



Supporting Information

for

Z-Selective semihydrogenation of alkynes via Ni/Lewis acid synergistic catalyzed system using DMF as hydrogen source and solvent

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Experimental procedure, compound characterization data, and copies of spectra

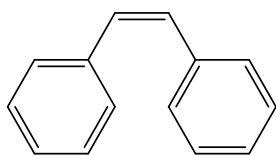
1. General information

Thin-layer chromatography (TLC) was performed using E. Merck Silica Gel 60 F254 precoated plates (0.25 mm). The developed chromatography plates were analyzed by a UV lamp (254 nm). Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature. Chemical shifts for ^1H NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent resonance as the internal standard (chloroform: δ 7.26 ppm). Chemical shifts for ^{13}C NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent as the internal standard (CDCl_3 : δ 77.16 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet, br = broad signal), coupling constant (Hz), and integration. The *Z/E* stereoisomeric ratio of the product was determined by gas chromatography (GC) analysis of the crude reaction mixture.

2. Experimental section

An oven-dried reaction vessel was charged with diphenylacetylene (0.2 mmol, 35.6 mg), $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (50 mol %, 22 mg), and NiCl_2 (20 mol %, 3.3 mg). DMF (0.8 mL) was then added, the vessel was sealed, and the mixture was stirred and heated at 150 °C (oil bath temperature) for 24 h. The reaction was monitored by GC analysis; upon complete consumption of the starting material, heating was discontinued. After cooling to room temperature, the volatiles were removed under reduced pressure. The resulting crude residue was purified by flash column chromatography on silica gel (eluent: petroleum ether) to afford pure (*Z*)-stilbene (**2a**) as a colorless solid in 95% isolated yield (34.4 mg). The *Z/E* ratio (98:2) was determined by GC analysis of the crude mixture.

3. Characterization data of products 2a–p

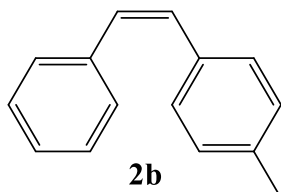


(2a)¹

2a

Yellow oil. ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.24–7.17 (m, 10H), 6.60 (s, 2H);

¹³C NMR (100 MHz, CDCl₃) δ 137.35, 130.37, 128.99, 128.33, 127.21.

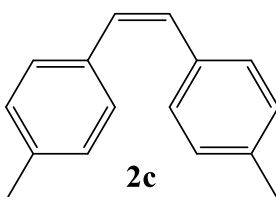


(2b)²

2b

¹H NMR (400 MHz, CDCl₃, TMS) δ 7.30 – 7.17 (m, 5H), 7.17 – 7.10 (m, 2H), 7.02 (d, *J* = 7.9 Hz, 2H), 6.55 (s, 2H), 2.31 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 137.53, 136.90, 134.29, 130.23, 129.58, 128.94, 128.88, 128.82, 128.22, 127.00, 21.27.

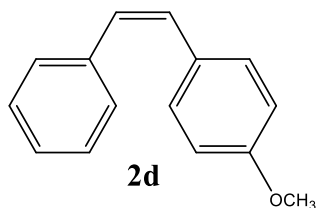


(2c)¹

2c

¹H NMR (400 MHz, CDCl₃, TMS) δ 7.16 (d, 4H, *J* = 8.2 Hz), 7.03 (d, 4H, *J* = 7.9 Hz), 6.51 (s, 2H), 2.31 (s, 6H);

¹³C NMR (100 MHz, CDCl₃) δ 136.75, 134.51, 129.53, 128.90, 128.77, 21.26.

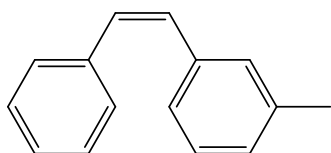


(2d)¹

2d

¹H NMR (400 MHz, CDCl₃, TMS) δ 7.50 – 6.91 (m, 7H), 6.75 (d, *J* = 8.8 Hz, 2H), 6.52 (d, *J* = 1.8 Hz, 2H), 3.78 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 158.69, 137.64, 130.17, 129.79, 129.68, 128.84, 128.78, 128.25, 126.92, 113.61, 55.21.

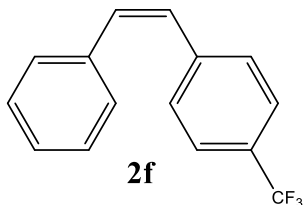


(2e)²

2e

¹H NMR (400 MHz, CDCl₃) δ 7.34 – 7.17 (m, 5H), 7.09 (m, 4H), 6.60 (s, 2H), 2.29 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 137.84, 137.41, 137.27, 130.45, 130.16, 129.69, 128.97, 128.24, 128.17, 127.94, 127.14, 125.96, 21.43.

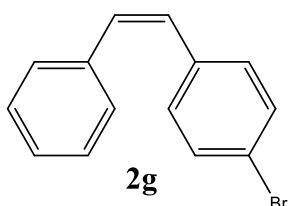


(2f)^{2,3}

2f

¹H NMR (400 MHz, CDCl₃) δ 7.47 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.30 – 7.17 (m, 5H), 6.73 (d, *J* = 12.3 Hz, 1H), 6.60 (d, *J* = 12.3 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 140.92, 136.56, 132.34, 129.14, 128.82, 128.75, 128.43, 127.58, 125.16 (q, *J*₁ = 3.7, *J*₂ = 3.8 Hz), 122.83.

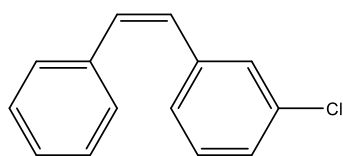


(2g)⁴

2g

¹H NMR (400 MHz, CDCl₃) δ 7.34 (d, *J* = 8.4 Hz, 2H), 7.25 – 7.20 (m, 5H), 7.10 (d, *J* = 8.3 Hz, 2H), 6.63 (d, *J* = 12.2 Hz, 1H), 6.50 (d, *J* = 12.2 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 136.86, 136.14, 131.39, 131.07, 130.57, 128.97, 128.83, 128.38, 127.38, 120.96.

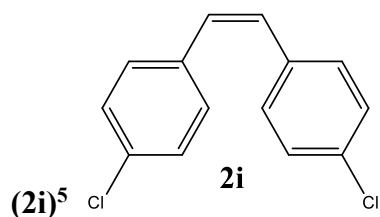


(2h)²

2h

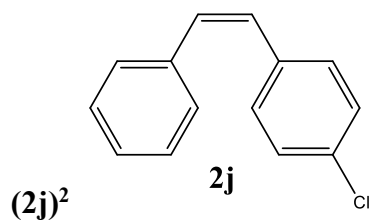
¹H NMR (400 MHz, CDCl₃) δ 7.35 – 7.03 (m, 9H), 6.68 (d, *J* = 12.2 Hz, 1H), 6.55 (d, *J* = 12.2 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 139.17, 136.68, 134.13, 131.64, 129.50, 128.91, 128.89, 128.78, 128.40, 127.52, 127.20, 127.07.



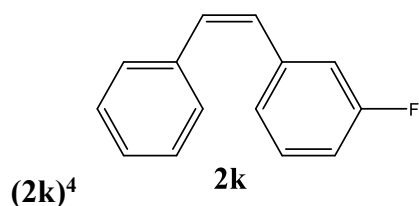
¹H NMR (400 MHz, CDCl₃) δ 7.23 (d, *J* = 8.5 Hz, 4H), 7.17 (d, *J* = 8.4 Hz, 4H), 6.58 (s, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 135.29, 133.06, 130.17, 129.64, 128.58.



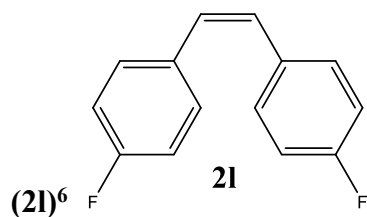
¹H NMR (400 MHz, CDCl₃) δ 7.35 – 7.08 (m, 9H), 6.62 (d, *J* = 12.2 Hz, 1H), 6.53 (d, *J* = 12.2 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 136.90, 135.68, 132.77, 130.98, 130.25, 128.95, 128.84, 128.44, 128.37, 127.35.



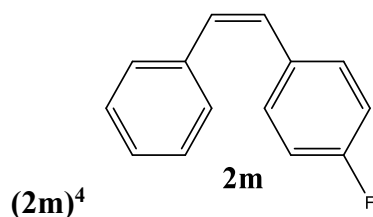
¹H NMR (400 MHz, CDCl₃) δ 7.27 – 7.12 (m, 6H), 7.01 (d, *J* = 7.7 Hz, 1H), 6.97 – 6.83 (m, 2H), 6.65 (d, *J* = 12.2 Hz, 1H), 6.54 (d, *J* = 12.2 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 162.73 (d, *J* = 245.2 Hz), 139.51 (d, *J* = 7.8 Hz), 129.69 (d, *J* = 8.4 Hz), 129.00 (d, *J* = 2.2 Hz), 115.56 (d, *J* = 21.7 Hz), 114.01 (d, *J* = 21.2 Hz).



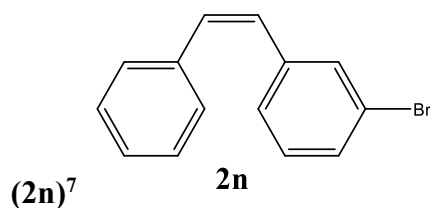
¹H NMR (400 MHz, CDCl₃) δ 7.29 – 7.07 (m, 4H), 7.00 – 6.83 (m, 4H), 6.54 (s, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 161.87 (d, *J* = 246.9 Hz), 132.98 (d, *J* = 3.4 Hz), 130.50 (d, *J* = 7.9 Hz), 129.11 (d, *J* = 1.2 Hz), 115.28 (d, *J* = 21.4 Hz).



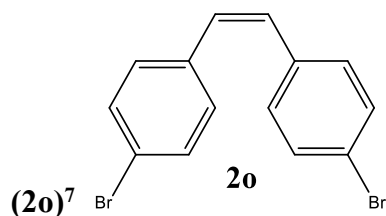
¹H NMR (400 MHz, CDCl₃) δ 7.27 – 7.16 (m, 7H), 6.95 – 6.85 (m, 2H), 6.59 (d, *J* = 12.2 Hz, 1H), 6.53 (d, *J* = 12.2 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 161.85 (d, *J* = 246.7 Hz), 133.21 (d, *J* = 3.4 Hz), 130.56 (d, *J* = 7.8 Hz), 130.28 (d, *J* = 1.0 Hz), 115.18 (d, *J* = 21.4 Hz).



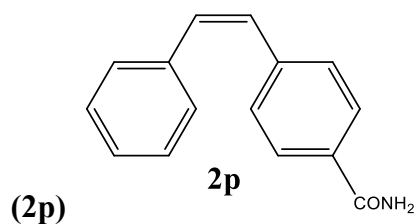
¹H NMR (400 MHz, CDCl₃) δ 7.39 – 7.05 (m, 9H), 6.64 (d, *J* = 12.2 Hz, 1H), 6.51 (d, *J* = 12.2 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 139.45, 136.61, 131.79, 131.66, 130.08, 129.74, 128.86, 128.64, 128.36, 127.51, 127.47, 122.31.



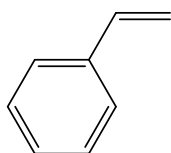
¹H NMR (400 MHz, CDCl₃) δ 7.36 (d, *J* = 8.5 Hz, 4H), 7.08 (d, *J* = 8.5 Hz, 4H), 6.54 (s, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 135.70, 131.68, 131.54, 130.47, 129.73, 121.25.



¹H NMR (400 MHz, CDCl₃) δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.28 – 7.12 (m, 5H), 6.70 (d, *J* = 12.2 Hz, 1H), 6.59 (d, *J* = 12.2 Hz, 1H), 5.93 (d, *J* = 94.6 Hz, 2H).

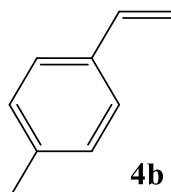
¹³C NMR (100 MHz, CDCl₃) δ 169.47, 141.20, 136.70, 132.10, 131.76, 129.10, 128.88, 128.39, 127.53, 127.38.



(4a)⁵ **4a**

¹H NMR (400 MHz, CDCl₃) δ 7.41 – 7.22 (m, 4H), 6.75 – 6.66 (m, 1H), 5.74 (d, *J* = 17.6 Hz, 1H), 5.23 (d, *J* = 11.0 Hz, 1H).

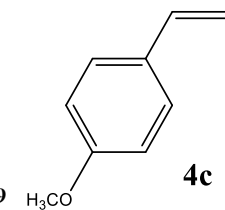
¹³C NMR (100 MHz, CDCl₃) δ 137.70, 137.02, 128.66, 127.94, 126.35, 113.94.



(4b)⁸ **4b**

¹H NMR (400 MHz, CDCl₃) δ 7.30 (d, *J* = 6.3 Hz, 2H), 7.12 (d, *J* = 6.6 Hz, 2H), 6.80 – 6.58 (m, 1H), 5.69 (d, *J* = 17.7 Hz, 1H), 5.18 (d, *J* = 10.9 Hz, 1H), 2.33 (s, 3H).

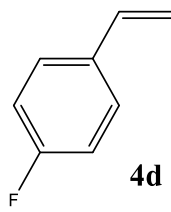
¹³C NMR (100 MHz, CDCl₃) δ 137.74, 136.84, 134.95, 129.35, 126.25, 112.89, 21.34.



(4c)^{5,9} **4c**

¹H NMR (400 MHz, CDCl₃) δ 7.34 (d, *J* = 8.9 Hz, 2H), 6.85 (d, *J* = 8.9 Hz, 2H), 6.65 (dd, *J* = 17.7, 10.9 Hz, 1H), 5.60 (d, *J* = 17.7 Hz, 1H), 5.12 (d, *J* = 11.9 Hz, 1H), 3.79 (s, 3H).

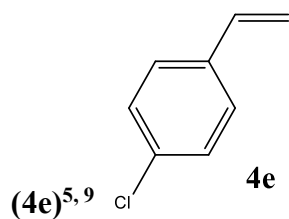
¹³C NMR (100 MHz, CDCl₃) δ 159.49, 136.34, 130.54, 127.50, 114.02, 111.68, 55.38.



(4d)⁹ **4d**

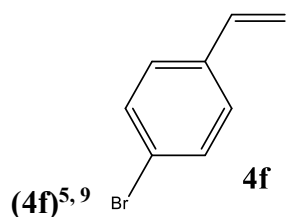
¹H NMR (400 MHz, CDCl₃) δ 7.36 (dd, *J* = 8.9, 5.3 Hz, 2H), 7.05 – 6.94 (m, 2H), 6.67 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.65 (d, *J* = 17.6 Hz, 1H), 5.21 (d, *J* = 10.9 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 162.58 (d, *J* = 246.6 Hz), 135.79, 133.84 (d, *J* = 3.4 Hz), 127.84 (d, *J* = 8.2 Hz), 115.51 (d, *J* = 21.7 Hz), 113.62 (d, *J* = 2.4 Hz).



¹H NMR (400 MHz, CDCl₃) δ 7.30 (q, *J* = 8.7 Hz, 4H), 6.65 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.71 (dd, *J* = 17.6, 0.8 Hz, 1H), 5.25 (dd, *J* = 10.9, 0.7 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 136.14, 135.78, 133.54, 128.79, 127.55, 114.57.



¹H NMR (400 MHz, CDCl₃) δ 7.43 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 11.0 Hz, 2H), 6.63 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.72 (d, *J* = 17.6 Hz, 1H), 5.26 (d, *J* = 10.9 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 136.57, 135.84, 131.74, 127.88, 121.72, 114.73.

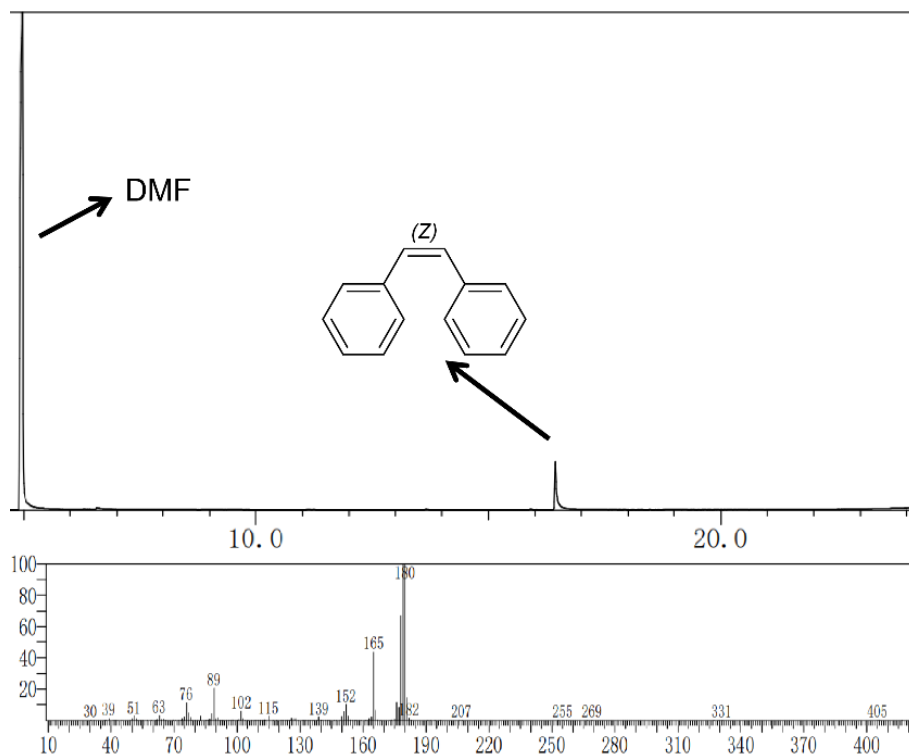


Figure S1: GC–MS chromatogram of diphenylacetylene reaction mixture after 48 h under standard conditions, showing no significant change in the (Z)-stilbene peak relative to the 24 h reaction. The peak labeled “DMF” corresponds to the solvent.

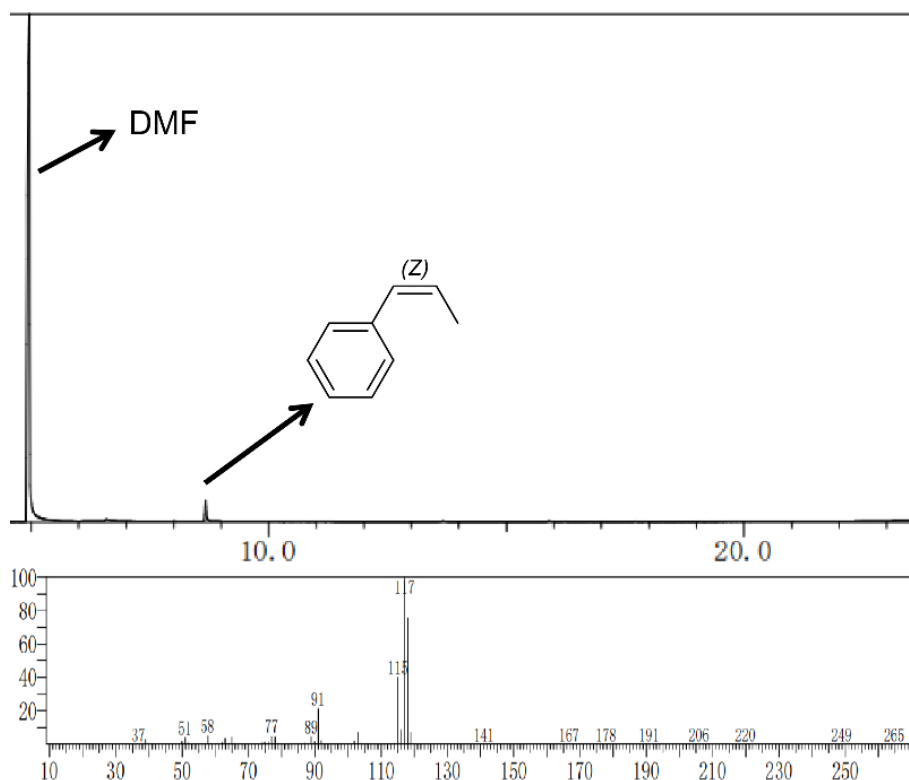


Figure S2: GC–MS chromatogram of the reaction mixture from 1-phenyl-1-propyne under standard conditions, showing complete conversion to (*Z*)-1-phenyl-1-propene ($m/z = 117$). The peak labeled “DMF” corresponds to the solvent.

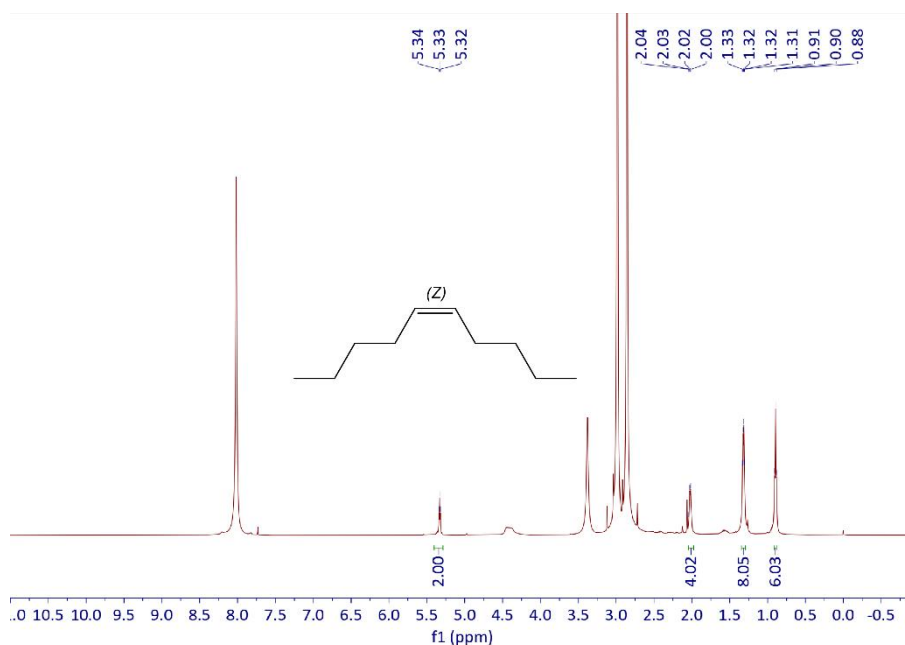
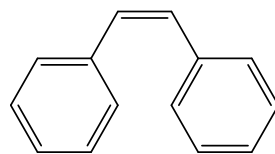


Figure S3: ^1H NMR spectrum of crude reaction mixture from 5-decyne after 24 h reaction, confirming the formation of (*Z*)-5-decene¹. (After 24 h of catalytic reaction, the crude mixture was extracted with CDCl_3 for ^1H NMR measurement.)

