

Supporting Information

Polycyclic Aromatic Hydrocarbons via Iron(III)-Catalyzed Carbonyl-Olefin Metathesis

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1. General Information

General Laboratory Procedures. All moisture-sensitive reactions were performed under an atmosphere of nitrogen in flame-dried round bottom flasks or glass vials fitted with rubber septa and/or septa equipped screw caps. Stainless steel syringes were used to transfer air or moisture-sensitive liquids. Flash chromatography was performed using silica gel Silia Flash[®] 40-63 micron (230-400 mesh) from Silicycle.

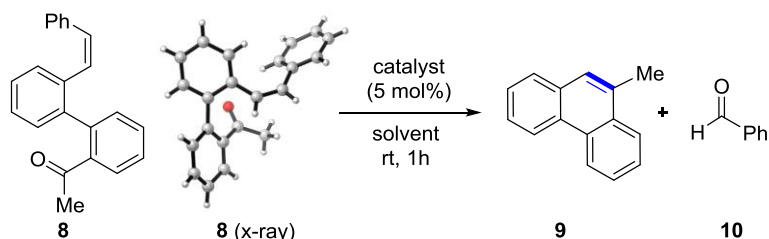
Materials and Instrumentation. All chemicals were purchased from SigmaAldrich, Alfa Aesar, Acros Organics, Oakwood, TCI America, Frontier Scientific, Matrix Scientific, Ark Pharm, and Chem Impex International, and were used as received unless otherwise stated. Tetrahydrofuran was dried by being passed through columns of activated alumina. Proton Nuclear Magnetic Resonance NMR (¹H NMR) spectra and carbon nuclear magnetic resonance (¹³C NMR) spectra were recorded on a Varian Unity Plus 400, Varian MR400, Varian vnmrs 500, Varian Inova 500, Varian Mercury 500, and Varian vnmrs 700 spectrometers. Chemical shifts for protons are reported in parts per million and are referenced to the NMR solvent peak (CDCl₃: δ 7.26; DMSO: δ 2.62). Chemical shifts for carbons are reported in parts per million and are referenced to the carbon resonances of the NMR solvent (CDCl₃: δ 77.23; DMSO: δ 40.76). Data are represented as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, dd = doublet of doublet, m = multiplet), and coupling constants in Hertz (Hz). Mass spectroscopic (MS) data was recorded at the Mass Spectrometry Facility at the Department of Chemistry of the University of Michigan in Ann Arbor, MI on an Agilent Q-TOF HPLC-MS with ESI high resolution mass spectrometer. Infrared (IR) spectra were obtained using either an Avatar 360 FT-IR or Perkin Elmer Spectrum BX FT-IR spectrometer. IR data are represented as frequency of absorption (cm⁻¹).

Abbreviations used: EtOAc = ethyl acetate, DMF = dimethylformamide, CH₃CN = acetonitrile, DCM = dichloromethane, DCE = 1,2-dichloroethane, HCl = hydrogen chloride, NaHCO₃ = sodium bicarbonate, K₂CO₃ = potassium carbonate, MeOH = methanol, THF = tetrahydrofuran Na₂SO₄ = sodium sulfate, MgSO₄ = magnesium sulfate, DMSO = dimethyl sulfoxide, TLC = thin layer chromatography, PhMe = toluene, IBX = 2-iodoxybenzoic acid, TBSCl = *tert*-butyldimethylsilyl chloride, DMAP = 4-(Dimethylamino)pyridine, Ac₂O = acetic anhydride, TEA = triethylamine, Tf₂O = trifluoromethanesulfonic anhydride, TBAF = tetrabutylammonium fluoride, TsCl = *p*-toluenesulfonyl chloride.

2. Reaction Optimization and Lewis Acid/Bronsted Acid Evaluation

A flame-dried 1 – dram vial was charged with Lewis or Bronsted acid (5 mol%), solvent (0.1-0.01 M) and stirred at room temperature. To this solution was added starting biaryl **8a** (0.13 mmol), and the resultant mixture was stirred at room temperature. After 1 h the reaction mixture was passed through a short silica plug eluting with DCM (25 mL). The filtrate was concentrated under reduced pressure and yield determined by NMR analysis of the crude reaction mixture with 1,3,5-trimethoxybenzene as internal standard.

Table S1. Evaluation of reaction conditions.



entry	Lewis Acid	solvent	yield 9 (%) ^a	conversion (%)
1	TiCl ₄	DCE (0.1M)	3	7
2	SnCl ₄	DCE (0.1M)	0	6
3	FeCl ₂	DCE (0.1M)	0	2
4	ZnCl ₂	DCE (0.1M)	22	26
5	InCl ₃	DCE (0.1M)	16	38
6	Yb(OTf) ₃	DCE (0.1M)	0	0
7	Dy(OTf) ₃	DCE (0.1M)	0	4
8	ScCl ₃	DCE (0.1M)	0	0
9	AlCl ₃	DCE (0.1M)	93	100
10	GaCl ₃	DCE (0.1M)	88	100
11	FeSO ₄ • 7H ₂ O	DCE (0.1M)	0	4
12	FeF ₃	DCE (0.1M)	0	7
13	Fe(acac) ₃	DCE (0.1M)	0	2
14	MgBr ₂	DCE (0.1M)	0	0
15	CuCl	DCE (0.1M)	0	0
16	BF ₃ • OEt ₂	DCE (0.1M)	31	35
17	SbCl ₃	DCE (0.1M)	0	0
18	FeBr ₂	DCE (0.1M)	0	0
19	Mg(OTf) ₂	DCE (0.1M)	88	100
20	Cu(OTf) ₂	DCE (0.1M)	0	0
21	Cu(OAc) ₂	DCE (0.1M)	0	0
22	Mn(acac) ₃	DCE (0.1M)	0	0
23	Fe(OAc) ₂	DCE (0.1M)	0	15
24	Fe(OTf) ₃	DCE (0.1M)	82	100
25	FeCl ₃	DCE (0.1M)	97	100
26	FeCl ₃	DCE (0.01M)	95	100
27	FeCl ₃	DCE (0.05M)	91	100
28	FeCl ₃	toluene (0.1M)	99	100
29	FeCl ₃	DMF (0.1M)	0	0
30	FeCl ₃	1,4-dioxane (0.1M)	0	6
31	HCl	DCE (0.1M)	0	0
32	pTsOH	DCE (0.1M)	0	0

3. Evaluation of Substituents on the Carbonyl Moiety

A flame-dried 1 – dram vial was charged with FeCl₃ (5 mol%), DCE (0.1 M) and stirred at room temperature. To this solution was added starting biaryl **22 a-l** (0.13 mmol), and the resultant mixture was stirred at room temperature unless noted otherwise. After completion of the reaction by TLC analysis, the mixture was passed through a short silica plug eluting with DCM (25 mL). The filtrate was concentrated under reduced pressure and purified by flash column chromatography.

Table S2. Evaluation of carbonyl functionalities for the iron(III)-catalyzed carbonyl-olefinmetathesis..

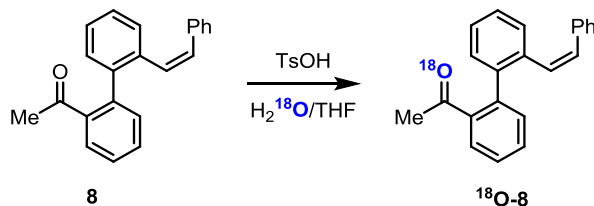
Reaction scheme: **22 a-l** (biaryl ketone with Ph and R groups) reacts with FeCl₃ (5 mol%) in DCE (0.1M) for 1-12 h to yield **9, 23 b-l** (biaryl product with R group) and benzaldehyde (H-C(=O)-Ph).

entry	substrate	yield (%)	entry	substrate	yield (%)
1	22a	99	7	22g^a	50
2	22b	75	8	22h	72
3	22c	79	9	22j^a	52
4	22d	55 ^a	10	22j^{b,c}	0
5	22e	67	11	22k^{b,d}	0
6	22f	53	12	22l^{b,d}	0

Conditions: biaryl (0.13 mmol), FeCl₃ (5 mol%) in dichloroethane (0.1M), rt, 1-12h; ^a reaction heated to 50°C. ^b only starting material observed by crude NMR after 24 h at room temperature. ^c only starting material and decomposition observed by crude NMR after 24 h at 80 °C. ^d only starting material observed by crude NMR after 24 h at 80 °C.

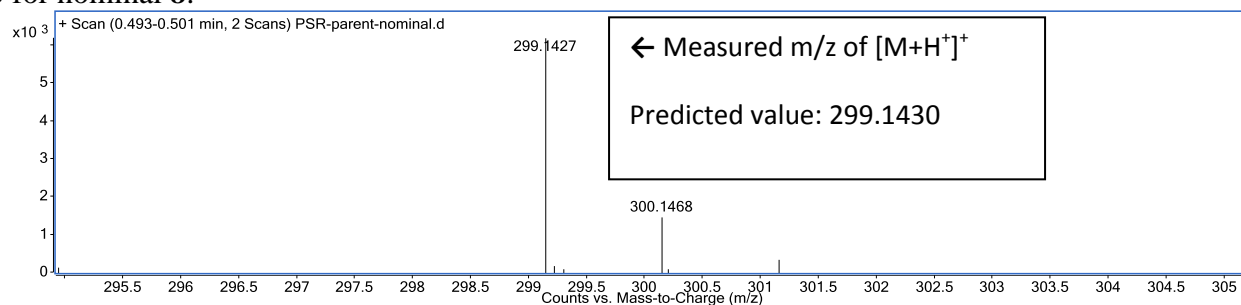
Both ketone substrates (**22a** and **22c-i**) and aldehyde **22b** underwent carbonyl-olefin metathesis. However, carboxylic acid derivatives (**22j-l**) failed to undergo the iron(III) chloride catalyzed carbonyl-olefin metathesis reaction, presumably as a result of their decreased electrophilicity as compared to ketones and aldehydes. Further, the enhanced Lewis basicity of **22j-l** can further inhibit catalysis.

4. ^{18}O Labeling Studies for Benzaldehyde Formation

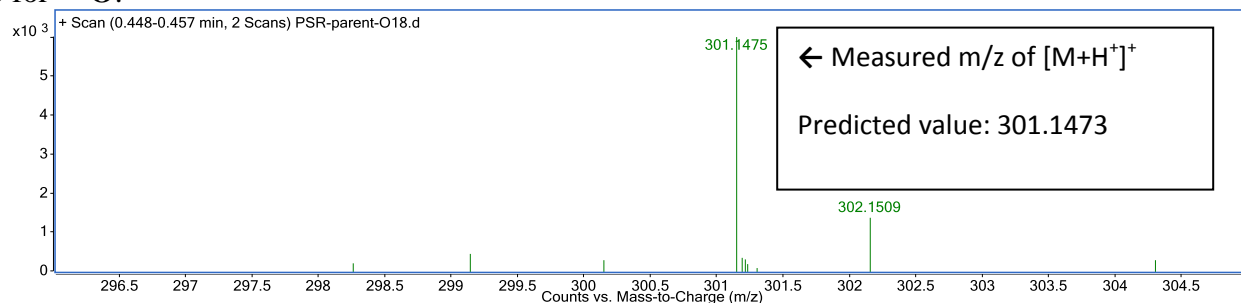


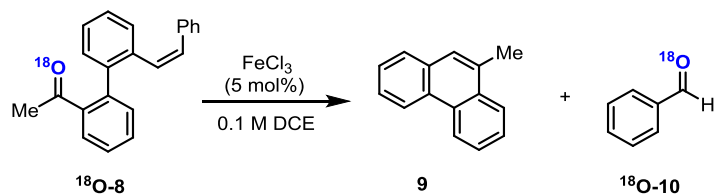
^{18}O -(Z)-1-(2'-styryl-[1,1'-biphenyl]-2-yl)ethan-1-one (^{18}O -8): *para*-Toluenesulfonic acid monohydrate (10 mg, 50 μmol) was placed in a screw-cap vial and 1 mL of benzene was added, then removed by rotary evaporator. This was repeated twice and the resulting solid was dried under high vacuum for 3 hours. Nominal (Z)-1-(2'-styryl-[1,1'-biphenyl]-2-yl)ethan-1-one (**8**) (100 mg, 0.34 mmol) was added to the vial and a 1:1 mixture of H_2^{18}O and THF (1.2 mL) was added. The reaction was heated to 70°C overnight. The reaction mixture was cooled to room temperature and EtOAc was added and the vial was capped and shaken. The layers were separated and the aqueous layer was washed with two additional portions of EtOAc. The combined organic layers were dried over Na_2SO_4 and concentrated by rotary evaporator to afford spectroscopically pure ^{18}O -8. **HRMS:** calculated for $\text{C}_{22}\text{H}_{19}^{18}\text{O}$ ($[\text{M}+\text{H}^+]^+$): 301.1473 Found: 301.1475.

HRMS for nominal **8**:



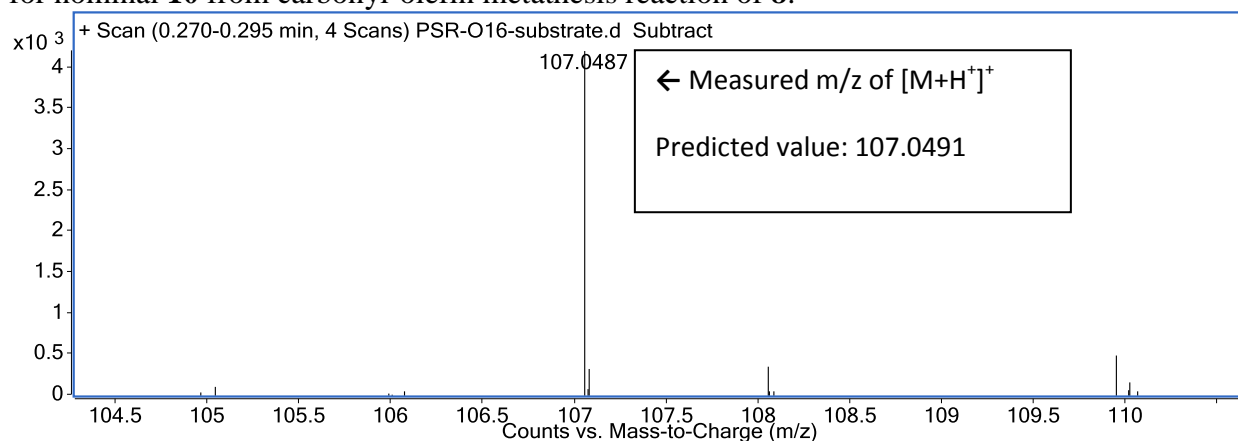
HRMS for ^{18}O -8:



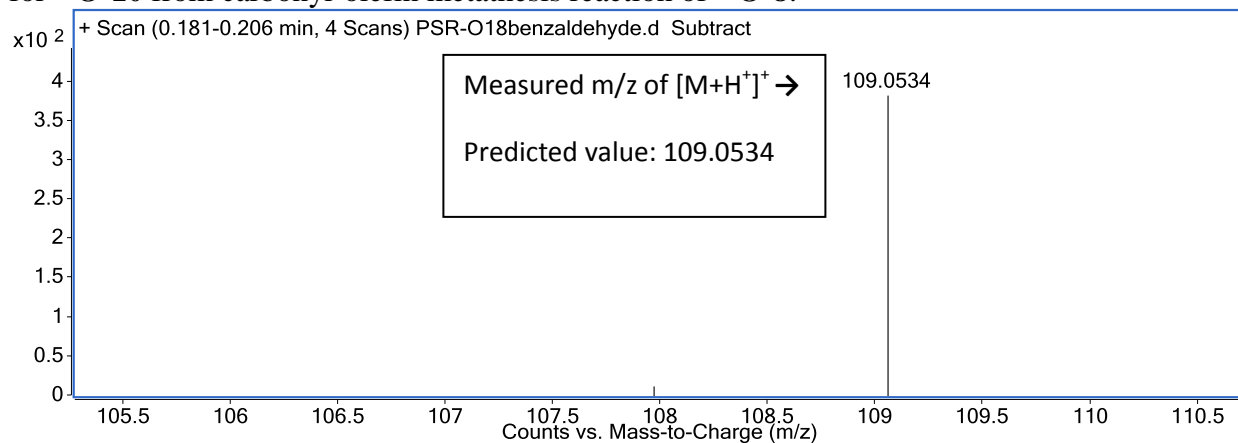


9-methylphenanthrene (9): The cyclization of $^{18}\text{O-8}$ was performed on a 0.13 mmol scale with a total reaction time of 1 h according to the general procedure for carbonyl-olefin metathesis (Section 6, Supporting Information). Purification by flash column chromatography eluting with hexanes/EtOAc provided 24 mg (96%) of **9** as a white solid. Before purification, an aliquot of the reaction mixture was removed and analyzed by HRMS and showed the formation of ^{18}O -benzaldehyde. **HRMS:** predicted for $\text{C}_7\text{H}_7^{18}\text{O}$ ($[\text{M}+\text{H}]^+$): 109.0534 Found: 109.0534.

HRMS for nominal 10 from carbonyl-olefin metathesis reaction of 8:



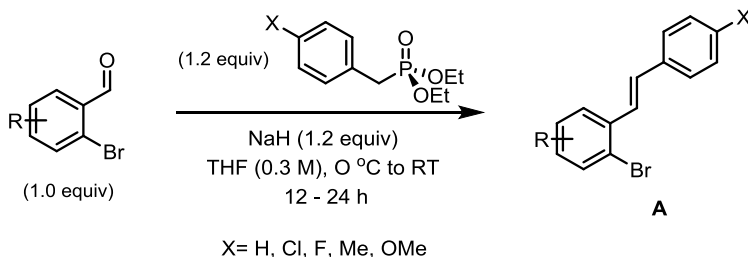
HRMS for $^{18}\text{O-10}$ from carbonyl-olefin metathesis reaction of $^{18}\text{O-8}$:



5. Synthesis of Starting Materials

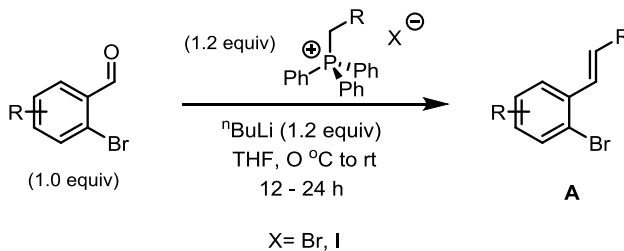
a. Synthesis of olefins

General olefination procedure A for substrate precursors (A):

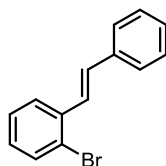


A 50 mL round bottom flask equipped with a magnetic stir bar was charged with diethyl benzylphosphonate (1.1 equiv) and dry THF (0.3 M). The solution was cooled to 0 °C with an ice bath followed by NaH addition (1.2 equiv). After stirring for 30 minutes at 0 °C the starting aryl aldehyde (1 equiv) was slowly added. The reaction was allowed to warm to room temperature and stirred until judged complete by TLC analysis (12-24 h). The reaction mixture was then cooled to 0 °C and quenched with aqueous ammonium chloride (n mL). The biphasic solution was extracted with ethyl acetate (3 × n mL). The combined organic phases were washed with brine (n mL), dried over MgSO₄ and concentrated under reduced pressure. The crude product was purified *via* flash column chromatography eluting with a mixture of hexanes and ethyl acetate to give the pure stilbene derivative (A).

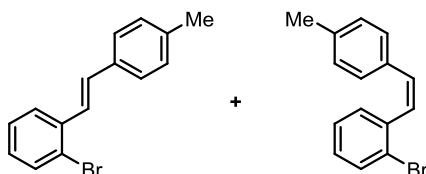
General olefination procedure B for substrate precursors (A):



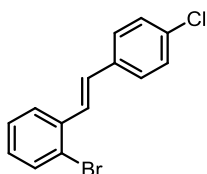
A 50 mL round bottom flask equipped with a magnetic stir bar was charged with Wittig salt (1.1 equiv) and dry THF (0.3 M). The solution was cooled to 0 °C with an ice bath followed by ⁿBuLi addition (1.2 equiv). After stirring for 30 minutes at 0 °C the starting aryl aldehyde (1 equiv) was slowly added. The reaction was allowed to warm to room temperature and stirred until judged complete by TLC analysis (12-24 h). The reaction mixture was then cooled to 0 °C and quenched with aqueous ammonium chloride (n mL). The biphasic solution was extracted with ethyl acetate (3 × n mL). The combined organic phases were washed with brine (n mL), dried over MgSO₄ and concentrated under reduced pressure. The crude product was purified *via* flash column chromatography eluting with a mixture of hexanes and ethyl acetate to give the pure olefin (A).



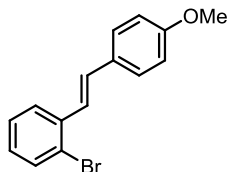
(E)-1-bromo-2-styrylbenzene (A1): General olefination procedure **A** was followed employing 2-bromobenzaldehyde (54 mmol). Purification by flash column chromatography eluting with hexanes/EtOAc provided 12.71 g (91%) of **A1** as a clear oil. Spectroscopic data matched reported literature data.¹ ¹H NMR (400 MHz, CDCl₃) δ 7.68 (d, *J* = 7.8 Hz, 1H), 7.63 – 7.51 (m, 3H), 7.47 (d, *J* = 16.2 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.35 – 7.27 (m, 2H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 16.2 Hz, 1H).



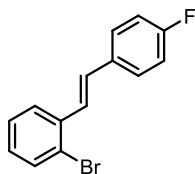
(E)-1-bromo-2-(4-methylstyryl)benzene + (Z)-1-bromo-2-(4-methylstyryl)benzene (E-A2 & Z-A2): General olefination procedure **A** was followed employing (2.72 mmol). Purification by flash column chromatography eluting with hexanes/EtOAc provided 218 mg (30%) of **E-A2** and 120 mg (16%) of **Z-A2** as a clear oil. Spectroscopic data matched reported literature data.² Spectral data for **E-A2**. ¹H NMR (700 MHz, CDCl₃) δ 7.67 (d, *J* = 7.8 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 16.2 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 7.9 Hz, 2H), 7.12 – 7.10 (m, 1H), 7.02 (d, *J* = 16.2 Hz, 1H), 2.38 (s, 3H). Spectral data for **Z-A2**. ¹H NMR (700 MHz, CDCl₃) δ 7.60 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.21 (dd, *J* = 7.1, 2.1 Hz, 1H), 7.12 – 7.07 (m, 2H), 7.04 (d, *J* = 8.1 Hz, 2H), 6.99 (d, *J* = 8.1 Hz, 2H), 6.65 (d, *J* = 12.1 Hz, 1H), 6.56 (d, *J* = 12.1 Hz, 1H), 2.29 (s, 3H).



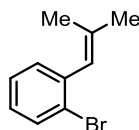
(E)-1-bromo-2-(4-chlorostyryl)benzene (A3): General olefination procedure **A** was followed (2.72 mmol scale). Purification by flash column chromatography eluting with hexanes/EtOAc provided 425 mg (56%) of **A3** as a white powder. Spectroscopic data matched reported literature data.³ ¹H NMR (500 MHz, CDCl₃) δ 7.65 (d, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.42 (s, 1H), 7.33 (m, 3H), 7.15 – 7.11 (m, 1H), 6.98 (d, *J* = 16.2 Hz, 1H).



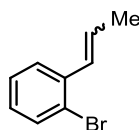
(E)-1-bromo-2-(4-methoxystyryl)benzene (A4): General olefination procedure **A** was followed (2.72 mmol scale). Purification by flash column chromatography eluting with hexanes/EtOAc provided 245 mg (31%) of **A4** as a white solid. Spectroscopic data matched reported literature data.³ ¹H NMR (500 MHz, CDCl₃) δ 7.65 (d, *J* = 7.8 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 8.6 Hz, 2H), 7.36 – 7.27 (m, 2H), 7.11 – 7.07 (m, 1H), 7.00 (d, *J* = 16.2 Hz, 1H), 6.92 (d, *J* = 8.7 Hz, 1H), 3.84 (s, 3H).



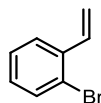
(E)-1-bromo-2-(4-fluorostyryl)benzene (A5): General olefination procedure **A** was followed (2.72 mmol scale). Purification by flash column chromatography eluting with hexanes/EtOAc provided 245 mg (53%) of **A5** as a clear oil. Spectroscopic data matched reported literature data.³ $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.66 (d, $J = 7.7$ Hz, 1H), 7.60 (d, $J = 8.0$ Hz, 1H), 7.54 (dd, $J = 8.4, 5.5$ Hz, 2H), 7.39 (d, $J = 16.2$ Hz, 1H), 7.33 (t, $J = 7.5$ Hz, 1H), 7.14 (t, $J = 7.4$ Hz, 1H), 7.09 (t, $J = 8.6$ Hz, 2H), 7.01 (d, $J = 16.2$ Hz, 1H).



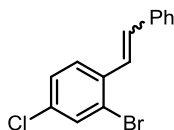
1-bromo-2-(2-methylprop-1-en-1-yl)benzene (A6): General olefination procedure **B** was followed employing 2-bromobenzaldehyde (12.4 mmol). Purification by flash column chromatography eluting with hexanes/EtOAc provided 2295 mg (89%) of **A6** as a clear oil. Spectroscopic data matched reported literature data.⁴ $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.59 – 7.56 (m, 1H), 7.30 – 7.23 (m, 2H), 7.10 – 7.06 (m, 1H), 6.27 (s, 1H), 1.96 (s, 3H), 1.77 (s, 3H).



1-bromo-2-(prop-1-en-1-yl)benzene (A7): General olefination procedure **B** was followed employing ethyl triphenylphosphonium bromide (5.43 mmol). Purification by flash column chromatography eluting with hexanes/EtOAc provided 756 mg (71%) of **A7** as a *E/Z* (3:1) mixture, as a clear oil. Spectroscopic data matched reported literature data.⁵

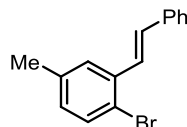


1-bromo-2-vinylbenzene (A8): General olefination procedure **B** was followed employing 2-bromobenzaldehyde (7.07 mmol). Purification by flash column chromatography eluting with hexanes/EtOAc provided 890 mg (69%) of **A8** as a clear oil. Spectroscopic data matched reported literature data.⁶ $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.55 (d, $J = 7.9$ Hz, 2H), 7.28 (t, $J = 7.6$ Hz, 1H), 7.12 (t, $J = 7.7$ Hz, 1H), 7.06 (dd, $J = 17.4, 11.0$ Hz, 1H), 5.71 (d, $J = 17.4$ Hz, 1H), 5.37 (d, $J = 10.9$ Hz, 1H).

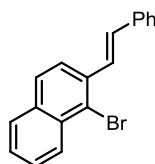


1-bromo-4-chloro-2-styrylbenzene (A9): General olefination procedure **A** was followed employing 2-bromo-5-chlorobenzaldehyde (2.62 mmol scale). Purification by flash column chromatography eluting with hexanes/EtOAc provided 395 mg (52%) of **A9** as an inseparable mixture of alkene isomers (3.88:1) as a white solid. $^1\text{H NMR}$ (500 MHz, CDCl_3 ;) δ 7.58 – 7.51 (m, 3H), 7.43 – 7.35 (m, 4H), 7.32 (t, $J = 7.3$ Hz, 1H), 7.04 (d, $J = 16.2$ Hz, 1H), 6.88 – 6.84 (m, 1H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 138.66, 136.51, 134.04, 132.63, 128.88, 128.79, 128.60, 128.46, 128.32, 126.97, 126.49, 126.25. IR (cm^{-1}): 2155.7, 1413.1, 1340.7, 1321.5,

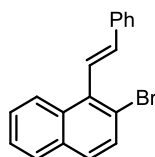
1251.0, 1107.8, 1079.4, 1023.3, 954.9, 822.7, 803.5, 752.0, 684.7. **HRMS**: Calculated for $C_{14}H_{10}BrCl^+$ ($[M]^+$): 291.9654 Found: 291.9659.



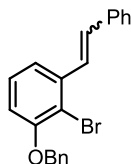
(E)-1-bromo-4-methyl-2-styrylbenzene (A10): General olefination procedure **A** was followed employing 2-bromo-5-methylbenzaldehyde (2.39 mmol). Purification by flash column chromatography eluting with hexanes/EtOAc provided 486 mg (74%) of **A10** as a white solid. 1H NMR (400 MHz, $CDCl_3$) δ 7.56 (t, $J = 8.2$ Hz, 1H), 7.48 – 7.34 (m, 1H), 7.32 – 7.24 (m, 1H), 7.12 (d, $J = 8.0$ Hz, 1H), 7.01 (d, $J = 16.2$ Hz, 1H), 2.34 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.34, 137.38, 1034.38, 133.65, 130.66, 128.92, 128.68, 128.08, 127.53, 126.94, 126.54, 124.15, 21.03. **IR** (cm^{-1}): 3045.3, 1594.0, 1492.9, 1483.5, 1448.1, 1228.2, 1037.9, 965.2, 954.5, 811.6, 751.6, 705.3, 689.9. **HRMS**: Calculated for $C_{15}H_{13}Br^+$ ($[M]^+$): 272.0201 Found: 272.0201.



(E)-1-bromo-2-styrylnaphthalene (A11): General olefination procedure **A** was followed employing 1-bromo-2-naphthaldehyde (3.25 mmol). Purification by flash column chromatography eluting with hexanes/EtOAc provided 624 mg (62%) of **A11** as a white solid. 1H NMR (500 MHz, $CDCl_3$) δ 8.37 (d, $J = 8.5$ Hz, 1H), 7.85 – 7.77 (m, 4H), 7.62 (d, $J = 5.1$ Hz, 2H), 7.60 – 7.58 (m, 1H), 7.53 – 7.49 (m, 1H), 7.41 (t, $J = 7.6$ Hz, 2H), 7.32 (t, $J = 7.4$ Hz, 1H), 7.18 (d, $J = 16.2$ Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.36, 134.91, 134.11, 132.99, 132.35, 129.01, 128.80, 128.38, 128.29, 127.98, 127.97, 127.86, 127.12, 126.76, 124.41, 124.15. **IR** (cm^{-1}): 3052.1, 1548.8, 1492.1, 1445.4, 1330.4, 1264.9, 1234.5, 958.3, 865.3, 804.5, 767.9, 738.5, 668.0, 657.0. **HRMS**: Calculated for $C_{18}H_{13}Br^+$ ($[M]^+$): 308.0201 Found: 308.0196.



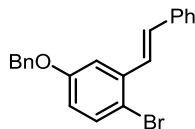
(E)-2-bromo-1-styrylnaphthalene (A12): General olefination procedure **A** was followed employing 2-bromo-1-naphthaldehyde⁷ (2.98 mmol). Purification by flash column chromatography eluting with hexanes/EtOAc provided 818 mg (89%) of **A12** as a white powder. 1H NMR (400 MHz, $CDCl_3$) δ 8.28 – 8.23 (m, 1H), 7.86 – 7.81 (m, 1H), 7.69 – 7.59 (m, 4H), 7.54 – 7.47 (m, 2H), 7.43 (m, 2H), 7.35 (m, 2H), 6.89 (d, $J = 16.6$ Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.10, 136.90, 135.67, 133.07, 133.02, 130.18, 129.00, 128.72, 128.57, 128.39, 127.08, 126.89, 126.39, 126.25, 126.17, 121.82. **IR** (cm^{-1}): 3050.8, 2919.6, 1561.5, 1499.1, 1449.2, 1378.3, 1114.5, 967.9, 891.1, 820.5, 801.7, 744.6, 724.2, 687.9. **HRMS**: Calculated for $C_{18}H_{13}Br^+$ ($[M]^+$): 308.0201 Found: 308.0196.



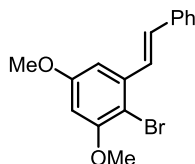
1-(benzyloxy)-2-bromo-3-styrylbenzene (A13): General olefination procedure **A** was followed employing 3-(benzyloxy)-2-bromobenzaldehyde⁸ (1.0 mmol). Purification by flash column chromatography eluting with hexanes/EtOAc provided 156 mg (43%) of **A13** as an inseparable *E/Z* mixture (3.3:1), as a clear oil. 1H NMR (500 MHz, $CDCl_3$; for major *E* isomer) δ 7.61 – 7.56 (m, 1H), 7.51 (dd, $J = 17.6, 11.1$ Hz, 2H), 7.46 – 7.28 (m,

4H), 7.27 – 7.22 (m, 1H), 7.21 – 7.12 (m, 3H), 7.10 – 6.98 (m, 1H), 6.90 – 6.77 (m, 2H), 6.75 – 6.61 (m, 1H), 5.19 (s, $J = 8.7$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3 ; for the *E/Z* mixture) δ 155.30, 139.91, 138.93, 137.05, 136.59, 136.58, 136.38, 131.71, 131.20, 129.73, 129.05, 128.73, 128.58, 128.09, 128.06, 127.92, 127.85, 127.75, 127.53, 127.26, 127.03, 126.99, 126.87, 123.21, 119.23, 114.54, 113.96, 112.37, 112.05, 70.95, 70.88.

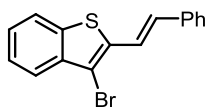
IR (cm^{-1}): 3024.3, 1588.2, 1561.4, 1494.5, 1446.0, 1425.9, 1378.1, 1289.7, 1267.4, 1054.9, 1026.8, 906.2, 772.9, 729.0, 691.5. **HRMS**: Calculated for $\text{C}_{21}\text{H}_{18}\text{BrO}^+$ ($[\text{M} + \text{H}]^+$): 365.0536 Found: 365.0532.



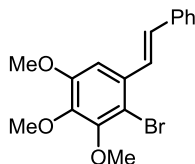
(E)-4-(benzyloxy)-1-bromo-2-styrylbenzene (A14): General olefination procedure **A** was followed employing 5-(benzyloxy)-2-bromobenzaldehyde⁹ (2.84 mmol). Purification by flash column chromatography eluting with hexanes/EtOAc provided 1.04 g (67%) of **A14** as a white solid. ^1H NMR (500 MHz, CDCl_3) δ 7.54 (d, $J = 7.4$ Hz, 2H), 7.50 – 7.25 (m, 11H), 6.99 (d, $J = 16.2$ Hz, 1H), 6.78 (dd, $J = 8.8, 3.0$ Hz, 1H), 5.10 (s, 2H). ^{13}C NMR (176 MHz, CDCl_3) δ 158.40, 138.13, 137.12, 136.77, 133.82, 131.80, 128.96, 128.89, 128.38, 128.36, 127.74, 127.66, 127.09, 116.00, 115.41, 113.22, 70.57. **IR** (cm^{-1}): 1584.4, 1474.5, 1461.8, 1405.5, 1380.9, 12229.4, 1206.6, 1173.6, 1115.9, 1003.5, 955.8, 833.6, 823.0, 771.8, 739.7, 695.2, 657.9. **HRMS**: Calculated for $\text{C}_{21}\text{H}_{18}\text{BrO}^+$ ($[\text{M} + \text{H}]^+$): 365.0536 Found: 365.0532.



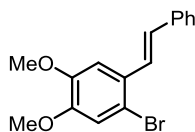
(E)-2-bromo-1,5-dimethoxy-3-styrylbenzene (A15): General olefination procedure **A** was followed employing 2-bromo-3,5-dimethoxybenzaldehyde¹⁰ (3.60 mmol). Purification by flash column chromatography eluting with hexanes/EtOAc provided 1.15 g (64%) of **A15** as a white solid. ^1H NMR (500 MHz, CDCl_3) δ 7.60-7.51 (m, 3H), 7.38 (t, $J = 7.6$ Hz, 2H), 7.32 – 7.27 (m, 1H), 7.02 (d, $J = 16.1$ Hz, 1H), 6.82 (d, $J = 2.7$ Hz, 1H), 6.45 (d, $J = 2.6$ Hz, 1H), 3.89 (s, 3H), 3.87 (s, 3H). ^{13}C NMR (176 MHz, CDCl_3) δ 159.81, 157.09, 138.93, 137.15, 131.84, 128.94, 128.31, 128.19, 127.08, 105.34, 102.89, 99.29, 56.59, 55.81. **IR** (cm^{-1}): 1580.5, 1446.0, 1414.7, 1349.9, 1282.6, 1204.5, 1165.4, 1070.5, 1019.7, 955.5, 822.8, 801.9, 750.1, 702.0, 688.7, 604.6. **HRMS**: Calculated for $\text{C}_{16}\text{H}_{16}\text{BrO}_2^+$: 319.0328 Found: 319.0332.



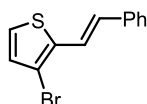
(E)-3-bromo-2-styrylbenzo[b]thiophene (A16): General olefination procedure **A** was followed employing 3-bromobenzo[b]thiophene-2-carbaldehyde (1.74 mmol). Purification by flash column chromatography eluting with hexanes/EtOAc provided 212 mg (67%) of **A16** as a white solid. ^1H NMR (500 MHz, CDCl_3) δ 7.78 (d, $J = 7.9$ Hz, 1H), 7.75 (d, $J = 7.9$ Hz, 1H), 7.58 (d, $J = 7.8$ Hz, 2H), 7.51 (d, $J = 16.1$ Hz, 1H), 7.45 – 7.35 (m, 4H), 7.32 (t, $J = 7.3$ Hz, 1H), 7.10 (d, $J = 16.1$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 139.04, 137.45, 136.69, 136.58, 132.91, 129.05, 128.72, 127.08, 126.23, 125.46, 123.25, 122.50, 120.81, 108.77. **IR** (cm^{-1}): 3023.3, 1488.7, 1430.0, 1318.0, 1295.4, 1253.9, 942.8, 921.8, 746.8, 721.8, 687.6. **HRMS**: Calculated for $\text{C}_{21}\text{H}_{18}\text{BrO}^+$ ($[\text{M}]^+$): 313.9765 Found: 313.9760.



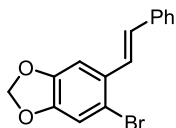
(E)-2-bromo-3,4,5-trimethoxy-1-styrylbenzene (A17): General olefination procedure **A** was followed employing 2-bromo-3,4,5-trimethoxybenzaldehyde¹¹ (3.64 mmol). Purification by flash column chromatography eluting with hexanes/EtOAc provided 1.27 g (51%) of **A17** as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.55 (d, *J* = 7.6 Hz, 2H), 7.47 (d, *J* = 16.1 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.01 (s, 1H), 6.94 (d, *J* = 16.1 Hz, 1H), 3.94 (s, 3H), 3.92 (s, 6H). ¹³C NMR (176 MHz, CDCl₃) δ 153.03, 151.20, 143.13, 137.20, 133.06, 130.94, 128.96, 128.22, 127.91, 126.97, 111.38, 105.45, 61.44, 61.17, 56.44. IR (cm⁻¹): 1479.0, 1447.6, 1422.3, 1388.8, 1345.6, 1238.2, 1207.8, 1166.3, 1104.4, 1050.5, 1005.8, 987.7, 957.8, 927.8, 862.4, 816.4, 752.4, 694.9. HRMS: Calculated for C₁₇H₁₈BrO₃⁺: 349.0434 Found: 349.0437.



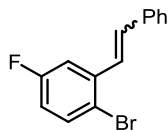
(E)-1-bromo-4,5-dimethoxy-2-styrylbenzene (A18): General olefination procedure **A** was followed employing 2-bromo-4,5-dimethoxybenzaldehyde (2.09 mmol). Purification by flash column chromatography eluting with hexanes/EtOAc provided 601 mg (90%) of **A18** as a white solid. Spectroscopic data matched reported literature data.¹² ¹H NMR (400 MHz, CDCl₃) δ 7.54 (d, *J* = 7.5 Hz, 2H), 7.38 (m, 3H), 7.29 (d, *J* = 7.2 Hz, 1H), 7.16 (s, 1H), 7.05 (s, 1H), 6.93 (d, *J* = 16.2 Hz, 1H), 3.95 (s, 3H), 3.90 (s, 3H).



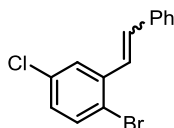
(E)-3-bromo-2-styrylthiophene (A19): General olefination procedure **A** was followed (3.85 mmol). Purification by flash column chromatography eluting with hexanes/EtOAc provided 652 mg (64%) of **A19** as a pale yellow solid. ¹H NMR (500 MHz, CDCl₃) δ 7.52 (d, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 6.0 Hz, 1H), 7.17 (d, *J* = 5.3 Hz, 1H), 6.99 (d, *J* = 4.3 Hz, 1H), 6.97 (d, *J* = 6.5 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 137.43, 136.84, 131.01, 130.51, 128.98, 128.30, 126.80, 124.13, 120.31, 111.13. IR (cm⁻¹): 3103.2, 3023.1, 1504.2, 1487.7, 1429.8, 1146.7, 952.6, 882.9, 838.1, 751.3, 707.3, 688.2. HRMS: Calculated for C₁₂H₉BrS⁺ ([M]⁺): 263.9603 Found: 263.9608.



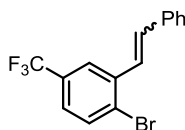
(E)-5-bromo-6-styrylbenzo[d][1,3]dioxole (A20): General olefination procedure **A** was followed employing 6-bromobenzo[d][1,3]dioxole-5-carbaldehyde (2.95 mmol). Purification by flash column chromatography eluting with hexanes/EtOAc provided 728 mg (82%) of **A20** as a white solid. Spectroscopic data matched reported literature data.¹³ ¹H NMR (500 MHz, CDCl₃) δ 7.52 (d, *J* = 7.5 Hz, 2H), 7.38 (m, 2H), 7.31 – 7.24 (m, 2H), 7.15 (s, 1H), 7.04 (s, 1H), 6.89 (d, *J* = 16.1 Hz, 1H), 6.00 (s, 2H).



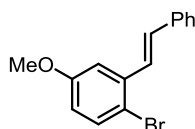
1-bromo-4-fluoro-2-styrylbenzene (A21): General olefination procedure **A** was followed employing 2-bromo-5-fluorobenzaldehyde (2.4 mmol). Purification by flash column chromatography eluting with hexanes/EtOAc provided 365 mg (55%) of **A21** as an inseparable mixture of alkene isomers (6.25:1) as a clear oil. $^1\text{H NMR}$ (500 MHz, CDCl_3 ; for major *E* isomer) δ 77.61 (d, $J = 2.4$ Hz, 1H), 77.53 (d, $J = 7.6$ Hz, 2H), 77.48 (d, $J = 8.5$ Hz, 1H), 77.36 (dd, $J = 15.3, 7.1$ Hz, 3H), 77.29 (t, $J = 7.3$ Hz, 1H), 77.07 (dd, $J = 8.6, 2.5$ Hz, 1H), 77.01 (d, $J = 16.2$ Hz, 1H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3 for major *E* isomer) δ 162.11 (d, $J = 245.0$), 138.7 (d, $J = 8.7$), 136.51, 134.17 (d, $J = 8.7$), 132.54, 128.79, 128.43, 126.96, 126.57 (d, $J = 2.5$), 115.95 (d, $J = 23.0$), 113.24 ($J = 23.5$). **IR** (cm^{-1}): 3024.0, 1599.1, 1571.3, 1457.9, 1410.0, 1255.6, 1159.6, 1027.7, 956.7, 746.6, 695.5, 596.0. **HRMS:** Calculated for $\text{C}_{14}\text{H}_{10}\text{BrF}^+$ ($[\text{M}]^+$): 275.9950 Found: 275.9949.



2-bromo-4-chloro-1-styrylbenzene (A22): General olefination procedure **A** was followed employing 2-bromo-4-chlorobenzaldehyde (2.39 mmol). Purification by flash column chromatography eluting with hexanes/EtOAc provided 357 mg (52%) as an inseparable mixture of alkene isomers (3.86:1) of **A22** as clear crystals. $^1\text{H NMR}$ (500 MHz, CDCl_3 ; for the mixture of isomers) δ 7.64 (d, $J = 2.4$ Hz, 1H), 7.55 (d, $J = 7.6$ Hz, 2.05H), 7.53 – 7.48 (m, 1.11H), 7.38 (m, 3.08H), 7.32 (t, $J = 7.3$ Hz, 1.07H), 7.26 – 7.19 (m, 0.79H), 7.14 (m, 0.75H), 7.11 – 7.08 (m, 1.11H), 7.04 (d, $J = 16.2$ Hz, 1.28H), 6.72 (d, $J = 12.1$ Hz, 0.31H), 6.53 (d, $J = 12.1$ Hz, 0.31H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 136.93, 135.98, 133.78, 132.82, 132.17, 129.01, 128.53, 128.09, 127.50, 127.09, 126.51, 124.35. **IR** (cm^{-1}): 3058.2, 1600.4, 1495.6, 1412.0, 1319.7, 1277.8, 1249.3, 1151.6, 1107.4, 1078.1, 1221.3, 954.4, 922.2, 822.2, 751.6, 709.9, 684.1. **HRMS:** Calculated for $\text{C}_{14}\text{H}_{10}\text{BrCl}^+$ ($[\text{M}]^+$): 291.9654 found: 291.9659.

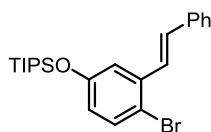


1-bromo-2-styryl-4-(trifluoromethyl)benzene (A23): General olefination procedure **A** was followed employing 2-bromo-5-(trifluoromethyl)benzaldehyde (2.39 mmol). Purification by flash column chromatography eluting with hexanes/EtOAc provided 249 mg (32%) of **A23** as an inseparable mixture of alkene isomers (6.25:1) as a white solid. $^1\text{H NMR}$ (500 MHz, CDCl_3 ; for major *E* isomer) δ 7.89 (s, 1H), 7.73 – 7.69 (m, 1H), 7.58 (d, $J = 7.5$ Hz, 2H), 7.45 (d, $J = 16.2$ Hz, 1H), 7.41 (t, $J = 7.5$ Hz, 2H), 7.37 – 7.31 (m, 2H), 7.14 – 7.09 (m, 1H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3 ; for major *E* isomer) δ 138.01, 136.37, 133.65, 133.16, 130.15 (q, $J = 33.7$), 128.83, 128.60, 127.01, 126.11, 124.95 (q, $J = 3.7$), 123.38 (q, $J = 3.7$). **IR** (cm^{-1}): 3058.2, 1631.2, 1600.4, 1495.6, 1412.0, 1319.7, 1277.8, 1249.3, 1151.6, 1107.4, 954.4, 751.6. **HRMS:** Calculated for $\text{C}_{15}\text{H}_{10}\text{BrF}_3^+$ ($[\text{M}]^+$): 325.9918 found: 325.9925



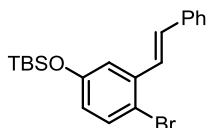
(E)-1-bromo-4-methoxy-2-styrylbenzene (A24): General olefination procedure **A** was followed employing 2-bromo-5-methoxybenzaldehyde (2.39 mmol). Purification by flash column chromatography eluting with hexanes/EtOAc provided 549 mg (80%) of **A24** as a white solid. Spectroscopic data matched reported literature

data.¹⁴ ¹H NMR (500 MHz, CDCl₃) δ 7.56 (d, *J* = 7.7 Hz, 2H), 7.49 – 7.36 (m, 4H), 7.30 (t, *J* = 7.3 Hz, 1H), 7.20 (d, *J* = 2.9 Hz, 1H), 7.02 (d, *J* = 16.2 Hz, 1H), 6.72 (dd, *J* = 8.8, 2.9 Hz, 1H), 3.85 (s, 3H)

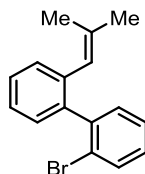


(E)-4-bromo-3-styrylphenoxytriisopropylsilane (A25): To a 50 mL round bottom flask equipped with a magnetic stir bar were added 2-bromo-5-hydroxy-benzaldehyde (500 mg, 2.49 mmol) and DMF (20 mL) at room temperature. To this reaction mixture was added imidazole (423 mg, 6.22 mmol) and triisopropylsilyl chloride (575 mg, 2.98 mmol). After 3 h, water was added and the mixture was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine (1 × 10 mL), dried over MgSO₄ and concentrated under reduced pressure to yield the crude 2-bromo-5-((triisopropylsilyloxy)benzaldehyde (844 mg). The aldehyde was used without further purification.

General olefination procedure **A** was followed employing 2-bromo-5-((triisopropylsilyloxy)benzaldehyde (1.69 mmol). Purification by flash column chromatography eluting with hexanes/EtOAc provided 325 mg (45%) of **A25** as a clear oil. ¹H NMR (500 MHz, CDCl₃) δ 7.57 (d, *J* = 7.6 Hz, 2H), 7.44 – 7.36 (m, 4H), 7.30 (t, *J* = 7.3 Hz, 1H), 7.20 (d, *J* = 2.8 Hz, 1H), 6.97 (d, *J* = 16.2 Hz, 1H), 6.69 (dd, *J* = 8.7, 2.8 Hz, 1H), 1.35 – 1.24 (m, 3H), 1.14 (d, *J* = 7.4 Hz, 18H). ¹³C NMR (125 MHz, CDCl₃) δ 155.79, 138.05, 137.17, 133.71, 131.45, 128.93, 128.28, 127.80, 127.07, 120.96, 118.05, 115.44, 18.15, 12.88. IR (cm⁻¹): 2942.9, 2865.3, 1586.6, 1461.3, 1403.9, 1291.0, 1173.6, 994.6, 958.6, 880.8, 826.4, 750.6, 720.2, 686.0, 434.1. HRMS: Calculated for C₂₃H₃₁BrOSi⁺ ([M]⁺): 430.1328 found: 430.1326.

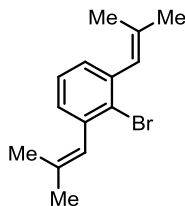


(E)-4-bromo-3-styrylphenoxy(tert-butyl)dimethylsilane (A26): General olefination procedure **A** was followed employing 2-bromo-5-((tert-butyl dimethylsilyloxy)benzaldehyde¹⁵ (1.90 mmol). Purification by flash column chromatography eluting with hexanes/EtOAc provided 385 mg (52%) of **A26** as a clear oil. ¹H NMR (500 MHz, CDCl₃) δ 7.56 (d, *J* = 7.6 Hz, 2H), 7.40 (m, 4H), 7.29 (t, *J* = 7.3 Hz, 1H), 7.13 (s, *J* = 2.1 Hz, 1H), 6.97 (d, *J* = 16.2 Hz, 1H), 6.64 (d, *J* = 8.6 Hz, 1H), 1.01 (s, 9H), 0.23 (s, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 155.40, 138.18, 137.17, 133.77, 131.57, 128.94, 128.30, 127.74, 127.08, 121.21, 118.34, 115.87, 25.91, 18.46, -4.15. IR (cm⁻¹): 2927.6, 2856.0, 1586.6, 1560.2, 1461.7, 1289.8, 1253.2, 1172.3, 993.4, 958.5, 860.6, 836.0, 779.8, 750.1. HRMS: Calculated for C₂₀H₂₅BrOSi⁺ ([M]⁺): 388.0858 found: 388.0864.

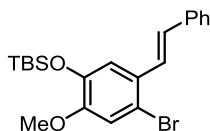


2-bromo-2'-(2-methylprop-1-en-1-yl)-1,1'-biphenyl (A27): General olefination procedure **A** was followed employing 2'-bromo-[1,1'-biphenyl]-2-carbaldehyde¹⁶ (2.68 mmol). Purification by flash column chromatography eluting with hexanes/EtOAc provided 414 mg (54%) of **A27** as a clear oil ¹H NMR (400 MHz, CDCl₃) δ 7.63 (dd, *J* = 7.5, 2.0 Hz, 1H), 7.38 – 7.27 (m, 5H), 7.23 – 7.11 (m, 3H), 5.87 (s, 1H), 1.75 (s, *J* = 0.6 Hz, 3H), 1.71 (s, *J* = 1.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 142.42, 140.54, 137.34, 135.61, 132.46, 131.37, 129.63, 129.53, 128.46, 127.35, 126.81, 125.80, 123.82, 123.80, 26.20, 19.42. IR (cm⁻¹): 2907.1,

1462.9, 1440.1, 1375.1, 1223.9, 1003.6, 827.6, 748.1, 699.7, 661.6, 617.1. **HRMS**: Calculated for $C_{16}H_{15}Br^+$ ($[M]^+$): 286.0357 found: 286.0359

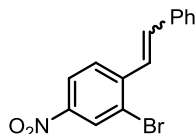


2-bromo-1,3-bis(2-methylprop-1-en-1-yl)benzene (A28): General olefination procedure **B** was followed employing 2-bromoisophthalaldehyde (0.8 mmol) and isopropyltriphenylphosphonium iodide (2.2 equiv) Purification by flash column chromatography eluting with hexanes/EtOAc provided 157 mg (74%) of **A28** as a clear oil. 1H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.16 (m, 1H), 7.07 (d, $J = 7.6$ Hz, 2H), 6.27 (s, 2H), 1.93 (s, $J = 1.4$ Hz, 6H), 1.74 (s, $J = 1.3$ Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.01, 135.89, 128.76, 126.21, 125.86, 125.56, 26.07, 19.34. **IR** (cm^{-1}): 2922.0, 1977.4, 1494.8, 1375.9, 1184.6, 1020.9, 905.1, 727.0. **HRMS**: Calculated for $C_{14}H_{17}Br^+$ ($[M]^+$): 264.0514 found: 264.0512.

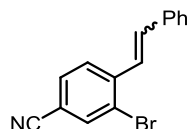


(E)-(4-bromo-2-methoxy-5-styrylphenoxy)(tert-butyl)dimethylsilane (A29): To a 100 mL round bottom flask equipped with a magnetic stir bar were added 2-bromo-5-hydroxy-4-methoxy-benzaldehyde (1500 mg, 6.49 mmol) and DCM (40 mL) at room temperature. To this reaction mixture was added imidazole (884 mg, 13.0 mmol) and TBSCl (1468 mg, 9.74 mmol). After 5 h, water was added and the mixture was extracted with DCM (3×20 mL). The combined organic layers were washed with brine (1×20 mL), dried over $MgSO_4$ and concentrated under reduced pressure to yield the crude 2-bromo-5-[tert-butyl(dimethyl)silyl]oxy-4-methoxy-benzaldehyde. Purification by flash column chromatography eluting with hexanes/EtOAc provided 1592 mg (71%) of 2-bromo-5-[tert-butyl(dimethyl)silyl]oxy-4-methoxy-benzaldehyde as a clear oil. 1H NMR (500 MHz, $CDCl_3$) δ 10.15 (s, 1H), 7.39 (s, 1H), 7.04 (s, 1H), 3.89 (s, 3H), 0.99 (s, 9H), 0.16 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.96, 156.94, 145.20, 126.98, 120.71, 120.62, 116.24, 56.16, 25.81, 18.62, -4.42. **IR** (cm^{-1}): 2929.0, 2856.3, 1683.2, 1587.6, 1498.5, 1438.0, 1275.7, 1251.6, 1213.8, 1155.4, 1026.3, 855.0, 836.4, 780.8. **HRMS**: Calculated for $C_{14}H_{21}O_3BrSi^+$ ($[M + H]^+$): 345.0516 found: 345.0516.

(E)-(4-bromo-2-methoxy-5-styrylphenoxy)(tert-butyl)dimethylsilane was prepared according to general olefination procedure **A** employing 2-bromo-5-[tert-butyl(dimethyl)silyl]oxy-4-methoxy-benzaldehyde (4.05 mmol). Purification by flash column chromatography eluting with hexanes/EtOAc provided 1100 mg (65%) of **A29** as a white solid. 1H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, $J = 7.6$ Hz, 2H), 7.36 (m, 3H), 7.28 – 7.24 (m, 1H), 7.16 (s, 1H), 7.03 (s, 1H), 6.86 (d, $J = 16.1$ Hz, 1H), 3.82 (s, 3H), 1.02 (s, 9H), 0.18 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.51, 144.87, 137.50, 129.77, 129.59, 128.88, 127.88, 127.34, 126.83, 118.49, 116.25, 115.77, 55.88, 25.94, 18.70, -4.37. **IR** (cm^{-1}): 2955.1, 2925.7, 2853.4, 1592.7, 1499.9, 1436.4, 1389.1, 1272.9, 1249.7, 1167.8, 1032.4, 956.6, 862.4, 832.1, 783.1, 794.3. **HRMS**: Calculated for $C_{21}H_{27}O_2BrSi^+$ ($[M]^+$): 418.0964 found: 418.0955.



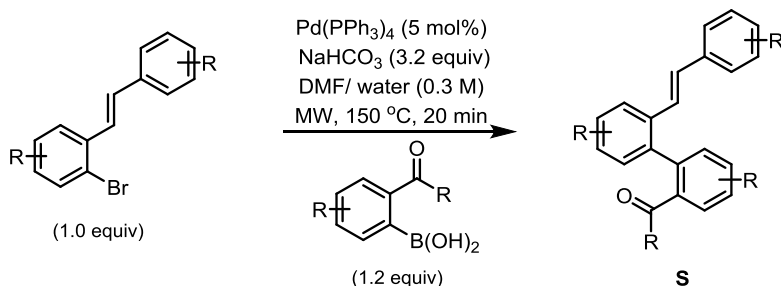
2-bromo-4-nitro-1-styrylbenzene (A30): General olefination procedure **B** was followed employing 2-bromo-4-nitrobenzaldehyde (2.17 mmol). Purification by flash column chromatography eluting with hexanes/EtOAc provided 485 mg (73%) as an inseparable mixture of alkene isomers (2.0:1.0) of **A30** as a yellow oil. **¹H NMR** (500 MHz, CDCl₃; for *E/Z* mixture) δ 8.50 (m, 1.12H), 8.19 (dd, *J* = 8.7, 2.2 Hz, 0.33H), 7.94 (dd, *J* = 8.6, 2.2 Hz, 0.91H), 7.84 (d, *J* = 8.7 Hz, 0.36H), 7.61 (d, *J* = 7.3 Hz, 0.78H), 7.50 (d, *J* = 16.2 Hz, 0.50H), 7.44 (t, *J* = 7.4 Hz, 0.73H), 7.38 (t, *J* = 7.3 Hz, 0.39H), 7.33 (d, *J* = 8.6 Hz, 0.95H), 7.26 – 7.21 (m, 3.30H), 7.13 (m, 1.92H), 6.89 (d, *J* = 12.1 Hz, 1H), 6.63 (d, *J* = 12.1 Hz, 0.96H). **¹³C NMR** (125 MHz, cdcl₃; for *E/Z* mixture) δ 147.16, 146.96, 145.13, 143.77, 136.20, 135.81, 135.55, 134.54, 131.56, 129.45, 129.16, 128.73, 128.67, 128.36, 128.23, 127.90, 127.54, 126.83, 125.66, 124.36, 123.90, 122.76, 122.12. **IR** (cm⁻¹): 3022.7, 2853.5, 1625.9, 1579.7, 1515.1, 1492.4, 1339.5, 1265.9, 1113.9, 1035.8, 892.4, 863.2, 771.0, 726.5, 695.4. **HRMS:** Calculated for C₁₄H₁₀BrNO₂⁺ ([M]⁺): 302.9895 found: 302.9898.



3-bromo-4-styrylbenzonitrile (A31): General olefination procedure **A** was followed employing 3-bromo-4-formylbenzonitrile¹⁷ (3.33 mmol). Purification by flash column chromatography afforded 200 mg (21% yield) of an *E/Z* mixture (1.5:1.0) of the title compound as a white solid. **¹H NMR** (700 MHz, CDCl₃, for *E/Z* mixture) δ 7.93 (d, *J* = 1.6 Hz, 1.5H), 7.72 (d, *J* = 8.3 Hz, 0.8H), 7.71 (d, *J* = 8.3 Hz, 1.5H), 7.57 (d, *J* = 7.5 Hz, 3.2H), 7.41 (t, *J* = 6.7 Hz, 25H), 7.39 – 7.32 (m, 4.7H), 7.24 – 7.20 (m, 2.6H), 7.11 – 7.06 (m, 3.4H), 6.81 (d, *J* = 12.0 Hz, 1H), 6.54 (d, *J* = 12.1 Hz, 1H). **¹³C NMR** (176 MHz, CDCl₃, for *E/Z* mixture) δ 139.77, 138.93, 136.26, 135.37, 134.35, 134.30, 134.09, 134.00, 133.71, 131.55, 131.23, 130.23, 129.67, 129.14, 129.08, 129.06, 128.99, 128.73, 128.31, 127.45, 127.29, 125.50, 118.30, 118.11, 112.06, 111.39. **IR** (cm⁻¹): 2229.4, 1467.2, 1222.9, 1156.4, 818.0, 754.5, 688.0, 607.3. **HRMS:** calculated for C₁₅H₁₀BrN⁺ ([M]⁺): 282.9997 Found: 282.9986.

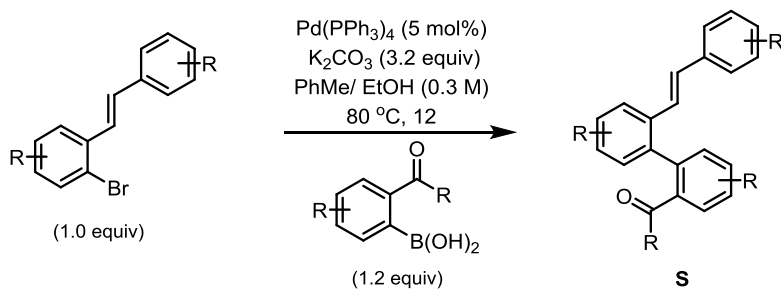
b. Synthesis of biaryl metathesis substrates

General cross-coupling procedure A for metathesis substrates (S):

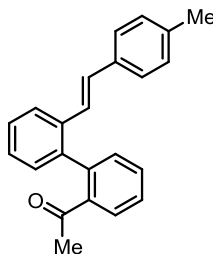


Procedure adopted from van der Eycken et al.¹⁸ To a Chemglass microwave vial equipped with a magnetic stir bar were added 2-bromo-aryl styrene (1.0 equiv), NaHCO₃ (3.2 equiv), aryl boronic acid (1.2 equiv), and Pd(PPh₃)₄ (5 mol%). A solution of DMF/ water (0.3 M; 1:1) was then added and the vial sealed. The vial was heated under microwave irradiation (150 °C, 20 min) at atmospheric pressure. After the reaction was allowed to cool to room temperature, it was diluted with ethyl acetate (n mL) and washed with water (3 × n mL) and brine (1 × n mL). The organic phase was dried over MgSO₄ and concentrated under reduced pressure. The crude product was purified *via* flash column chromatography eluting with a mixture of hexanes and ethyl acetate to give the pure coupled product (S).

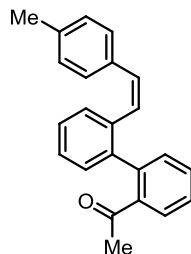
General cross-coupling procedure B for metathesis substrates (S):



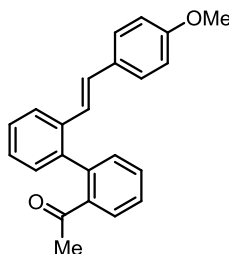
To a Chemglass reaction tube equipped with a magnetic stir bar were added aryl bromide (1.0 equiv), K₂CO₃ (3.2 equiv), aryl boronic acid (1.2 equiv), and Pd(PPh₃)₄ (5 mol%). A solution of toluene/ ethanol (0.3 M; 1:1) was then added and the vial sealed. The reaction was heated to 80 °C for 12 h. After the reaction was allowed to cool to room temperature, it was diluted with ethyl acetate (15 mL) and washed with water (3 × n mL) and brine (1 × n mL). The organic phase was dried over MgSO₄ and concentrated under reduced pressure. The crude product was purified *via* flash column chromatography eluting with a mixture of hexanes and ethyl acetate to give the pure cross coupled product (S).



(E)-1-(2'-(4-methylstyryl)-[1,1'-biphenyl]-2-yl)ethan-1-one (12): Prepared according to general cross coupling procedure **A** between **E-A2** (0.55 mmol) and 2-acetylphenylboronic acid. Purification by flash column chromatography eluting with hexanes/EtOAc afforded 109 mg (64% yield) of **12** as a white solid. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.76 (d, $J = 7.7$ Hz, 1H), 7.71 (d, $J = 6.9$ Hz, 1H), 7.53 (t, $J = 7.4$ Hz, 1H), 7.46 (t, $J = 7.5$ Hz, 1H), 7.41 (t, $J = 7.5$ Hz, 1H), 7.31 (t, $J = 7.5$ Hz, 2H), 7.20 (t, $J = 8.7$ Hz, 3H), 7.09 (d, $J = 7.6$ Hz, 2H), 7.00 (d, $J = 16.2$ Hz, 1H), 6.83 (d, $J = 16.2$ Hz, 1H), 2.32 (s, 3H), 2.00 (s, 3H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 202.93, 141.08, 140.03, 139.88, 137.88, 136.00, 134.73, 131.72, 131.03, 130.62, 130.52, 129.57, 128.48, 128.44, 127.82, 127.59, 126.72, 125.72, 125.65, 29.94, 21.47. **HRMS**: calculated for $\text{C}_{23}\text{H}_{20}\text{ONa}^+$ ($[\text{M} + \text{Na}]^+$): 335.1406 Found 335.1404.

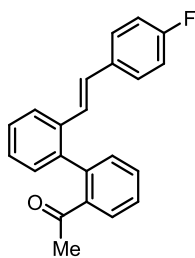


(Z)-1-(2'-(4-methylstyryl)-[1,1'-biphenyl]-2-yl)ethan-1-one (13): Prepared according to general cross coupling procedure **A** between **Z-A2** (0.40 mmol) and 2-acetylphenylboronic acid. Purification by flash column chromatography eluting with hexanes/EtOAc afforded 61 mg (49% yield) of the title compound as a white solid. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.65 (d, $J = 7.6$ Hz, 1H), 7.48 – 7.38 (m, 2H), 7.35 (d, $J = 7.6$ Hz, 1H), 7.27 (s, $J = 4.7$ Hz, 2H), 7.23 – 7.15 (m, 2H), 7.13 (d, $J = 8.0$ Hz, 2H), 7.02 (d, $J = 8.0$ Hz, 2H), 6.41 (d, $J = 12.3$ Hz, 1H), 6.16 (d, $J = 12.2$ Hz, 1H), 2.31 (s, 3H), 2.12 (s, 3H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 202.84, 140.64, 140.14, 137.31, 136.08, 133.99, 131.54, 130.95, 130.88, 130.21, 129.70, 129.55, 129.12, 128.98, 128.44, 128.12, 127.64, 127.60, 126.70, 29.66, 21.47. **IR** (cm^{-1}): 3059.2, 3015.0, 2922.2, 1688.6, 1594.0, 1509.1, 1437.4, 1354.1, 1267.7, 1246.3, 908.5, 822.9, 761.0, 729.6. **HRMS**: calculated for $\text{C}_{23}\text{H}_{20}\text{ONa}^+$ ($[\text{M} + \text{Na}]^+$): 335.1406 Found 335.1404.

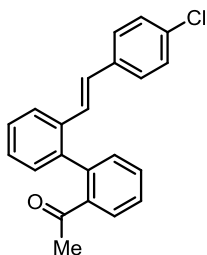


(E)-1-(2'-(4-methoxystyryl)-[1,1'-biphenyl]-2-yl)ethan-1-one (14): Prepared according to general cross coupling procedure **A** between **A4** (0.52 mmol) and 2-acetylphenylboronic acid. Purification by flash column chromatography eluting with hexanes/EtOAc afforded 123 mg (72% yield) of the title compound as a white solid. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.74 (d, $J = 7.9$ Hz, 1H), 7.70 (d, $J = 7.7$ Hz, 1H), 7.53 (t, $J = 7.5$ Hz, 1H), 7.46 (t, $J = 7.5$ Hz, 1H), 7.40 (t, $J = 7.6$ Hz, 1H), 7.32 – 7.27 (m, 2H), 7.27 – 7.23 (m, 2H), 7.19 (d, $J = 7.6$ Hz,

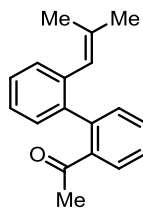
1H), 6.98 (d, $J = 16.2$ Hz, 1H), 6.83 (d, $J = 8.6$ Hz, 2H), 6.74 (d, $J = 16.2$ Hz, 1H), 3.79 (s, 3H), 1.99 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 202.99, 159.58, 141.10, 139.92, 139.87, 136.11, 131.68, 131.03, 130.49, 130.33, 130.16, 128.47, 128.41, 128.02, 127.79, 127.40, 125.45, 124.55, 114.30, 55.51, 29.93. HRMS: calculated for $\text{C}_{23}\text{H}_{24}\text{O}_2\text{N}^+$ ($[\text{M} + \text{NH}_4^+]^+$): 346.1802 Found 346.1801.



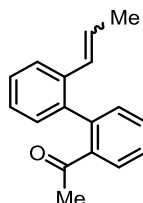
(E)-1-(2'-(4-fluorostyryl)-[1,1'-biphenyl]-2-yl)ethan-1-one (15): Prepared according to general cross coupling procedure A between A5 (0.54 mmol) and 2-acetylphenylboronic acid. Purification by flash column chromatography eluting with hexanes/EtOAc afforded 121 mg (71% yield) of the title compound as a white solid. ^1H NMR (500 MHz, CDCl_3) δ 7.74 (d, $J = 7.9$ Hz, 1H), 7.71 (d, $J = 7.7$ Hz, 1H), 7.54 (t, $J = 7.3$ Hz, 1H), 7.47 (t, $J = 7.5$ Hz, 1H), 7.42 (t, $J = 7.6$ Hz, 1H), 7.35 – 7.30 (m, 2H), 7.29 – 7.24 (m, 3H), 7.21 (d, $J = 7.5$ Hz, 1H), 6.99 – 6.95 (m, 2H), 6.77 (d, $J = 16.2$ Hz, 1H), 1.99 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 202.63, 162.33 (d, $J = 247.4$), 140.85, 139.91, 139.48, 135.47, 133.43 (d, $J = 3.2$), 131.39, 130.86, 130.24, 129.17, 128.28, 128.22, 128.08, 128.02, 127.63 (d, $J = 11.0$), 126.21 (d, $J = 2.0$), 125.36, 115.64, 115.47, 29.66. IR (cm^{-1}): 3053.1, 1673.7, 1596.6, 1509.1, 1463.6, 1270.8, 1229.4, 1158.9, 973.8, 823.9, 759.7. HRMS: calculated for $\text{C}_{22}\text{H}_{17}\text{OFNa}^+$ ($[\text{M} + \text{Na}^+]^+$): 339.1161 Found 339.1159.



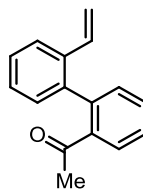
(E)-1-(2'-(4-chlorostyryl)-[1,1'-biphenyl]-2-yl)ethan-1-one (16): Prepared according to general cross coupling procedure A between A3 (0.34 mmol) and 2-acetylphenylboronic acid. Purification by flash column chromatography eluting with hexanes/EtOAc afforded 53 mg (47% yield) of the title compound as a white solid. ^1H NMR (500 MHz, CDCl_3) δ 7.74 (d, $J = 7.8$ Hz, 1H), 7.71 (d, $J = 7.6$ Hz, 1H), 7.54 (t, $J = 6.9$ Hz, 1H), 7.48 (t, $J = 7.0$ Hz, 1H), 7.42 (t, $J = 7.6$ Hz, 1H), 7.33 (m, 3H), 7.24 – 7.20 (m, 4H), 6.96 (d, $J = 16.2$ Hz, 1H), 6.82 (d, $J = 16.2$ Hz, 1H), 2.00 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 202.79, 141.07, 140.27, 139.64, 135.98, 135.54, 133.51, 131.64, 131.11, 130.49, 129.31, 129.01, 128.53, 128.47, 128.01, 127.96, 127.93, 127.30, 125.68, 29.89. IR (cm^{-1}): 3054.0, 2249.2, 1683.6, 1491.5, 1354.4, 1245.4, 1088.2, 905.7, 812.3, 726.2, 430.0. HRMS: calculated for $\text{C}_{22}\text{H}_{21}\text{OCIN}^+$ ($[\text{M} + \text{NH}_4^+]^+$): 350.1306 Found 350.1305.



1-(2'-(2-methylprop-1-en-1-yl)-[1,1'-biphenyl]-2-yl)ethan-1-one (17): Prepared according to general cross coupling procedure **B** between **A6** (2.15 mmol) and 2-acetylphenylboronic acid. Purification by flash column chromatography eluting with hexanes/EtOAc afforded 335 mg (62% yield) of the title compound as a clear oil. $^1\text{H NMR}$ (700 MHz, CDCl_3) δ 7.63 (d, $J = 7.7$ Hz, 1H), 7.51 – 7.46 (m, 1H), 7.39 (td, $J = 7.6, 1.1$ Hz, 1H), 7.37 – 7.33 (m, 1H), 7.31 – 7.26 (m, 2H), 7.26 – 7.21 (m, 2H), 5.79 (s, 1H), 1.97 (s, 3H), 1.75 (s, 3H), 1.72 (s, 3H). $^{13}\text{C NMR}$ (176 MHz, CDCl_3) δ 202.47, 140.81, 140.60, 140.55, 137.19, 136.43, 131.33, 130.91, 130.12, 129.81, 128.13, 127.64, 127.44, 126.71, 124.44, 29.56, 26.46, 19.37. **IR** (cm^{-1}): 2972.3, 2907.9, 1682.9, 1593.5, 1436.2, 1375.8, 1351.9, 1263.1, 1243.9, 1233.4, 952.9, 830.8, 750.2, 593.4. **HRMS**: calculated for $\text{C}_{18}\text{H}_{18}\text{ONa}^+$ ($[\text{M} + \text{Na}^+]^+$): 250.1358 Found 250.1354.

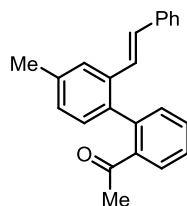


1-(2'-(prop-1-en-1-yl)-[1,1'-biphenyl]-2-yl)ethan-1-one (18): Prepared according to general cross coupling procedure **A** between **A7** (0.76 mmol) and 2-acetylphenylboronic acid. Purification by flash column chromatography eluting with hexanes/EtOAc afforded 105 mg (58% yield) of the title compound as a clear oil. $^1\text{H NMR}$ (700 MHz, CDCl_3) δ 7.68 (dd, $J = 10.1, 5.0$ Hz, 1H), 7.65 (dd, $J = 7.7, 1.2$ Hz, 0.5H), 7.56 (d, $J = 7.8$ Hz, 1H), 7.51 (td, $J = 7.4, 1.2$ Hz, 1H), 7.50 – 7.47 (m, 0.5H), 7.43 (td, $J = 7.6, 1.2$ Hz, 1H), 7.41 (td, $J = 7.6, 1.2$ Hz, 0.5H), 7.39 – 7.36 (m, 1H), 7.34 (td, $J = 7.7, 1.3$ Hz, 1H), 7.32 – 7.29 (m, 0.5H), 7.28 – 7.22 (m, 3H), 7.14 (dd, $J = 7.6, 1.1$ Hz, 1H), 6.18 – 6.10 (m, 2H), 6.05 (dd, $J = 11.5, 1.8$ Hz, 0.5H), 5.67 (dq, $J = 11.6, 7.1$ Hz, 0.5H), 1.98 (s, 1.5H), 1.95 (s, 3H), 1.80 (dd, $J = 7.1, 1.8$ Hz, 3H), 1.75 (d, $J = 4.8$ Hz, 6H). $^{13}\text{C NMR}$ (176 MHz, CDCl_3) δ 203.18, 202.85, 141.04, 140.79, 140.77, 140.43, 140.22, 139.20, 136.60, 136.00, 131.58, 131.39, 131.06, 131.01, 130.30, 130.04, 129.88, 129.09, 129.02, 128.45, 128.41, 128.34, 128.09, 127.95, 127.72, 127.71, 127.68, 127.21, 127.07, 125.76, 29.94, 29.78, 18.97, 14.58. **IR** (cm^{-1}): 3018.0, 2362.3, 1681.9, 1593.2, 1468.3, 1435.6, 1352.5, 1263.7, 1232.9, 964.2, 749.8, 593.8. **HRMS**: calculated for $\text{C}_{17}\text{H}_{17}\text{O}^+$ ($[\text{M} + \text{H}^+]^+$): 237.1274 Found 237.1278.

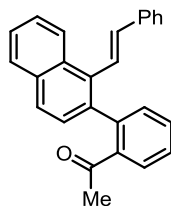


1-(2'-vinyl-[1,1'-biphenyl]-2-yl)ethan-1-one (19): Prepared according to general cross coupling procedure **A** between **A8** (0.82 mmol) and 2-acetylphenylboronic acid. Purification by flash column chromatography eluting with hexanes/EtOAc afforded 42 mg (23% yield) of the title compound as a clear oil. $^1\text{H NMR}$ (700 MHz, CDCl_3) δ 7.69 (dd, $J = 7.7, 1.3$ Hz, 1H), 7.65 (d, $J = 7.8$ Hz, 1H), 7.51 (td, $J = 7.5, 1.3$ Hz, 1H), 7.44 (tt, $J = 7.7, 3.9$ Hz, 1H), 7.39 (dt, $J = 7.5, 3.6$ Hz, 1H), 7.31 (td, $J = 7.5, 1.1$ Hz, 1H), 7.29 – 7.25 (m, 1H), 7.17 (dd, $J = 7.6,$

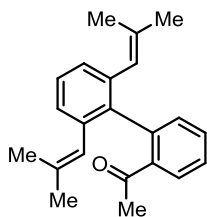
1.2 Hz, 1H), 6.49 (dd, $J = 17.5, 11.0$ Hz, 1H), 5.68 (dd, $J = 17.4, 0.7$ Hz, 1H), 5.17 (dd, $J = 11.0, 0.8$ Hz, 1H), 1.97 (s, 3H). ^{13}C NMR (175 MHz, CDCl_3) δ 203.03, 140.89, 139.89, 139.78, 136.22, 134.93, 131.51, 131.00, 130.24, 128.43, 128.42, 127.93, 127.80, 125.60, 115.90, 29.90. IR (cm^{-1}): 3067.3, 2251.0, 1683.6, 1417.3, 1355.0, 1268.8, 1245.3, 907.4, 762.7, 726.7, 647.7, 459.0. HRMS: calculated for $\text{C}_{25}\text{H}_{28}\text{ON}^+$ ($[\text{M} + \text{H}]^+$): 223.1117 Found 223.1121.



(E)-1-(4'-methyl-2'-styryl-[1,1'-biphenyl]-2-yl)ethan-1-one (S2): Prepared according to general cross coupling procedure **A** between **A10** (0.55 mmol) and 2-acetylphenylboronic acid. Purification by flash column chromatography eluting with hexanes/EtOAc afforded 155 mg (90% yield) of the title compound as a clear oil. ^1H NMR (500 MHz, CDCl_3) δ 7.70 (d, $J = 7.7$ Hz, 1H), 7.67 (d, $J = 8.0$ Hz, 1H), 7.52 (t, $J = 7.4$ Hz, 1H), 7.46 (t, $J = 7.5$ Hz, 1H), 7.30 (m, 5H), 7.25 – 7.17 (m, 2H), 7.03 – 6.95 (m, 2H), 6.86 (d, $J = 16.2$ Hz, 1H), 2.38 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 202.83, 140.81, 139.85, 139.69, 137.45, 137.41, 132.77, 131.44, 130.89, 130.76, 129.45, 129.11, 128.57, 128.16, 127.53, 127.49, 126.44, 126.34, 125.37, 29.73, 21.13. IR (cm^{-1}): 3021.1, 1680.3, 1594.6, 1353.5, 1266.4, 965.7, 812.8, 757.2, 730.6, 690.3, 595.0. HRMS: calculated for $\text{C}_{23}\text{H}_{24}\text{ON}^+$ ($[\text{M} + \text{NH}_4]^+$): 330.1852 Found 300.1856.

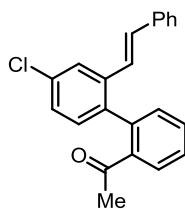


(E)-1-(2-(1-styrylnaphthalen-2-yl)phenyl)ethan-1-one (S3): Prepared according to general cross coupling procedure **B** between **A12** (0.97 mmol) and 2-acetylphenylboronic acid. Purification by flash column chromatography eluting with hexanes/EtOAc afforded 154 mg (46% yield) of the title compound as a white solid. ^1H NMR (500 MHz, CDCl_3) δ 8.37 – 8.29 (m, 1H), 7.94 – 7.89 (m, 1H), 7.85 (d, $J = 8.4$ Hz, 1H), 7.68 (d, $J = 7.7$ Hz, 1H), 7.56 – 7.49 (m, 3H), 7.40 (m, 3H), 7.34 – 7.29 (m, 4H), 7.28 – 7.22 (m, 1H), 7.17 (d, $J = 16.6$ Hz, 1H), 6.60 (d, $J = 16.6$ Hz, 1H), 2.06 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 202.30, 141.22, 140.55, 137.62, 137.51, 136.82, 133.57, 133.54, 131.97, 131.88, 131.12, 128.84, 128.67, 128.50, 128.07, 127.99, 127.67, 127.53, 126.75, 126.55, 126.22, 126.04, 125.42, 29.75. IR (cm^{-1}): 3054.7, 1682.3, 1594.2, 1484.5, 1354.1, 1264.2, 1247.5, 969.2, 820.1, 732.6, 692.8, 597.0. HRMS: calculated for $\text{C}_{26}\text{H}_{24}\text{ON}^+$ ($[\text{M} + \text{NH}_4]^+$): 366.1852 Found 366.1857.

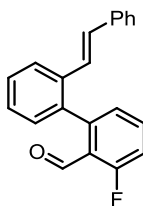


1-(2',6'-bis(2-methylprop-1-en-1-yl)-[1,1'-biphenyl]-2-yl)ethan-1-one (S4): Prepared according to general cross coupling procedure **B** between **A28** (0.97 mmol) and 2-acetylphenylboronic acid. Purification by flash column chromatography eluting with hexanes/EtOAc afforded 154 mg (46% yield) of the title compound as a

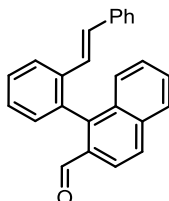
clear oil. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.68 (d, $J = 7.7$ Hz, 1H), 7.45 (t, $J = 7.4$ Hz, 1H), 7.37 (t, $J = 7.5$ Hz, 1H), 7.30 (t, $J = 7.6$ Hz, 1H), 7.17 (d, $J = 7.6$ Hz, 2H), 7.07 (d, $J = 7.5$ Hz, 1H), 5.67 (s, 2H), 1.93 (s, 3H), 1.75 (s, 6H), 1.66 (s, 6H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 201.37, 140.38, 139.87, 139.59, 137.34, 135.38, 131.61, 130.91, 128.32, 128.19, 127.23, 126.82, 124.97, 29.13, 26.40, 19.41. **IR** (cm^{-1}): 2970.5, 2913.6, 2853.1, 1682.7, 1441.3, 1419.9, 1375.2, 1351.8, 1278.0, 1246.7, 847.0, 758.0, 730.9. **HRMS**: calculated for $\text{C}_{22}\text{H}_{28}\text{ON}^+$ ($[\text{M} + \text{NH}_4^+]^+$): 322.2165 Found 322.2165



(E)-1-(4'-chloro-2'-styryl-[1,1'-biphenyl]-2-yl)ethan-1-one (S5): Prepared according to general cross coupling procedure **A** between **A22** (0.51 mmol) and 2-acetylphenylboronic acid. Purification by flash column chromatography eluting with hexanes/EtOAc afforded 132 mg (78% yield) of the title compound as clear crystals. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.72 (m, 2H), 7.54 (t, $J = 7.4$ Hz, 1H), 7.49 (t, $J = 7.6$ Hz, 1H), 7.28 (m, 6H), 7.23 (m, 1H), 7.13 (d, $J = 8.2$ Hz, 1H), 7.02 (d, $J = 16.2$ Hz, 1H), 6.77 (d, $J = 16.2$ Hz, 1H), 2.09 (s, 3H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 202.21, 140.74, 138.71, 138.65, 137.52, 136.99, 134.38, 131.80, 131.70, 131.58, 131.27, 128.90, 128.62, 128.30, 128.19, 127.65, 126.91, 125.58, 125.47, 29.87. **IR** (cm^{-1}): 1687.6, 1595.8, 1468.8, 1354.6, 1264.0, 1094.4, 964.3, 909.7, 823.0, 731.0, 702.6, 595.2. **HRMS**: calculated for $\text{C}_{22}\text{H}_{21}\text{OCIN}^+$ ($[\text{M} + \text{NH}_4^+]^+$): 350.1306 Found 350.1311

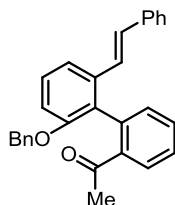


(E)-3-fluoro-2'-styryl-[1,1'-biphenyl]-2-carbaldehyde (S6): Prepared according to general cross coupling procedure **A** between 2-bromo-6-fluorobenzaldehyde (0.74 mmol) and (*E*)-(2-styrylphenyl)boronic acid. Purification by flash column chromatography eluting with hexanes/EtOAc afforded 153 mg (69% yield) of the title compound as a pale yellow oil. $^1\text{H NMR}$ (700 MHz, CDCl_3) δ 9.91 (s, 1H), 7.63 – 7.59 (m, 1H), 7.47 (ddd, $J = 8.0, 7.5, 0.8$ Hz, 1H), 7.35 (td, $J = 7.5, 1.1$ Hz, 1H), 7.32 – 7.27 (m, 4H), 7.25 – 7.20 (m, 3H), 7.17 – 7.14 (m, 1H), 7.04 (d, $J = 16.2$ Hz, 1H), 6.78 (d, $J = 16.2$ Hz, 1H). $^{13}\text{C NMR}$ (175 MHz, CDCl_3) δ 188.90, 162.45 (d, $J = 263.5$), 145.63, 137.01, 136.36 (d, $J = 2.1$), 136.20, 134.54 (d, $J = 10.3$), 131.09, 130.49, 128.78, 128.64, 127.90, 127.41 (d, $J = 3.6$), 127.35, 126.61, 125.94, 125.53, 123.17 (d, $J = 6.8$), 116.19 (d, $J = 21.3$). **IR** (cm^{-1}): 3023.3, 2851.2, 1696.2, 1603.6, 1238.7, 1189.8, 962.0, 913.9, 798.5, 756.5, 735.3, 689.6. **HRMS**: calculated for $\text{C}_{21}\text{H}_{15}\text{OFNa}^+$ ($[\text{M} + \text{Na}^+]^+$): 325.0999 Found 325.1003.

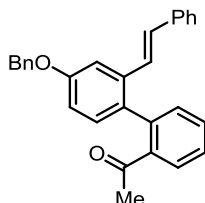


(E)-1-(2-styrylphenyl)-2-naphthaldehyde (S7): Prepared according to general cross coupling procedure **B** between 1-bromo-2-naphthaldehyde (1.28 mmol) and (*E*)-(2-styrylphenyl)boronic acid. Purification by flash column chromatography eluting with hexanes/EtOAc afforded 322 mg (75% yield) of the title compound as a

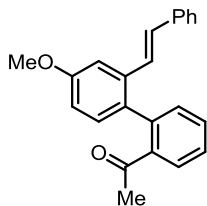
white solid. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 9.82 (s, 1H), 8.10 (d, $J = 8.6$ Hz, 1H), 7.97 (m, 2H), 7.91 (d, $J = 7.9$ Hz, 1H), 7.62 (t, $J = 7.5$ Hz, 1H), 7.55 (m, 2H), 7.43 (dd, $J = 18.1, 7.6$ Hz, 2H), 7.30 (d, $J = 7.5$ Hz, 1H), 7.18 – 7.12 (m, 2H), 7.08 (d, $J = 7.4$ Hz, 2H), 7.03 (d, $J = 16.2$ Hz, 1H), 6.51 (d, $J = 16.2$ Hz, 1H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 192.53, 145.19, 137.52, 136.83, 136.12, 134.09, 132.46, 131.70, 131.57, 130.80, 128.95, 128.91, 128.63, 128.46, 128.28, 127.76, 127.66, 127.24, 127.12, 126.52, 125.83, 125.20, 122.09. **IR** (cm^{-1}): 3057.1, 1688.0, 1594.3, 1493.6, 1429.1, 1379.3, 1330.2, 1264.0, 1239.8, 961.8, 821.6, 732.1, 691.0. **HRMS**: calculated for $\text{C}_{25}\text{H}_{22}\text{ON}^+$ ($[\text{M} + \text{NH}_4^+]^+$): 357.1250 Found 357.1256.



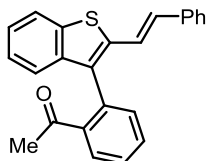
(E)-1-(2'-(benzyloxy)-6'-styryl-[1,1'-biphenyl]-2-yl)ethan-1-one (S8): Prepared according to general cross coupling procedure **A** between **A13** (0.41 mmol) and 2-acetylphenylboronic acid. Purification by flash column chromatography eluting with hexanes/EtOAc afforded 62 mg (37% yield) of the title compound as a clear oil. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.80 (d, $J = 7.7$ Hz, 1H), 7.54 (t, $J = 7.5$ Hz, 1H), 7.47 (t, $J = 7.6$ Hz, 1H), 7.43 (d, $J = 7.9$ Hz, 1H), 7.33 (t, $J = 7.8$ Hz, 1H), 7.30 – 7.17 (m, 9H), 7.12 (d, $J = 7.3$ Hz, 2H), 7.00 (dd, $J = 16.2, 1.8$ Hz, 1H), 6.91 (d, $J = 8.1$ Hz, 1H), 6.76 (dd, $J = 16.2, 2.3$ Hz, 1H), 5.00 (s, 2H), 2.09 (s, 3H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 201.55, 155.74, 140.78, 137.50, 137.41, 137.27, 135.83, 132.53, 131.23, 130.54, 130.28, 128.93, 128.77, 128.53, 128.43, 127.81, 127.71, 127.68, 126.95, 126.76, 118.52, 111.87, 70.46, 29.19. **IR** (cm^{-1}): 3024.3, 1683.0, 1596.4, 1569.1, 1451.0, 1263.4, 1057.4, 960.0, 786.9, 731.8, 692.0, 599.2. **HRMS**: calculated for $\text{C}_{29}\text{H}_{28}\text{O}_2\text{N}^+$ ($[\text{M} + \text{NH}_4^+]^+$): 422.2115 Found 422.2119.



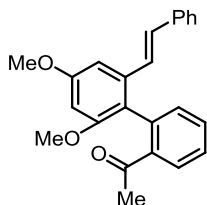
(E)-1-(4'-(benzyloxy)-2'-styryl-[1,1'-biphenyl]-2-yl)ethan-1-one (S9): Prepared according to general cross coupling procedure **A** between **A14** (2 x 211 mg, 0.58 mmol) and 2-acetylphenylboronic acid. Purification by flash column chromatography eluting with hexanes/EtOAc afforded 63 mg (combined) (13% yield) of the title compound as a white solid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.68 (d, $J = 7.6$ Hz, 1H), 7.60 – 7.19 (m, 14H), 7.12 (d, $J = 8.4$ Hz, 1H), 7.04 – 6.91 (m, 2H), 6.86 (d, $J = 16.2$ Hz, 1H), 5.17 (s, 2H), 2.00 (s, 3H). $^{13}\text{C NMR}$ (176 MHz, CDCl_3) δ 203.32, 159.01, 141.42, 139.40, 137.33, 137.04, 136.99, 133.10, 131.98, 131.71, 130.95, 130.87, 128.87, 128.85, 128.38, 128.34, 128.02, 127.86, 127.67, 126.83, 126.62, 114.39, 111.83, 70.43, 30.02. **IR** (cm^{-1}): 1681.8, 1597.4, 1499.5, 1466.1, 1279.0, 1229.9, 1026.4, 996.6, 963.0, 756.3, 728.6. **HRMS**: calculated for $\text{C}_{29}\text{H}_{28}\text{O}_2\text{N}^+$ ($[\text{M} + \text{NH}_4^+]^+$): 422.2115 Found: 422.2118.



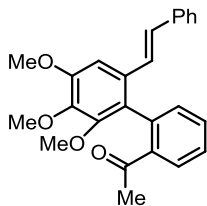
(E)-1-(4'-methoxy-2'-styryl-[1,1'-biphenyl]-2-yl)ethan-1-one (S10): Prepared according to general cross coupling procedure **A** between **A24** (150 mg, 0.52 mmol) and 2-acetylphenylboronic acid. Purification by flash column chromatography eluting with hexanes/EtOAc afforded 128 mg (75% yield) of the title compound as a white solid. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.68 (d, $J = 7.7$ Hz, 1H), 7.51 (t, $J = 7.4$ Hz, 1H), 7.44 (t, $J = 7.5$ Hz, 1H), 7.35 – 7.27 (m, 6H), 7.22 (t, $J = 6.9$ Hz, 1H), 7.12 (d, $J = 8.4$ Hz, 1H), 7.01 (d, $J = 7.8$ Hz, 1H), 6.89 (dd, $J = 15.6, 9.4$ Hz, 2H), 3.91 (s, 3H), 2.00 (s, 3H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 203.34, 159.79, 141.43, 139.45, 137.35, 136.97, 132.86, 132.01, 131.71, 130.94, 130.80, 128.86, 128.37, 128.01, 127.65, 126.84, 126.72, 113.70, 110.69, 55.62, 30.02. **IR** (cm^{-1}): 2833.2, 1683.7, 1603.1, 1473.8, 1281.5, 1243.7, 1212.0, 1165.8, 1048.1, 971.0, 882.9, 809.2, 758.3, 728.1, 695.7, 596.6. **HRMS**: calculated for $\text{C}_{23}\text{H}_{24}\text{O}_2\text{N}^+$ ($[\text{M} + \text{NH}_4^+]^+$): 346.1802 Found 346.1807..



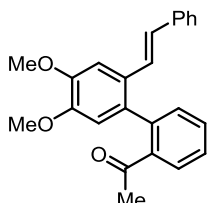
(E)-1-(2-(2-styrylbenzo[b]thiophen-3-yl)phenyl)ethan-1-one (S11): Prepared according to general cross coupling procedure **A** between **A16** (100 mg, 0.32 mmol) and 2-acetylphenylboronic acid. Purification by flash column chromatography eluting with hexanes/EtOAc afforded 98 mg (87% yield) of the title compound as a white solid. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.83 (d, $J = 7.8$ Hz, 2H), 7.64 (t, $J = 7.4$ Hz, 1H), 7.57 (t, $J = 7.6$ Hz, 1H), 7.42 (d, $J = 7.5$ Hz, 1H), 7.37 (t, $J = 7.1$ Hz, 3H), 7.31 (m, 4H), 7.23 (d, $J = 7.3$ Hz, 1H), 7.05 (d, $J = 16.0$ Hz, 1H), 6.98 (d, $J = 16.0$ Hz, 1H), 1.97 (s, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 202.64, 141.91, 140.73, 139.81, 138.00, 136.70, 134.49, 133.42, 132.37, 132.10, 131.68, 129.05, 128.92, 128.69, 128.41, 126.93, 125.70, 125.17, 122.93, 122.50, 120.61, 29.36. **IR** (cm^{-1}): 1681.9, 1351.9, 1431.0, 1351.9, 1273.8, 1236.3, 948.9, 765.0, 752.0, 732.4, 689.5, 472.2. **HRMS**: calculated for $\text{C}_{24}\text{H}_{22}\text{ONS}^+$ ($[\text{M} + \text{NH}_4^+]^+$): 372.1417 Found 372.1422.



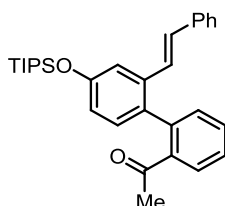
(E)-1-(2',4'-dimethoxy-6'-styryl-[1,1'-biphenyl]-2-yl)ethan-1-one (S12): Prepared according to General Cross Coupling Procedure **A** between **A15** (185 mg, 0.58 mmol) and 2-acetylphenylboronic acid. Purification by flash column chromatography eluting with hexanes/EtOAc afforded 103 mg (50% yield) of the title compound as a white solid. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.75 (d, $J = 7.6$ Hz, 1H), 7.51 (t, $J = 7.4$ Hz, 1H), 7.44 (t, $J = 7.5$ Hz, 1H), 7.27 (s, 1H), 7.23 – 7.14 (m, 2H), 6.99 (d, $J = 16.2$ Hz, 1H), 6.91 (d, $J = 2.0$ Hz, 1H), 6.75 (d, $J = 16.2$ Hz, 1H), 6.48 (d, $J = 2.0$ Hz, 1H), 3.93 (s, 3H), 3.69 (s, 3H), 2.10 (s, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 202.20, 160.57, 157.84, 141.48, 137.76, 137.39, 135.32, 133.00, 131.06, 130.53, 128.81, 128.19, 127.91, 127.59, 127.18, 126.81, 122.48, 101.52, 98.34, 55.82, 55.64, 29.22. **IR** (cm^{-1}): 1683.8, 1597.2, 1575.8, 1456.8, 1349.1, 1276.5, 1245.3, 1199.6, 1154.4, 1079.2, 1059.3, 960.3, 757.4, 736.8, 691.7. **HRMS**: calculated for $\text{C}_{24}\text{H}_{23}\text{O}_3^+$ ($[\text{M} + \text{H}^+]^+$): 359.1642 Found: 359.1650.



(E)-1-(2',3',4'-trimethoxy-6'-styryl-[1,1'-biphenyl]-2-yl)ethan-1-one (S13): Prepared according to General cross coupling procedure **A** between **A17** (150 mg, 0.43 mmol) and 2-acetylphenylboronic acid. Purification by flash column chromatography eluting with hexanes/EtOAc afforded 70 mg (42% yield) of the title compound as a white solid. $^1\text{H NMR}$ (700 MHz, CDCl_3) δ 7.78 (dd, $J = 7.7, 1.0$ Hz, 1H), 7.53 (td, $J = 7.5, 1.3$ Hz, 1H), 7.47 (td, $J = 7.6, 1.1$ Hz, 1H), 7.30 – 7.23 (m, 5H), 7.20 (td, $J = 5.8, 3.0$ Hz, 1H), 7.05 (s, 1H), 6.89 (d, $J = 16.1$ Hz, 1H), 6.69 (d, $J = 16.2$ Hz, 1H), 3.99 (s, 3H), 3.92 (s, 3H), 3.57 (s, 3H), 2.18 (s, 3H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 201.69, 153.45, 151.06, 142.23, 140.99, 137.45, 135.28, 132.74, 131.59, 131.03, 129.58, 128.82, 128.44, 127.78, 127.74, 126.94, 126.66, 104.29, 61.27, 60.74, 56.24, 29.22. **IR** (cm^{-1}): 1687.8, 1591.3, 1475.8, 1400.5, 1345.5, 1235.2, 1094.3, 1003.1, 960.0, 753.0, 693.9. **HRMS**: calculated for $\text{C}_{25}\text{H}_{22}\text{O}_4\text{Na}$ ($[\text{M} + \text{Na}^+]^+$): 411.1567 Found: 411.1572.

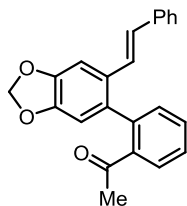


(E)-1-(4',5'-dimethoxy-2'-styryl-[1,1'-biphenyl]-2-yl)ethan-1-one (S14): Prepared according to general cross coupling procedure **A** between **A18** (150 mg, 0.47 mmol) and 2-acetylphenylboronic acid. Purification by flash column chromatography eluting with hexanes/EtOAc afforded 121 mg (72% yield) of the title compound as a white solid. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.68 (d, $J = 7.4$ Hz, 1H), 7.54 – 7.51 (m, 1H), 7.46 (t, $J = 7.2$ Hz, 1H), 7.35 – 7.24 (m, 6H), 7.20 (t, $J = 6.9$ Hz, 1H), 6.93 (d, $J = 16.2$ Hz, 1H), 6.85 (d, $J = 16.2$ Hz, 1H), 6.69 (d, $J = 2.7$ Hz, 1H), 4.02 (s, 3H), 3.87 (s, 3H), 2.01 (s, 3H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 203.49, 149.24, 148.95, 141.52, 139.36, 137.62, 132.94, 131.90, 130.92, 128.84, 128.65, 128.39, 128.32, 127.83, 127.67, 126.58, 126.47, 113.30, 108.02, 56.28, 56.23, 30.00. **IR** (cm^{-1}): 3010.6, 1692.2, 1513.4, 1470.9, 1239.2, 1207.5, 1140.6, 1023.1, 947.6, 879.2, 831.6, 763.9, 751.9, 695.2. **HRMS**: calculated for $\text{C}_{24}\text{H}_{26}\text{O}_3\text{N}^+$ ($[\text{M} + \text{NH}_4^+]^+$): 376.1807 Found 376.1899.

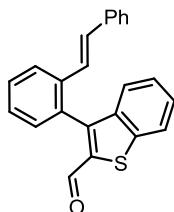


(E)-1-(2'-styryl-4'-((triisopropylsilyl)oxy)-[1,1'-biphenyl]-2-yl)ethan-1-one (S15): Prepared according to general cross coupling procedure **A** between **A25** (150 mg, 0.34 mmol) and 2-acetylphenylboronic acid. Purification by flash column chromatography eluting with hexanes/EtOAc afforded 97 mg (59% yield) of the title compound as a clear oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.65 (d, $J = 7.7$ Hz, 1H), 7.49 (t, $J = 7.4$, 1H), 7.42 (t, $J = 7.5$, 1H), 7.35 – 7.23 (m, 7H), 7.20 (m, 1H), 7.03 (d, $J = 8.3$ Hz, 1H), 6.99 – 6.91 (m, 1H), 6.88 – 6.81 (m, 2H), 1.92 (s, 3H), 1.37 – 1.23 (m, 3H), 1.14 (d, $J = 7.3$ Hz, 18H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 203.70, 156.47, 141.60, 139.47, 137.35, 136.96, 134.03, 133.84, 133.07, 131.89, 131.73, 130.86, 130.56, 128.90, 128.83, 128.72, 128.65, 128.35, 127.97, 127.62, 126.84, 126.66, 119.66, 116.79, 30.02, 18.18, 12.93. **IR** (cm^{-1}):

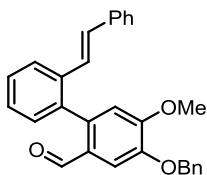
2943.9, 2866.2, 1682.0, 1596.9, 1467.2, 1282.1, 1212.1, 994.9, 906.3, 881.8, 728.5, 689.4. **HRMS**: calculated for $C_{31}H_{42}O_2NSi^+$ ($[M + NH_4^+]^+$): 488.2979 Found 488.2983.



(E)-1-(2-(6-styrylbenzo[d][1,3]dioxol-5-yl)phenyl)ethan-1-one (S16): Prepared according to general cross coupling procedure **A** between **A20** (200 mg, 0.66 mmol) and 2-acetylphenylboronic acid. Purification by flash column chromatography eluting with hexanes/EtOAc afforded 72 mg (32% yield) of the title compound as a white solid. 1H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, $J = 7.6$ Hz, 1H), 7.54 (t, $J = 7.2$ Hz, 1H), 7.48 (t, $J = 7.4$ Hz, 1H), 7.29 (m, 6H), 7.25 – 7.16 (m, 1H), 6.90 (d, $J = 16.1$ Hz, 1H), 6.77 (d, $J = 16.2$ Hz, 1H), 6.70 (s, 1H), 6.06 (s, 2H), 2.10 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.84, 148.24, 147.49, 141.27, 139.46, 137.54, 134.34, 131.88, 131.09, 130.02, 128.84, 128.82, 128.40, 127.89, 127.69, 126.60, 126.38, 110.33, 105.16, 101.66, 29.95. **IR** (cm^{-1}): 2889.6, 1681.7, 1474.4, 1234.7, 1206.7, 1037.8, 966.7, 935.8, 756.0, 725.0, 696.4, 590.7. **HRMS**: calculated for $C_{23}H_{22}O_3N^+$ ($[M + NH_4^+]^+$): 360.1594 Found 360.1598

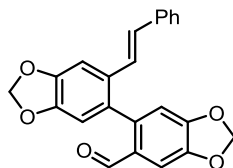


(E)-3-(2-styrylphenyl)benzo[b]thiophene-2-carbaldehyde (S17): Prepared according to general cross coupling procedure **B** between 3-bromobenzothiophene-2-carbaldehyde (1.24 mmol) and (*E*)-(2-styrylphenyl)boronic acid. Purification by flash column chromatography eluting with hexanes/EtOAc afforded 285 mg (67% yield) of the title compound as a white solid. 1H NMR (500 MHz, $CDCl_3$) δ 9.81 (s, 1H), 7.97 (d, $J = 8.2$ Hz, 1H), 7.92 (d, $J = 7.9$ Hz, 1H), 7.60 – 7.50 (m, 3H), 7.43 (t, $J = 7.4$ Hz, 1H), 7.38 (dd, $J = 14.9$, 7.6 Hz, 2H), 7.24 – 7.16 (m, 5H), 7.10 (d, $J = 16.2$ Hz, 1H), 6.78 (d, $J = 16.2$ Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 185.95, 146.65, 141.94, 139.92, 139.72, 137.58, 137.02, 131.74, 131.36, 131.31, 129.67, 128.80, 128.68, 128.14, 127.70, 126.80, 126.00, 125.95, 125.93, 125.53, 123.49. **IR** (cm^{-1}): 3025.1, 1661.9, 1520.2, 1346.8, 1264.3, 1208.4, 1168.7, 961.8, 905.7, 761.2, 726.7, 689.8, 664.2, 611.2. **HRMS**: calculated for $C_{23}H_{16}OSNa^+$ ($[M + Na^+]^+$): 363.0814 Found 363.0819.

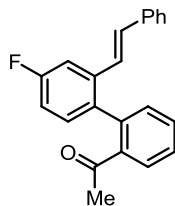


(E)-4-(benzyloxy)-5-methoxy-2'-styryl-[1,1'-biphenyl]-2-carbaldehyde (S18): Prepared according to general cross coupling procedure **B** between 5-(benzyloxy)-2-bromo-4-methoxybenzaldehyde¹⁹ (300 mg, 0.93 mmol) and (*E*)-(2-styrylphenyl)boronic acid. Purification by flash column chromatography eluting with hexanes/EtOAc afforded 162 mg (41% yield) of the title compound as a white solid. 1H NMR (500 MHz, $CDCl_3$) δ 9.59 (s, 1H), 7.80 (d, $J = 7.8$ Hz, 1H), 7.63 (s, 1H), 7.52 (d, $J = 7.4$ Hz, 2H), 7.46 (t, $J = 7.6$ Hz, 1H), 7.41 (t, $J = 7.5$ Hz, 2H), 7.35 (t, $J = 7.3$ Hz, 2H), 7.28 (m, 4H), 7.24 – 7.19 (m, 1H), 7.04 (d, $J = 16.2$ Hz, 1H), 6.82 (m, 2H), 5.33 – 5.11 (m, 2H), 3.91 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.98, 154.12, 148.24, 140.21,

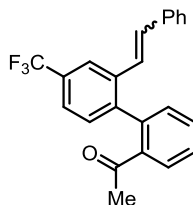
137.29, 137.07, 136.61, 136.53, 131.45, 130.92, 128.87, 128.79, 128.37, 128.06, 127.89, 127.84, 127.40, 126.80, 126.55, 125.56, 113.77, 110.51, 71.12, 56.52. **IR** (cm⁻¹): 1671.5, 1588.0, 1506.0, 1346.7, 1277.6, 1236.2, 1134.6, 1013.9, 756.1, 746.0, 736.1, 691.6. **HRMS**: calculated for C₂₉H₂₈O₃N⁺ ([M + NH₄⁺]⁺): 438.2064 Found 438.2067.



(E)-6'-styryl-[5,5'-bibenzo[d][1,3]dioxole]-6-carbaldehyde (S19): Prepared according to general cross coupling procedure **A** between **A20** (150 mg, 0.50 mmol) and (6-formylbenzo[d][1,3]dioxol-5-yl)boronic acid. Purification by flash column chromatography eluting with hexanes/EtOAc afforded 98 mg (53% yield) of the title compound as a white powder. **¹H NMR** (500 MHz, CDCl₃) δ 9.57 (s, 1H), 7.47 – 7.46 (s, 1H), 7.31 – 7.17 (m, 6H), 6.90 (d, *J* = 16.1 Hz, 2H), 6.76 – 6.65 (m, 3H), 6.12 (d, *J* = 15.4 Hz, 2H), 6.05 (s, 2H). **¹³C NMR** (125 MHz, CDCl₃) δ 190.53, 152.37, 148.54, 148.22, 147.32, 141.84, 137.35, 131.37, 130.54, 130.00, 129.35, 128.82, 127.86, 126.69, 126.10, 111.21, 110.98, 106.21, 105.00, 102.40, 101.78. **IR** (cm⁻¹): 2848.0, 1681.7, 1609.3, 1497.5, 1473.2, 1421.6, 1346.5, 1243.8, 1208.0, 1036.4, 928.0, 874.1, 756.2, 691.9. **HRMS**: calculated for C₂₃H₁₆O₅Na⁺ ([M + Na⁺]⁺): 395.0890 Found 395.0894.

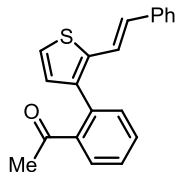


(E)-1-(4'-fluoro-2'-styryl-[1,1'-biphenyl]-2-yl)ethan-1-one (S20): Prepared according to general cross coupling procedure **A** between **A21** (150 mg, 0.54 mmol) and 2-acetylphenylboronic acid. Purification by flash column chromatography eluting with hexanes/EtOAc afforded 81 mg (48% yield) as an *E/Z* mixture (3.33:1) of the title compound as a clear oil. **¹H NMR** (500 MHz, CDCl₃; for major *E* isomer) δ 7.72 (d, *J* = 7.6 Hz, 1H), 7.54 (m, 1H), 7.47 (m, 2H), 7.33 – 7.26 (m, 4H), 7.26 – 7.20 (m, 2H), 7.16 (m, 2H), 7.02 (m, 2H), 6.81 (d, *J* = 16.2 Hz, 1H), 2.06 (s, *J* = 4.4 Hz, 3H). **¹³C NMR** (125 MHz, CDCl₃; for major *E* isomer) δ 202.51, 162.93 (d, *J* = 245.0), 141.05, 138.82, 137.91 (d, *J* = 7.5), 136.99, 132.02, 131.95, 131.88, 131.72, 131.19, 128.92, 128.56, 128.32, 128.09, 126.94, 125.75, 114.76 (d, *J* = 21.2), 112.06 (d, *J* = 22.5) 29.91. **IR** (cm⁻¹): 3056.2, 1685.7, 1602.9, 1578.3, 1498.3, 1468.4, 1354.0, 1264.4, 1196.4, 1158.5, 961.6, 757.3, 731.2. **HRMS**: calculated for C₂₂H₂₁OFN⁺ ([M + NH₄⁺]⁺): 334.1632 Found 334.1604.

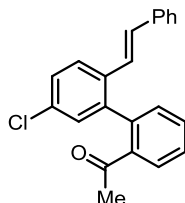


1-(2'-styryl-4'-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)ethan-1-one (S21): Prepared according to general cross coupling procedure **A** between **A23** (200 mg, 0.66 mmol) and 2-acetylphenylboronic acid. Purification by flash column chromatography eluting with hexanes/EtOAc afforded 72 mg (32% yield) as an *E/Z* mixture (3.33:1.0) of the title compound as a white solid. **¹H NMR** (700 MHz, CDCl₃; for *E/Z* mixture) δ 7.99 (s, 1H),

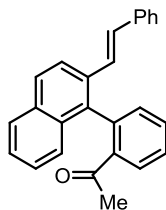
7.78 (dt, $J = 10.1, 0.96\text{H}$), 7.76 – 7.72 (m, 0.28H), 7.61 – 7.56 (m, 1.89H), 7.55 – 7.51 (m, 1.45H), 7.51 – 7.44 (m, 0.60H), 7.32 (m, 5.89H), 7.27 – 7.16 (m, 2.62H), 7.07 (d, $J = 16.2\text{ Hz}$, 1H), 6.82 (d, $J = 16.2\text{ Hz}$, 0.30H), 6.51 (d, $J = 12.2\text{ Hz}$, 0.28H), 6.15 (d, $J = 12.2\text{ Hz}$, 1H), 2.32 (s, 0.79H), 2.17 (s, 3H). $^{13}\text{C NMR}$ (175 MHz, CDCl_3 , for *E* isomer) δ 201.21, 143.60, 139.97, 138.54, 136.69, 136.36, 131.99, 131.32, 131.29, 130.41, 128.70, 128.57, 128.24, 128.16, 126.70, 125.26, 124.15 (q, $J = 271.2\text{ Hz}$), 123.83 (q, $J = 8.6\text{ Hz}$), 122.29 (q, $J = 3.7\text{ Hz}$), 29.36. **IR** (cm^{-1}): 3057.9, 2360.1, 1687.7, 1324.3, 1244.8, 1160.8, 1112.2, 1081.7, 968.0, 771.7, 757.1, 735.8, 692.2. **HRMS**: calculated for $\text{C}_{23}\text{H}_{21}\text{OF}_3\text{N}^+$ ($[\text{M} + \text{NH}_4^+]^+$): 384.1570 Found 384.1575



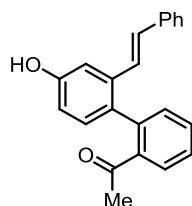
(E)-1-(2-(2-styrylthiophen-3-yl)phenyl)ethan-1-one (S22): Prepared according to General cross coupling procedure **A** between **A19** (150 mg, 0.57 mmol) and 2-acetylphenylboronic acid. Purification by flash column chromatography eluting with hexanes/EtOAc afforded 98 mg (57% yield) of the title compound as a pale yellow solid. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.67 (d, $J = 7.7\text{ Hz}$, 1H), 7.55 (t, $J = 7.0\text{ Hz}$, 1H), 7.47 (t, $J = 7.2\text{ Hz}$, 1H), 7.35 (d, $J = 7.9\text{ Hz}$, 3H), 7.30 (t, $J = 7.6\text{ Hz}$, 2H), 7.23 (t, $J = 6.2\text{ Hz}$, 2H), 6.97 – 6.92 (m, 3H), 2.08 (s, 3H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 203.72, 141.55, 139.20, 139.11, 136.99, 134.72, 131.45, 131.17, 130.42, 130.03, 128.89, 128.47, 128.14, 128.01, 126.66, 123.87, 120.30, 29.79. **IR** (cm^{-1}): 3102.9, 3026.1, 1670.0, 1593.1, 1443.2, 1350.7, 1279.8, 1268.2, 1233.7, 951.8, 768.2, 733.9, 713.3, 683.9, 665.9. **HRMS**: calculated for $\text{C}_{20}\text{H}_{17}\text{OS}^+$ ($[\text{M} + \text{H}^+]^+$): 305.0995 Found 305.0992.



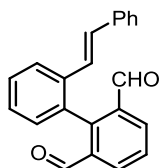
(E)-1-(5'-chloro-2'-styryl-[1,1'-biphenyl]-2-yl)ethan-1-one (S23): Prepared according to general cross coupling procedure **A** between **A9** (150 mg, 0.51 mmol) and 2-acetylphenylboronic acid. Purification by flash column chromatography eluting with hexanes/EtOAc afforded 103 mg (63% yield) of the title compound as a white solid. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.75 (d, $J = 8.6\text{ Hz}$, 1H), 7.69 (d, $J = 8.5\text{ Hz}$, 1H), 7.57 (t, $J = 7.5\text{ Hz}$, 1H), 7.53 – 7.49 (m, 1H), 7.39 (dd, $J = 8.4, 2.1\text{ Hz}$, 1H), 7.33 – 7.26 (m, 5H), 7.26 – 7.19 (m, 2H), 6.99 (d, $J = 16.2\text{ Hz}$, 1H), 6.76 (d, $J = 16.2\text{ Hz}$, 1H), 2.13 (s, 3H). $^{13}\text{C NMR}$ (175 MHz, CDCl_3) δ 201.75, 141.83, 140.45, 138.58, 137.18, 134.48, 133.28, 131.58, 131.40, 131.09, 129.99, 128.87, 128.68, 128.47, 128.33, 128.11, 126.88, 126.79, 125.57, 29.74. **IR** (cm^{-1}): 3058.2, 1687.1, 1494.8, 1464.8, 1354.1, 1264.1, 1097.0, 963.4, 813.4, 758.6, 731.8, 690.4. **HRMS**: calculated for $\text{C}_{22}\text{H}_{21}\text{OCIN}^+$ ($[\text{M} + \text{NH}_4^+]^+$): 350.1306 Found 350.1308.



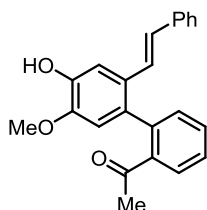
(E)-1-(2-(2-styrylnaphthalen-1-yl)phenyl)ethan-1-one (S24): Prepared according to general cross coupling procedure **A** between **A11** (200 mg, 0.65 mmol) and 2-acetylphenylboronic acid. Purification by flash column chromatography eluting with hexanes/EtOAc afforded 89 mg (40% yield) of the title compound as a white solid. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.92 (q, $J = 8.8$ Hz, 3H), 7.86 (d, $J = 8.1$ Hz, 1H), 7.64 (t, $J = 7.5$ Hz, 1H), 7.59 (t, $J = 7.5$ Hz, 1H), 7.45 (t, $J = 7.4$ Hz, 1H), 7.36 (t, $J = 7.5$ Hz, 1H), 7.33 – 7.27 (m, 6H), 7.23 – 7.19 (m, 1H), 7.15 (d, $J = 16.3$ Hz, 1H), 6.87 (d, $J = 16.3$ Hz, 1H), 1.85 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 201.67, 141.26, 137.70, 137.51, 137.15, 133.16, 133.06, 132.99, 132.53, 131.69, 130.61, 129.00, 128.84, 128.62, 128.31, 128.23, 127.95, 126.99, 126.95, 126.80, 126.48, 126.17, 122.97, 29.56. **IR** (cm^{-1}): 3056.9, 1680.9, 1594.1, 1353.5, 1273.7, 1244.7, 958.3, 811.2, 760.7, 739.7, 791.1, 596.1. **HRMS:** calculated for $\text{C}_{26}\text{H}_{24}\text{ON}^+$ ($[\text{M} + \text{NH}_4^+]^+$): 366.1852 Found 366.1857.



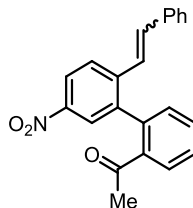
(E)-1-(4'-hydroxy-2'-styryl-[1,1'-biphenyl]-2-yl)ethan-1-one (S25): Prepared according to general cross coupling procedure **A** between **A26** (150 mg, 0.35mmol) and 2-acetylphenylboronic acid. Purification by flash column chromatography eluting with hexanes/EtOAc afforded 71 mg (66% yield) of the title compound as a pale white solid. The *tert*-butyldimethylsilyl ether was cleaved under the reaction conditions. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.68 (d, $J = 7.6$ Hz, 1H), 7.52 (t, $J = 7.1$ Hz, 1H), 7.45 (t, $J = 7.5$ Hz, 1H), 7.30 (m, 5H), 7.22 (m, 2H), 7.06 (d, $J = 8.2$ Hz, 1H), 6.99 (d, $J = 16.2$ Hz, 1H), 6.84 (d, $J = 16.2$ Hz, 1H), 6.79 (dd, $J = 8.2, 2.1$ Hz, 1H), 5.16 (s, 1H), 2.02 (s, 3H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 203.70, 155.85, 141.39, 139.39, 137.28, 137.24, 132.91, 132.03, 131.90, 131.02, 130.94, 128.87, 128.37, 128.06, 127.69, 126.85, 126.38, 115.20, 112.09, 30.03. **IR** (cm^{-1}): 3207.0, 1679.1, 1572.4, 1475.5, 1305.9, 1213.9, 963.3, 833.6, 773.6, 759.9, 728.2, 696.0. **HRMS:** calculated for $\text{C}_{22}\text{H}_{22}\text{O}_2\text{N}^+$ ($[\text{M} + \text{NH}_4^+]^+$): 332.1645 Found 332.1648.



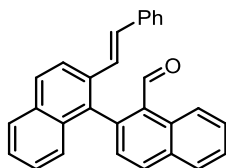
(E)-2'-styryl-[1,1'-biphenyl]-2,6-dicarbaldehyde (S26): Prepared according to general cross coupling procedure **B** between 2-bromoisophthalaldehyde (300 mg, 1.41 mmol) and (*E*)-(2-styrylphenyl)boronic acid 2-acetylphenylboronic acid. Purification by flash column chromatography eluting with hexanes/EtOAc afforded 89 mg (40% yield) of the title compound as a white solid. $^1\text{H NMR}$ (700 MHz, CDCl_3) δ 9.74 (s, $J = 0.6$ Hz, 1H), 8.30 (d, $J = 7.7$ Hz, 2H), 7.85 (d, $J = 7.9$ Hz, 1H), 7.72 (t, $J = 7.7$ Hz, 1H), 7.55 (td, $J = 7.8, 0.7$ Hz, 1H), 7.41 (td, $J = 7.5, 1.1$ Hz, 1H), 7.30 (dd, $J = 7.5, 1.0$ Hz, 1H), 7.25 (d, $J = 7.1$ Hz, 2H), 7.23 – 7.19 (m, 3H), 7.04 (d, $J = 16.1$ Hz, 1H), 6.61 (d, $J = 16.1$ Hz, 1H). $^{13}\text{C NMR}$ (175 MHz, CDCl_3) δ 190.92, 147.16, 137.77, 136.75, 135.15, 132.94, 132.48, 131.69, 131.40, 129.86, 129.00, 128.85, 128.42, 127.65, 126.87, 125.91, 125.34. **IR** (cm^{-1}): 3061.7, 2868.2, 1678.0, 1449.2, 1386.1, 1232.3, 963.8, 921.3, 794.4, 763.0, 746.5, 691.4. **HRMS:** calculated for $\text{C}_{22}\text{H}_{20}\text{O}_2\text{N}^+$ ($[\text{M} + \text{NH}_4^+]^+$): 330.1489 Found 330.1493.



(E)-1-(4'-hydroxy-5'-methoxy-2'-styryl-[1,1'-biphenyl]-2-yl)ethan-1-one (S27): Prepared according to general cross coupling procedure A between **A29** (150 mg, 0.35 mmol) and 2-acetylphenylboronic acid. Purification by flash column chromatography eluting with hexanes/EtOAc afforded 107 mg (87% yield) of the title compound as a pale white solid. The *tert*-butyldimethylsilyl ether was cleaved under the reaction conditions. $^1\text{H NMR}$ (700 MHz, CDCl_3) δ 7.67 (d, $J = 7.7$ Hz, 1H), 7.52 (t, $J = 7.5$ Hz, 1H), 7.46 (t, $J = 7.6$ Hz, 1H), 7.36 (s, 1H), 7.32 – 7.26 (m, 5H), 7.19 (t, $J = 6.9$ Hz, 1H), 6.93 (d, $J = 16.1$ Hz, 1H), 6.82 (d, $J = 16.1$ Hz, 1H), 6.65 (s, 1H), 5.66 (s, 1H), 3.87 (s, 3H), 2.01 (s, 3H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 203.75, 146.46, 145.88, 141.59, 139.37, 137.62, 132.30, 131.95, 130.85, 129.18, 129.07, 128.80, 128.25, 127.77, 127.63, 126.62, 126.03, 112.71, 111.31, 56.31, 30.05. **IR** (cm^{-1}): 3535.8, 1677.3, 1594.1, 1509.6, 1278.0, 1238.4, 1141.7, 905.2, 724.1, 647.3. **HRMS**: calculated for $\text{C}_{23}\text{H}_{20}\text{O}_3\text{Na}$ ($[\text{M} + \text{Na}^+]^+$): 367.1305, found: 367.1302.

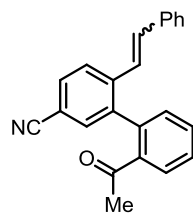


1-(5'-nitro-2'-styryl-[1,1'-biphenyl]-2-yl)ethan-1-one (S28): Prepared according to general cross coupling procedure A between **A30** (100 mg, 0.33 mmol) and 2-acetylphenylboronic acid. Purification by flash column chromatography eluting with hexanes/EtOAc afforded 71 mg (63% yield) of the title compound as a pale yellow foam and an *E/Z* mixture (1.62:1.0). $^1\text{H NMR}$ (700 MHz, CDCl_3 , for *E/Z* mixture) δ 8.23 (dd, $J = 8.7$, 2.2 Hz, 1H), 8.09 (dd, $J = 12.3$, 2.3 Hz, 1.41H), 7.97 (dd, $J = 8.6$, 2.3 Hz, 0.63H), 7.84 (t, $J = 12.4$, 2H), 7.81 – 7.78 (m, 0.61H), 7.61 (tt, $J = 7.0$, 3.5 Hz, 1H), 7.59 – 7.48 (m, 2.36H), 7.40 (d, $J = 8.6$ Hz, 0.72H), 7.34 – 7.17 (m, 9.95H), 7.13 (d, $J = 16.2$ Hz, 1.15H), 6.76 (d, $J = 16.3$ Hz, 1.11H), 6.56 (d, $J = 12.3$ Hz, 0.72H), 6.10 (d, $J = 12.3$ Hz, 0.68H), 2.43 (s, 1.86H), 2.28 (s, 3H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3 , for *E/Z* mixture) δ 200.38, 200.34, 146.87, 146.66, 142.95, 142.87, 142.39, 141.78, 139.37, 139.01, 138.46, 138.13, 136.52, 135.92, 134.36, 133.69, 131.97, 131.90, 131.76, 131.46, 130.19, 129.18, 128.99, 128.95, 128.90, 128.82, 128.70, 128.59, 128.23, 127.35, 127.15, 126.04, 124.93, 124.89, 124.66, 123.00, 122.05, 29.26, 28.74. **IR** (cm^{-1}): 2954.2, 1733.9, 1688.2, 1516.9, 1343.4, 1283.6, 1246.5, 1232.9, 1044.2, 943.8, 759.0, 707.5. **HRMS**: Calculated for $\text{C}_{22}\text{H}_{17}\text{O}_3\text{N}^+$ ($[\text{M}]^+$): 343.1208 found: 343.1205.

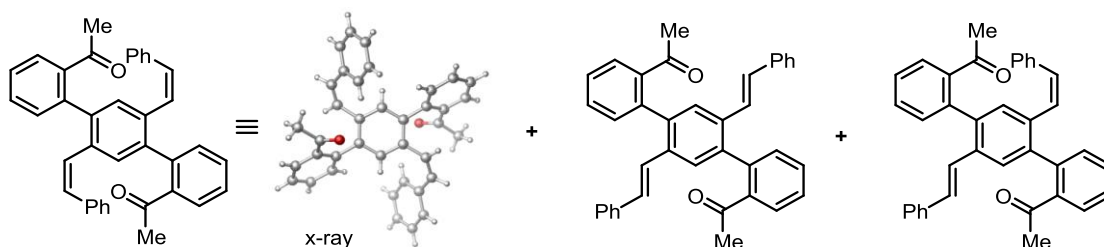


(E)-2-styryl-[1,2'-binaphthalene]-1'-carbaldehyde (S29): Prepared according to general cross coupling procedure A between 2-bromo-1-naphthaldehyde (150 mg, 0.64 mmol) and (*E*)-(2-styrylnaphthalen-1-yl)boronic acid. Purification by flash column chromatography eluting with hexanes/EtOAc afforded 103 mg (42% yield) of **S29** as a white solid. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 9.95 (s, 1H), 9.40 (d, $J = 8.6$ Hz, 1H), 8.20 (d, $J = 8.3$ Hz, 1H), 8.02 (d, $J = 8.0$ Hz, 1H), 7.97 (q, $J = 8.8$ Hz, 2H), 7.90 (d, $J = 8.1$ Hz, 1H), 7.78 – 7.75 (m,

1H), 7.68 (t, $J = 7.5$ Hz, 1H), 7.45 (m, 2H), 7.35 – 7.31 (m, 1H), 7.29 (d, $J = 6.9$ Hz, 1H), 7.23 – 7.15 (m, 7H), 6.83 (d, $J = 16.2$ Hz, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 194.59, 146.04, 137.20, 135.00, 134.41, 134.00, 133.81, 133.68, 132.85, 131.32, 130.85, 130.17, 129.75, 129.65, 129.07, 128.87, 128.81, 128.72, 128.30, 128.11, 127.34, 127.29, 126.88, 126.80, 126.59, 126.44, 126.38, 122.87. IR (cm^{-1}): 2858.1, 2361.9, 1678.2, 1590.9, 1558.1, 1505.4, 1429.6, 1180.0, 1147.6, 1059.2, 966.5, 817.6, 745.7. HRMS: calculated for $\text{C}_{29}\text{H}_{24}\text{ON}^+$ ($[\text{M} + \text{NH}_4^+]$): 402.1852 Found 402.1853.

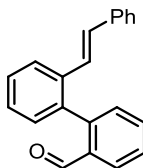


2'-acetyl-6-styryl-[1,1'-biphenyl]-3-carbonitrile (S30): Prepared according to general cross coupling procedure **A** between 3-bromo-4-styrylbenzonitrile (**A31**) (130 mg, 0.46 mmol) and 2-acetylphenylboronic acid. Purification by flash column chromatography eluting with hexanes/EtOAc afforded 79 mg (53% yield) of an *E/Z* mixture (3.0:1.0) of the title compound as a yellow-white solid. ^1H NMR (500 MHz, CDCl_3 , for *E/Z* mixture) δ 7.99 (s, 1H), 7.81 – 7.73 (m, 1.3H), 7.63 – 7.45 (m, 4.2H), 7.35 – 7.20 (m, 9.3H), 7.17 (t, $J = 6.7$ Hz, 1H), 7.02 (d, $J = 16.2$ Hz, 1.1H), 6.71 (d, $J = 16.2$ Hz, 1.1H), 6.50 (d, $J = 12.2$ Hz, 0.4H), 6.04 (d, $J = 12.2$ Hz, 0.4H). ^{13}C NMR (126 MHz, CDCl_3 , for *E/Z* mixture) δ 200.79, 200.64, 145.15, 139.60, 138.51, 137.16, 136.64, 133.05, 132.84, 131.75, 131.70, 131.36, 131.08, 130.82, 130.78, 130.54, 130.50, 129.38, 129.02, 128.97, 128.83, 128.76, 128.73, 128.60, 128.50, 128.25, 126.97, 126.93, 124.72, 119.01, 112.15, 29.32, 28.80. IR (cm^{-1}): 2223.6, 1682.8, 1245.6, 973.0, 894.6, 827.8, 777.6, 756.4, 732.4, 695.7, 606.7. HRMS: calculated for $\text{C}_{23}\text{H}_{18}\text{NO}$ ($[\text{M} + \text{H}^+]$): 324.1383 Found: 324.1381.

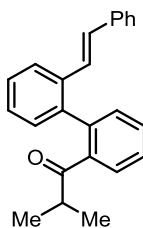


1,1'-(2',5'-distyryl-[1,1':4',1''-terphenyl]-2,2''-diyl)bis(ethan-1-one) (58): Prepared according to general cross coupling procedure **A** between ((2,5-dibromo-1,4-phenylene)bis(ethene-2,1-diyl))dibenzene²⁰ (100 mg, 0.23 mmol), 2-acetylphenylboronic acid (93 mg, 0.57 mmol), $\text{Pd}(\text{PPh}_3)_4$ (26 mg, 10 mol%), NaHCO_3 (115 mg, 1.36 mmol) and DMF/ H_2O (1:1; 0.1 M). Purification by flash column chromatography eluting with hexanes/EtOAc afforded 39 mg (33% yield) of an inseparable *Z/Z'*, *E/E'* and *E/Z'* mixture as a yellow-white solid. This isomeric mixture was used in the title reaction without further resolution. ^1H NMR (700 MHz, CDCl_3 , for *Z/Z'*, *E/E'* and *E/Z'* mixture) δ 7.79 (d, $J = 11.2$ Hz, 0.49H), 7.73 (m, 1.42H), 7.69 (d, $J = 7.3$ Hz, 0.76H), 7.67 – 7.58 (m, 2.66H), 7.58 – 7.51 (m, 1.03H), 7.50 – 7.33 (m, 7.62H), 7.33 – 7.15 (m, 16.90H), 7.02 (m, 2.76H), 6.94 – 6.87 (m, 0.64H), 6.75 (m, $J = 19.2$ Hz, 0.66H), 6.43 (d, $J = 12.1$ Hz, 1.75H), 6.26 (d, $J = 12.2$ Hz, 0.57H), 6.18 (d, $J = 12.2$ Hz, 1.72H), 2.31 (s, 6H), 2.18 (s, 0.84H), 2.14 (s, 1.24H). ^{13}C NMR (175 MHz, CDCl_3 , *Z/Z'*, *E/E'* and *E/Z'* mixture) δ 202.66, 201.67 (broad), 141.22, 140.88, 140.30, 140.15, 139.73 (broad), 139.24, 137.32, 136.96 (broad), 136.83, 135.38, 135.34, 135.30, 135.27 (overlap), 135.23, 135.14, 135.06, 134.91, 132.36, 132.30, 132.01, 131.58 (overlap), 131.51 (overlap), 131.30, 131.22, 131.08, 130.86, 130.72 (overlap), 130.69, 130.47, 129.85, 129.07 (broad), 128.86, 128.81, 128.68, 128.54 (overlap), 128.43 (overlap), 128.30 (overlap), 128.27, 128.24, 128.21, 128.18, 128.15, 128.09, 127.95 (overlap), 127.46 (overlap), 127.28 (overlap), 126.85, 126.80, 125.84, 125.63, 30.13 (broad), 30.01 (overlap), 29.93 (overlap), 29.77. IR

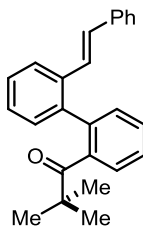
(cm^{-1}): 3052.7, 1688.1, 1595.2, 1354.2, 1264.0, 963.6, 923.6, 762.3, 732.1, 697.0. **HRMS**: calculated for $\text{C}_{38}\text{H}_{34}\text{NO}_2^+$ ($[\text{M}+\text{NH}_4^+]^+$): 536.2584 Found: 536.2575.



(E)-2'-styryl-[1,1'-biphenyl]-2-carbaldehyde (22b): Prepared according to general cross coupling procedure **A** between **A1** (6 x 150 mg) and 2-formylphenylboronic acid. Purification by flash column chromatography eluting with hexanes/EtOAc afforded 500 mg (51% yield) of the title compound as a clear oil. $^1\text{H NMR}$ (700 MHz, CDCl_3) δ 9.79 (s, 1H), 8.08 – 8.06 (m, 1H), 7.80 (d, $J = 7.9$ Hz, 1H), 7.67 (t, $J = 7.5$ Hz, 1H), 7.55 (t, $J = 7.6$ Hz, 1H), 7.49 – 7.45 (m, 1H), 7.40 – 7.34 (m, 3H), 7.30 – 7.25 (m, 7H), 7.21 (ddd, $J = 8.6, 5.7, 3.3$ Hz, 1H), 7.03 (d, $J = 16.2$ Hz, 1H), 6.78 (d, $J = 16.2$ Hz, 1H). $^{13}\text{C NMR}$ (175 MHz, CDCl_3) δ 192.26, 144.81, 137.27, 136.84, 134.55, 133.81, 131.67, 131.27, 131.16, 128.85, 128.83, 128.35, 128.05, 127.53, 127.48, 126.80, 126.47, 125.68. **IR** (cm^{-1}): 1686.9, 1596.6, 1498.7, 1466.8, 1279.2, 1264.8, 1230.4, 1204.8, 1171.3, 999.9, 962.8, 756.4, 729.4, 690.9. **HRMS**: calculated for $\text{C}_{21}\text{H}_{17}\text{O}^+$ ($[\text{M} + \text{H}^+]^+$): 307.1090 Found: 307.1099.

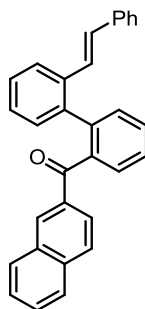


(E)-2-methyl-1-(2'-styryl-[1,1'-biphenyl]-2-yl)propan-1-one (22c): Prepared according to general cross coupling procedure **A** between 1-(2-bromophenyl)-2-methylpropan-1-one.²¹ (131 mg) and (*E*)-(2-styrylphenyl)boronic acid. Purification by flash column chromatography eluting with hexanes/EtOAc afforded 90 mg (48% yield) of the title compound as a white solid. $^1\text{H NMR}$ (700 MHz, CDCl_3) δ 7.79 (d, $J = 7.9$ Hz, 1H), 7.55 (t, $J = 14.4$ Hz, 1H), 7.49 (t, $J = 7.4$ Hz, 1H), 7.45 (t, $J = 7.5$ Hz, 1H), 7.40 (t, $J = 7.6$ Hz, 1H), 7.36 – 7.27 (m, 6H), 7.22 (t, $J = 7.2$ Hz, 1H), 7.15 (d, $J = 7.6$ Hz, 1H), 7.05 (d, $J = 16.2$ Hz, 1H), 6.94 (d, $J = 16.2$ Hz, 1H), 2.62 – 2.49 (m, 1H), 0.89 (d, $J = 6.8$ Hz, 3H), 0.81 (d, $J = 6.6$ Hz, 3H). $^{13}\text{C NMR}$ (17 MHz, CDCl_3) δ 210.94, 141.27, 139.81, 138.87, 137.59, 135.70, 131.74, 130.79, 130.33, 130.16, 128.83, 128.40, 128.32, 127.87, 127.79, 127.60, 126.90, 126.82, 125.70, 39.72, 19.37, 18.31. **IR** (cm^{-1}): 1735.0, 1685.8, 1594.4, 1495.4, 1465.0, 1379.9, 1212.2, 977.7, 760.3, 734.9, 690.1. **HRMS**: calculated for $\text{C}_{24}\text{H}_{26}\text{ON}^+$ ($[\text{M} + \text{NH}_4^+]^+$): 344.2009 Found: 344.2015.



