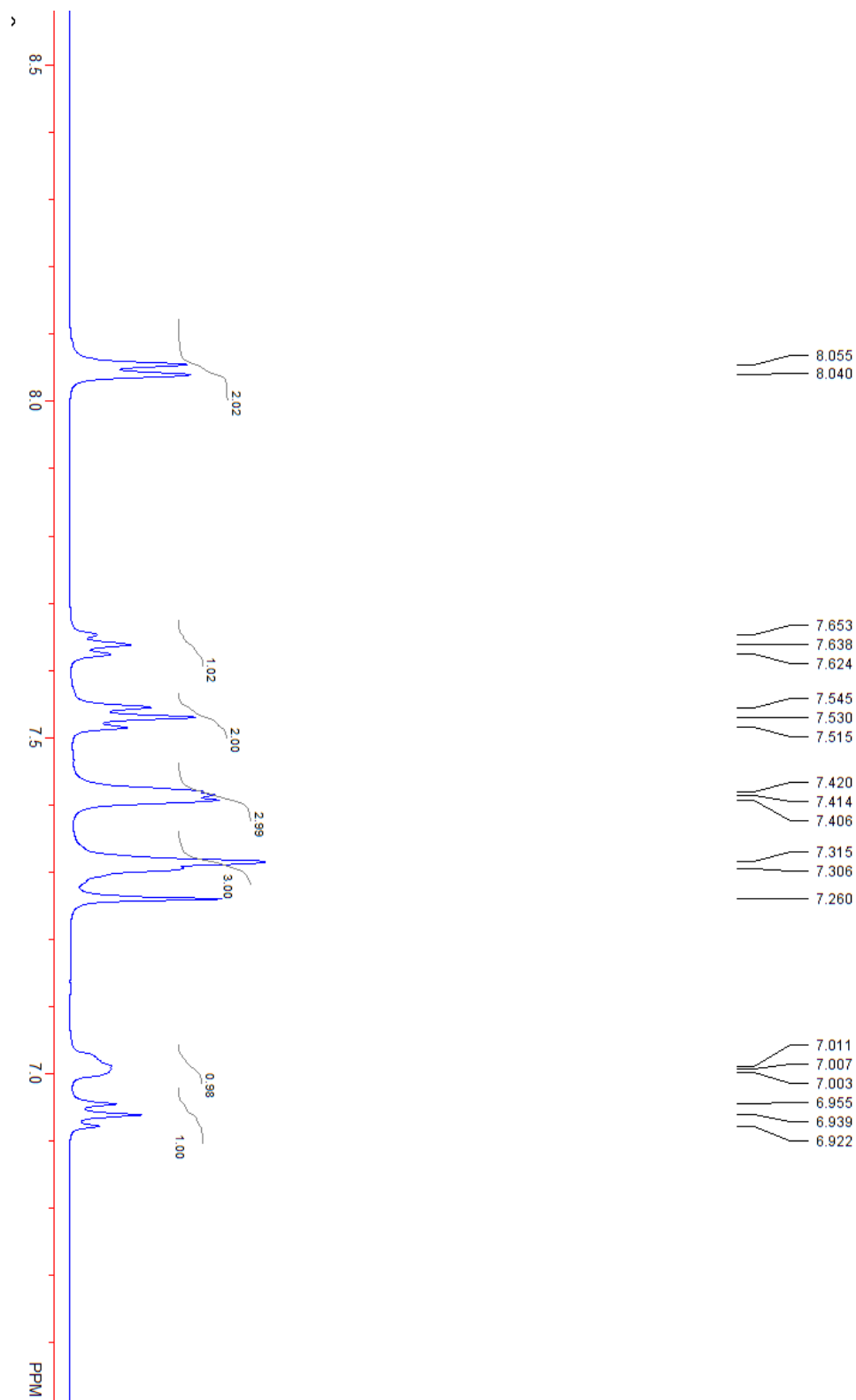


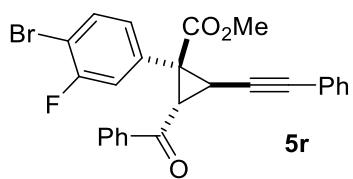
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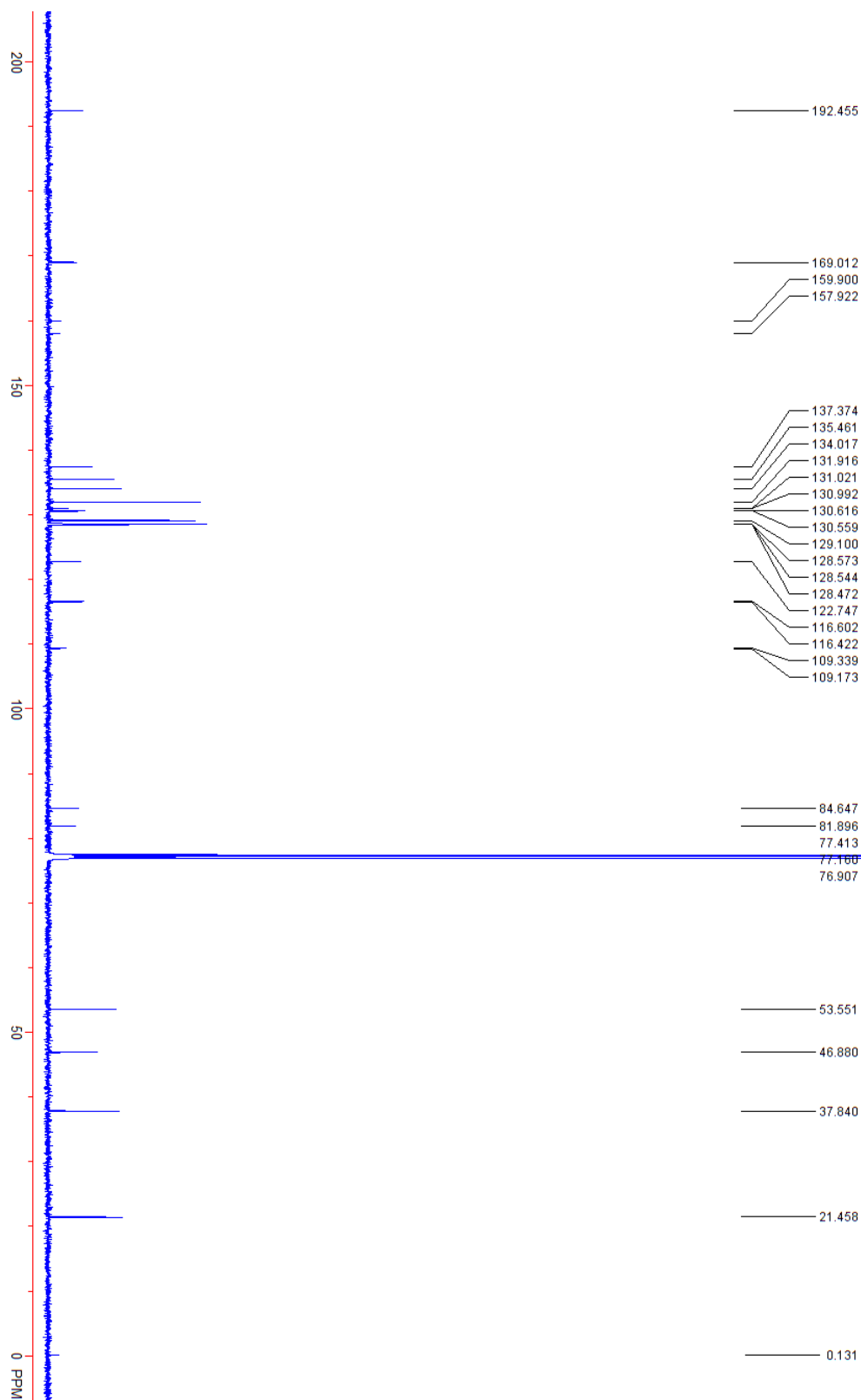


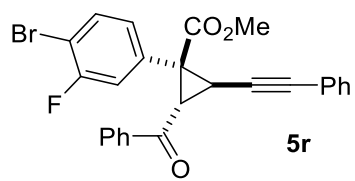
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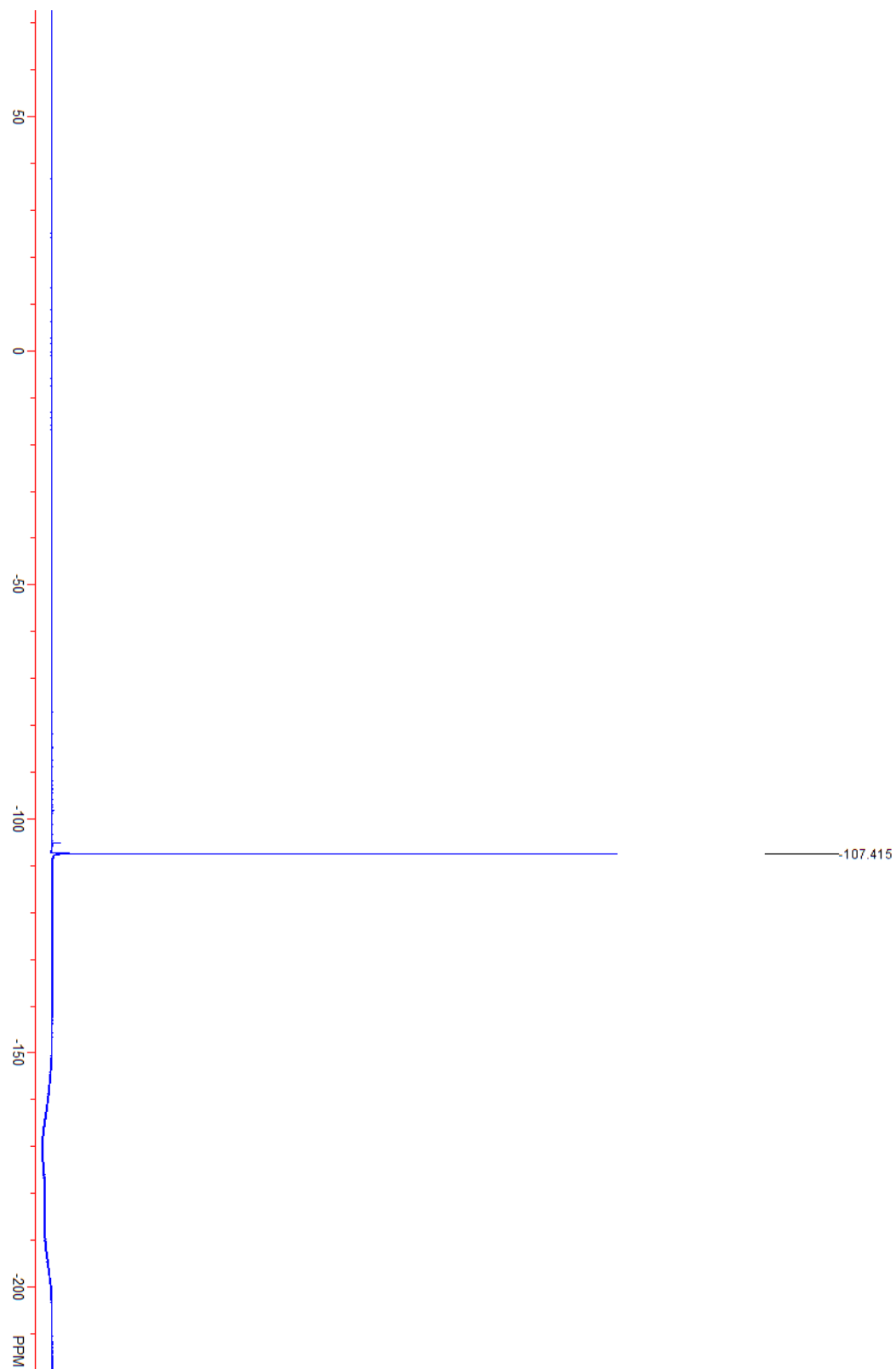


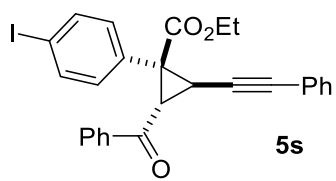
$^{13}\text{C}\{^1\text{H}\}$ NMR:



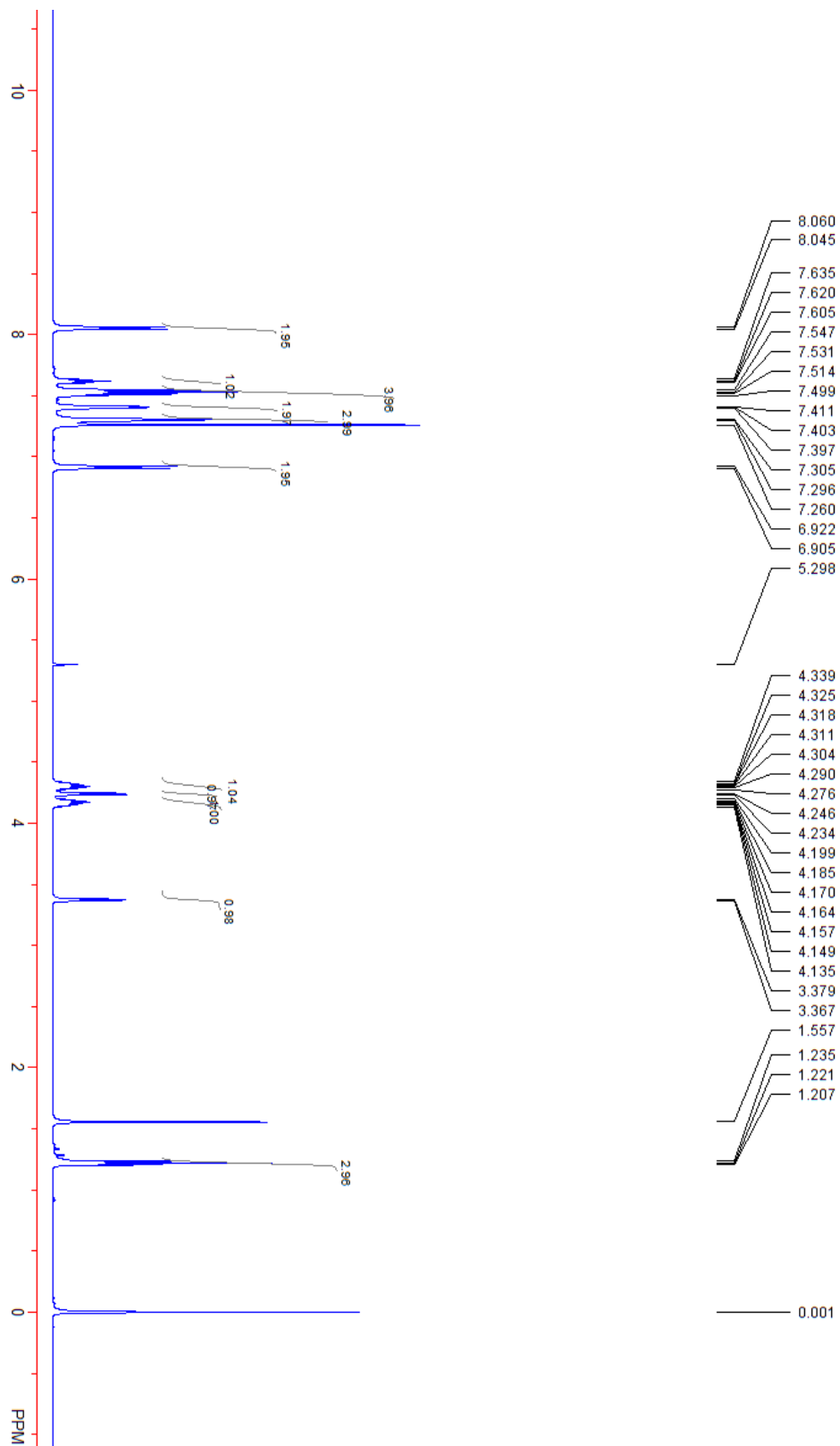


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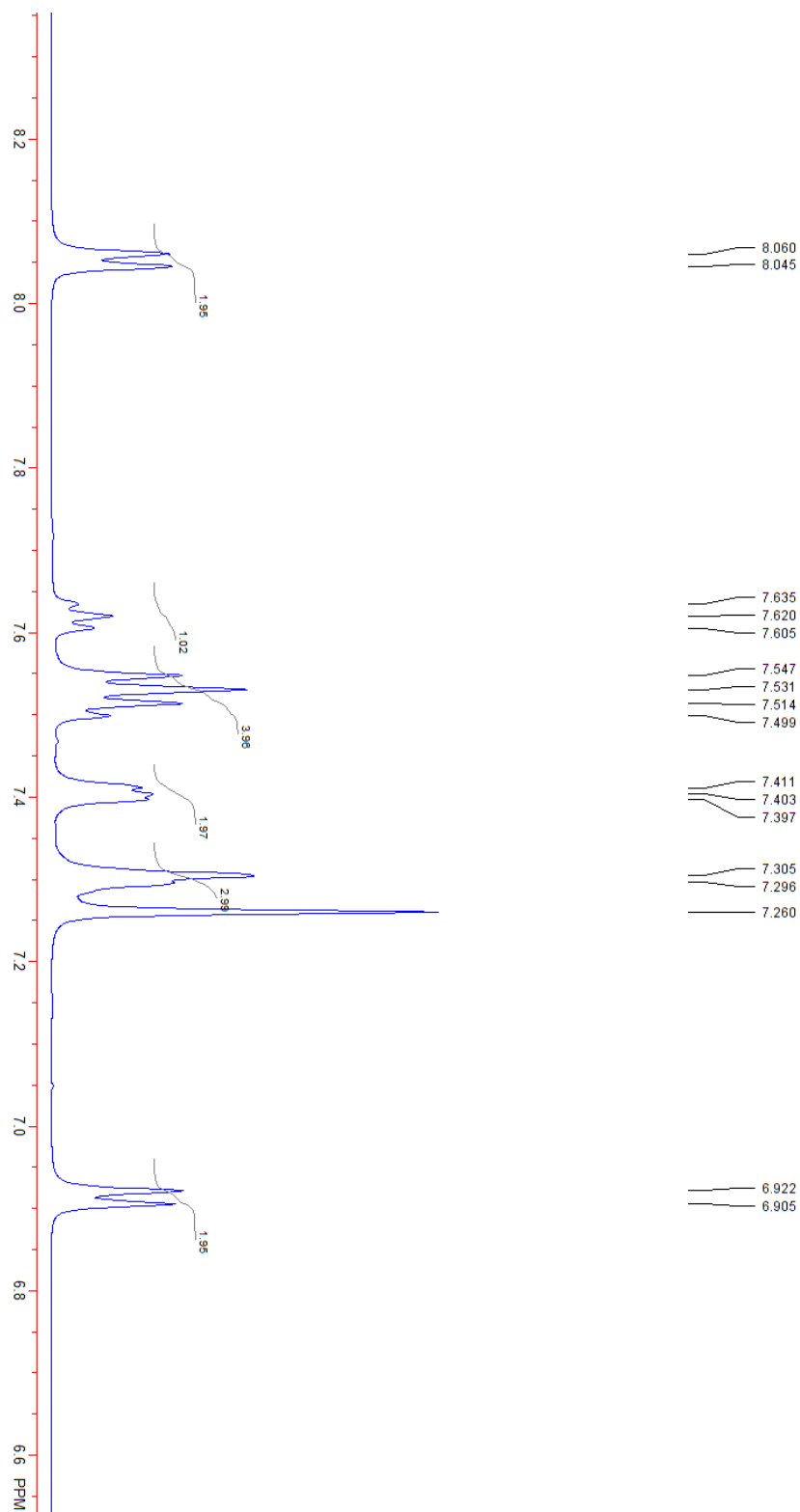
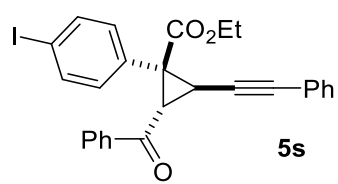


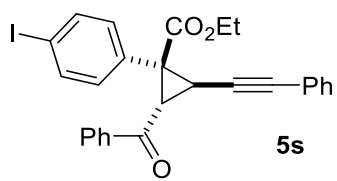


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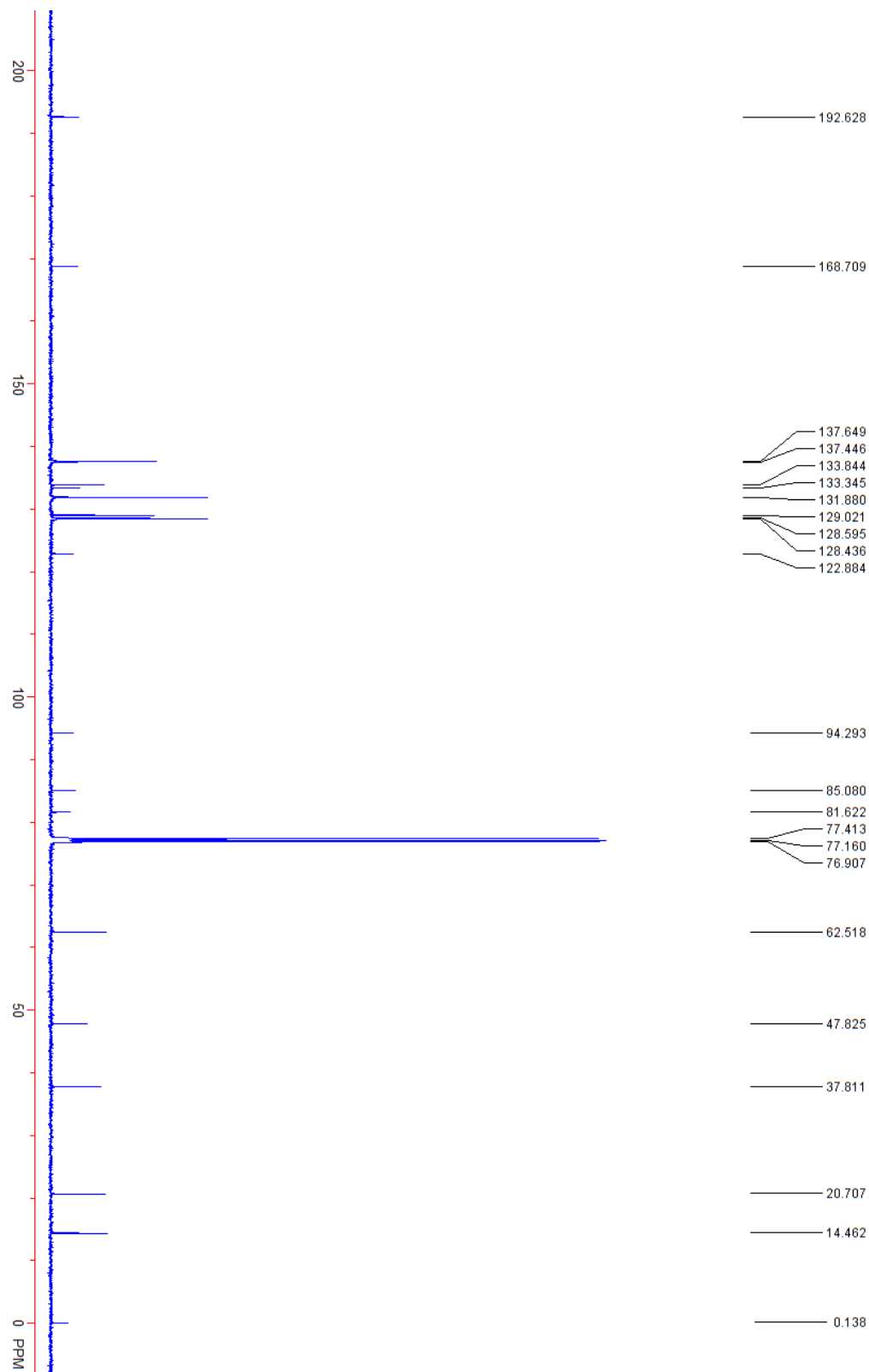


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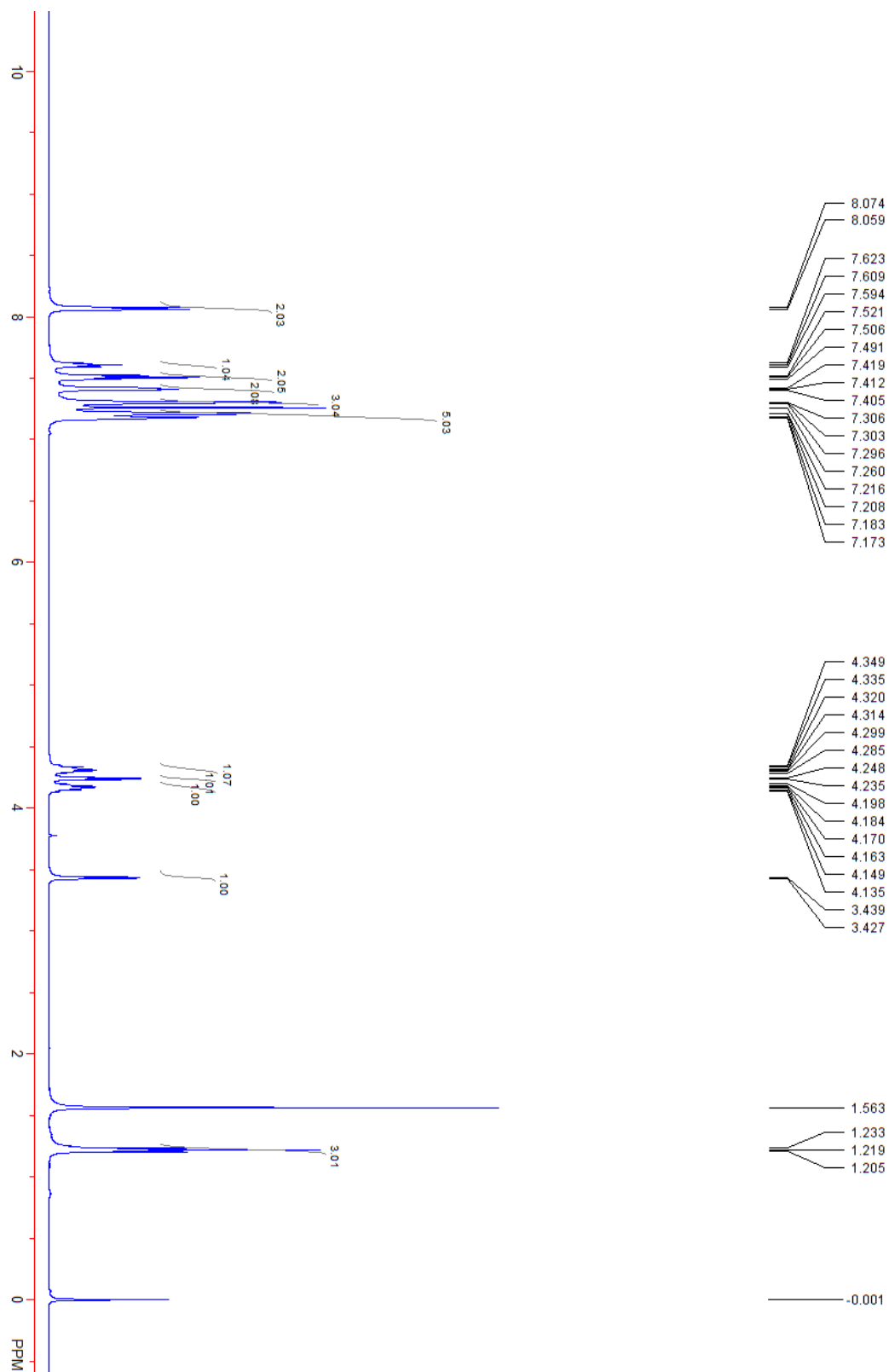
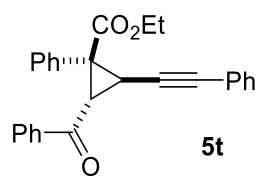


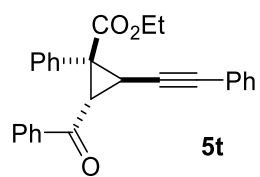


$^{13}\text{C}\{^1\text{H}\}$ NMR:

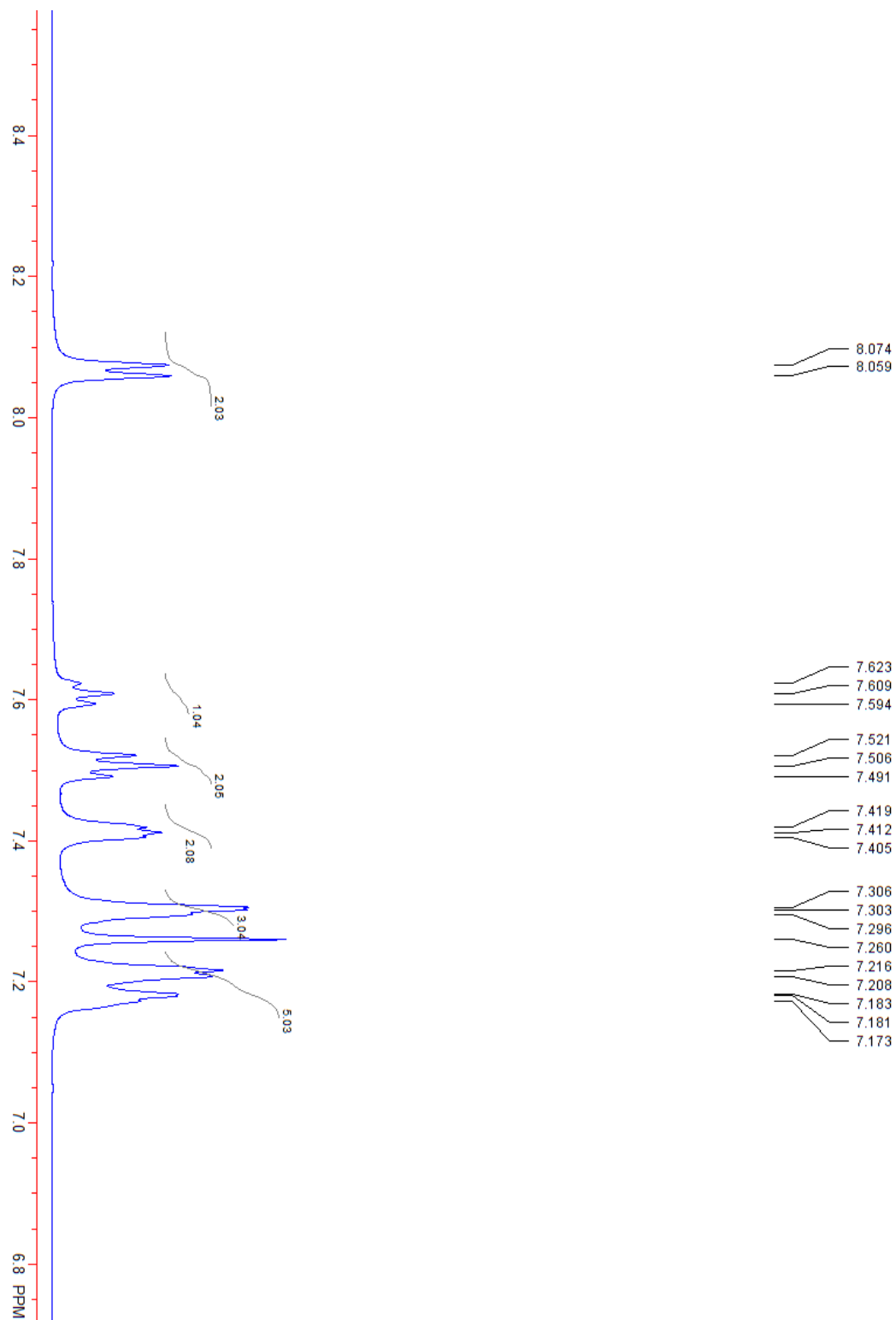


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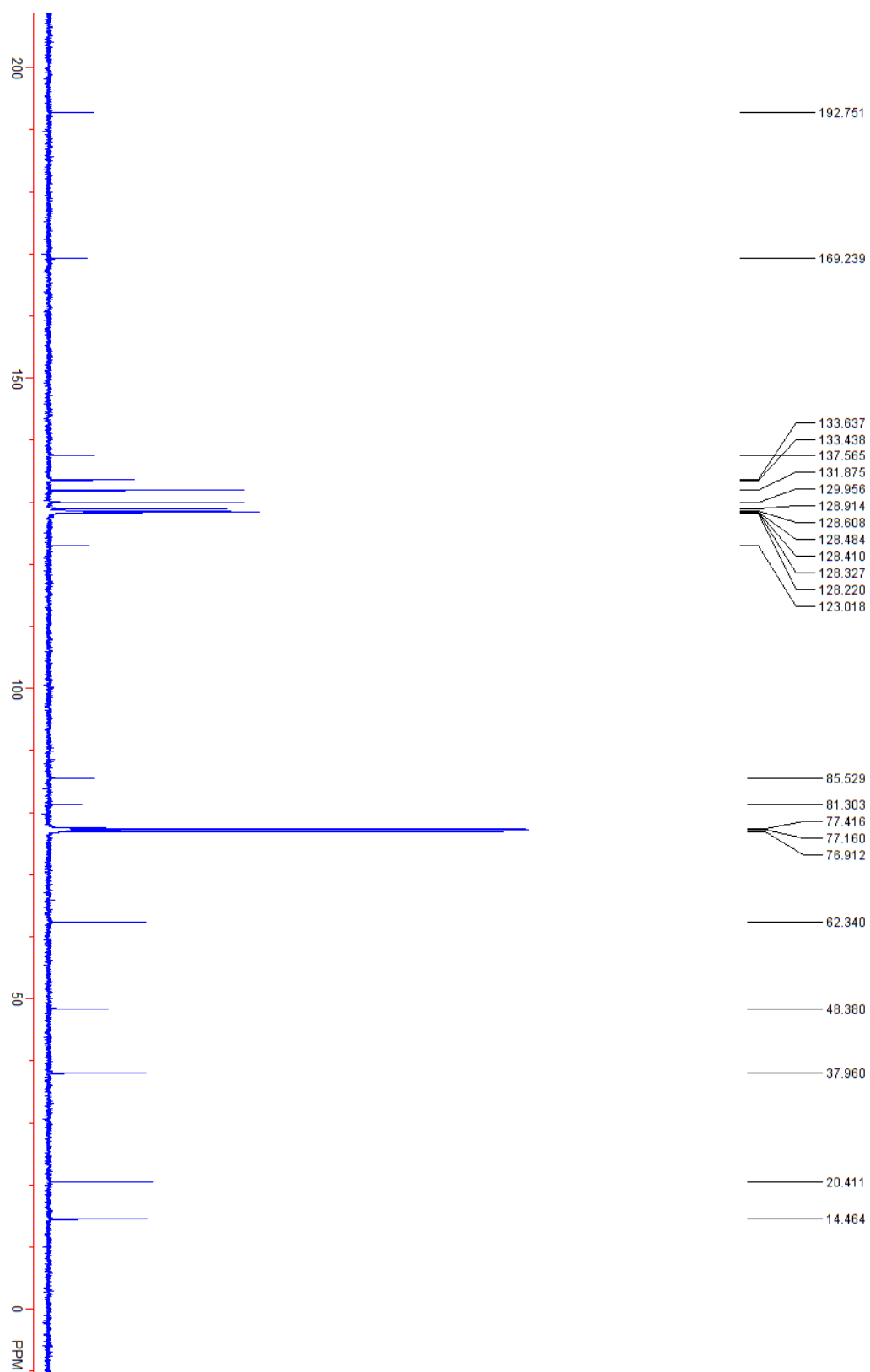
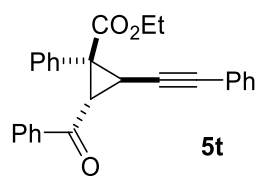


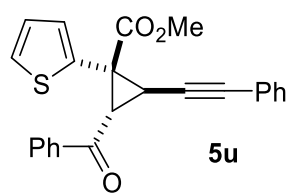


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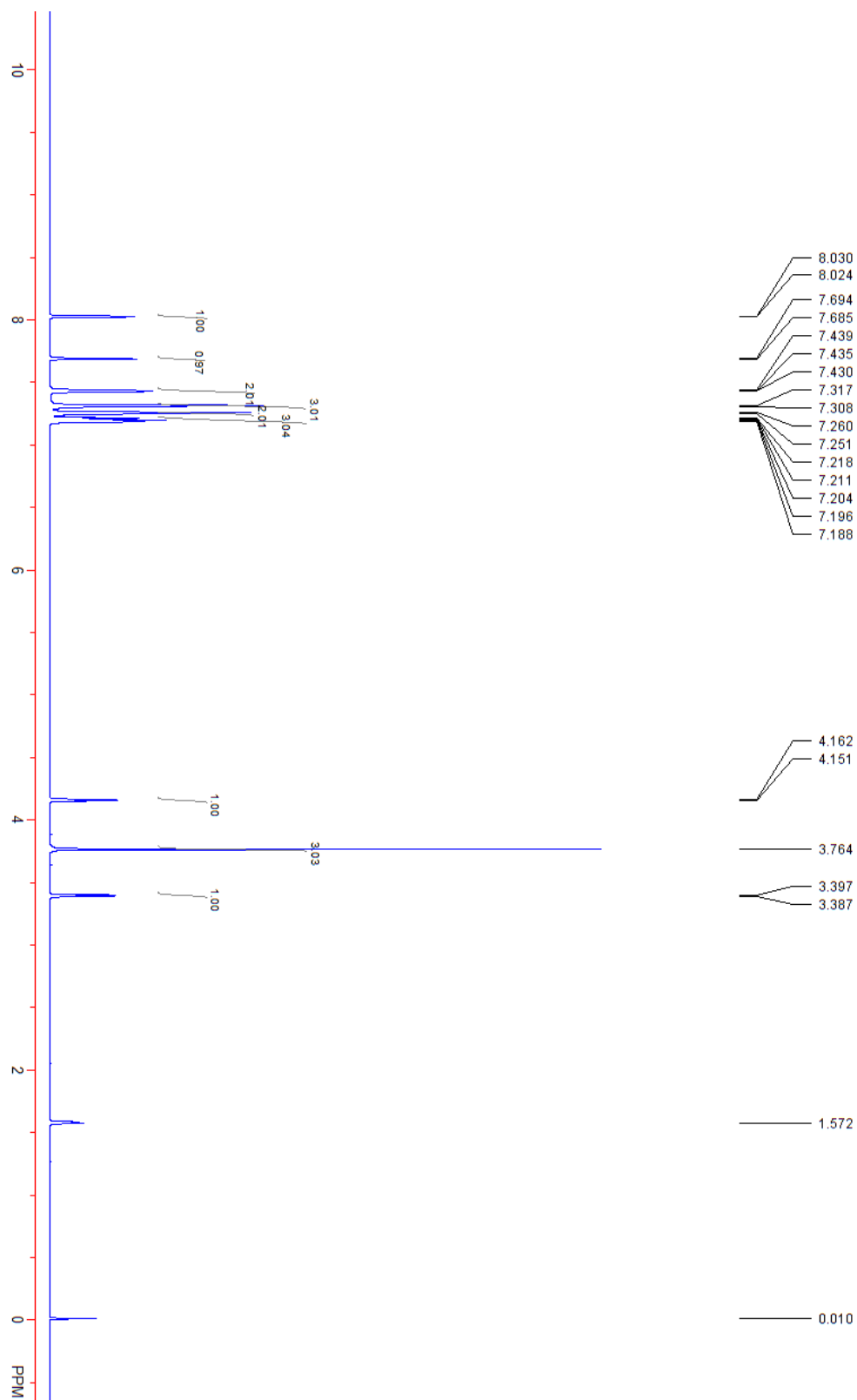


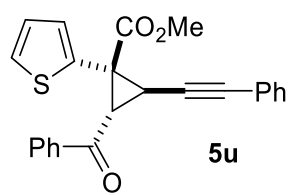
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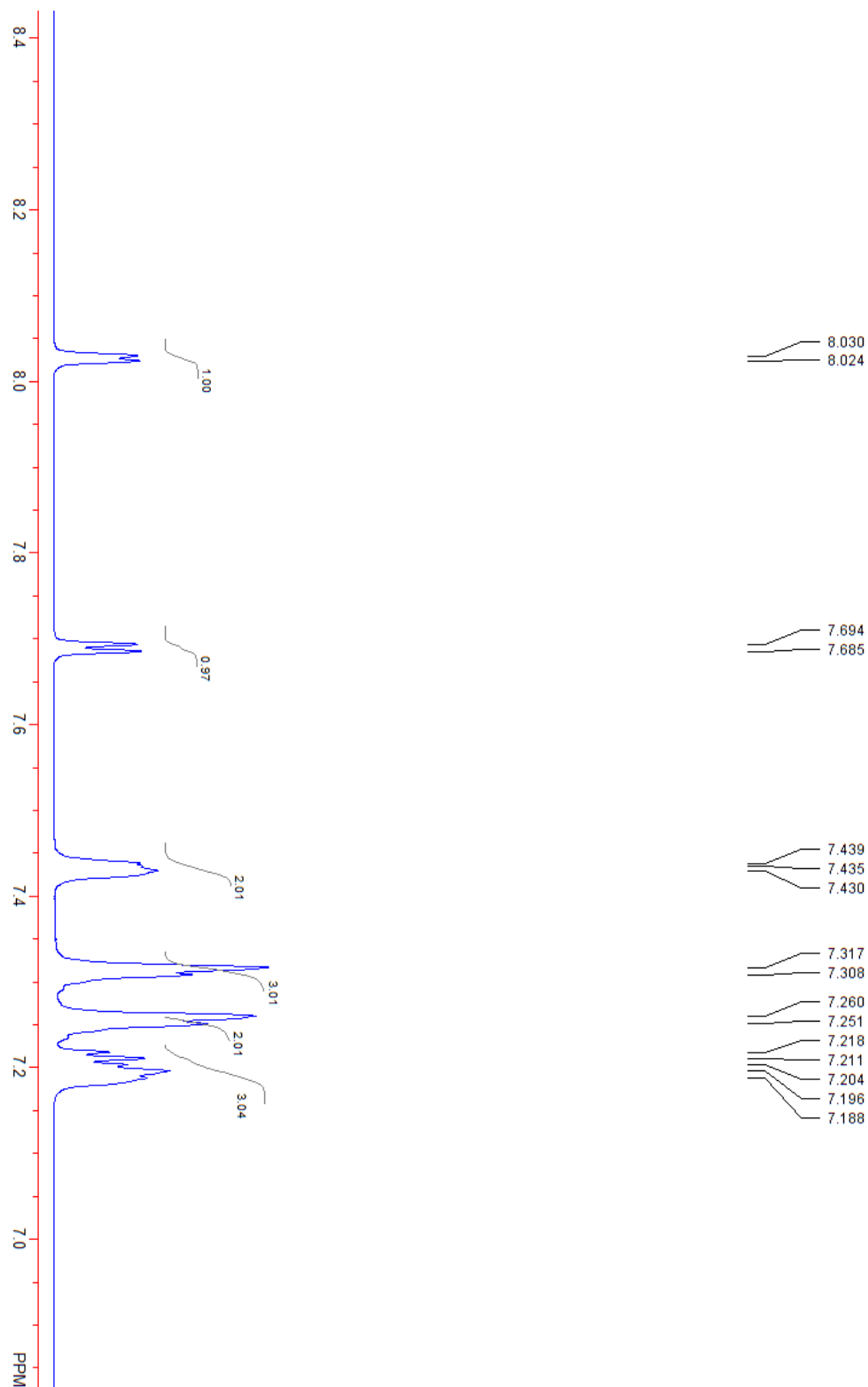


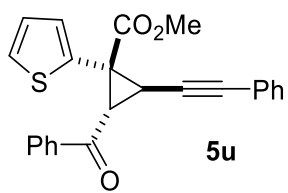
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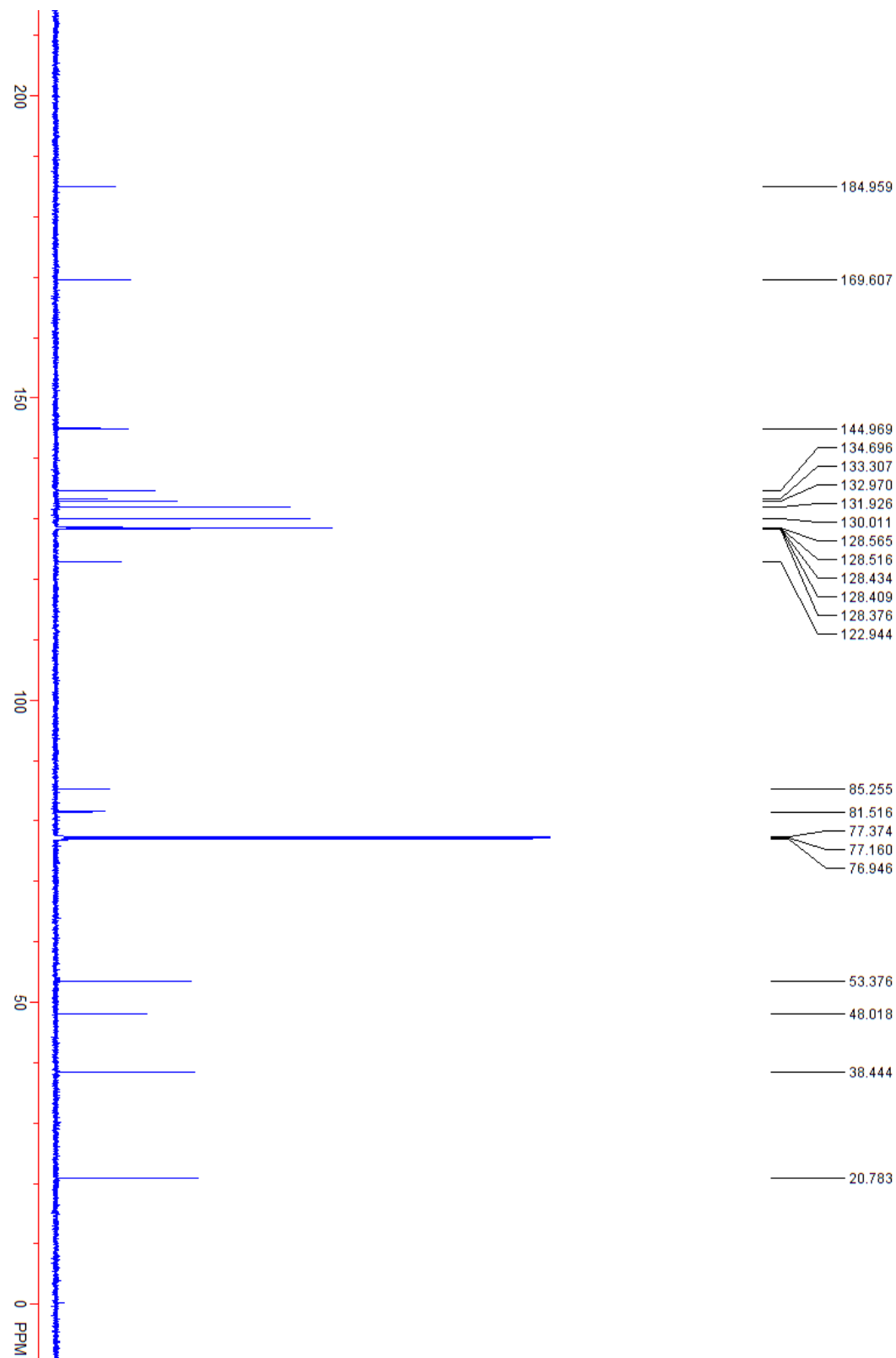


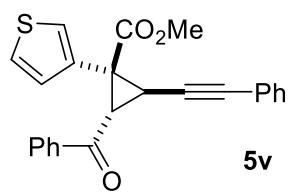
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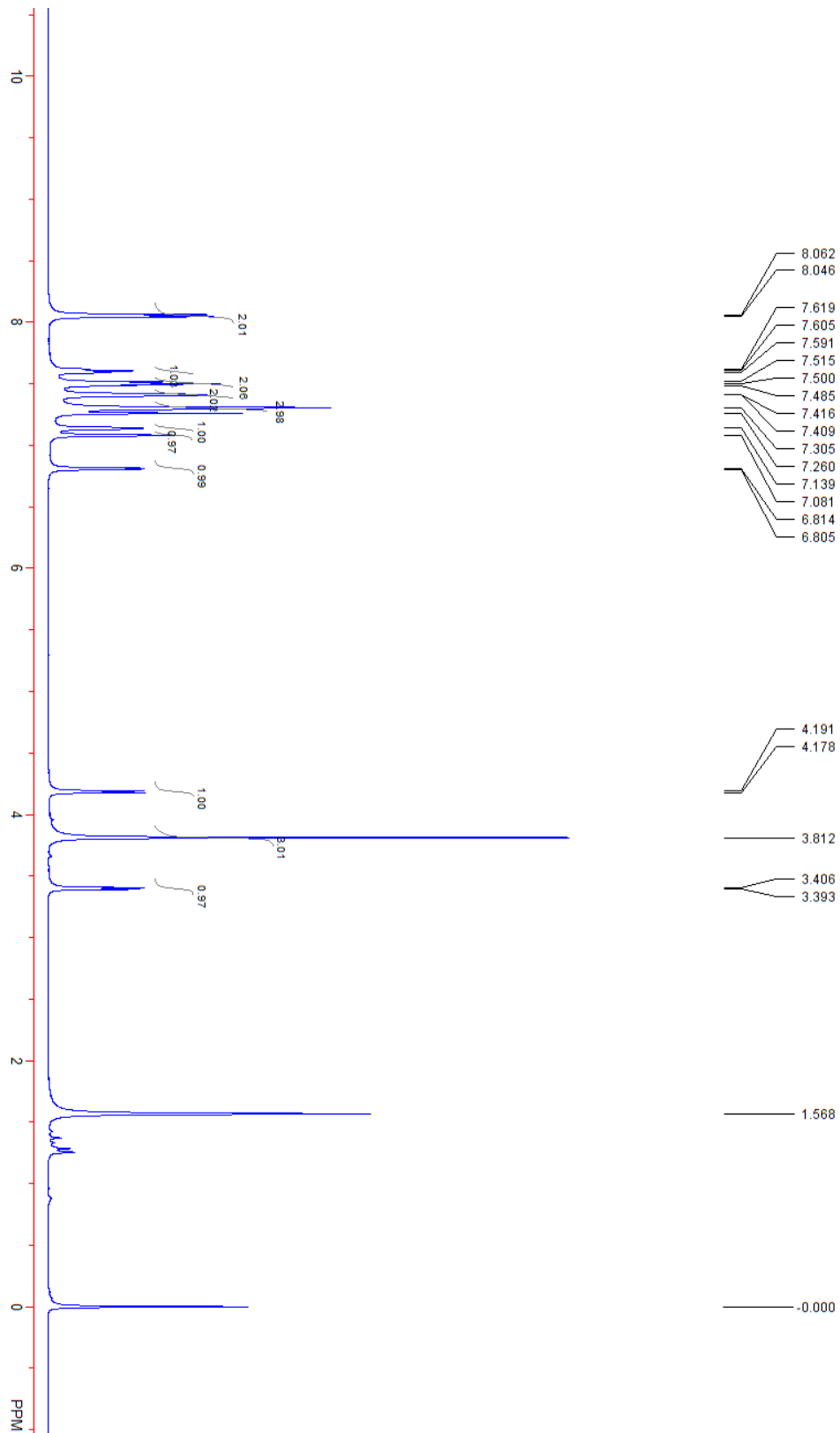


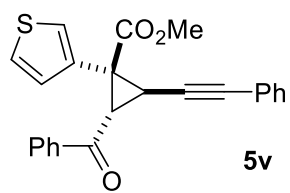
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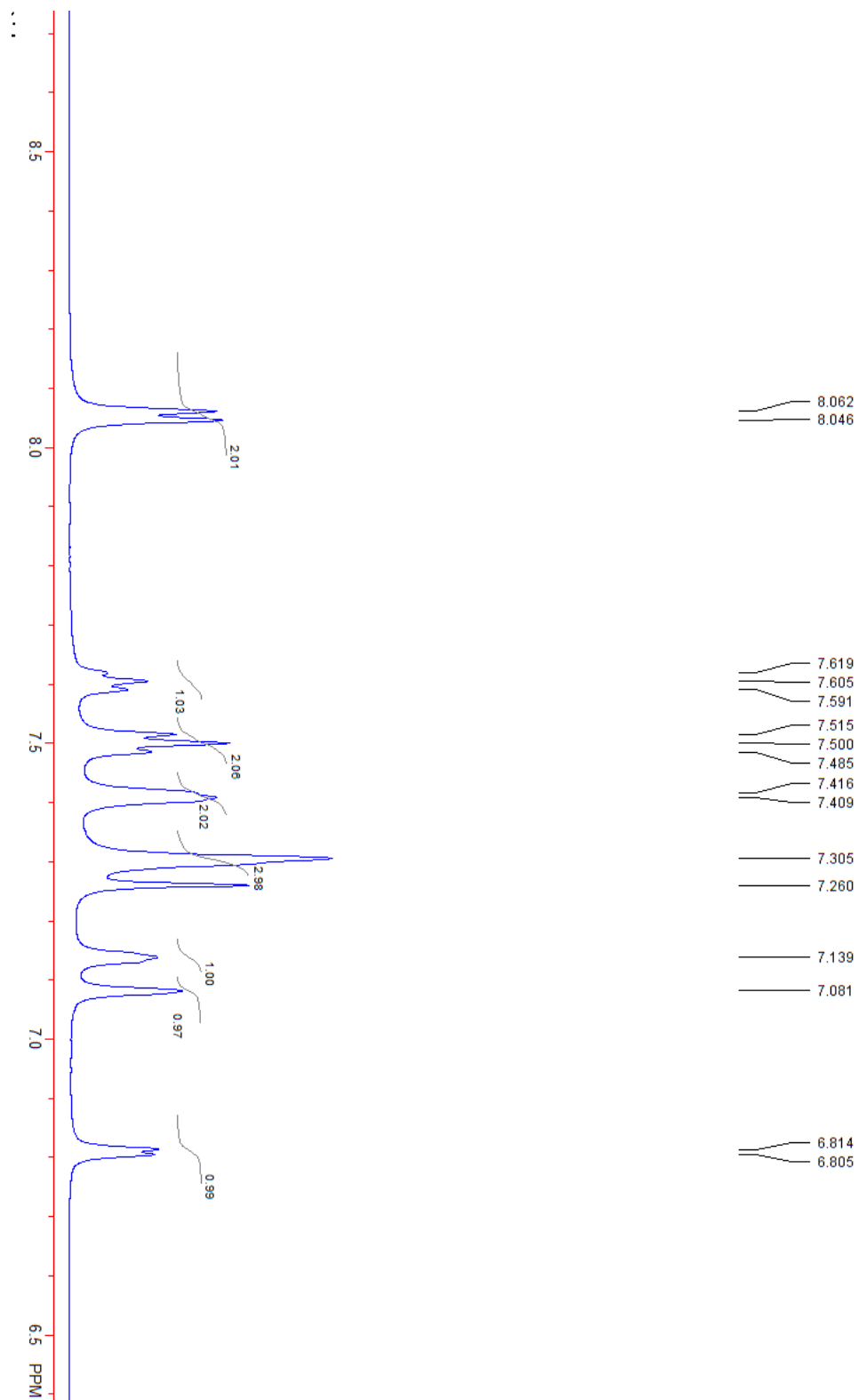


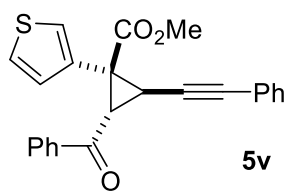
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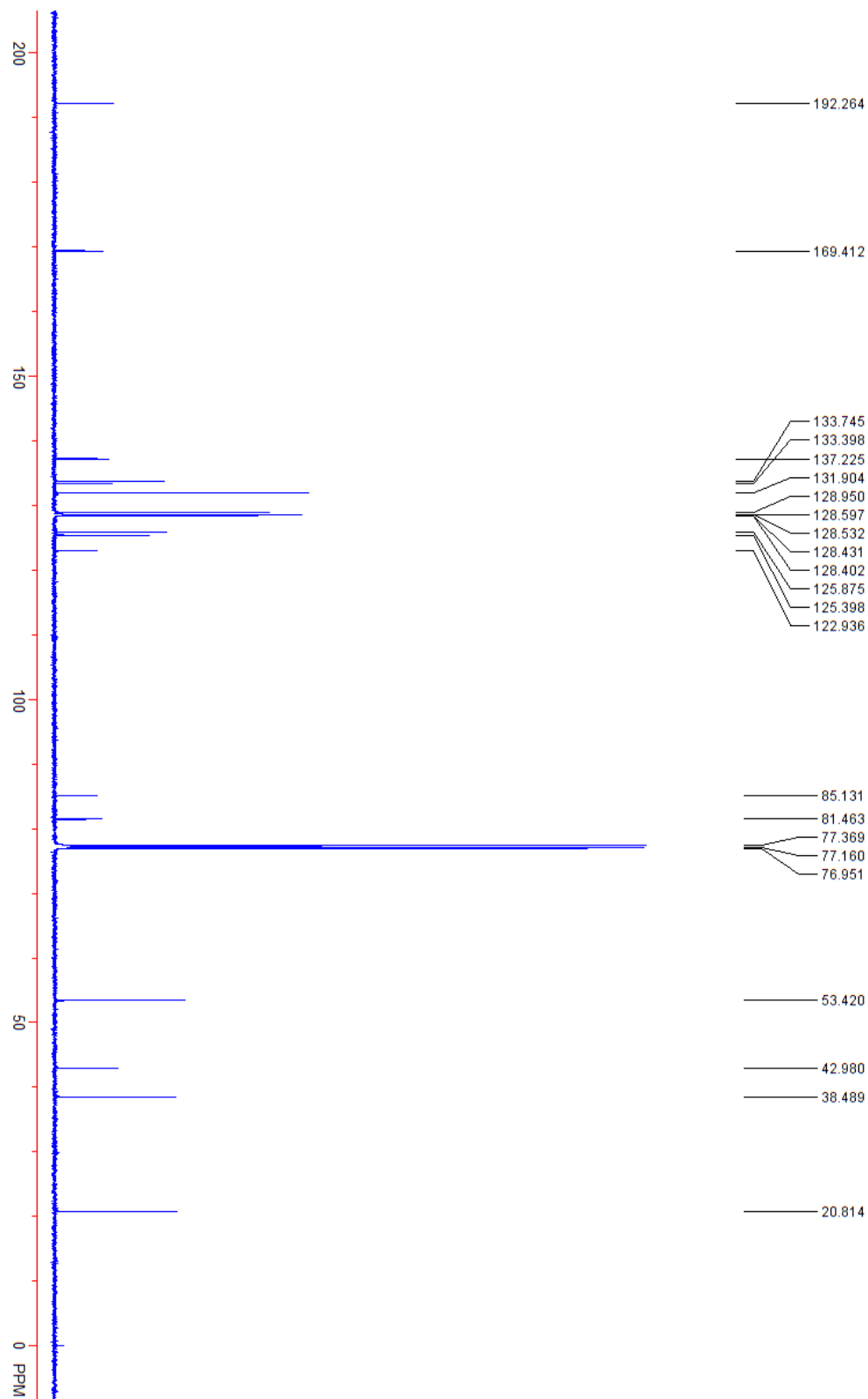


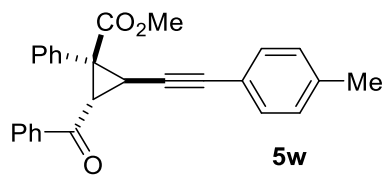
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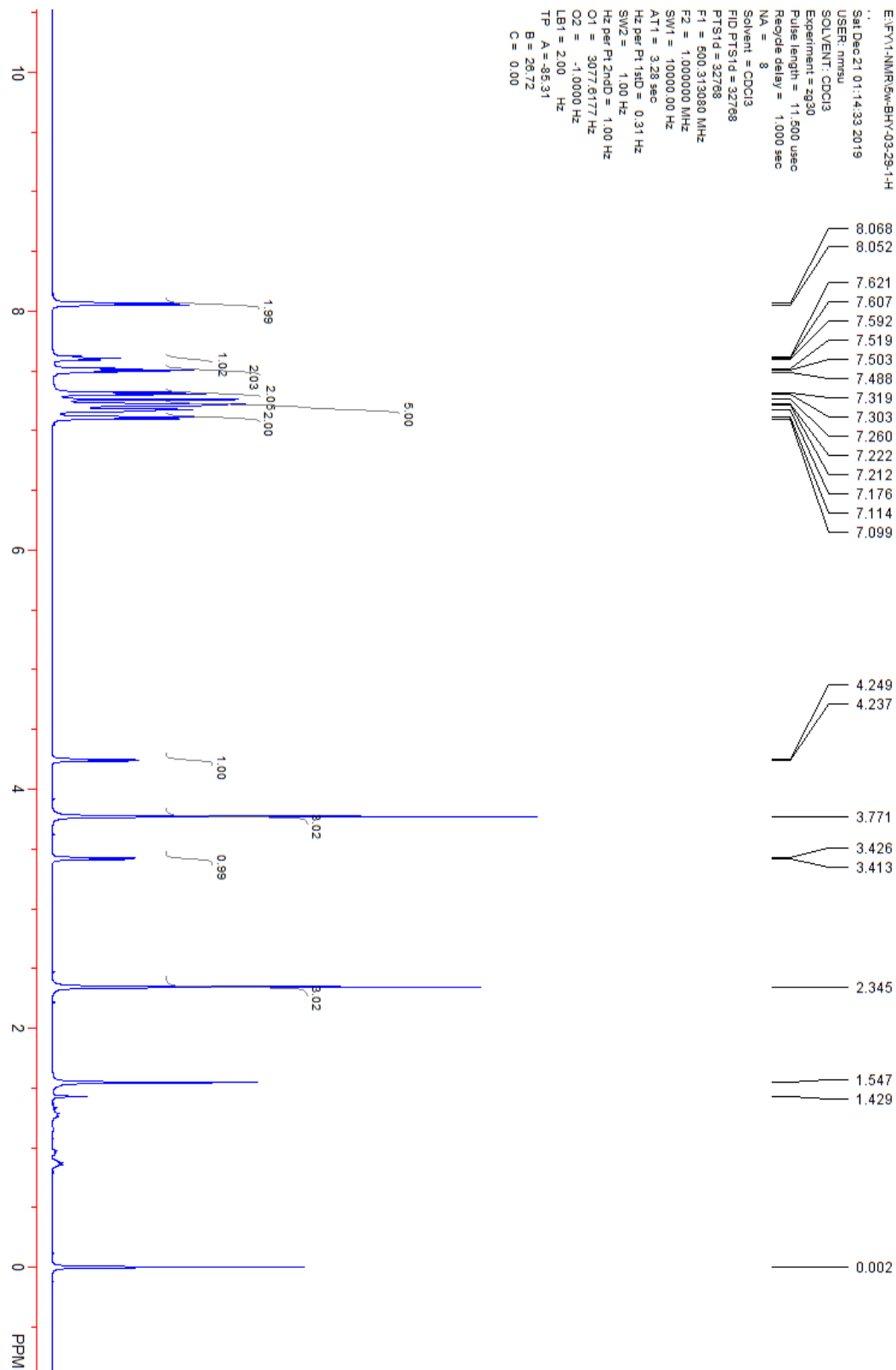


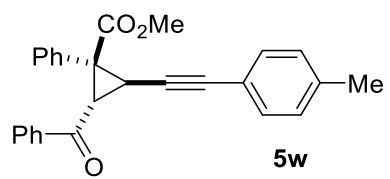
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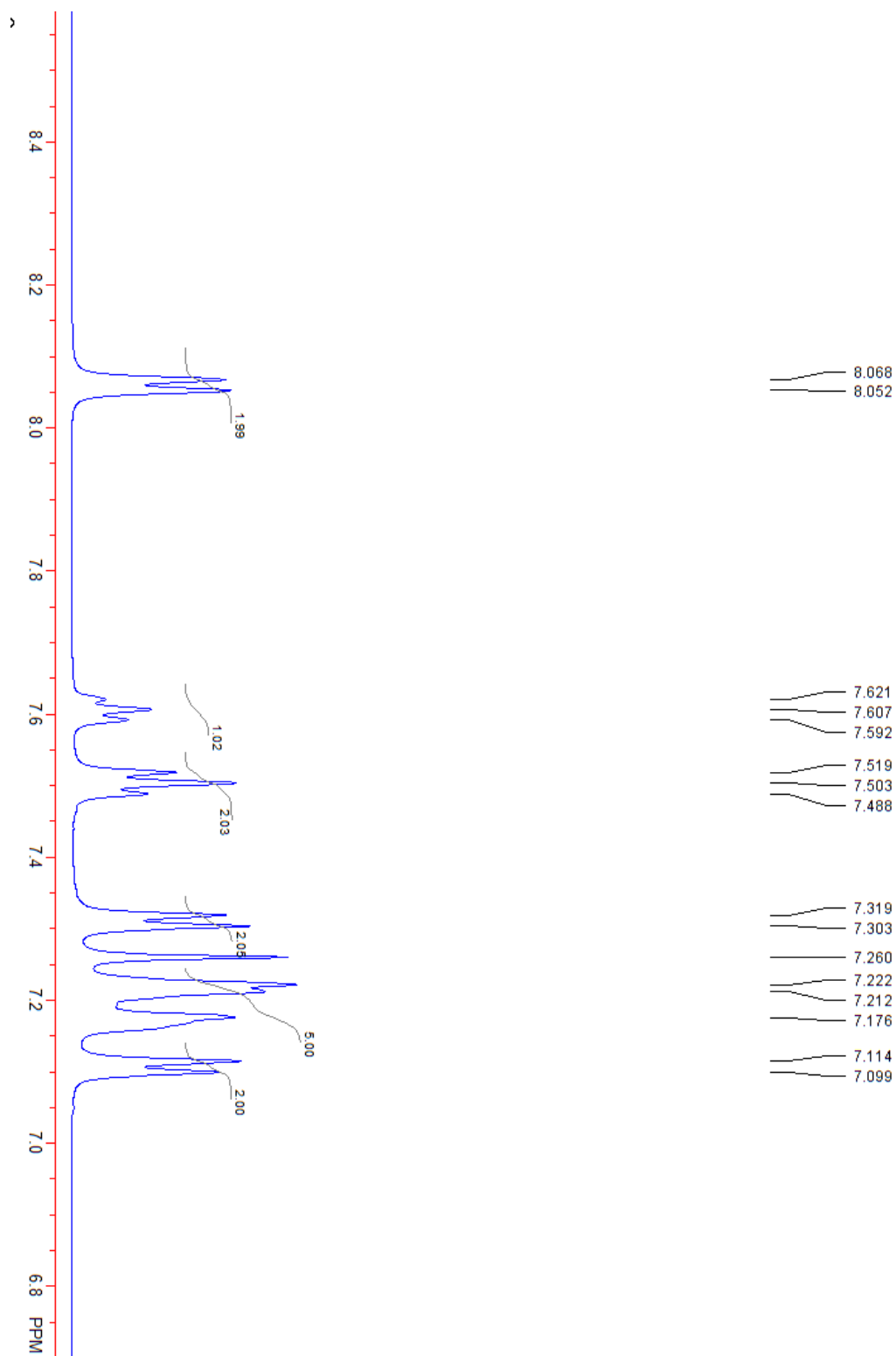


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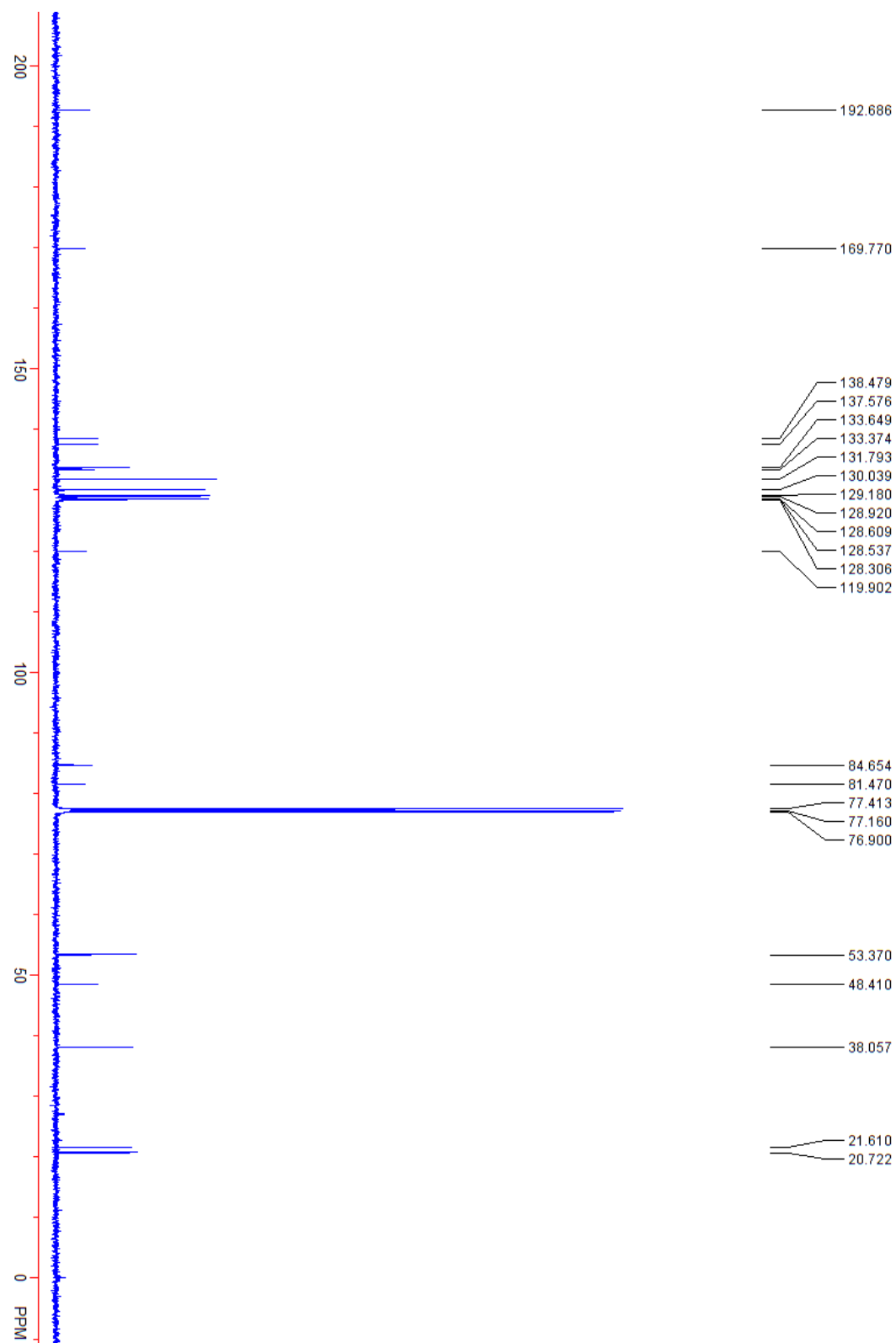
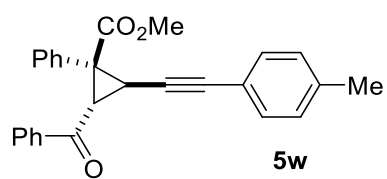




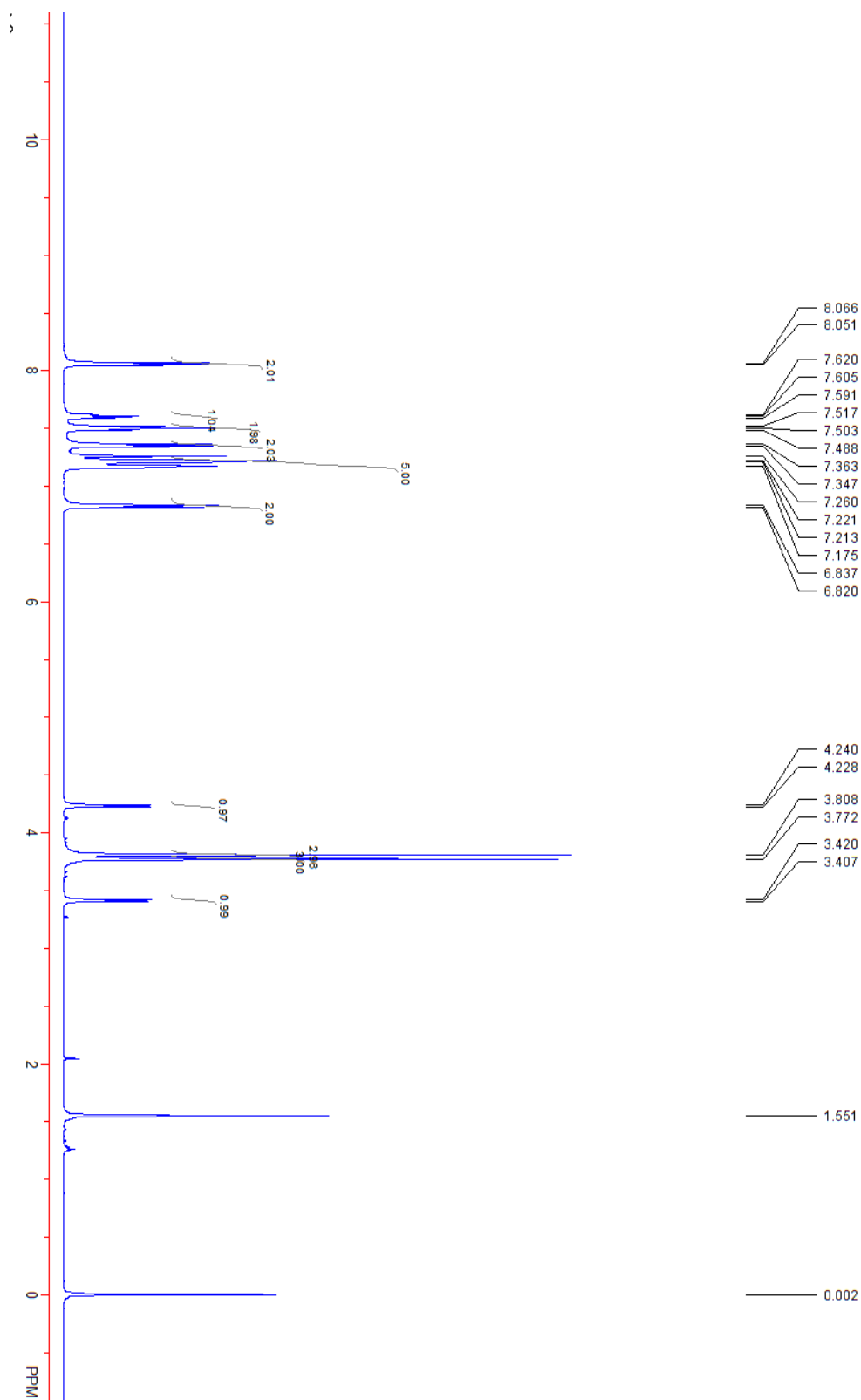
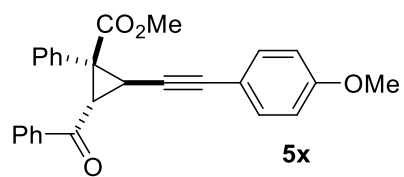
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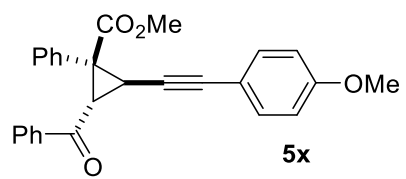


$^{13}\text{C}\{^1\text{H}\}$ NMR:

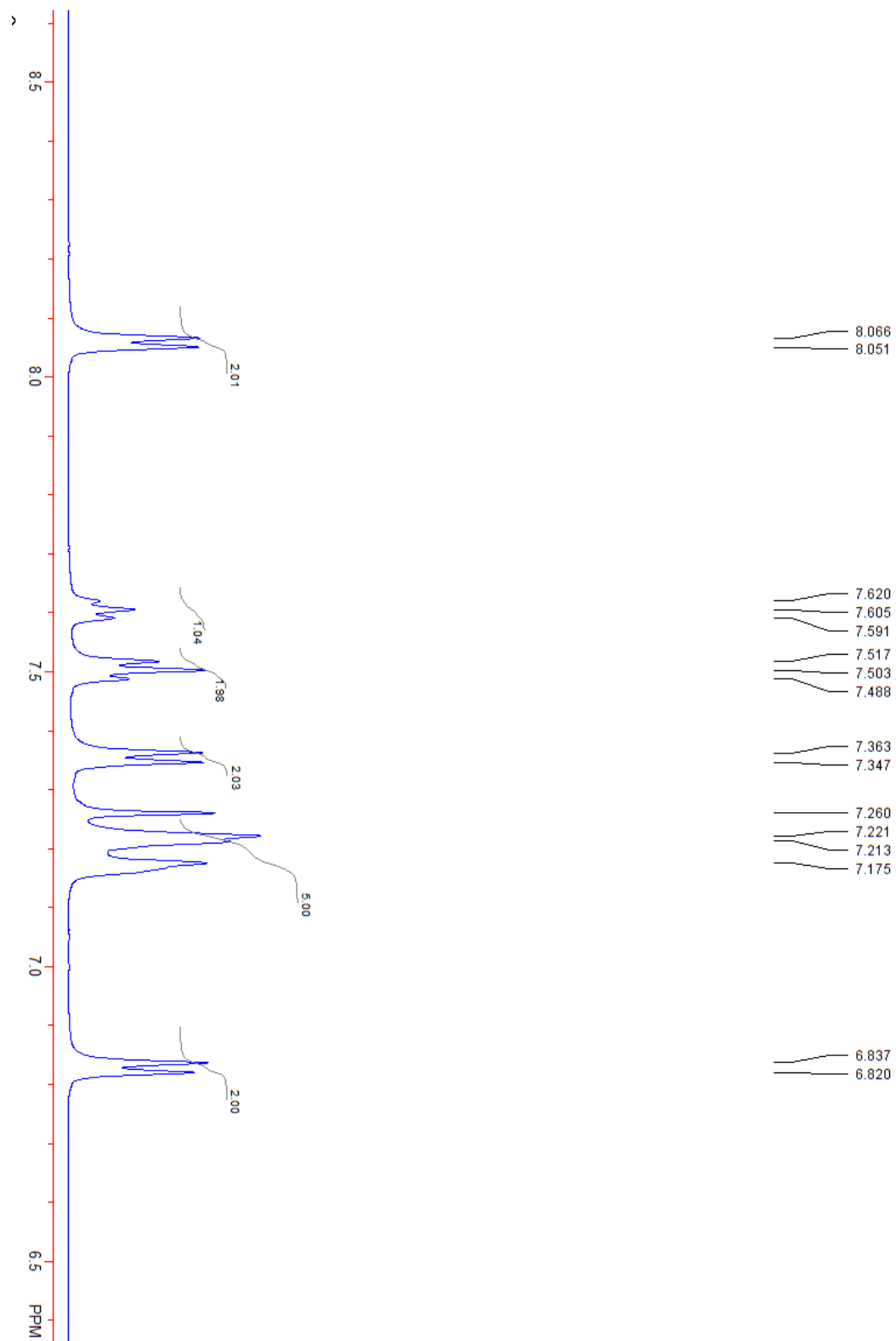


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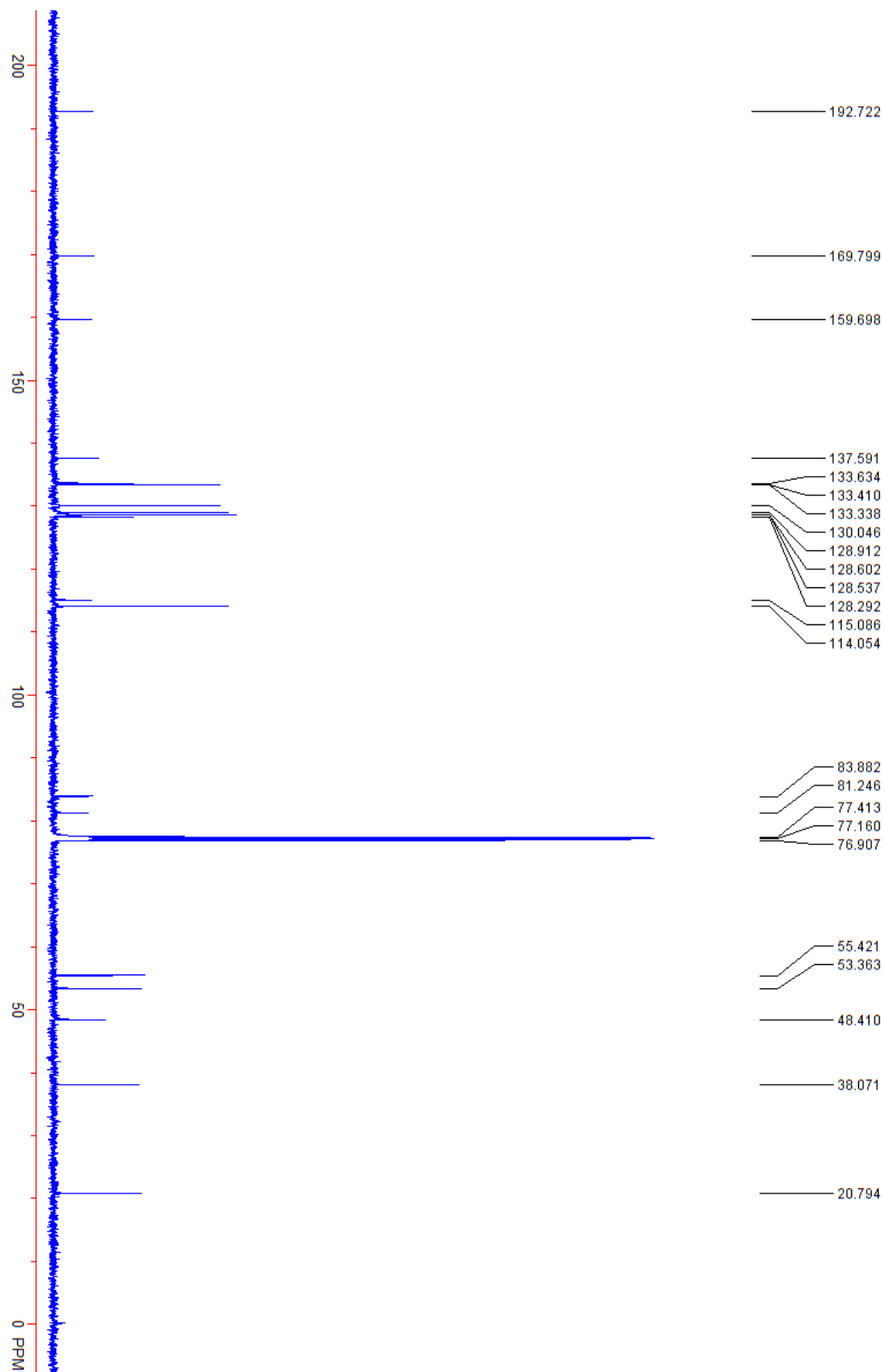
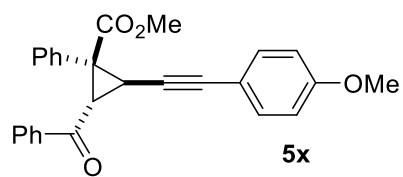




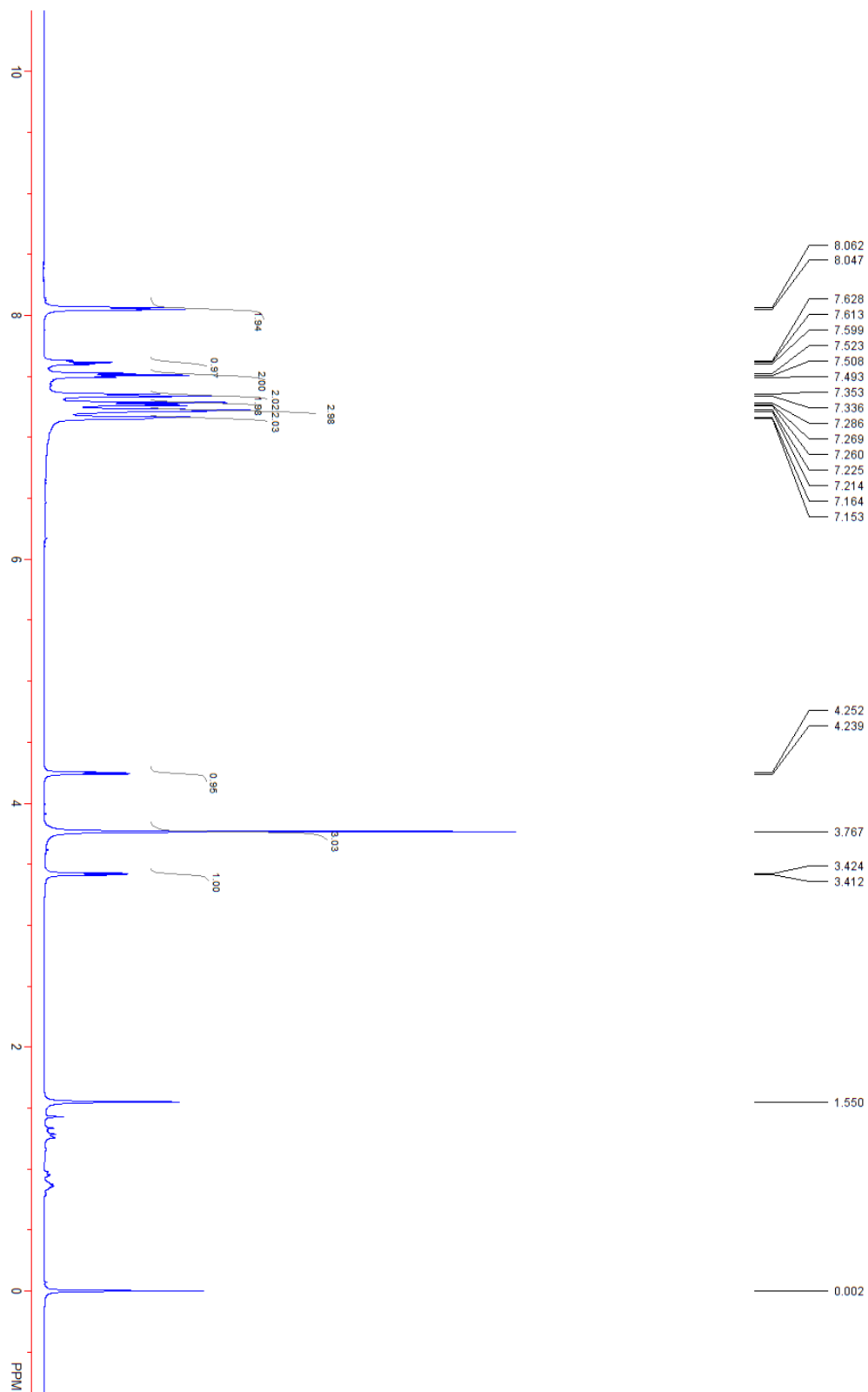
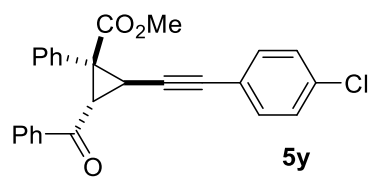
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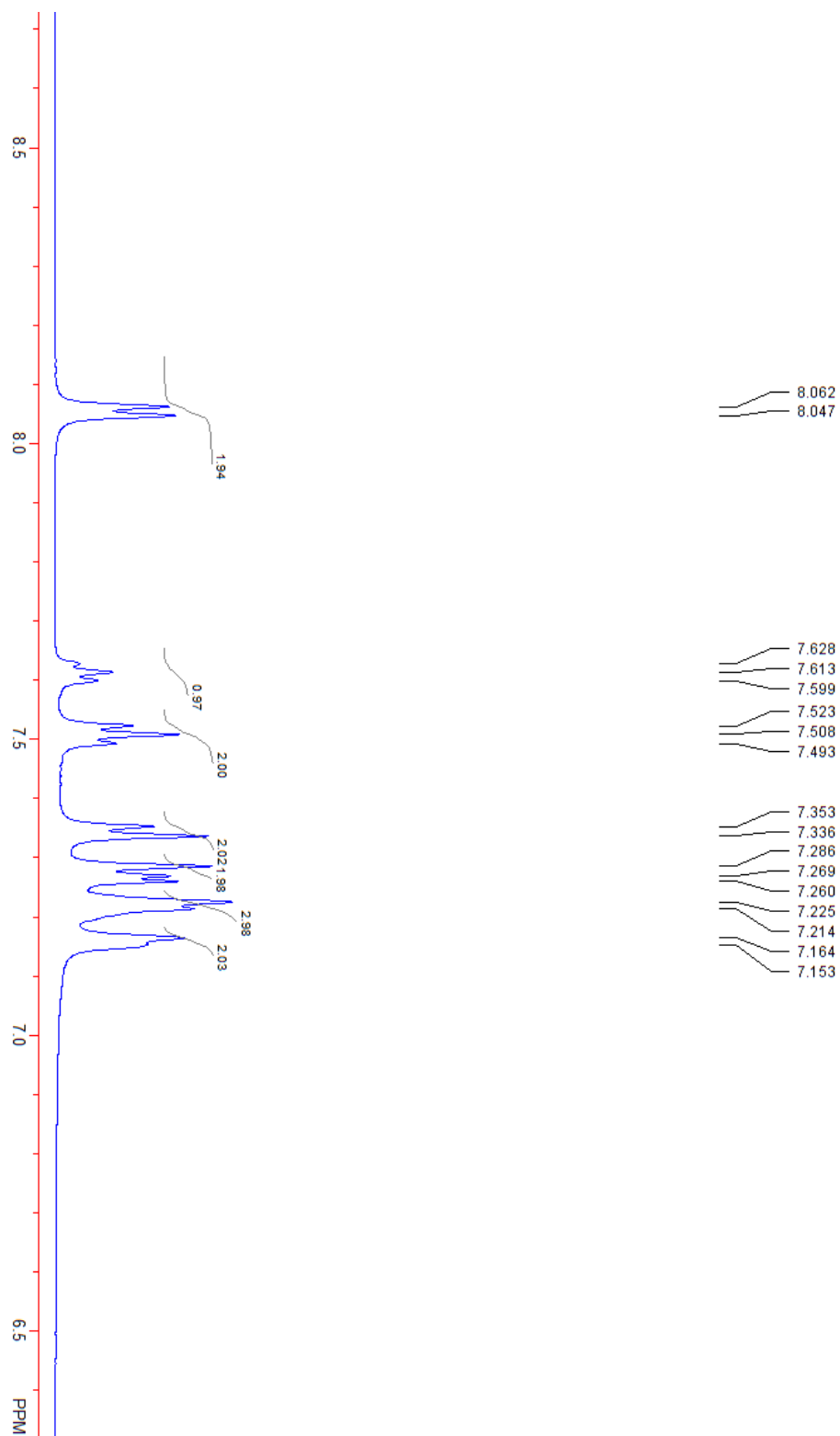
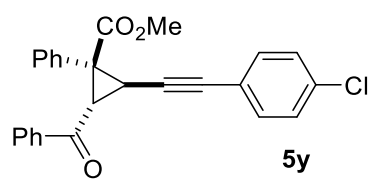
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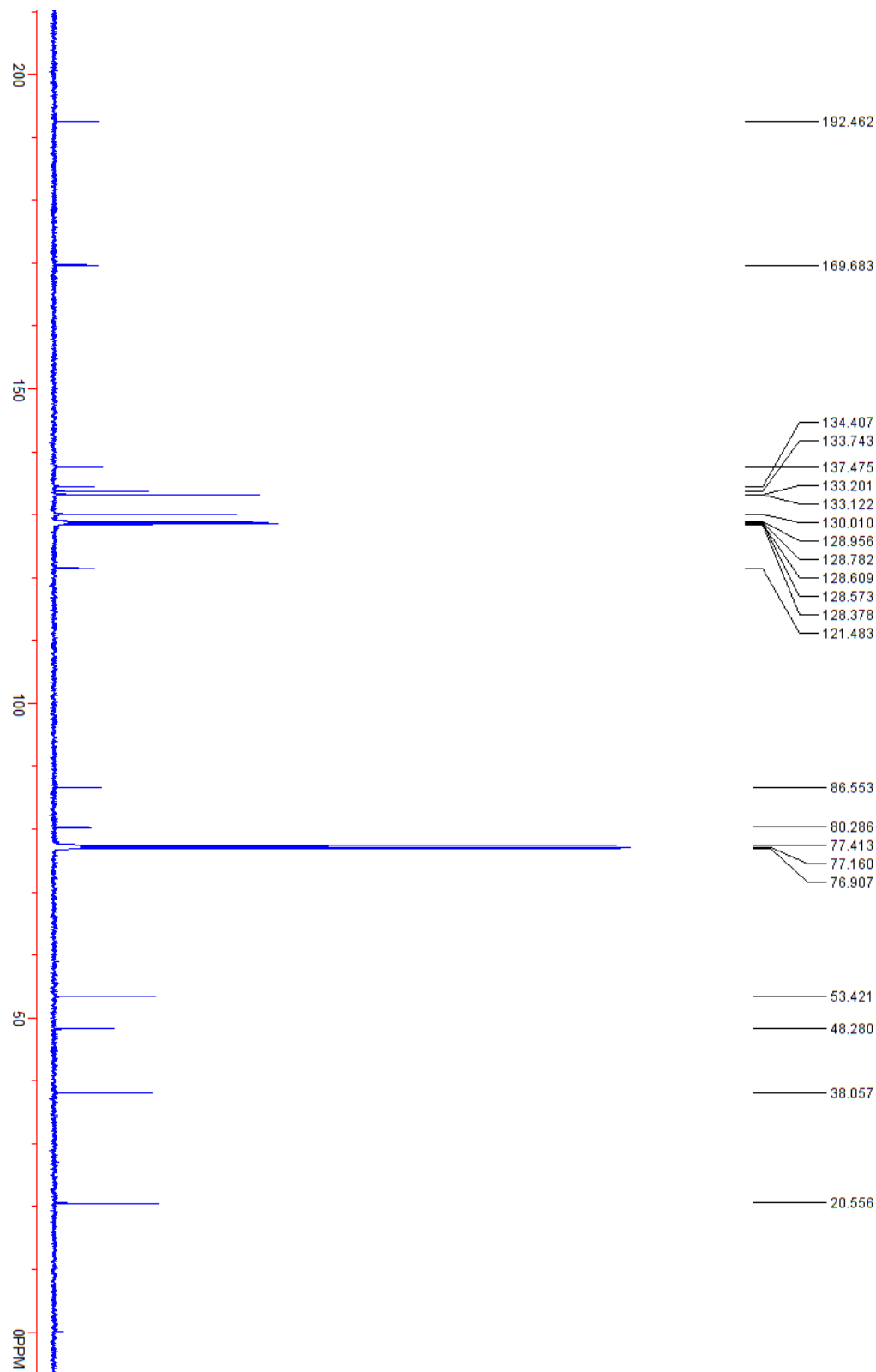
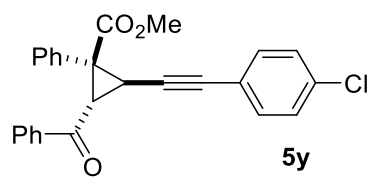
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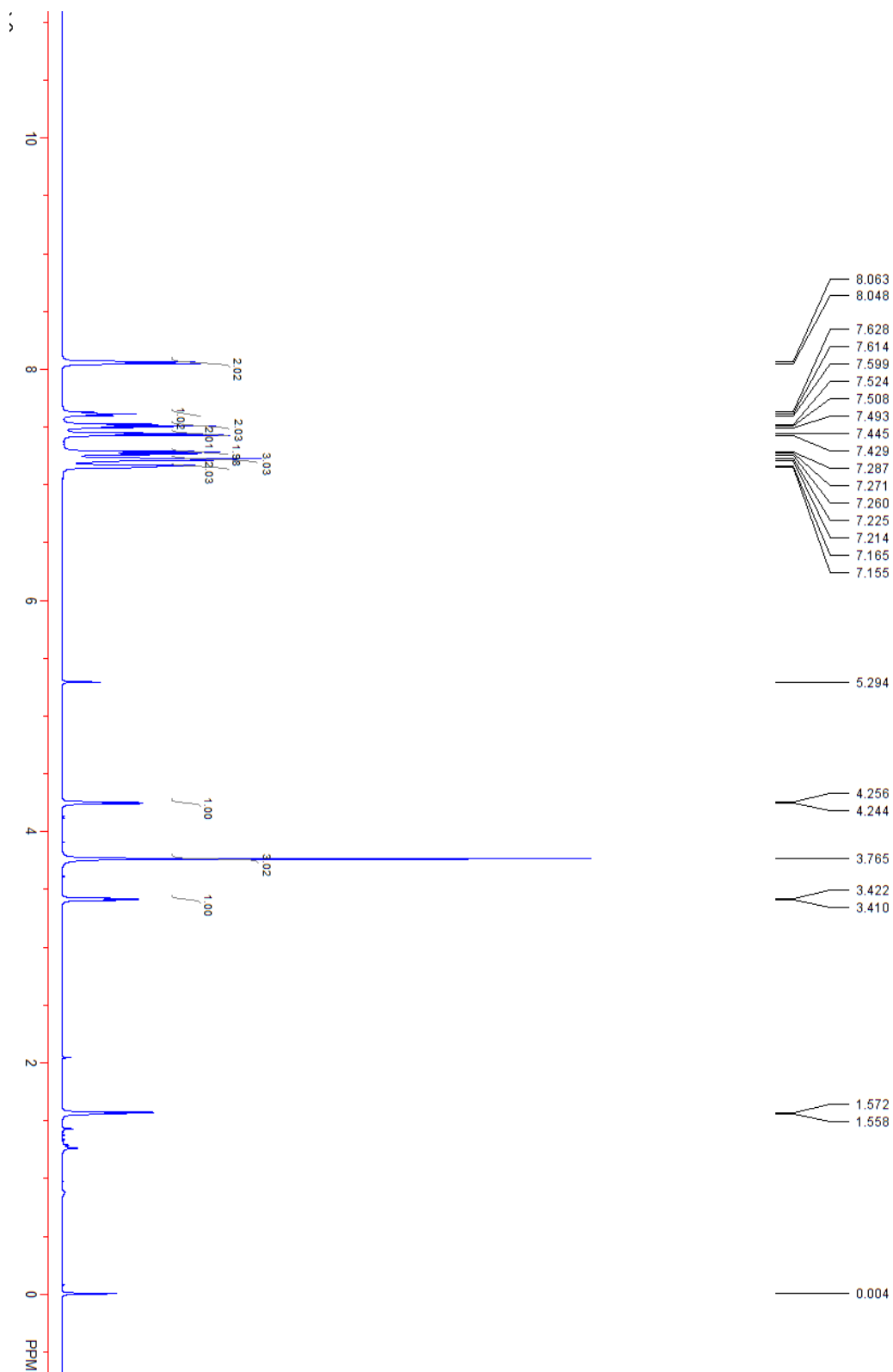
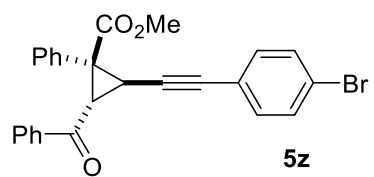
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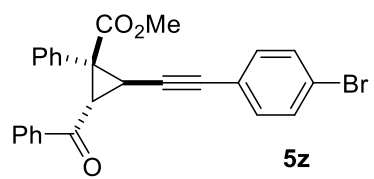


$^{13}\text{C}\{^1\text{H}\}$ NMR:

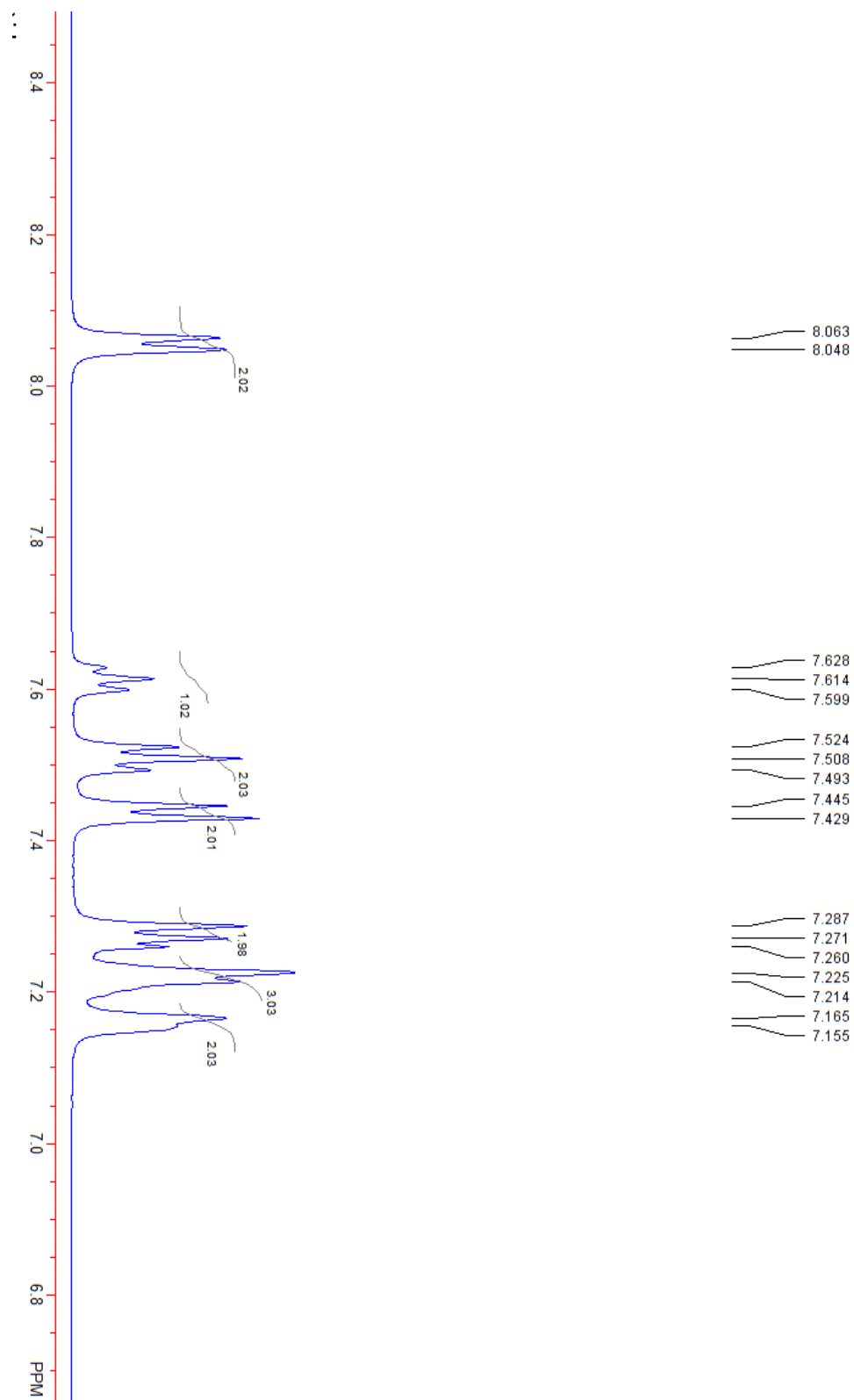


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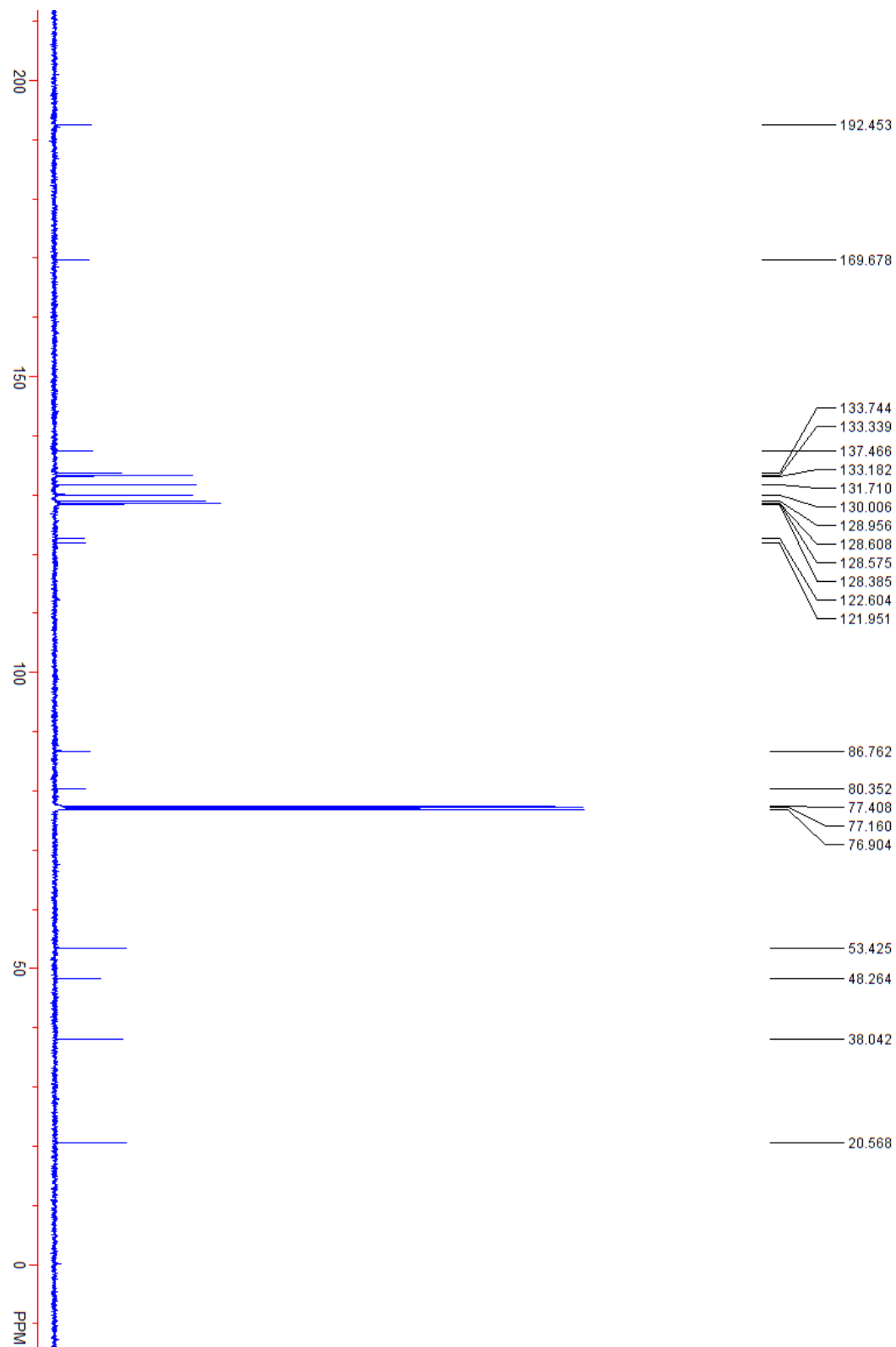
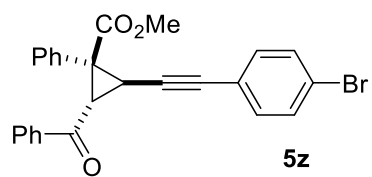




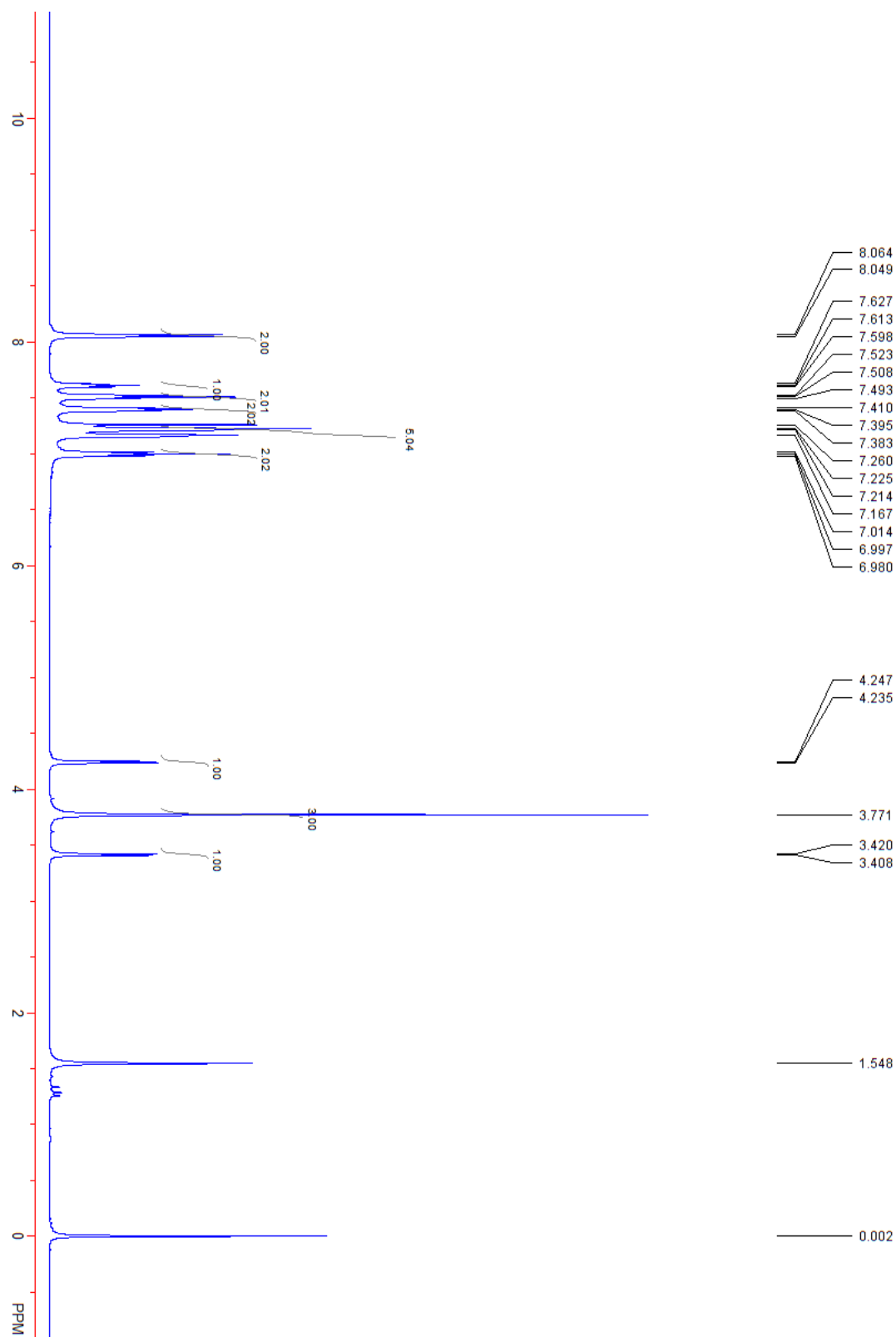
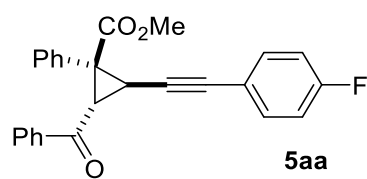
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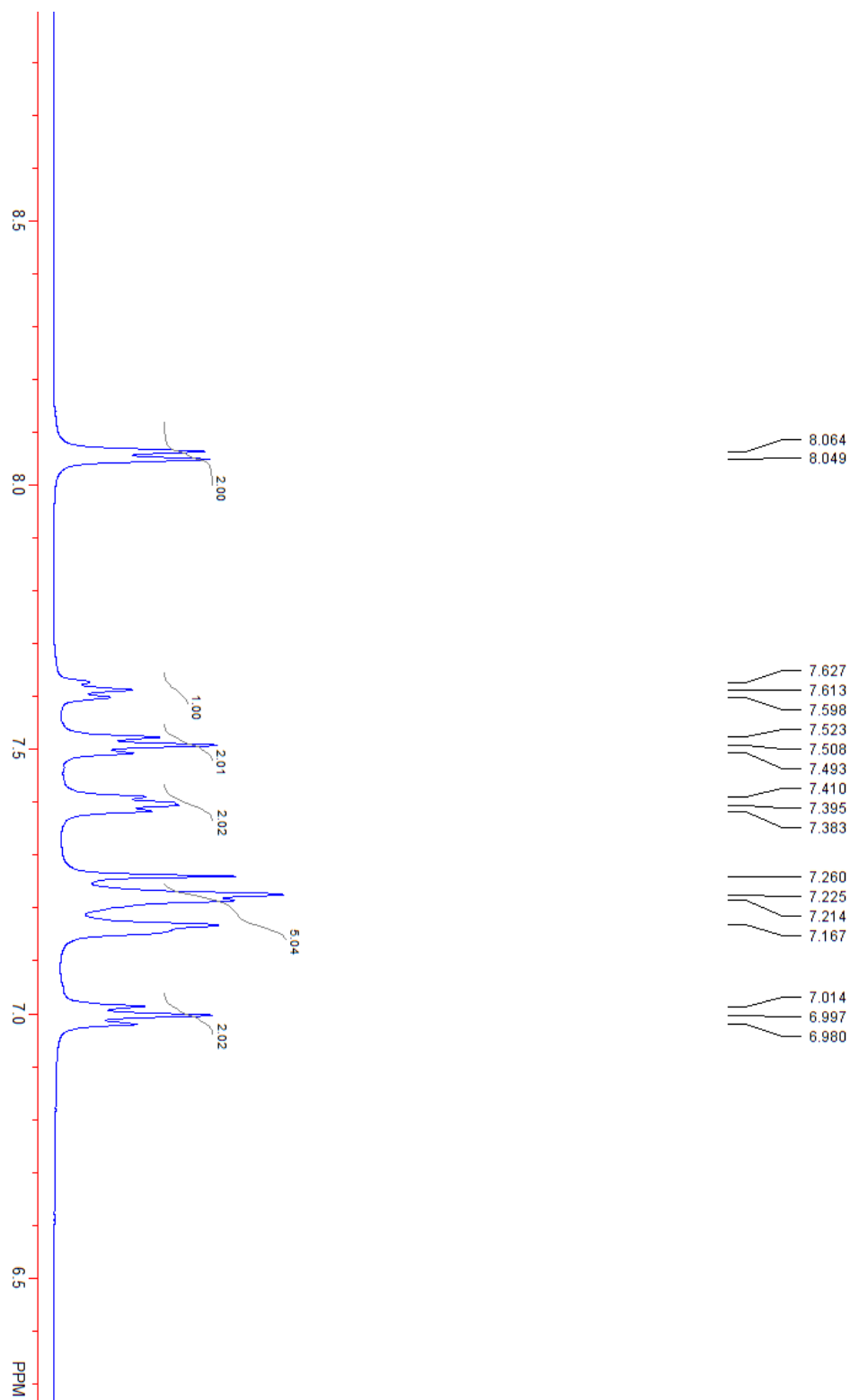
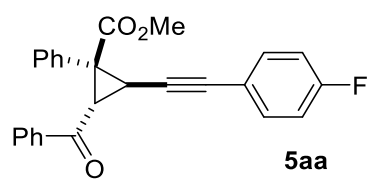
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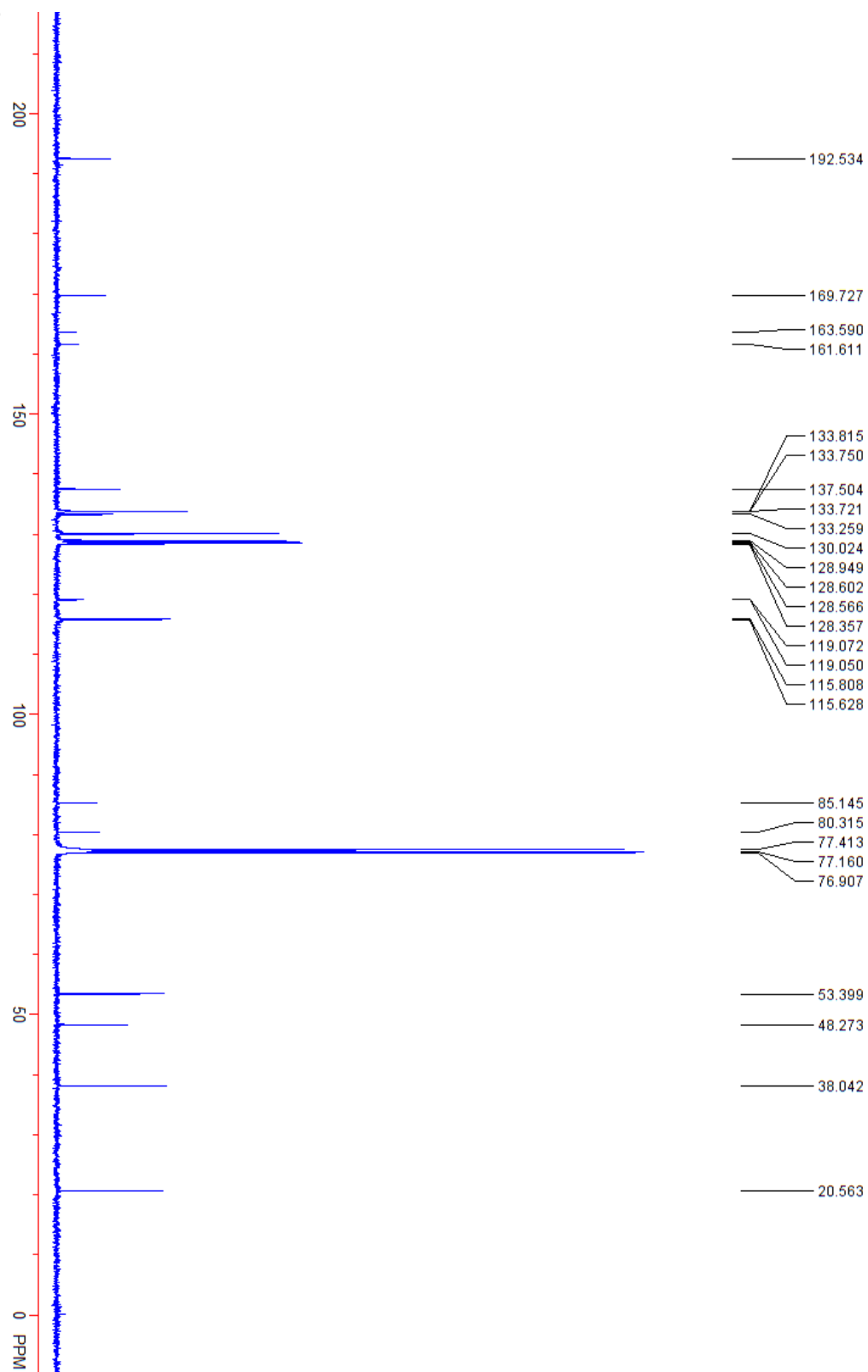
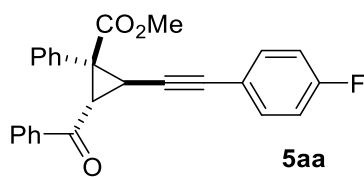
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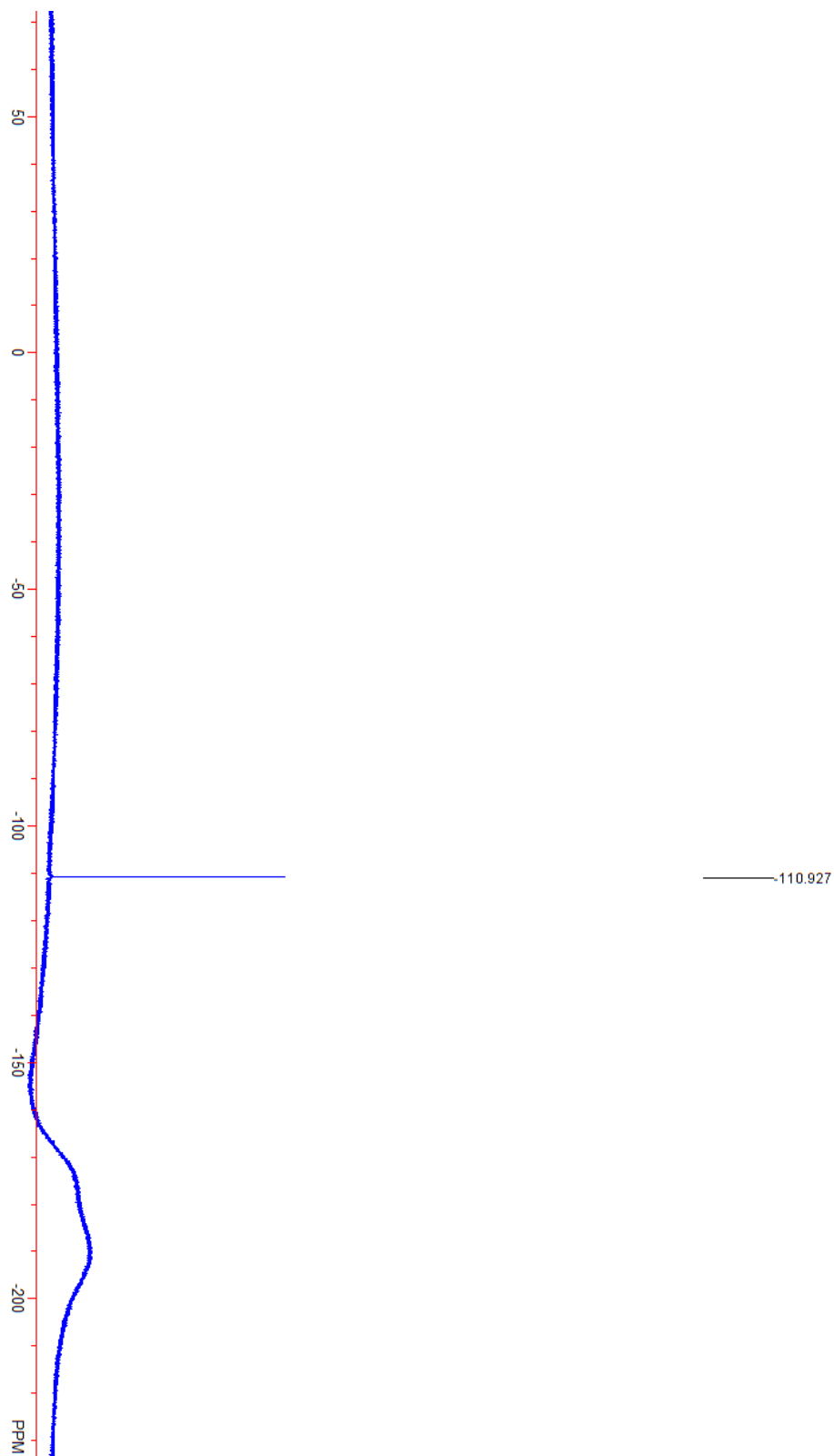
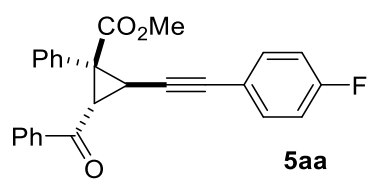
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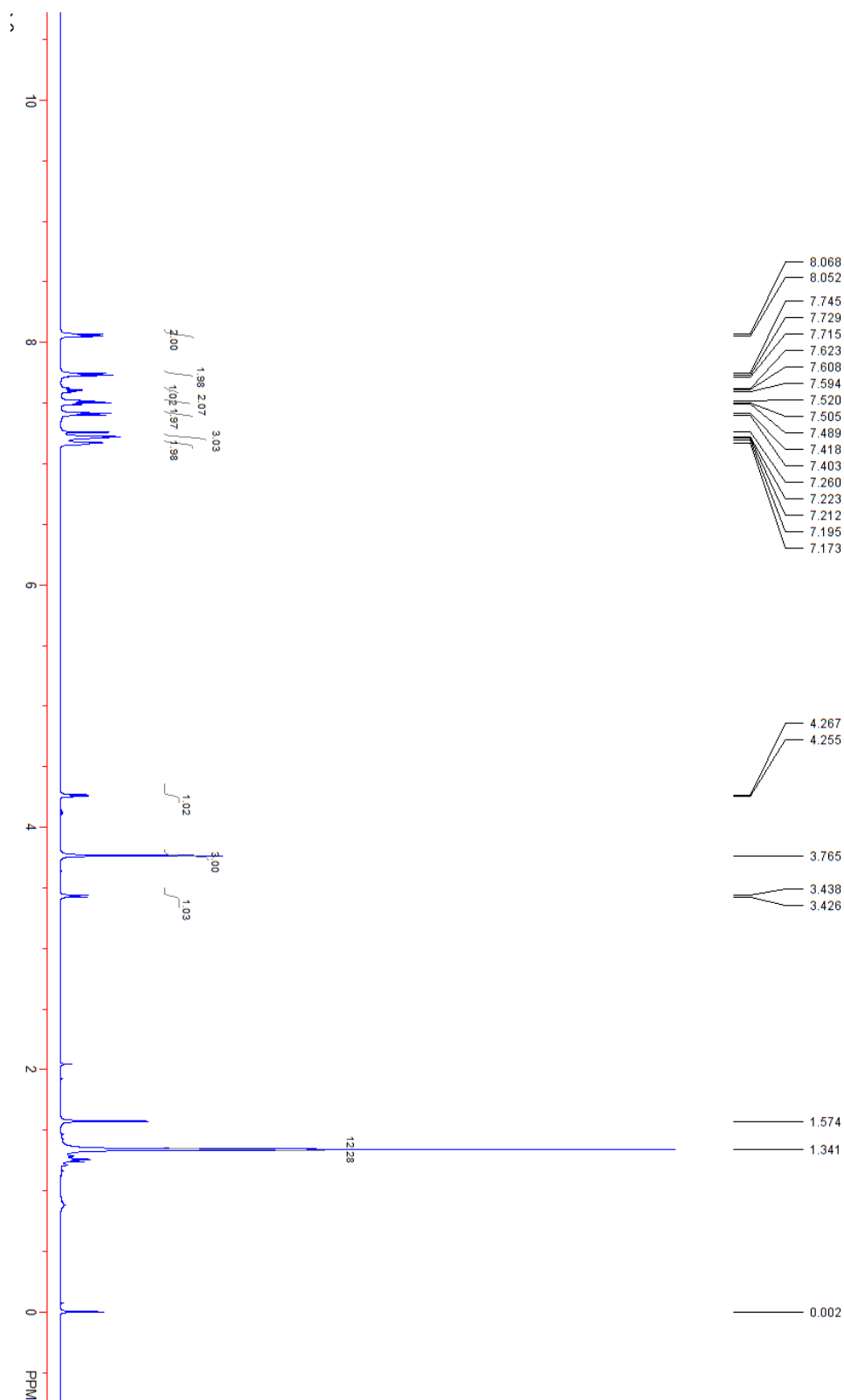
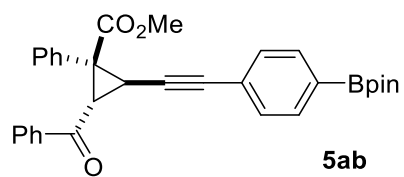
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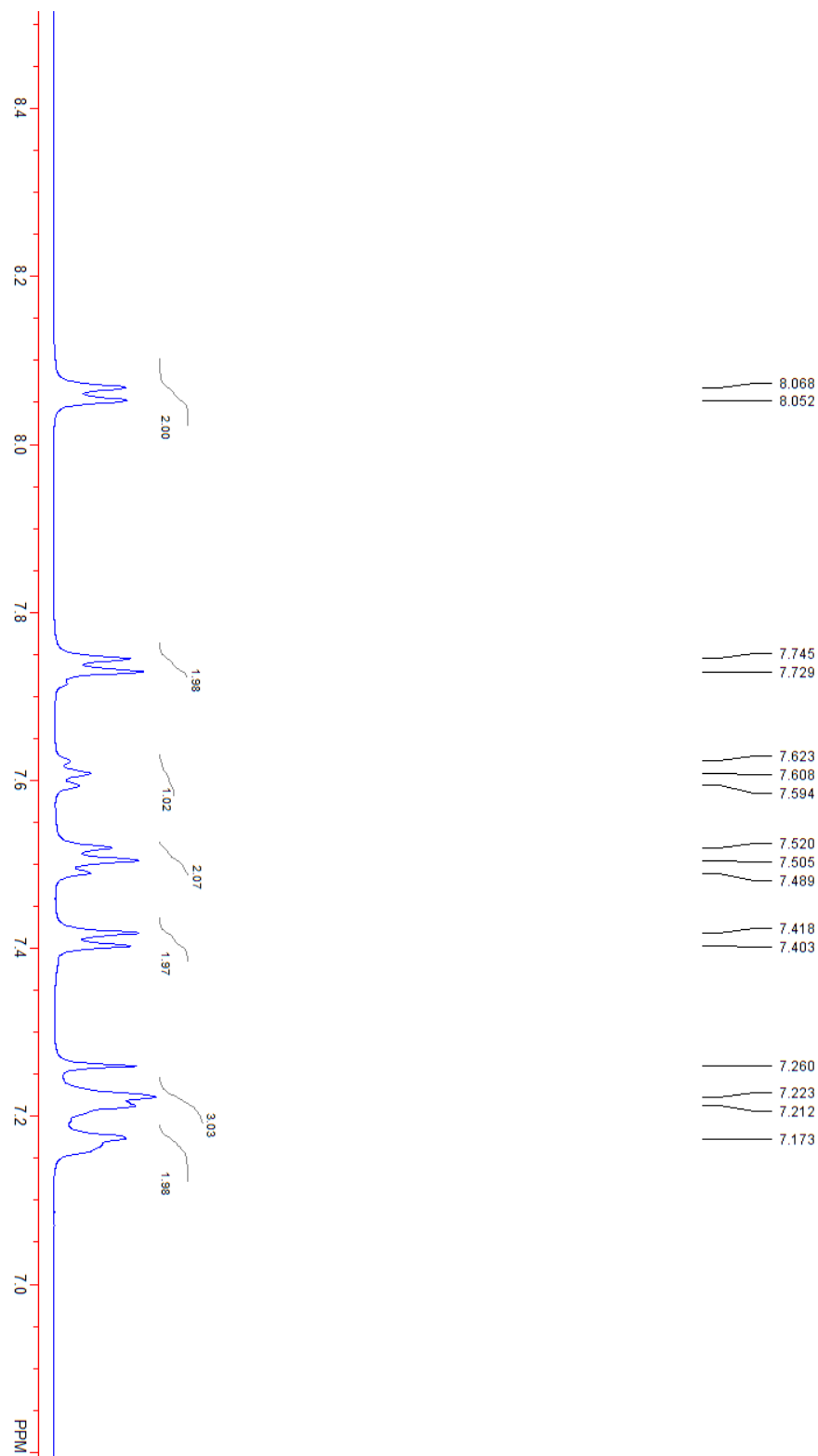
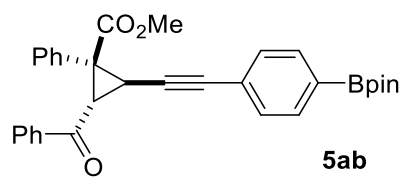
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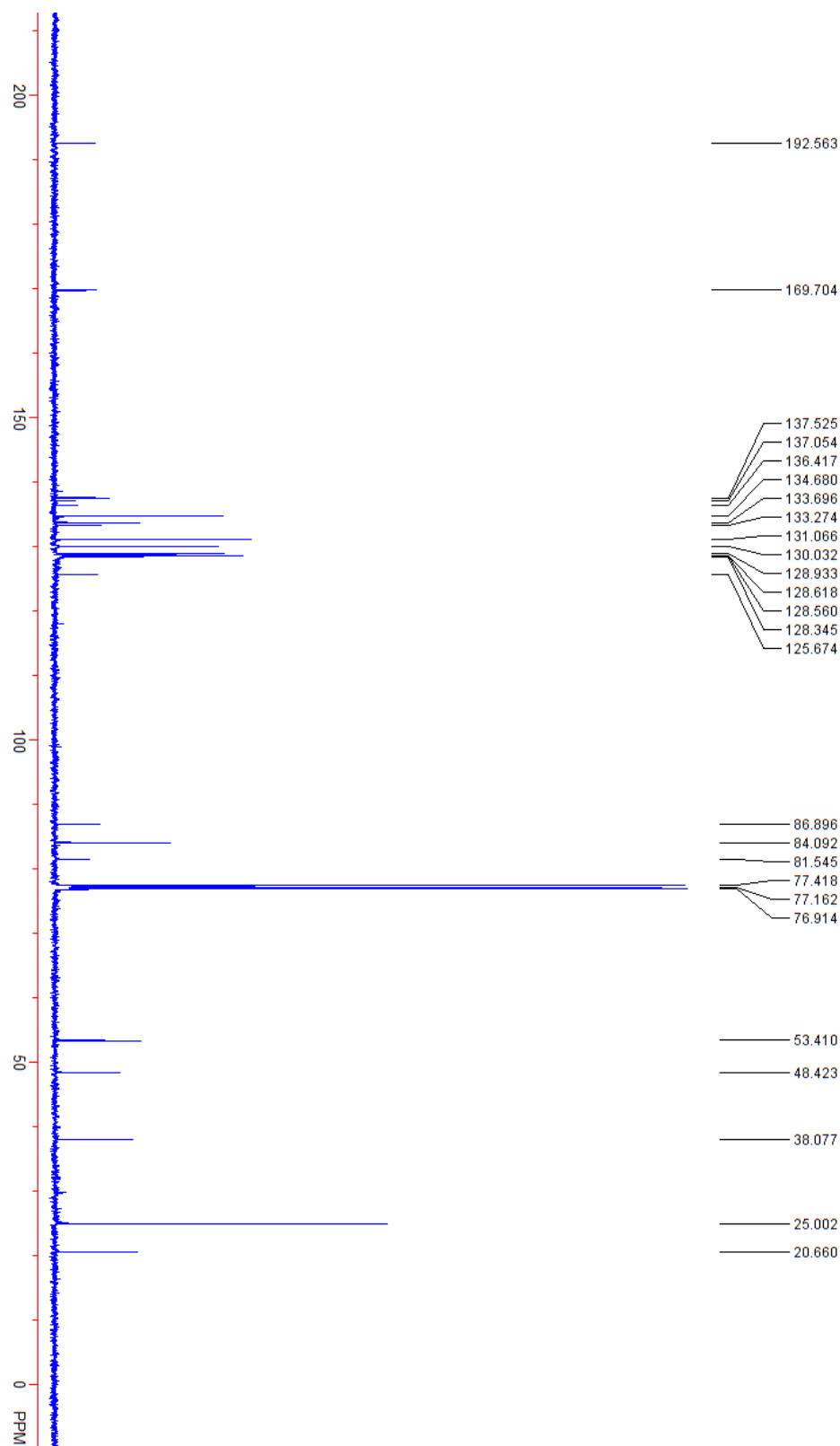
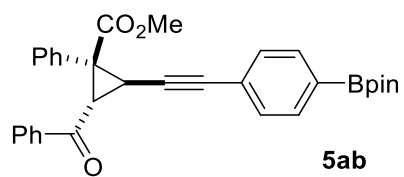
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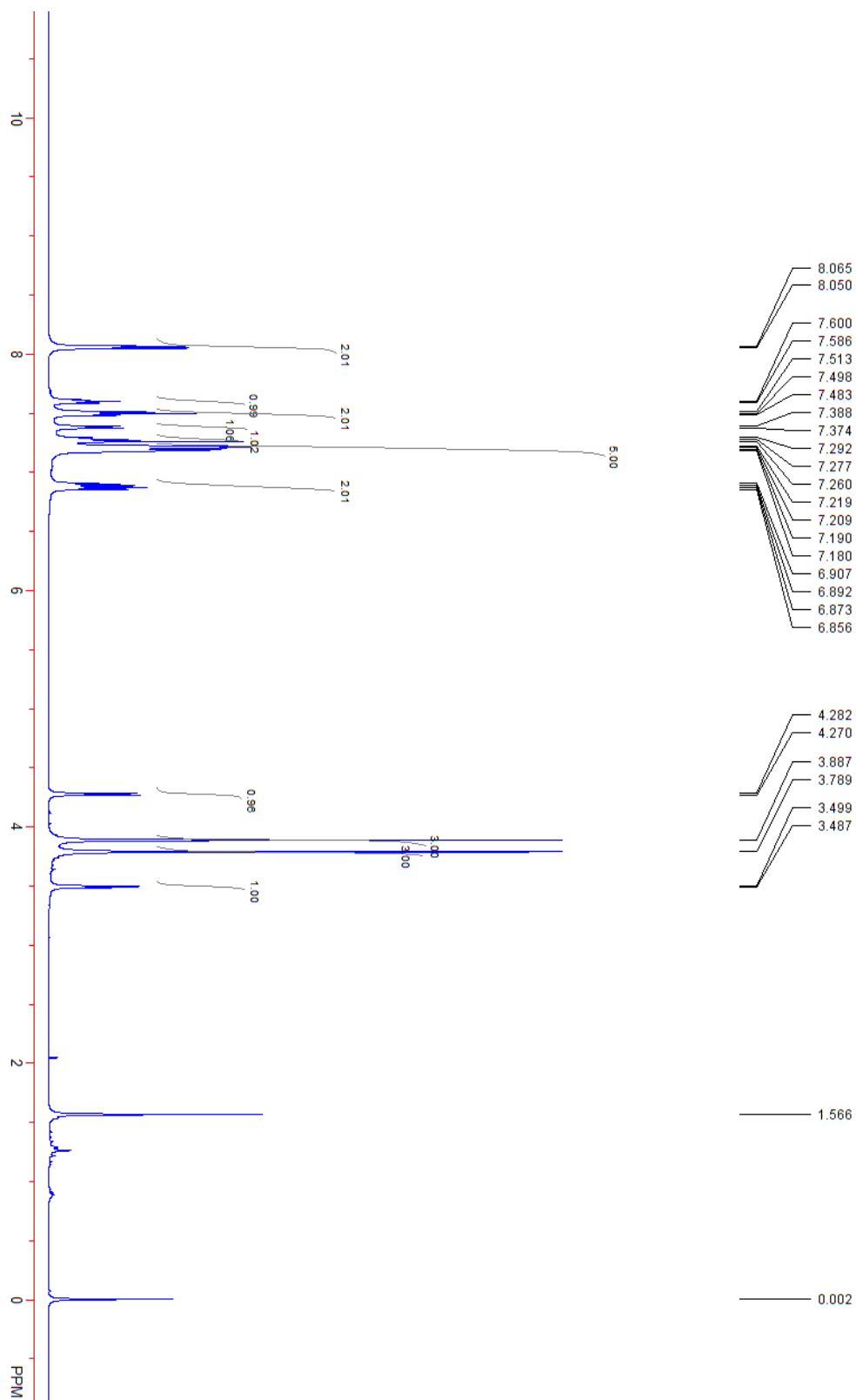
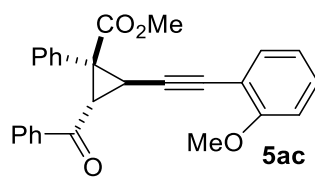
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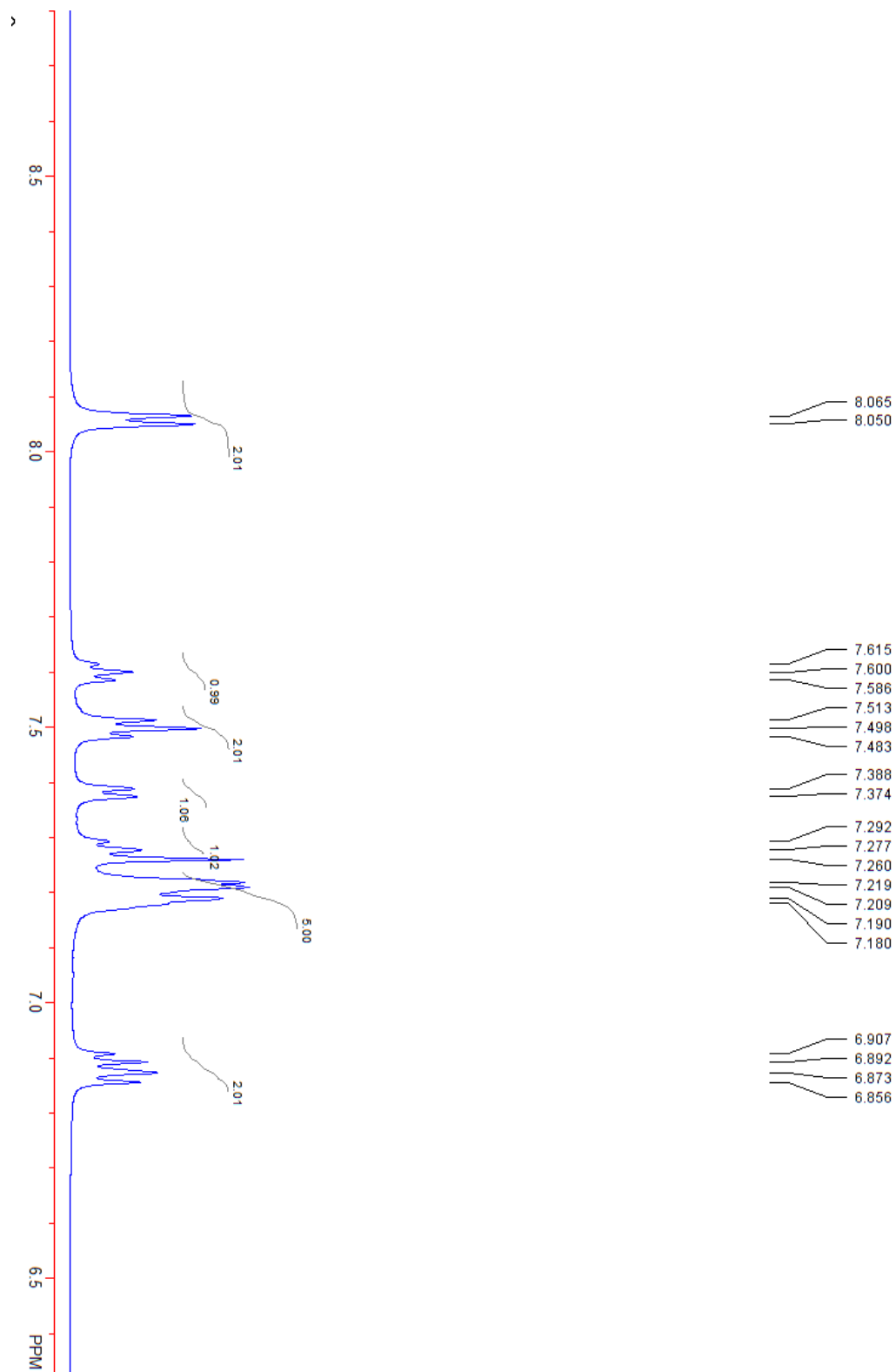
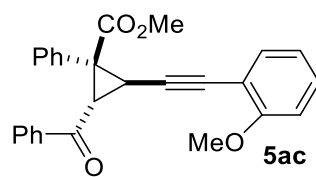
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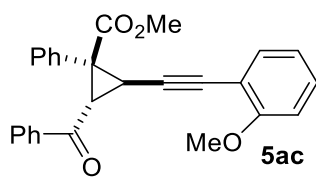


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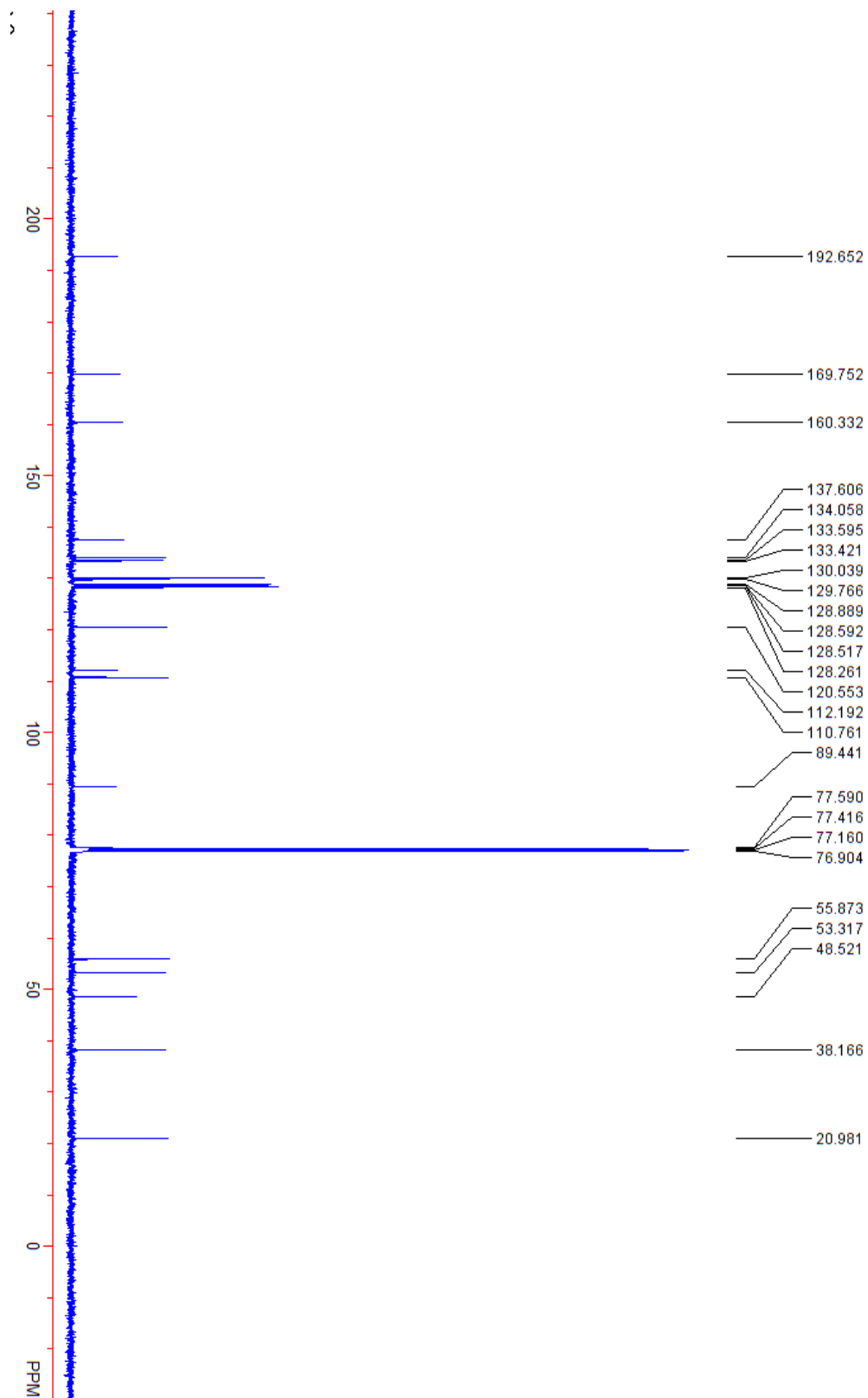


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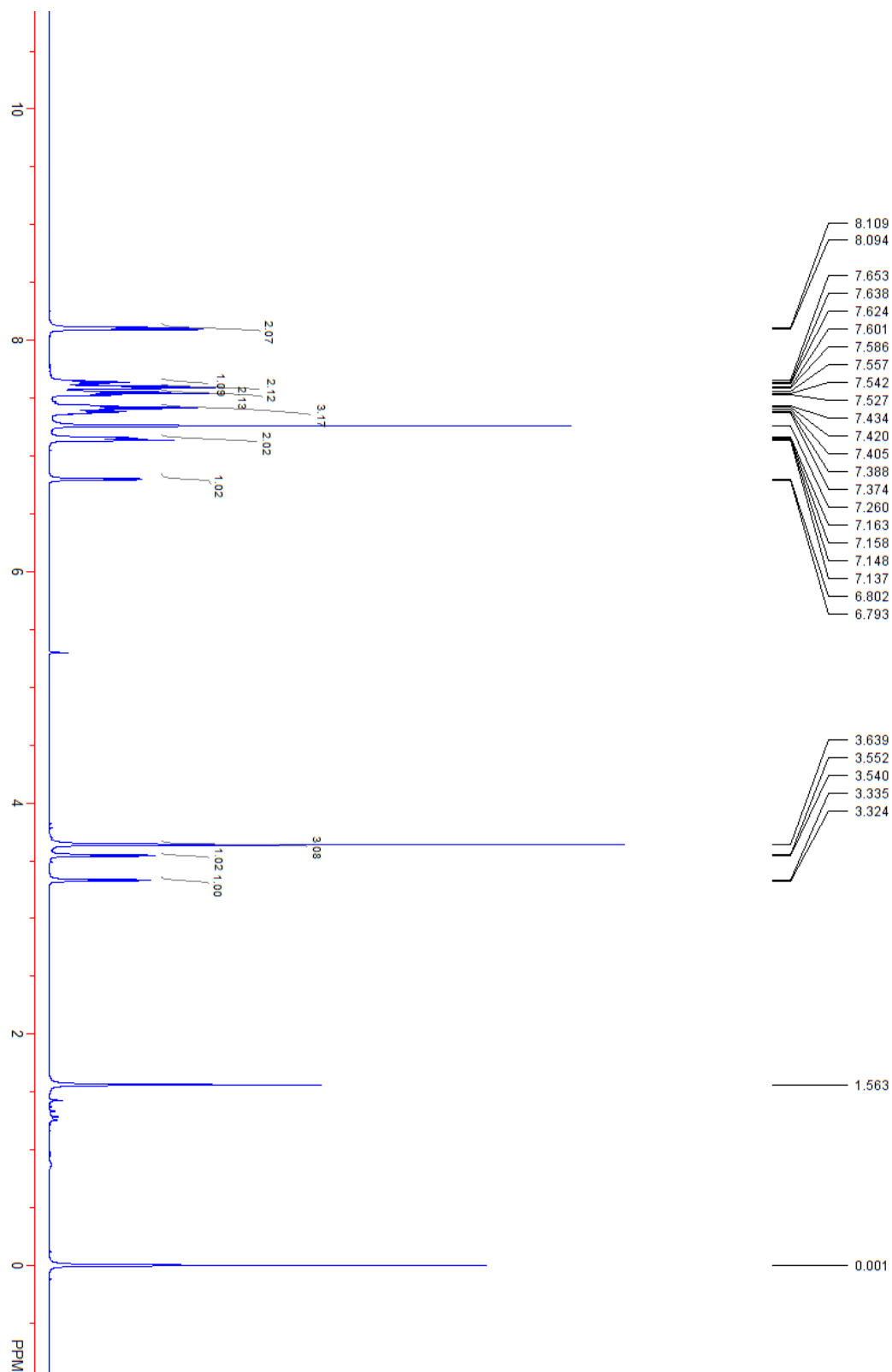
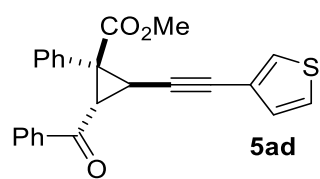




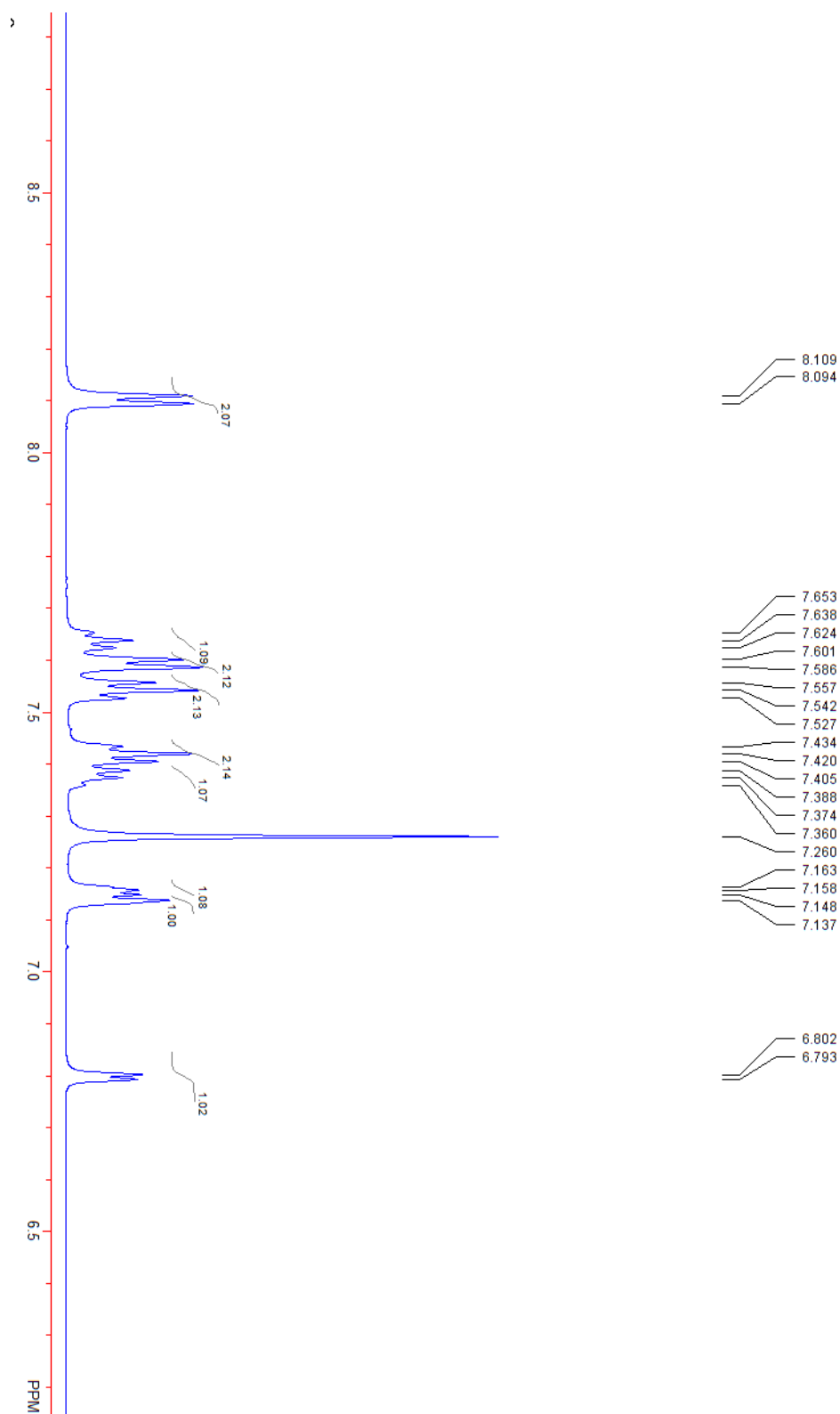
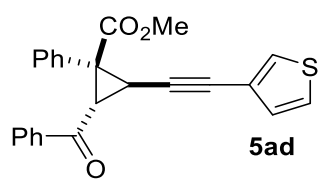
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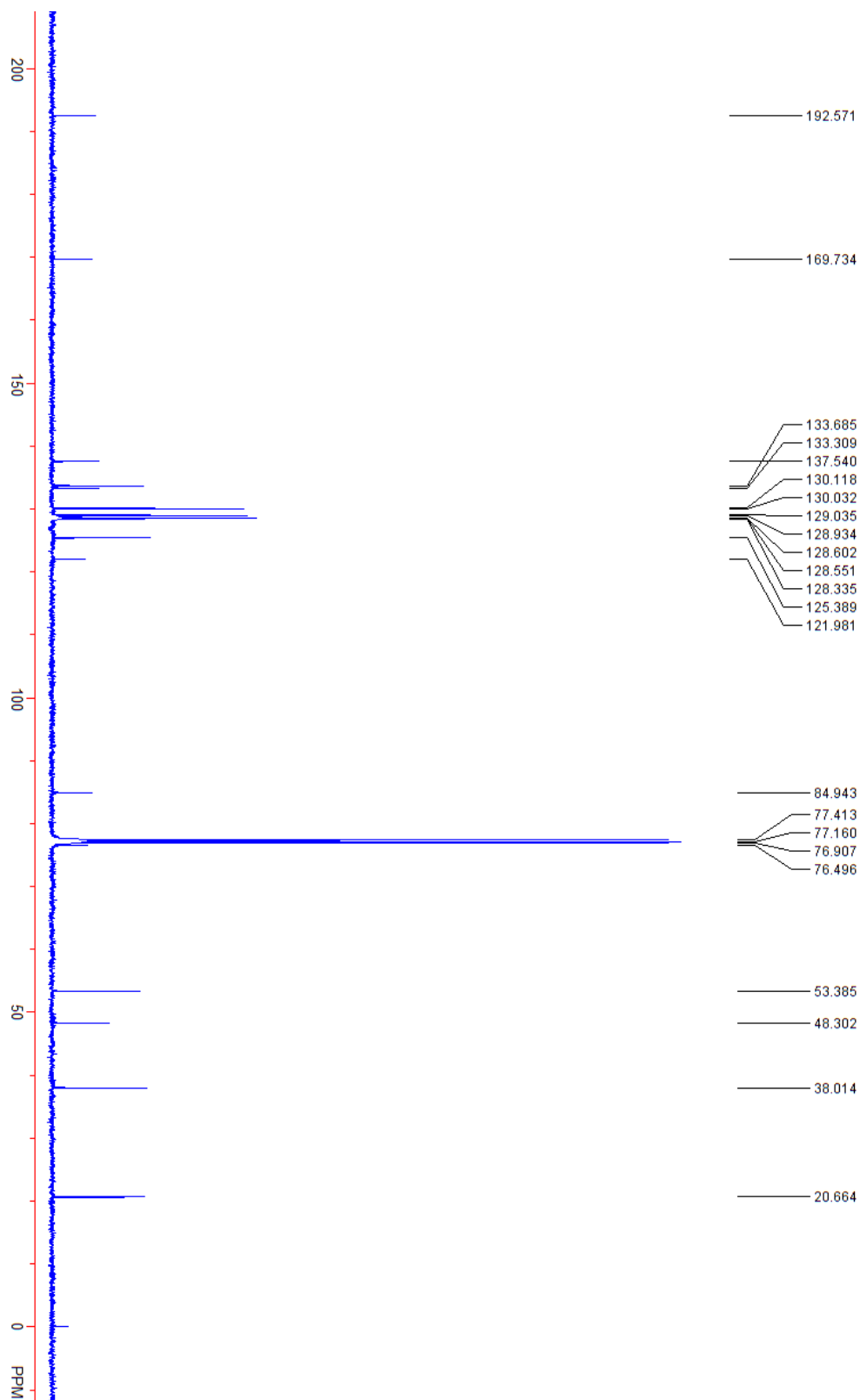
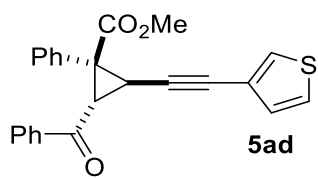
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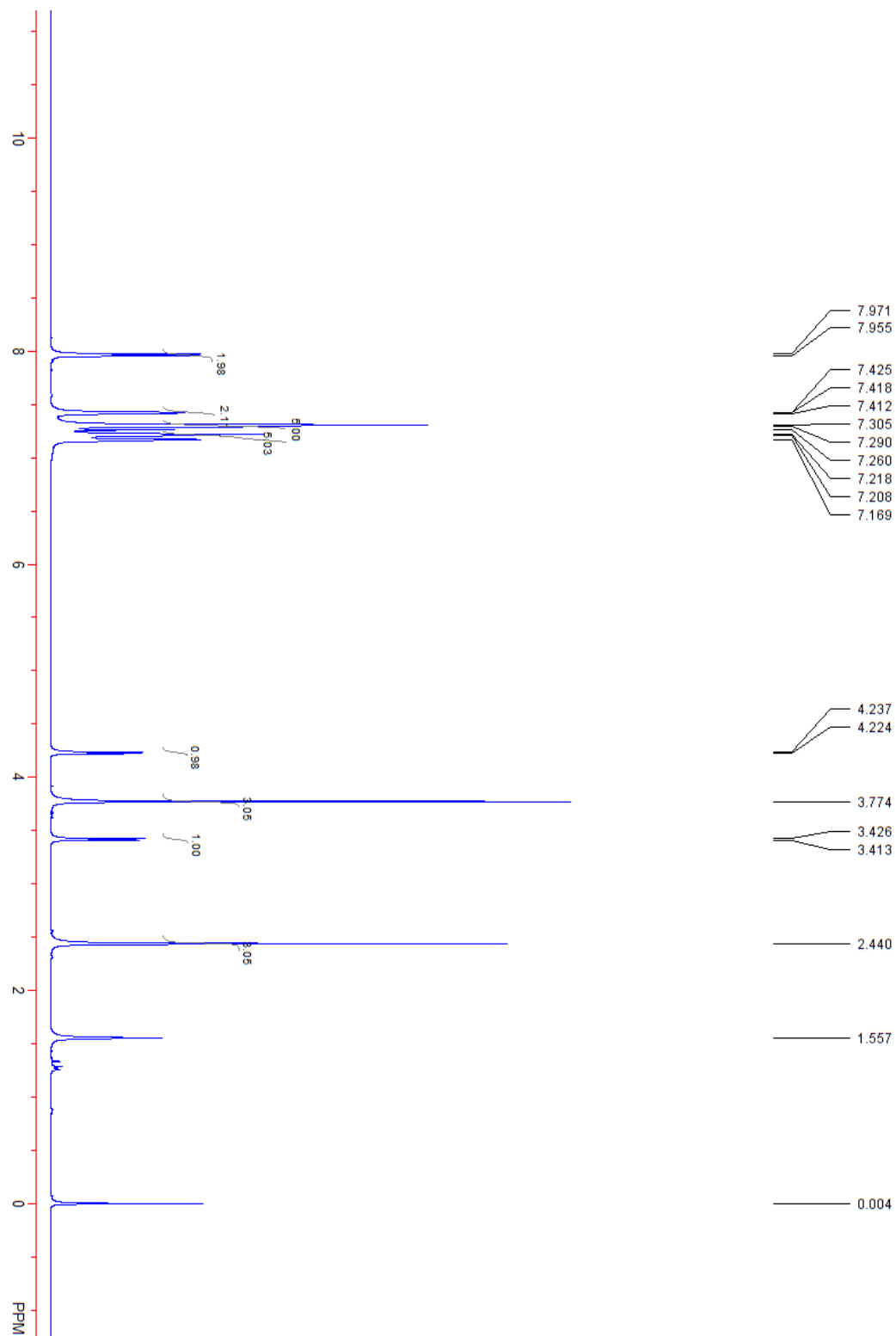
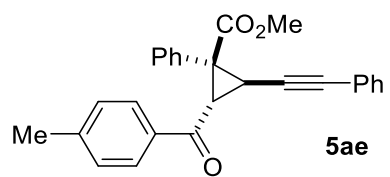
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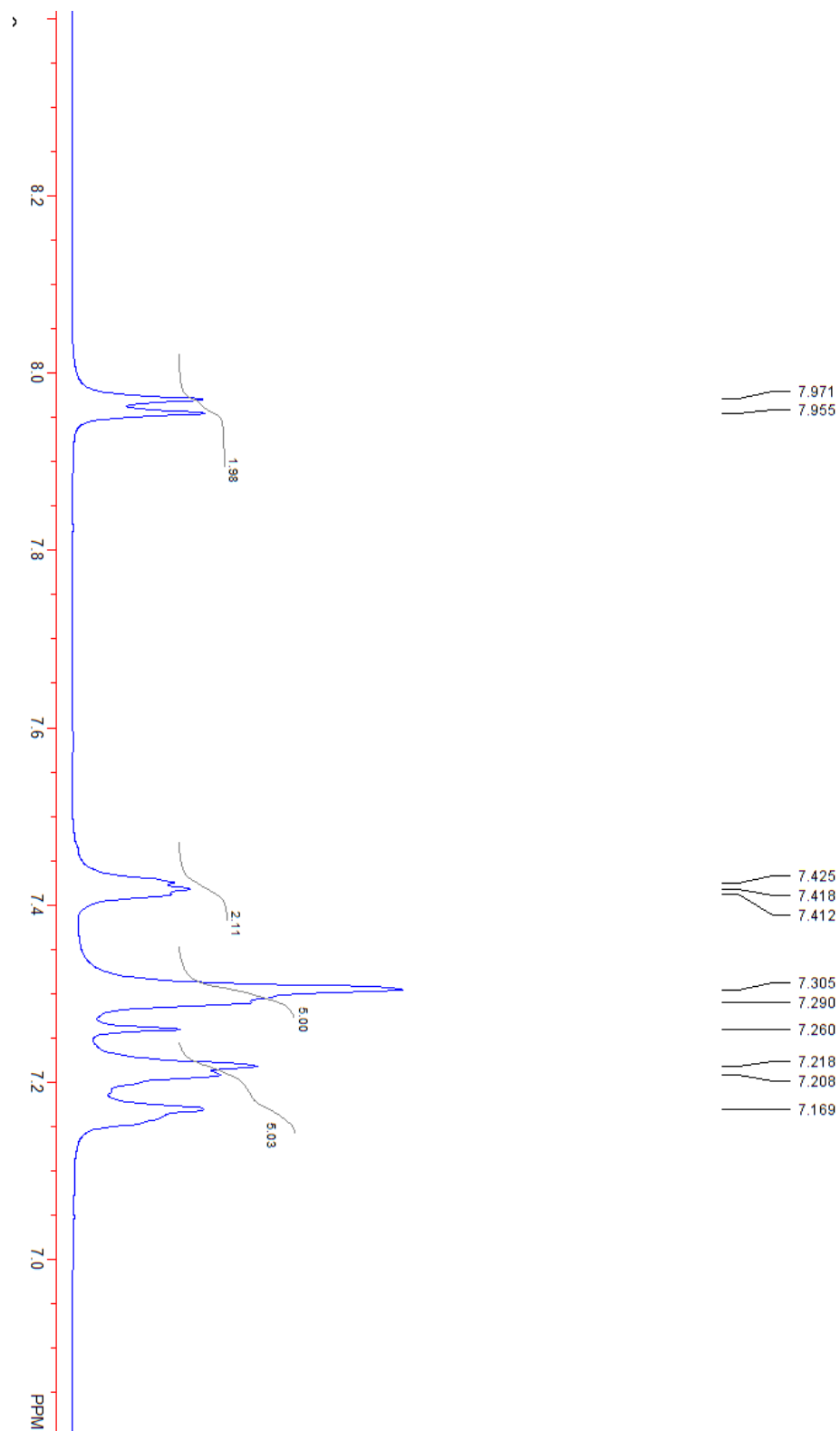
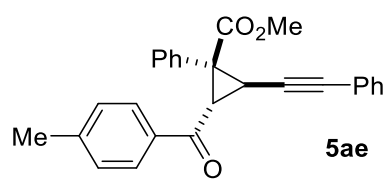
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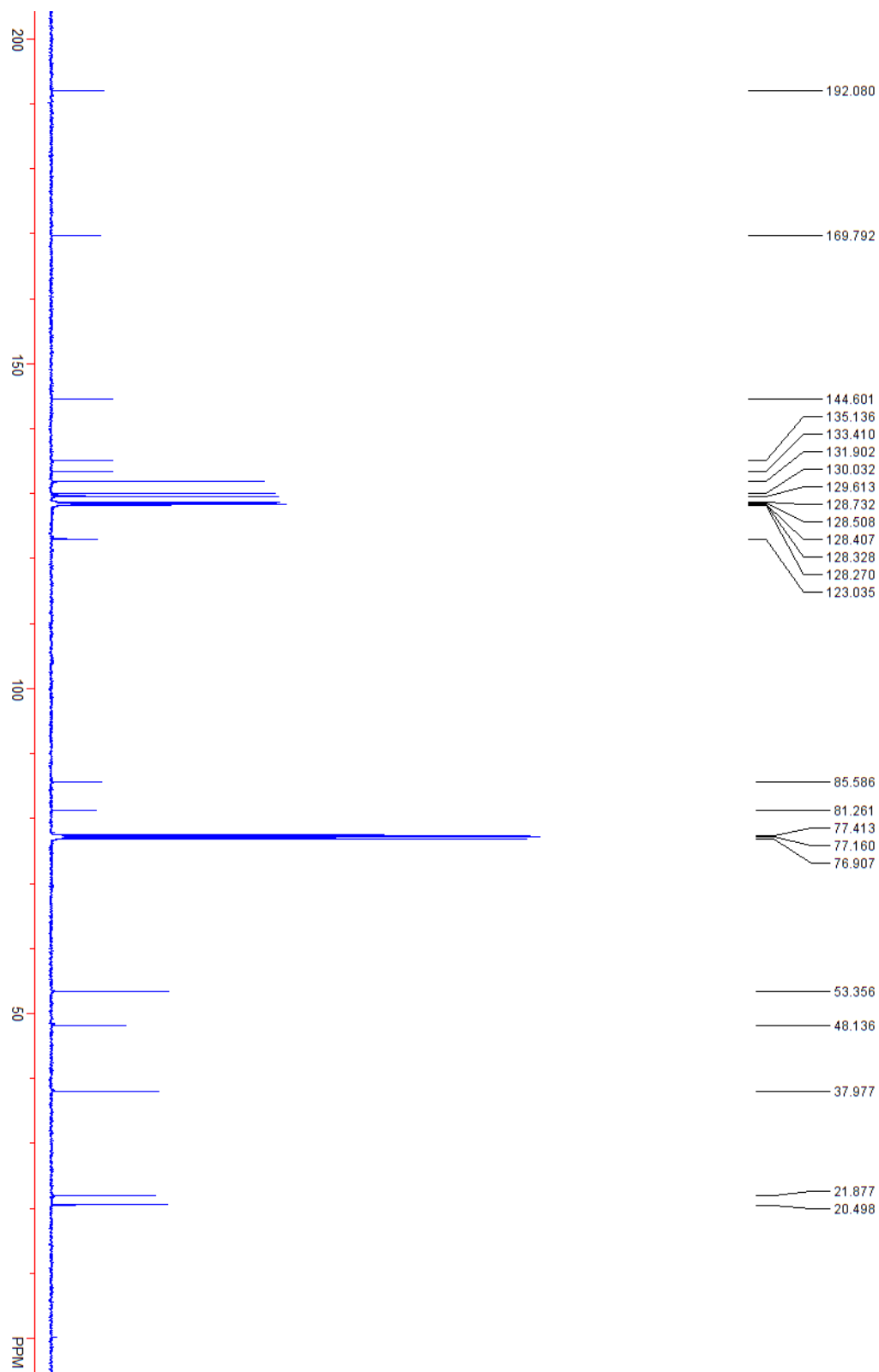
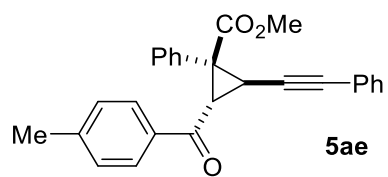
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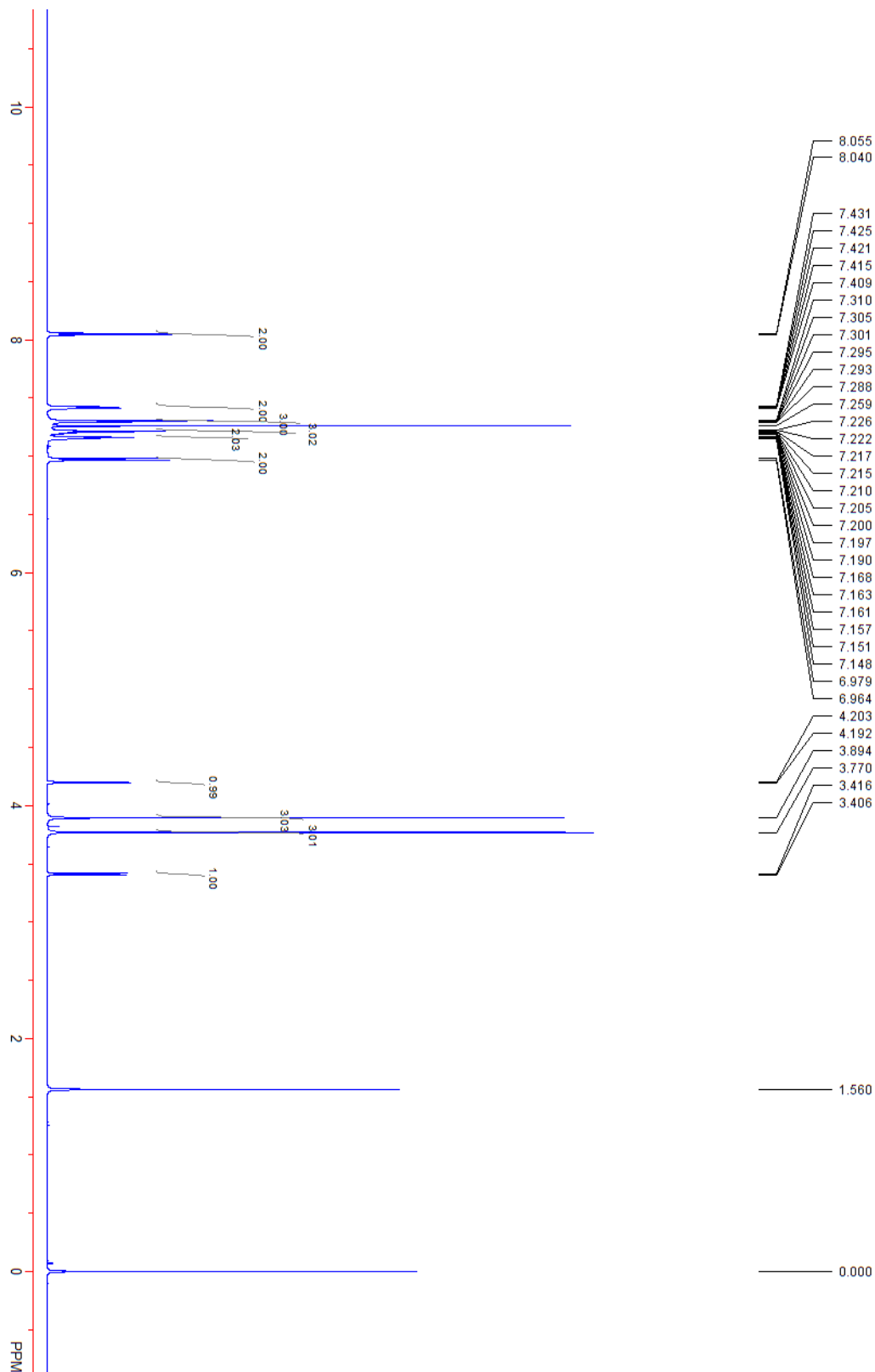
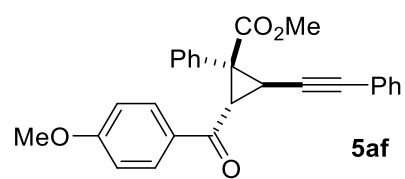
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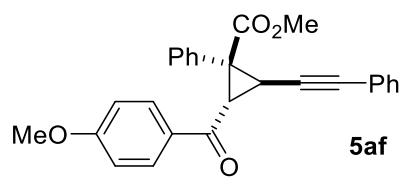


$^{13}\text{C}\{^1\text{H}\}$ NMR:

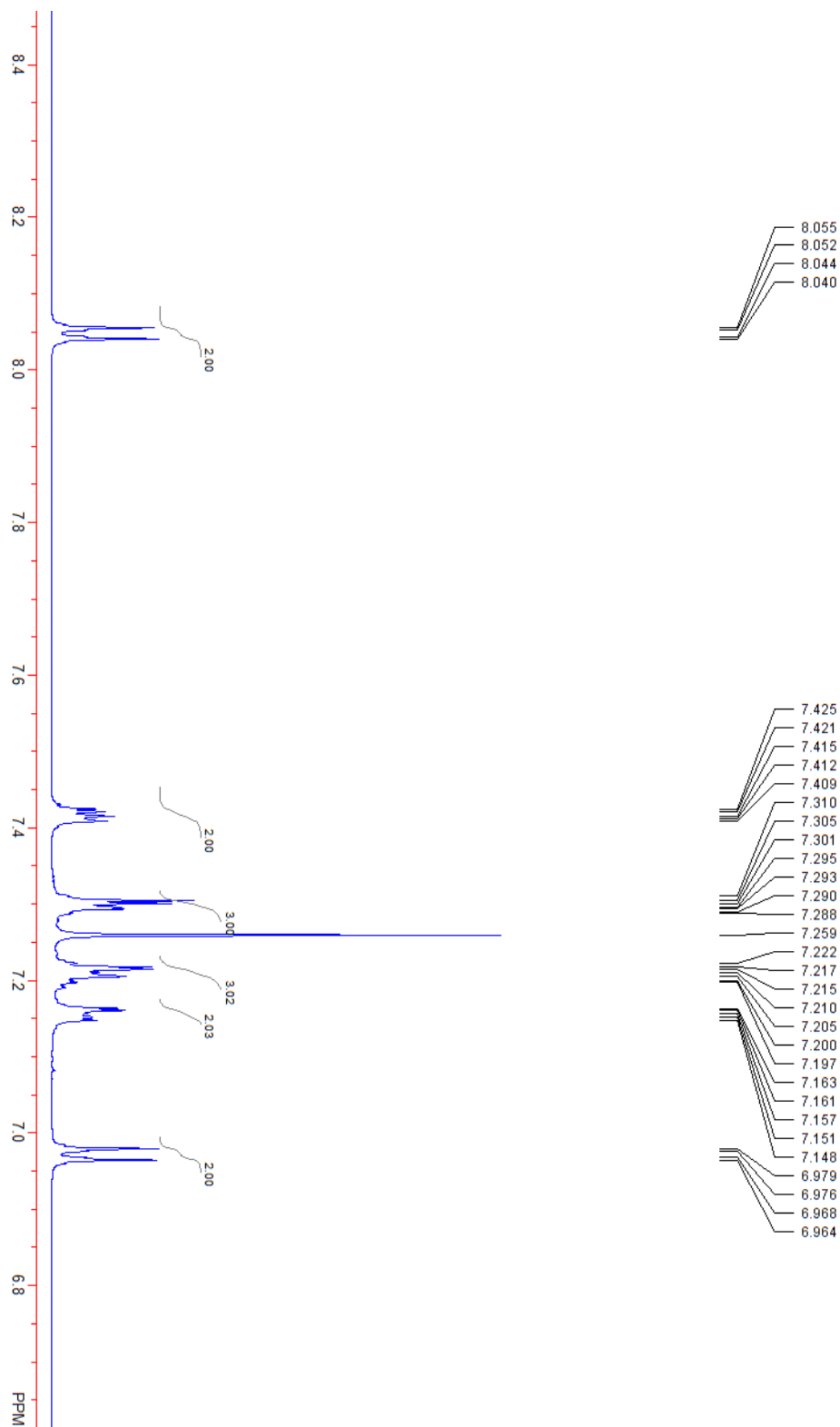


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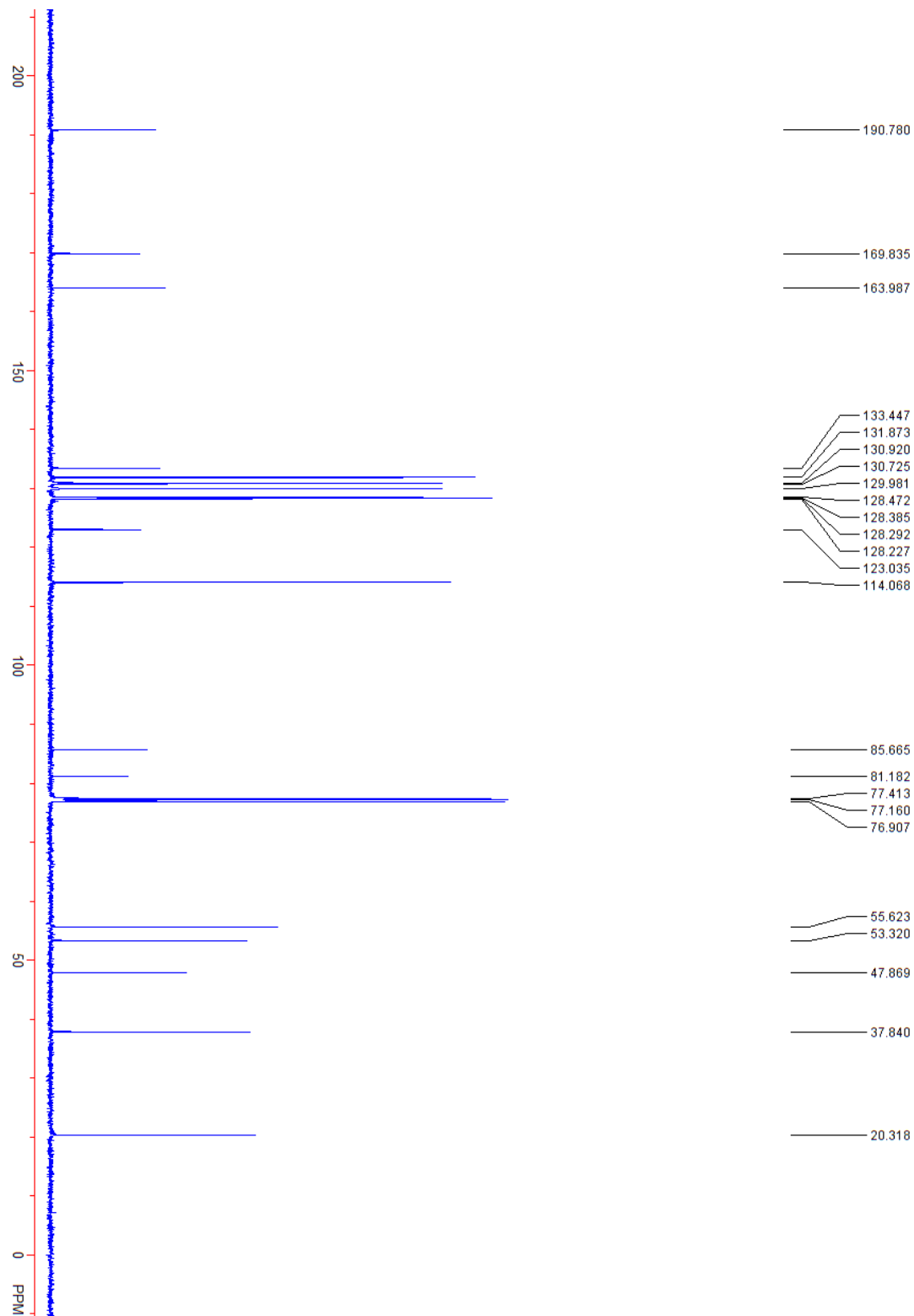
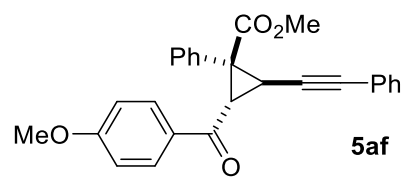




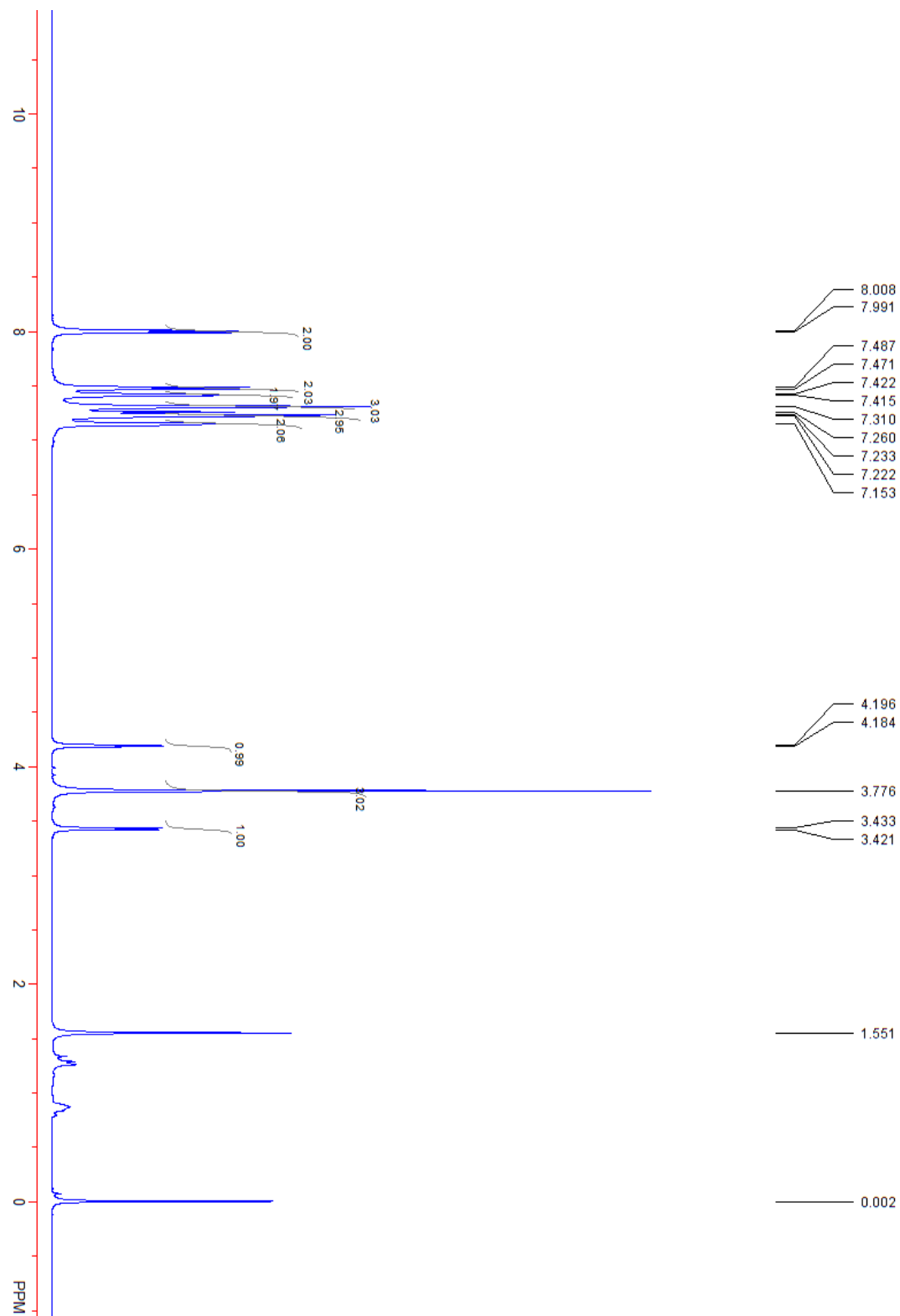
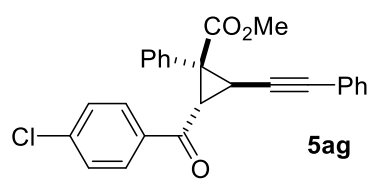
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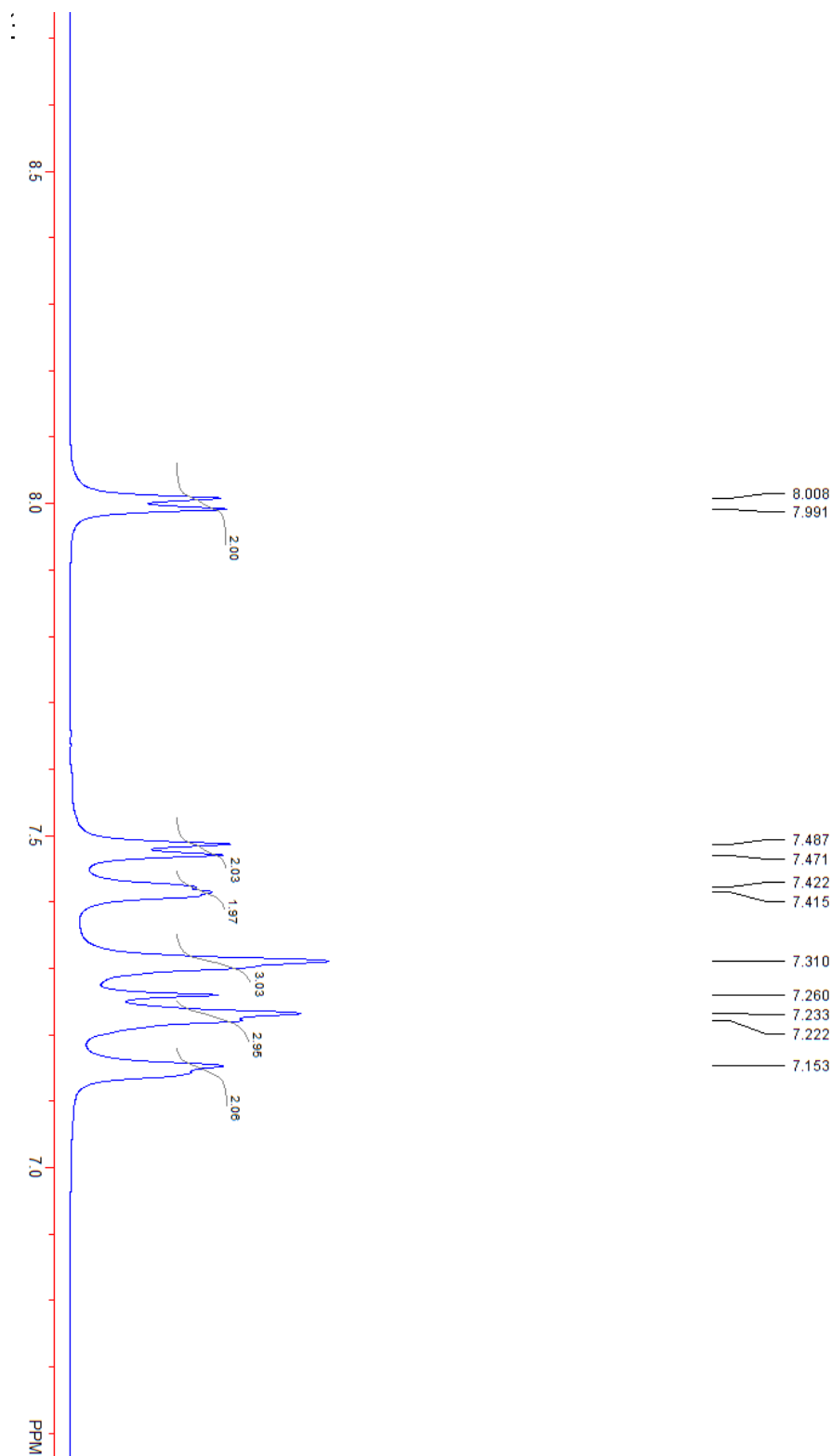
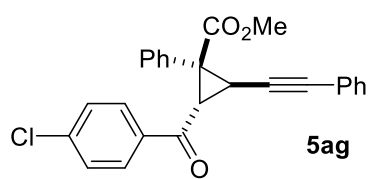
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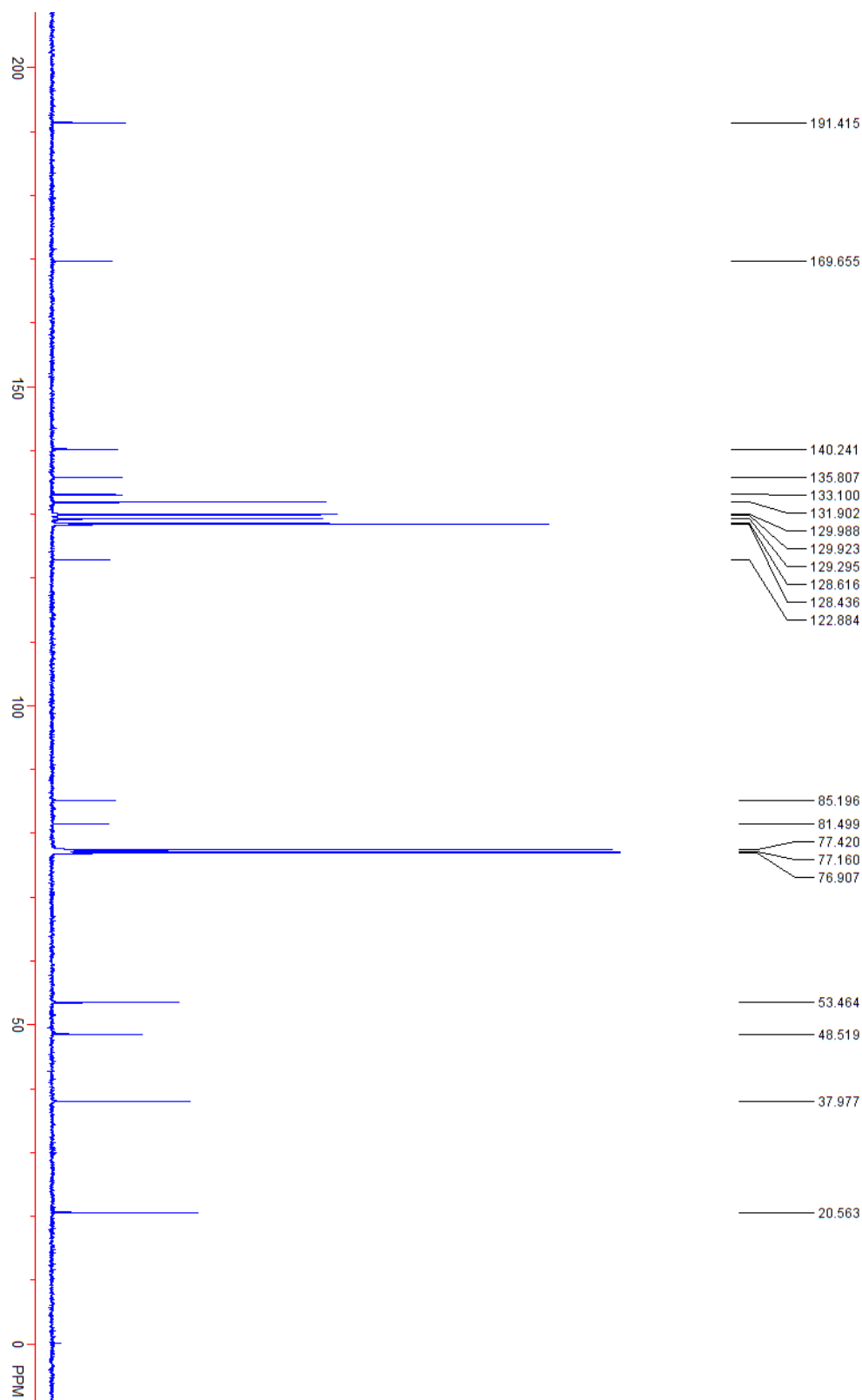
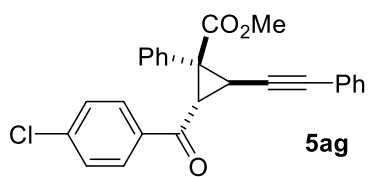
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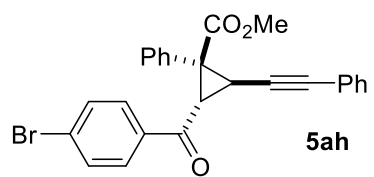


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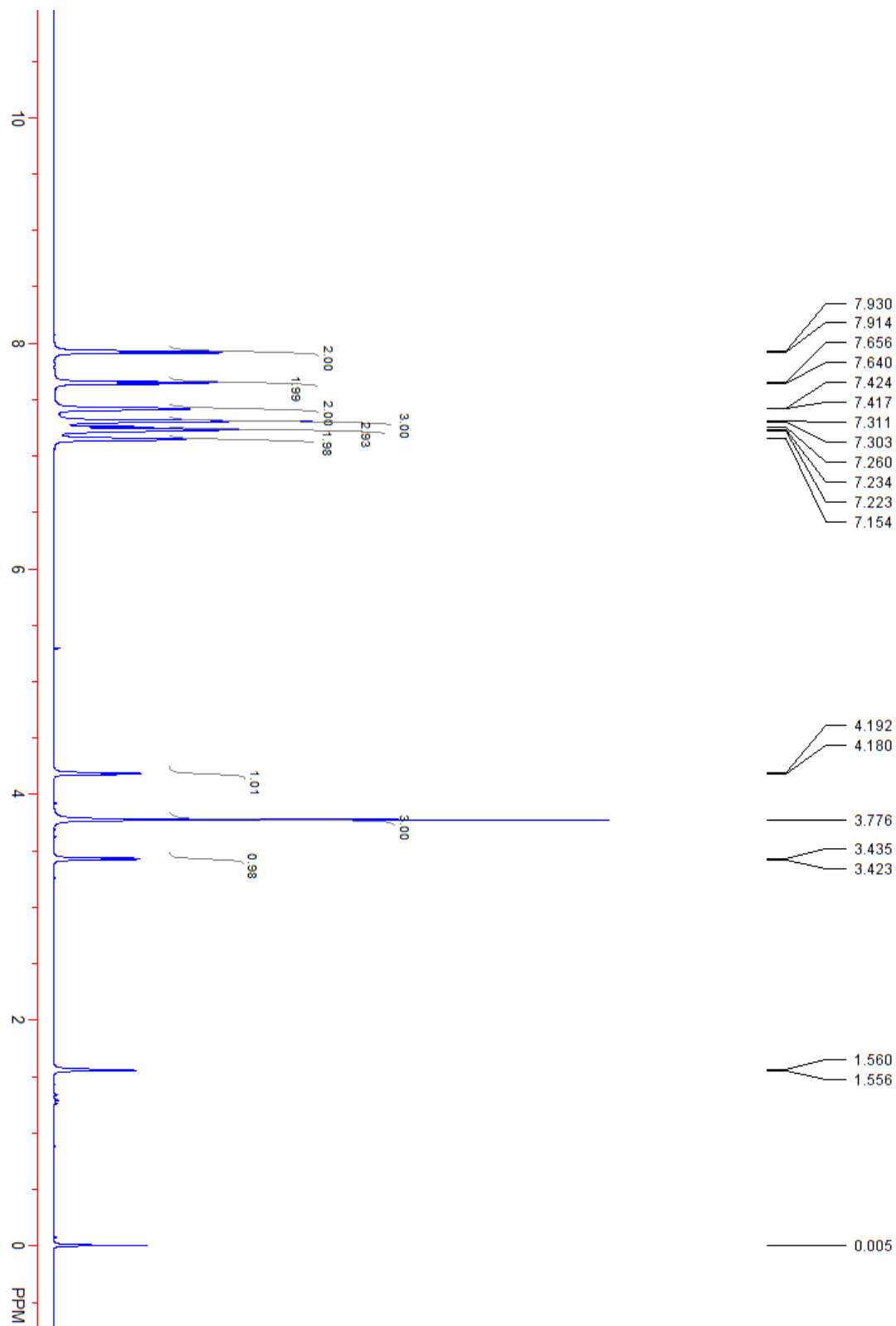


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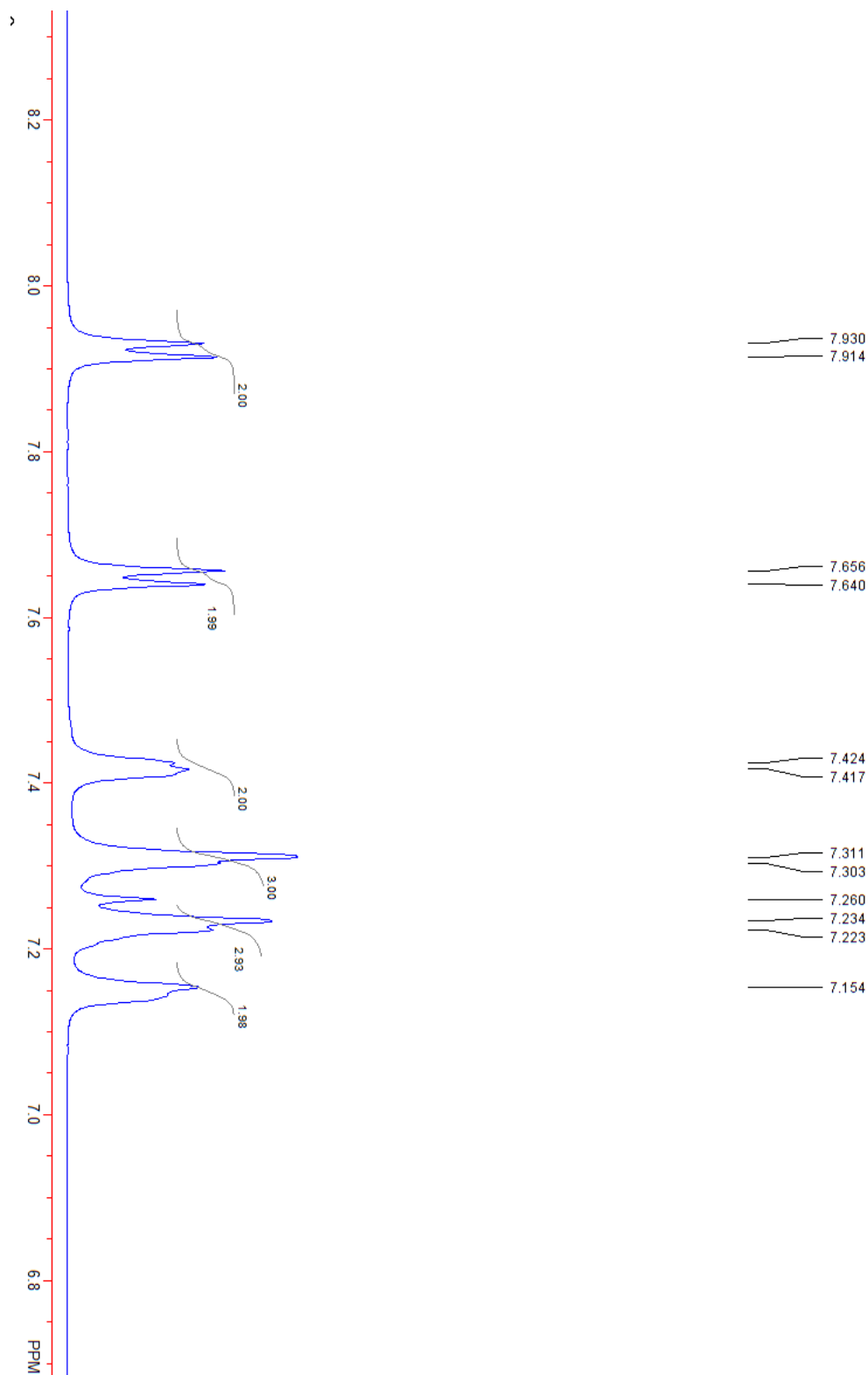
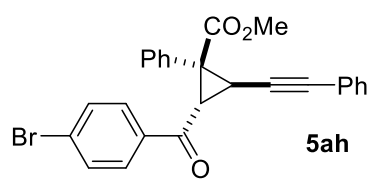




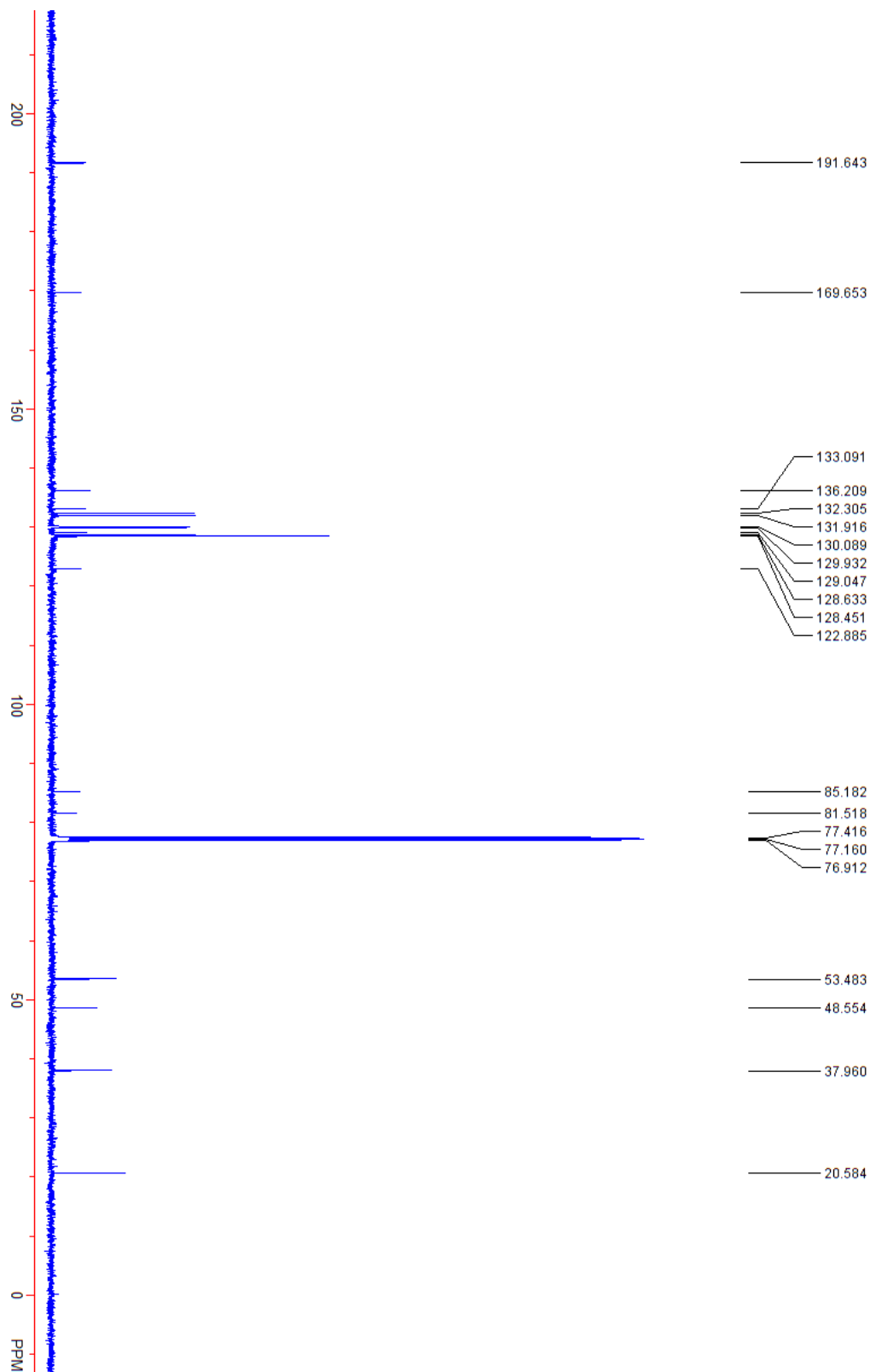
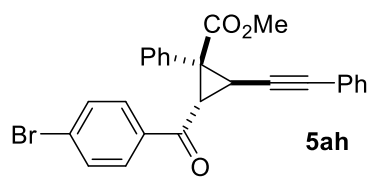
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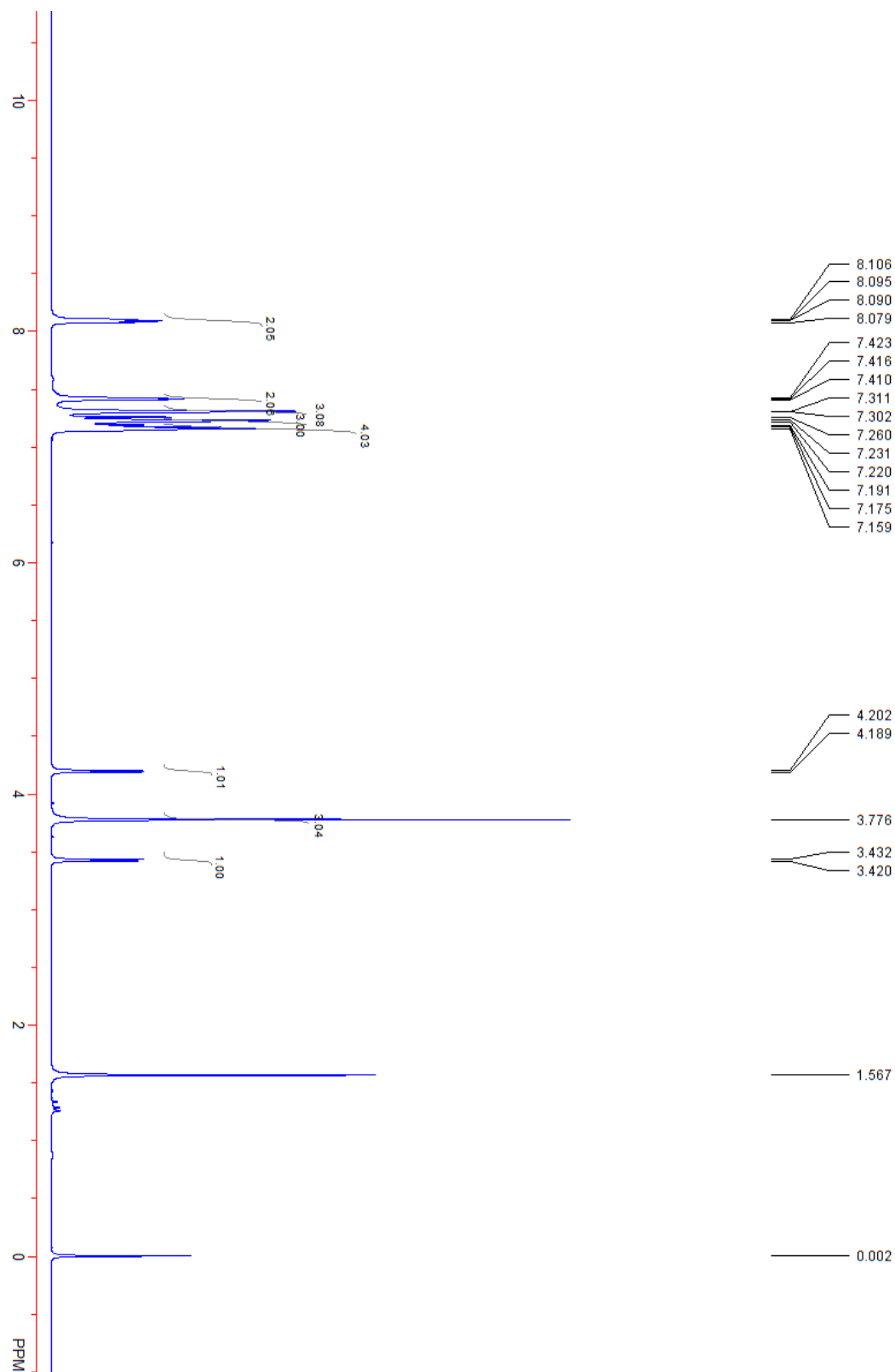
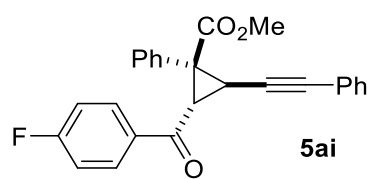
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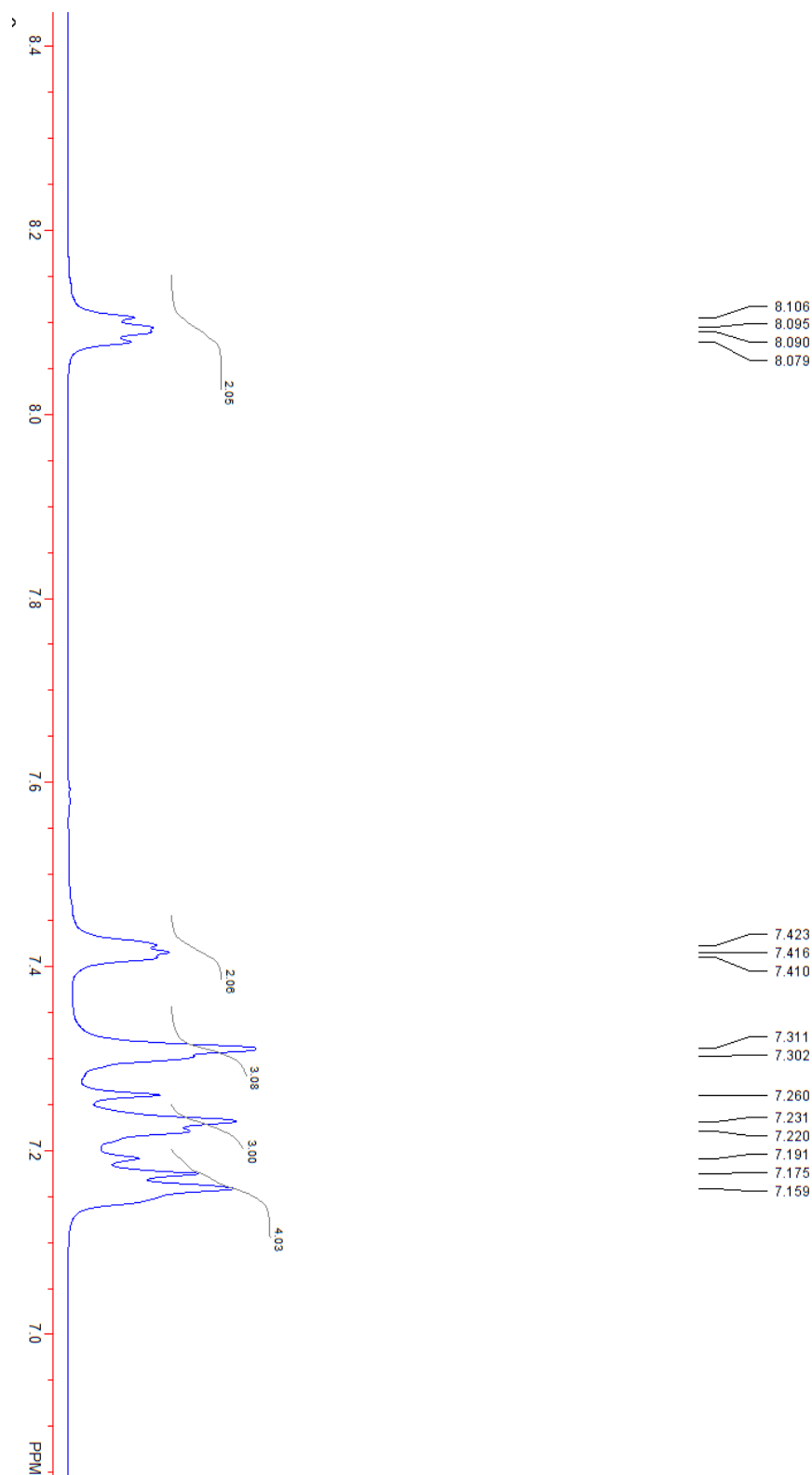
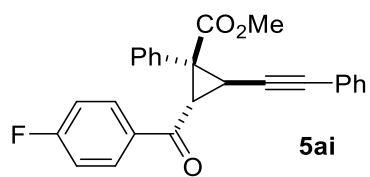
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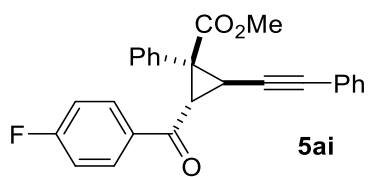