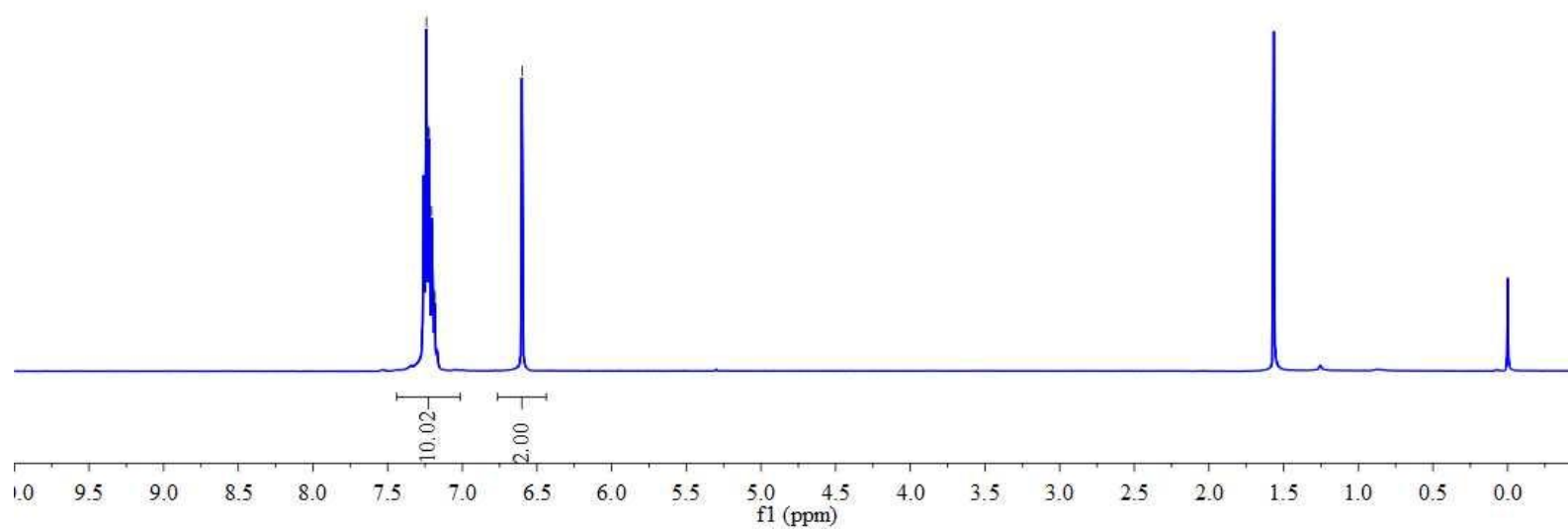
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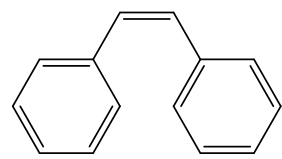
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7.223
7.205
7.193
7.184
— 6.600



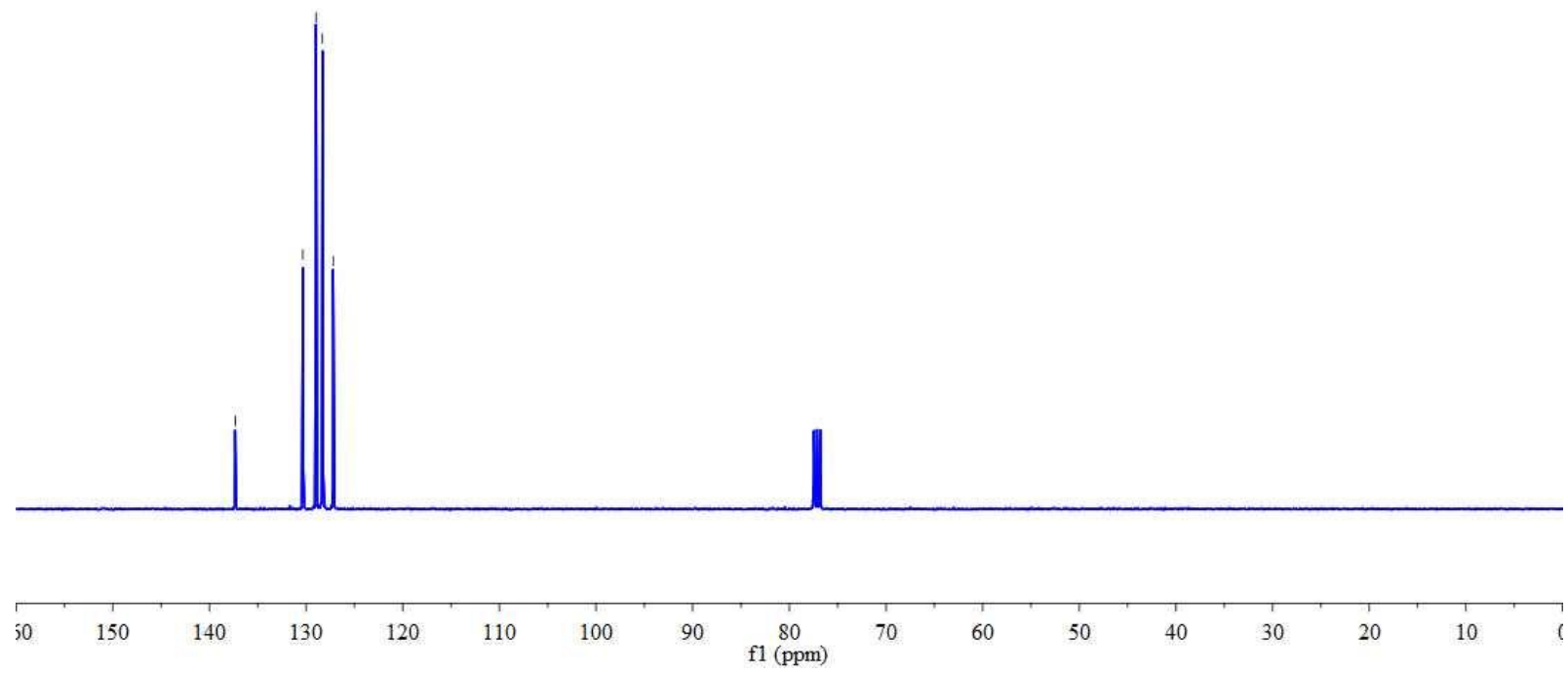
2a

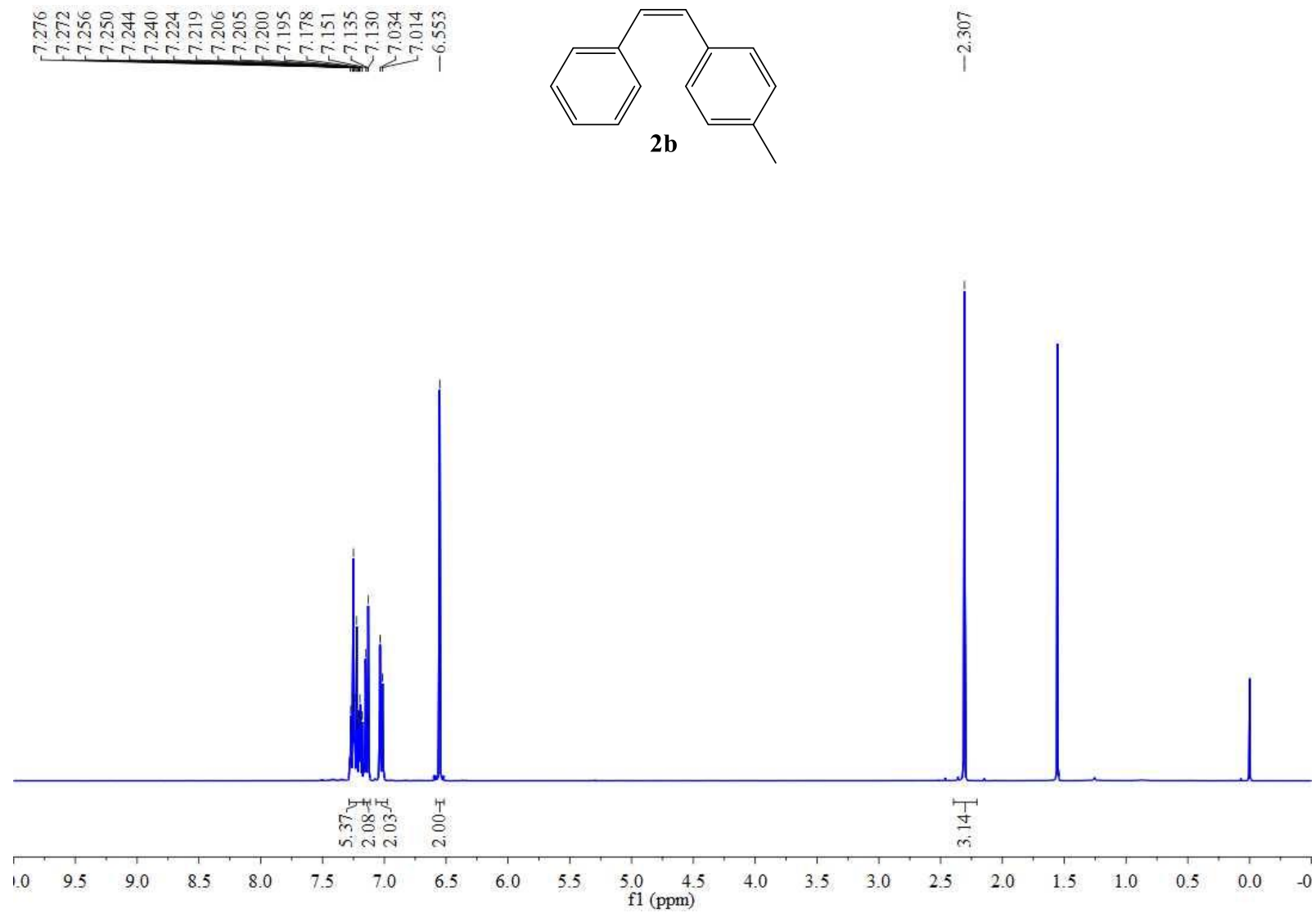


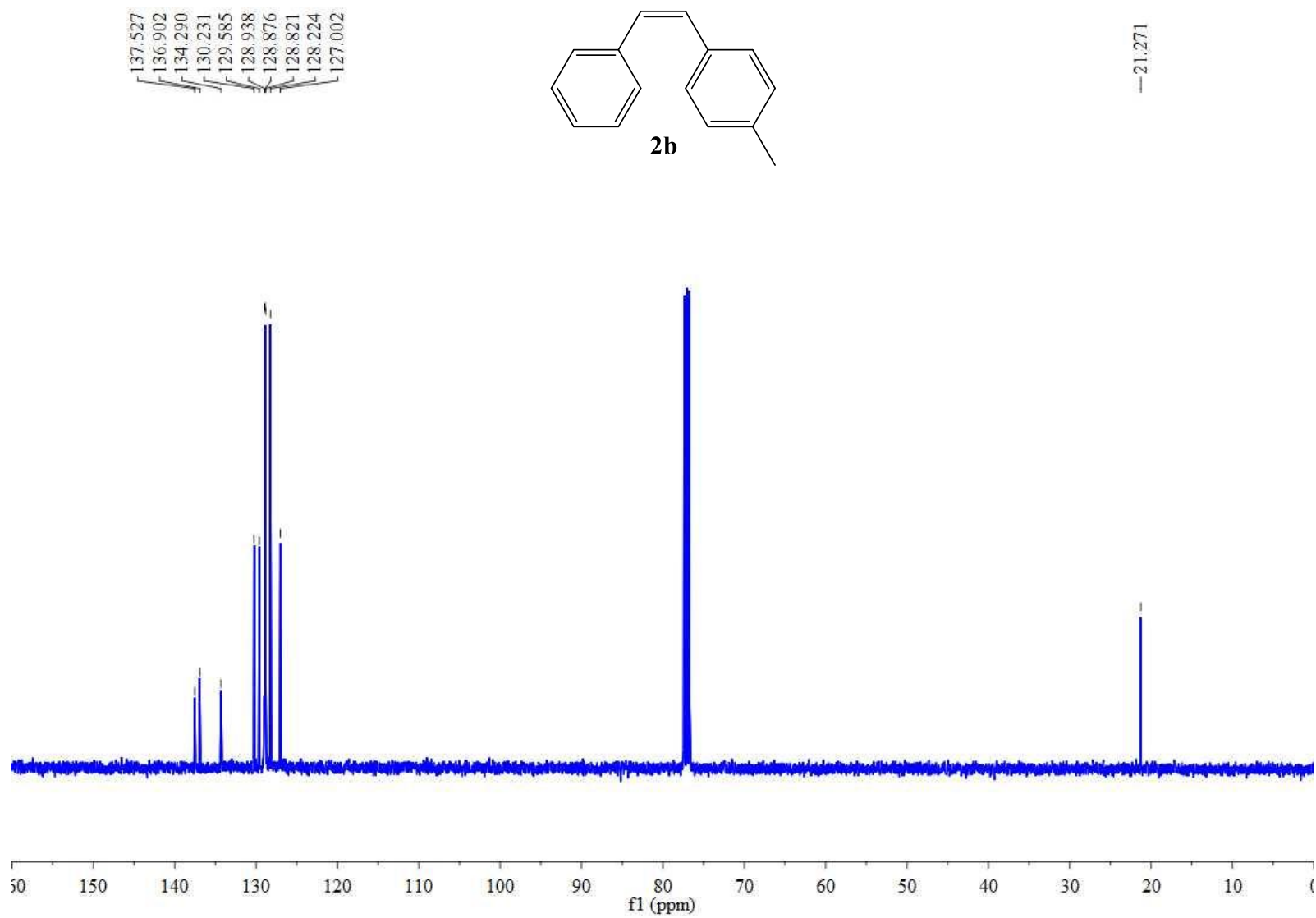
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130.339
128.966
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127.184

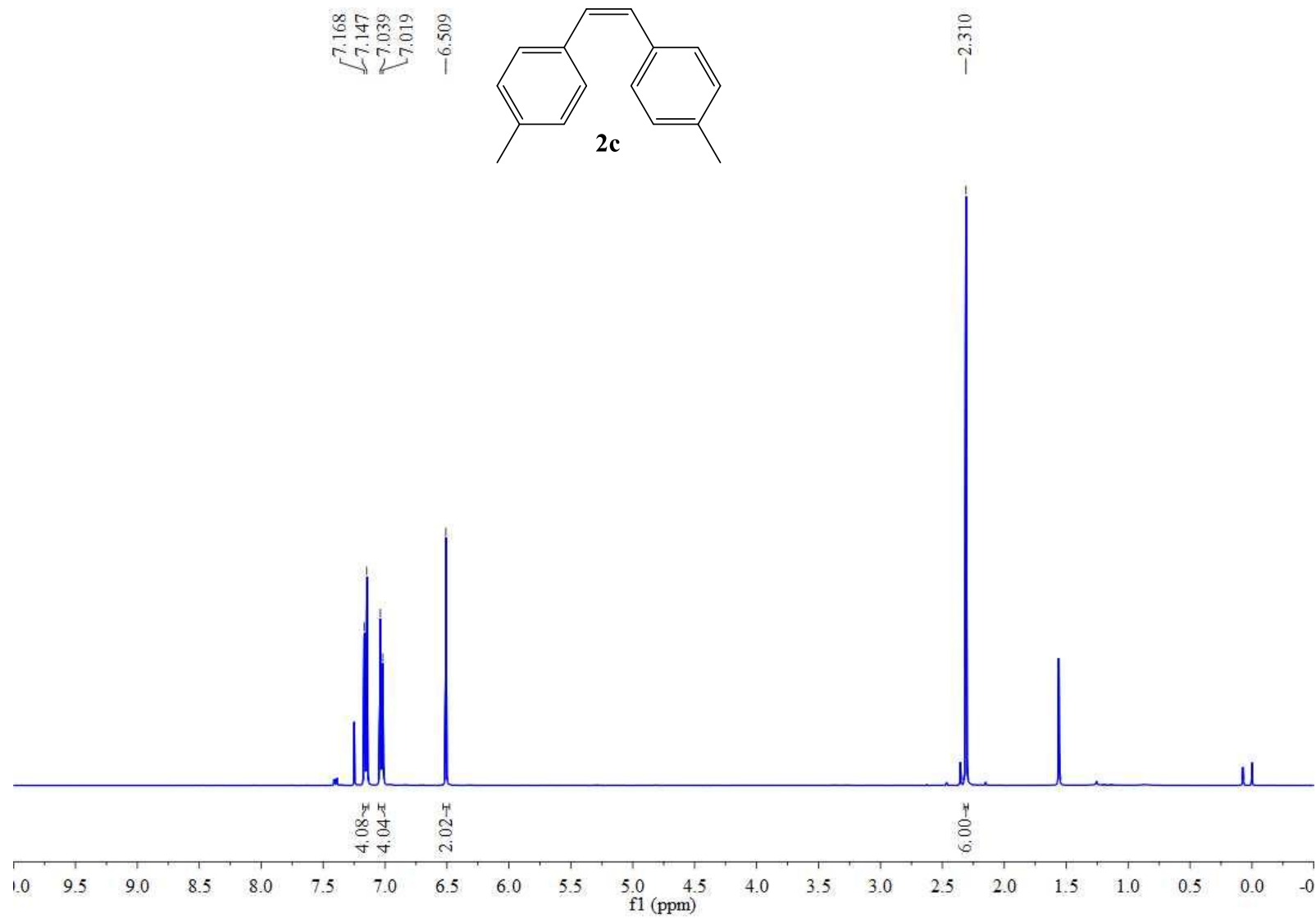


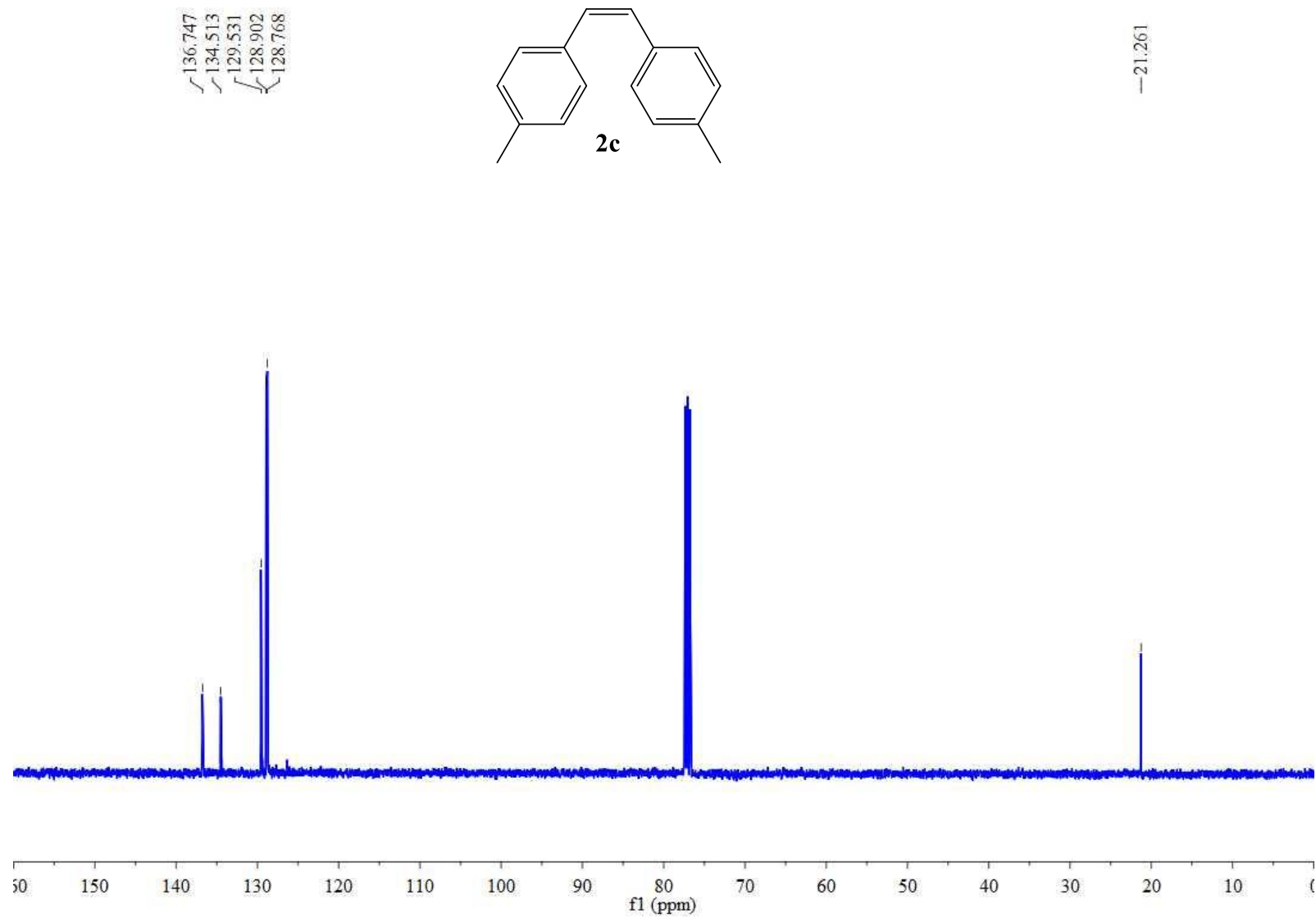
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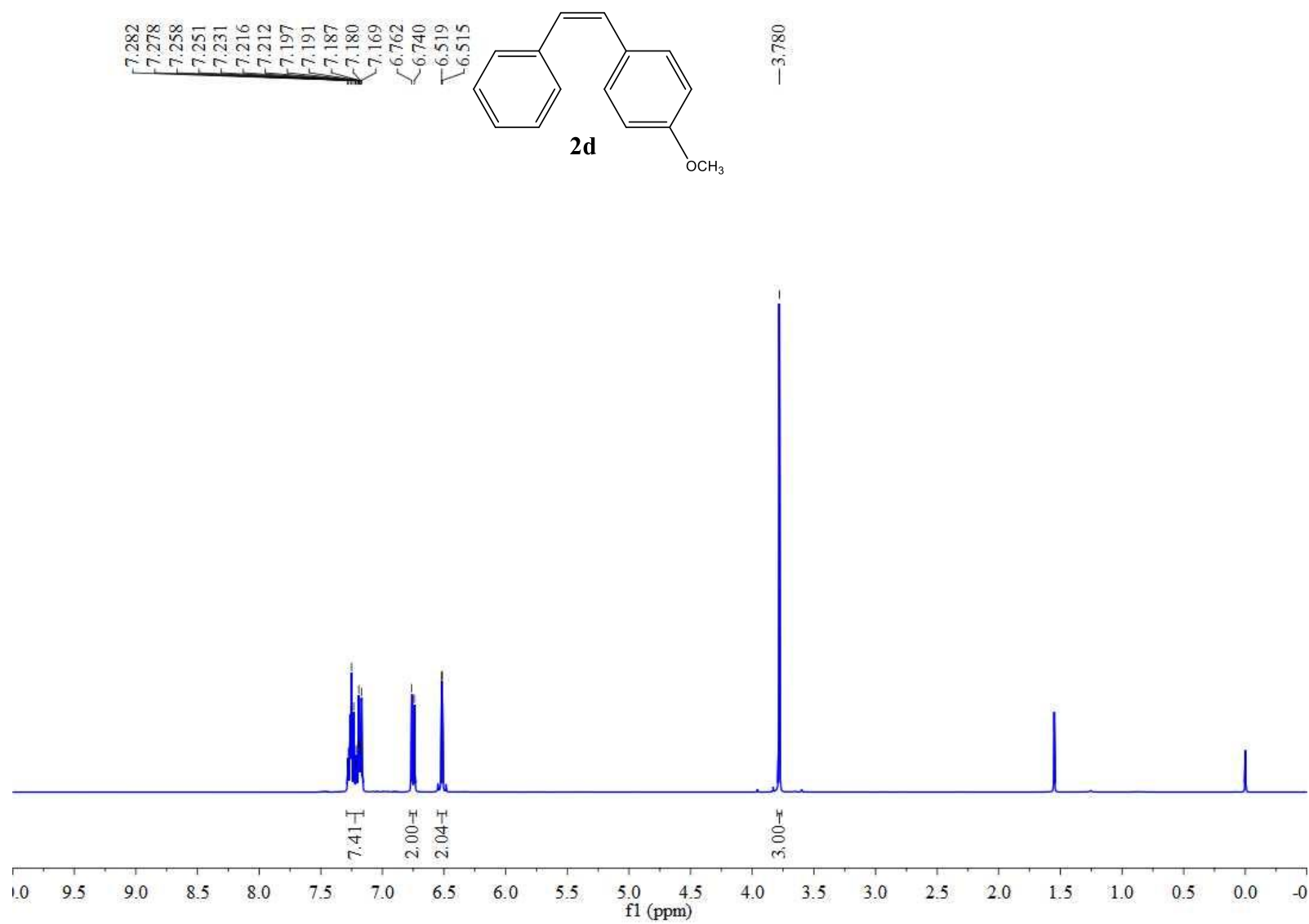