(E)-2,2-dimethyl-1-(2'-styryl-[1,1'-biphenyl]-2-yl)propan-1-one (22d): Prepared according to general cross coupling procedure **A** between 1-(2-bromophenyl)-2,2-dimethylpropan-1-one.²² (150 mg) and (*E*)-(2-styrylphenyl)boronic acid. Purification by flash column chromatography eluting with hexanes/EtOAc afforded 92 mg (43% yield) of the title compound as a white solid. $^1\text{H NMR}$ (401 MHz, CDCl_3) δ 7.77 (d, $J = 7.8$ Hz,

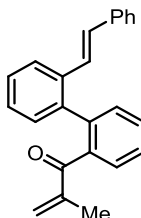
1H), 7.44 – 7.17 (m, 14H), 7.03 (d, $J = 8.3$ Hz, 2H), 0.93 (s, 9H). ^{13}C NMR (175 MHz, CDCl_3) δ 215.51, 142.18, 139.33, 137.73, 136.64, 135.96, 131.95, 131.85, 129.86, 128.84, 128.31, 128.19, 127.78, 127.48, 127.27, 127.11, 126.80, 125.87, 125.62, 44.93, 27.61. IR (cm^{-1}): 1683.9, 1235.5, 963.6, 759.1, 690.5. HRMS: calculated for $\text{C}_{25}\text{H}_{28}\text{ON}^+$ ($[\text{M} + \text{NH}_4^+]$): 358.2165 Found: 358.2169.



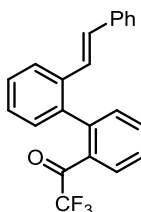
(E)-naphthalen-2-yl(2'-styryl-[1,1'-biphenyl]-2-yl)methanone (22f): To a 50 mL round bottom flask equipped with a magnetic stir bar was added a solution of 2-bromonaphthalene (1455 mg, 7.03 mmol) and 20 mL of THF. To this solution was added magnesium shavings (158 mg, 6.49 mmol) and a crystal of I_2 . The mixture was allowed to stir at rt for 1 h. Next, the mixture was cooled to 0°C with an ice-bath and at which time 2-bromobenzaldehyde (1000 mg, 5.40 mmol) in a solution of THF (5 mL) was added. The reaction mixture was allowed to stir at 0°C and slowly warmed to rt. When judged complete by TLC analysis, the reaction was quenched with NH_4Cl (aq.) (20 mL) and extracted with Et_2O (3 x 20 mL). The combined organic layers were washed with brine (1 x 20 mL), dried over MgSO_4 , and concentrated in *vacuo* to yield the crude alcohol (1002 mg). This was used in the next step without further purification.

To a 50 mL round bottom flask was added the crude alcohol (1000 mg) and 15 mL of DMSO. Next, IBX (1341 mg, 4.79 mmol) was added to the reaction solution at rt and allowed to stir for 3 h. The reaction was quenched with water (20 mL) and stirred for an additional 1 h. Next the reaction was filtered and extracted with EtOAc (3 x 20 mL). The combined organic layers were dried with MgSO_4 and concentrated in *vacuo*. The crude ketone was purified by flash column chromatography with hexanes/ EtOAc to afford 756 mg (44% over two steps) of (2-bromophenyl)(naphthalen-2-yl)methanone as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 8.17 (s, 1H), 8.02 (dd, $J = 8.6, 1.5$ Hz, 1H), 7.94 (s, 1H), 7.90 (m, 3H), 7.70 (d, $J = 7.8$ Hz, 1H), 7.62 (t, $J = 7.5$ Hz, 1H), 7.54 (t, $J = 7.5$ Hz, 1H), 7.50 – 7.34 (m, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 196.08, 141.08, 136.13, 133.75, 133.48, 133.32, 132.64, 131.39, 129.99, 129.30, 129.15, 128.88, 128.08, 127.46, 127.07, 125.00, 119.89. IR (cm^{-1}): 3057.8, 1660.1, 1430.1, 1290.7, 1232.9, 1200.2, 1112.4, 919.3, 850.3, 926.8, 778.5, 754.0, 735.5, 689.1. HRMS: calculated for $\text{C}_{17}\text{H}_{11}\text{OBrNa}^+$ ($[\text{M} + \text{Na}^+]$): 332.9885 Found 332.9884.

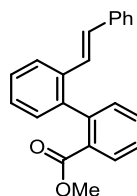
(E)-naphthalen-2-yl(2'-styryl-[1,1'-biphenyl]-2-yl)methanone was prepared according to general cross coupling procedure A between (2-bromophenyl)(naphthalen-2-yl)methanone (150 mg, 0.48 mmol) and (E)-(2-styrylphenyl)boronic acid. Purification by flash column chromatography eluting with hexanes/ EtOAc afforded 93 mg (47% yield) of **22f** as a white solid. ^1H NMR (500 MHz, CDCl_3) δ 7.98 (s, 1H), 7.77 – 7.71 (m, 2H), 7.68 – 7.60 (m, 3H), 7.58 – 7.43 (m, 5H), 7.36 (t, $J = 7.5$ Hz, 1H), 7.25 (m, 4H), 7.22 – 7.16 (m, 2H), 7.16 – 7.09 (m, 2H), 7.05 (d, $J = 16.2$ Hz, 1H), 6.78 (d, $J = 16.2$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 197.83, 140.54, 140.08, 139.44, 137.70, 135.70, 135.43, 134.90, 132.48, 132.14, 131.74, 130.82, 130.55, 130.34, 129.71, 129.36, 128.74, 128.38, 128.11, 127.99, 127.77, 127.38, 127.35, 127.32, 126.73, 126.52, 125.58, 125.08. IR (cm^{-1}): 3051.7, 1660.8, 1623.2, 1291.7, 1117.7, 964.3, 919.4, 781.2, 759.6, 748.8, 732.0, 695.3. HRMS: calculated for $\text{C}_{31}\text{H}_{23}\text{O}^+$ ($[\text{M} + \text{H}^+]$): 411.1743 Found 411.1751.



(E)-2-methyl-1-(2'-styryl-[1,1'-biphenyl]-2-yl)prop-2-en-1-one (22g): Prepared according to general cross coupling procedure **A** between 1-(2-bromophenyl)-2-methylprop-2-en-1-one (150 mg, 0.66 mmol) and (*E*)-(2-styrylphenyl)boronic acid. Purification by flash column chromatography eluting with hexanes/EtOAc afforded 127 mg (59% yield) of the title compound as a clear oil. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.73 (d, $J = 7.8$ Hz, 1H), 7.55 – 7.48 (m, 2H), 7.46 (t, $J = 7.2$ Hz, 1H), 7.37 – 7.28 (m, 6H), 7.24 (q, $J = 7.6$ Hz, 2H), 7.11 (d, $J = 7.5$ Hz, 1H), 7.02 (d, $J = 16.2$ Hz, 1H), 6.93 (d, $J = 16.2$ Hz, 1H), 5.55 (s, 1H), 5.39 (s, 1H), 1.68 (s, 3H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 200.34, 145.28, 140.32, 139.64, 139.62, 137.67, 135.58, 131.53, 130.94, 130.03, 129.70, 128.78, 128.57, 128.08, 127.91, 127.77, 127.35, 127.32, 127.29, 126.73, 125.56, 17.41. **IR** (cm^{-1}): 3055.8, 1657.2, 1494.5, 1435.7, 1327.9, 1264.3, 1196.0, 1015.2, 963.2, 906.2, 760.5, 732.5, 690.4. **HRMS**: calculated for $\text{C}_{24}\text{H}_{24}\text{ON}^+$ ($[\text{M} + \text{NH}_4^+]^+$): 342.1852 Found 342.1860.



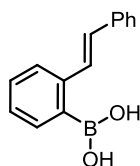
(E)-2,2,2-trifluoro-1-(2'-styryl-[1,1'-biphenyl]-2-yl)ethan-1-one (22i): Prepared according to general cross coupling procedure **A** between 1-(2-bromophenyl)-2,2,2-trifluoroethan-1-onemethanone (200 mg, 0.79 mmol) and (*E*)-(2-styrylphenyl)boronic acid. Purification by flash column chromatography eluting with hexanes/EtOAc afforded 115 mg (41% yield) of the title compound as a clear oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.86 (d, $J = 7.9$ Hz, 1H), 7.73 – 7.64 (m, 2H), 7.54 (td, $J = 7.7, 1.2$ Hz, 1H), 7.45 – 7.37 (m, 2H), 7.32 (td, $J = 7.5, 1.1$ Hz, 1H), 7.29 – 7.23 (m, 4H), 7.23 – 7.18 (m, 1H), 7.15 (dd, $J = 7.6, 1.0$ Hz, 1H), 6.96 (d, $J = 16.2$ Hz, 1H), 6.73 (d, $J = 16.2$ Hz, 1H). $^{13}\text{C NMR}$ (175 MHz, CDCl_3) δ 183.12 (q, $J = 35$), 142.72, 138.62, 137.17, 135.59, 133.18, 132.44, 131.77, 130.94, 129.61, 128.99, 128.97, 128.50, 128.29, 127.66, 127.58, 127.51, 126.53, 126.19, 125.73, 115.94 (q, $J = 292$). **IR** (cm^{-1}): 3024.4, 1725.4, 1594.7, 1494.9, 1199.5, 1182.5, 1140.8, 962.1, 933.9, 757.8, 736.0, 689.8, 661.0. **HRMS**: calculated for $\text{C}_{22}\text{H}_{16}\text{OF}_3^+$ ($[\text{M} + \text{H}^+]^+$): 353.1148 Found 353.1149.



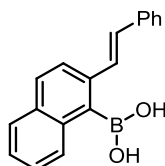
Methyl (*E*)-2'-styryl-[1,1'-biphenyl]-2-carboxylate (22j): Prepared according to general cross coupling procedure **A** between methyl 2-bromobenzoate (6 x 258 mg) and (*E*)-(2-styrylphenyl)boronic acid. Purification by flash column chromatography eluting with hexanes/EtOAc afforded 652 mg (29% yield) of the title compound as a thick clear oil. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.96 (d, $J = 7.8$ Hz, 1H), 7.74 (d, $J = 7.8$ Hz, 1H), 7.56 (t, $J = 7.5$ Hz, 1H), 7.46 (t, $J = 7.6$ Hz, 1H), 7.38 (t, $J = 7.5$ Hz, 1H), 7.34 – 7.26 (m, 6H), 7.19 (m, 2H), 7.00 (d, $J = 16.2$ Hz, 1H), 6.81 (d, $J = 16.2$ Hz, 1H), 3.54 (s, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ 168.09, 141.91, 140.83, 137.69, 135.55, 131.89, 131.67, 131.51, 130.12, 129.86, 129.62, 128.75, 127.84, 127.68,

127.63, 127.33, 127.15, 126.72, 125.07, 52.16. **IR** (cm⁻¹): 1727.4, 1596.8, 1430.3, 1250.6, 1124.6, 1082.1, 961.0, 749.1, 7124, 690.1 **HRMS**: calculated for C₂₂H₁₉O₂⁺([M + H]⁺): 315.1380 Found: 315.1380.

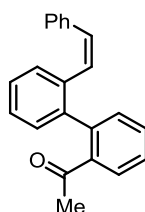
c. Miscellaneous procedures



(E)-(2-styrylphenyl)boronic acid: Prepared according to the reported literature procedure:²³ (*E*)-1-bromo-2-styrylbenzene (**A1**) (3.0 g, 11.6 mmol) was dissolved in THF (60 mL) and cooled to -78°C. Next, *n*BuLi (2.5 M in hexane, 7.0 mL, 17.4 mmol) was added dropwise and the reaction mixture was stirred for 30 minutes before triisopropoxyborate (4.0 mL, 17.4 mmol) was added slowly. The reaction mixture was allowed to warm to rt with stirring overnight. The reaction mixture was quenched with 1M HCl and allowed to stir for 1 hour before being concentrated by rotary evaporator and extracted with two portions of DCM (3 x 30 mL). The combined organic layers were dried over Na₂SO₄ and concentrated by rotary evaporator. The solid product was dried under high vacuum and used without further purification.

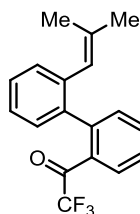


(E)-(2-styrylnaphthalen-1-yl)boronic acid: (*E*)-1-bromo-2-styrylnaphthalene (**A11**) (300 mg, 0.97 mmol) was dissolved in THF (9 mL) and cooled to -78 °C. Next, *n*BuLi (2.5 M in hexane, 0.47 mL, 1.07 mmol) was added dropwise and the reaction mixture was stirred for 30 minutes before triisopropoxyborate (0.34 mL, 1.46 mmol) was added slowly. The reaction mixture was allowed to warm to rt with stirring overnight. The reaction mixture was quenched with 1M HCl and allowed to stir for 1 hour before being concentrated by rotary evaporator and extracted with two portions of DCM (3 x 5 mL). The combined organic layers were dried over Na₂SO₄ and concentrated by rotary evaporator. The orange semi-solid product was dried under high vacuum and used without further purification.

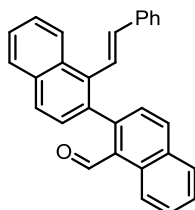


(Z)-1-(2'-styryl-[1,1'-biphenyl]-2-yl)ethan-1-one (8): General olefination procedure **B** was followed employing 2'-acetyl-[1,1'-biphenyl]-2-carbaldehyde²⁶ (9.37 mmol). Purification by flash column chromatography eluting with hexanes/EtOAc provided 1485 mg (53%) of **8** and its alkene isomer (*E*:*Z*; 2.2:1) as a clear oil. Recrystallization from hexanes afforded exclusively the *Z* alkene (**8**). Spectroscopic data for *E*/*Z* mixture prior to recrystallization: ¹H NMR (700 MHz, CDCl₃) δ 7.77 (d, *J* = 7.9 Hz, 1H), 7.71 (d, *J* = 7.7 Hz, 1H), 7.65 (d, *J* = 7.5 Hz, 0.5H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.45 – 7.39 (m, 1.5H), 7.30 (m, 9.5H), 7.23 – 7.15 (m, 4H), 7.02 (d, *J* = 16.2 Hz, 1H), 6.88 (d, *J* = 16.2 Hz, 1H), 6.45 (d, *J* = 12.2 Hz, 0.5H), 6.22 (d, *J* = 12.2 Hz, 0.5H), 2.14 (d, *J* = 0.5 Hz, 1.5H), 2.00 (d, *J* = 0.4 Hz, 3H). ¹³C NMR (175 MHz, CDCl₃) δ 202.88, 202.75, 141.04, 140.61, 140.17, 140.10, 139.79, 137.47, 136.94, 135.87, 135.80, 131.69, 131.53, 131.04, 130.91, 130.64, 130.52, 130.22, 129.71, 129.24, 129.21, 129.05, 128.84, 128.75, 128.49, 128.46, 128.41, 128.15, 127.92, 127.87, 127.77, 127.70, 127.65, 127.45, 126.79, 126.68, 125.71, 29.93, 29.66.

IR (cm⁻¹): 1684.6, 1593.5, 1494.4, 1467.9, 1453.8, 1352.4, 1244.0, 1073.6, 1003.7, 962.2, 757.2, 732.5, 690.4. Spectroscopic data for **8**: **¹H NMR** (400 MHz, CDCl₃) δ 7.66 (d, *J* = 6.7 Hz, 1H), 7.43 (pd, *J* = 7.4, 1.6 Hz, 2H), 7.32 (dd, *J* = 10.3, 4.3 Hz, 1H), 7.29 – 7.14 (m, 9H), 6.45 (d, *J* = 12.3 Hz, 1H), 6.22 (d, *J* = 12.3 Hz, 1H), 2.14 (s, 3H). **¹³C NMR** (175 MHz, CDCl₃) δ 202.77, 140.72, 140.60, 140.10, 136.94, 135.87, 131.54, 131.03, 130.91, 130.22, 129.71, 129.21, 129.05, 128.41, 128.15, 127.70, 127.66, 127.45, 29.67. **IR** (cm⁻¹): 3014.2, 1688.4, 1591.9, 1473.5, 1444.4, 1350.8, 1245.4, 965.9, 776.0, 762.5, 703.8, 692.9, 596.0. **HRMS**: calculated for C₂₂H₁₈O⁺ ([M]⁺): 298.1358 Found 298.1365.

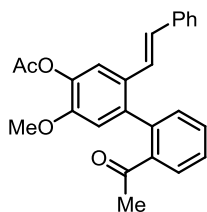


2,2,2-trifluoro-1-(2'-(2-methylprop-1-en-1-yl)-[1,1'-biphenyl]-2-yl)ethan-1-one (S31): A 25 mL round bottom flask containing a stirred solution of 2-bromo-2'-(2-methylprop-1-en-1-yl)-1,1'-biphenyl (**A27**, 350 mg, 1.22 mmol) in THF (10 mL), was cooled to -78°C. At which time, ⁿBuLi (2.5 M in hexanes, 0.54 mL, 1.34 mmol) was slowly added. This solution was allowed to stir for 30 min. Next, ethyl trifluoroacetate (0.26 mL, 2.19 mmol) was added. The resultant mixture was allowed to slowly warm to room temperature over 3 h. The reaction mixture was quenched with NH₄Cl⁺ (aq) (10 mL) and extracted with EtOAc (3 x 15 mL). The combined organic layers were dried over MgSO₄ and concentrated under reduced pressure. Purification was accomplished employing flash column chromatography with hexanes/EtOAc to afford 156 mg (42%) of **S31** as a clear oil. **¹H NMR** (500 MHz, CDCl₃) δ 7.79 (d, *J* = 7.9 Hz, 1H), 7.66 (td, *J* = 7.6, 1.2 Hz, 1H), 7.48 (td, *J* = 7.8, 1.1 Hz, 1H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.36 – 7.30 (m, 2H), 7.27 – 7.20 (m, 2H), 5.68 (s, 1H), 1.71 (s, 3H), 1.67 (s, 3H). **¹³C NMR** (175 MHz, CDCl₃) δ 181.89 (q, *J* = 34.6), 143.35, 139.05, 137.45, 136.13, 133.29, 132.00, 131.44, 129.98, 129.09, 128.39, 128.38, 127.38, 127.07, 126.79, 123.75, 116.10 (q, *J* = 292.9). **IR** (cm⁻¹): 3072.0, 1454.2, 1435.9, 1229.8, 1162.6, 1138.1, 1115.3, 1056.5, 1016.2, 927.8, 736.3, 694.6, 647.8. **HRMS**: calculated for C₁₈H₁₉OF₃N⁺ ([M + NH₄⁺]⁺): 322.1413 Found 322.1414.

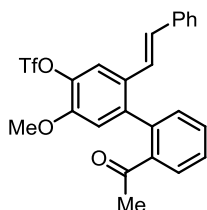


(E)-1'-styryl-[2,2'-binaphthalene]-1-carbaldehyde (S32): Sodium hydride (60% dispersion in mineral oil, 31mg, 0.77 mmol) was suspended in THF (6 mL) and cooled on an ice bath. Diethyl benzylphosphonate (0.134 mL, 0.64 mmol) was added via syringe and stirred for 30 minutes. [2,2'-binaphthalene]-1,1'-dicarbaldehyde²⁵ was added as a solid and the reaction mixture was allowed to warm to room temperature over 1 hour. The reaction mixture was then heated to 50°C for 6 hours. The mixture was allowed to cool to room temperature and quenched with water, then neutralized with saturated aqueous ammonium chloride. The aqueous layer was extracted twice with ethyl acetate and the combined organic layers were washed with brine and dried over Na₂SO₄. The resulting crude product was purified by silica gel column chromatography eluting with hexanes/EtOAc to afford 136 mg (27%) of the title compound as a foamy yellow solid. **¹H NMR** (700 MHz, CDCl₃) δ 10.22 (s, 1H), 9.30 (d, *J* = 8.6 Hz, 1H), 8.35 (dd, *J* = 6.1, 3.5 Hz, 1H), 8.05 (d, *J* = 8.3 Hz, 1H), 7.96 (dd, *J* = 6.1, 3.4 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 8.3 Hz, 1H), 7.70 – 7.66 (m, 1H), 7.62 – 7.56 (m, 3H), 7.48 (d, *J* = 8.3 Hz, 1H), 7.45 (d, *J* = 8.3 Hz, 1H), 7.25 – 7.16 (m, 6H), 6.65 (d, *J* = 16.5 Hz, 1H). **¹³C NMR** (176 MHz, CDCl₃) δ 194.59, 149.05, 137.57, 137.20, 135.13, 134.97, 134.16, 133.78, 133.28, 131.89, 130.71, 129.48, 129.29, 128.88, 128.78, 128.72, 128.53, 128.12, 127.34, 127.20, 127.01, 126.71, 126.62, 126.17,

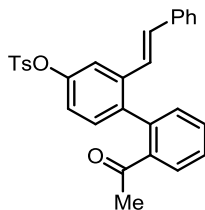
126.06, 125.29. **IR** (cm^{-1}): 3048.5, 1680.9, 1590.0, 1503.3, 1429.8, 1264.0, 1175.8, 1057.3, 964.5, 819.8, 733.7. **HRMS**: calculated for $\text{C}_{29}\text{H}_{20}\text{O}^+$ ($[\text{M}]^+$): 384.1514 Found: 384.1518. .



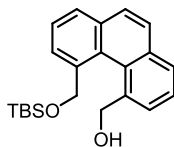
(E)-2'-acetyl-5-methoxy-2-styryl-[1,1'-biphenyl]-4-yl acetate (S34): To a 10 mL flame-dried round bottom flask was added **S27** (100 mg, 0.29 mmol) along with DCM (2 mL) under an atmosphere of nitrogen. After cooling the resultant mixture to 0 °C, DMAP (0.35 mg, 2.9 μmol), Ac_2O (41.2 μL , 0.47 mmol) and TEA (60.5 μL , 0.44 mmol) were successively added. The reaction mixture was slowly allowed to warm to room temperature. After 8 h, the reaction was quenched with NH_4Cl^+ (aq) (5 mL) and extracted with EtOAc (3 x 5 mL). The combined organic layers were dried over MgSO_4 and concentrated under reduced pressure. Purification was accomplished employing flash column chromatography with hexanes/EtOAc to afford 109 mg (97%) of **S34** as a clear foam. **^1H NMR** (500 MHz, CDCl_3) δ 7.71 (d, $J = 7.6$ Hz, 1H), 7.56 (td, $J = 7.5, 1.3$ Hz, 1H), 7.53 – 7.46 (m, 2H), 7.35 (d, $J = 7.5$ Hz, 1H), 7.33 – 7.27 (m, 4H), 7.21 (dq, $J = 8.6, 4.3$ Hz, 1H), 6.92 (d, $J = 16.2$ Hz, 1H), 6.79 (m, 2H), 3.83 (s, 3H), 2.39 (s, 3H), 2.06 (s, 3H). **^{13}C NMR** (125 MHz, CDCl_3) δ 202.98, 169.07, 150.57, 141.19, 139.99, 138.85, 138.51, 137.40, 131.58, 131.02, 129.48, 128.82, 128.78, 128.34, 128.11, 127.73, 126.59, 125.38, 119.94, 114.25, 56.25, 29.98, 20.88. **IR** (cm^{-1}): 3053.8, 2056.0, 1759.6, 1685.6, 1506.0, 1438.2, 1205.0, 1133.4, 1022.1, 961.9, 732.2. **HRMS**: calculated for $\text{C}_{25}\text{H}_{26}\text{O}_4\text{N}$ ($[\text{M} + \text{NH}_4^+]^+$): 404.1856, found: 404.1856.



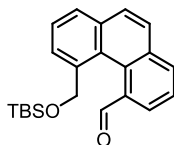
(E)-2'-acetyl-5-methoxy-2-styryl-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate (S35): To a 10 mL flame-dried round bottom flask was added **S27** (100 mg, 0.29 mmol) along with DCM (4 mL) under an atmosphere of nitrogen. After cooling the resultant mixture to 0 °C, Tf_2O (58. μL , 0.35 mmol) and TEA (88 μL , 0.58 mmol) were successively added. The reaction mixture was slowly allowed to warm to room temperature. After 4 h, the reaction was quenched with NH_4Cl^+ (aq) (5 mL) and extracted with EtOAc (3 x 5 mL). The combined organic layers were dried over MgSO_4 and concentrated under reduced pressure. Purification was accomplished employing flash column chromatography with hexanes/EtOAc to afford 97 mg (70%) of **S35** as a white solid. **^1H NMR** (500 MHz, CDCl_3) δ 7.74 (d, $J = 7.6$ Hz, 1H), 7.60 – 7.55 (m, 2H), 7.52 (m, 1H), 7.34 – 7.30 (m, 1H), 7.29 (d, $J = 4.3$ Hz, 4H), 7.25 – 7.20 (m, 1H), 6.88 (d, $J = 16.2$ Hz, 1H), 6.85 (s, 1H), 6.70 (d, $J = 16.2$ Hz, 1H), 3.90 (s, 3H), 2.13 (s, 3H). **^{13}C NMR** (125 MHz, CDCl_3) δ 201.91, 150.42, 141.12, 140.59, 138.75, 138.23, 136.99, 131.47, 131.38, 130.62, 129.35, 128.89, 128.64, 128.57, 128.15, 126.75, 124.74, 119.55, 114.84, 119.01 (q, $J = 318.8$), 56.62, 29.69. **IR** (cm^{-1}): 3032.2, 1688.9, 1609.7, 1503.3, 1419.3, 1320.0, 1240.0, 1204.5, 1136.6, 1101.0, 856.2, 756.2, 734.5. **HRMS**: calculated for $\text{C}_{24}\text{H}_{23}\text{O}_5\text{NF}_3\text{S}$ ($[\text{M} + \text{NH}_4^+]^+$): 494.1244, found: 494.1244.



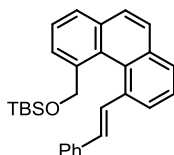
(E)-2'-acetyl-2-styryl-[1,1'-biphenyl]-4-yl 4-methylbenzenesulfonate (S36): To a 10 mL flame-dried round bottom flask was added **S25** (120 mg, 0.38 mmol) along with DCM (4 mL) under an atmosphere of nitrogen. After cooling the resultant mixture to 0 °C, TsCl (87 mg, 0.38 mmol) and TEA (0.16 mL, 1.15 mmol) were successively added. The reaction mixture was slowly allowed to warm to room temperature. After 12 h, the reaction was quenched with NH_4Cl^+ (aq) (5 mL) and extracted with EtOAc (3 x 5 mL). The combined organic layers were dried over MgSO_4 and concentrated under reduced pressure. Purification was accomplished employing flash column chromatography with hexanes/EtOAc to afford 85 mg (48%) of **S36** as a pale yellow foam. $^1\text{H NMR}$ (700 MHz, CDCl_3) δ 7.78 (d, $J = 6.9$ Hz, 2H), 7.70 (d, $J = 7.7$ Hz, 1H), 7.53 (t, $J = 7.5$ Hz, 1H), 7.47 (t, $J = 7.6$ Hz, 1H), 7.36 (m, 3H), 7.31 – 7.21 (m, 6H), 7.09 (d, $J = 8.3$, 1H), 6.90 (d, $J = 8.3$ Hz, 1H), 6.81 (d, $J = 16.2$ Hz, 1H), 6.71 (d, $J = 16.2$ Hz, 1H), 2.46 (s, 3H), 1.98 (s, 3H). $^{13}\text{C NMR}$ (176 MHz, CDCl_3) δ 202.08, 149.78, 145.74, 140.84, 138.99, 138.49, 137.62, 136.86, 132.55, 132.06, 131.59, 131.53, 131.25, 130.02, 128.92, 128.63, 128.38, 128.27, 126.89, 125.36, 121.34, 119.42, 29.80, 21.98. **IR** (cm^{-1}): 2959.5, 1687.5, 1448.5, 1428.9, 1284.2, 1232.5, 1178.1, 1092.1, 943.9, 880.6, 707.6. **HRMS**: calculated for $\text{C}_{29}\text{H}_{28}\text{O}_4\text{NS}^+$ ($[\text{M} + \text{NH}_4^+]$): 486.1734, found: 486.1730.



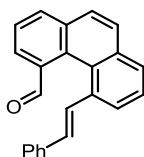
(5-(((tert-butyl dimethylsilyl)oxy)methyl)phenanthren-4-yl)methanol (S37i-a): Phenanthrene-4,5-diyl dimethanol²⁶ (893 mg, 3.75 mmol) was dissolved in DMF (4 mL). TBSCl (678 mg, 4.5 mmol) and imidazole (765 mg, 11.2 mmol) were added and the reaction mixture was stirred overnight. The reaction was diluted with water and diethyl ether. The layers were separated and the aqueous layer was washed with two portions of ether. The combined organic layers were washed with brine and dried over MgSO_4 , then concentrated by rotary evaporator. The product was purified by silica gel column chromatography eluting with hexanes/ethyl acetate to afford 281 mg (21% yield) of the title product as a clear oil. This reaction was carried out twice and the combined product was used in the next step. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.89 – 7.73 (m, 4H), 7.69 – 7.54 (m, 4H), 5.06 (d, $J = 12.1$ Hz, 1H), 4.99 (d, $J = 12.1$ Hz, 1H), 4.86 (d, $J = 12.2$ Hz, 1H), 4.75 (d, $J = 12.1$ Hz, 1H), 0.76 (s, 9H), -0.22 (s, 3H), -0.33 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 139.62, 139.33, 133.54, 127.89, 127.71, 127.65, 127.15, 127.04, 126.96, 126.88, 126.86, 126.72, 126.56, 63.82, 63.54, 25.96, 18.34, -5.29, -5.37. **IR** (cm^{-1}): 2926.2, 2884.4, 2854.1, 1469.7, 1251.3, 1164.4, 1101.7, 1066.3, 1004.1, 955.6, 889.6, 824.3, 772.6, 723.7, 673.8. **HRMS**: calculated for $\text{C}_{22}\text{H}_{28}\text{O}_2\text{SiNa}^+$ ($[\text{M} + \text{Na}^+]$): 375.1751 Found: 375.1753.



5-(((tert-butyldimethylsilyl)oxy)methyl)phenanthrene-4-carbaldehyde (S37i-b): (5-(((tert-butyldimethylsilyl)oxy)methyl)phenanthren-4-yl)methanol (**S37i-a**) (514 mg, 1.50 mmol), tetrapropylammonium perruthenate (26 mg, 0.07 mmol) and N-methylmorpholine N-oxide (256 mg, 2.1 mmol) were combined and dissolved in DCM (15 mL). The reaction mixture was stirred at room temperature until judged complete by TLC. The reaction mixture was filtered through a plug of silica eluting with DCM and the solvent was removed by rotary evaporator. The crude product was purified by silica gel column chromatography eluting with hexanes/ethyl acetate, affording 416 mg (81% yield) of product as a clear oil. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 9.93 (s, 1H), 8.22 (d, $J = 7.3$ Hz, 1H), 8.11 (d, $J = 7.7$ Hz, 1H), 7.94 (d, $J = 7.4$ Hz, 1H), 7.88 (d, $J = 7.6$ Hz, 1H), 7.79 – 7.65 (m, 4H), 5.03 (br d, $J = 79.4$ Hz, 2H), 0.75 (s, 9H), -0.12 – -0.37 (br m, 6H). $^{13}\text{C NMR}$ (176 MHz, CDCl_3): δ 191.83, 140.94, 135.38, 134.14, 133.84, 133.09, 129.91, 128.38, 128.29, 128.10, 127.20, 126.79, 126.55, 126.48, 126.00, 63.50, 25.95, 18.35, -5.33. **IR** (cm^{-1}): 1685.4, 1469.9, 1249.6, 1219.7, 1074.3, 832.0, 774.1, 723.9. **HRMS**: calculated for $\text{C}_{22}\text{H}_{26}\text{O}_2\text{SiNa}^+$ ($[\text{M}+\text{Na}]^+$): 373.1594 Found: 373.1596.

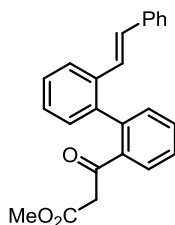


(E)-tert-butyldimethyl((5-styrylphenanthren-4-yl)methoxy)silane (S37i-c): NaH (1.33 g, 5.85 mmol) was added to a solution of diethyl benzylphosphonate (1.33 g, 5.85 mmol) in DMF (5 mL) at 0°C and allowed to stir for 30 minutes, at which time a solution of 5-(((tert-butyldimethylsilyl)oxy)methyl)phenanthrene-4-carbaldehyde (**S37i-b**) (410 mg, 1.17 mmol) in DMF (3 mL) was added slowly. The reaction mixture was allowed to warm to room temperature and stirred for 2 hours, before cooling to 0°C and quenching with water. The aqueous layer was washed with three portions of ethyl acetate and the combined organic layers were washed with brine and dried over Na_2SO_4 . The crude product was purified by silica gel column chromatography eluting with hexanes/ethyl acetate to afford 374 mg (75% yield) of the title compound as a clear oil. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.92 (d, $J = 7.5$ Hz, 1H), 7.85 (d, $J = 7.5$ Hz, 1H), 7.79 (dd, $J = 12.7, 7.7$ Hz, 2H), 7.71 – 7.55 (m, 4H), 7.45 (d, $J = 7.8$ Hz, 2H), 7.33 (dd, $J = 19.3, 11.8$ Hz, 3H), 7.25 (m, $J = 13.4$ Hz, 2H), 7.05 (d, $J = 16.4$ Hz, 1H), 5.05 (d, $J = 12.9$ Hz, 1H), 4.75 (d, $J = 13.0$ Hz, 1H), 0.66 (s, 9H), -0.33 (s, 3H), -0.45 (s, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ 140.29, 137.72, 137.01, 134.48, 133.32, 130.41, 129.11, 128.98, 128.80, 128.30, 127.85, 127.34, 127.32, 126.99, 126.81, 126.62, 126.57, 126.40, 124.25, 64.70, 25.98, 18.39, -5.43, -5.47. **IR** (cm^{-1}): 1470.0, 1251.4, 1070.4, 973.1, 834.0, 775.1, 755.4, 721.6, 960.0, 667.7. **HRMS**: Calculated for $\text{C}_{25}\text{H}_{23}\text{OSi}^+$ ($[\text{M}-\text{C}_4\text{H}_9]^+$): 367.1518 Found: 367.1518

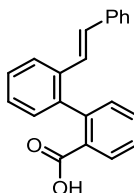


(E)-5-styrylphenanthrene-4-carbaldehyde (S37): (E)-tert-butyldimethyl((5-styrylphenanthren-4-yl)methoxy)silane (**S37i-d**) (360 mg, 0.85 mmol) was dissolved in THF (8.5 mL) and cooled to 0°C before a solution of TBAF (1M in THF, 2.2 mL, 2.20 mmol) was added slowly. The reaction mixture was allowed to warm to room temperature and stirred for 3 hours, at which time the reaction mixture was diluted with water and diethyl ether. The layers were separated and the organic layer was washed with saturated aqueous

ammonium chloride and brine and dried over MgSO₄. The solvent was removed by rotary evaporator and the crude material was dissolved in DMSO (3 mL) and IBX (285 mg, 1.01 mmol) was added and the reaction mixture was stirred at room temperature for 4 hours. The mixture was diluted with water and diethyl ether and filtered through a pad of Celite. The layers were separated and the aqueous layer was extracted with two more portions of ether. The combined organic layers were washed with brine and dried over MgSO₄ and concentrated by rotary evaporator. The crude product was purified by silica gel column chromatography to afford 106 mg (41% yield) of the title compound as a yellow-white foam. ¹H NMR (401 MHz, CDCl₃): δ 10.04 (s, 1H), 8.21 (d, *J* = 7.4 Hz, 1H), 8.09 (d, *J* = 7.8 Hz, 1H), 7.90 (dd, *J* = 15.6, 7.5 Hz, 2H), 7.84 – 7.63 (m, 5H), 7.44 (d, *J* = 7.5 Hz, 2H), 7.40 – 7.33 (m, 3H), 7.29 (d, *J* = 7.4 Hz, 2H). ¹³C NMR (176 MHz, CDCl₃): δ 189.13, 138.51, 137.43, 135.70, 134.71, 133.95, 132.82, 132.67, 129.97, 128.94, 128.70, 128.32, 128.06, 127.99, 127.57, 127.37, 127.03, 126.89, 126.82, 126.81, 126.27. IR (cm⁻¹): 1725.7, 1684.3, 1447.6, 1275.5, 1213.9, 1133.5, 1018.3, 969.2, 907.5, 831.5, 761.3, 719.3, 690.1, 646.2. HRMS: calculated for C₂₃H₁₇O⁺ ([M+H]⁺): 309.1274 Found: 309.1270.

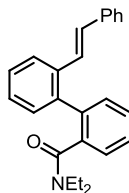


Methyl (*E*)-3-oxo-3-(2'-styryl-[1,1'-biphenyl]-2-yl)propanoate (22h): Sodium hydride (60% dispersion in mineral oil, 181 mg, 4.5 mmol) was suspended in dimethyl carbonate (10 mL) and a solution of **11** (450 mg, 1.5 mmol) in dimethyl carbonate (5 mL) was added dropwise at room temperature. The reaction mixture was then heated to reflux and monitored until complete by TLC analysis. Purification by flash column chromatography eluting with hexanes/EtOAc afforded 174 mg (33% yield) as a mixture of keto/enol tautomers. NMR spectra in CDCl₃ appeared as a mixture of keto/enol tautomers. ¹H NMR (500 MHz, DMSO) δ 7.83 (t, *J* = 8.0 Hz, 2H), 7.65 (t, *J* = 7.1 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.38 – 7.26 (m, 5H), 7.16 (dd, *J* = 29.9, 22.6 Hz, 3H), 6.73 (d, *J* = 16.3 Hz, 1H), 3.70 (d, *J* = 16.6 Hz, 1H), 3.58 – 3.52 (m, 1H), 3.48 (s, 2H). ¹³C NMR (126 MHz, DMSO) δ 196.16, 167.31, 139.41, 139.38, 138.30, 136.91, 134.96, 131.67, 131.61, 129.95, 129.84, 128.74, 128.70, 128.09, 127.91, 127.74, 127.48, 126.26, 126.20, 125.93, 125.37, 51.74, 47.48. IR (cm⁻¹): 1741.0, 1692.7, 1616.5, 1593.4, 1470.7, 1436.2, 1388.6, 1319.3, 1273.1, 1241.4, 1092.8, 1073.1, 983.4, 962.8, 823.9. HRMS: calculated for C₂₄H₂₄O₃N⁺: 374.1751 Found: 374.1755.



(*E*)-2'-styryl-[1,1'-biphenyl]-2-carboxylic acid (22k): Potassium trimethylsilanoate (1.16g, 9.1 mmol) was dissolved in THF (10 mL) and transferred to a solution of ester **22j** (570 mg, 1.83 mmol) in THF (8 mL) and the mixture was stirred overnight at room temperature. The solvent was then stripped by rotary evaporator and the crude mixture was taken up in diethyl ether and extracted with two portions of aqueous sodium hydroxide (1M). The combined aqueous layers were then acidified to pH 1 with concentrated HCl and extracted with four portions of diethyl ether. The combined organic layers were dried over MgSO₄ and concentrated by rotary evaporator to afford 545 mg (83% yield) of the title compound as a white solid. ¹H NMR (700 MHz, CDCl₃): δ 8.03 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.58 (td, *J* = 7.5, 1.3 Hz, 1H), 7.47 (td, *J* = 7.8, 1.1 Hz,

1H), 7.36 (t, $J = 7.6$ Hz, 1H), 7.32 – 7.23 (m, 6H), 7.19 (ddd, $J = 8.5, 5.8, 2.8$ Hz, 1H), 7.16 (dd, $J = 7.5, 0.9$ Hz, 1H), 6.95 (d, $J = 16.2$ Hz, 1H), 6.79 (d, $J = 16.2$ Hz, 1H). $^{13}\text{C NMR}$ (176 MHz, CDCl_3): δ 171.54, 142.60, 140.50, 137.69, 135.58, 132.41, 132.20, 131.02, 130.12, 129.95, 129.60, 128.73, 127.91, 127.68, 127.67, 127.30, 127.05, 126.74, 125.26. **IR** (cm^{-1}): 2534.3, 1691.0, 1570.9, 1470.9, 1405.9, 1293.6, 1276.9, 1145.9, 965.9, 805.0, 767.8, 754.8, 691.8, 659.6 **HRMS**: calculated for $\text{C}_{21}\text{H}_{16}\text{O}_2\text{Na}^+$ ($[\text{M}+\text{Na}^+]^+$): 323.1043 Found: 323.1043.



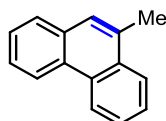
(E)-N,N-diethyl-2'-styryl-[1,1'-biphenyl]-2-carboxamide (22l): (*E*)-2'-styryl-[1,1'-biphenyl]-2-carboxylic acid (**22k**) (250 mg, 0.83 mmol) was treated with thionyl chloride (0.60 mL, 8.3 mmol) and heated to reflux for 3 hours, at which time the reaction mixture was allowed to cool and volatiles were removed by rotary evaporator. The resulting crude material was dissolved in DCM (10 mL) and diethylamine (0.17 mL, 1.66 mmol) was added. The reaction mixture was stirred until judged complete by TLC. The solvent was removed by rotary evaporator and the crude material was purified directly by silica gel column chromatography eluting with hexanes/EtOAc to afford 296 mg (61% yield) of the title compound as a thick yellow oil. $^1\text{H NMR}$ (700 MHz, CDCl_3) δ 7.76 (d, $J = 7.8$ Hz, 1H), 7.43 (s, 3H), 7.38 – 7.13 (m, 9H), 7.05 (m, 2H), 3.73 (s, 1H), 2.94 (m, 2H), 2.63 (br s, 1H), 0.96 (br s, 1H), 0.86 – 0.65 (m, 5H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 170.15, 137.70, 131.55, 129.79, 128.84, 128.19, 127.88, 126.72, 125.35, 42.71, 38.16, 13.90, 12.08. **IR** (cm^{-1}): 1623.3, 1494.1, 1424.4, 1379.3, 1362.2, 1312.3, 1287.7, 1220.0, 1085.8, 962.3, 910.7, 760.0, 729.4, 690.8. **HRMS**: calculated for $\text{C}_{25}\text{H}_{26}\text{NO}$ ($[\text{M}+\text{H}^+]^+$): 356.2009 Found: 356.2012.

6. Synthesis of metathesis products



General procedure for Carbonyl-Olefin Metathesis:

A flame-dried 1 – dram vial was charged with FeCl₃ (1 mg, 0.13 mmol) and DCE (1.3 mL), and stirred at room temperature. To this solution was added starting ketone **S** (0.13 mmol), and the resultant mixture was stirred for the indicated time at room temperature, unless otherwise specified. Upon completion (as determined by TLC analysis), the reaction mixture was passed through a short silica plug eluting with DCM (25 mL). The filtrate was concentrated under reduced pressure, and the crude material was purified using column chromatography, with the indicated eluent to give the pure metathesis adducts.



9-methylphenanthrene (9): The cyclization of **8** was performed on 0.13 mmol scale with a total reaction time of 1 h. Purification by flash column chromatography eluting with hexanes/EtOAc (19:1) provided 25 mg (99%) of **9** as a white solid. Spectroscopic data matched reported literature data.²⁴ ¹H NMR (500 MHz, CDCl₃) δ 8.73 (d, *J* = 7.8 Hz, 1H), 8.66 (d, *J* = 7.9 Hz, 1H), 8.07 (d, *J* = 7.7 Hz, 1H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.71 – 7.62 (m, 2H), 7.62 – 7.53 (m, 3H), 2.75 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 132.46, 132.06, 132.00, 130.36, 129.65, 127.80, 126.71, 126.55, 126.49, 126.19, 125.78, 124.64, 122.98, 122.43, 20.02.

9-methylphenanthrene (9): The cyclization of **11** was performed on 0.13 mmol scale with a total reaction time of 24 h. Purification by flash column chromatography eluting with hexanes/EtOAc (19:1) provided 22.5 mg (90%) of **9** as a white solid.

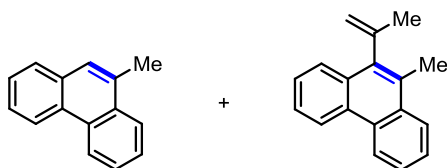
9-methylphenanthrene (9): The cyclization of **12** was performed on 0.13 mmol scale with a total reaction time of 8 h at 50 °C. Purification by flash column chromatography eluting with hexanes/EtOAc (19:1) provided 20.5 mg (82%) of **9** as a white solid.

9-methylphenanthrene (9): The cyclization of **13** was performed on 0.13 mmol scale with a total reaction time of 8 h at 50 °C. Purification by flash column chromatography eluting with hexanes/EtOAc (19:1) provided 22.2 mg (89%) of **9** as a white solid.

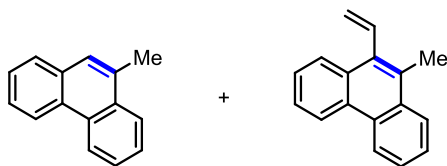
9-methylphenanthrene (9): The cyclization of **14** was performed on 0.13 mmol scale with a total reaction time of 6 h at 50 °C. Purification by flash column chromatography eluting with hexanes/EtOAc (19:1) provided 21.4 mg (86%) of **9** as a white solid.

9-methylphenanthrene (9): The cyclization of **15** was performed on 0.13 mmol scale with a total reaction time of 6 h 50 °C. Purification by flash column chromatography eluting with hexanes/EtOAc (19:1) provided 20.0 mg (80%) of **9** as a white solid.

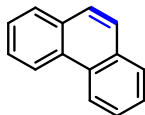
9-methylphenanthrene (9): The cyclization of **16** was performed on 0.13 mmol scale with a total reaction time of 6 h 50 °C. Purification by flash column chromatography eluting with hexanes/EtOAc (19:1) provided 21.0 mg (84%) of **9** as a white solid.



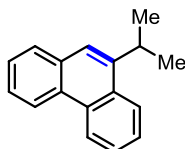
9-methylphenanthrene + 9-methyl-10-(prop-1-en-2-yl)phenanthrene²⁷ (9 + 20): The cyclization of **17** was performed on 0.13 mmol scale with a total reaction time of 1 h at rt . Purification by flash column chromatography eluting with hexanes/EtOAc (19:1) provided 26 mg of **9** (19.8 mg, 79%) and **9b** (6.2 mg, 21%) as an inseparable mixture (1.0:0.26; ratio by NMR analysis), as a white solid. ¹H NMR (500 MHz, CDCl₃; as a mixture of **9** and **9b**) δ 8.73 (d, *J* = 11.4 Hz, 1.10H), 8.70 (d, *J* = 8.9 Hz, 0.34H), 8.66 (d, *J* = 8.0 Hz, 0.94H), 8.15 – 8.10 (m, 0.25H), 8.10 – 8.04 (m, 0.92H), 8.01 (d, *J* = 7.8 Hz, 0.25H), 7.81 (d, *J* = 7.4 Hz, 0.98H), 7.66 (m, 2.24H), 7.62 – 7.52 (m, 3.04H), 5.57 (s, 0.26H), 5.00 (s, 0.28H), 2.74 (s, 3H), 2.69 (s, 0.69H), 2.14 (s, 0.57H). ¹³C NMR (125 MHz, CDCl₃; as a mixture of **9** and **9b**) δ 144.46, 138.48, 132.48, 132.09, 132.02, 131.98, 130.46, 130.38, 129.68, 129.61, 129.53, 128.86, 128.68, 128.56, 128.30, 127.82, 127.58, 126.73, 126.63, 126.57, 126.51, 126.21, 125.90, 125.80, 125.60, 124.89, 124.66, 123.00, 122.77, 122.53, 122.45, 116.71, 24.86, 20.04, 16.49.



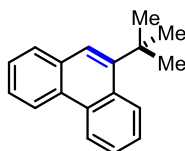
9-methylphenanthrene + 9-methyl-10-vinylphenanthrene (9 + 21): The cyclization of **18** was performed on 0.12 mmol scale with a total reaction time of 6 h at 50 °C . Purification by flash column chromatography eluting with hexanes/EtOAc (19:1) provided 19 mg of **9** (4.5 mg, 18%) and **9c** (13.3 mg, 47%) as an inseparable mixture (0.4:1.0; ratio by NMR analysis), as a white solid. ¹H NMR (500 MHz, CDCl₃; as a mixture of **9** and **9c**) δ 8.72 (m, 2.19H), 8.67 (d, *J* = 7.9 Hz, 0.36H), 8.14 (m, 1.74H), 8.08 (d, *J* = 7.6 Hz, 0.36H), 7.82 (d, *J* = 7.5 Hz, 0.45H), 7.72 – 7.63 (m, 2.38H), 7.63 – 7.53 (m, 2.39H), 7.13 (dt, *J* = 25.0, 12.5 Hz, 1.05H), 5.85 (d, *J* = 11.4 Hz, 1H), 5.42 (d, *J* = 17.9 Hz, 0.97H), 2.76 (s, 3.82H). ¹³C NMR (125 MHz, CDCl₃; as a mixture of **9** and **9c**) δ 135.75, 133.93, 132.69, 132.30, 132.23, 131.35, 130.59, 129.93, 129.89, 129.55, 129.36, 129.29, 129.22, 128.04, 126.94, 126.88, 126.79, 126.73, 126.62, 126.46, 126.42, 126.26, 126.01, 125.90, 125.32, 124.87, 123.21, 122.98, 122.77, 122.66, 121.79, 20.25, 17.17.



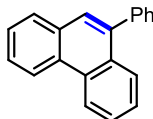
Phenanthrene (23b): The cyclization of **22b** was performed on 0.13 mmol scale (37 mg) with a total reaction time of 4 h. Purification by flash column chromatography eluting with hexanes/EtOAc provided 18 mg (75%) of **23b** as a white solid. Spectroscopic data matched that reported.²⁸ ¹H NMR (401 MHz, CDCl₃) δ 8.70 (d, *J* = 8.2 Hz, 2H), 7.90 (d, *J* = 7.8 Hz, 2H), 7.75 (s, 2H), 7.67 (t, *J* = 7.5 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 2H). ¹³C NMR (176 MHz, CDCl₃) δ 132.26, 130.52, 128.78, 127.13, 126.77, 122.87.



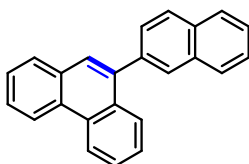
9-Isopropylphenanthrene (23c): The cyclization of **22c** was performed on 0.13 mmol scale with a total reaction time of 4 h. Purification by flash column chromatography eluting with hexanes/EtOAc provided 23 mg (79%) of **23c** as a colorless oil.²⁹ **¹H NMR** (400 MHz, CDCl₃) δ 8.81 – 8.71 (m, 1H), 8.69 – 8.62 (m, 1H), 8.21 (m, 1H), 7.91 – 7.80 (m, 1H), 7.74 – 7.46 (m, 5H), 3.82 – 3.69 (m, 1H), 1.49 (s, 3H), 1.47 (s, 3H). **¹³C NMR** (175 MHz, CDCl₃) δ 142.80, 132.19, 131.12, 130.96, 129.59, 128.51, 126.75, 126.66, 126.16, 126.12, 124.17, 123.52, 122.59, 122.42, 28.83, 23.55.



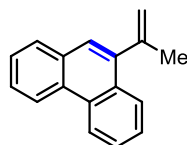
9-(tert-butyl)phenanthrene (23d): The cyclization of **22d** was performed on 0.13 mmol scale with a total reaction time of 12 h at 50 °C. Purification by flash column chromatography eluting with hexanes/EtOAc provided 16.4 mg (55%) of **23d** as a white solid. Spectroscopic data matched that reported.³⁰ **¹H NMR** (700 MHz, CDCl₃) δ 8.82 – 8.77 (m, 1H), 8.64 (d, *J* = 8.1 Hz, 1H), 8.54 (dd, *J* = 7.3, 1.4 Hz, 1H), 7.86 (d, *J* = 7.7 Hz, 1H), 7.76 (s, 1H), 7.61 (m, 4H), 1.70 (s, 9H). **¹³C NMR** (175 MHz, CDCl₃) δ 144.19, 132.01, 131.87, 131.06, 129.86, 128.89, 127.88, 126.78, 126.44, 125.58, 125.52, 124.31, 123.87, 122.40, 36.15, 32.06.



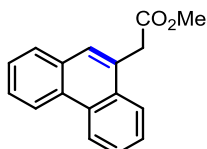
9-Phenylphenanthrene (23e): The cyclization of **22e** was performed on 0.13 mmol scale (47 mg) with a total reaction time of 24 h. Purification by flash column chromatography eluting with hexanes/EtOAc provided 22 mg (67%) of **23e** as a white solid. Spectroscopic data matched that reported.³¹ **¹H NMR** (401 MHz, CDCl₃) δ 8.79 (d, *J* = 8.3 Hz, 1H), 8.74 (d, *J* = 8.2 Hz, 1H), 7.92 (t, *J* = 8.7 Hz, 2H), 7.79 – 7.38 (m, 10H). **¹³C NMR** (176 MHz, CDCl₃) δ 141.02, 139.00, 131.78, 131.36, 130.84, 130.28, 130.17, 128.88, 128.52, 127.72, 127.58, 127.15, 127.06, 126.80, 126.71, 126.66, 123.11, 122.75.



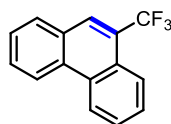
9-(naphthalen-2-yl)phenanthrene (23f): The cyclization of **22f** was performed on 0.13 mmol scale with a total reaction time of 24 h. Purification by flash column chromatography eluting with hexanes/EtOAc (19:1) provided 21 mg (53%) of **23f** as a white solid. Spectroscopic data matched reported literature data.³² **¹H NMR** (500 MHz, CDCl₃) δ 8.81 (d, *J* = 8.3 Hz, 1H), 8.76 (d, *J* = 8.2 Hz, 1H), 8.03 (s, 1H), 8.00 – 7.89 (m, 5H), 7.79 (s, 1H), 7.69 (m, 3H), 7.64 (t, *J* = 7.3 Hz, 1H), 7.60 – 7.50 (m, 3H). **¹³C NMR** (125 MHz, CDCl₃) δ 138.92, 138.60, 133.70, 132.89, 131.82, 131.46, 130.89, 130.26, 128.92, 128.91, 128.65, 128.29, 128.08, 128.00, 127.88, 127.24, 127.11, 126.87, 126.78, 126.73, 126.56, 126.31, 123.16, 122.79.



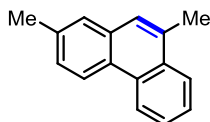
9-(prop-1-en-2-yl)phenanthrene (23g): The cyclization of **22g** was performed on 0.13 mmol scale with a total reaction time of 12 h at 50°C. Purification by flash column chromatography eluting with hexanes/EtOAc (9:1) provided 14 mg (50%) of **23g** as a yellow solid. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.73 (d, $J = 8.2$ Hz, 1H), 8.68 (d, $J = 8.1$ Hz, 1H), 8.09 (d, $J = 8.1$ Hz, 1H), 7.86 (d, $J = 7.7$ Hz, 1H), 7.69 – 7.55 (m, 5H), 5.44 (s, 1H), 5.15 (s, 1H), 2.25 (s, 3H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 145.25, 141.05, 131.89, 130.49, 130.02, 128.65, 126.90, 126.67, 126.66, 126.54, 126.52, 125.14, 123.14, 122.69, 116.33, 25.25. **IR** (cm^{-1}): 3072.8, 2923.1, 1492.8, 1449.3, 1372.0, 1258.0, 1040.0, 905.3, 767.6. **HRMS**: calculated for $\text{C}_{17}\text{H}_{14}$ $[\text{M}]^+$: 218.1096, found: 218.1096.



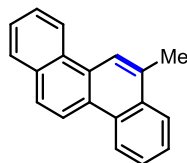
Methyl 2-(phenanthren-9-yl)acetate (23h): The cyclization of **22h** was performed on 0.13 mmol scale (49 mg) with a total reaction time of 24 h. Purification by flash column chromatography eluting with hexanes/EtOAc provided 24 mg (72%) of **23h** as a pale yellow solid. Spectroscopic data matched that reported.³³ $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.77 – 8.72 (m, 1H), 8.67 (d, $J = 8.2$ Hz, 1H), 8.07 – 8.01 (m, 1H), 7.88 – 7.83 (m, 1H), 7.72 – 7.54 (m, 5H), 4.13 (s, 2H), 3.70 (s, 3H). $^{13}\text{C NMR}$ (175 MHz, CDCl_3) δ 172.26, 131.76, 131.29, 130.95, 130.45, 129.19, 129.12, 128.60, 127.13, 126.98, 126.91, 126.73, 124.62, 123.44, 122.73, 52.44, 39.86.



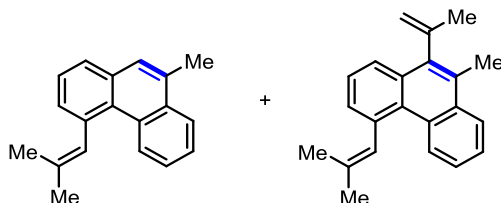
9-(trifluoromethyl)phenanthrene (23i): The cyclization of **22i** was performed on 0.13 mmol scale (47 mg) with a total reaction time of 1 h at 50 °C. Purification by flash column chromatography eluting with hexanes/EtOAc provided 16.5 mg (52%) of **23i** as a white solid. Spectroscopic data matched that reported.³⁴ $^1\text{H NMR}$ (700 MHz, CDCl_3) δ 8.77 (d, $J = 8.2$ Hz, 1H), 8.71 (d, $J = 8.3$ Hz, 1H), 8.25 (d, $J = 8.2$ Hz, 1H), 8.19 (s, 1H), 7.97 (t, $J = 9.5$ Hz, 1H), 7.78 (t, $J = 7.1$ Hz, 1H), 7.75 (t, $J = 7.6$ Hz, 1H), 7.71 (t, $J = 7.6$ Hz, 1H), 7.68 (t, $J = 7.0$ Hz, 1H). $^{13}\text{C NMR}$ (175 MHz, CDCl_3) δ 132.02, 131.20, 130.14, 129.68, 129.21, 127.69, 127.58, 127.55, 127.27 (q, $J = 6.3$ Hz), 127.04, 125.41 (q, $J = 2.7$ Hz), 124.89 (q, $J = 29.8$), 123.40, 122.91.



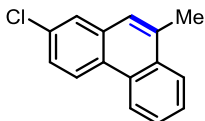
2,9-dimethylphenanthrene (24): The cyclization of **S2** was performed on 0.13 mmol scale with a total reaction time of 1 h. Purification by flash column chromatography eluting with hexanes/EtOAc (19:1) provided 24 mg (89%) of **24** as a white solid. Spectroscopic data matched reported literature data.³⁵ $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.79 – 8.67 (m, 1H), 8.46 (s, 1H), 8.11 – 8.01 (m, 1H), 7.72 (d, $J = 8.0$ Hz, 1H), 7.70 – 7.60 (m, 2H), 7.56 (s, 1H), 7.39 (dd, $J = 24.8, 8.0$ Hz, 1H), 2.73 (s, 3H), 2.63 (s, 3H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 135.60, 132.43, 131.60, 130.36, 130.16, 129.92, 128.50, 127.89, 126.77, 126.57, 126.19, 124.84, 123.18, 122.44, 22.31, 20.19.



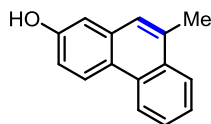
6-methylchrysene (25): The cyclization of **S3** was performed on 0.15 mmol scale with a total reaction time of 1 h. Purification by flash column chromatography eluting with hexanes/EtOAc (19:1) provided 29 mg (80%) of **25** as a white solid. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.81 (dd, $J = 14.7, 8.3$ Hz, 2H), 8.71 (d, $J = 9.1$ Hz, 1H), 8.58 (s, 1H), 8.21 – 8.12 (m, 1H), 8.03 – 7.90 (m, 2H), 7.71 (qdd, $J = 6.8, 6.2, 1.4$ Hz, 3H), 7.66 – 7.56 (m, 1H), 2.91 (s, 3H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 133.38, 132.49, 132.17, 130.87, 130.42, 128.74, 127.53, 126.73, 126.68, 126.56, 126.51, 126.46, 124.93, 123.79, 123.32, 121.75, 121.36, 20.85. **IR** (cm^{-1}): 2923.8, 1596.5, 1513.9, 1483.1, 1438.3, 1399.6, 1244.5, 1156.1, 1035.6, 873.9, 823.3, 755.2. **HRMS**: calculated for $\text{C}_{19}\text{H}_{14}$ $[\text{M}]^+$: 242.1096 found: 242.1095..



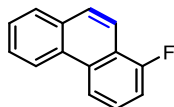
9-methyl-4-(2-methylprop-1-en-1-yl)phenanthrene + 9-methyl-4-(2-methylprop-1-en-1-yl)-10-(prop-1-en-2-yl)phenanthrene (26 + 26b): The cyclization of **S4** was performed on 0.12 mmol scale with a total reaction time of 1 h. Purification by flash column chromatography eluting with hexanes/EtOAc (19:1) provided 28 mg of **26** (18 mg, 64%) and **26b** (10 mg, 30%) as an inseparable mixture (1:0.69; ratio by NMR analysis), as a clear oil. $^1\text{H NMR}$ (500 MHz, CDCl_3 ; as a mixture of **26** and **26b**) δ 9.28 (d, $J = 8.4$ Hz, 1H), 9.24 (d, $J = 8.5$ Hz, 0.57H), 8.13 (d, $J = 8.2$ Hz, 0.66H), 8.06 (d, $J = 8.0$ Hz, 1H), 7.96 (d, $J = 8.1$ Hz, 0.64H), 7.72 (d, $J = 7.8$ Hz, 1H), 7.66 – 7.55 (m, 3.62H), 7.52 (m, 1.76H), 7.37 (t, $J = 8.3$ Hz, 1.66H), 6.83 (s, 1H), 6.81 (s, 0.55H), 5.57 (s, 0.63H), 5.01 (s, 0.62H), 2.73 (s, 3H), 2.69 (s, 1.52H), 2.15 (s, 1.64H), 2.10 (s, $J = 3.6$ Hz, 4.43H), 1.88 (s, 1.60H), 1.83 (s, 3H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3 ; as a mixture of **26** and **26b**) δ 145.22, 139.09, 136.66, 136.55, 133.45, 133.28, 133.14, 132.80, 132.37, 132.35, 132.00, 131.80, 131.10, 130.45, 130.20, 130.02, 129.92, 128.81, 128.75, 128.31, 127.94, 127.67, 127.14, 126.26, 126.11, 125.89, 125.71, 125.49, 125.30, 124.81, 124.53, 124.41, 116.94, 26.14, 26.09, 25.17, 20.22, 19.88, 19.80, 16.85. **HRMS (26)**: calculated for $\text{C}_{19}\text{H}_{18}$ $[\text{M}]^+$: 246.1409, found: 246.1405. **HRMS (26b)**: calculated for $\text{C}_{19}\text{H}_{18}$ $[\text{M}]^+$: 286.1722, found: 286.1721.



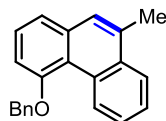
2-chloro-9-methylphenanthrene (27): The cyclization of **S5** was performed on 0.13 mmol scale with a total reaction time of 1 h. Purification by flash column chromatography eluting with hexanes/EtOAc (19:1) provided 25 mg (85%) of **27** as a white solid. Spectroscopic data matched reported literature data.³⁵ $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.65 (dd, $J = 9.7, 7.0$ Hz, 1H), 8.55 (dd, $J = 8.8, 2.3$ Hz, 1H), 8.05 (d, $J = 7.6$ Hz, 1H), 7.81 – 7.74 (m, 1H), 7.72 – 7.62 (m, 2H), 7.52 (d, $J = 8.8$ Hz, 1H), 7.46 (d, $J = 15.8$ Hz, 1H), 2.74 (d, $J = 7.7$ Hz, 3H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 134.24, 133.26, 132.52, 132.15, 130.15, 128.21, 127.01, 126.93, 126.84, 126.42, 125.85, 125.00, 124.35, 123.13.



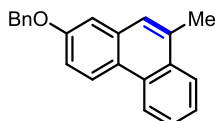
9-methylphenanthren-2-ol (28): The cyclization of **S25** was performed on 0.13 mmol scale with a total reaction time of 12 h. Purification by flash column chromatography eluting with hexanes/EtOAc (9:1) provided 24 mg (75%) of **28** as a yellow solid. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.60 (d, $J = 8.2$ Hz, 1H), 8.54 (d, $J = 8.5$ Hz, 1H), 8.02 (d, $J = 8.1$ Hz, 1H), 7.64 (t, $J = 7.4$ Hz, 1H), 7.58 (t, $J = 7.4$ Hz, 1H), 7.46 (s, 1H), 7.17 – 7.13 (m, 2H), 4.95 (b, 1H), 2.72 (s, 3H). $^{13}\text{C NMR}$ (175 MHz, CDCl_3) δ 154.13, 133.51, 133.42, 131.03, 130.48, 126.36, 125.89, 125.59, 124.68, 124.43, 124.14, 122.42, 115.76, 111.06, 20.06.



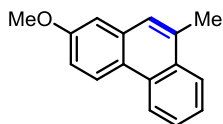
1-fluorophenanthrene (29): The cyclization of **S6** was performed on 0.13 mmol scale with a total reaction time of 1 h. Purification by flash column chromatography eluting with hexanes/EtOAc (19:1) provided 26 mg (99%) of **29** as a pale yellow solid. Spectroscopic data matched reported literature data.³⁶ $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.67 (d, $J = 8.2$ Hz, 1H), 8.47 (d, $J = 8.4$ Hz, 1H), 8.04 (d, $J = 9.1$ Hz, 1H), 7.92 (d, $J = 9.0$ Hz, 1H), 7.81 (d, $J = 9.1$ Hz, 1H), 7.71 – 7.54 (m, 3H), 7.29 (m, 1H). $^{13}\text{C NMR}$ (175 MHz, CDCl_3) δ 159.28 (d, $J = 250.1$ Hz), 132.15 (d, $J = 4.4$ Hz), 132.08, 129.64 (d, $J = 2.6$ Hz), 128.78, 127.37 (d, $J = 1.8$ Hz), 127.10, 127.0, 126.47 (d, $J = 8.7$ Hz), 123.01, 121.56 (d, $J = 15.4$ Hz), 118.51 (d, $J = 7.0$ Hz), 118.39 (d, $J = 3.9$ Hz), 111.01 (d, $J = 20.4$ Hz).



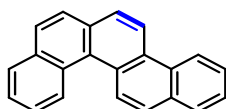
4-(benzyloxy)-9-methylphenanthrene (30): The cyclization of **S8** was performed on 0.13 mmol scale with a total reaction time of 12 h. Purification by flash column chromatography eluting with hexanes/EtOAc (19:1) provided 24 mg (71%) of **30** as a white solid. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 9.83 (t, $J = 12.2$ Hz, 1H), 8.07 (d, $J = 8.0$ Hz, 1H), 7.65 – 7.52 (m, 5H), 7.50 – 7.42 (m, 4H), 7.38 (t, $J = 7.3$ Hz, 1H), 7.17 (dd, $J = 5.9, 3.1$ Hz, 1H), 5.40 (s, $J = 11.4$ Hz, 2H), 2.74 (s, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 157.57, 137.00, 134.59, 133.07, 132.59, 130.47, 129.03, 128.65, 128.00, 127.66, 127.23, 126.45, 125.98, 125.80, 123.97, 121.25, 120.30, 109.39, 71.24, 20.15. **IR** (cm^{-1}): 2921.0, 1567.5, 1441.5, 1301.0, 1241.4, 1229.9, 1055.6, 880.7, 744.7, 757.7, 715.8, 691.5. **HRMS**: calculated for $\text{C}_{22}\text{H}_{19}\text{O}$ ($[\text{M} + \text{H}]^+$): 299.1436, found: 299.1430.



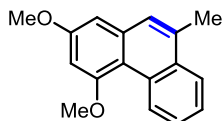
2-(benzyloxy)-9-methylphenanthrene (31): The cyclization of **S9** was performed on 0.13 mmol scale with a total reaction time of 12 h. Purification by flash column chromatography eluting with hexanes/EtOAc (19:1) provided 38 mg (97%) of **31** as a yellow-white solid. $^1\text{H NMR}$ (700 MHz, CDCl_3) δ 8.62 (d, $J = 8.2$ Hz, 1H), 8.56 (d, $J = 8.9$ Hz, 1H), 8.03 (d, $J = 8.2$ Hz, 1H), 7.66 – 7.61 (m, 1H), 7.60 – 7.54 (m, 1H), 7.51 (m, $J = 8.2$ Hz, 3H), 7.42 (t, $J = 7.6$ Hz, 2H), 7.36 (d, $J = 7.4$ Hz, 1H), 7.30 (dd, $J = 9.0, 2.6$ Hz, 1H), 7.27 (d, $J = 2.6$ Hz, 1H), 5.23 (s, 2H), 2.73 (s, 3H). $^{13}\text{C NMR}$ (175 MHz, CDCl_3) δ 157.73, 137.19, 133.57, 133.41, 131.29, 130.71, 128.84, 128.23, 127.79, 126.58, 126.53, 125.78, 124.88, 124.39, 124.38, 122.74, 116.88, 109.52, 70.34, 20.28. **IR** (cm^{-1}): 1600.2, 1492.1, 1447.3, 1382.6, 1363.1, 1305.8, 1228.0, 1181.0, 1020.4, 995.7, 887.6, 827.8, 777.5, 7449, 720.7, 694.1. **HRMS**: Calculated for $\text{C}_{22}\text{H}_{19}\text{O}^+$ ($[\text{M} + \text{H}]^+$): 299.1430 Found: 299.1433.



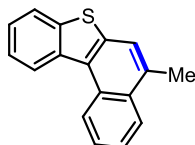
2-methoxy-9-methylphenanthrene (32): The cyclization of **S10** was performed on 0.13 mmol scale with a total reaction time of 12 h. Purification by flash column chromatography eluting with hexanes/EtOAc (19:1) provided 25 mg (86%) of **32** as a white solid. Spectroscopic data matched reported literature data.³⁵ **¹H NMR** (500 MHz, CDCl₃) δ 8.62 (dd, *J* = 8.2, 0.5 Hz, 1H), 8.55 (d, *J* = 9.0 Hz, 1H), 8.02 (dt, *J* = 10.1, 5.0 Hz, 1H), 7.66 – 7.61 (m, 1H), 7.61 – 7.55 (m, 1H), 7.52 (s, 1H), 7.23 (dd, *J* = 9.0, 2.7 Hz, 1H), 7.19 (d, *J* = 2.6 Hz, 1H), 3.96 (s, 1H), 2.73 (d, *J* = 0.6 Hz, 1H). **¹³C NMR** (125 MHz, CDCl₃) δ 158.55, 133.62, 133.40, 131.26, 130.75, 126.59, 126.52, 125.73, 124.88, 124.33, 124.23, 122.72, 116.41, 108.21, 55.60, 20.28.



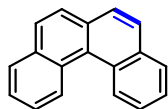
benzo[c]chrysene (33): The cyclization of **S29** was performed on 0.13 mmol scale with a total reaction time of 12 h. Purification by flash column chromatography eluting with hexanes/EtOAc (9:1) provided 35 mg (96%) of **33** as a white solid. Spectroscopic data matched reported literature data.³⁷ **¹H NMR** (400 MHz, CDCl₃) δ 9.07 (t, *J* = 8.3 Hz, 2H), 8.89 – 8.80 (m, 2H), 8.09 – 8.00 (m, 3H), 7.97 (d, *J* = 9.2 Hz, 1H), 7.94 – 7.86 (m, 2H), 7.77 – 7.62 (m, 4H). **¹³C NMR** (125 MHz, CDCl₃) δ 133.85, 131.83, 131.24, 130.77, 130.43, 130.27, 128.74, 128.71, 128.39, 128.27, 127.75, 127.26, 126.87, 126.85, 126.80, 126.64, 126.44, 126.31, 126.16, 123.57, 122.08.



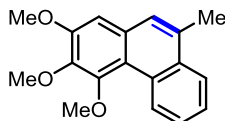
2,4-dimethoxy-9-methylphenanthrene (34): The cyclization of **S12** was performed on 0.13 mmol scale with a total reaction time of 12 h at 50°C. Purification by flash column chromatography eluting with hexanes/EtOAc (9:1) provided 19 mg (57%) of **34** as a white solid. Starting material was not fully consumed in the reaction. **¹H NMR** (700 MHz, CDCl₃) δ 9.61 (d, *J* = 8.6 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.62 (t, *J* = 7.7 Hz, 1H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.50 (s, 1H), 6.85 (s, 1H), 6.74 (s, 1H), 4.10 (d, *J* = 1.5 Hz, 3H), 3.96 (d, *J* = 1.6 Hz, 3H), 2.71 (s, 3H). **¹³C NMR** (176 MHz, CDCl₃) δ 160.03, 158.39, 135.61, 133.85, 131.77, 130.92, 128.11, 127.29, 126.31, 125.07, 124.25, 115.16, 101.04, 98.95, 55.94, 55.58, 20.39. **IR** (cm⁻¹): 1613.2, 1572.0, 1449.7, 1345.8, 1325.2, 1208.3, 1158.8, 1104.8, 1062.2, 1004.8, 890.9, 802.5, 753.4, 717.9, 626.2. **HRMS**: Calculated for C₁₇H₁₇O₂⁺ ([M + H]⁺): 253.1223 Found: 253.1224.



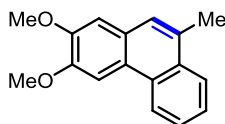
5-methylbenzo[b]naphtho[1,2-d]thiophene (35): The cyclization of **S11** was performed on 0.13 mmol scale with a total reaction time of 4 h at 50 °C and 20 mol% FeCl₃. Purification by flash column chromatography eluting with hexanes/EtOAc (19:1) provided 20 mg (62%) of **35** as a pale yellow solid. **¹H NMR** (500 MHz, CDCl₃) δ 9.05 (d, *J* = 8.5 Hz, 1H), 8.83 (d, *J* = 8.3 Hz, 1H), 8.18 (d, *J* = 8.3 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.79 (s, 1H), 7.75 (t, *J* = 7.6 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.59 (t, *J* = 7.7 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 2.82 (s, 3H). **¹³C NMR** (125 MHz, CDCl₃) δ 139.56, 138.74, 137.08, 134.26, 131.51, 131.03, 128.01, 126.99, 125.67, 125.07, 125.01, 124.99, 124.63, 123.89, 123.42, 121.78, 20.44. **IR** (cm⁻¹): 2920.2, 1594.0, 1510.6, 1461.3, 1373.9, 1235.6, 1211.7, 1163.8, 886.0, 745.4. **HRMS**: calculated for C₁₇H₁₂S [M]⁺: 248.0660 found: 248.0662.



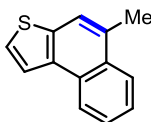
benzo[c]phenanthrene (36): The cyclization of **S7** was performed on 0.14 mmol scale with a total reaction time of 1 h. Purification by flash column chromatography eluting with hexanes/EtOAc (19:1) provided 29 mg (89%) of **36** as a white solid. Spectroscopic data matched reported literature data.³⁸ **¹H NMR** (500 MHz, CDCl₃) δ 9.16 (d, *J* = 8.5 Hz, 2H), 8.04 (d, *J* = 7.9 Hz, 2H), 7.92 (d, *J* = 8.5 Hz, 2H), 7.84 (d, *J* = 8.5 Hz, 2H), 7.72 – 7.68 (m, 2H), 7.64 (m, 2H). **¹³C NMR** (125 MHz, CDCl₃) δ 133.49, 130.97, 130.30, 128.52, 127.89, 127.45, 127.33, 126.83, 126.10, 125.83.



2,3,4-Trimethoxy-9-methylphenanthrene (37): The cyclization of **S13** was performed on 0.13 mmol scale (51 mg) with heating to 50°C for a total reaction time of 12 h. Purification by flash column chromatography eluting with hexanes/EtOAc provided 32 mg (87%) of **37** as a white solid. **¹H NMR** (400 MHz, CDCl₃) δ 9.62 – 9.53 (m, 1H), 8.08 – 7.99 (m, 1H), 7.68 – 7.55 (m, 2H), 7.47 (s, 1H), 7.03 (s, 1H), 4.03 (s, 3H), 4.01 (s, 6H), 2.70 (s, 3H). **¹³C NMR** (175 MHz, CDCl₃) δ 152.70, 152.61, 142.49, 132.52, 131.89, 130.35, 130.28, 127.21, 126.87, 126.56, 125.69, 124.43, 118.31, 104.79, 61.52, 60.47, 56.06, 20.30. **IR** (cm⁻¹): 1598.3, 1493.4, 1449.7, 1399.5, 1356.0, 1248.0, 1140.7, 1089.1, 1000.6, 890.2, 760.1, 750.5, 701.4. **HRMS:** Calculated for C₁₈H₁₉O₃⁺: 283.1329 Found: 283.1329.

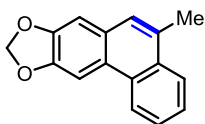


2,3-dimethoxy-9-methylphenanthrene (38): The cyclization of **S14** was performed on 0.13 mmol scale with a total reaction time of 12 h. Purification by flash column chromatography eluting with hexanes/EtOAc (9:1) provided 28 mg (86%) of **38** as a white solid. **¹H NMR** (500 MHz, CDCl₃) δ 8.56 (d, *J* = 7.9 Hz, 1H), 8.07 – 8.01 (m, 1H), 7.99 (s, 1H), 7.67 – 7.61 (m, 1H), 7.61 – 7.56 (m, 1H), 7.50 (s, 1H), 7.18 (s, 1H), 4.11 (s, 3H), 4.04 (s, 3H), 2.72 (s, 3H). **¹³C NMR** (125 MHz, CDCl₃) δ 149.57, 148.98, 131.48, 130.94, 130.10, 127.33, 126.14, 126.06, 125.70, 125.00, 124.25, 122.72, 107.96, 103.53, 56.22, 56.11, 20.11. **IR** (cm⁻¹): 2935.6, 1604.6, 1504.5, 1463.5, 1437.4, 1391.4, 1251.0, 1216.2, 1193.9, 1154.7, 1021.6, 752.1. **HRMS:** calculated for C₁₇H₁₇O₂ ([M + H]⁺): 253.1223, found: 253.1224.

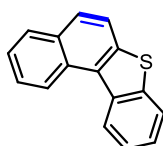


5-methylnaphtho[2,1-b]thiophene (39): The cyclization of **S22** was performed on 0.13 mmol scale with a total reaction time of 12 h 50 °C. Purification by flash column chromatography eluting with hexanes/EtOAc (9:1) provided 13 mg (51%) of **39** as a white solid. Starting material decomposition was observed at elevated reaction temperatures Spectroscopic data matched reported literature data.³⁹ **¹H NMR** (400 MHz, CDCl₃) δ 8.38 – 8.33 (m, 1H), 8.10 – 8.05 (m, 1H), 7.98 – 7.93 (m, 1H), 7.75 (s, 1H), 7.65 – 7.60 (m, 1H), 7.60 – 7.55 (m, 1H), 7.50

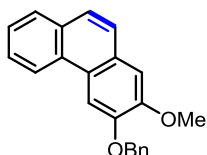
(d, $J = 5.4$ Hz, 1H), 2.77 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 137.48, 135.01, 131.42, 130.71, 129.58, 126.34, 125.36, 125.08, 124.71, 124.29, 122.19, 121.02, 20.25.



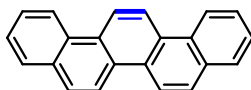
5-methylphenanthro[2,3-d][1,3]dioxole (40): The cyclization of **S16** was performed on 0.13 mmol scale with a total reaction time of 1 h. Purification by flash column chromatography eluting with hexanes/EtOAc (9:1) provided 31 mg (99%) of **40** as a white solid. ^1H NMR (500 MHz, CDCl_3) δ 8.53 – 8.47 (m, 1H), 8.05 – 8.01 (m, 1H), 8.00 (s, 1H), 7.66 – 7.55 (m, 2H), 7.47 (s, 1H), 7.15 (s, 1H), 6.09 (s, 2H), 2.71 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 147.71, 147.68, 131.49, 131.01, 130.40, 128.58, 126.63, 126.13, 125.85, 125.79, 124.92, 122.98, 105.36, 101.39, 101.04, 20.04. IR (cm^{-1}): 2902.5, 1482.0, 1451.9, 1395.9, 1225.8, 1180.6, 1036.5, 938.4, 881.8, 847.4, 758.2, 701.0. HRMS: calculated for $\text{C}_{16}\text{H}_{13}\text{O}_2$ ($[\text{M} + \text{H}]^+$): 237.0910, found: 237.0910.



benzo[b]naphtho[1,2-d]thiophene (41): The cyclization of **S17** was performed on 0.13 mmol scale with a total reaction time of 6 h at 50 °C and 20 mol% FeCl_3 . Purification by flash column chromatography eluting with hexanes/EtOAc (9:1) provided 21 mg (67%) of **41** as a pale yellow solid. Spectroscopic data matched reported literature data.⁴⁰ ^1H NMR (500 MHz, CDCl_3) δ 9.02 (d, $J = 8.5$ Hz, 1H), 8.87 (d, $J = 8.3$ Hz, 1H), 8.03 (dd, $J = 11.6, 8.3$ Hz, 2H), 7.91 (q, $J = 8.7$ Hz, 2H), 7.75 (t, $J = 7.7$ Hz, 1H), 7.63 – 7.58 (m, 2H), 7.51 (t, $J = 7.5$ Hz, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 139.72, 138.60, 136.70, 131.92, 130.64, 129.44, 129.03, 127.84, 127.13, 125.21, 124.89, 124.80, 124.71, 123.20, 123.18, 121.07.

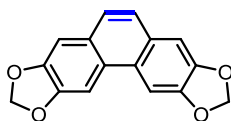


3-(benzyloxy)-2-methoxyphenanthrene (42): The cyclization of **S18** was performed on 0.13 mmol scale with a total reaction time of 12 h. Purification by flash column chromatography eluting with hexanes/EtOAc (9:1) provided 31 mg (75%) of **42** as a white solid. ^1H NMR (500 MHz, CDCl_3) δ 8.54 (d, $J = 8.3$ Hz, 1H), 8.04 (s, $J = 5.3$ Hz, 1H), 7.86 (t, $J = 8.3$ Hz, 1H), 7.62 (m, 2H), 7.56 – 7.50 (m, 1H), 7.43 – 7.37 (m, 1H), 7.33 (dd, $J = 13.5, 6.1$ Hz, 1H), 7.29 (s, 1H), 5.32 (s, 1H), 4.12 (d, $J = 3.6$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 150.05, 148.71, 137.05, 131.60, 129.91, 128.87, 128.85, 128.17, 127.57, 127.26, 126.38, 126.20, 125.80, 125.35, 122.38, 110.86, 103.95, 71.08, 56.34. IR (cm^{-1}): 2930.4, 1602.1, 1506.5, 1467.2, 1379.8, 1265.1, 1216.8, 1156.0, 1012.3, 855.1, 739.8, 695.6. HRMS: calculated for $\text{C}_{22}\text{H}_{19}\text{O}_2$ ($[\text{M} + \text{NH}_4]^+$): 332.1645, found: 332.1644.

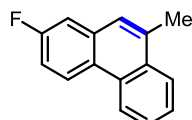


Picene (43): The cyclization of **S32** was performed on 0.13 mmol scale with a total reaction time of 12 h. Purification by preparative thin layer chromatography eluting with hexanes/EtOAc (4:1) provided 19 mg (53%) of **43** as a pale brown solid. Picene **43** is very insoluble in organic solvents. Spectroscopic data matched

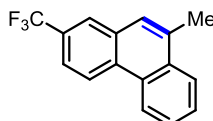
reported literature data.⁴¹ $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.97 (s, 2H), 8.87 (d, $J = 8.4$ Hz, 2H), 8.80 (d, $J = 9.2$ Hz, 2H), 8.03 (t, $J = 9.0$ Hz, 3H), 7.75 (t, $J = 7.1$ Hz, 2H), 7.67 (t, $J = 7.3$ Hz, 3H).



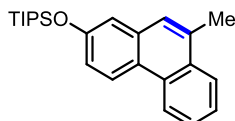
phenanthro[2,3-d:6,7-d']bis([1,3]dioxole) (44): The cyclization of **S19** was performed on 0.11 mmol scale with a total reaction time of 12 h. Purification by flash column chromatography eluting with hexanes/EtOAc (9:1) provided 20 mg (68%) of **44** as a white solid. Spectroscopic data matched reported literature data.⁴² $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.79 (s, 1H), 7.50 (s, 1H), 7.18 (s, 1H), 6.08 (s, 2H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 148.17, 147.20, 127.96, 126.56, 124.99, 105.70, 101.43, 100.66.



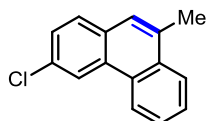
2-fluoro-9-methylphenanthrene (45): The cyclization of **S20** was performed on 0.14 mmol scale with a total reaction time of 12 h. Purification by flash column chromatography eluting with hexanes/EtOAc (9:1) provided 26 mg (87%) of **45** as a white solid. Spectroscopic data matched reported literature data.³⁵ $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.62 (dd, $J = 14.5, 6.7$ Hz, 1H), 8.06 (d, $J = 8.1$ Hz, 1H), 7.66 (qd, $J = 13.6, 6.9$ Hz, 1H), 7.55 – 7.48 (m, 1H), 7.49 – 7.39 (m, 1H), 7.32 (tt, $J = 16.1, 8.1$ Hz, 1H), 2.74 (s, 2H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 161.63 (d, $J = 245.8$ Hz), 134.25, 133.62 (d, $J = 8.7$ Hz), 131.75, 130.38, 126.55, 126.48, 126.20 (d, $J = 3.6$ Hz), 125.02, 125.0 (d, $J = 8.7$), 123.02, 114.87 (d, $J = 23.7$ Hz), 112.03 (d, $J = 20.3$ Hz), 20.27.



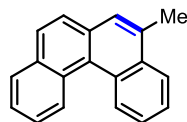
9-methyl-2-(trifluoromethyl)phenanthrene (46): The cyclization of **S21** was performed on 0.13 mmol scale with a total reaction time of 12 h. Purification by flash column chromatography eluting with hexanes/EtOAc (12:1) provided 31 mg (93%) of **46** as a white solid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.73 (m, 3H), 8.13 – 8.06 (m, 2H), 7.78 (dd, $J = 8.7, 1.4$ Hz, 1H), 7.75 – 7.68 (m, 2H), 7.63 (s, 1H), 2.76 (s, 3H). $^{13}\text{C NMR}$ (175 MHz, CDCl_3) δ 134.22, 132.74, 131.67, 131.29, 129.62, 128.32 (q, $J = 32.2$ Hz), 127.61, 126.76, 126.43, 125.07 (q, $J = 4.2$ Hz), 124.85, 124.45 (q, $J = 271.3$), 123.40, 123.31, 121.60 (q, $J = 3.2$ Hz). **IR** (cm^{-1}): 2923.3, 1361.7, 1331.8, 1279.8, 1200.6, 1165.7, 1114.1, 1075.8, 906.2, 825.4, 754.8, 723.6, 706.0. **HRMS:** Calculated for $\text{C}_{16}\text{H}_{11}\text{F}_3^+$ ($[\text{M}]^+$): 260.0813 found: 260.0813.



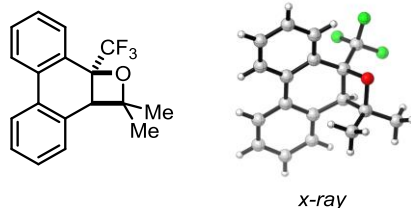
triisopropyl((9-methylphenanthren-2-yl)oxy)silane (47): The cyclization of **S15** was performed on 0.13 mmol scale with a total reaction time of 6 h at 50 °C. Purification by flash column chromatography eluting with hexanes/EtOAc (19:1) provided 15 mg (65% brsm) of **47** as a white solid and 10 mg of recovered **S15** (75% conv). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.61 (d, $J = 8.2$ Hz, 1H), 8.51 (d, $J = 8.9$ Hz, 1H), 8.01 (d, $J = 8.0$ Hz, 1H), 7.63 (t, $J = 7.5$ Hz, 1H), 7.57 (t, $J = 7.5$ Hz, 1H), 7.23 (d, $J = 2.3$ Hz, 1H), 7.19 (dd, $J = 8.8, 2.4$ Hz, 1H), 2.71 (s, 3H), 1.33 (h, $J = 7.4$ Hz, 3H), 1.15 (d, $J = 7.5$ Hz, 18H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 155.01, 133.68, 133.10, 131.34, 130.75, 126.48, 125.75, 124.86, 124.49, 124.15, 122.75, 120.49, 116.19, 20.26, 18.21, 12.98. **IR** (cm^{-1}): 2943.0, 2866.7, 1611.6, 1491.8, 1462.6, 1450.2, 1308.0, 1251.9, 1175.7, 967.9, 884.1, 858.6, 737.8. **HRMS:** Calculated for $\text{C}_{24}\text{H}_{32}\text{OSi}^+$ ($[\text{M}]^+$): 364.2222 found: 364.2230.



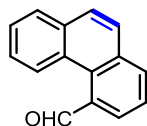
3-chloro-9-methylphenanthrene (48): The cyclization of **S23** was performed on 0.13 mmol scale with a total reaction time of 12 h. Purification by flash column chromatography eluting with hexanes/EtOAc (9:1) provided 24 mg (92%) of **48** as a white solid. $^1\text{H NMR}$ (700 MHz, CDCl_3) δ 8.65 – 8.62 (m, 1H), 8.61 (d, $J = 1.5$ Hz, 1H), 8.08 – 8.04 (m, 1H), 7.74 (d, $J = 8.4$ Hz, 1H), 7.70 – 7.65 (m, 2H), 7.55 (s, 1H), 7.51 (dd, $J = 8.4, 2.0$ Hz, 1H), 2.73 (s, 3H). $^{13}\text{C NMR}$ (176 MHz, CDCl_3) δ 133.16, 132.50, 131.93, 130.97, 130.48, 129.62, 129.41, 127.37, 127.28, 126.73, 126.24, 124.96, 123.27, 122.41, 20.24. **IR** (cm^{-1}): 1750.7, 1594.9, 1491.1, 1445.6, 1429.2, 1410.0, 1371.0, 1214.3, 1160.8, 1093.6, 1065.2, 1019.4, 944.8, 870.6, 803.9, 743.7, 715.7, 684.1. **HRMS**: calculated for $\text{C}_{15}\text{H}_{11}\text{Cl}$ $[\text{M}]^+$: 226.0549 found: 226.0546.



5-methylbenzo[c]phenanthrene (49): The cyclization of **S24** was performed on 0.12 mmol scale with a total reaction time of 12 h at 50 °C. Purification by flash column chromatography eluting with hexanes/EtOAc (9:1) provided 14 mg (48%) of **49** as a yellow solid. Spectroscopic data matched reported literature data.³⁵ $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 9.14 (d, $J = 8.3$ Hz, 1H), 9.08 (d, $J = 8.5$ Hz, 1H), 8.19 (d, $J = 7.6$ Hz, 1H), 8.01 (d, $J = 7.9$ Hz, 1H), 7.88 (d, $J = 8.5$ Hz, 1H), 7.77 (d, $J = 8.5$ Hz, 1H), 7.73 – 7.64 (m, 4H), 7.60 (t, $J = 7.4$ Hz, 1H), 2.82 (s, 3H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 133.45, 133.28, 130.99, 130.67, 130.43, 128.74, 128.60, 128.07, 127.70, 127.33, 126.66, 126.56, 126.29, 126.01, 125.86, 125.65, 124.64, 19.98.

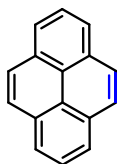


(2aR,10bS)-2,2-dimethyl-10b-(trifluoromethyl)-2a,10b-dihydro-2H-phenanthro[9,10-b]oxete (6): The cyclization of **S31** was performed on 0.13 mmol scale in PhMe with a total reaction time of 4 h. Purification by preparative thin layer chromatography eluting with hexanes/EtOAc (9:1) provided 17.8 mg (45%) of **6** as a white solid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.97 (dd, $J = 7.9, 2.3$ Hz, 2H), 7.65 (d, $J = 7.8$ Hz, 1H), 7.48 (t, $J = 7.0$ Hz, 1H), 7.37 (t, $J = 7.9$ Hz, 2H), 7.29 (d, $J = 7.4$ Hz, 1H), 7.03 (d, $J = 7.3$ Hz, 1H), 4.34 (s, 1H), 1.66 (s, 3H), 1.02 (s, 3H). $^{13}\text{C NMR}$ (175 MHz, CDCl_3) δ 132.78, 131.92, 130.34, 130.24, 129.72, 129.09, 128.93, 128.89, 128.68, 128.67, 123.71, 123.51, 88.47, 46.43, 30.76, 24.98. **IR** (cm^{-1}): 2924.2, 2851.2, 1449.9, 1303.9, 1259.8, 1227.9, 1154.4, 1019.4, 974.2, 940.1, 844.2, 774.4, 757.7, 738.5, 731.0. Unable to observe the trifluoromethyl quartet after 3000 scans. **HRMS**: calculated for $\text{C}_{17}\text{H}_{14}$ $[\text{M}]^+$: 304.1075 found: 304.1080.

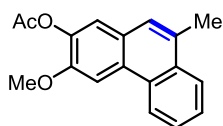


phenanthrene-4-carbaldehyde (50): The cyclization of **S26** was performed on 0.13 mmol scale with a total reaction time of 12 h. Purification by flash column chromatography eluting with hexanes/EtOAc (9:1) provided 27 mg (90%) of **50** as a pale yellow solid. Spectroscopic data matched reported literature data.⁴⁰ $^1\text{H NMR}$ (500

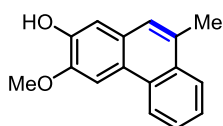
MHz, CDCl₃) δ 10.69 (s, 1H), 8.14 – 8.07 (m, 3H), 8.00 (d, J = 7.1 Hz, 1H), 7.86 (d, J = 8.8 Hz, 1H), 7.81 (d, J = 8.8 Hz, 1H), 7.75 – 7.68 (m, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 193.33, 135.53, 133.73, 133.46, 133.39, 130.68, 129.33, 128.87, 128.47, 128.20, 127.83, 127.03, 126.81, 126.33.



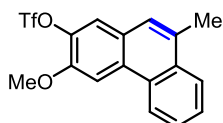
pyrene (51): The cyclization of **S37** was performed on 0.13 mmol scale with a total reaction time of 30 minutes. Purification by flash column chromatography eluting with hexanes/EtOAc provided 18 mg (70%) of **51** as an off-white solid. Spectroscopic data matched reported literature data.⁴⁴ ¹H NMR (700 MHz, CDCl₃): δ 8.19 (d, J = 7.5 Hz, 2H), 8.09 (s, 2H), 8.02 (t, J = 7.5 Hz, 1H). ¹³C NMR (176 MHz, CDCl₃): δ 131.34, 127.61, 126.08, 125.16, 124.87.



3-methoxy-9-methylphenanthren-2-yl acetate (52): The cyclization of **S34** was performed on 0.13 mmol scale with a total reaction time of 4 h. Purification by flash column chromatography eluting with hexanes/EtOAc (9:1) provided 33 mg (90%) of **52** as a pale yellow solid. ¹H NMR (500 MHz, CDCl₃) δ 8.62 – 8.57 (m, 1H), 8.08 (s, 1H), 8.07 – 8.03 (m, 1H), 7.67 – 7.62 (m, 2H), 7.47 (s, 2H), 4.06 (s, 3H), 2.71 (s, 3H), 2.40 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 169.42, 150.19, 140.31, 132.33, 131.22, 129.87, 128.82, 126.80, 126.68, 126.22, 126.05, 125.06, 123.16, 121.00, 104.54, 56.26, 20.99, 20.10. IR (cm⁻¹): 2938.3, 1761.7, 1620.9, 1607.1, 1503.6, 1463.4, 1440.0, 1366.9, 1254.9, 1211.1, 1195.4, 1135.2, 1027.7, 908.7, 754.2, 734.2, 624.9. HRMS: calculated for C₁₈H₁₇O₃ ([M + H]⁺): 281.1172, found: 281.1172.

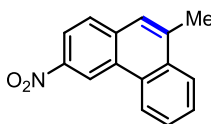


3-methoxy-9-methylphenanthren-2-ol (53): The cyclization of **S27** was performed on 0.13 mmol scale with a total reaction time of 12 h. Purification by flash column chromatography eluting with hexanes/EtOAc (9:1) provided 24 mg (78%) of **53** as a white solid. ¹H NMR (500 MHz, CDCl₃) δ 8.54 (d, J = 8.1 Hz, 1H), 8.03 (d, J = 8.1 Hz, 1H), 7.98 (s, 1H), 7.62 (t, J = 7.6 Hz, 1H), 7.58 (t, J = 7.4 Hz, 1H), 7.46 (s, 1H), 7.28 (s, 1H), 5.90 (s, 1H), 4.12 (s, 3H), 2.71 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 146.81, 145.95, 131.42, 131.04, 130.24, 127.87, 126.14, 126.03, 125.62, 125.04, 124.04, 122.58, 111.05, 102.79, 56.25, 20.12. IR (cm⁻¹): 3396.0, 2932.2, 1529.5, 1503.2, 1438.0, 1246.4, 1216.6, 1157.6, 1029.4, 840.1, 750.0. HRMS: calculated for C₁₆H₁₅O₂ ([M + H]⁺): 239.1067, found: 239.1064.

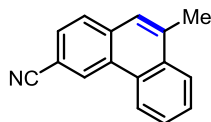


3-methoxy-9-methylphenanthren-2-yl trifluoromethanesulfonate (54): The cyclization of **S35** was performed on 0.13 mmol scale with a total reaction time of 2 h. Purification by flash column chromatography eluting with hexanes/EtOAc (10:1) provided 42 mg (87%) of **54** as a pale yellow solid ¹H NMR (500 MHz,

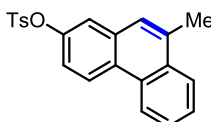
cdcl₃) δ 8.60 – 8.56 (m, 1H), 8.11 (s, 1H), 8.08 – 8.02 (m, 1H), 7.71 – 7.66 (m, 2H), 7.64 (m, 1H), 7.48 (s, 1H), 4.12 (s, 3H), 2.71 (s, 3H). ¹³C NMR (125 MHz, cdcl₃) δ 149.40, 138.68, 132.45, 132.10, 129.92, 129.11, 127.26, 126.39, 126.13, 125.48, 124.95, 123.10, 120.66, 118.82 (q, J = 318.8), 105.13, 56.29, 19.84. **IR** (cm⁻¹): 2930.0, 1622.4, 1506.0, 1418.7, 1246.1, 1201.3, 1139.0, 1101.3, 1026.3, 968.0, 862.4, 755.5. **HRMS**: Calculated for C₁₇H₁₃O₄F₃S⁺ ([M]⁺): 370.0487 found: 370.0486.



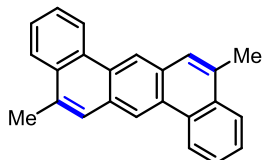
9-methyl-3-nitrophenanthrene (55): The cyclization of **S28** was performed on 0.13 mmol scale with a total reaction time of 12 h. Purification by flash column chromatography eluting with hexanes/EtOAc (9:1) provided 26 mg (93%) of **55** as a pale yellow solid. ¹H NMR (500 MHz, CDCl₃) δ 9.54 (s, 1H), 8.76 (d, J = 7.5 Hz, 1H), 8.34 (dd, J = 8.7, 2.2 Hz, 1H), 8.12 (d, J = 7.5 Hz, 1H), 7.89 (d, J = 8.7 Hz, 1H), 7.76 (pd, J = 7.0, 1.5 Hz, 2H), 7.64 (s, 1H), 2.79 (s, J = 0.7 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 145.64, 137.86, 135.93, 132.55, 130.53, 129.40, 129.05, 128.17, 127.75, 125.99, 125.29, 123.49, 120.72, 119.26, 20.57. **IR** (cm⁻¹): 3085.7, 1609.8, 1503.9, 1333.3, 1302.0, 1100.1, 889.2, 872.3, 750.0, 741.9, 710.4. **HRMS**: Calculated for C₁₅H₁₁NO₂⁺ ([M]⁺): 237.0790 found: 237.0786.



9-methylphenanthrene-2-carbonitrile (56): The cyclization of **S30** was performed on a 0.13 mmol scale with a total reaction time of 25 h. Purification by flash column chromatography eluting with hexanes/EtOAc provided 25 mg (90%) of **56** as a white solid. ¹H NMR (700 MHz, CDCl₃) δ 8.72 (d, J = 8.0 Hz, 2H), 8.16 (s, 1H), 8.11 (dd, J = 7.1, 1.9 Hz, 1H), 7.80 – 7.70 (m, 3H), 7.59 (s, 1H), 2.77 (s, 3H). ¹³C NMR (176 MHz, CDCl₃) δ 135.17, 133.26, 133.05, 132.41, 131.66, 129.58, 128.44, 127.46, 127.28, 125.90, 125.19, 123.80, 123.79, 119.55, 110.03, 20.32. ¹³C NMR (176 MHz, CDCl₃) δ 135.17, 133.26, 133.05, 132.41, 131.66, 129.58, 128.44, 127.46, 127.28, 125.90, 125.19, 123.80, 123.79, 119.55, 110.03, 20.32. **IR** (cm⁻¹): 2225.4, 1487.6, 1438.5, 1407.9, 1245.7, 1212.6, 1155.9, 892.0, 860.3, 825.1, 775.7, 751.3, 717.9, 622.7, 606.9. **HRMS**: calculated for C₁₆H₁₁N ([M+H]⁺): 218.0964 Found: 218.0960.



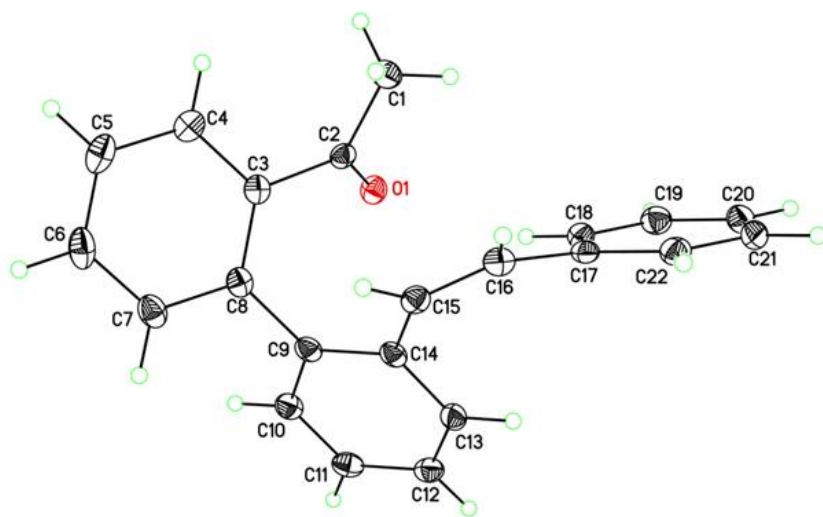
9-methylphenanthren-2-yl 4-methylbenzenesulfonate (57): The cyclization of **S36** was performed on 0.13 mmol scale with a total reaction time of 4 h. Purification by flash column chromatography eluting with hexanes/EtOAc (9:1) provided 45 mg (96%) of **57** as a white solid. ¹H NMR (500 MHz, CDCl₃) δ 8.64 – 8.57 (m, 1H), 8.53 (d, J = 9.0 Hz, 1H), 8.07 – 8.01 (m, 1H), 7.74 (d, J = 8.1 Hz, 2H), 7.69 – 7.62 (m, 2H), 7.45 (d, J = 2.2 Hz, 2H), 7.29 (d, J = 8.3 Hz, 2H), 7.18 (dd, J = 9.0, 2.3 Hz, 1H), 2.71 (s, 3H), 2.44 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 148.20, 145.53, 134.28, 132.91, 132.63, 132.21, 130.00, 129.96, 128.78, 128.49, 127.13, 126.89, 126.28, 125.00, 124.46, 123.24, 120.41, 120.33, 21.92, 20.23. **IR** (cm⁻¹): 3065.9, 2925.3, 1611.2, 1597.2, 1491.1, 1448.8, 1368.6, 1189.6, 1177.0, 1091.5, 947.4, 829.6, 737.2. **HRMS**: calculated for C₂₂H₂₂O₃NS⁺ ([M + NH₄]⁺): 380.1315 found: 380.1312.



5,12-dimethylbenzo[k]tetraphene (59): The cyclization of **58** was performed on 0.075 mmol scale with a total reaction time of 4 h and 10 mol% FeCl₃. Purification by flash column chromatography eluting with hexanes/EtOAc (9:1) provided 21 mg (90%) of **59** as a pale yellow solid. **¹H NMR** (700 MHz, CDCl₃) δ 9.03 (s, 2H), 8.89 (d, *J* = 7.9 Hz, 2H), 8.08 (d, *J* = 7.9 Hz, 2H), 7.79 (s, 2H), 7.73 (t, *J* = 7.4 Hz, 2H), 7.69 (t, *J* = 6.6 Hz, 2H), 2.78 (s, 6H). **¹³C NMR** (125 MHz, CDCl₃) δ 132.55, 132.49, 130.59, 130.56, 129.04, 127.40, 127.10, 126.62, 124.97, 123.39, 121.31, 20.46. **IR** (cm⁻¹): 2920.0, 1628.1, 1438.4, 1273.5, 1028.7, 897.9, 859.4, 755.5, 700.5. **HRMS:** Calculated for C₂₄H₁₈⁺ ([M]⁺): 306.1409 found: 306.1401.

7. X-Ray Crystallographic Data

Structure Determination of (Z)-1-(2'-styryl-[1,1'-biphenyl]-2-yl)ethan-1-one (9)



(CCDC 1505968)

Colorless block-like crystals of (Z)-1-(2'-styryl-[1,1'-biphenyl]-2-yl)ethan-1-one were grown from a hexane/ethyl acetate solution of the compound at 22 deg. C. A crystal of dimensions 0.16 x 0.16 x 0.14 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode ($\lambda = 1.54187$ Å) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 2028 images were collected with an oscillation width of 1.0° in ω . The exposure times were 1 sec. for the low angle images, 5 sec. for high angle. The integration of the data yielded a total of 12297 reflections to a maximum 2θ value of 136.43° of which 2831 were independent and 2729 were greater than $2\sigma(I)$. The final cell constants (Table 1) were based on the xyz centroids 5758 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection; the data were processed with CrystalClear 2.0 and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2014/6) software package, using the space group $P1\bar{1}$ with $Z = 2$ for the formula $C_{22}H_{18}O$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. Full matrix least-squares refinement based on F^2 converged at $R1 = 0.0446$ and $wR2 = 0.1039$ [based on $I > 2\sigma(I)$], $R1 = 0.0454$ and $wR2 = 0.1045$ for all data. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.

Sheldrick, G.M. SHELXTL, v. 2014/6; Bruker Analytical X-ray, Madison, WI, 2014.

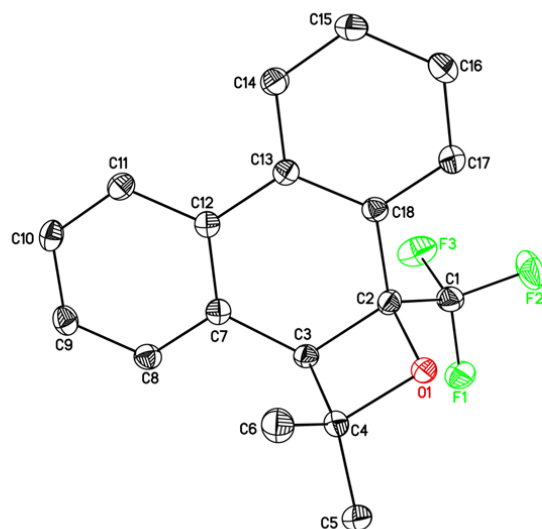
CrystalClear Expert 2.0 r16, Rigaku Americas and Rigaku Corporation (2014), Rigaku Americas, 9009, TX, USA 77381-5209, Rigaku Tokyo, 196-8666, Japan.

Crystal data and structure refinement for (Z)-1-(2'-styryl-[1,1'-biphenyl]-2-yl)ethan-1-one

Identification code	(Z)-1-(2'-styryl-[1,1'-biphenyl]-2-yl)ethan-1-one
Empirical formula	$C_{22}H_{18}O$
Formula weight	298.36
Temperature	85(2) K

Wavelength 1.54178 Å
Crystal system, space group Triclinic, P-1
Unit cell dimensions a = 7.85230(10) Å alpha = 77.261(5) deg.
b = 9.3906(2) Å beta = 84.541(6) deg.
c = 11.5779(8) Å gamma = 71.939(5) deg.
Volume 791.35(6) Å³
Z, Calculated density 2, 1.252 Mg/m³
Absorption coefficient 0.580 mm⁻¹
F(000) 316
Crystal size 0.160 x 0.160 x 0.140 mm
Theta range for data collection 3.916 to 68.215 deg.
Limiting indices -9<=h<=9, -11<=k<=11, -13<=l<=13
Reflections collected / unique 12297 / 2831 [R(int) = 0.0465]
Completeness to theta = 67.679 97.8 %
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 0.925 and 0.843
Refinement method Full-matrix least-squares on F²
Data / restraints / parameters 2831 / 0 / 210
Goodness-of-fit on F² 1.122
Final R indices [I>2sigma(I)] R1 = 0.0446, wR2 = 0.1039
R indices (all data) R1 = 0.0454, wR2 = 0.1045
Extinction coefficient 0.077(3)
Largest diff. peak and hole 0.239 and -0.296 e.Å⁻³

Structure Determination of 2,2-dimethyl-10b-(trifluoromethyl)-2a,10b-dihydro-2H-phenanthro[9,10-b]oxete (6)



(CCDC 1505967)

Colorless plates of 2,2-dimethyl-10b-(trifluoromethyl)-2a,10b-dihydro-2H-phenanthro[9,10-b]oxete were grown from a dichloromethane solution of the compound at 22 deg. C. A crystal of dimensions 0.17 x 0.12 x 0.04 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode ($\lambda = 1.54187$ Å) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 2028 images were collected with an oscillation width of 1.0° in ω . The exposure times were 1 sec. for the low angle images, 4 sec. for high angle. Rigaku d*trek images were exported to CrysAlisPro for processing and corrected for absorption. The integration of the data yielded a total of 21527 reflections to a maximum 2θ value of 138.38° of which 2617 were independent and 2584 were greater than $2\sigma(I)$. The final cell constants (Table 1) were based on the xyz centroids 17451 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection; the data were processed with CrystalClear 2.0 and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2014/6) software package, using the space group P2(1)/n with $Z = 4$ for the formula $C_{18}H_{15}OF_3$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. Full matrix least-squares refinement based on F^2 converged at $R1 = 0.0478$ and $wR2 = 0.1172$ [based on $I > 2\sigma(I)$], $R1 = 0.0480$ and $wR2 = 0.1175$ for all data. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.

Sheldrick, G.M. SHELXTL, v. 2014/6; Bruker Analytical X-ray, Madison, WI, 2014.

CrystalClear Expert 2.0 r16, Rigaku Americas and Rigaku Corporation (2014), Rigaku Americas, 9009, TX, USA 77381-5209, Rigaku Tokyo, 196-8666, Japan.

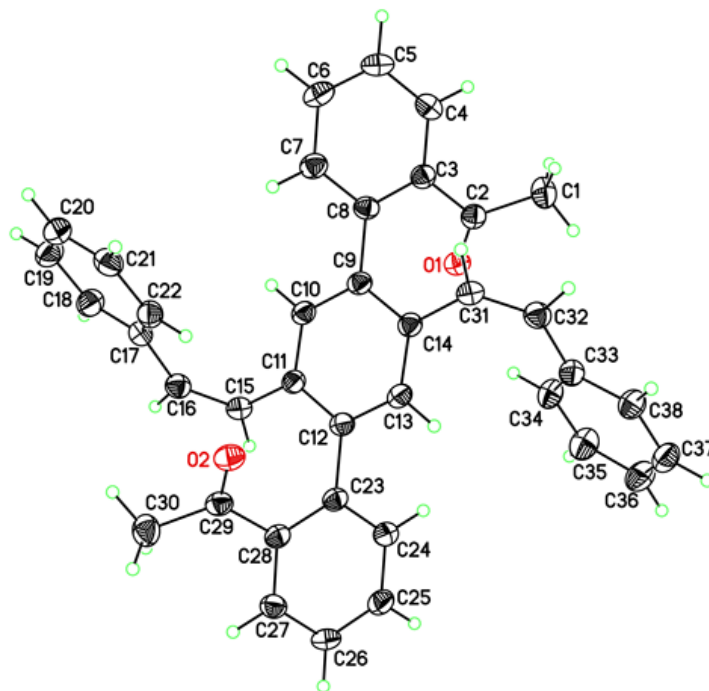
CrysAlisPro 1.171.38.41 (Rigaku Oxford Diffraction, 2015).

Crystal data and structure refinement for **2,2-dimethyl-10b-(trifluoromethyl)-2a,10b-dihydro-2H-phenanthro[9,10-b]oxete**

Identification code **2,2-dimethyl-10b-(trifluoromethyl)-2a,10b-dihydro-2H-phenanthro[9,10-b]oxete**

Empirical formula C18 H15 F3 O
Formula weight 304.30
Temperature 85(2) K
Wavelength 1.54184 Å
Crystal system, space group Monoclinic, P2(1)/n
Unit cell dimensions a = 7.88370(10) Å alpha = 90 deg.
b = 12.60220(10) Å beta = 95.2380(10) deg.
c = 14.49740(10) Å gamma = 90 deg.
Volume 1434.33(2) Å³
Z, Calculated density 4, 1.409 Mg/m³
Absorption coefficient 0.955 mm⁻¹
F(000) 632
Crystal size 0.170 x 0.120 x 0.040 mm
Theta range for data collection 4.658 to 69.189 deg.
Limiting indices -9<=h<=9, -15<=k<=15, -17<=l<=17
Reflections collected / unique 21527 / 2617 [R(int) = 0.0536]
Completeness to theta = 67.684 98.2 %
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 1.00000 and 0.91522
Refinement method Full-matrix least-squares on F²
Data / restraints / parameters 2617 / 0 / 202
Goodness-of-fit on F² 1.136
Final R indices [I>2sigma(I)] R1 = 0.0478, wR2 = 0.1172
R indices (all data) R1 = 0.0480, wR2 = 0.1175
Extinction coefficient 0.0278(14)
Largest diff. peak and hole 0.326 and -0.401 e.Å⁻³

Structure Determination for 1,1'-(2',5'-di((Z)-styryl)-[1,1':4',1''-terphenyl]-2,2''-diyl)bis(ethan-1-one)



(CCDC 1530039)

Colorless block-like crystals of 1,1'-(2',5'-di((Z)-styryl)-[1,1':4',1''-terphenyl]-2,2''-diyl)bis(ethan-1-one) were grown from a dichloromethane/hexane solution of the compound at 22 deg. C. A crystal of dimensions 0.21 x 0.11 x 0.10 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode ($\lambda = 1.54187$ Å) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 2028 images were collected with an oscillation width of 1.0° in ω . The exposure times were 1 sec. for the low angle images, 5 sec. for high angle. Rigaku d*trek images were exported to CrysAlisPro for processing and corrected for absorption. The integration of the data yielded a total of 41858 reflections to a maximum 2θ value of 138.66° of which 5089 were independent and 4803 were greater than $2\sigma(I)$. The final cell constants (Table 1) were based on the xyz centroids 21176 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection. The structure was solved and refined with the Bruker SHELXTL (version 2014/6) software package, using the space group P2(1)/n with $Z = 4$ for the formula $C_{38}H_{30}O_2$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. Full matrix least-squares refinement based on F^2 converged at $R1 = 0.0597$ and $wR2 = 0.1647$ [based on $I > 2\sigma(I)$], $R1 = 0.0615$ and $wR2 = 0.1673$ for all data. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.

Sheldrick, G.M. SHELXTL, v. 2014/6; Bruker Analytical X-ray, Madison, WI, 2014.

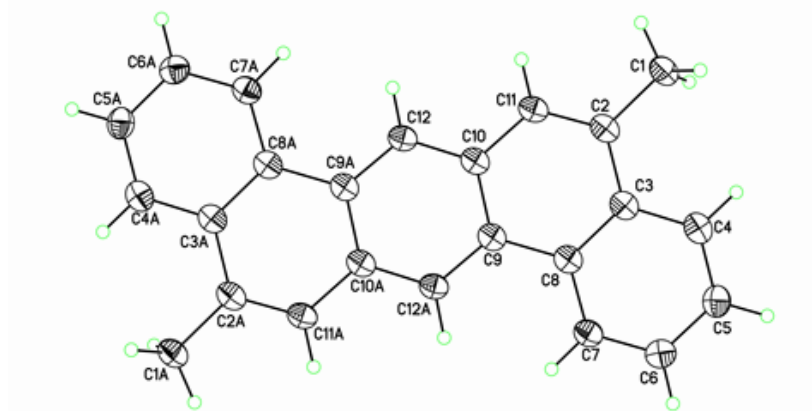
CrystalClear Expert 2.0 r16, Rigaku Americas and Rigaku Corporation (2014), Rigaku Americas, 9009, TX, USA 77381-5209, Rigaku Tokyo, 196-8666, Japan.

CrysAlisPro 1.171.38.41 (Rigaku Oxford Diffraction, 2015).

Crystal data and structure refinement for **1,1'-(2',5'-di((Z)-styryl)-[1,1':4',1''-terphenyl]-2,2''-diyl)bis(ethan-1-one)**

Identification code	1,1'-(2',5'-di((Z)-styryl)-[1,1':4',1''-terphenyl]-2,2''-diyl)bis(ethan-1-one)
Empirical formula	C ₃₈ H ₃₀ O ₂
Formula weight	518.62
Temperature	85(2) K
Wavelength	1.54184 Å
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 10.62617(10) Å alpha = 90 deg. b = 19.11003(16) Å beta = 90.5435(8) deg. c = 13.49063(11) Å gamma = 90 deg.
Volume	2739.37(4) Å ³
Z, Calculated density	4, 1.257 Mg/m ³
Absorption coefficient	0.590 mm ⁻¹
F(000)	1096
Crystal size	0.210 x 0.110 x 0.100 mm
Theta range for data collection	4.011 to 69.330 deg.
Limiting indices	-12<=h<=12, -23<=k<=22, -16<=l<=16
Reflections collected / unique	41858 / 5089 [R(int) = 0.0539]
Completeness to theta = 67.684	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.84698
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5089 / 0 / 364
Goodness-of-fit on F ²	1.035
Final R indices [I>2sigma(I)]	R1 = 0.0597, wR2 = 0.1647
R indices (all data)	R1 = 0.0615, wR2 = 0.1673
Extinction coefficient	0.0013(3)
Largest diff. peak and hole	0.581 and -0.346 e.Å ⁻³

Structure Determination for 5,12-dimethylbenzo[k]tetraphene



(CCDC 1530358)

Yellow plates of **5,12-dimethylbenzo[k]tetraphene** were grown from a dichloromethane/hexane solution of the compound at 22 deg. C. A crystal of dimensions 0.17 x 0.11 x 0.11 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode ($\lambda = 1.54187$ Å) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 2028 images were collected with an oscillation width of 1.0° in ω . The exposure times were 1 sec. for the low angle images, 4 sec. for high angle. Rigaku d*trek images were exported to CrysAlisPro for processing and corrected for absorption. The integration of the data yielded a total of 22025 reflections to a maximum 2θ value of 138.26° of which 1452 were independent and 1420 were greater than $2\sigma(I)$. The final cell constants (Table 1) were based on the xyz centroids 14219 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection. The structure was solved and refined with the Bruker SHELXTL (version 2014/6) software package, using the space group *Pbca* with $Z = 4$ for the formula $C_{24}H_{18}$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. The molecule lies on an inversion center of the crystal lattice. Full matrix least-squares refinement based on F^2 converged at $R1 = 0.0399$ and $wR2 = 0.0975$ [based on $I > 2\sigma(I)$], $R1 = 0.0404$ and $wR2 = 0.0979$ for all data. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.

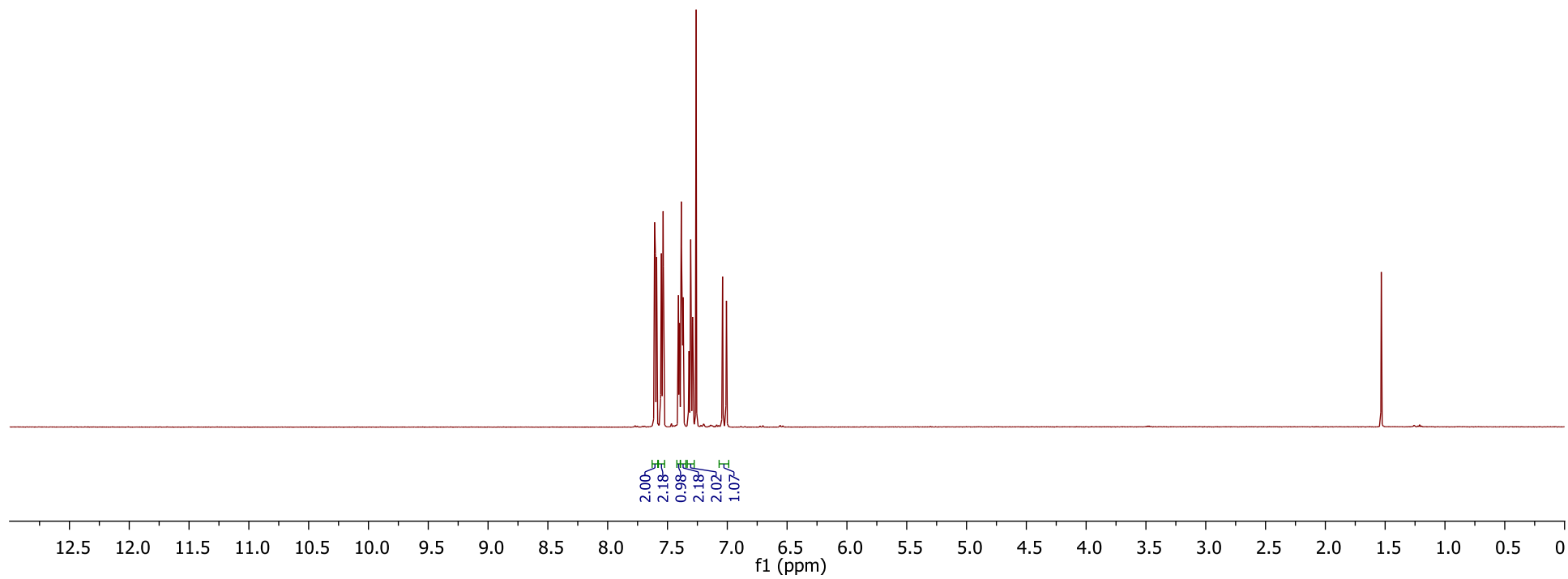
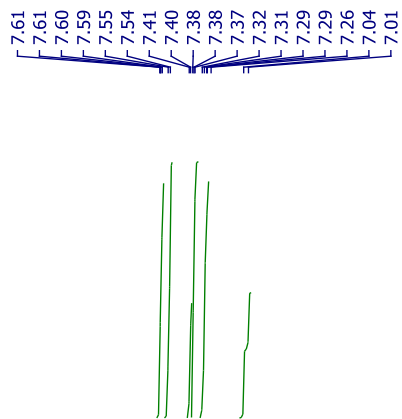
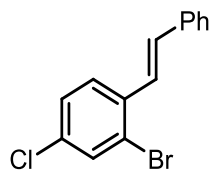
Sheldrick, G.M. SHELXTL, v. 2014/6; Bruker Analytical X-ray, Madison, WI, 2014.

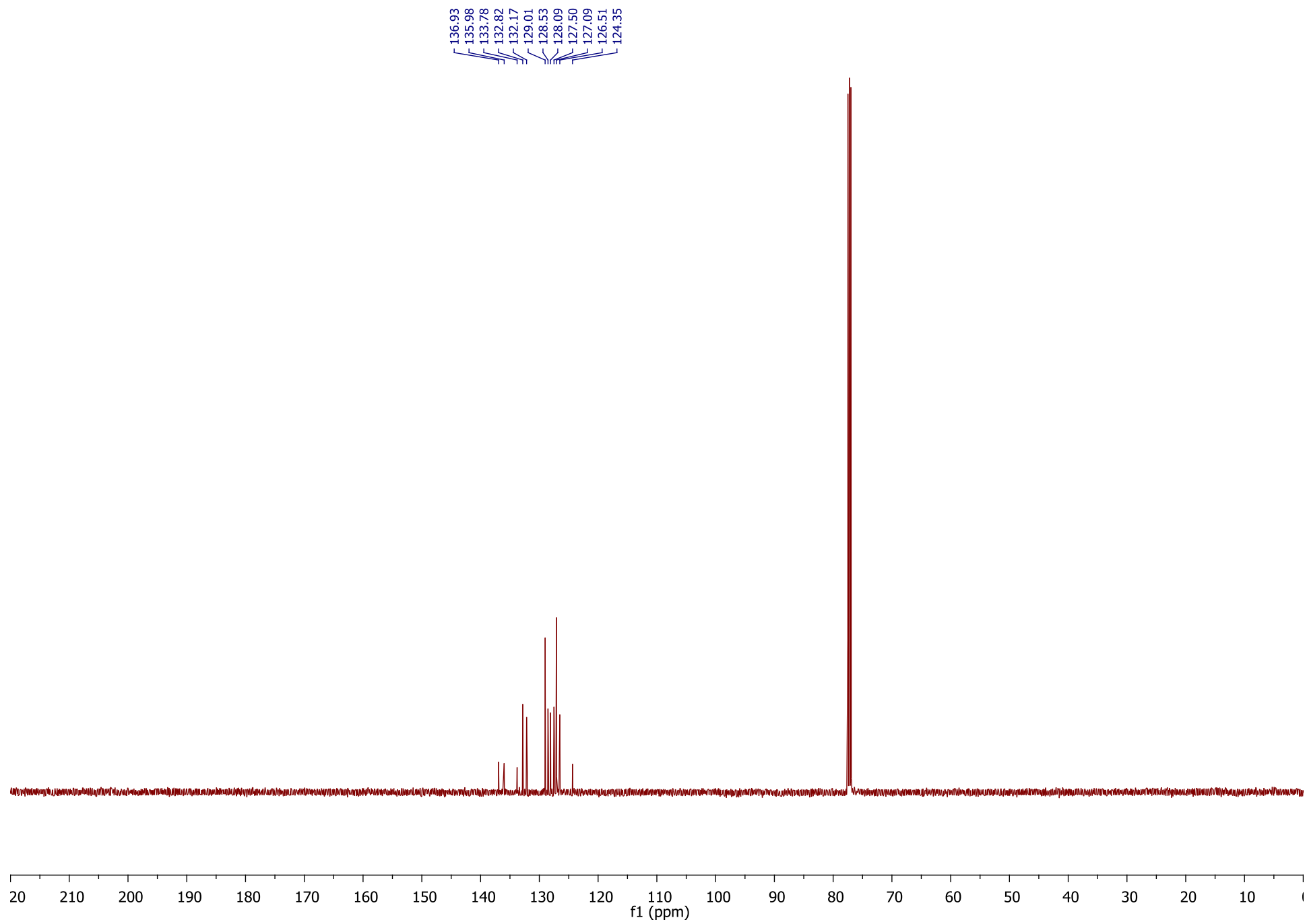
CrystalClear Expert 2.0 r16, Rigaku Americas and Rigaku Corporation (2014), Rigaku Americas, 9009, TX, USA 77381-5209, Rigaku Tokyo, 196-8666, Japan.