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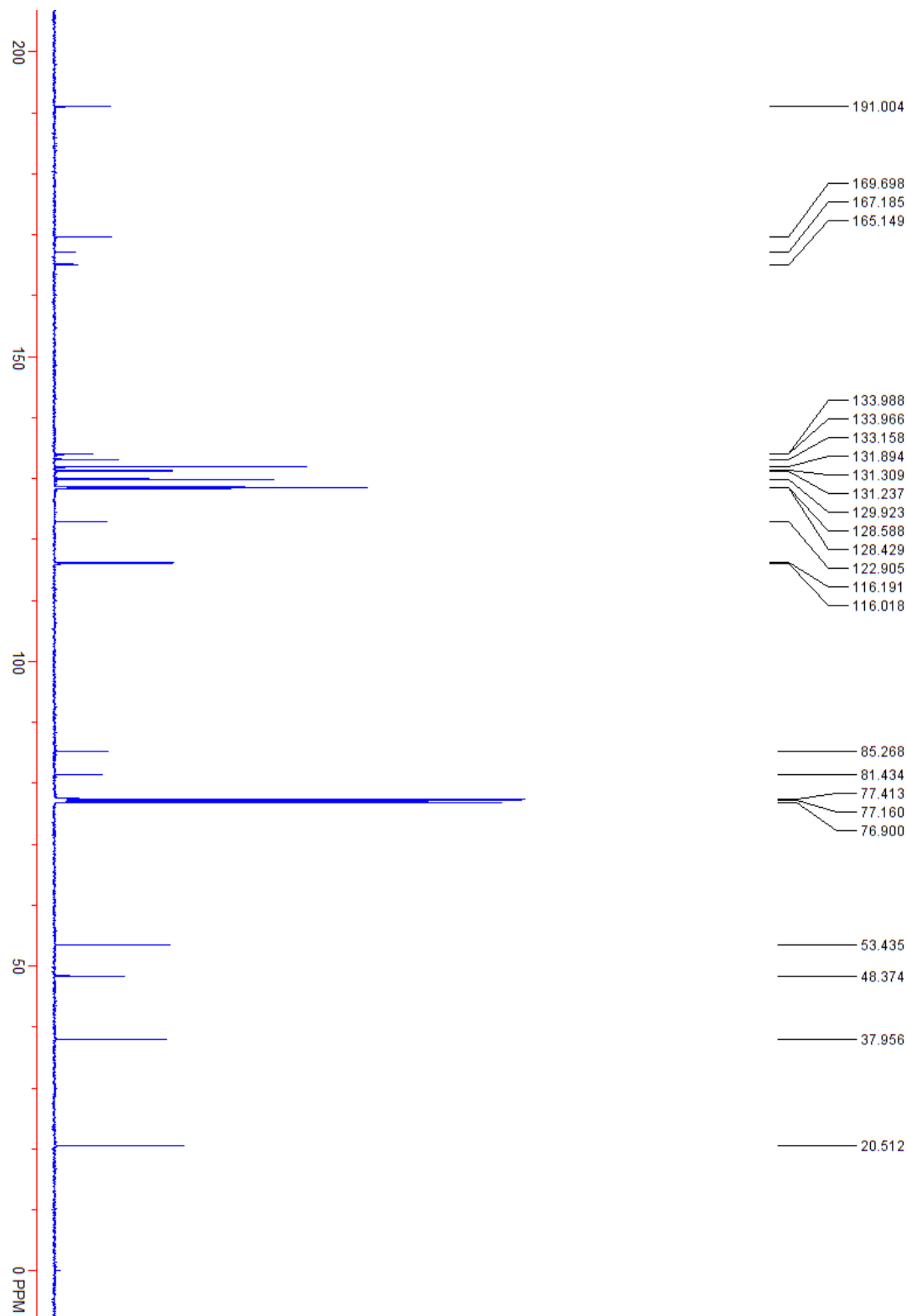


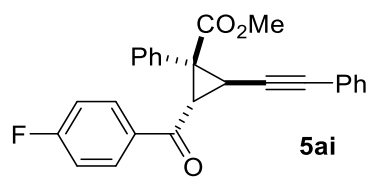
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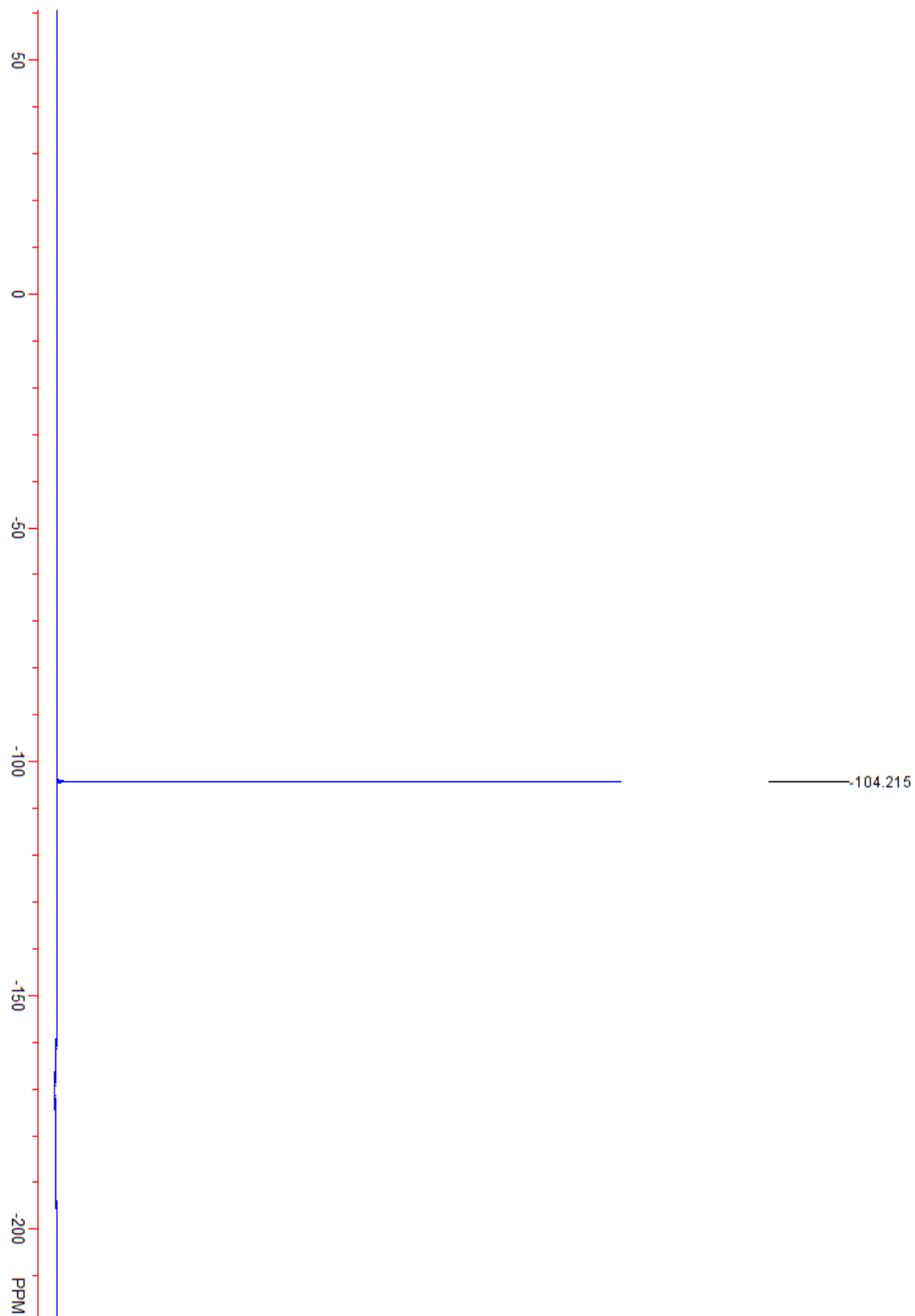


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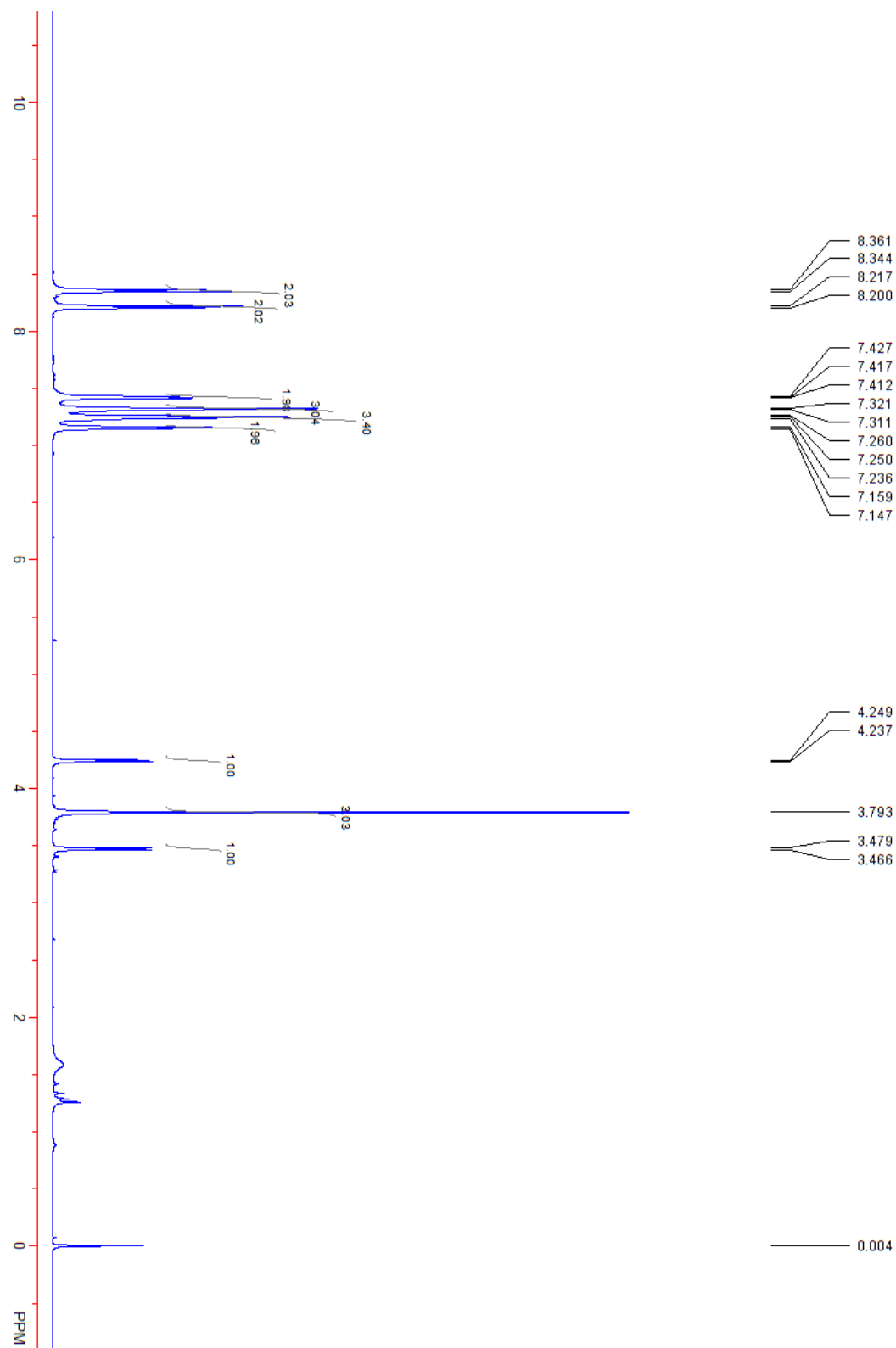
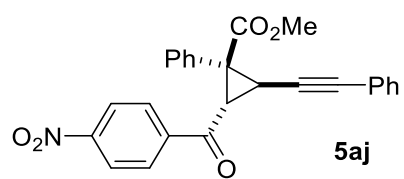




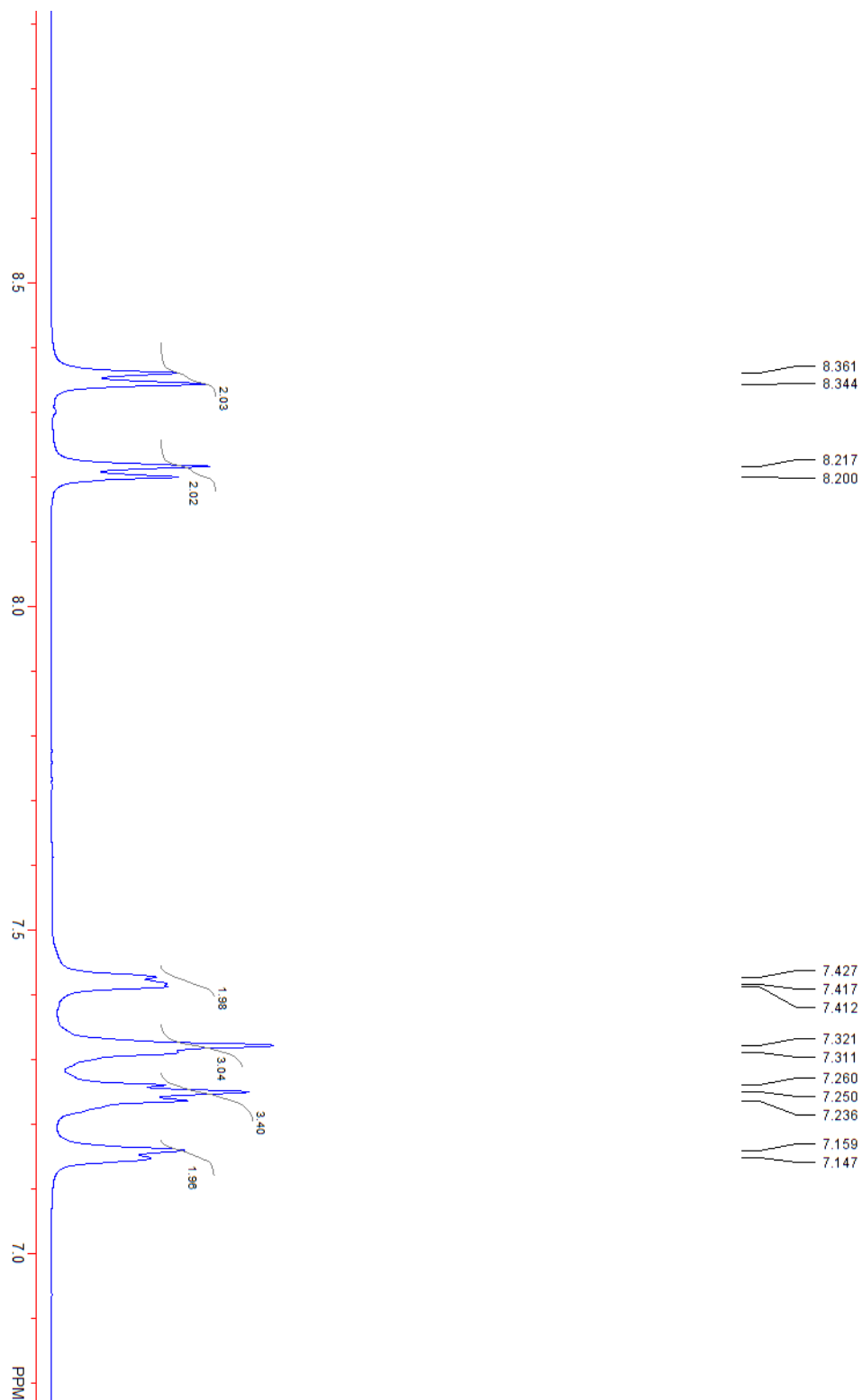
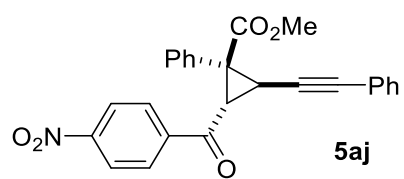
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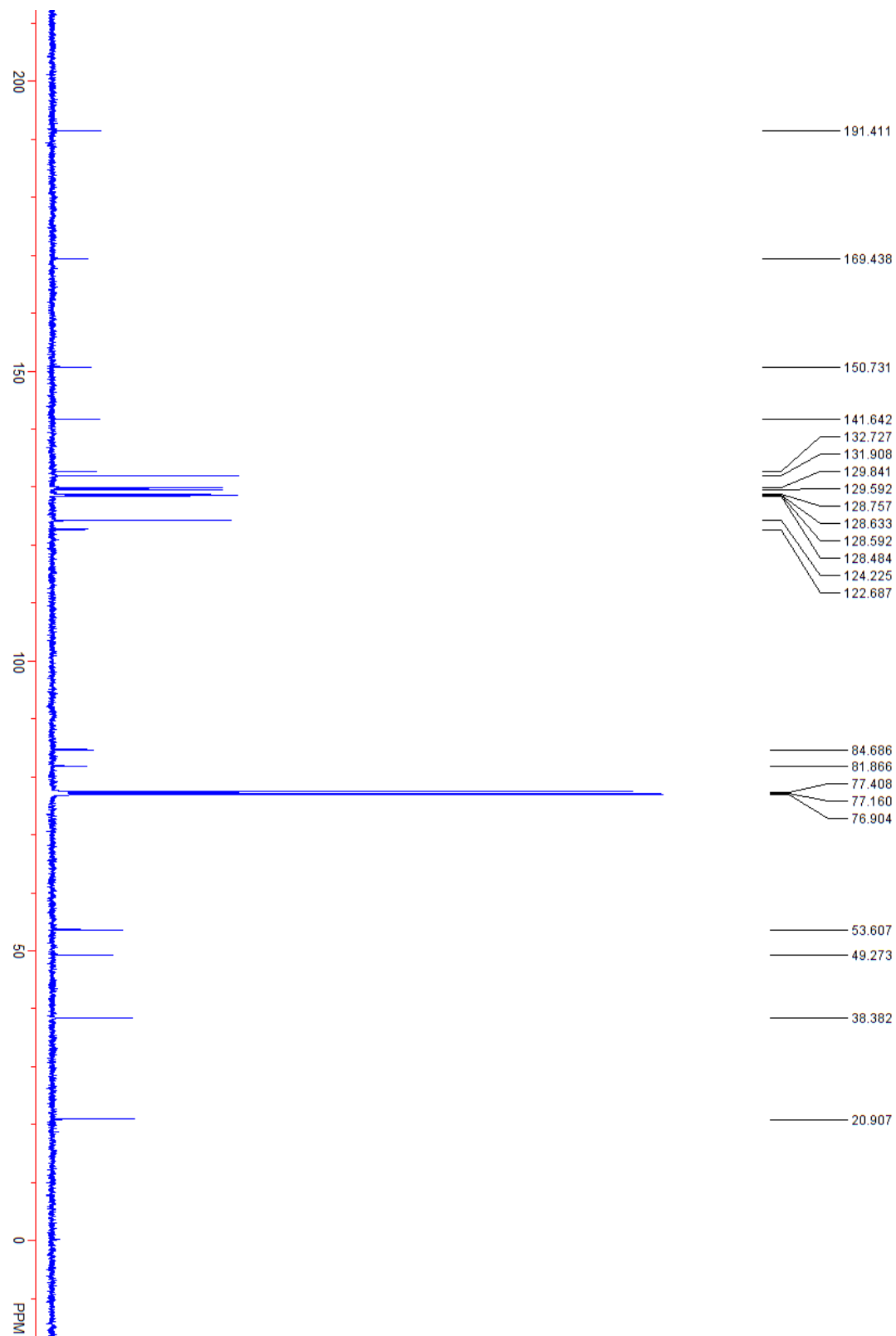
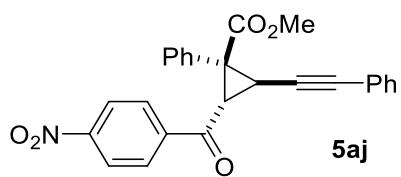
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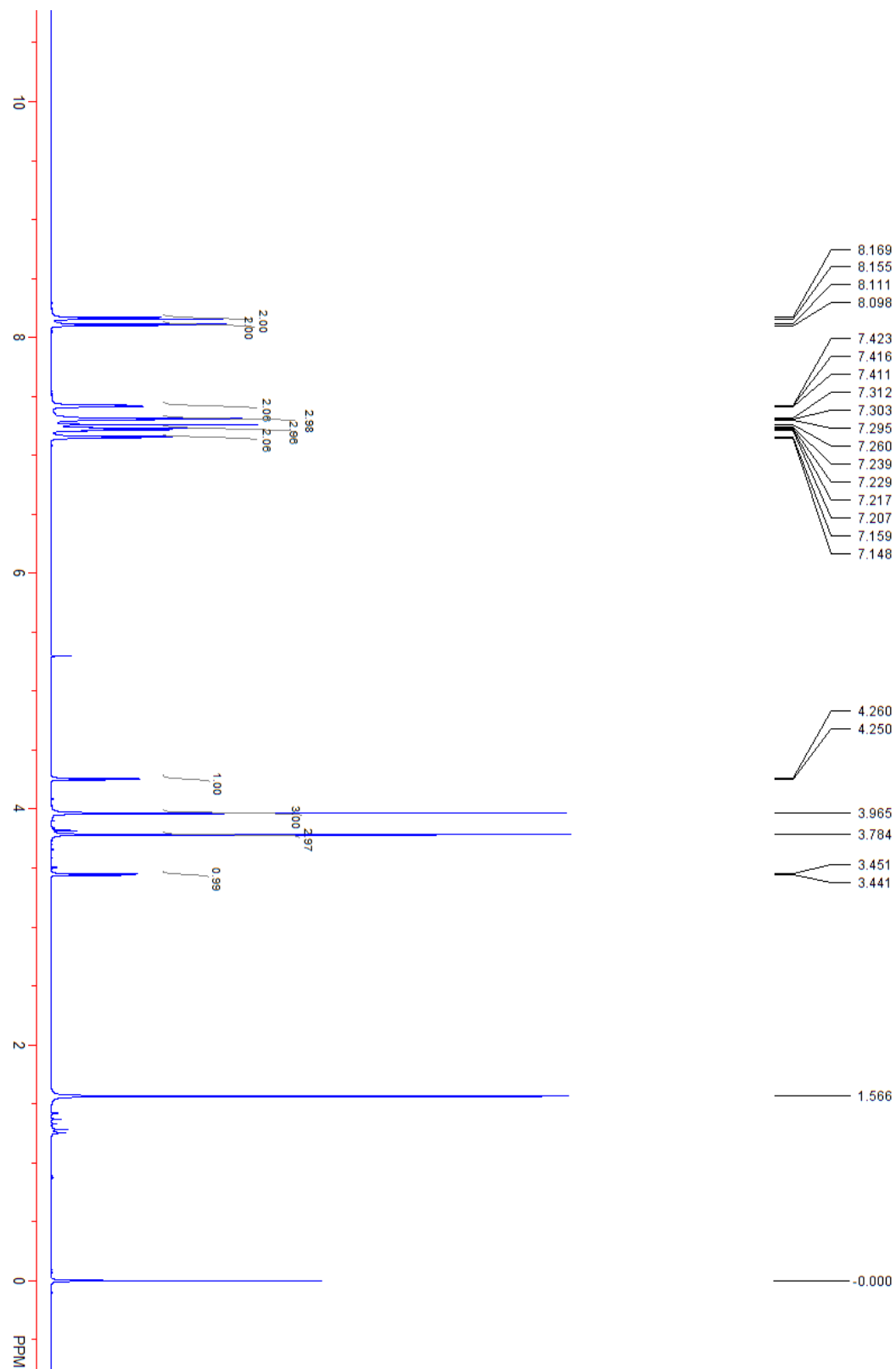
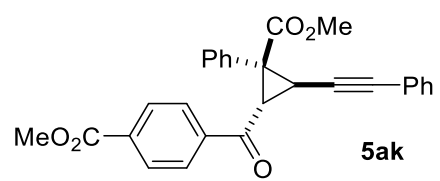
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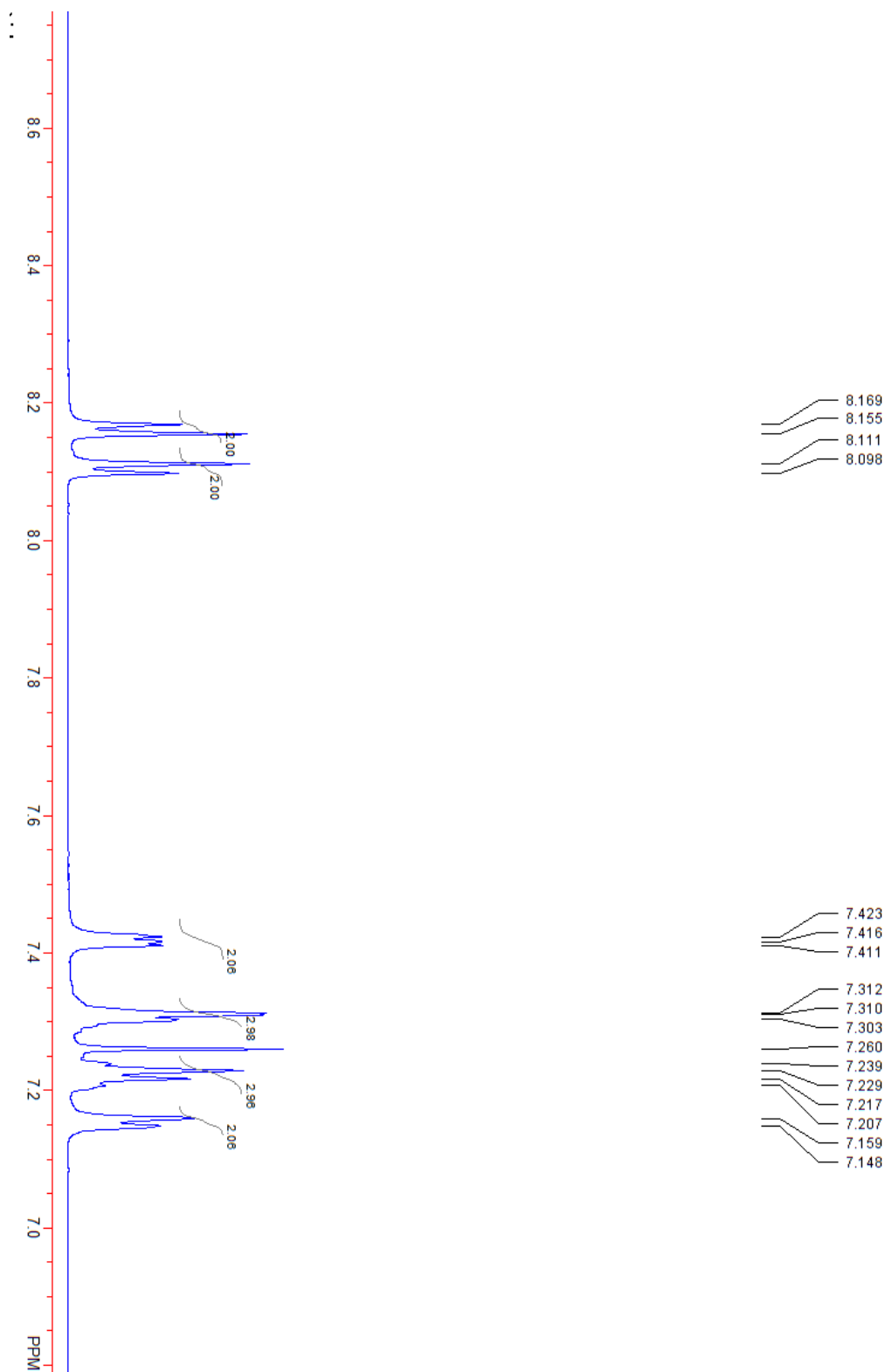
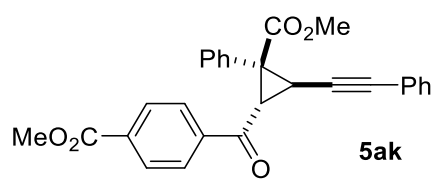
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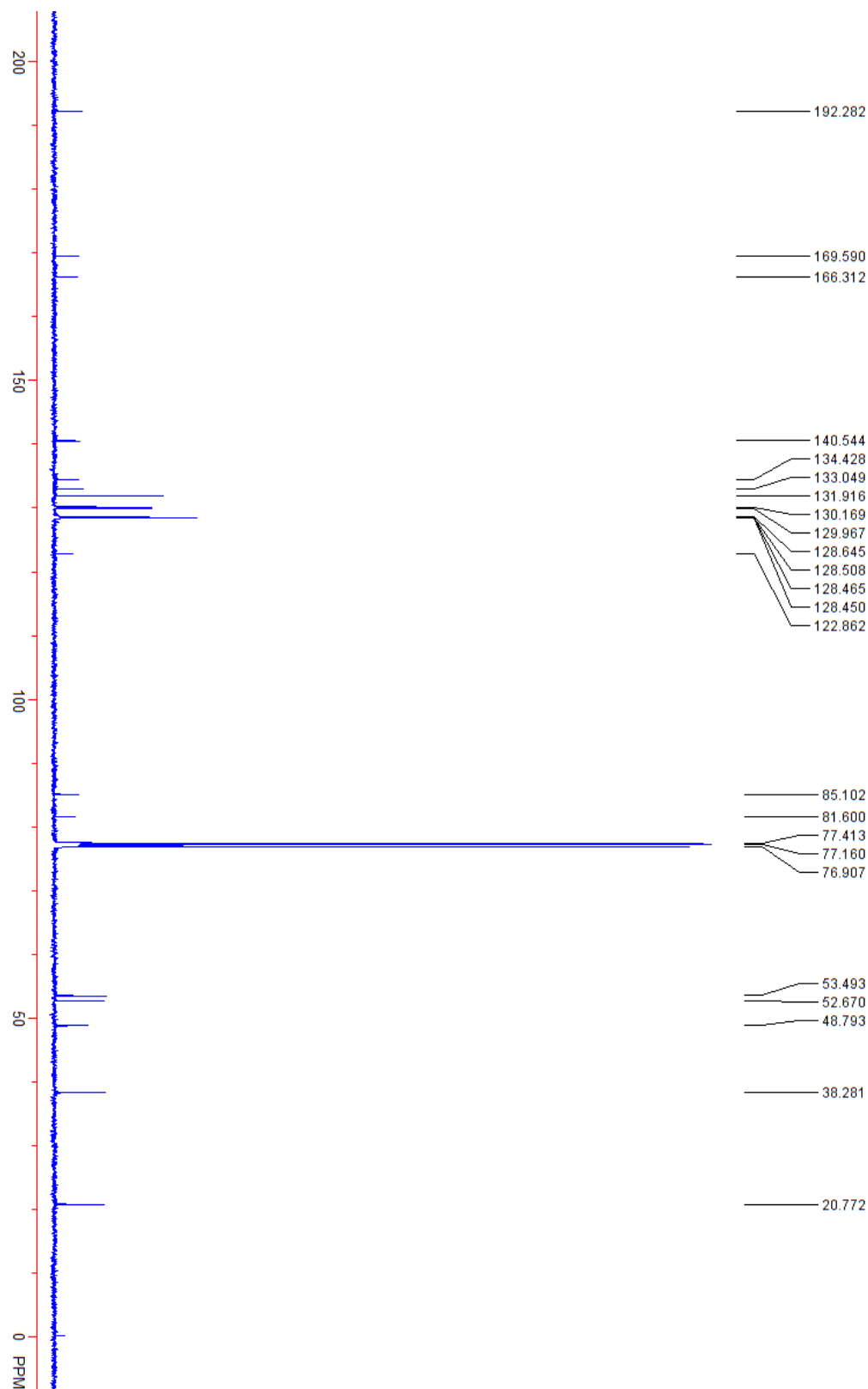
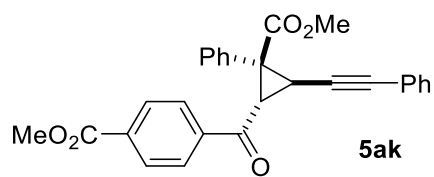
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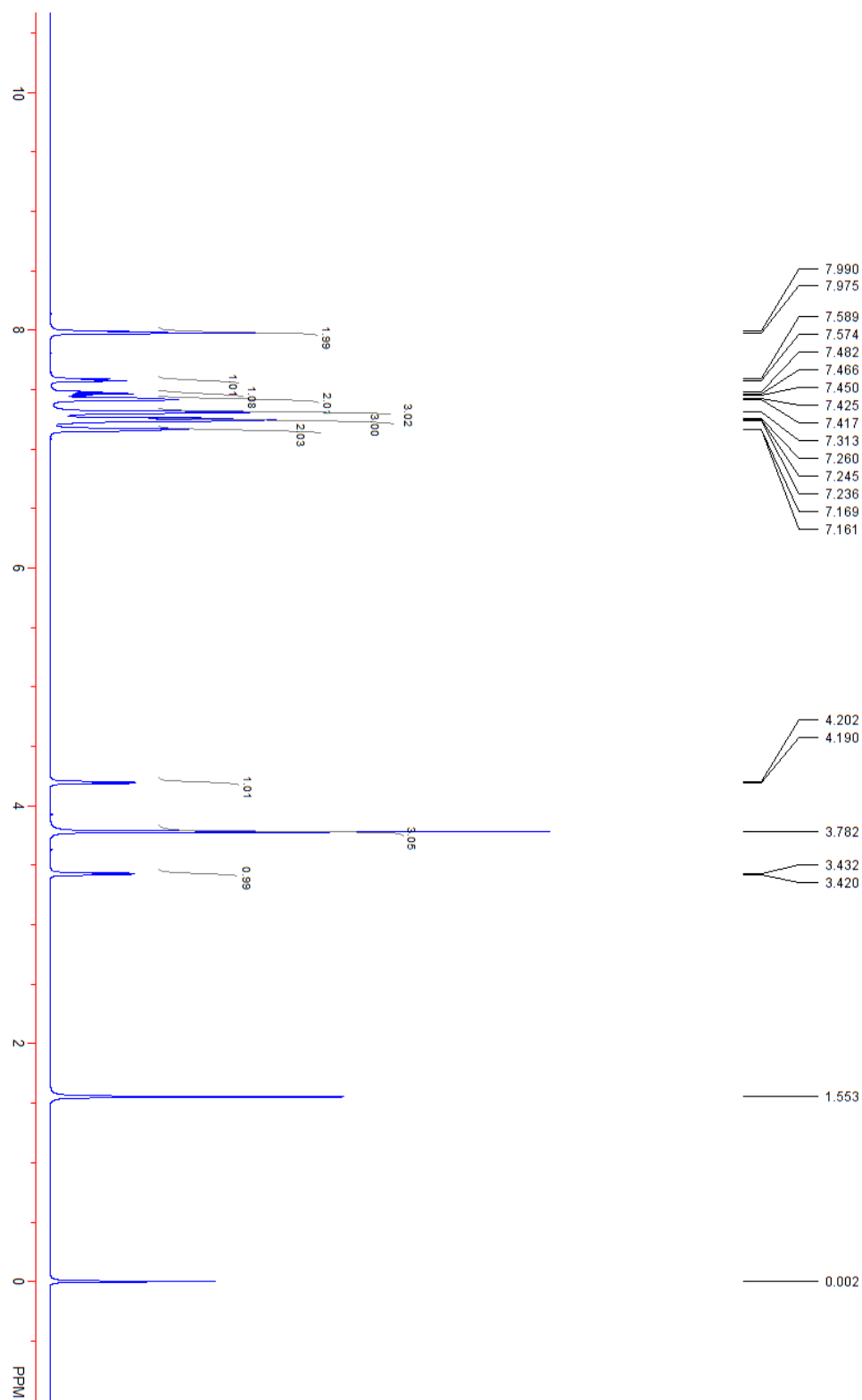
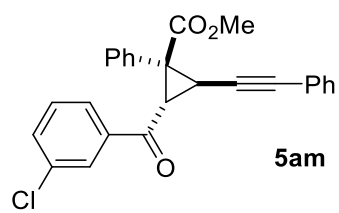
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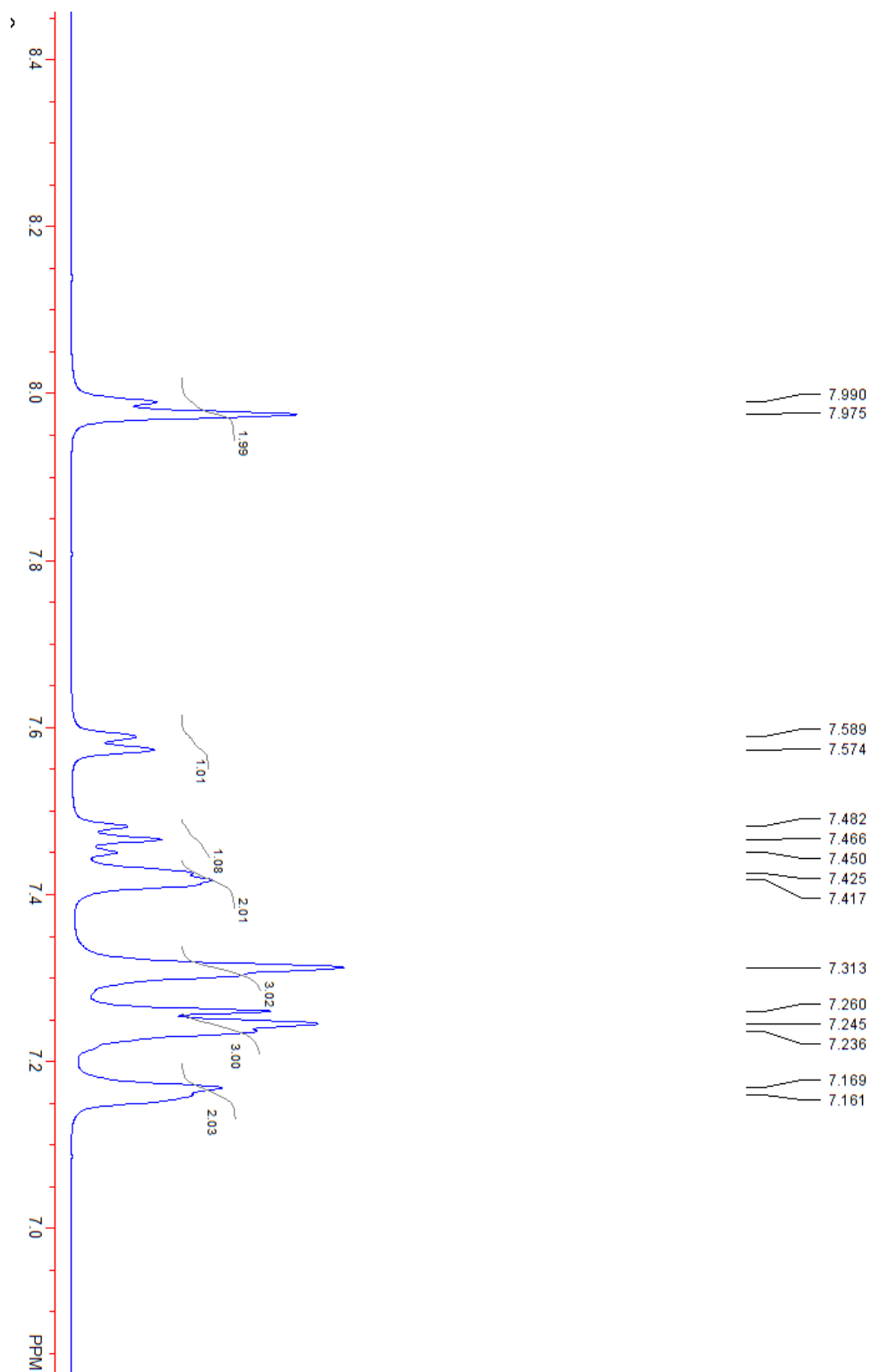
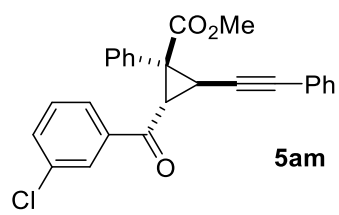
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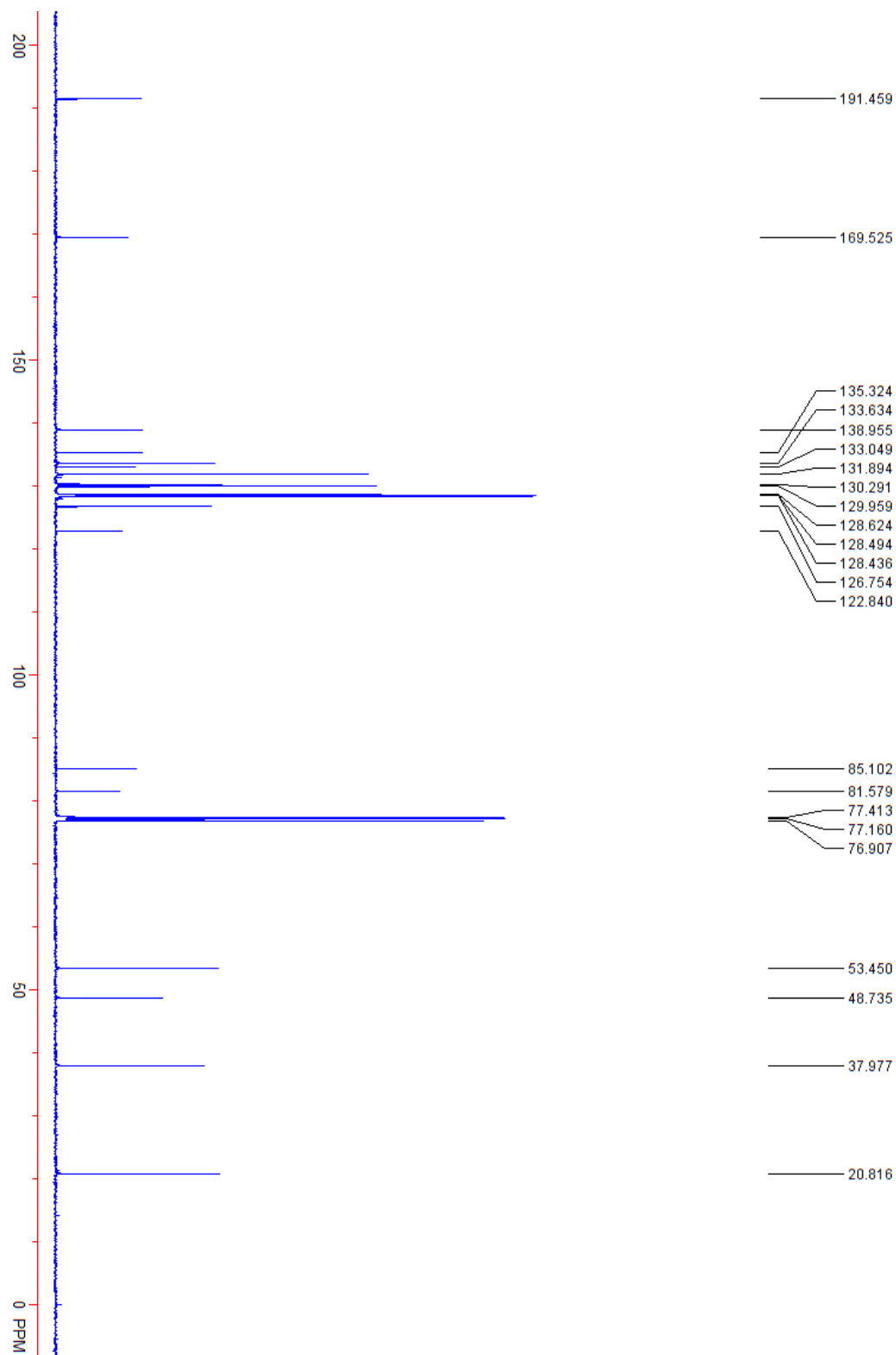
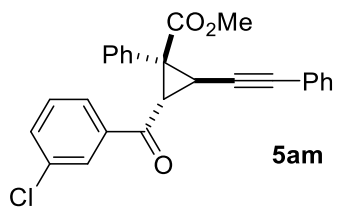
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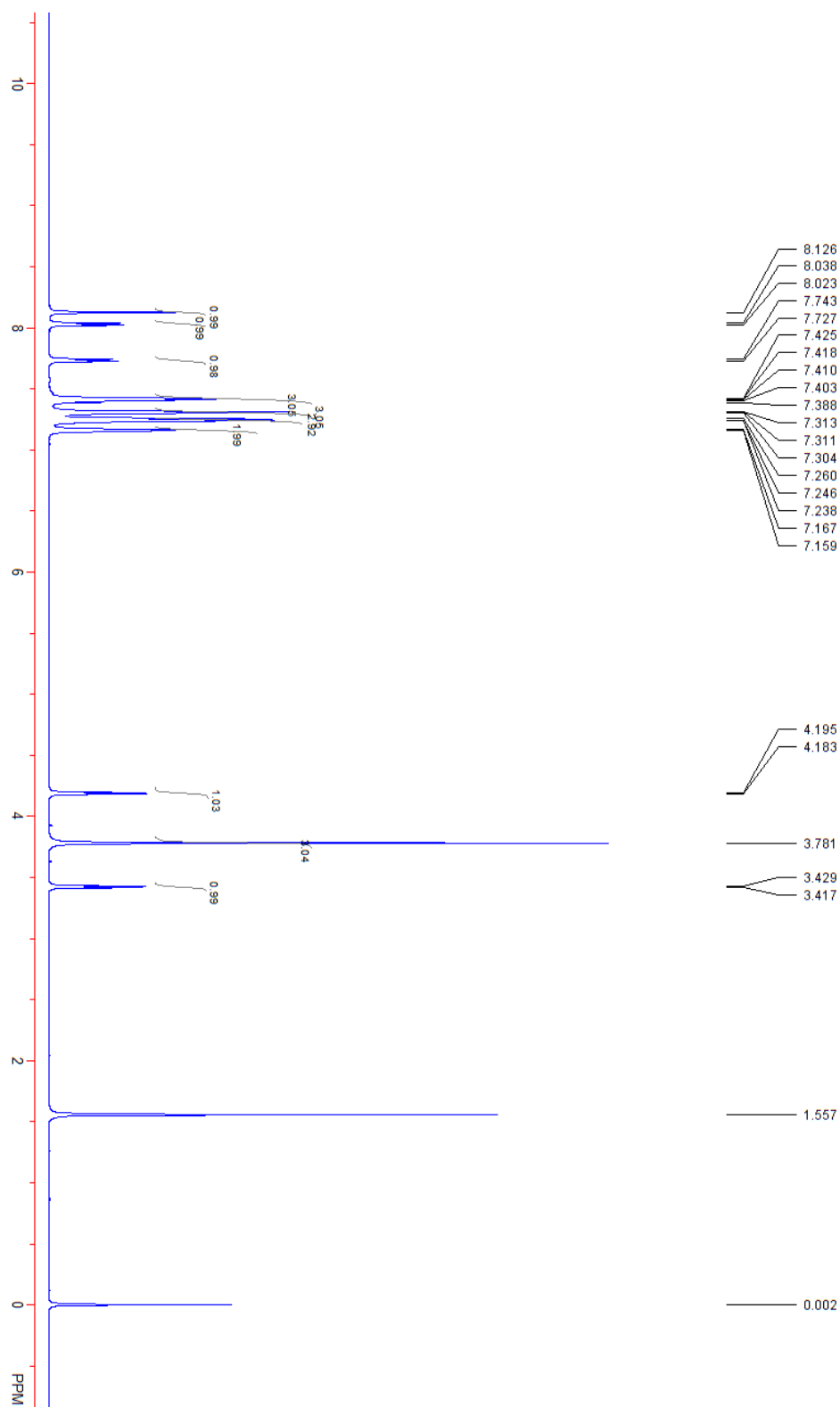
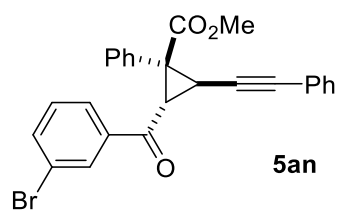
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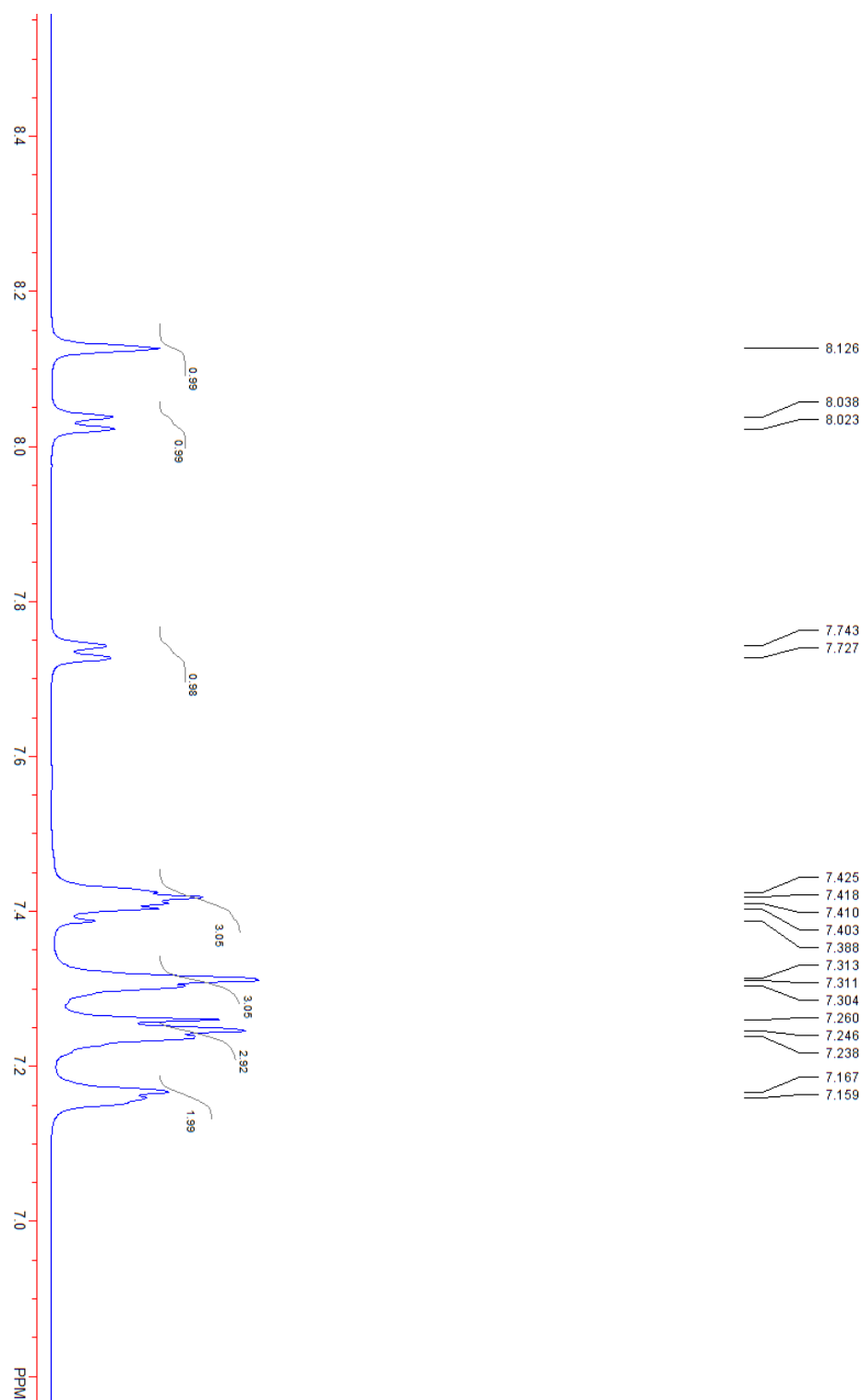
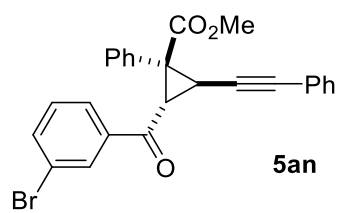
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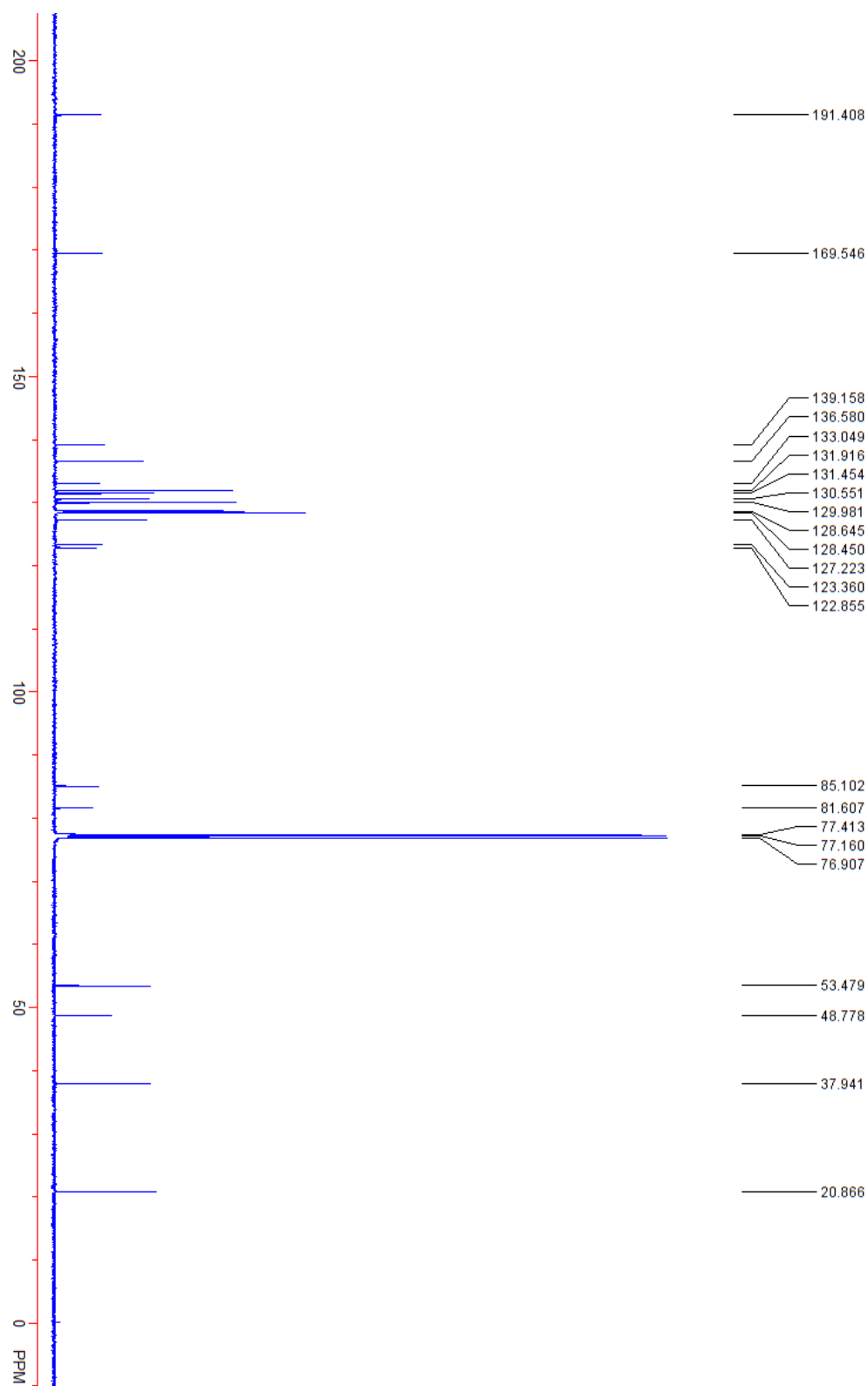
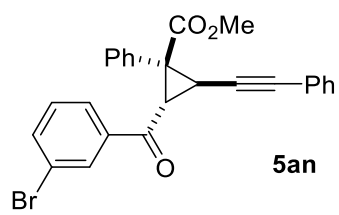
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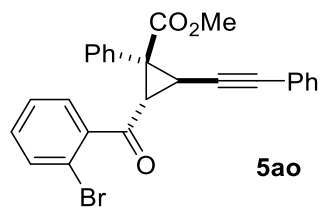


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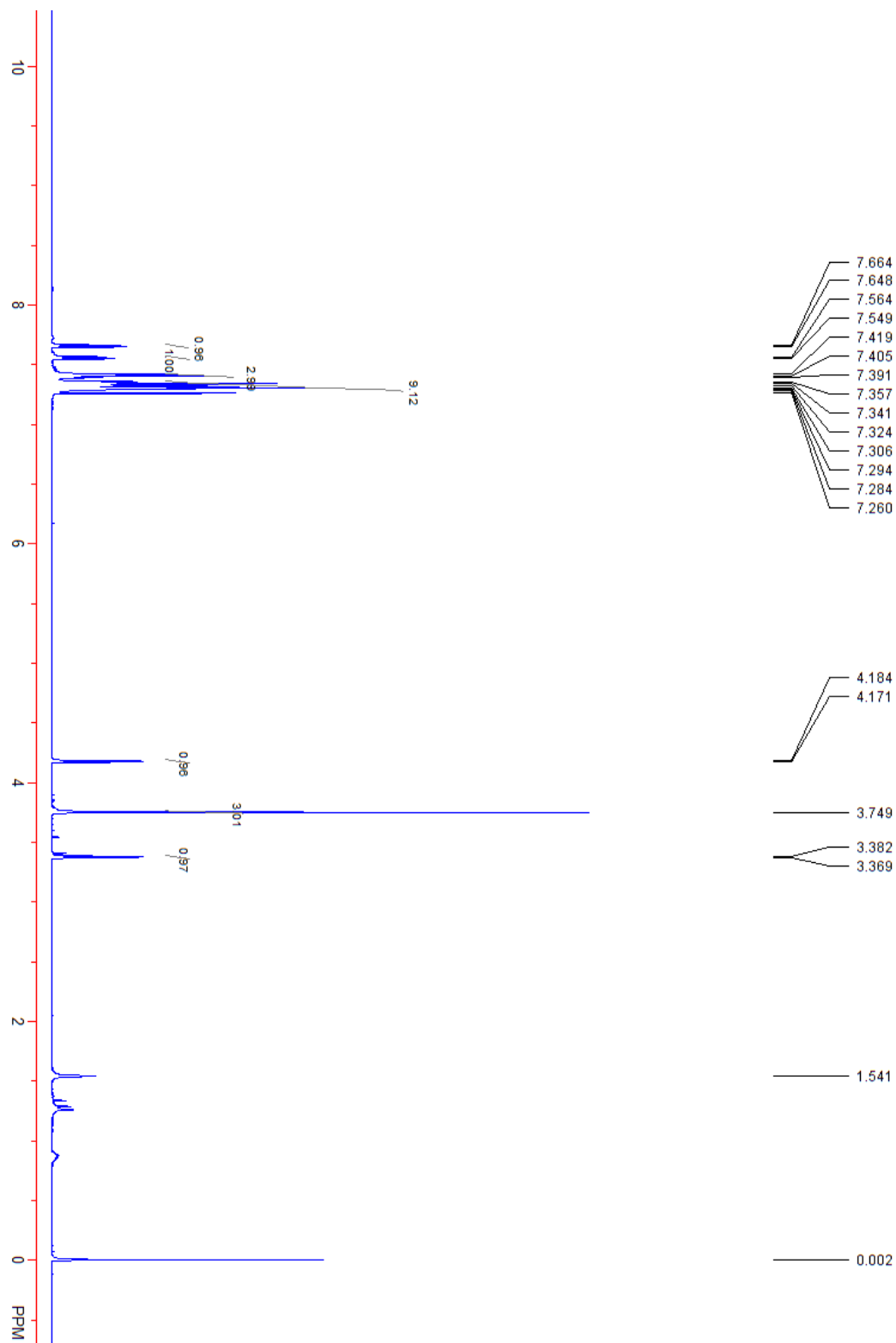


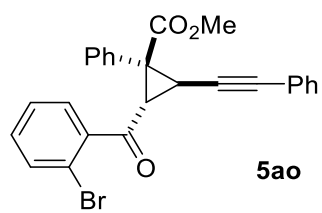
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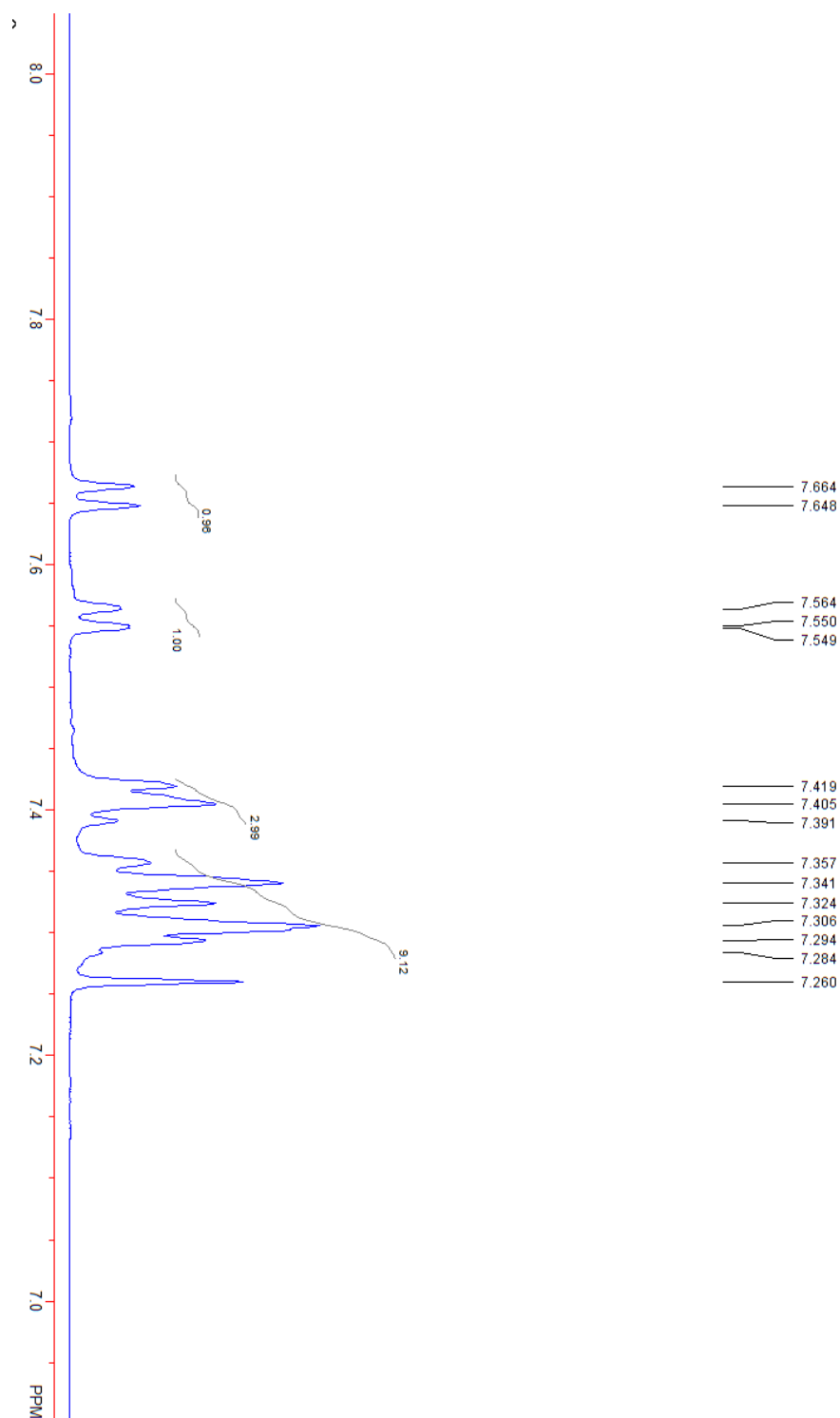


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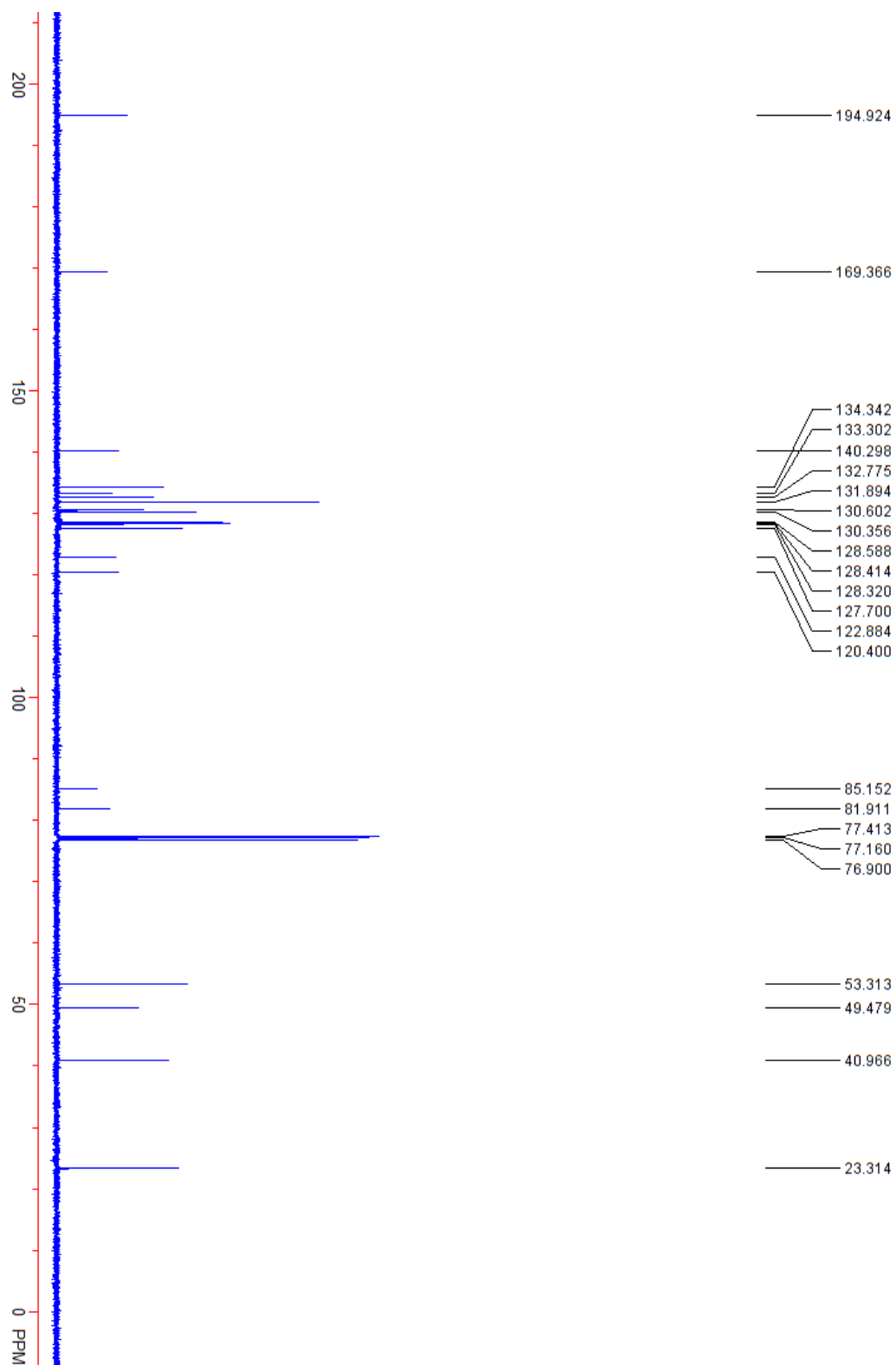
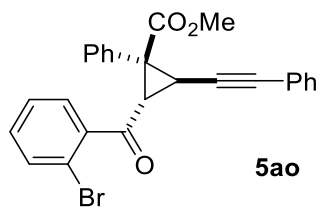




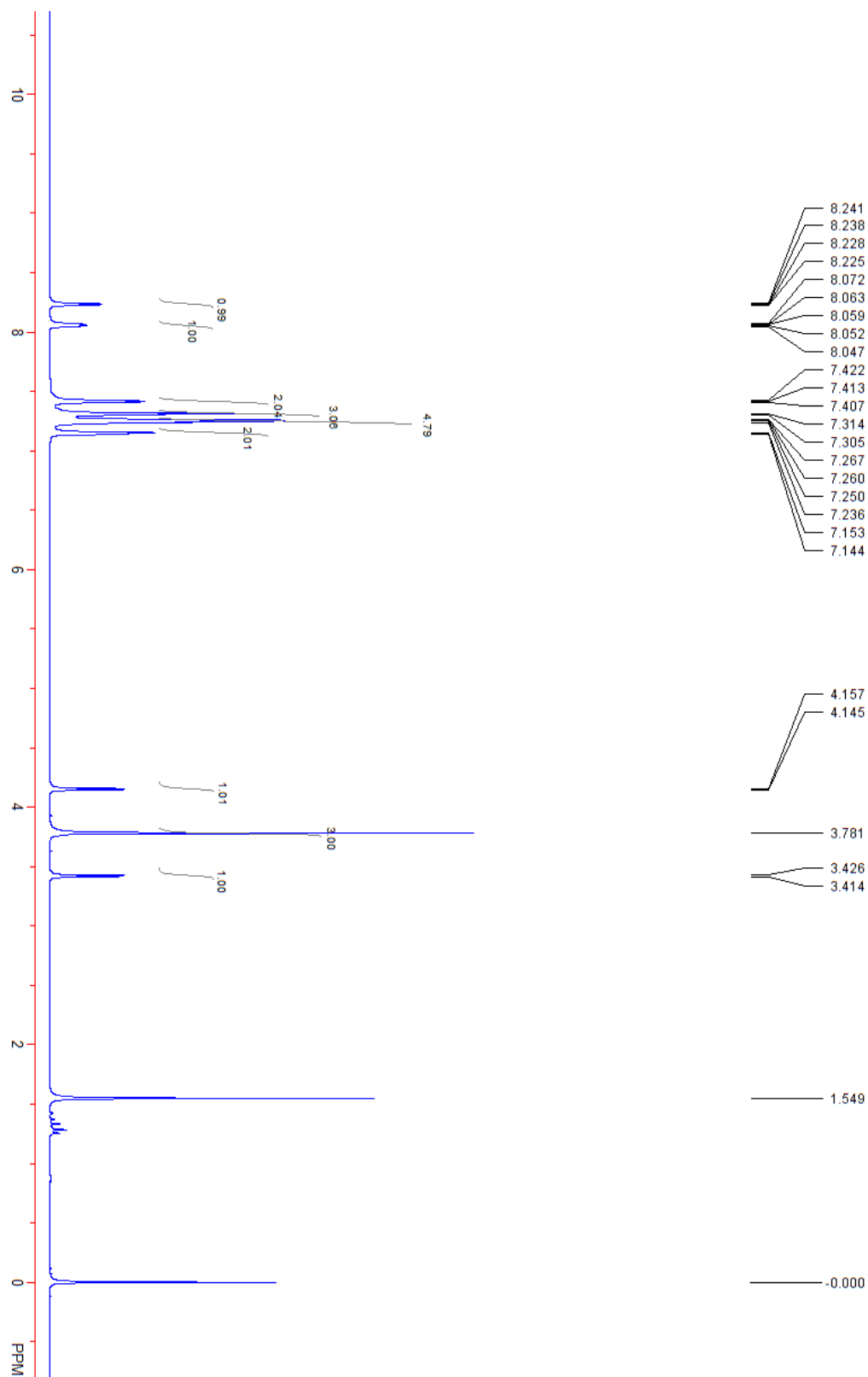
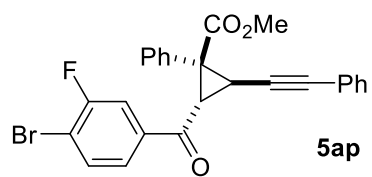
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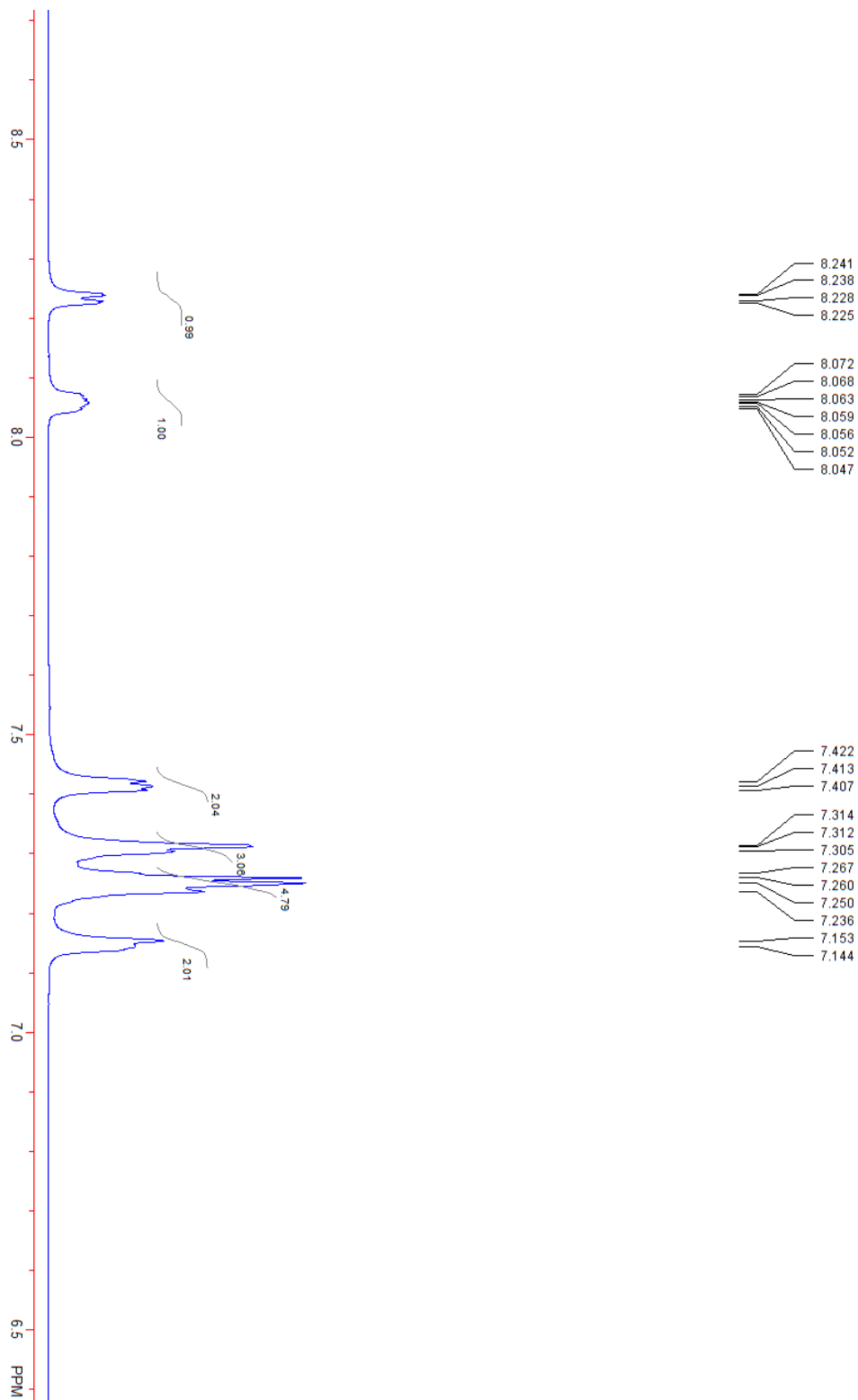
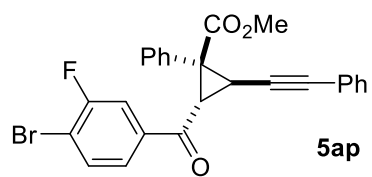
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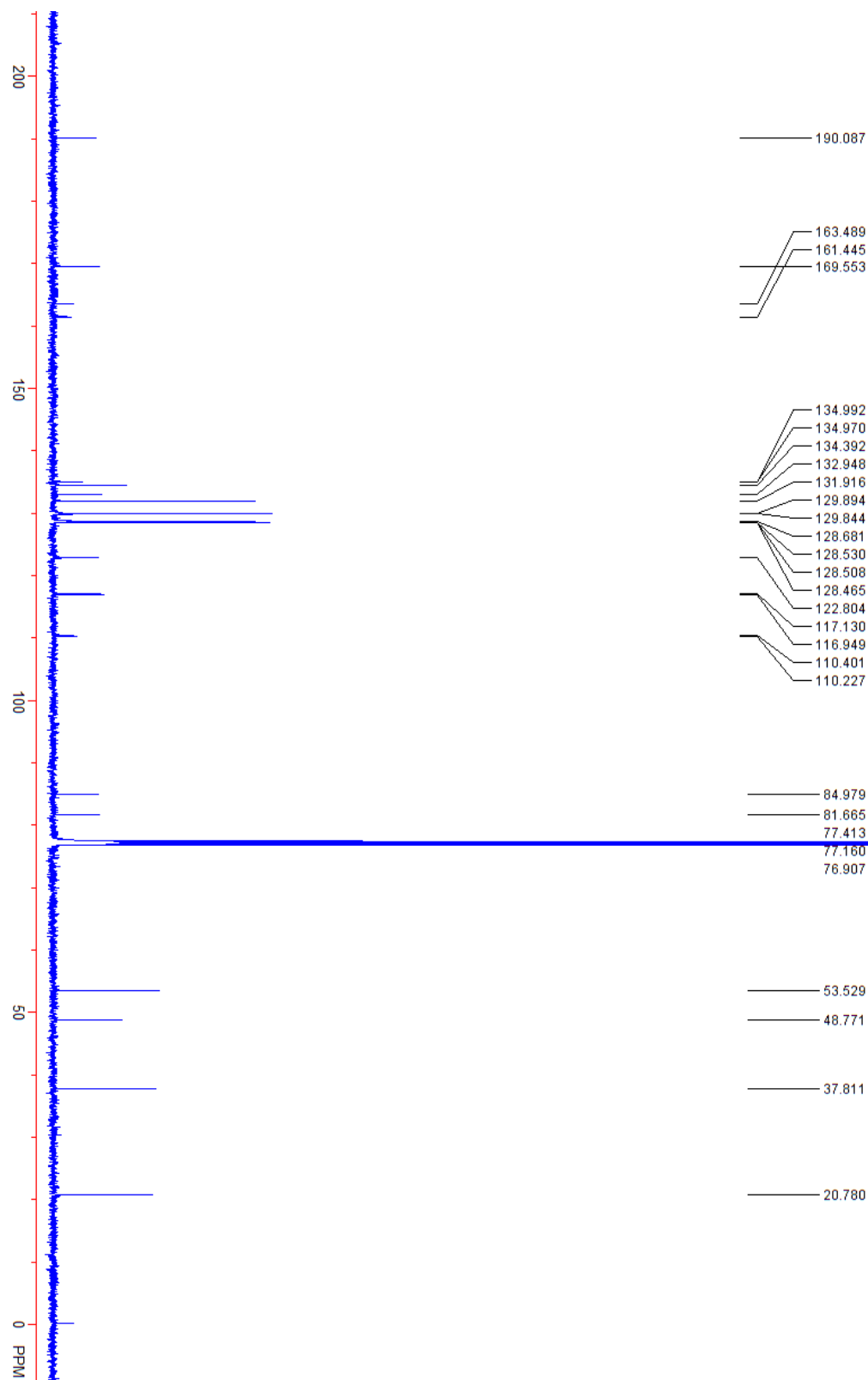
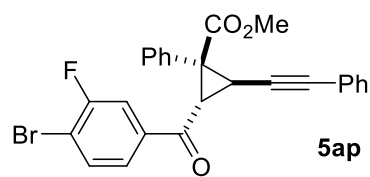
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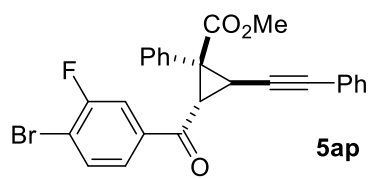


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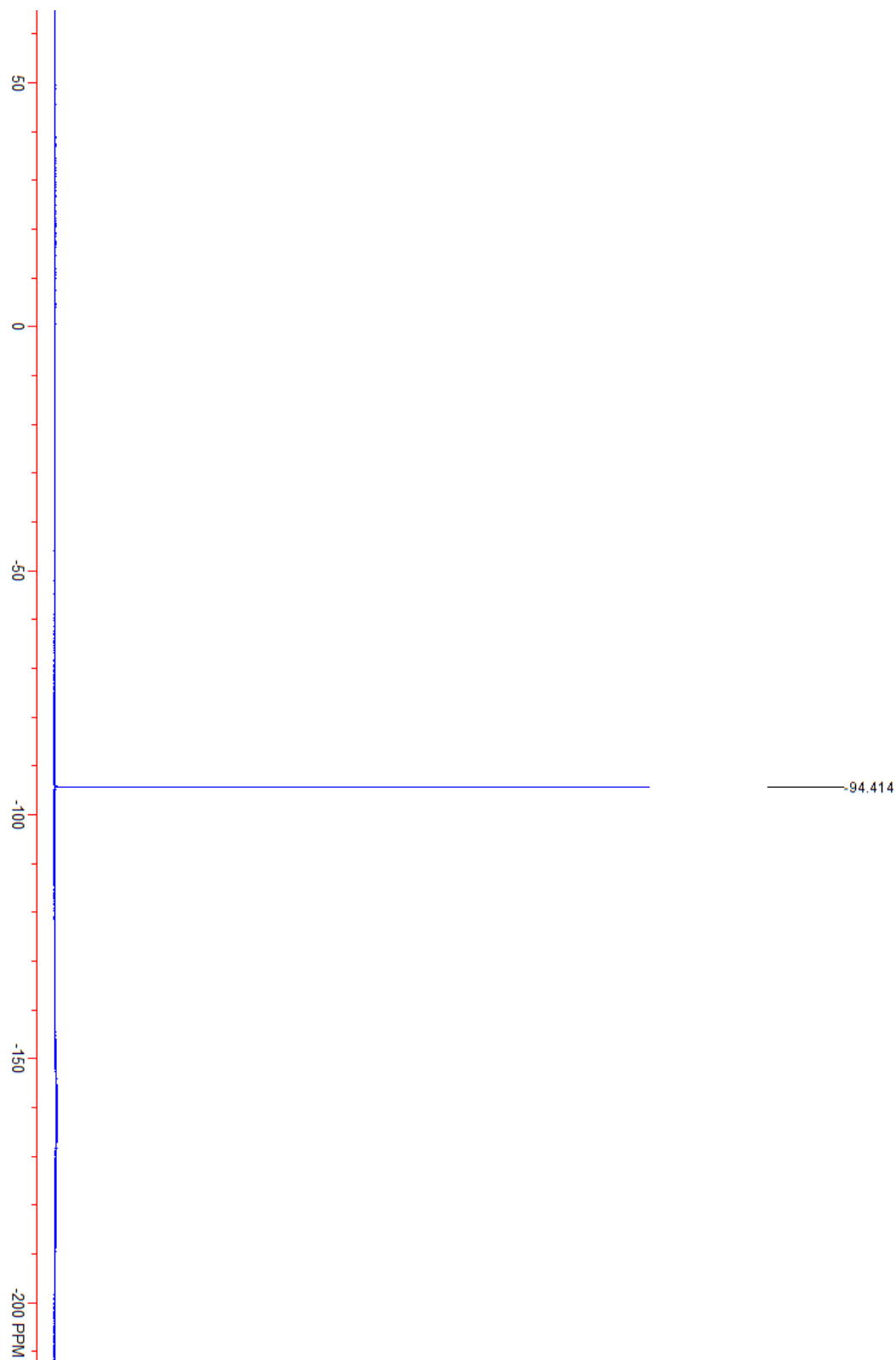


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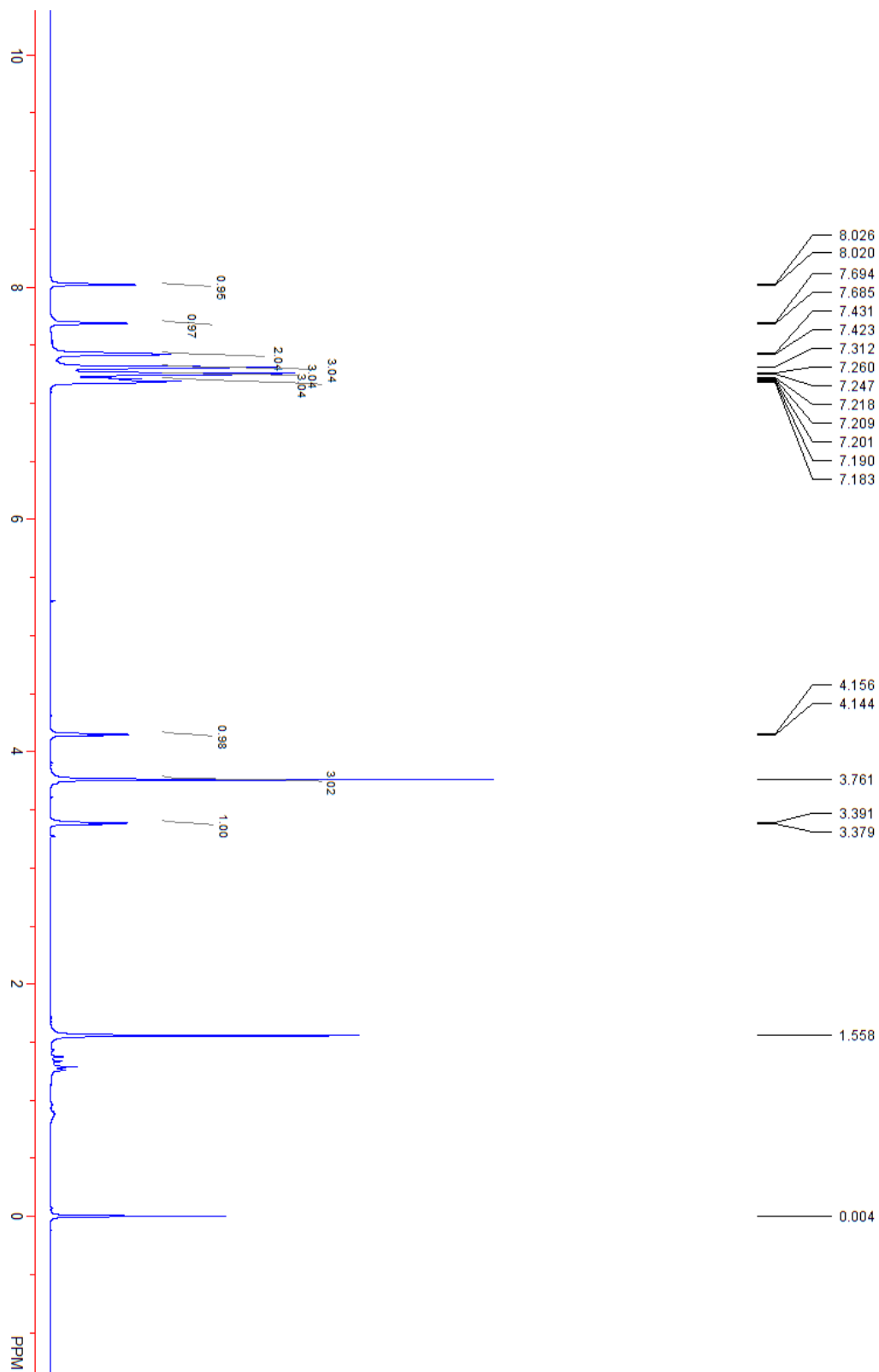
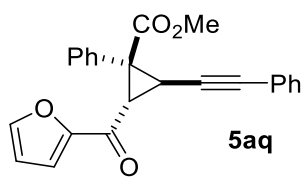




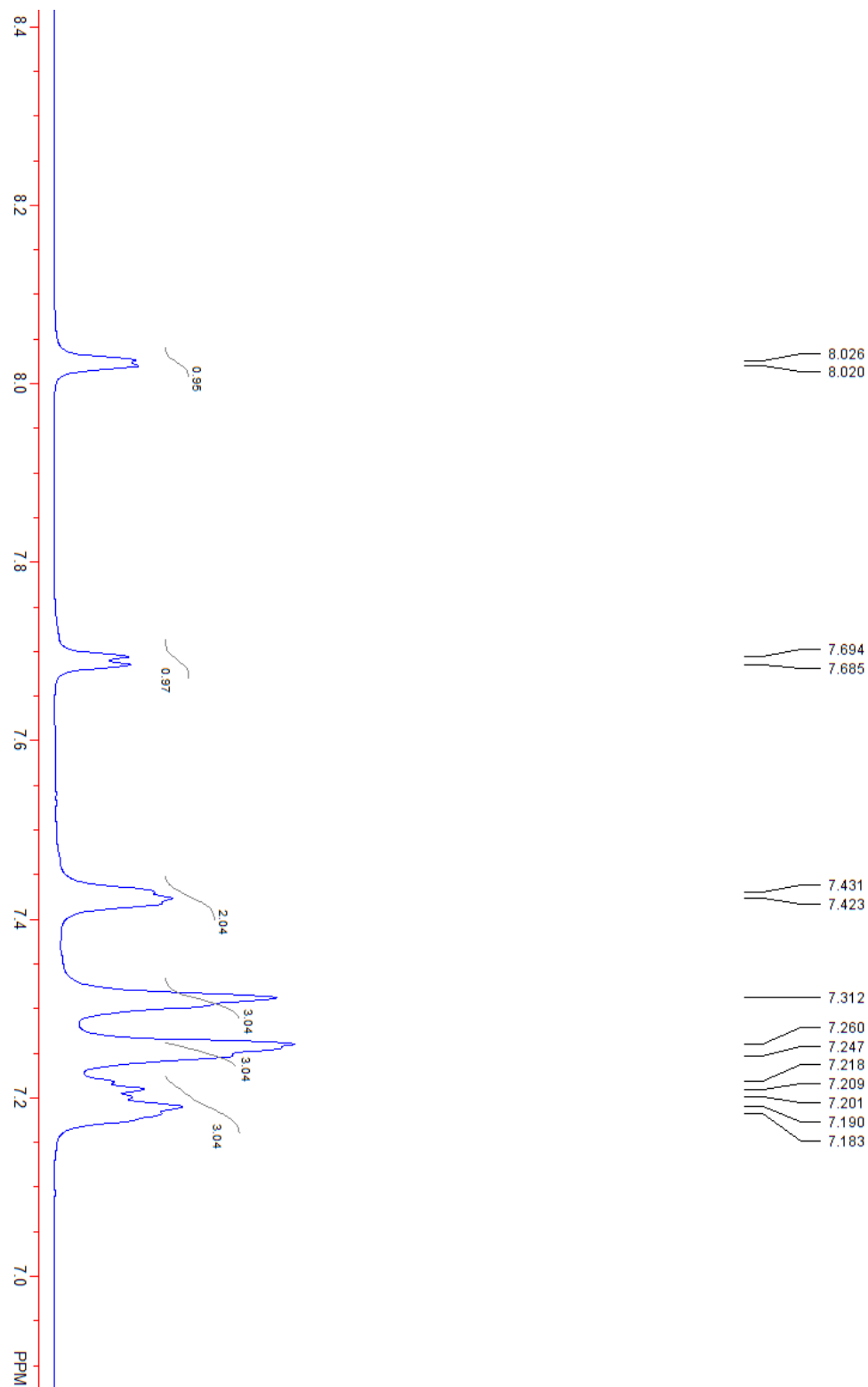
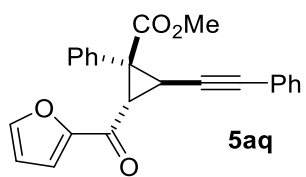
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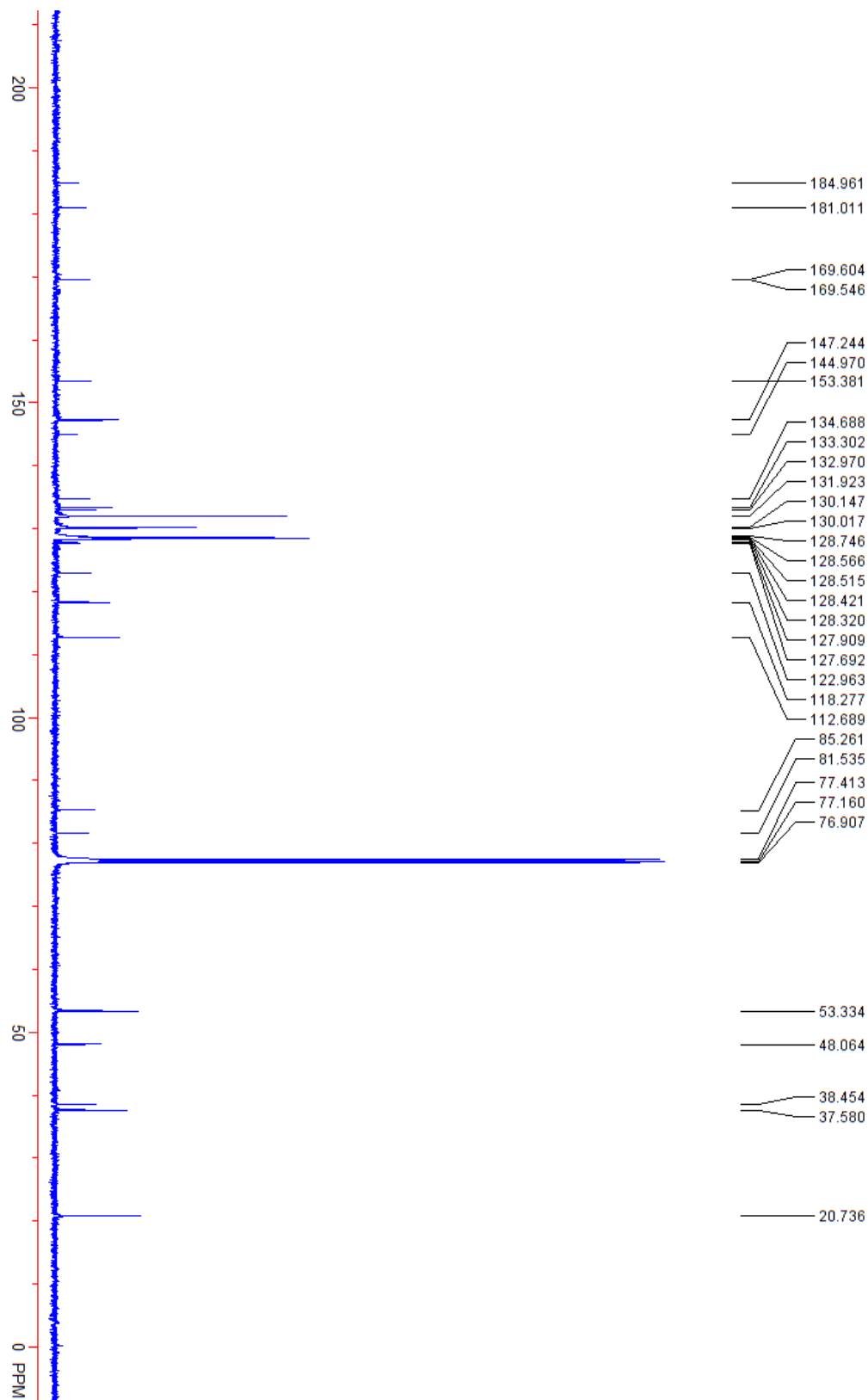
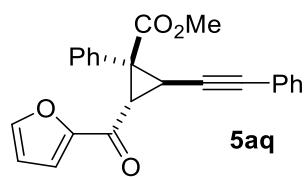
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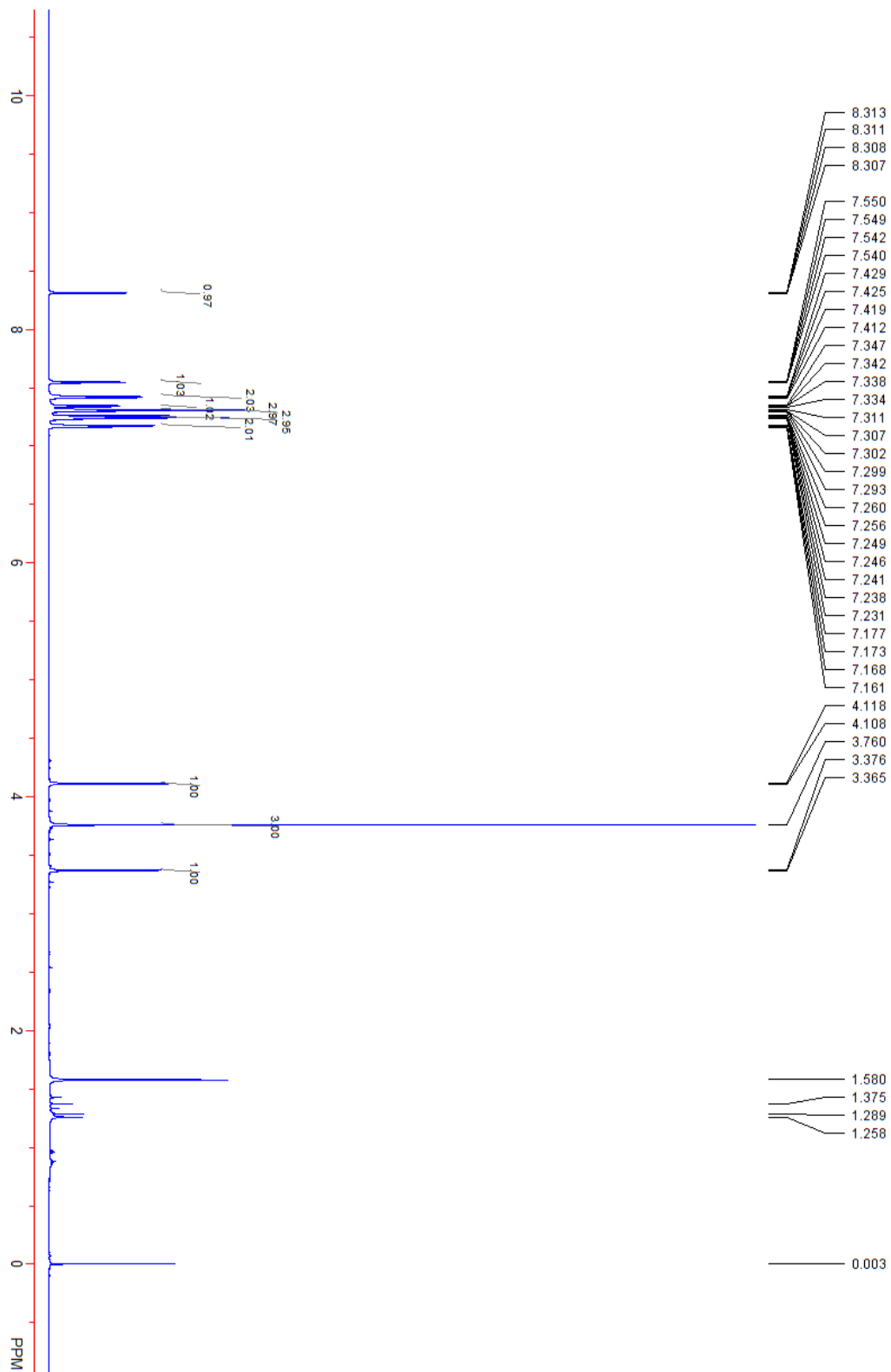
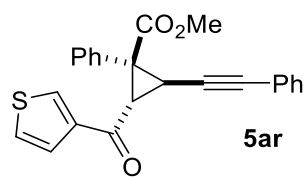
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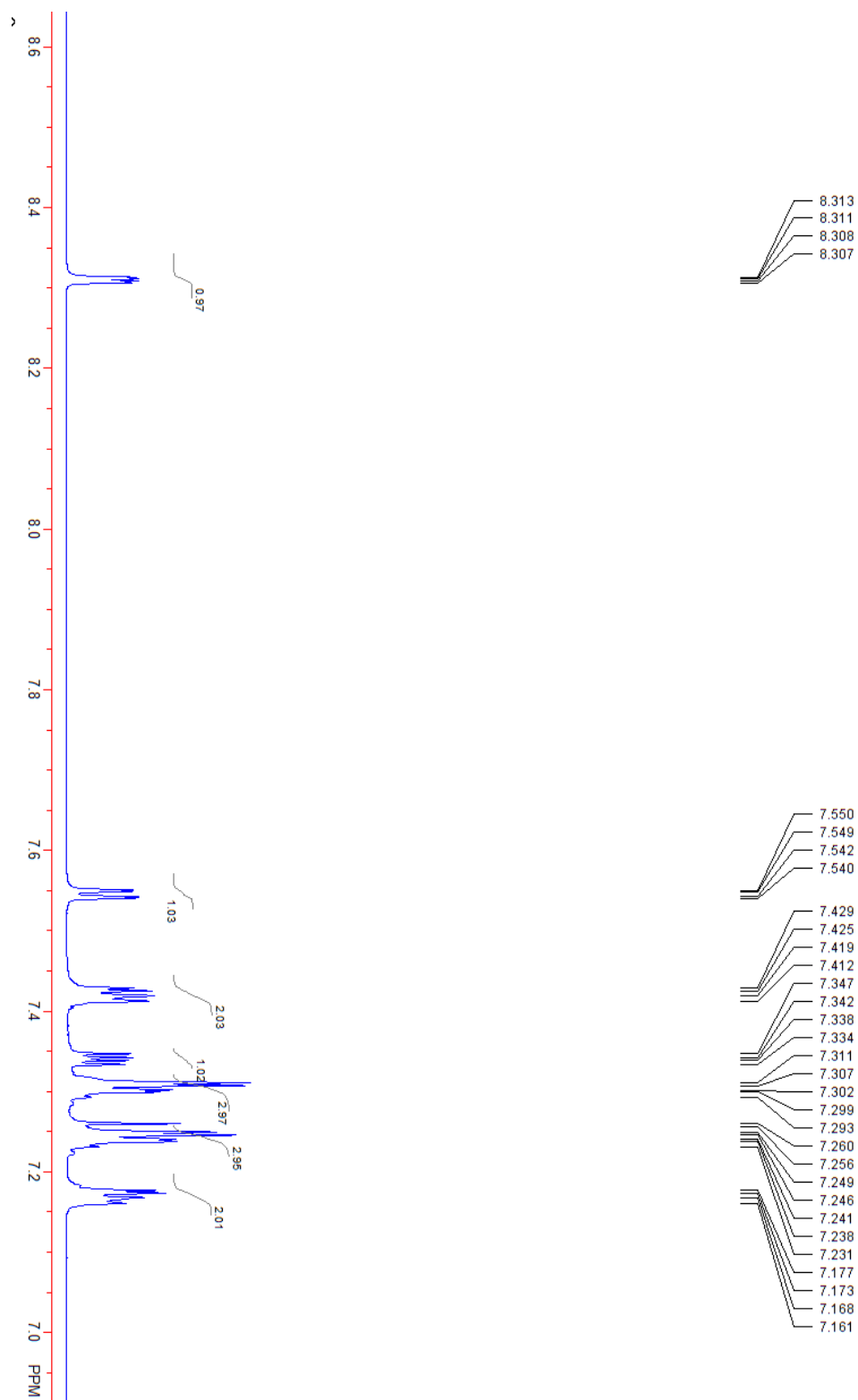
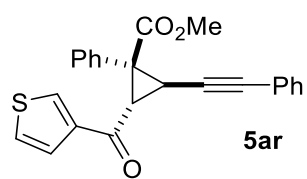
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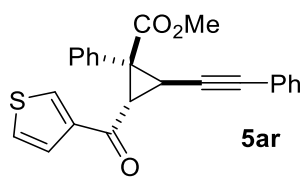


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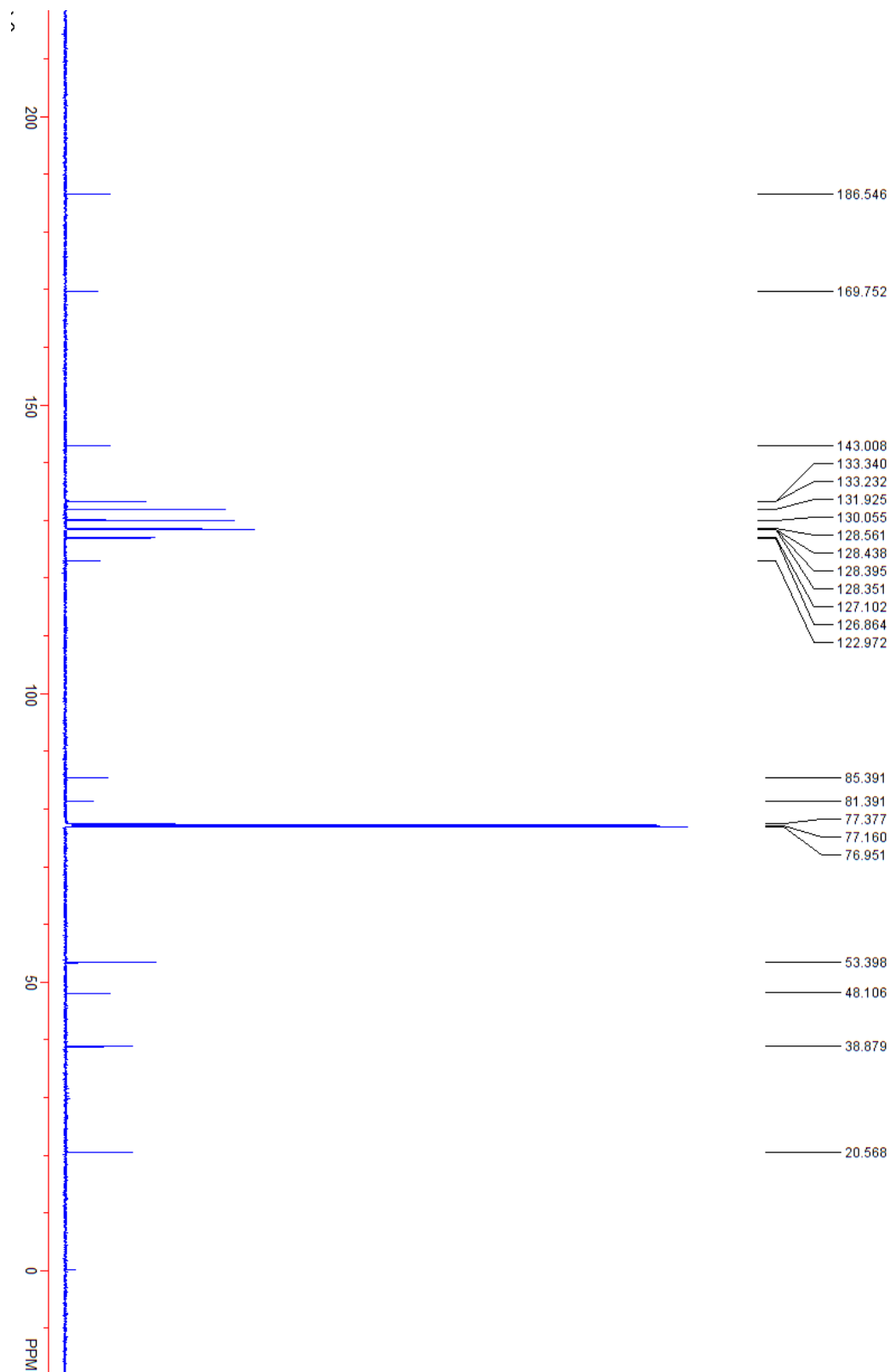


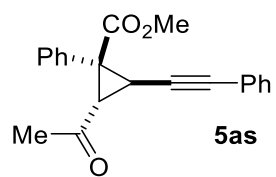
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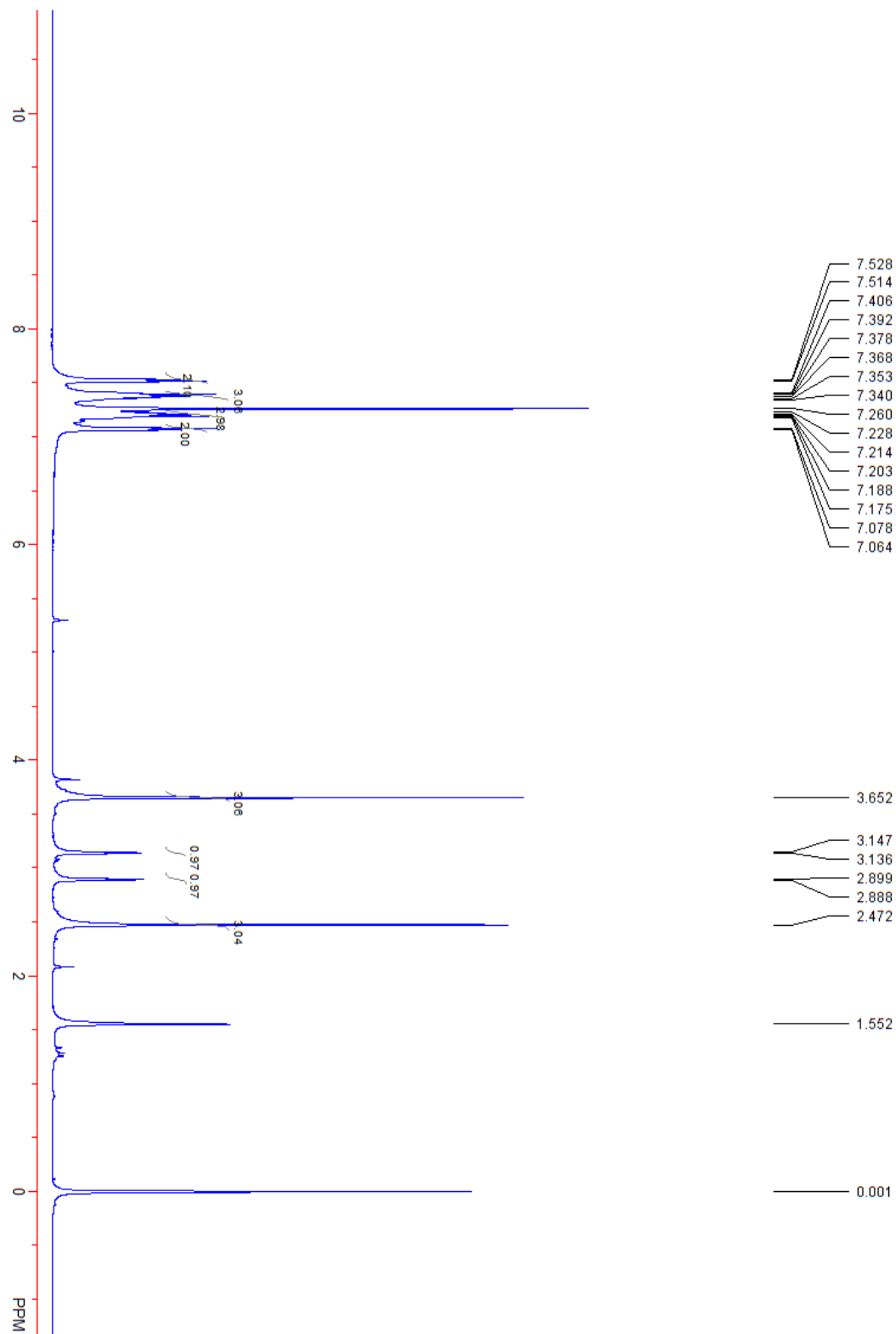


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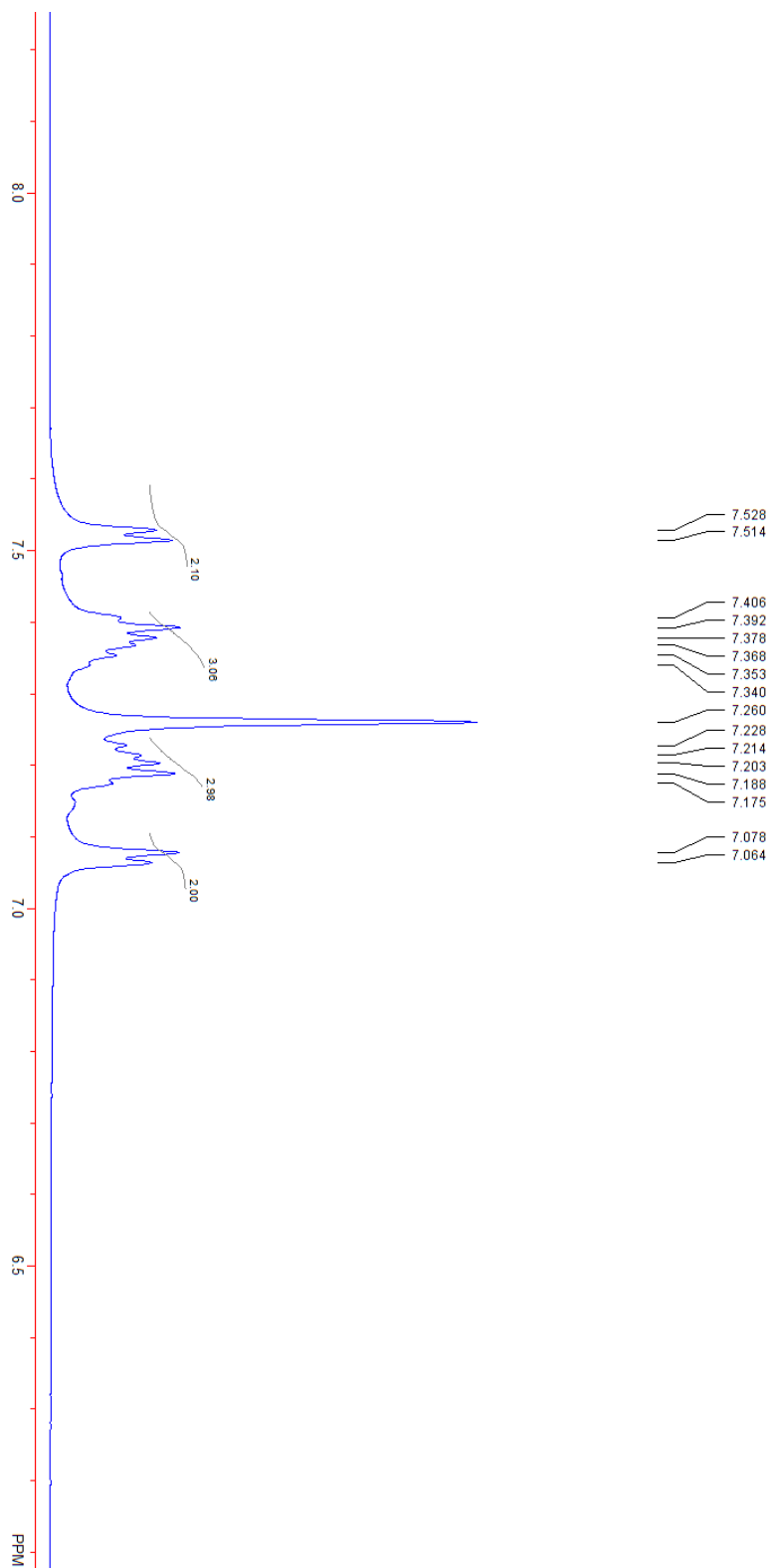
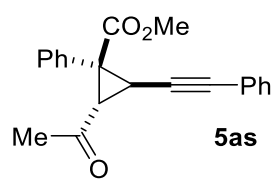


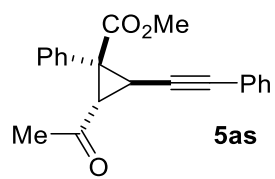


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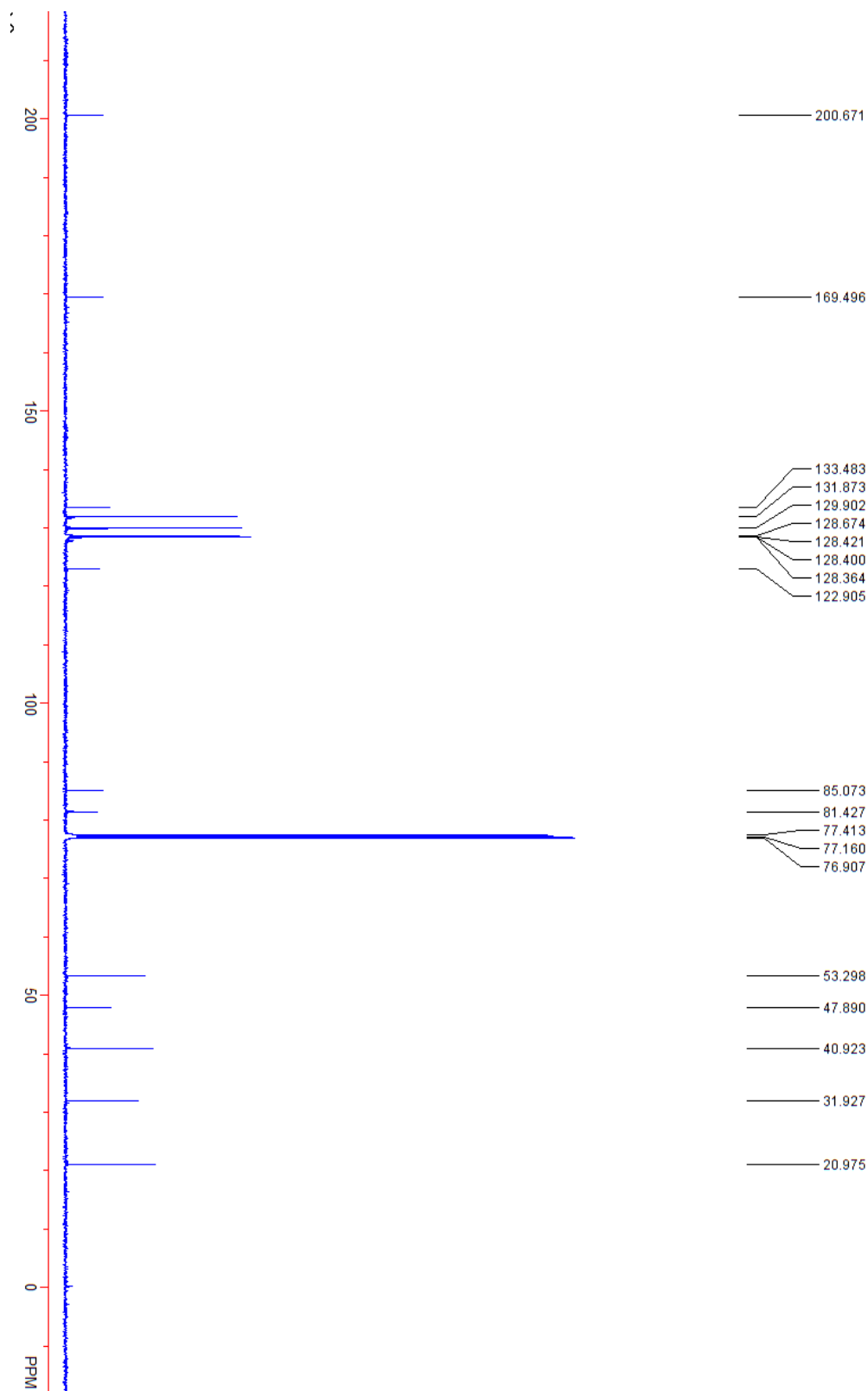


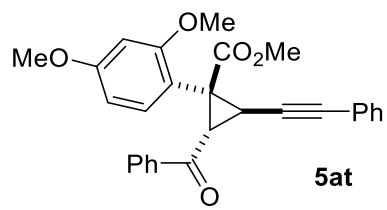
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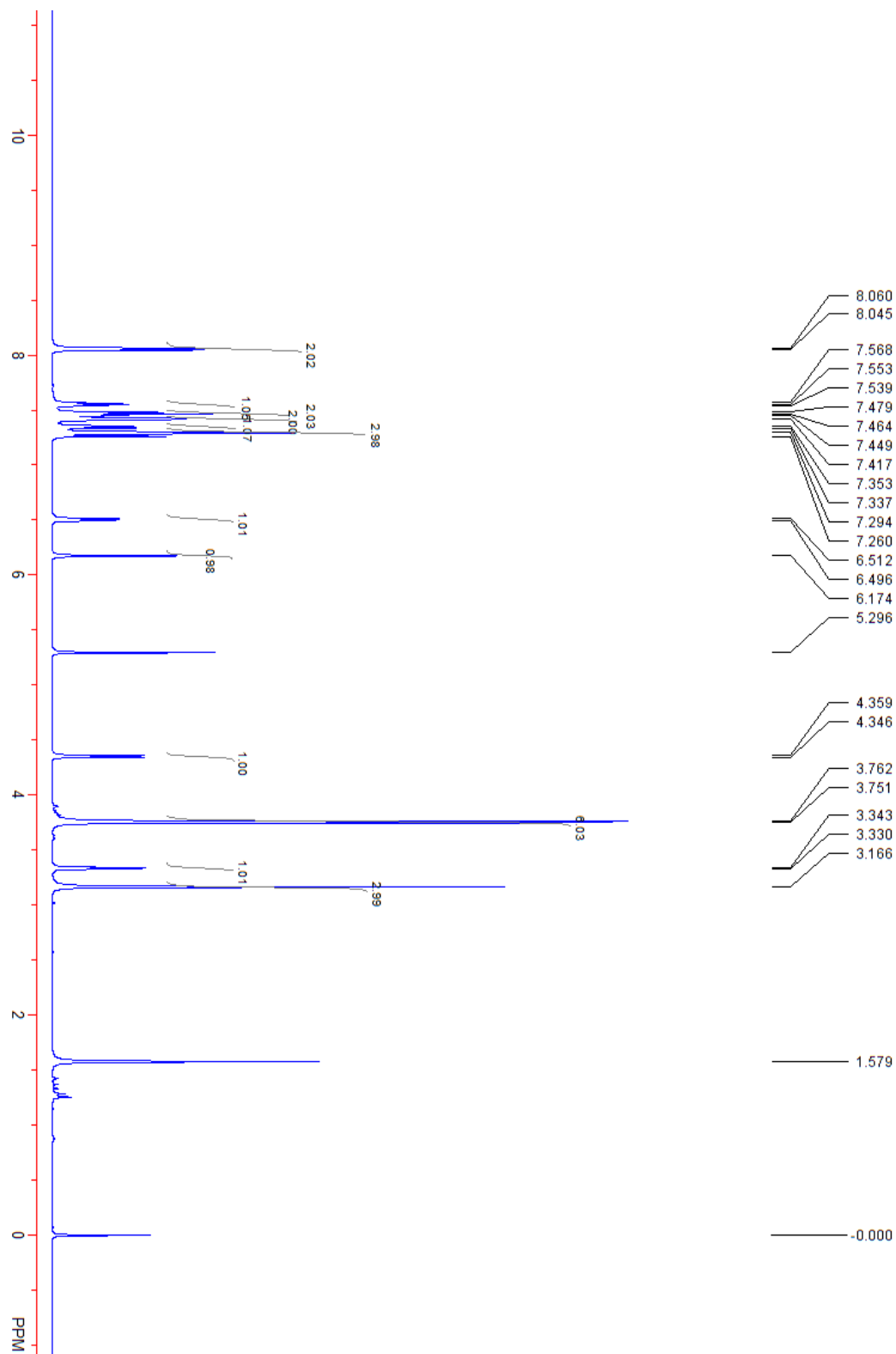


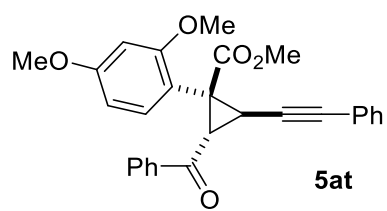
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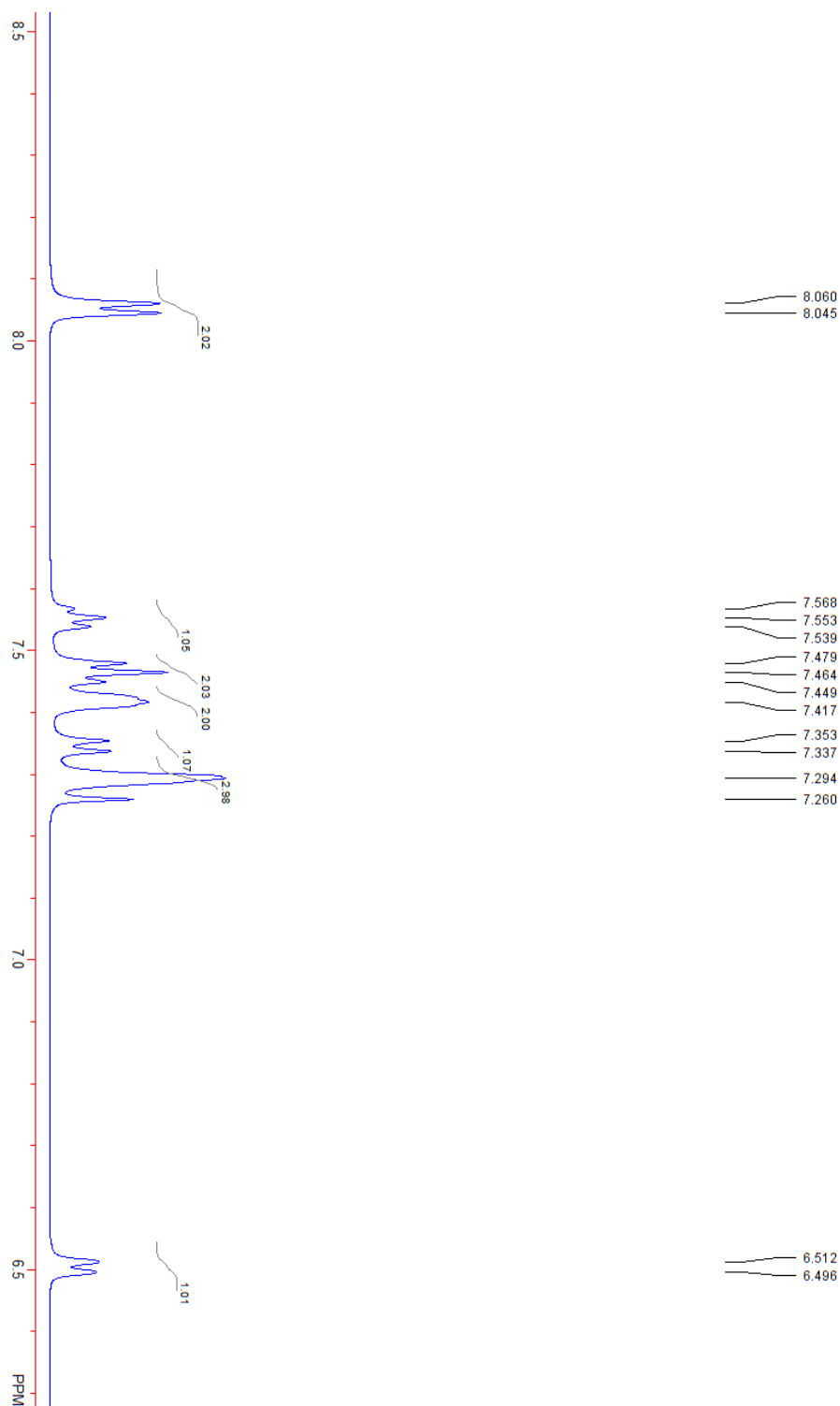


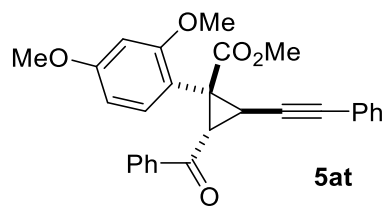
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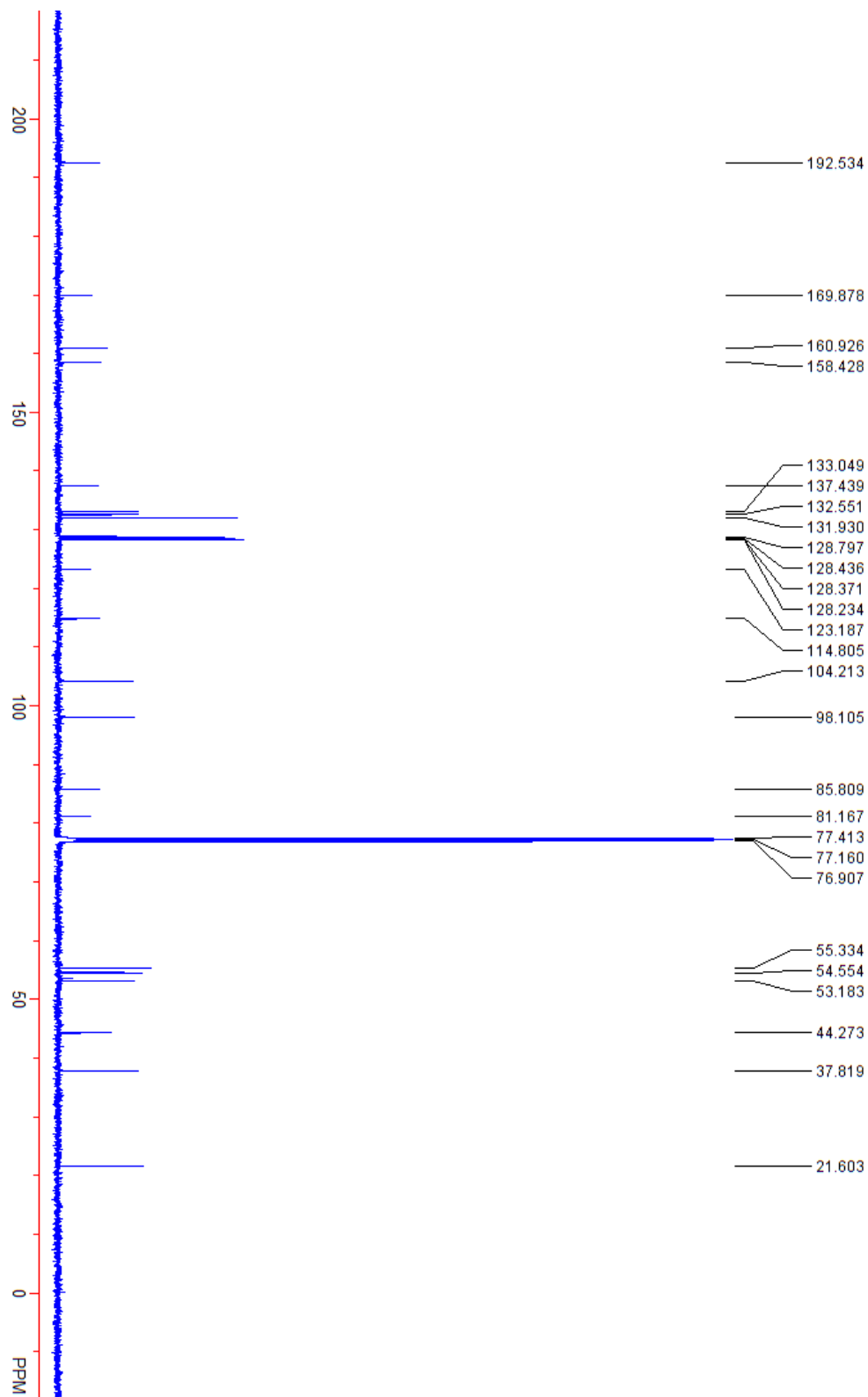


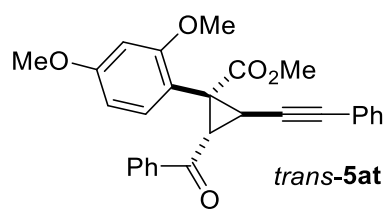
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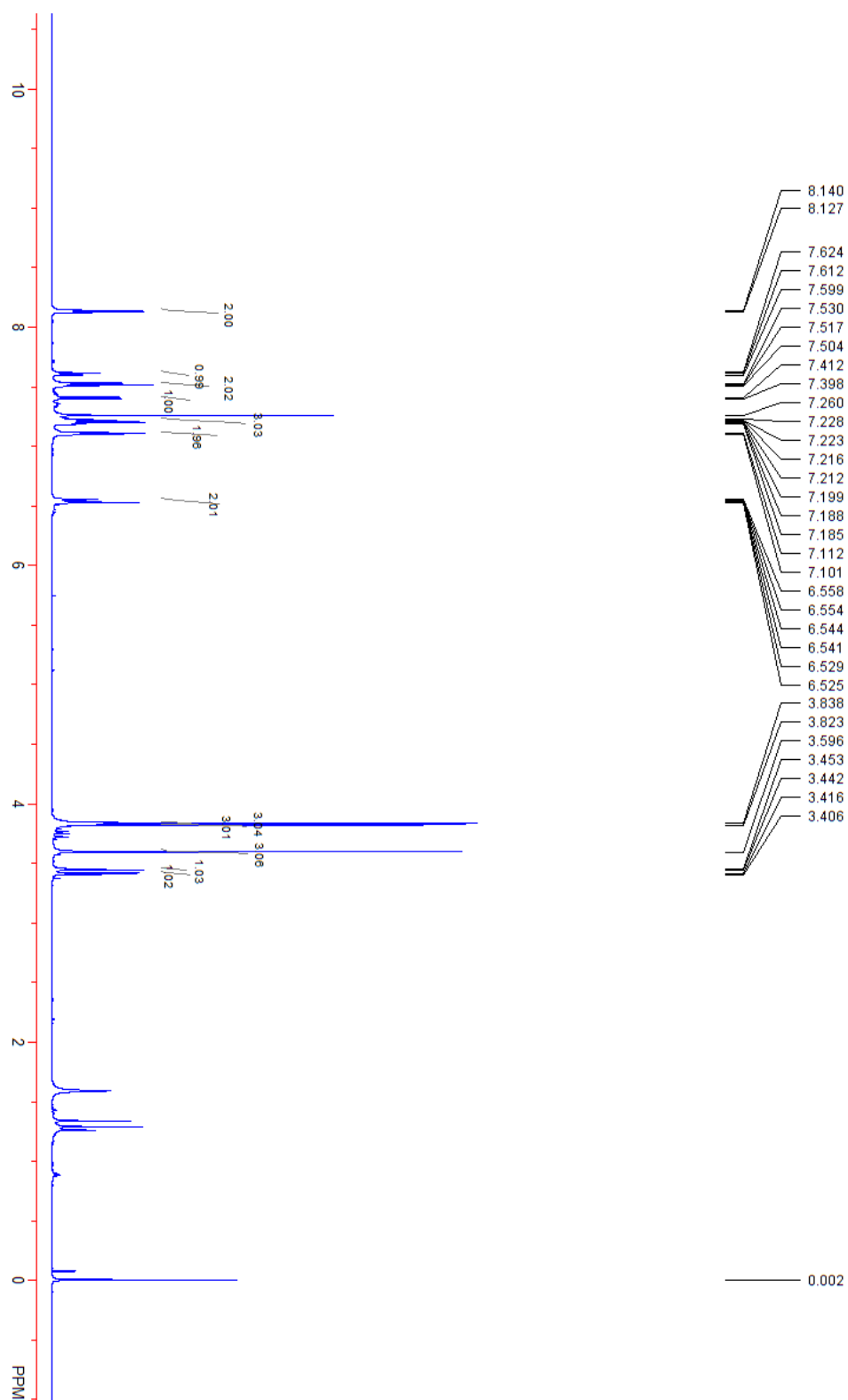


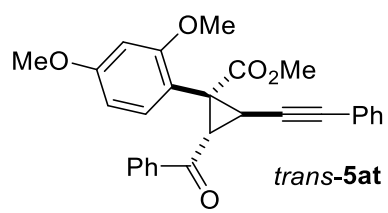
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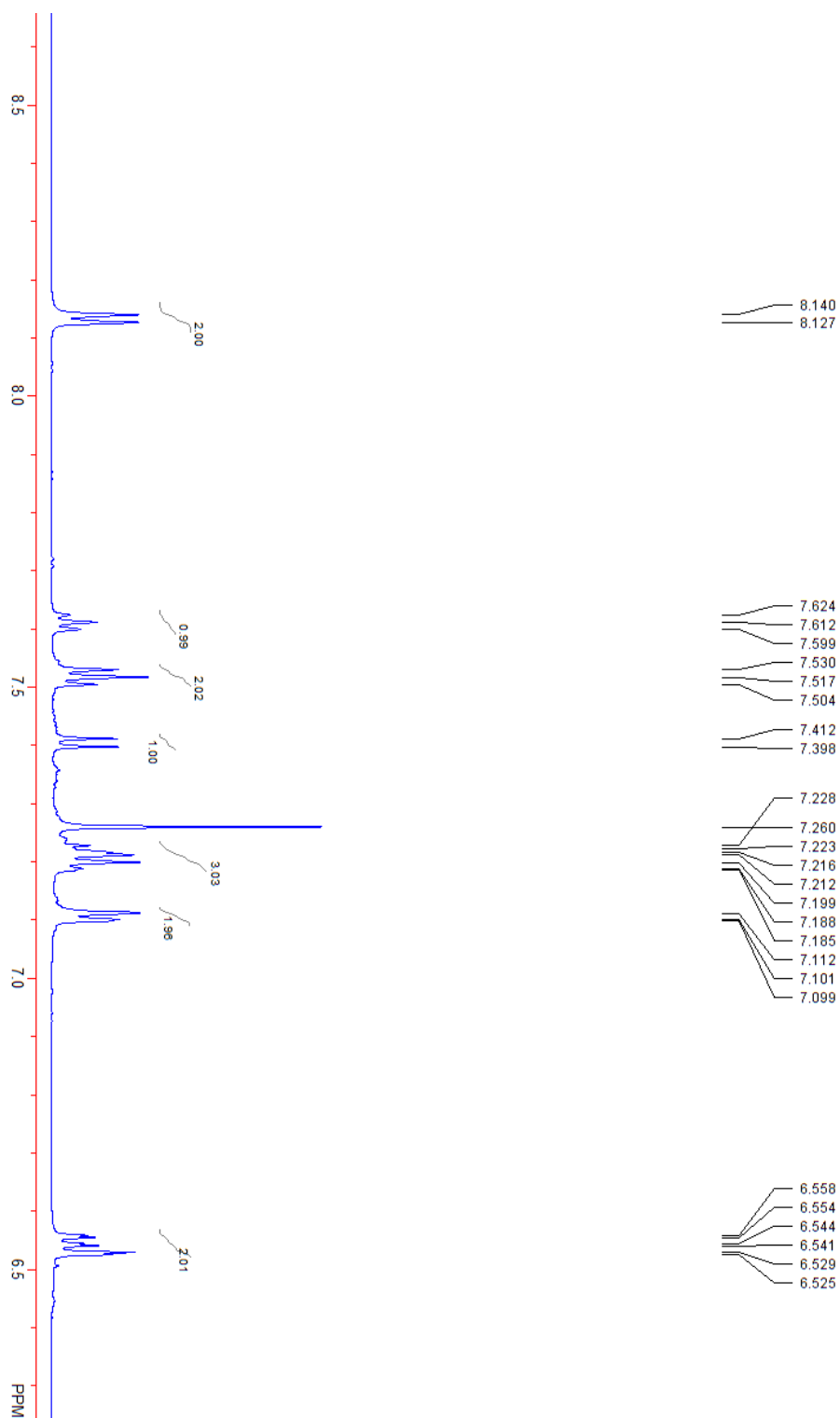


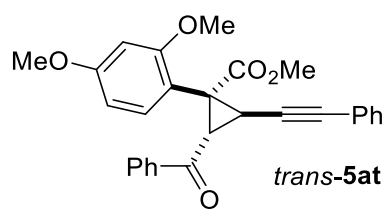
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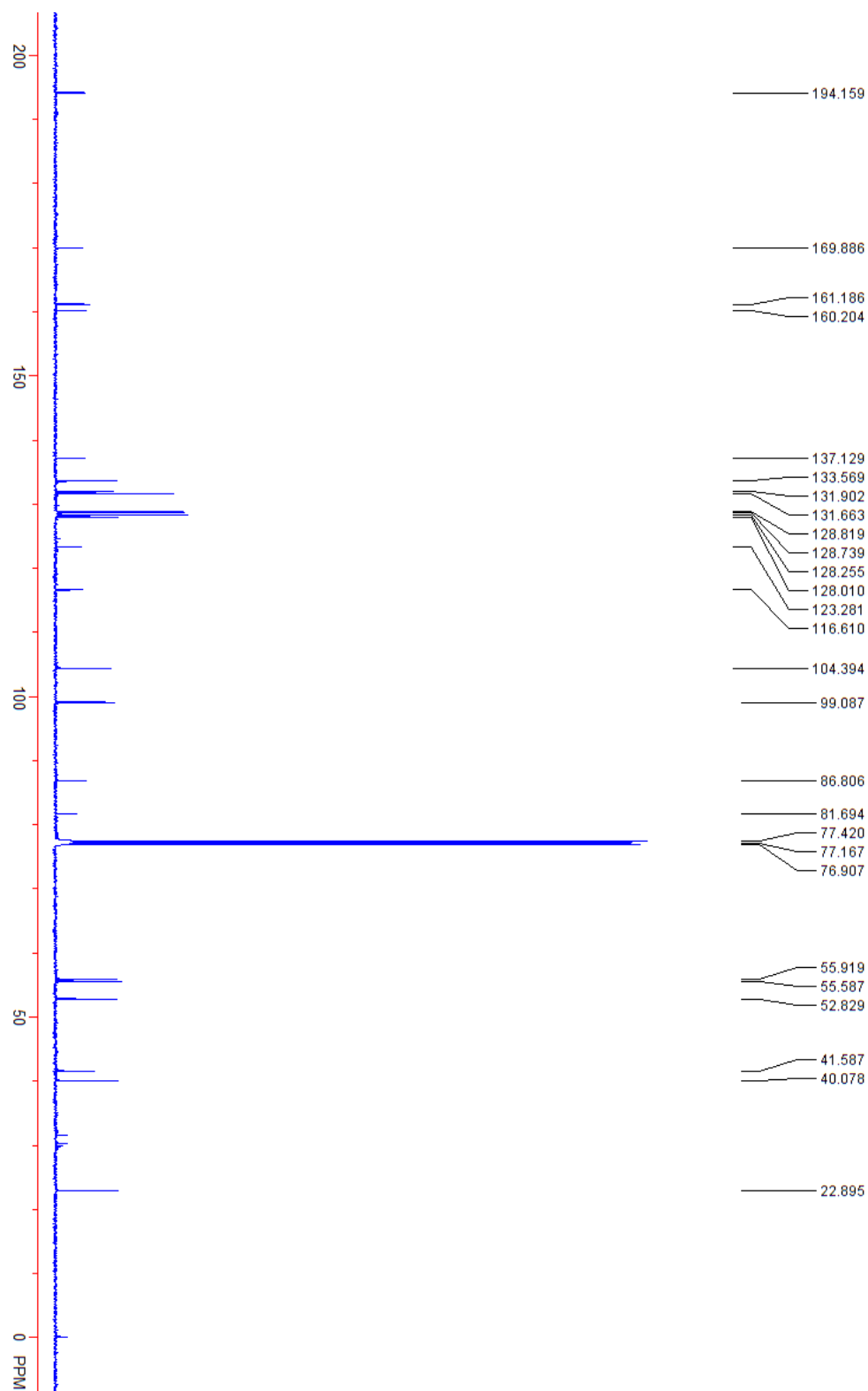


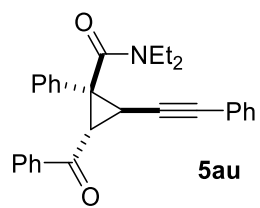
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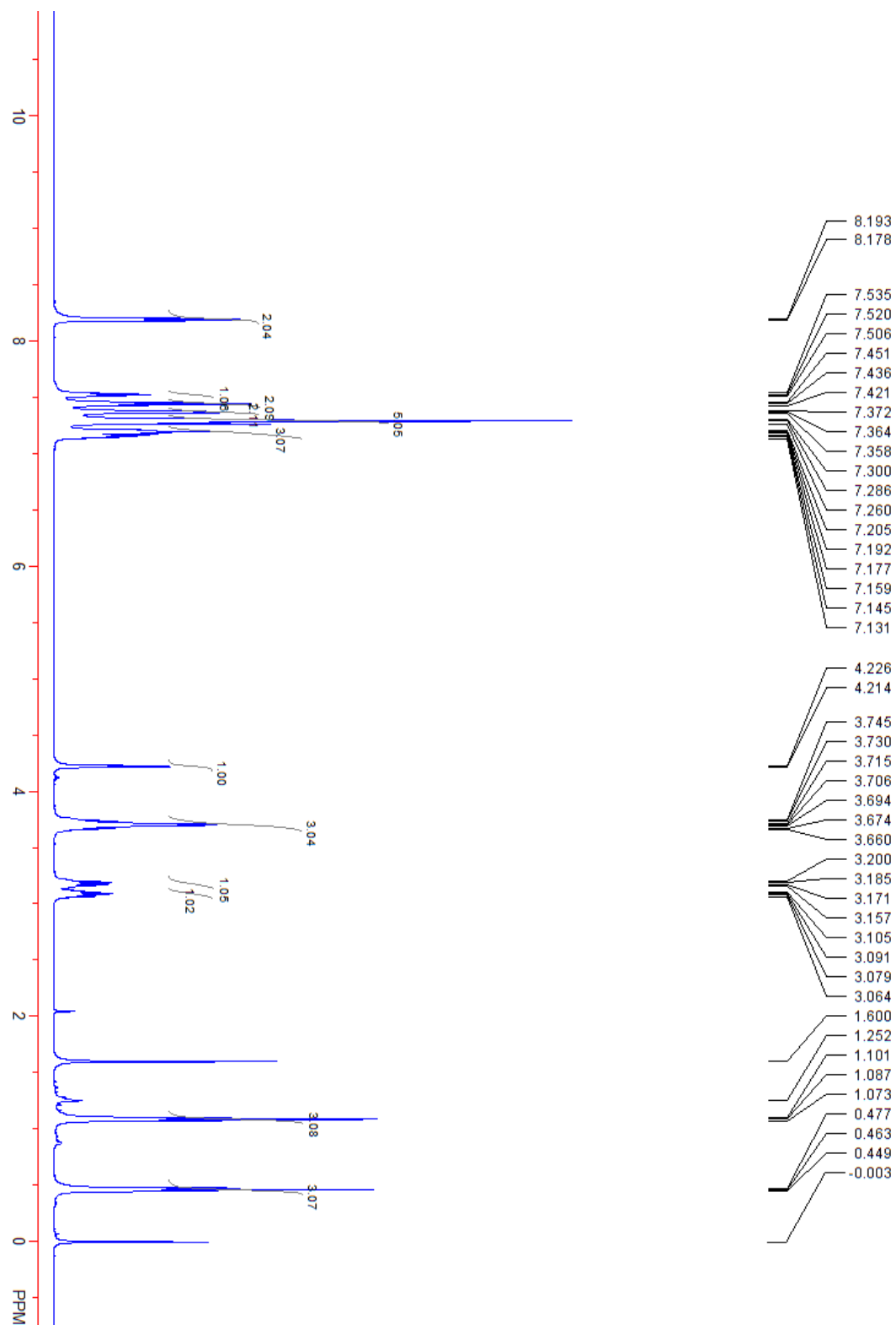


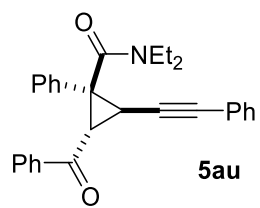
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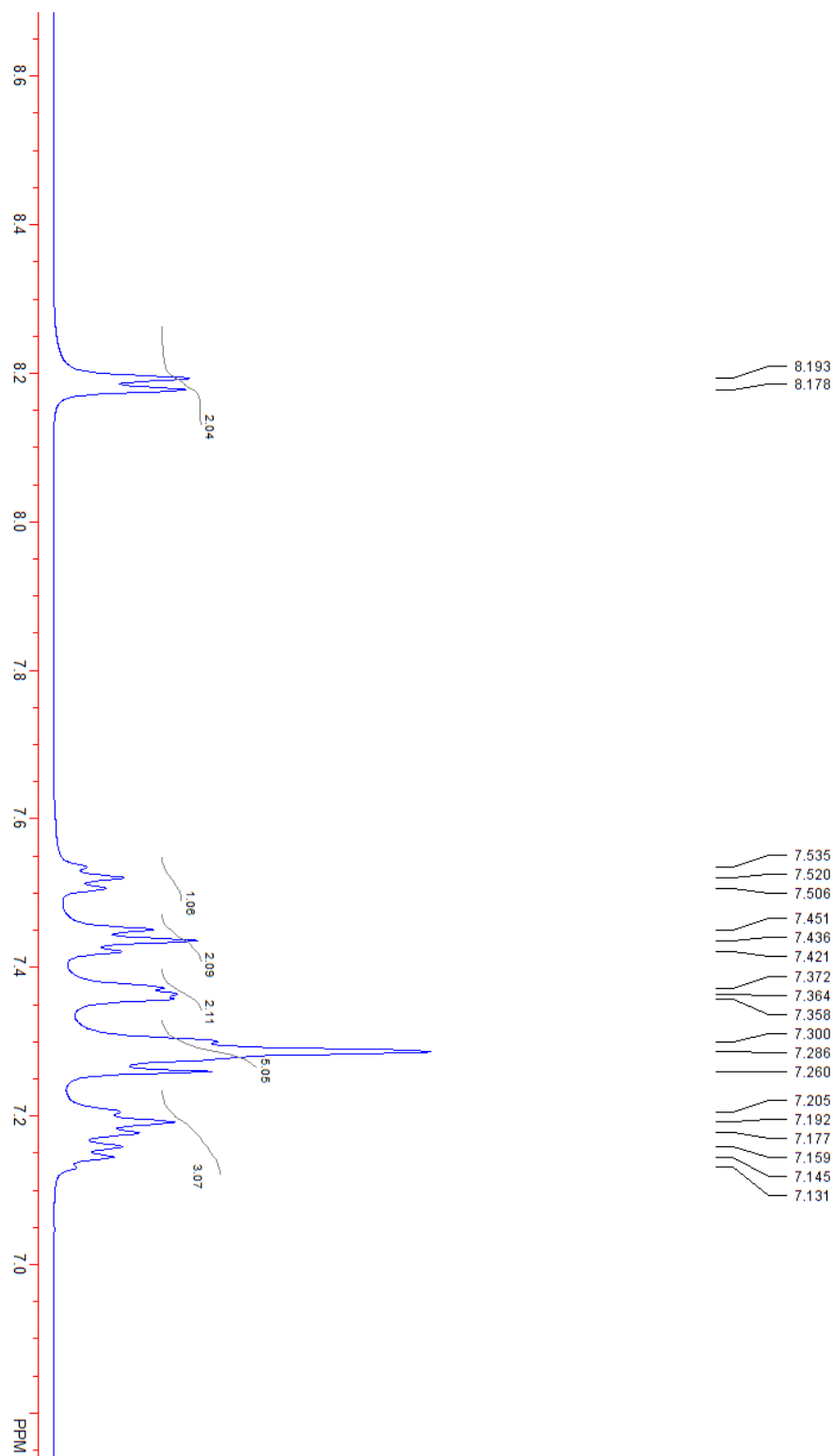


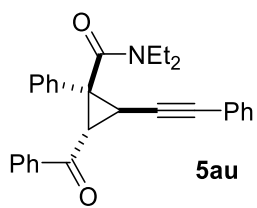
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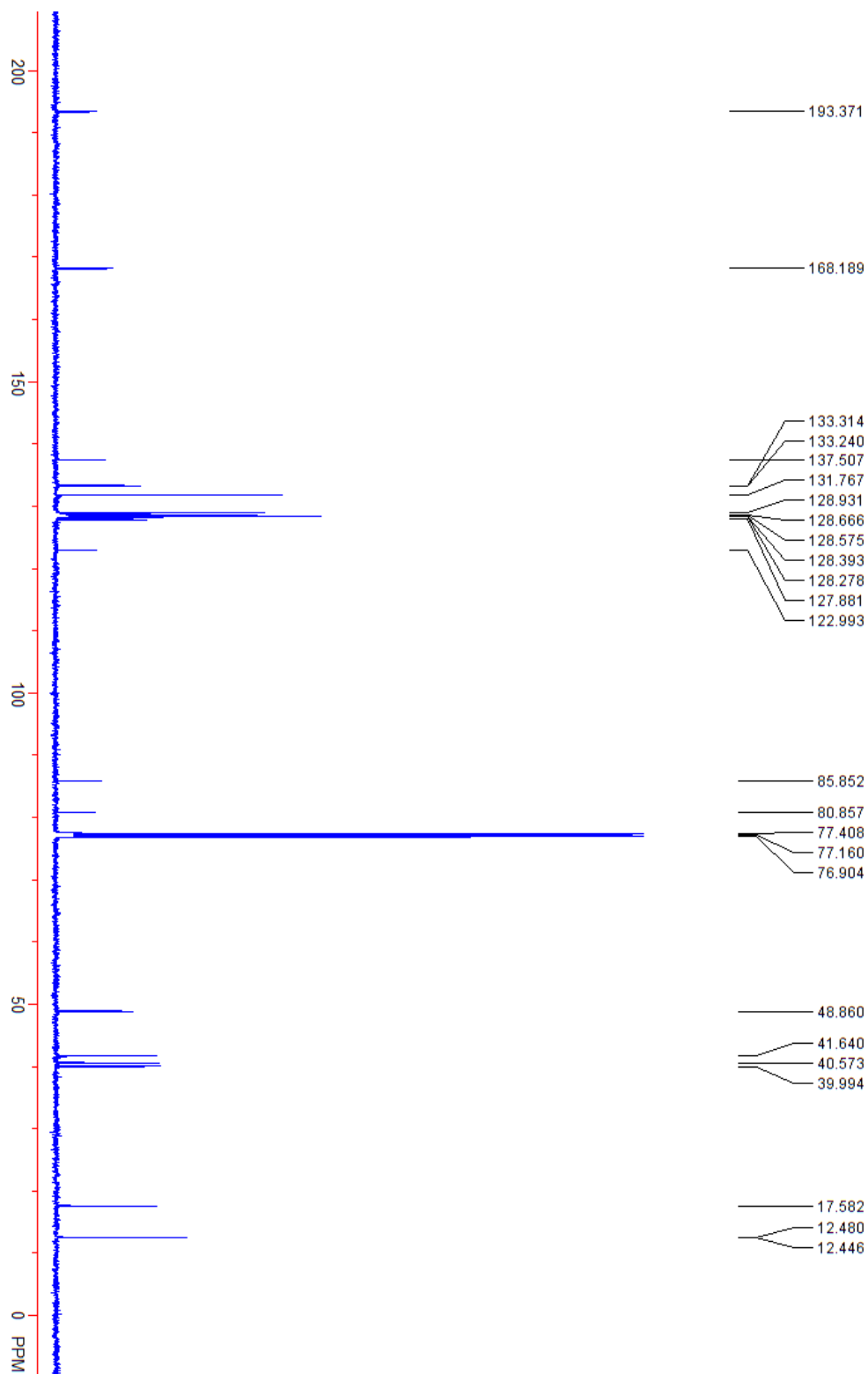


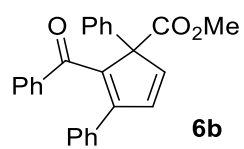
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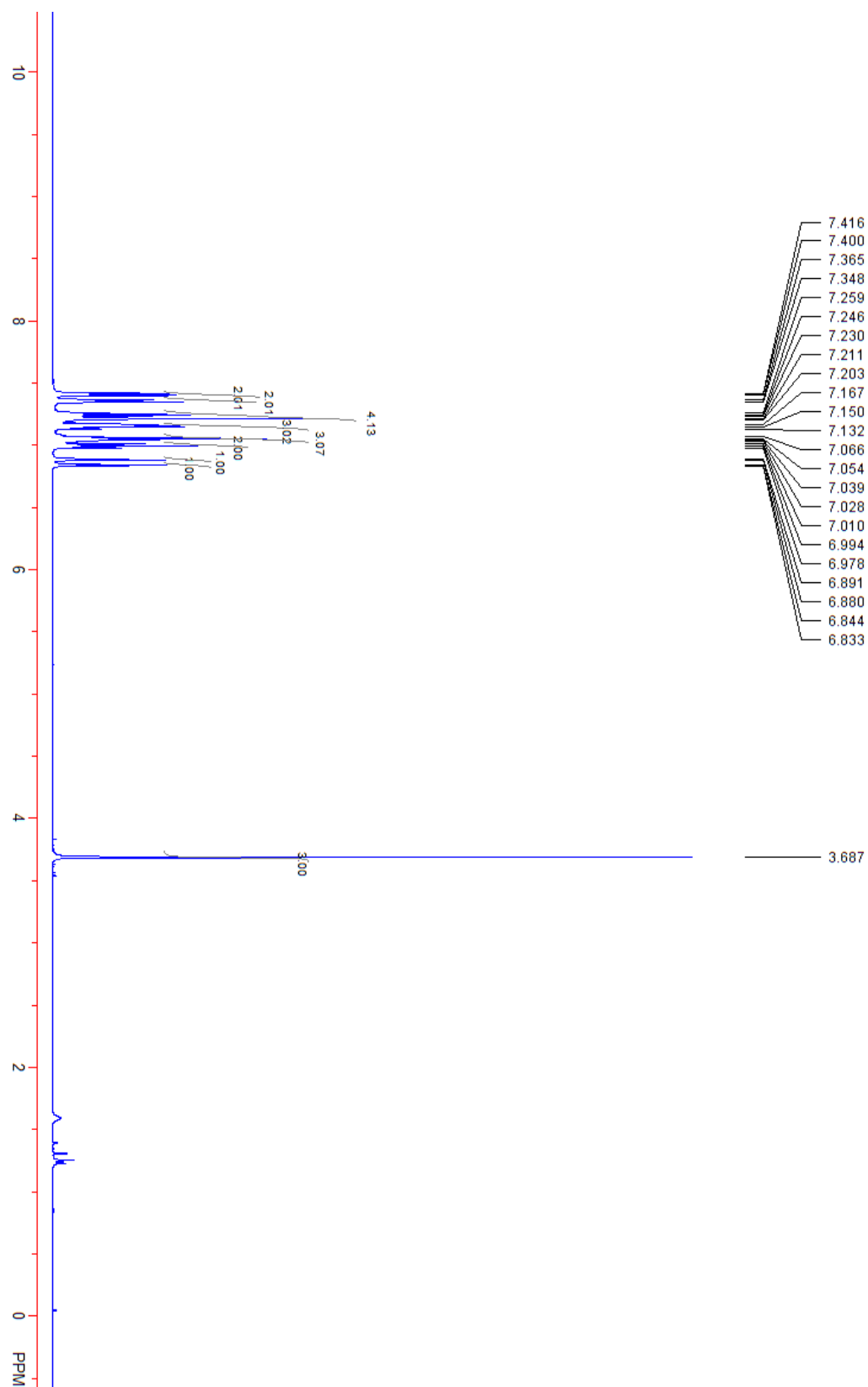


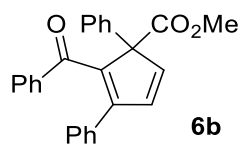
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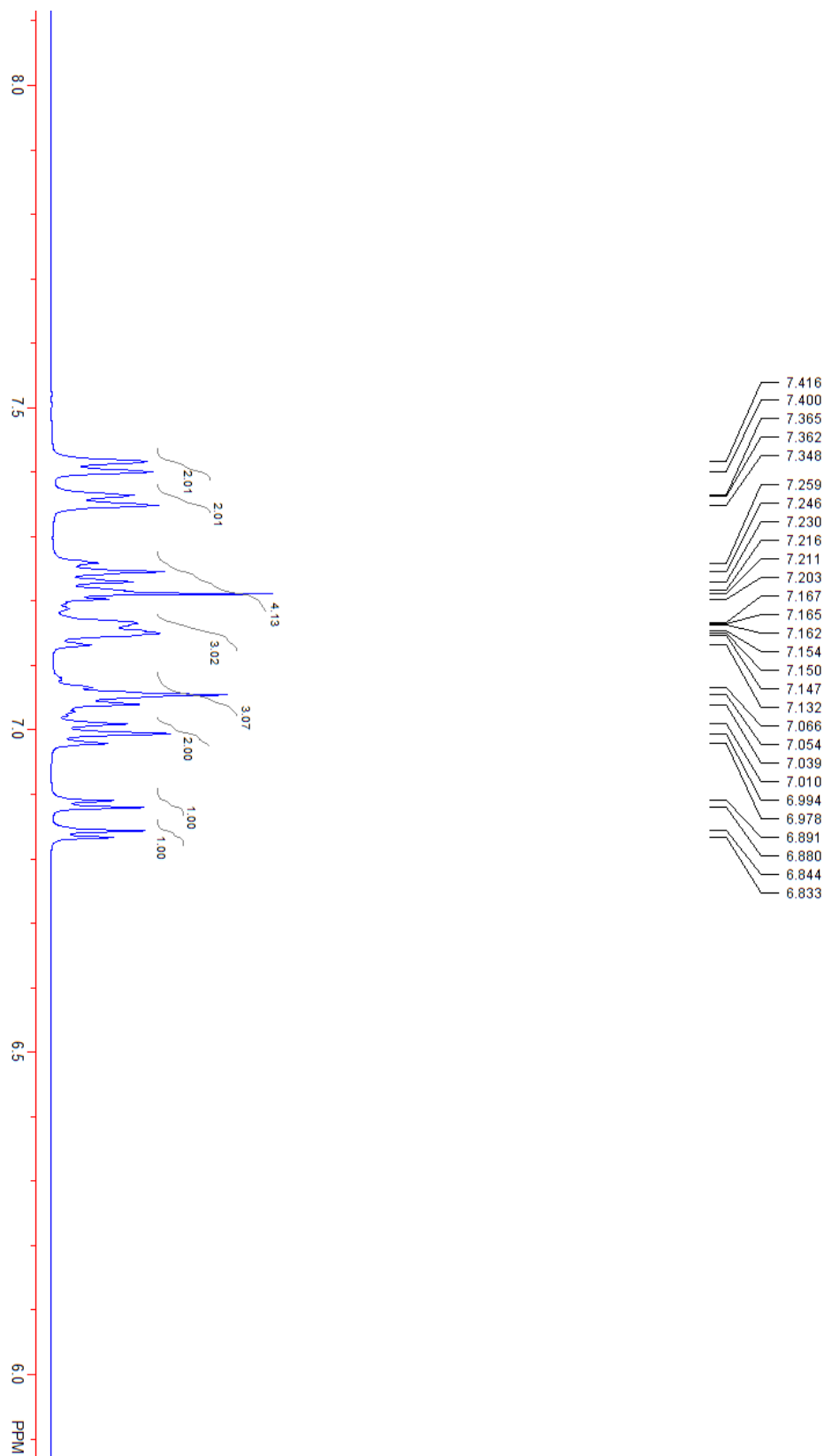


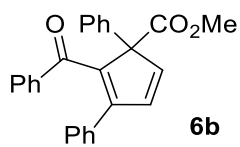
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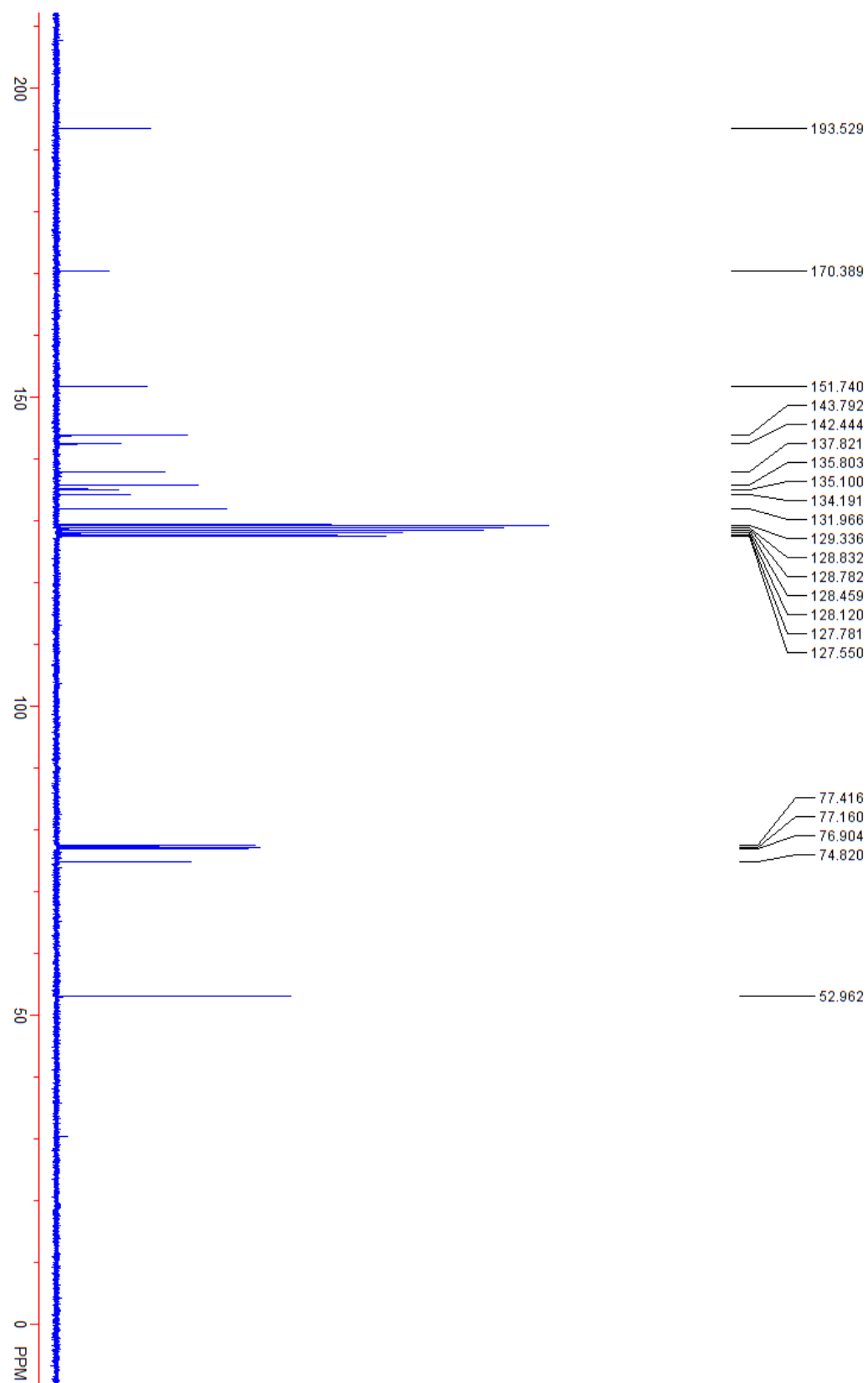


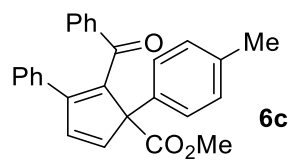
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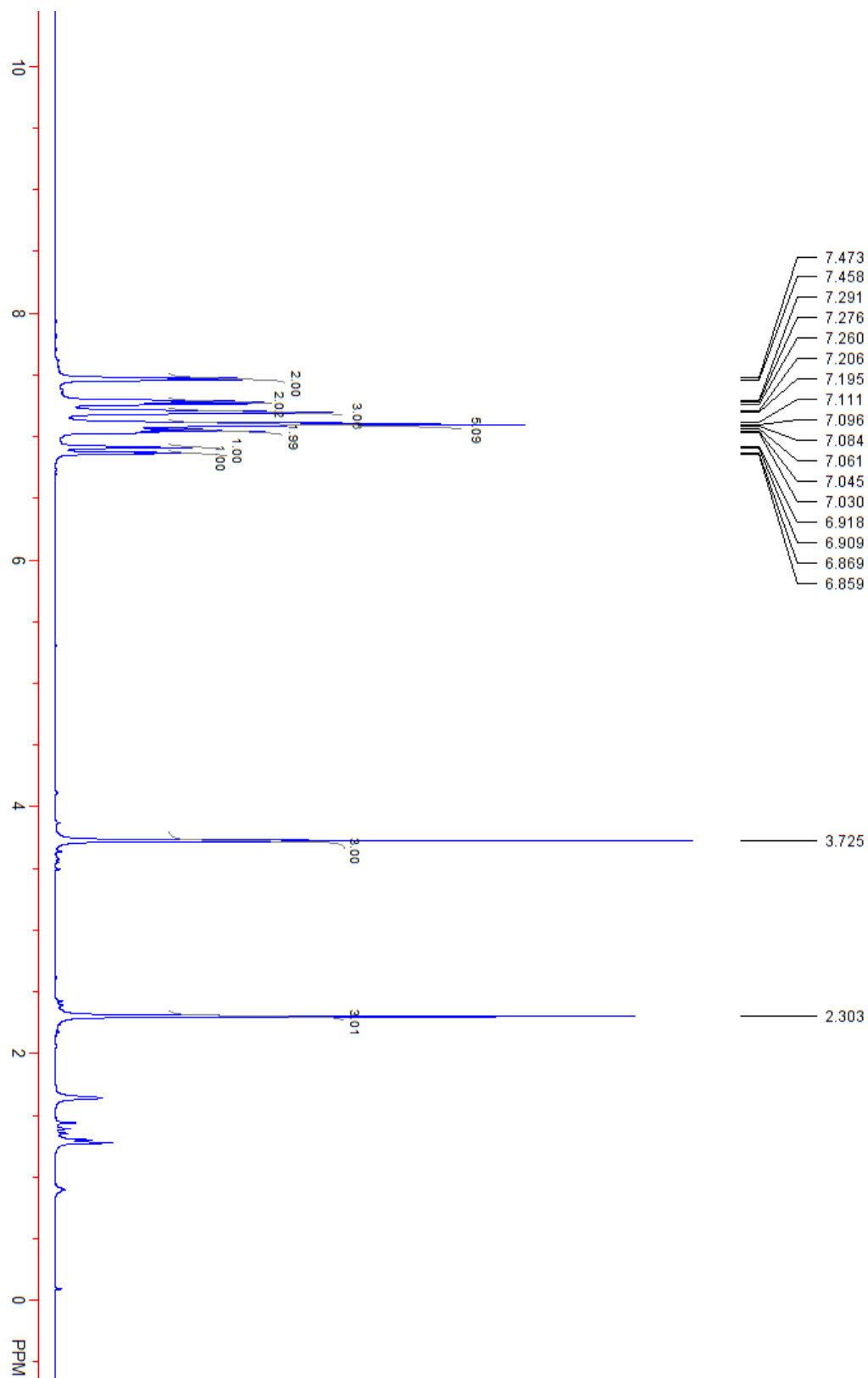


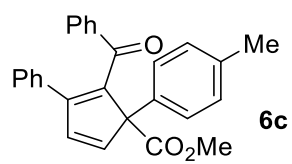
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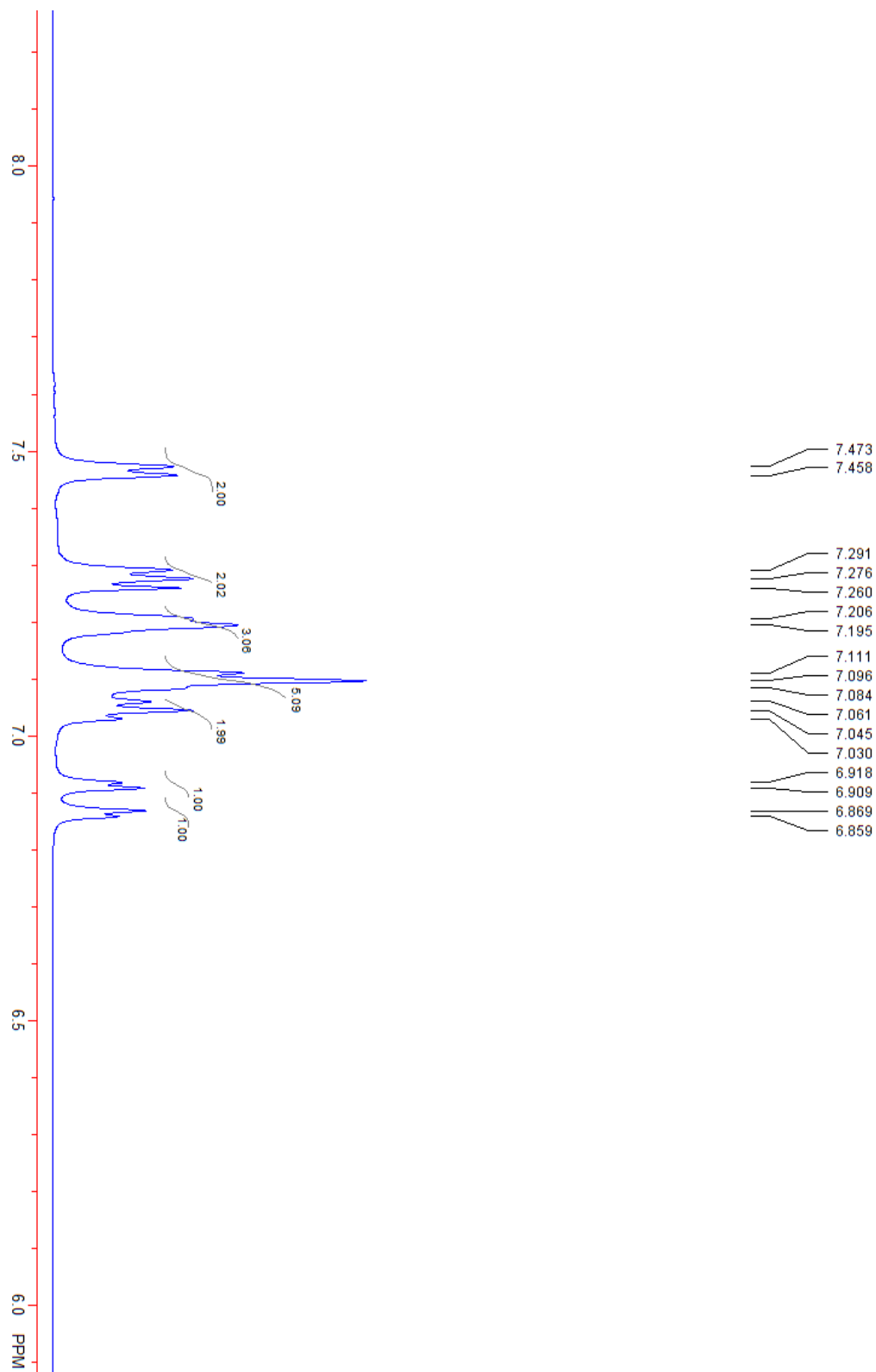


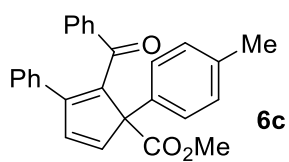
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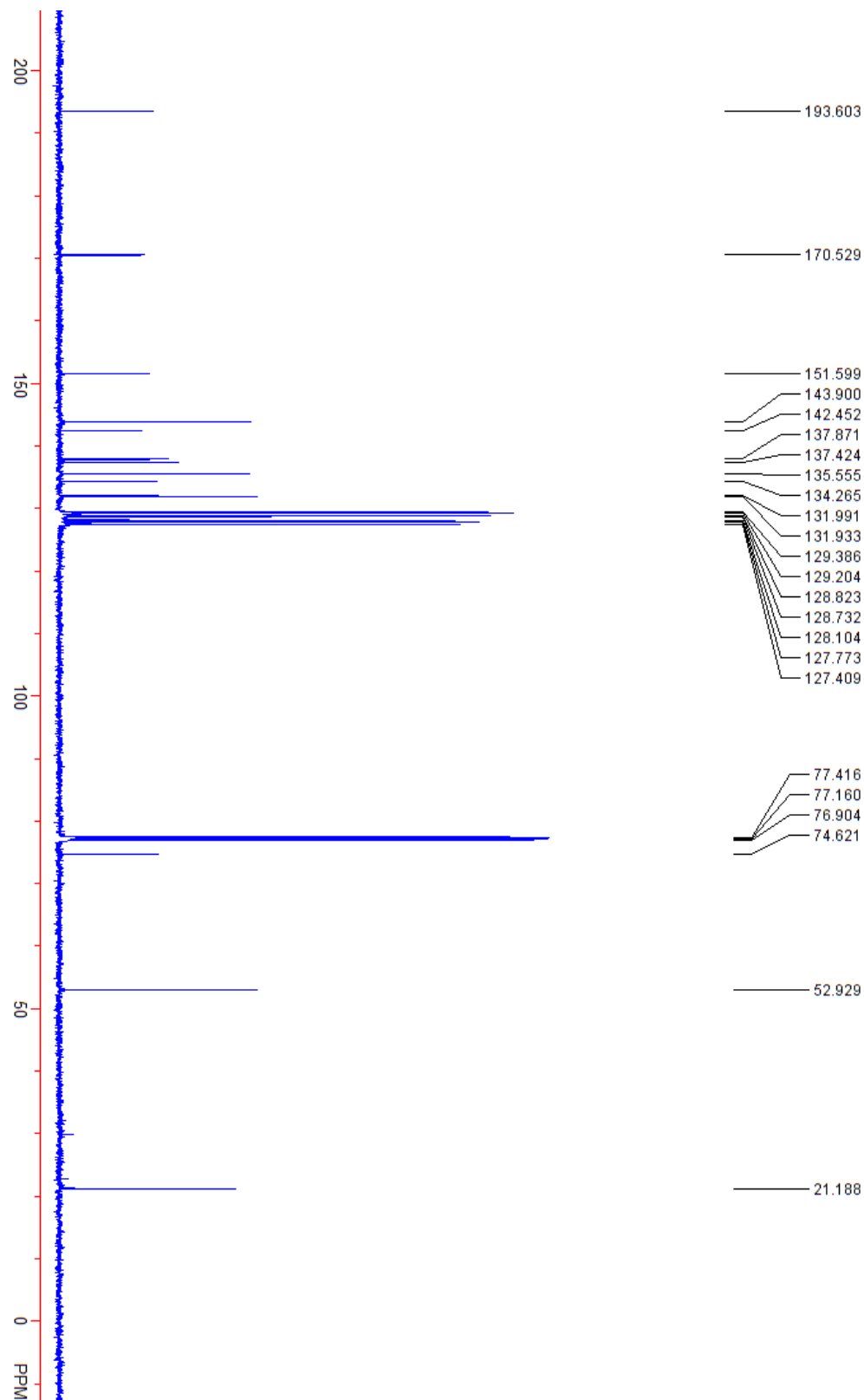


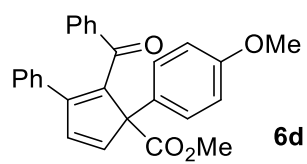
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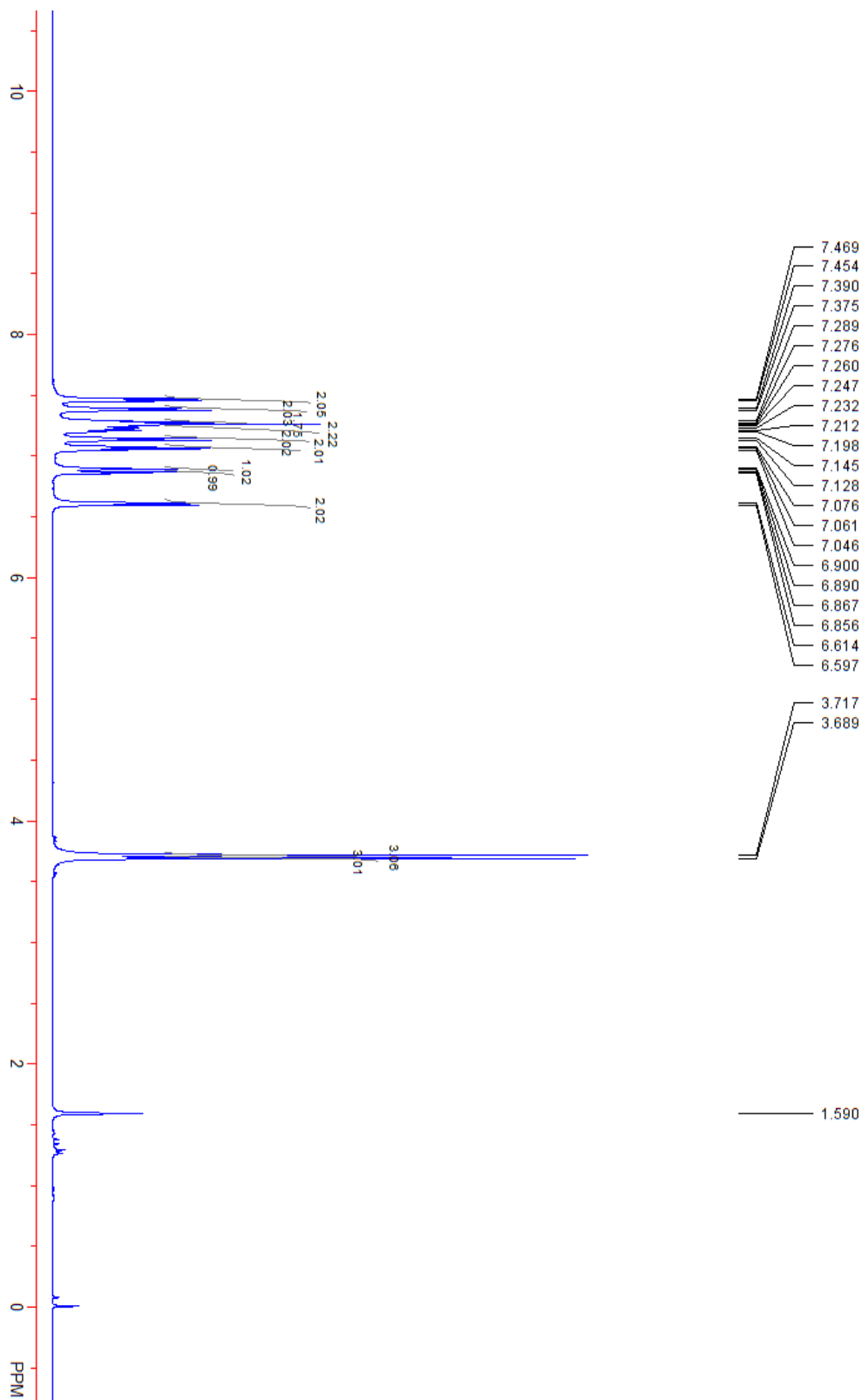


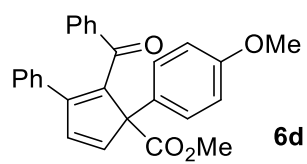
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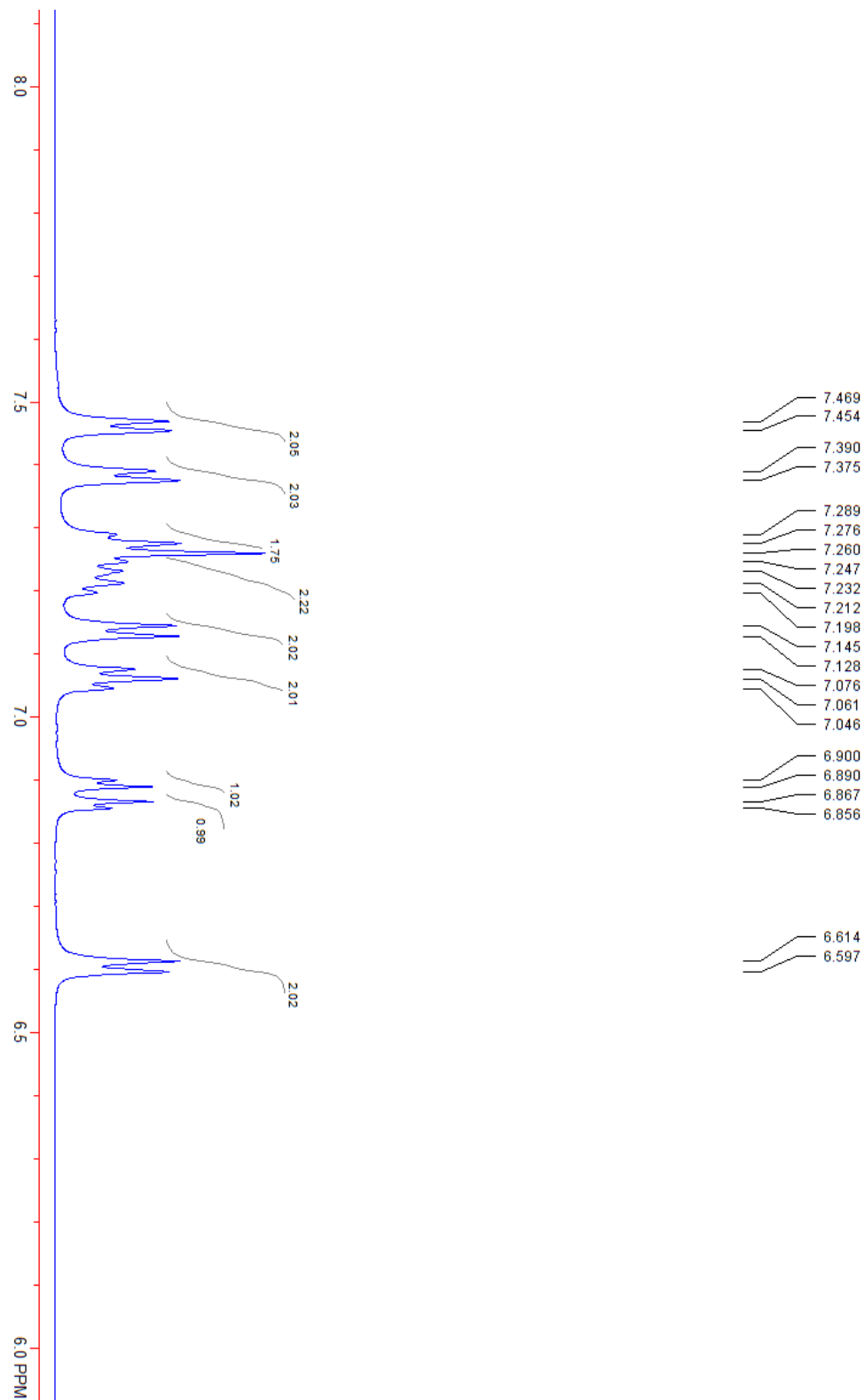


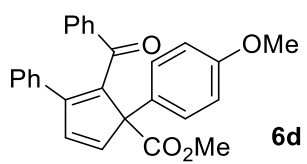
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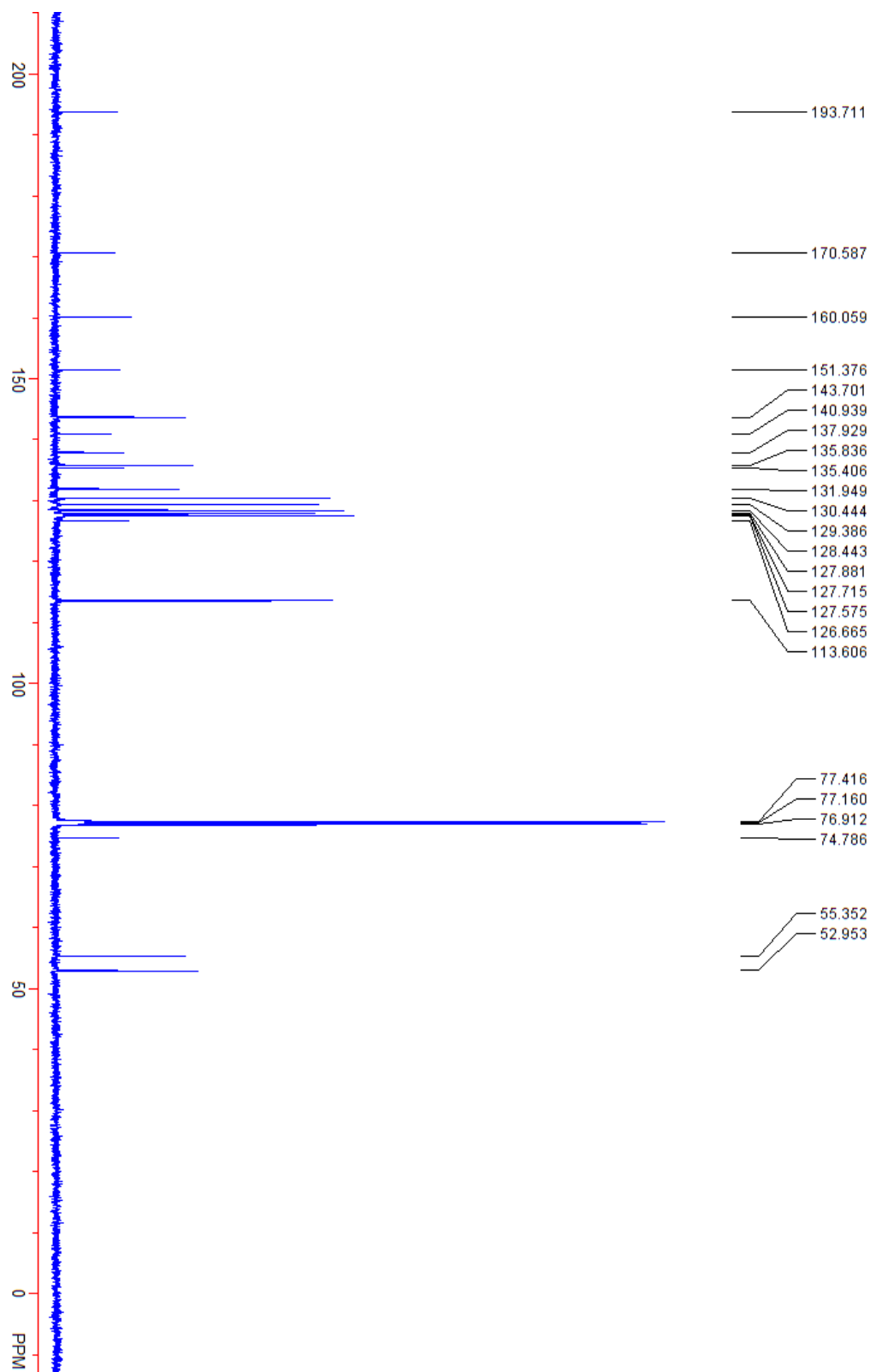


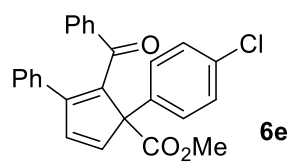
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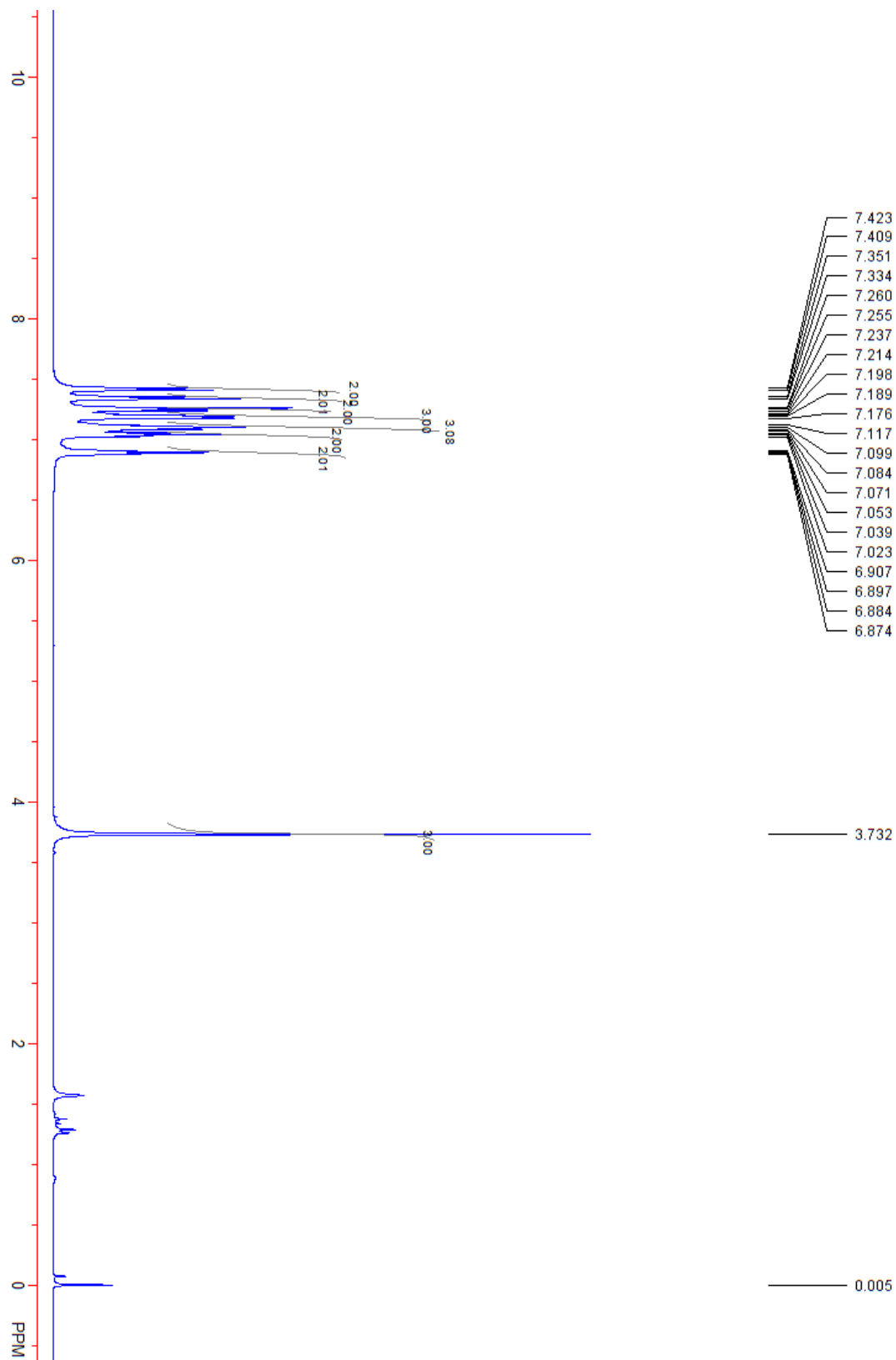


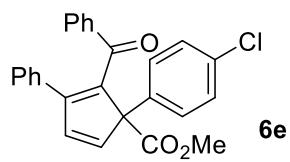
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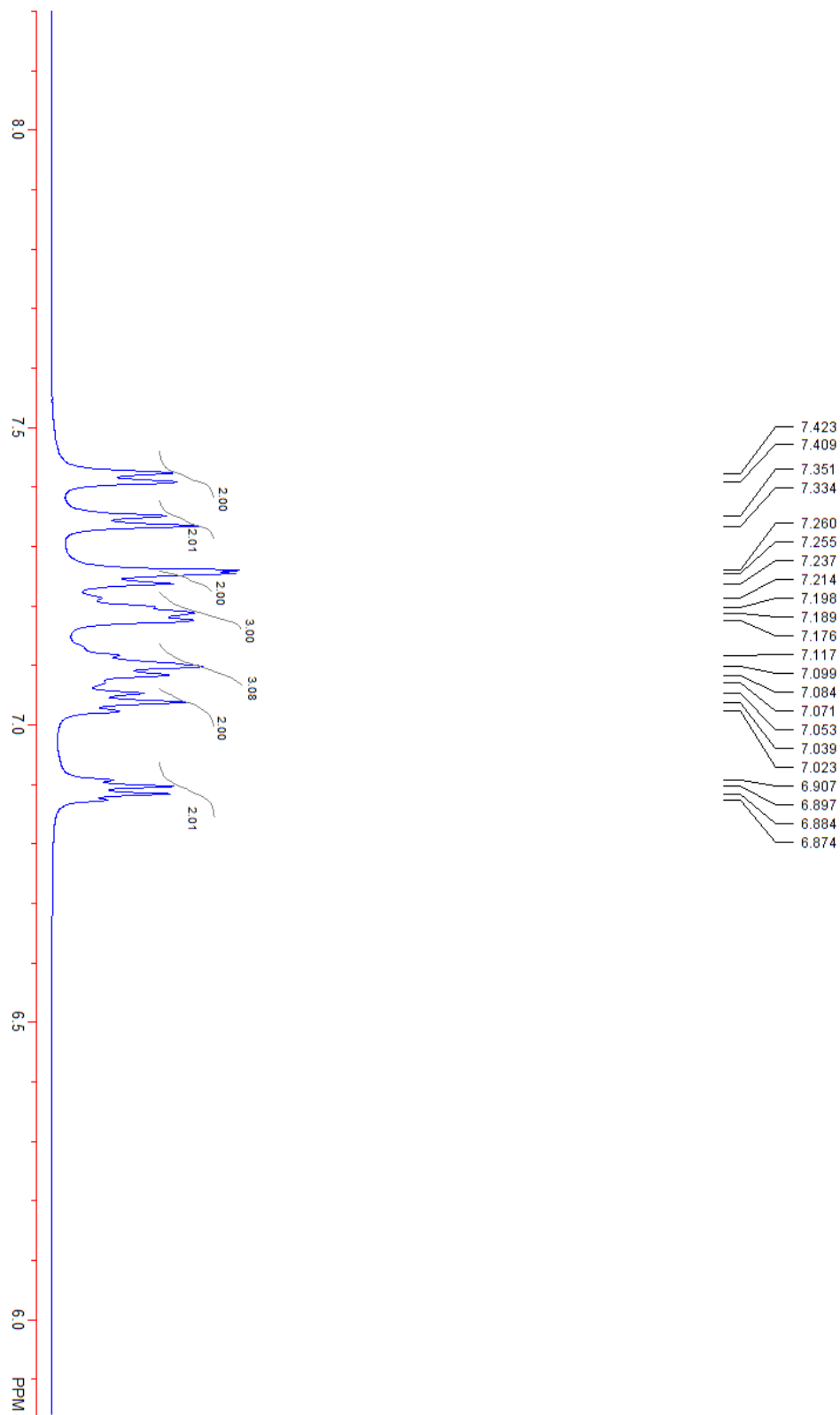


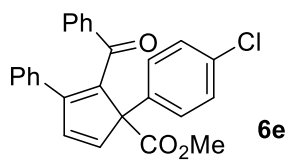
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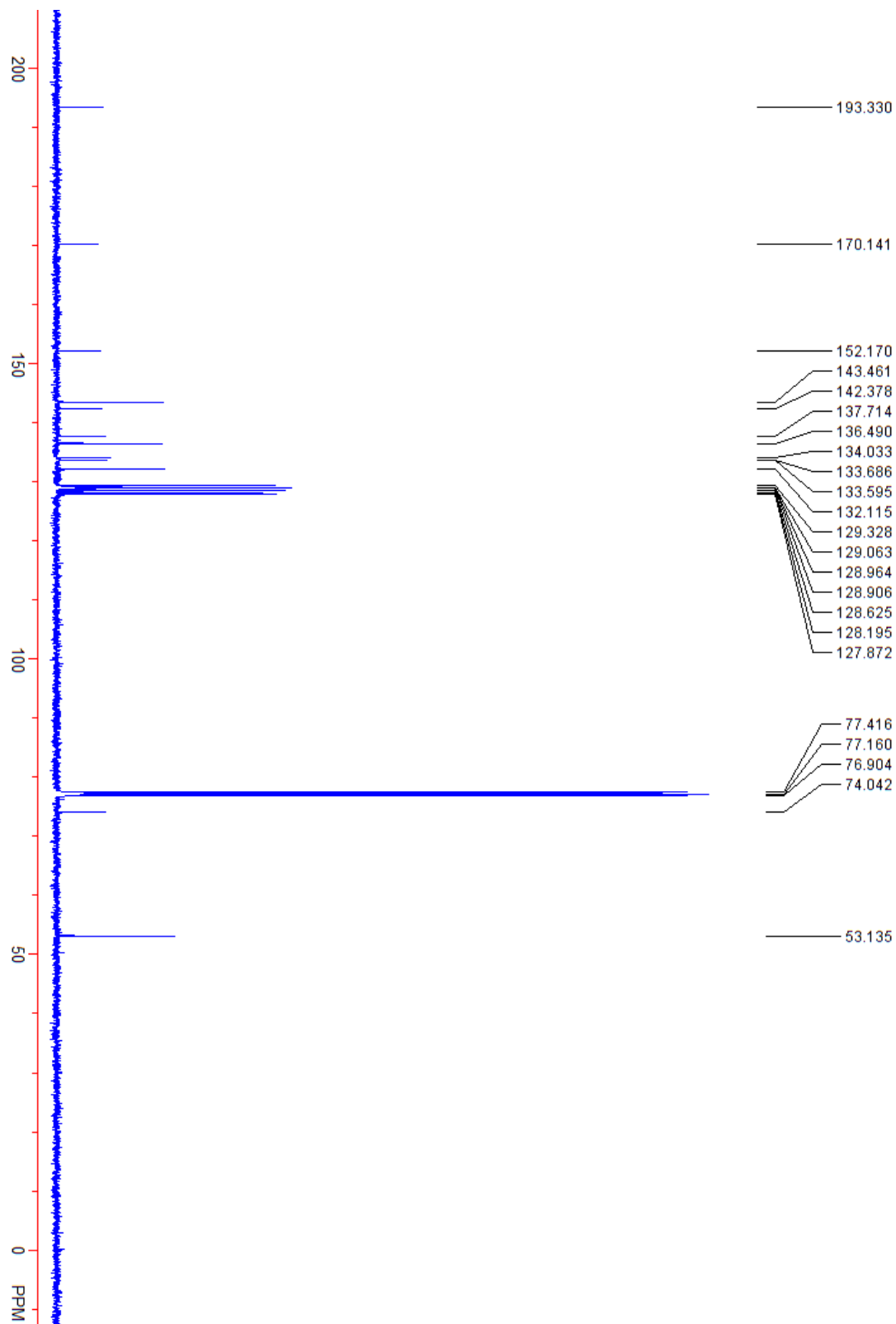


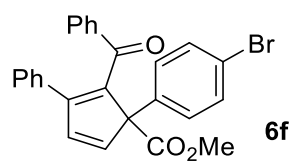
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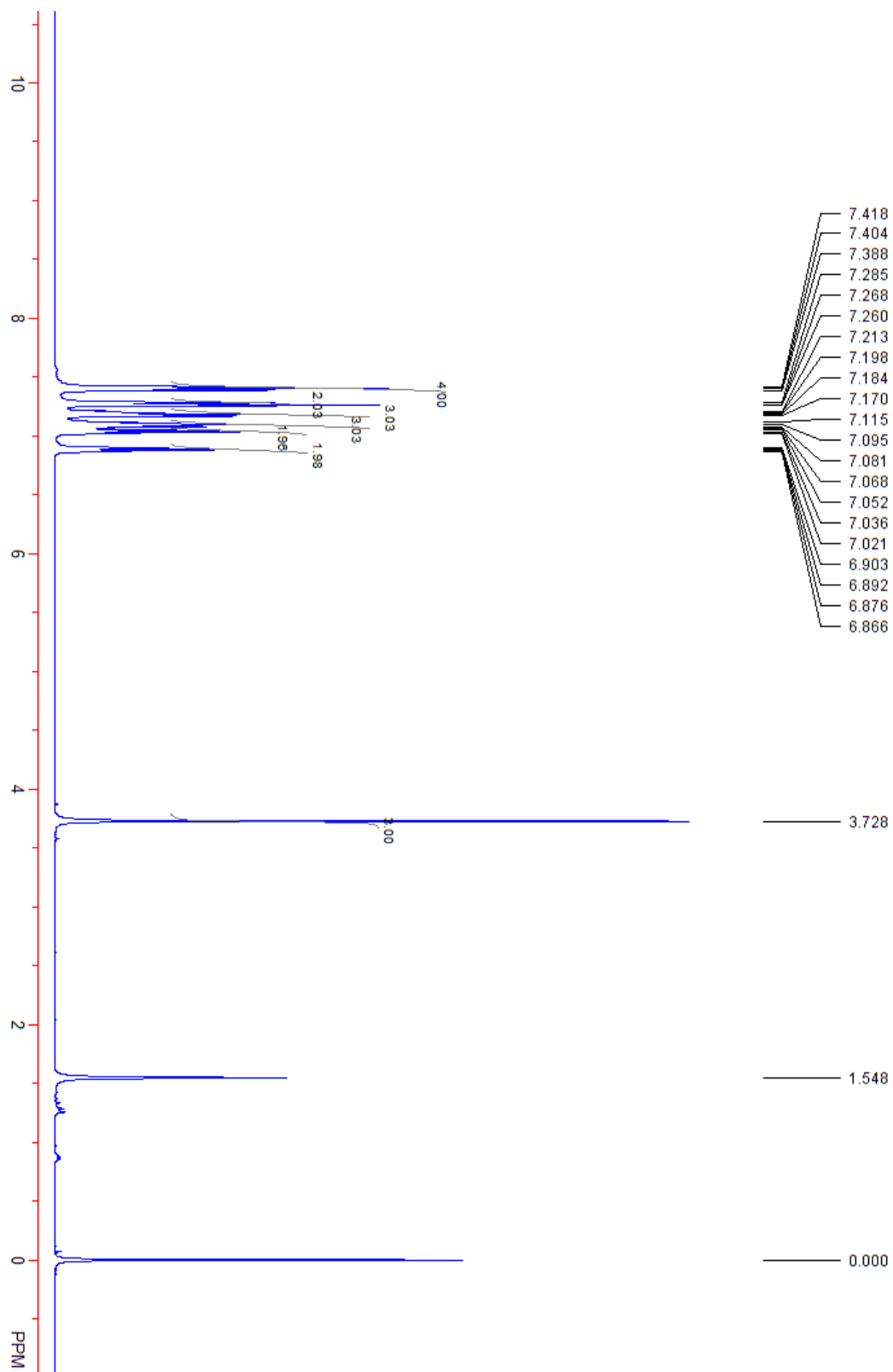