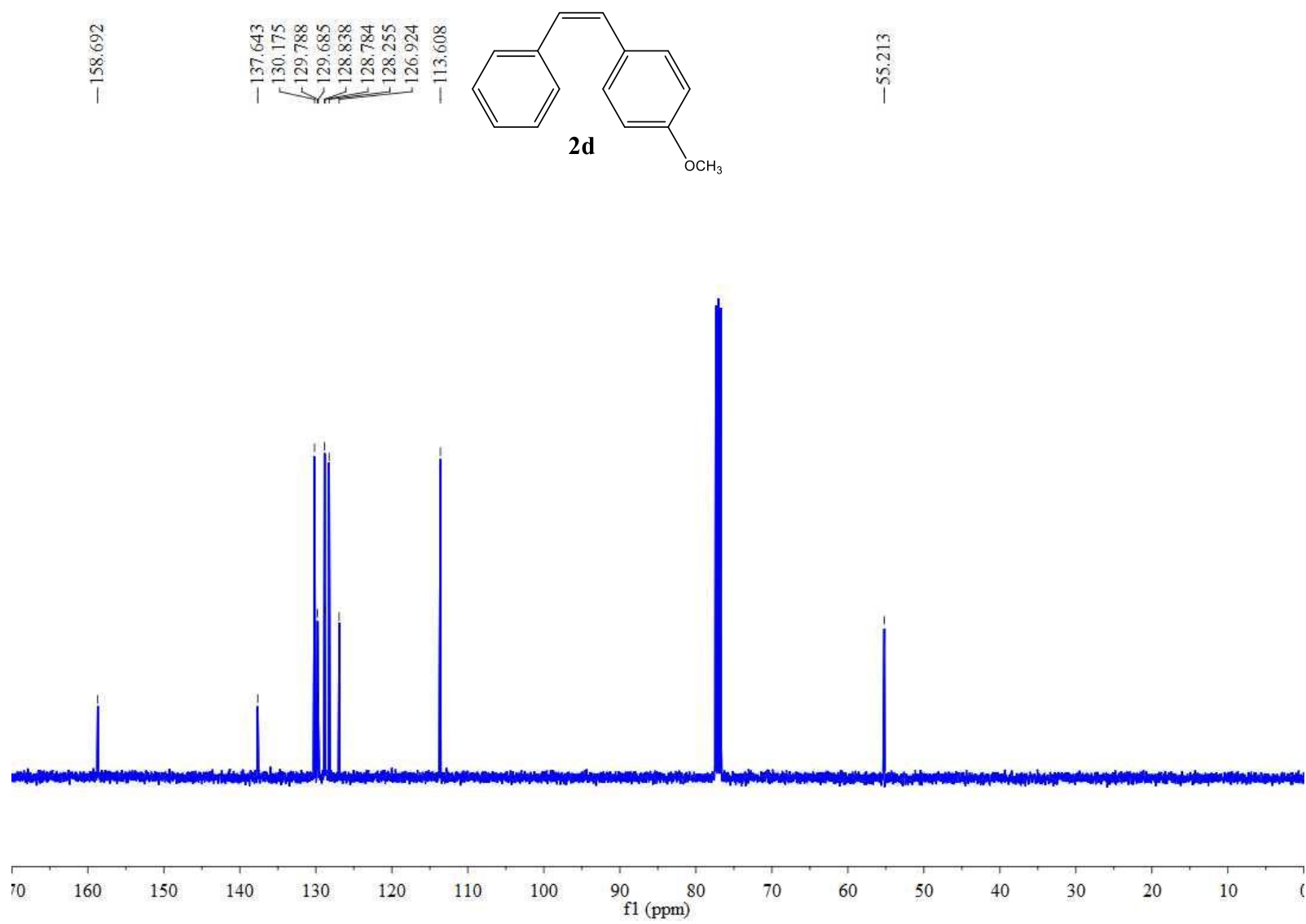


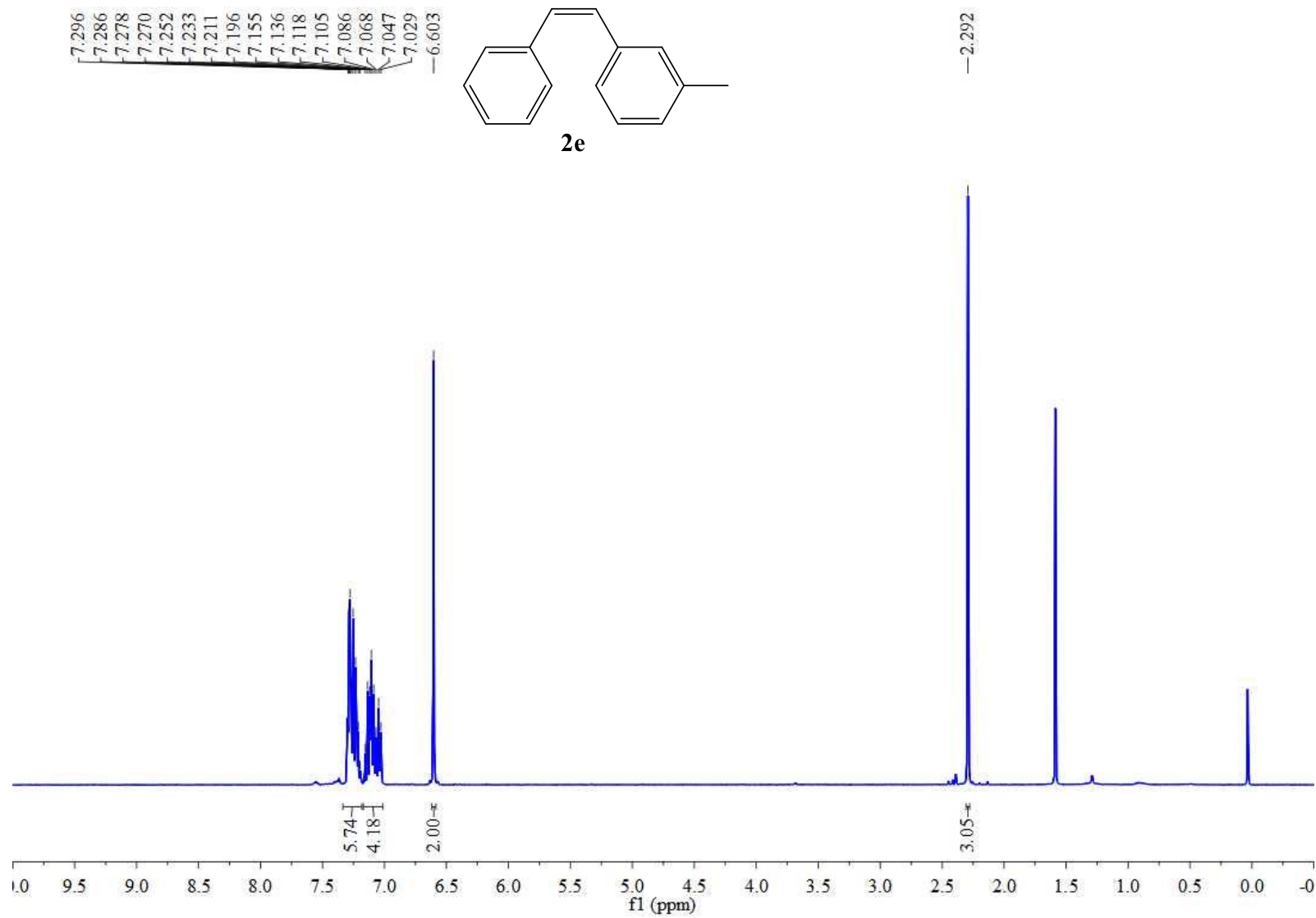


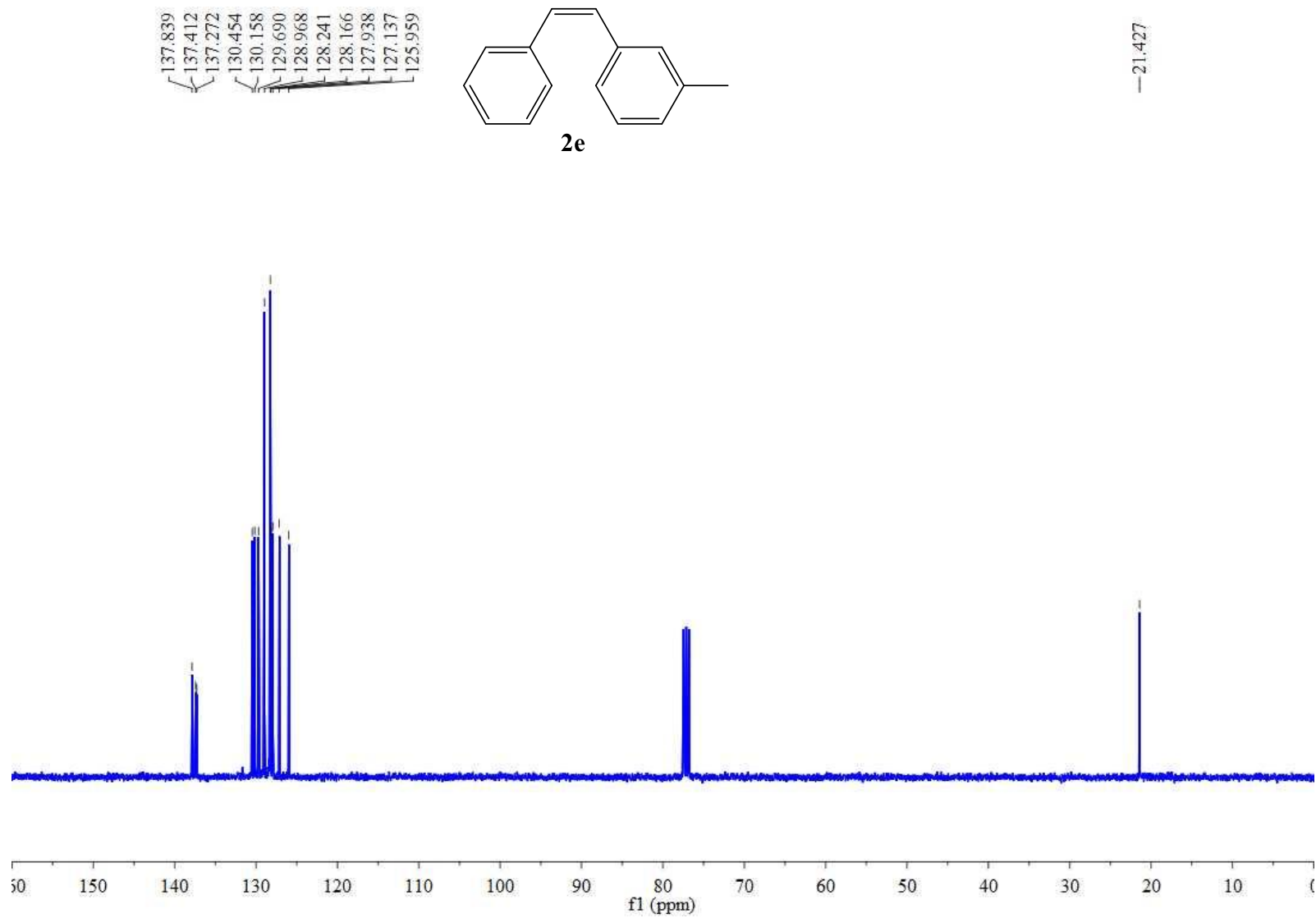


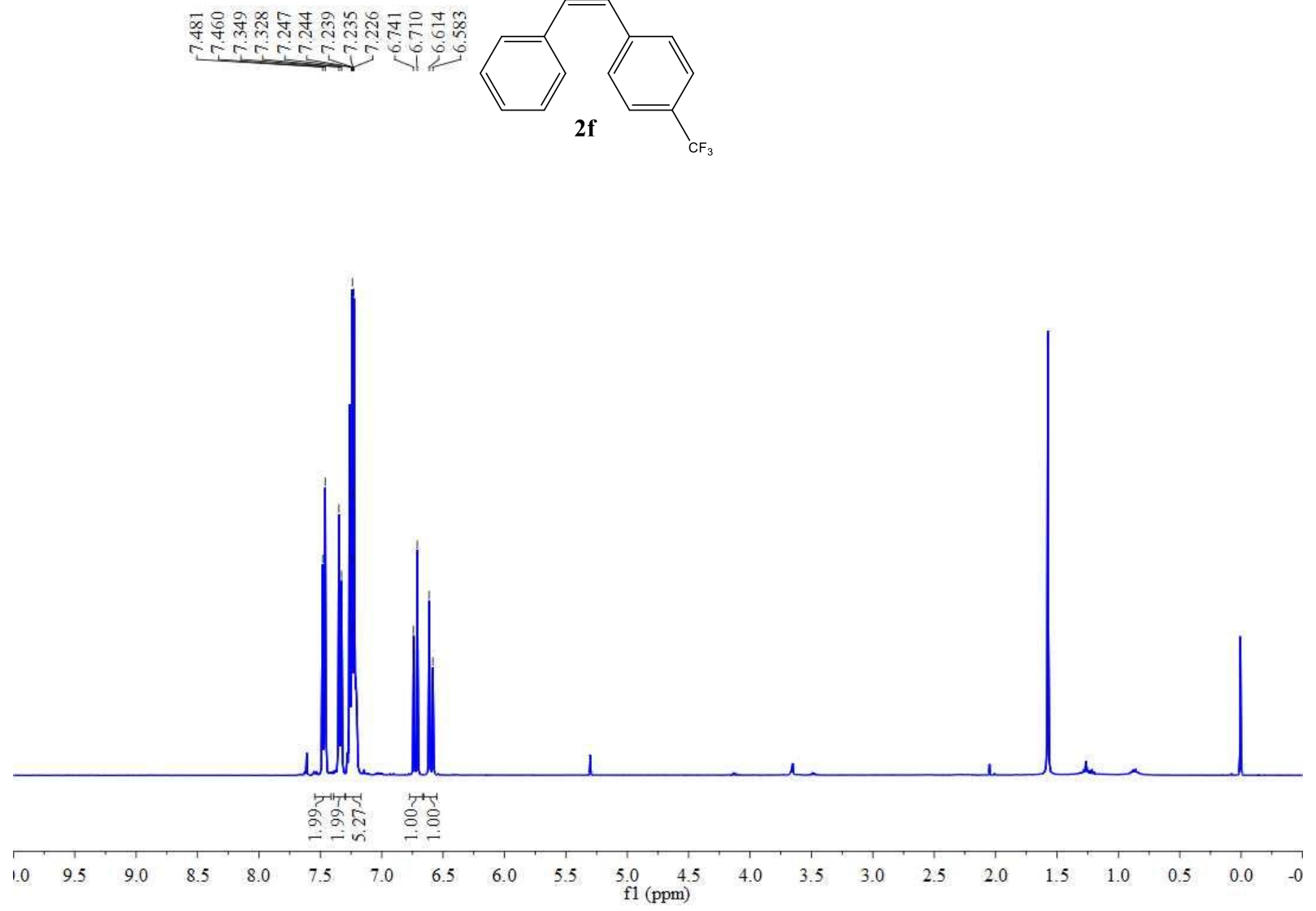
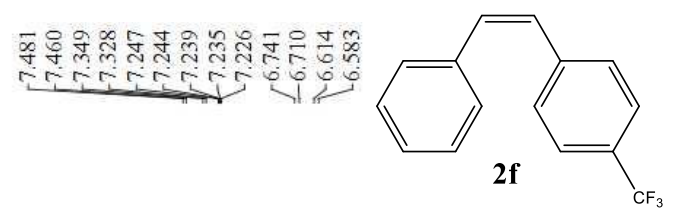