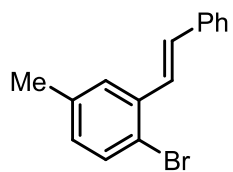
Crystal data and structure refinement for **5,12-dimethylbenzo[k]tetrathene**

Identification code	ccm530
Empirical formula	C ₂₄ H ₁₈
Formula weight	306.38
Temperature	85(2) K
Wavelength	1.54184 Å
Crystal system, space group	Orthorhombic, Pbc _a
Unit cell dimensions	a = 13.92565(12) Å alpha = 90 deg. b = 6.76441(5) Å beta = 90 deg. c = 16.55751(12) Å gamma = 90 deg.
Volume	1559.70(2) Å ³
Z, Calculated density	4, 1.305 Mg/m ³
Absorption coefficient	0.556 mm ⁻¹
F(000)	648
Crystal size	0.170 x 0.110 x 0.110 mm
Theta range for data collection	5.343 to 69.132 deg.
Limiting indices	-16 ≤ h ≤ 16, -8 ≤ k ≤ 8, -20 ≤ l ≤ 20
Reflections collected / unique	22025 / 1452 [R(int) = 0.0537]
Completeness to theta = 67.684	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.88200
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	1452 / 0 / 111
Goodness-of-fit on F ²	1.122
Final R indices [I > 2σ(I)]	R1 = 0.0399, wR2 = 0.0975
R indices (all data)	R1 = 0.0404, wR2 = 0.0979
Extinction coefficient	0.0197(14)
Largest diff. peak and hole	0.226 and -0.285 e.Å ⁻³

8. ^1H NMR and ^{13}C NMR

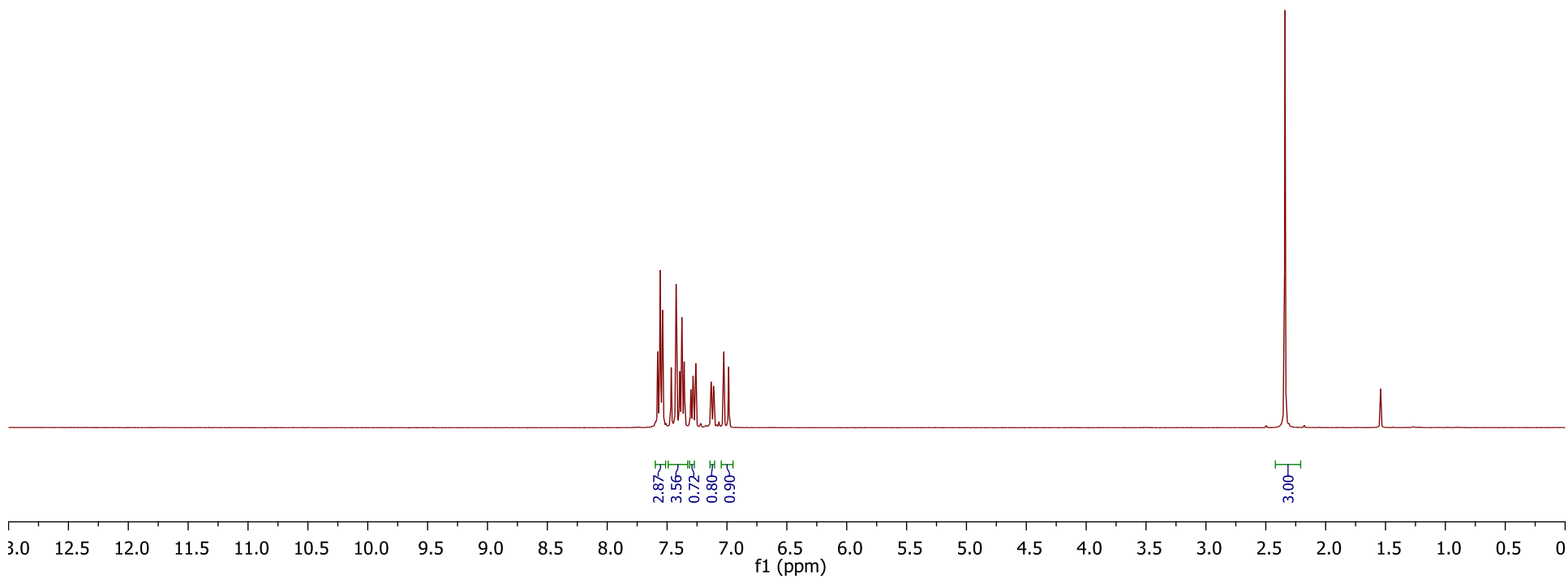


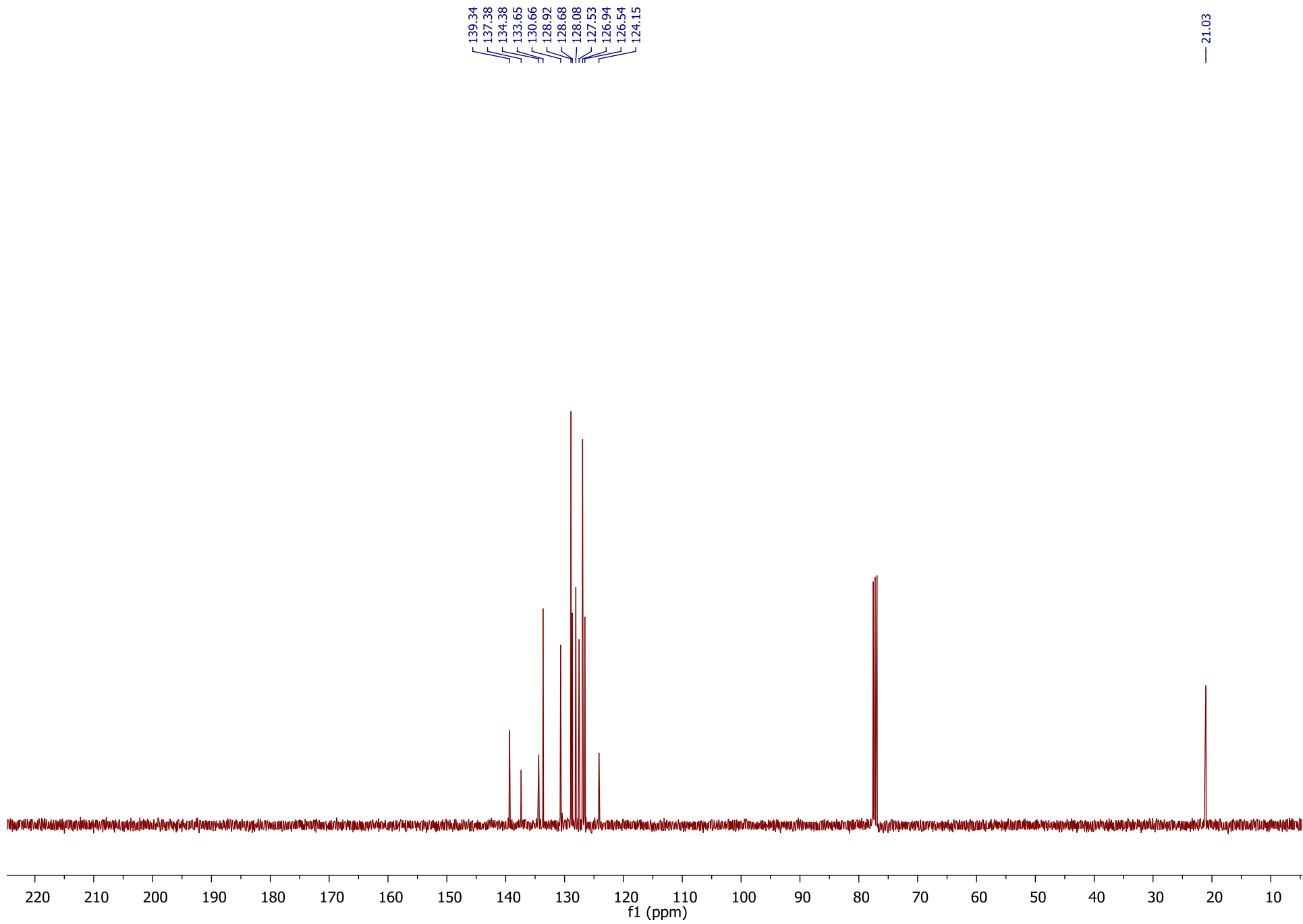


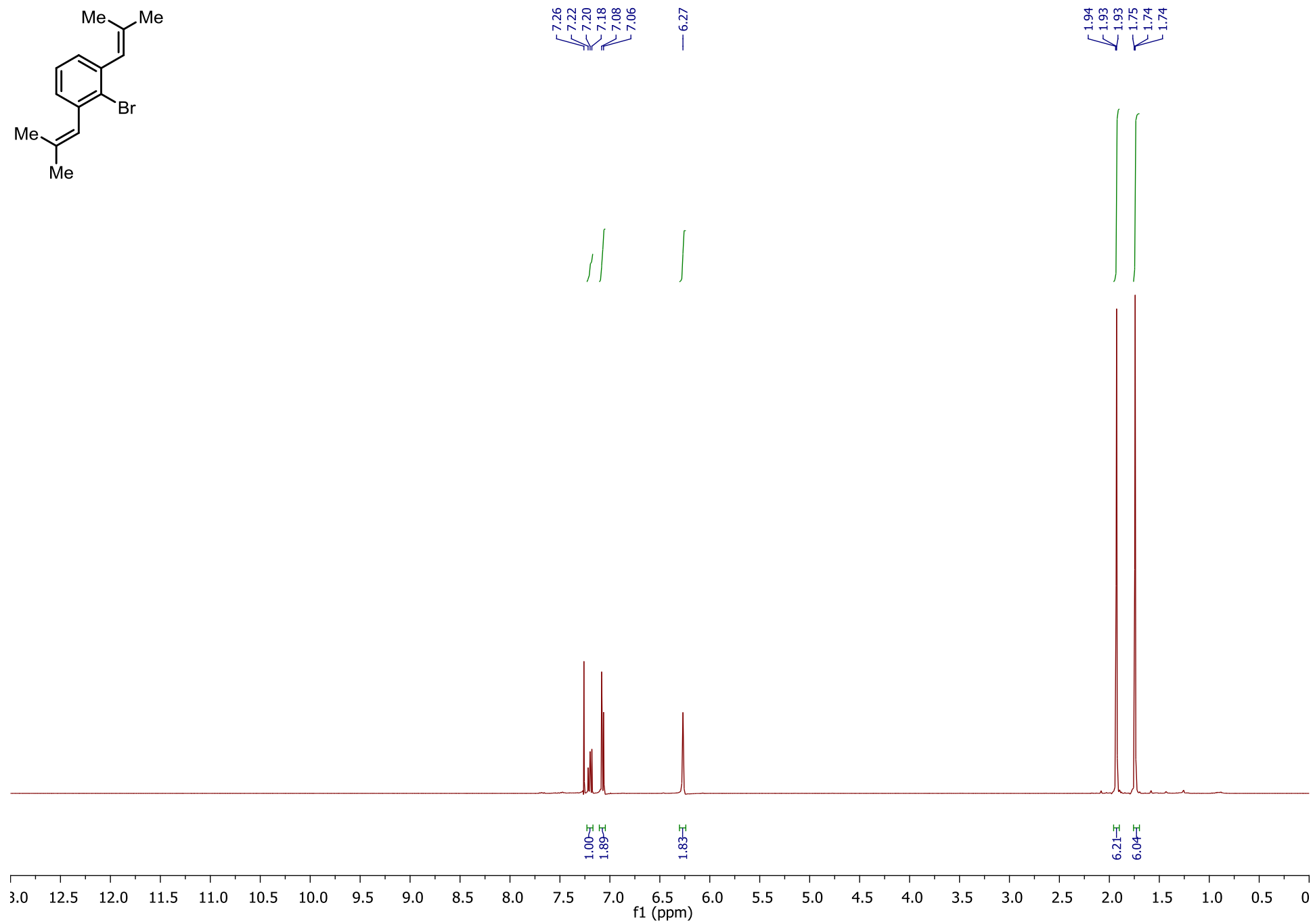
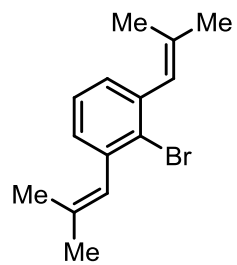


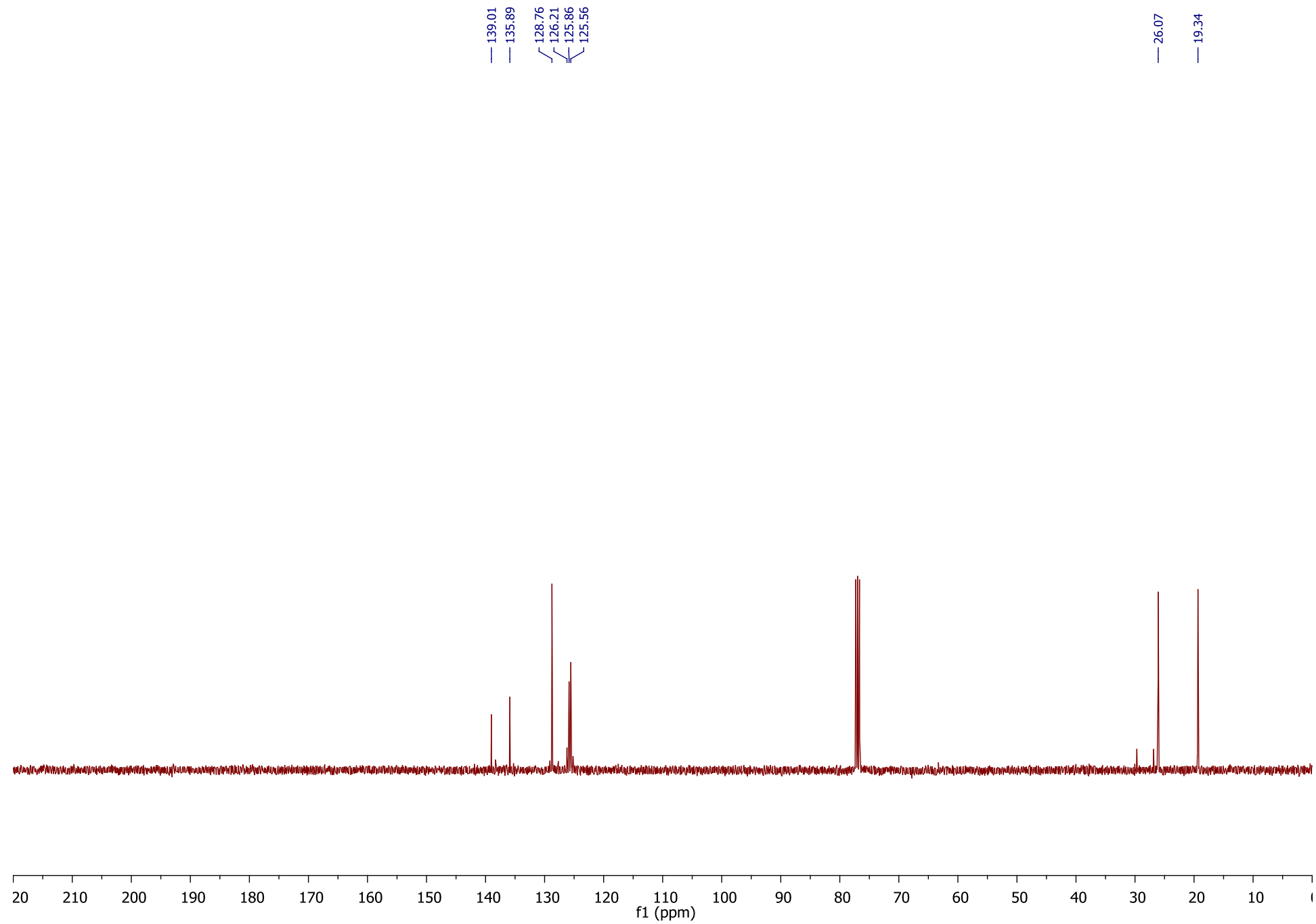
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7.54
7.47
7.42
7.39
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7.36
7.30
7.28
7.26
7.13
7.11
7.03
6.99

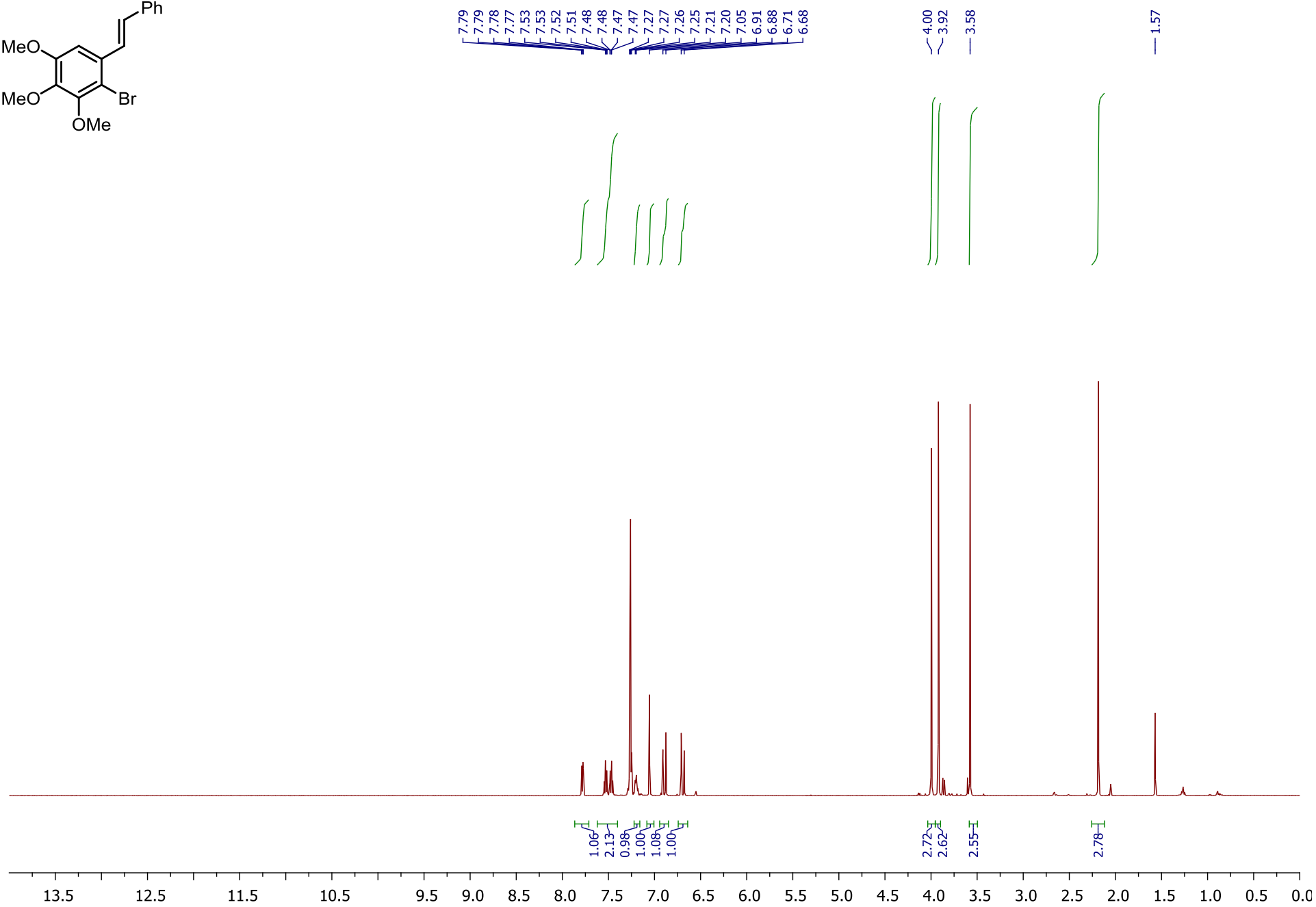
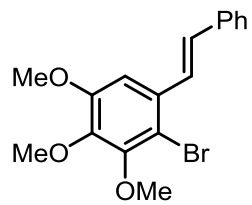
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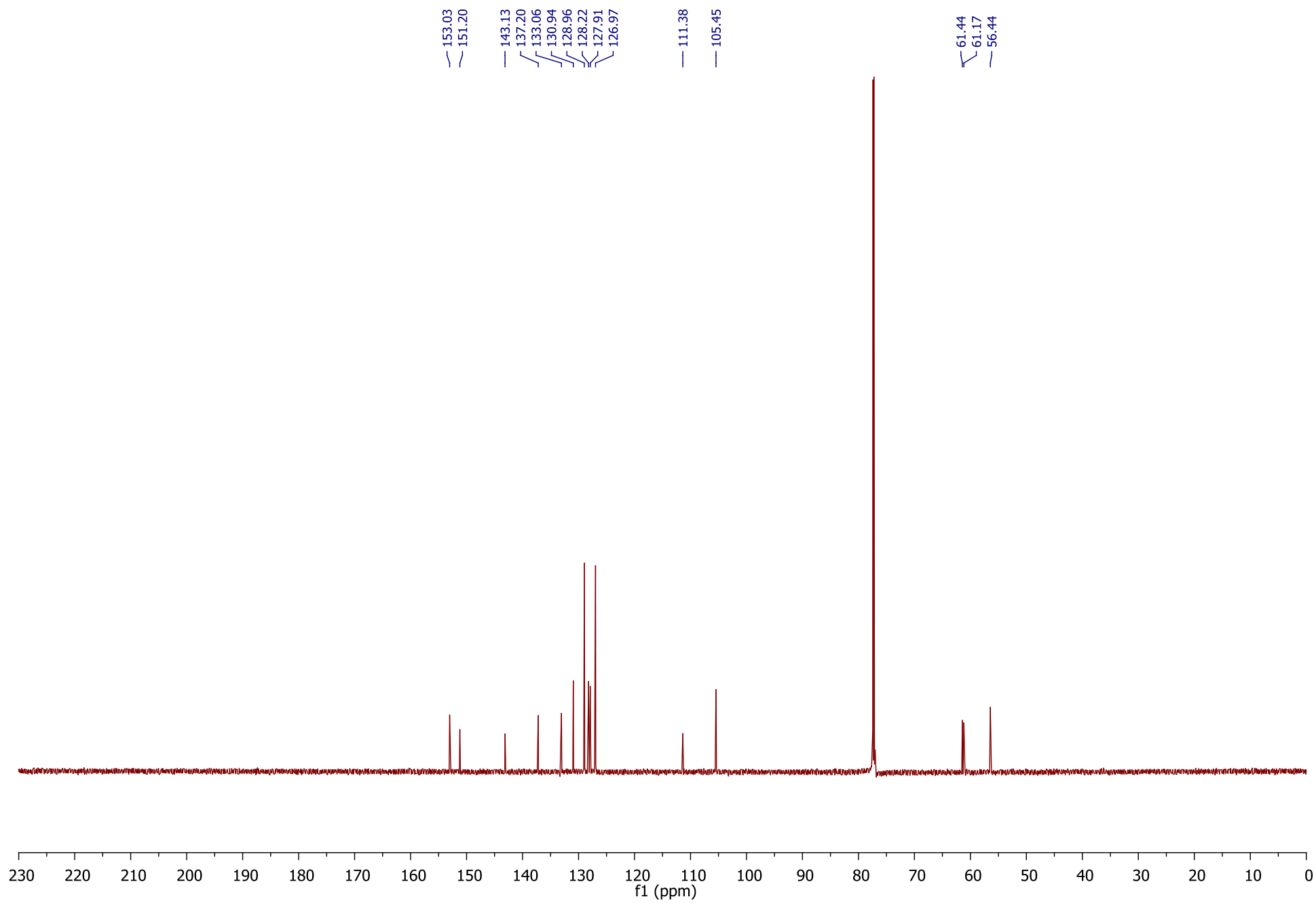


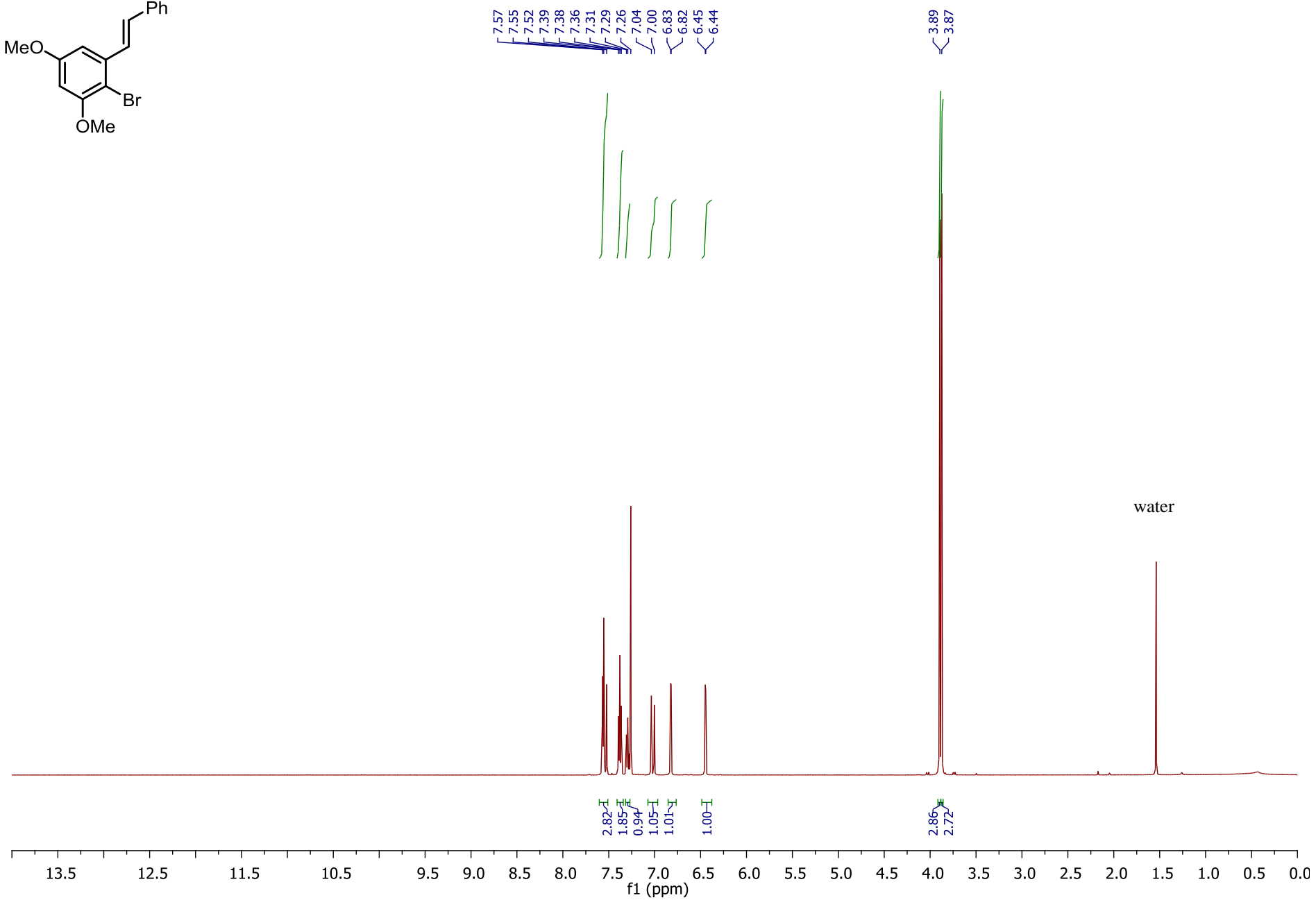
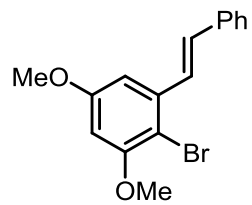


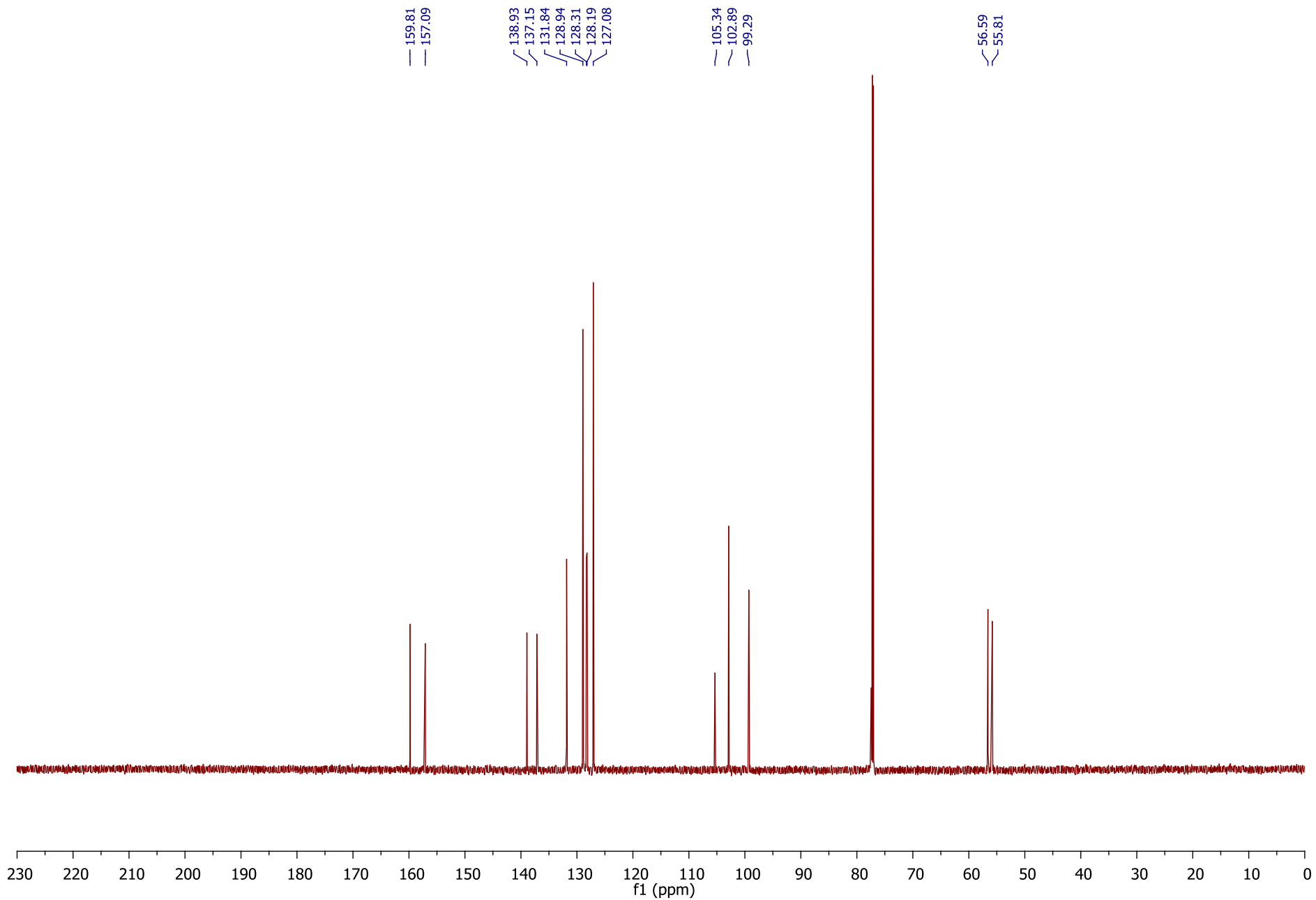


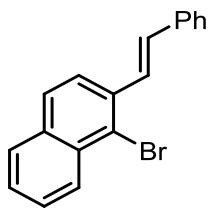




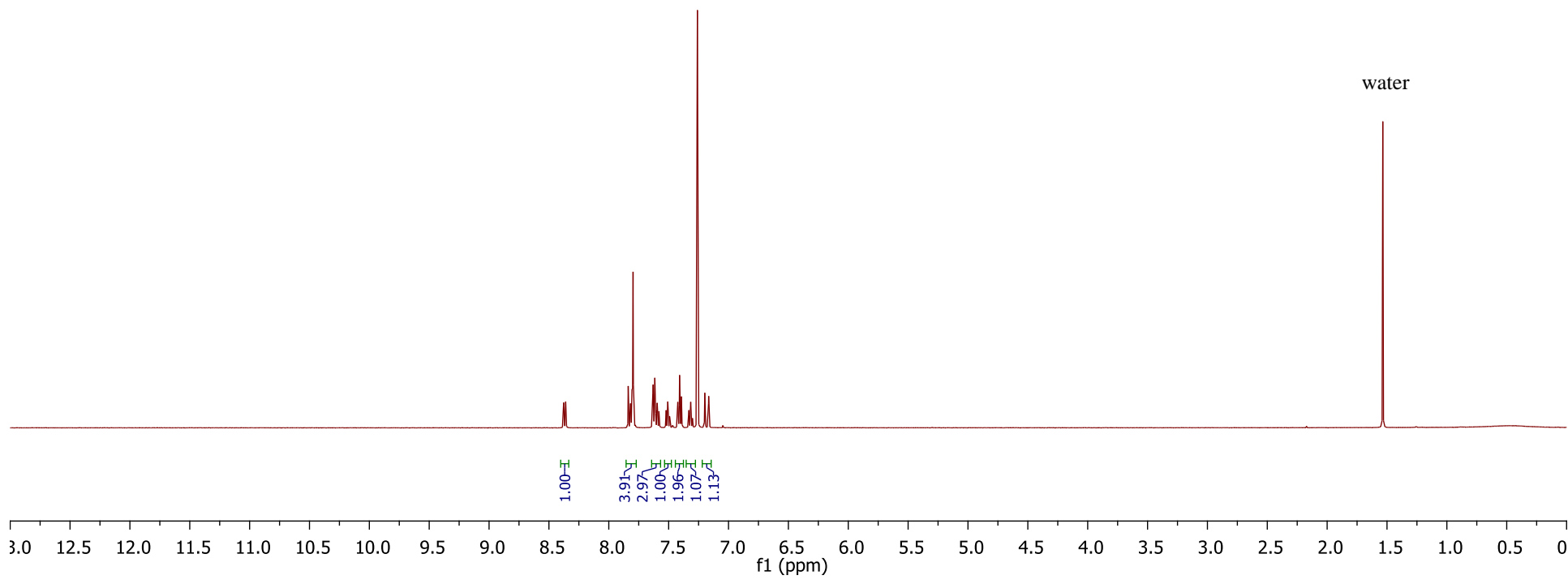


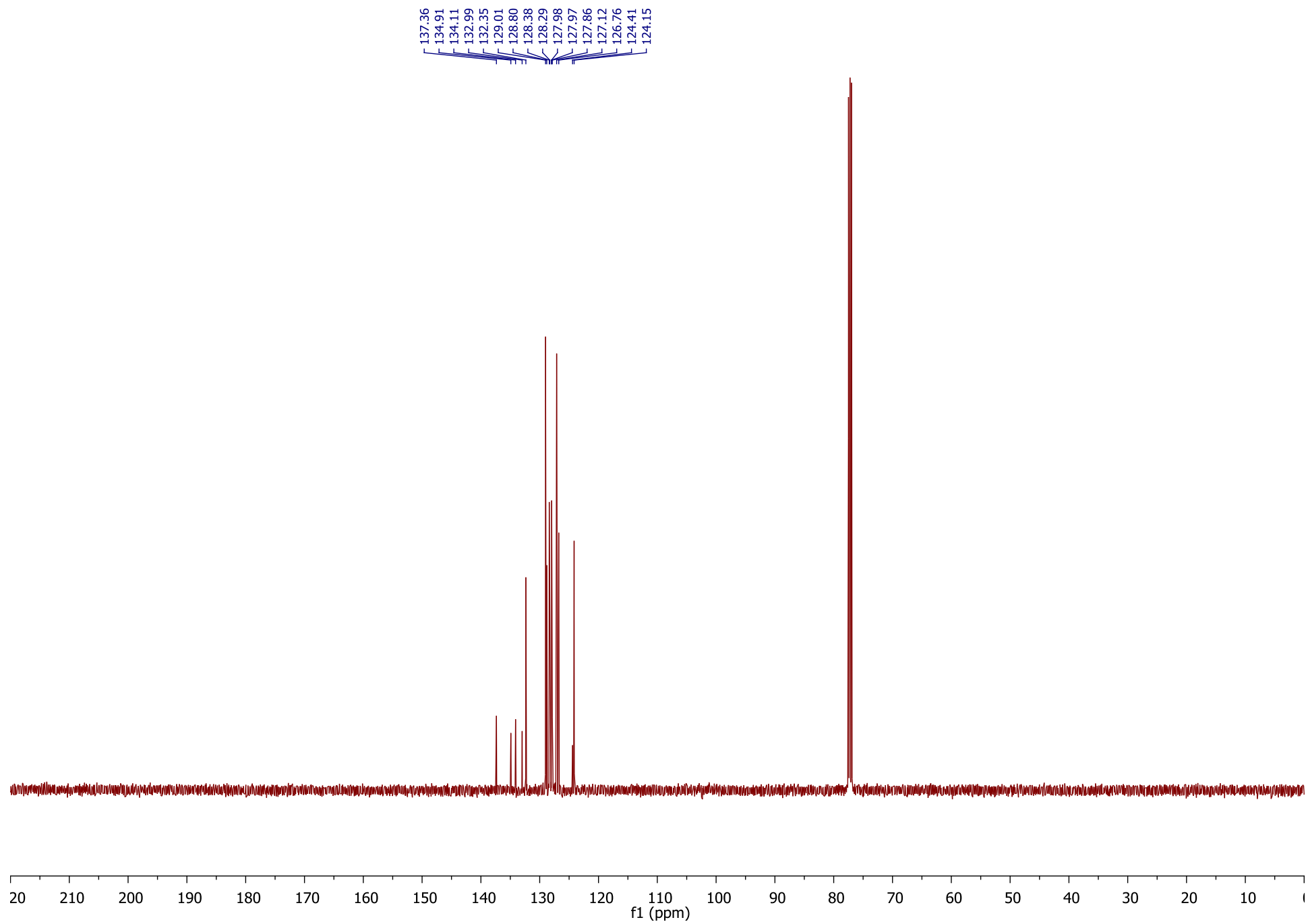


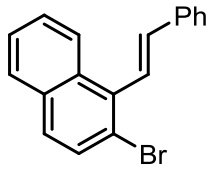




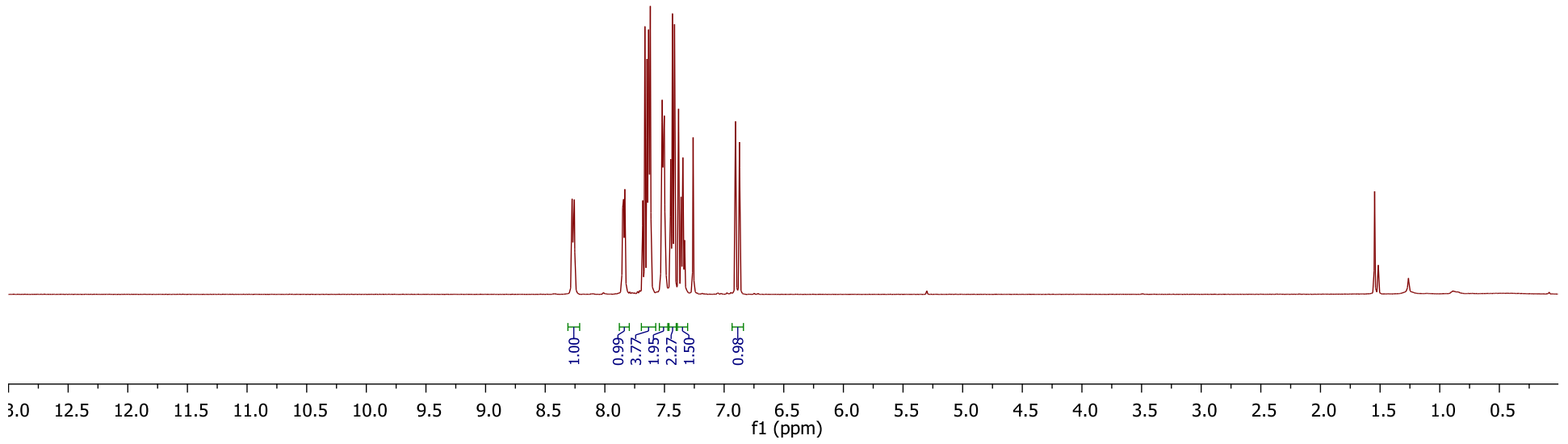
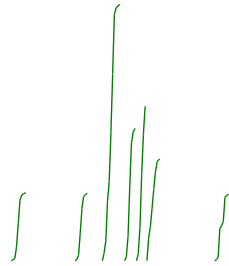
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7.62
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7.60
7.58
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7.41
7.39
7.33
7.32
7.26
7.20
7.17



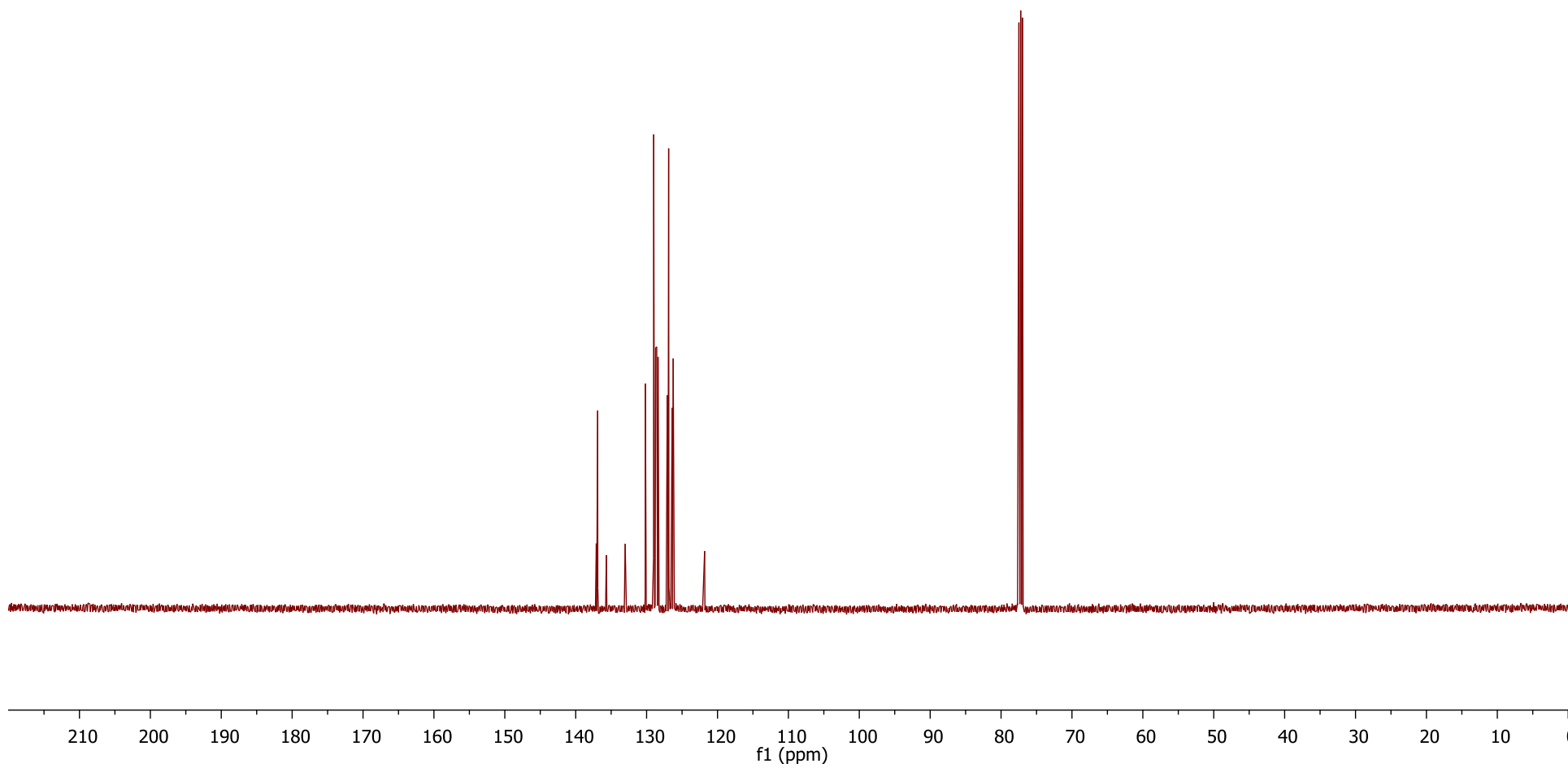


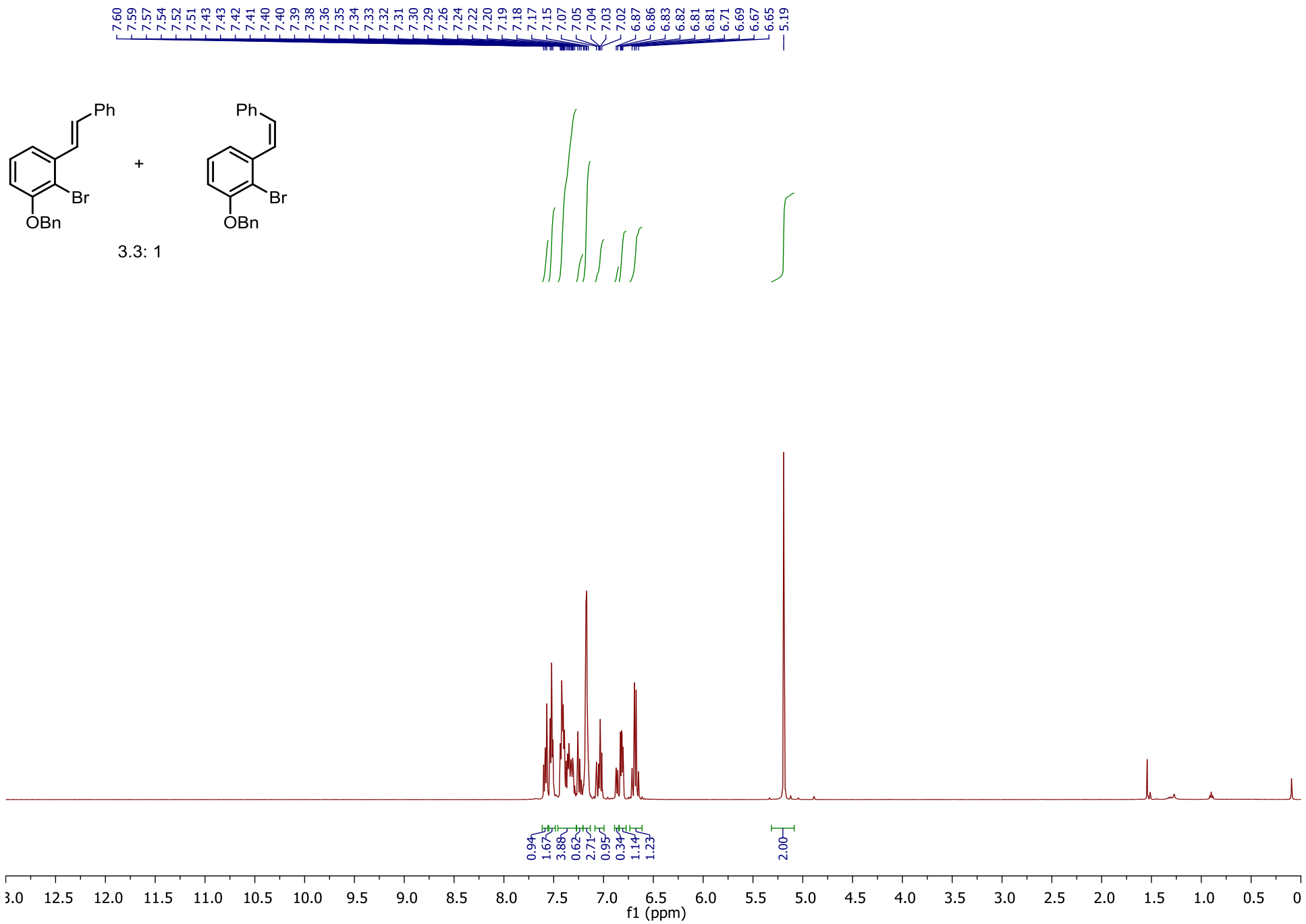


8.27
8.26
8.26
7.66
7.65
7.63
7.62
7.43
6.96
6.87



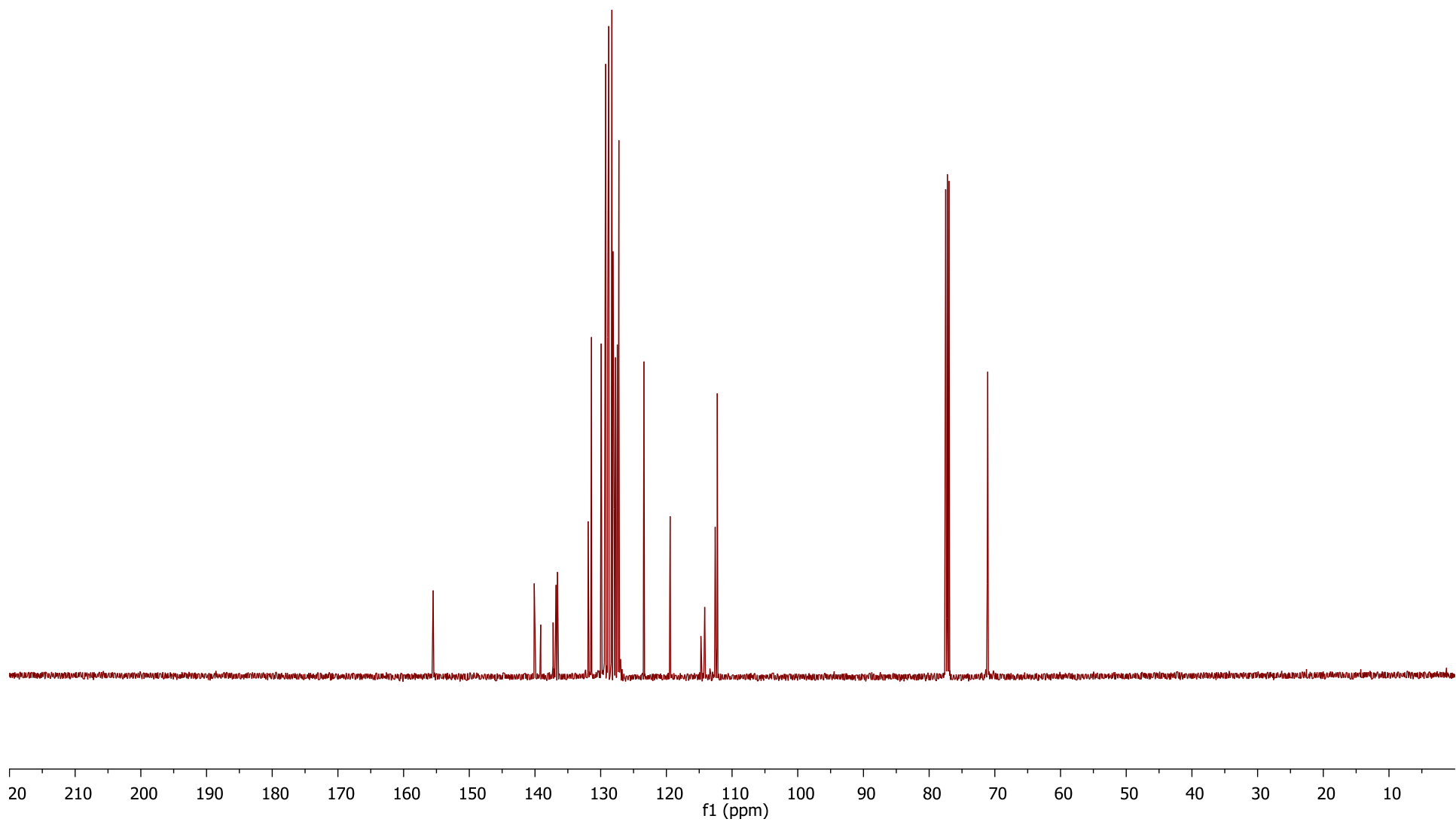
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136.90
135.67
133.07
133.02
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129.00
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128.39
127.08
126.89
126.39
126.25
126.17
121.82

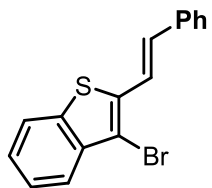




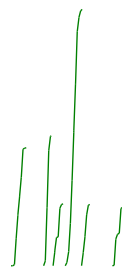
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139.13
137.25
136.80
136.78
136.58
131.91
131.40
129.93
129.25
128.93
128.78
128.29
128.26
128.12
128.05
127.95
127.73
127.46
127.23
127.19
127.07
123.42
119.43
114.74
114.17
112.57
112.25

71.16
71.08

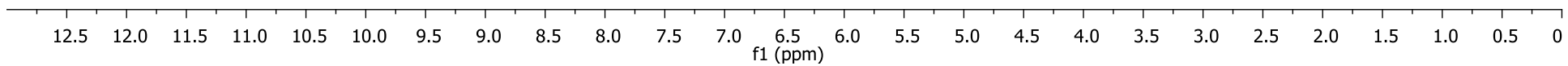


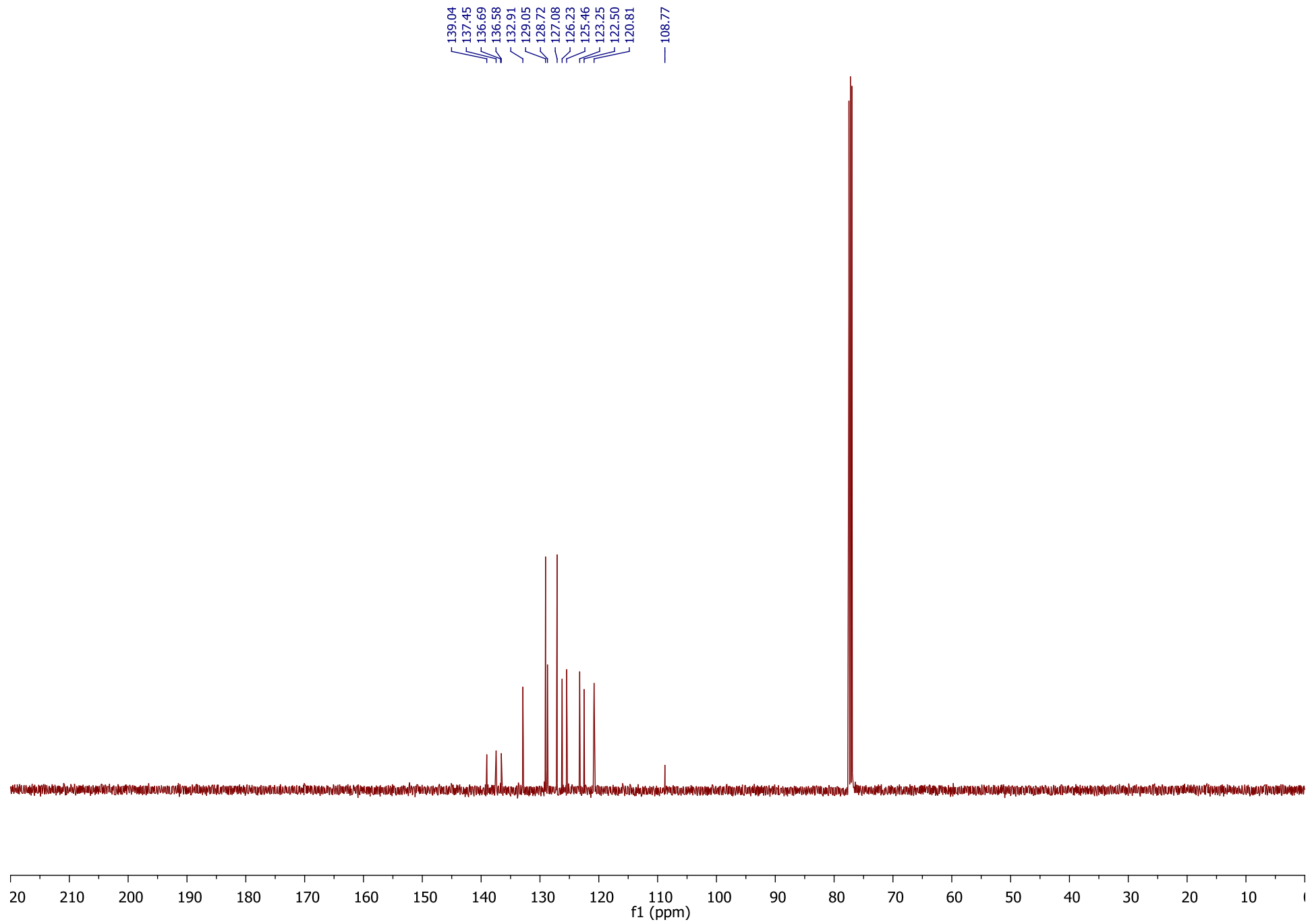


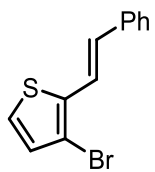
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7.76
7.75
7.58
7.57
7.52
7.49
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7.43
7.41
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7.36
7.33
7.32
7.30
7.26
7.11
7.08



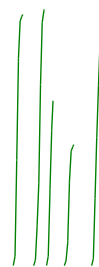
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2.20
1.05
4.35
1.04
0.99



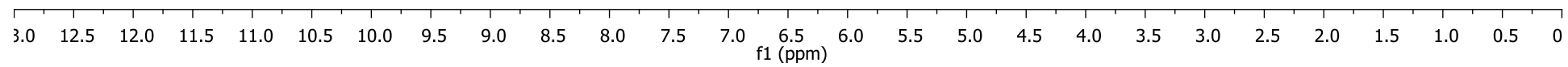


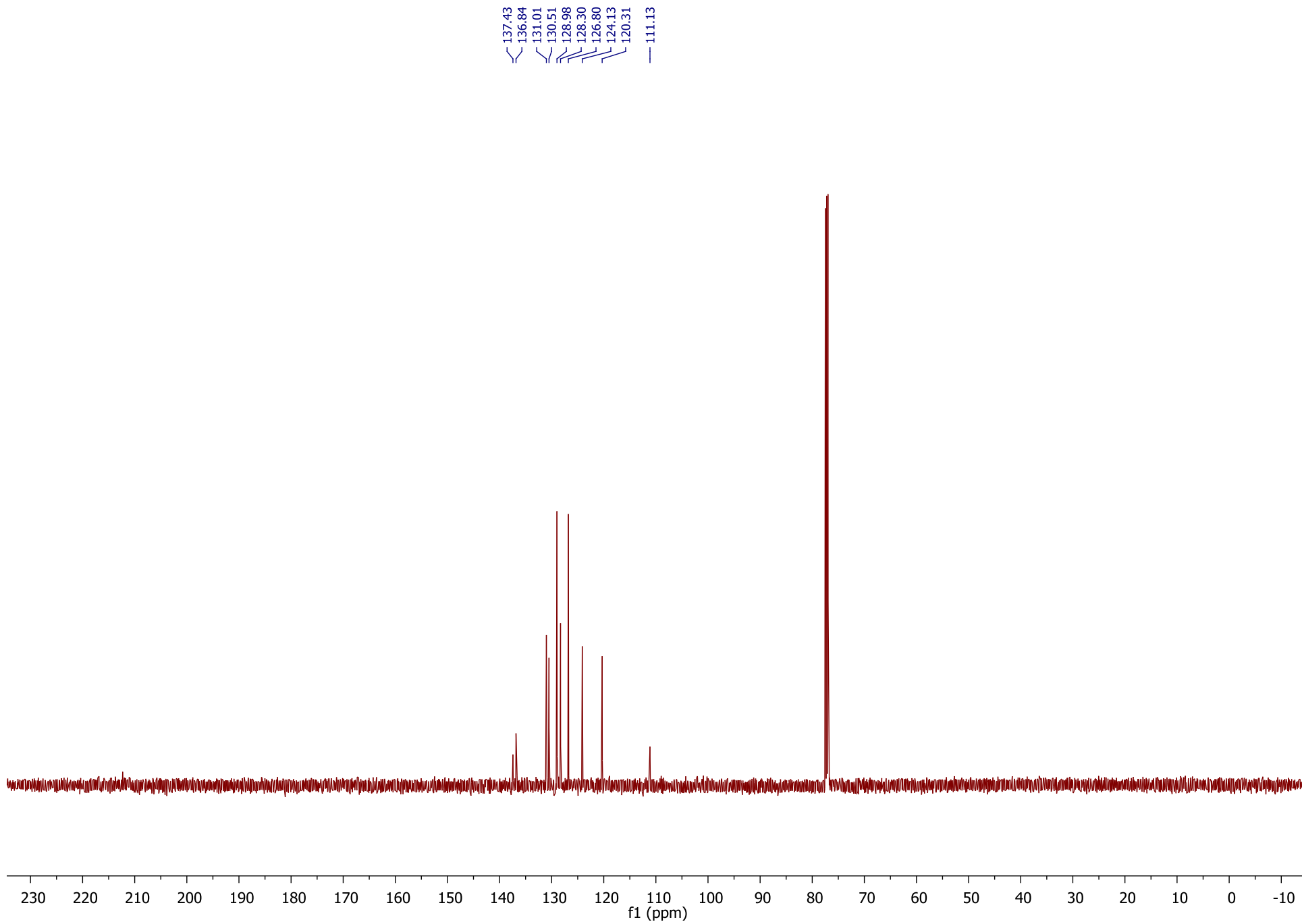


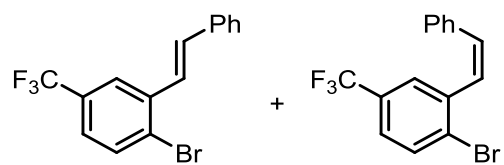
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7.51
7.38
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7.26
7.17
7.16
6.99
6.98
6.97
6.96



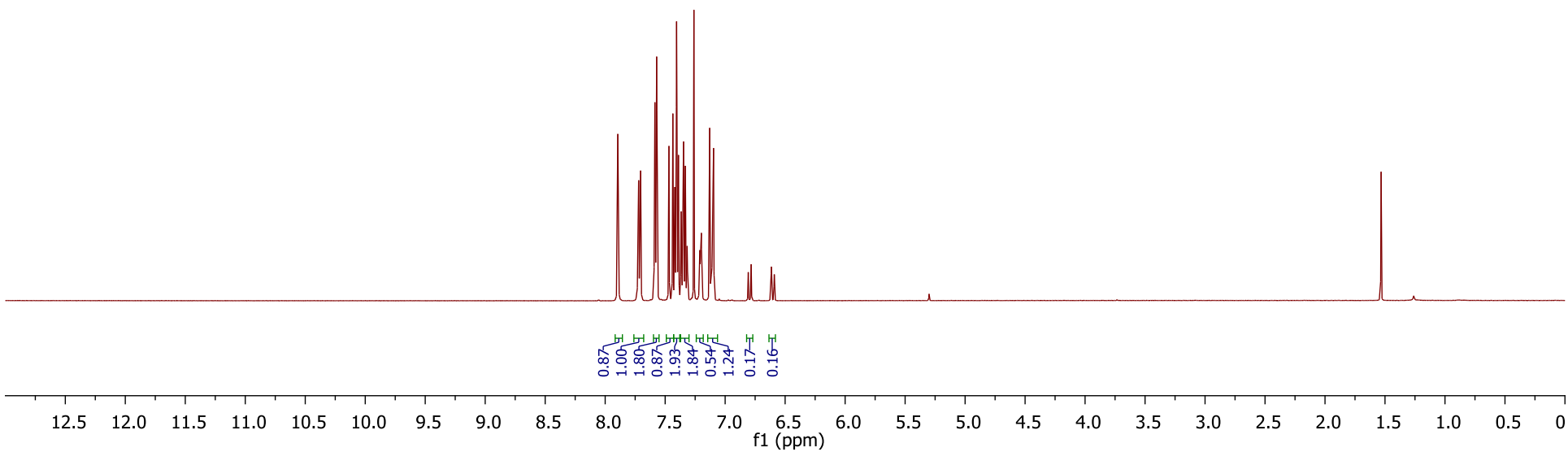
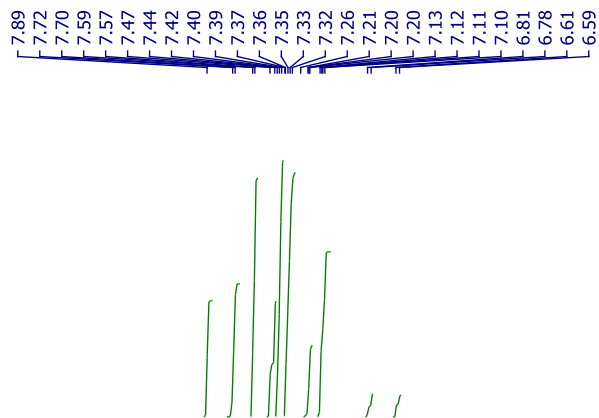
2.00
2.04
1.31
0.96
1.86

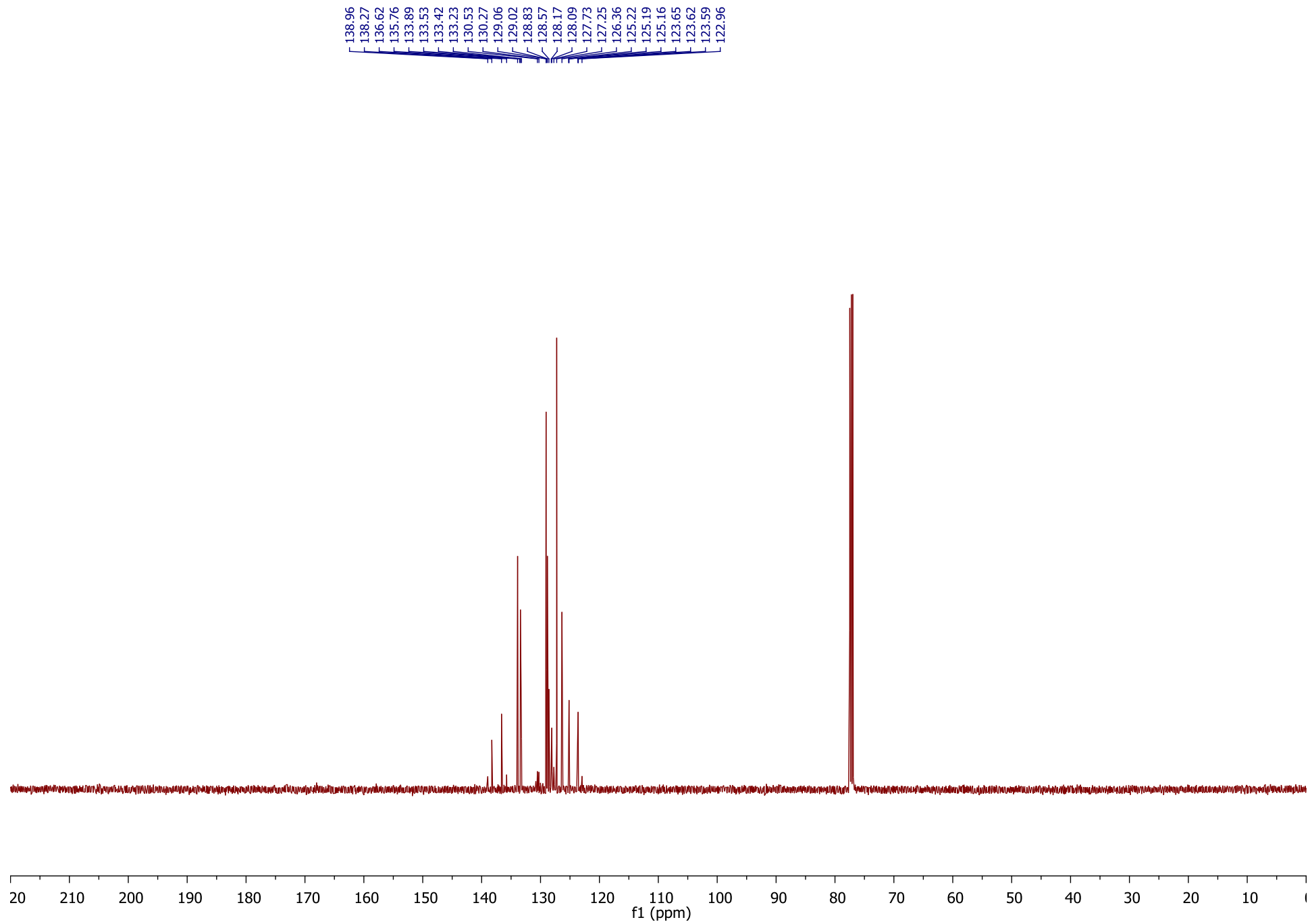


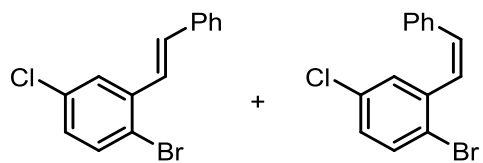




6.25: 1

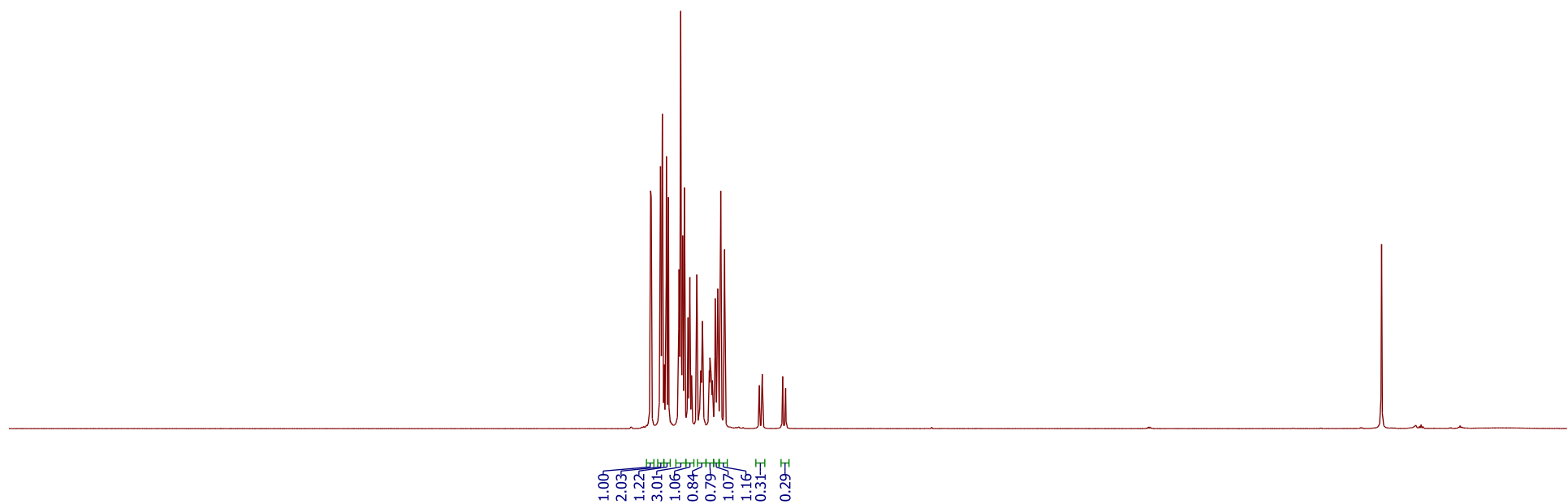
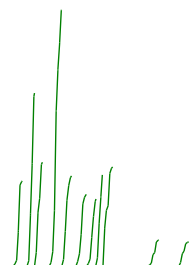






3.86: 1

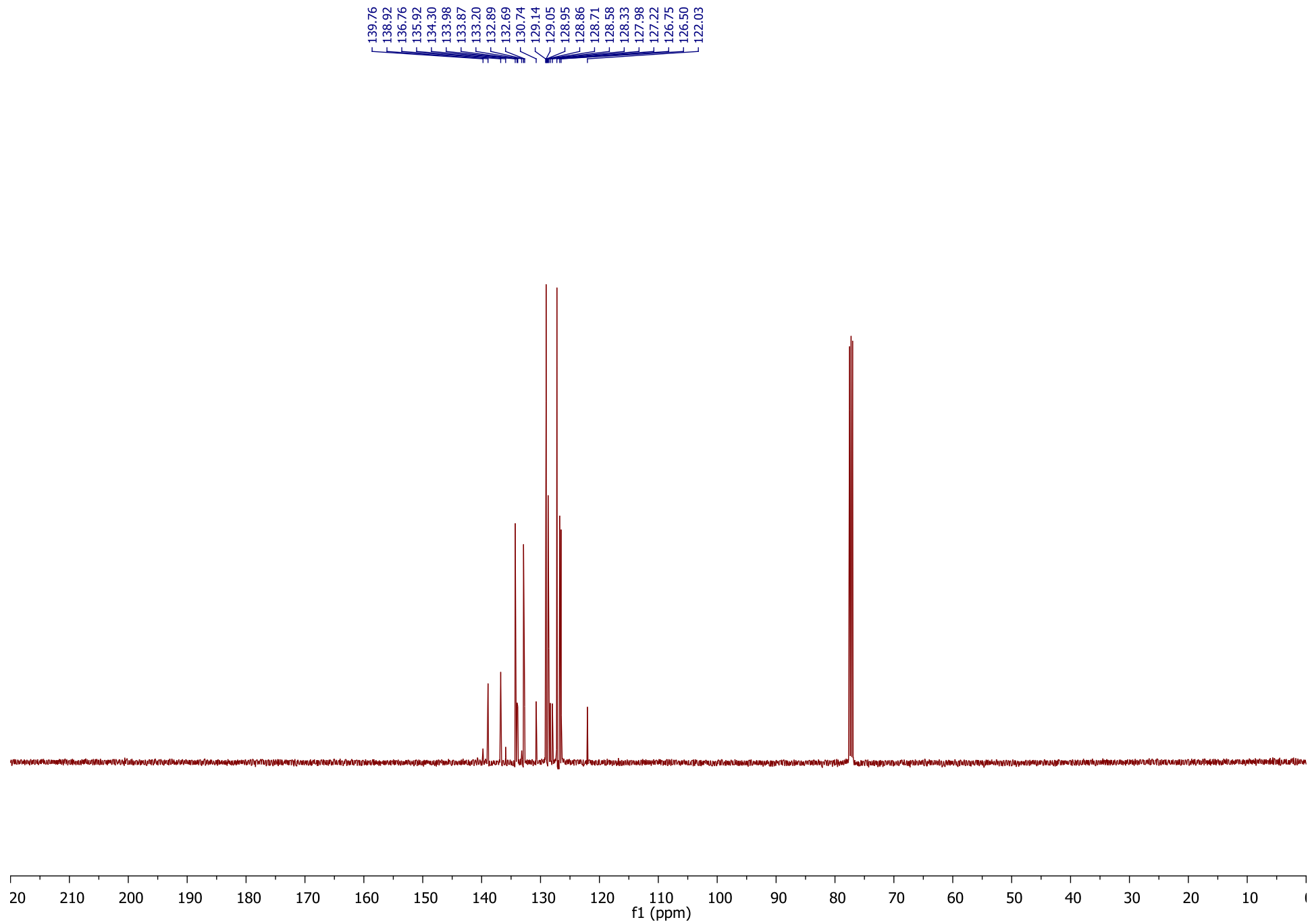
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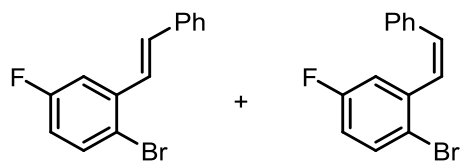


3.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0

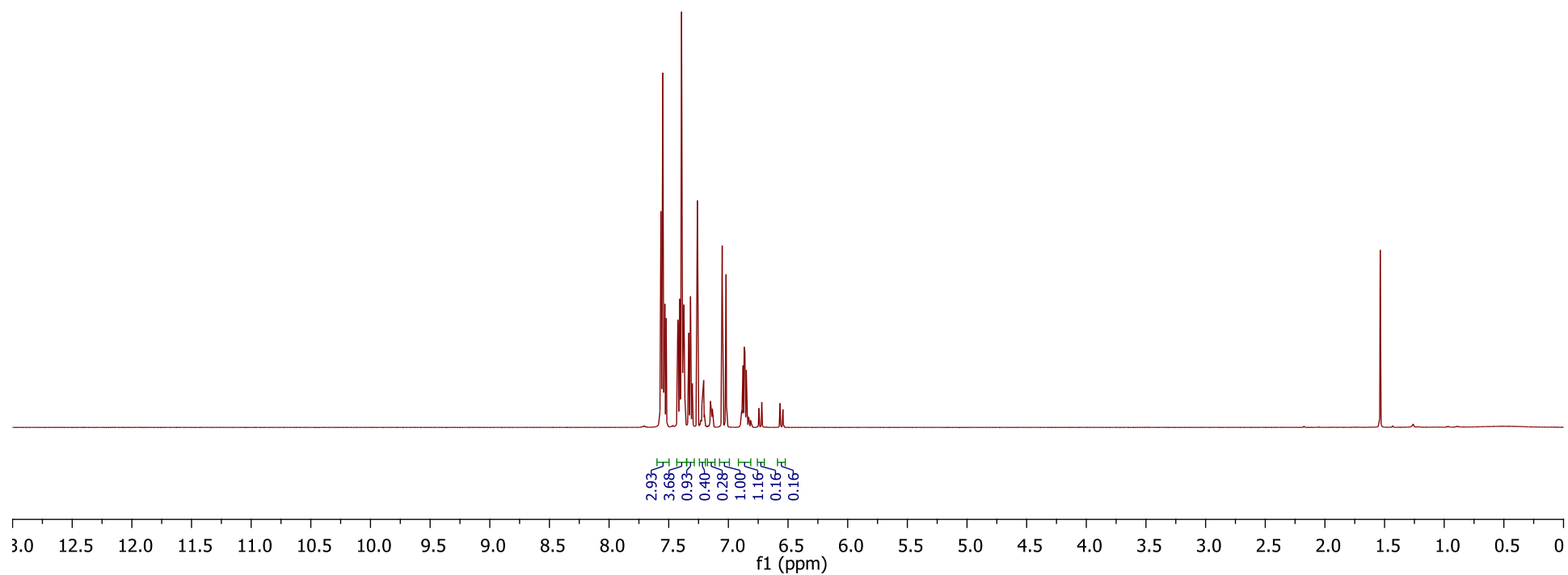
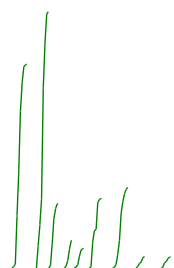
f1 (ppm)

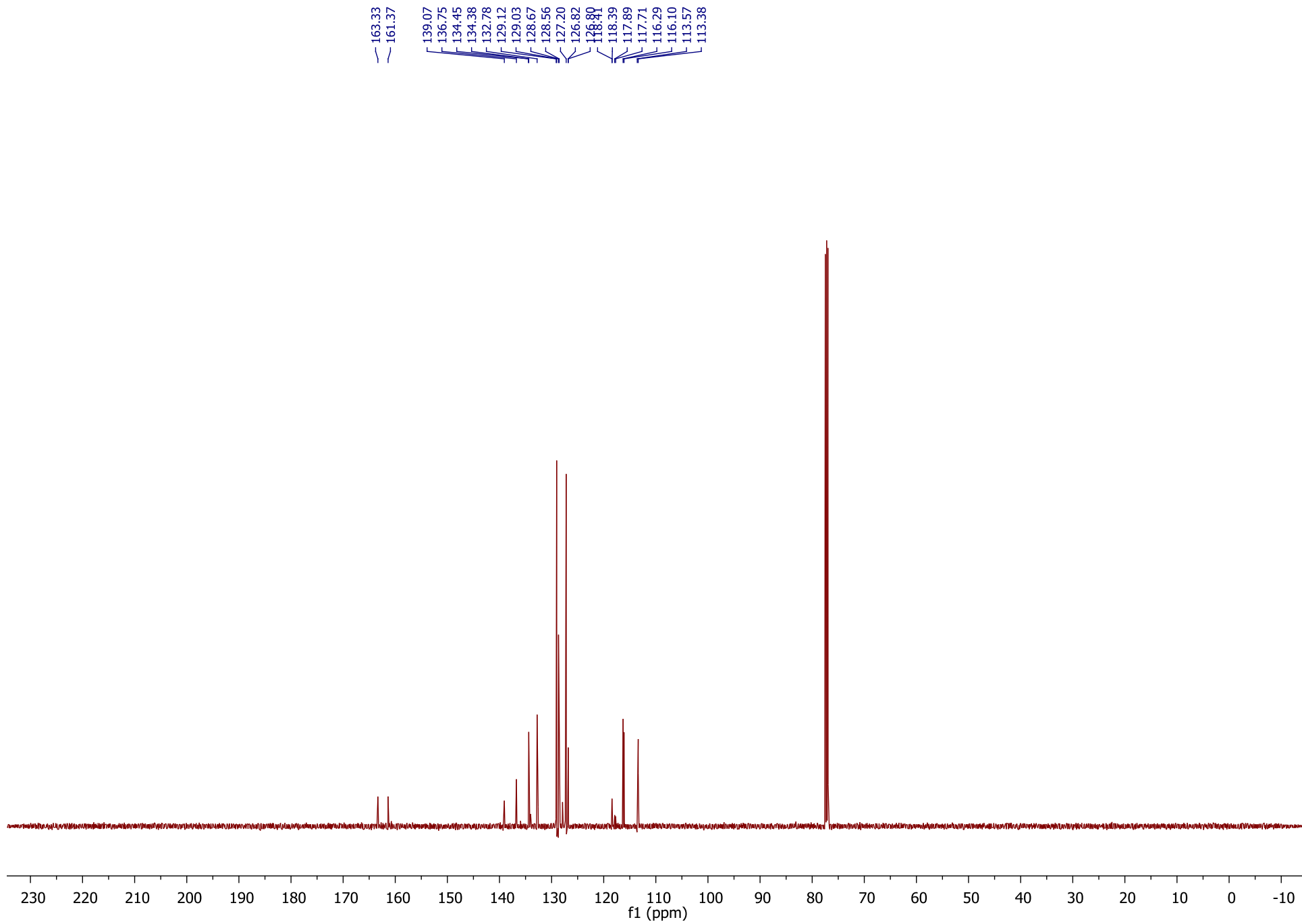
1.00 2.03 1.22 3.01 1.06 0.84 0.79 1.07 1.16 0.31 0.29

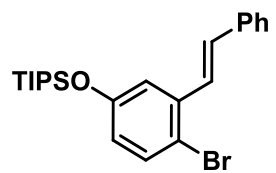




6.25: 1





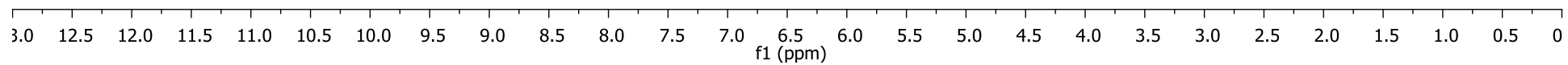


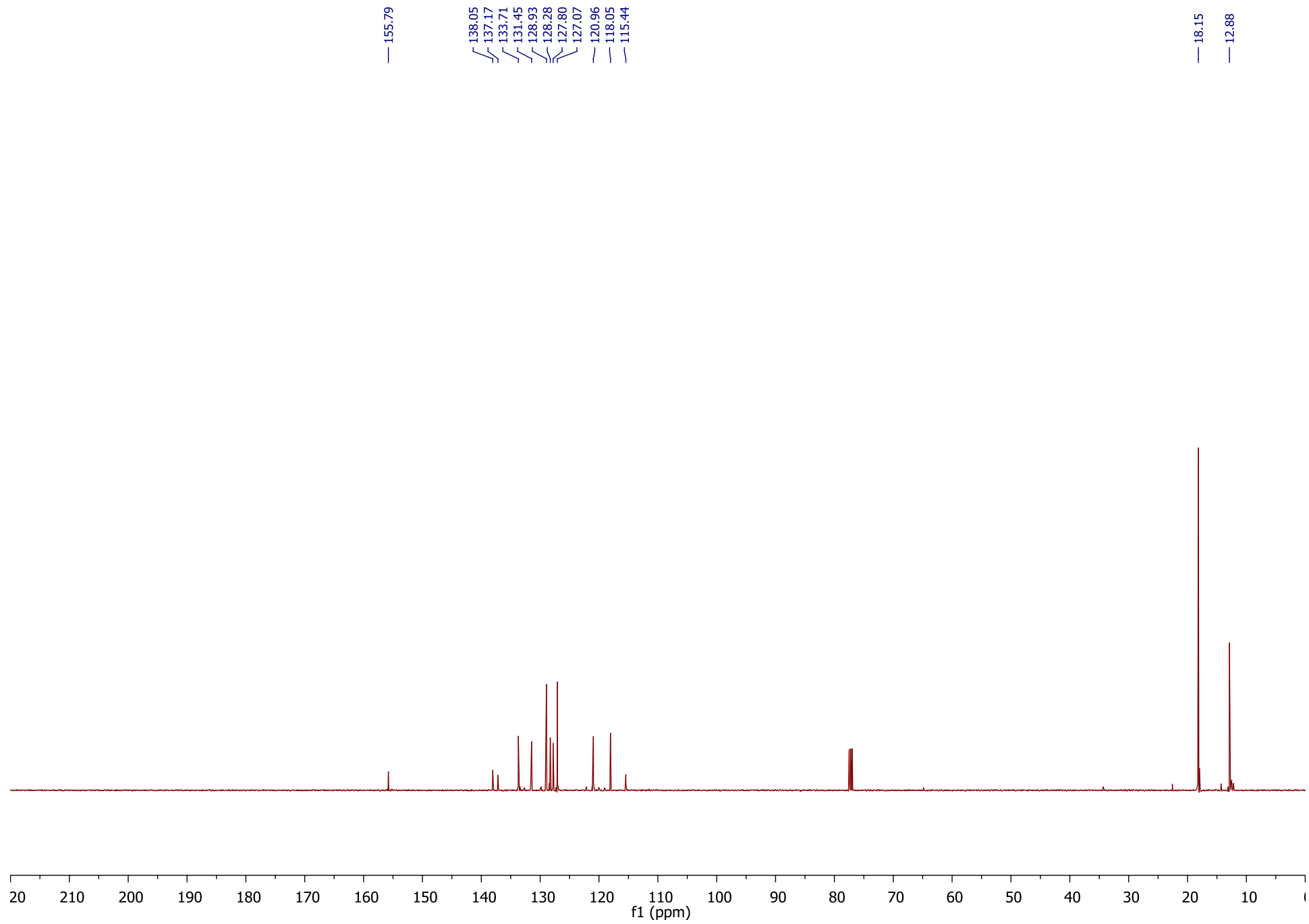
7.58
7.56
7.43
7.42
7.40
7.40
7.39
7.38
7.32
7.30
7.29
7.26
7.20
7.19
7.19
6.99
6.96
6.71
6.70
6.69
6.68

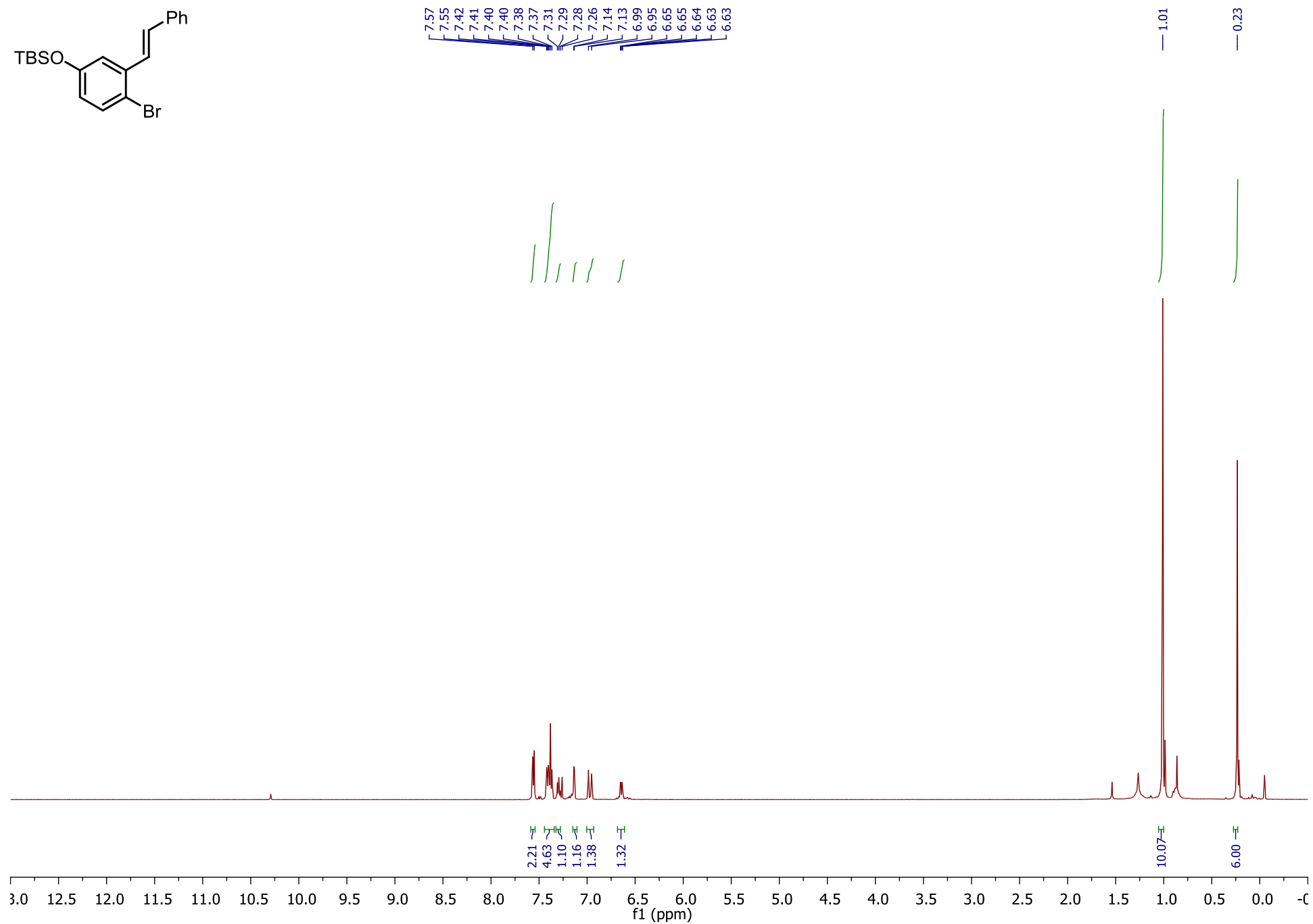
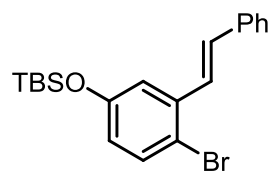
1.33
1.31
1.30
1.28
1.27
1.27
1.26
1.25
1.15
1.14

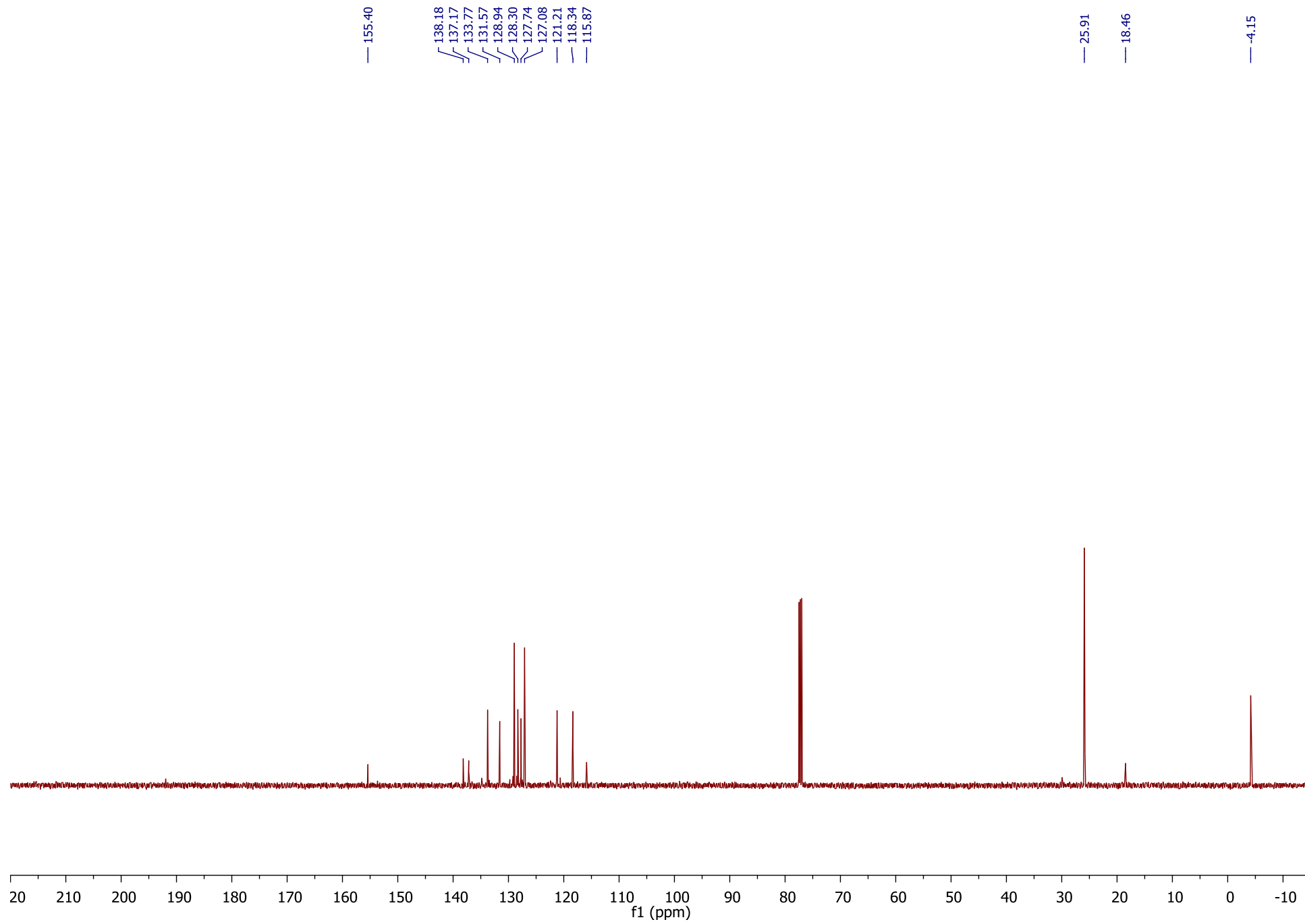
Integration values for the aromatic region (6.68-7.58 ppm):
2.00
3.84
1.05
1.19
1.03
1.07

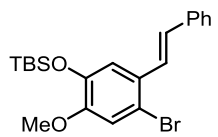
Integration values for the aliphatic region (1.14-1.33 ppm):
3.86
16.18









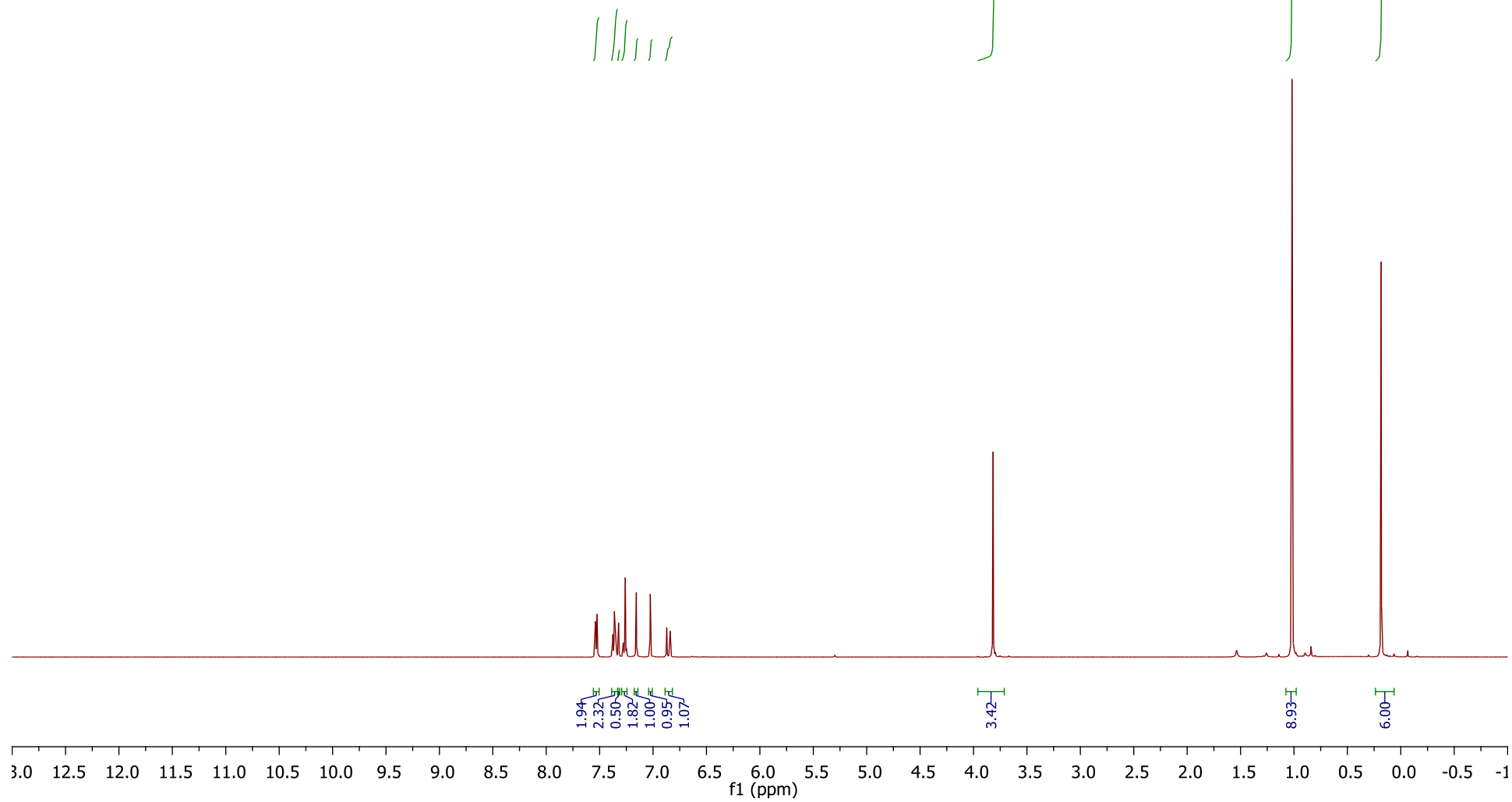


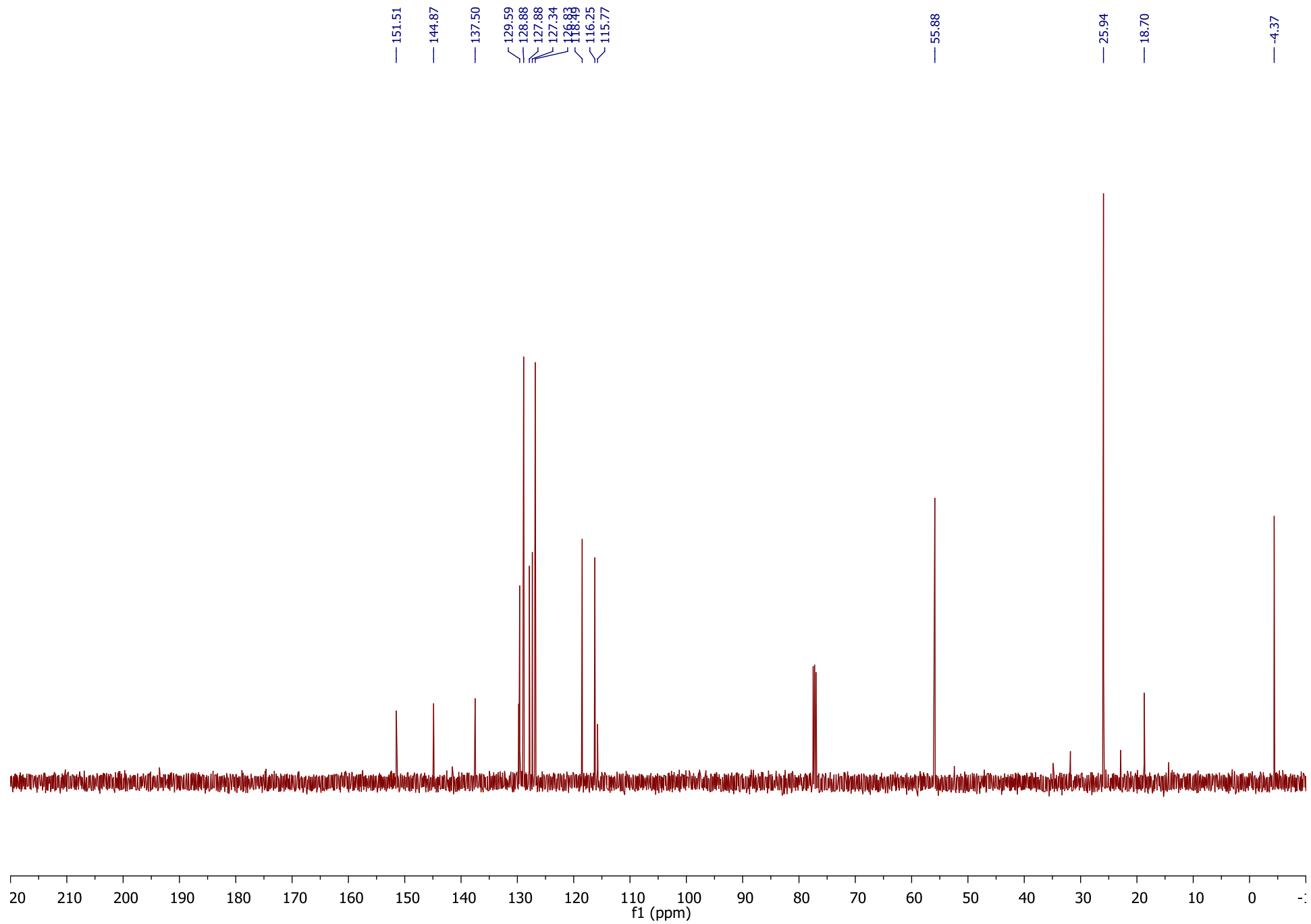
7.54
7.52
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7.28
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7.25
7.16
7.03
6.87
6.84

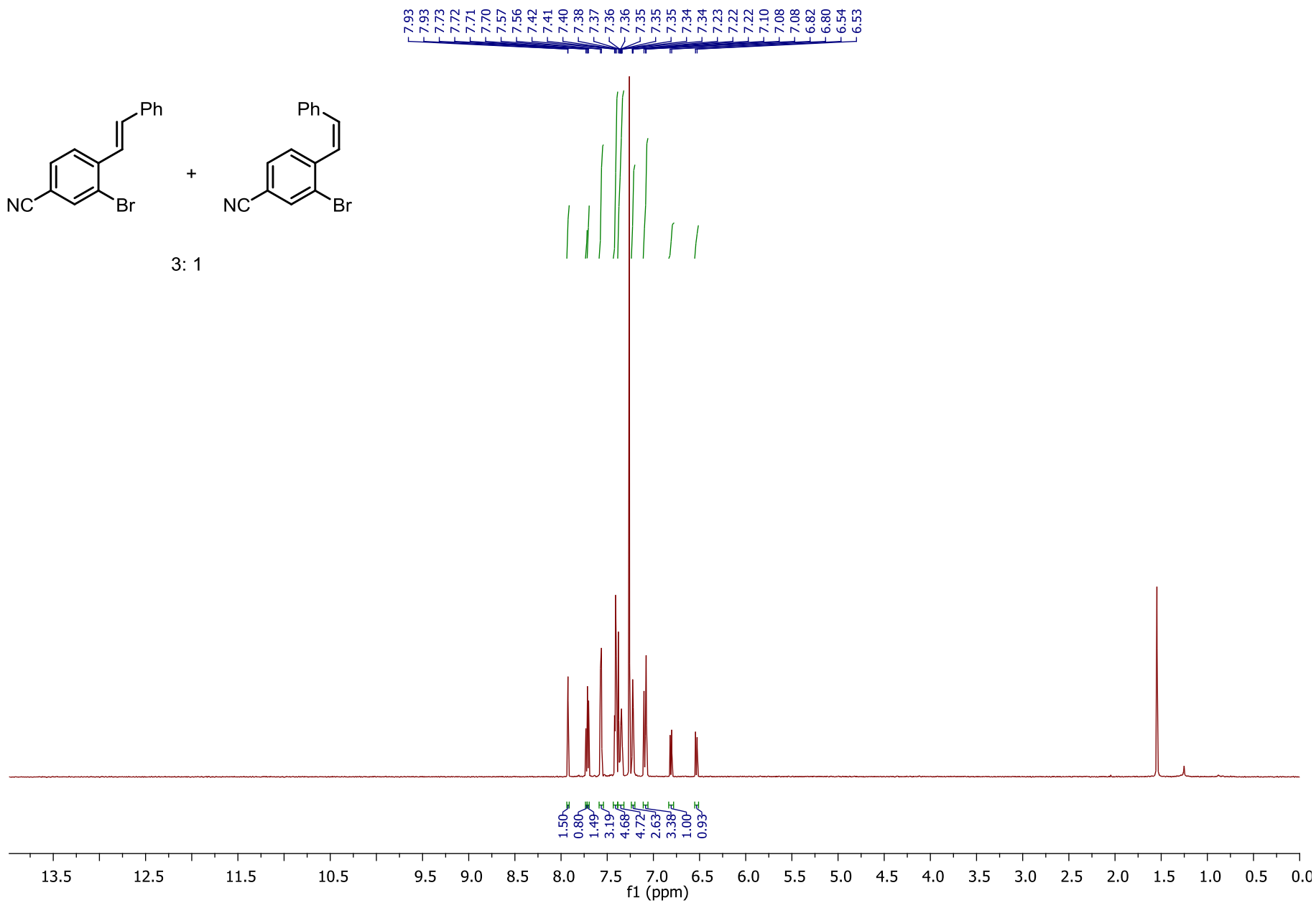
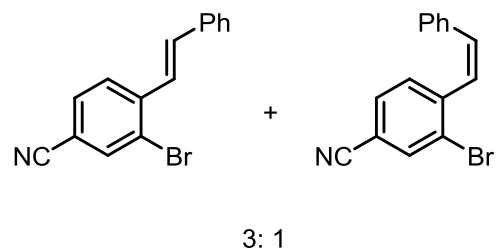
3.82

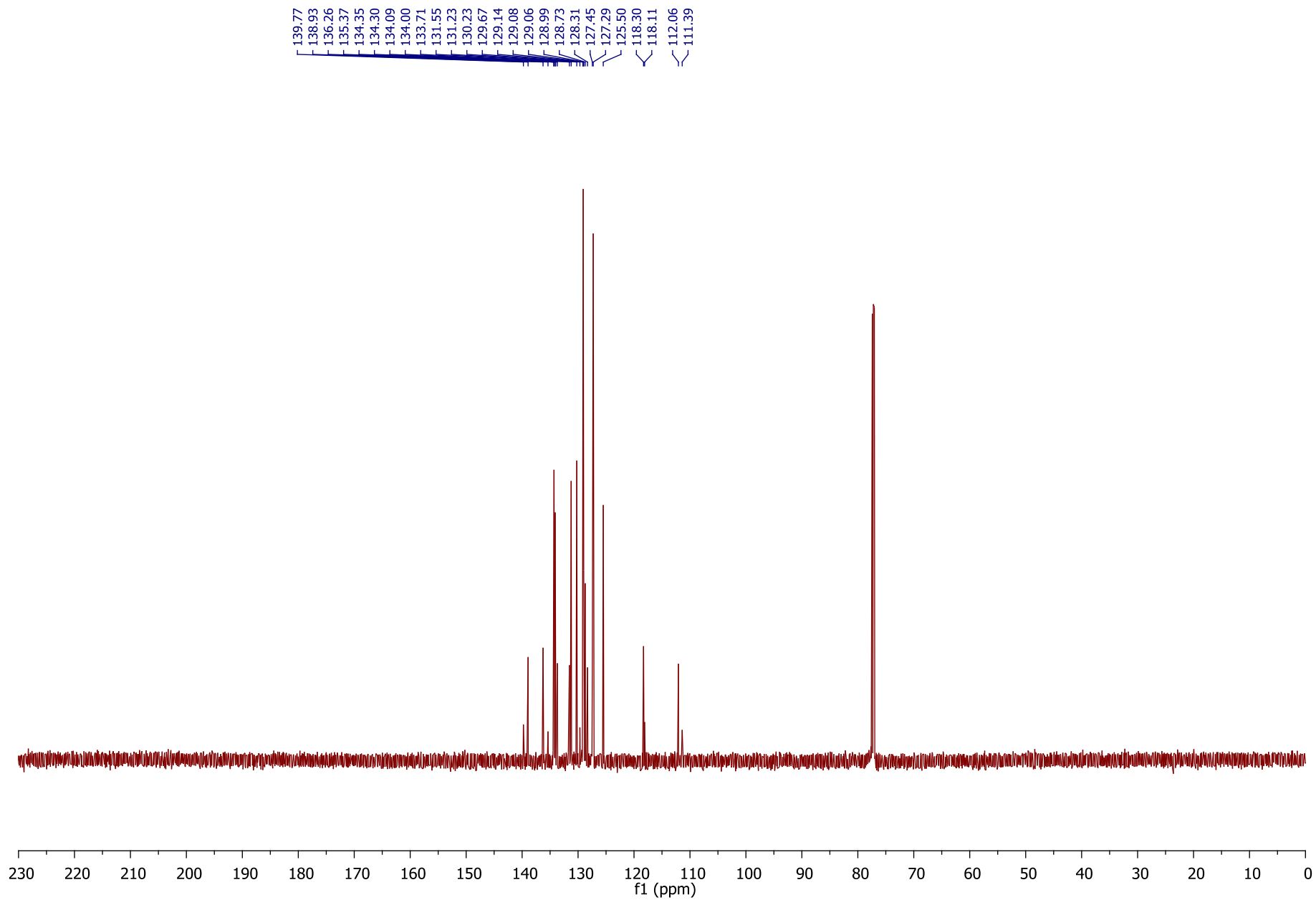
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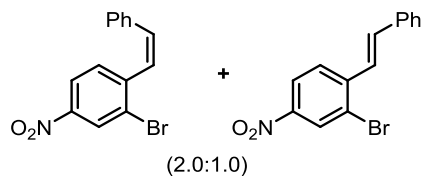
0.18



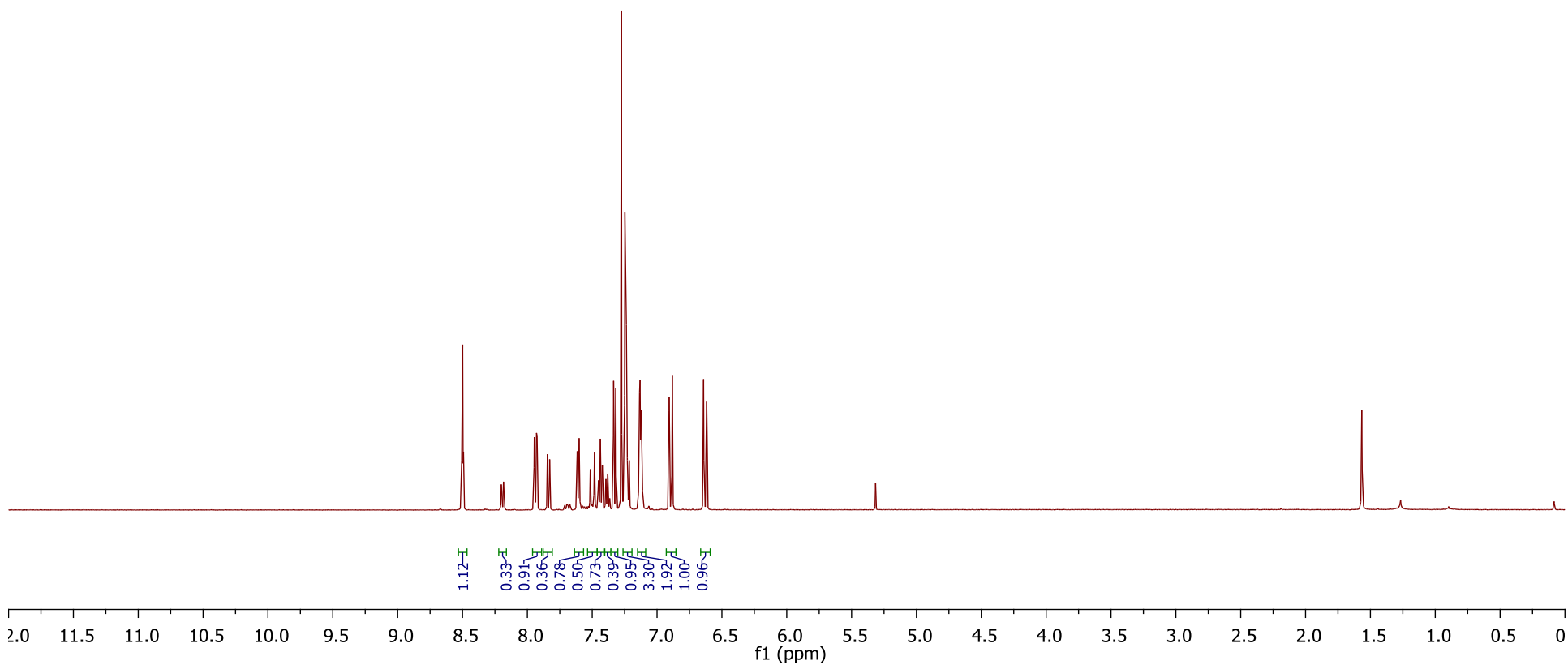
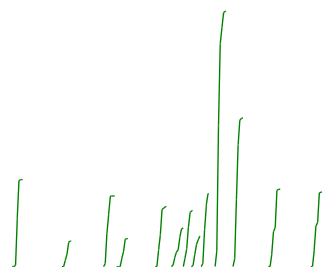


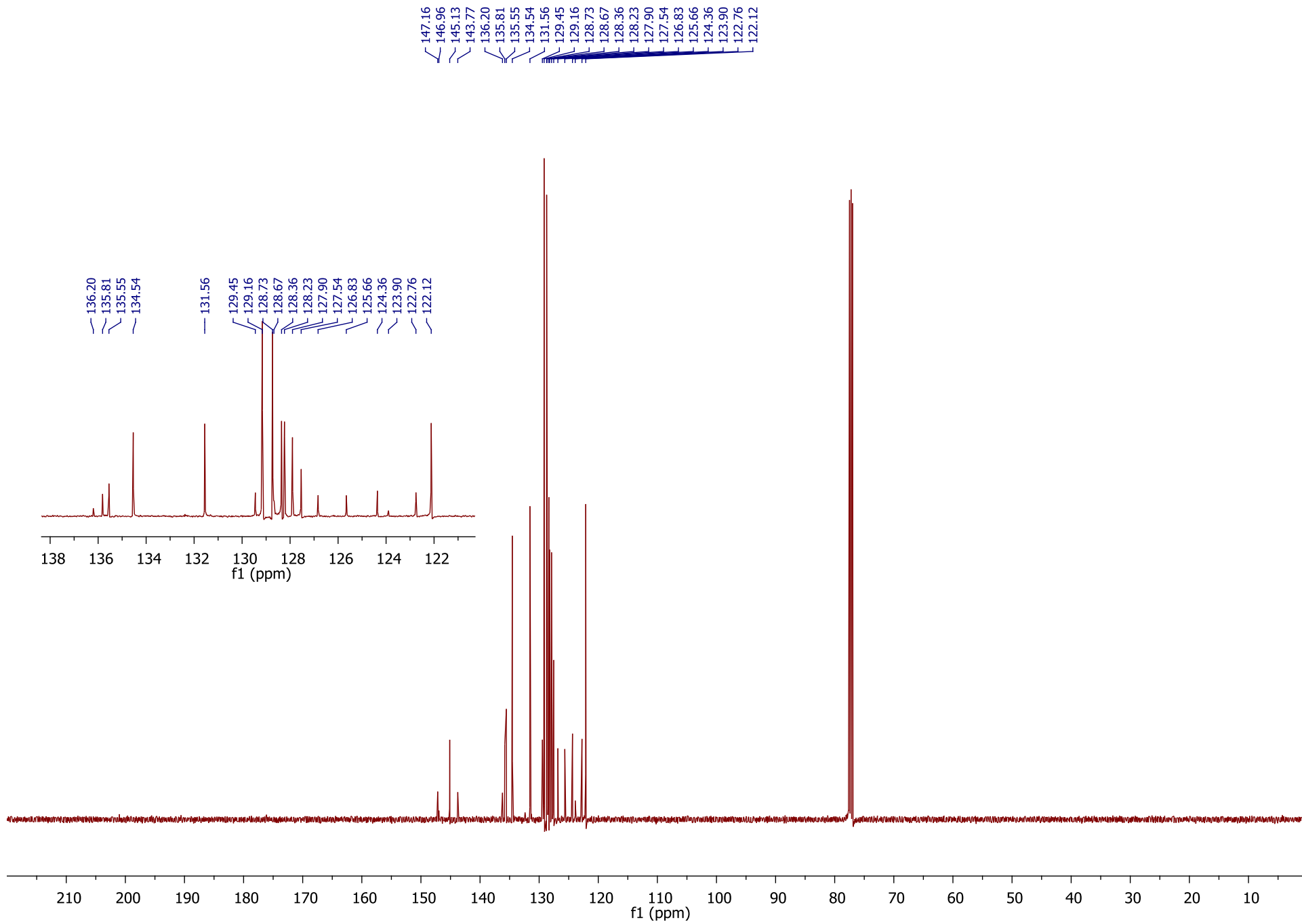


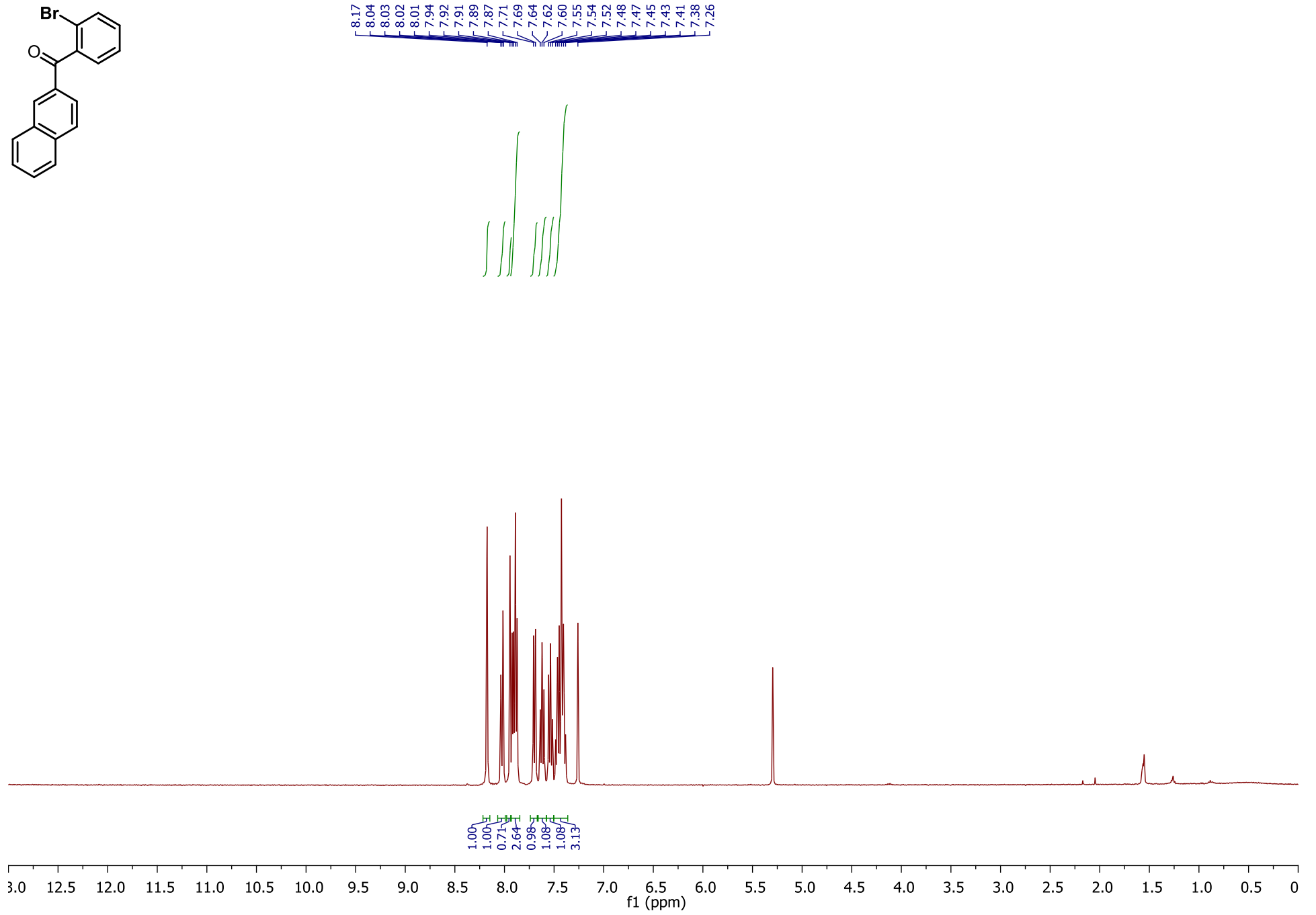
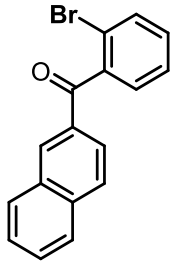


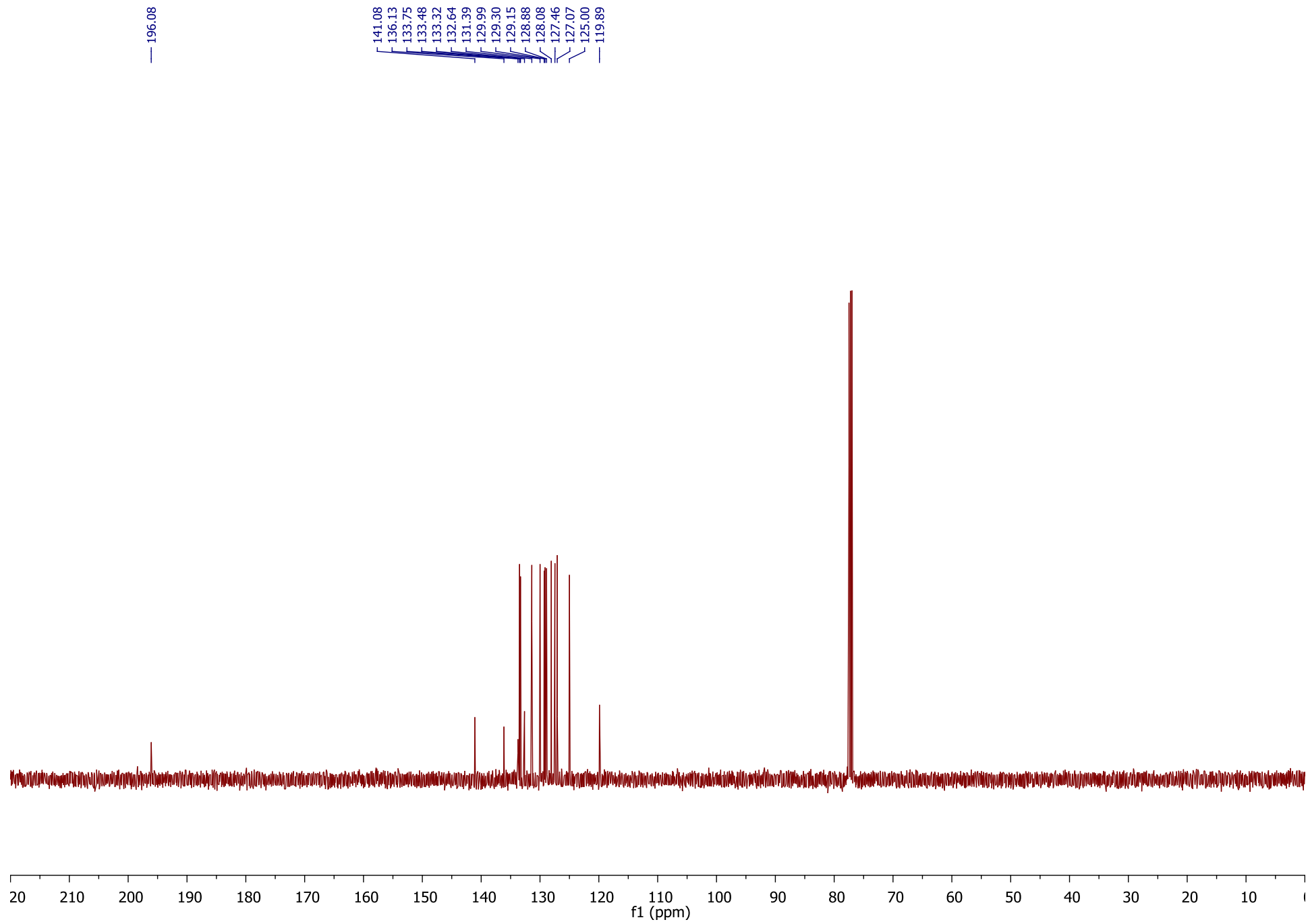


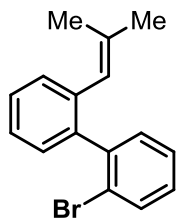
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8.50
8.49
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7.95
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7.93
7.85
7.83
7.62
7.60
7.51
7.48
7.45
7.44
7.42
7.39
7.38
7.37
7.33
7.32
7.27
7.26
7.26
7.25
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7.13
7.12
7.12
6.91
6.88
6.64
6.62





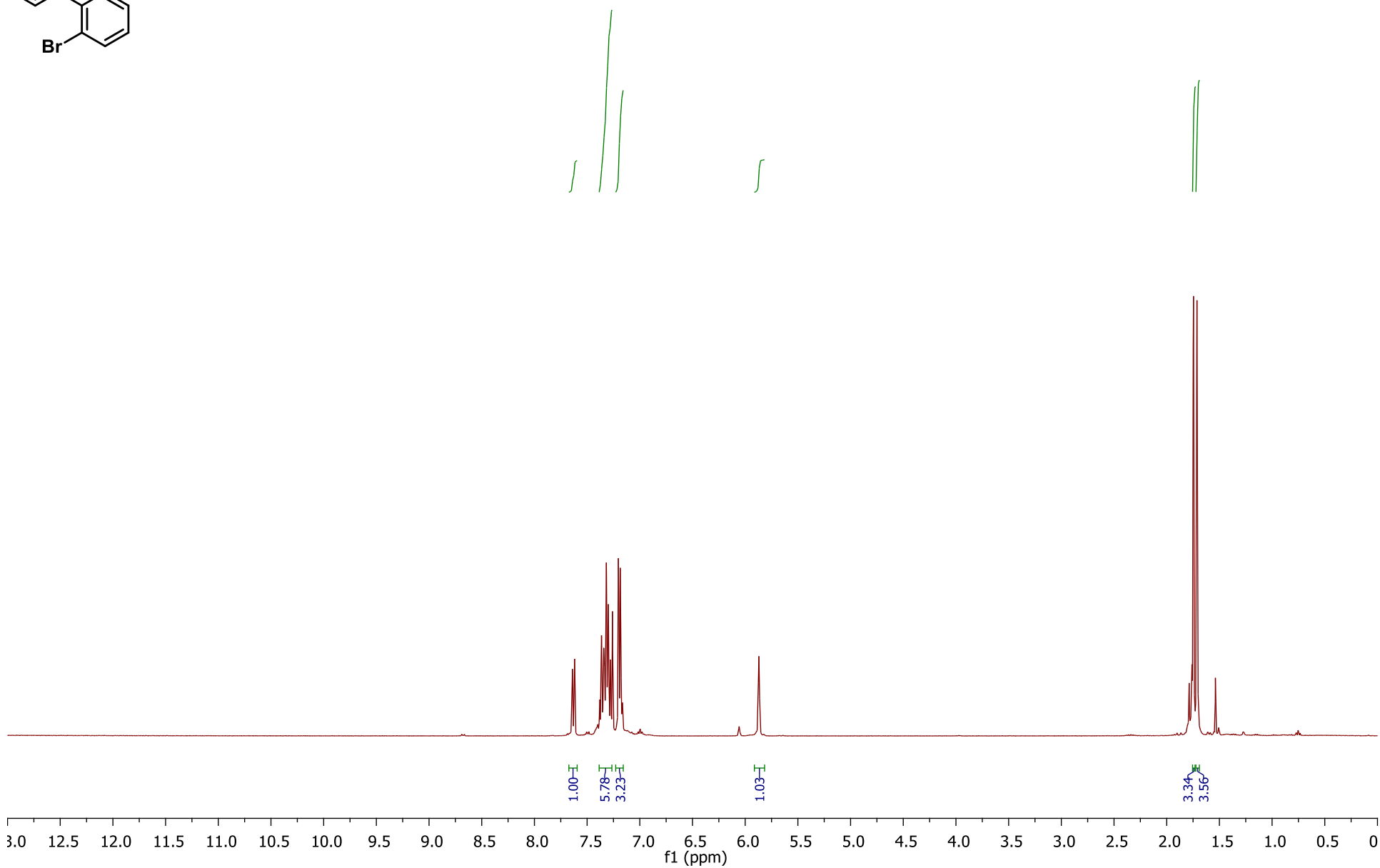


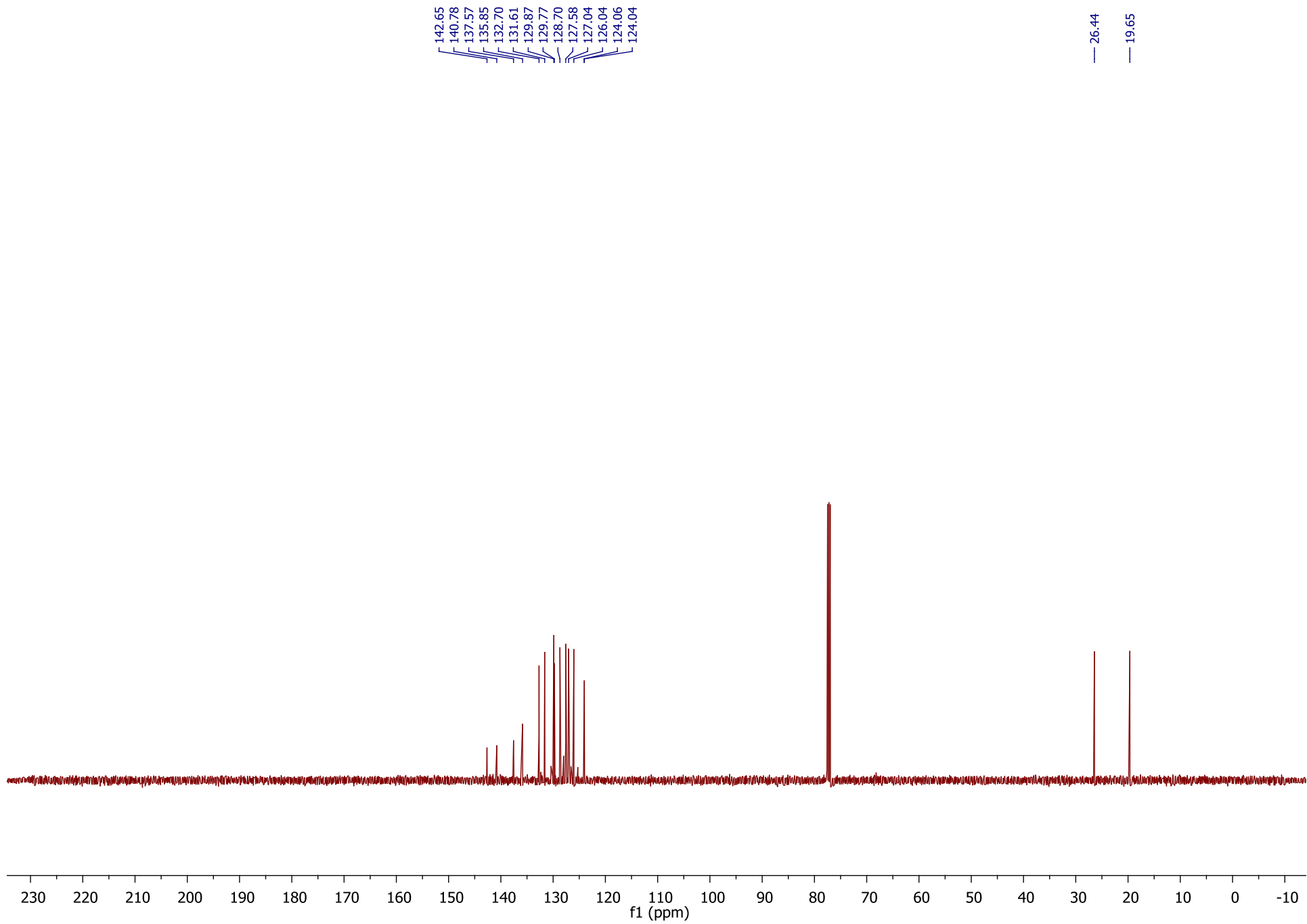


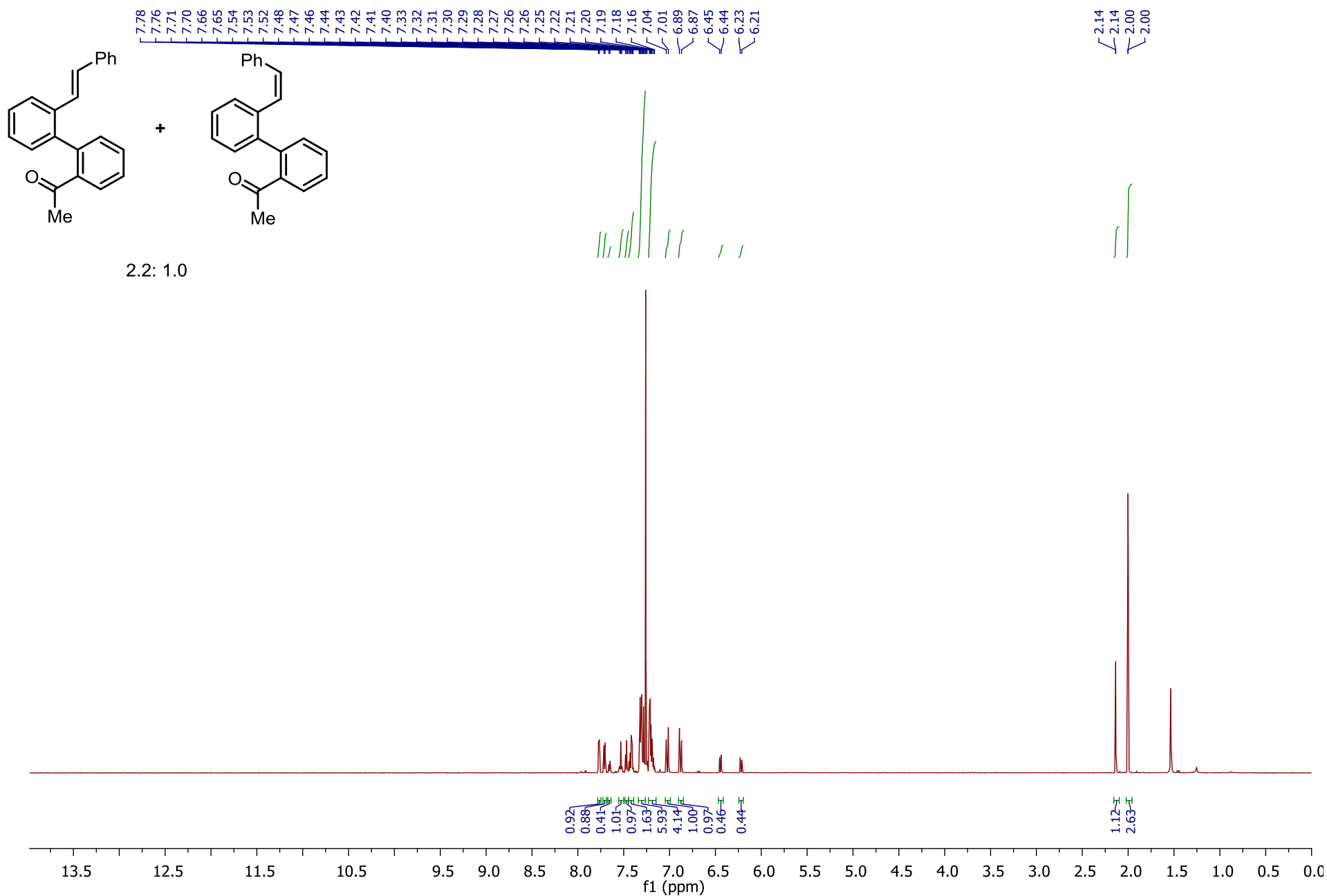


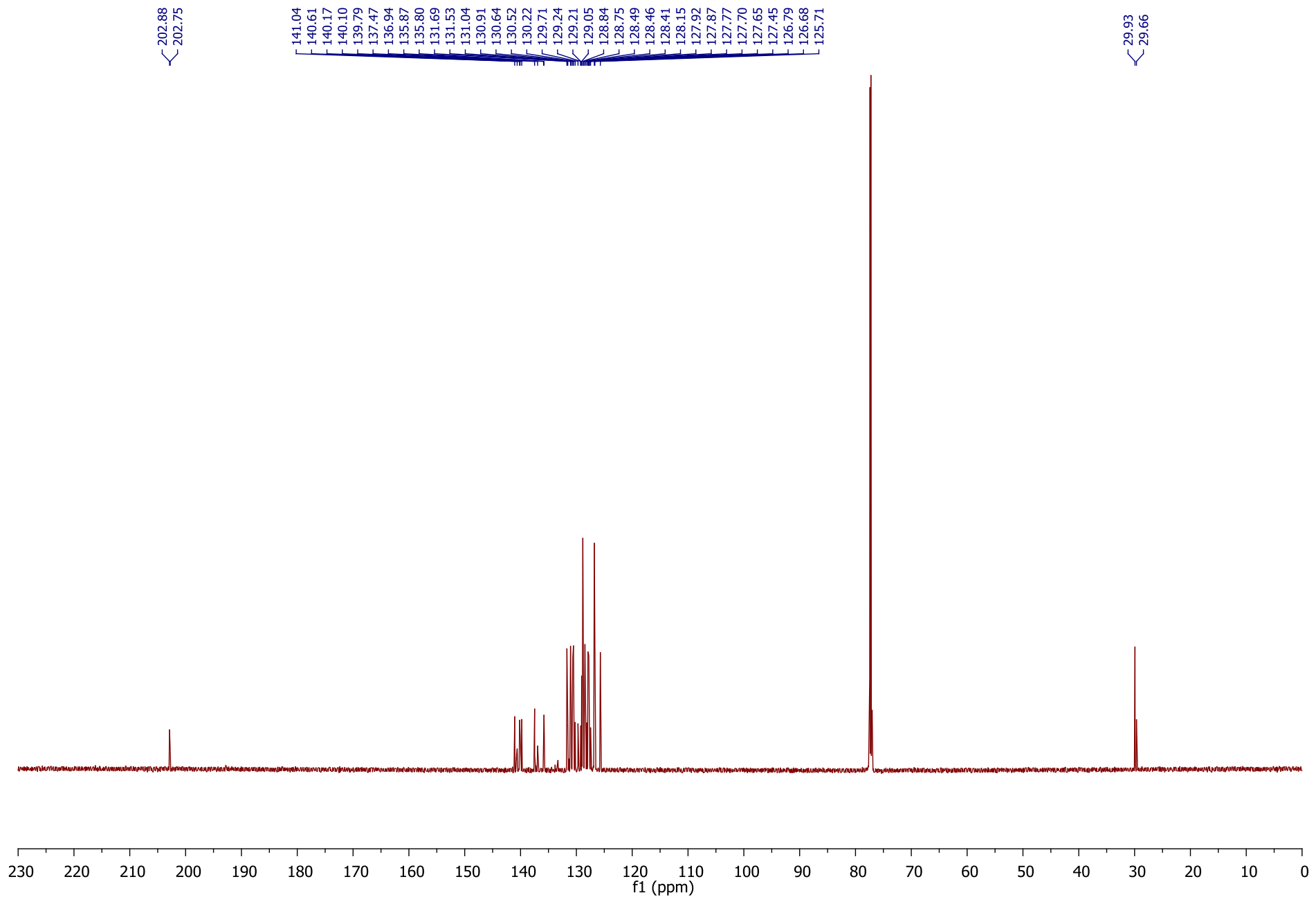
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7.34
7.34
7.33
7.32
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5.87

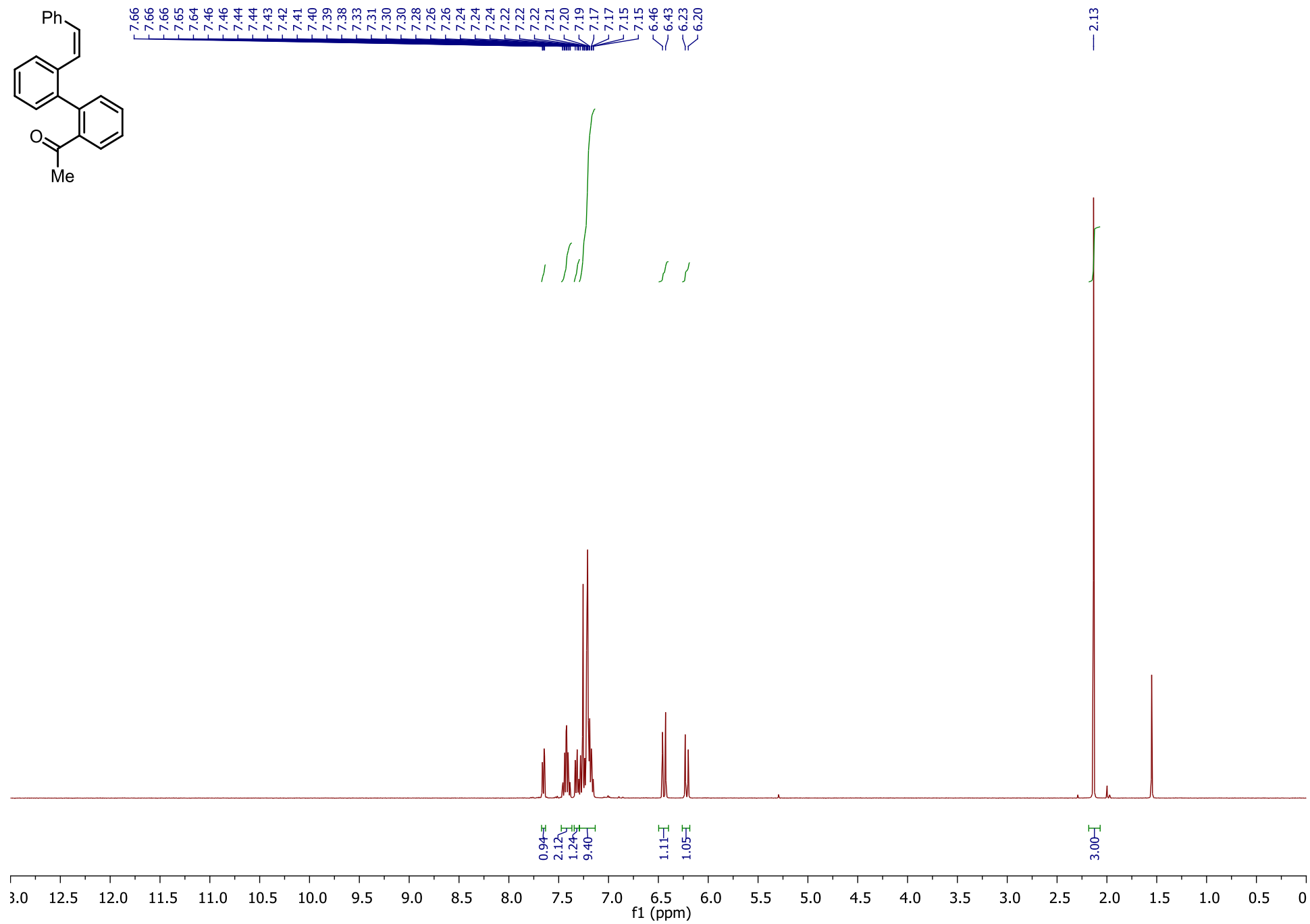
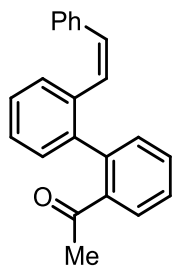
1.75
1.75
1.71
1.71