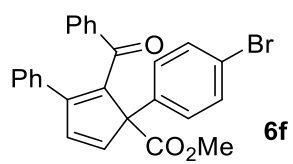
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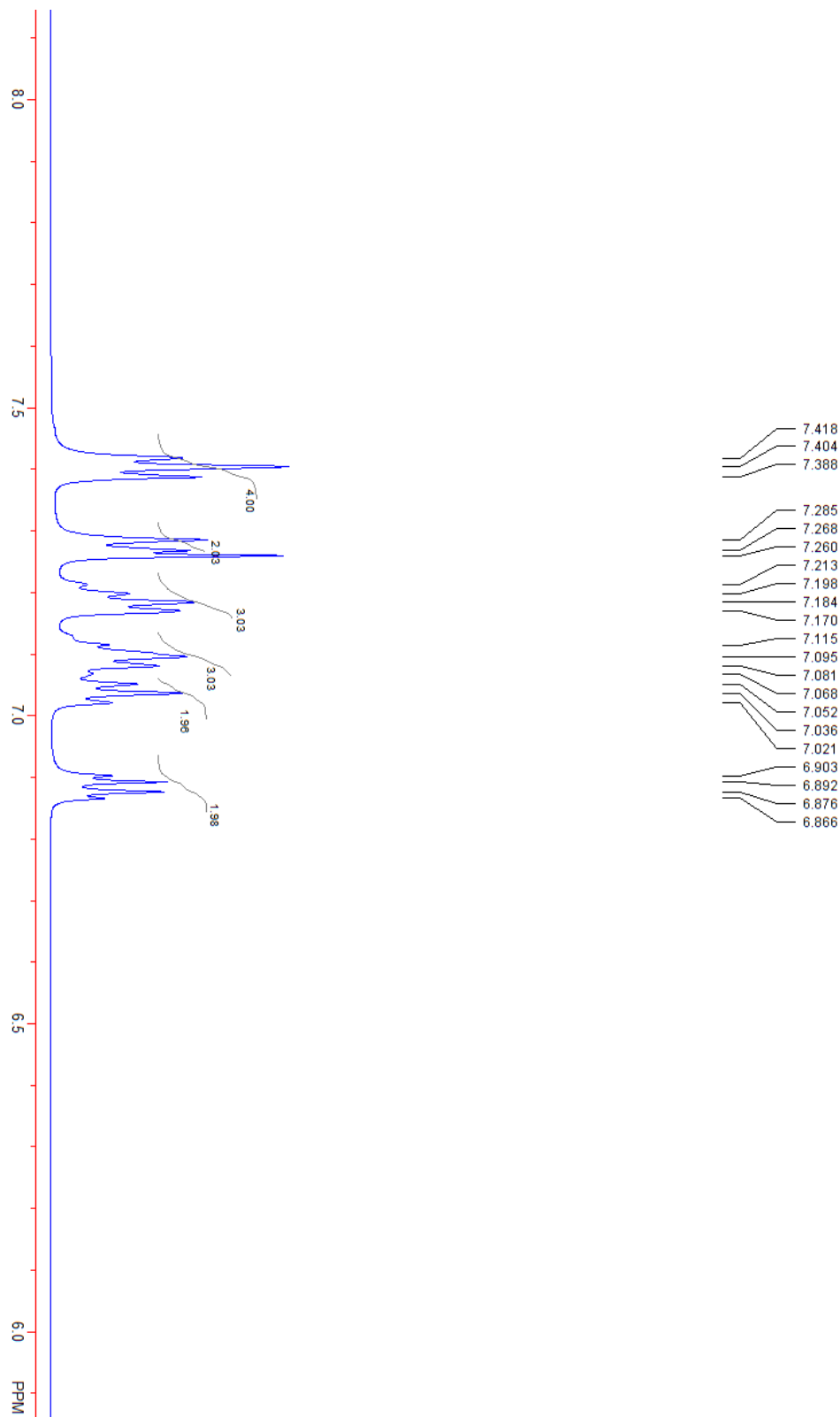


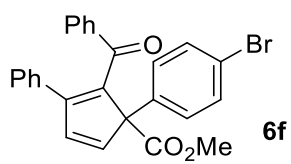
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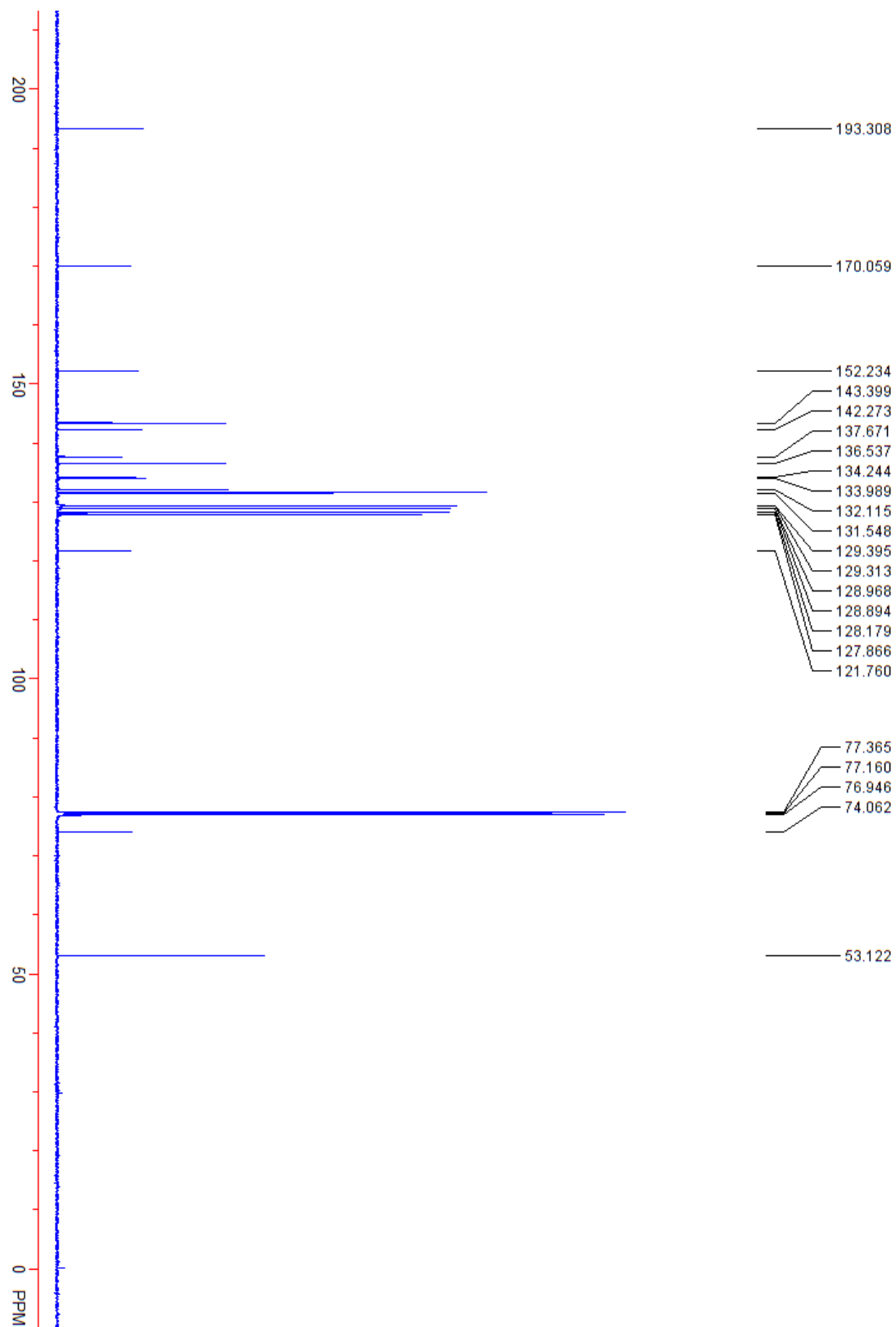


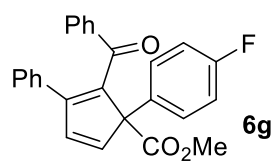
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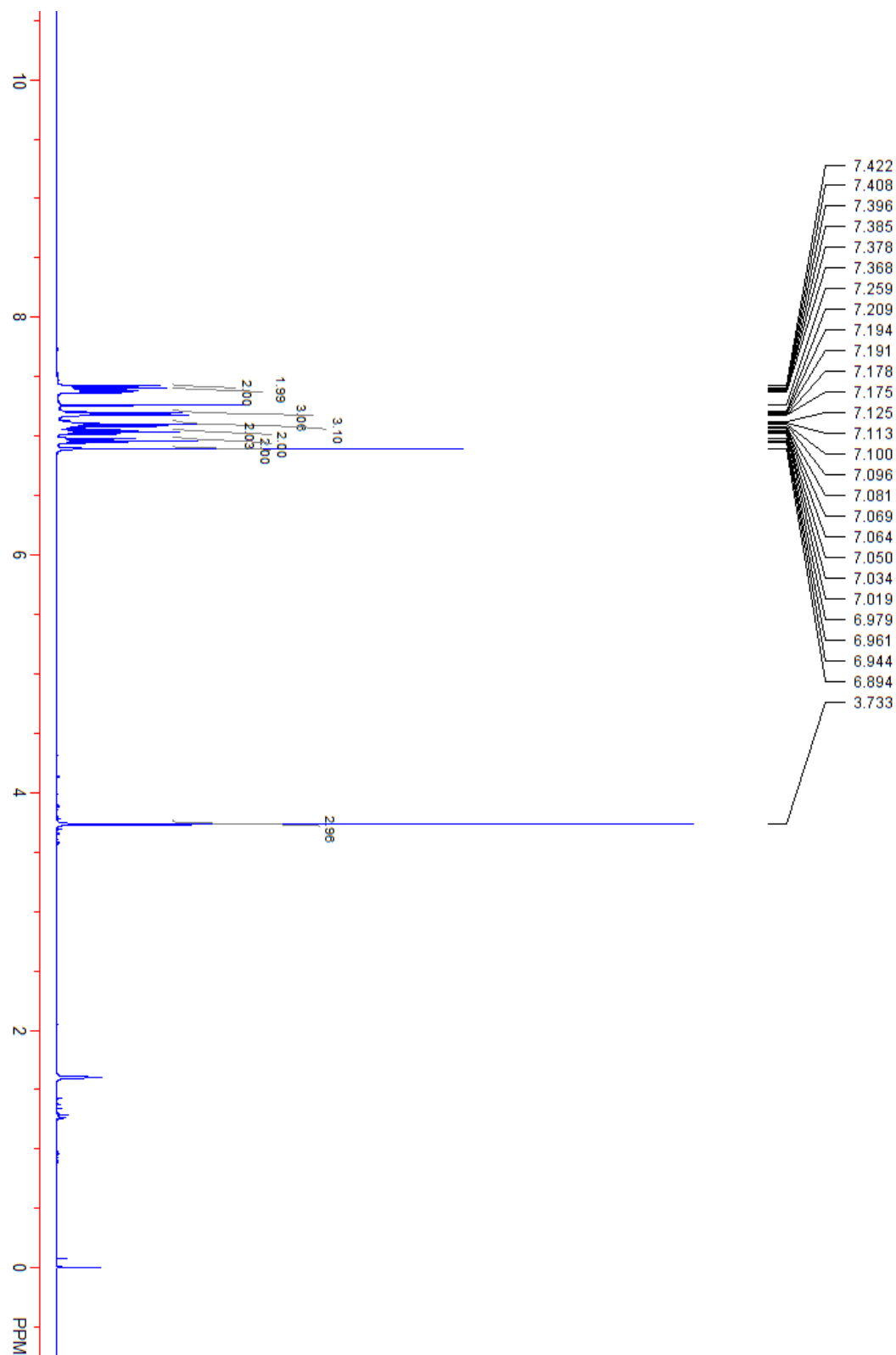


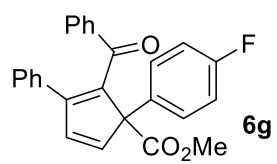
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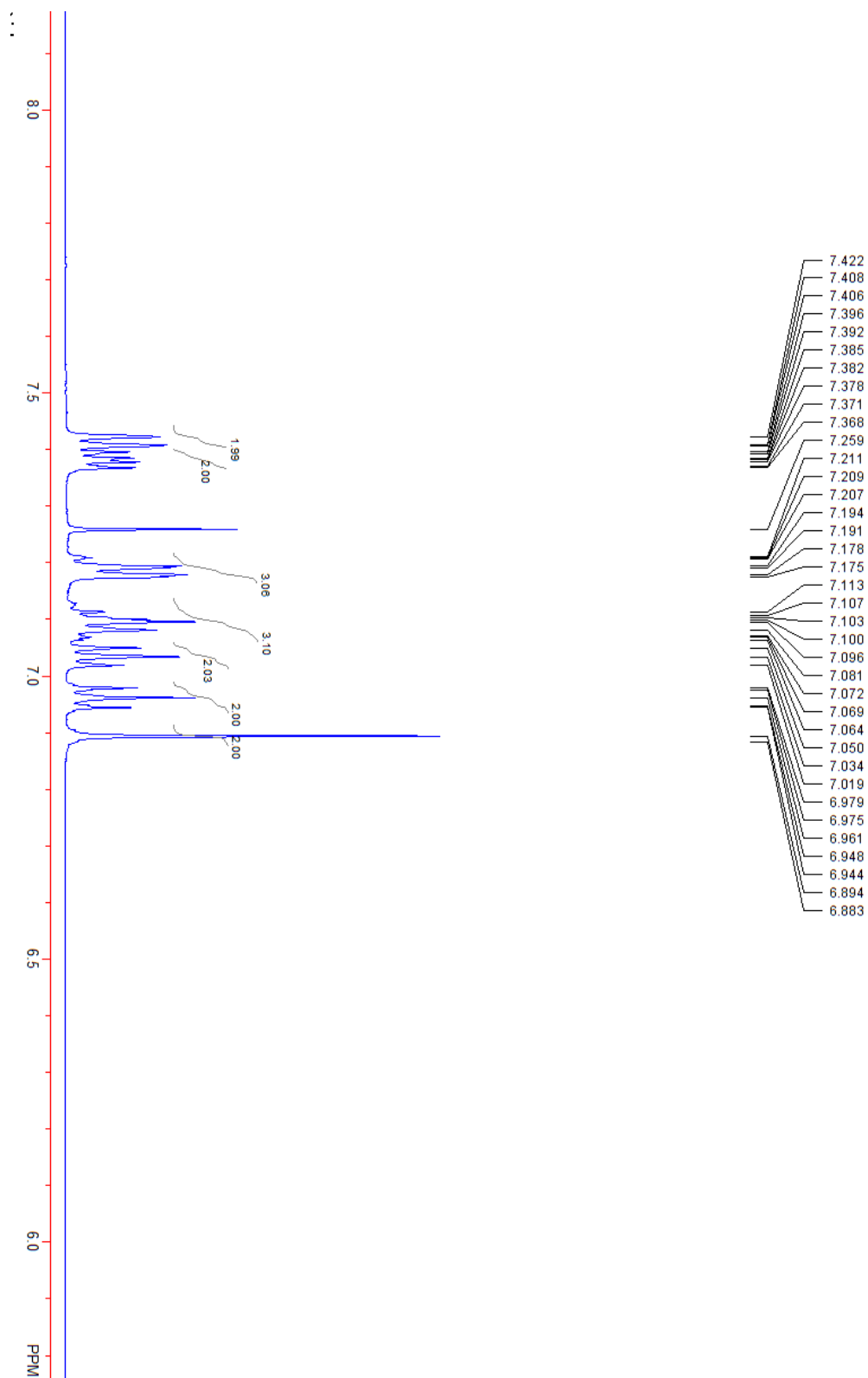


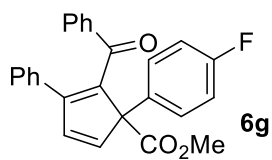
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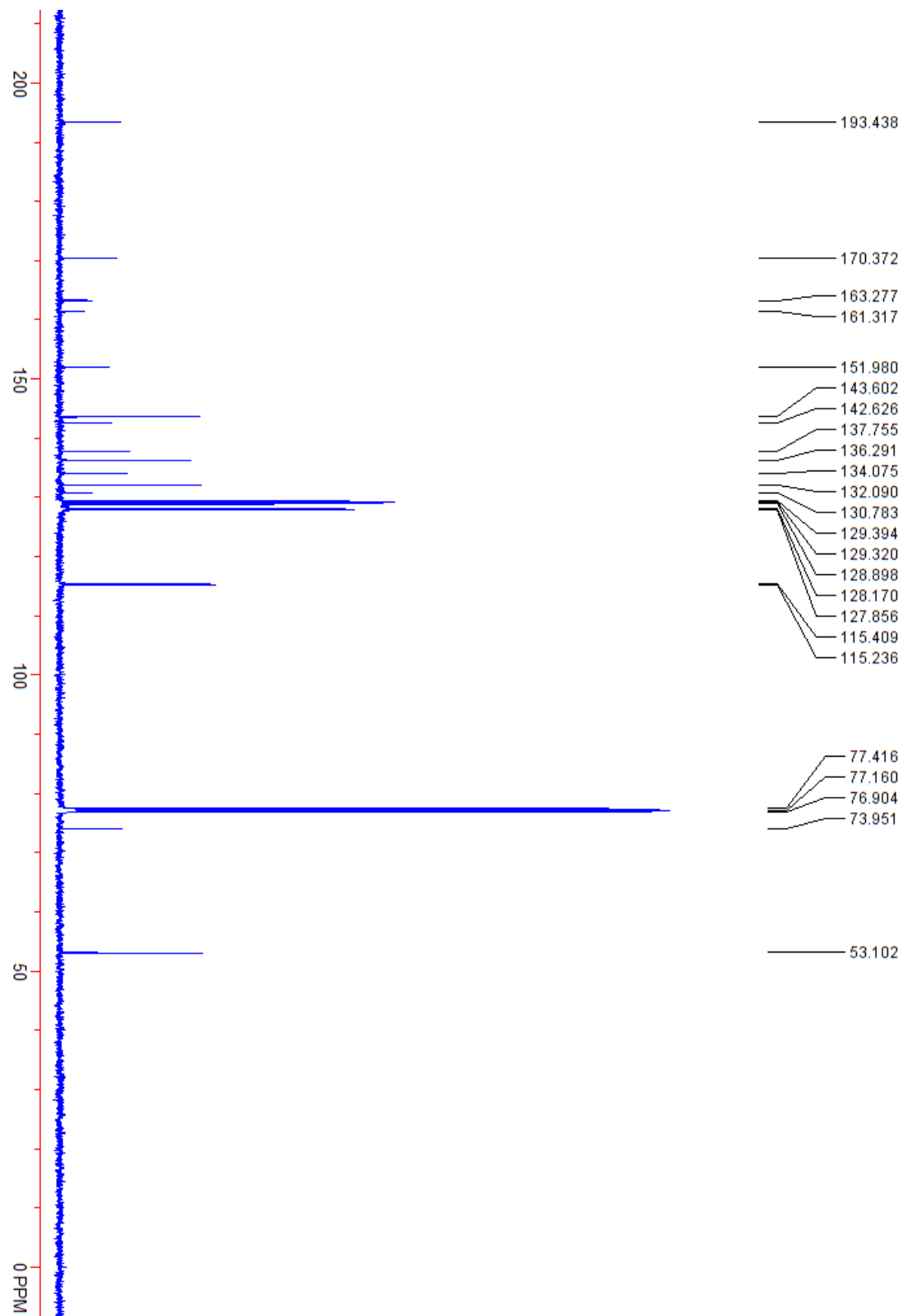


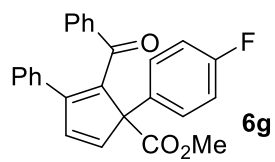
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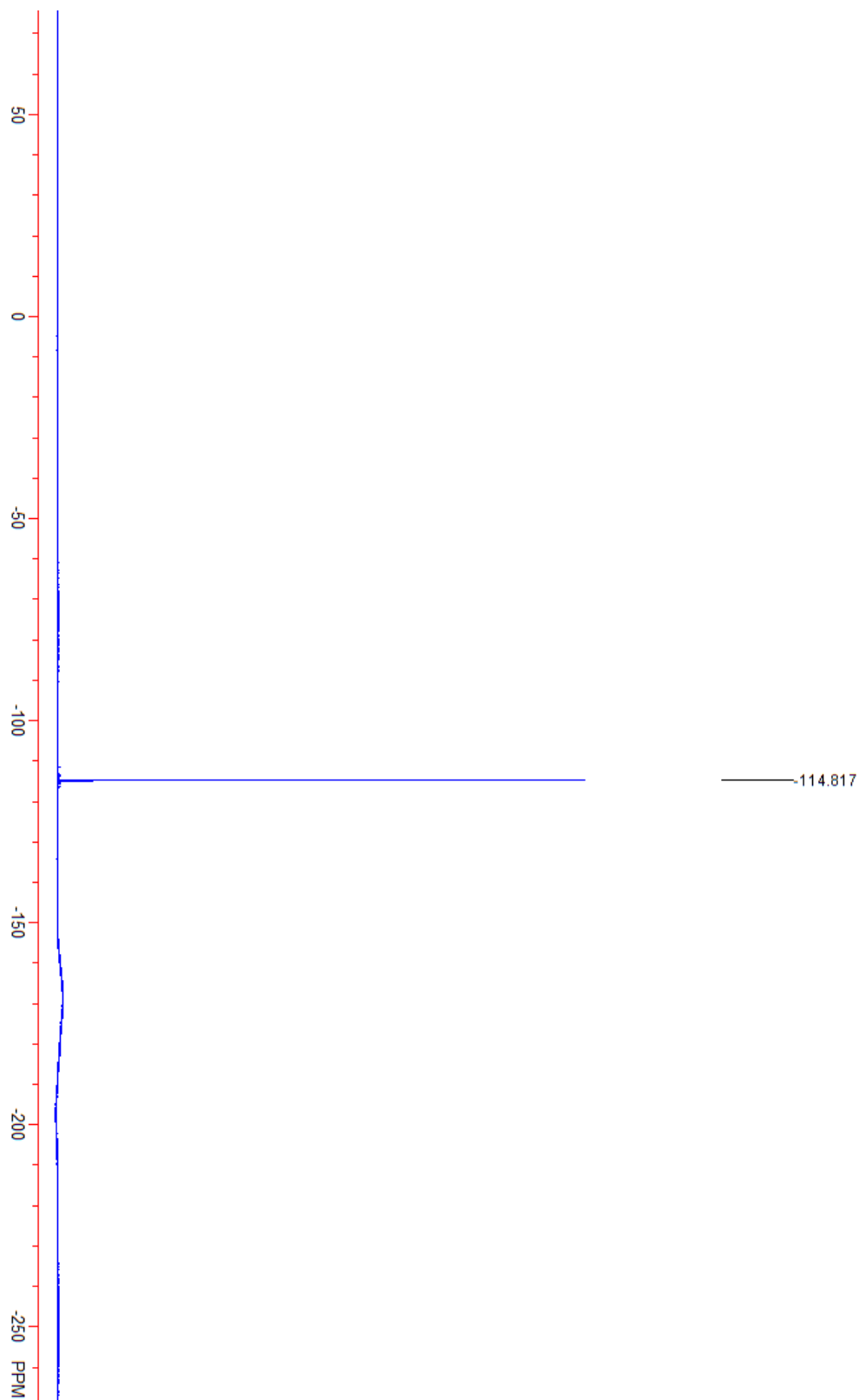


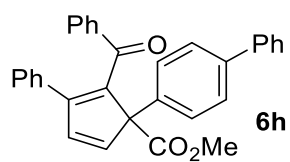
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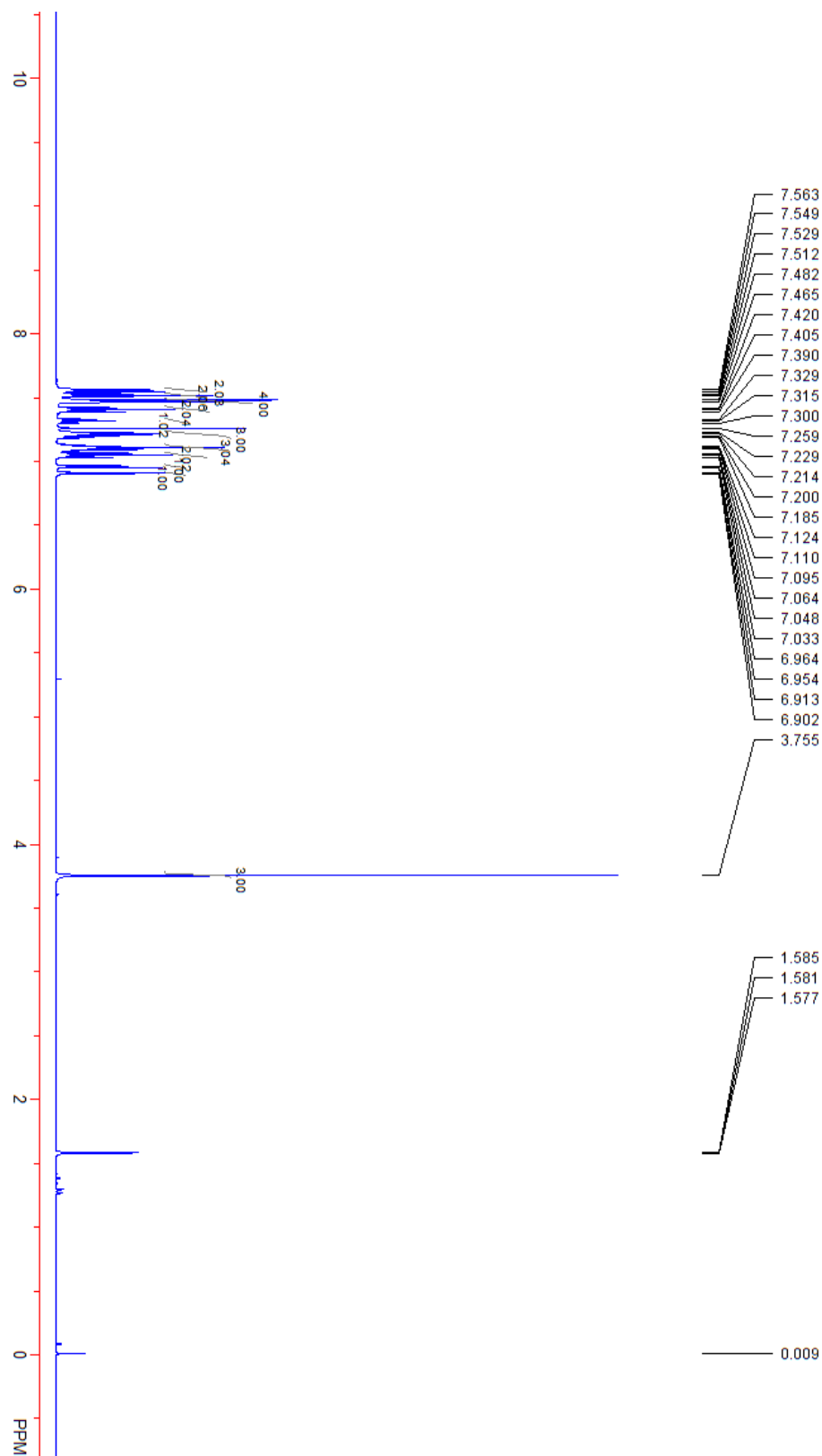


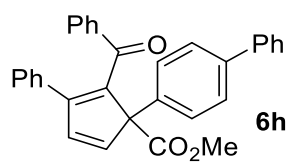
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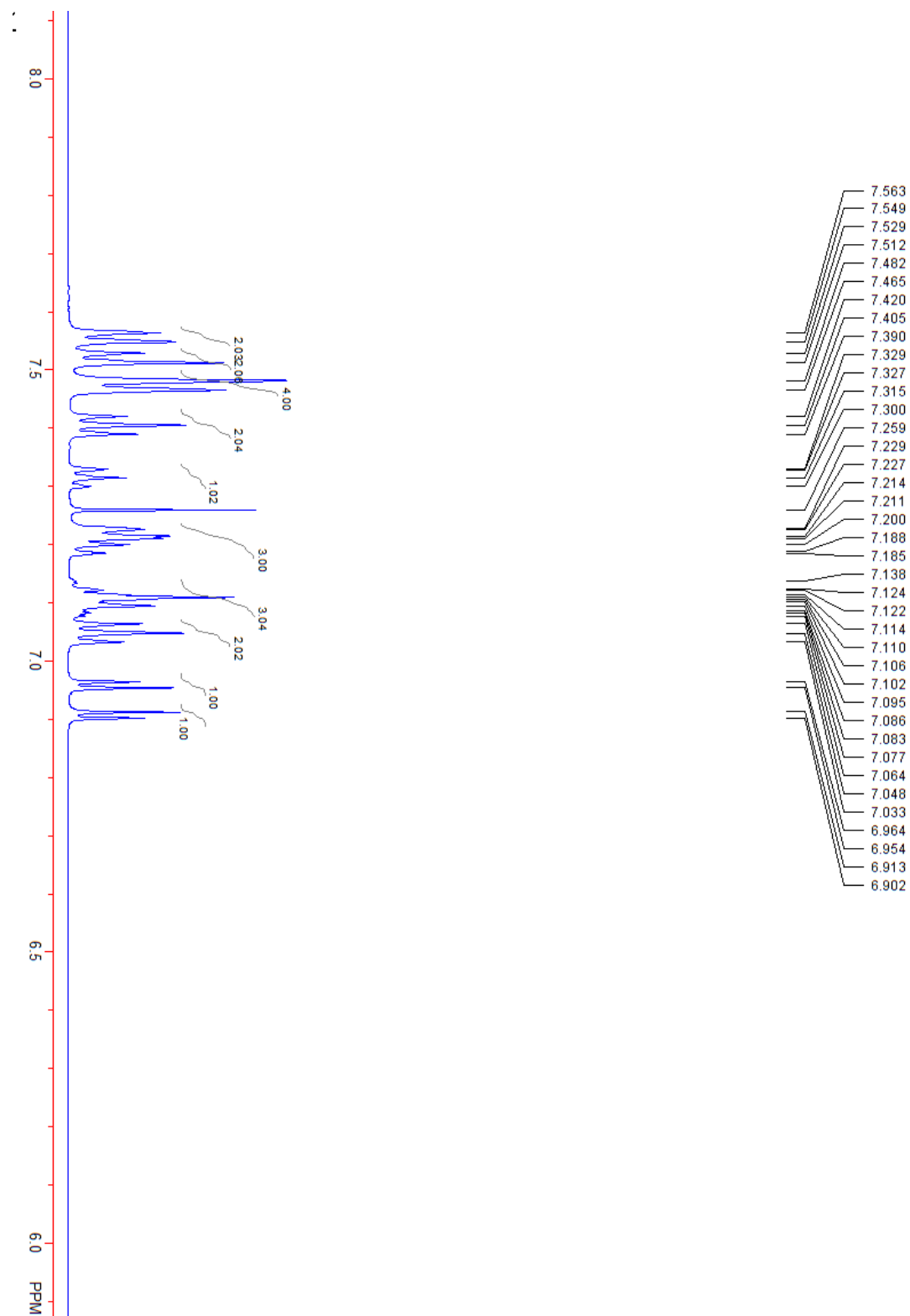


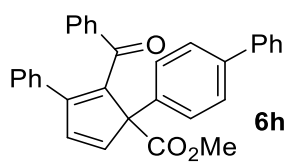
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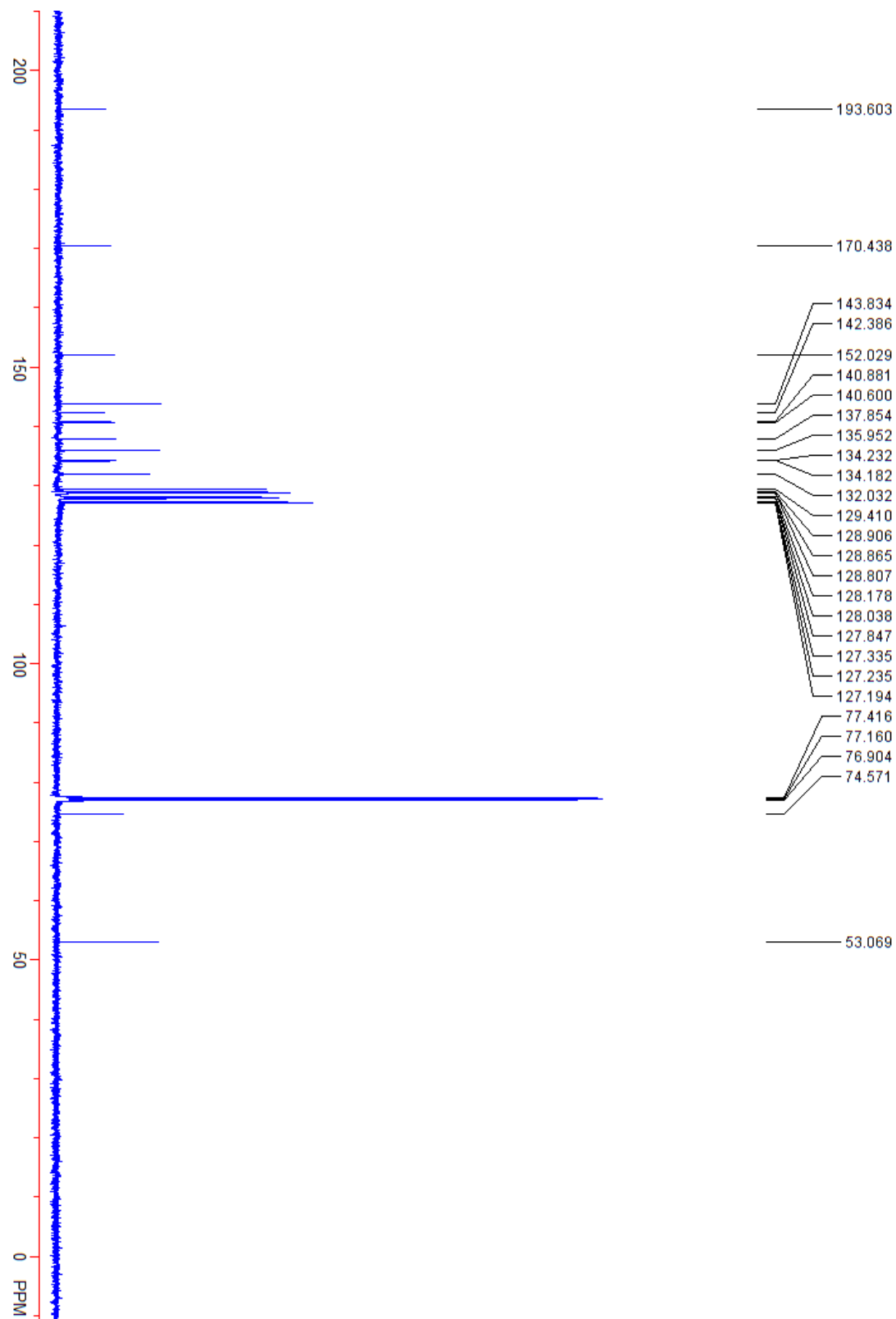


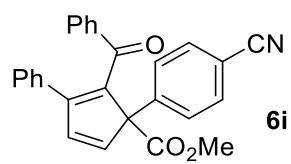
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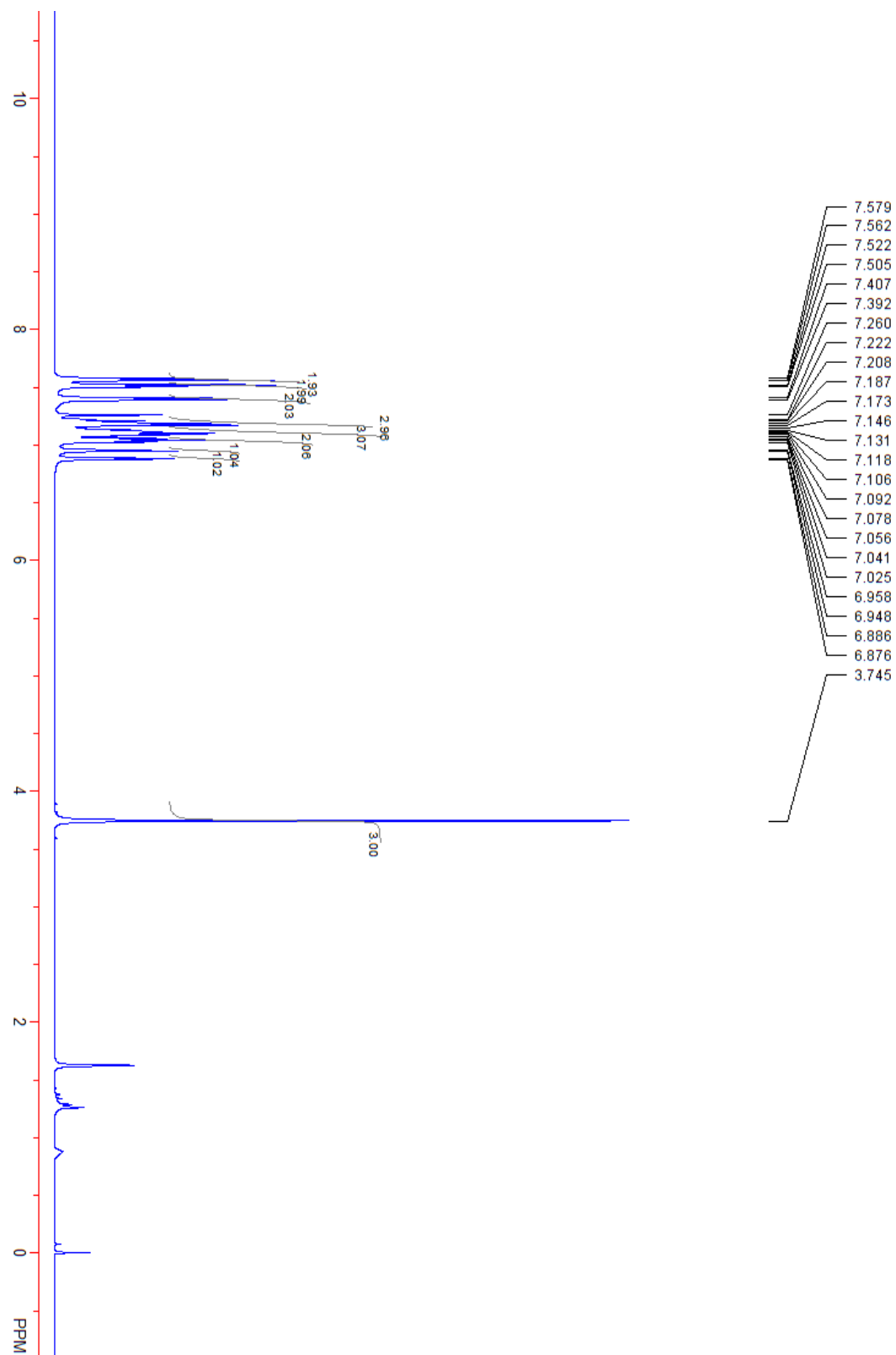


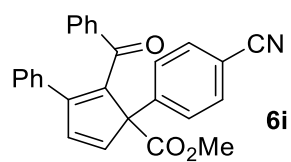
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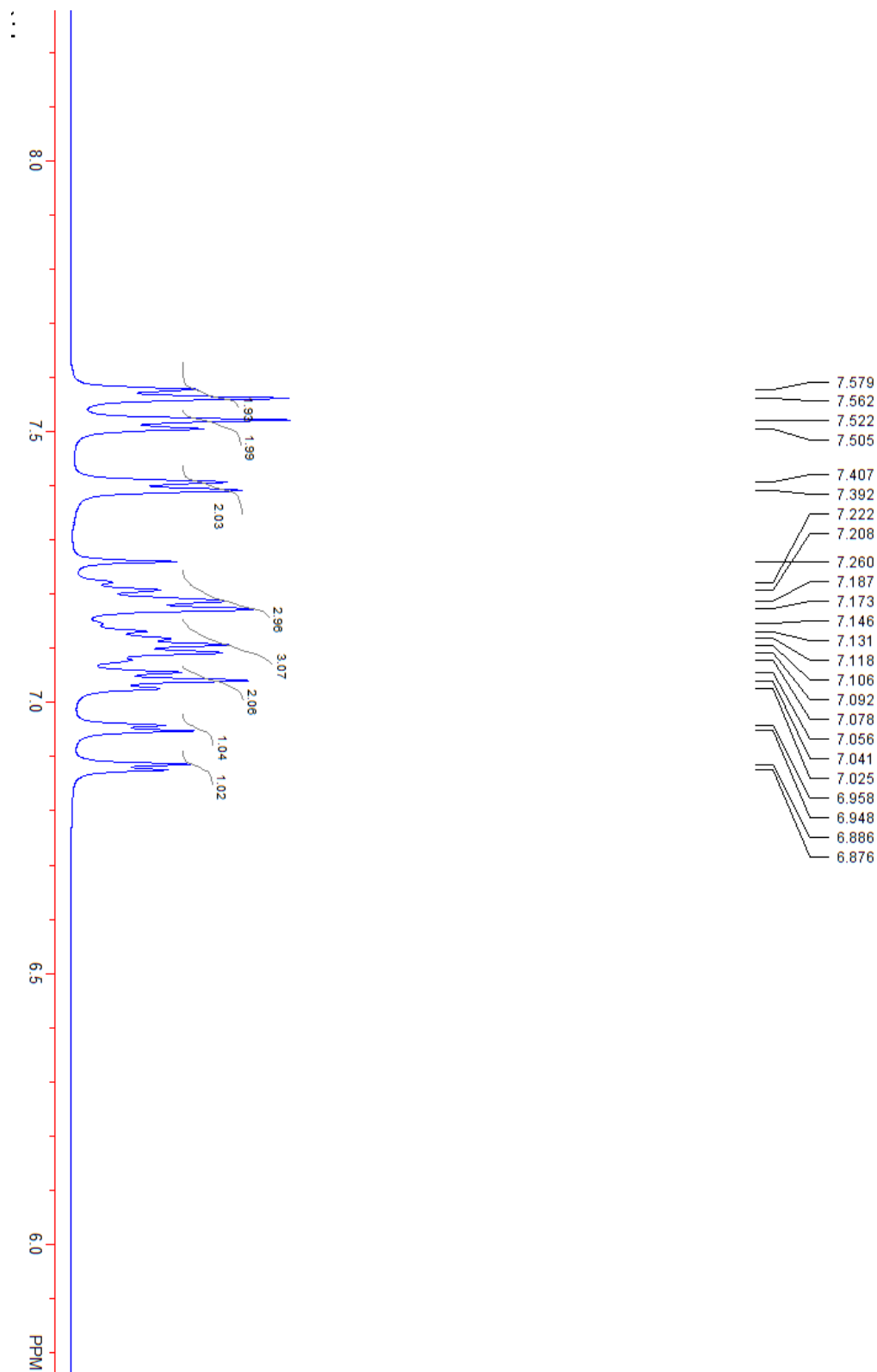


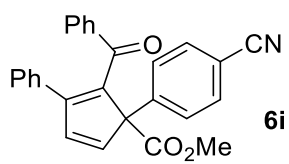
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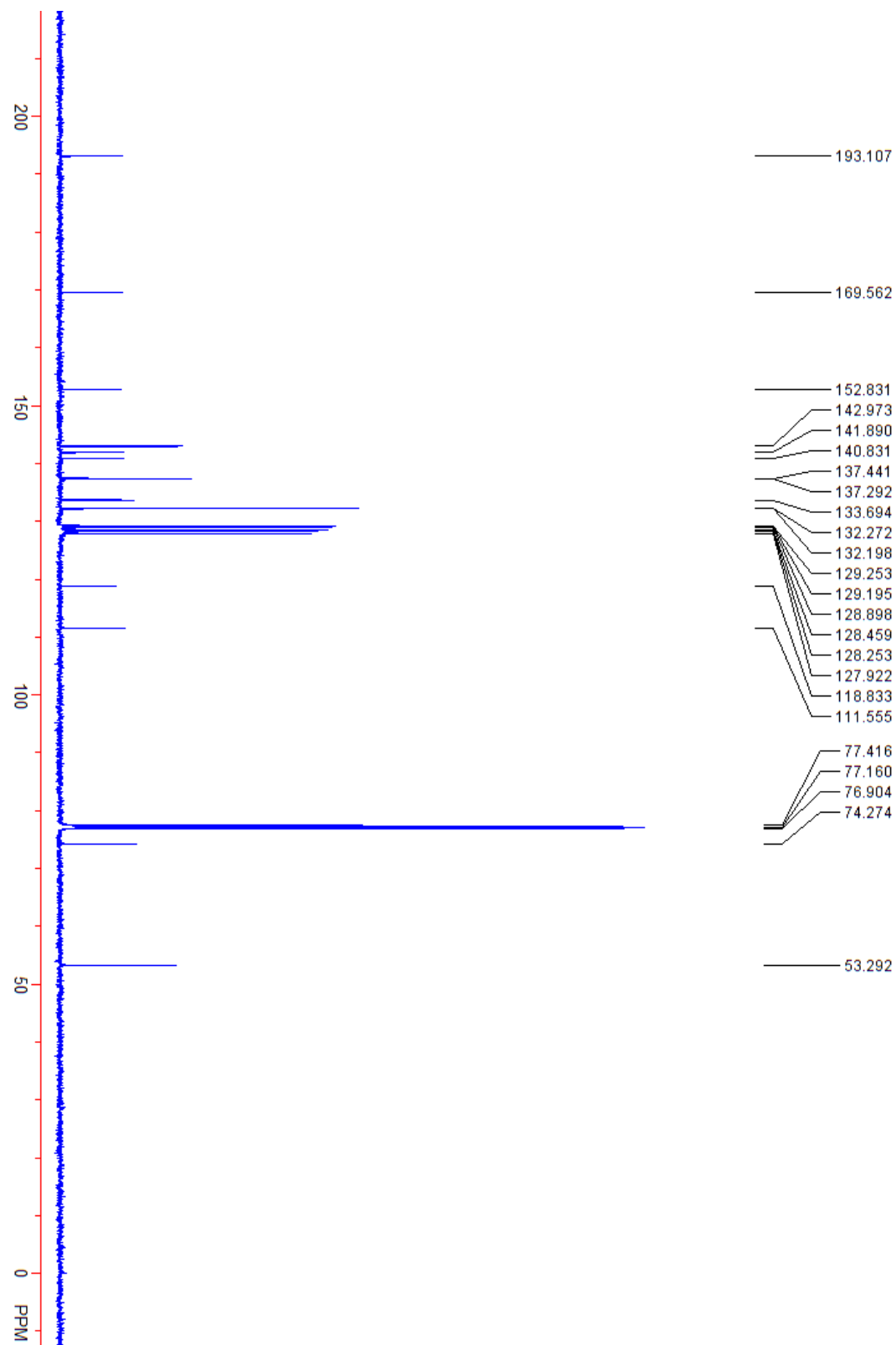


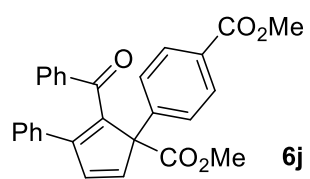
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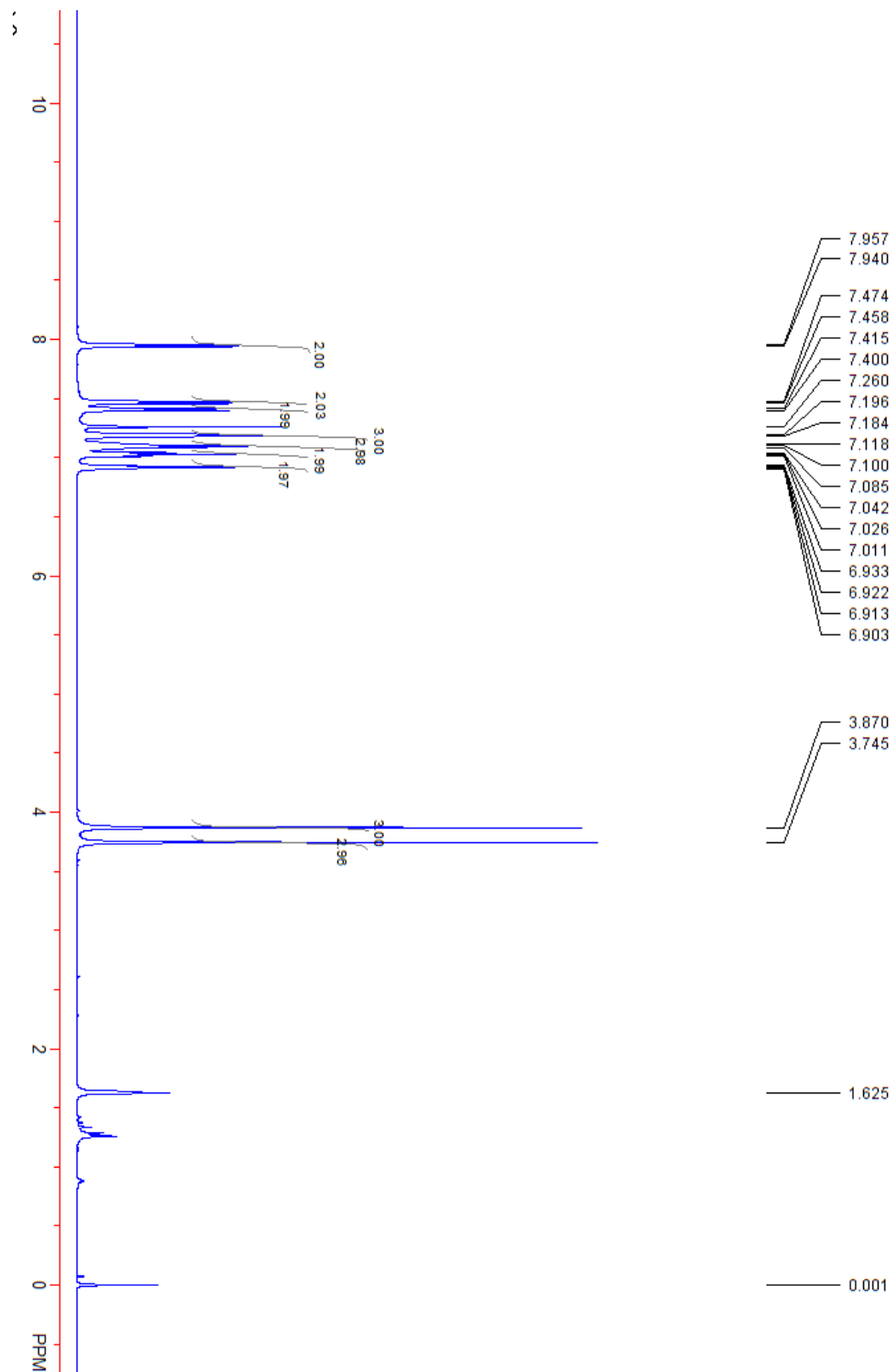


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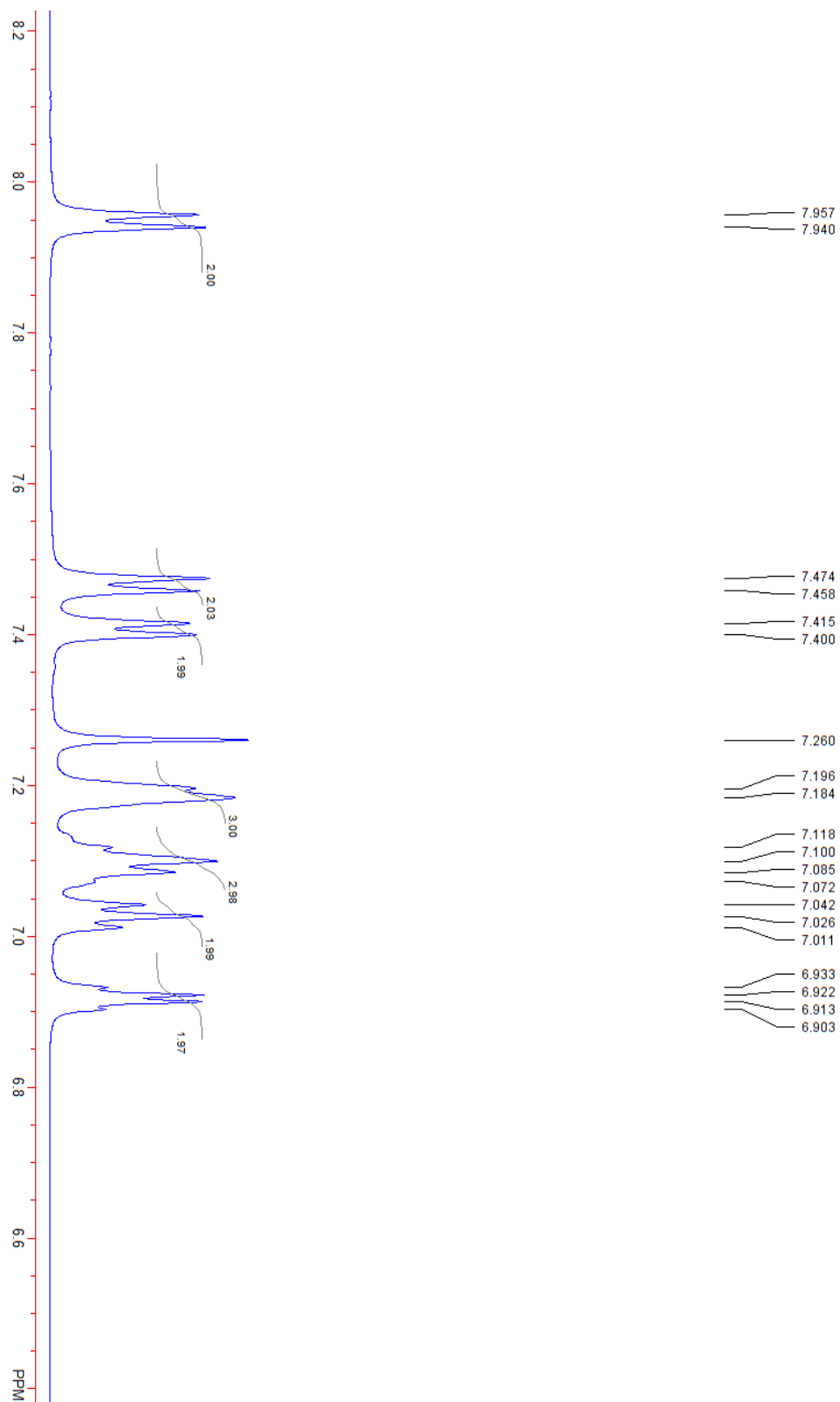
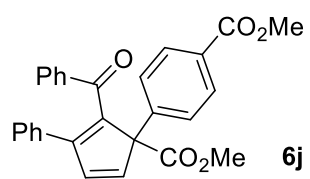


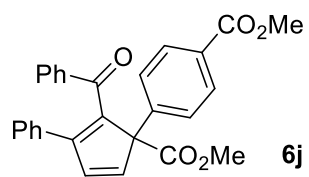


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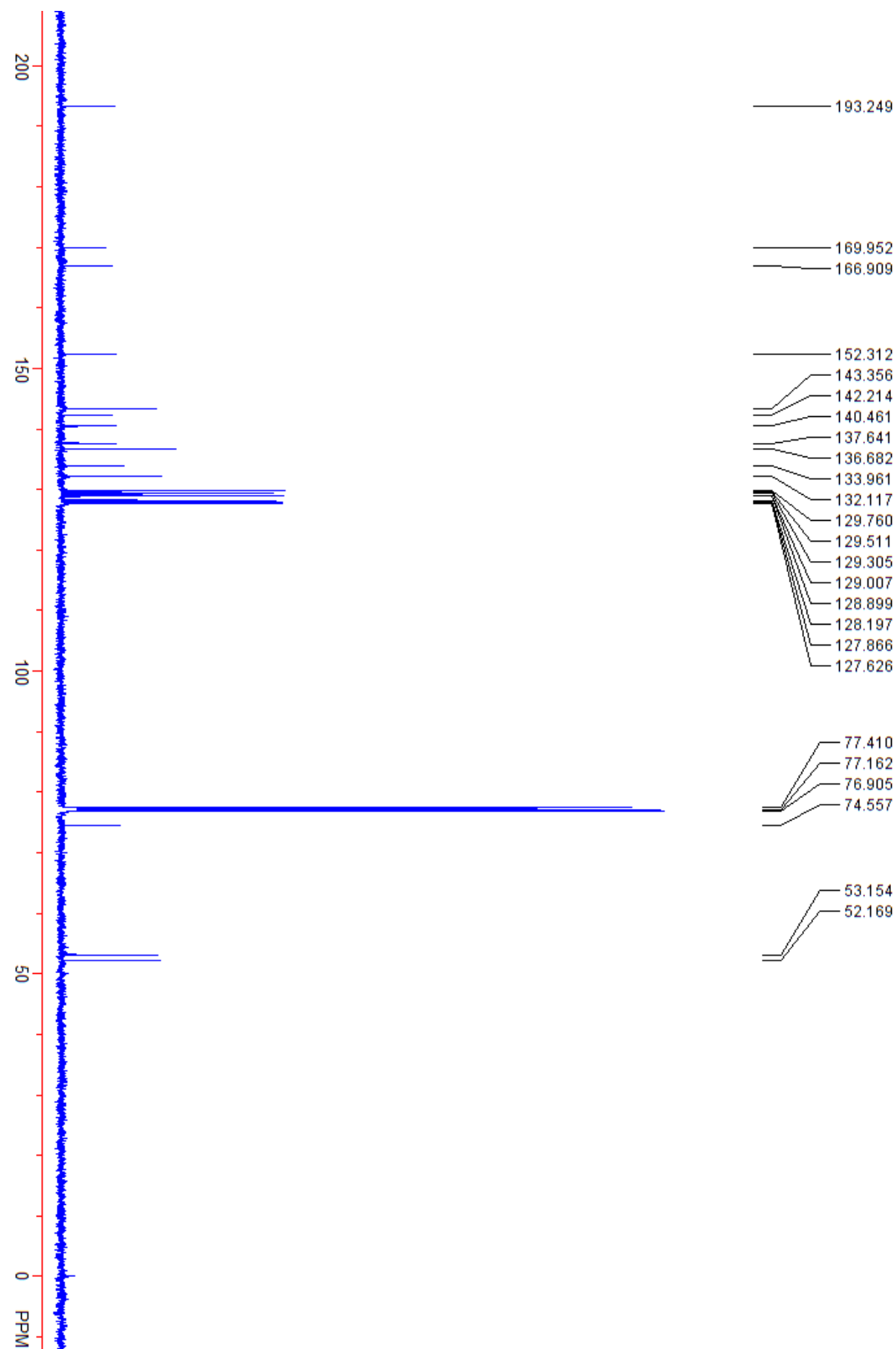


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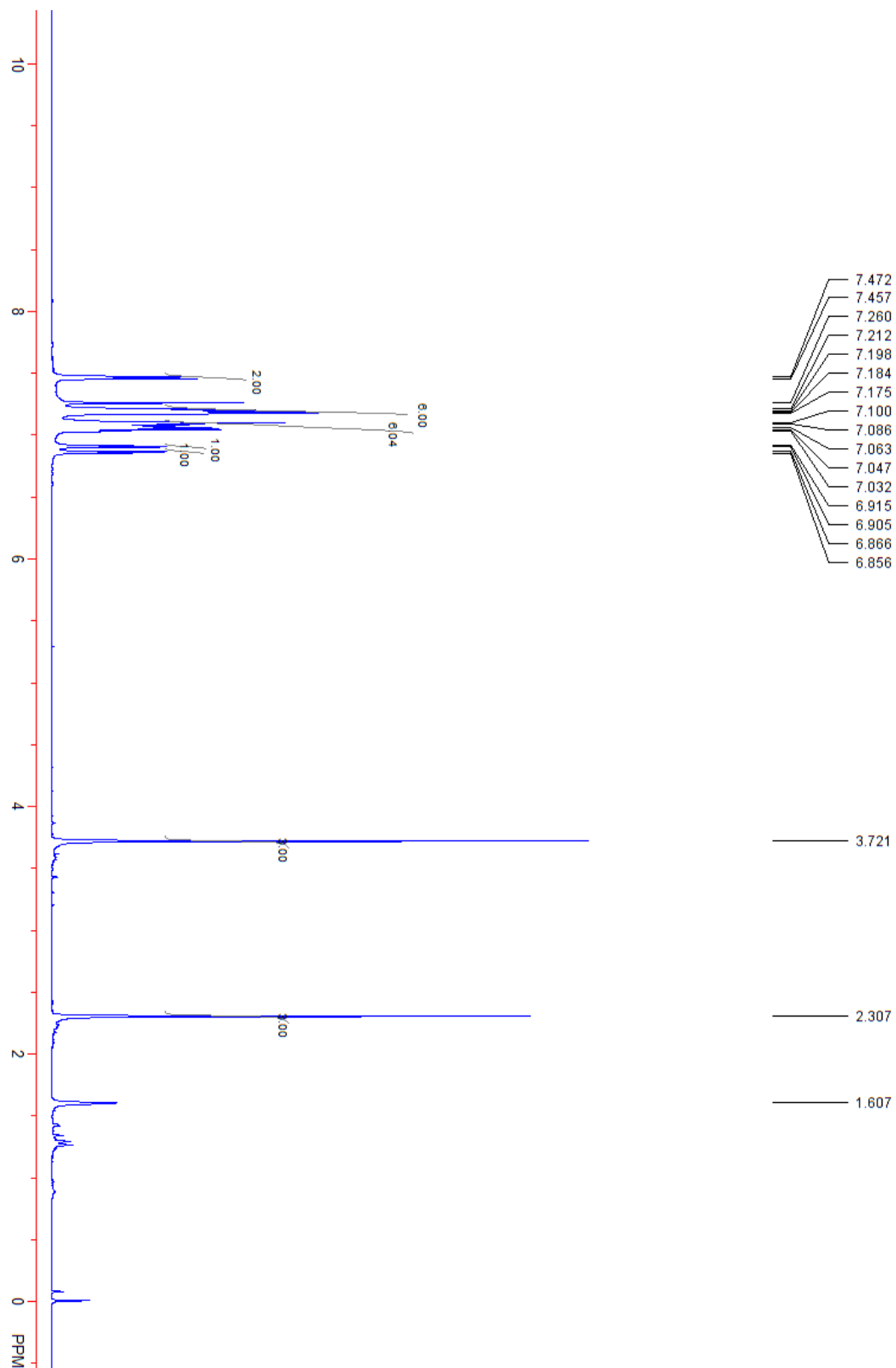
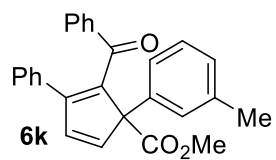




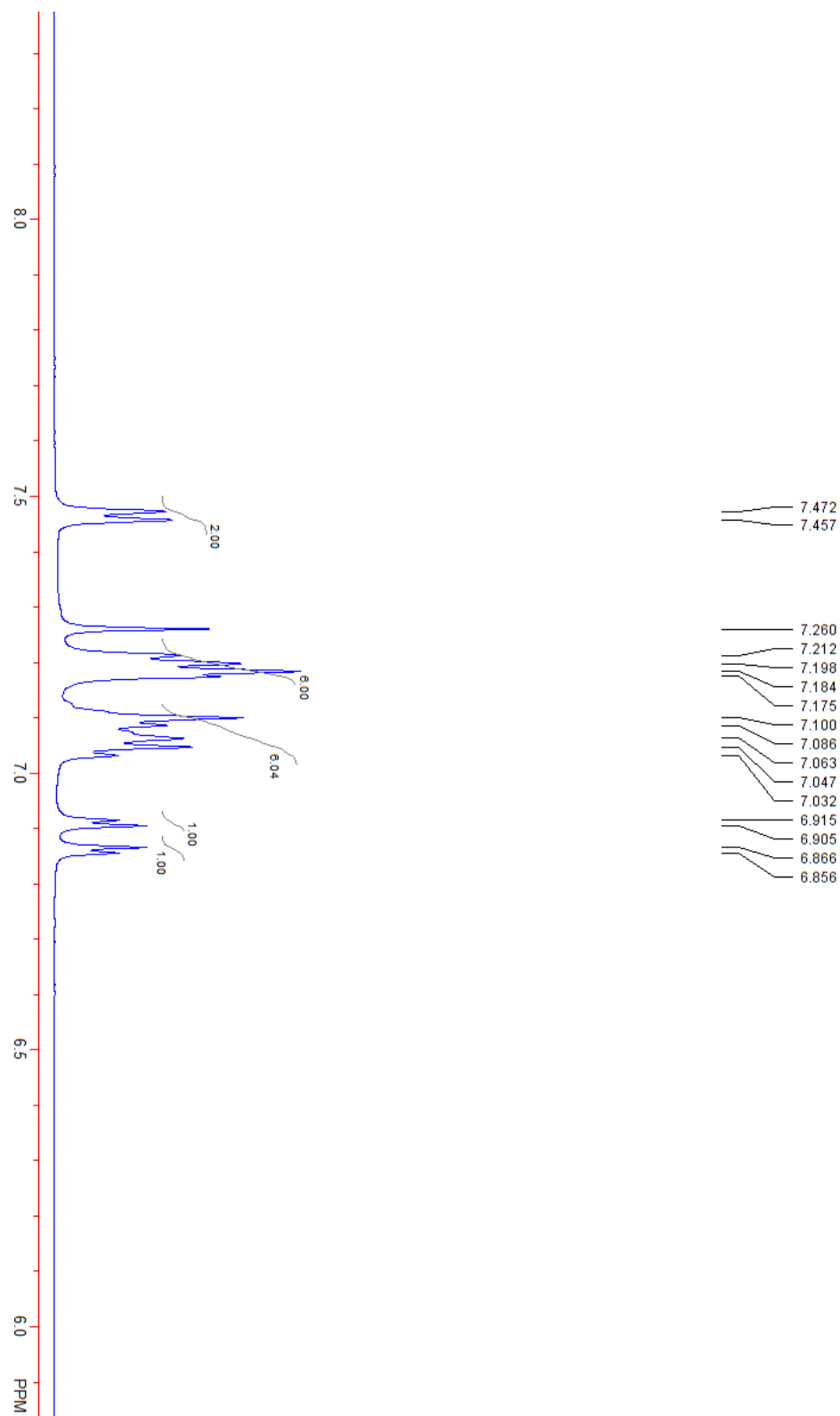
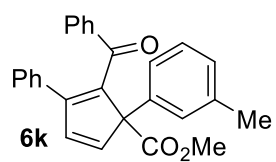
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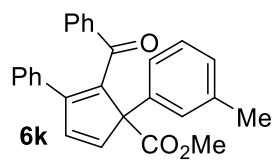


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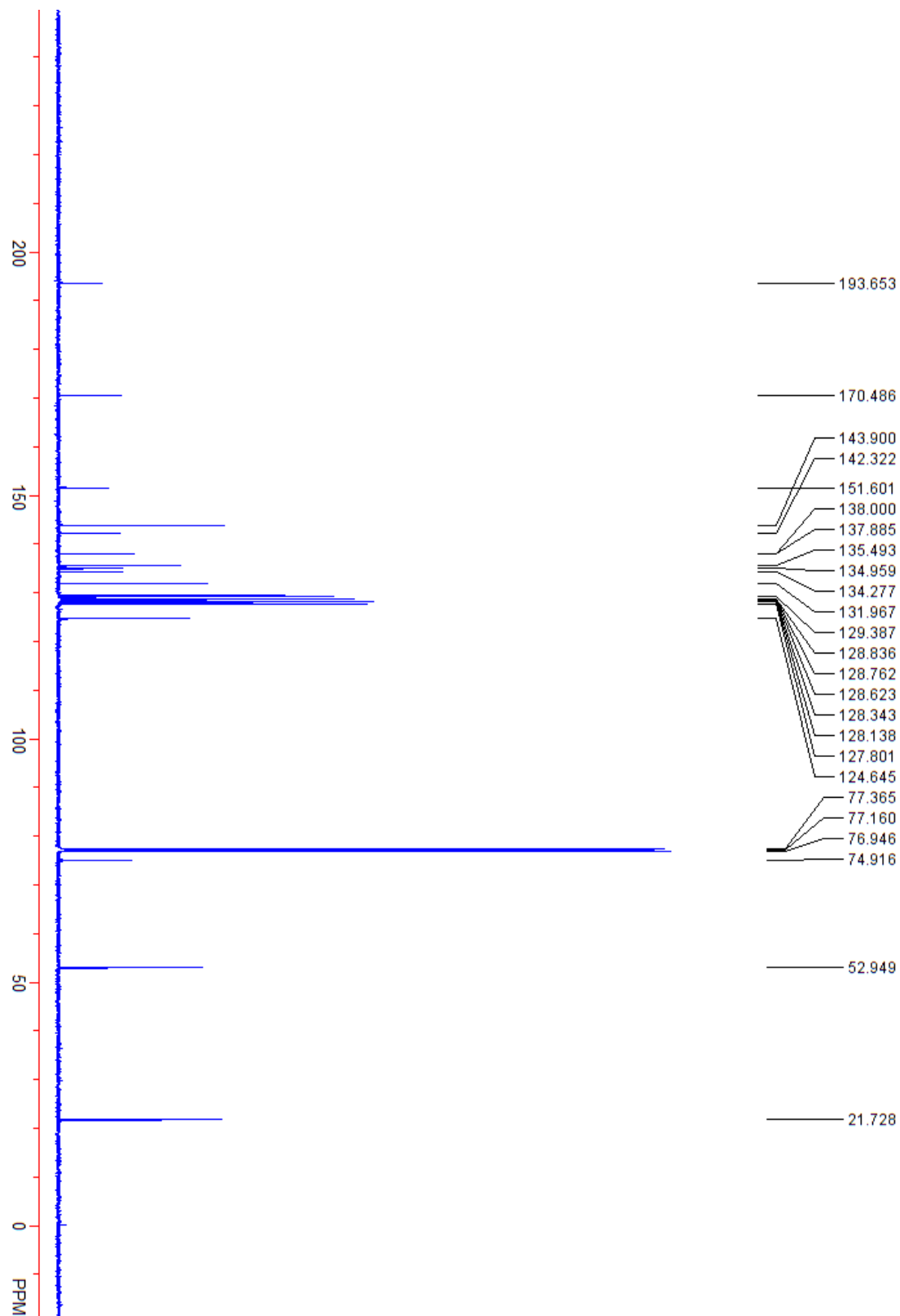


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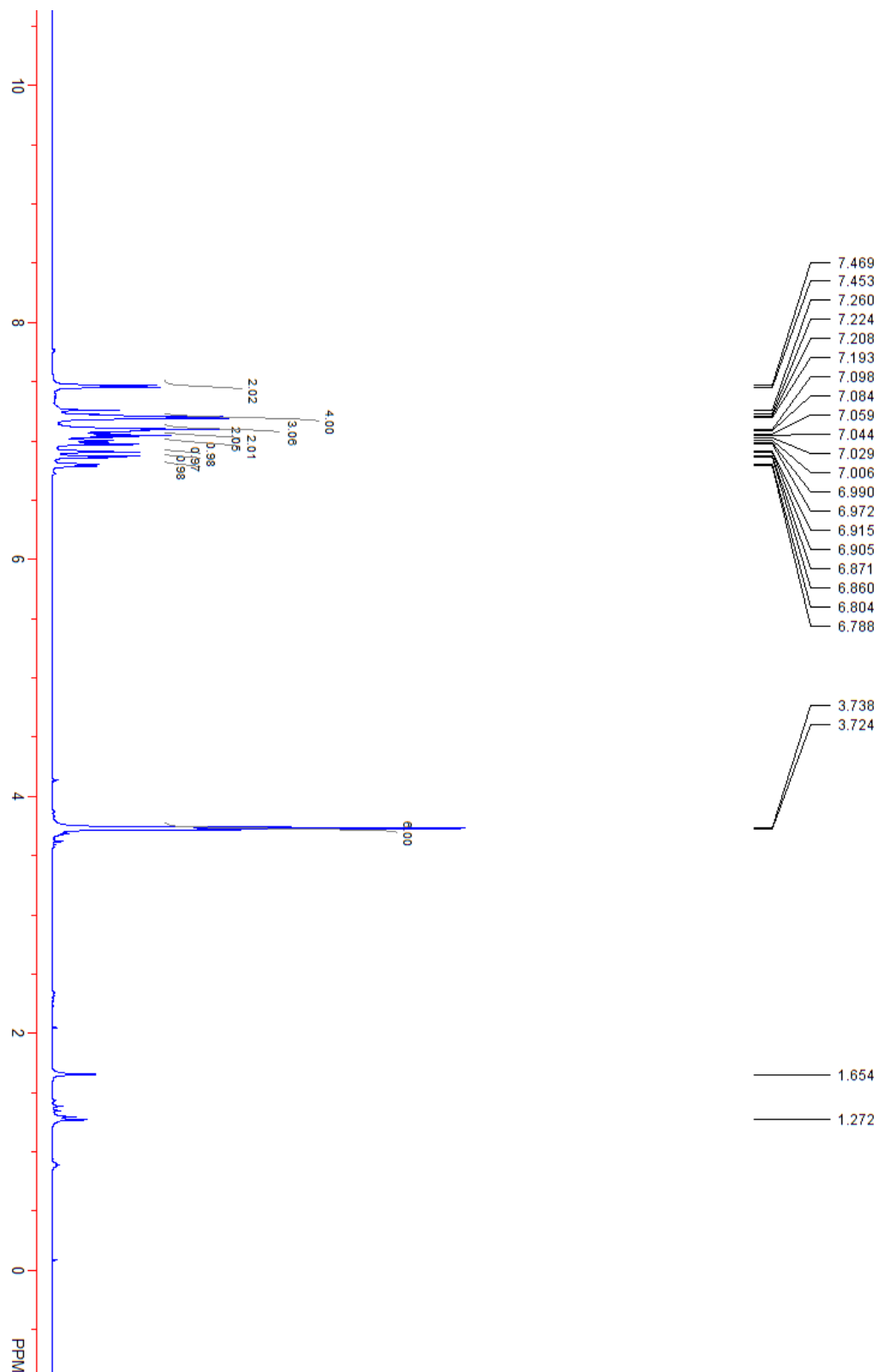
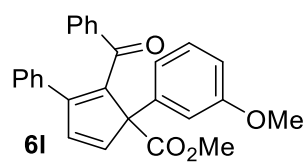




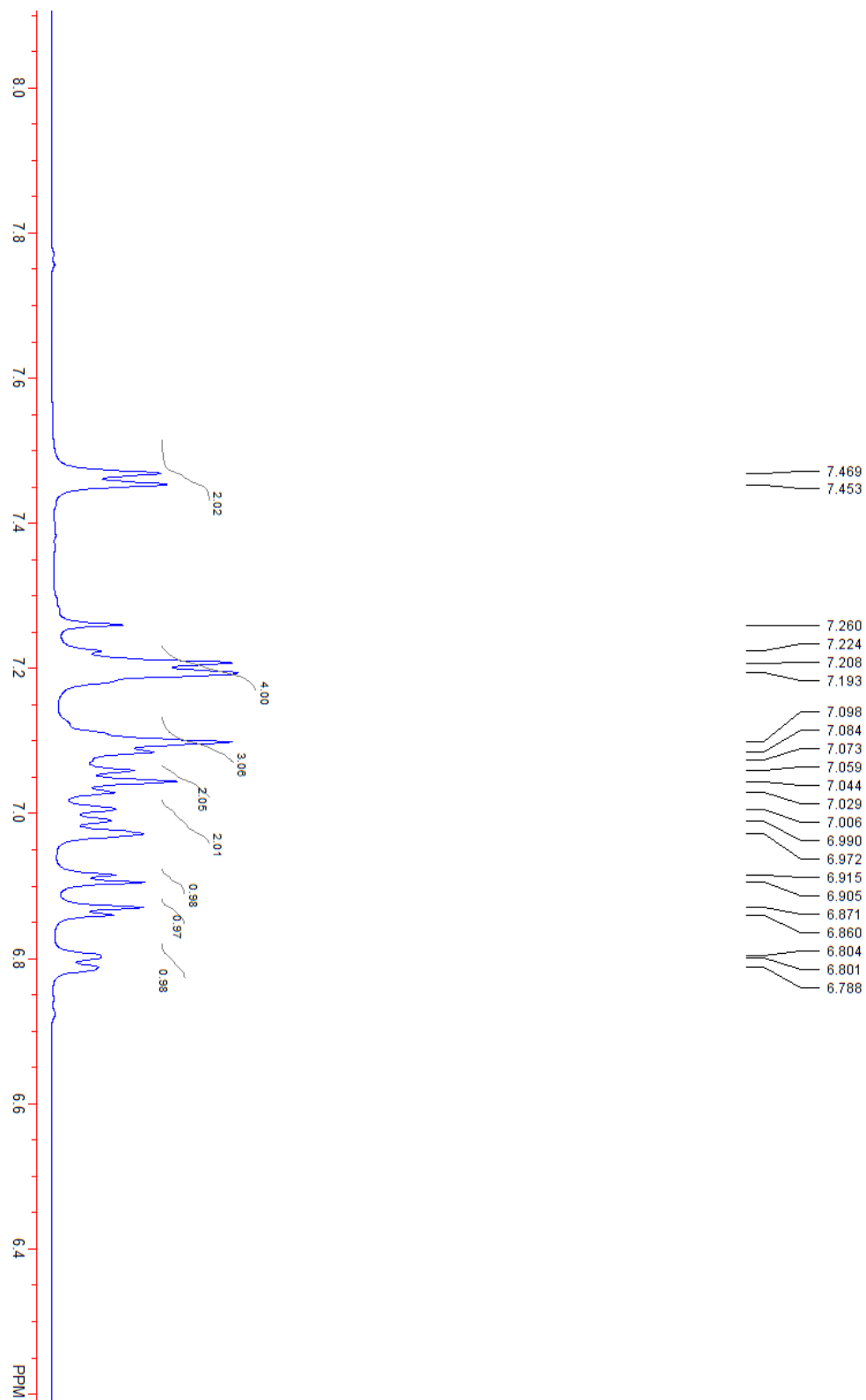
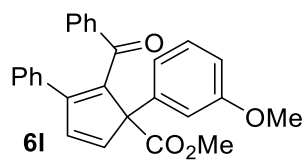
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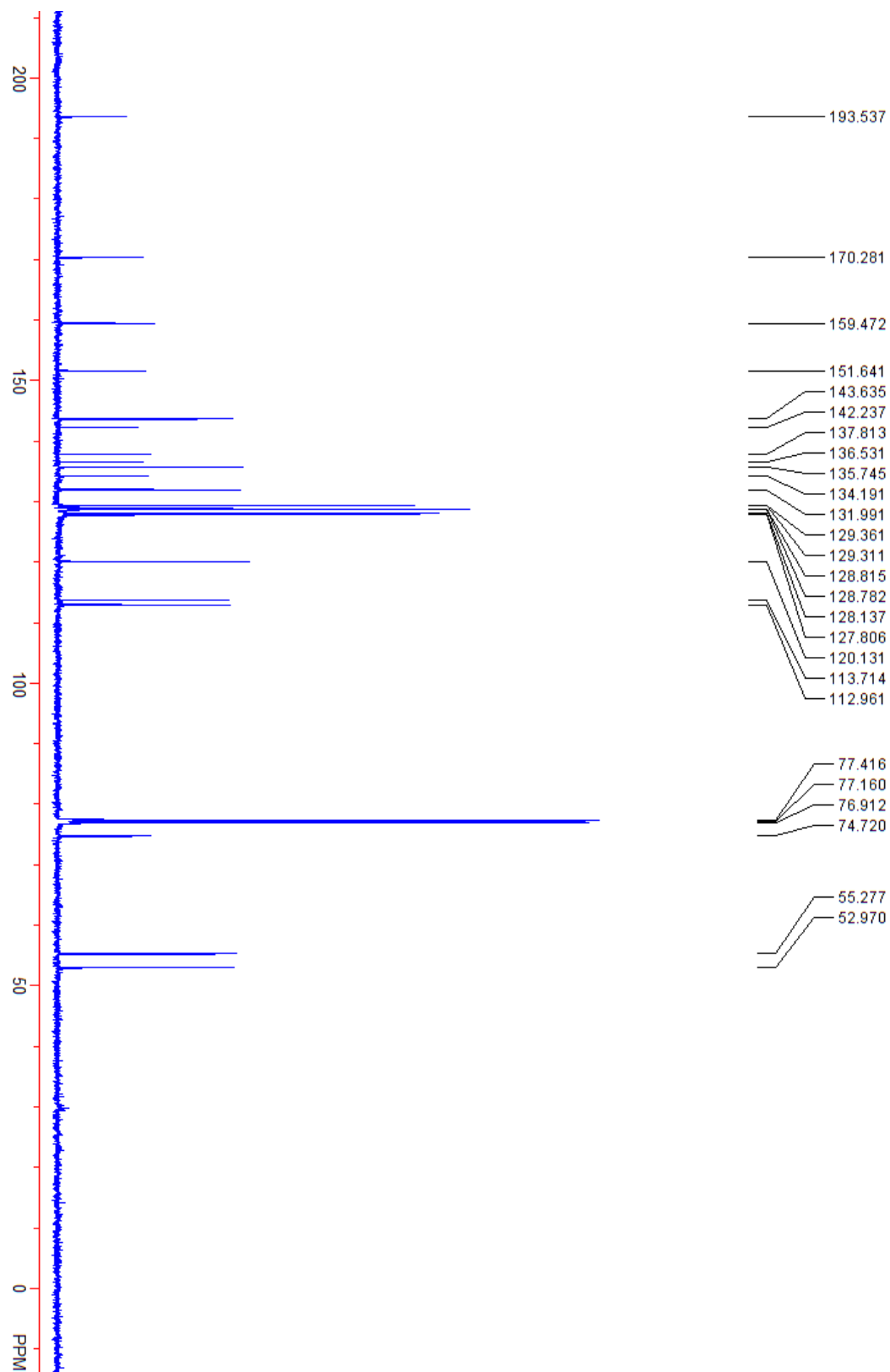
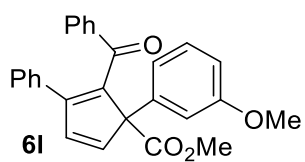
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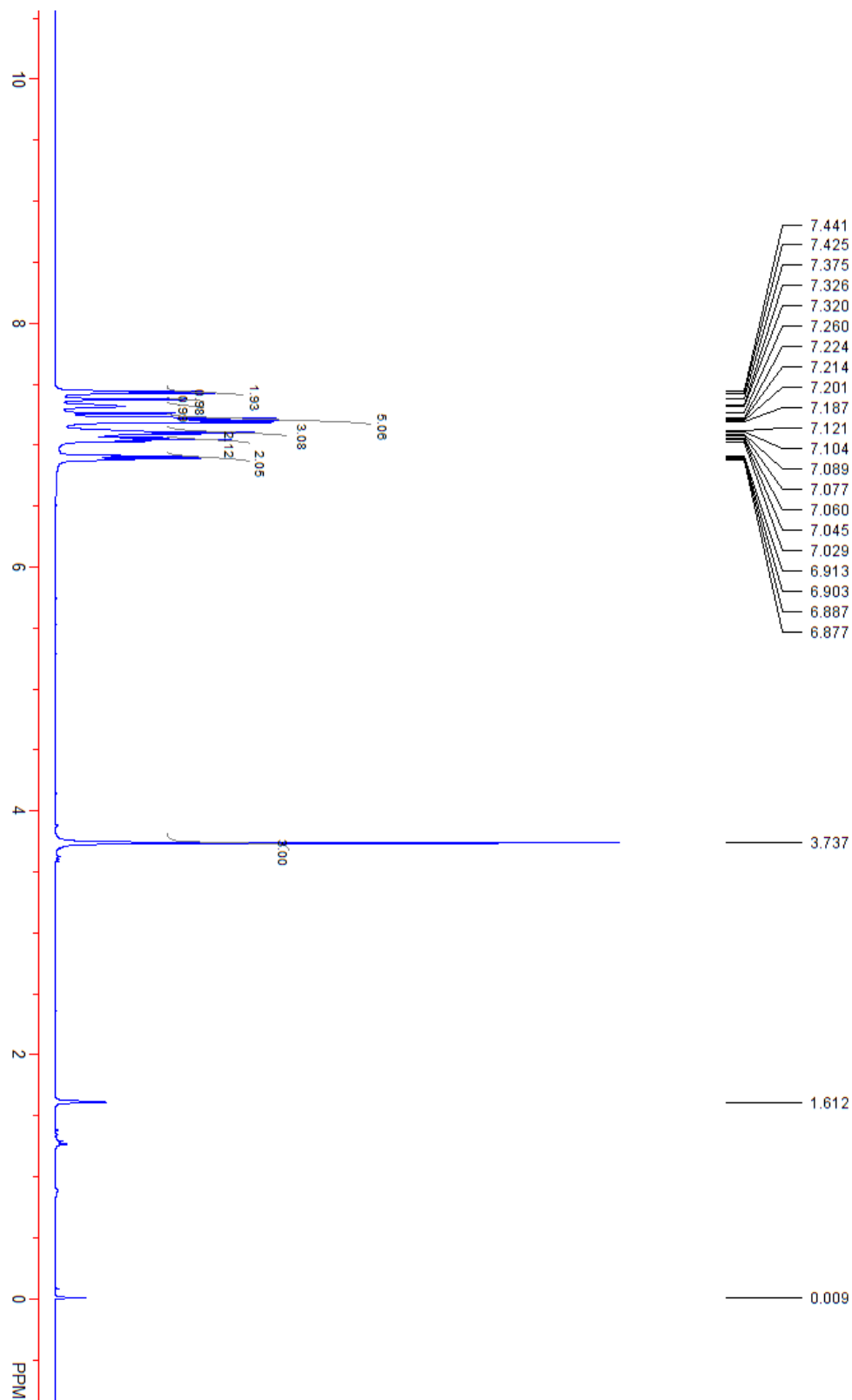
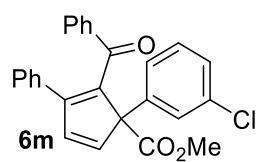
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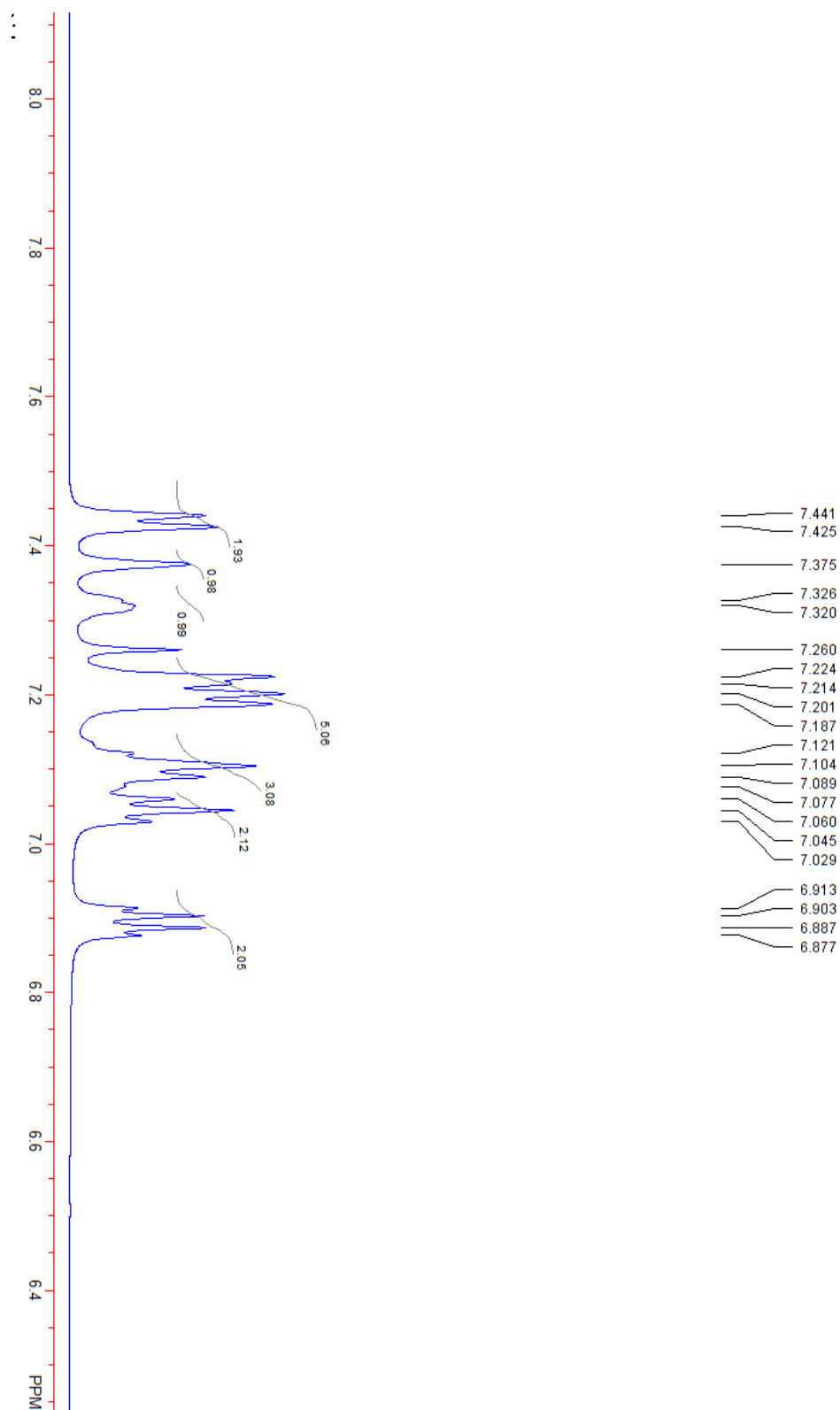
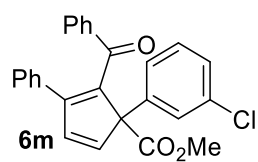
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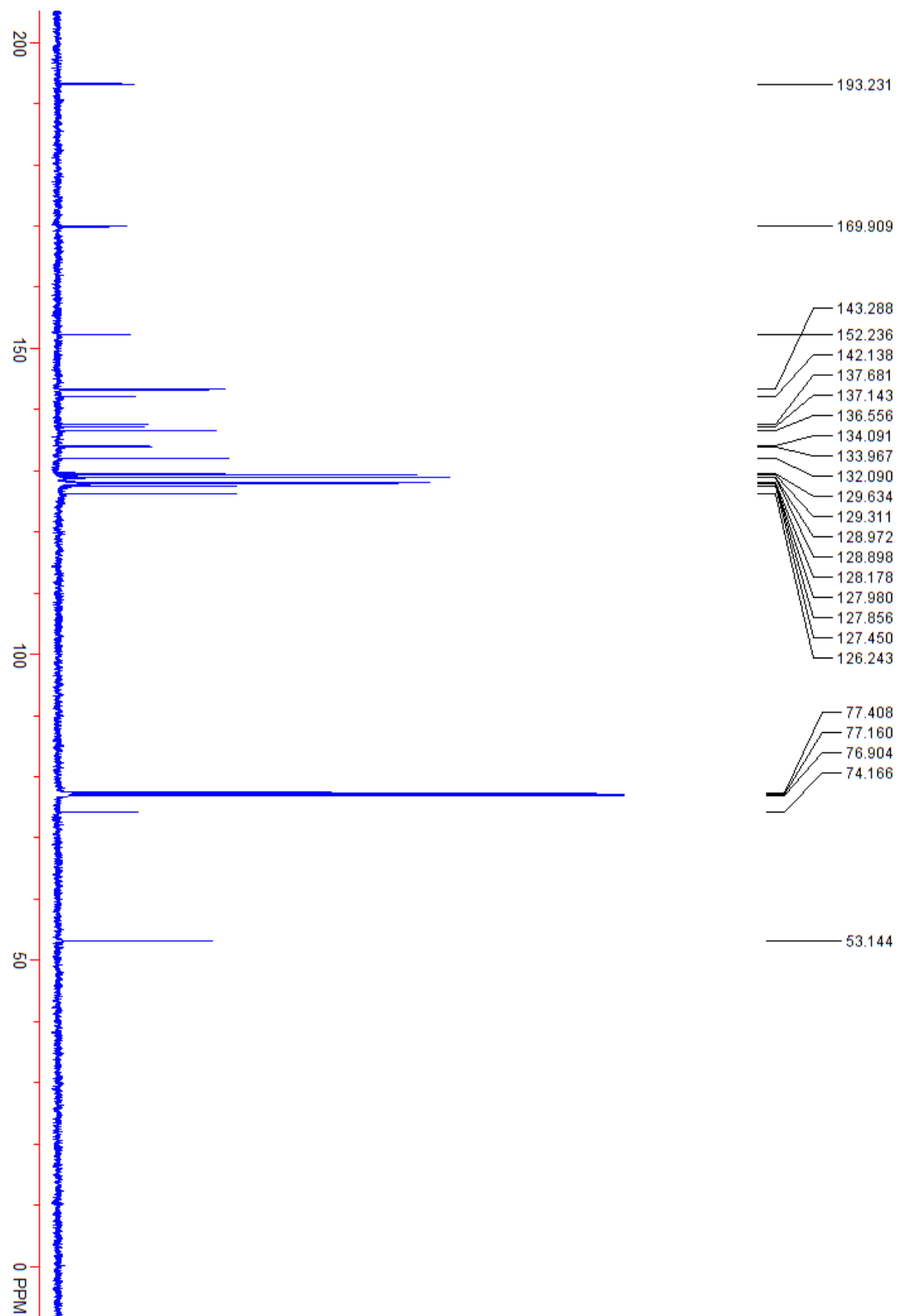
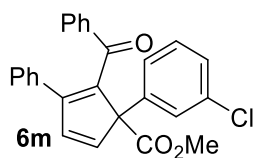
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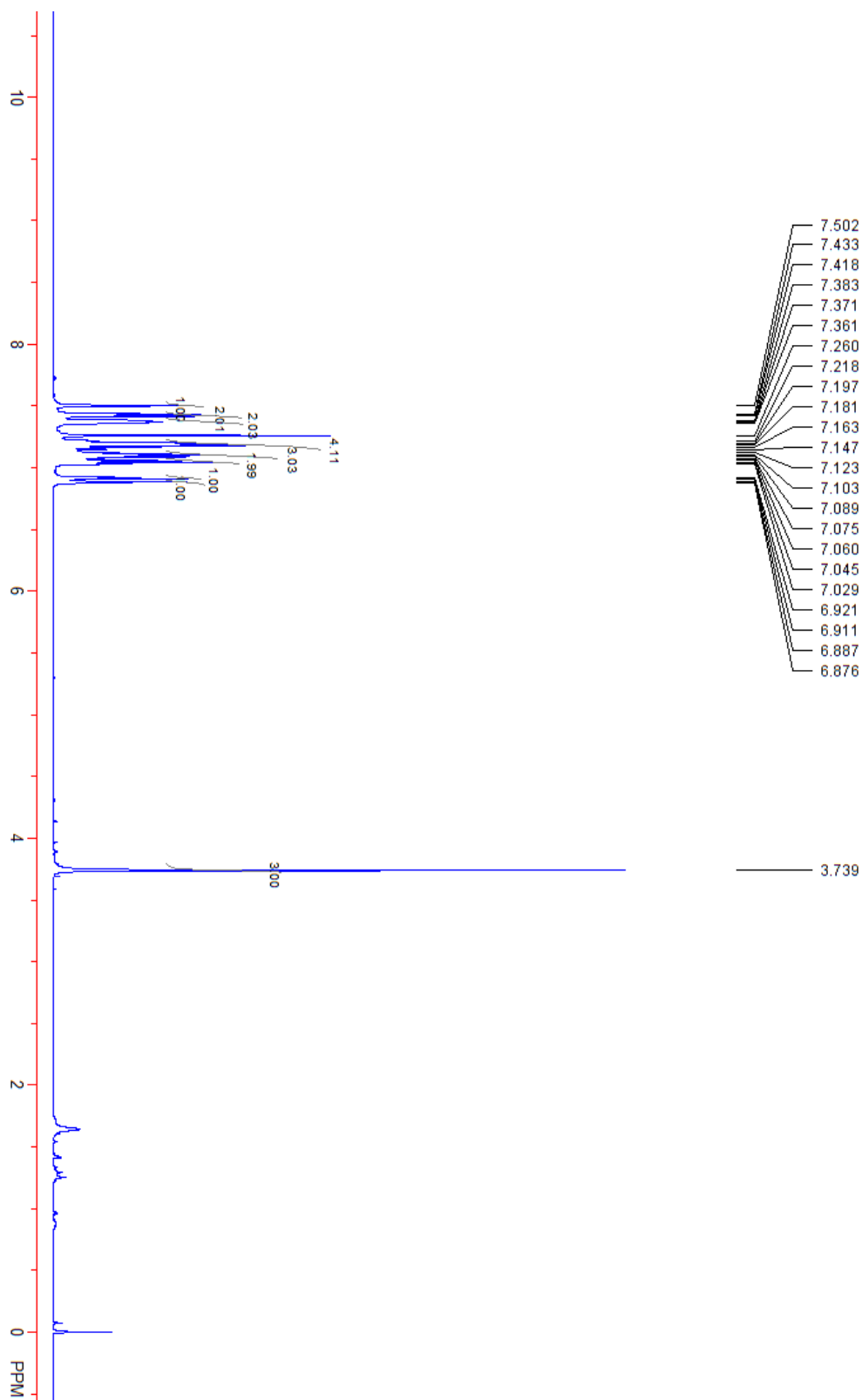
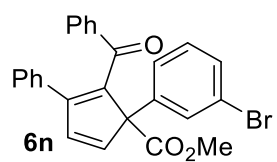
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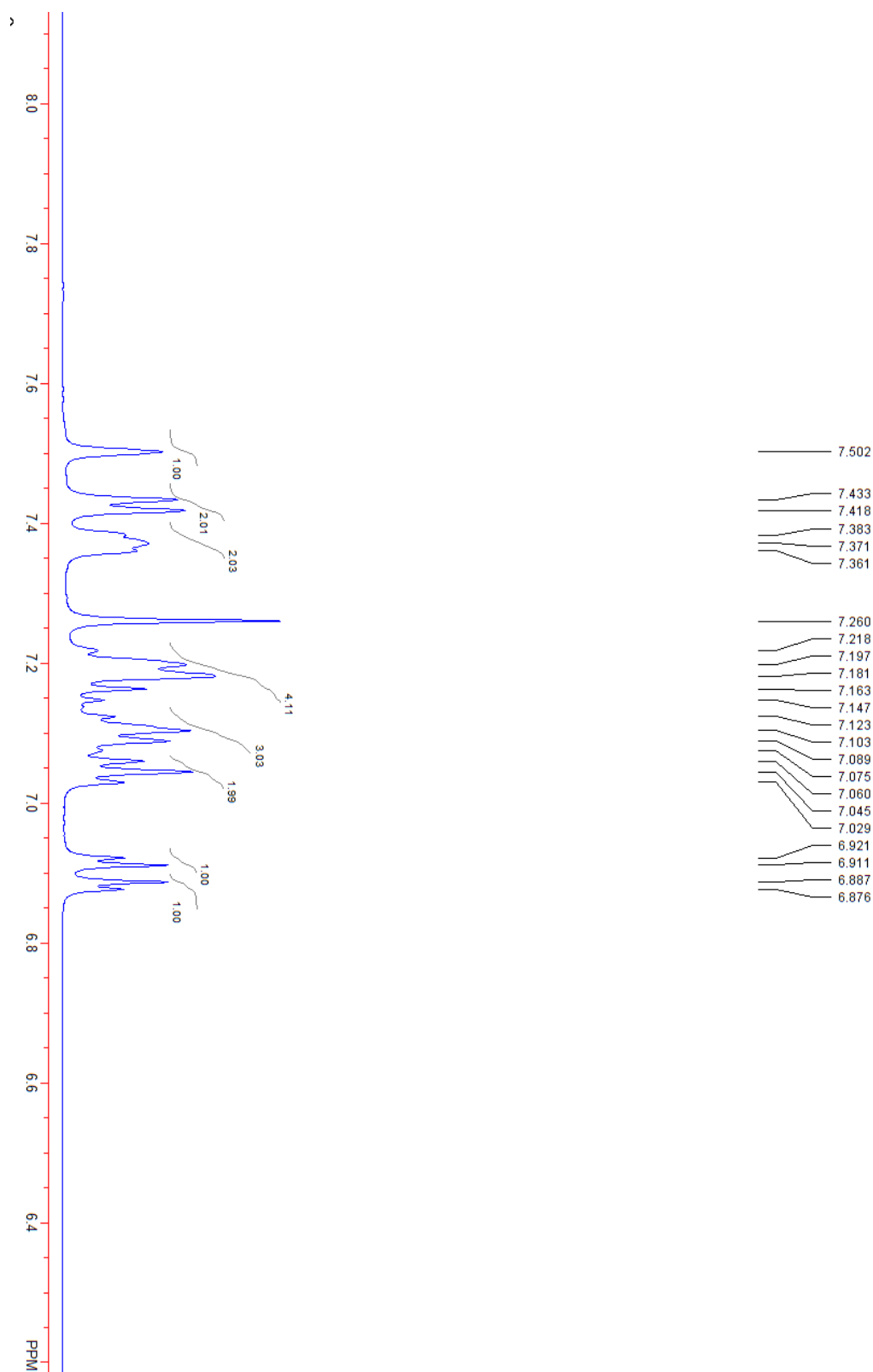
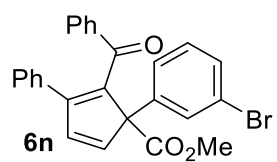
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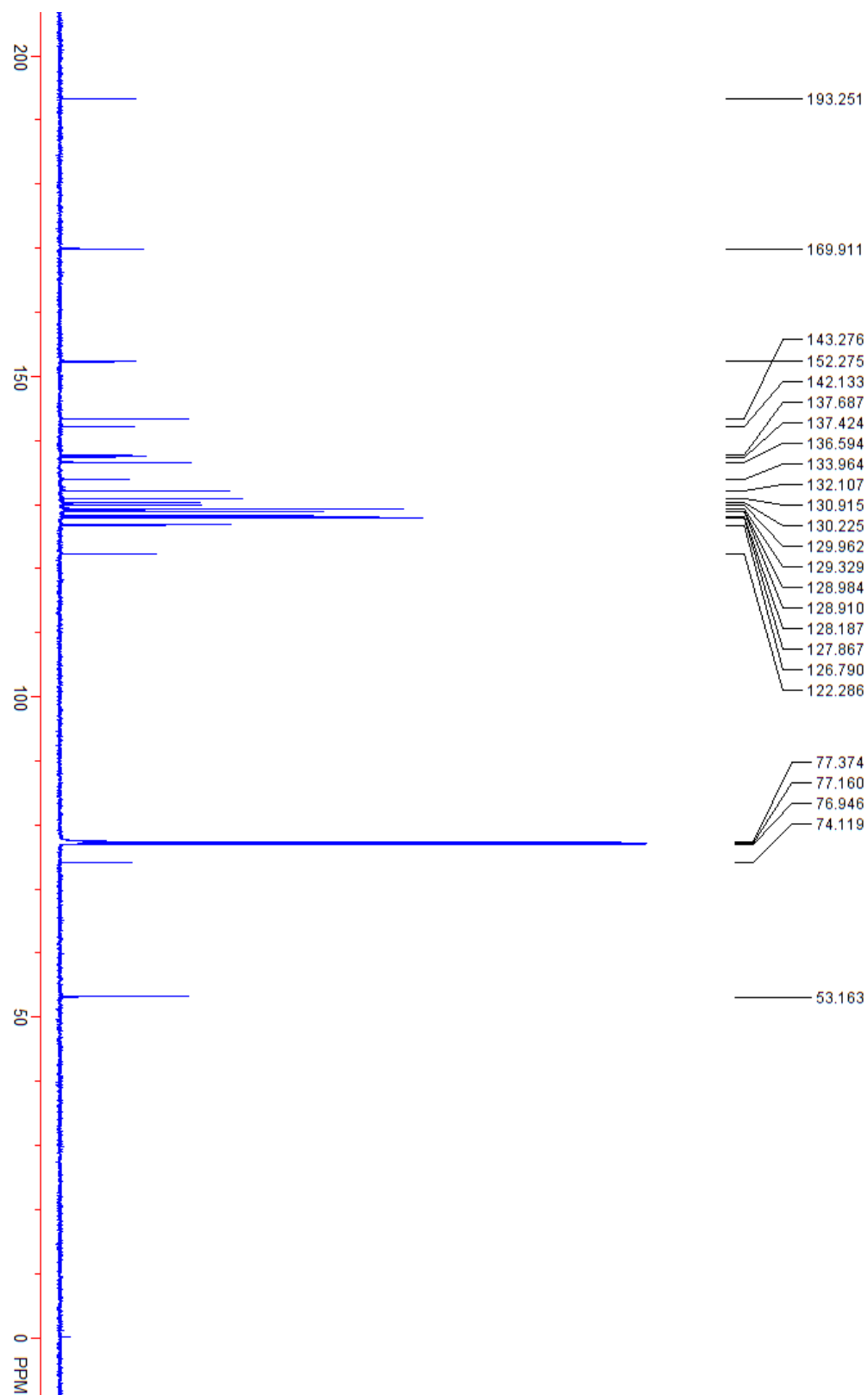
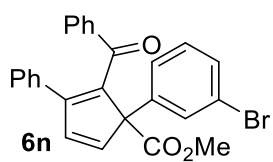
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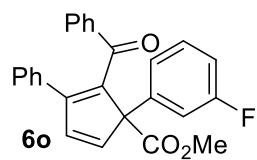


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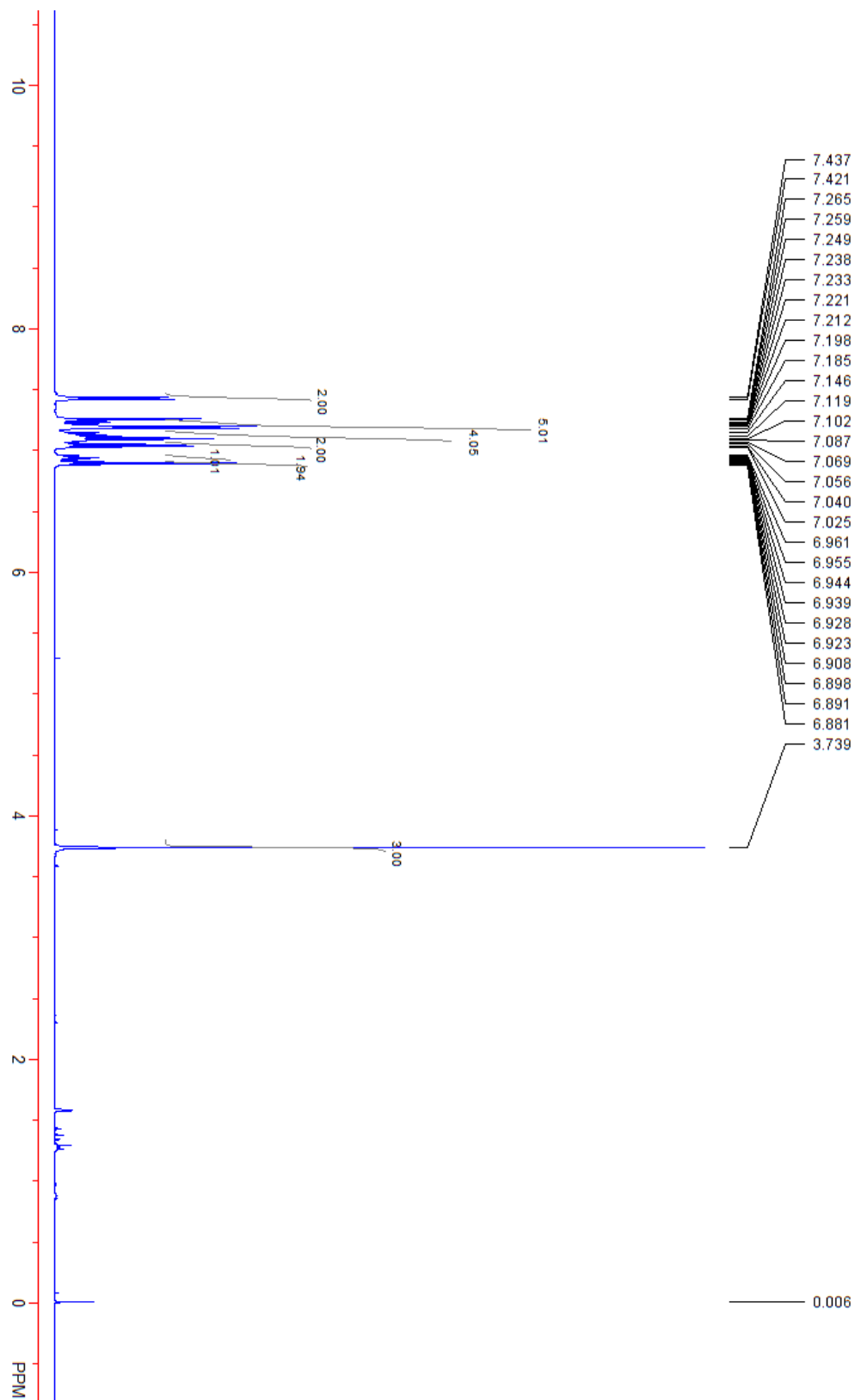


$^{13}\text{C}\{^1\text{H}\}$ NMR:

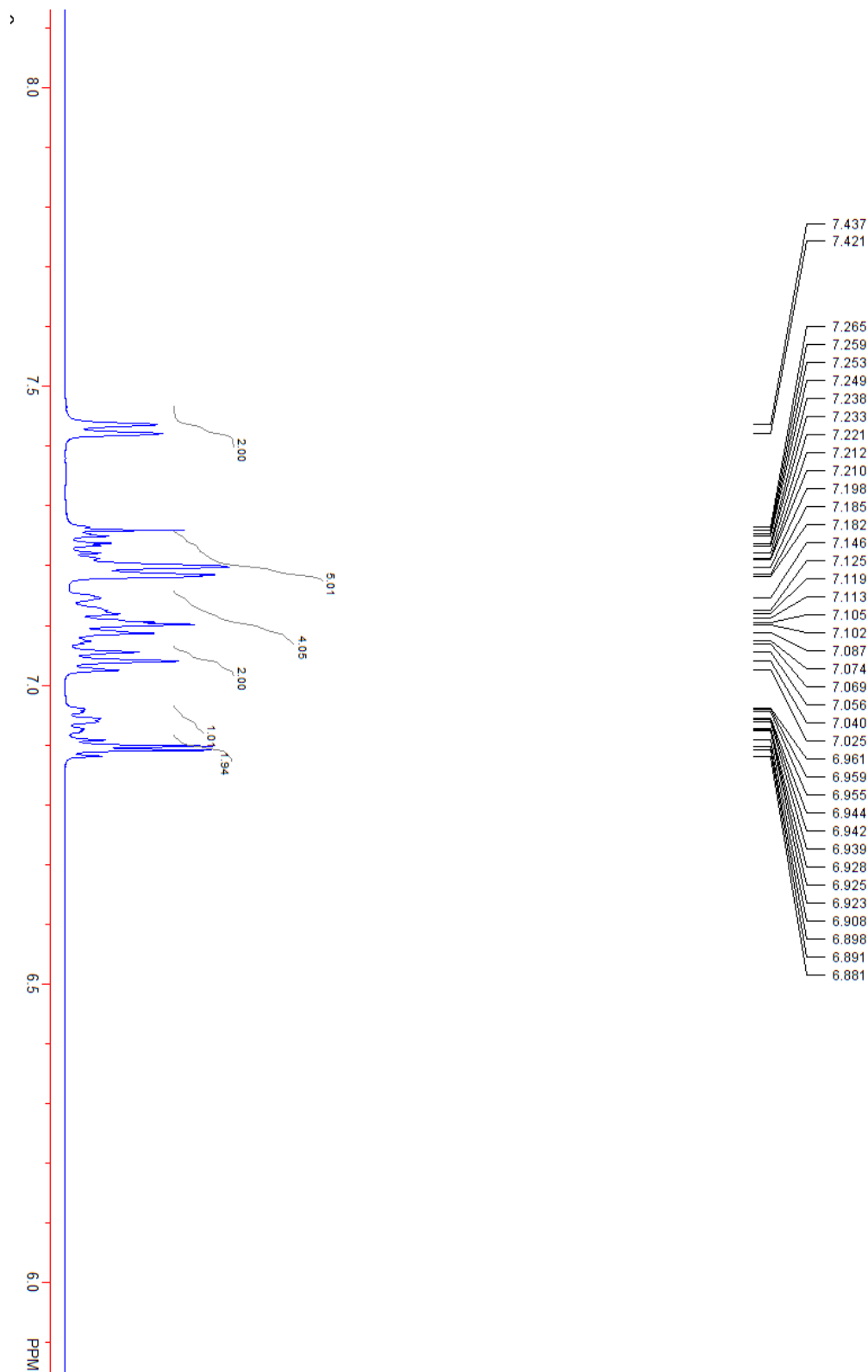
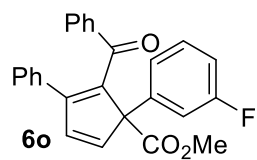




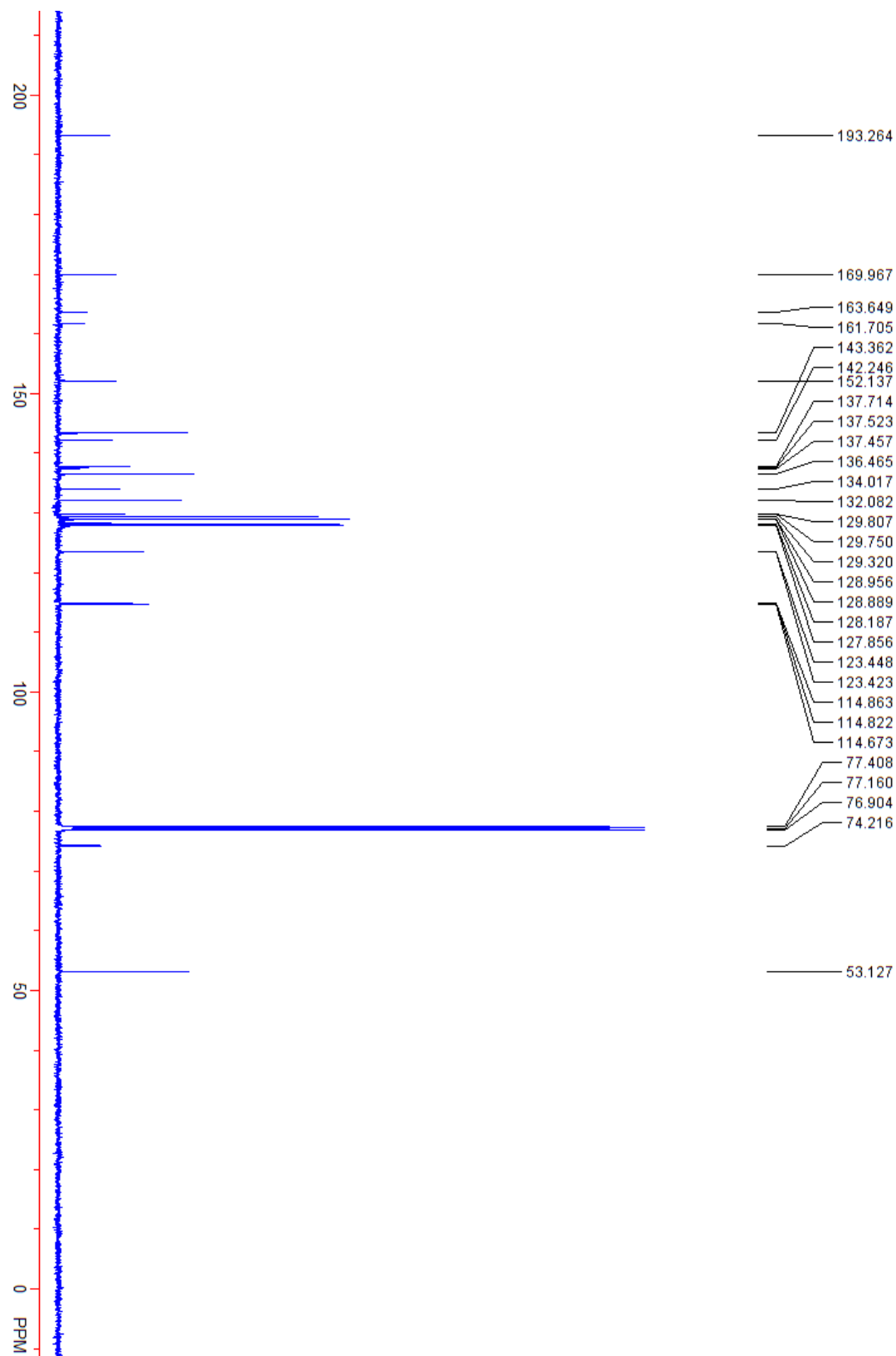
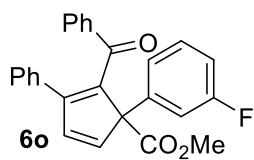
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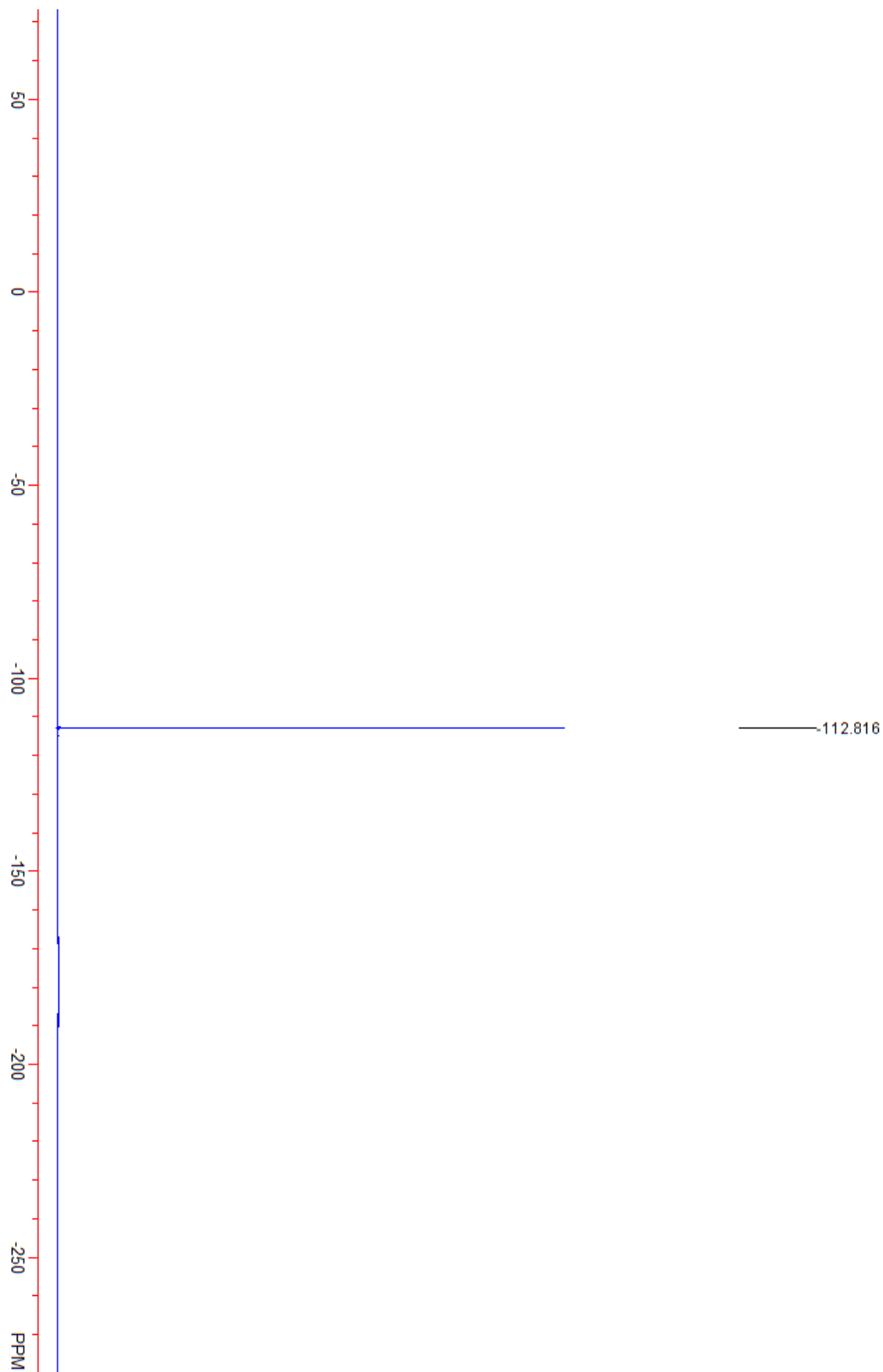
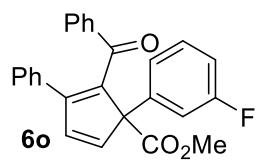
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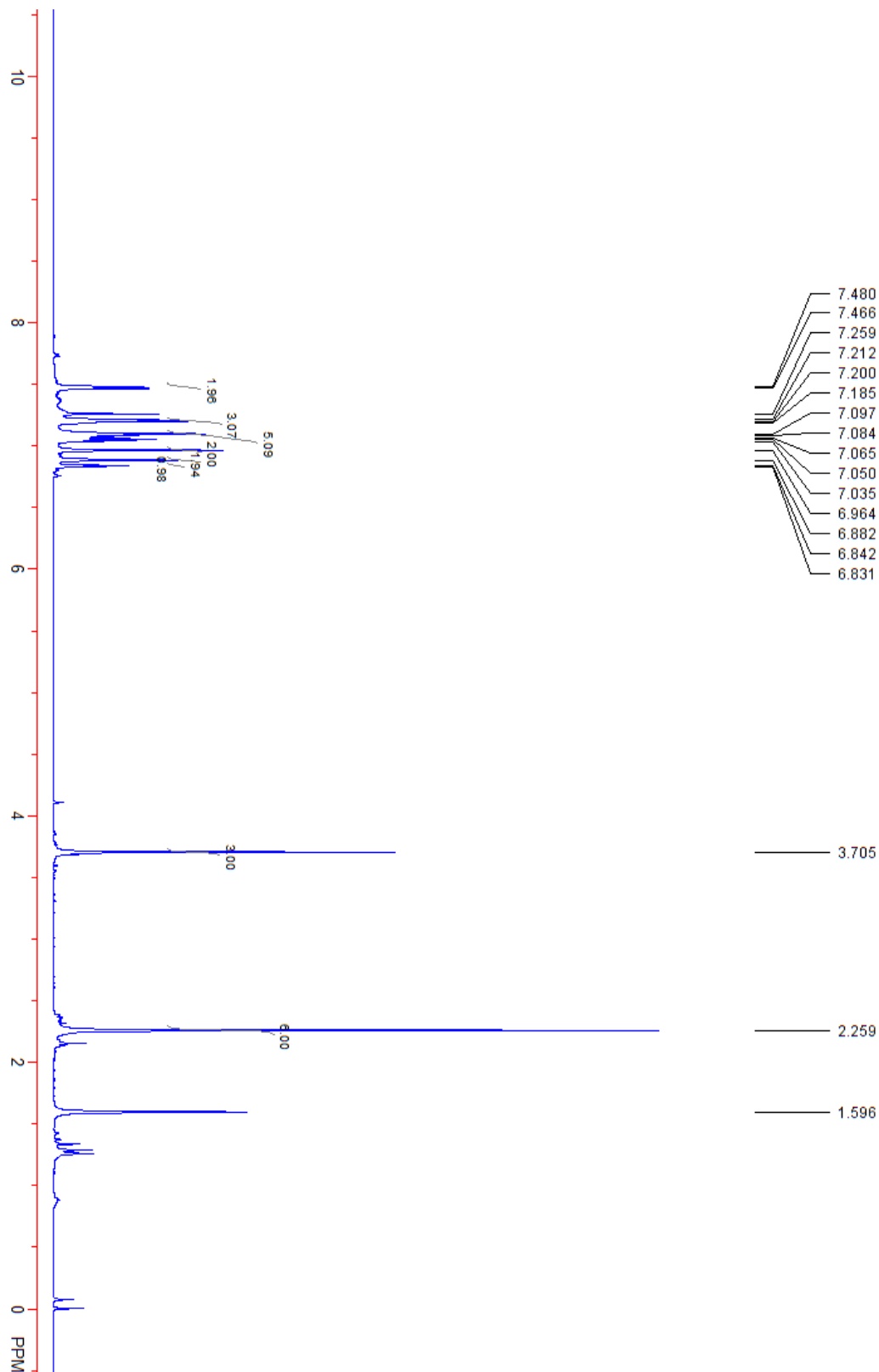
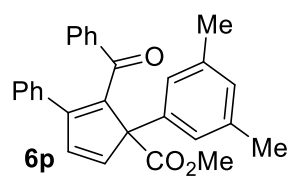
$^{13}\text{C}\{^1\text{H}\}$ NMR:



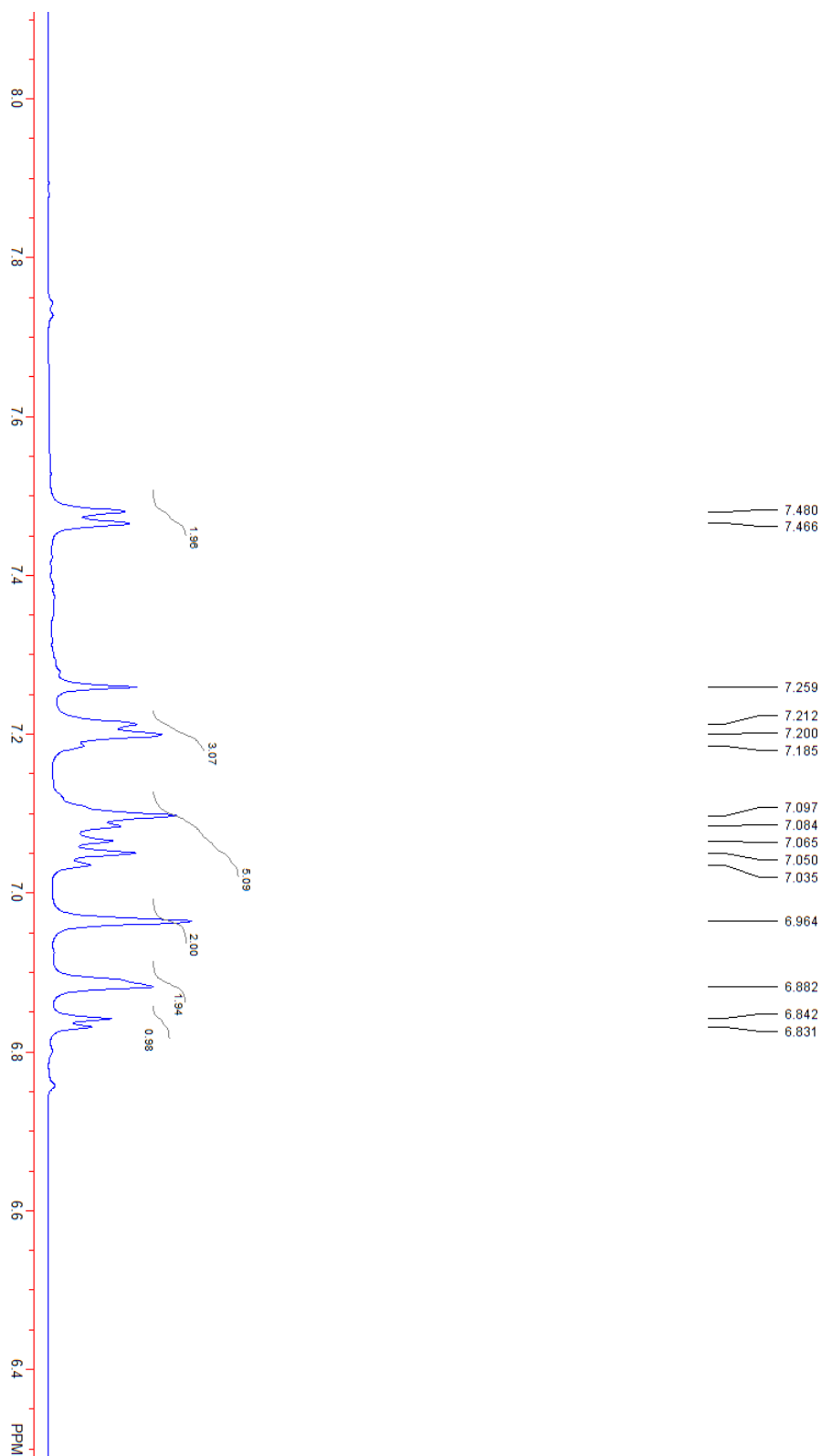
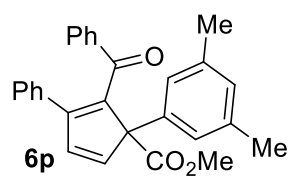
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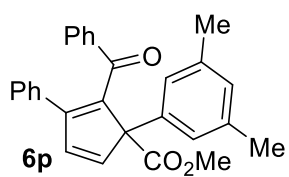


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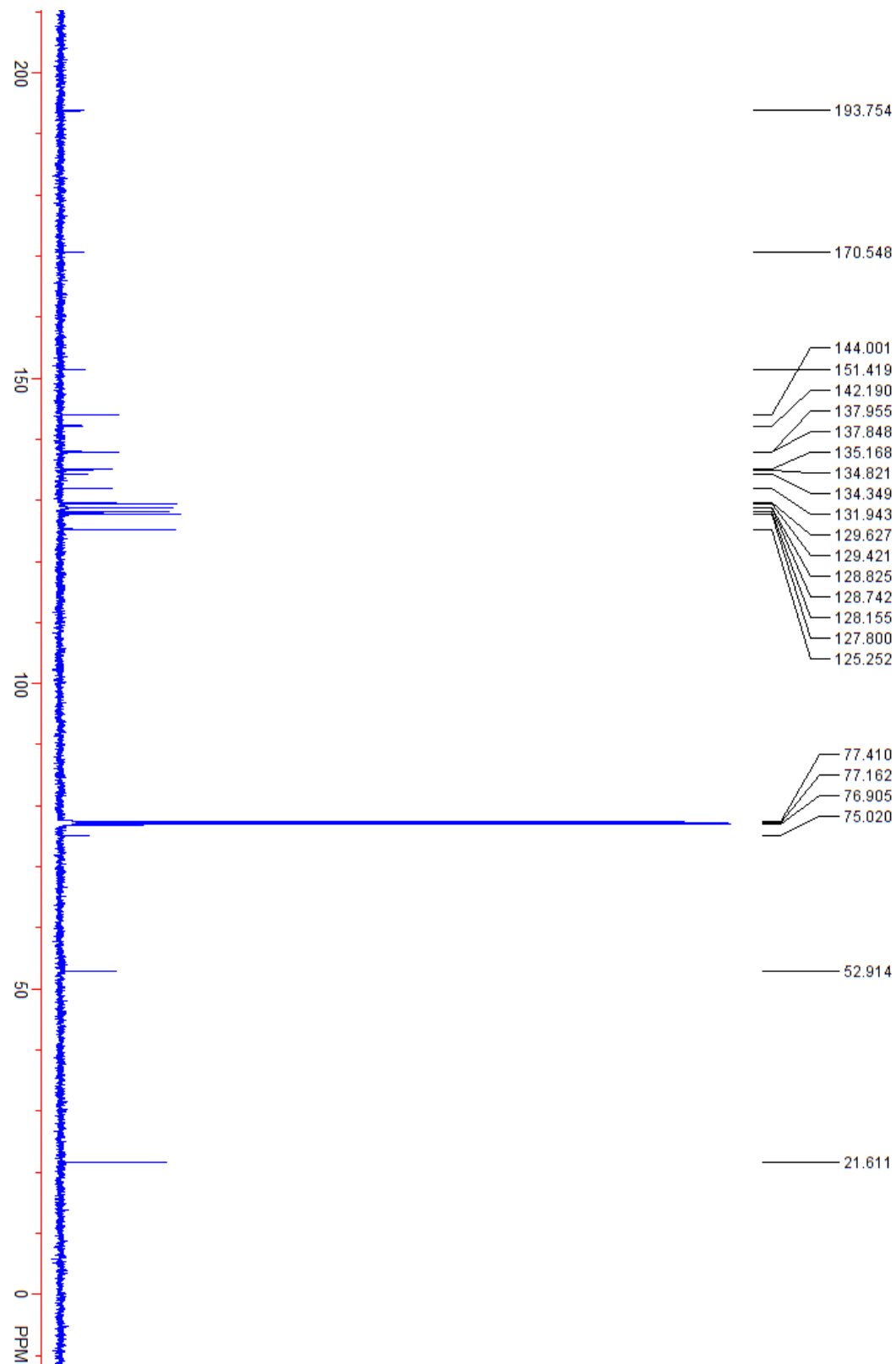


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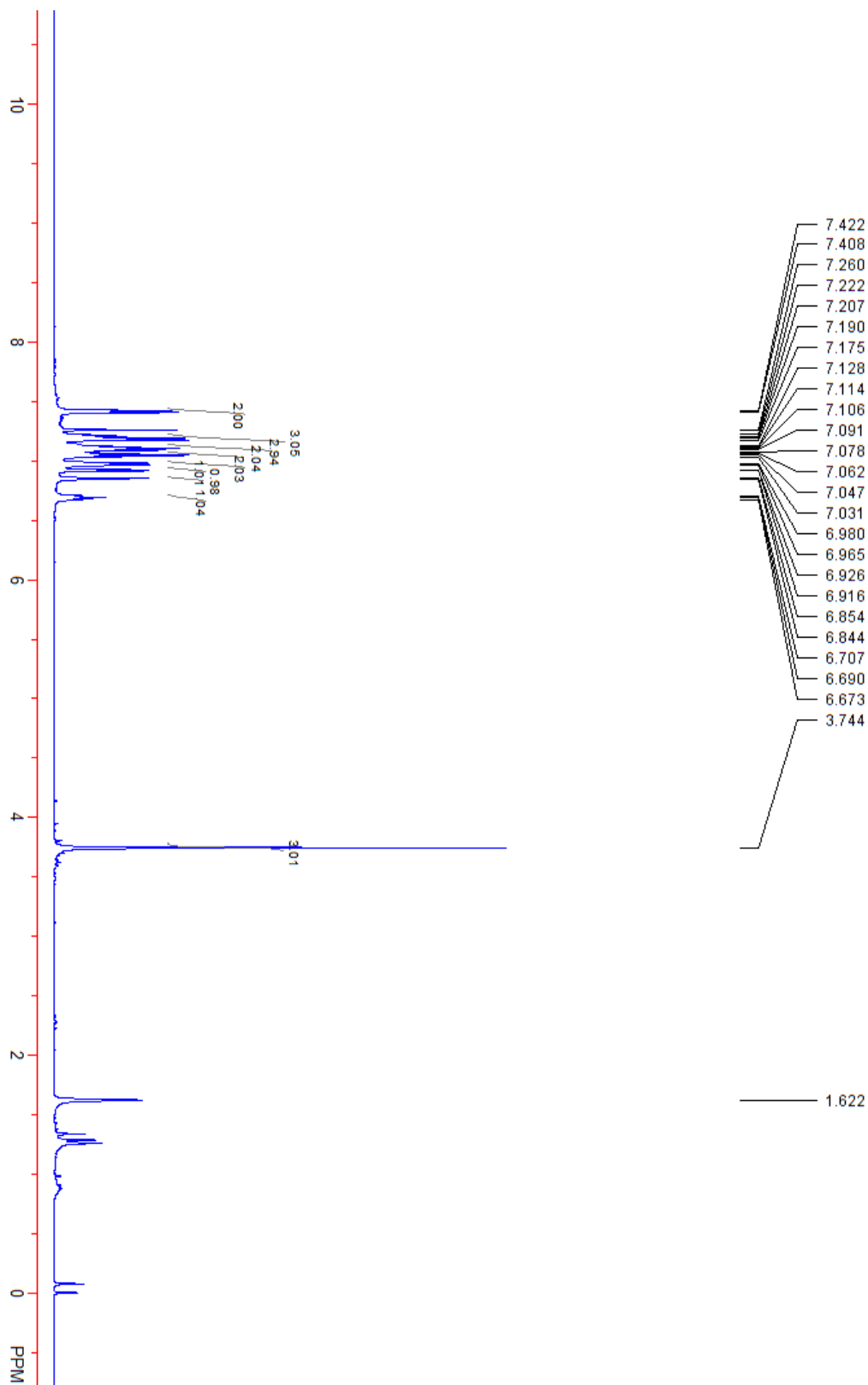
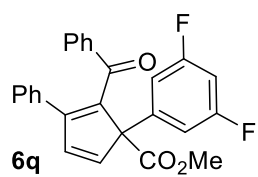




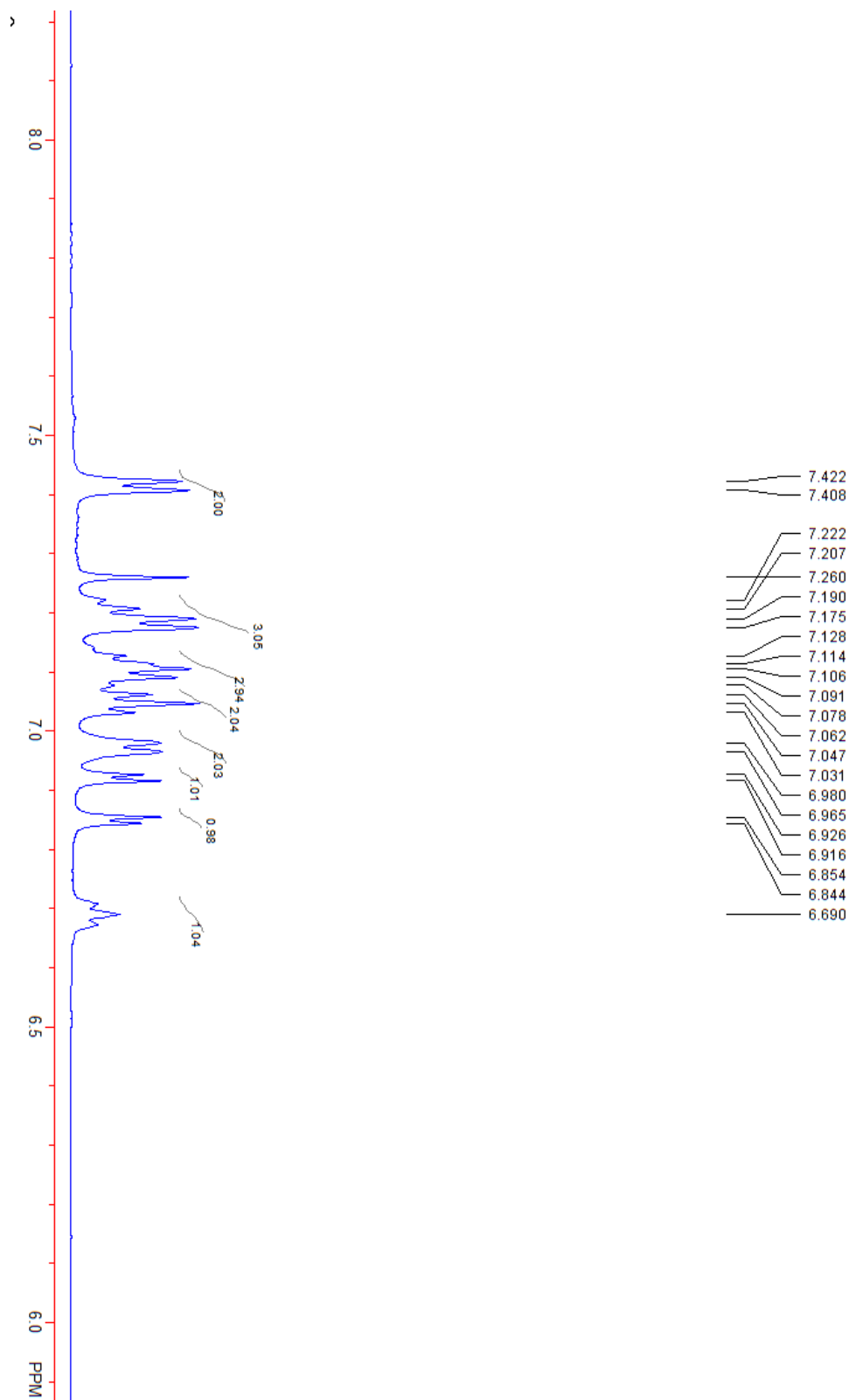
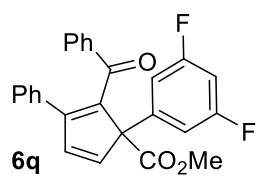
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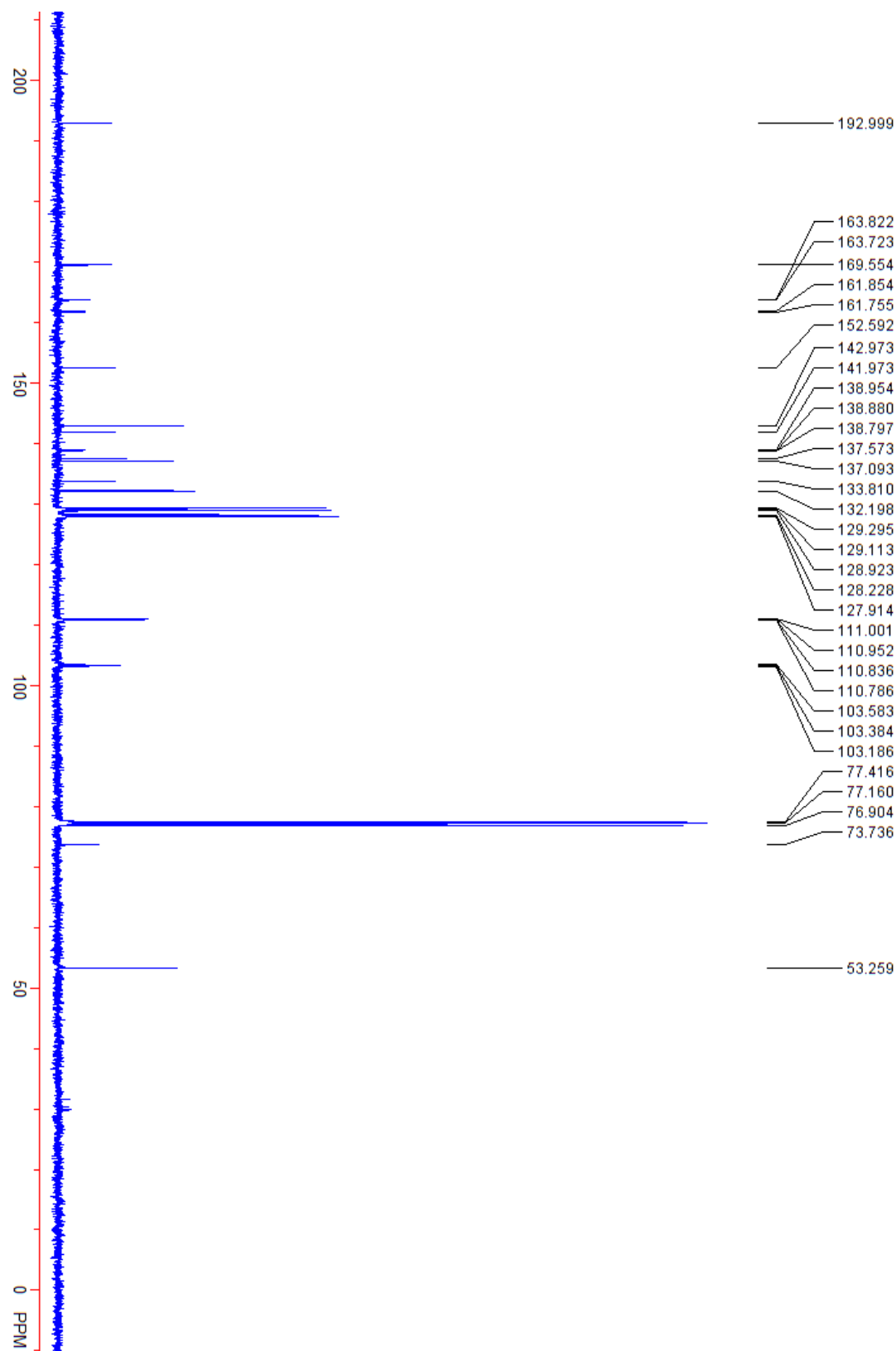
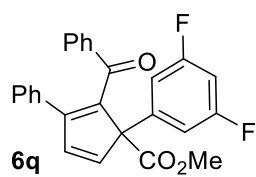
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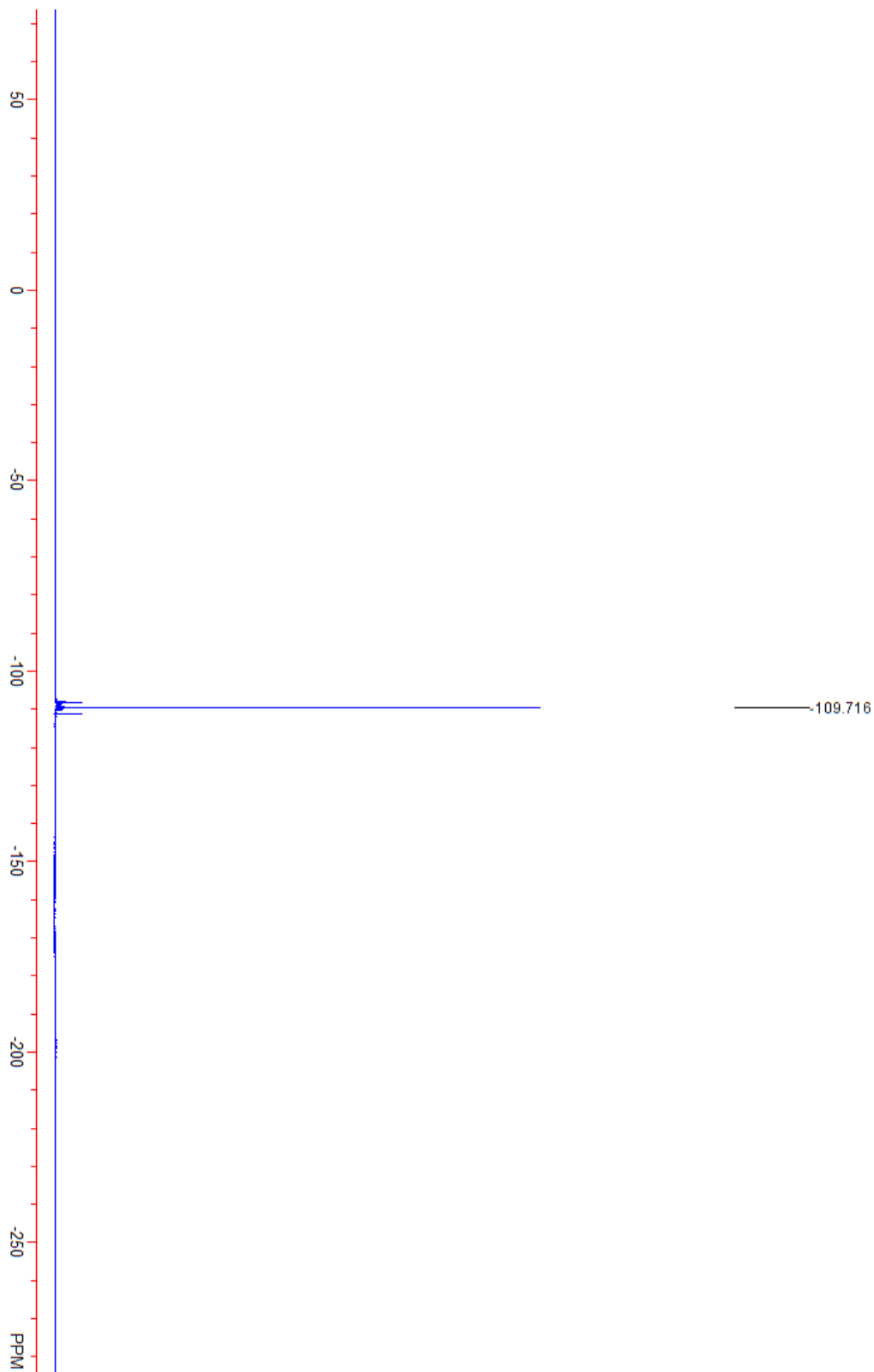
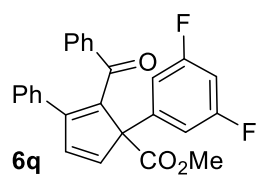
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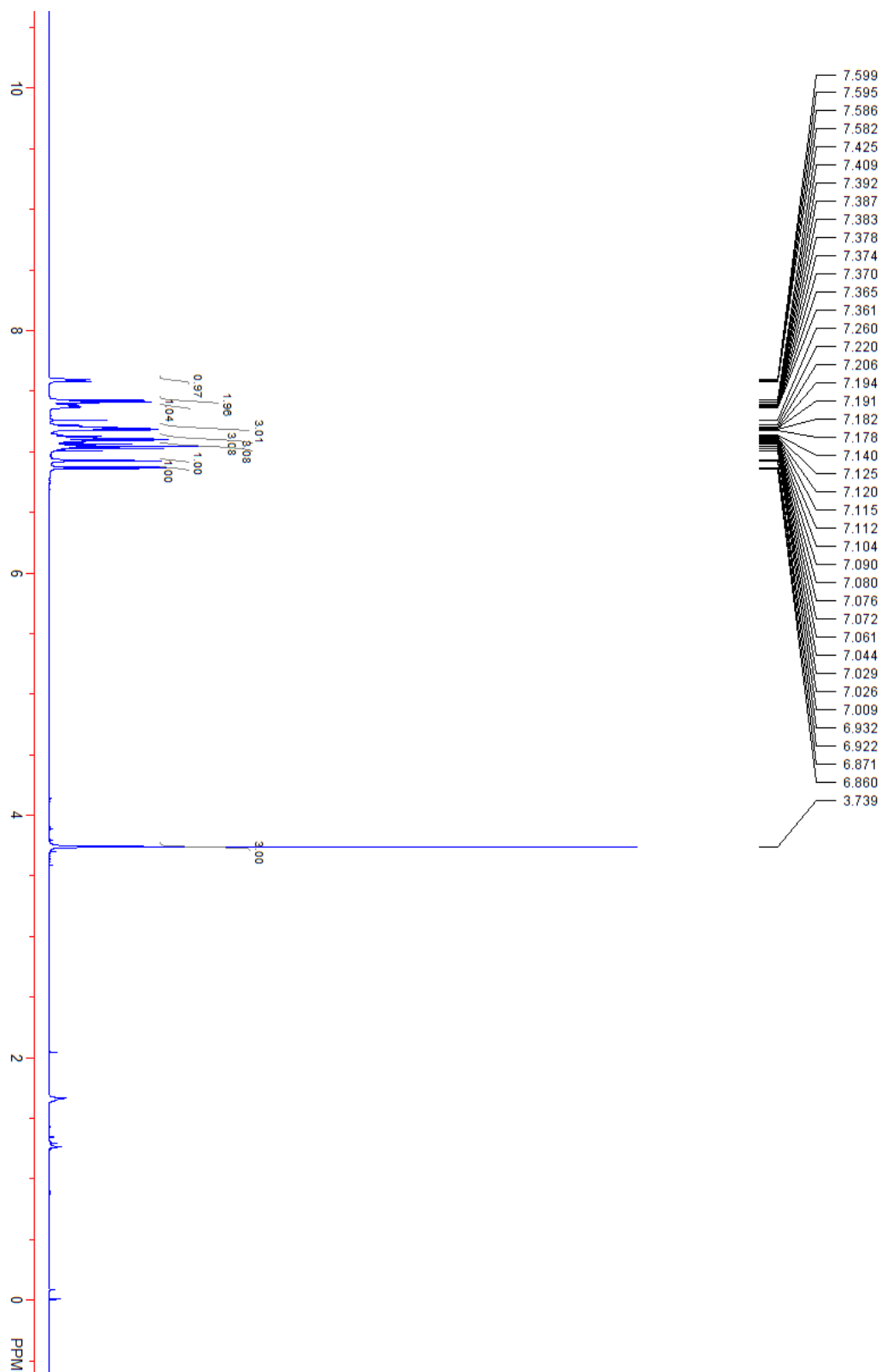
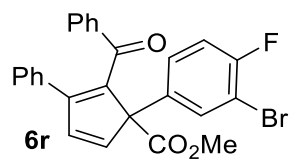
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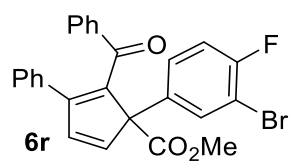


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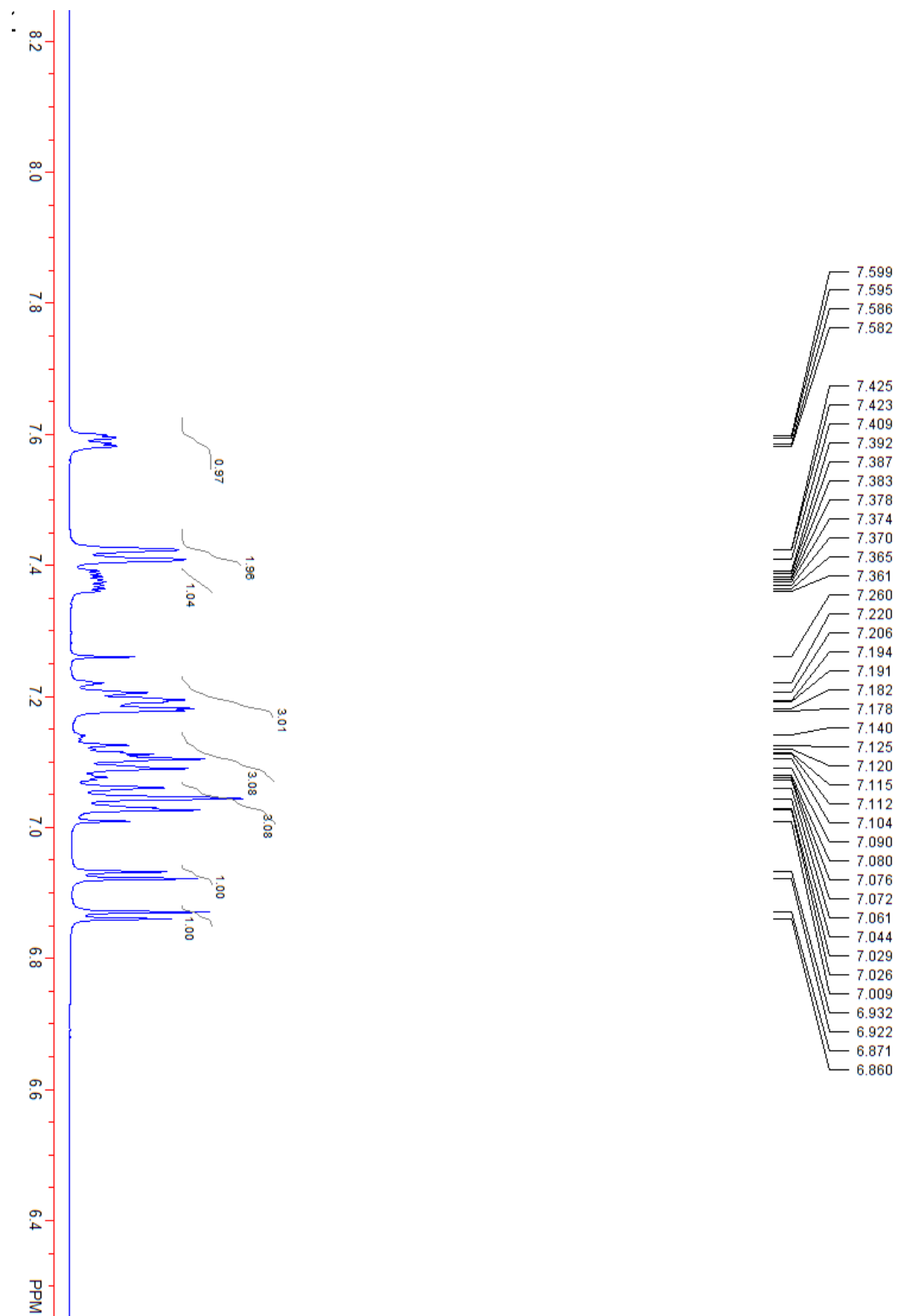


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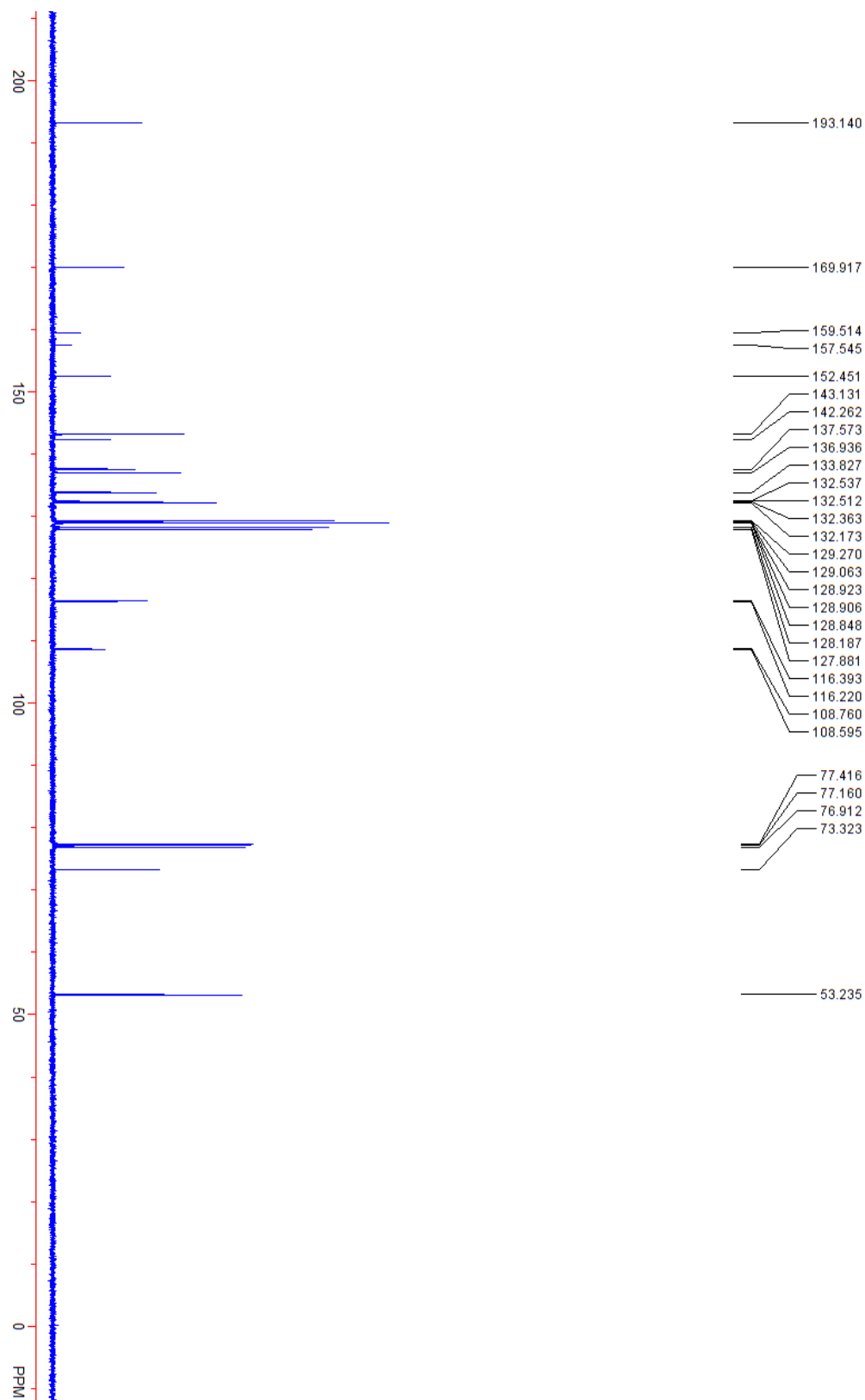
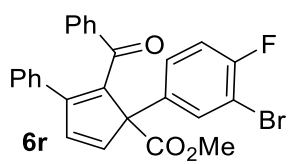




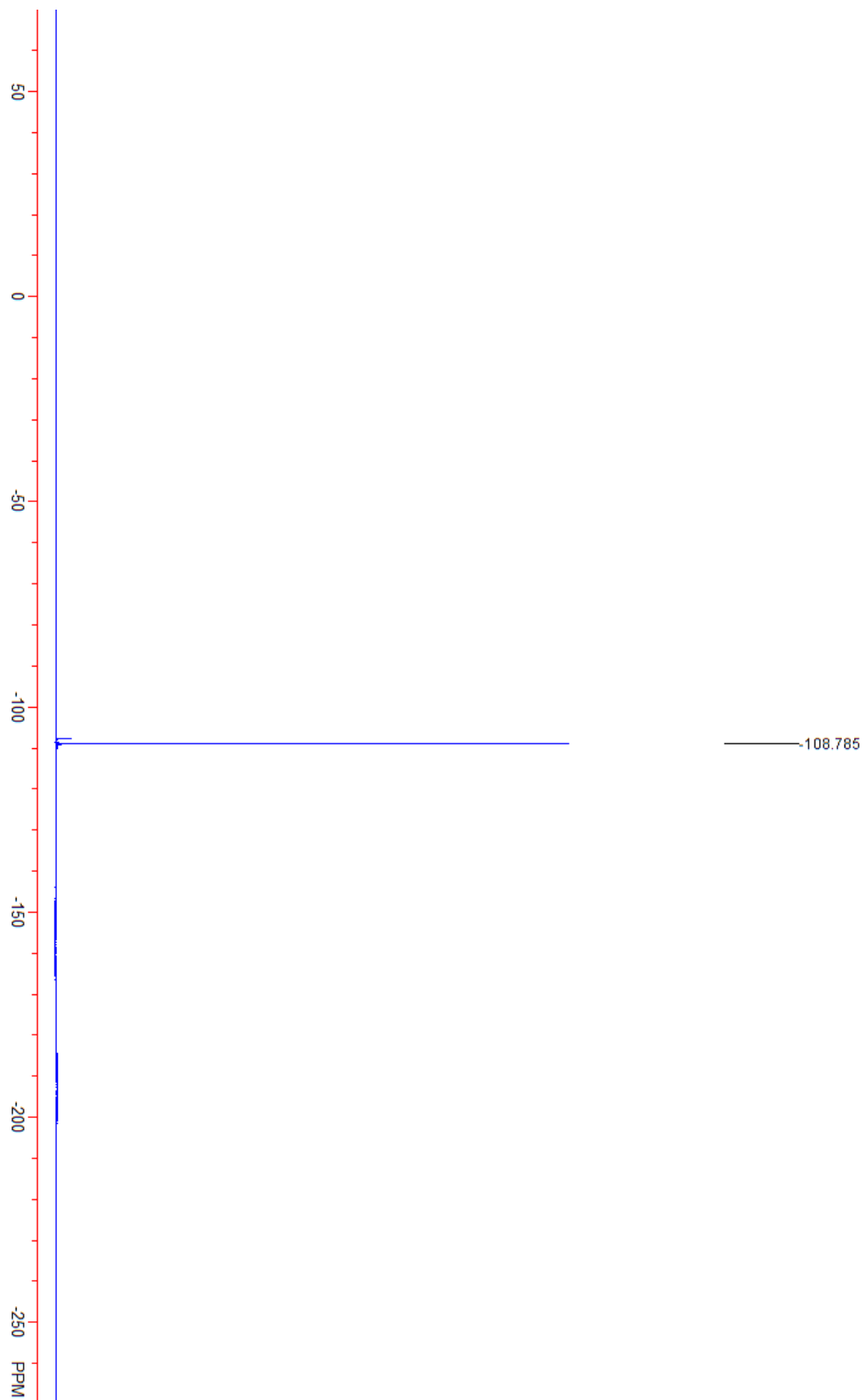
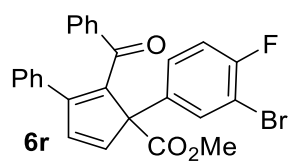
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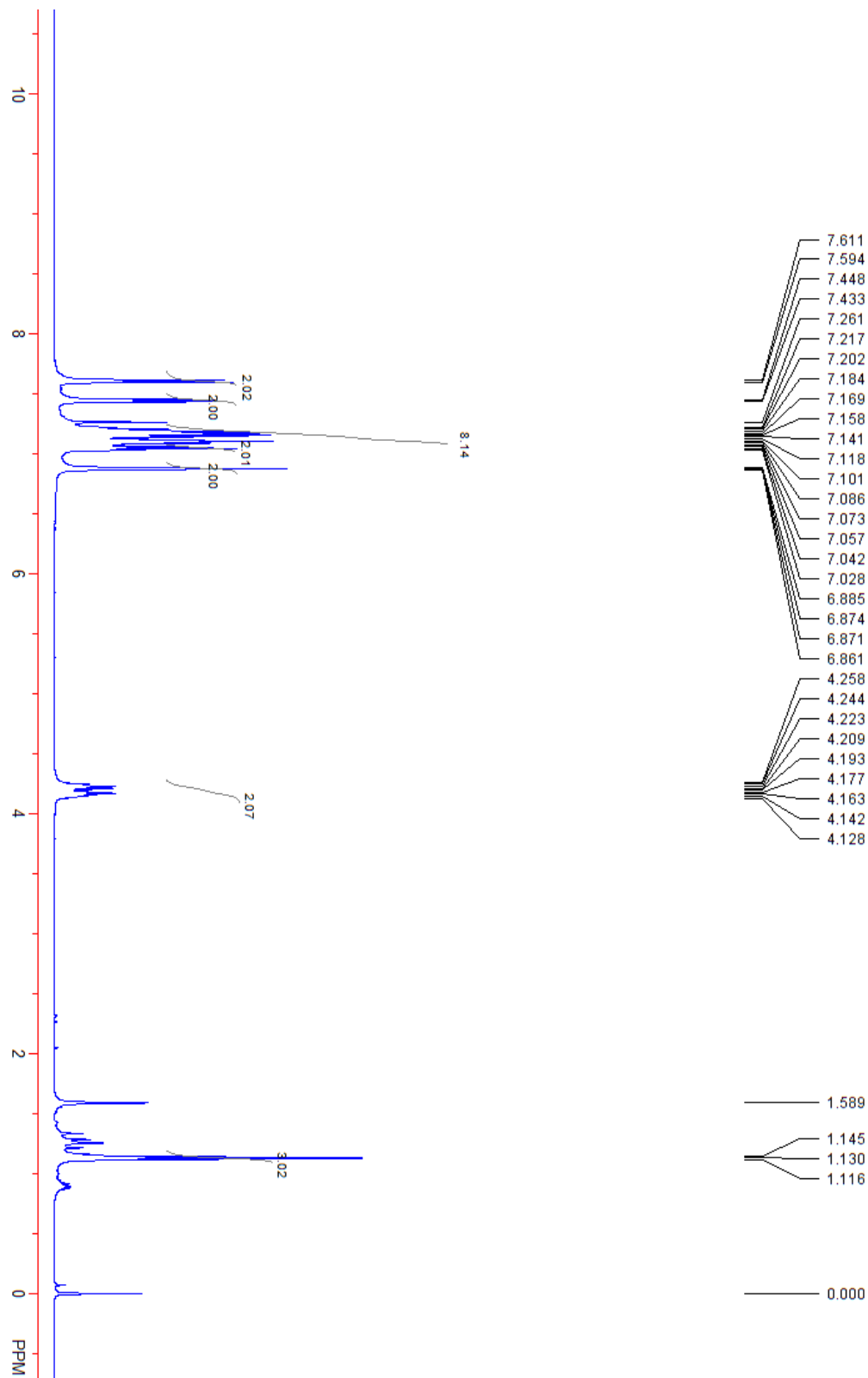
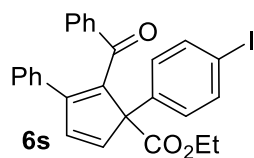
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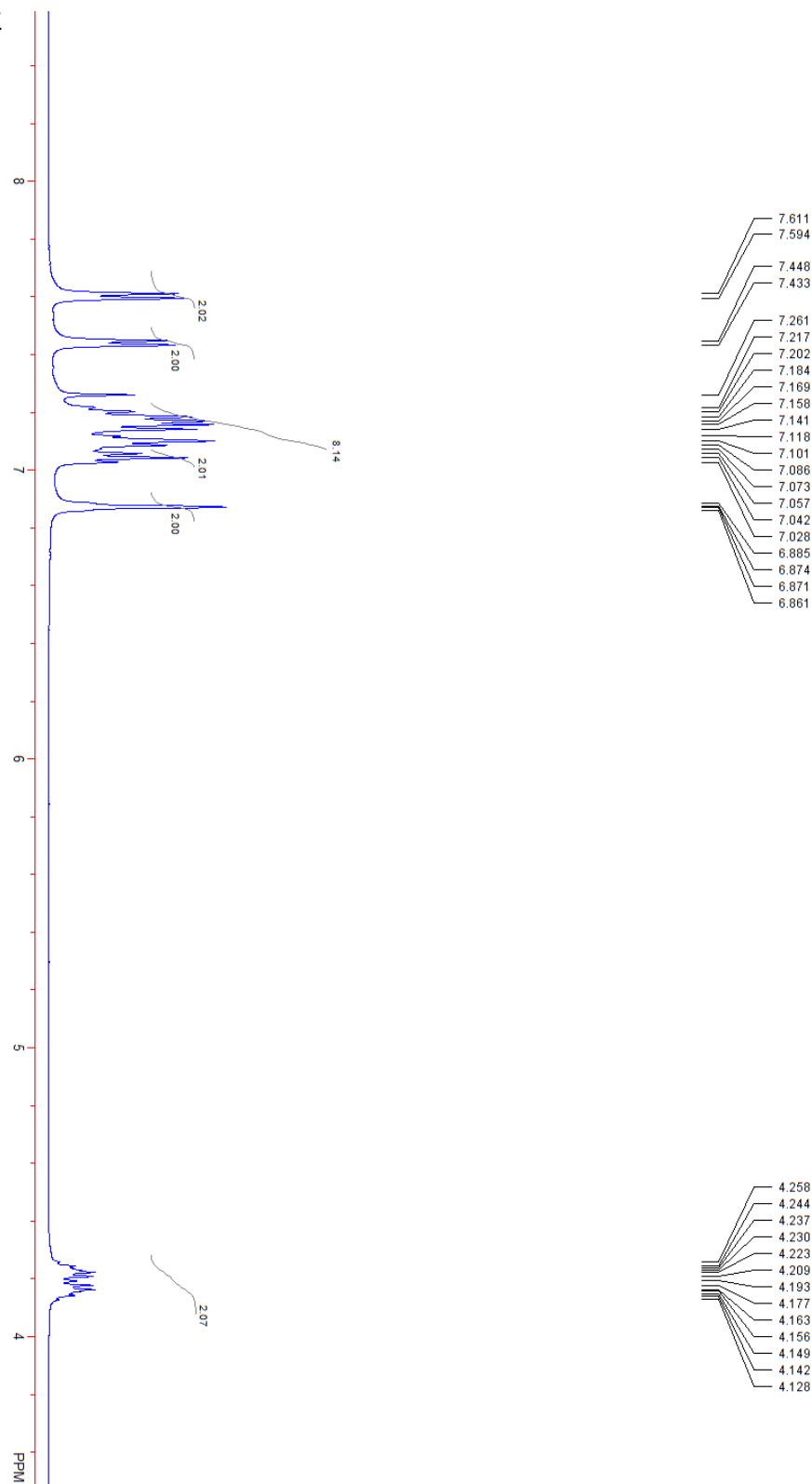
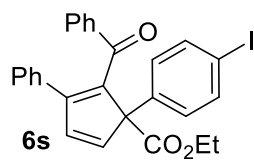
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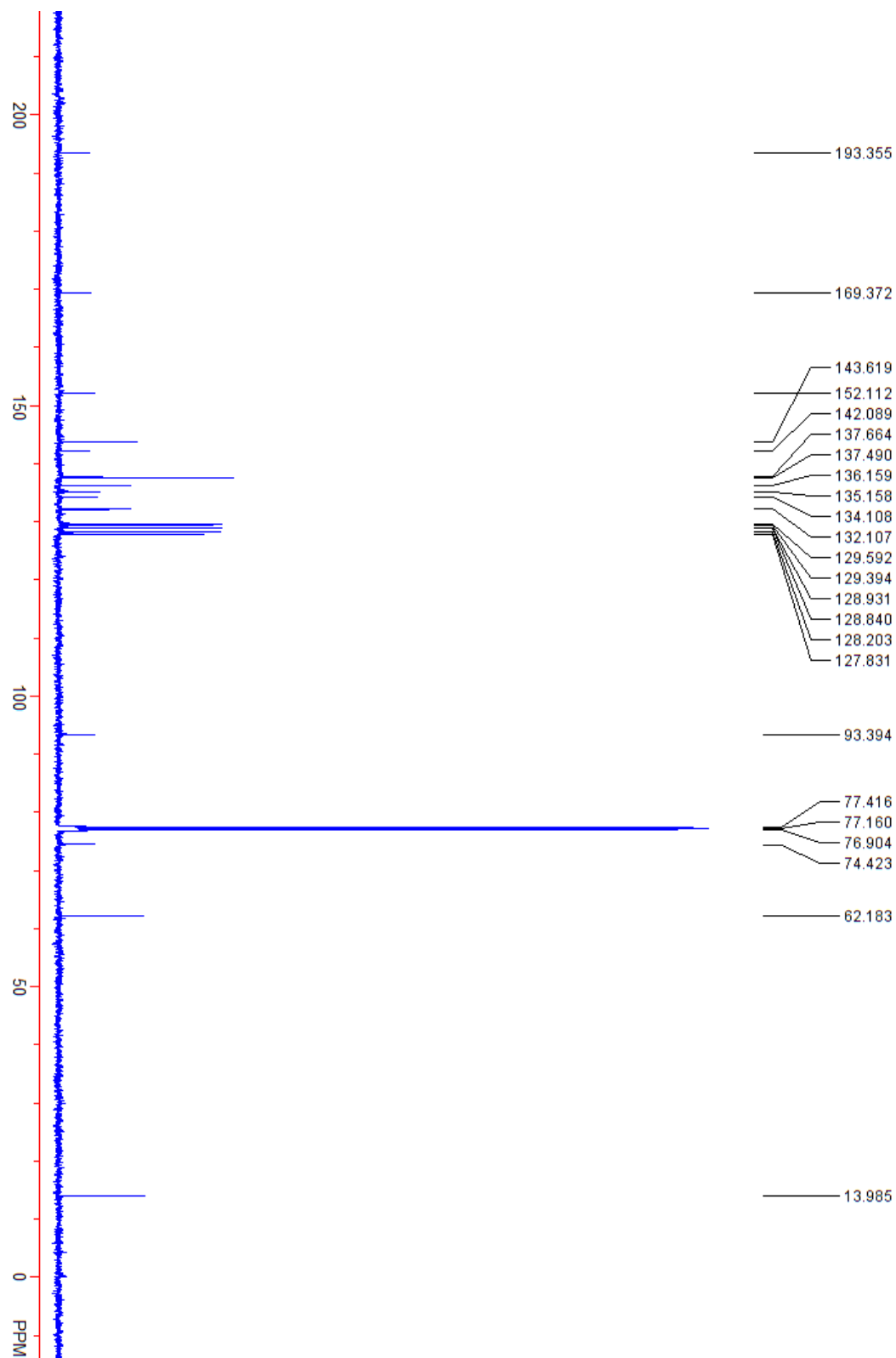
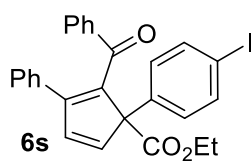
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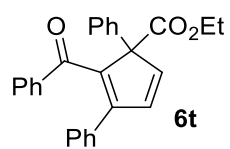


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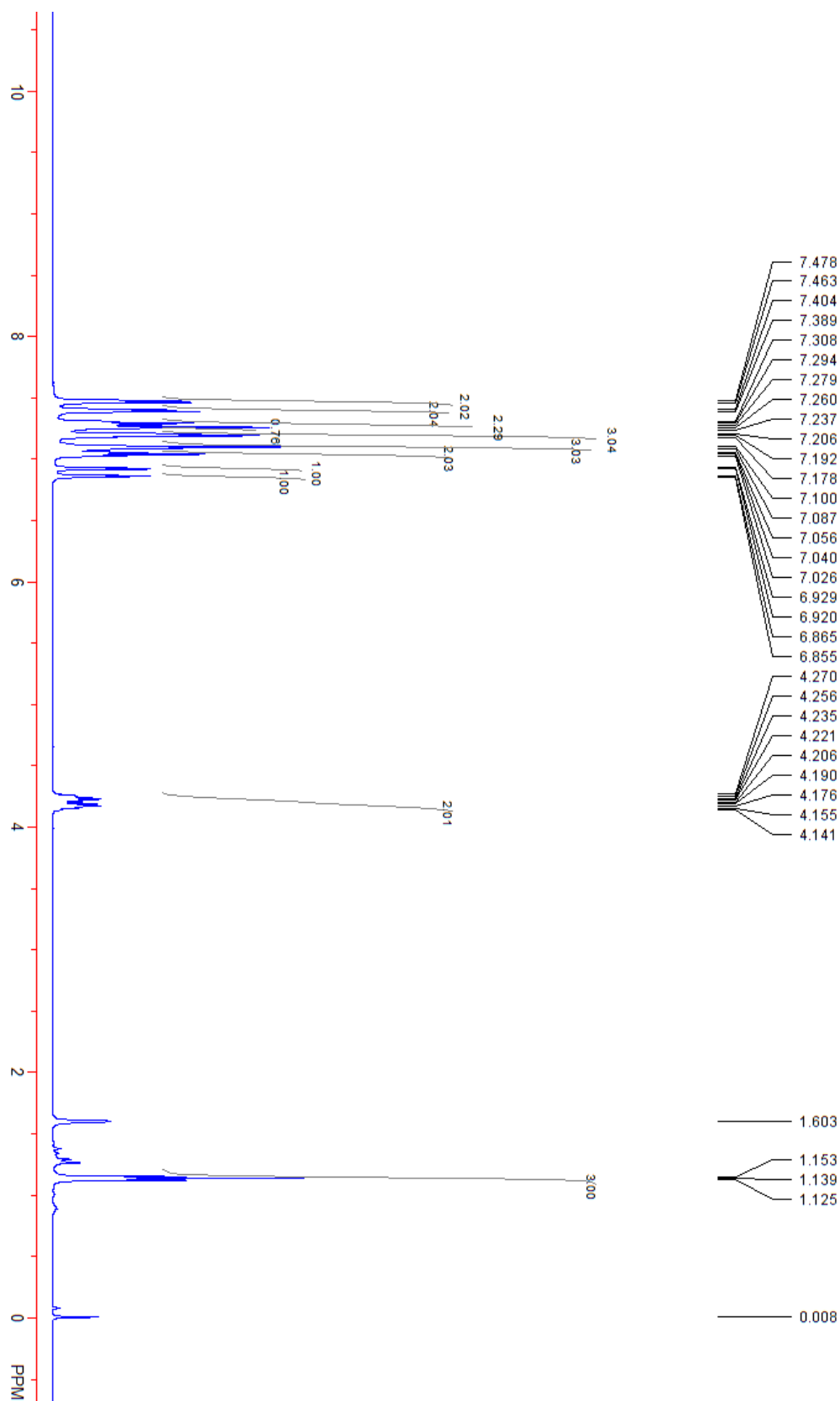


$^{13}\text{C}\{^1\text{H}\}$ NMR:

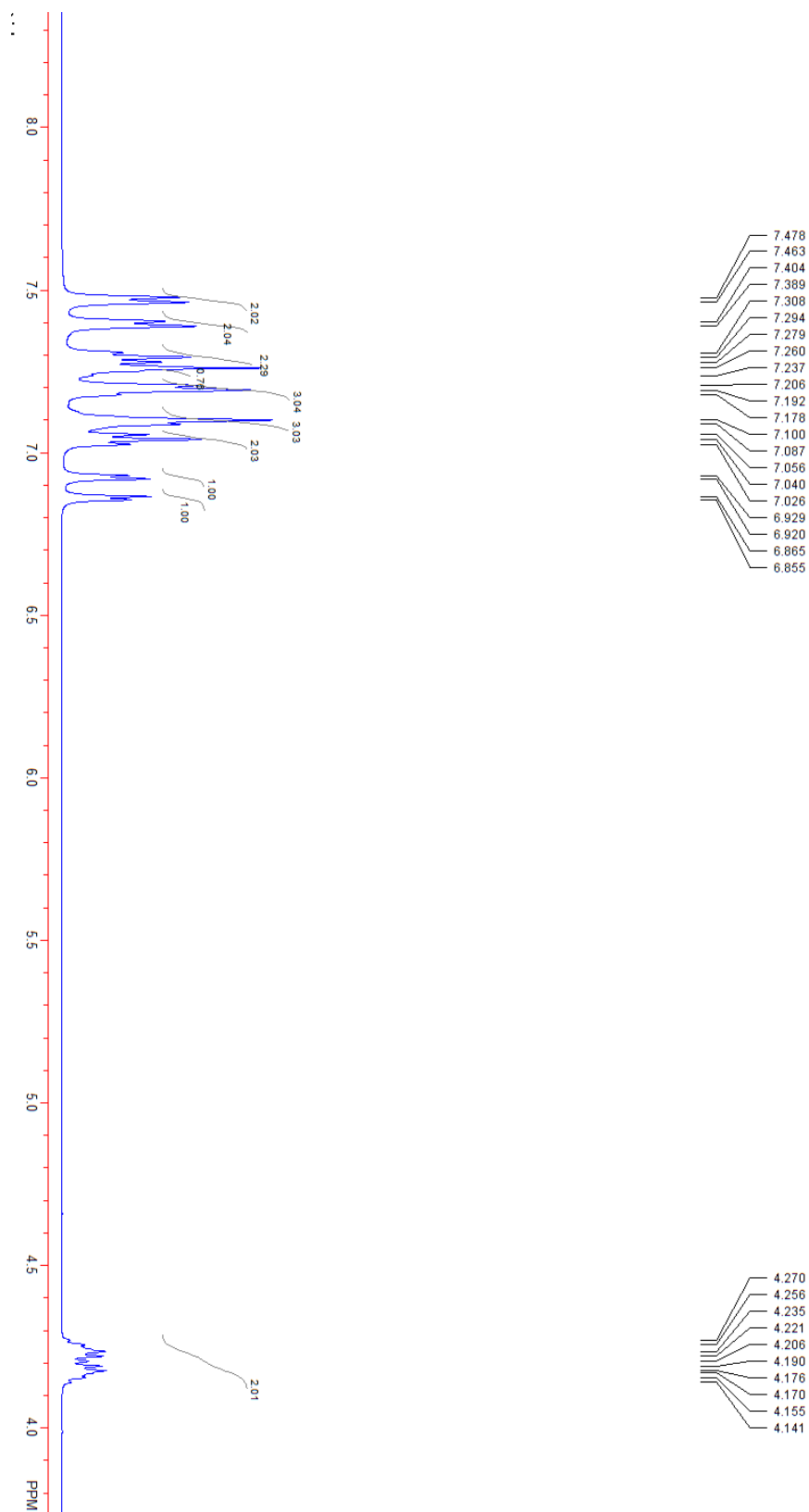
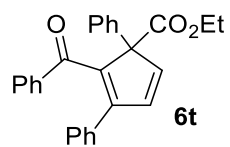


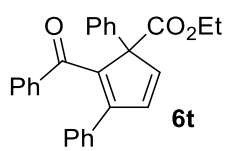


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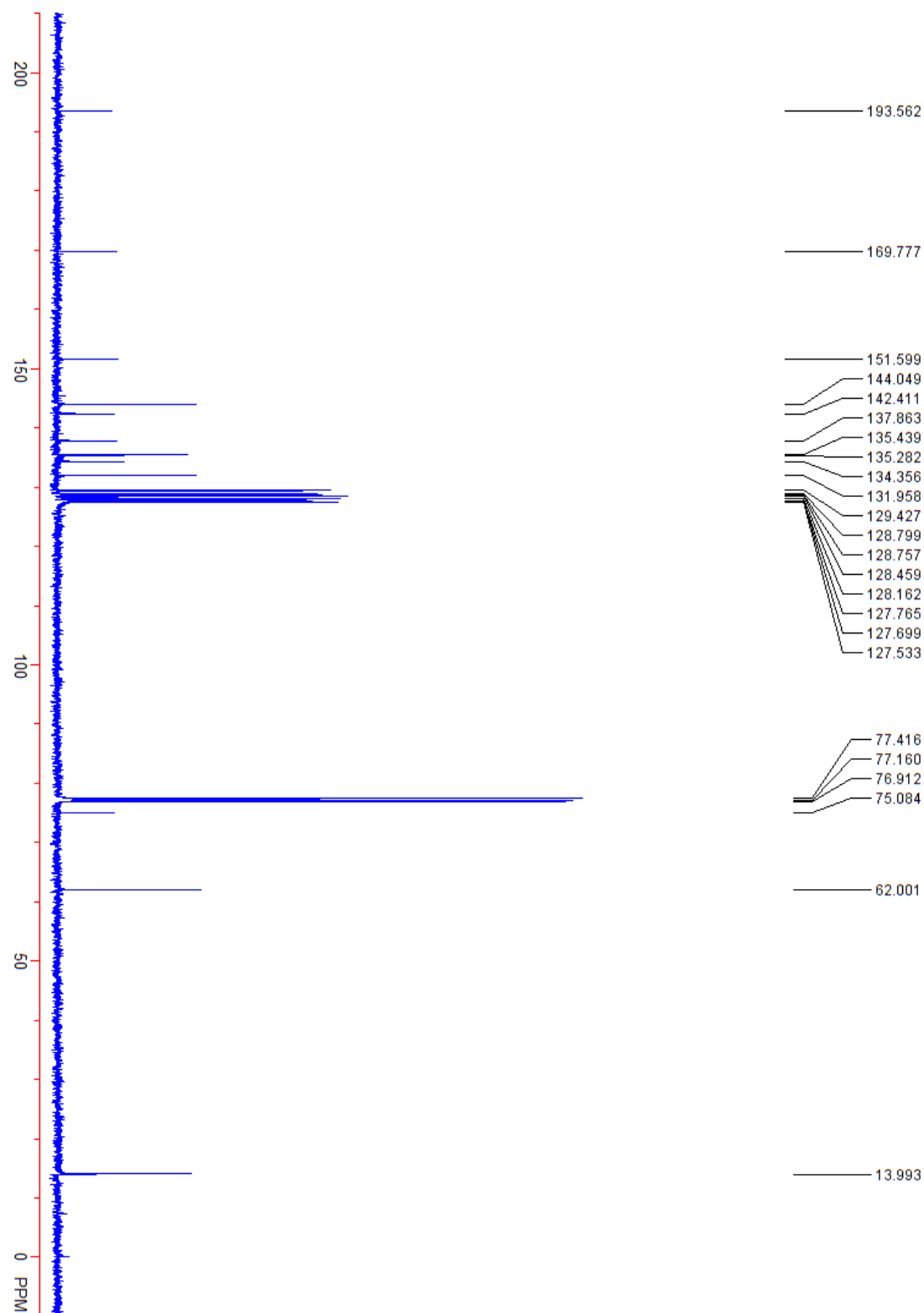


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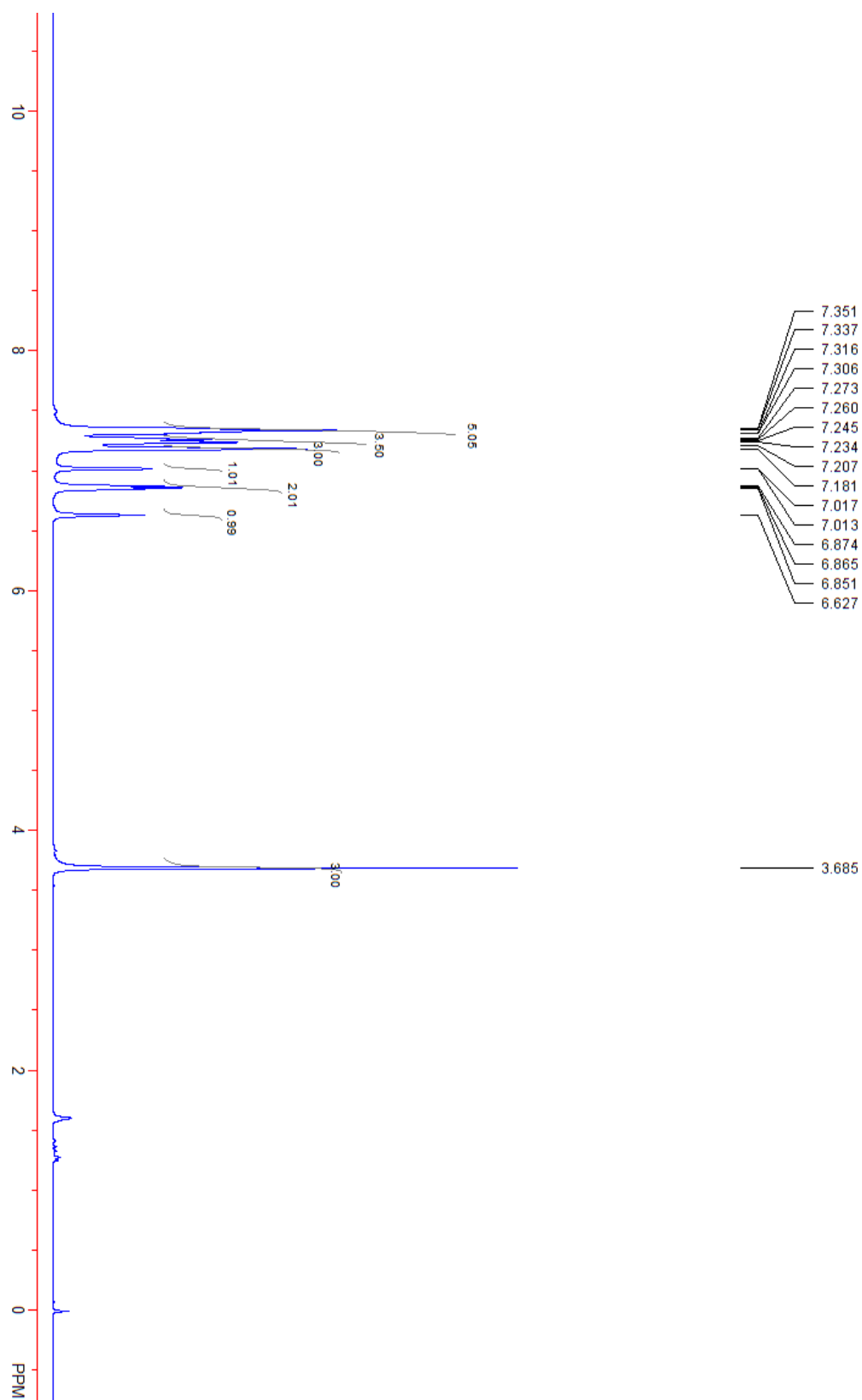
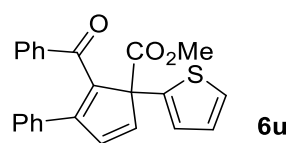




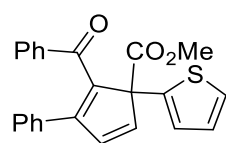
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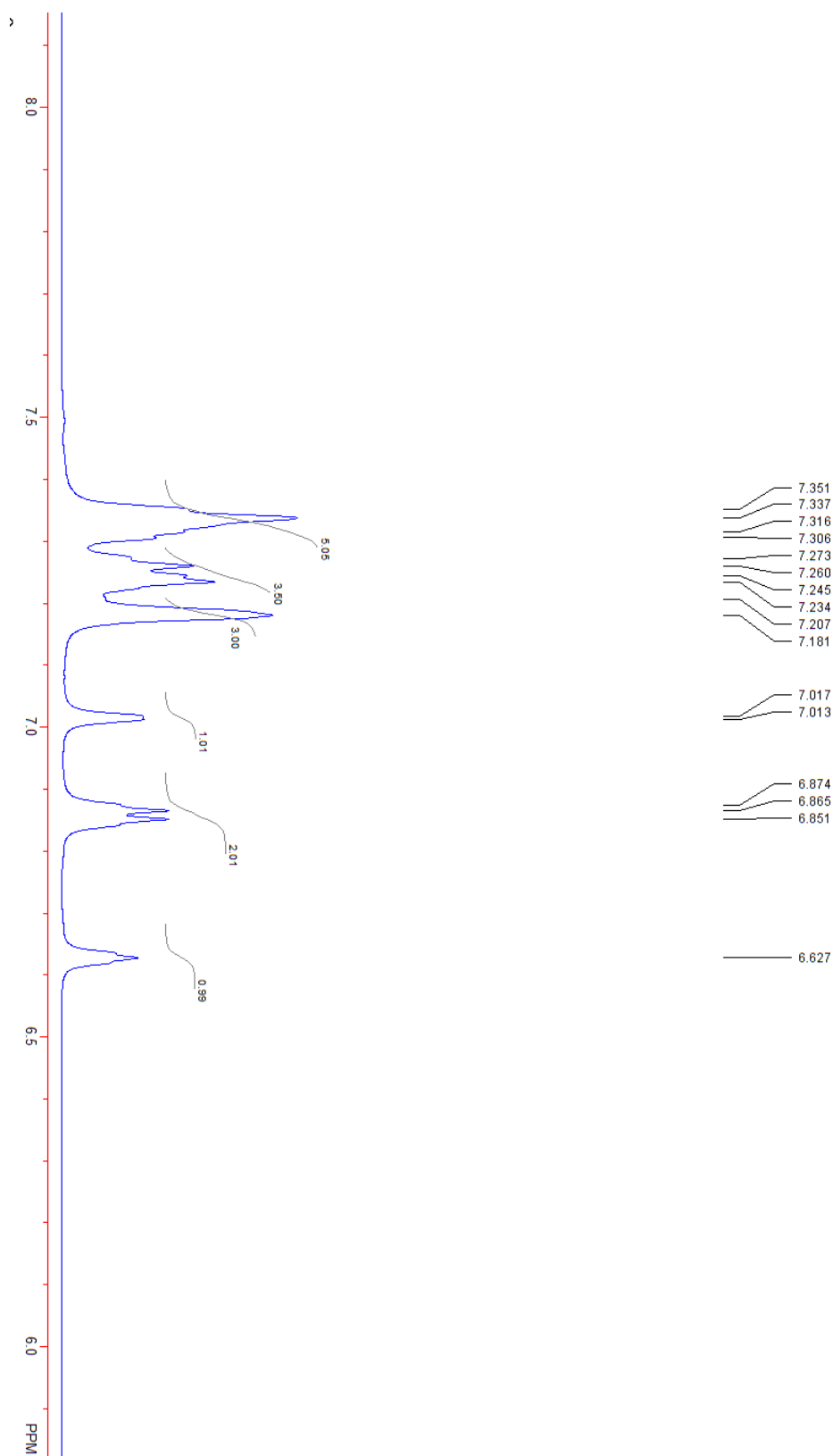
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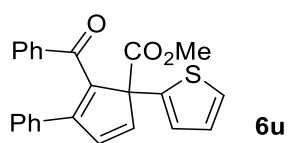


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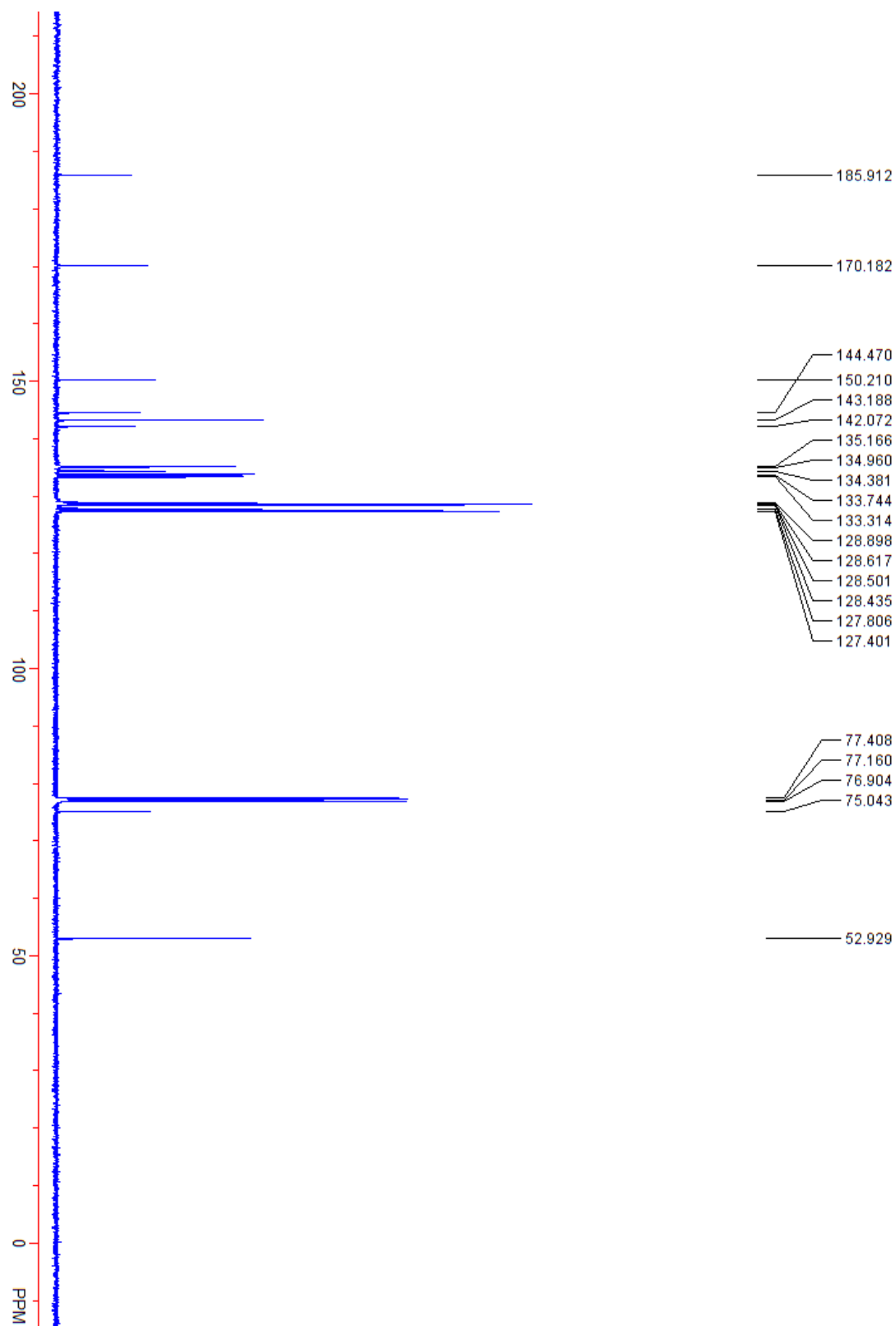


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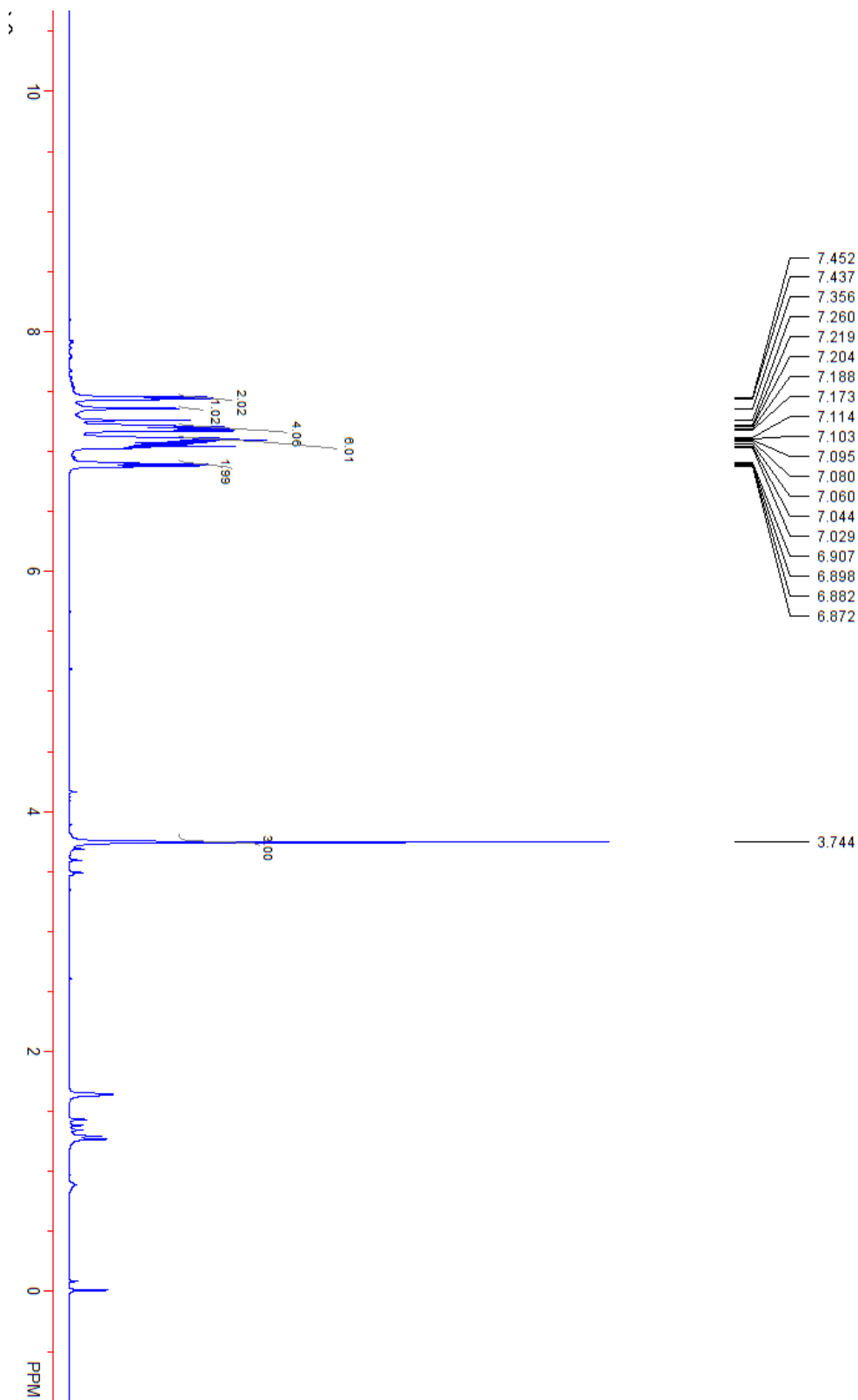
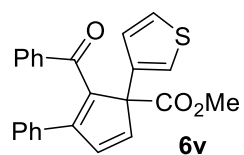




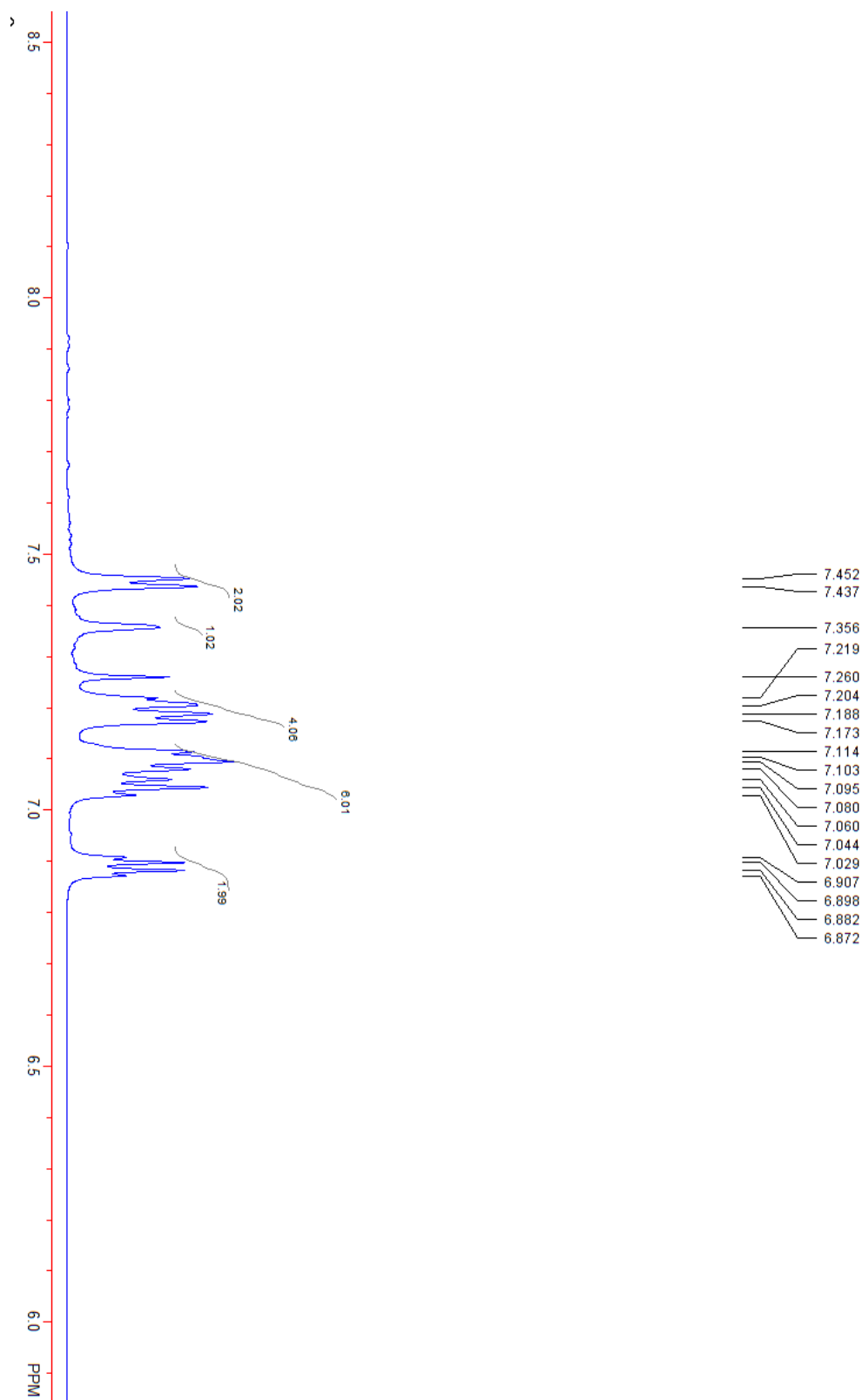
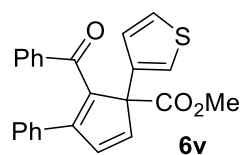
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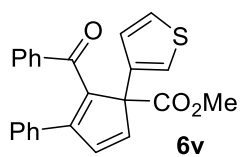


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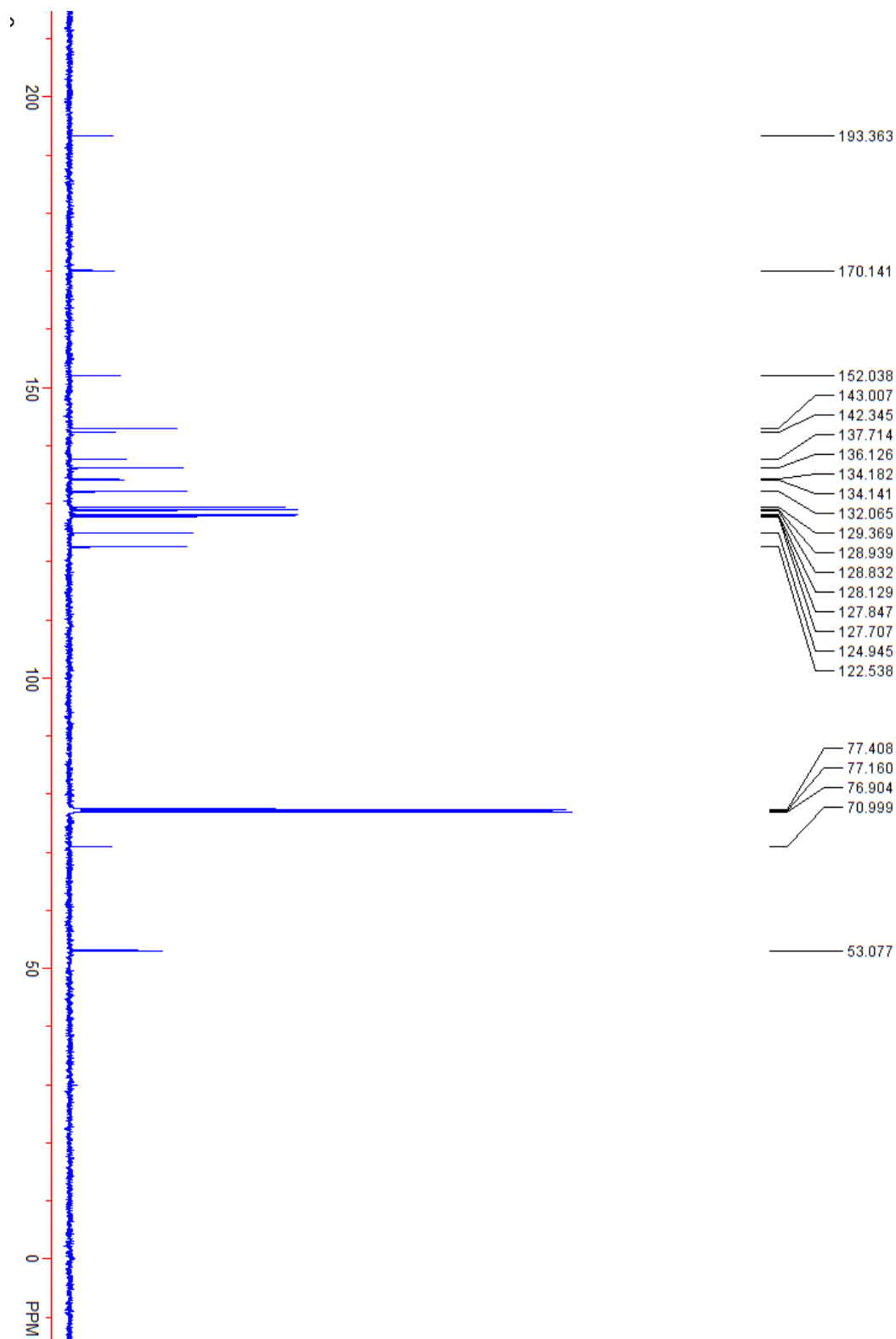