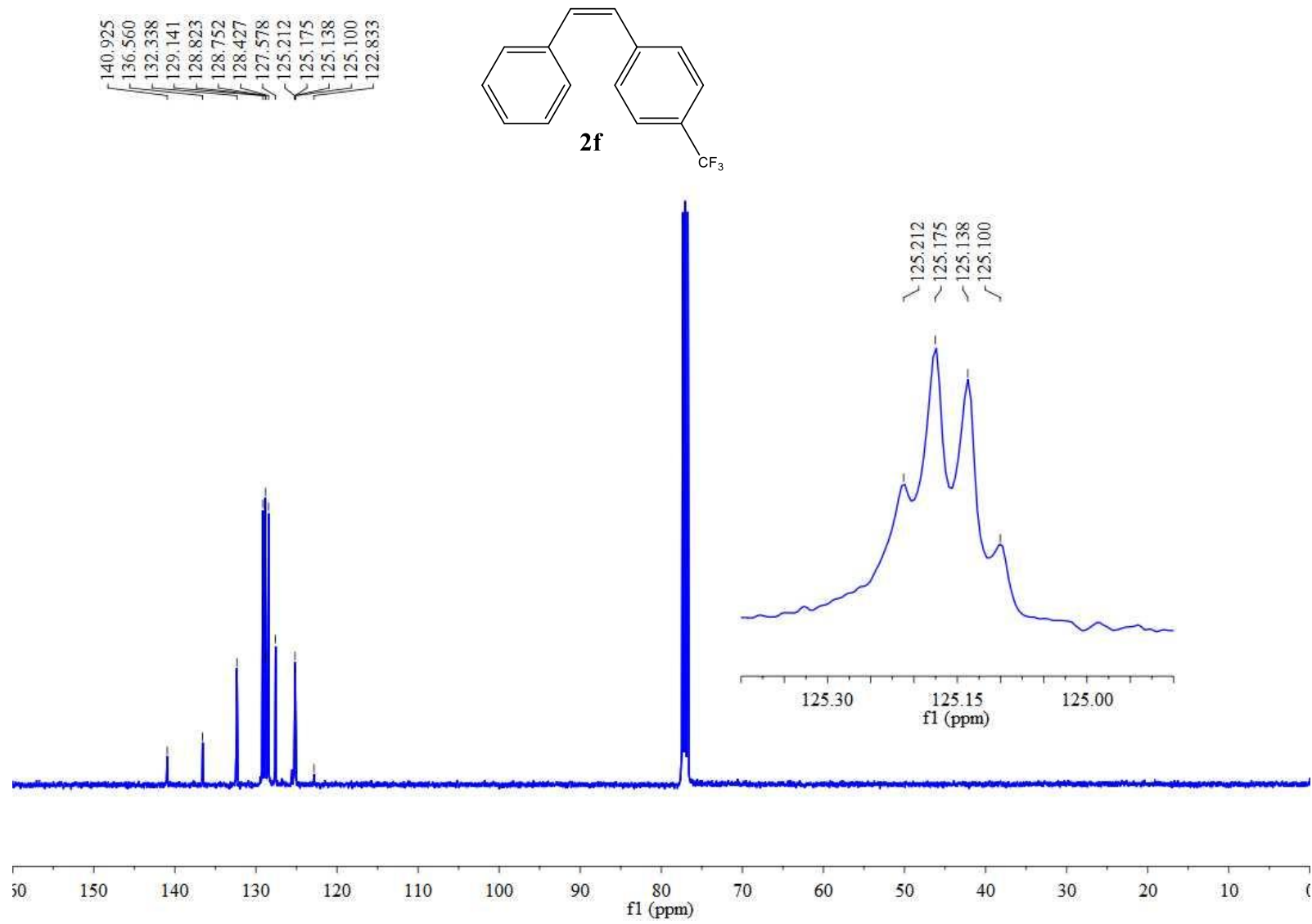


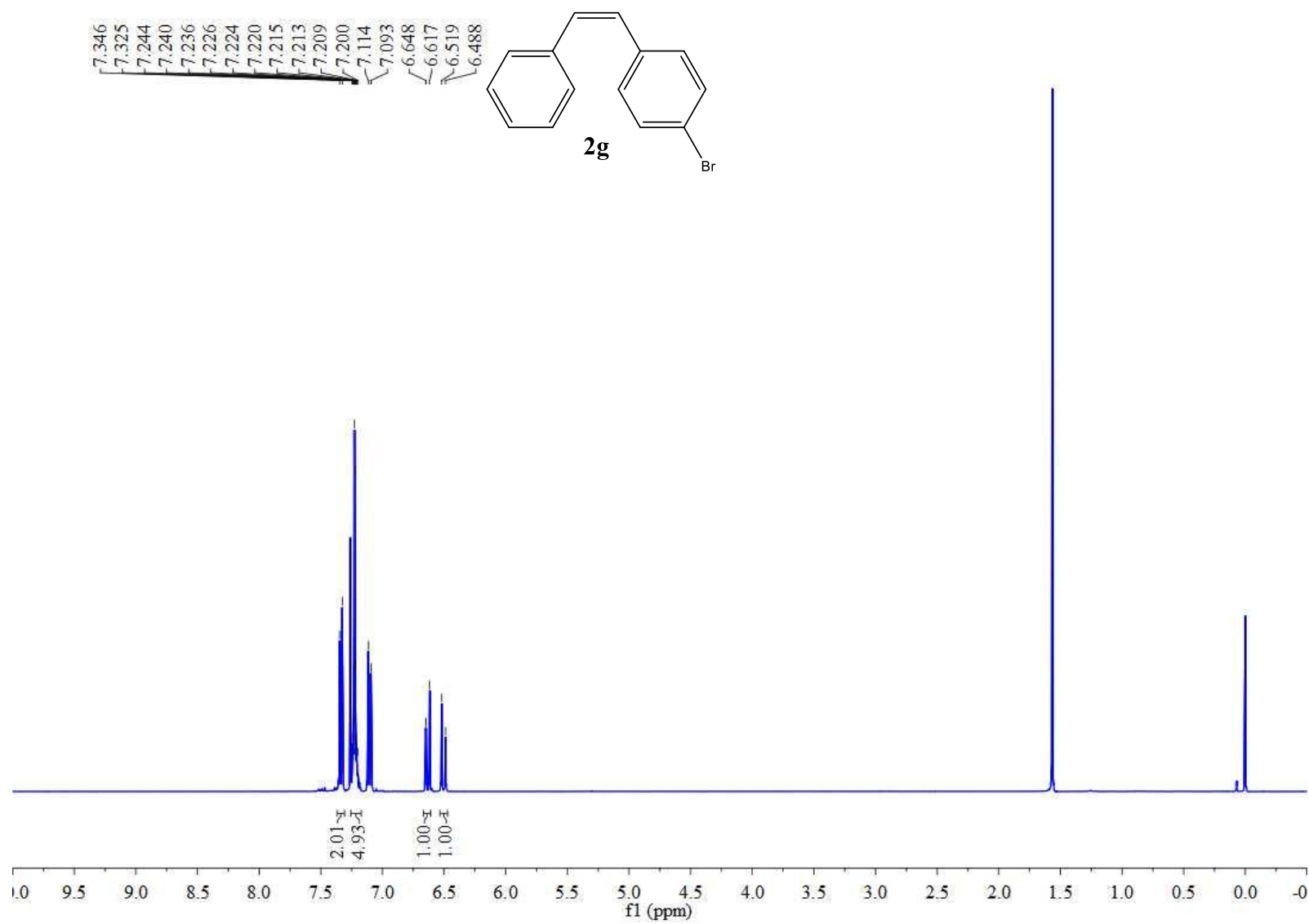


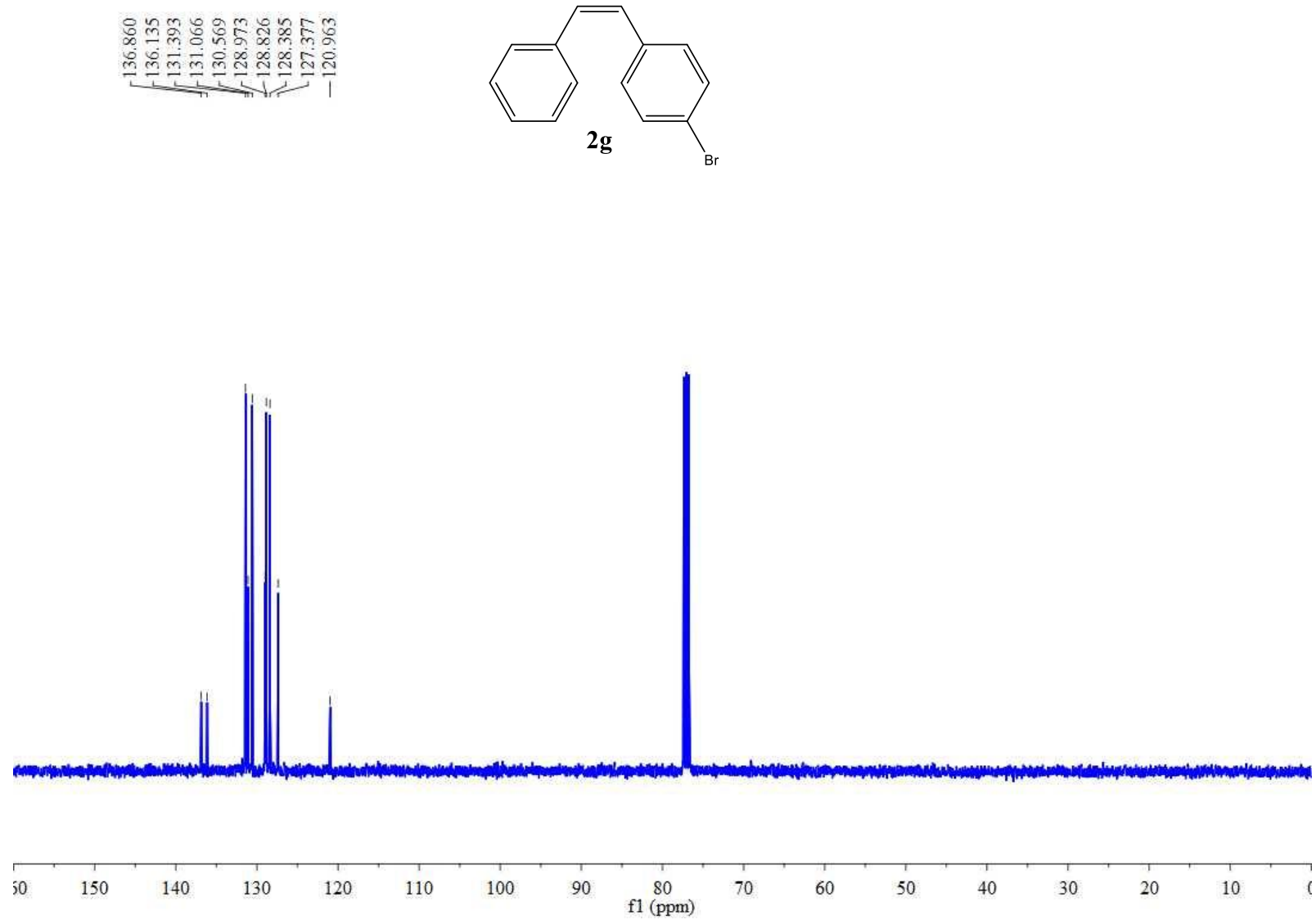




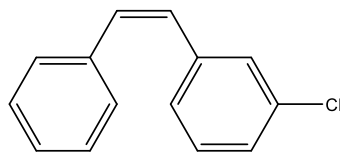




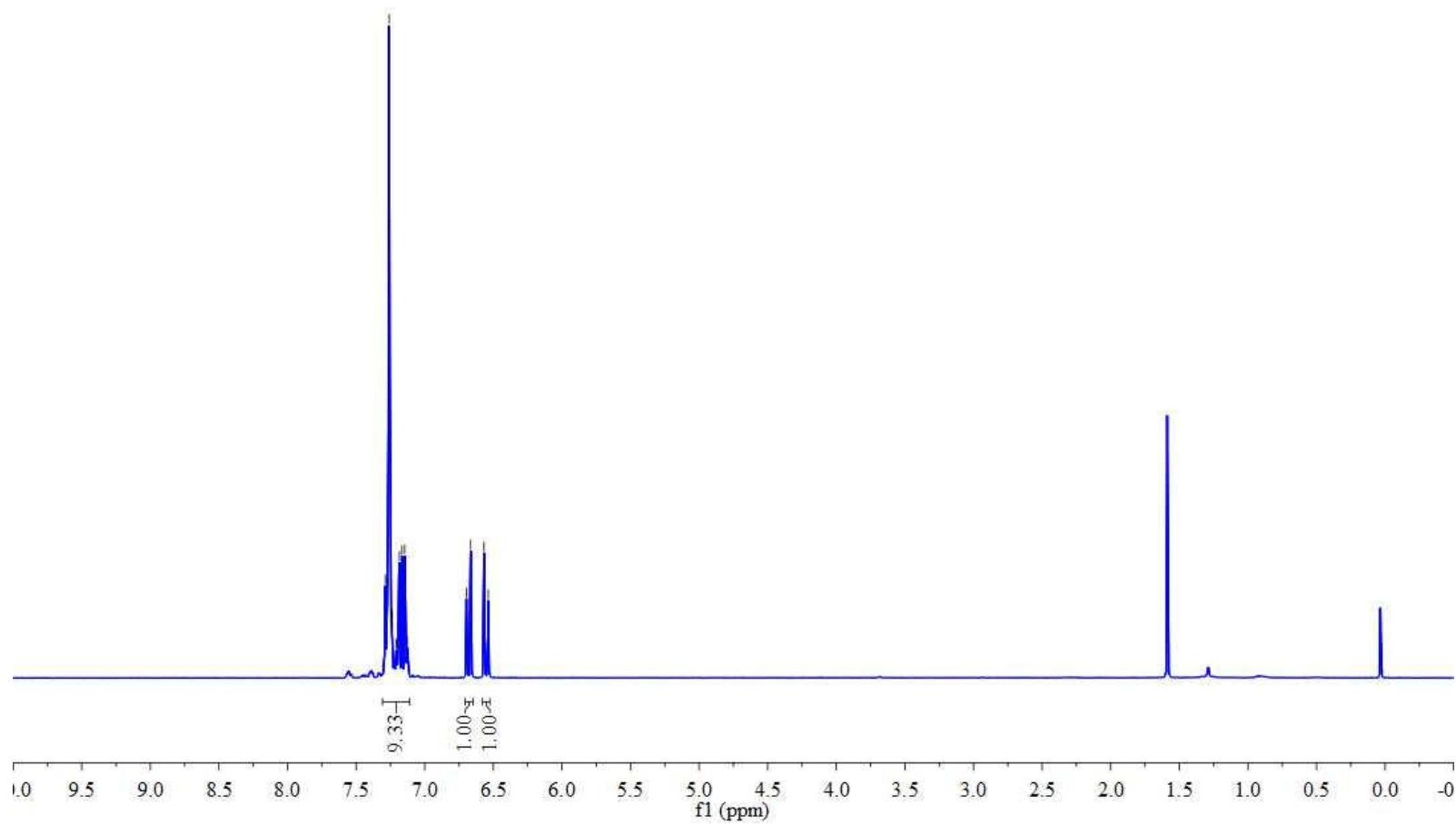




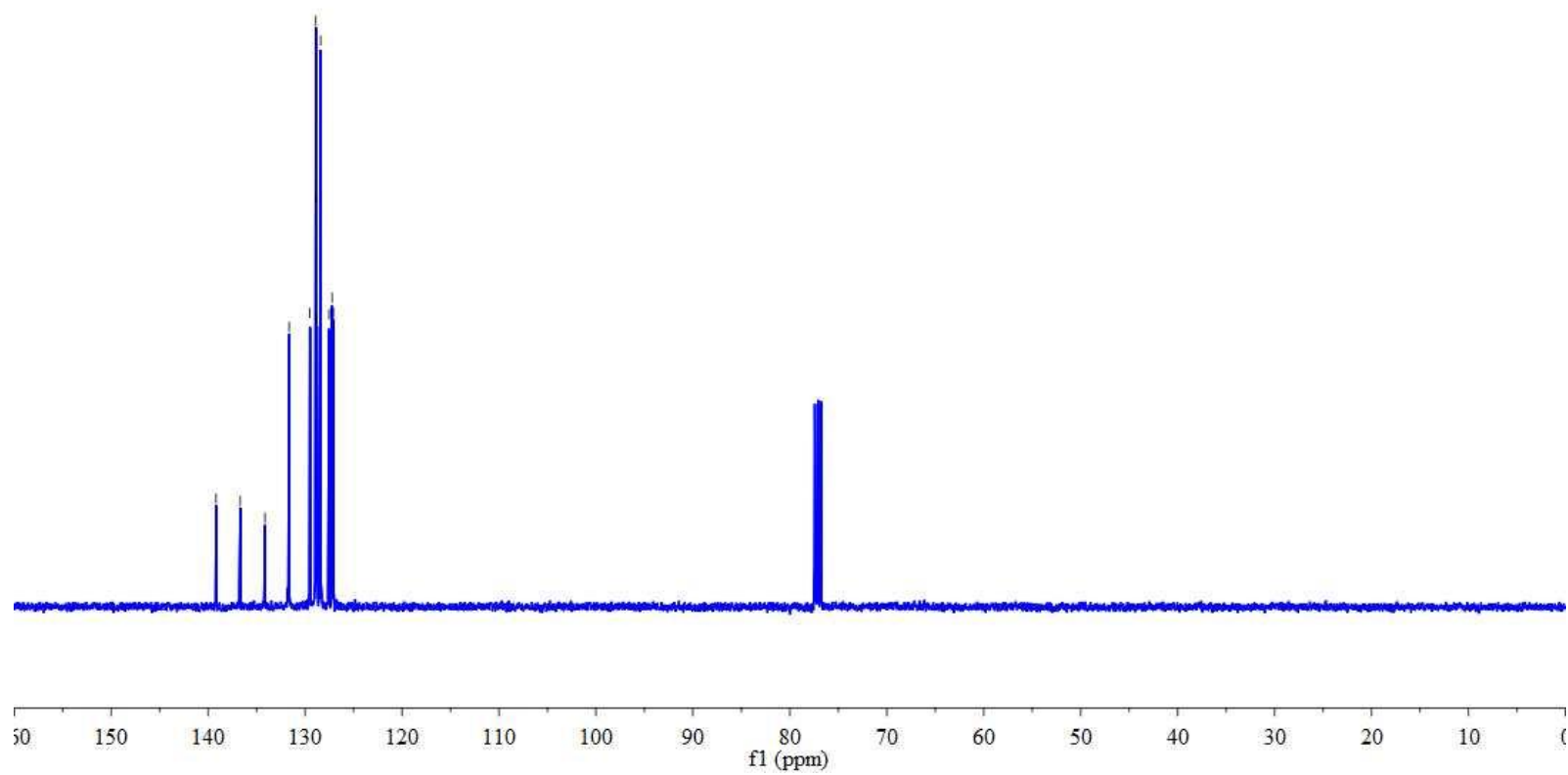
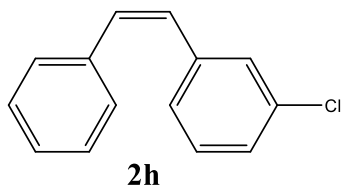
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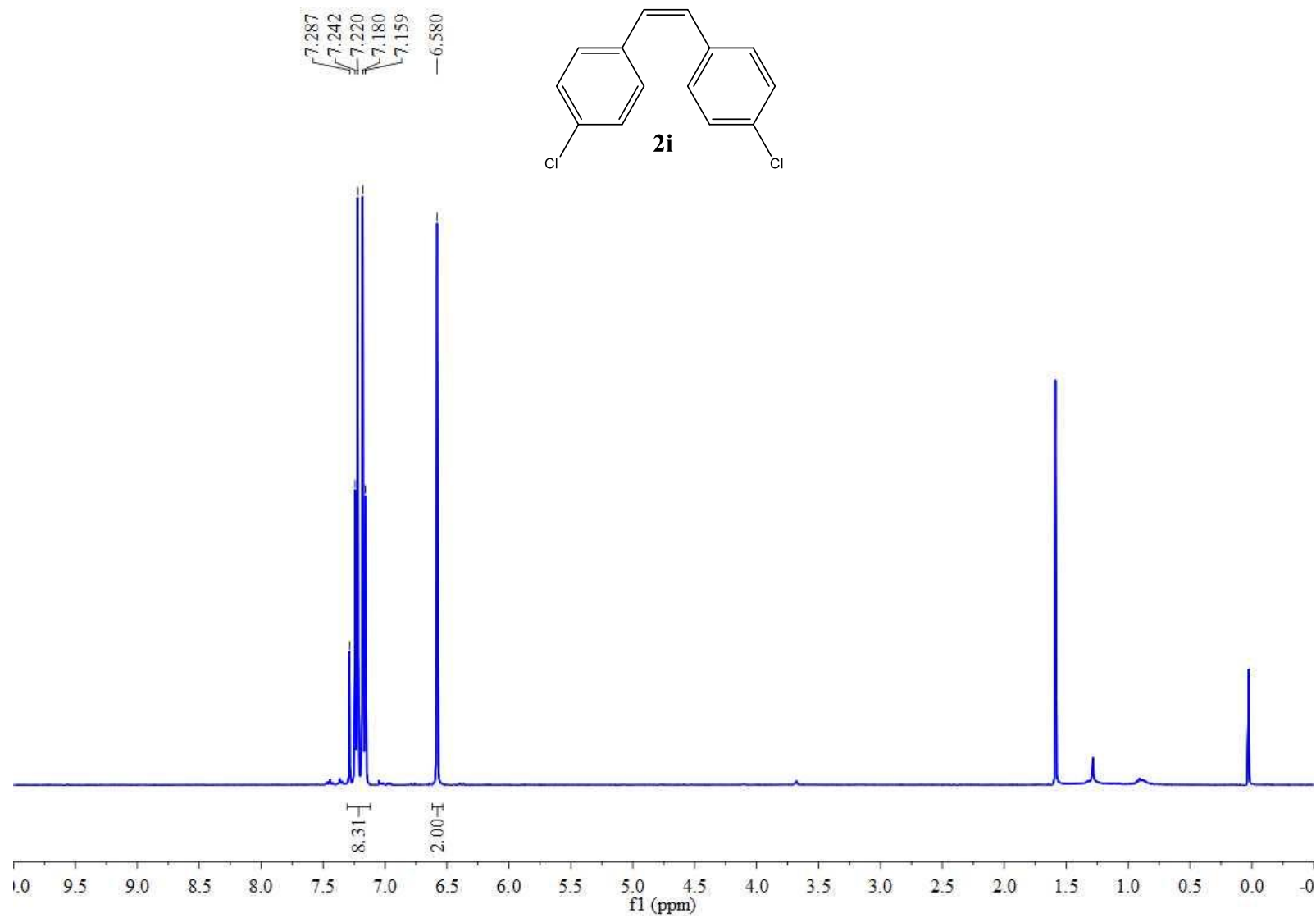


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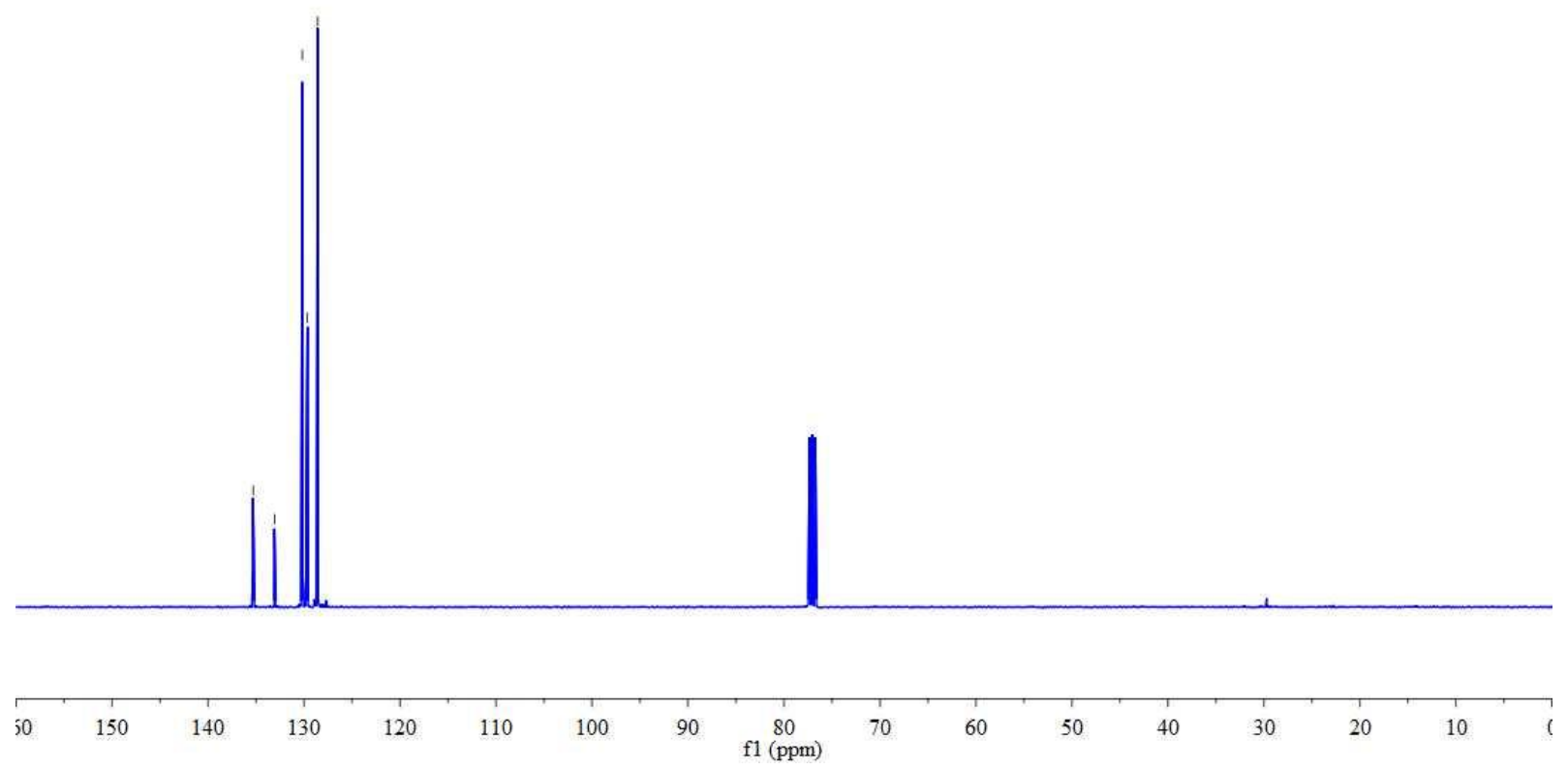
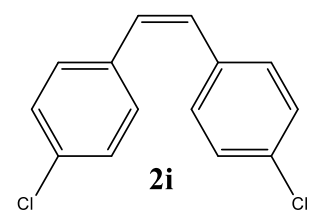