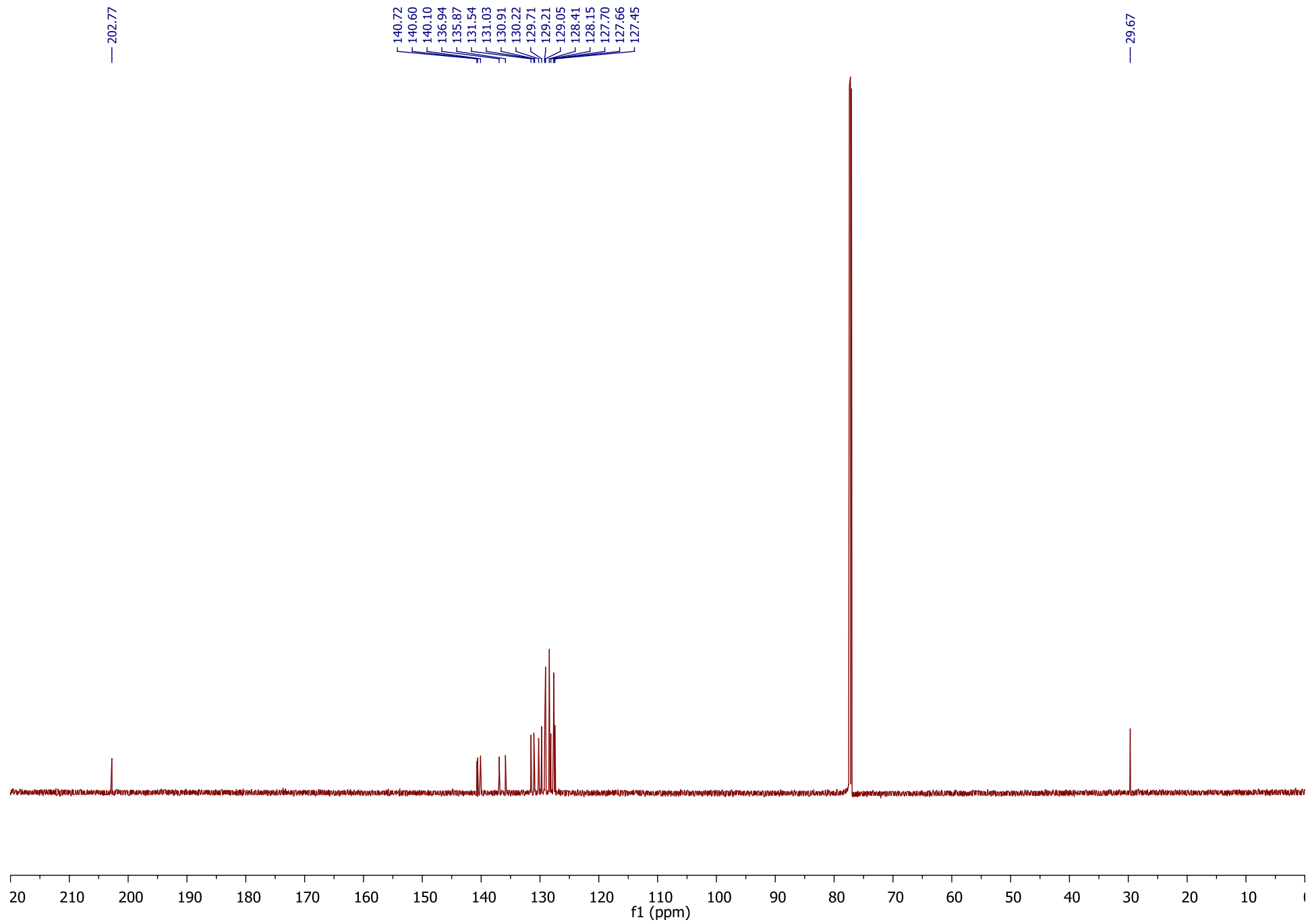


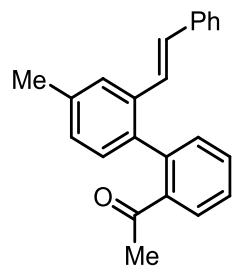




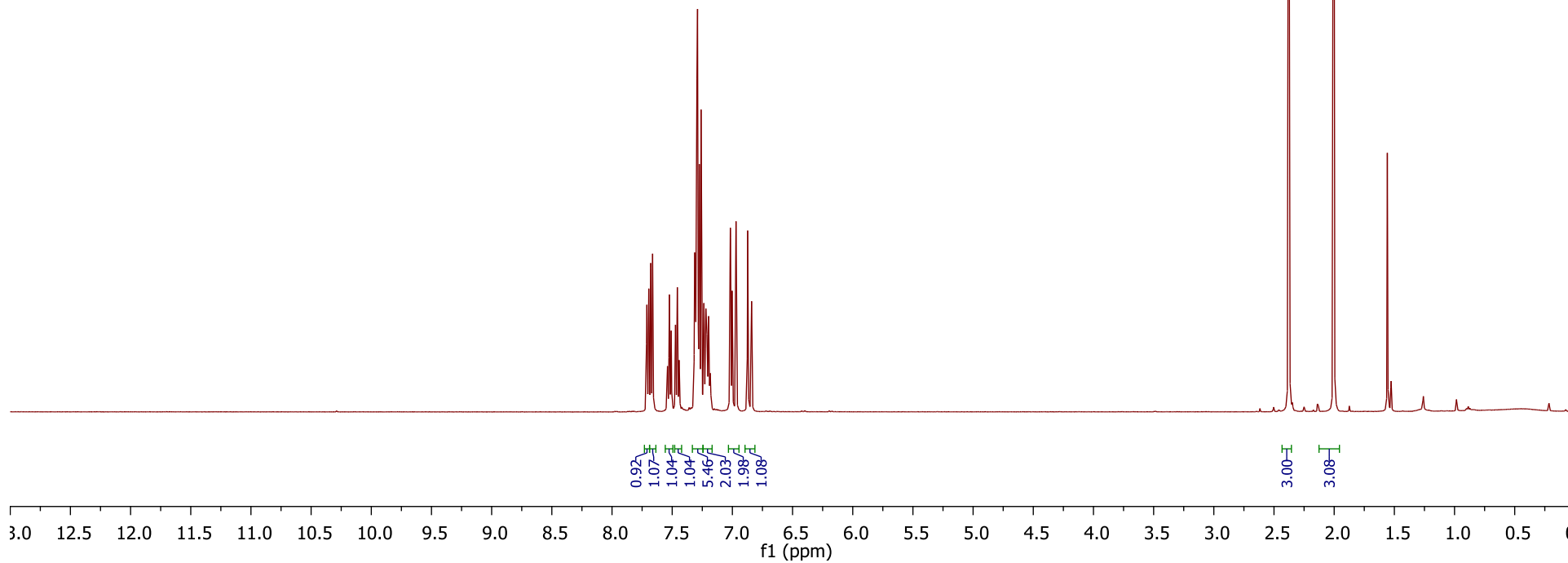


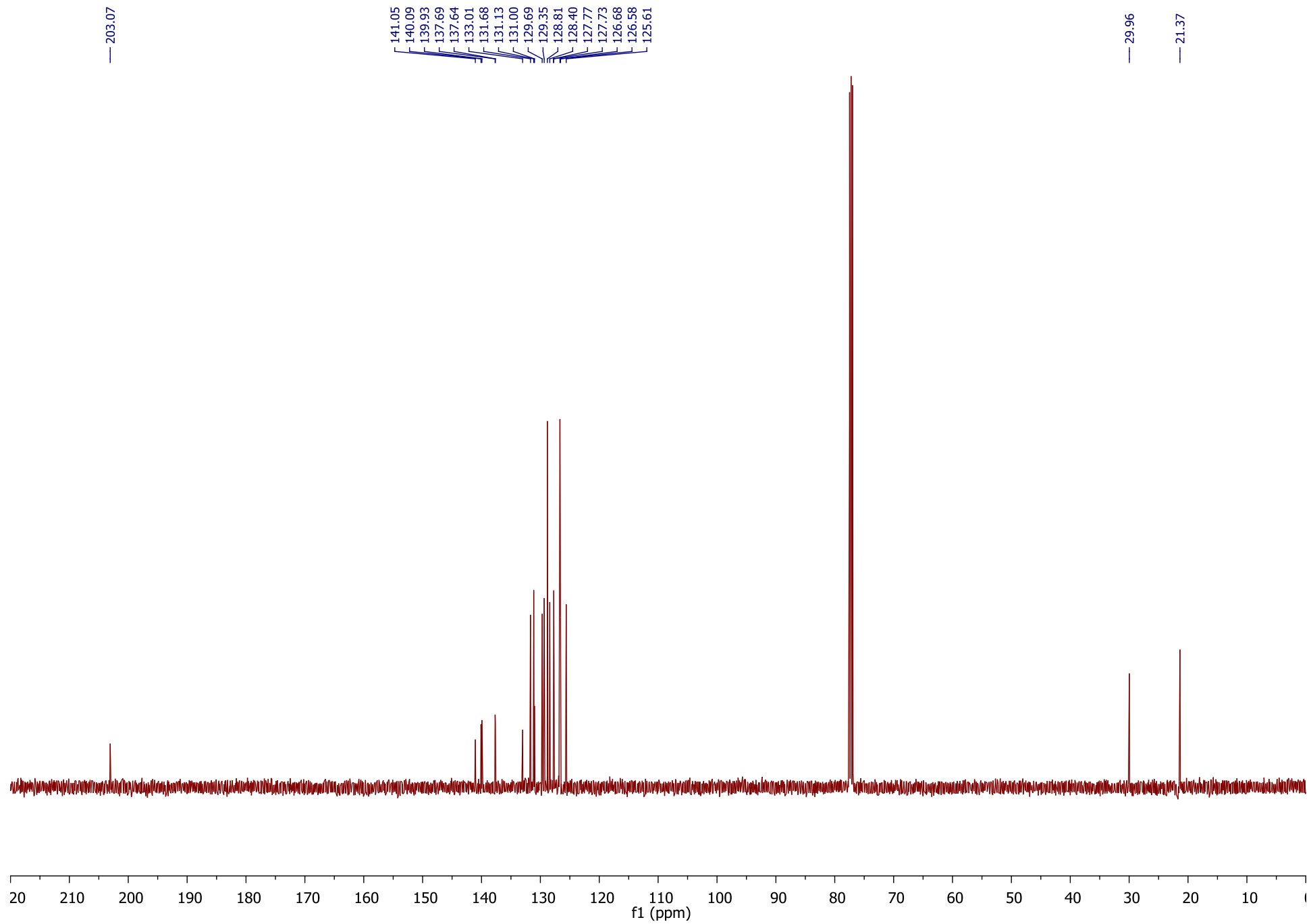


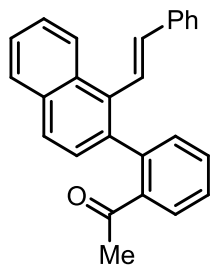




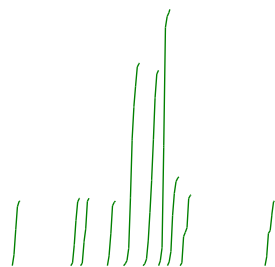
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7.44
7.31
7.31
7.29
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7.20
7.18
7.02
7.00
6.97
6.87
6.84







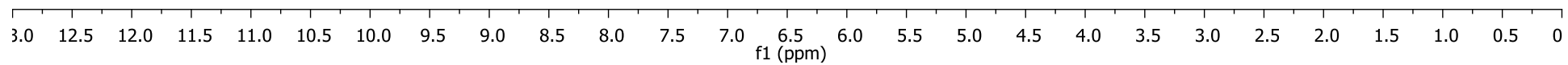
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6.58

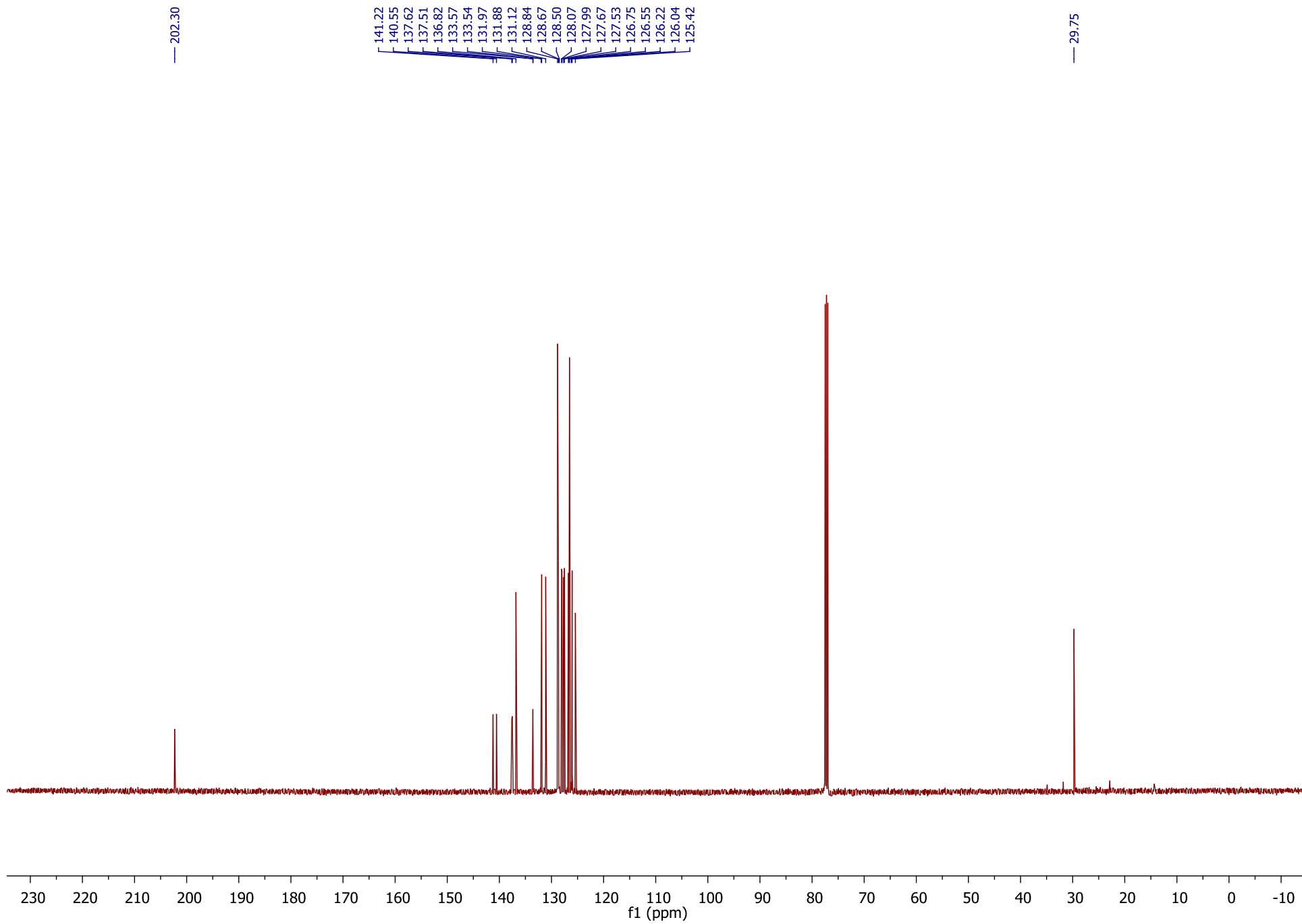


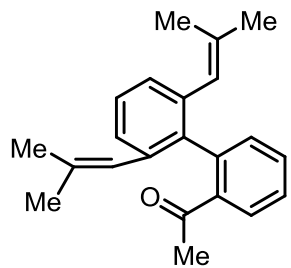
2.06

1.00
1.05
1.05
1.00
3.14
3.03
3.97
1.38
1.10
1.01

3.06



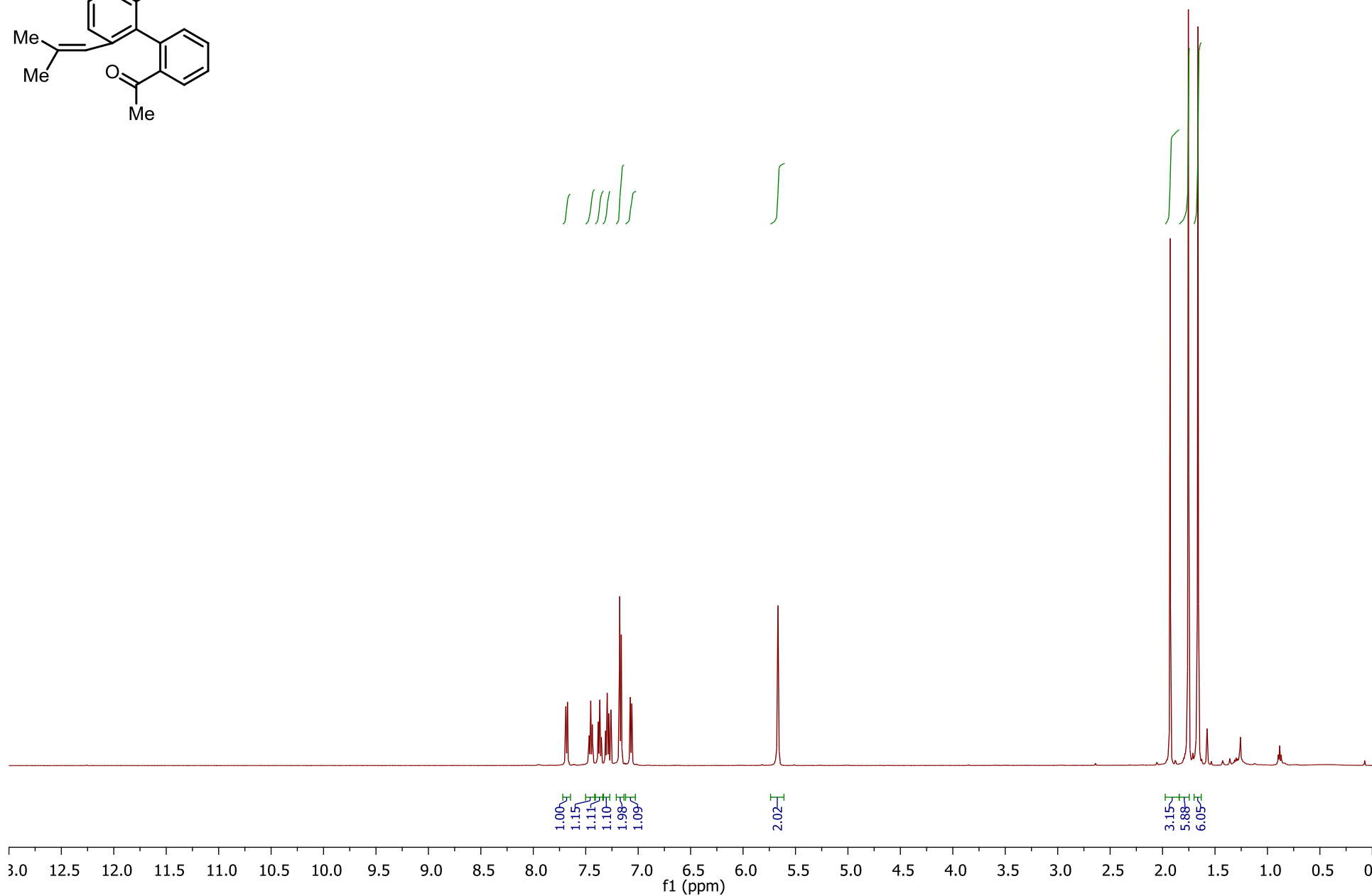


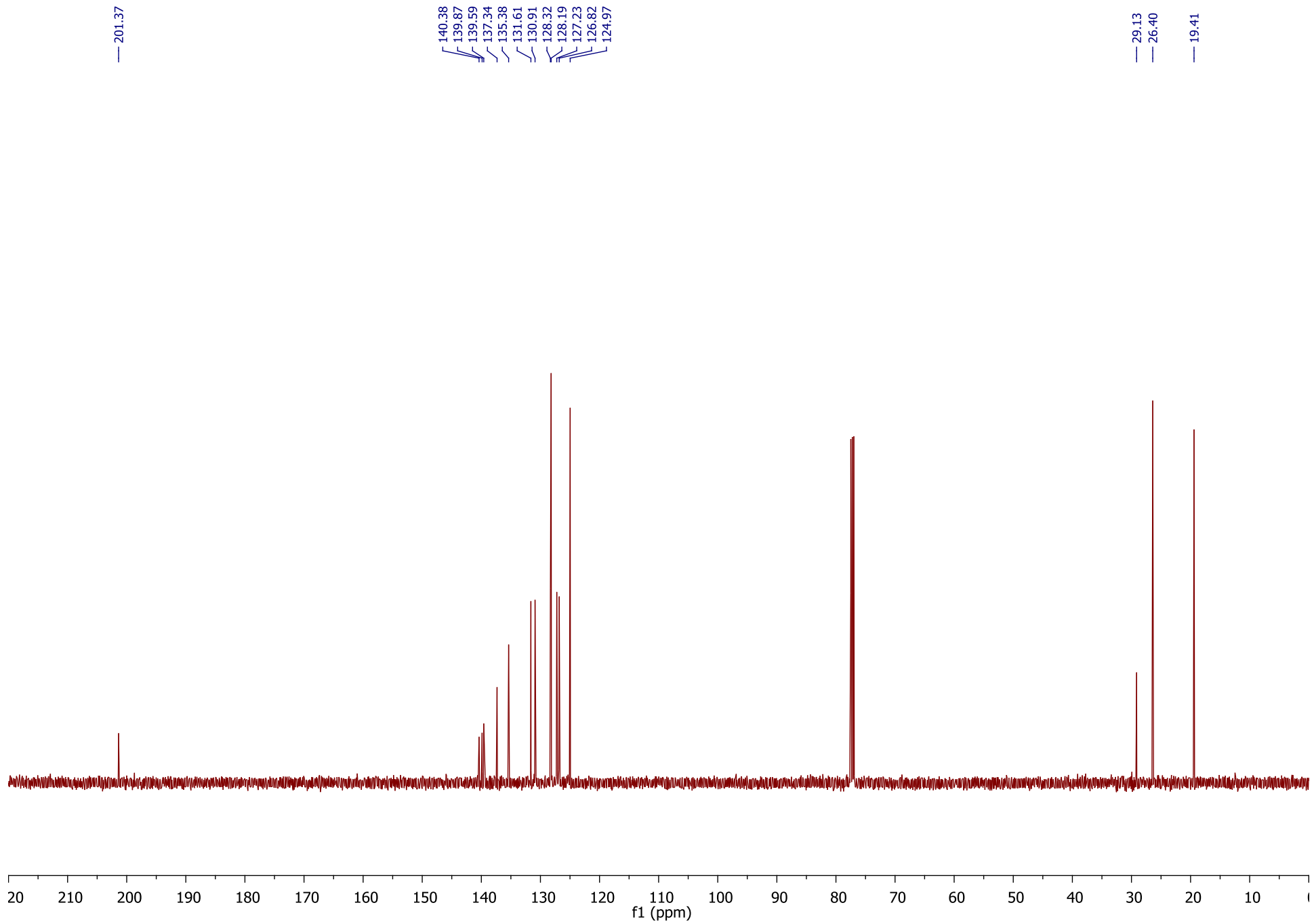


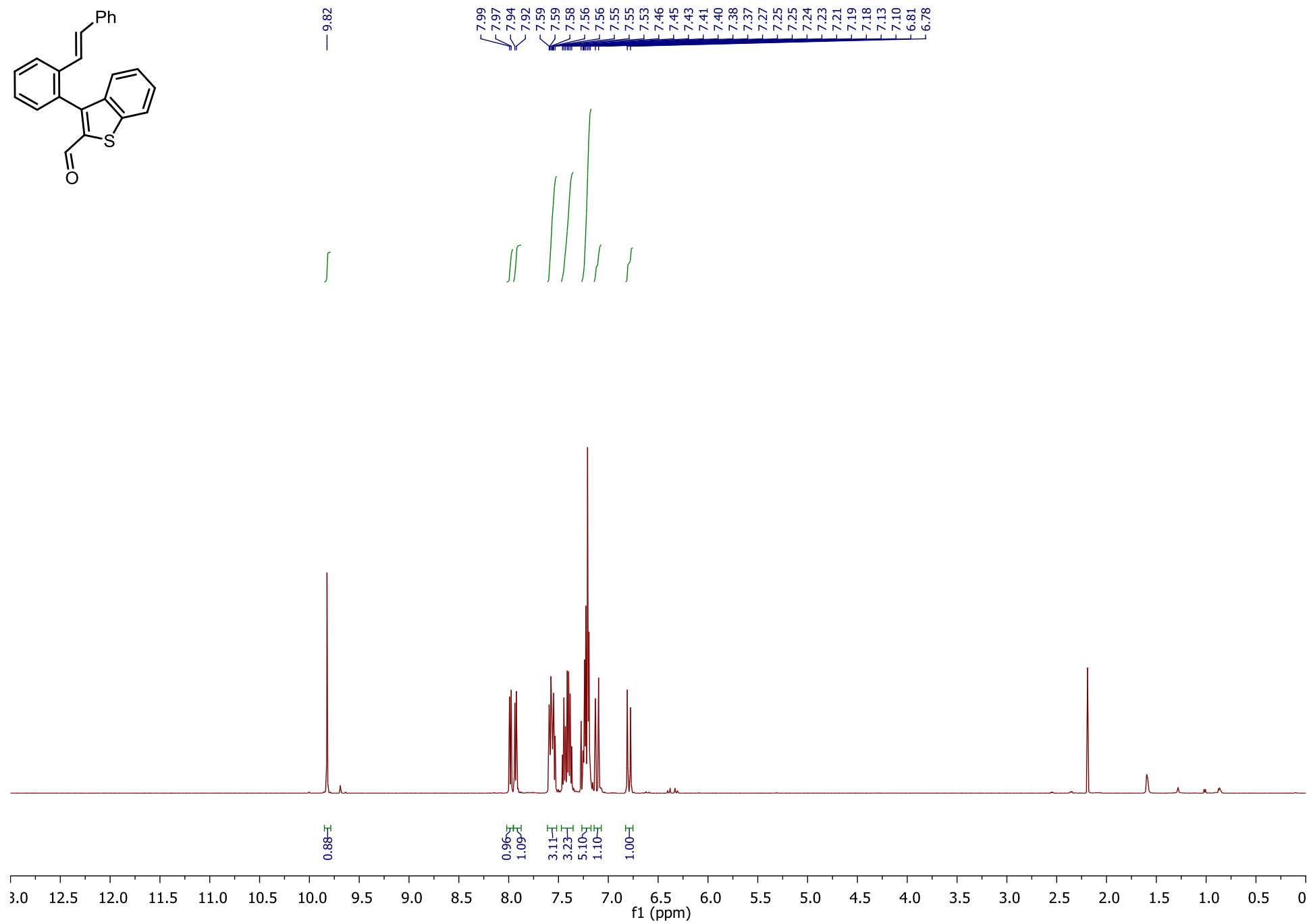
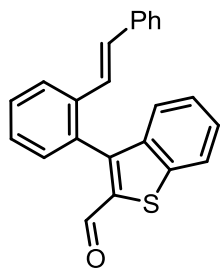
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7.08
7.06

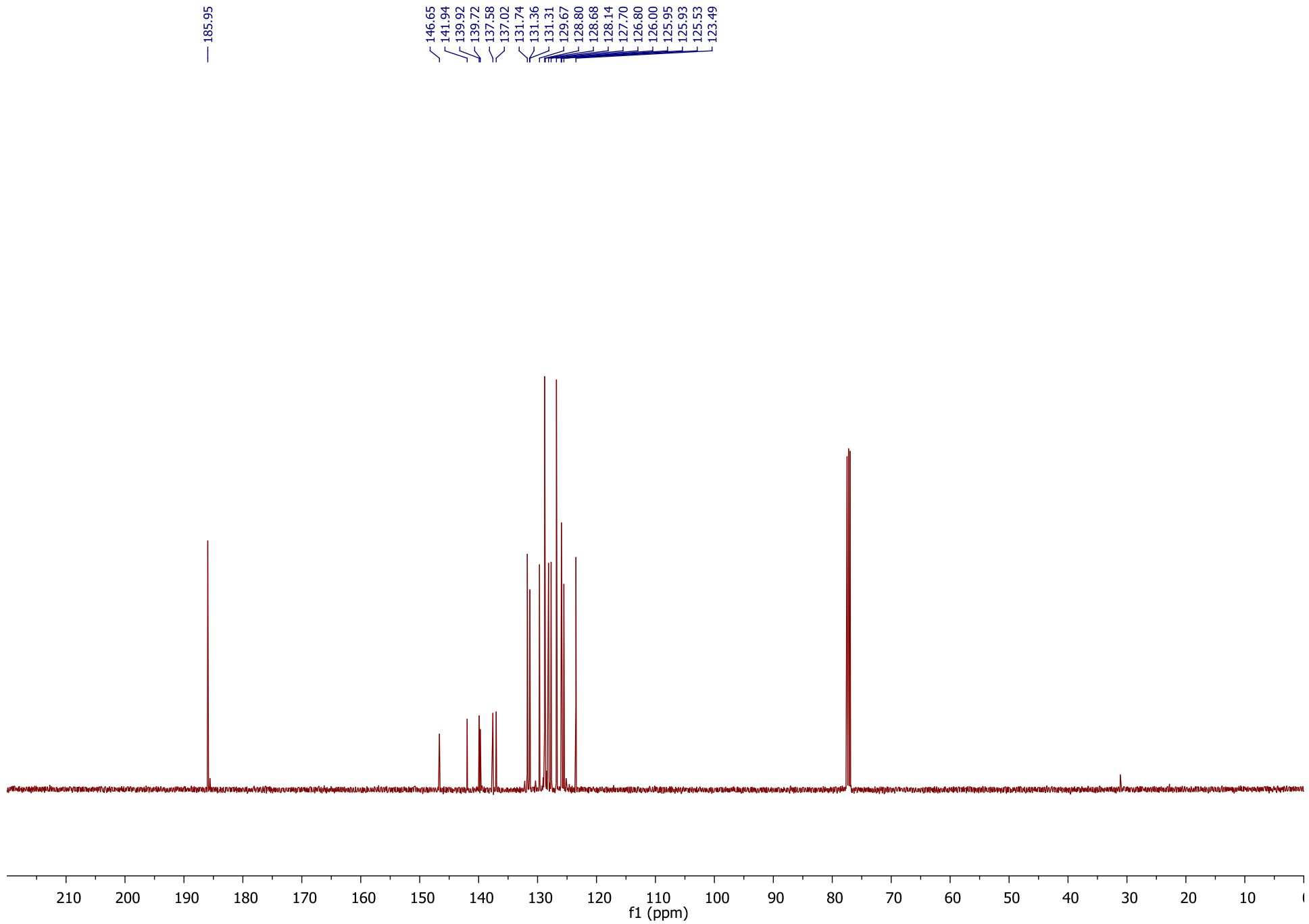
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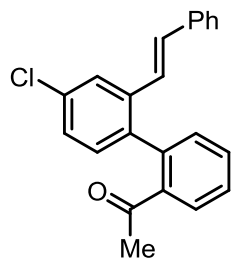
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1.75
1.66





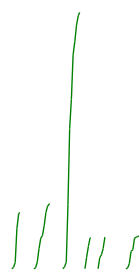






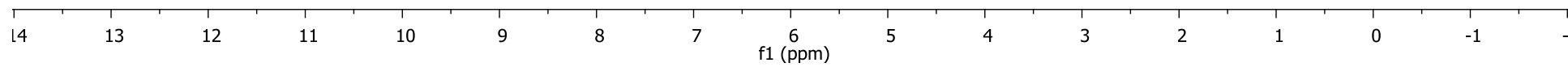
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6.78
6.75

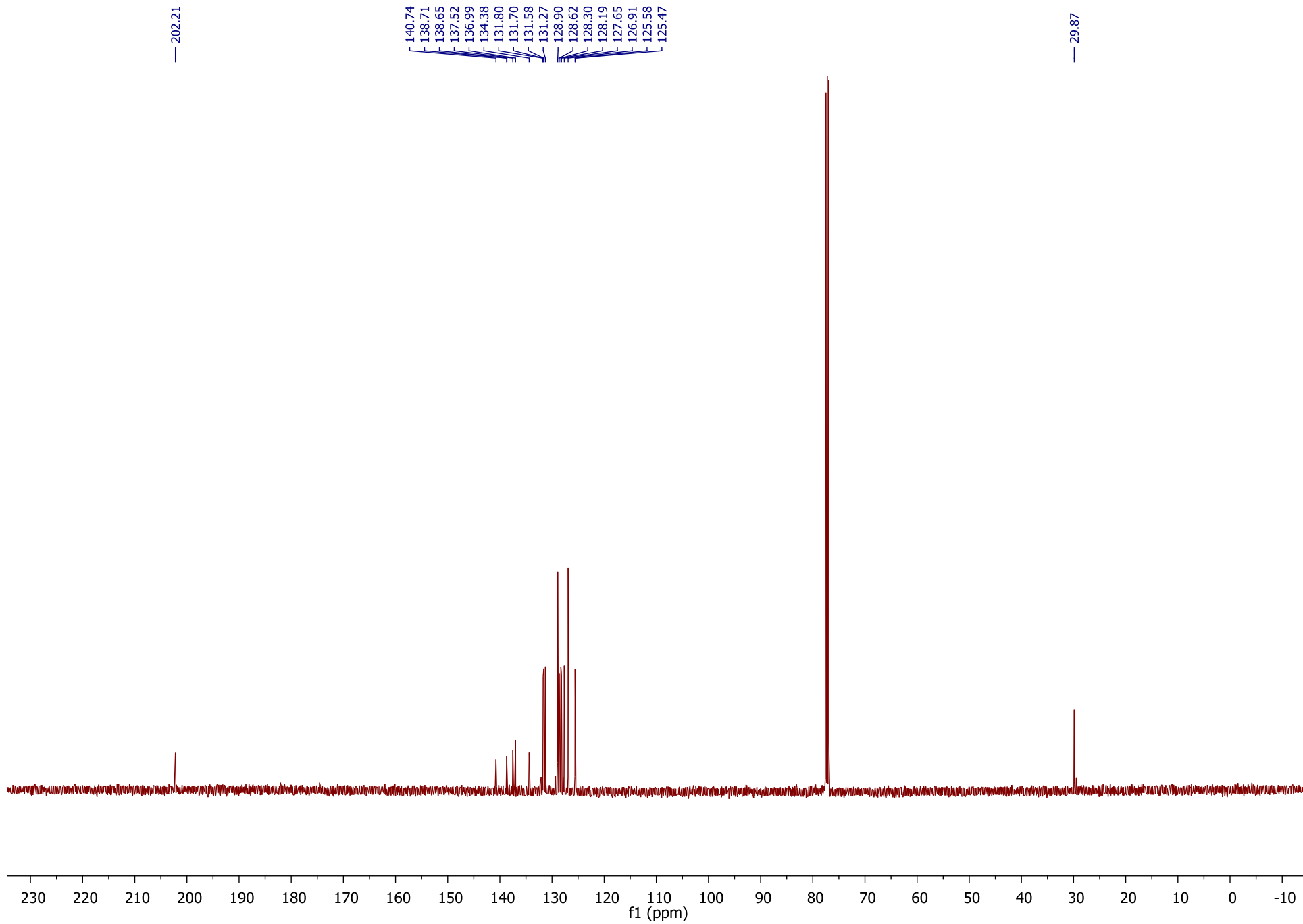
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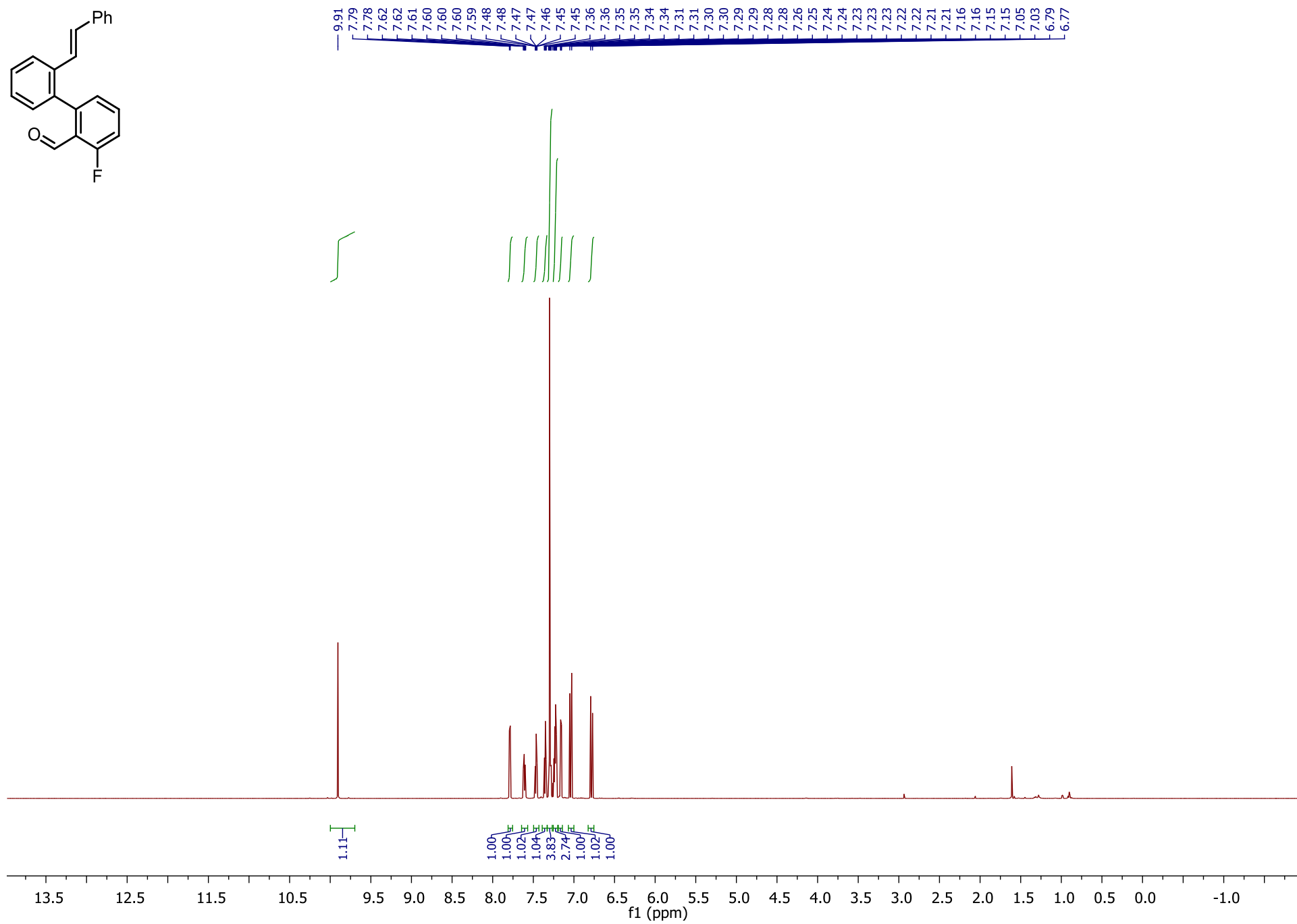
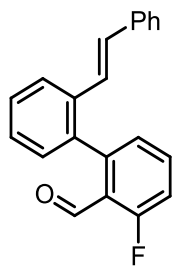


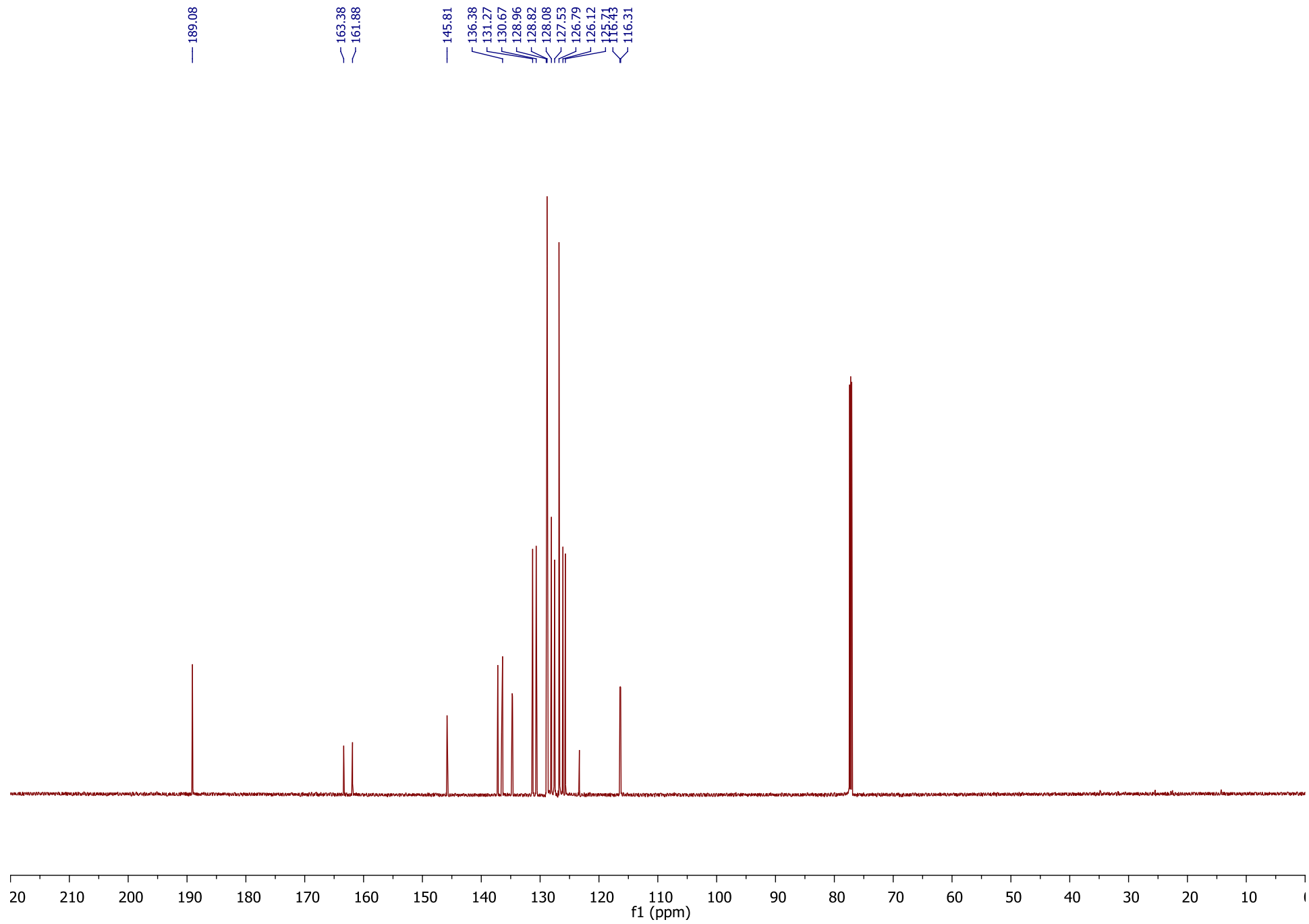
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1.00
1.04

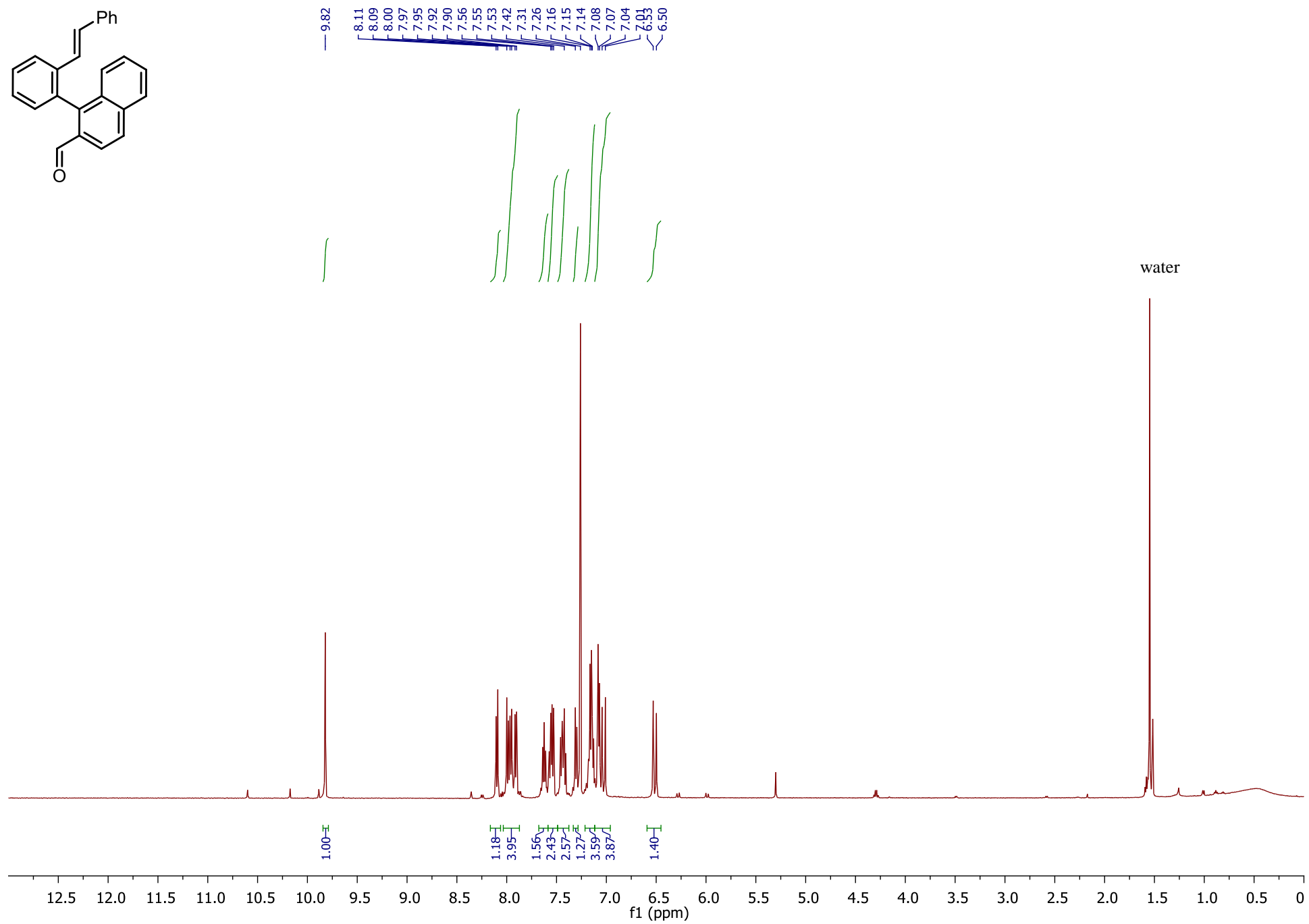
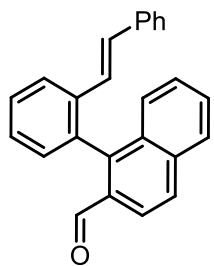
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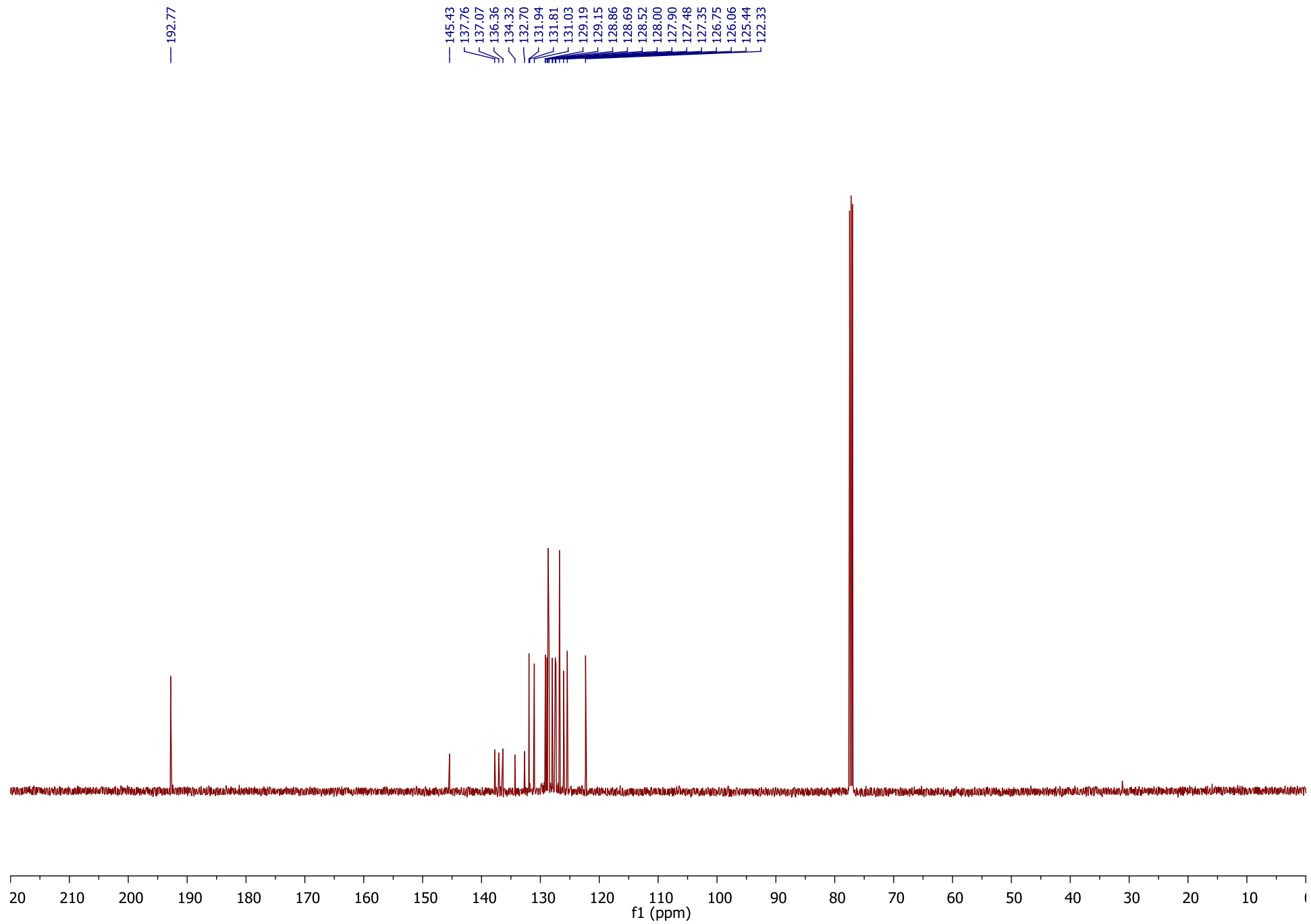


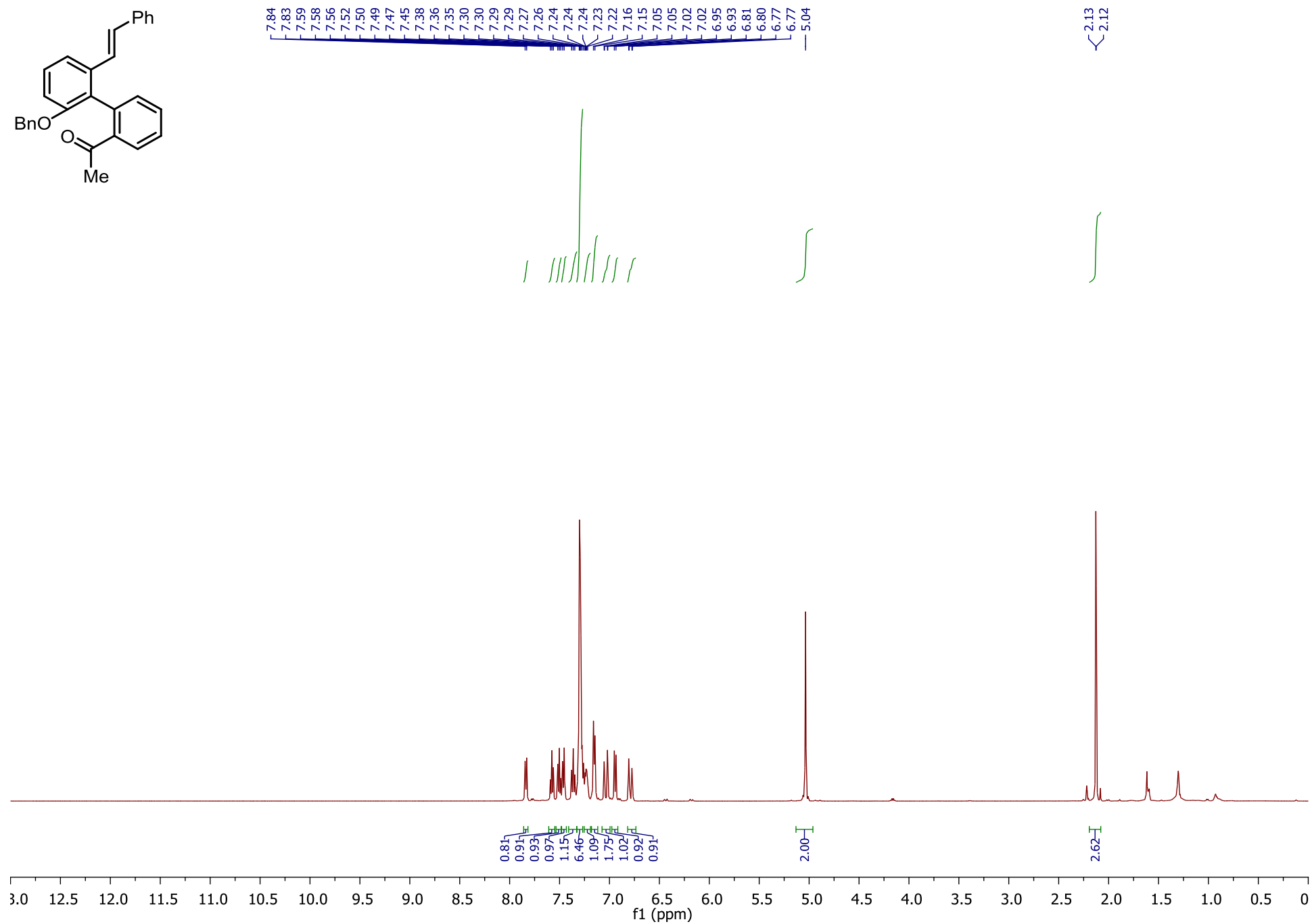
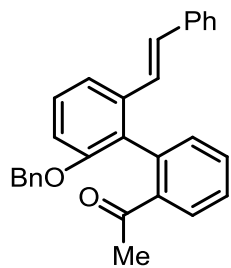


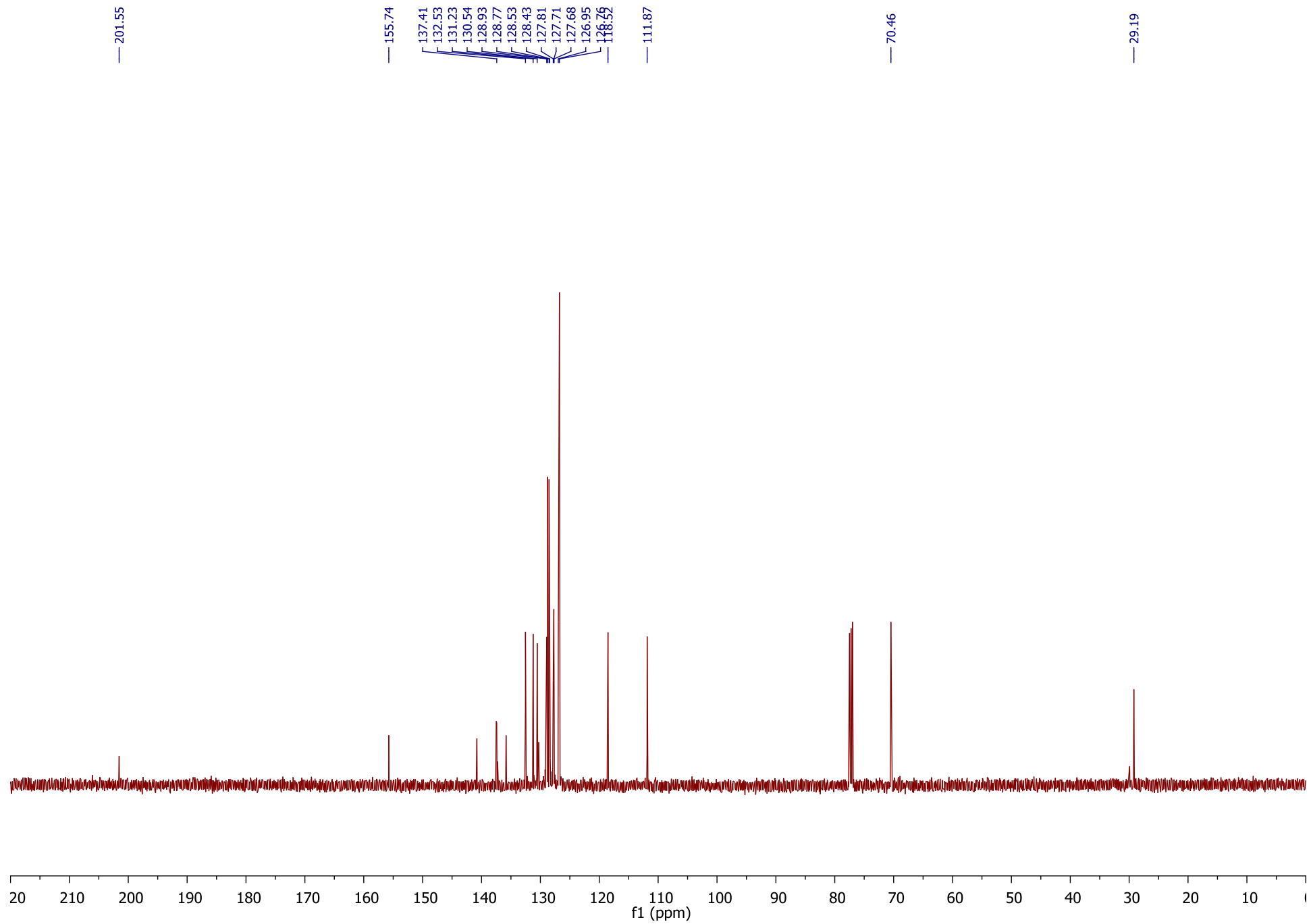


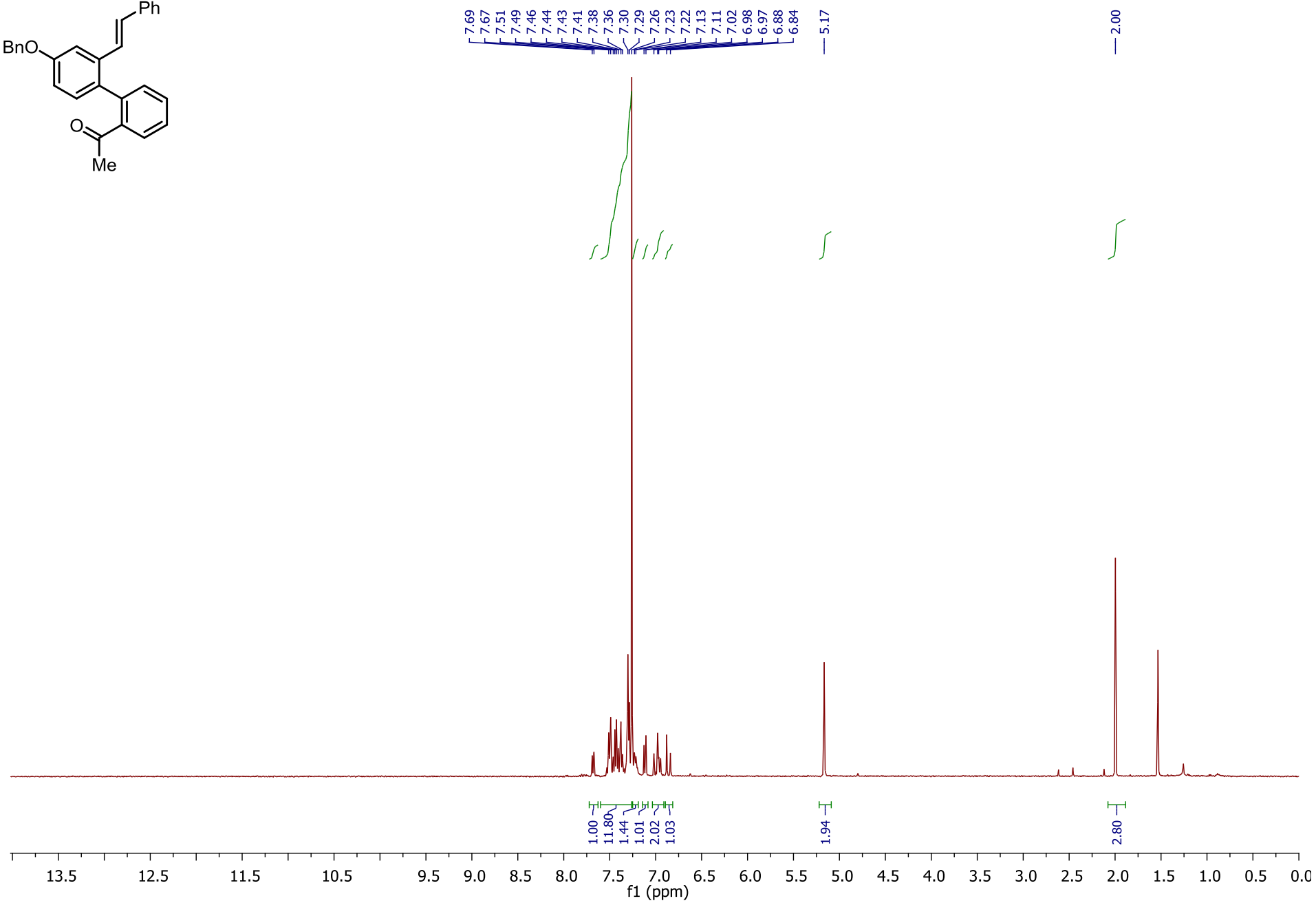
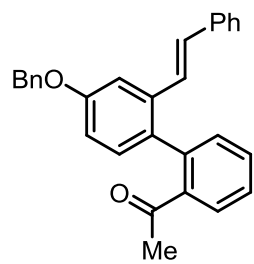


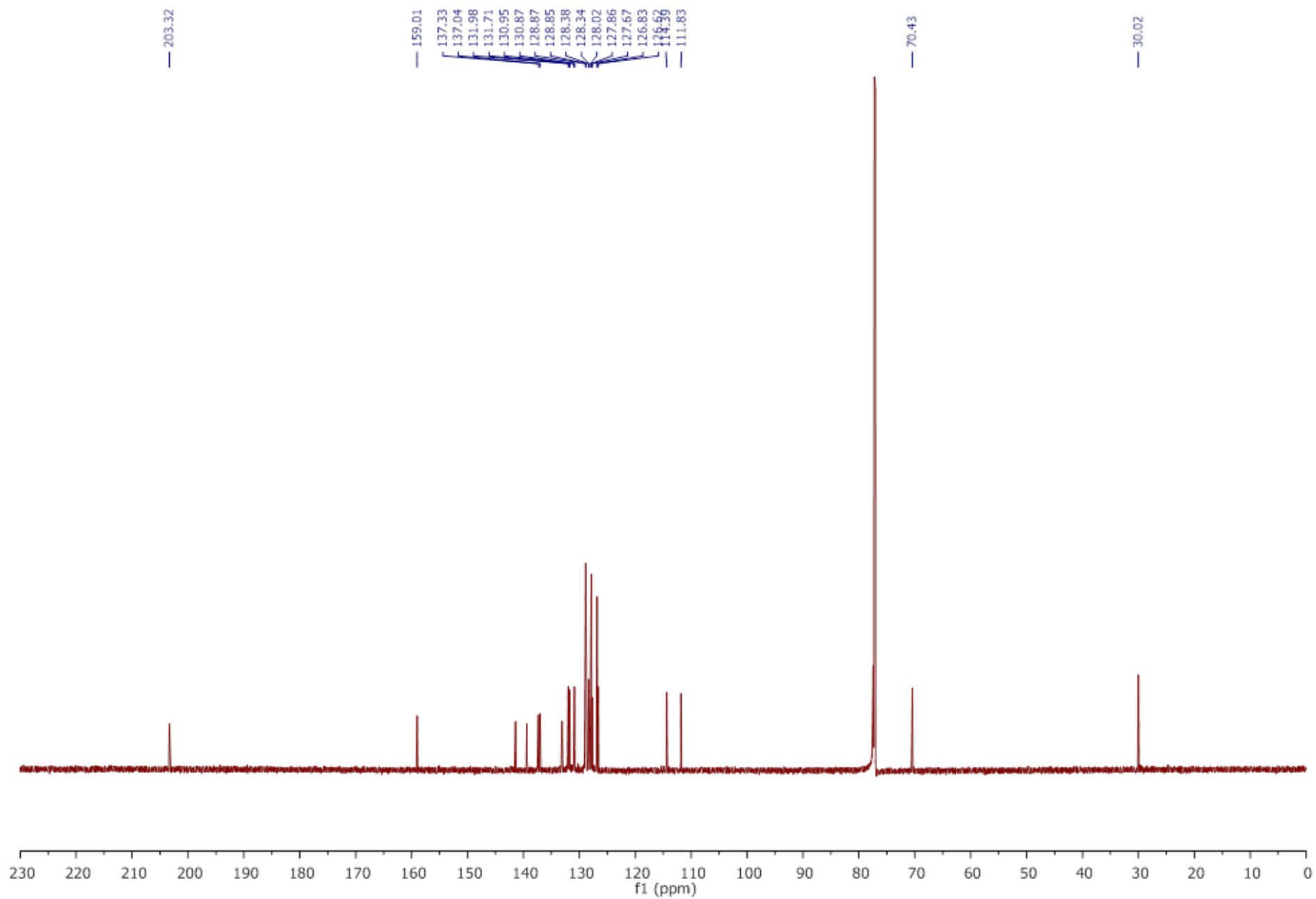


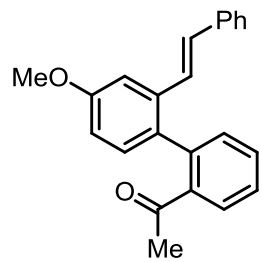




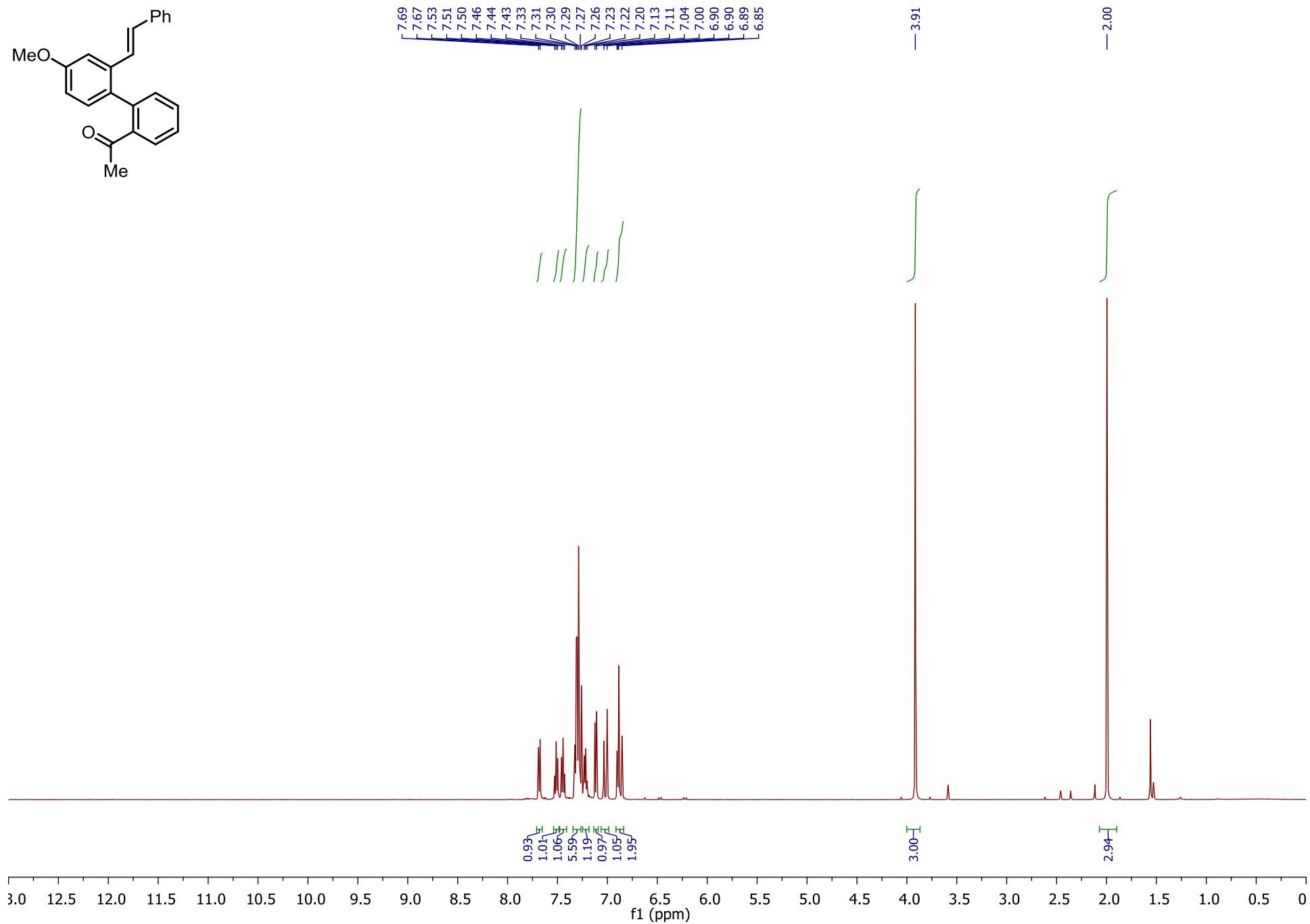


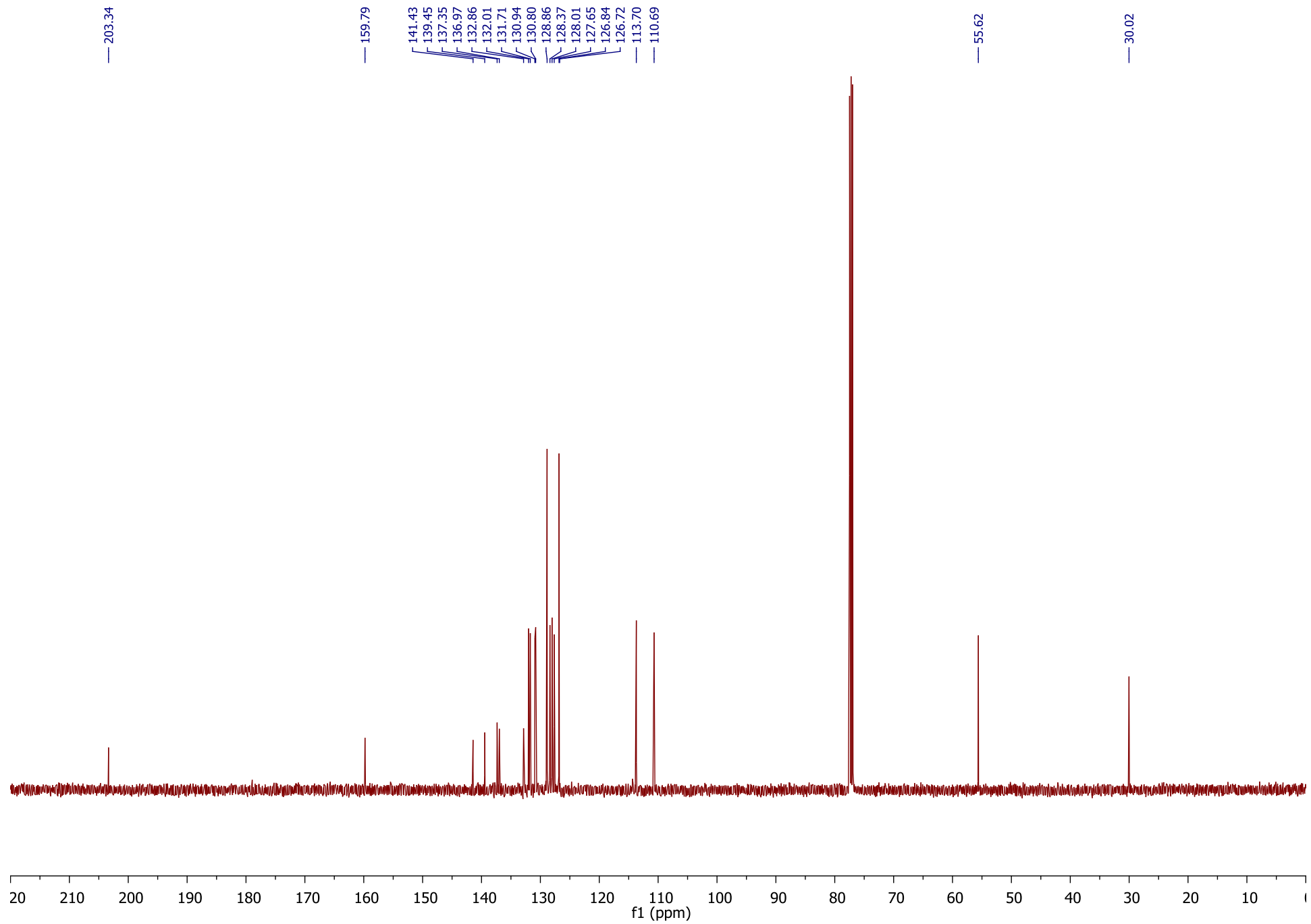


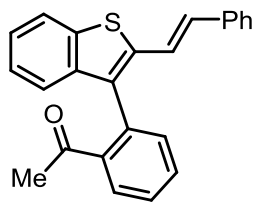




7.69
7.67
7.53
7.51
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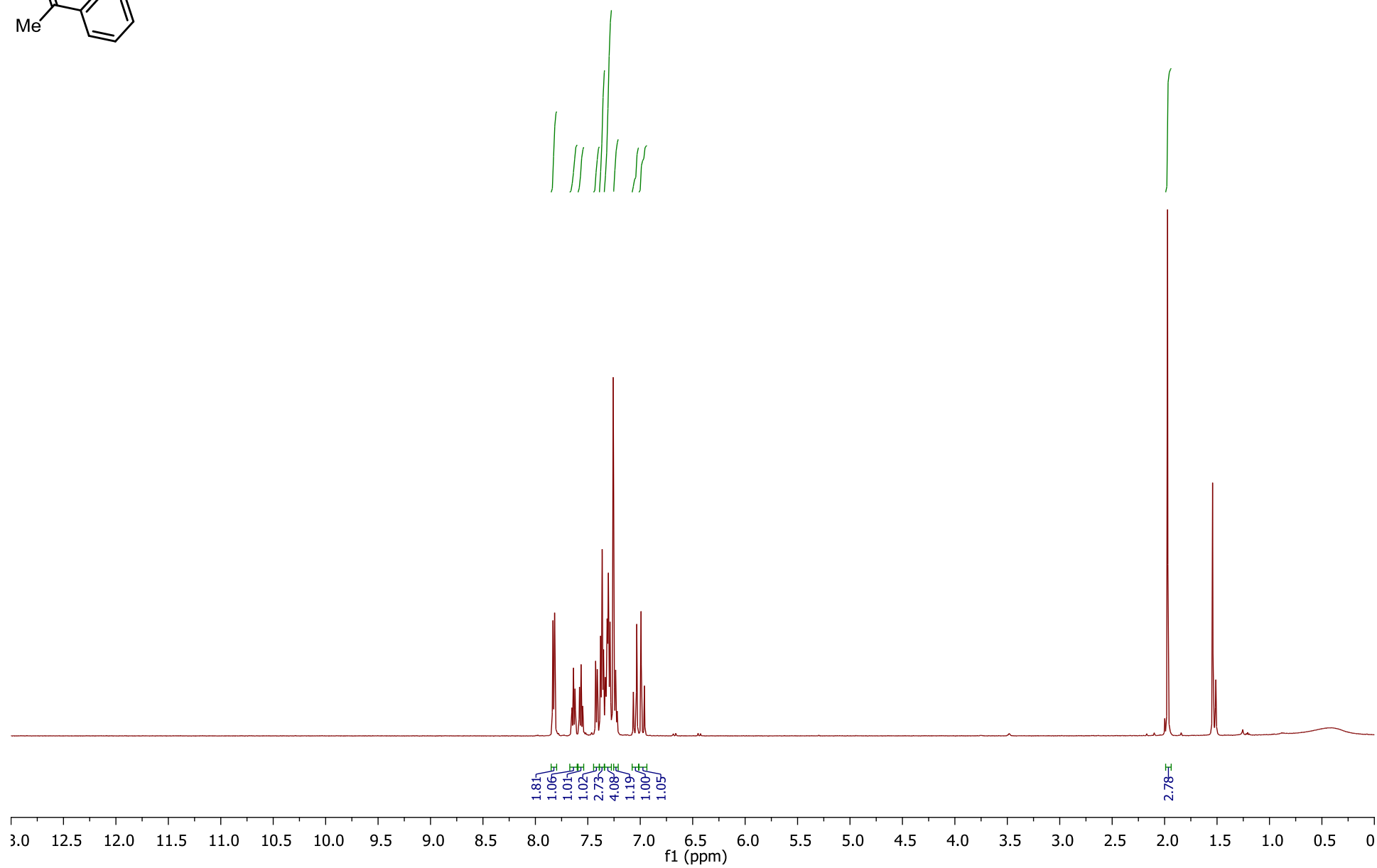


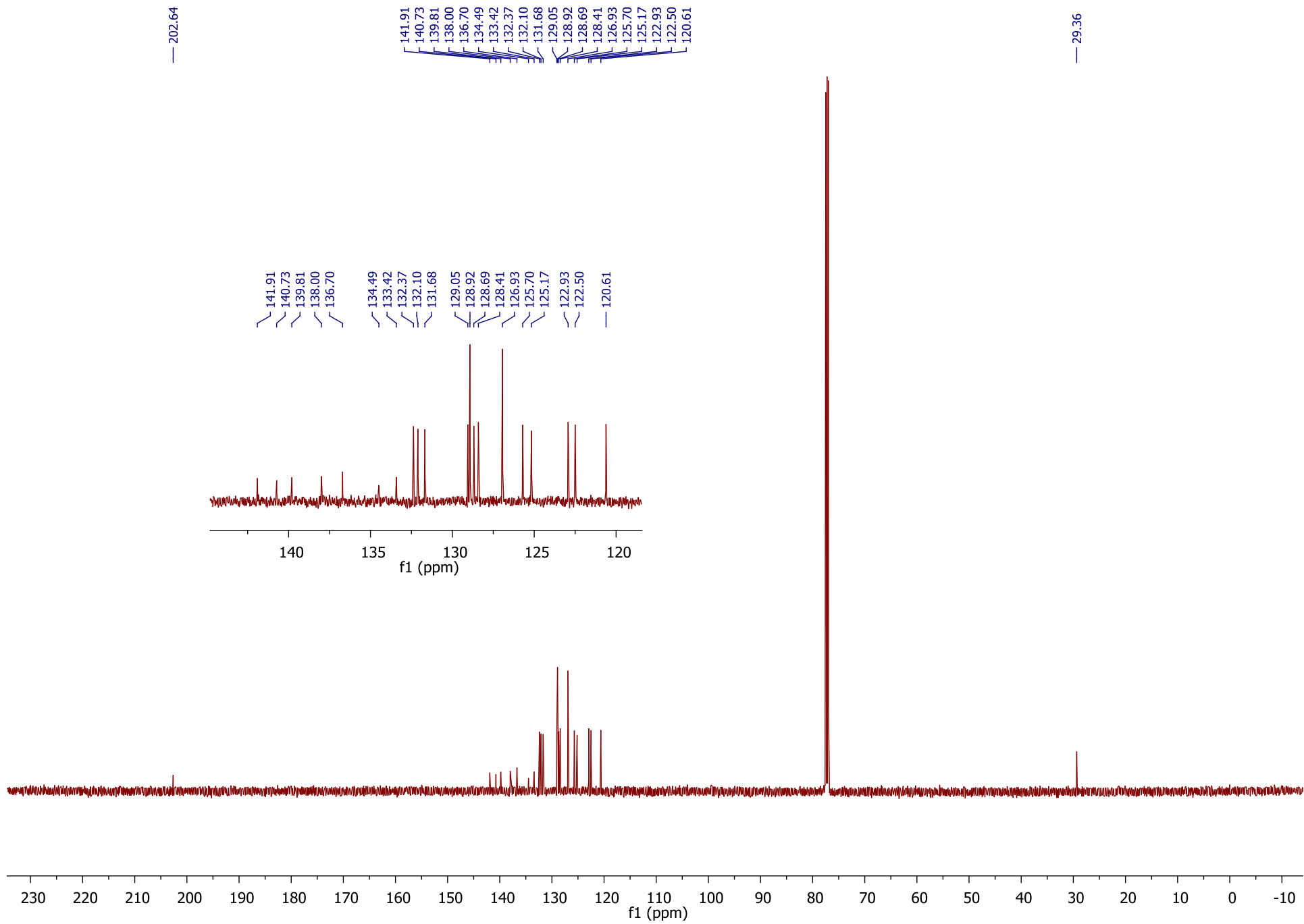


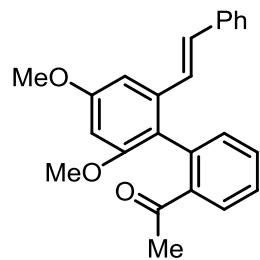


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1.97

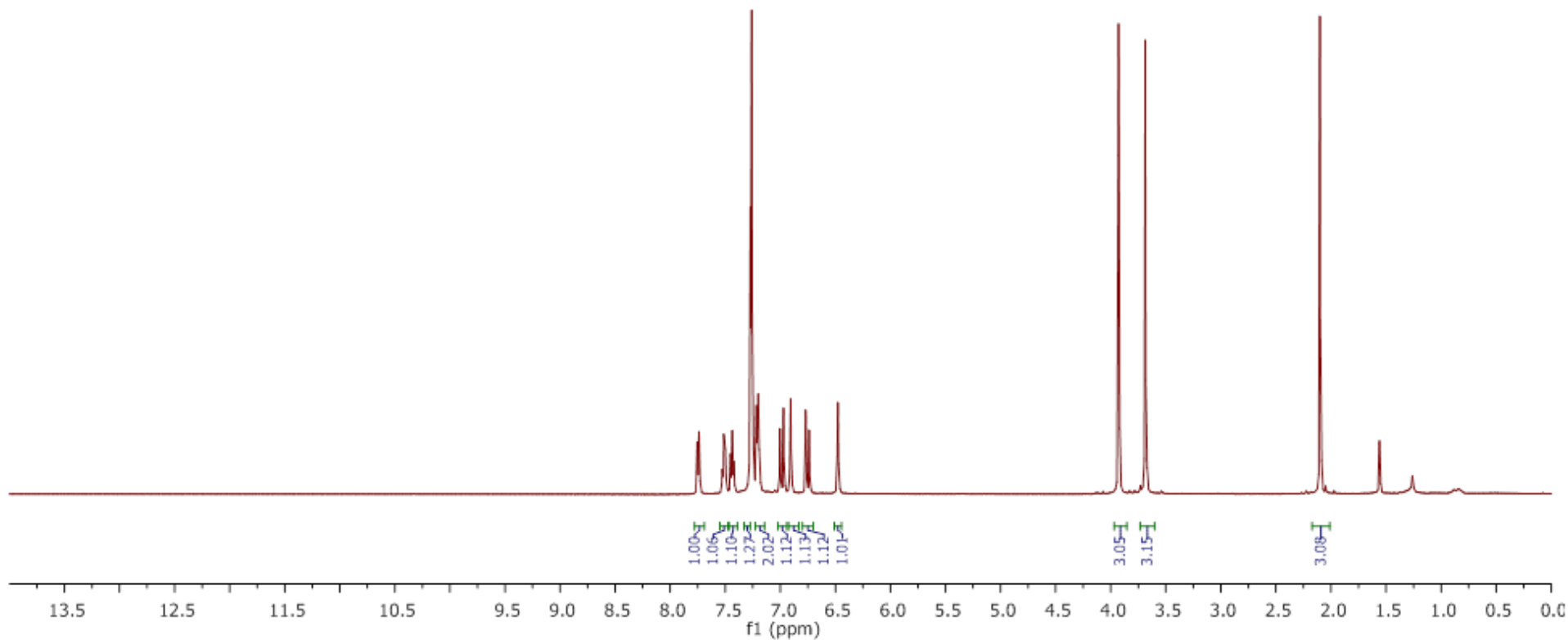


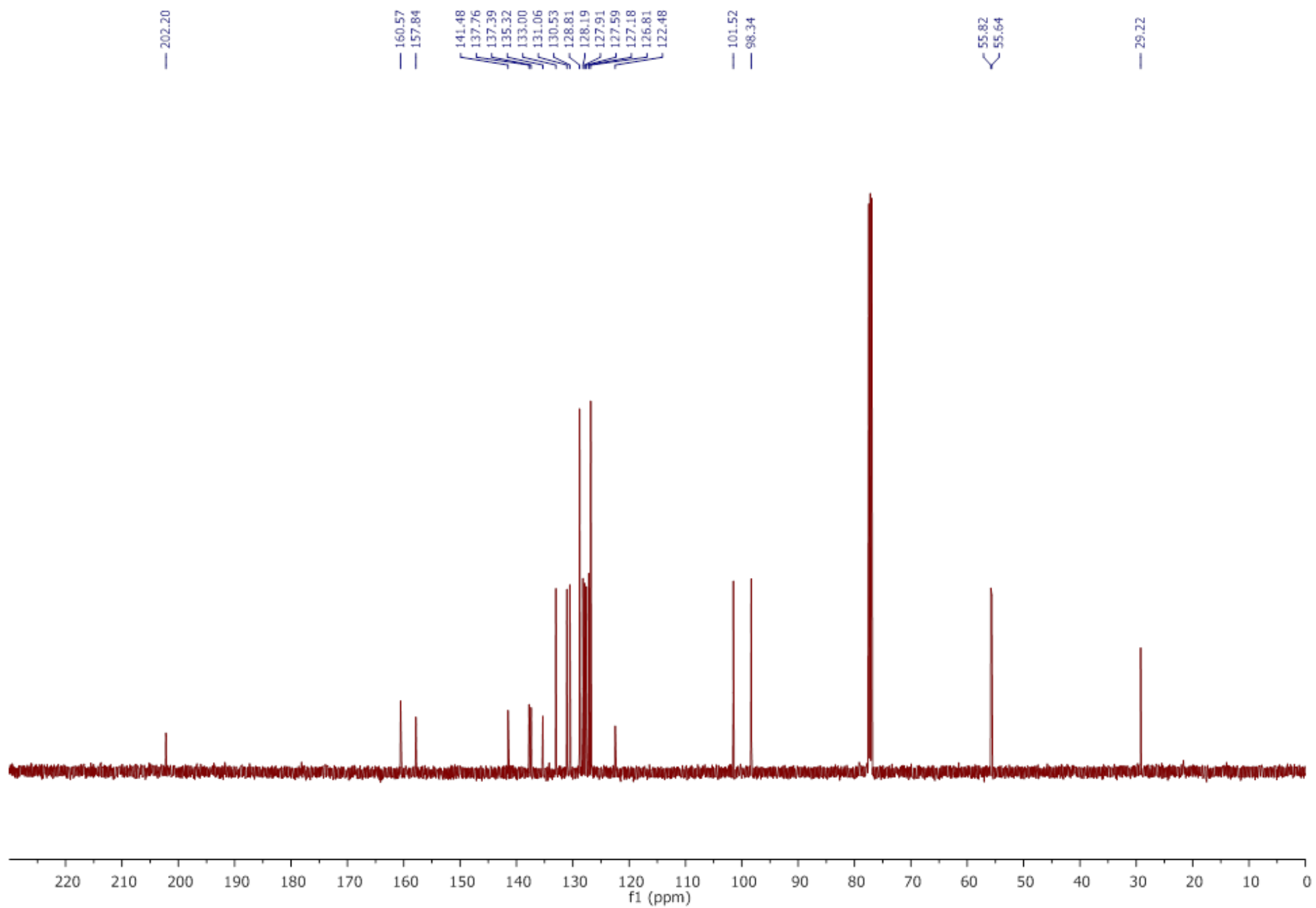


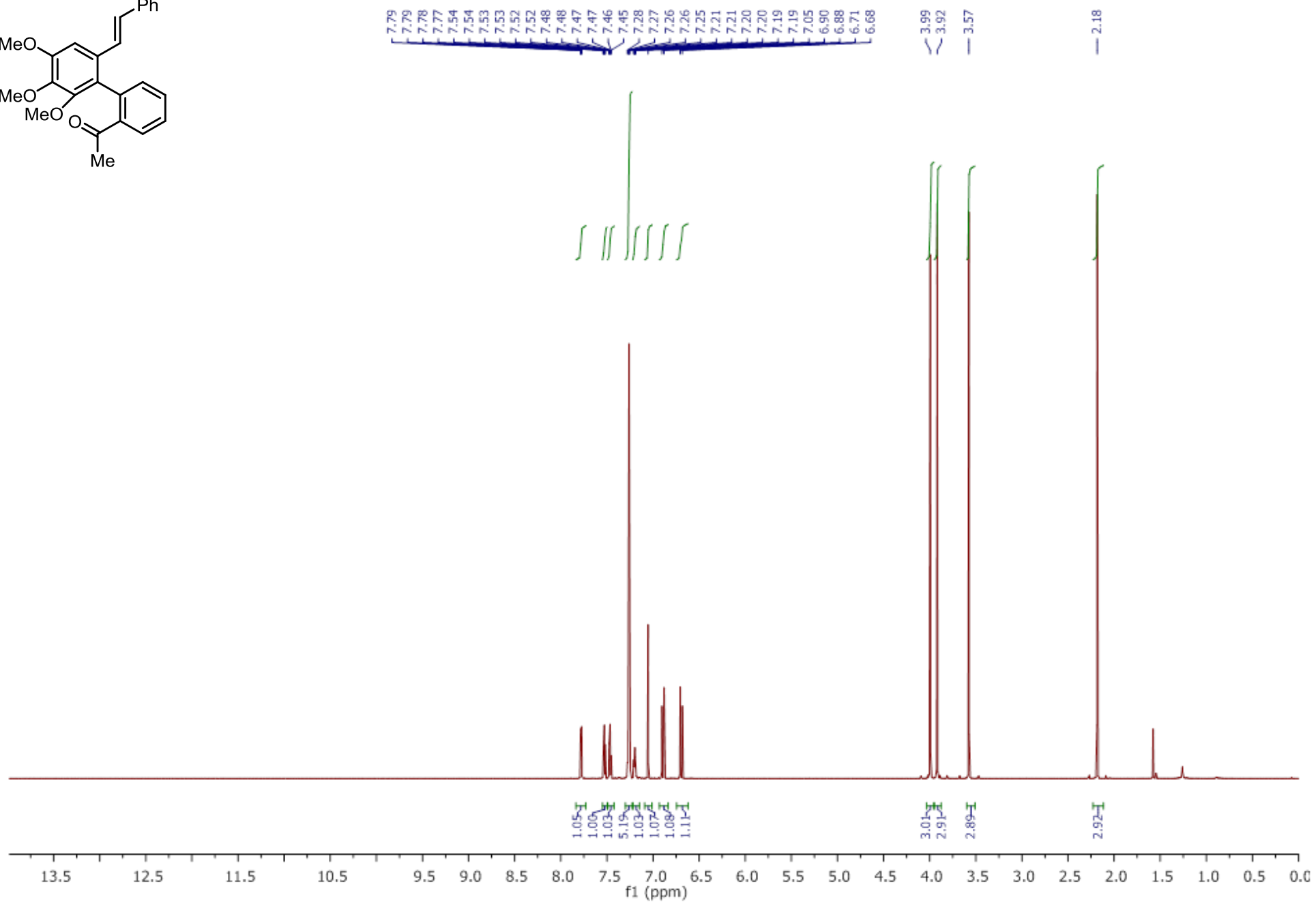
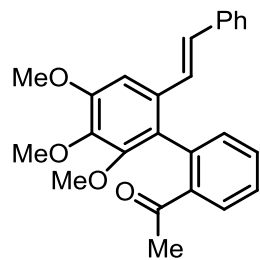


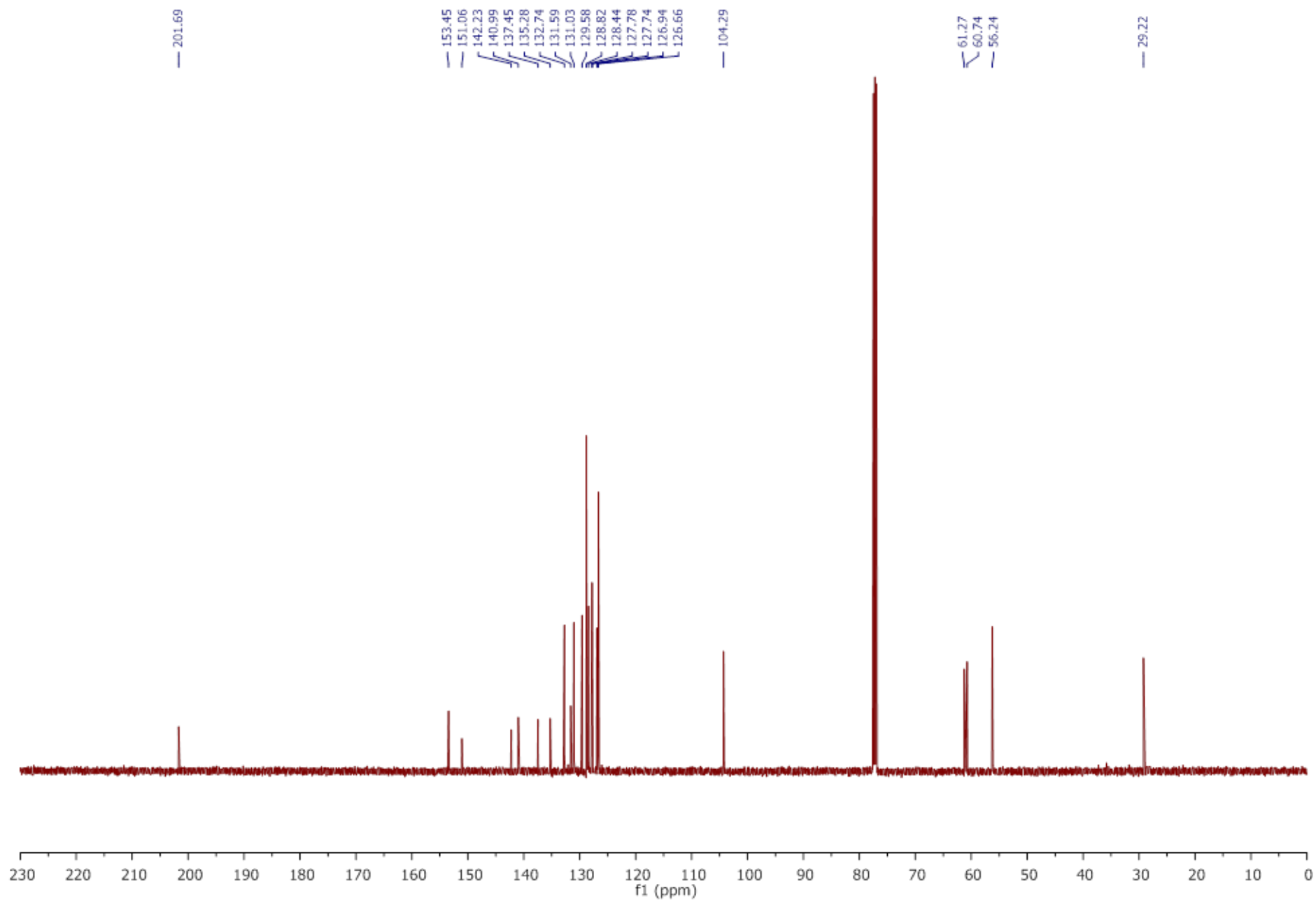
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6.48

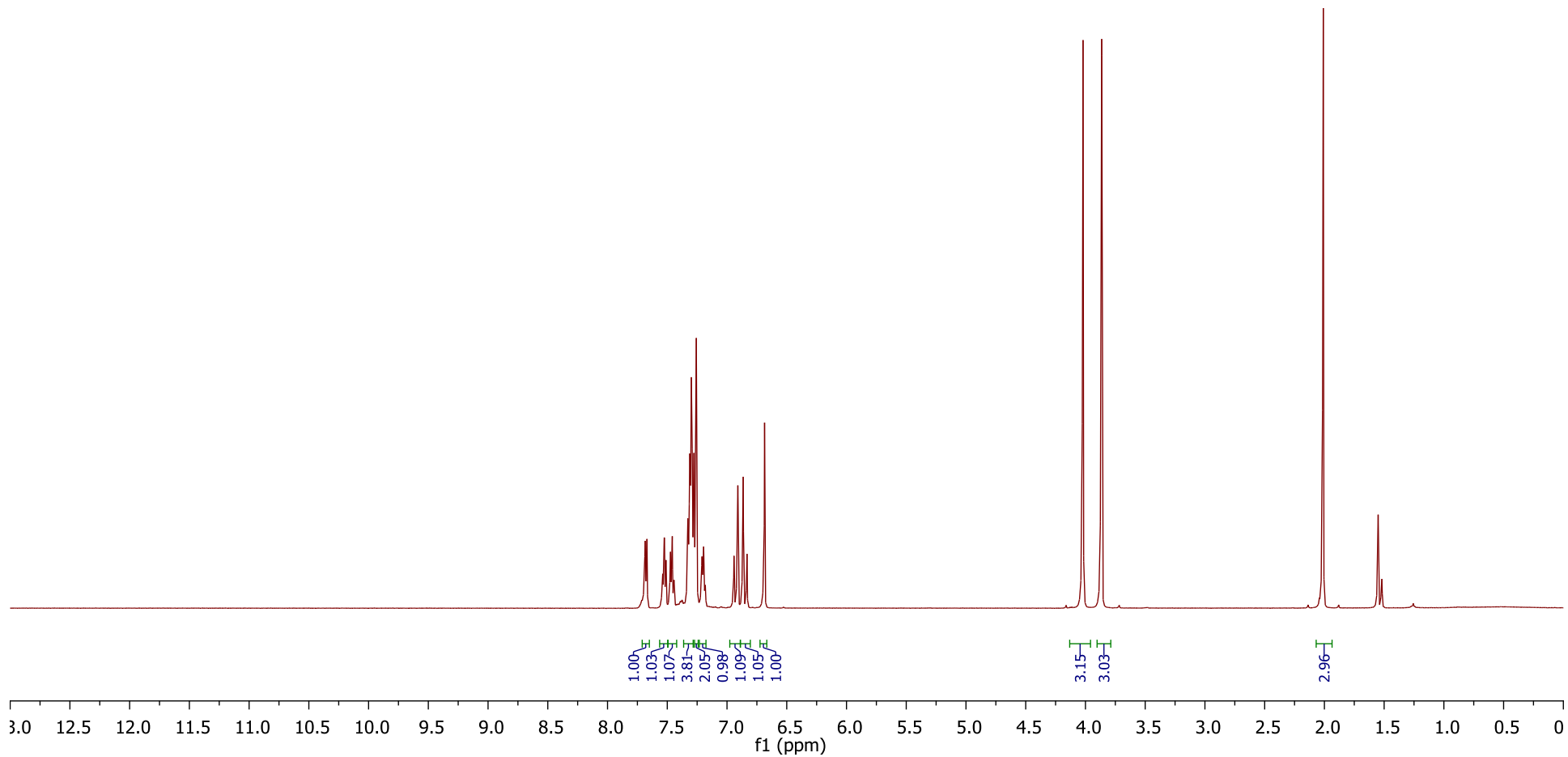
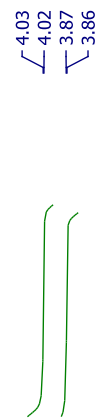
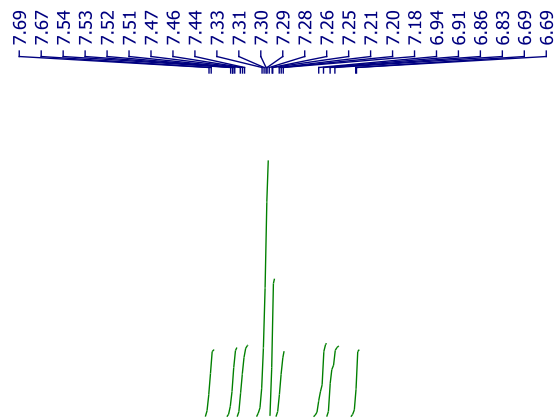
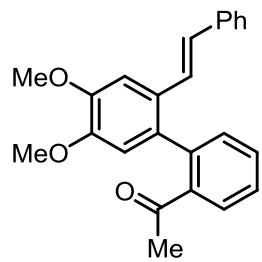
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3.69
2.10

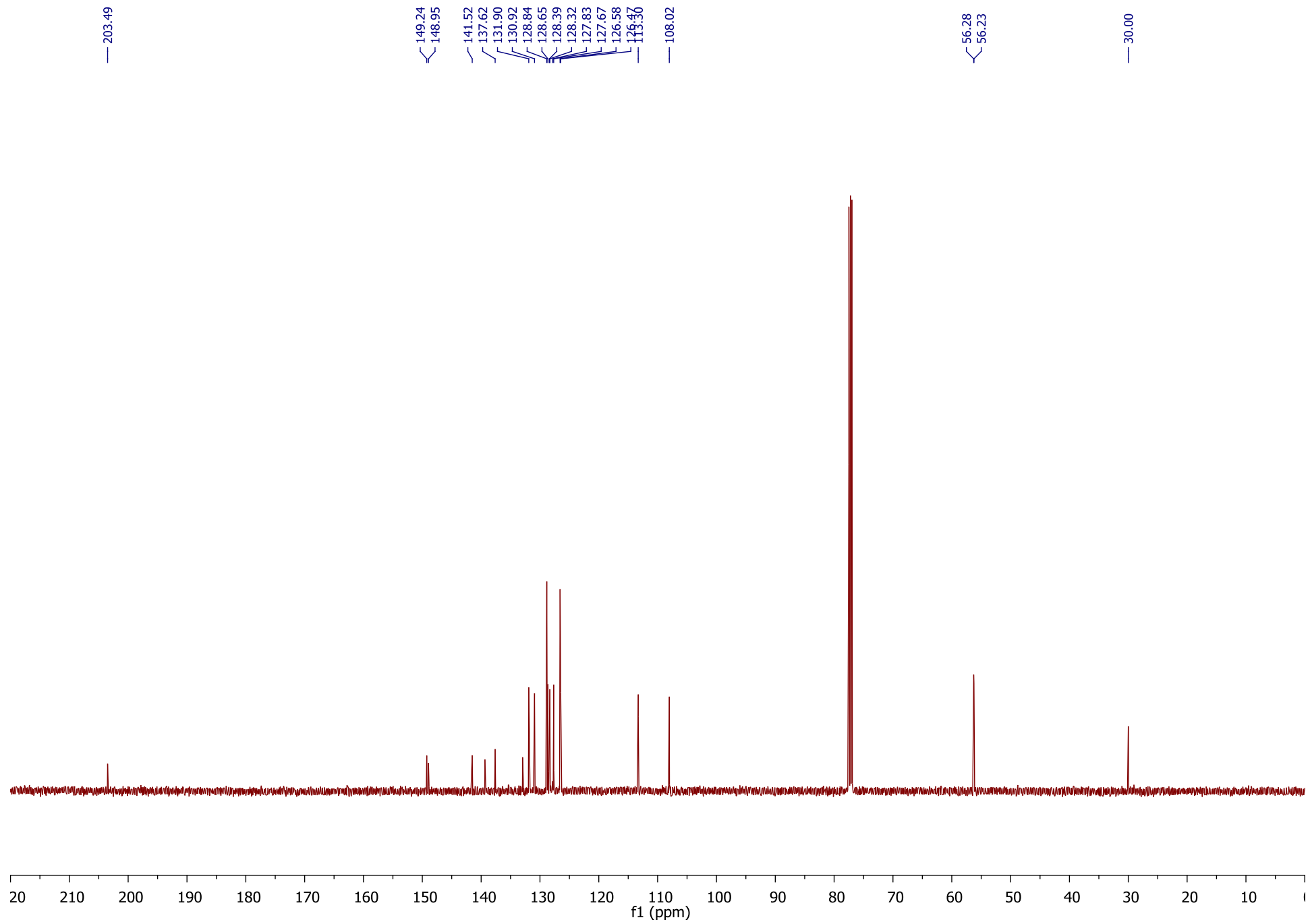


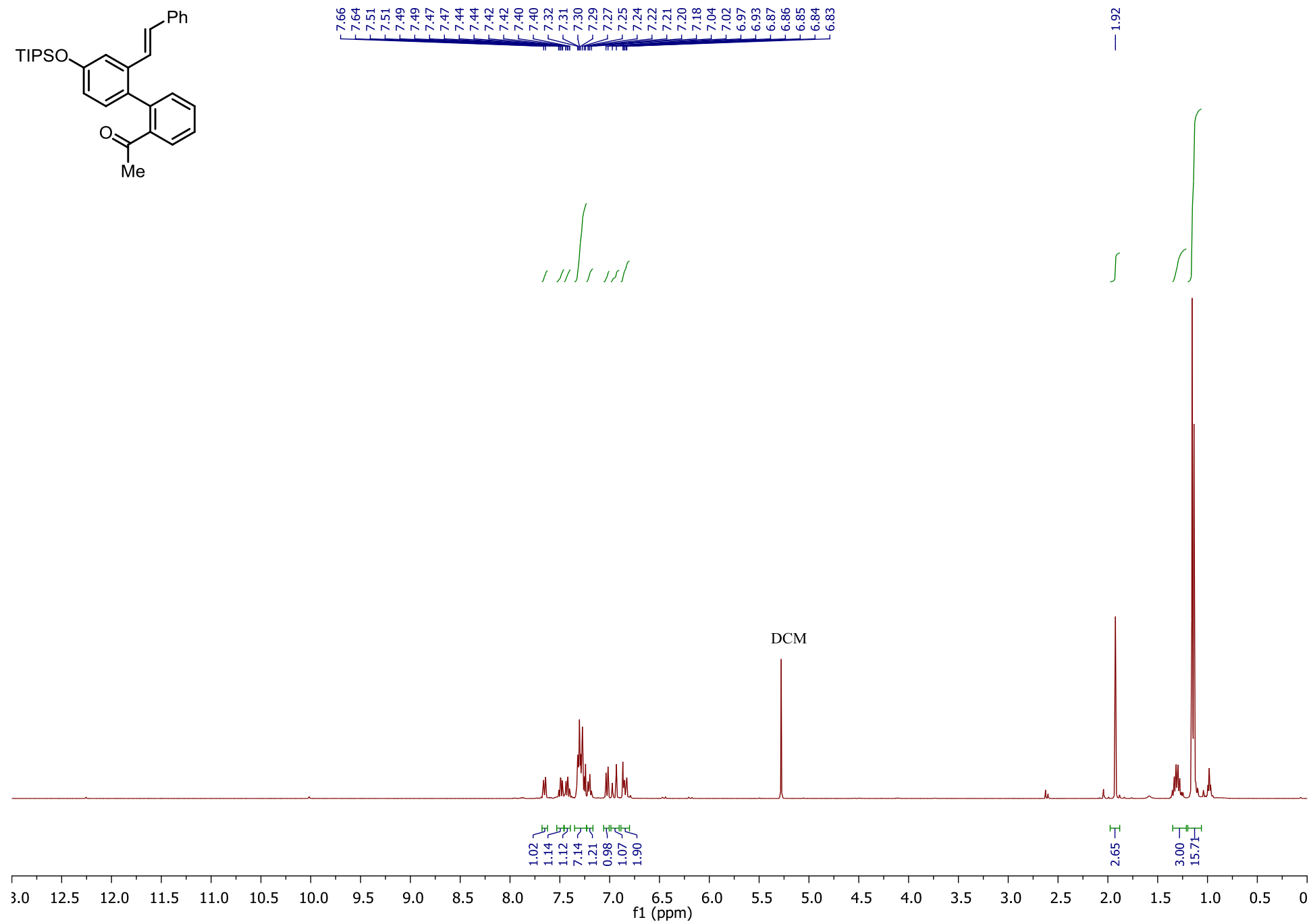
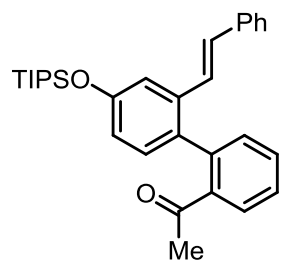


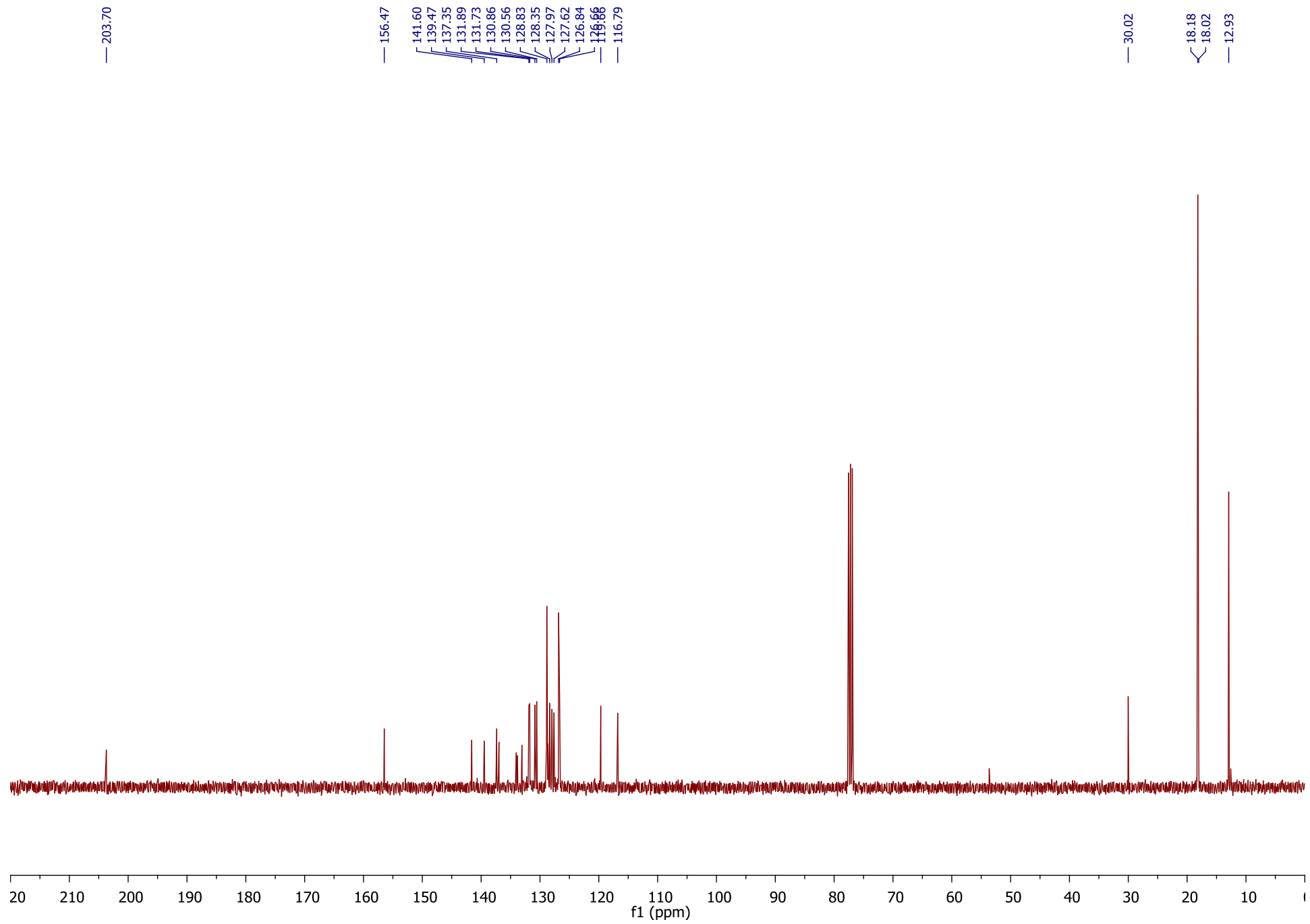


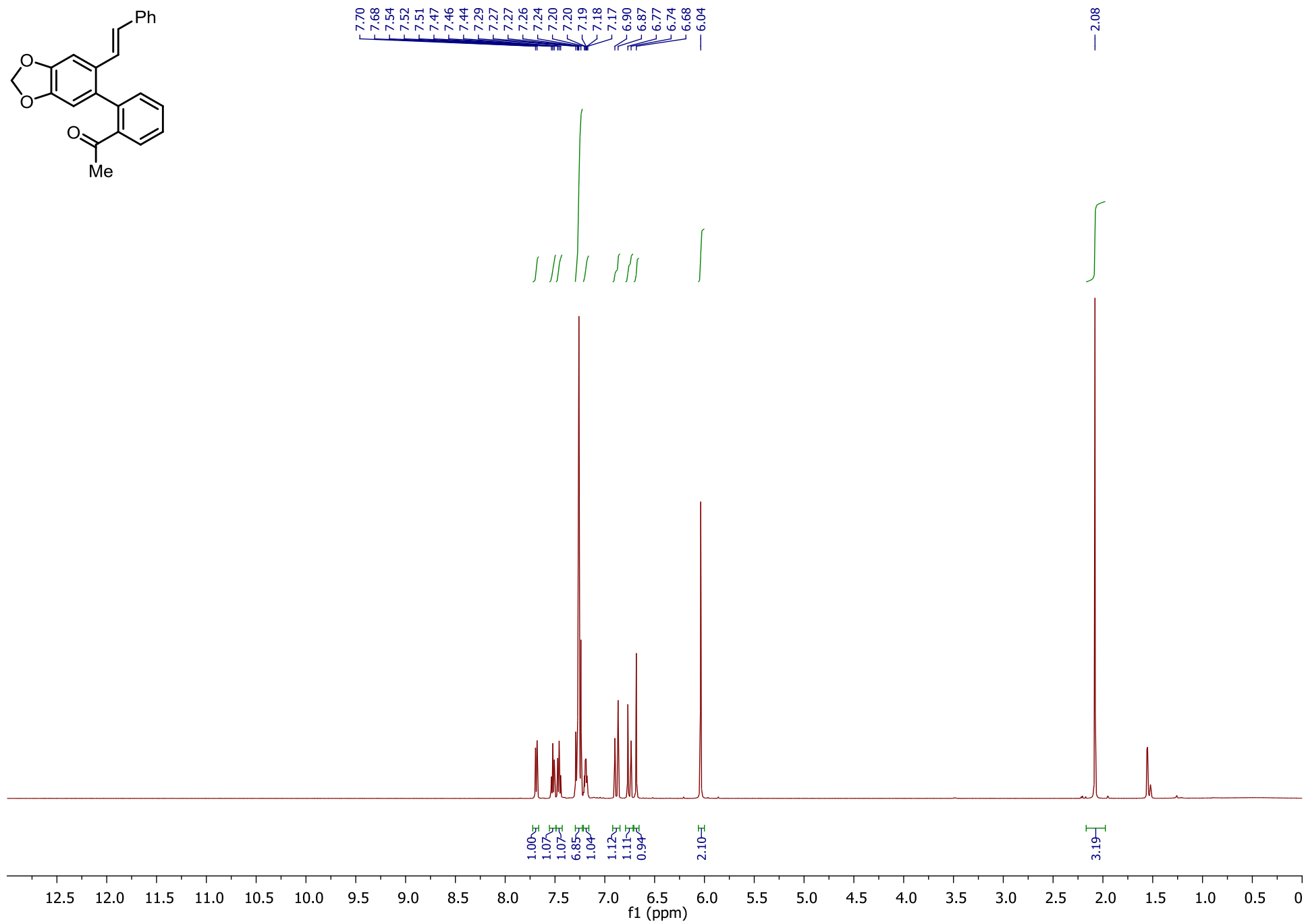
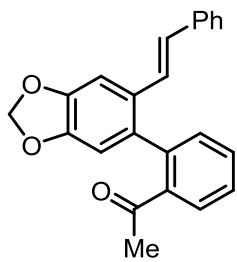


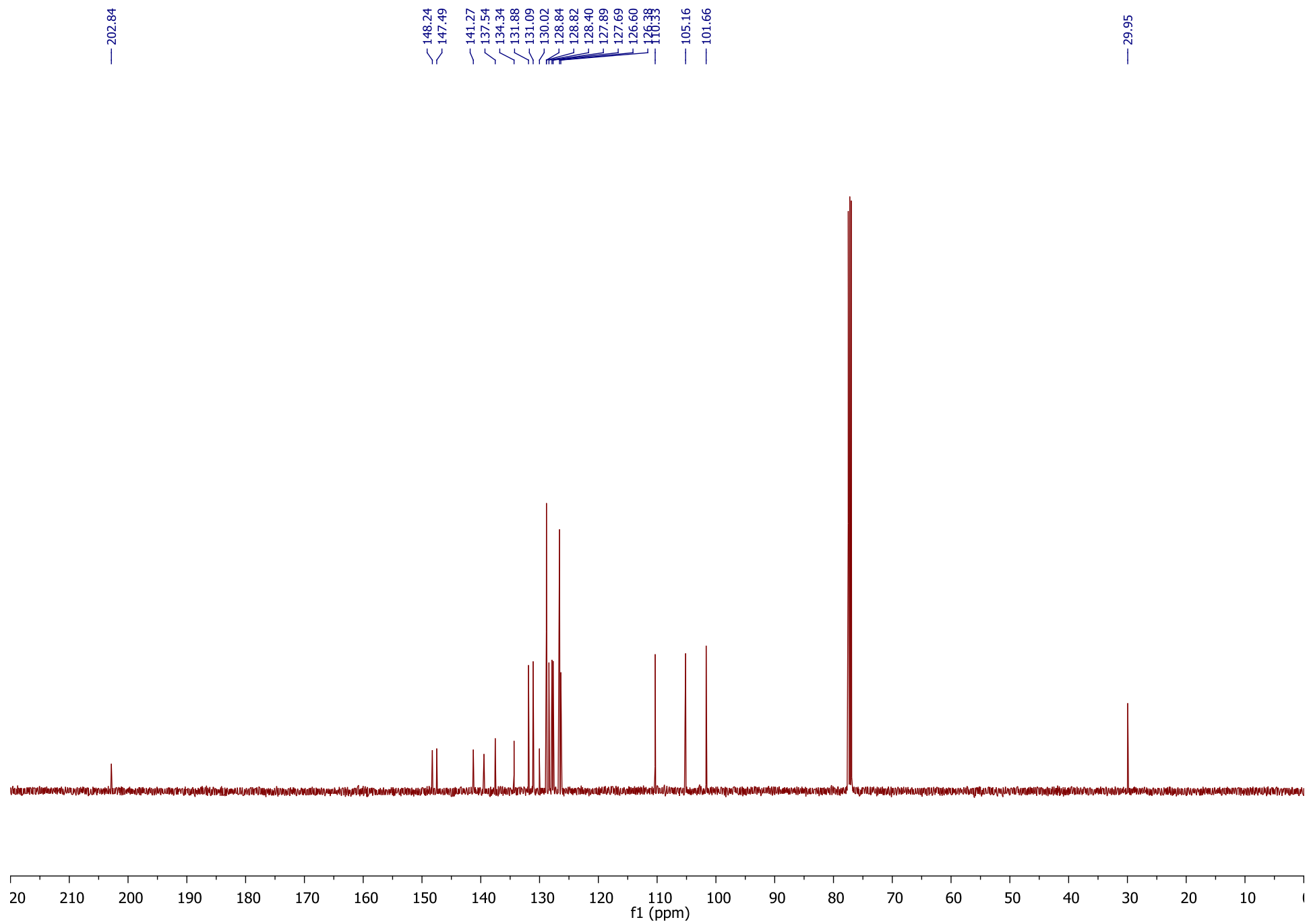


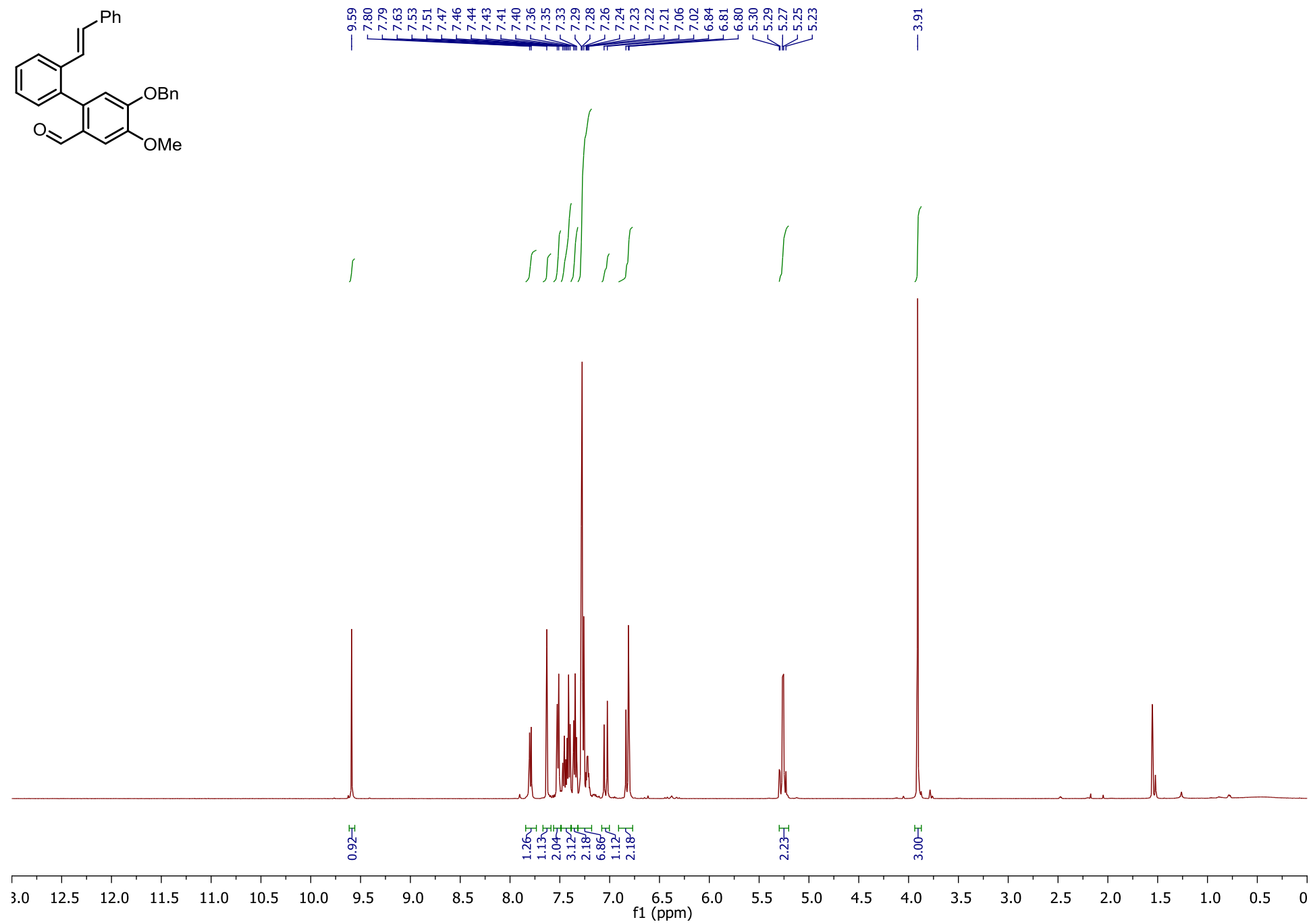
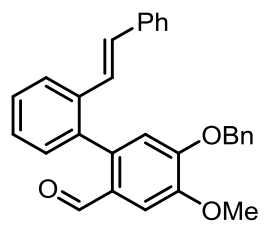


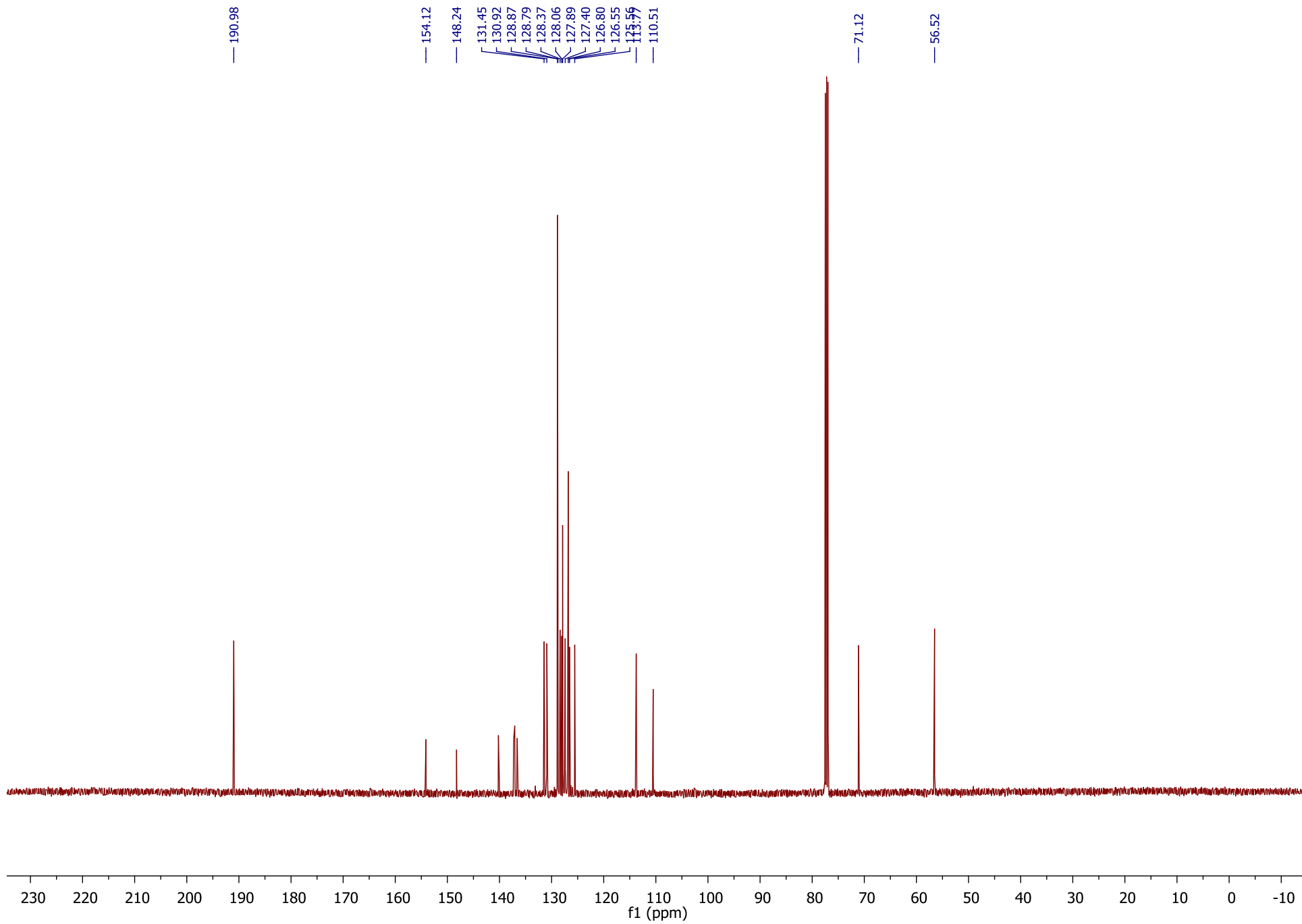


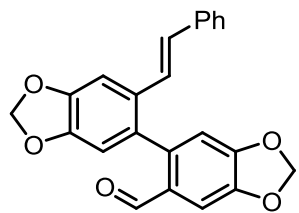




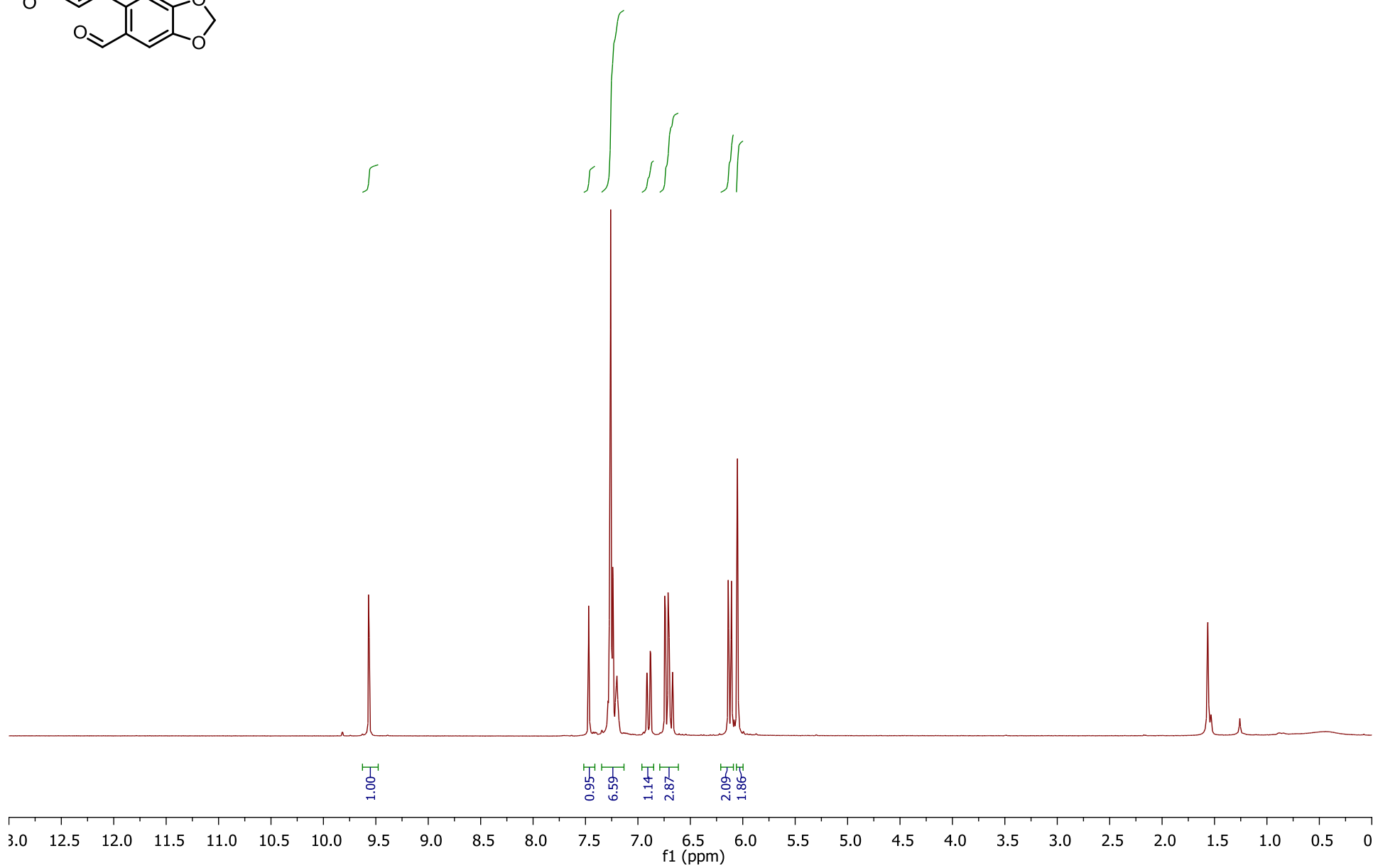


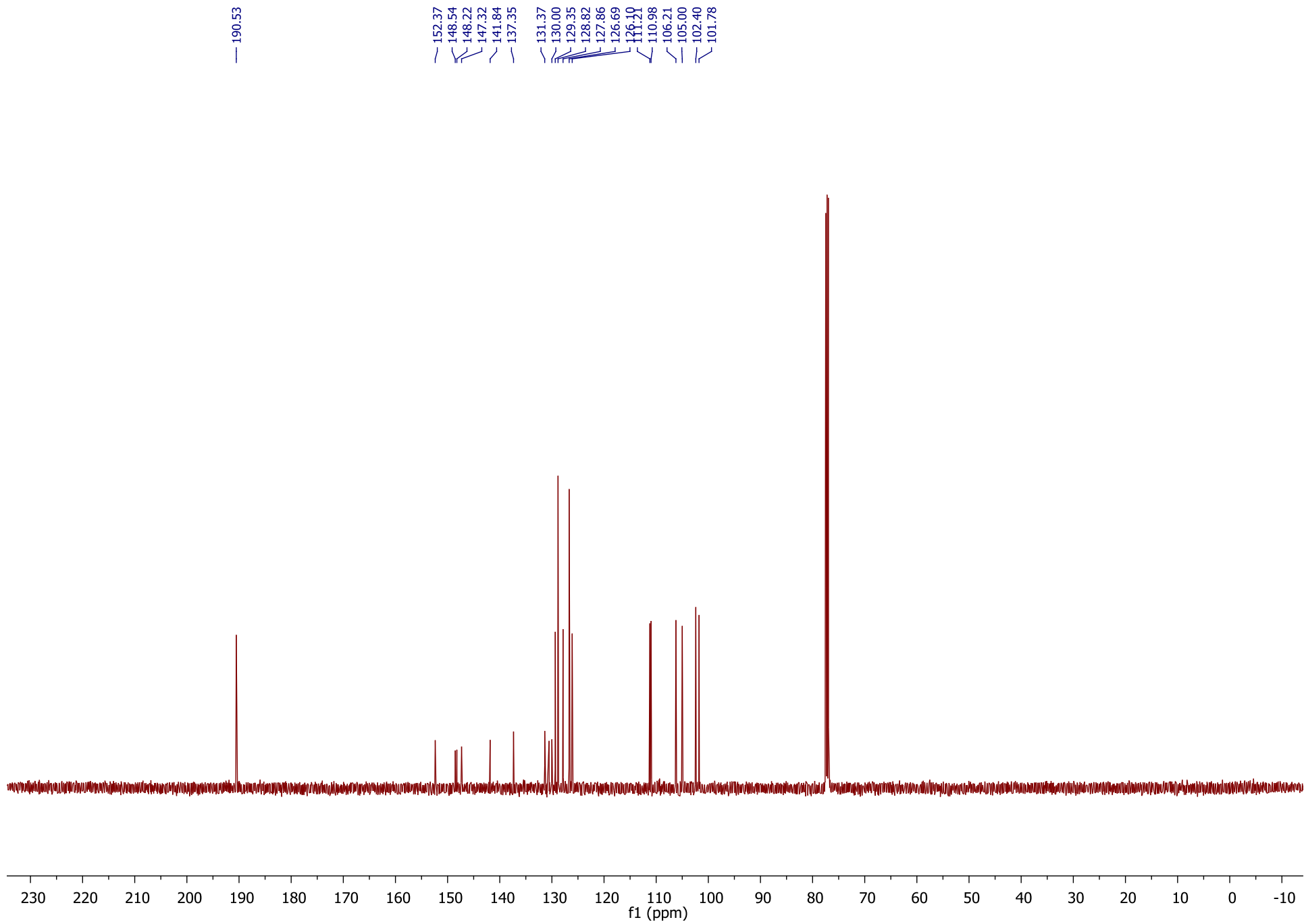






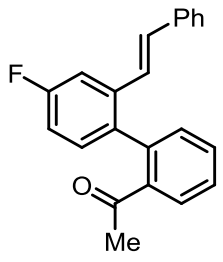
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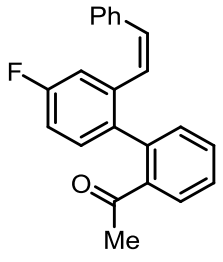


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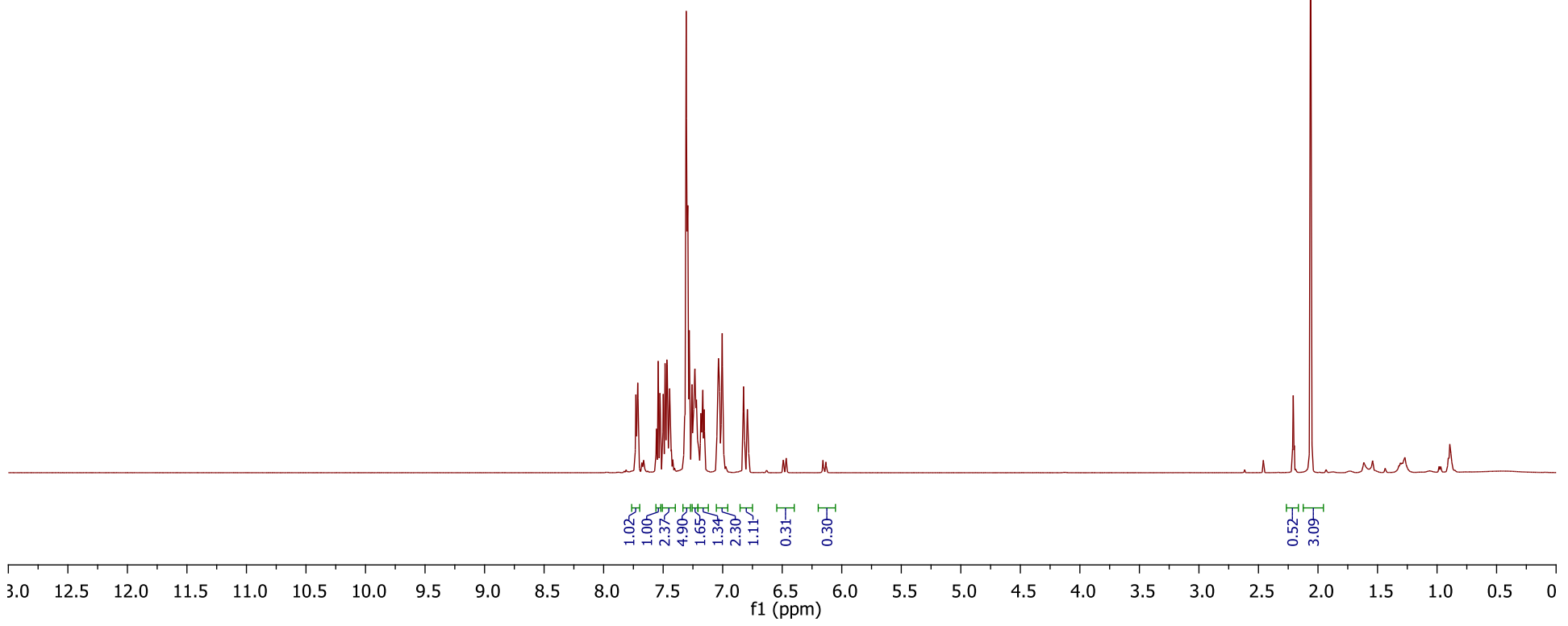
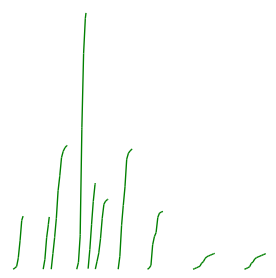
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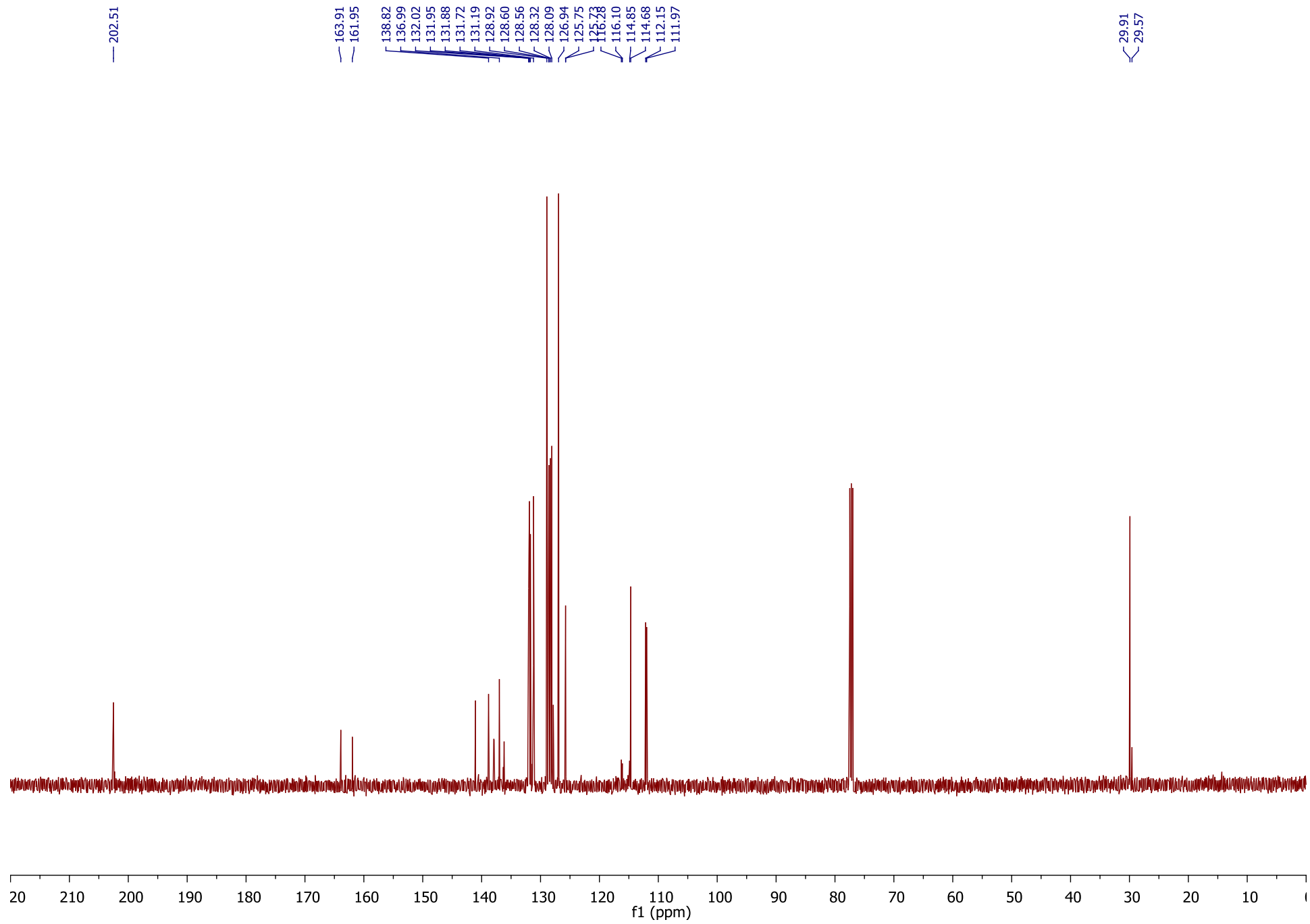