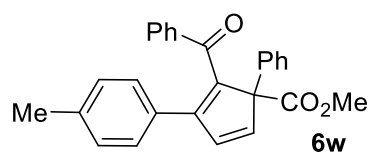
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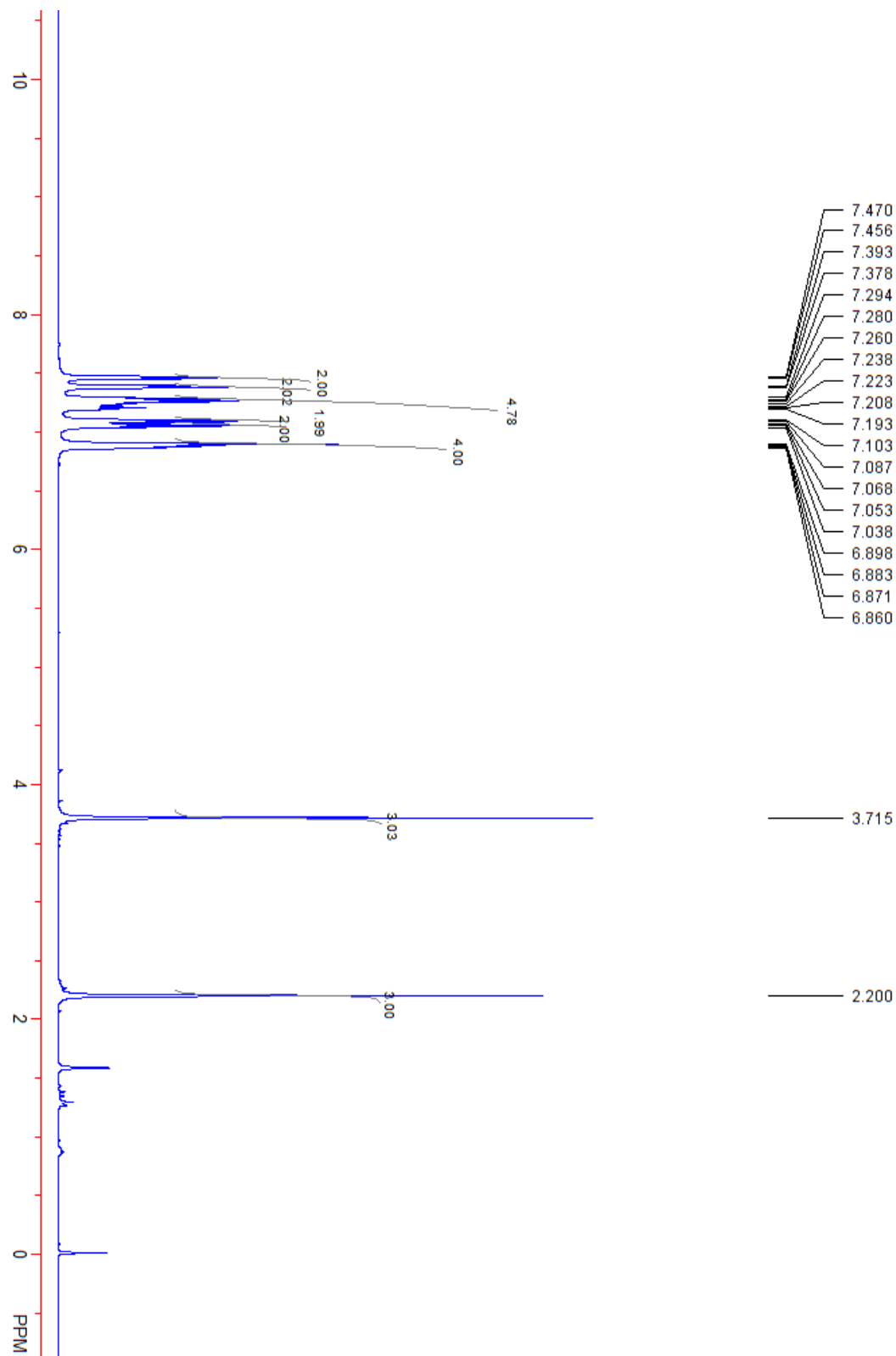


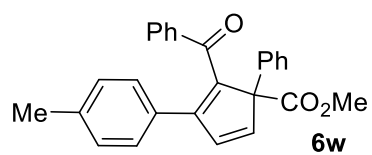
$^{13}\text{C}\{^1\text{H}\}$ NMR:



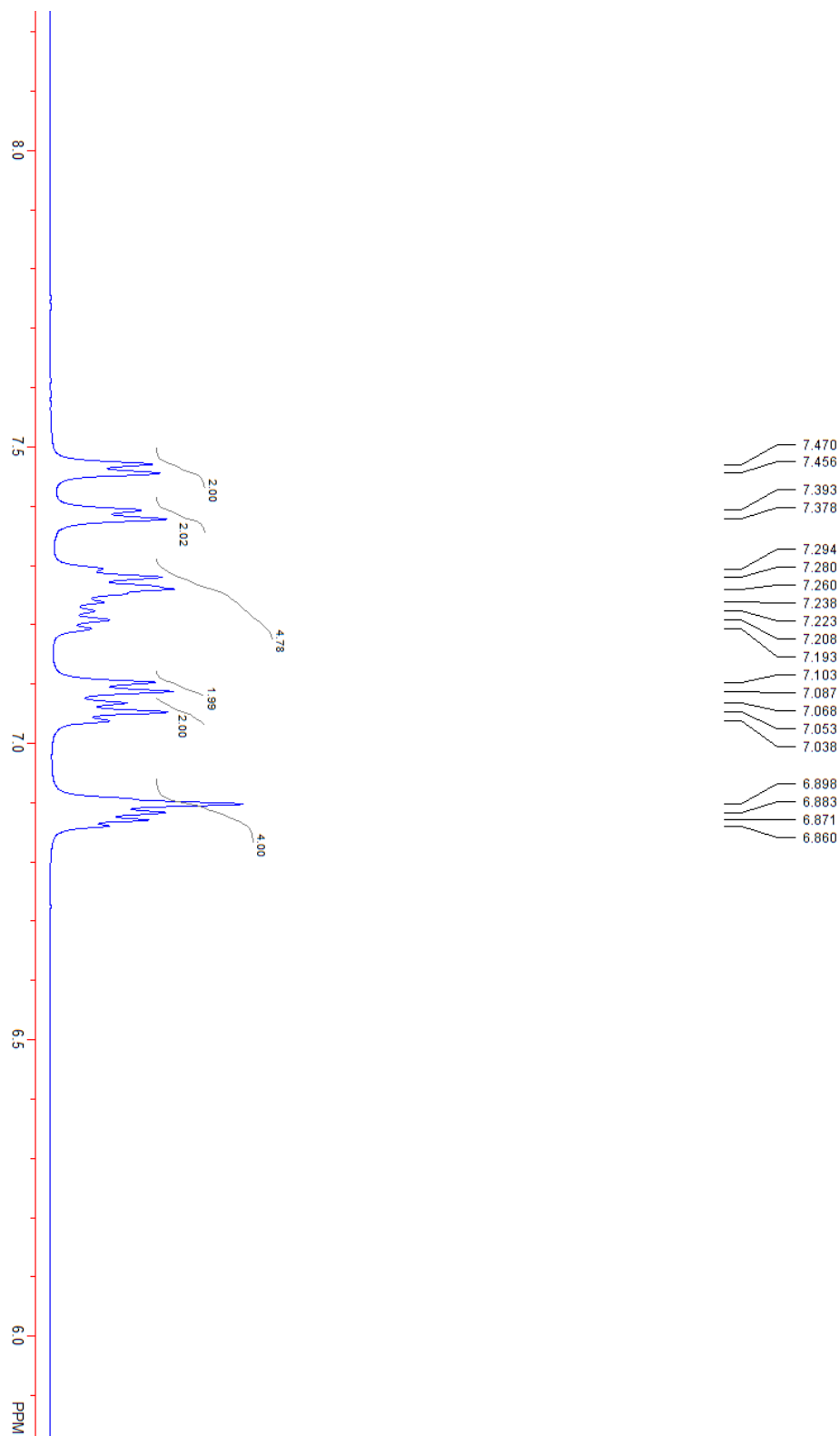


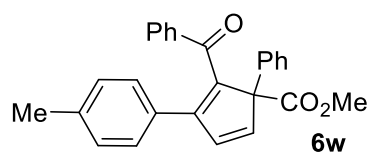
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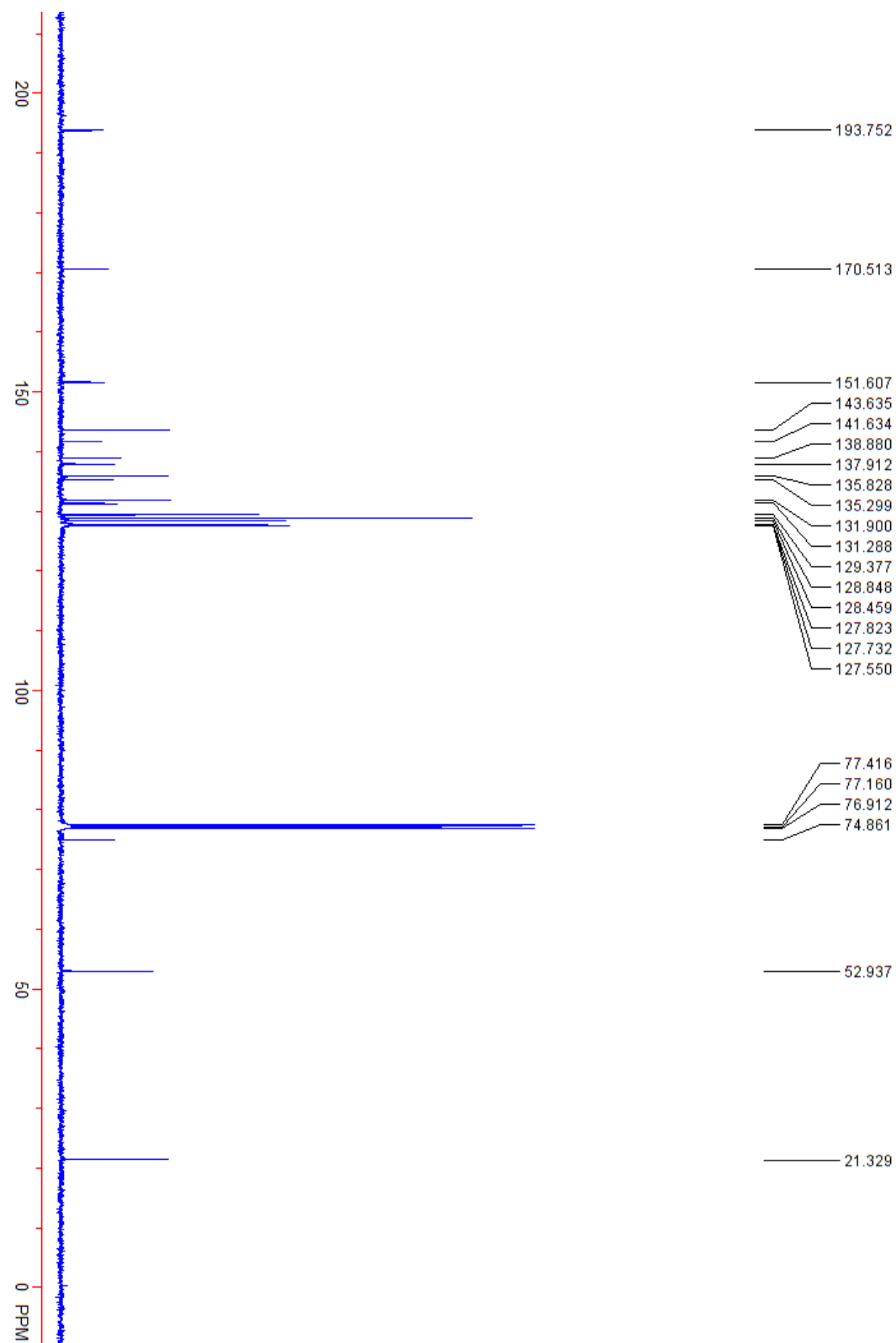


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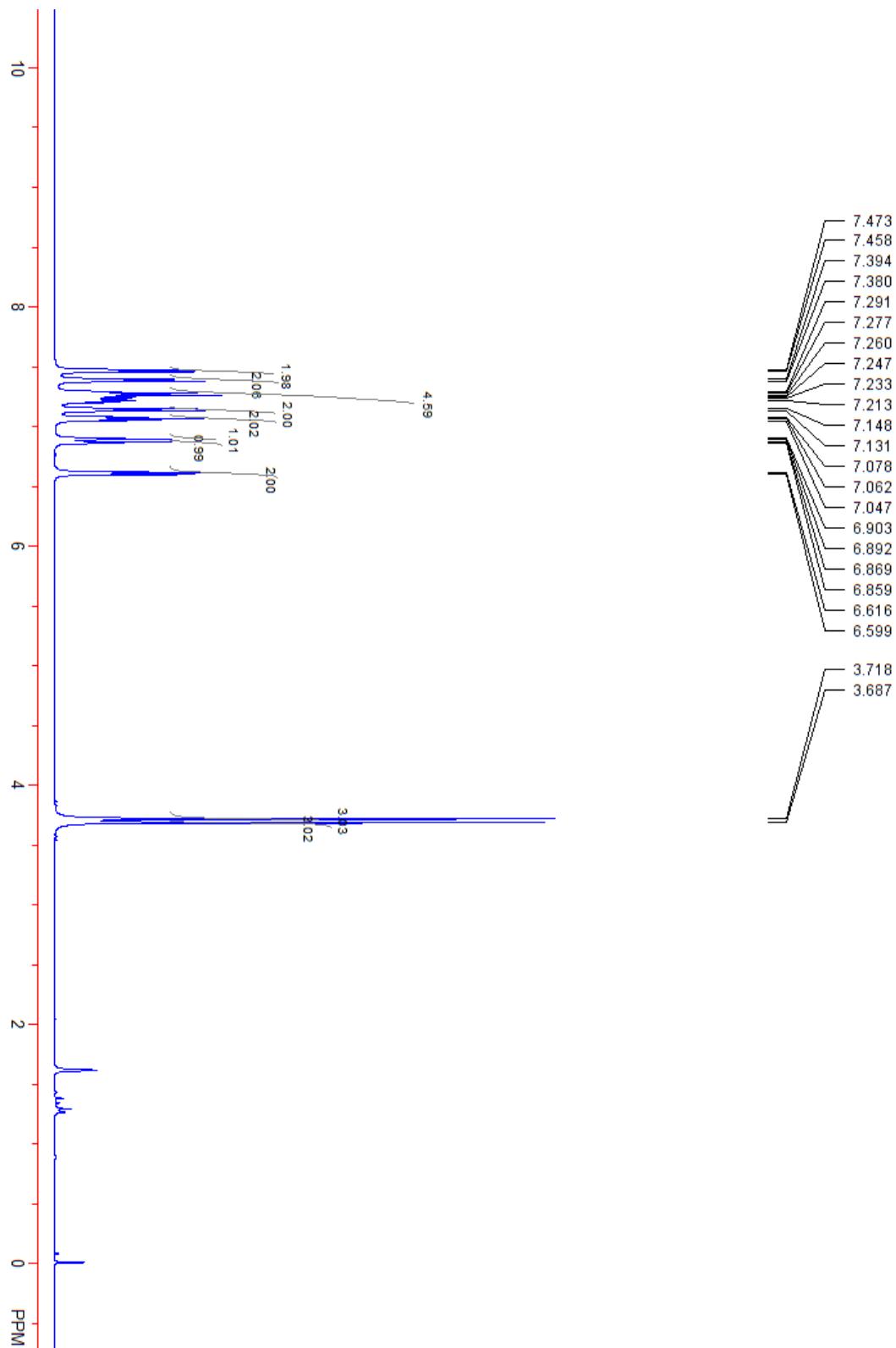
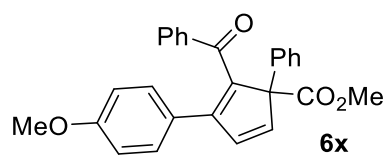




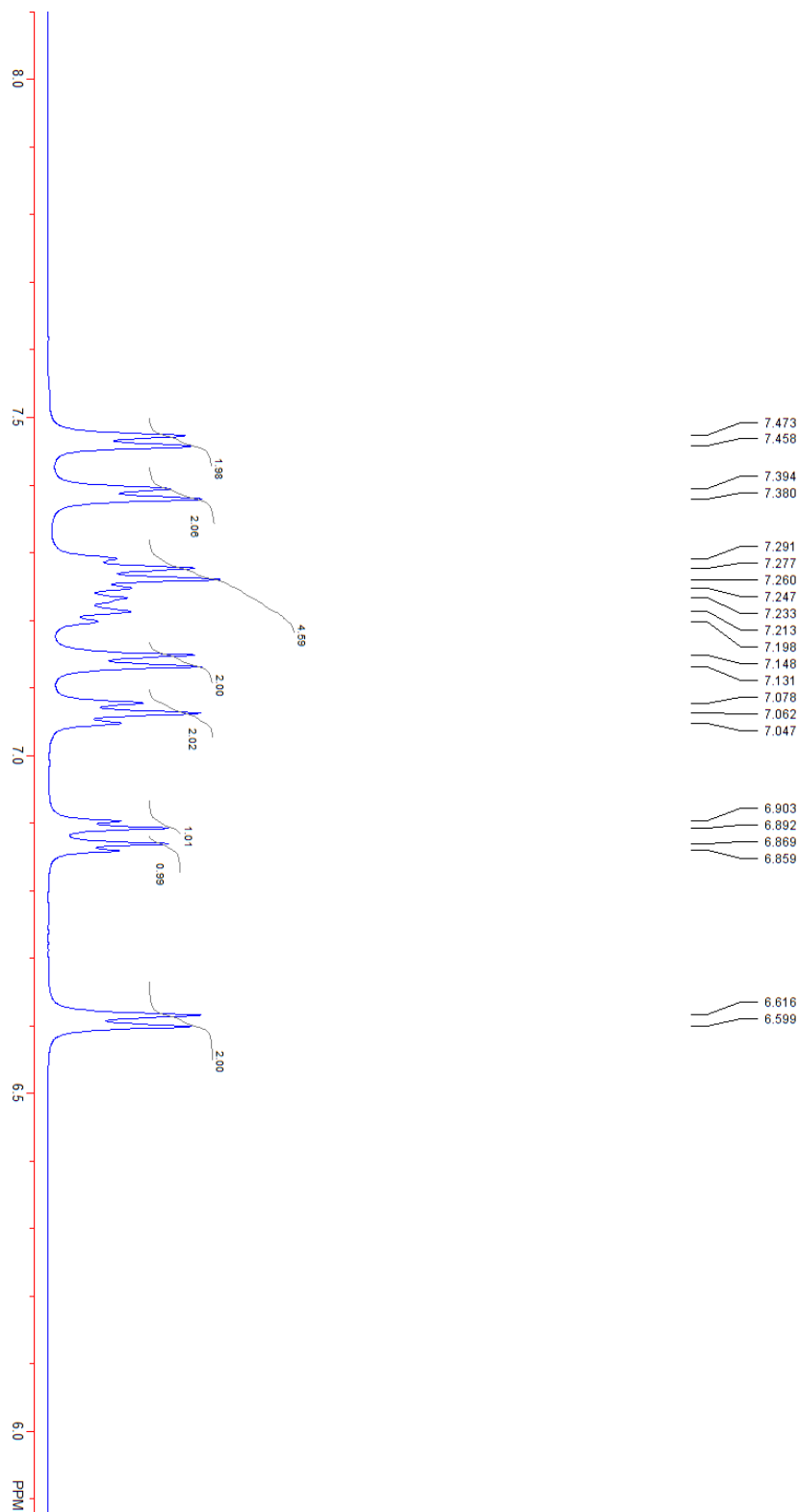
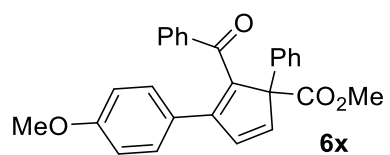
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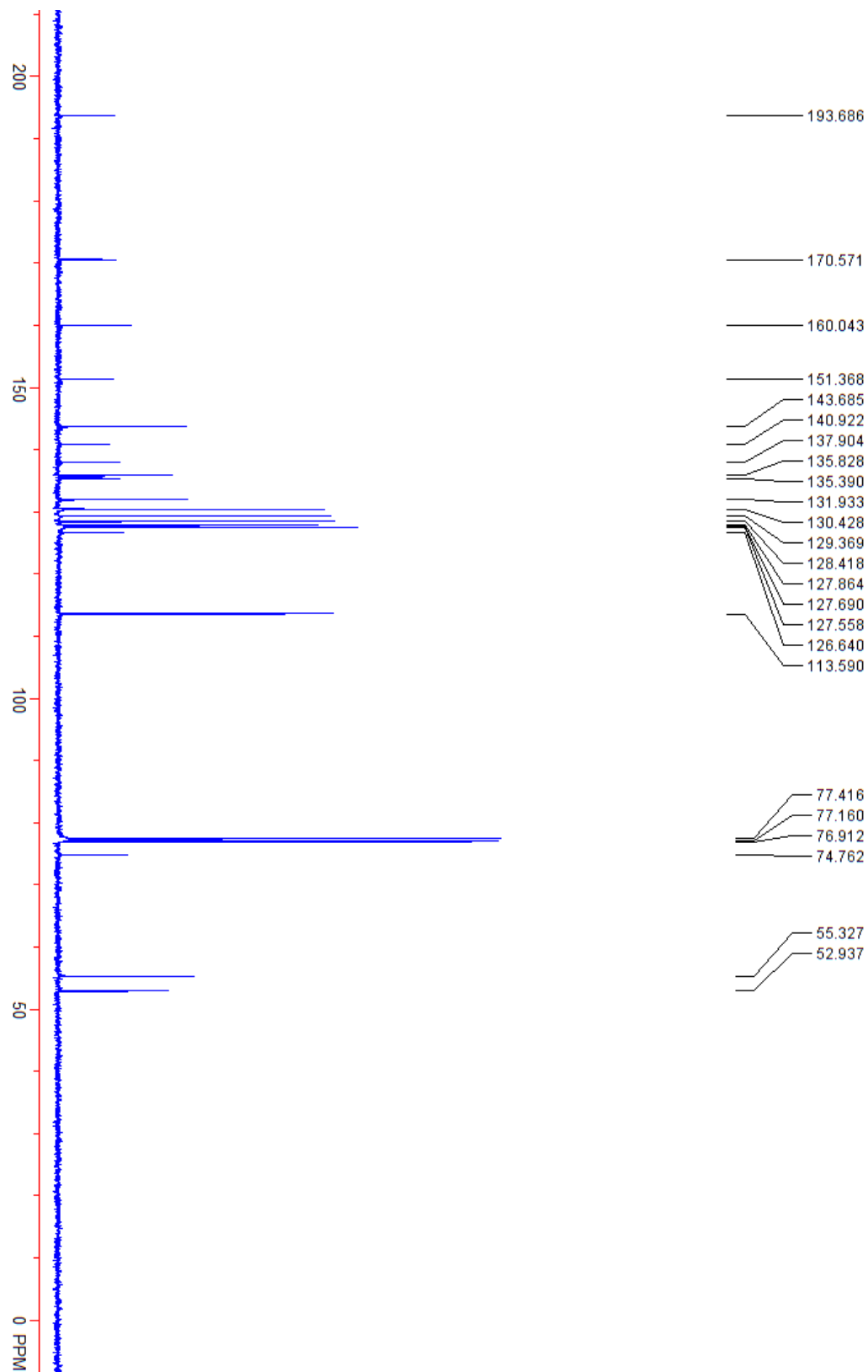
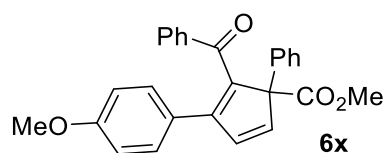
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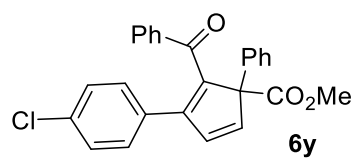


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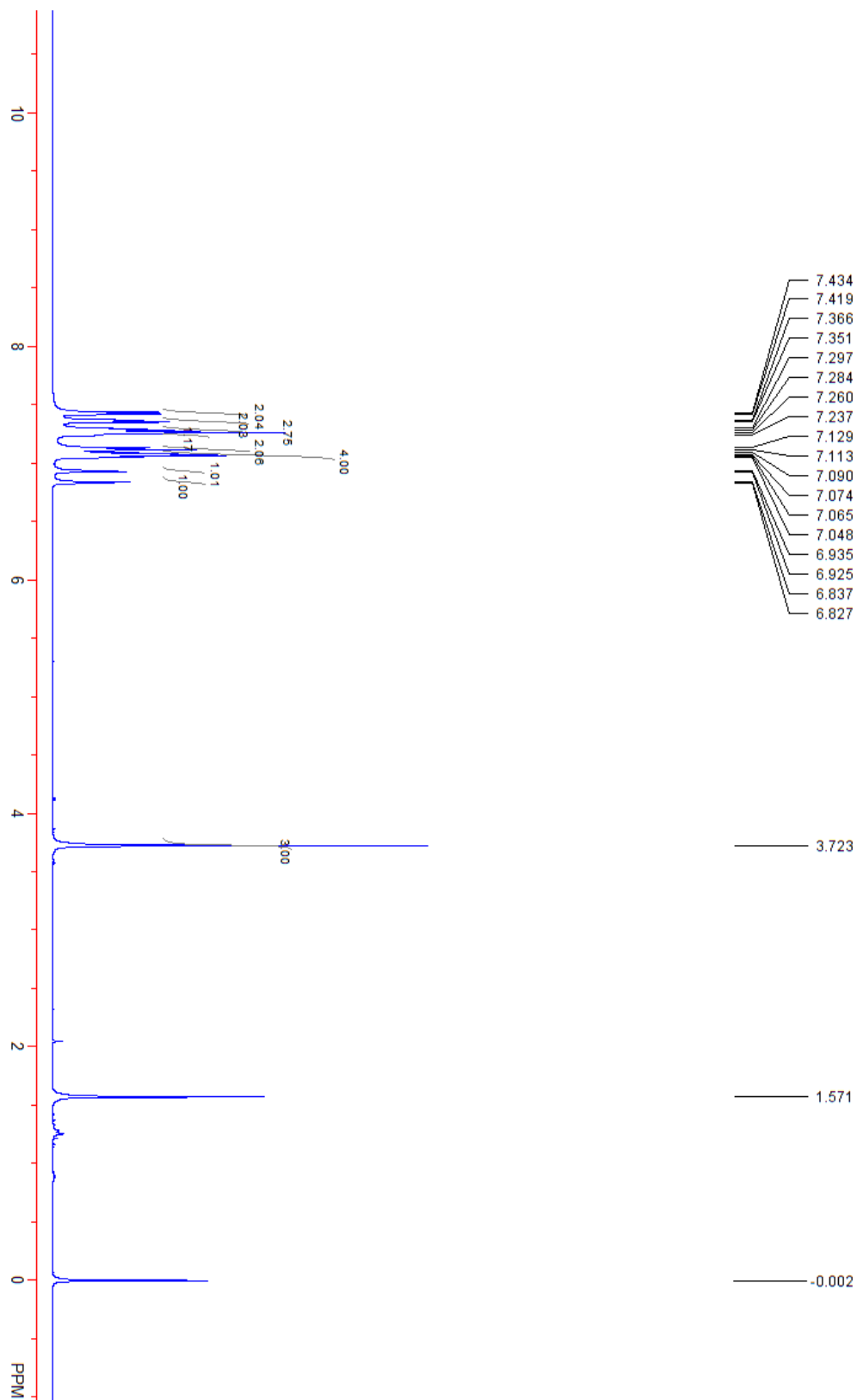


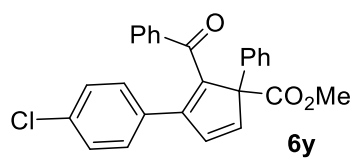
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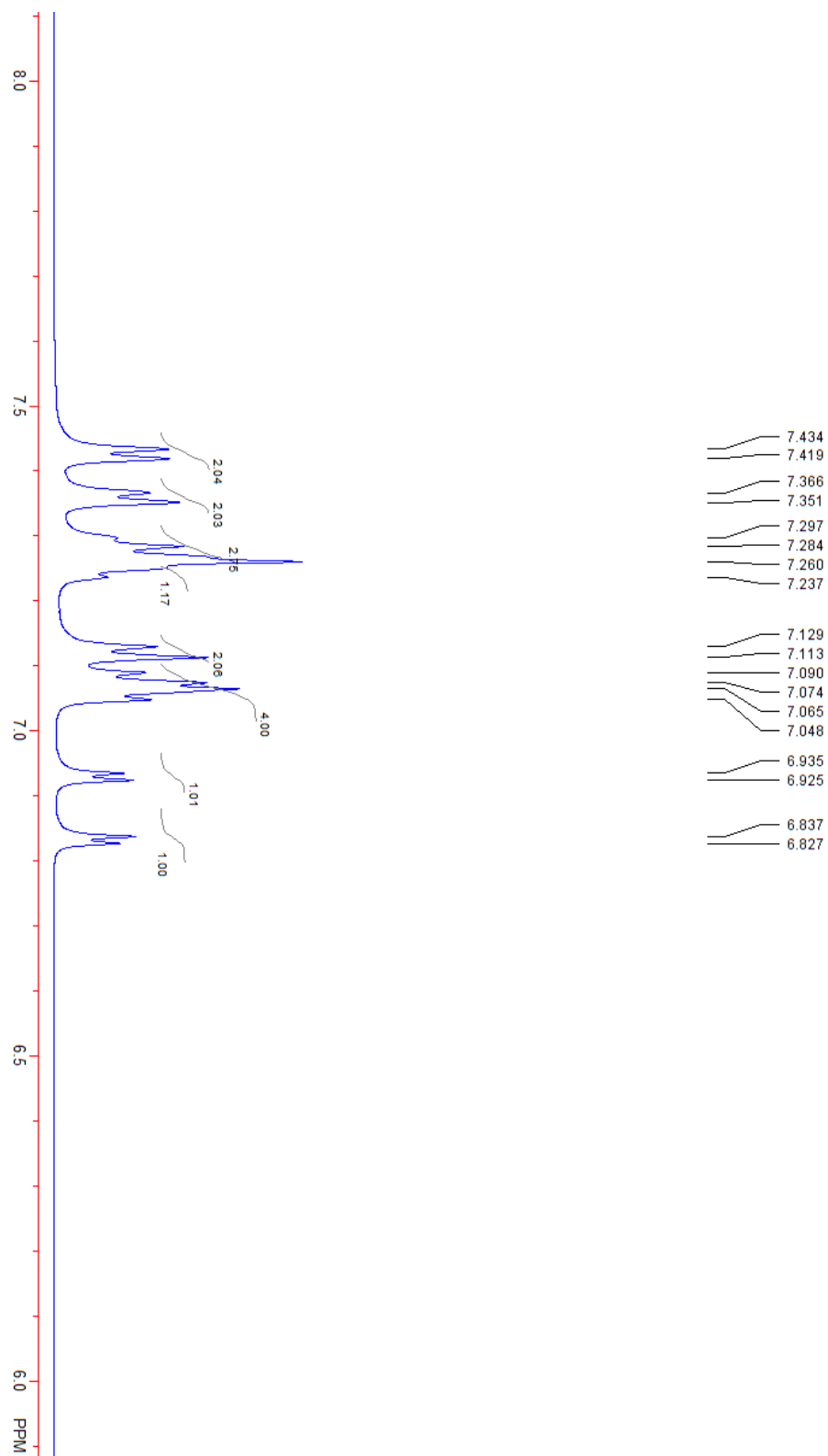


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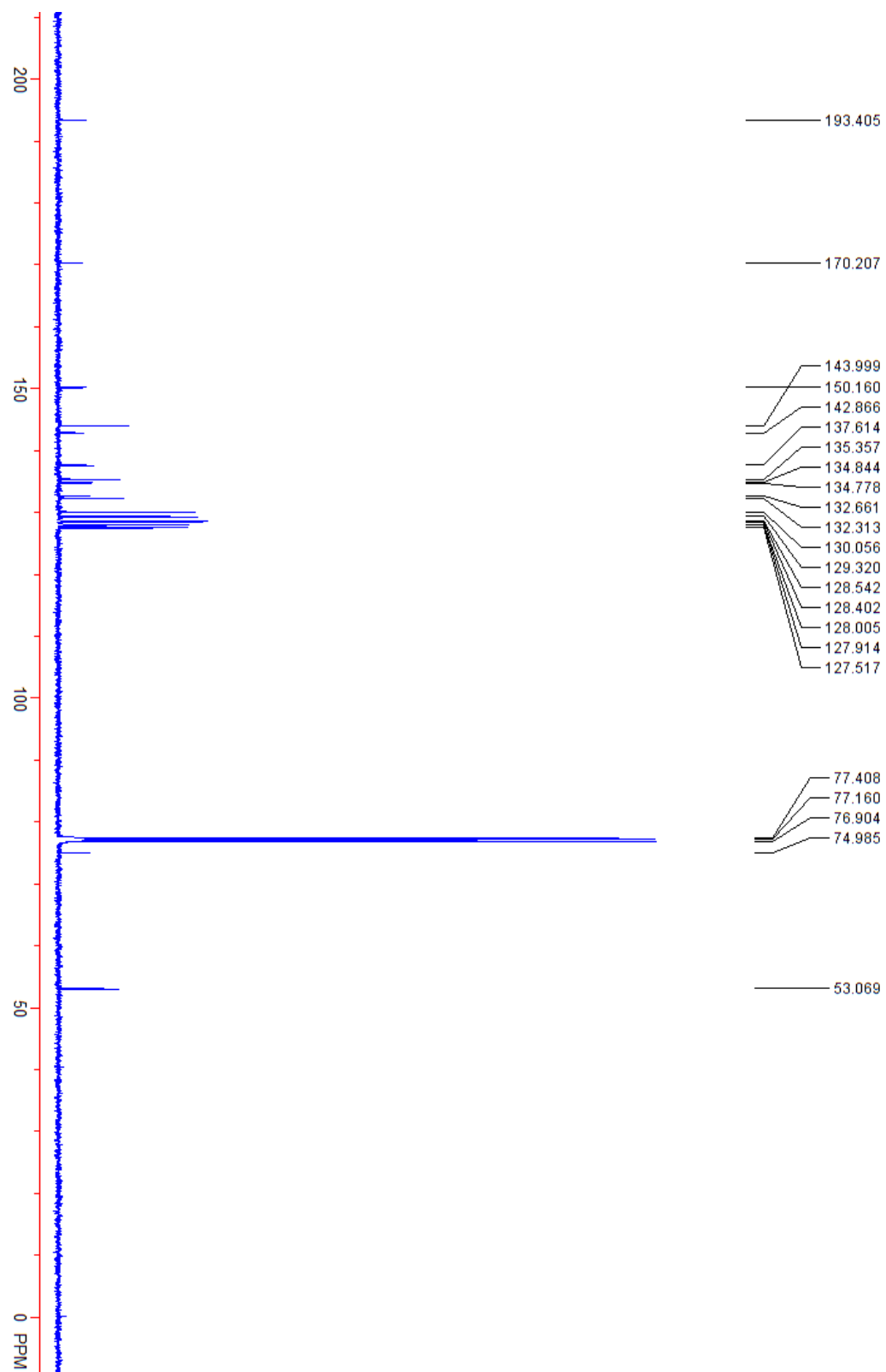
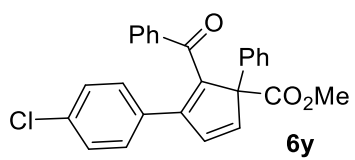




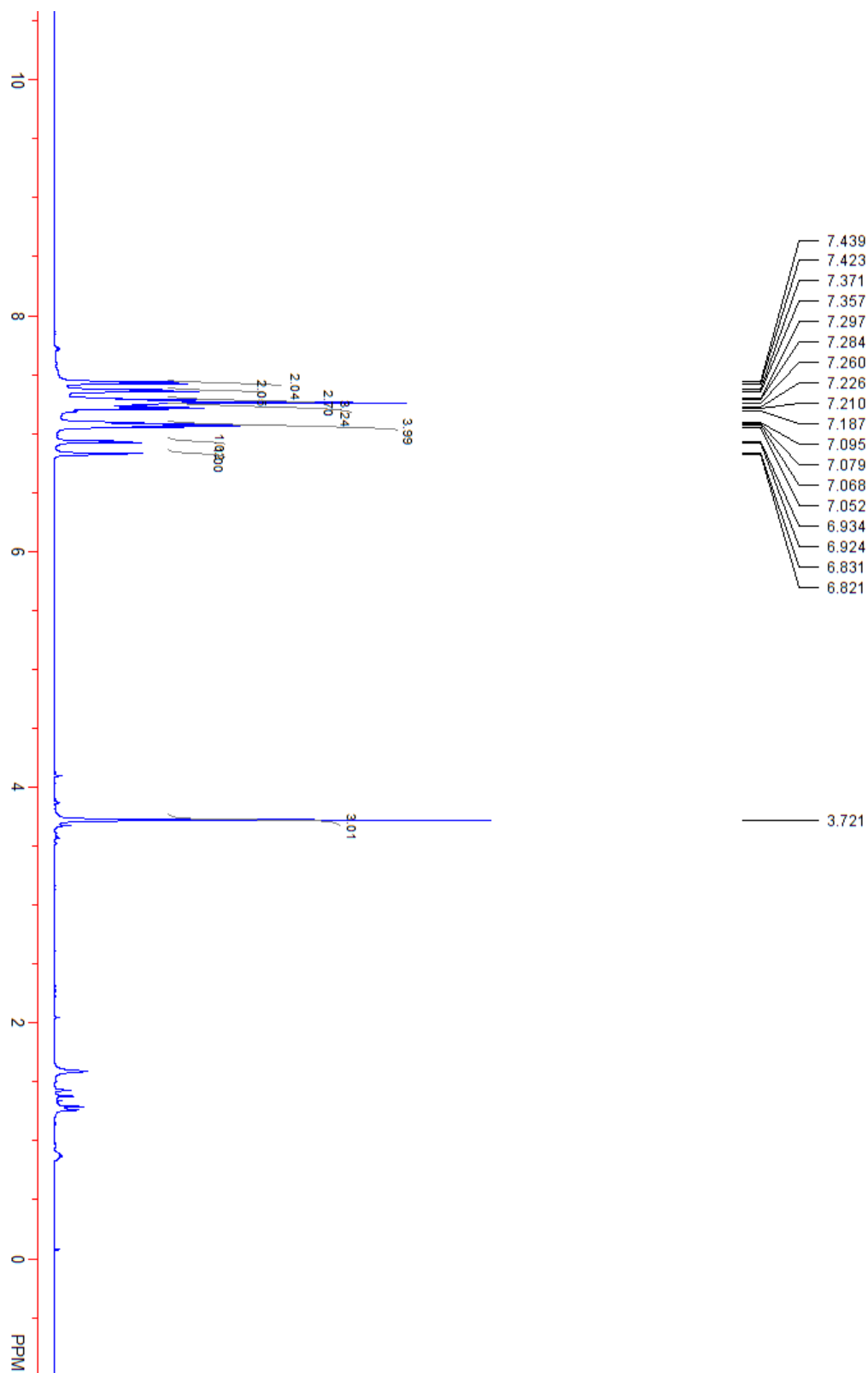
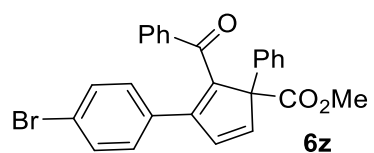
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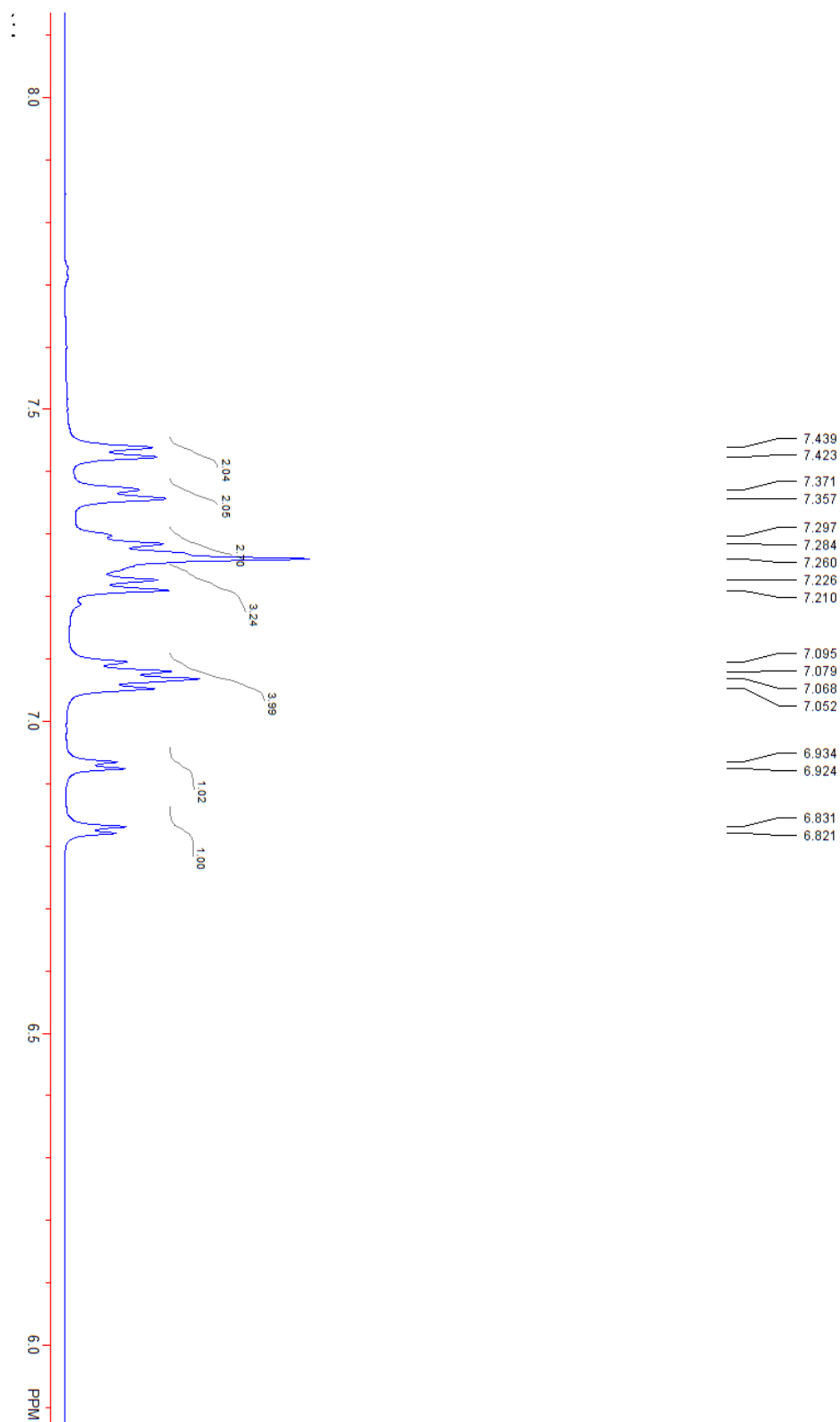
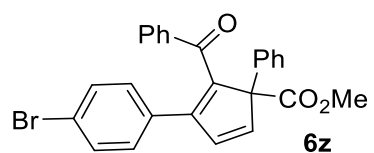
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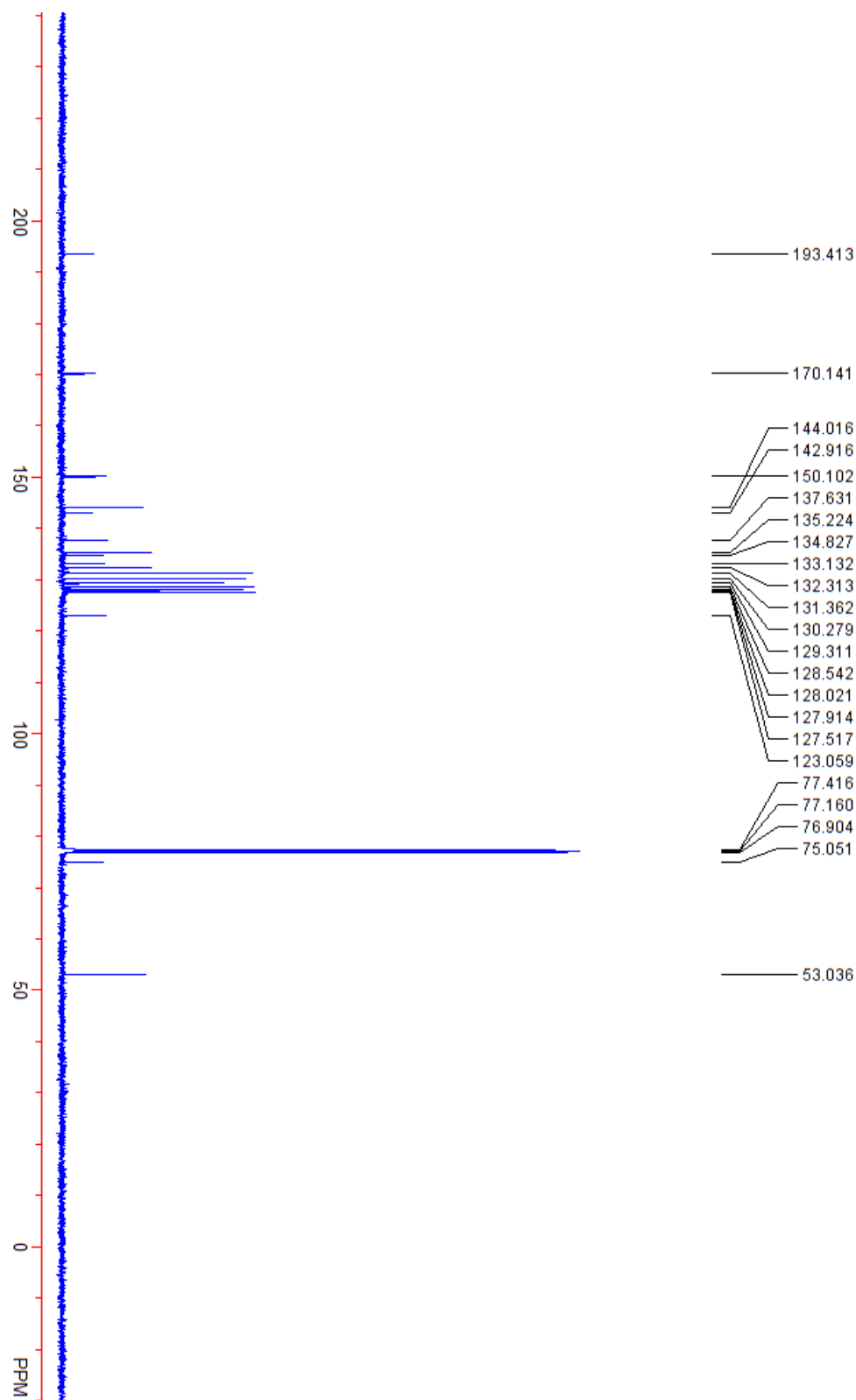
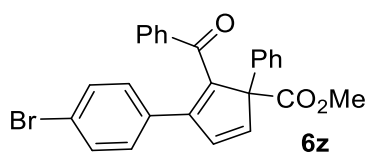
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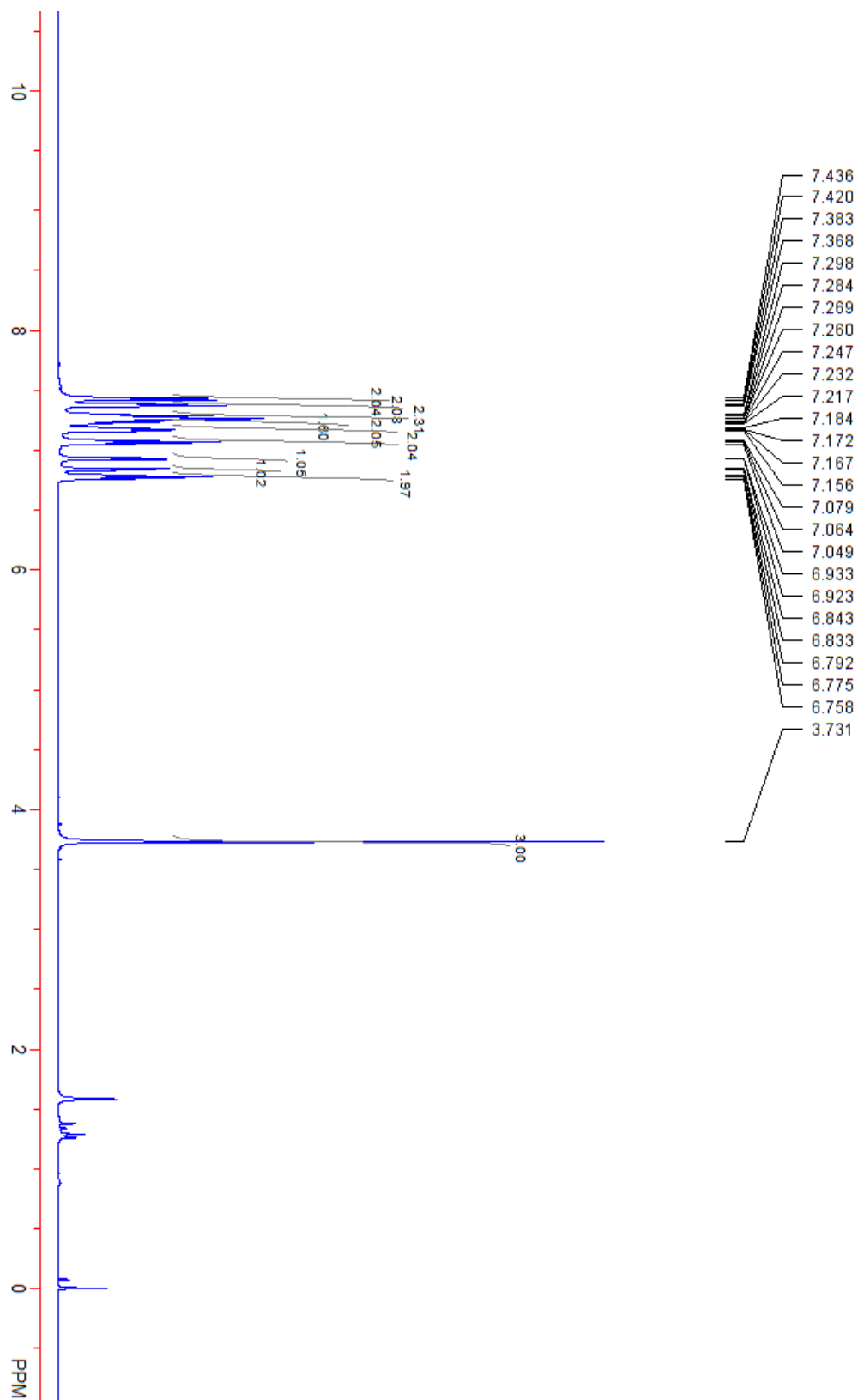
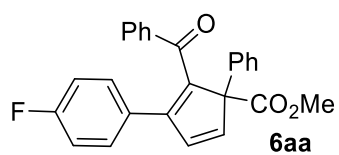
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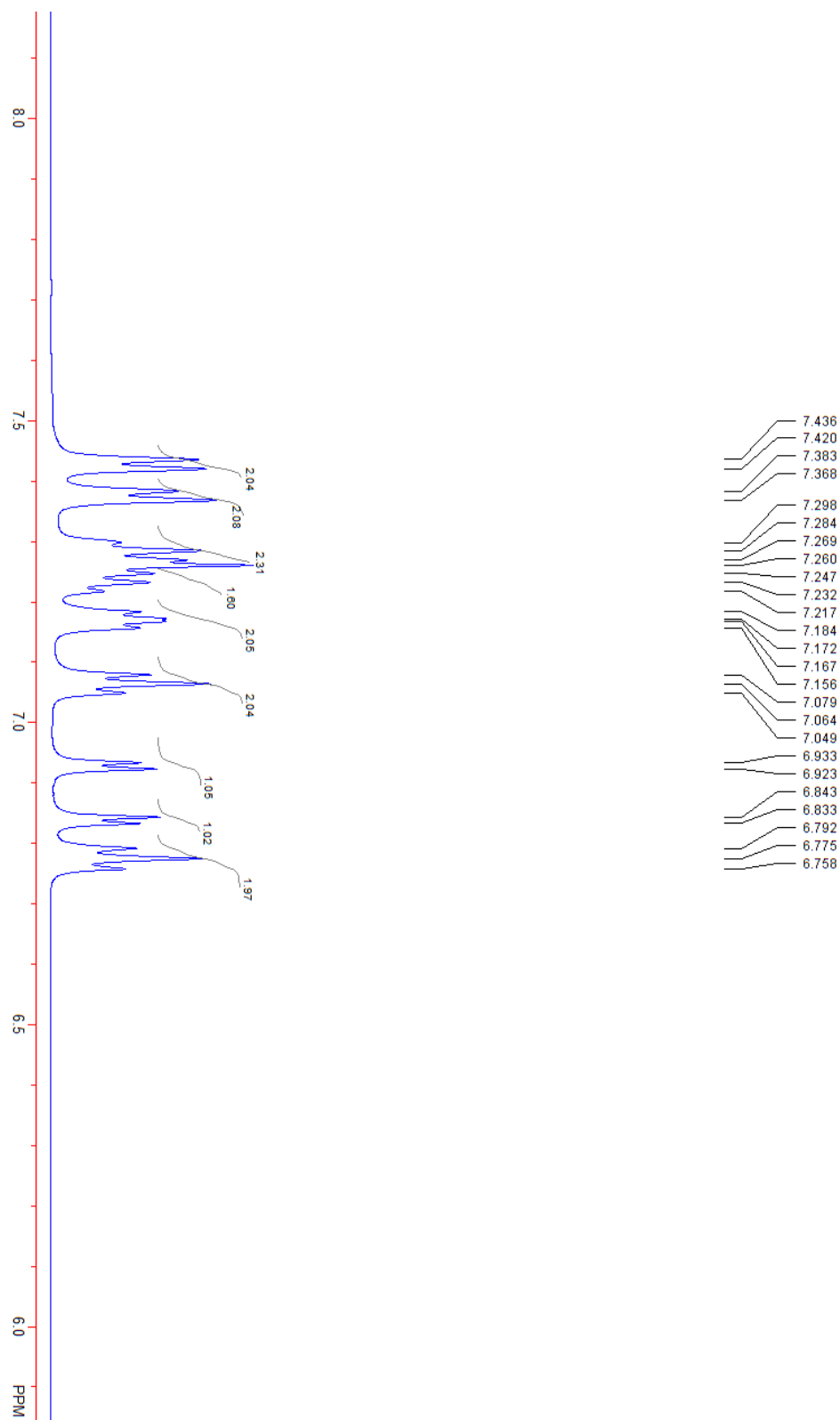
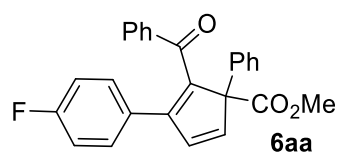
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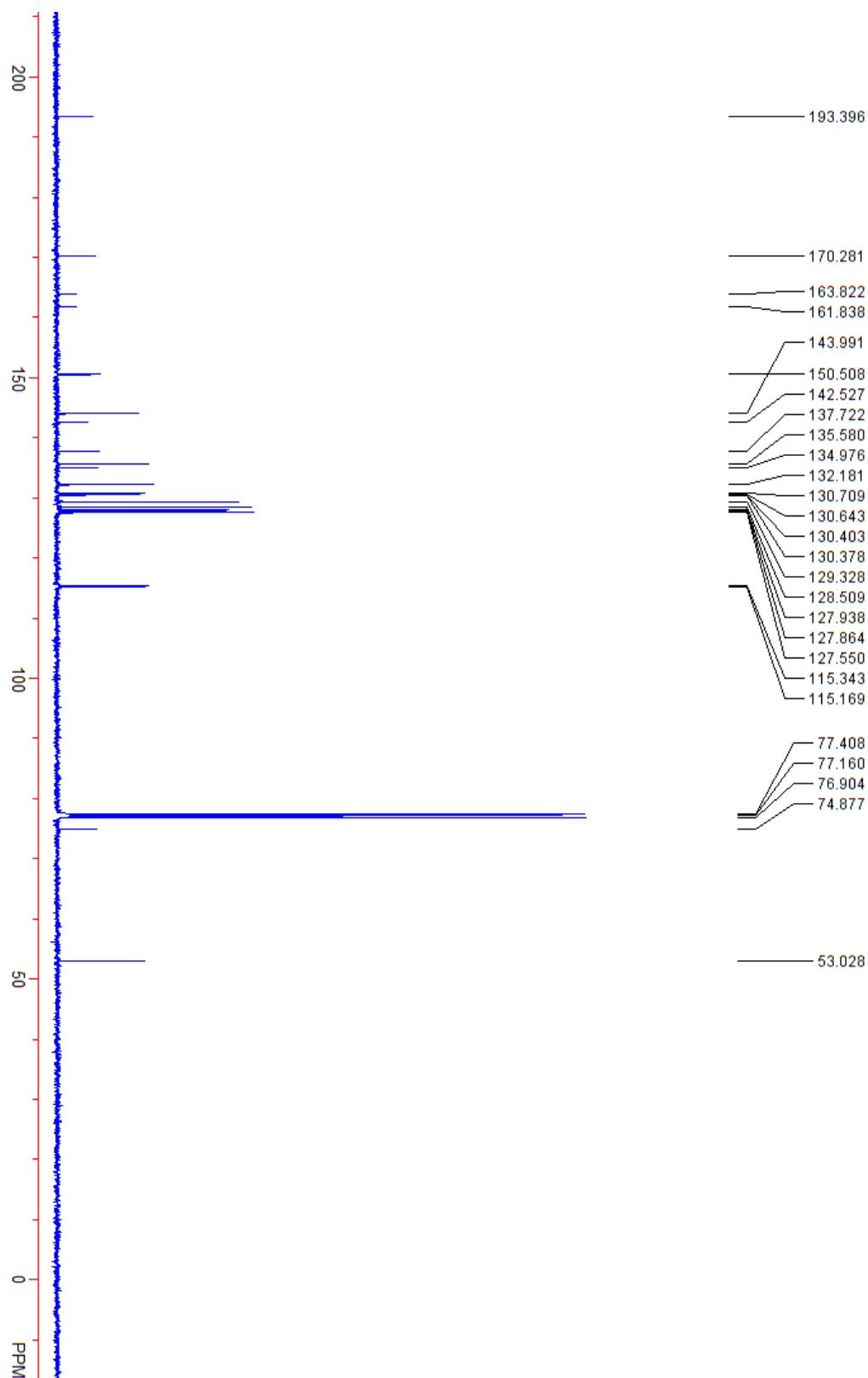
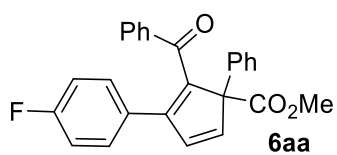
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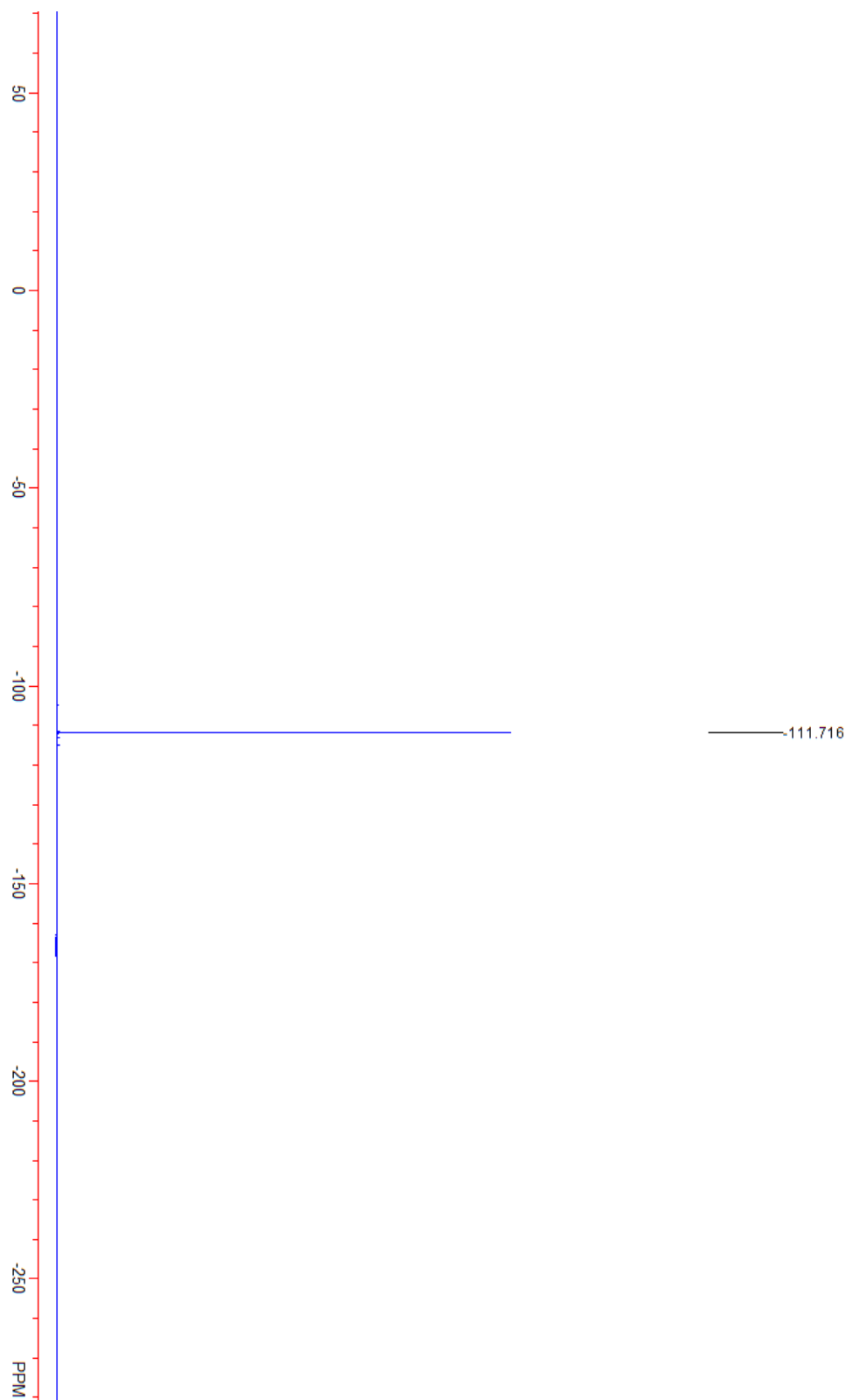
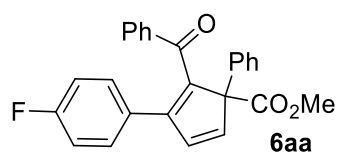
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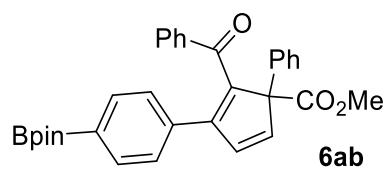


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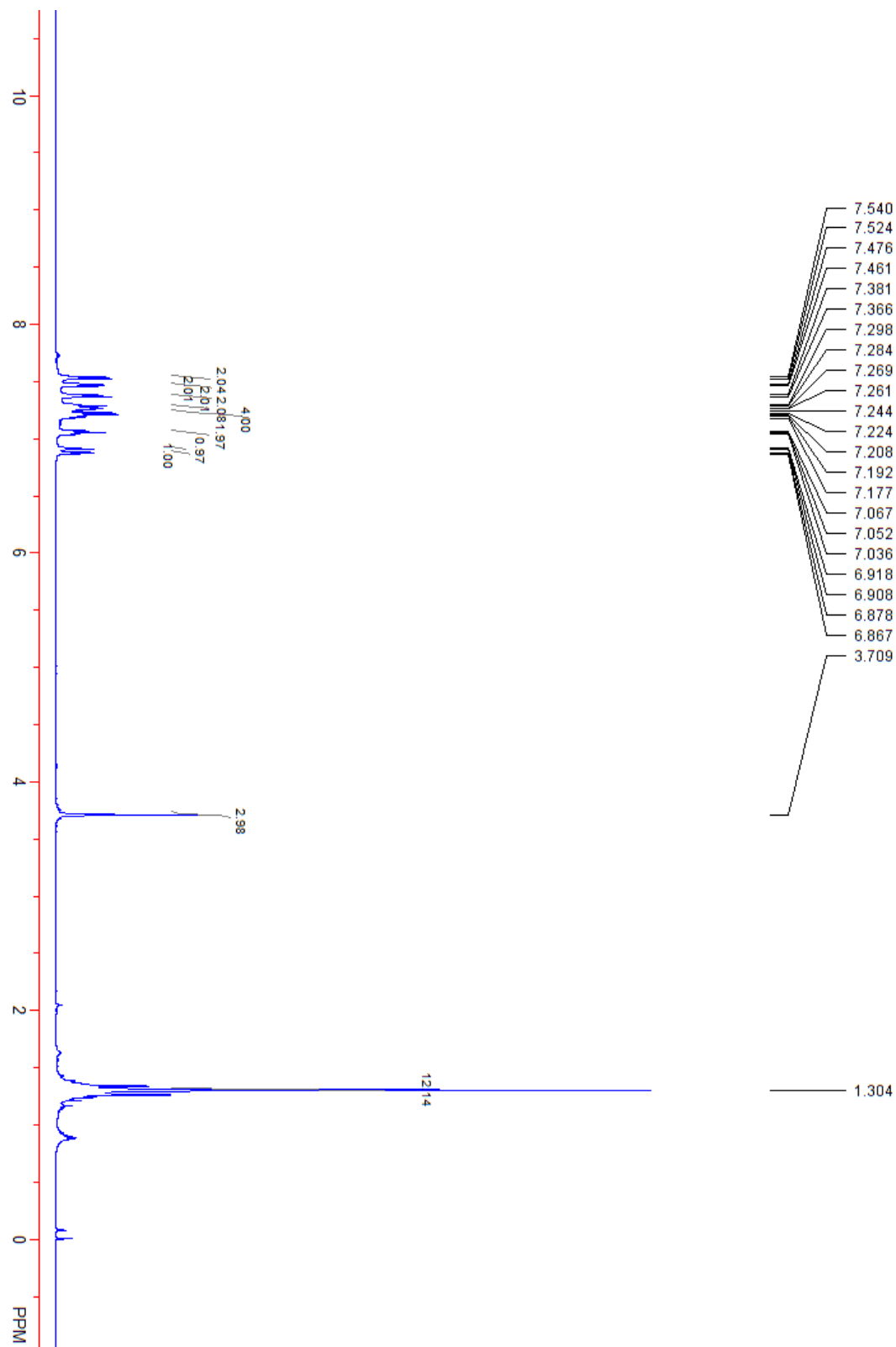


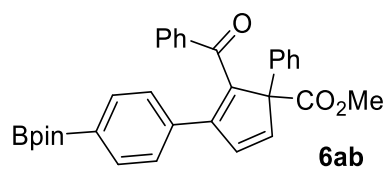
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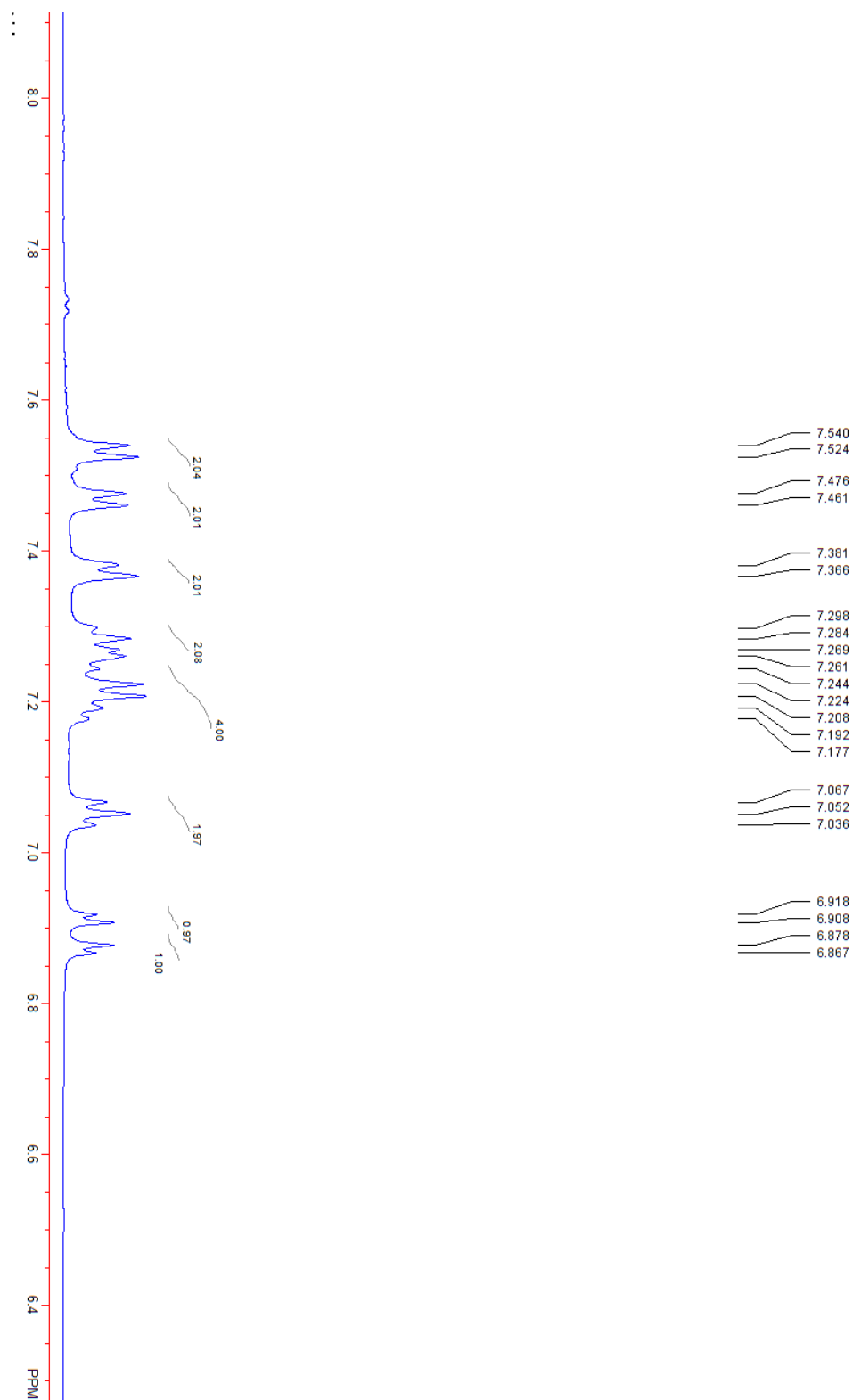


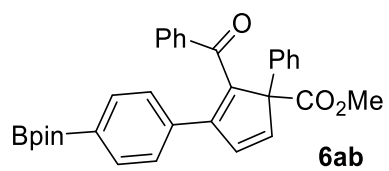
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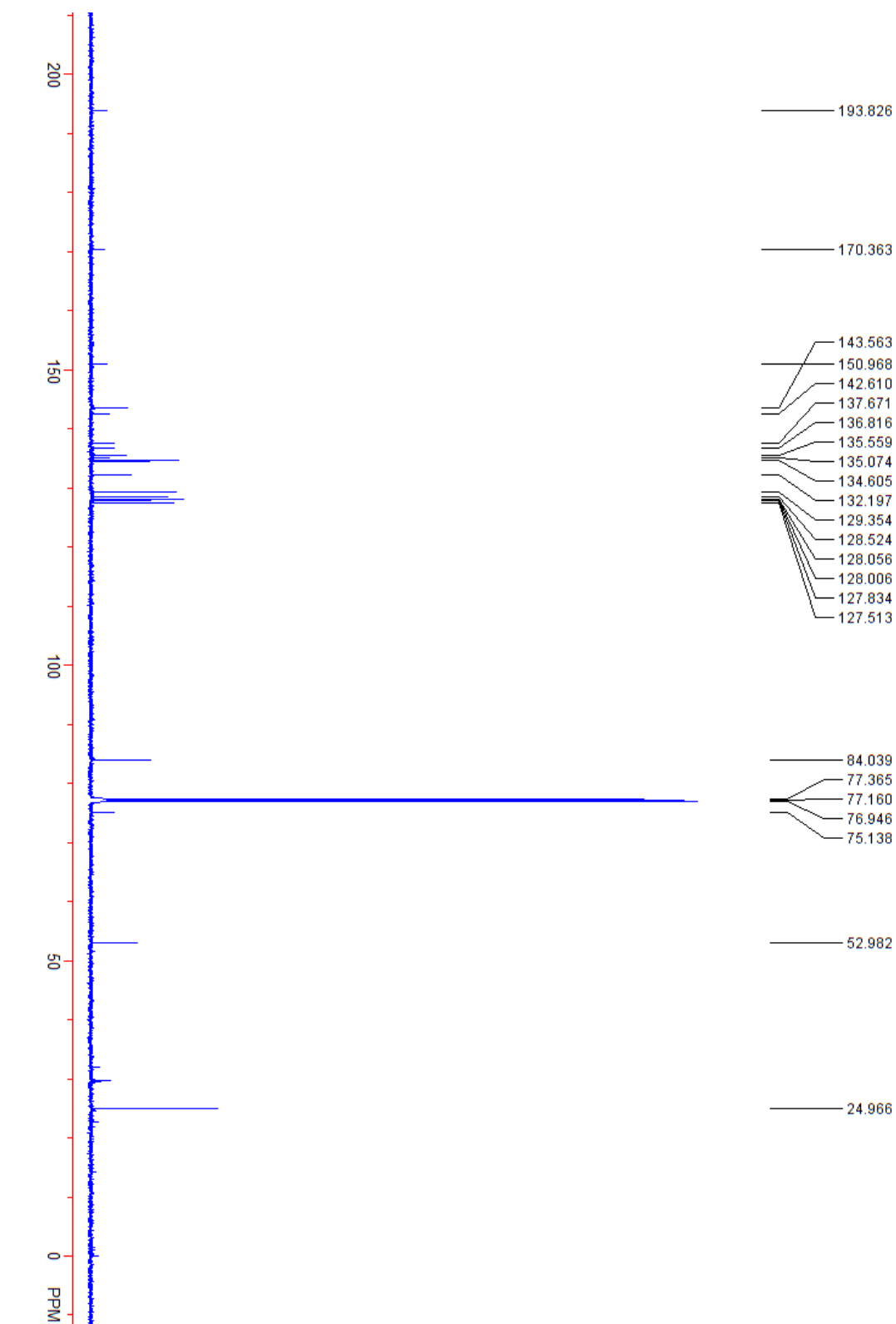


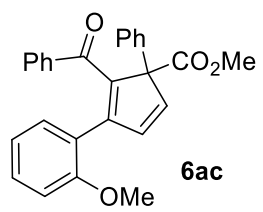
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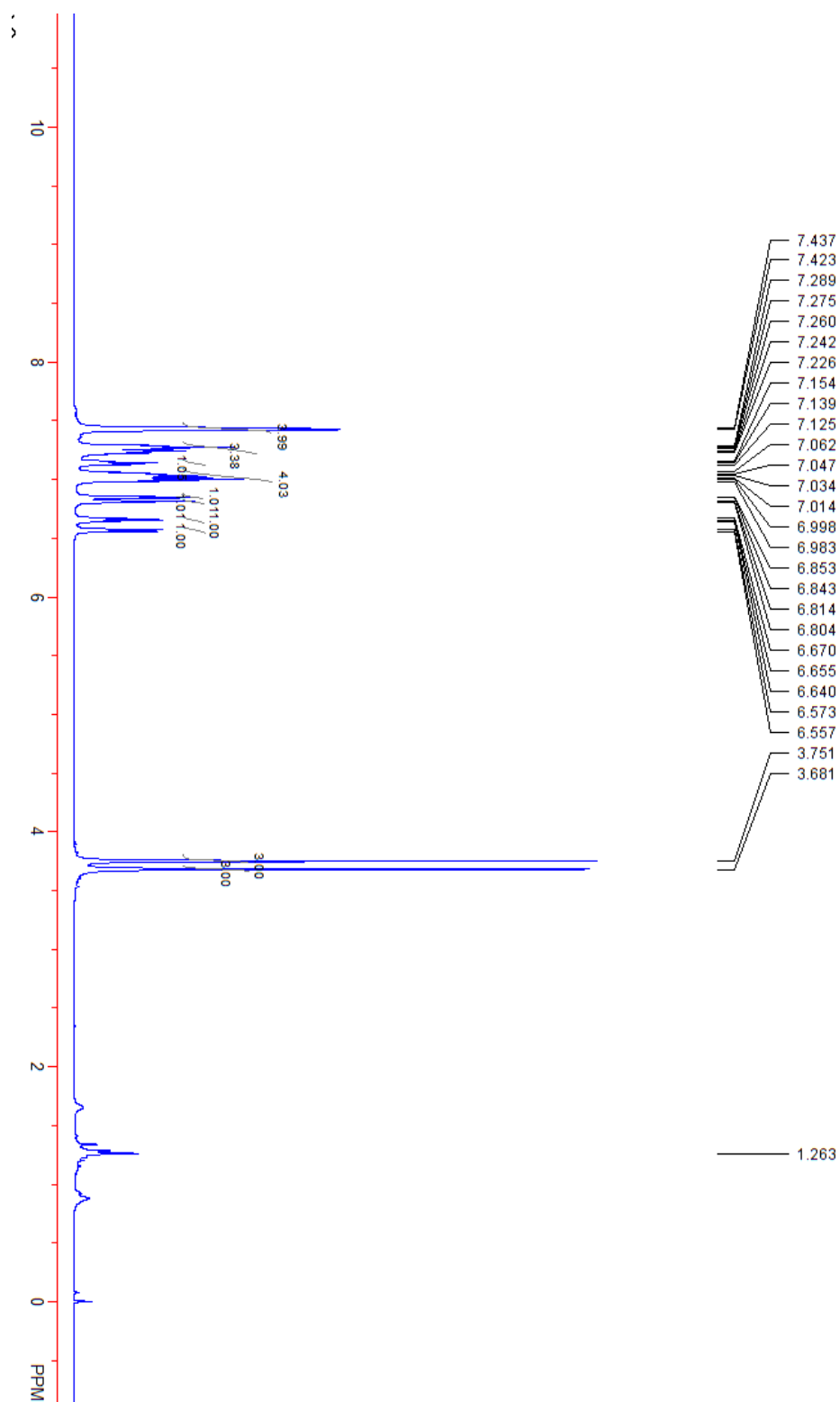


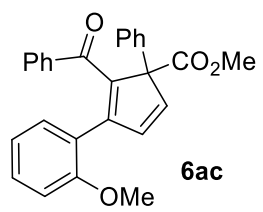
$^{13}\text{C}\{^1\text{H}\}$ NMR:



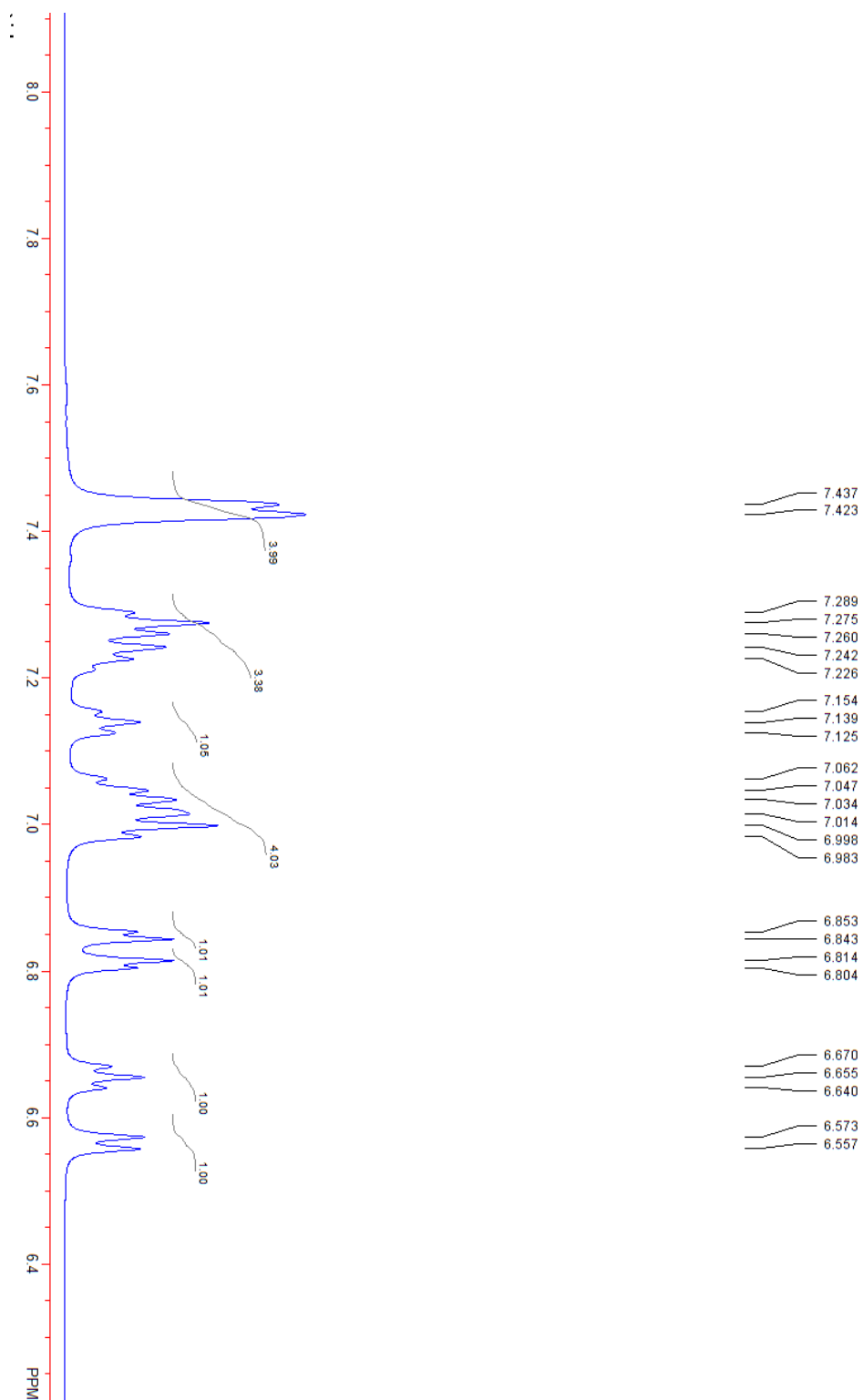


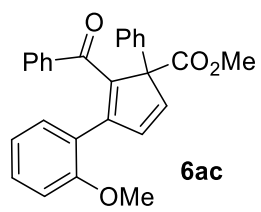
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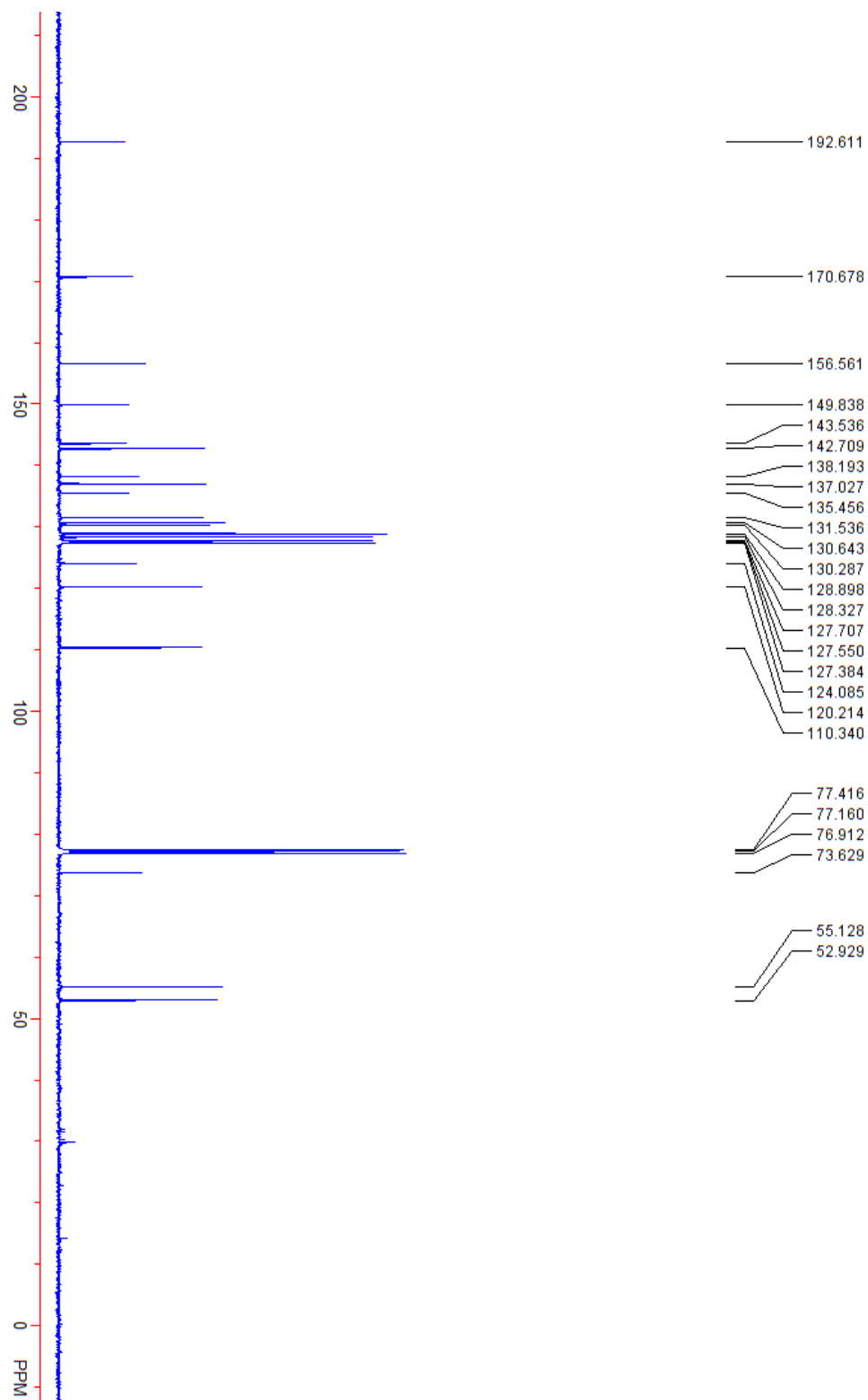


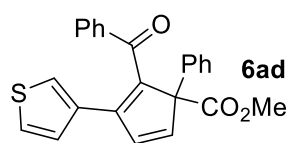
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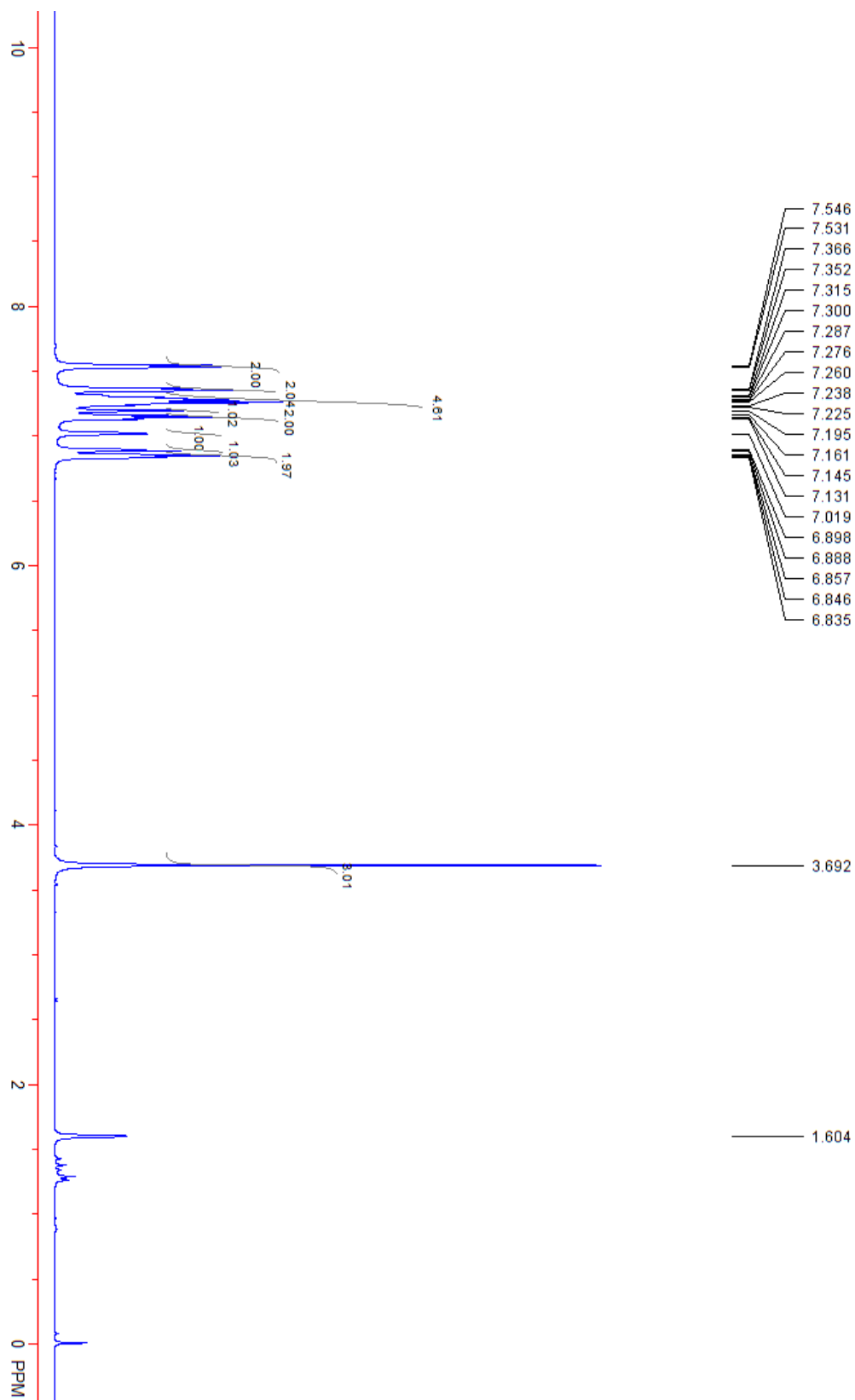


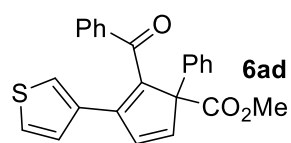
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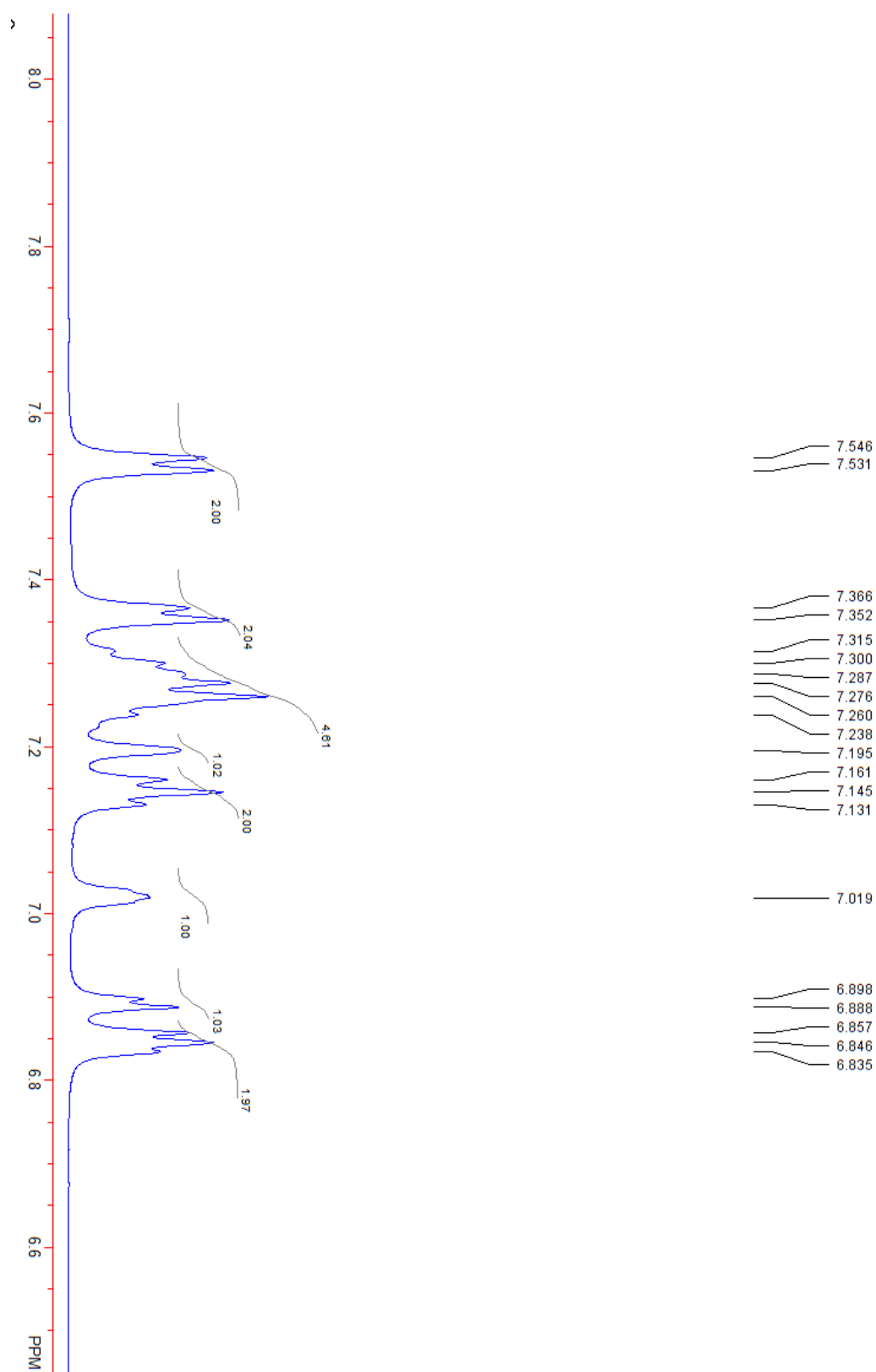


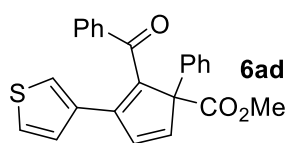
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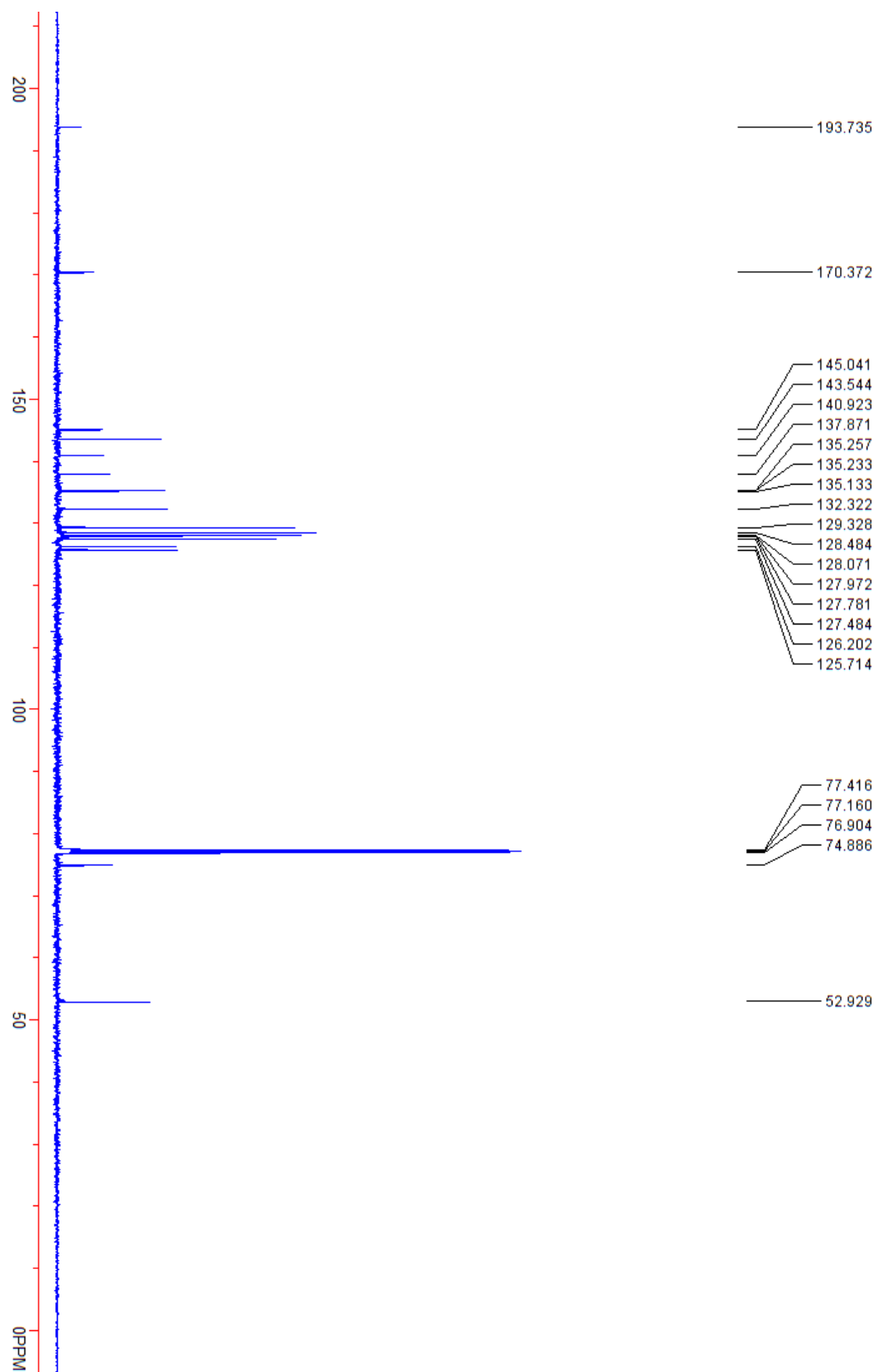


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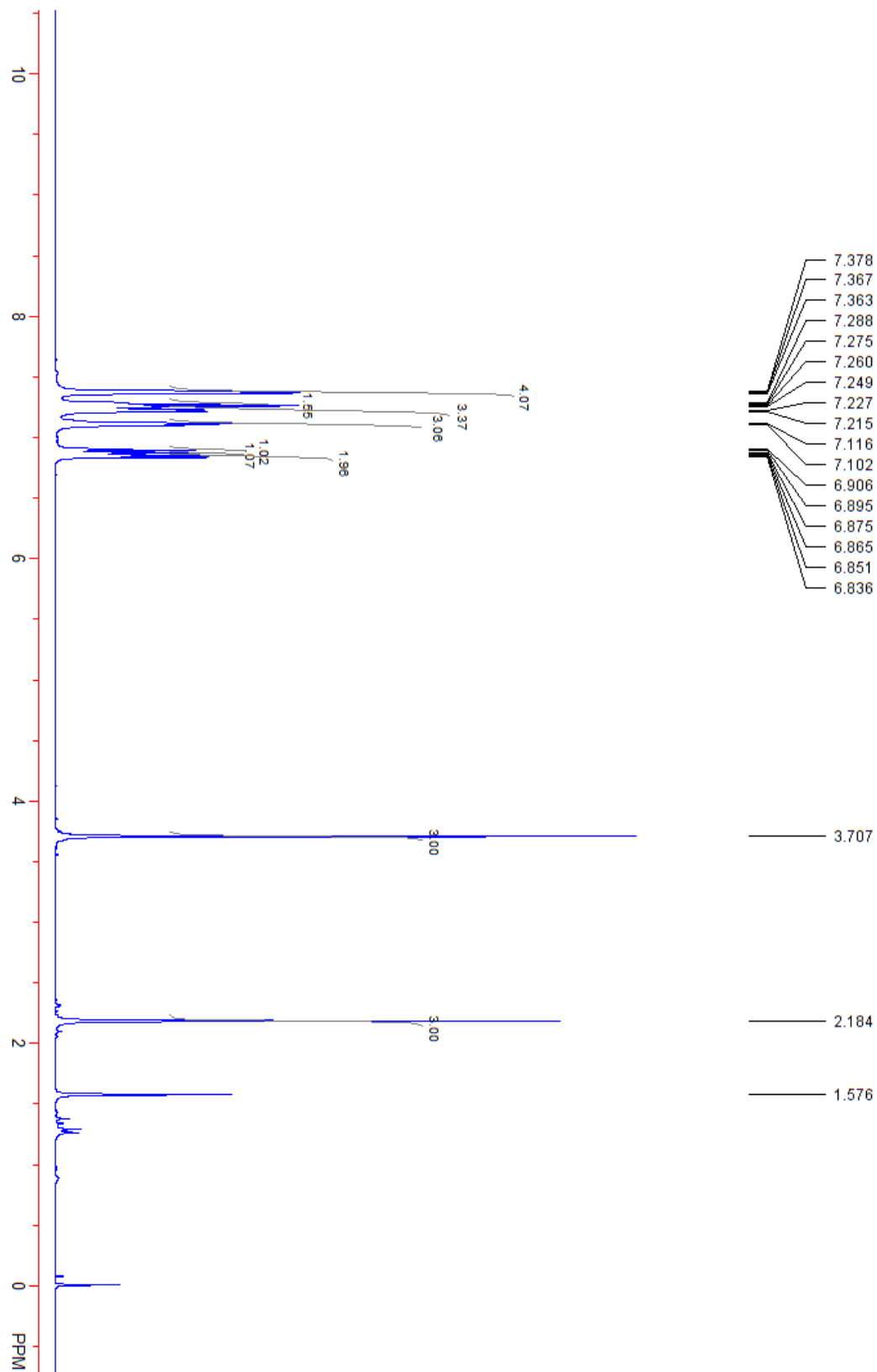
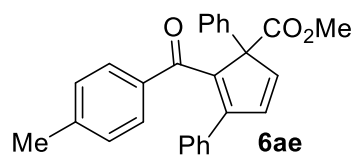




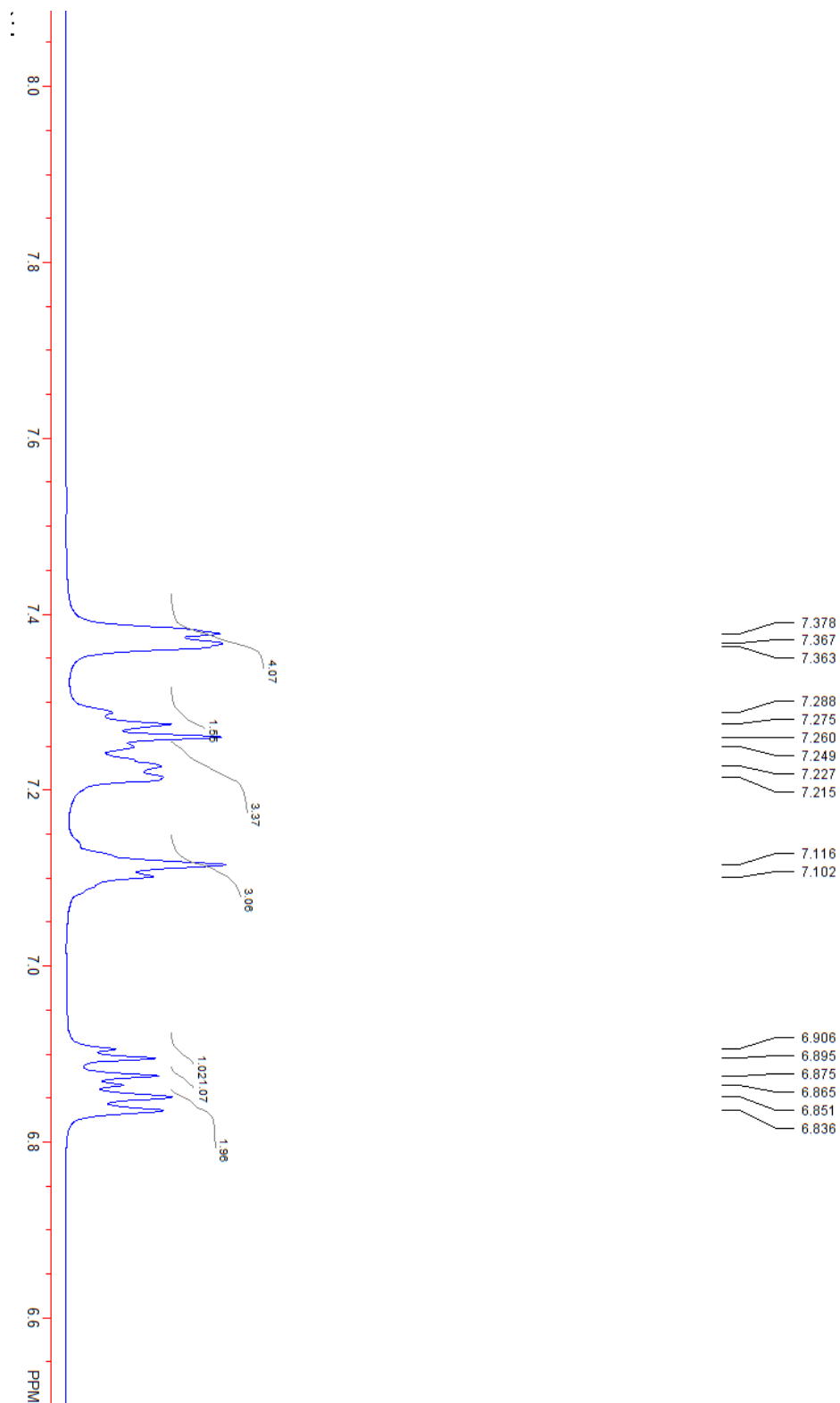
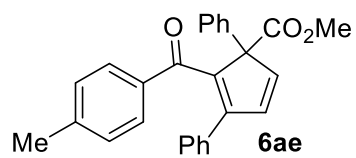
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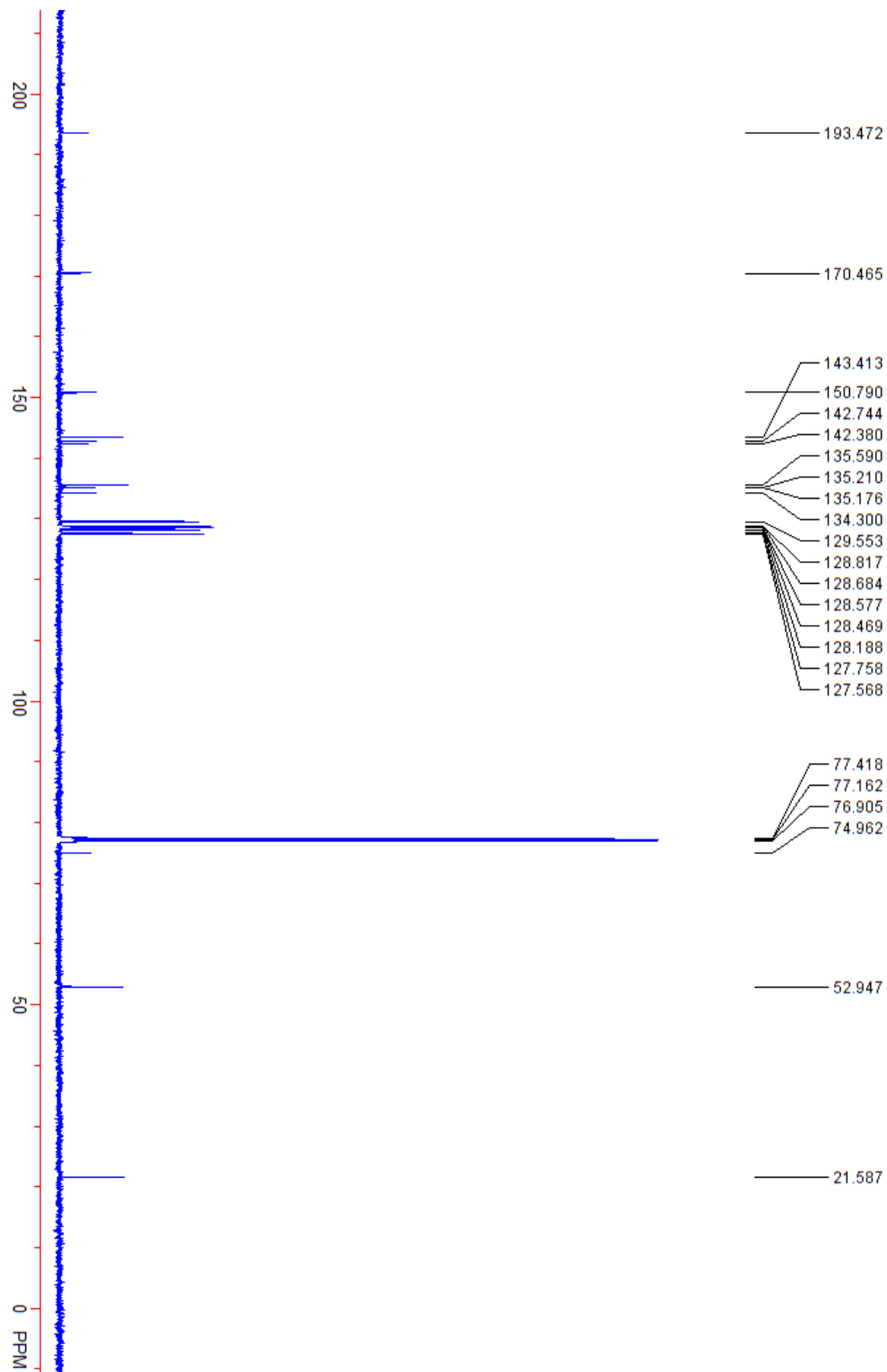
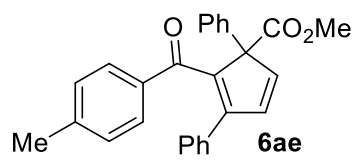
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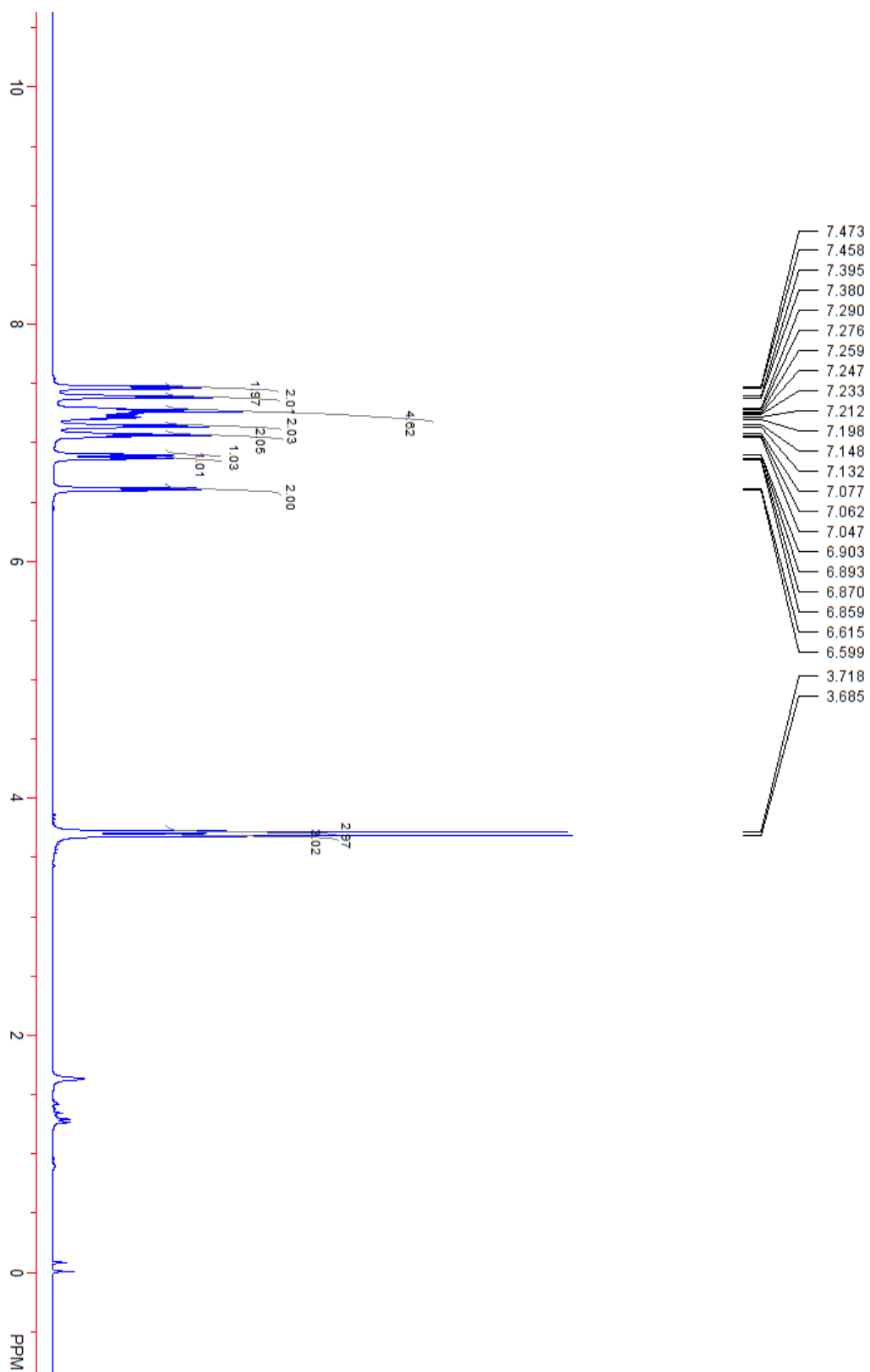
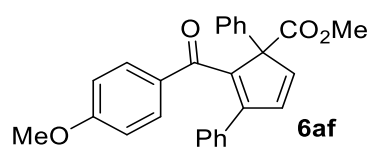
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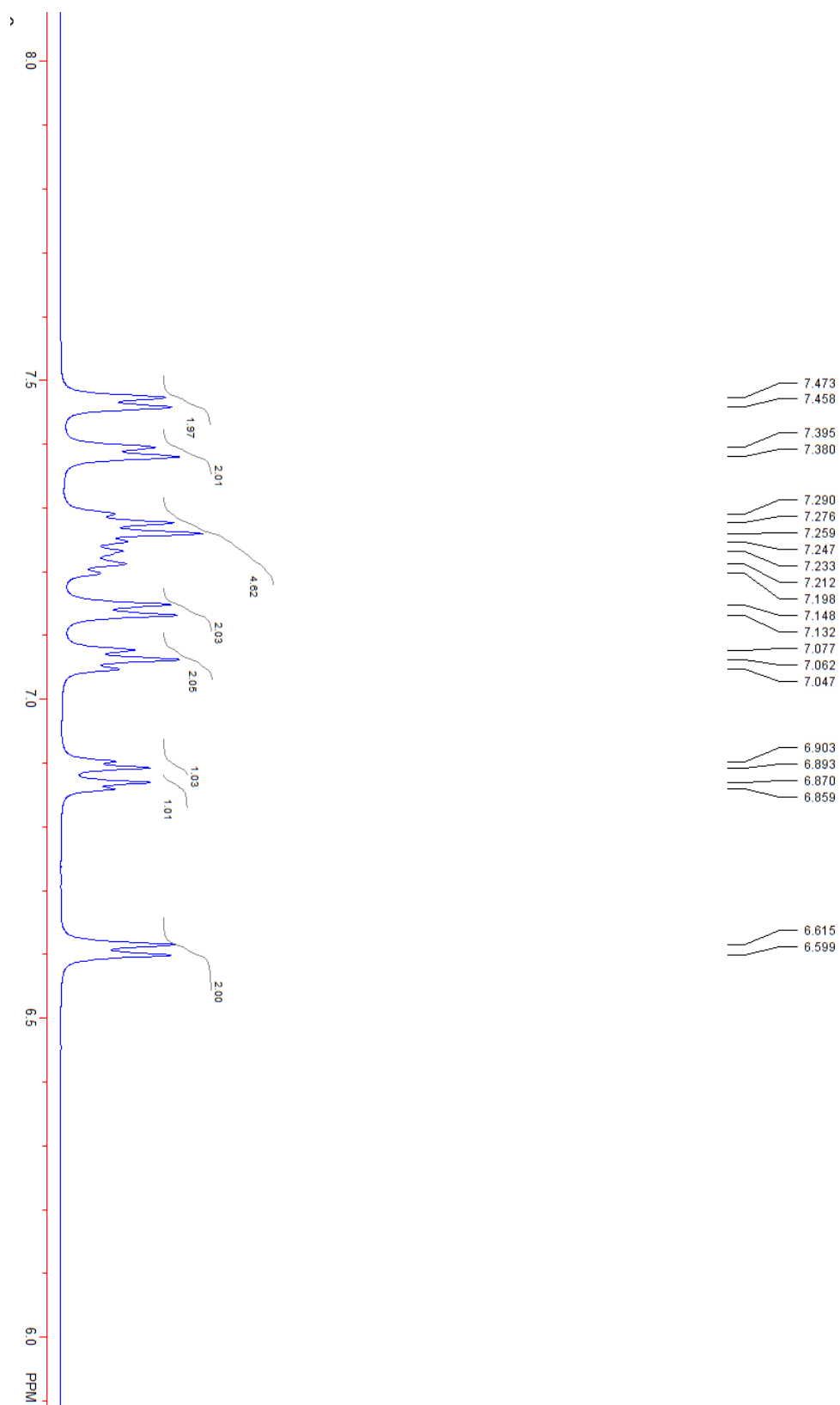
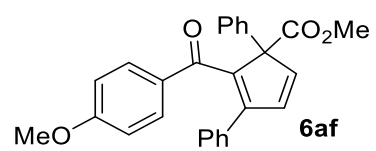
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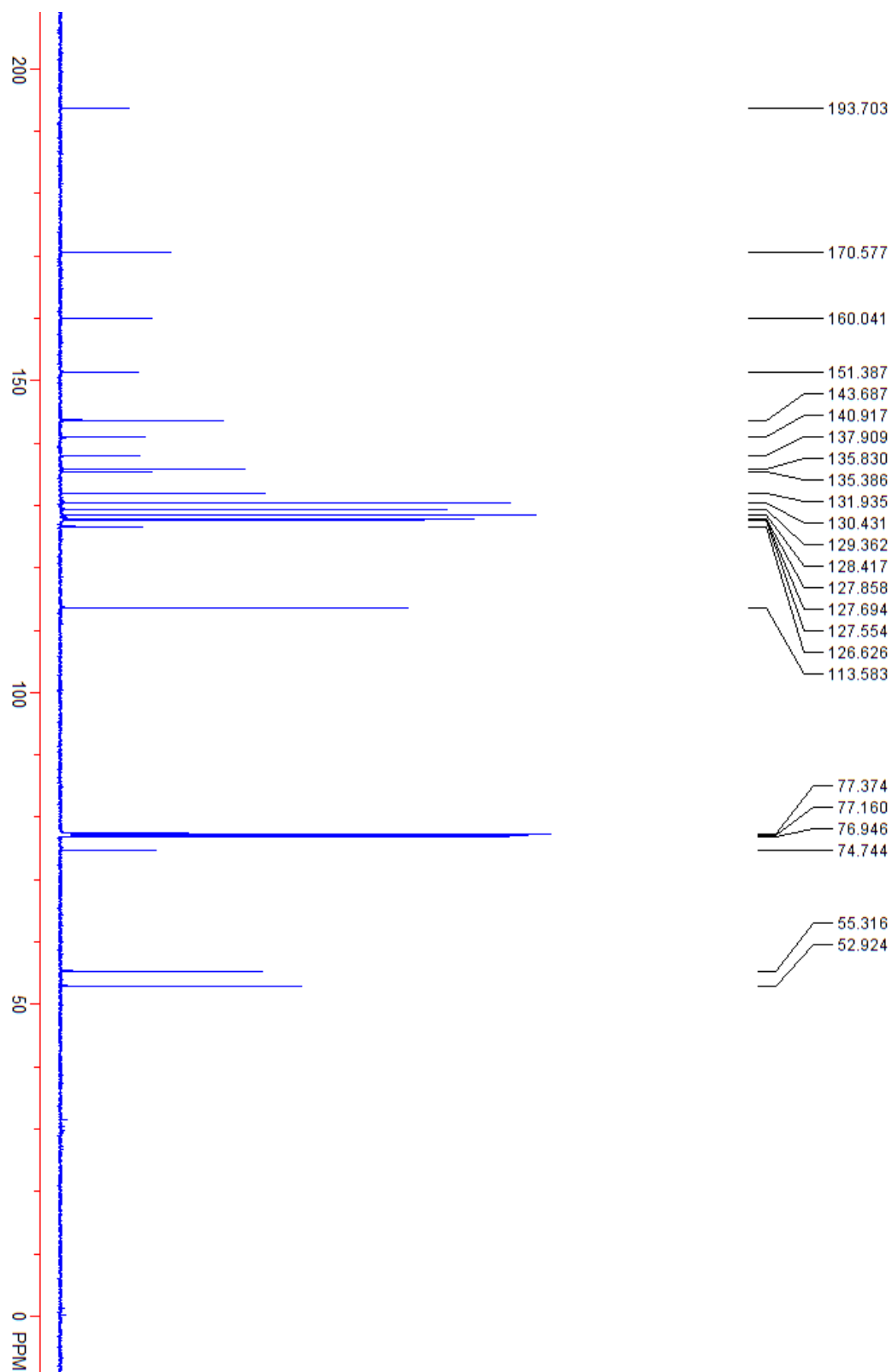
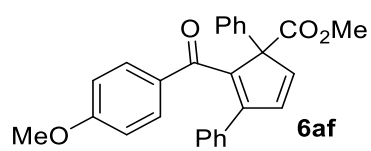
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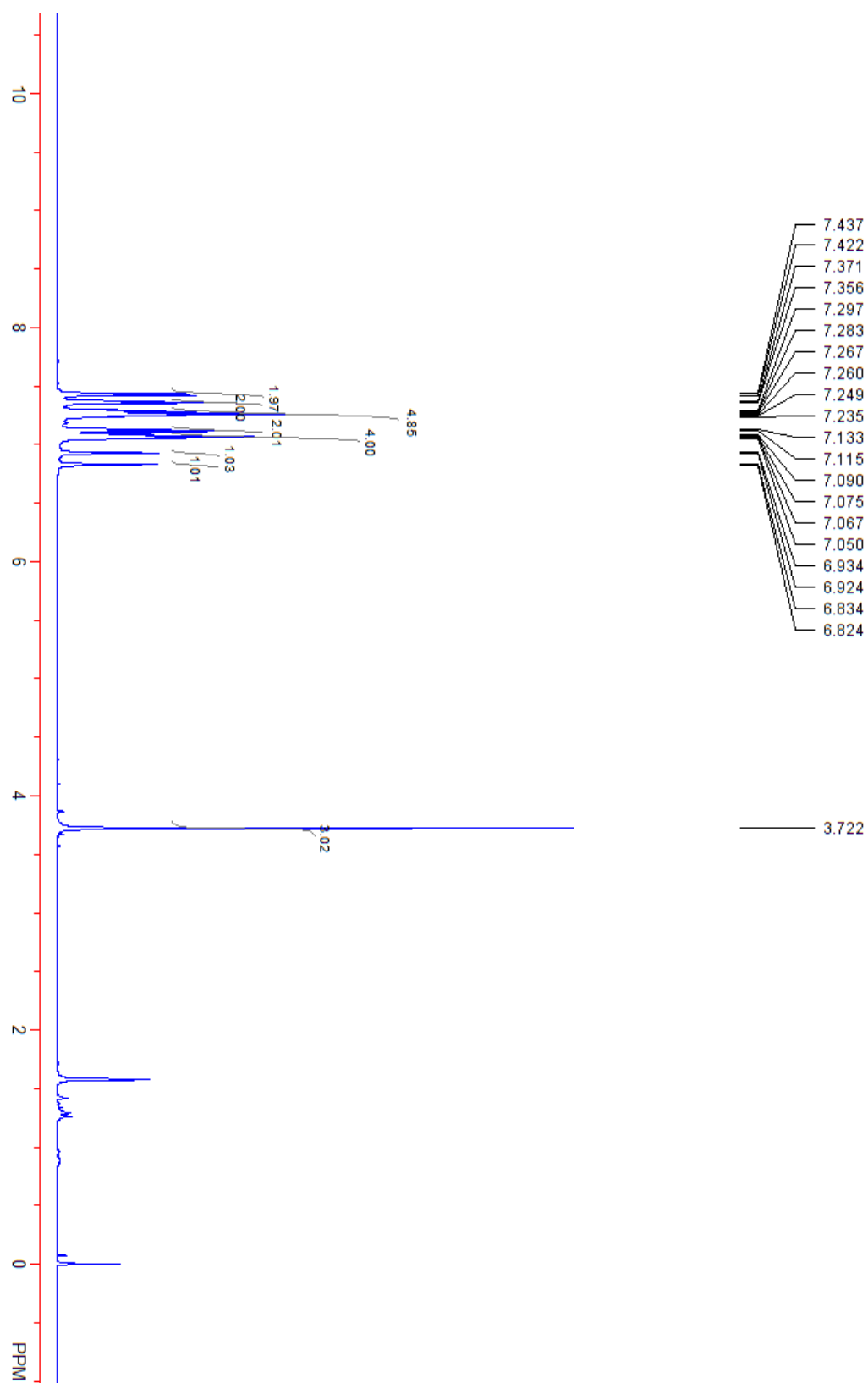
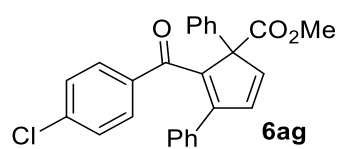
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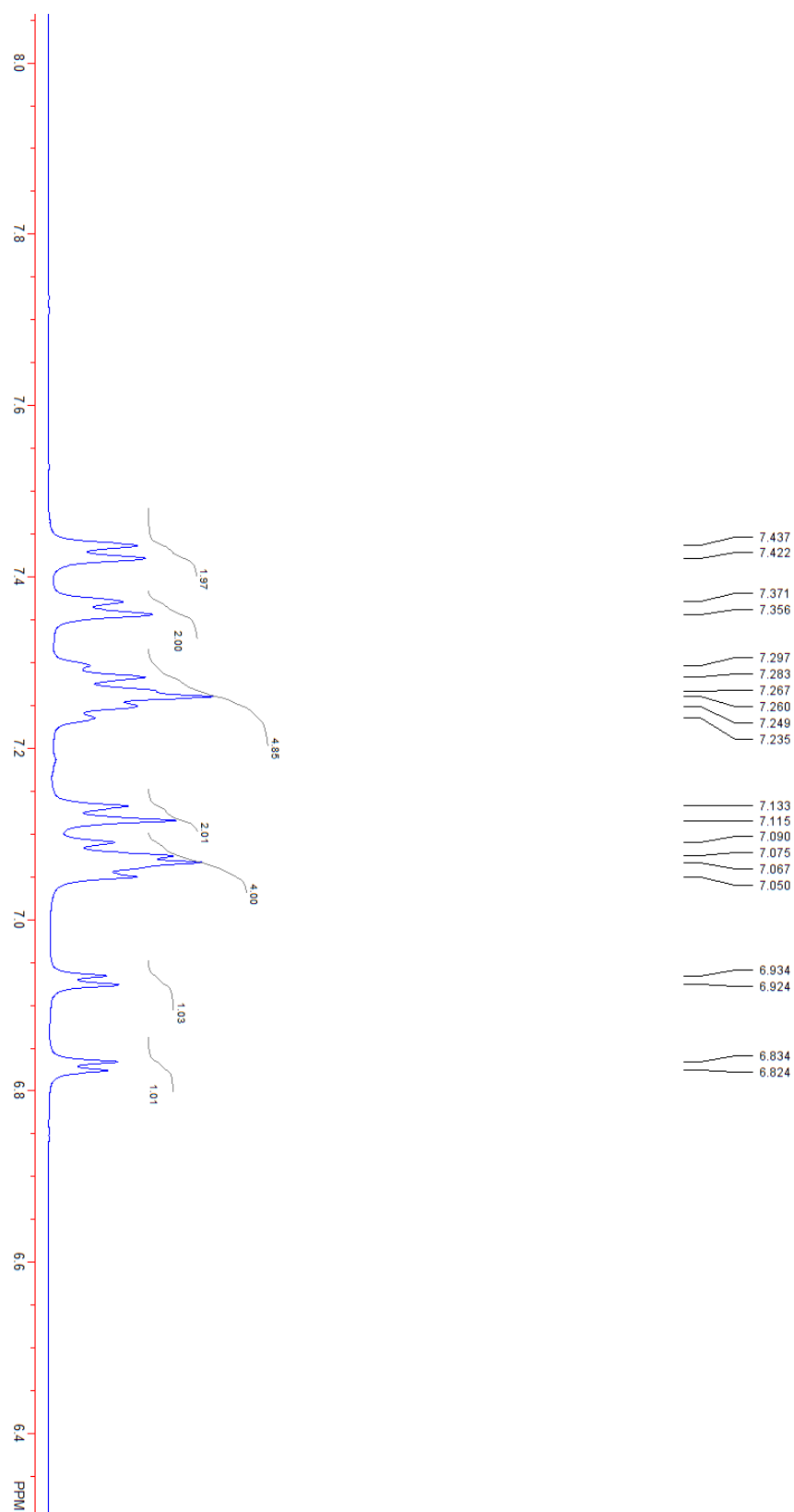
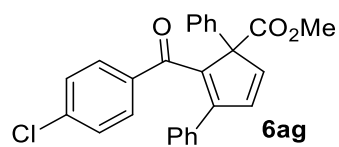
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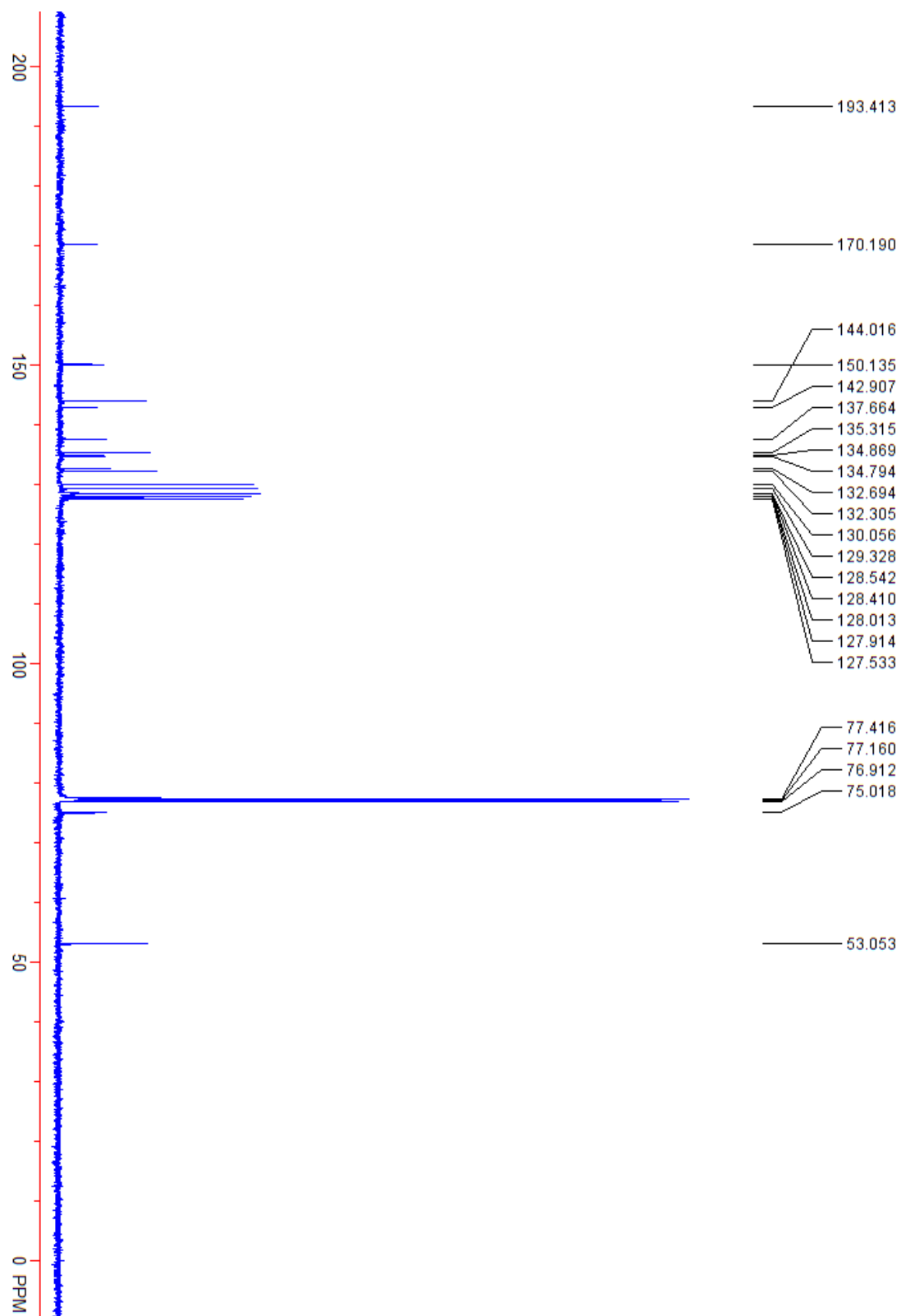
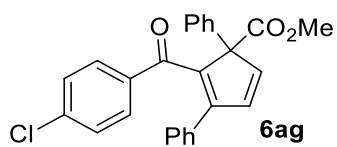
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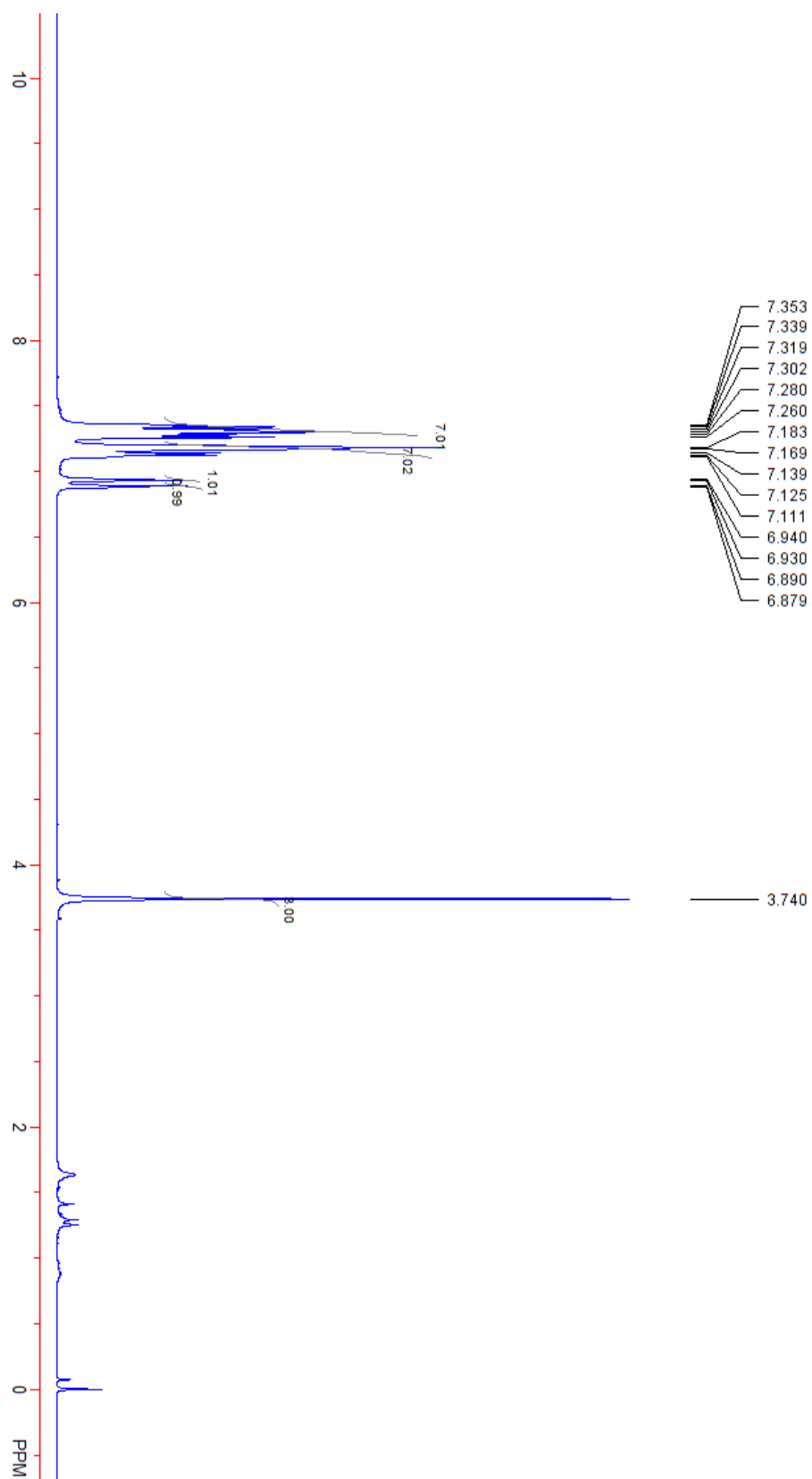
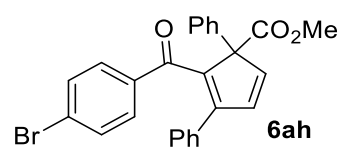
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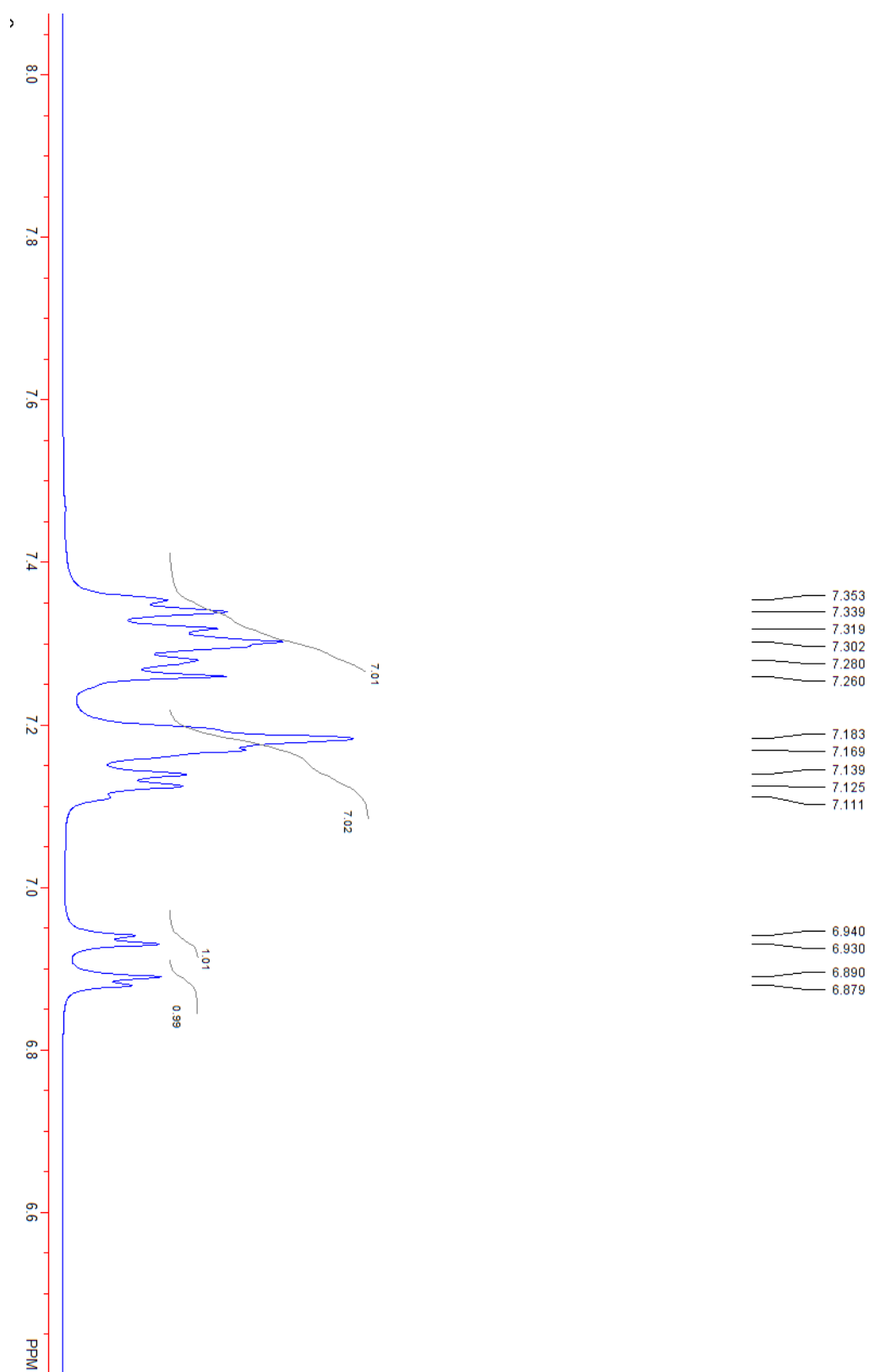
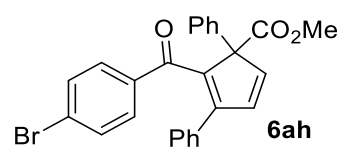
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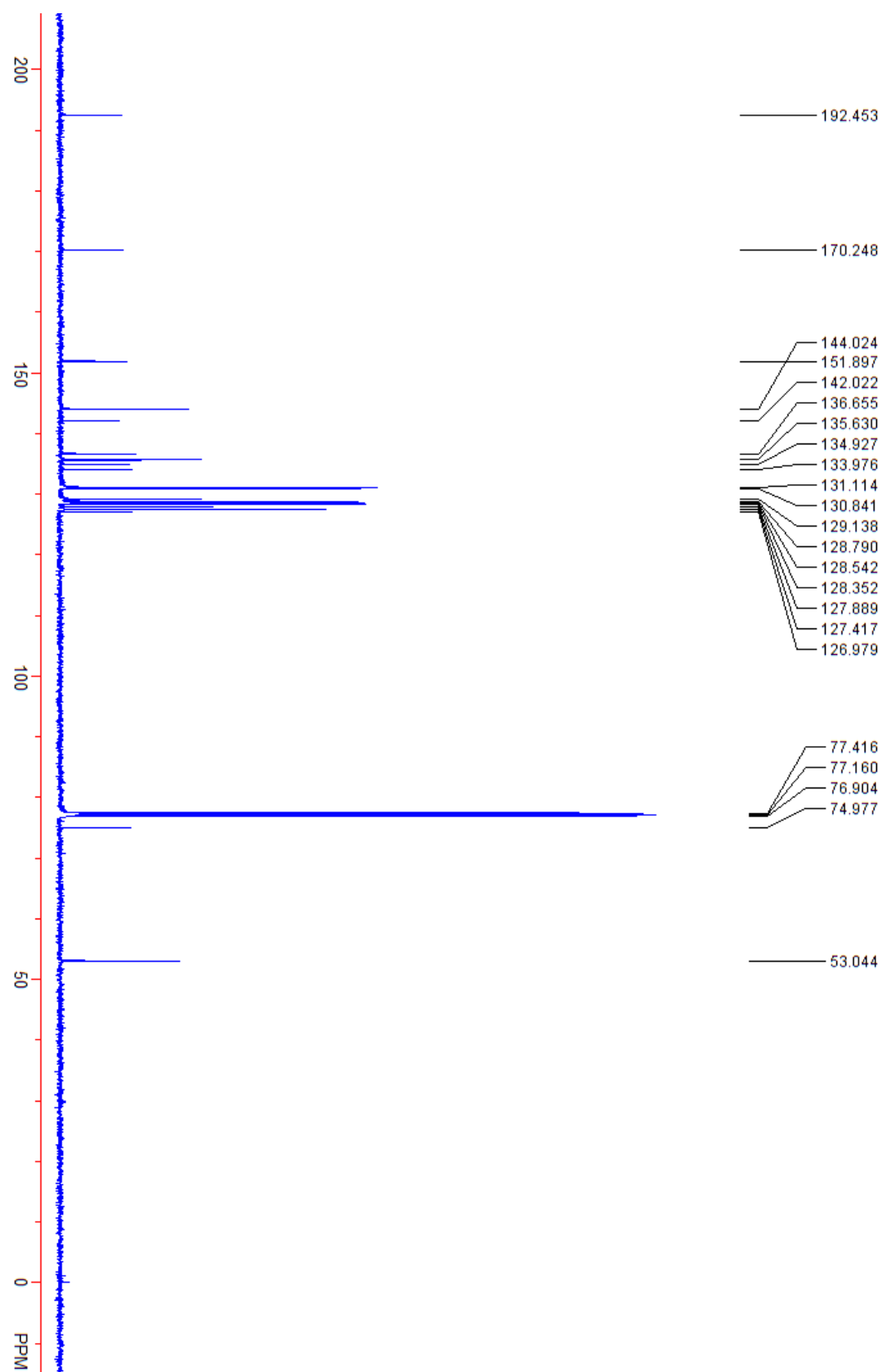
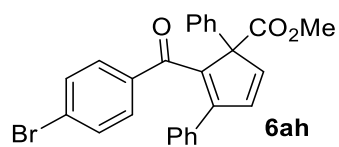
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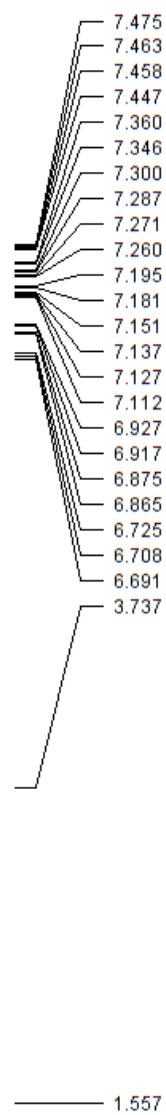
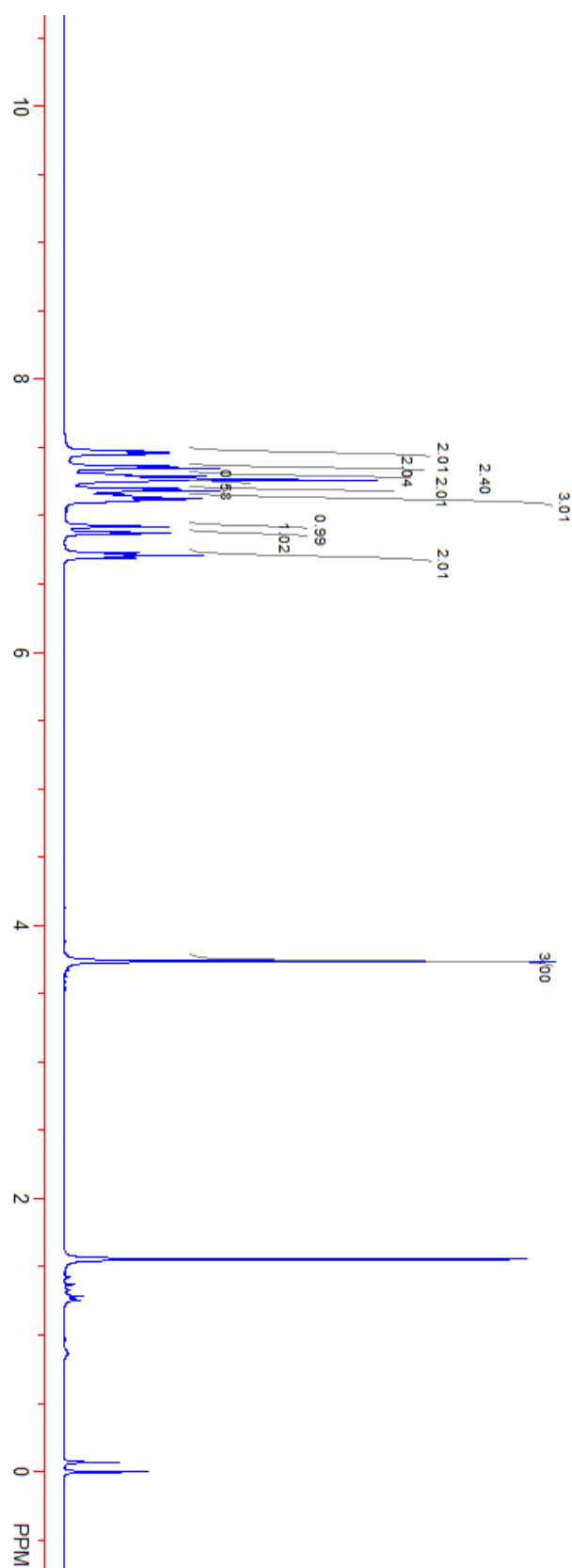
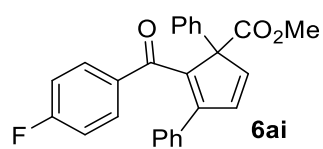
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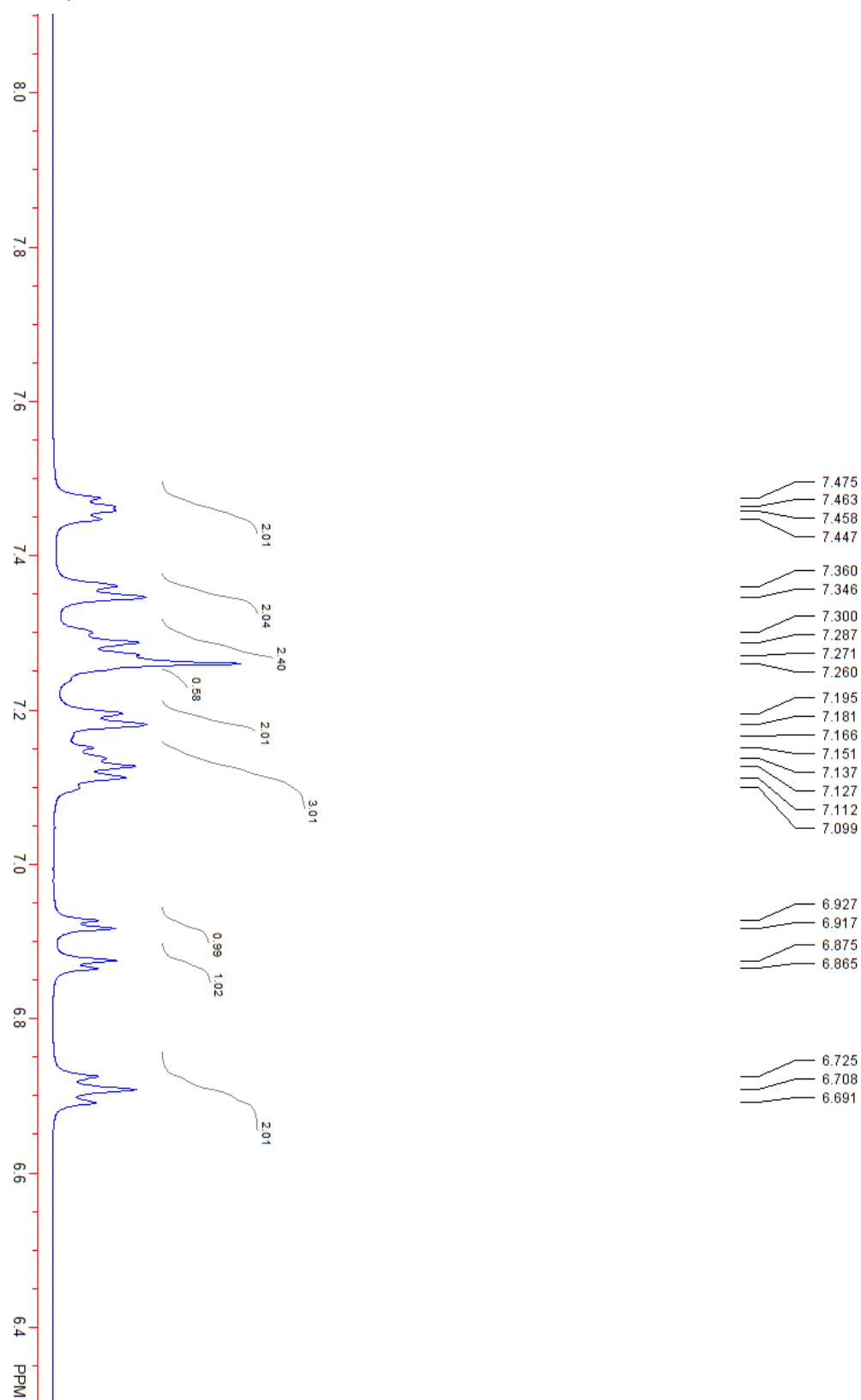
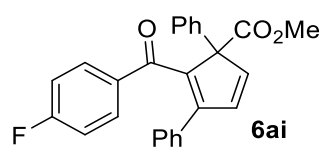
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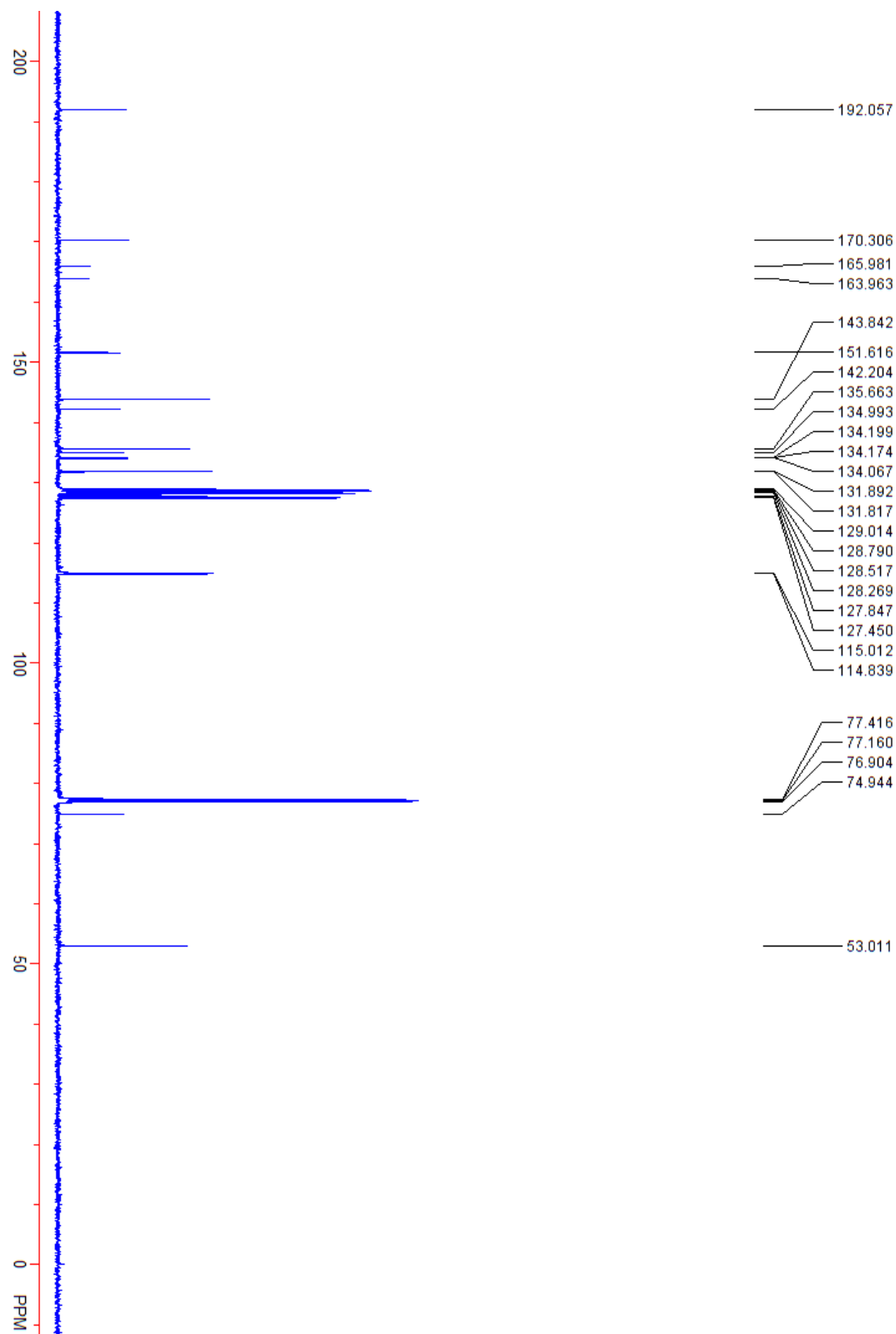
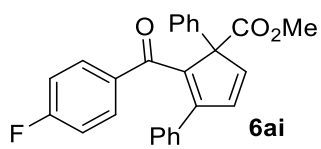
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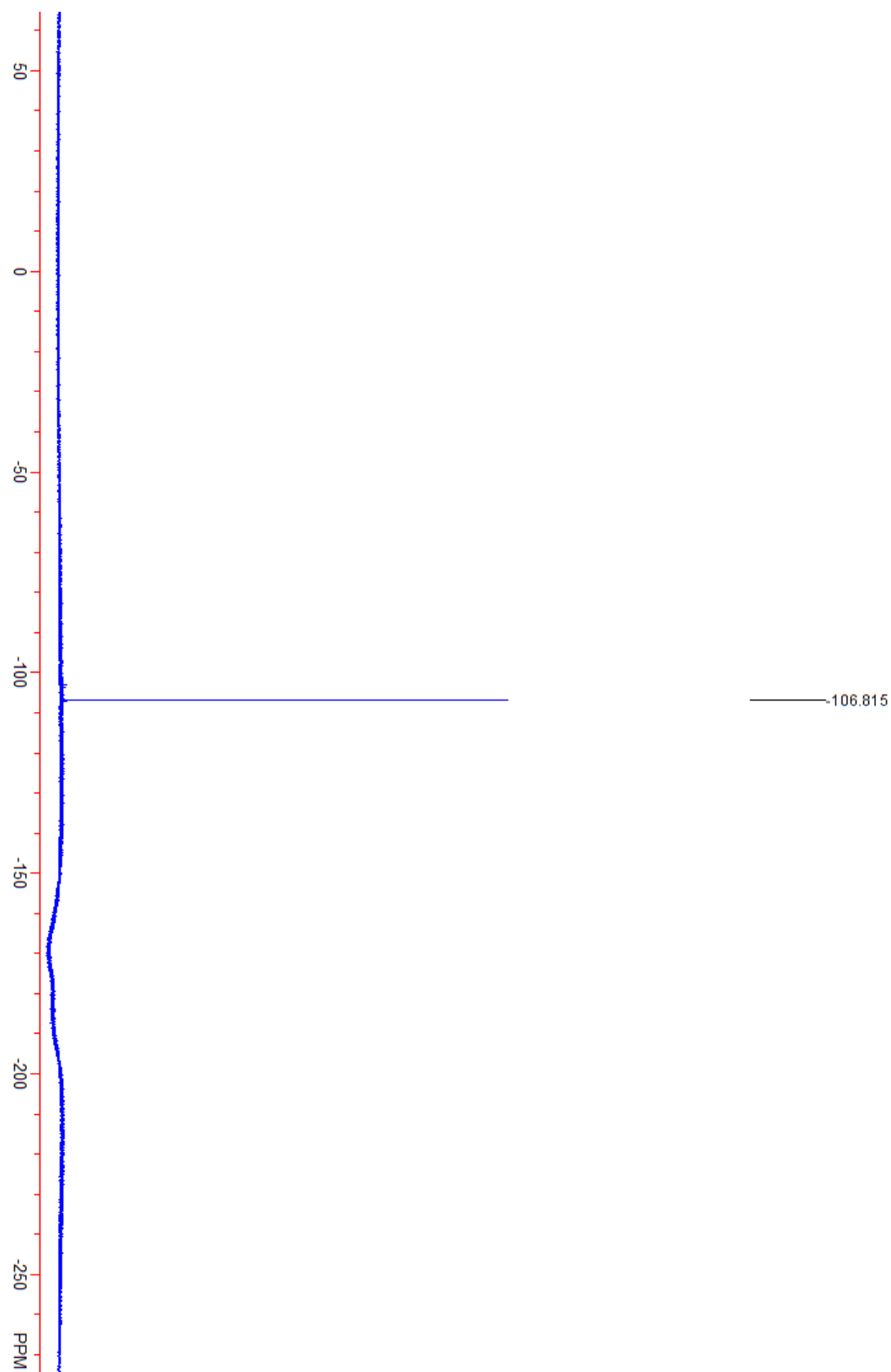
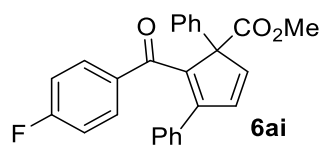
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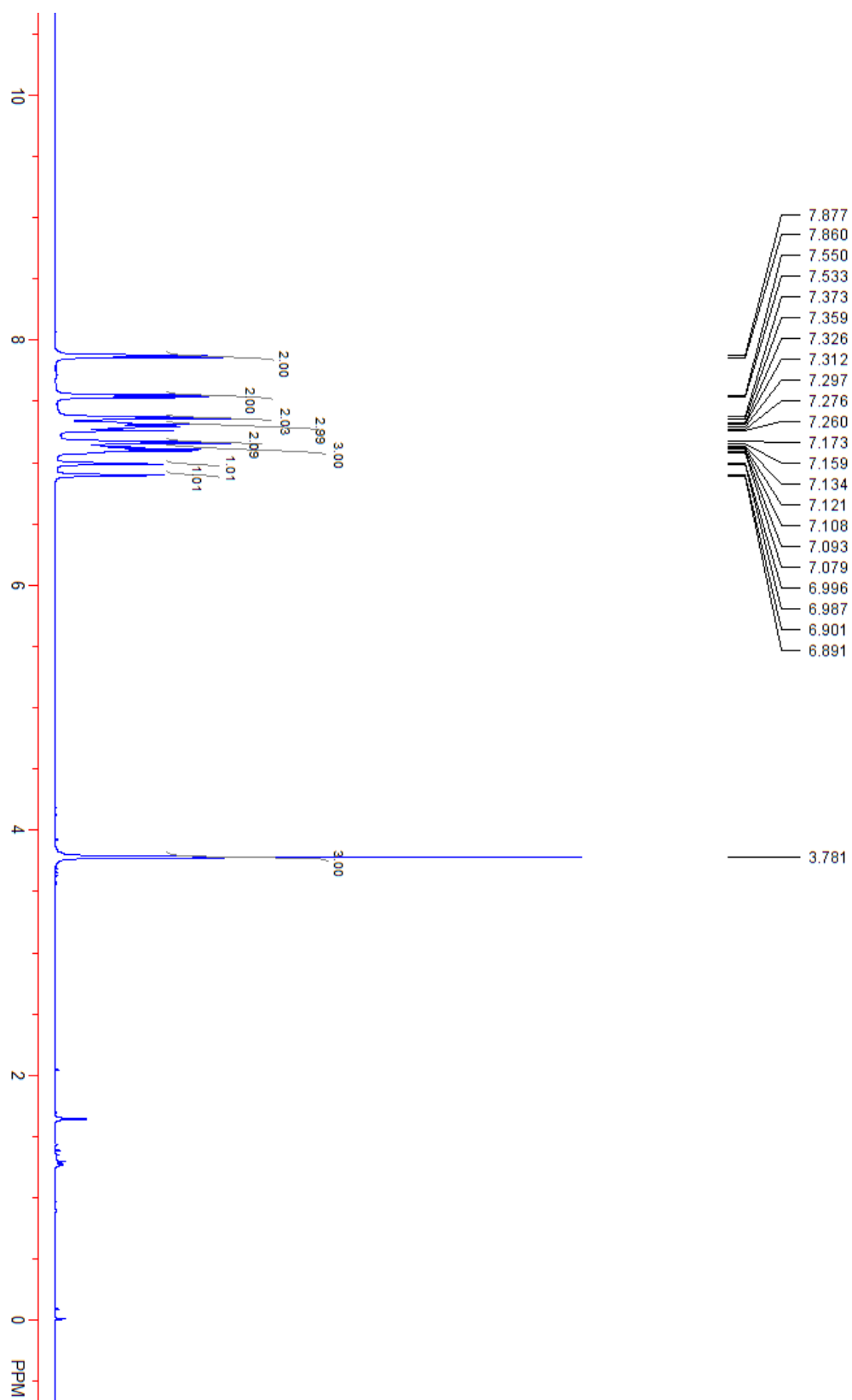
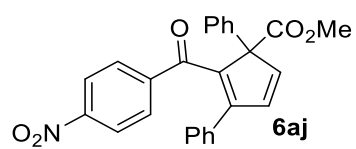
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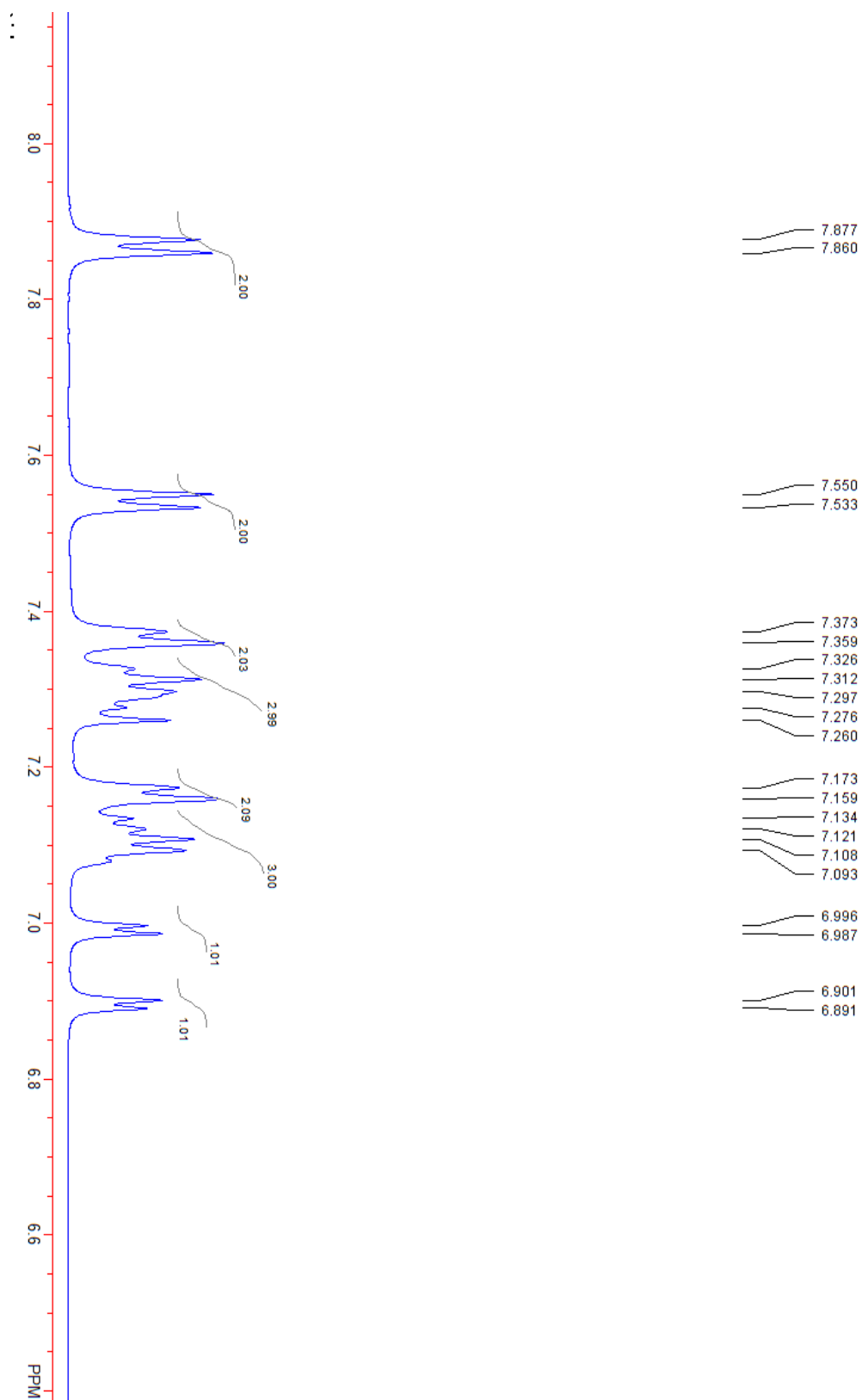
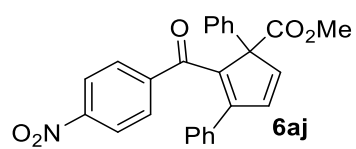
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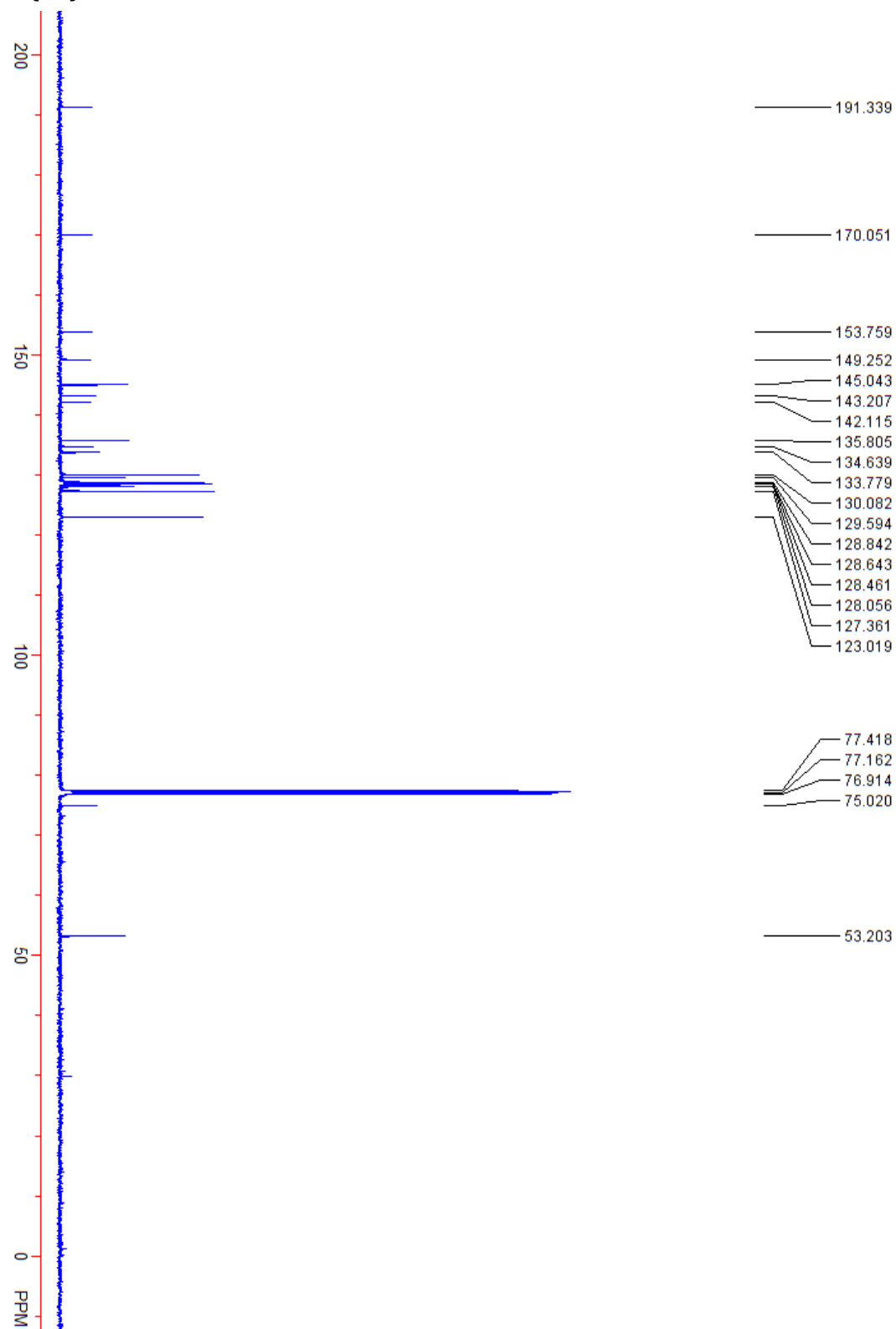
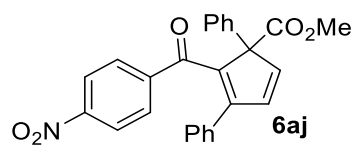
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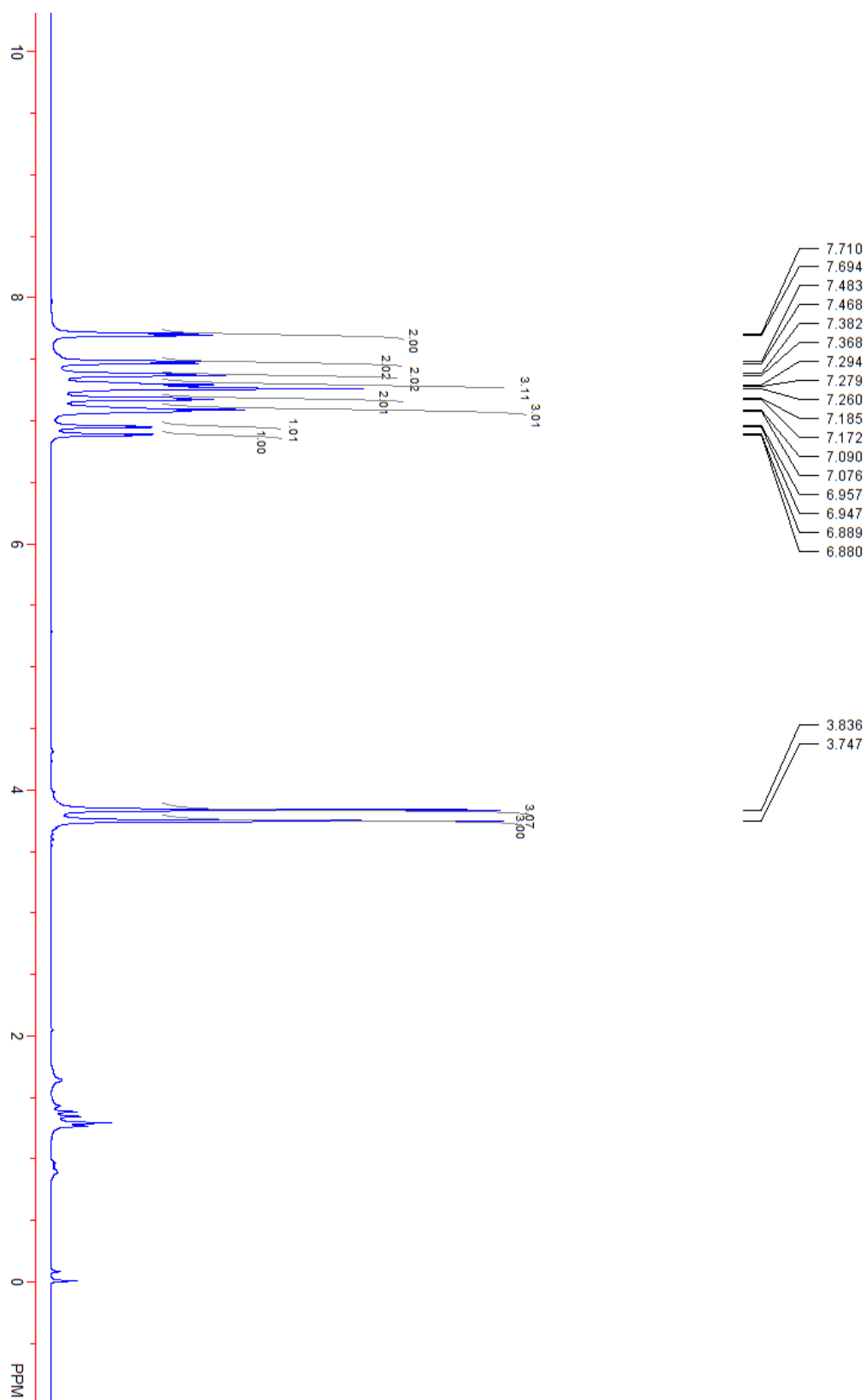
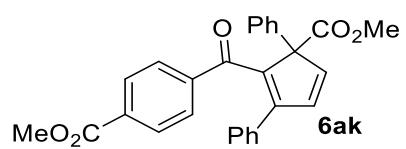
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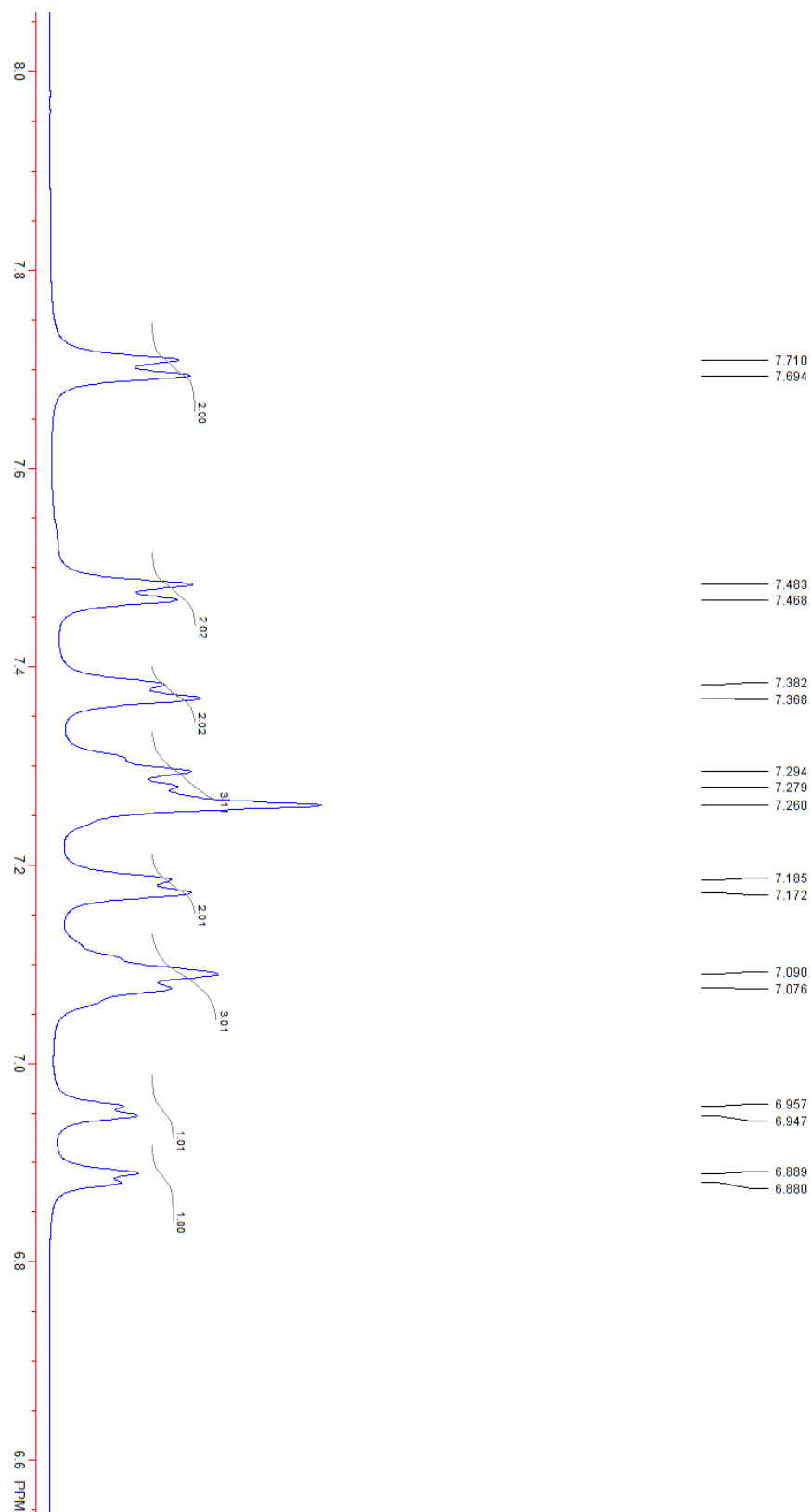
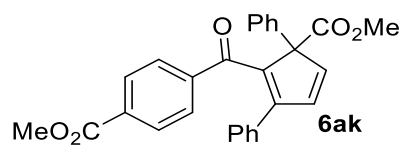
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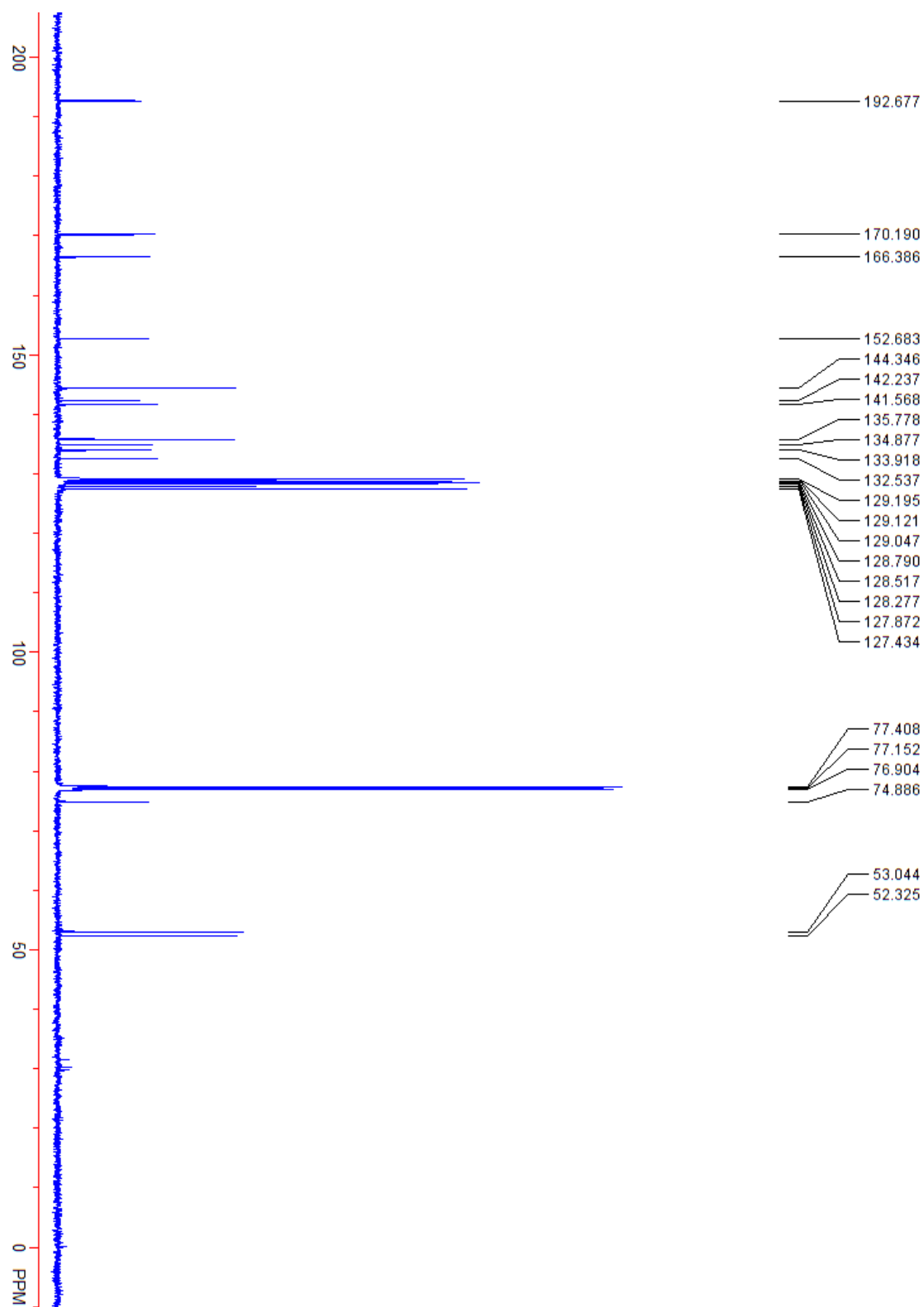
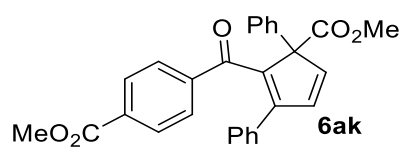
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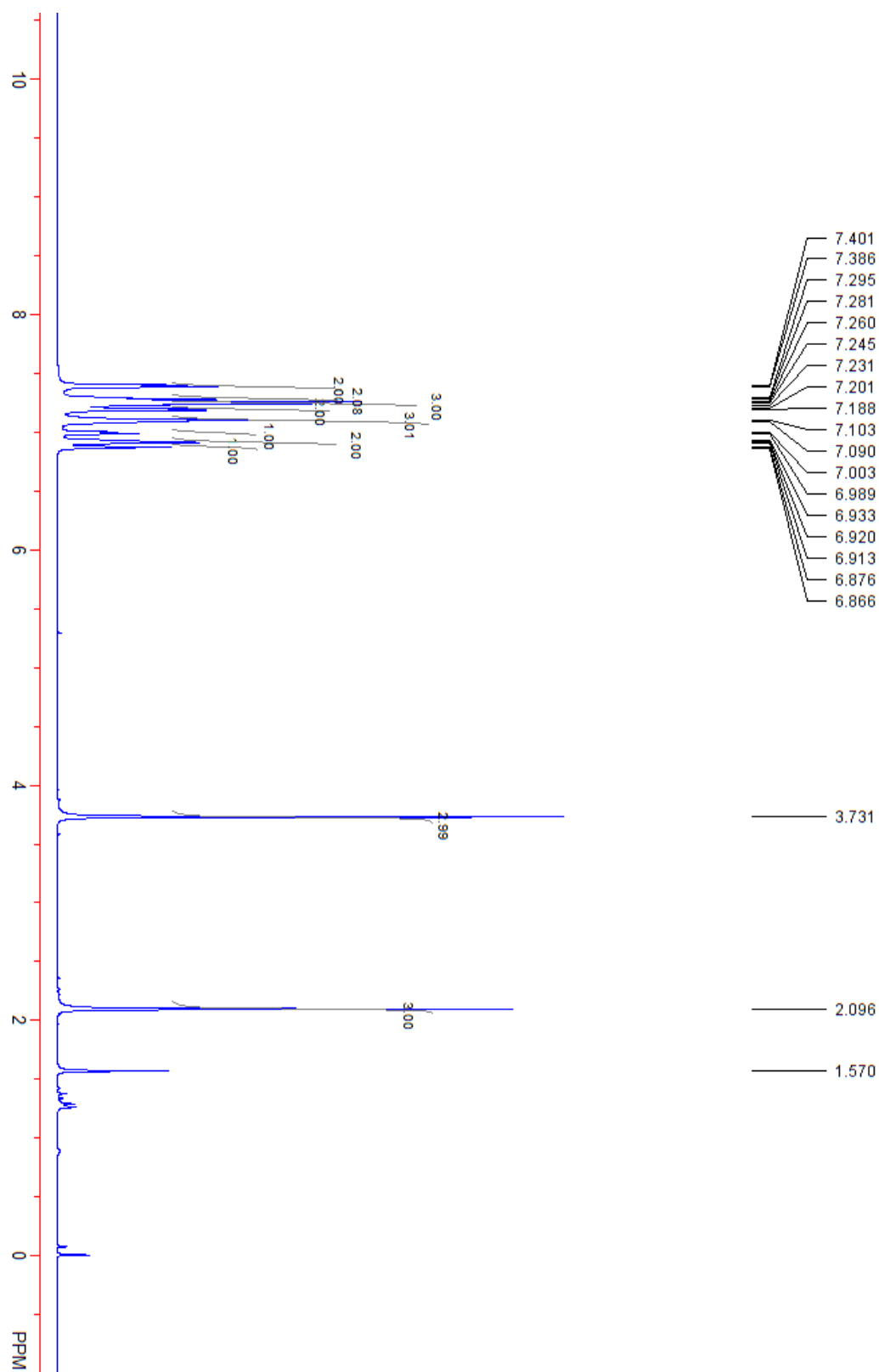
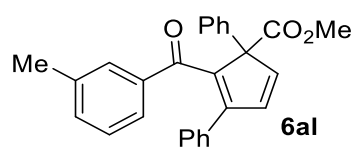
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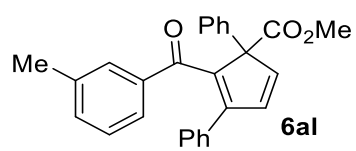


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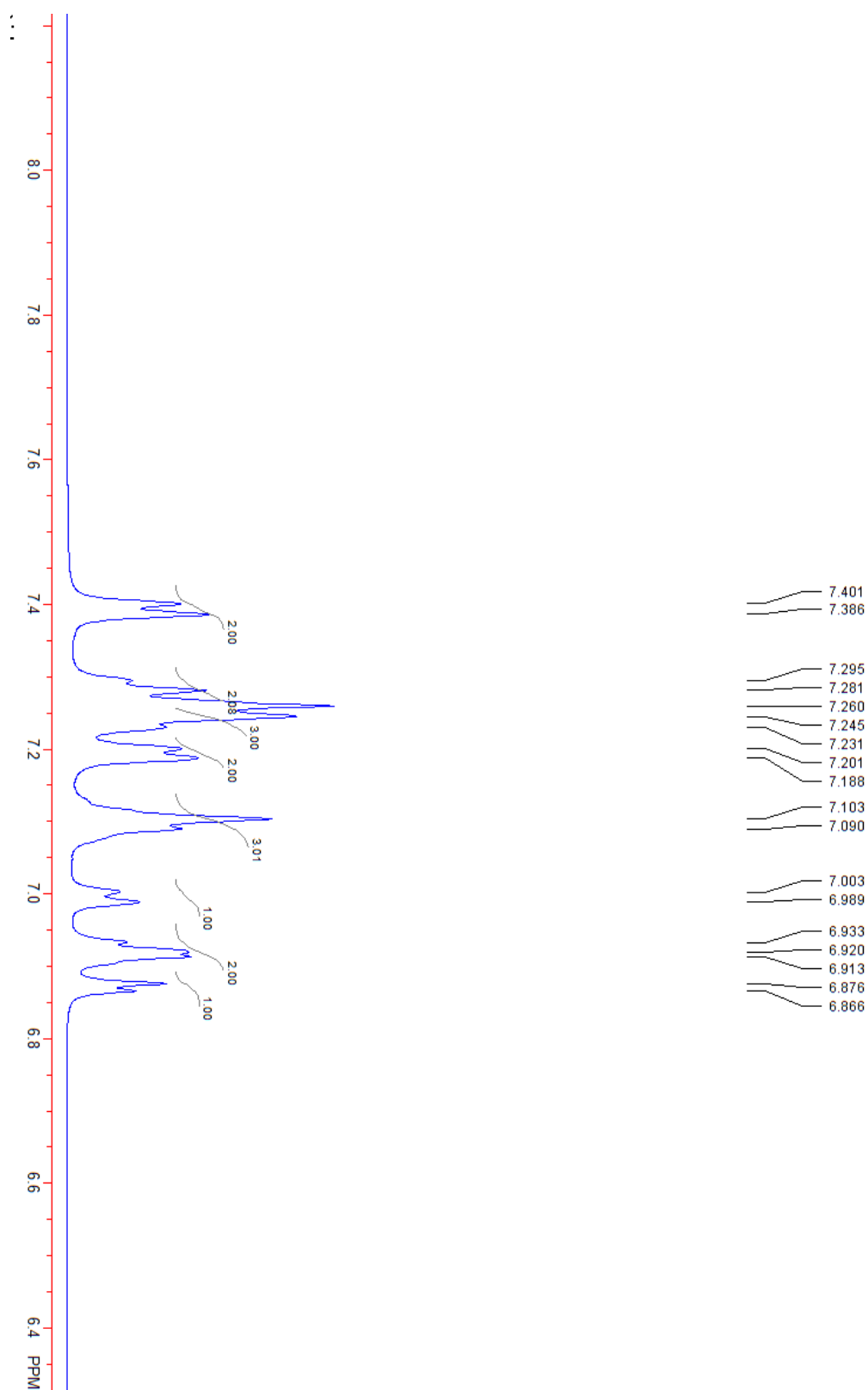


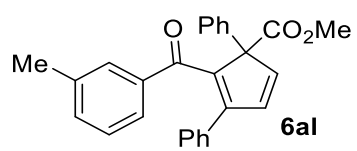
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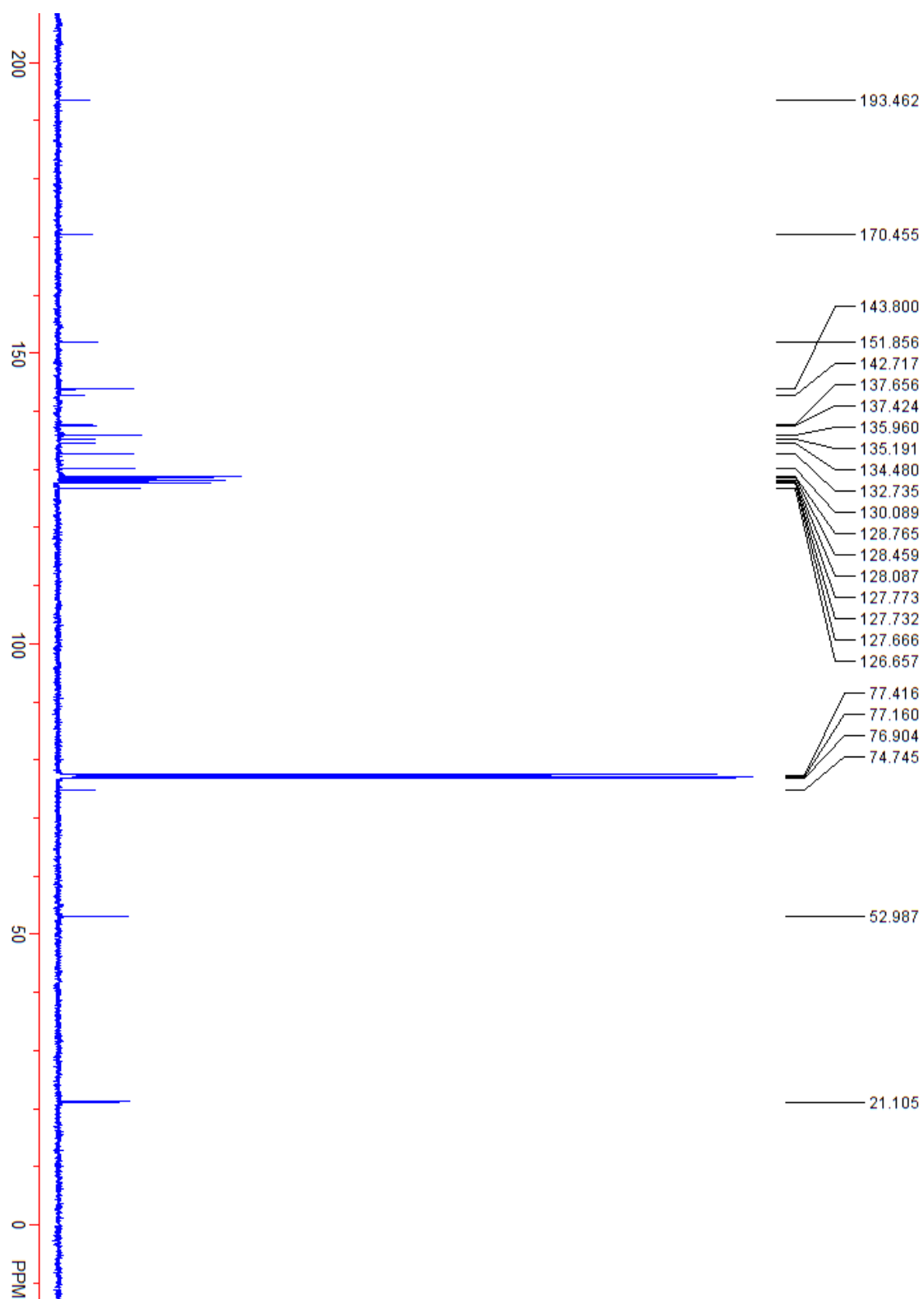


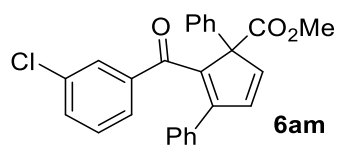
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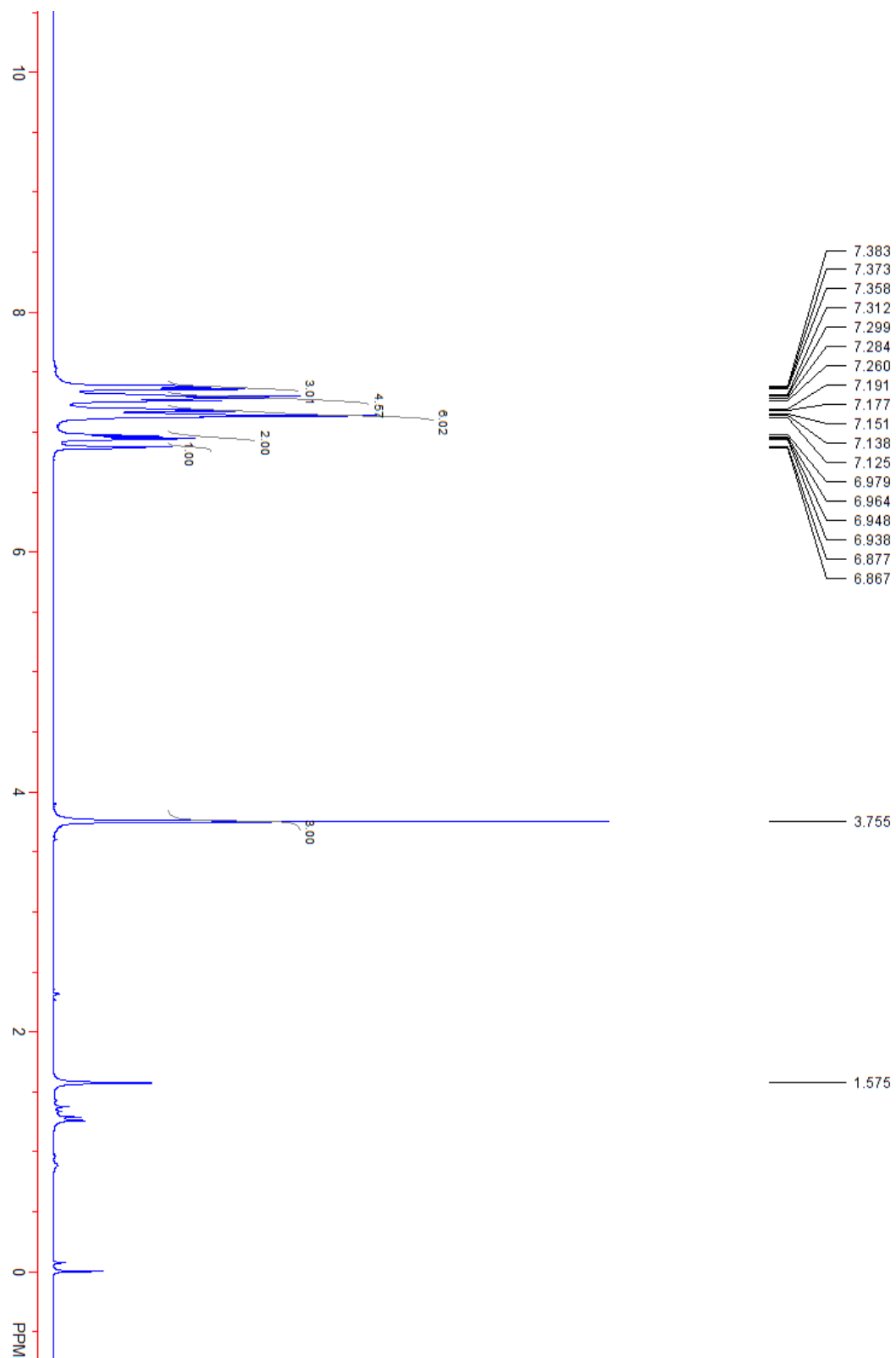


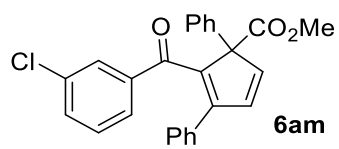
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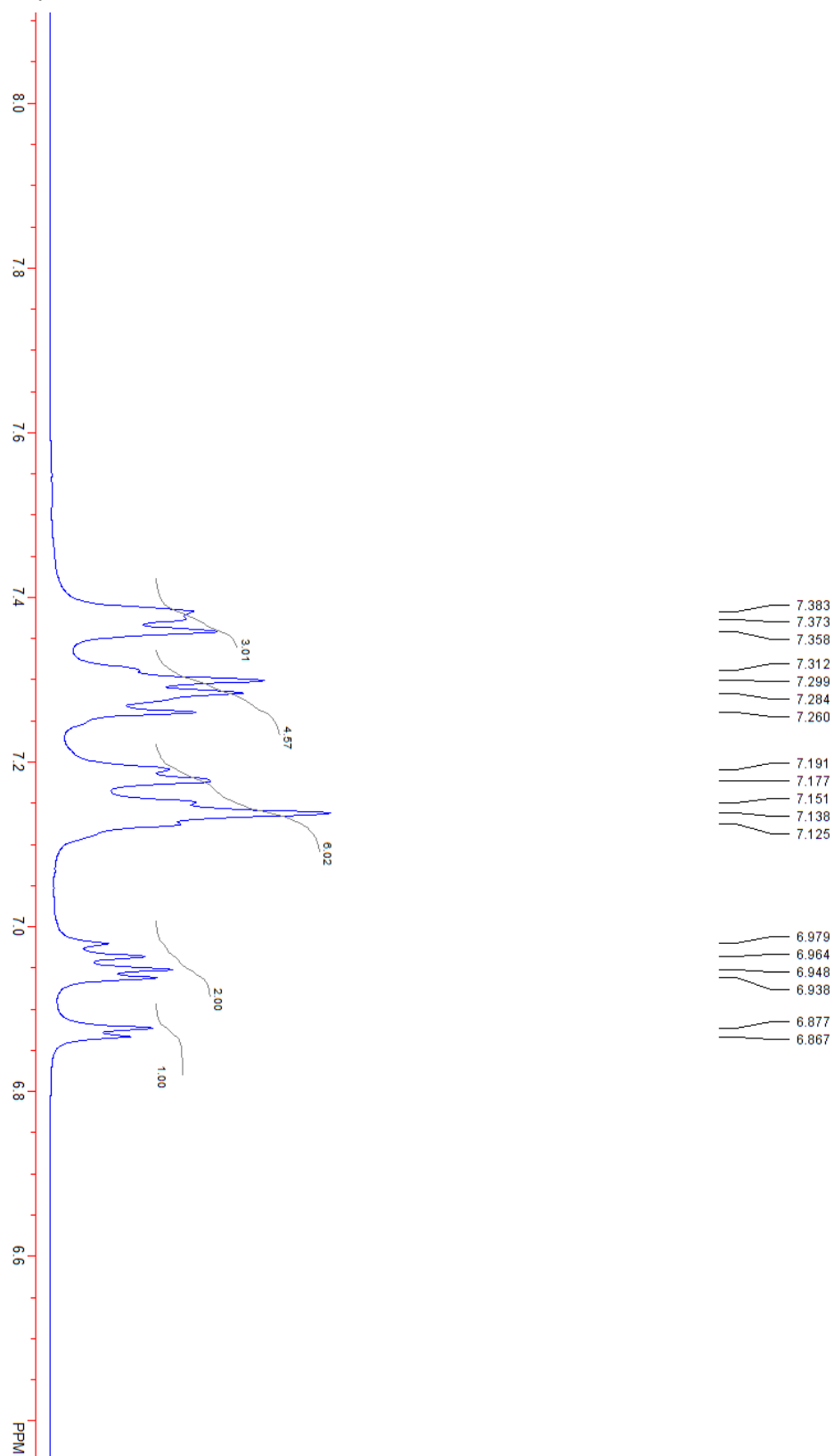


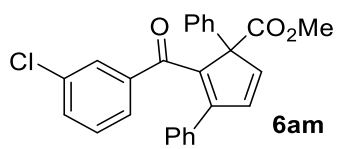
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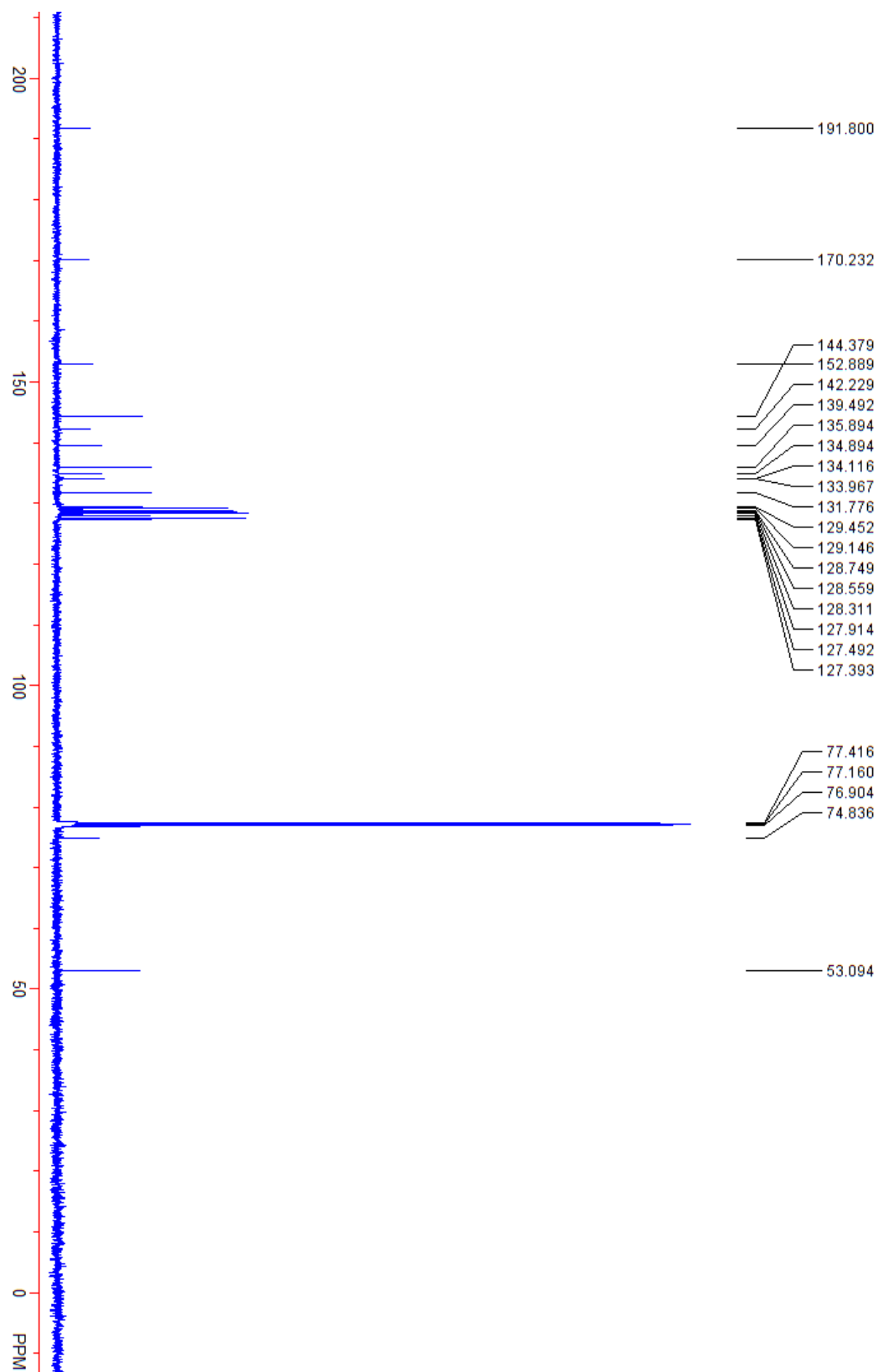