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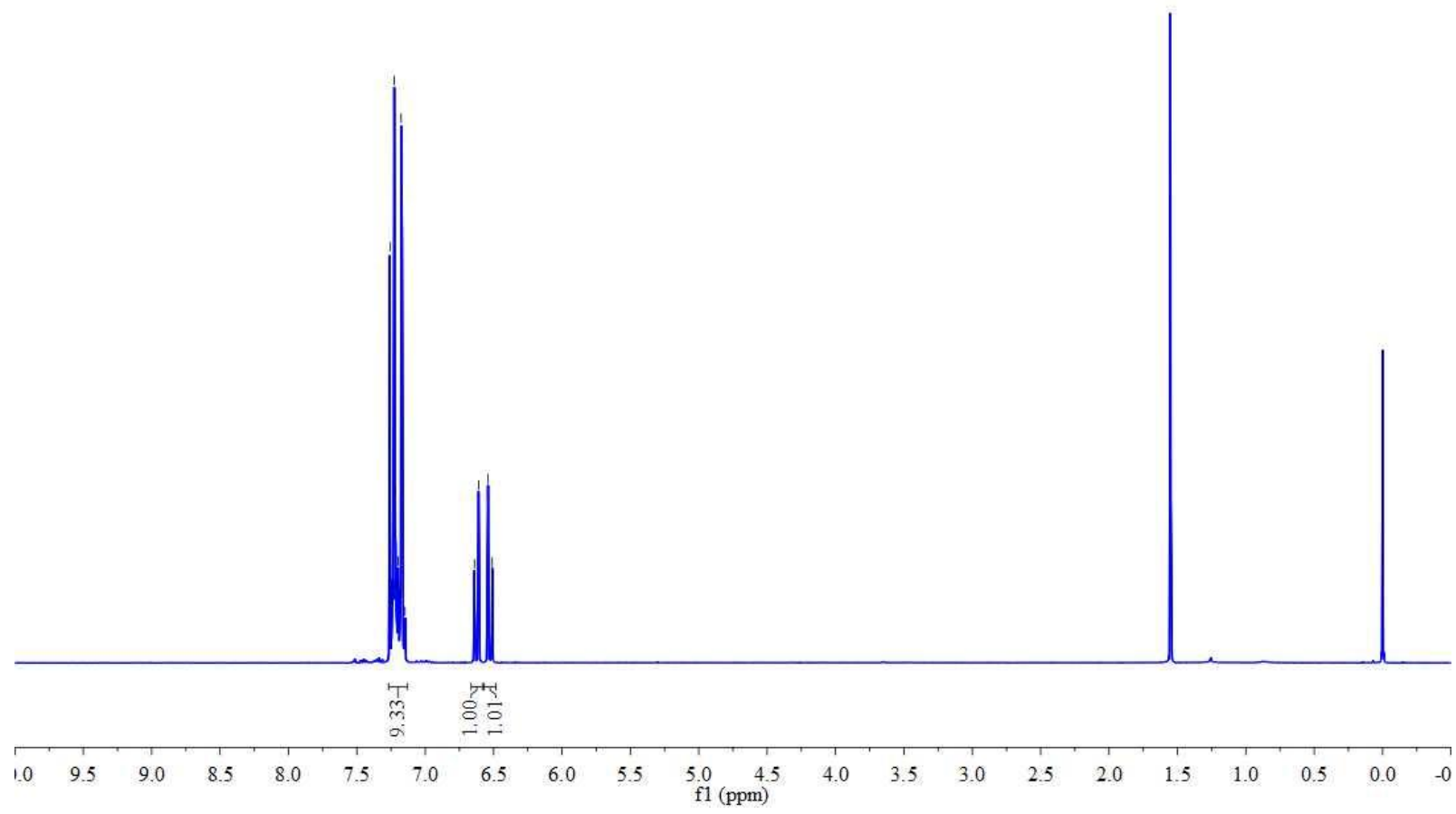
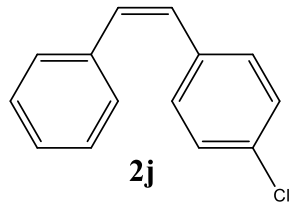




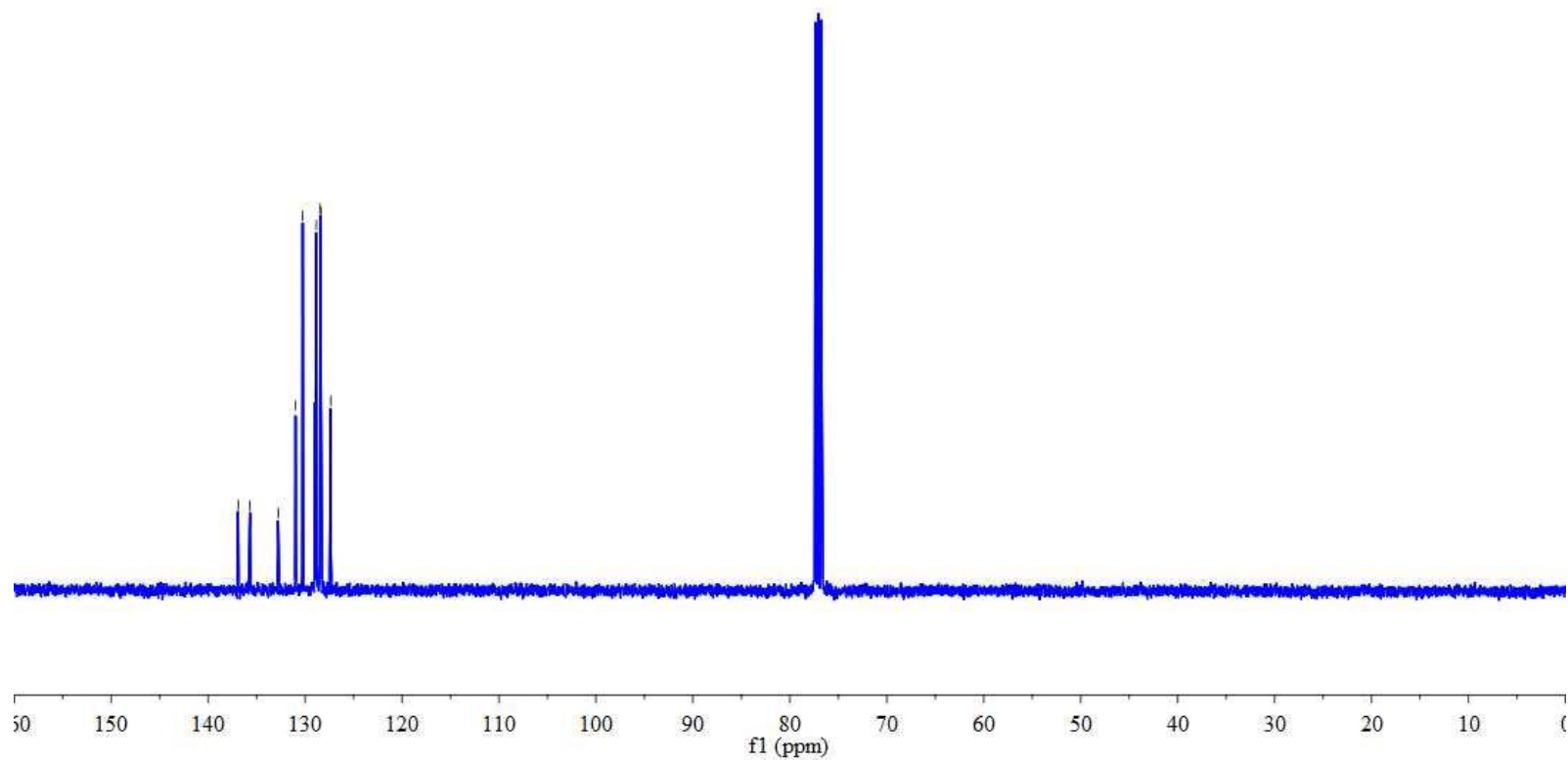
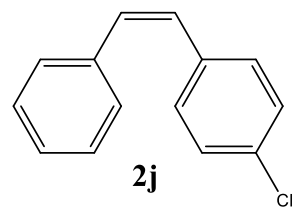
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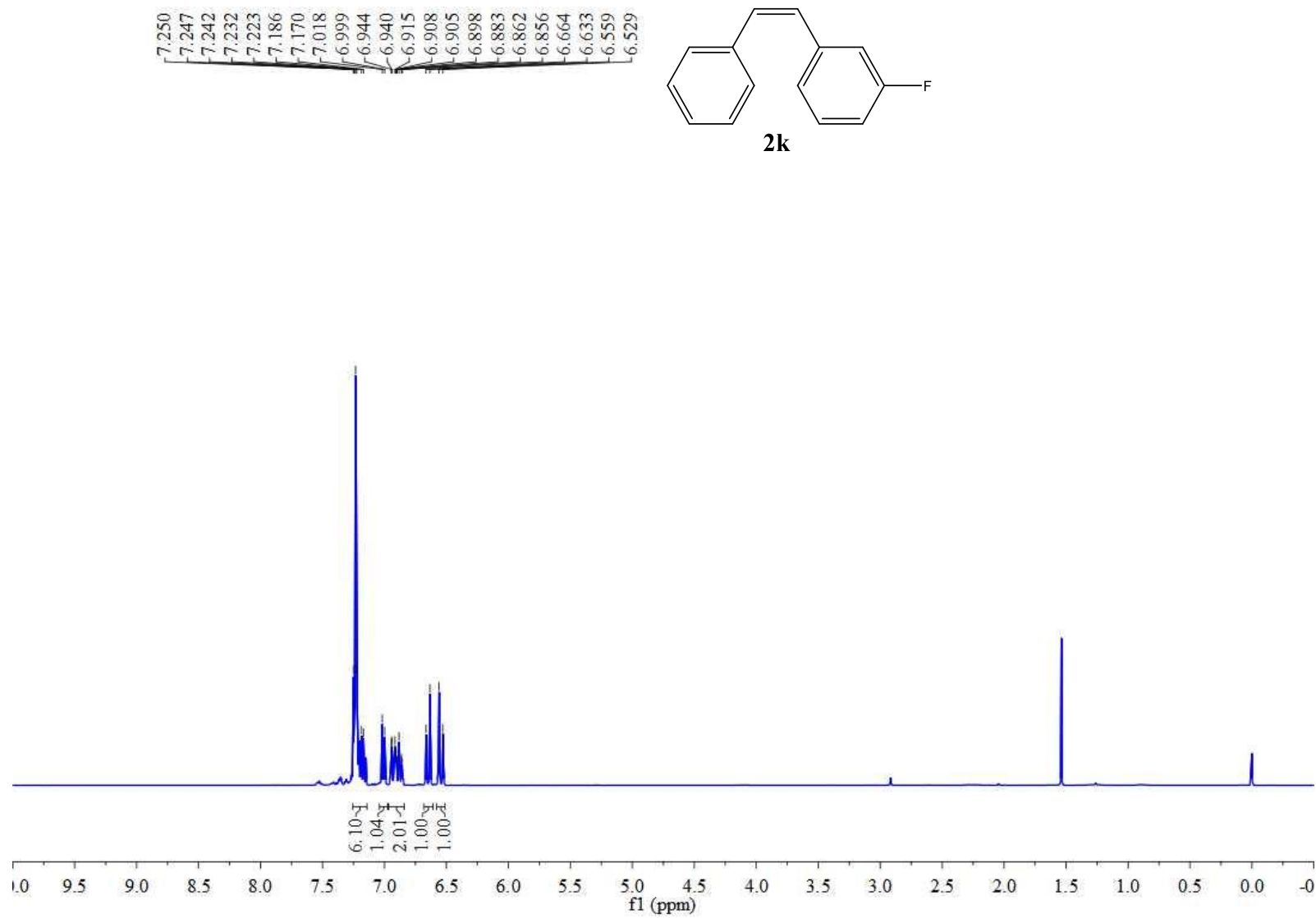


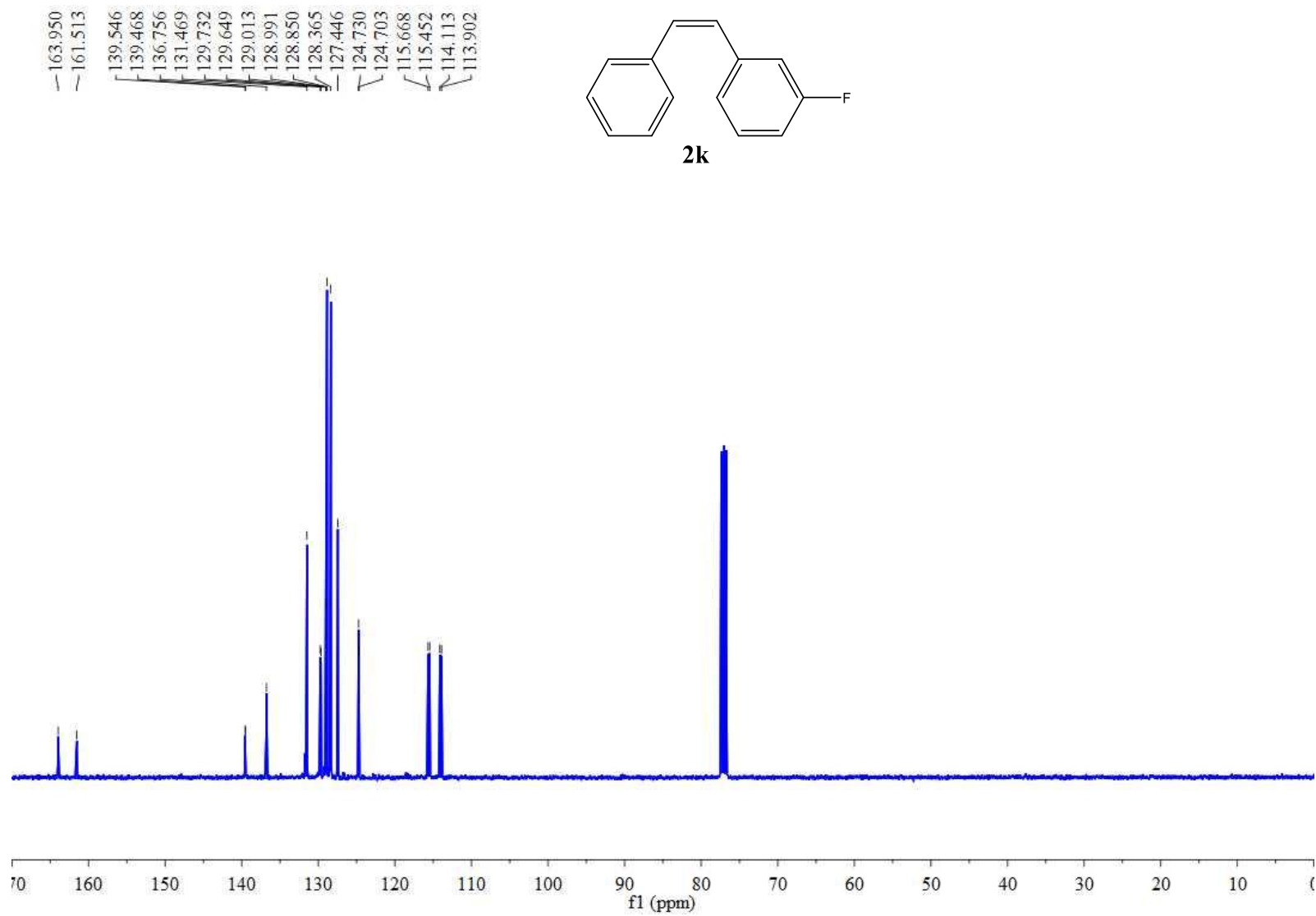
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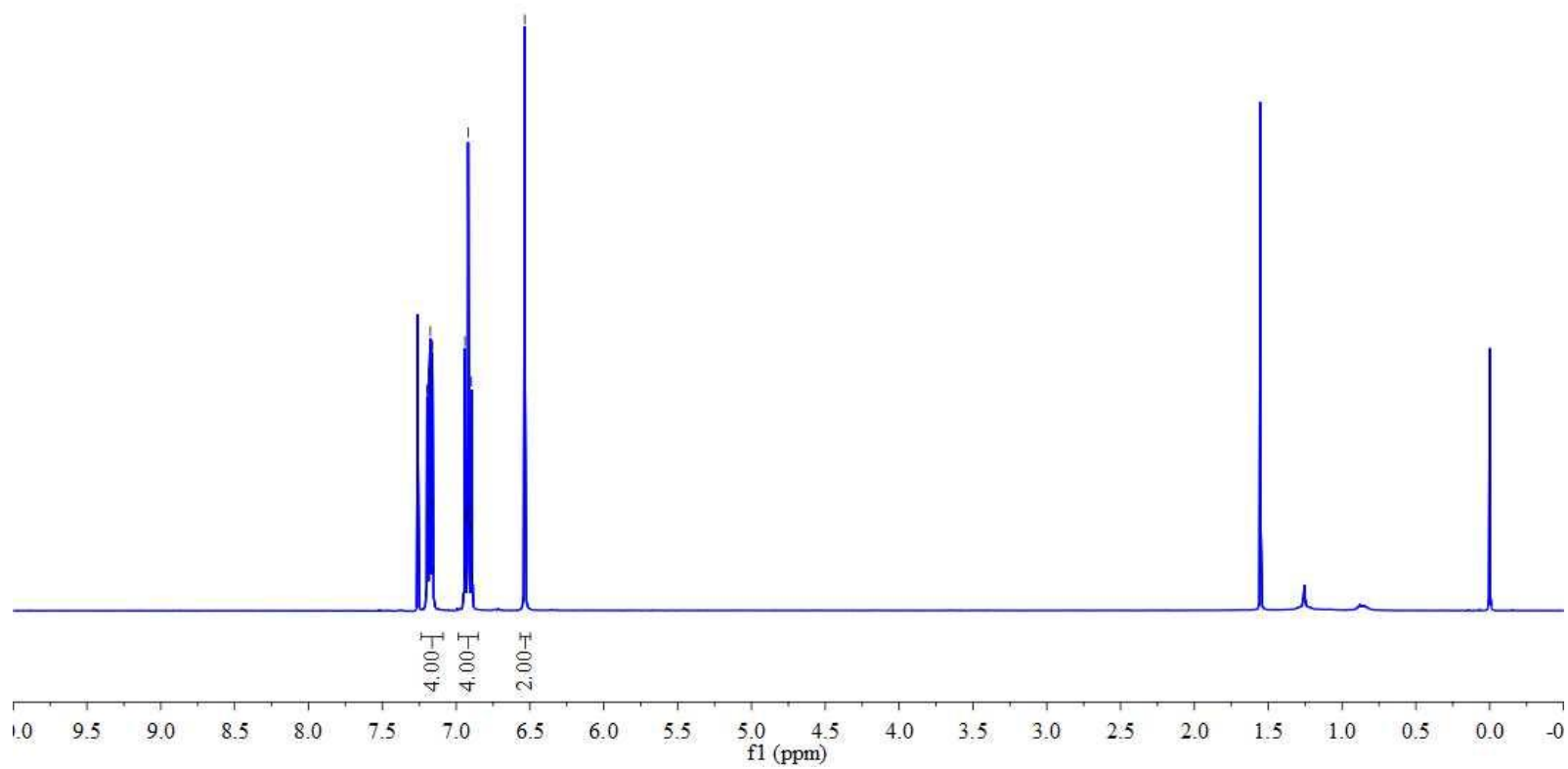
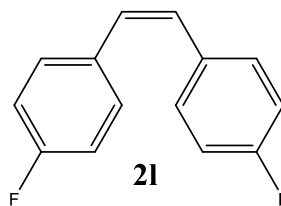
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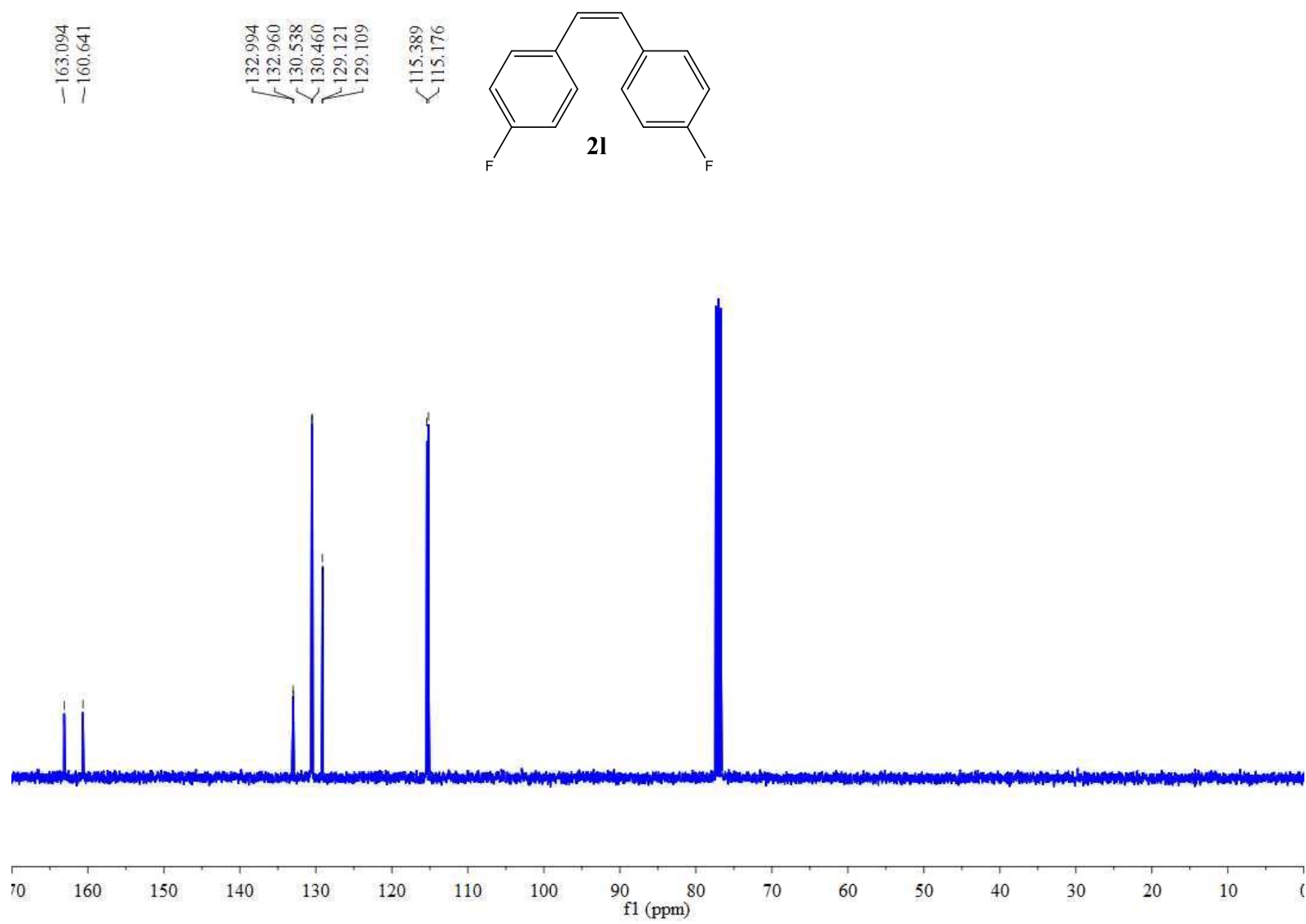