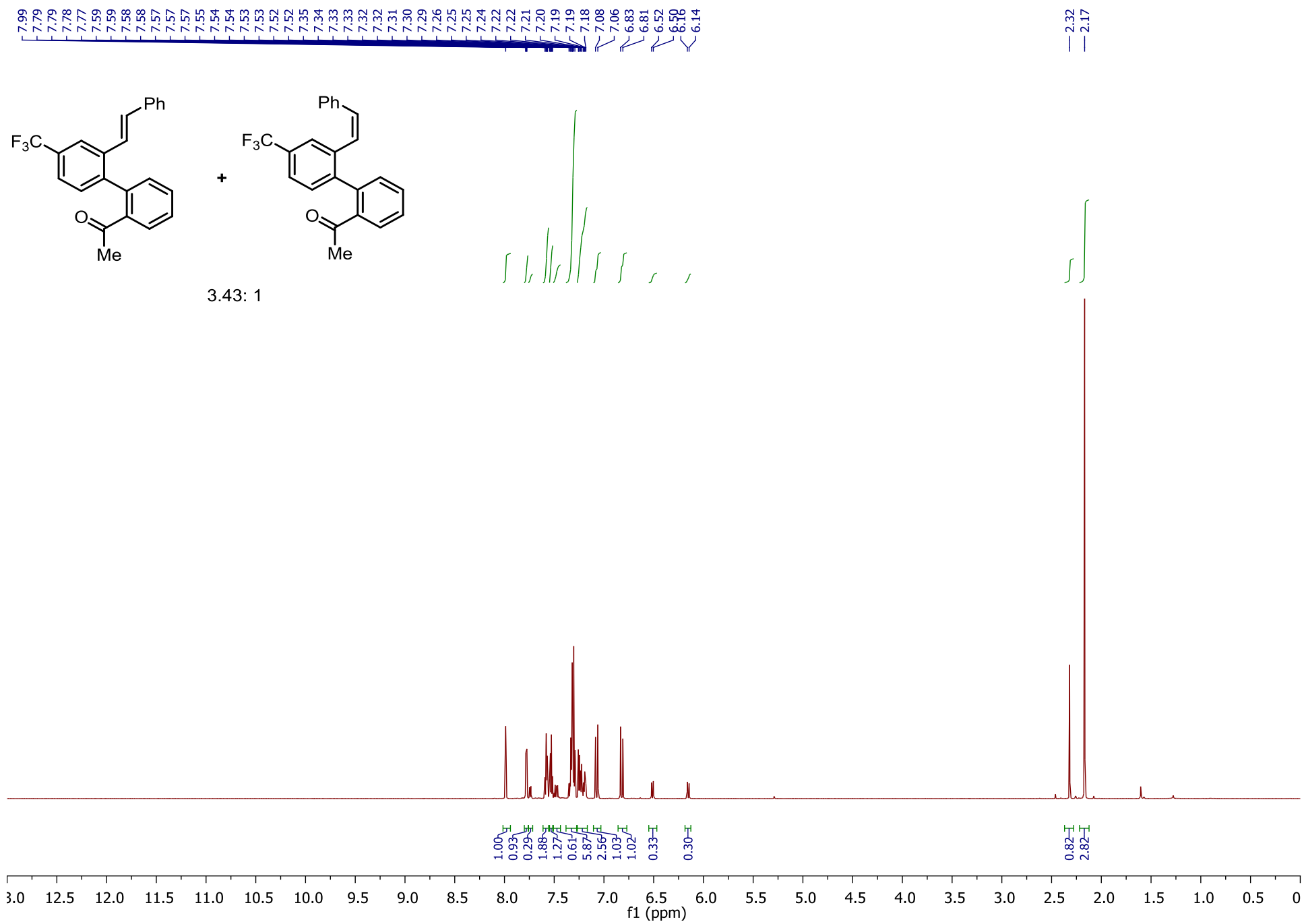
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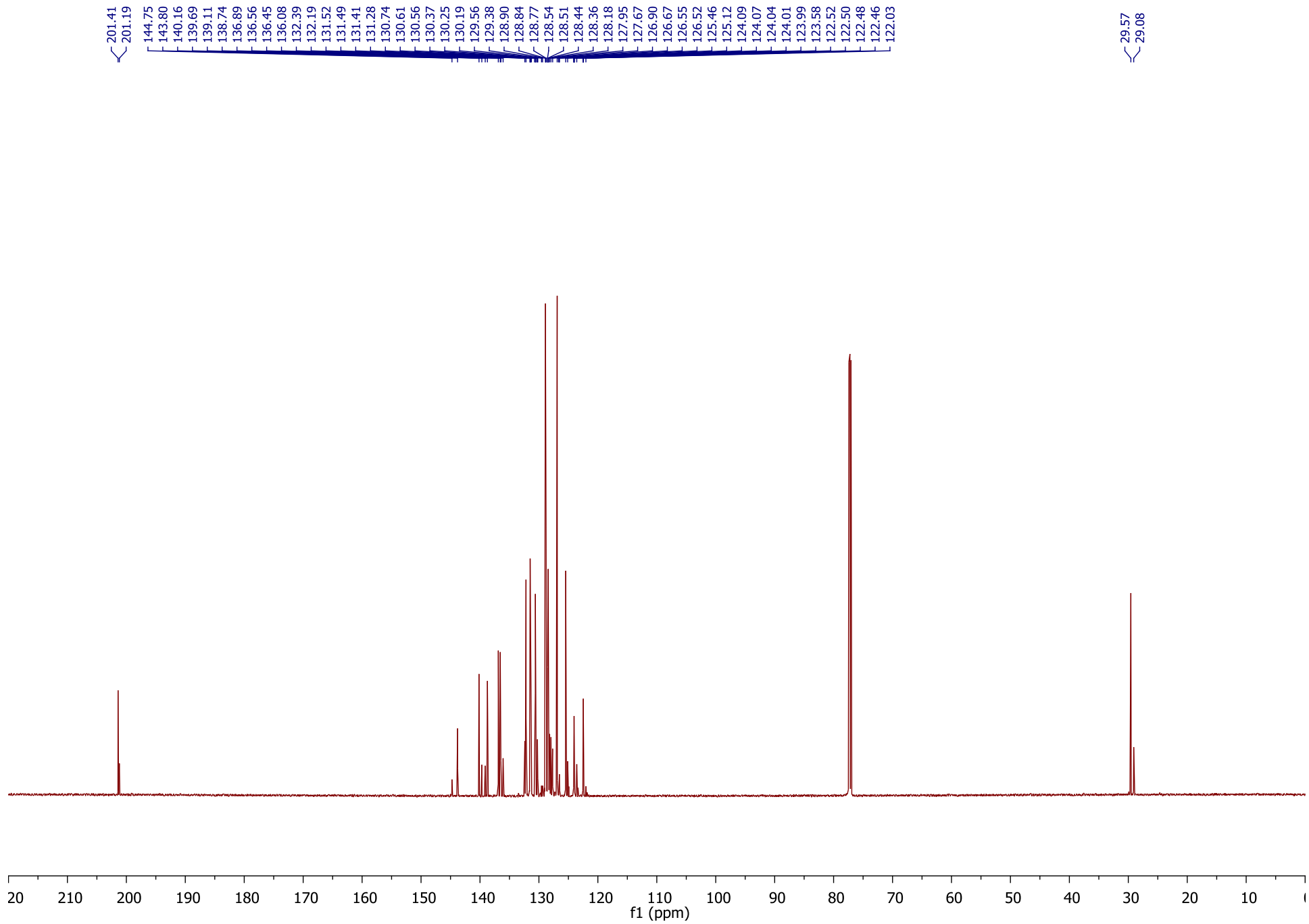


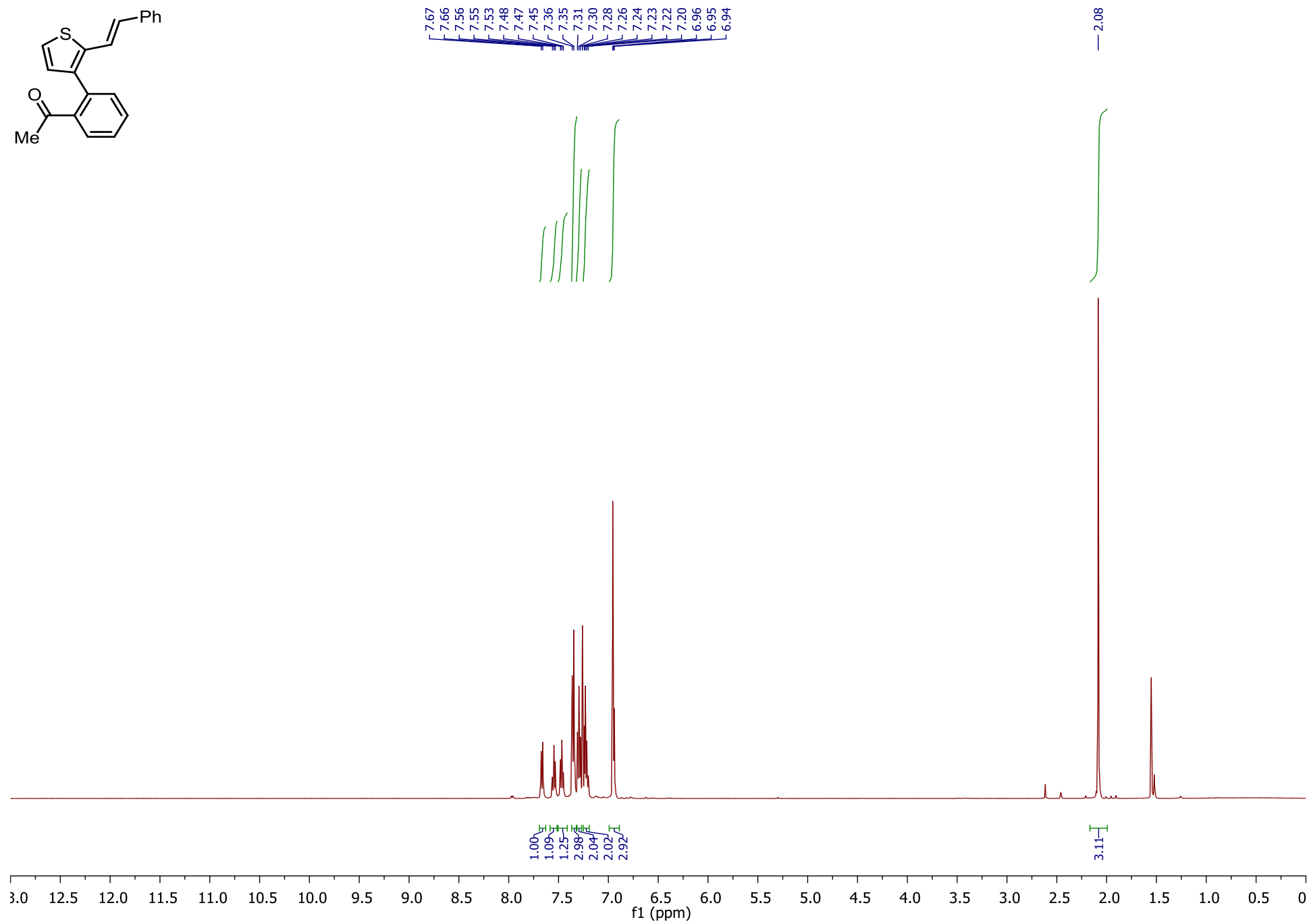
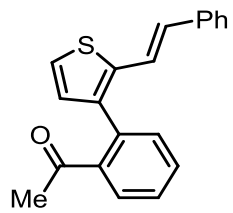
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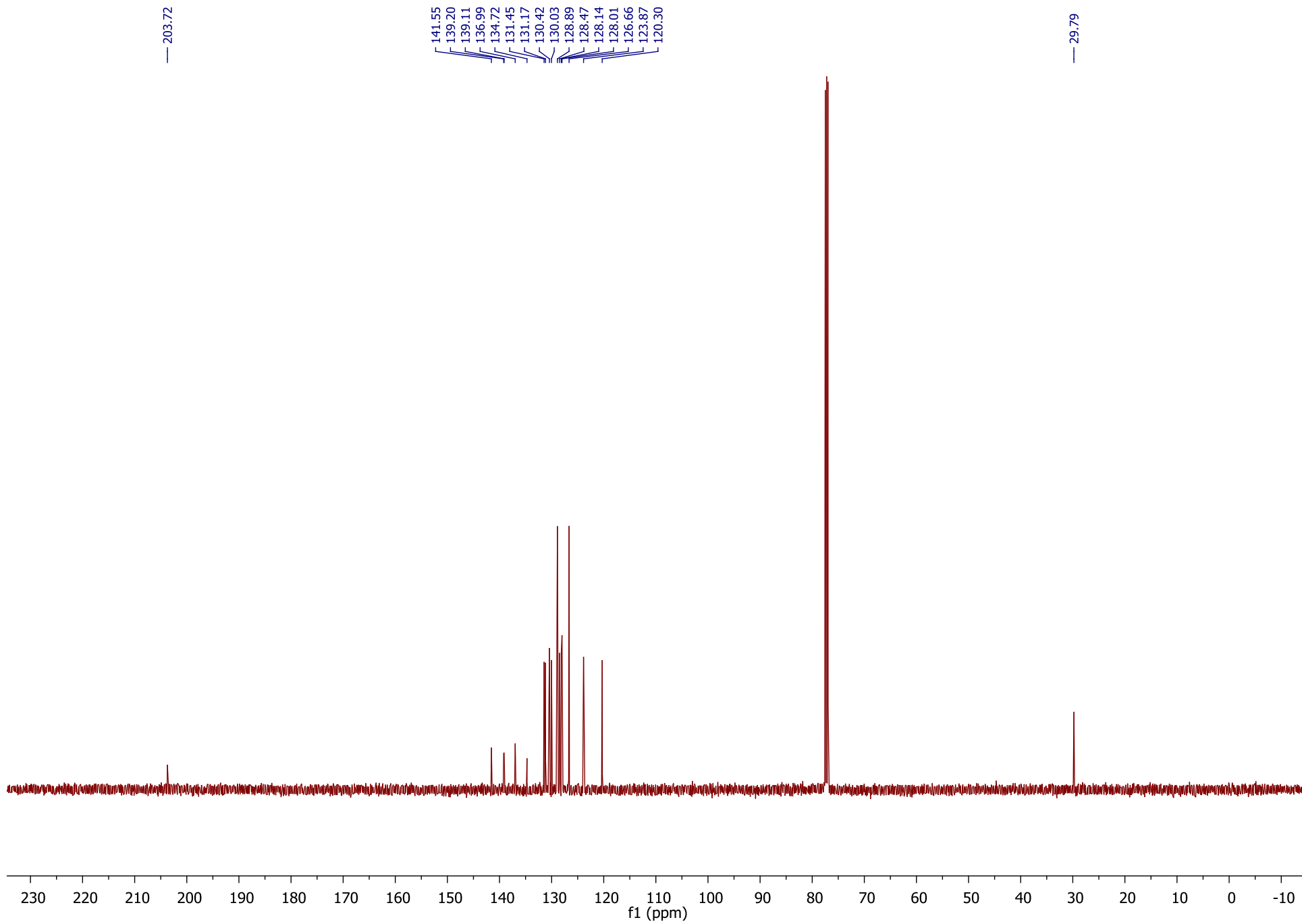
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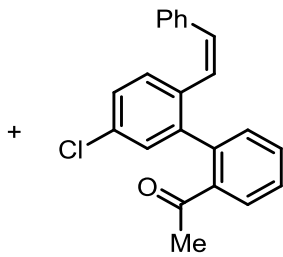
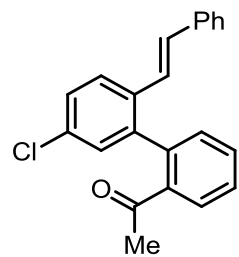




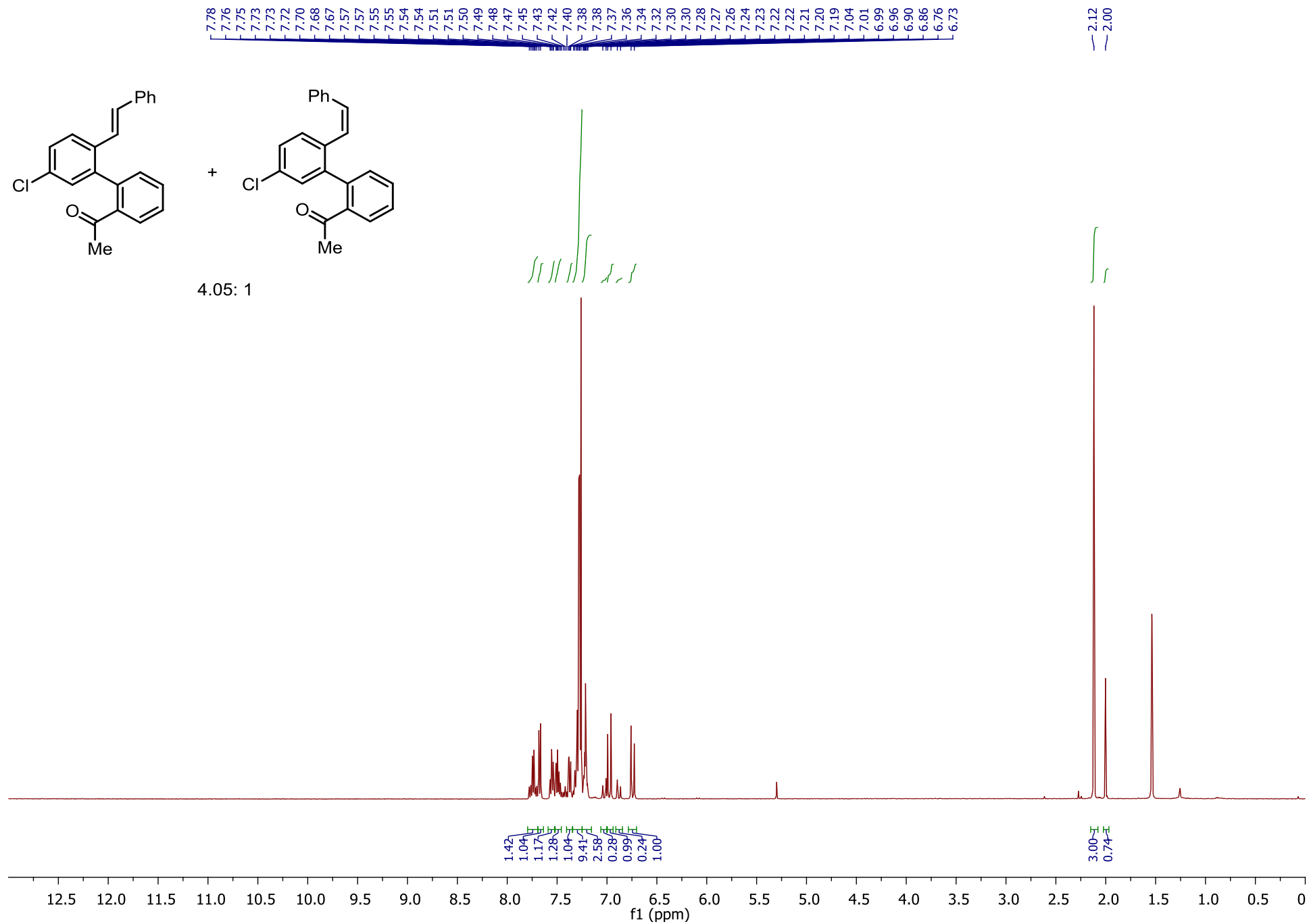


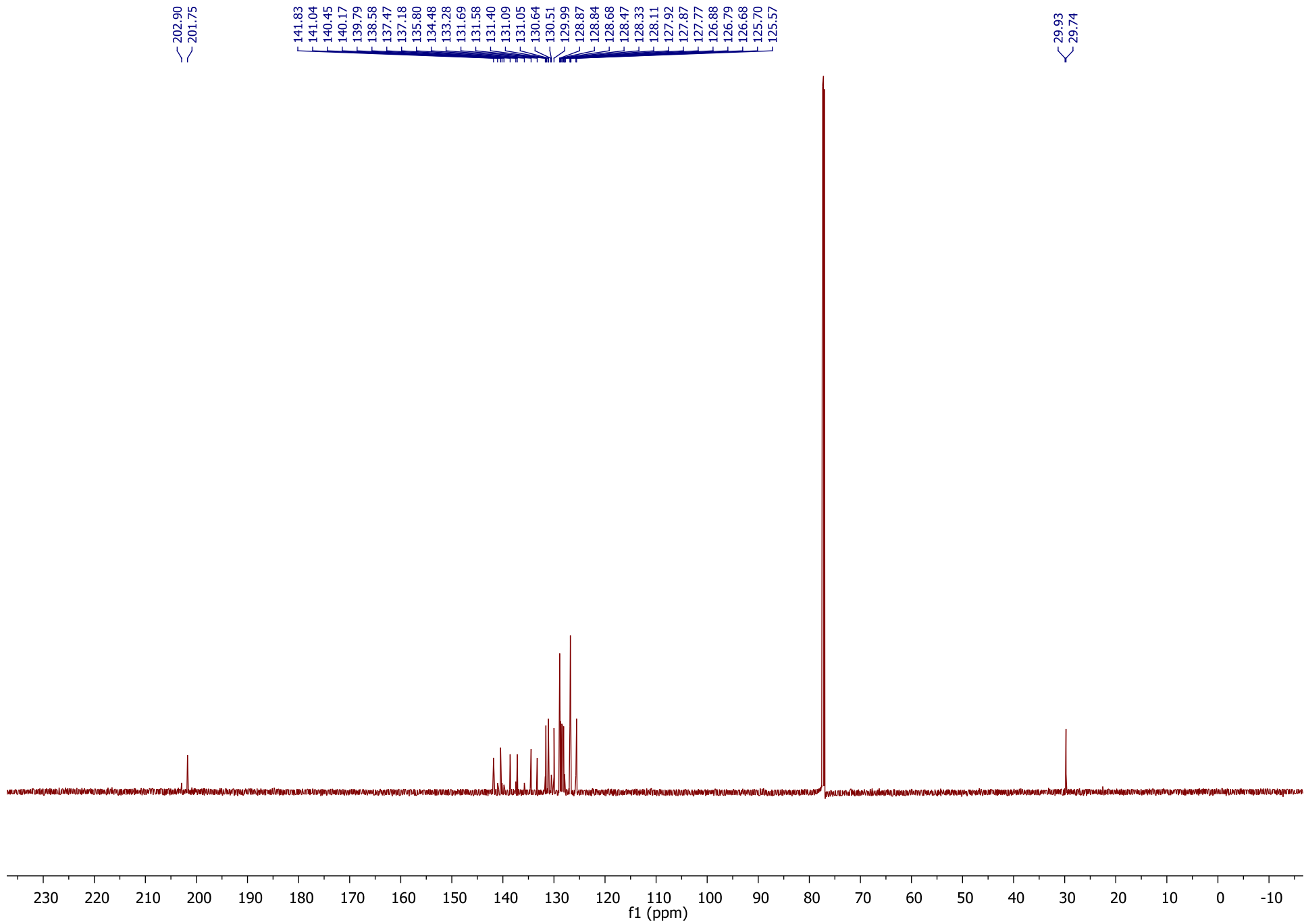


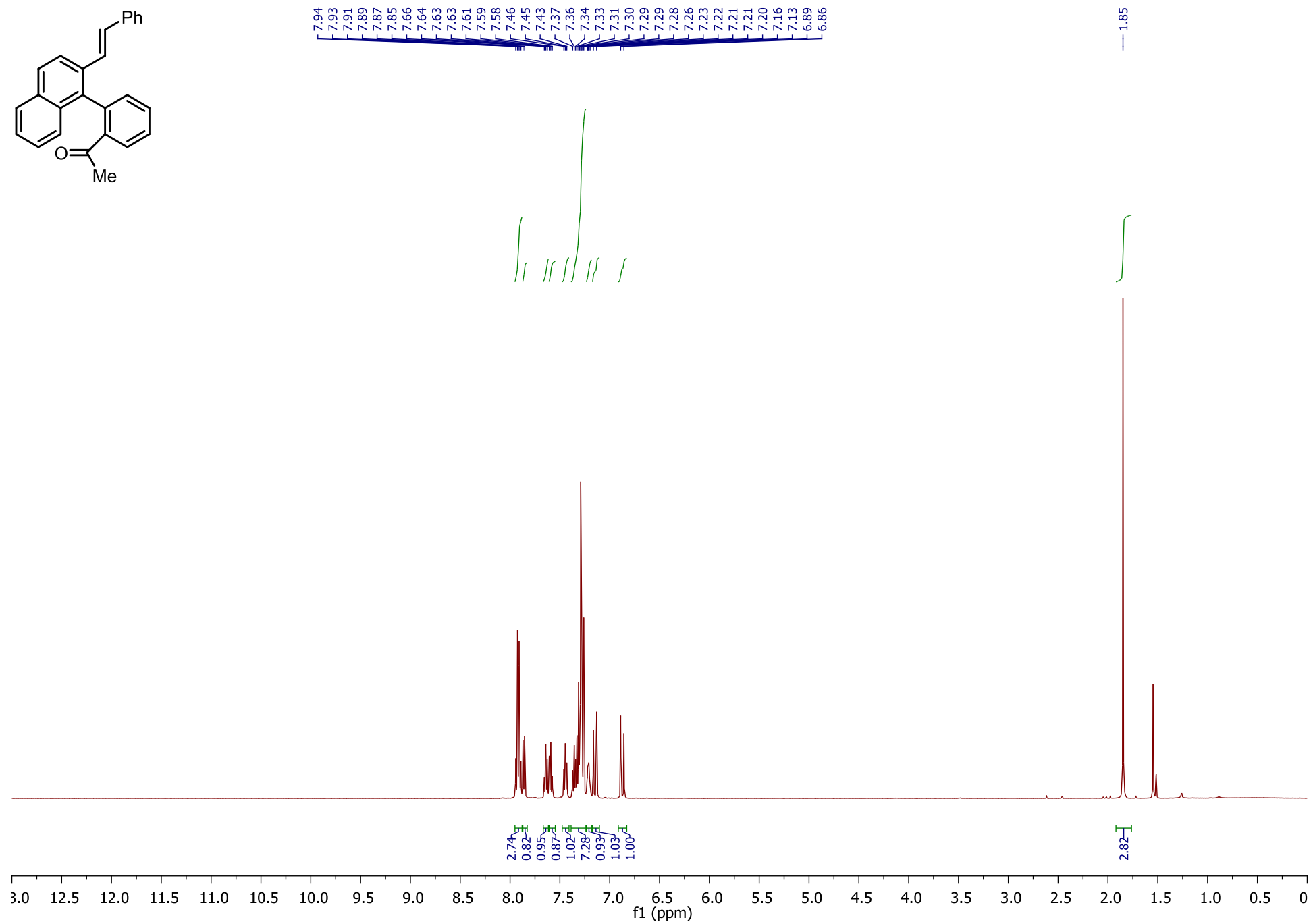
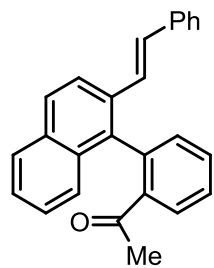


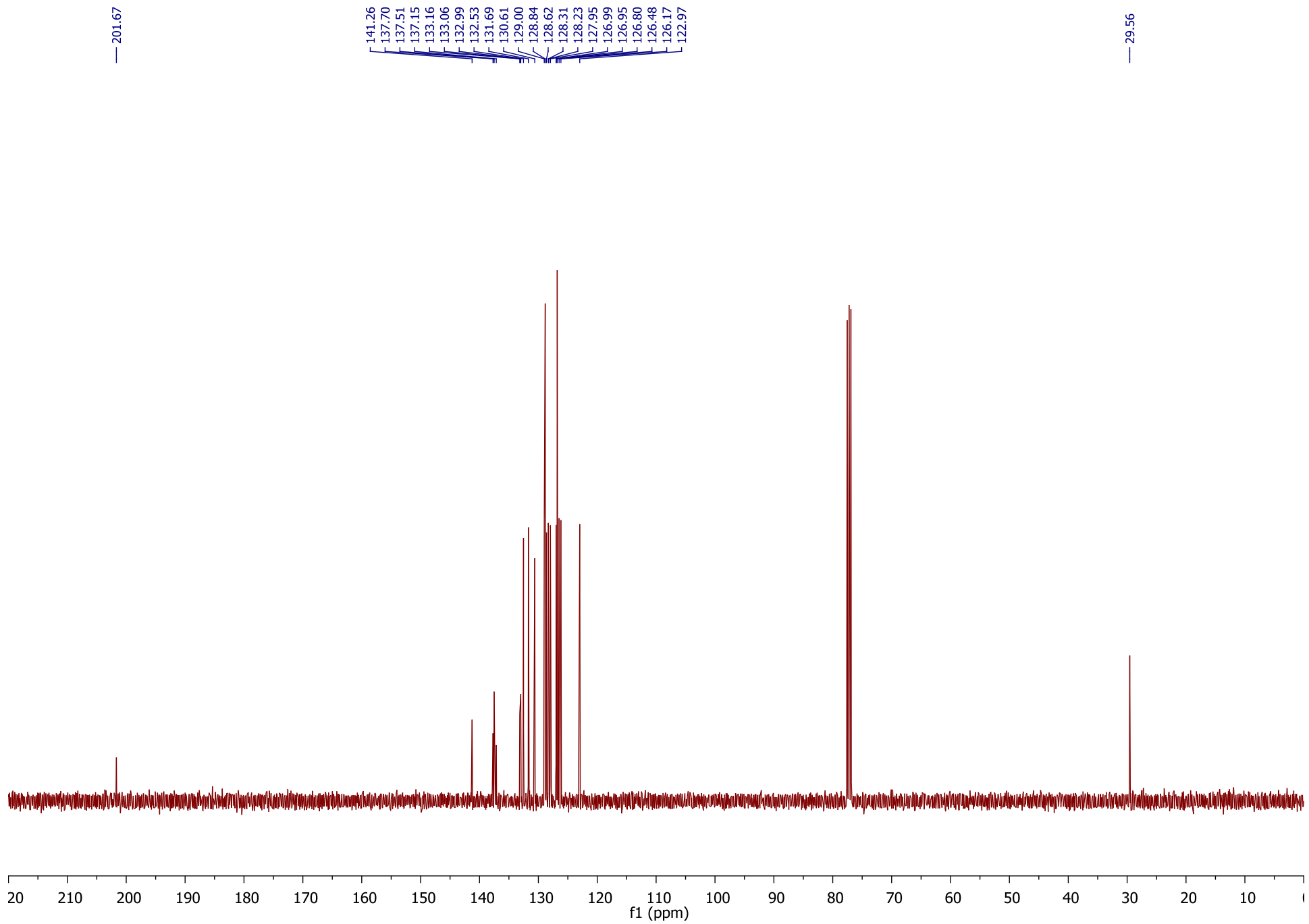


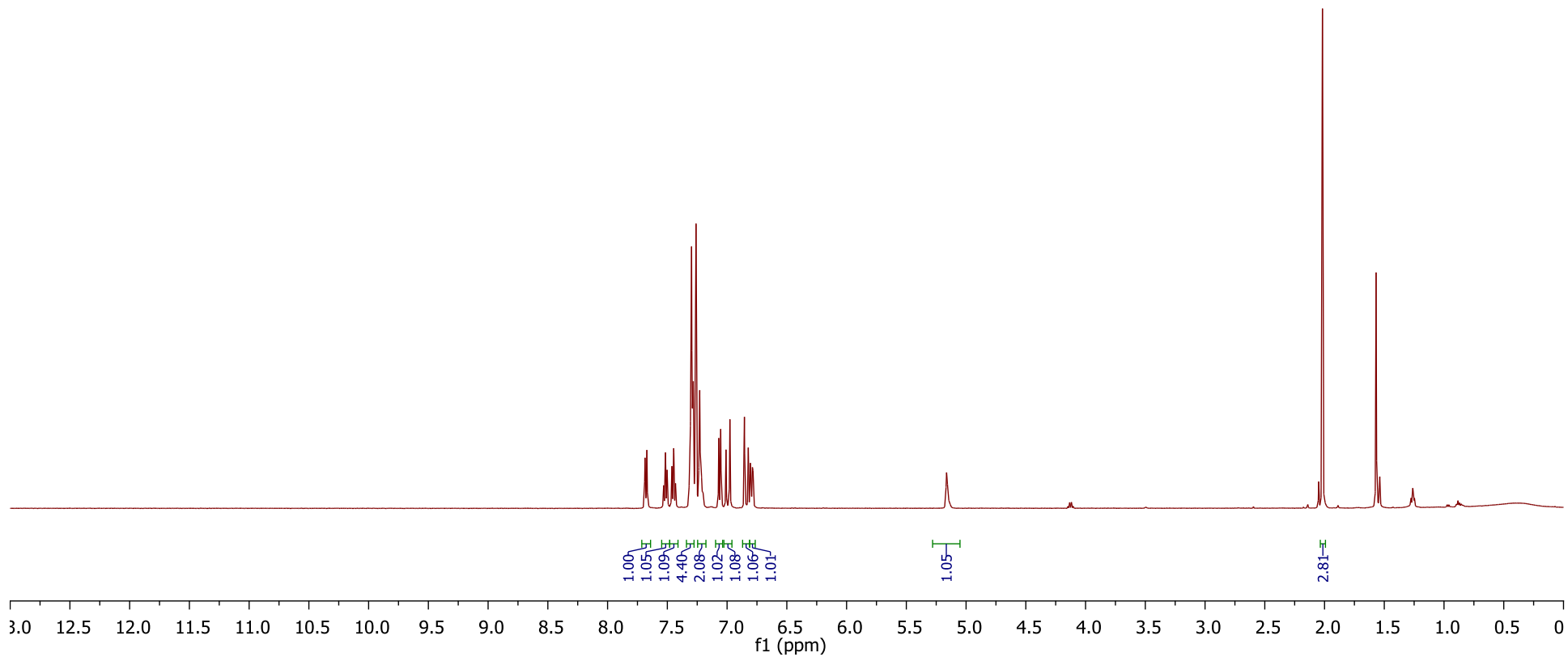
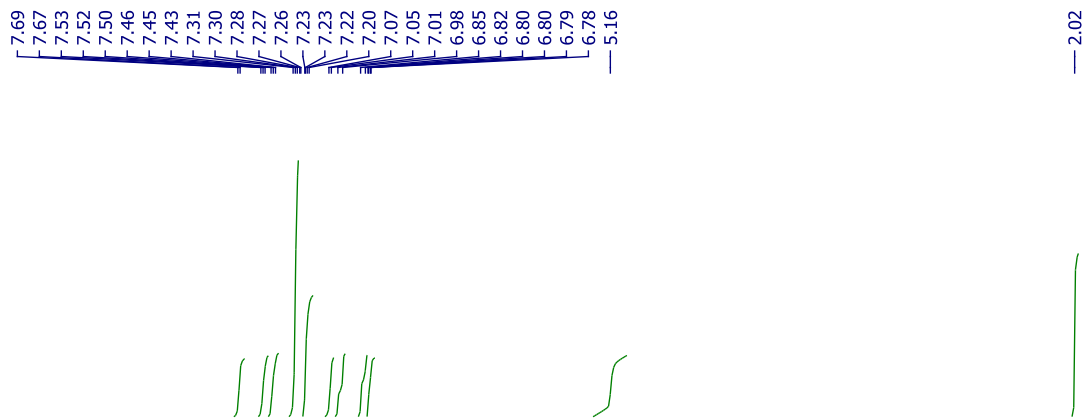
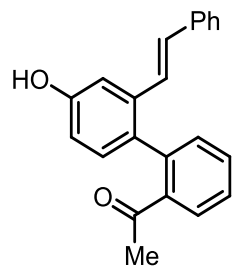
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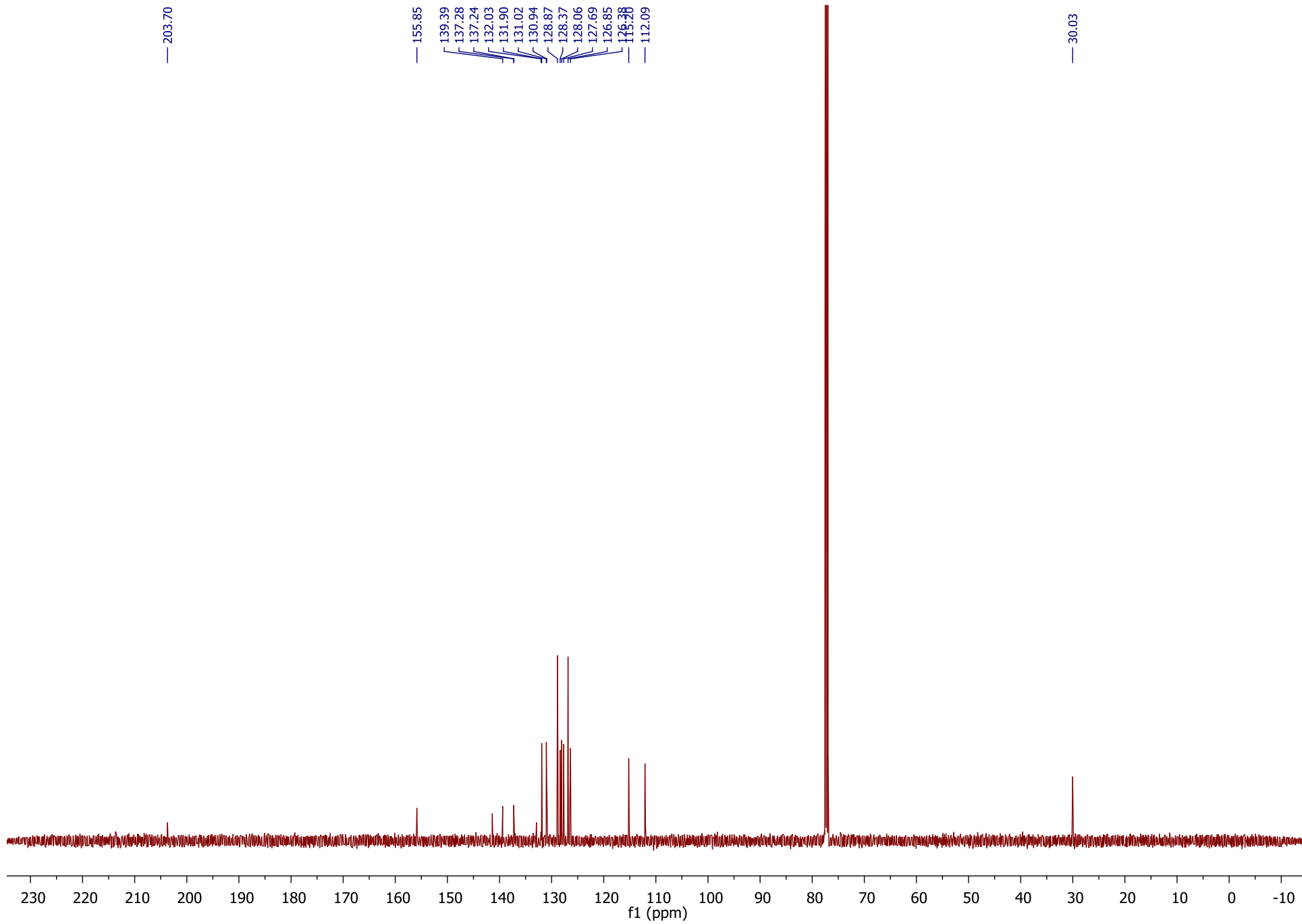


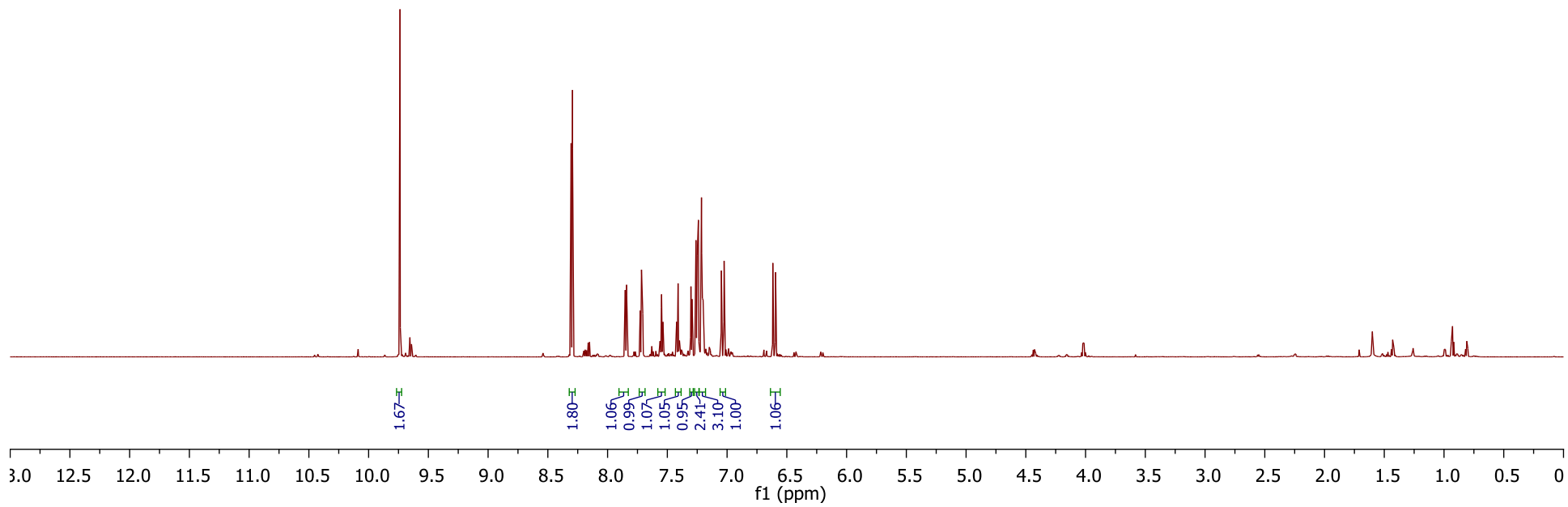
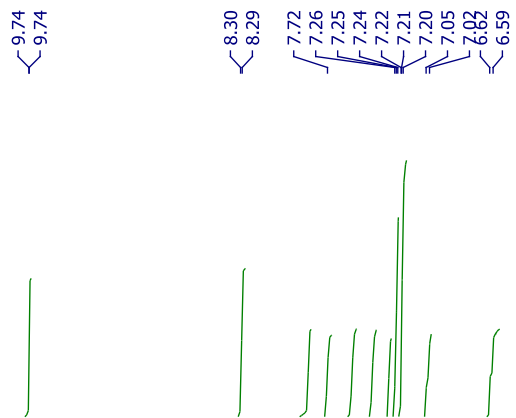
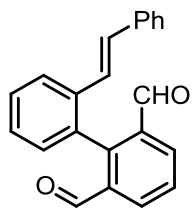


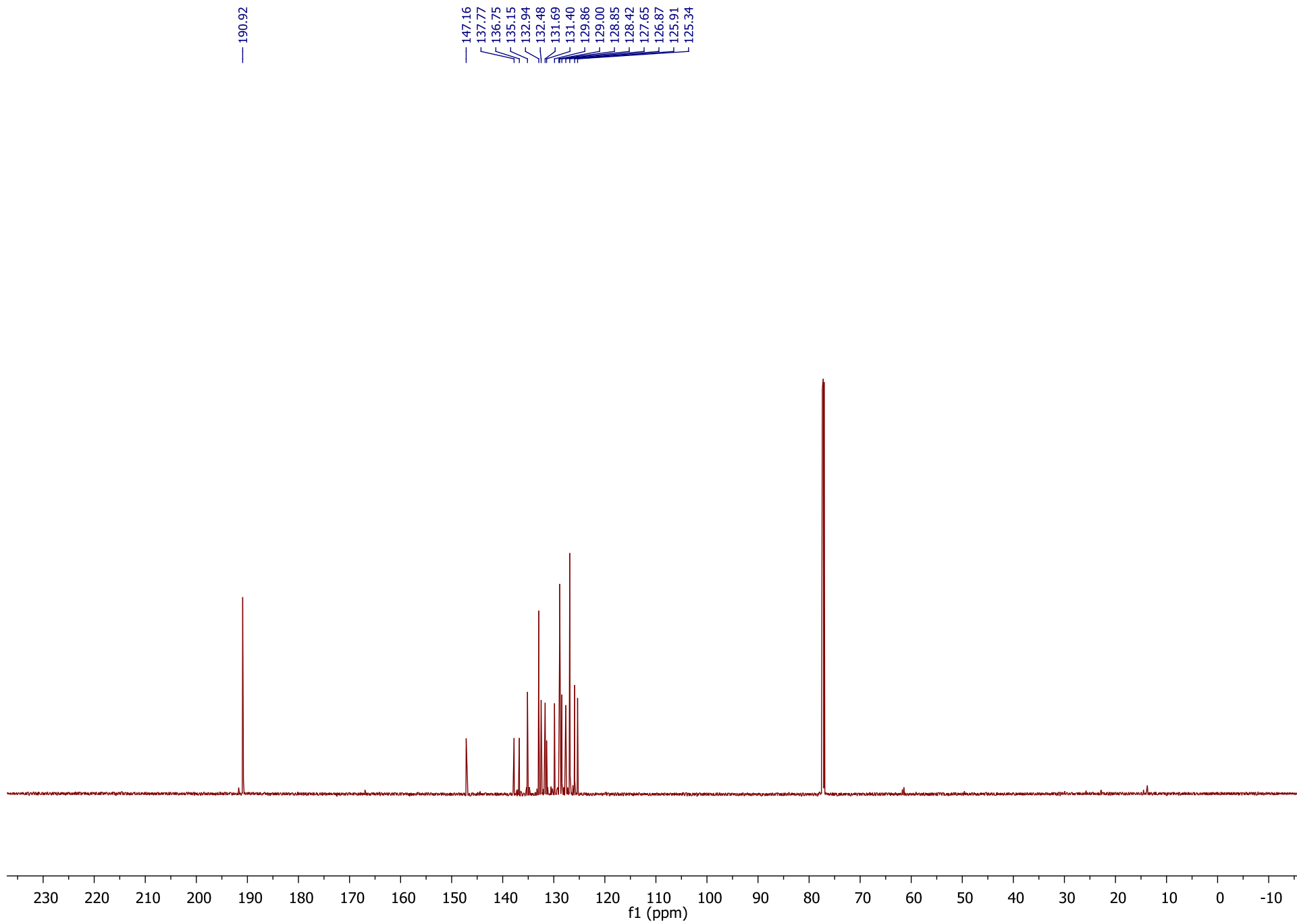


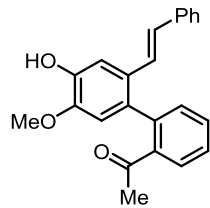








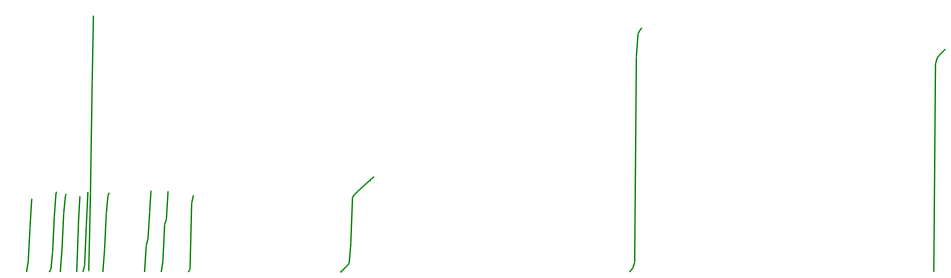




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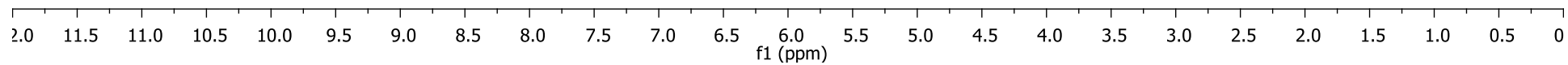


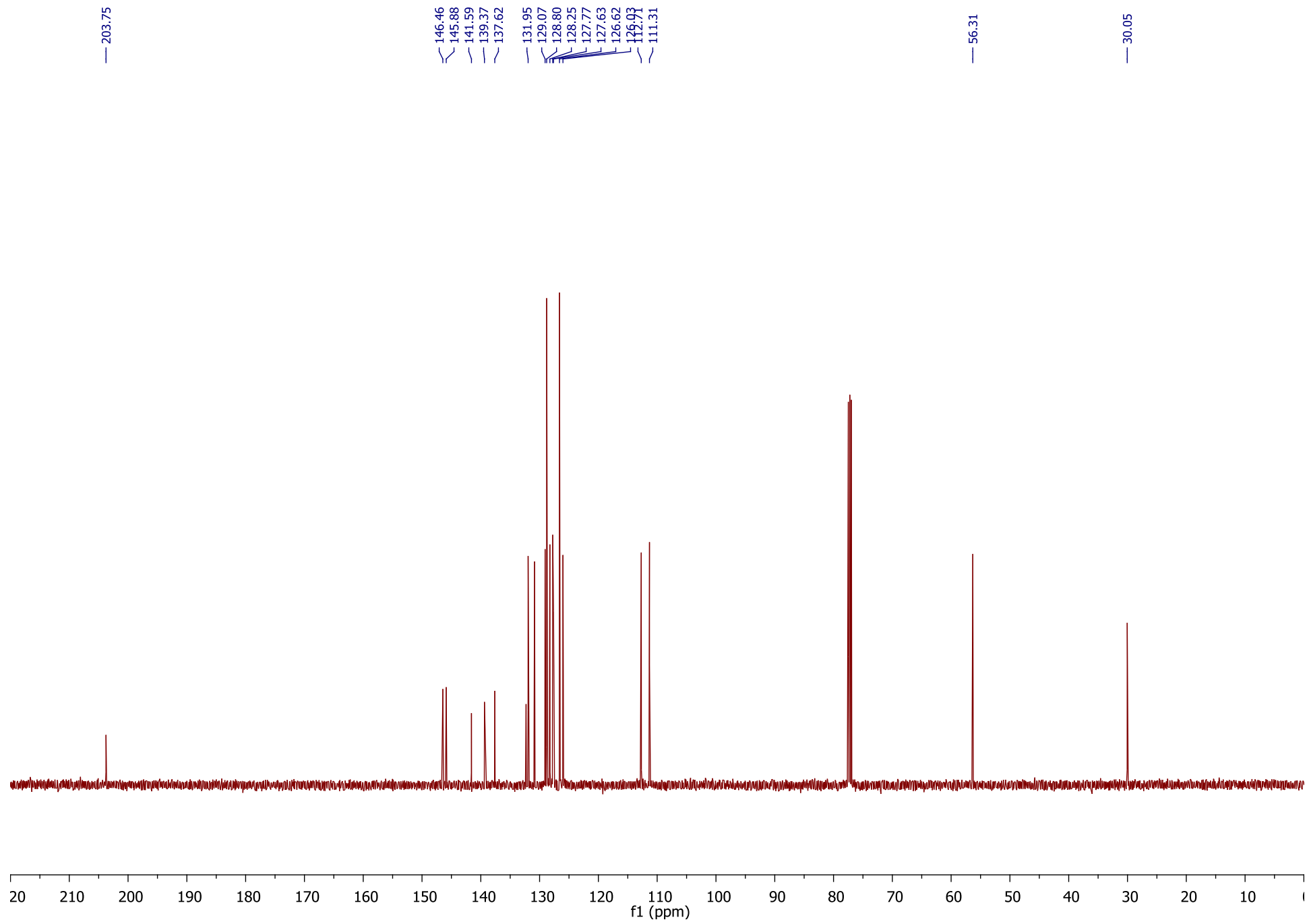
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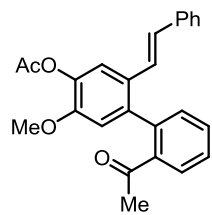
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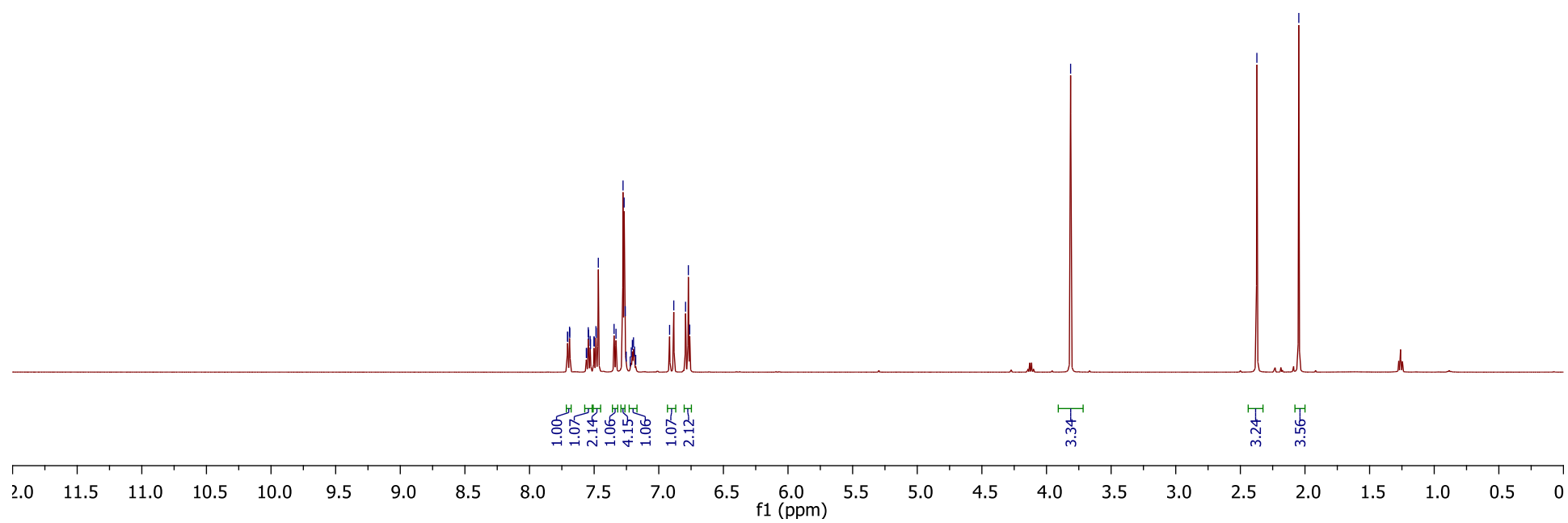
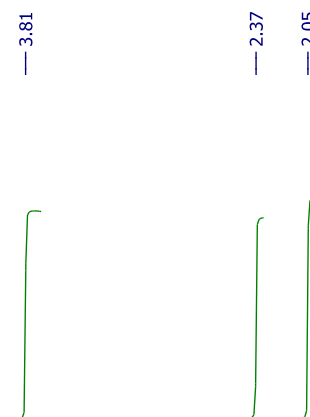
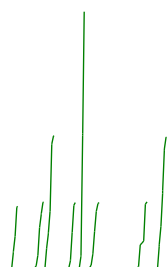
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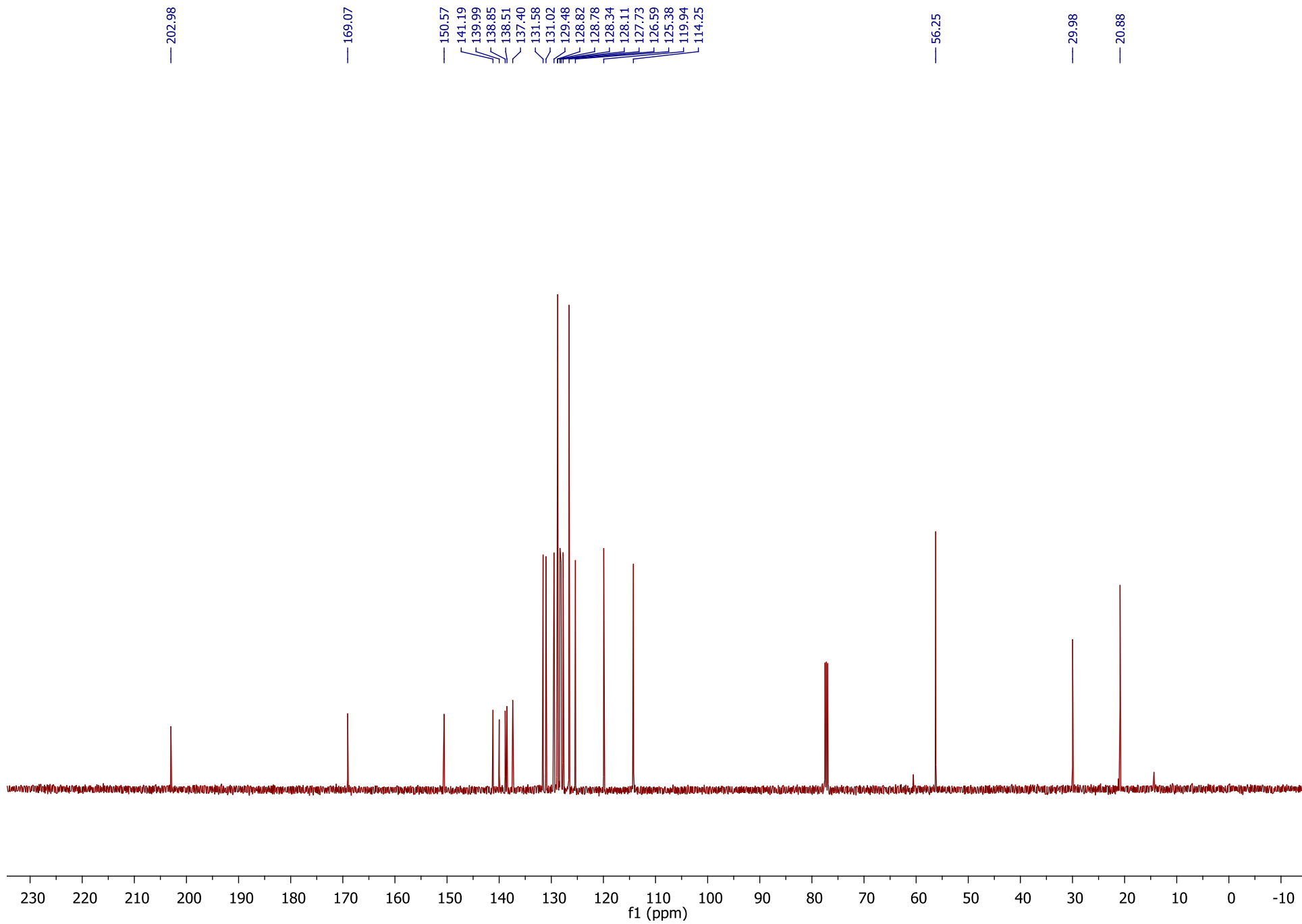


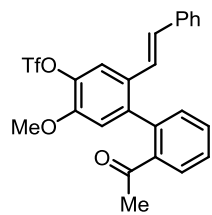




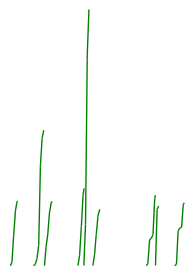
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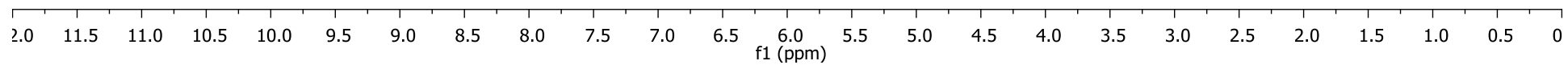
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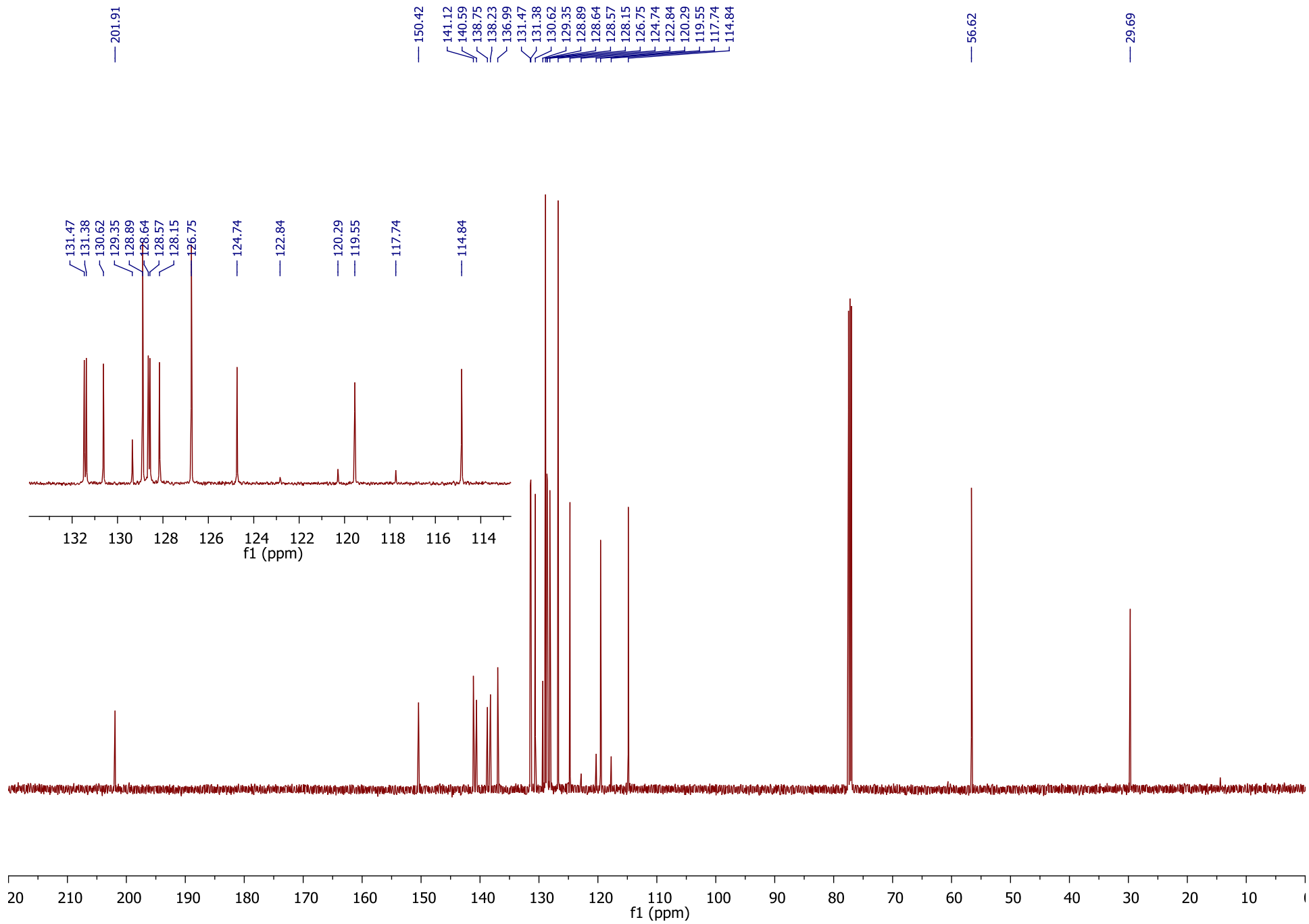


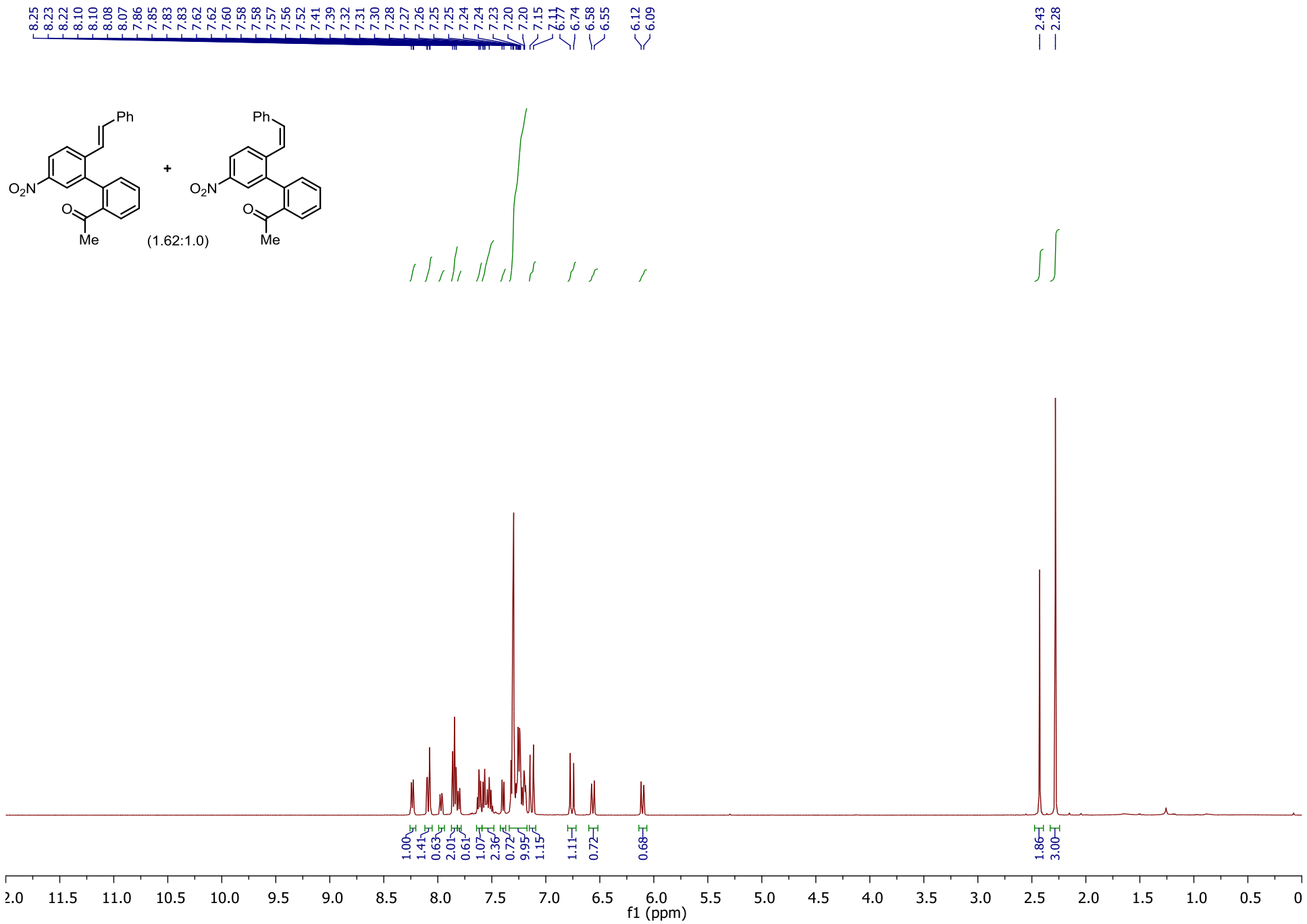
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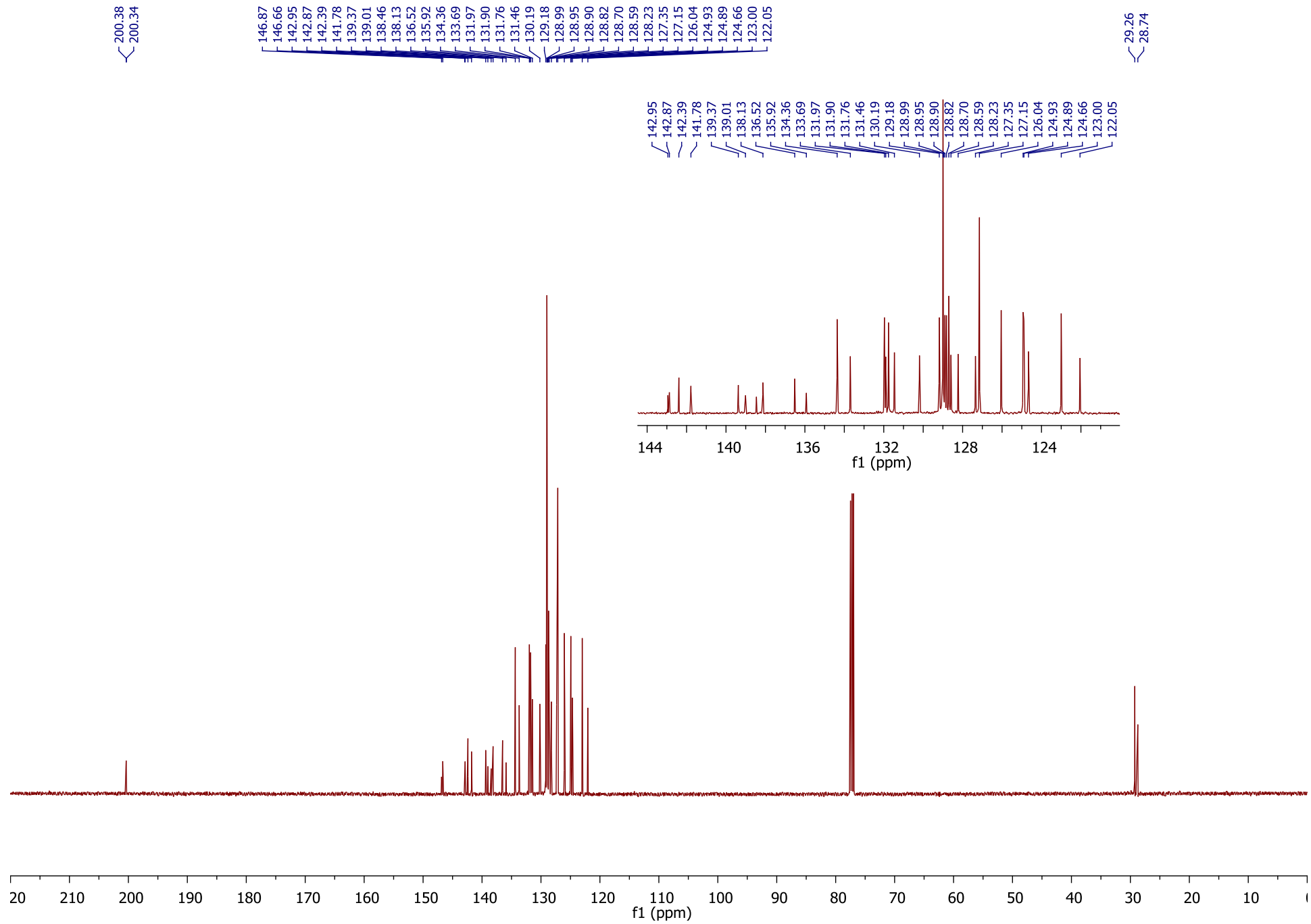
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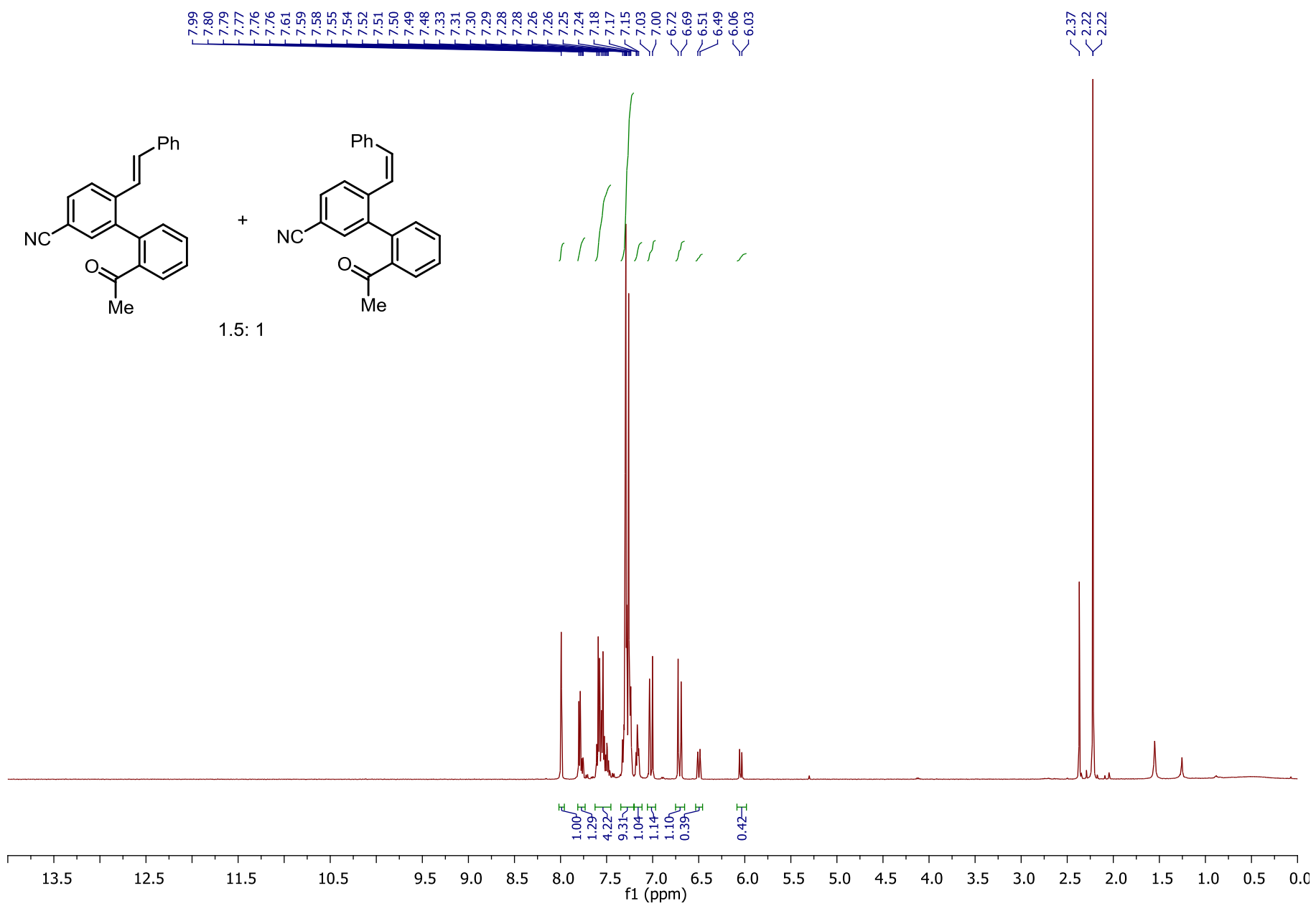
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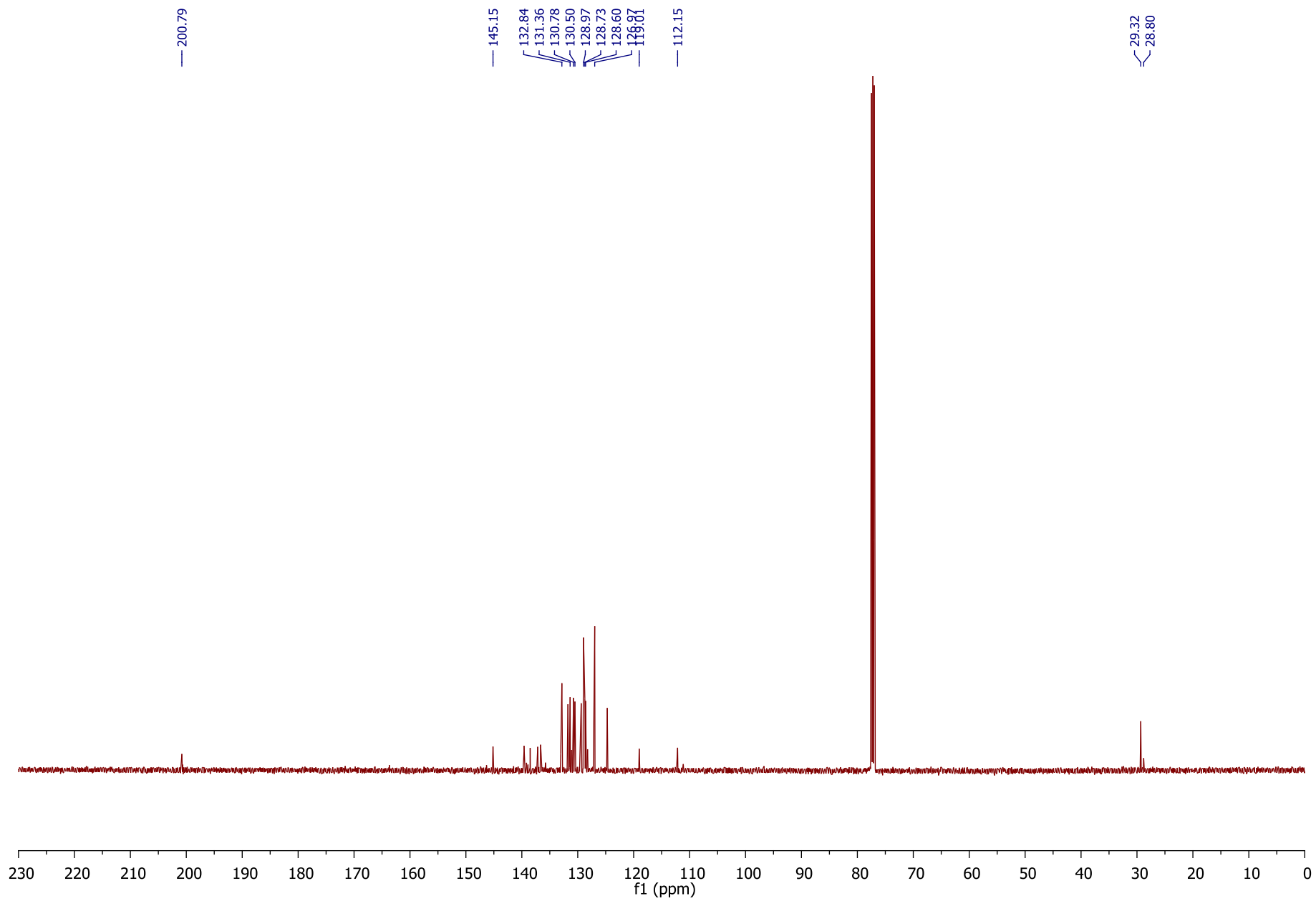


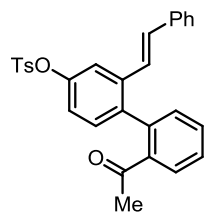




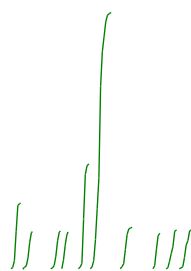




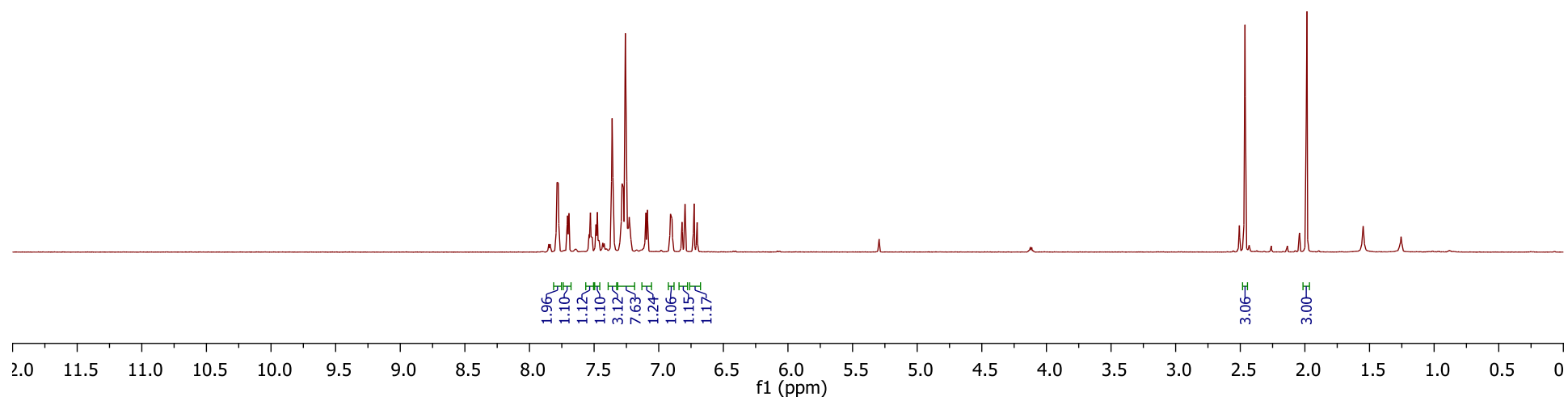
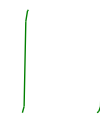


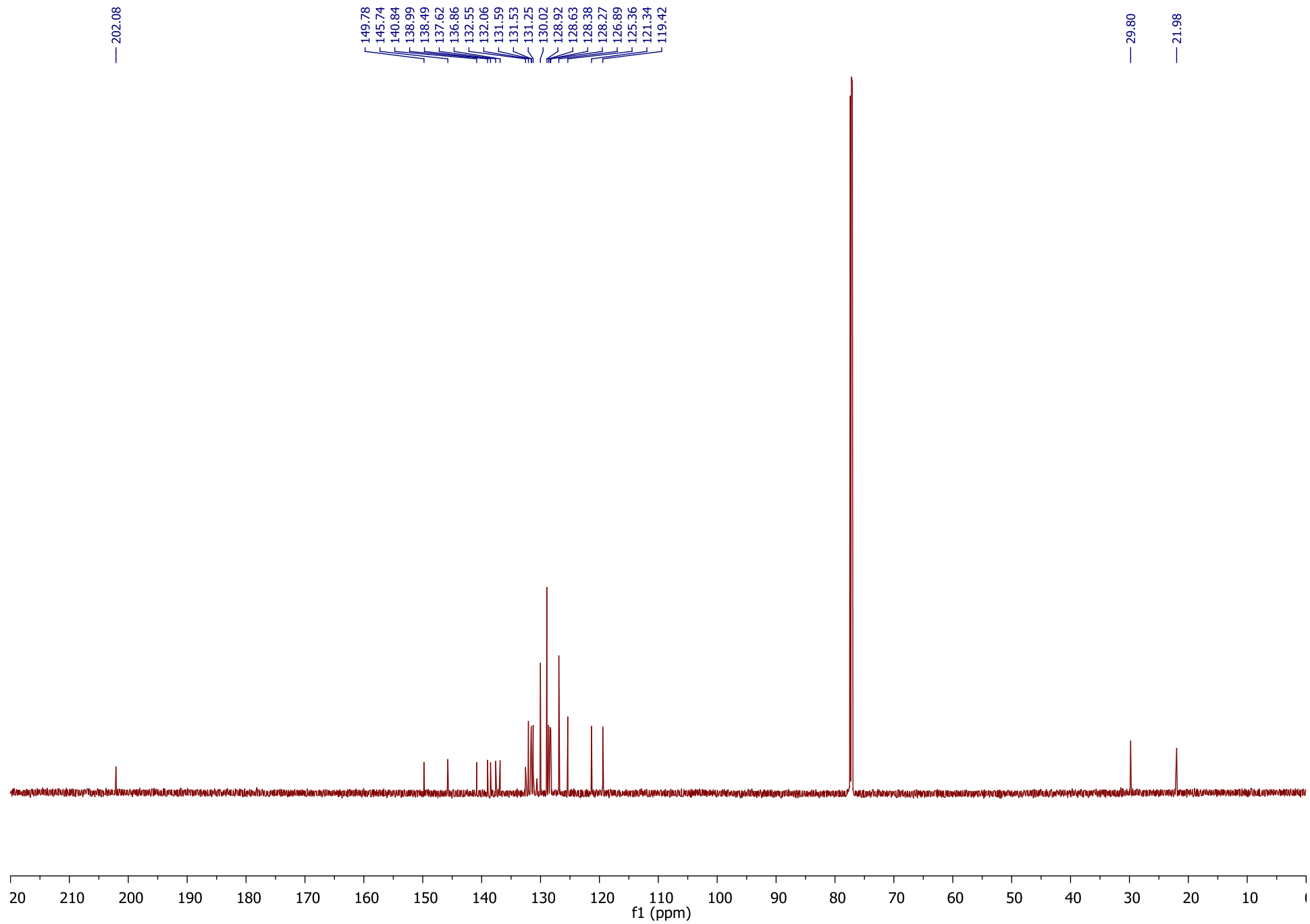


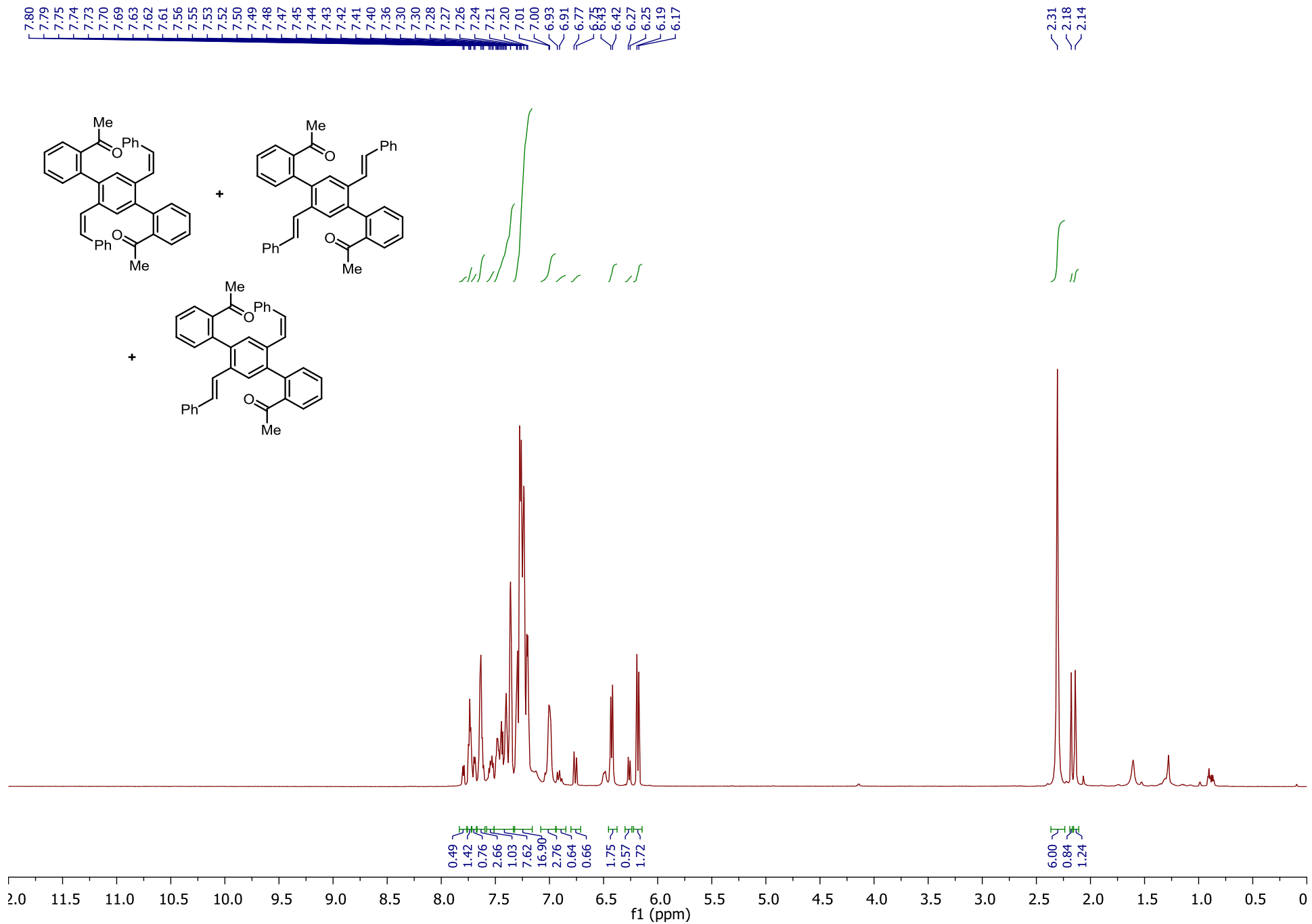
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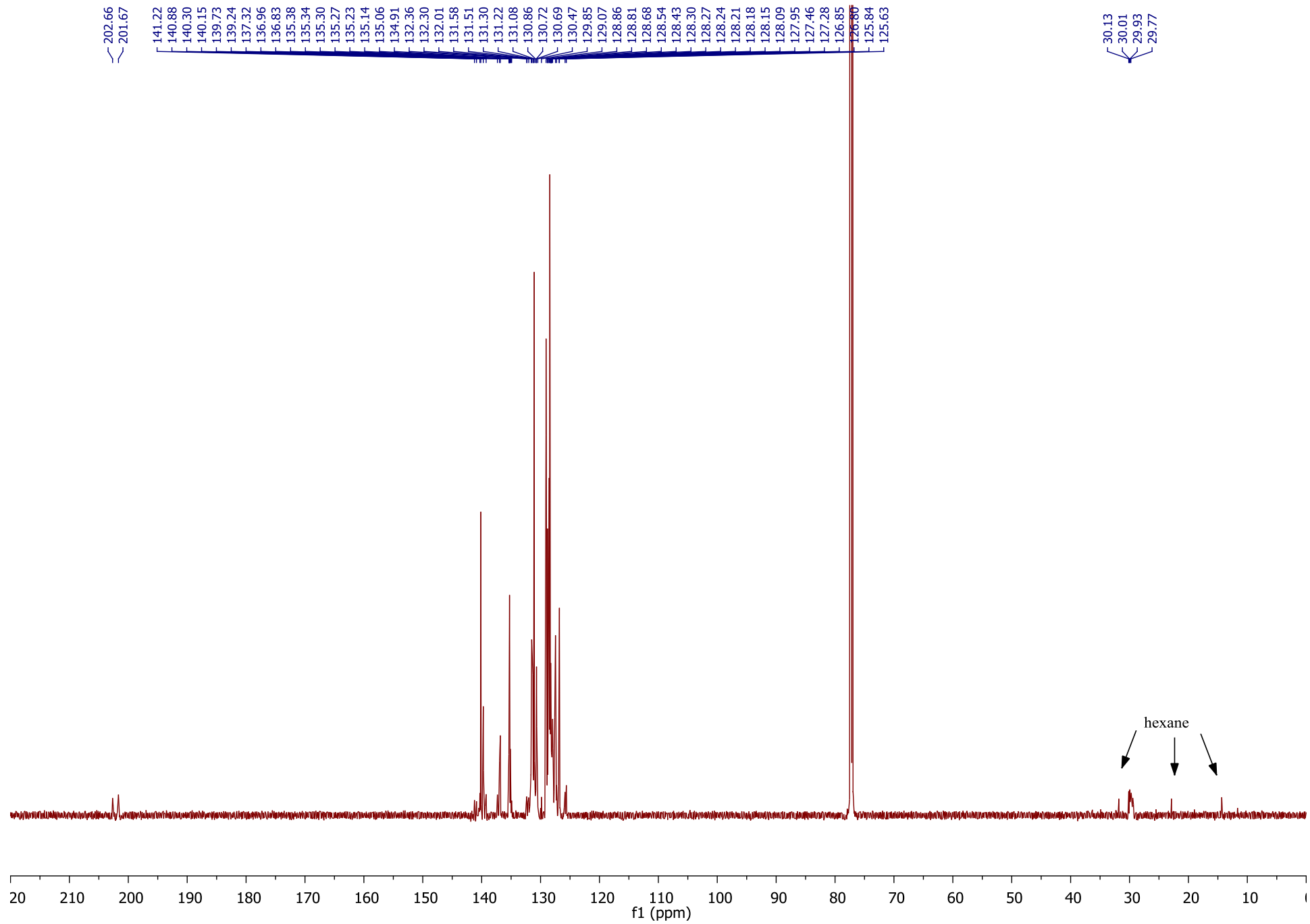


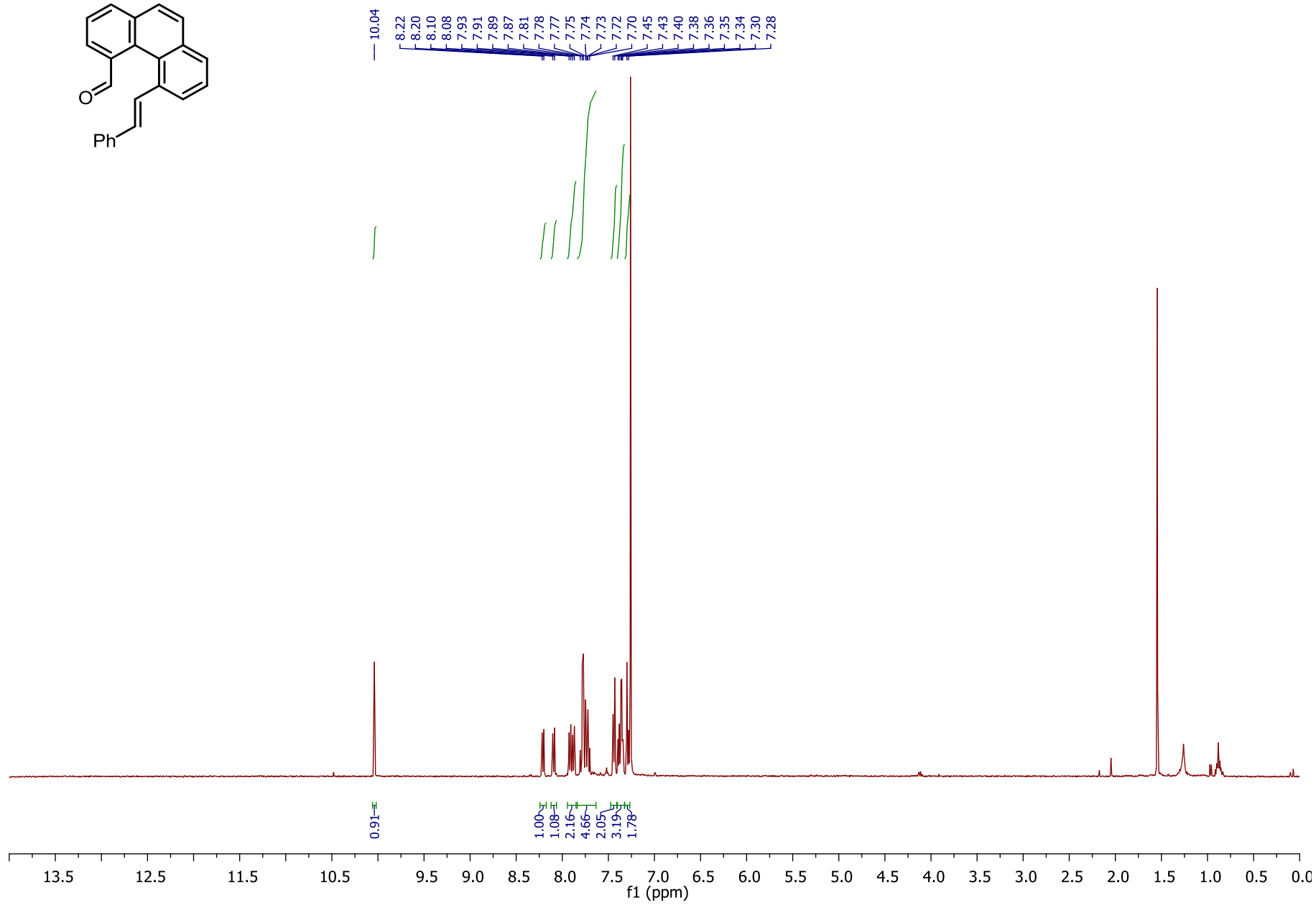
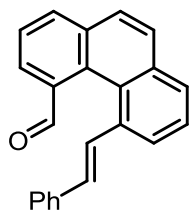
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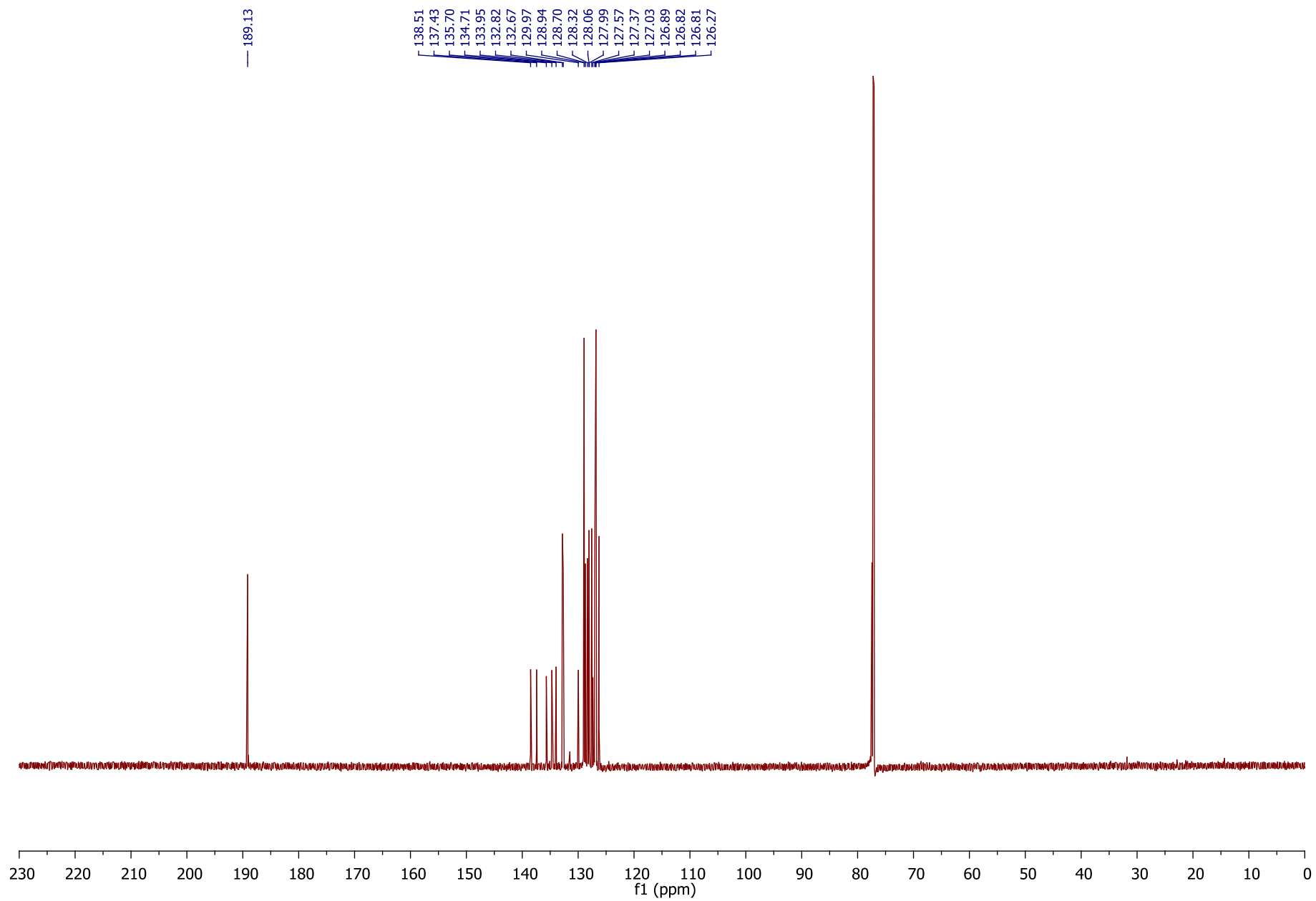


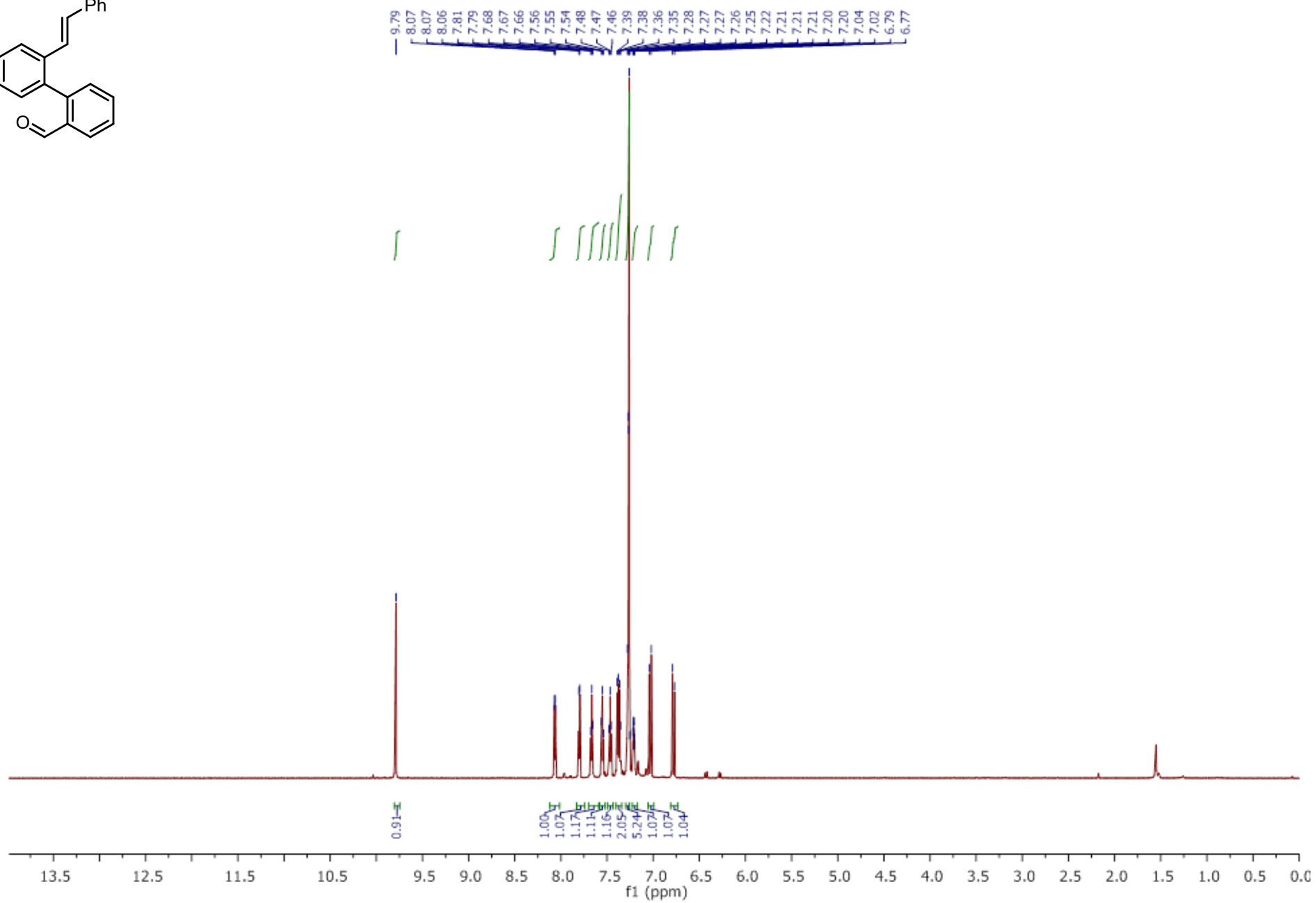
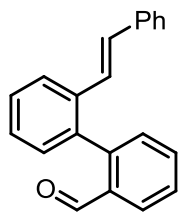


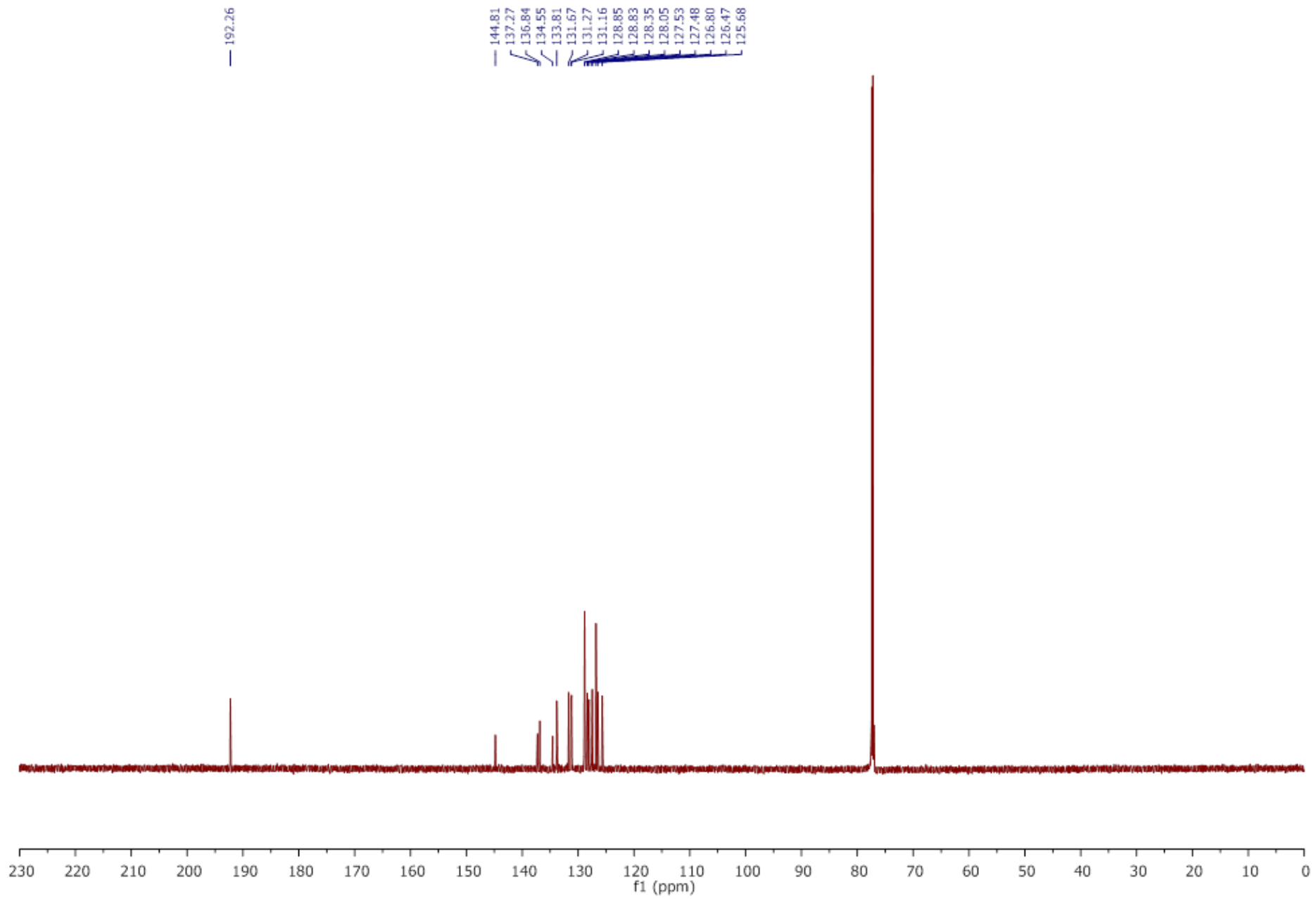


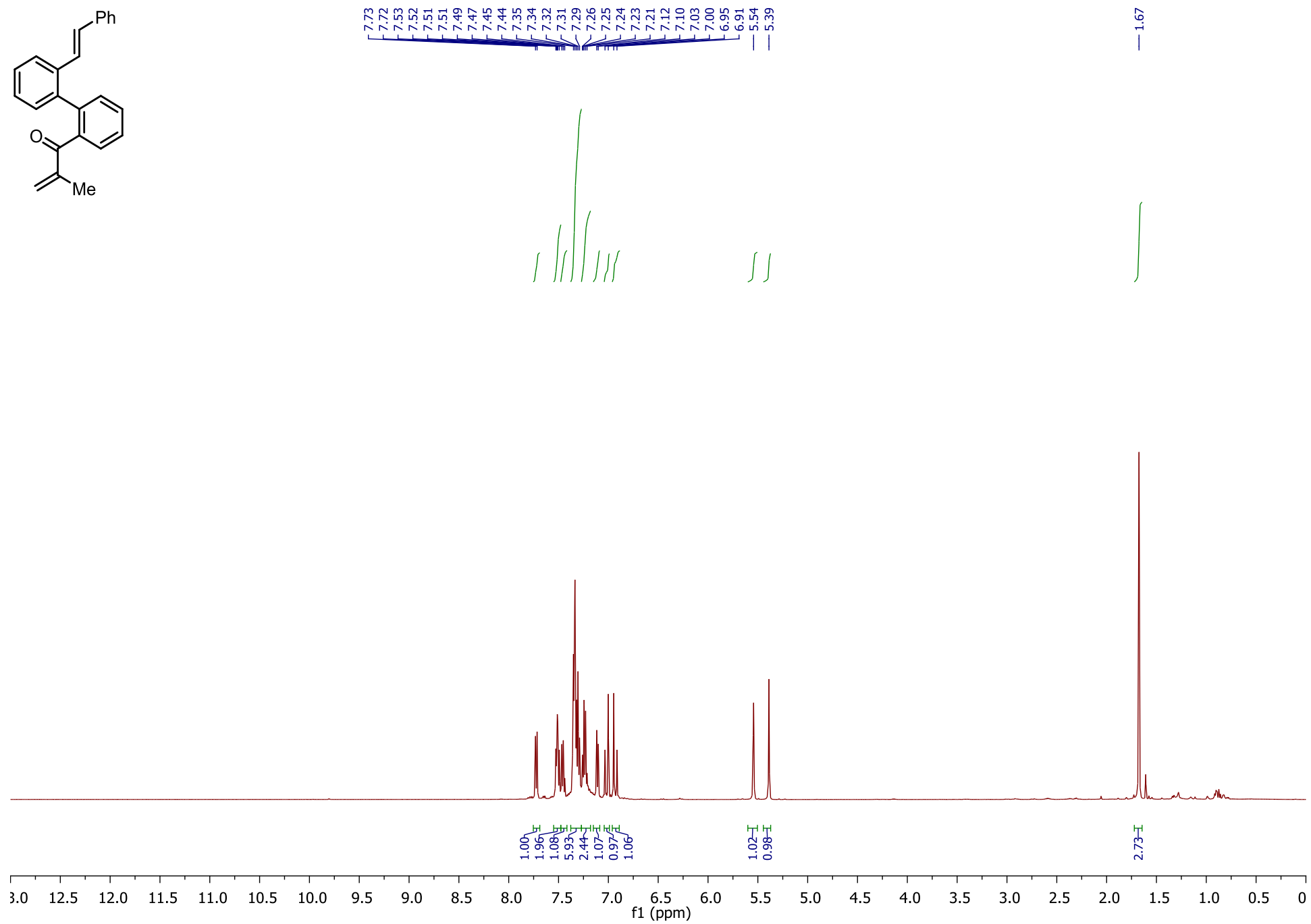
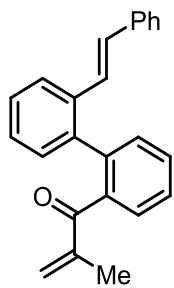


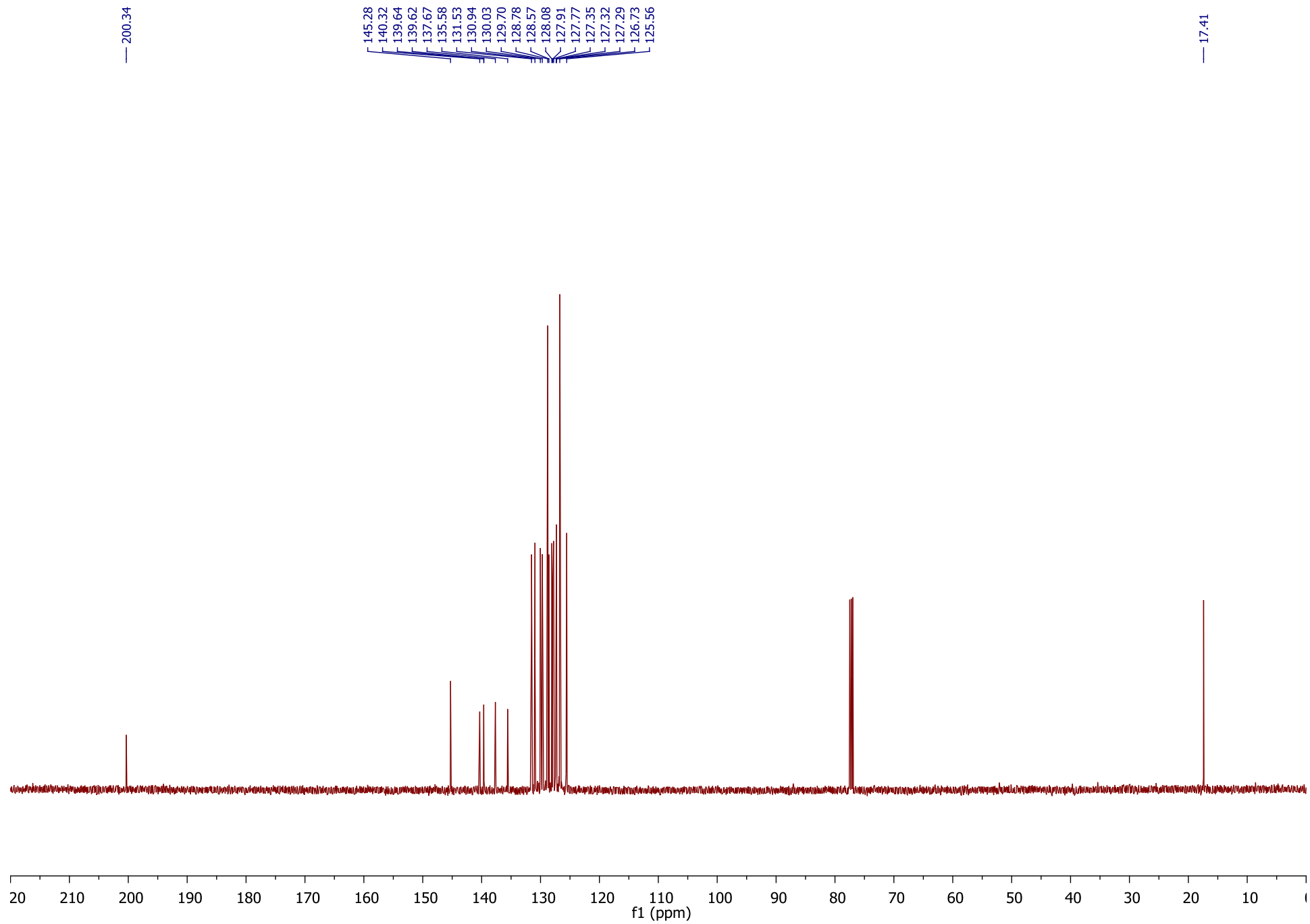


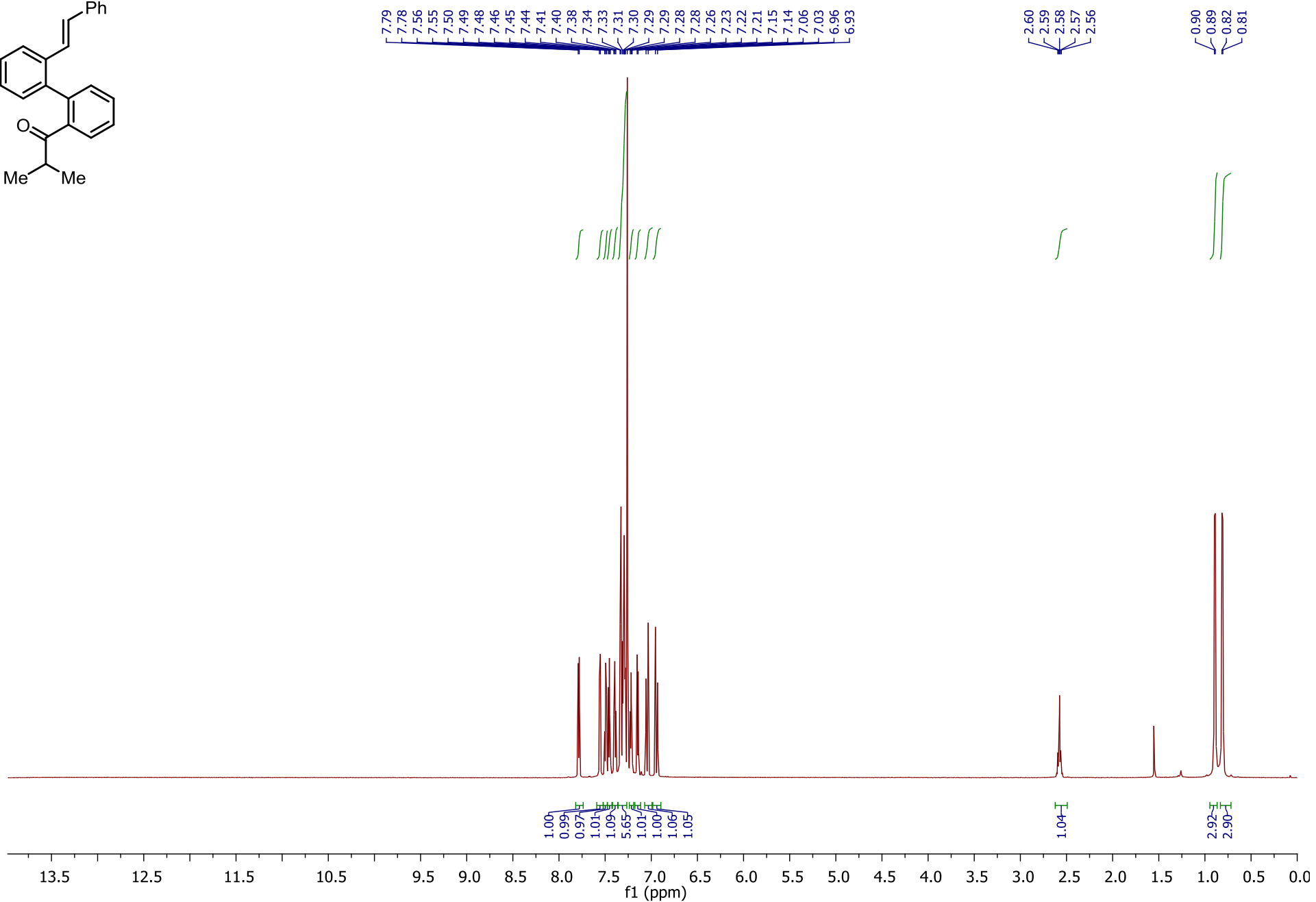
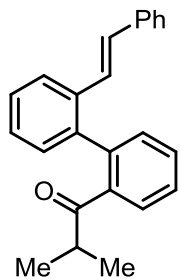


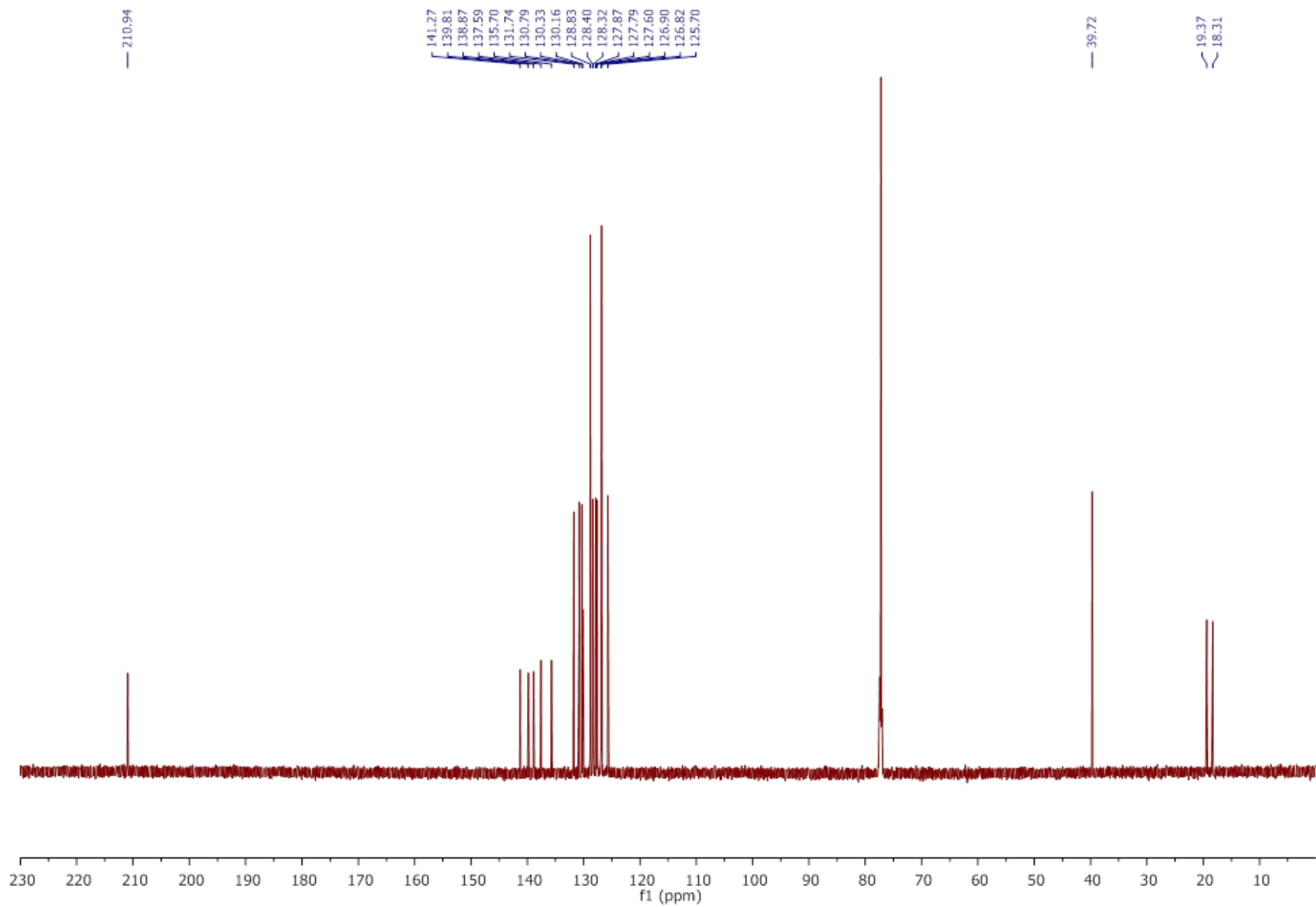


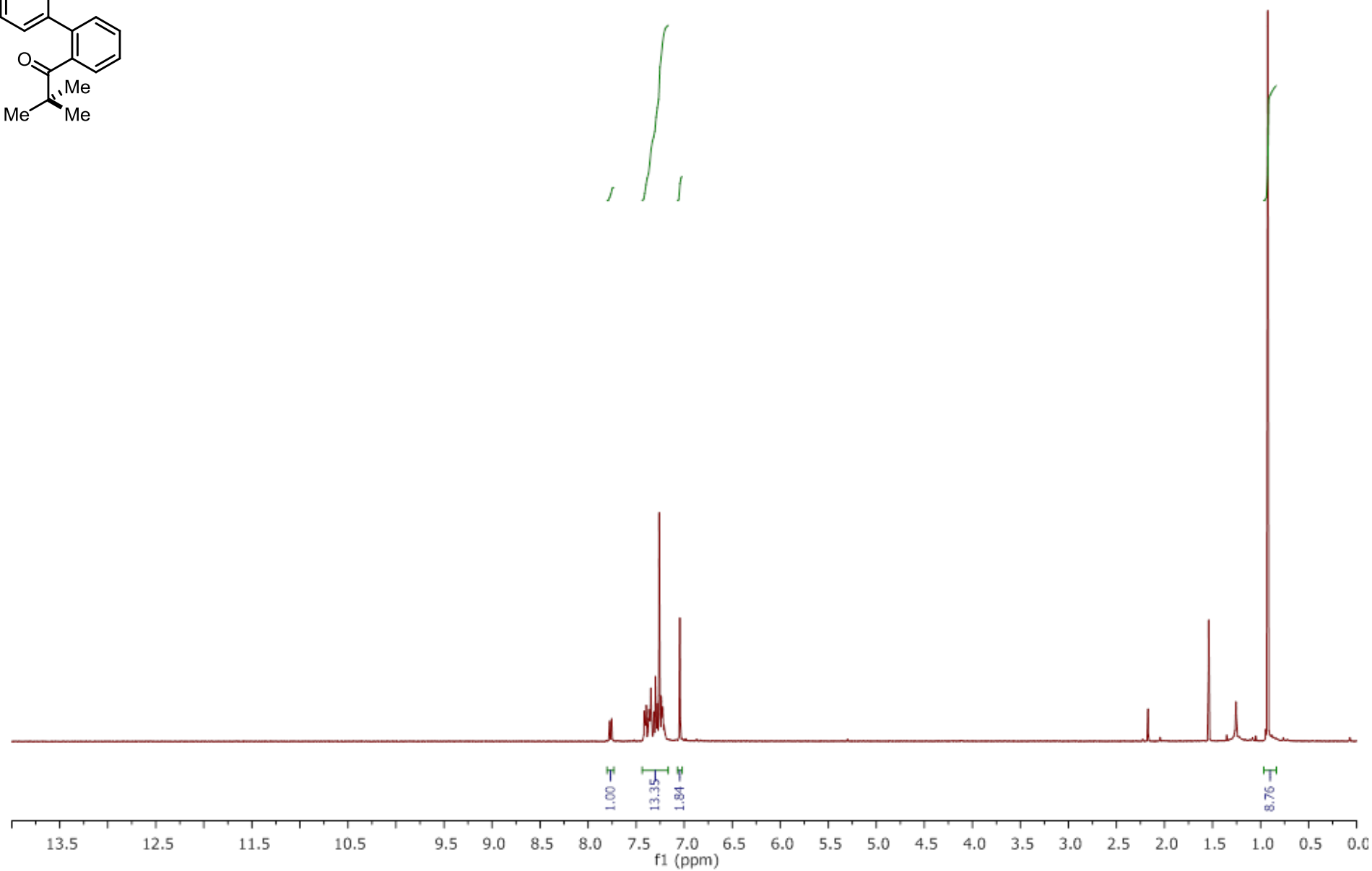
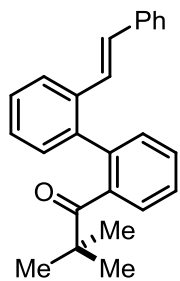


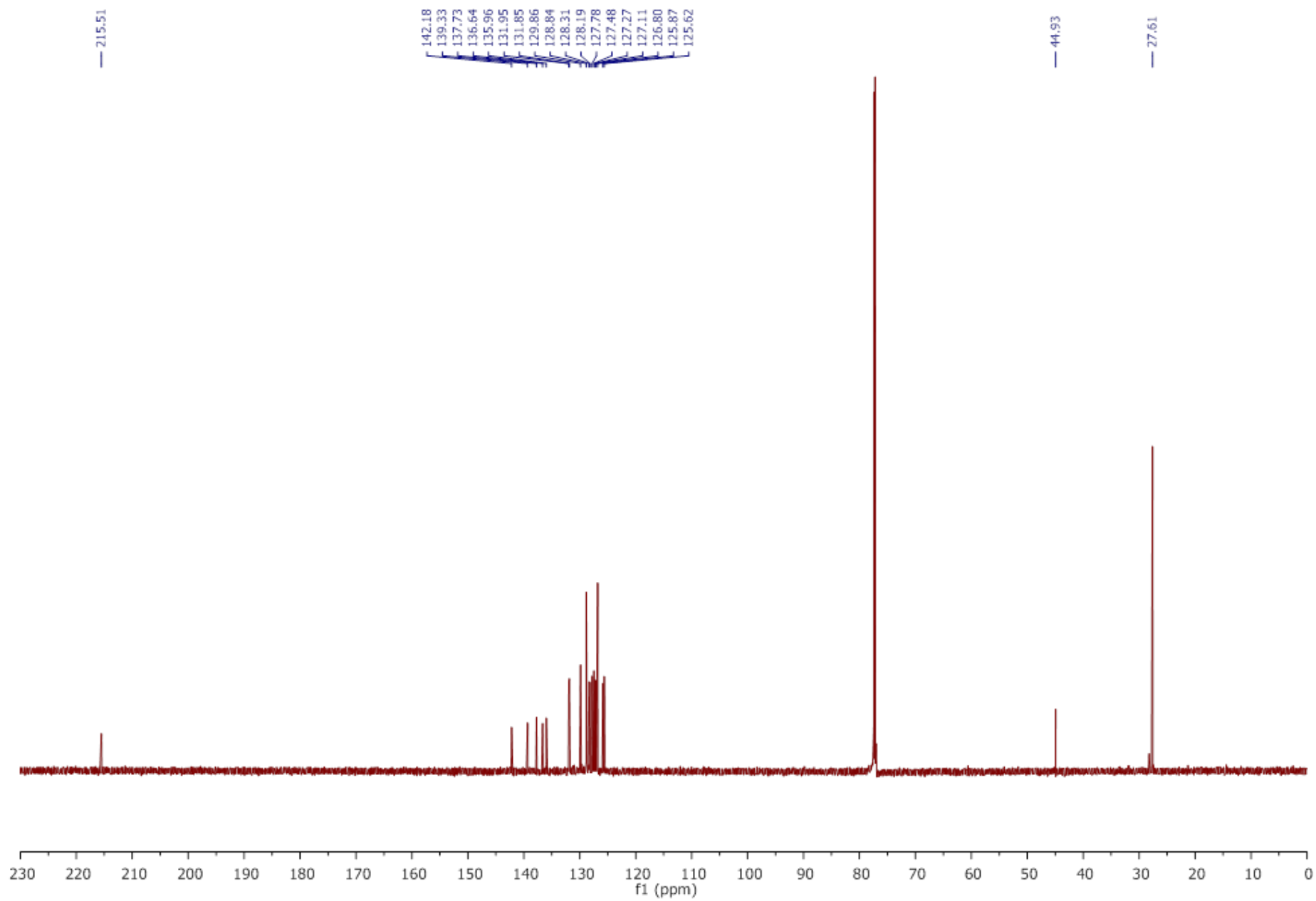


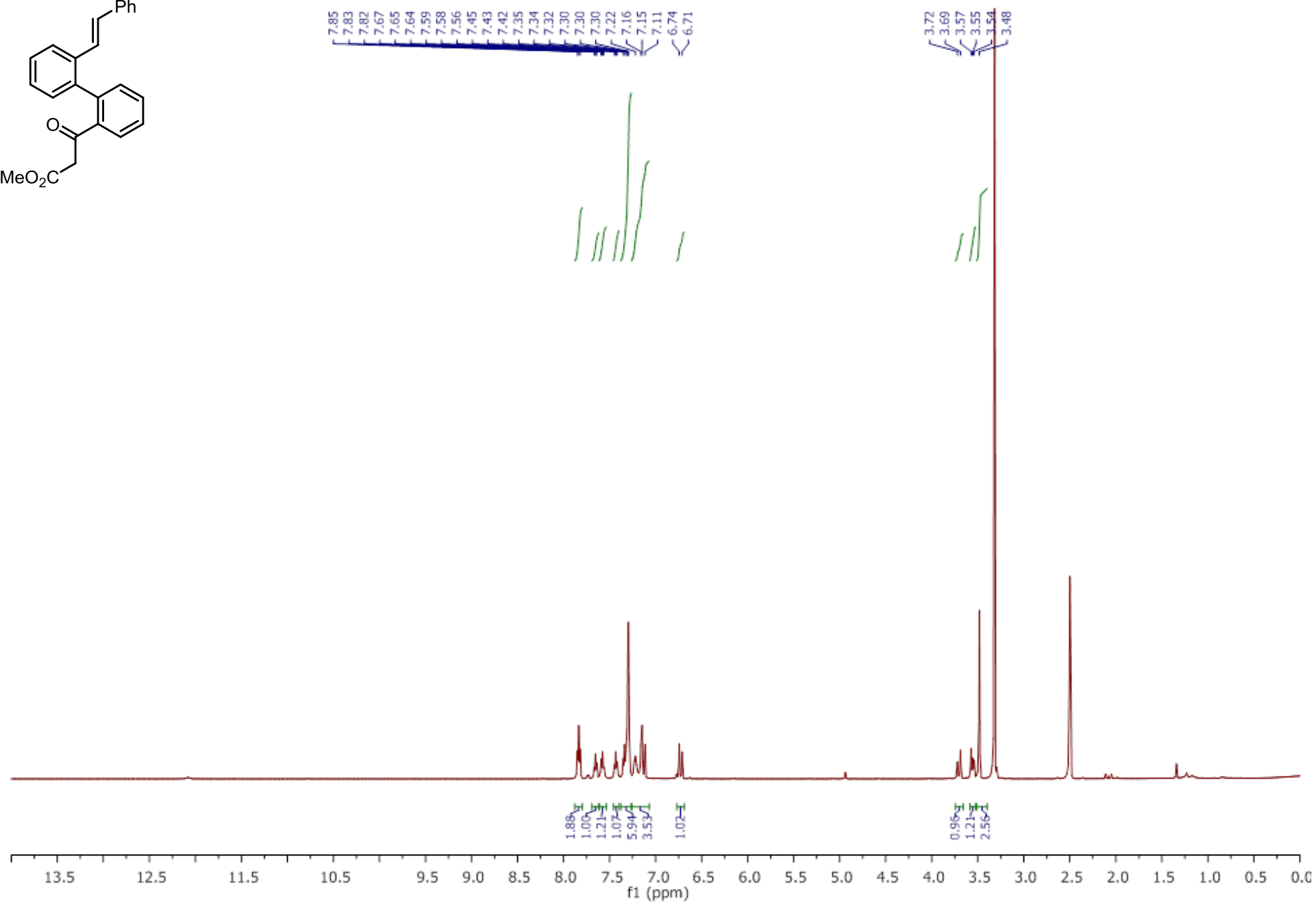
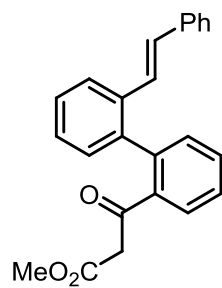


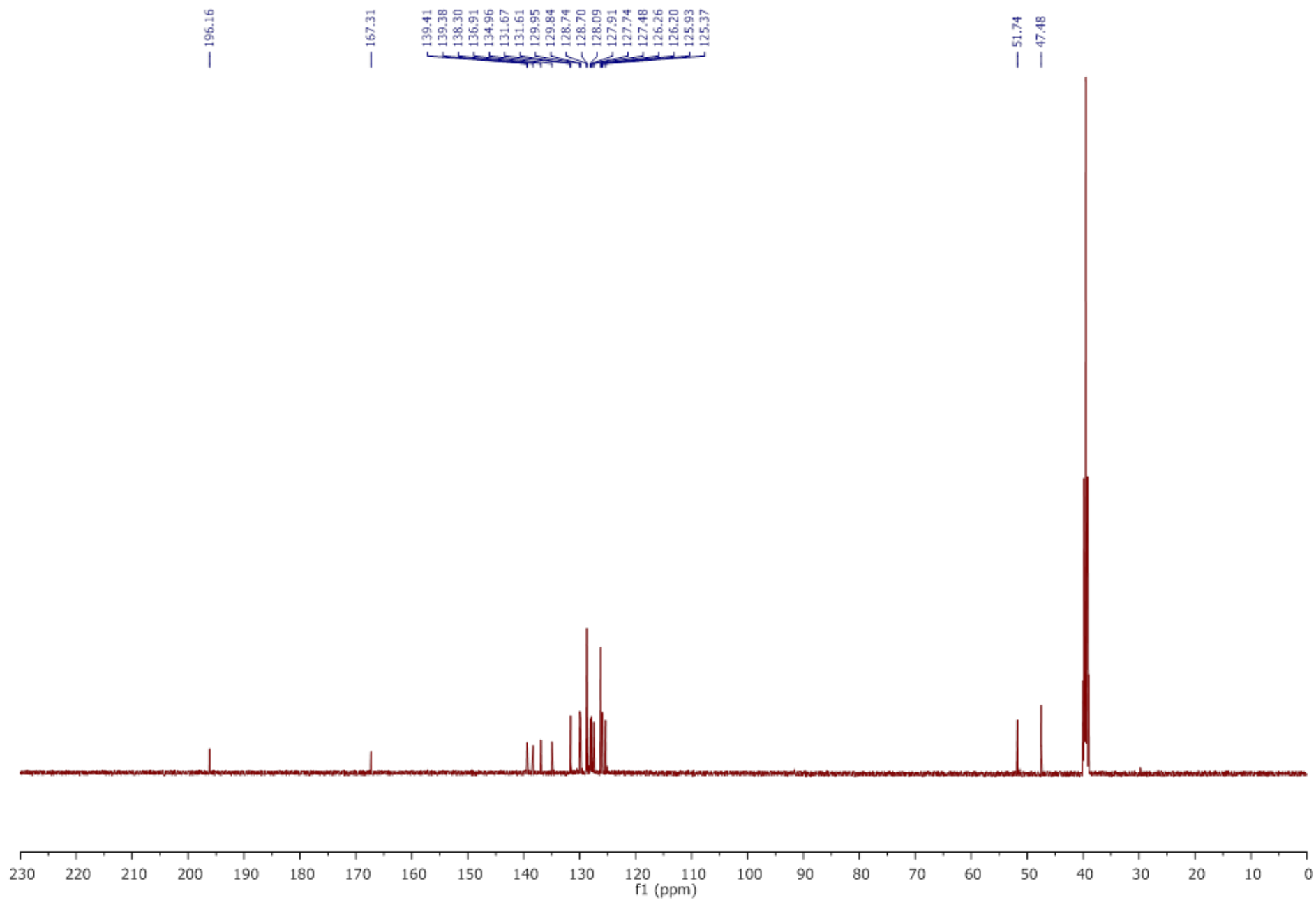


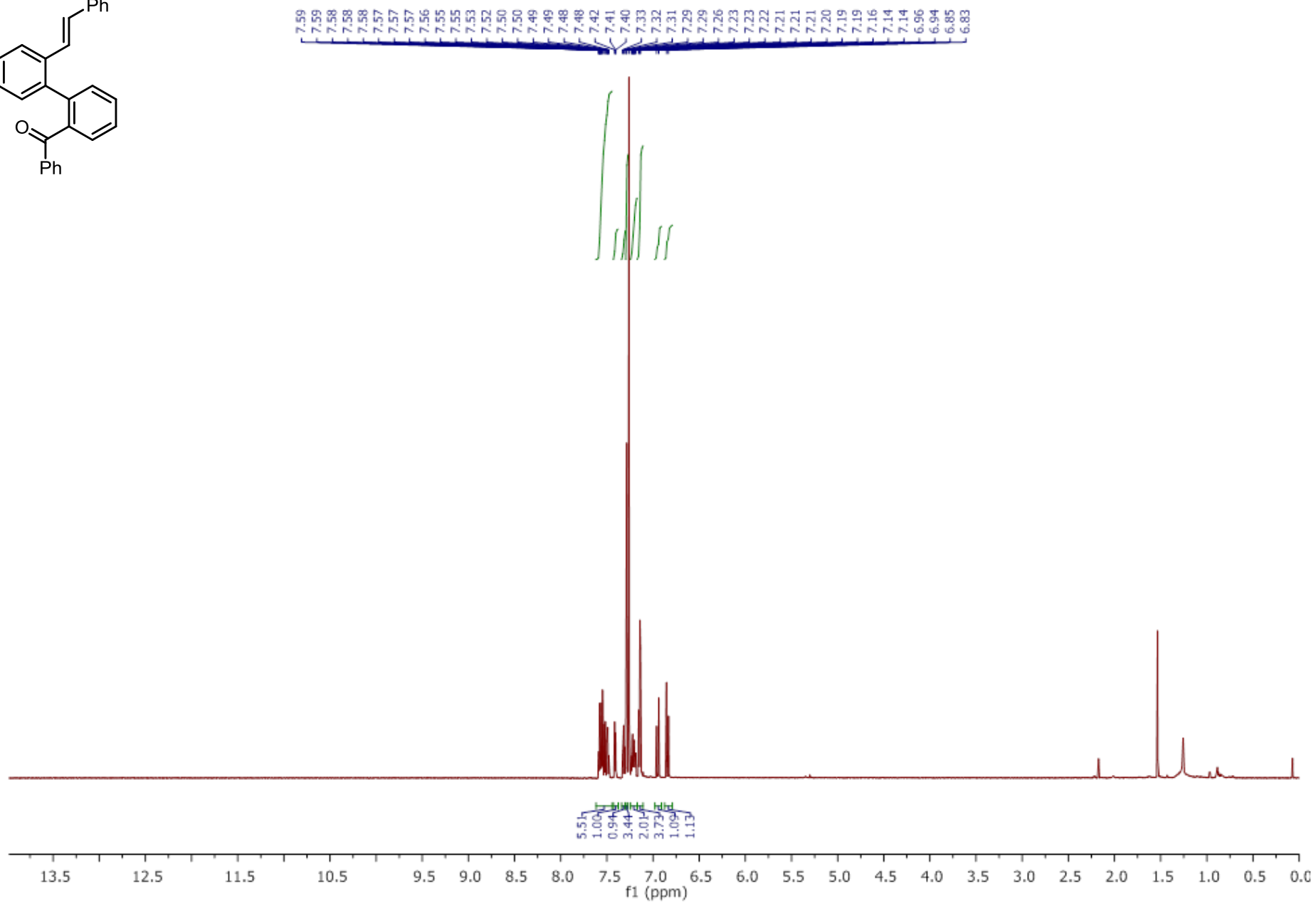
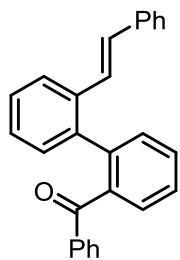