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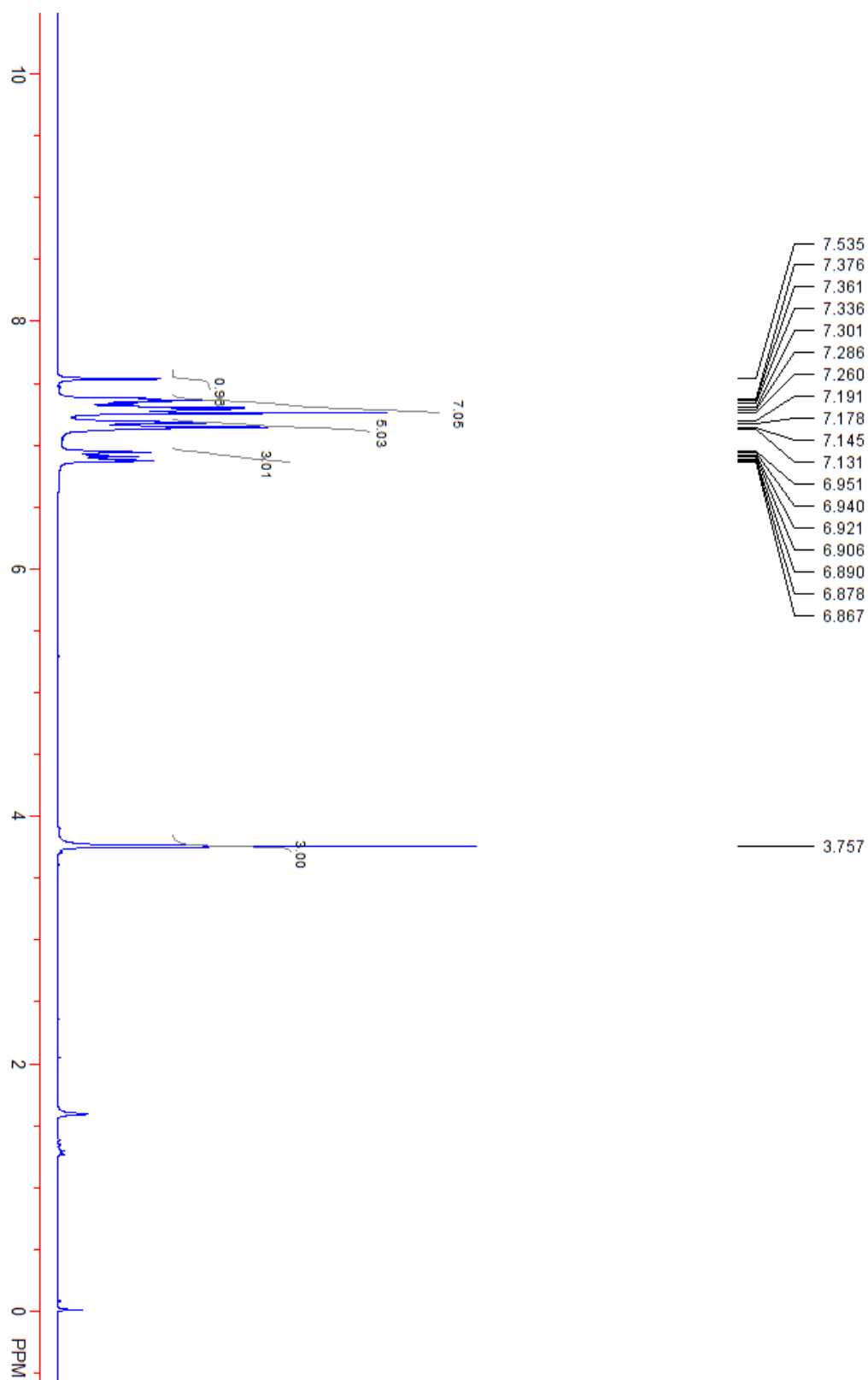
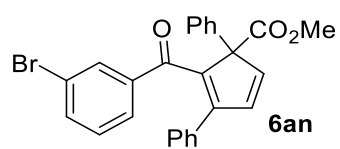




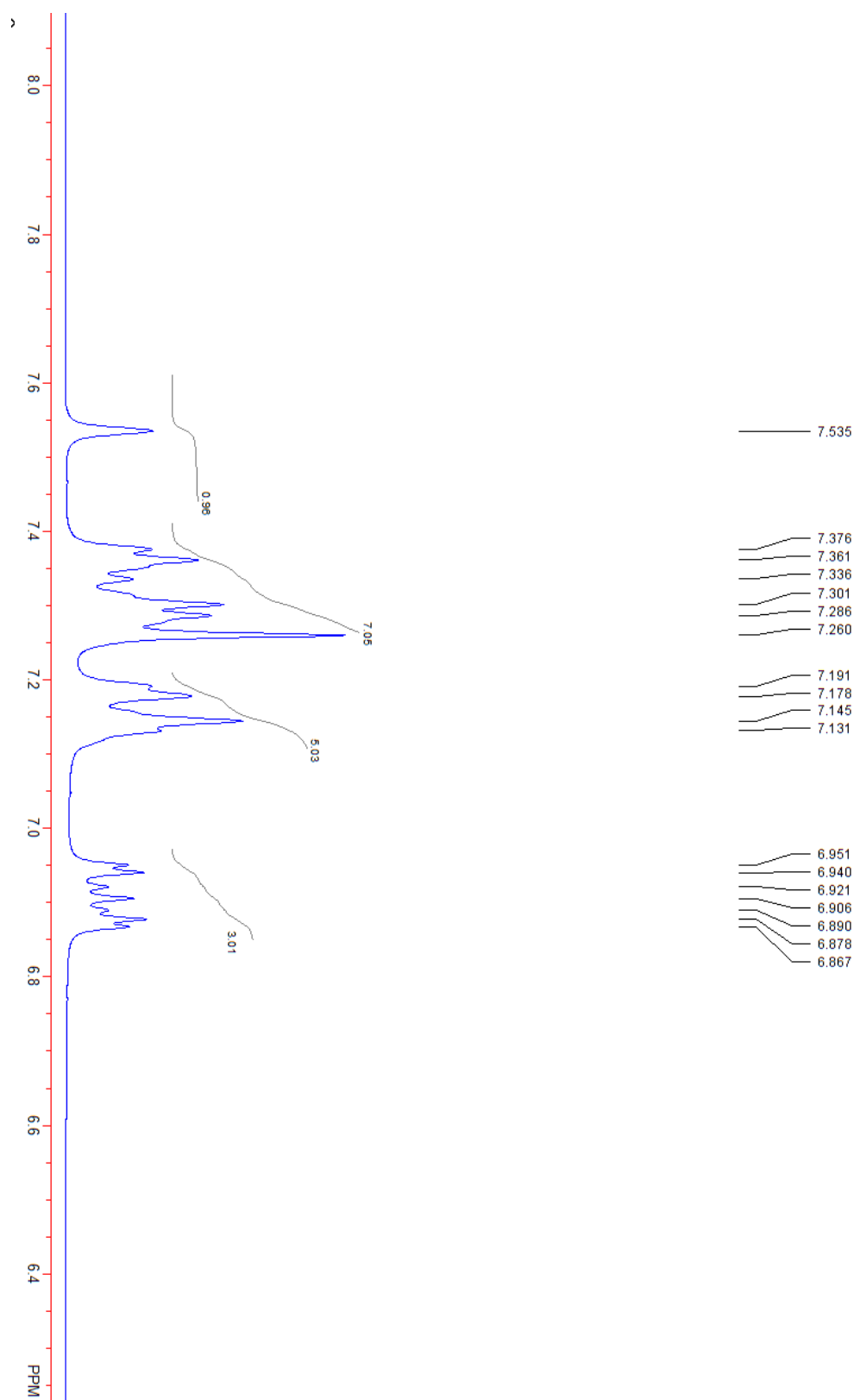
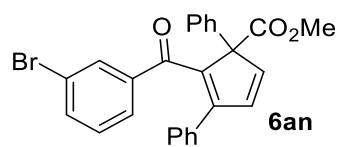
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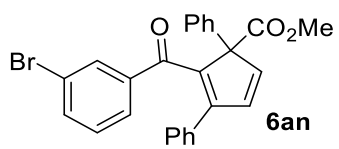


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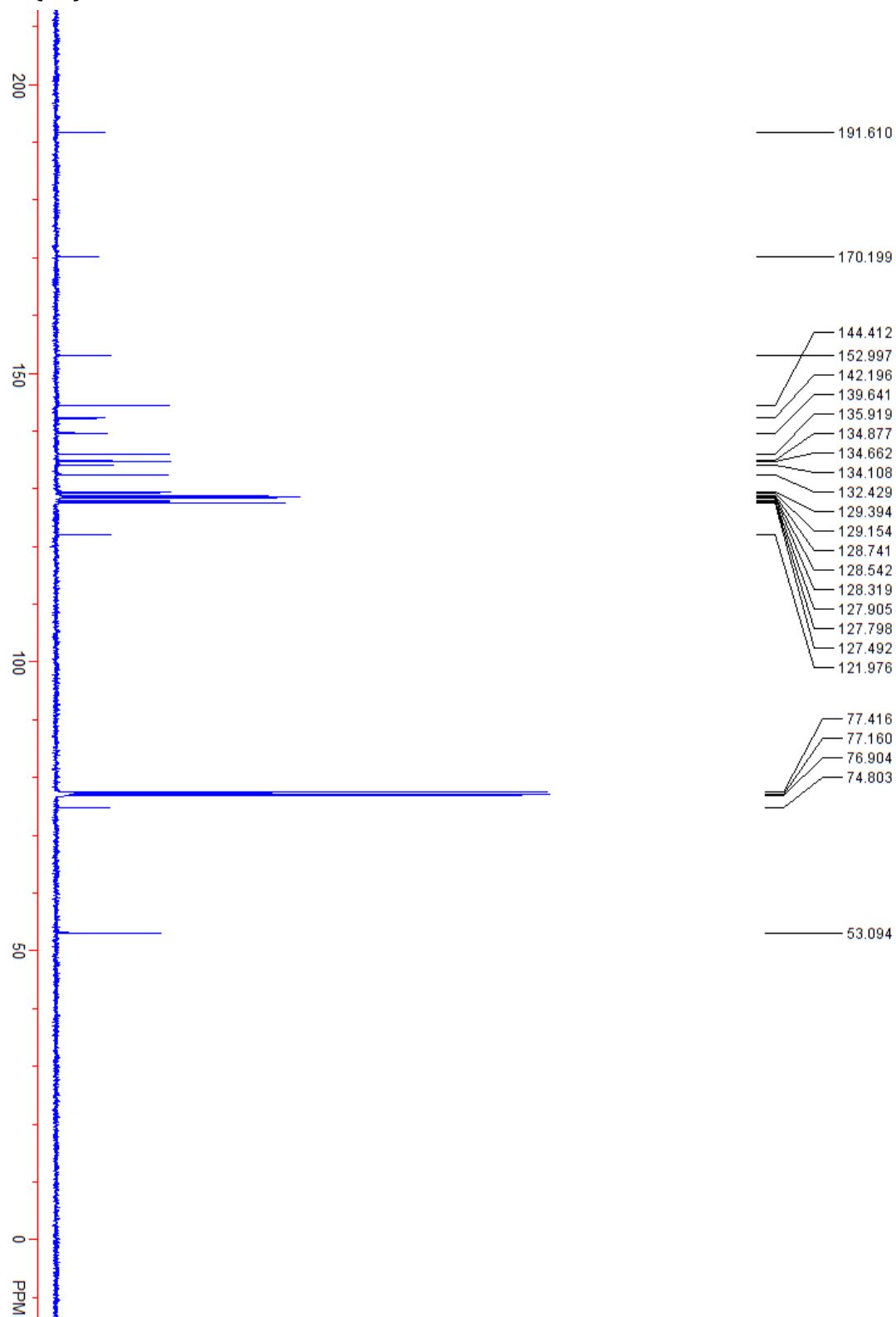


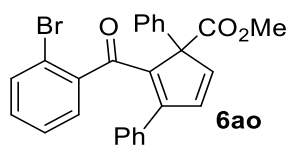
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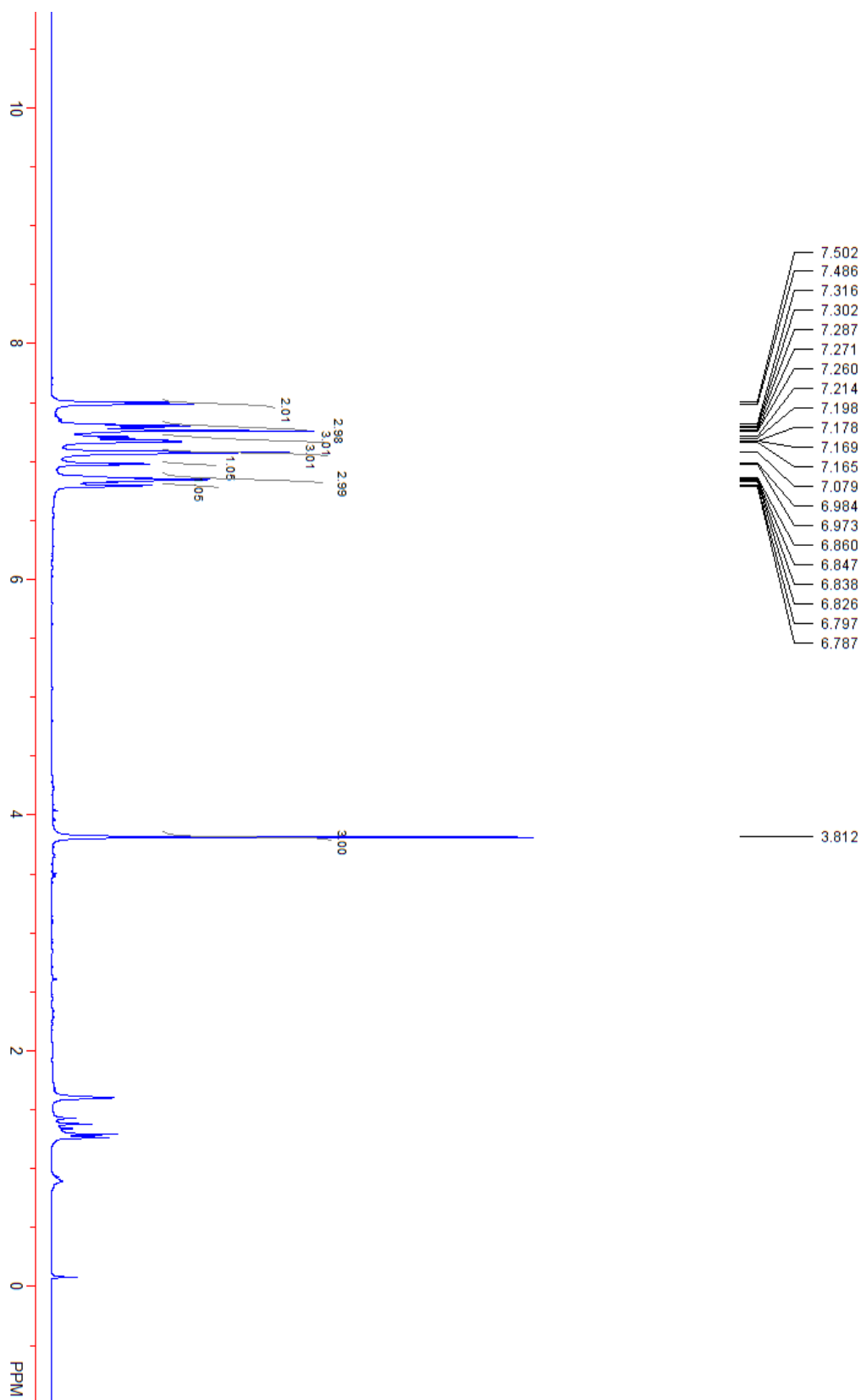


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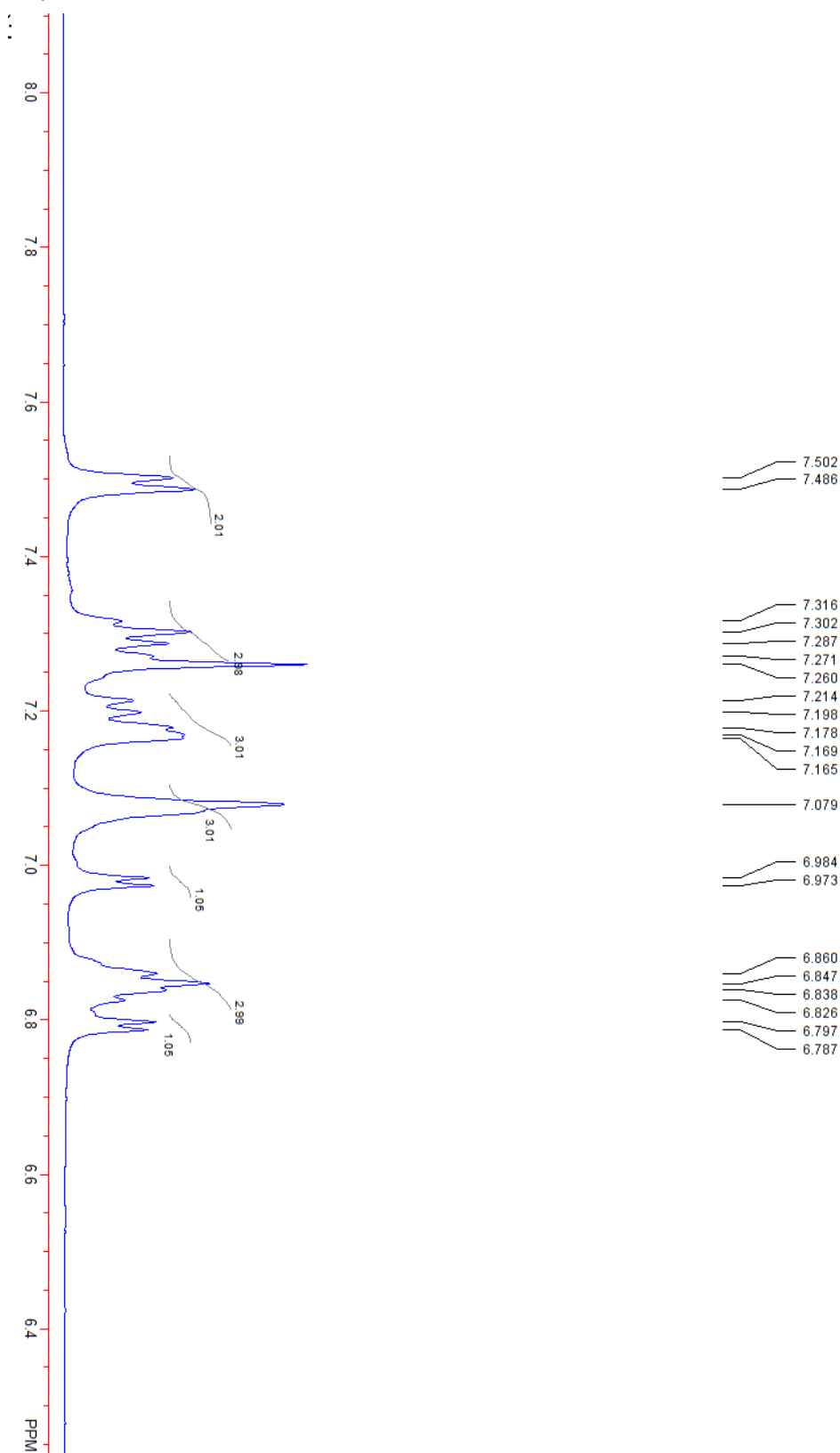
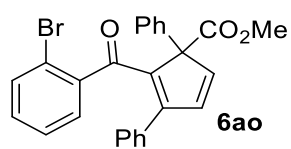




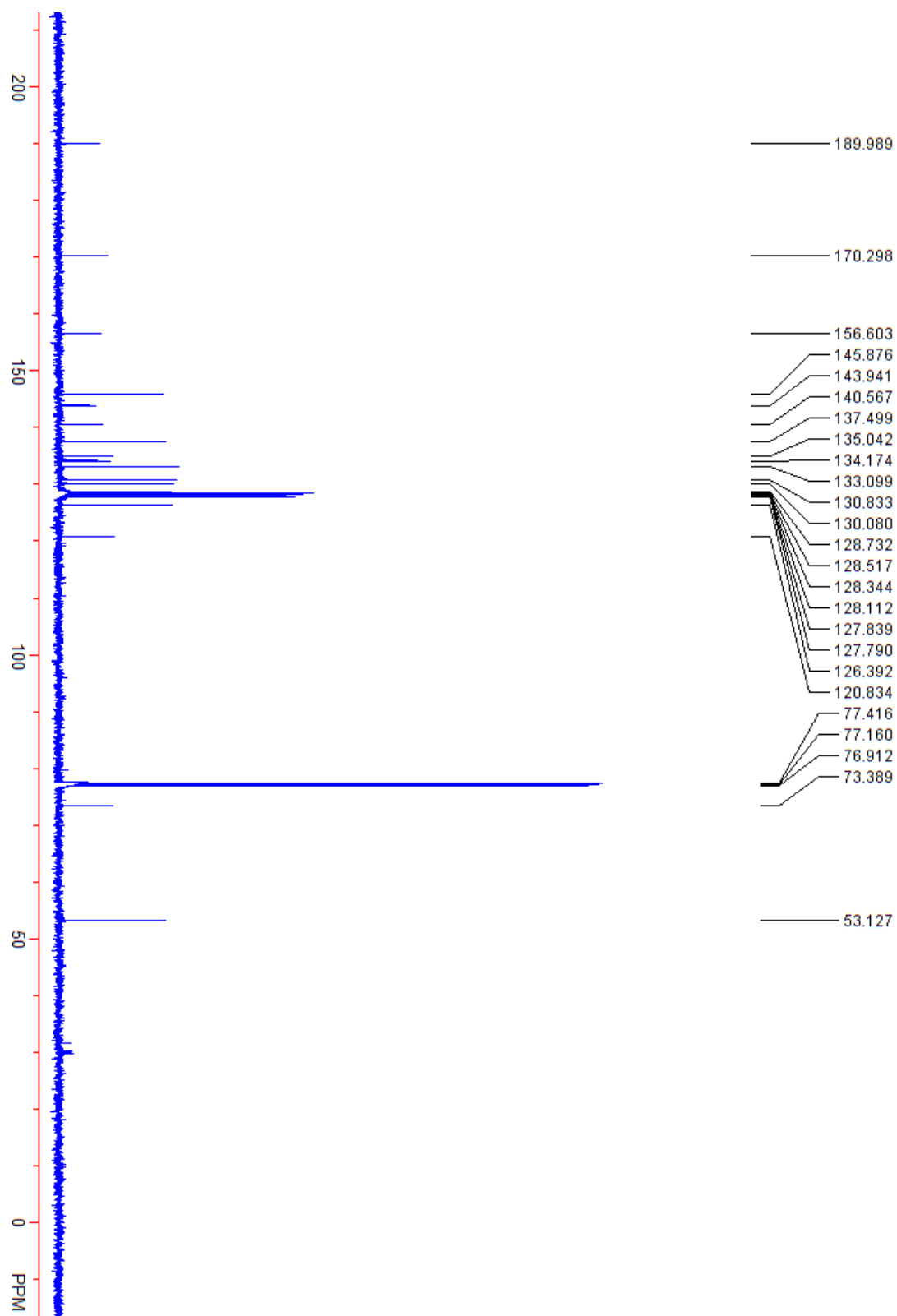
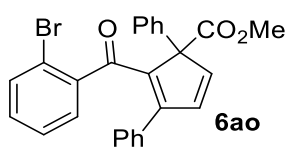
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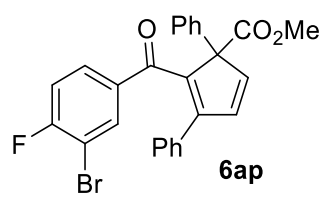


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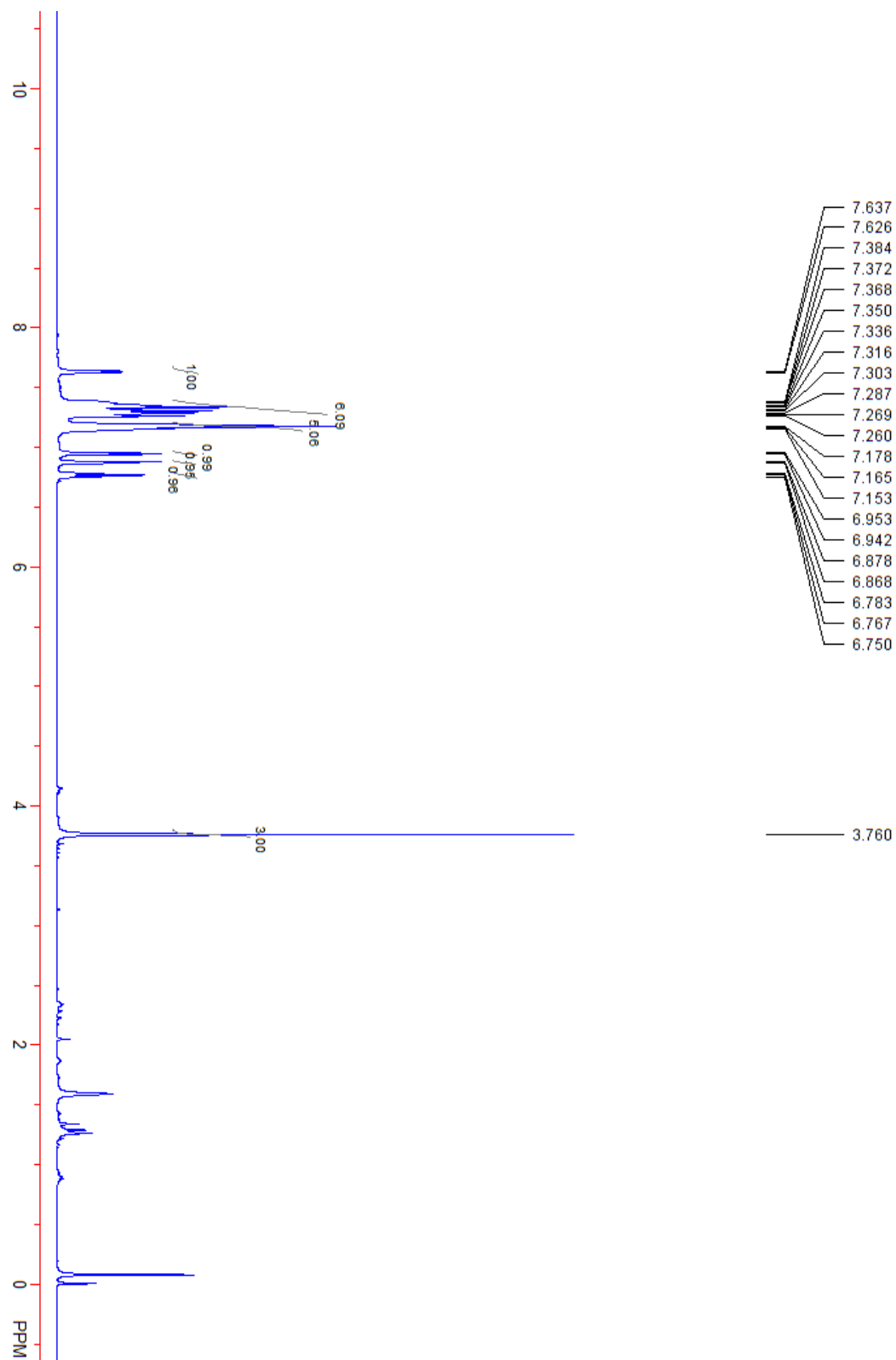


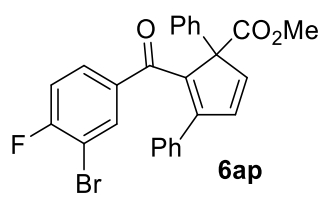
$^{13}\text{C}\{^1\text{H}\}$ NMR:



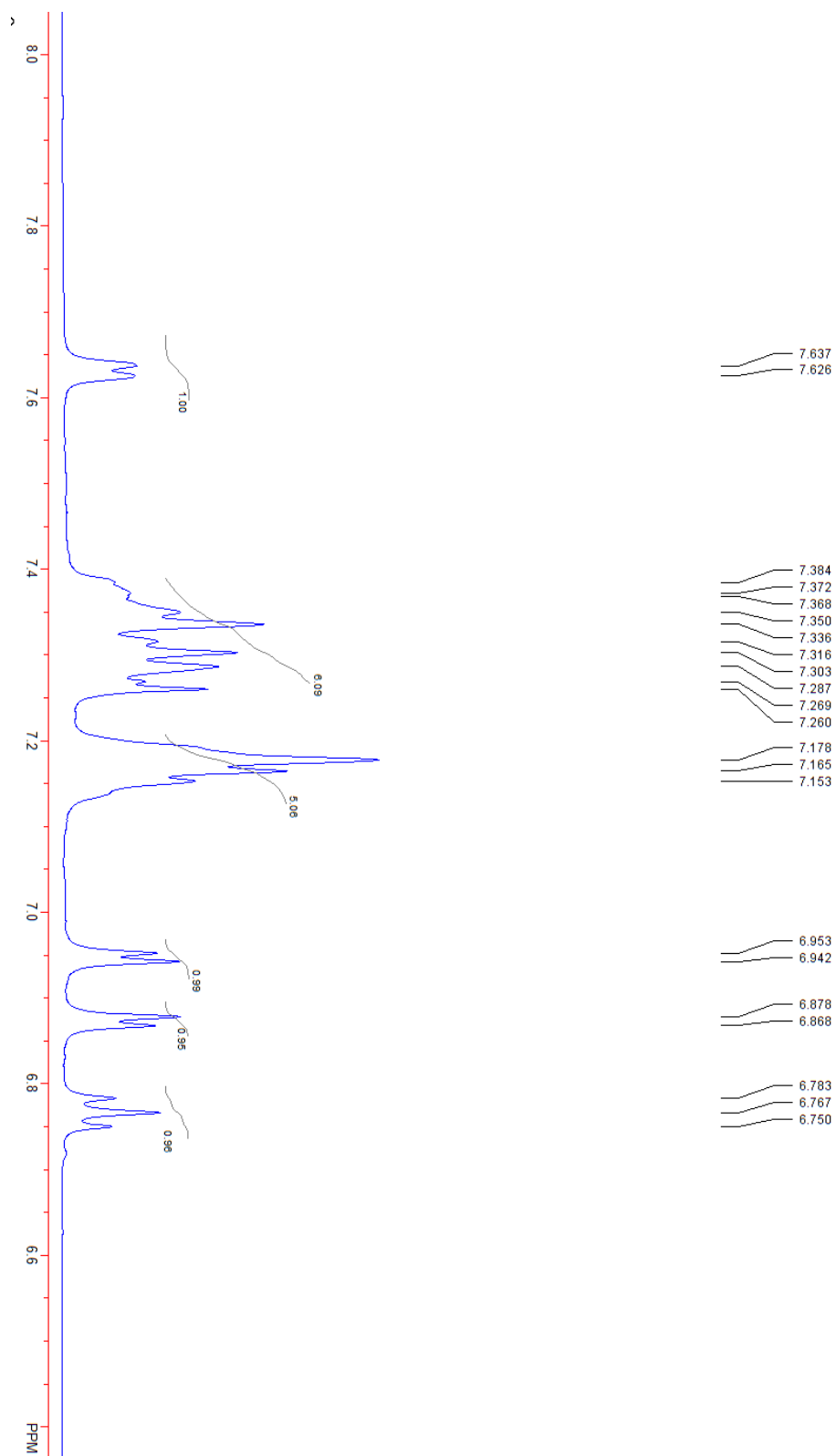


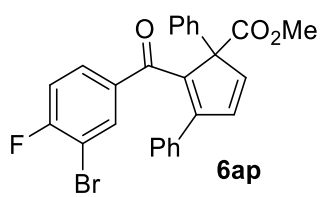
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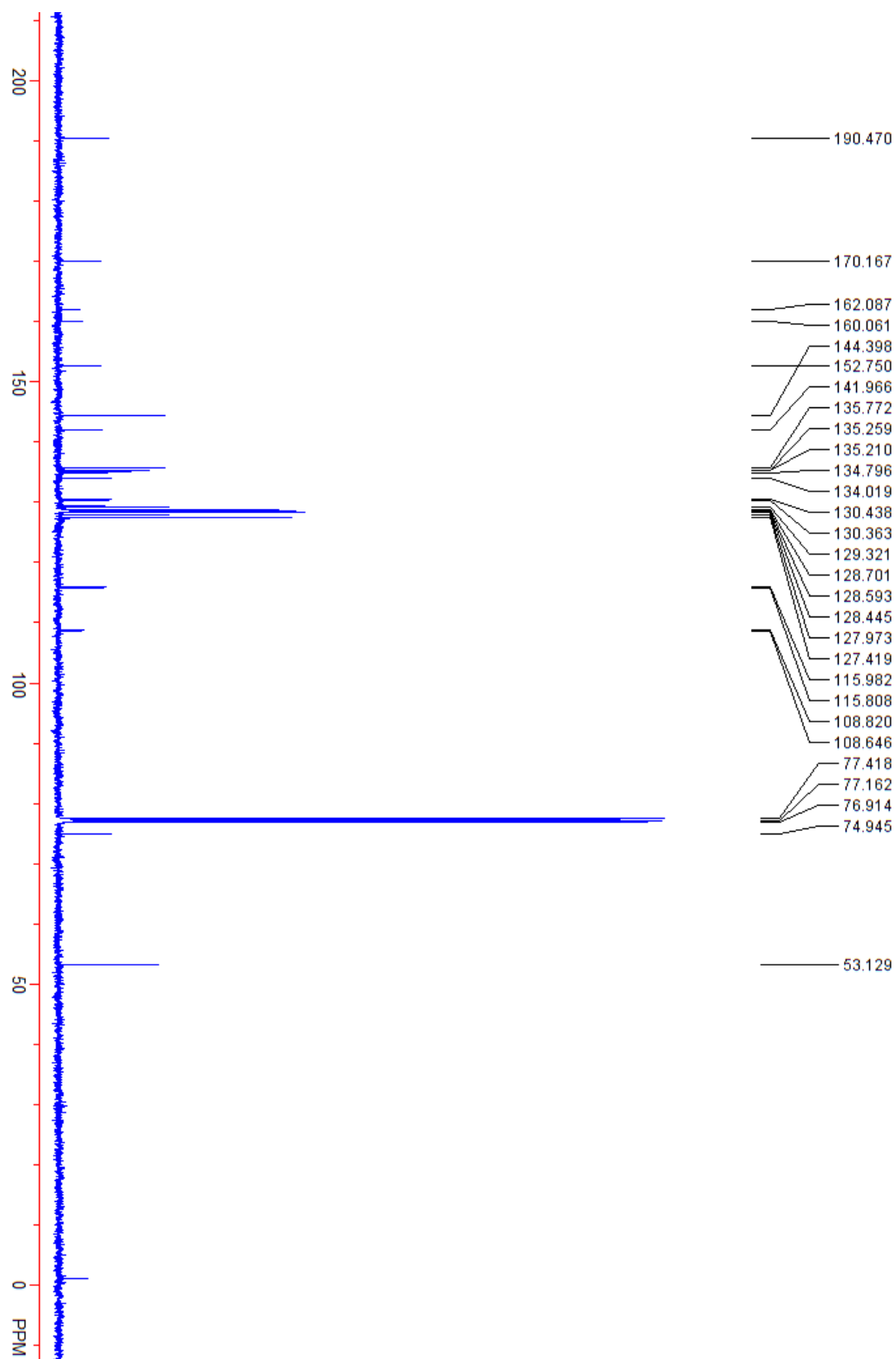


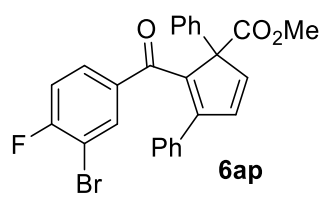
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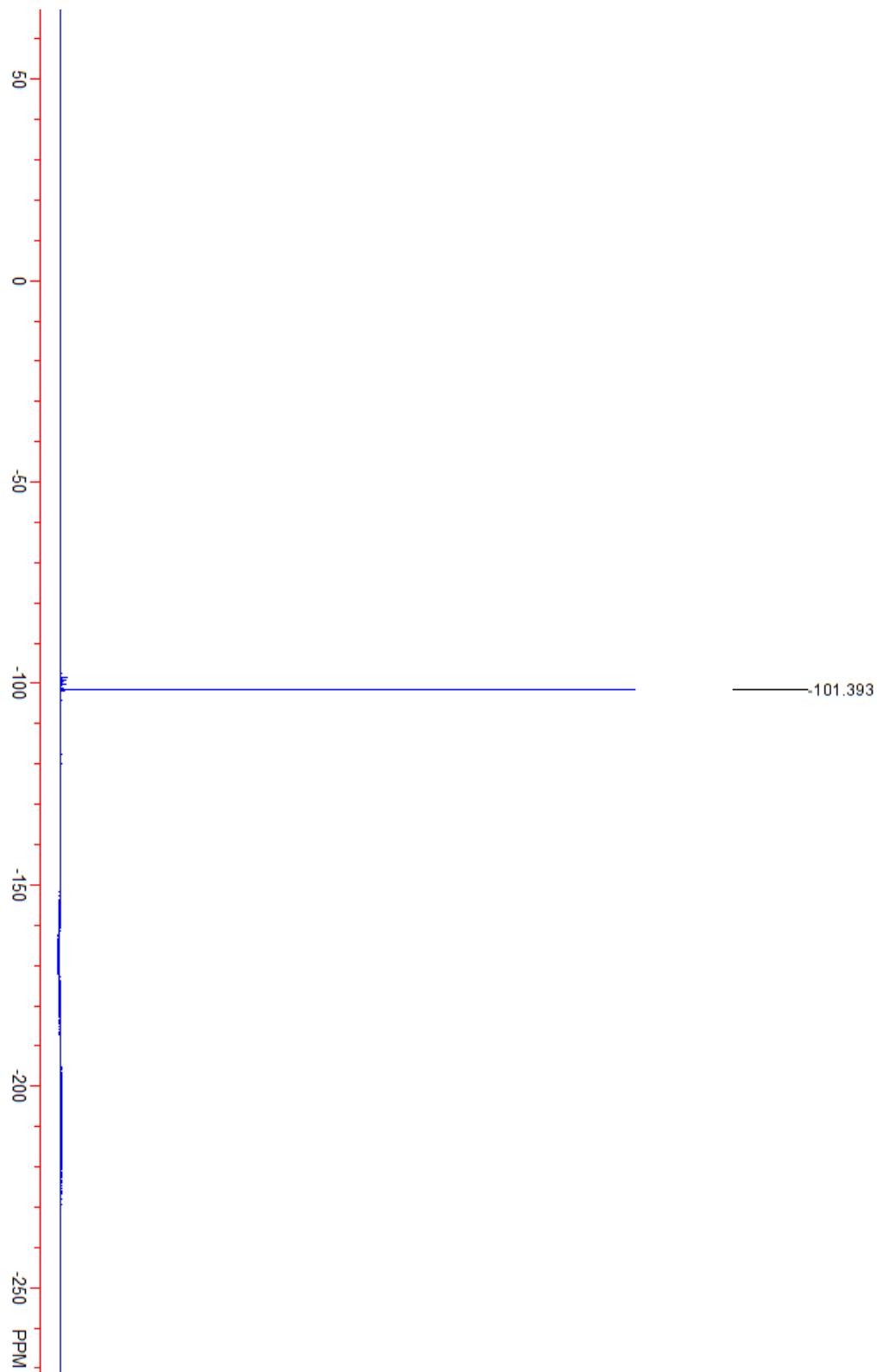


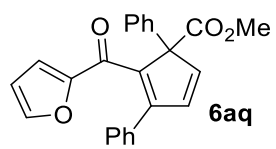
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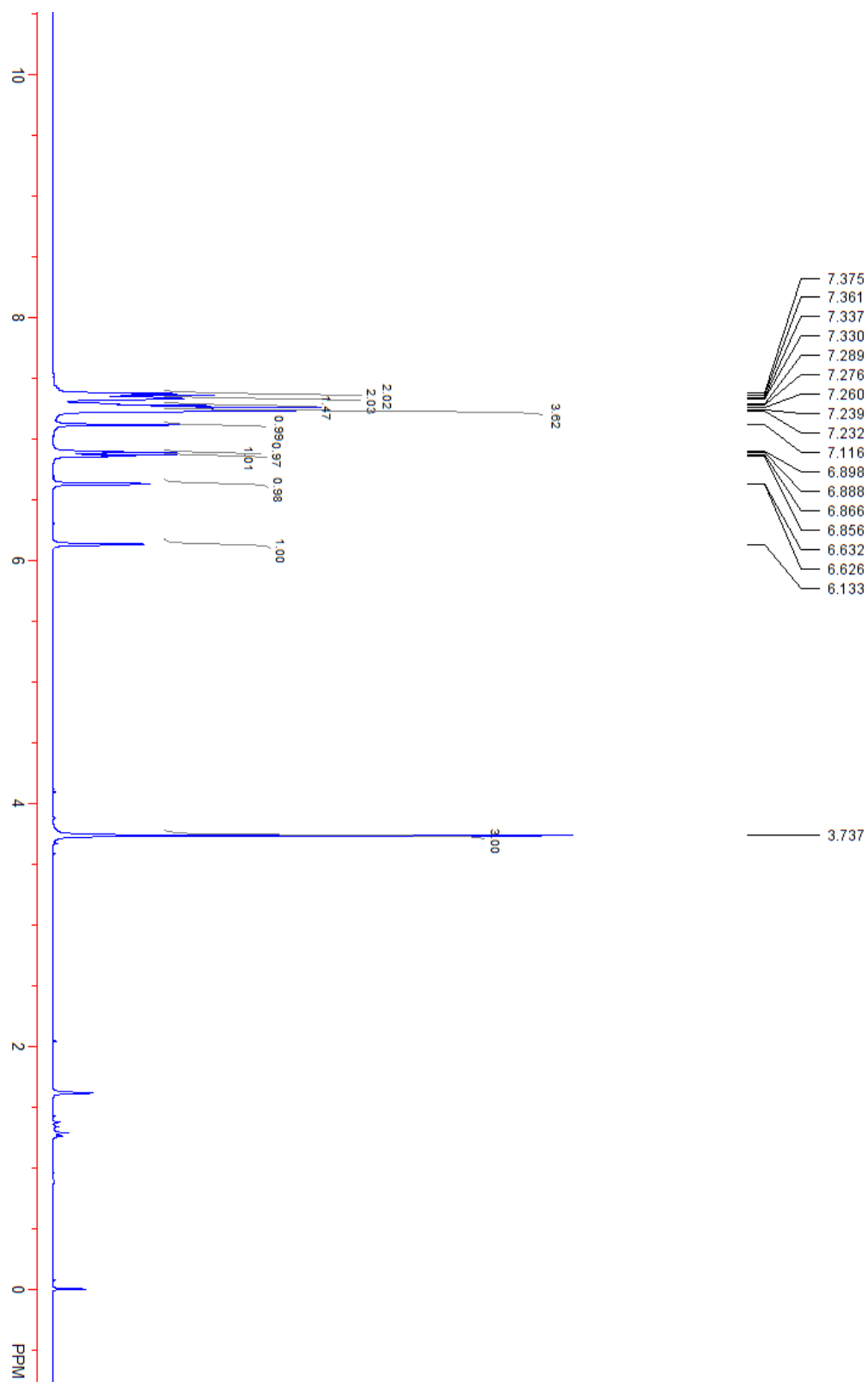


^{19}F NMR:

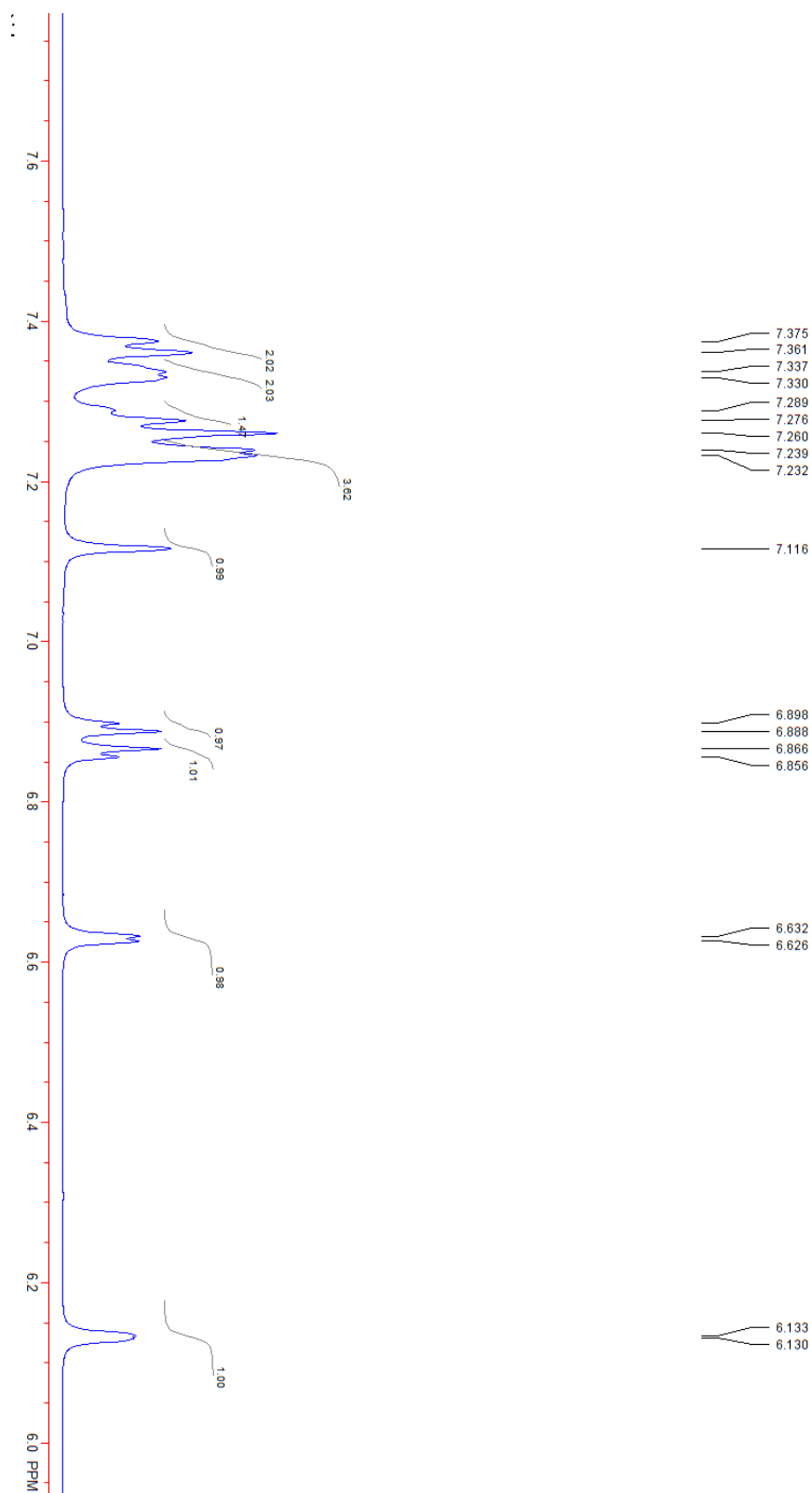
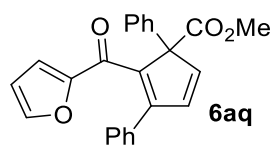


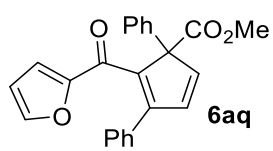


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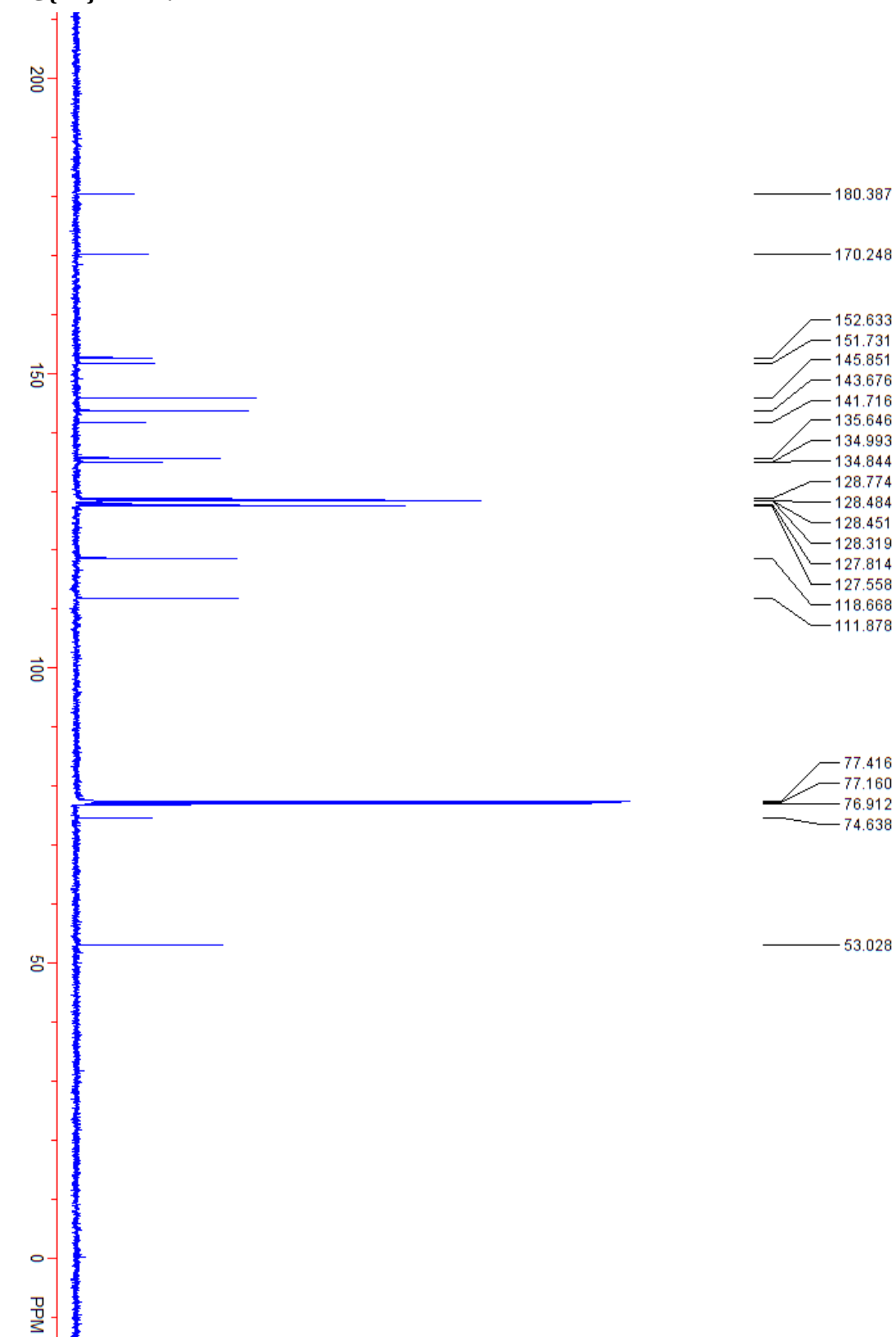


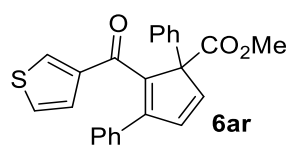
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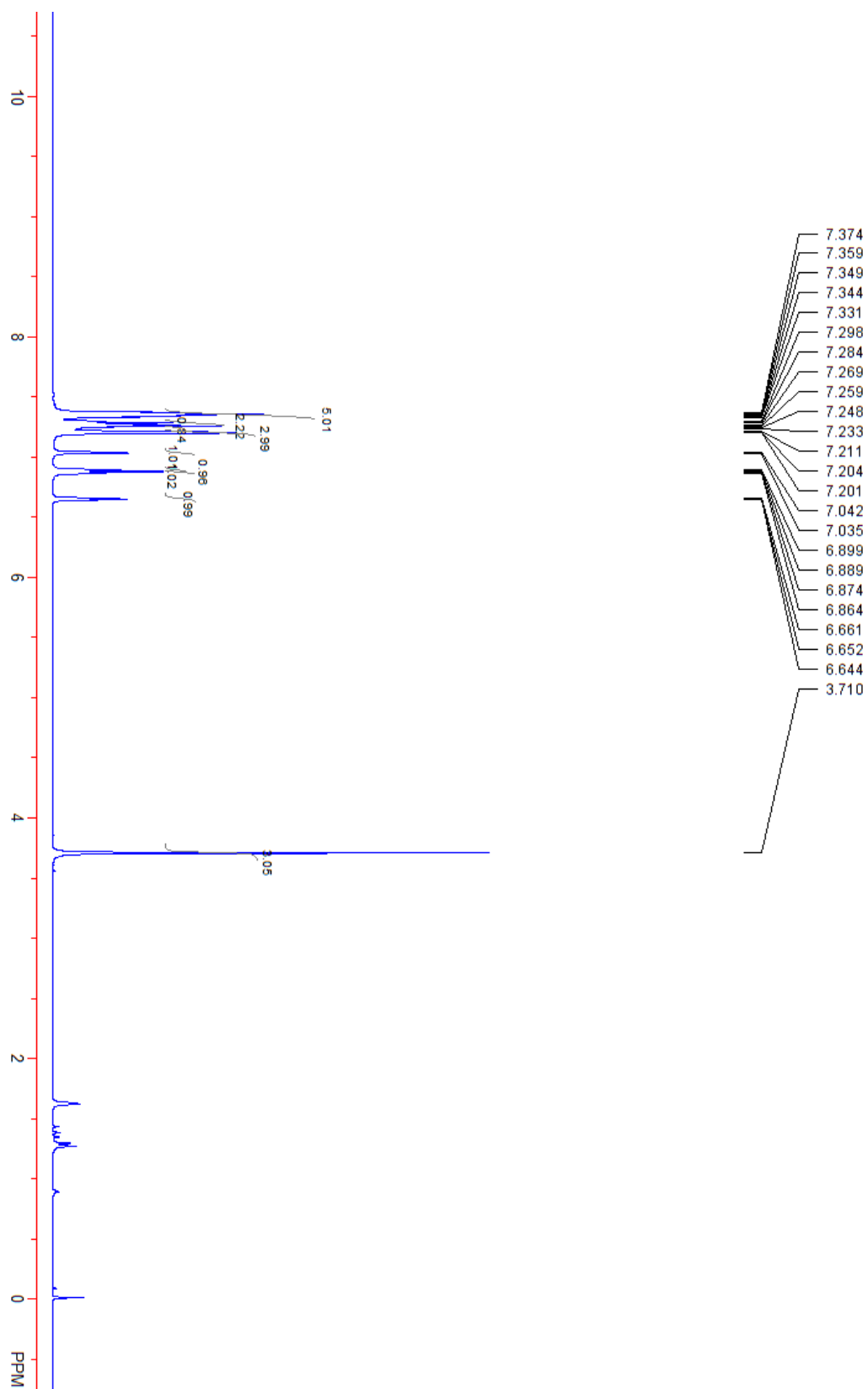


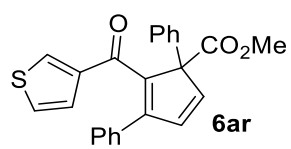
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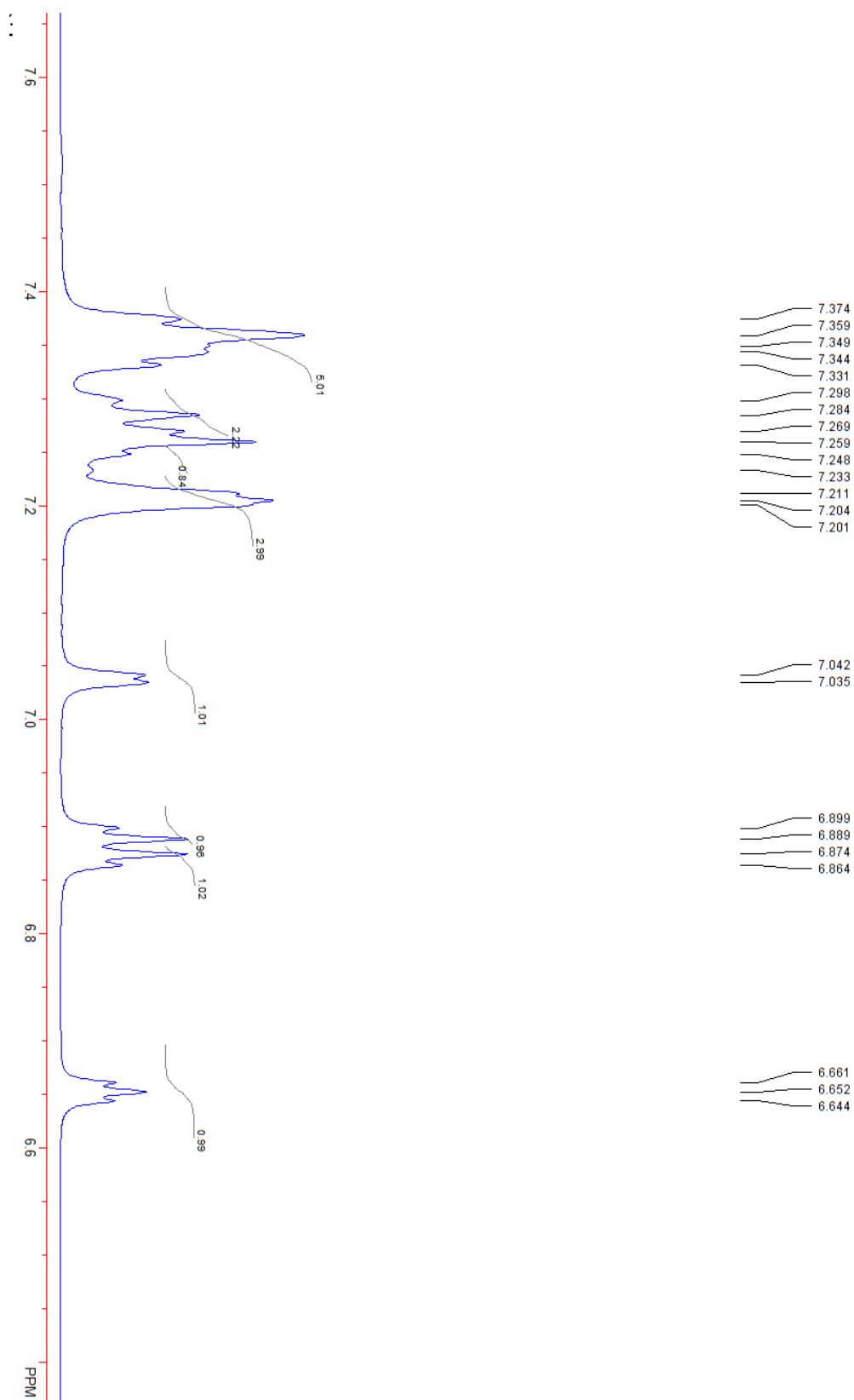


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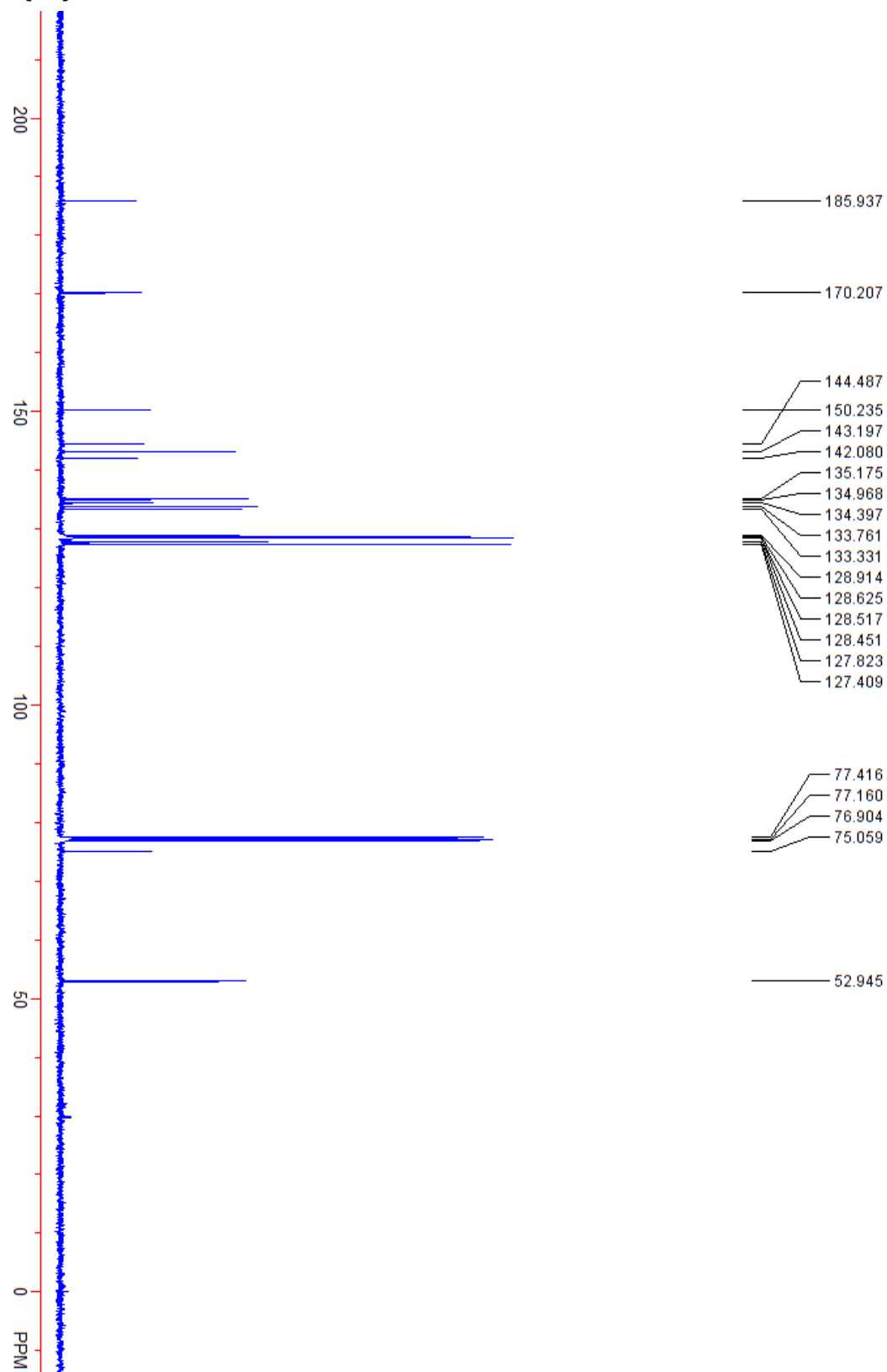
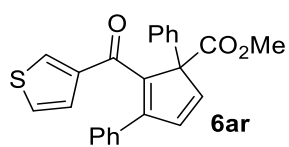


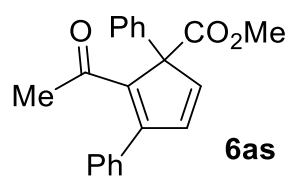


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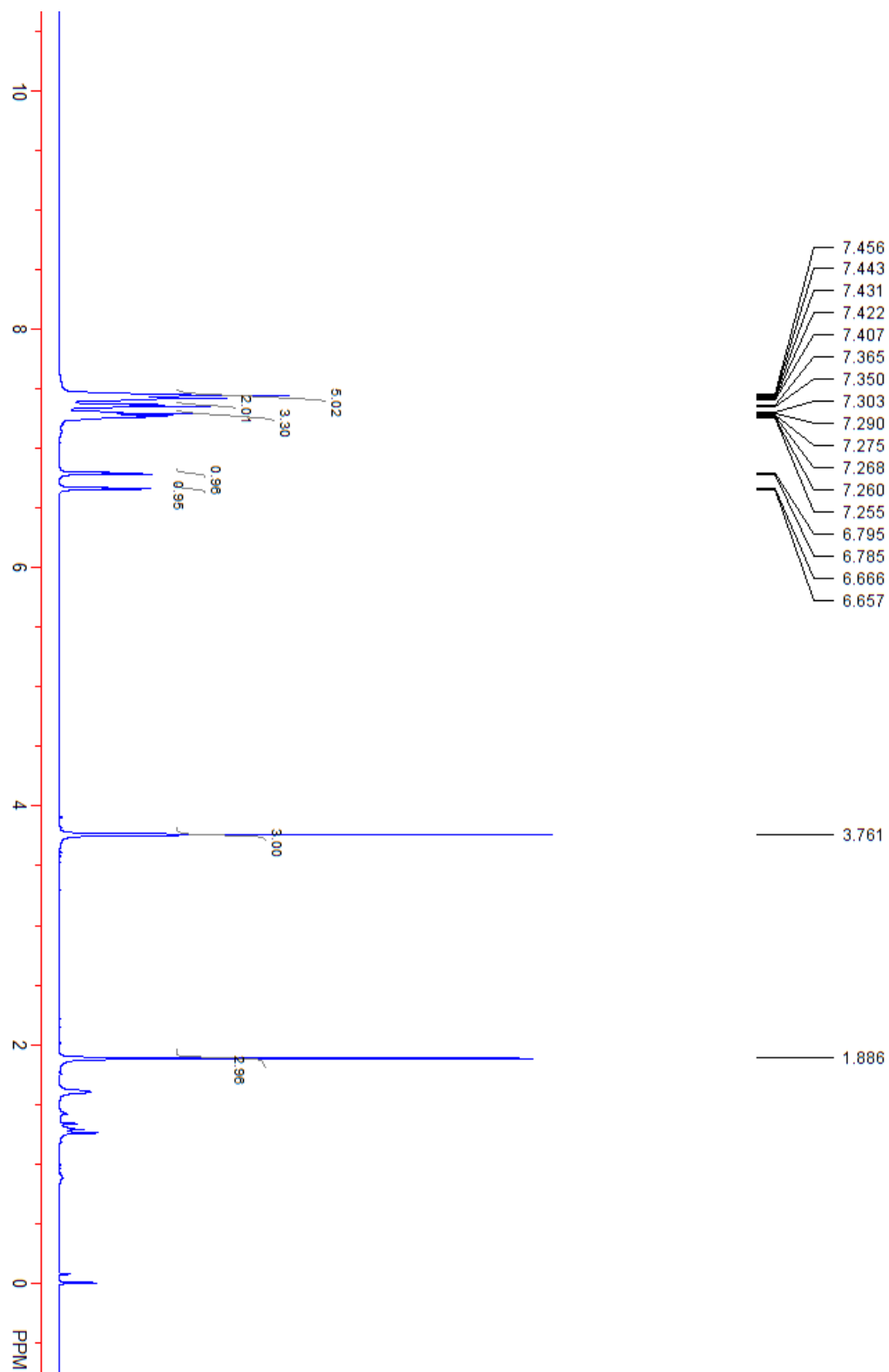


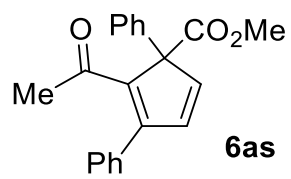
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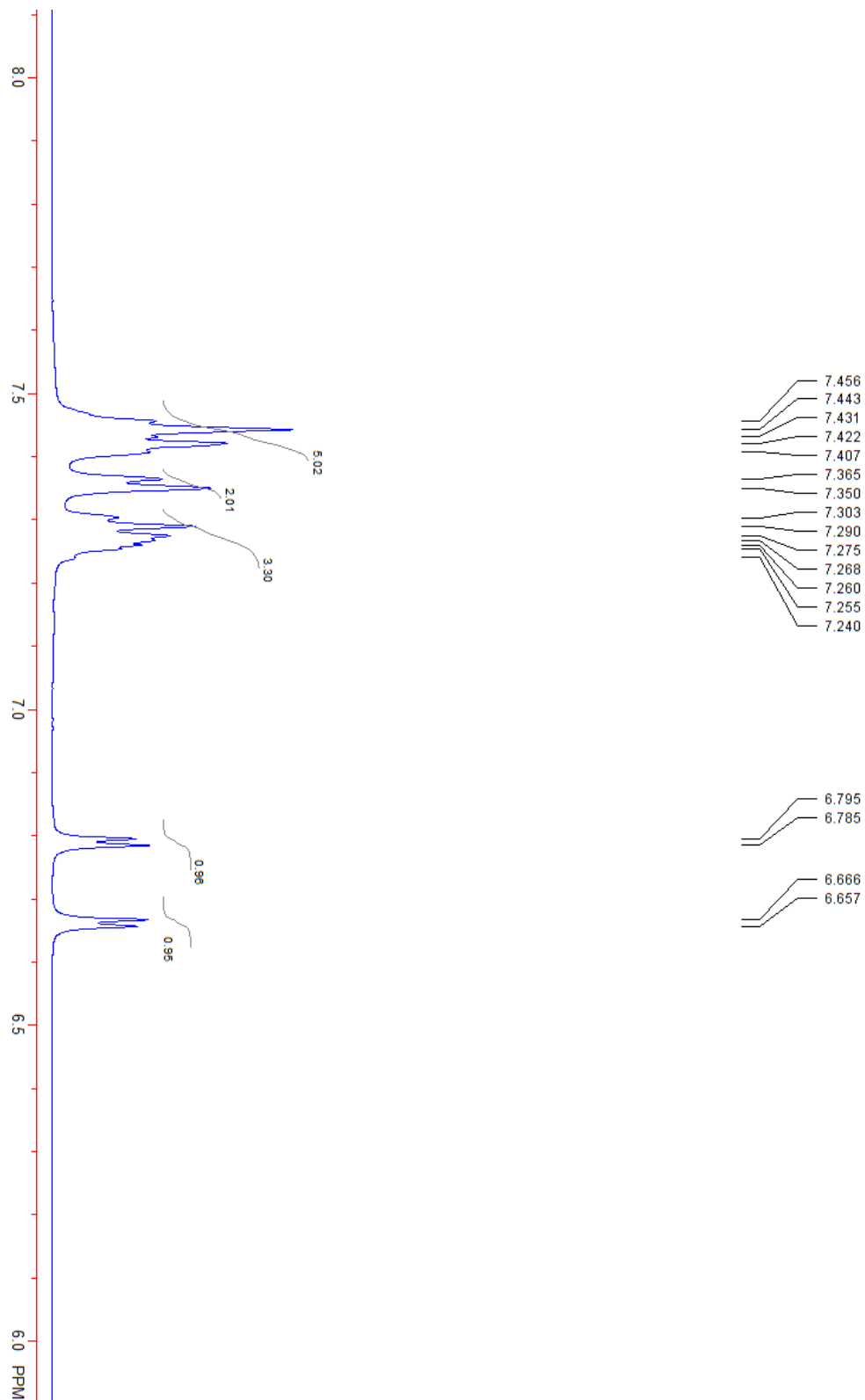


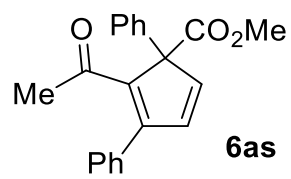
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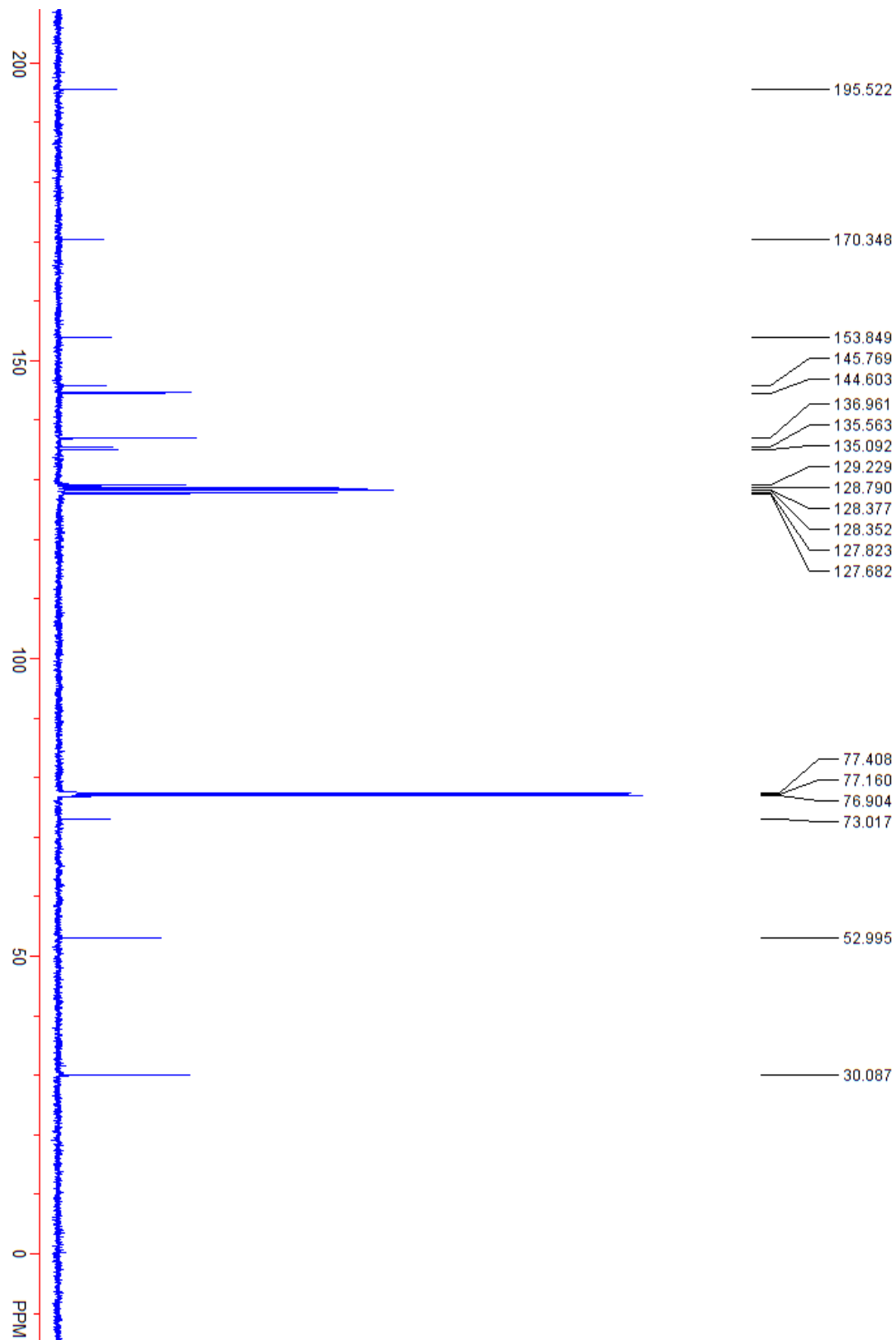


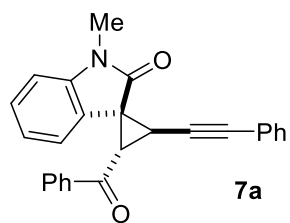
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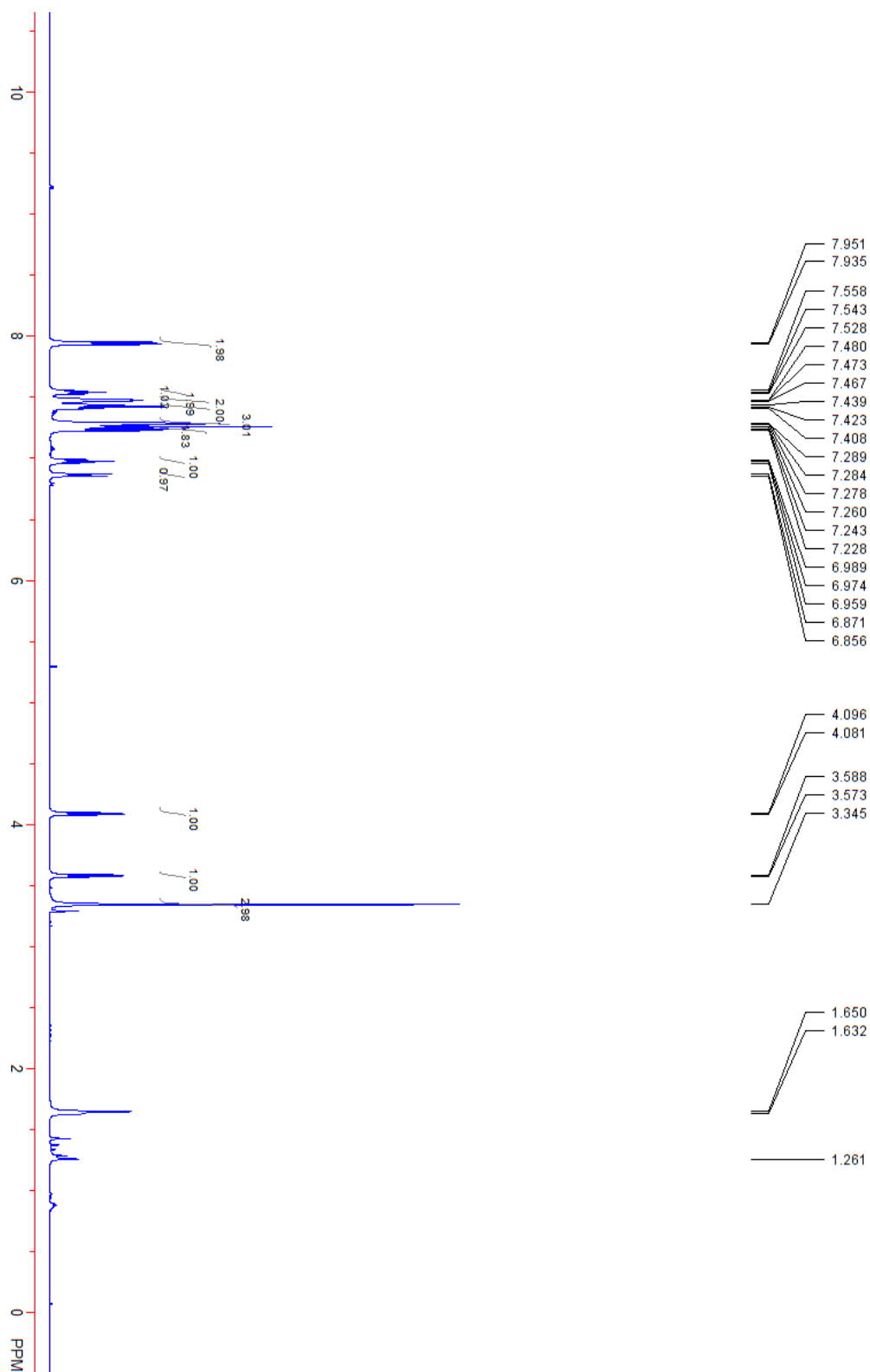


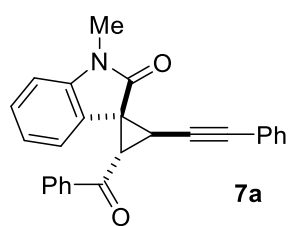
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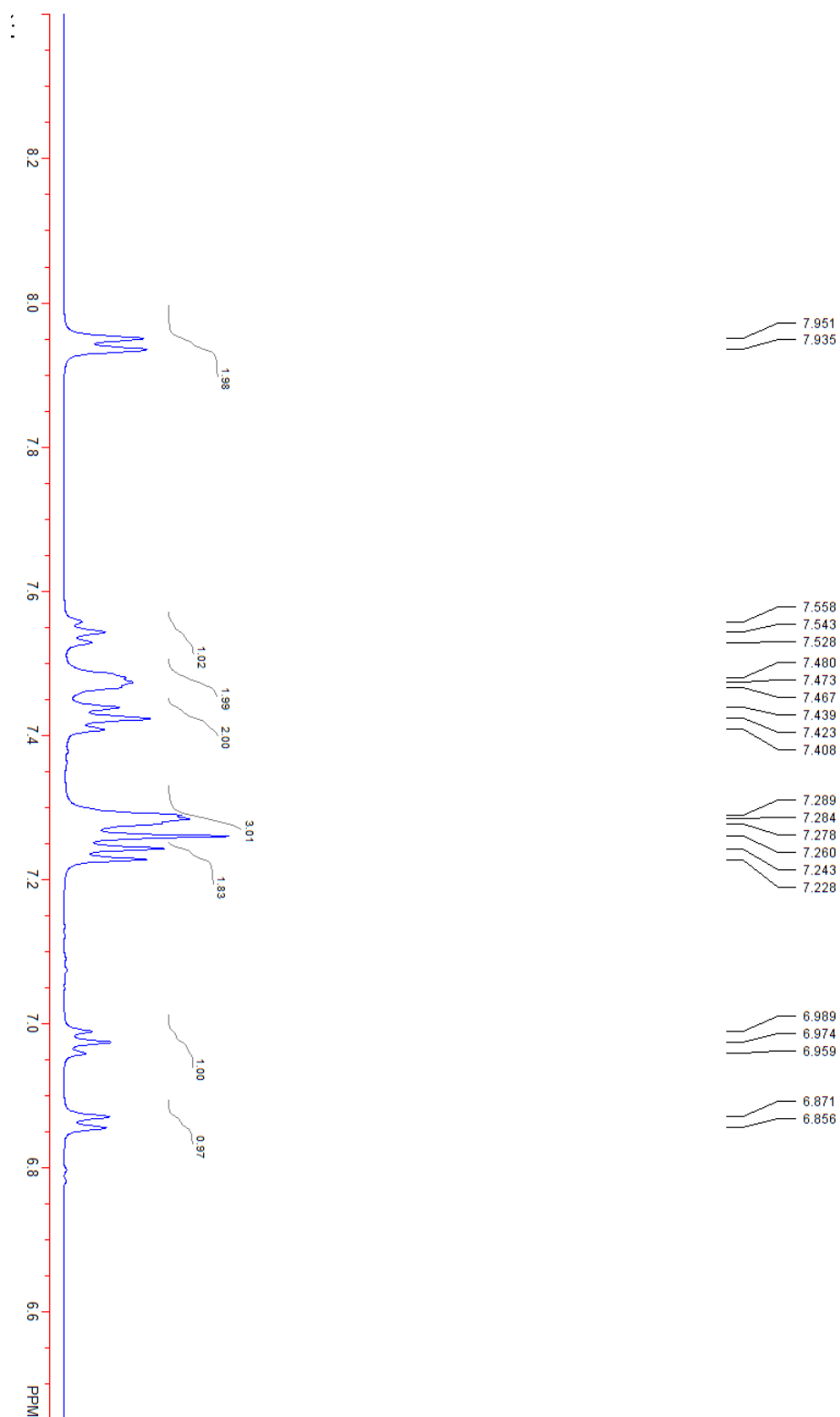


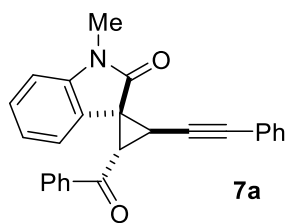
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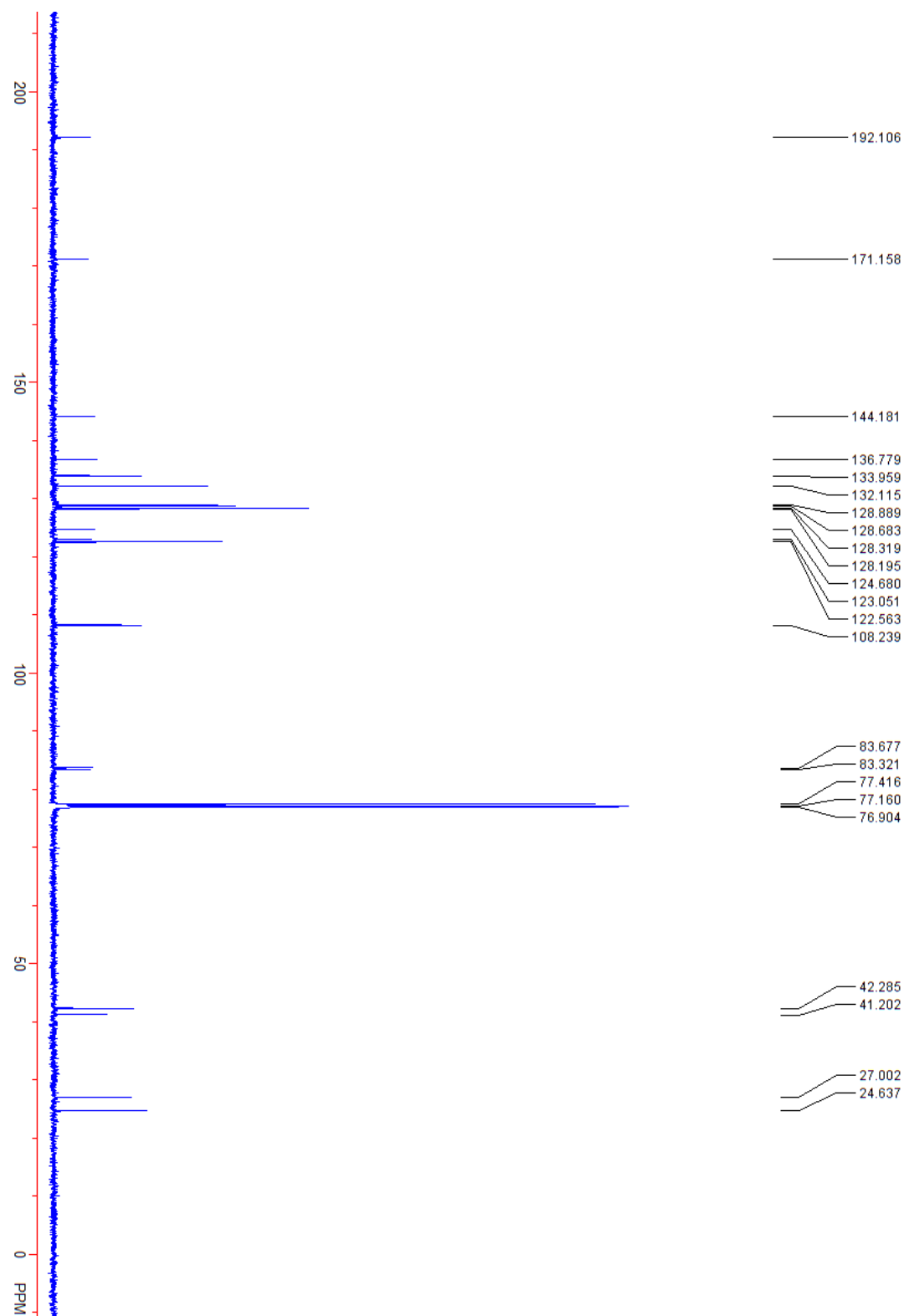


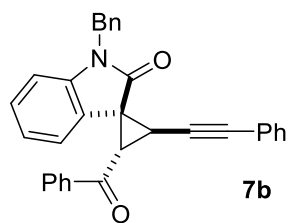
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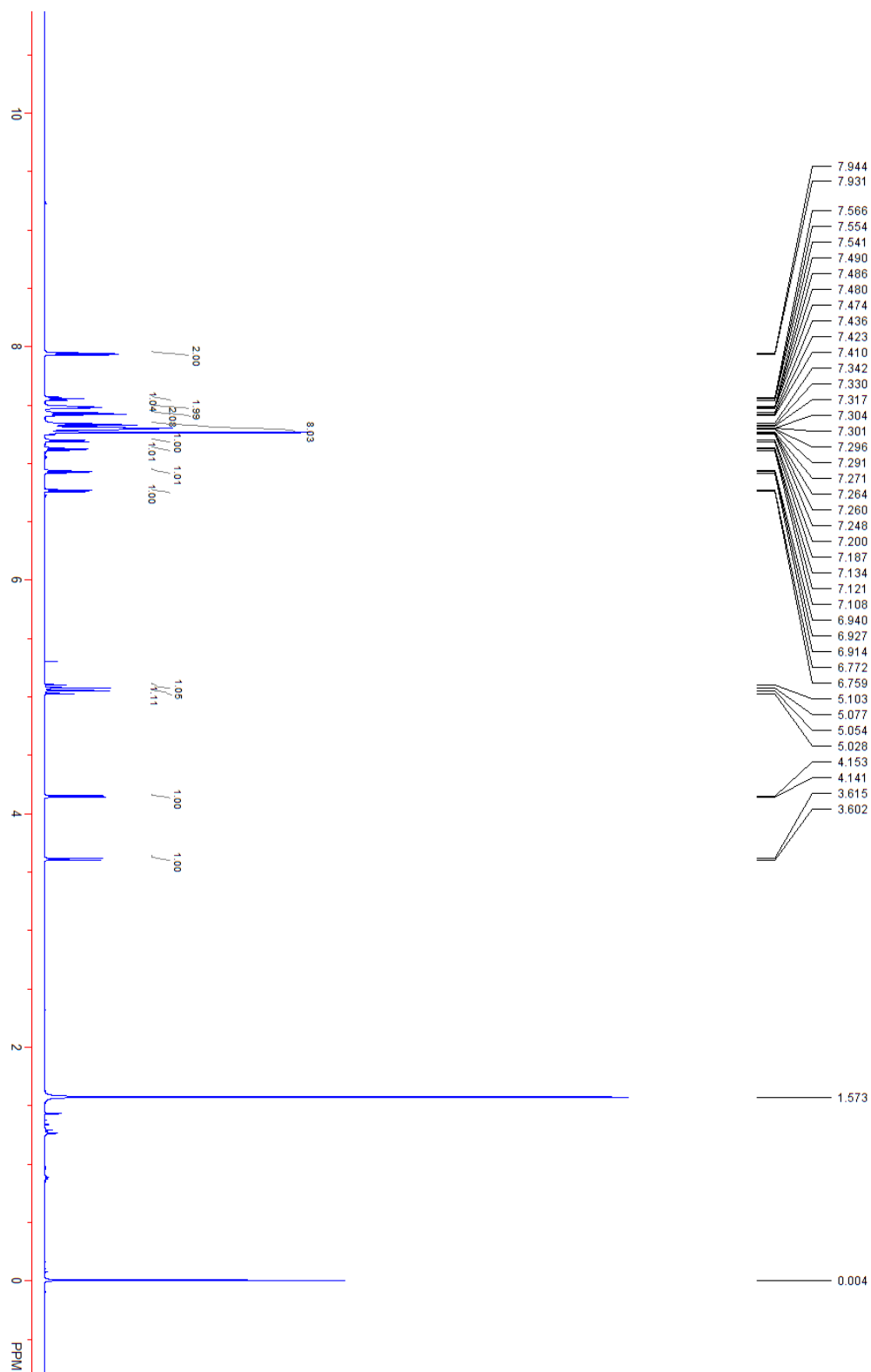


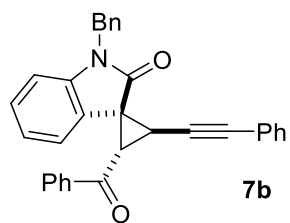
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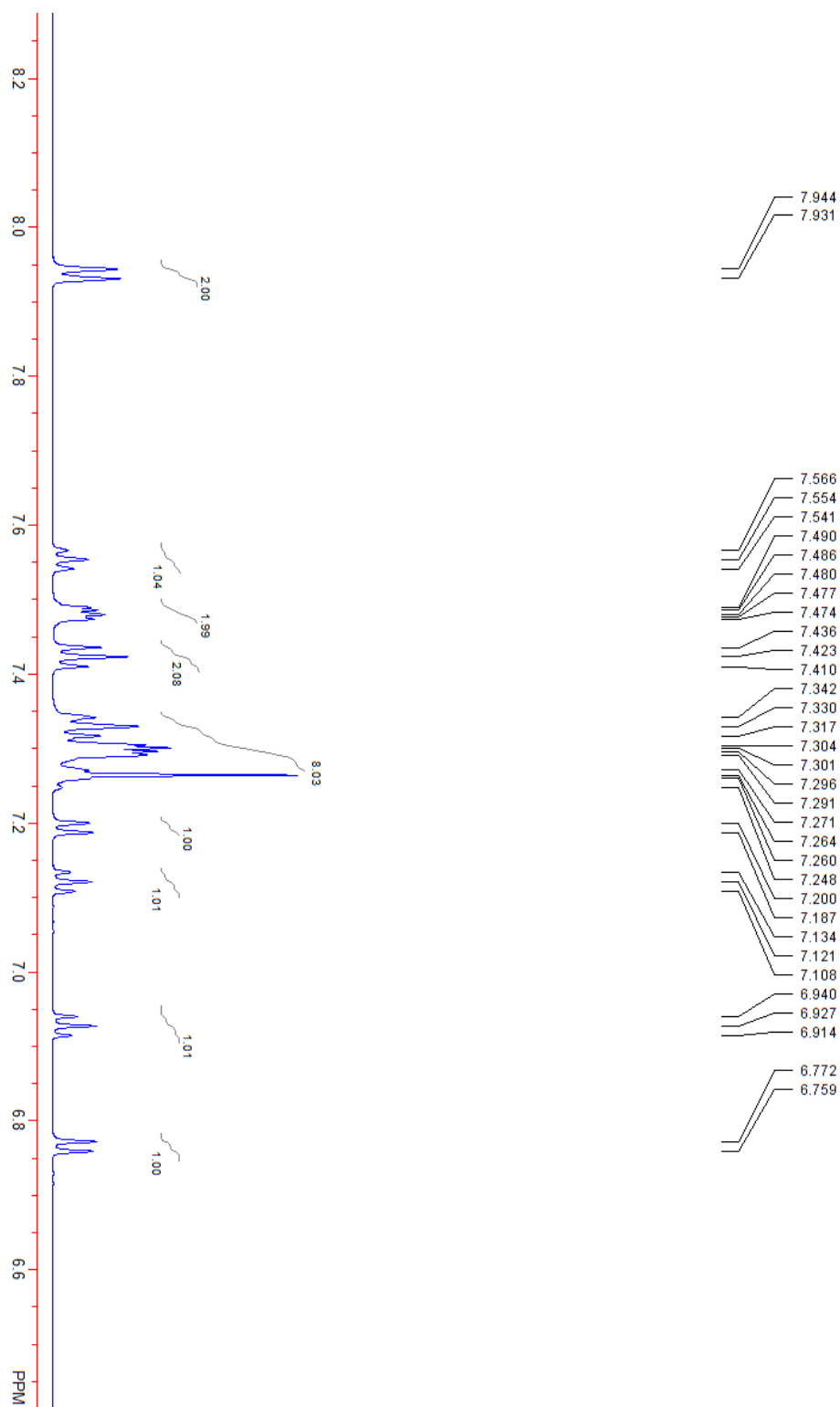


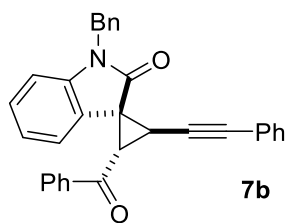
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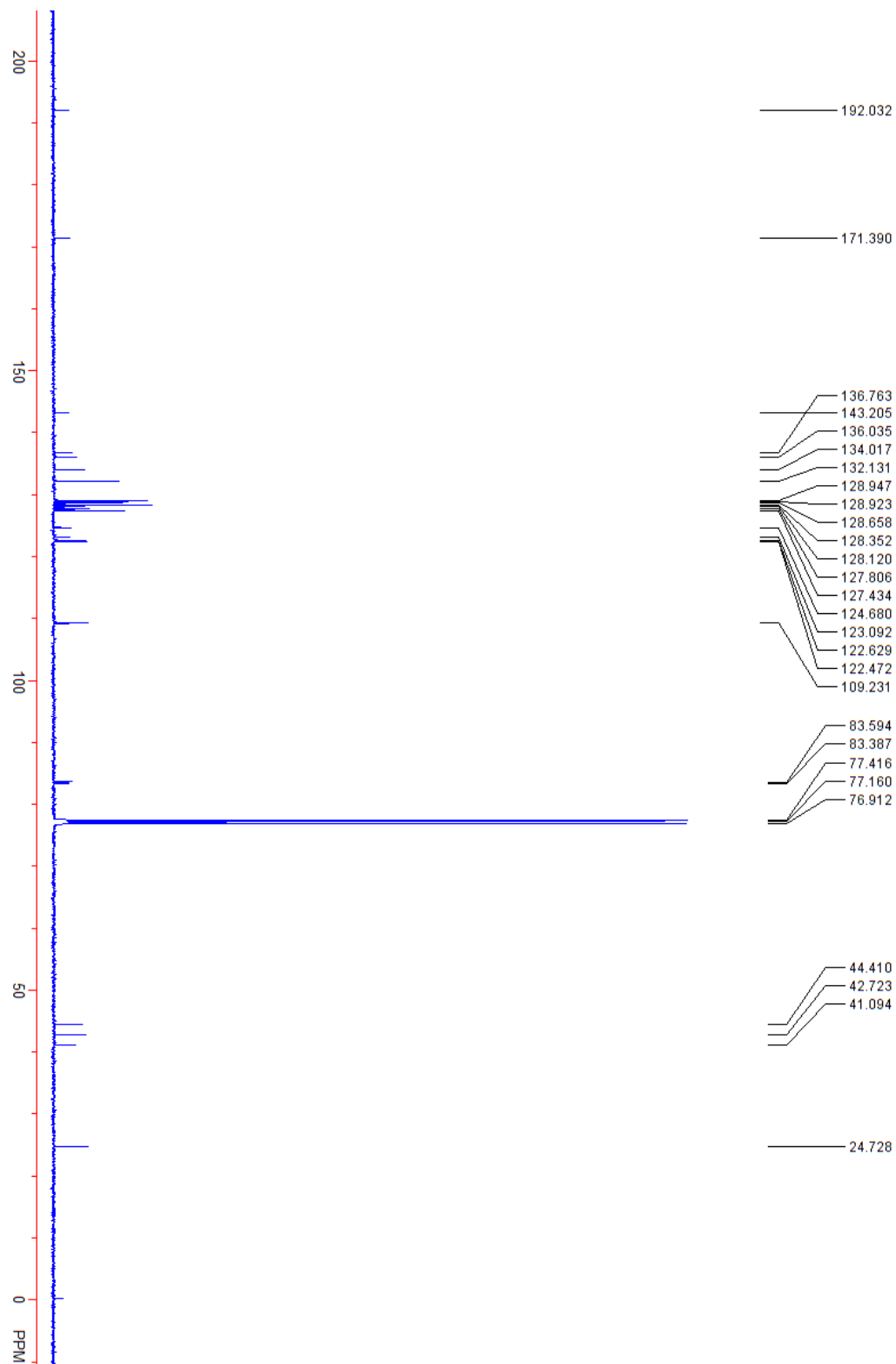


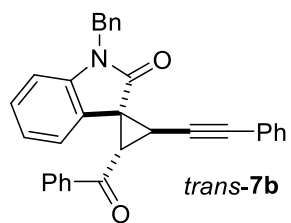
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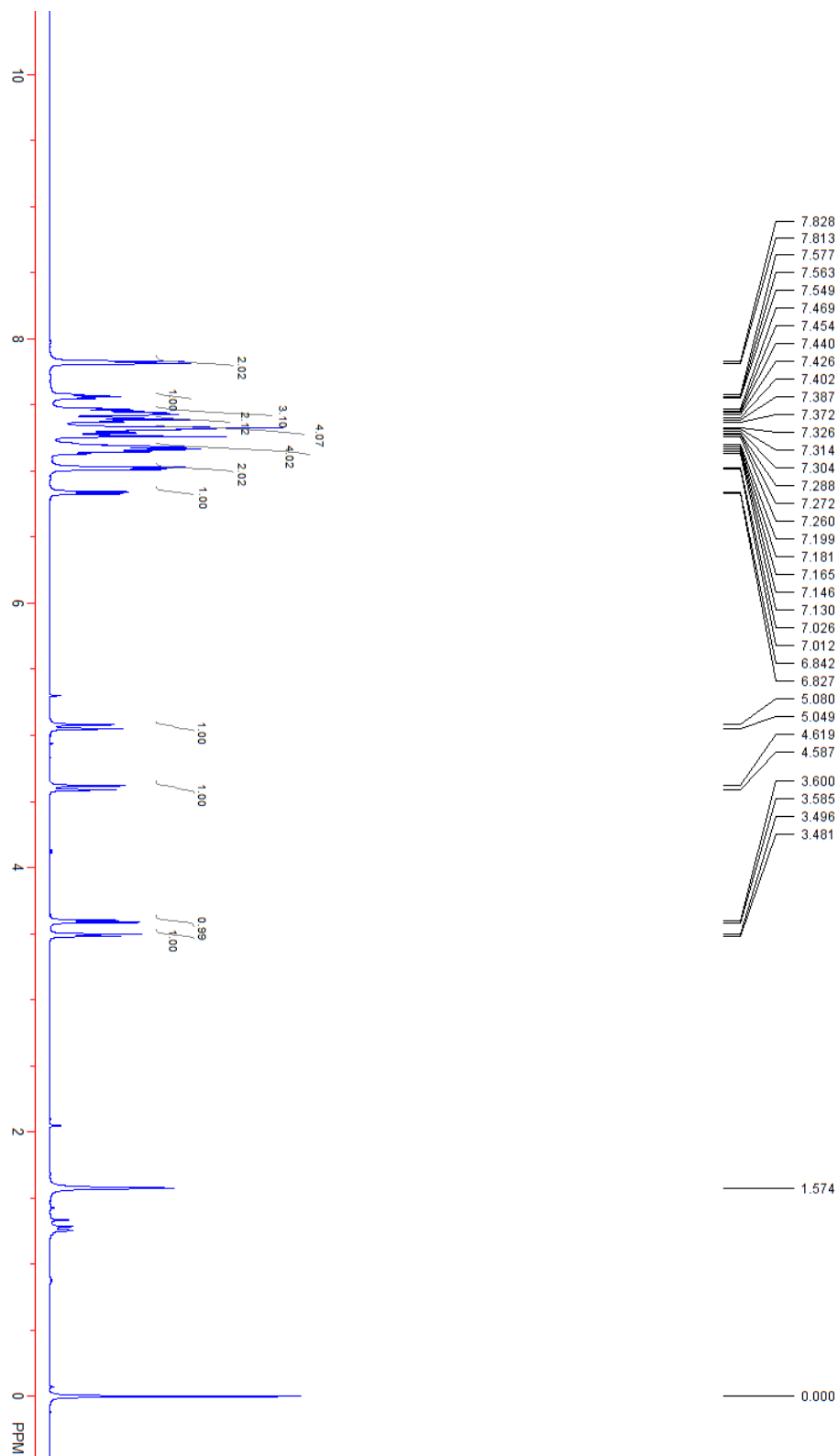


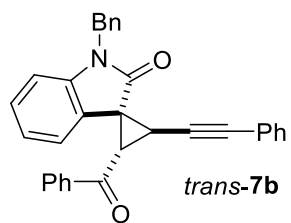
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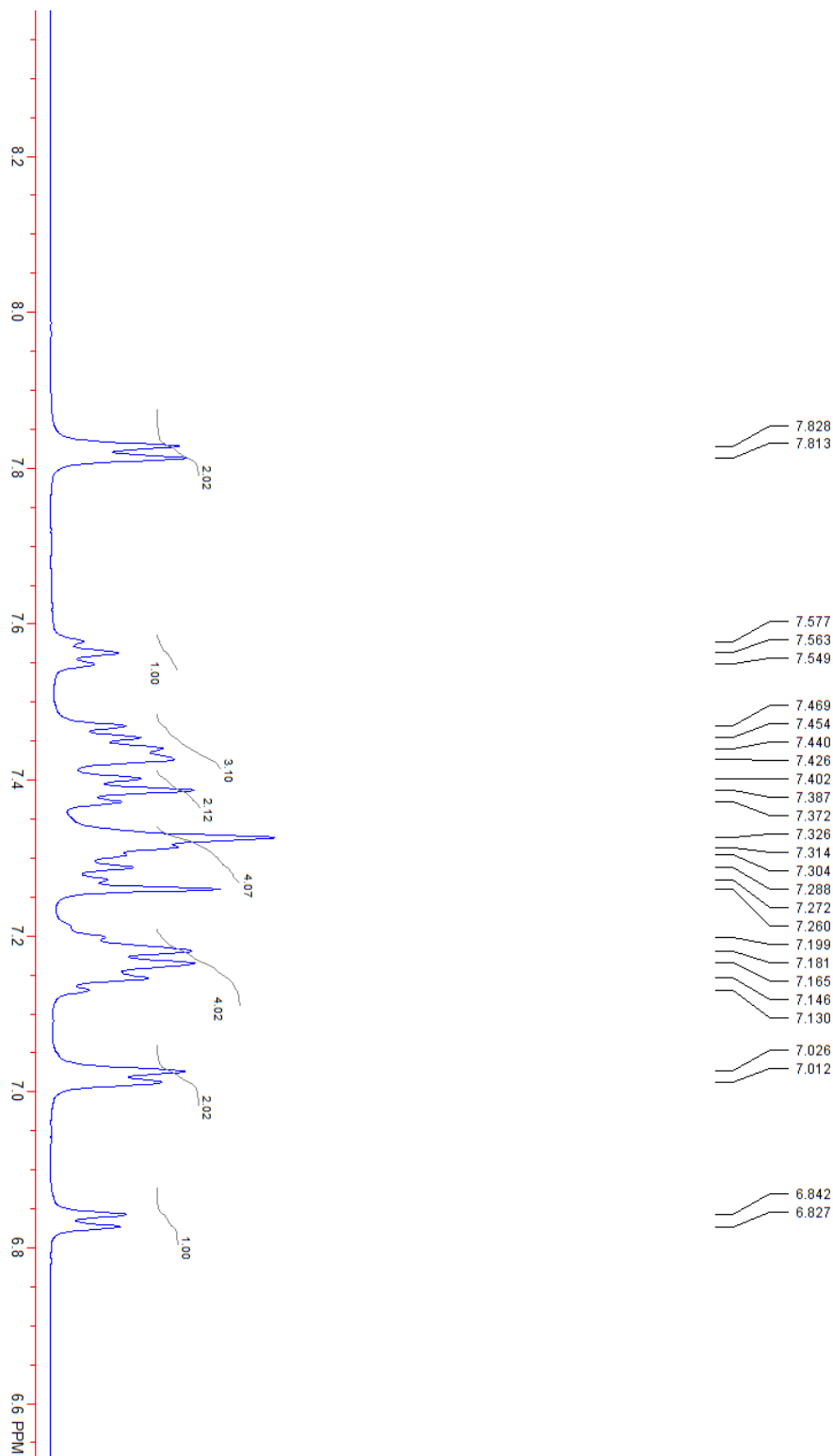


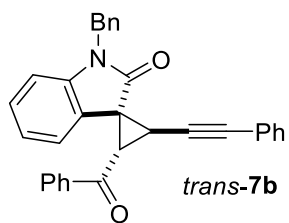
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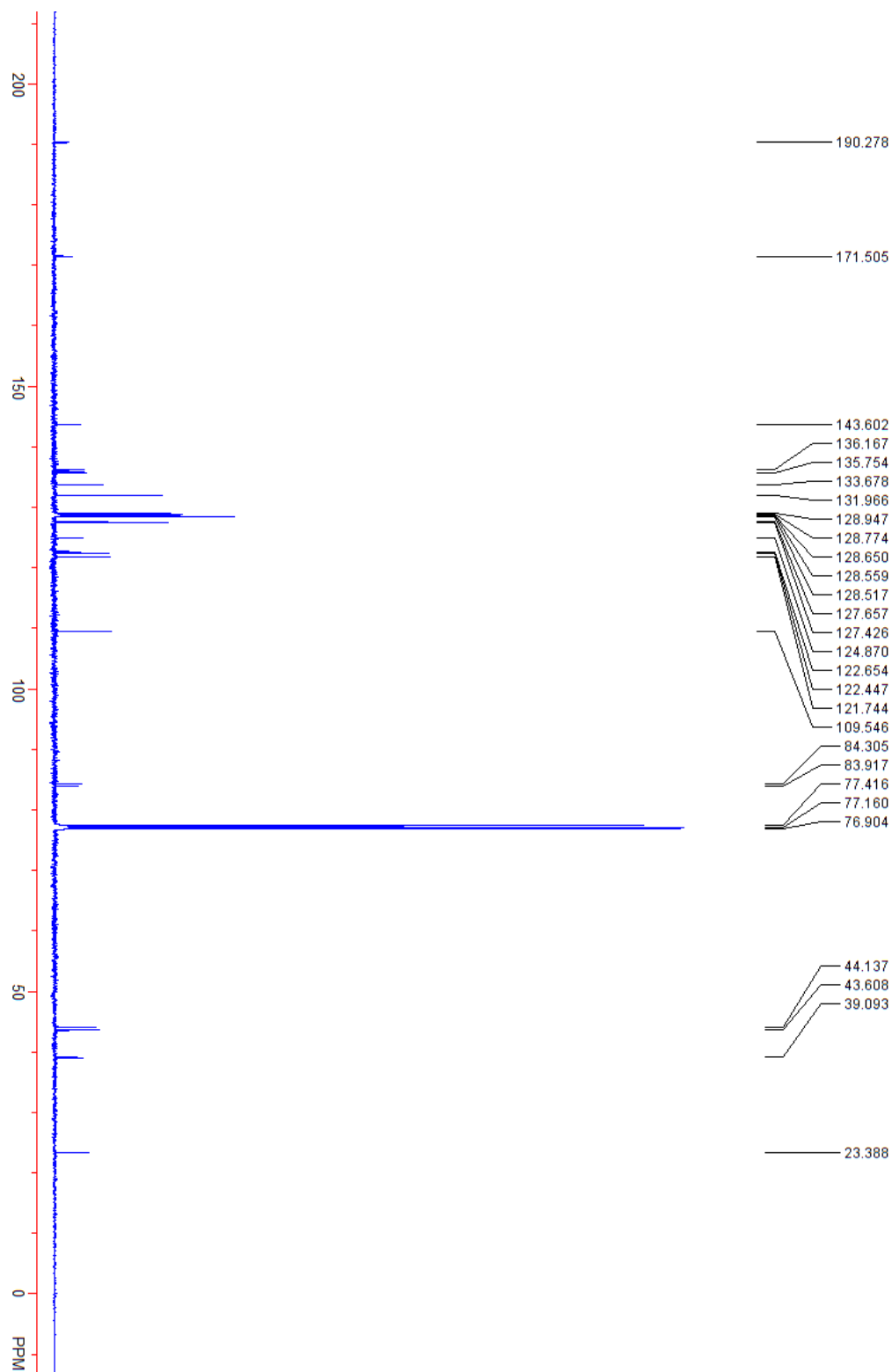


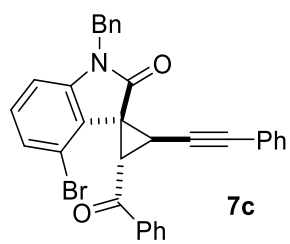
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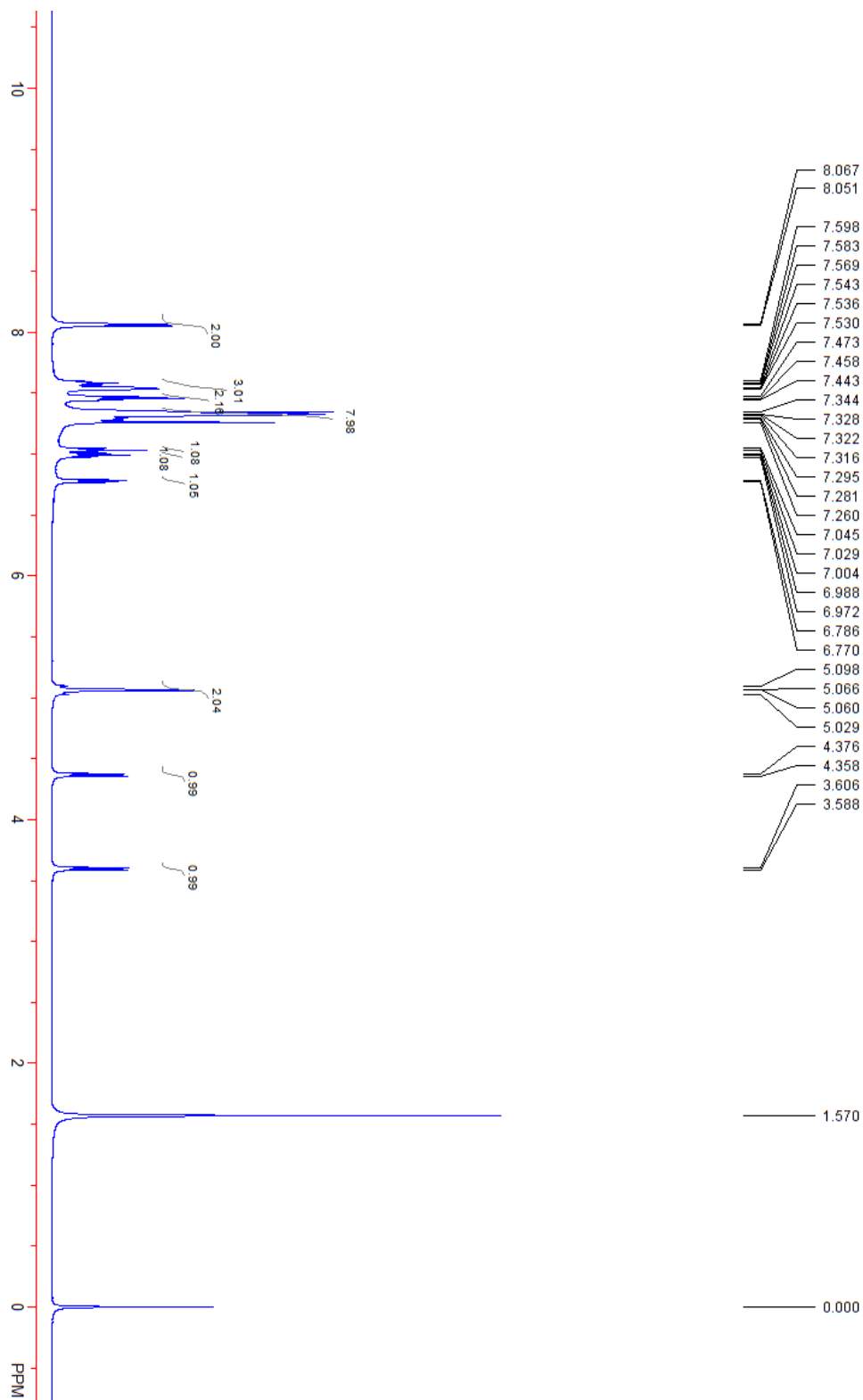


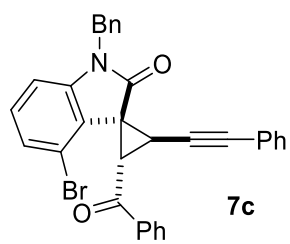
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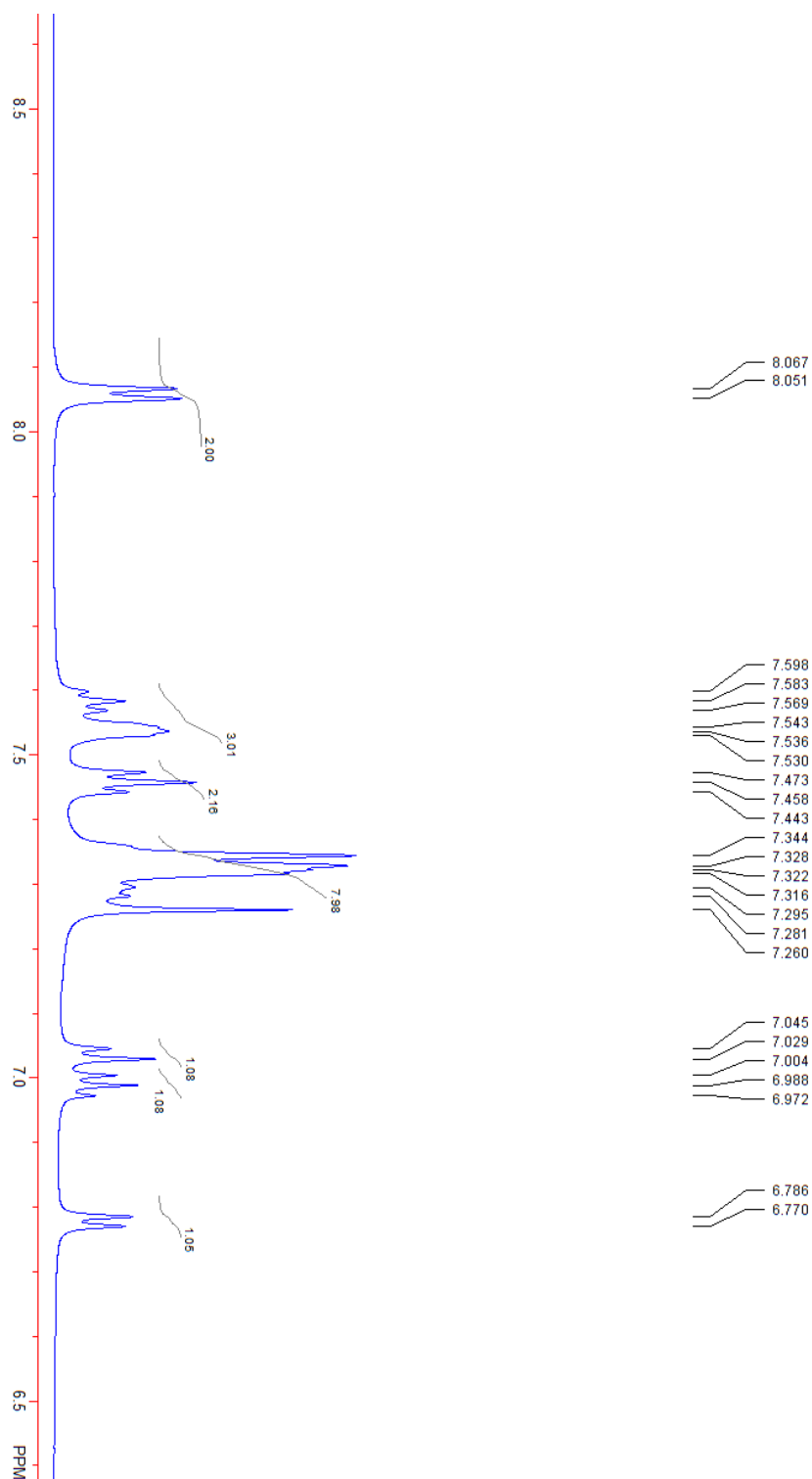


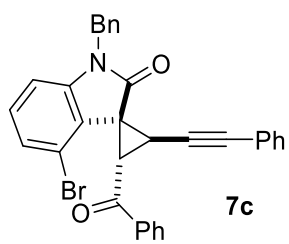
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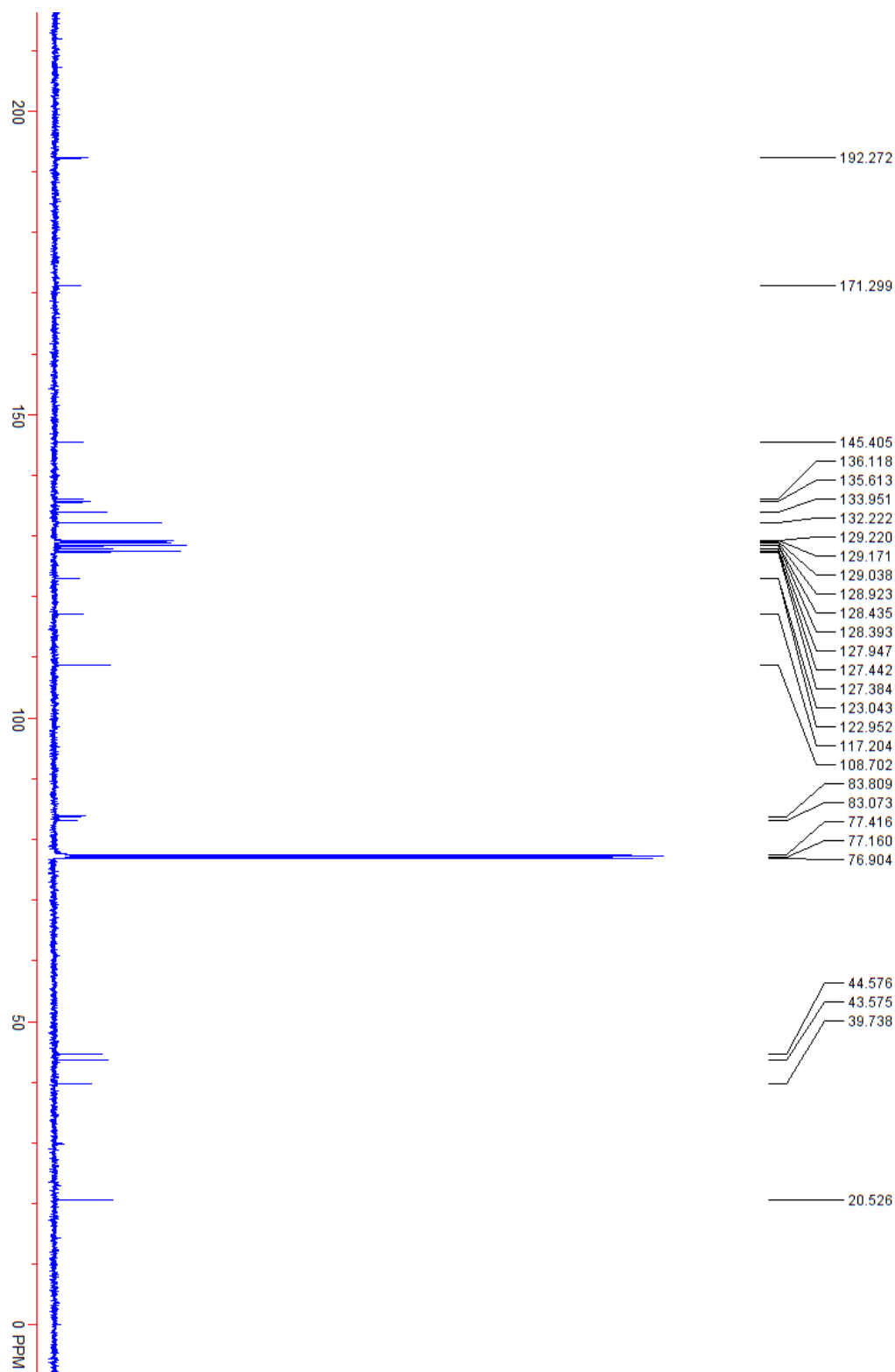


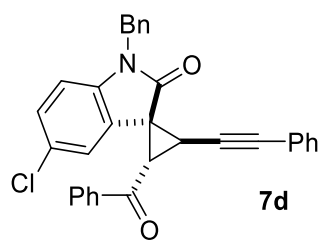
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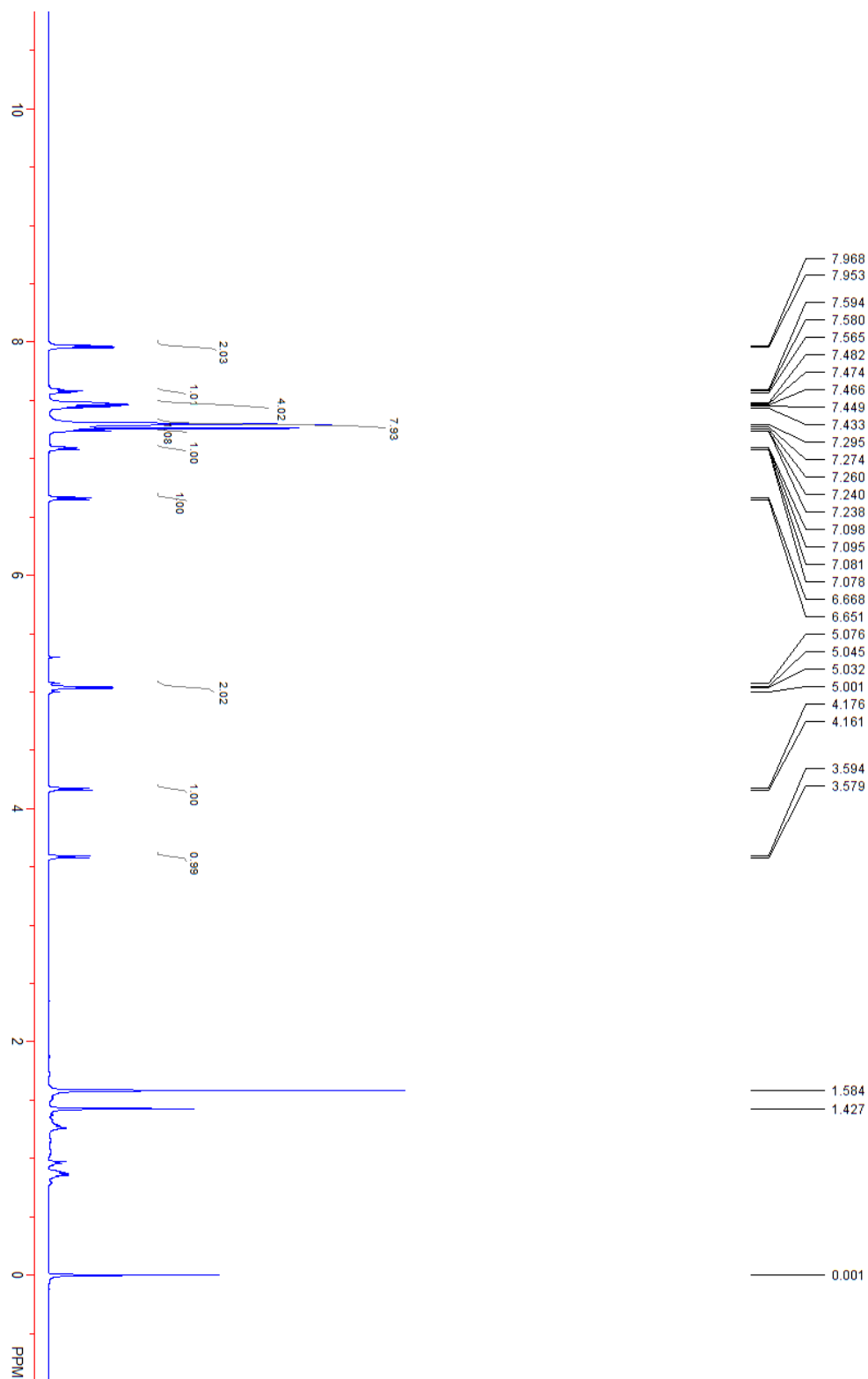


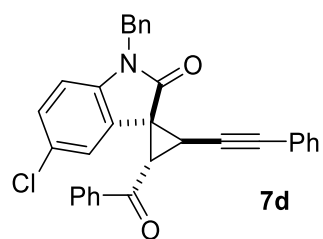
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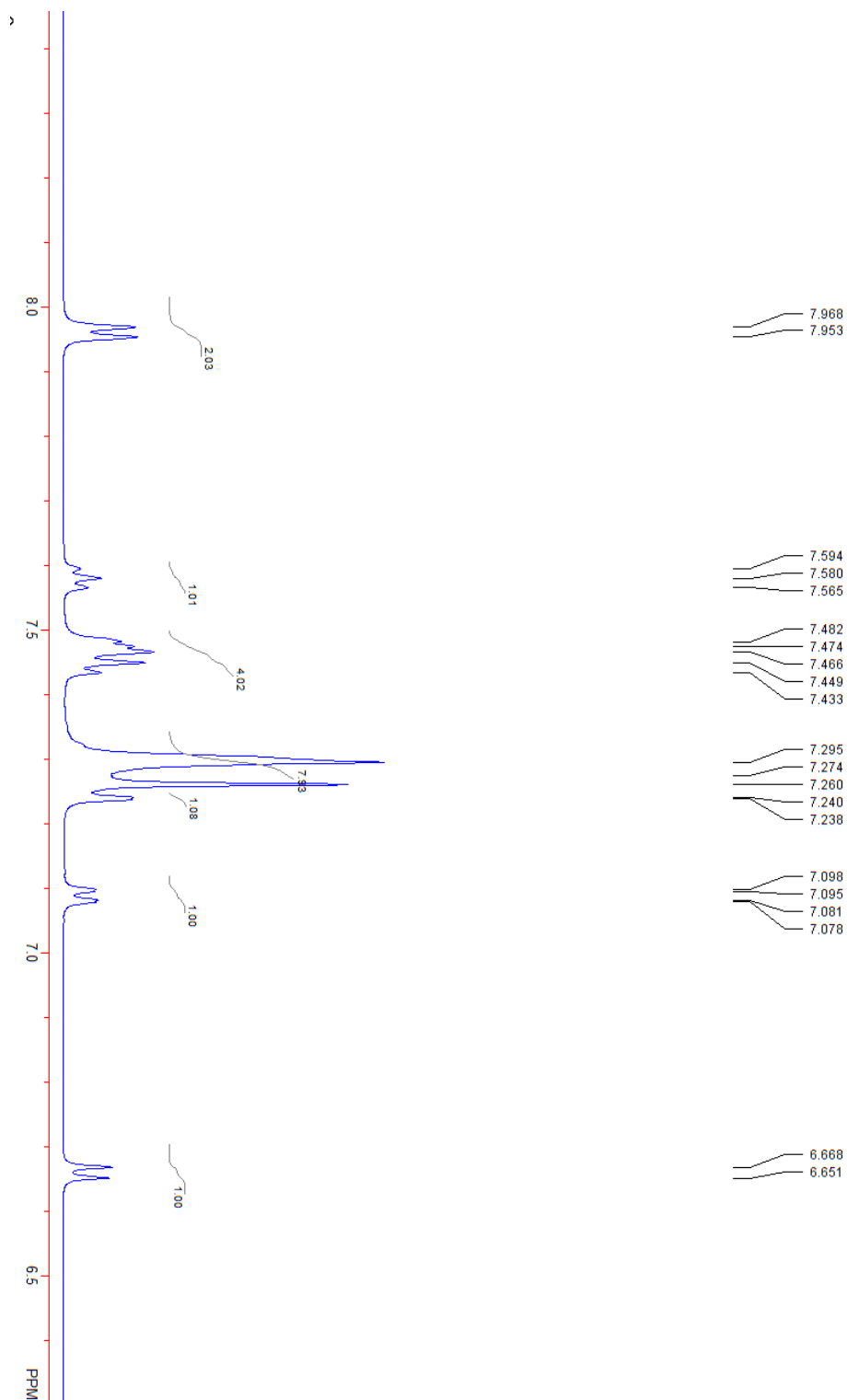


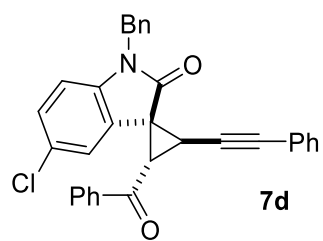
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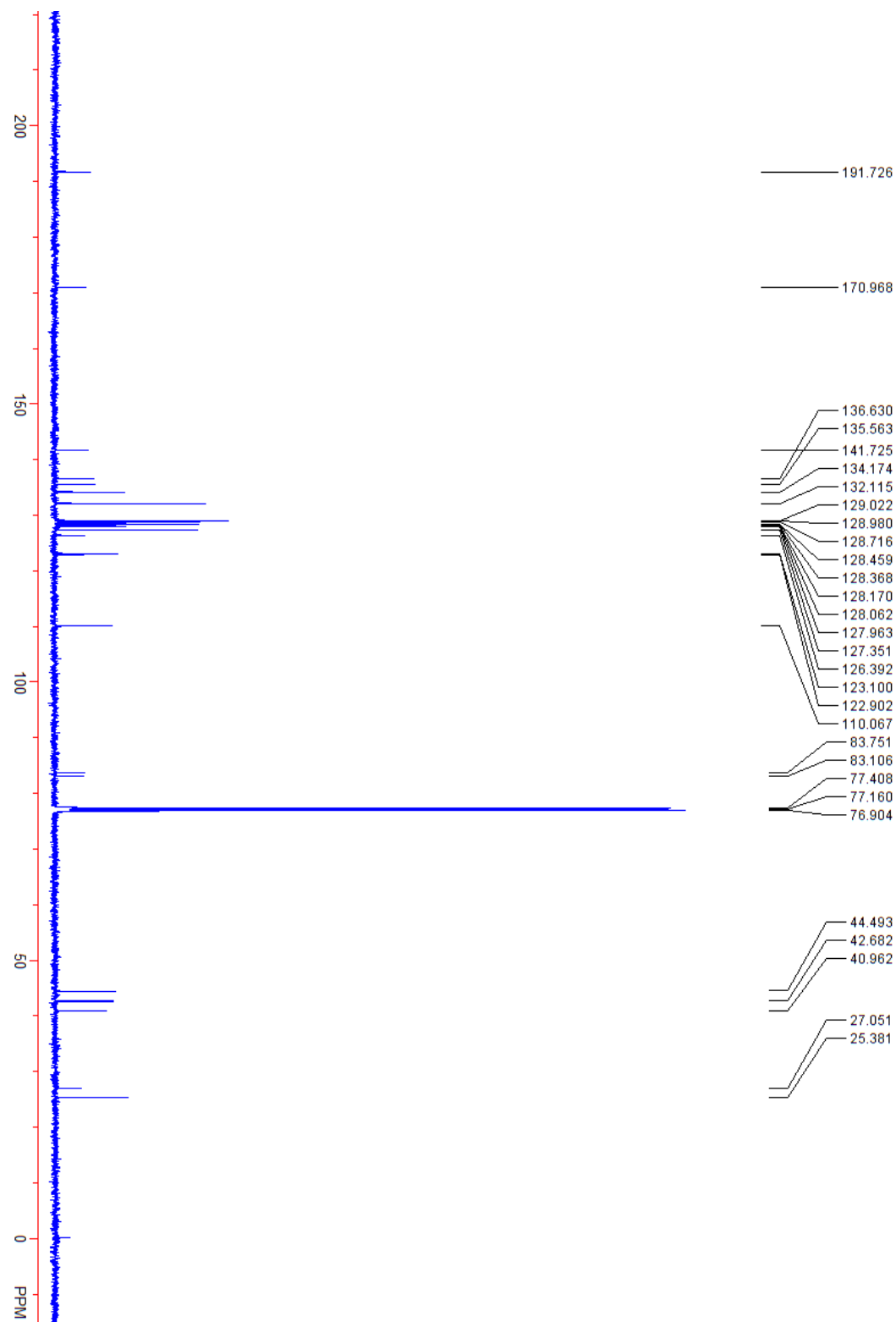


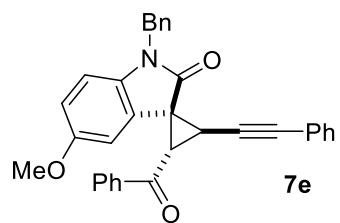
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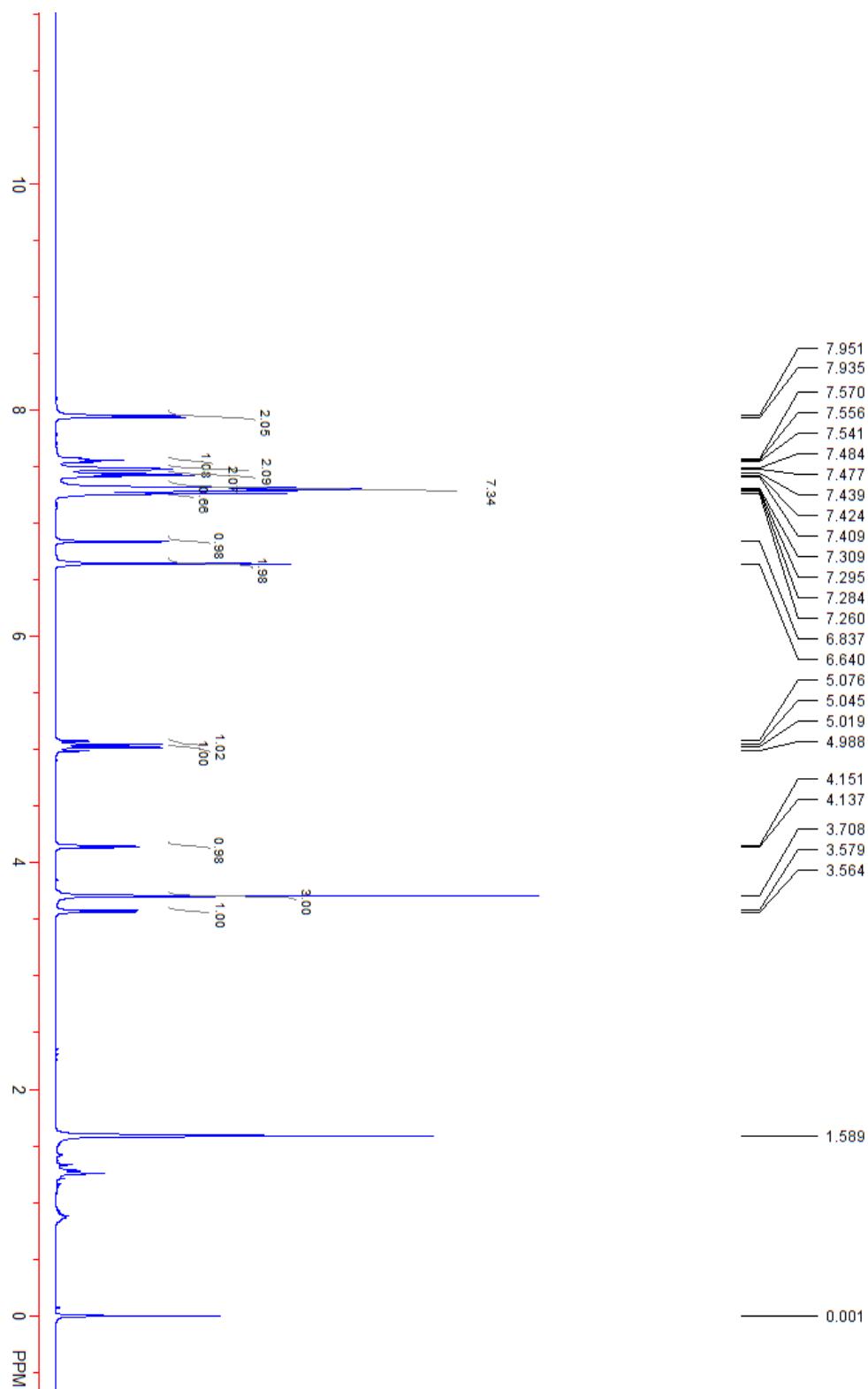


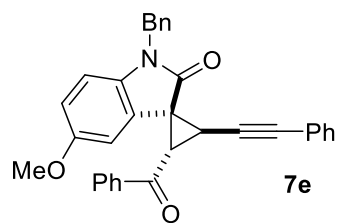
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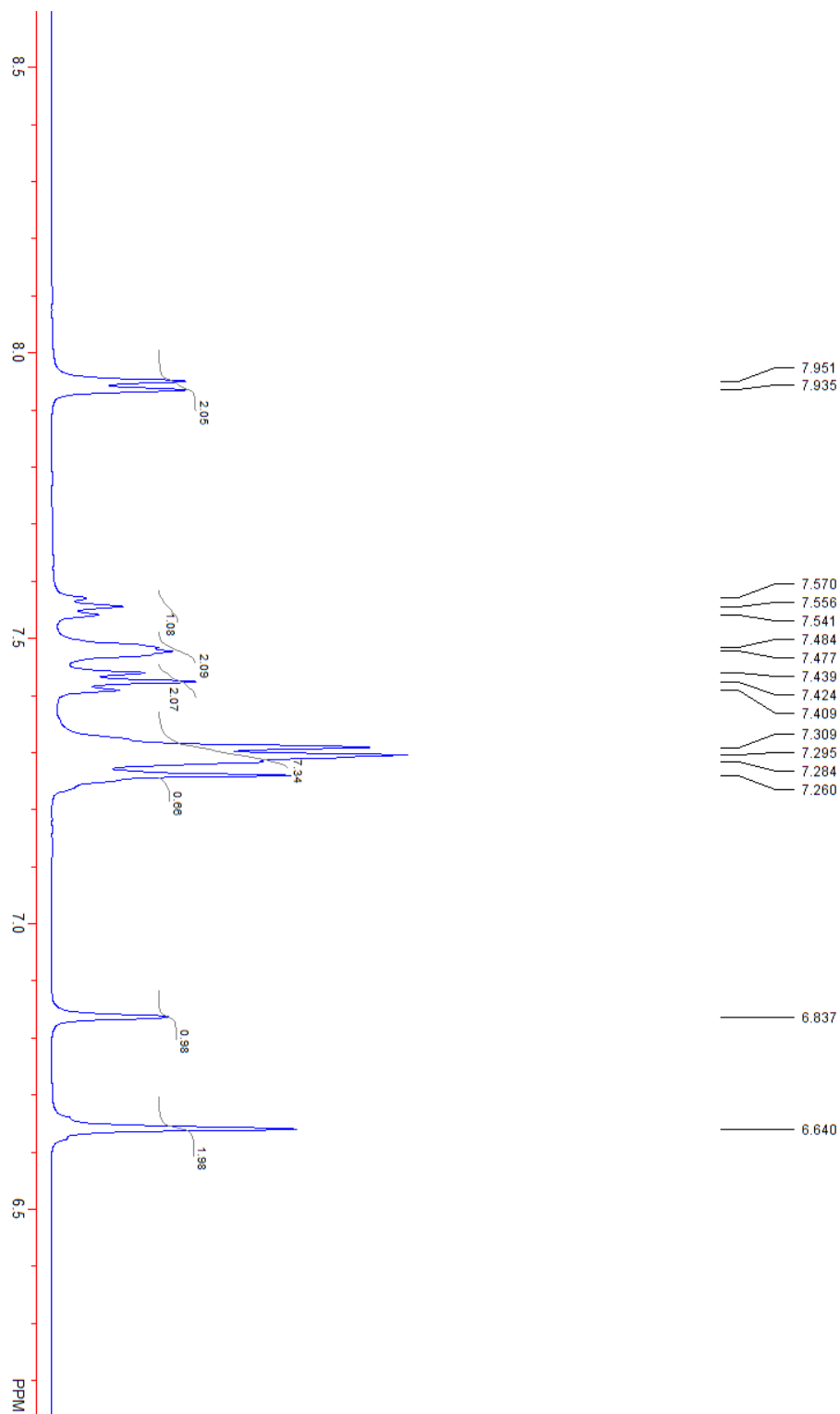


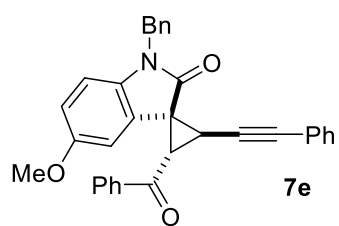
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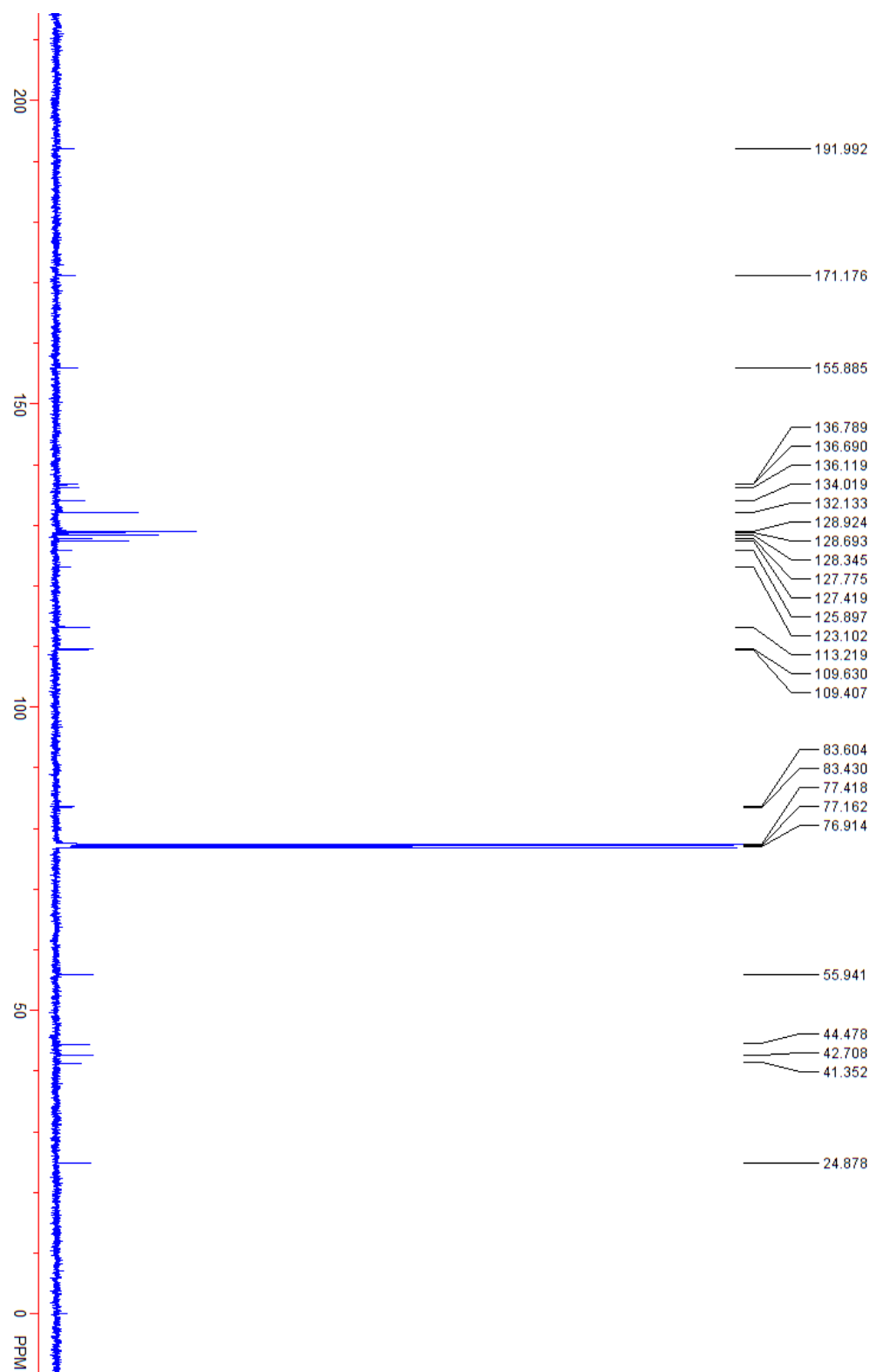


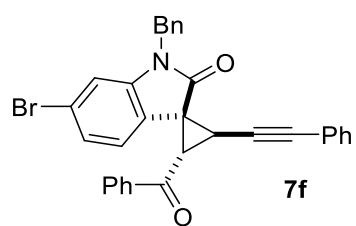
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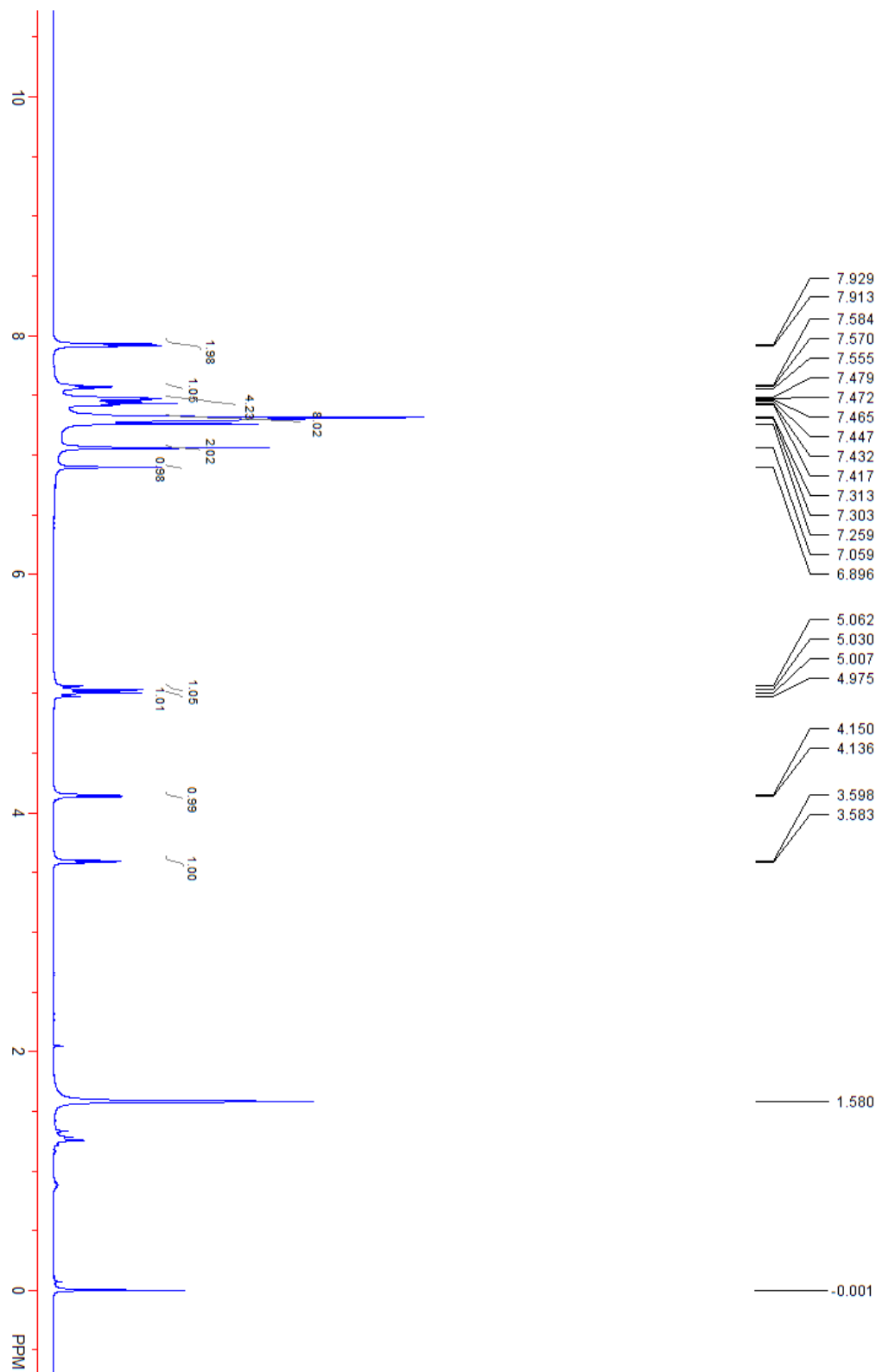


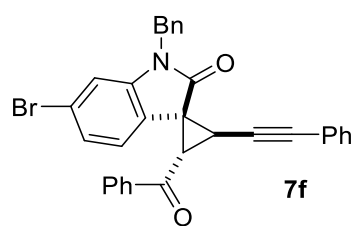
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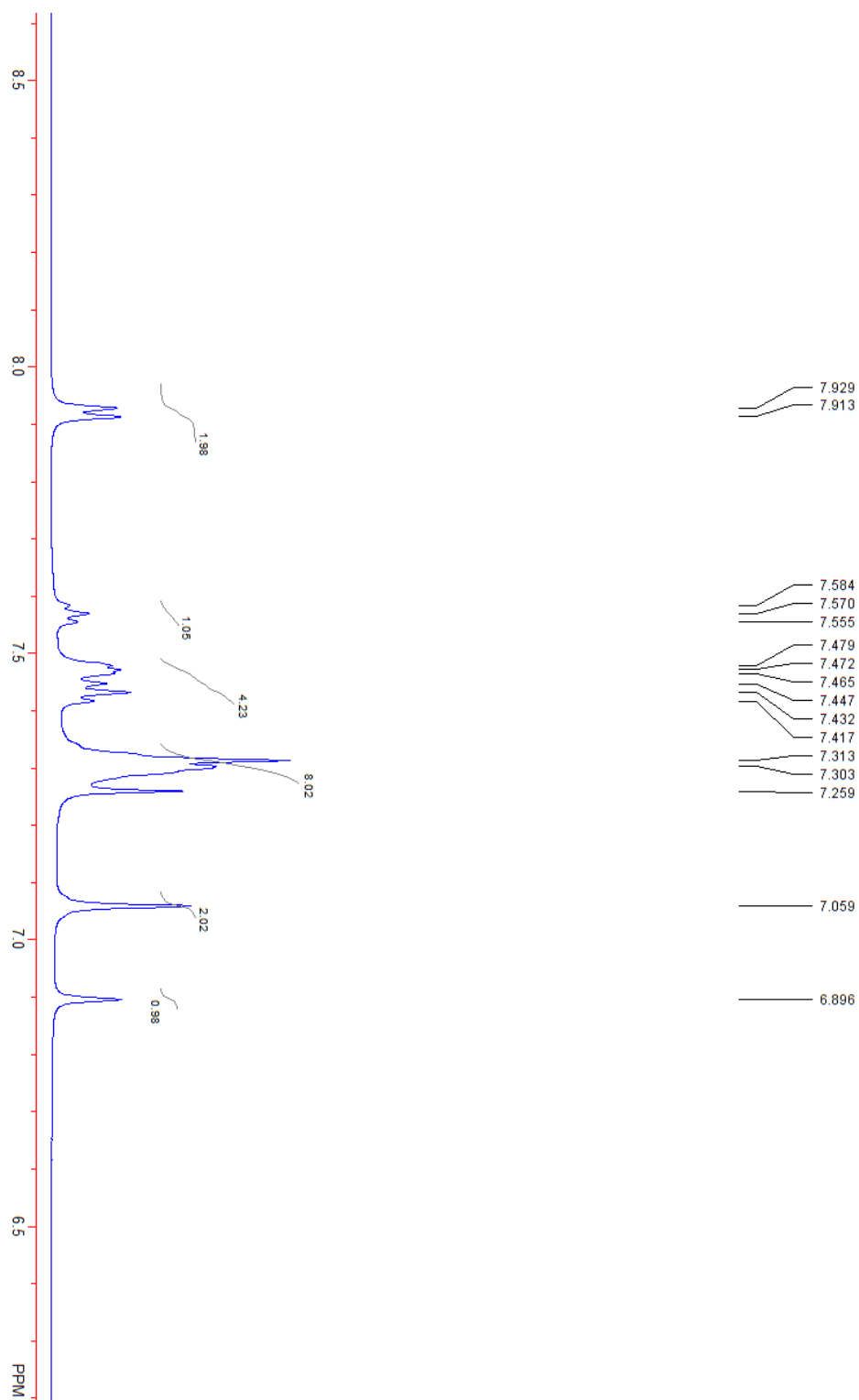


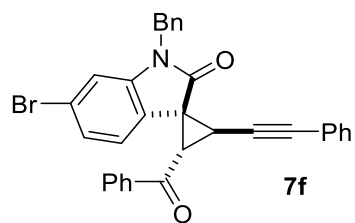
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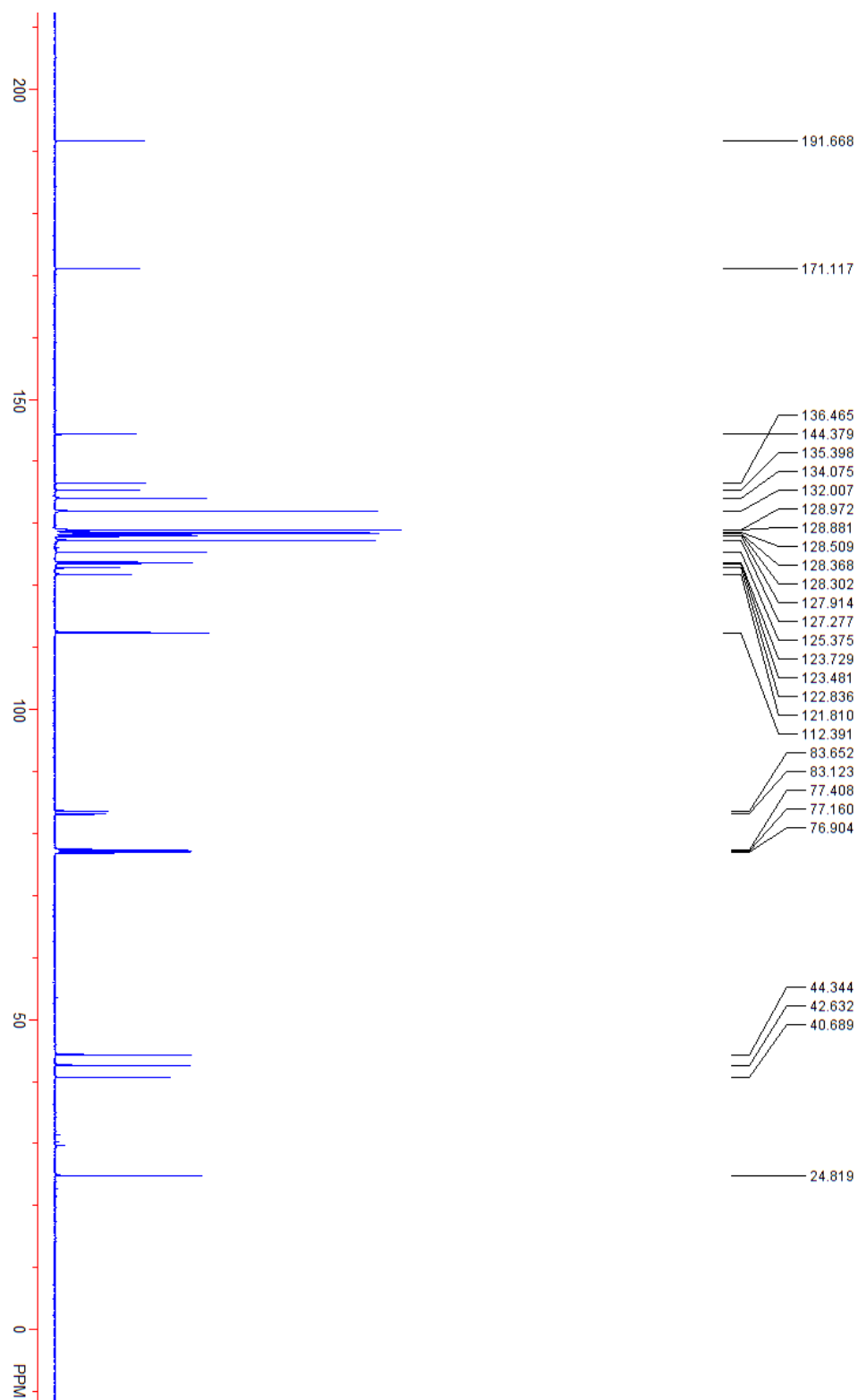


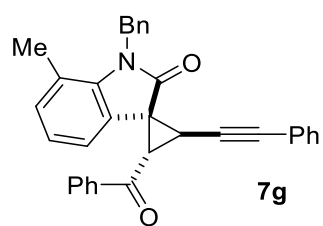
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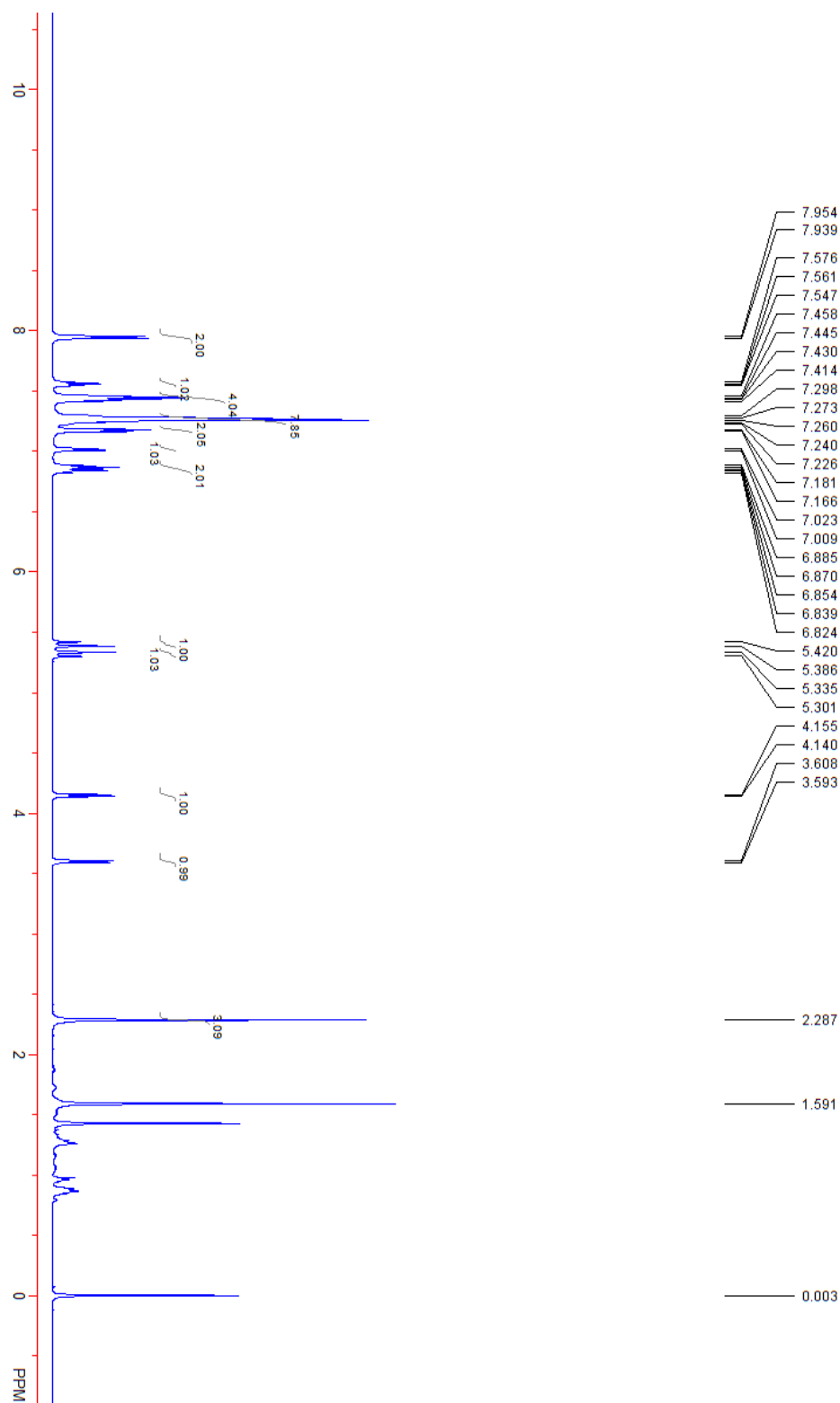


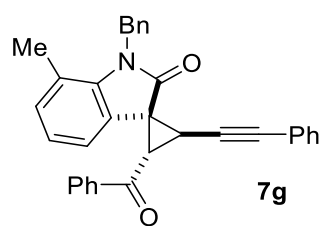
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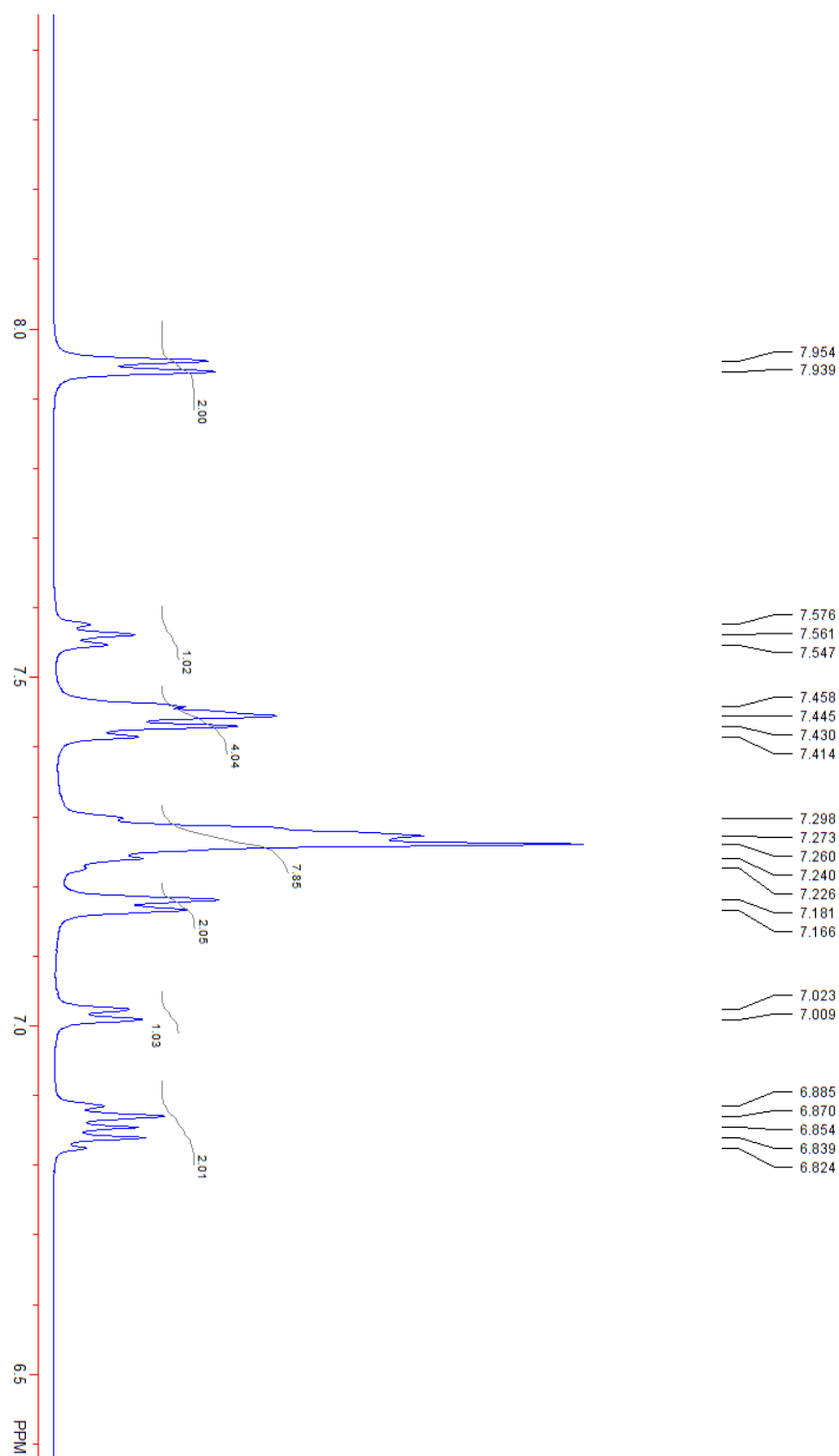


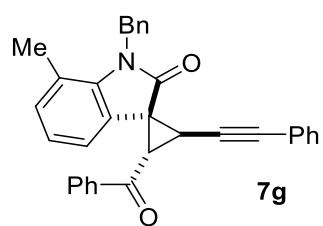
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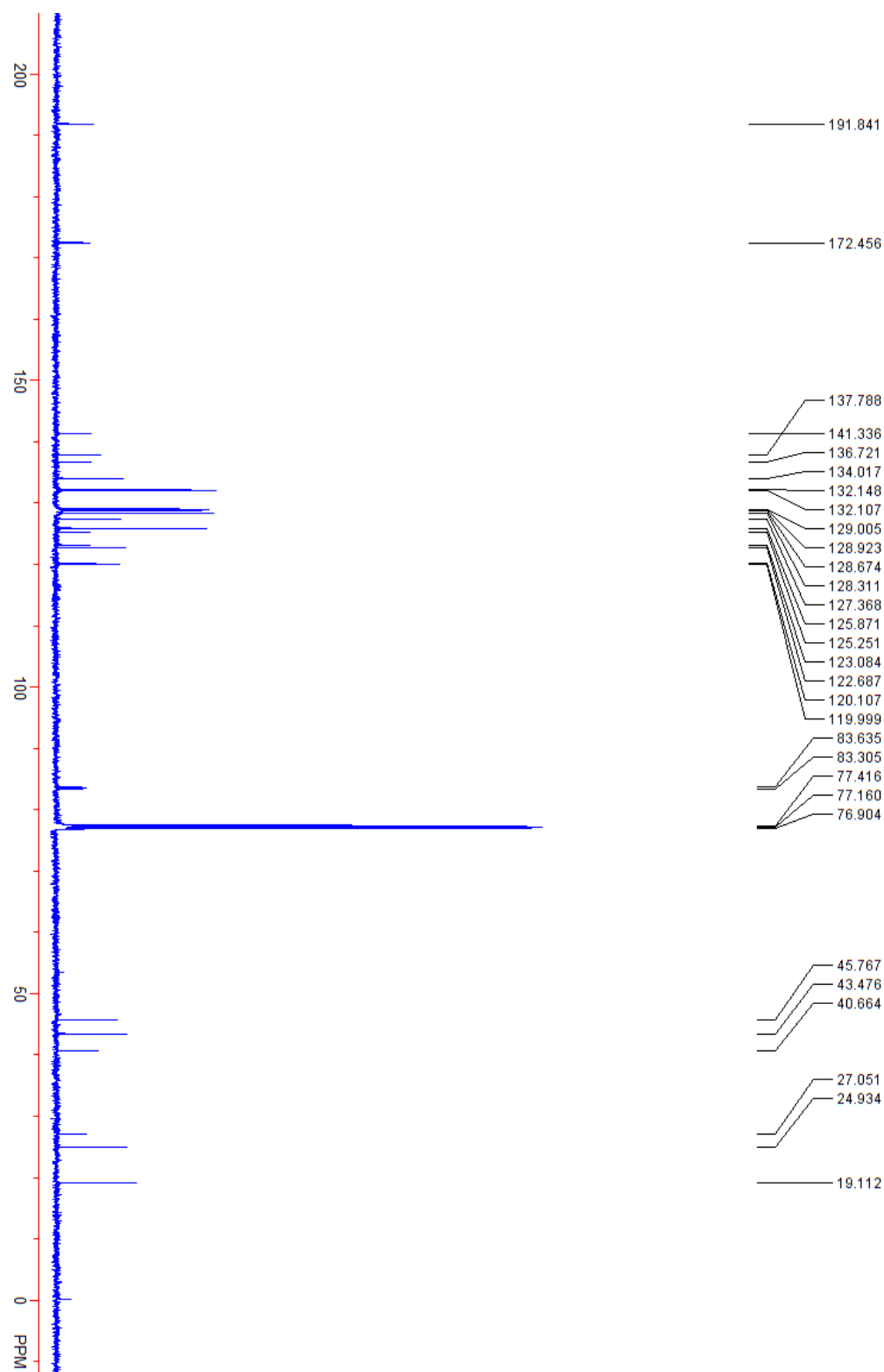


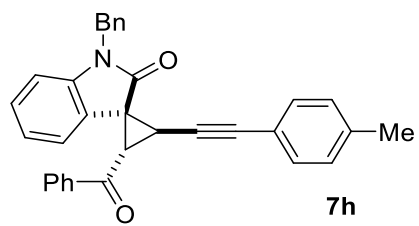
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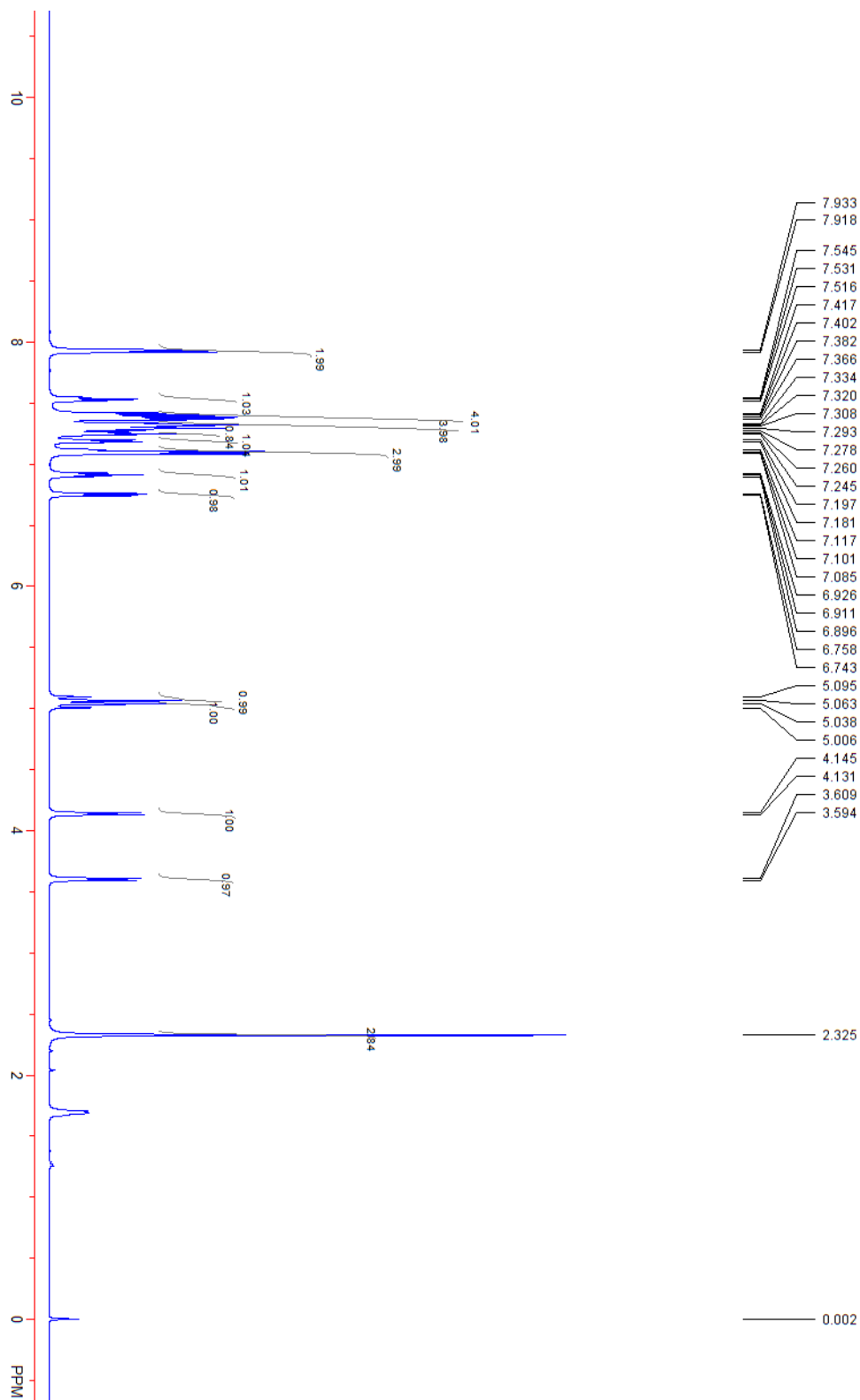


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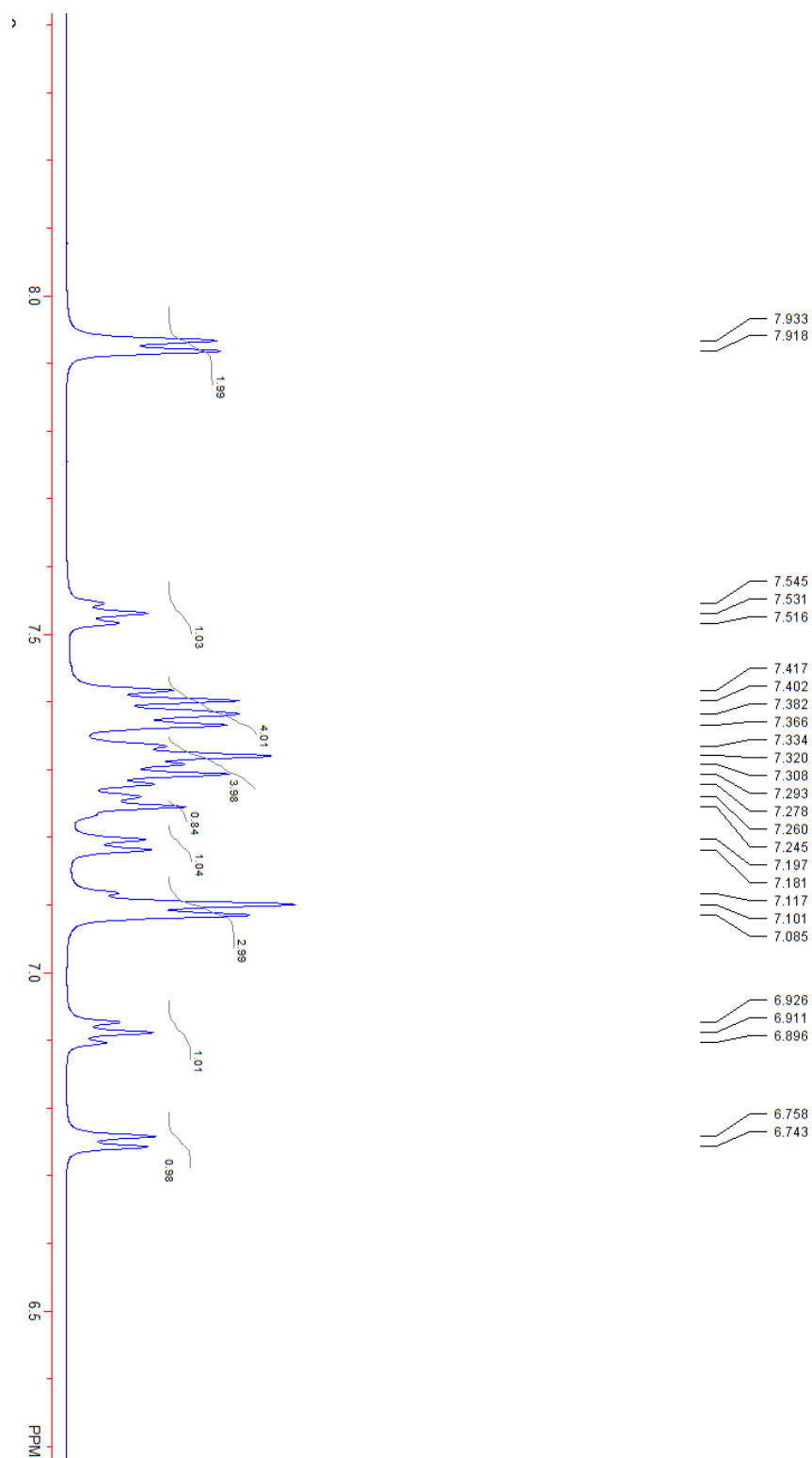


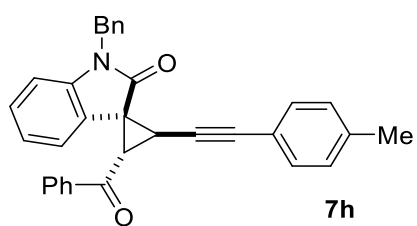


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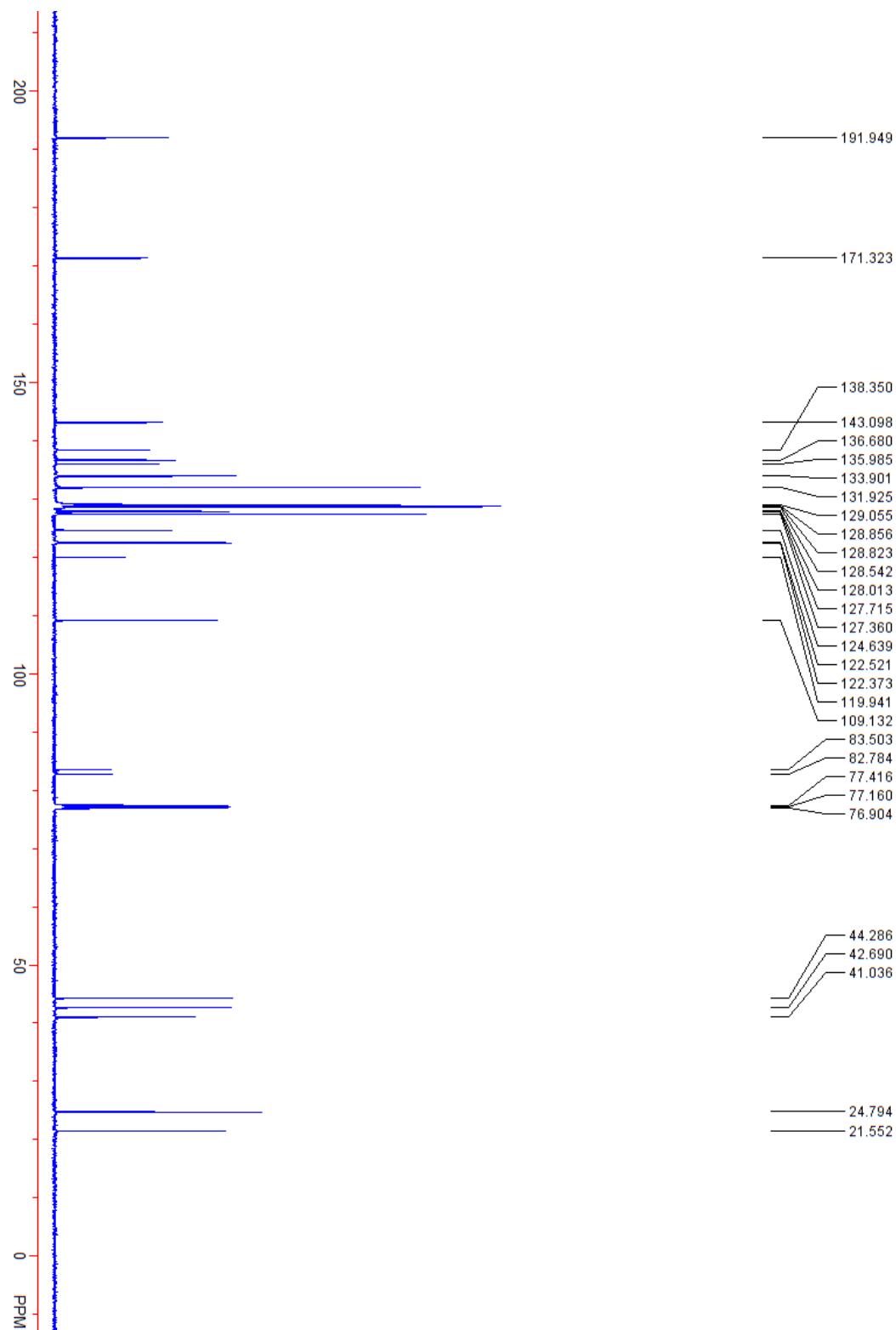


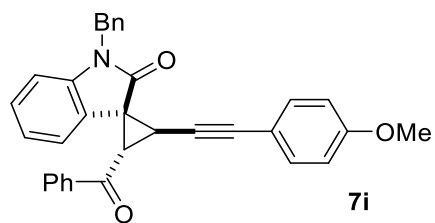
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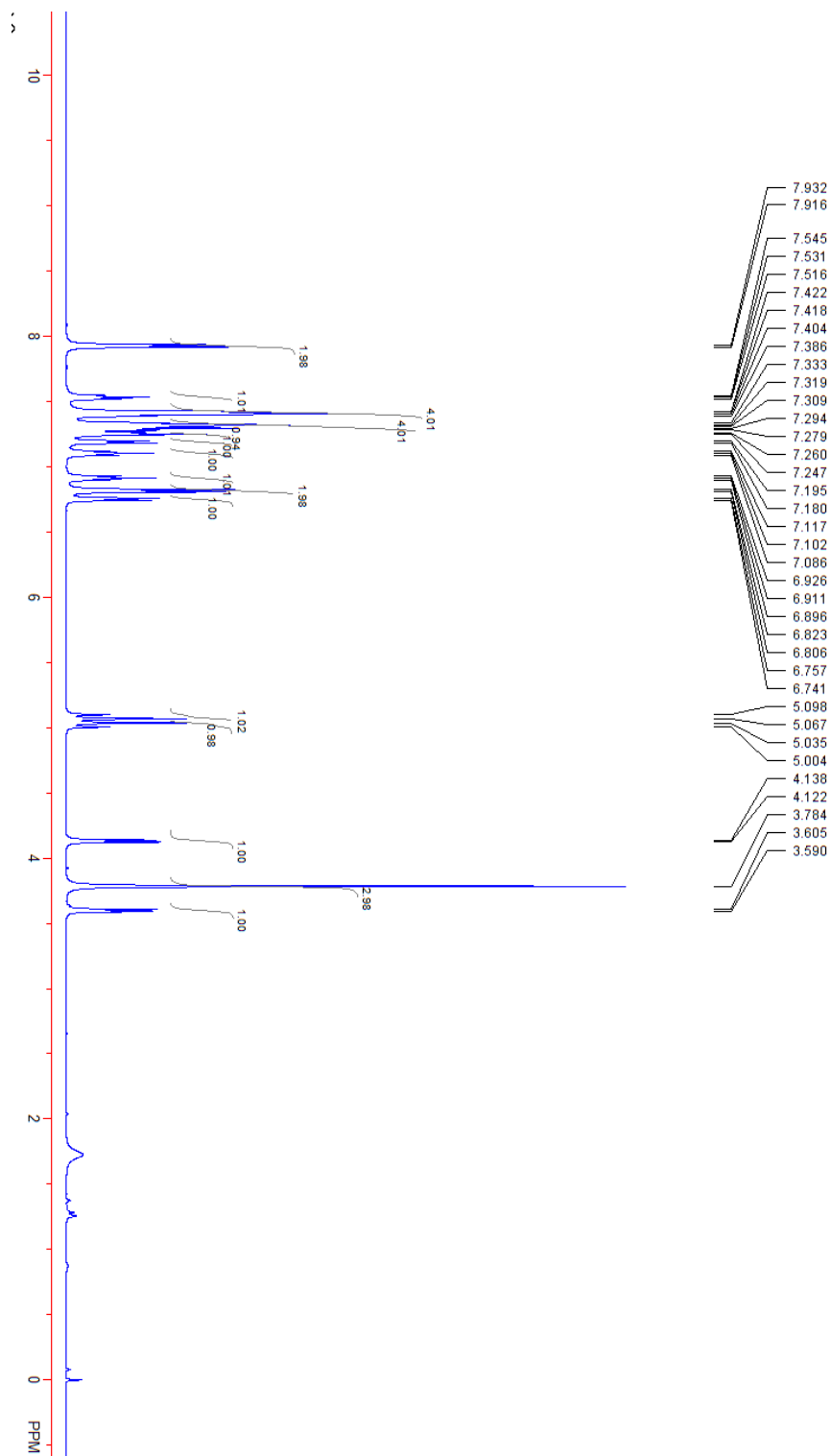


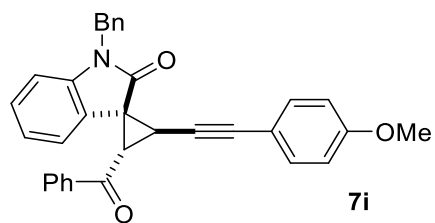
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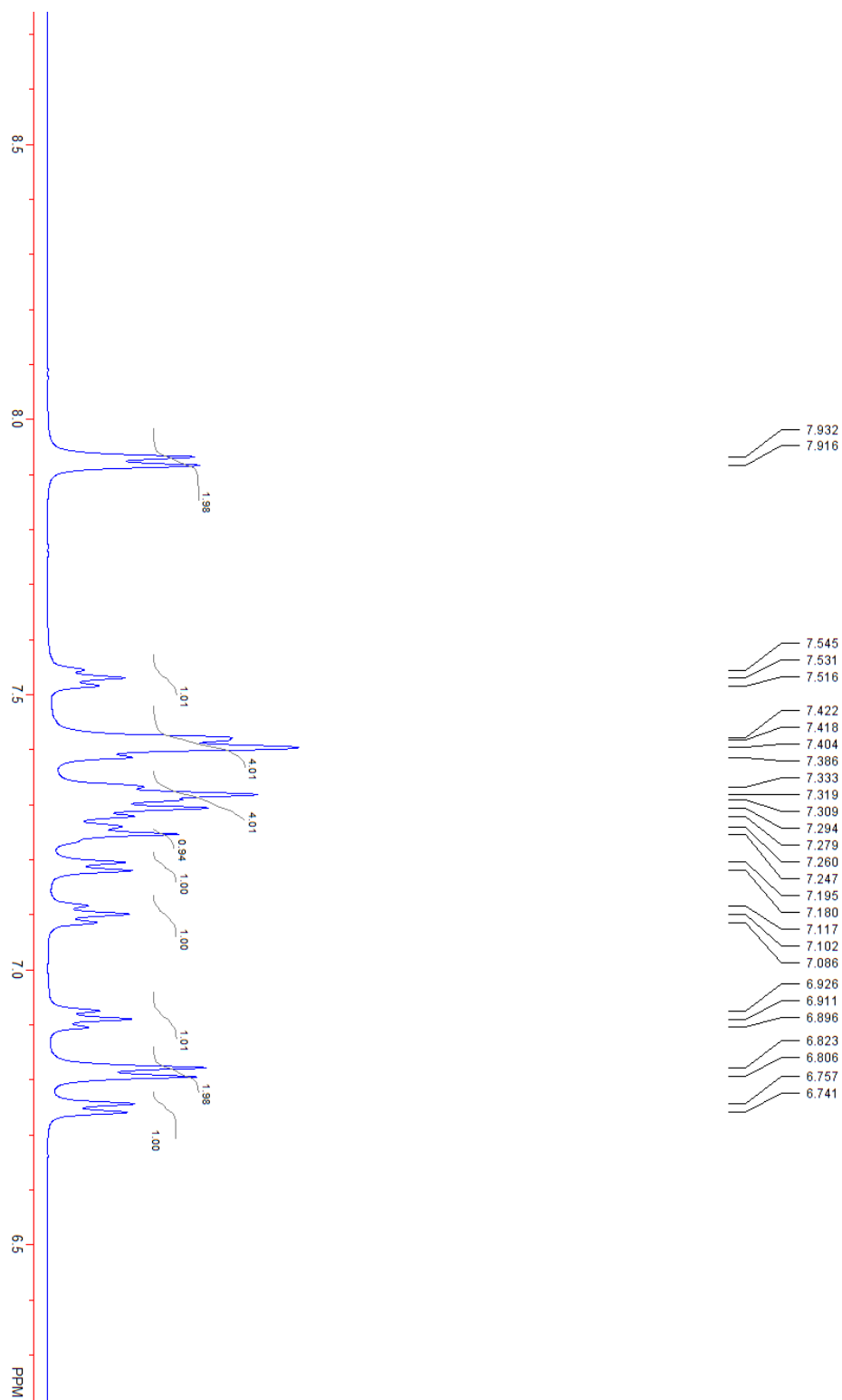


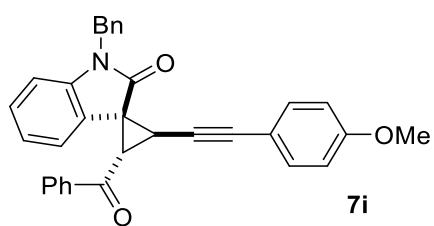
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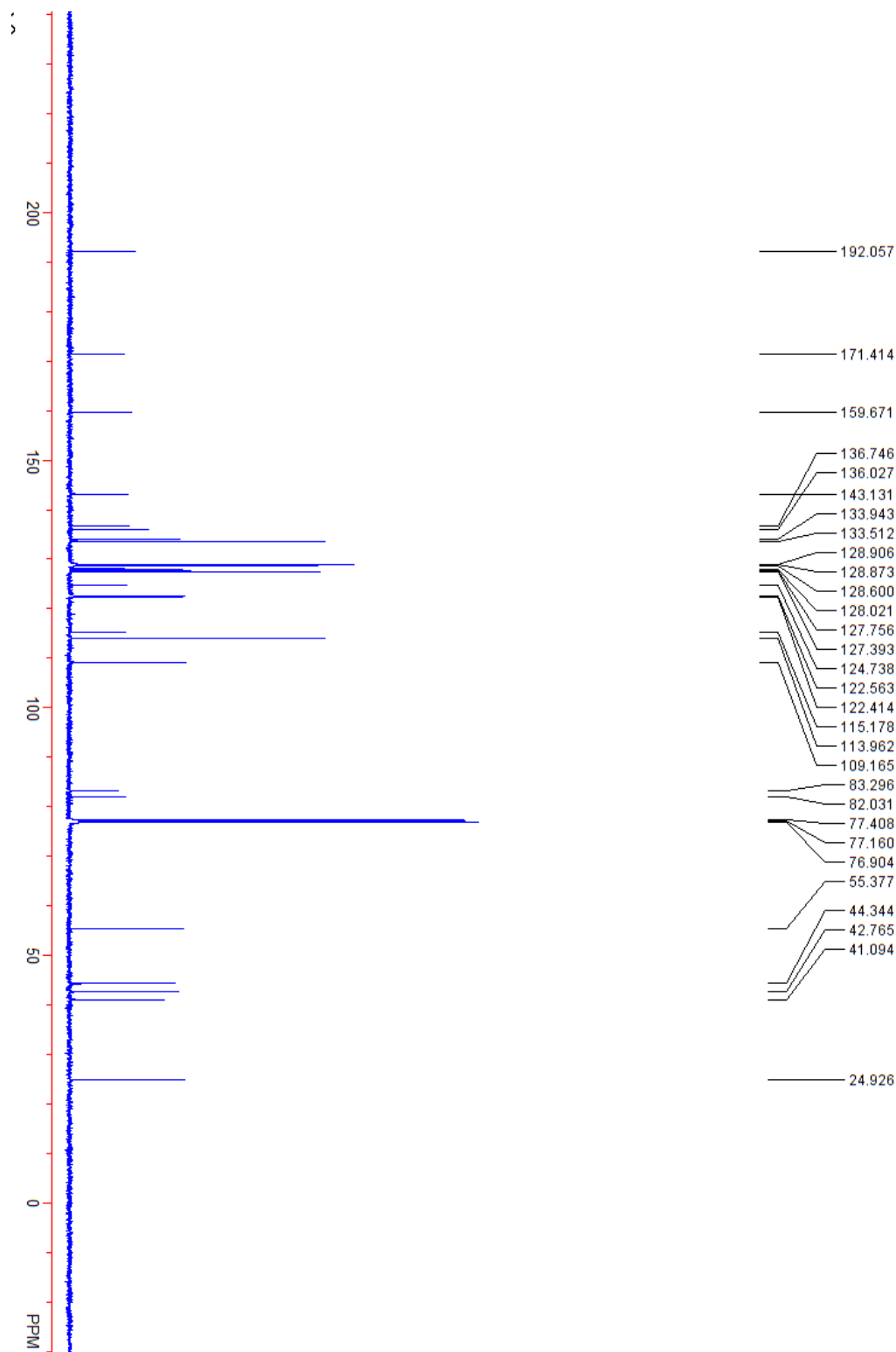


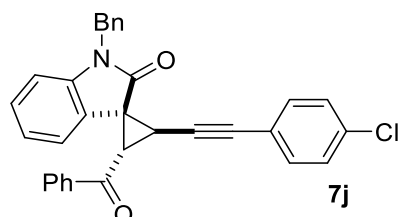
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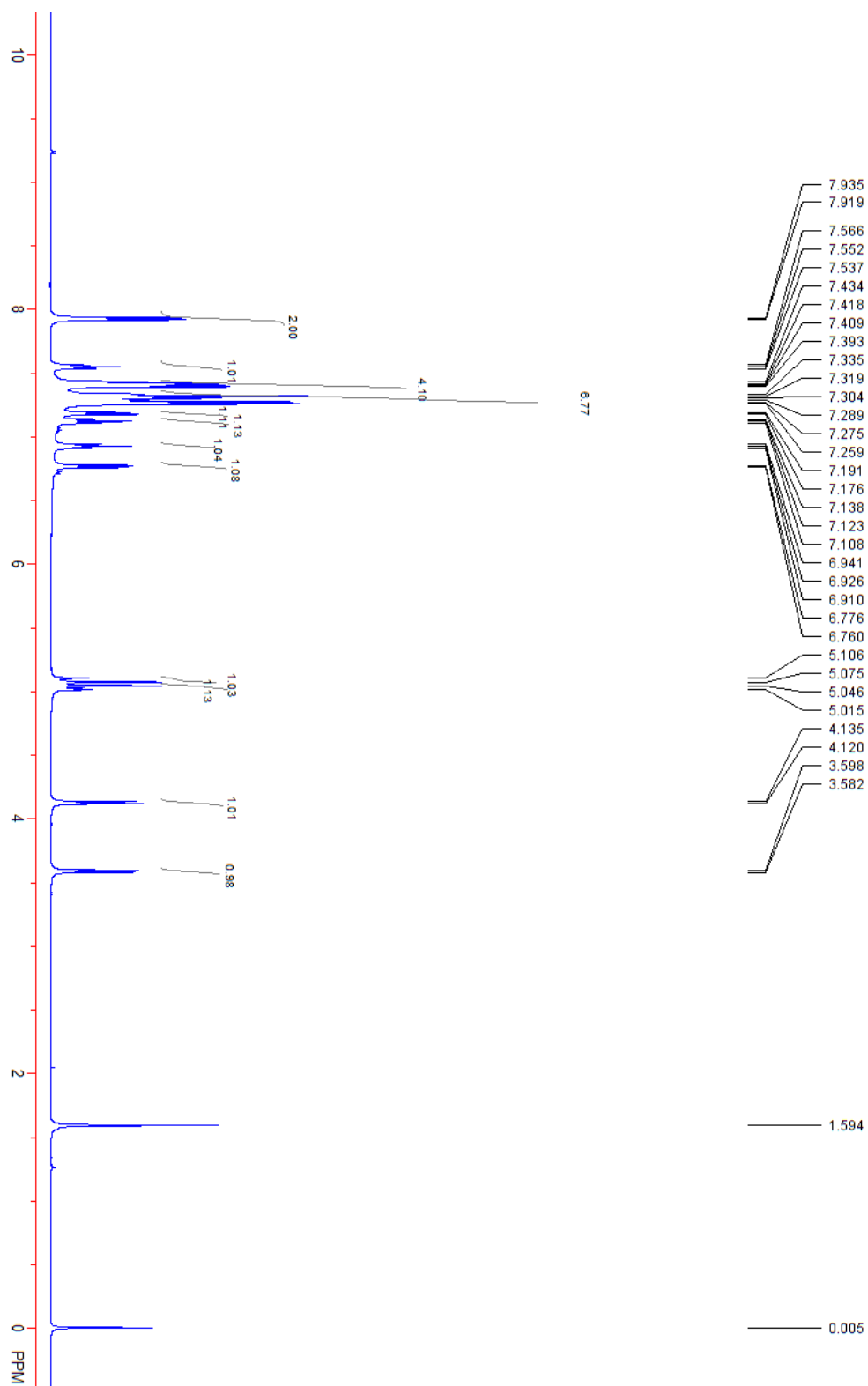


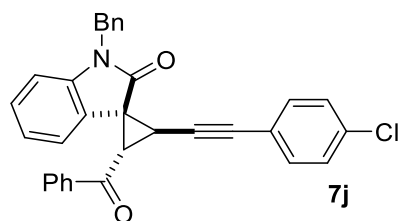
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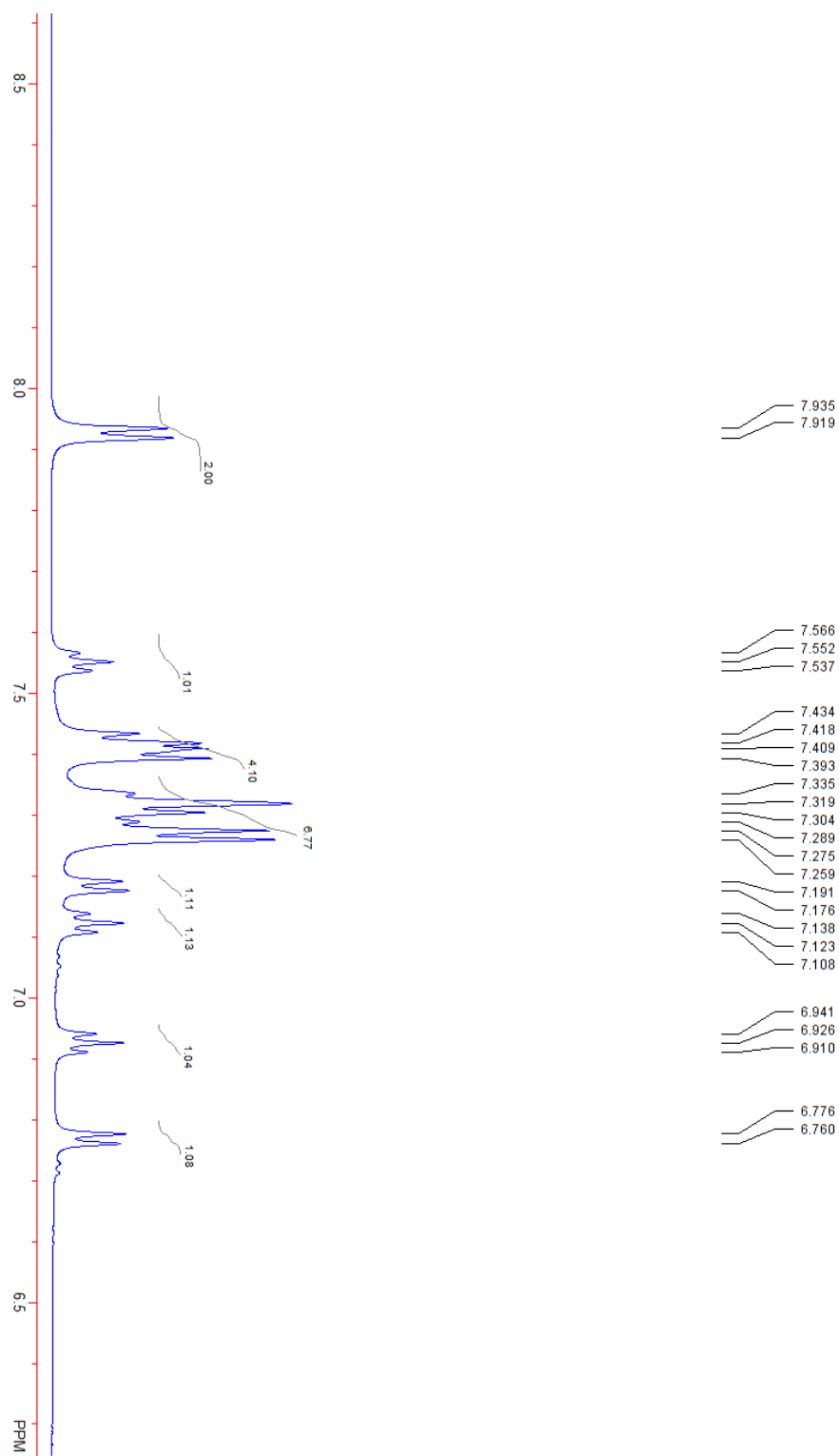


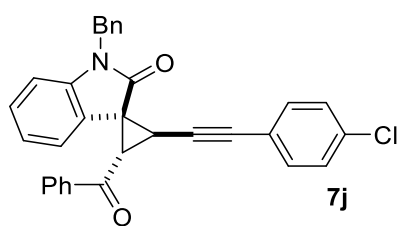
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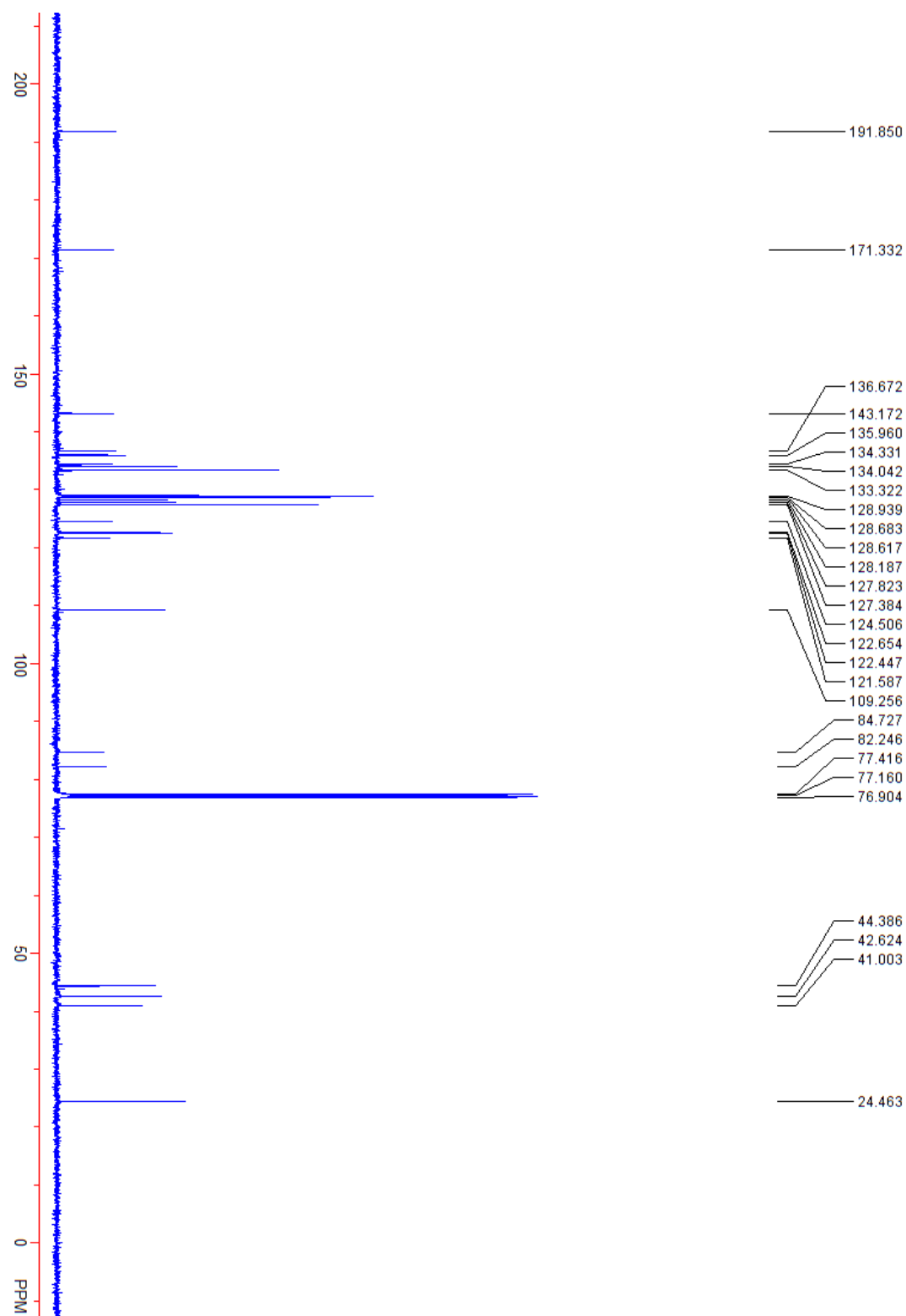


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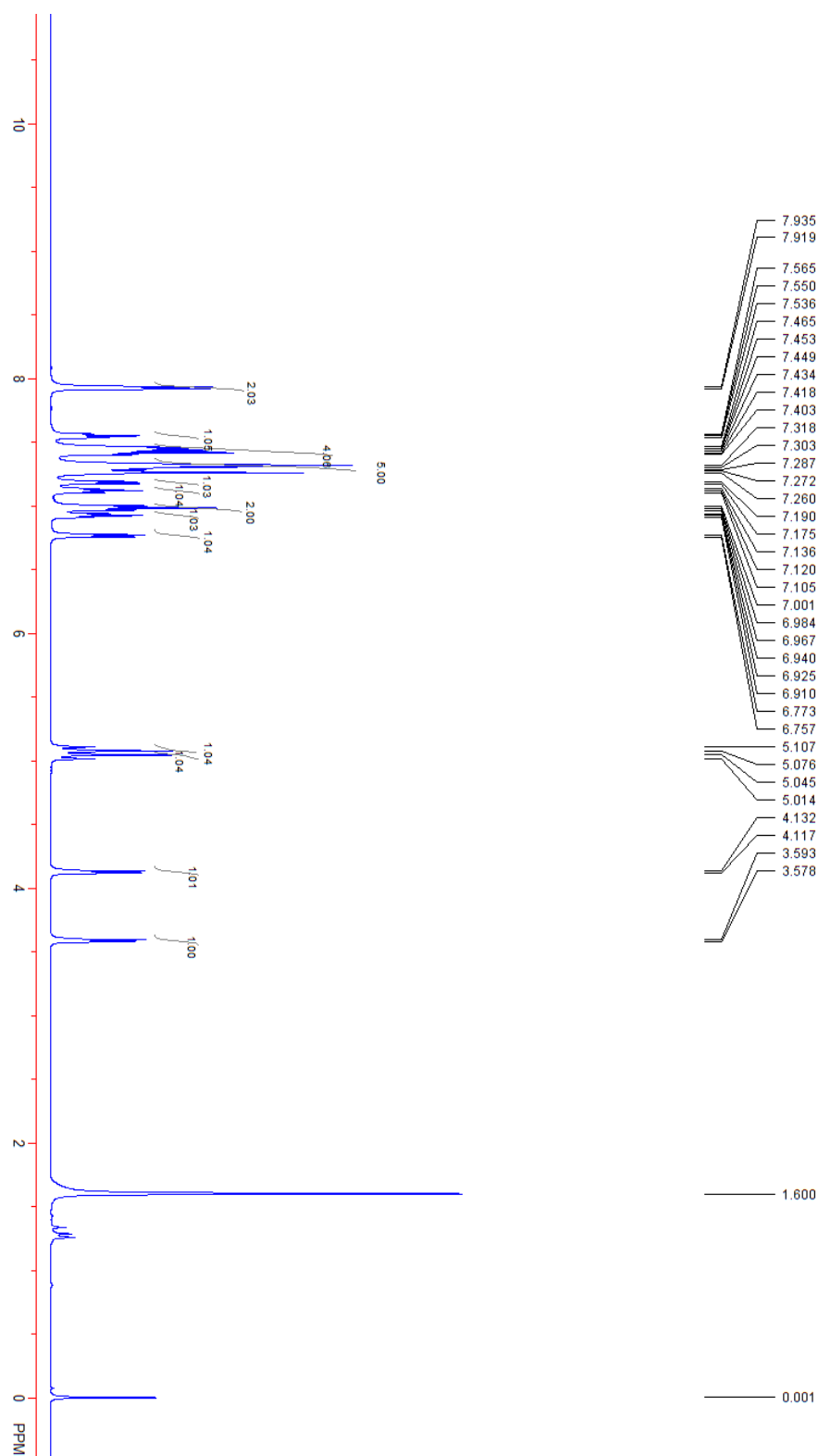
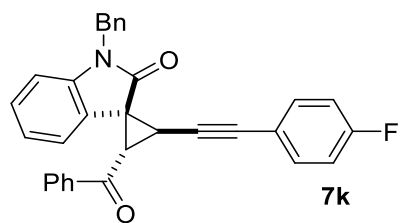