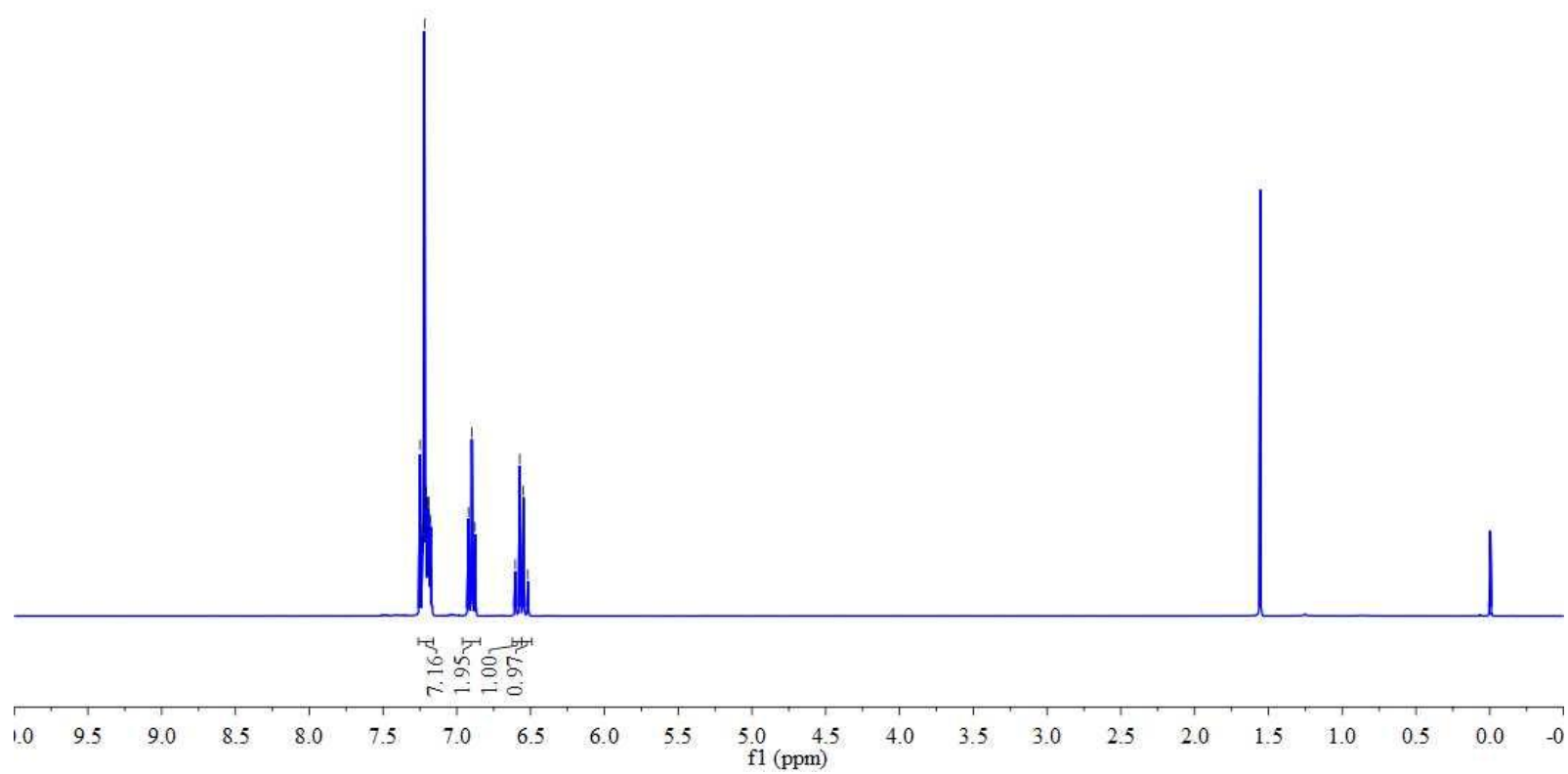
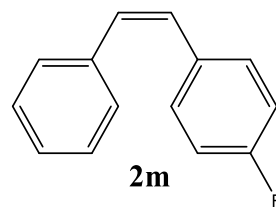


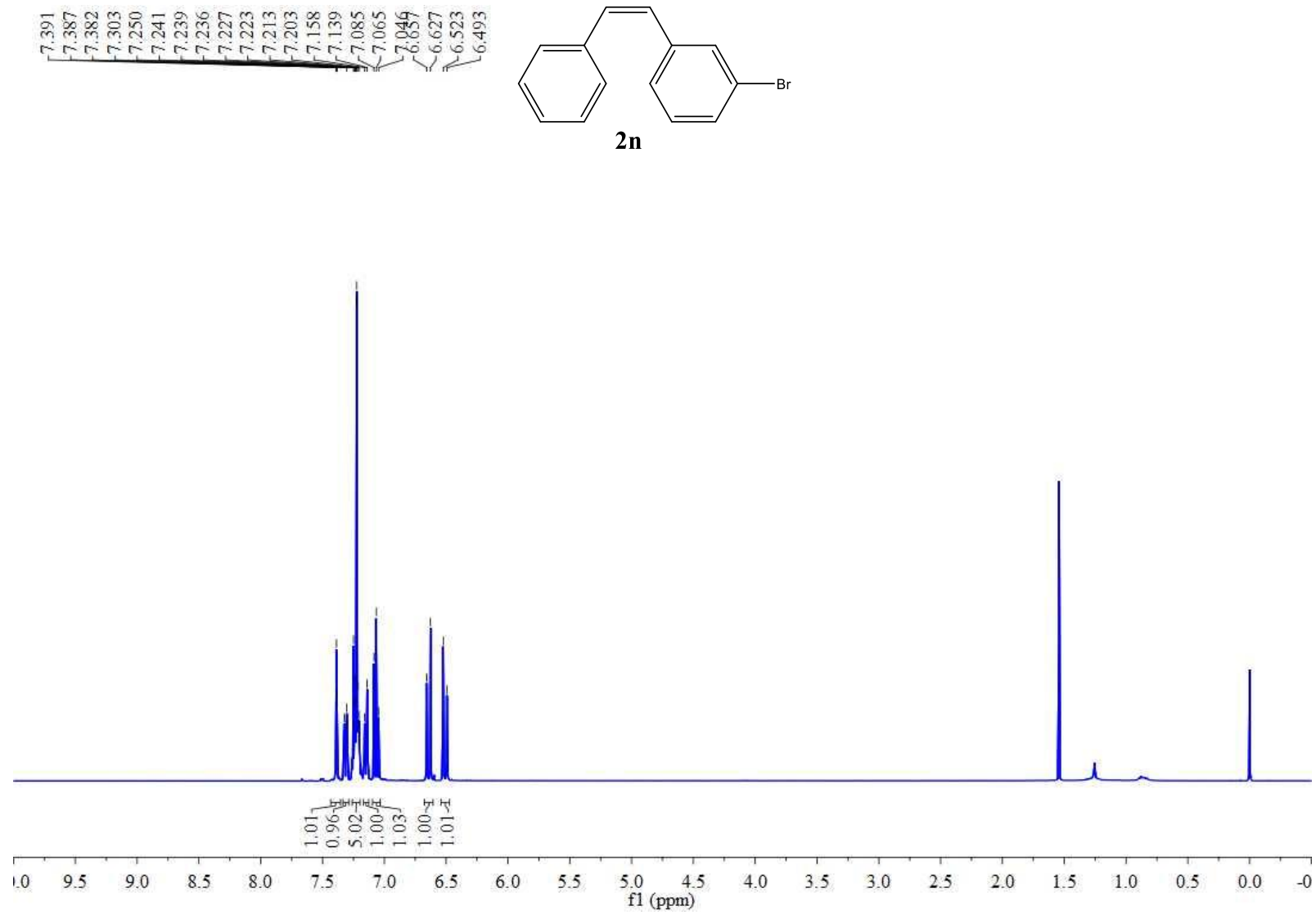
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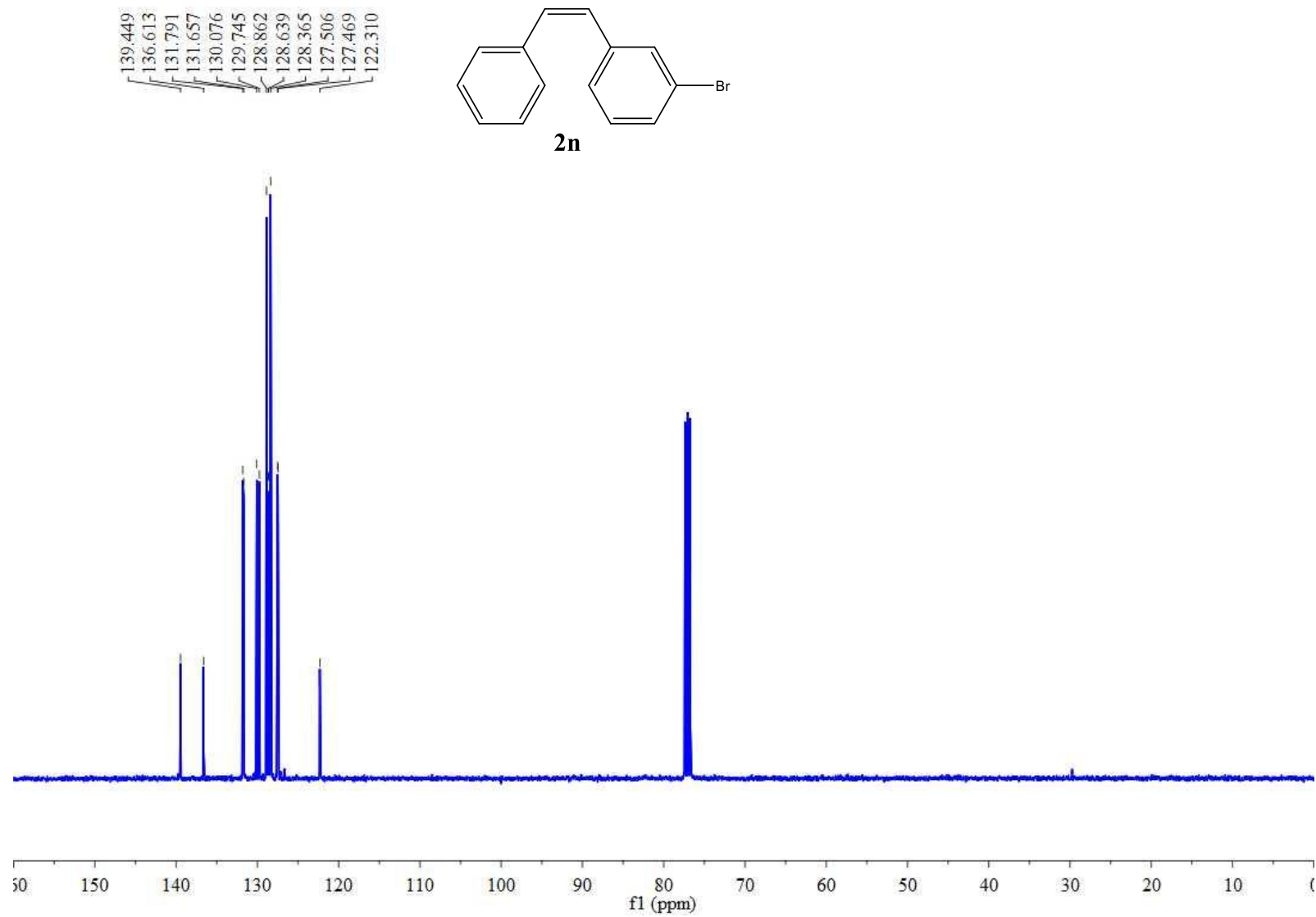


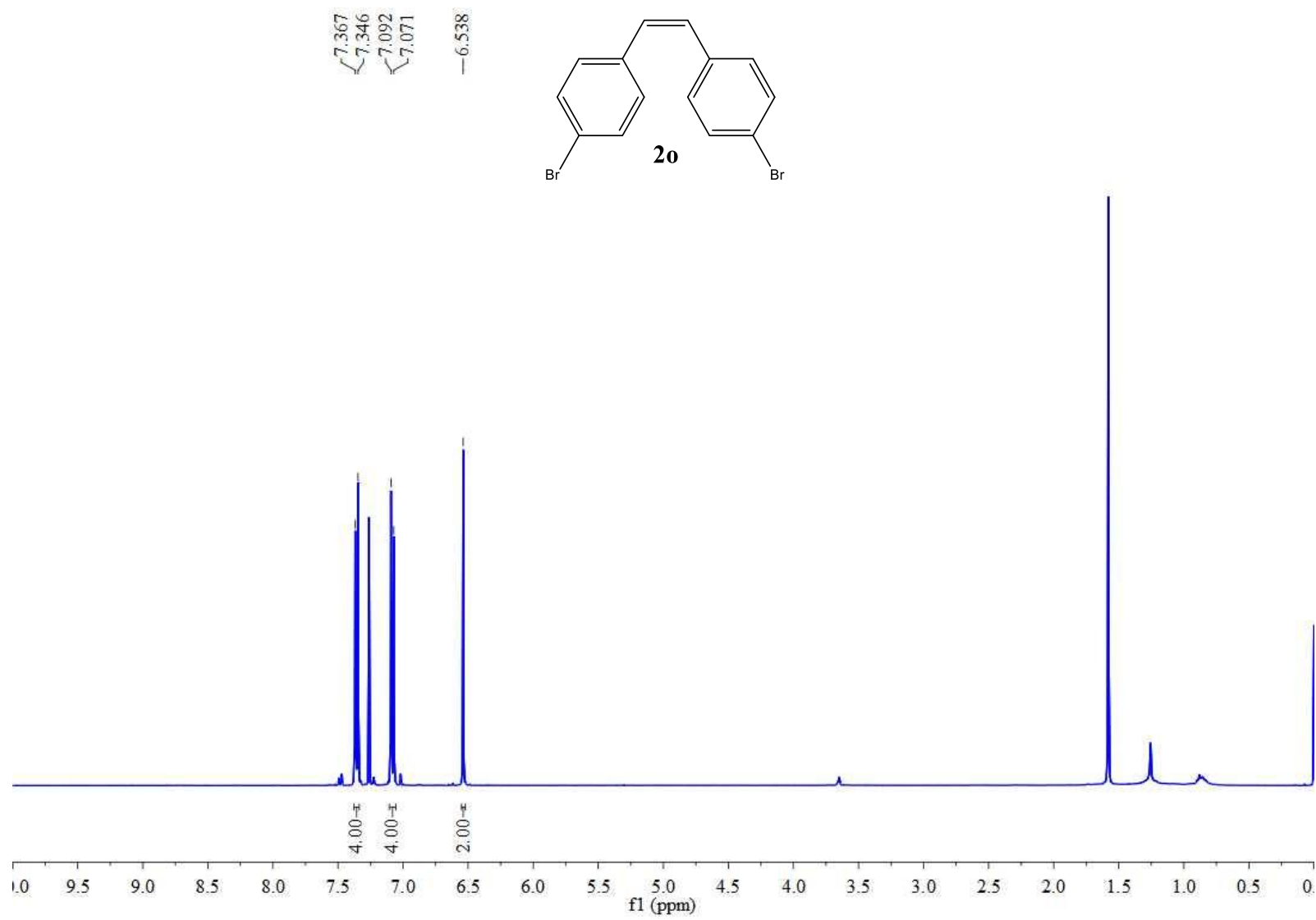


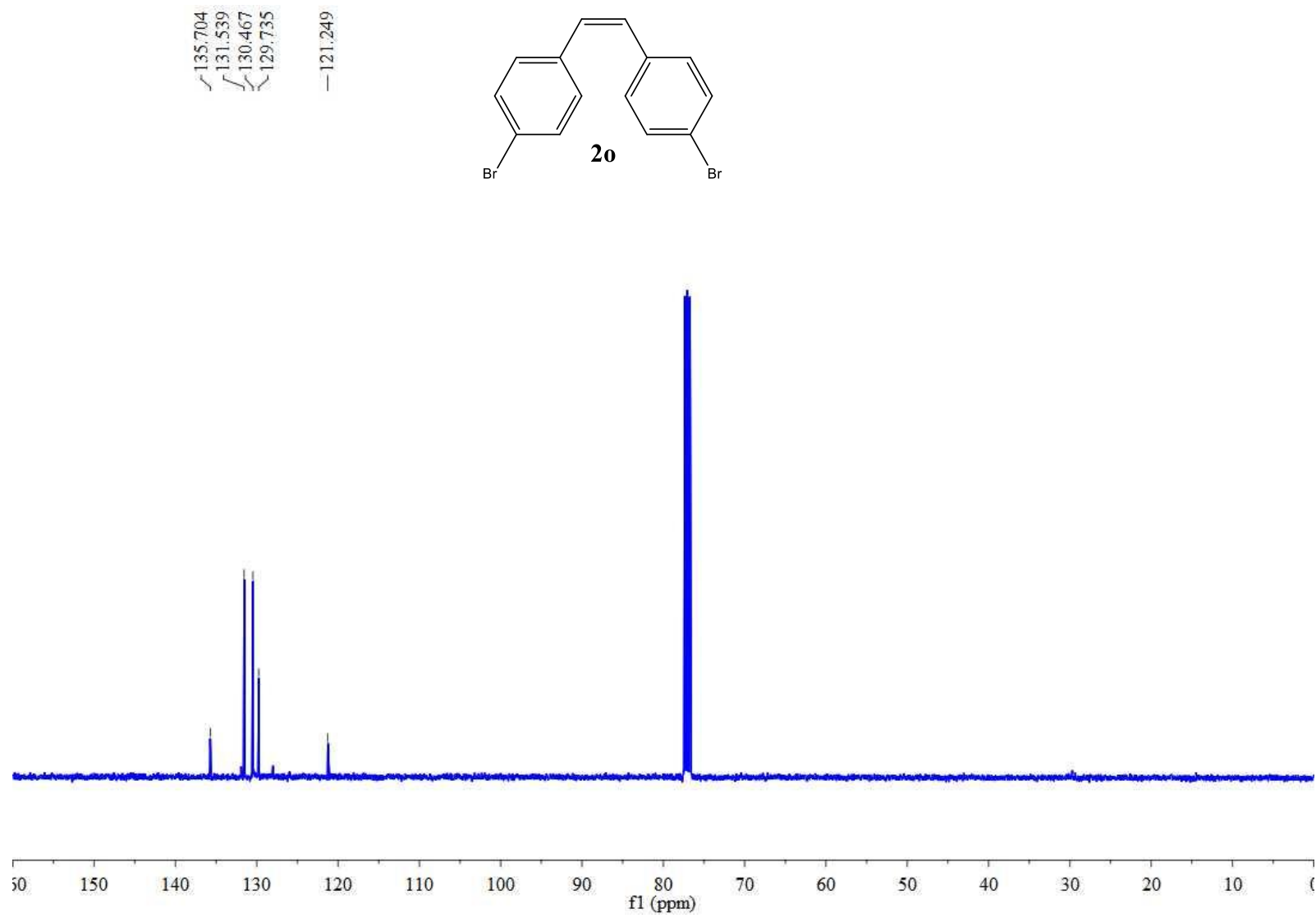
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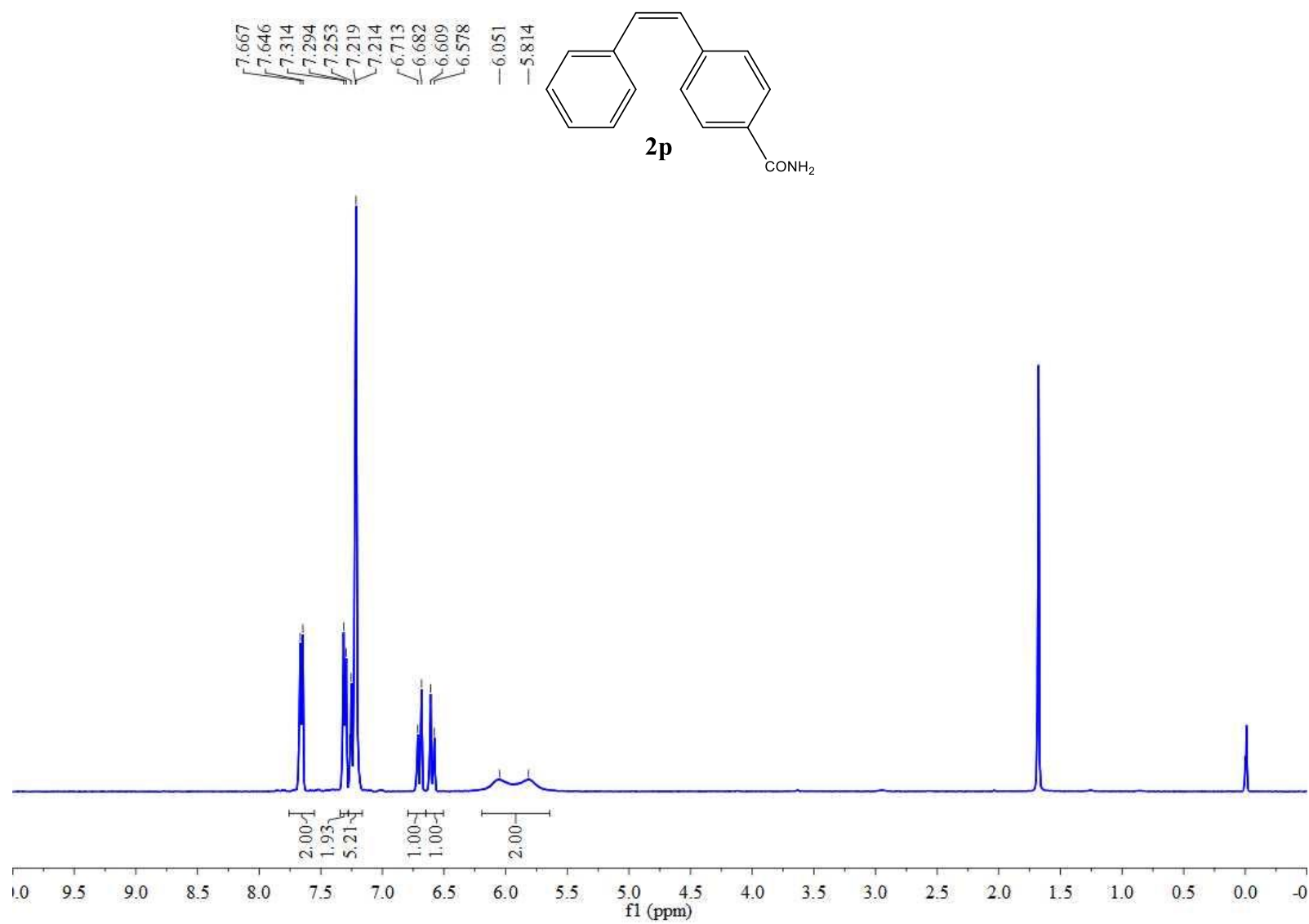