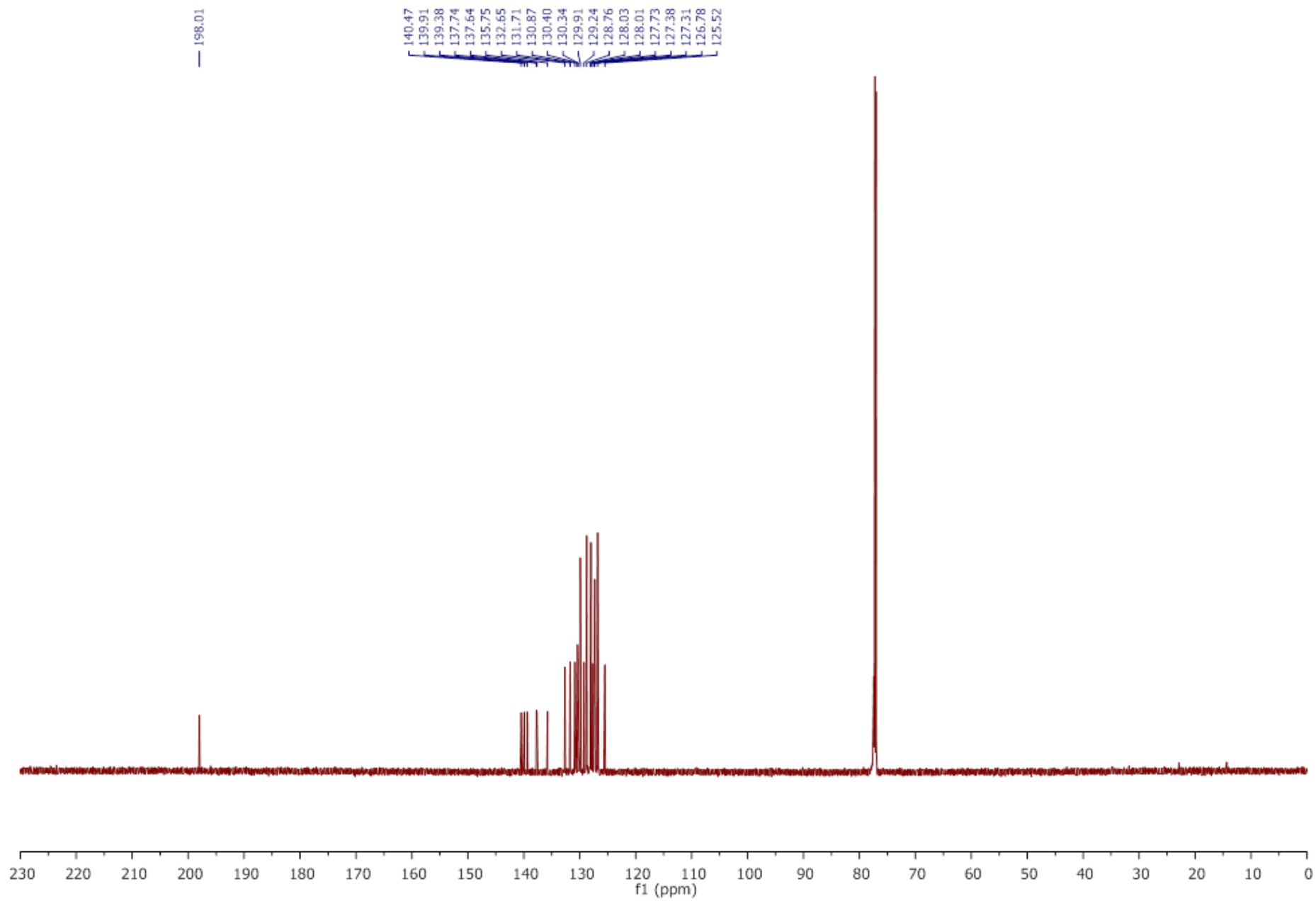


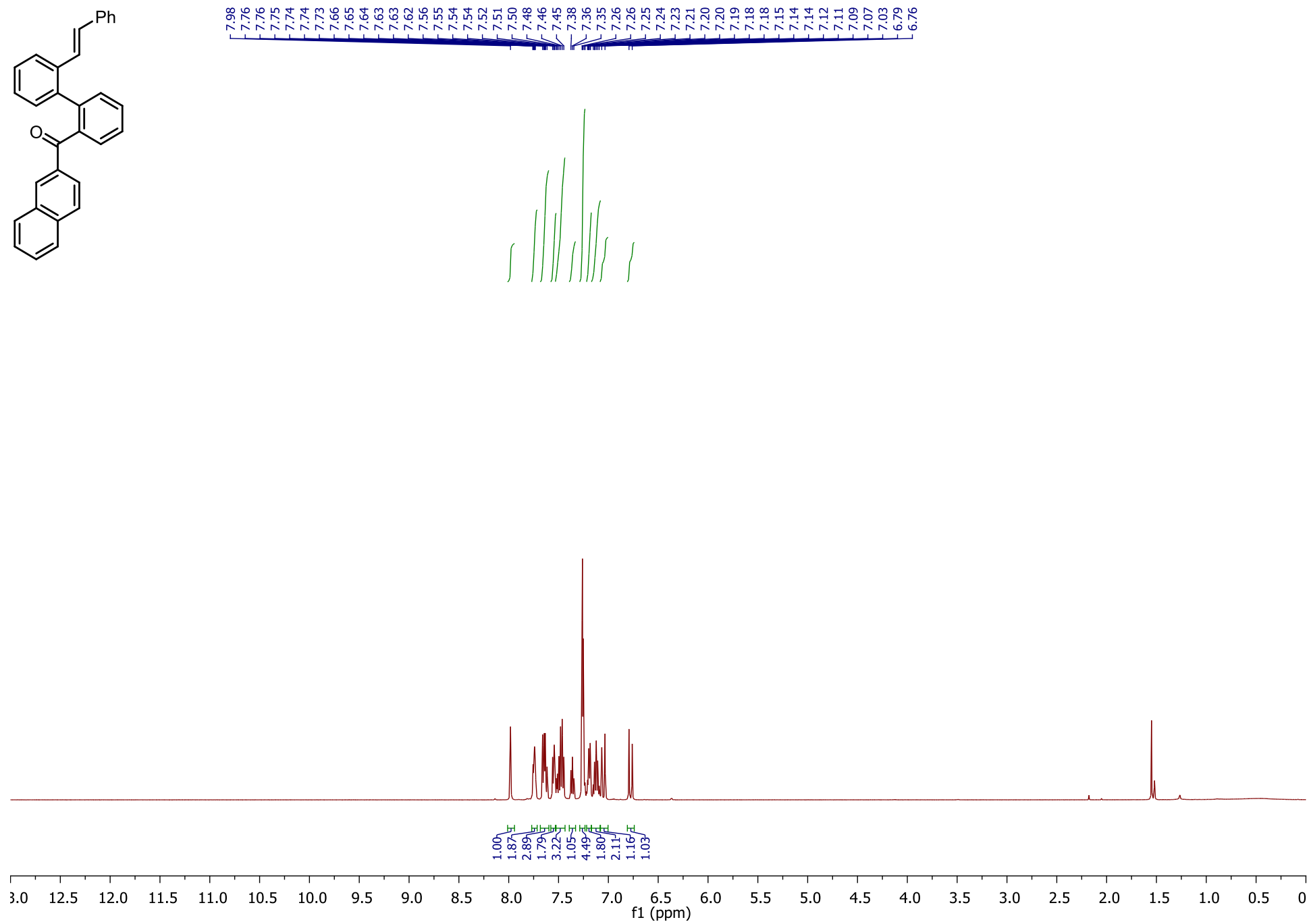
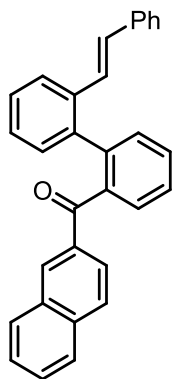


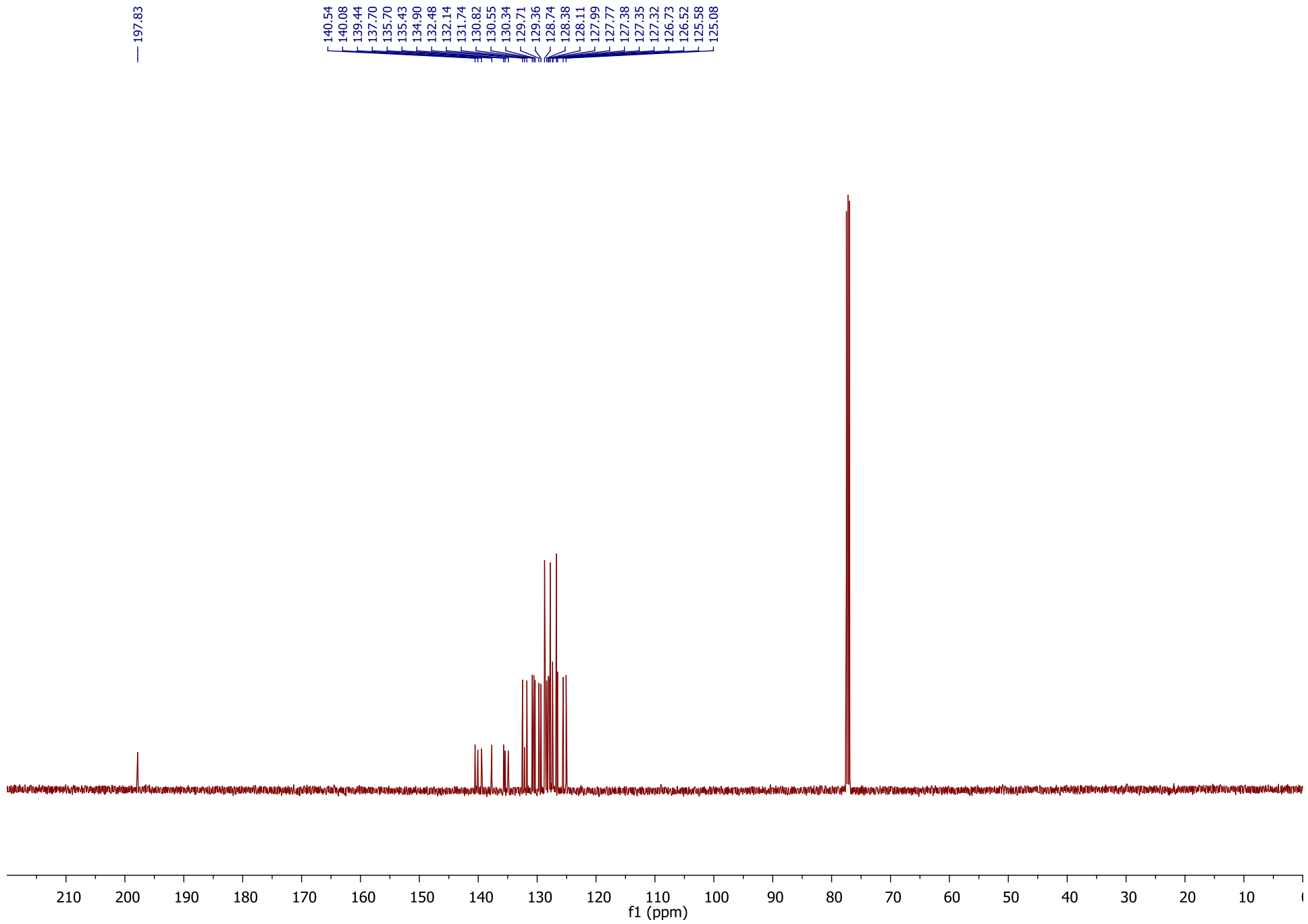


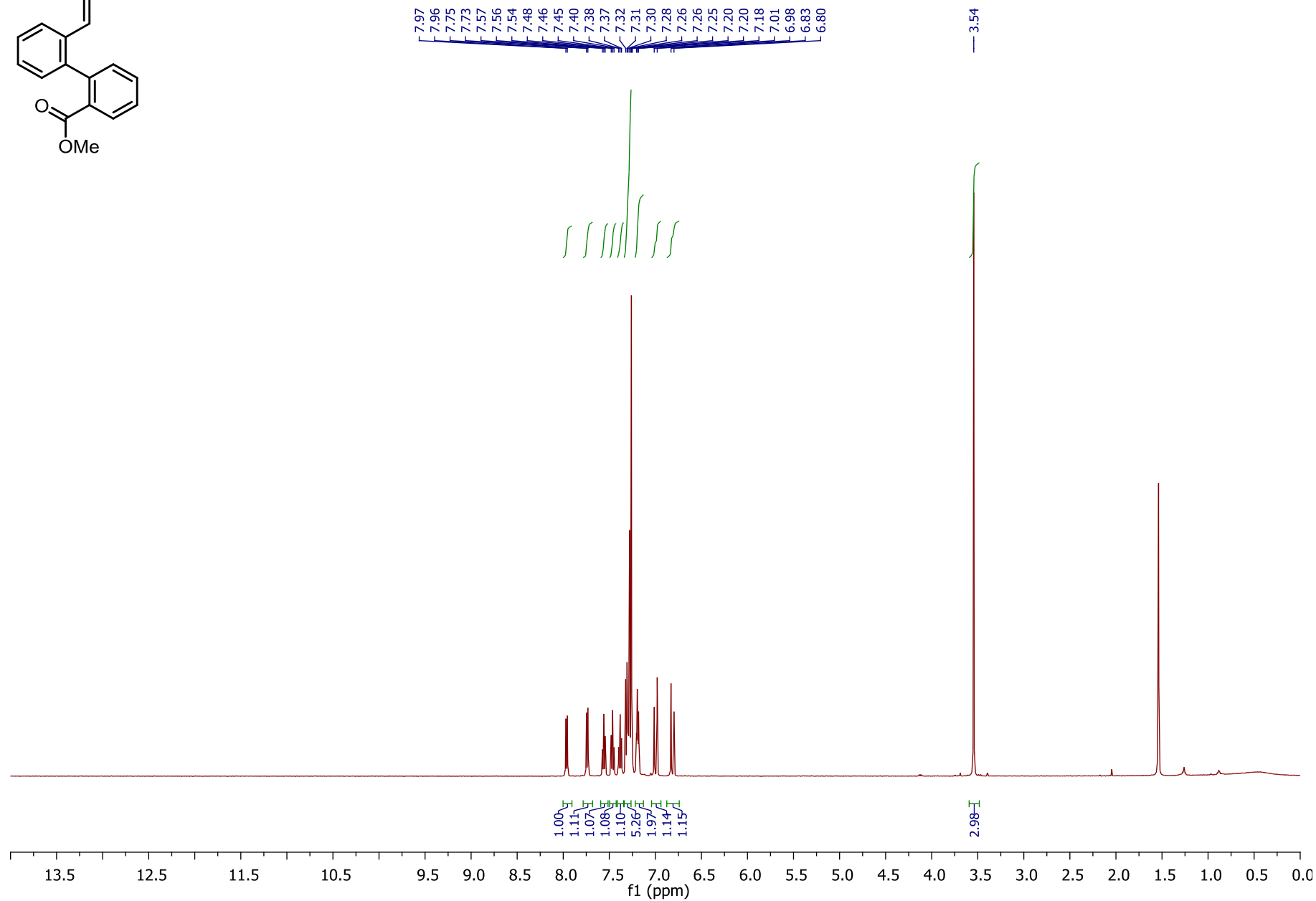
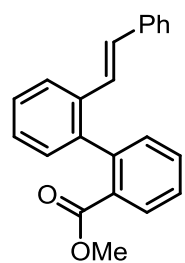


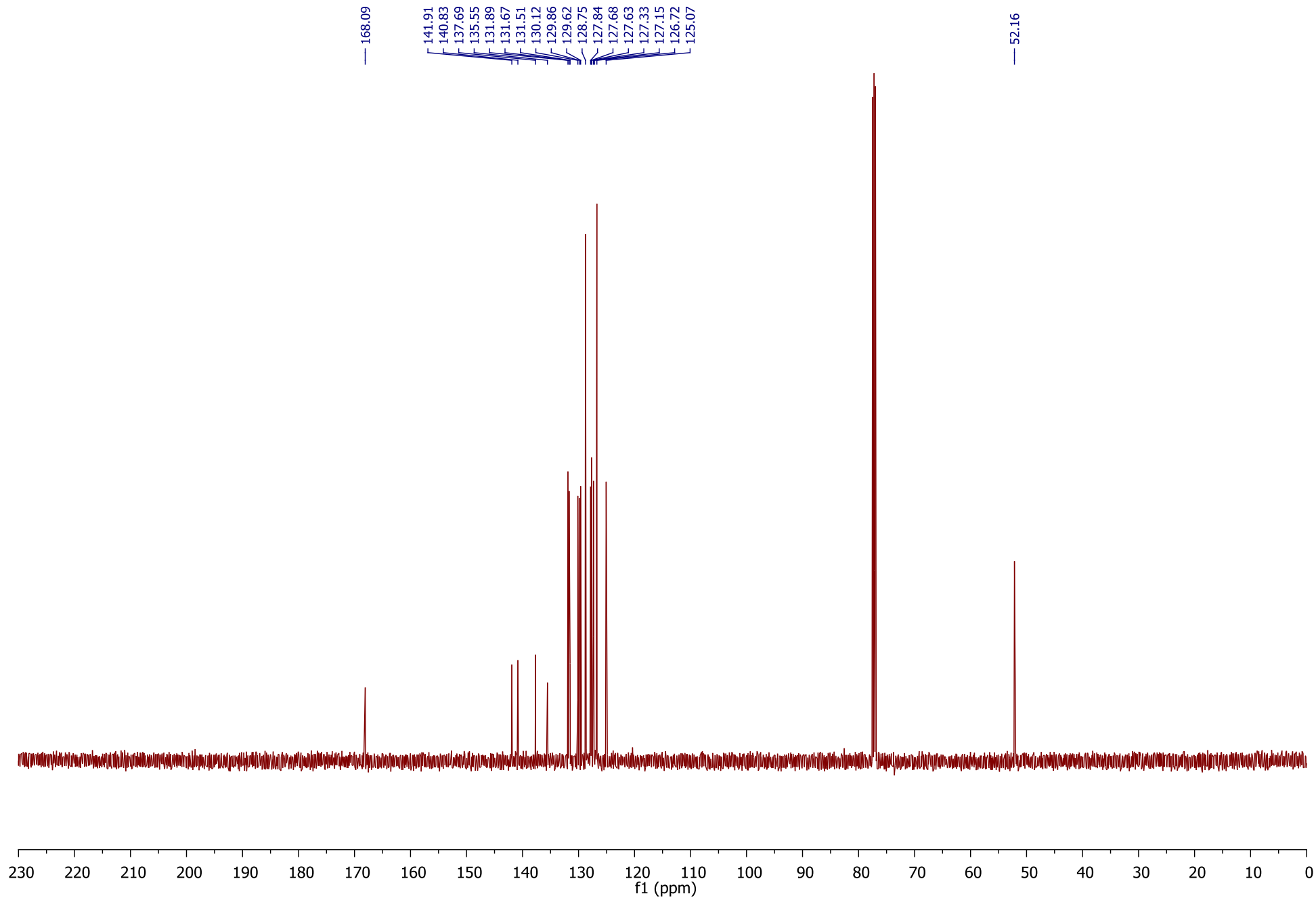


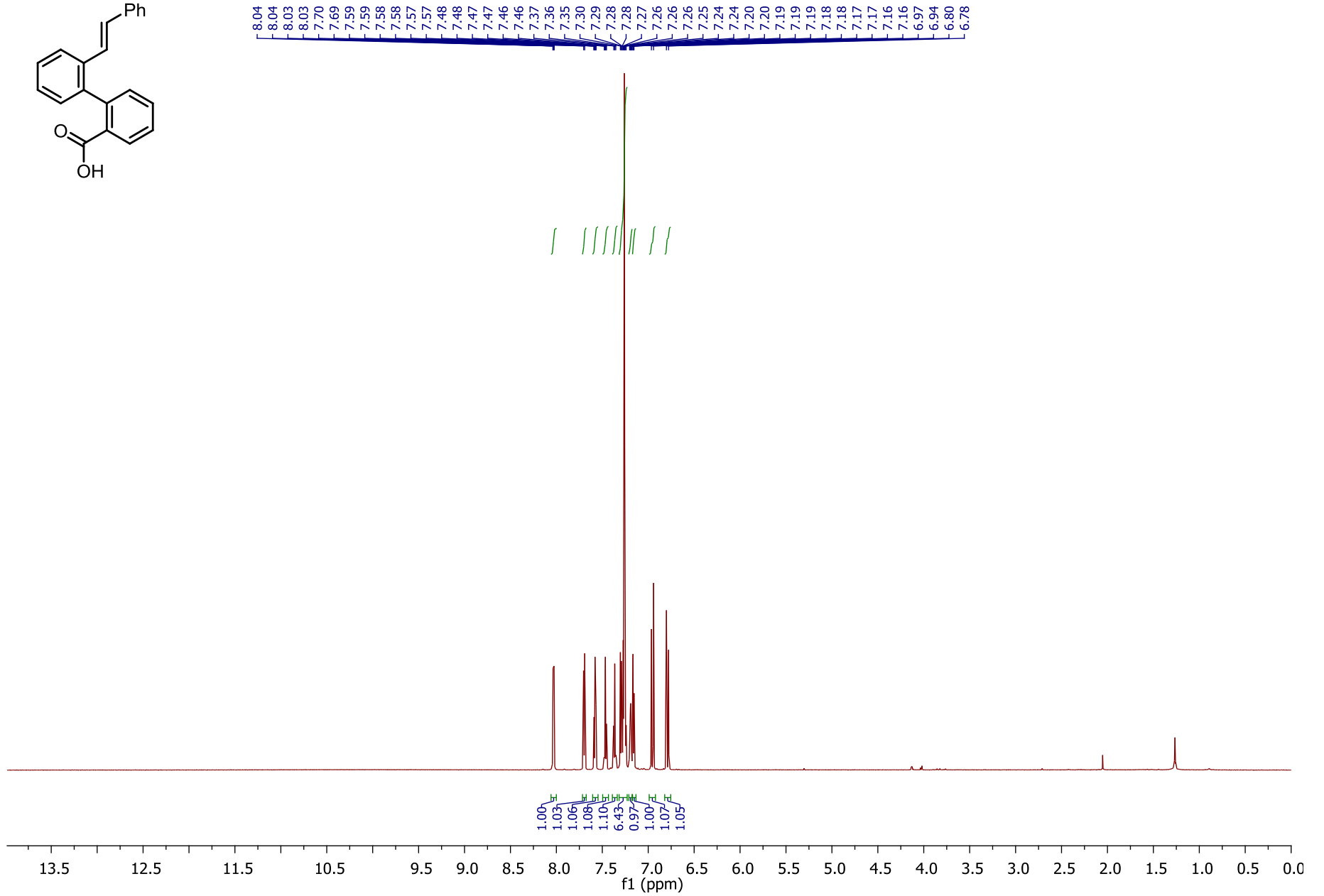
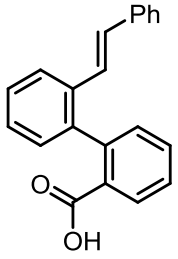


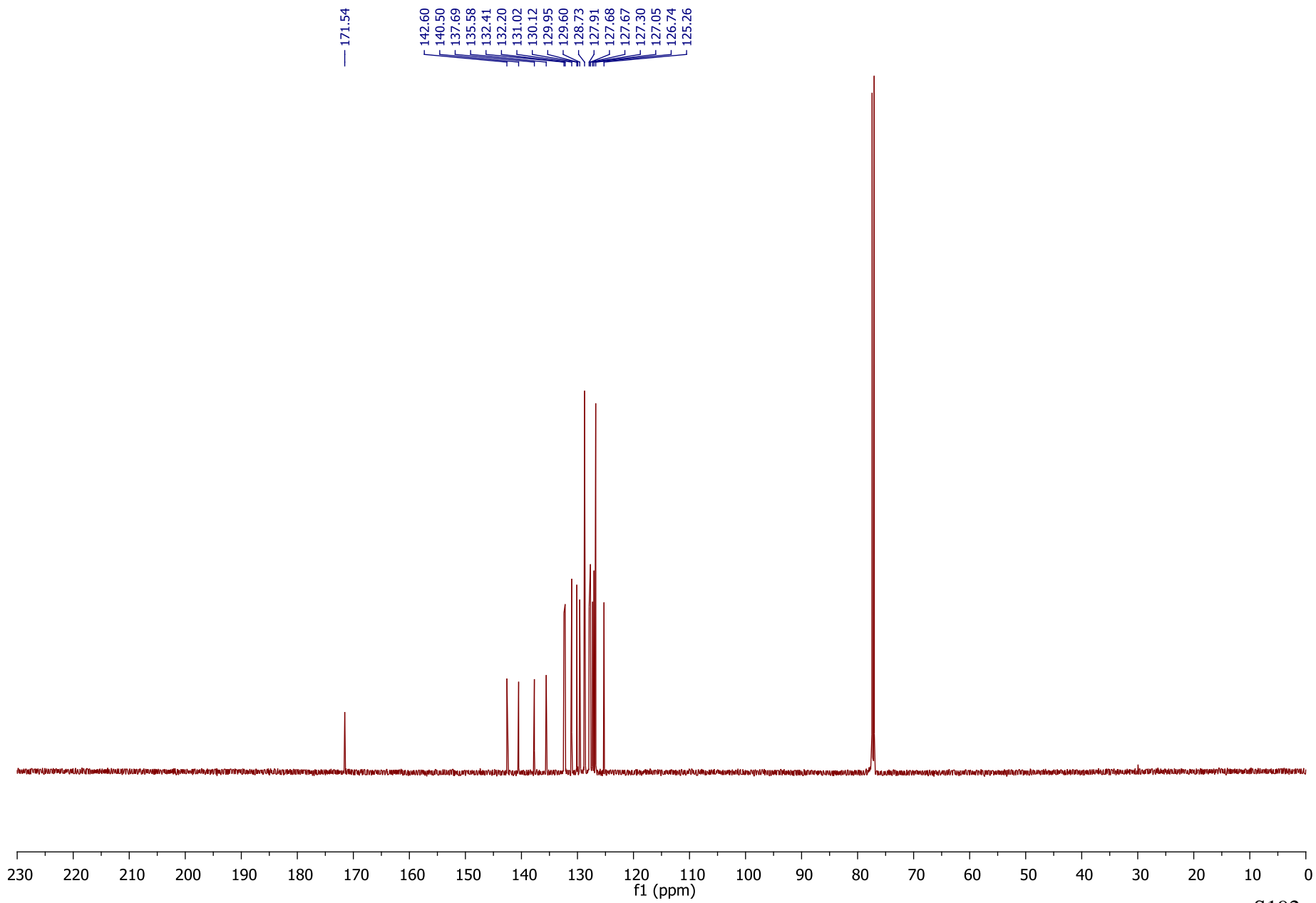


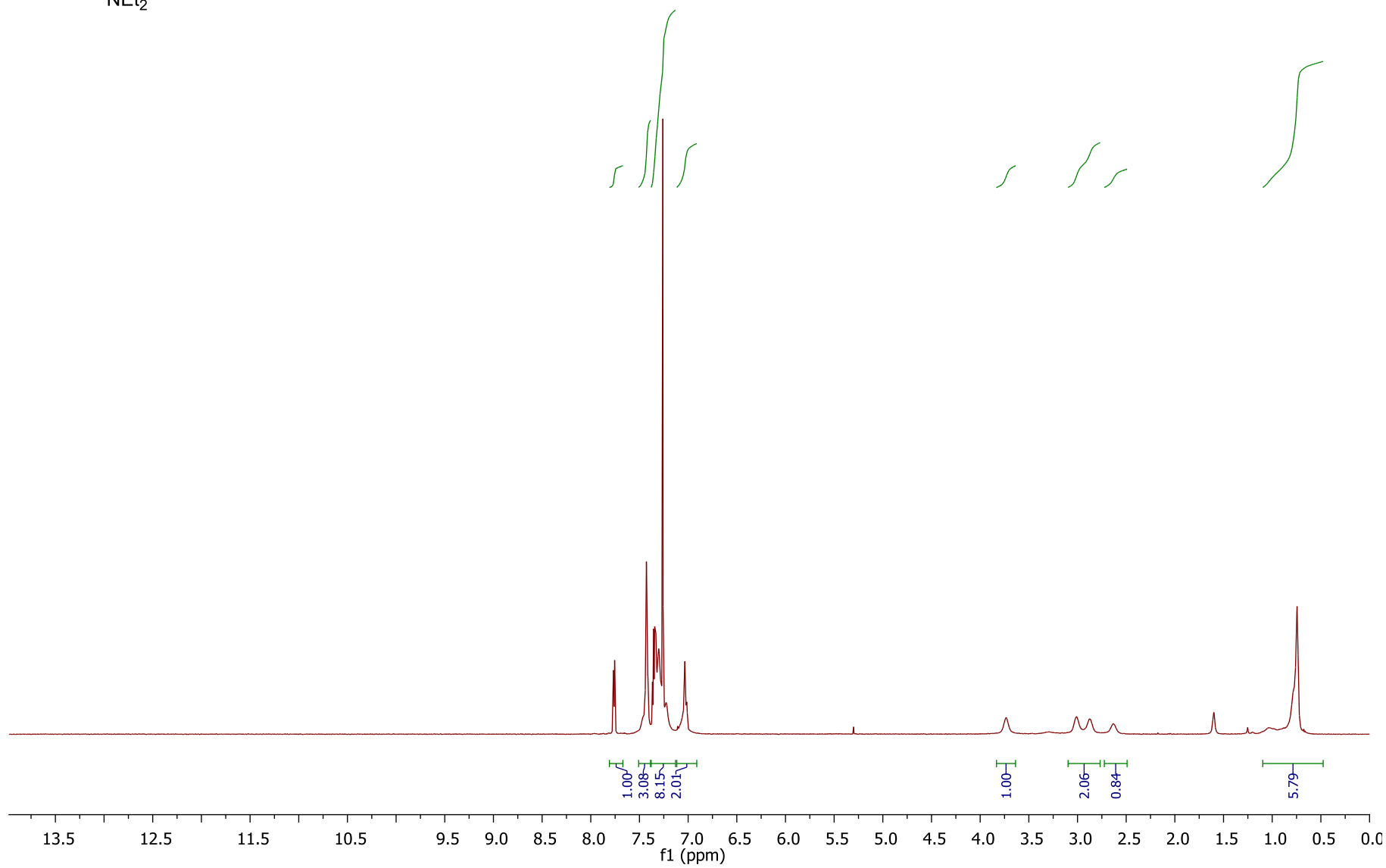
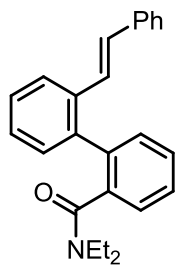


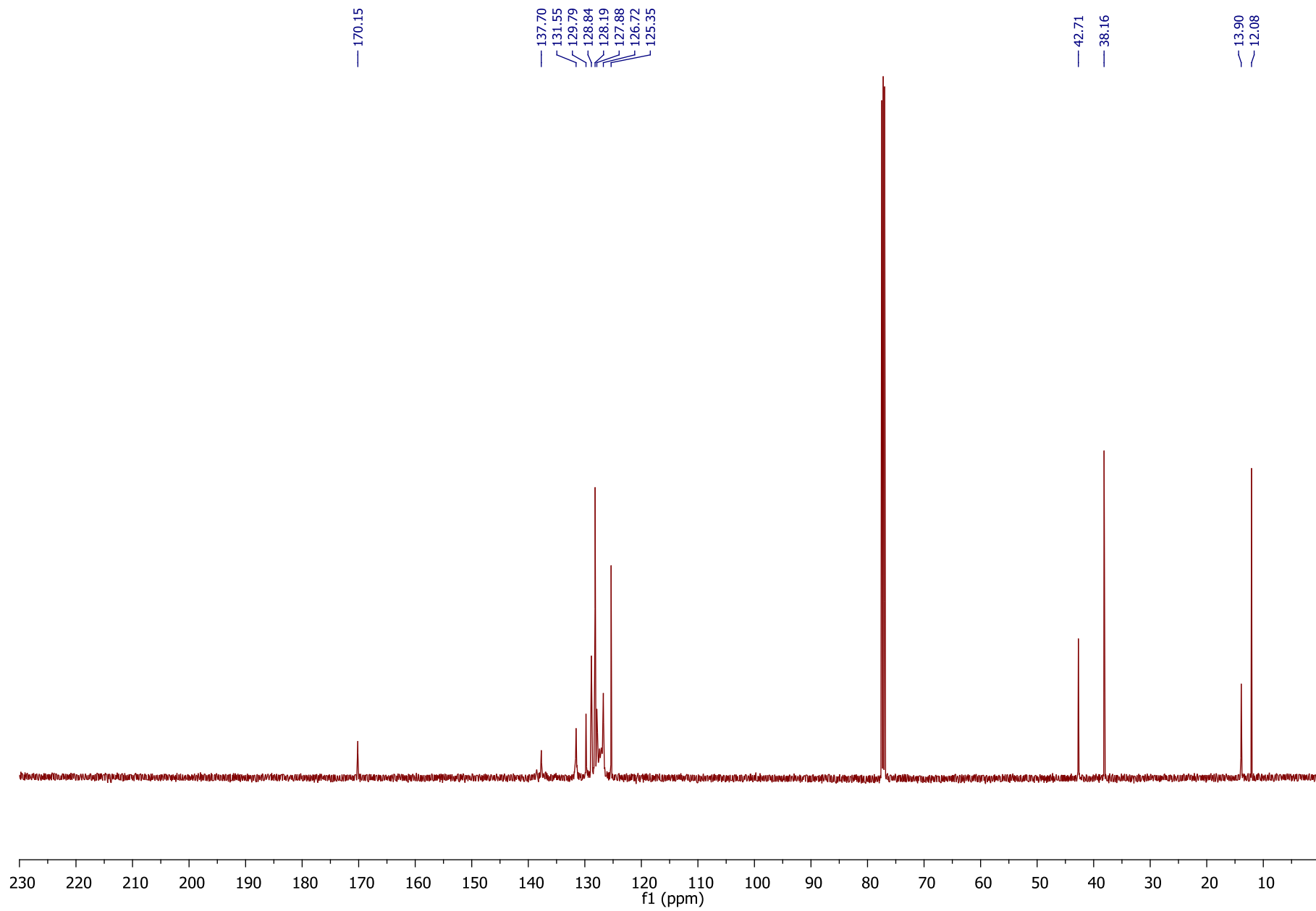


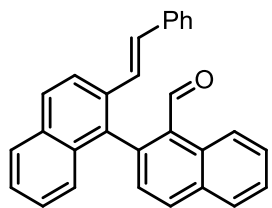




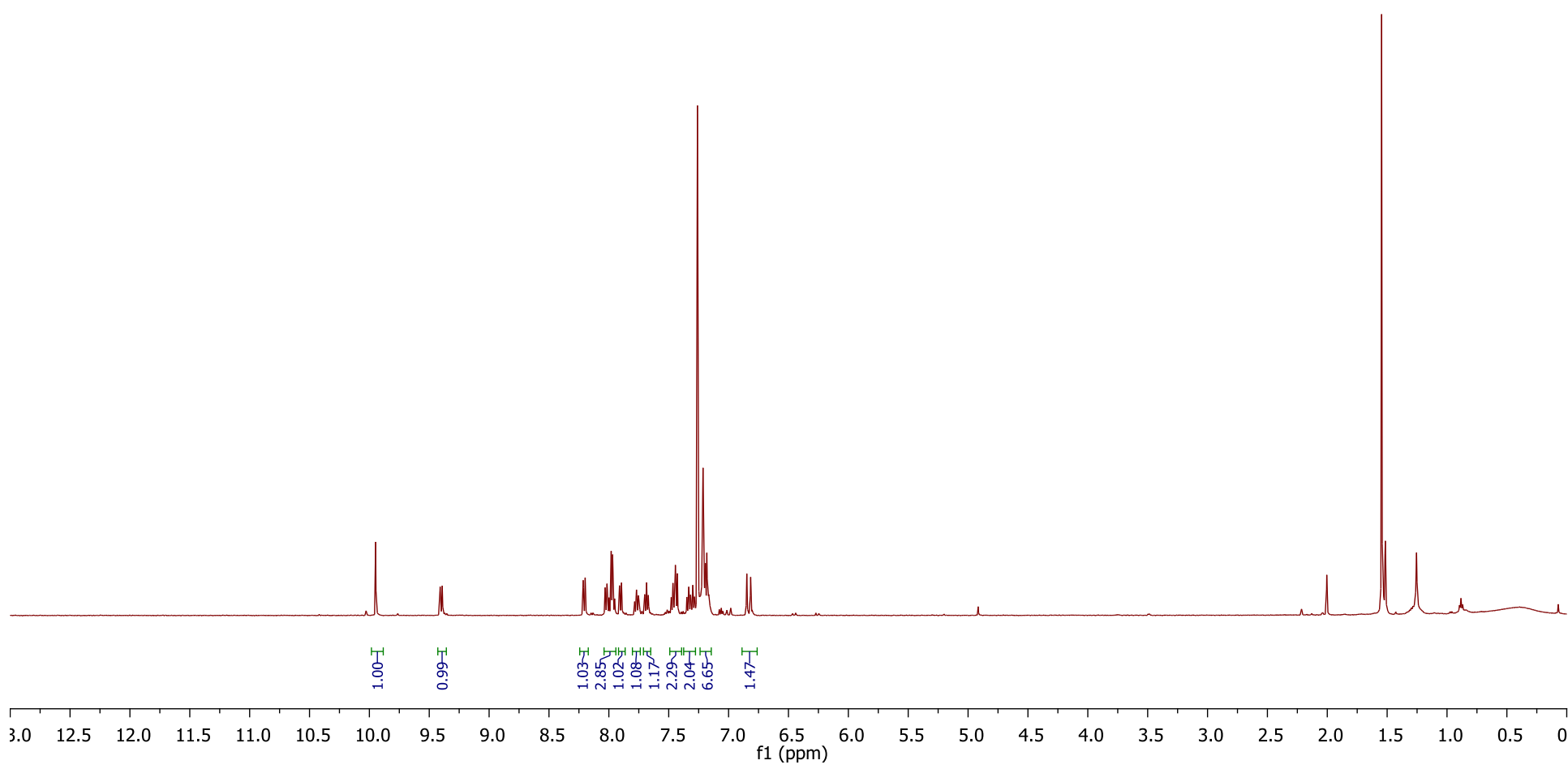


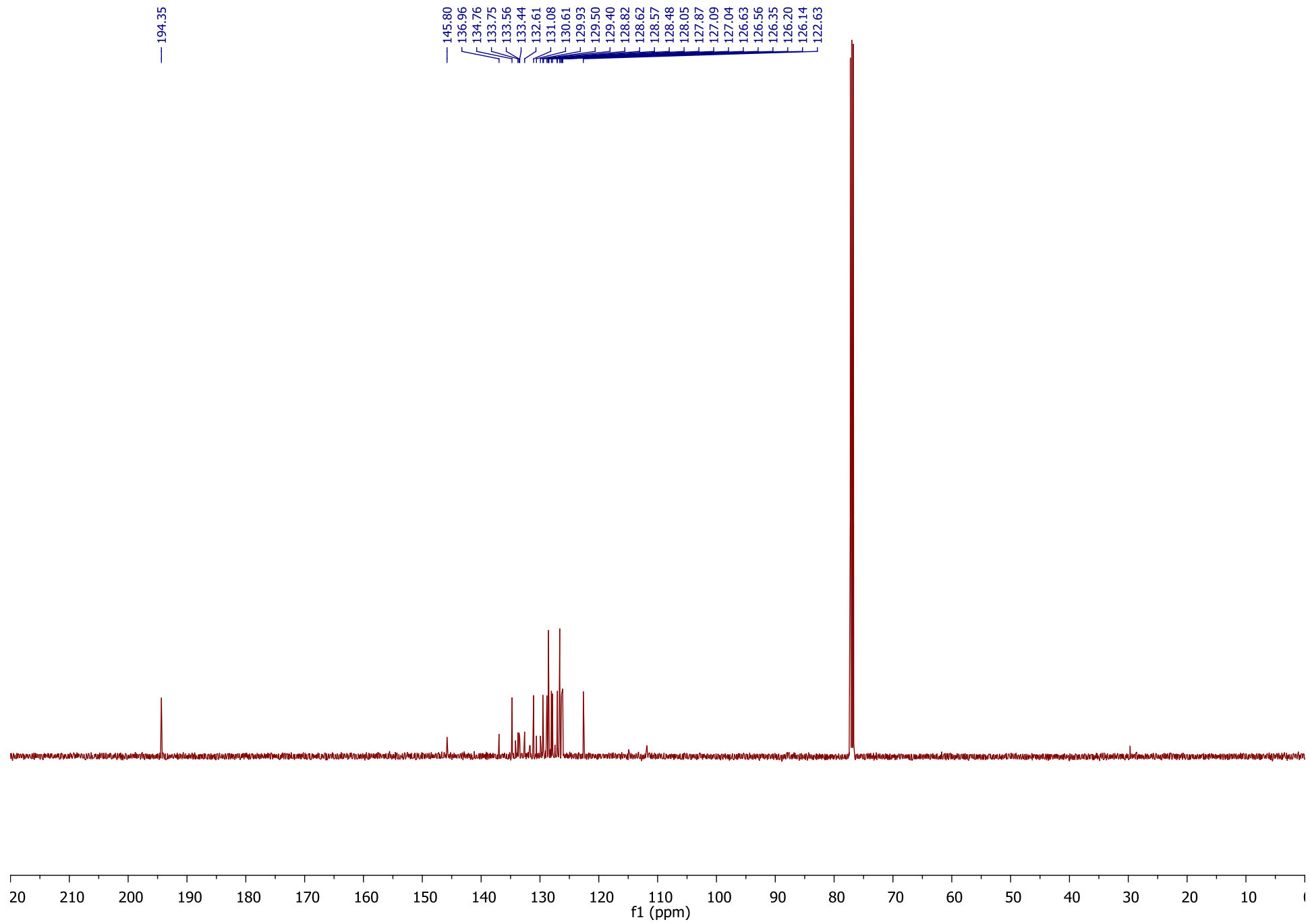


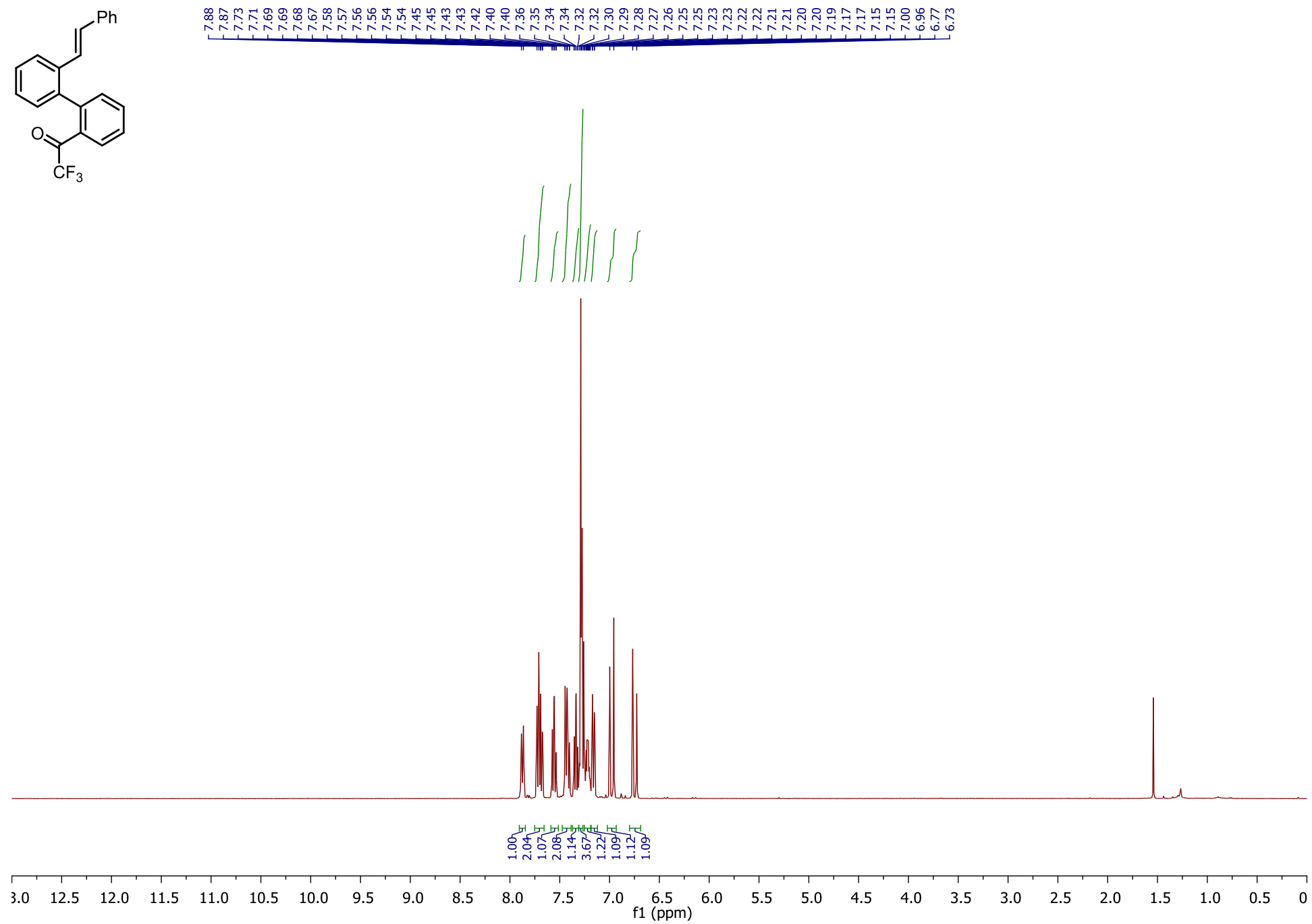
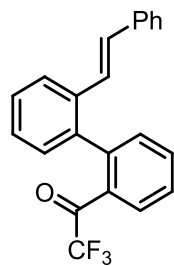


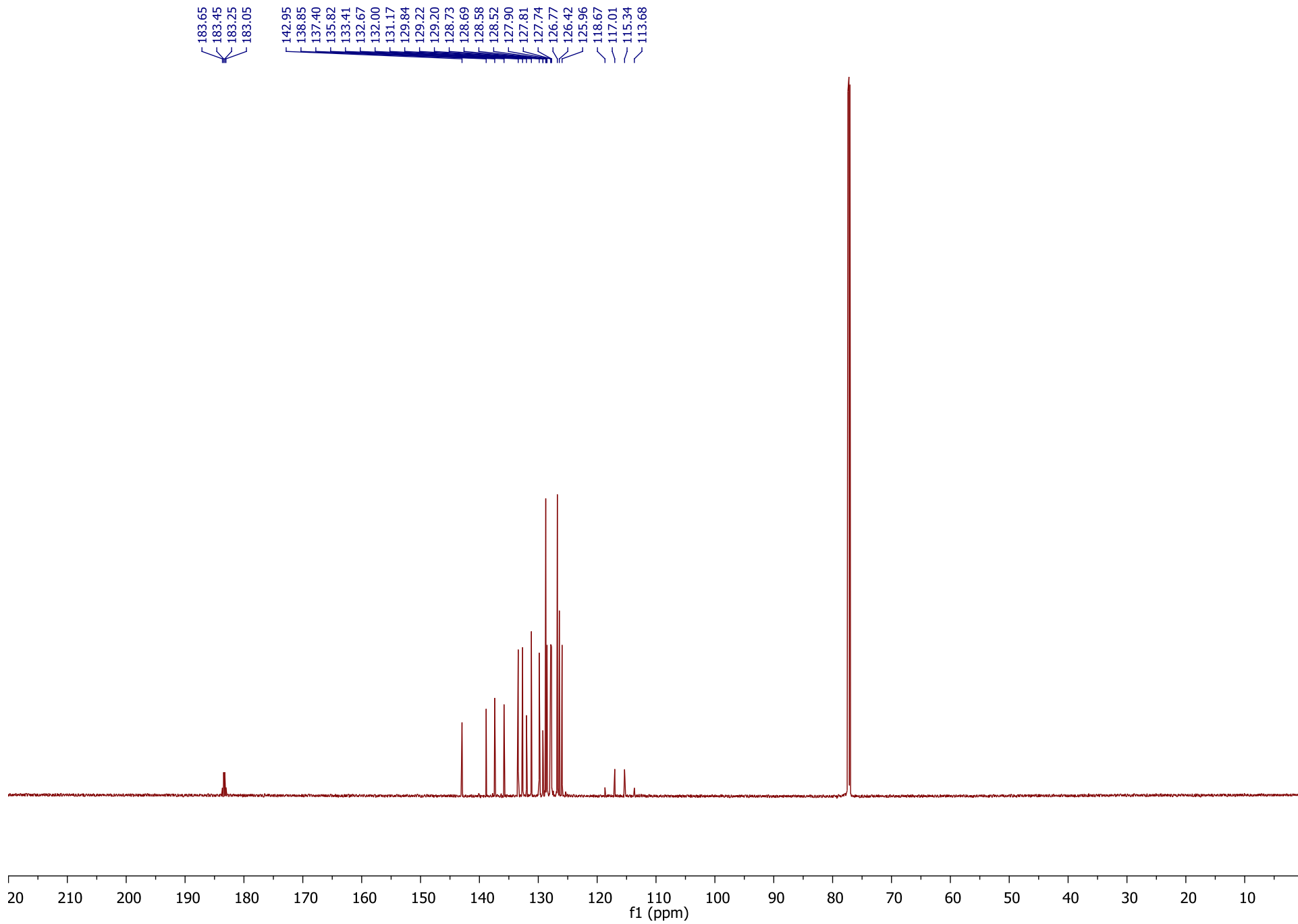


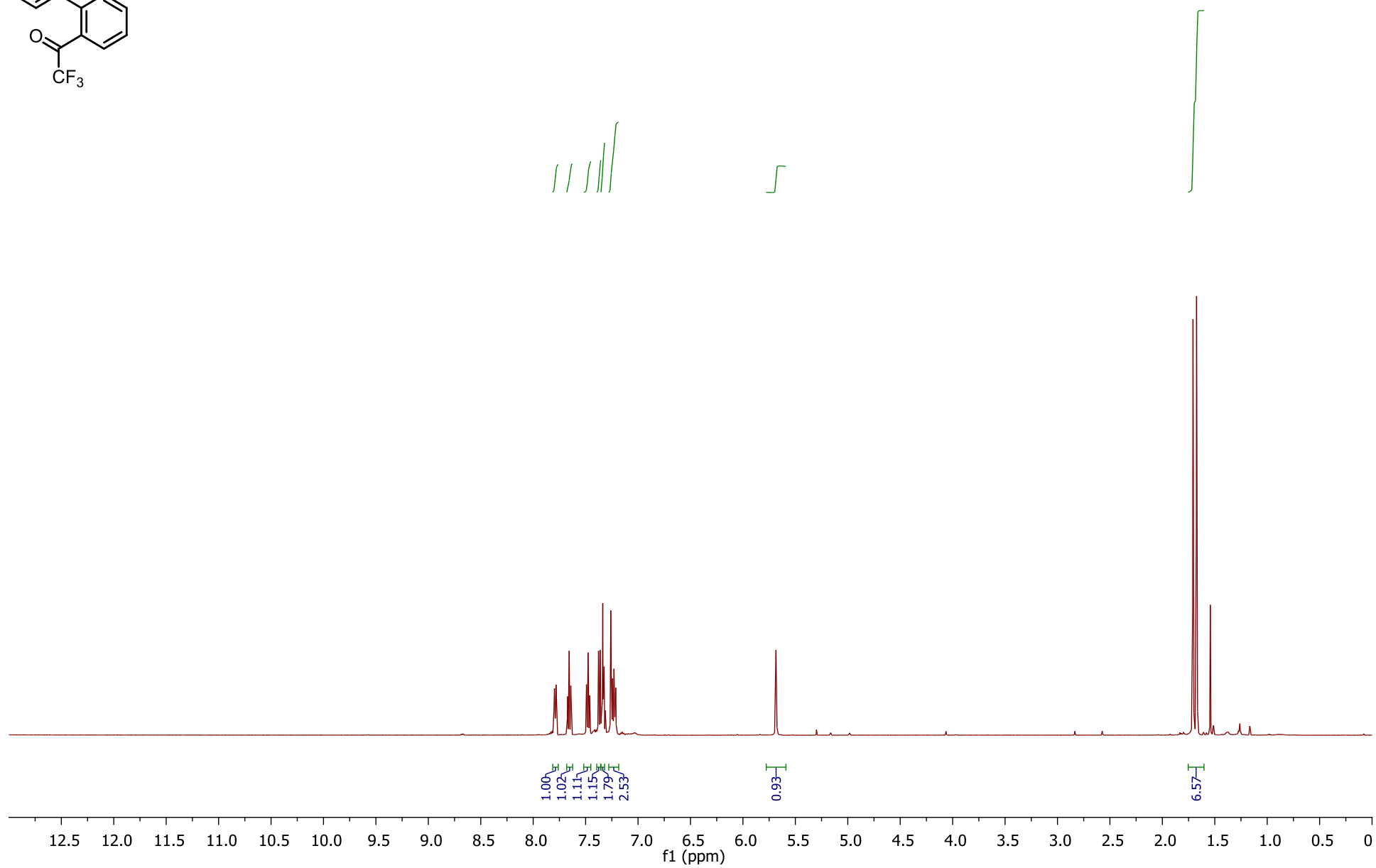
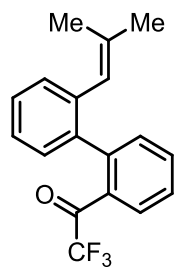
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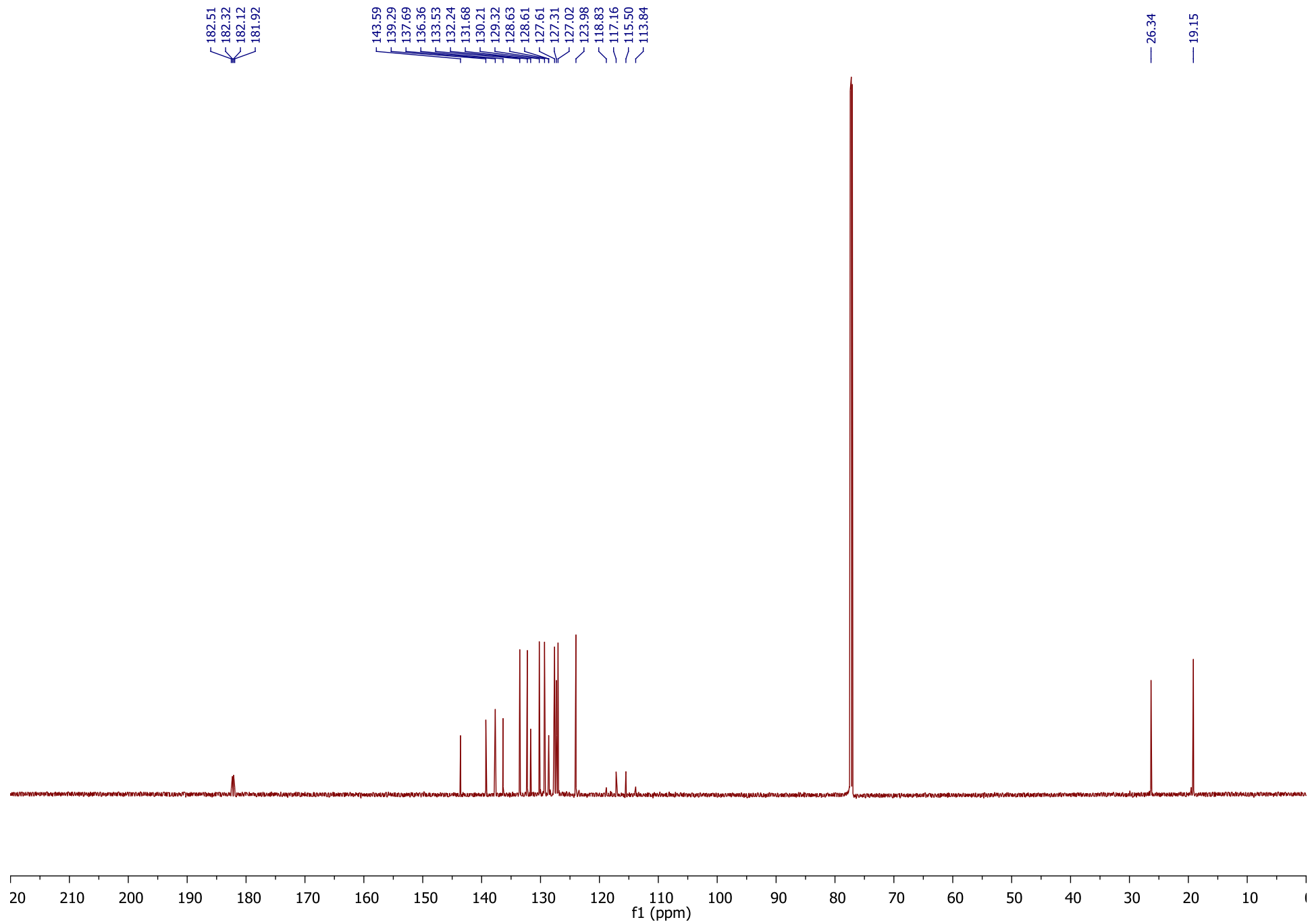


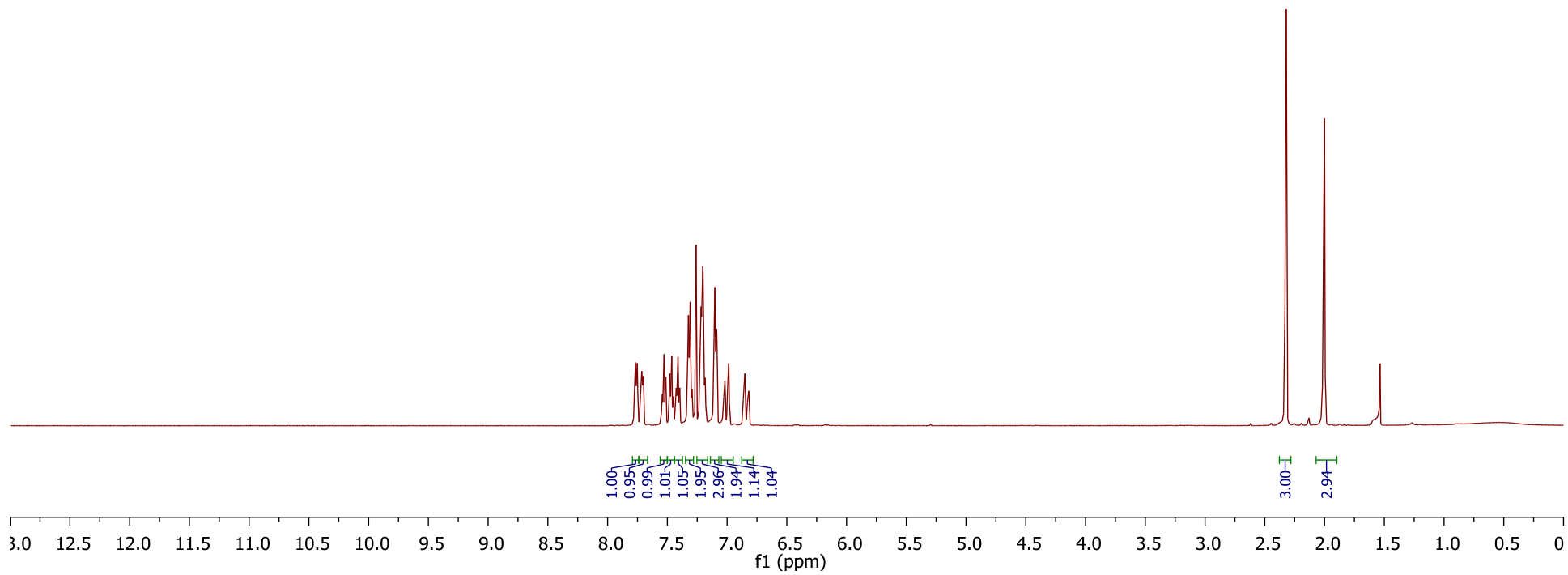
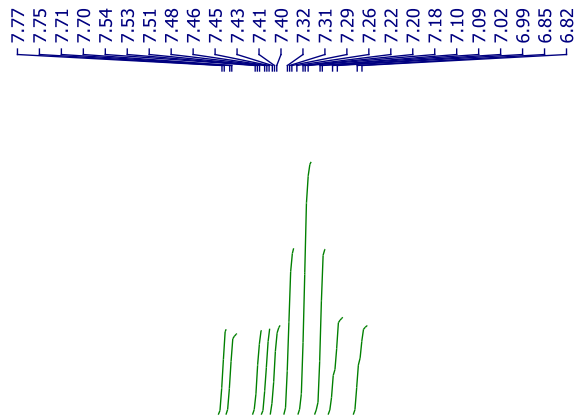
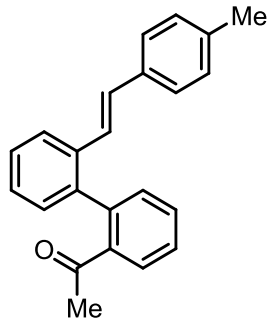


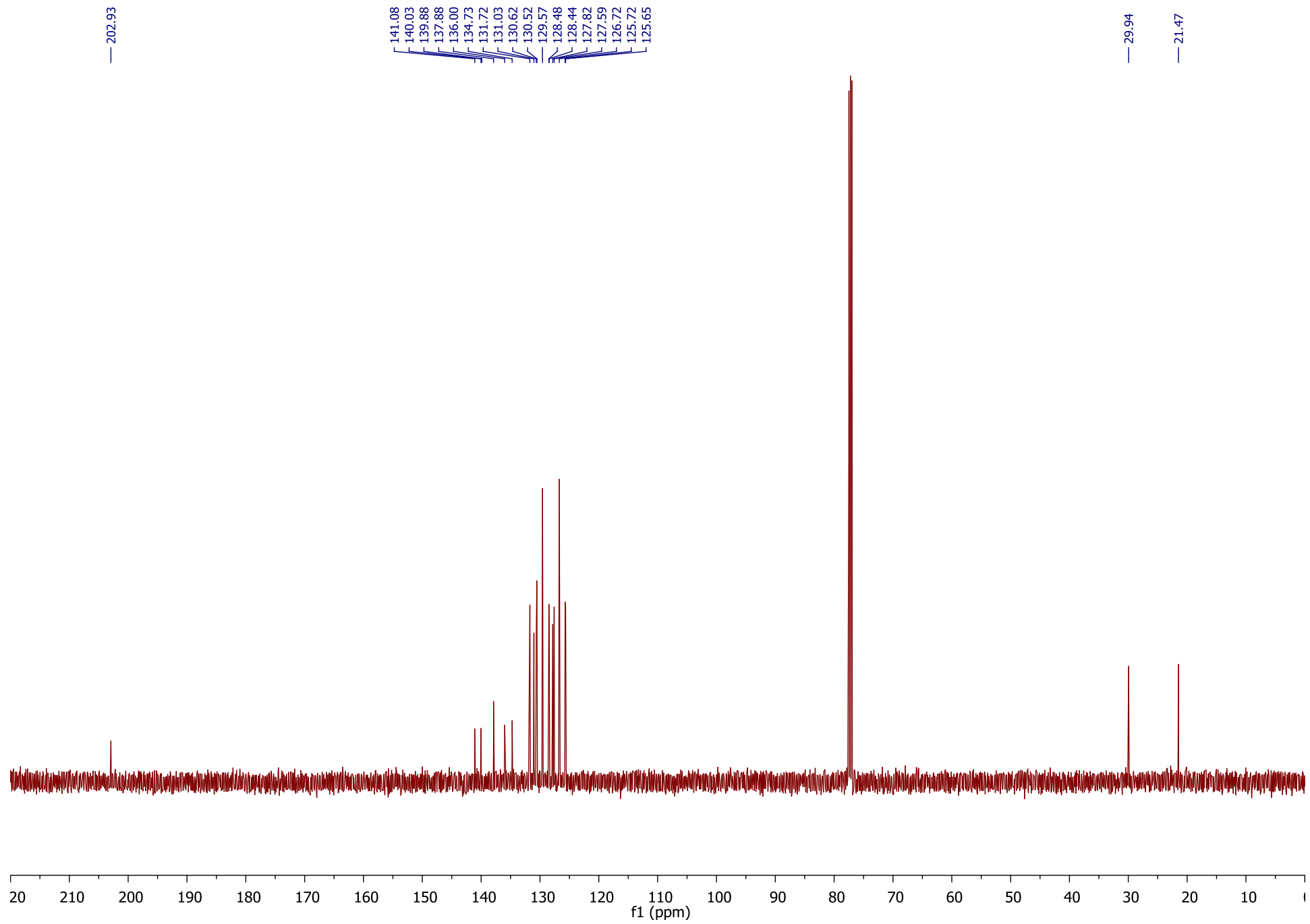


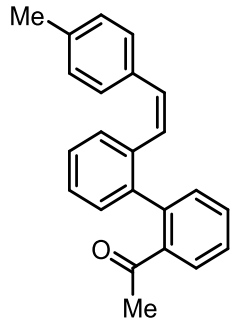






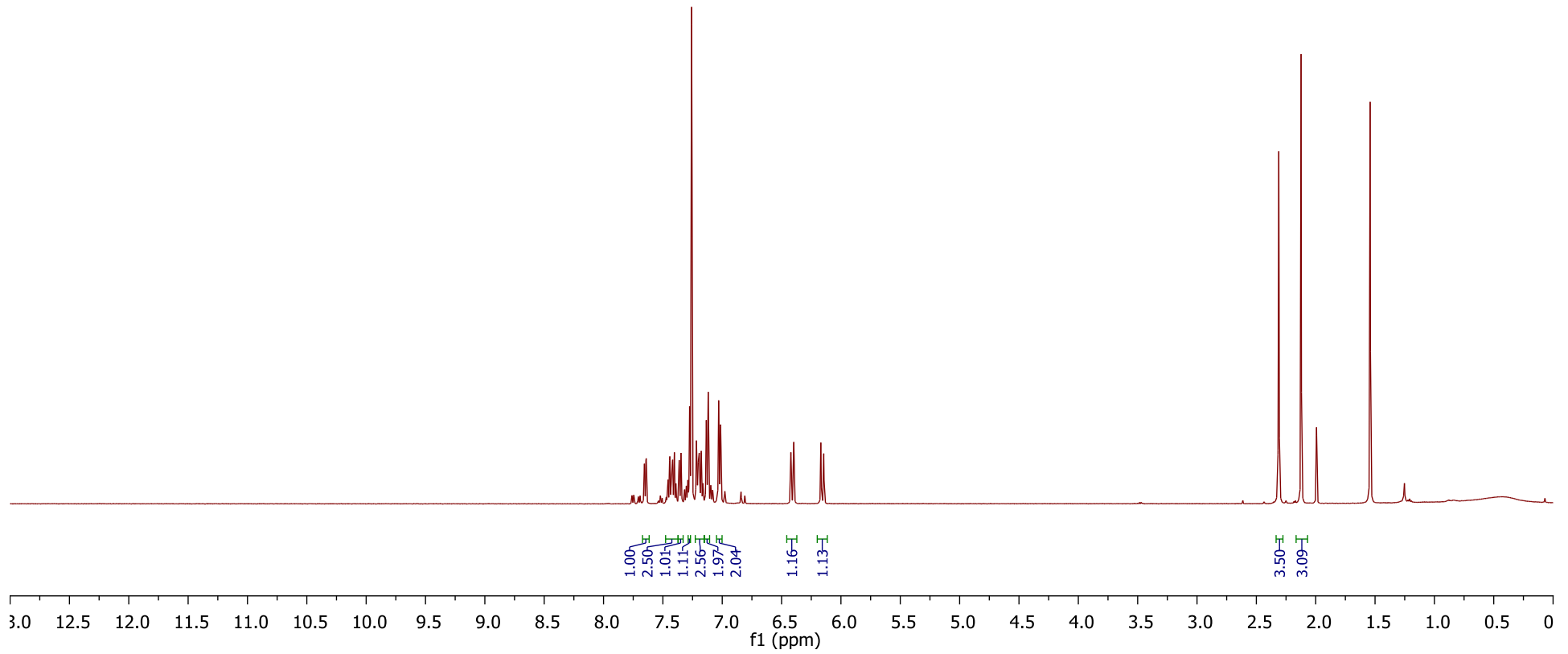
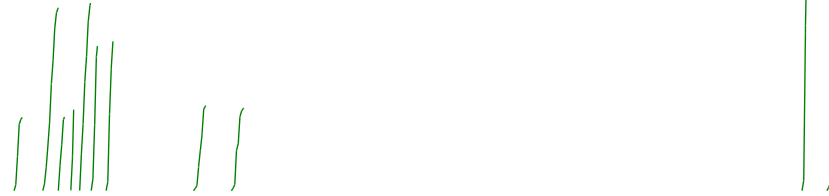


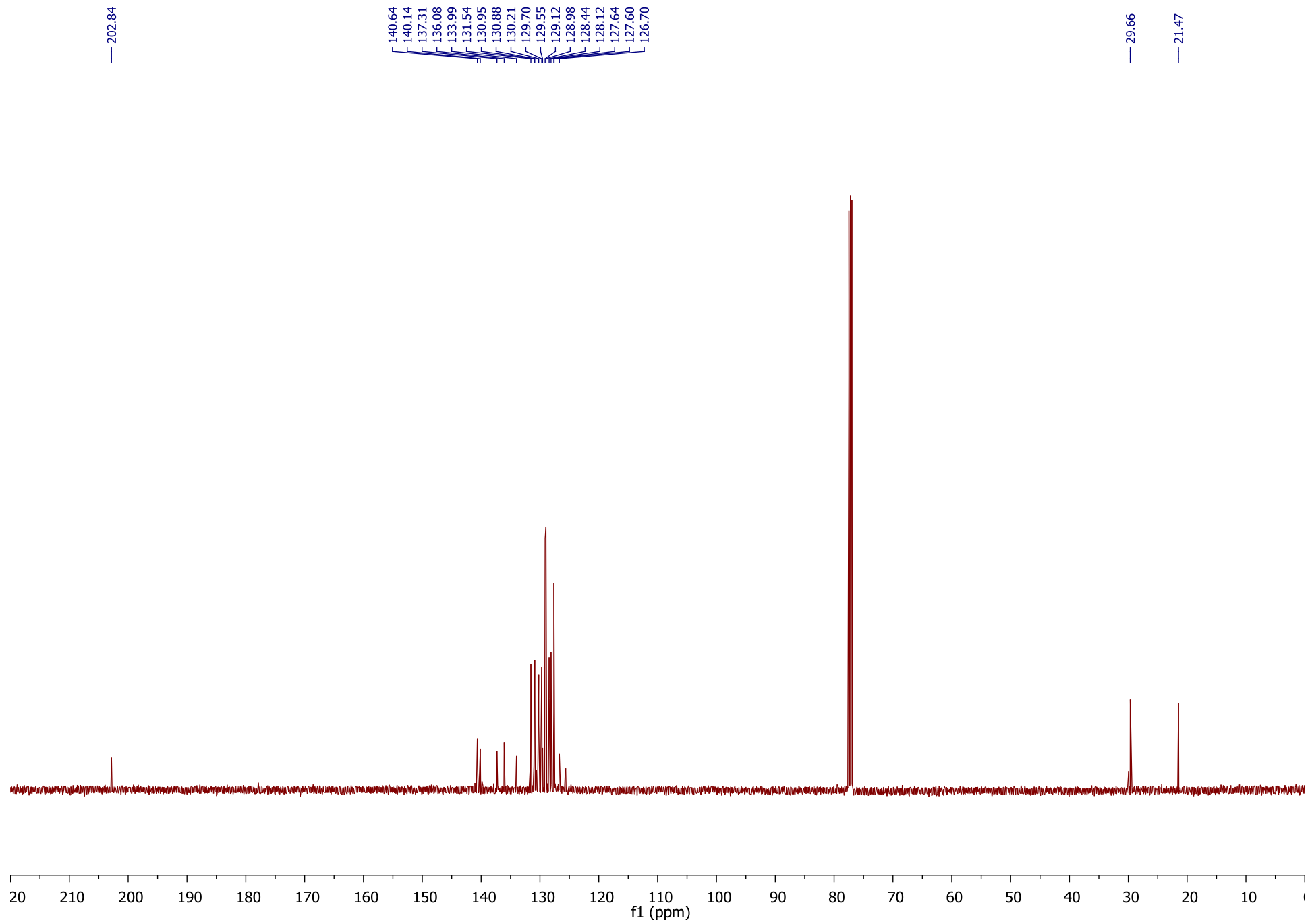


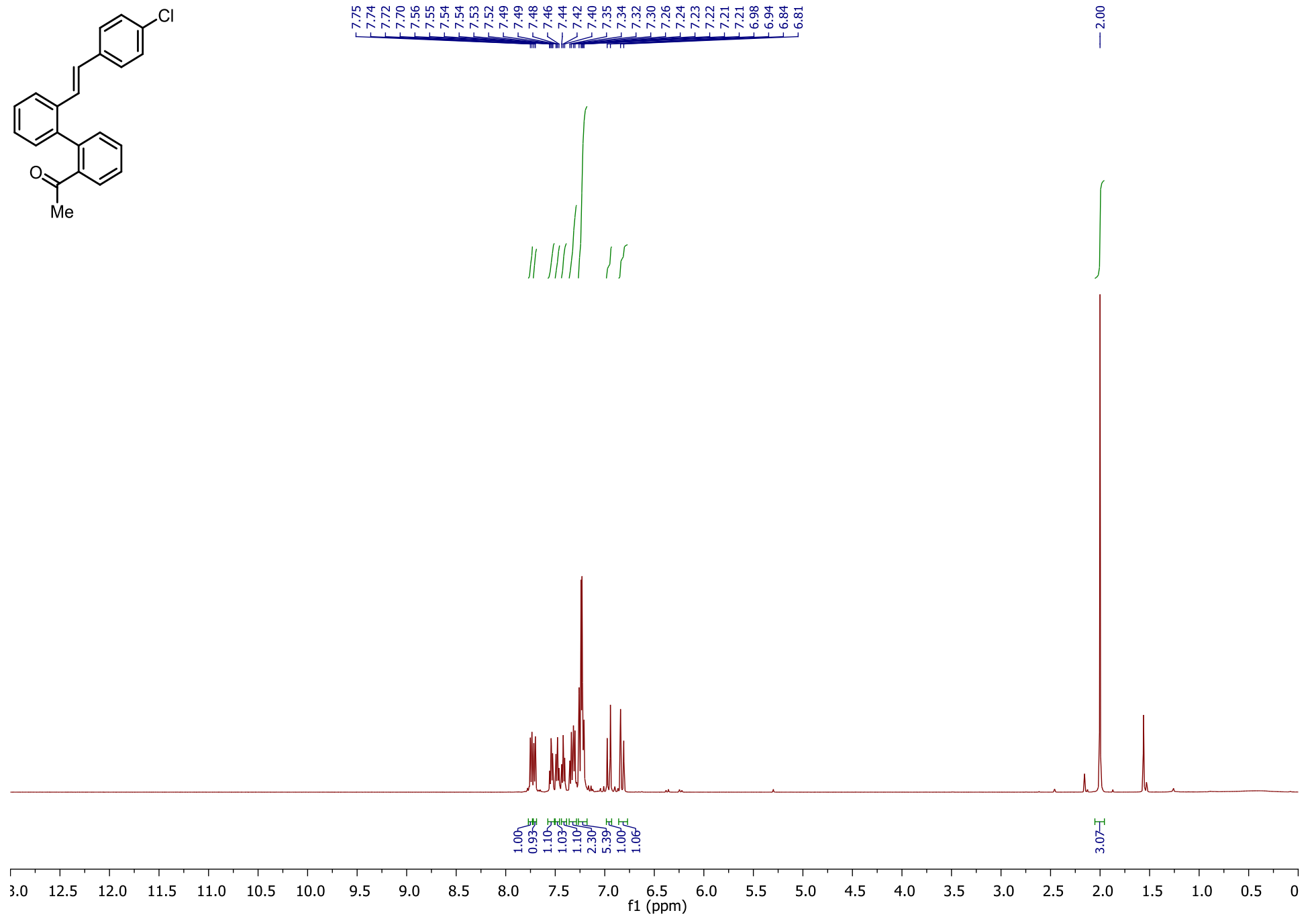
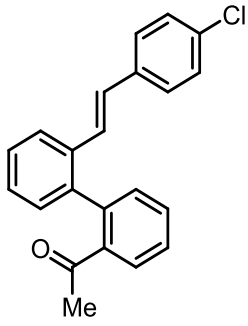


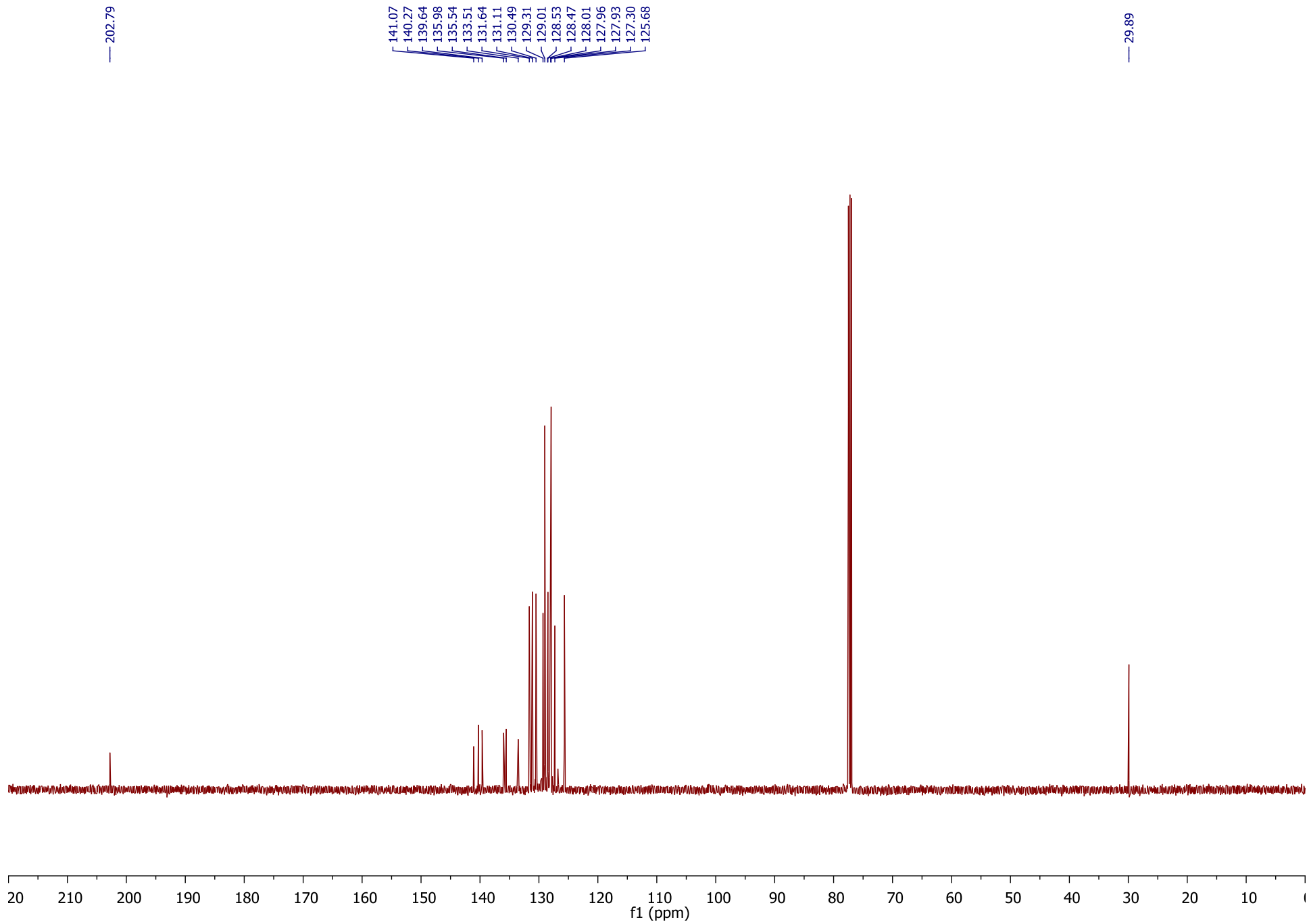
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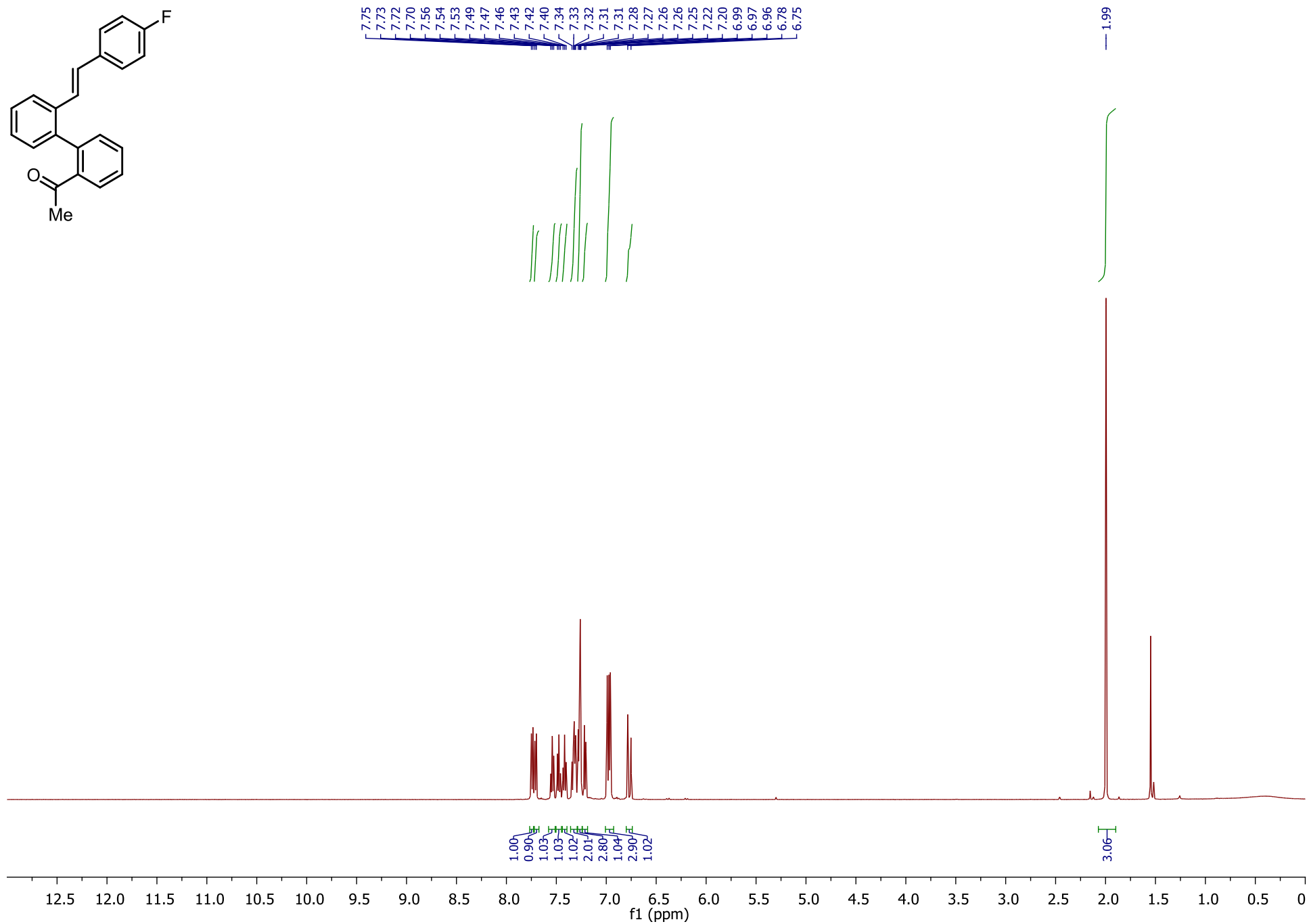
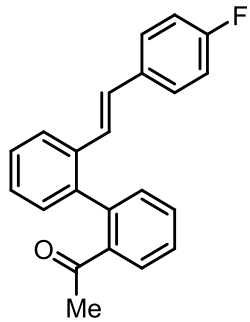
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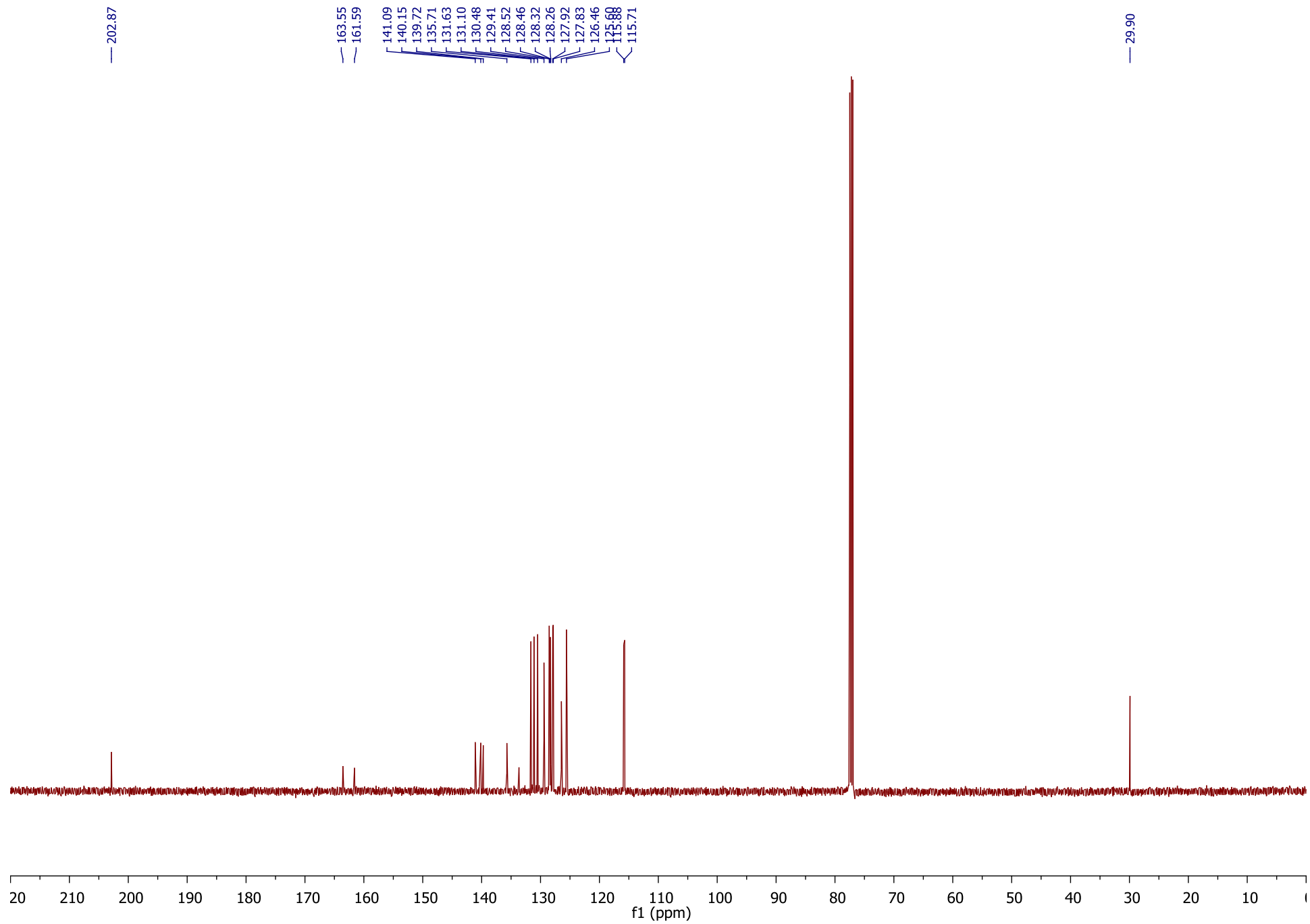


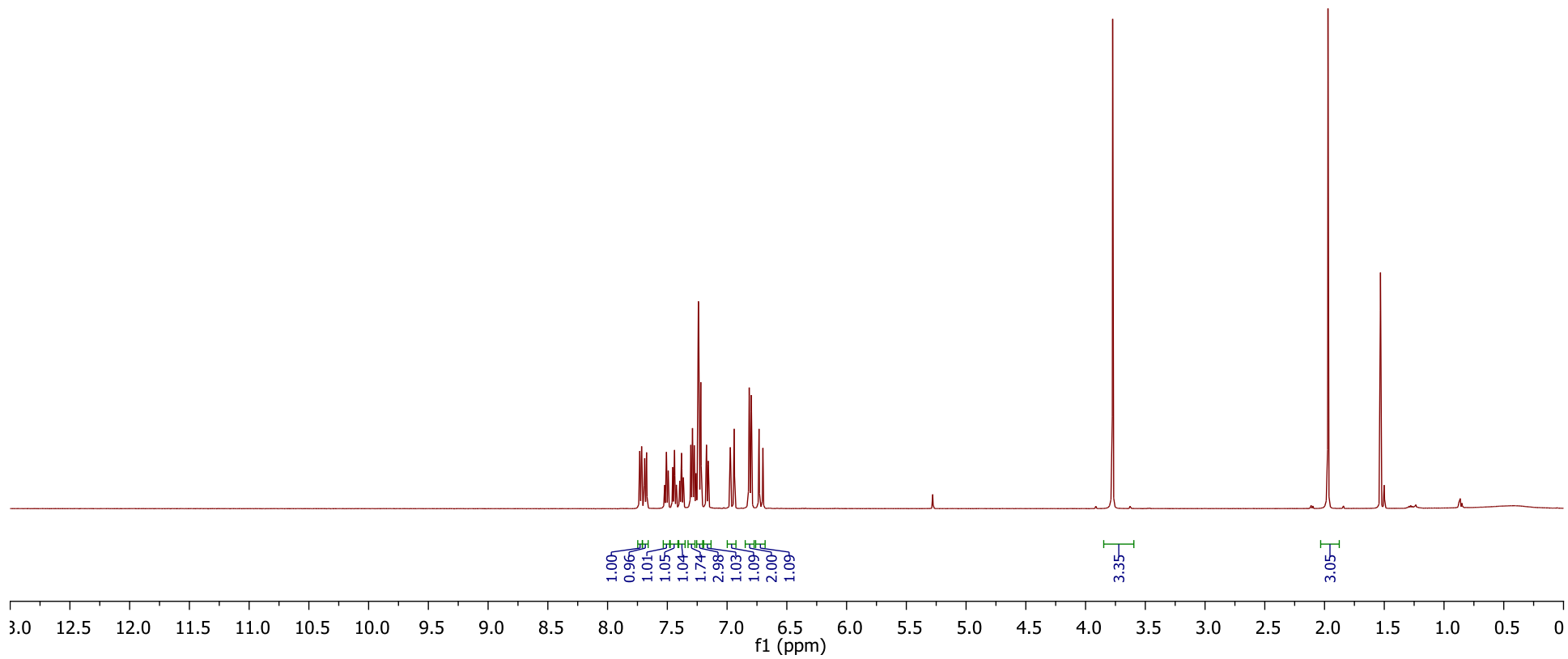
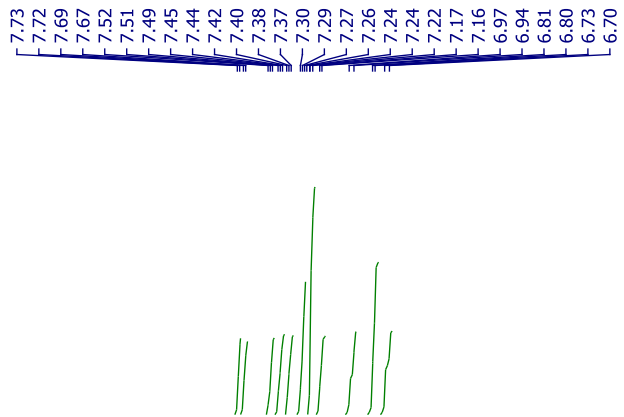
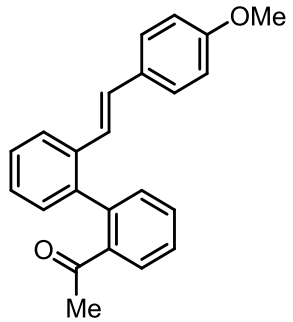


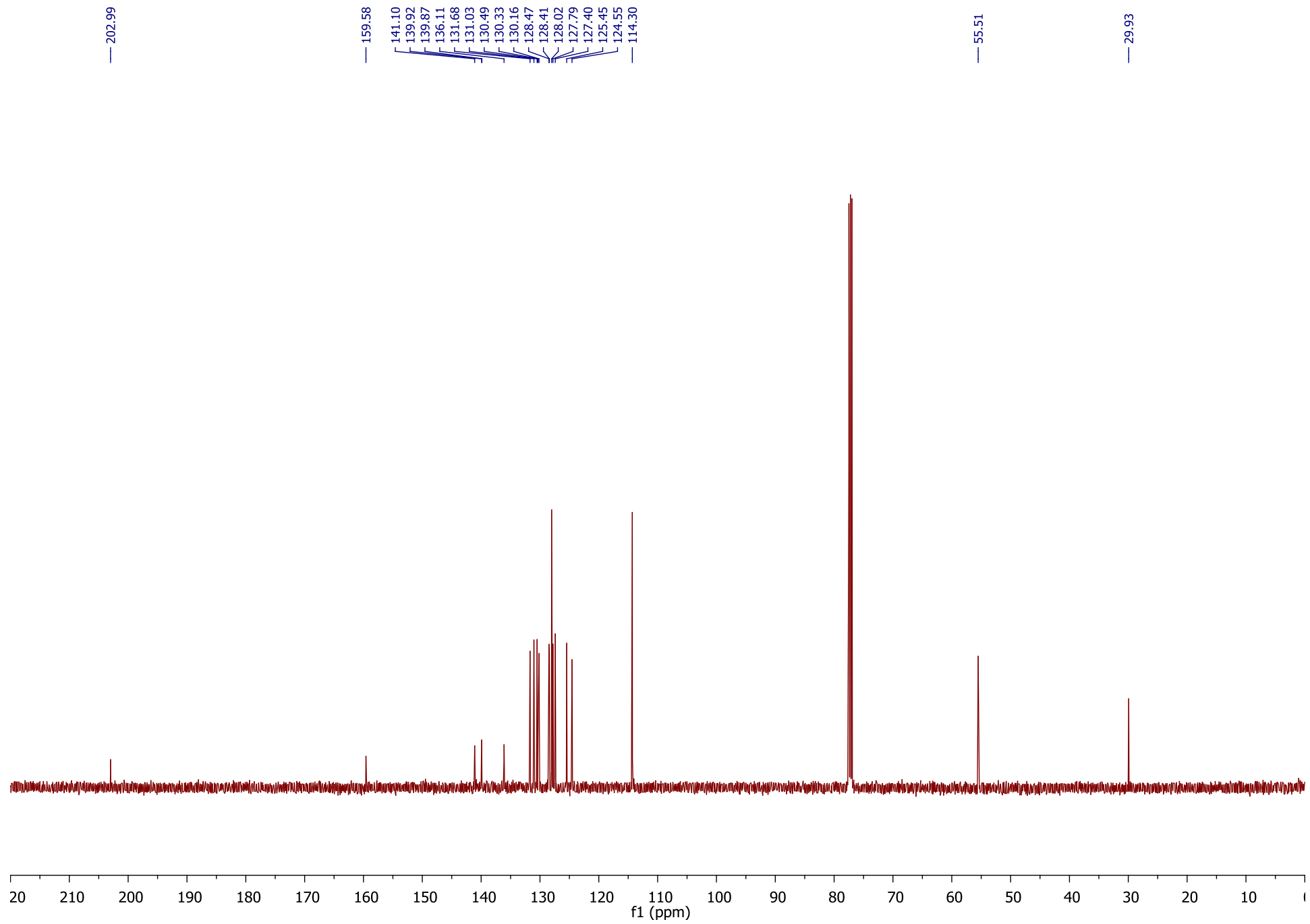


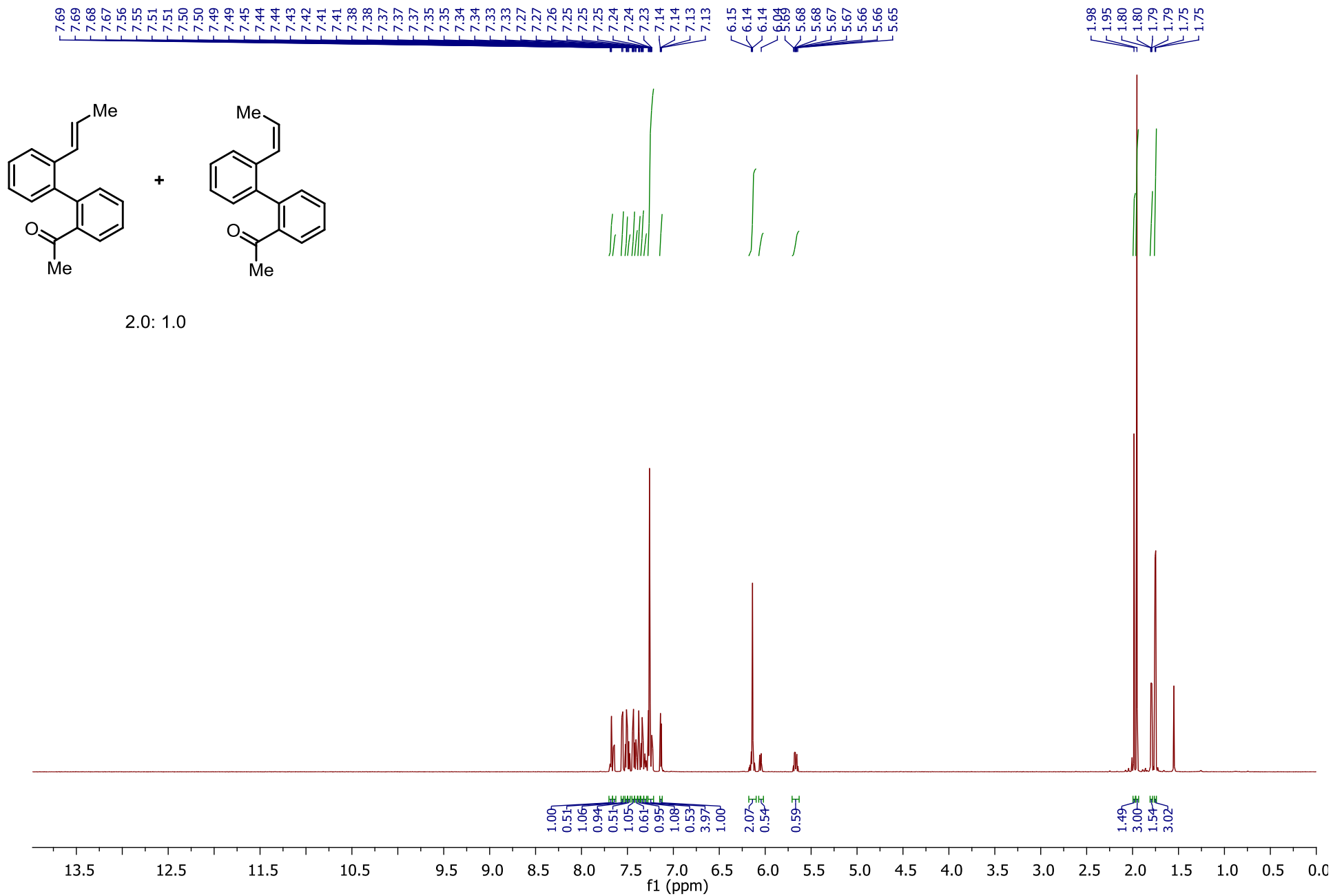


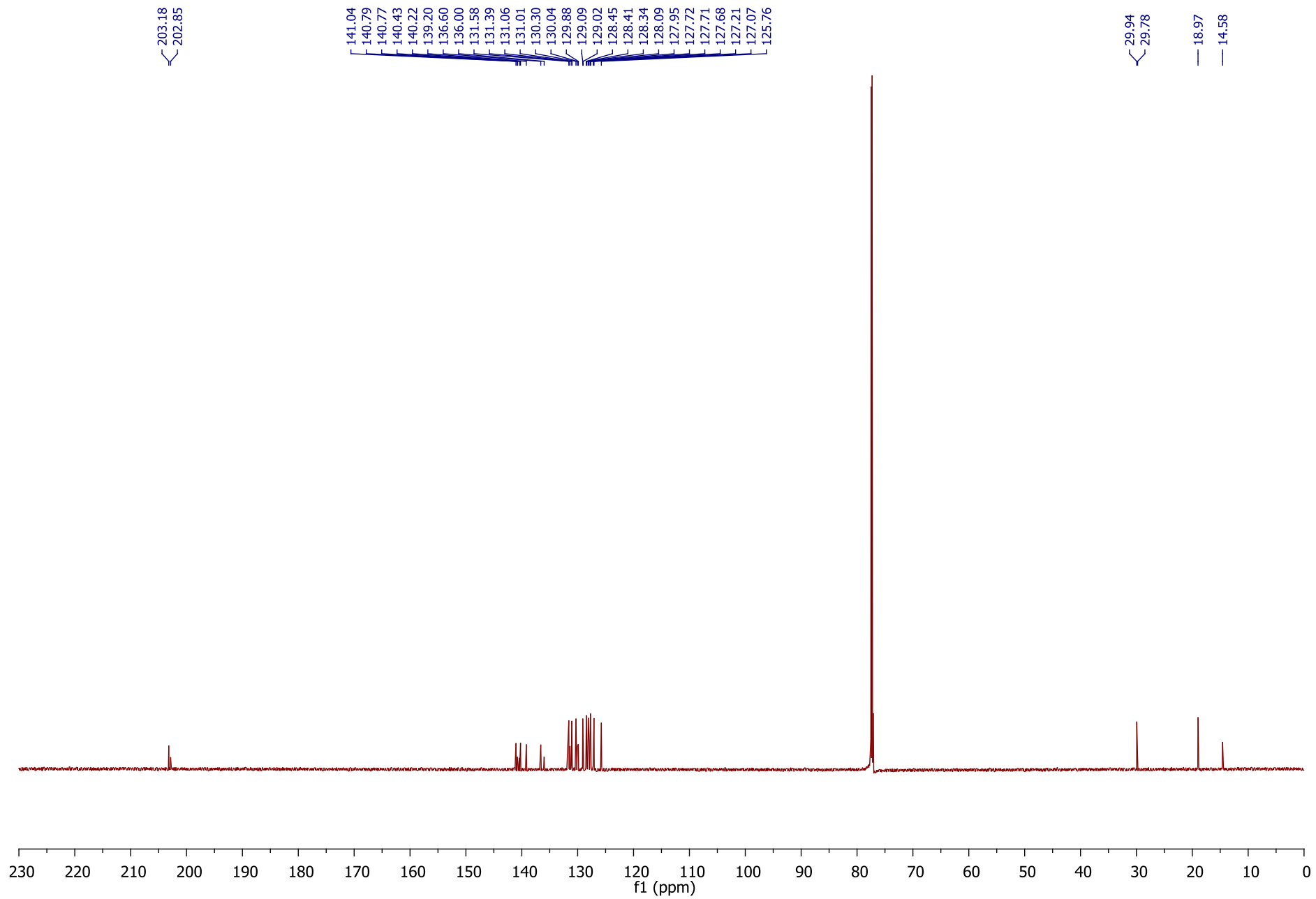


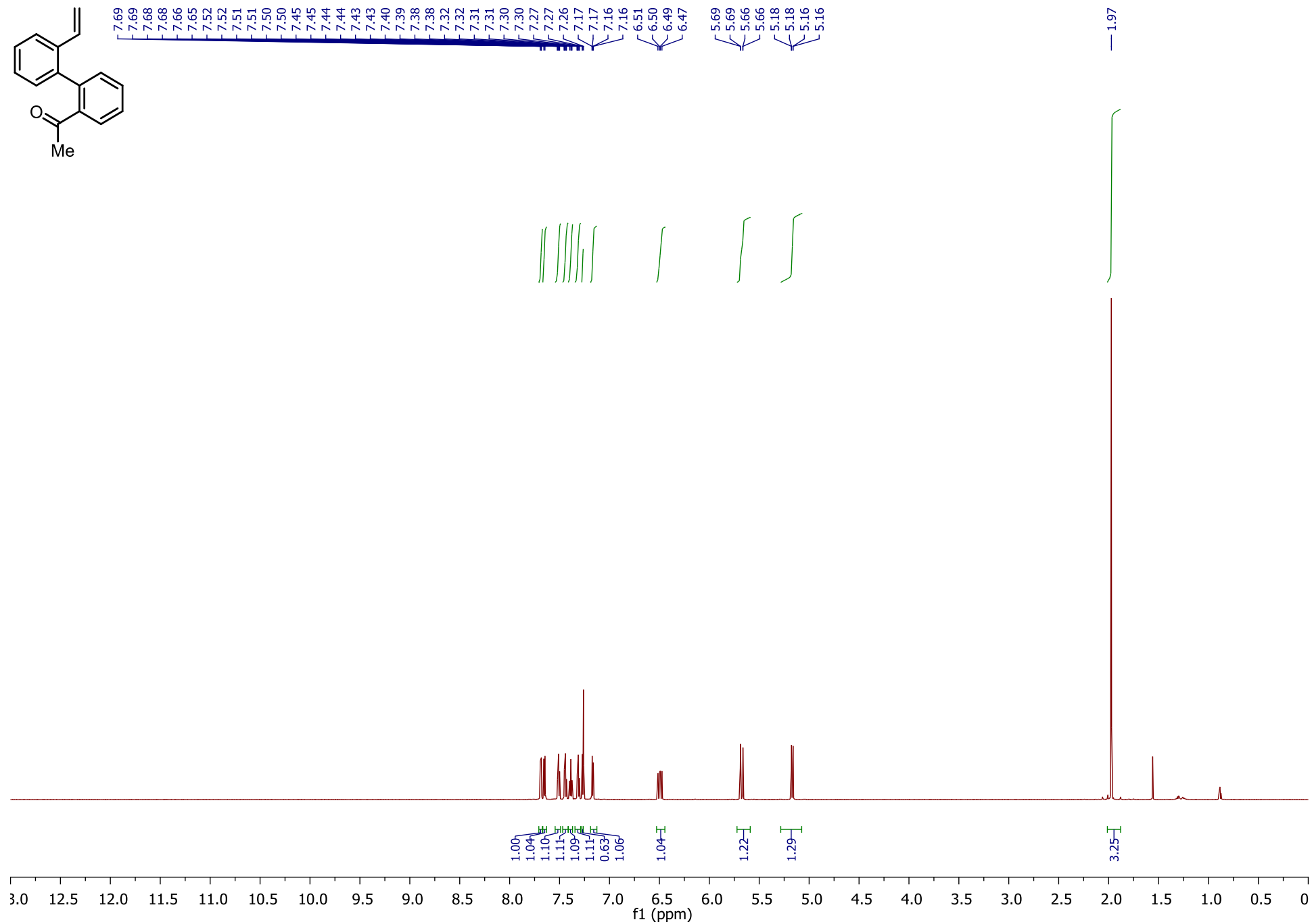
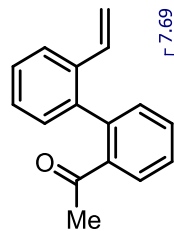


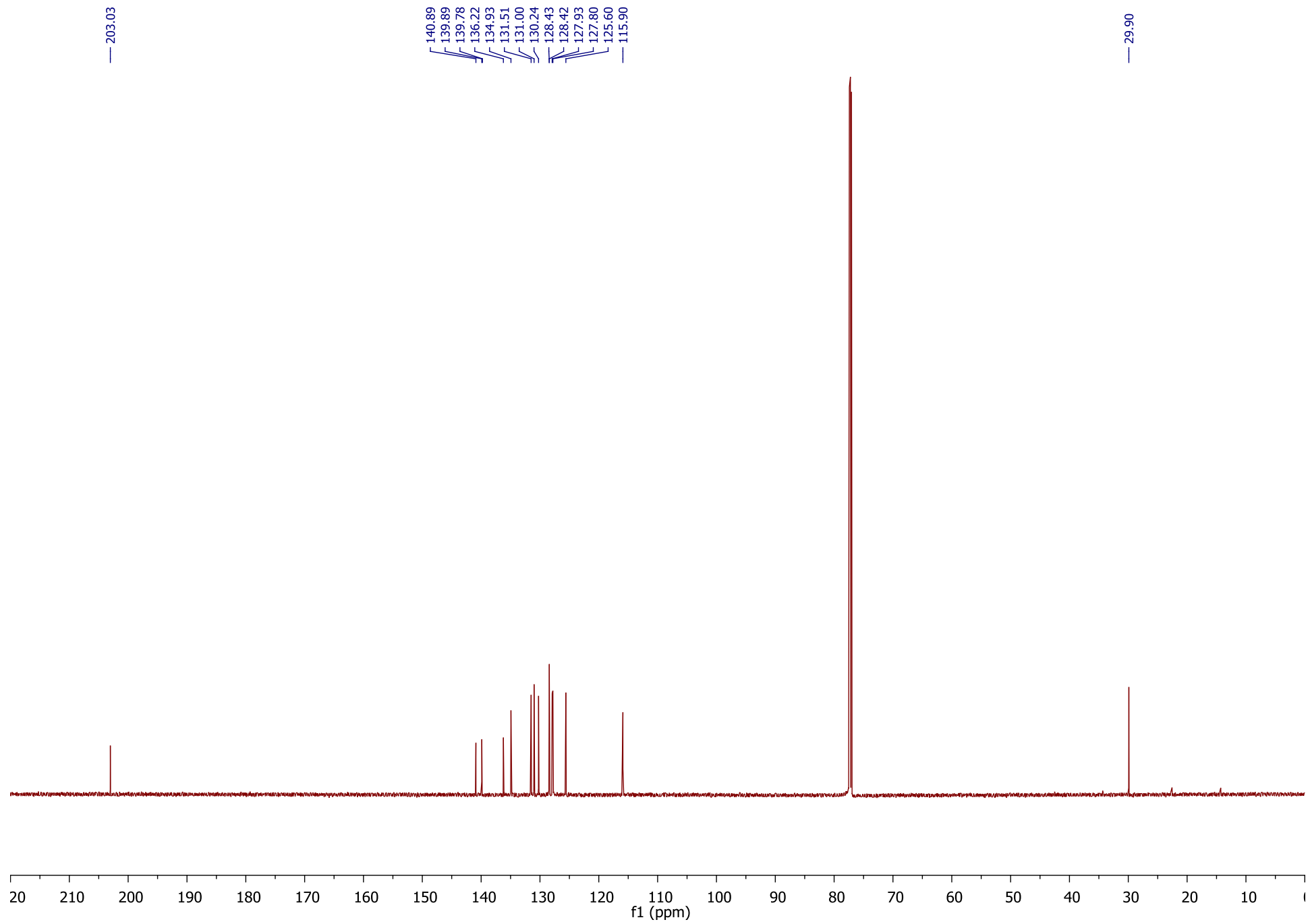


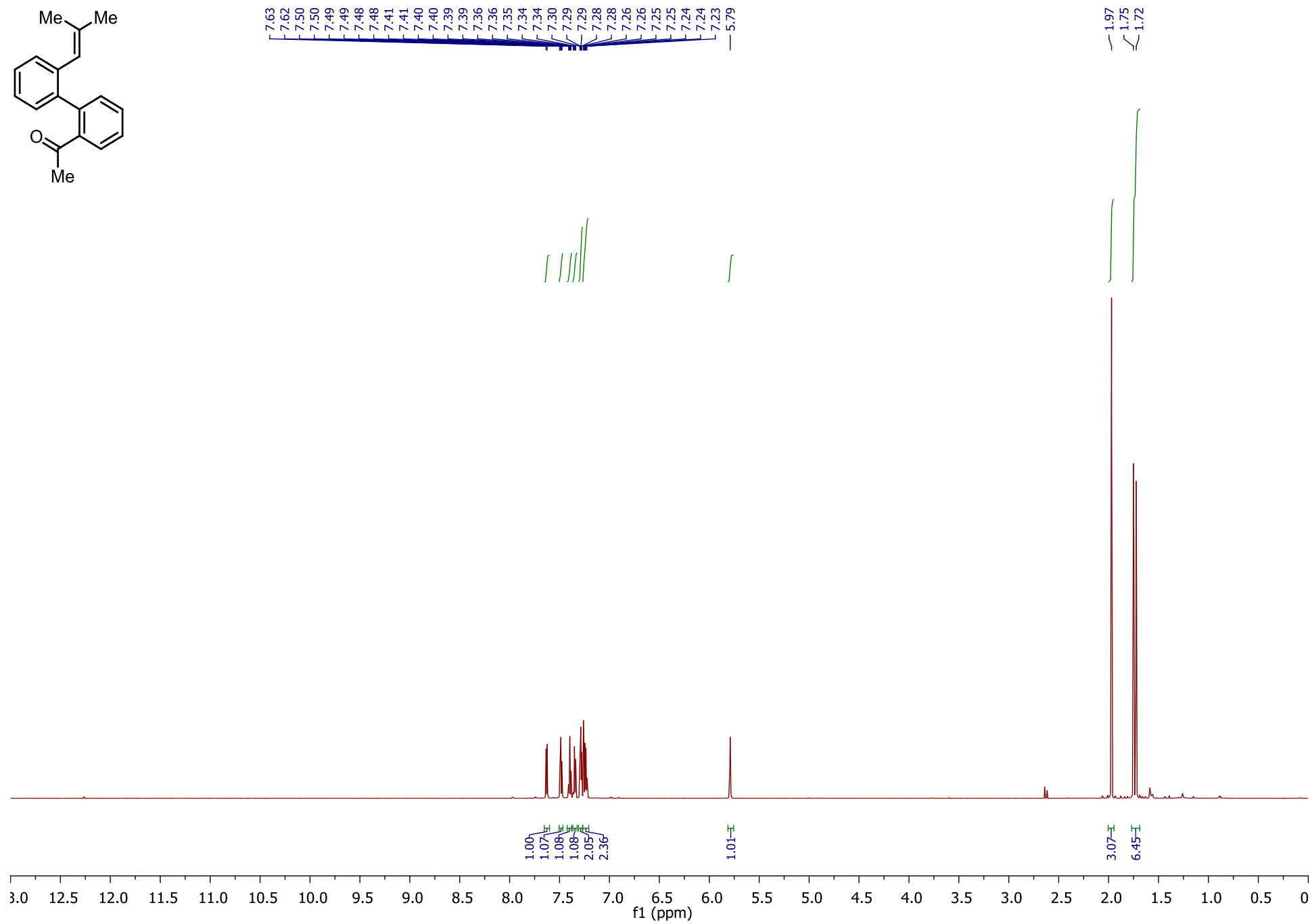
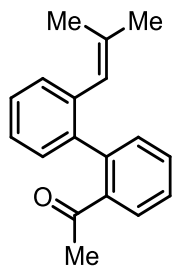


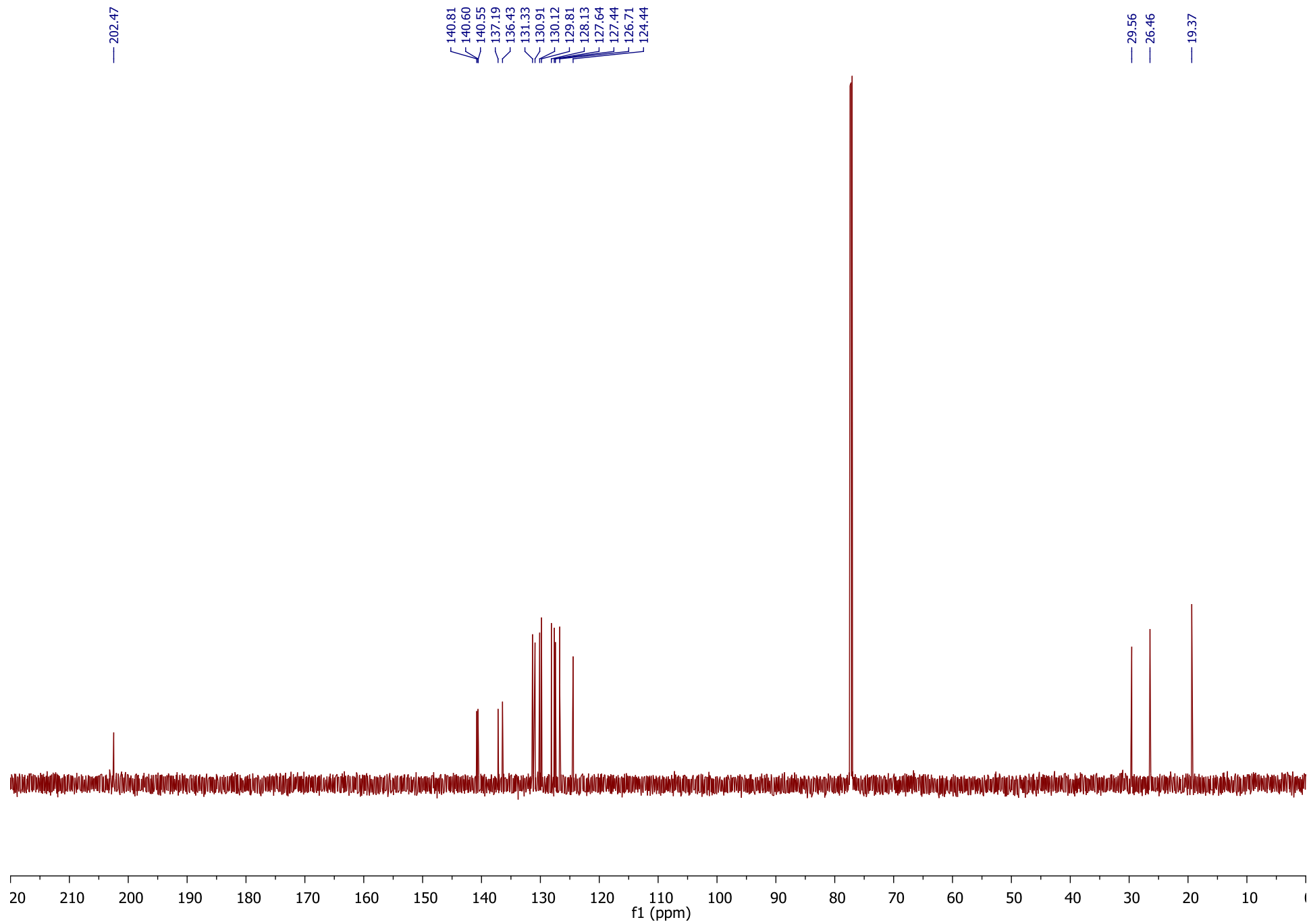


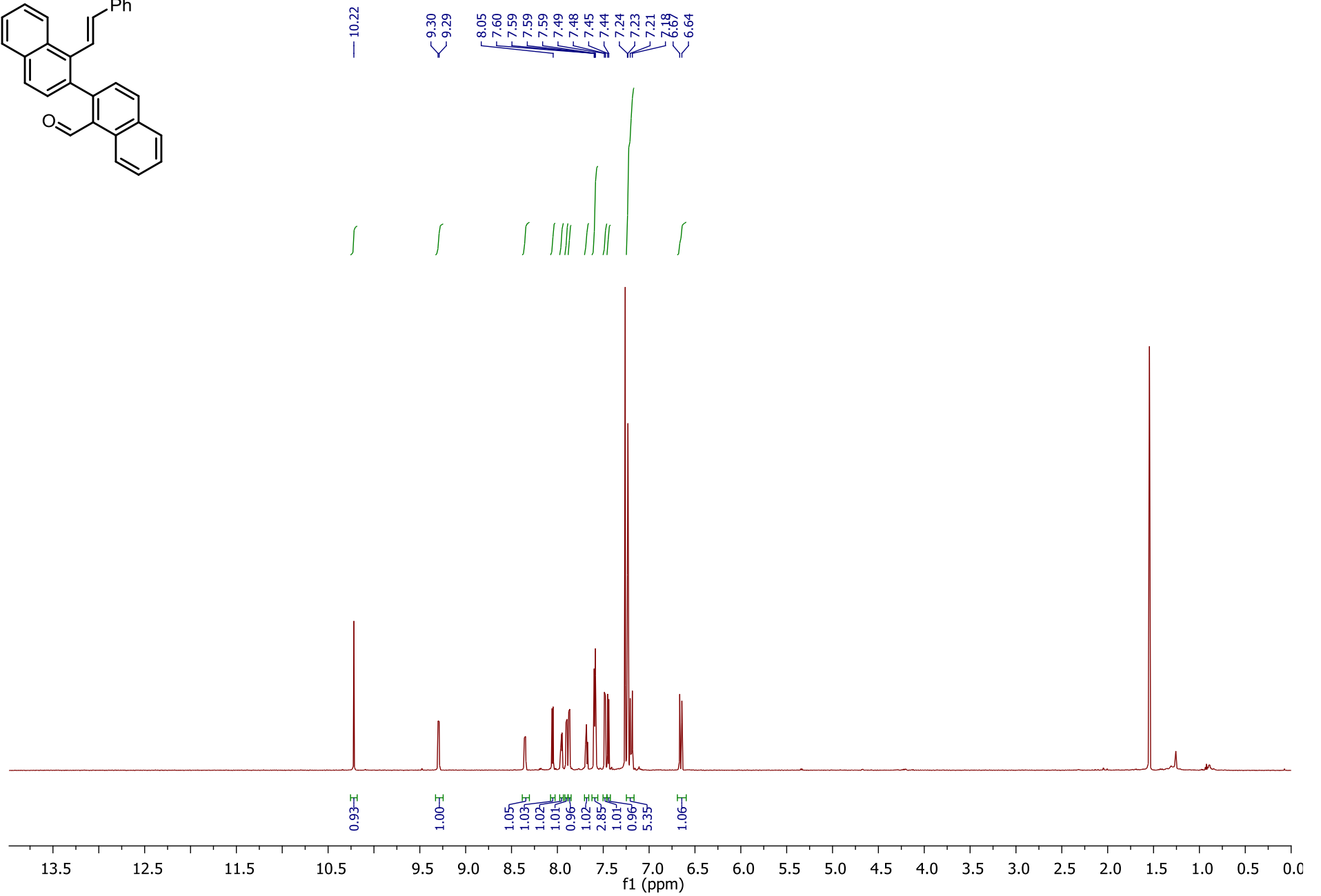
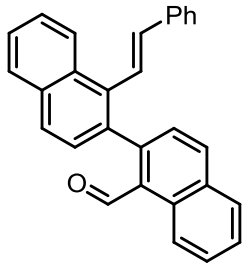


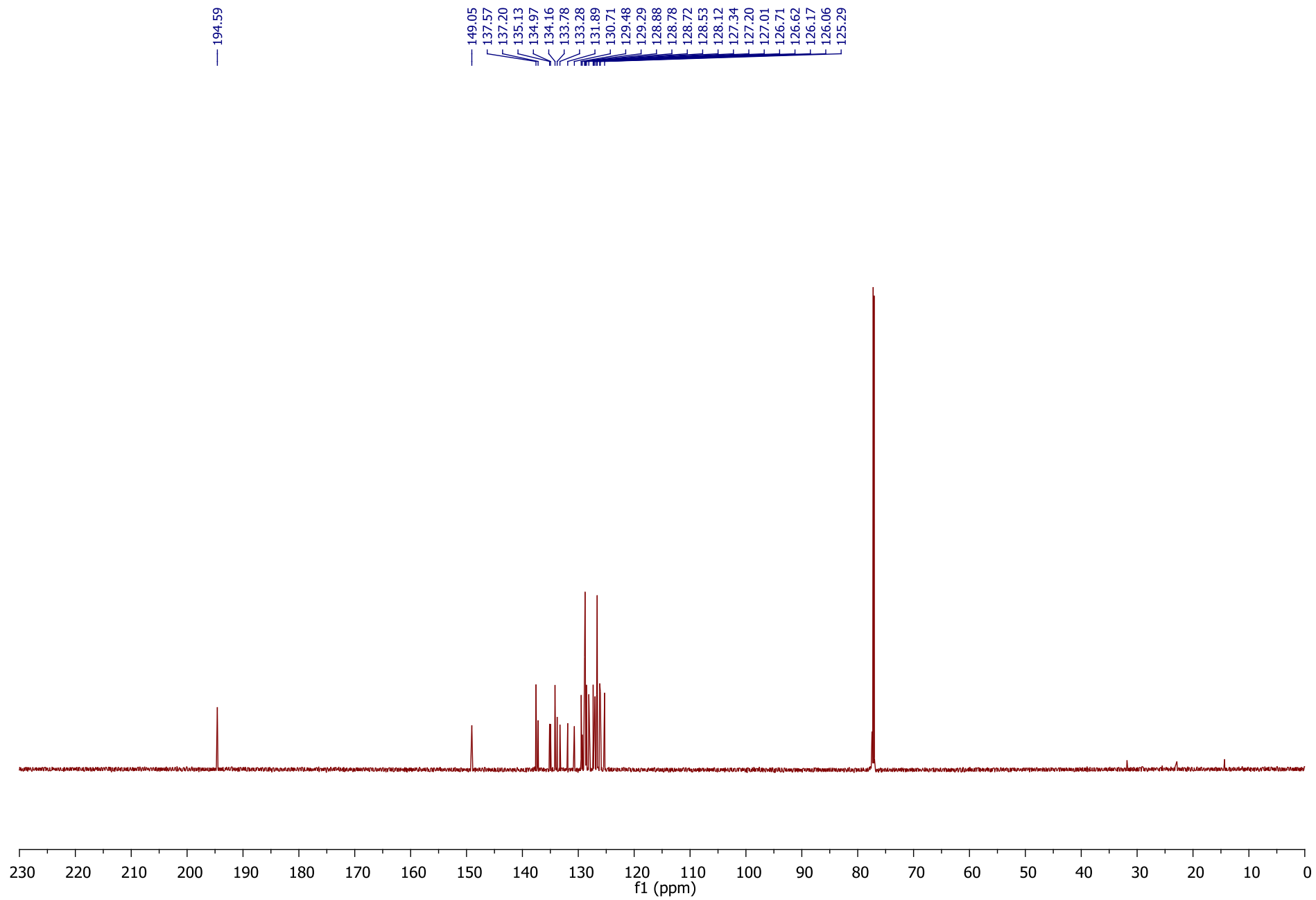


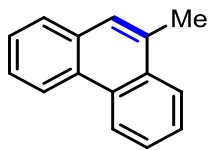












8.74
8.72
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8.65
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8.06
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7.64
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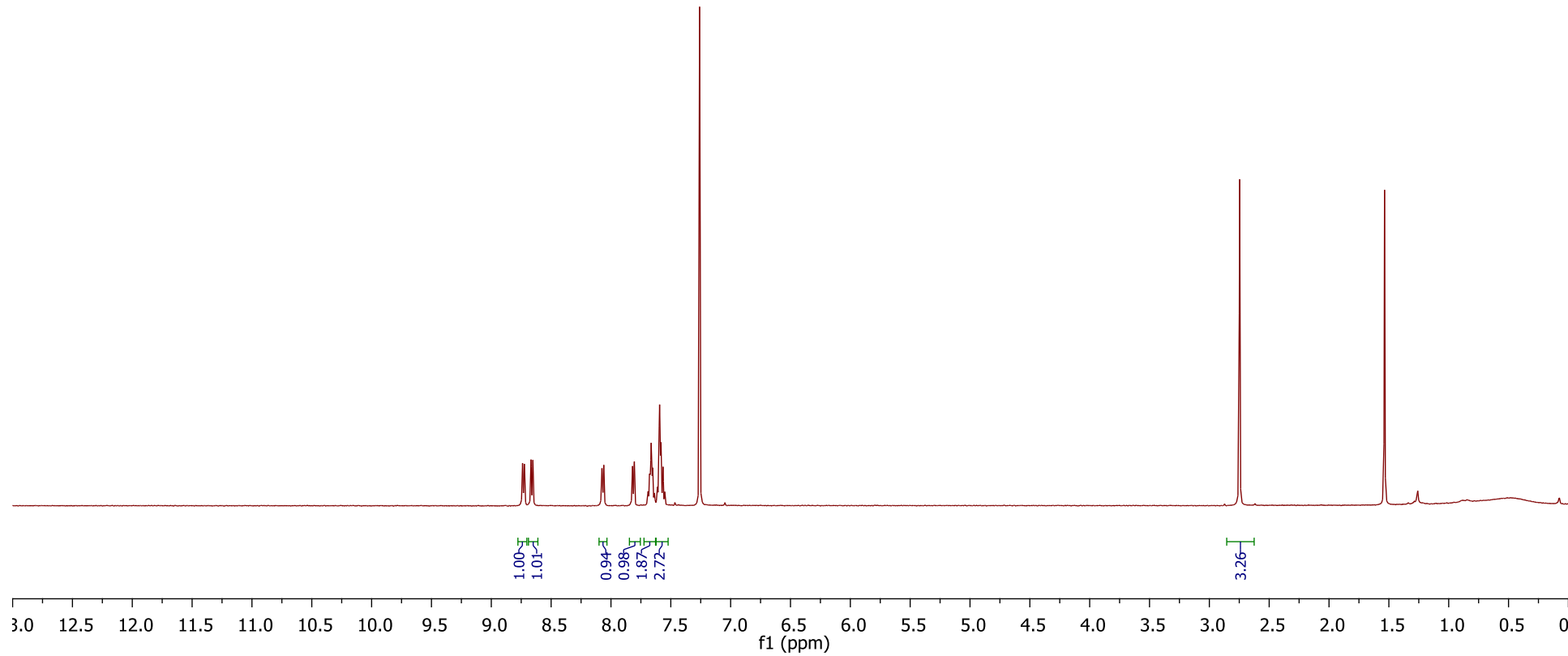
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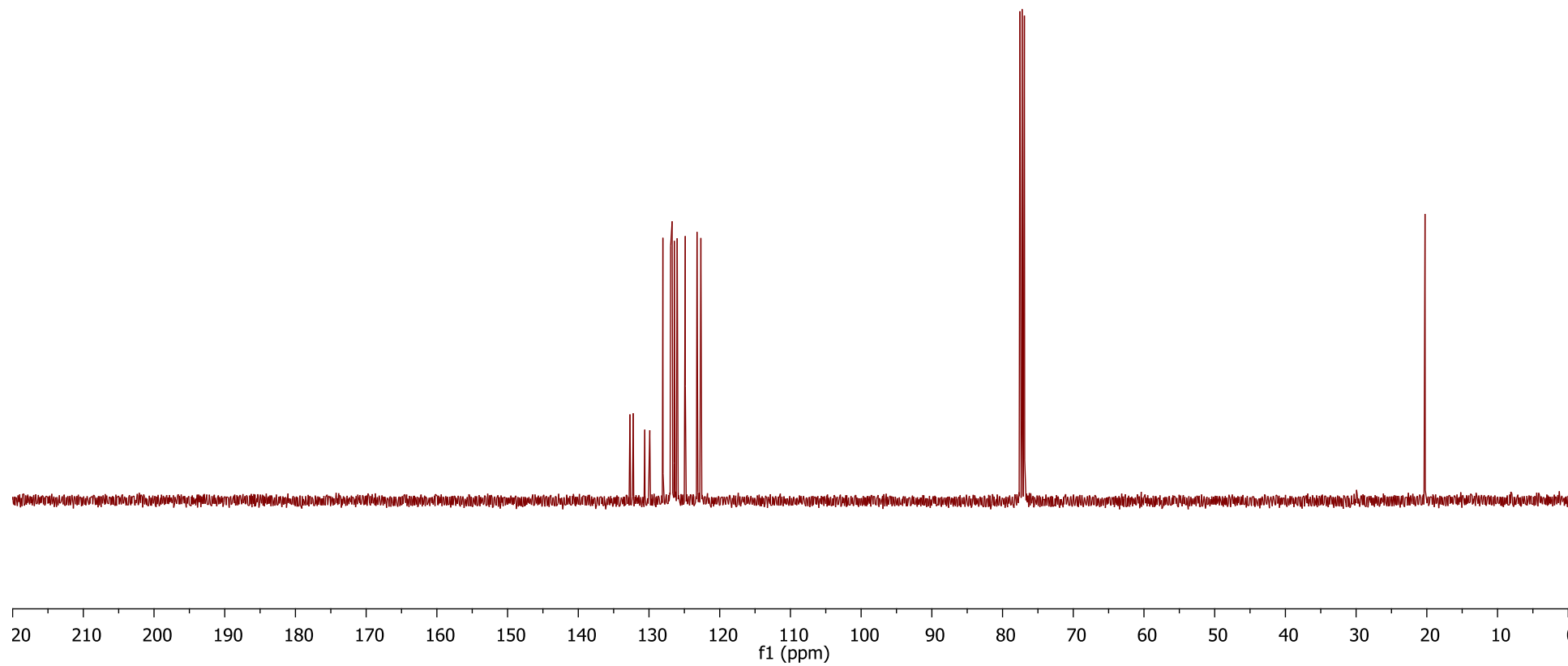
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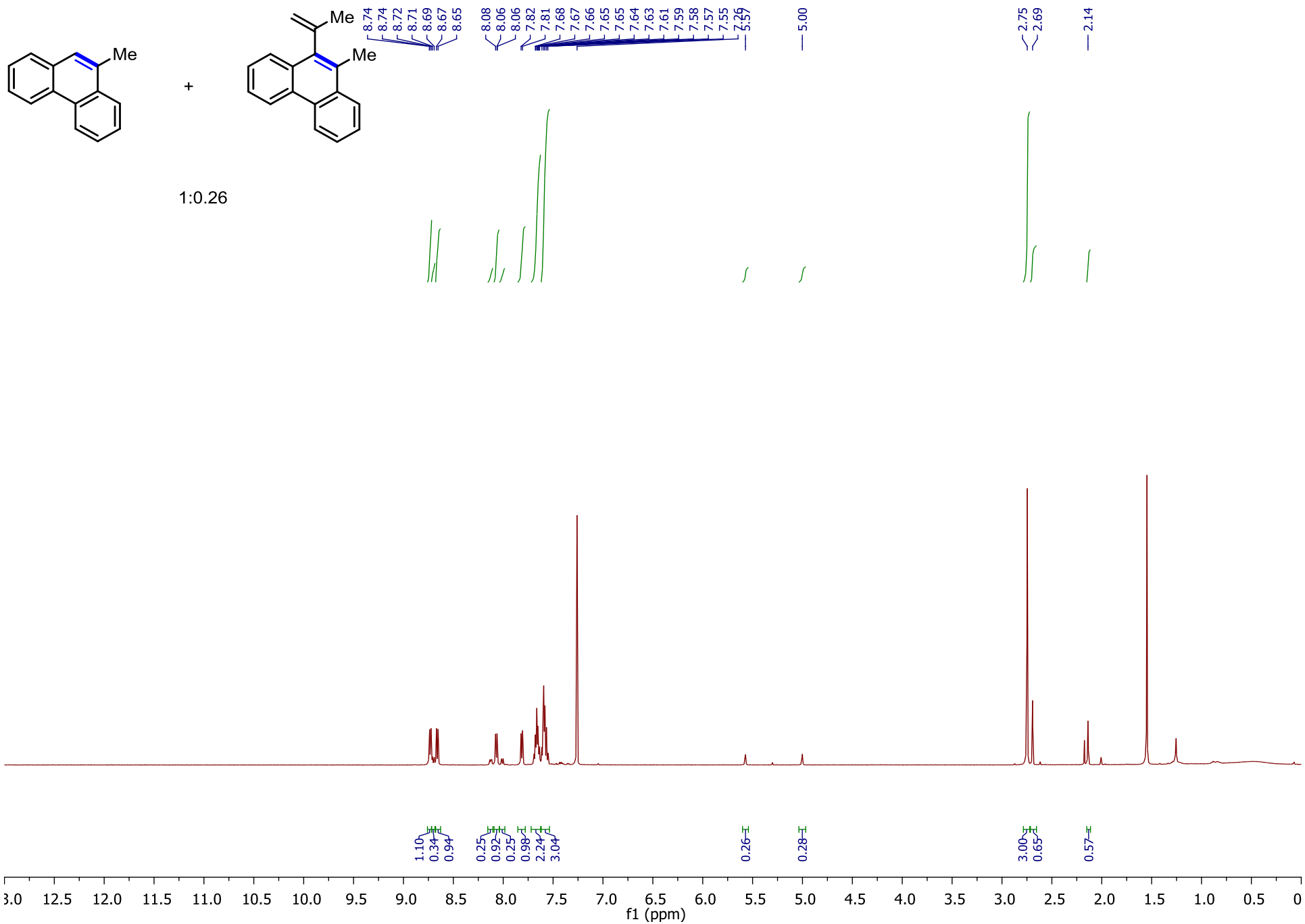
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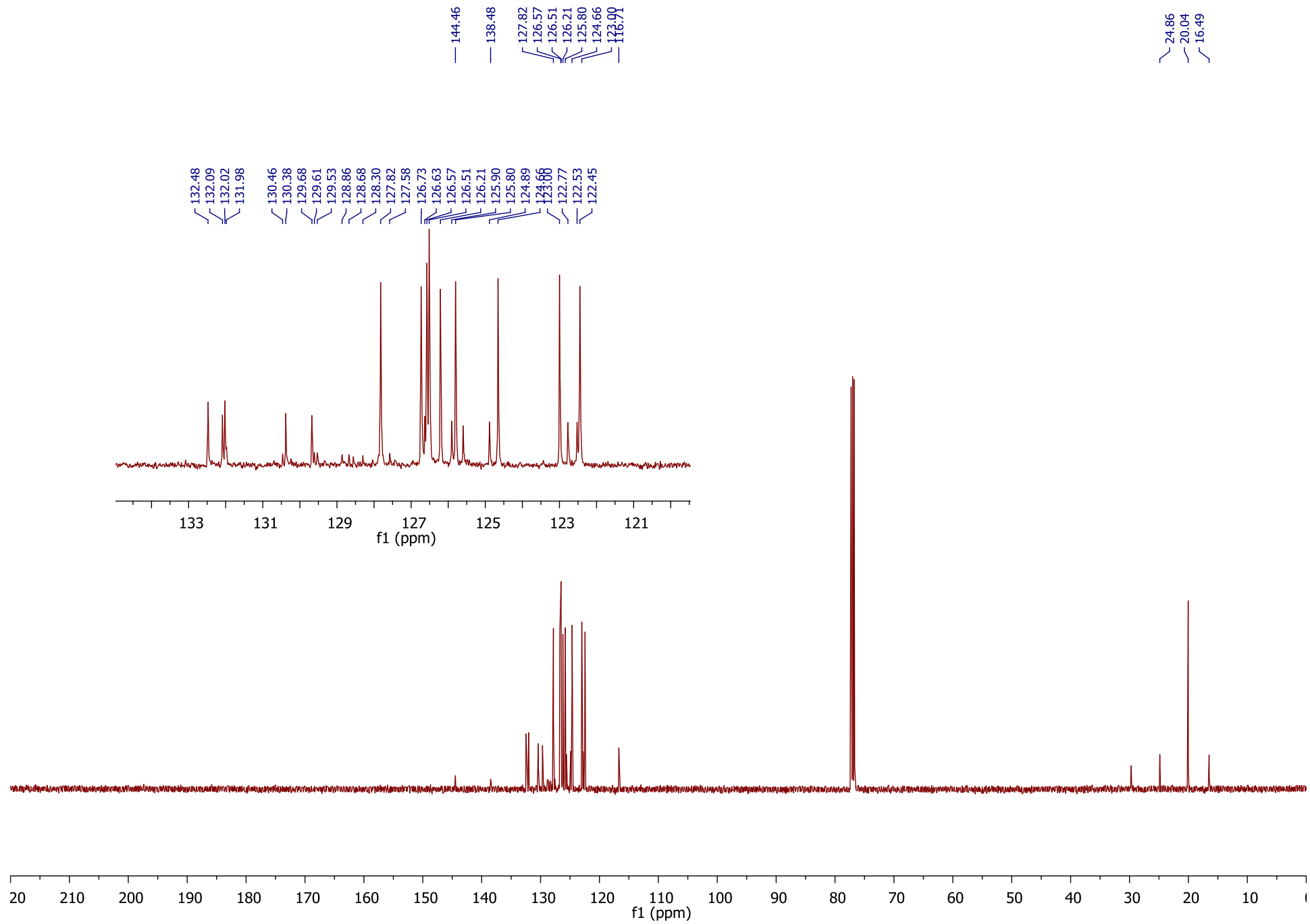


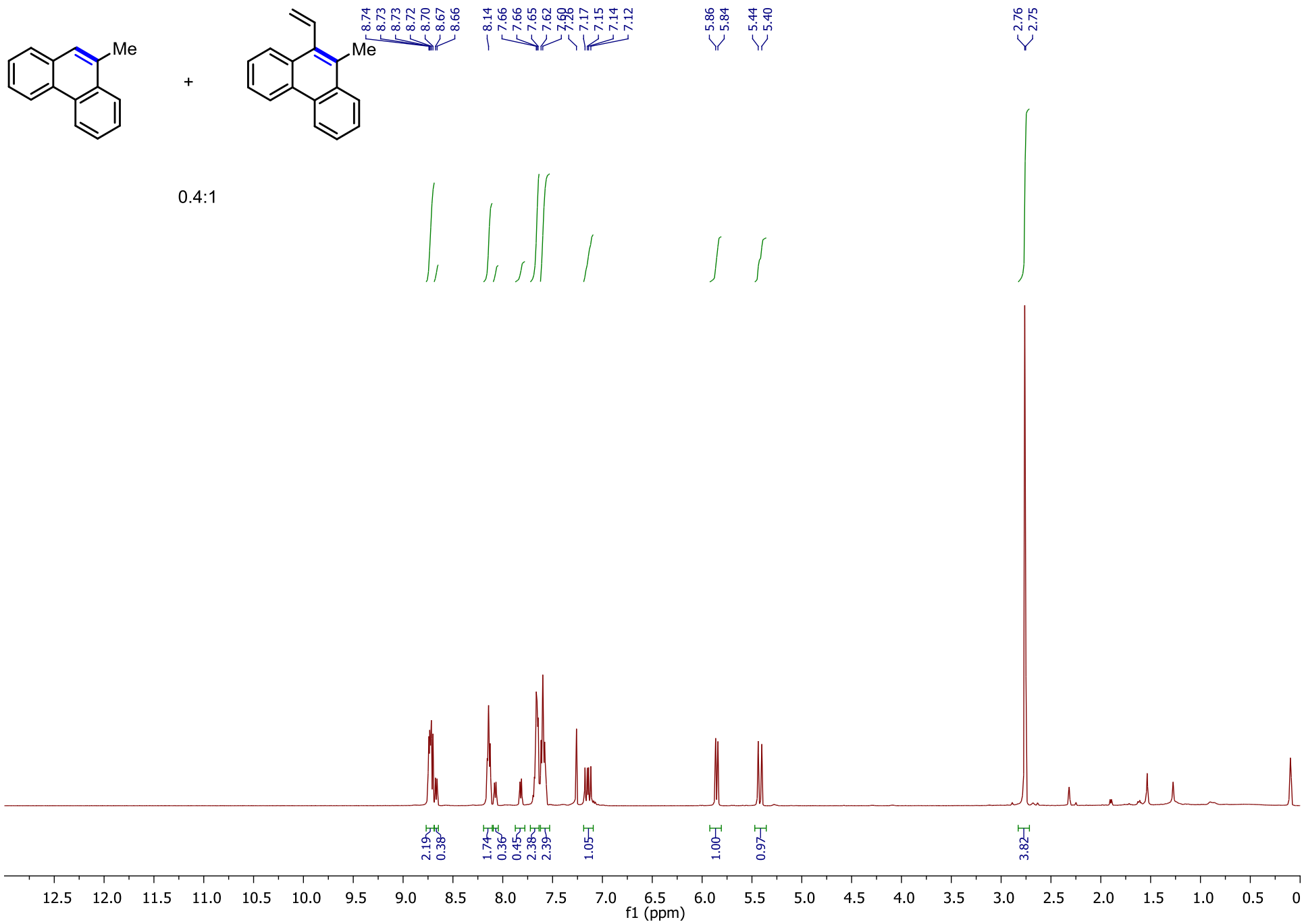
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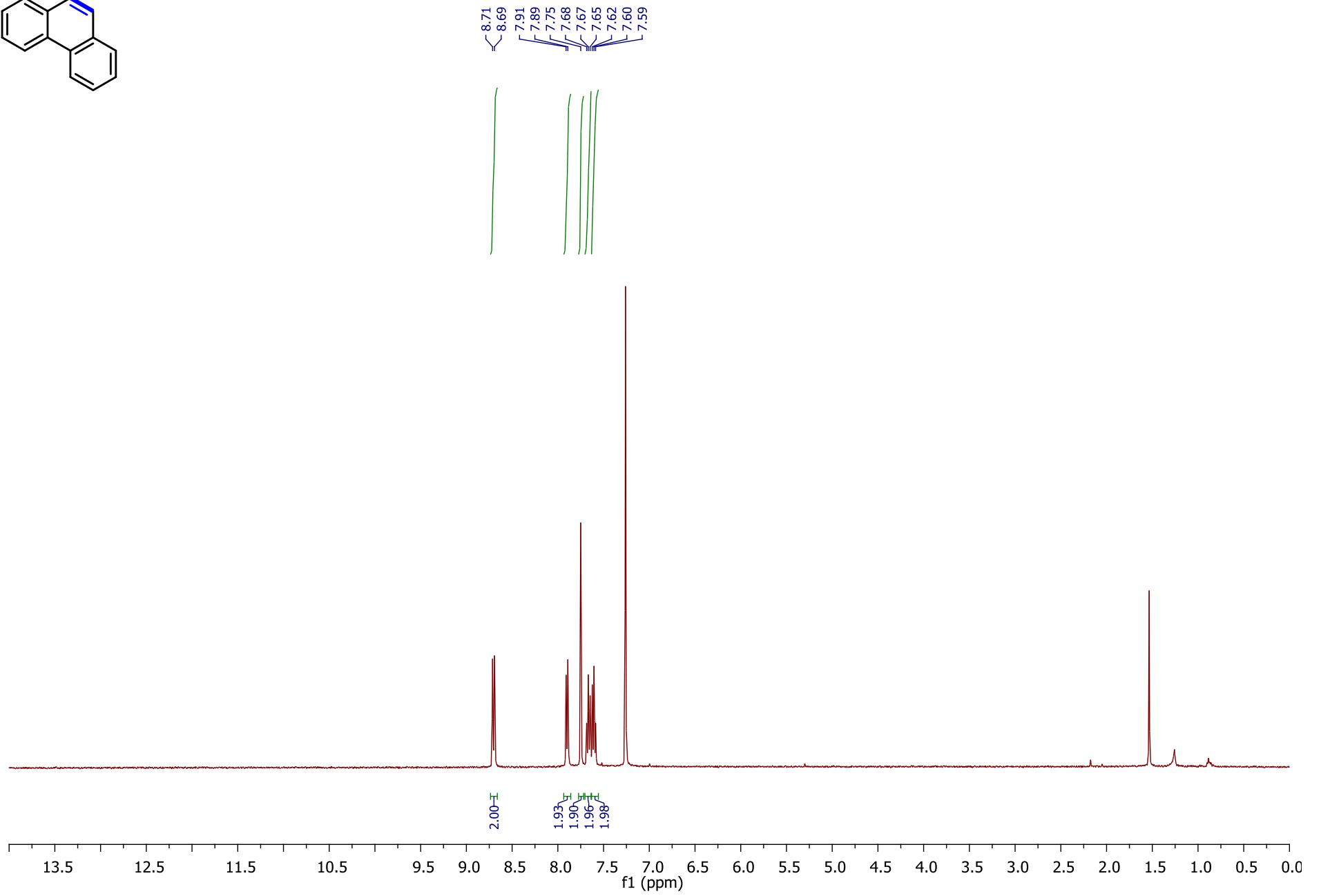
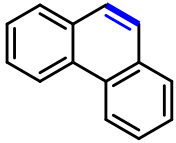
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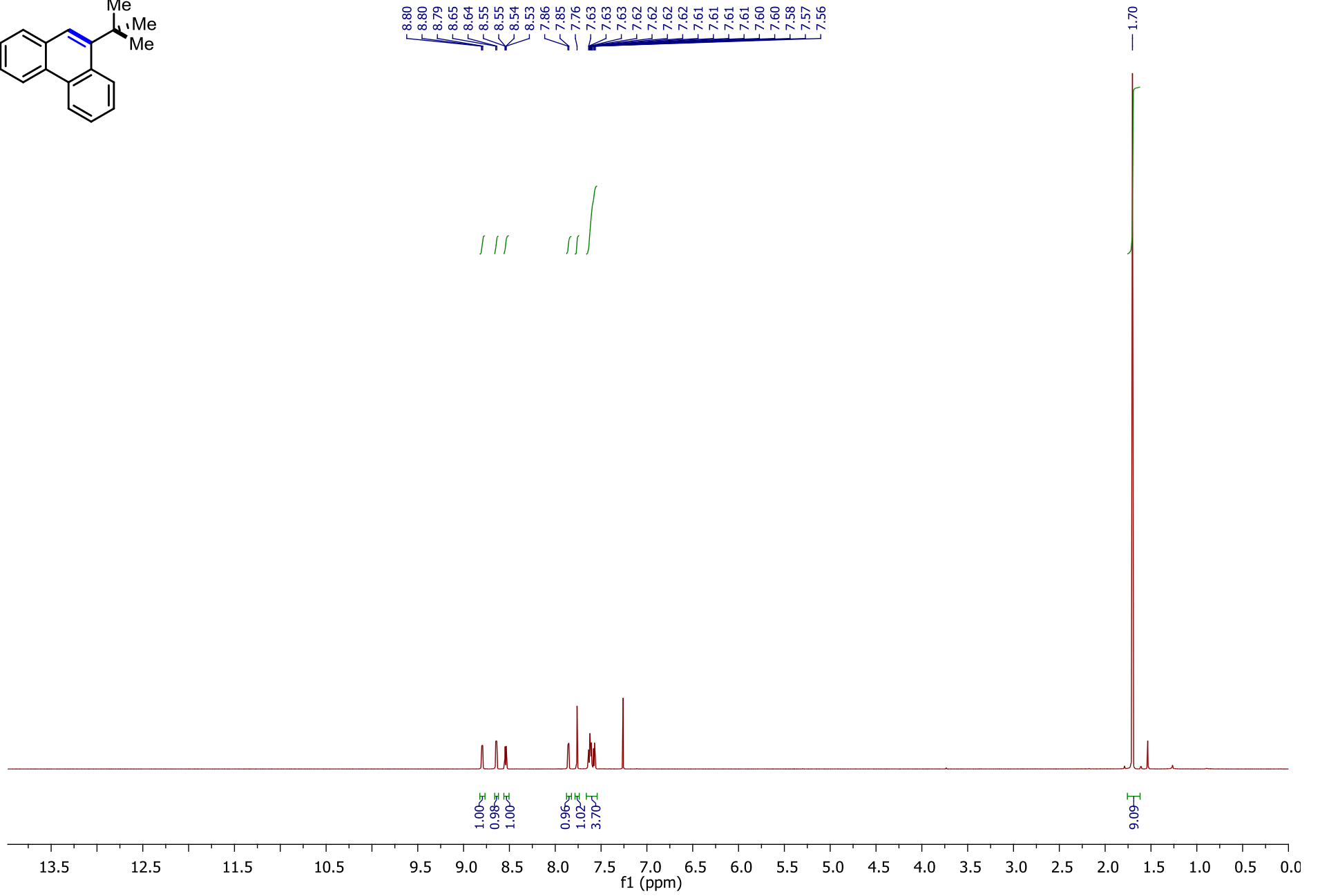
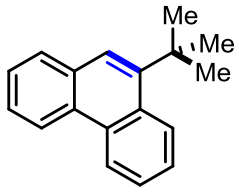


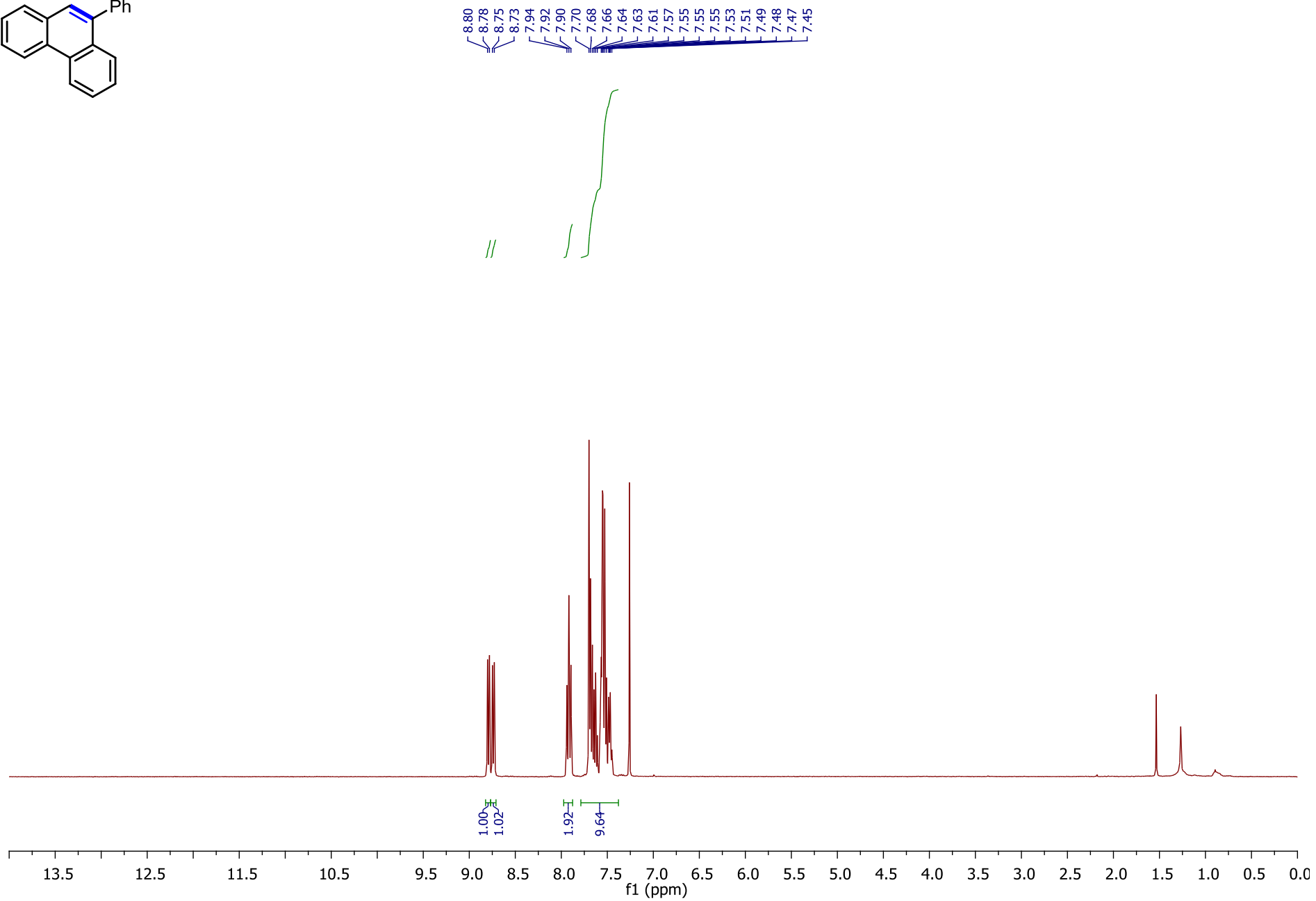
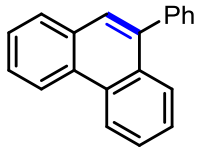


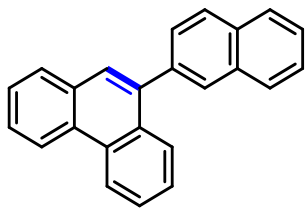




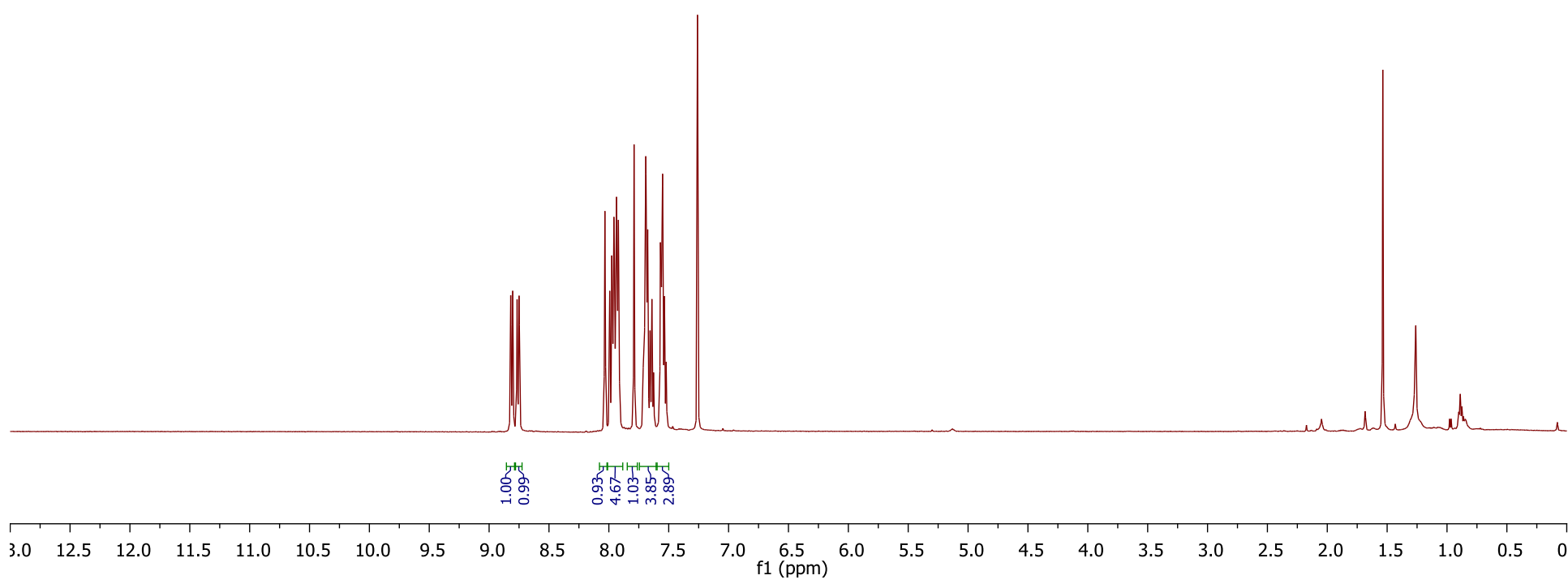


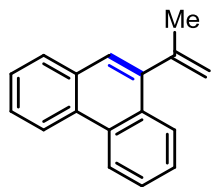






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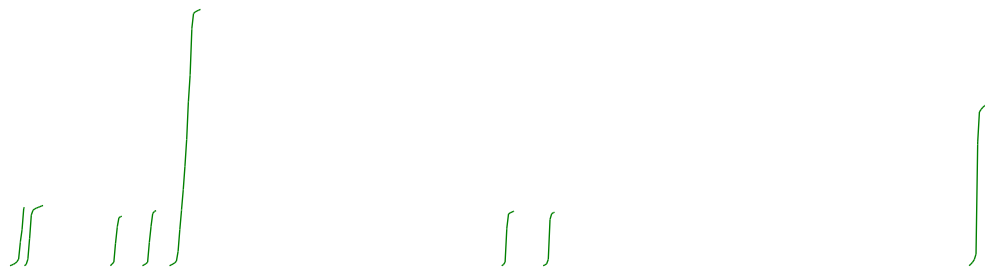




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2.26
2.26

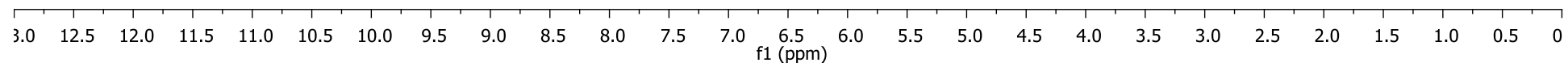


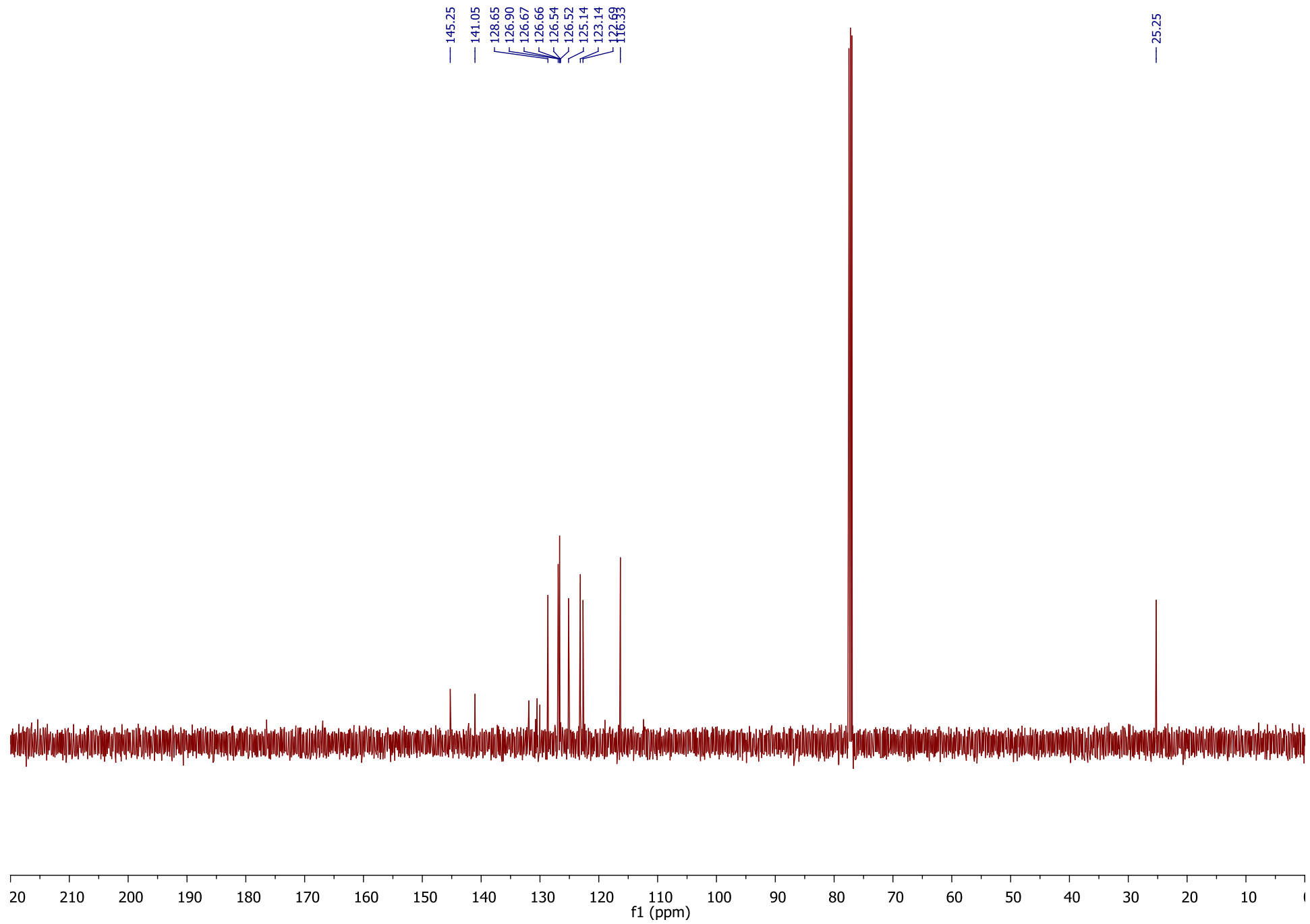
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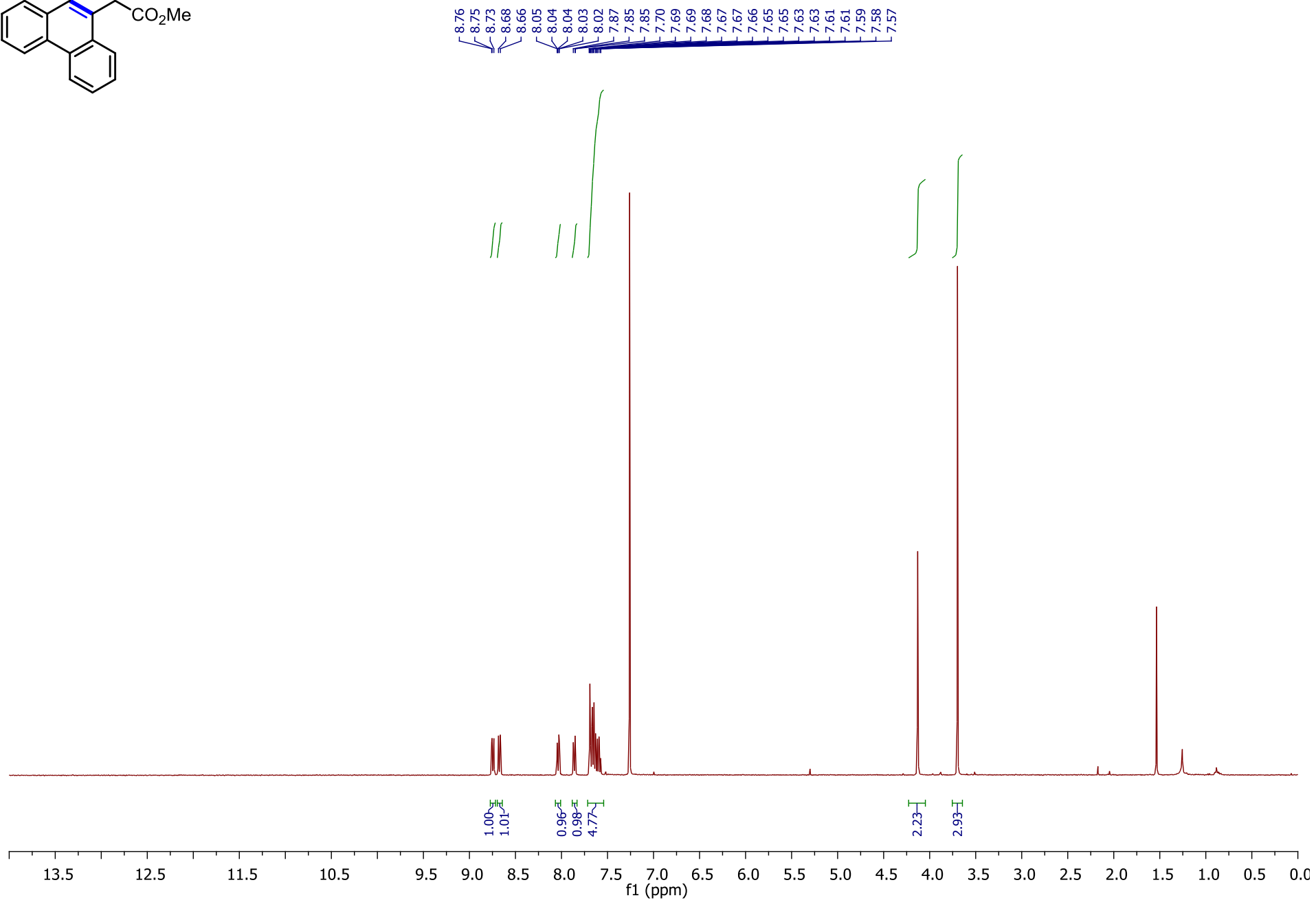
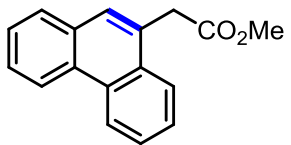
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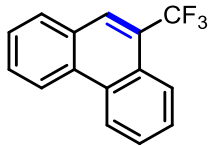
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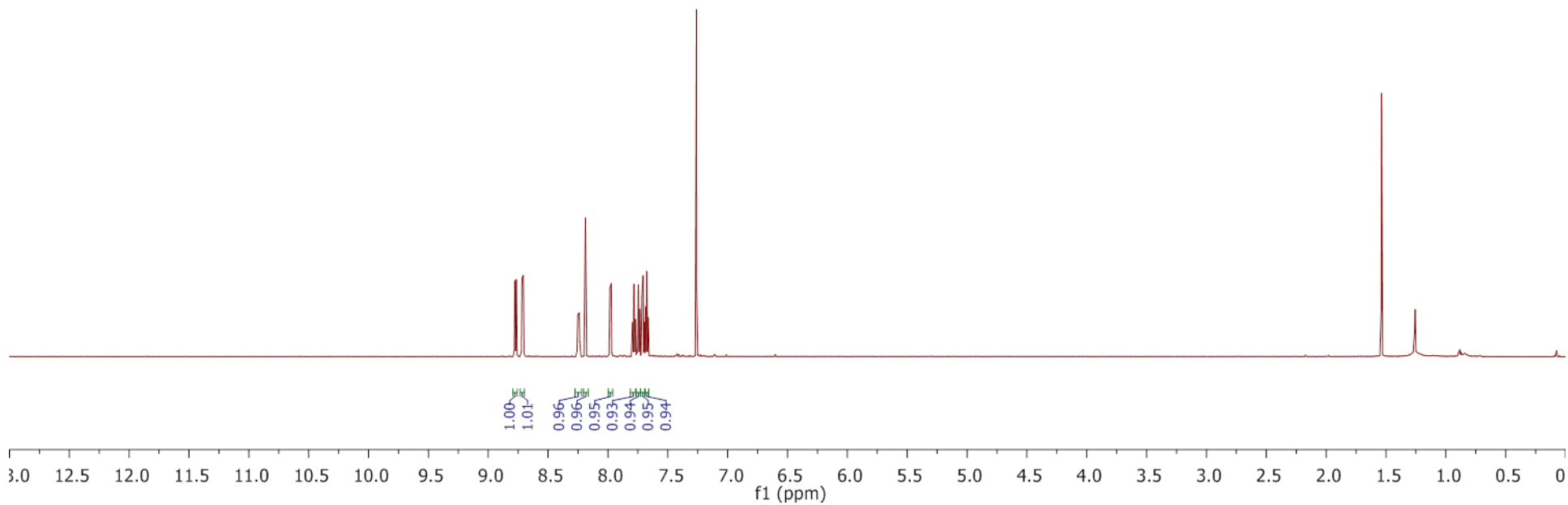
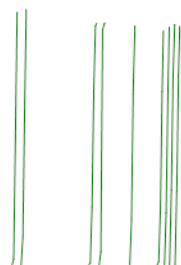


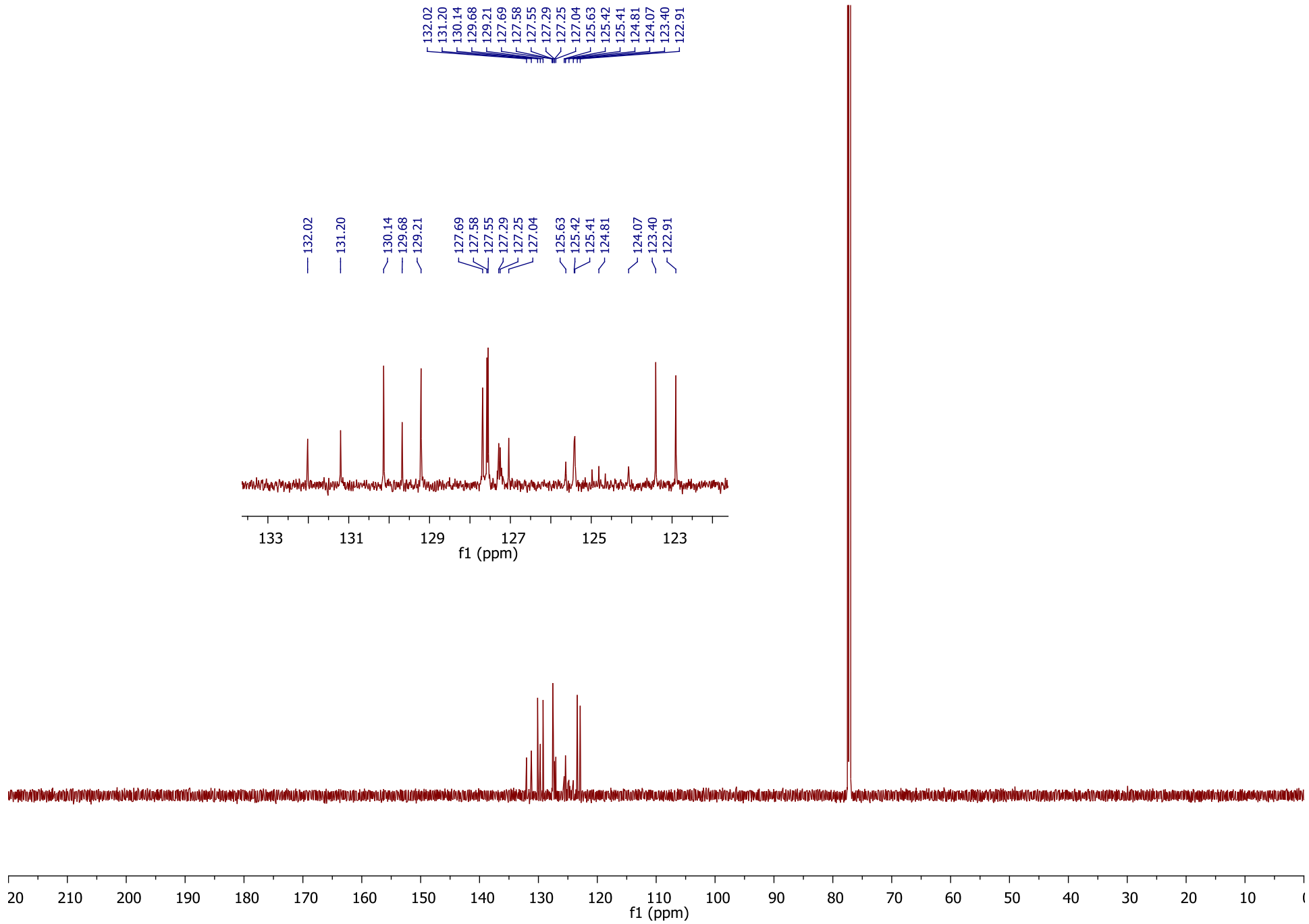


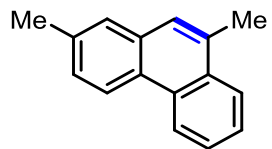




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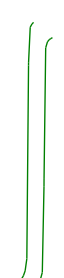
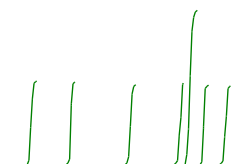






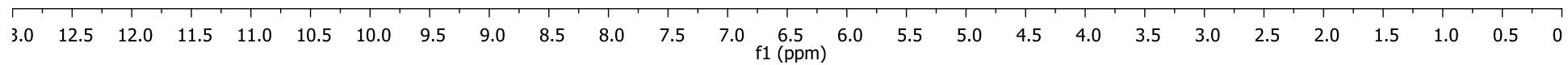
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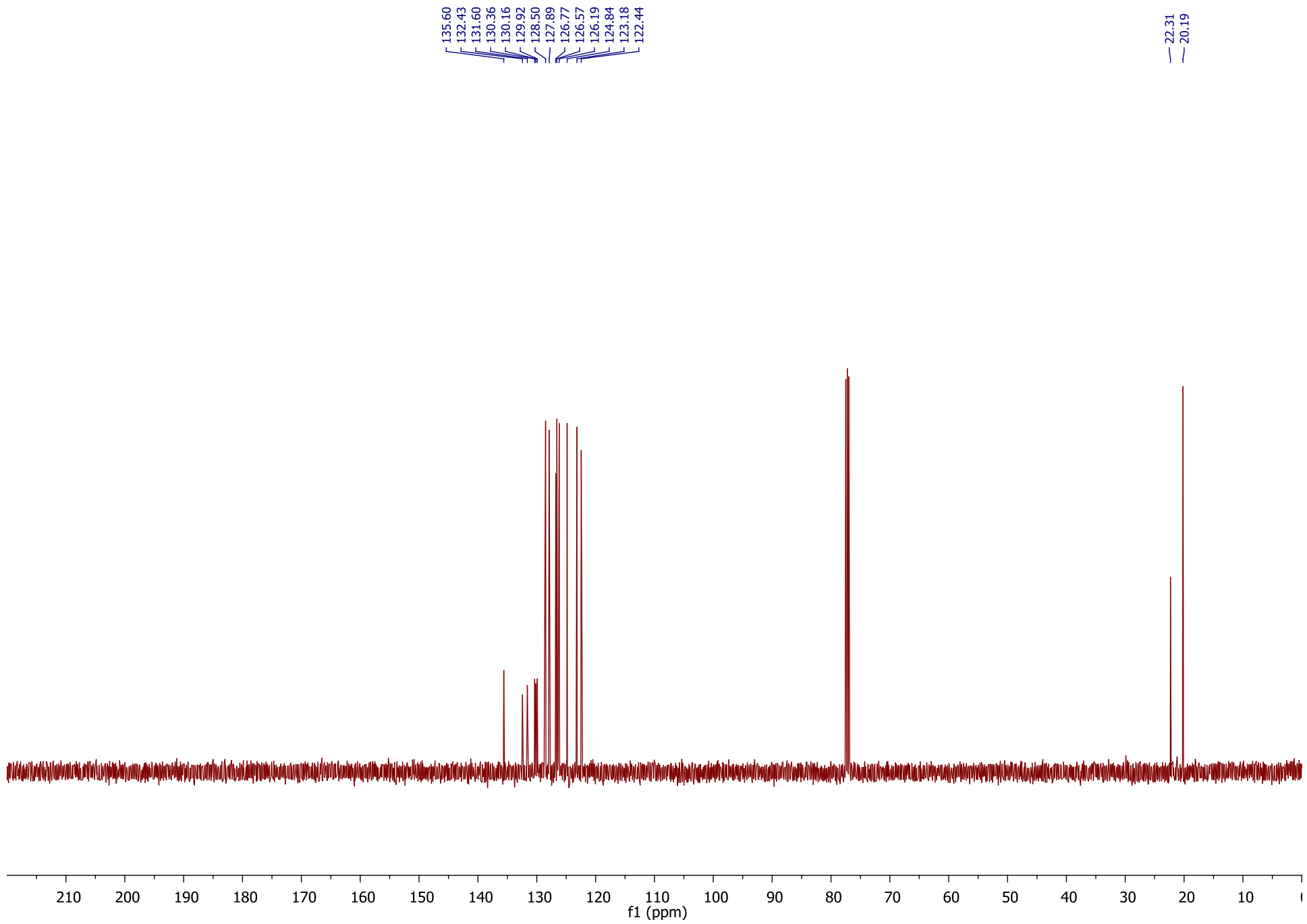
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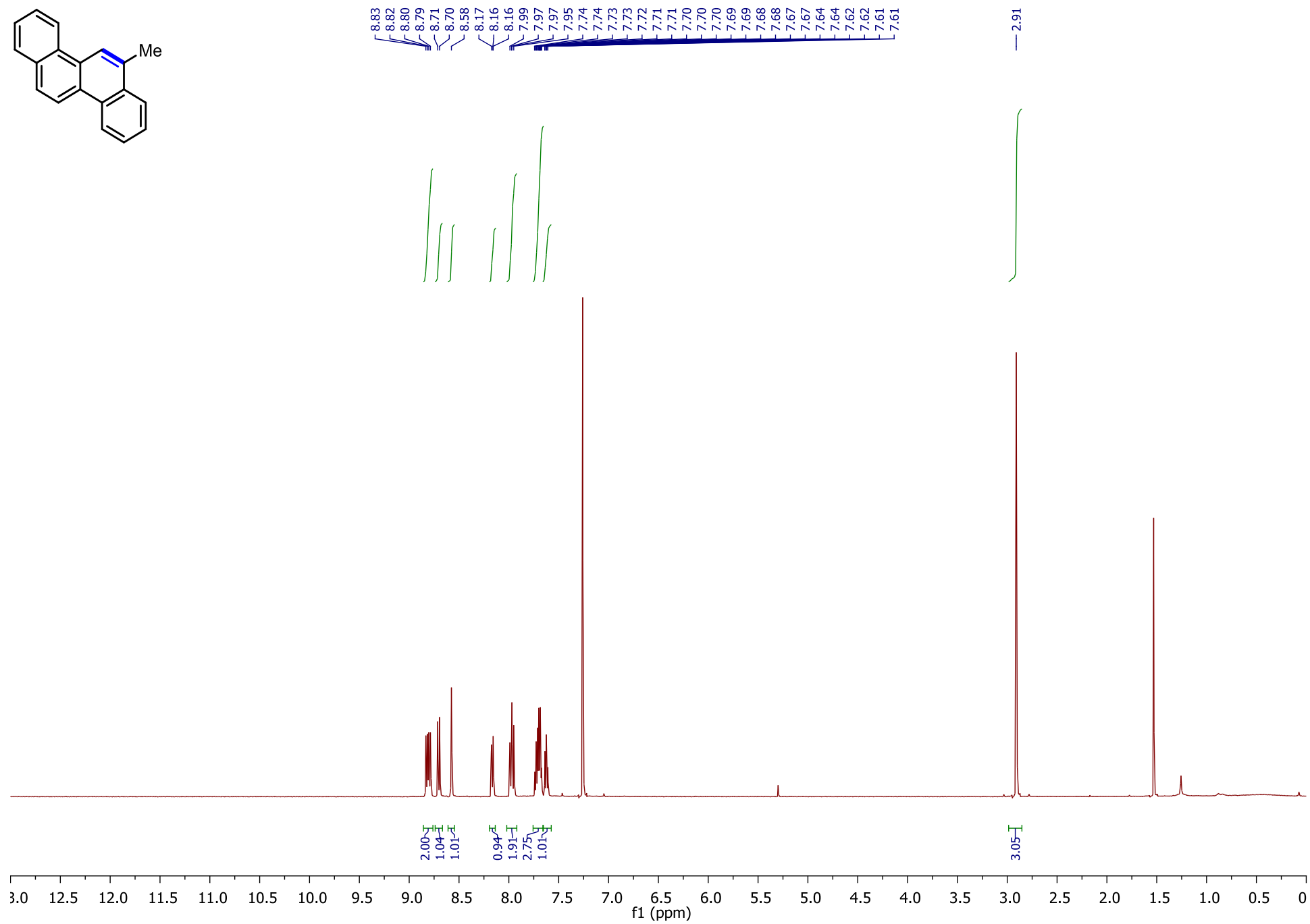
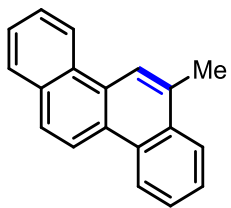


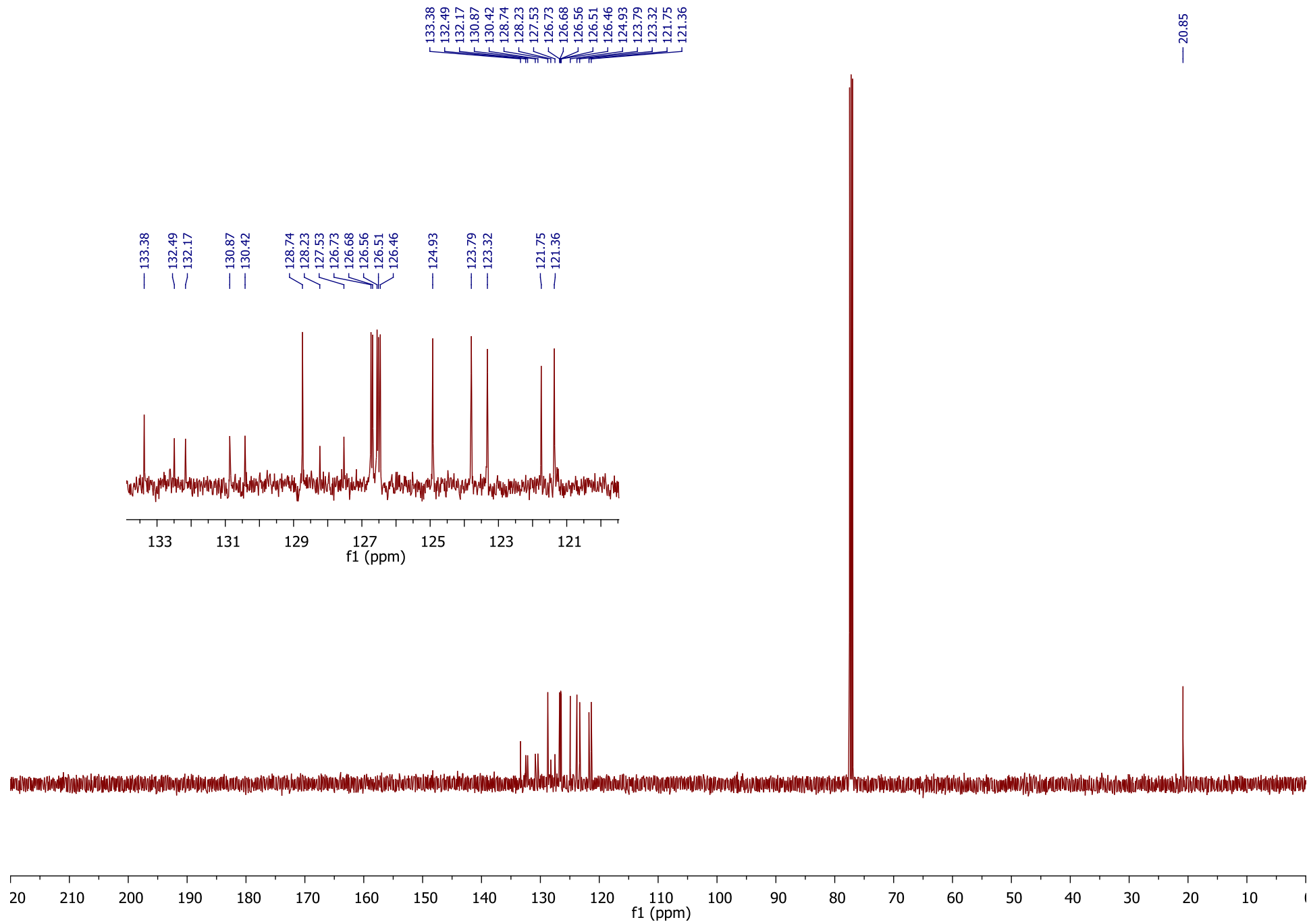
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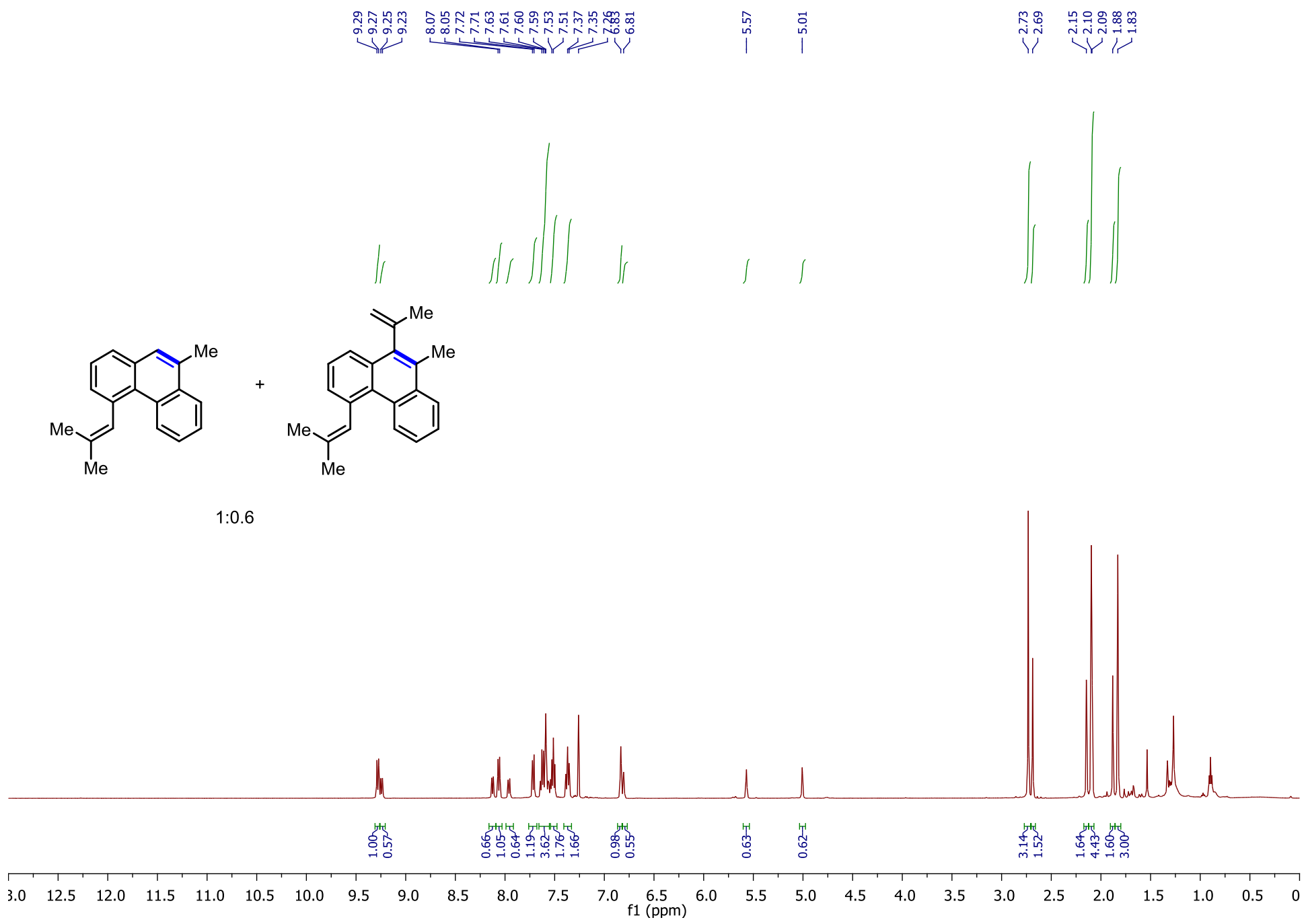
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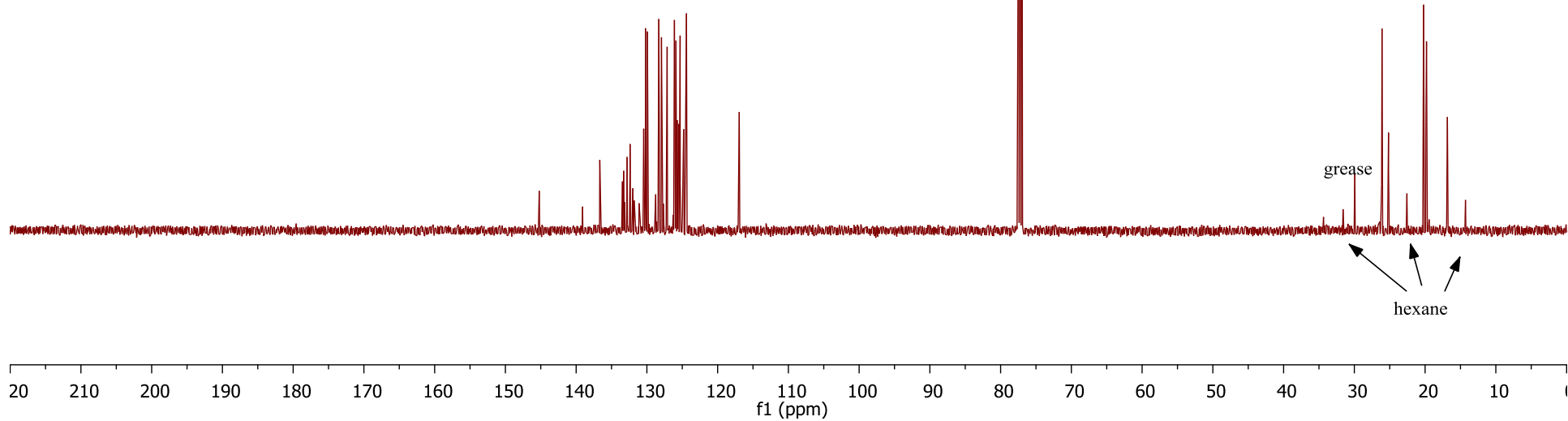
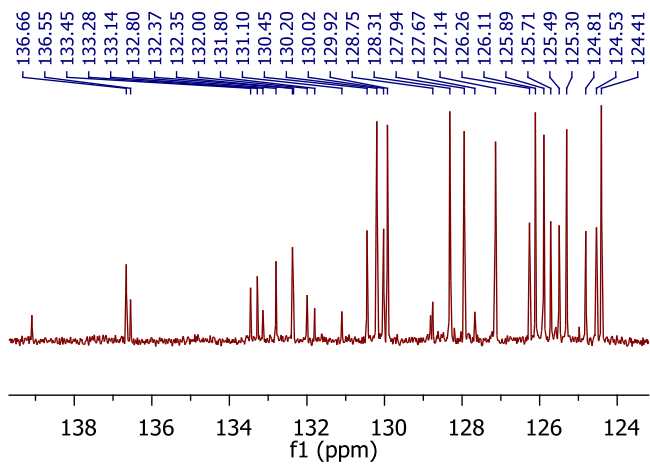


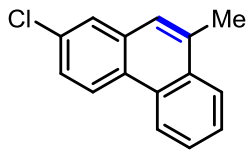




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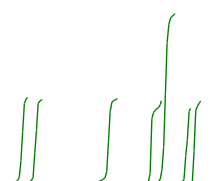
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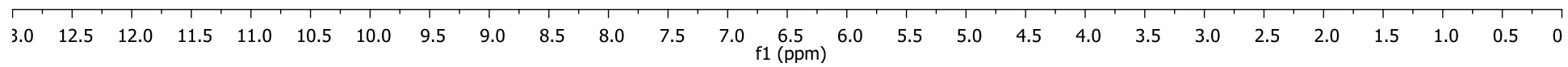
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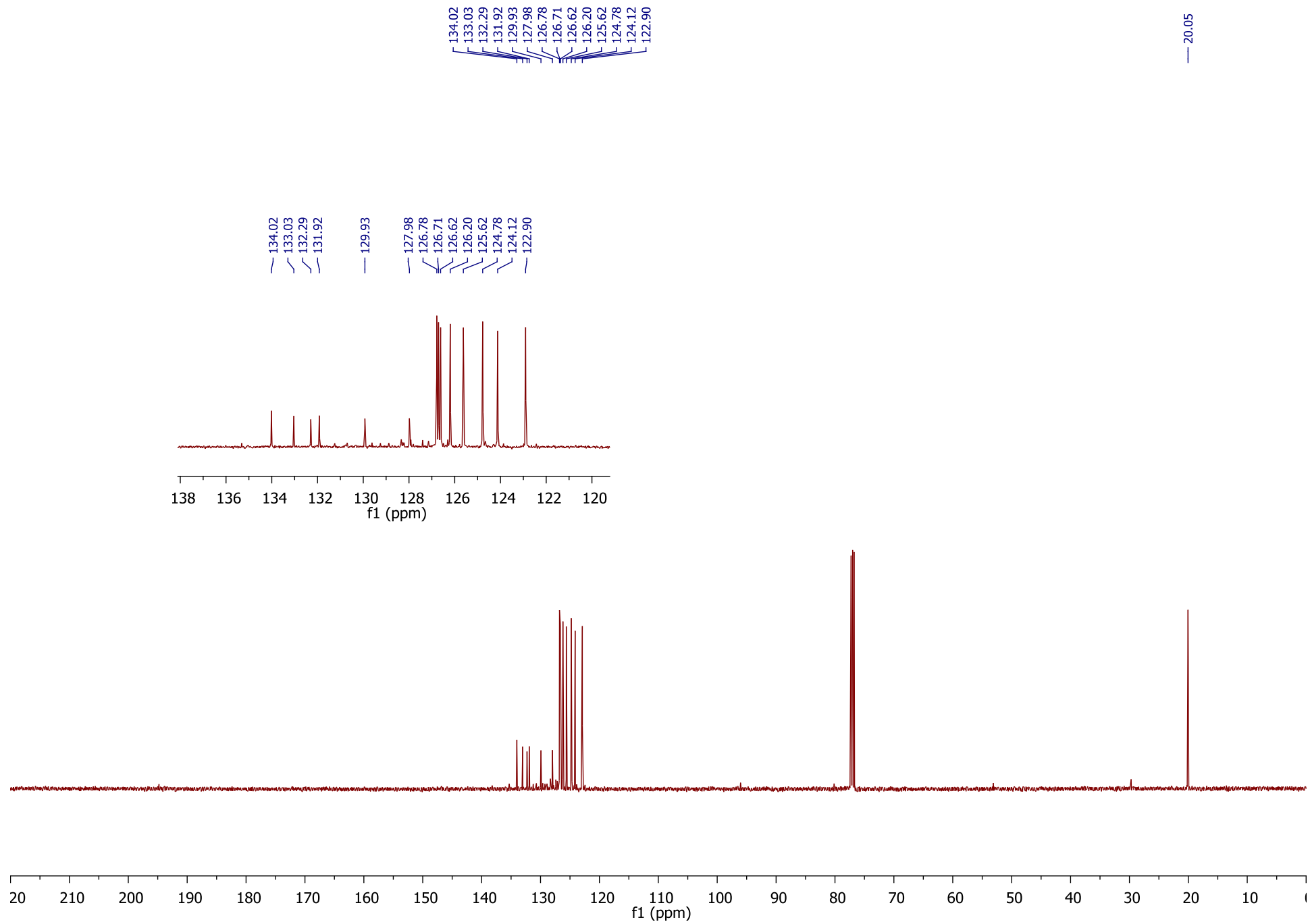
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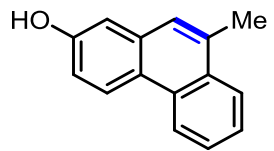
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3.04





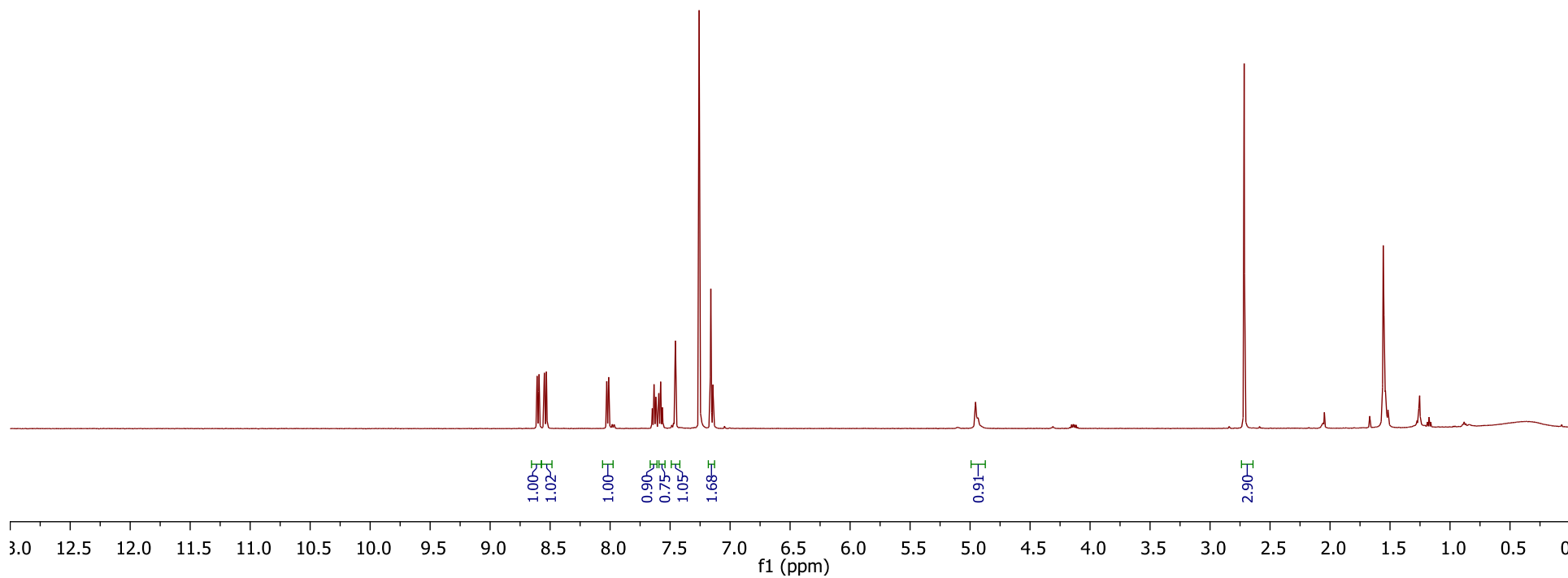
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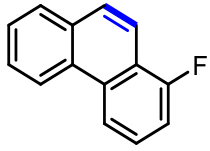


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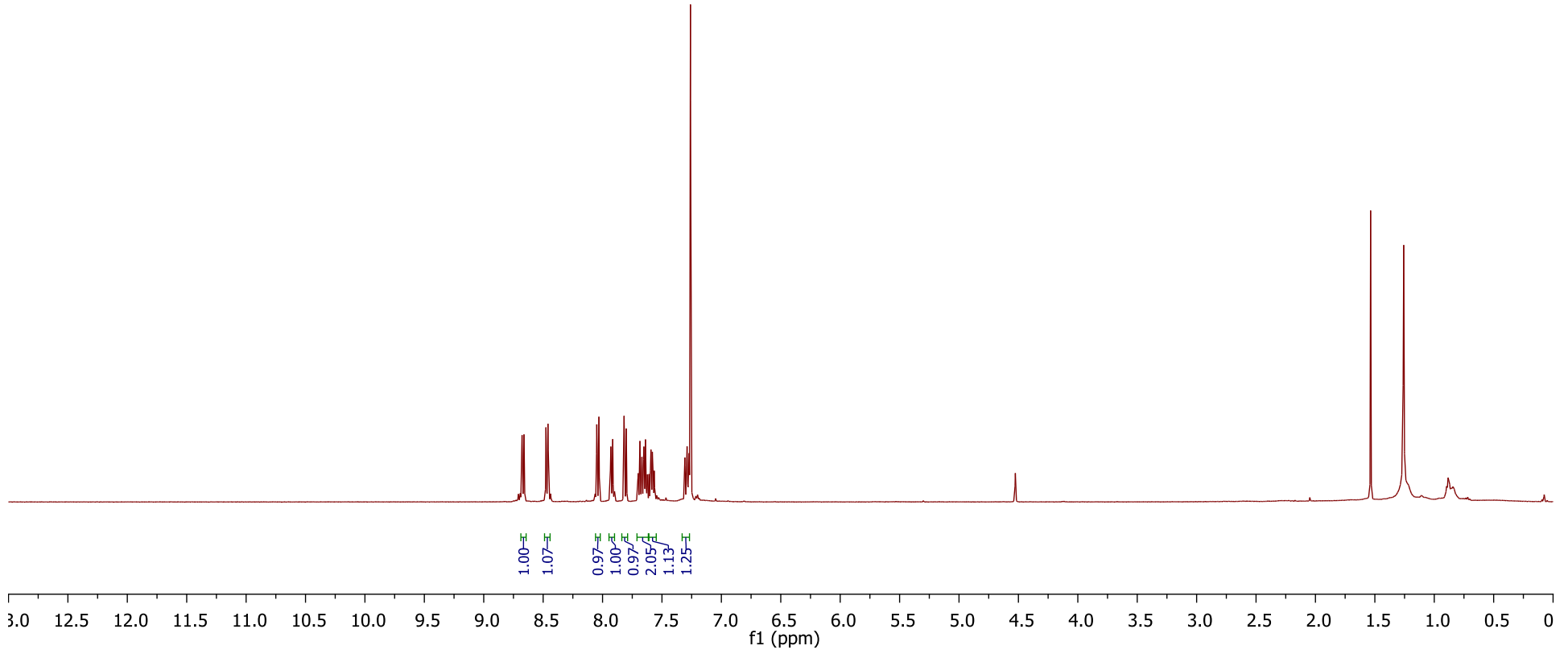
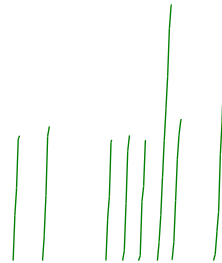
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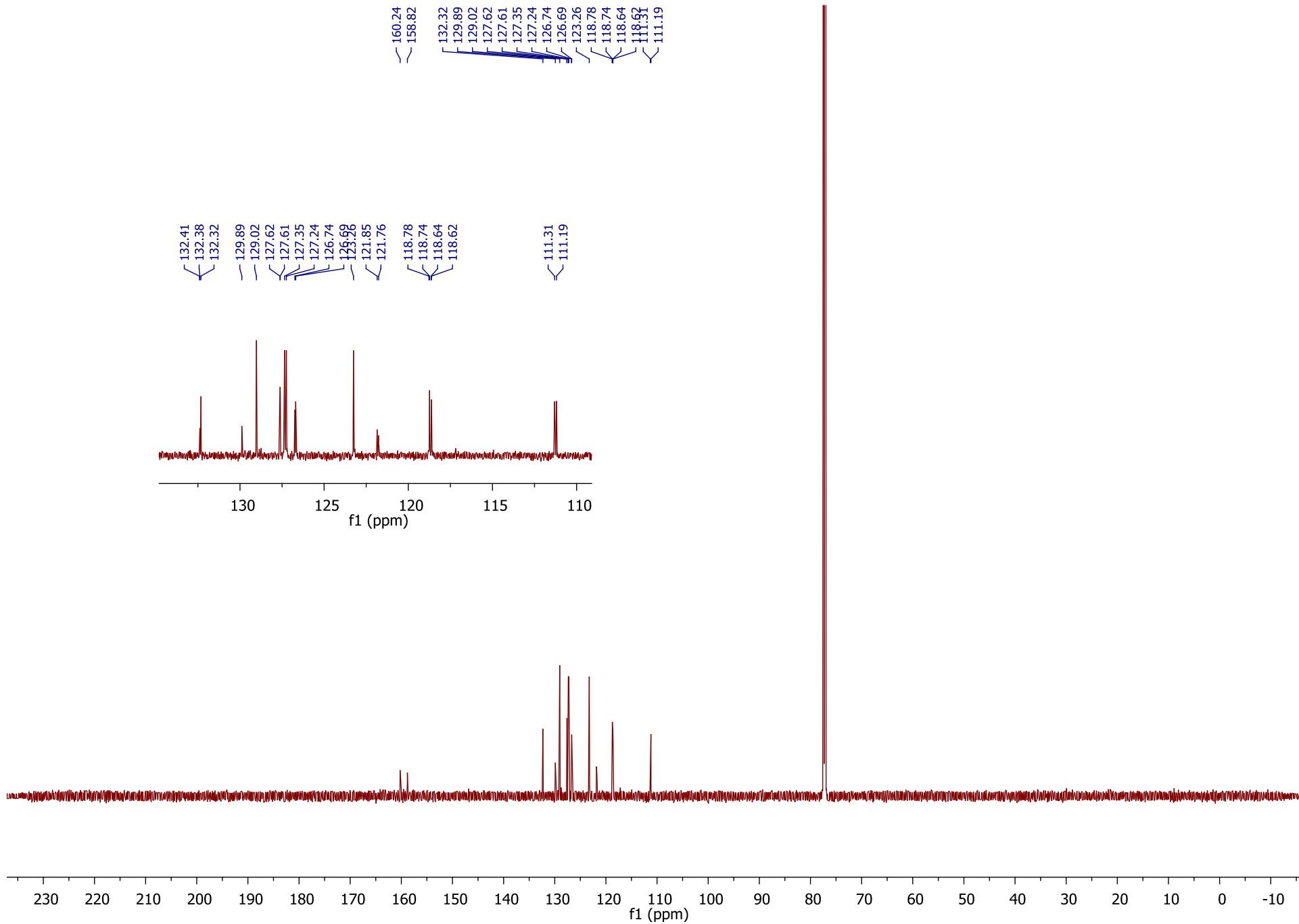
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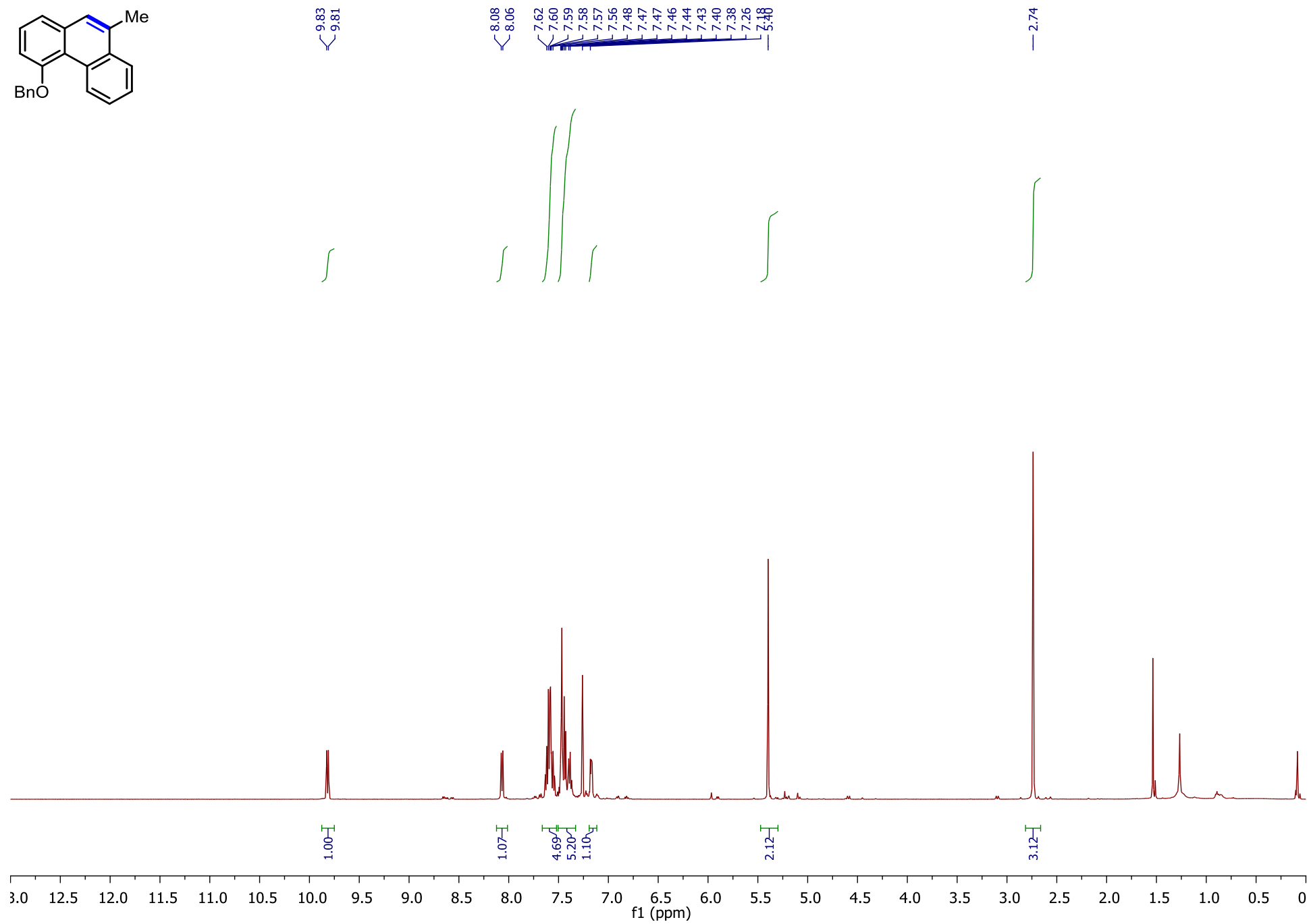
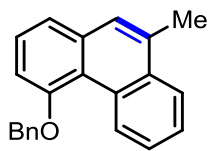


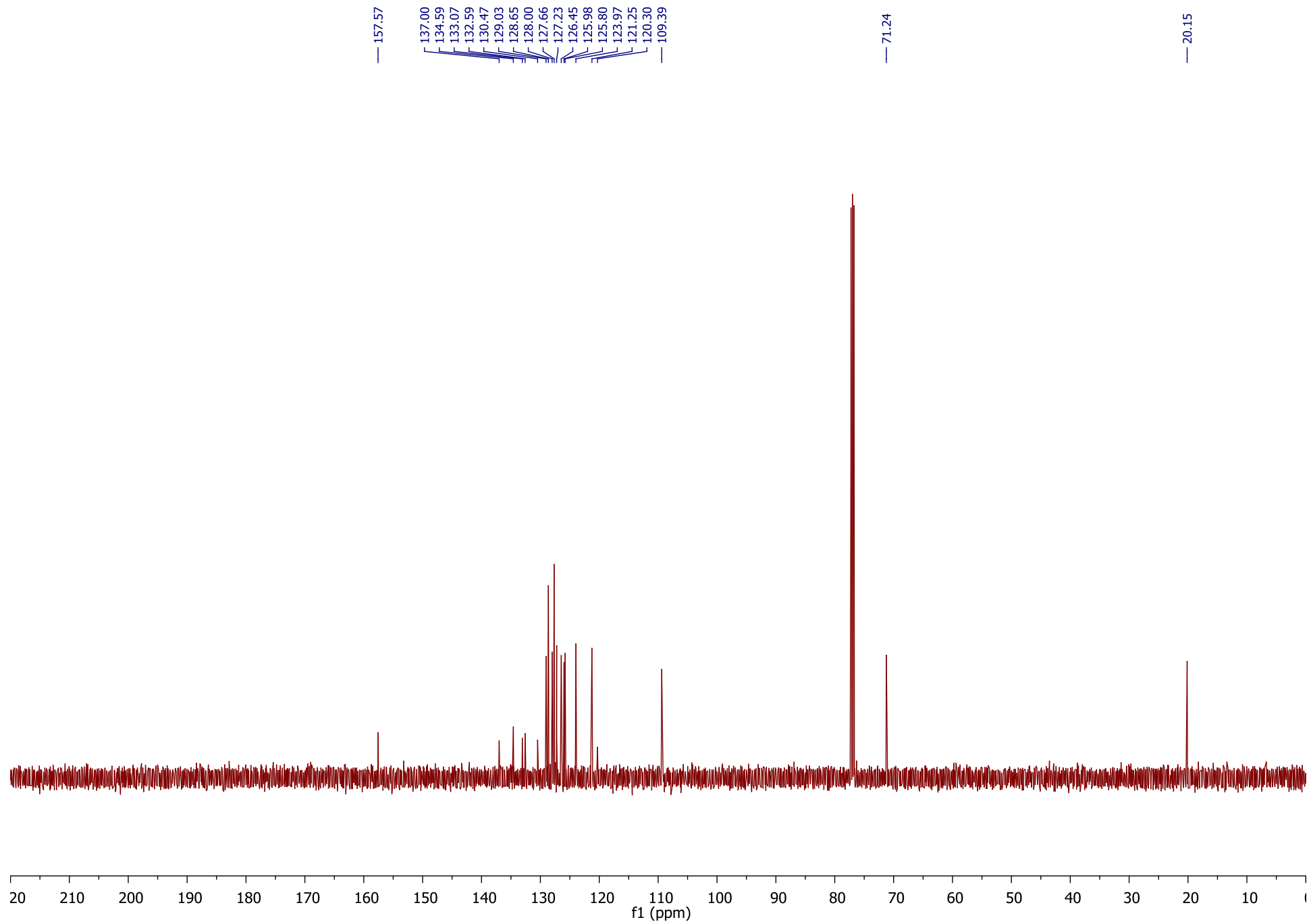


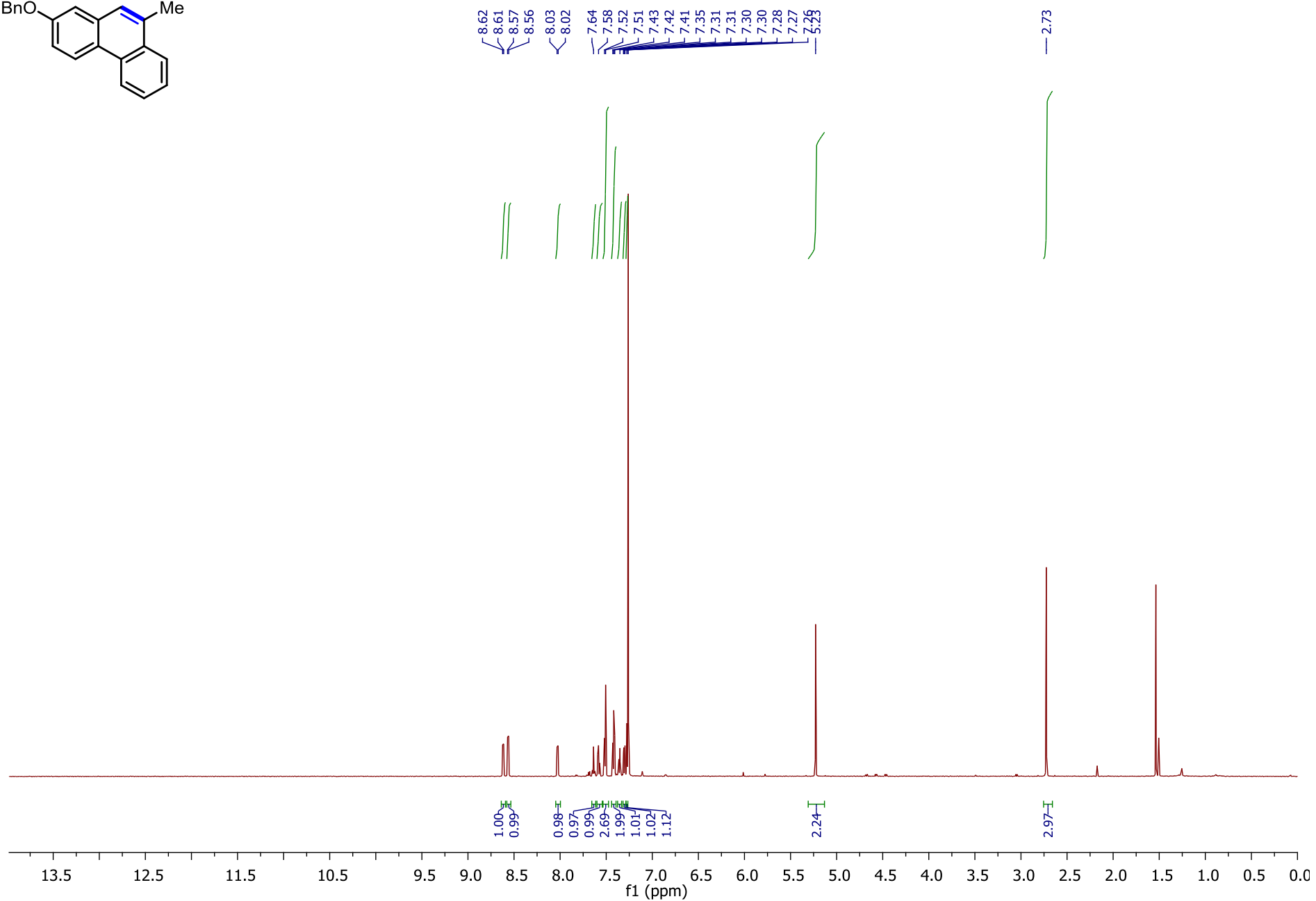
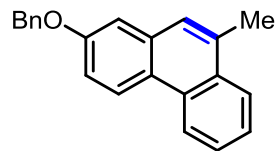
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7.93
7.91
7.82
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7.70
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7.67
7.67
7.65
7.65
7.64
7.64
7.62
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7.26

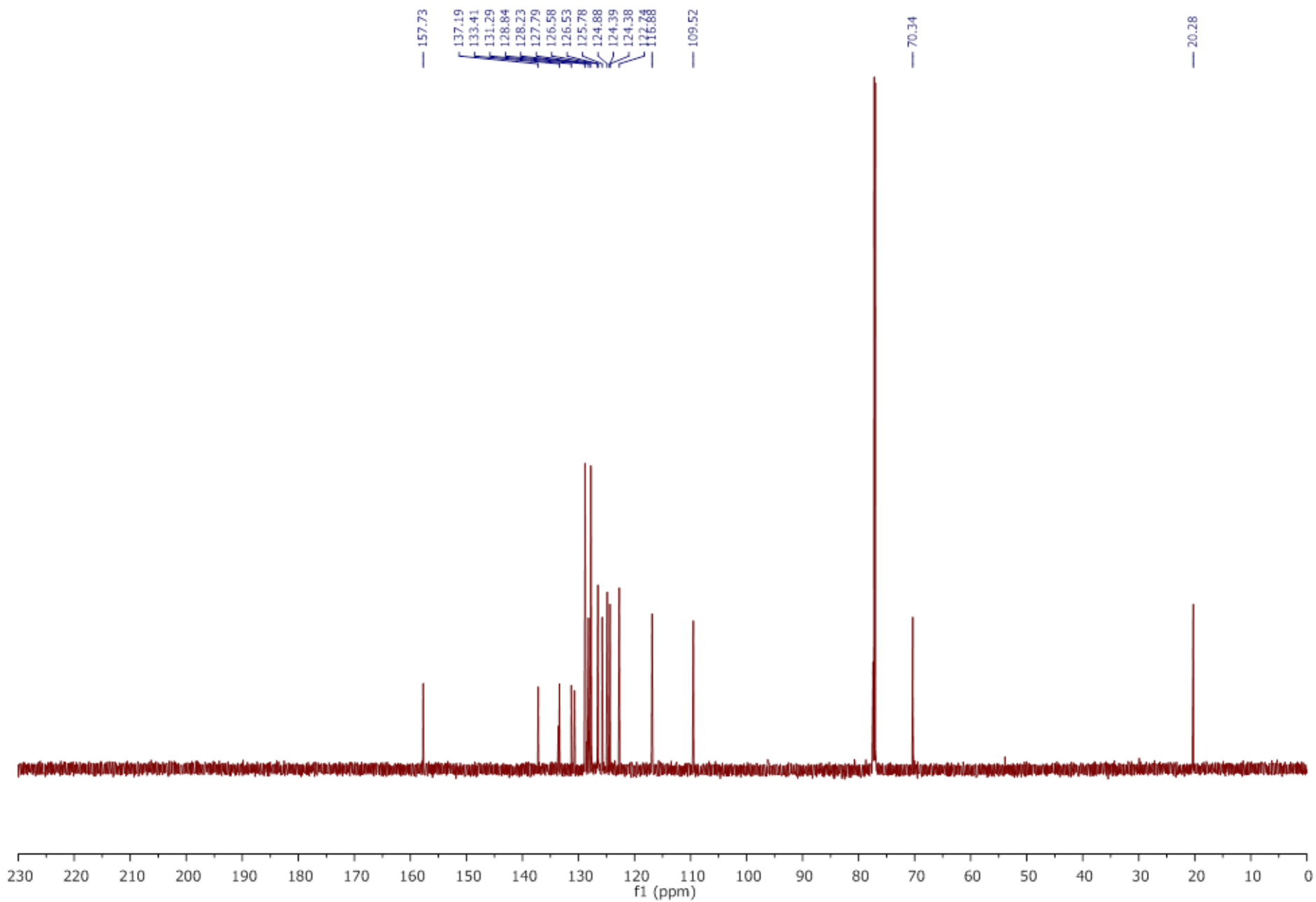


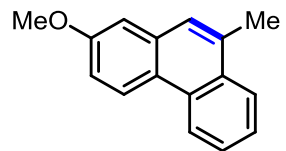








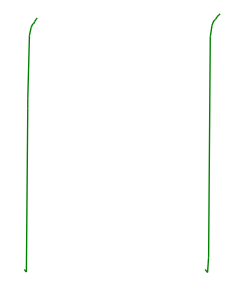
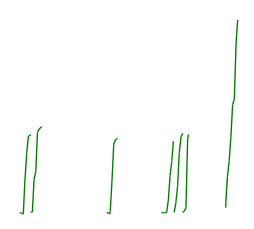




8.63
8.61
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7.60
7.60
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7.58
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7.22
7.20
7.19

3.96
3.80

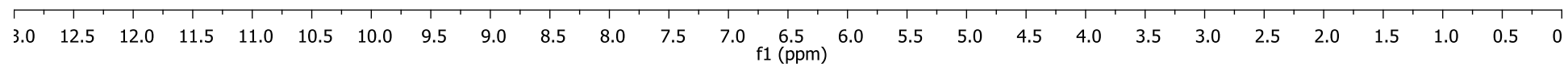
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2.73

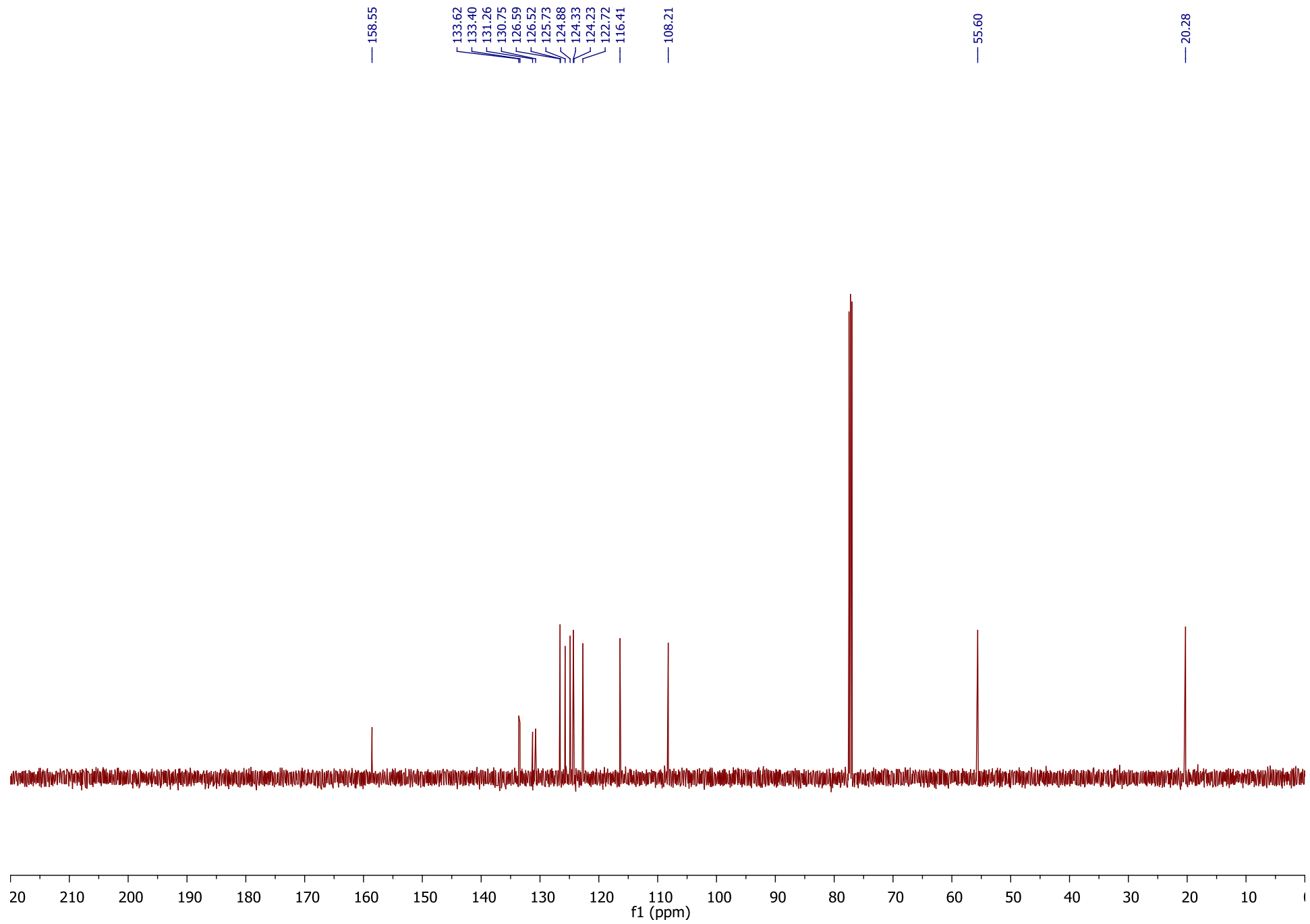


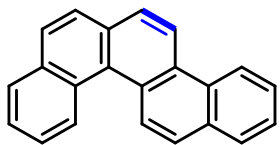
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0.95
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0.78
0.87
0.86
2.12

2.77

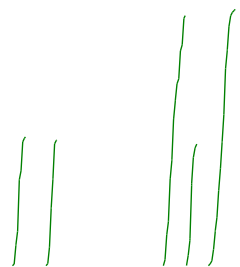
2.82



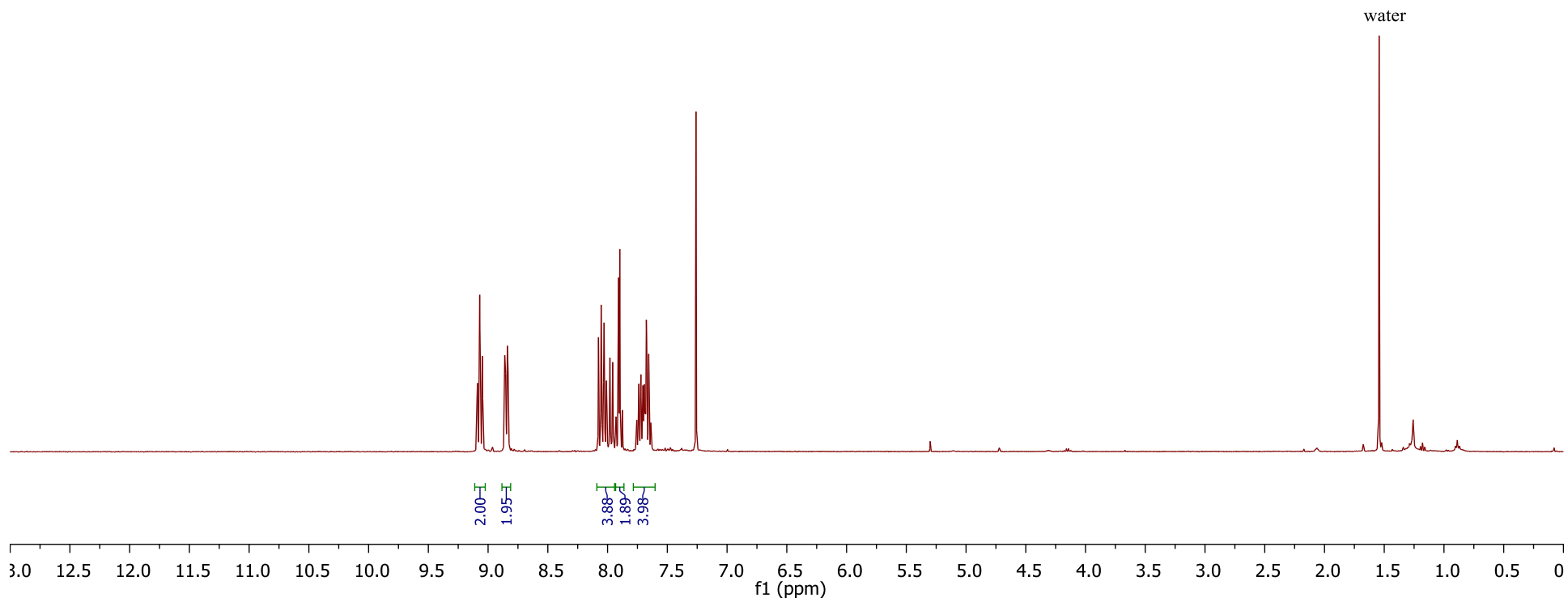


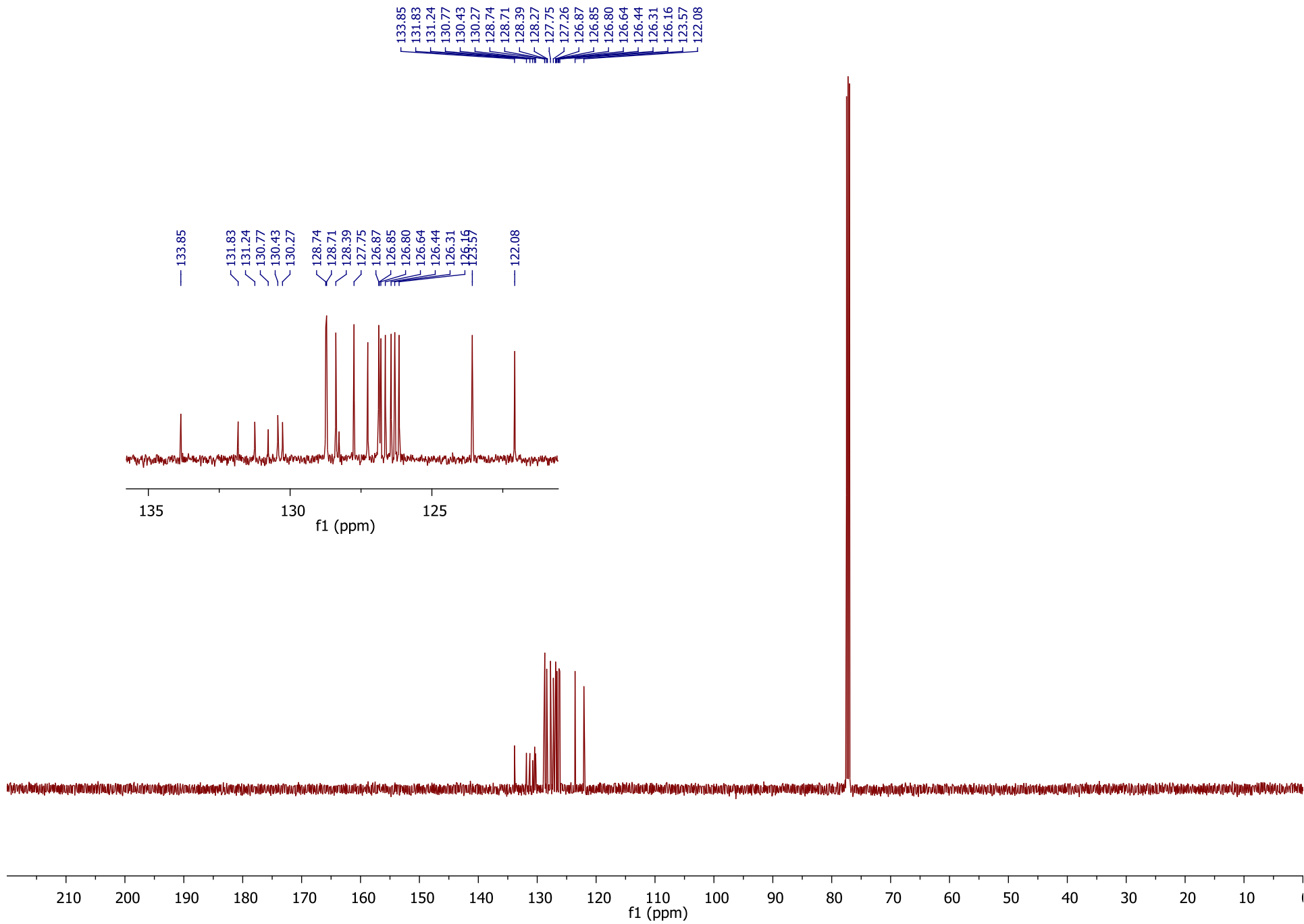


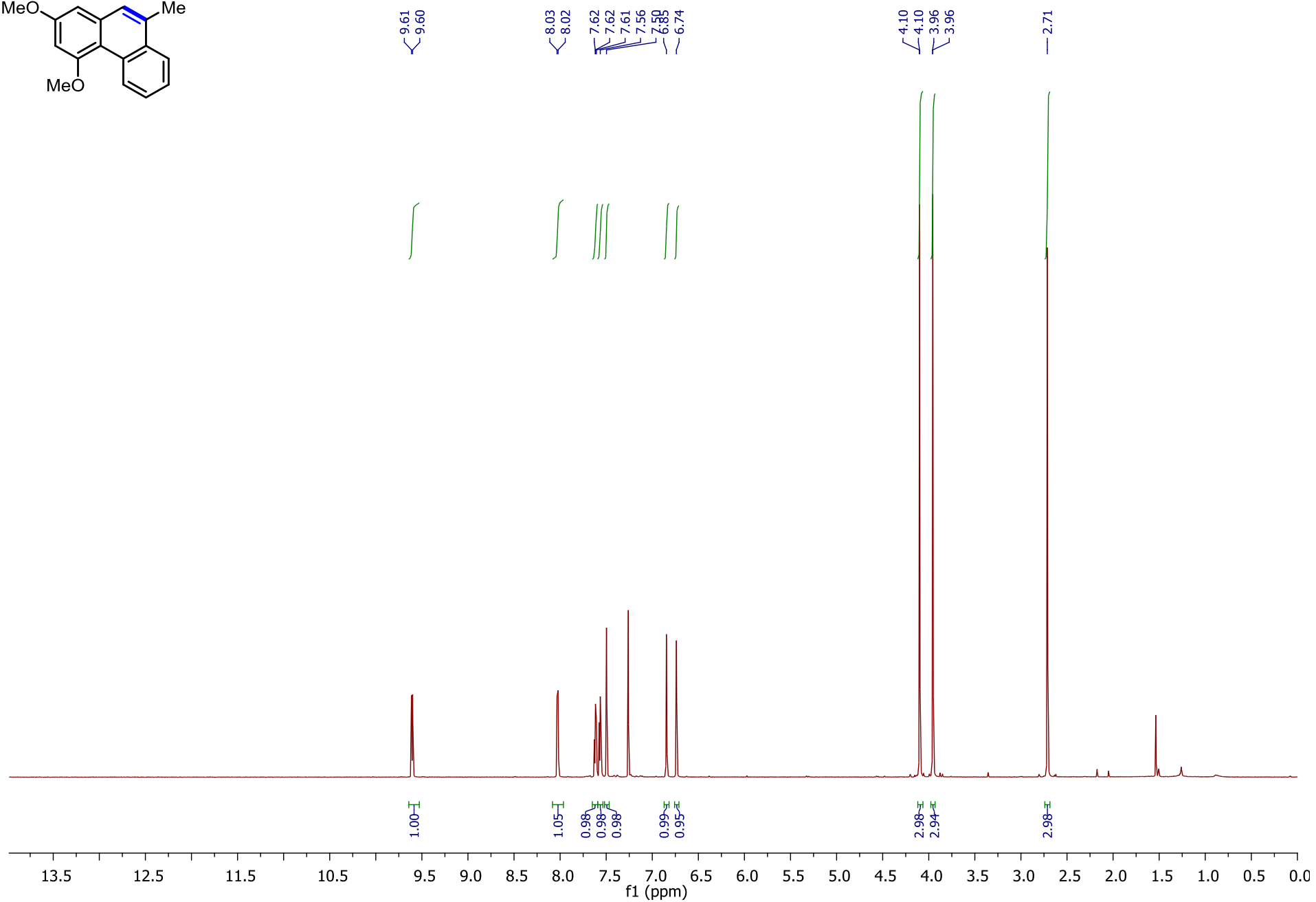
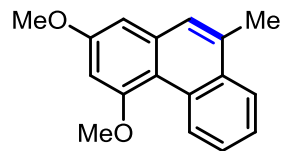
9.09
9.07
9.05
8.86
8.85
8.84
8.83
8.08
8.05
8.03
7.91
7.90
7.68
7.56

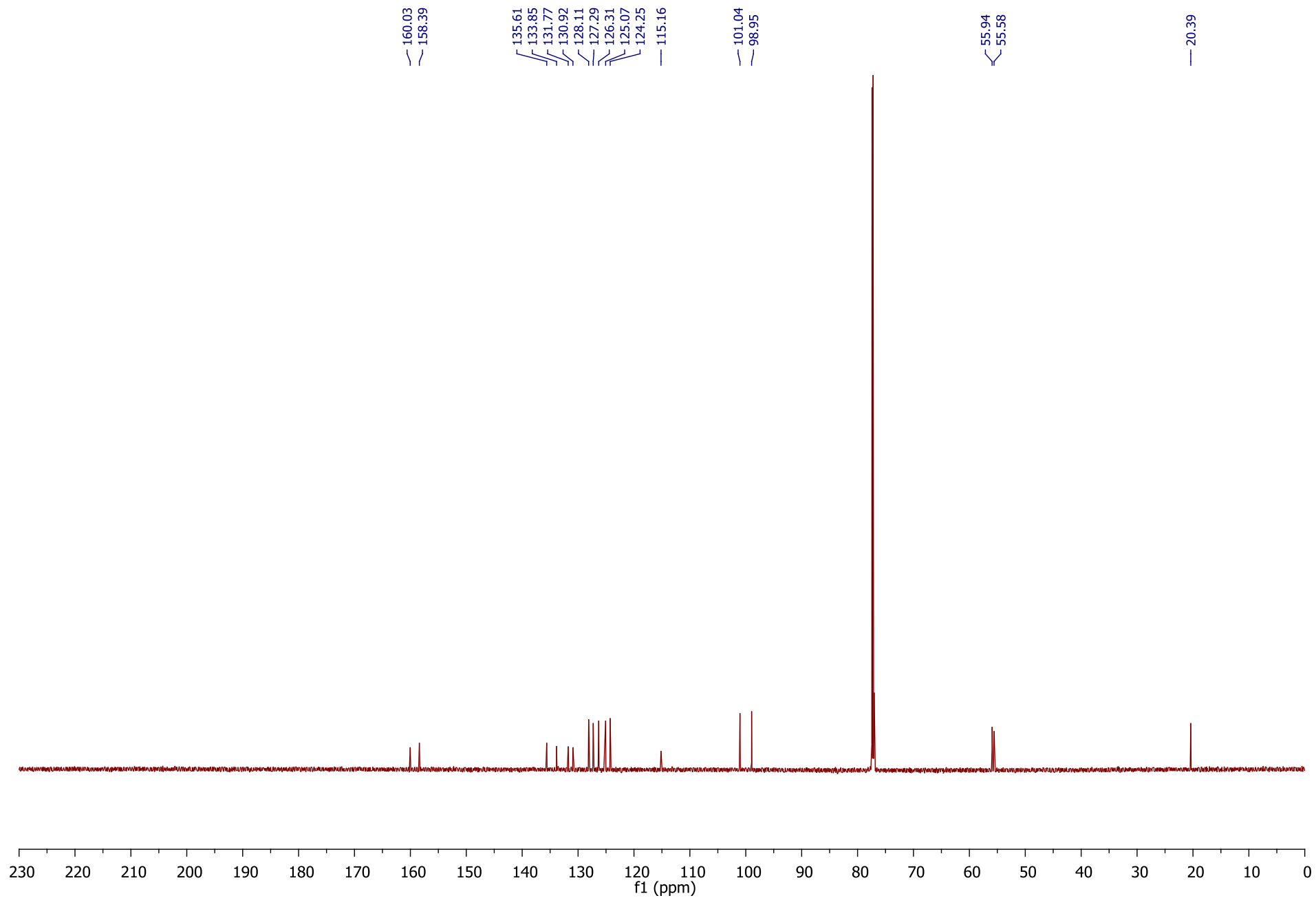


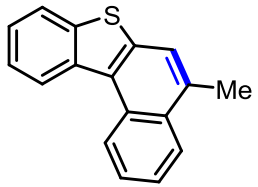
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1.89
3.98





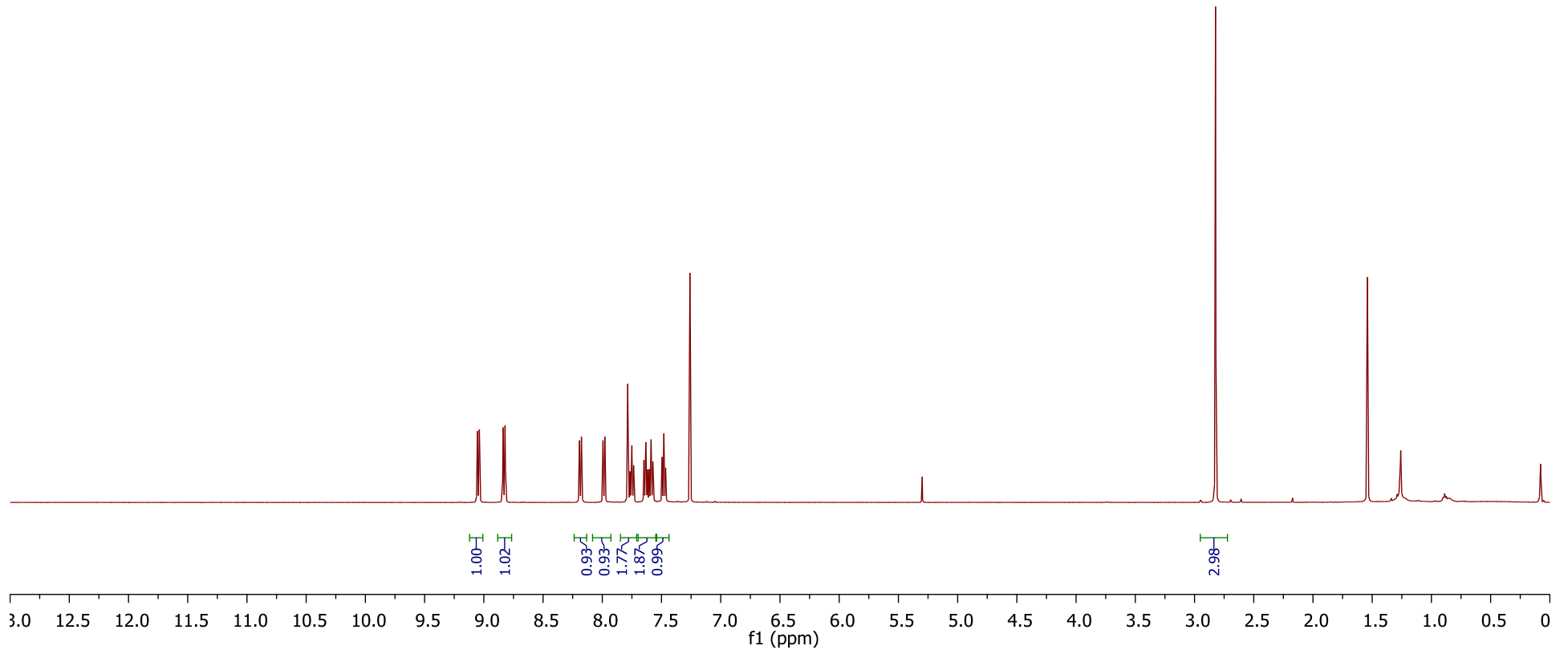
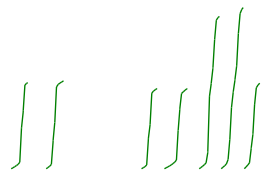


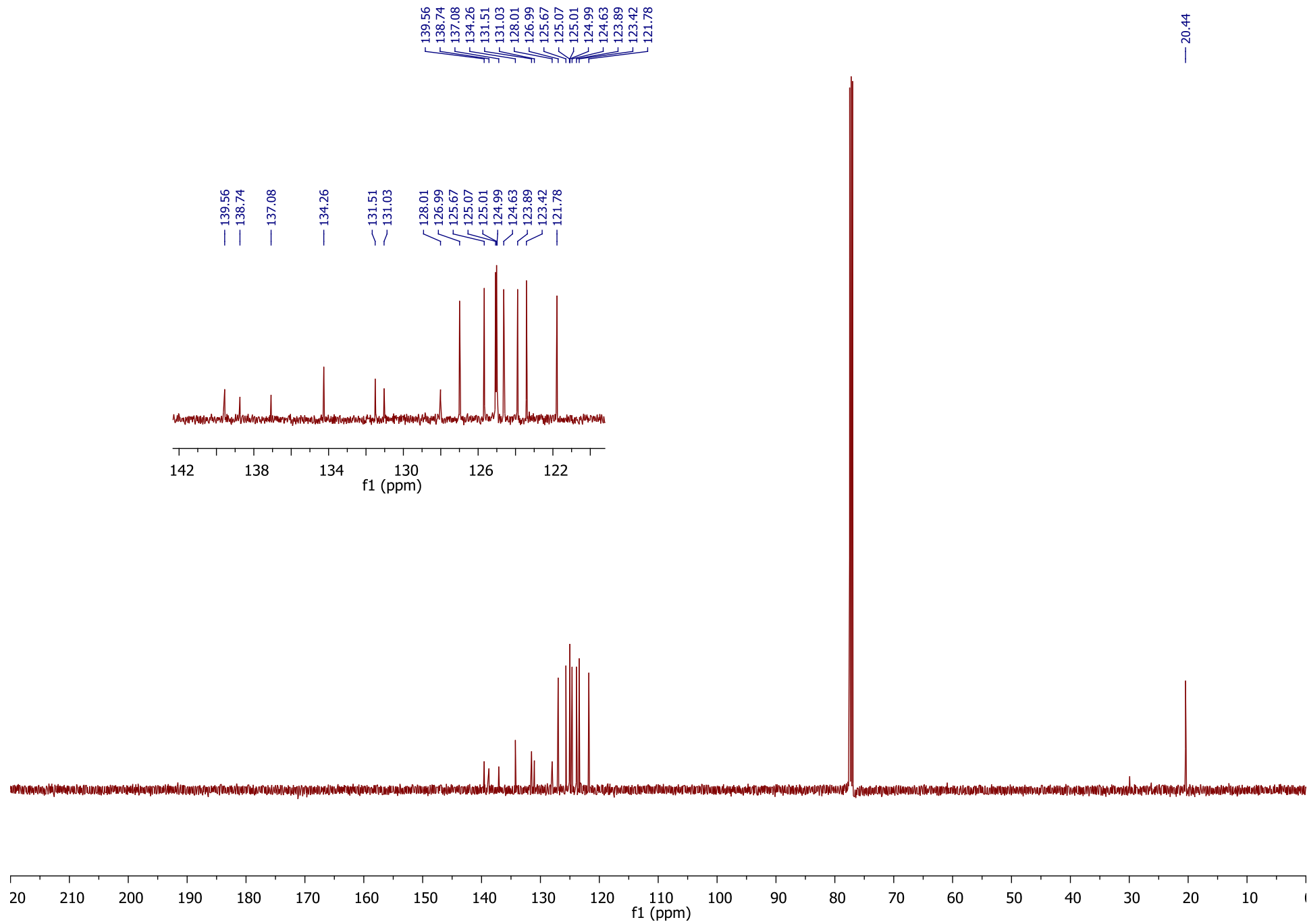




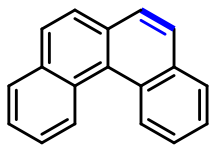
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9.04
8.84
8.82
8.19
8.18
7.99
7.98
7.79
7.77
7.75
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7.59
7.57
7.50
7.48
7.47
7.26

2.82

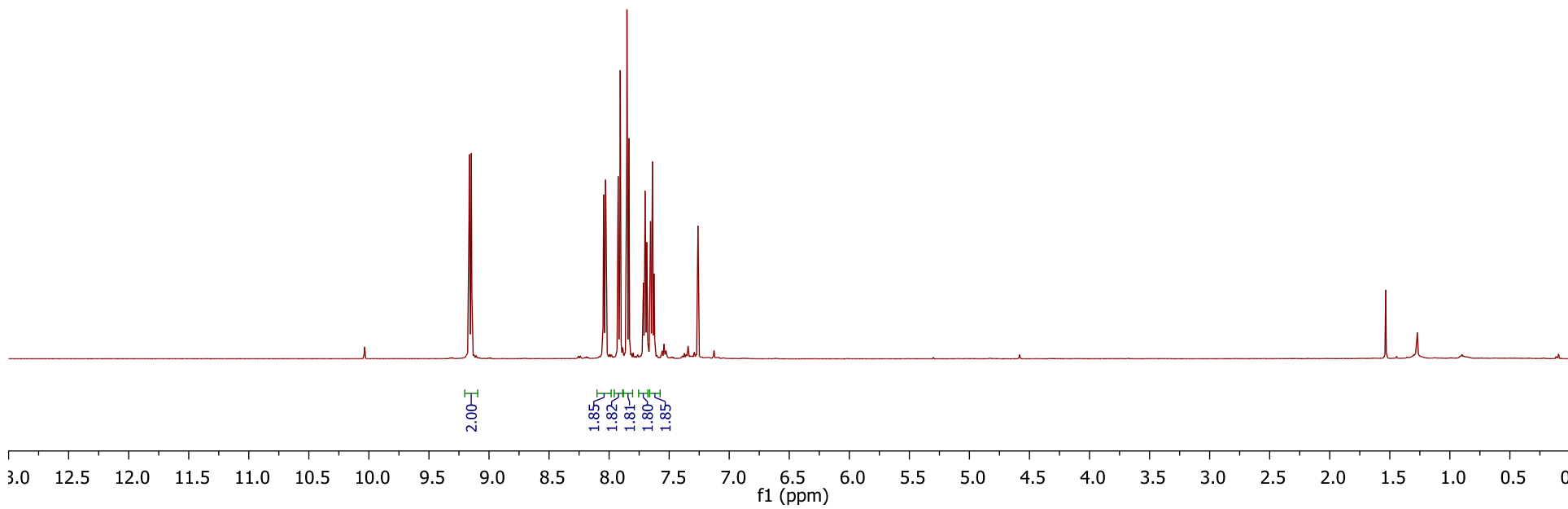
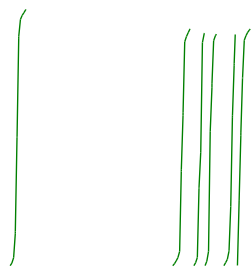


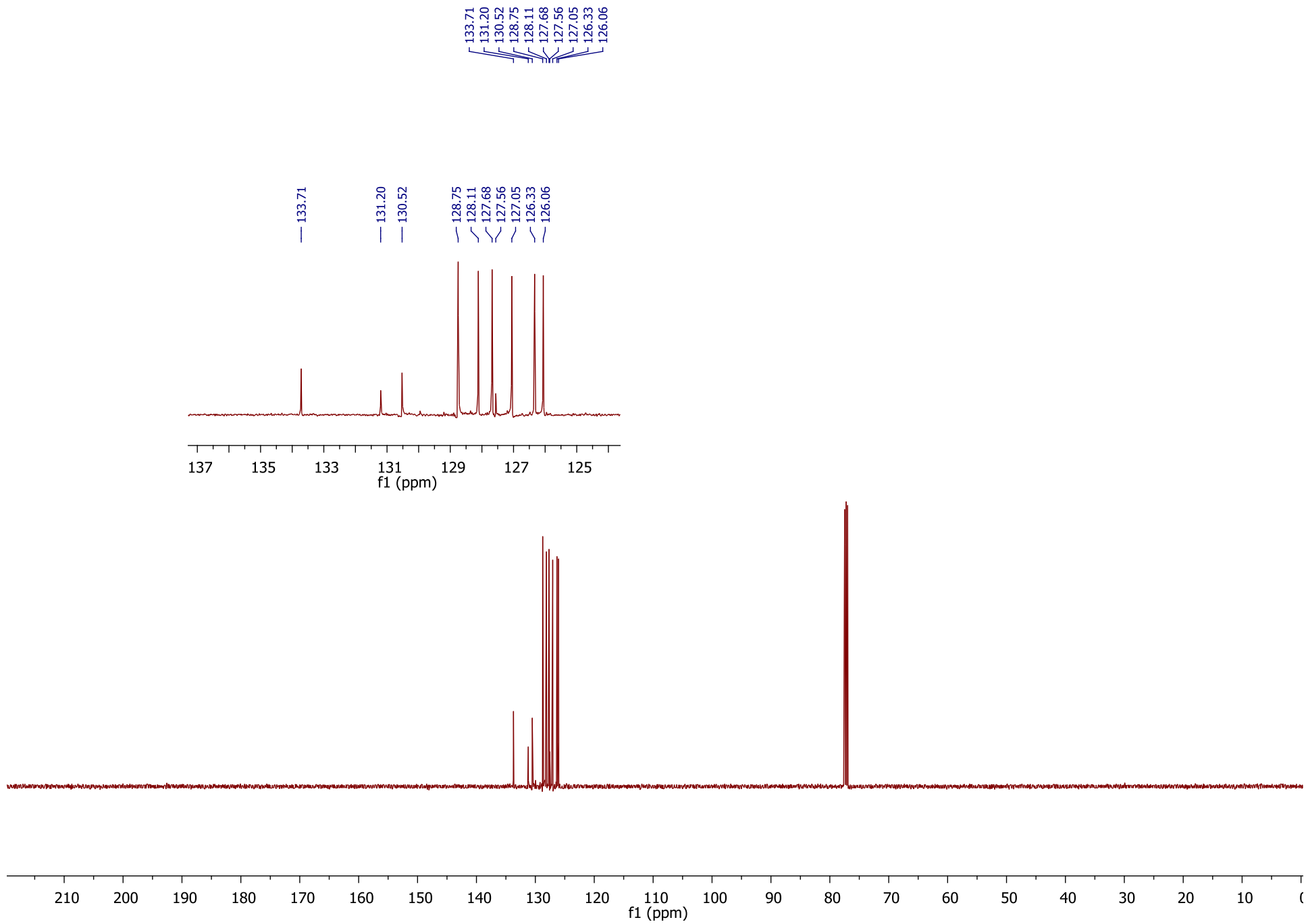


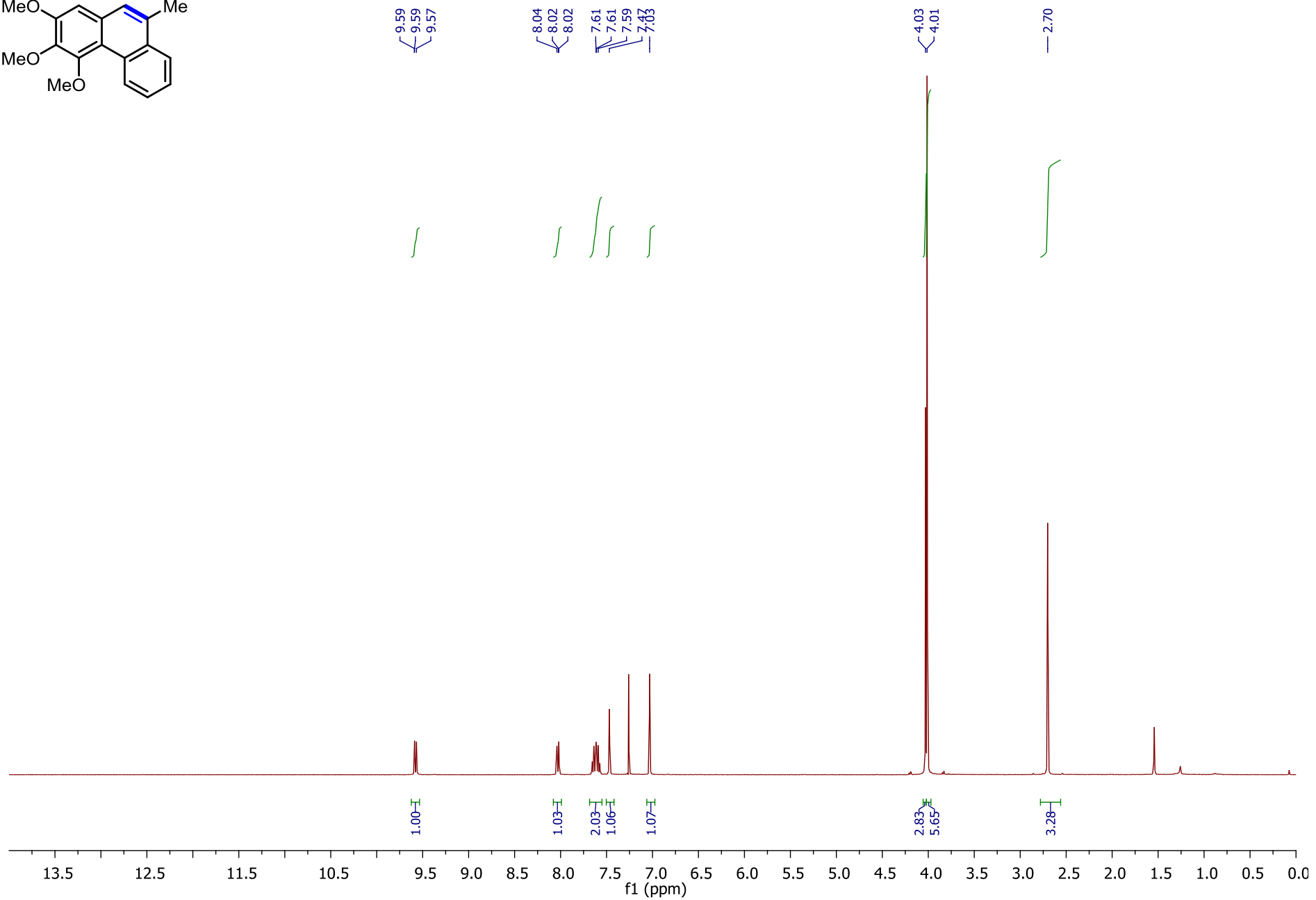
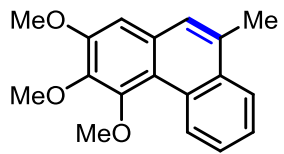
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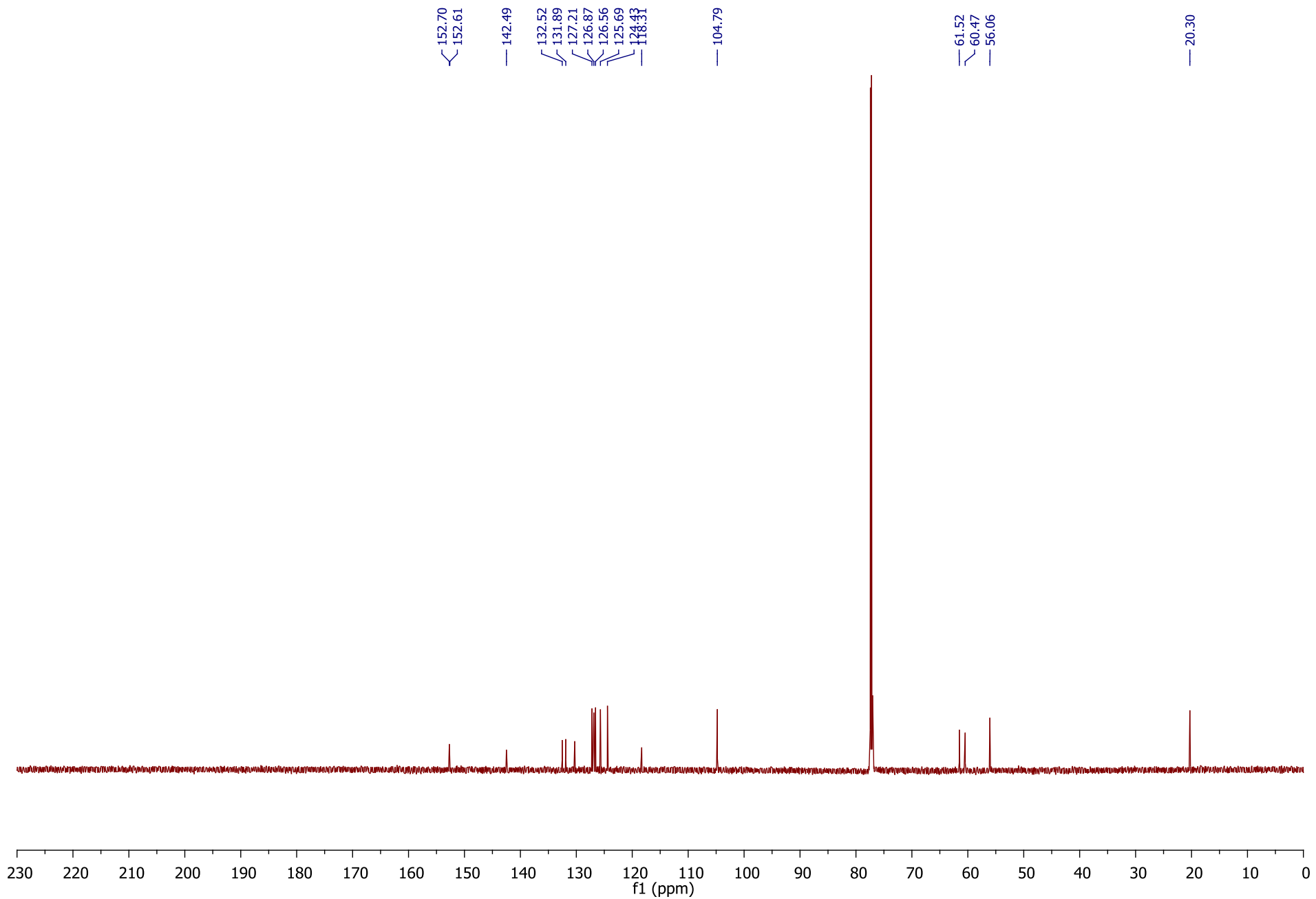


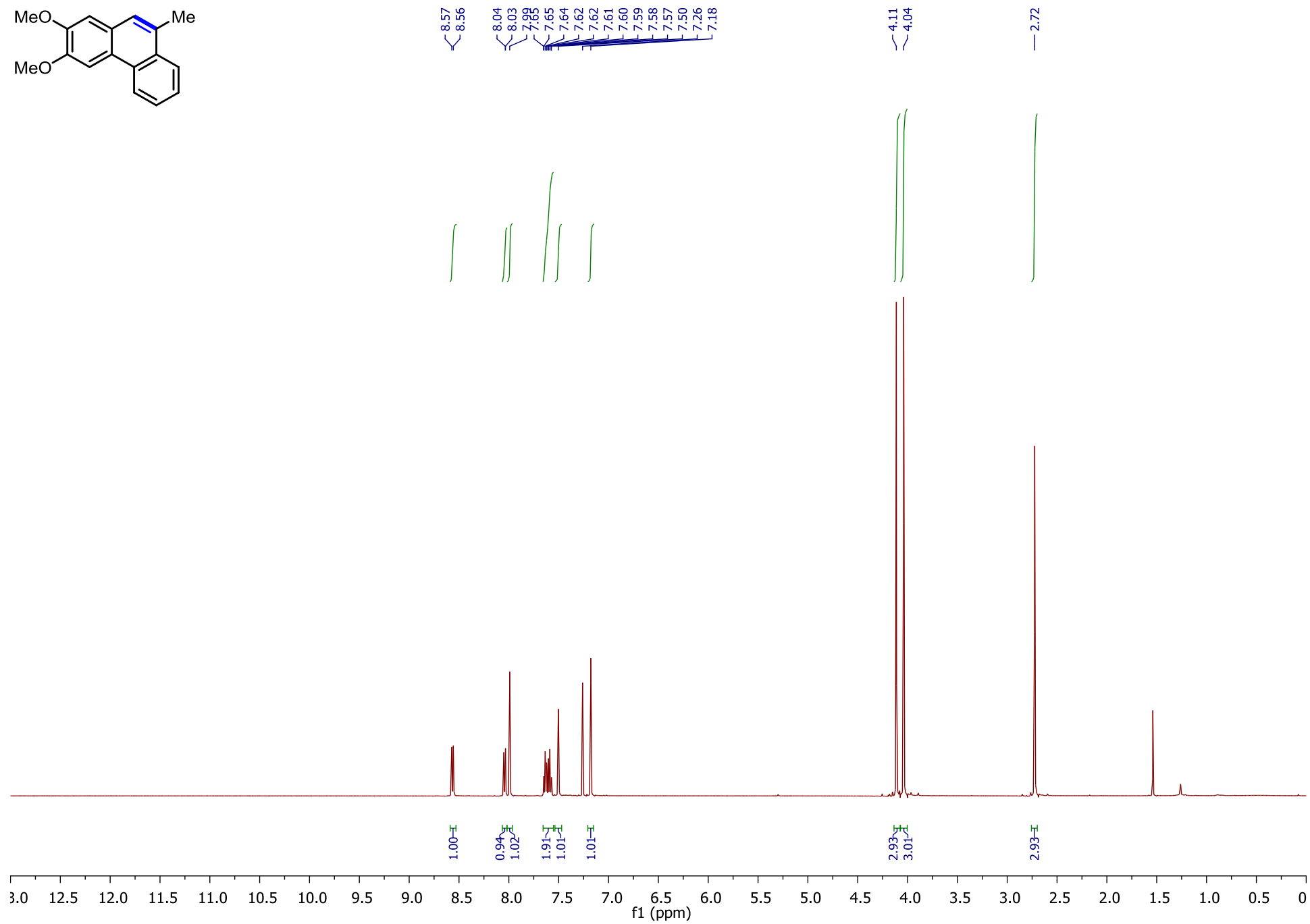
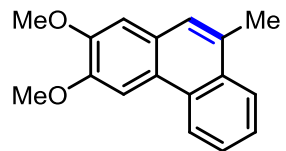
9.16
9.15
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7.92
7.91
7.85
7.83
7.70
7.70
7.65
7.65
7.54

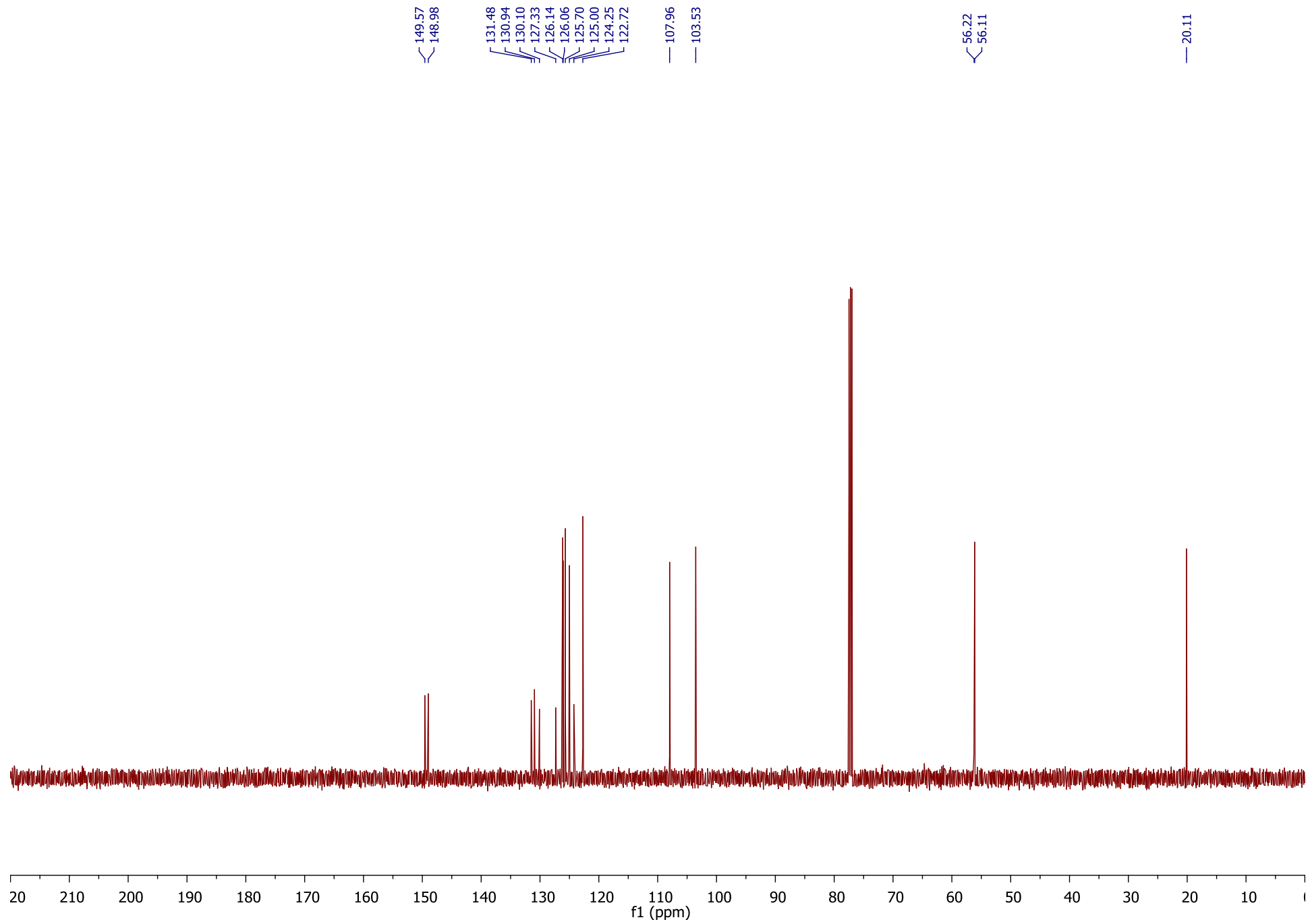


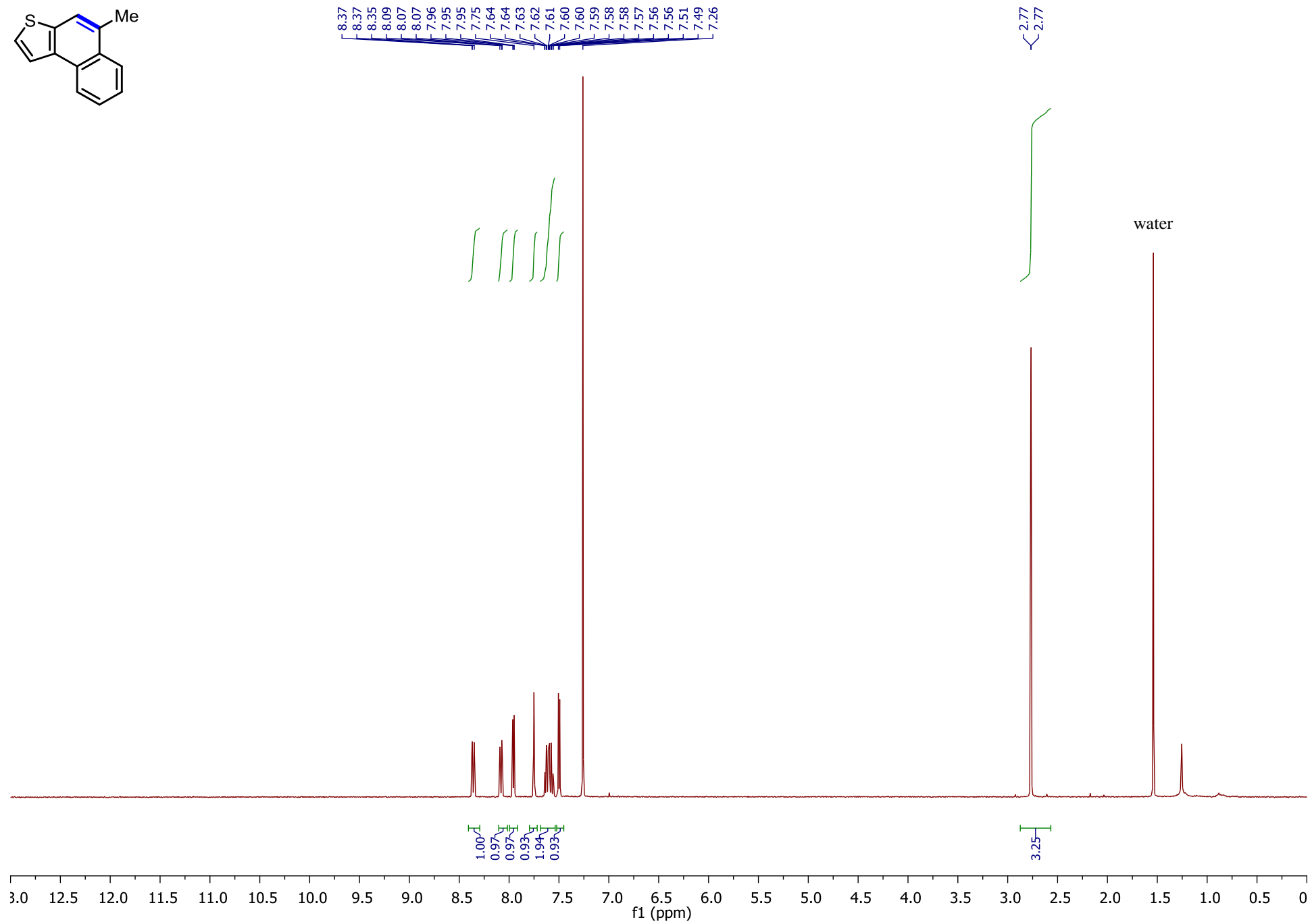
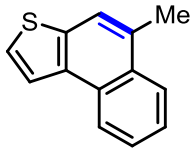






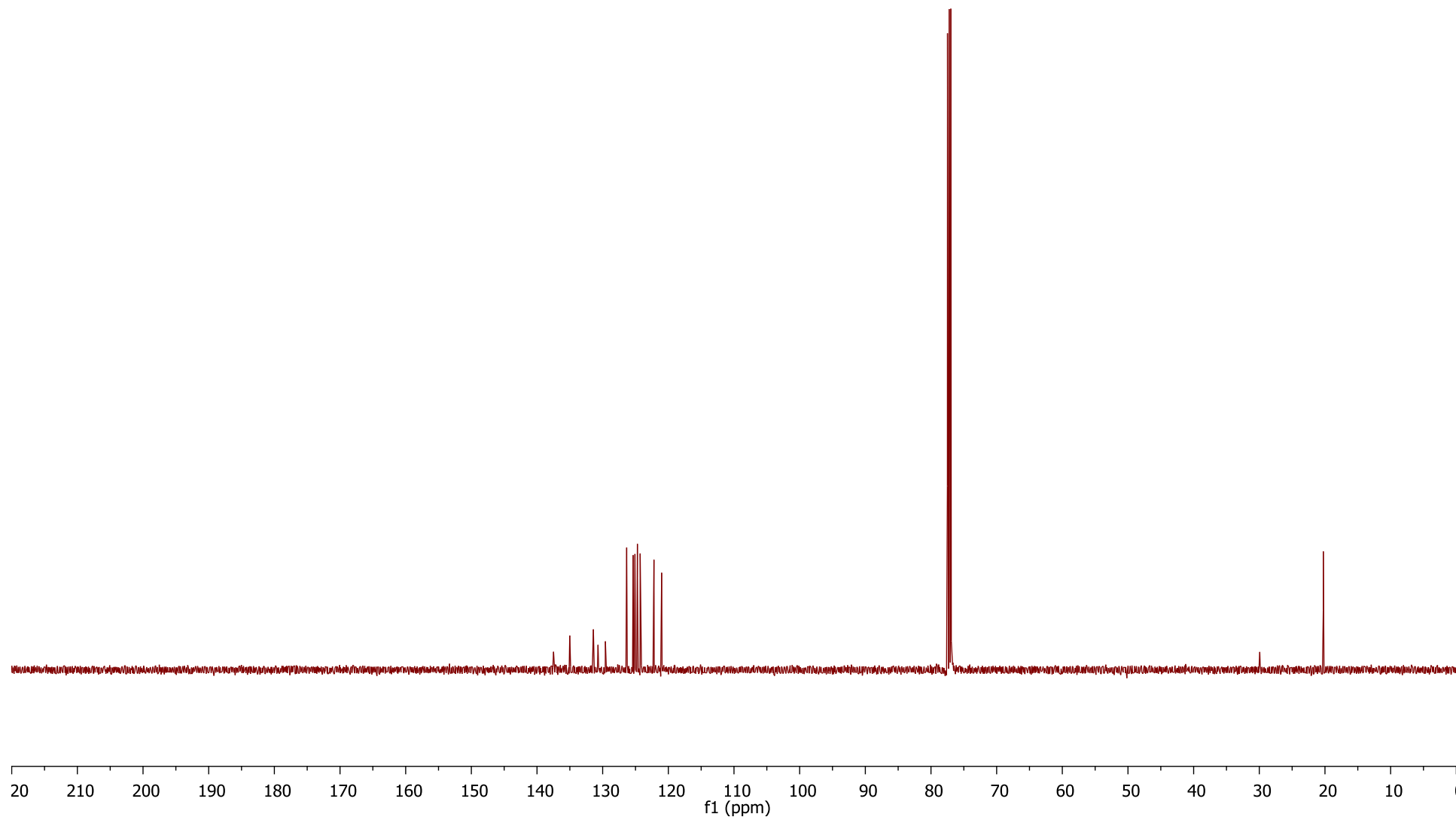


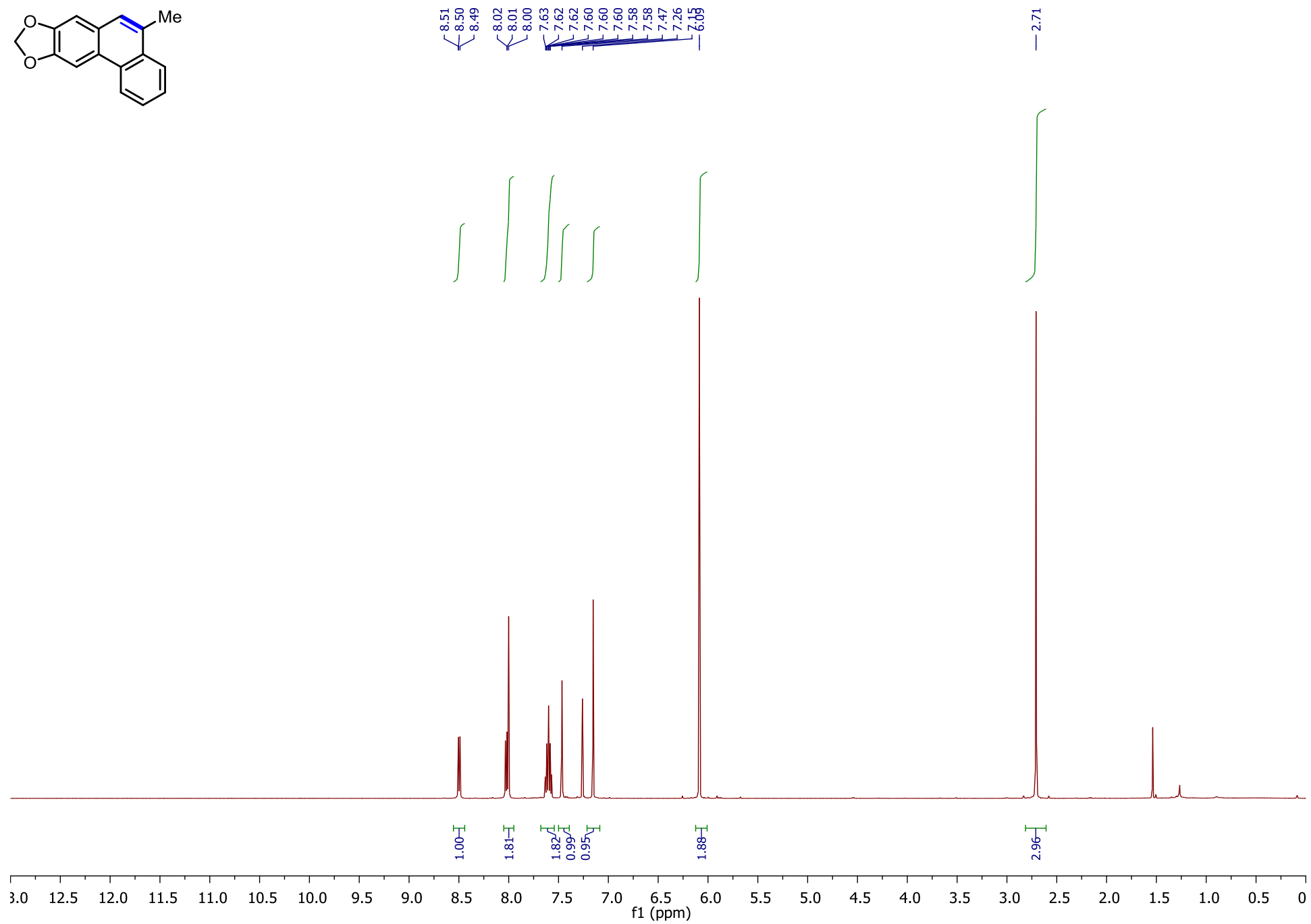
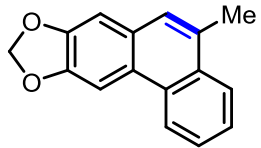


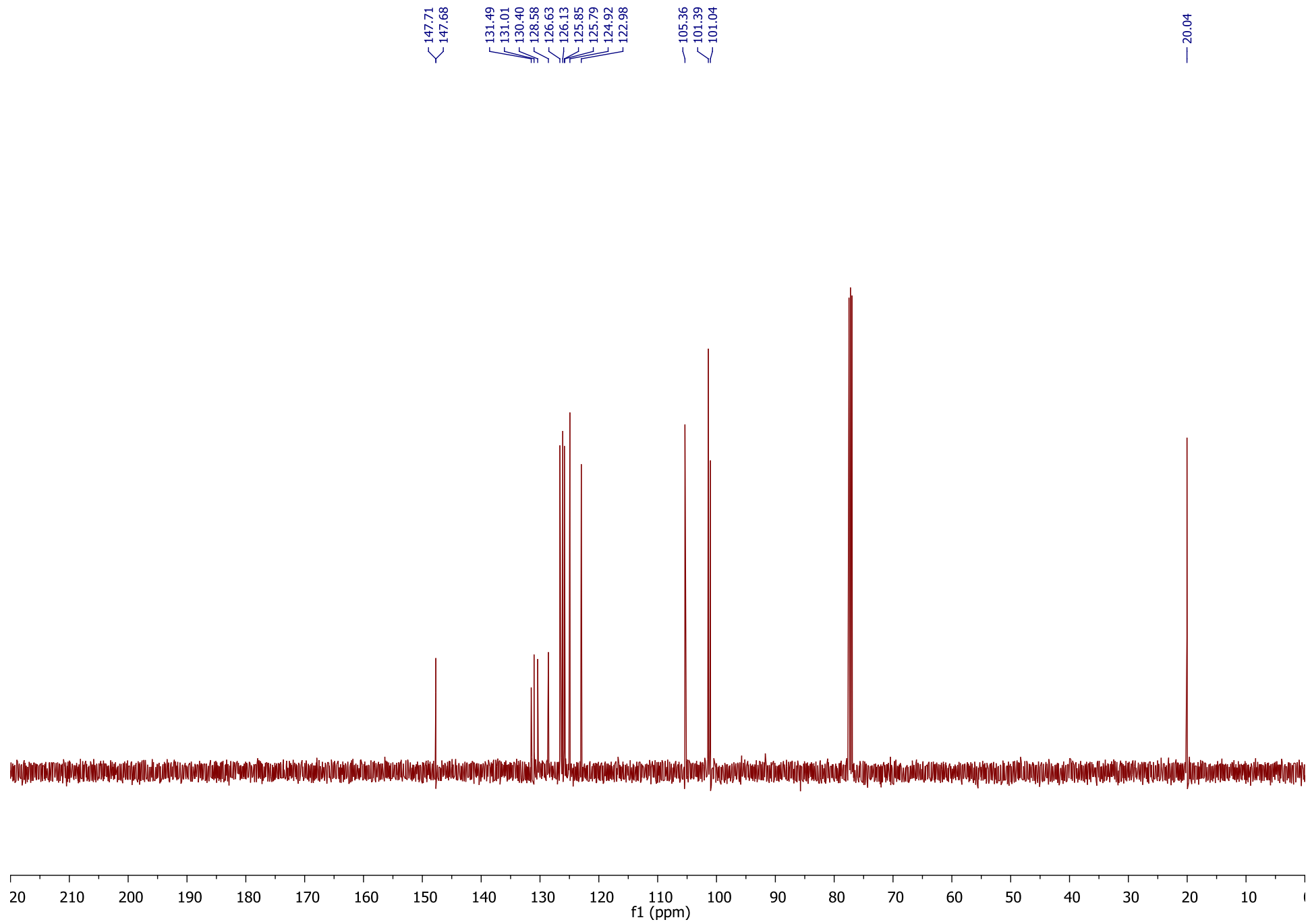


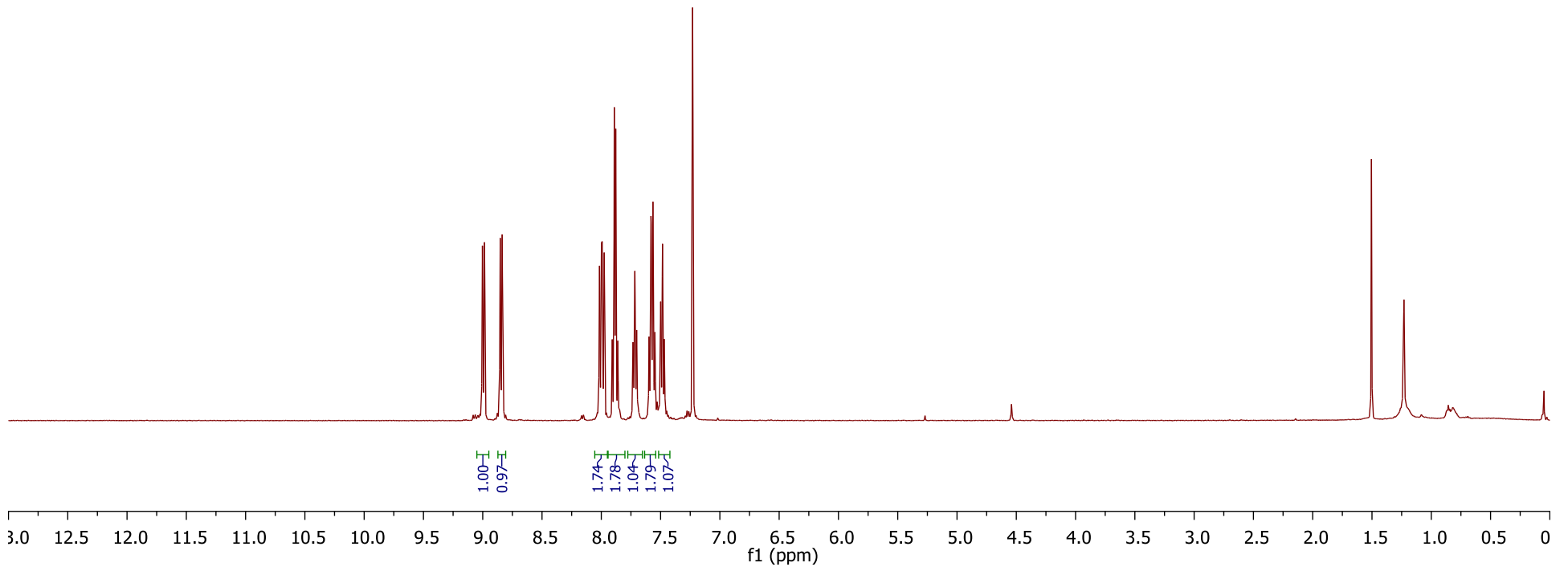
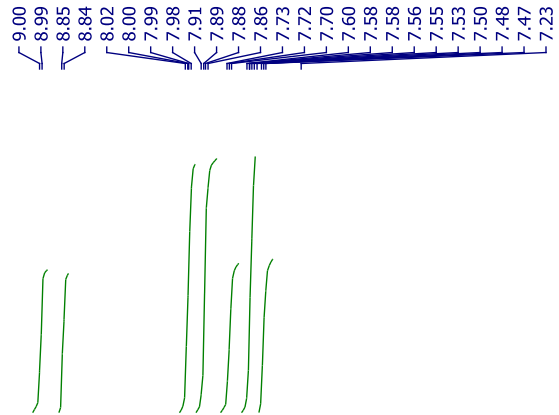
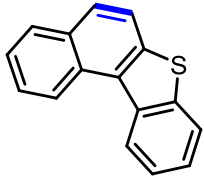
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126.35
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125.09
124.71
124.29
122.19
121.02

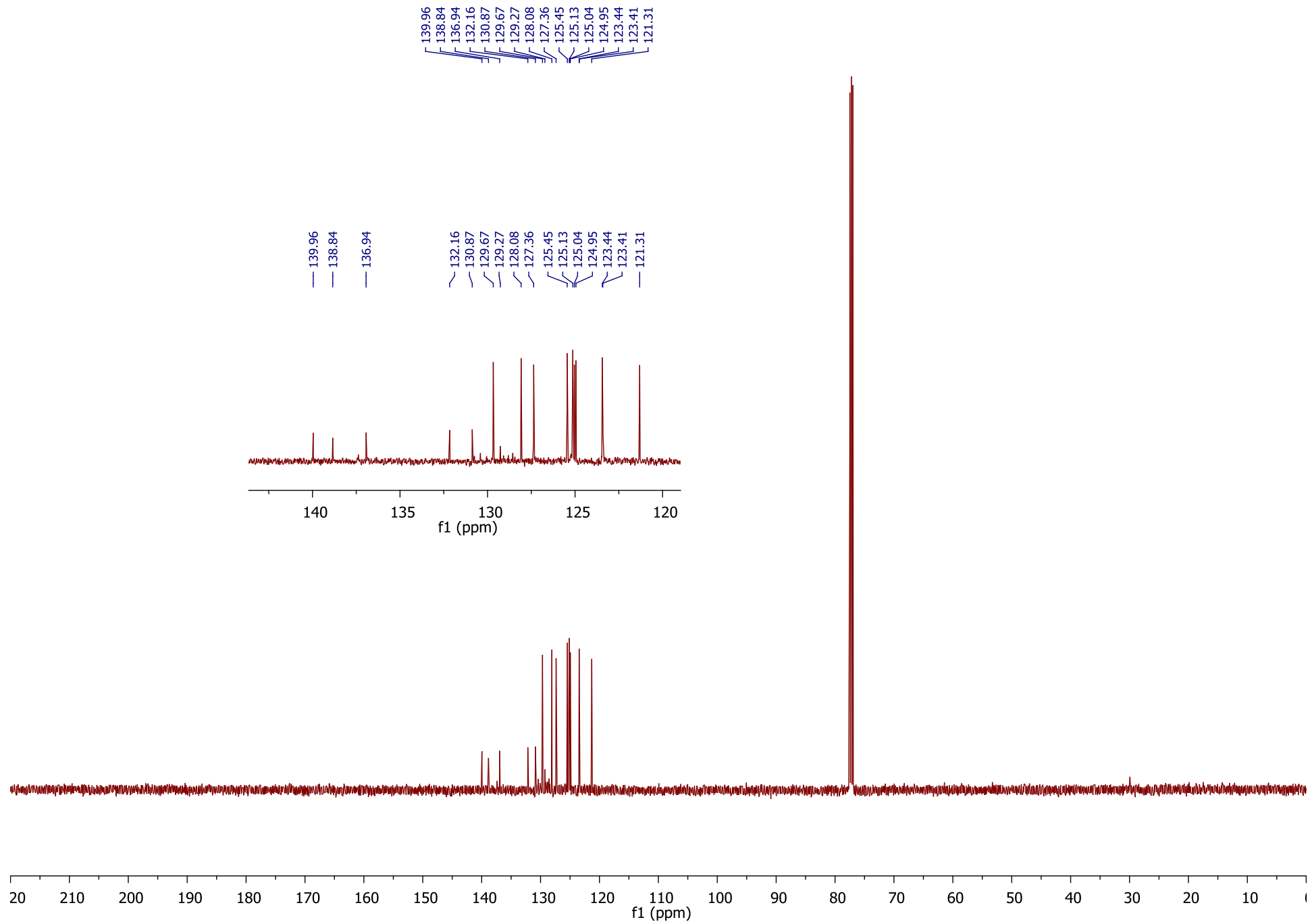
— 20.25

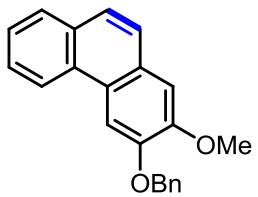








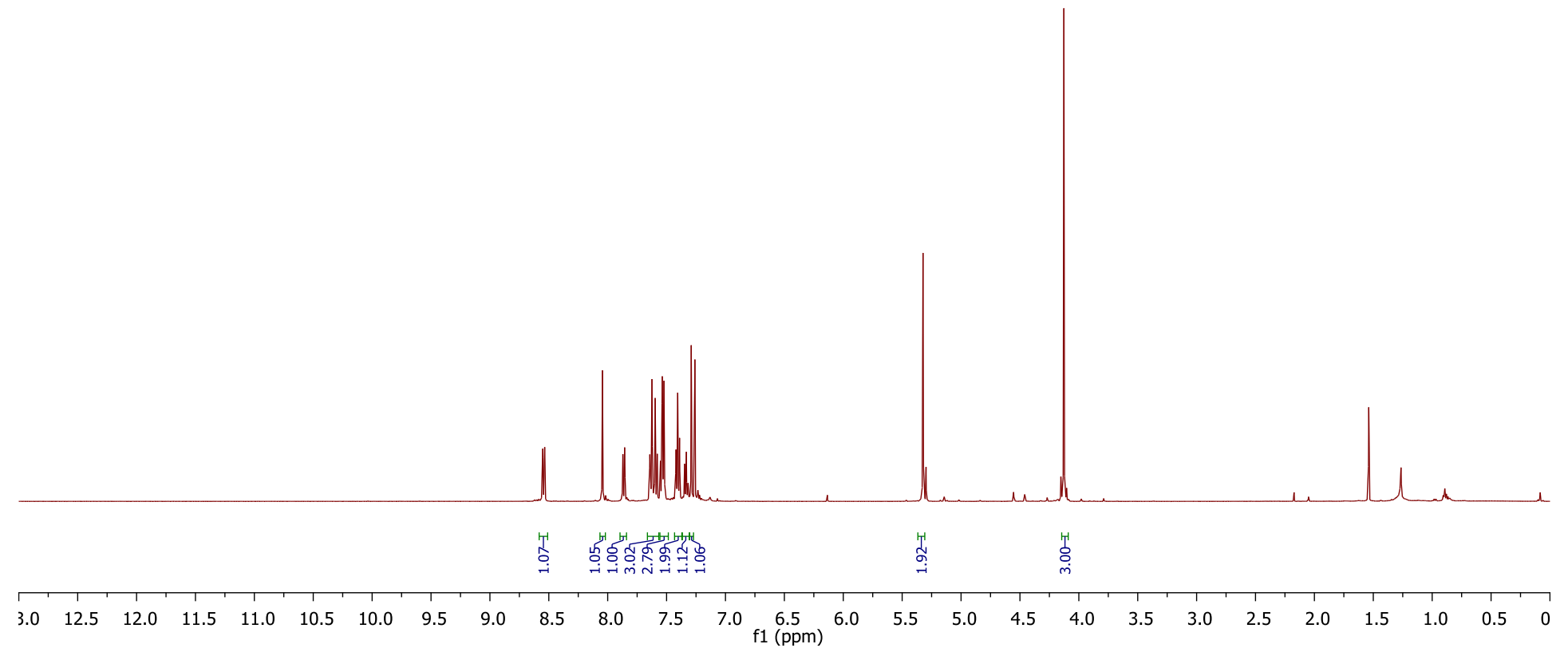


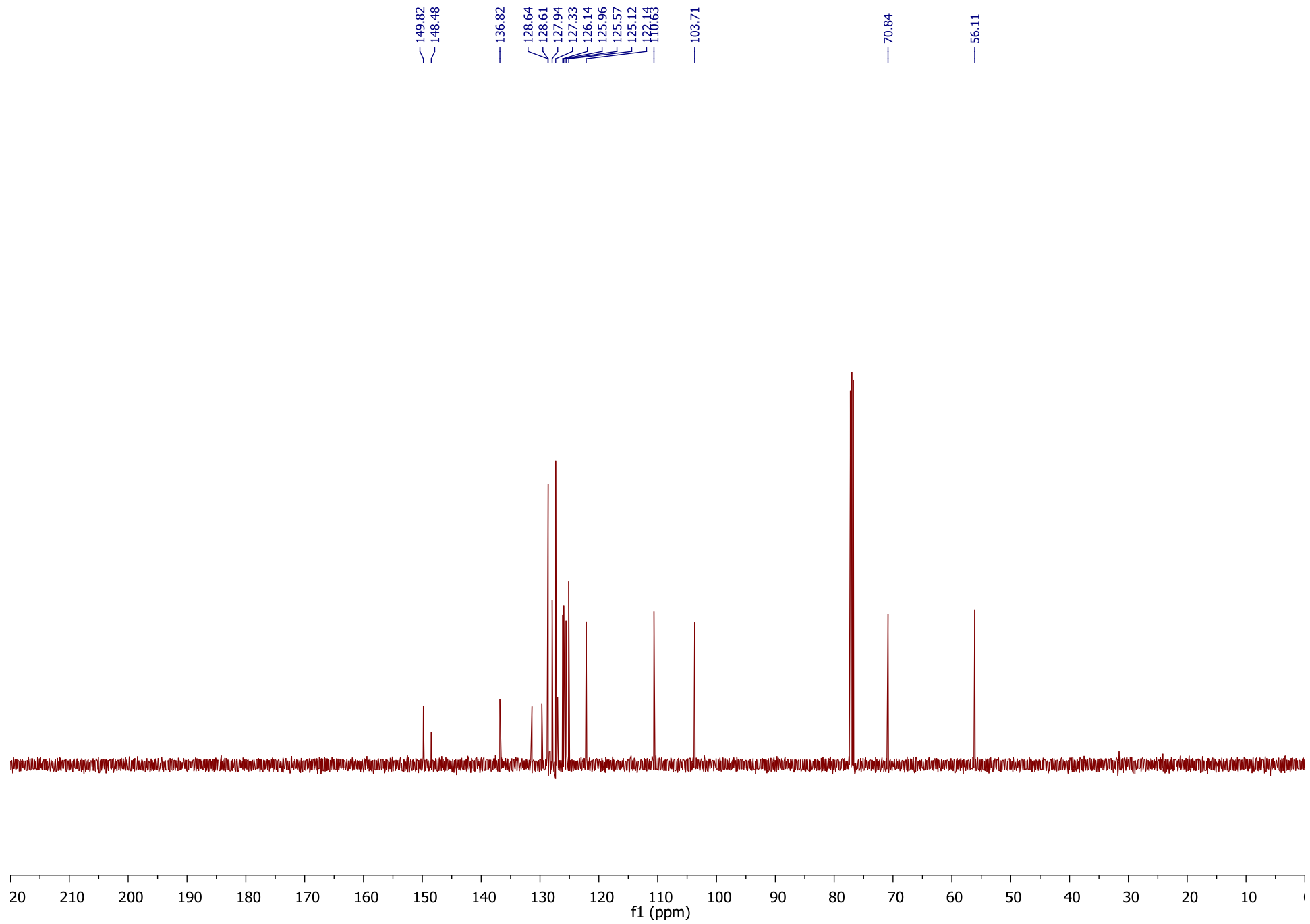


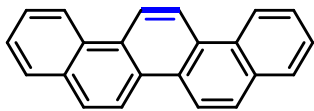
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7.86
7.64
7.62
7.61
7.60
7.58
7.55
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7.52
7.42
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7.35
7.33
7.29
7.26
5.39
4.13



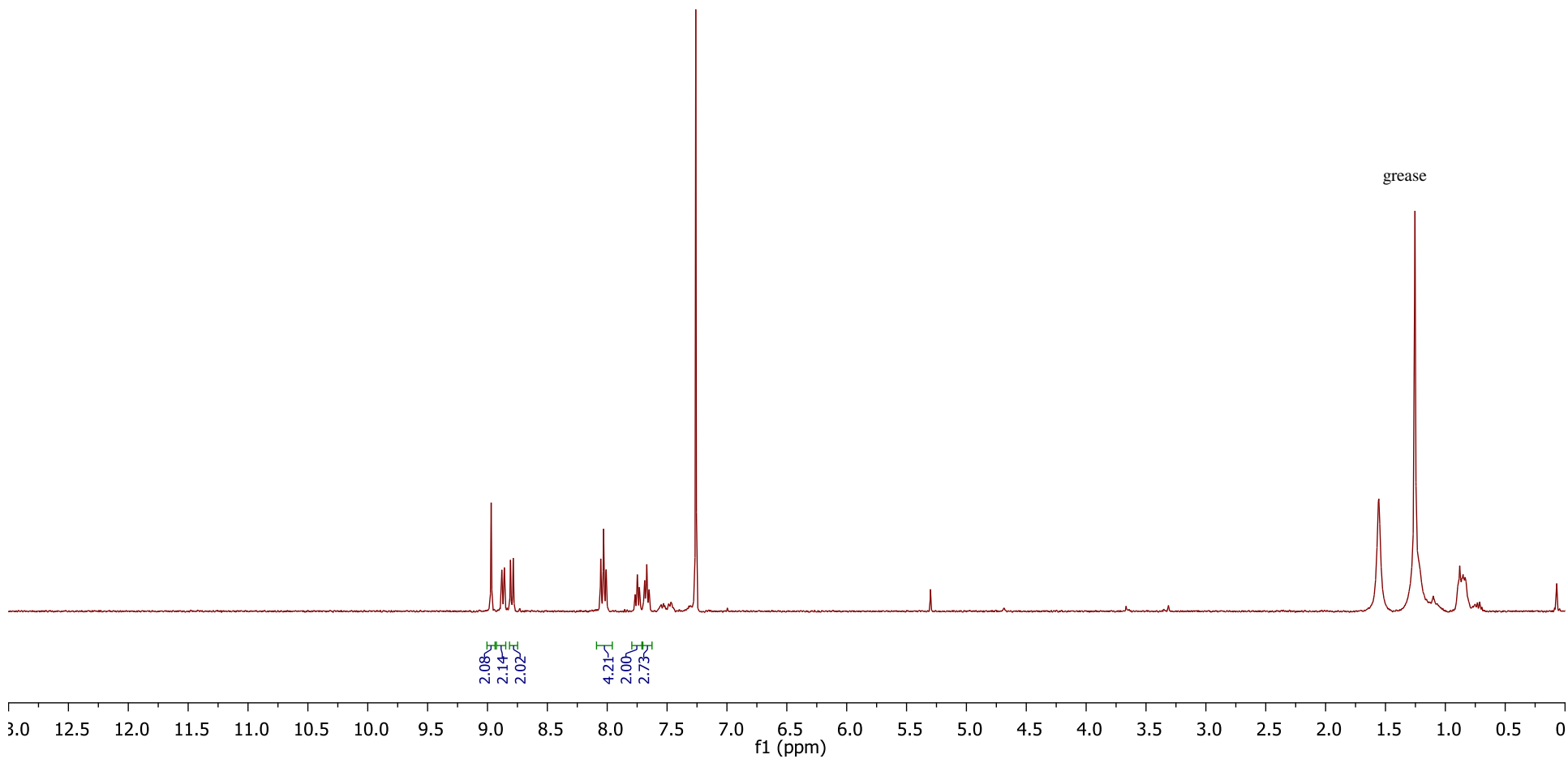
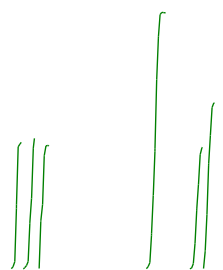
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1.05
1.00
3.02
2.79
1.99
1.12
1.06
1.92
3.00

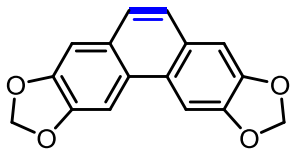






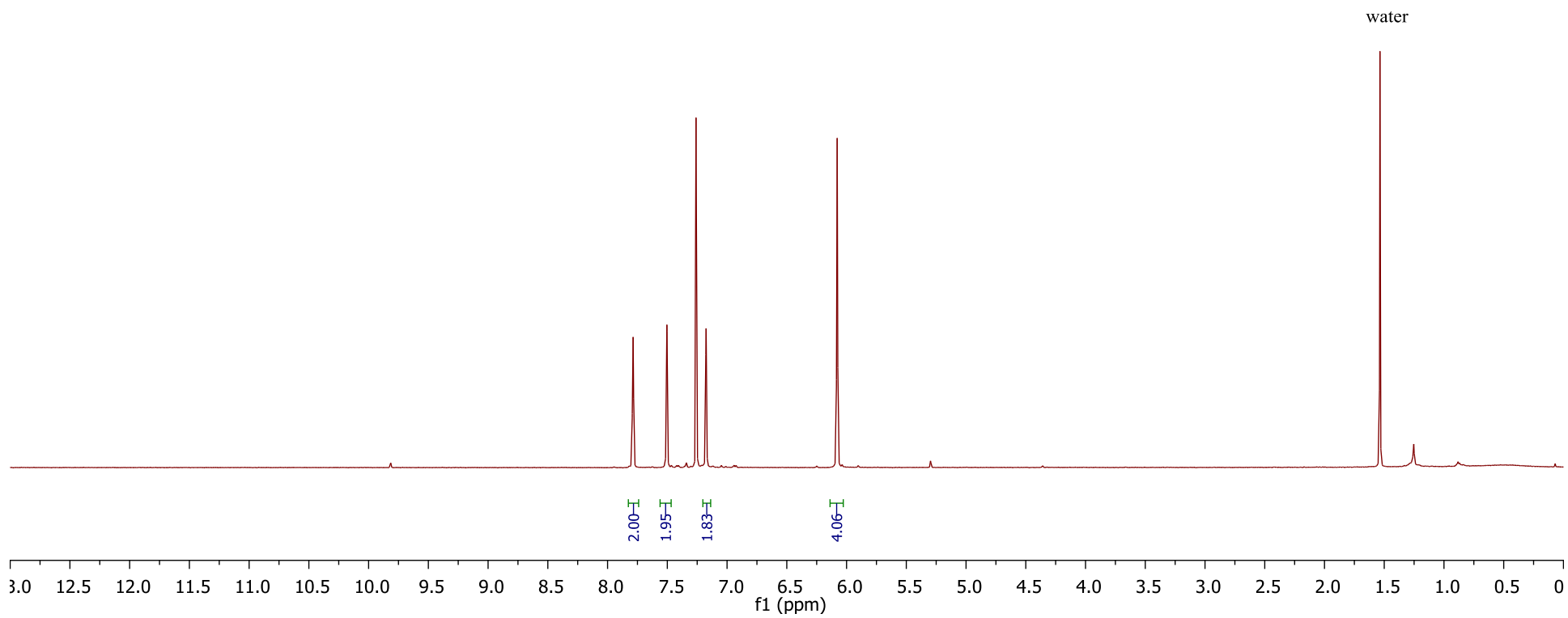
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8.88
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8.05
8.03
8.01
7.75
7.73
7.69
7.56

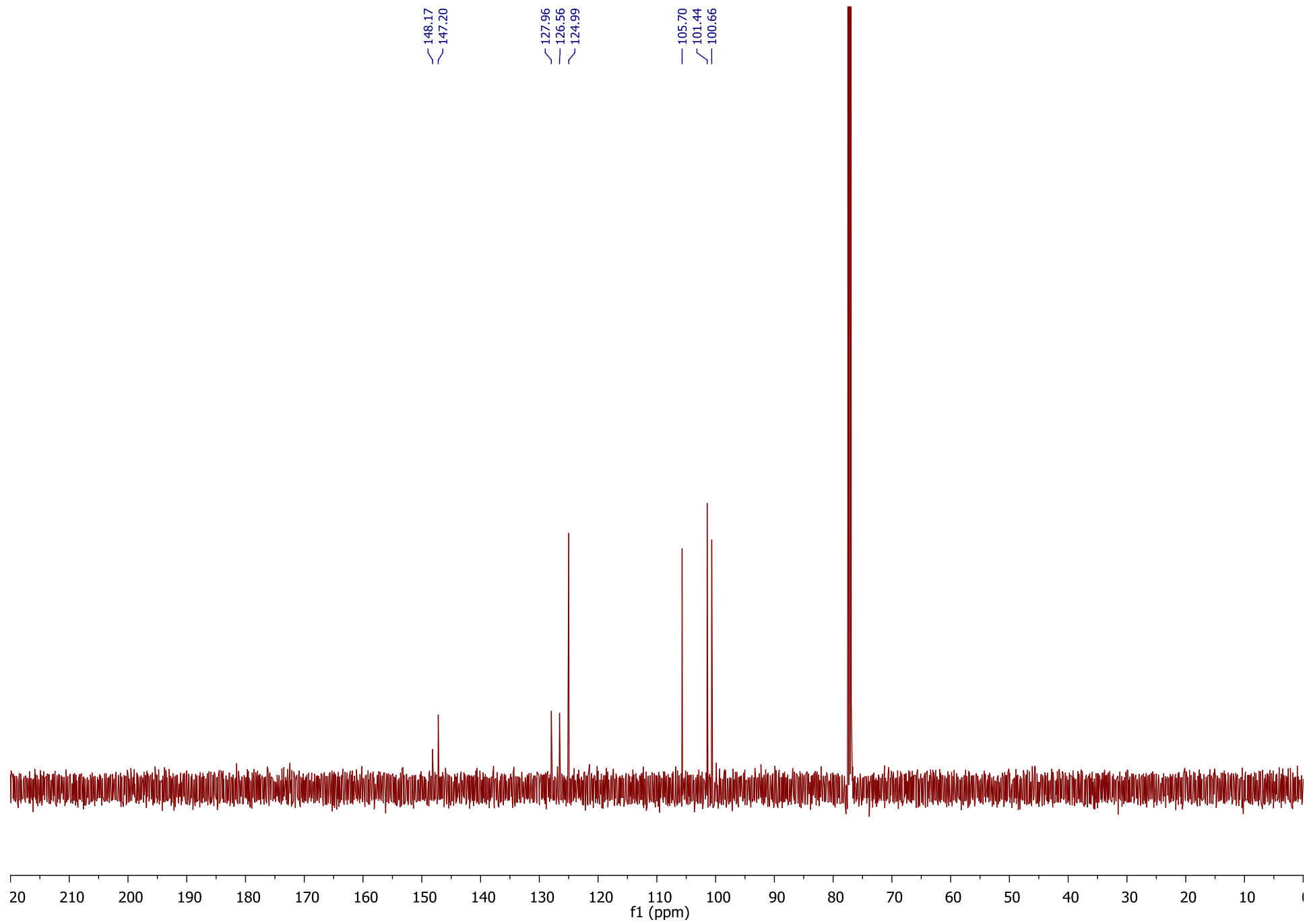


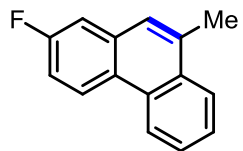


7.79
7.50
7.26
7.18

6.08





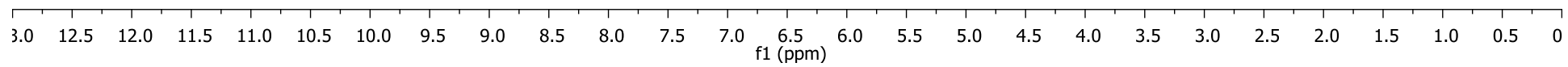


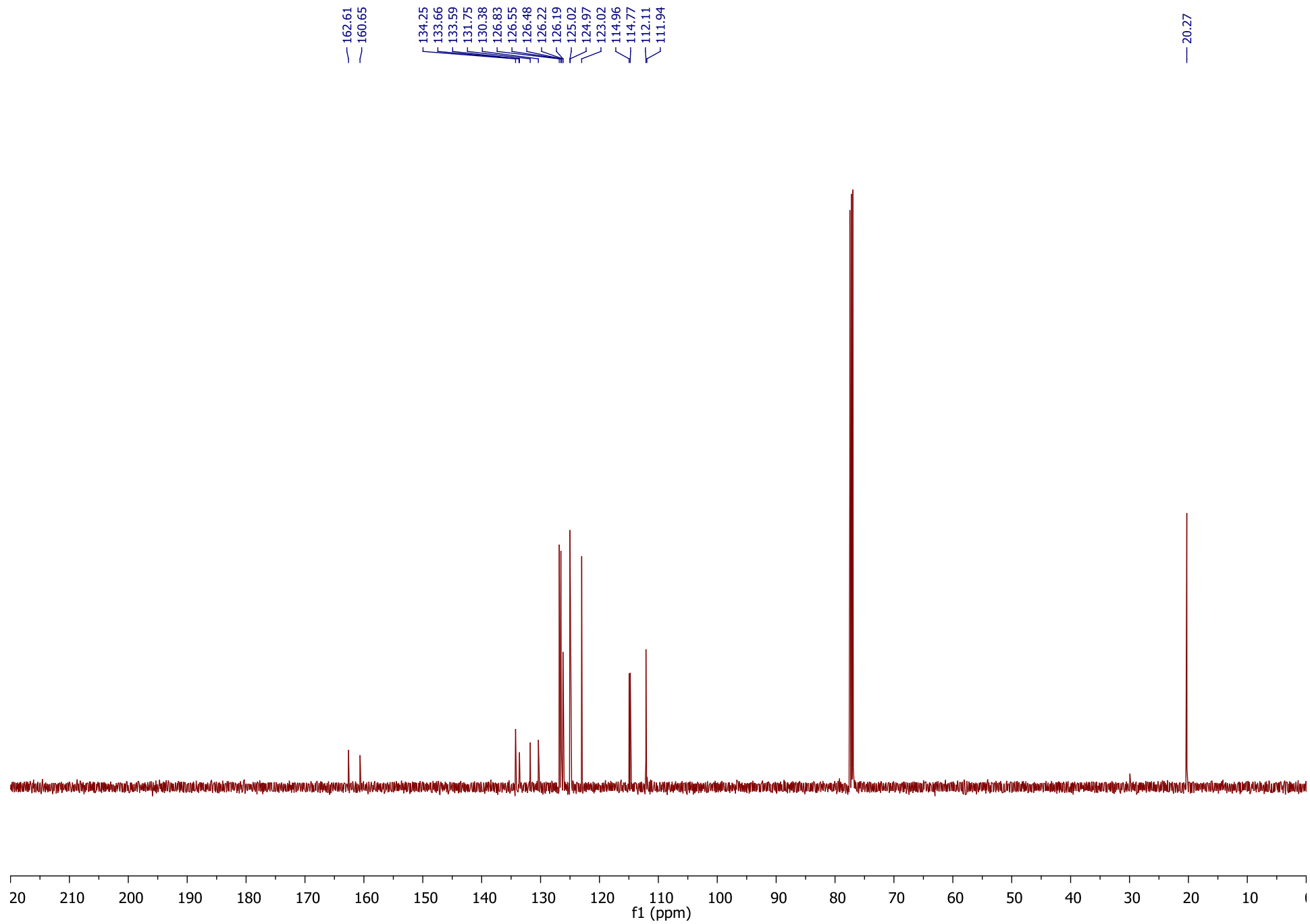
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8.63
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8.61
8.07
8.05
7.69
7.68
7.66
7.66
7.66
7.65
7.64
7.63
7.52
7.45
7.44
7.43
7.42
7.35
7.34
7.33
7.31
7.31
7.26

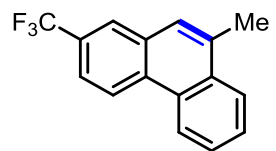
2.74



1.94
0.95
1.82
0.97
0.94
0.93
3.00

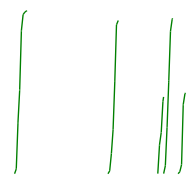






8.74
8.73
8.11
8.10
8.10
8.09
7.74
7.73
7.71
7.63

2.76



2.00

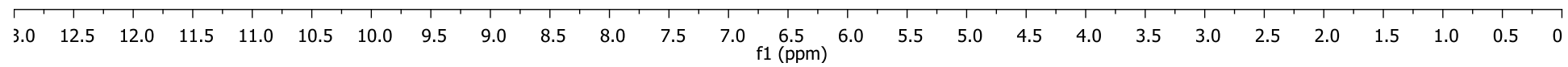
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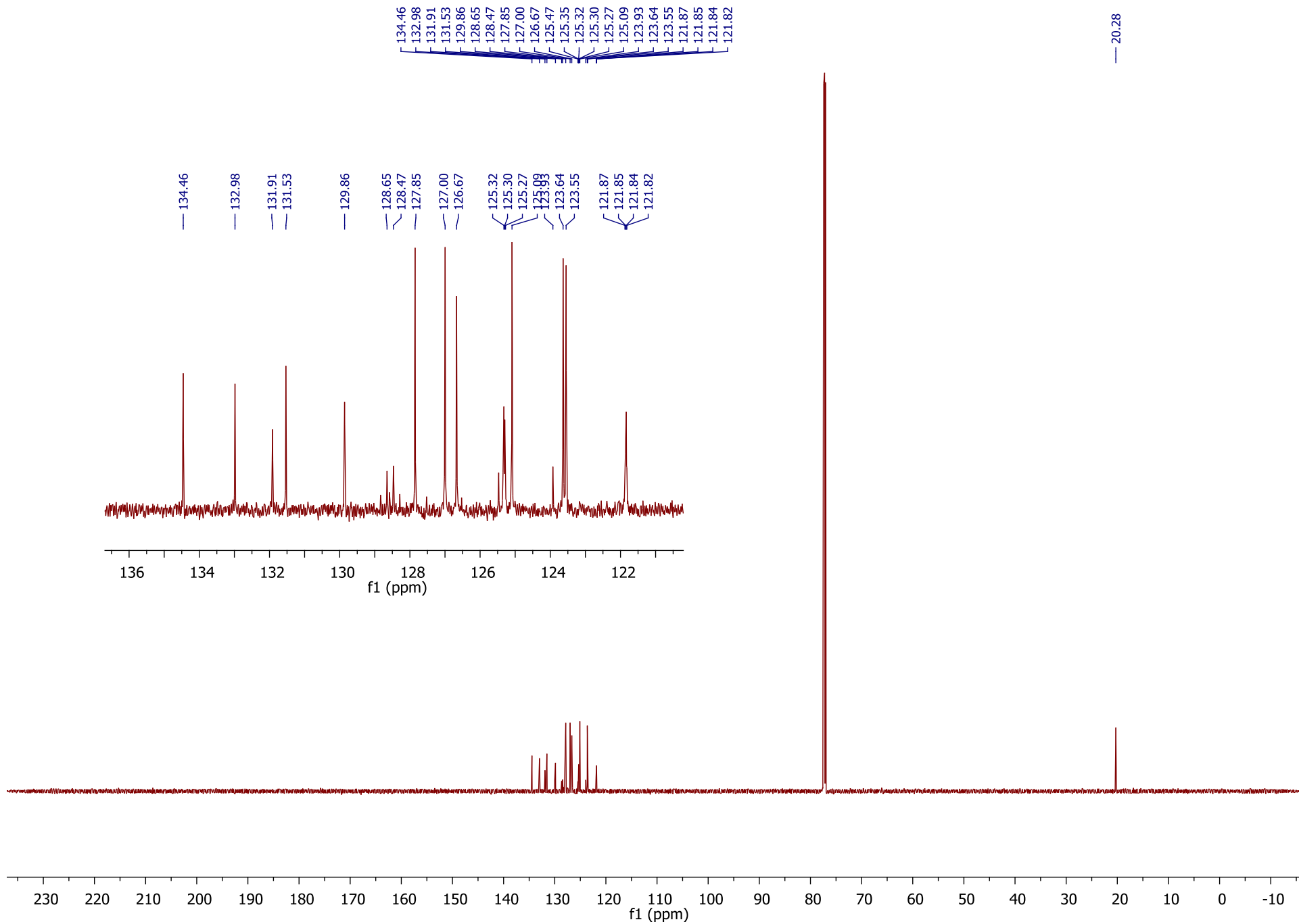
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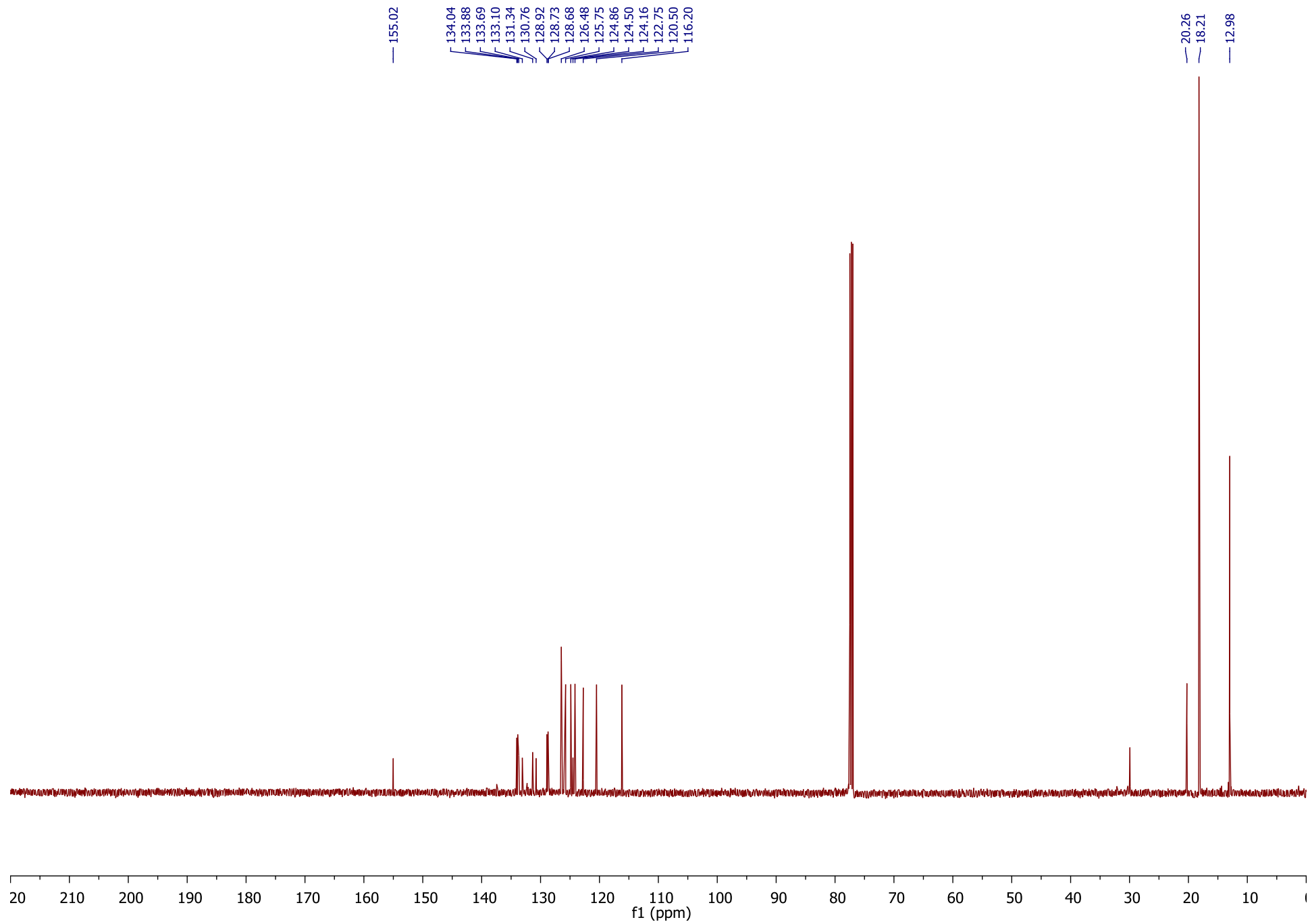
1.91

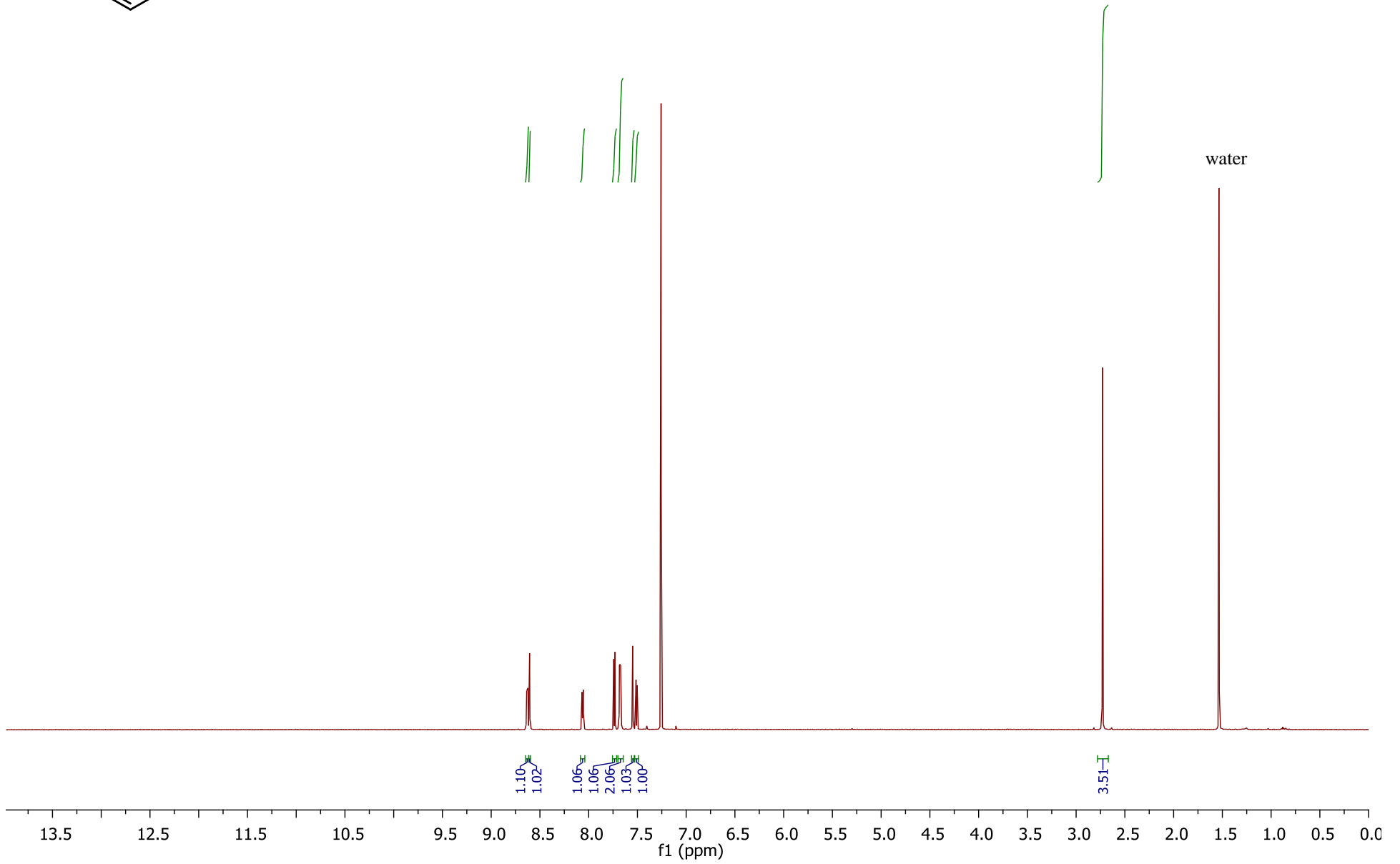
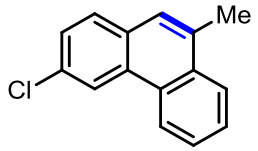
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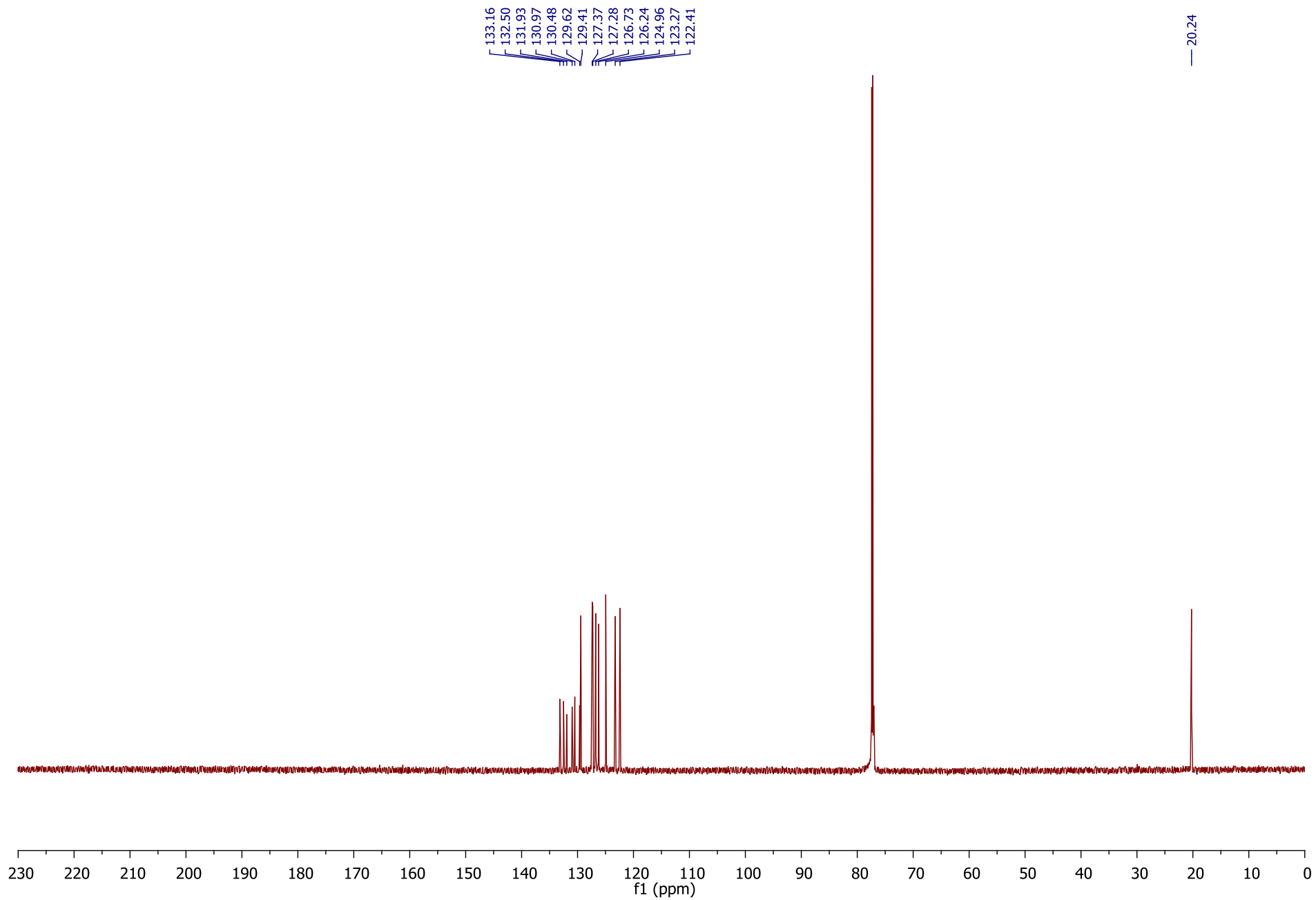
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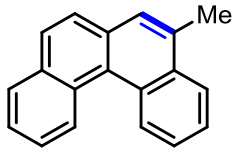






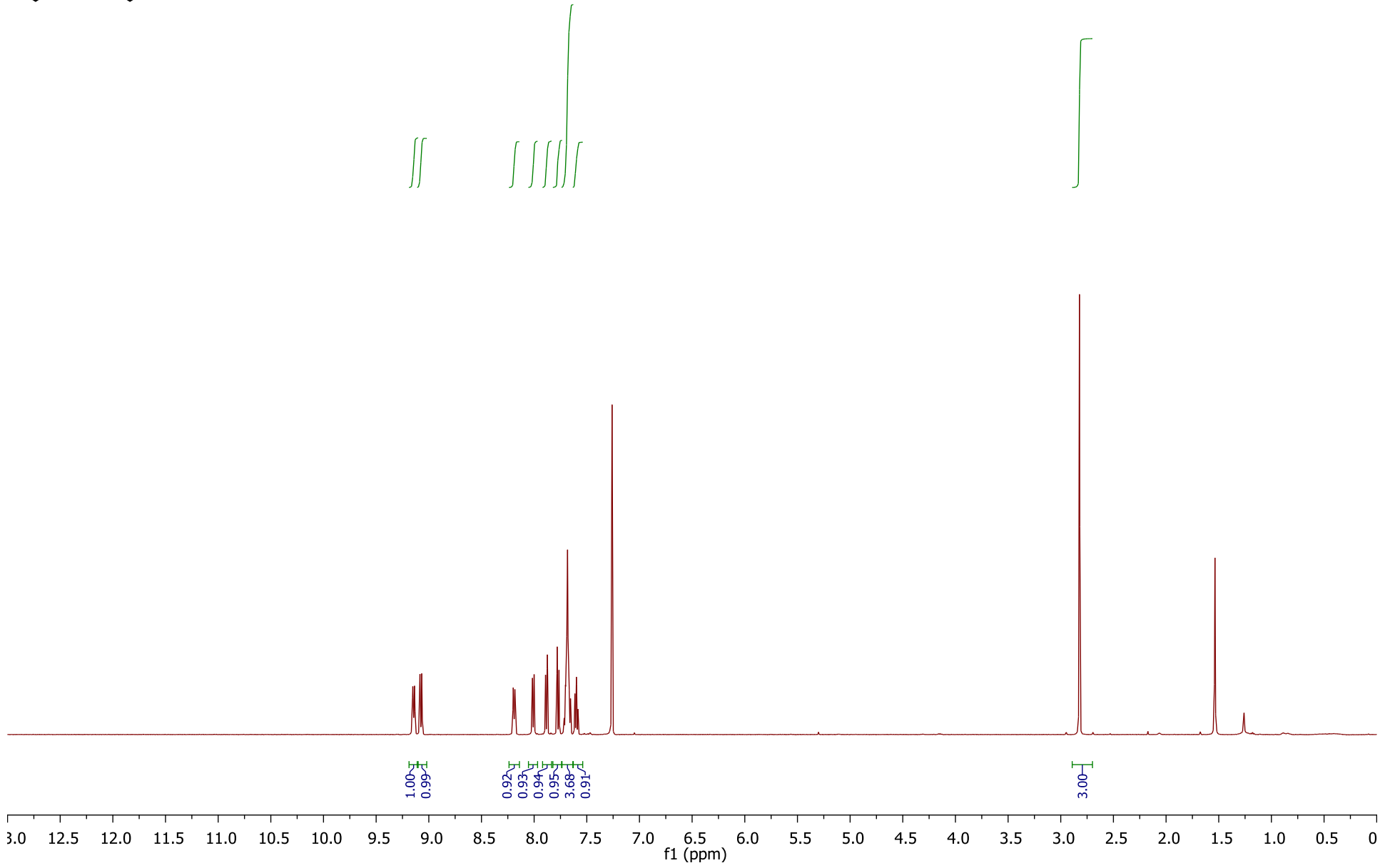


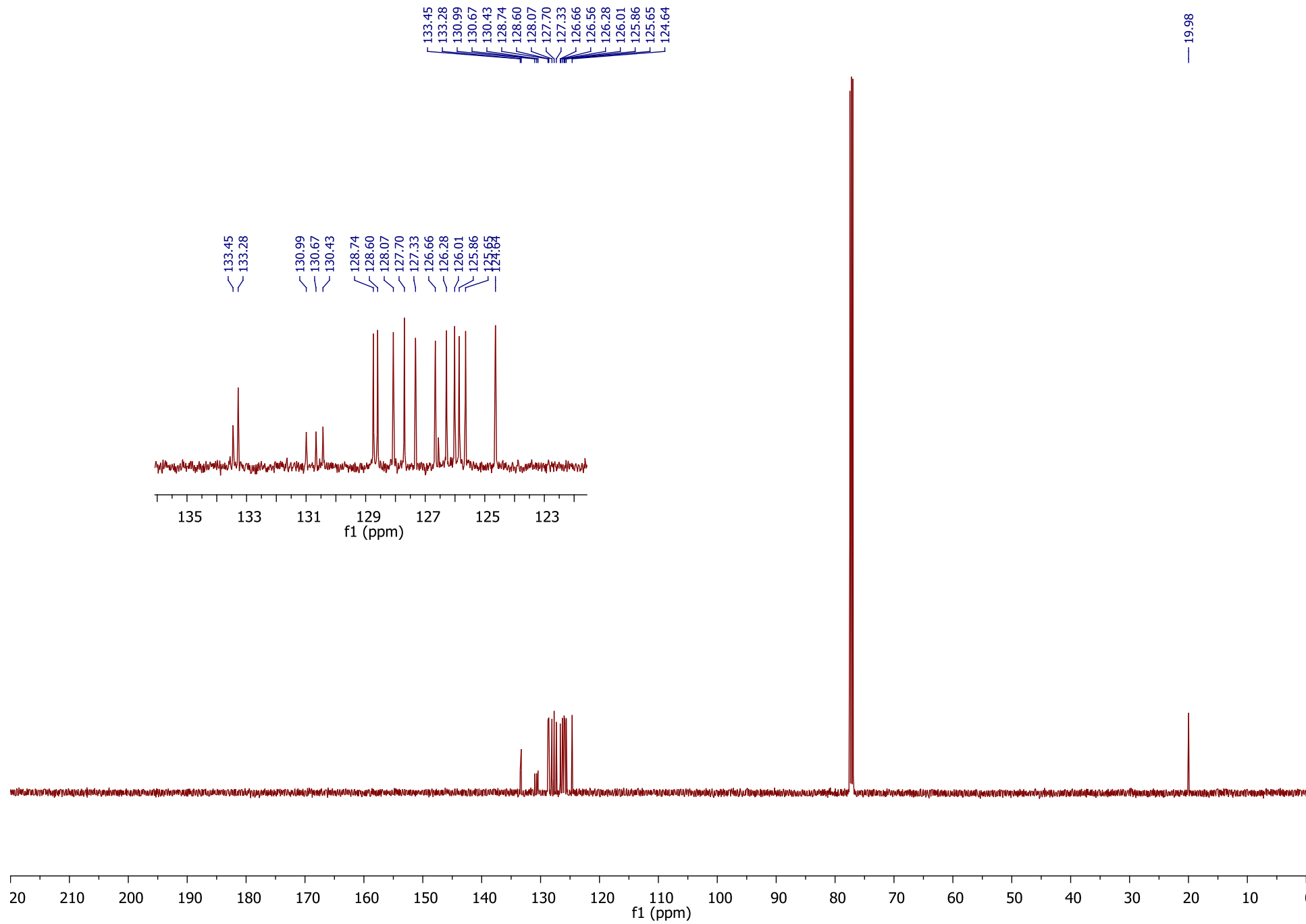


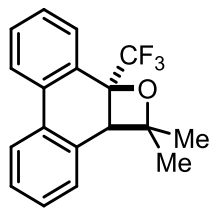


9.15
9.14
9.08
9.07
8.00
7.89
7.87
7.78
7.76
7.69
7.68
7.67
7.58

2.82





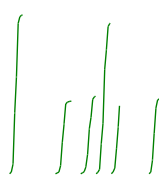


7.99
7.98
7.97
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7.50
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7.48
7.46
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7.28
7.26
7.04
7.02

4.34

1.66

1.02

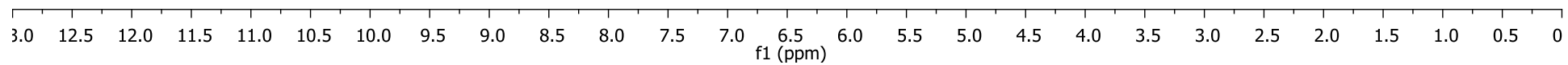


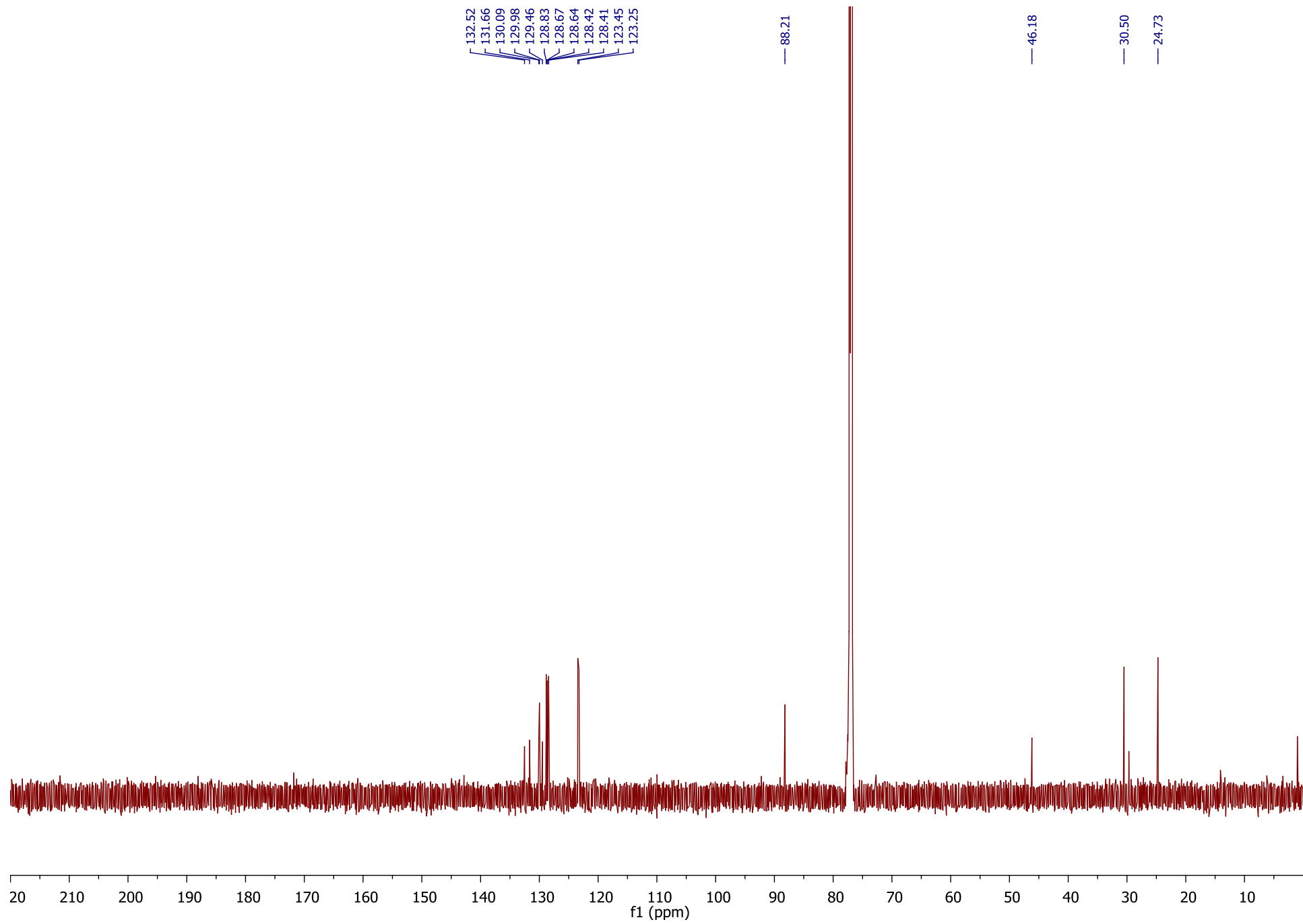
2.00
0.91
0.98
1.90
0.86
0.94

0.98

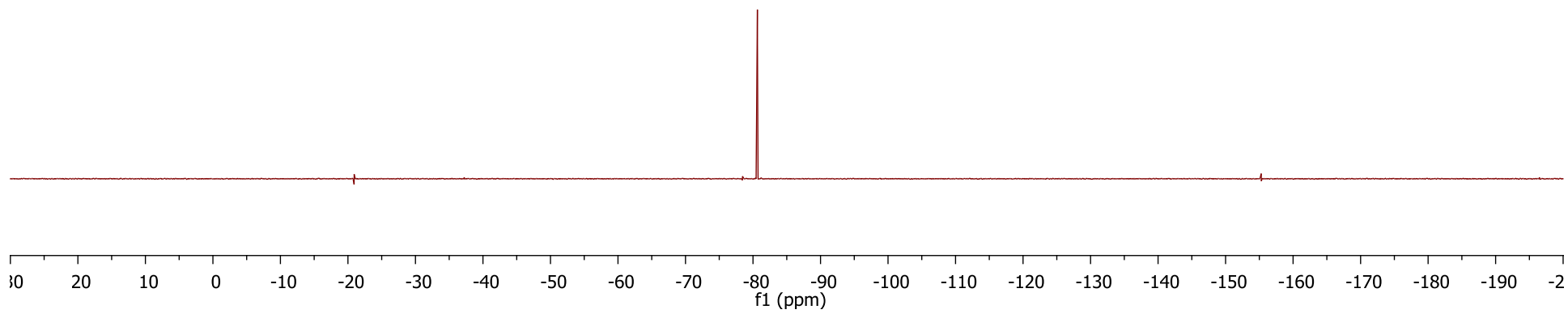
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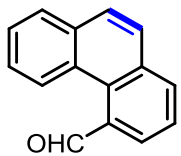
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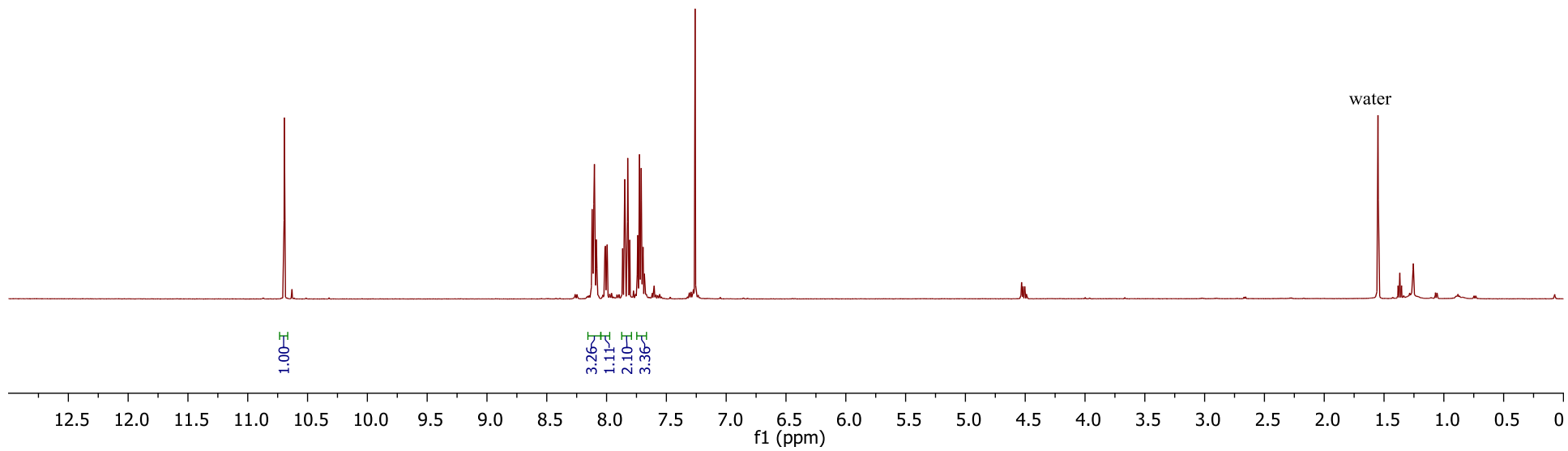


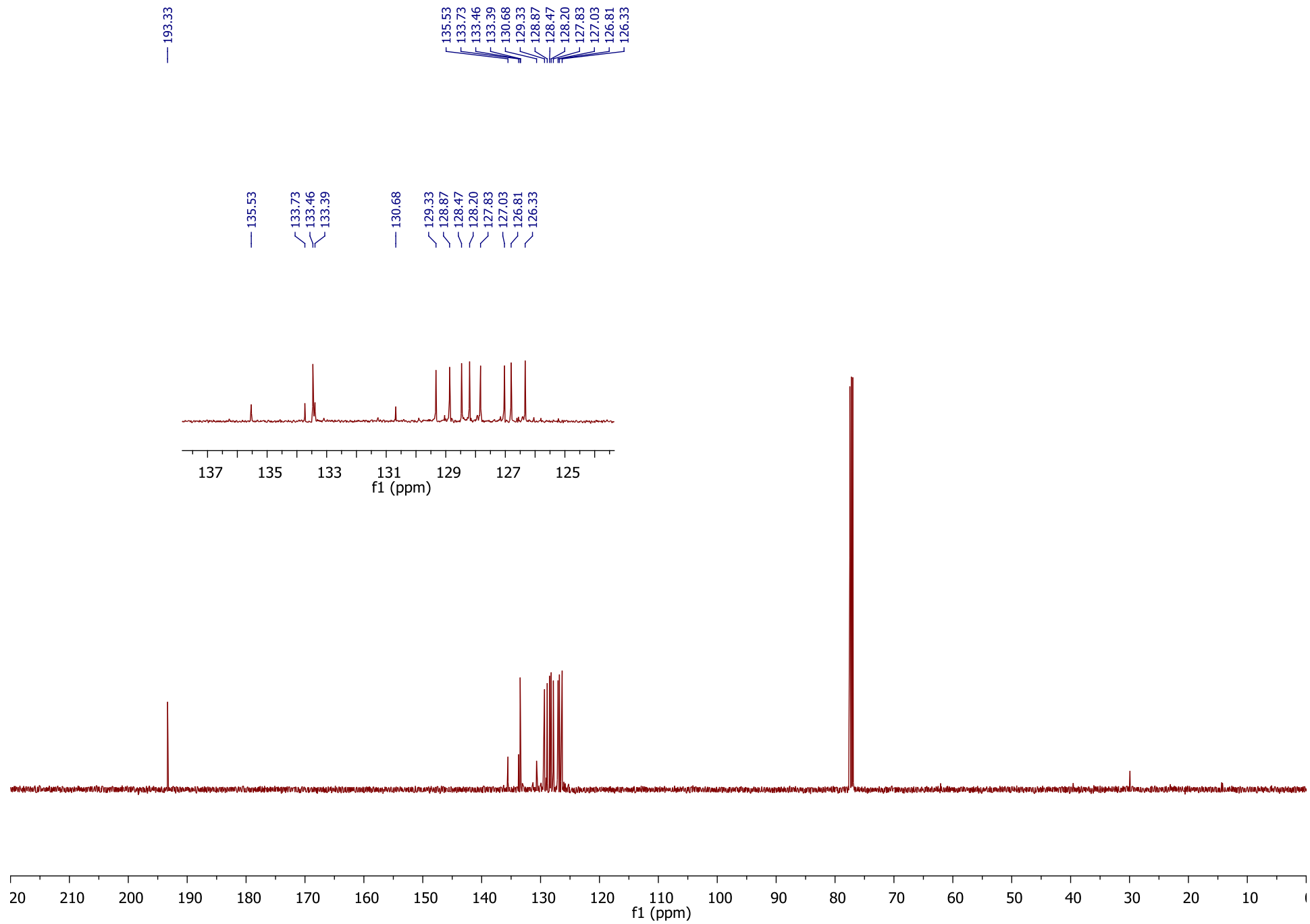
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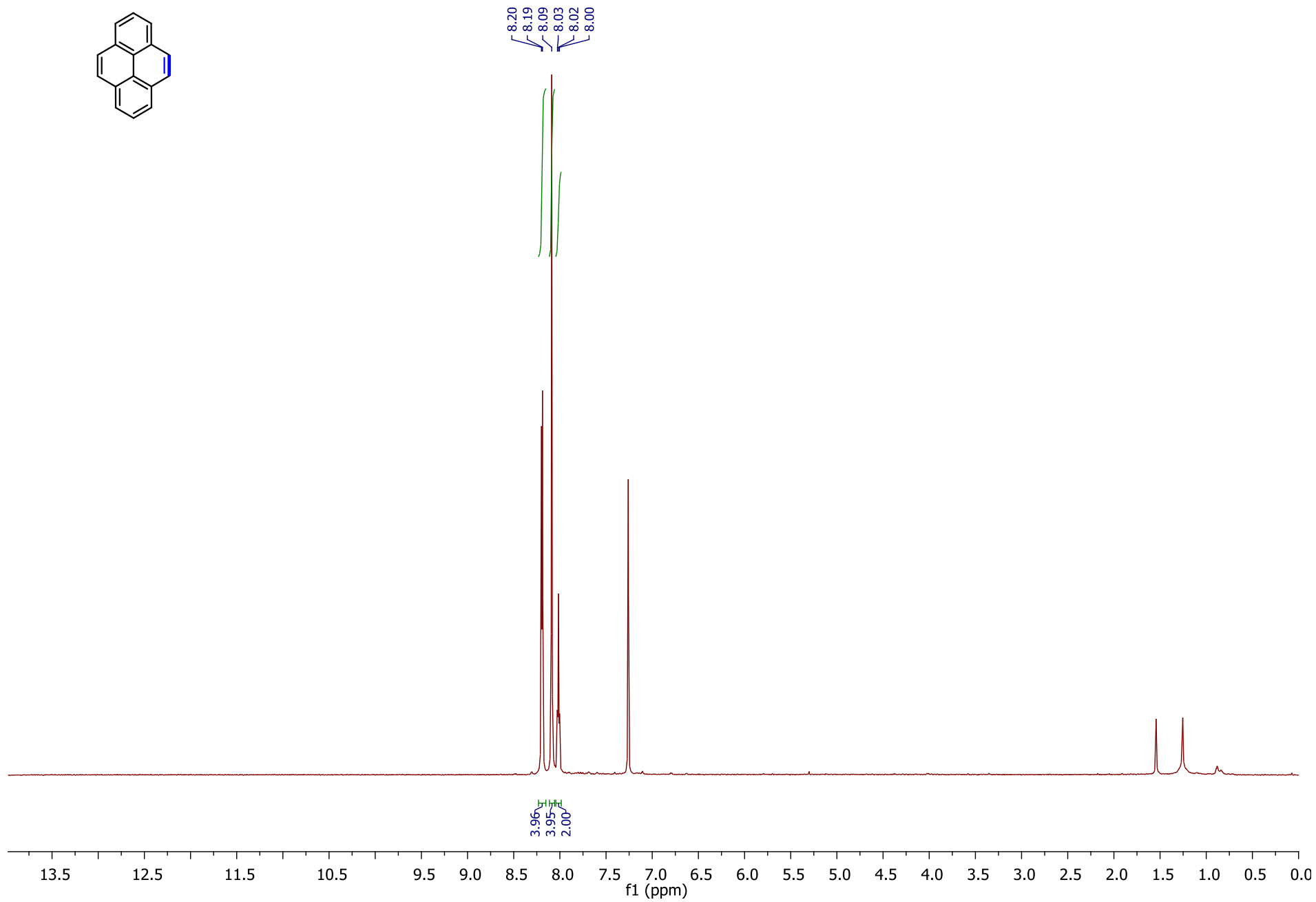
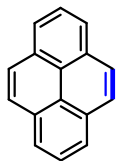


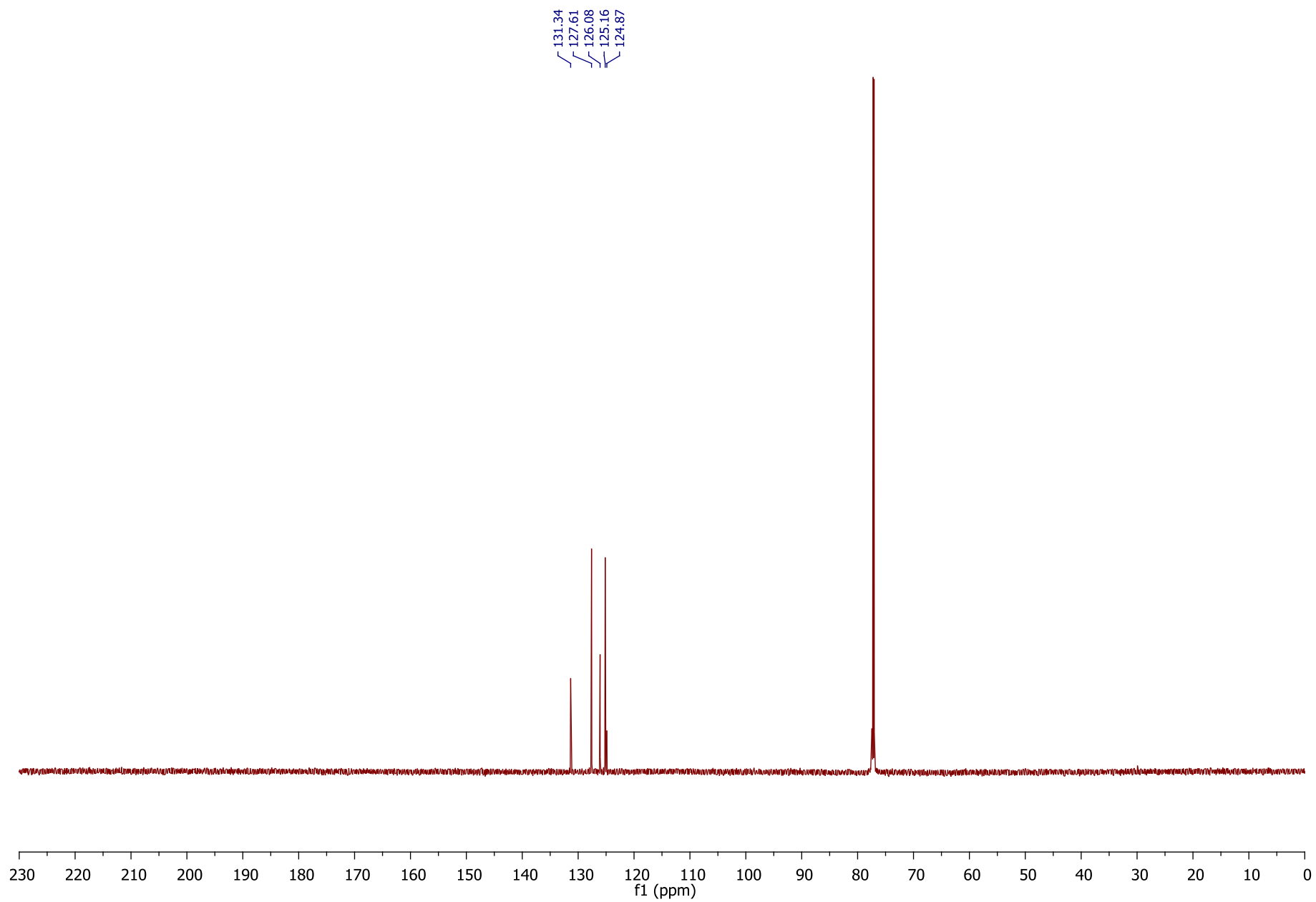


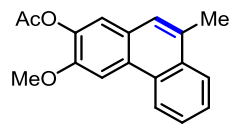
10.69
8.12
8.11
8.10
8.09
8.08
8.01
8.01
7.99
7.87
7.85
7.82
7.81
7.74
7.74
7.73
7.71
7.71
7.70
7.69
7.68
7.68







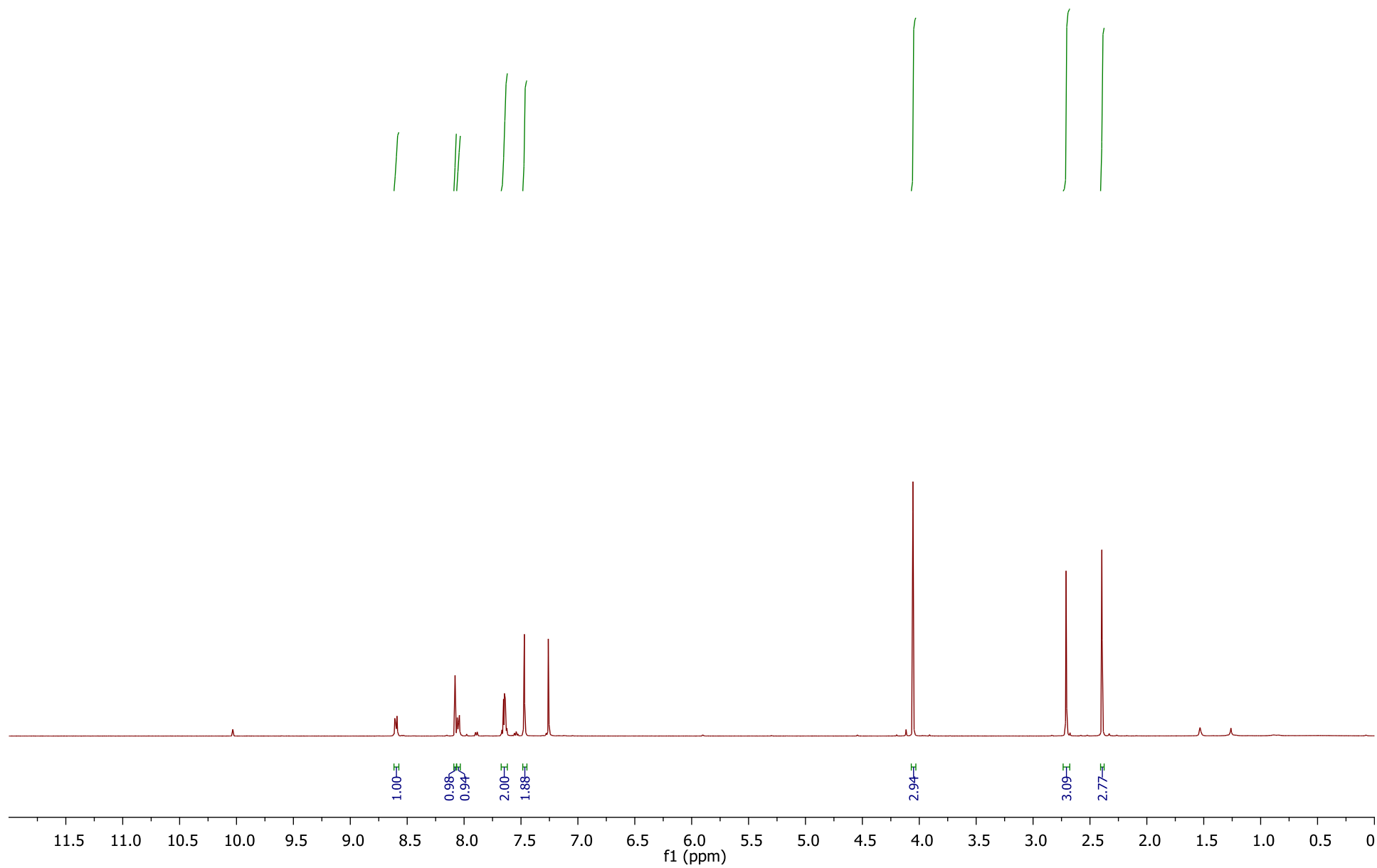


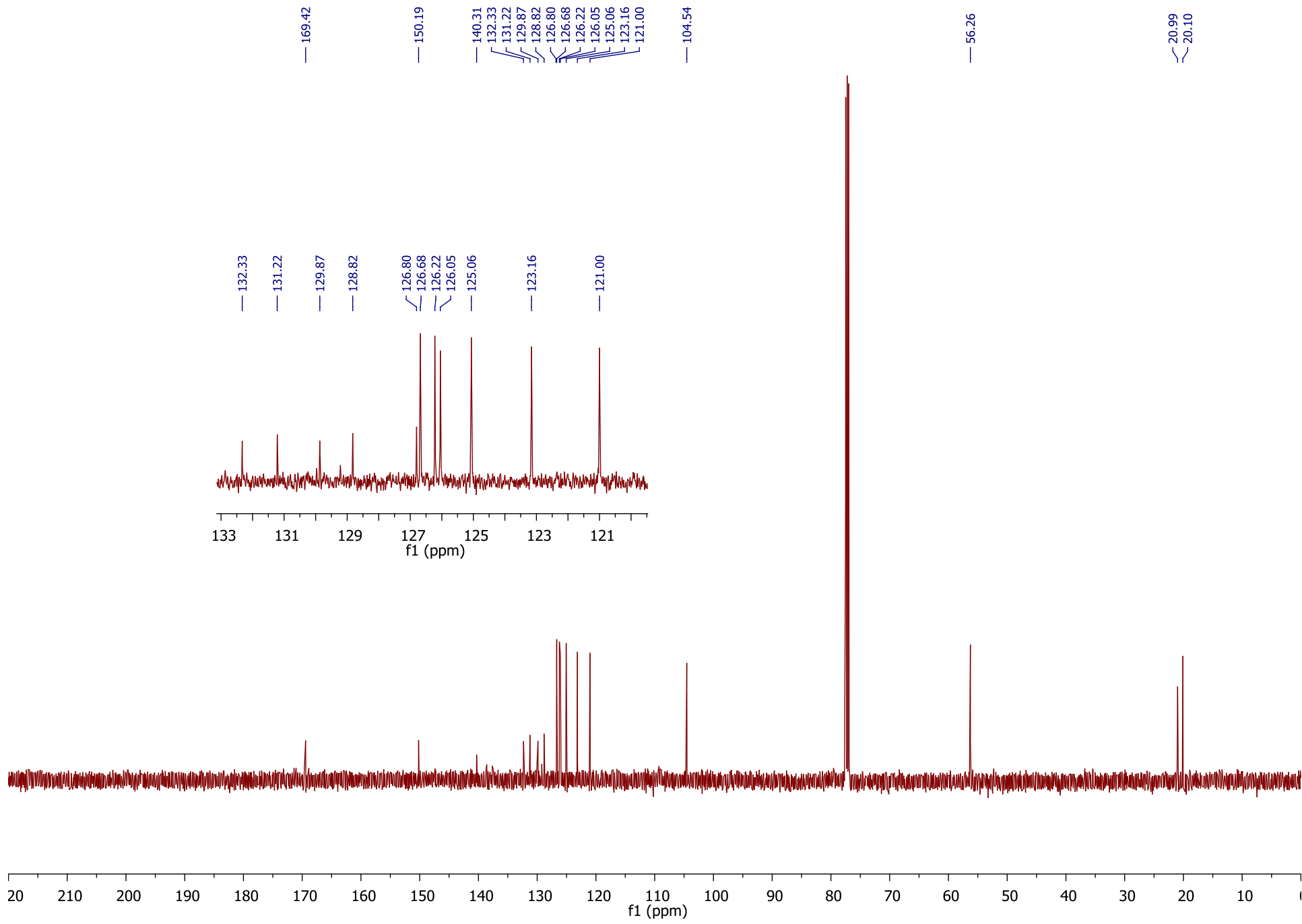


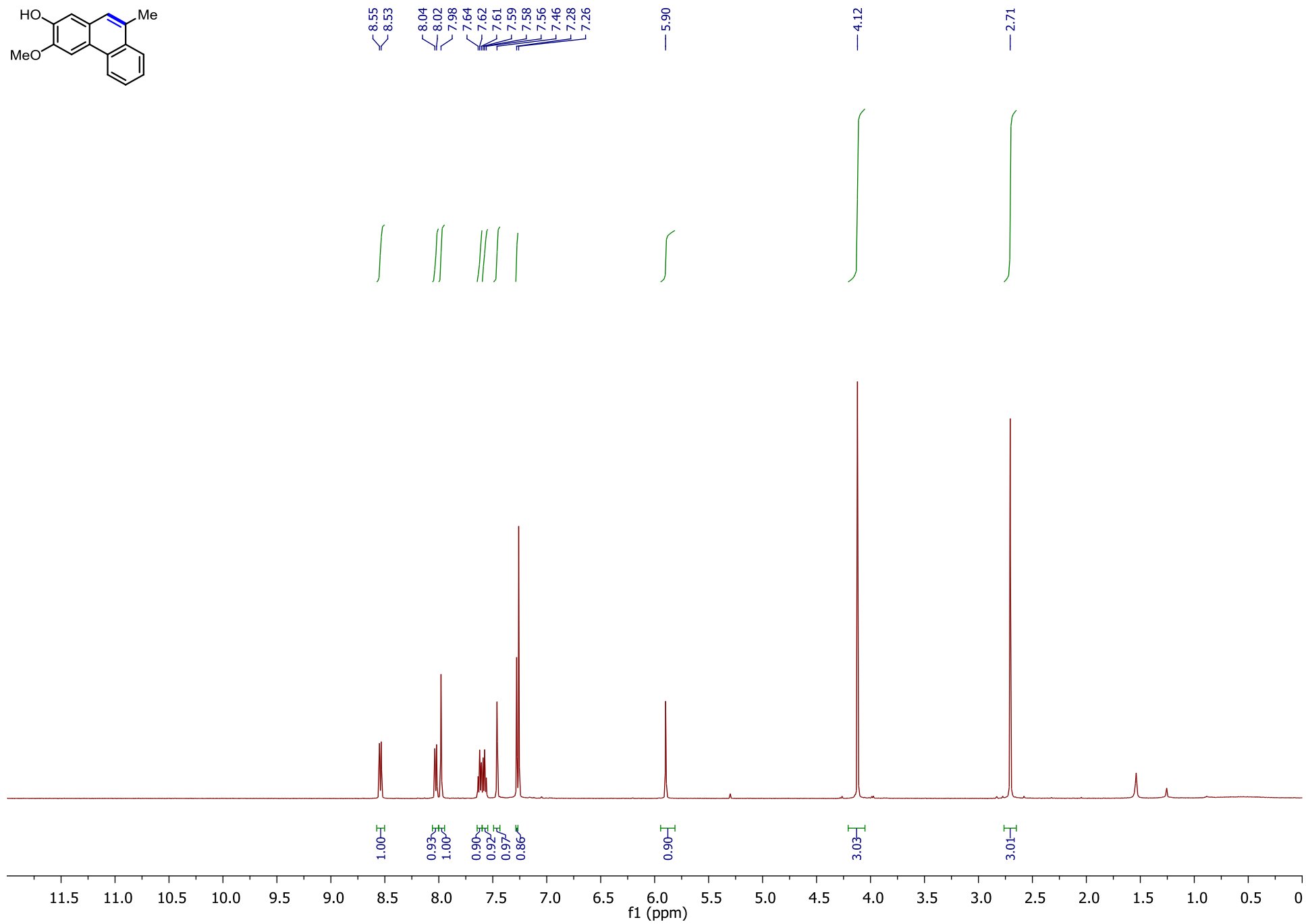
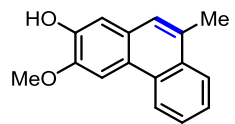
8.61
8.60
8.60
8.59
8.08
8.06
8.04
7.87
7.66
7.65
7.65
7.64
7.63
7.62
7.47
7.26

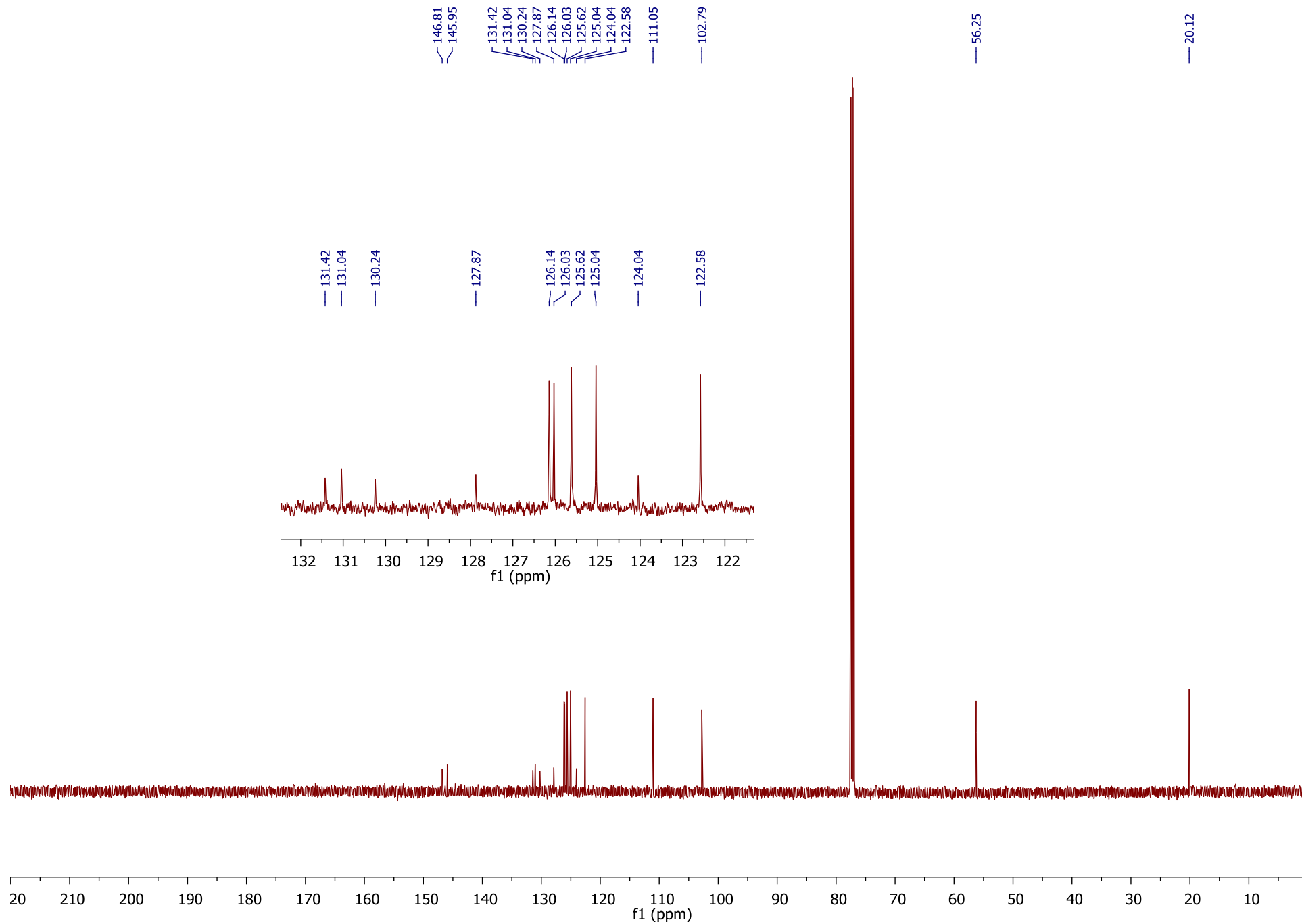
4.06

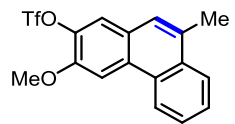
2.71
2.71
2.40



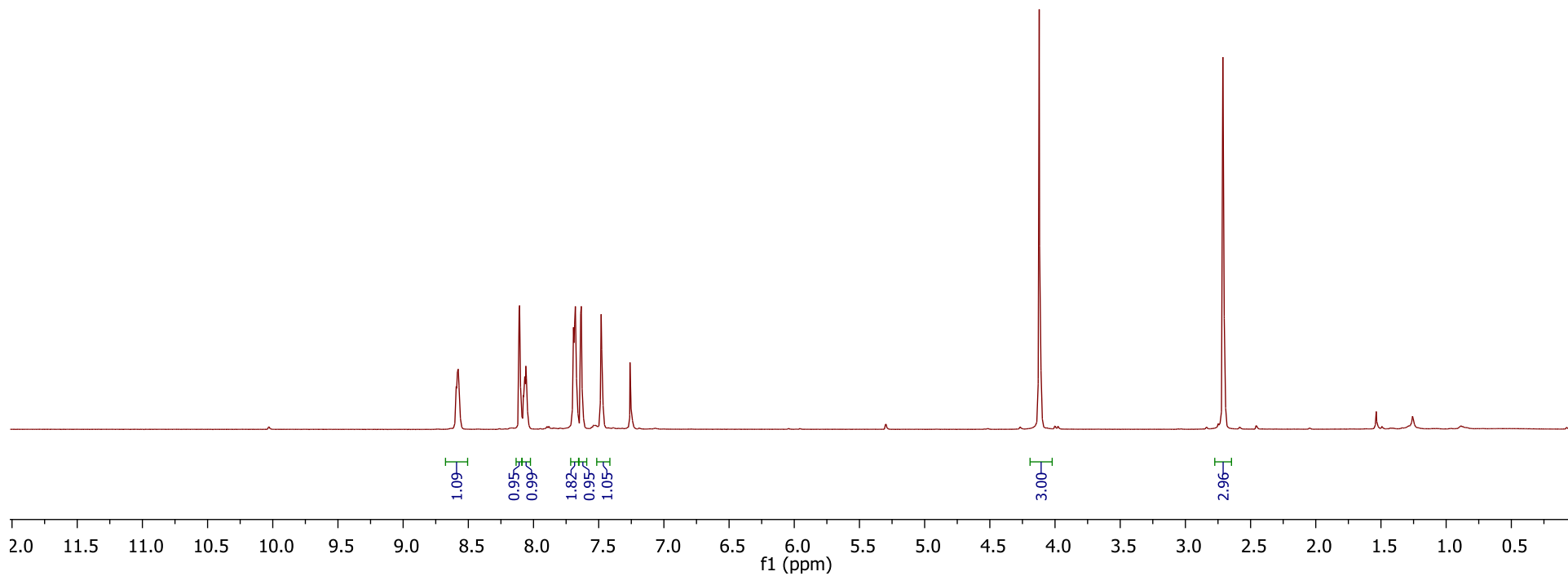


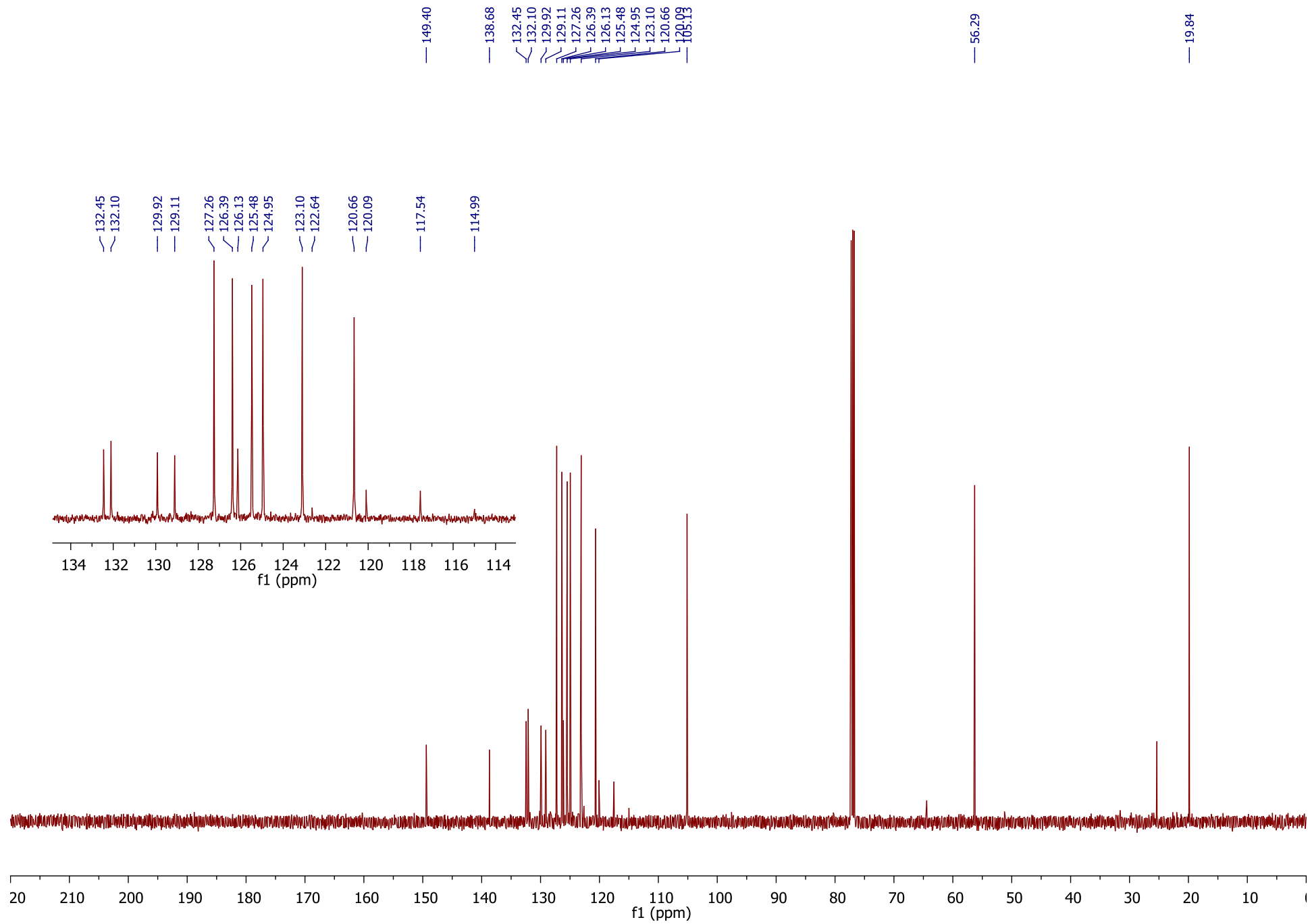


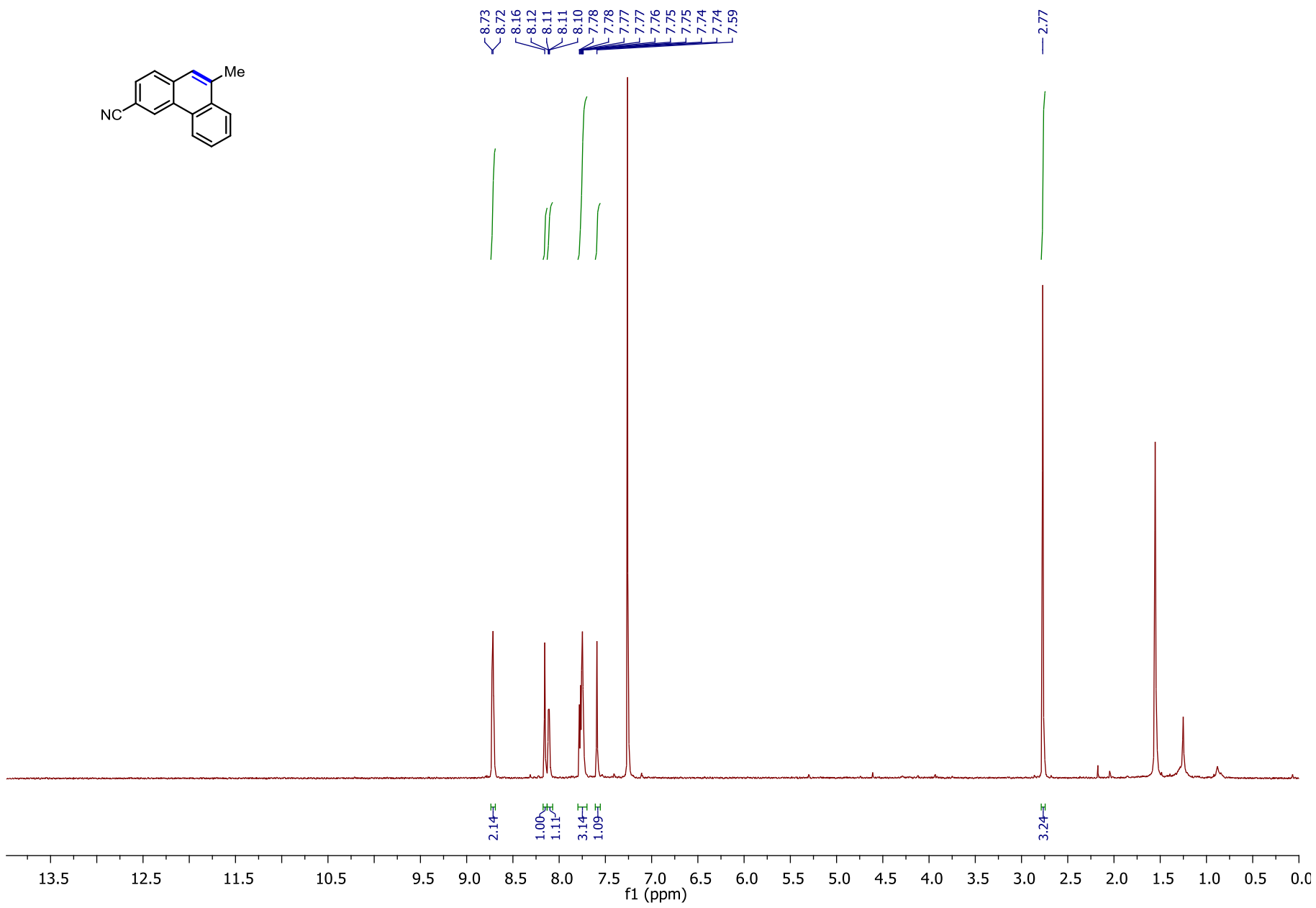
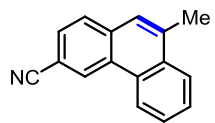


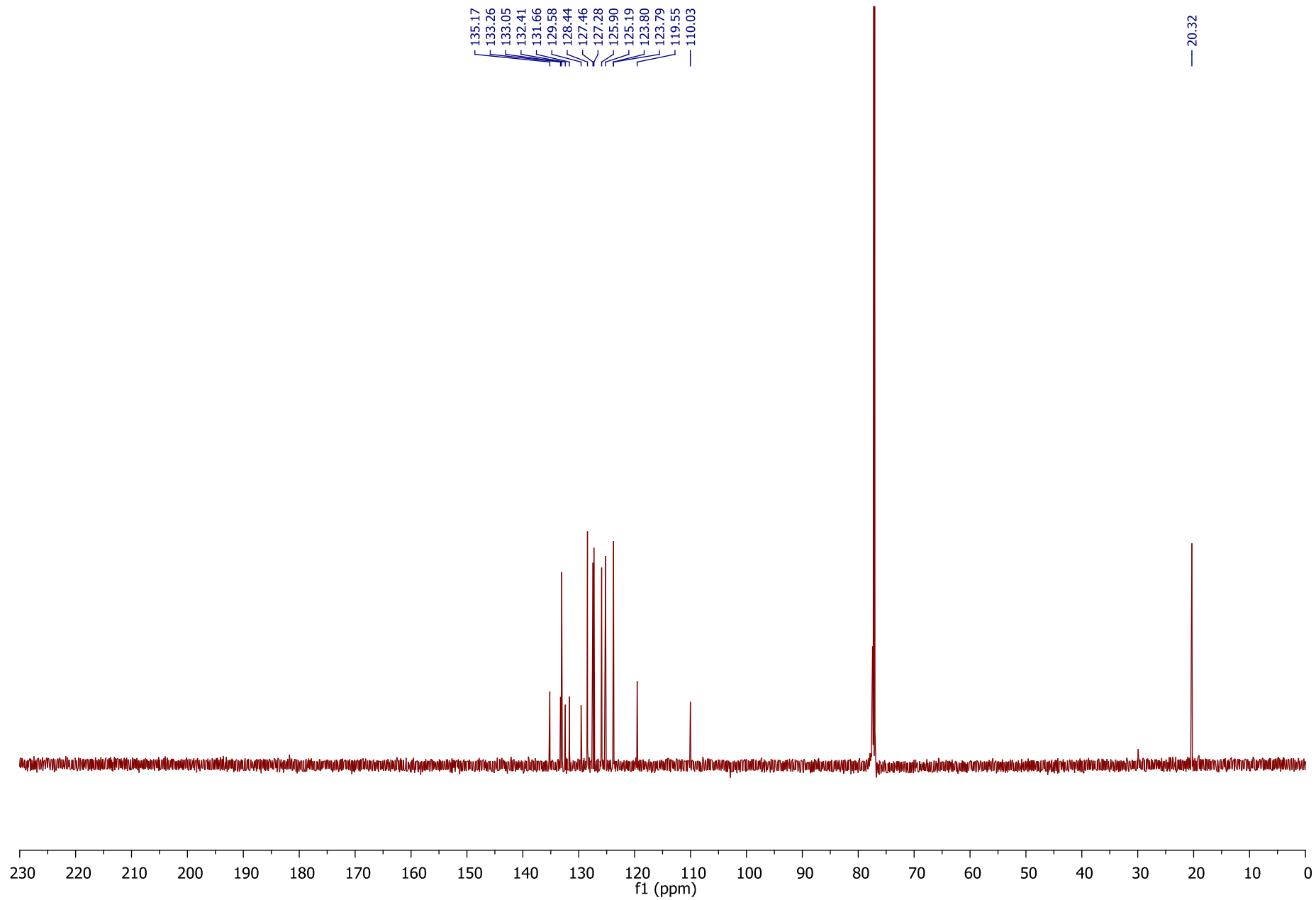


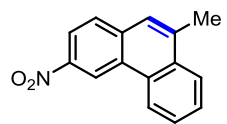
8.60
8.59
8.58
8.58
8.57
8.11
8.11
9.96
7.69
7.69
7.68
7.68
7.67
7.64
7.63
7.48
7.26
7.26
4.13
4.12
4.11
2.71
2.71







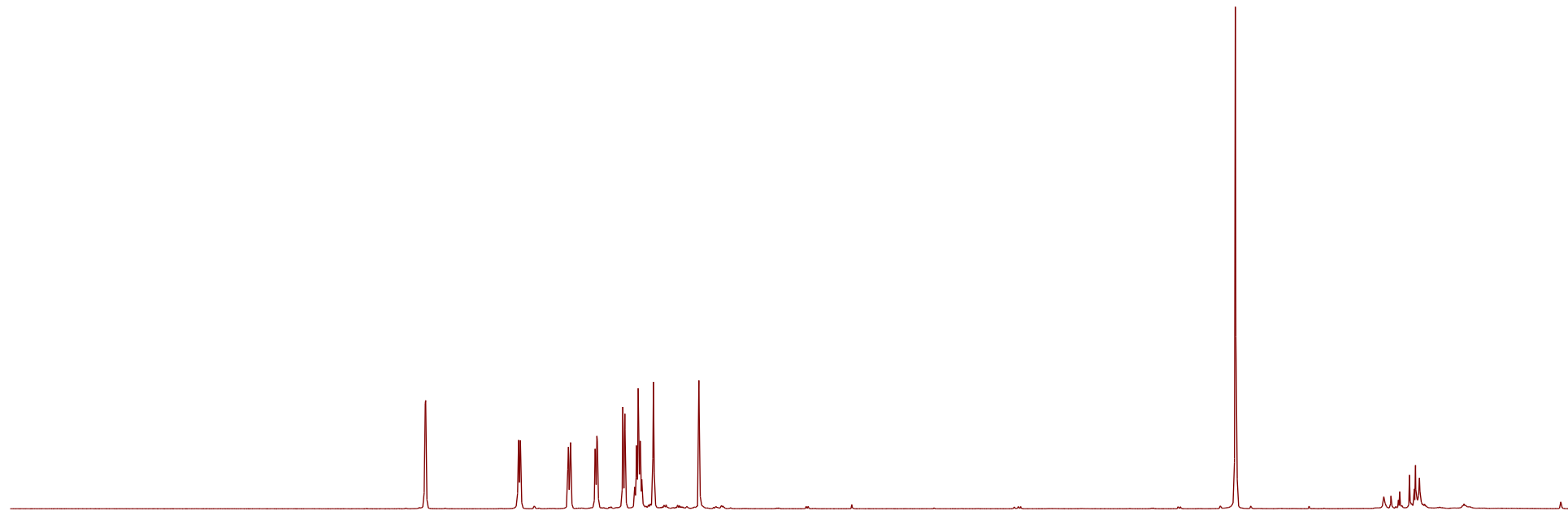




9.54
8.76
8.75
8.11
7.89
7.88
7.77
7.76
7.75
7.54
7.26



2.79

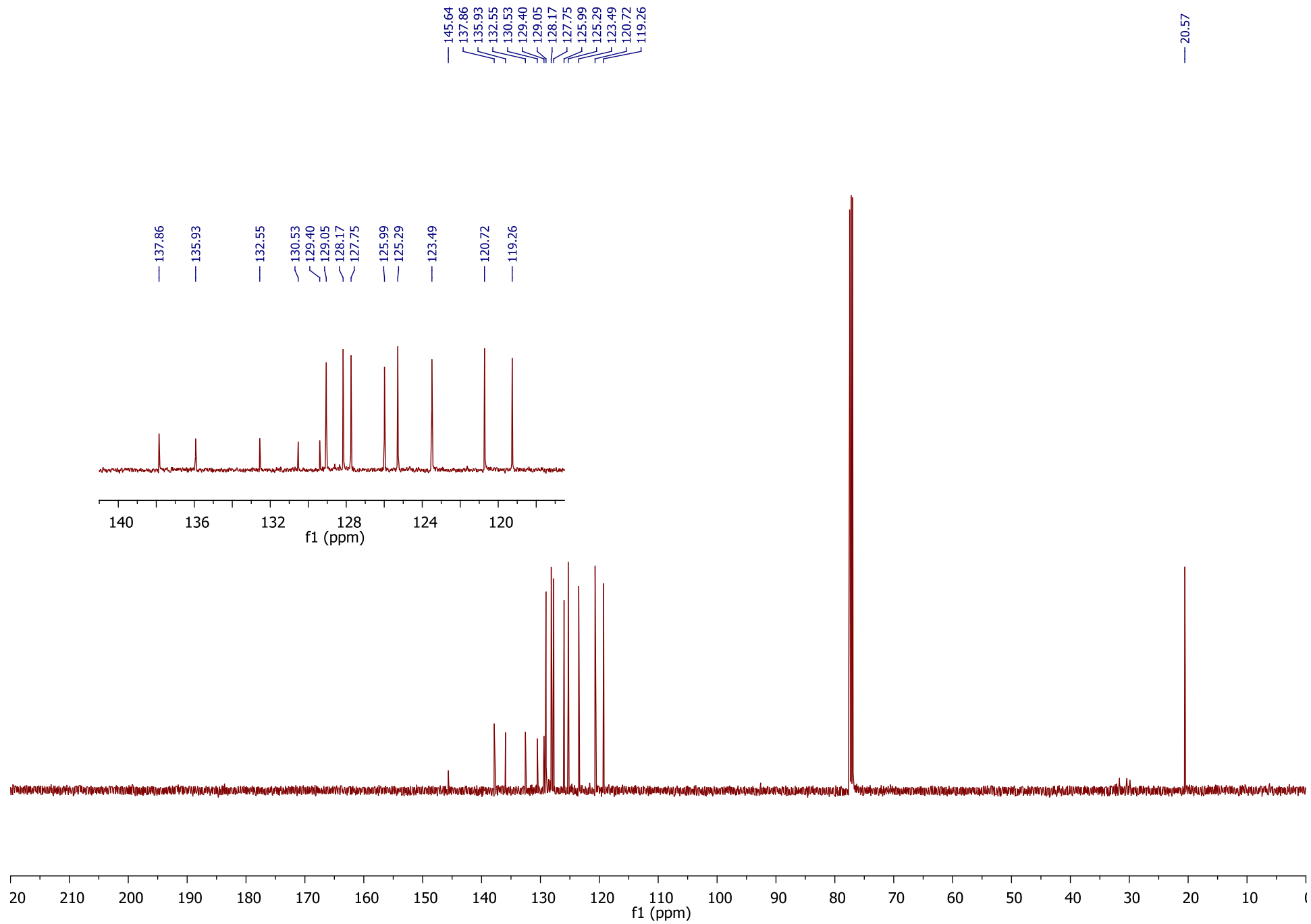


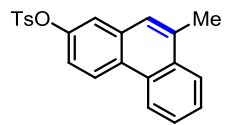
1.00
1.05
0.92
0.99
1.01
1.96
1.02

3.18

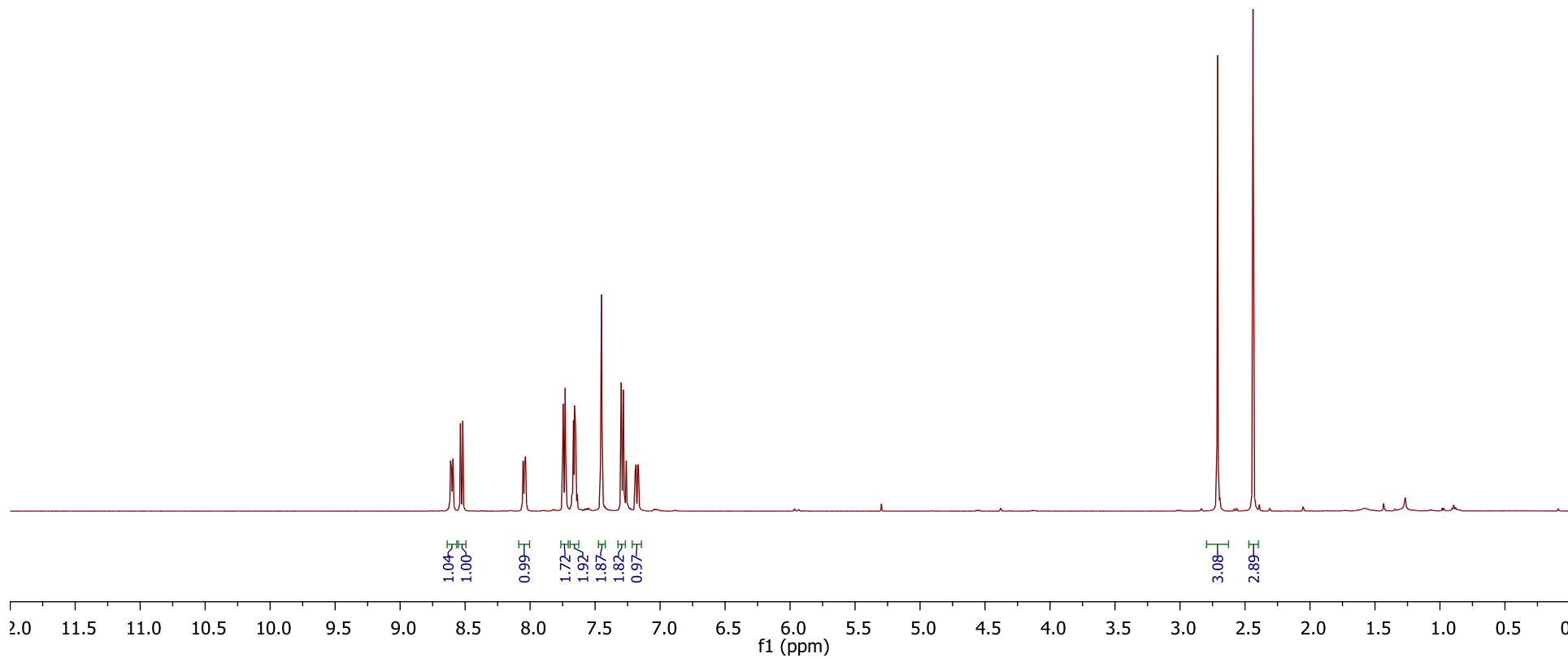
3.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0

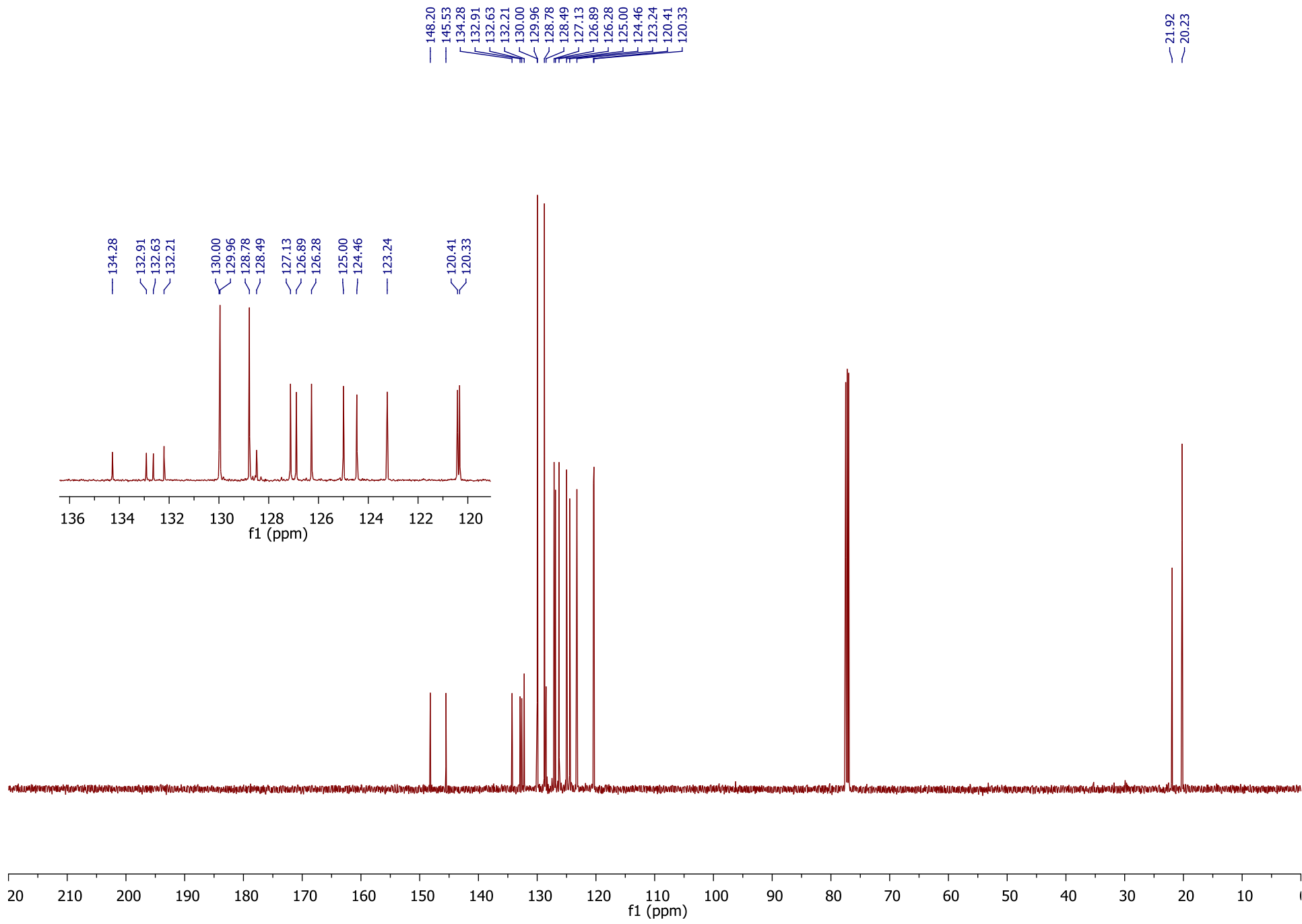
f1 (ppm)

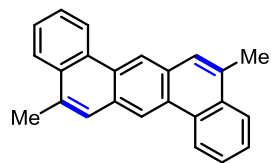




8.61
8.61
8.60
8.59
8.54
8.52
8.05
8.04
7.73
7.68
7.67
7.66
7.65
7.64
7.46
7.45
7.30
7.28
7.19
7.19
7.17
7.17
2.71
2.44







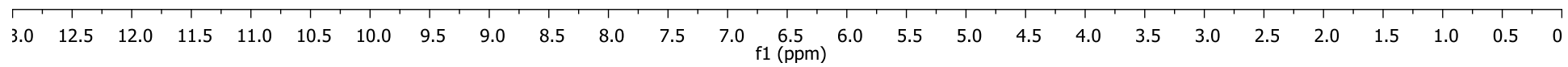
9.03
8.90
8.89
8.09
8.07
7.79
7.74
7.73
7.72
7.70
7.69
7.68

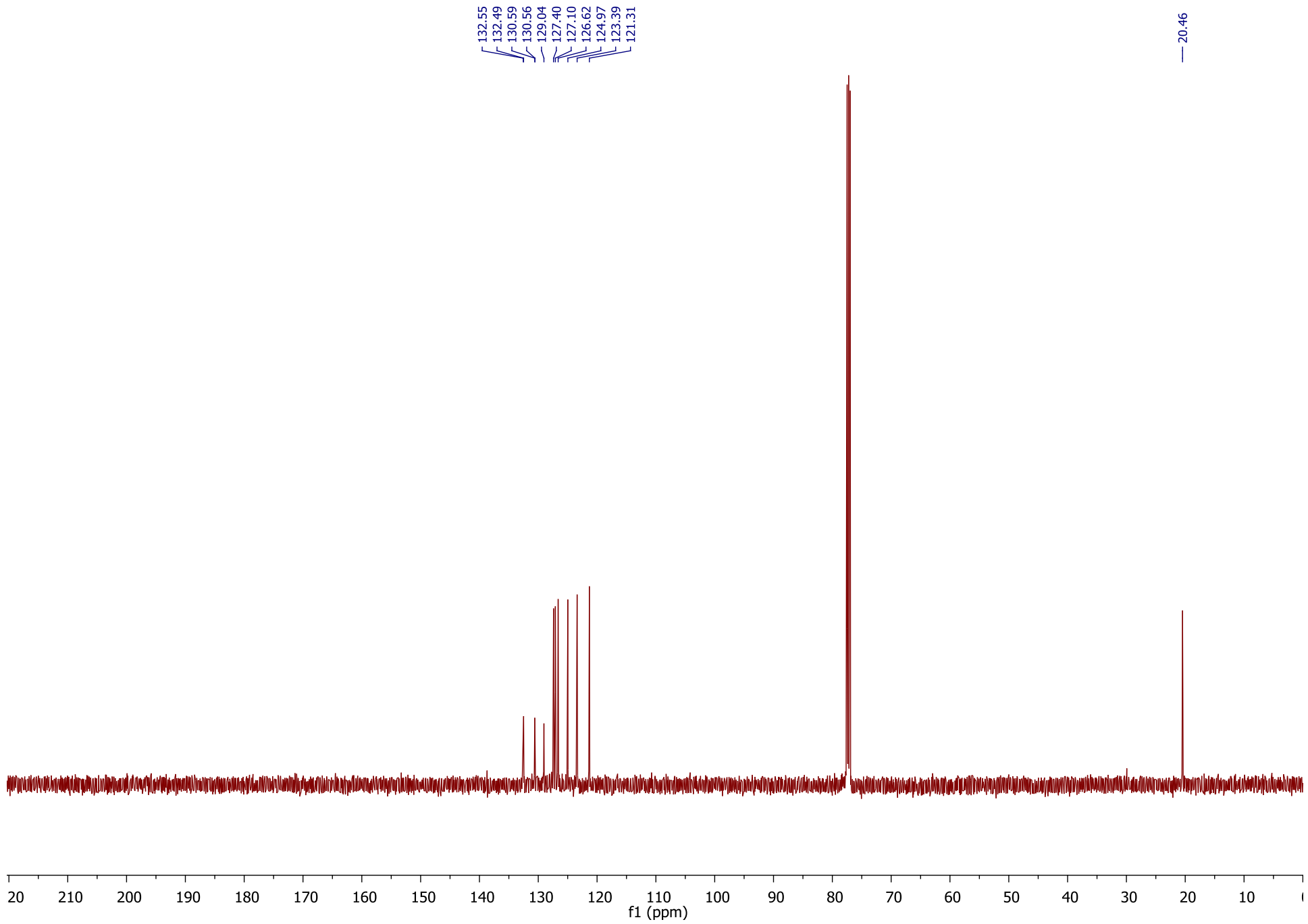
2.78



2.00
1.97
1.95
1.98
2.11
2.04

6.00





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