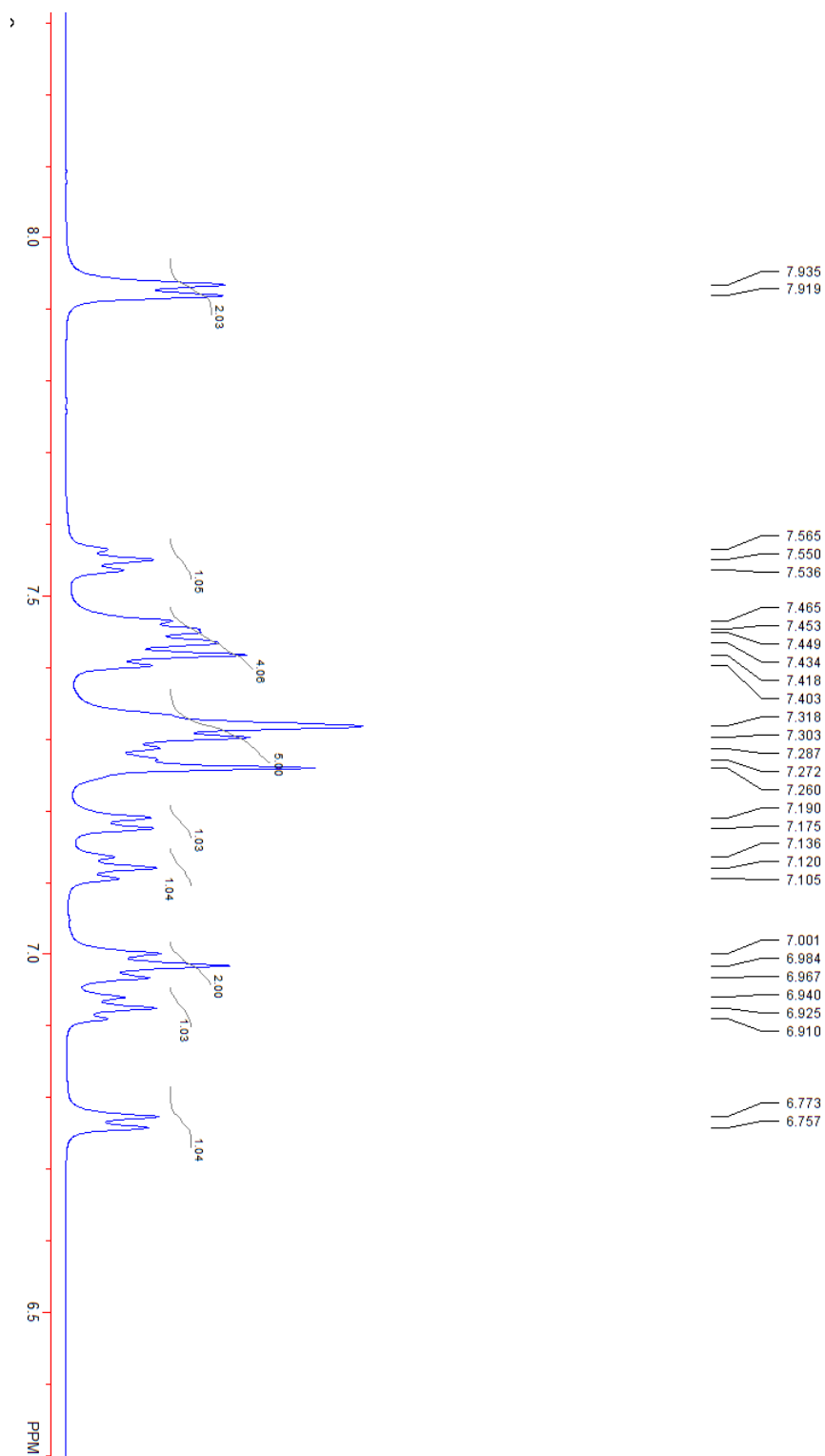
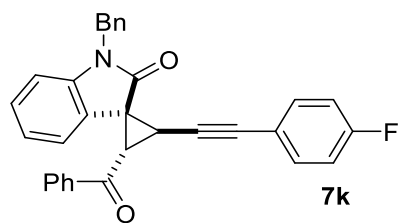
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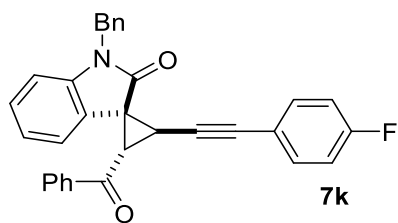


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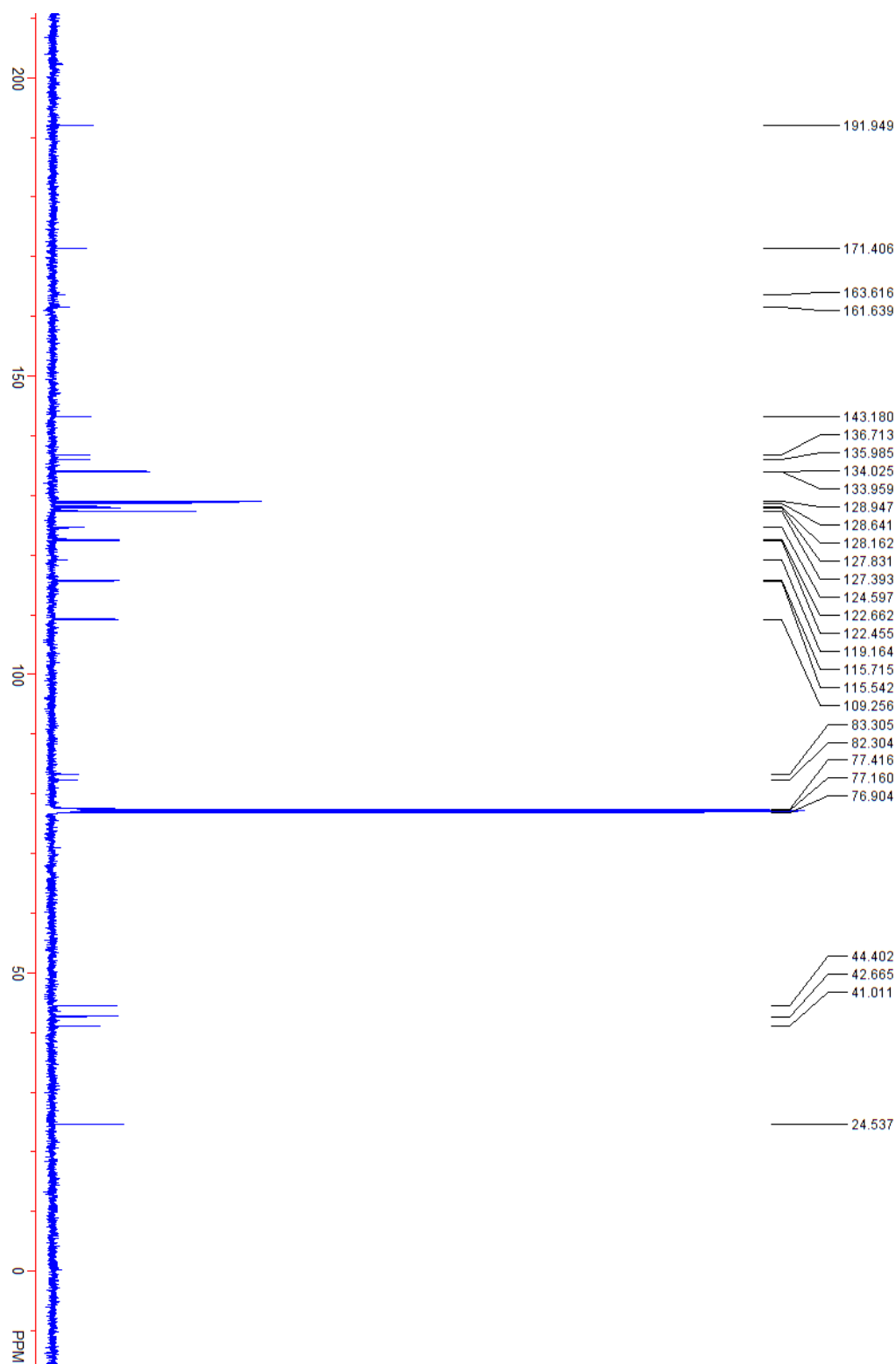


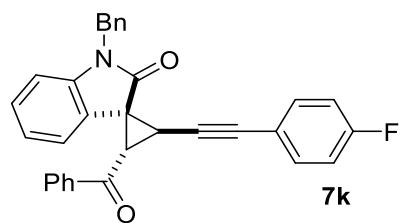
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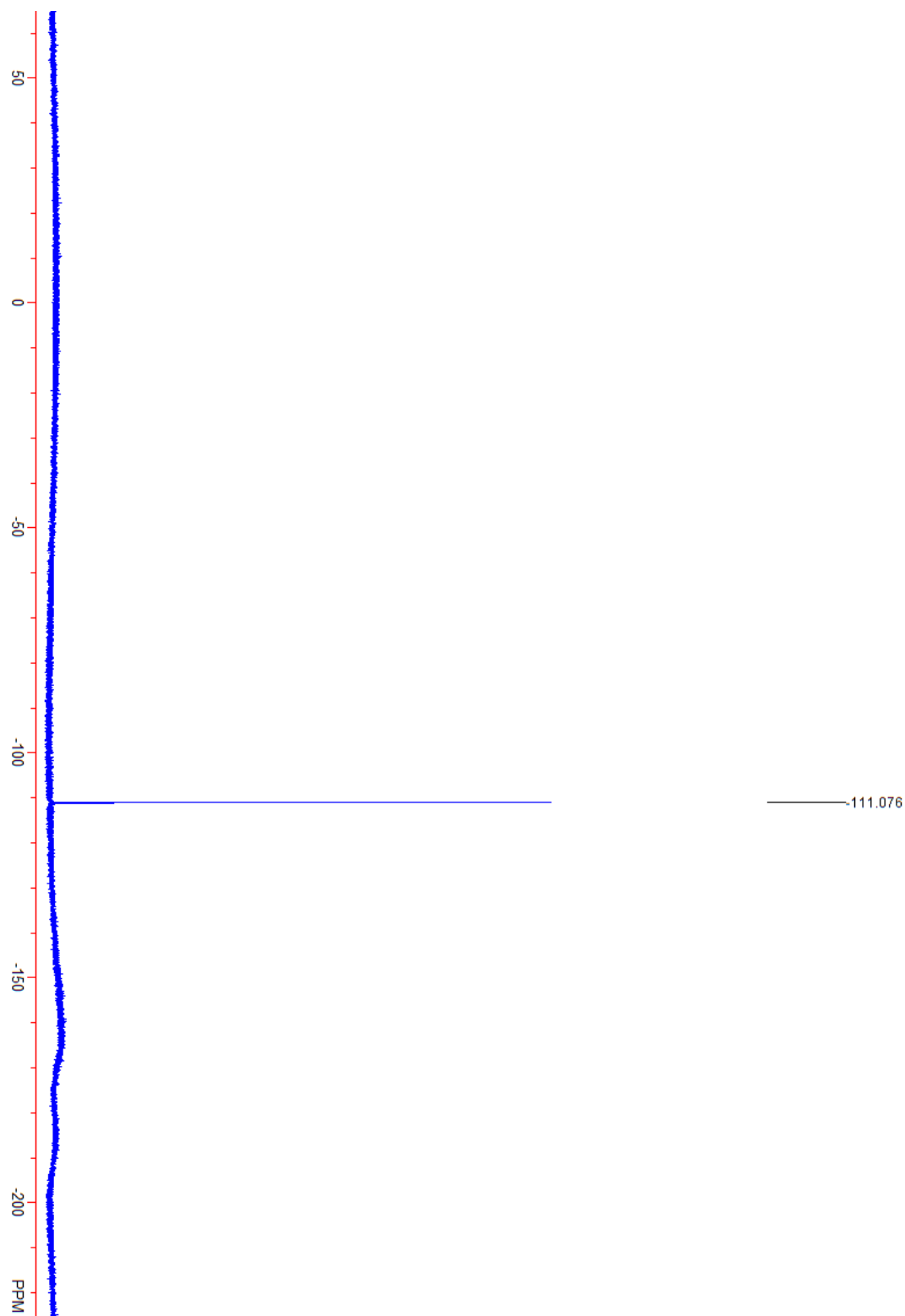


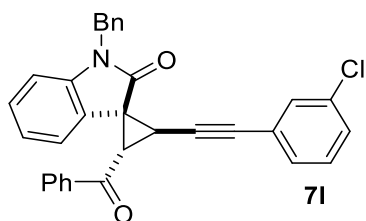
$^{13}\text{C}\{^1\text{H}\}$ NMR:



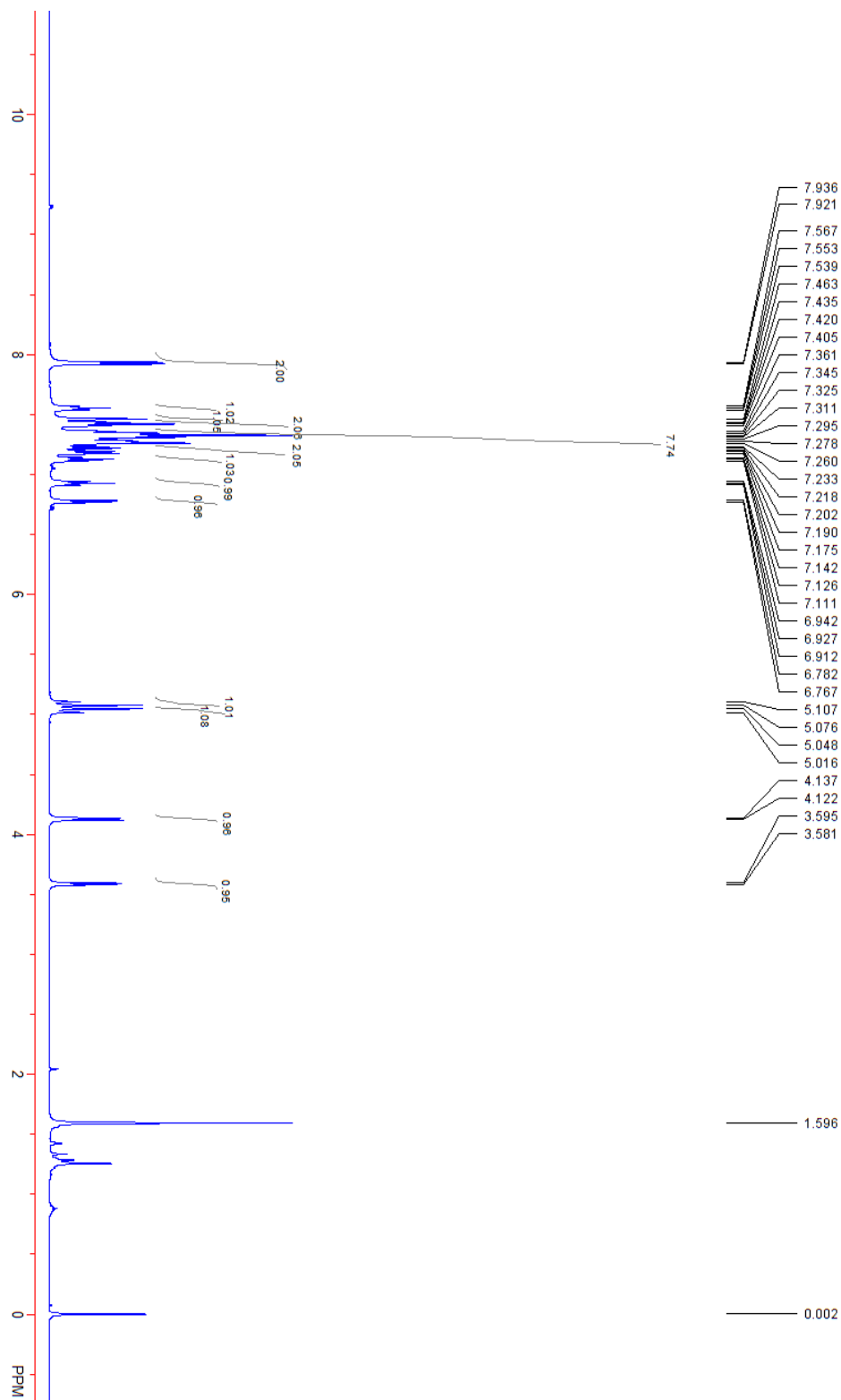


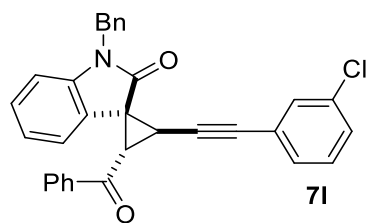
^{19}F NMR:



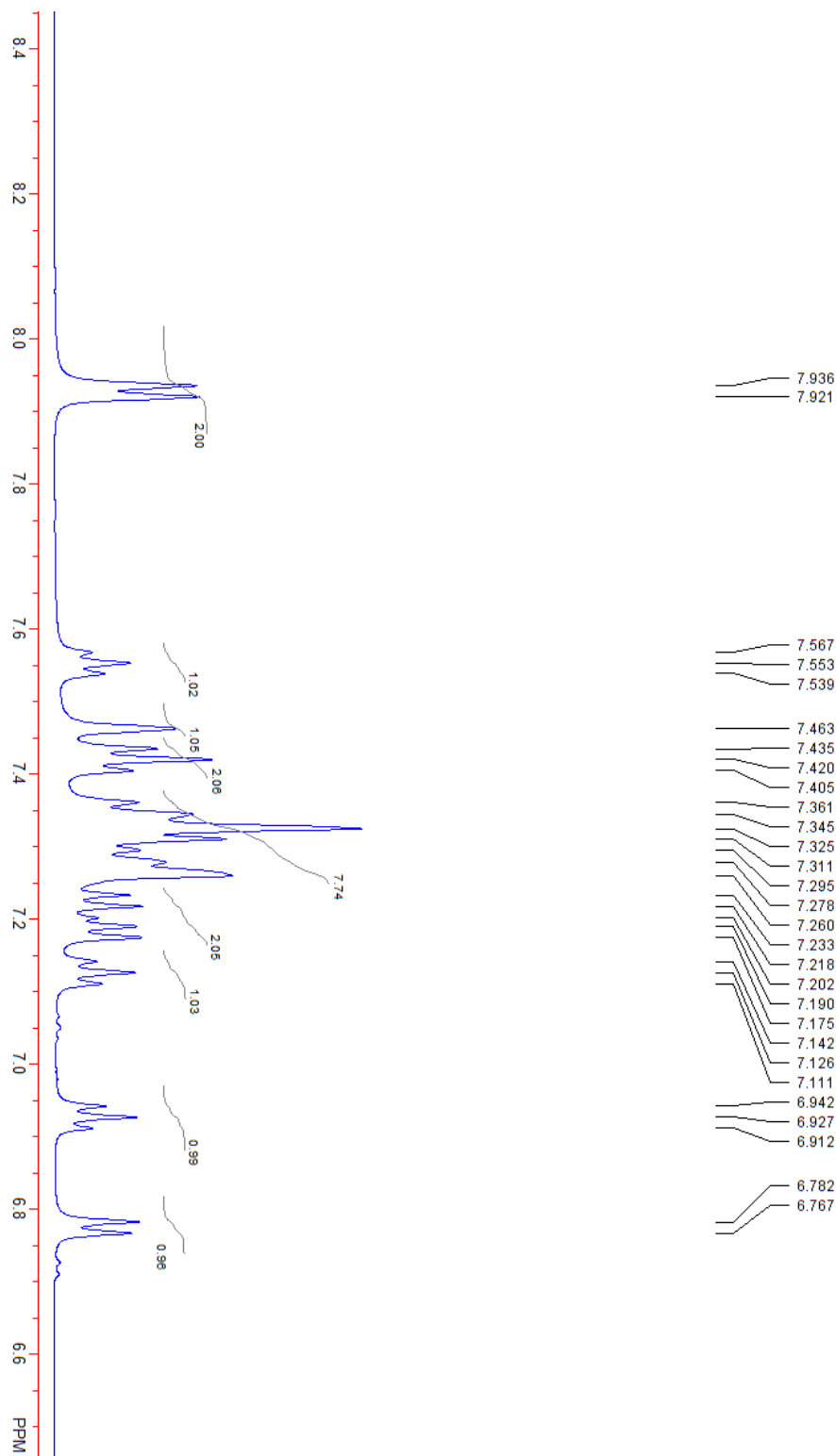


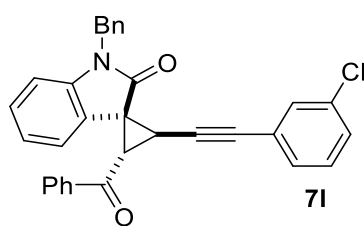
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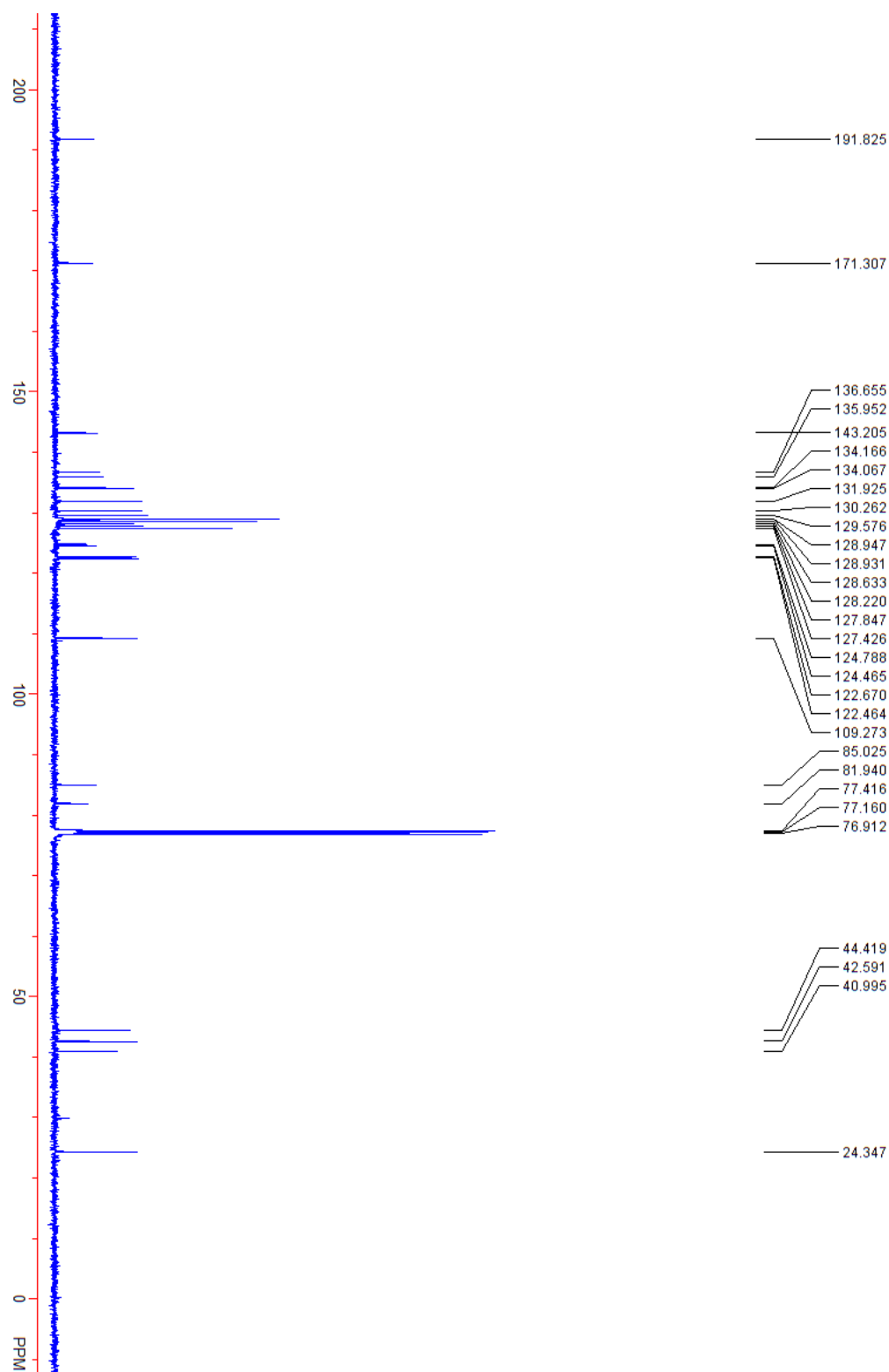


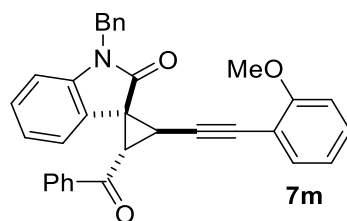
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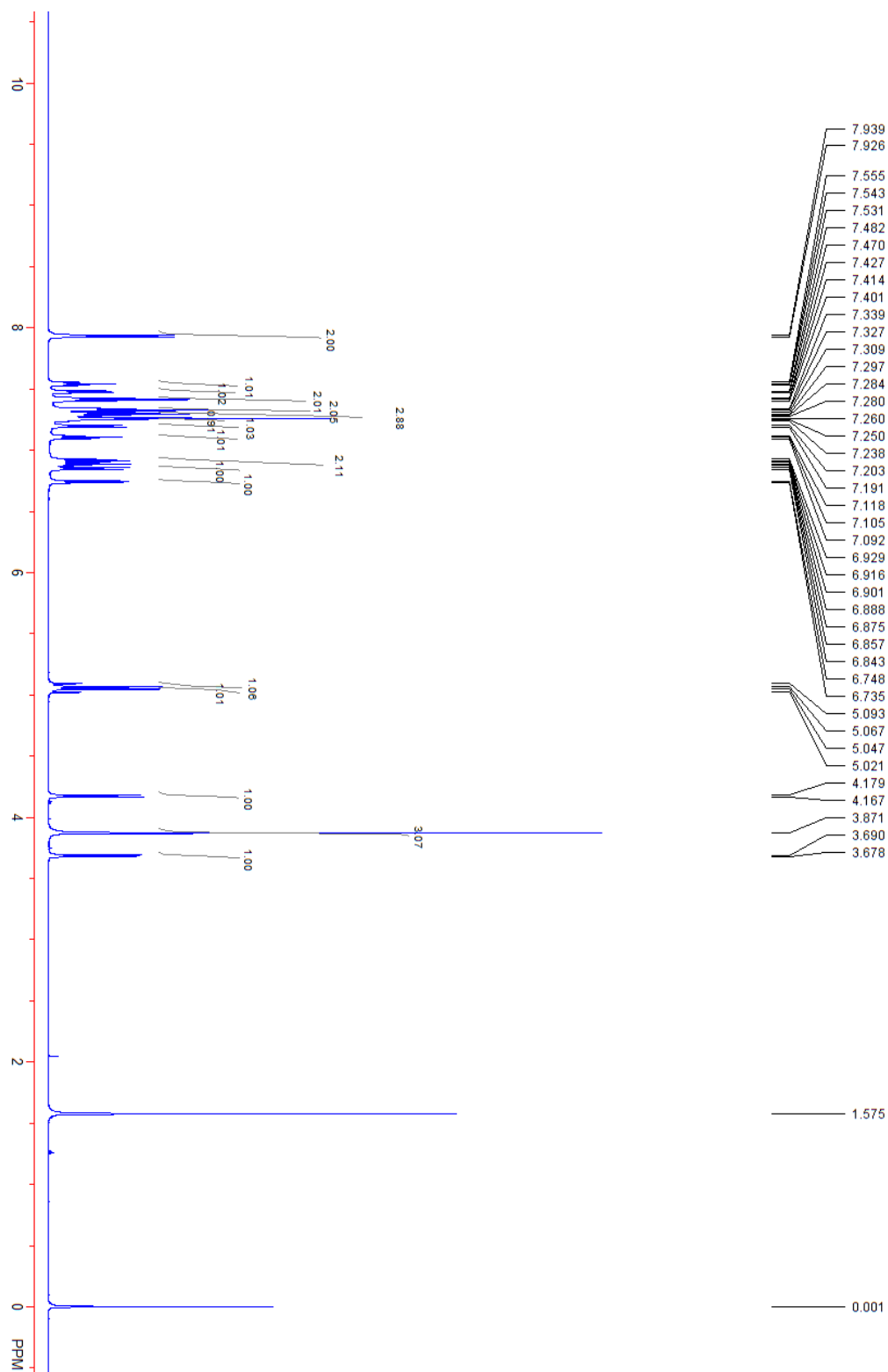


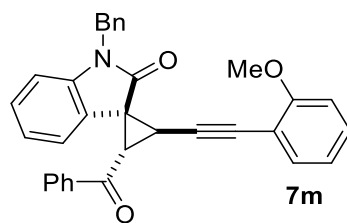
$^{13}\text{C}\{^1\text{H}\}$ NMR:



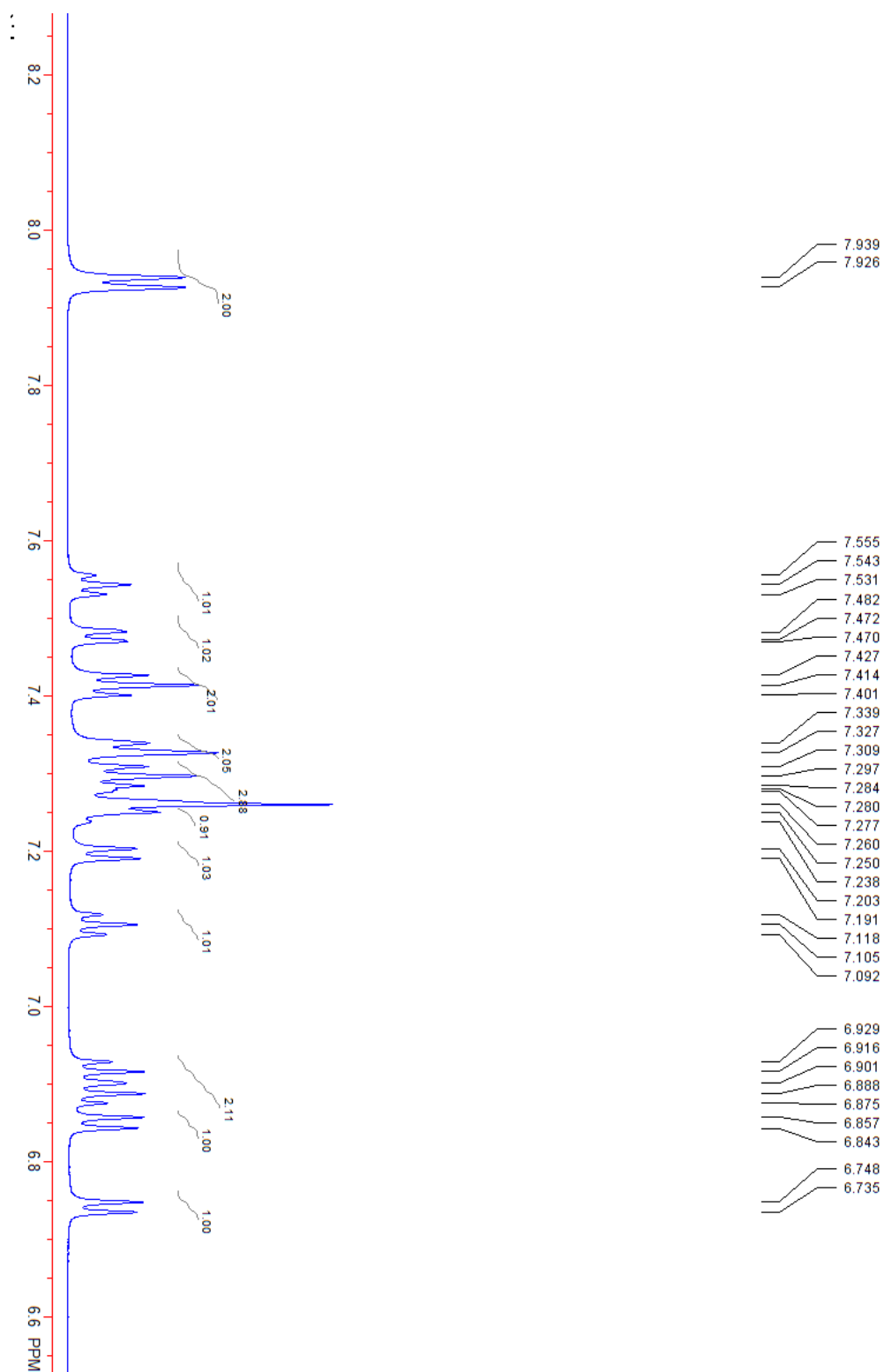


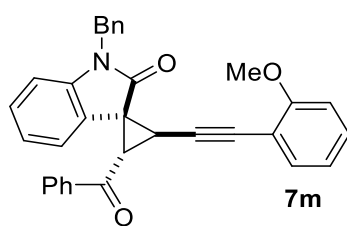
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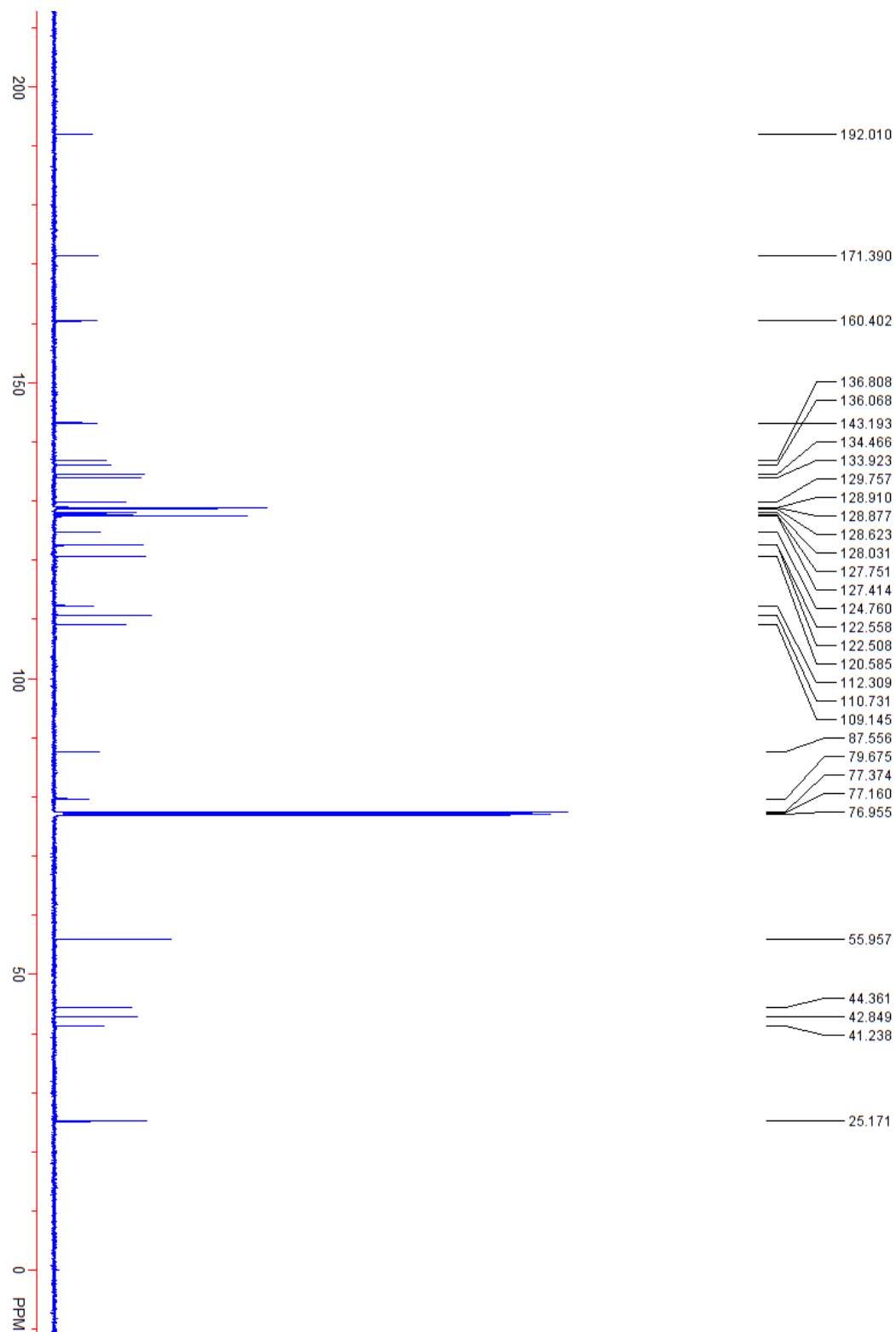


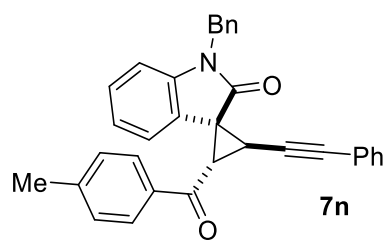
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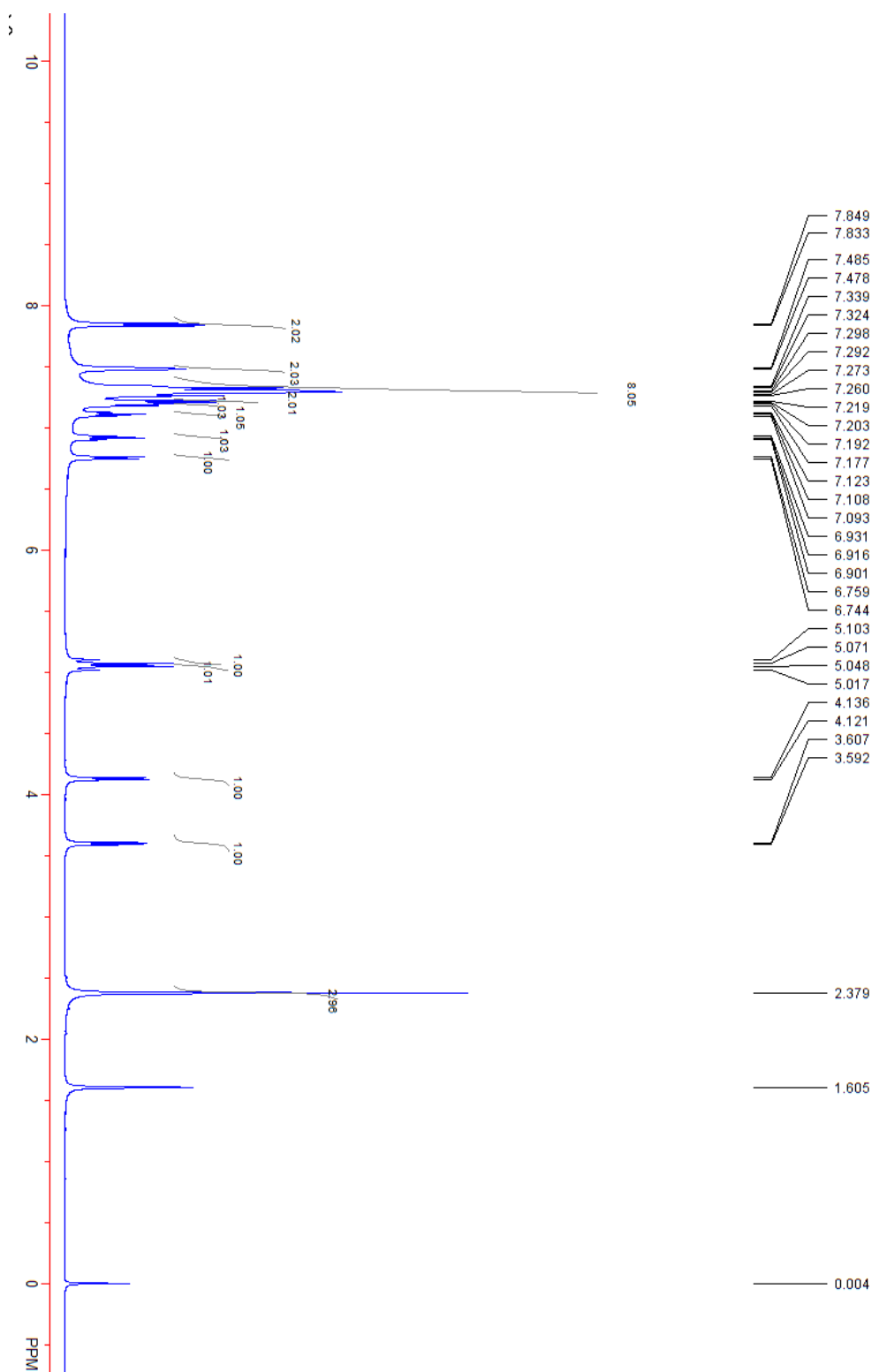


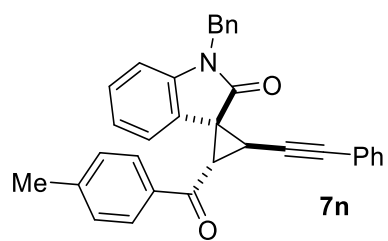
$^{13}\text{C}\{^1\text{H}\}$ NMR:



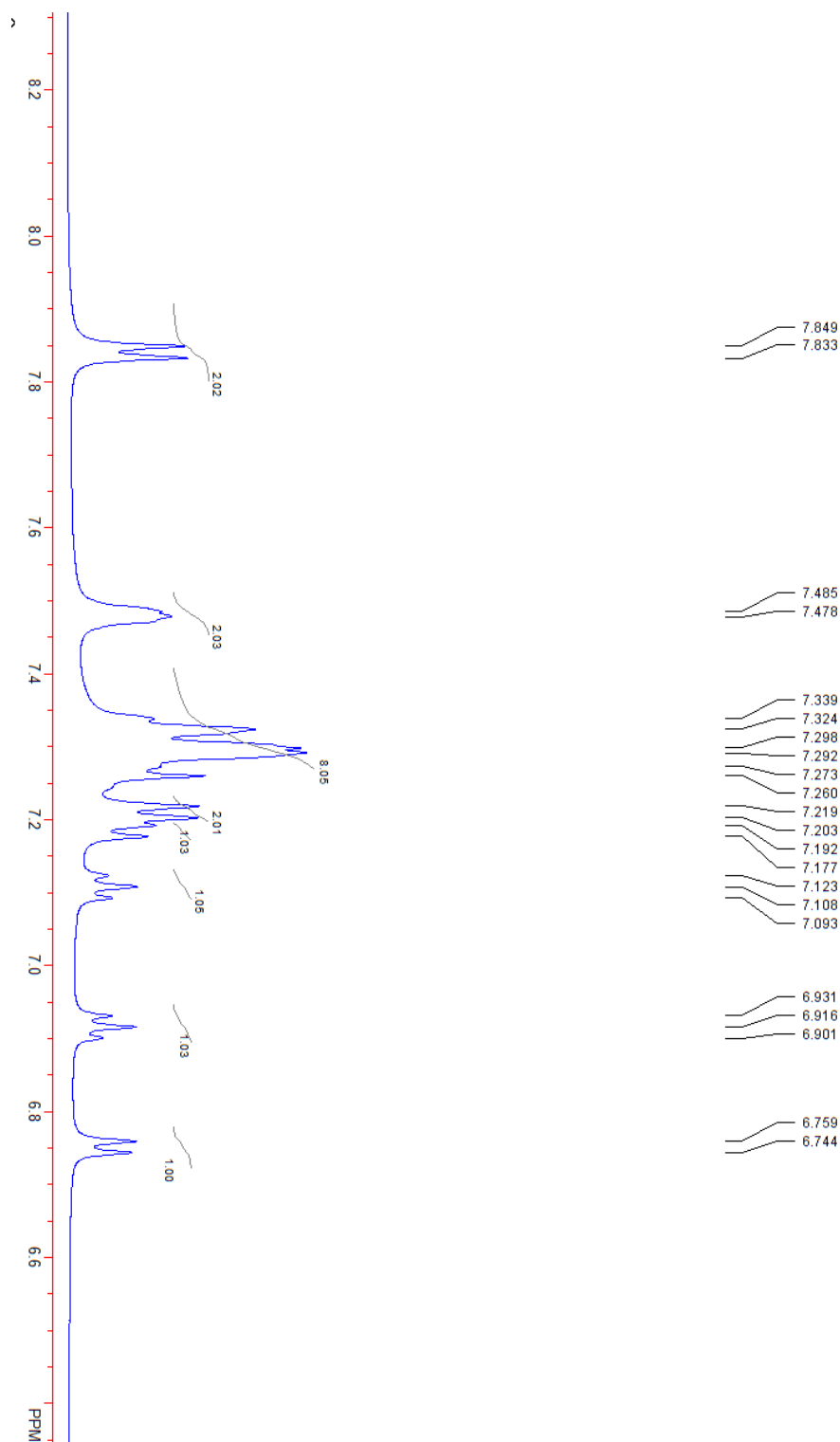


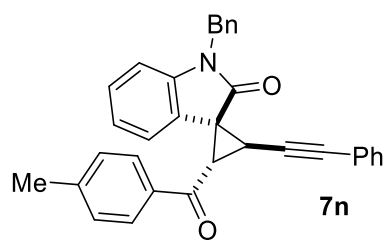
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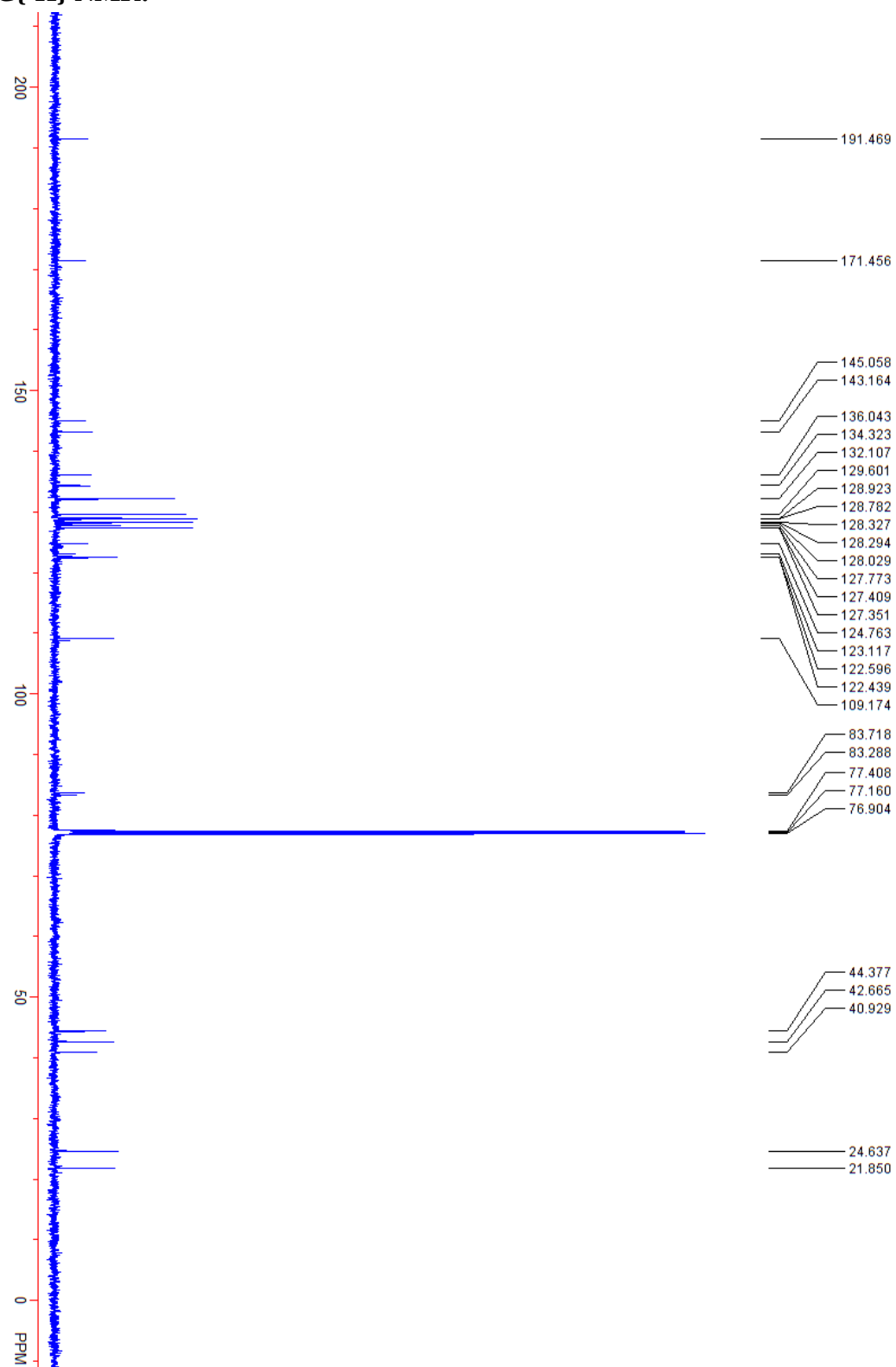


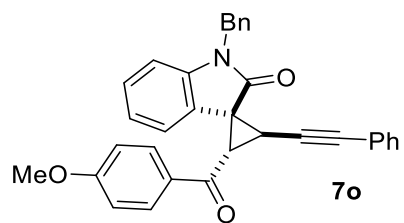
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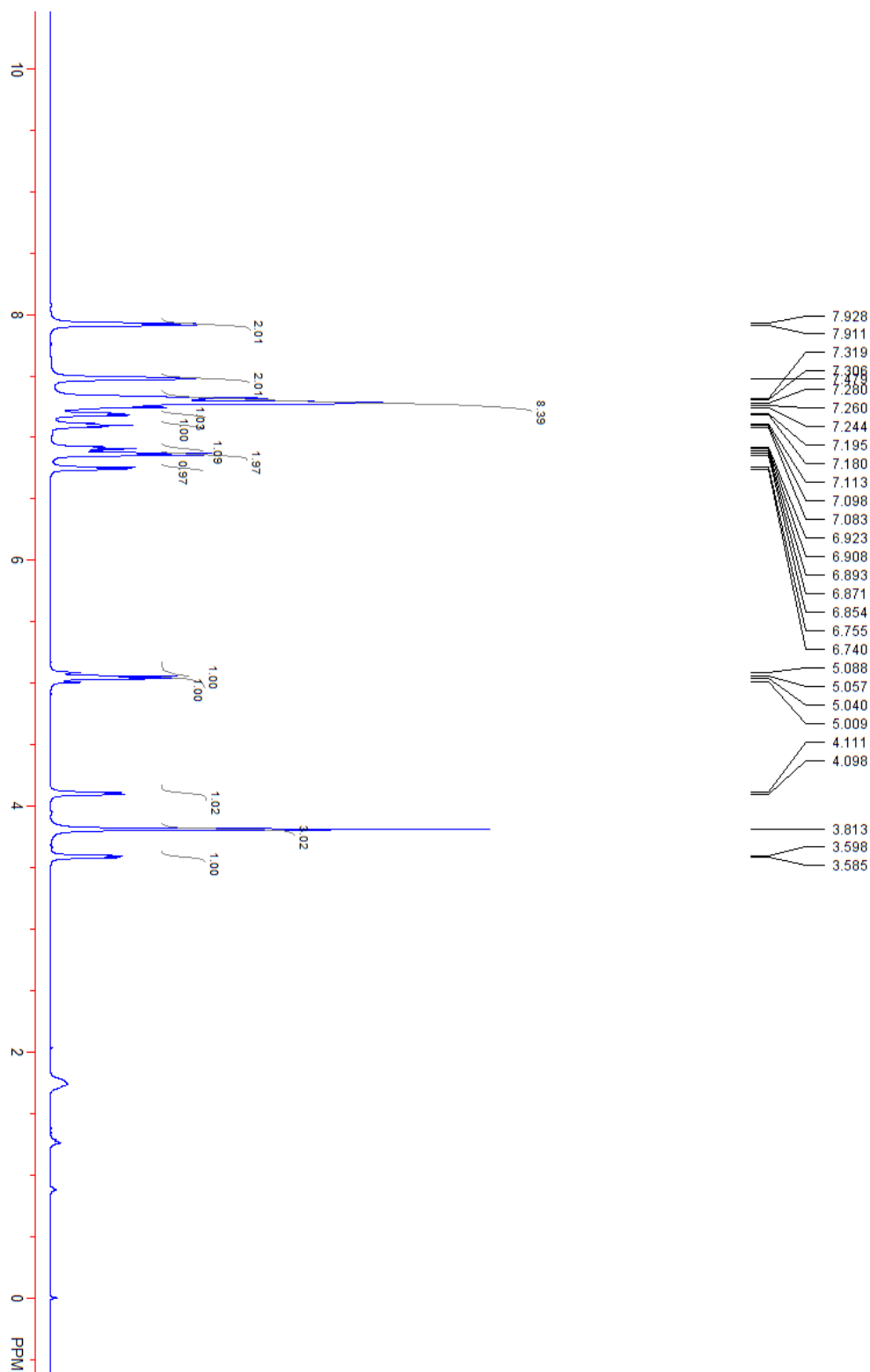


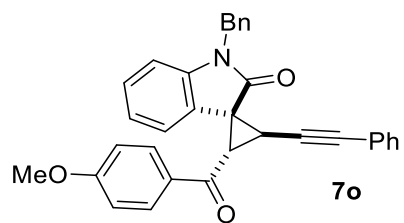
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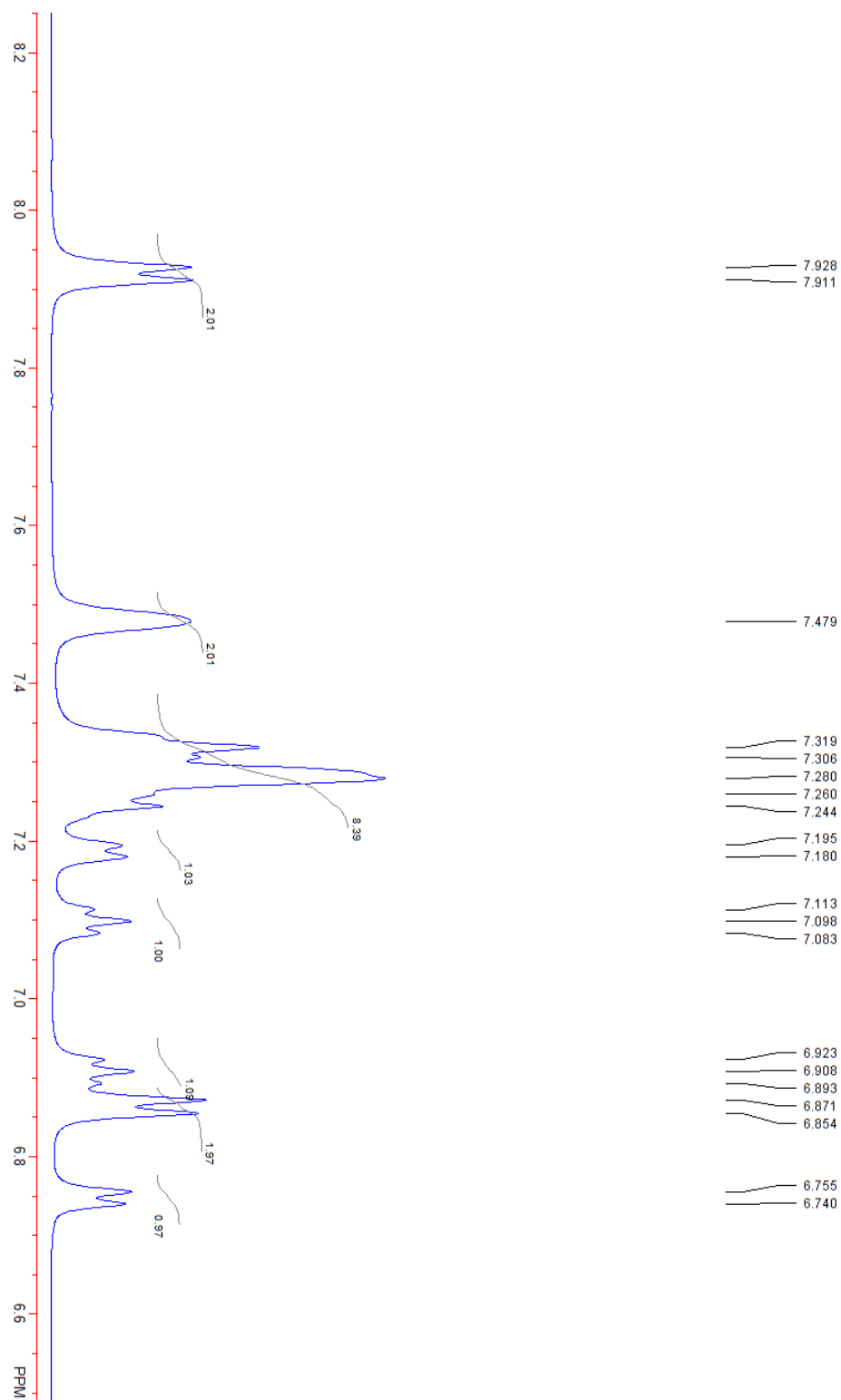


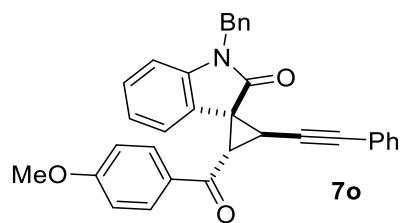
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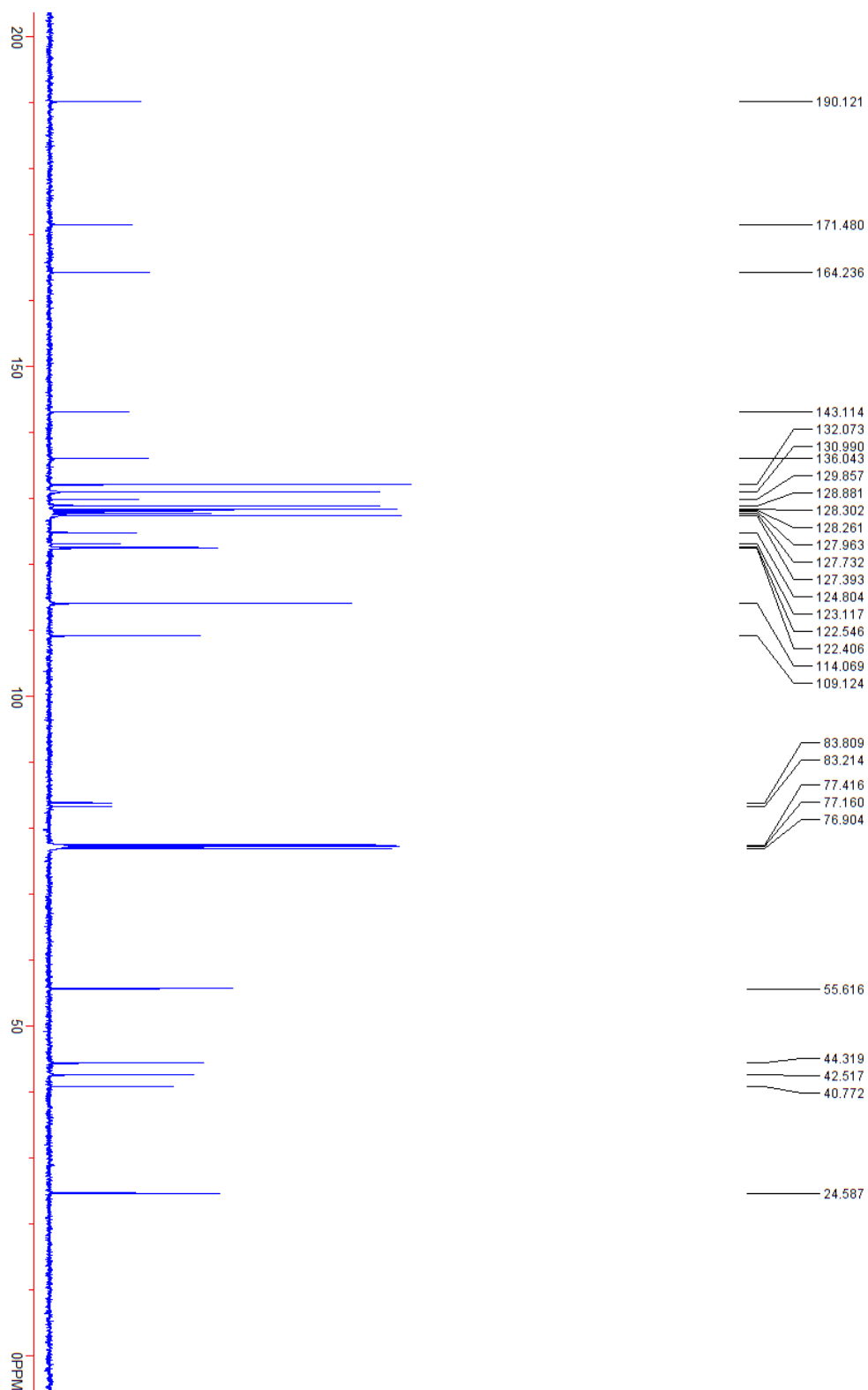


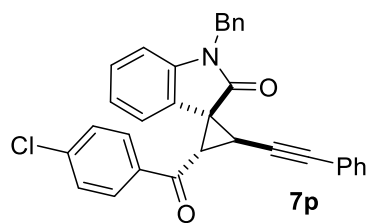
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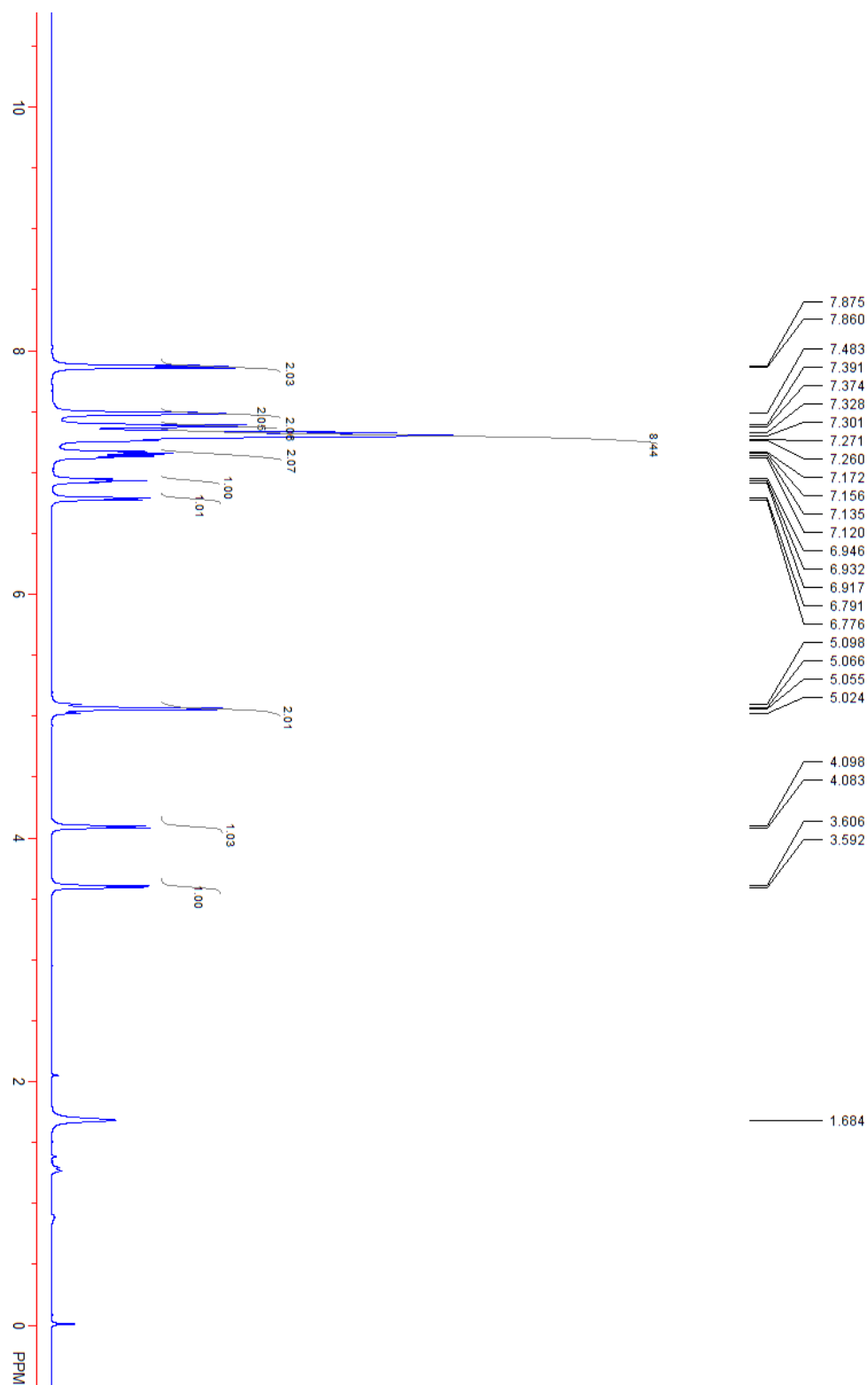


$^{13}\text{C}\{^1\text{H}\}$ NMR:

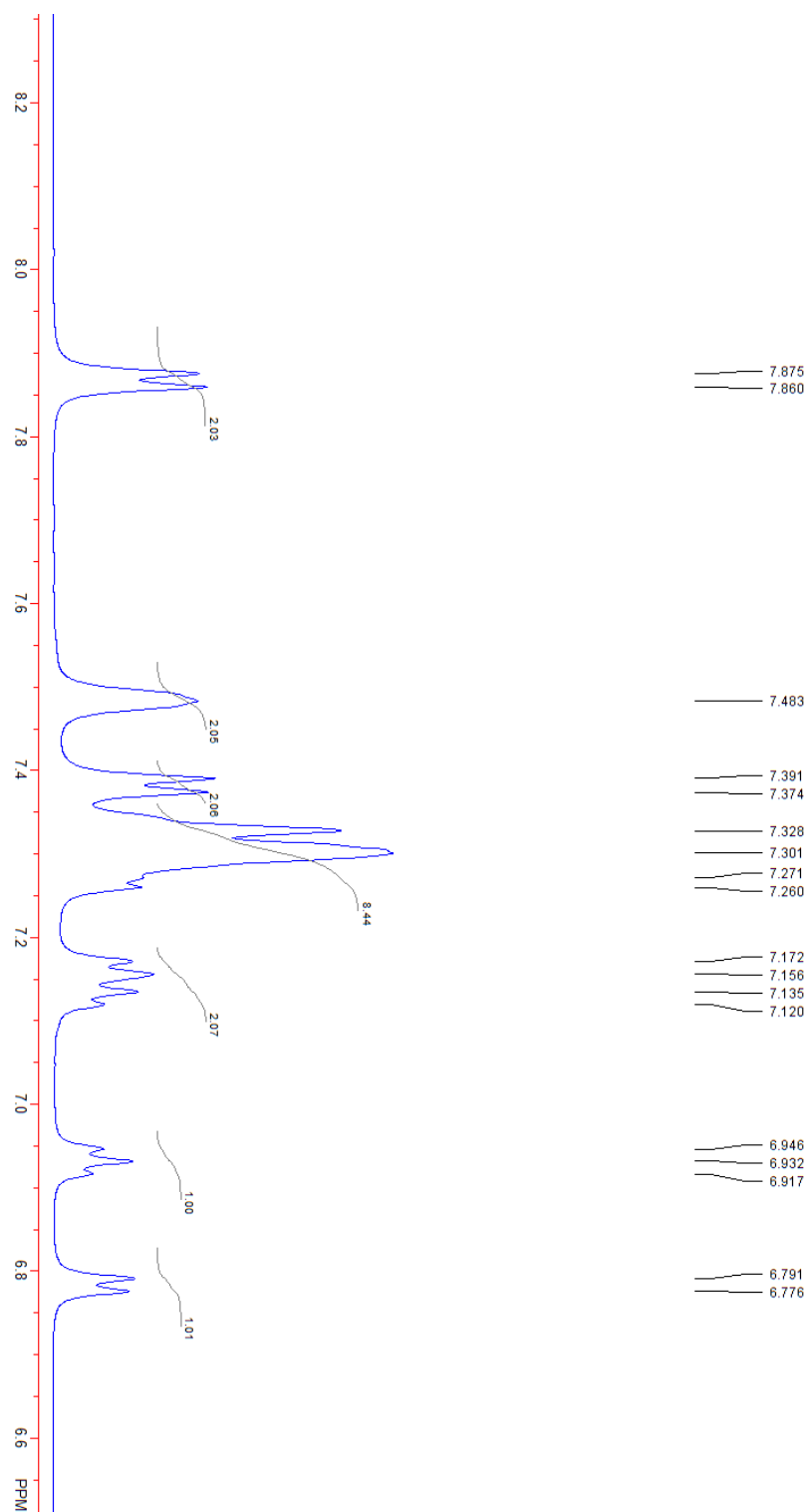
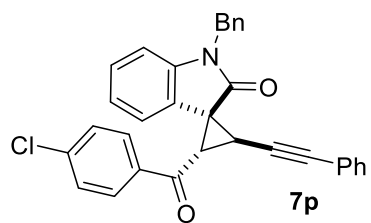


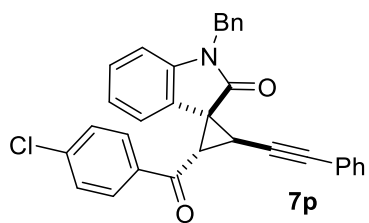


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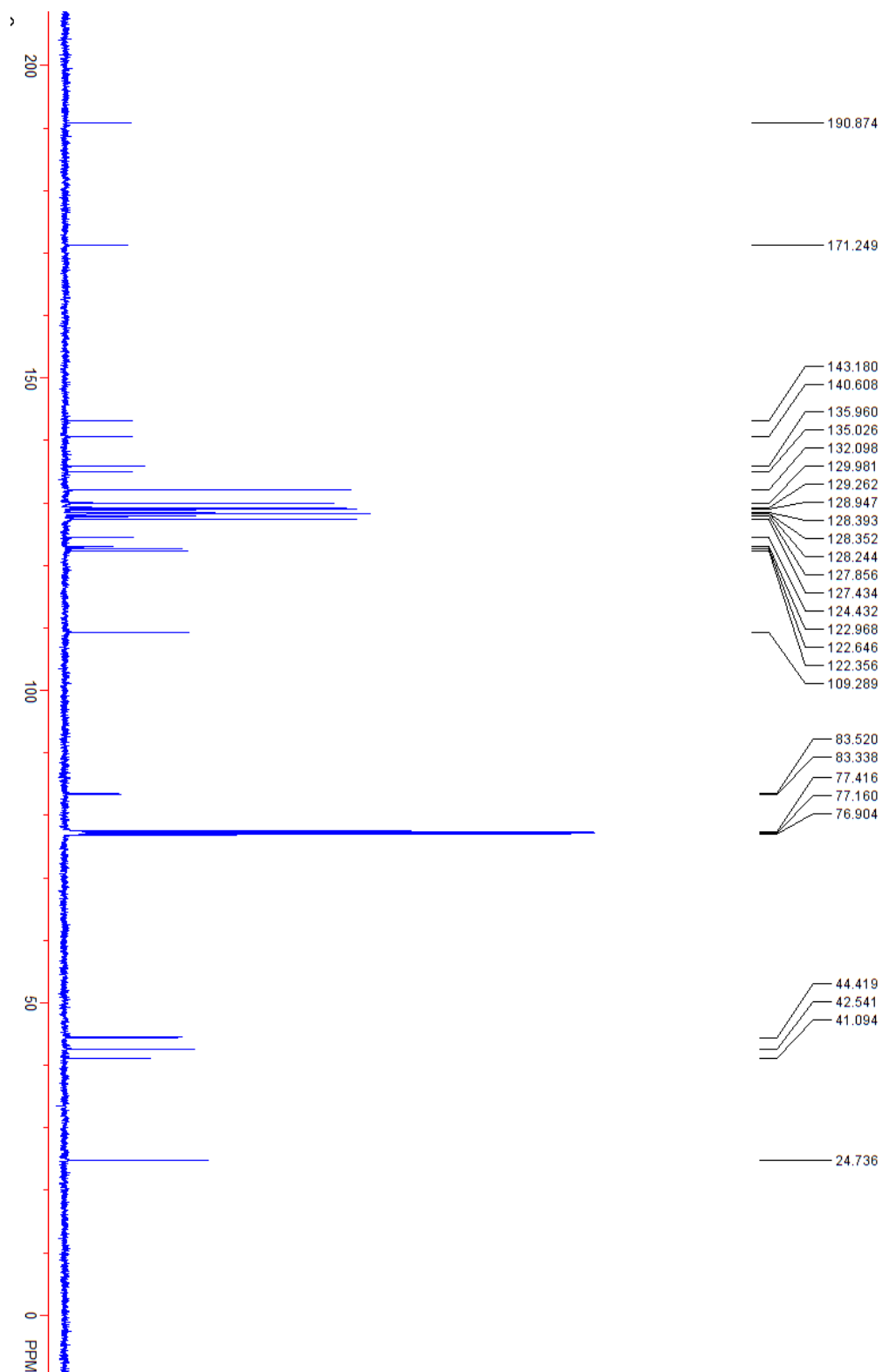


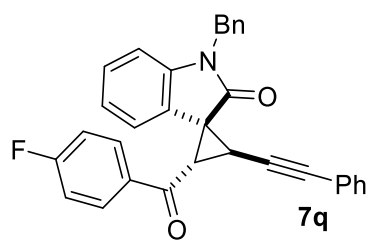
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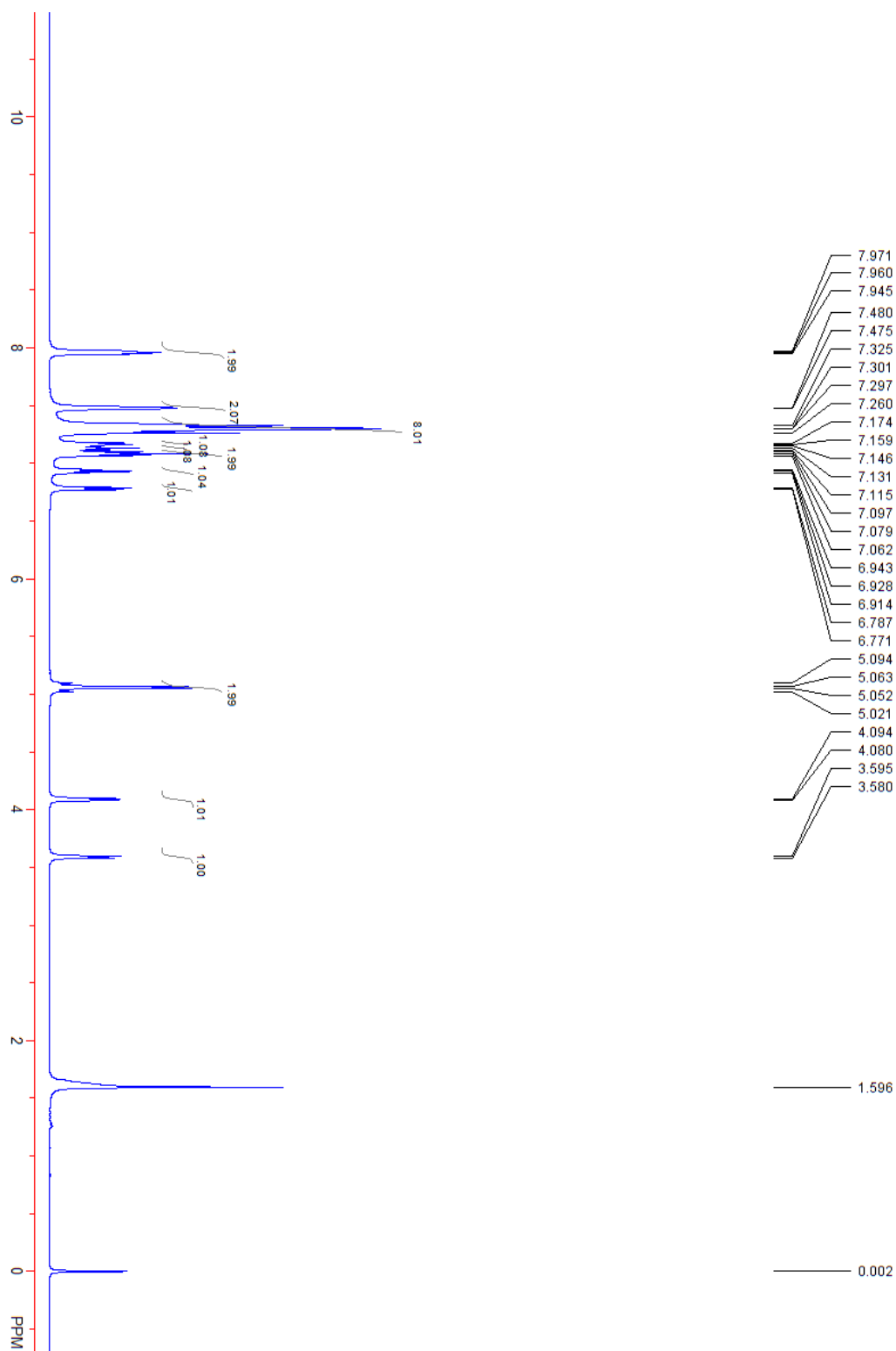


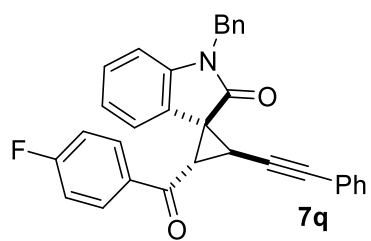
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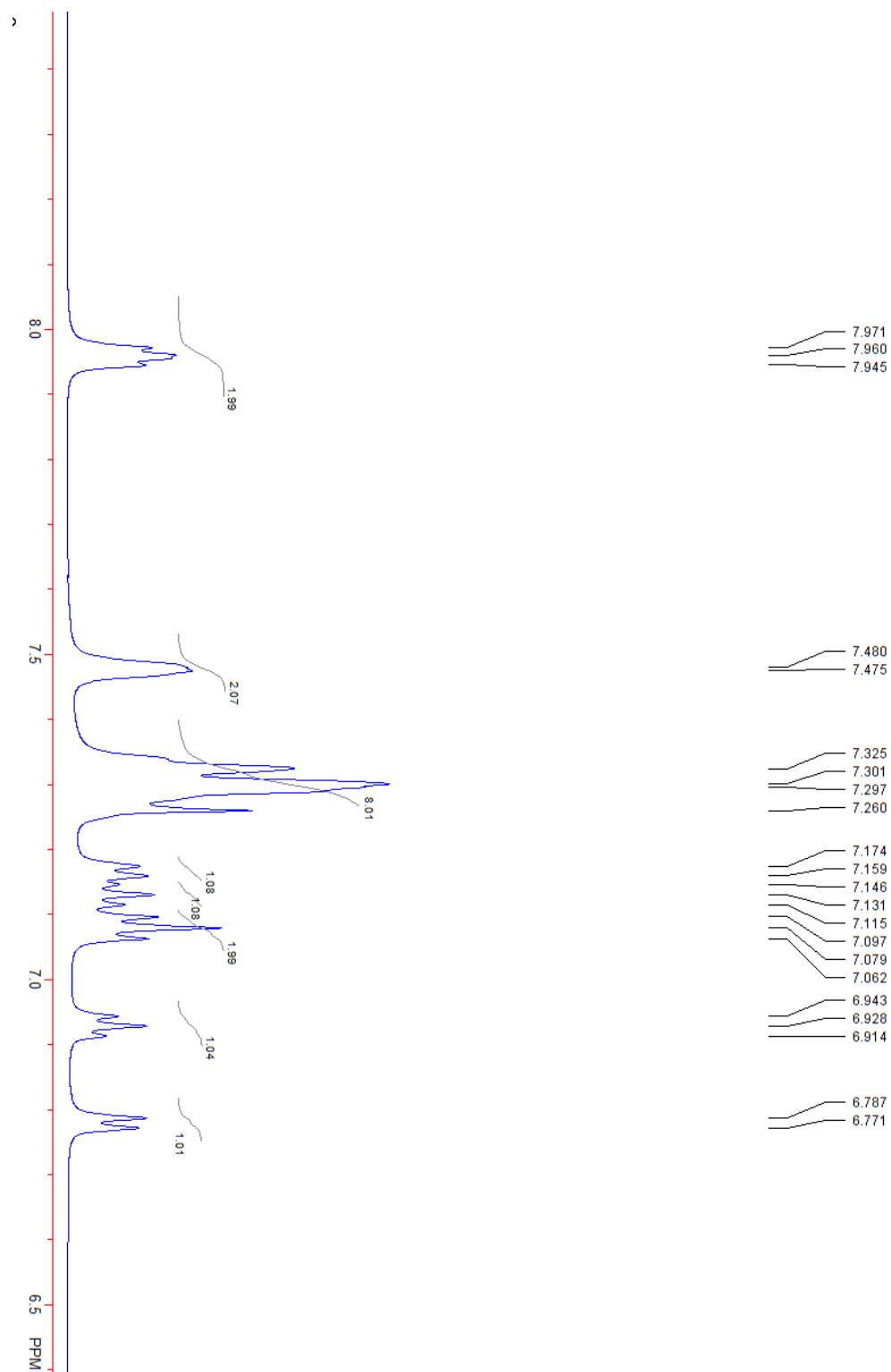


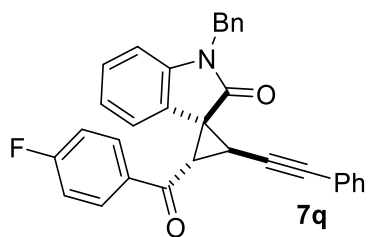
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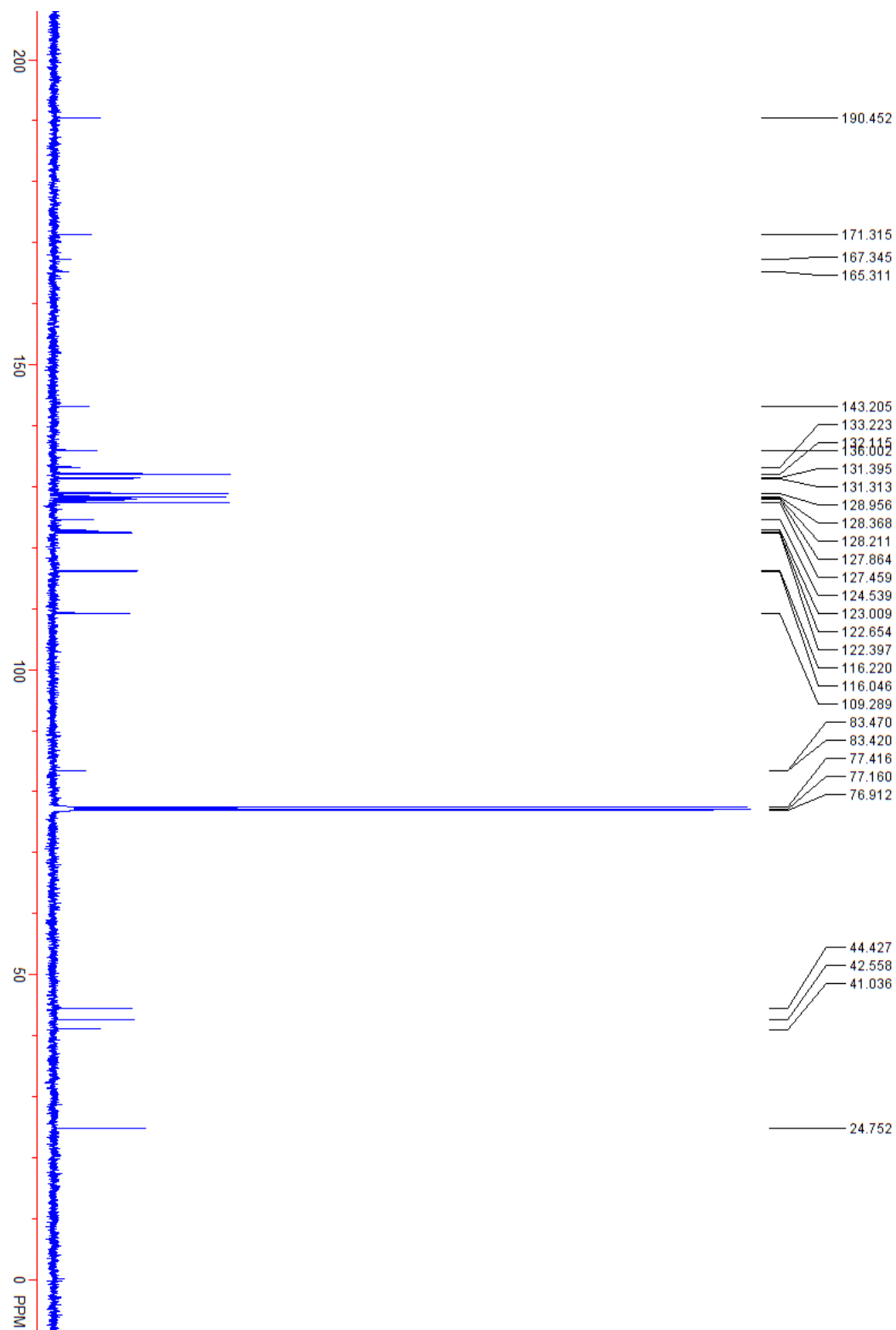


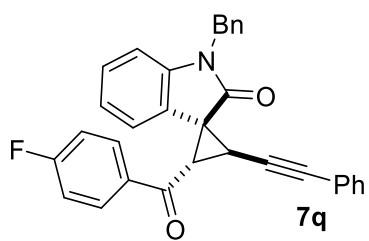
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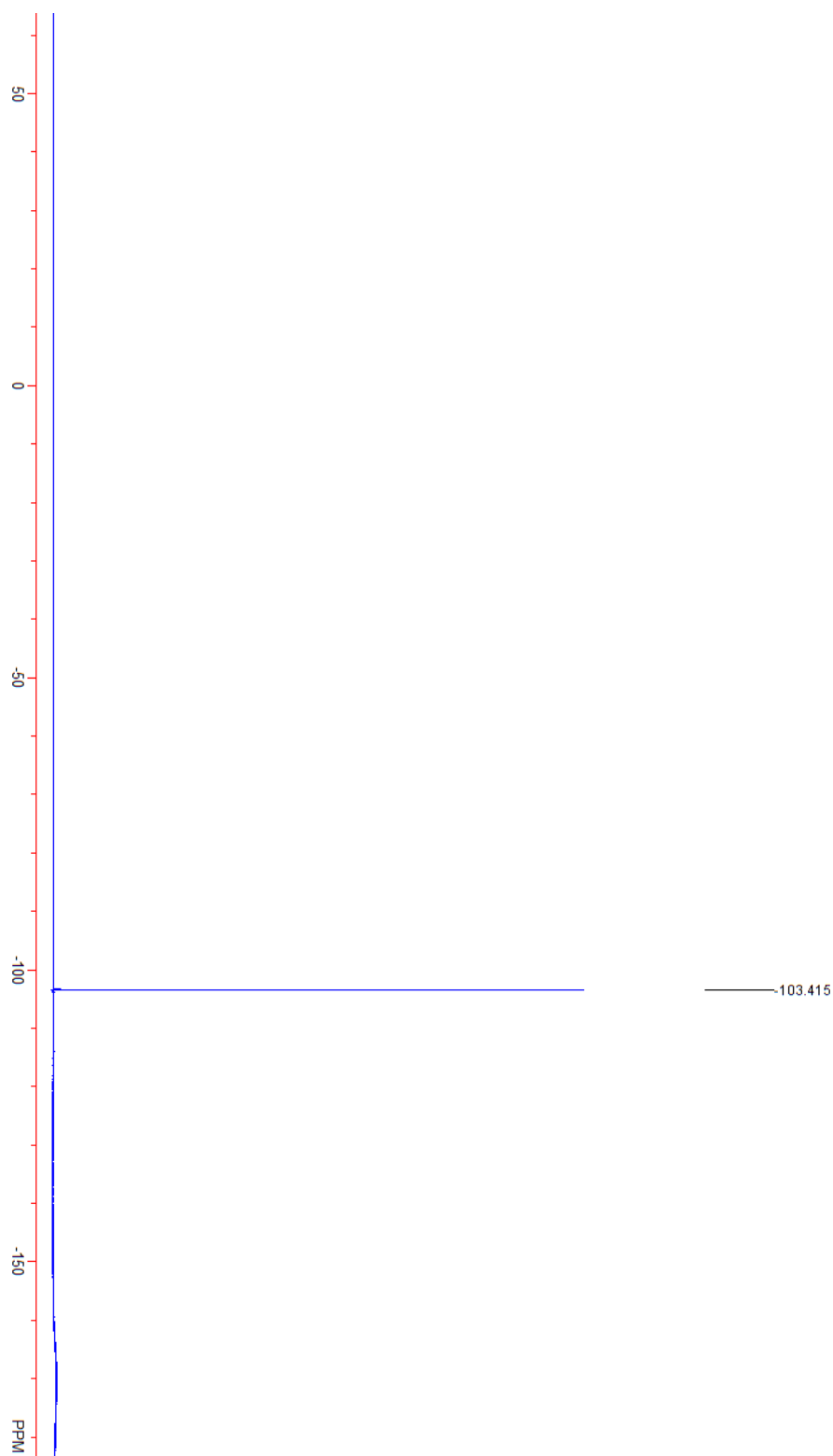


$^{13}\text{C}\{^1\text{H}\}$ NMR:

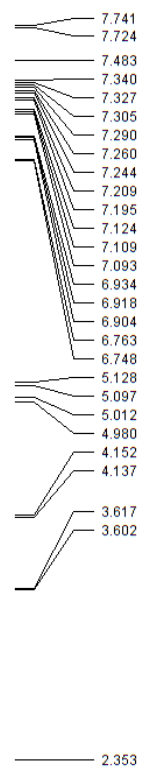
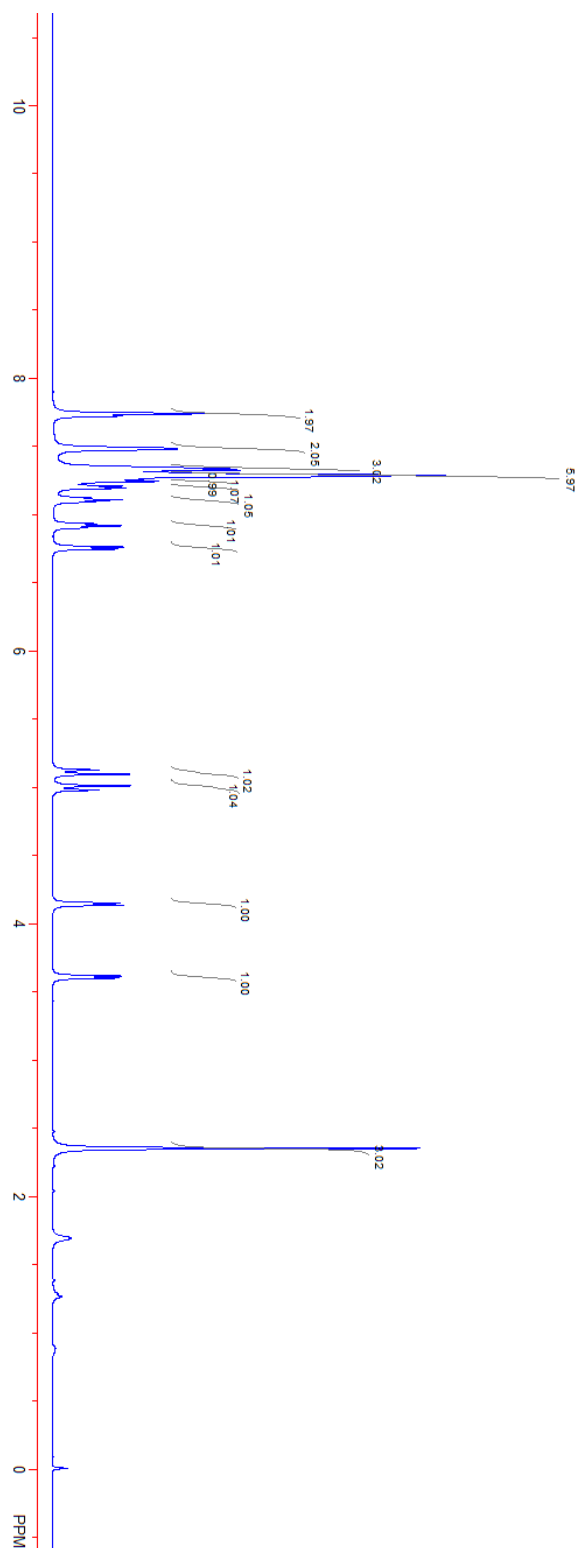
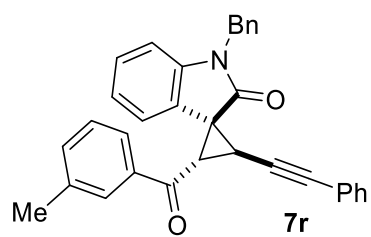


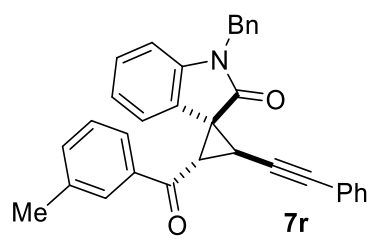


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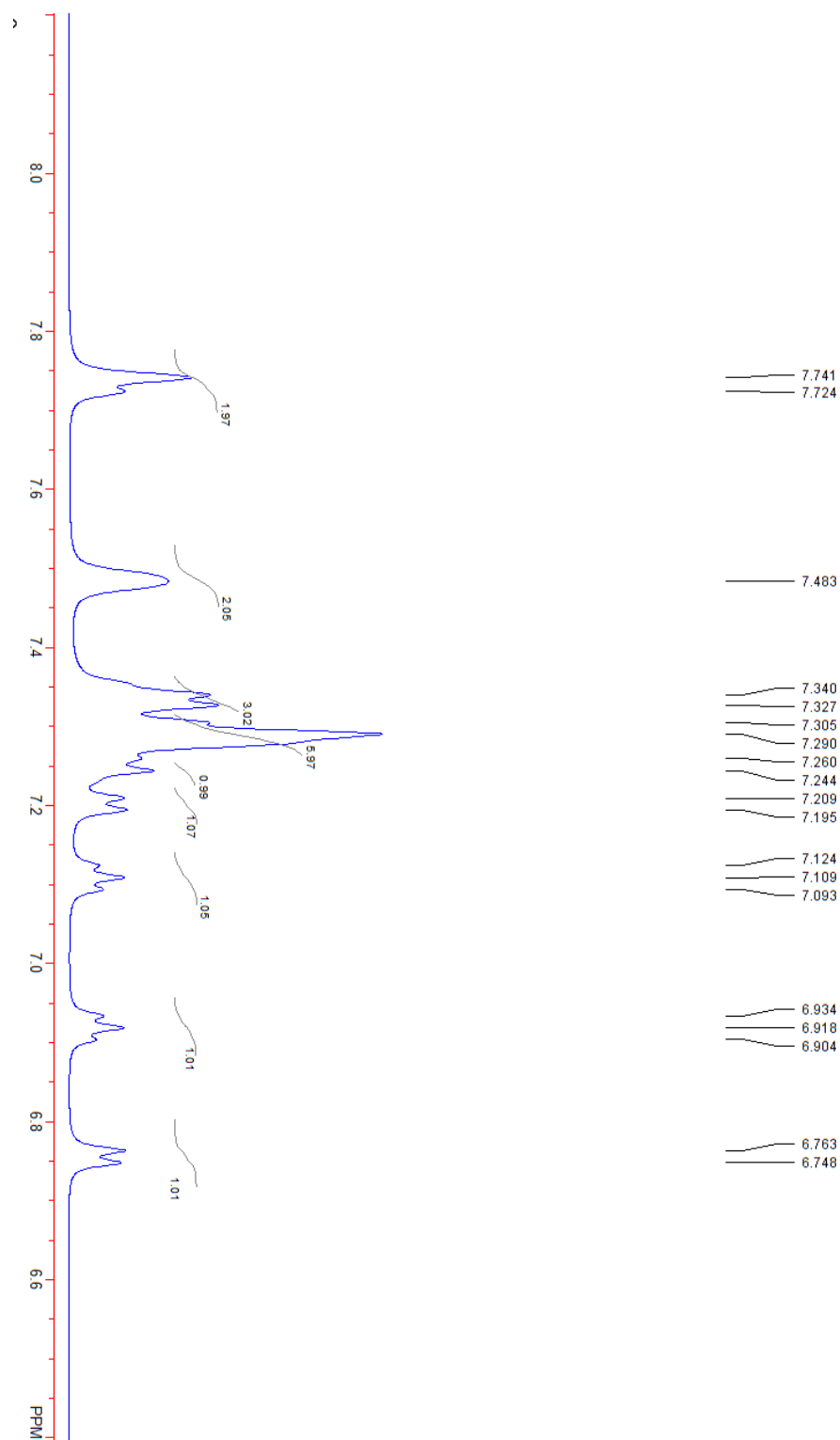


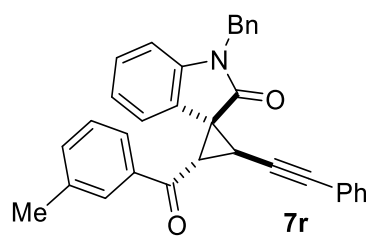
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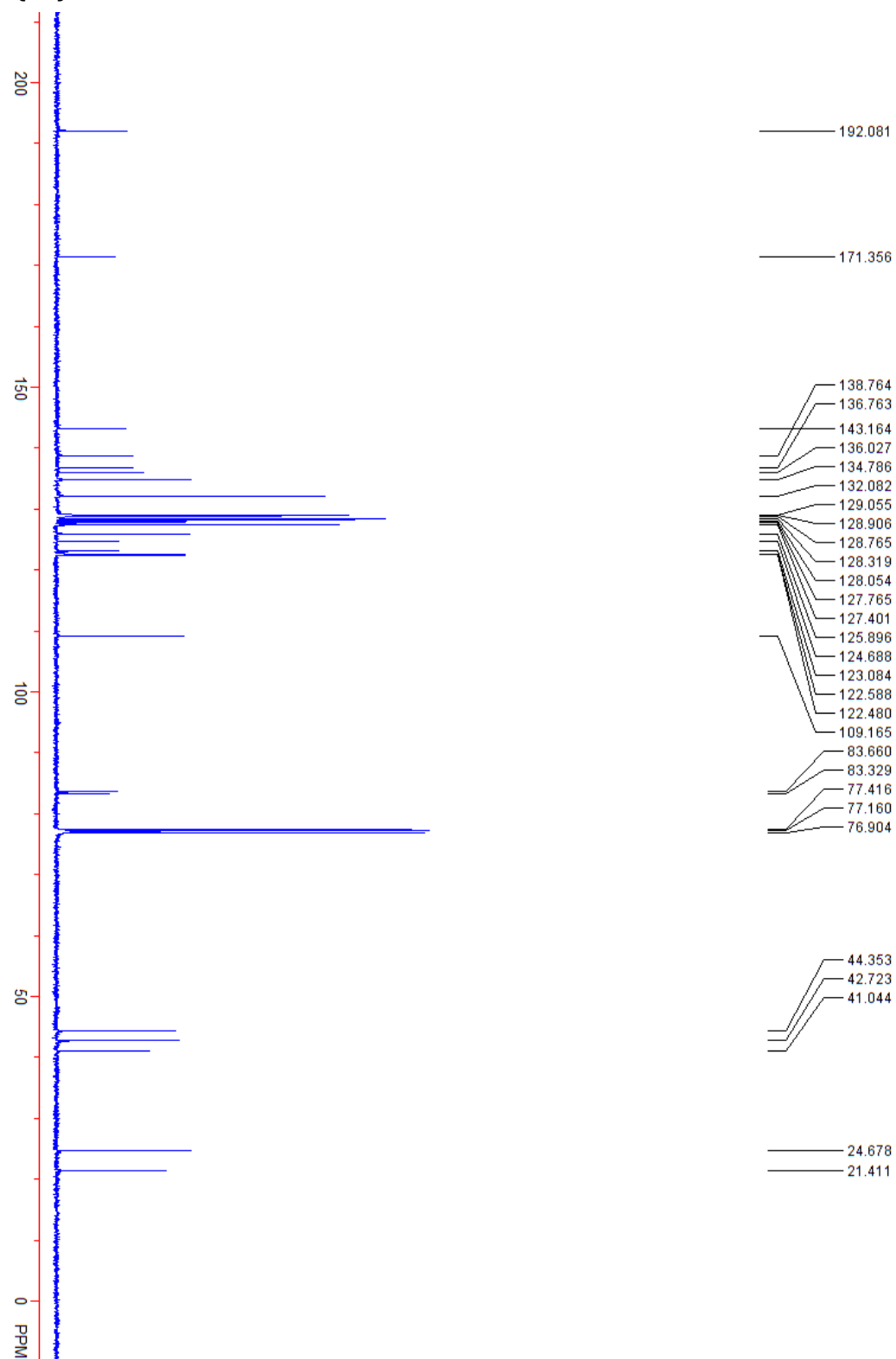


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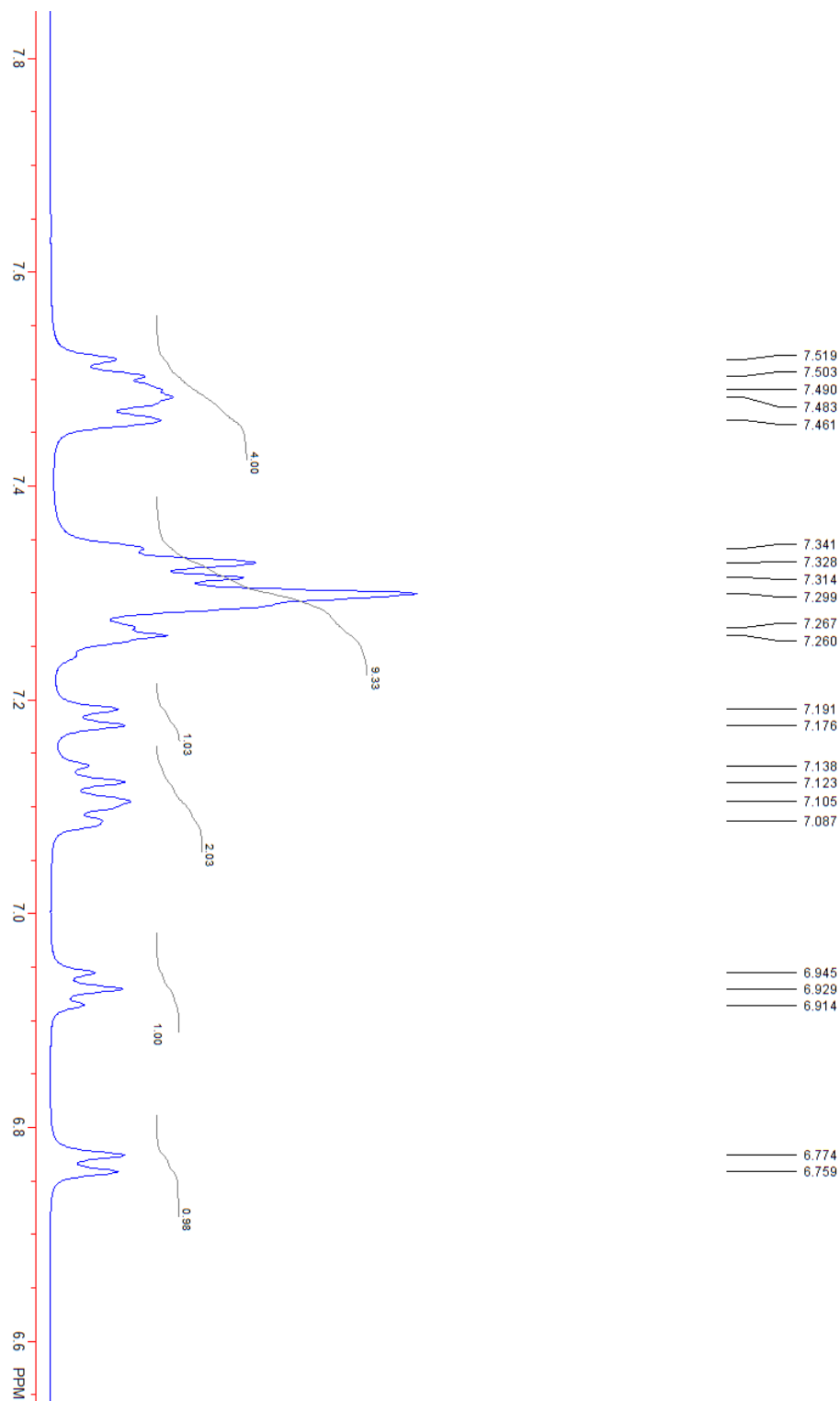
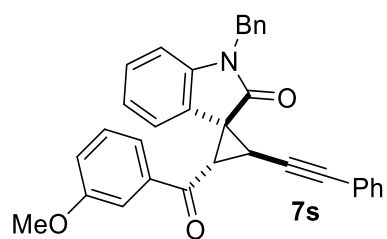


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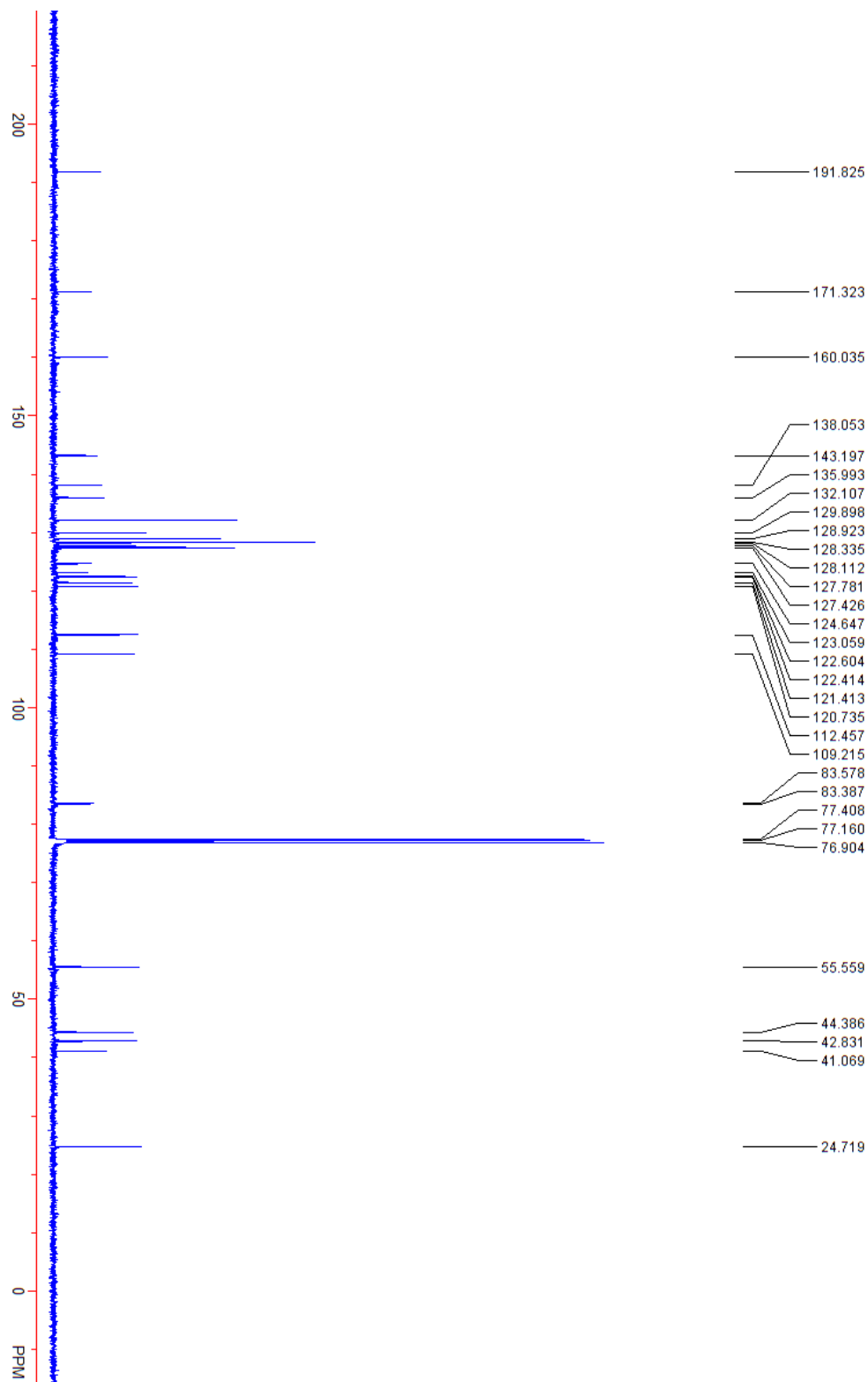
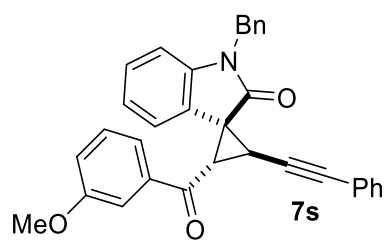




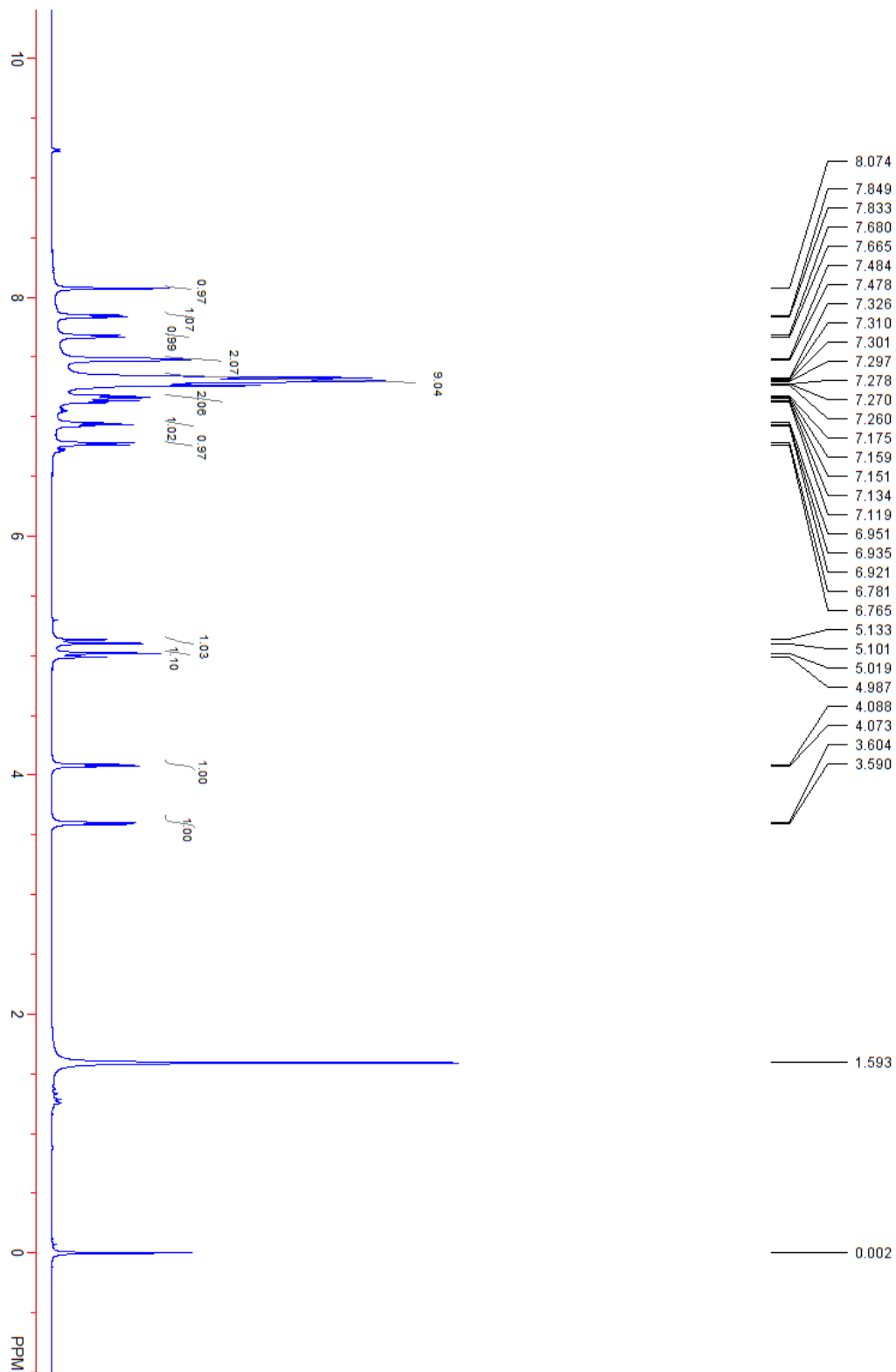
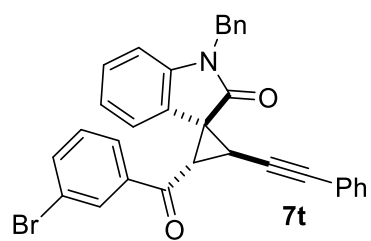
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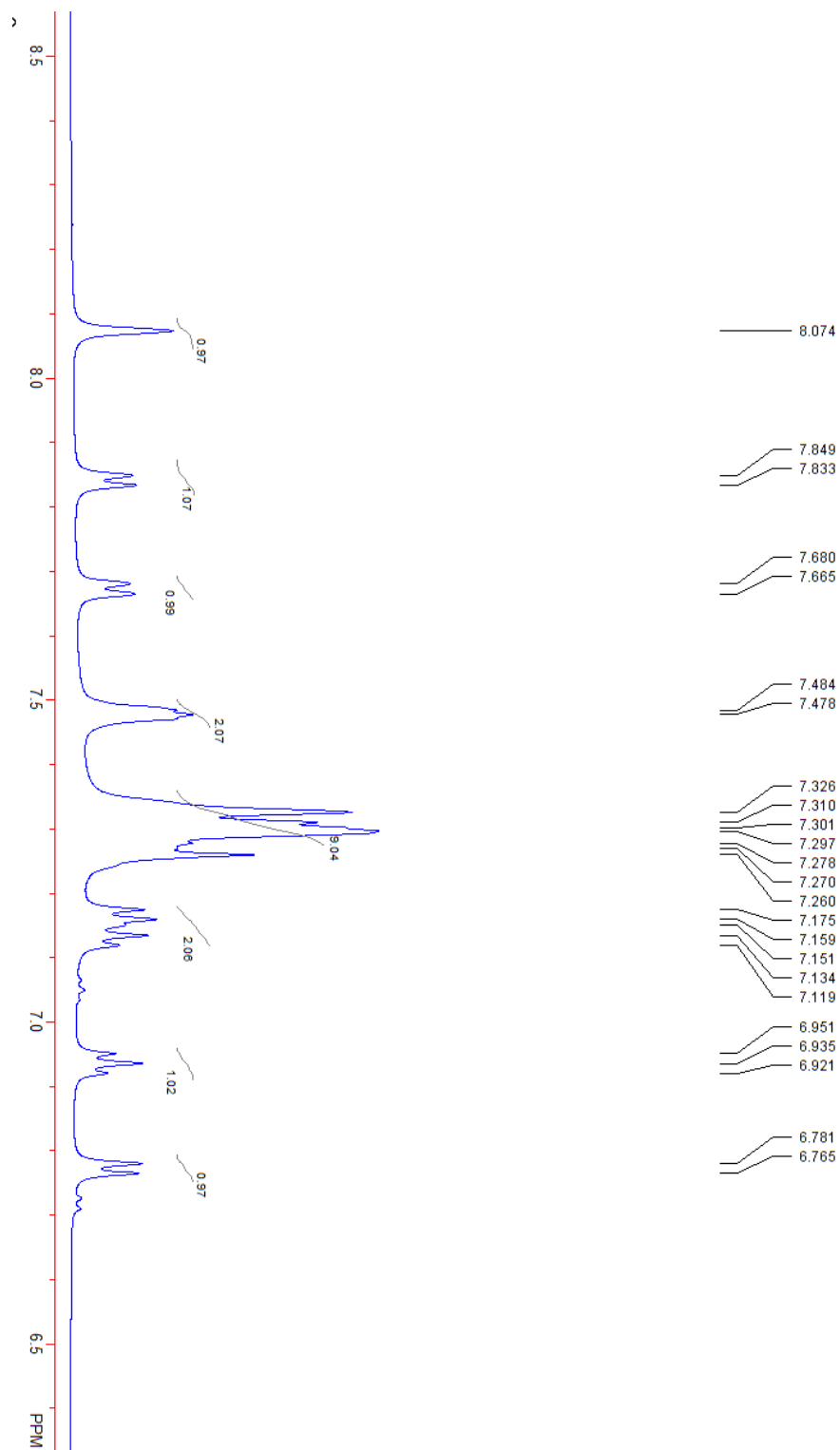
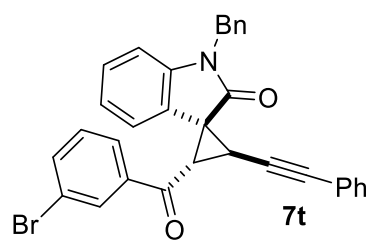
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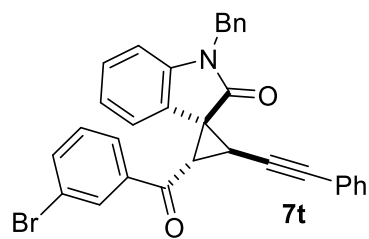


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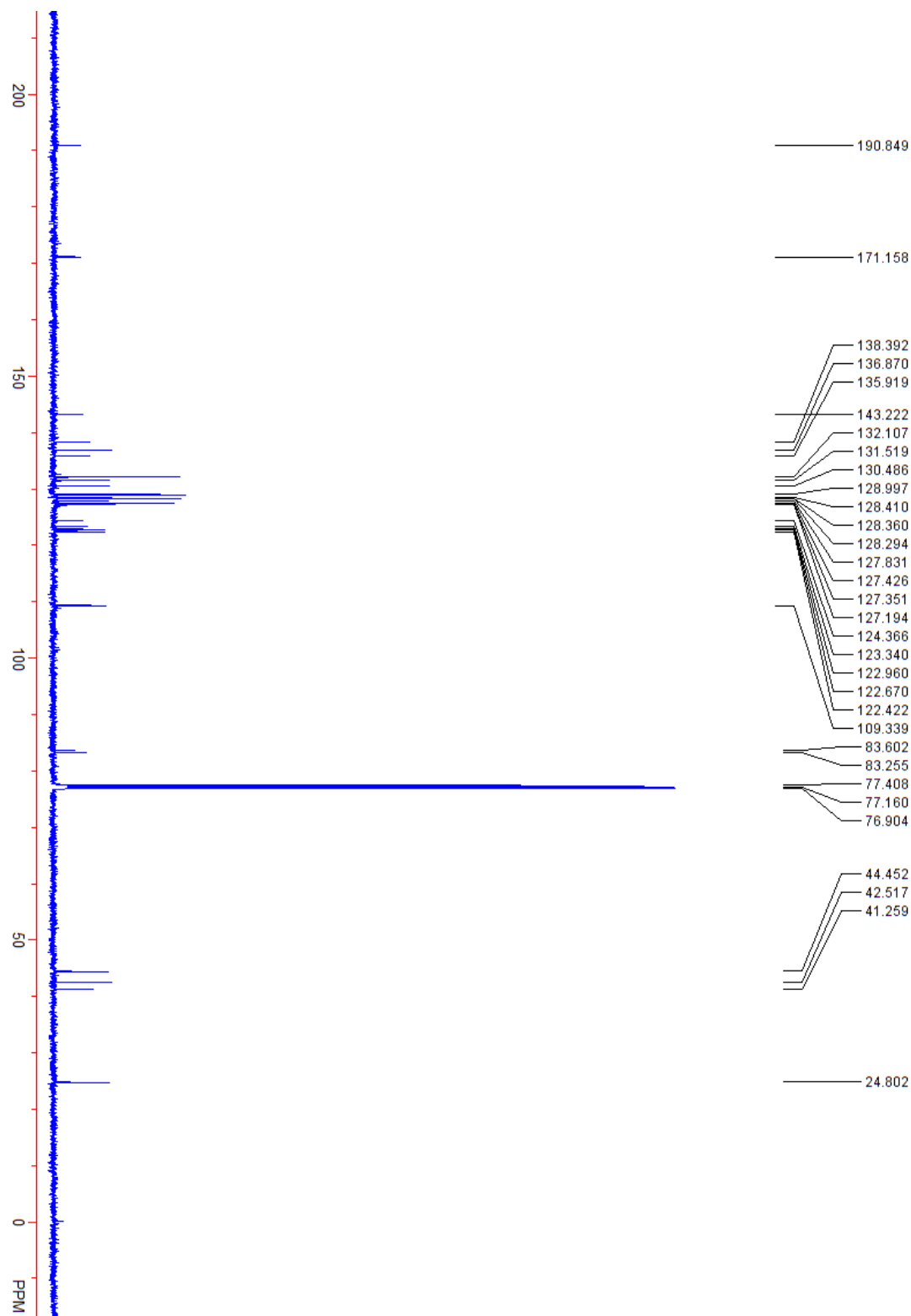


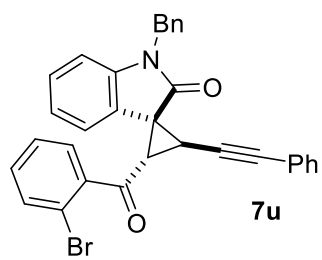
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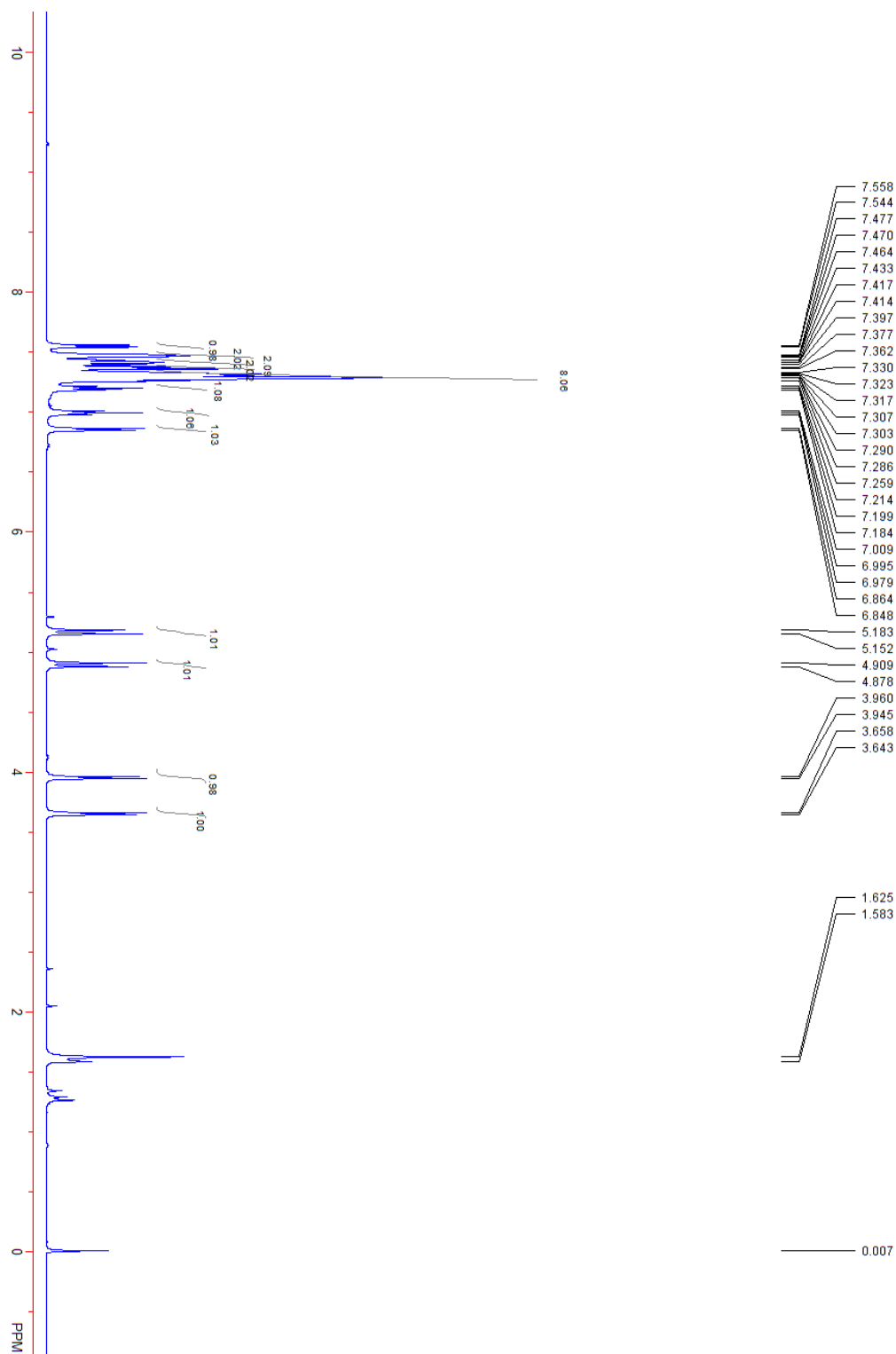


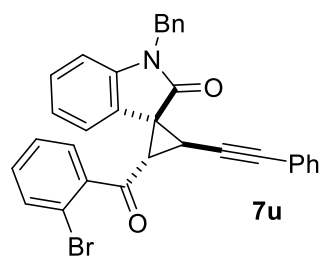
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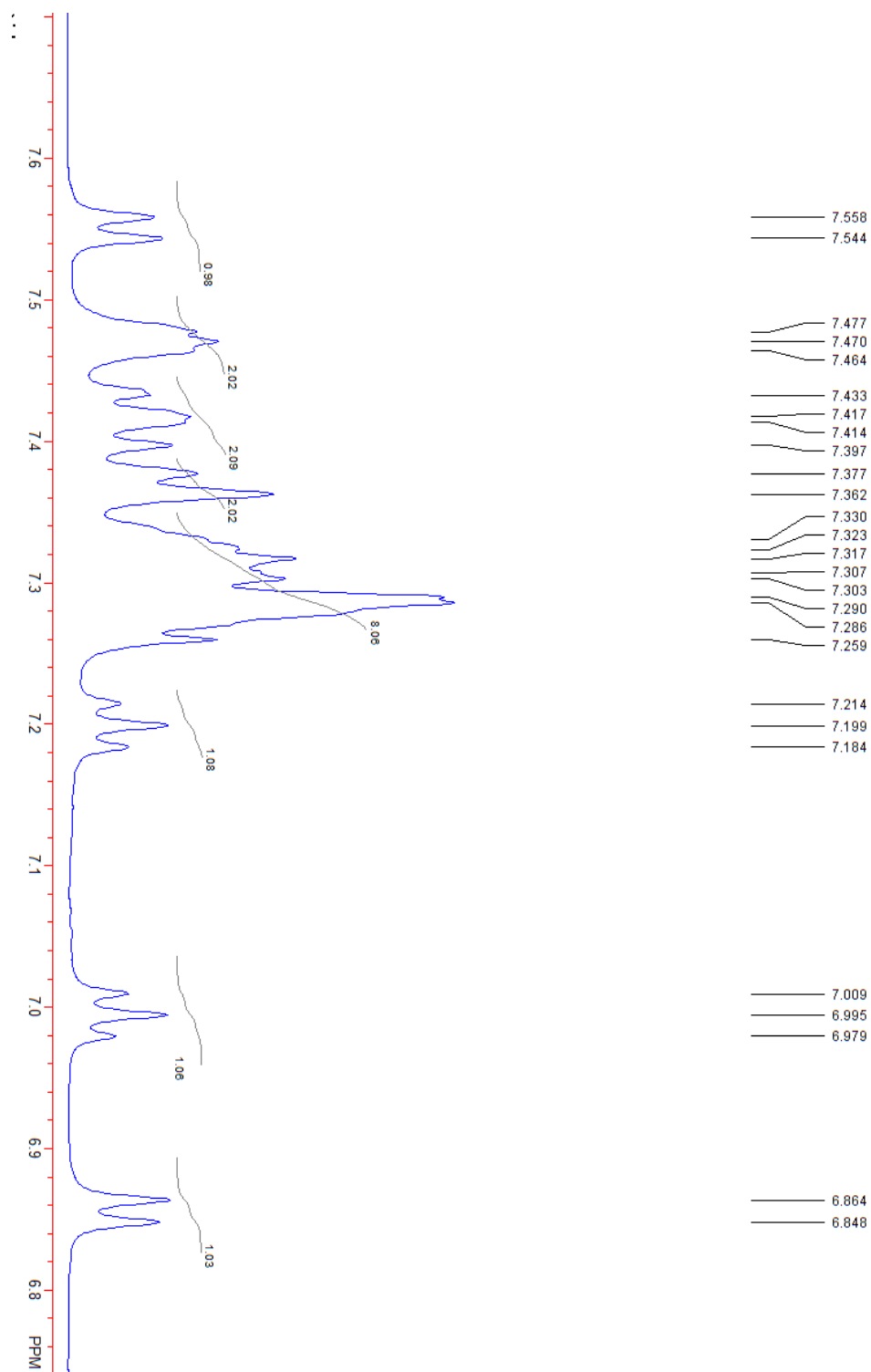


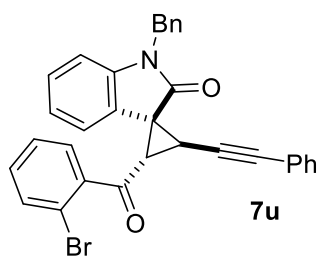
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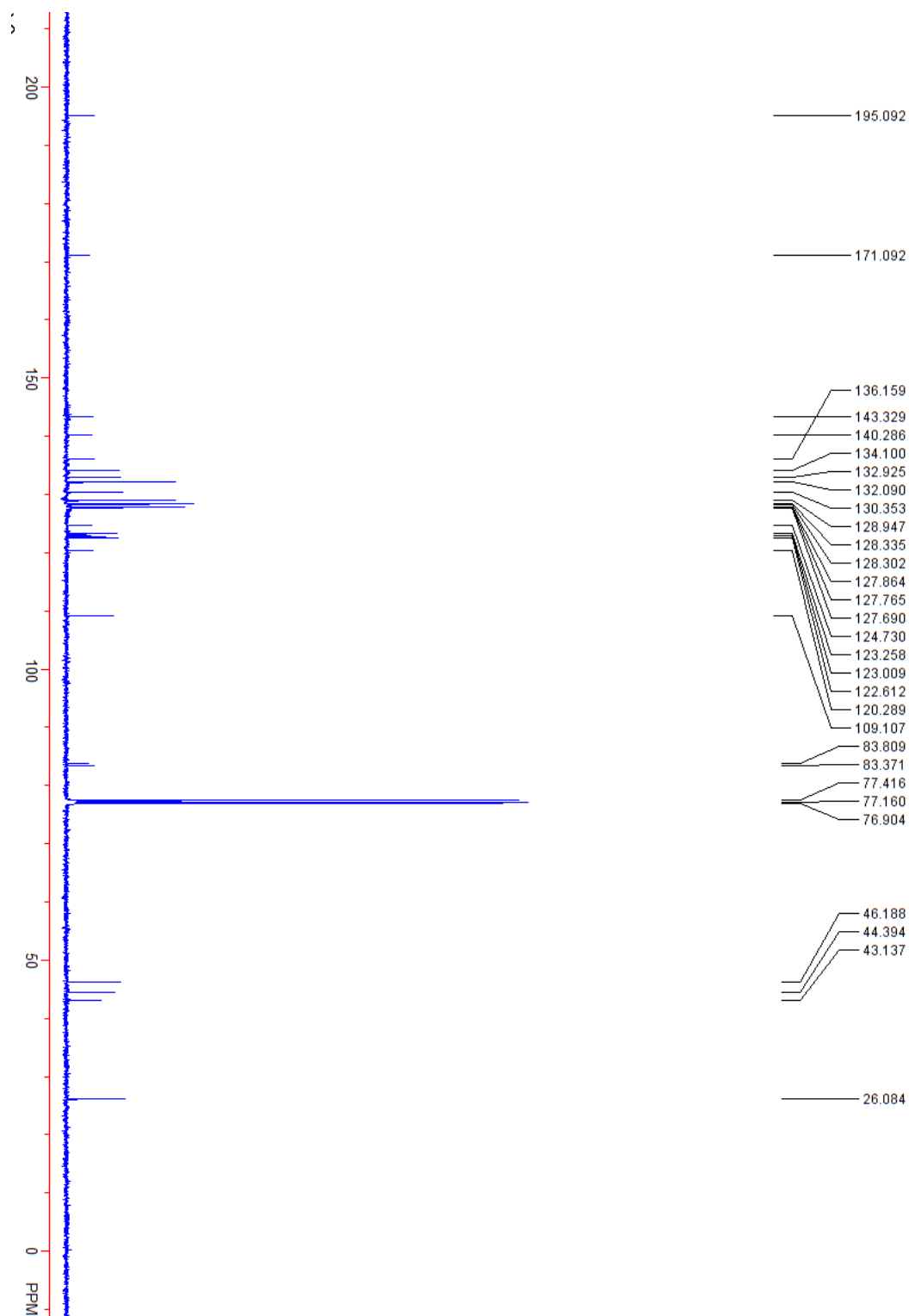


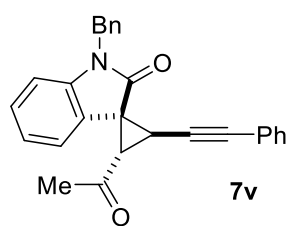
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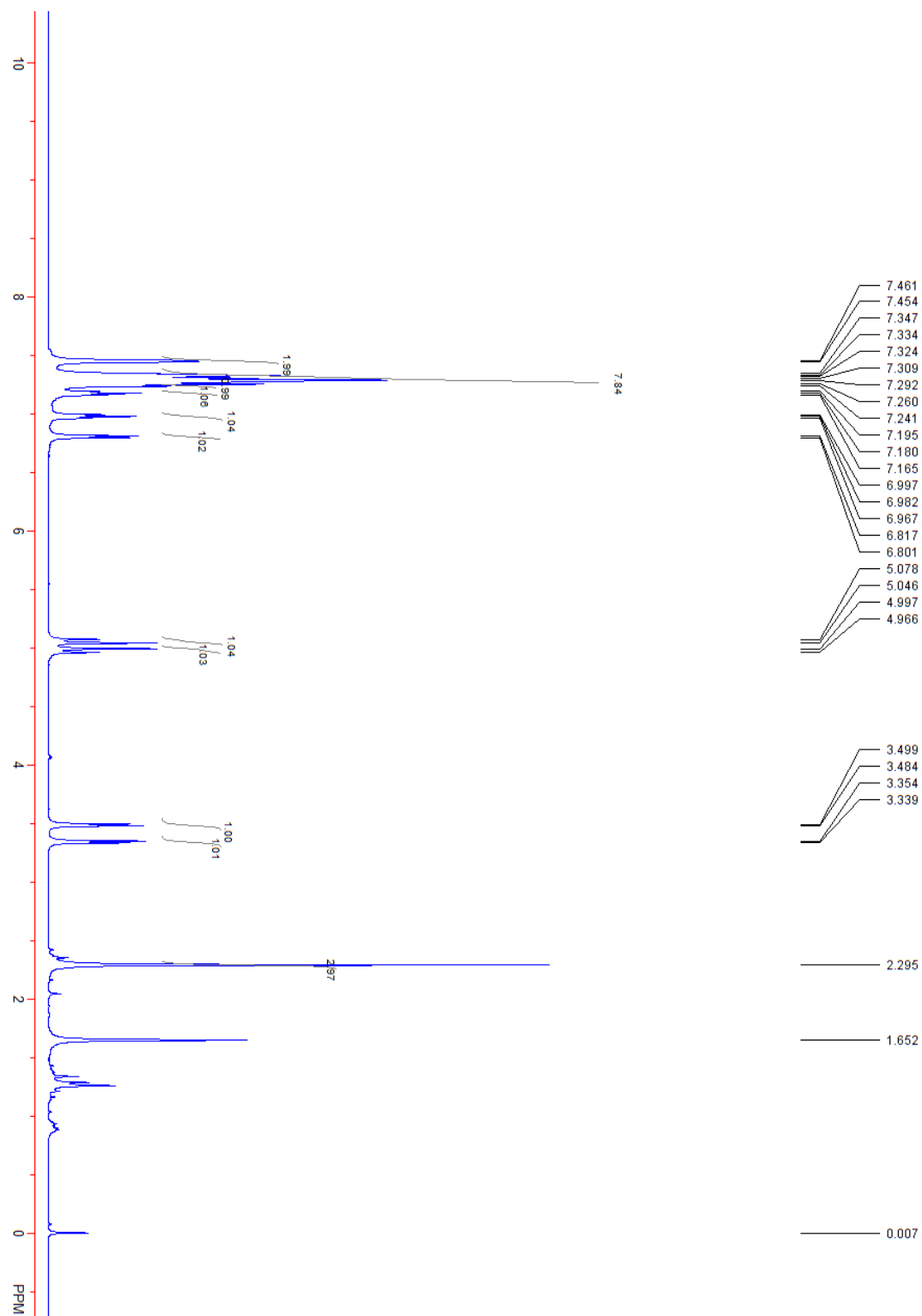


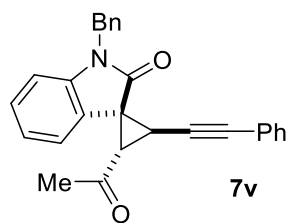
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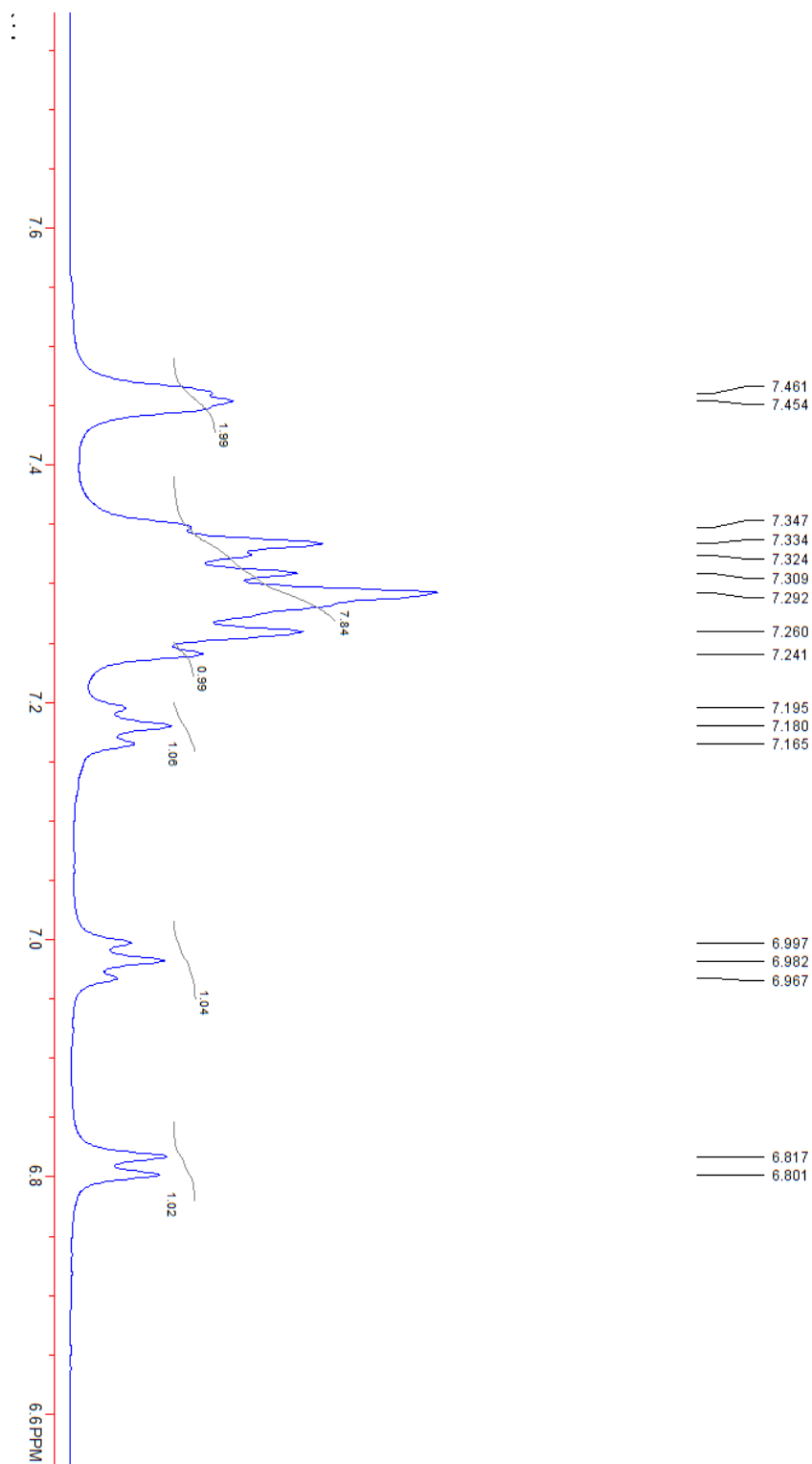


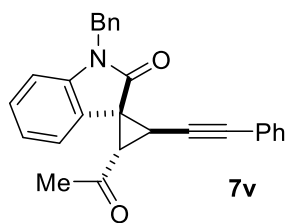
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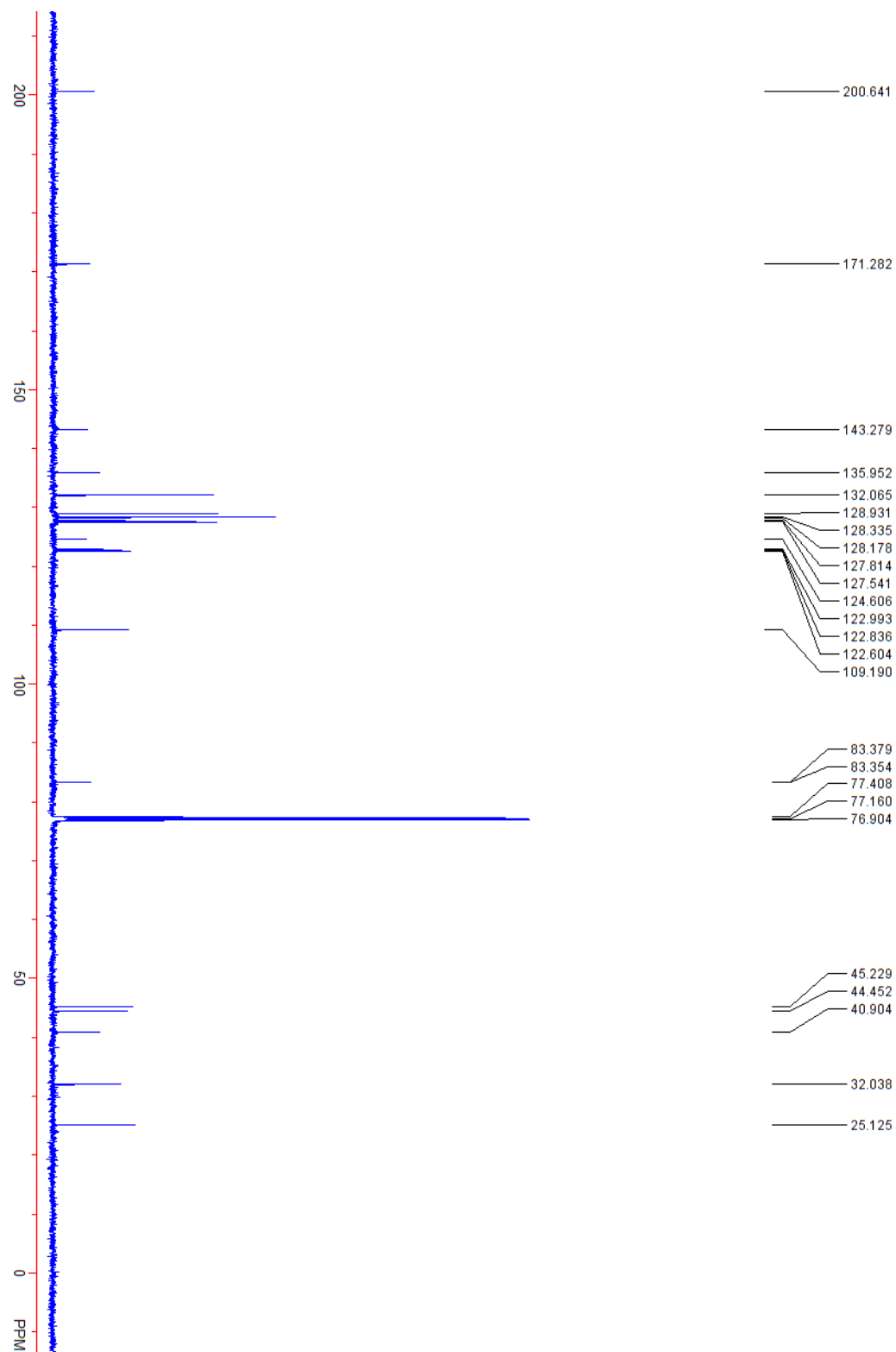


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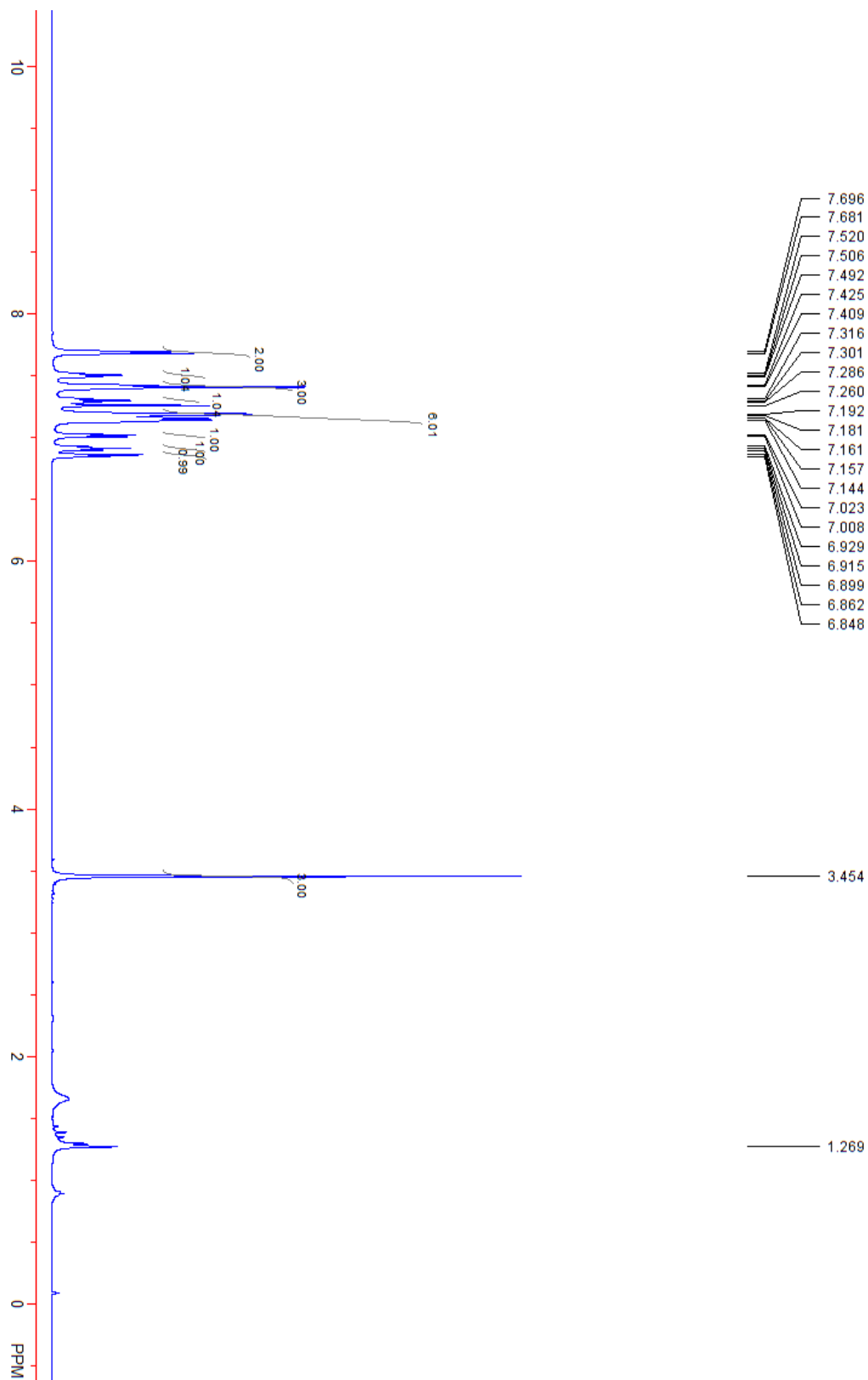
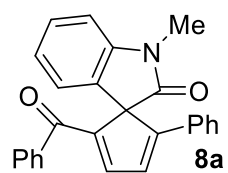




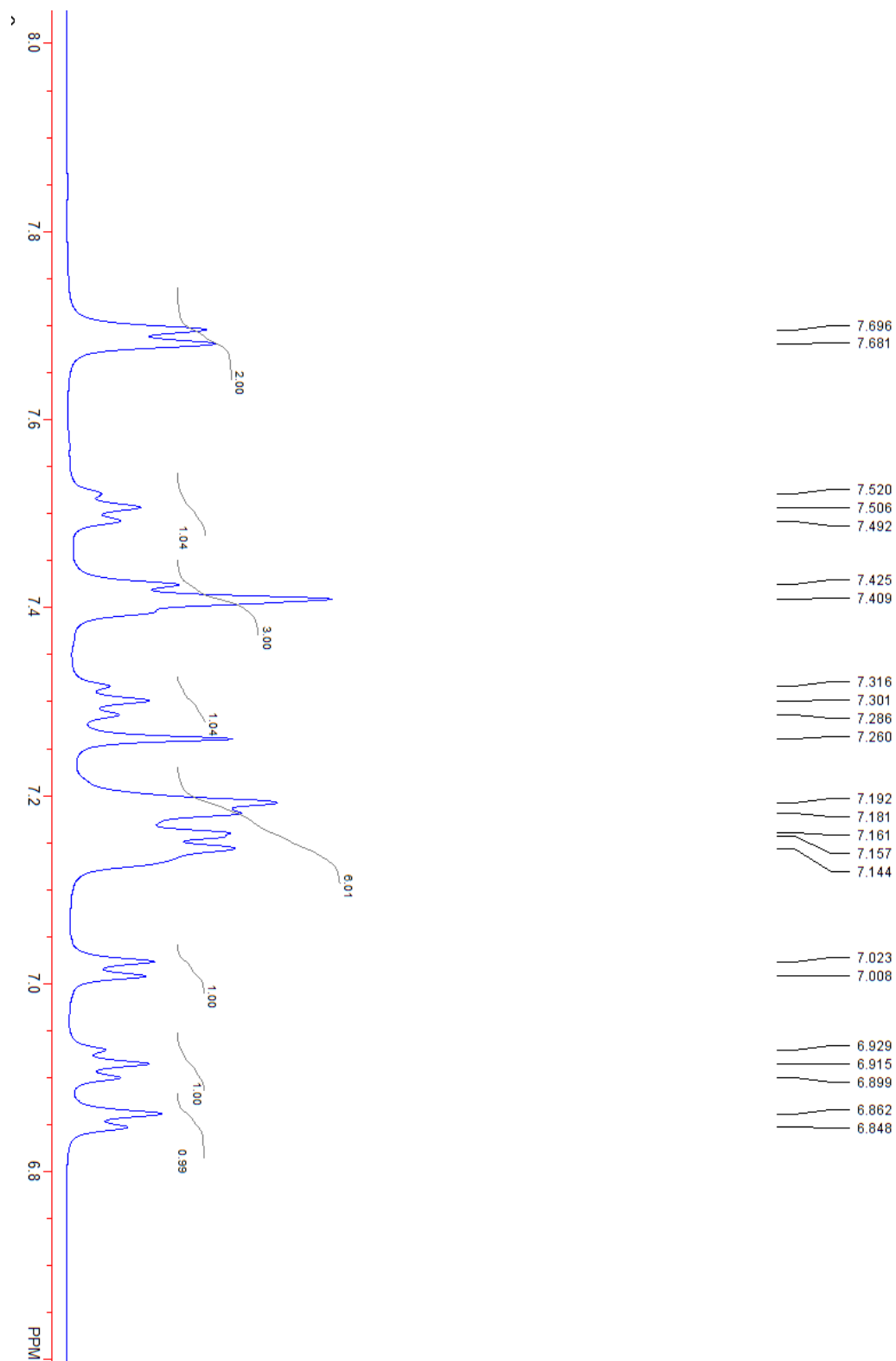
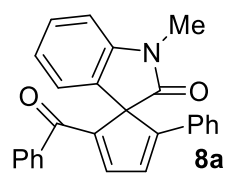
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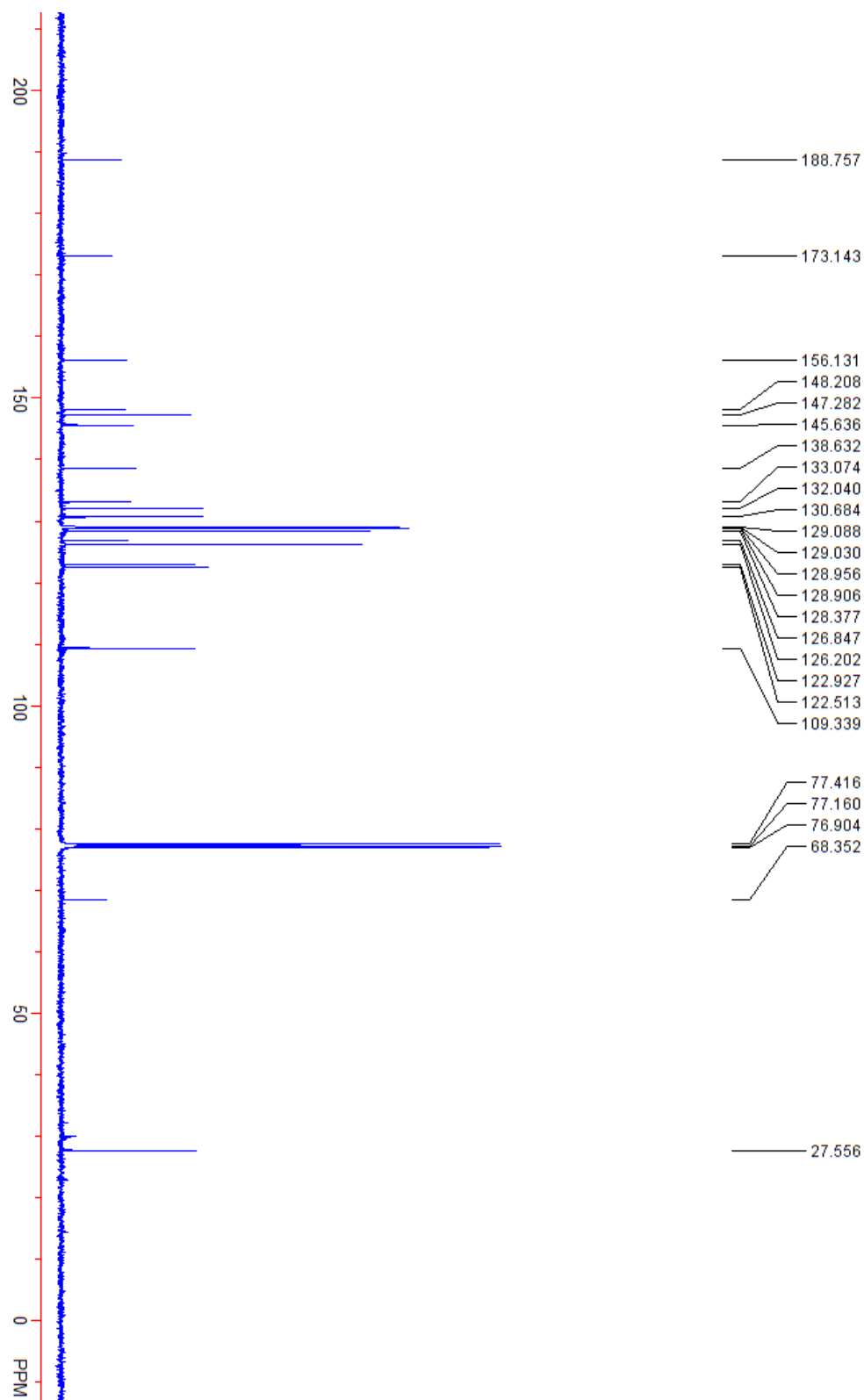
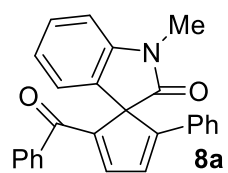
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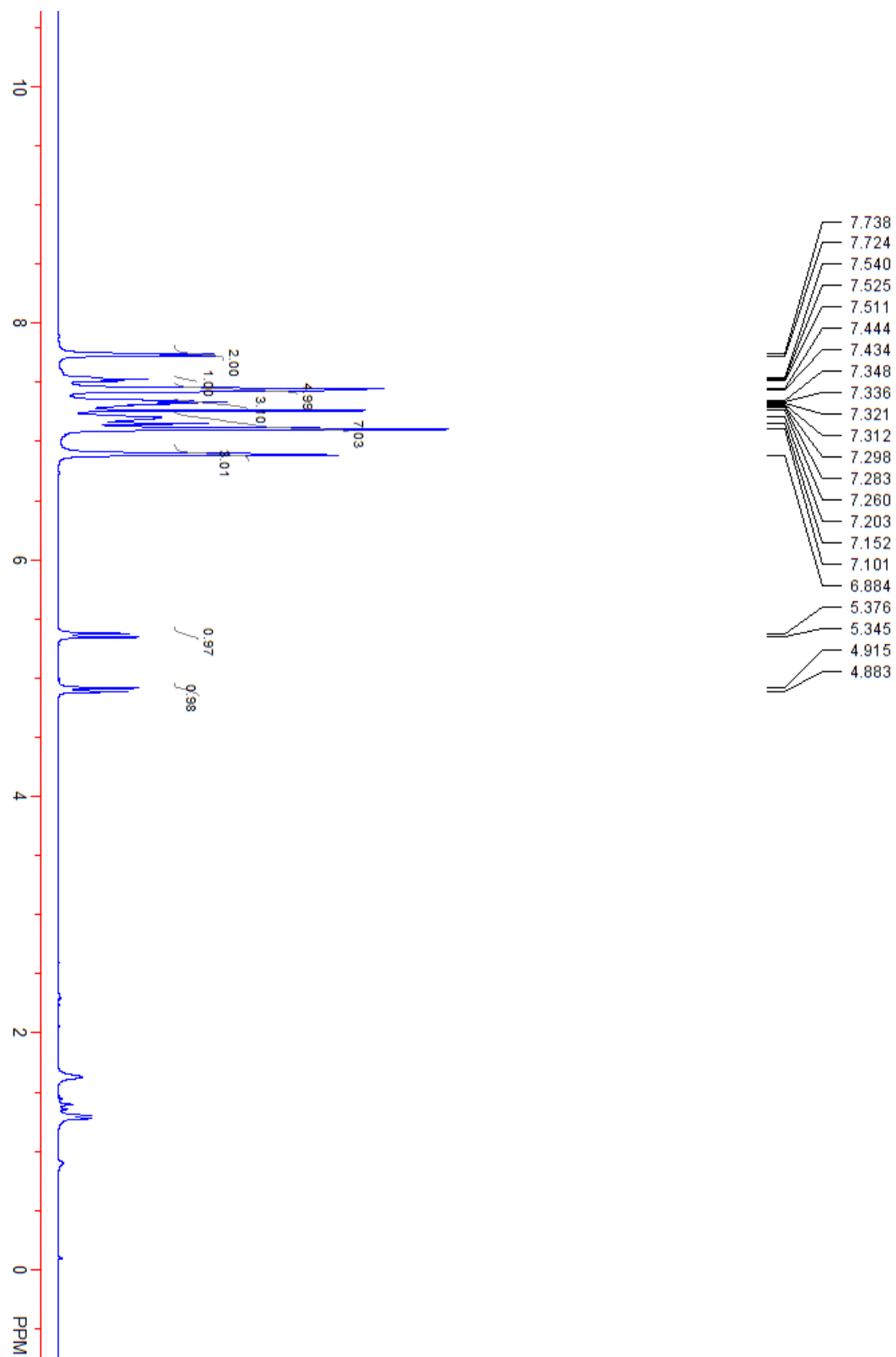
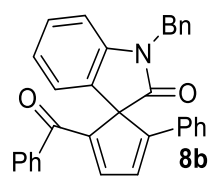
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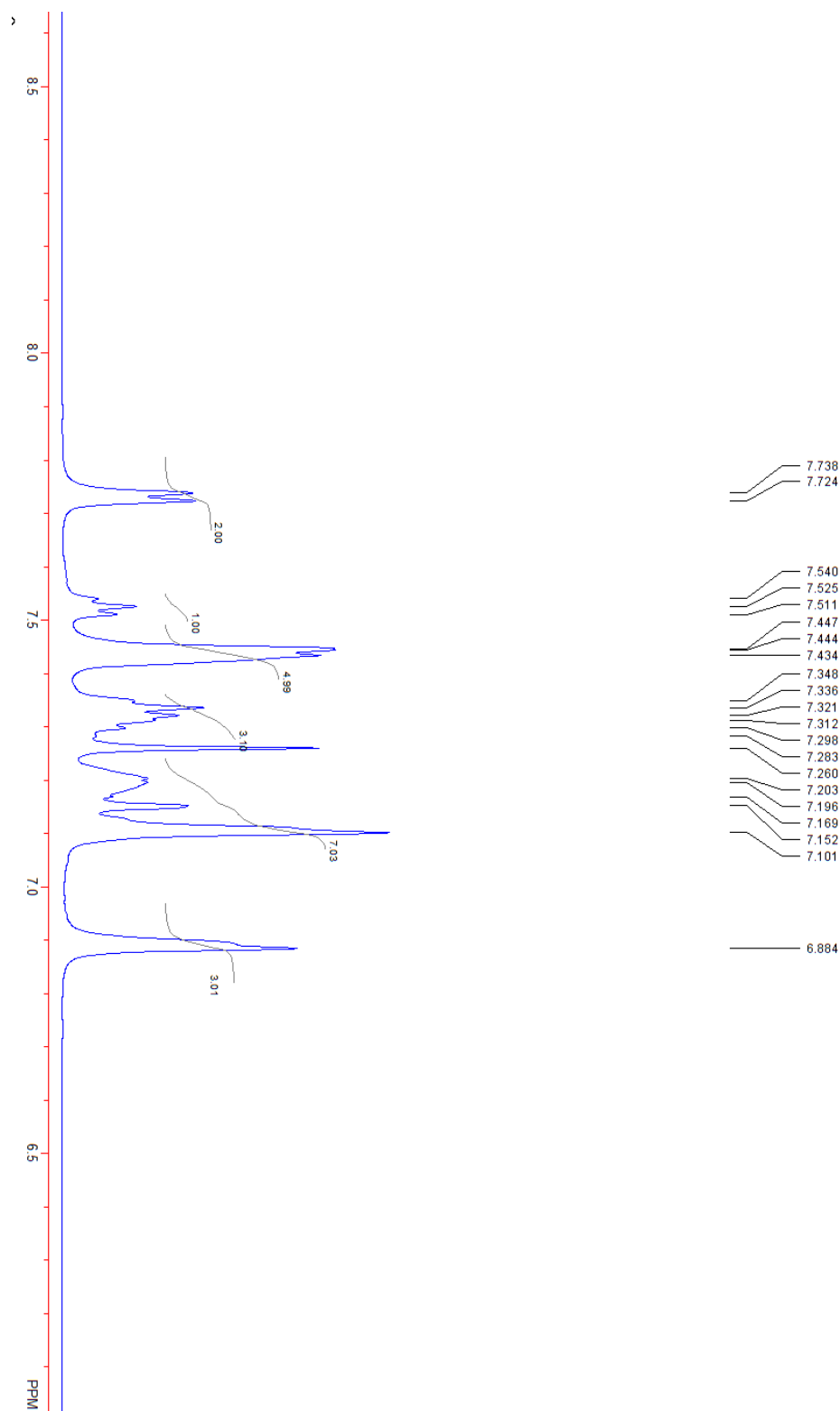
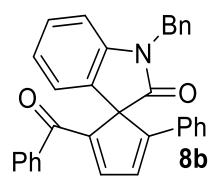
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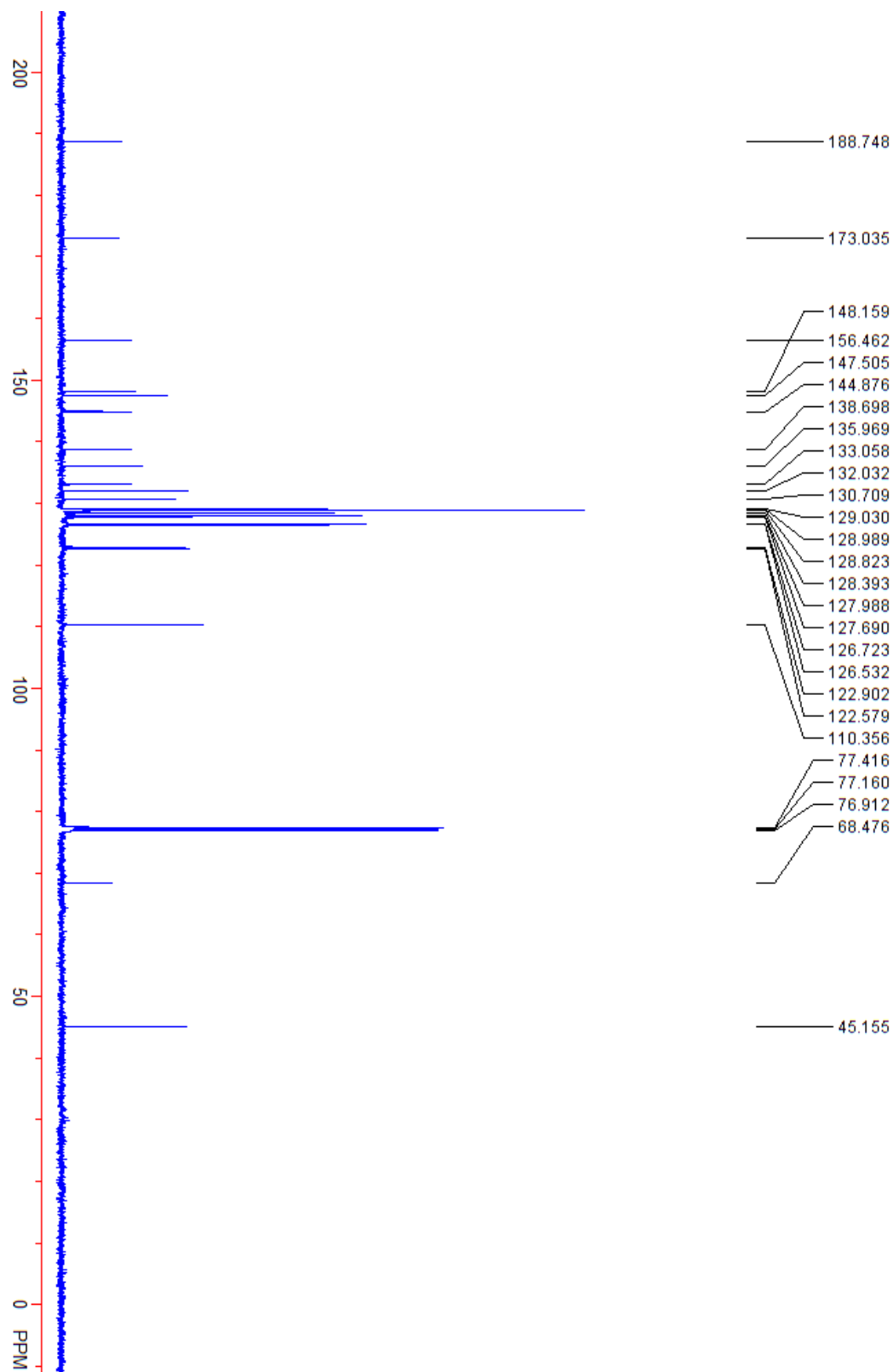
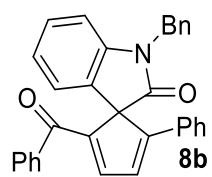
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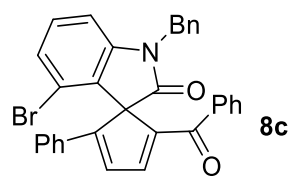


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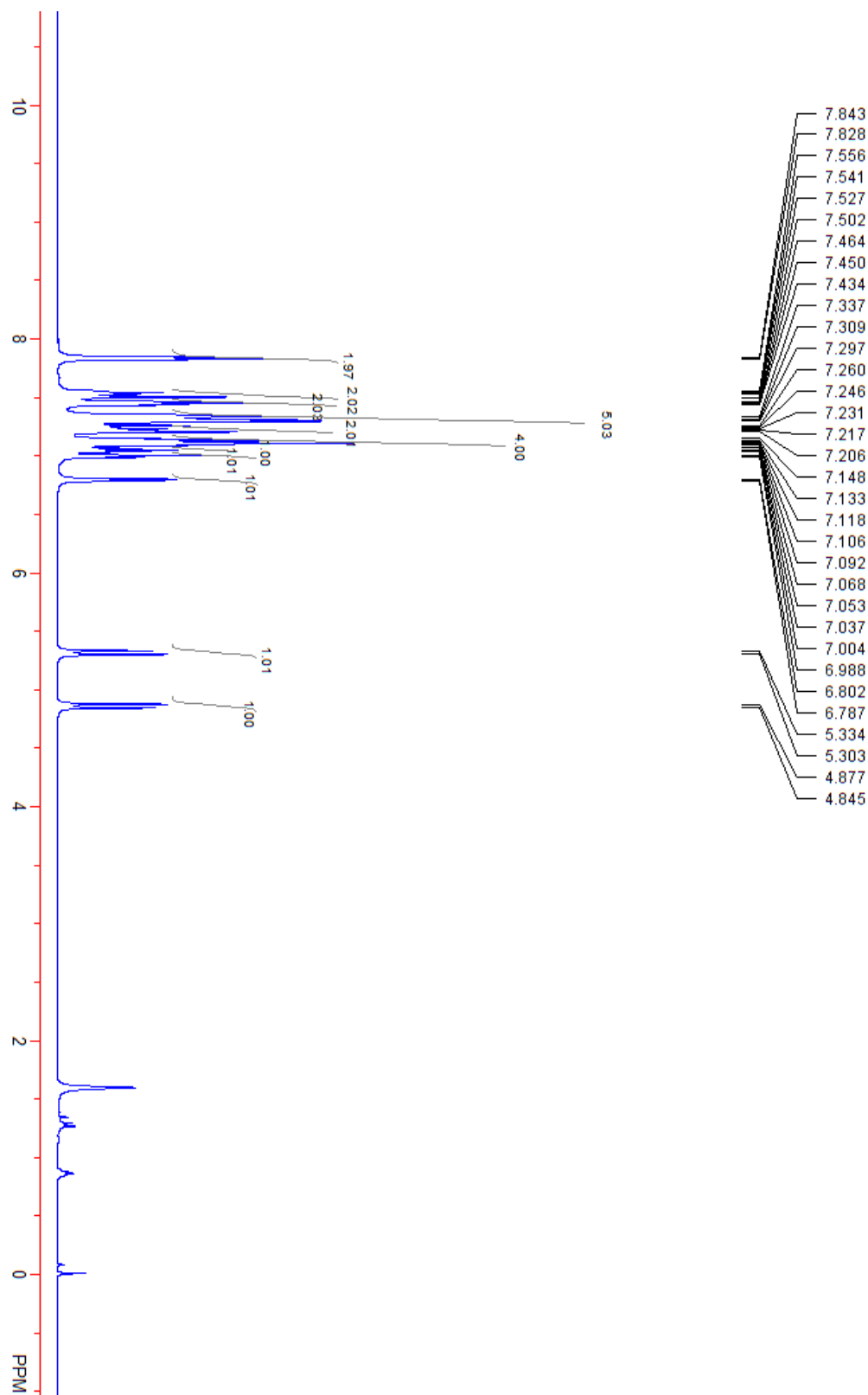


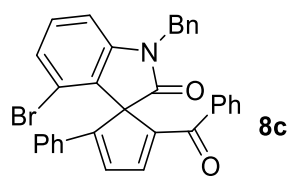
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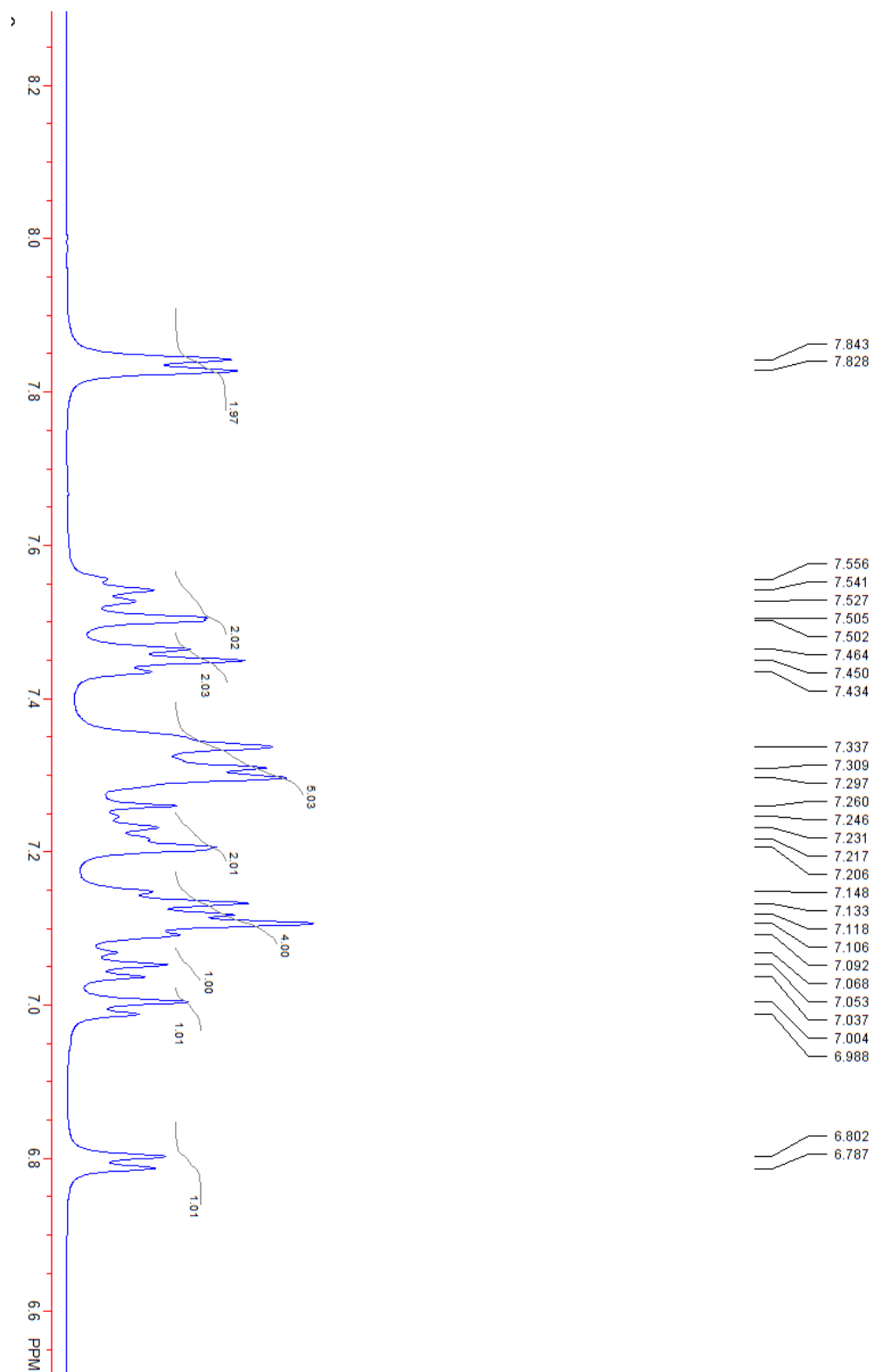


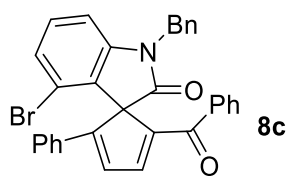
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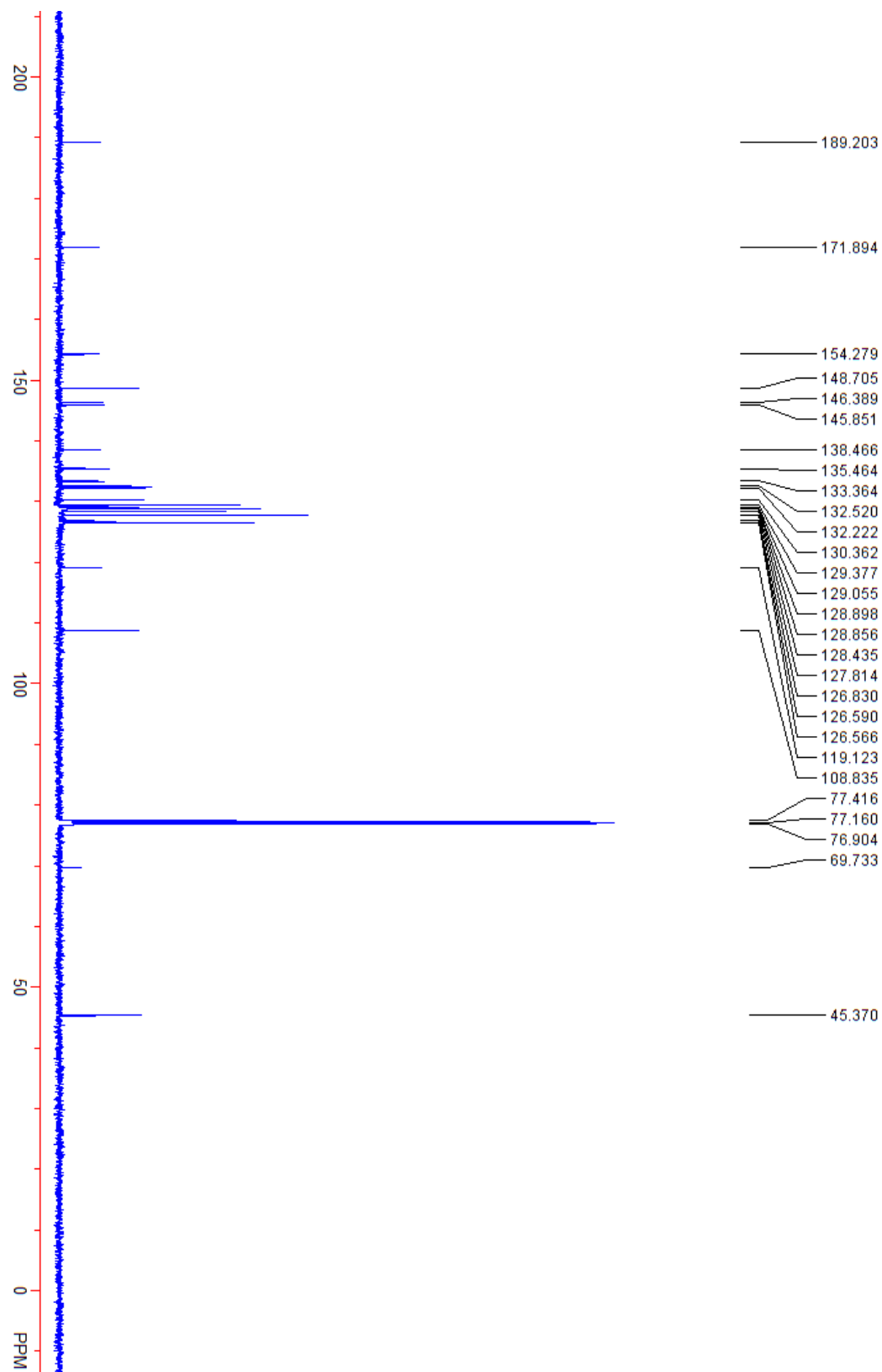


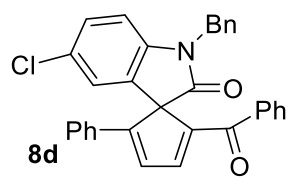
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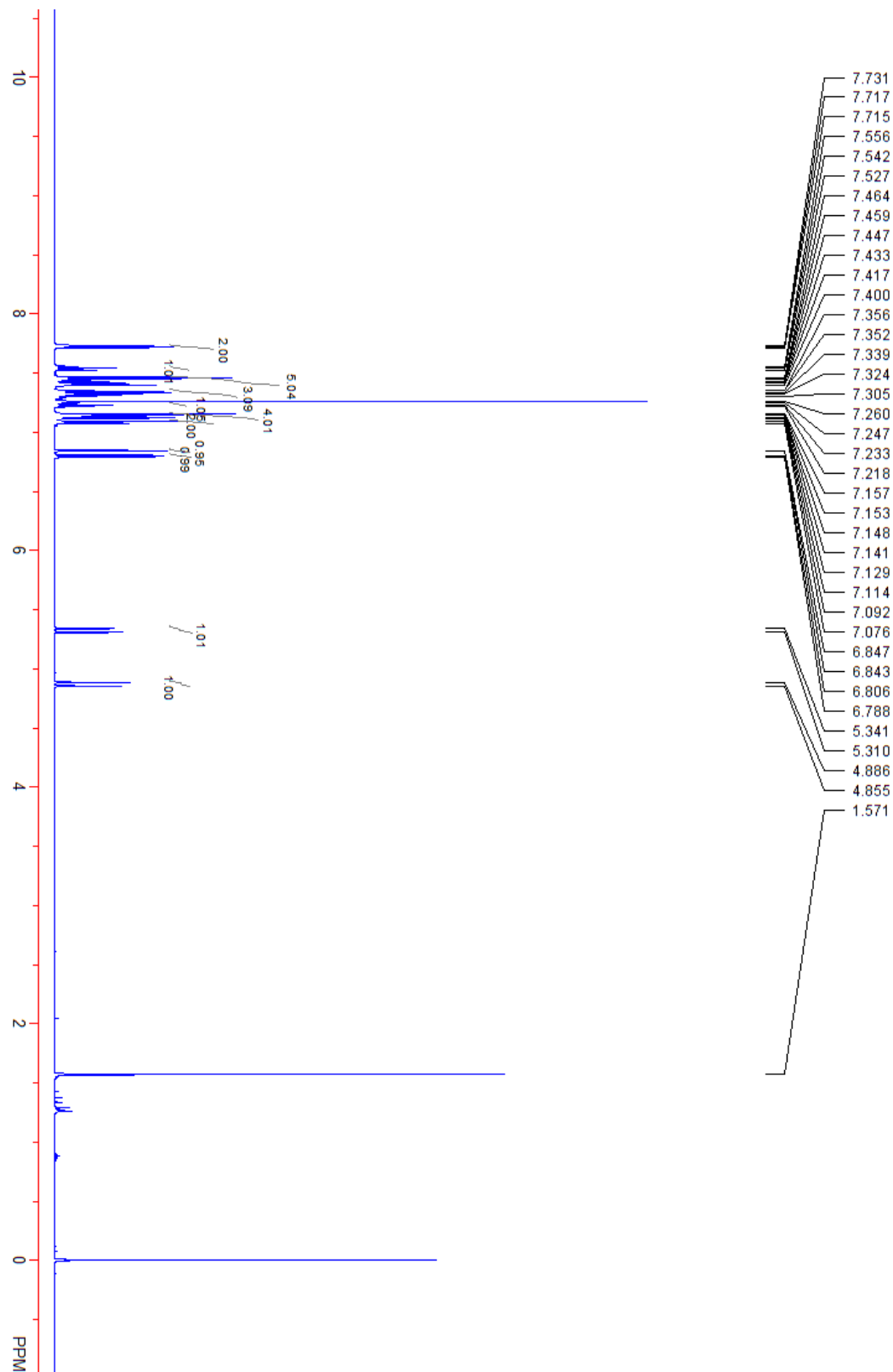


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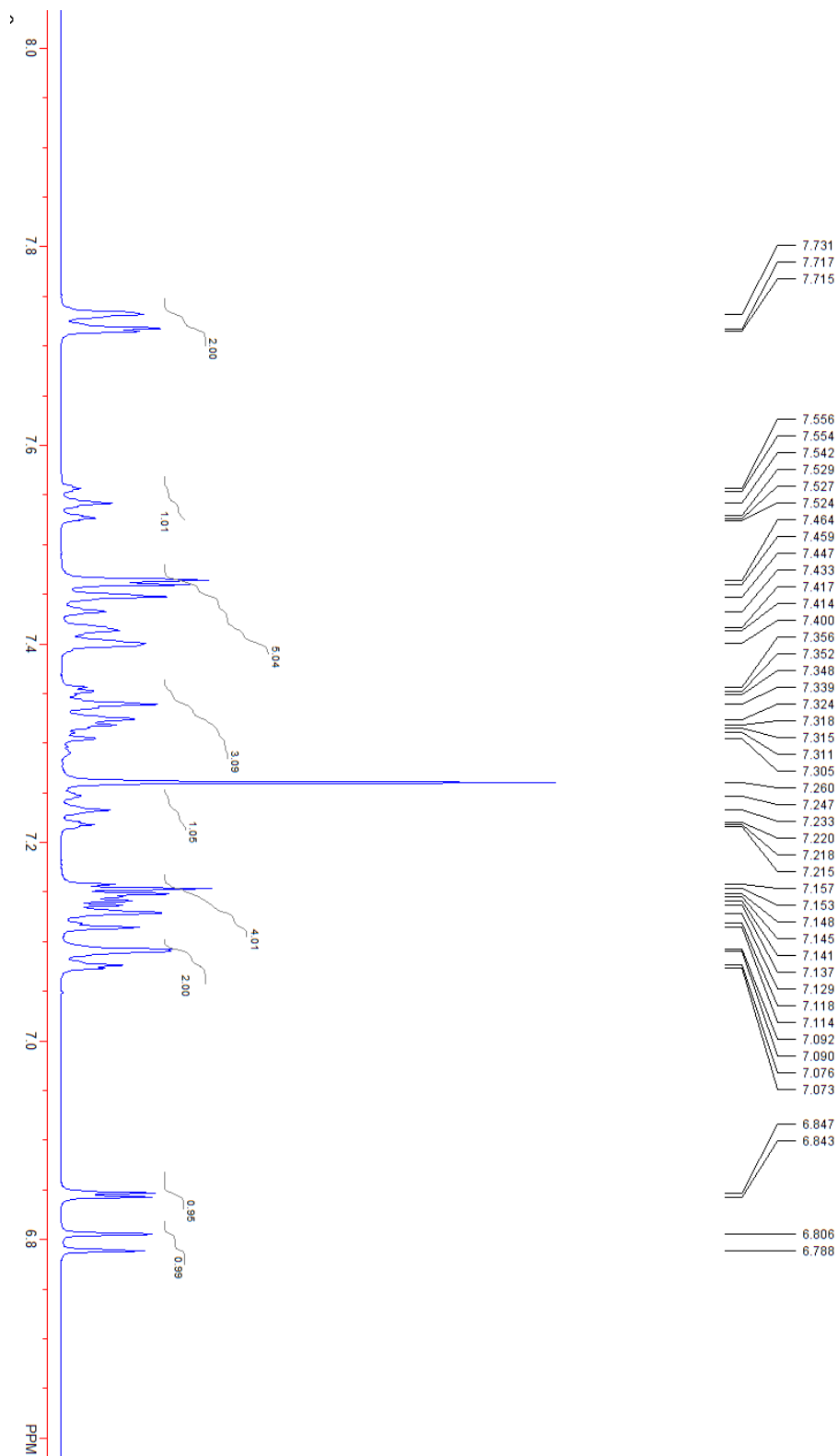
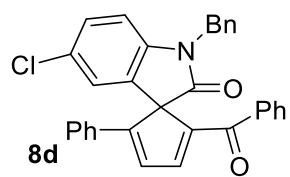




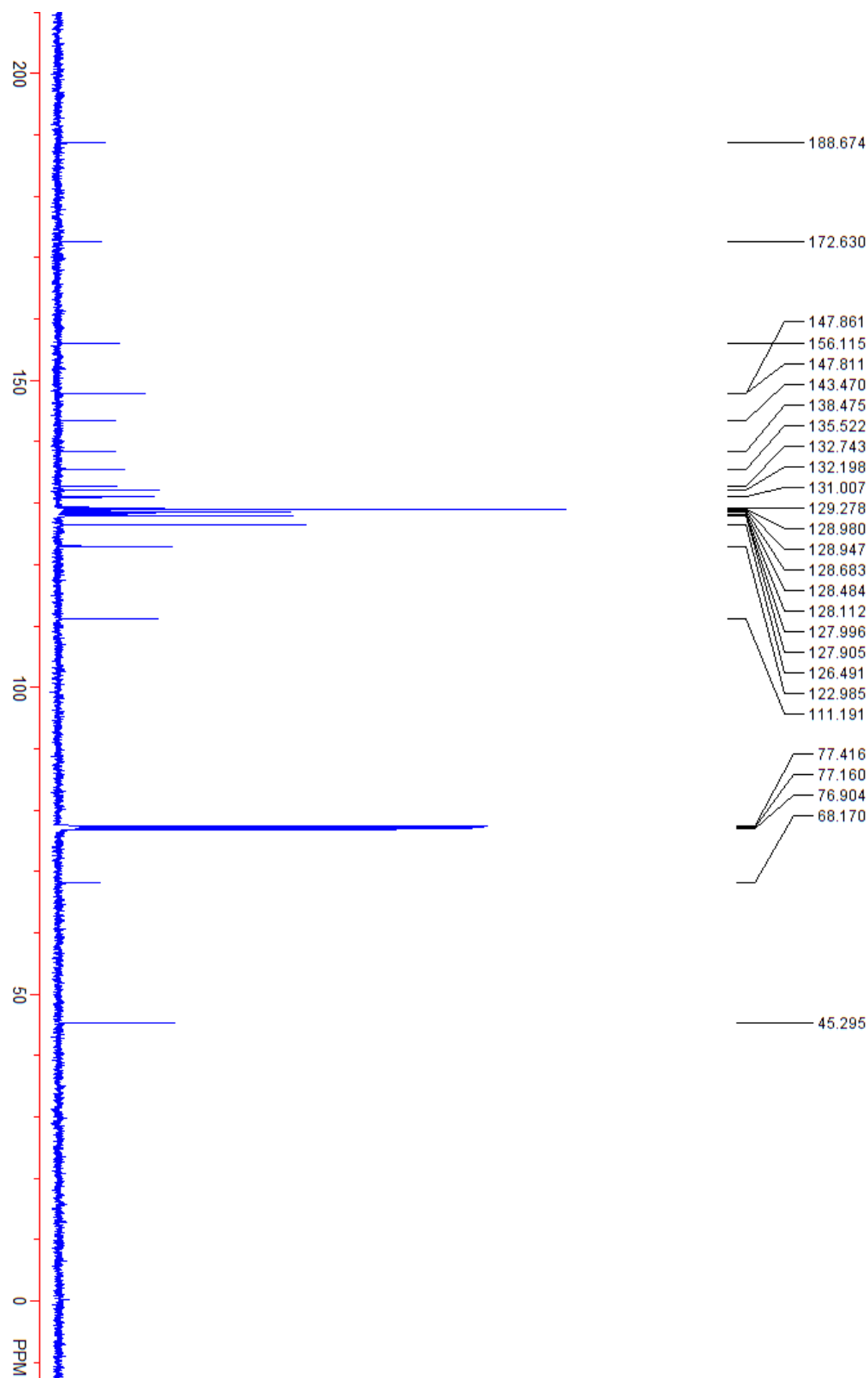
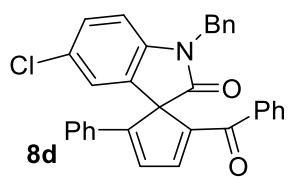
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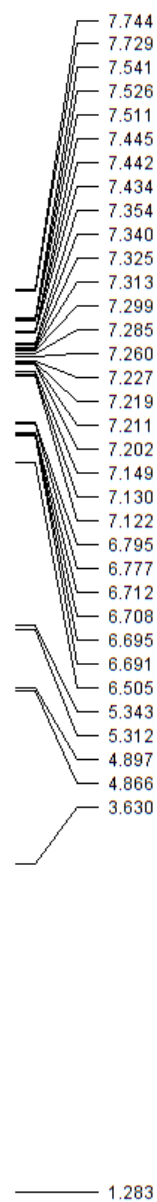
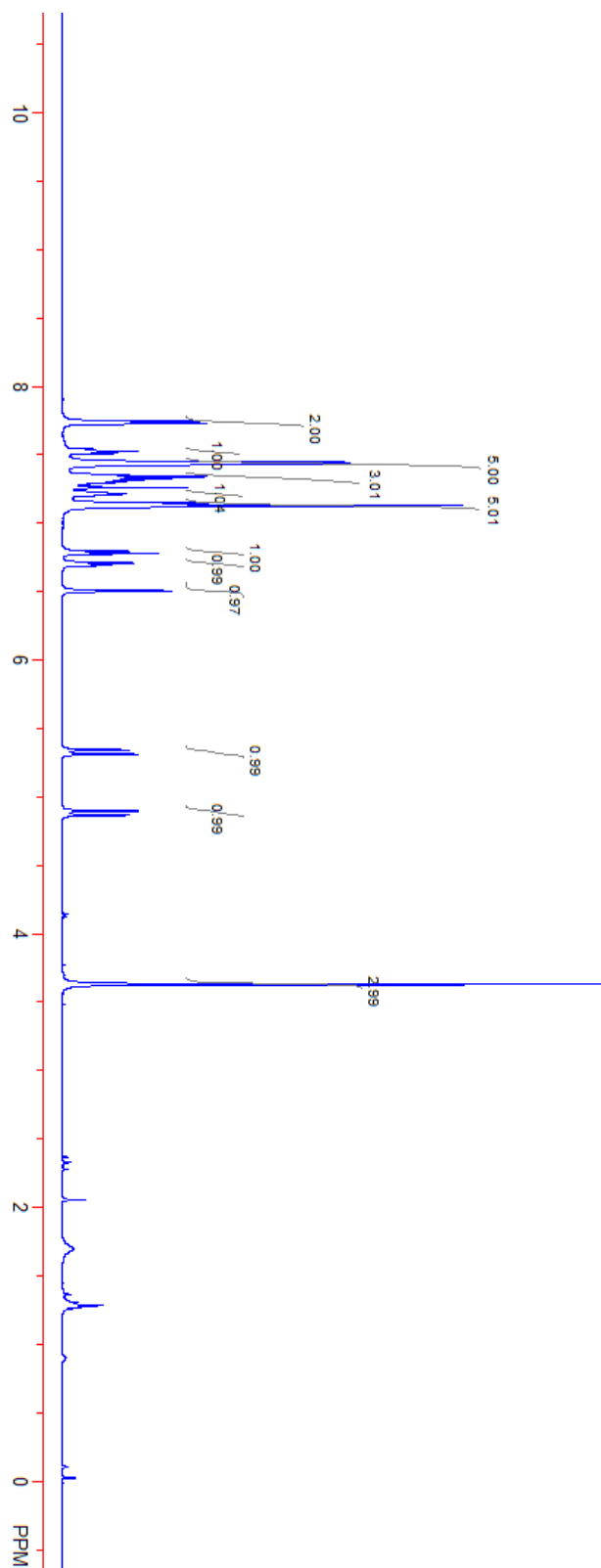
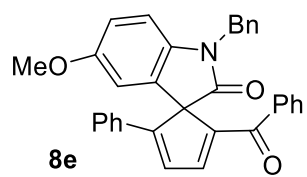
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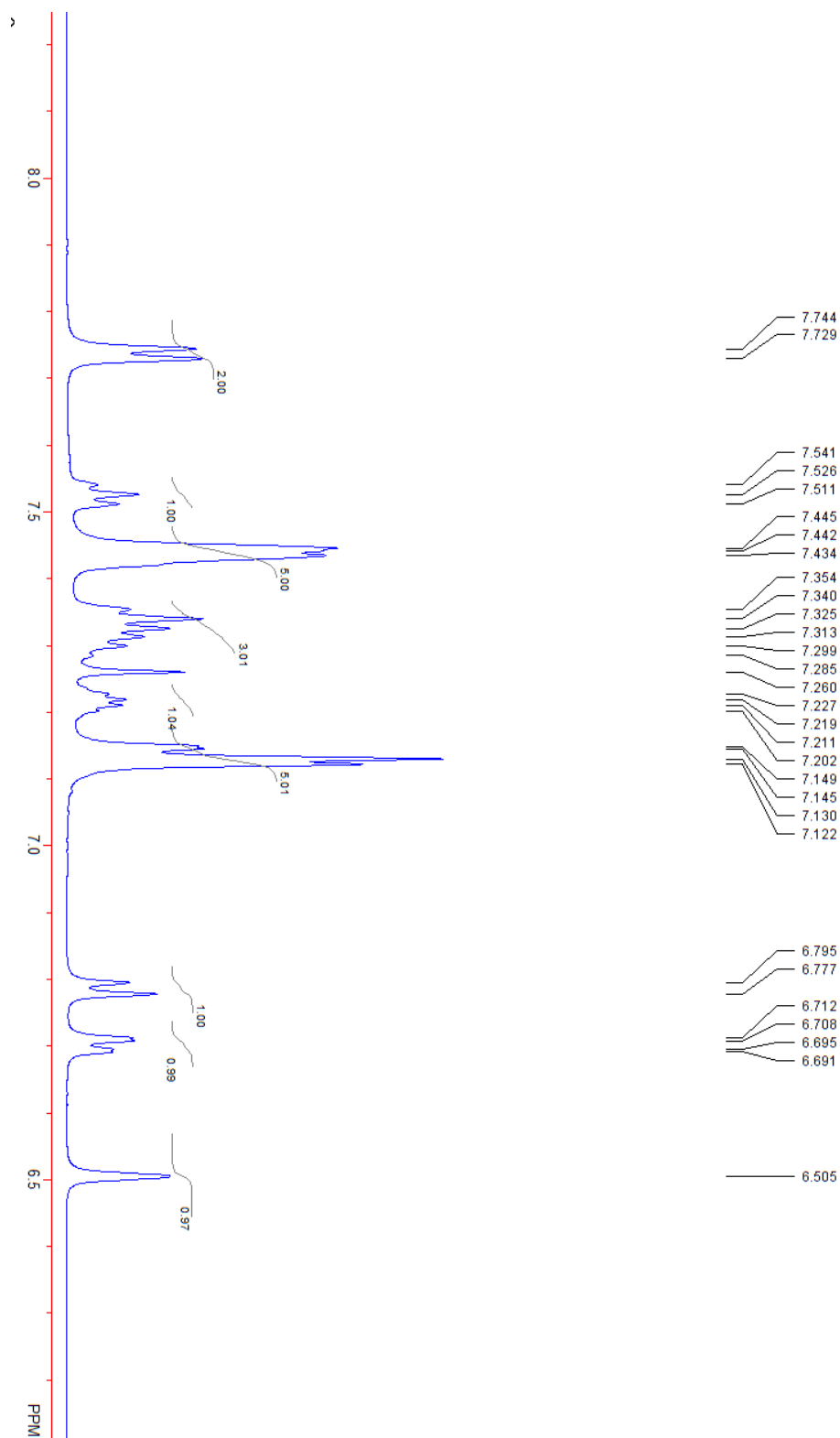
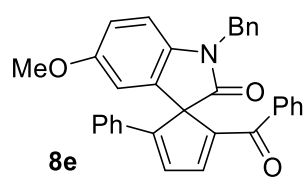
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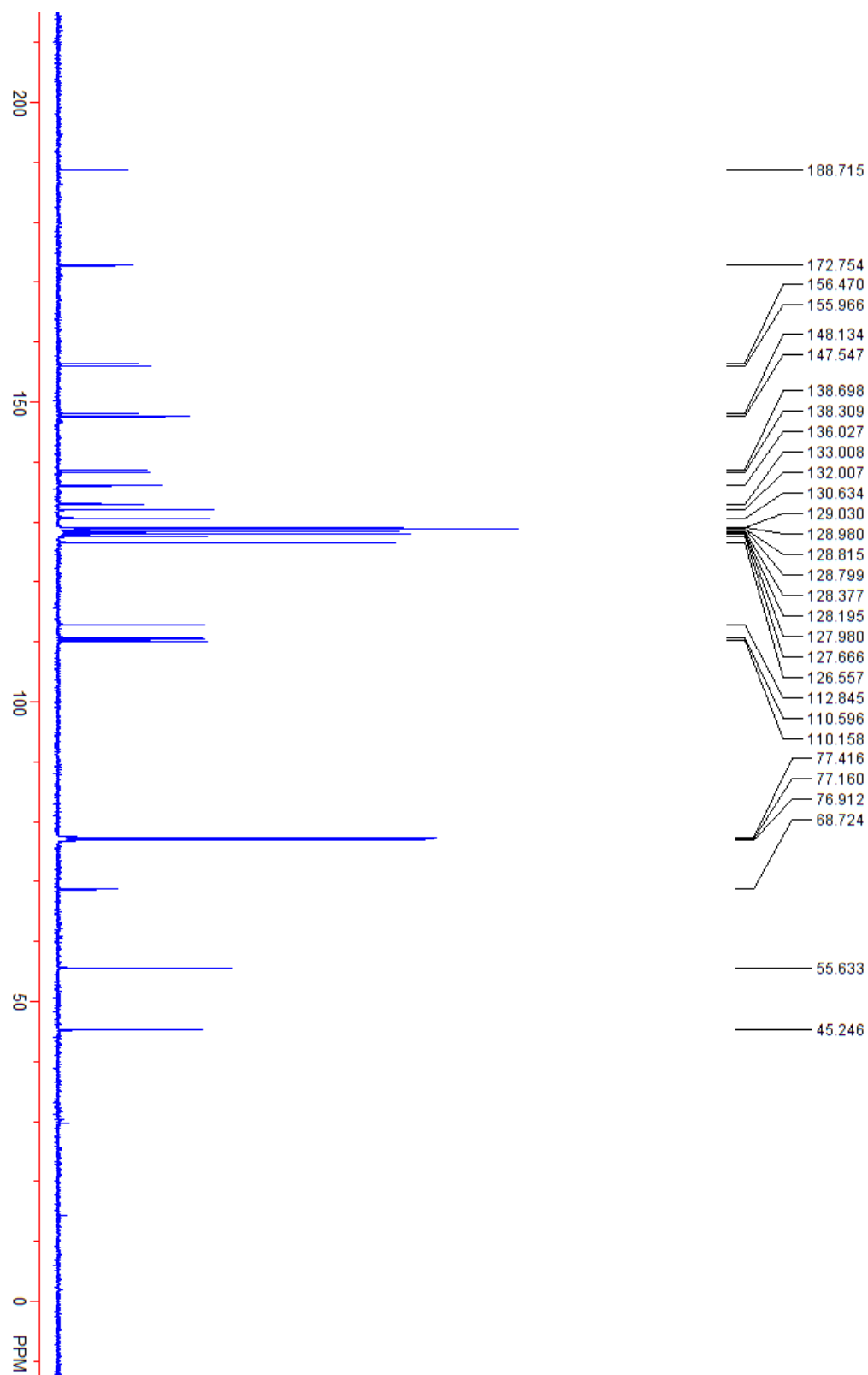
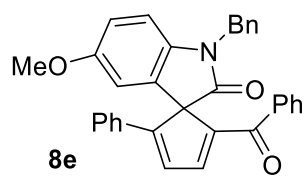
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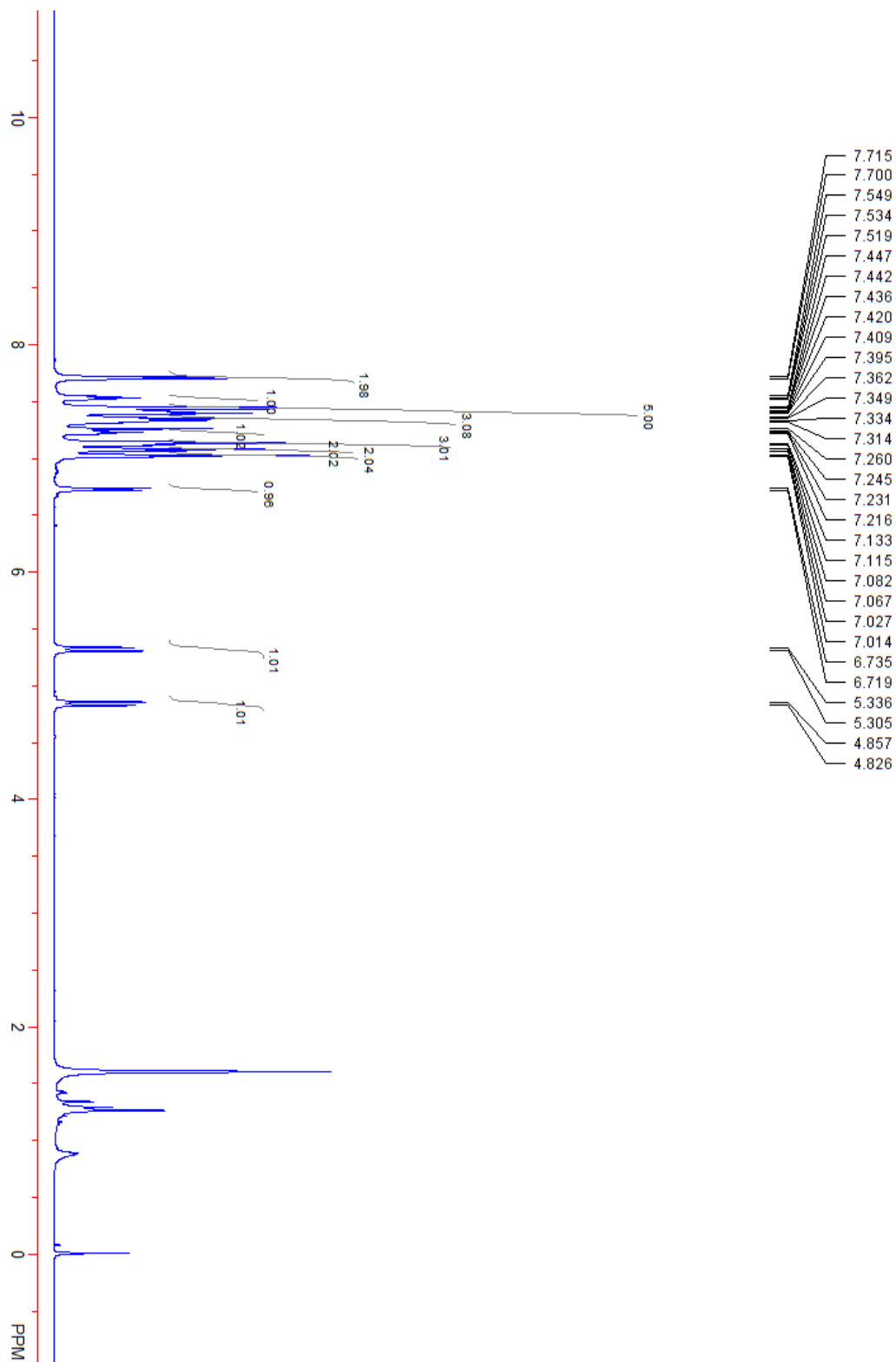
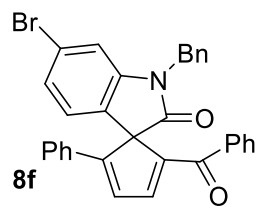
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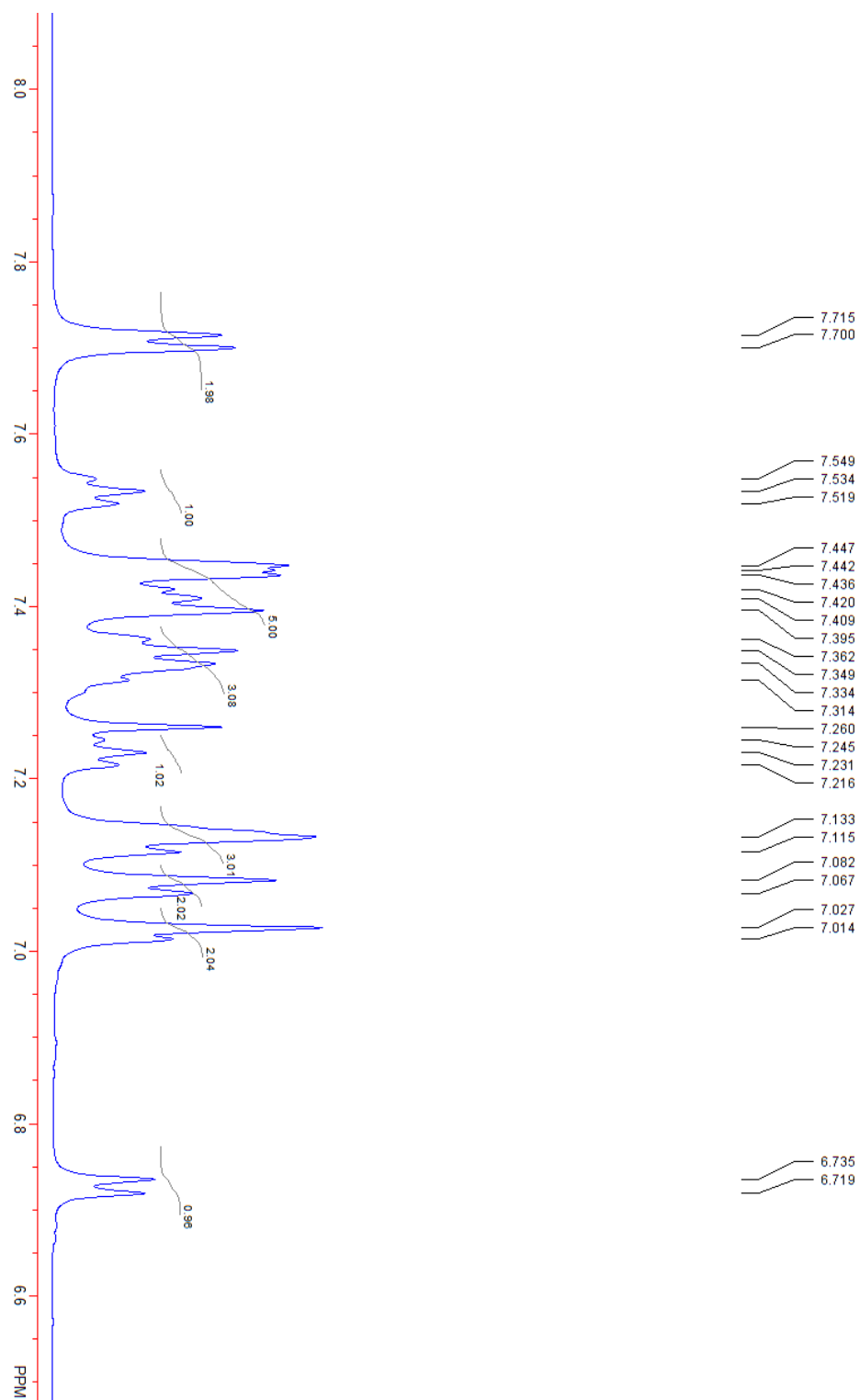
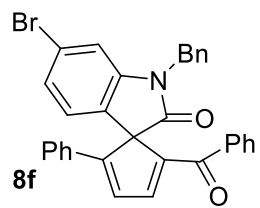
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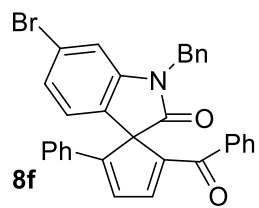