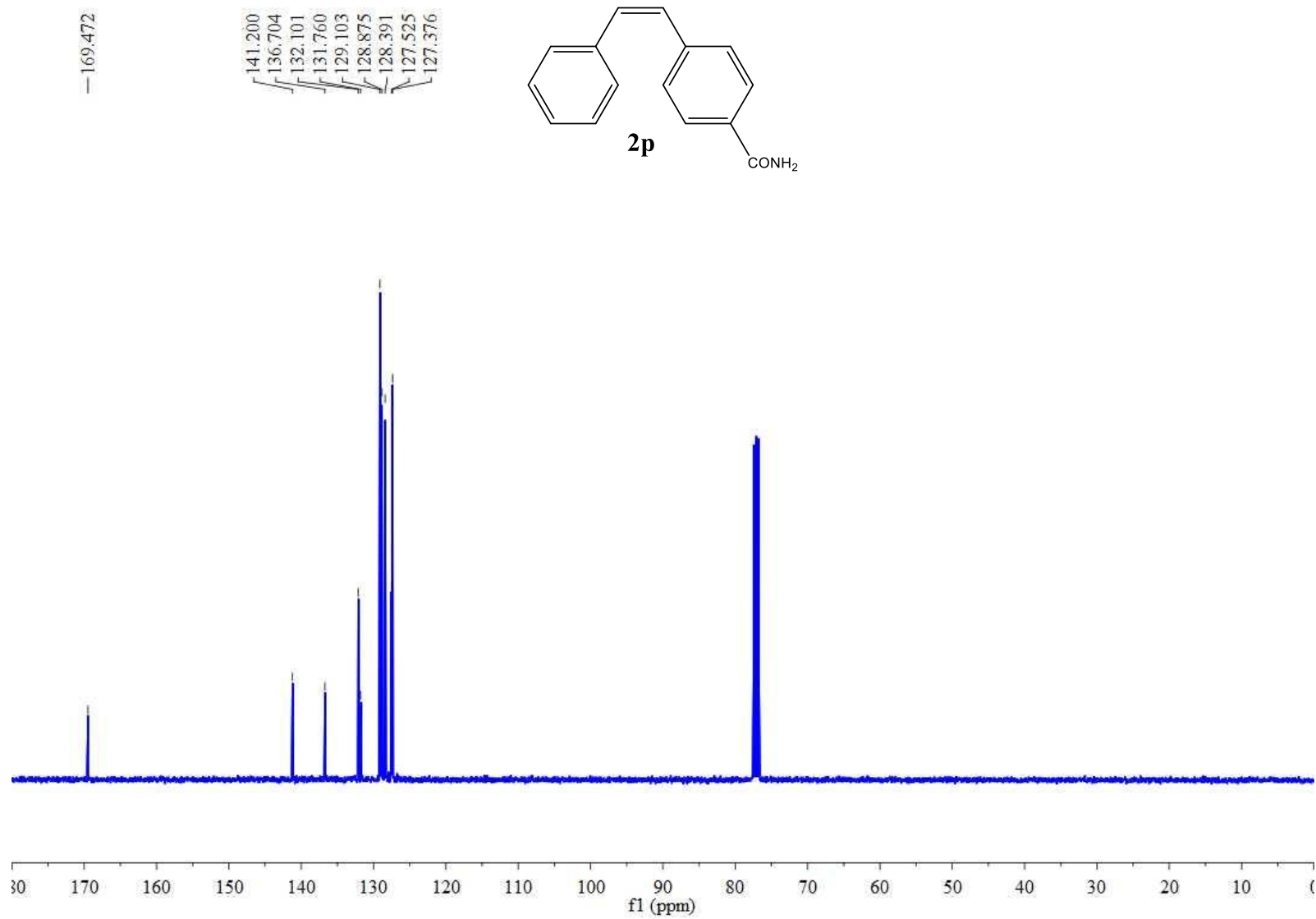


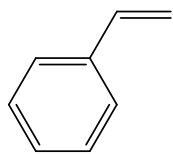




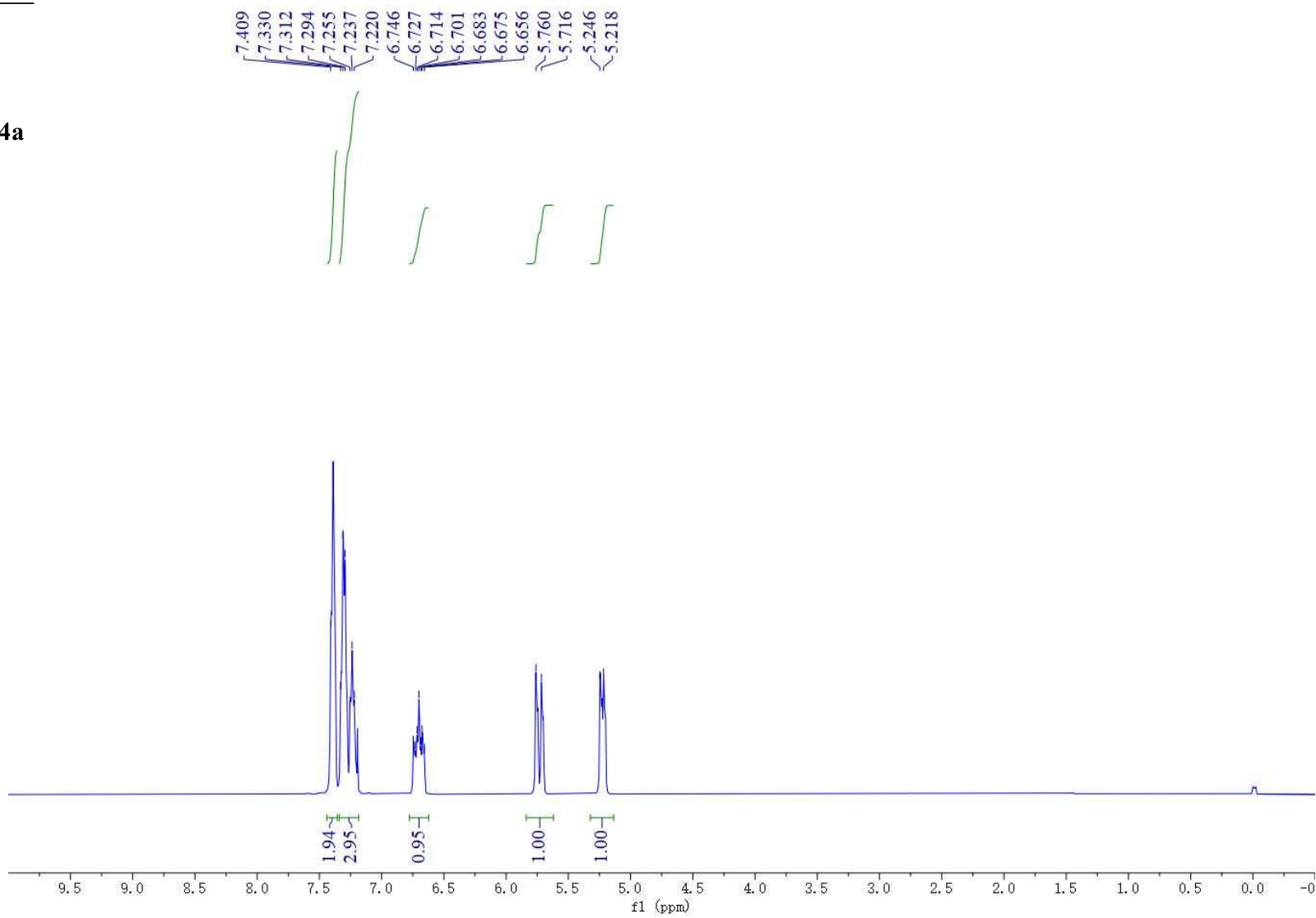


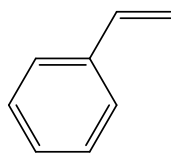






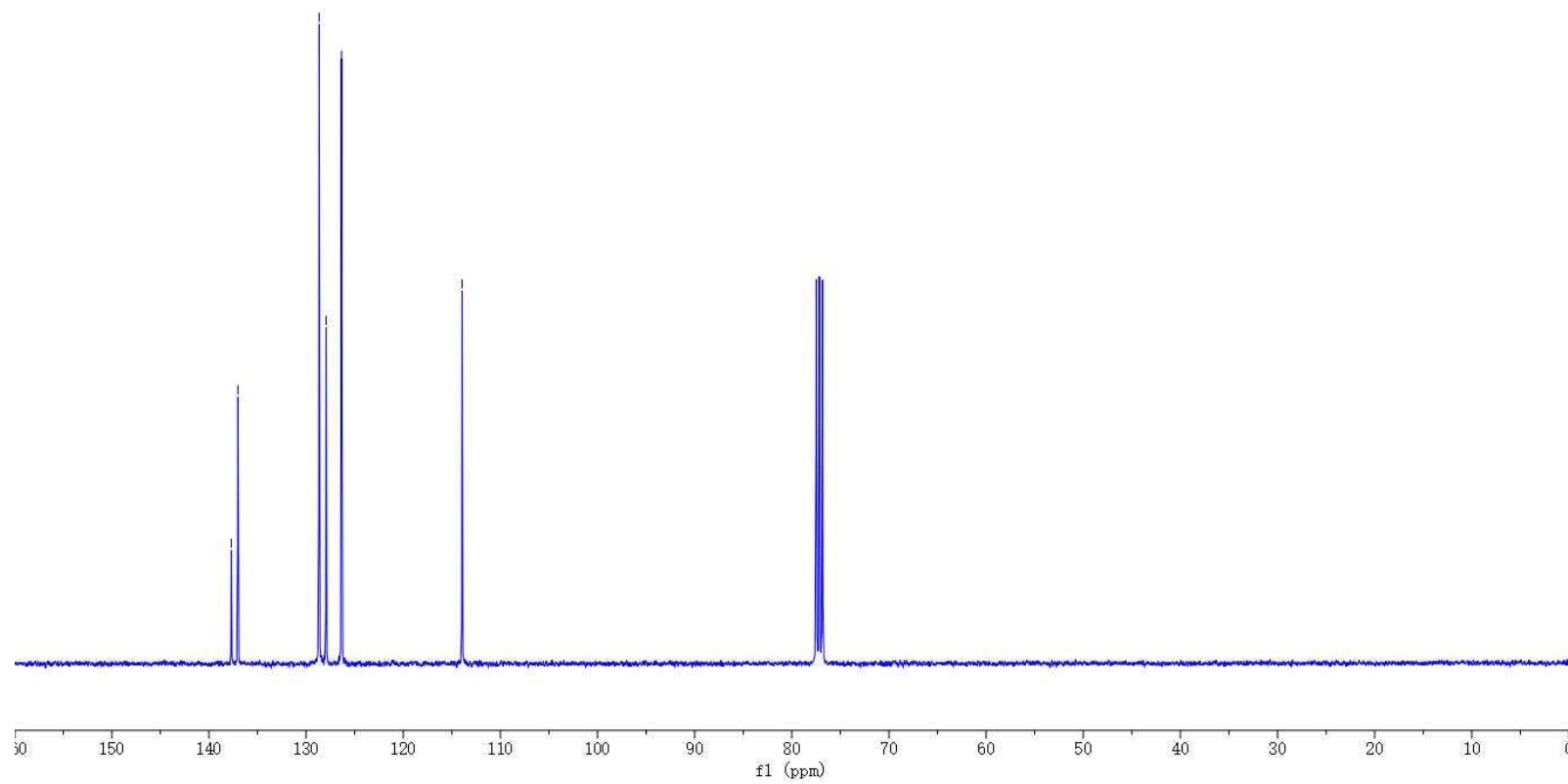
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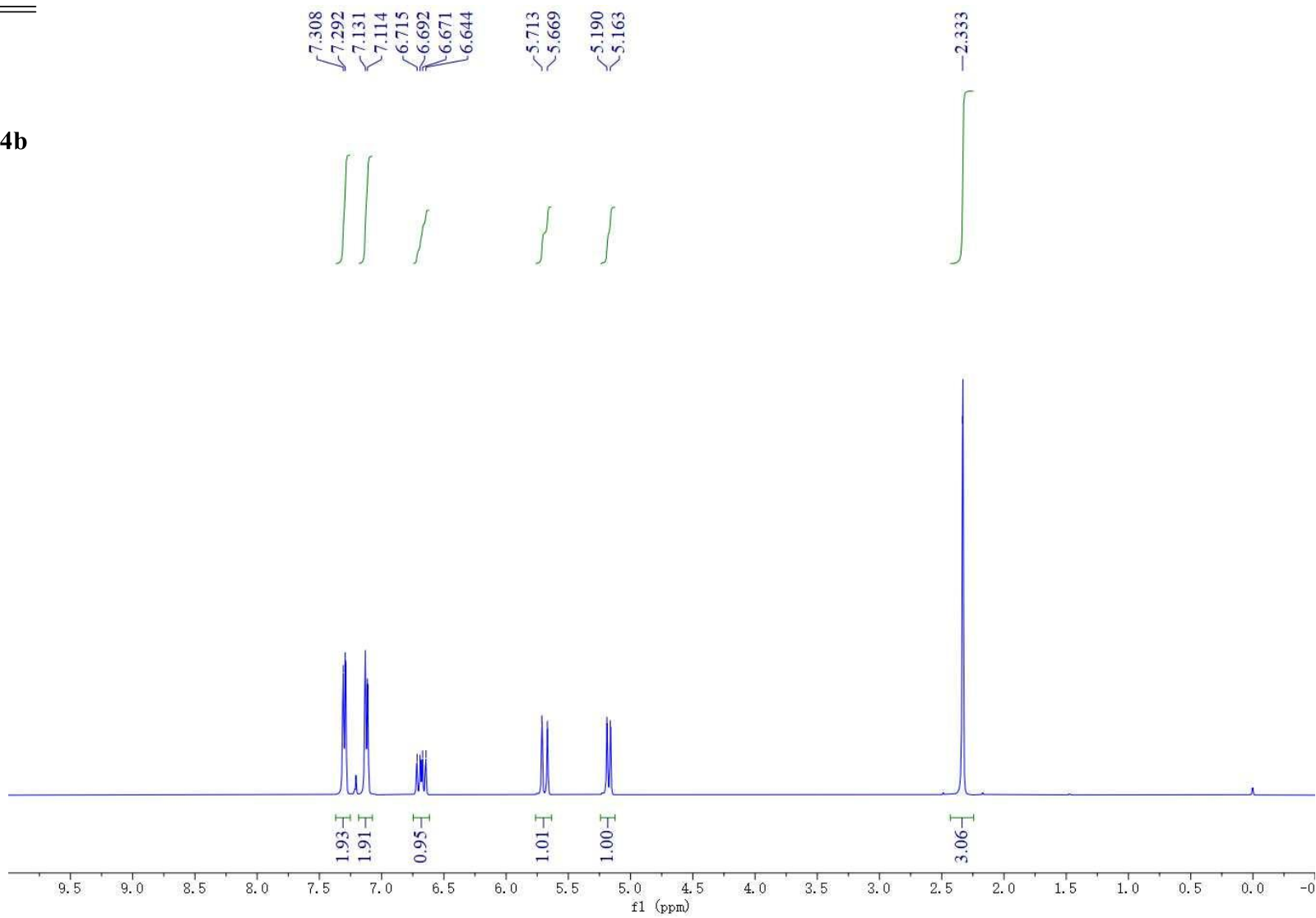
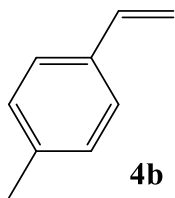


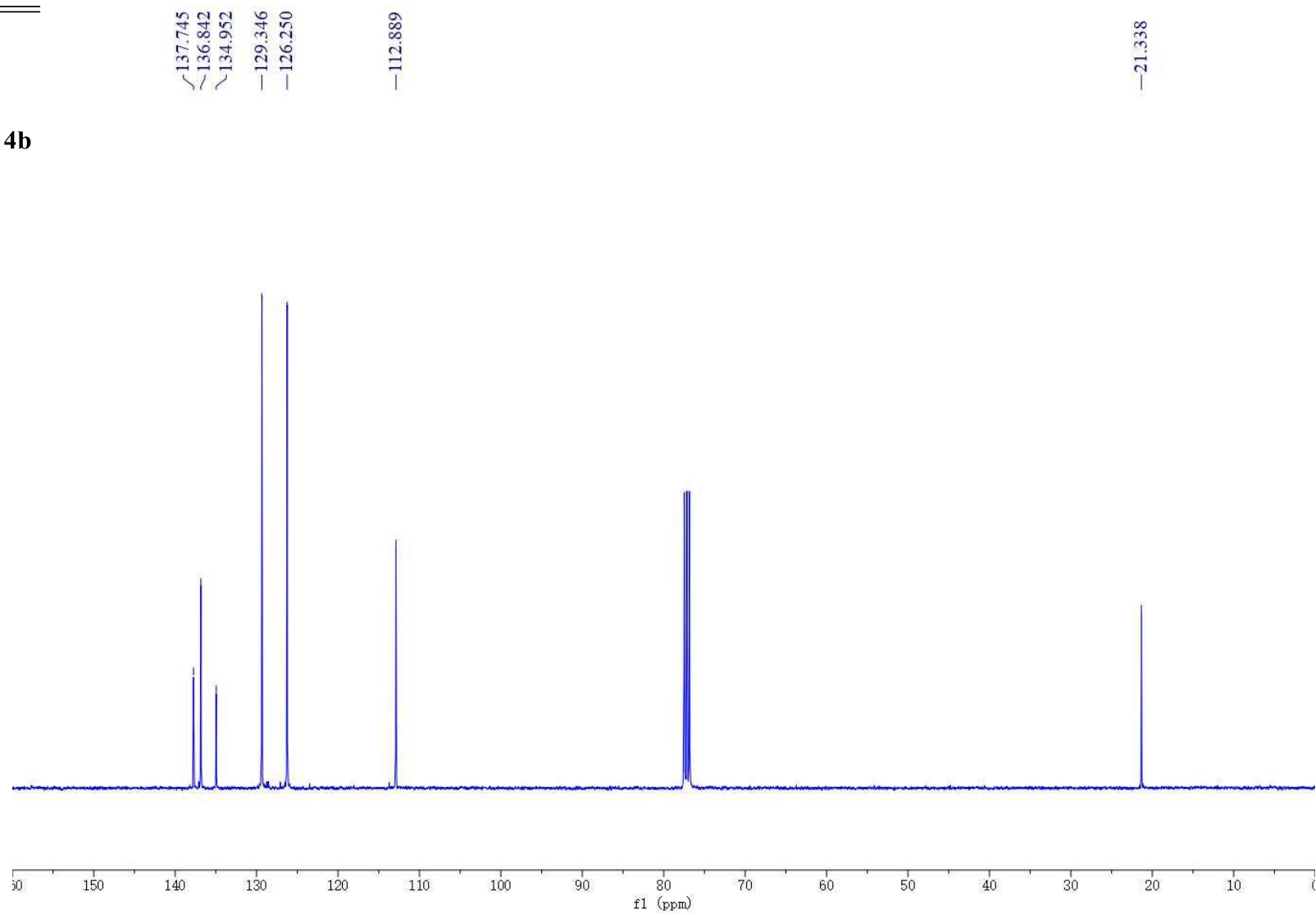
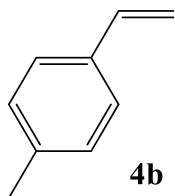


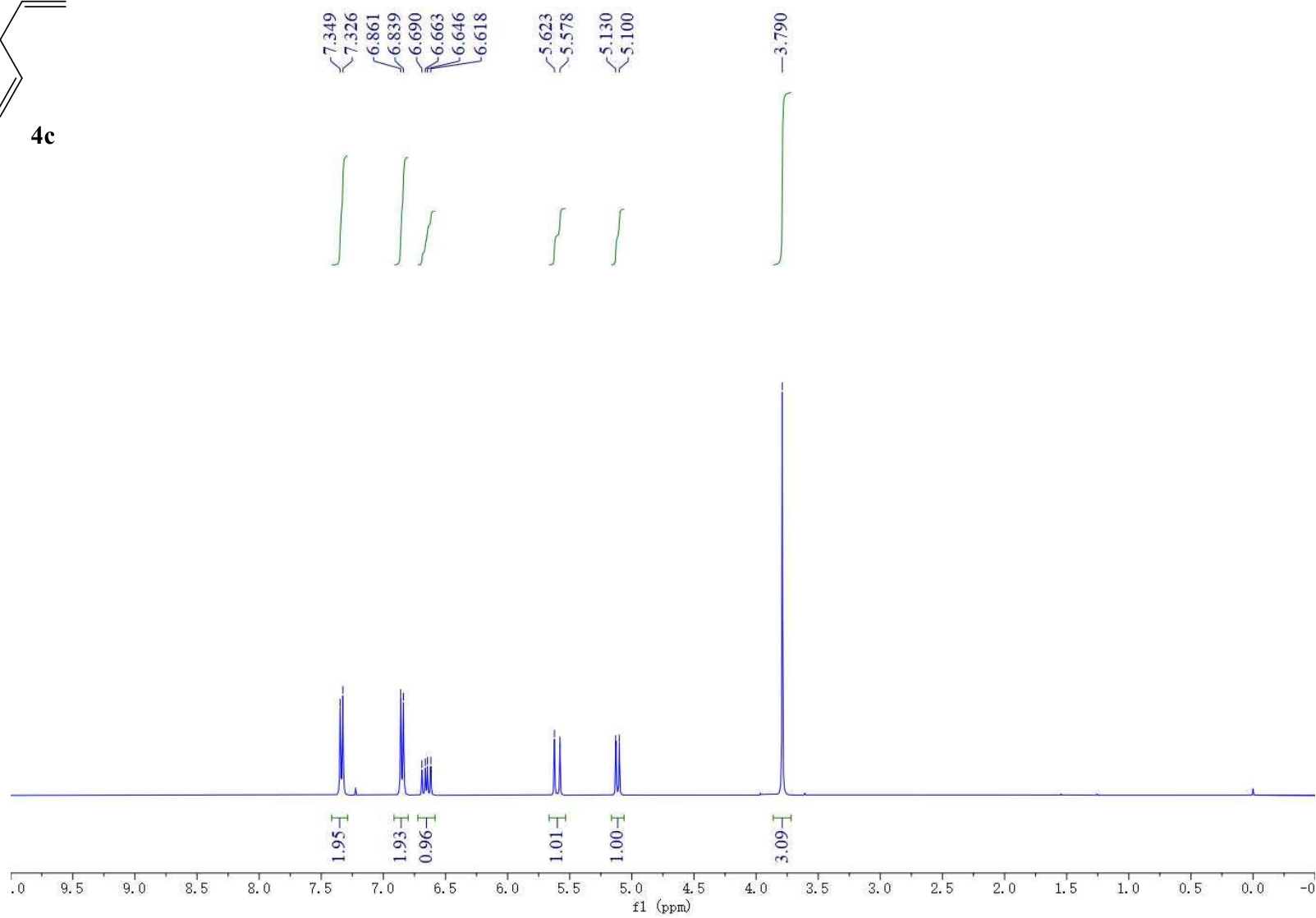
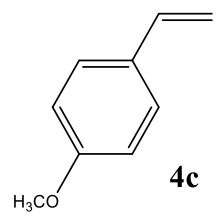
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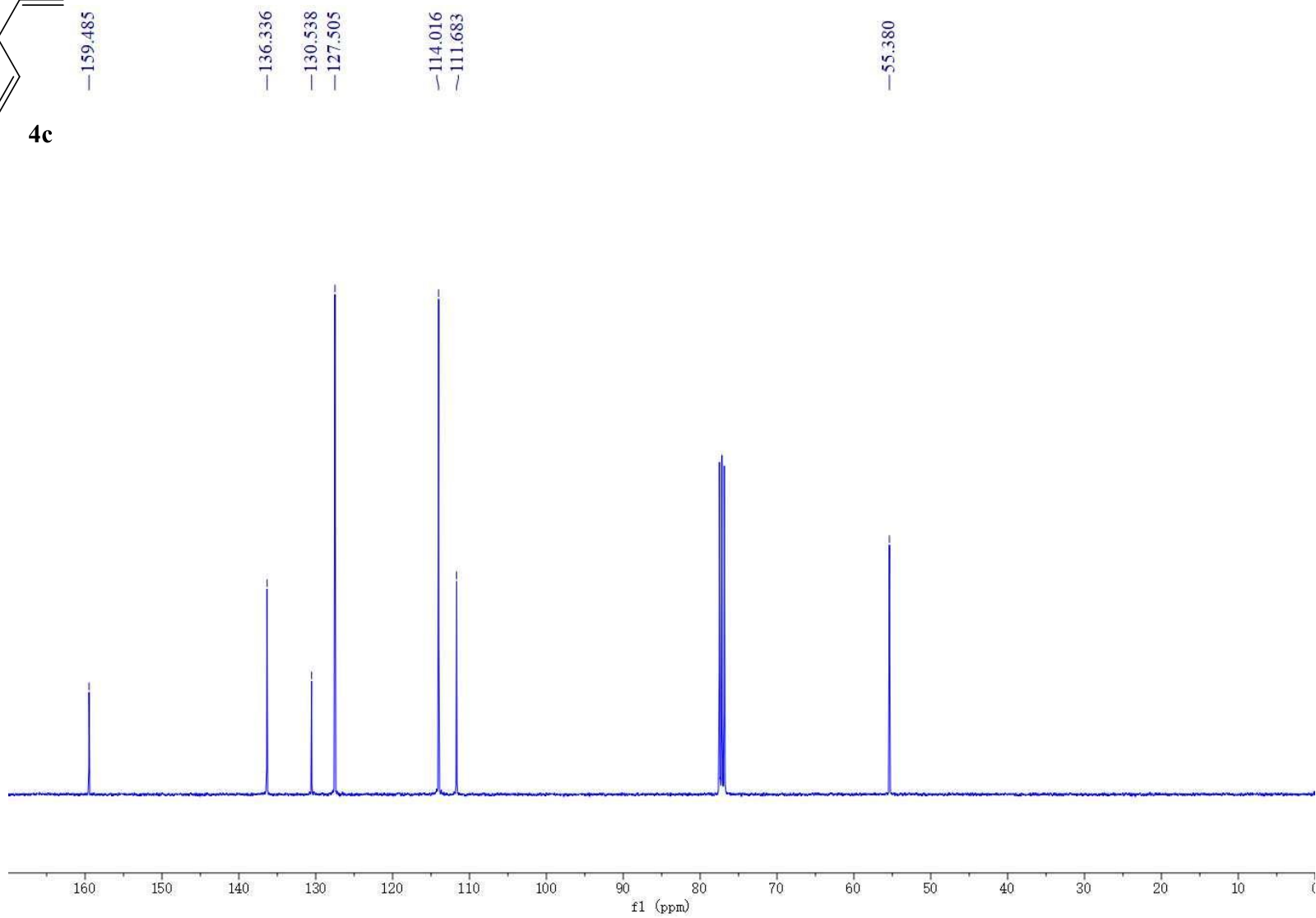
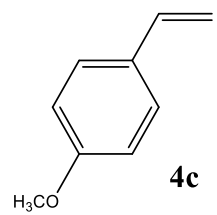
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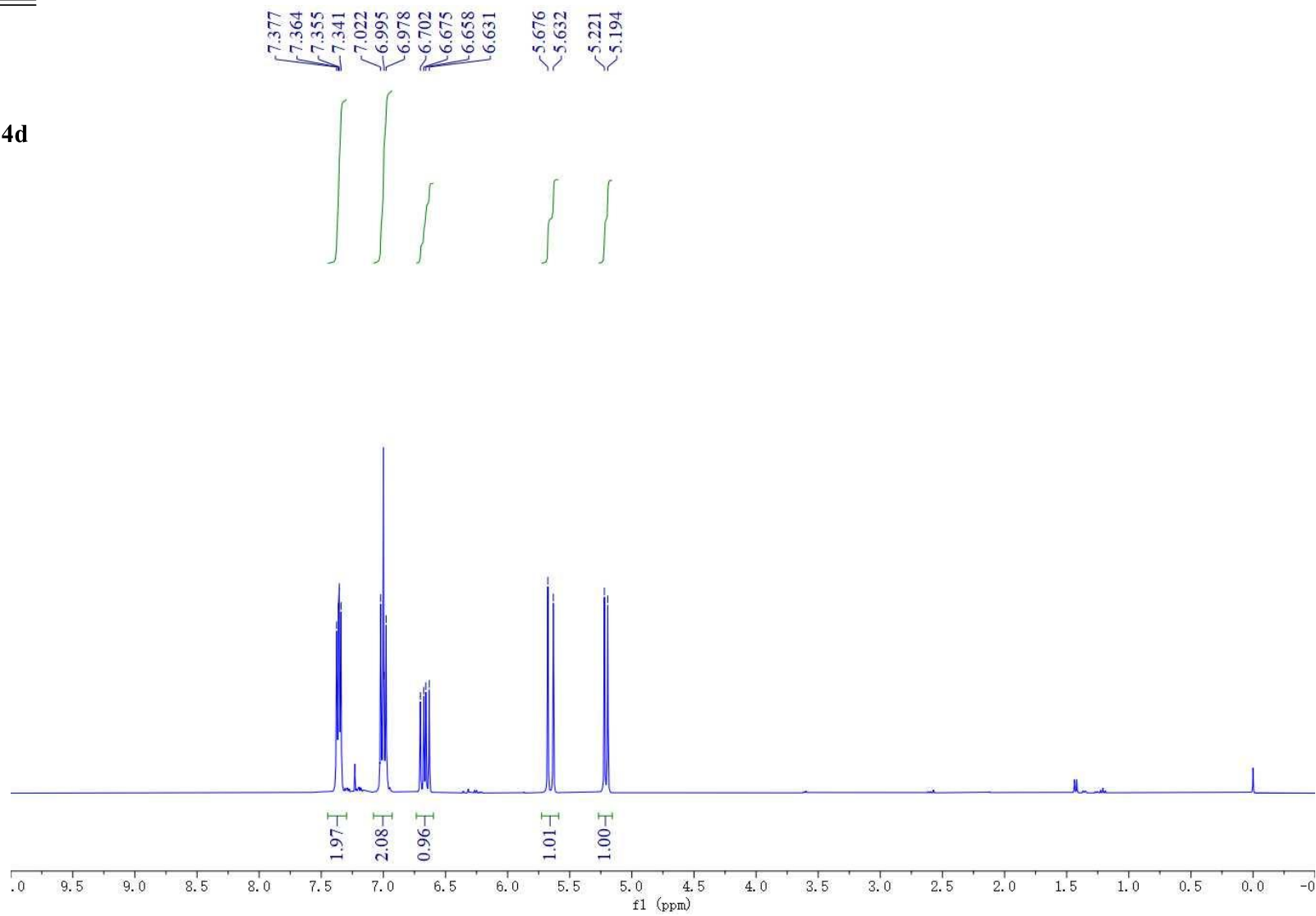
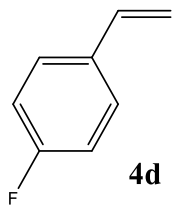


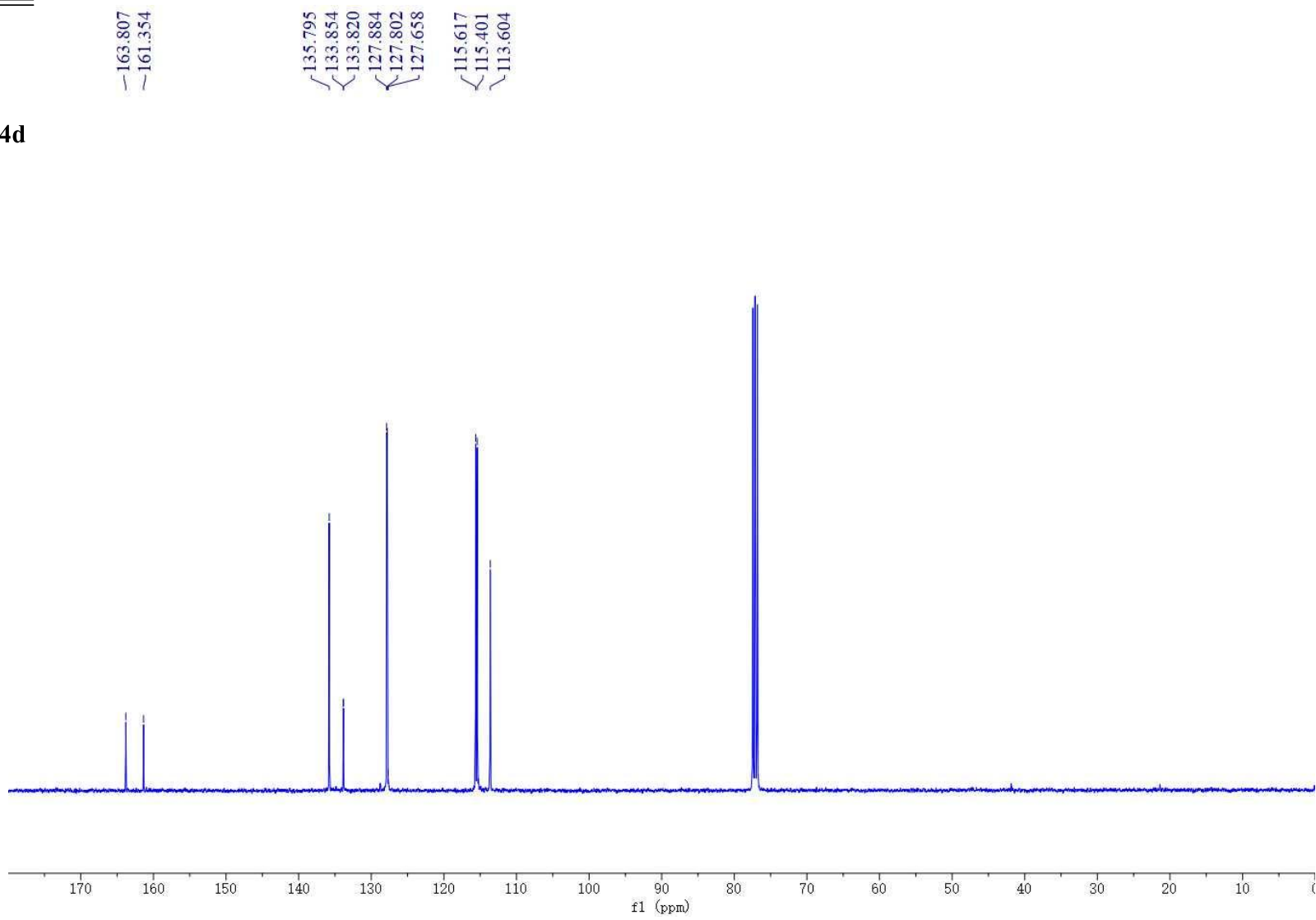
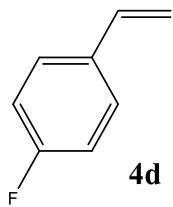


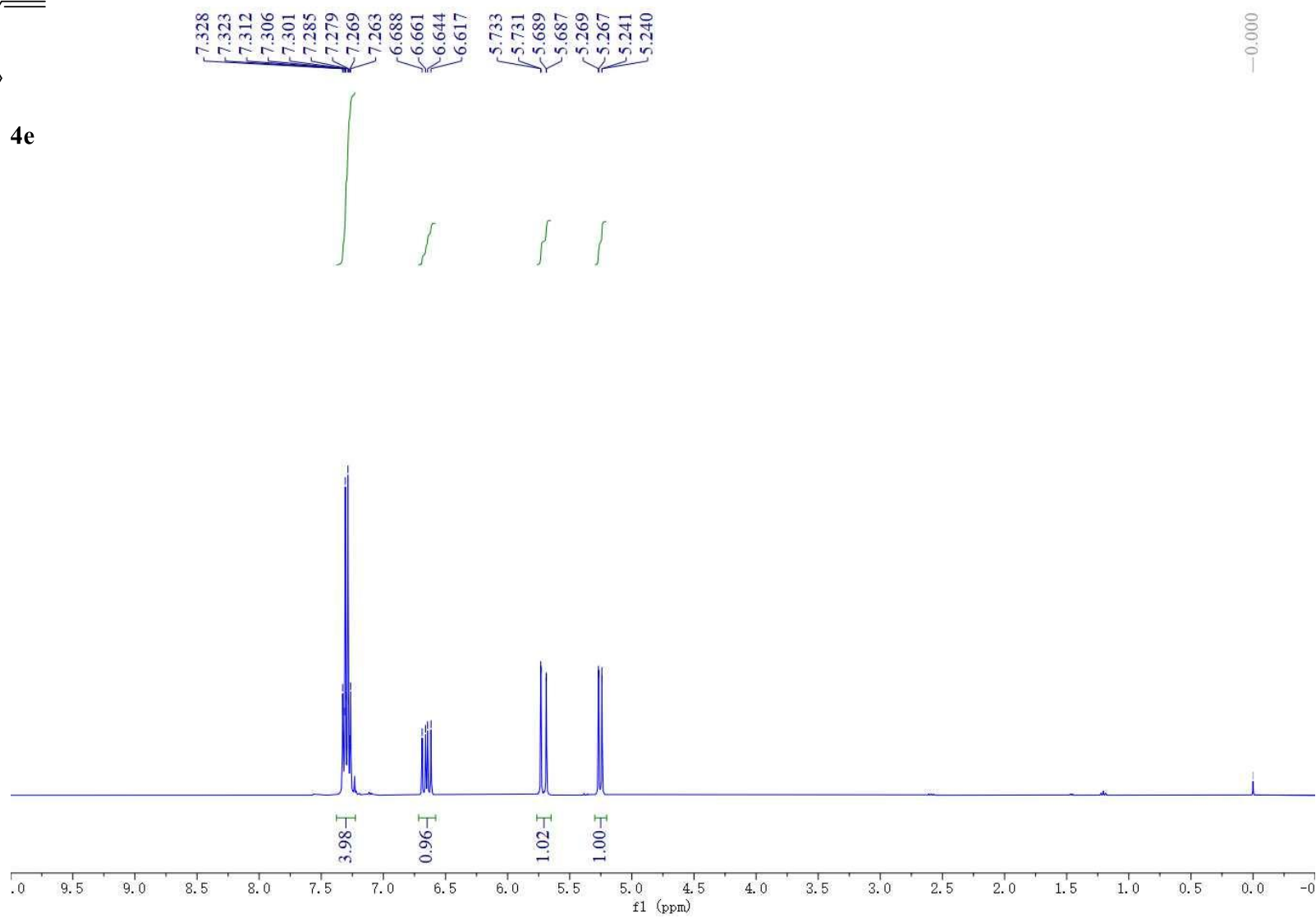
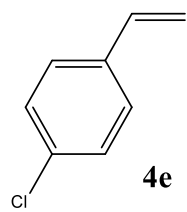


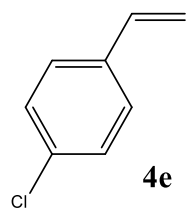




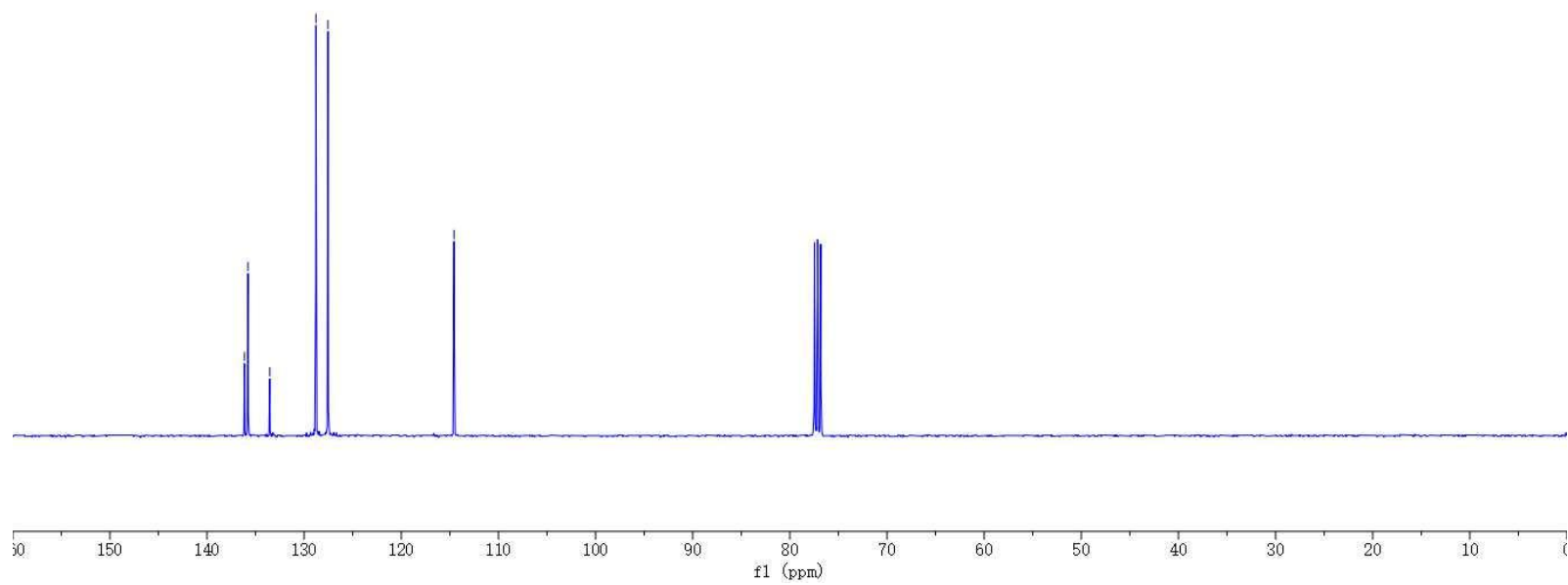


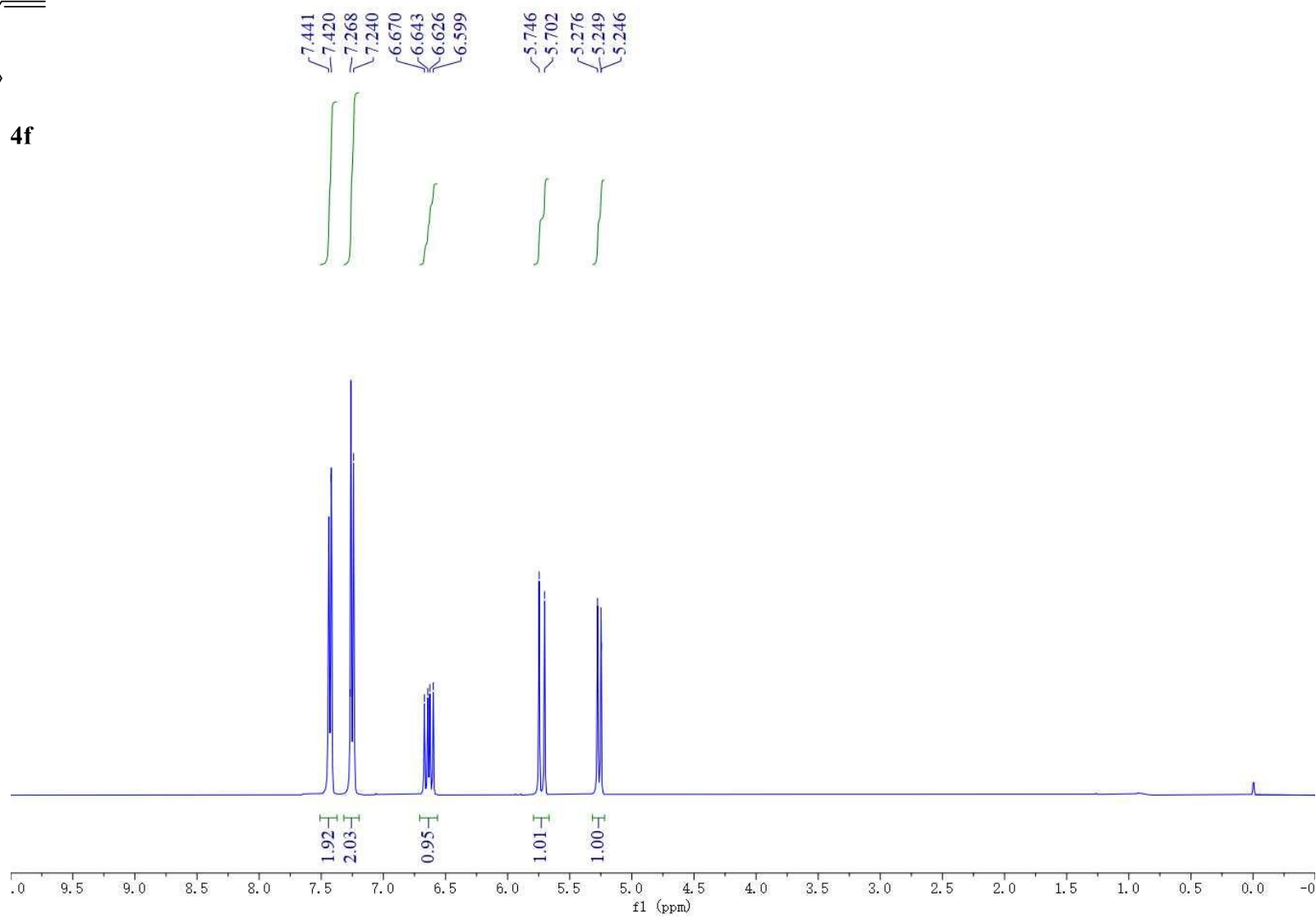
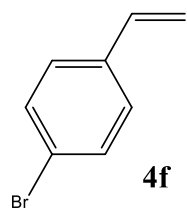


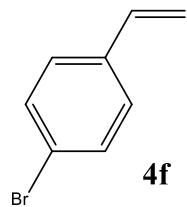




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