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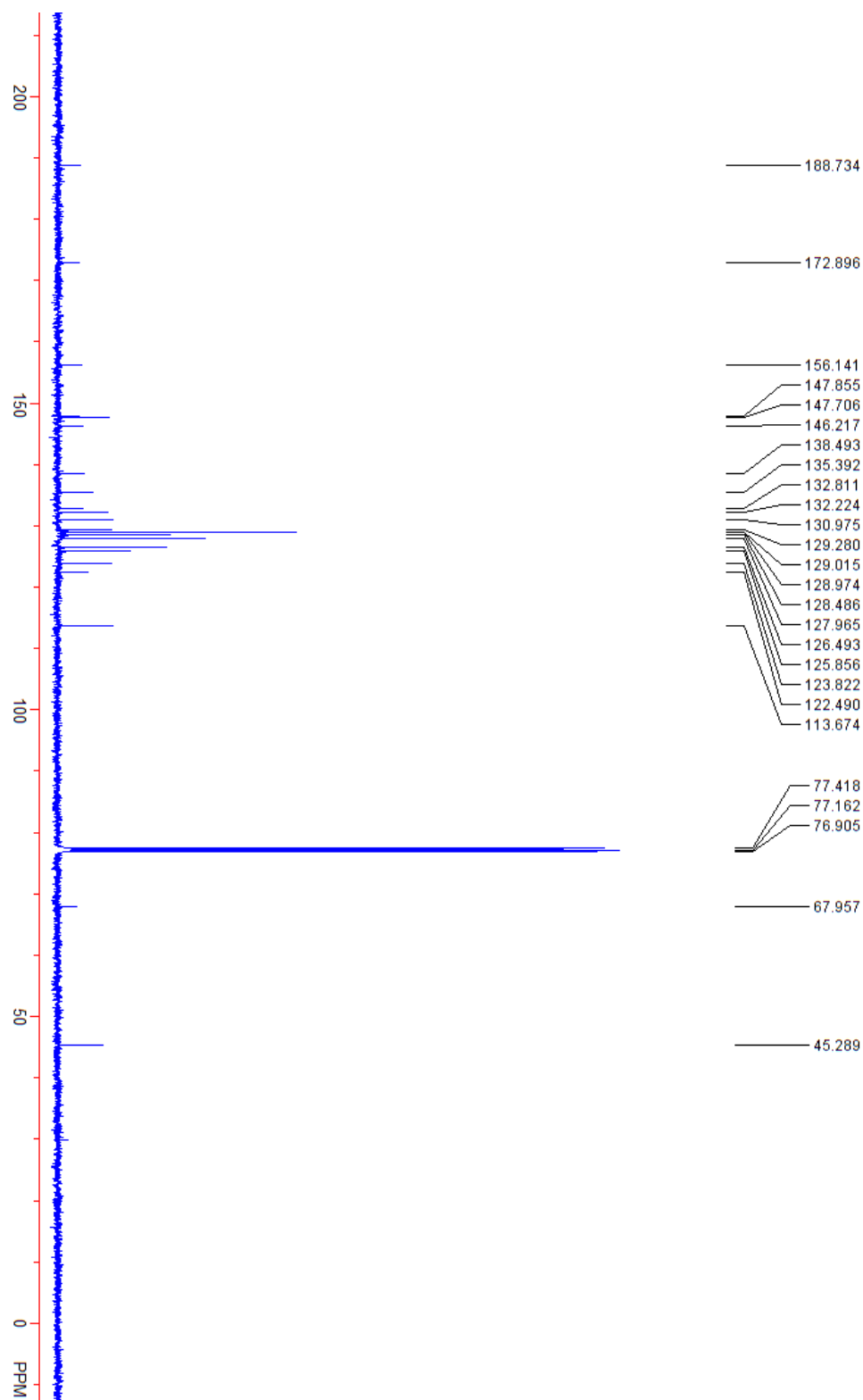


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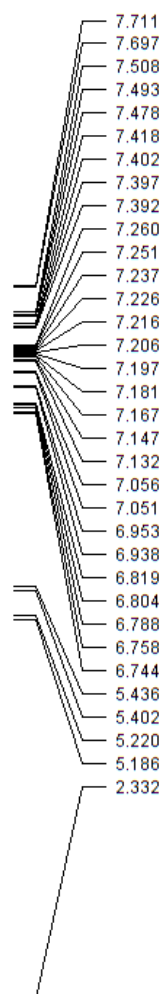
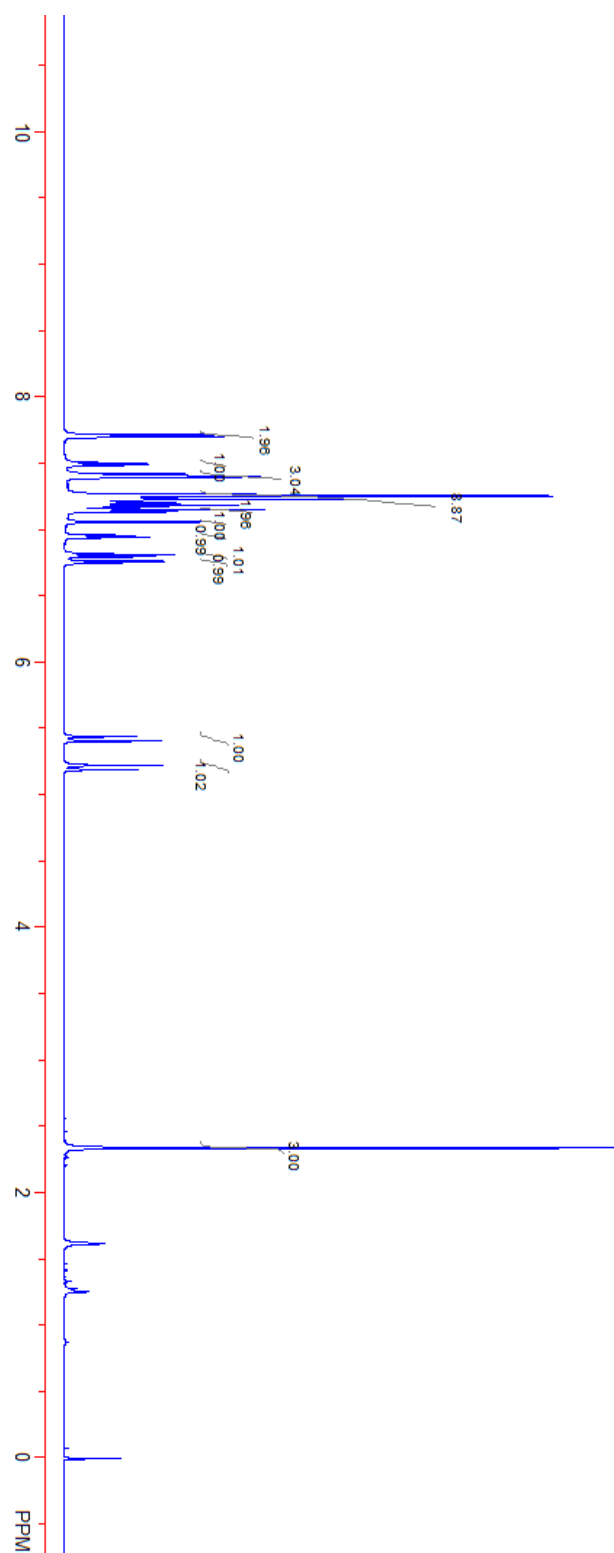
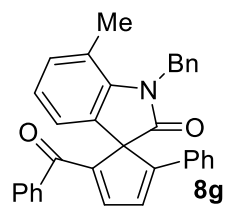




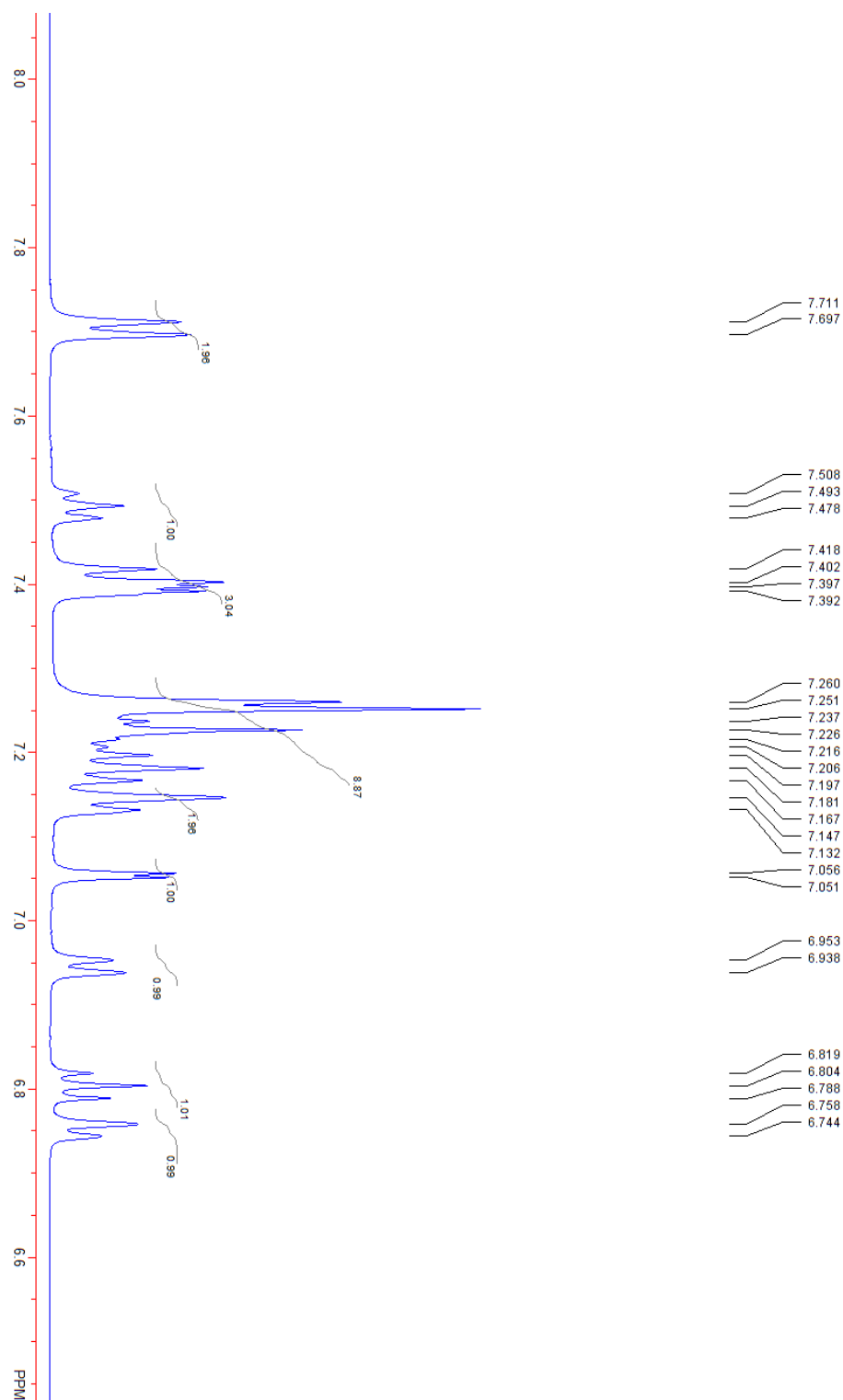
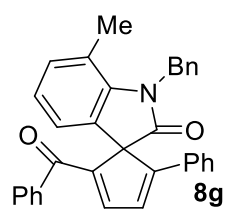
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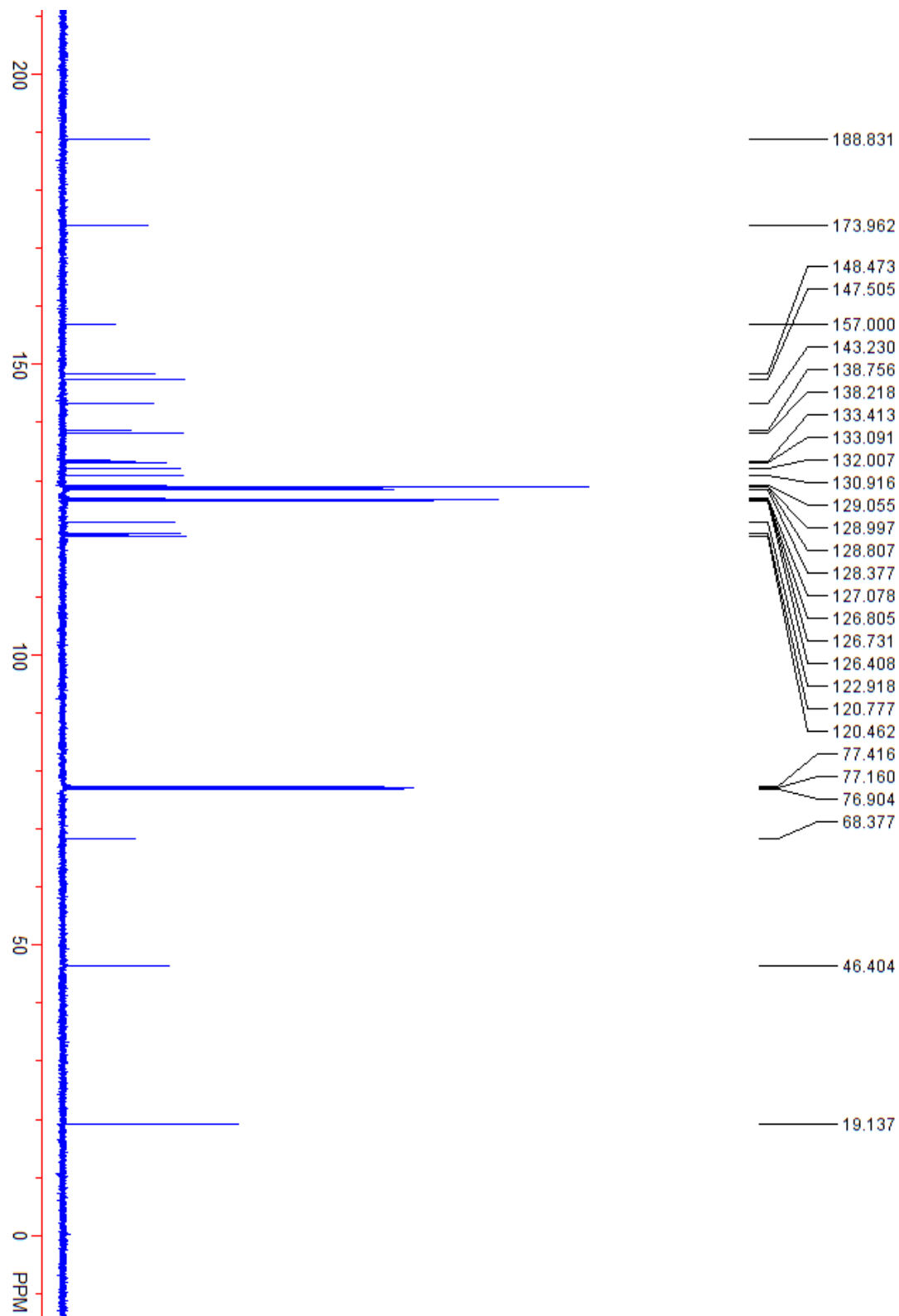
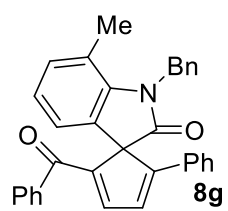
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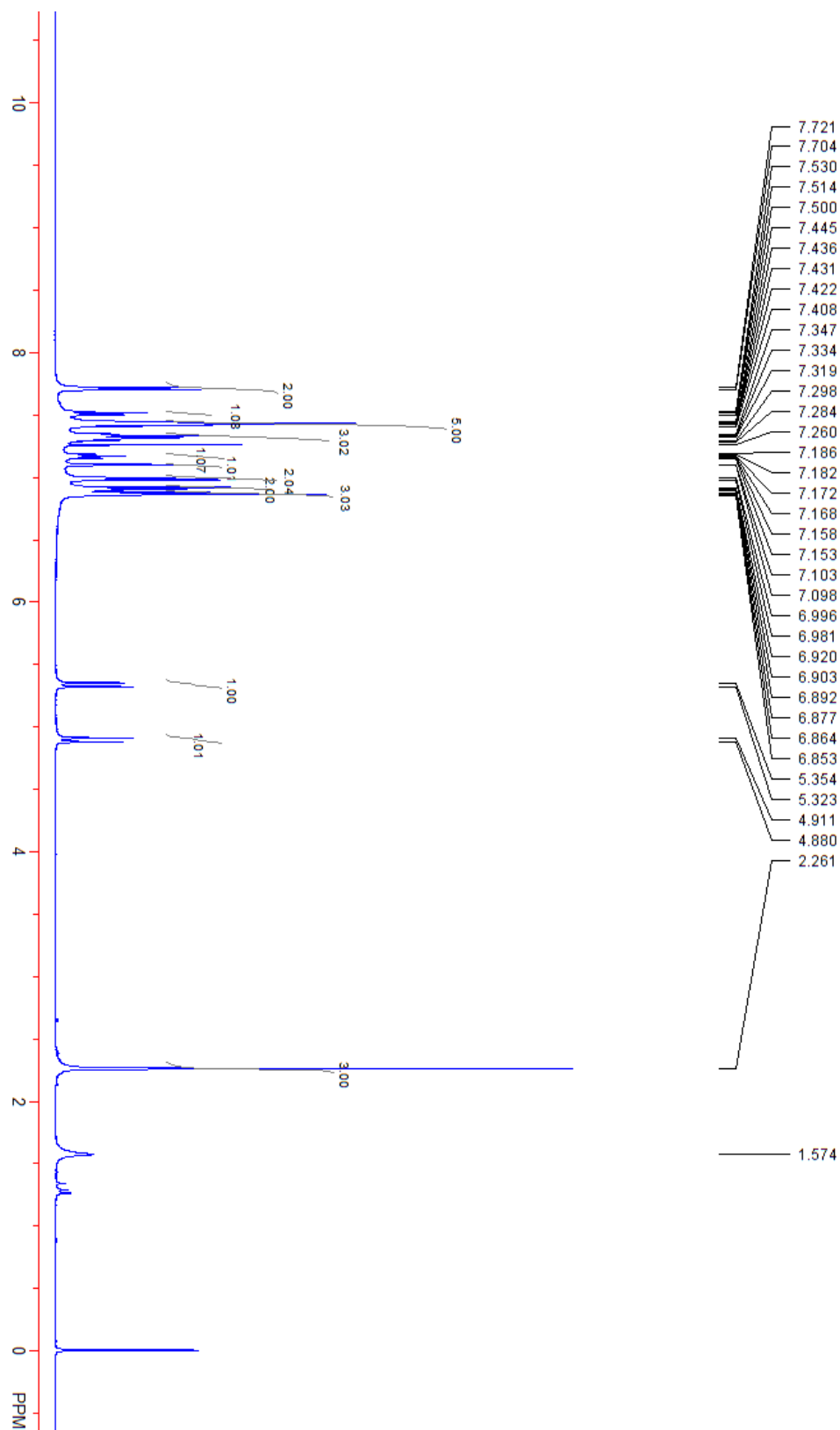
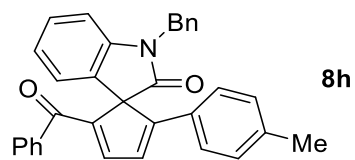
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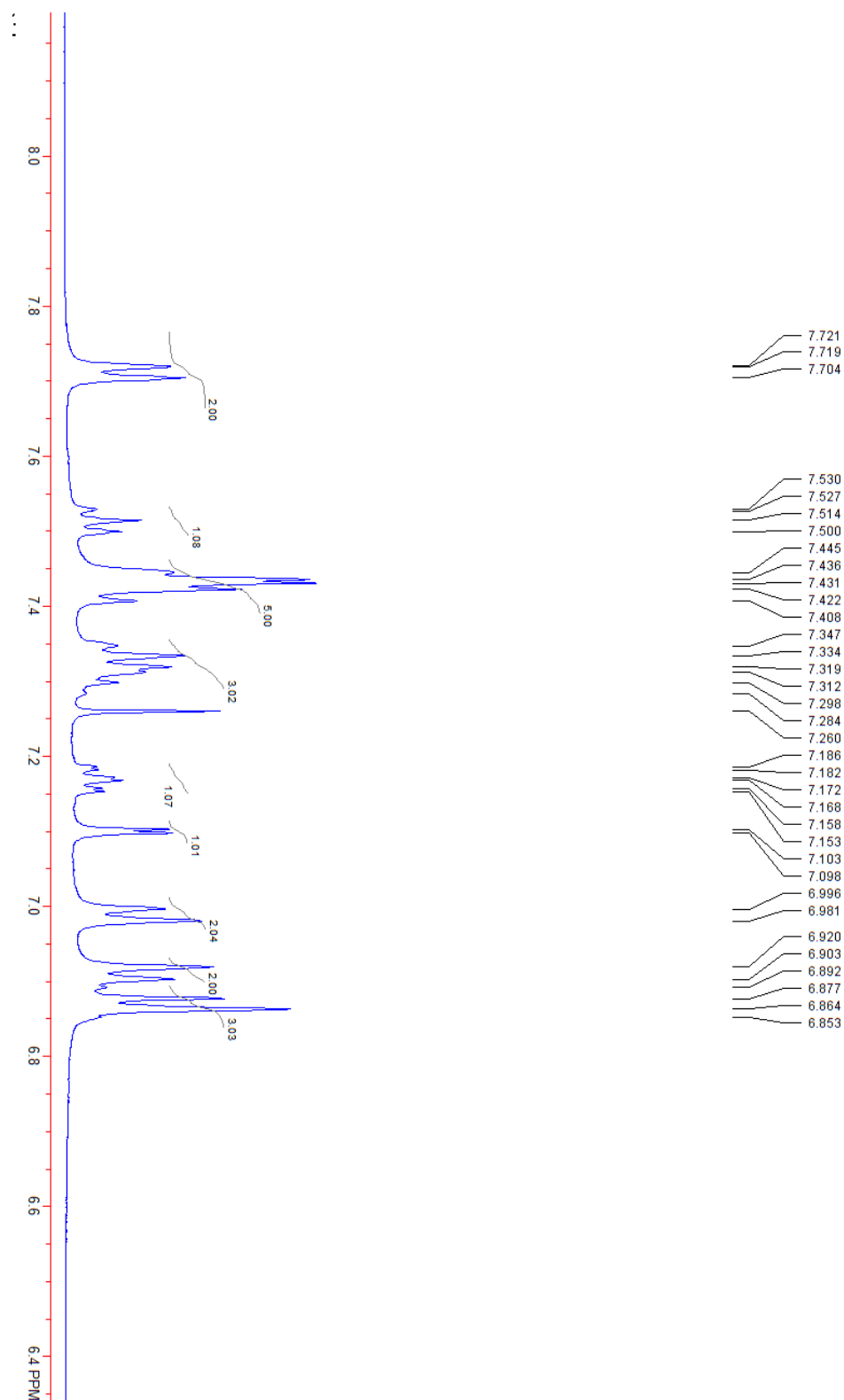
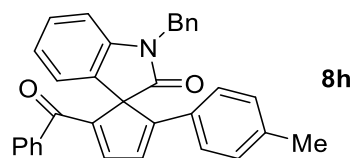
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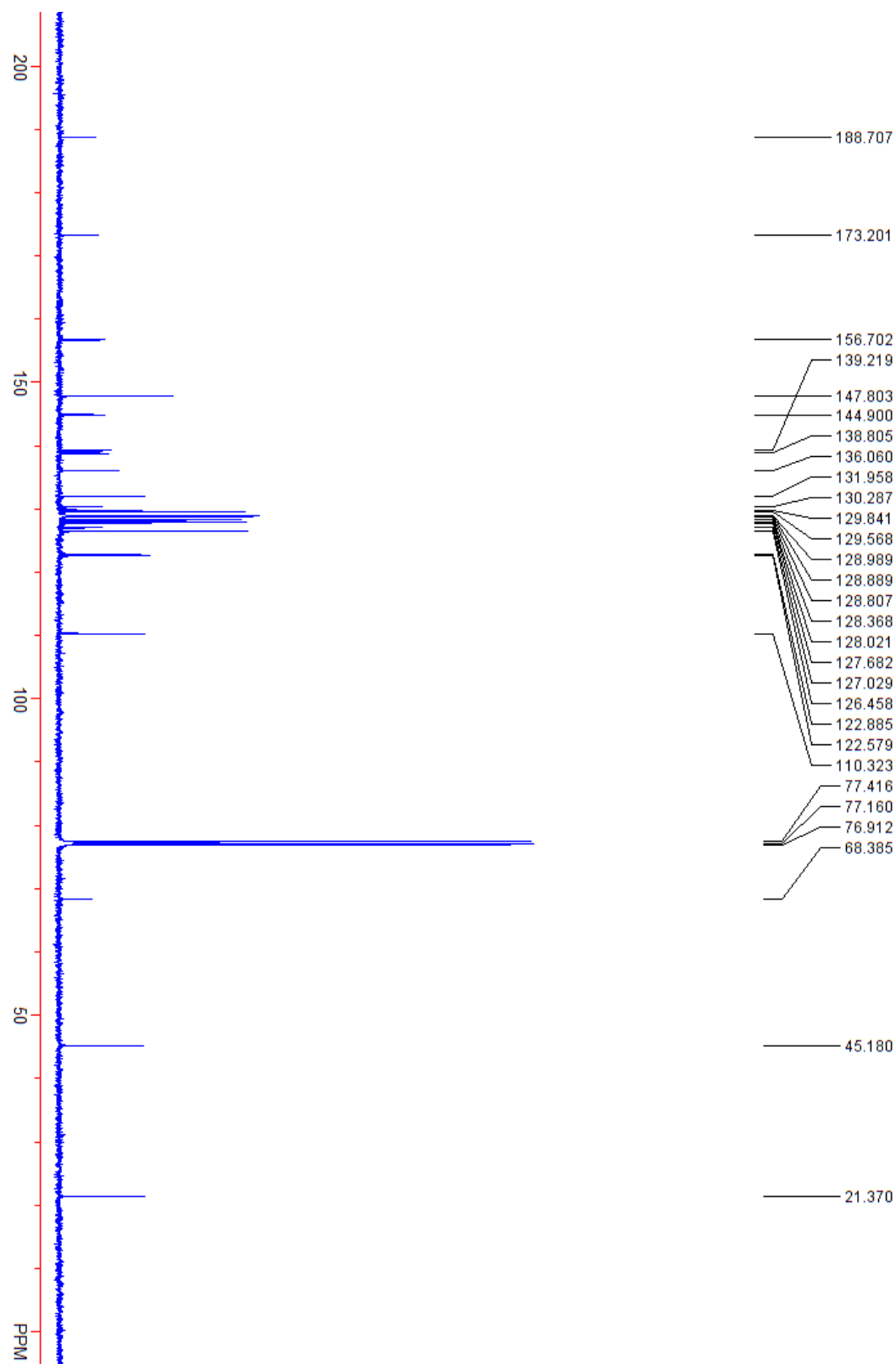
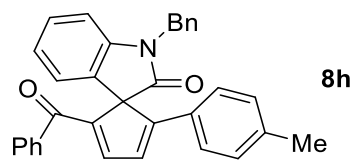
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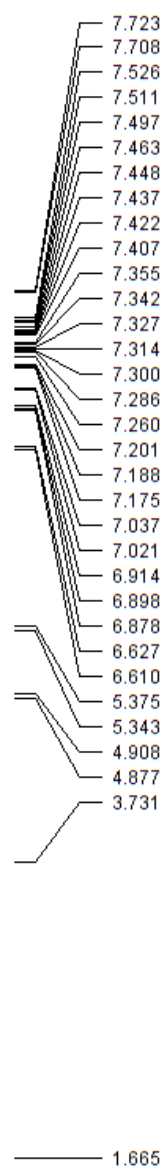
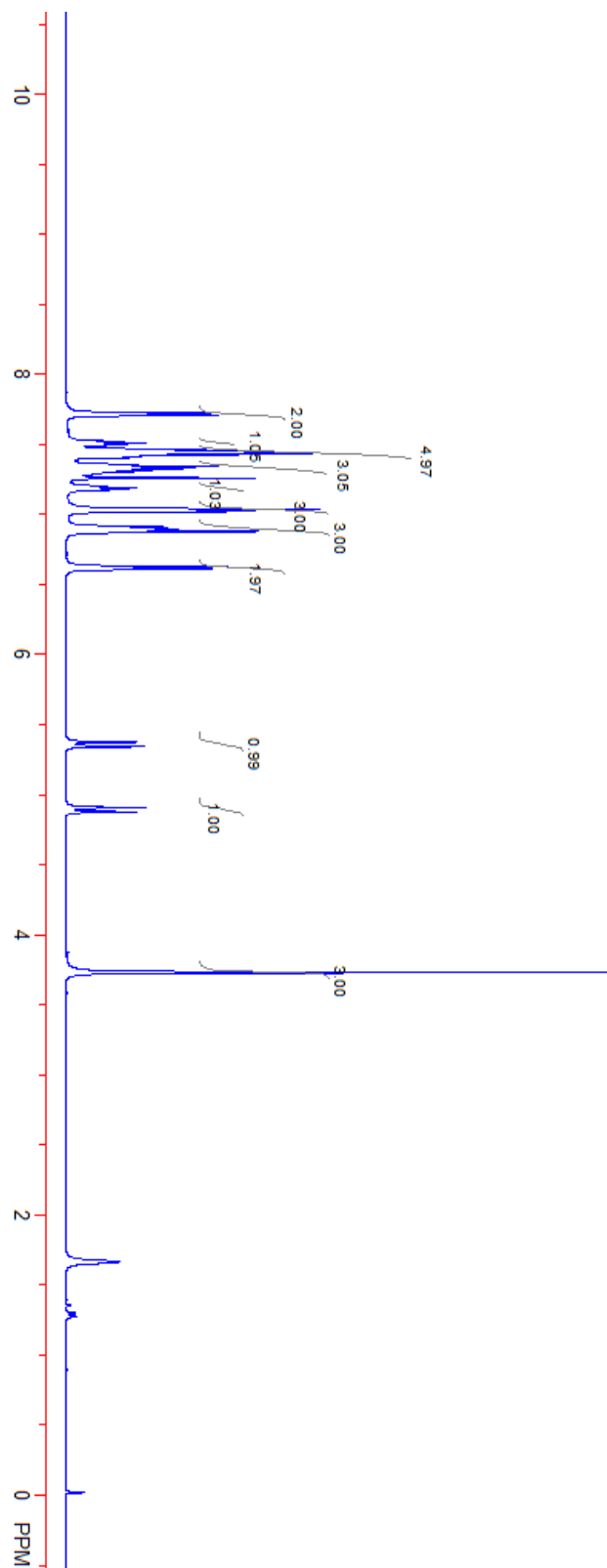
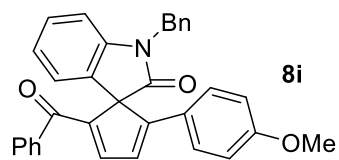
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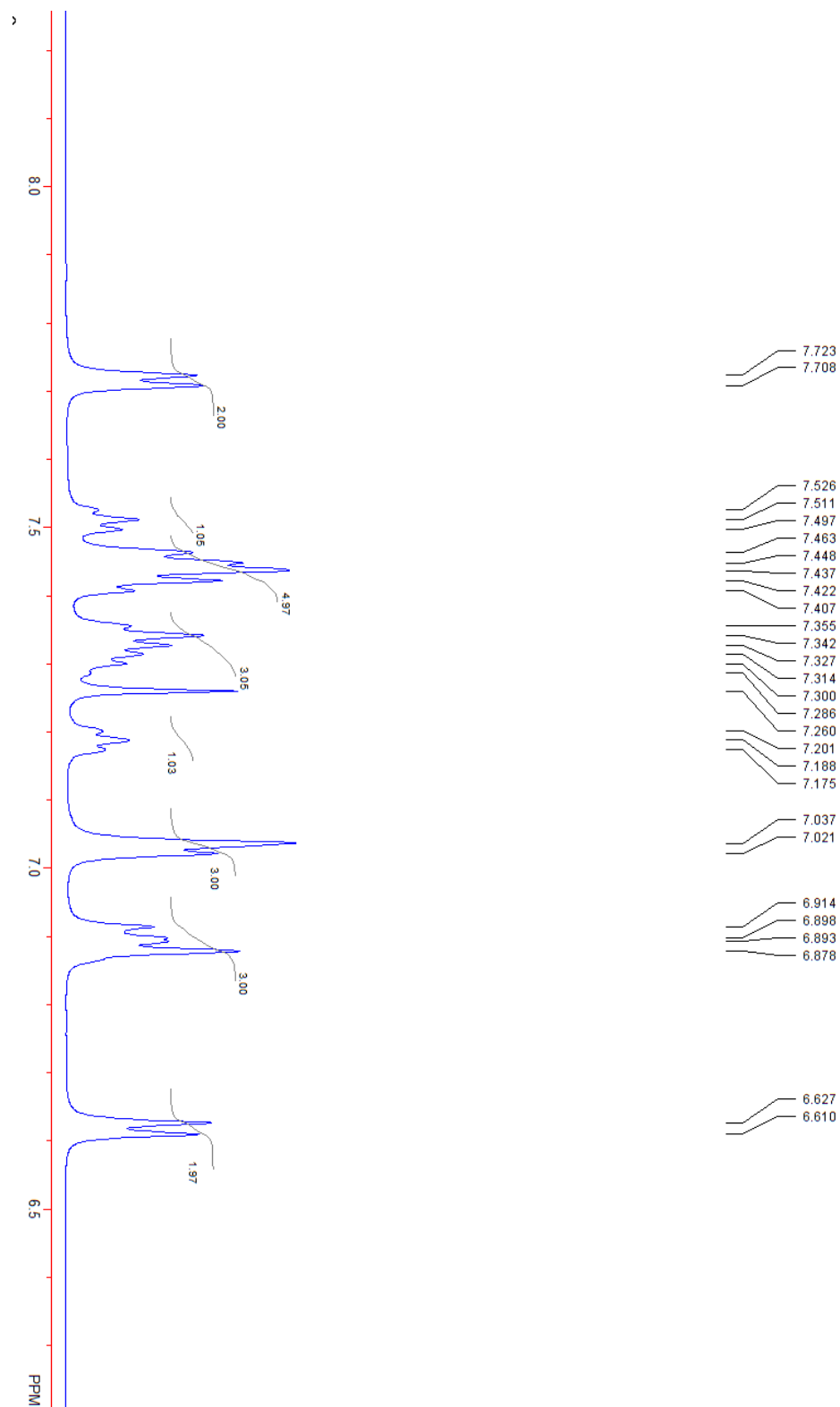
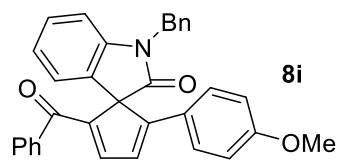
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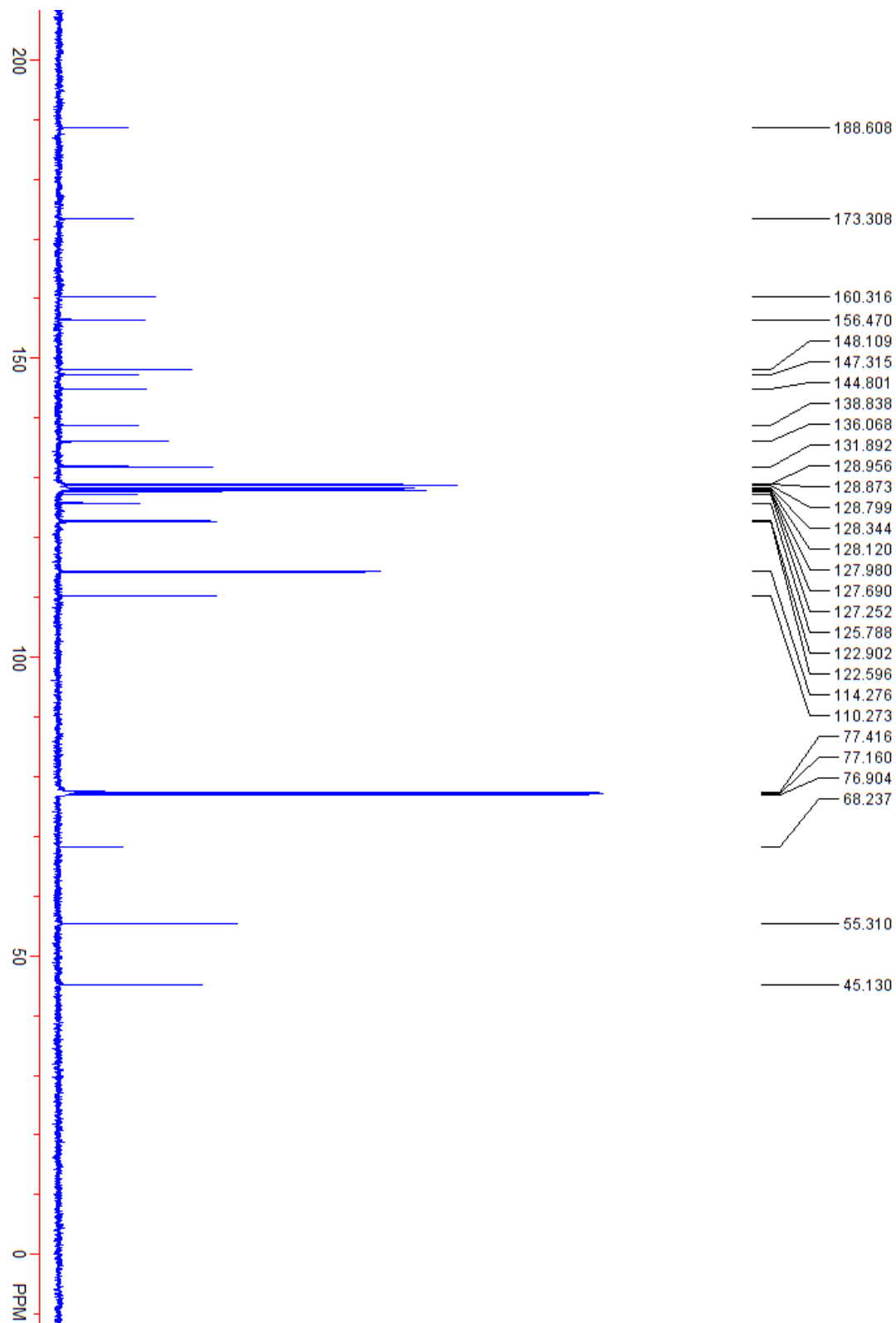
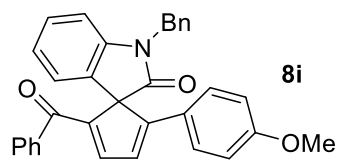
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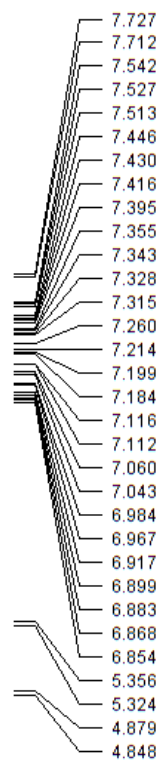
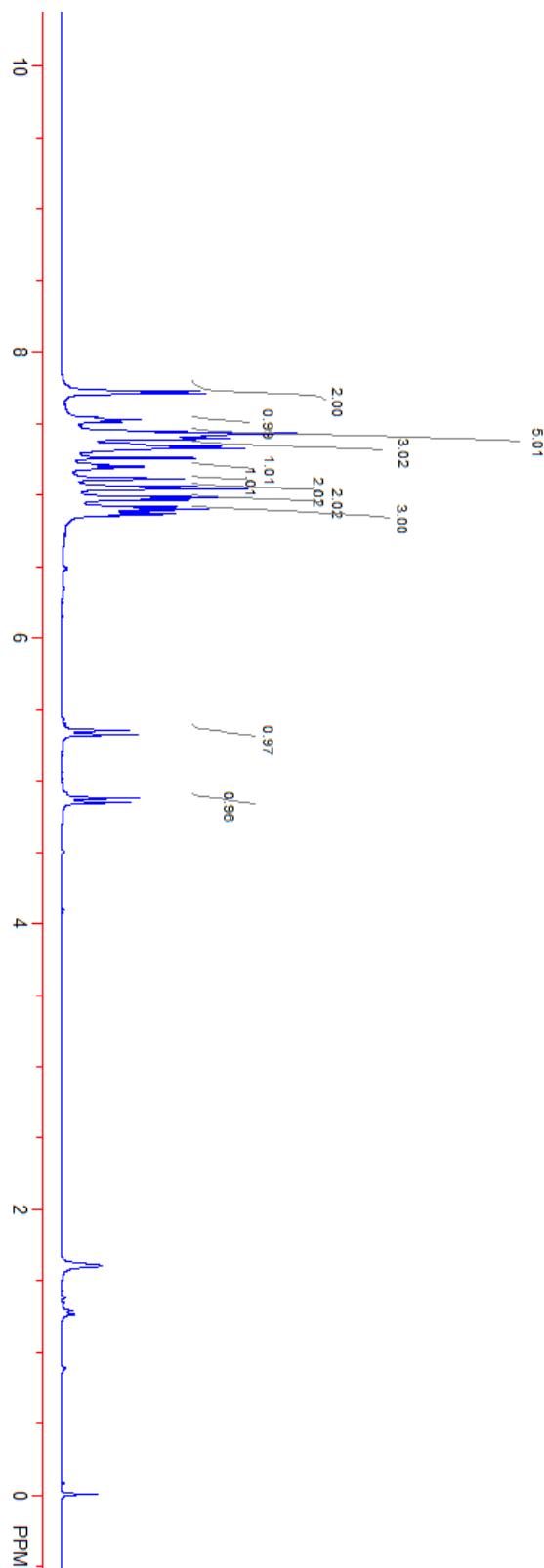
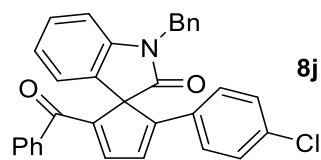
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$^{13}\text{C}\{^1\text{H}\}$ NMR:

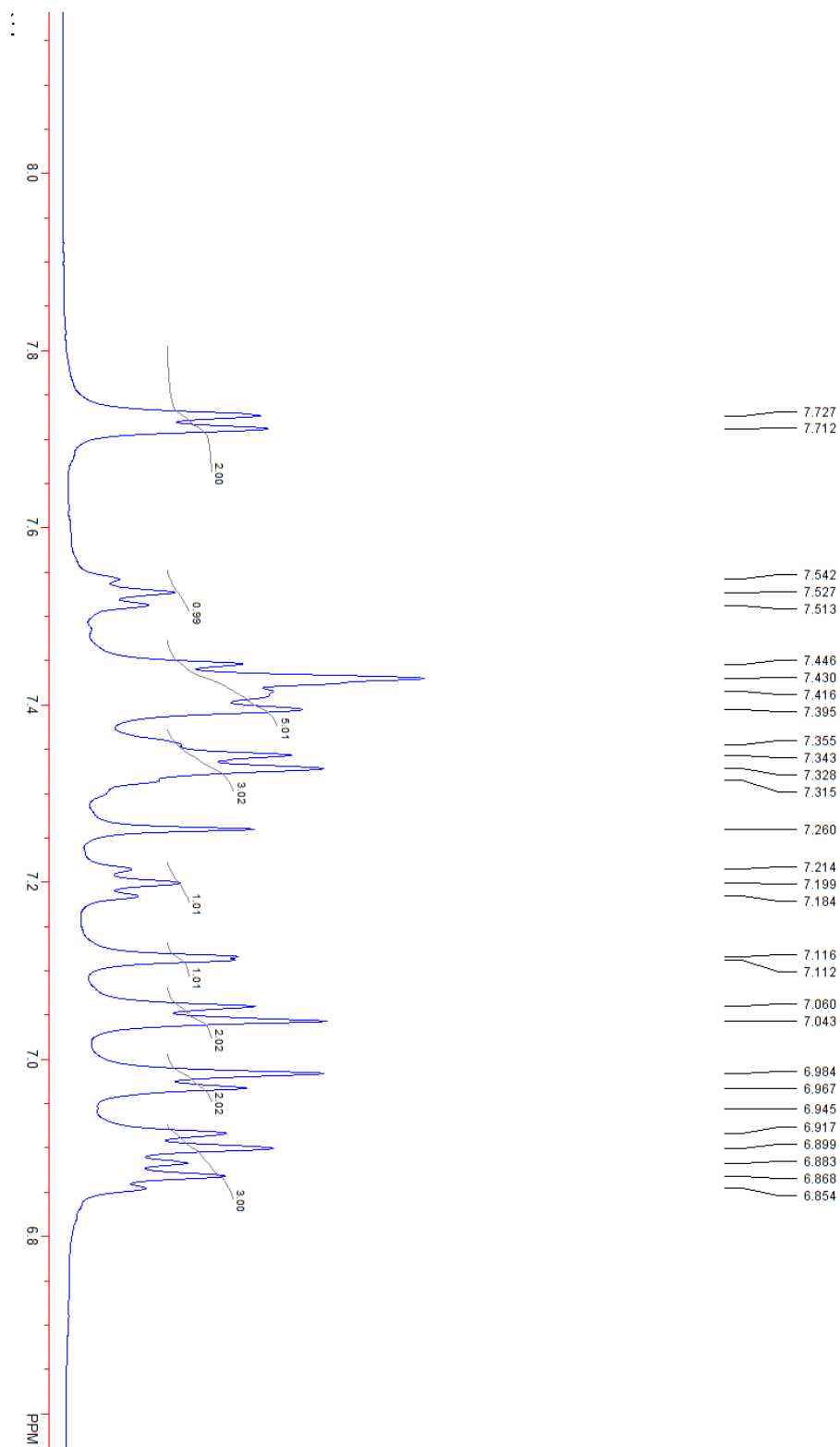
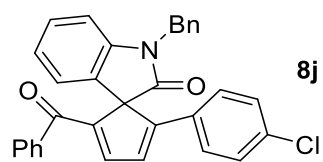


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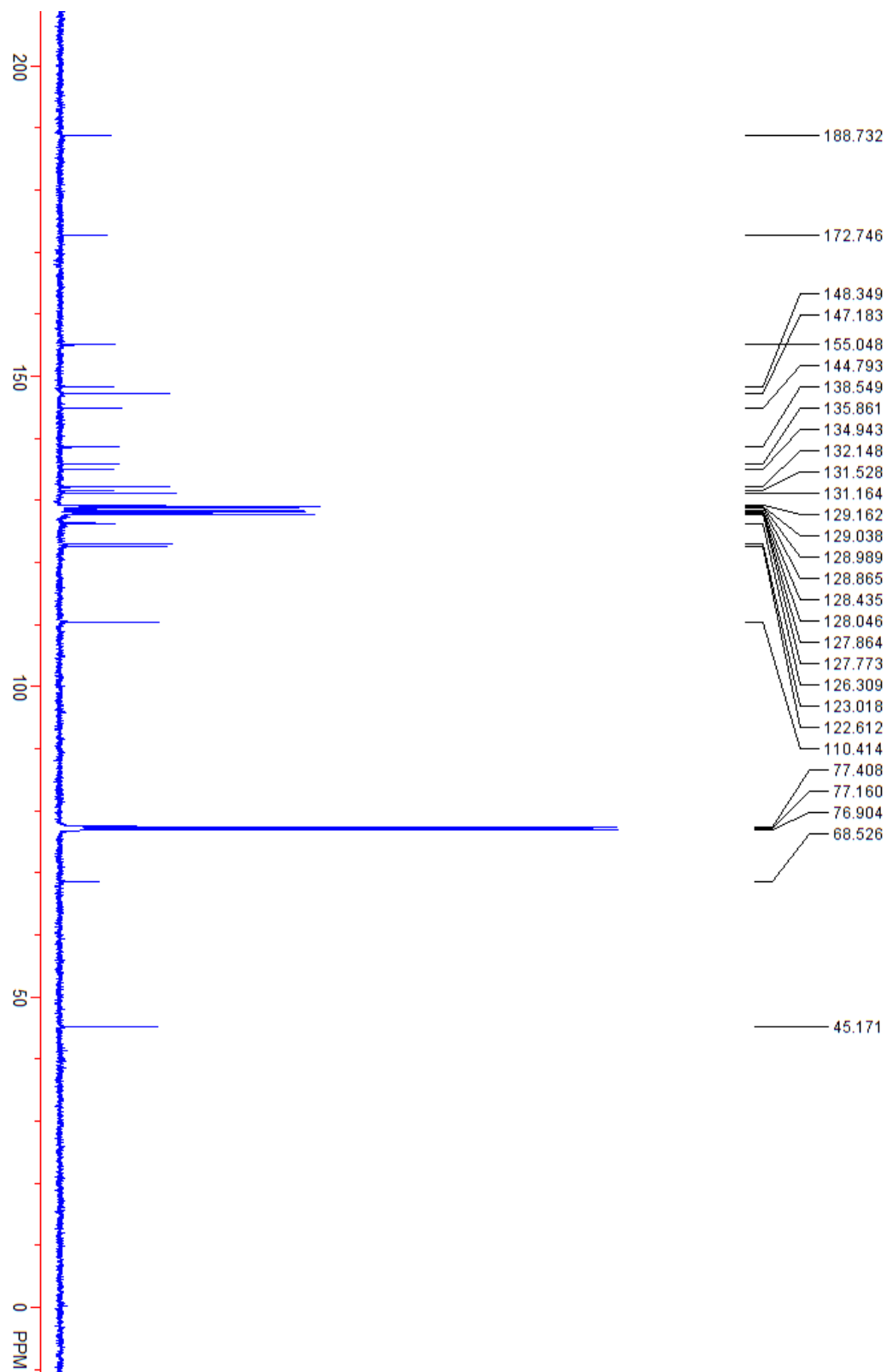
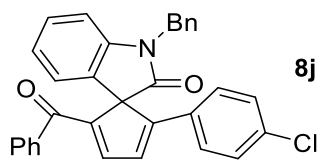


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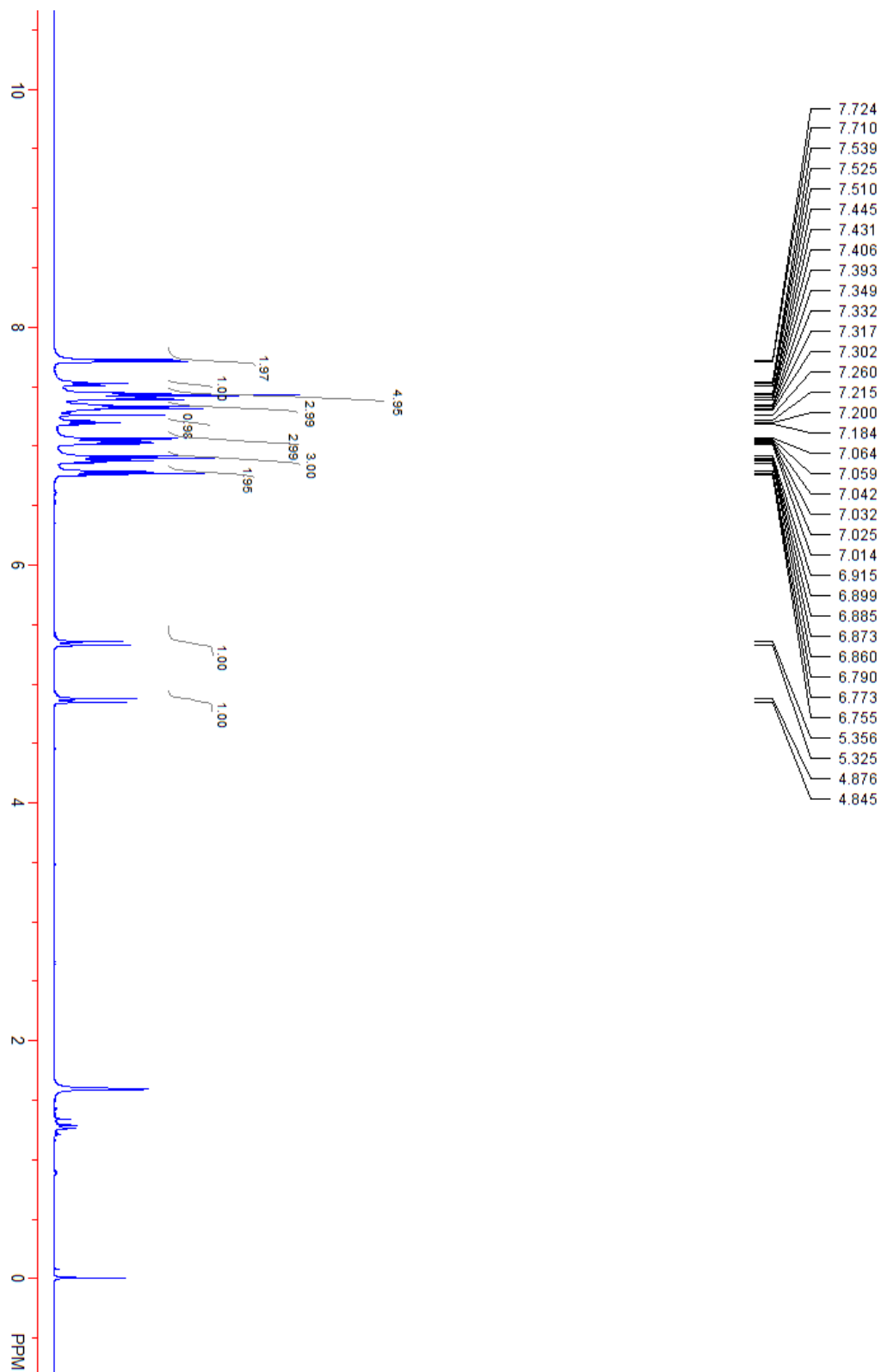
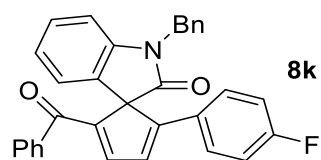
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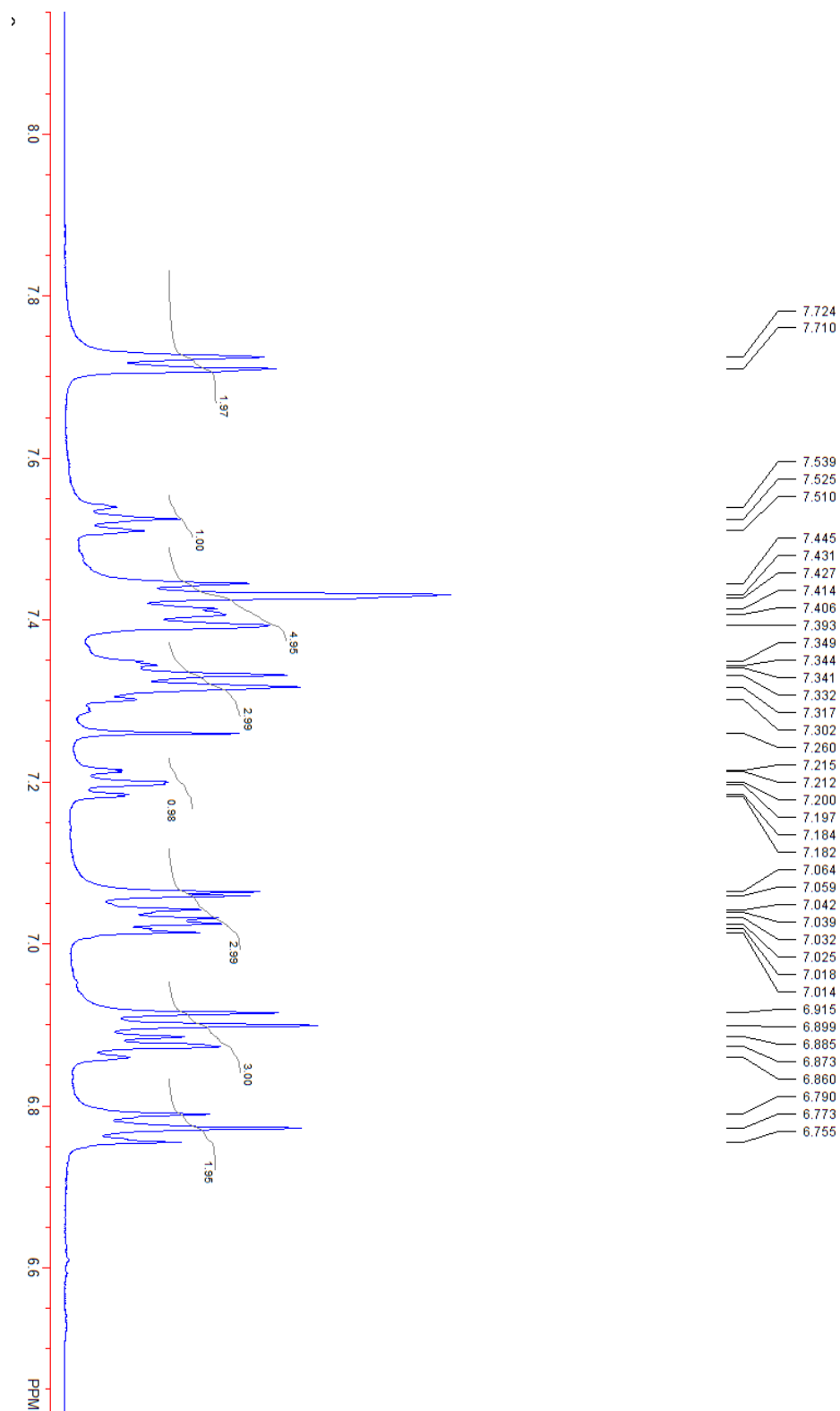
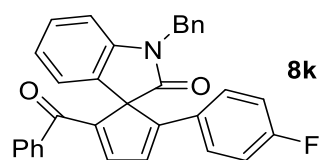
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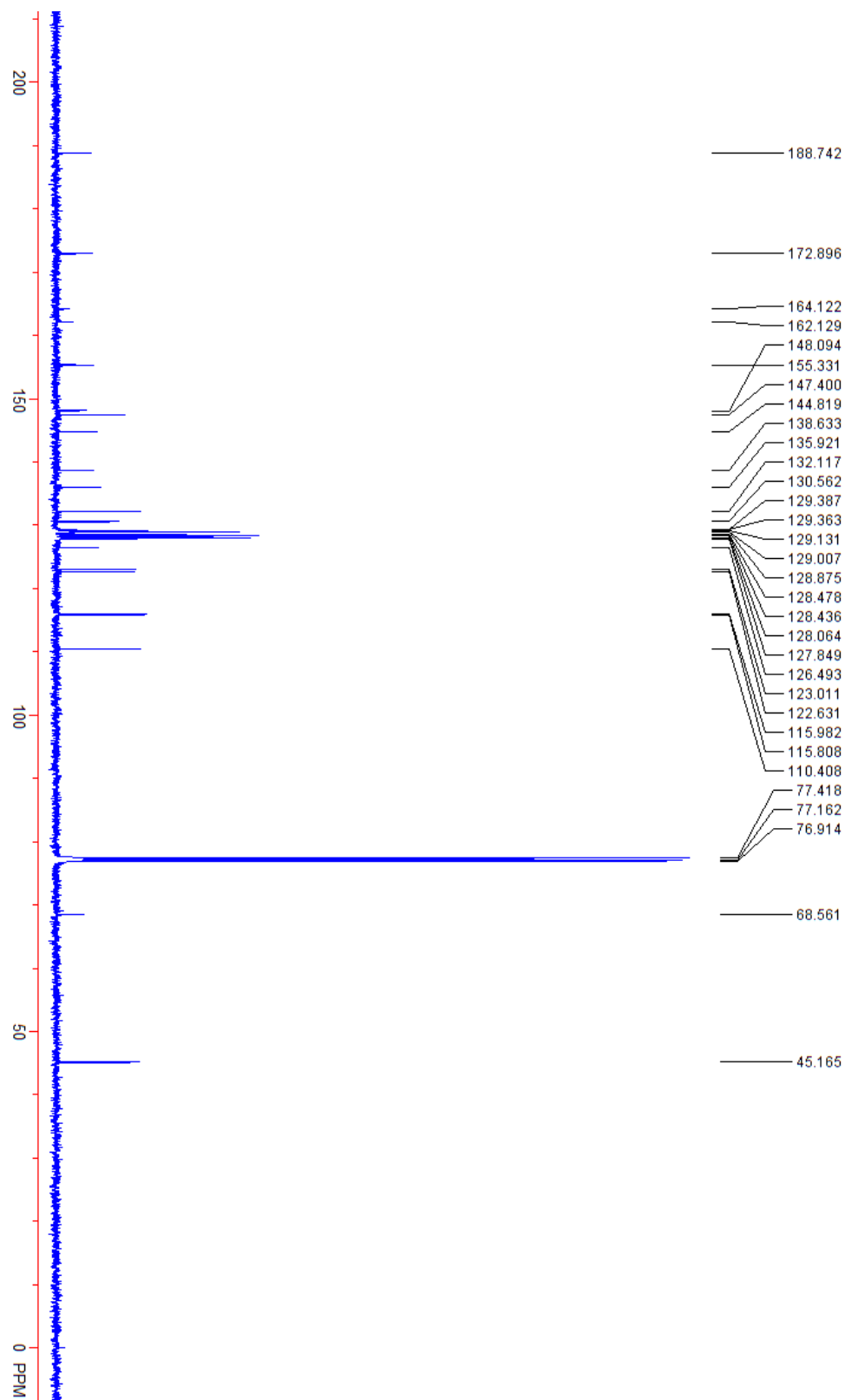
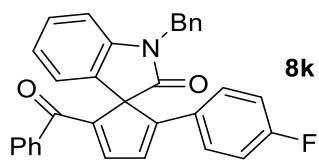
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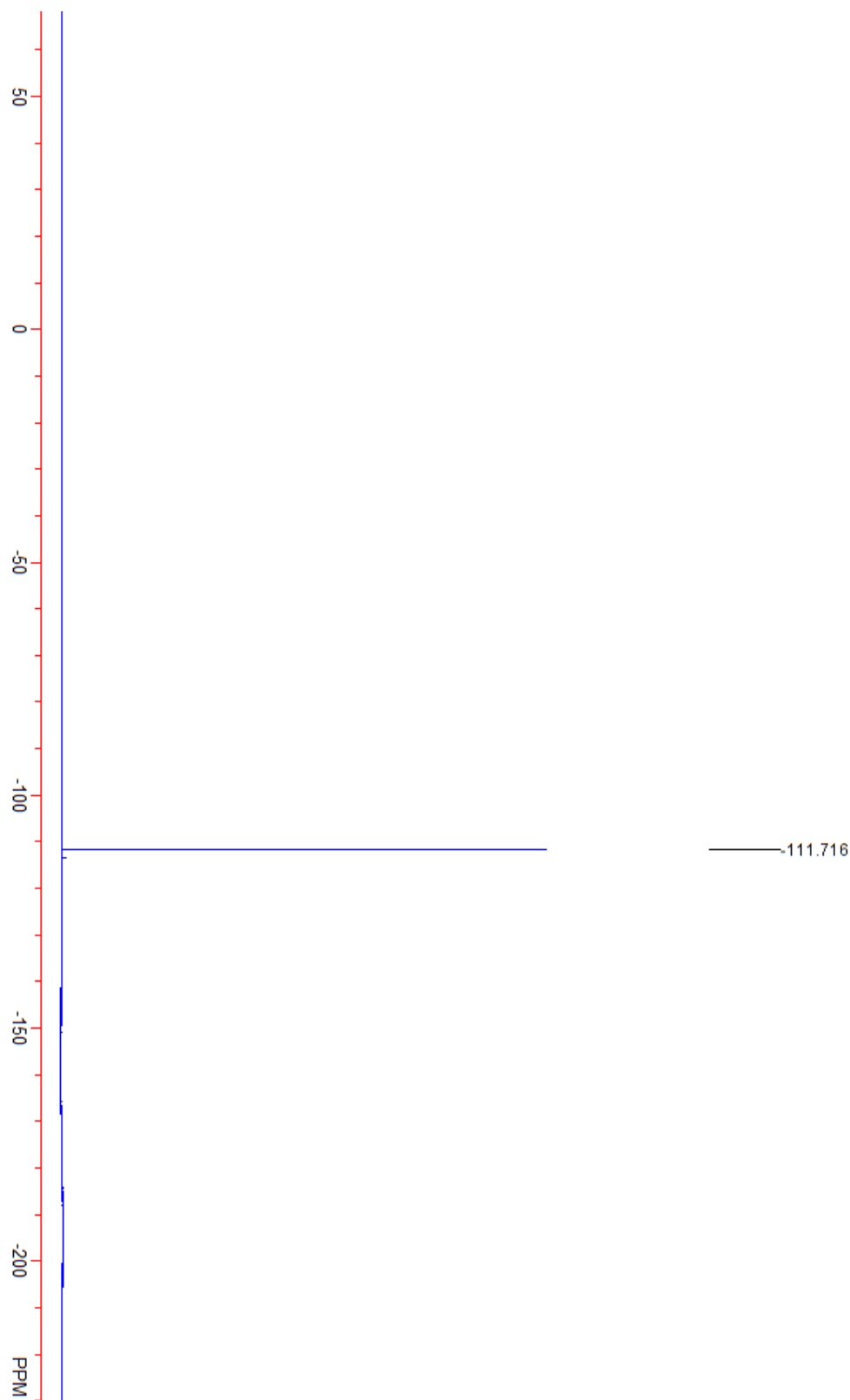
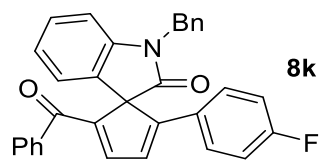
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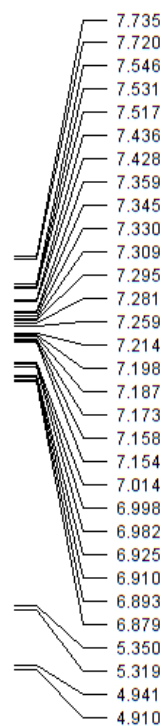
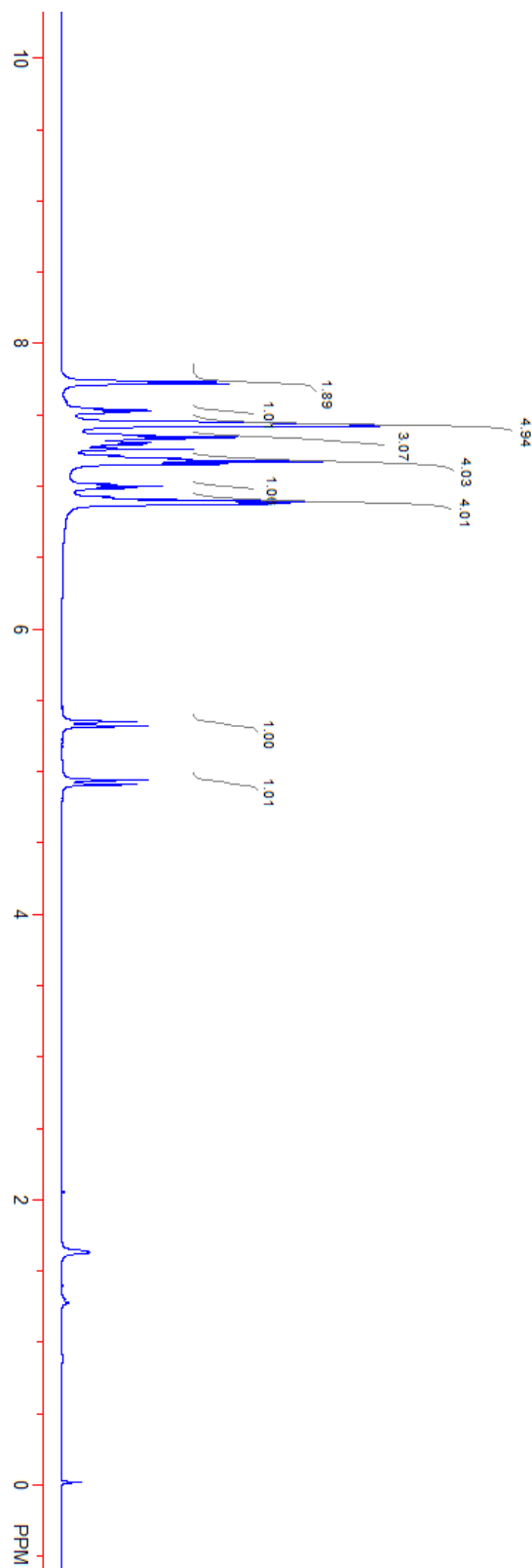
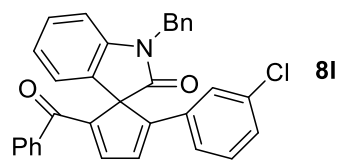
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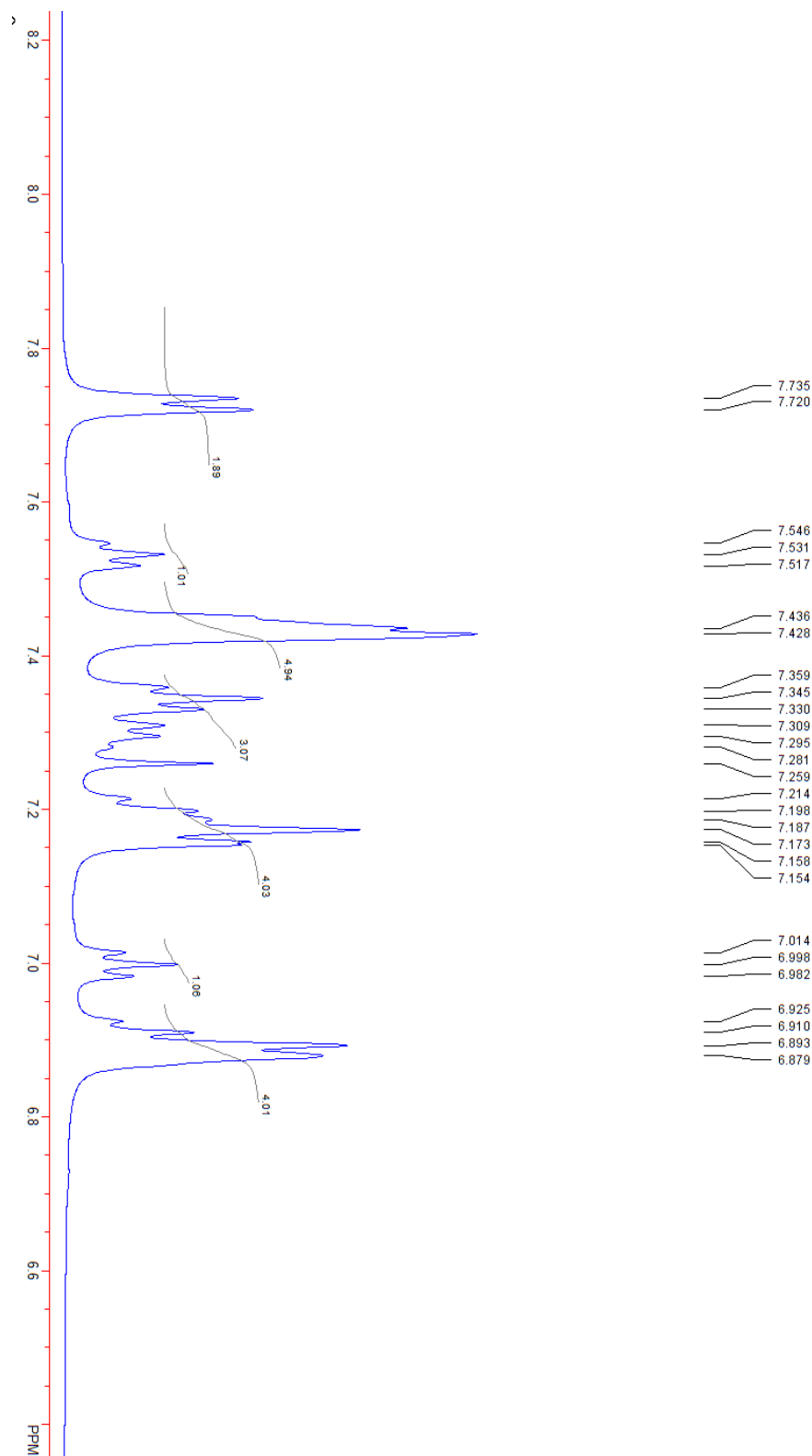
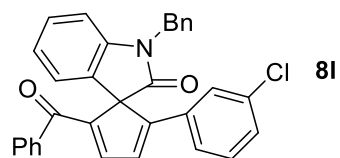
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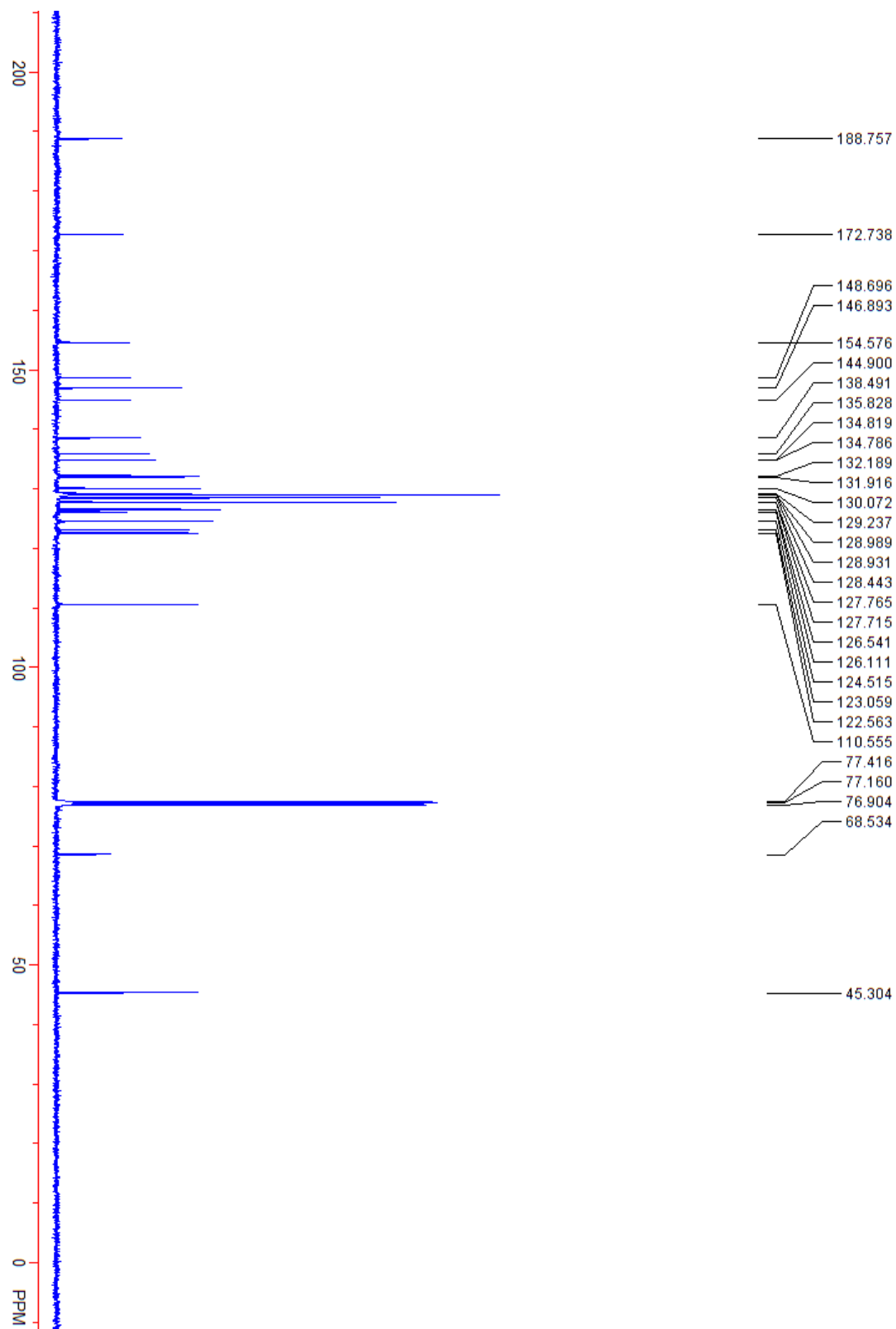
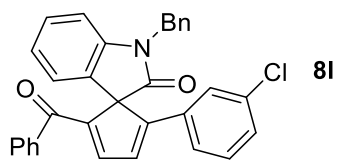
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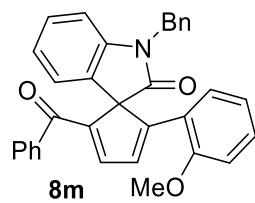


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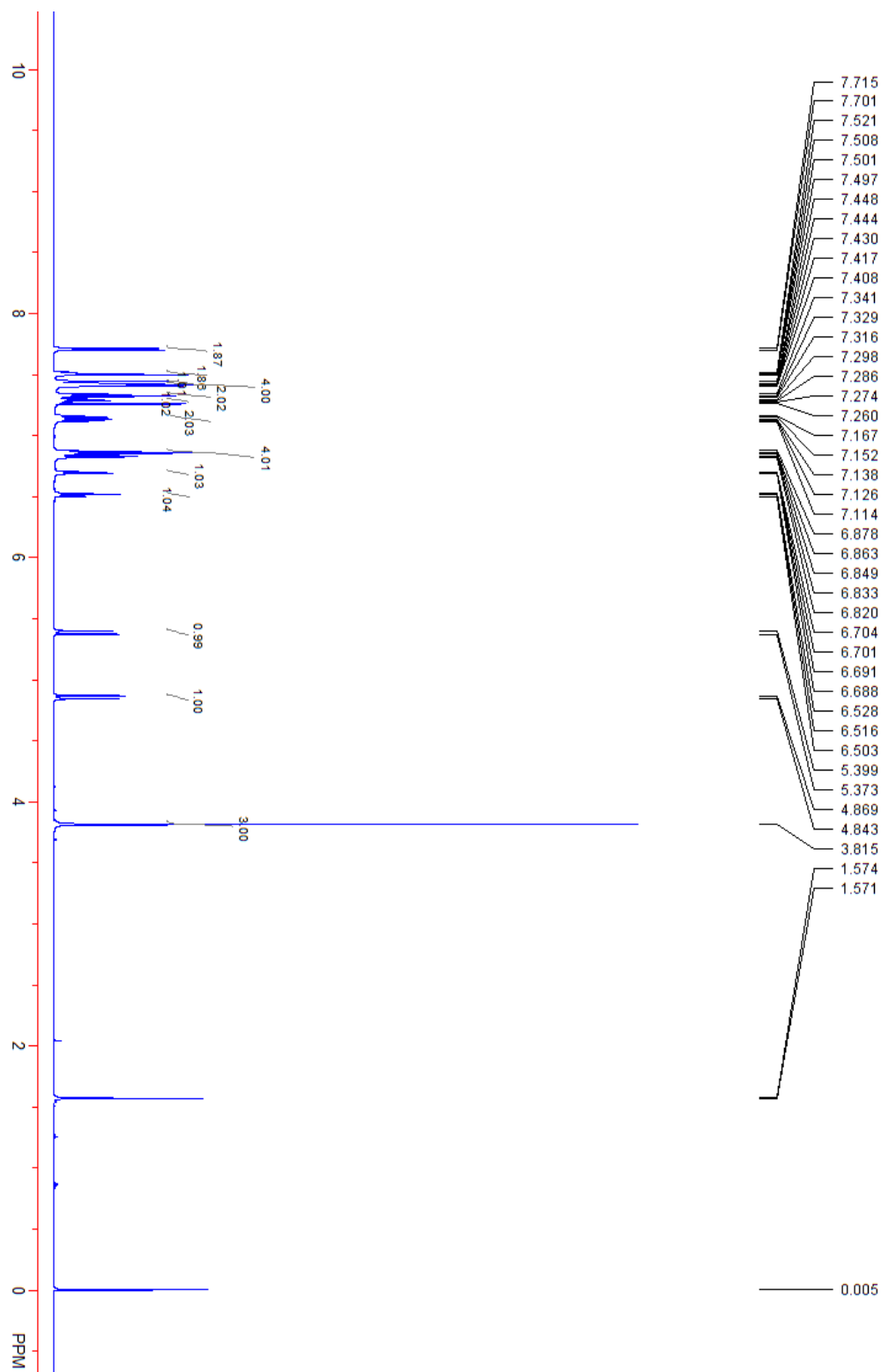


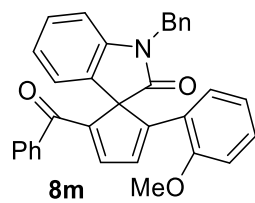
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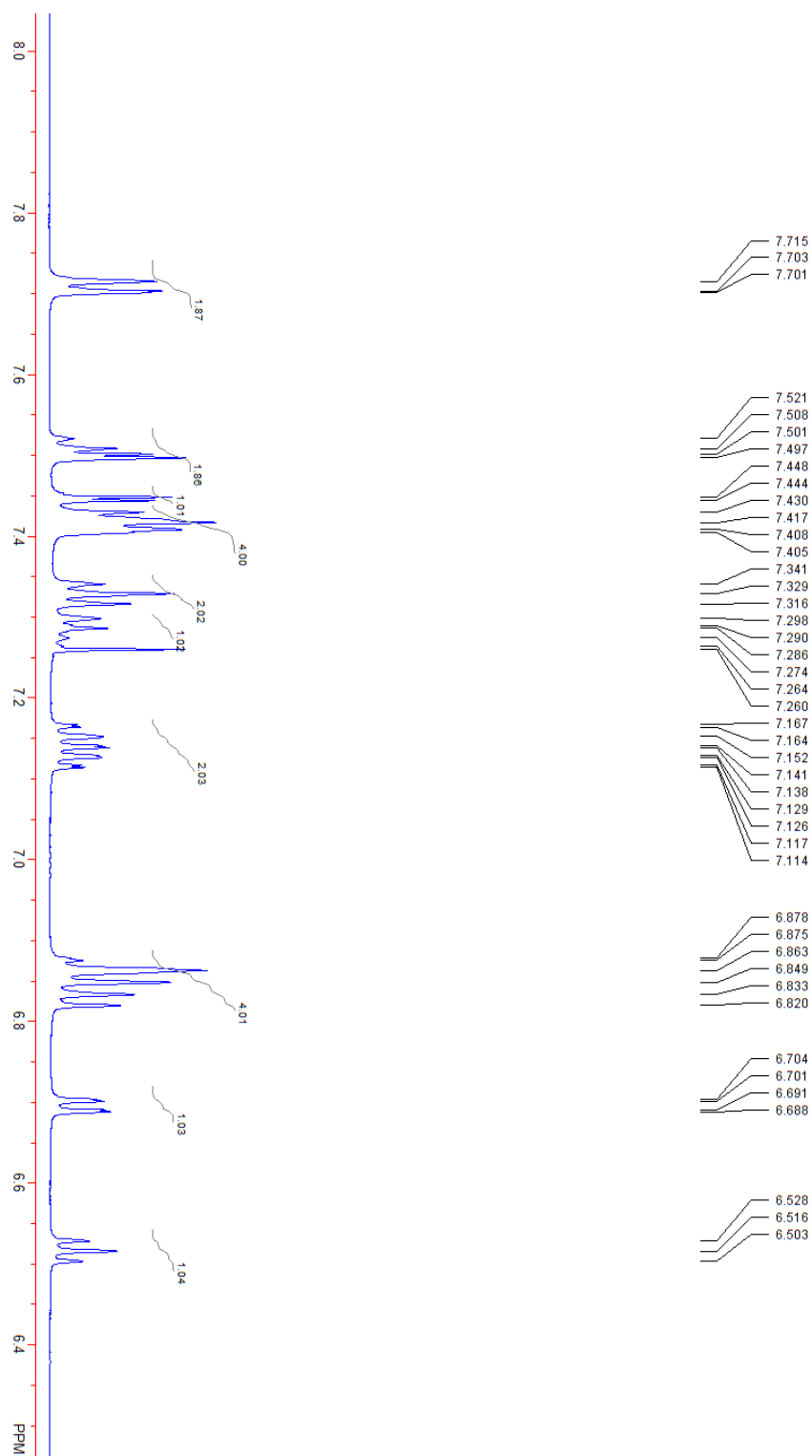


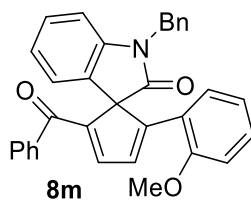
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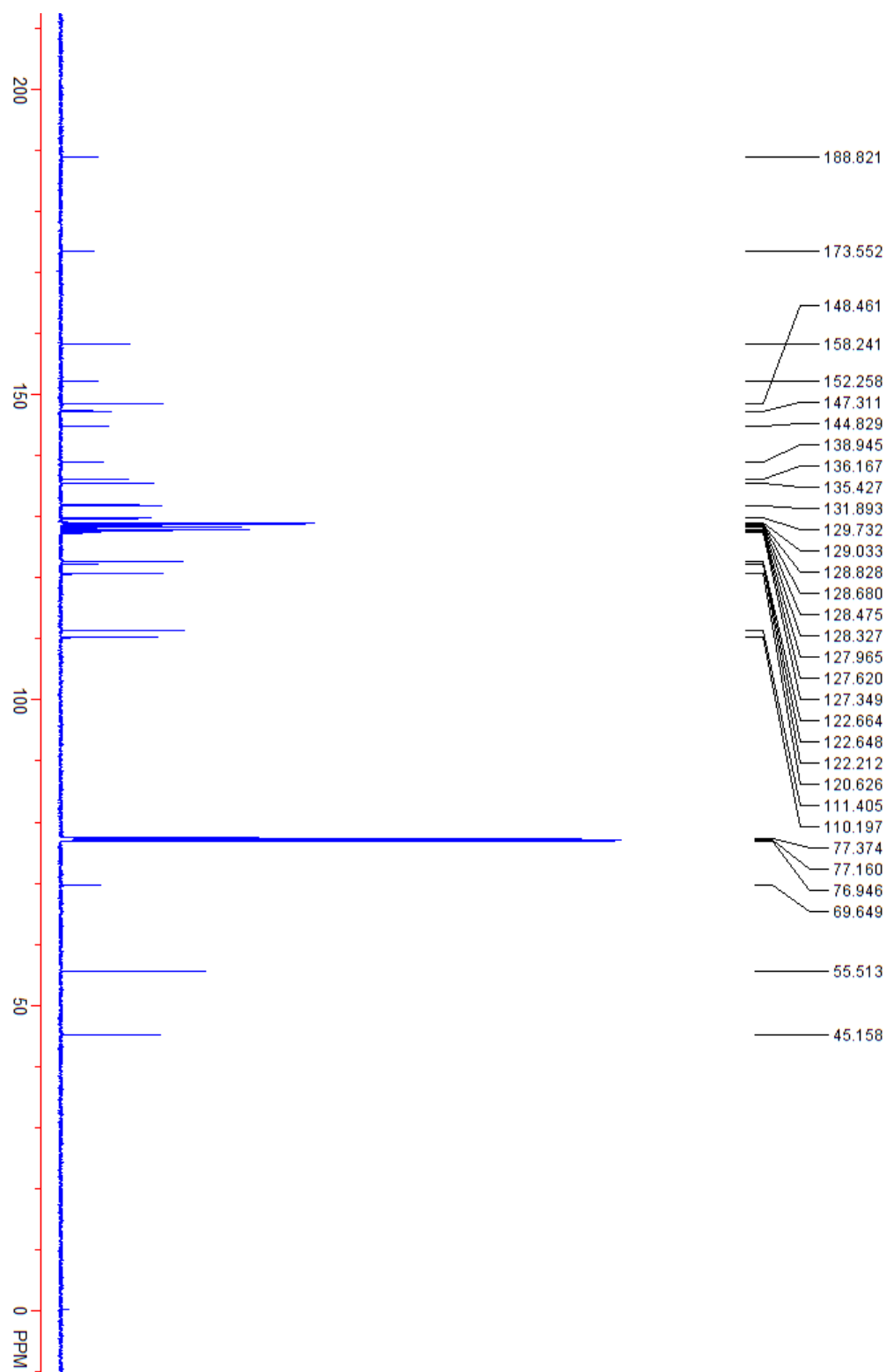


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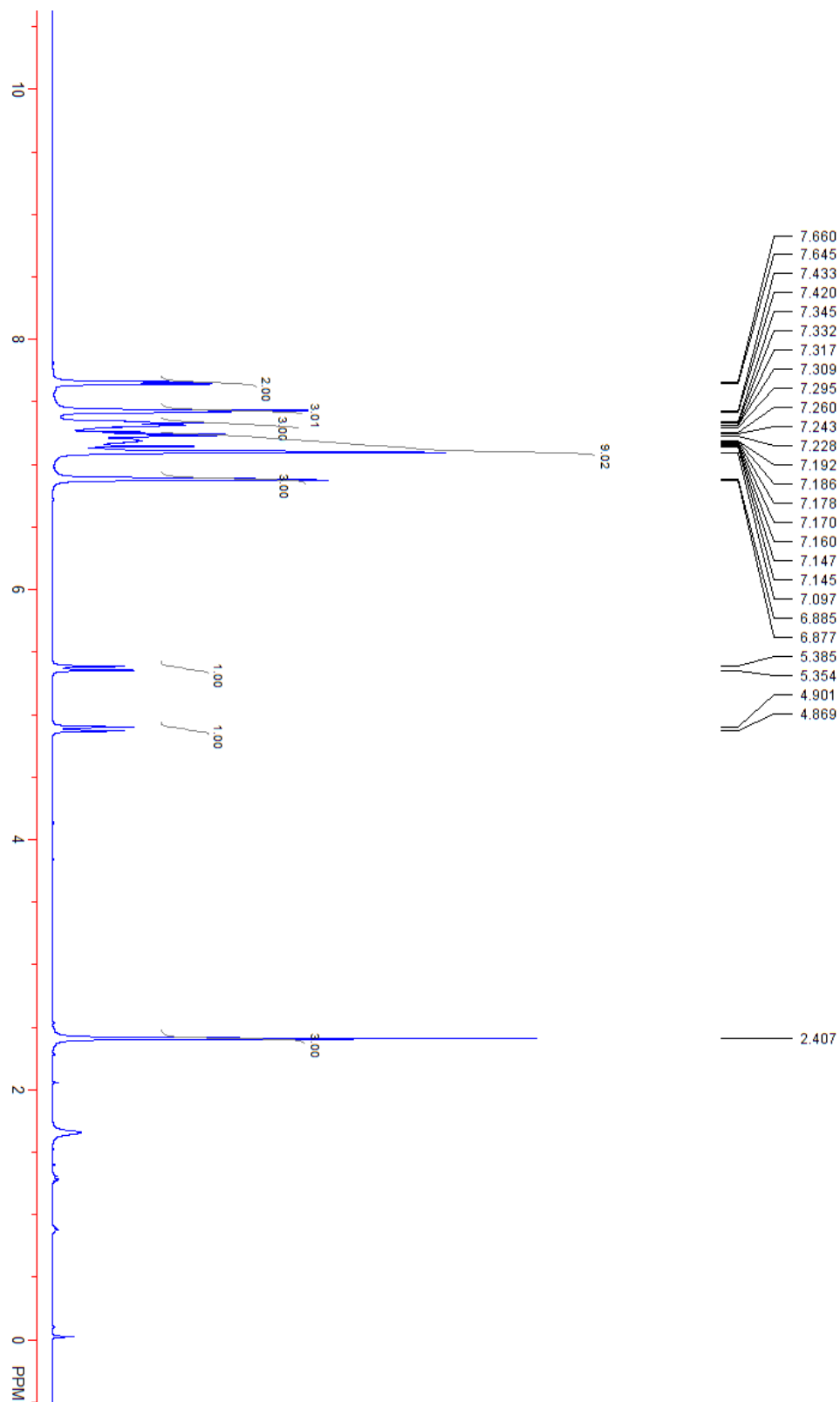
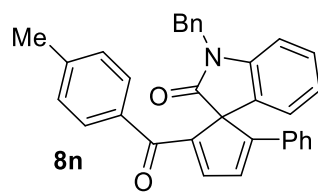




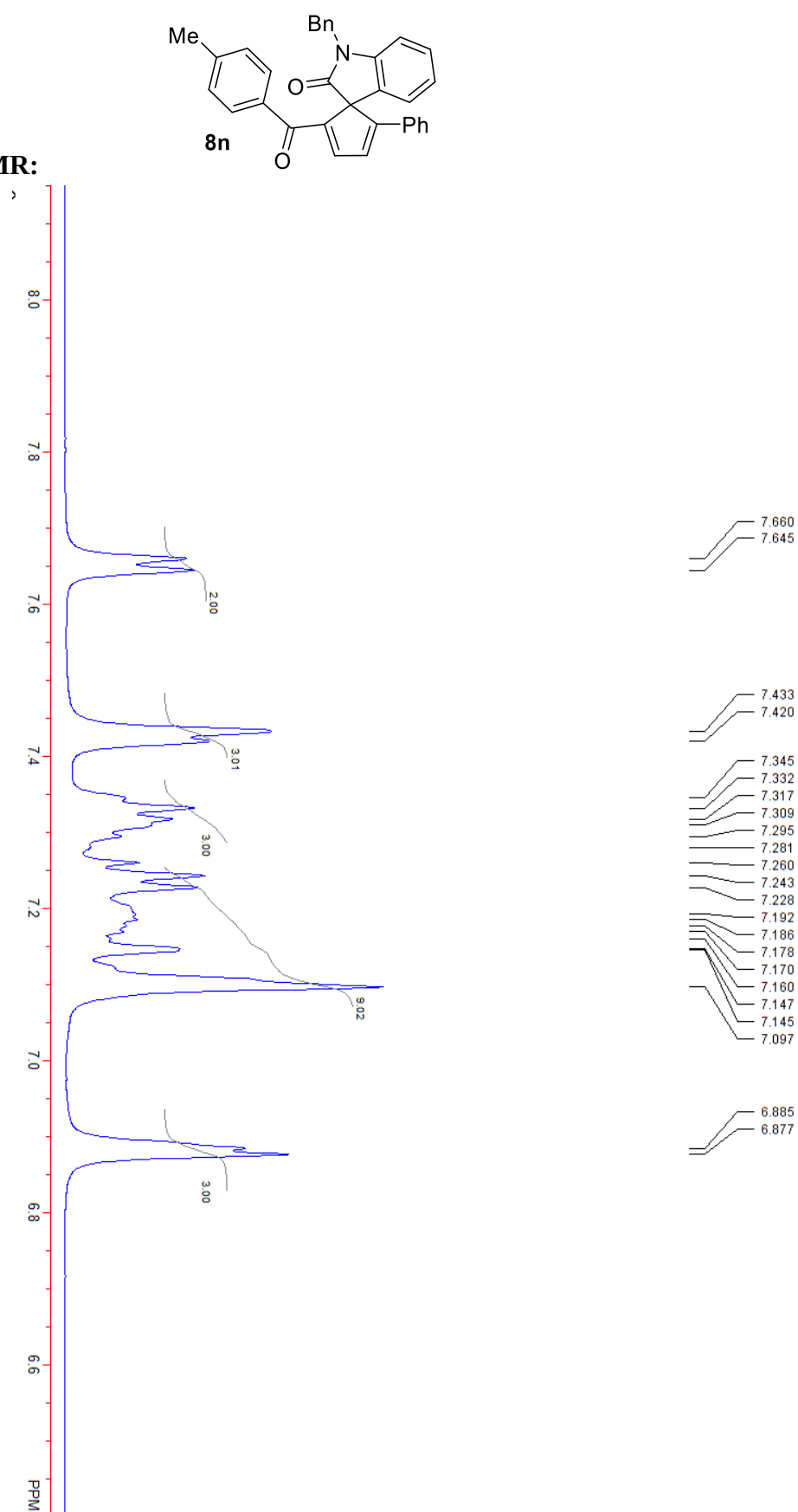
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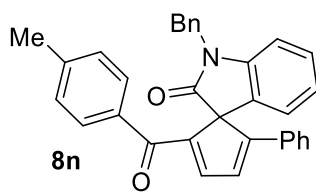


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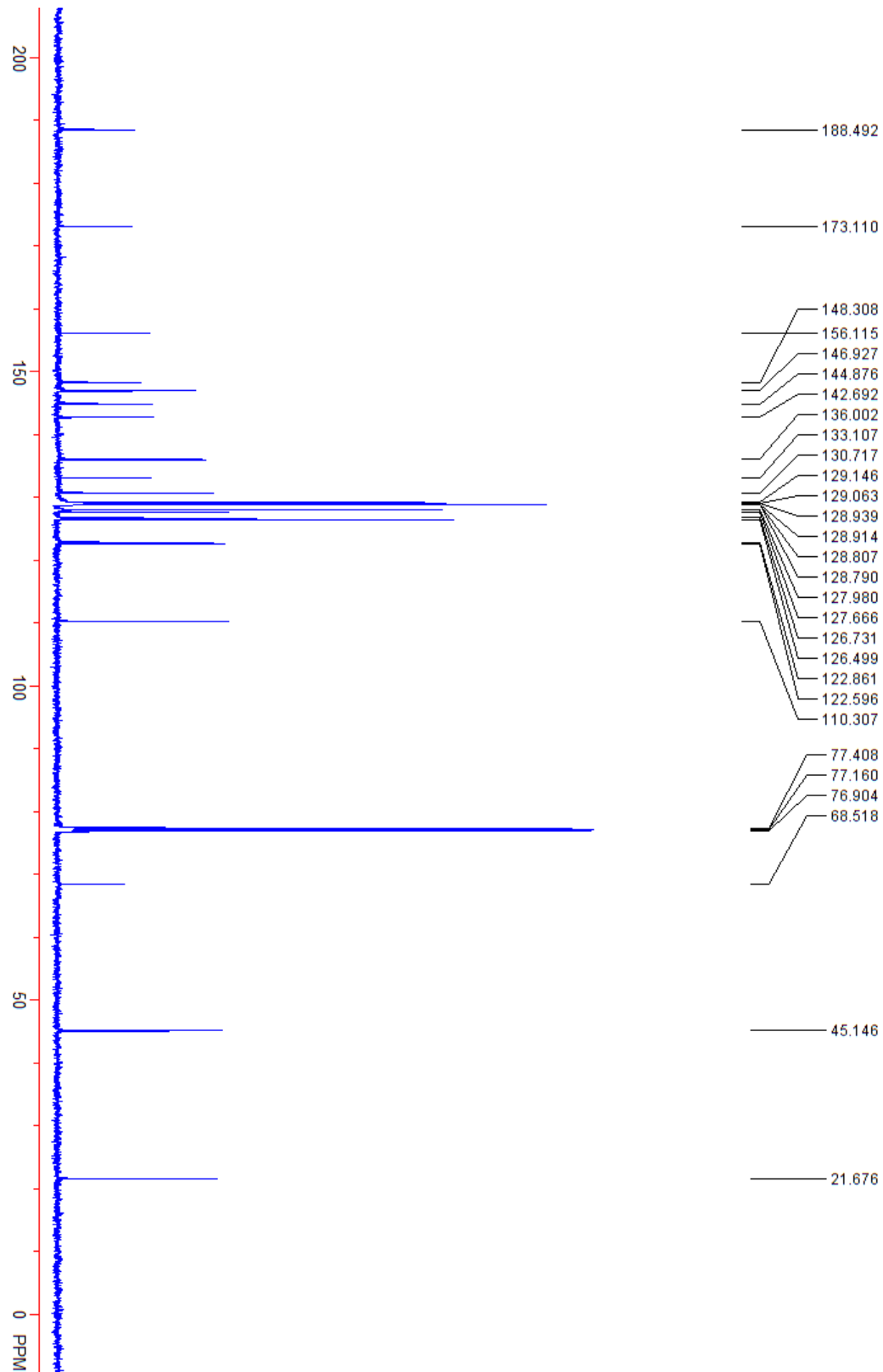


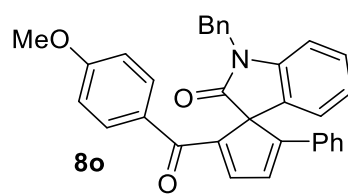
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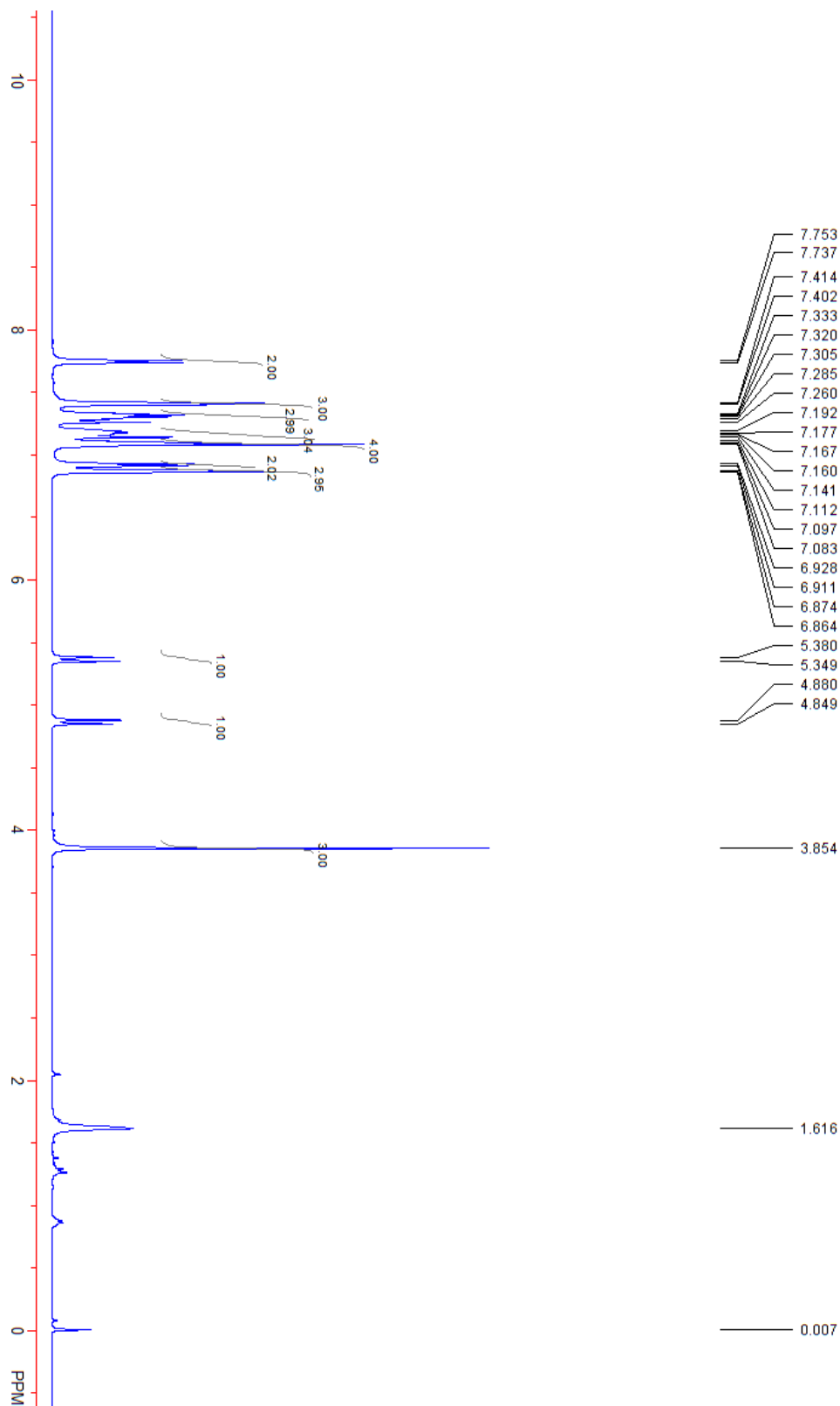


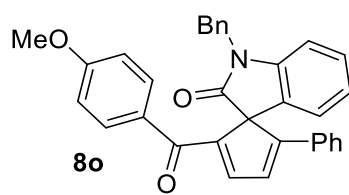
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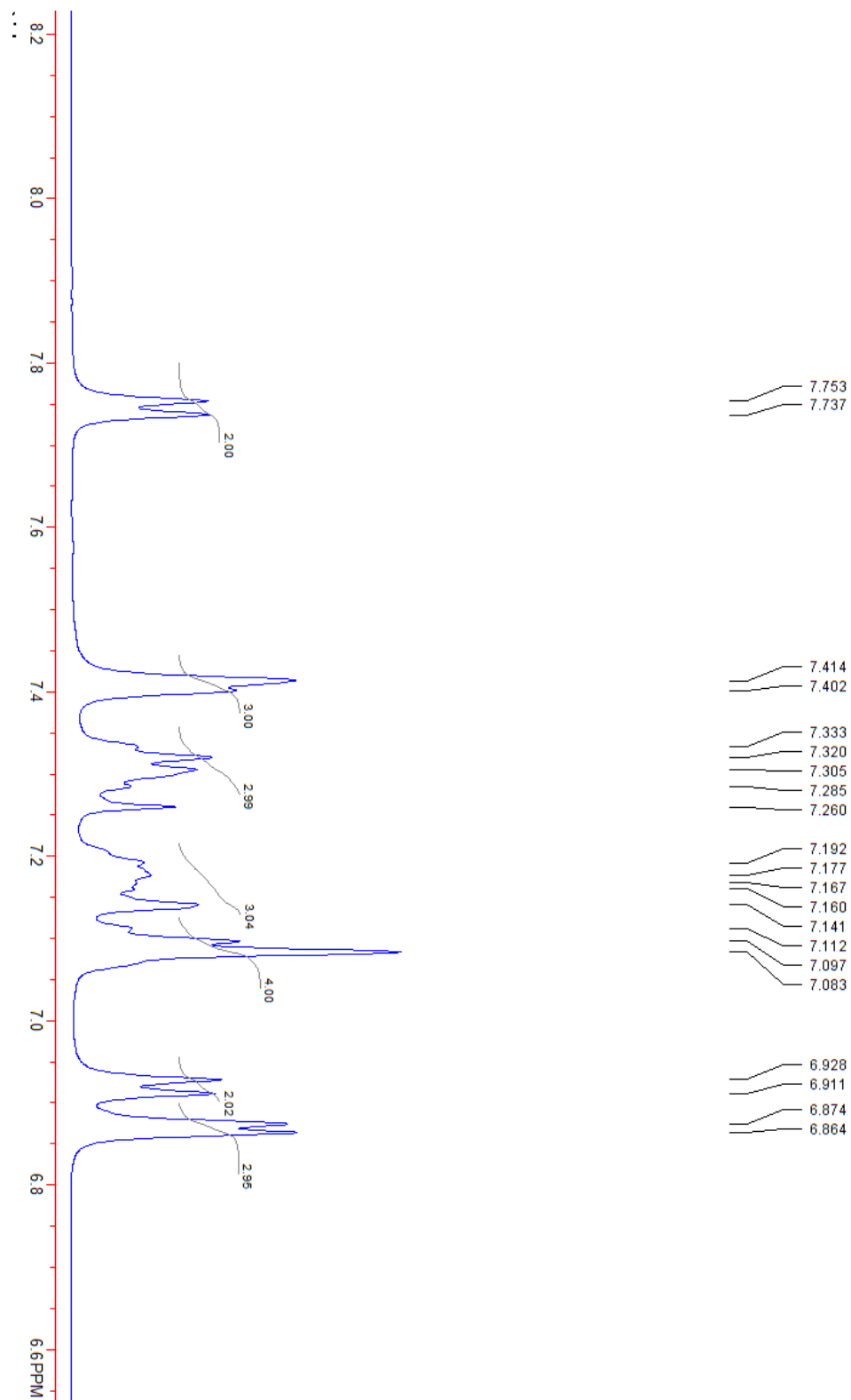


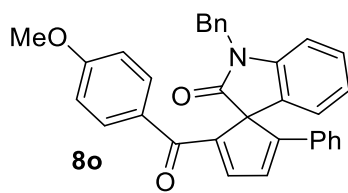
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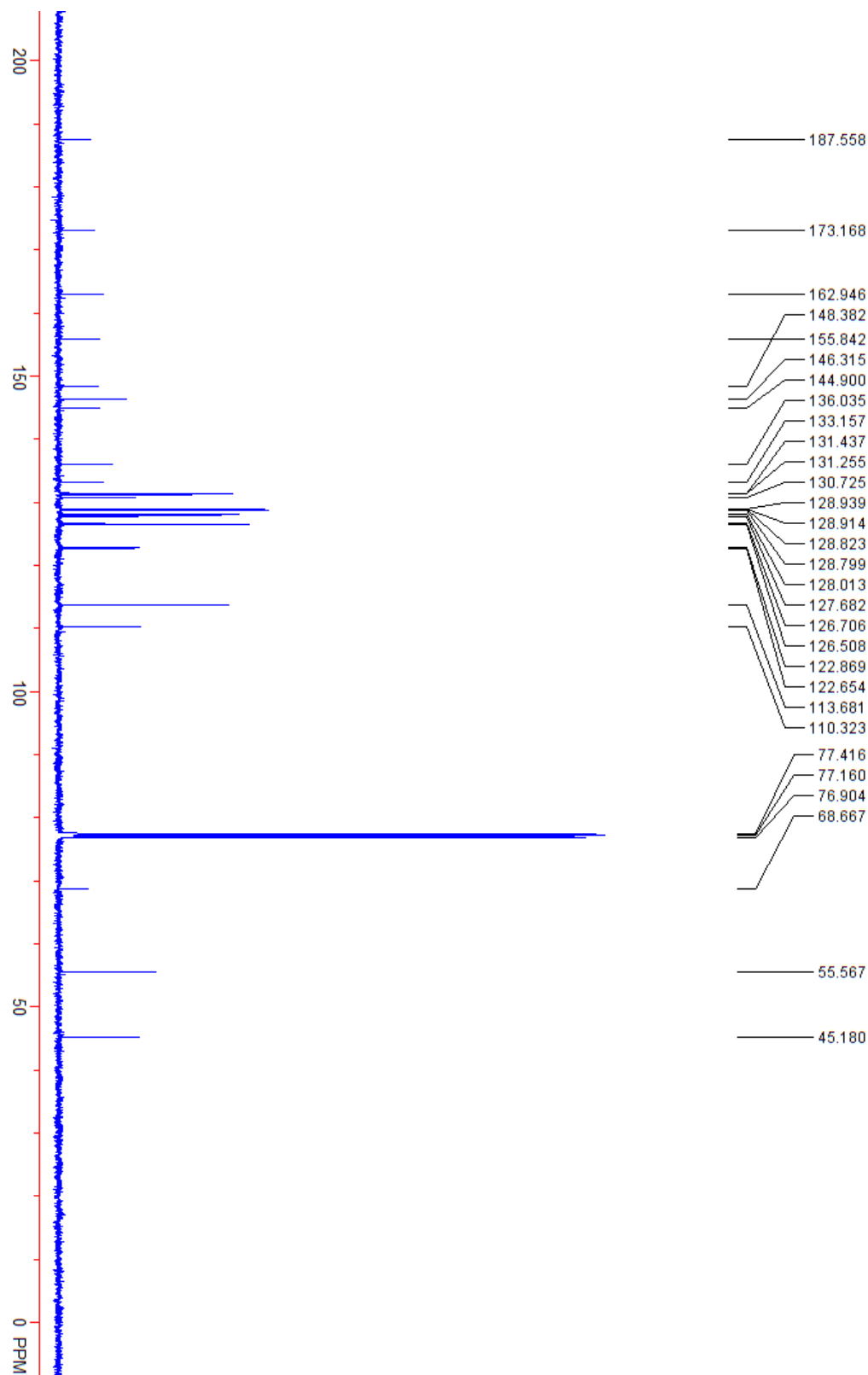


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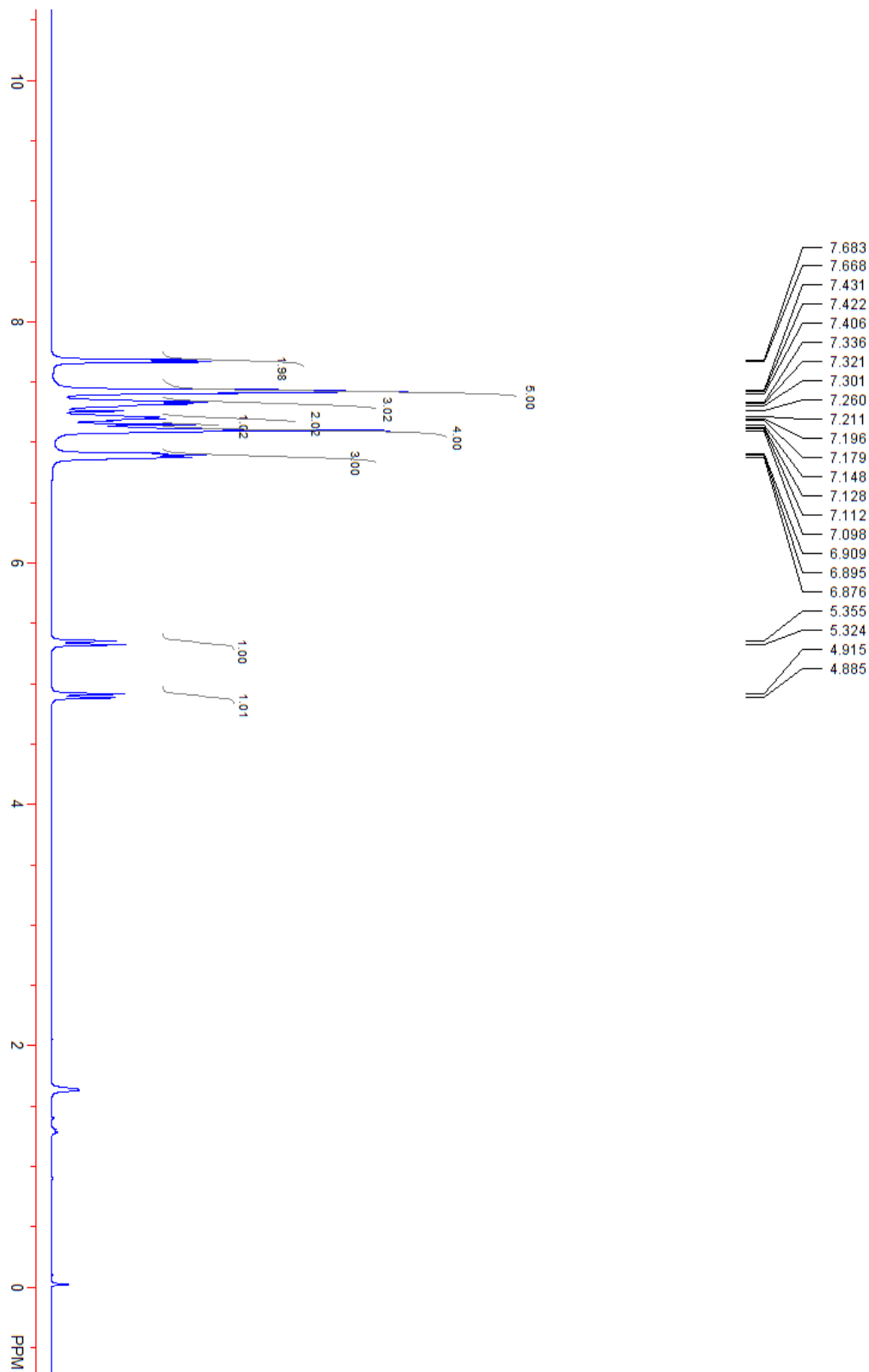
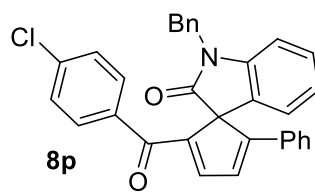




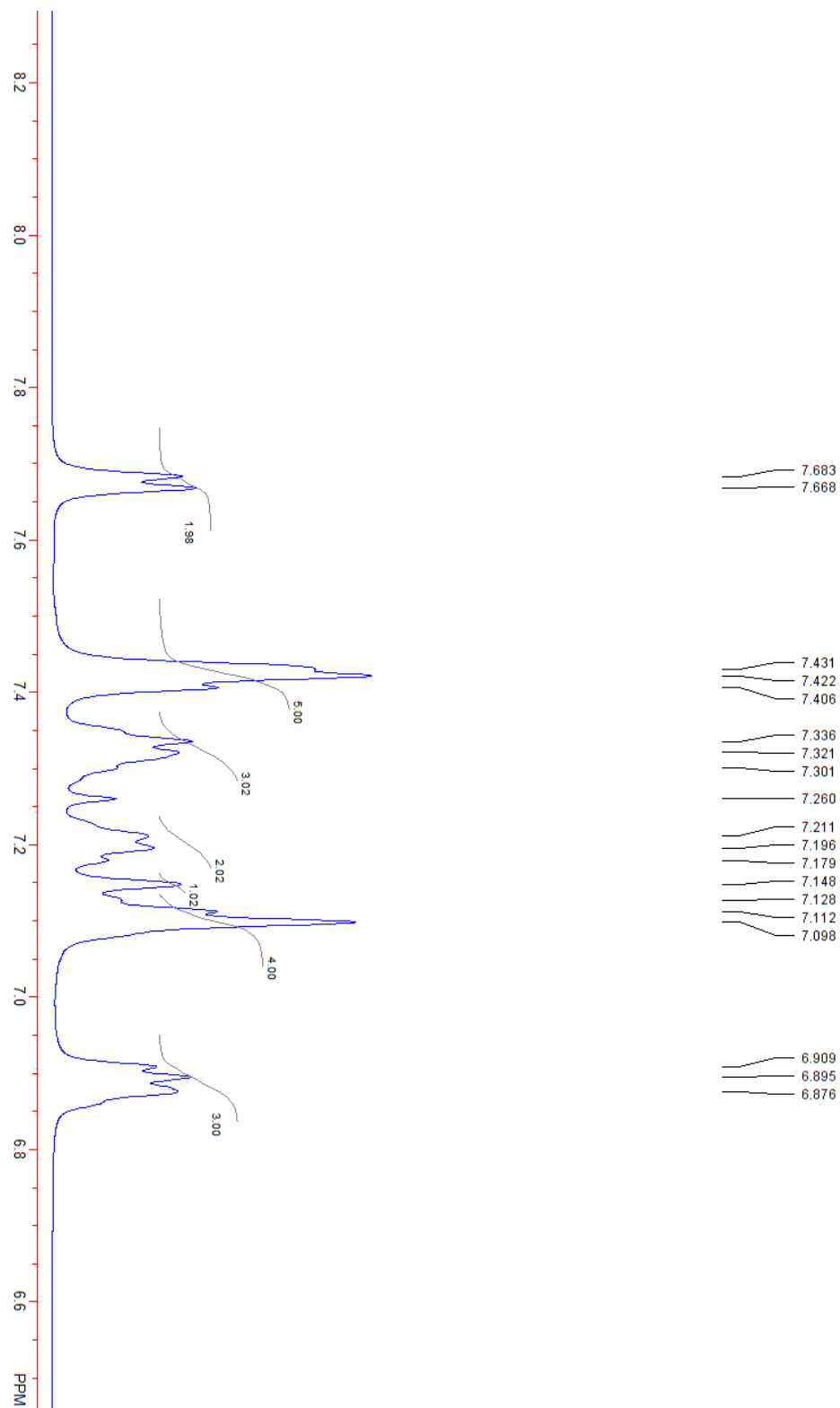
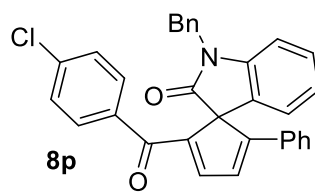
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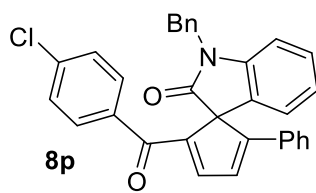


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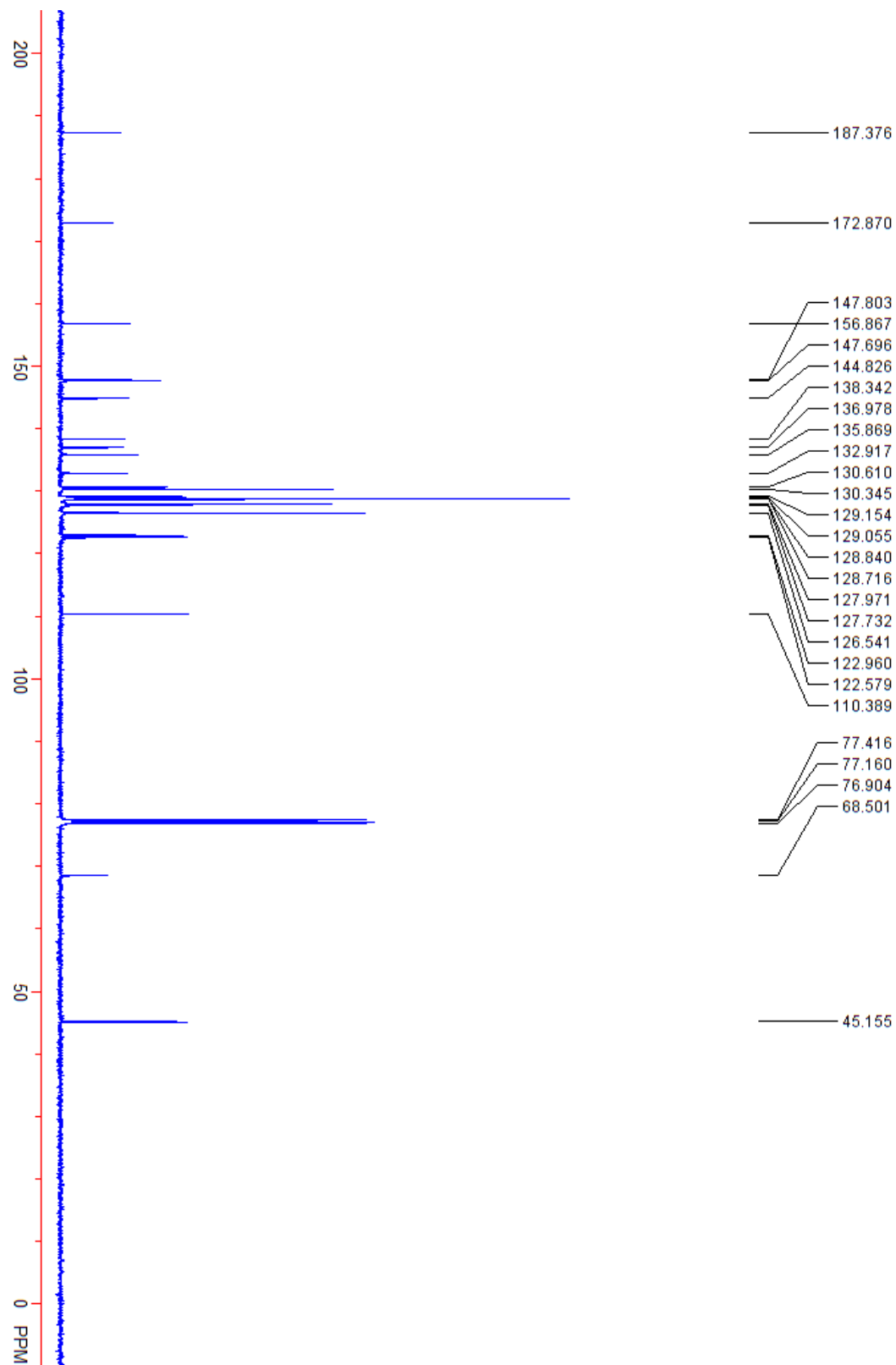


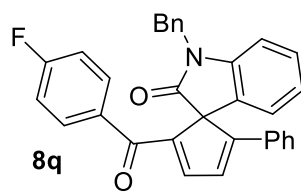
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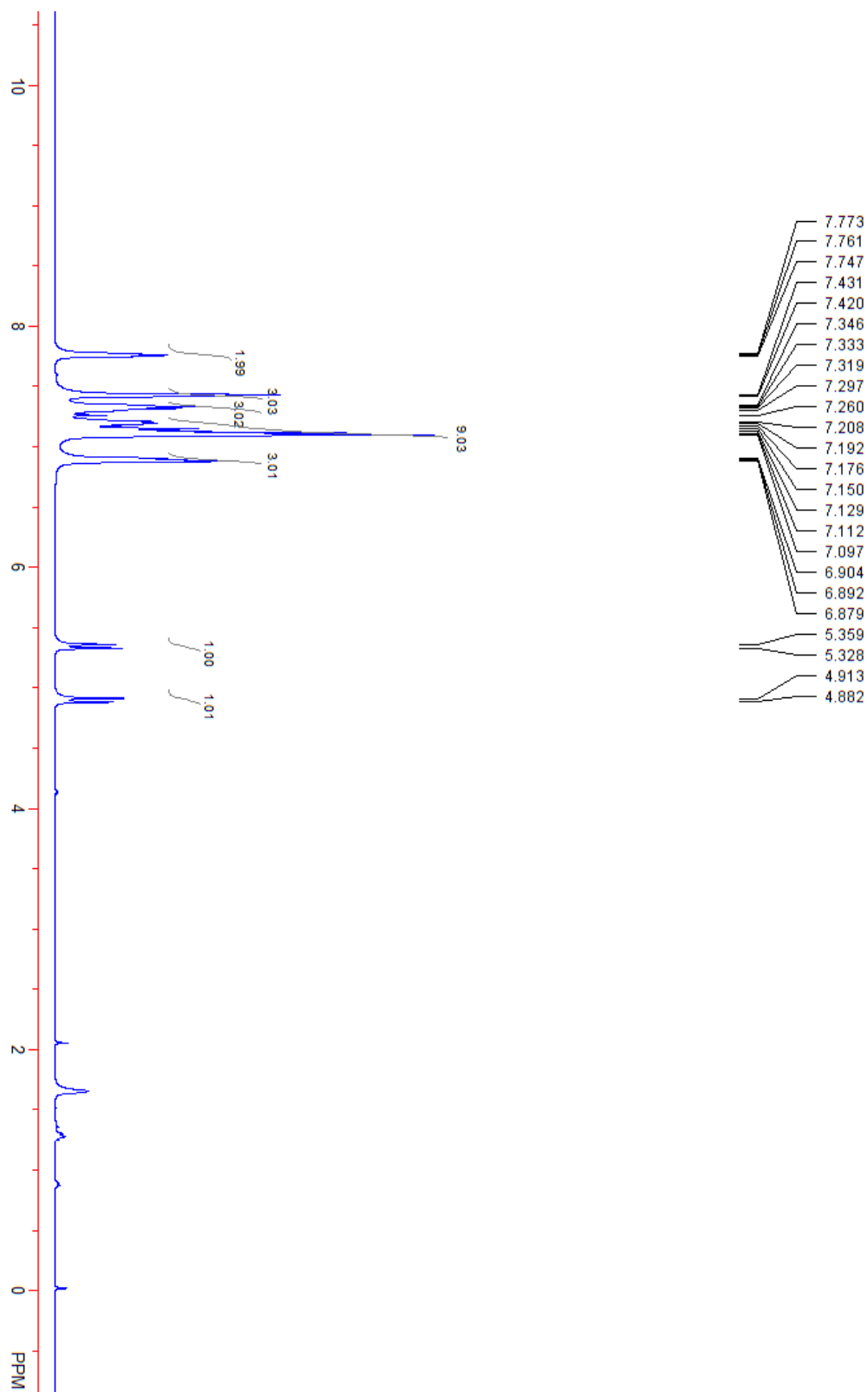


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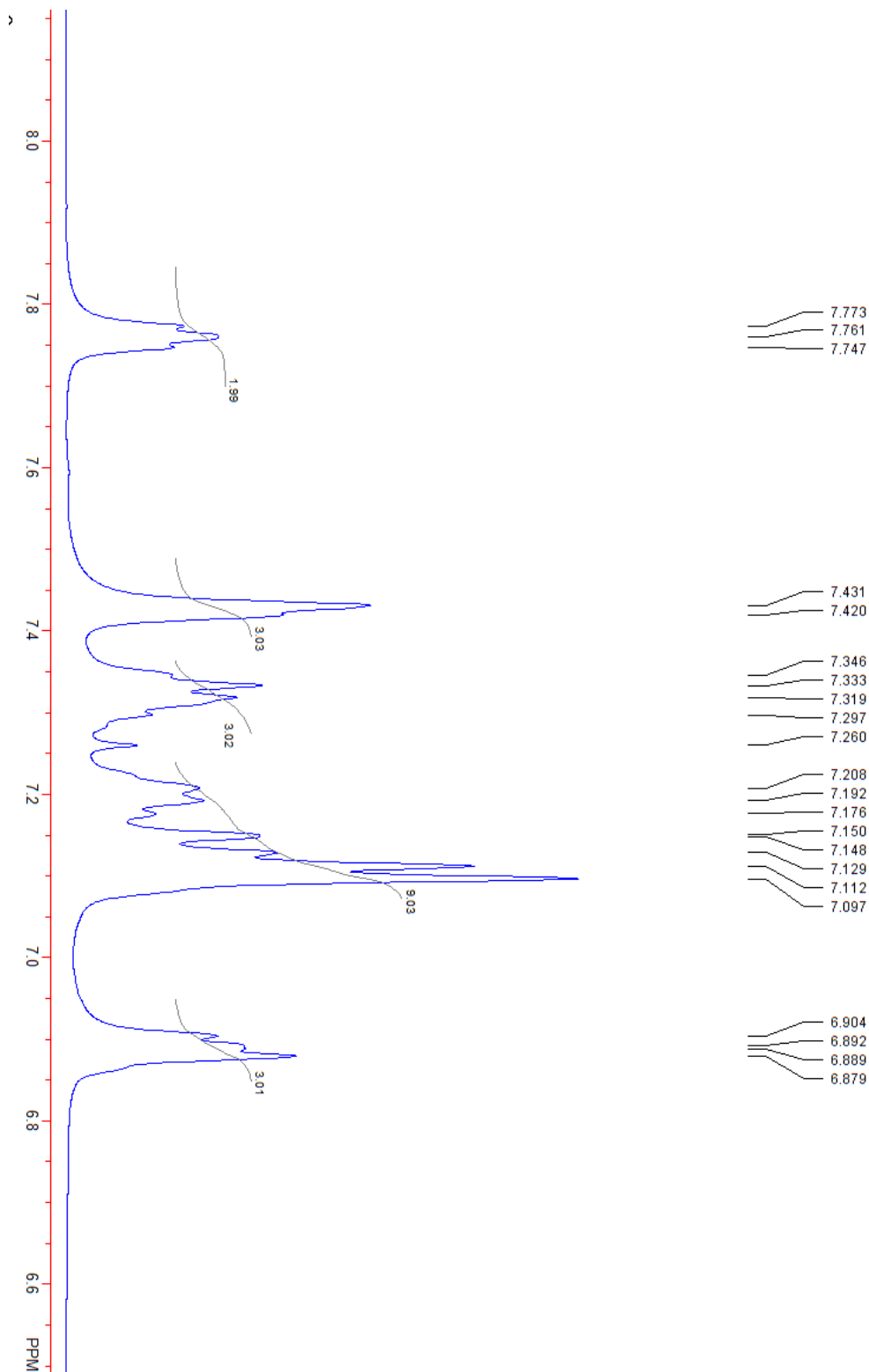
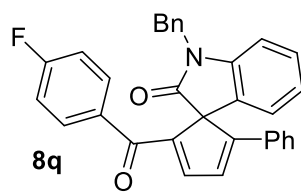


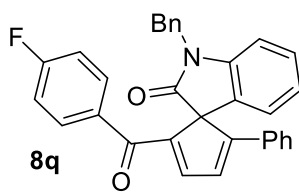


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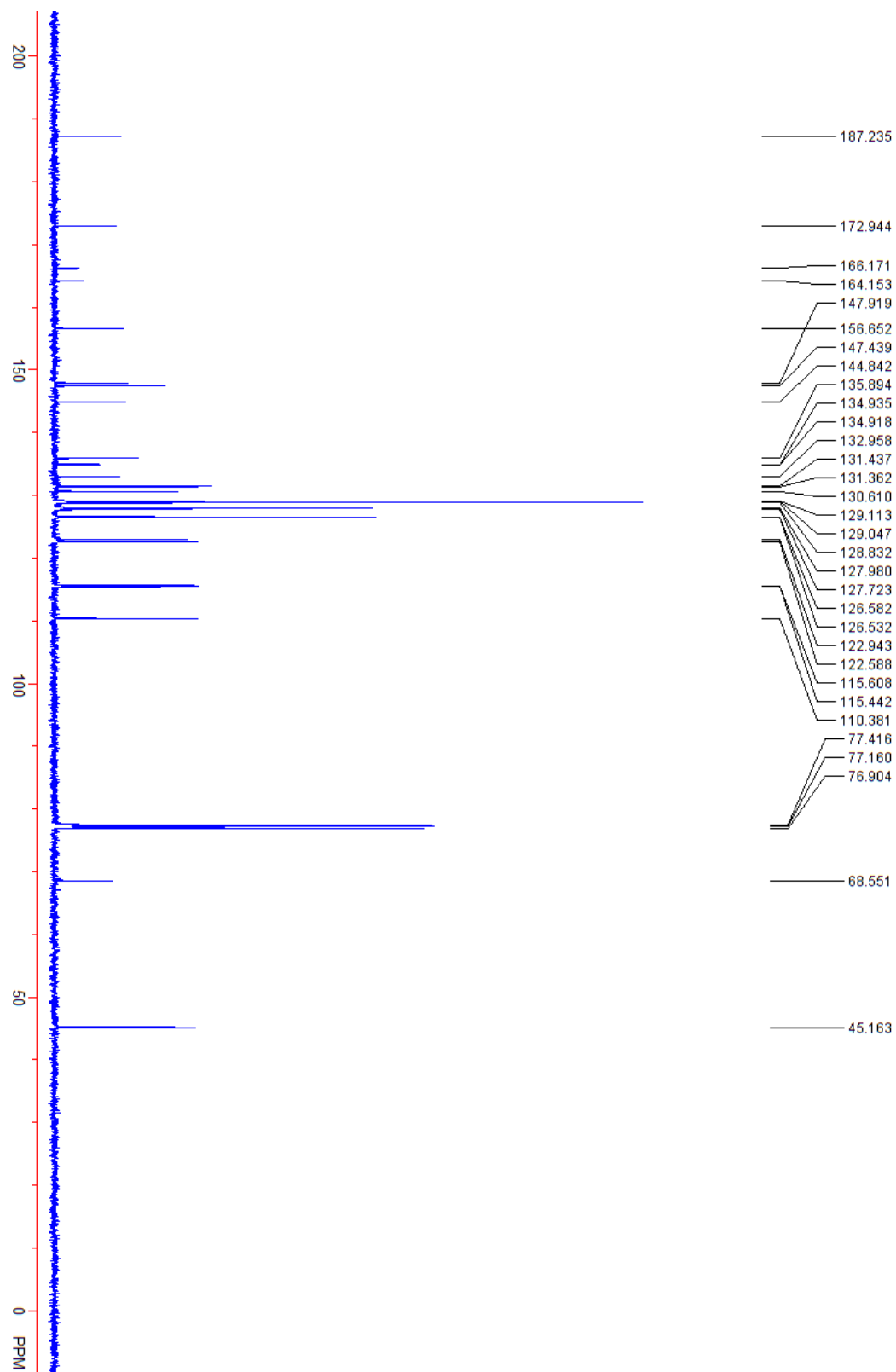


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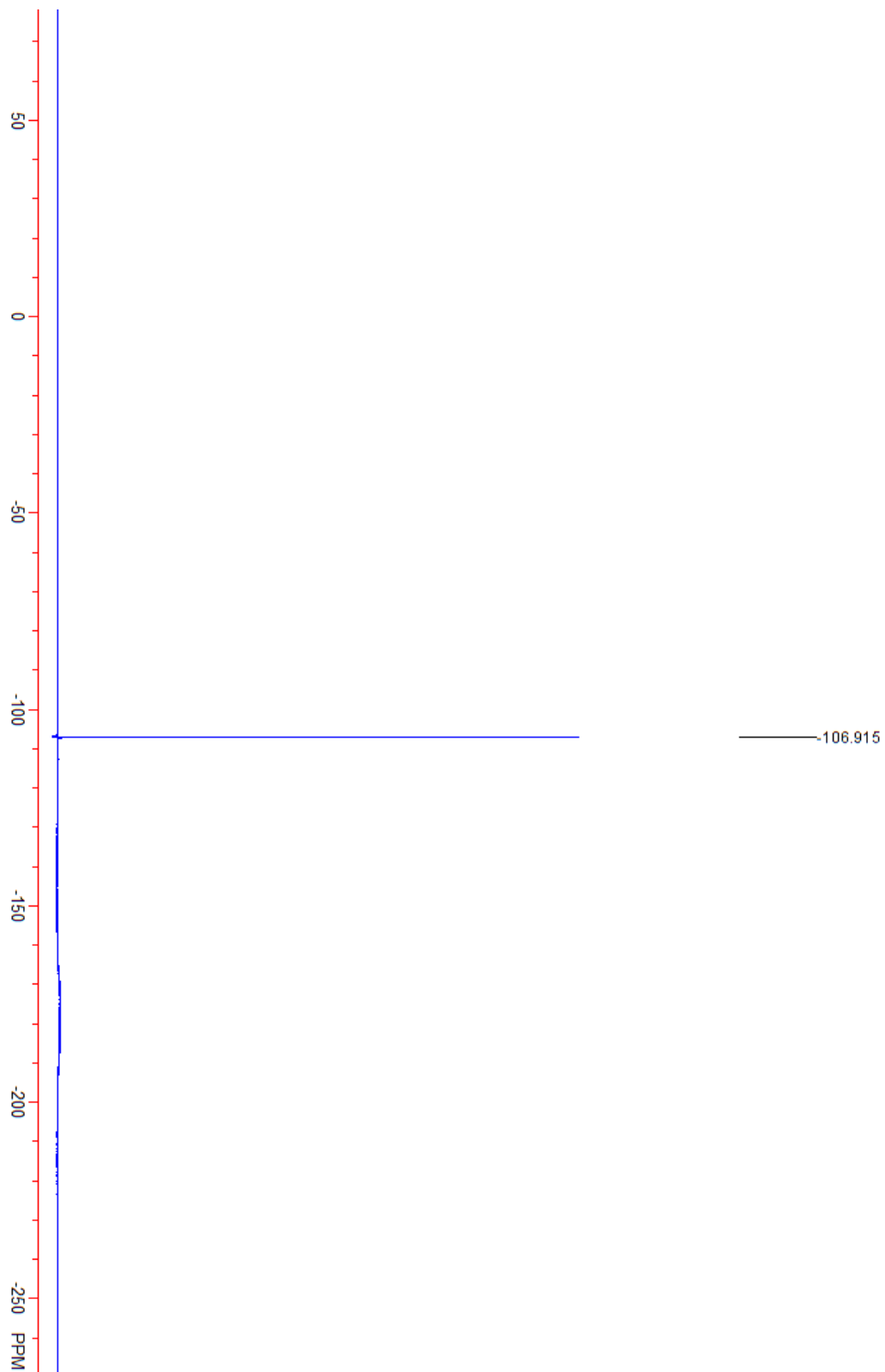
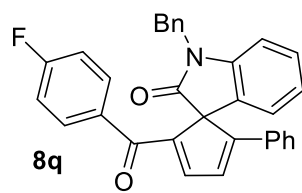


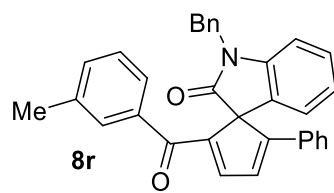


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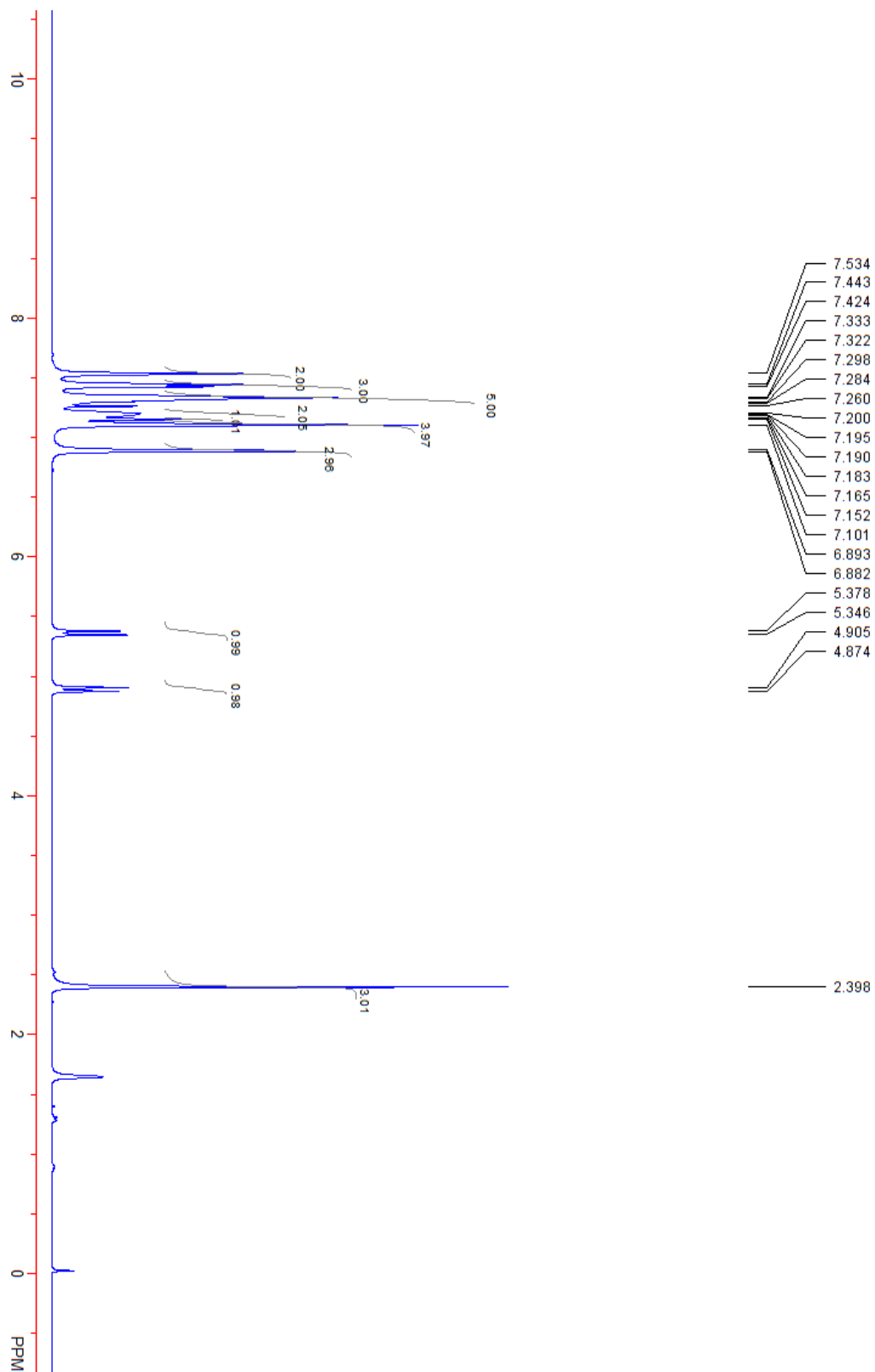


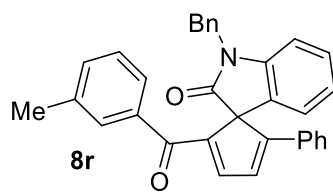
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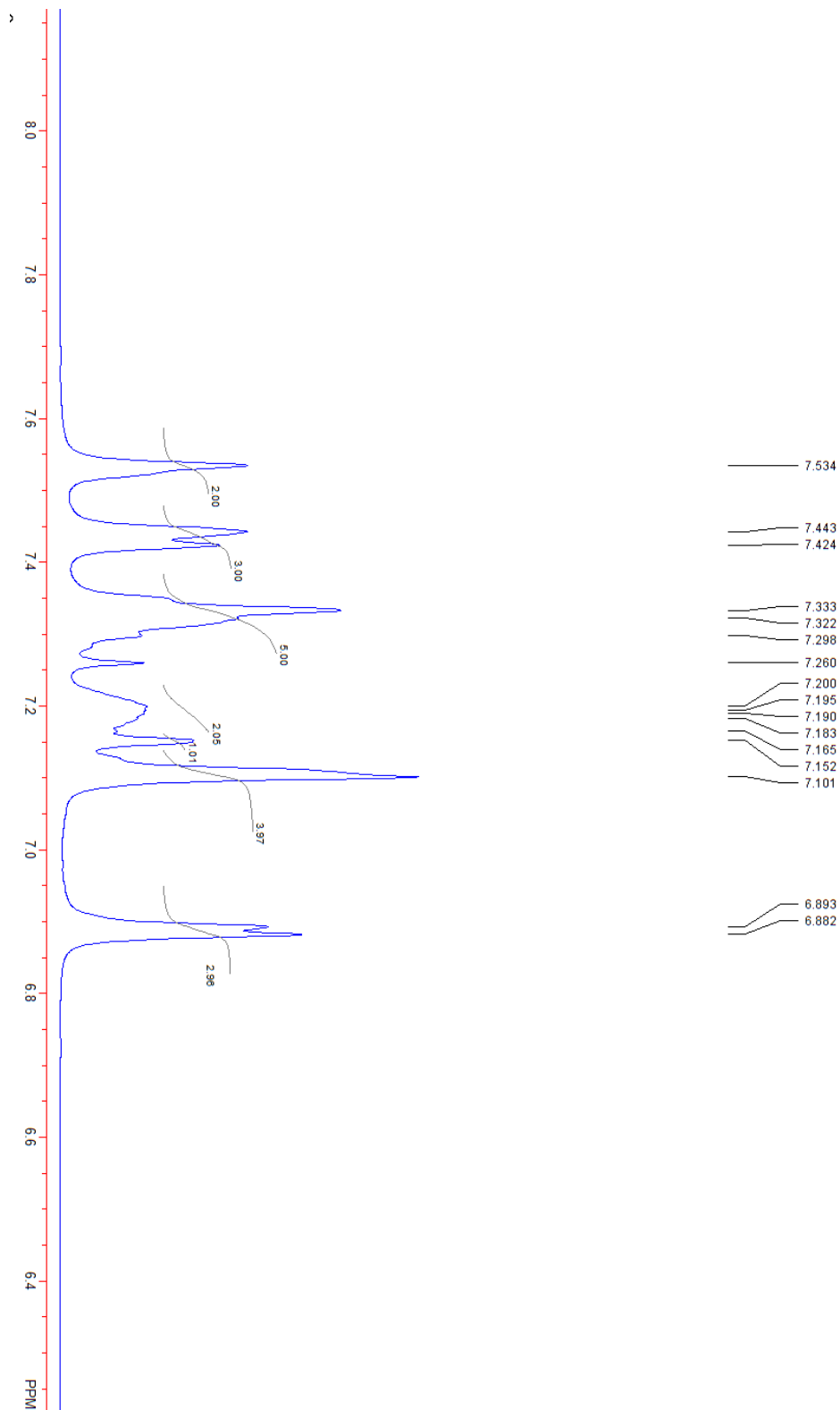


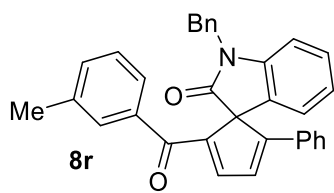
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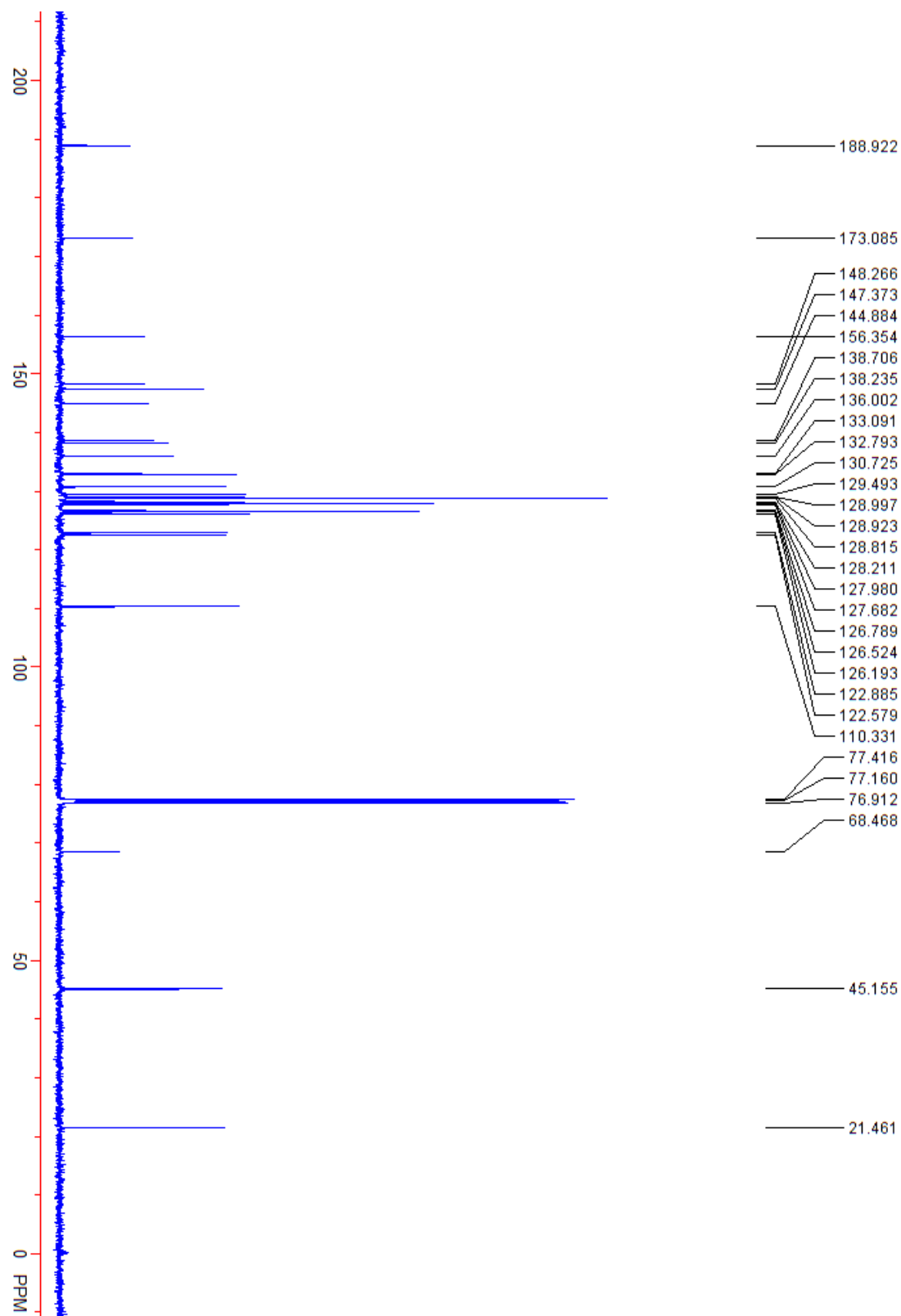


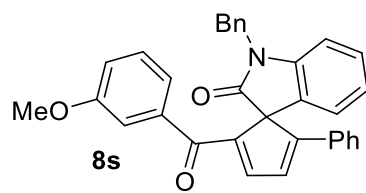
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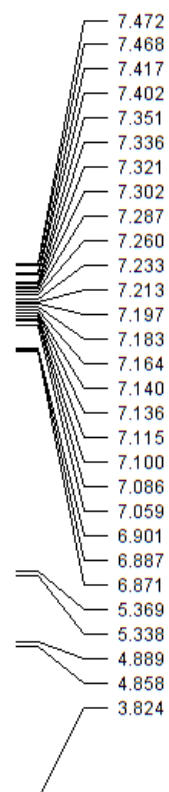
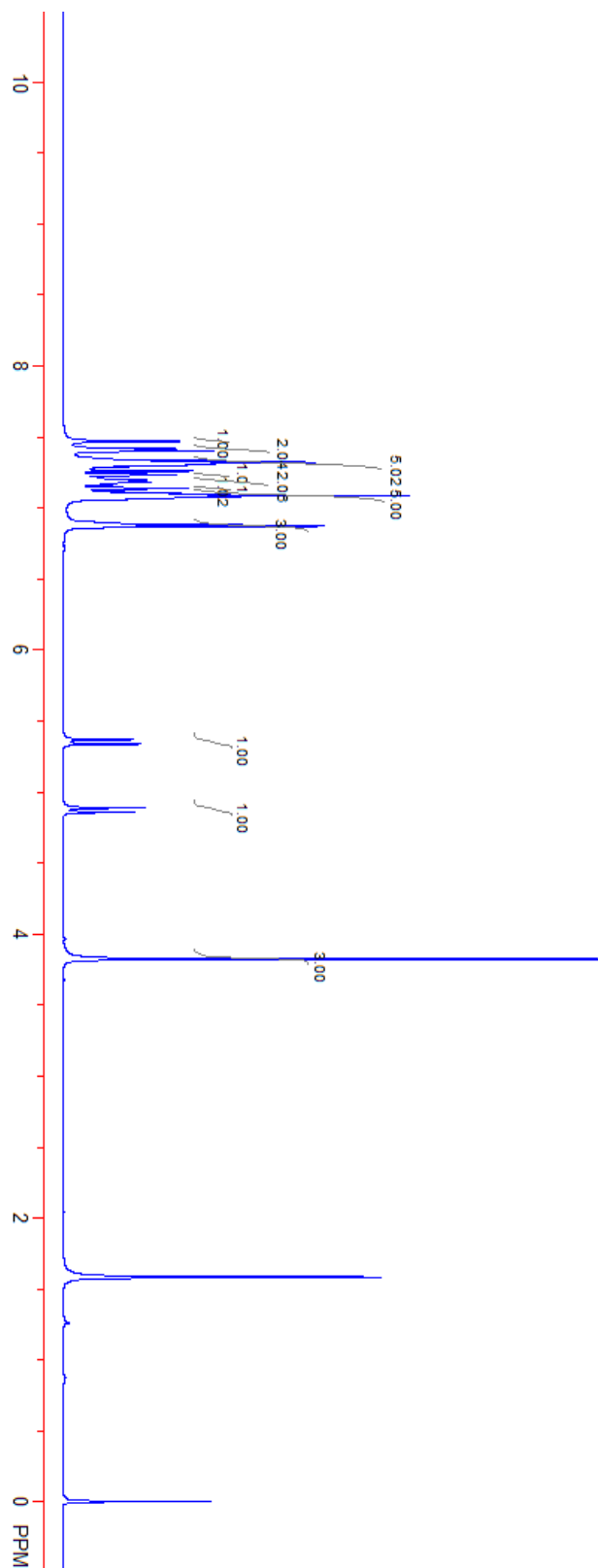


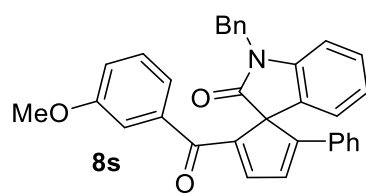
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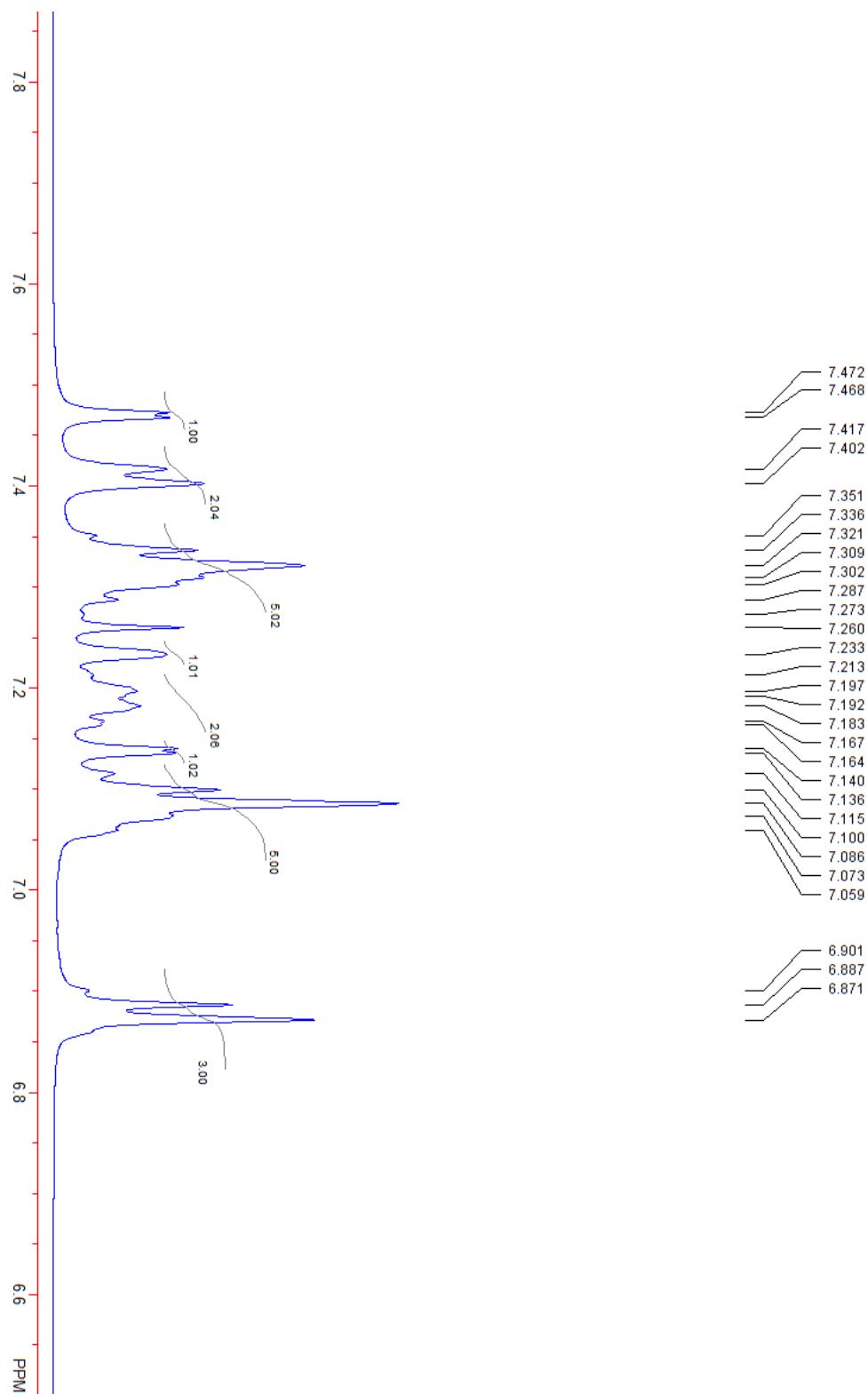


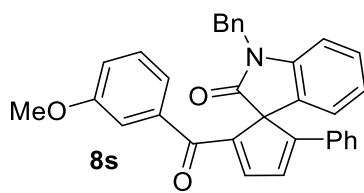
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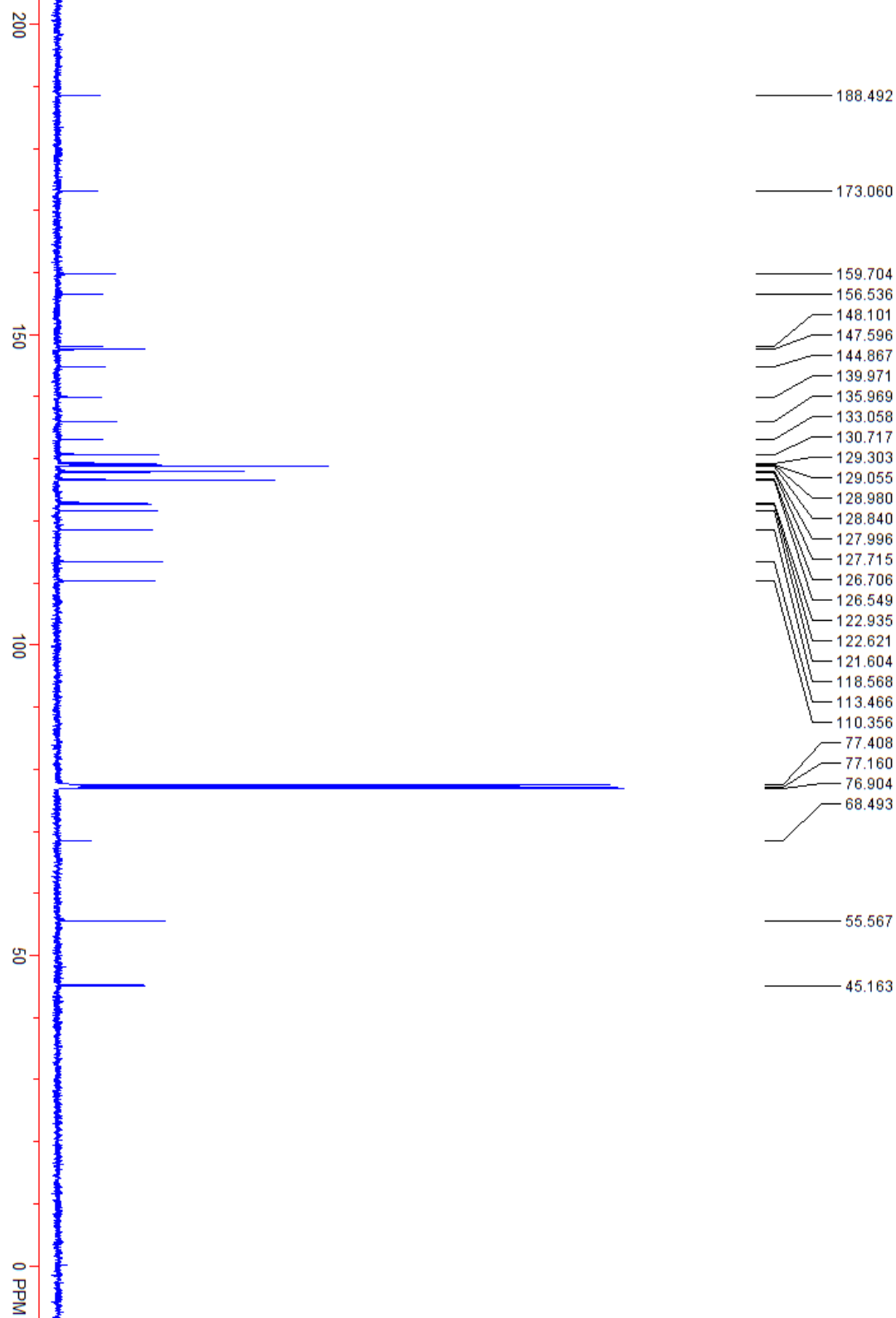


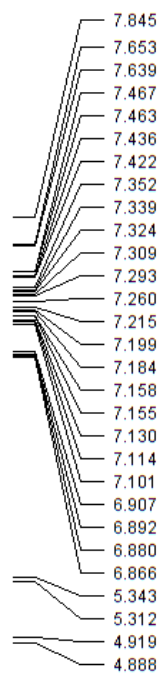
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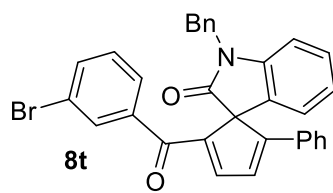




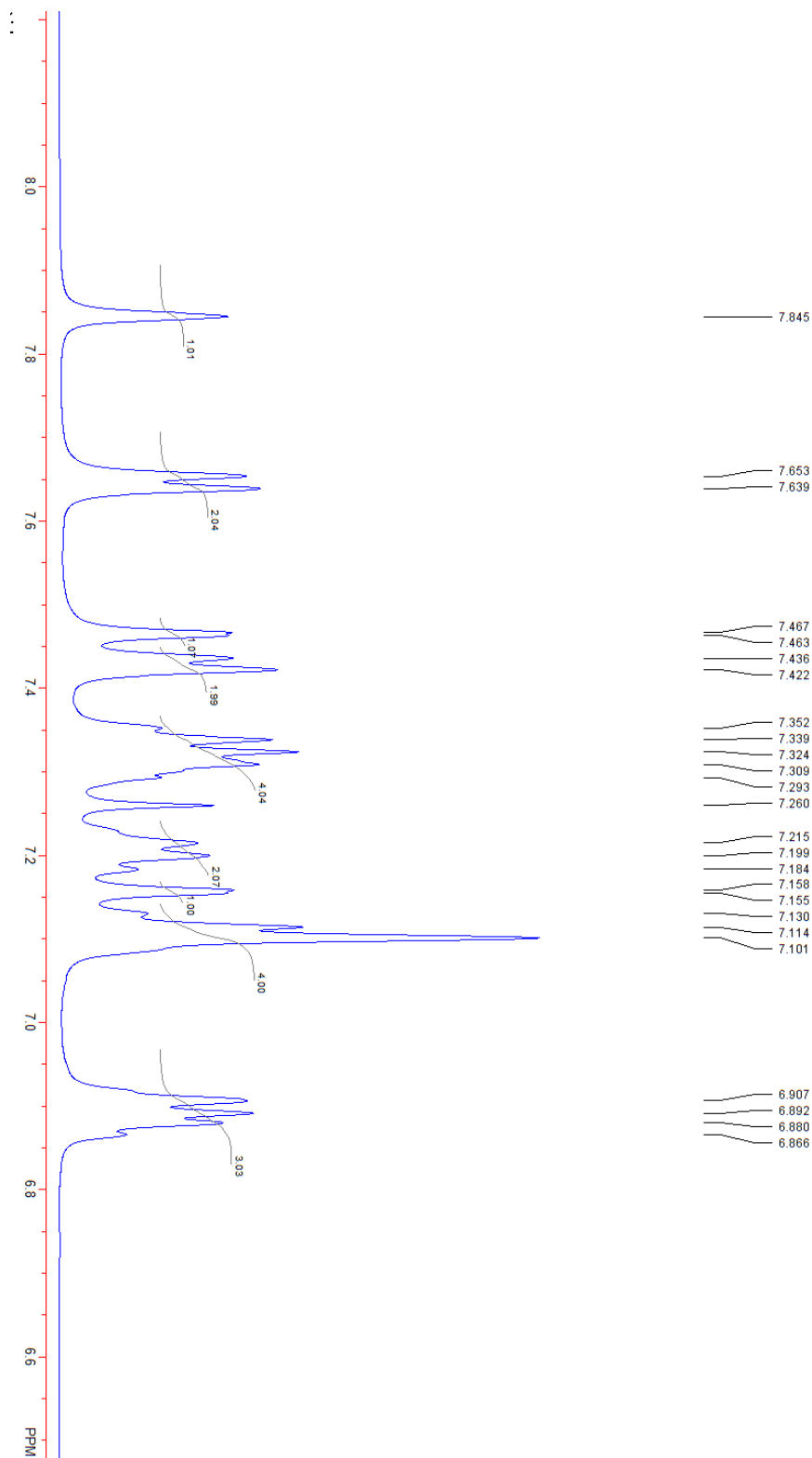
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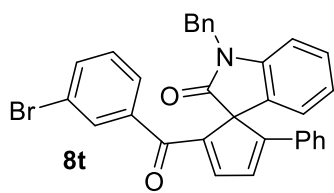




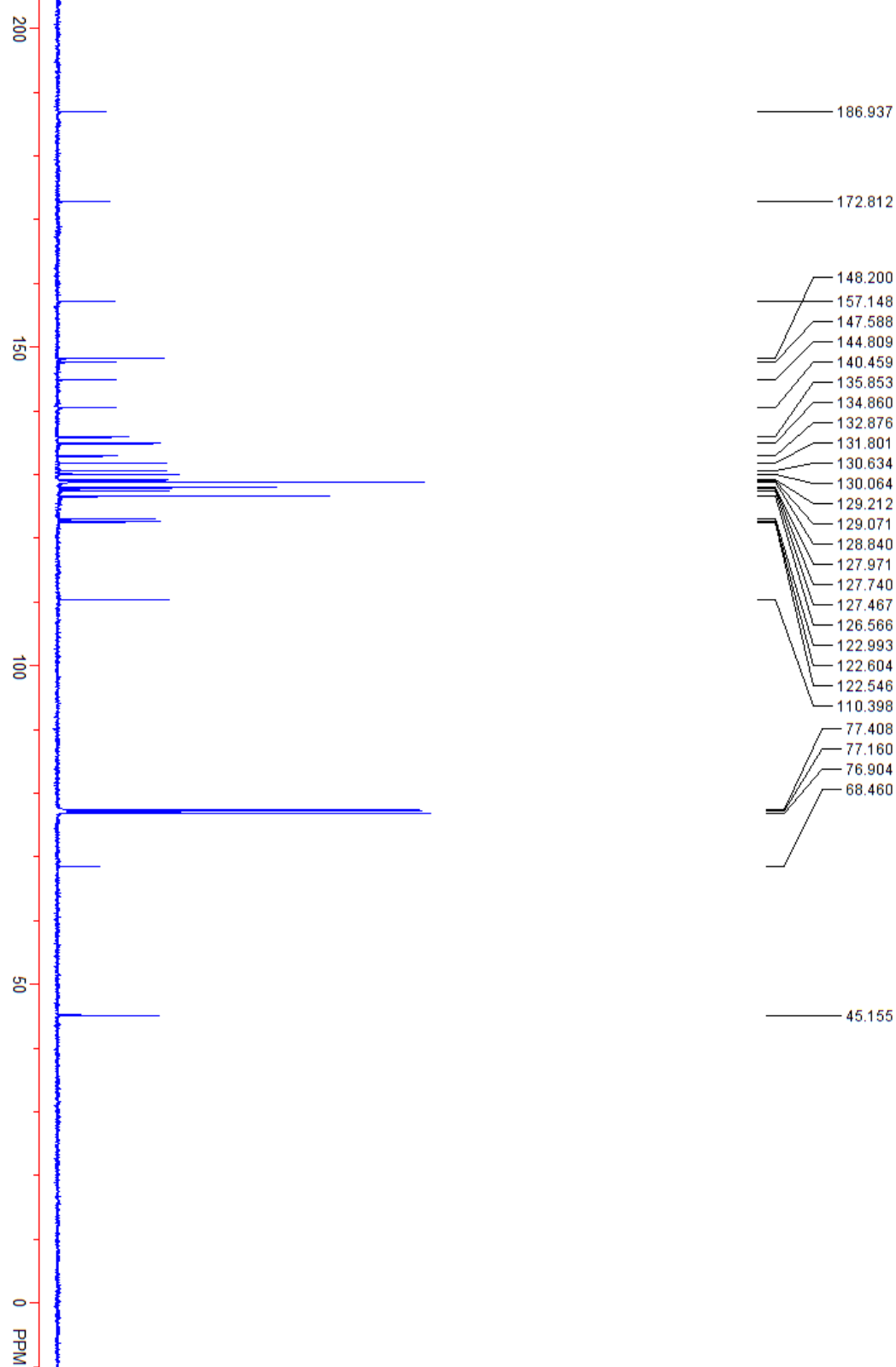


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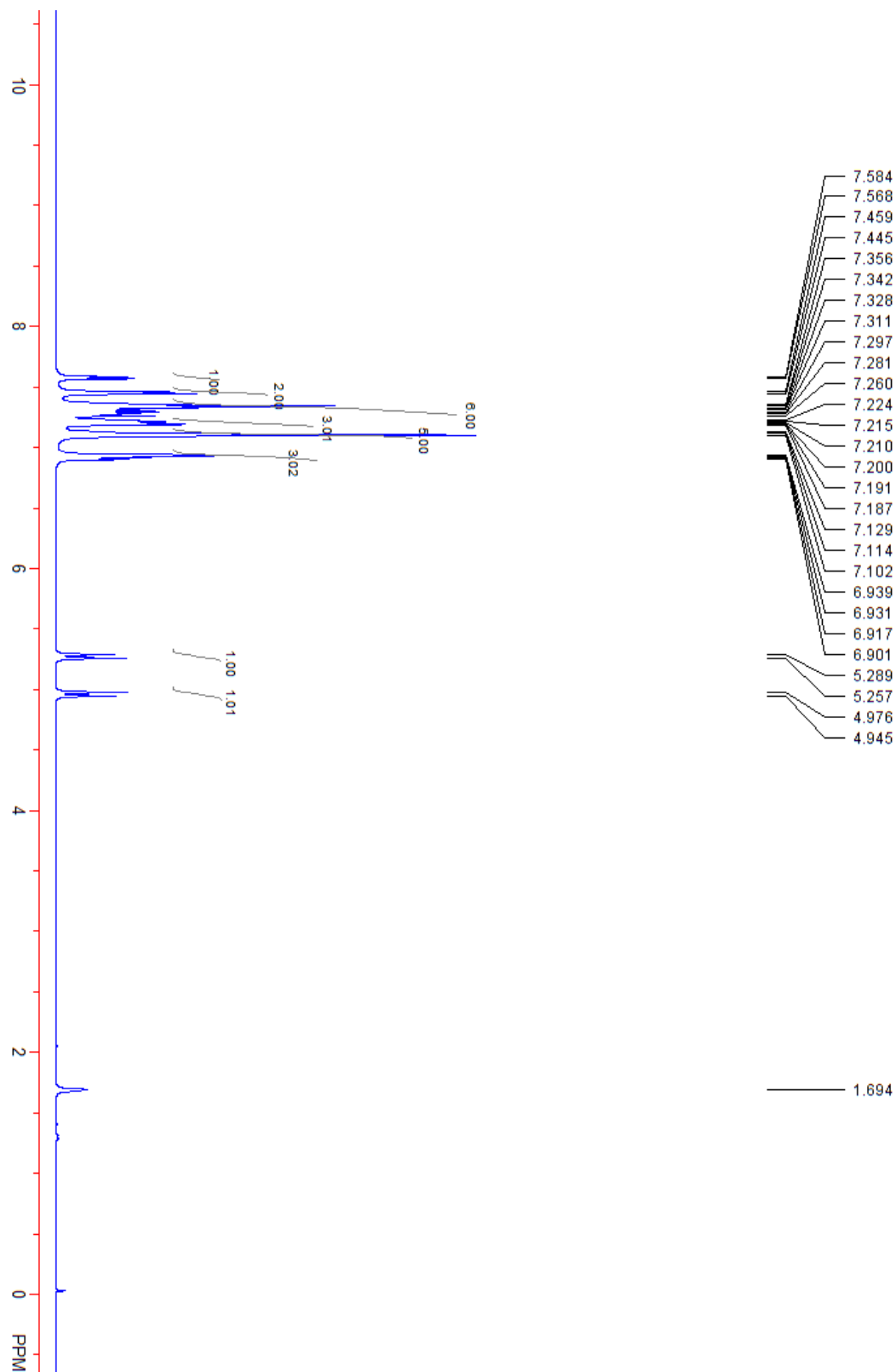
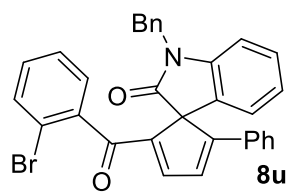




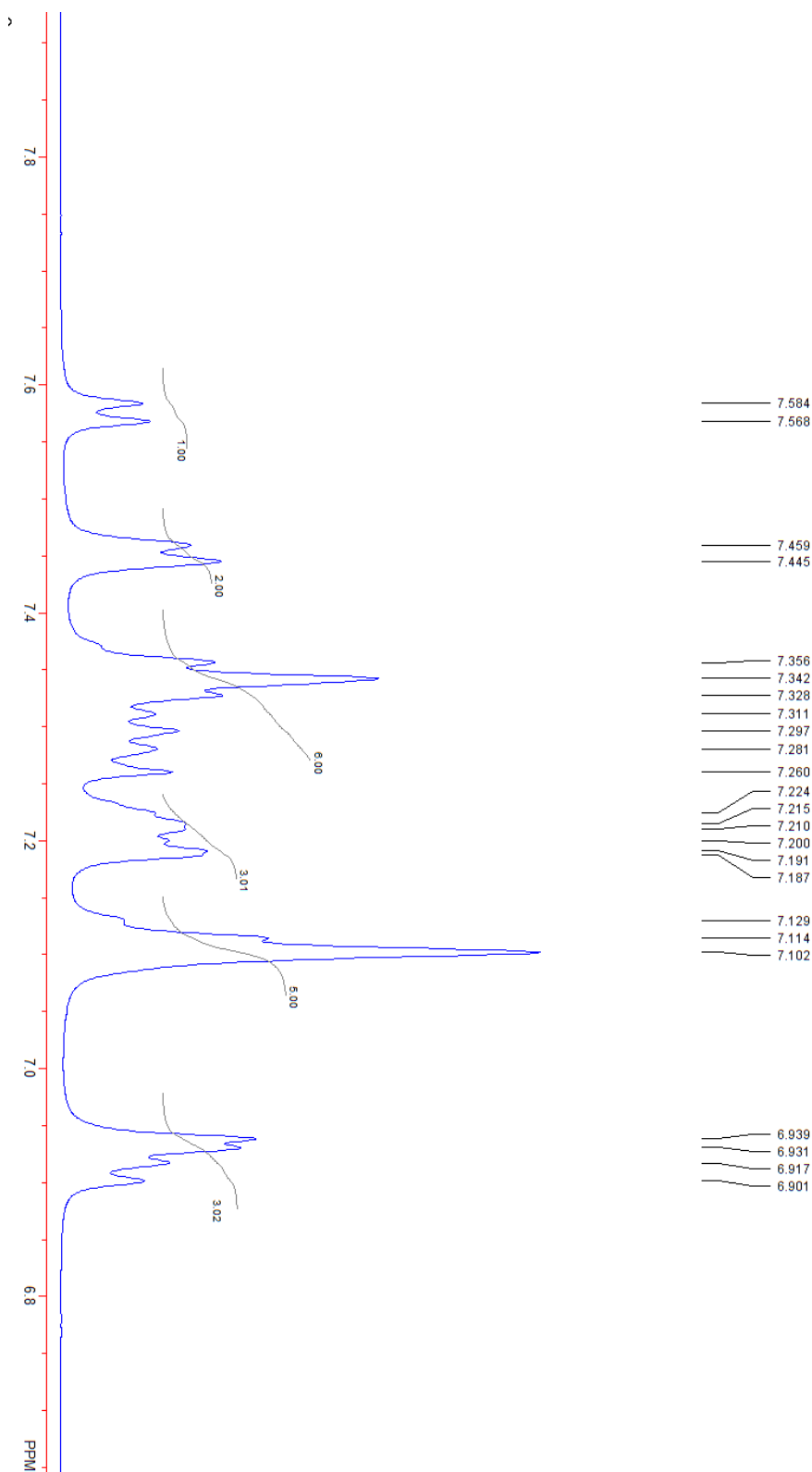
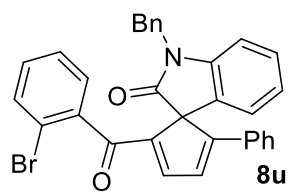
$^{13}\text{C}\{^1\text{H}\}$ NMR:



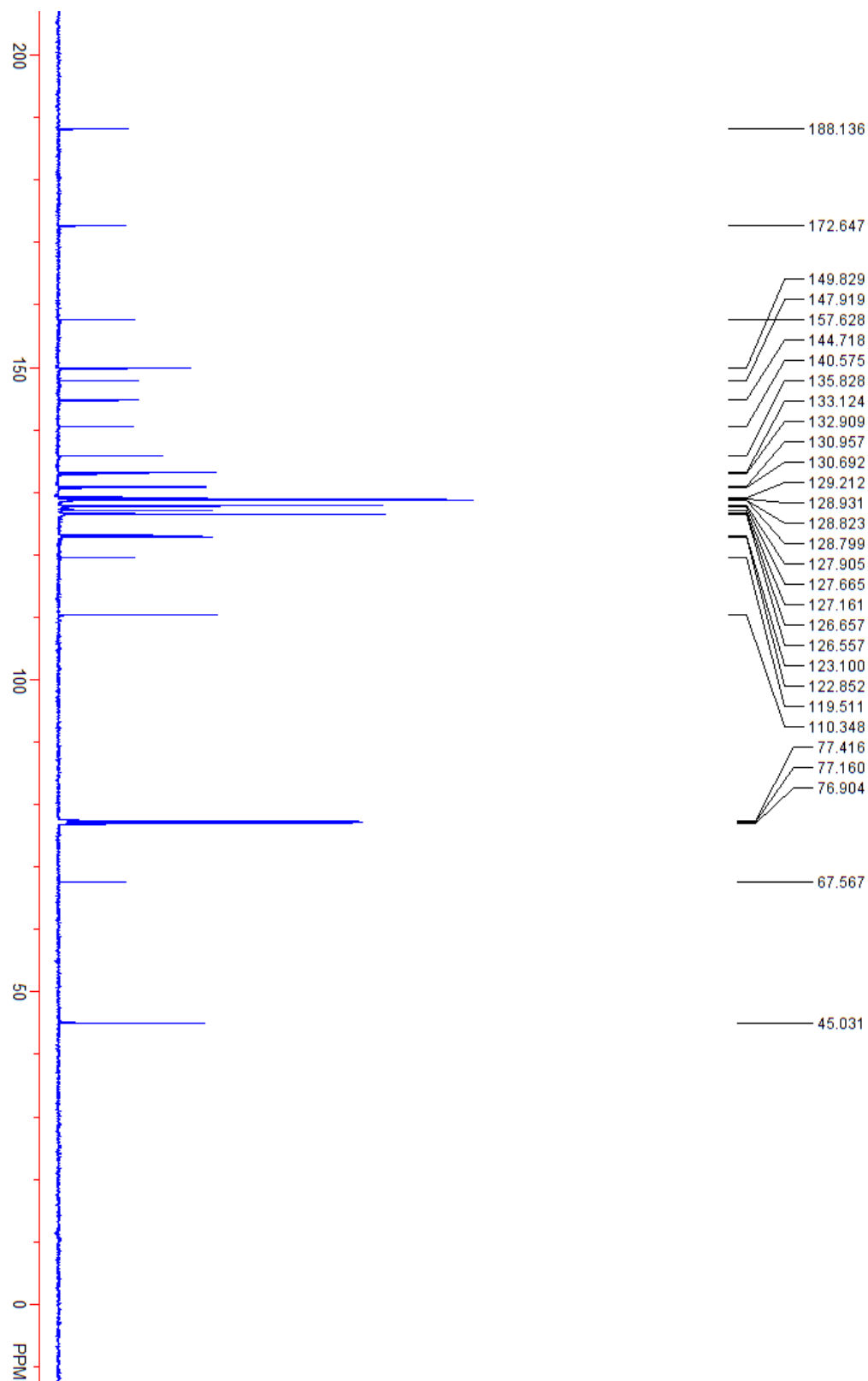
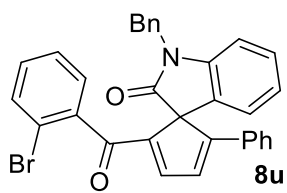
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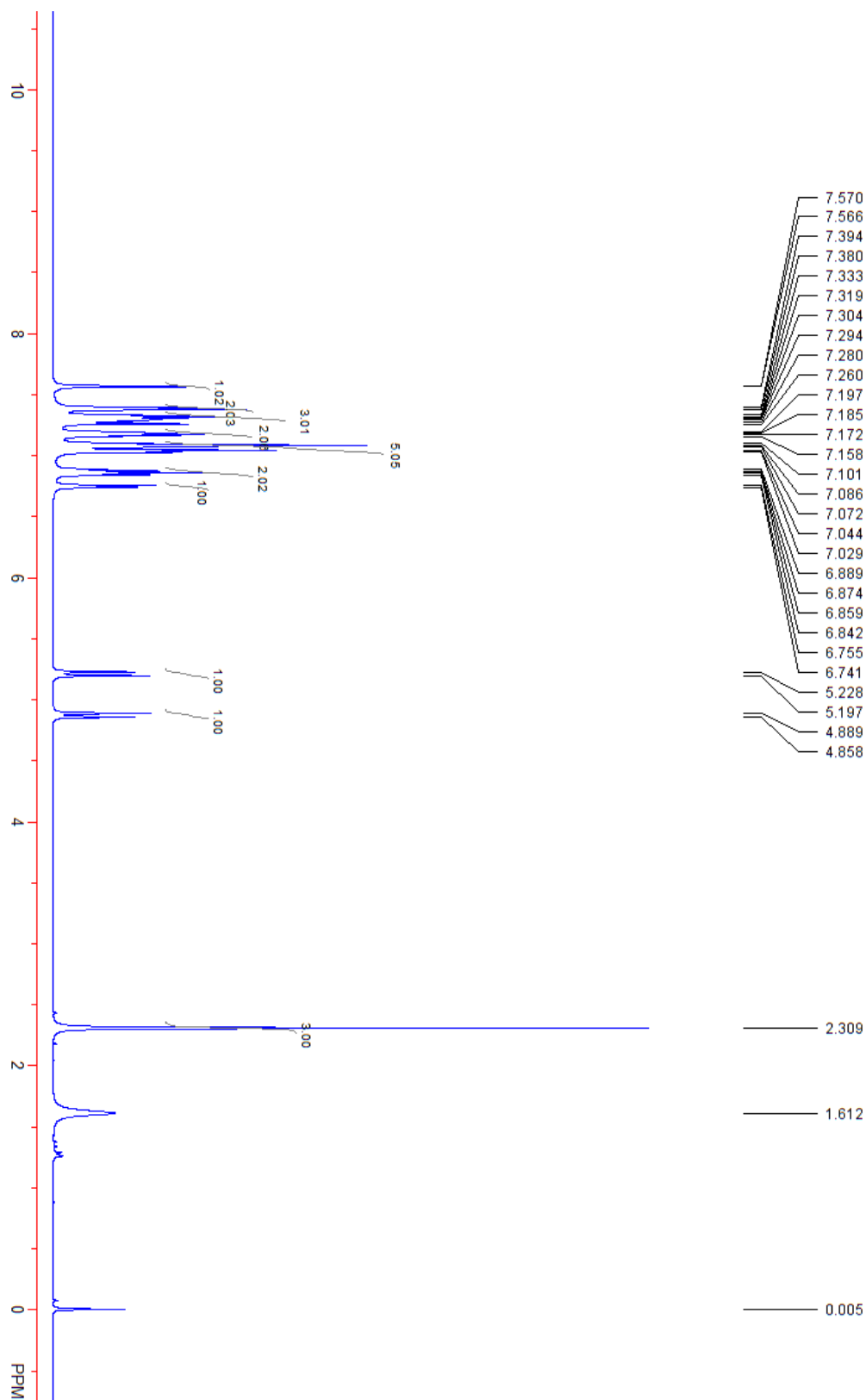
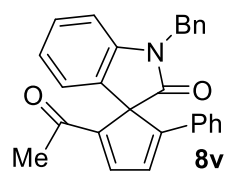
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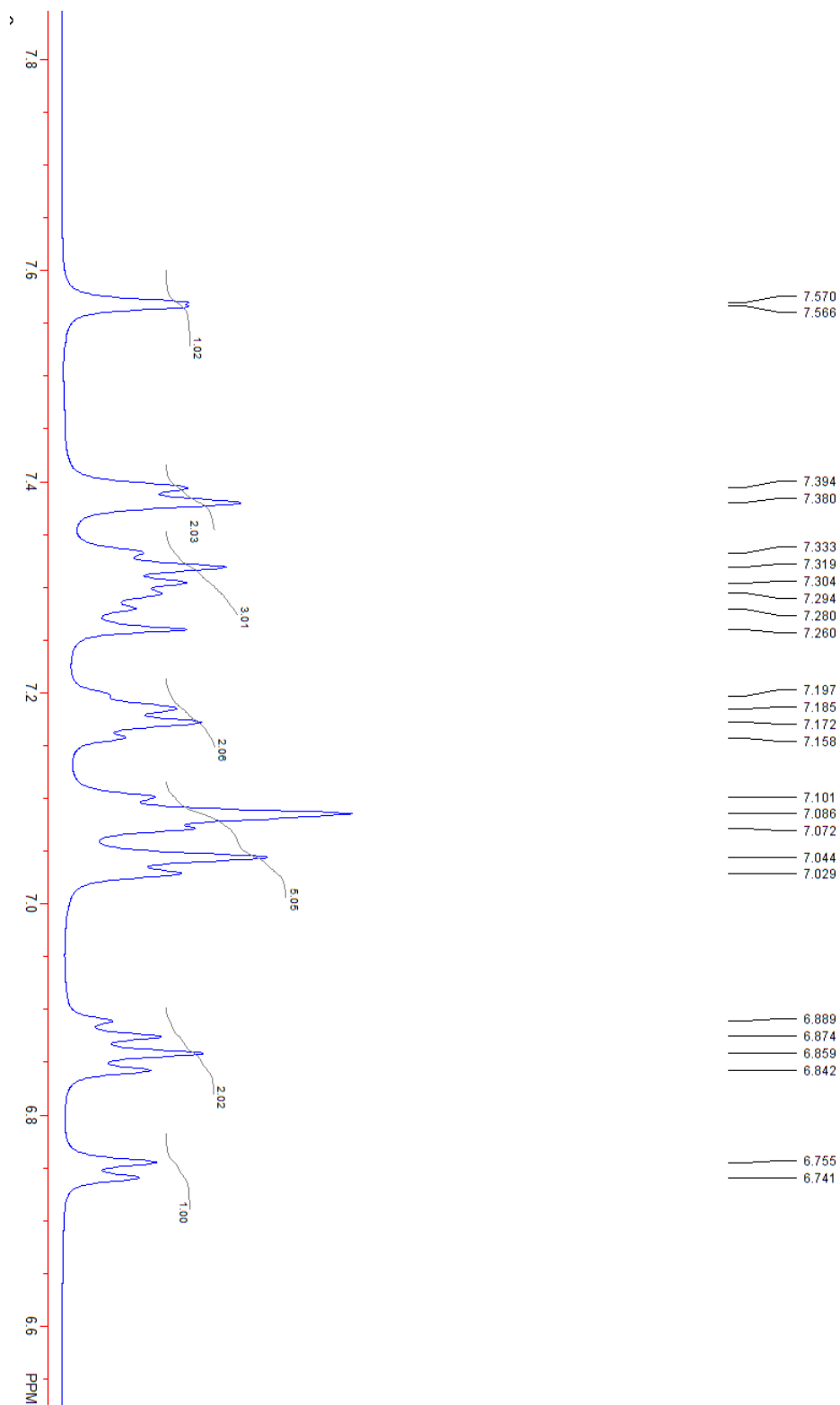
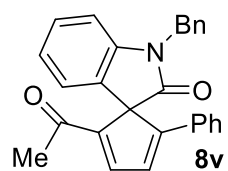
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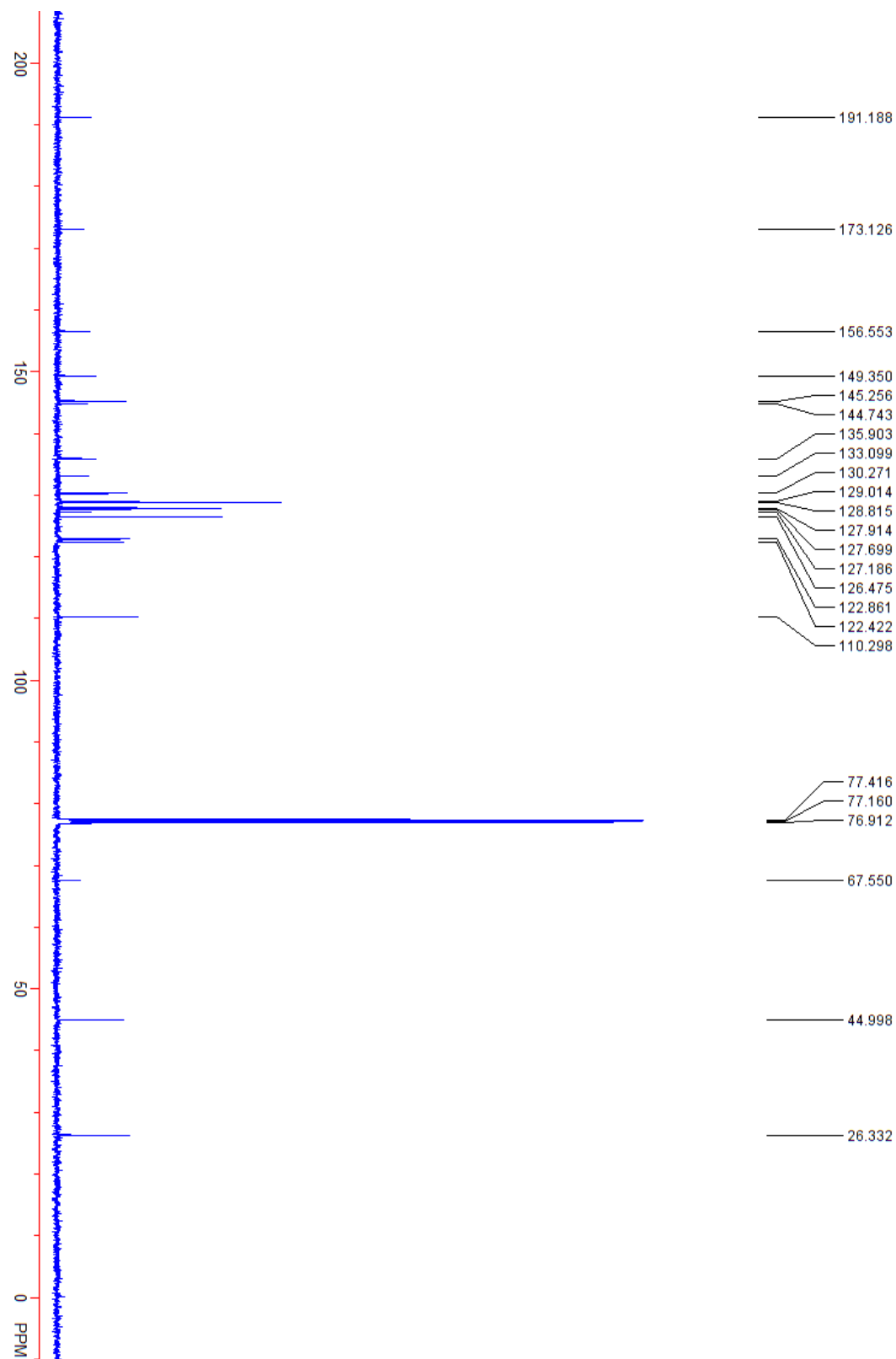
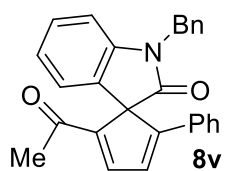
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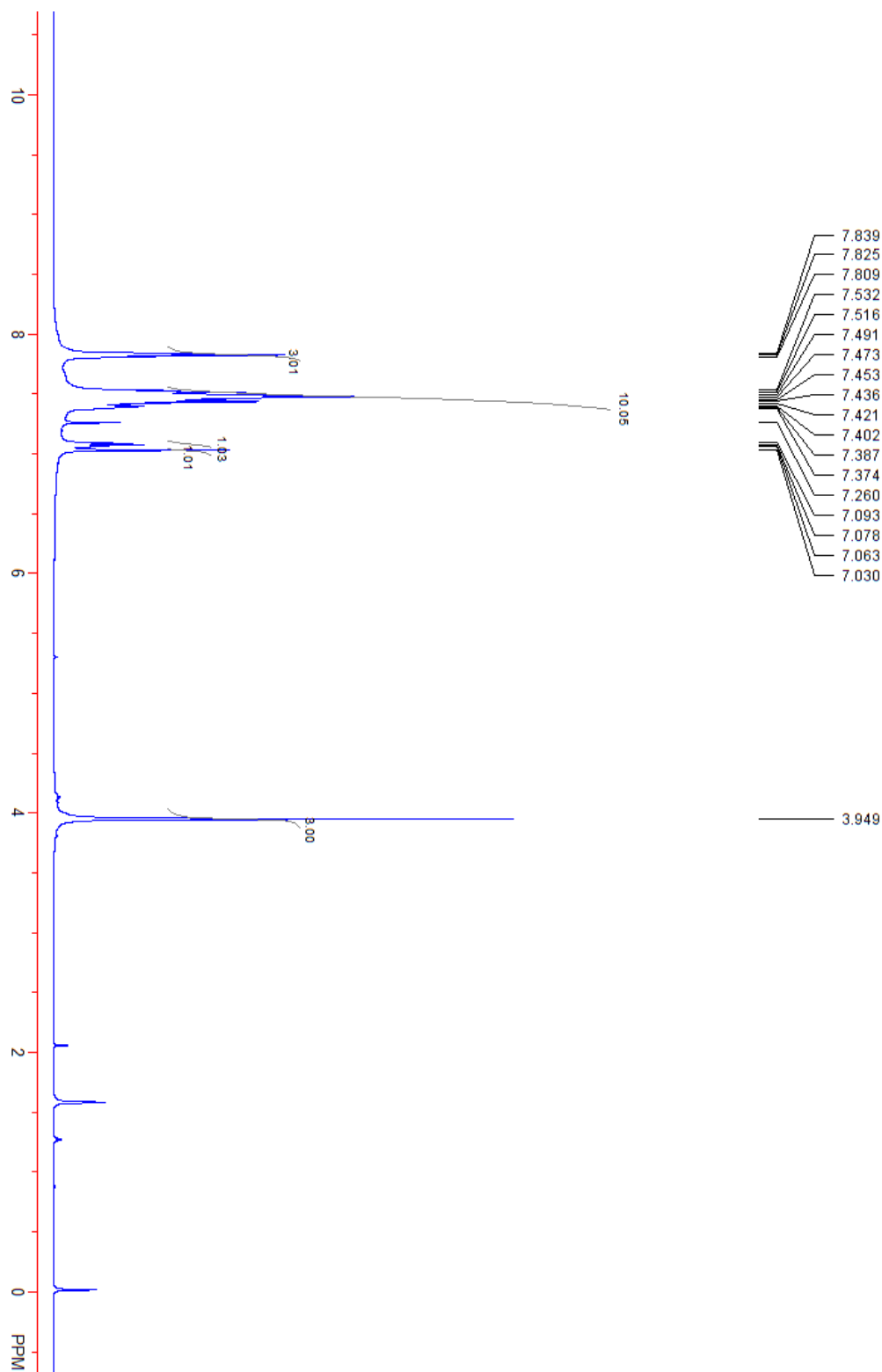
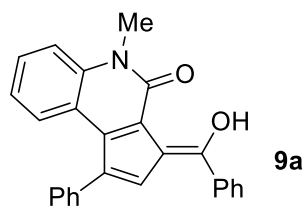
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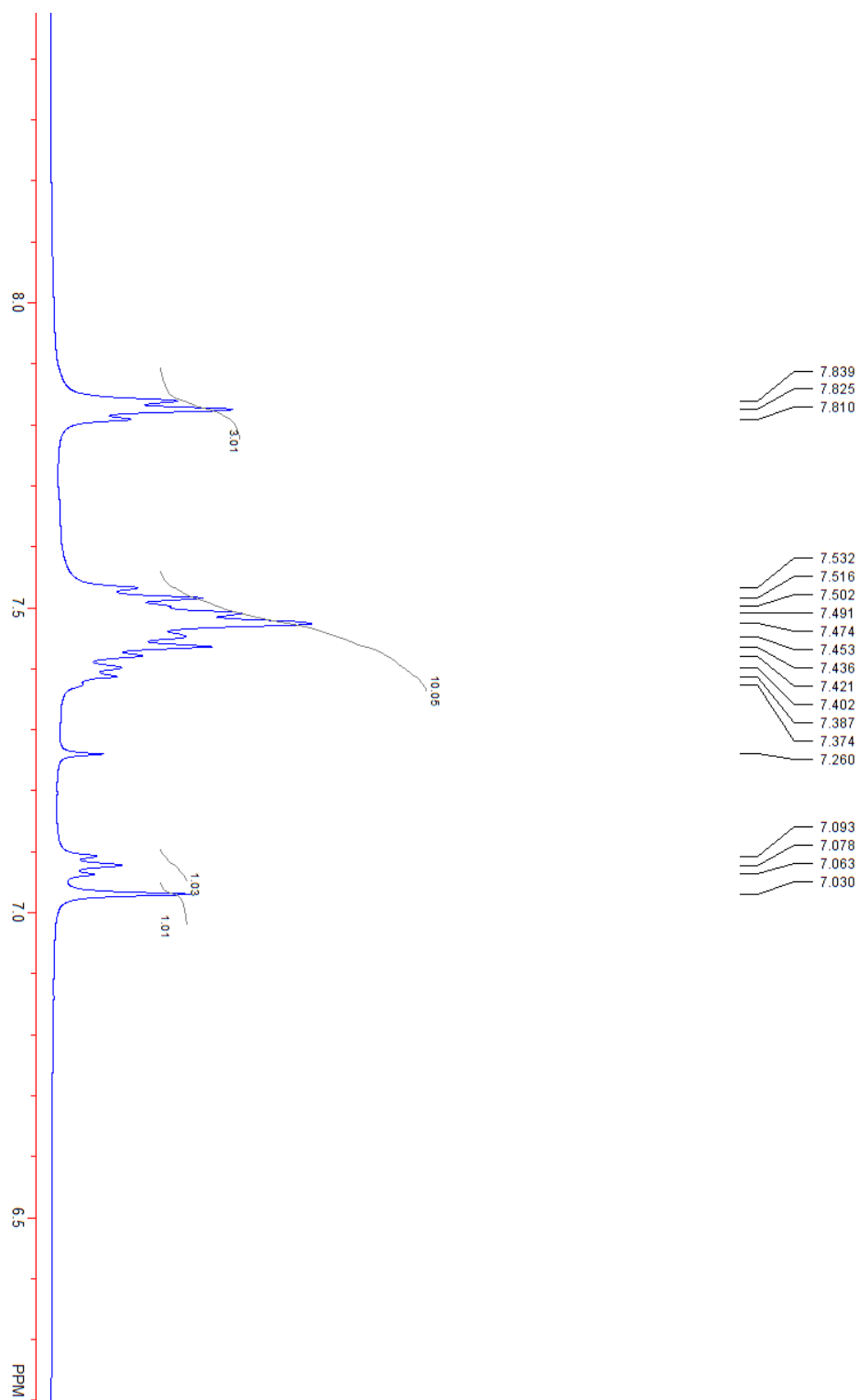
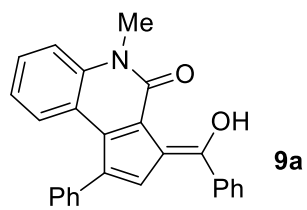
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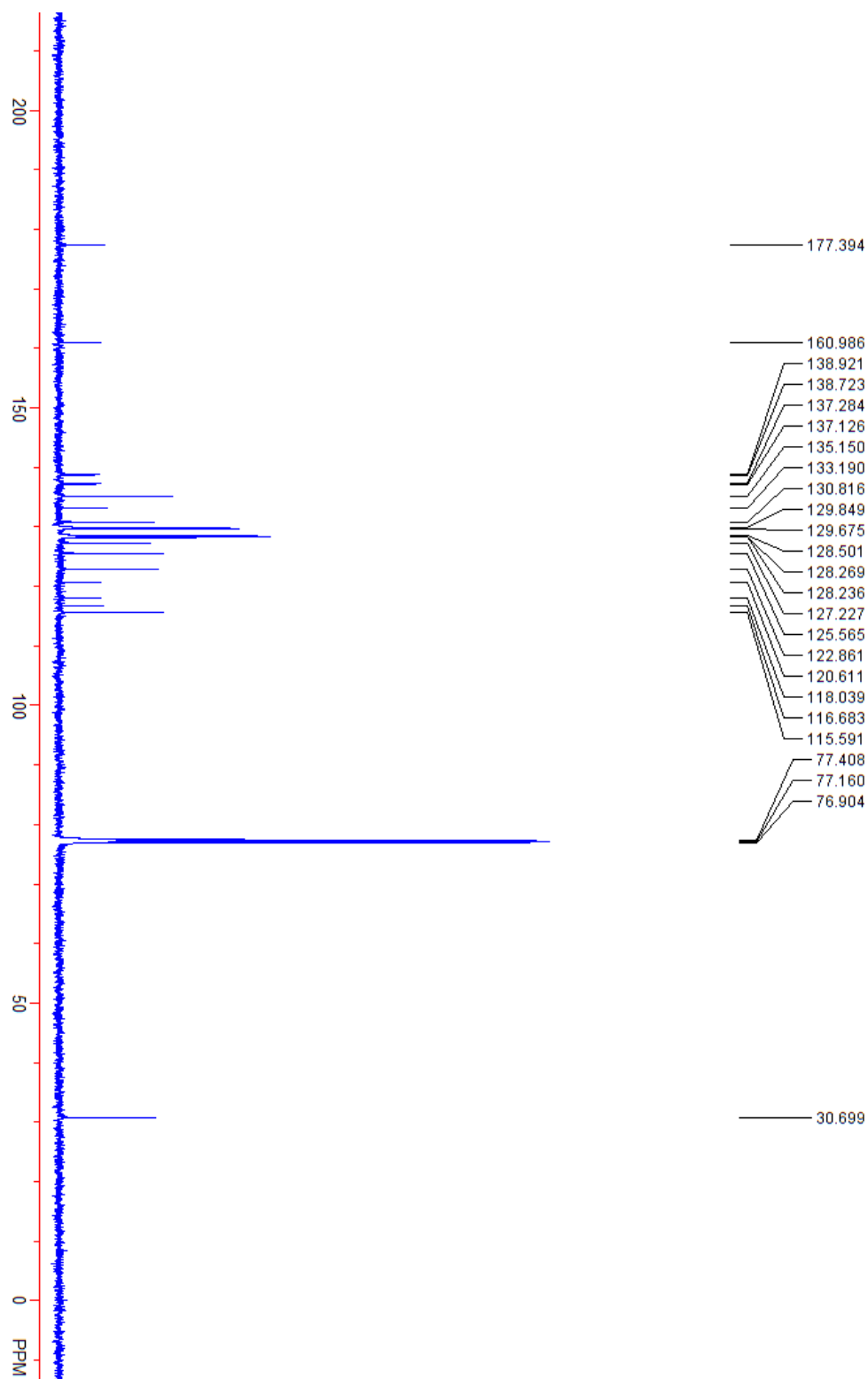
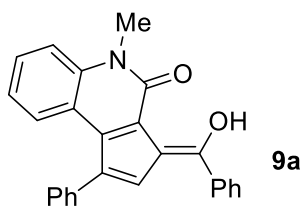
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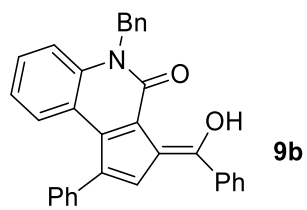


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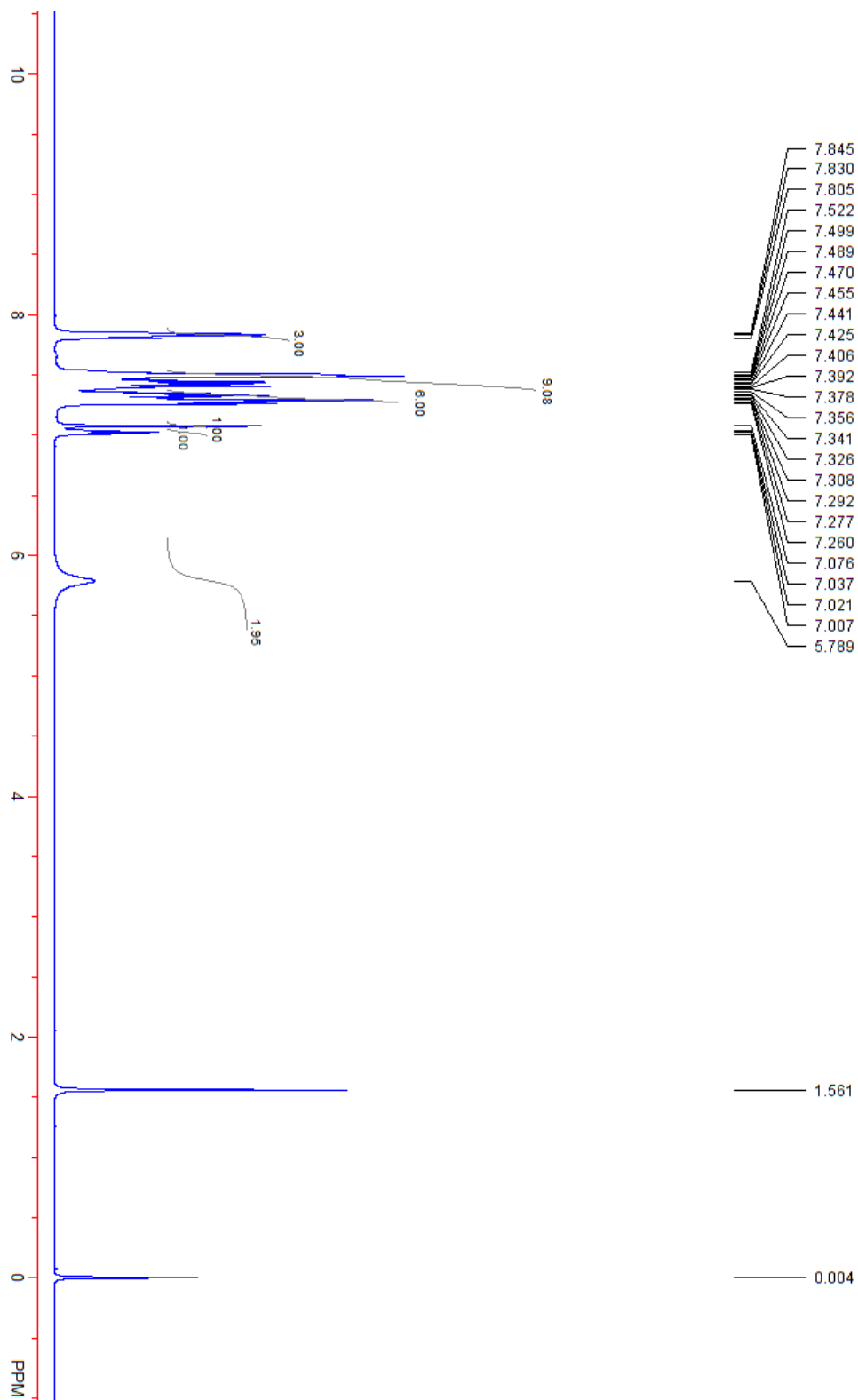


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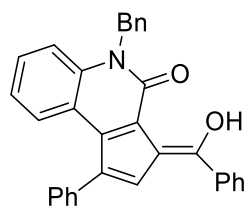




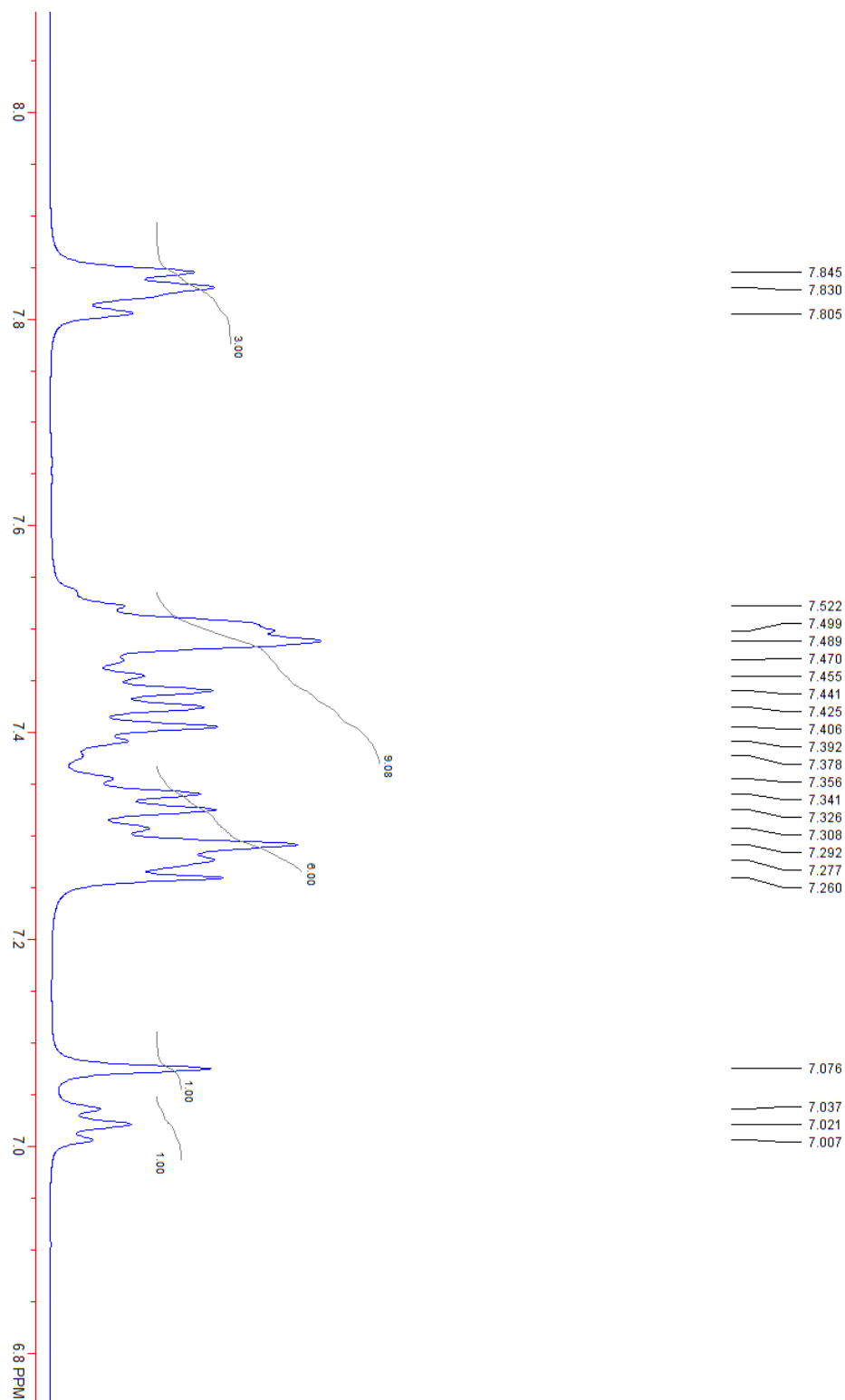
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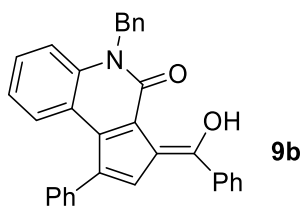


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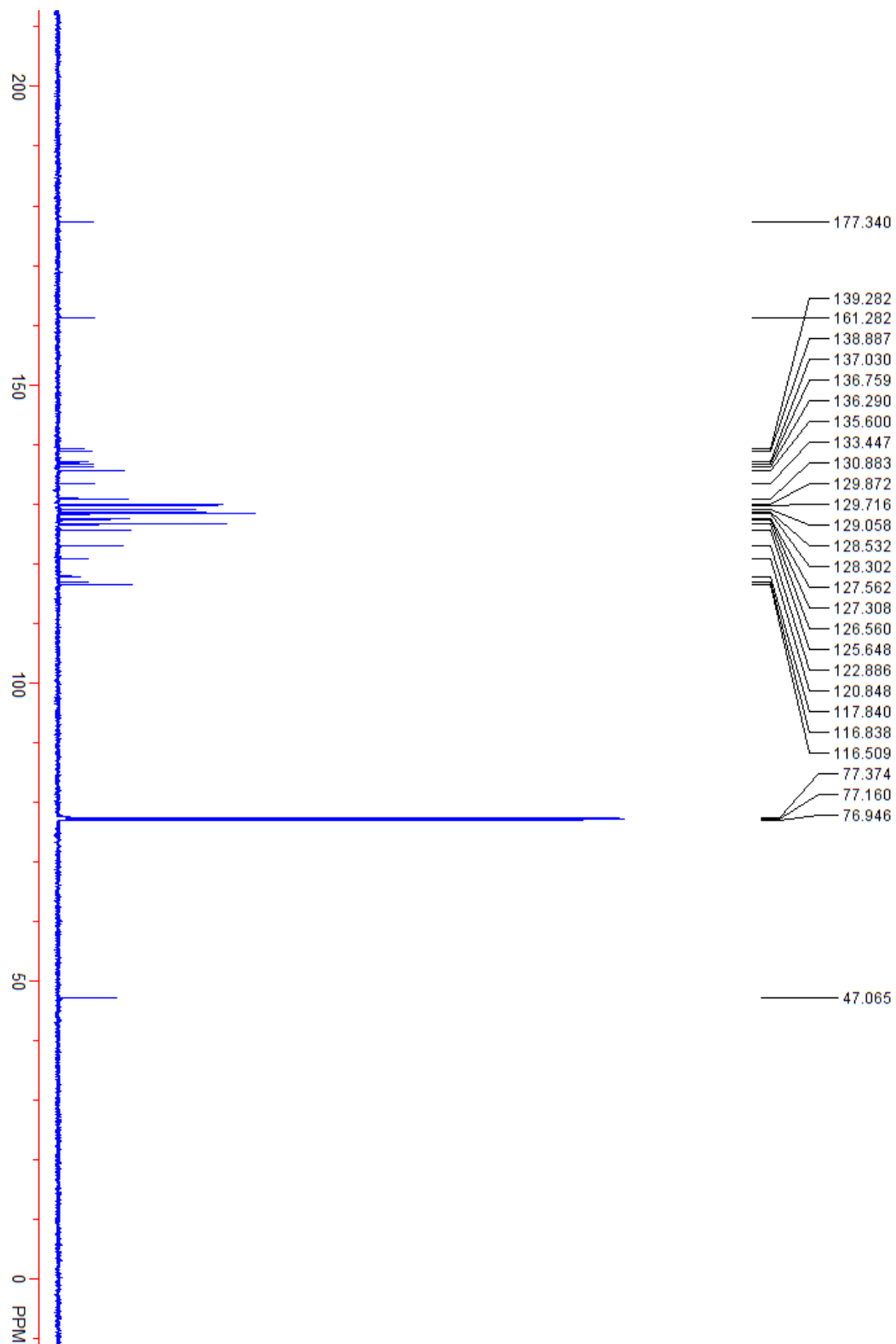


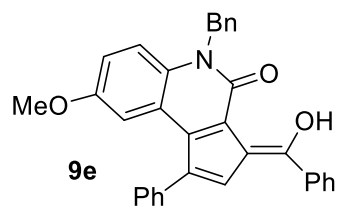
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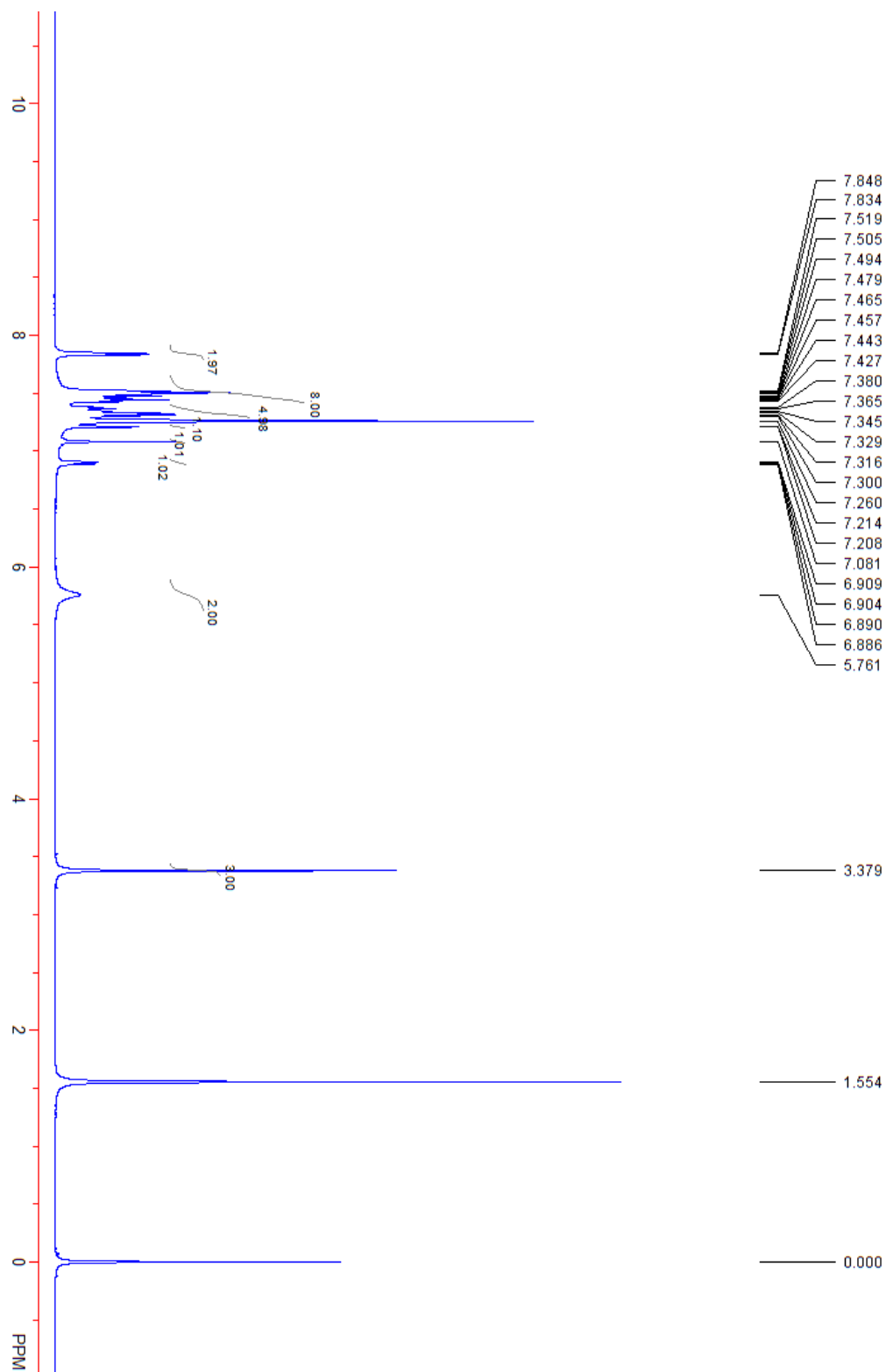


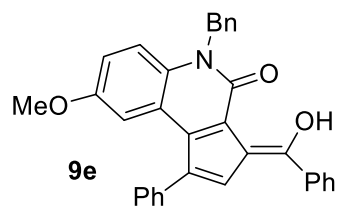
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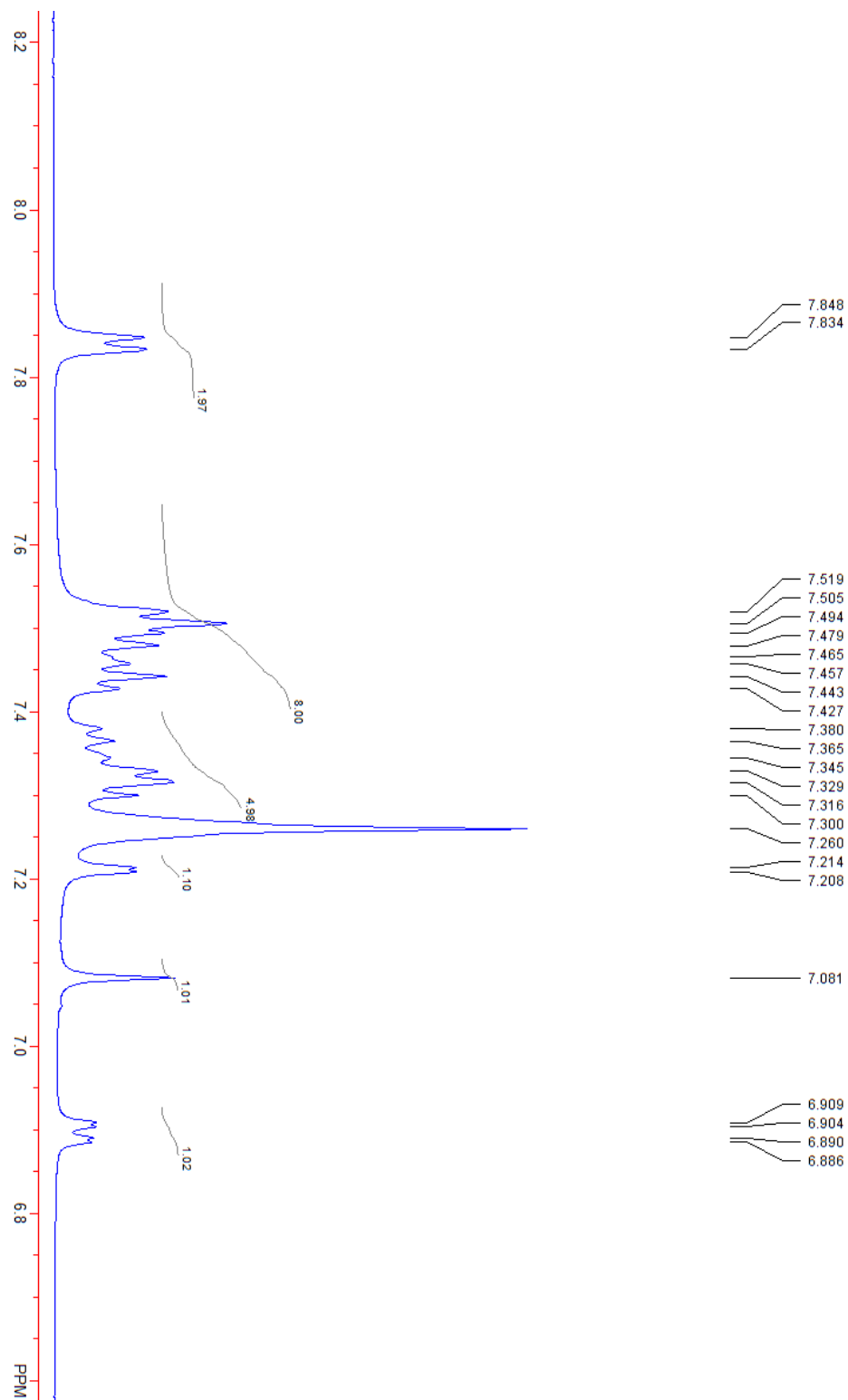


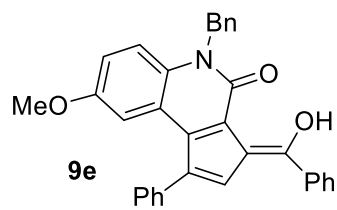
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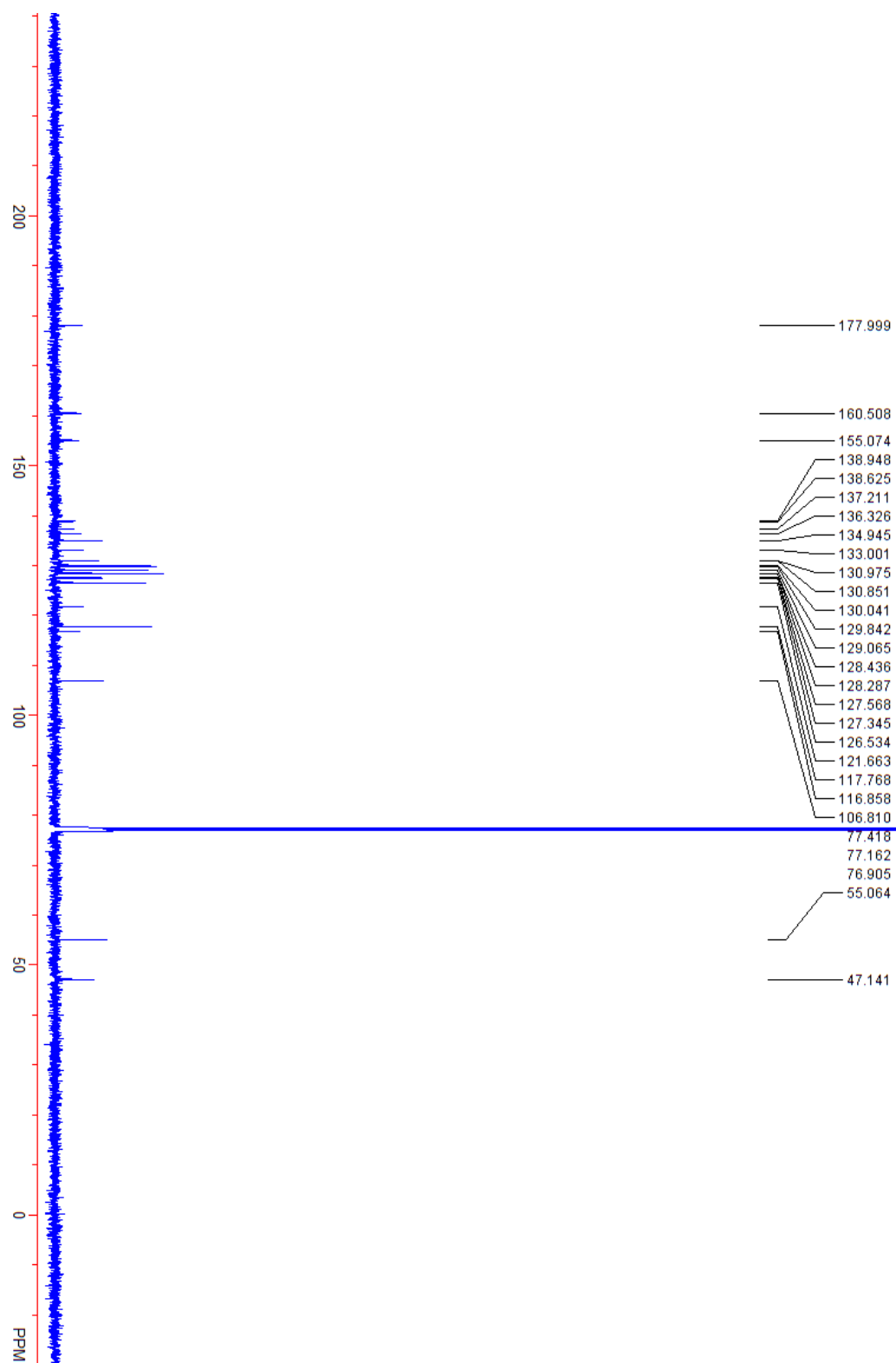


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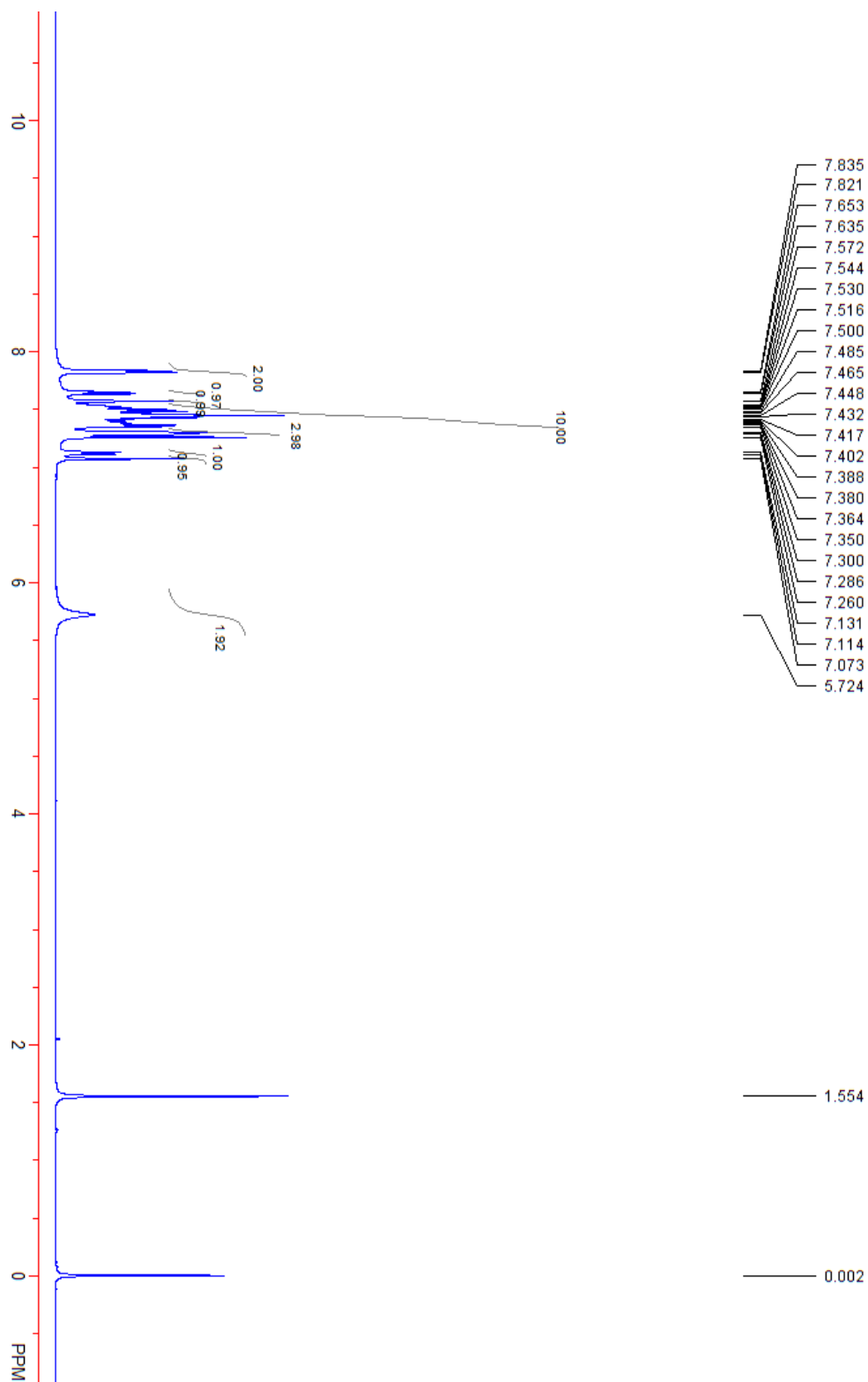
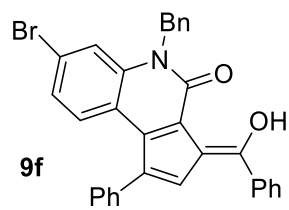




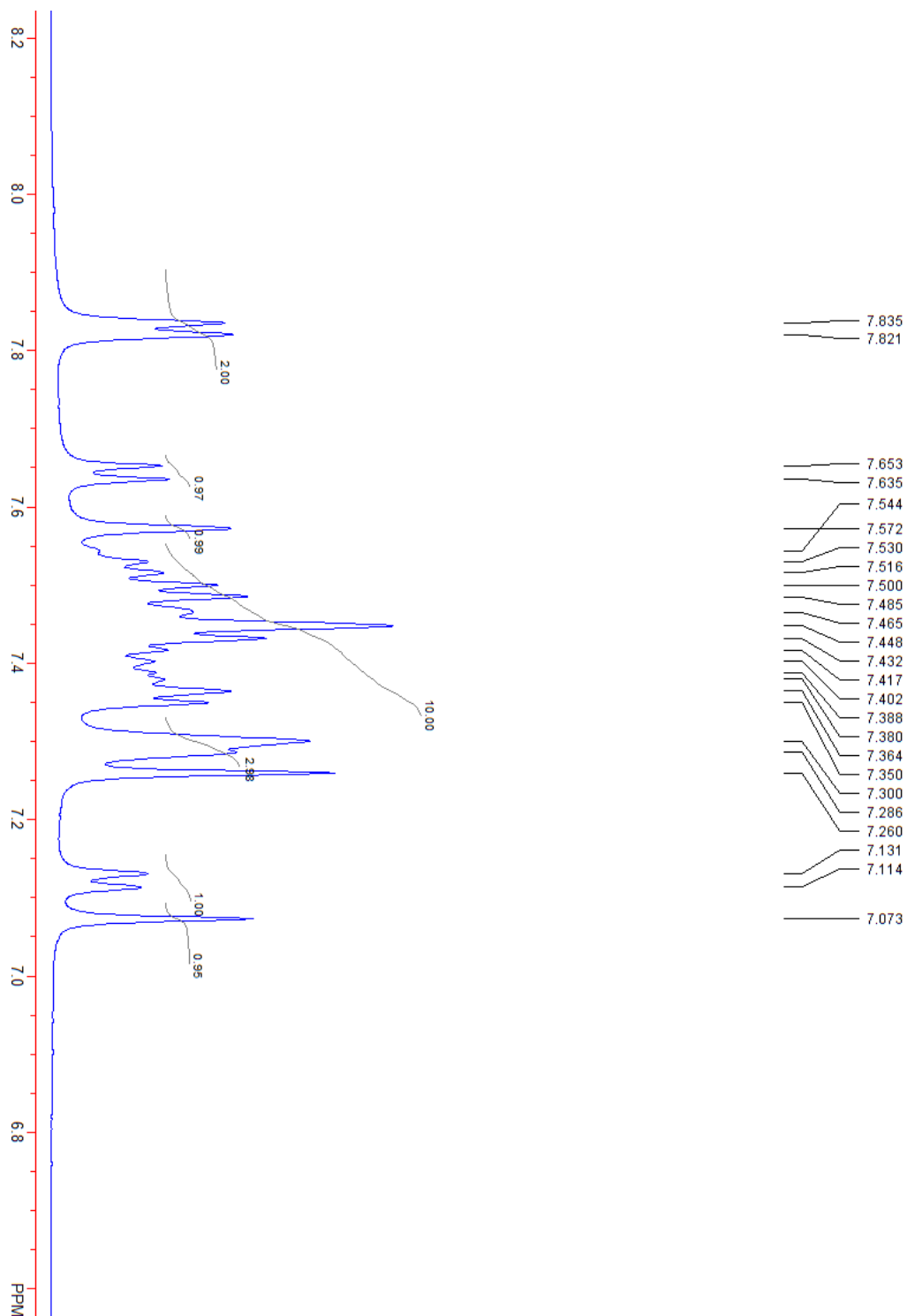
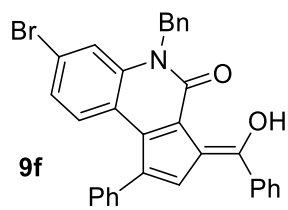
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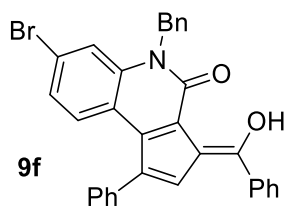


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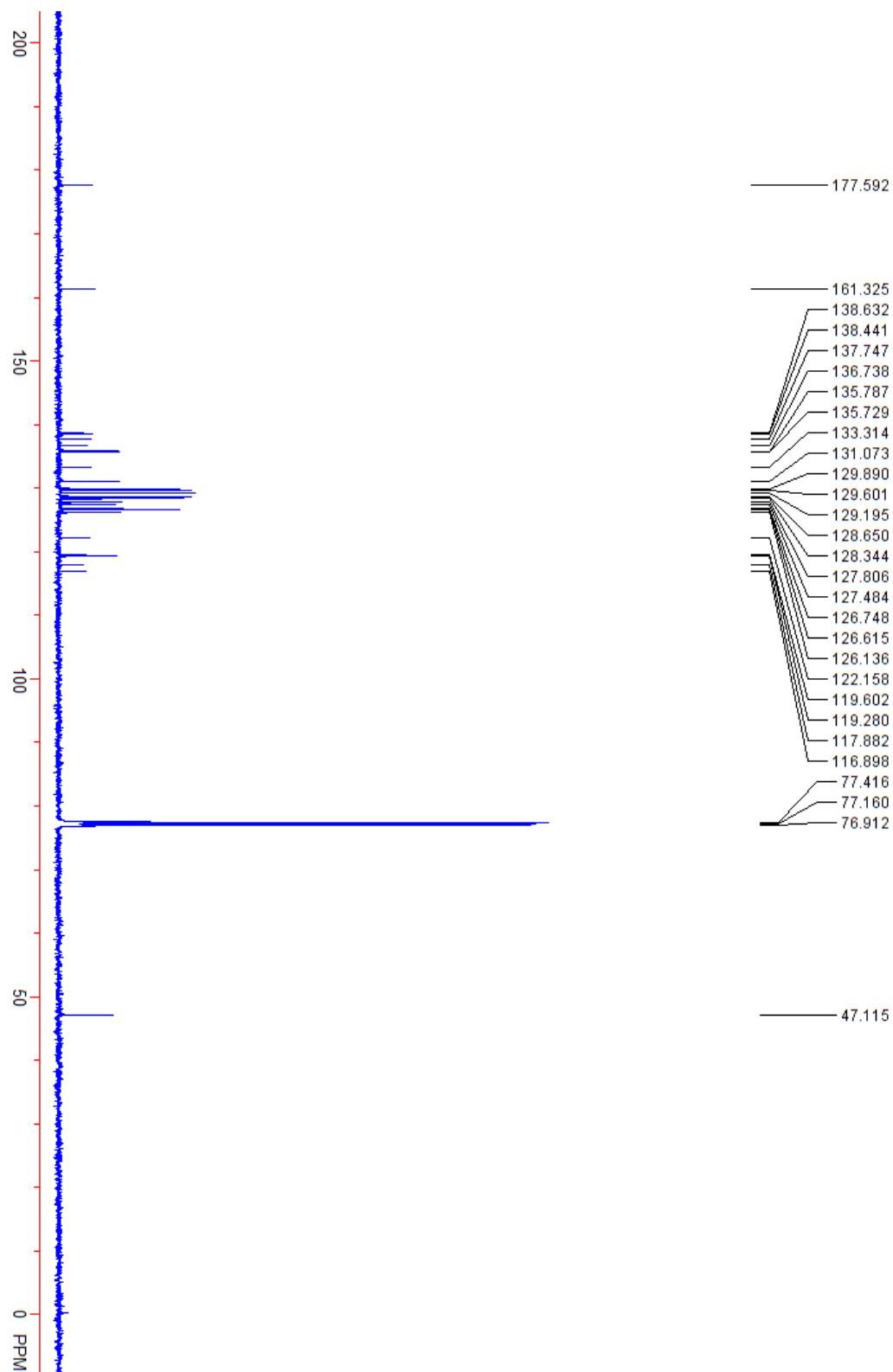


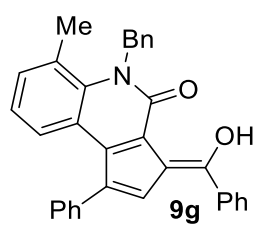
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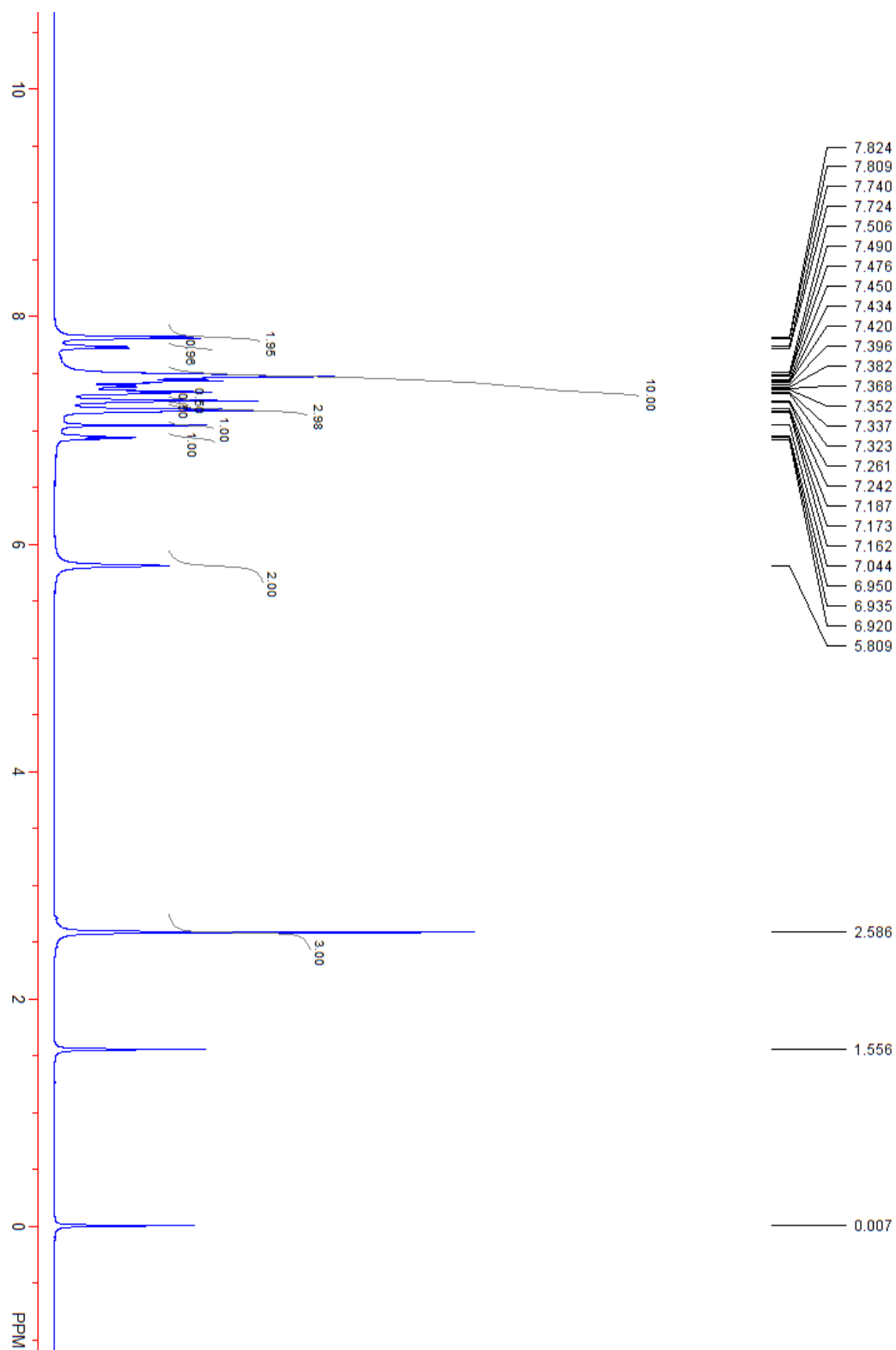


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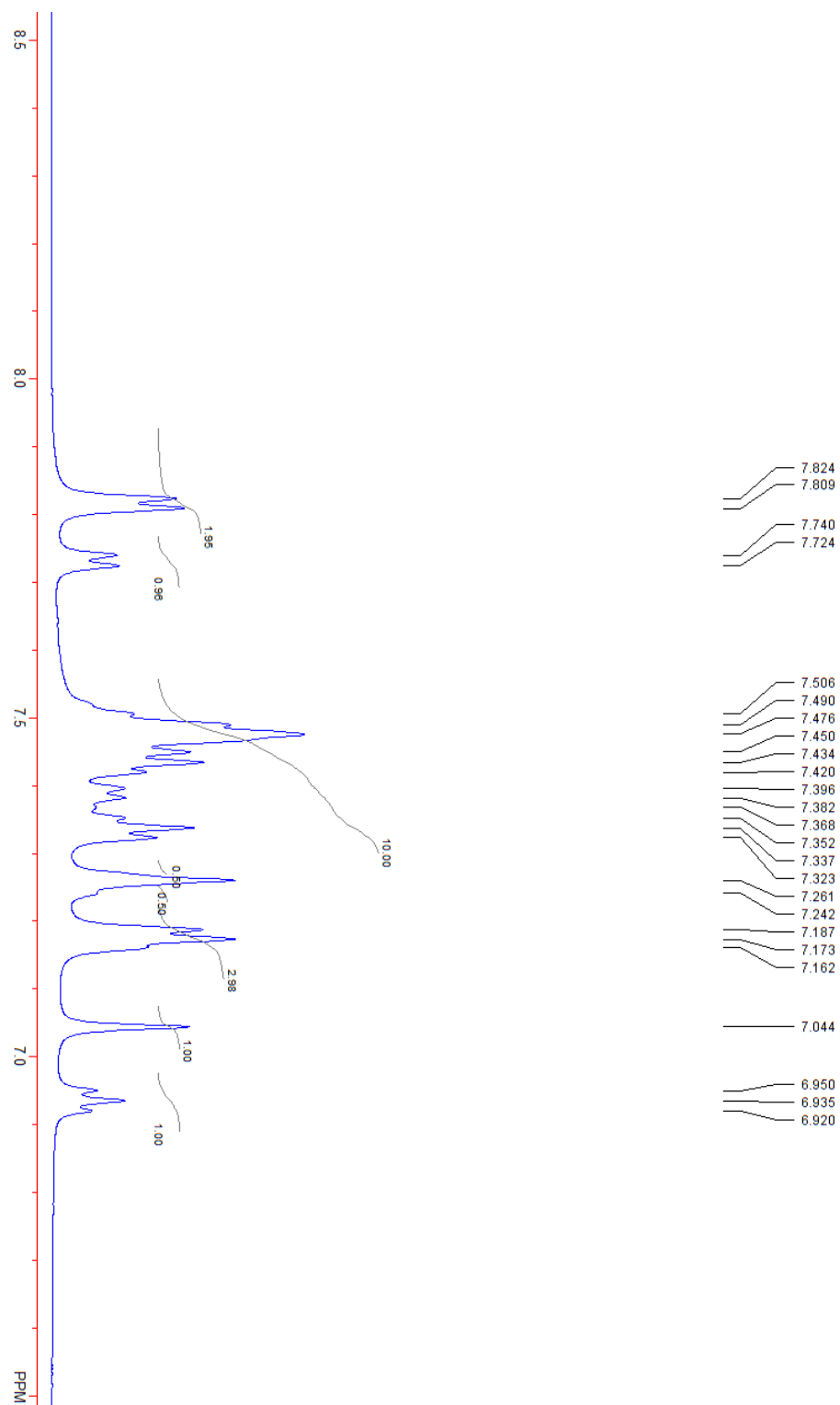
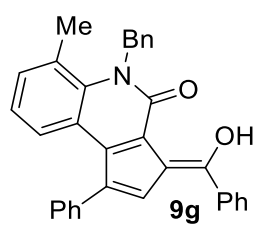


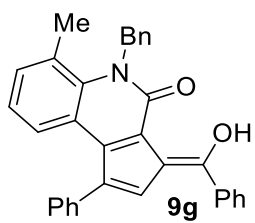


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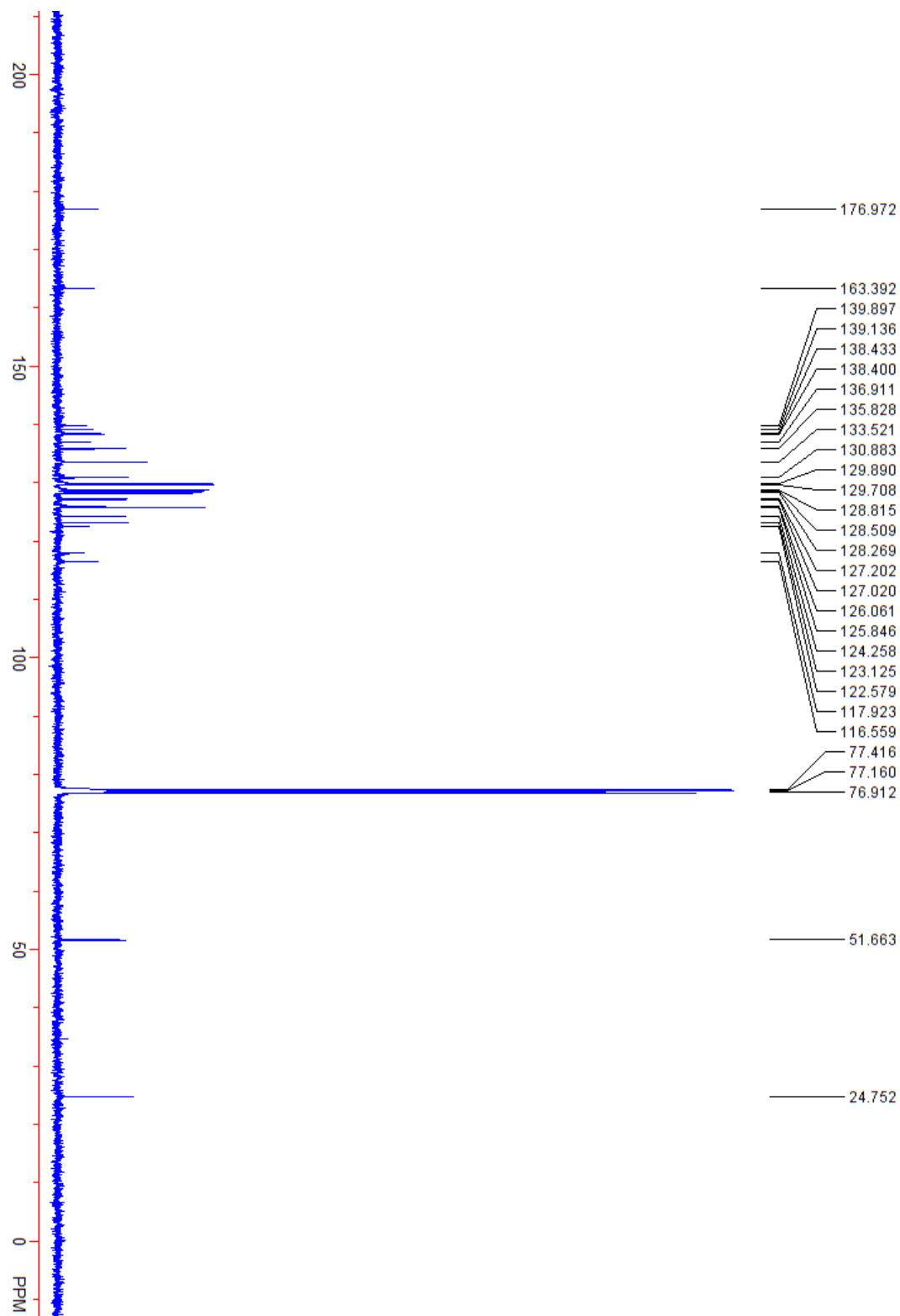


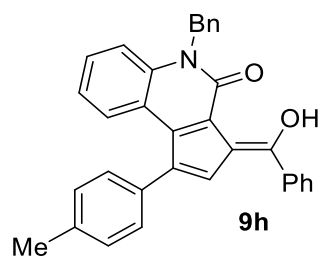
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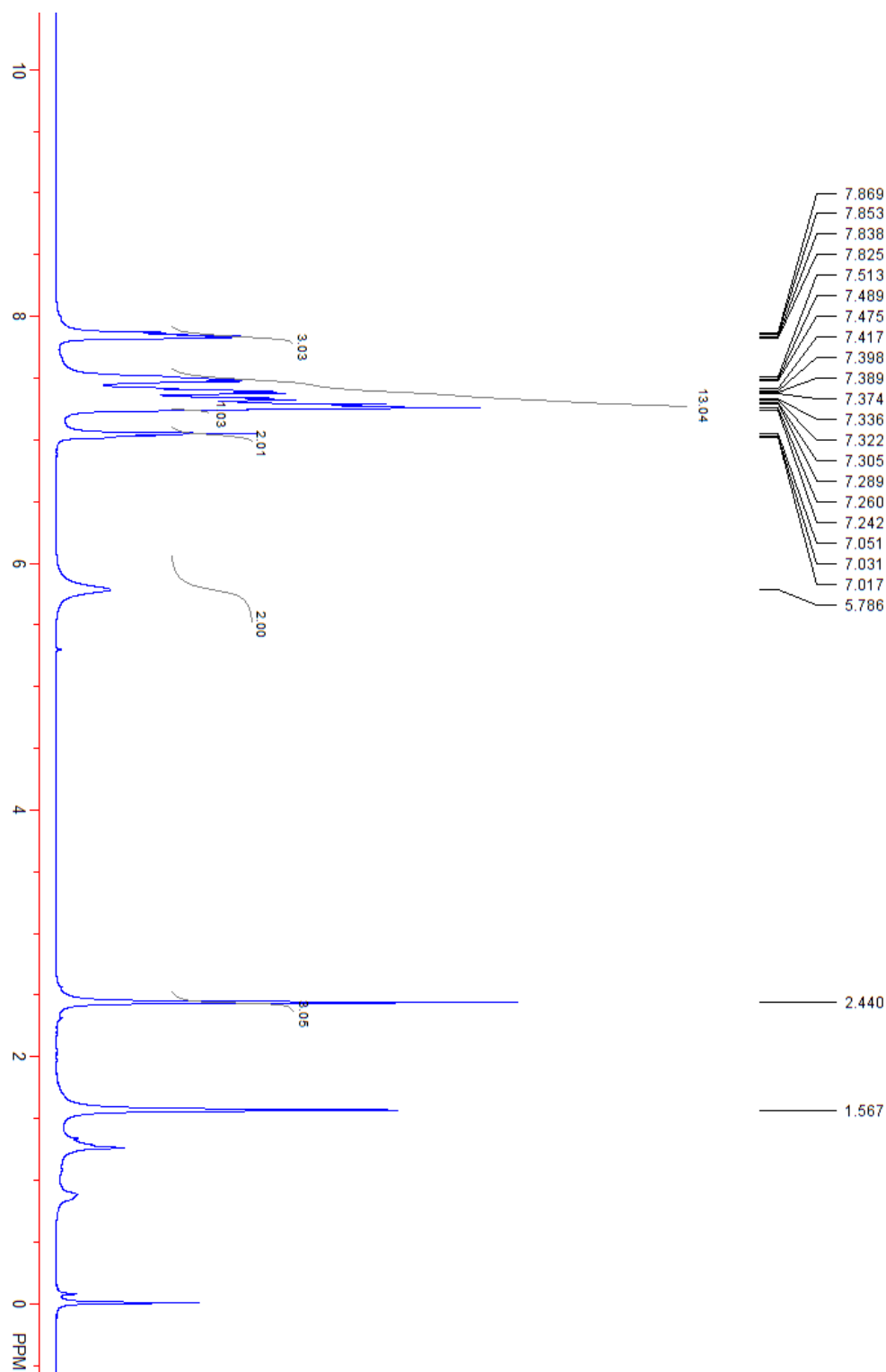


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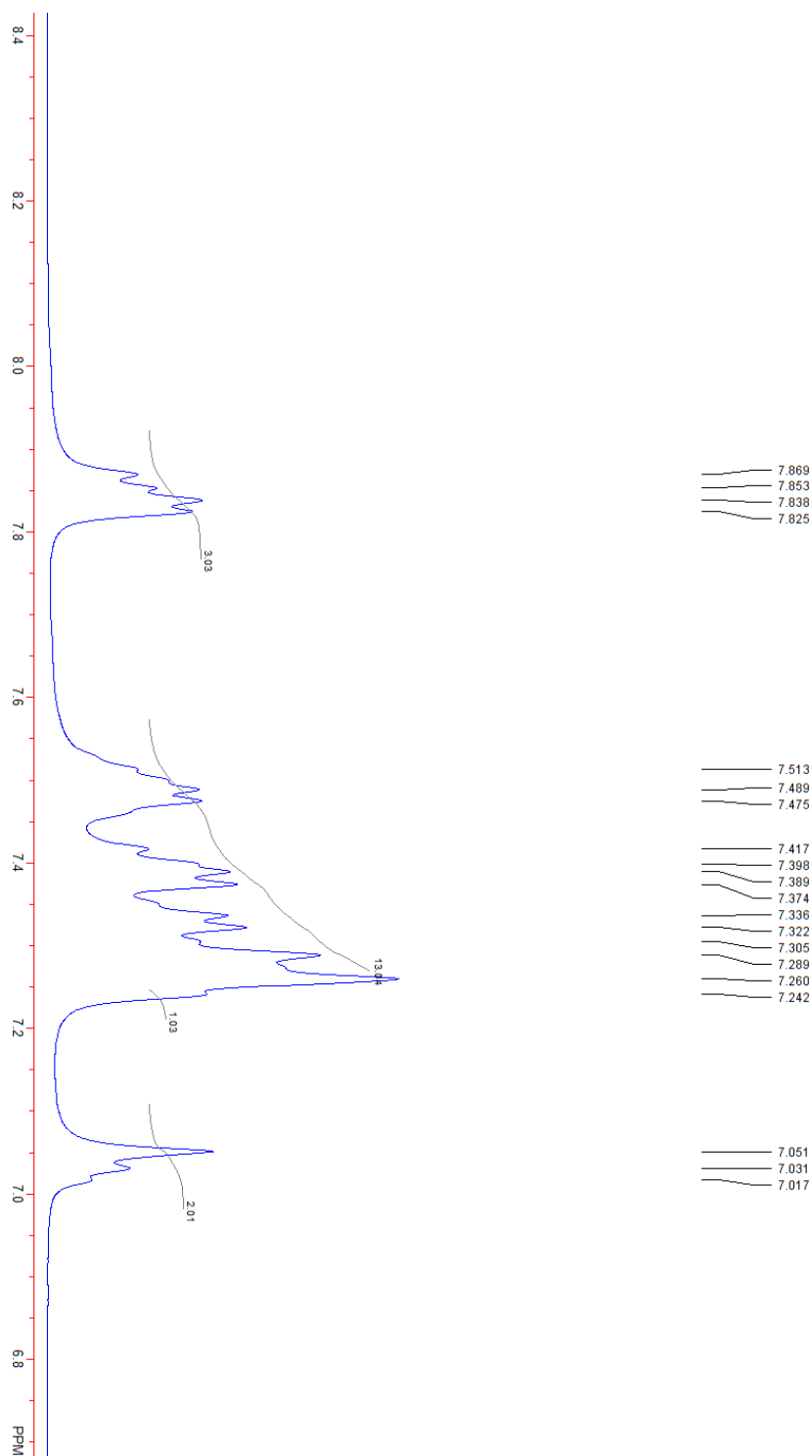
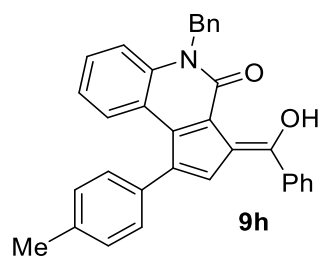


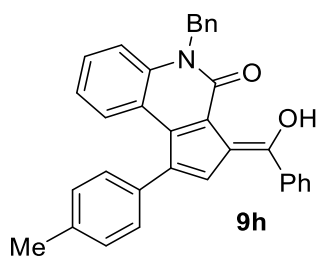


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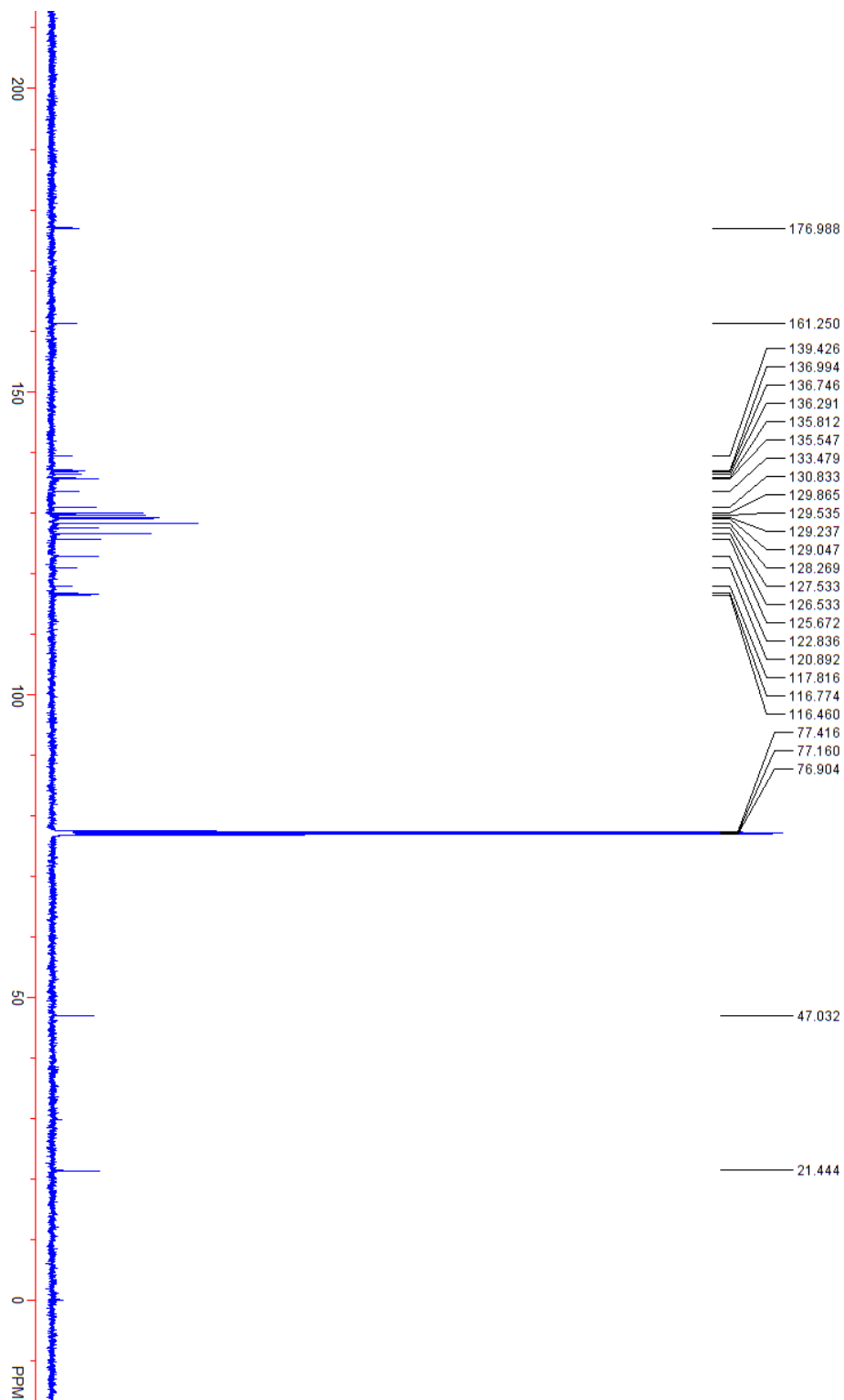


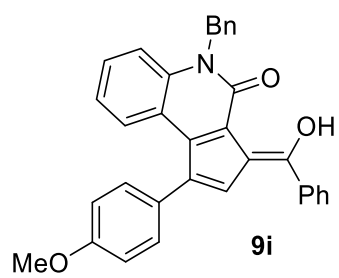
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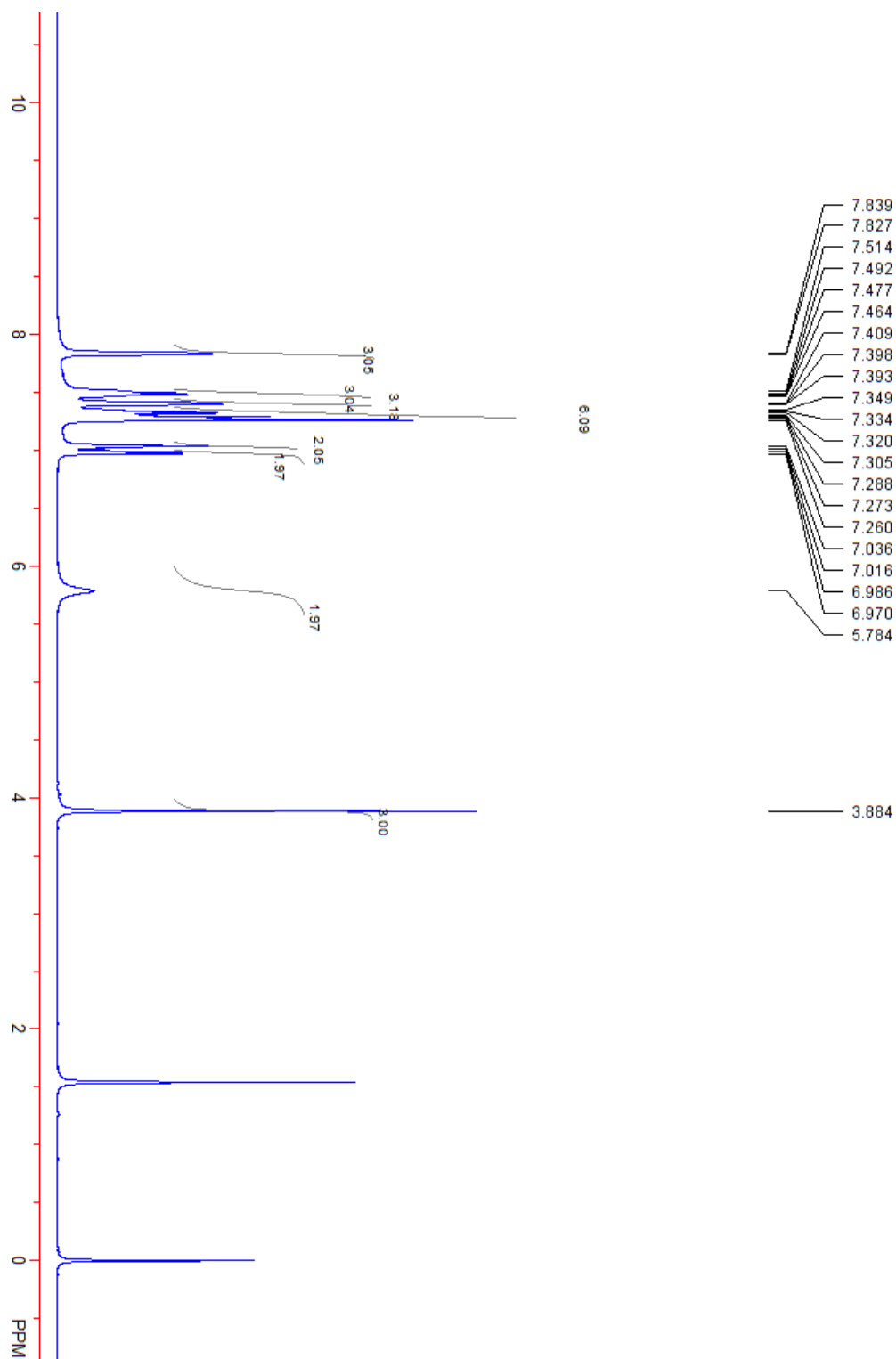


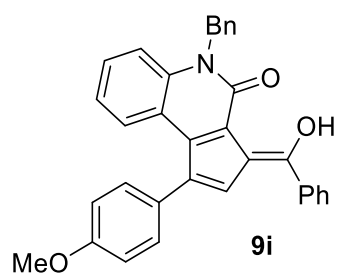
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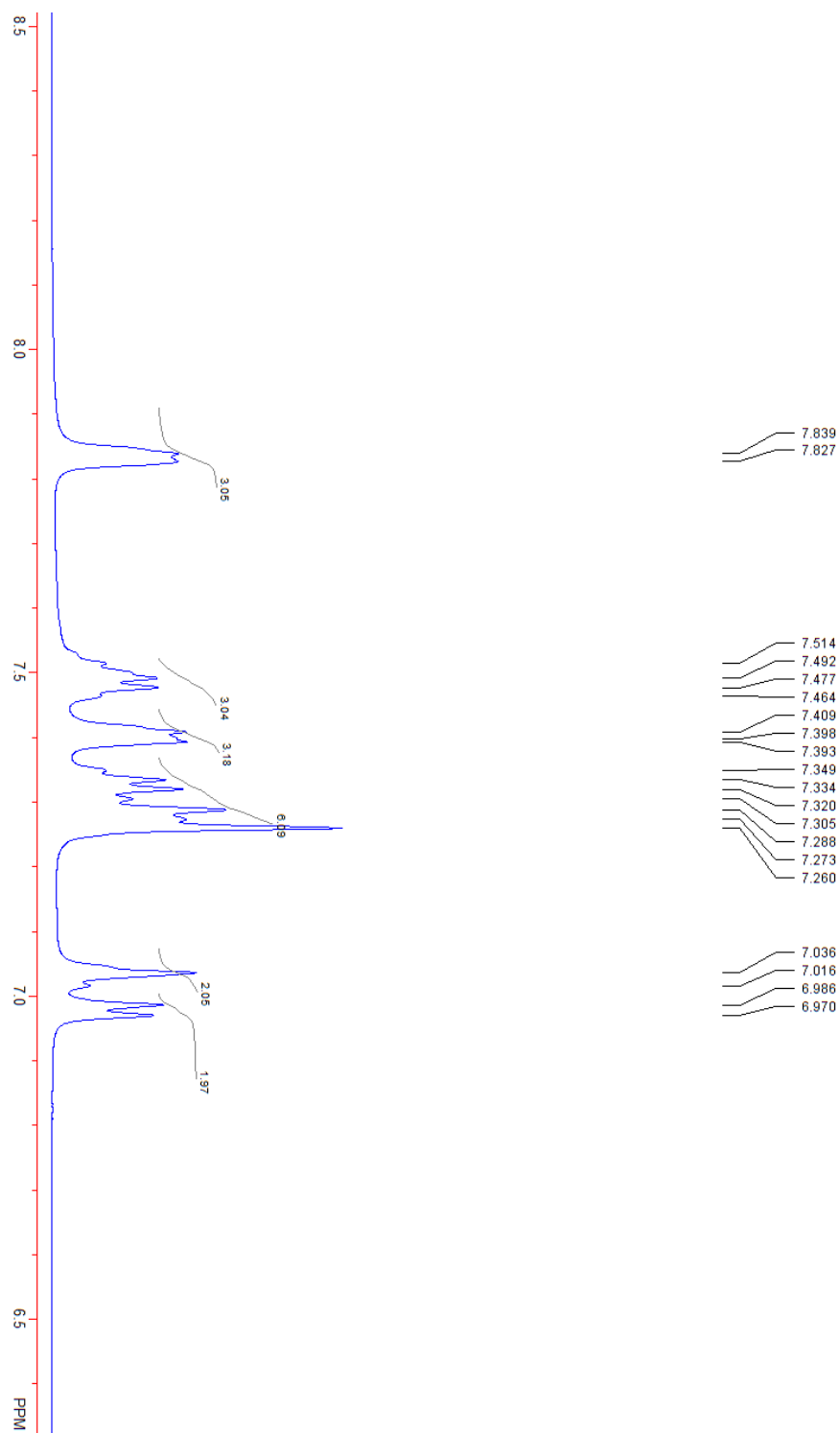


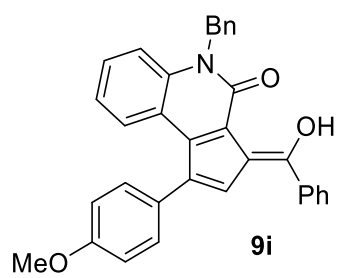
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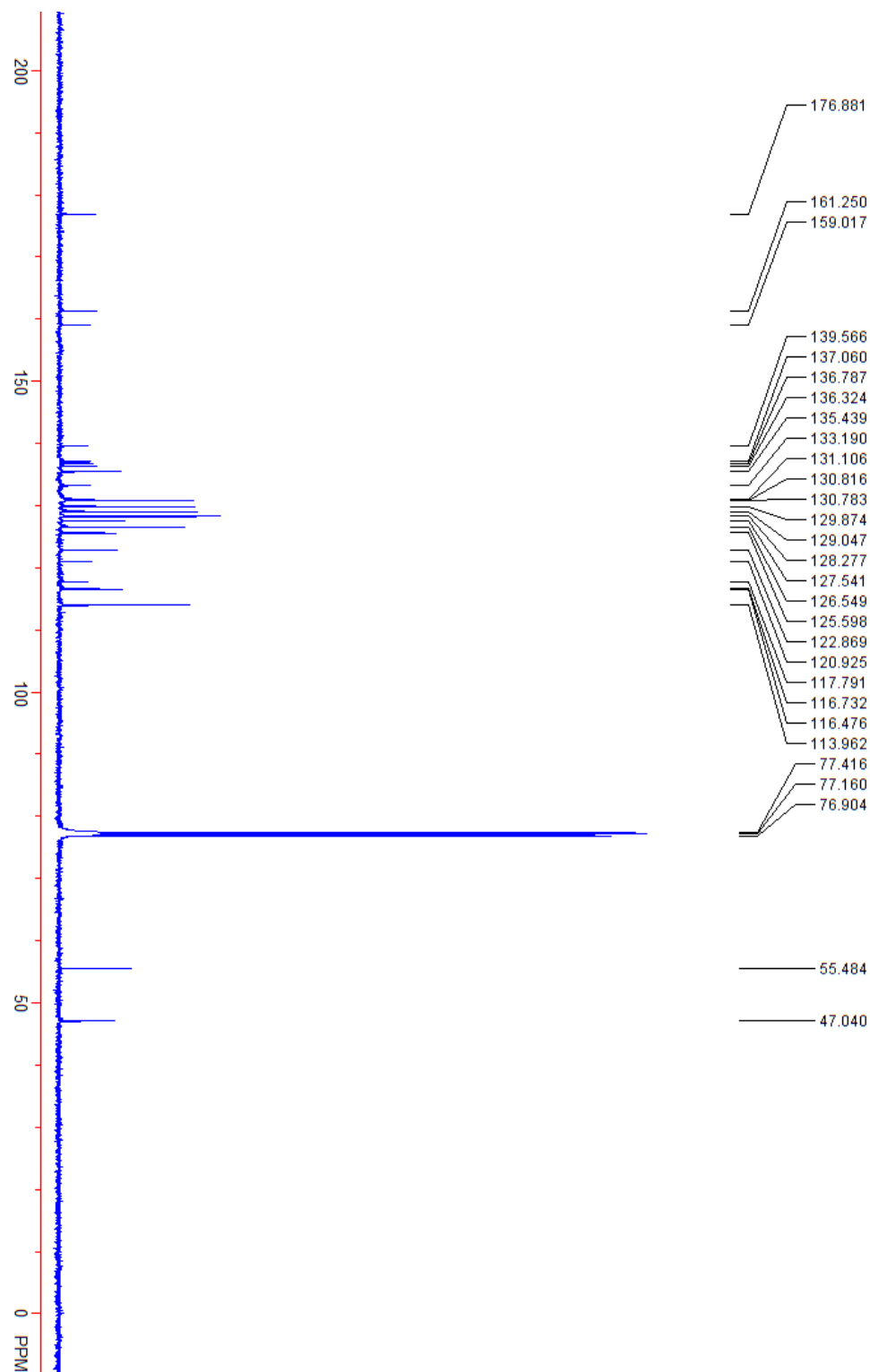


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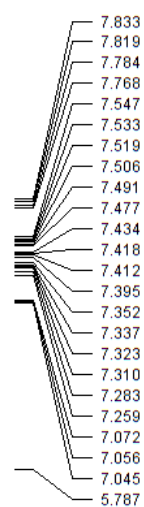
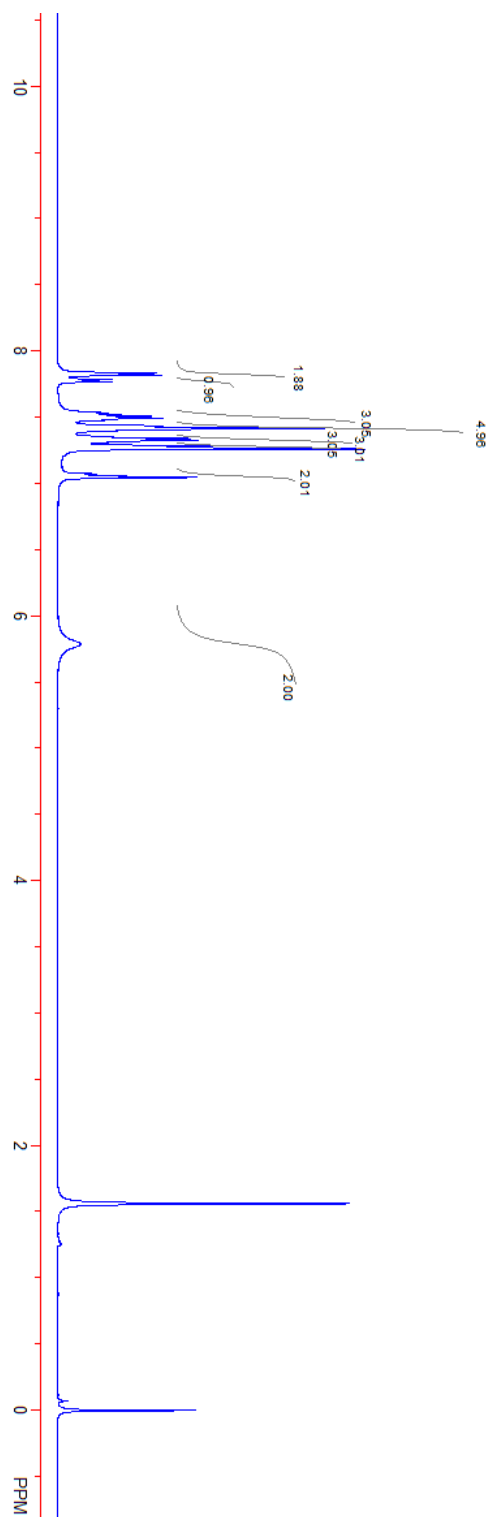
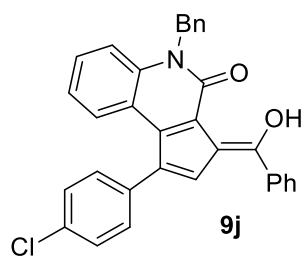




$^{13}\text{C}\{^1\text{H}\}$ NMR:



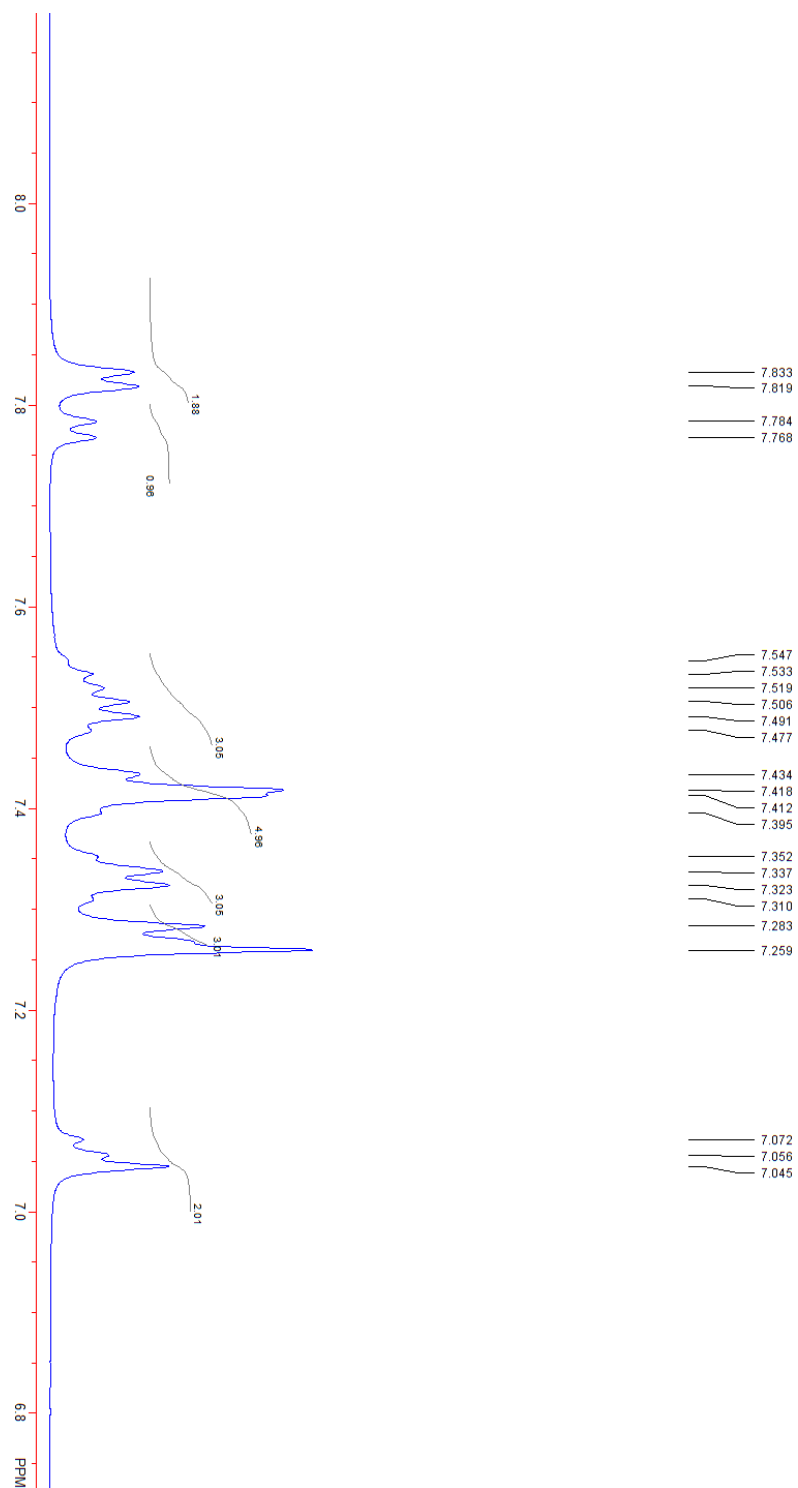
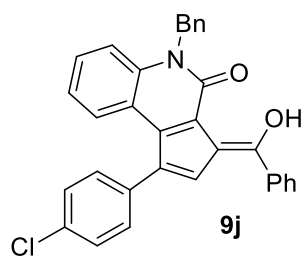
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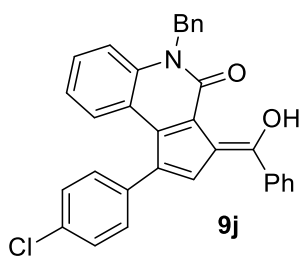


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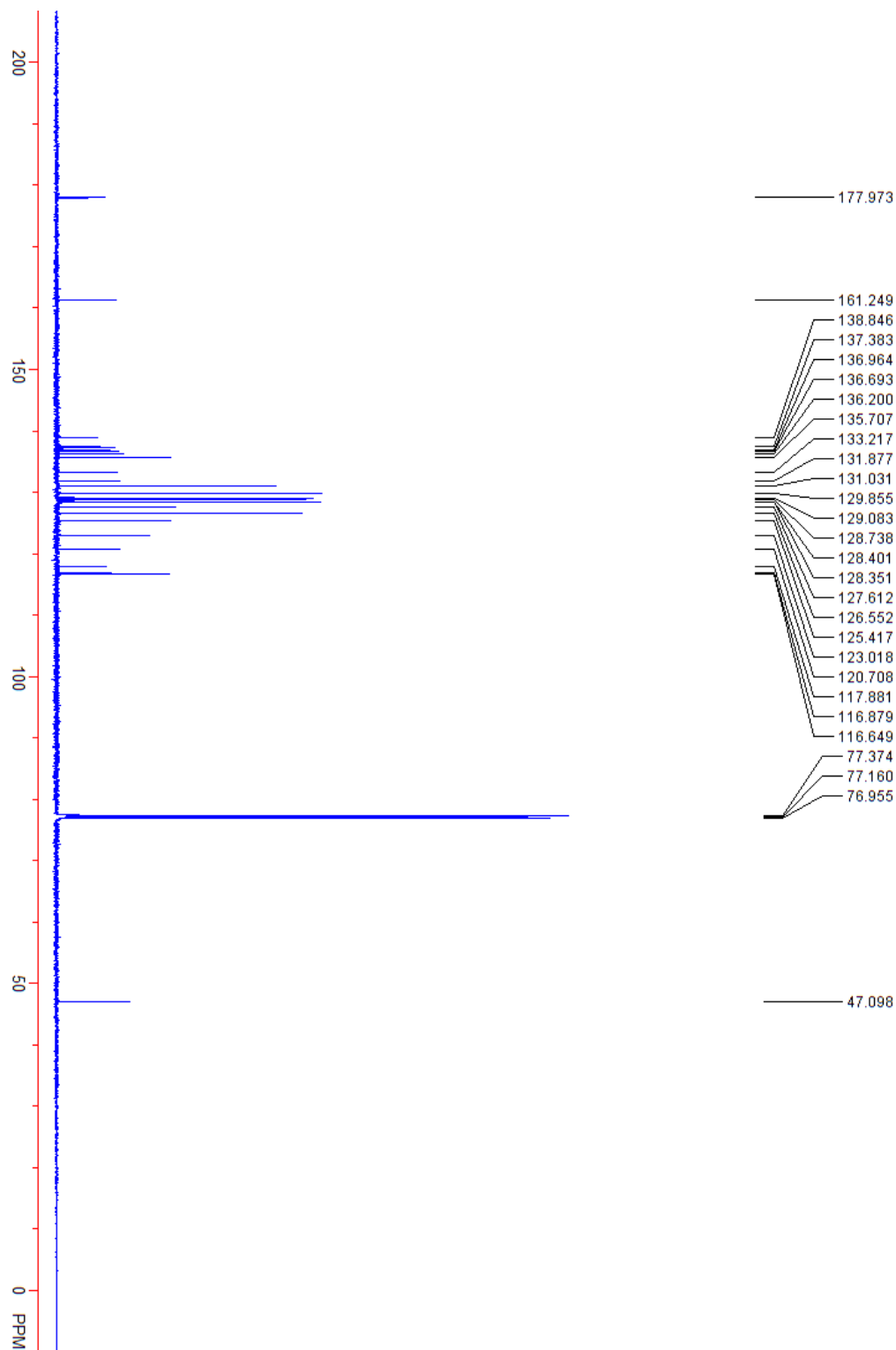
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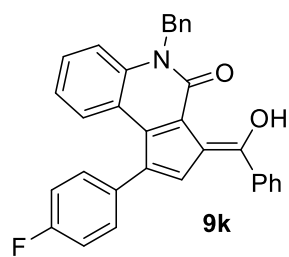
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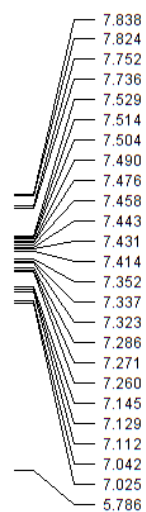
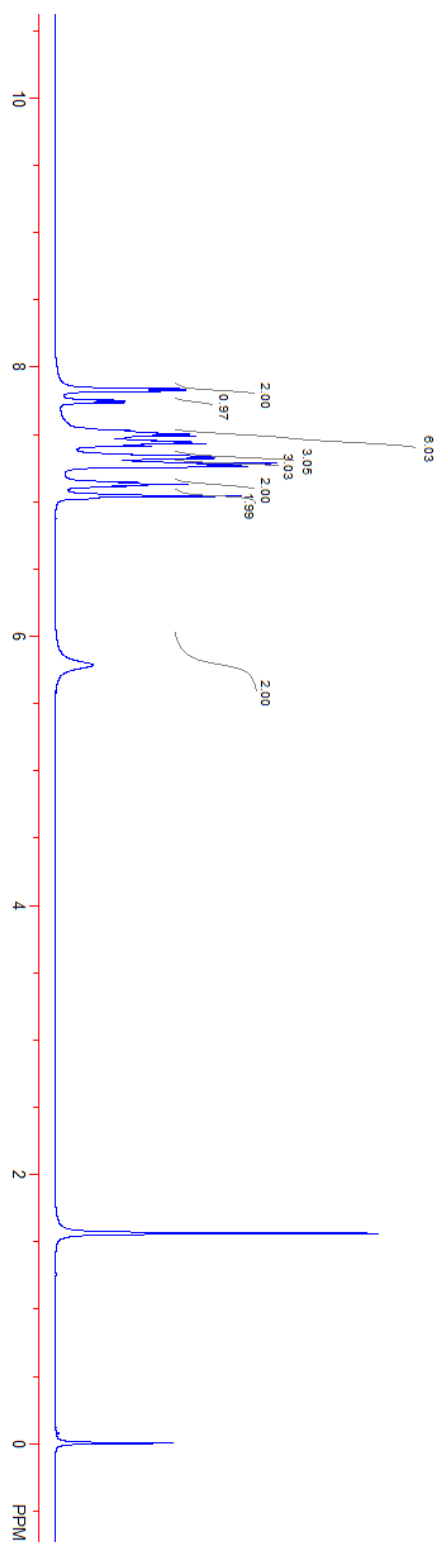


$^{13}\text{C}\{^1\text{H}\}$ NMR:



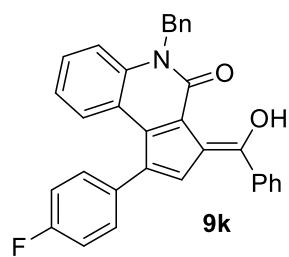


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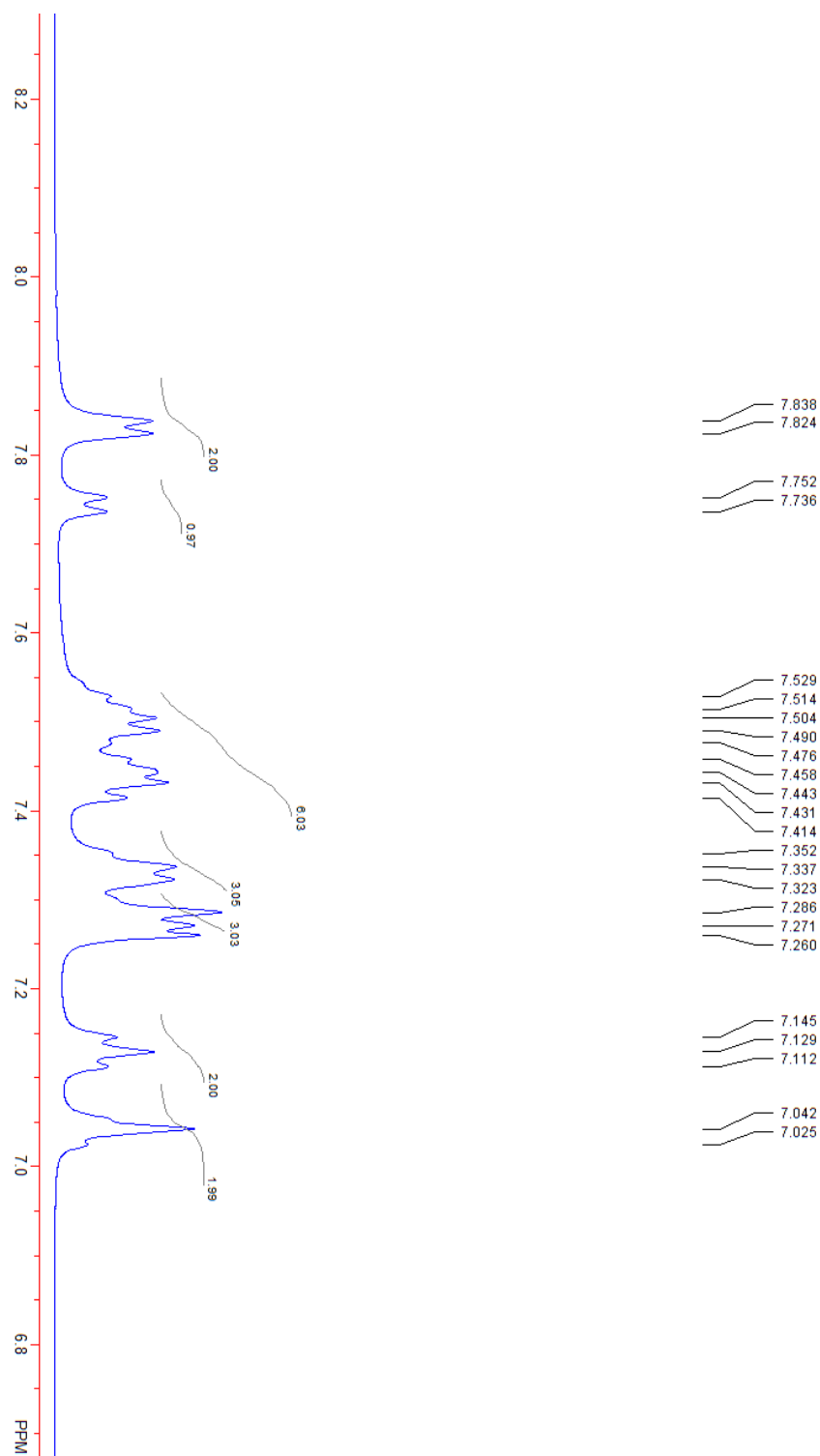


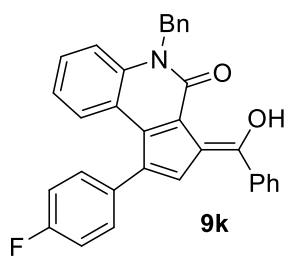
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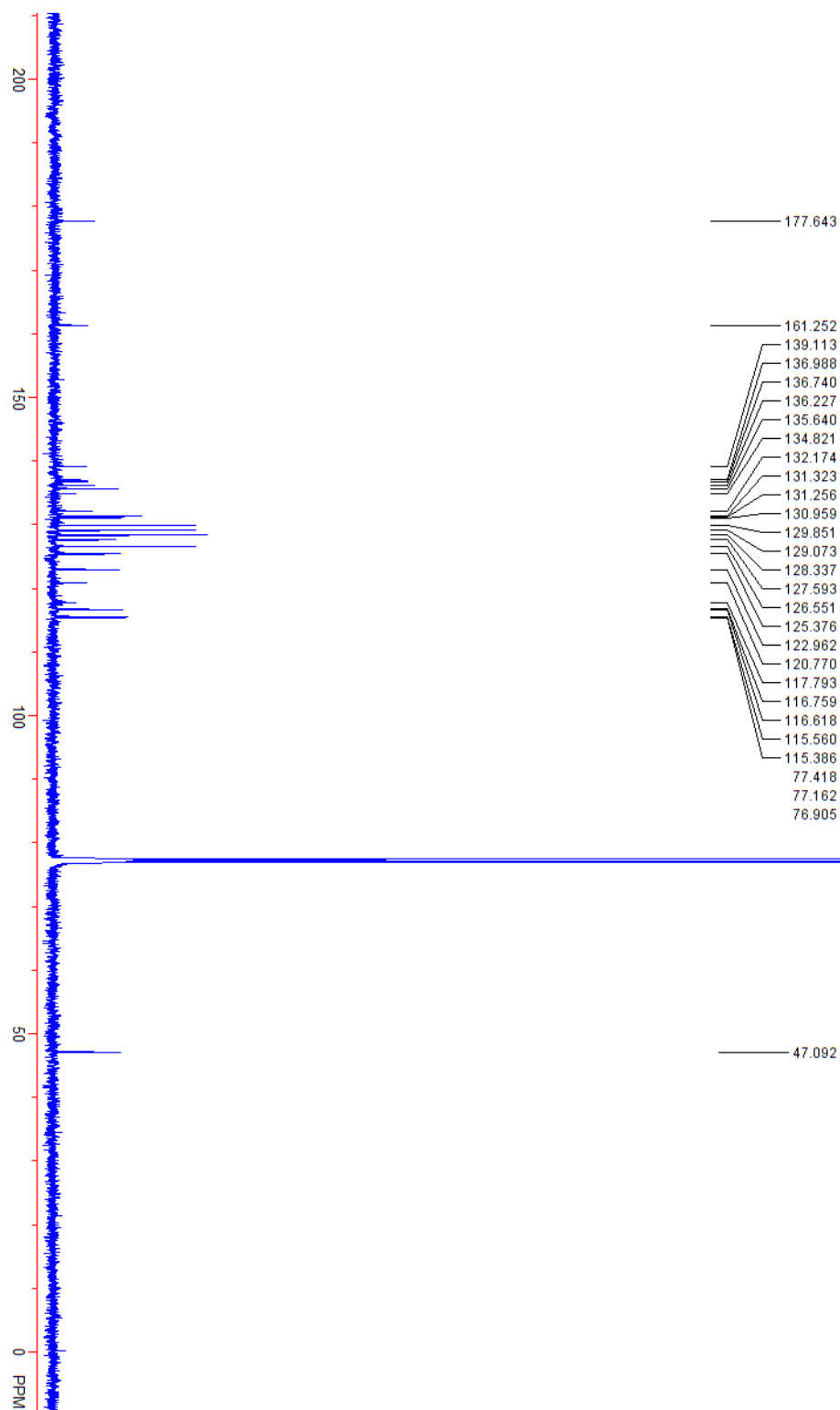


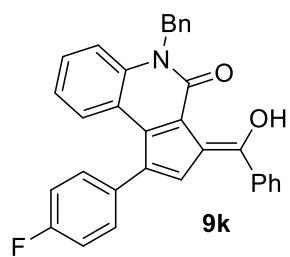
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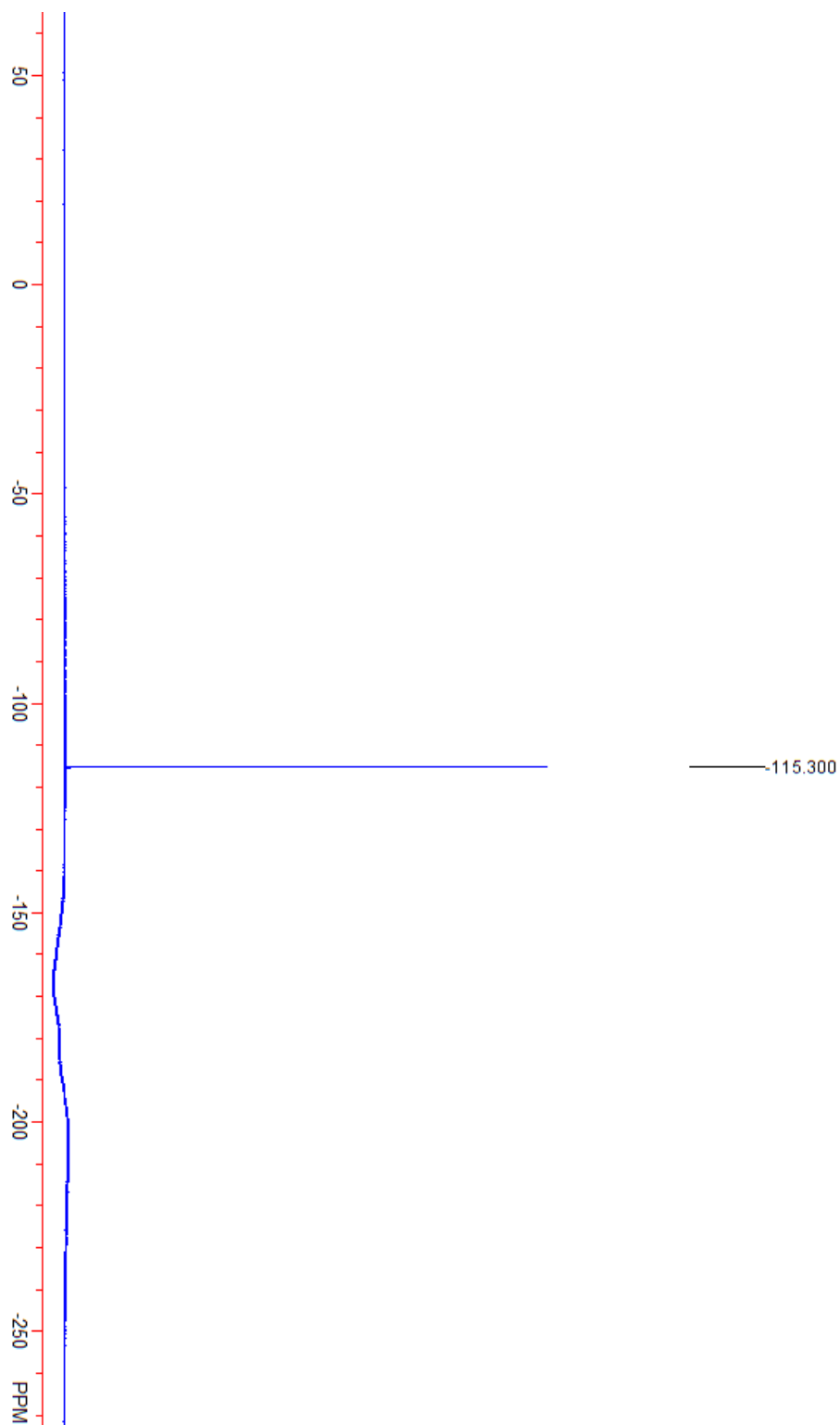


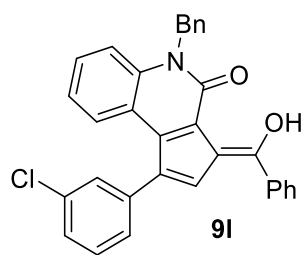
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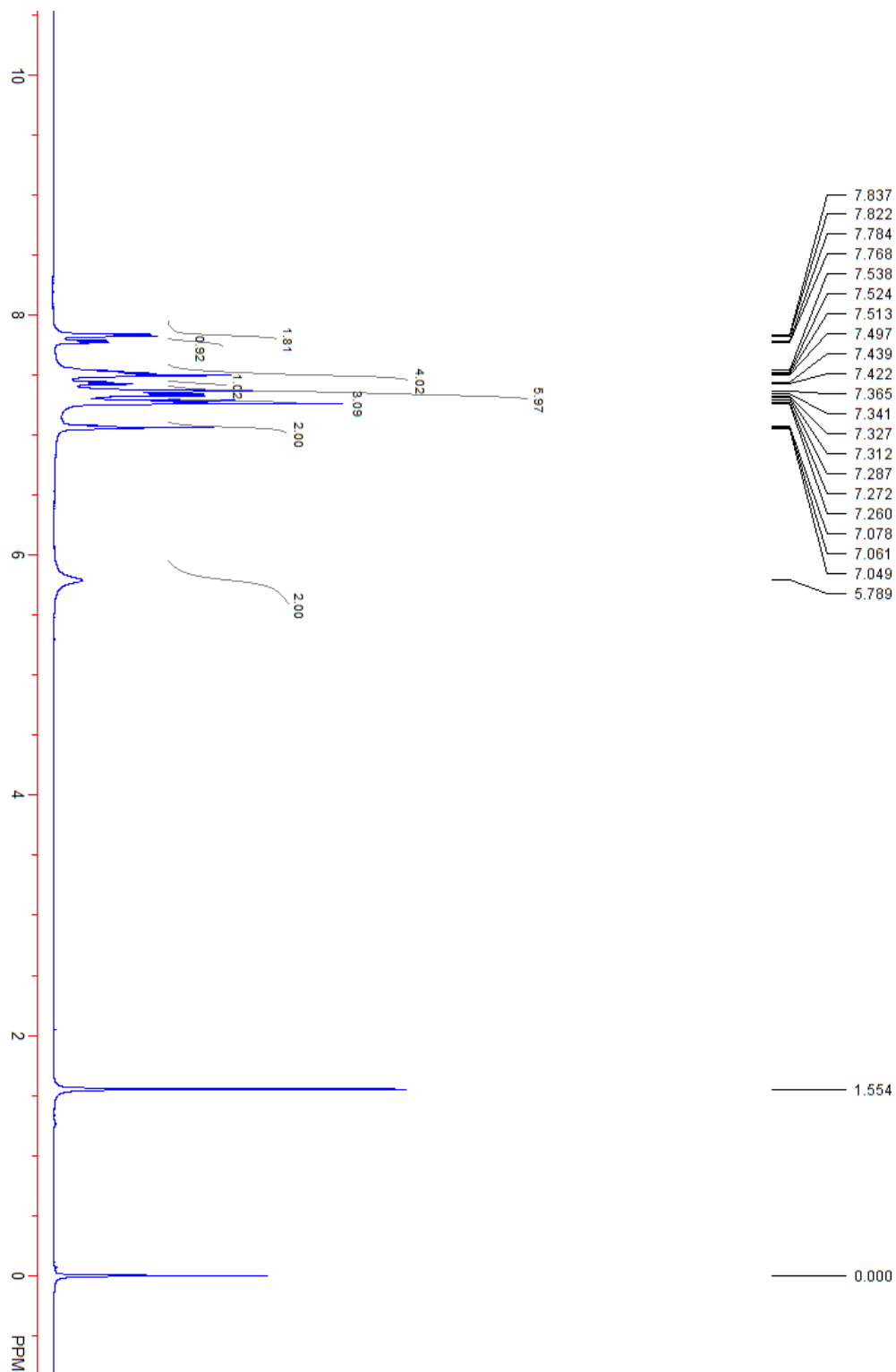


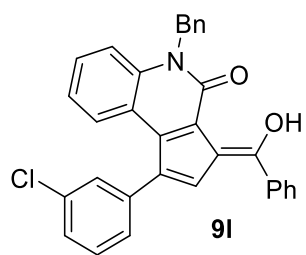
^{19}F NMR:



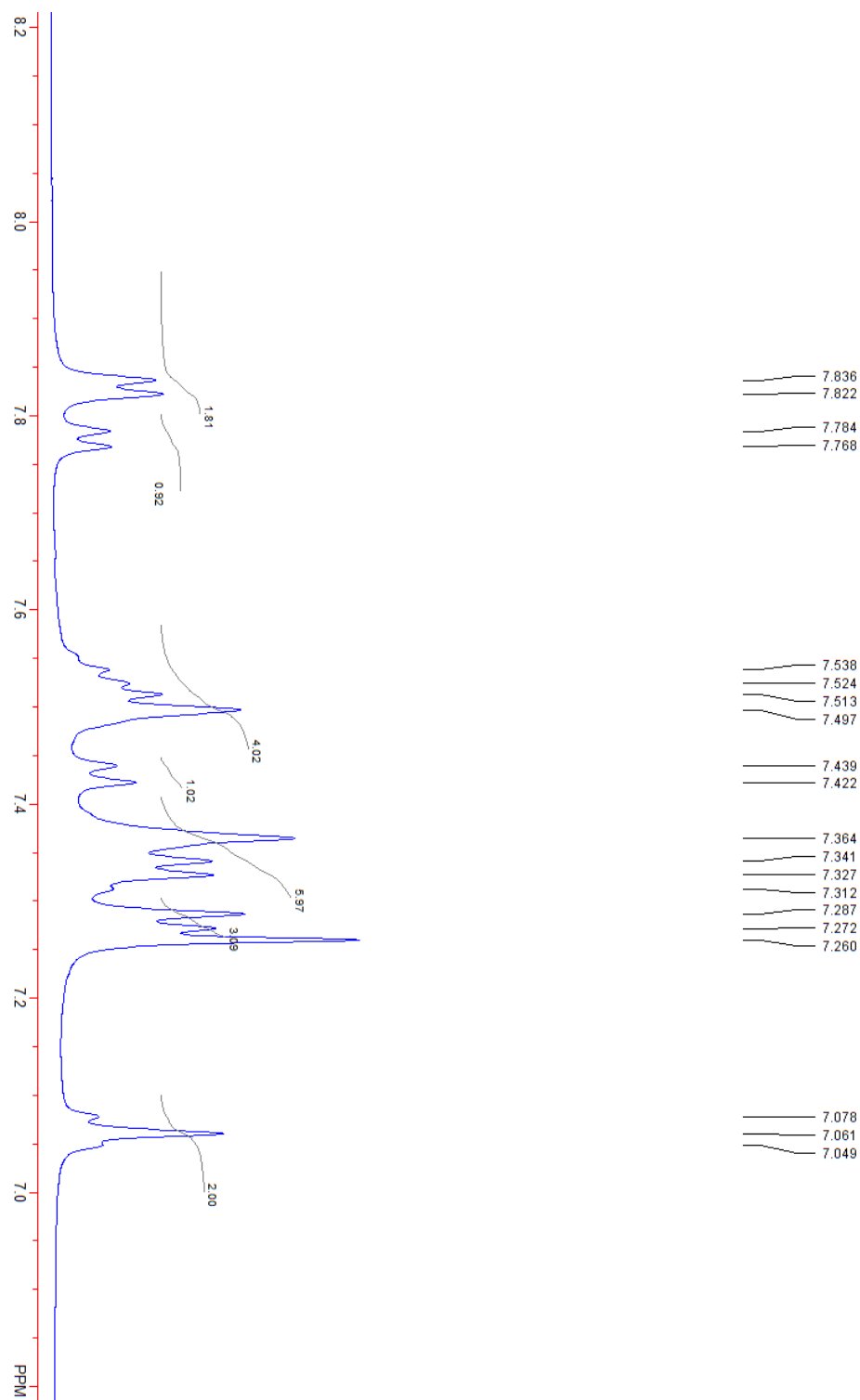


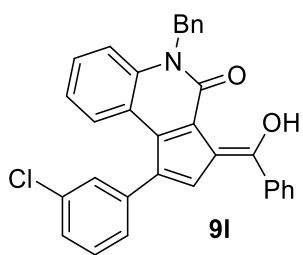
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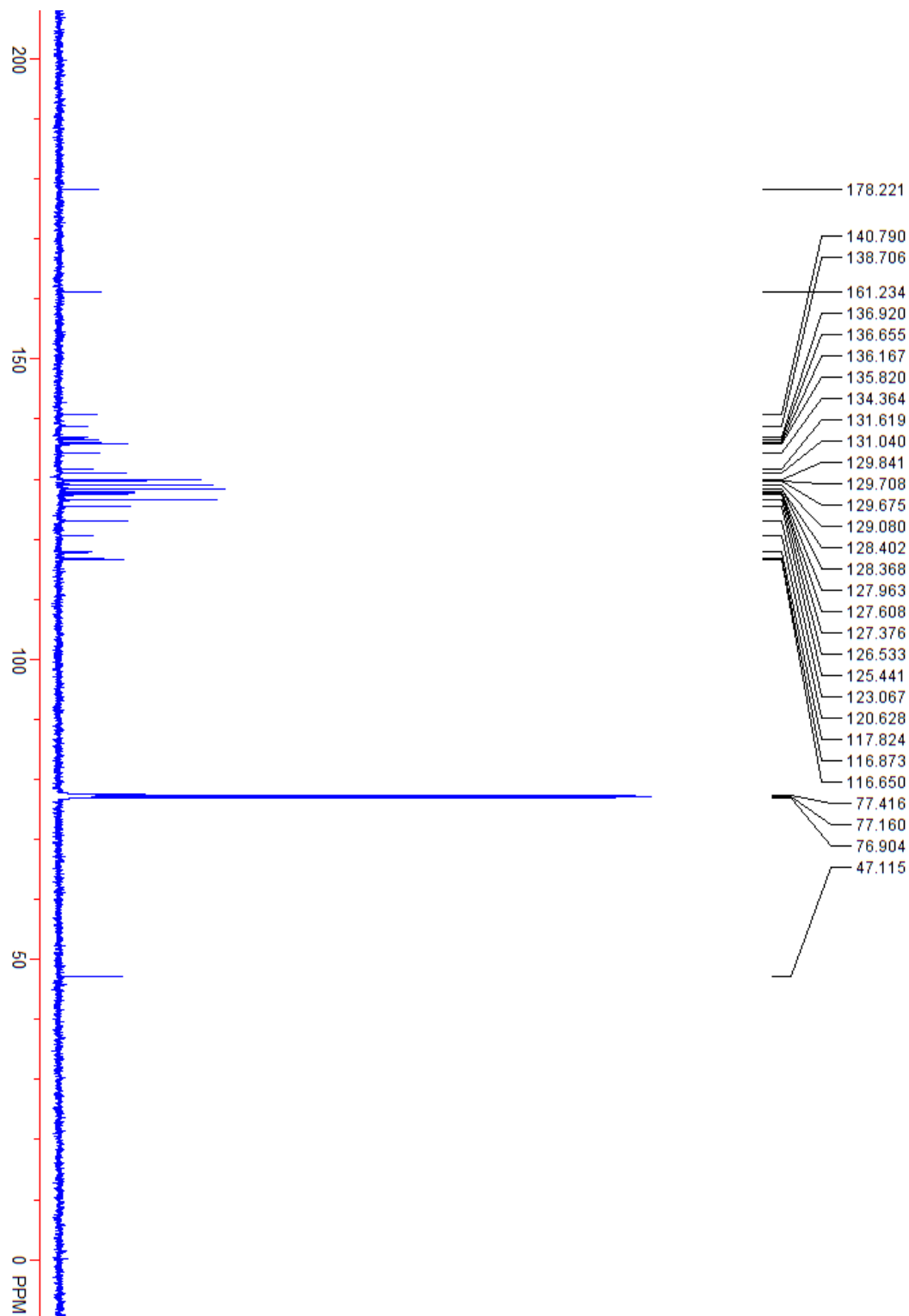


¹H NMR:

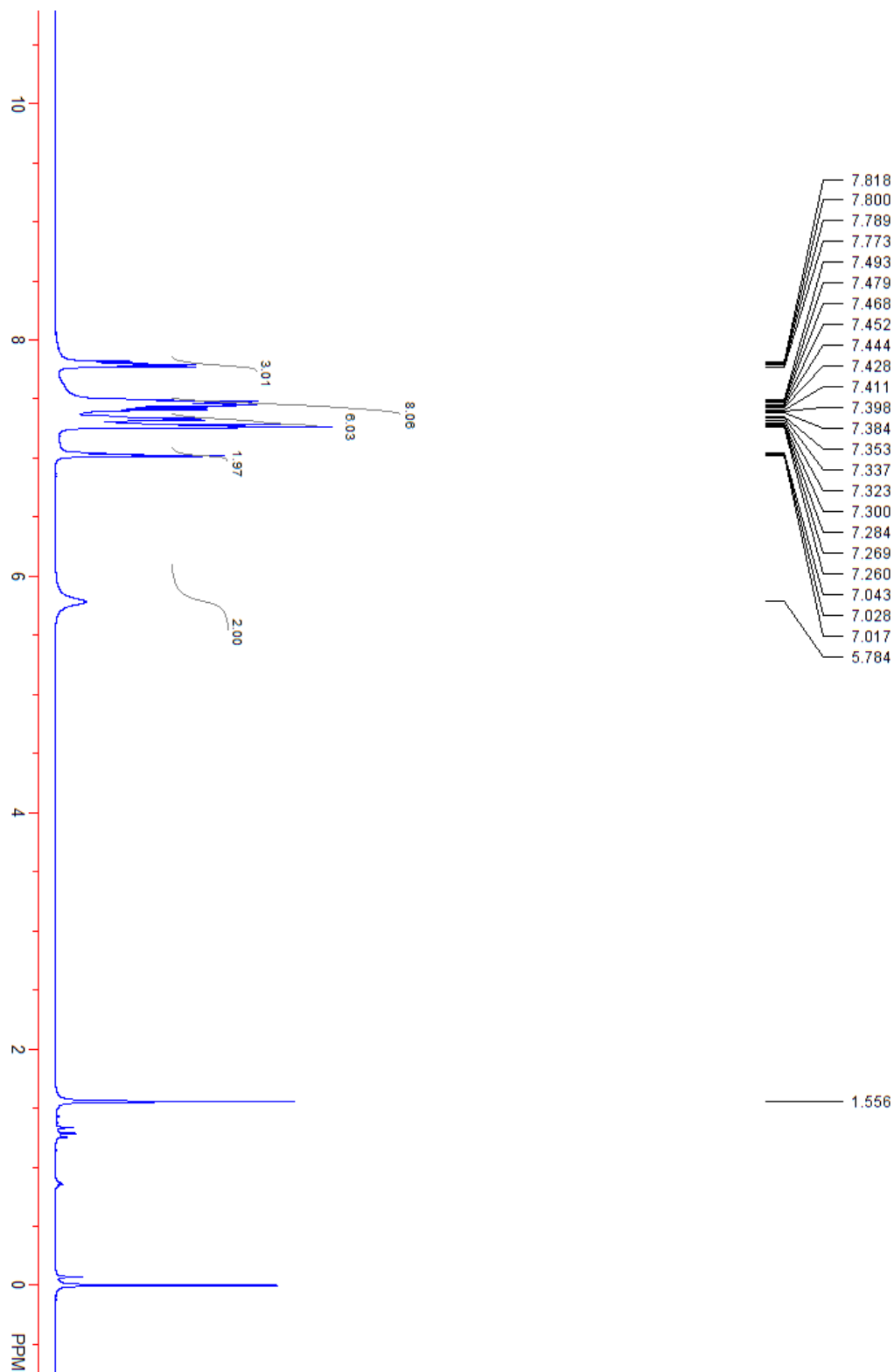
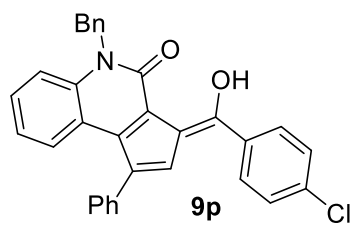




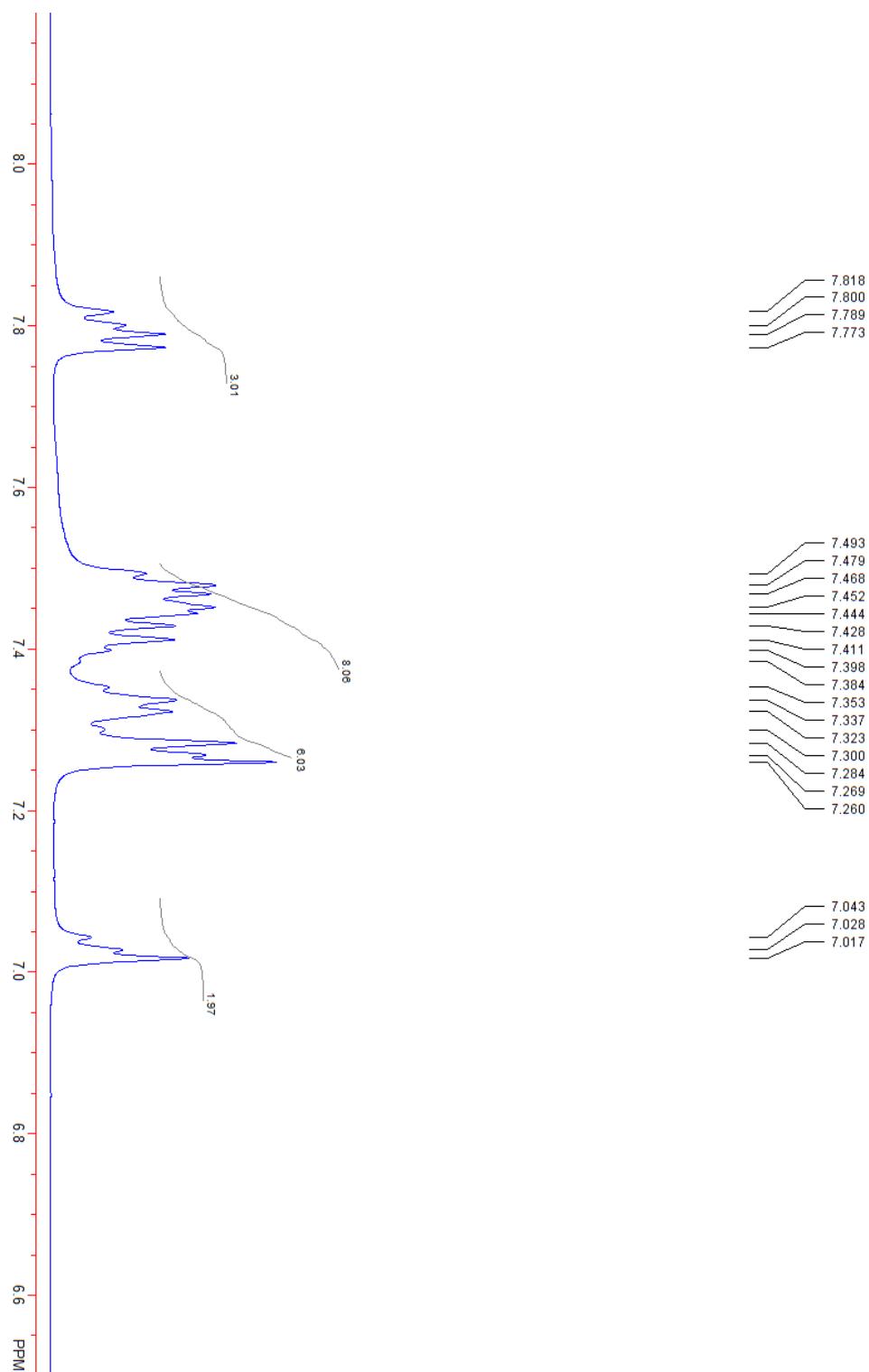
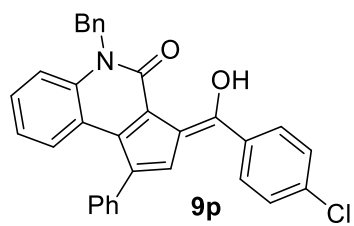
$^{13}\text{C}\{^1\text{H}\}$ NMR:

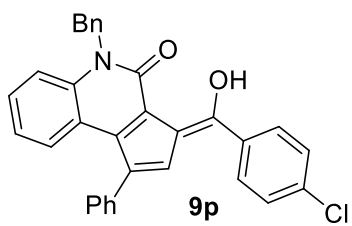


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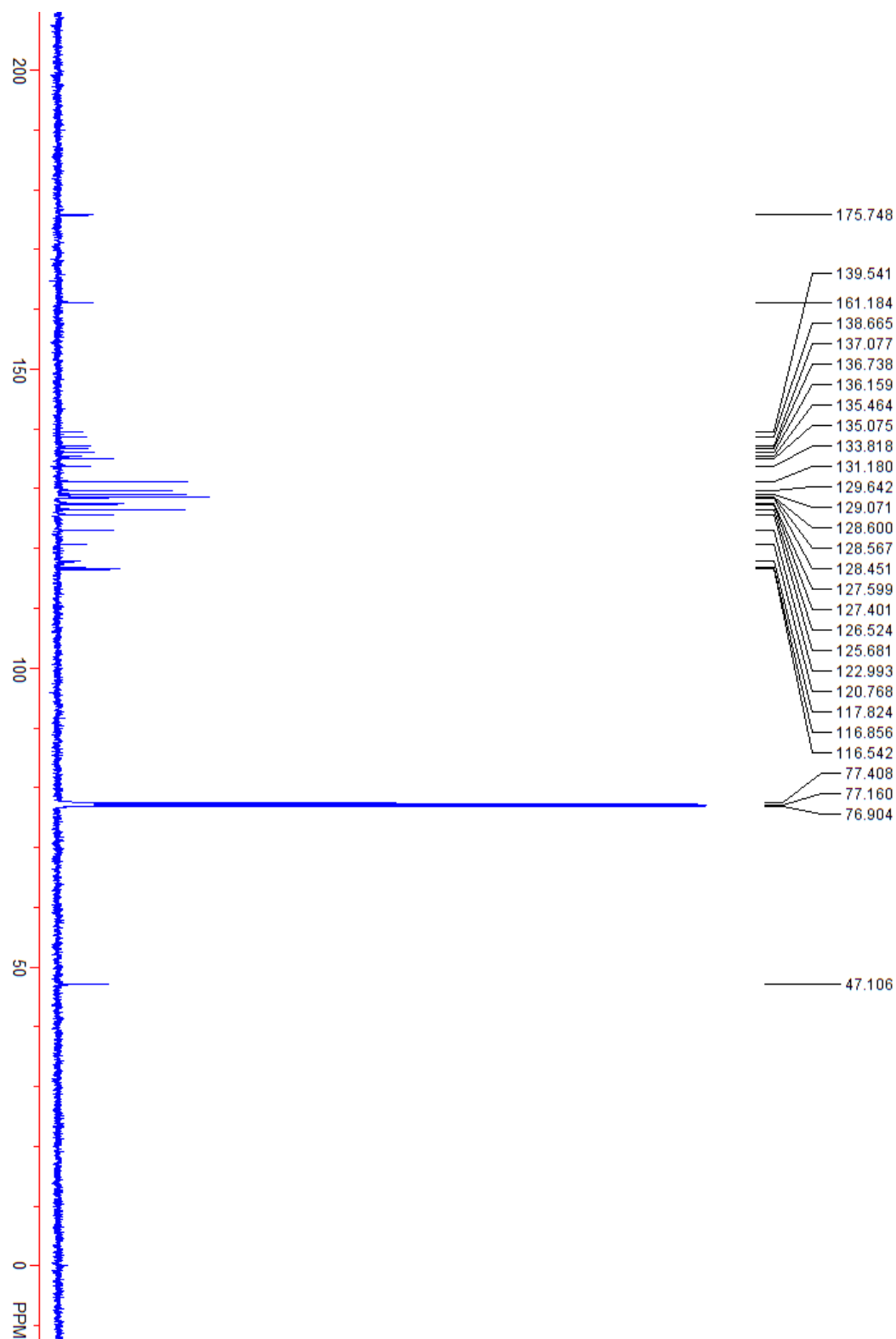


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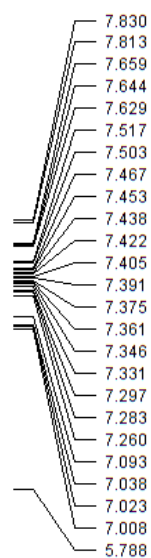
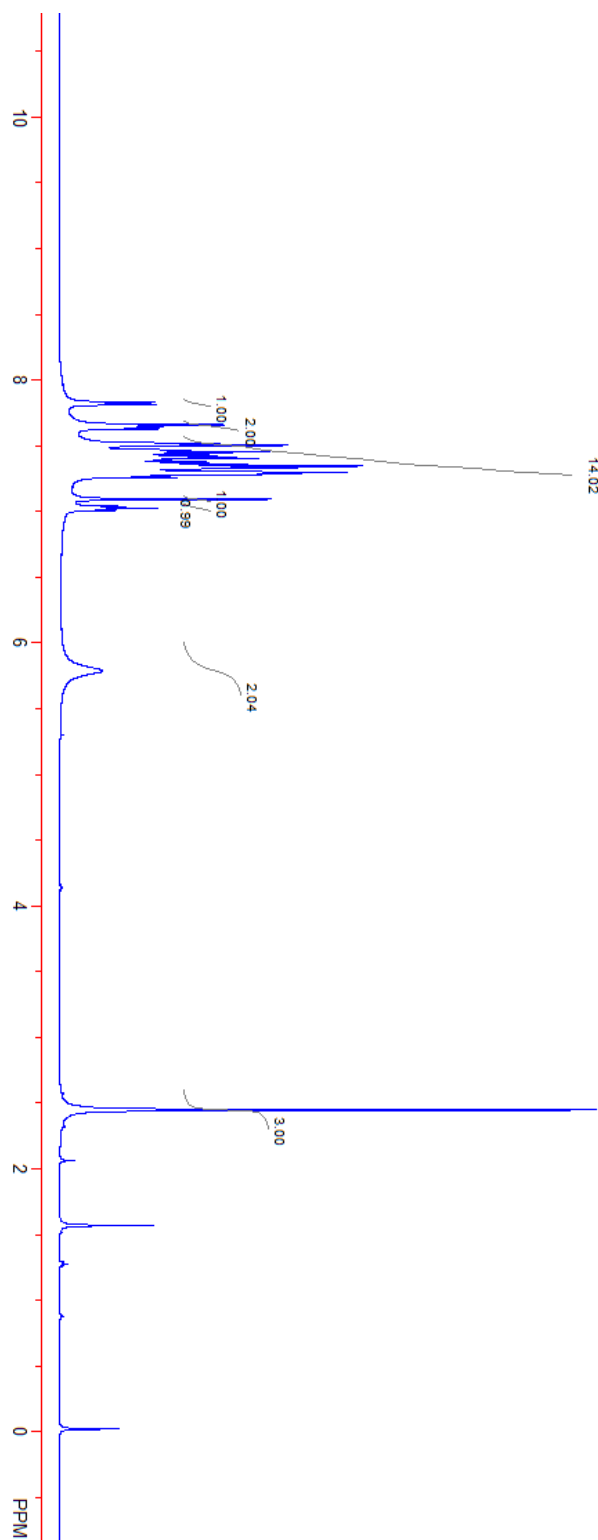
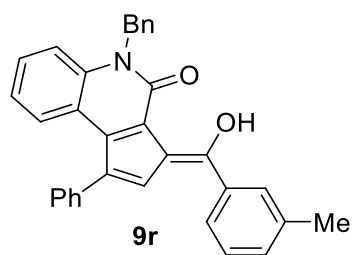




$^{13}\text{C}\{^1\text{H}\}$ NMR:

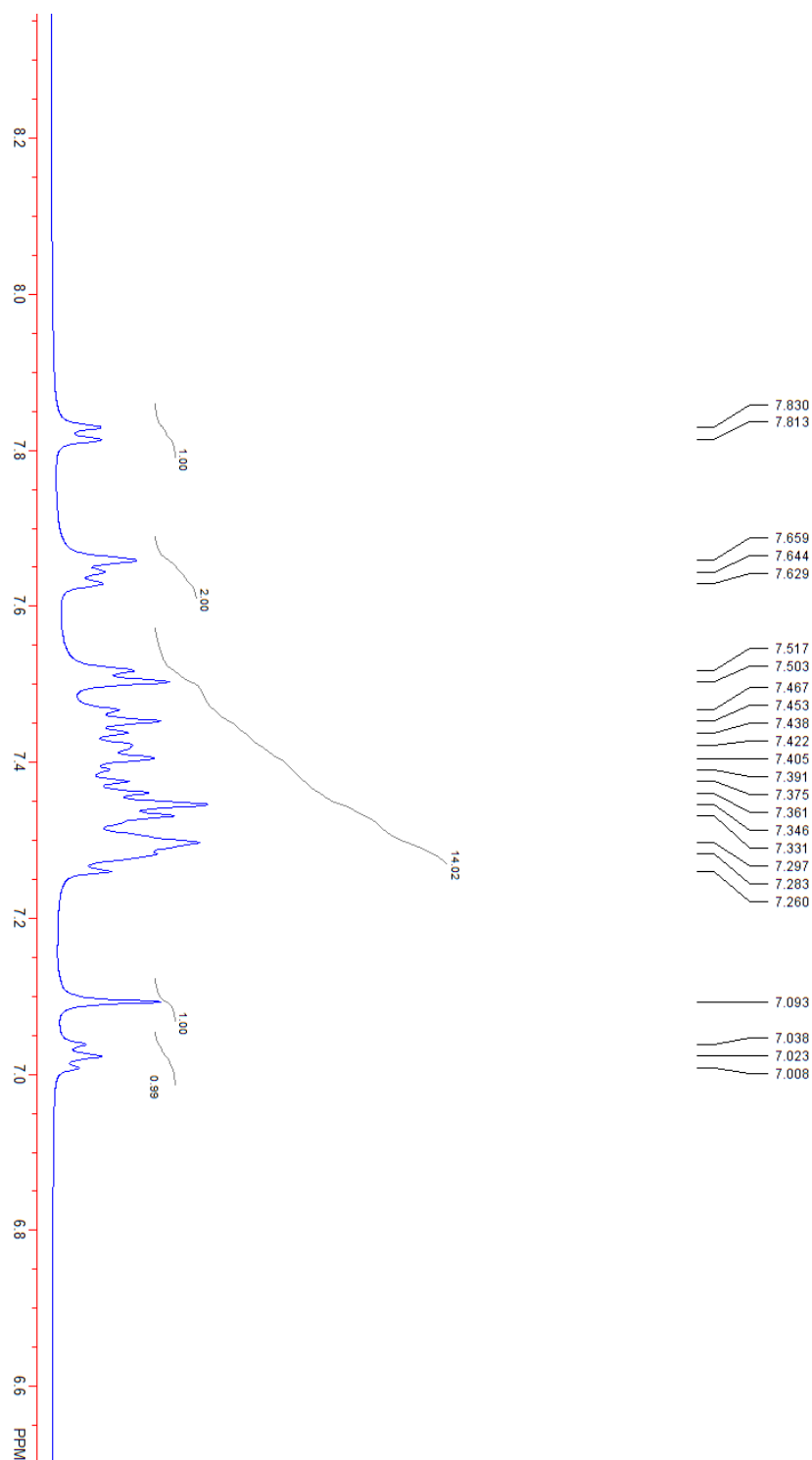
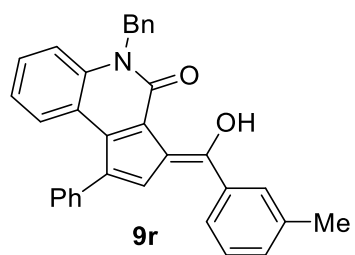


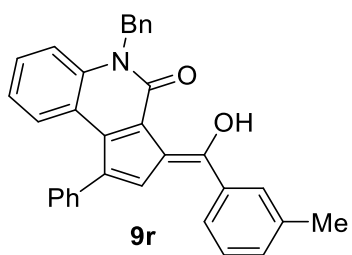
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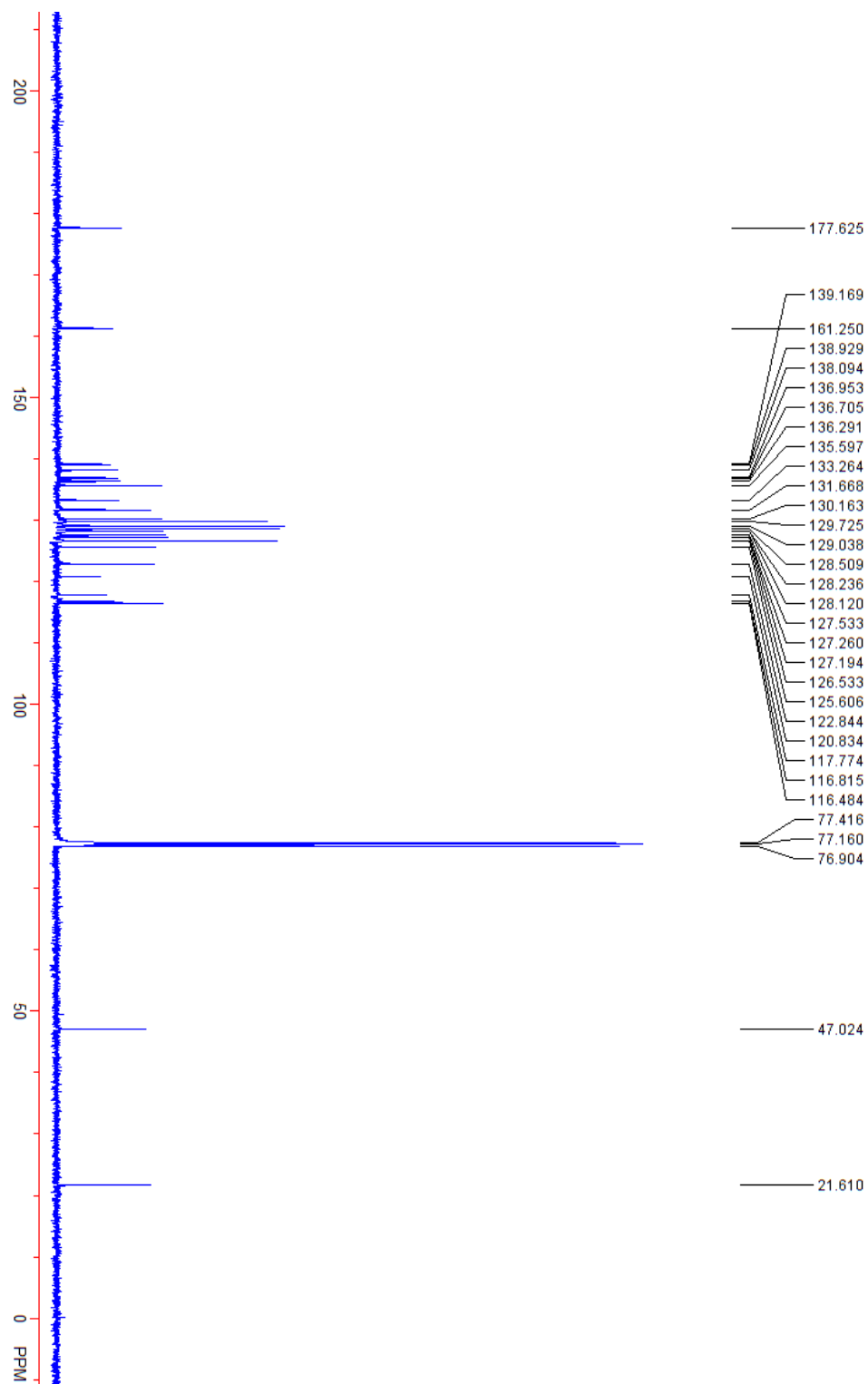
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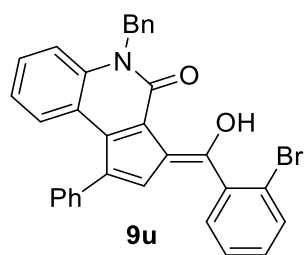
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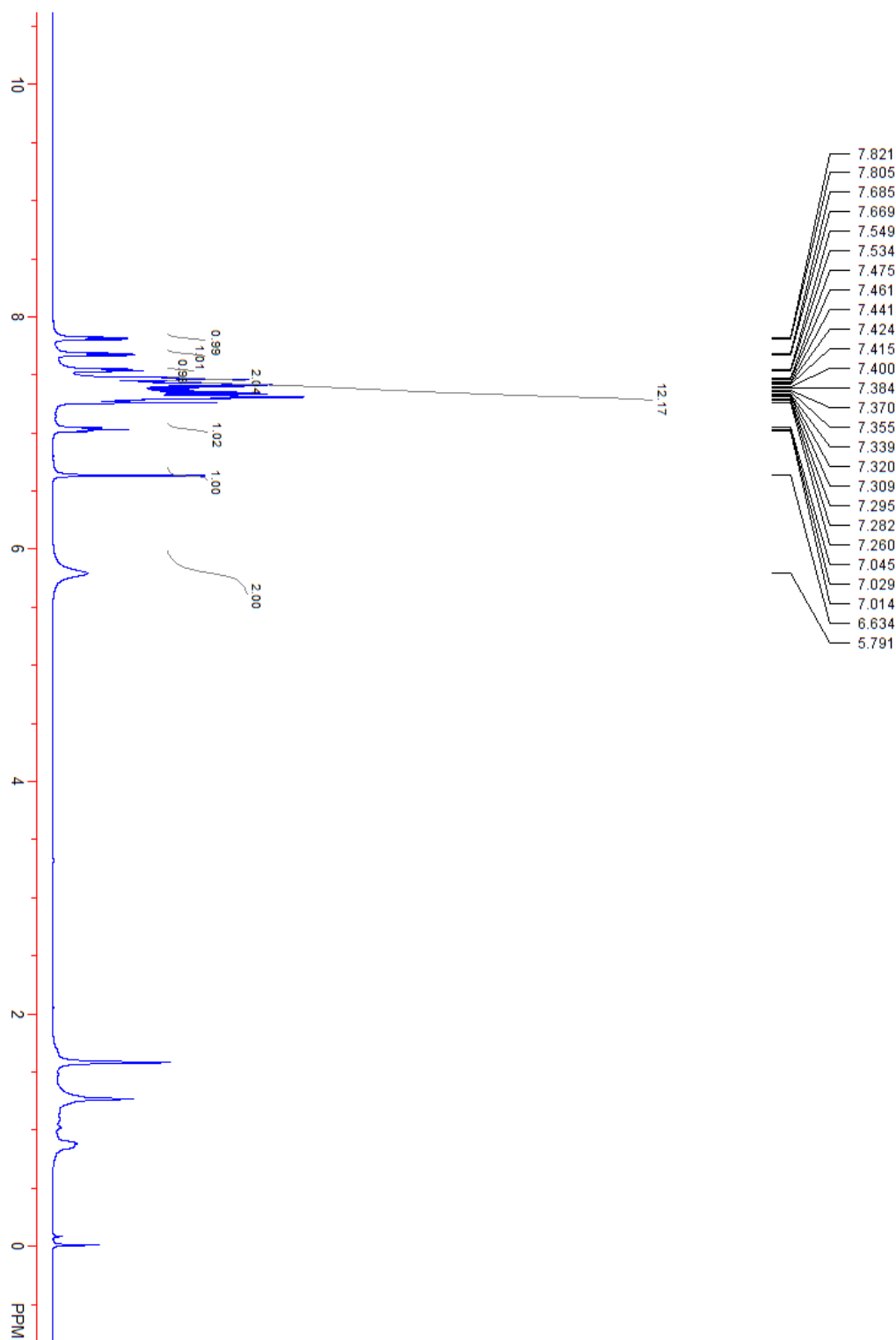


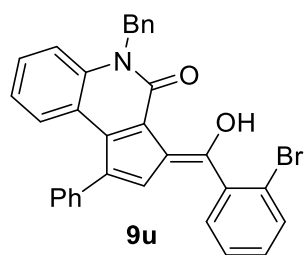
$^{13}\text{C}\{^1\text{H}\}$ NMR:



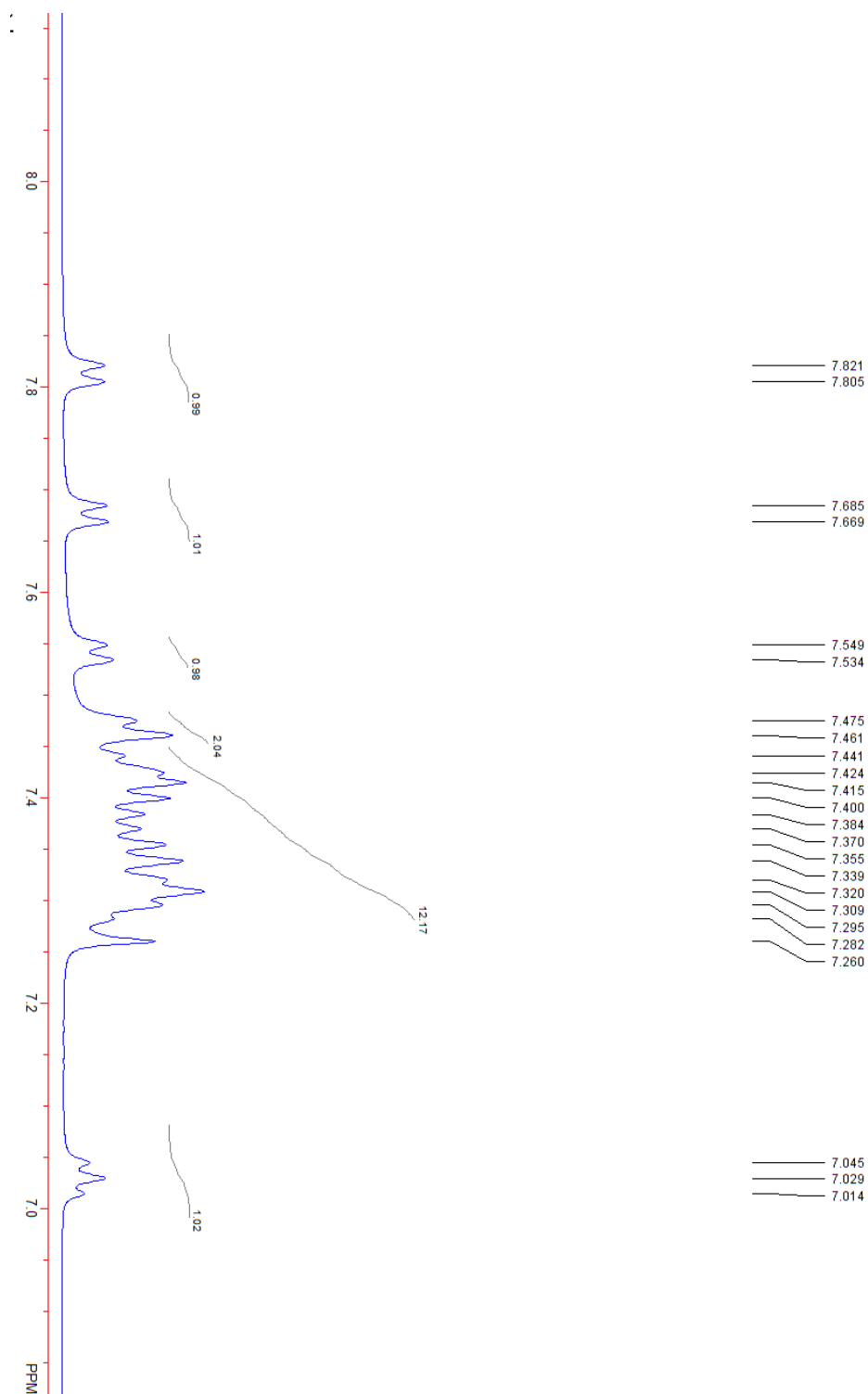


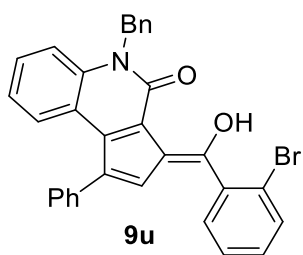
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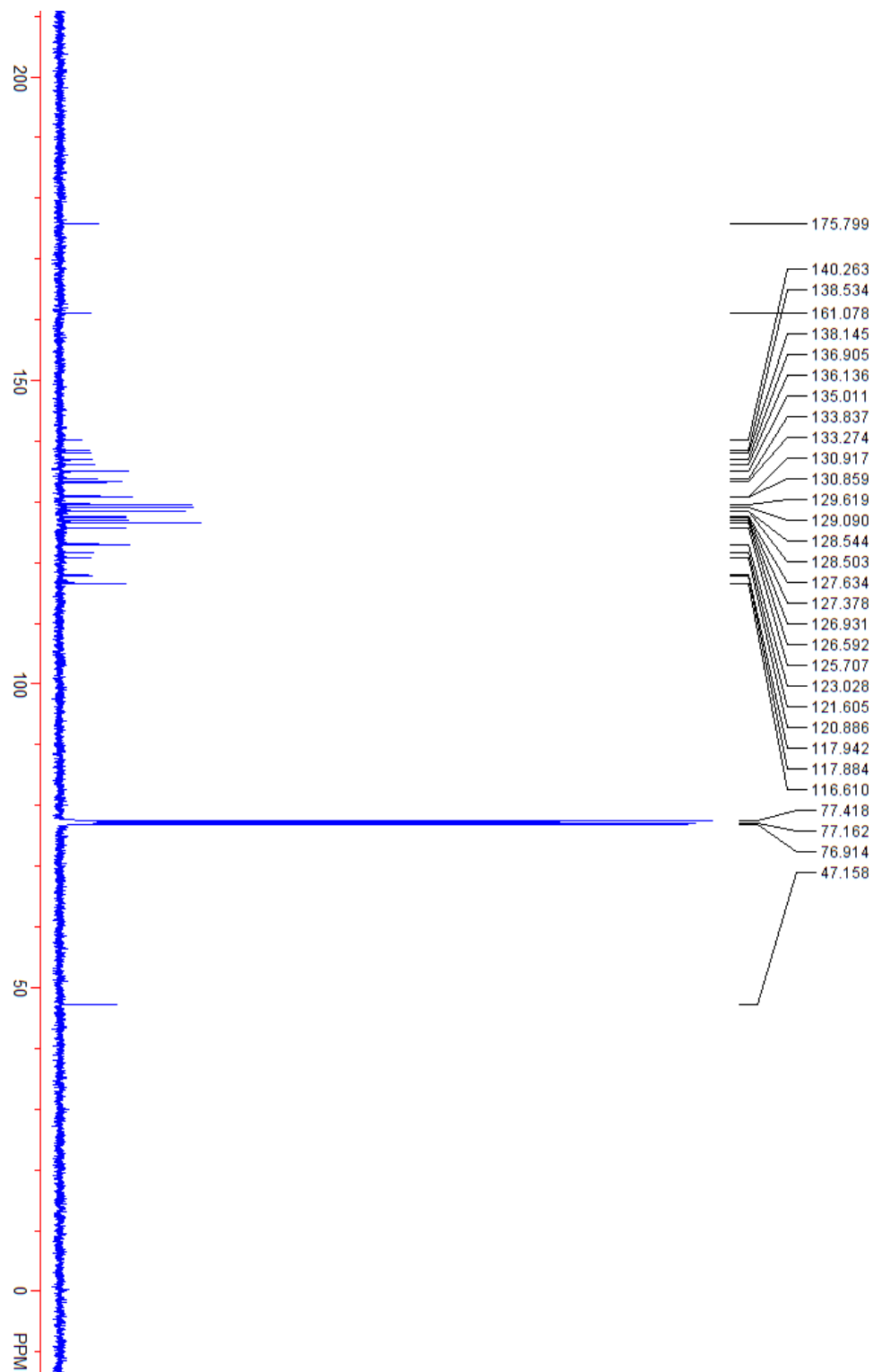


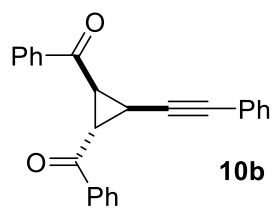
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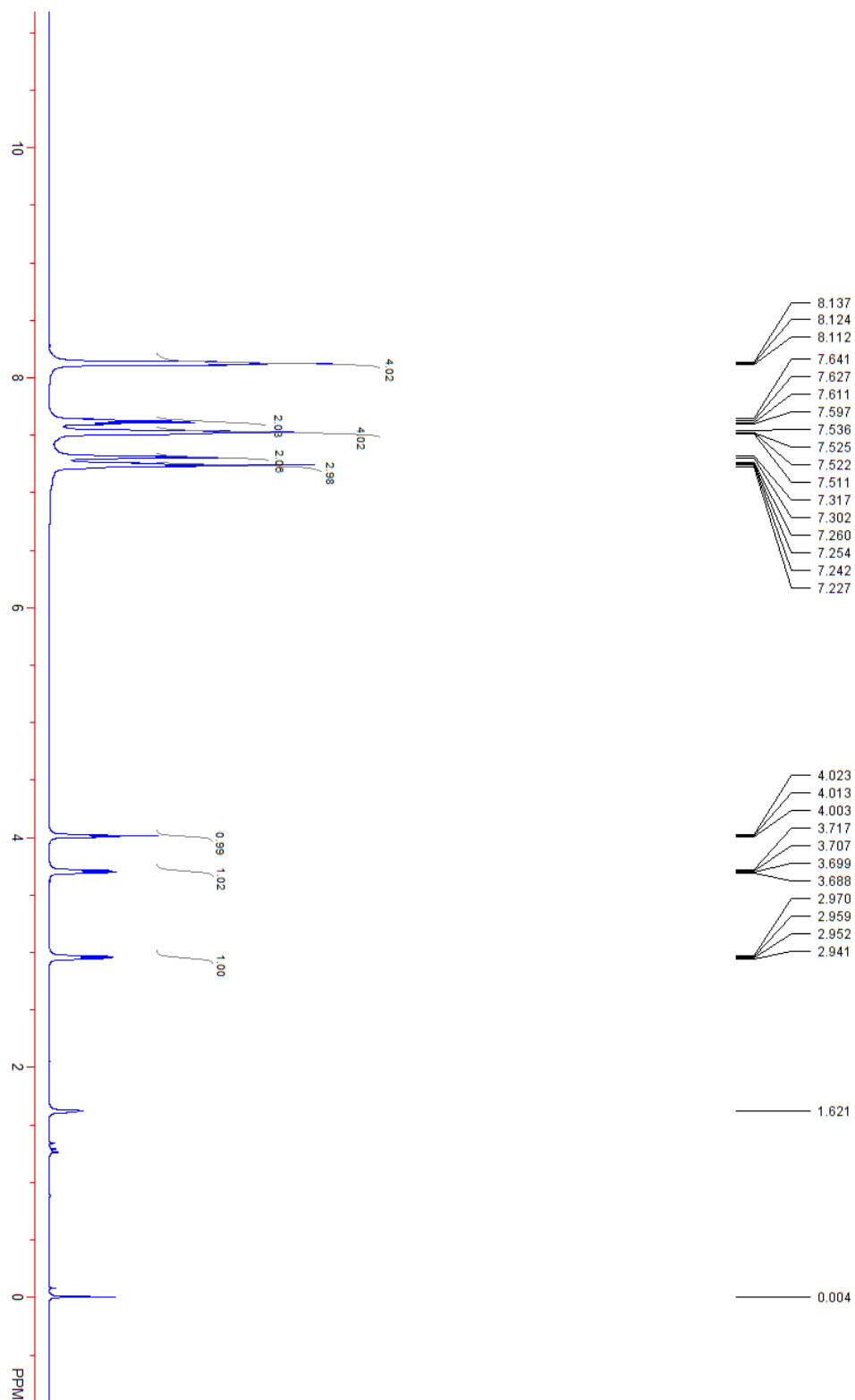


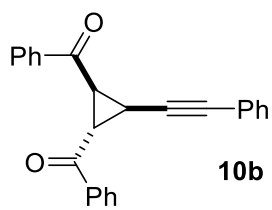
$^{13}\text{C}\{^1\text{H}\}$ NMR:



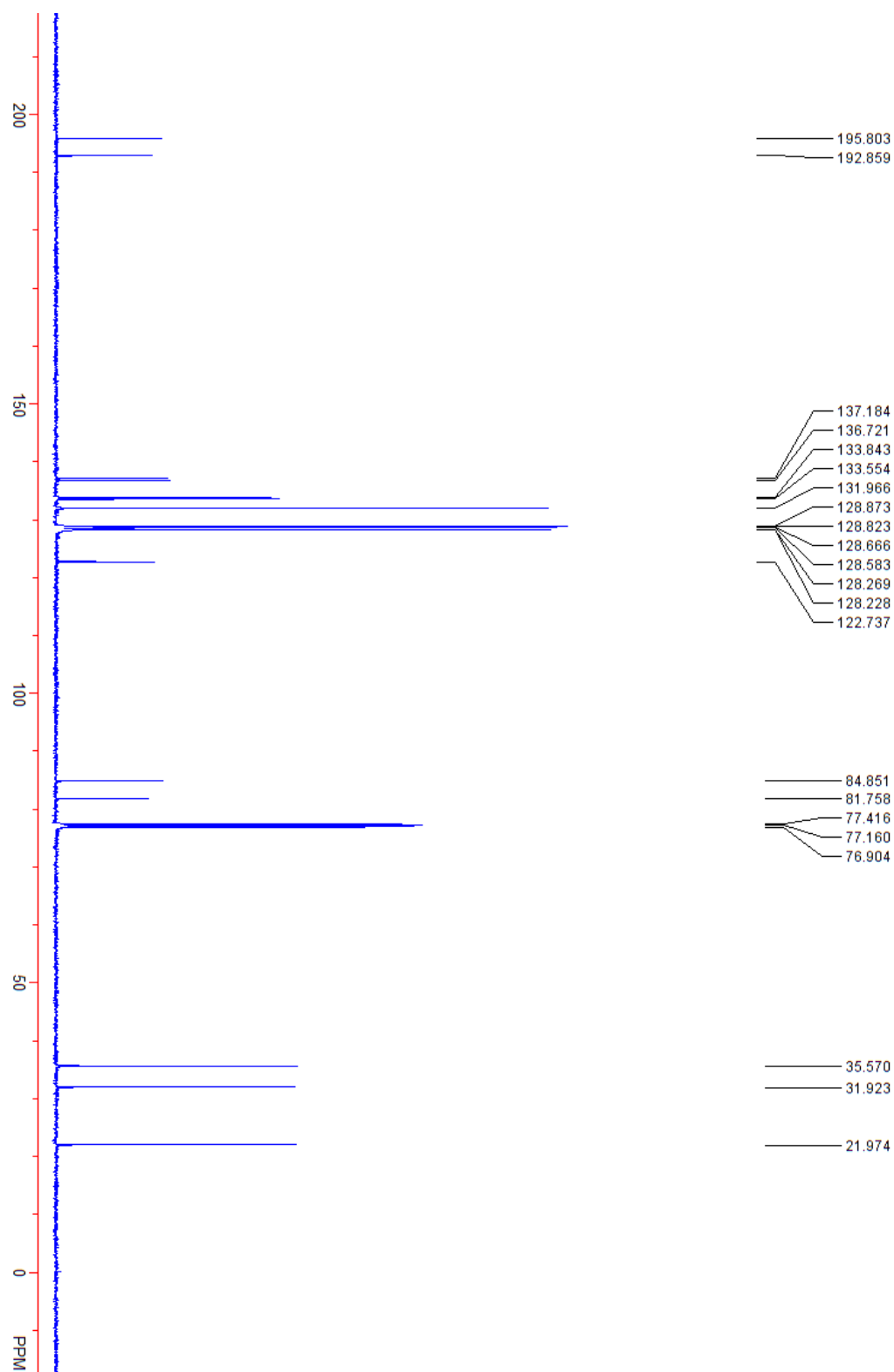


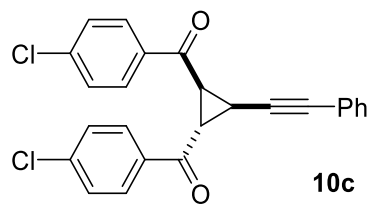
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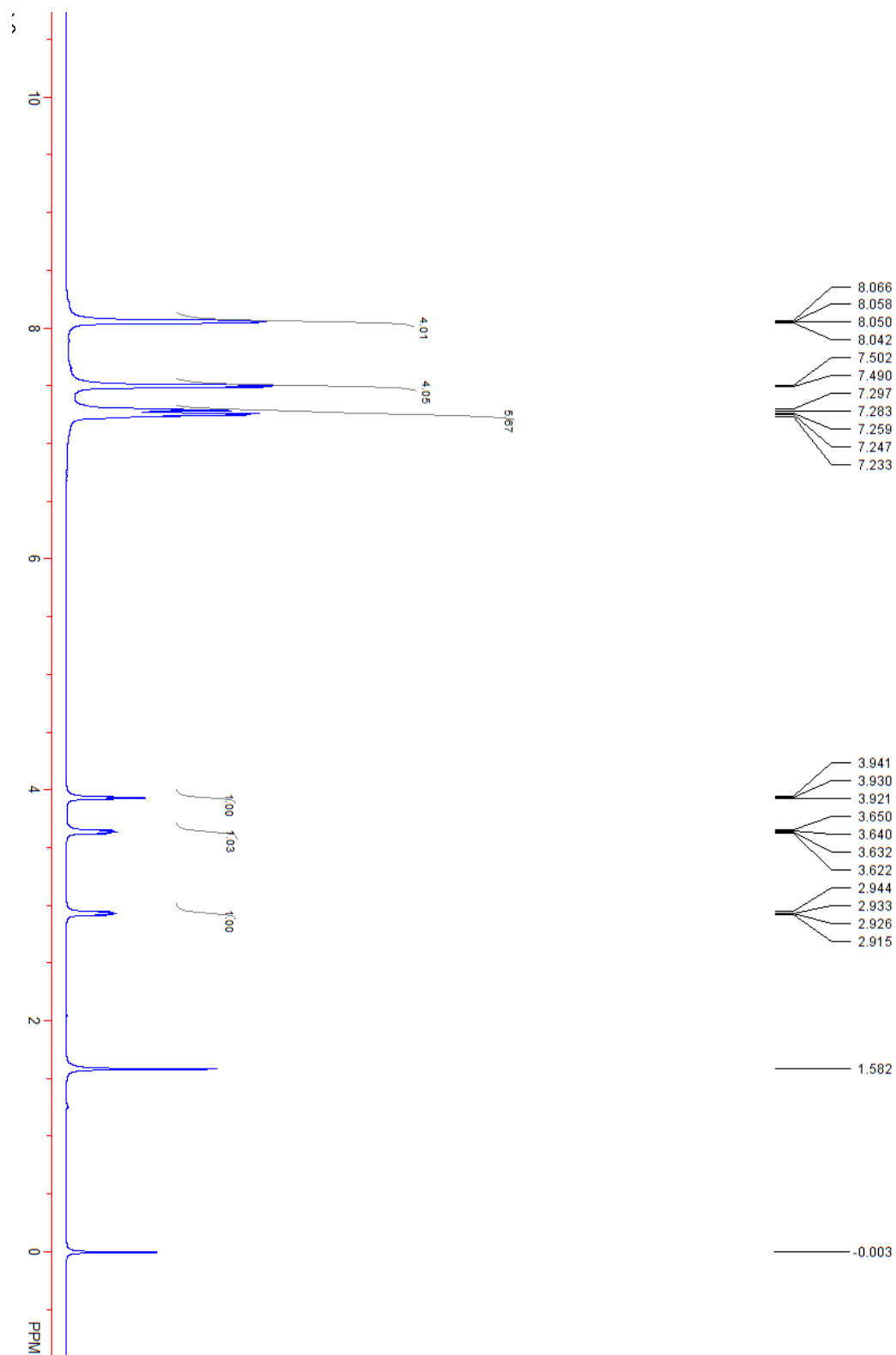


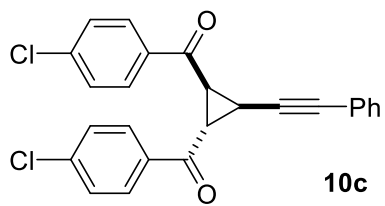
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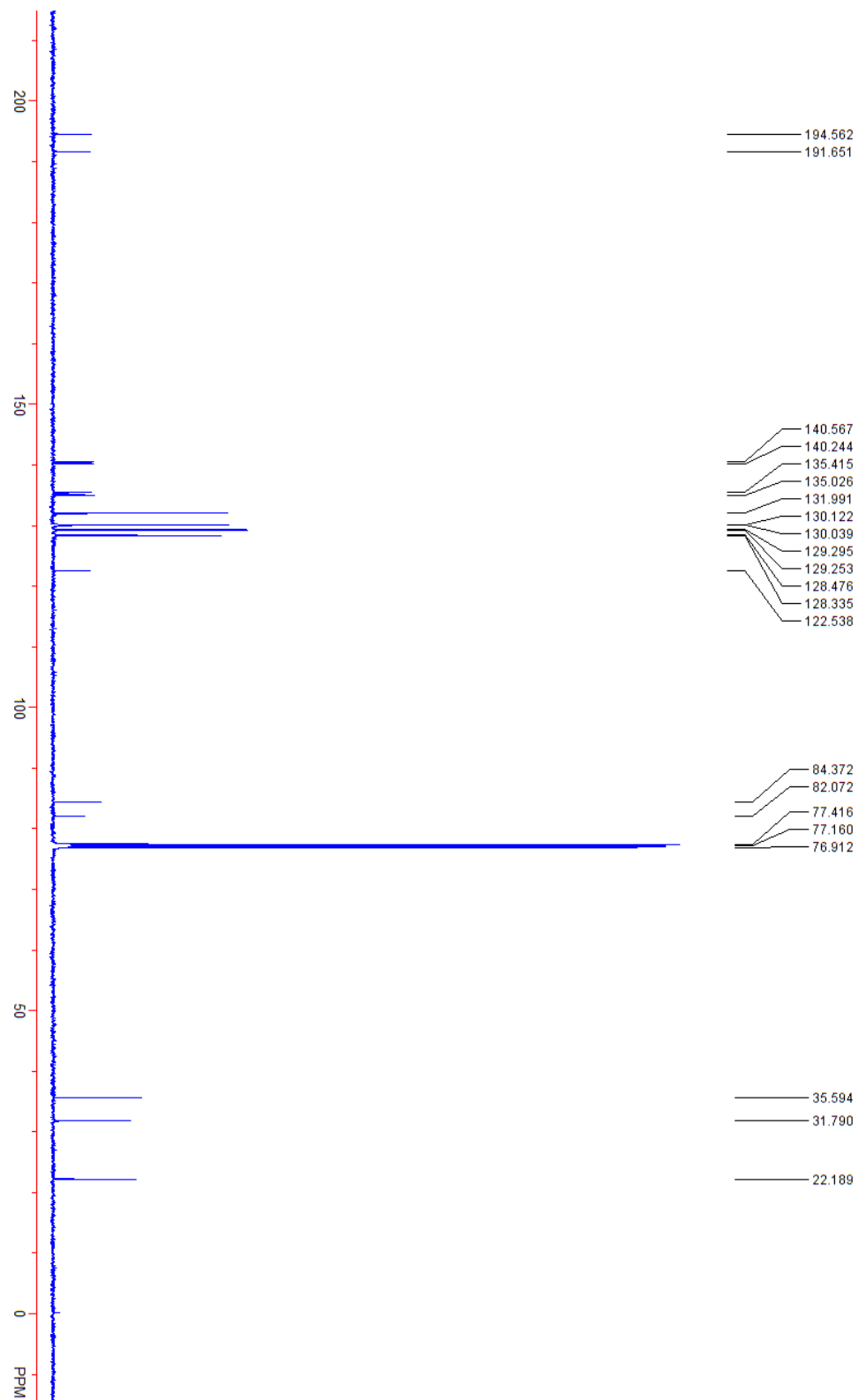


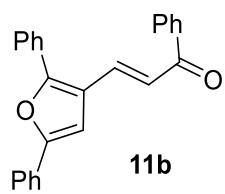
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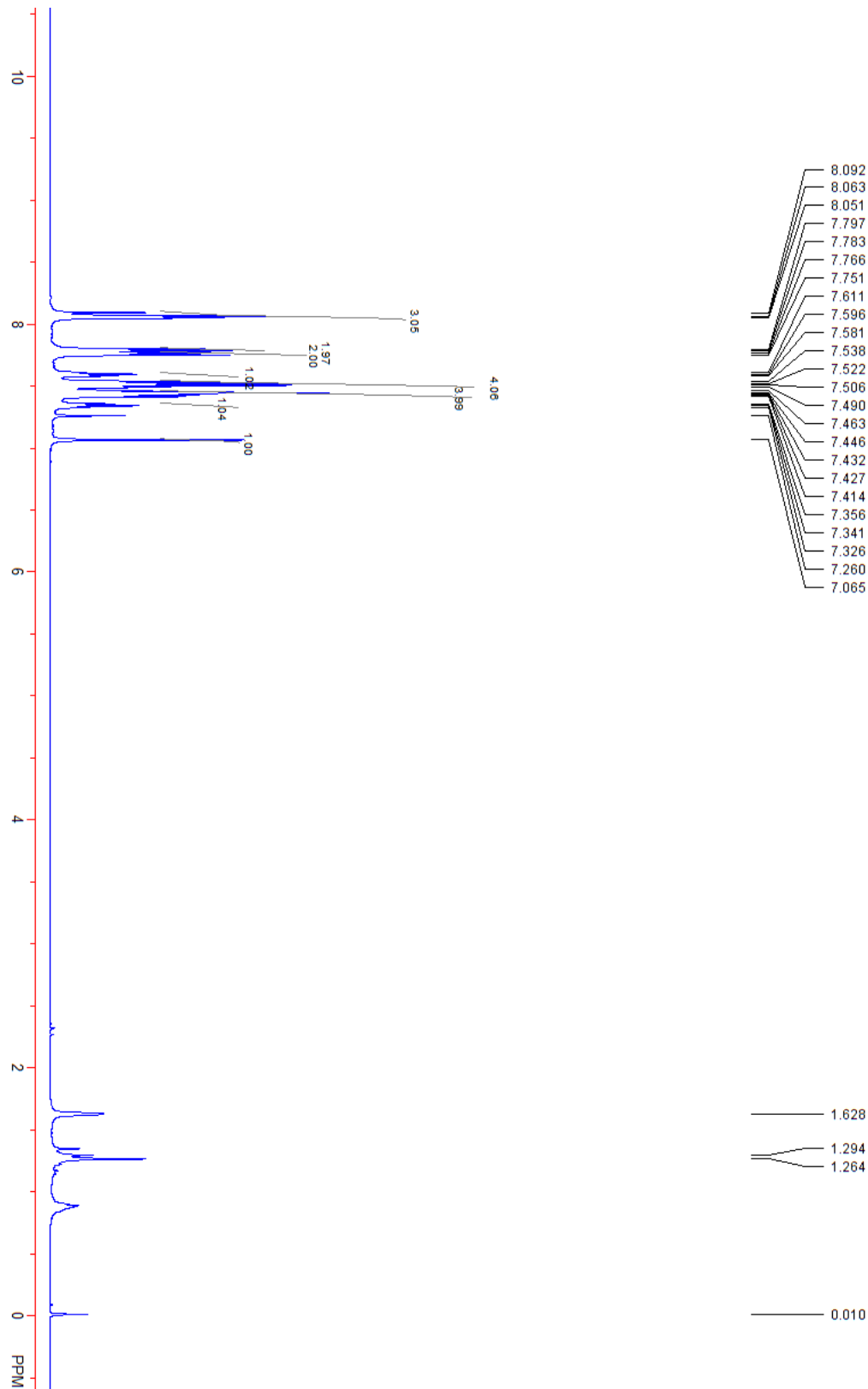


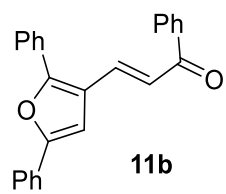
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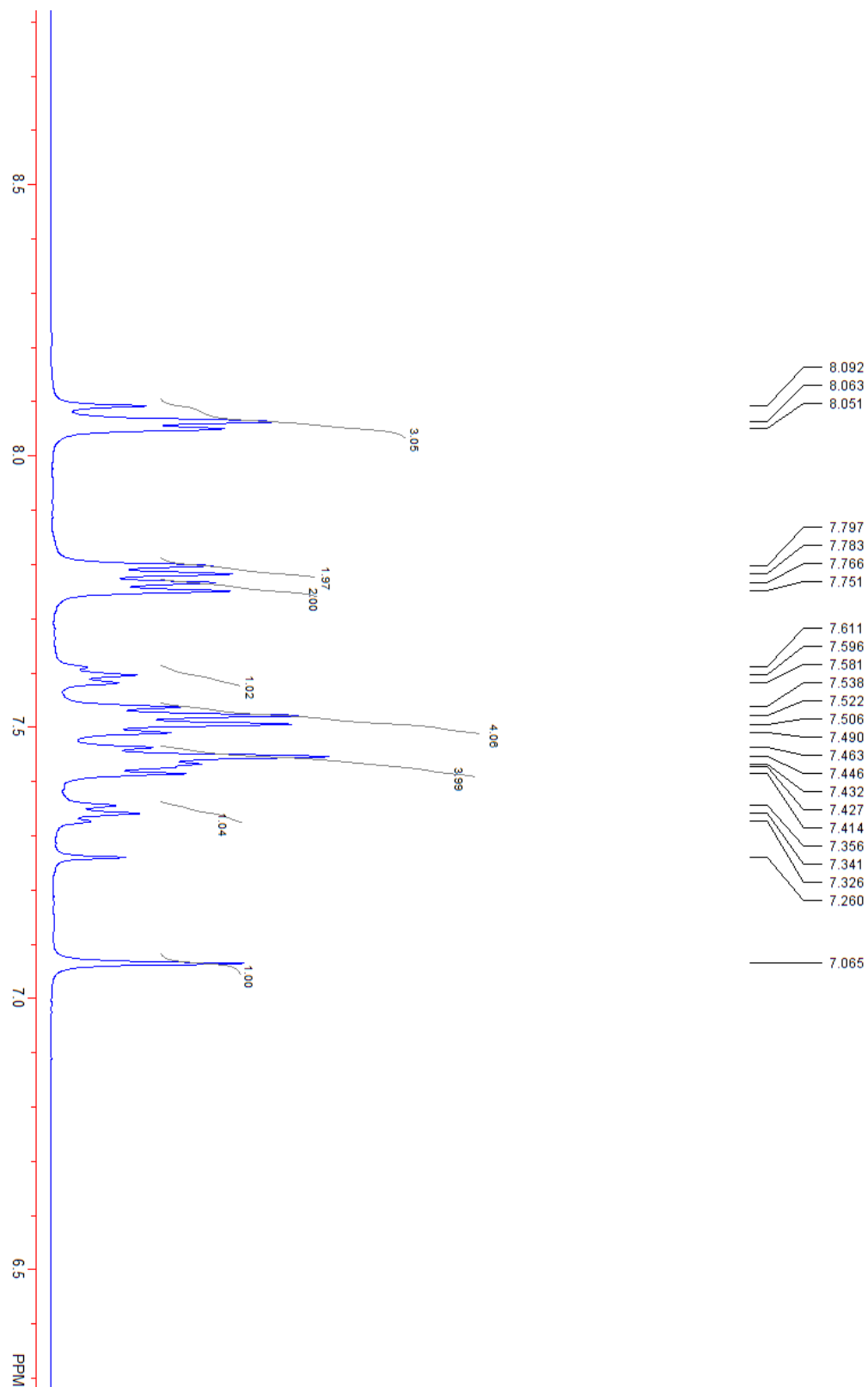


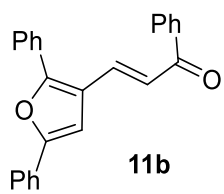
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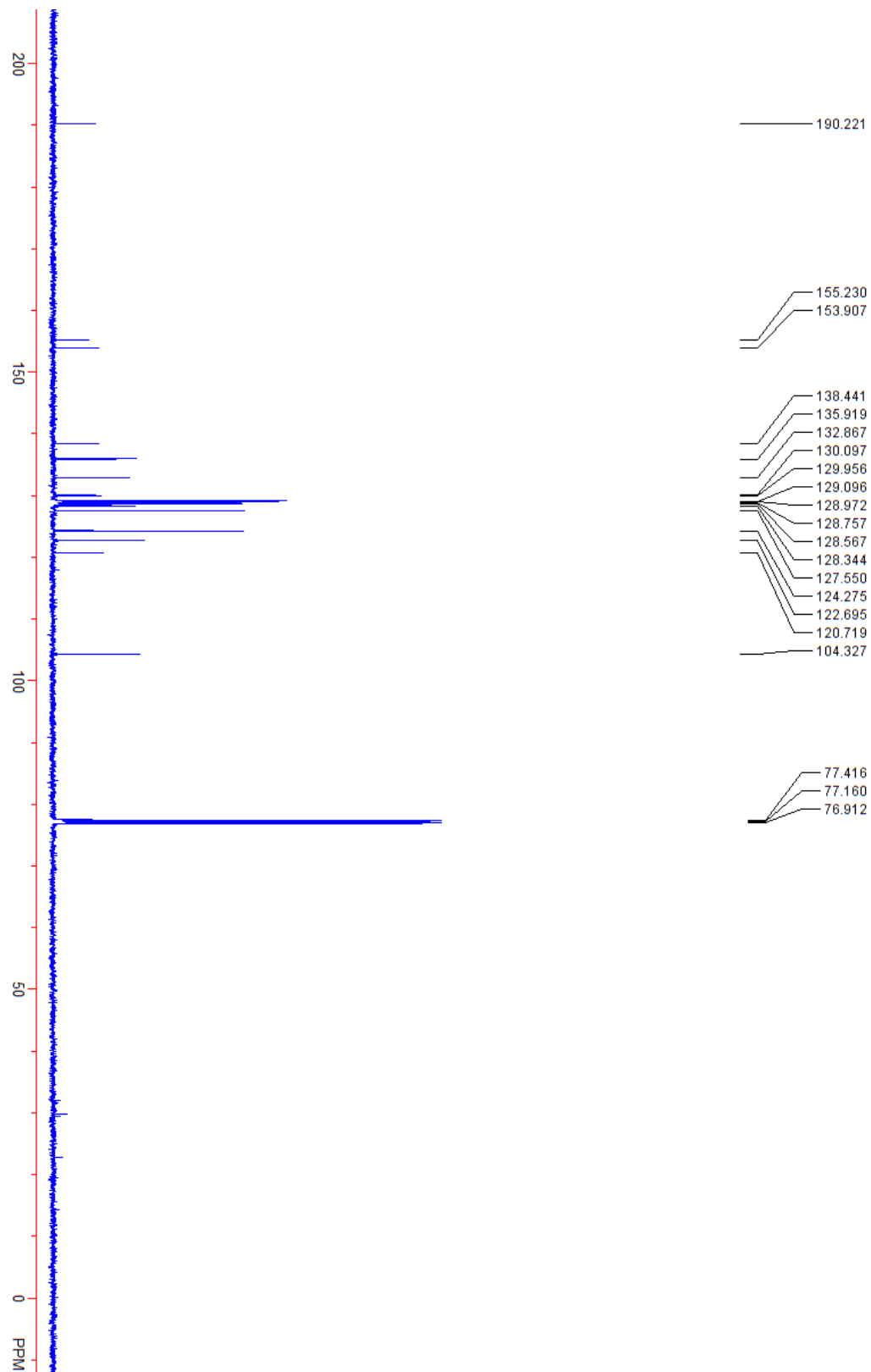


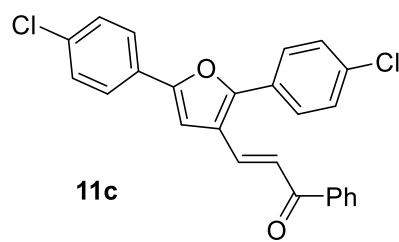
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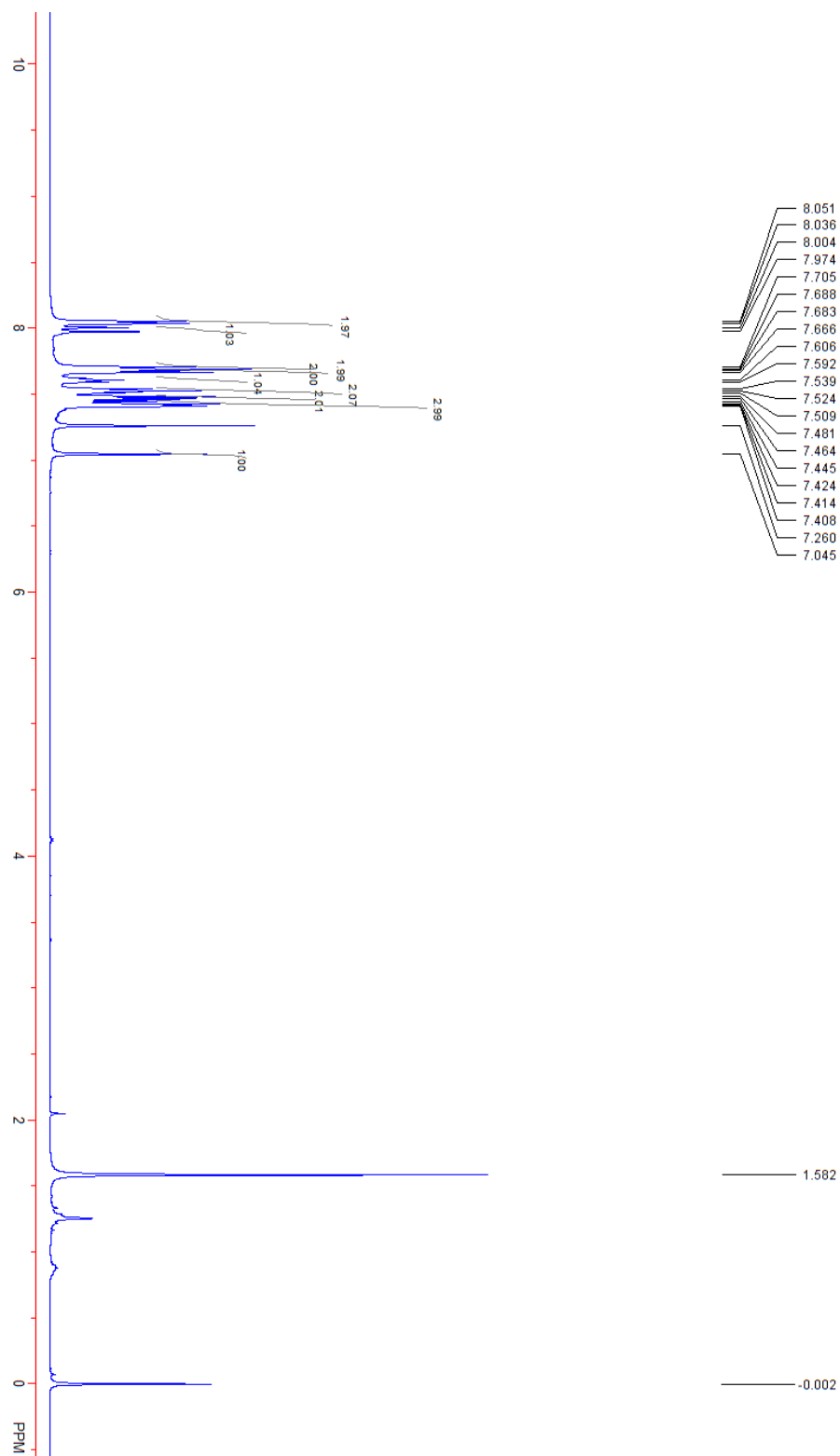


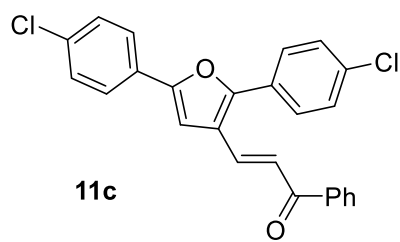
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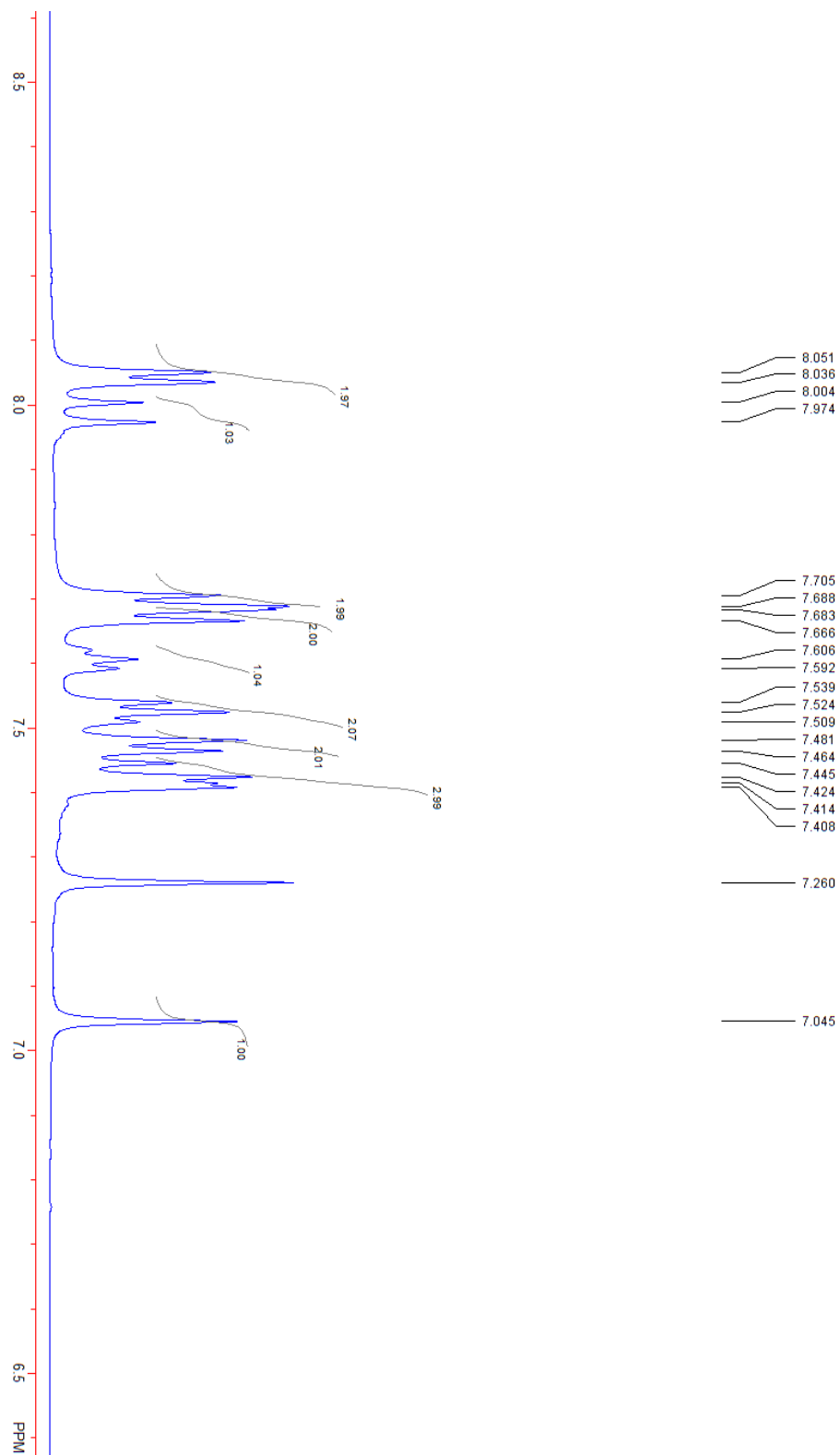


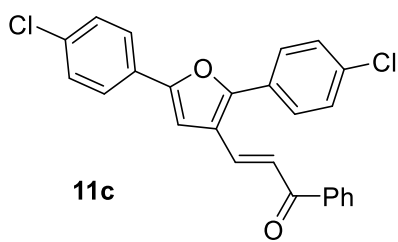
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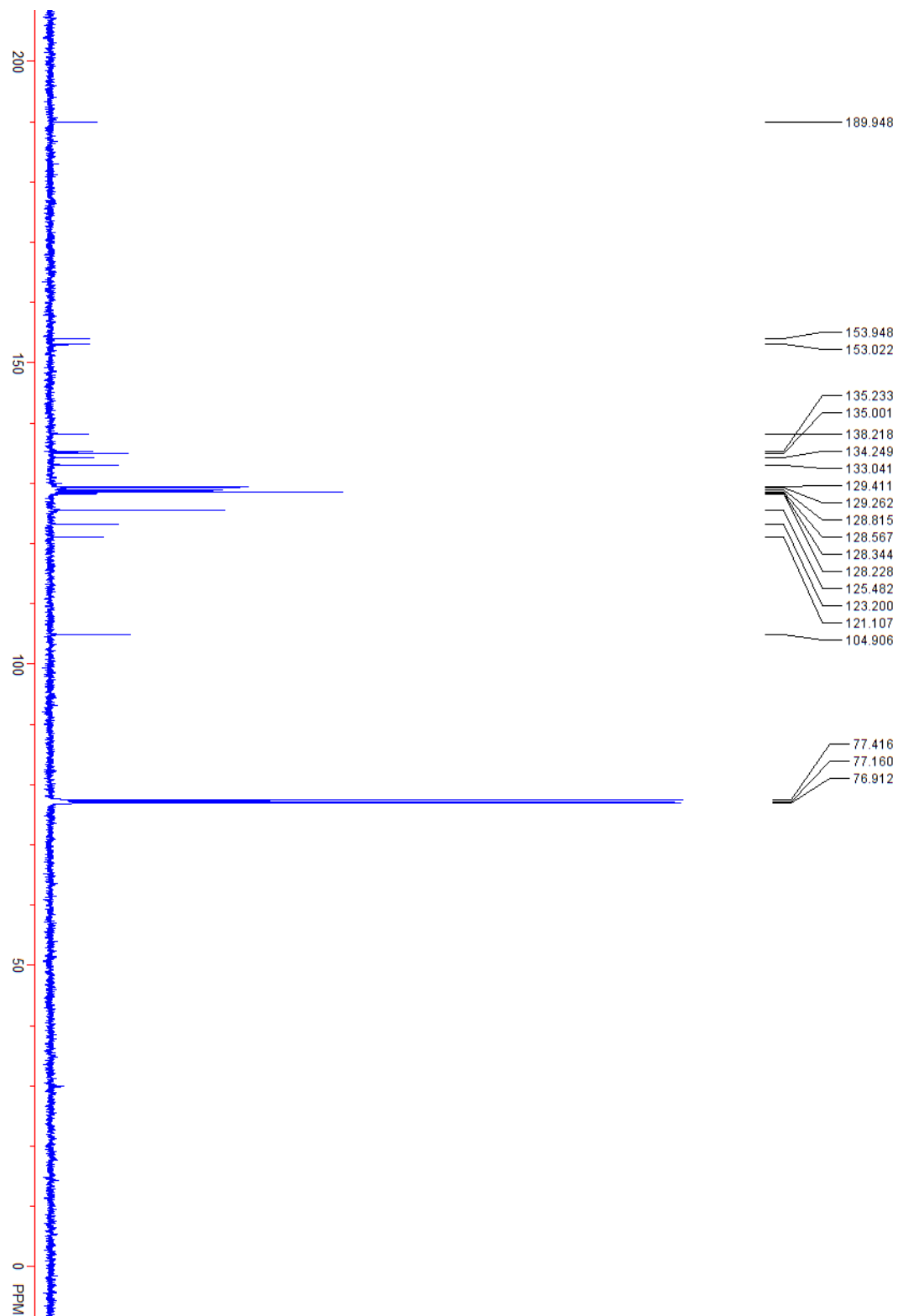


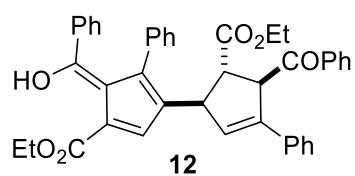
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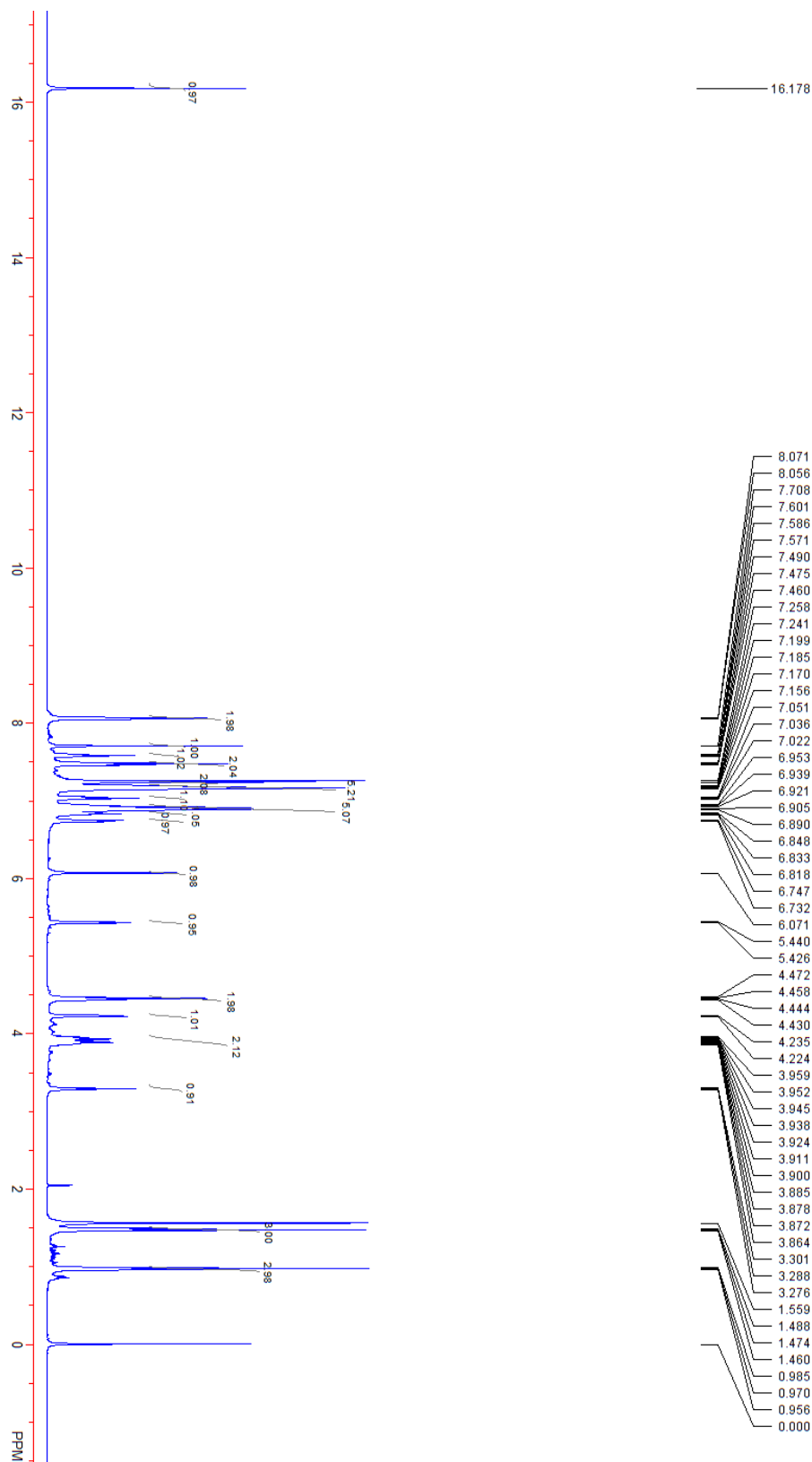


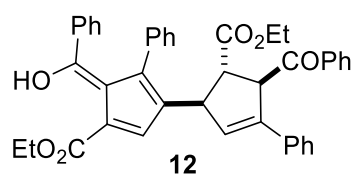
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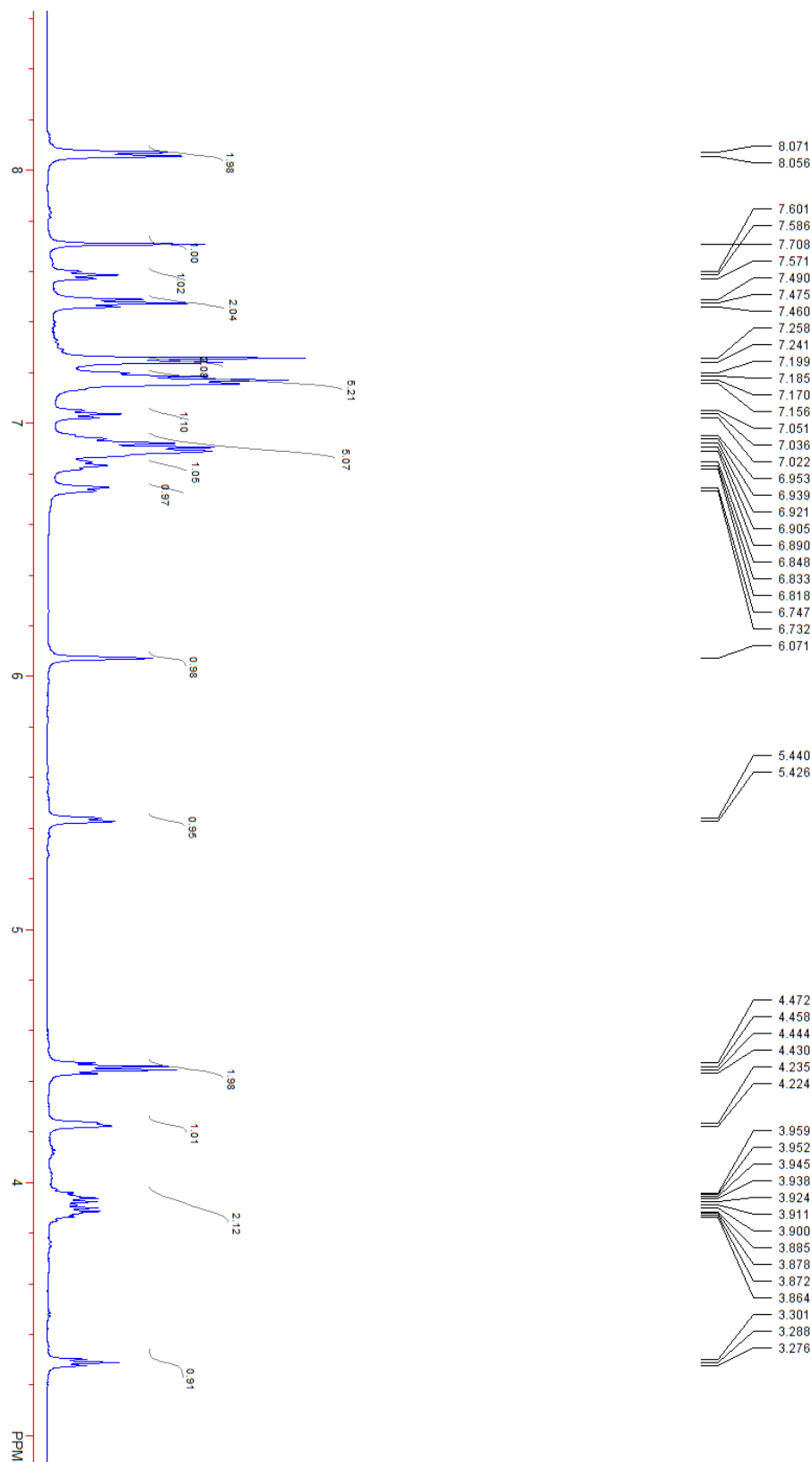


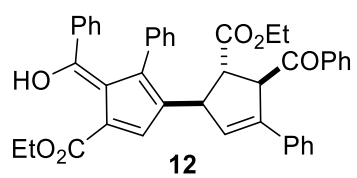
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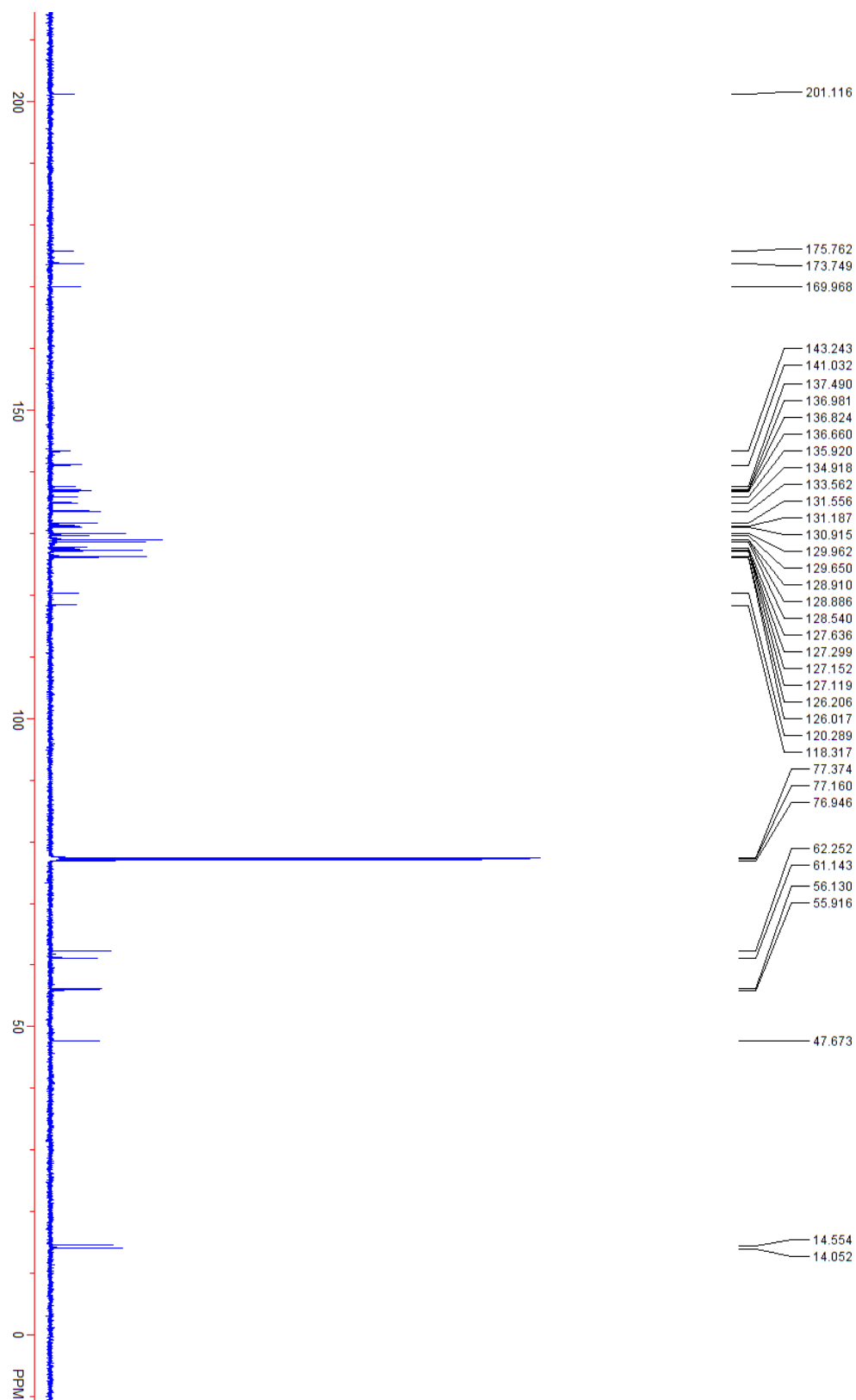


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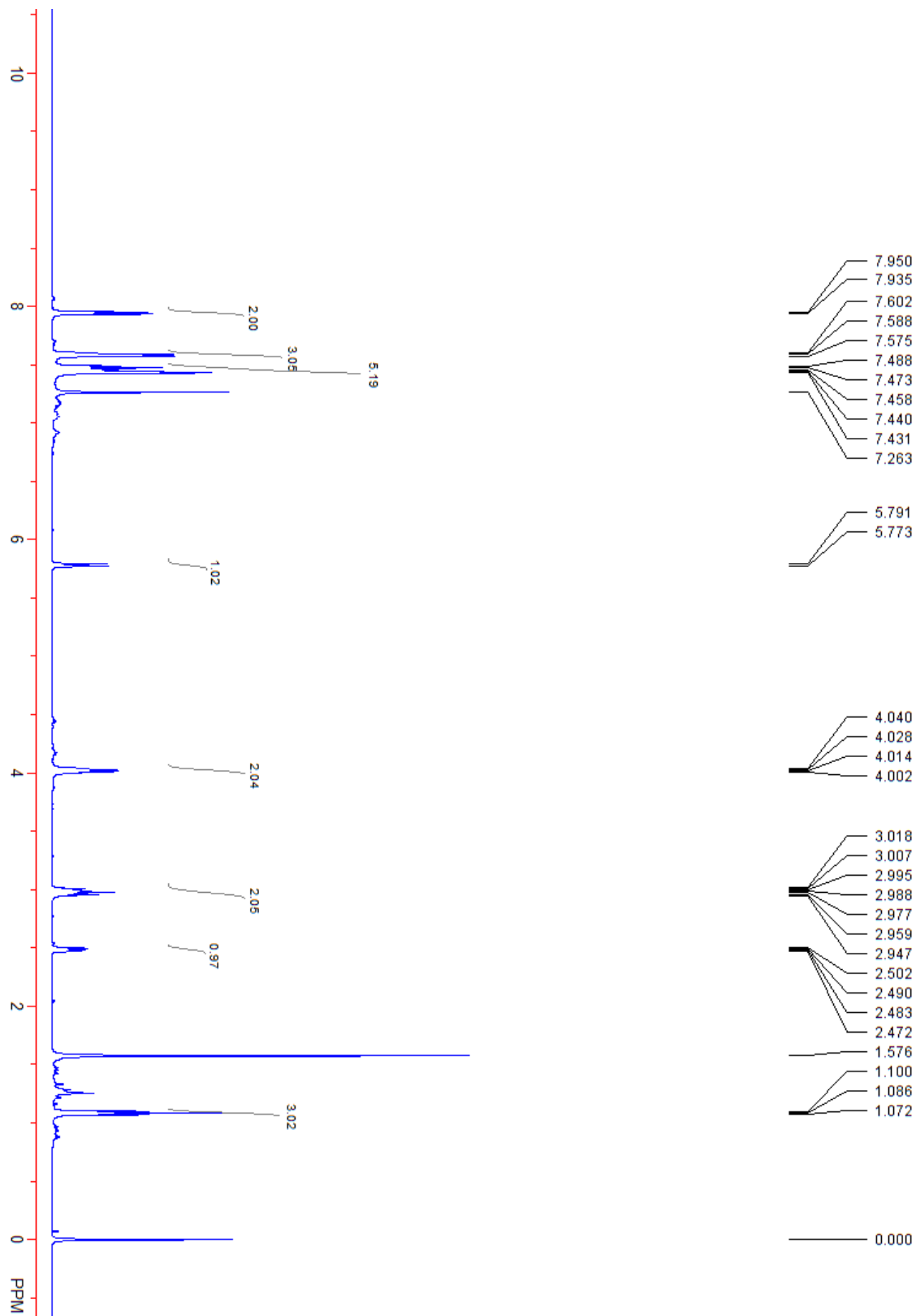
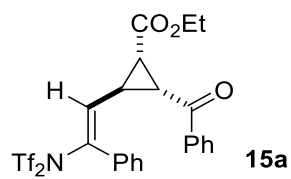




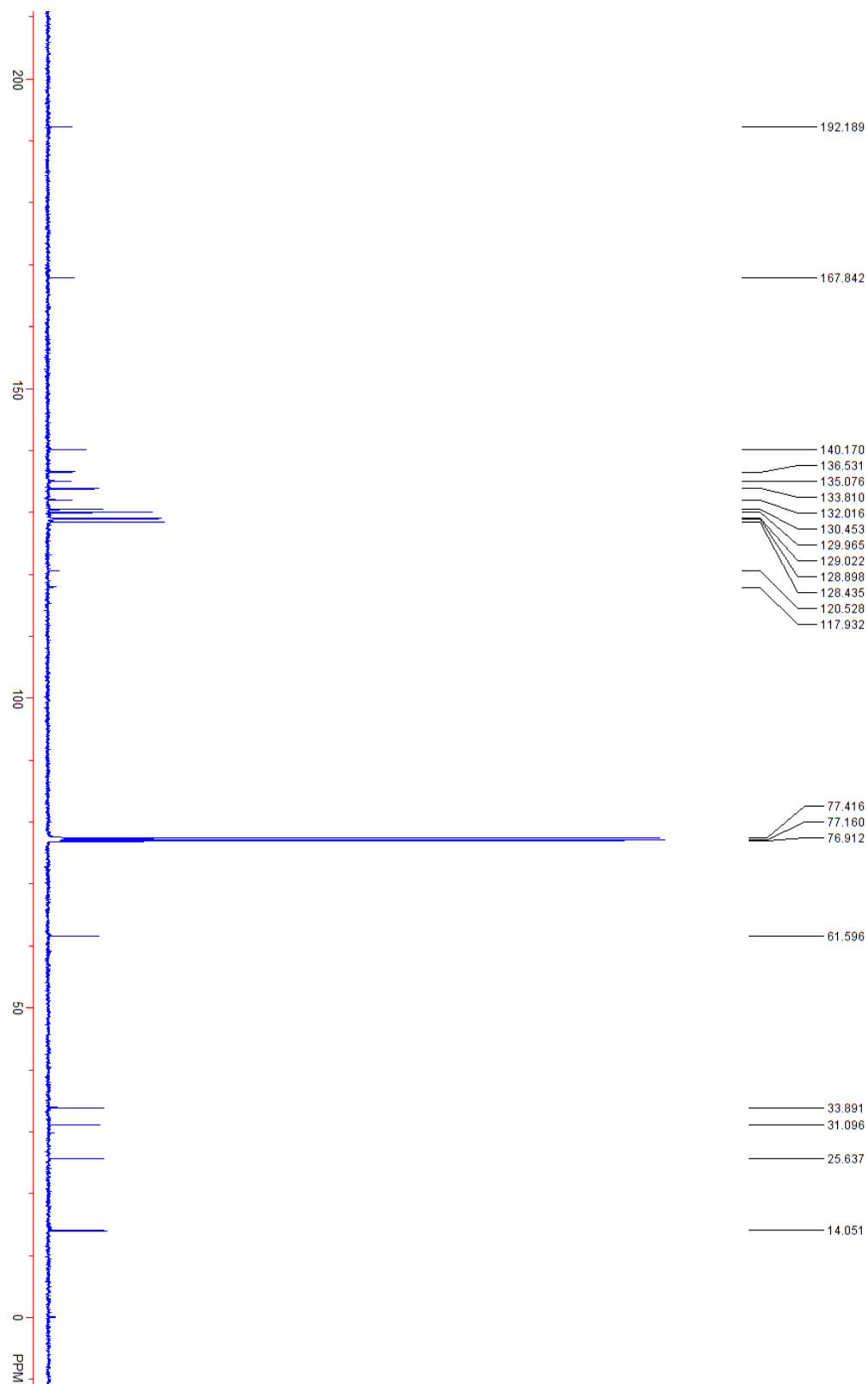
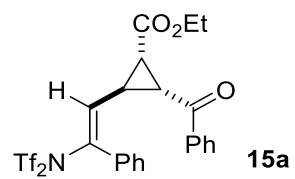
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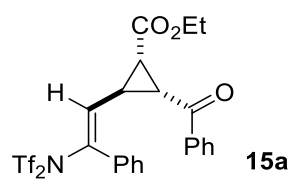
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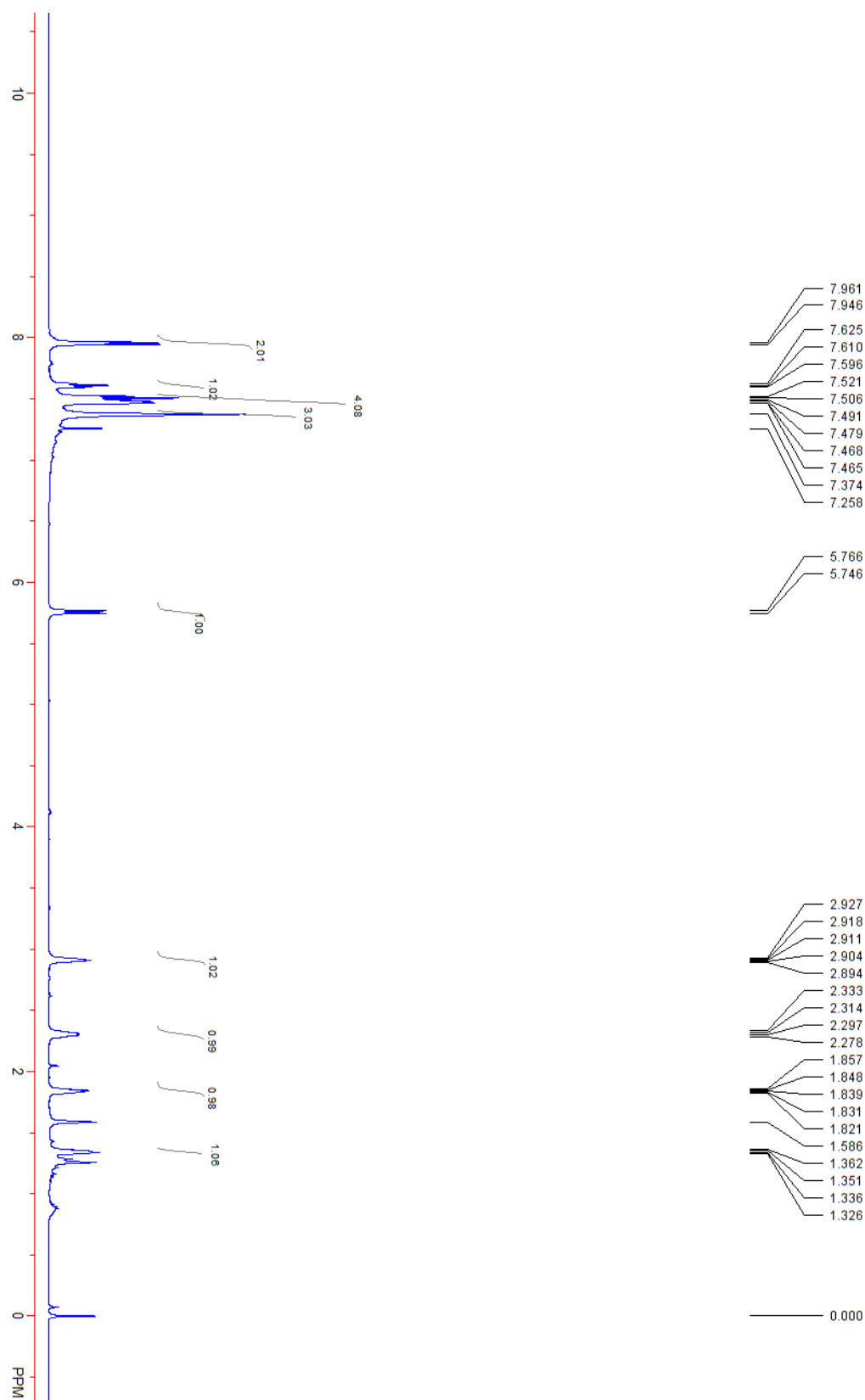
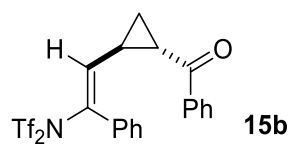
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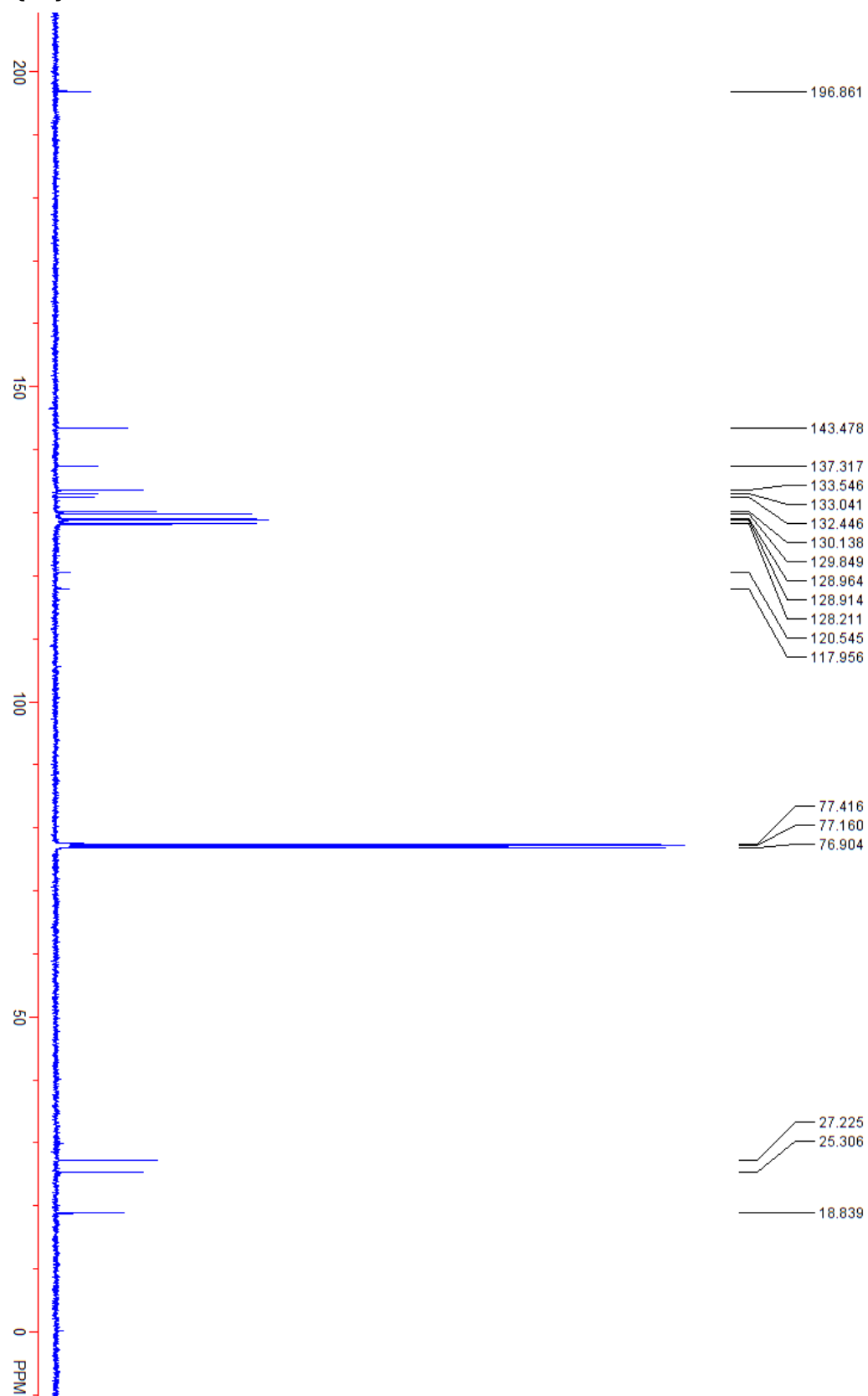
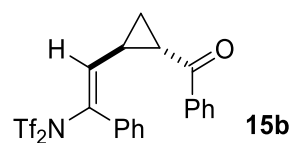
¹⁹F NMR:



¹H NMR:



$^{13}\text{C}\{^1\text{H}\}$ NMR:



¹⁹F NMR:

