

Electrochemical Gold Redox Catalysis for Selective Oxidative Arylation

Shuyao Zhang,^a Xiaohan Ye^a, Lukasz Wojtas^a, Wenyan Hao^b, and Xiaodong Shi^{a,*}

^a*Department of Chemistry, University of South Florida, Tampa, FL 33620, USA*

^b*College of Chemistry & Chemical Engineering, Jiangxi Normal University, Nanchang 330022, People's Republic of China*

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I. General Methods and Materials

All of the reactions dealing with air and/or moisture-sensitive compounds were carried out under an atmosphere of argon using oven/flame-dried glassware and standard syringe/septa techniques. Unless otherwise noted, all commercial reagents and solvents were obtained from the commercial provider and used without further purification. ^1H NMR and ^{13}C NMR spectra were recorded on Agilent 400/600 MHz spectrometers spectrometers. Chemical shifts were reported relative to internal tetramethylsilane (δ 0.00 ppm) or CDCl_3 (δ 7.26 ppm) for ^1H and CDCl_3 (δ 77.00 ppm) for ^{13}C . Flash column chromatography was performed on 230-430 mesh silica gel. Analytical thin layer chromatography was performed with precoated glass baked plates (250 μ) and visualized by fluorescence and by charring after treatment with potassium permanganate stain.

II. General Procedures

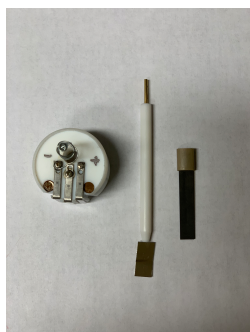
2.0 General procedure for the ElectraSyn Set-up

Handmade cell connection with IKA ElectraSyn

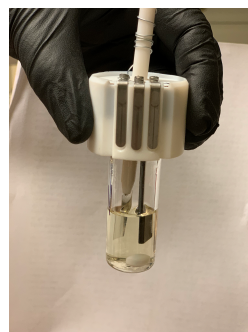


1. Remove the top cover

2. Wind a thin wire and attach to the screw on cathode(-)



3. Assemble both graphite electrode and Pt electrode.

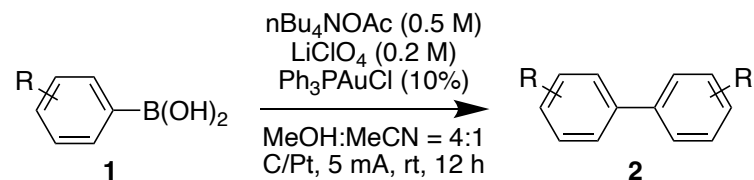


4. Complete the vial set up



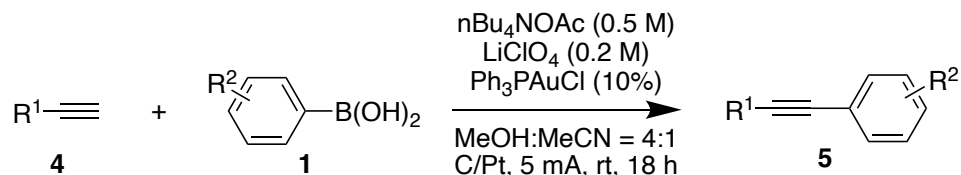
5. Connection the vials to IKA Carousel

2.1 General procedure for EAO promoted diaryl oxidative coupling reaction



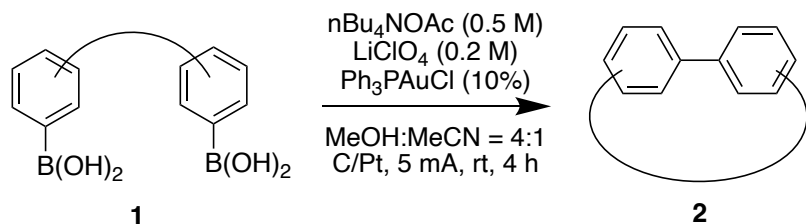
To a 10 mL ElectraSyn screwed vial with 0.5 M $n\text{Bu}_4\text{NOAc}$ (2.5 mmol, purchased from TCI, catalog# T2694) and 0.2 M LiClO_4 (1 mmol) in $\text{MeOH}:\text{MeCN} = 4:1$ (5mL), aryl-boronic acid **1** (0.5 mmol, 1.0 equiv.), Ph_3PAuCl (0.025mmol, 5 mol%) was added. The vial was placed on IKA Carousel and run under constant current at 5 mA for 12 h. After the reaction was completed, the solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel to give desired product **2**.

2.2 General procedure for EAO promoted terminal alkyne arylation reaction



To a 10 mL ElectraSyn screwed vial with 0.5 M $n\text{Bu}_4\text{NOAc}$ (2.5 mmol, purchased from TCI, catalog# T2694) and 0.2 M LiClO_4 (1 mmol) in $\text{MeOH}:\text{MeCN} = 4:1$ (5mL), aryl-boronic acid **1** (0.5 mmol, 2.0 equiv.), terminal alkyne **4** (0.25 mmol, 1.0 equiv.), Ph_3PAuCl (0.025mmol, 10 mol%) was added. The vial was placed on IKA Carousel and run under constant current at 5 mA for 18 h. After the reaction was completed, the solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel to give desired product **5**.

2.3 General procedure for EAO promoted aryl boronic acid macrocyclization reaction

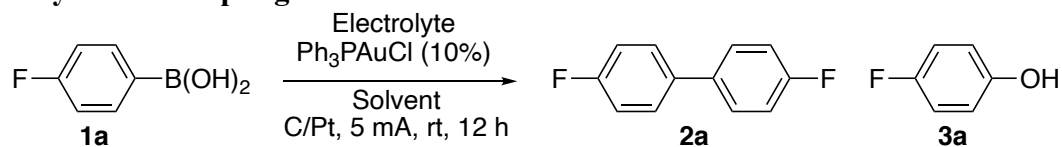


To a 10 mL ElectraSyn screwed vial with 0.5 M $n\text{Bu}_4\text{NOAc}$ (2.5 mmol, purchased from TCI, catalog# T2694) and 0.2 M LiClO_4 (1

mmol) in MeOH:MeCN = 4:1 (5mL), aryl-boronic acid **1** (0.05 mmol, 1.0 equiv.), Ph₃PAuCl (0.005mmol, 10 mol%) was added. The vial was placed on IKA Carousel and run under constant current at 5 mA for 4 h. After the reaction was completed, the solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel to give desired product **2**.

III. Condition Optimization and Mechanistic Studies

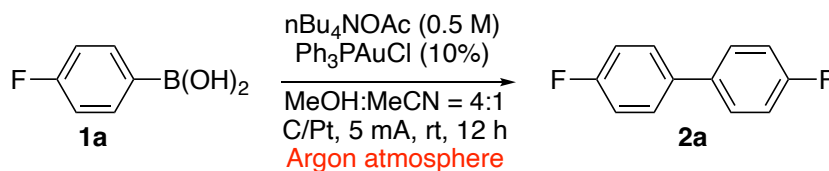
3.1 Optimization studies of aryl homo-coupling reaction



Entry	Electrolyte		Solvent		Yield		Note
	nBu ₄ NOAc	LiClO ₄	MeOH	MeCN	2a	3a	
1	0.5 M	-	4 mL	1 mL	23%	10%	-
2	0.2 M	0.2 M	4 mL	1 mL	36%	16%	-
3	0.5 M	0.2 M	4 mL	1 mL	78%	<5%	-
4	0.2 M	0.5 M	4 mL	1 mL	14%	35%	-
5	0.5 M	0.2 M	5 mL	0 mL	15%	10%	-
6	0.5 M	0.2 M	3 mL	2 mL	49%	7%	-
7	0.5 M	0.2 M	2.5 mL	2.5 mL	51%	<5%	-
8	0.5 M	0.2 M	2 mL	3 mL	42%	<5%	-
9	0.5 M	0.2 M	1 mL	4 mL	23%	8%	-
10	0.5 M LiOAc.2H ₂ O		4 mL	1 mL	36%	<5%	-
11	0.5 M	0.2 M	4 mL	1 mL	trace	0%	Argon
12	0.75 M	0.2 M	4 mL	1 mL	36%	15%	-
13	0.5 M	0.02 M	4 mL	1 mL	8%	<5%	-
14	0.5 M	0.05 M	4 mL	1 mL	14%	<5%	-
15	0.5 M	0.1 M	4 mL	1 mL	41%	10%	-
16	0.5 M	0.15 M	4 mL	1 mL	74%	<5%	-
17	0.5 M	0.2 M	4 mL	1 mL	75%	<5%	-

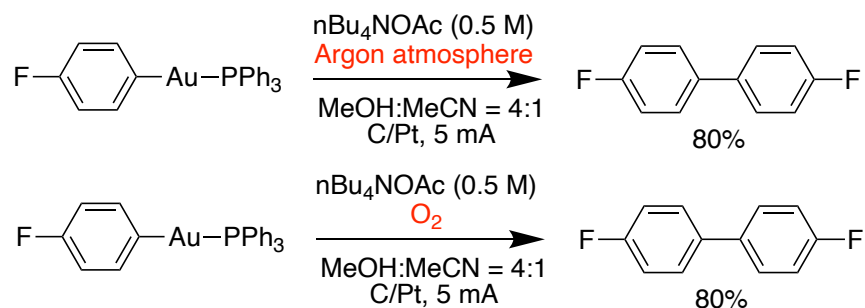
18	0.5 M	0.25 M	4 mL	1 mL	72%	<5%	-
19	0.5 M	0.3 M	4 mL	1 mL	30%	<5%	-
20	0.5 M	0.4 M	4 mL	1 mL	10%	<5%	-
21	0.5 M	0.5 M	4 mL	1 mL	<5%	<5%	-
23	0.5 M	0.2 M	4 mL	1 mL	38%	<5%	Water-free
24	0.5 M	0.2 M	4 mL	1 mL	72%	<5%	Add 1 eq water
25	0.5 M	0.2 M	4 mL	1 mL	70%	<5%	Add 2 eq water
26	0.5 M	0.2 M	4 mL	1 mL	72%	<5%	Add 3 eq water
27	0.5 M	0.2 M	4 mL	1 mL	74%	<5%	Add 5 eq water
28	0.5 M	0.2 M	4 mL	1 mL	75%	<5%	Add 10 eq water
29	0.5 M	0.2 M	4 mL	1 mL	40%	<5%	25% concentration
30	0.5 M	0.2 M	4 mL	1 mL	0%	<5%	No [Au]

3.2 Study of “oxygen effect”



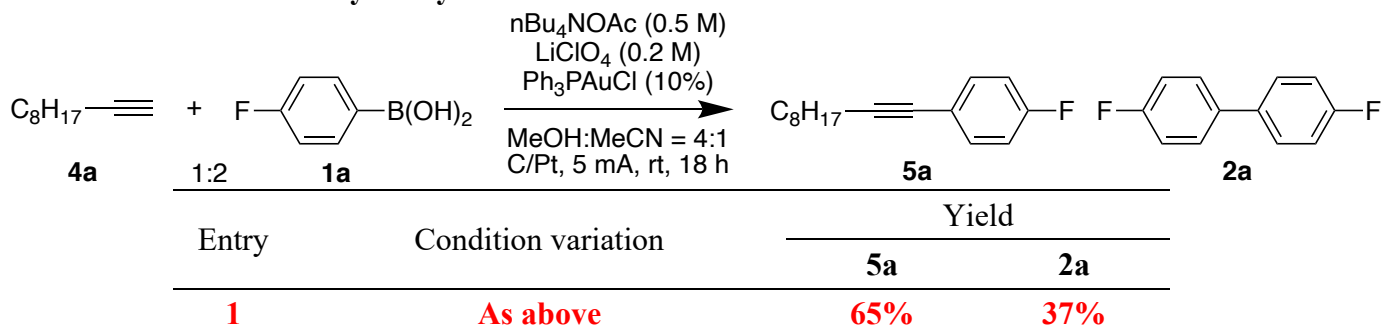
Entry	Adduct	Result
1	N/A	No rxn, fast gold decomposition
2	50 μL H_2O	No rxn, fast gold decomposition
3	500 μL H_2O	No rxn, fast gold decomposition
4	50 μL H_2O + 2 eq Li_2CO_3	No rxn, fast gold decomposition
5	2 eq NaOH	No rxn, fast gold decomposition
6	2 eq LiOMe	No rxn, fast gold decomposition
7	O_2	25% yield

We started our investigation on performing our standard reaction in glovebox (Entry 1). We observed that gold will decompose on cathode quickly (usually in 1 h). Then we start to wonder which adduct stopped the gold decomposition. We tried to add water, base and oxygen separately (Entry 2-8). Only entries with oxygen gave us desired product **2a** without gold decomposition. However, it was still not clear that whether oxygen helped with the gold oxidation on anode or simply serve as a sacrificial oxidant (perform reduction on cathode instead of gold), so we designed two more experiment to study on it.



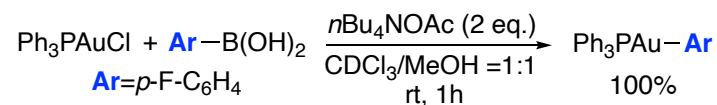
We prepared Ph₃PAu(p-FPh) as starting material, and charged them into standard reaction condition, one under argon and one under oxygen. If the one with argon did not give desired diaryl product, then oxygen should play an important role in gold oxidation. If both of them reacted well, then oxygen should serve as a sacrificial oxidant. The result showed that both reactions worked well, generated the desired product at 80% yield. This result clearly indicated that oxygen is a sacrificial oxidant, it was reduced on cathode to prevent the gold decomposition.

3.3 Optimization studies of terminal alkyne arylation reaction



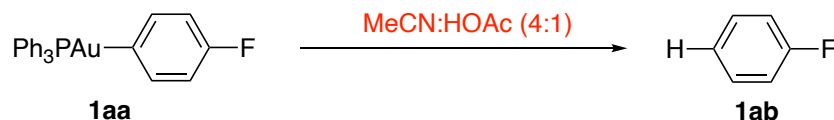
2	0.1 M LiClO ₄	30%	26%
3	No LiClO ₄	21%	30%
4	0.3 M LiClO ₄	34%	18%
5	5 mL MeOH	32%	25%
6	3 mL MeOH 2 mL MeCN	41%	46%
7	2 mL MeOH 3 mL MeCN	<5%	12%
8	5 eq 4a , 1 eq 1a	10%	<5%
9	3 eq 1a , no LiClO ₄	18%	30%
10	3 eq 1a	40%	35%

3.4 General procedures and results for mechanistic studies



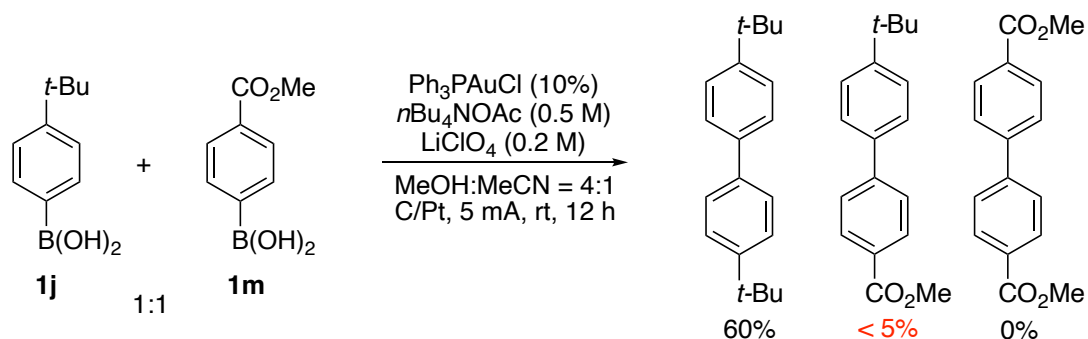
To a 5 mL vial with 0.2 mmol *n*Bu₄NOAc in 1 ml CDCl₃/MeOH = 1:1 solvent was added 0.1 mmol Ph₃PAuCl and 0.1 mmol *p*-FPhB(OH)₂. The reaction was stirred at room temperature for 1 h, and the resulted solution was directly used to perform ¹⁹F and ³¹P NMR study without further operation.

Result: The conversion of Ph₃PAuCl and the yield of Ph₃PAu-Ar were both 100%.



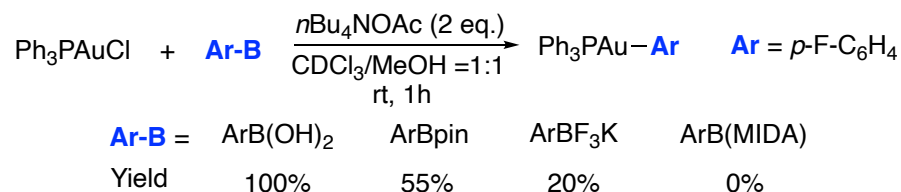
To a 5 mL vial was added 0.1 mmol **1aa**, 0.8 mL MeCN and 0.2 mL HOAc. The reaction was stirred at room temperature for 30 min, then the resulted solution was directly used to perform ¹⁹F and ³¹P NMR study with CDCl₃ as deuterium solvent.

Result: Purple precipitation started to form within 10 min. **1aa** was completely consumed after 30 min and the yield of **1ab** was 100%



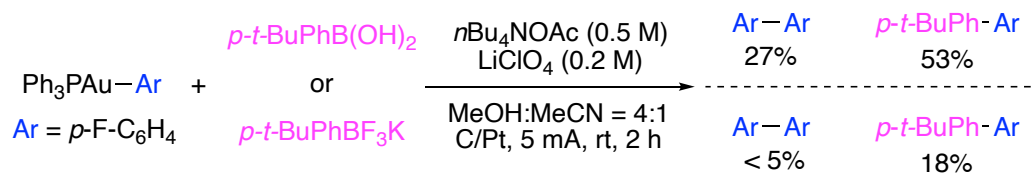
To a 10 mL ElectraSyn screwed vial with 0.5 M *n*Bu₄NOAc (2.5 mmol, purchased from TCI, catalog# T2694) and 0.2 M LiClO₄ (1 mmol) in MeOH:MeCN = 4:1 (5mL), **1j** (0.25 mmol, 1.0 equiv.), **1m** (0.25 mmol, 1.0 equiv.) and Ph₃PAuCl (0.025mmol, 10 mol%) was added. The vial was placed on IKA Carousel and run under constant current at 5 mA for 12 h. After the reaction was completed, 0.25 mmol 1,3,5-trimethoxybenzene was added to the solution to perform ¹H NMR study.

Result: Homocoupling product **2j** was detected in 60% yield, the cross-coupling product has only trace amount yield.



To a 5 mL vial with 0.2 mmol *n*Bu₄NOAc in 1 ml CDCl₃/MeOH = 1:1 solvent was added 0.1 mmol Ph₃PAuCl and 0.1 mmol corresponding boron compounds. The reaction was stirred at room temperature for 1 h, and the resulted solution was directly used to perform ¹⁹F and ³¹P NMR study without further operation.

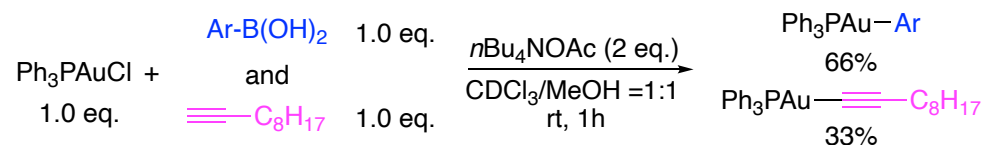
Result: as shown above.



To a 10 mL ElectraSyn screwed vial with 0.5 M *n*Bu₄NOAc (2.5 mmol, purchased from TCI, catalog# T2694) and 0.2 M LiClO₄ (1 mmol) in MeOH:MeCN = 4:1 (5mL), 0.25 mmol Ph₃PAuPhF and 0.25 mmol corresponding boron compound was added. The vial was placed on IKA Carousel and run under constant current at 5 mA for 2 h. After the reaction was completed, the solution was directly used

to perform ^{19}F NMR study with CDCl_3 as deuterium solution.

Result: Reaction of p - $t\text{BuC}_6\text{H}_4\text{B}(\text{OH})_2$ and Ph_3PAuPhF gave 53% cross coupling product and 27% homocoupling product. Reaction of p - $t\text{BuC}_6\text{H}_4\text{BF}_3\text{K}$ and Ph_3PAuPhF gave 18% cross coupling product, while no homocoupling product was observed.



To a 5 mL vial with 0.2 mmol $n\text{Bu}_4\text{NOAc}$ in 1 ml $\text{CDCl}_3/\text{MeOH} = 1:1$ solvent was added 0.1 mmol Ph_3PAuCl , 0.1 mmol **1a** and 0.1 mmol **4a**. The reaction was stirred at room temperature for 1 h, and the resulted solution was directly used to perform ^{19}F and ^{31}P NMR study without further operation.

Result: The conversion of Ph_3PAuCl was 100%. Aryl gold species was generated in 66% yield and the gold acetylene was generated in 33% yield.

IV. ORTEP Drawing of Crystal Structures

X-ray diffraction data were measured on Bruker D8 Venture PHOTON II CPAD diffractometer equipped with a Cu K α INCOATEC ImuS micro-focus source ($\lambda = 1.54178 \text{ \AA}$). Indexing was performed using *APEX3* [1] (Difference Vectors method). Data integration and reduction were performed using SaintPlus [2]. Absorption correction was performed by multi-scan method implemented in SADABS [3]. Space groups were determined using XPREP implemented in APEX3 [1]. Structure was solved using SHELXT [4] and refined using SHELXL-2018 [5] (full-matrix least-squares on F^2) through OLEX2 interface program [6]. Crystal data and refinement conditions are shown in Tables 1 - 4.

[1] Bruker (2019). *APEX3* Bruker AXS Inc., Madison, Wisconsin, USA.

[2] Bruker (2019) SAINT V8.35A. Data Reduction Software.

[3] Sheldrick, G. M. (1996). *SADABS. Program for Empirical Absorption Correction*. University of Gottingen, Germany.

[4] XT, G.M. Sheldrick, Acta Cryst. (2015). A71, 3-8

[5] XL, Sheldrick, G. M. (2008). Acta Cryst. A64, 112-122.

[6] Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H., OLEX2: A complete structure solution, refinement and analysis program (2009). J. Appl. Cryst., 42, 339-341

Table 1 Crystal data and structure refinement for 2r.	
Identification code	2r
Empirical formula	C ₁₉ H ₁₈ O ₄
Formula weight	310.33
Temperature/K	100.0
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	10.6865(4)
b/Å	4.4027(2)
c/Å	32.2490(10)
α/°	90
β/°	96.691(2)
γ/°	90
Volume/Å ³	1506.96(10)
Z	4
ρ _{calc} /g/cm ³	1.368
μ/mm ⁻¹	0.779
F(000)	656.0
Crystal size/mm ³	0.2 × 0.05 × 0.04
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	5.518 to 157.686
Index ranges	-13 ≤ h ≤ 12, -5 ≤ k ≤ 5, -41 ≤ l ≤ 39
Reflections collected	15842
Independent reflections	3216 [R _{int} = 0.0428, R _{sigma} = 0.0328]
Data/restraints/parameters	3216/0/208
Goodness-of-fit on F ²	1.042
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0417, wR ₂ = 0.1036
Final R indexes [all data]	R ₁ = 0.0521, wR ₂ = 0.1141
Largest diff. peak/hole / e Å ⁻³	0.23/-0.22

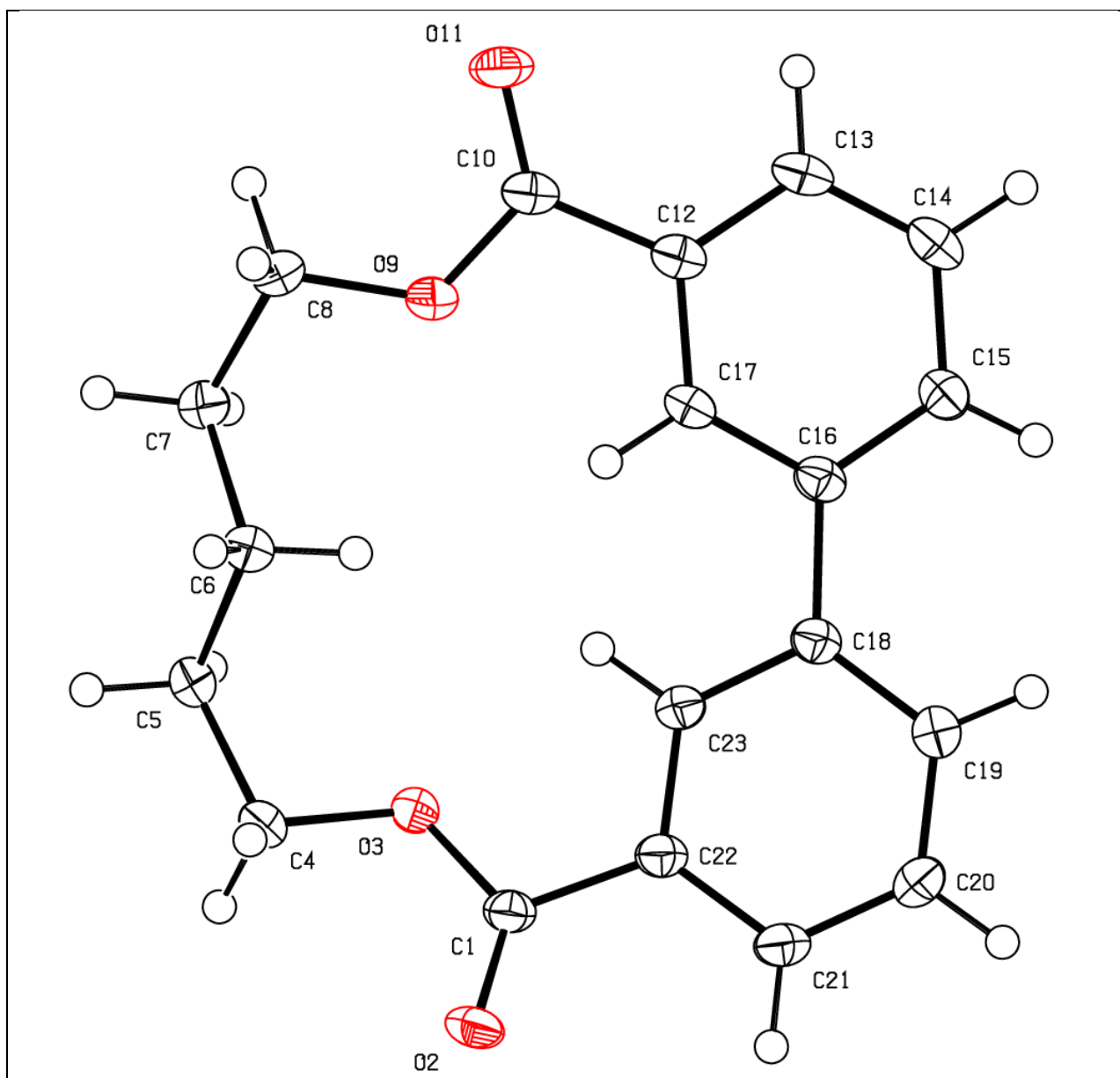


Fig.1. Asymmetric unit of **2r**. Anisotropic displacement parameters were drawn at 50% probability level. CCDC: 2048962

Table 2 Crystal data and structure refinement for 2t.

Identification code	2t
Empirical formula	C ₂₄ H ₃₂ O ₂
Formula weight	352.49
Temperature/K	100.0
Crystal system	monoclinic
Space group	C2/c
a/Å	11.4588(5)
b/Å	7.6111(3)
c/Å	22.9097(9)
α/°	90
β/°	94.3530(10)
γ/°	90
Volume/Å ³	1992.28(14)
Z	4
ρ _{calc} /cm ³	1.175
μ/mm ⁻¹	0.559
F(000)	768.0
Crystal size/mm ³	0.18 × 0.17 × 0.12
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	7.74 to 159.884
Index ranges	-14 ≤ h ≤ 14, -9 ≤ k ≤ 9, -29 ≤ l ≤ 29
Reflections collected	15199
Independent reflections	2150 [R _{int} = 0.0413, R _{sigma} = 0.0269]
Data/restraints/parameters	2150/0/118
Goodness-of-fit on F ²	1.045
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0359, wR ₂ = 0.0982

Final R indexes [all data] $R_1 = 0.0367$, $wR_2 = 0.0992$
 Largest diff. peak/hole / $e \text{ \AA}^{-3}$ 0.23/-0.18

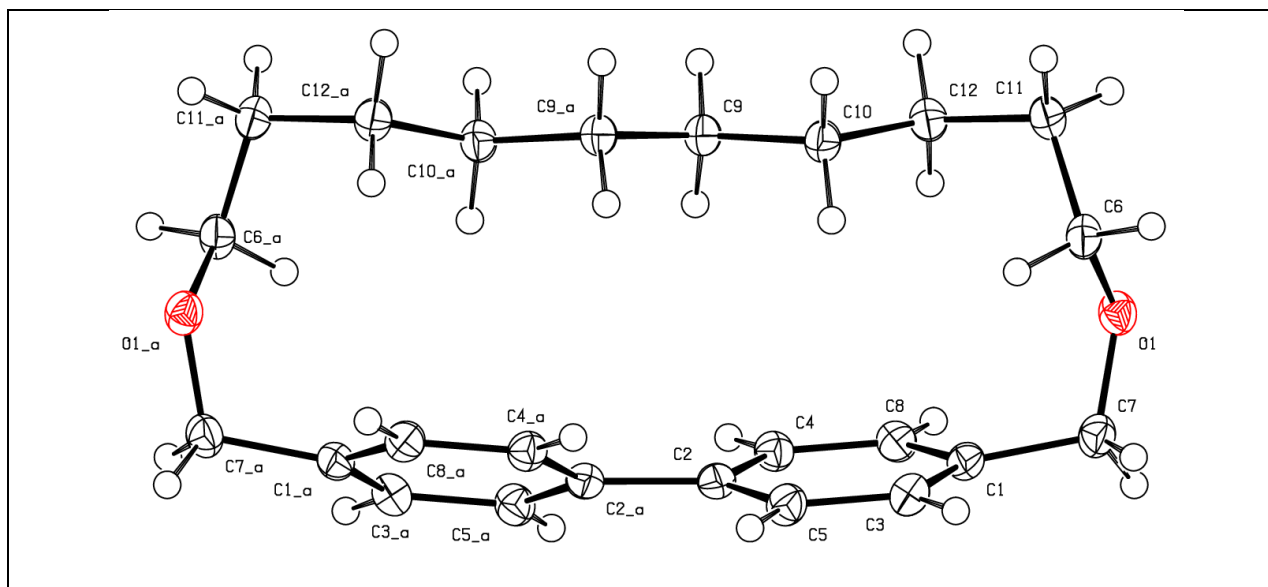


Fig.2. Ellipsoid plot of **2t**. Anisotropic displacement parameters were drawn at 50% probability level. CCDC: 2048963

Table 3 Crystal data and structure refinement for 2v.

Identification code	2v
Empirical formula	$C_{20}H_{24}O_2$
Formula weight	296.39
Temperature/K	100.0
Crystal system	monoclinic
Space group	$C2/c$
$a/\text{\AA}$	21.5319(9)

b/Å	7.5076(3)
c/Å	11.3927(5)
α /°	90
β /°	119.9544(9)
γ /°	90
Volume/Å ³	1595.66(12)
Z	4
ρ_{calc} /cm ³	1.234
μ /mm ⁻¹	0.607
F(000)	640.0
Crystal size/mm ³	0.2 × 0.16 × 0.1
Radiation	CuK α (λ = 1.54178)
2 Θ range for data collection/°	9.482 to 159.858
Index ranges	-27 ≤ h ≤ 27, -9 ≤ k ≤ 9, -13 ≤ l ≤ 14
Reflections collected	19312
Independent reflections	1702 [R_{int} = 0.0426, R_{sigma} = 0.0233]
Data/restraints/parameters	1702/0/100
Goodness-of-fit on F ²	1.043
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0385, wR_2 = 0.1053
Final R indexes [all data]	R_1 = 0.0395, wR_2 = 0.1067
Largest diff. peak/hole / e Å ⁻³	0.24/-0.26

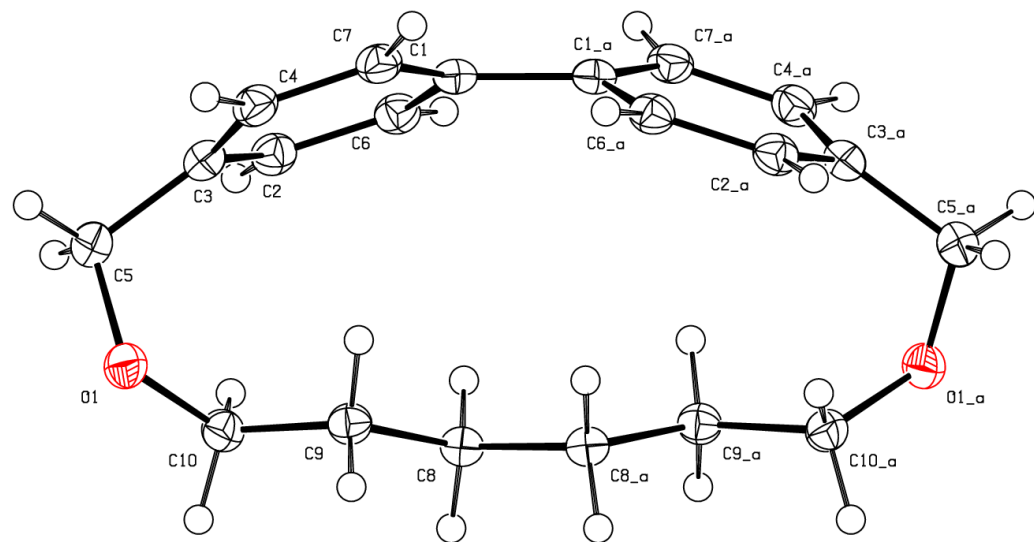
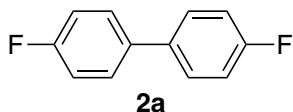


Fig.3. Ellipsoid plot of **2v**. Anisotropic displacement parameters were drawn at 50% probability level. CCDC: 2048964

V. Compound Characterization



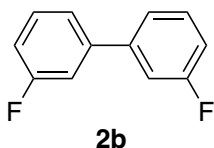
4,4'-difluoro-1,1'-biphenyl

2a was prepared following the general procedure 2.1 and purified by column chromatography (hexane) as a white solid

$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.49 (dd, $J = 8.5, 5.4$ Hz, 4H), 7.13 (t, $J = 8.6$ Hz, 4H).

$^{13}\text{C NMR}$ (151 MHz, Chloroform-*d*) δ 162.44 (d, $J = 246.3$ Hz), 136.41 (d, $J = 3.3$ Hz), 128.60 (d, $J = 8.0$ Hz), 115.72 (d, $J = 21.5$ Hz).

$^{19}\text{F NMR}$ (564 MHz, Chloroform-*d*) δ -115.72.



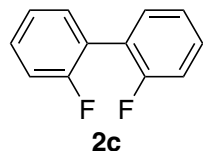
3,3'-difluoro-1,1'-biphenyl

2b was prepared following the general procedure 2.1 and purified by column chromatography (hexane) as a white solid

$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.40 (td, $J = 7.9, 5.9$ Hz, 2H), 7.34 (dt, $J = 7.8, 1.3$ Hz, 2H), 7.26 (ddd, $J = 10.3, 2.7, 1.8$ Hz, 2H), 7.06 (tdd, $J = 8.3, 2.5, 1.0$ Hz, 2H).

$^{13}\text{C NMR}$ (151 MHz, Chloroform-*d*) δ 163.19 (d, $J = 245.9$ Hz), 142.18 (d, $J = 7.9$ Hz), 130.42 (d, $J = 8.6$ Hz), 122.76 (d, $J = 3.1$ Hz), 114.69 (d, $J = 21.3$ Hz), 114.07 (d, $J = 22.1$ Hz).

$^{19}\text{F NMR}$ (564 MHz, Chloroform-*d*) δ -112.75.



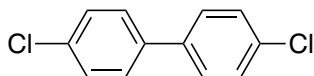
2,2'-difluoro-1,1'-biphenyl

2c was prepared following the general procedure 2.1 and purified by column chromatography (hexane) as a white solid

$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.43 – 7.34 (m, 2H), 7.22 (td, $J = 7.5, 1.2$ Hz, 1H), 7.20 – 7.14 (m, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.85 (d, $J = 249.8$ Hz), 131.63, 129.79 (t, $J = 4.3$ Hz), 124.09, 123.54 (d, $J = 11.7$ Hz), 115.81 (dd, $J = 17.6, 4.7$ Hz).

^{19}F NMR (564 MHz, Chloroform-*d*) δ -114.82.



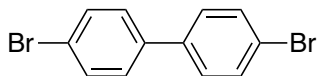
2d

4,4'-dichloro-1,1'-biphenyl

2d was prepared following the general procedure 2.1 and purified by column chromatography (hexane) as a white solid

^1H NMR (600 MHz, Chloroform-*d*) δ 7.47 (d, $J = 8.6$ Hz, 1H), 7.40 (d, $J = 8.5$ Hz, 1H).

^{13}C NMR (151 MHz, CDCl_3) δ 138.44, 133.75, 129.07, 128.25.



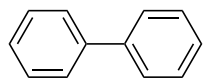
2e

4,4'-dibromo-1,1'-biphenyl

2e was prepared following the general procedure 2.1 and purified by column chromatography (hexane) as a white solid

^1H NMR (600 MHz, Chloroform-*d*) δ 7.56 (d, $J = 8.5$ Hz, 4H), 7.42 (d, $J = 8.5$ Hz, 4H).

^{13}C NMR (151 MHz, CDCl_3) δ 138.93, 132.05, 128.54, 121.97.



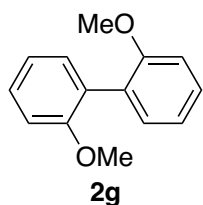
2f

1,1'-biphenyl

2f was prepared following the general procedure 2.1 and purified by column chromatography (hexane) as a white solid

^1H NMR (600 MHz, Chloroform-*d*) δ 7.66 – 7.57 (m, 4H), 7.50 – 7.42 (m, 4H), 7.36 (d, $J = 7.4$ Hz, 2H).

^{13}C NMR (151 MHz, CDCl_3) δ 141.25, 128.78, 127.28, 127.20.

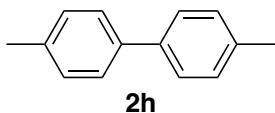


2,2'-dimethoxy-1,1'-biphenyl

2g was prepared following the general procedure 2.1 and purified by column chromatography (hexane/EA = 10:1) as a white solid

$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.33 (ddd, $J = 8.2, 7.4, 1.8$ Hz, 2H), 7.25 (dd, $J = 7.5, 1.9$ Hz, 2H), 7.06 – 6.96 (m, 4H), 3.77 (s, 6H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 157.04, 131.50, 128.66, 127.80, 120.37, 111.09, 55.72.

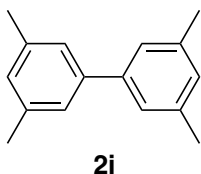


4,4'-dimethyl-1,1'-biphenyl

2h was prepared following the general procedure 2.1 and purified by column chromatography (hexane) as a white solid

$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.47 (d, $J = 8.1$ Hz, 4H), 7.23 (d, $J = 7.9$ Hz, 4H), 2.38 (s, 6H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 138.32, 136.75, 129.49, 126.86, 21.15.

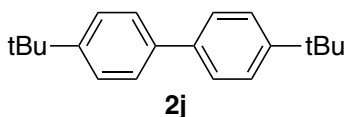


3,3',5,5'-tetramethyl-1,1'-biphenyl

2i was prepared following the general procedure 2.1 and purified by column chromatography (hexane) as a colorless oil

$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.23 – 7.14 (m, 4H), 6.98 (d, $J = 1.7$ Hz, 2H), 2.37 (s, 12H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 141.47, 138.14, 128.76, 125.14, 21.45.

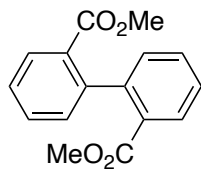


4,4'-di-tert-butyl-1,1'-biphenyl

2j was prepared following the general procedure 2.1 and purified by column chromatography (hexane) as a white solid

$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.53 (d, $J = 8.4$ Hz, 4H), 7.45 (d, $J = 8.4$ Hz, 4H), 1.36 (s, 18H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 149.93, 138.23, 126.71, 125.68, 34.55, 31.44.



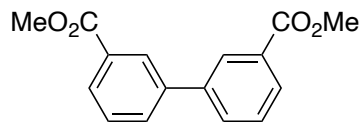
2k

dimethyl [1,1'-biphenyl]-2,2'-dicarboxylate

2k was prepared following the general procedure 2.1 and purified by column chromatography (hexane/EA = 10:1) as a colorless oil

$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 8.01 (dt, $J = 7.9, 0.9$ Hz, 2H), 7.54 (td, $J = 7.5, 1.4$ Hz, 2H), 7.43 (td, $J = 7.6, 1.3$ Hz, 2H), 7.21 (dt, $J = 7.6, 0.9$ Hz, 2H), 3.62 (s, 6H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 167.43, 143.31, 131.51, 130.20, 129.87, 129.32, 127.20, 51.86.



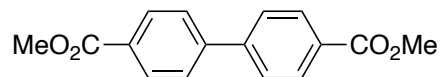
2l

dimethyl [1,1'-biphenyl]-3,3'-dicarboxylate

2l was prepared following the general procedure 2.1 and purified by column chromatography (hexane/EA = 10:1) as a white solid

$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 8.30 (t, $J = 1.8$ Hz, 2H), 8.05 (dt, $J = 7.8, 1.4$ Hz, 2H), 7.81 (ddd, $J = 7.7, 2.0, 1.2$ Hz, 2H), 7.53 (t, $J = 7.7$ Hz, 2H), 3.96 (s, 6H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 166.93, 140.38, 131.56, 130.84, 129.05, 128.84, 128.27, 52.30.



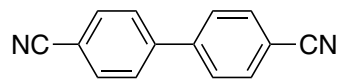
2m

dimethyl [1,1'-biphenyl]-4,4'-dicarboxylate

2m was prepared following the general procedure 2.1 and purified by column chromatography (hexane/EA = 10:1) as a white solid

$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 8.19 – 8.11 (m, 4H), 7.75 – 7.61 (m, 4H), 3.95 (s, 8H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 166.84, 144.36, 130.23, 129.69, 127.28, 52.28.



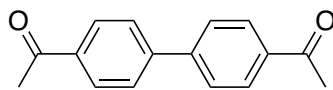
2n

[1,1'-biphenyl]-4,4'-dicarbonitrile

2n was prepared following the general procedure 2.1 and purified by column chromatography (hexane/EA = 5:1) as a white solid

¹H NMR (600 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 8.5 Hz, 4H), 7.70 (d, *J* = 8.4 Hz, 4H).

¹³C NMR (151 MHz, CDCl₃) δ 143.54, 132.93, 127.97, 118.46, 112.43.



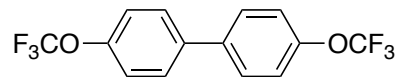
2o

1,1'-([1,1'-biphenyl]-4,4'-diyl)bis(ethan-1-one)

2o was prepared following the general procedure 2.1 and purified by column chromatography (hexane/EA = 10:1) as a white solid

¹H NMR (600 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 8.4 Hz, 4H), 7.73 (d, *J* = 8.4 Hz, 4H), 2.66 (s, 6H).

¹³C NMR (151 MHz, CDCl₃) δ 197.72, 144.37, 136.55, 129.05, 127.48, 26.77.



2p

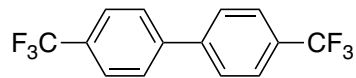
4,4'-bis(trifluoromethoxy)-1,1'-biphenyl

2p was prepared following the general procedure 2.1 and purified by column chromatography (hexane) as a white solid

¹H NMR (600 MHz, Chloroform-*d*) δ 7.63 – 7.50 (m, 4H), 7.29 (dt, *J* = 7.7, 1.1 Hz, 4H).

¹³C NMR (151 MHz, CDCl₃) δ 148.94, 138.59, 128.49, 121.38, 120.52 (q, *J* = 258.1 Hz).

¹⁹F NMR (564 MHz, Chloroform-*d*) δ -57.85.



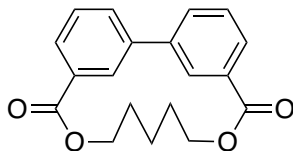
2q

4,4'-bis(trifluoromethyl)-1,1'-biphenyl

2q was prepared following the general procedure 2.1 and purified by column chromatography (hexane) as a white solid

¹H NMR (600 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 8.4 Hz, 4H), 7.70 (d, *J* = 8.3 Hz, 4H).

^{13}C NMR (151 MHz, CDCl_3) δ 143.26, 130.28 (q, $J = 32.5$ Hz), 127.66, 125.97 (q, $J = 3.8$ Hz), 124.12 (q, $J = 272.1$ Hz).



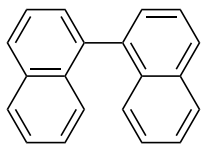
2r

4,10-dioxa-1,2(1,3)-dibenzenacycloundecaphane-3,11-dione

2r was prepared following the general procedure 2.3 and purified by column chromatography (hexane/EA = 10:1) as a white solid

^1H NMR (600 MHz, Chloroform-*d*) δ 8.90 (t, $J = 1.9$ Hz, 2H), 7.93 (ddd, $J = 7.7, 1.8, 0.9$ Hz, 2H), 7.88 (ddd, $J = 7.6, 2.1, 0.9$ Hz, 2H), 7.54 (t, $J = 7.7$ Hz, 2H), 4.45 – 4.32 (m, 4H), 2.14 (qd, $J = 10.5, 9.4, 5.7$ Hz, 2H), 1.86 (dddd, $J = 10.7, 9.0, 6.7, 5.0$ Hz, 4H).

^{13}C NMR (151 MHz, CDCl_3) δ 165.35, 139.06, 133.68, 131.79, 129.23, 128.59, 127.50, 64.14, 30.12, 22.85.

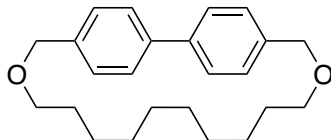


2s

2s was prepared following the general procedure 2.1 and purified by column chromatography (hexane) as a white solid

^1H NMR (600 MHz, Chloroform-*d*) δ 7.95 (ddt, $J = 7.7, 5.2, 1.0$ Hz, 2H), 7.59 (dd, $J = 8.3, 6.9$ Hz, 1H), 7.52 – 7.45 (m, 2H), 7.39 (dd, $J = 8.6, 1.2$ Hz, 1H), 7.28 (ddd, $J = 8.3, 6.7, 1.3$ Hz, 1H).

^{13}C NMR (151 MHz, CDCl_3) δ 138.46, 133.52, 132.85, 128.17, 127.91, 127.85, 126.58, 126.00, 125.83, 125.41.



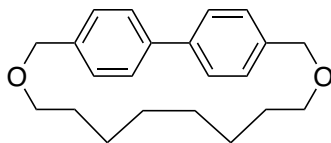
2t

4,15-dioxa-1,2(1,4)-dibenzenacyclohexadecaphane

2t was prepared following the general procedure 2.3 and purified by column chromatography (hexane/EA = 20:1) as a white solid

^1H NMR (600 MHz, Chloroform-*d*) δ 7.68 (d, $J = 8.2$ Hz, 3H), 7.45 (d, $J = 8.2$ Hz, 3H), 4.48 (s, 4H), 3.31 (dd, $J = 6.0, 4.8$ Hz, 4H), 1.30 – 1.20 (m, 6H), 0.87 (tt, $J = 12.0, 5.7$ Hz, 5H), 0.50 (dt, $J = 7.9, 3.4$ Hz, 4H), 0.32 – 0.20 (m, 5H).

^{13}C NMR (151 MHz, CDCl_3) δ 139.75, 137.96, 130.44, 126.40, 72.21, 65.17, 31.55, 29.95, 29.25, 25.10.



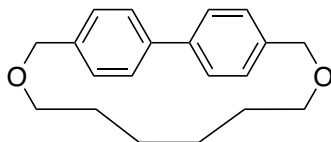
2u

4,13-dioxa-1,2(1,4)-dibenzenacyclotetradecaphane

2u was prepared following the general procedure 2.3 and purified by column chromatography (hexane/EA = 20:1) as a white solid

$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.70 (d, $J = 8.2$ Hz, 4H), 7.45 (d, $J = 8.2$ Hz, 4H), 4.52 (s, 4H), 3.21 (t, $J = 6.5$ Hz, 4H), 0.63 – 0.47 (m, 8H), 0.35 (p, $J = 3.1$ Hz, 4H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 140.12, 137.94, 130.92, 126.71, 73.61, 68.46, 30.83, 30.13, 26.00.



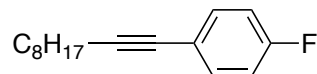
2v

4,11-dioxa-1,2(1,4)-dibenzenacyclododecaphane

2v was prepared following the general procedure 2.3 and purified by column chromatography (hexane/EA = 20:1) as a white solid

$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.75 (d, $J = 8.4$ Hz, 4H), 7.40 (d, $J = 8.4$ Hz, 4H), 4.45 (s, 4H), 3.09 – 2.97 (m, 4H), 0.14 (dt, $J = 8.6, 3.6$ Hz, 4H), -0.00 – -0.06 (m, 4H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 140.23, 136.68, 131.27, 126.97, 73.85, 68.47, 31.01, 25.96.



5a

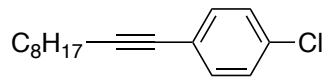
1-(dec-1-yn-1-yl)-4-fluorobenzene

5a was prepared following the general procedure 2.2 and purified by column chromatography (hexane) as a colorless oil.

$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.43 – 7.31 (m, 2H), 6.97 (t, $J = 8.7$ Hz, 2H), 2.38 (t, $J = 7.2$ Hz, 2H), 1.59 (p, $J = 7.2$ Hz, 2H), 1.48 – 1.38 (m, 2H), 1.36 – 1.22 (m, 8H), 0.94 – 0.85 (m, 3H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 162.01 (d, $J = 248.1$ Hz), 133.30 (d, $J = 8.2$ Hz), 120.15 (d, $J = 3.5$ Hz), 115.37 (d, $J = 21.8$ Hz), 90.11, 79.47, 31.88, 29.24, 29.16, 28.97, 28.74, 22.70, 19.36, 14.14.

$^{19}\text{F NMR}$ (564 MHz, Chloroform-*d*) δ -112.48.



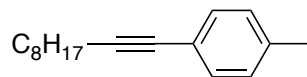
5b

1-chloro-4-(dec-1-yn-1-yl)benzene

5b was prepared following the general procedure 2.2 and purified by column chromatography (hexane) as a colorless oil.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.31 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 2H), 2.39 (t, *J* = 7.2 Hz, 2H), 1.59 (p, *J* = 7.3 Hz, 2H), 1.43 (p, *J* = 7.0 Hz, 2H), 1.34 – 1.27 (m, 8H), 0.89 (t, *J* = 6.9 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 133.36, 132.78, 128.49, 122.61, 91.61, 79.50, 31.87, 29.22, 29.14, 28.96, 28.67, 22.69, 19.42, 14.15.



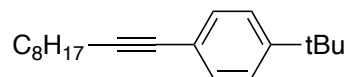
5c

1-(dec-1-yn-1-yl)-4-methylbenzene

5c was prepared following the general procedure 2.2 and purified by column chromatography (hexane) as a colorless oil.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.28 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 2.39 (t, *J* = 7.2 Hz, 2H), 2.33 (s, 3H), 1.64 – 1.58 (m, 2H), 1.49 – 1.40 (m, 2H), 1.35 – 1.27 (m, 8H), 0.88 (t, *J* = 7.0 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 137.42, 131.41, 128.95, 120.99, 89.69, 80.54, 31.88, 29.24, 29.17, 28.97, 28.85, 22.70, 21.43, 19.45, 14.15.



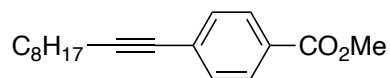
5d

1-(tert-butyl)-4-(dec-1-yn-1-yl)benzene

5d was prepared following the general procedure 2.2 and purified by column chromatography (hexane) as a colorless oil.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.33 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.7 Hz, 2H), 1.64 – 1.57 (m, 2H), 1.43 (q, *J* = 7.0 Hz, 2H), 1.30 (s, 17H), 0.88 (t, *J* = 7.0 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 150.58, 131.22, 125.18, 121.08, 89.72, 80.52, 34.67, 31.88, 31.22, 29.25, 29.17, 28.95, 28.86, 22.70, 19.45, 14.15.



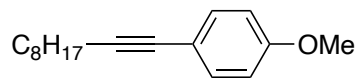
5e

methyl 4-(dec-1-yn-1-yl)benzoate

5e was prepared following the general procedure 2.2 and purified by column chromatography (hexane/EA = 10:1) as a colorless oil.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.95 (d, J = 8.6 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H), 3.91 (s, 3H), 2.42 (t, J = 7.1 Hz, 2H), 1.61 (p, J = 7.2 Hz, 2H), 1.45 (dq, J = 9.5, 7.2 Hz, 2H), 1.34 – 1.27 (m, 8H), 0.91 – 0.87 (m, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 166.73, 131.48, 129.41, 128.96, 128.79, 94.08, 80.10, 52.19, 31.86, 29.22, 29.13, 28.96, 28.59, 22.69, 19.53, 14.15.



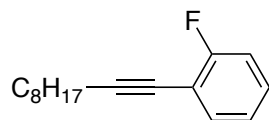
5f

1-(dec-1-yn-1-yl)-4-methoxybenzene

5f was prepared following the general procedure 2.2 and purified by column chromatography (hexane/EA = 10:1) as a colorless oil.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.33 (d, J = 8.7 Hz, 2H), 6.81 (d, J = 8.8 Hz, 2H), 3.80 (s, 3H), 2.38 (t, J = 7.1 Hz, 2H), 1.59 (p, J = 7.3 Hz, 2H), 1.49 – 1.39 (m, 2H), 1.36 – 1.26 (m, 8H), 0.88 (t, J = 6.9 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 158.95, 132.86, 116.26, 113.79, 88.86, 80.21, 55.27, 31.88, 29.25, 29.17, 28.98, 28.90, 22.70, 19.44, 14.15.



5g

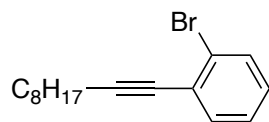
1-(dec-1-yn-1-yl)-2-fluorobenzene

5g was prepared following the general procedure 2.2 and purified by column chromatography (hexane) as a colorless oil.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.39 (td, J = 7.5, 1.9 Hz, 1H), 7.26 – 7.21 (m, 1H), 7.08 – 7.02 (m, 2H), 2.45 (t, J = 7.1 Hz, 2H), 1.62 (p, J = 7.2 Hz, 2H), 1.46 (tt, J = 9.4, 6.1 Hz, 2H), 1.30 (ddd, J = 15.3, 8.4, 3.0 Hz, 8H), 0.95 – 0.84 (m, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 162.81 (d, J = 249.9 Hz), 129.07 (d, J = 7.8 Hz), 123.78 (d, J = 3.8 Hz), 115.35 (d, J = 21.0 Hz), 112.53 (d, J = 15.8 Hz), 133.56, 96.04, 73.85, 31.87, 29.23, 29.14, 28.91, 28.63, 22.70, 19.63, 14.15.

¹⁹F NMR (564 MHz, Chloroform-*d*) δ -111.14.



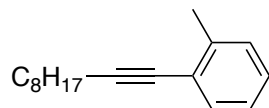
5h

1-bromo-2-(dec-1-yn-1-yl)benzene

5h was prepared following the general procedure 2.2 and purified by column chromatography (hexane) as a colorless oil.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.55 (dd, $J = 8.1, 1.2$ Hz, 1H), 7.42 (dd, $J = 7.7, 1.7$ Hz, 1H), 7.22 (td, $J = 7.6, 1.2$ Hz, 1H), 7.11 (td, $J = 7.7, 1.7$ Hz, 1H), 2.46 (t, $J = 7.1$ Hz, 2H), 1.64 (p, $J = 7.1$ Hz, 2H), 1.53 – 1.46 (m, 2H), 1.35 – 1.27 (m, 8H), 0.92 – 0.86 (m, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 133.31, 132.27, 128.64, 126.90, 126.10, 125.46, 95.69, 79.35, 31.88, 29.25, 29.14, 28.90, 28.58, 22.70, 19.60, 14.16.



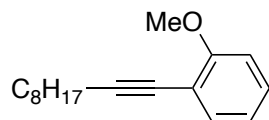
5i

1-(dec-1-yn-1-yl)-2-methylbenzene

5i was prepared following the general procedure 2.2 and purified by column chromatography (hexane) as a colorless oil.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.36 (d, $J = 7.2$ Hz, 1H), 7.19 – 7.14 (m, 2H), 7.13 – 7.06 (m, 1H), 2.45 (t, $J = 7.1$ Hz, 2H), 2.41 (s, 3H), 1.61 (p, $J = 7.2$ Hz, 2H), 1.51 – 1.44 (m, 2H), 1.33 – 1.27 (m, 8H), 0.89 (t, $J = 6.9$ Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 139.94, 131.78, 129.28, 127.44, 125.41, 123.86, 94.50, 79.43, 31.88, 29.26, 29.15, 28.92, 28.84, 22.70, 20.77, 19.57, 14.15.



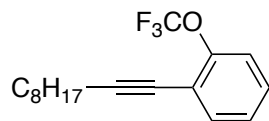
5j

1-(dec-1-yn-1-yl)-2-methoxybenzene

5j was prepared following the general procedure 2.2 and purified by column chromatography (hexane/EA = 20:1) as a colorless oil.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.38 (dd, $J = 7.5, 1.8$ Hz, 1H), 7.24 (ddd, $J = 8.2, 7.5, 1.8$ Hz, 1H), 6.90 – 6.84 (m, 2H), 3.88 (s, 3H), 2.47 (t, $J = 7.2$ Hz, 2H), 1.63 (p, $J = 7.3$ Hz, 2H), 1.50 – 1.43 (m, 2H), 1.30 (ddd, $J = 14.6, 8.2, 3.3$ Hz, 6H), 0.88 (t, $J = 6.9$ Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 159.79, 133.68, 128.86, 120.39, 113.13, 110.49, 94.80, 76.58, 55.80, 31.88, 29.27, 29.18, 28.98, 28.88, 22.71, 19.82, 14.15.



5k

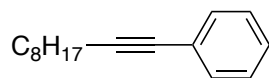
1-(dec-1-yn-1-yl)-2-(trifluoromethoxy)benzene

5k was prepared following the general procedure 2.2 and purified by column chromatography (hexane) as a colorless oil.

^1H NMR (600 MHz, Chloroform-*d*) δ 7.45 (dd, $J = 7.6, 1.8$ Hz, 1H), 7.29 (ddd, $J = 8.8, 7.3, 1.7$ Hz, 1H), 7.25 – 7.20 (m, 2H), 2.44 (t, $J = 7.0$ Hz, 2H), 1.61 (p, $J = 7.1$ Hz, 2H), 1.50 – 1.43 (m, 2H), 1.34 – 1.27 (m, 8H), 0.91 – 0.86 (m, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 149.40, 133.60, 128.56, 126.61, 121.21, 120.86 (q, $J = 258.1$ Hz), 118.82, 96.37, 74.76, 31.86, 29.21, 29.15, 28.79, 28.54, 22.69, 19.55, 14.12.

^{19}F NMR (564 MHz, Chloroform-*d*) δ -57.52.



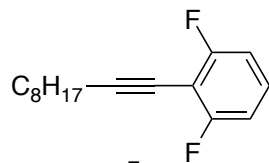
5l

dec-1-yn-1-ylbenzene

5l was prepared following the general procedure 2.2 and purified by column chromatography (hexane) as a colorless oil.

^1H NMR (600 MHz, Chloroform-*d*) δ 7.42 – 7.34 (m, 2H), 7.32 – 7.26 (m, 2H), 2.41 (d, $J = 7.2$ Hz, 2H), 1.64 – 1.58 (m, 2H), 1.45 (p, $J = 7.0$ Hz, 2H), 1.33 – 1.27 (m, 8H), 0.89 (t, $J = 6.8$ Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 131.55, 128.20, 127.47, 124.09, 90.53, 80.54, 31.88, 29.24, 29.16, 28.96, 28.79, 22.70, 19.44, 14.15.



5m

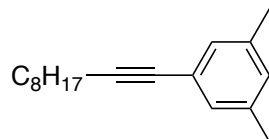
2-(dec-1-yn-1-yl)-1,3-difluorobenzene

5m was prepared following the general procedure 2.2 and purified by column chromatography (hexane) as a colorless oil.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.19 (tt, *J* = 8.4, 6.3 Hz, 1H), 6.87 (dd, *J* = 8.4, 6.9 Hz, 2H), 2.49 (t, *J* = 7.1 Hz, 2H), 1.64 (p, *J* = 7.2 Hz, 2H), 1.50 – 1.43 (m, 2H), 1.36 – 1.26 (m, 8H), 0.88 (t, *J* = 7.0 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 163.29 (d, *J* = 252.2 Hz), 128.63, 111.02 (dd, *J* = 20.3, 4.6 Hz), 102.87 (t, *J* = 19.7 Hz), 101.25, 67.38, 31.84, 29.20, 29.10, 28.83, 28.46, 22.69, 19.81, 14.14.

¹⁹F NMR (564 MHz, Chloroform-*d*) δ -108.66.



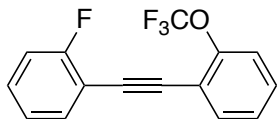
5n

1-(dec-1-yn-1-yl)-3,5-dimethylbenzene

5n was prepared following the general procedure 2.2 and purified by column chromatography (hexane) as a colorless oil.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.03 (d, *J* = 1.8 Hz, 2H), 6.94 – 6.84 (m, 1H), 2.38 (t, *J* = 7.1 Hz, 2H), 2.27 (s, 8H), 1.59 (dd, *J* = 15.0, 7.6 Hz, 3H), 1.49 – 1.39 (m, 2H), 1.34 – 1.27 (m, 8H), 0.89 (t, *J* = 6.9 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 137.72, 129.38, 129.24, 123.67, 89.74, 80.74, 31.89, 29.24, 29.17, 28.95, 28.84, 22.70, 21.12, 19.42, 14.16.



5o

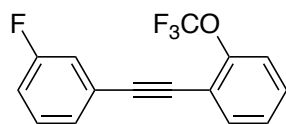
1-fluoro-2-((2-(trifluoromethoxy)phenyl)ethynyl)benzene

5o was prepared following the general procedure 2.2 and purified by column chromatography (hexane) as a colorless oil.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.64 – 7.60 (m, 1H), 7.53 (td, *J* = 7.3, 1.8 Hz, 1H), 7.41 – 7.36 (m, 1H), 7.35 – 7.28 (m, 3H), 7.18 – 7.10 (m, 2H).

¹³C NMR (151 MHz, Chloroform-*d*) δ 162.72 (d, *J* = 252.4 Hz), 149.33, 133.56 (d, *J* = 3.1 Hz), 130.51 (d, *J* = 8.1 Hz), 129.81, 126.82, 124.03 (d, *J* = 3.7 Hz), 121.43, 120.60 (q, *J* = 249.1 Hz), 117.81, 115.62 (d, *J* = 20.6 Hz), 111.48 (d, *J* = 15.6 Hz), 88.47 (d, *J* = 3.1 Hz).

¹⁹F NMR (564 MHz, Chloroform-*d*) δ -57.61, -109.50.



5p

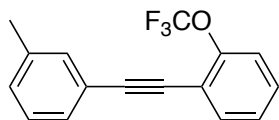
1-((3-fluorophenyl)ethynyl)-2-(trifluoromethoxy)benzene

5p was prepared following the general procedure 2.2 and purified by column chromatography (hexane) as a colorless oil.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.59 (dd, $J = 8.0, 1.7$ Hz, 1H), 7.41 – 7.37 (m, 1H), 7.35 – 7.28 (m, 4H), 7.24 (ddd, $J = 10.0, 2.3, 1.3$ Hz, 1H), 7.09 – 7.05 (m, 1H).

¹³C NMR (151 MHz, Chloroform-*d*) δ 162.39 (d, $J = 246.9$ Hz), 149.40, 133.53, 130.02 (d, $J = 8.5$ Hz), 129.82, 127.64 (d, $J = 3.0$ Hz), 126.85, 124.61 (d, $J = 9.3$ Hz), 121.44, 120.60 (q, $J = 252.2$ Hz), 118.47 (d, $J = 22.7$ Hz), 117.67, 116.10 (d, $J = 21.1$ Hz), 93.30, 84.34.

¹⁹F NMR (564 MHz, Chloroform-*d*) δ -57.53, -112.79.



5q

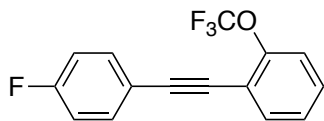
1-(m-tolylethynyl)-2-(trifluoromethoxy)benzene

5q was prepared following the general procedure 2.2 and purified by column chromatography (hexane) as a colorless oil.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.63 – 7.55 (m, 1H), 7.38 – 7.33 (m, 3H), 7.31 – 7.28 (m, 2H), 7.28 – 7.23 (m, 1H), 7.19 – 7.16 (m, 1H), 2.37 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 149.29, 138.12, 133.48, 132.26, 129.66, 129.35, 128.85, 128.31, 126.79, 122.60, 121.40, 120.85 (q, $J = 256.4$ Hz), 118.25, 94.91, 83.14, 21.28.

¹⁹F NMR (564 MHz, Chloroform-*d*) δ -57.48.



5r

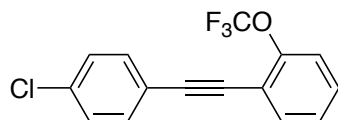
1-((4-fluorophenyl)ethynyl)-2-(trifluoromethoxy)benzene

5r was prepared following the general procedure 2.2 and purified by column chromatography (hexane) as a colorless oil.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.58 (dd, $J = 8.0, 1.7$ Hz, 1H), 7.55 – 7.50 (m, 2H), 7.39 – 7.35 (m, 1H), 7.31 – 7.27 (m, 2H), 7.10 – 7.04 (m, 2H).

¹³C NMR (151 MHz, Chloroform-*d*) δ 162.79 (d, $J = 250.5$ Hz), 149.29, 133.67 (d, $J = 8.5$ Hz), 133.39, 129.52, 126.83, 121.42, 120.63 (q, $J = 256.5$ Hz), 118.96 (d, $J = 3.1$ Hz), 117.97, 115.76 (d, $J = 22.4$ Hz), 93.60, 83.22.

¹⁹F NMR (564 MHz, Chloroform-*d*) δ -57.51, -110.17.



5s

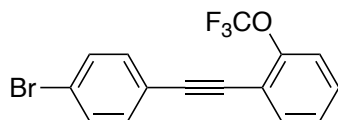
1-((4-chlorophenyl)ethynyl)-2-(trifluoromethoxy)benzene

5s was prepared following the general procedure 2.2 and purified by column chromatography (hexane) as a colorless oil.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.58 (dd, $J = 8.0, 1.7$ Hz, 1H), 7.49 – 7.45 (m, 2H), 7.40 – 7.36 (m, 1H), 7.36 – 7.33 (m, 2H), 7.32 – 7.28 (m, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 149.32, 134.80, 133.44, 132.93, 129.69, 128.79, 126.84, 121.42, 121.28, 120.65 (q, $J = 255.2$ Hz), 117.81, 93.50, 84.44.

¹⁹F NMR (564 MHz, Chloroform-*d*) δ -57.51.



5t

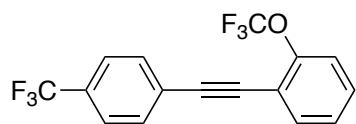
1-((4-bromophenyl)ethynyl)-2-(trifluoromethoxy)benzene

5t was prepared following the general procedure 2.2 and purified by column chromatography (hexane) as a white solid.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.58 (dd, $J = 8.0, 1.7$ Hz, 1H), 7.52 – 7.49 (m, 2H), 7.42 – 7.39 (m, 2H), 7.39 – 7.36 (m, 1H), 7.32 – 7.28 (m, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 149.32, 133.44, 133.13, 131.72, 129.73, 126.85, 123.06, 121.75, 121.43, 120.66 (q, $J = 256.5$ Hz), 117.79, 93.56, 84.62.

¹⁹F NMR (564 MHz, Chloroform-*d*) δ -57.50.



5u

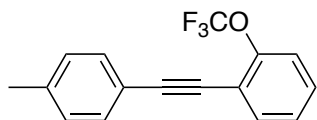
1-(trifluoromethoxy)-2-((4-(trifluoromethyl)phenyl)ethynyl)benzene

5u was prepared following the general procedure 2.2 and purified by column chromatography (hexane) as a white solid.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.66 – 7.58 (m, 5H), 7.40 (ddd, *J* = 8.4, 7.3, 1.7 Hz, 1H), 7.31 (dd, *J* = 7.9, 6.8 Hz, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 149.47, 133.58, 131.94, 130.37(q, *J* = 32.7 Hz), 129.54, 126.89, 126.59, 125.36 (q, *J* = 3.9 Hz), 123.90 (q, *J* = 272.1 Hz), 121.46, 120.61 (q, *J* = 258.0 Hz), 117.44, 93.09, 85.78.

¹⁹F NMR (564 MHz, Chloroform-*d*) δ -57.55, -62.86.



5v

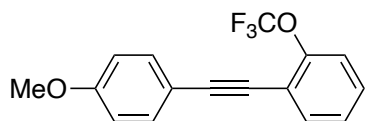
1-(p-tolyethynyl)-2-(trifluoromethoxy)benzene

5v was prepared following the general procedure 2.2 and purified by column chromatography (hexane) as a colorless oil.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.58 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.35 (ddd, *J* = 8.5, 7.1, 1.7 Hz, 1H), 7.30 – 7.27 (m, 2H), 7.20 – 7.15 (m, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 149.25, 138.97, 133.40, 131.63, 129.22, 129.18, 126.77, 121.39, 120.65 (q, *J* = 258.1 Hz), 119.72, 118.36, 94.95, 82.88, 21.60.

¹⁹F NMR (564 MHz, Chloroform-*d*) δ -57.49.



5w

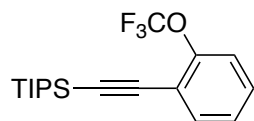
1-((4-methoxyphenyl)ethynyl)-2-(trifluoromethoxy)benzene

5w was prepared following the general procedure 2.2 and purified by column chromatography (hexane/EA = 20:1) as a colorless oil.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.58 – 7.56 (m, 1H), 7.51 – 7.47 (m, 2H), 7.34 (ddd, *J* = 8.5, 7.1, 1.7 Hz, 1H), 7.31 – 7.27 (m, 2H), 6.94 – 6.87 (m, 2H), 3.84 (s, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 159.97, 149.15, 133.25, 129.03, 126.76, 121.38, 120.66 (q, $J = 258.0$ Hz), 118.49, 114.90, 114.06, 94.84, 82.30, 55.36.

^{19}F NMR (564 MHz, Chloroform-*d*) δ -57.48.



5x

triisopropyl((2-(trifluoromethoxy)phenyl)ethynyl)silane

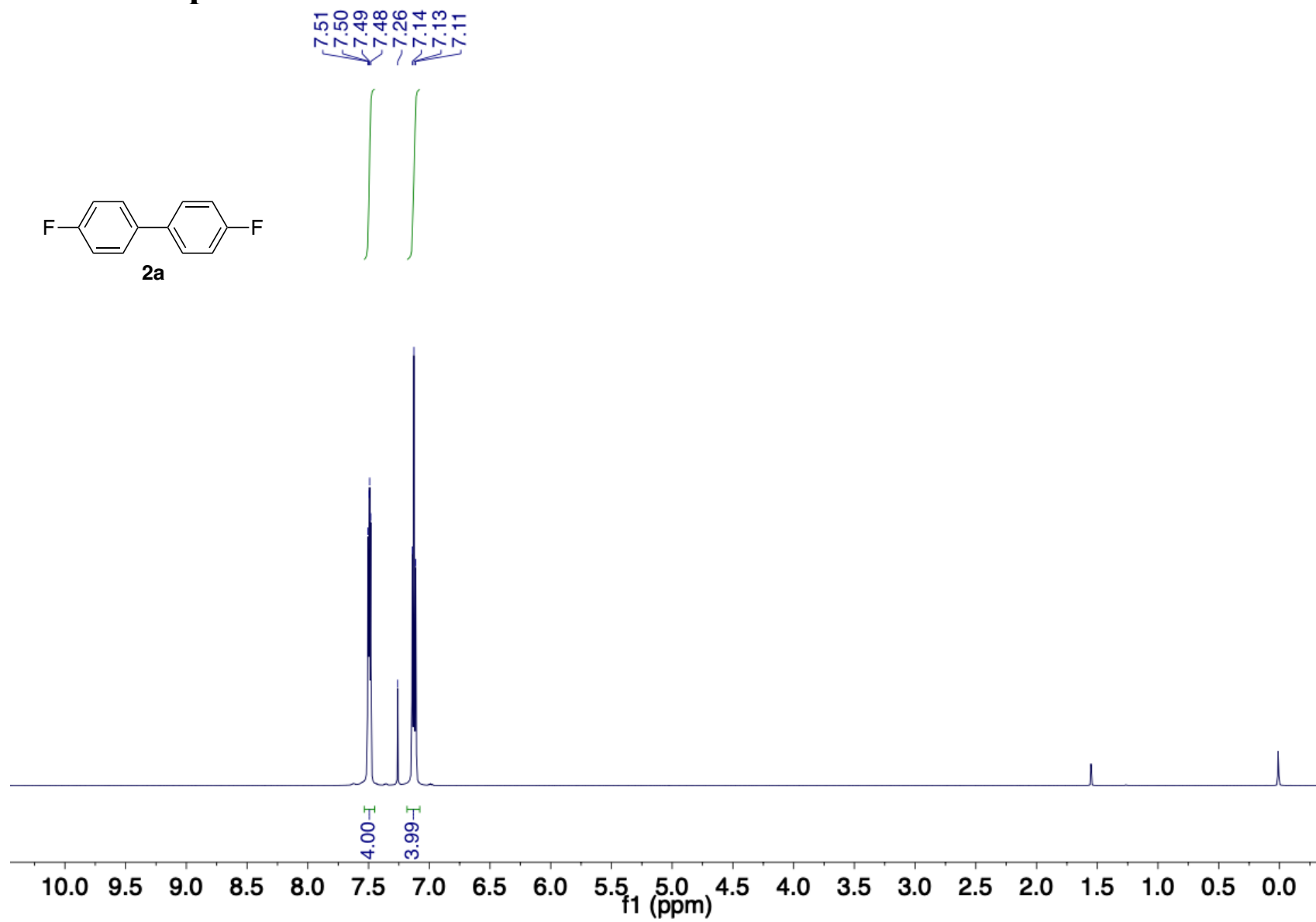
5x was prepared following the general procedure 2.2 and purified by column chromatography (hexane) as a colorless oil.

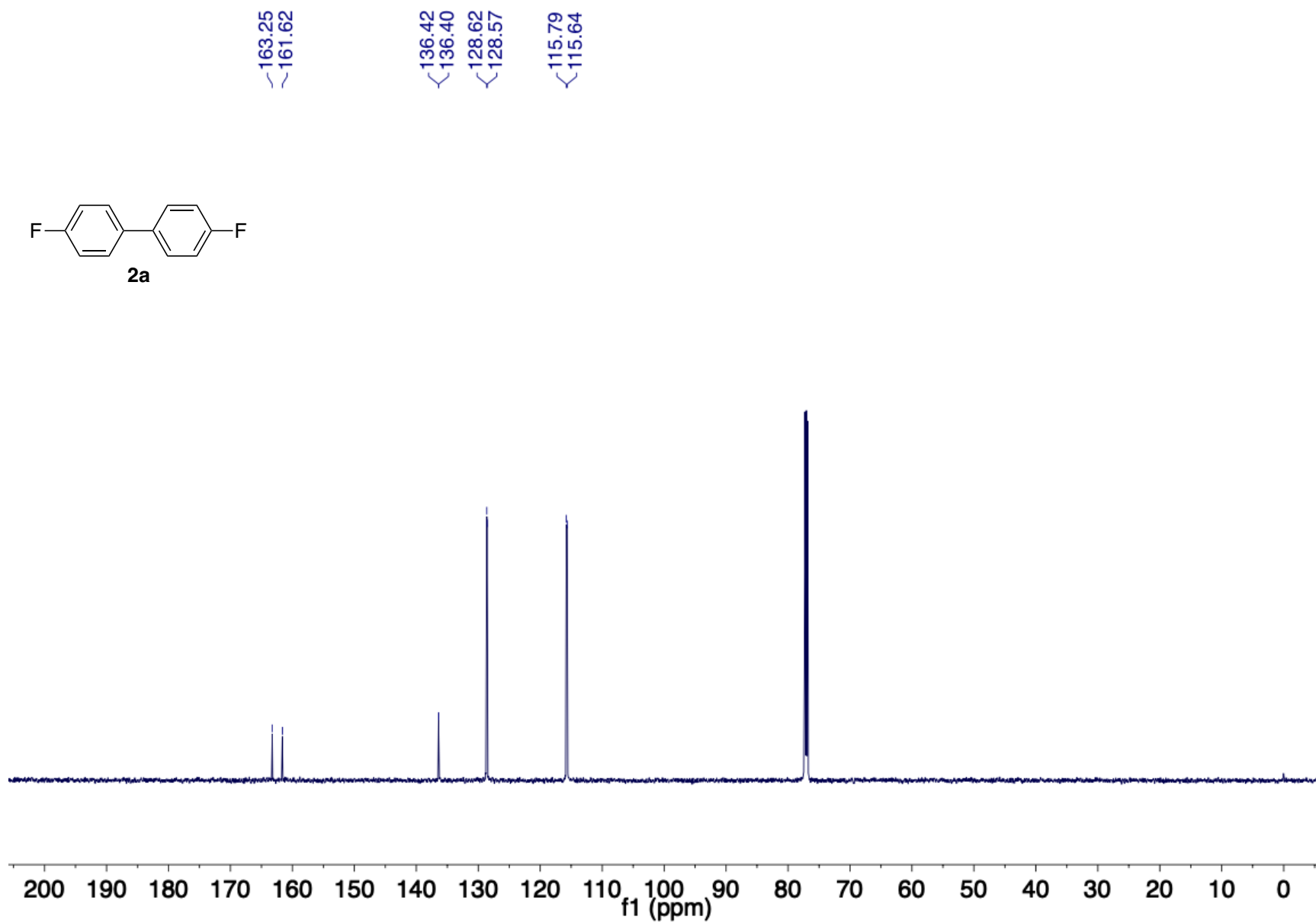
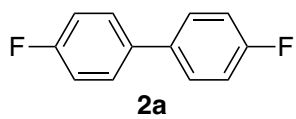
^1H NMR (600 MHz, Chloroform-*d*) δ 7.54 (dd, $J = 7.6, 1.7$ Hz, 1H), 7.34 (ddd, $J = 8.8, 7.4, 1.7$ Hz, 1H), 7.26 – 7.22 (m, 2H), 1.13 (d, $J = 2.8$ Hz, 21H).

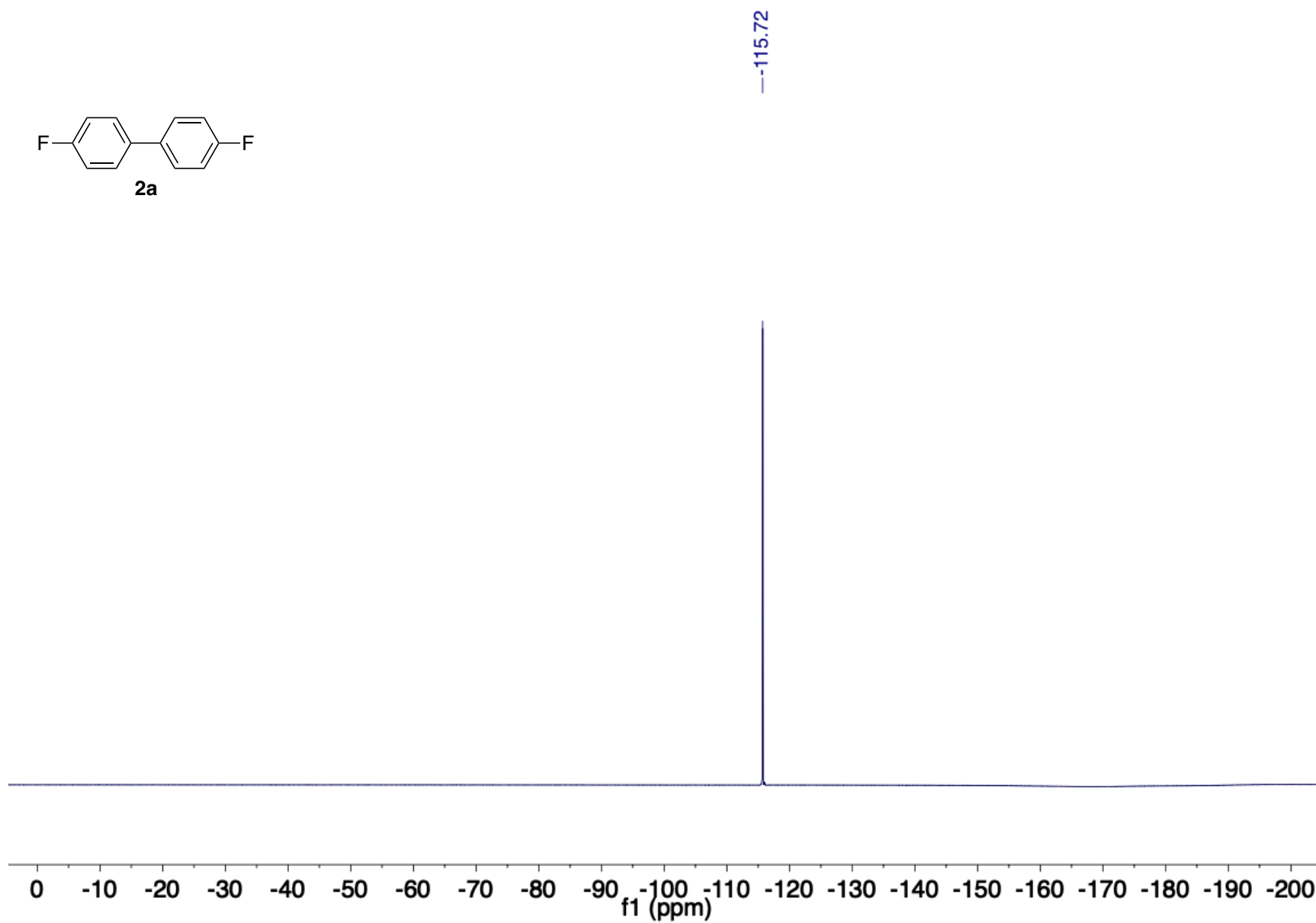
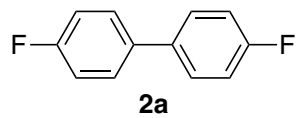
^{13}C NMR (151 MHz, CDCl_3) δ 149.73, 134.08, 129.42, 126.61, 121.27, 120.57 (q, $J = 252.0$ Hz), 118.33, 100.42, 97.08, 18.55, 11.22.

^{19}F NMR (564 MHz, Chloroform-*d*) δ -57.50.

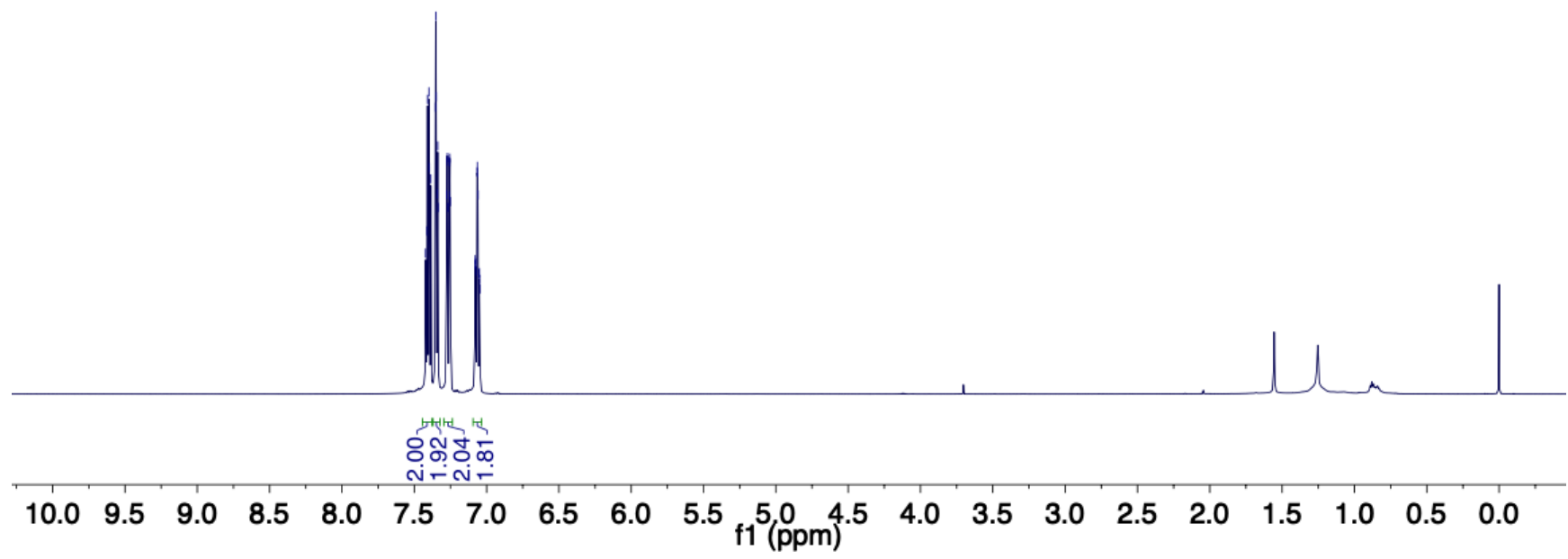
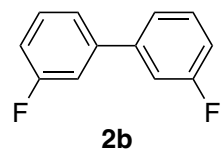
VI. NMR Spectra Data

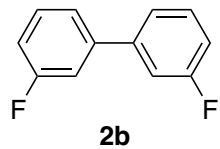






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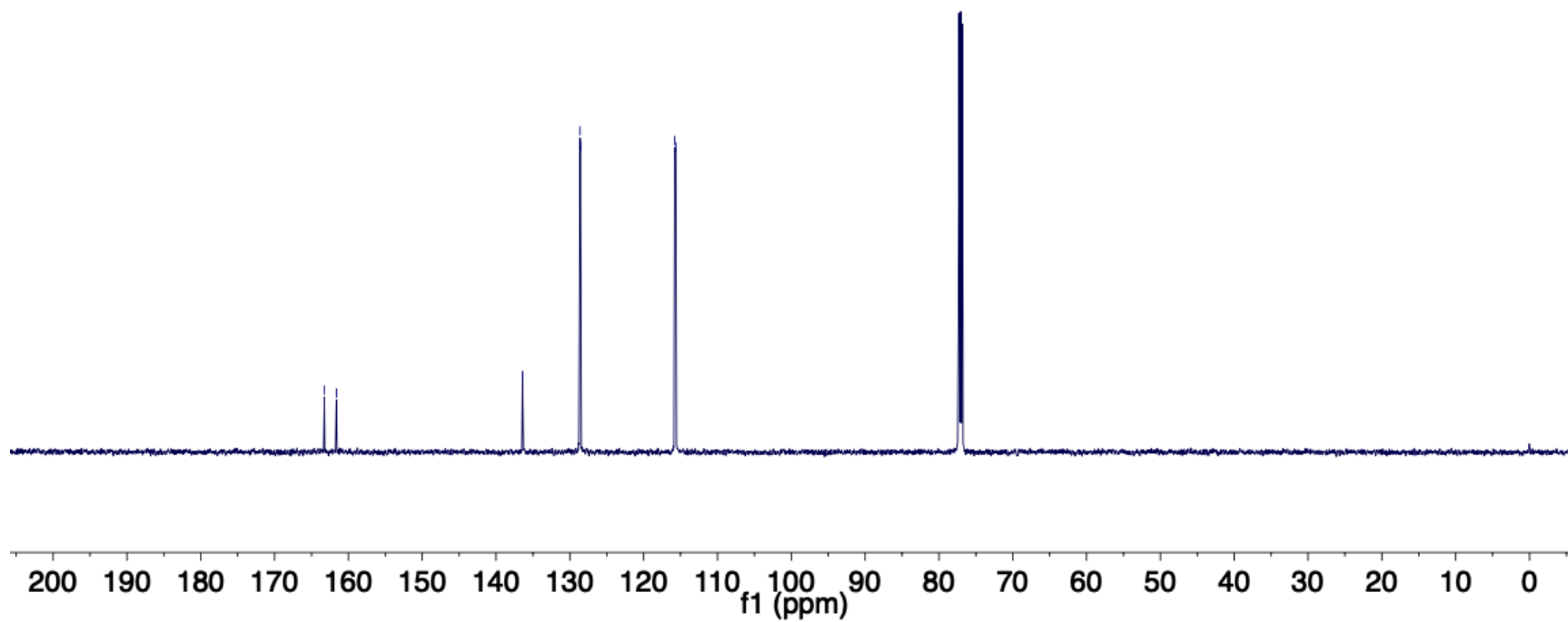


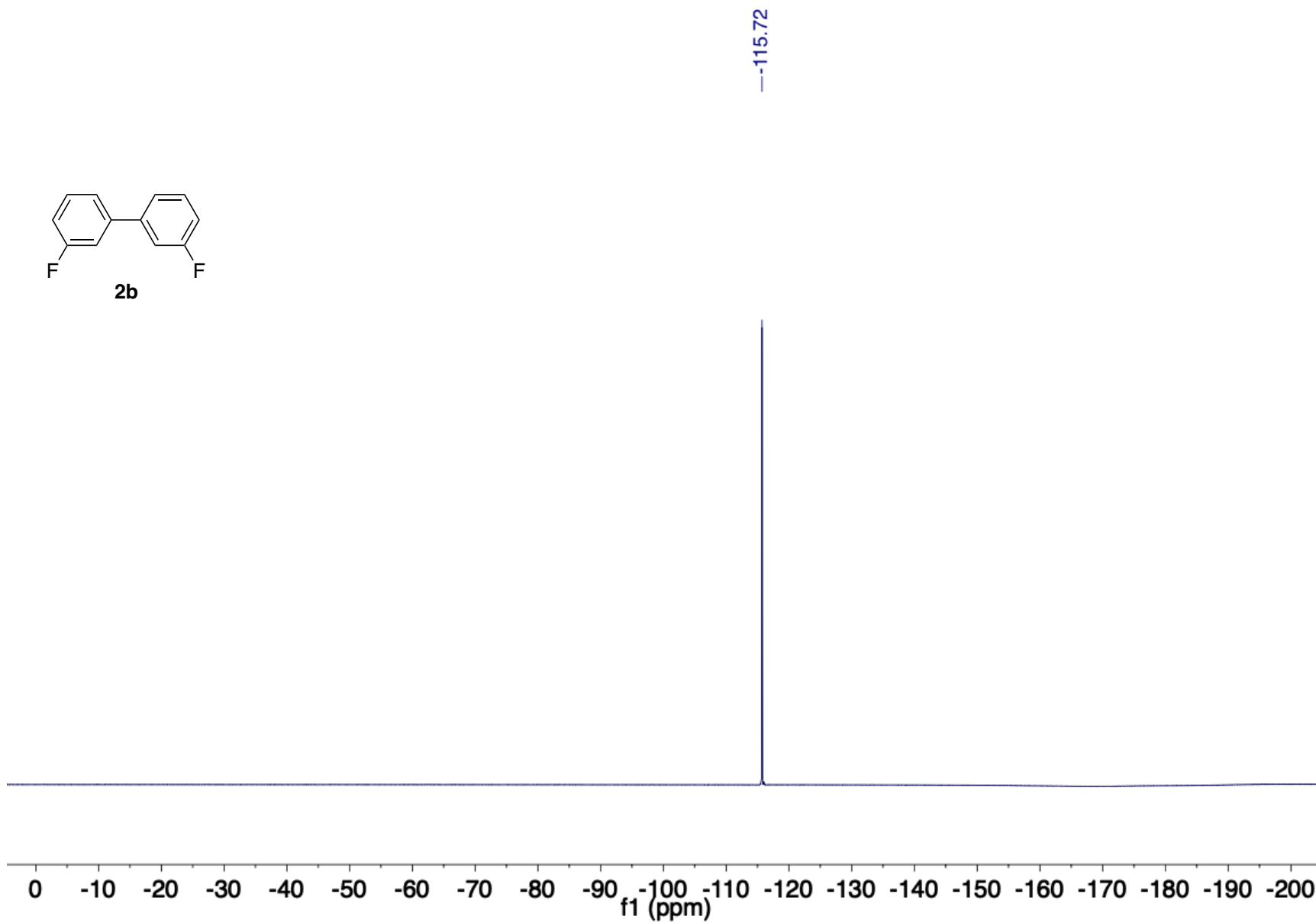
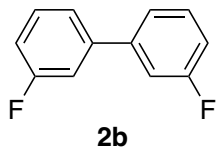


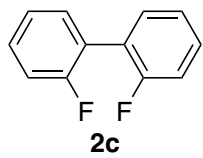
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161.62

136.42
136.40
128.62
128.57

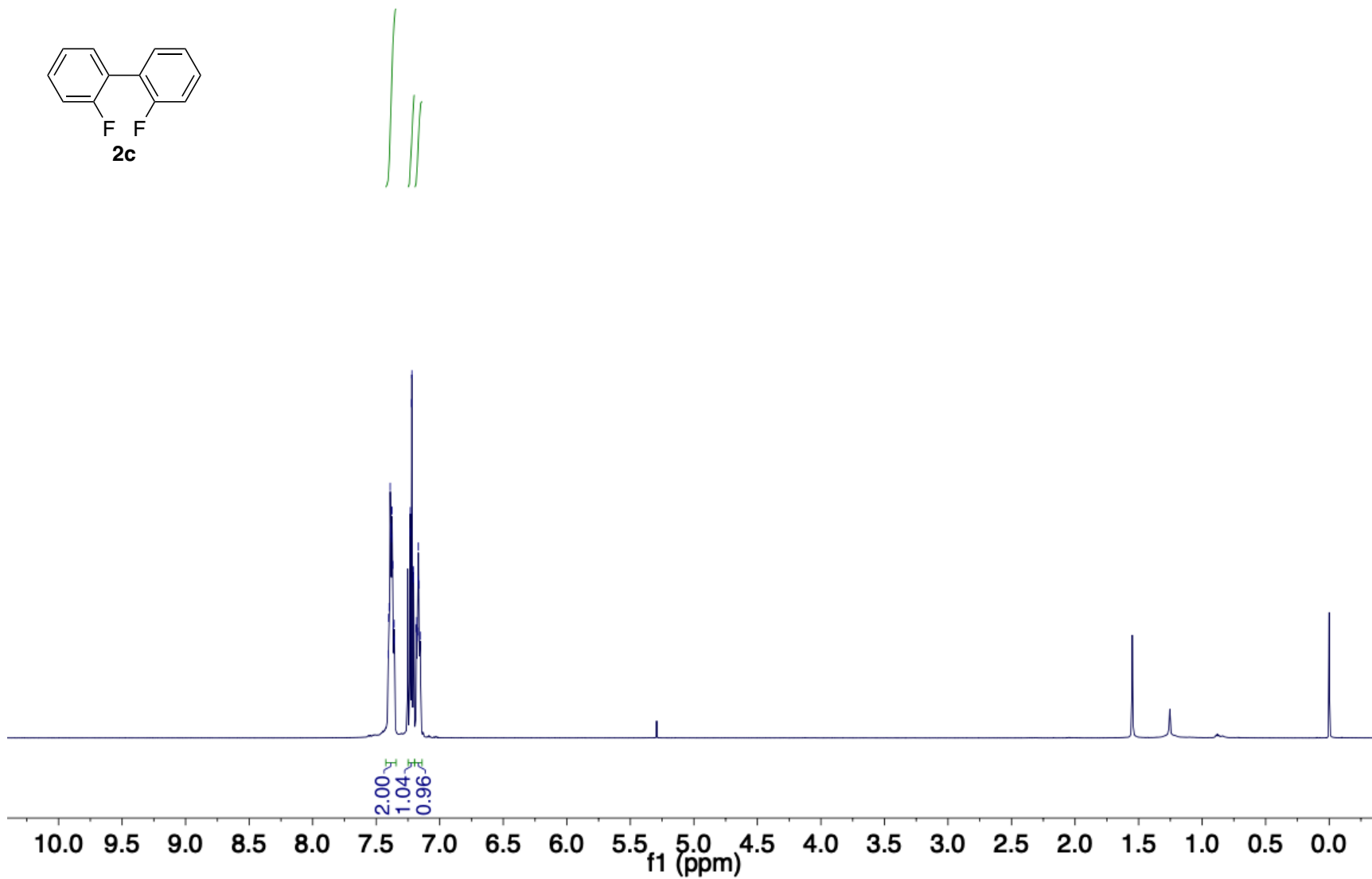
115.79
115.64

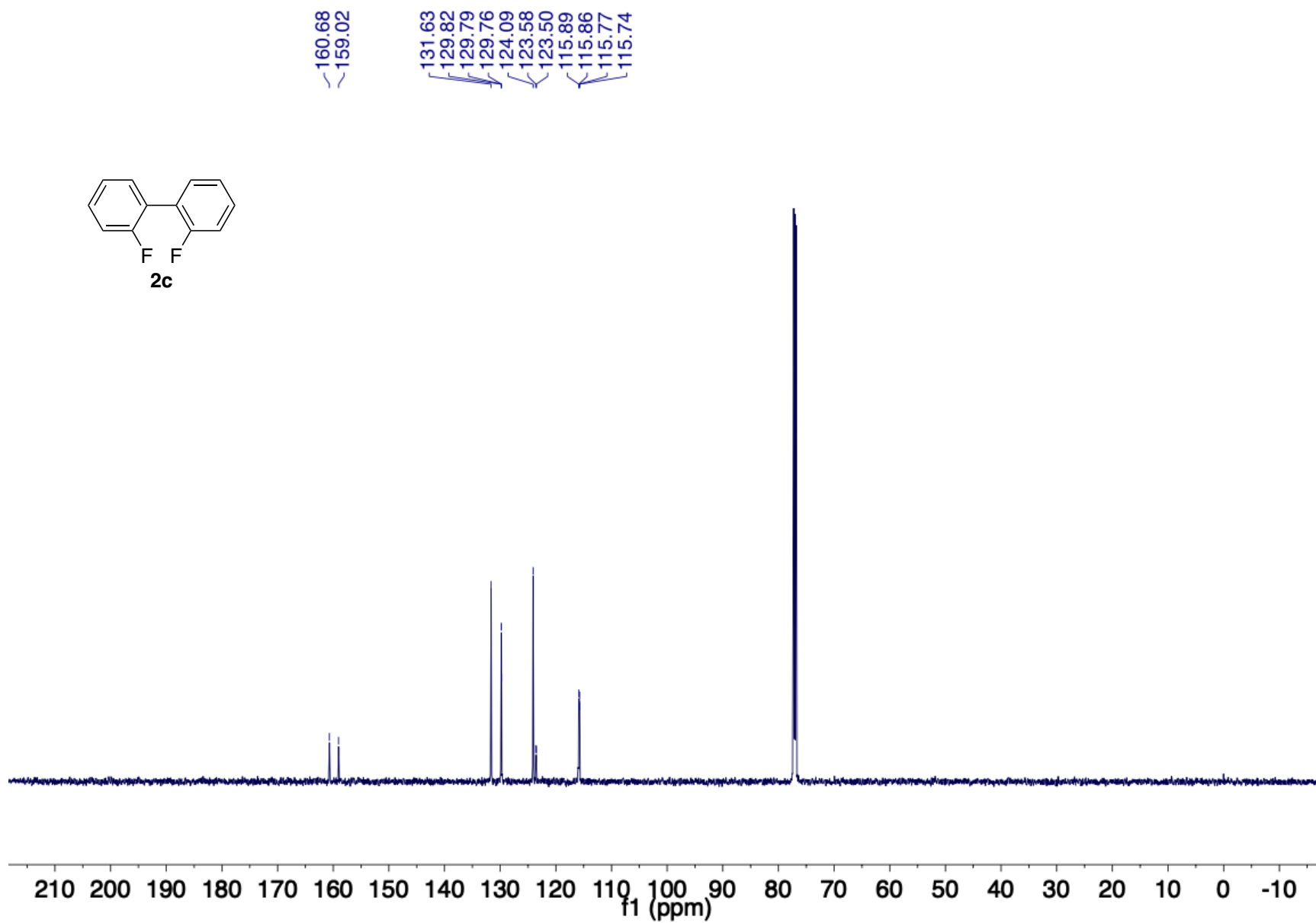
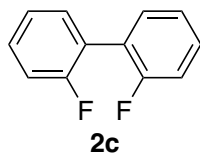


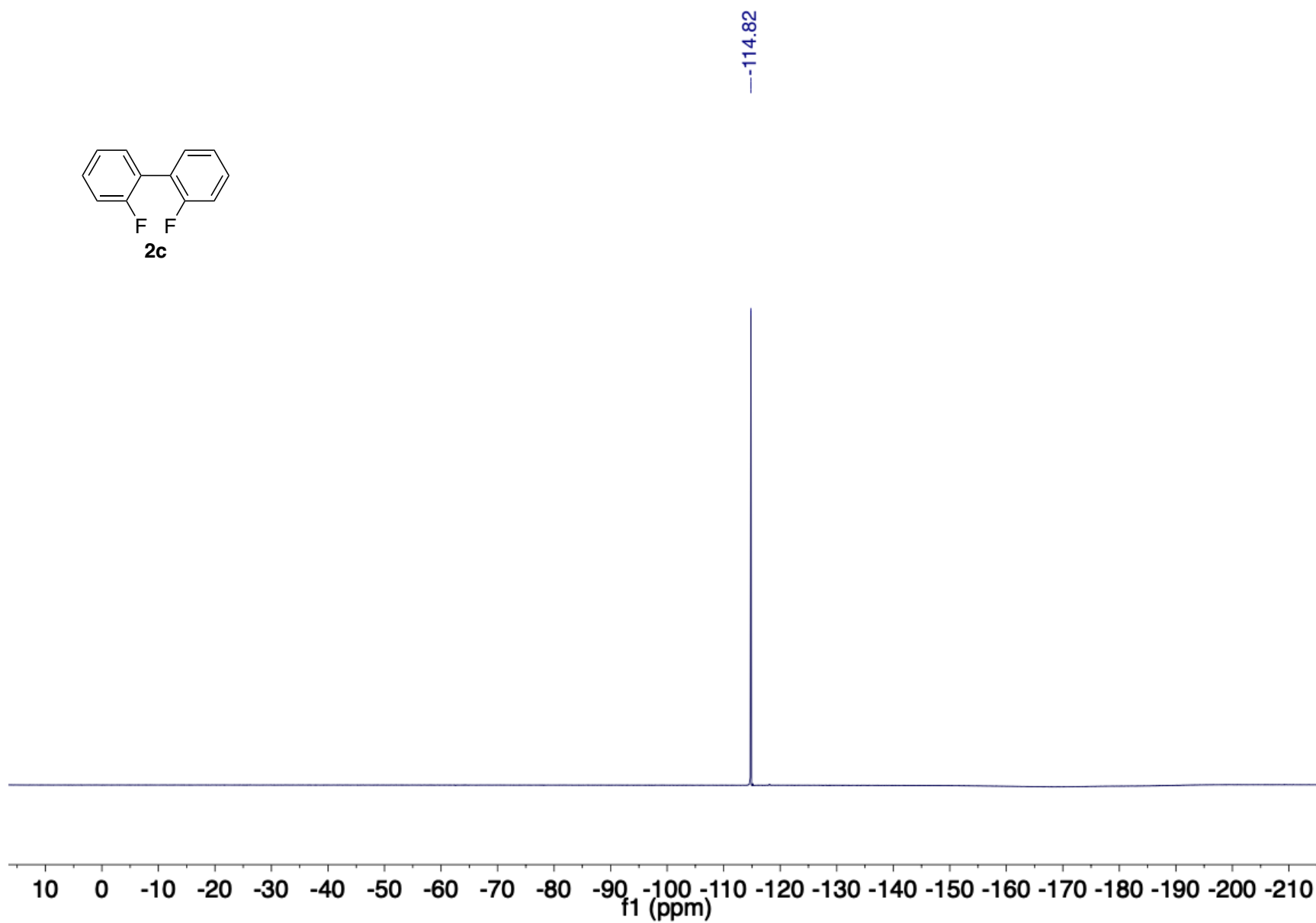
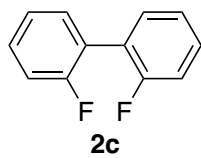


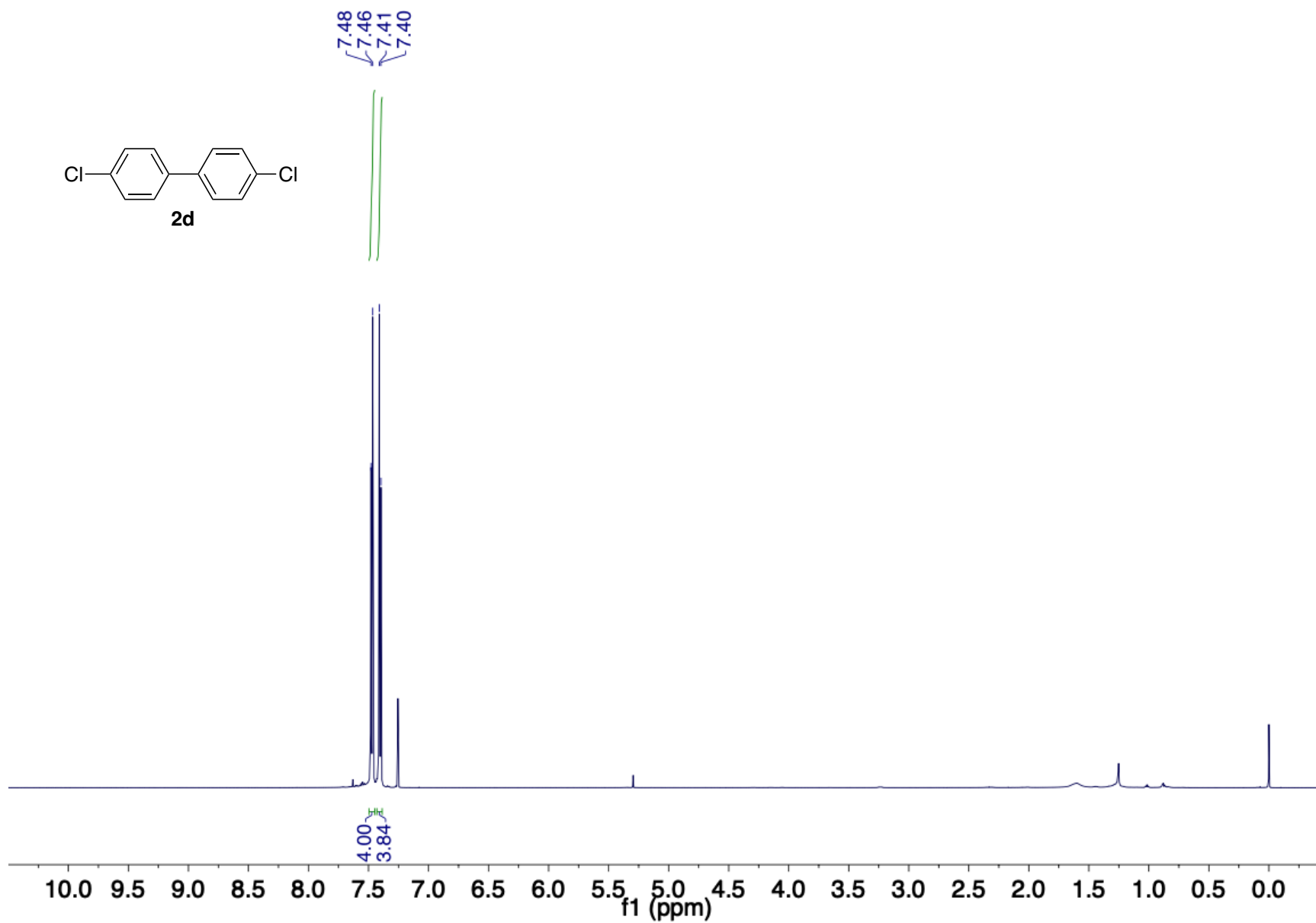
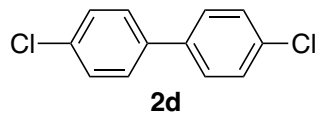


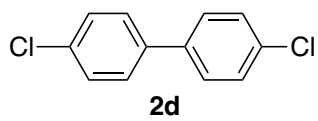
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7.15



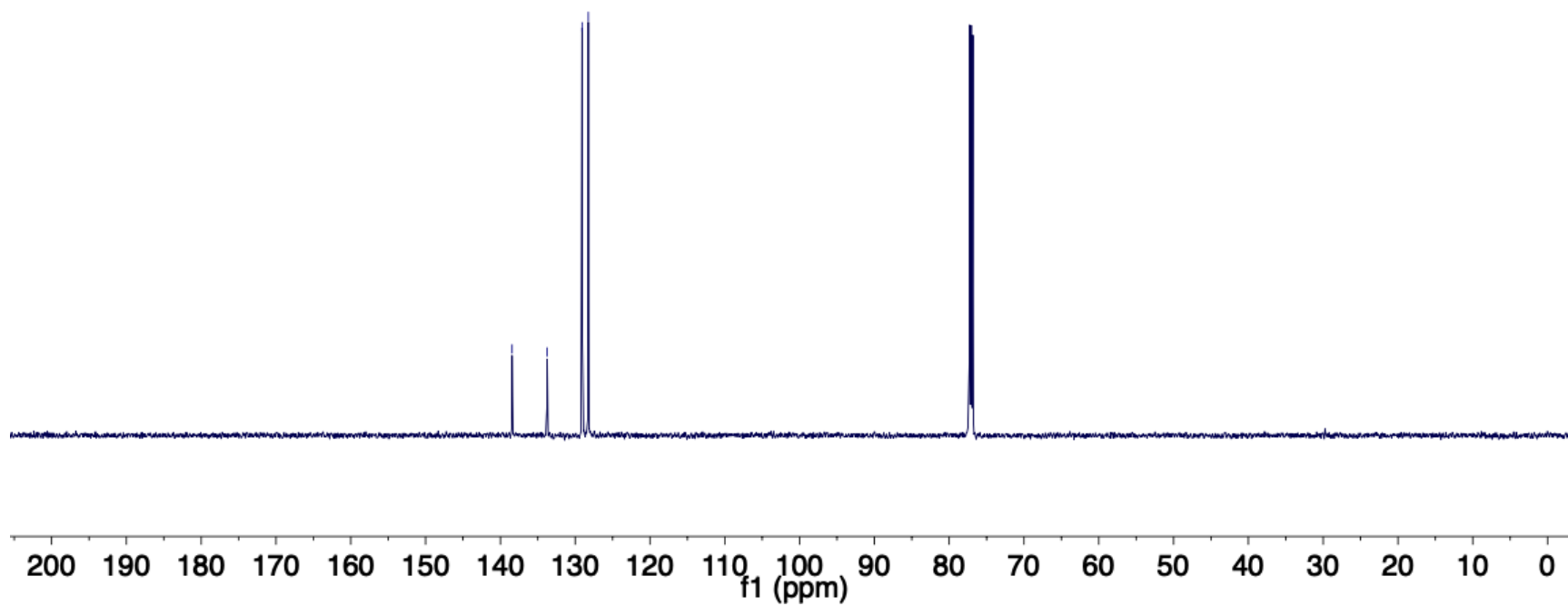


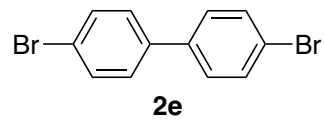




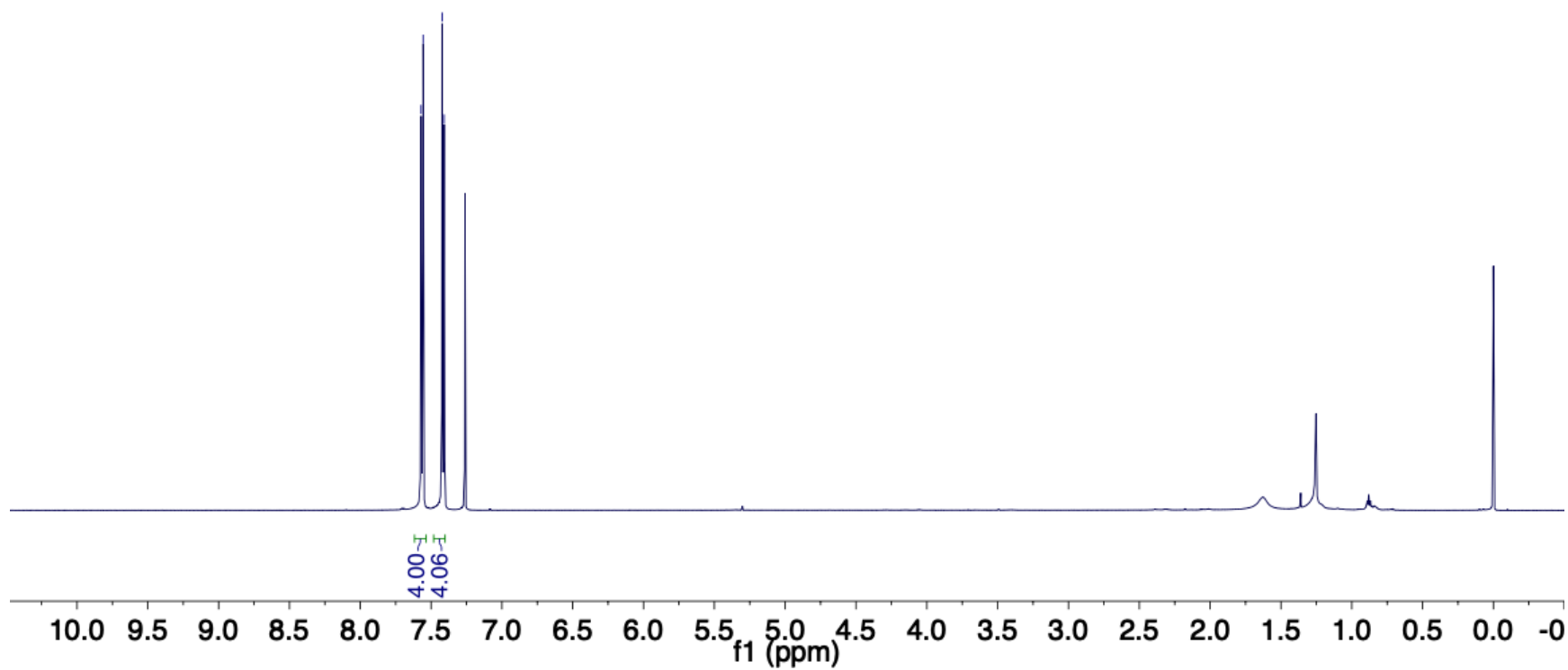


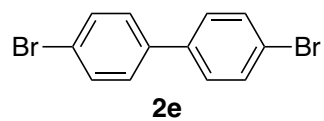
138.44
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128.25



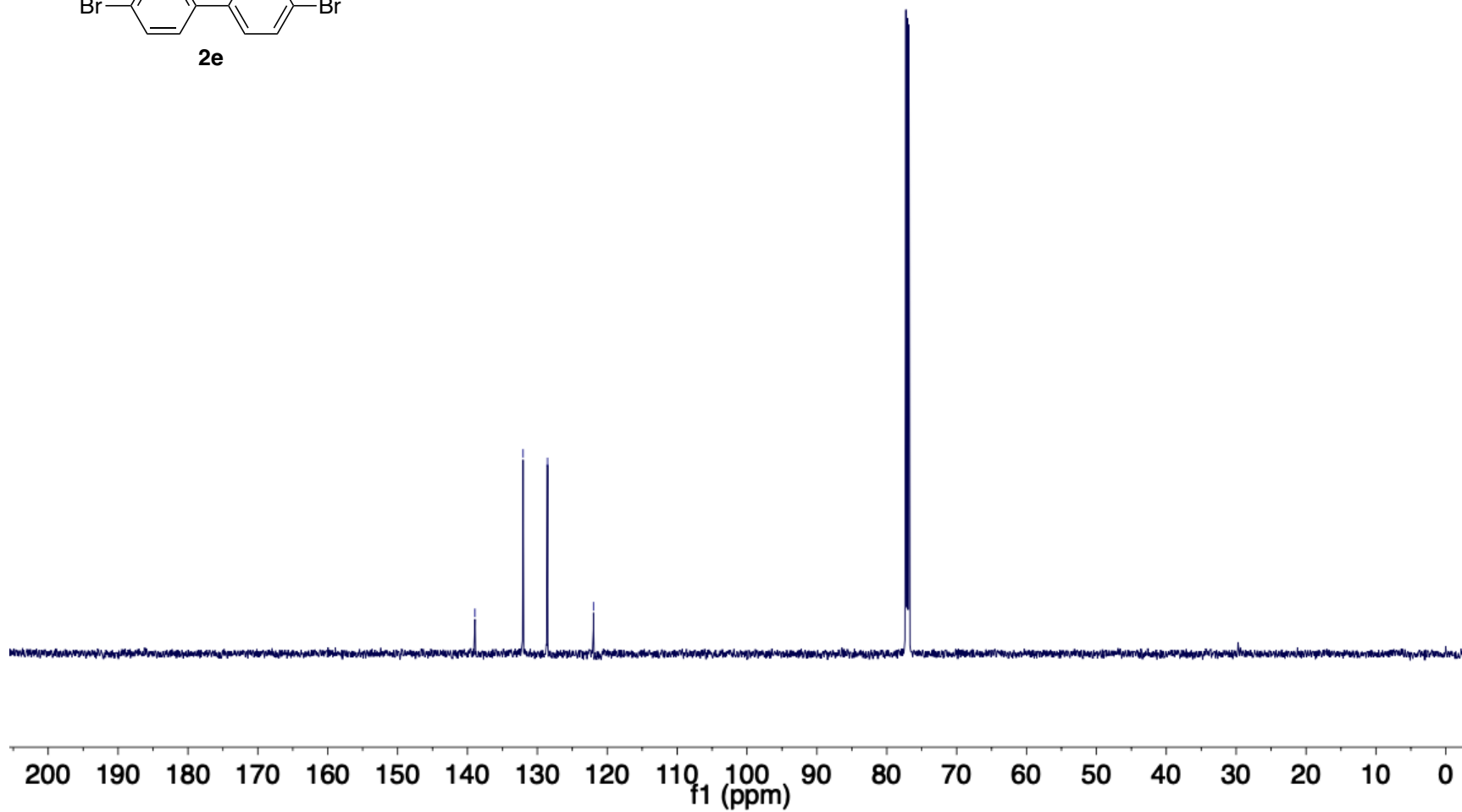


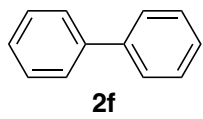
7.57
7.56
7.42
7.41



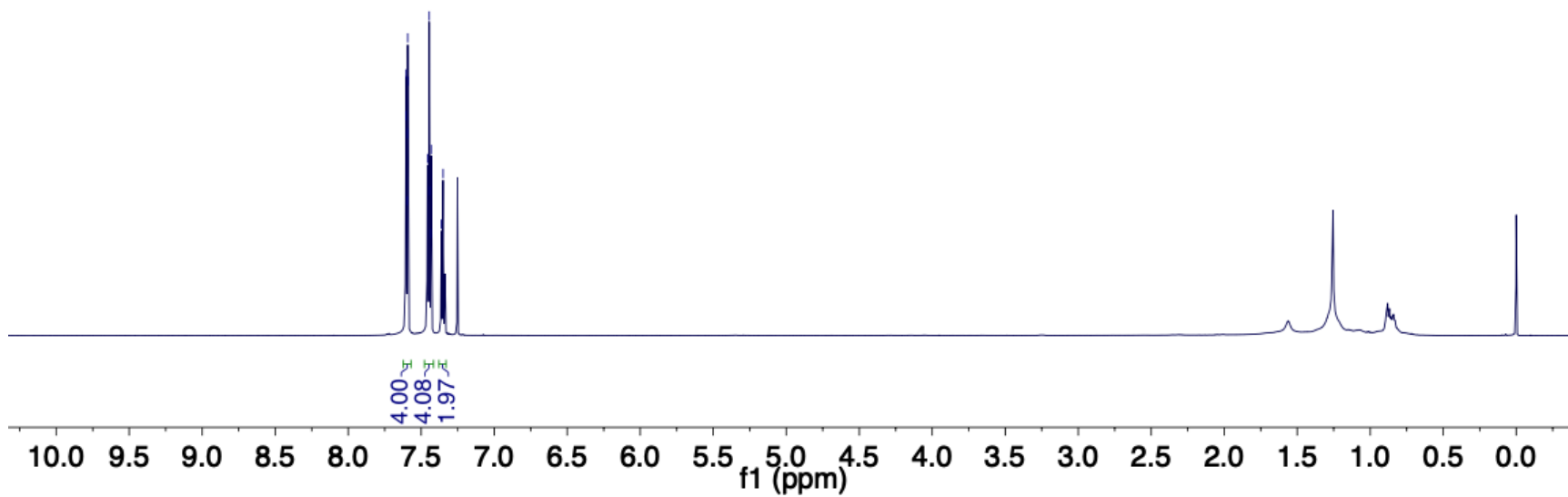


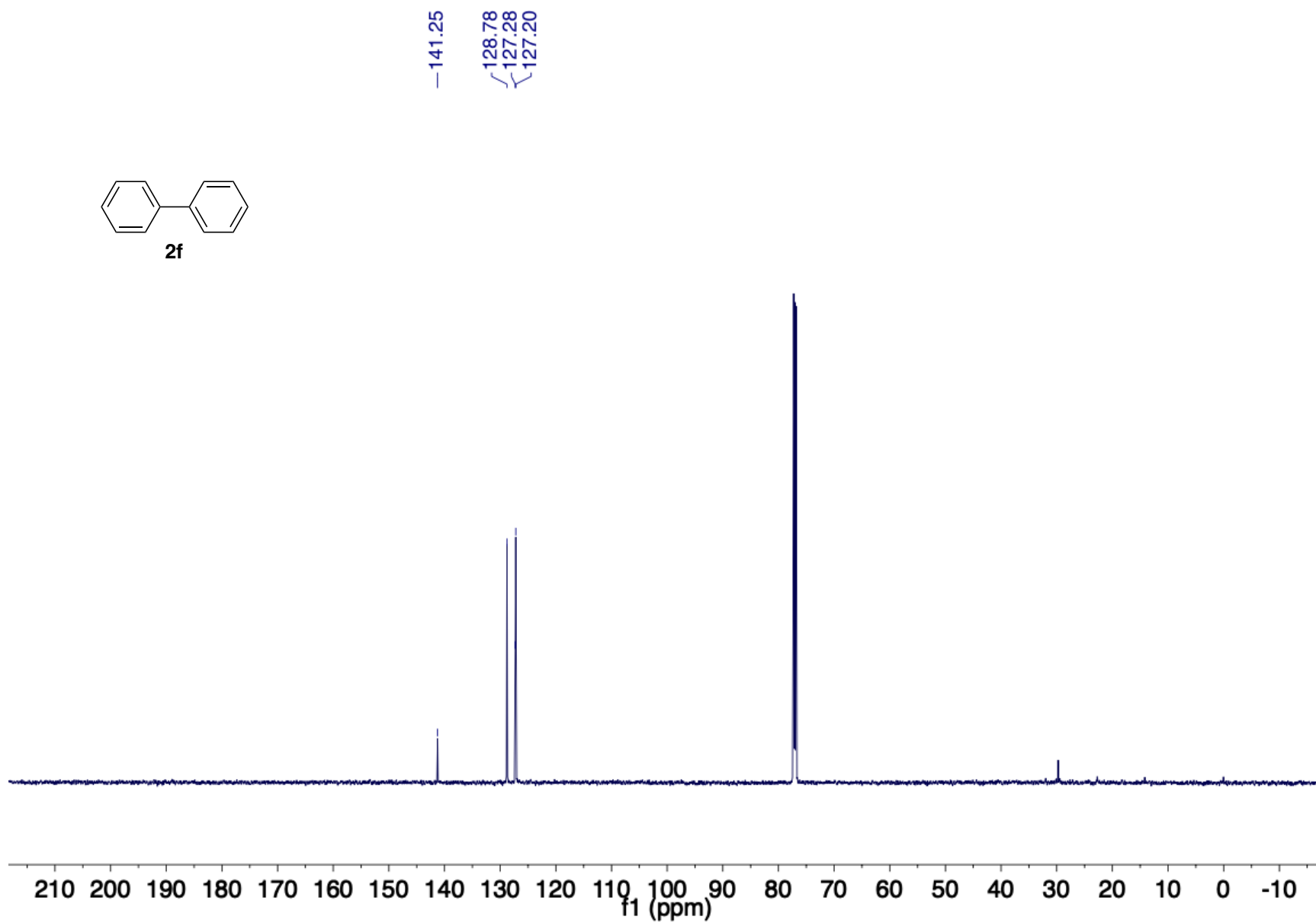
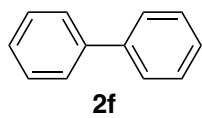
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—132.05
—128.54
—121.97

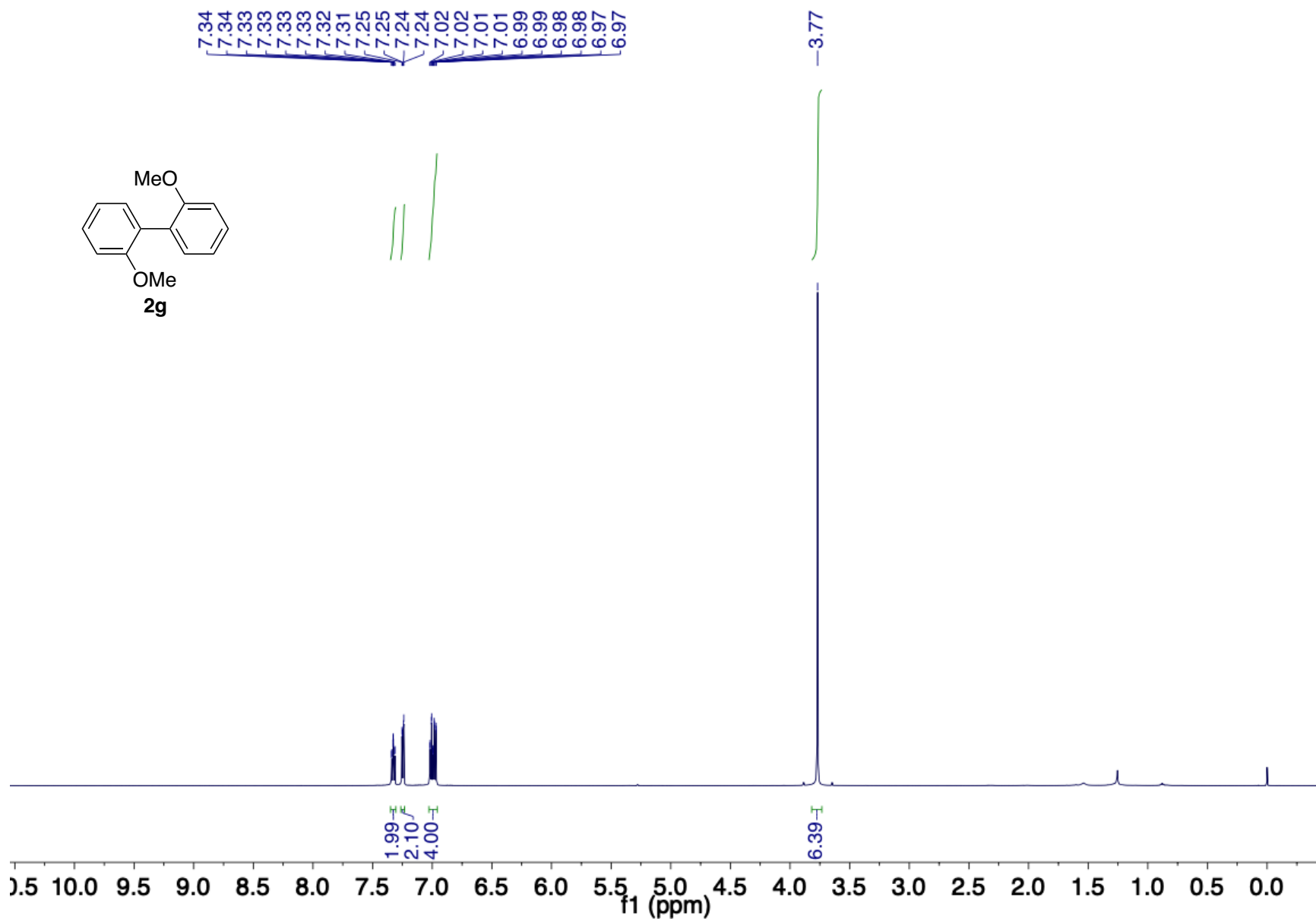


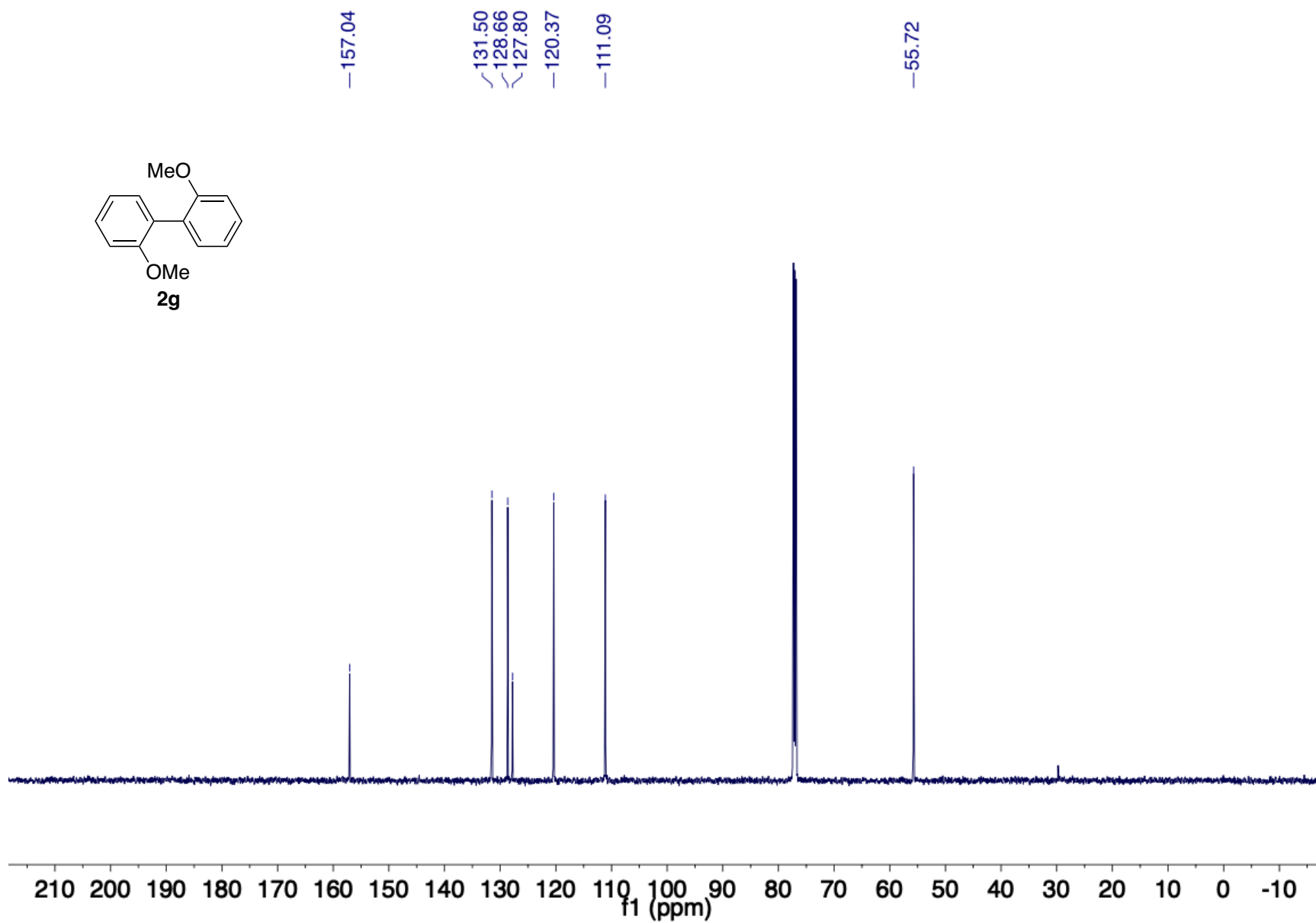
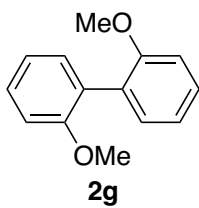


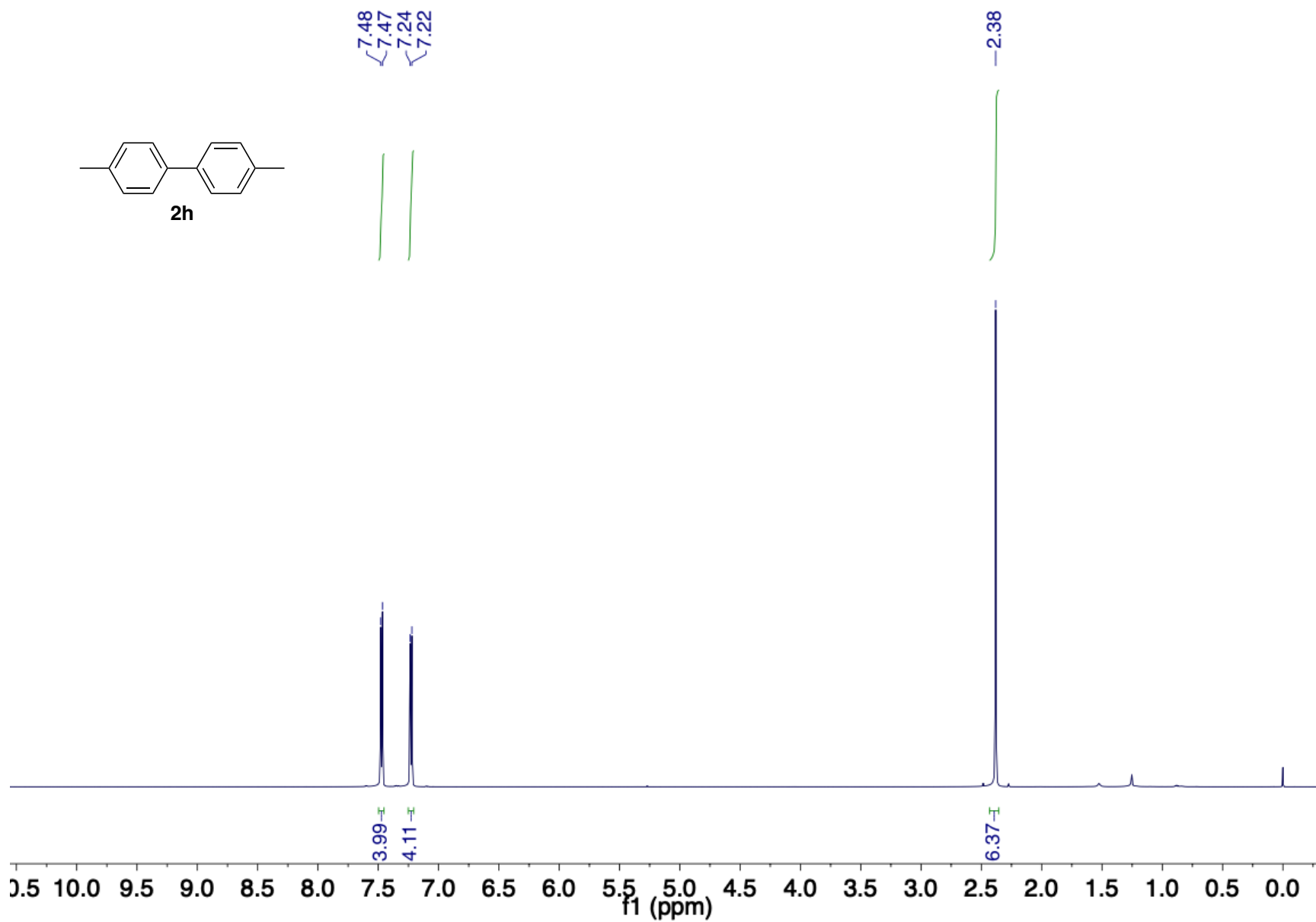
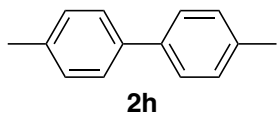
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7.36
7.35

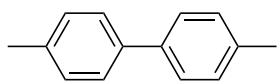








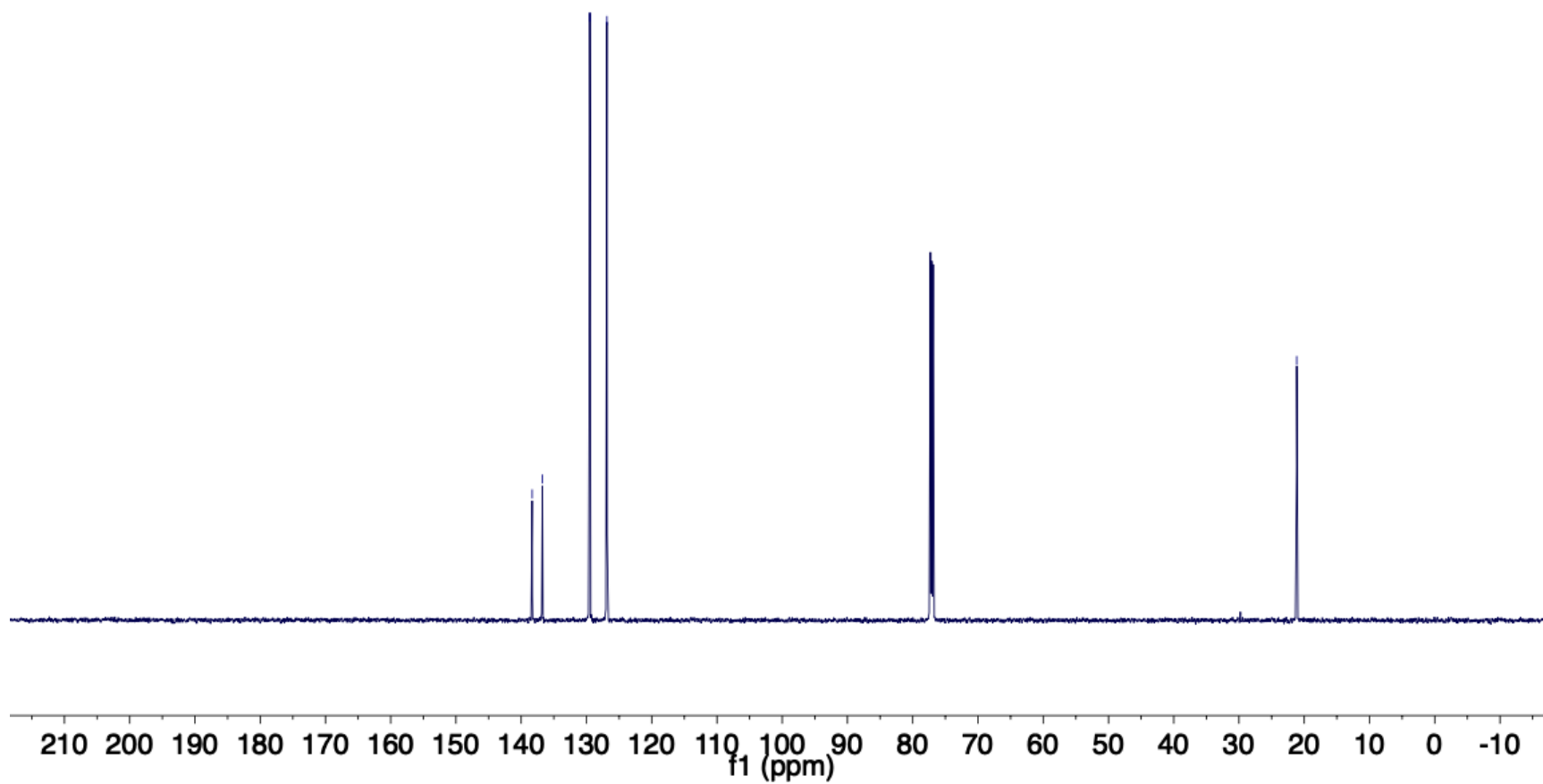


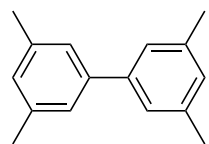


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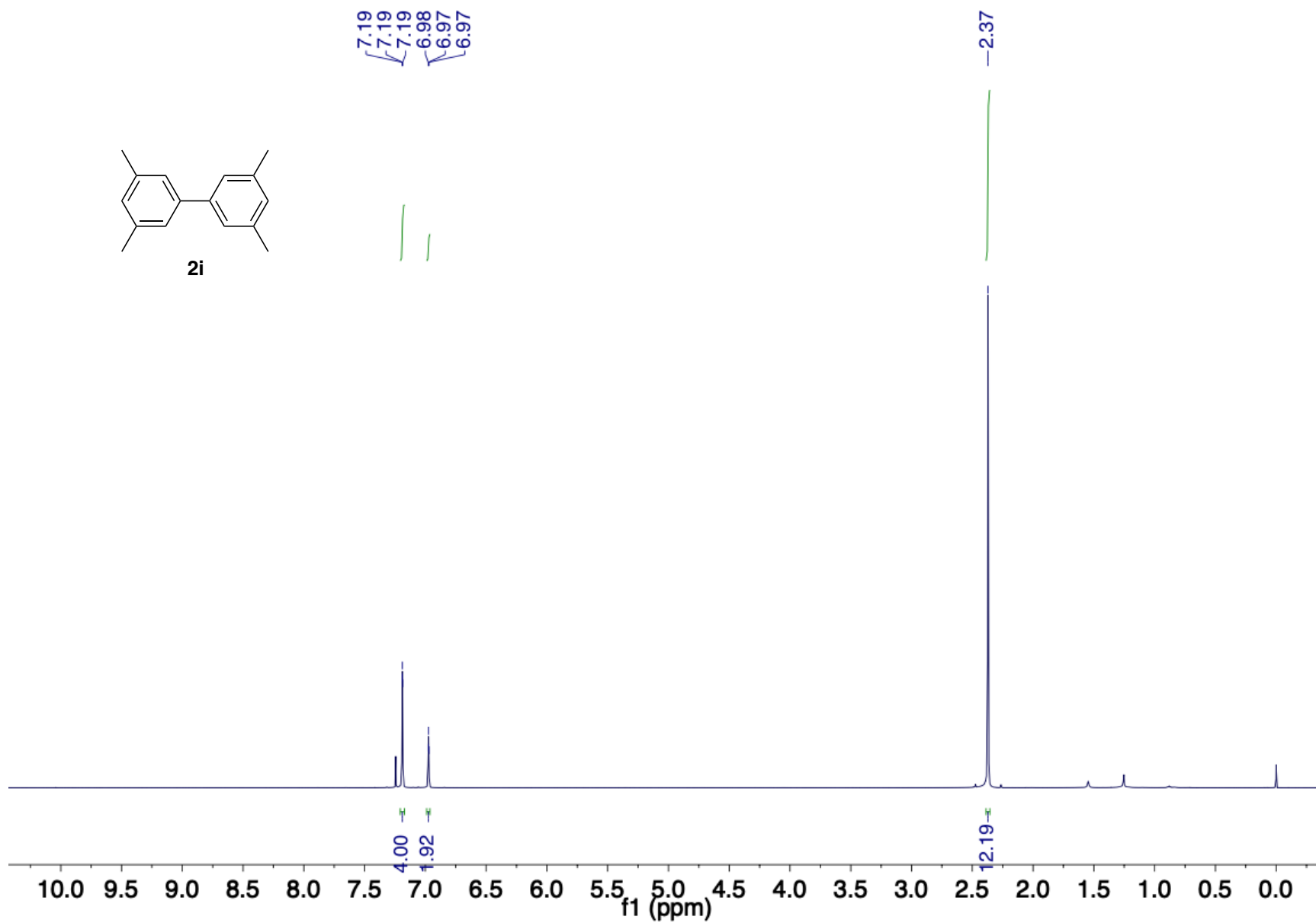
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136.75
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126.86

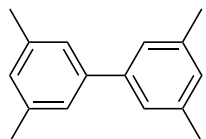
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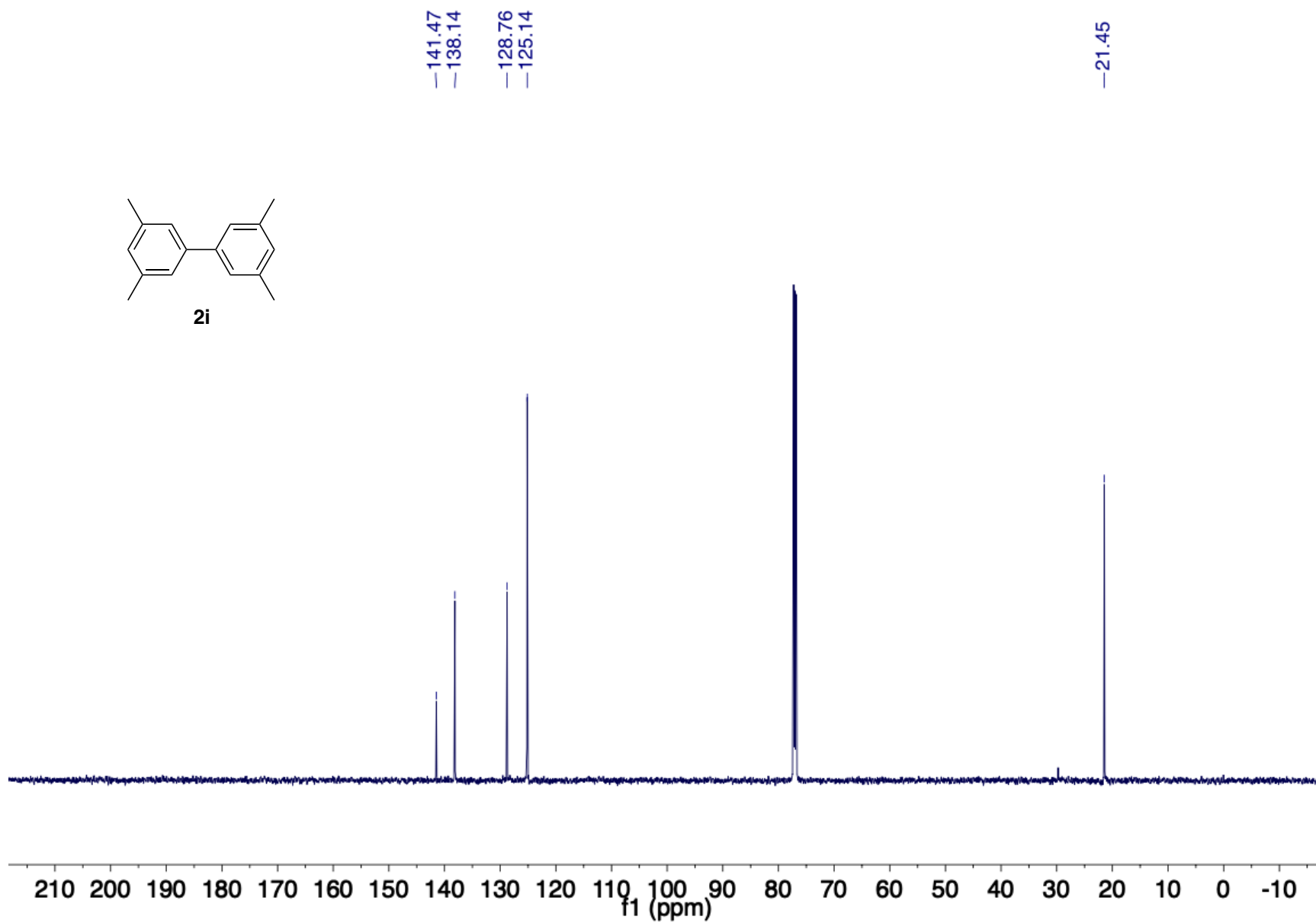


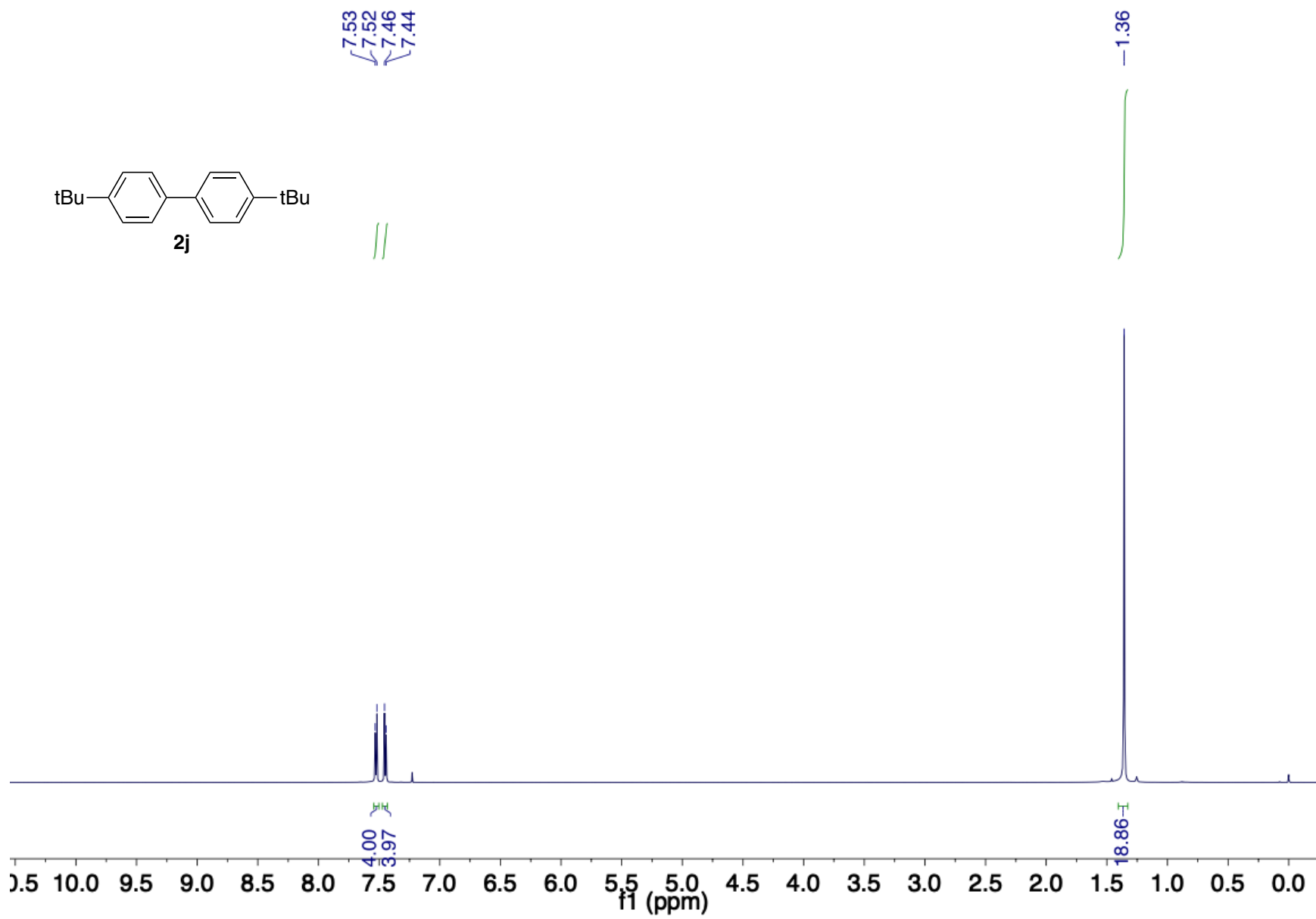
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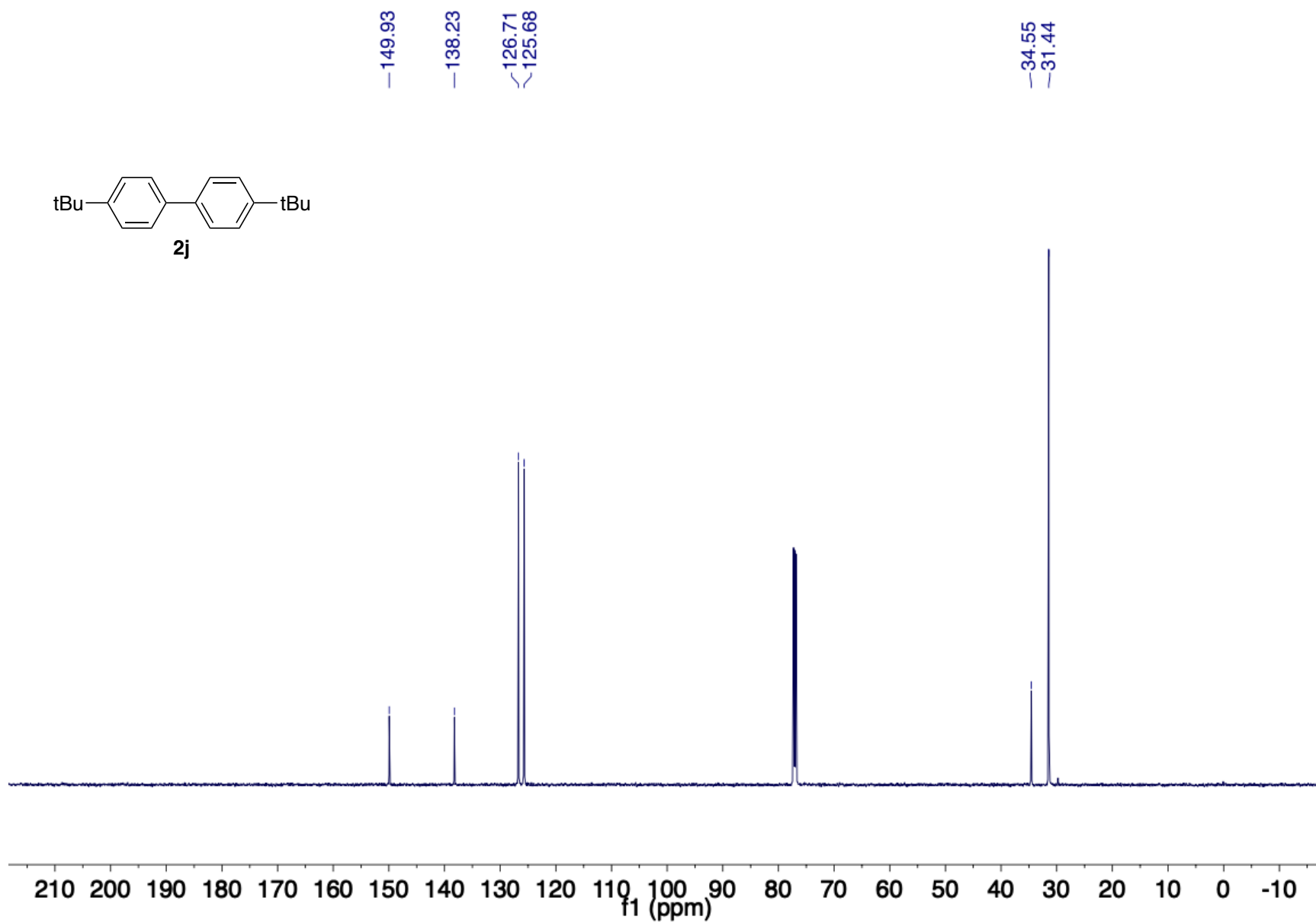
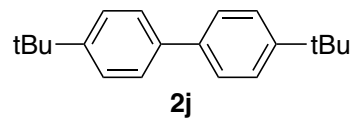


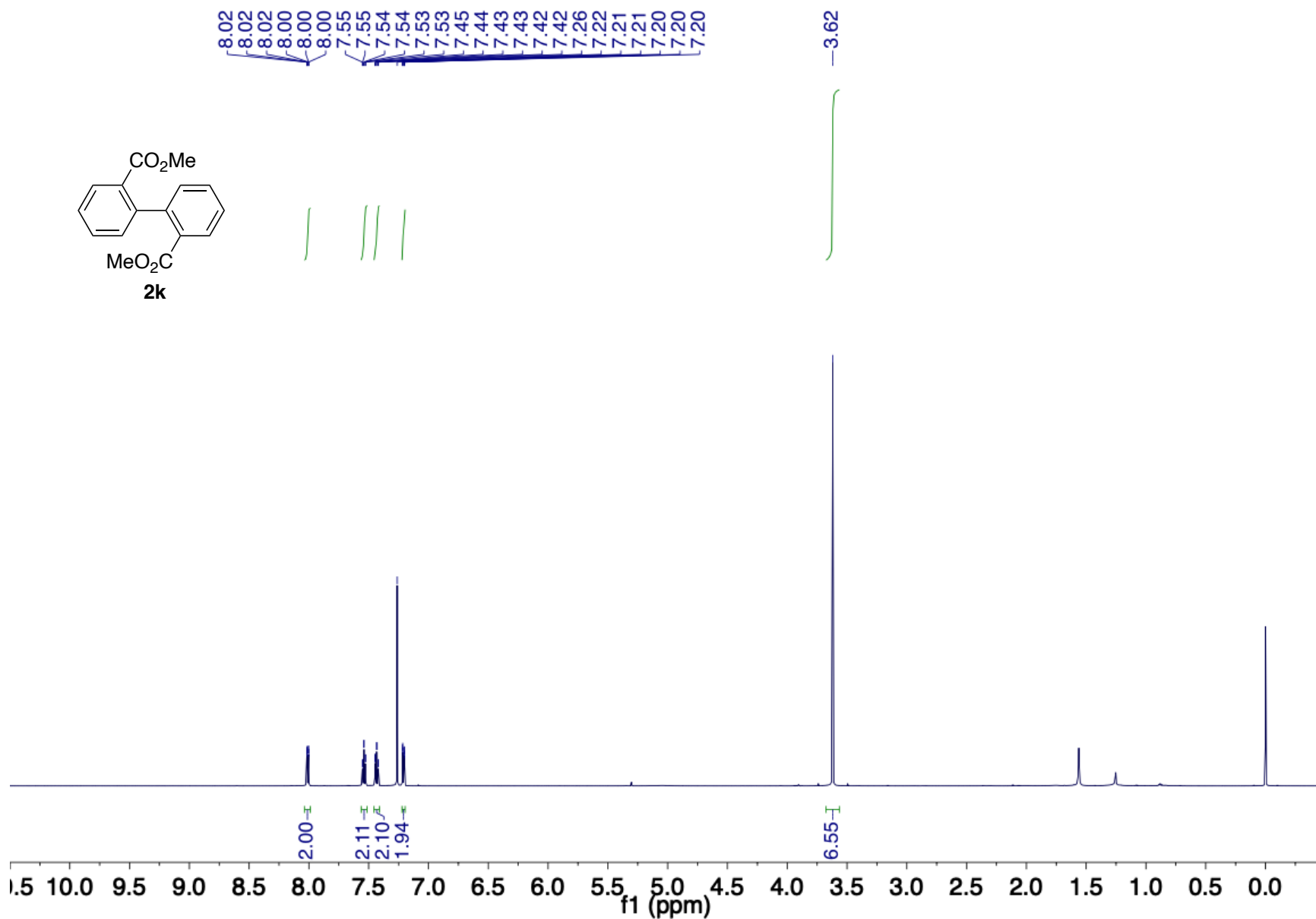


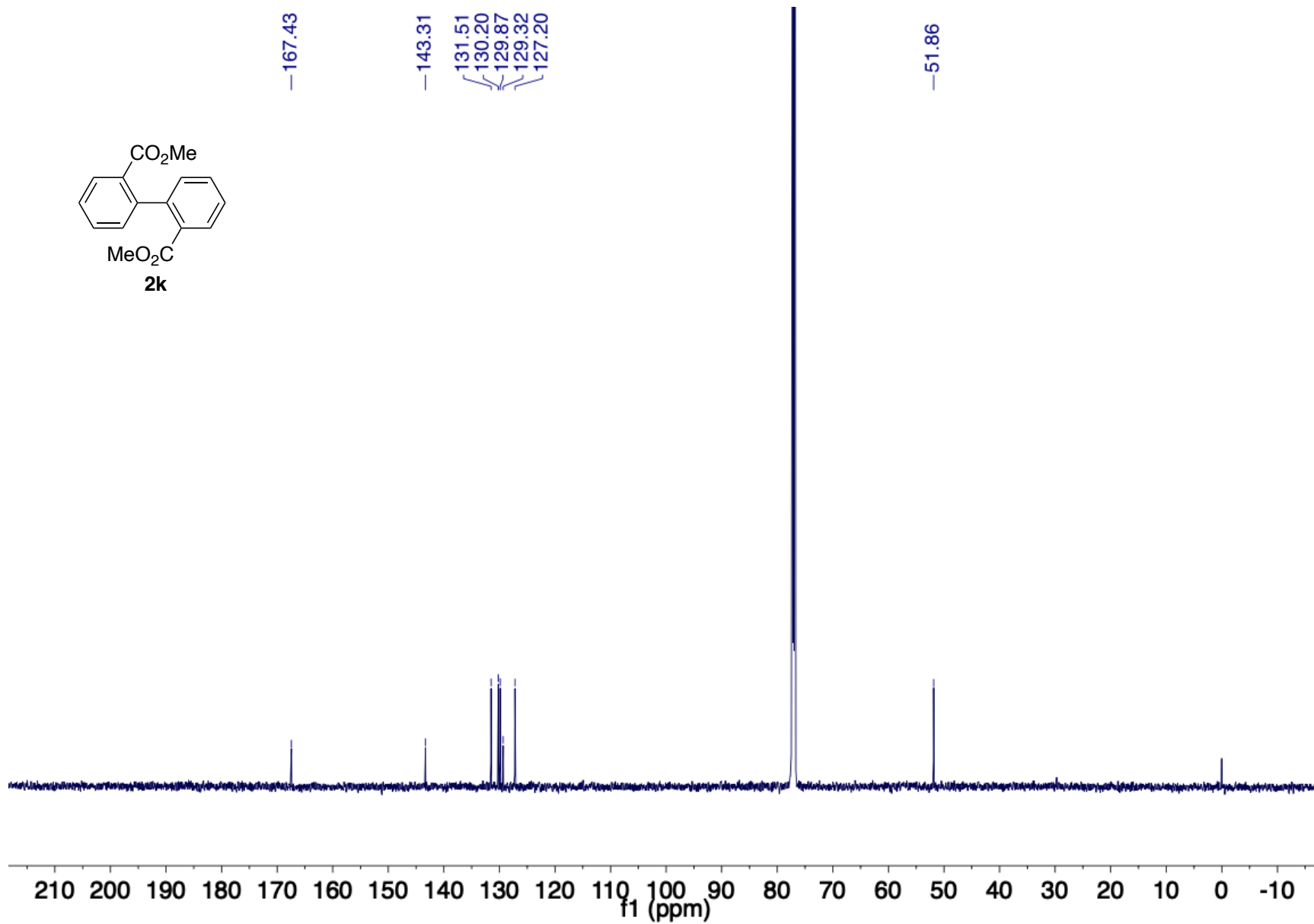
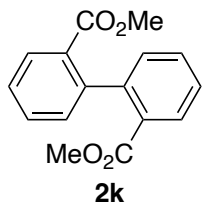
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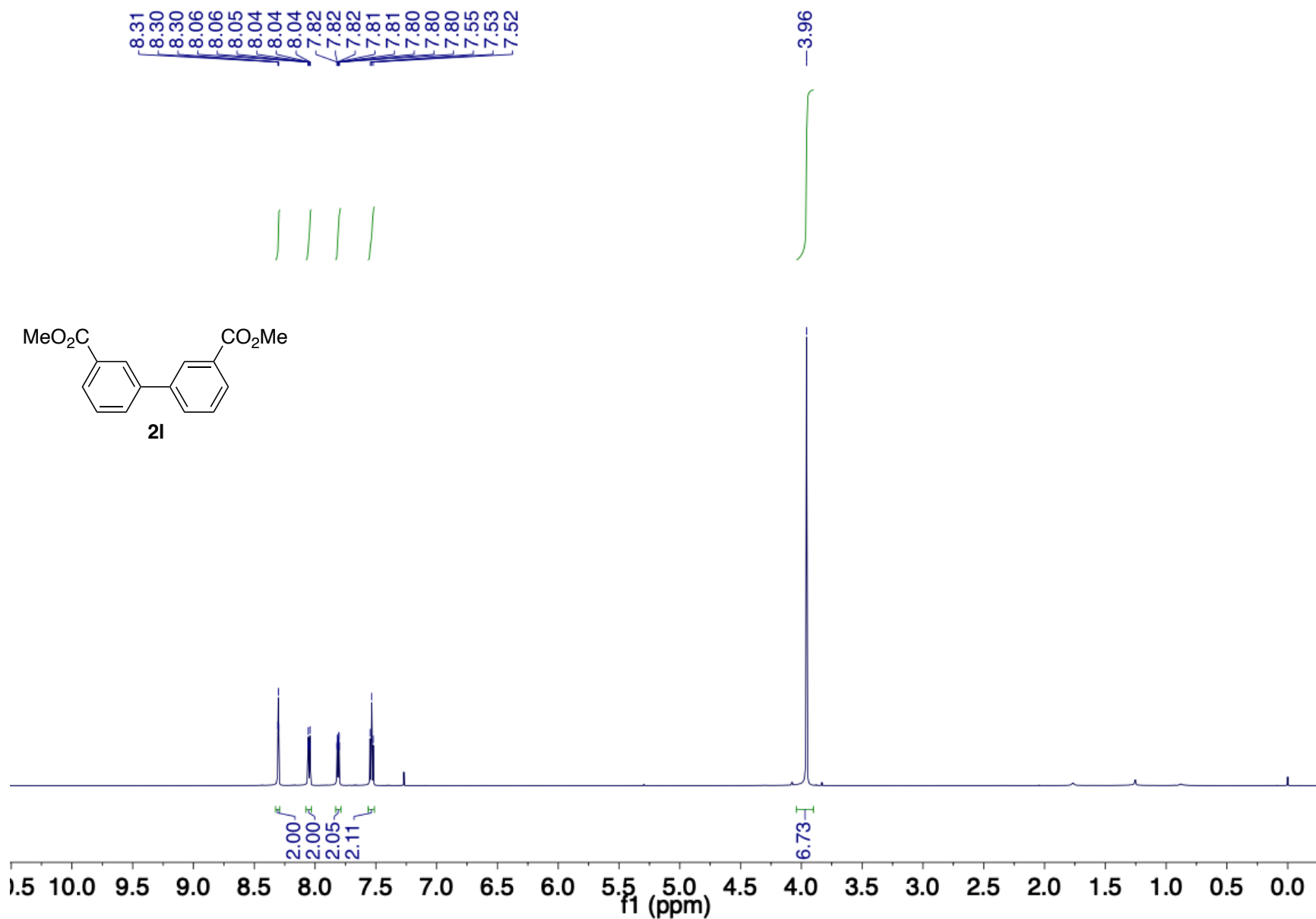


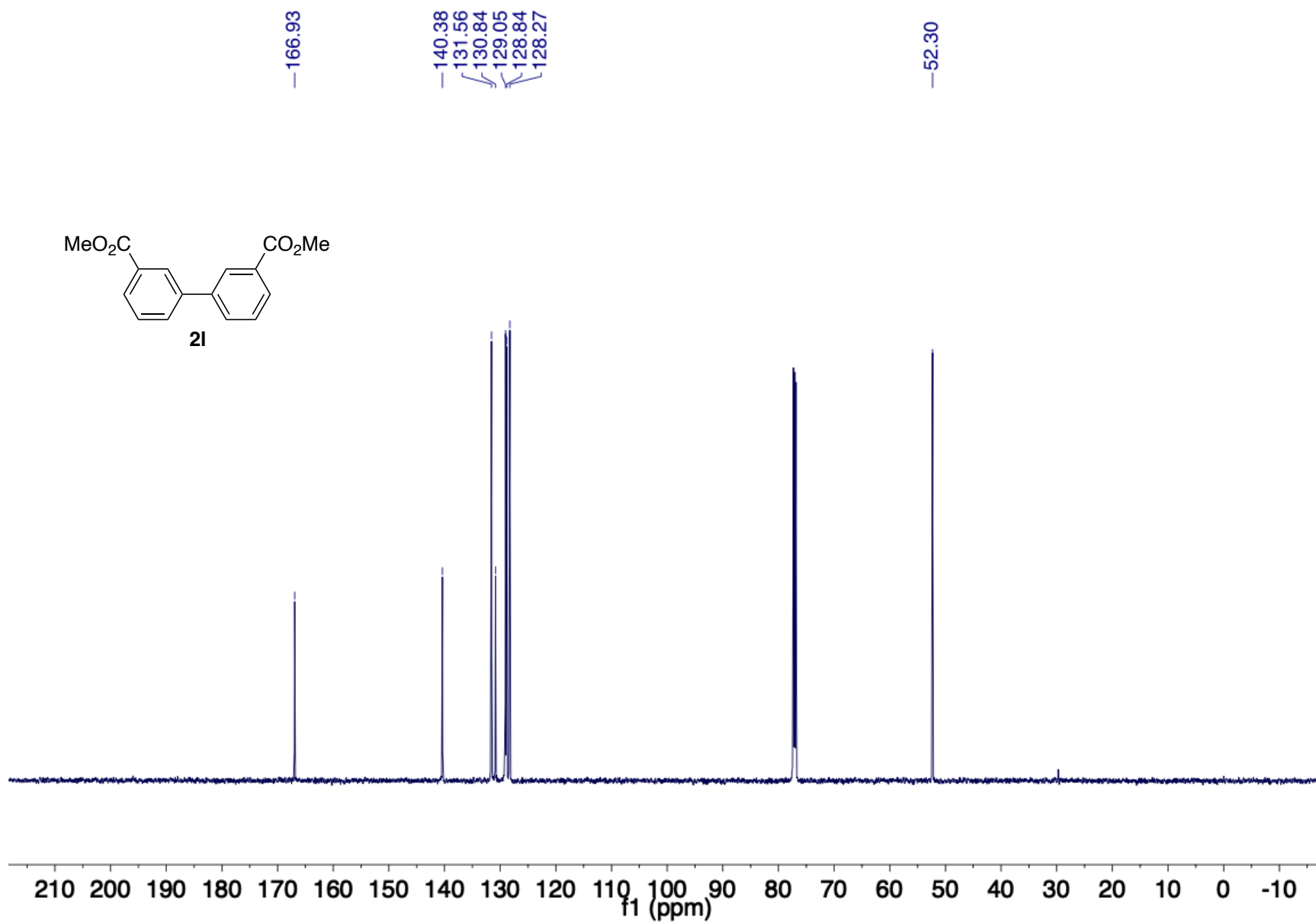
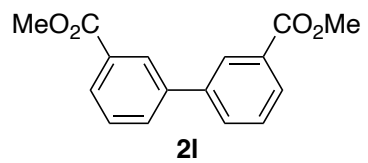


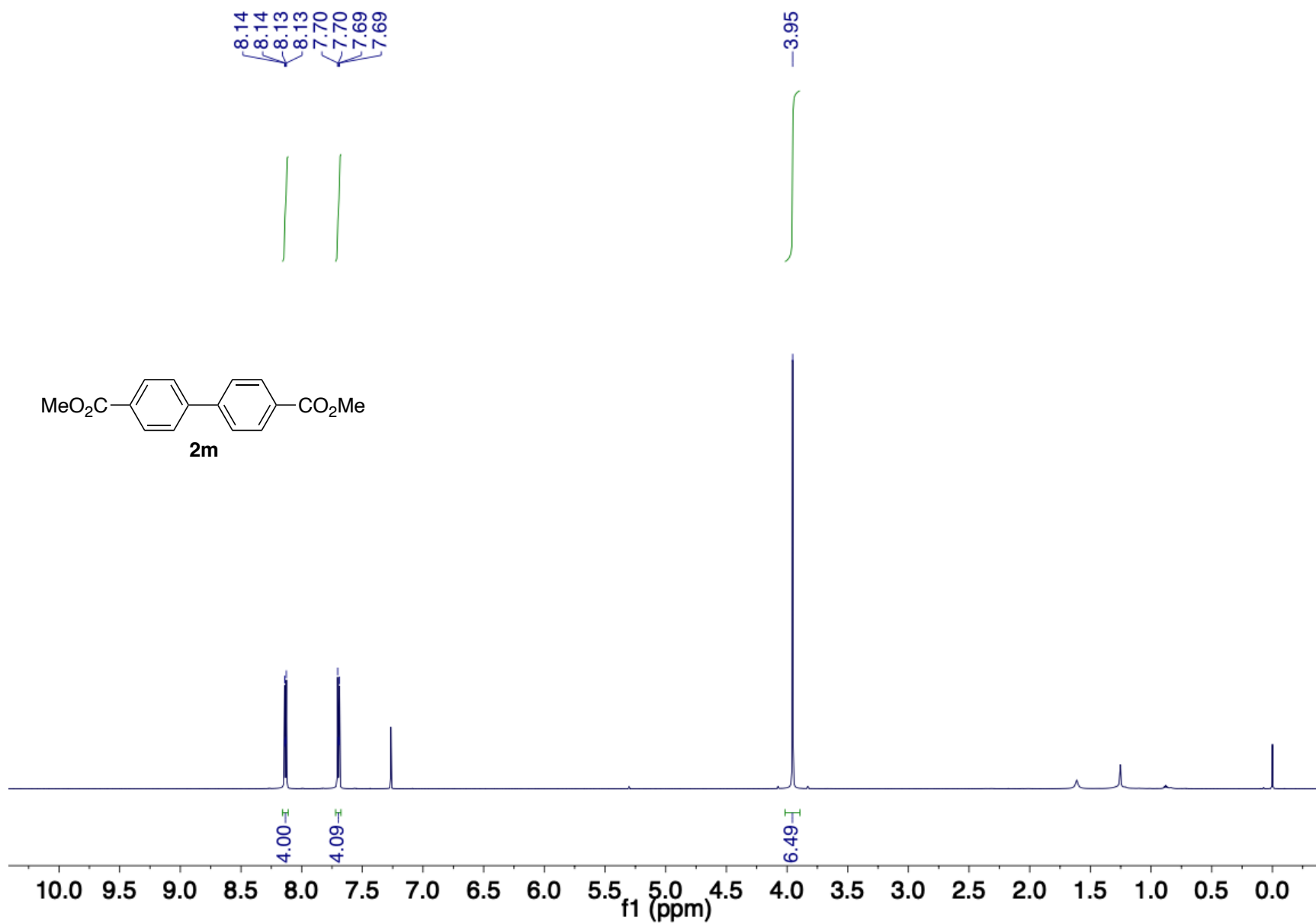


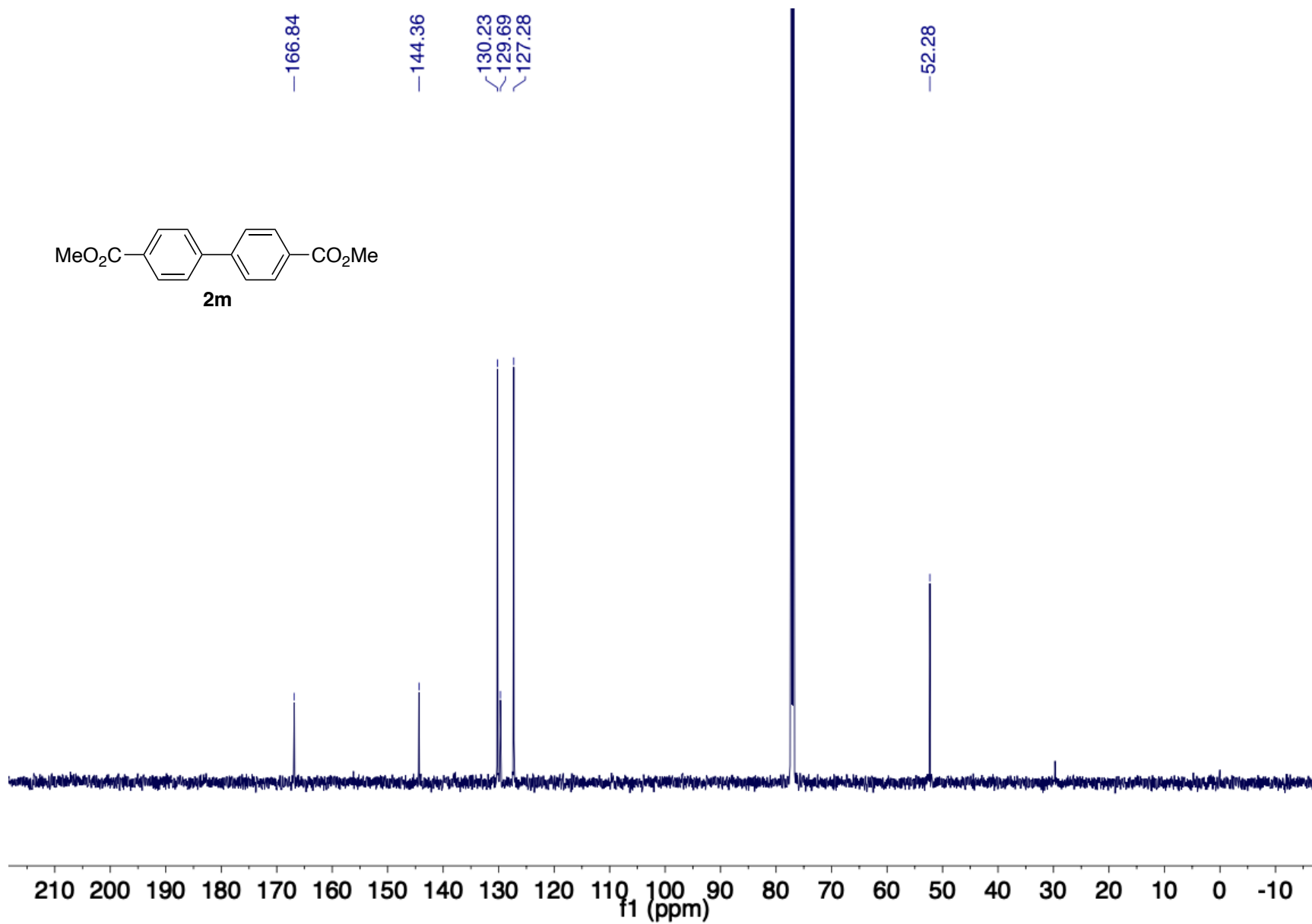
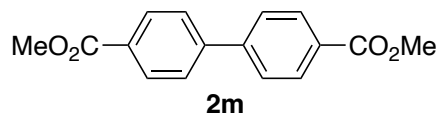


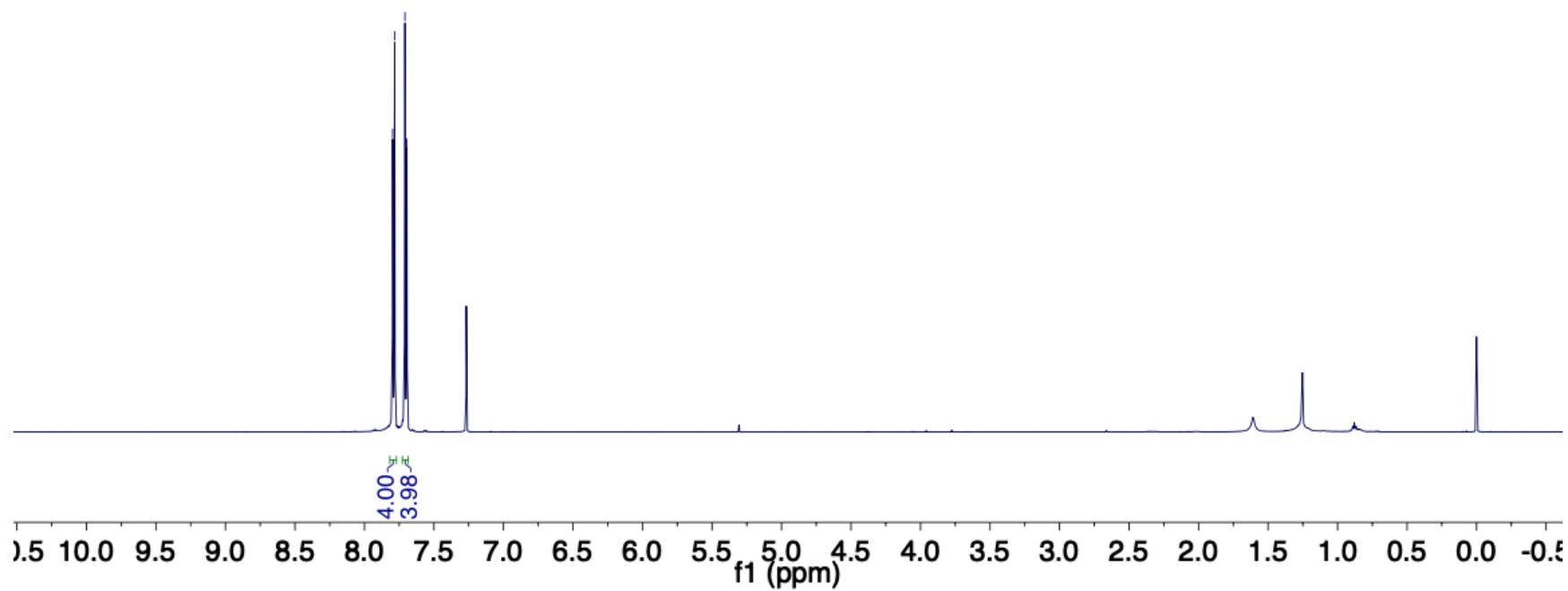
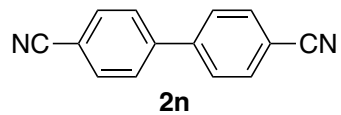


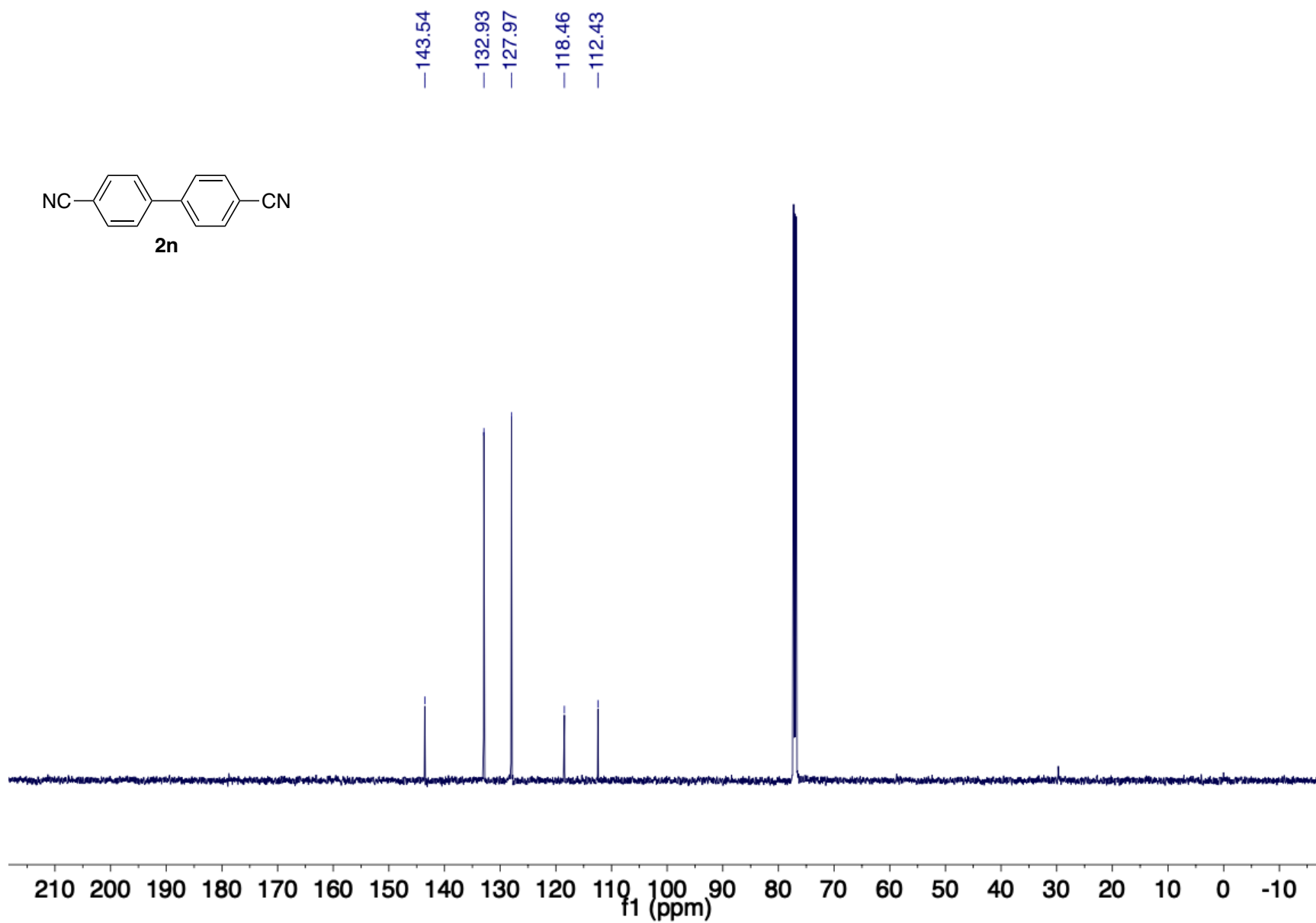
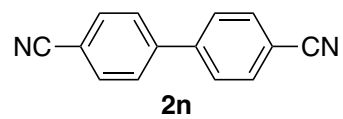


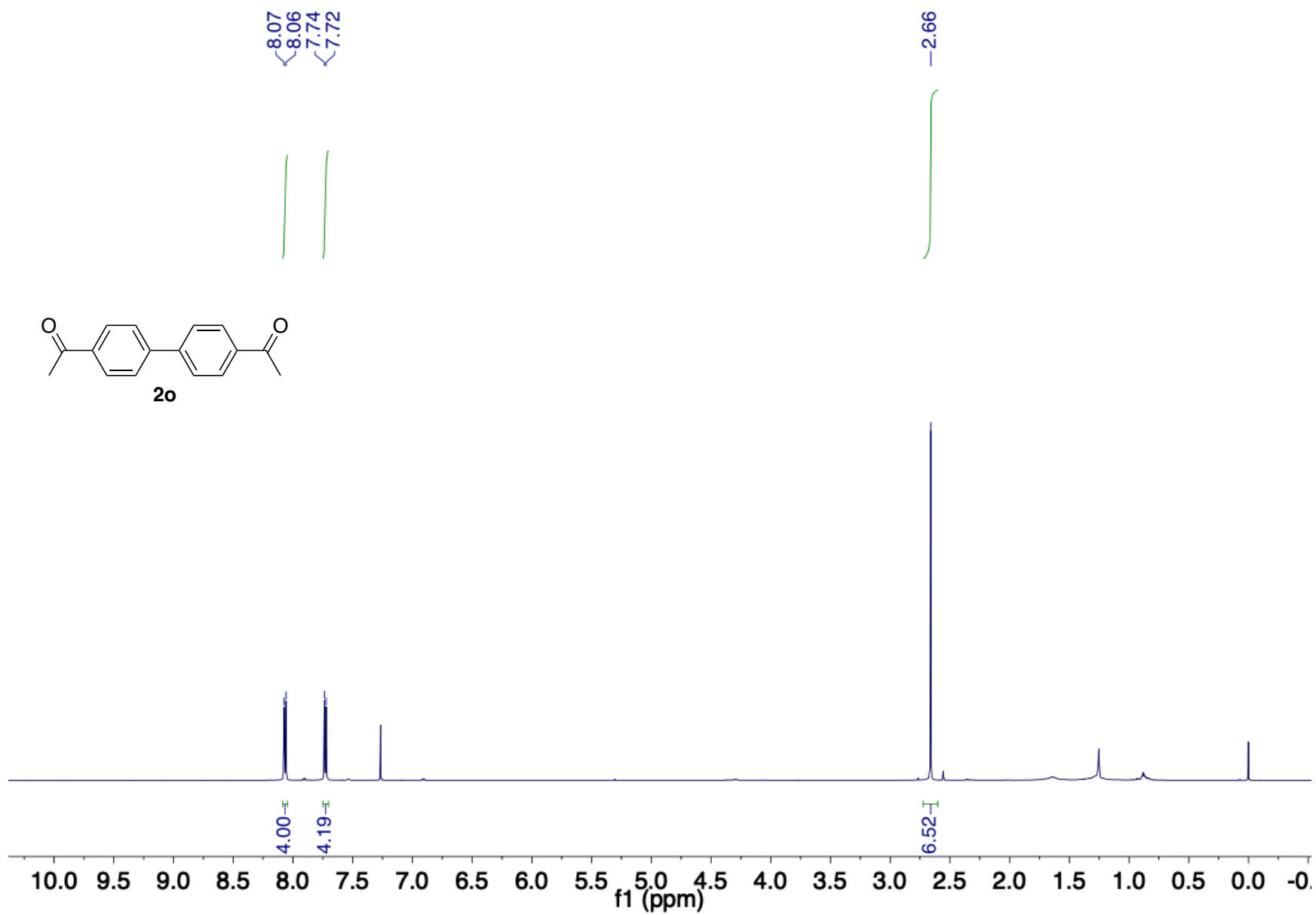


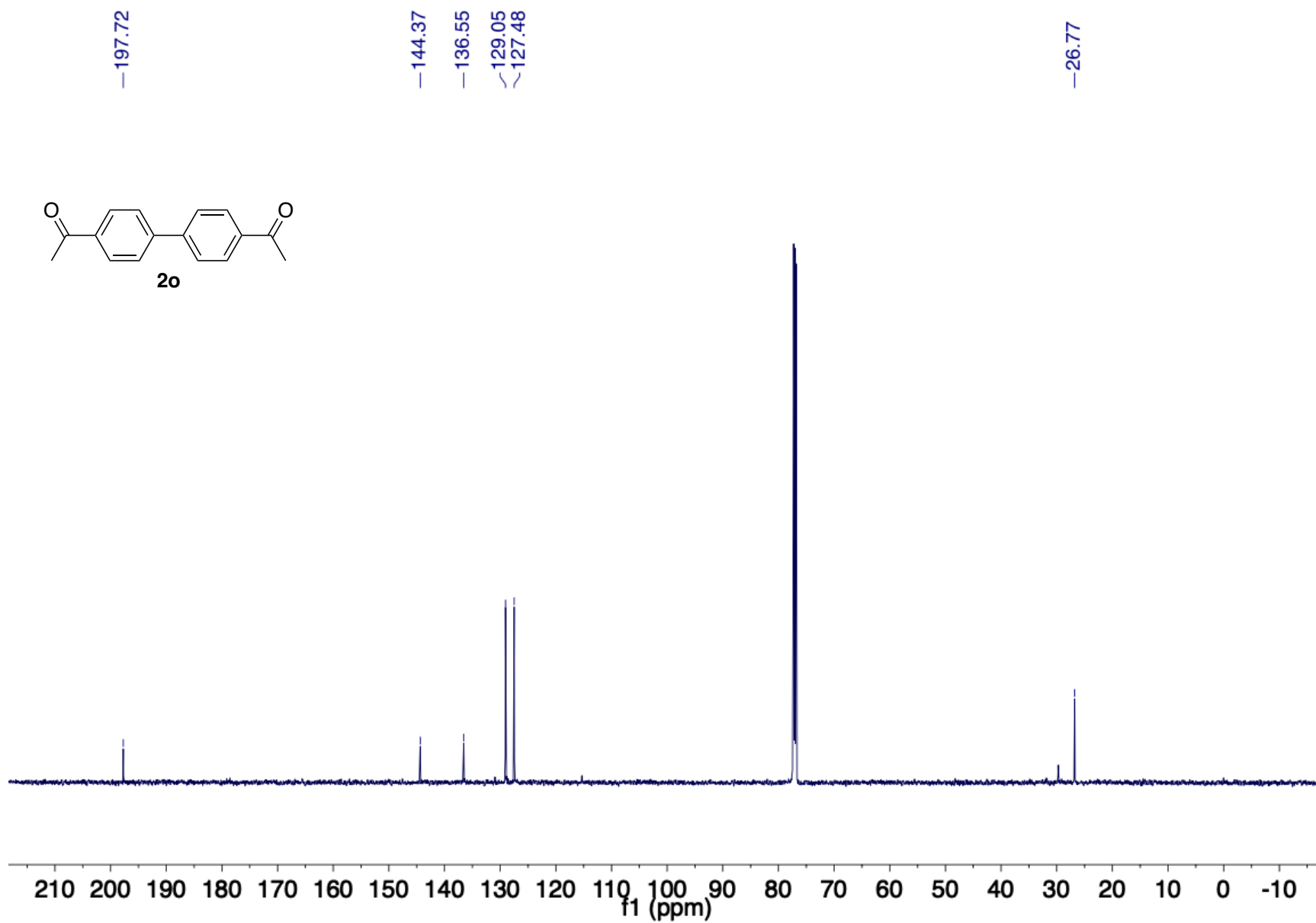
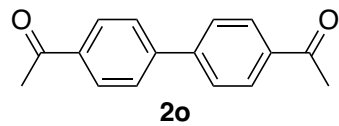


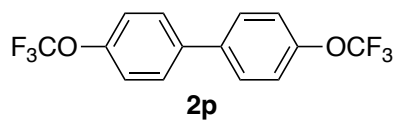




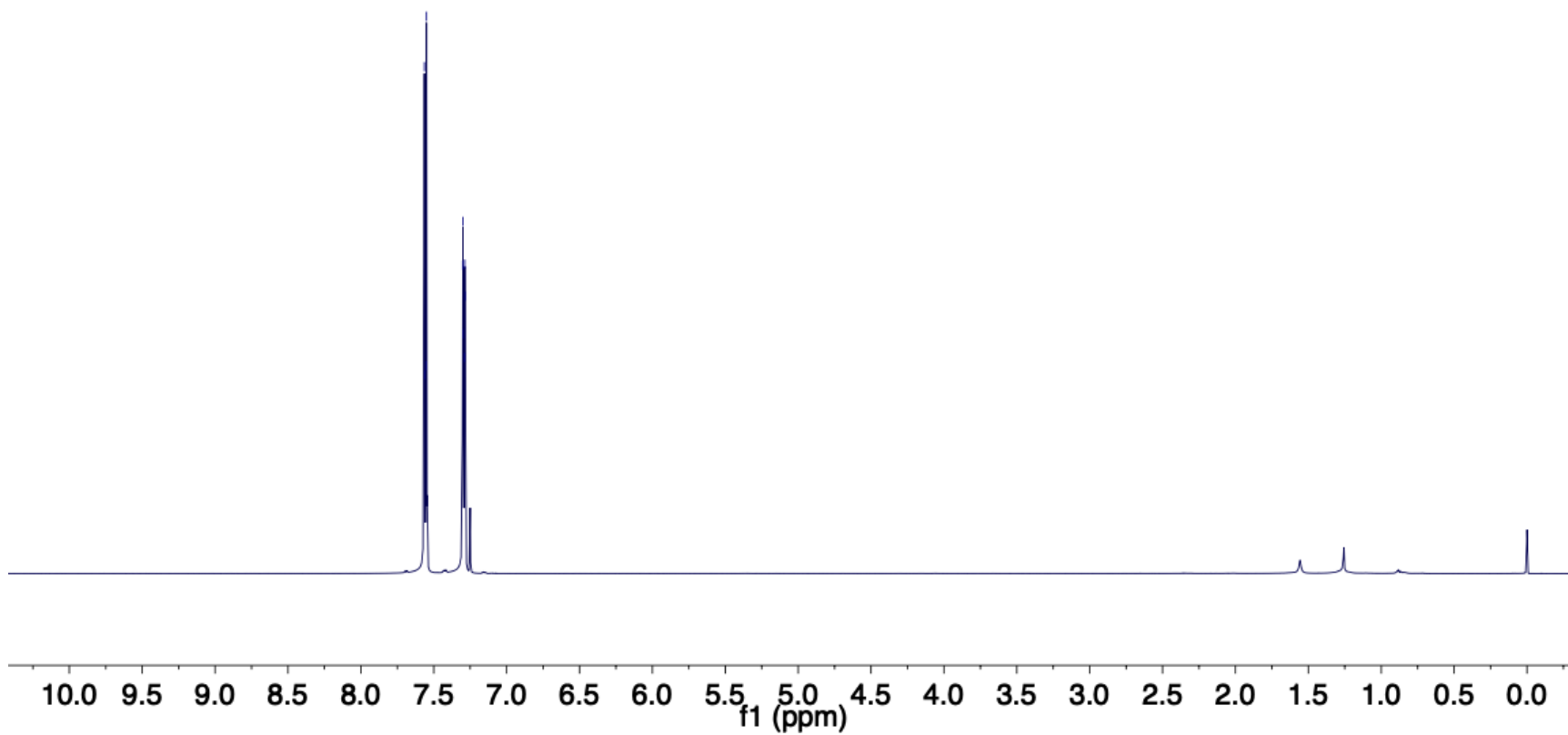


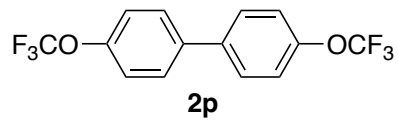




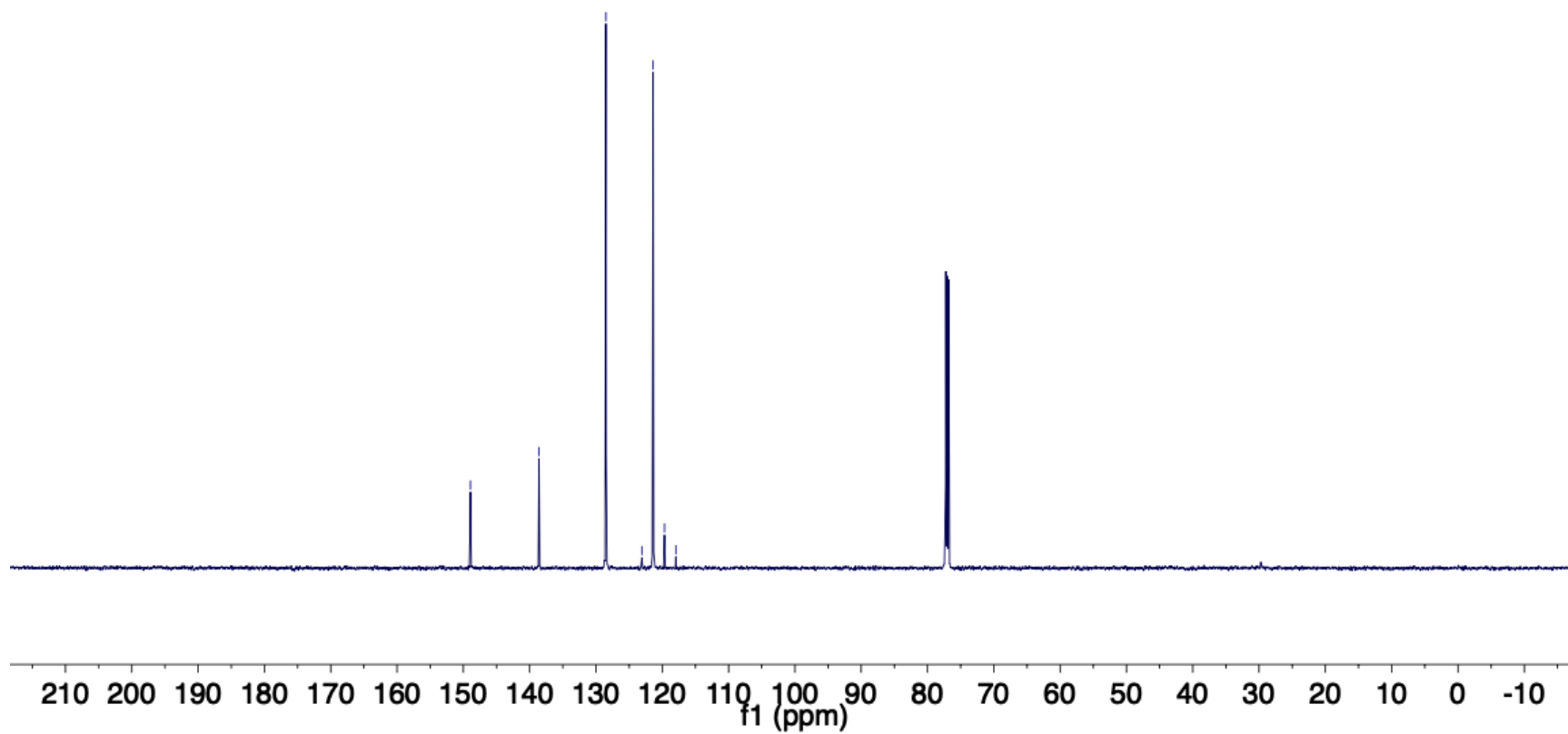


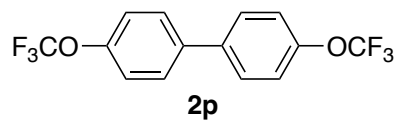
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7.55
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7.30
7.29
7.29
7.28



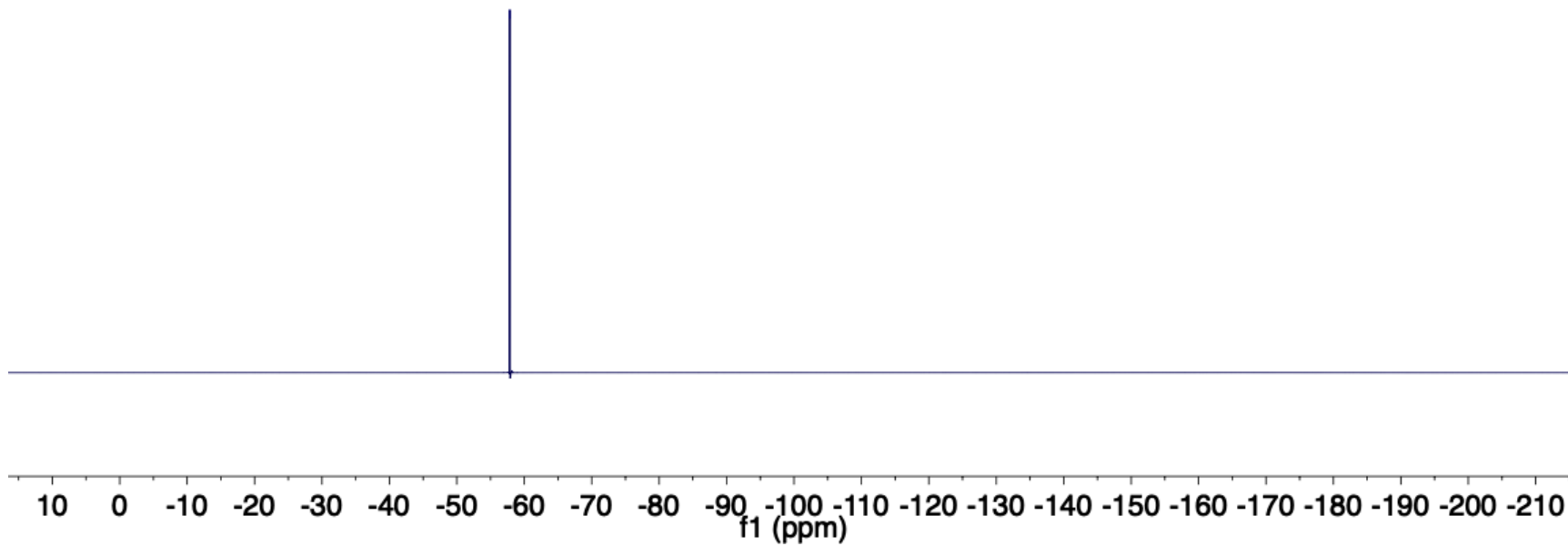


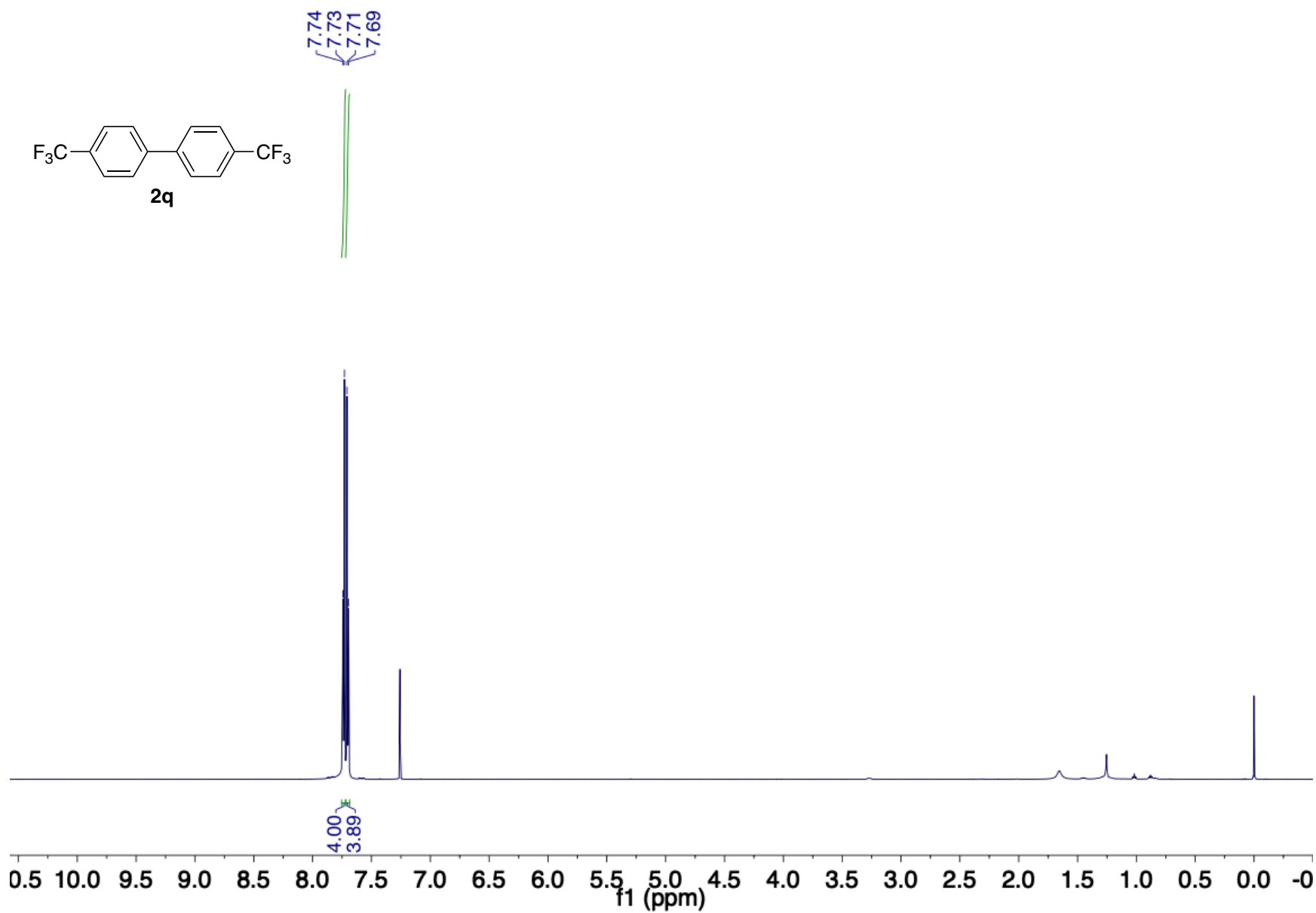
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—138.59
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123.07
121.38
119.66
117.96

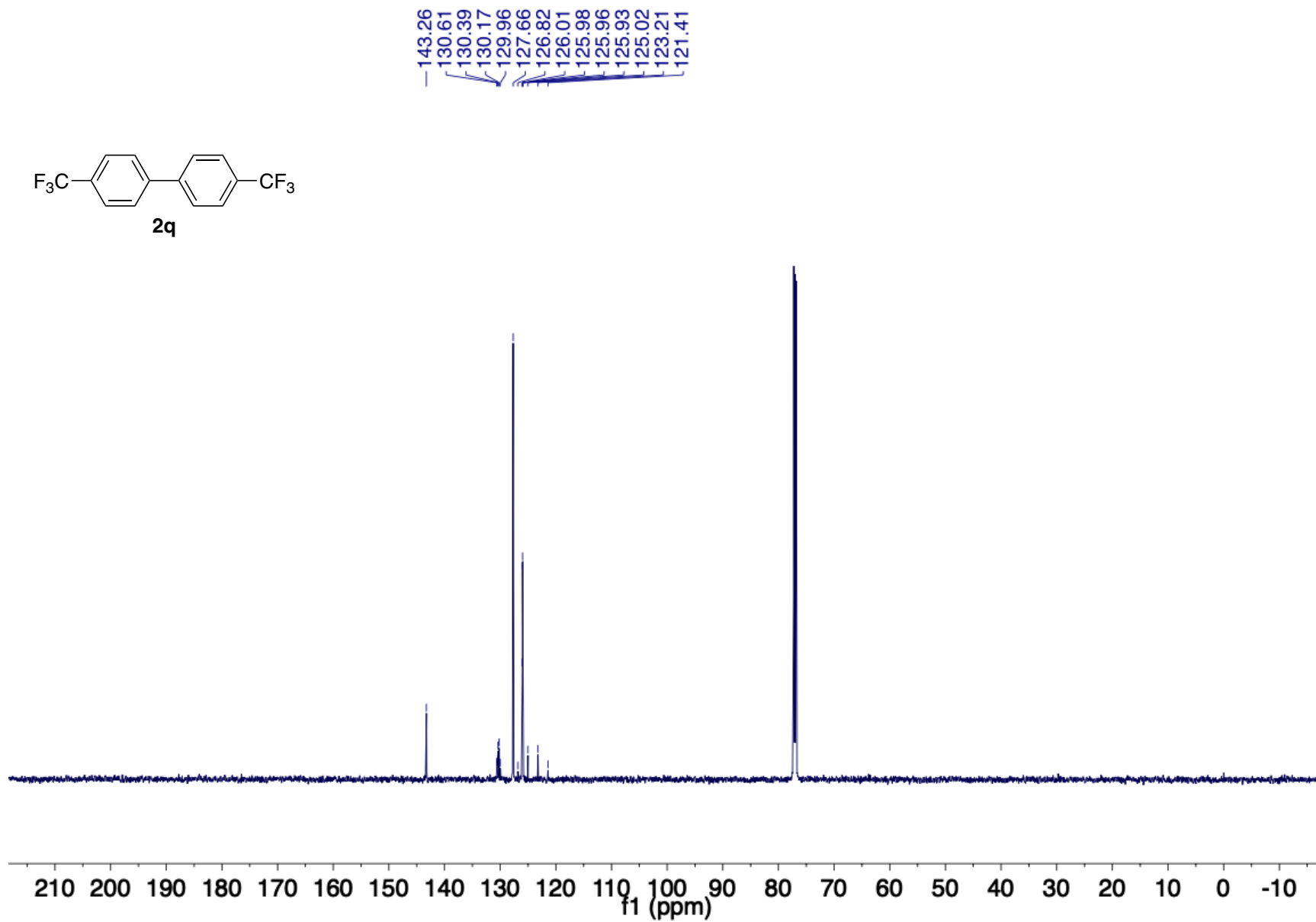
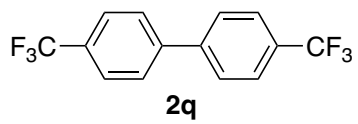


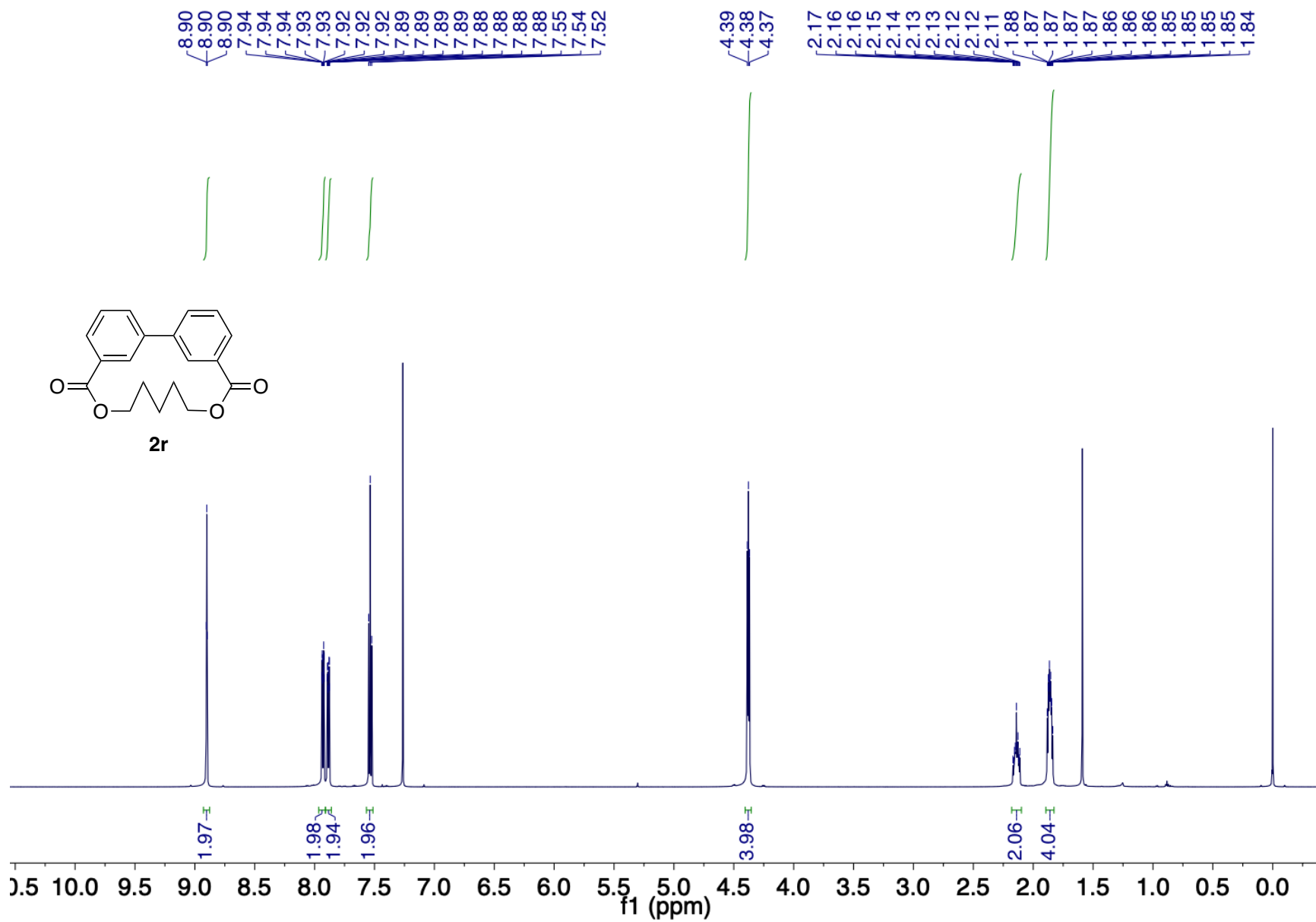


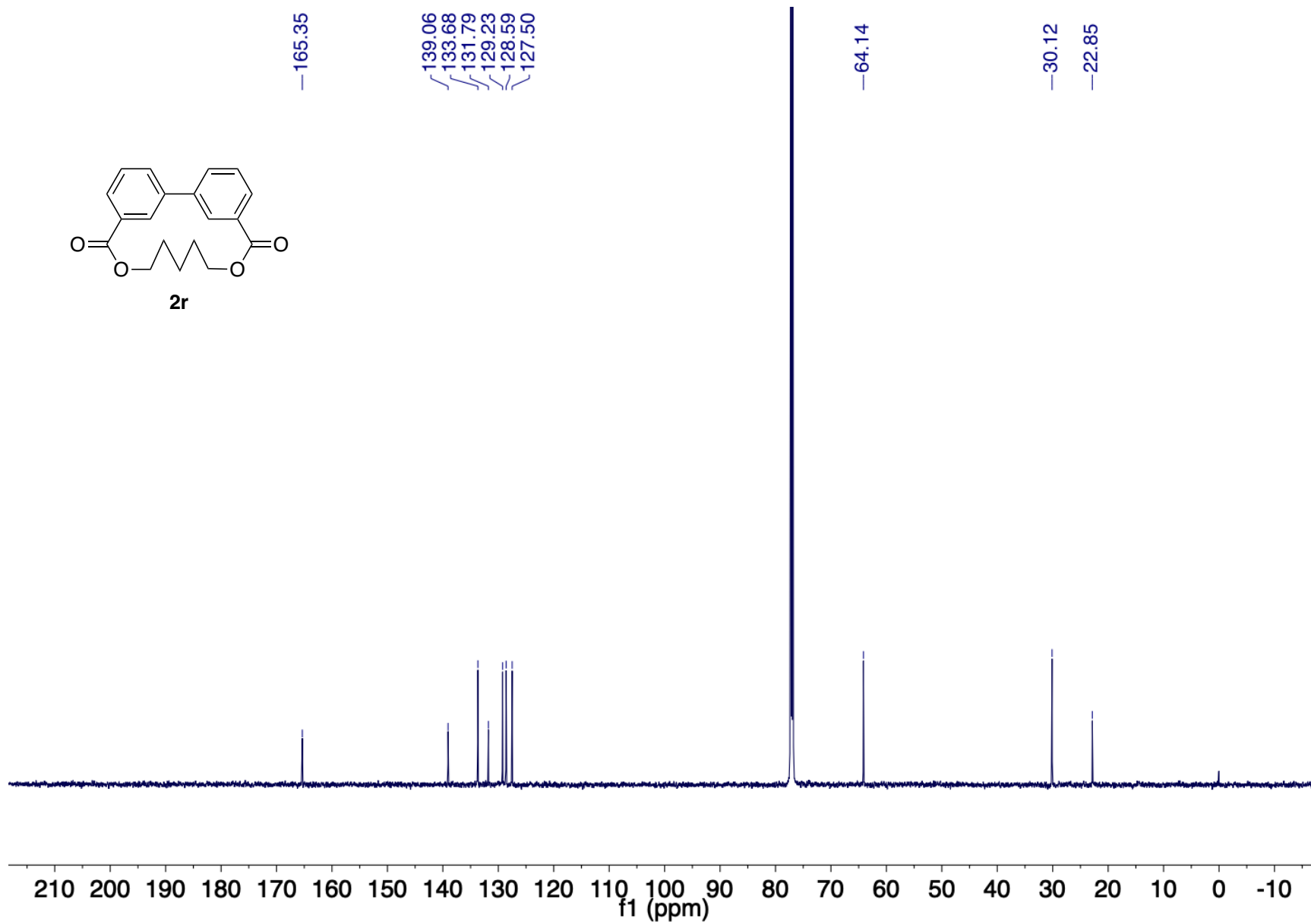
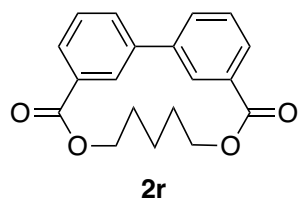
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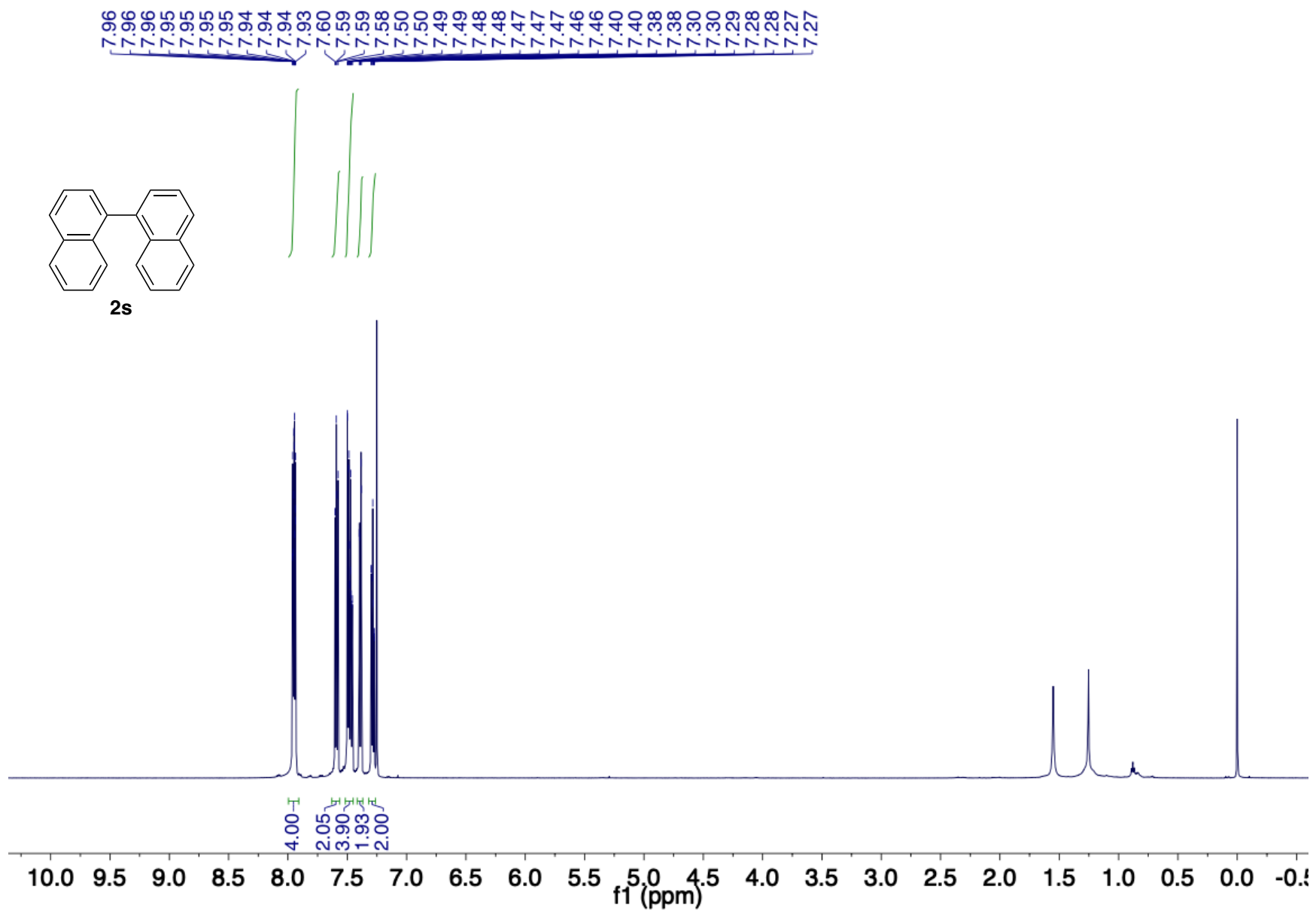


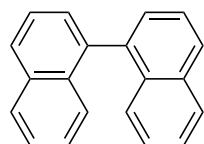






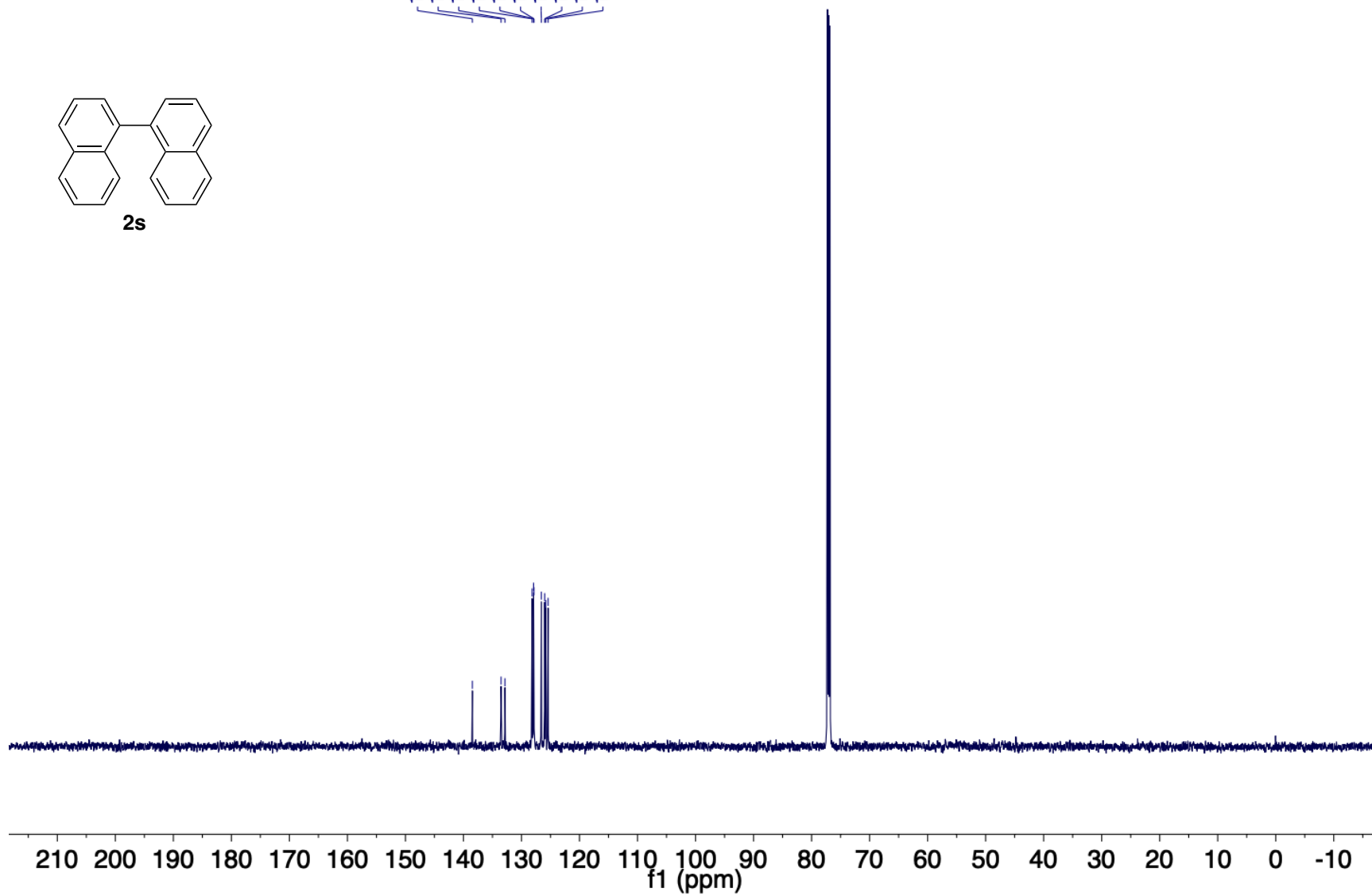


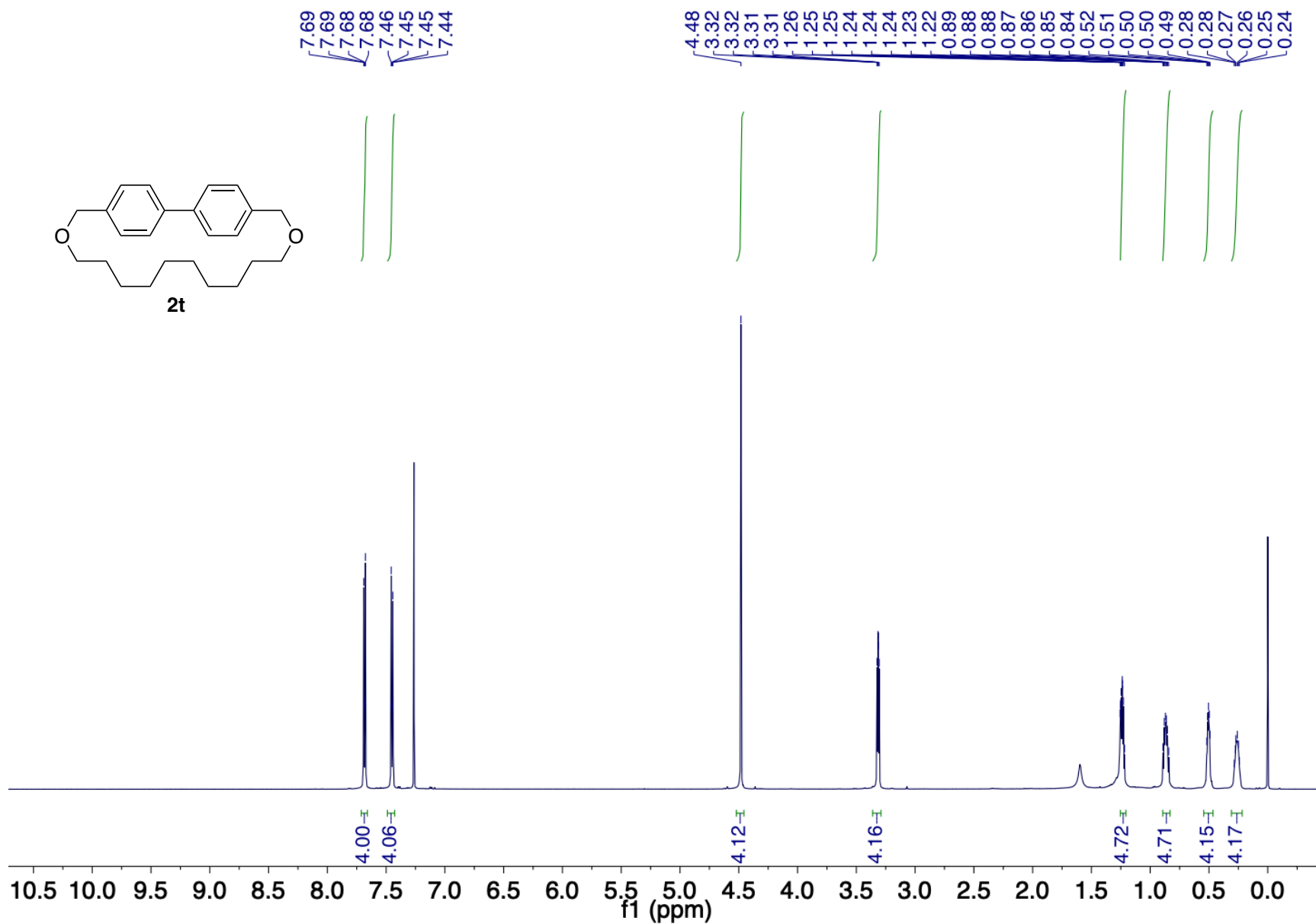
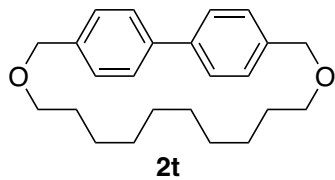


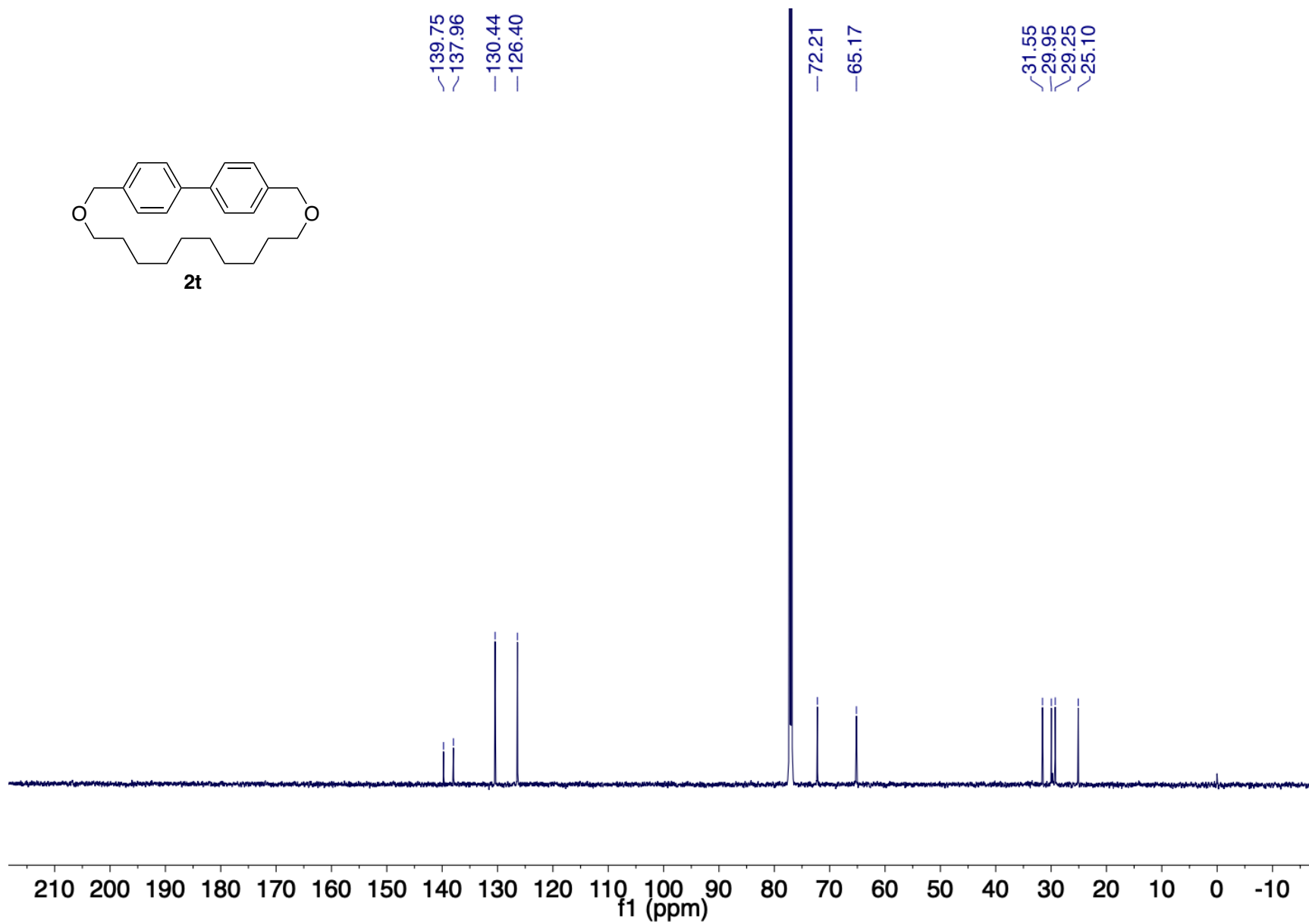
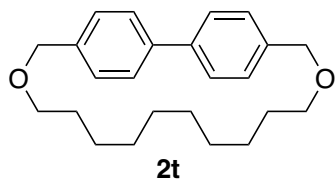


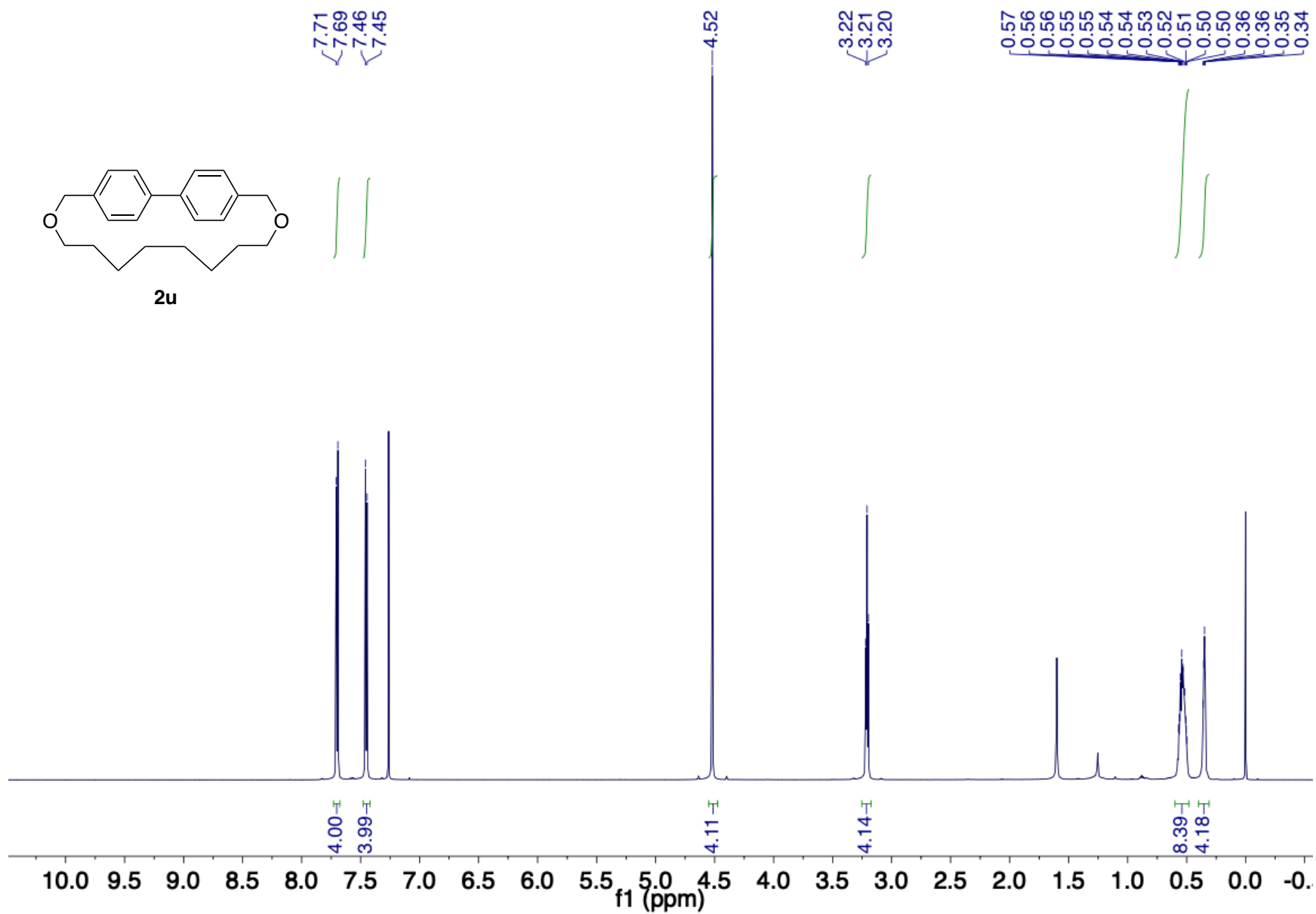
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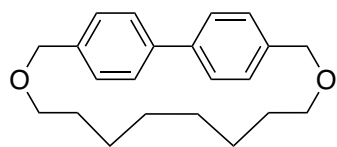
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126.00
125.83
125.41



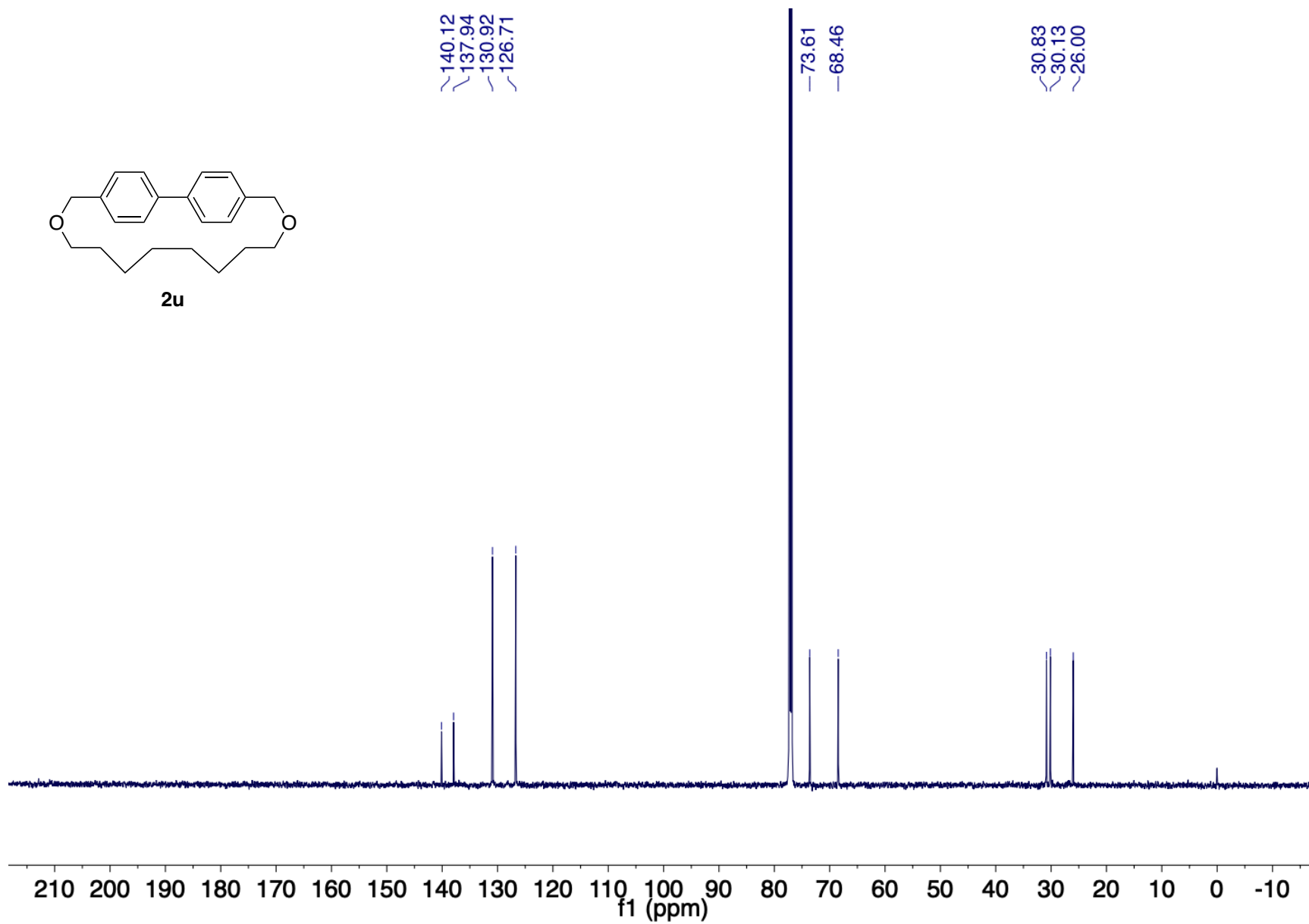


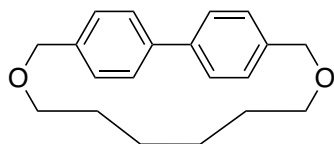




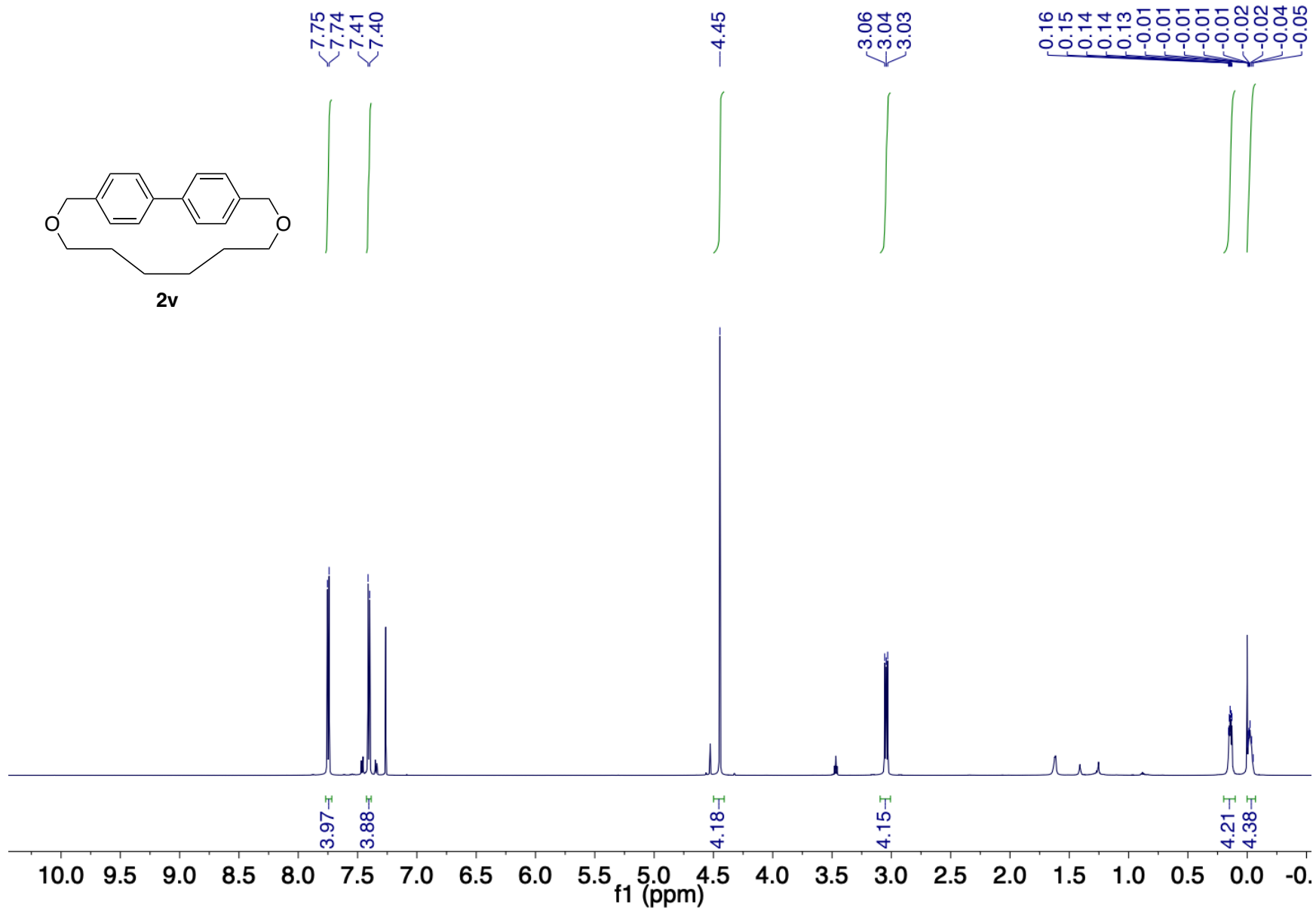


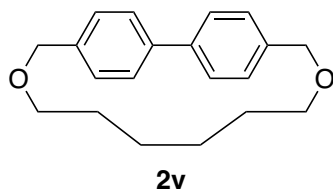
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2v

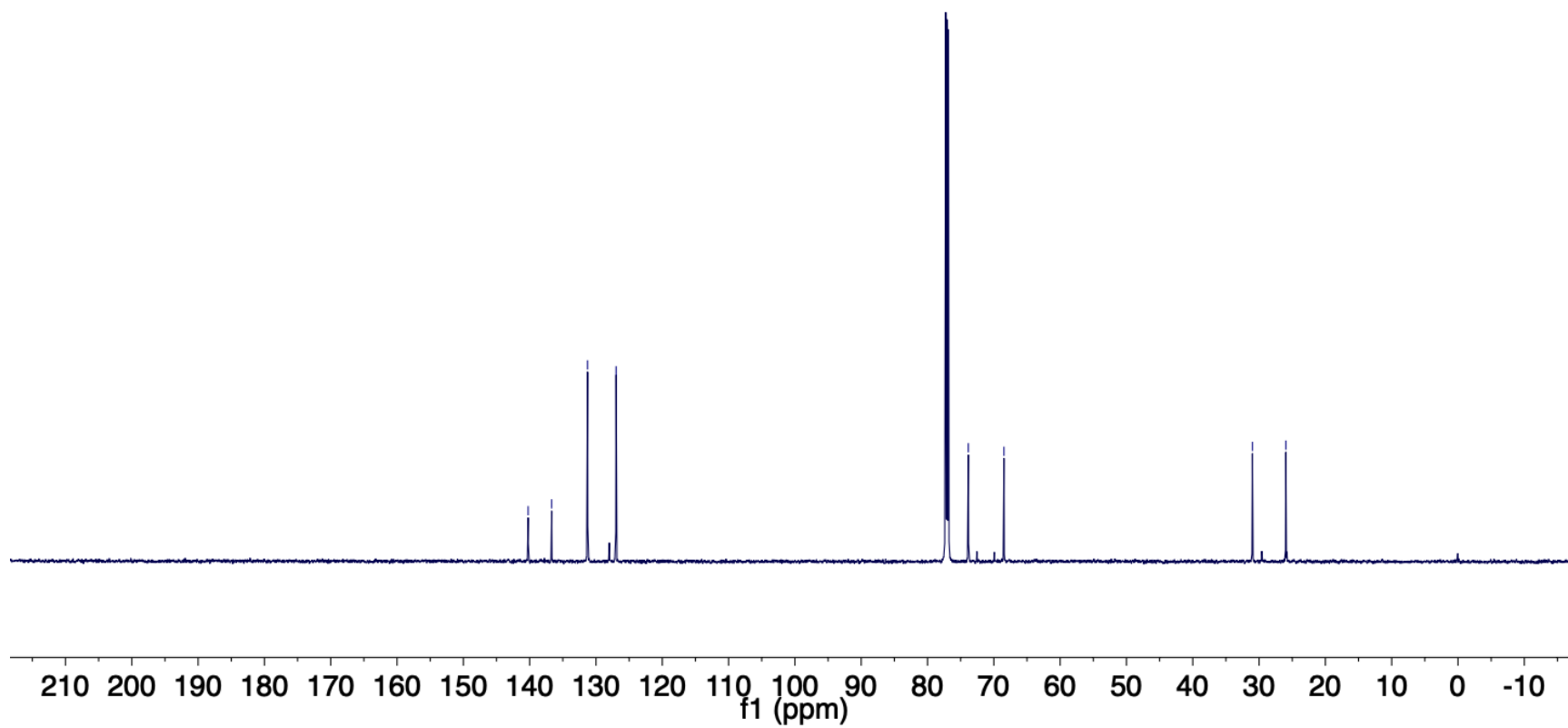


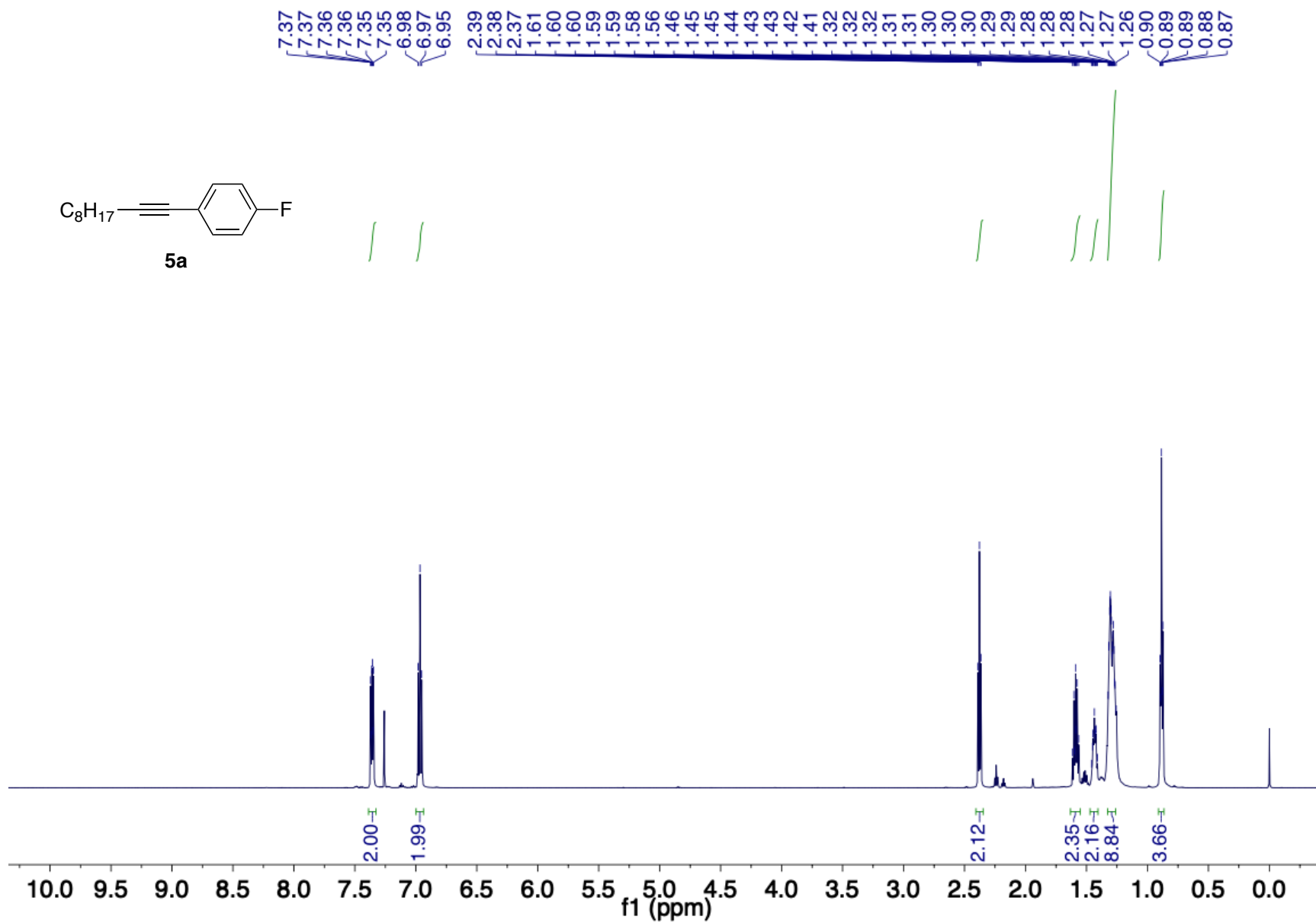
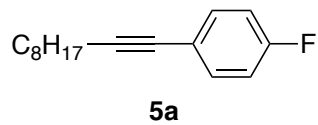


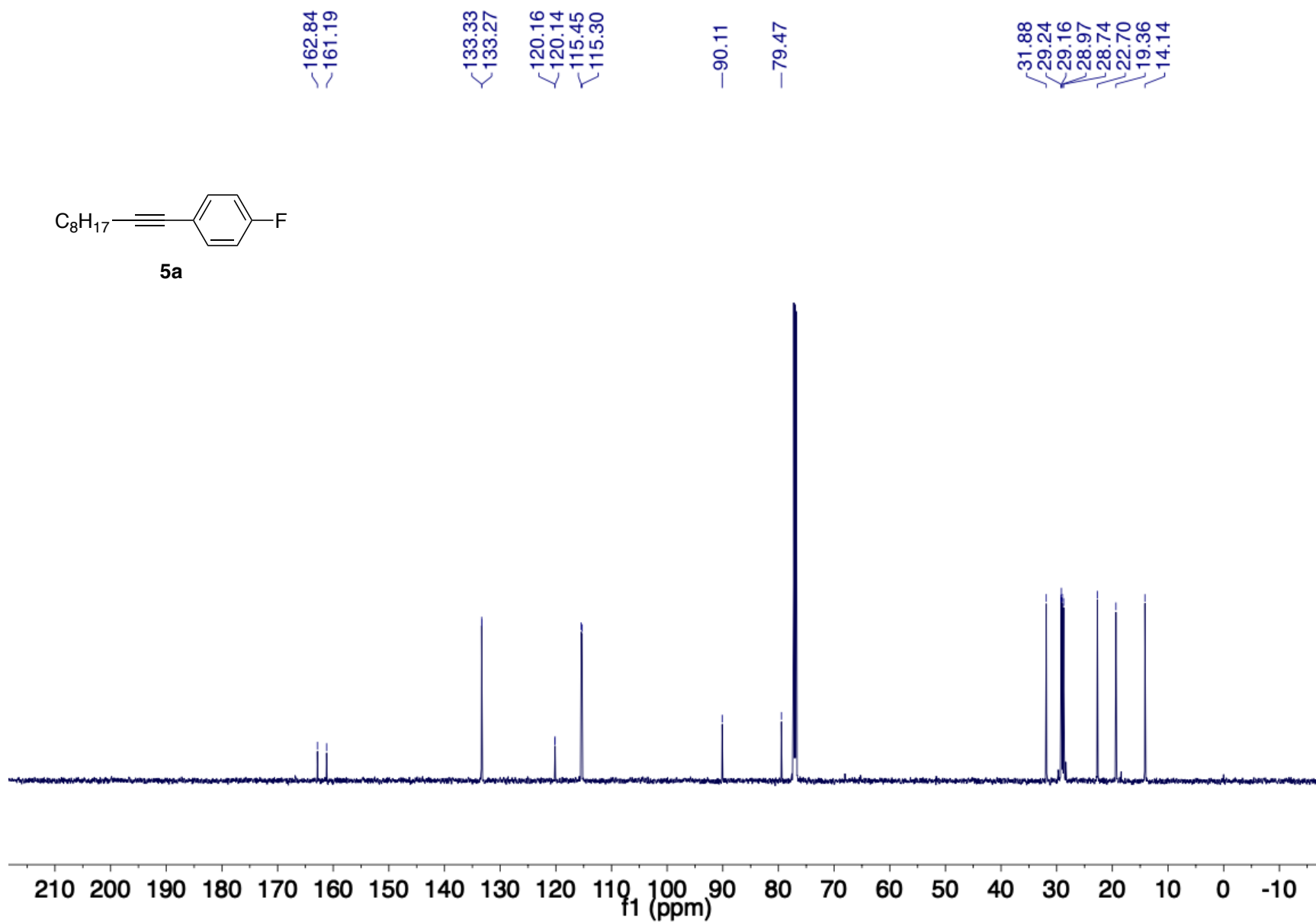
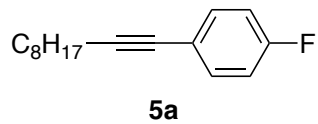
~140.23
~136.68
~131.27
~126.97

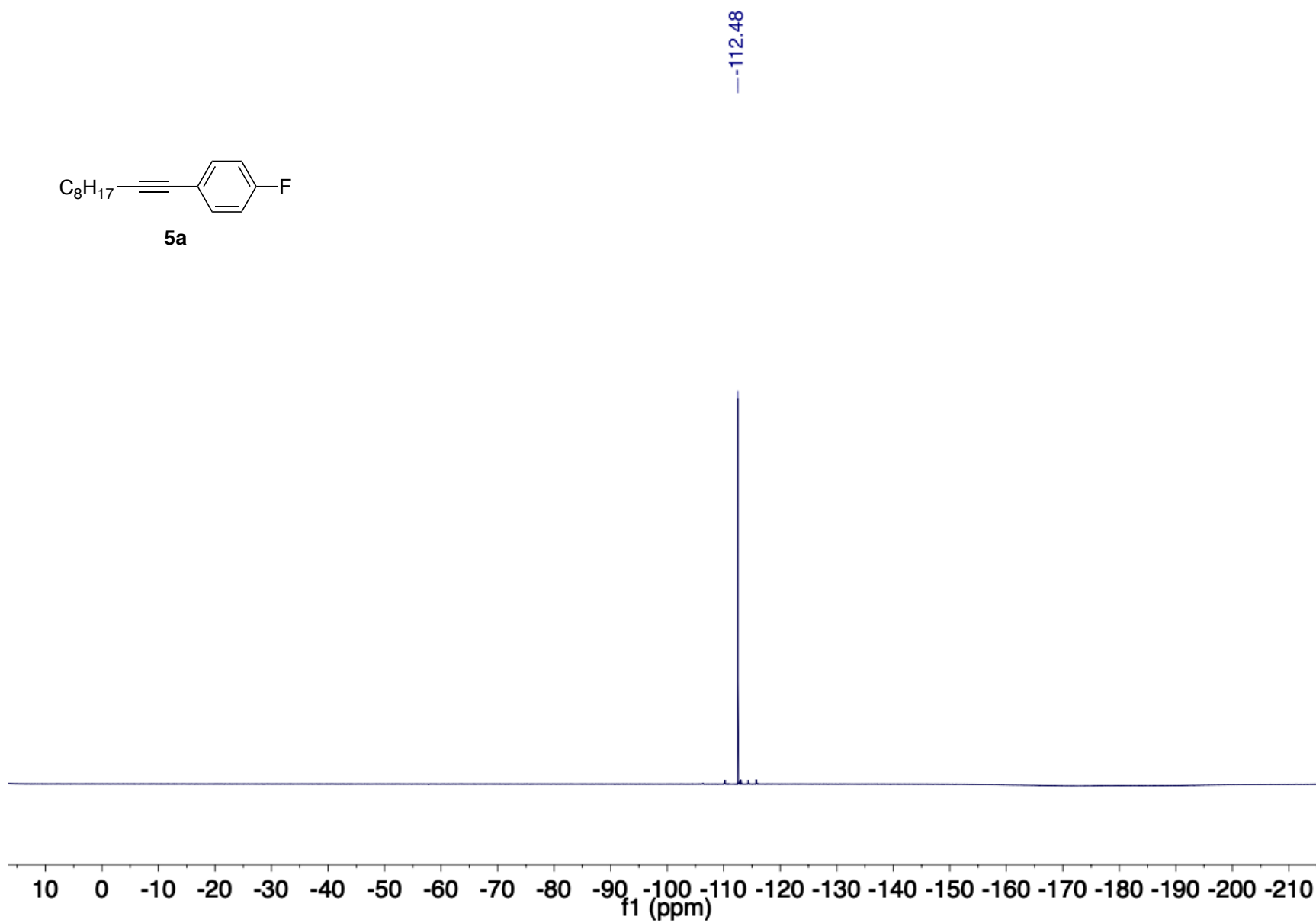
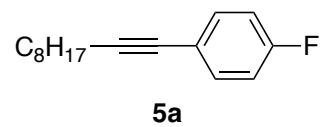
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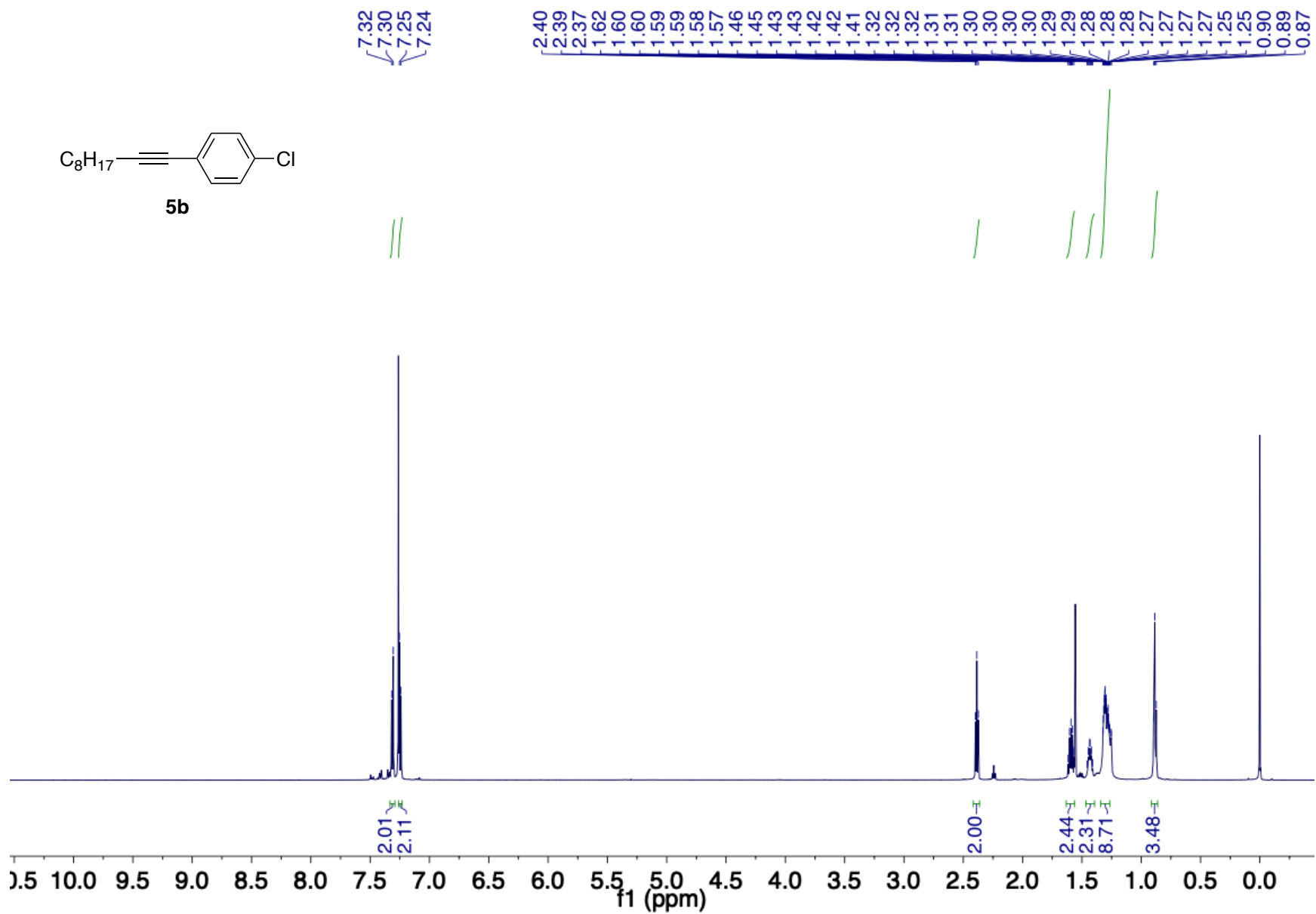
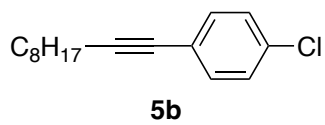
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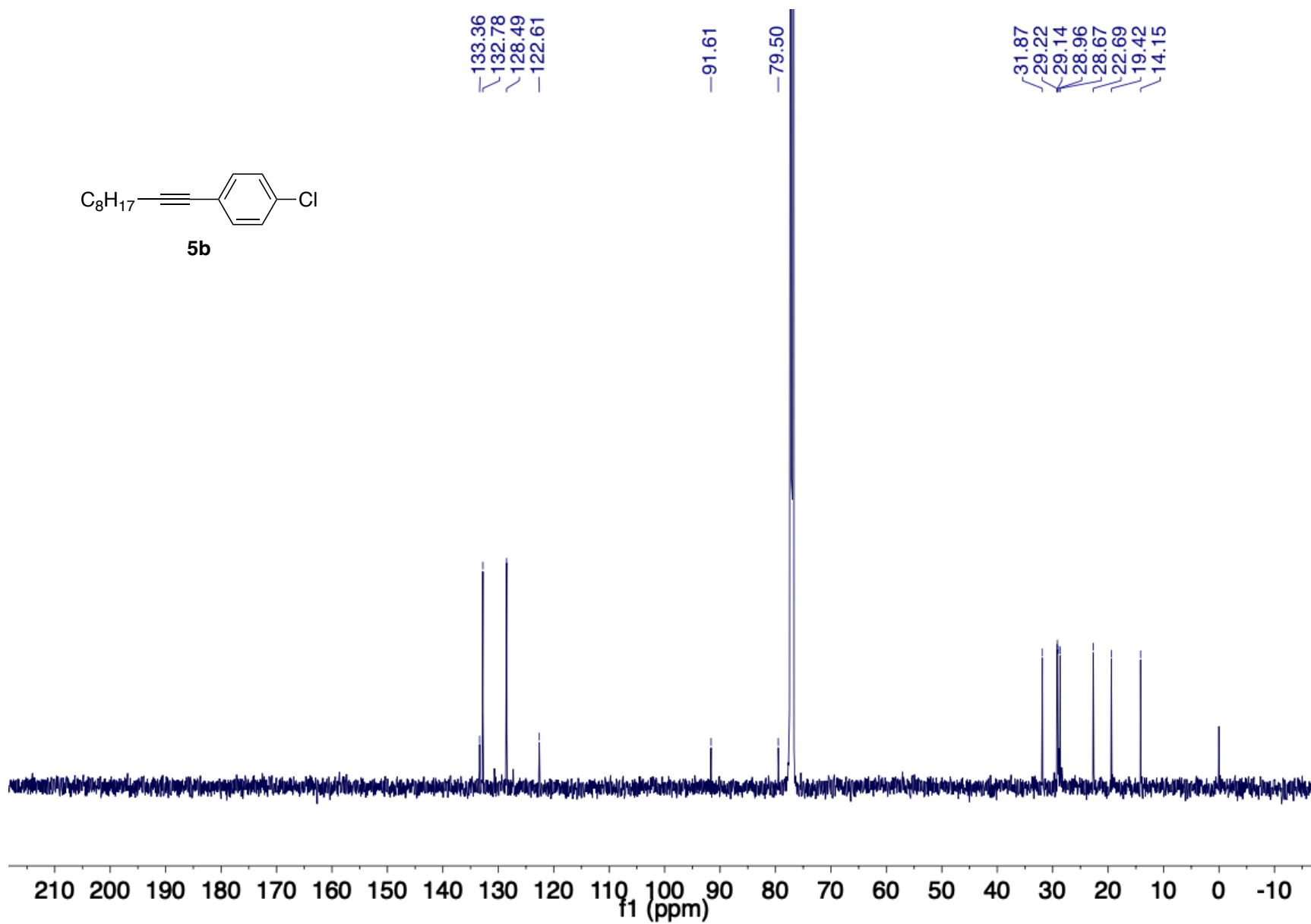
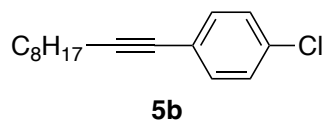


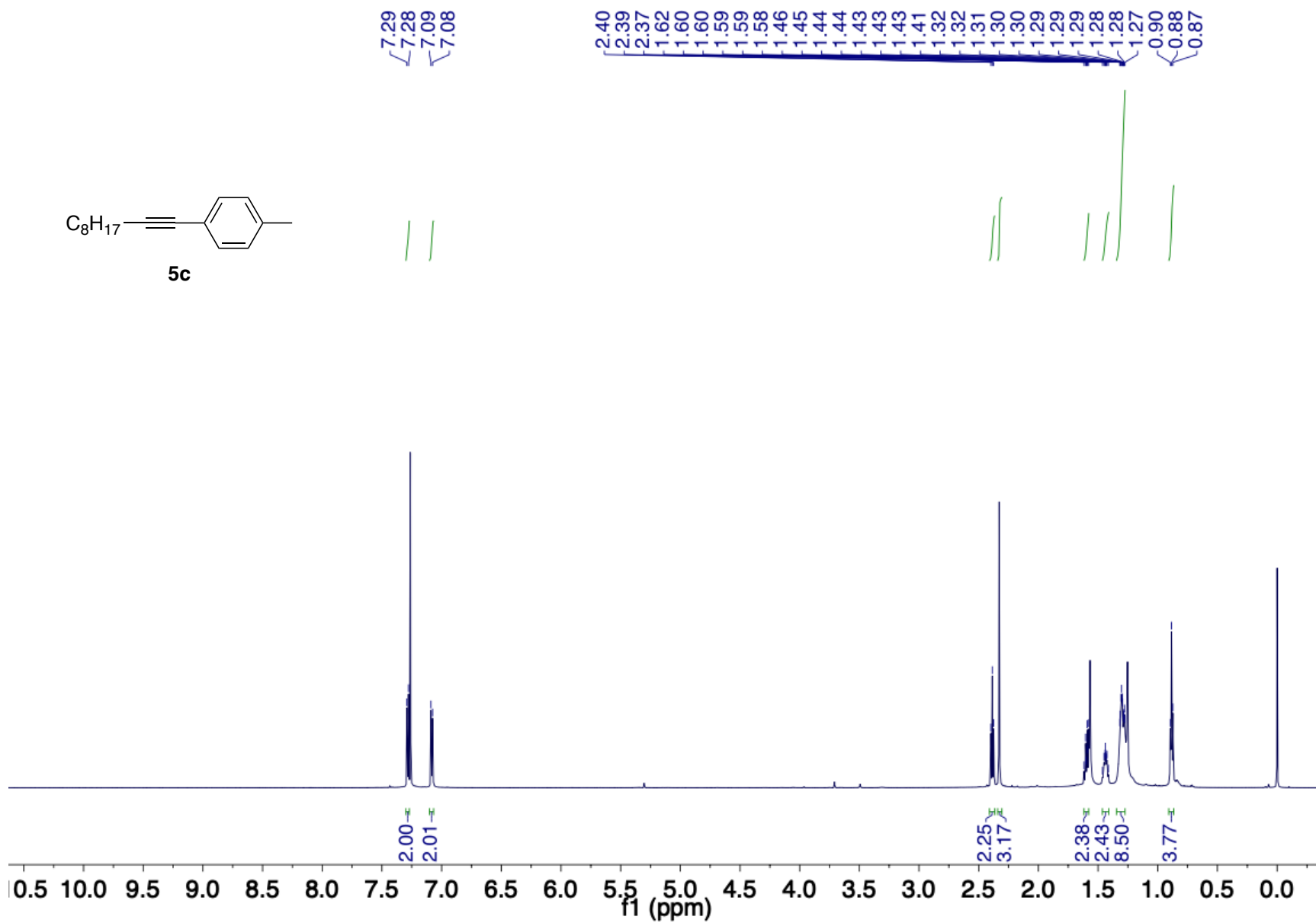
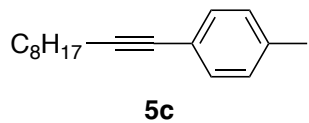


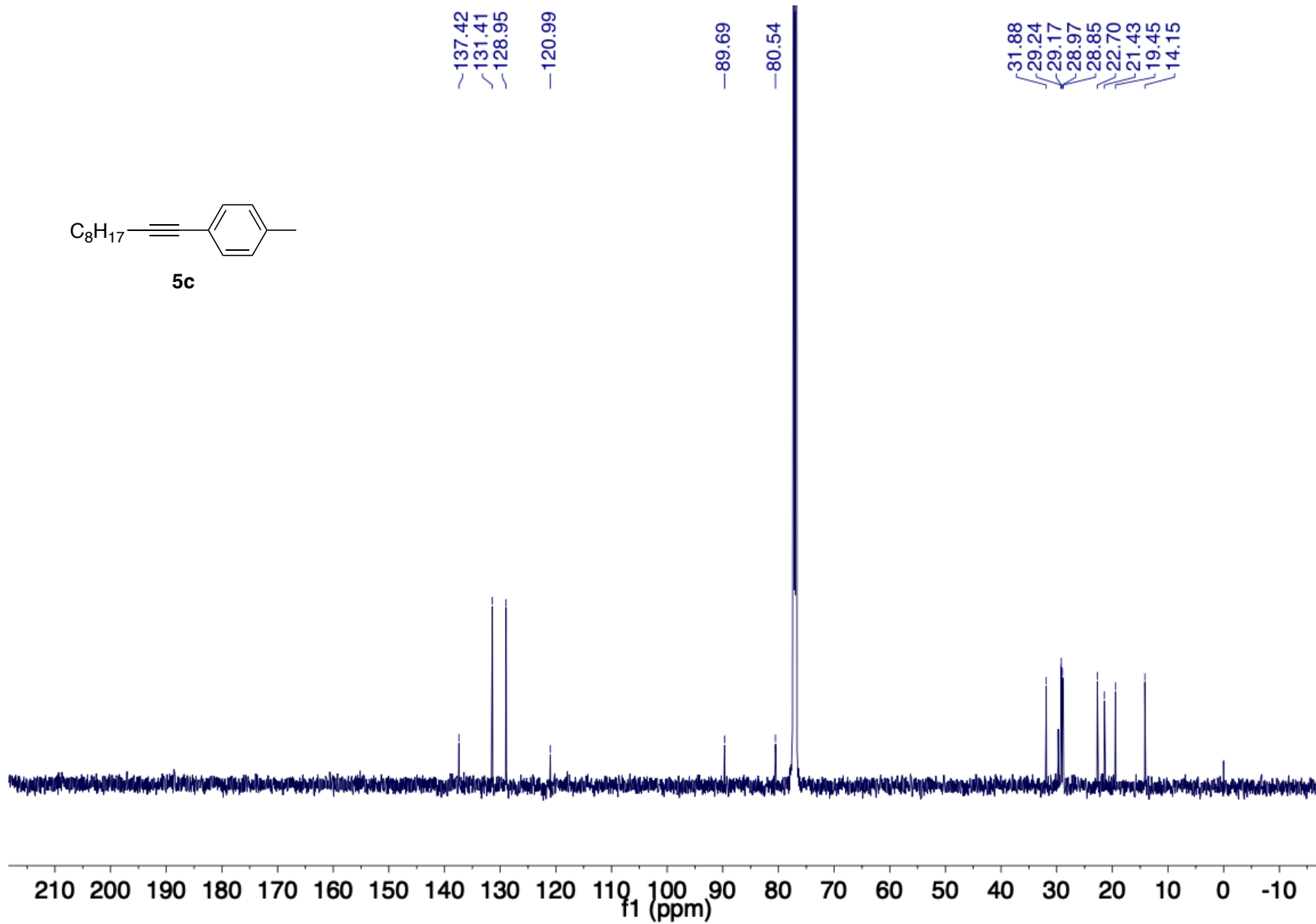
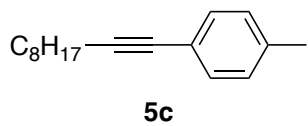


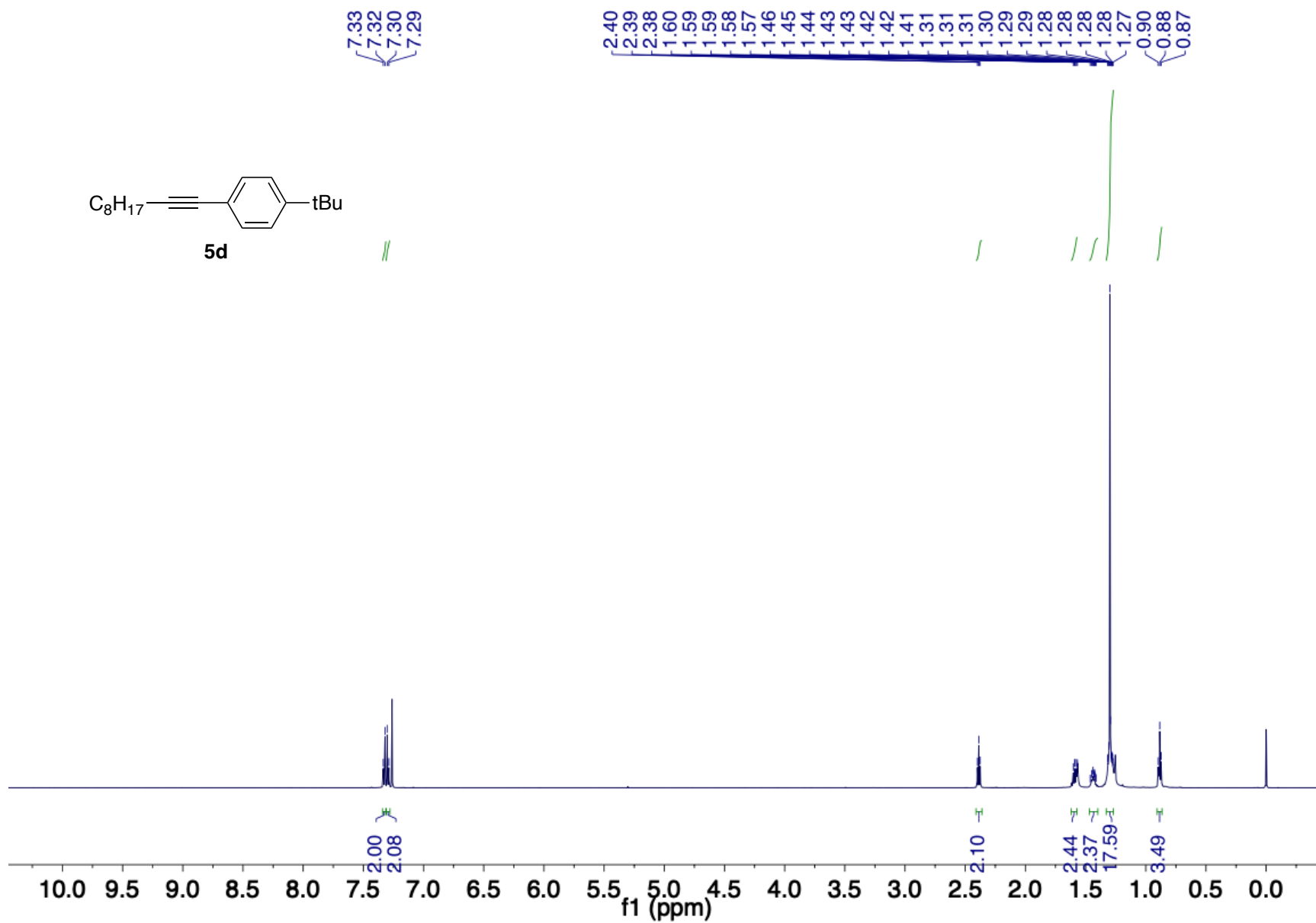
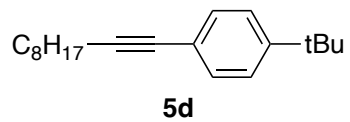


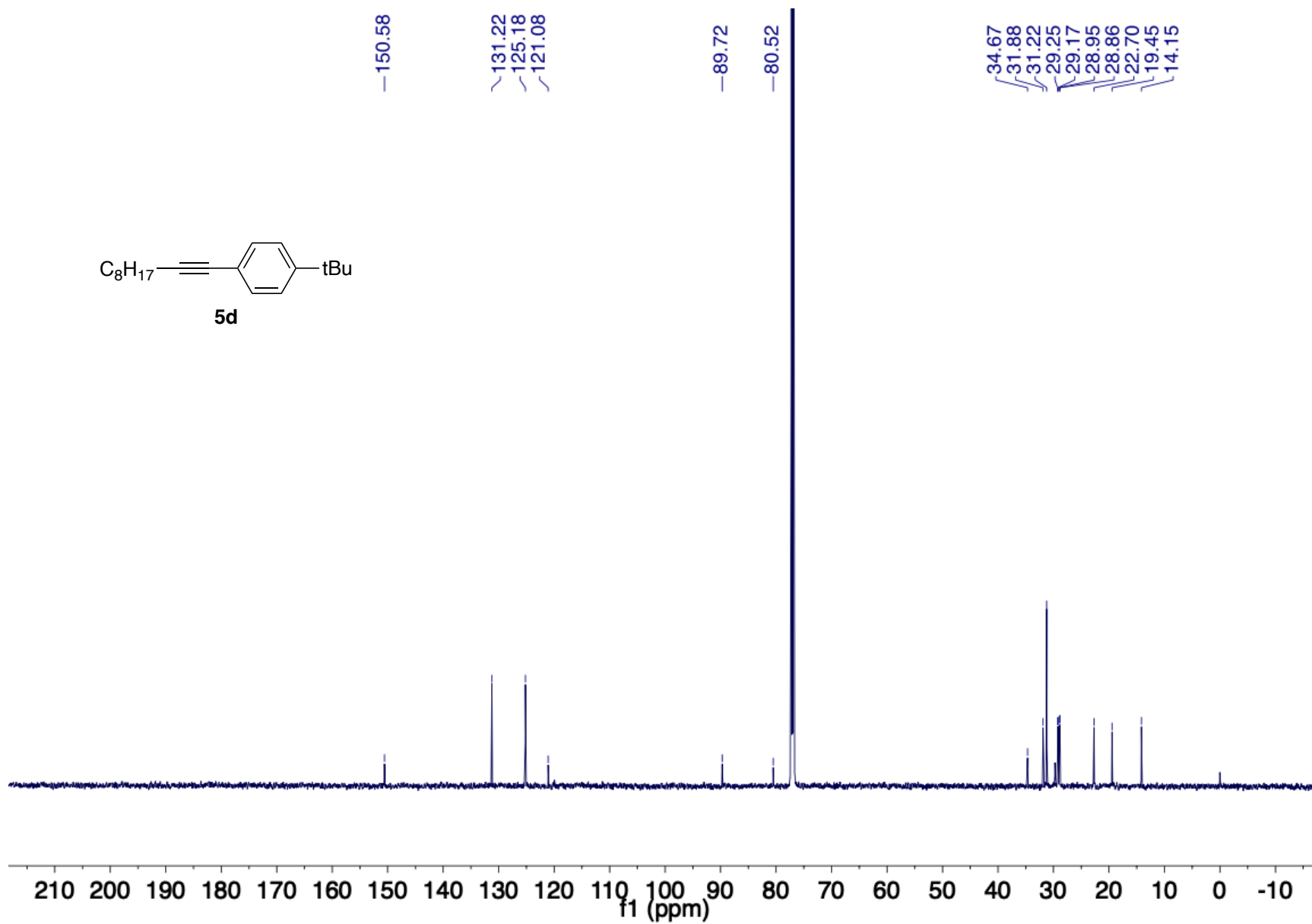
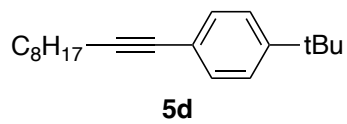


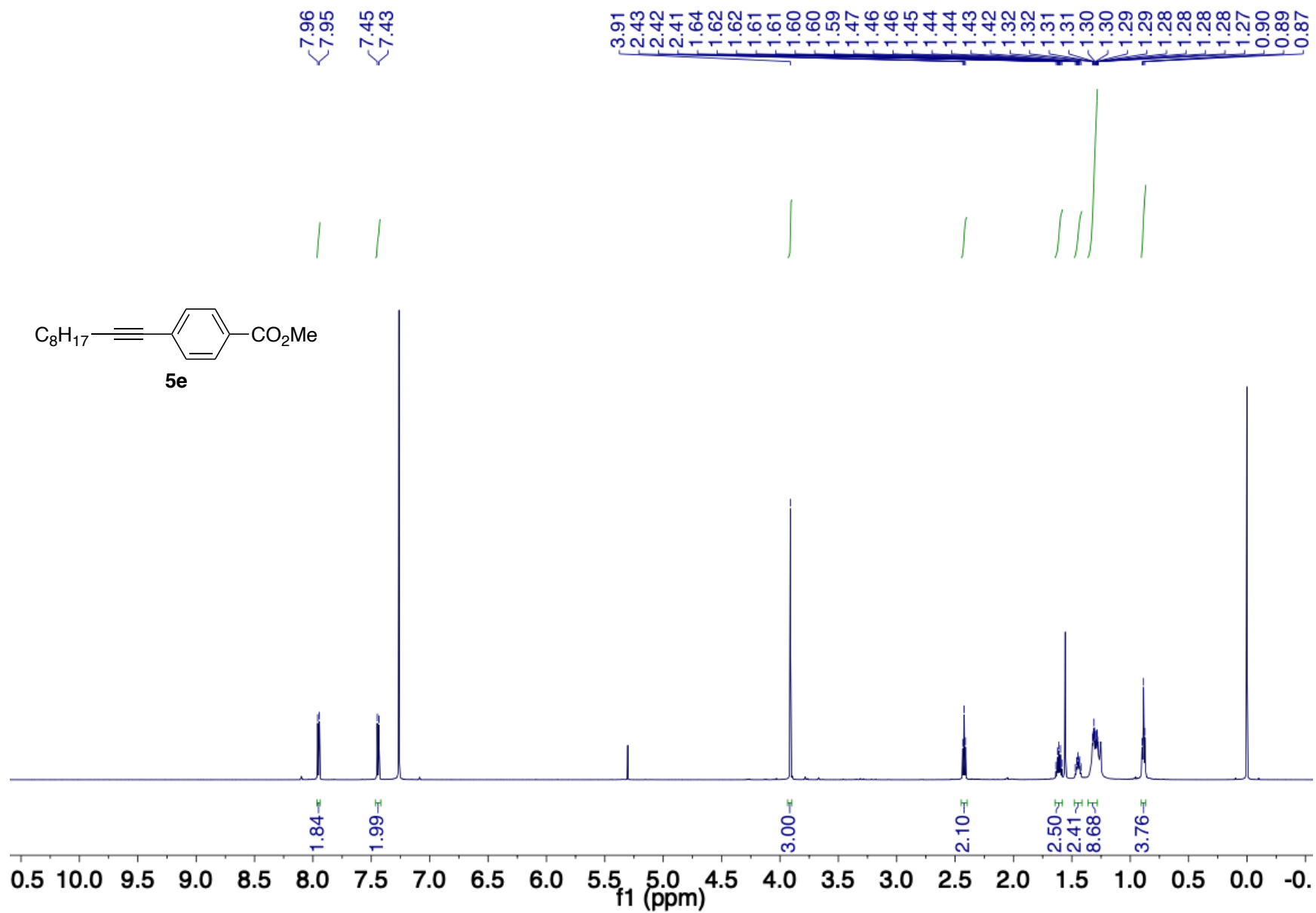


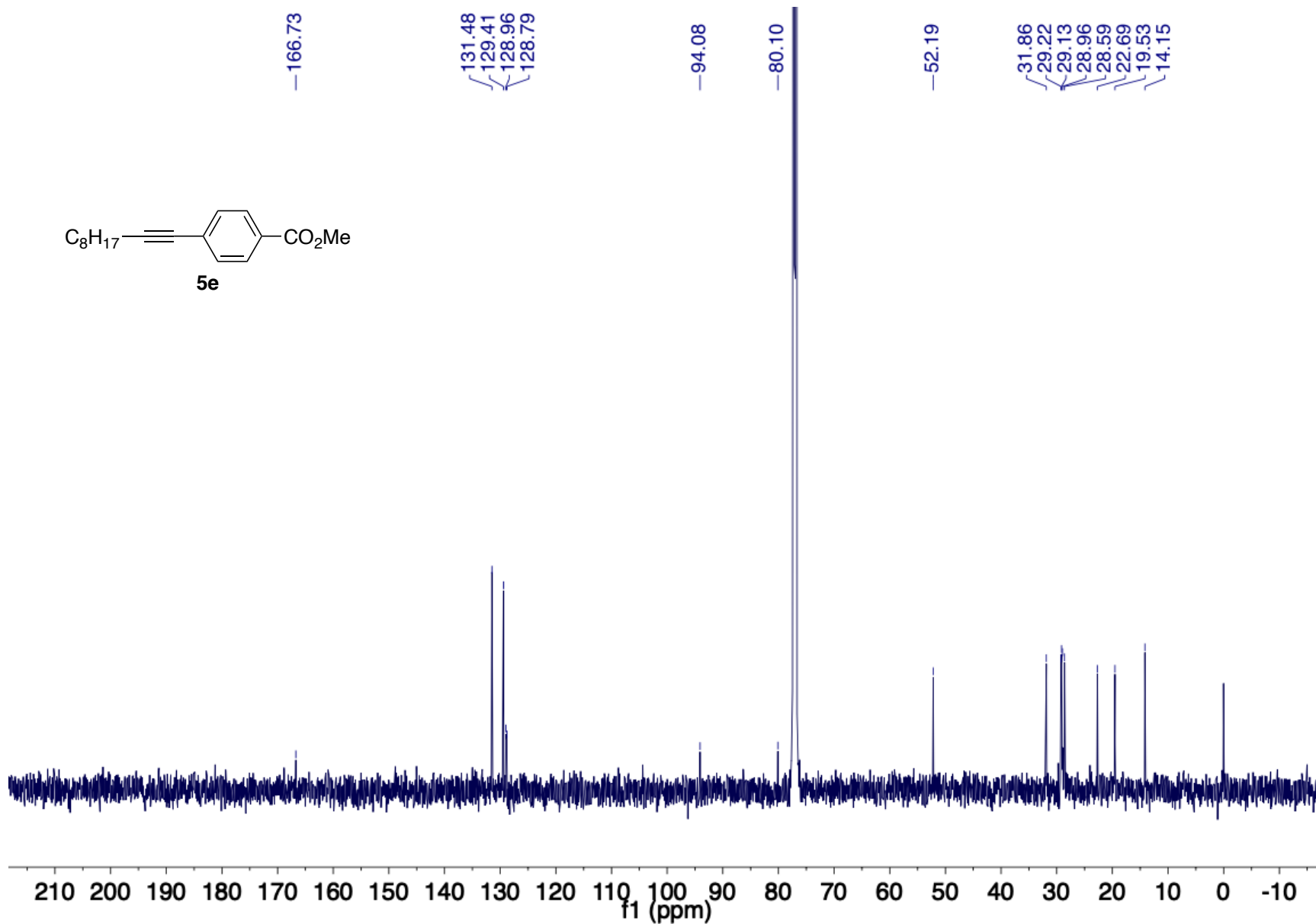
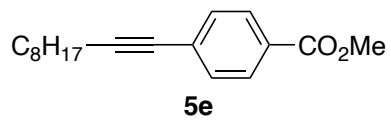


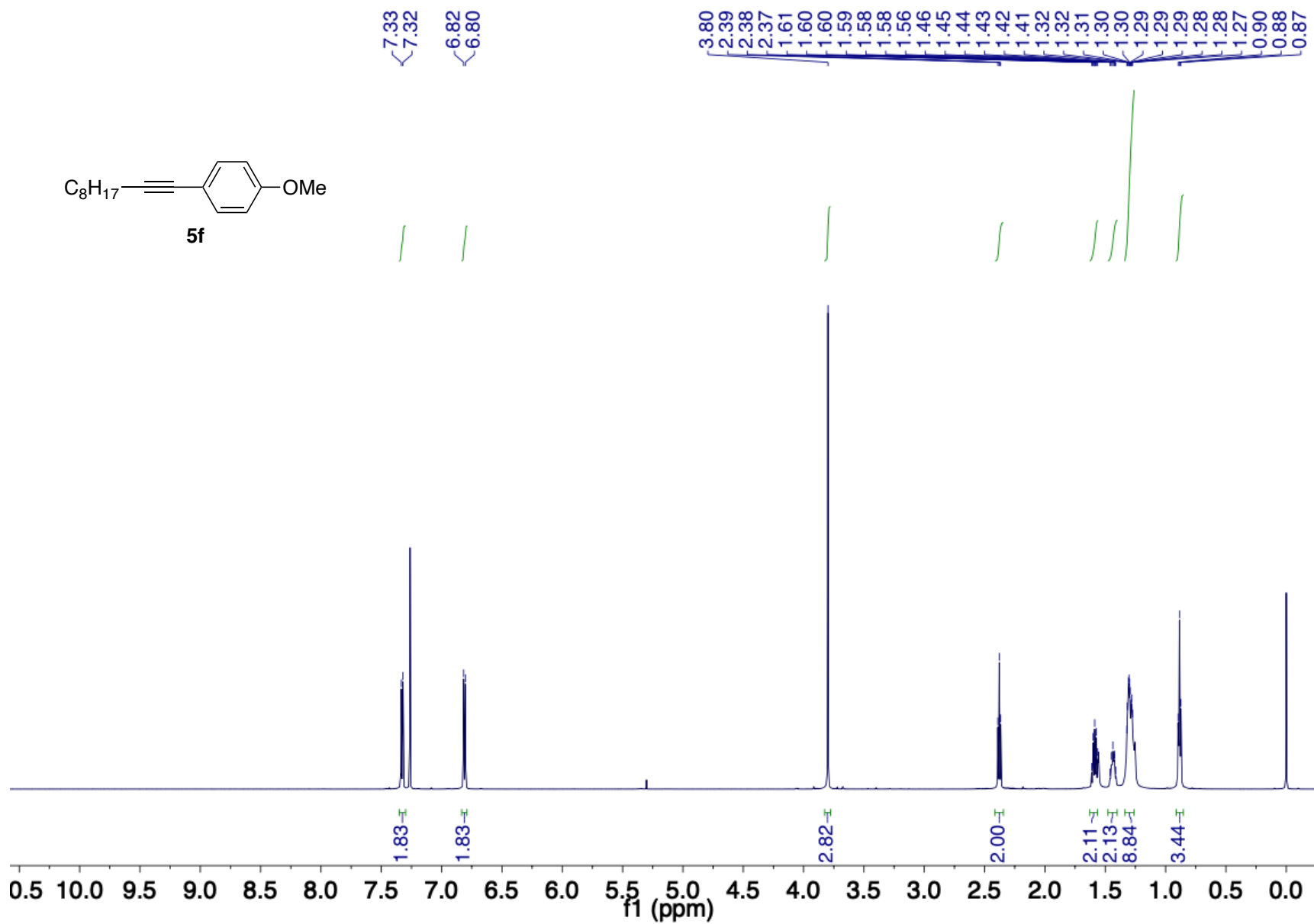
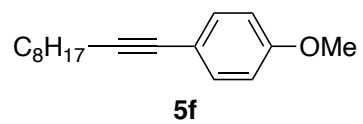


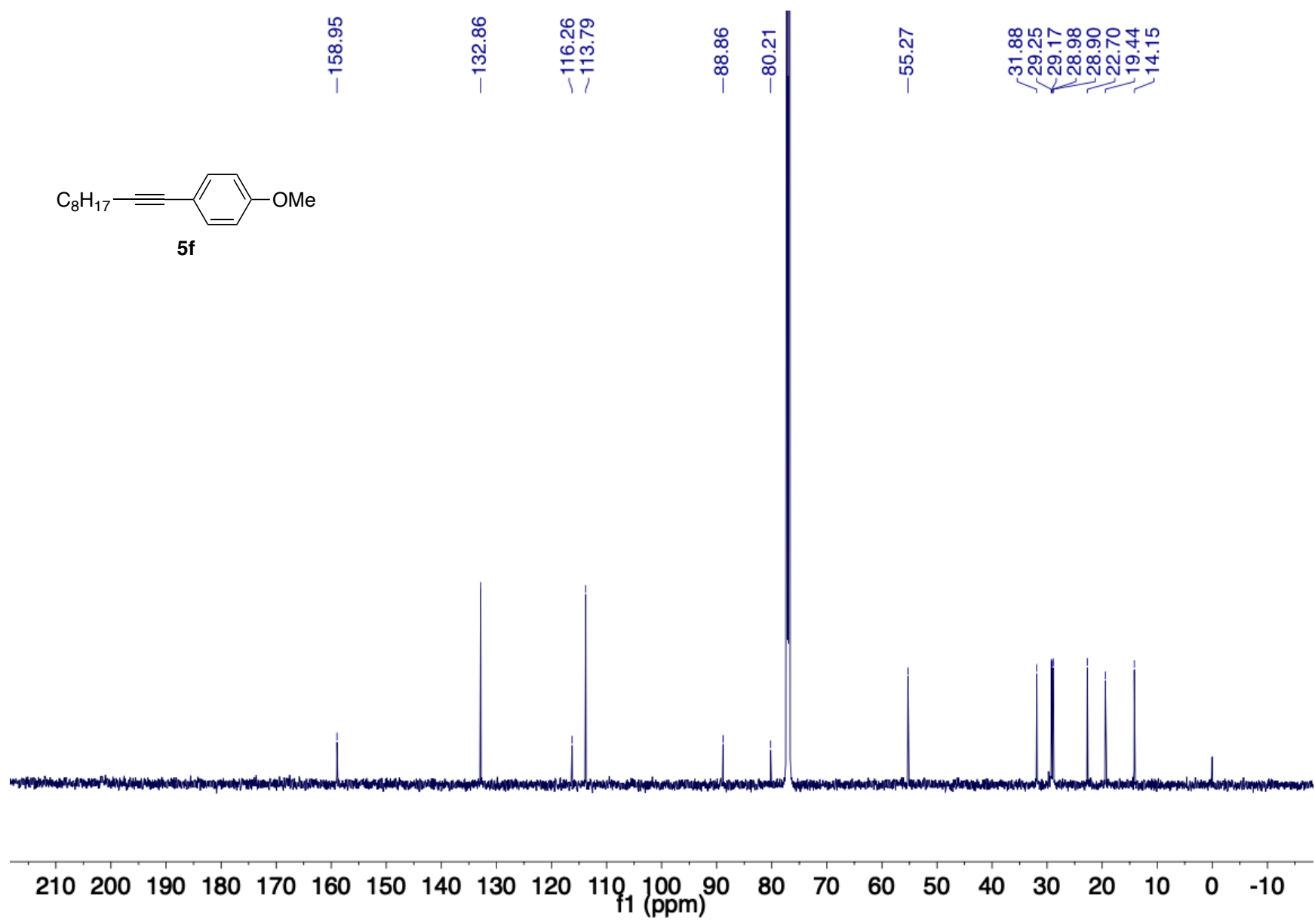
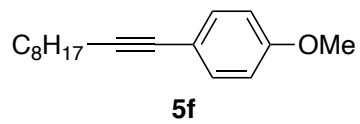


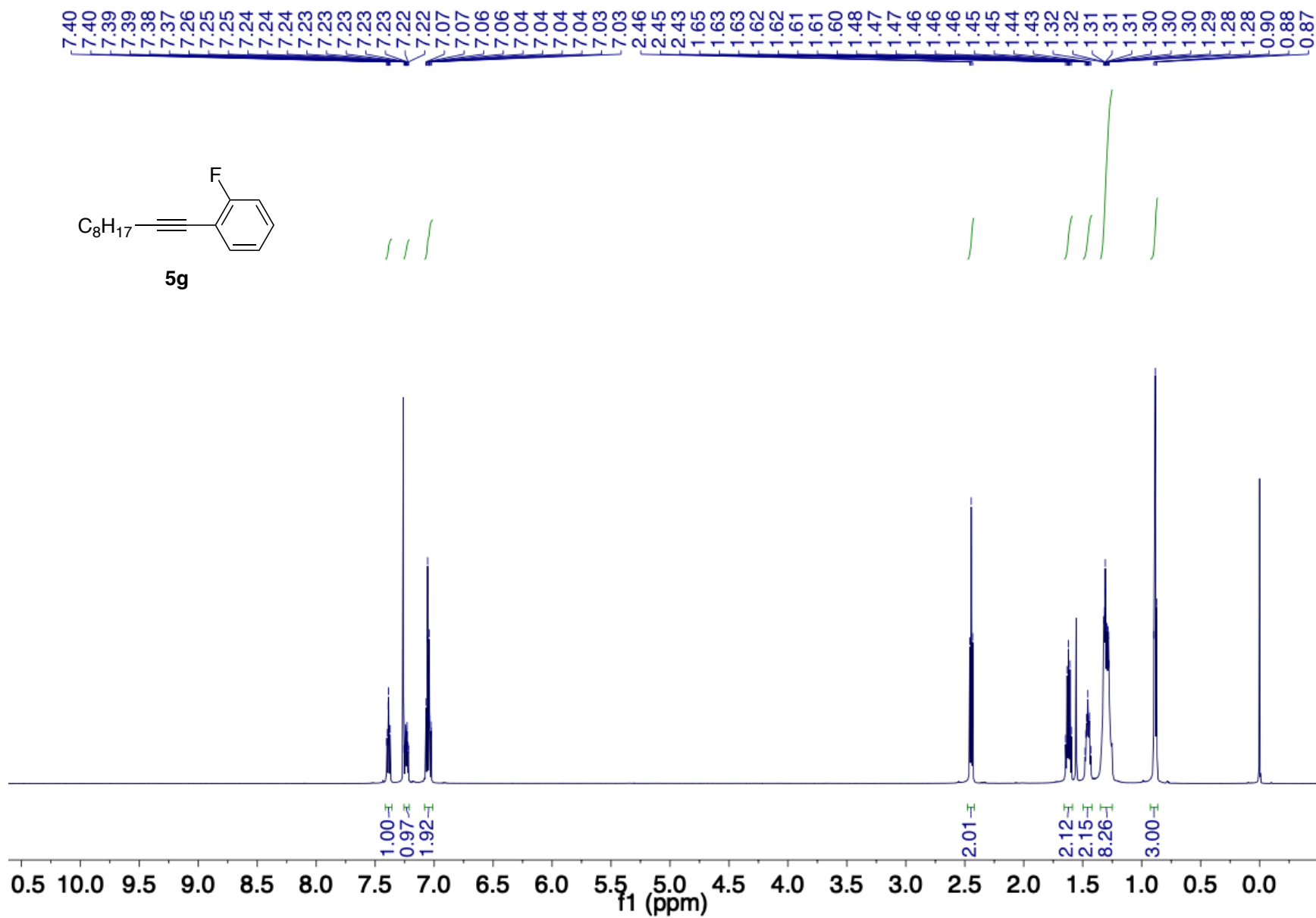


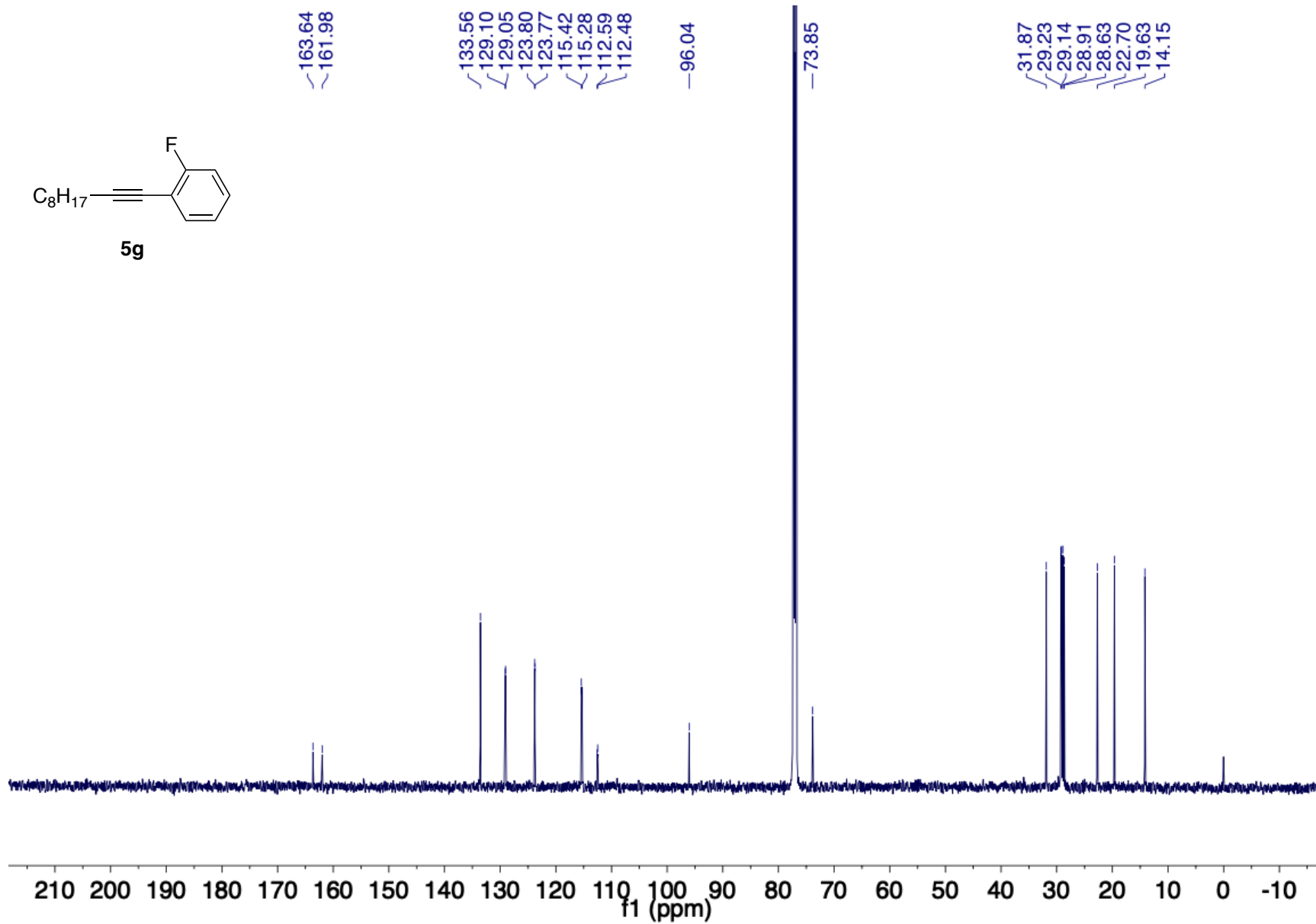
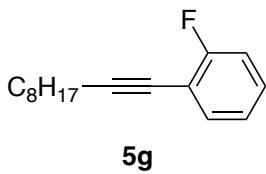


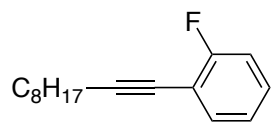




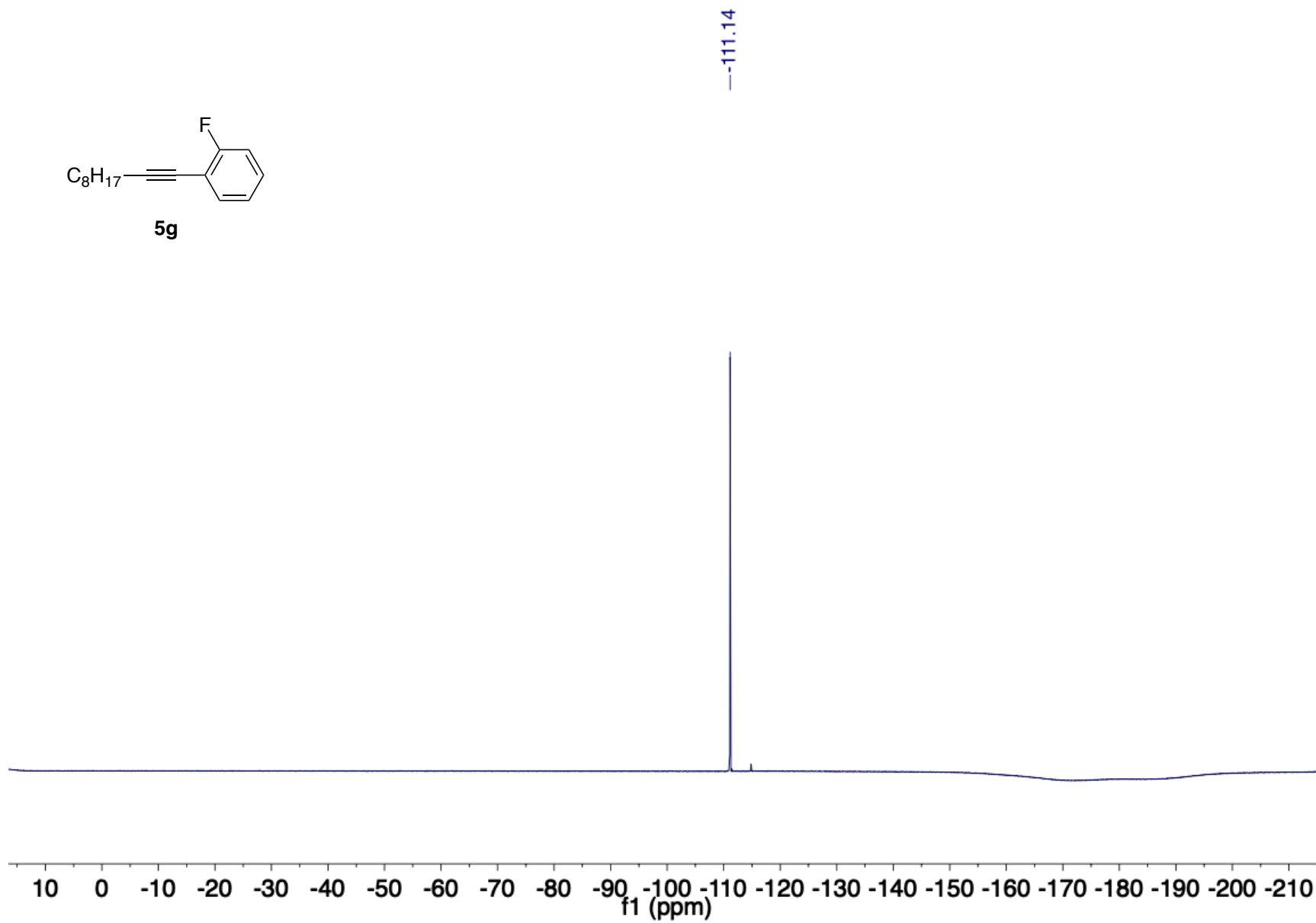


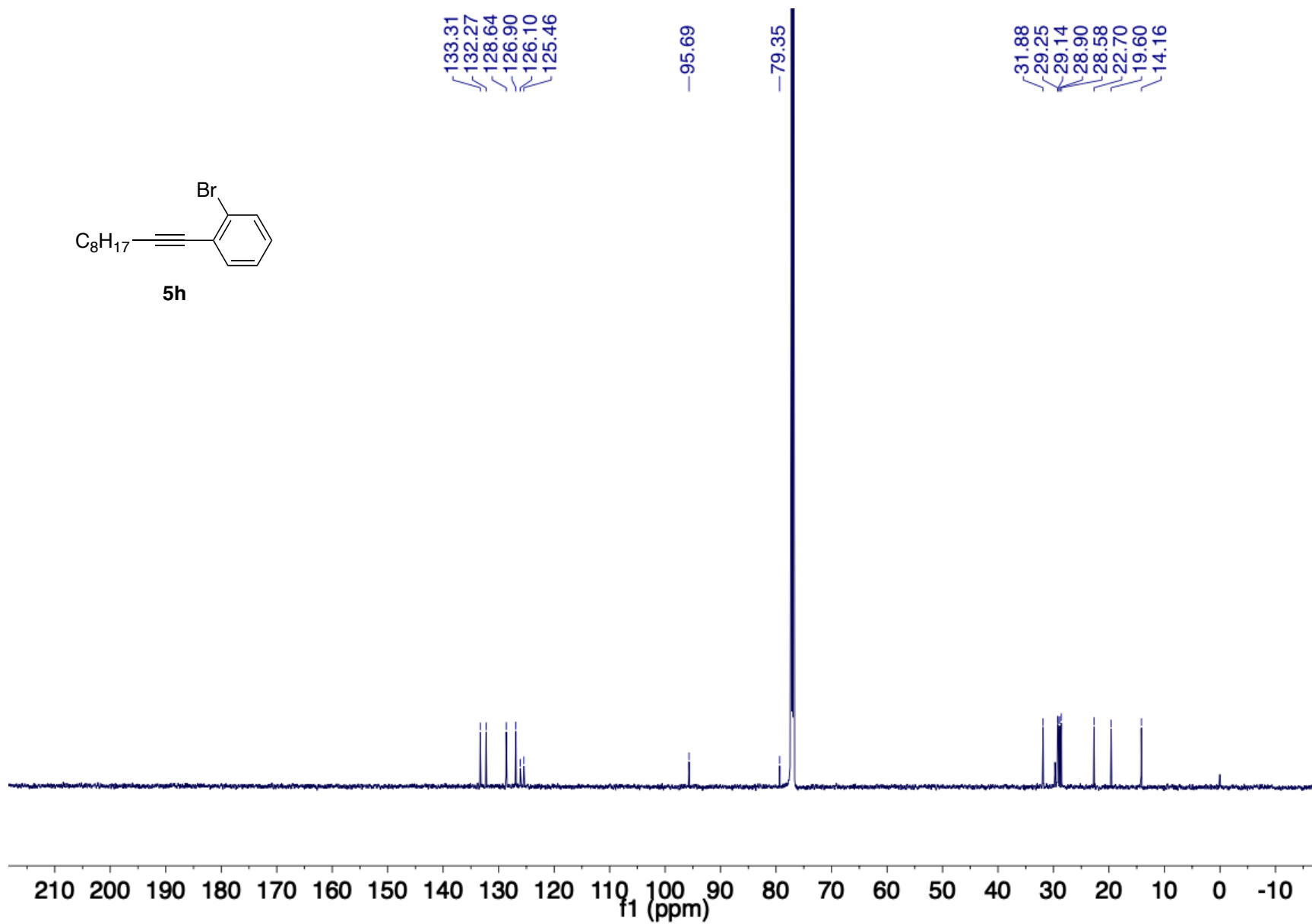
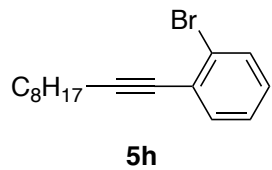


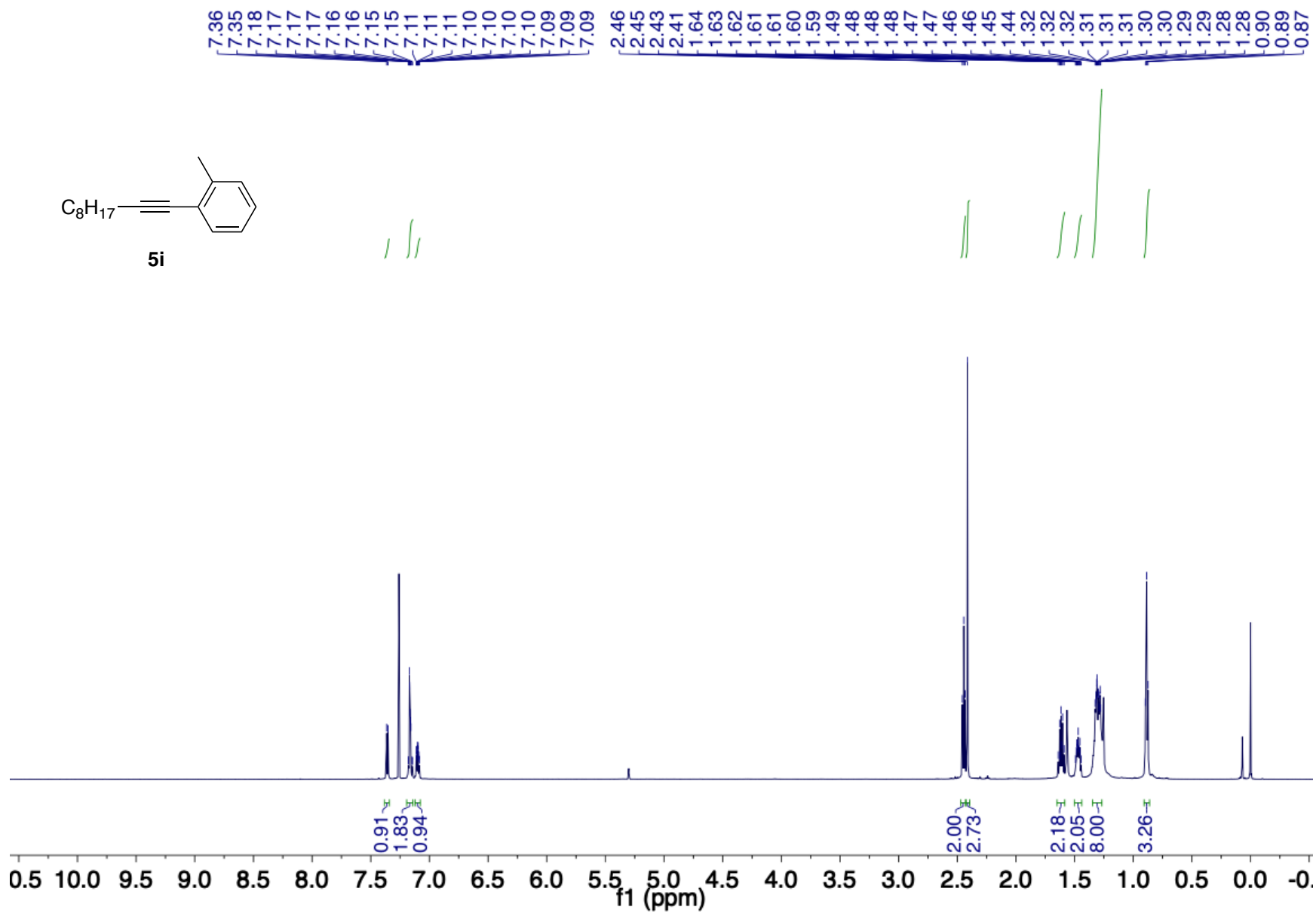
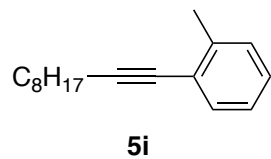


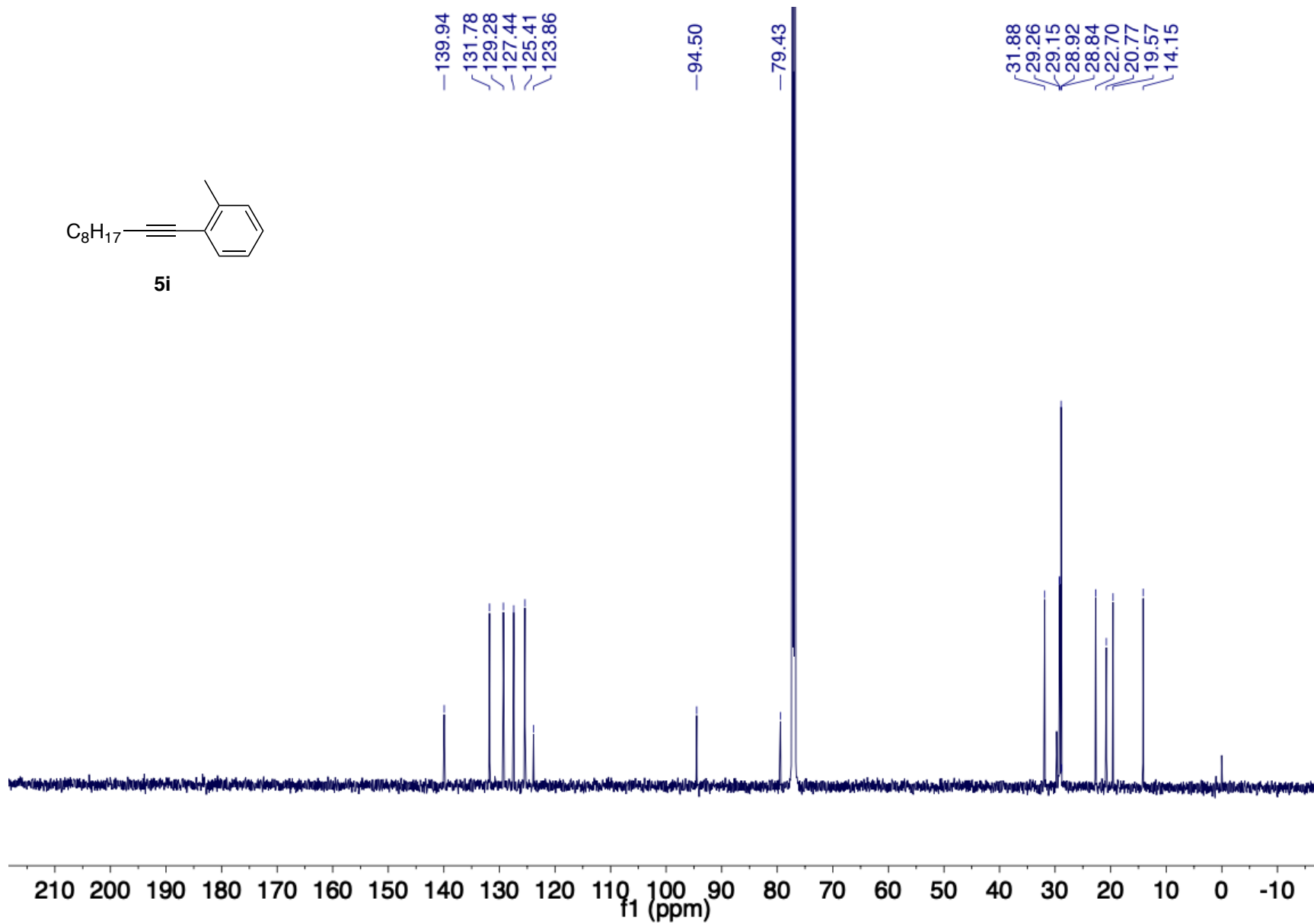
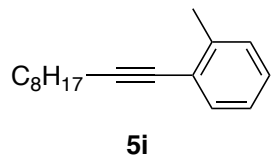


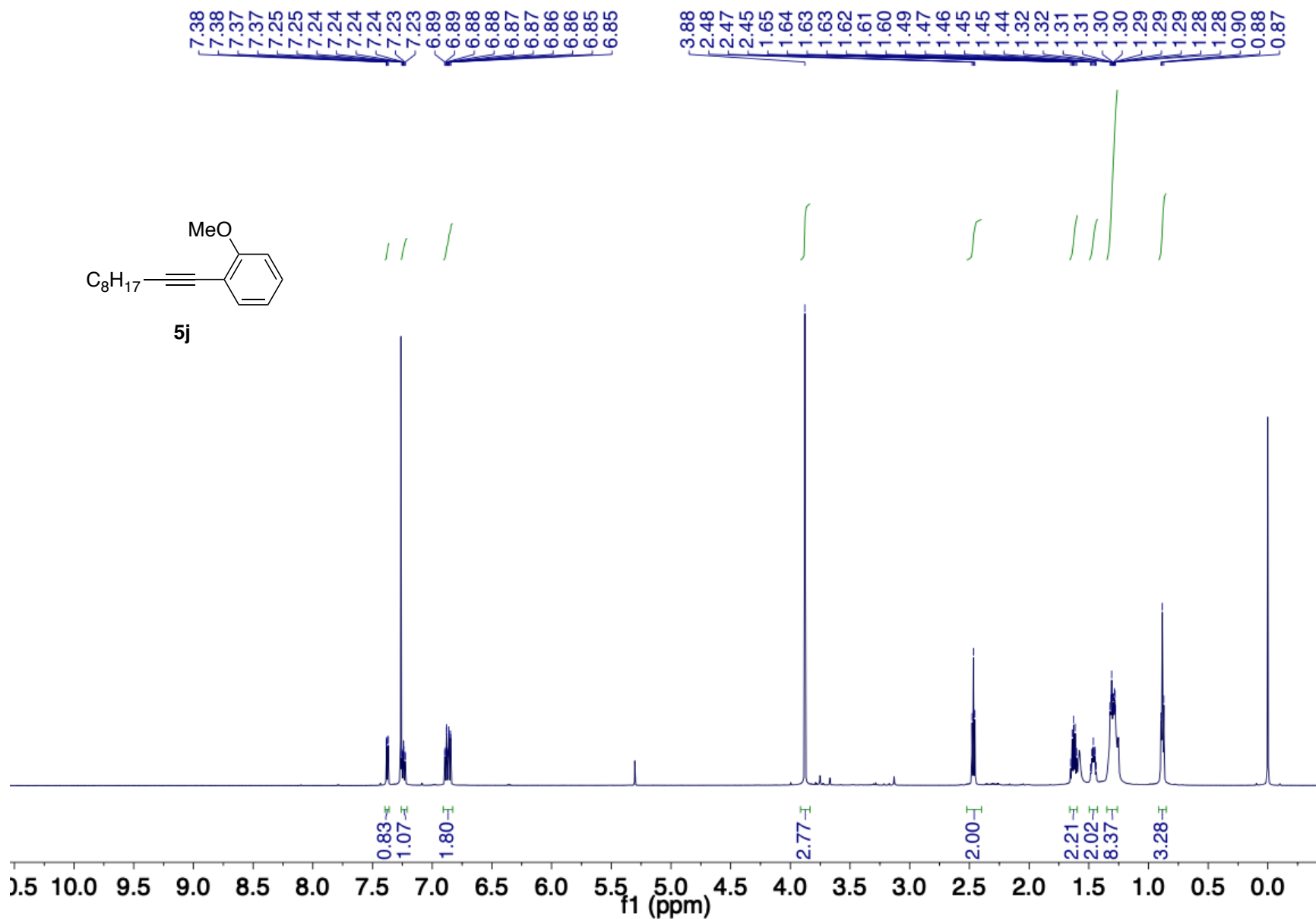
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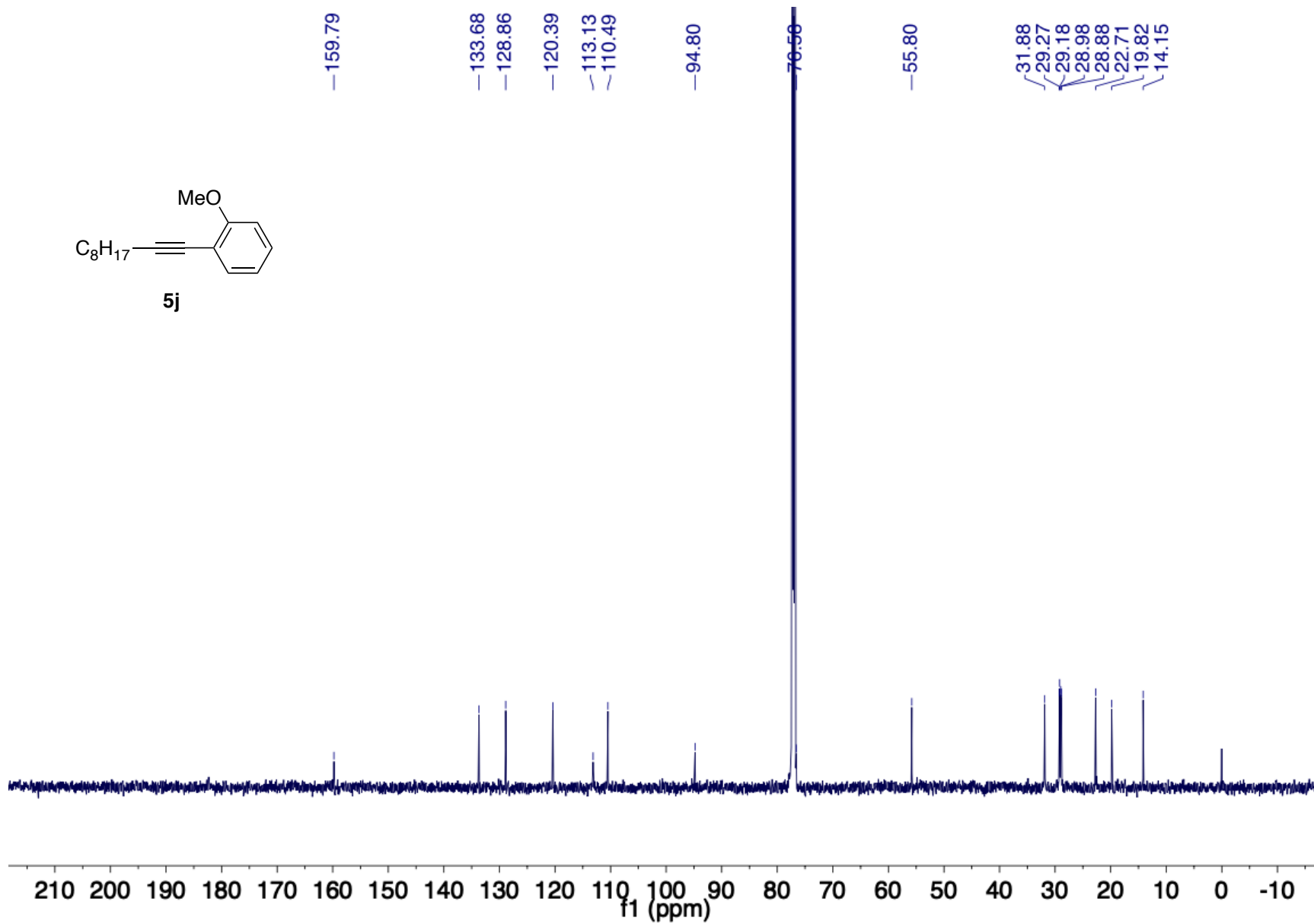
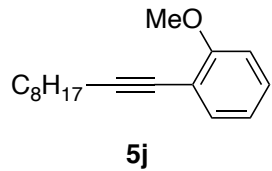


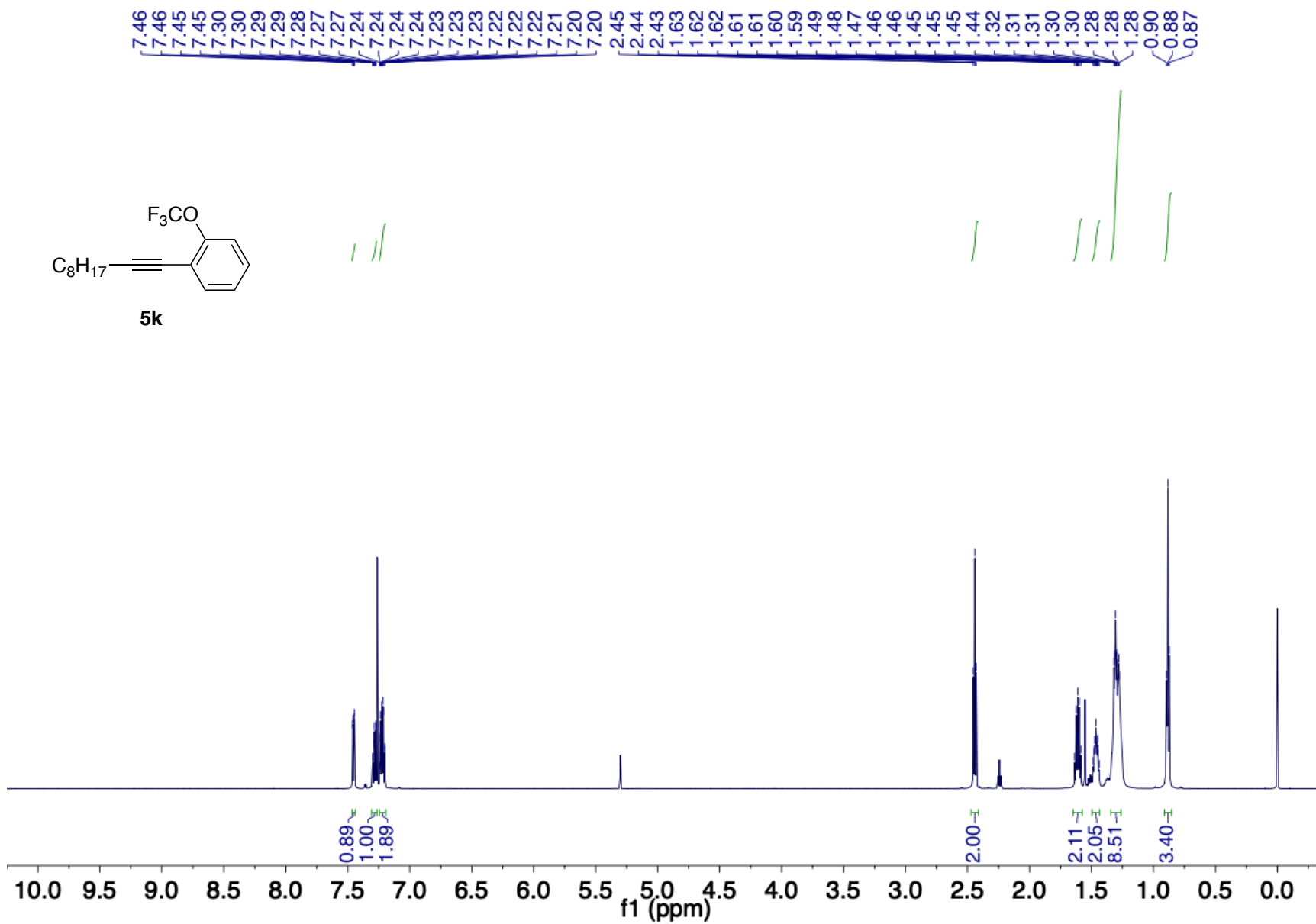
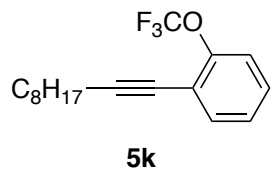


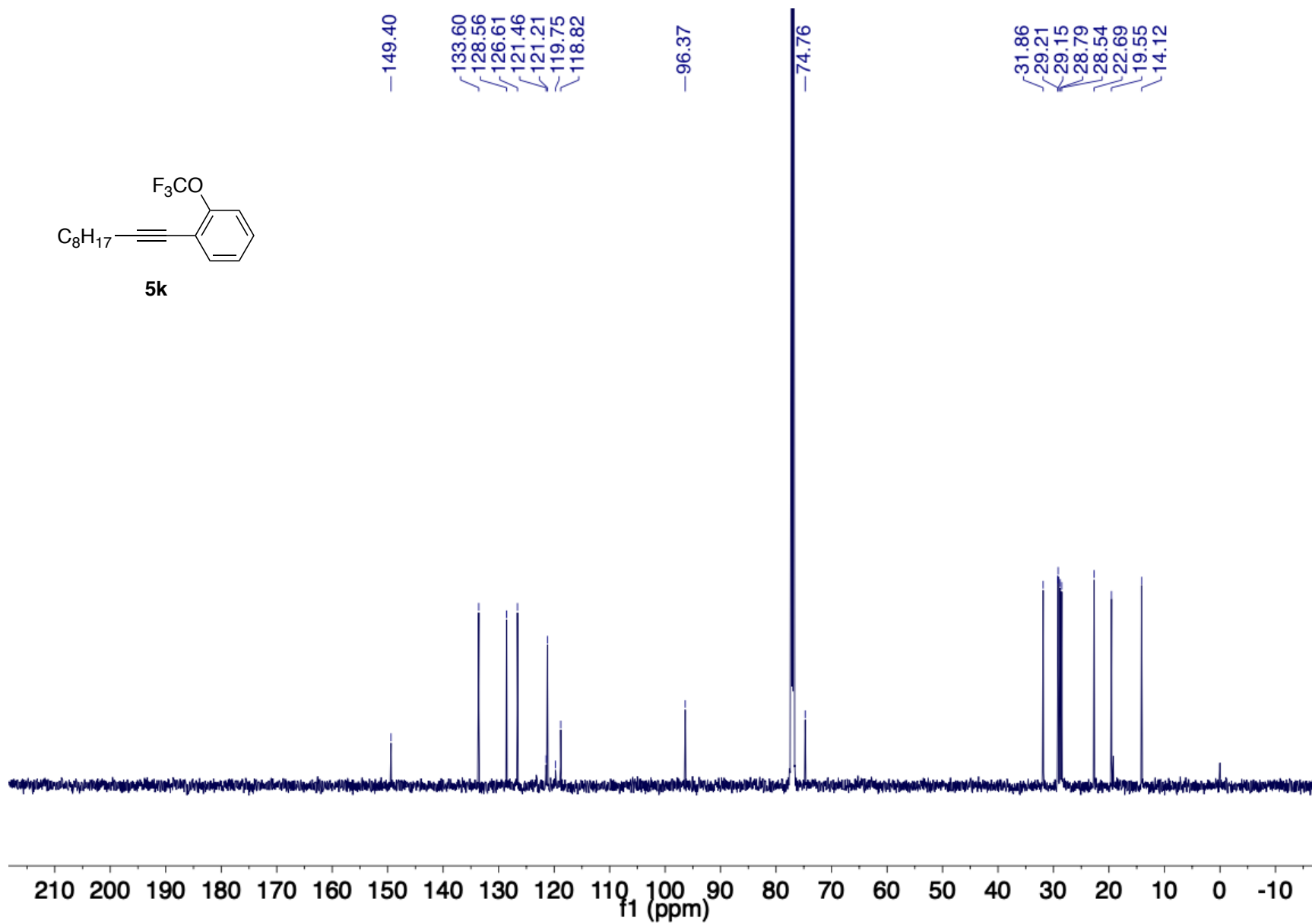
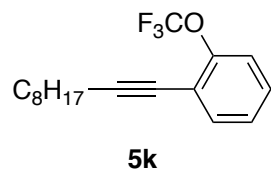


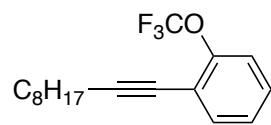






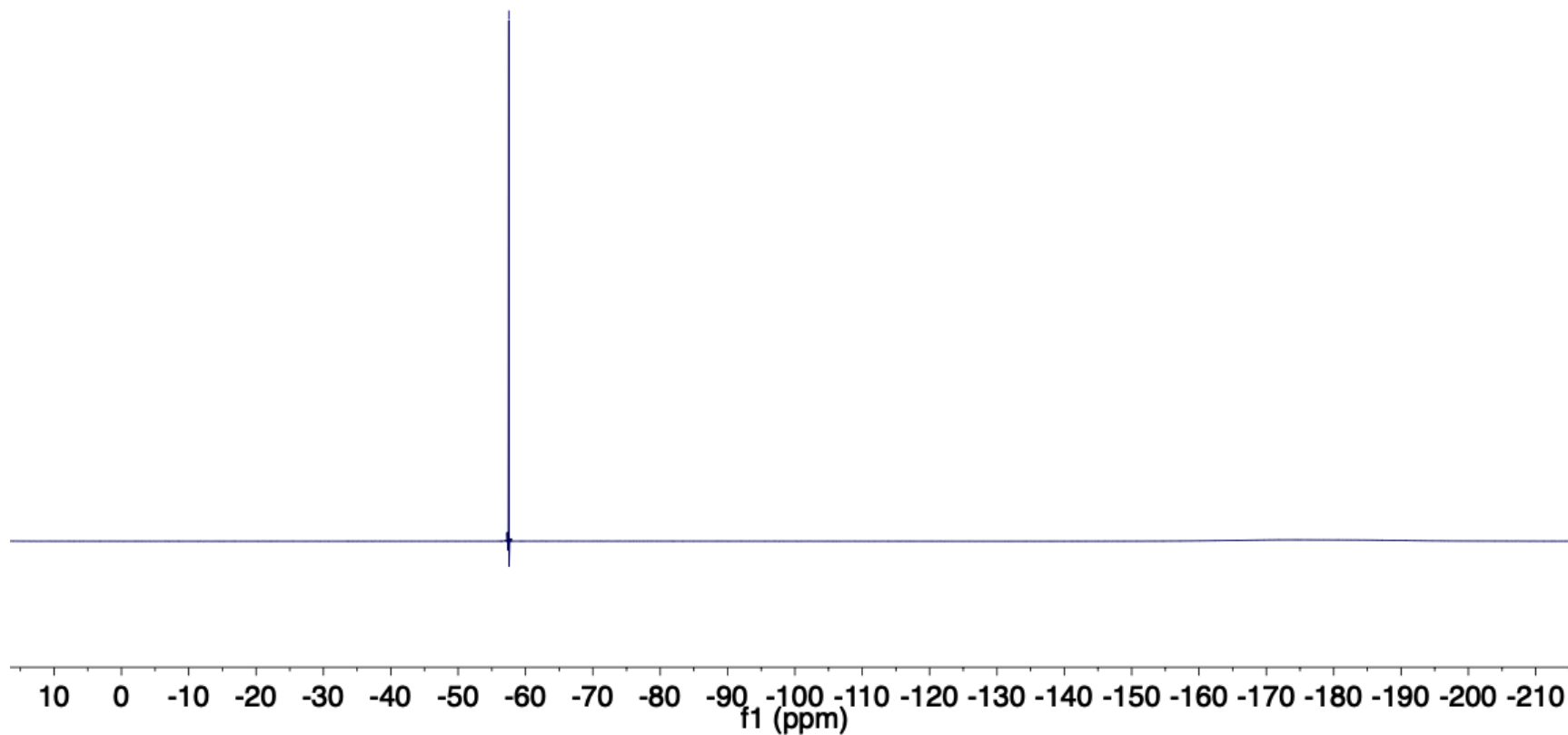


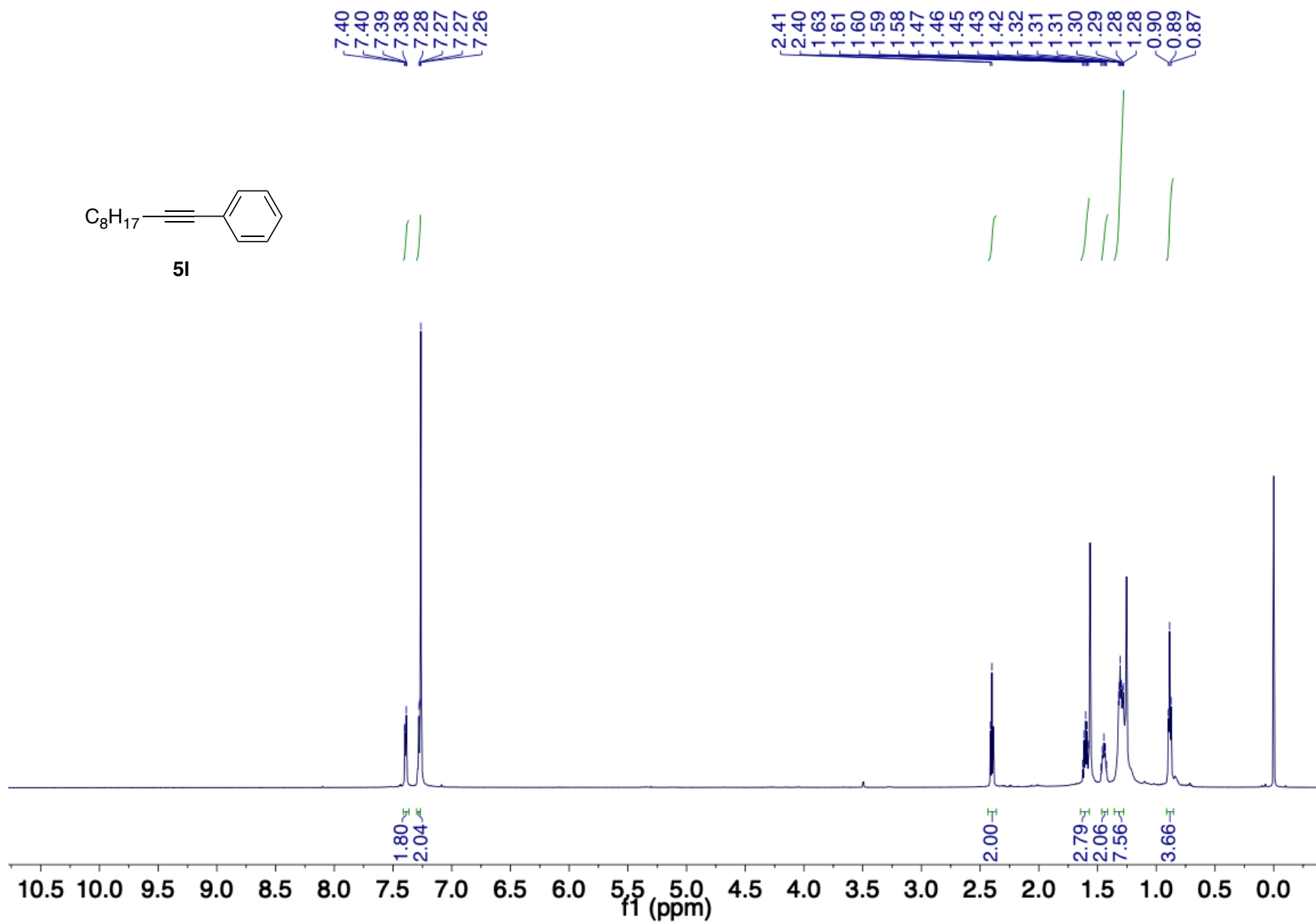
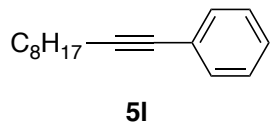


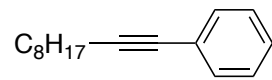


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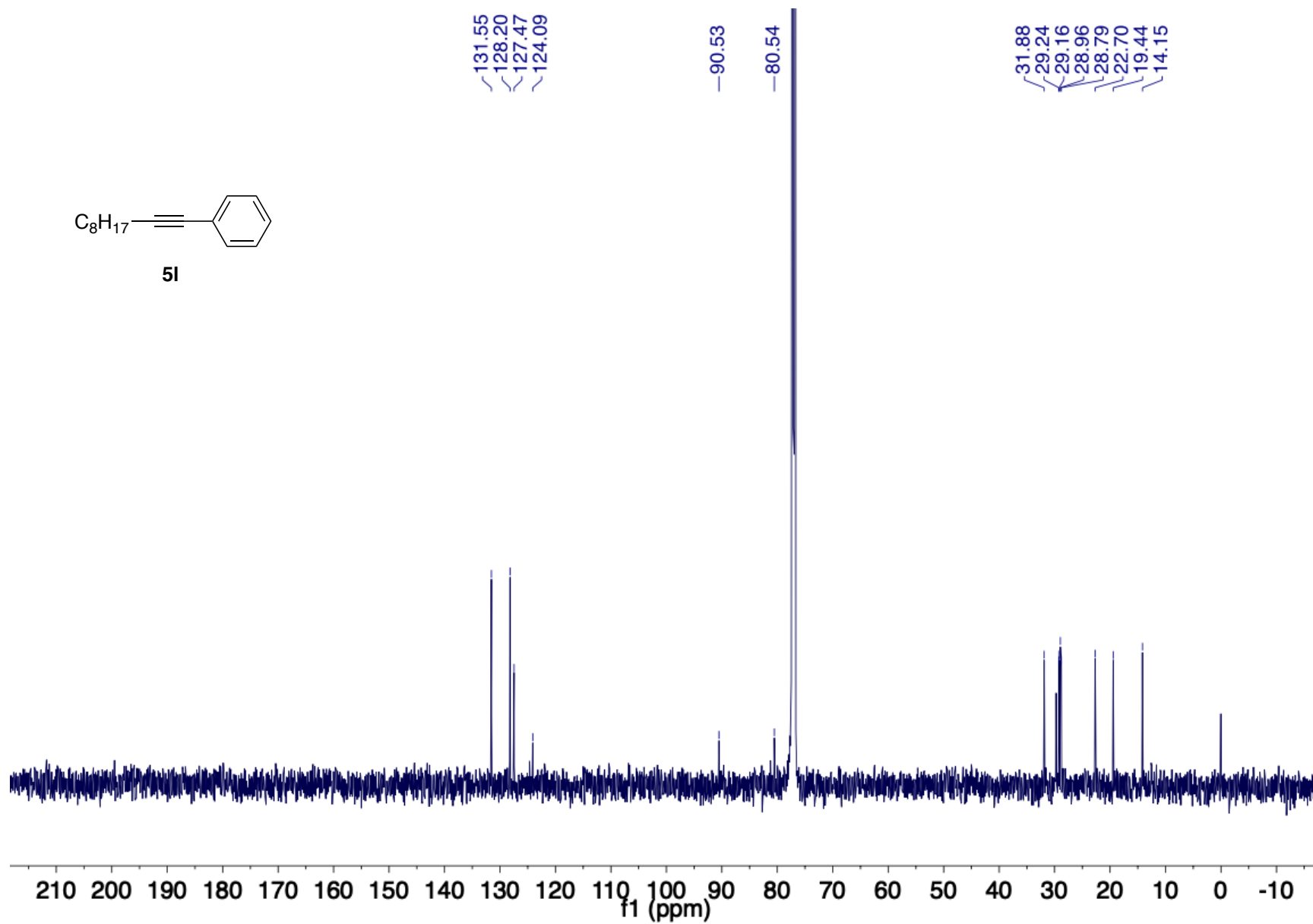
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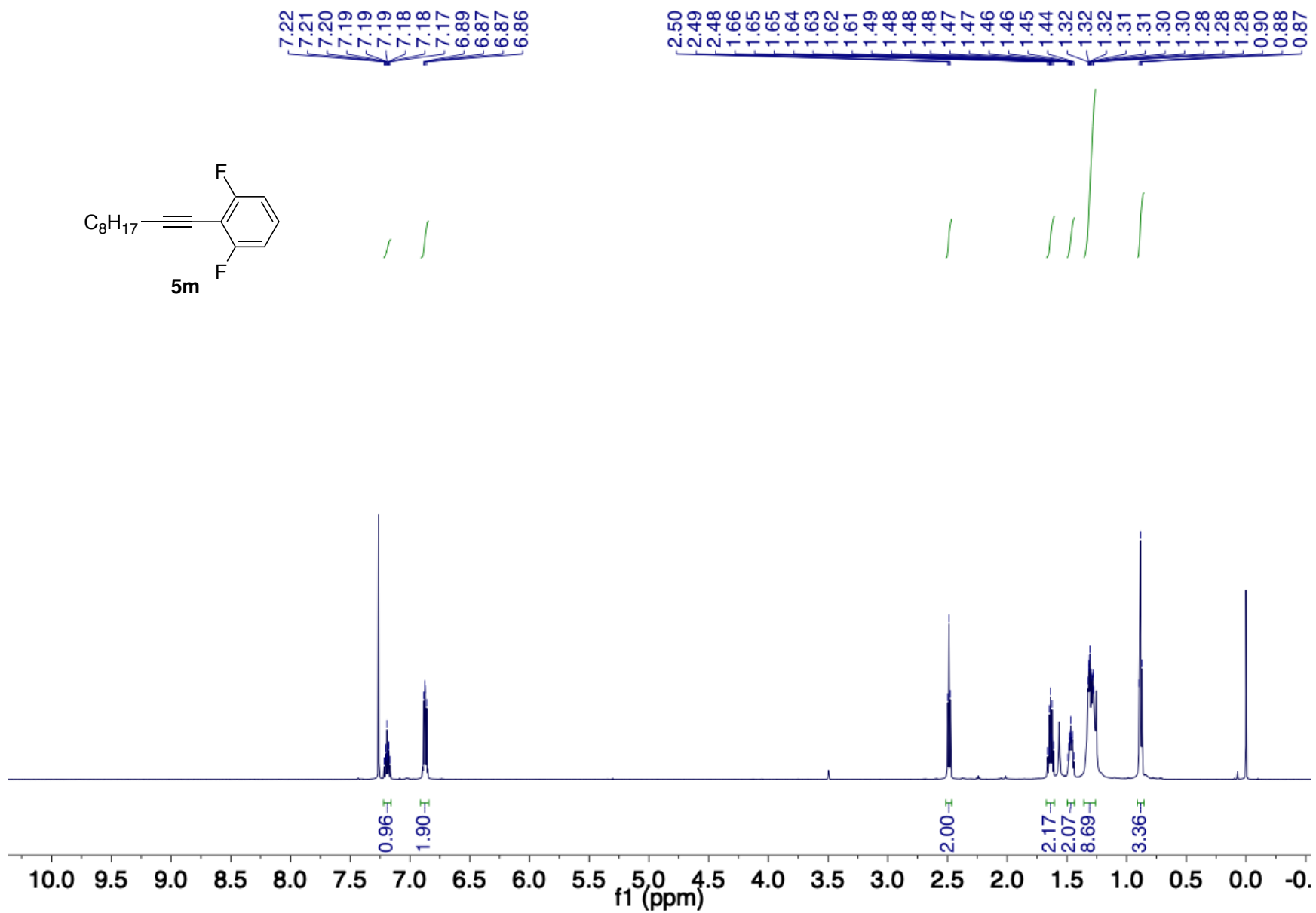
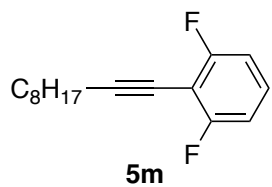


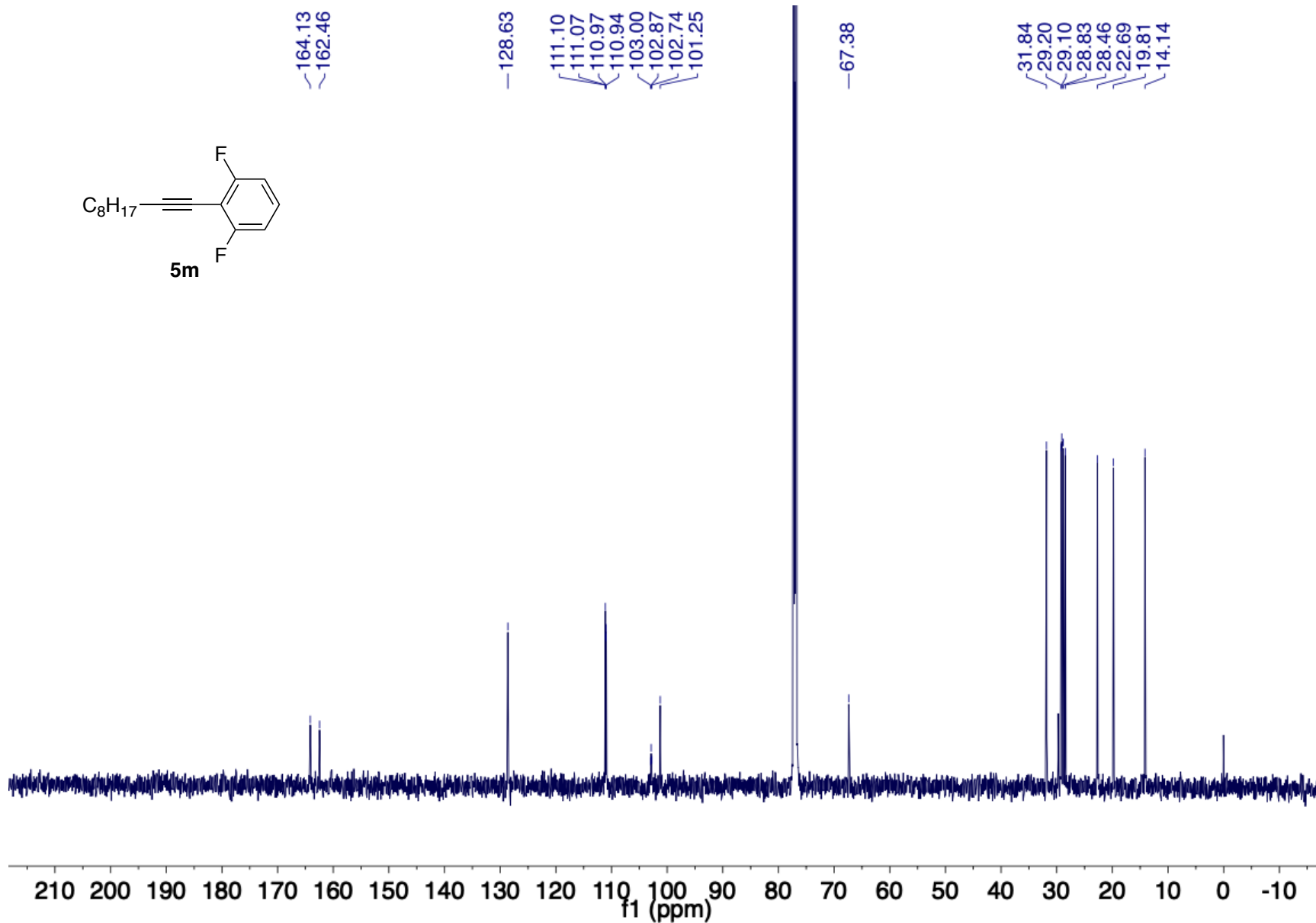
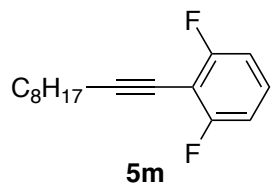


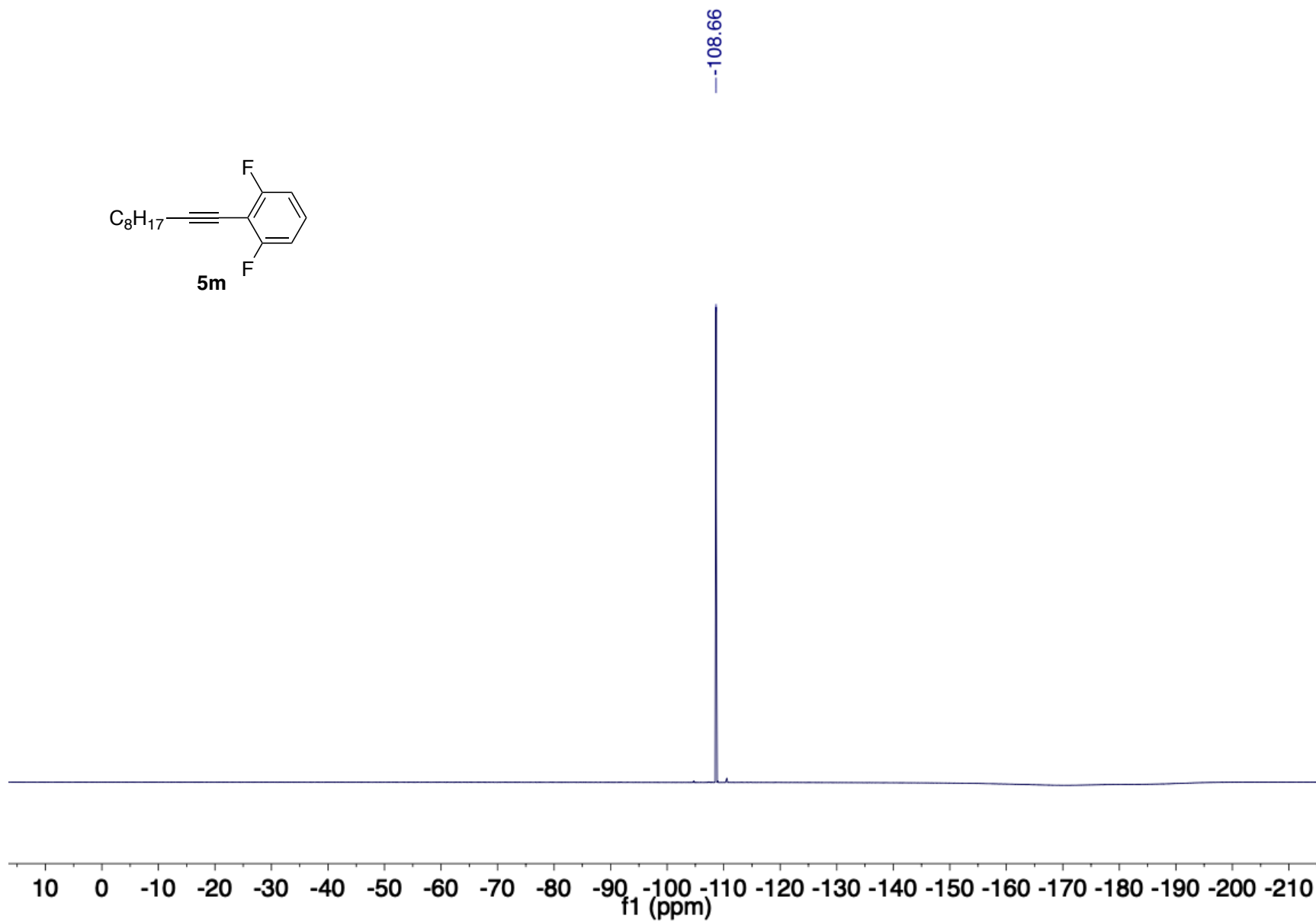
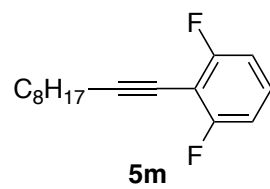


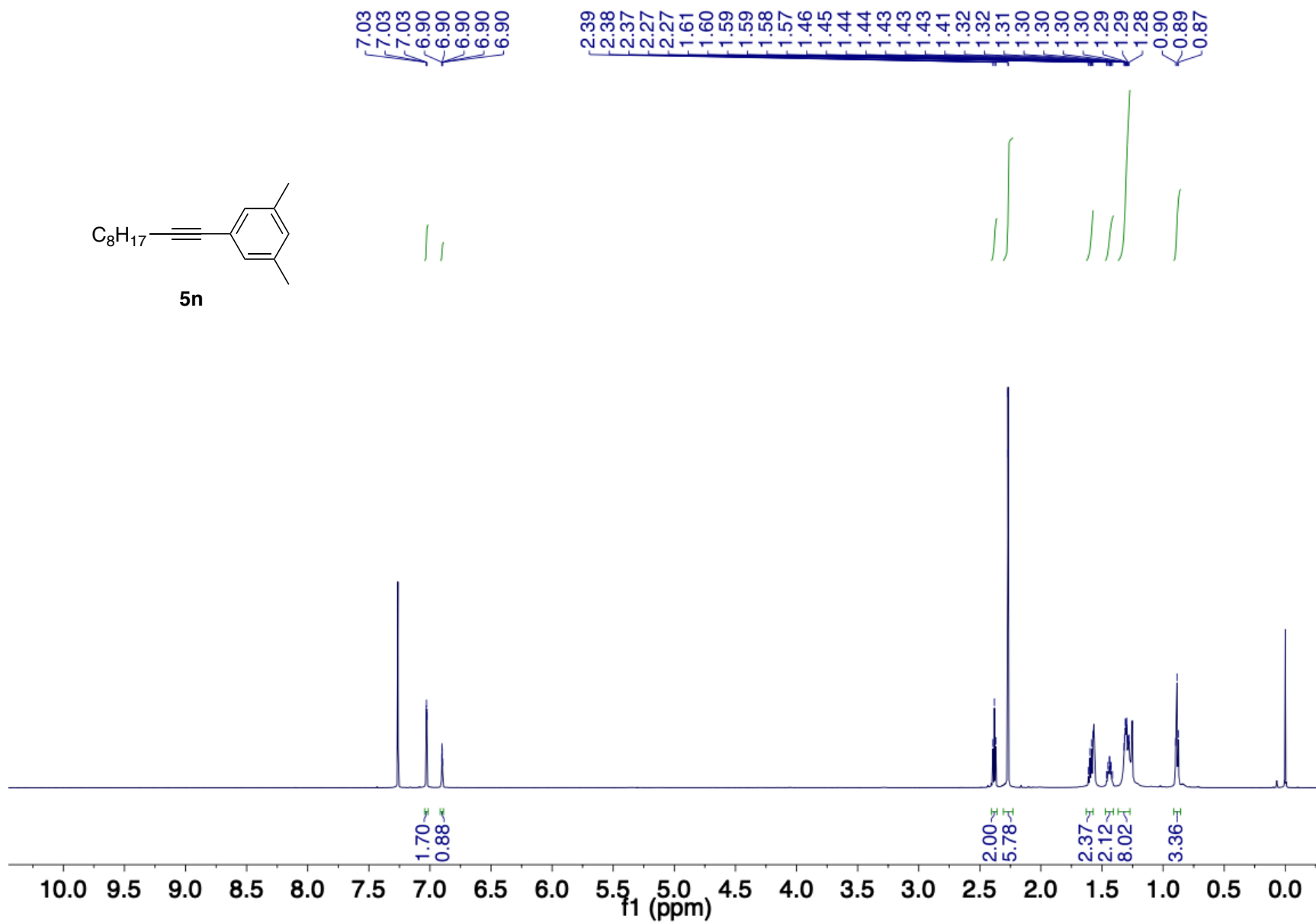
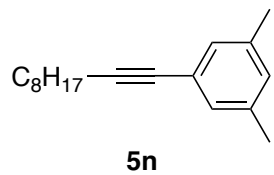
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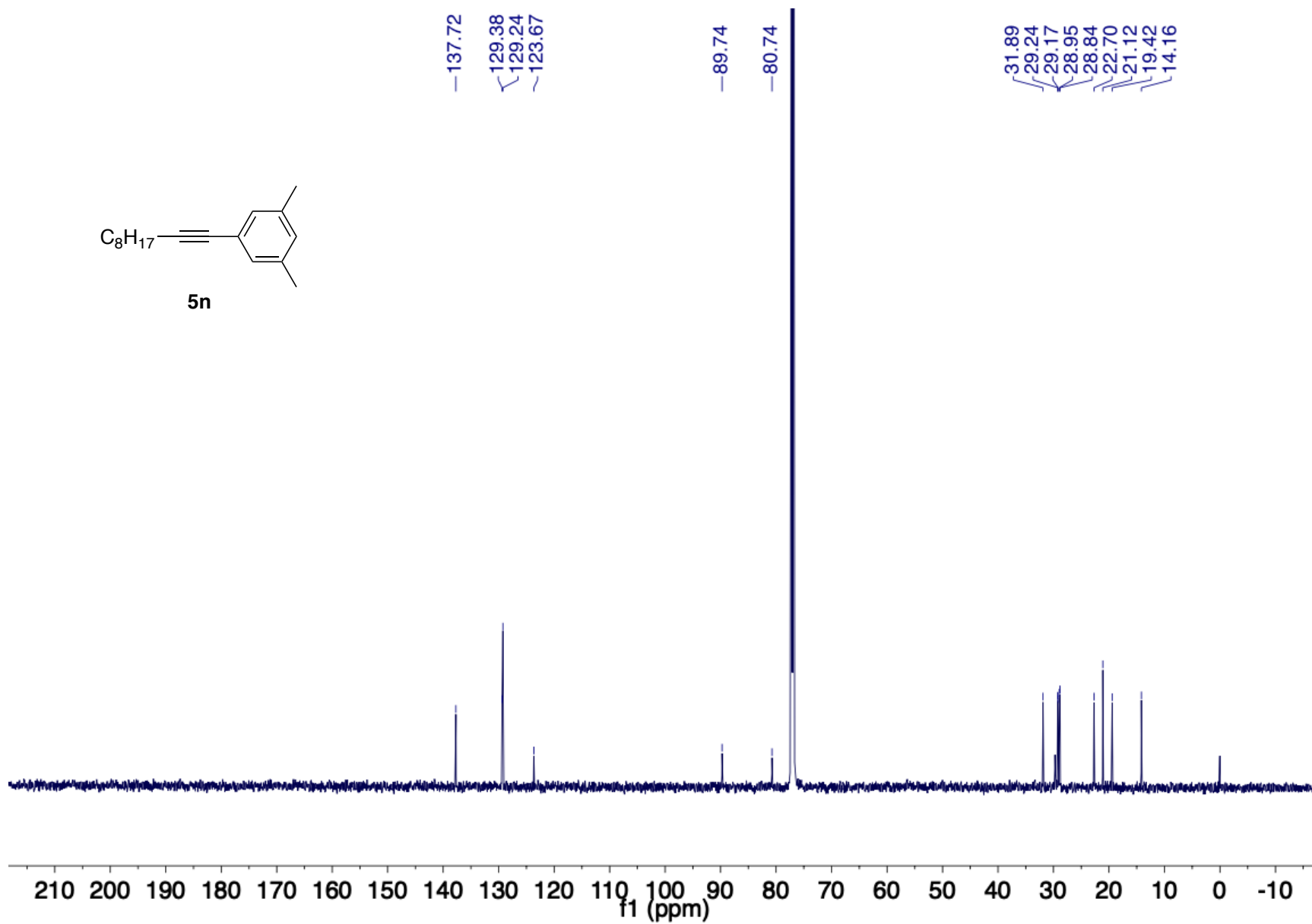
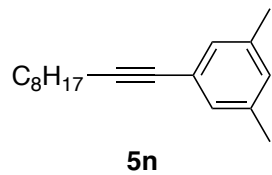




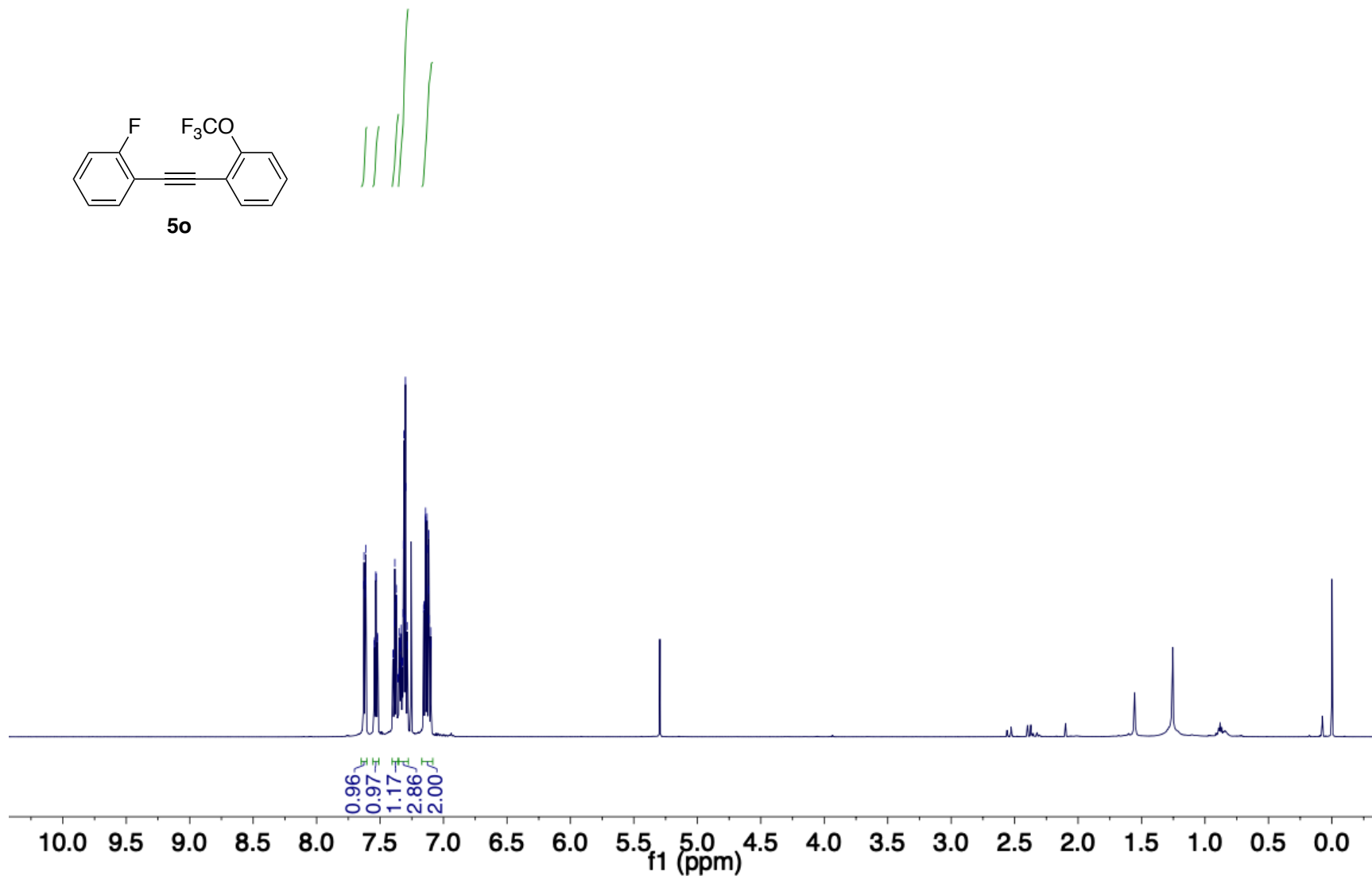
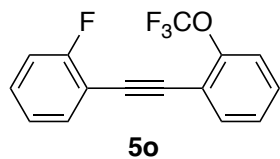


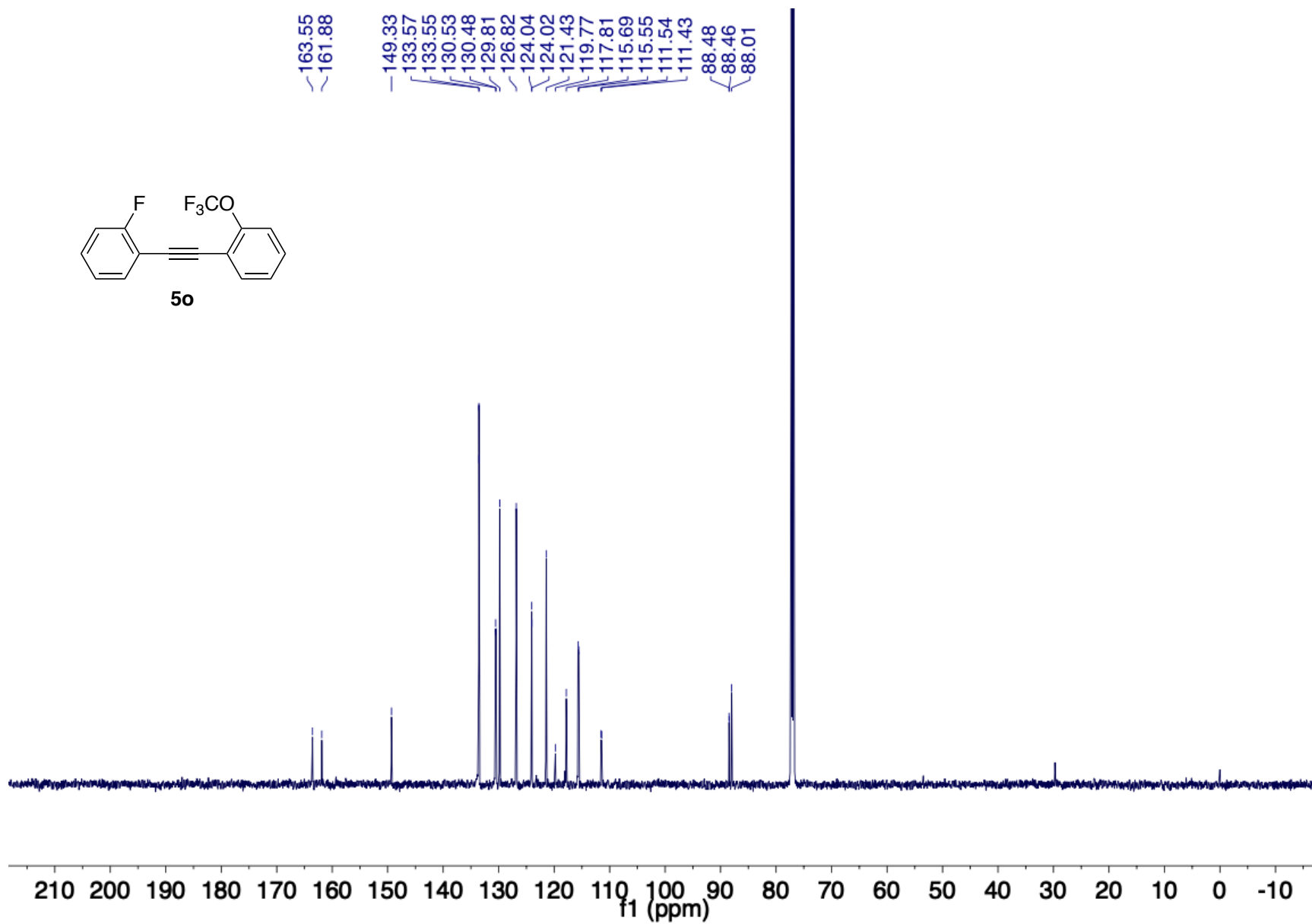
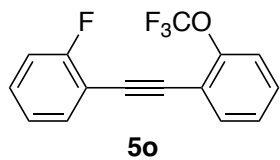


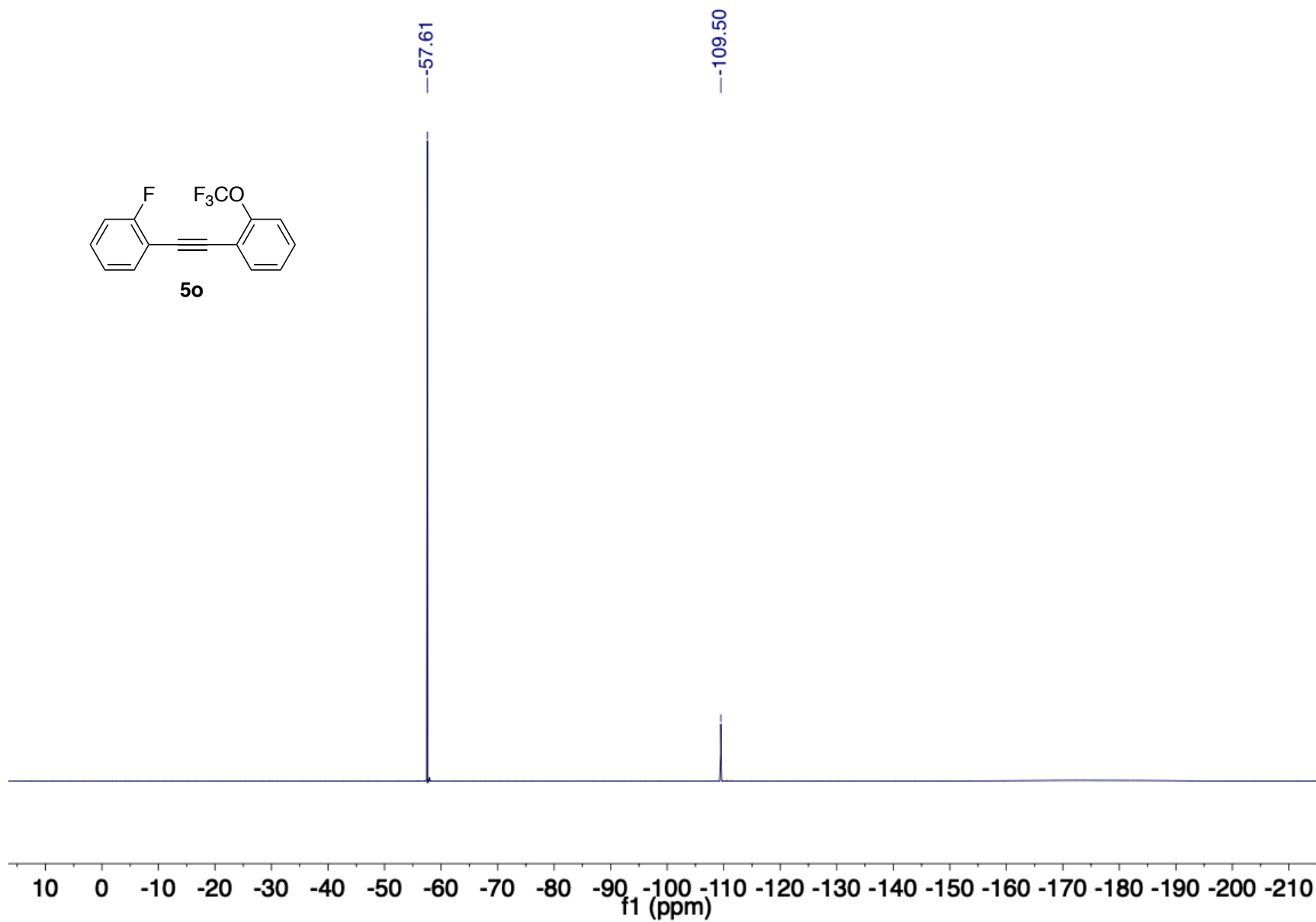
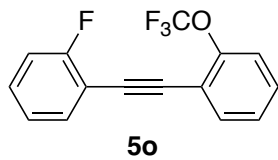




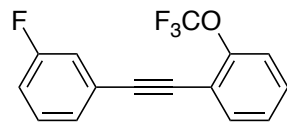
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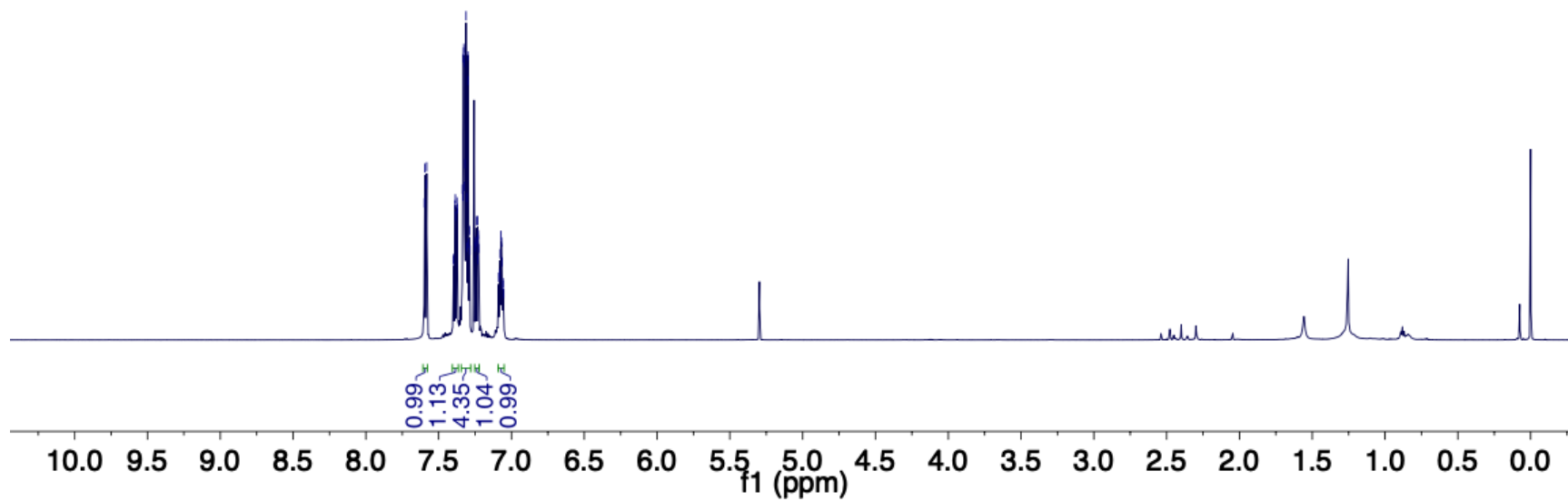


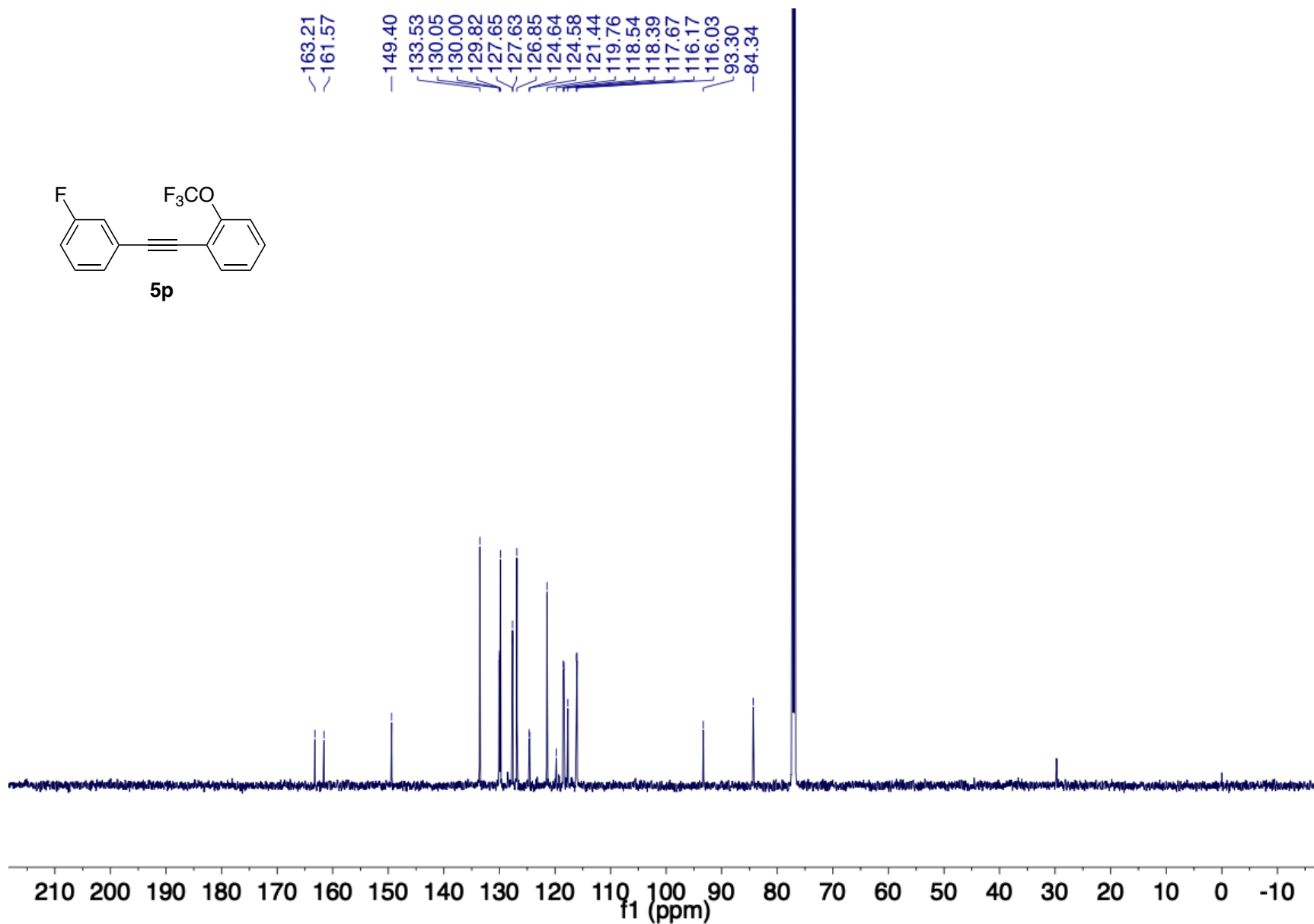
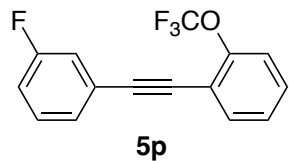


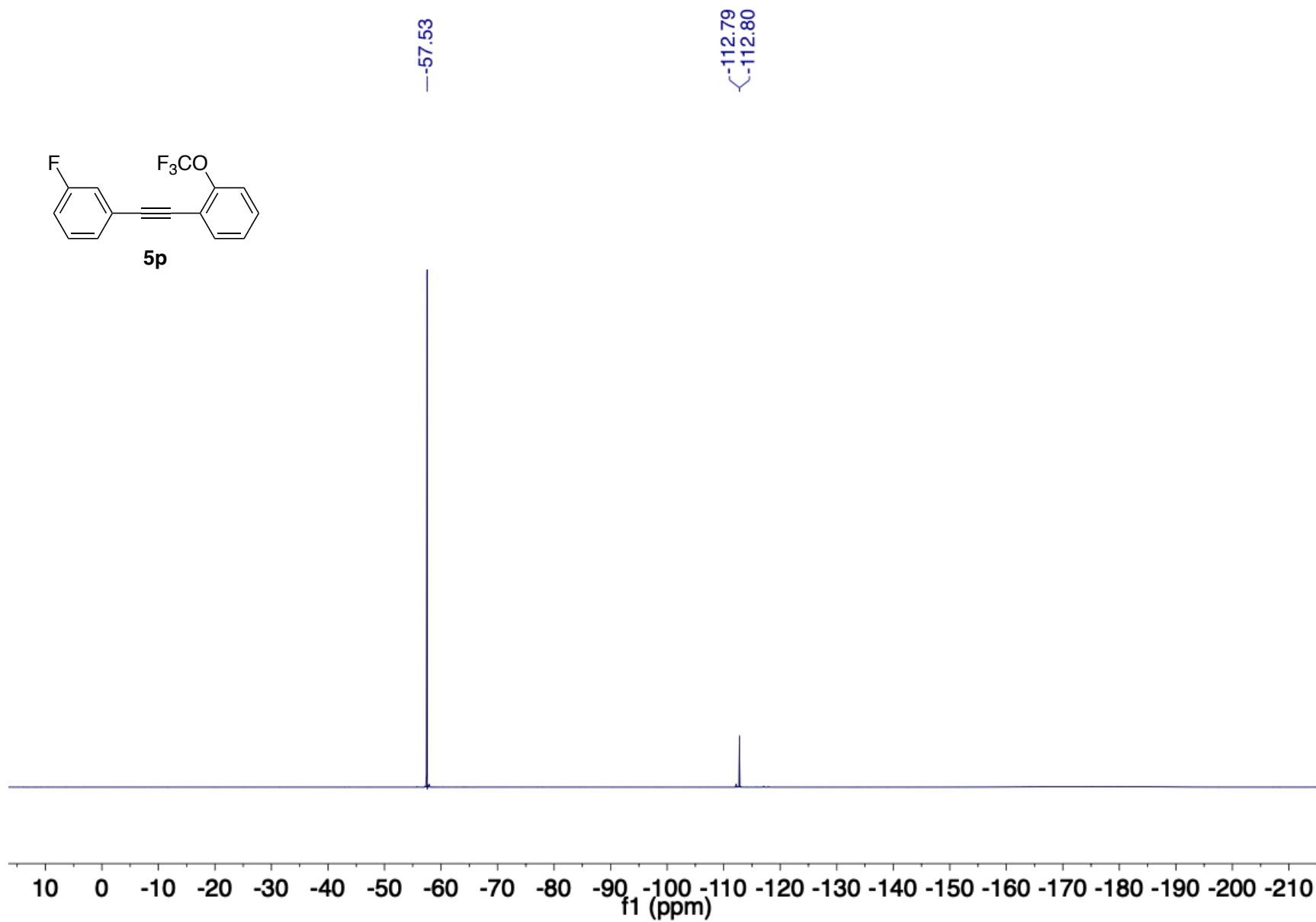
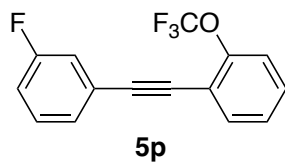
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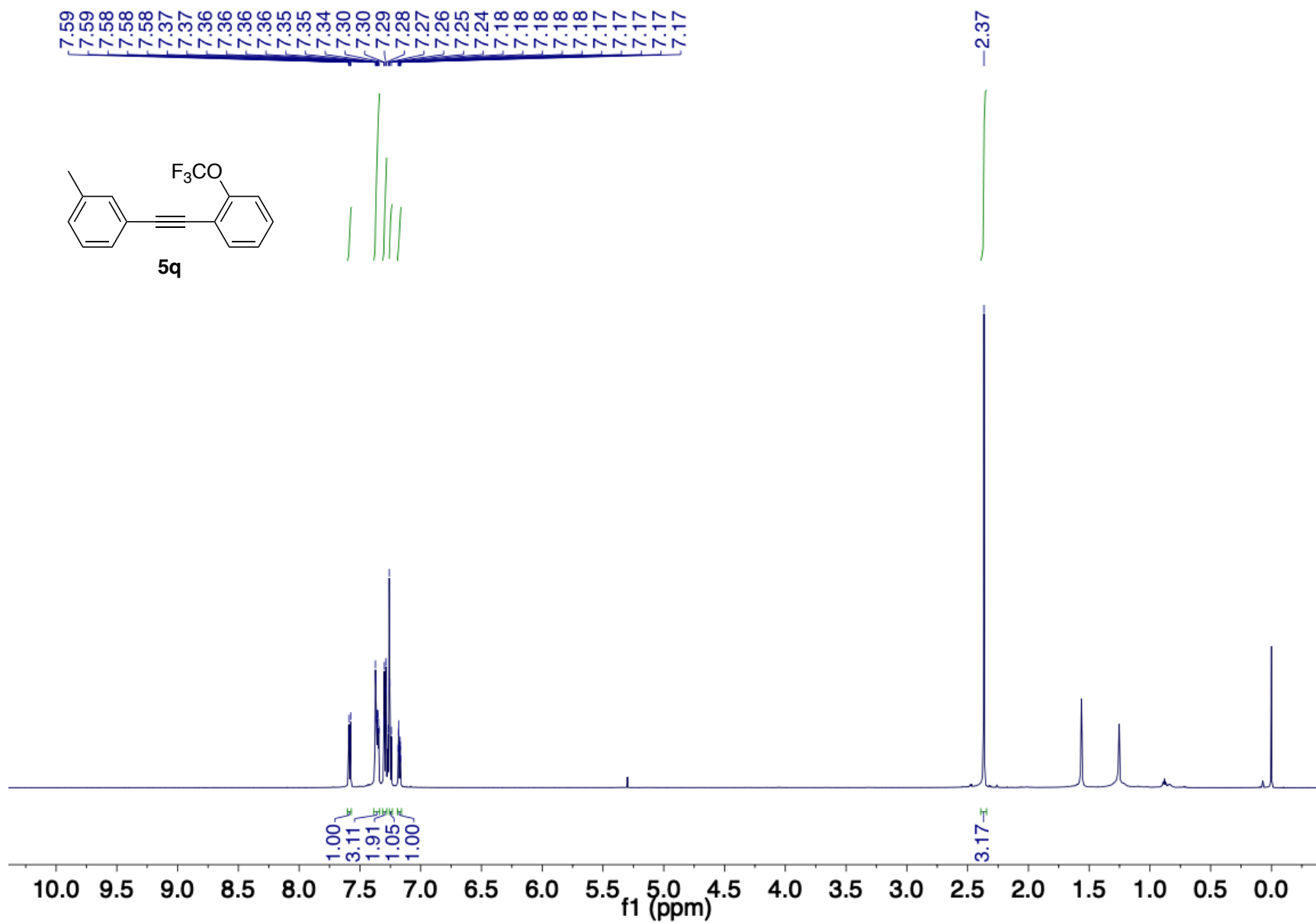


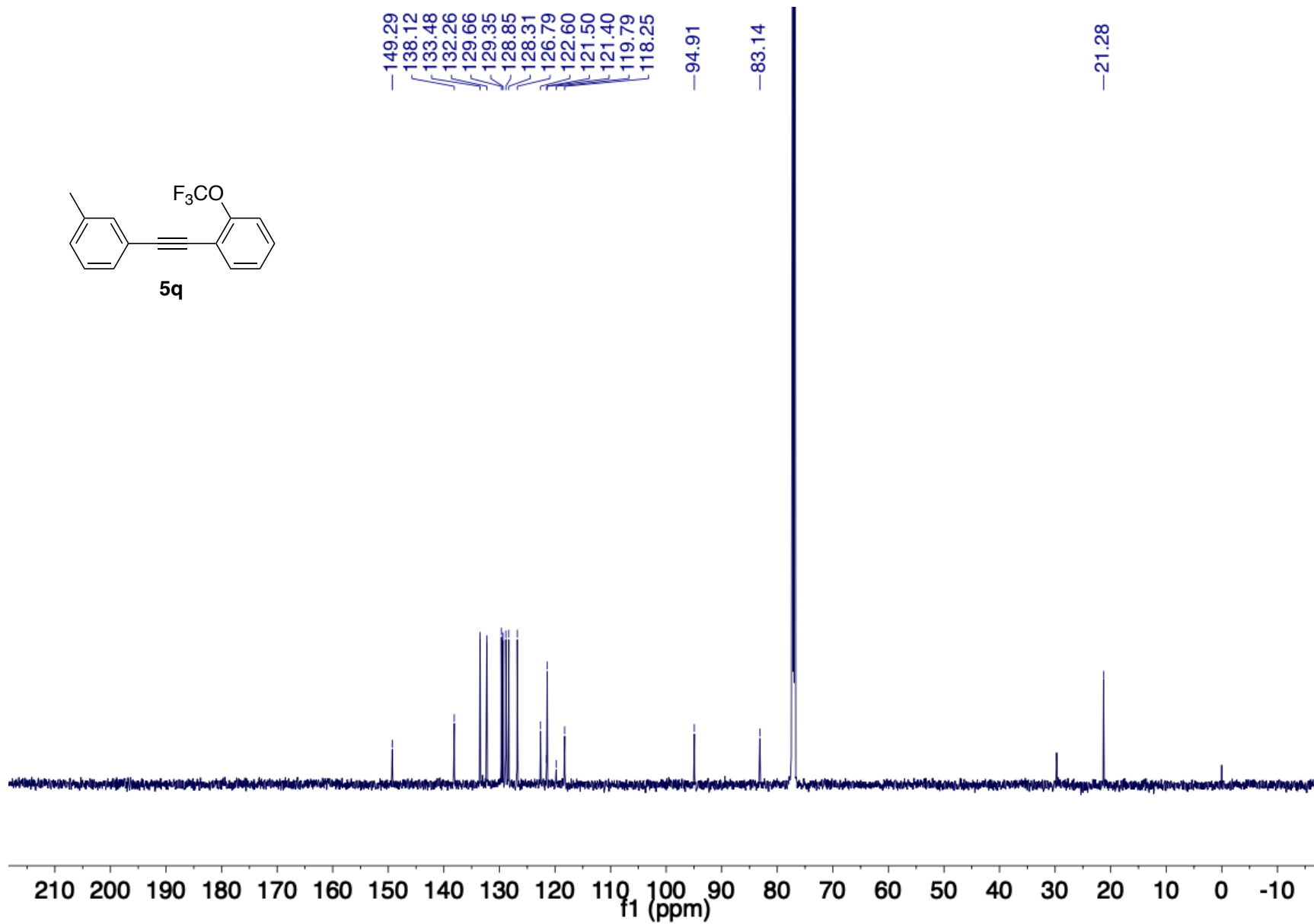
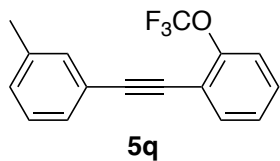
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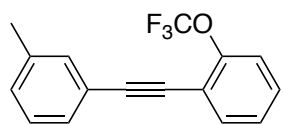






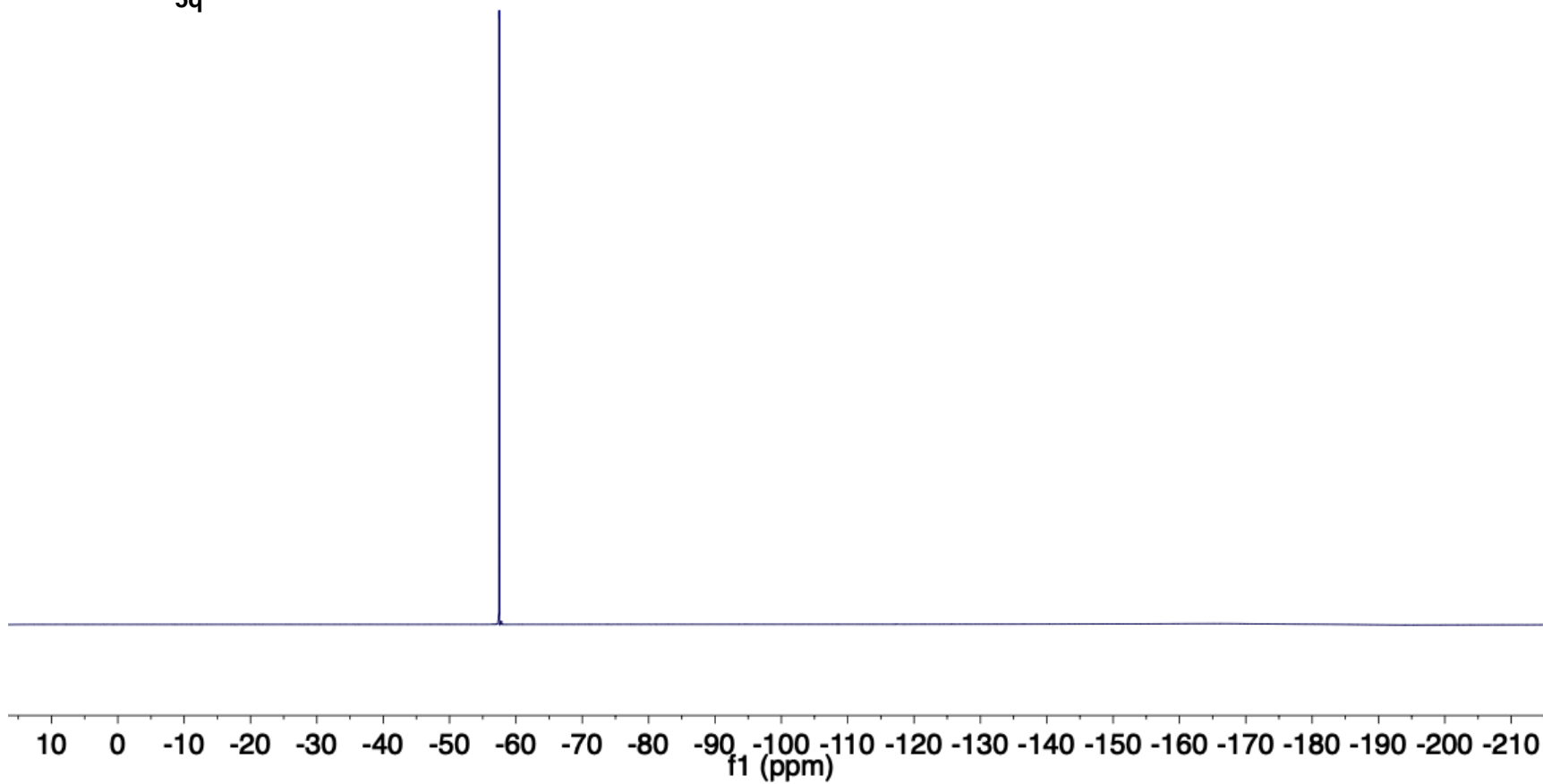


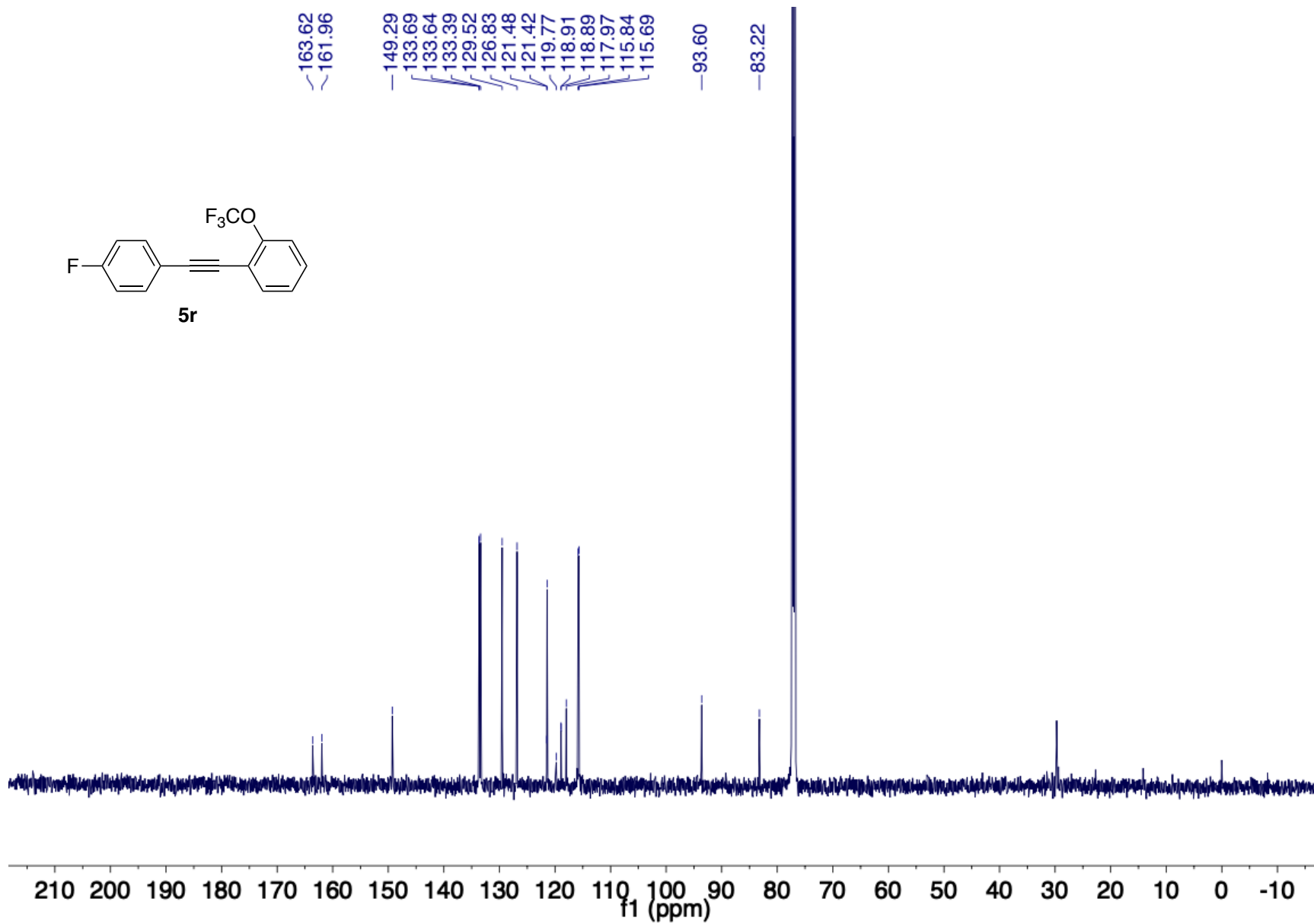
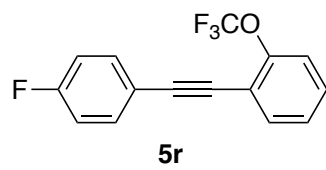


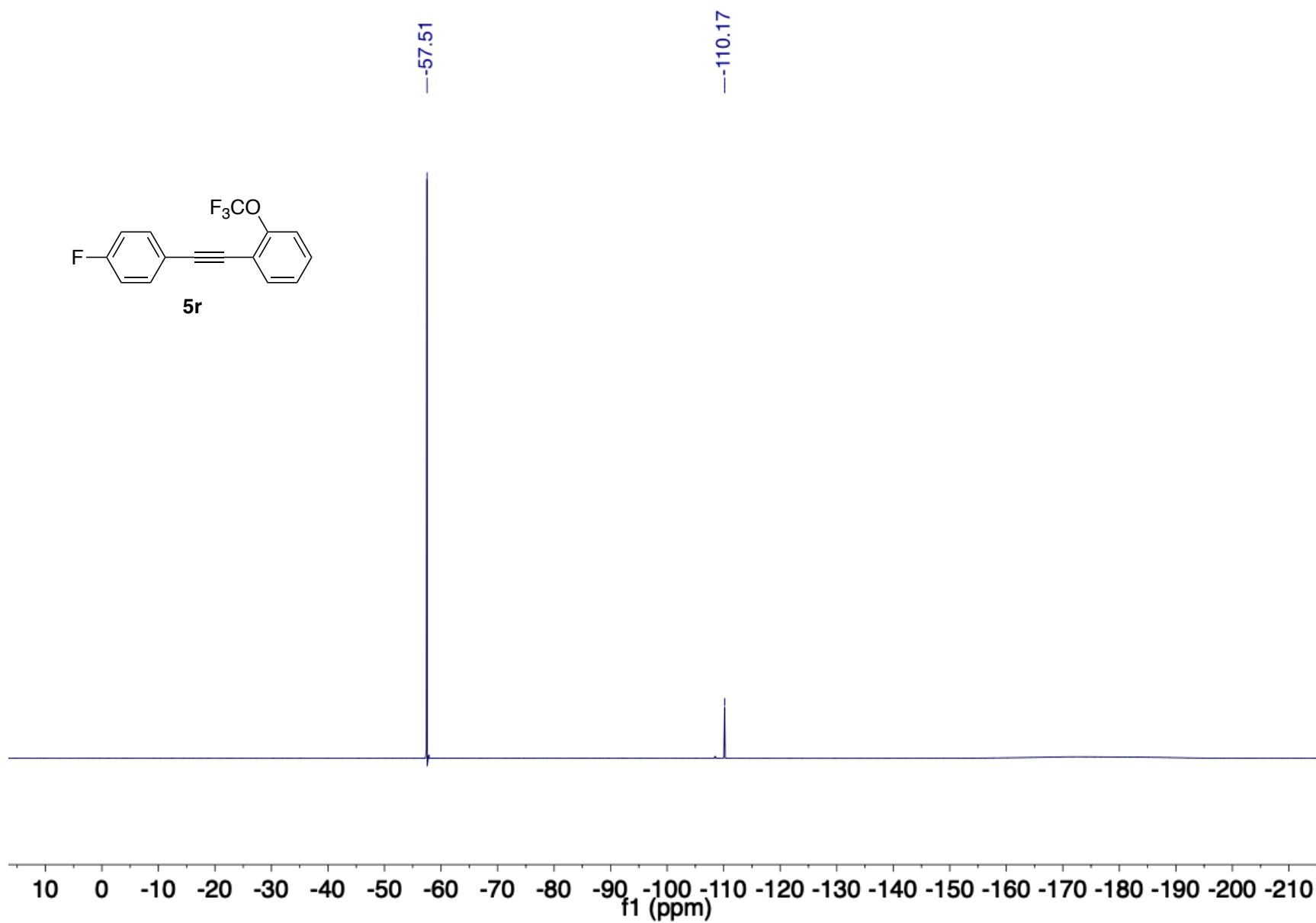
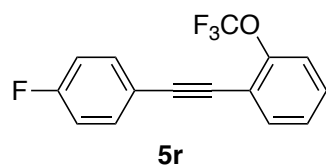


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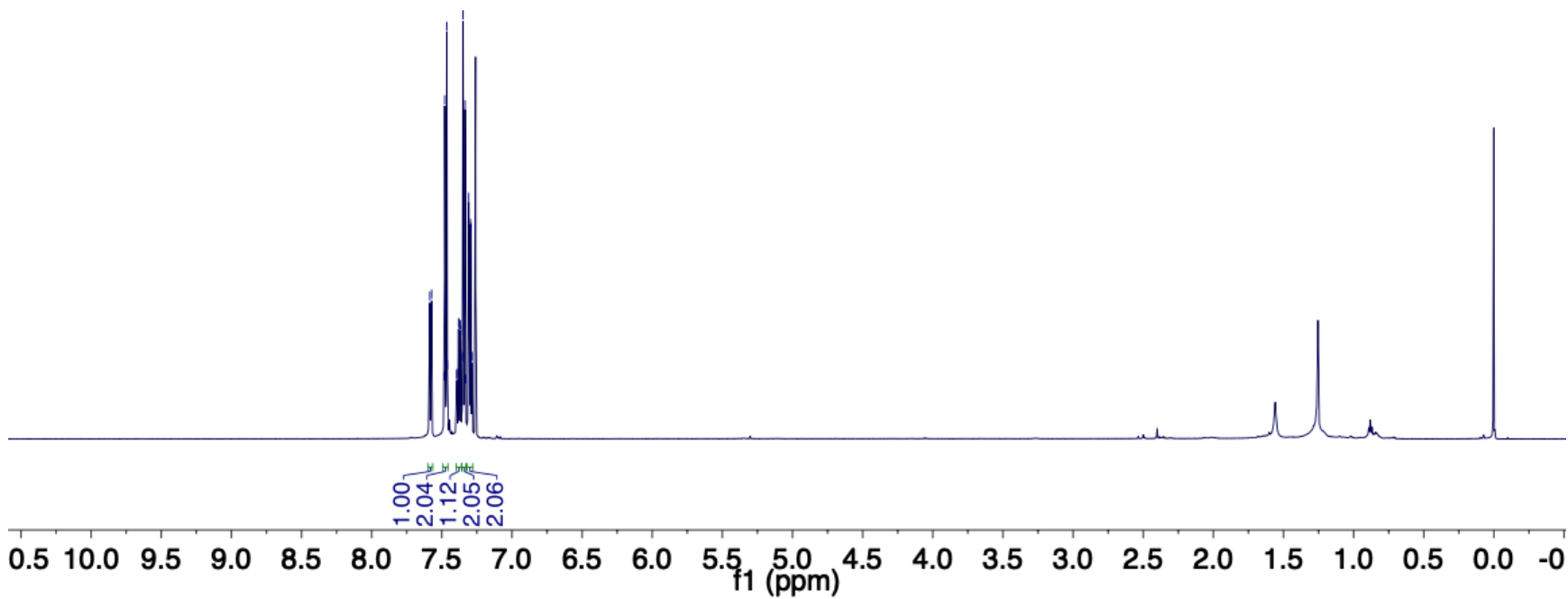
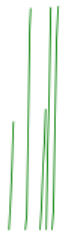
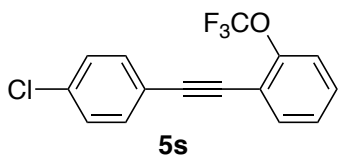
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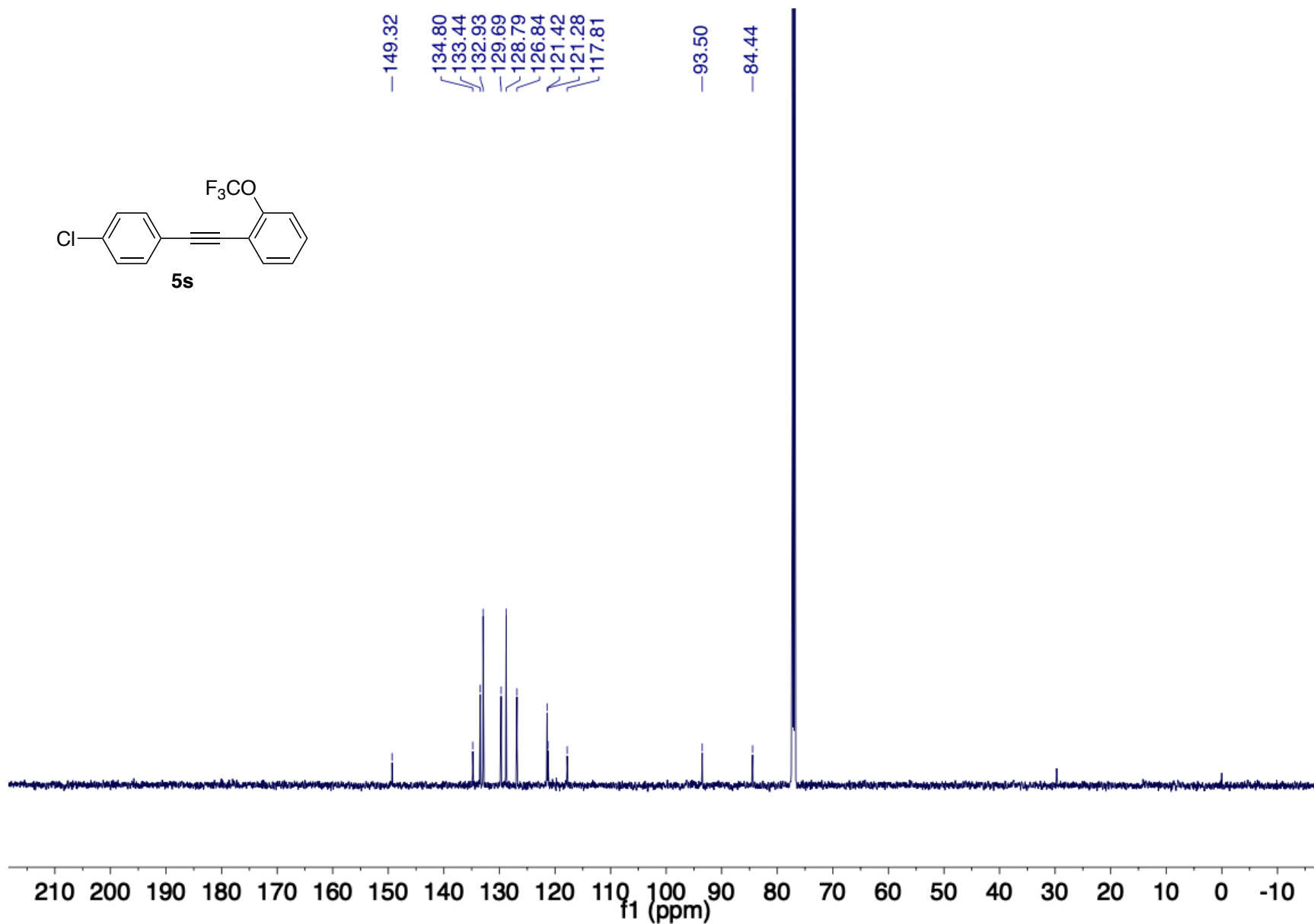
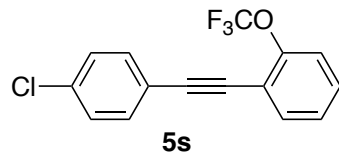


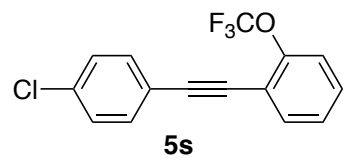




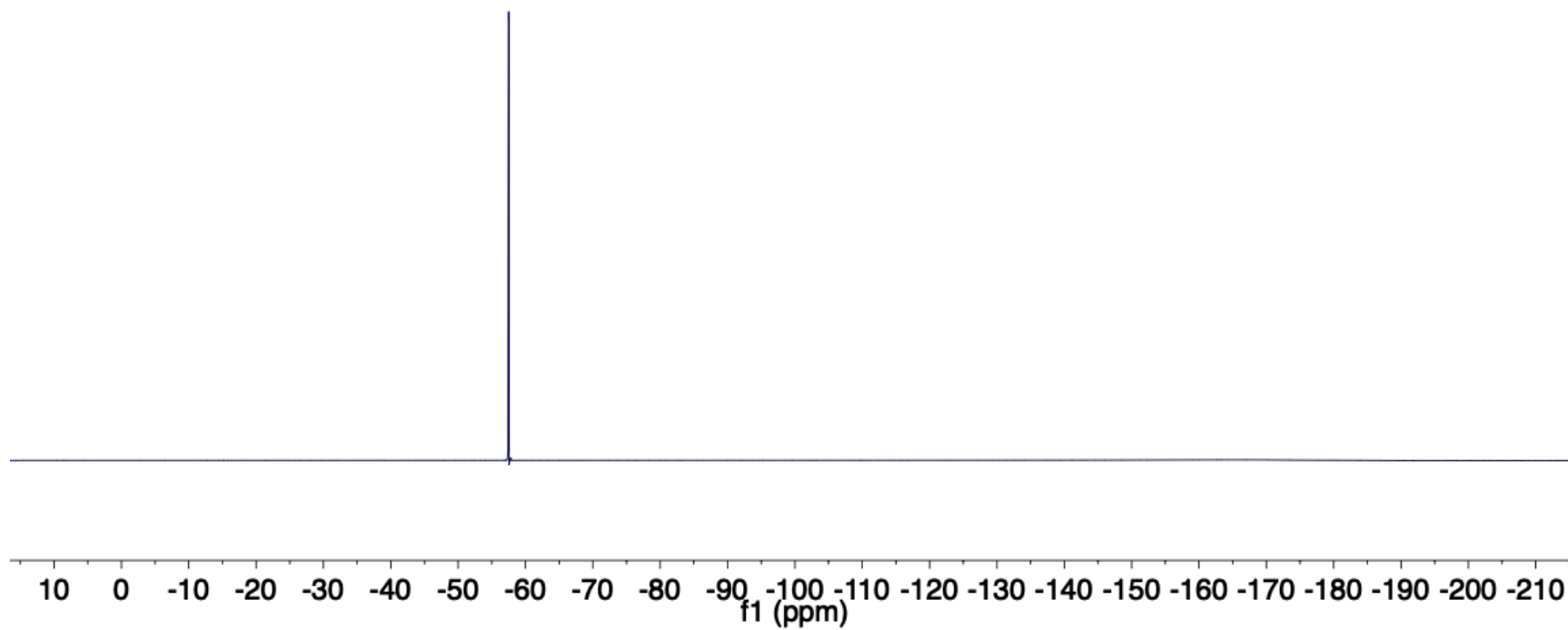
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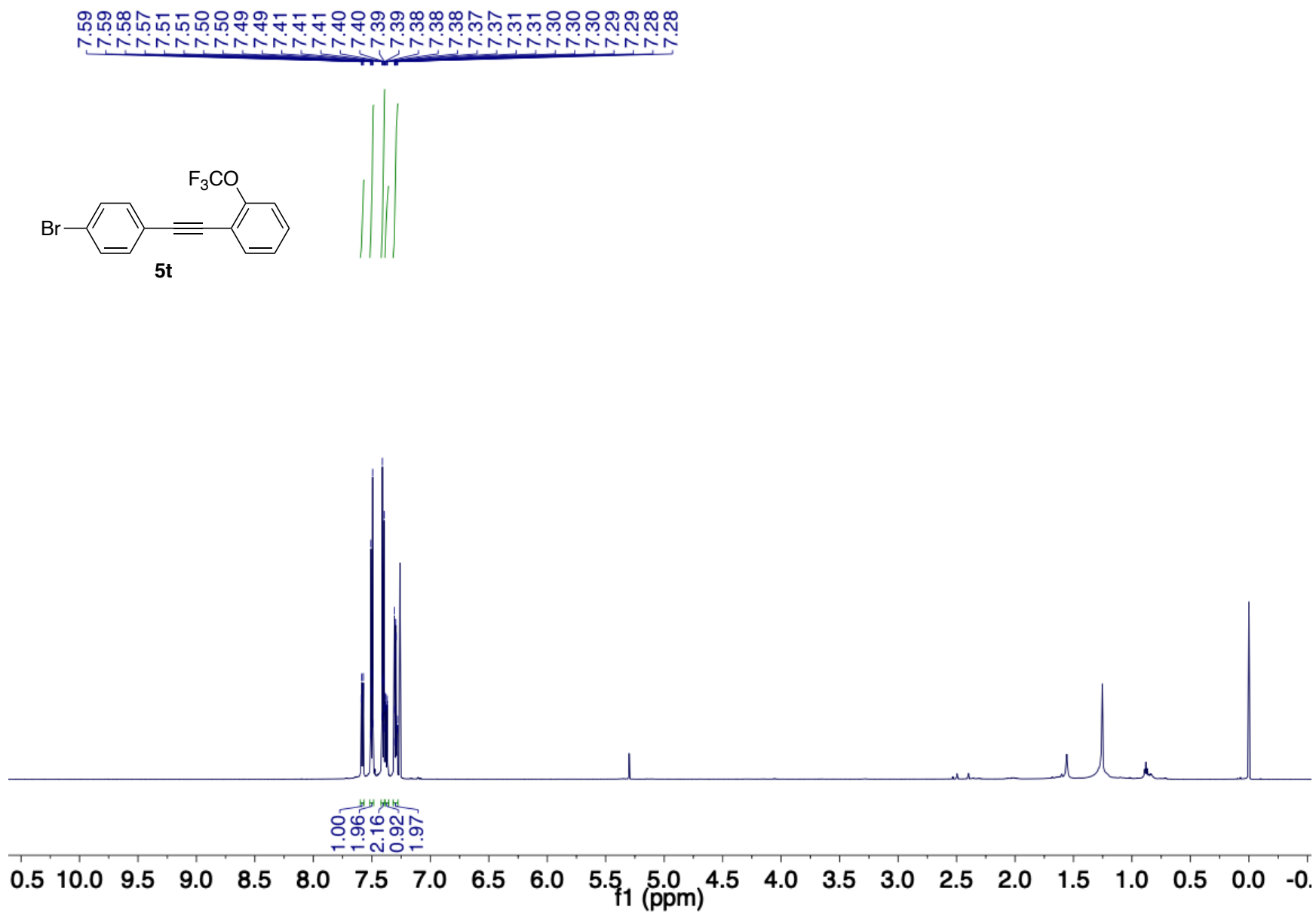


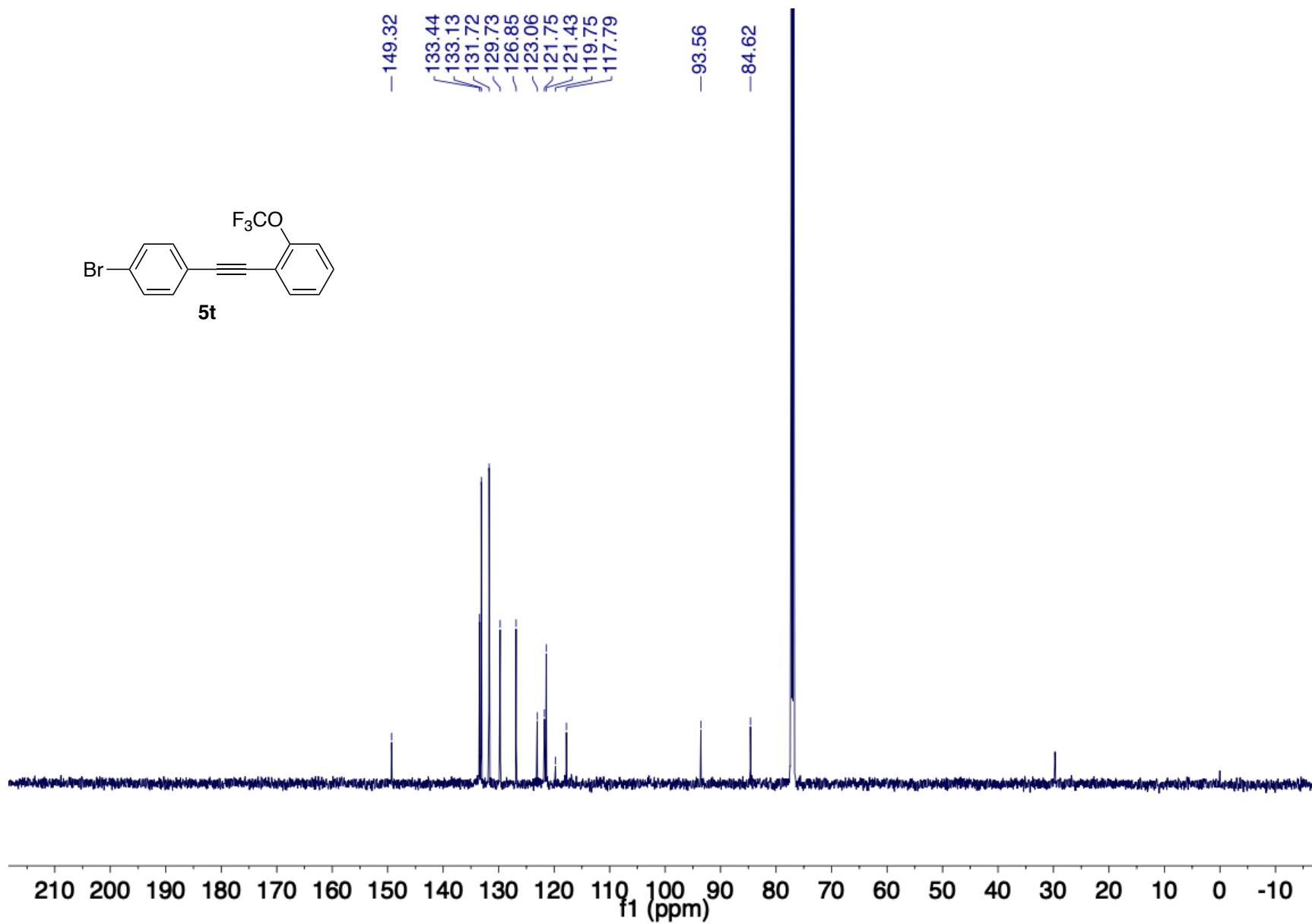
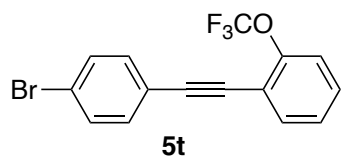


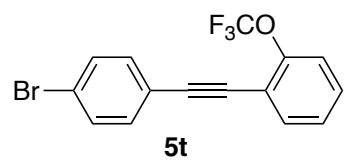


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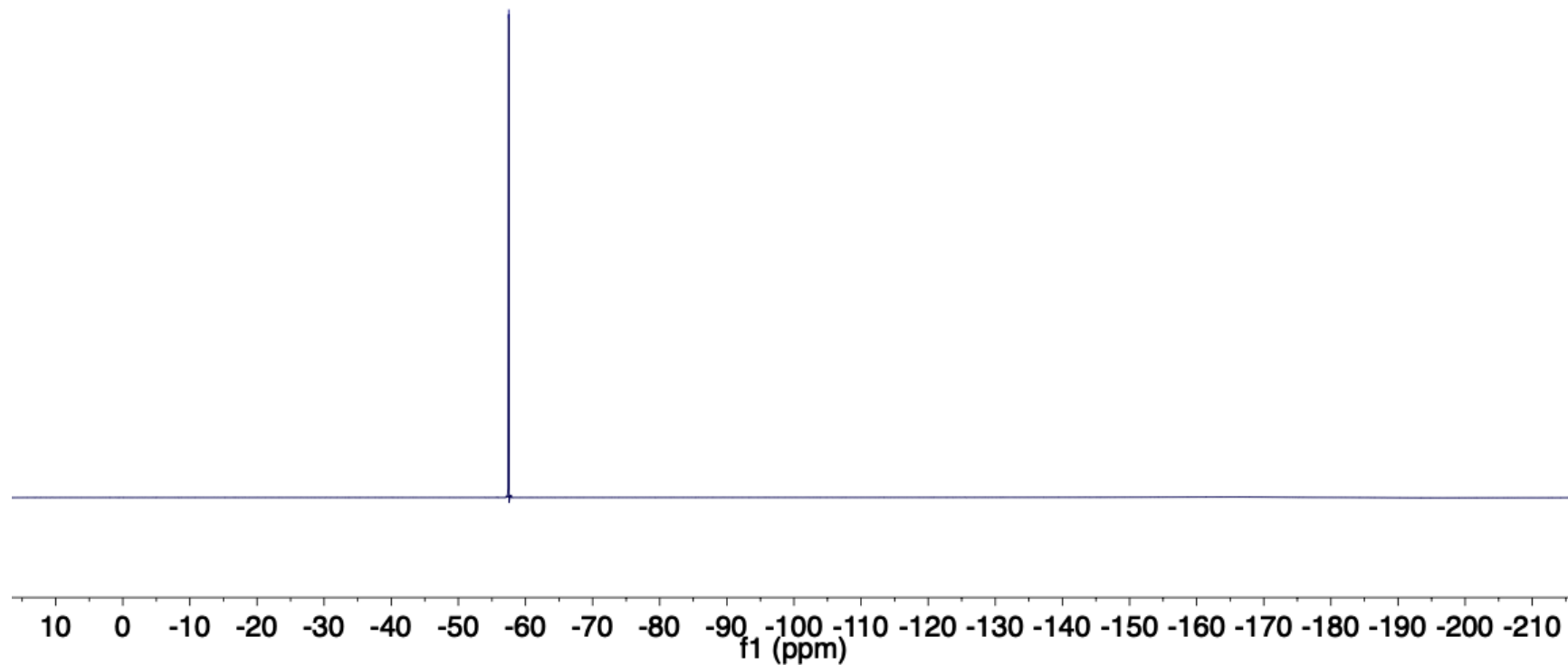


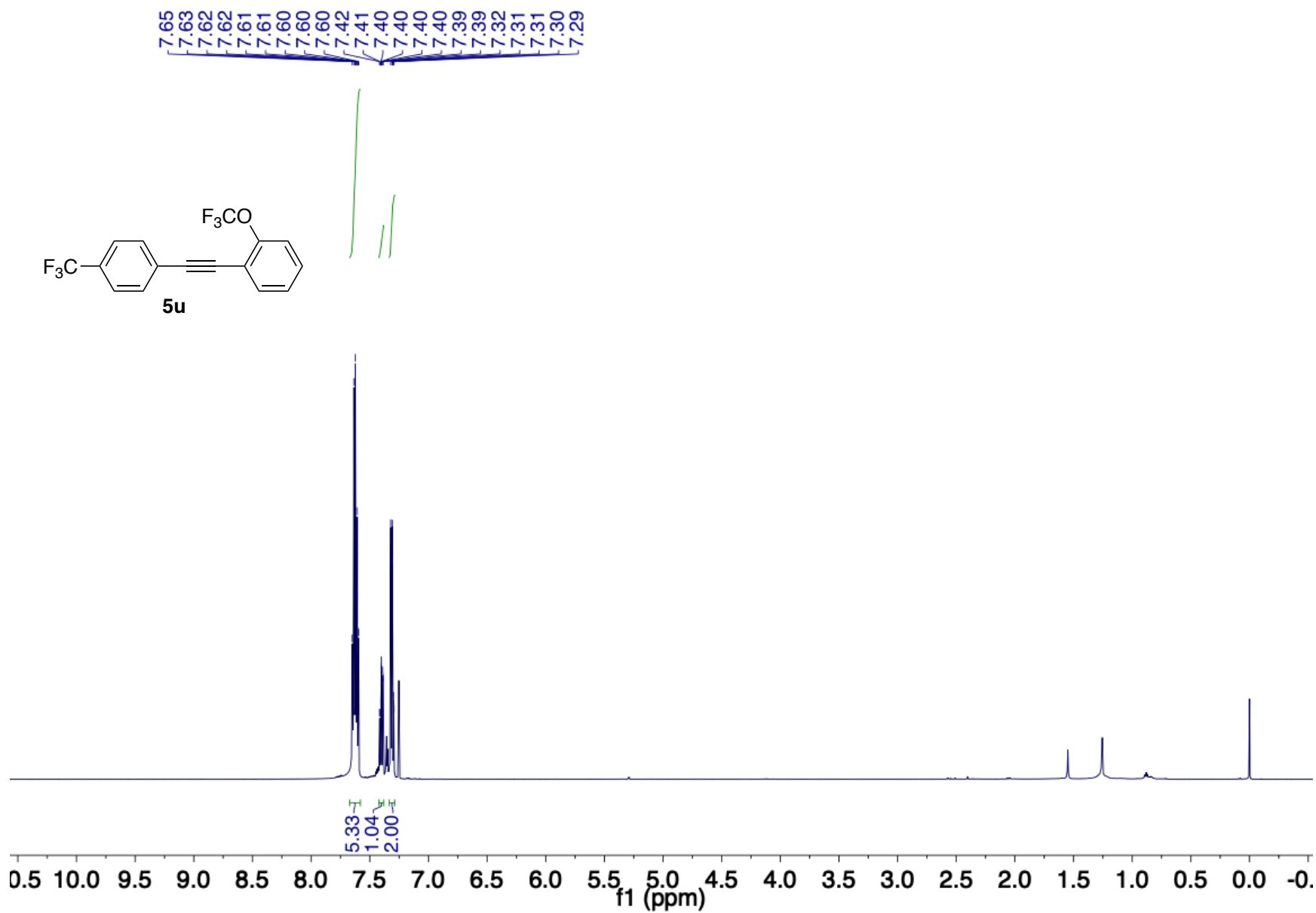


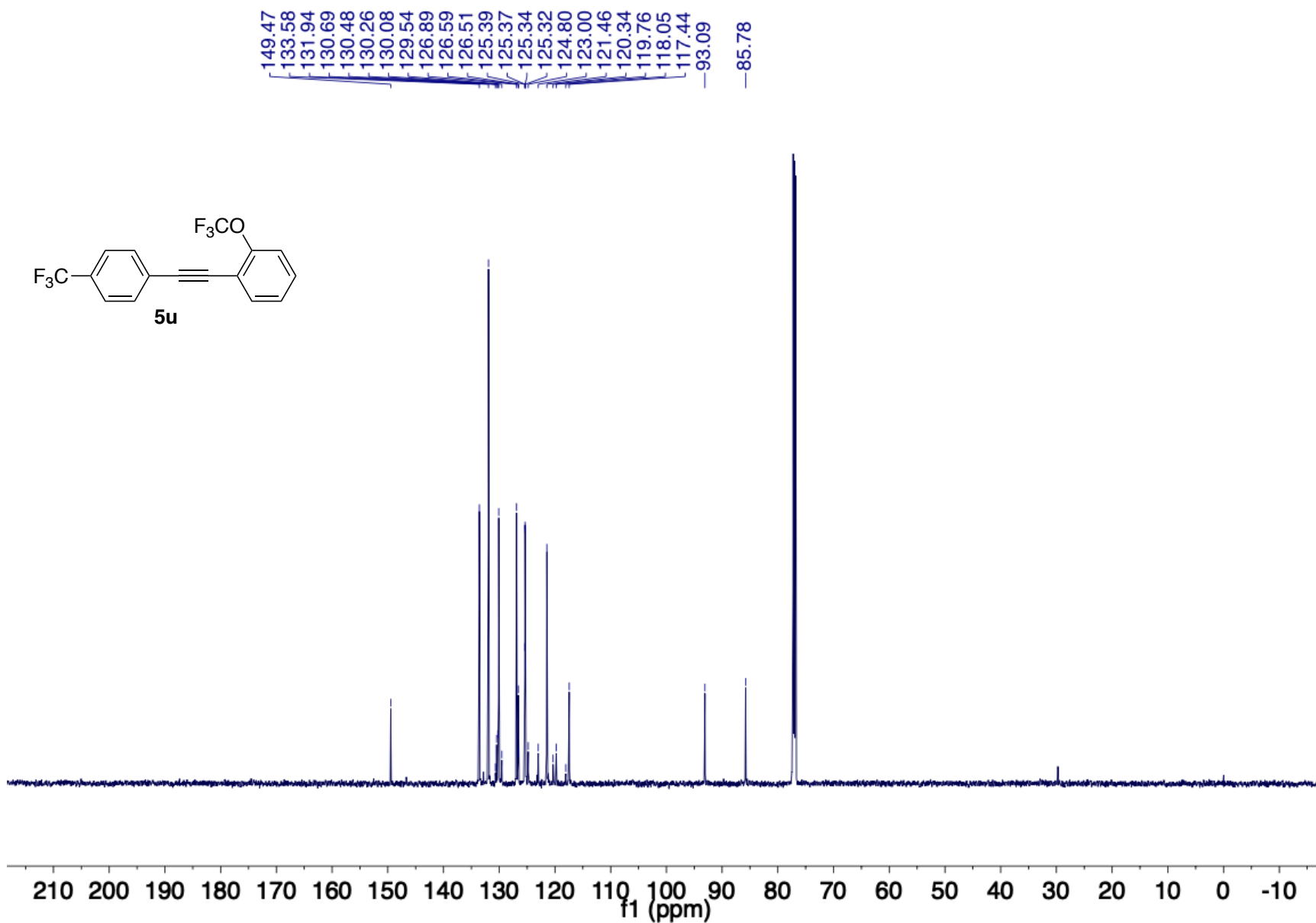
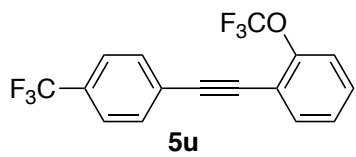


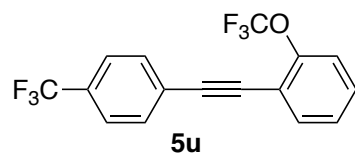


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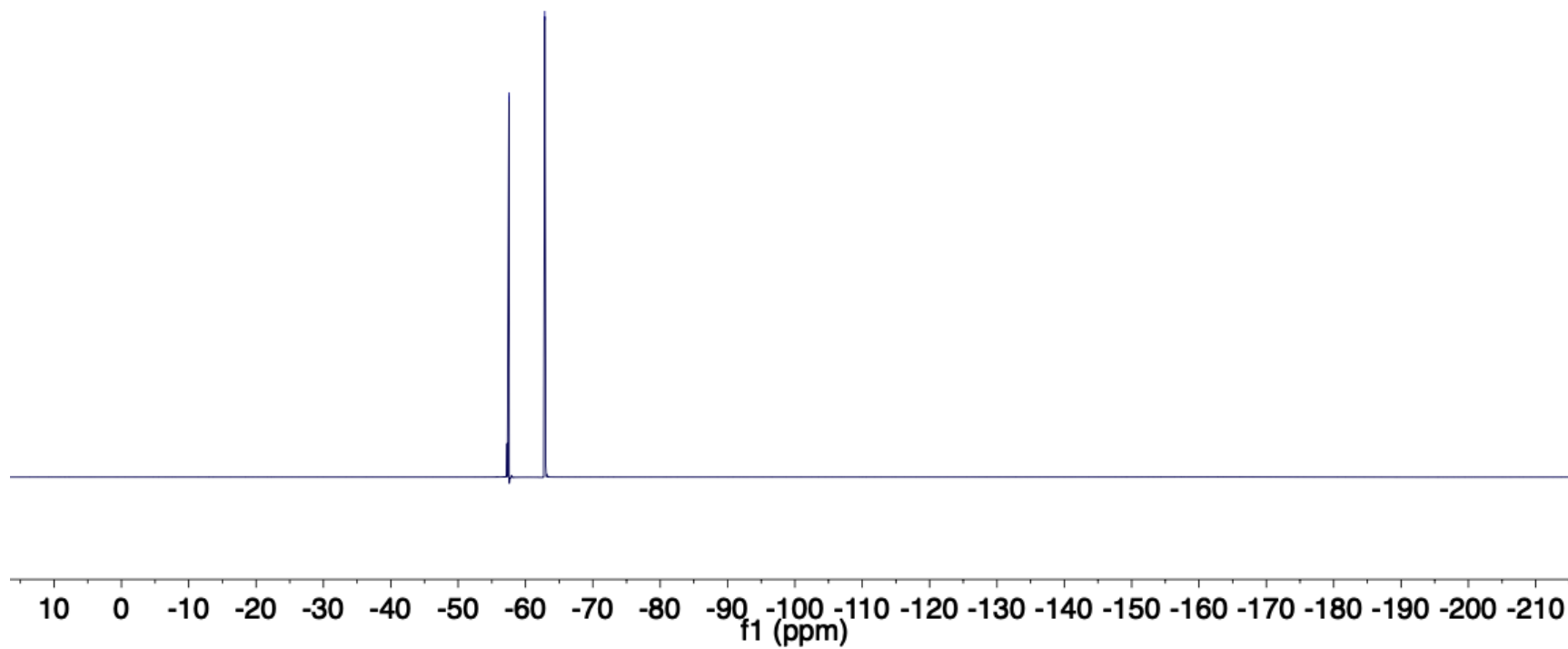


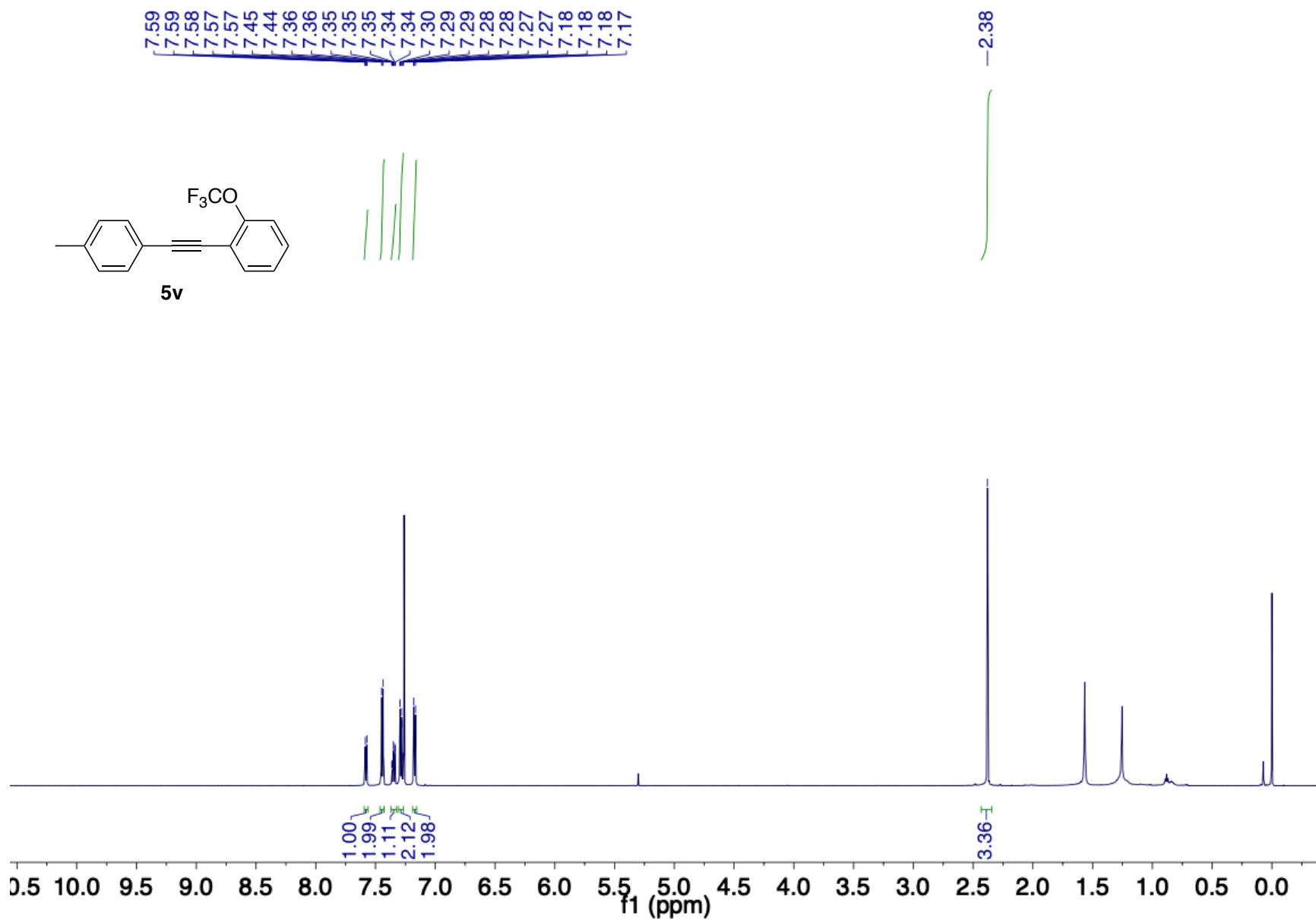


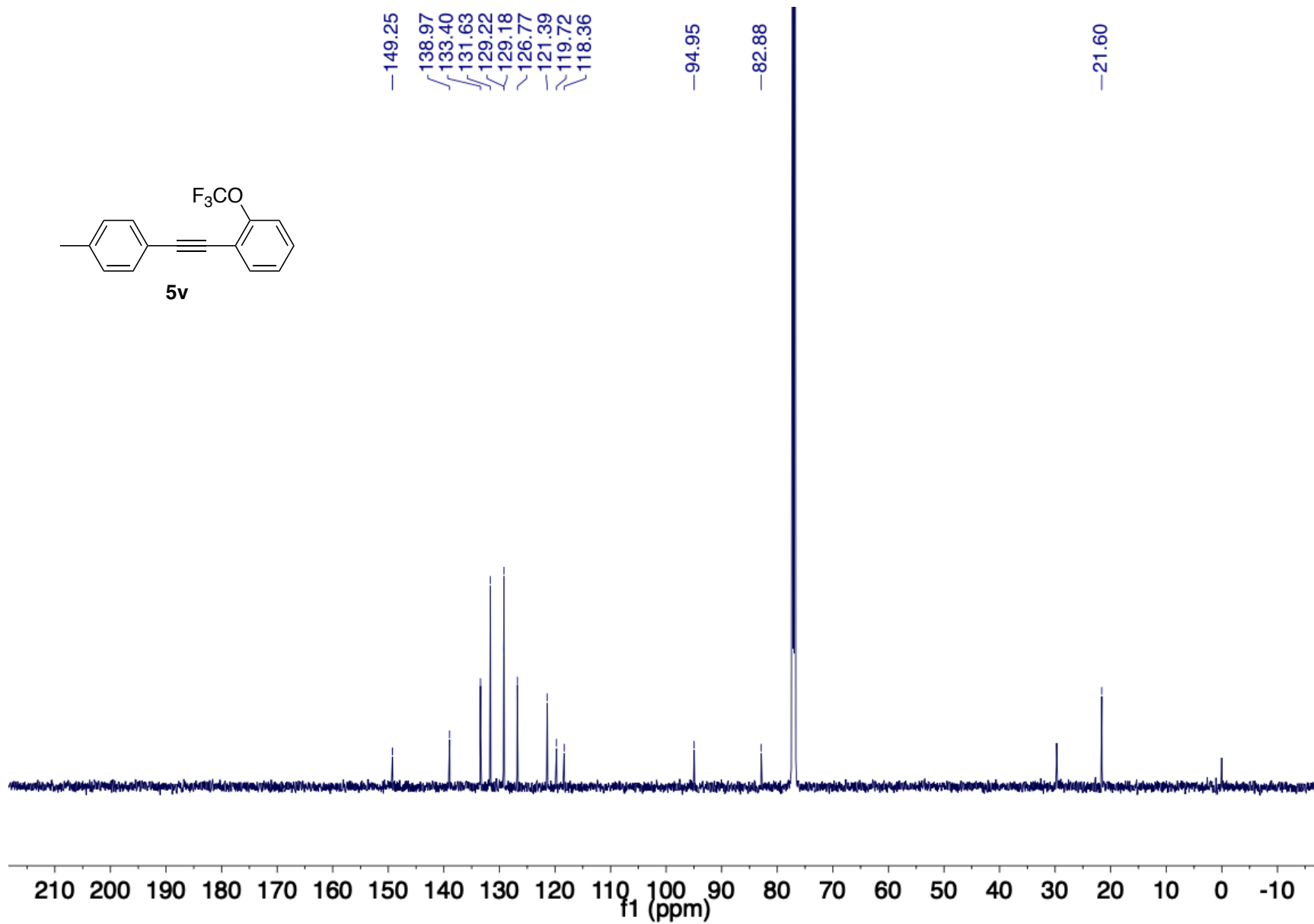
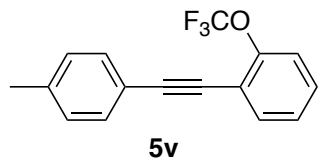


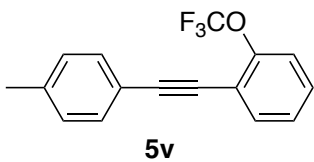


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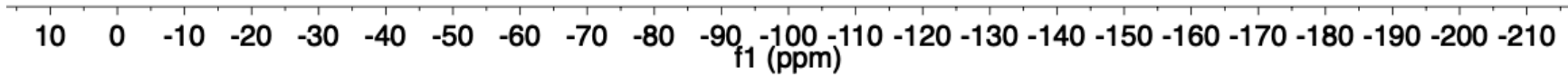


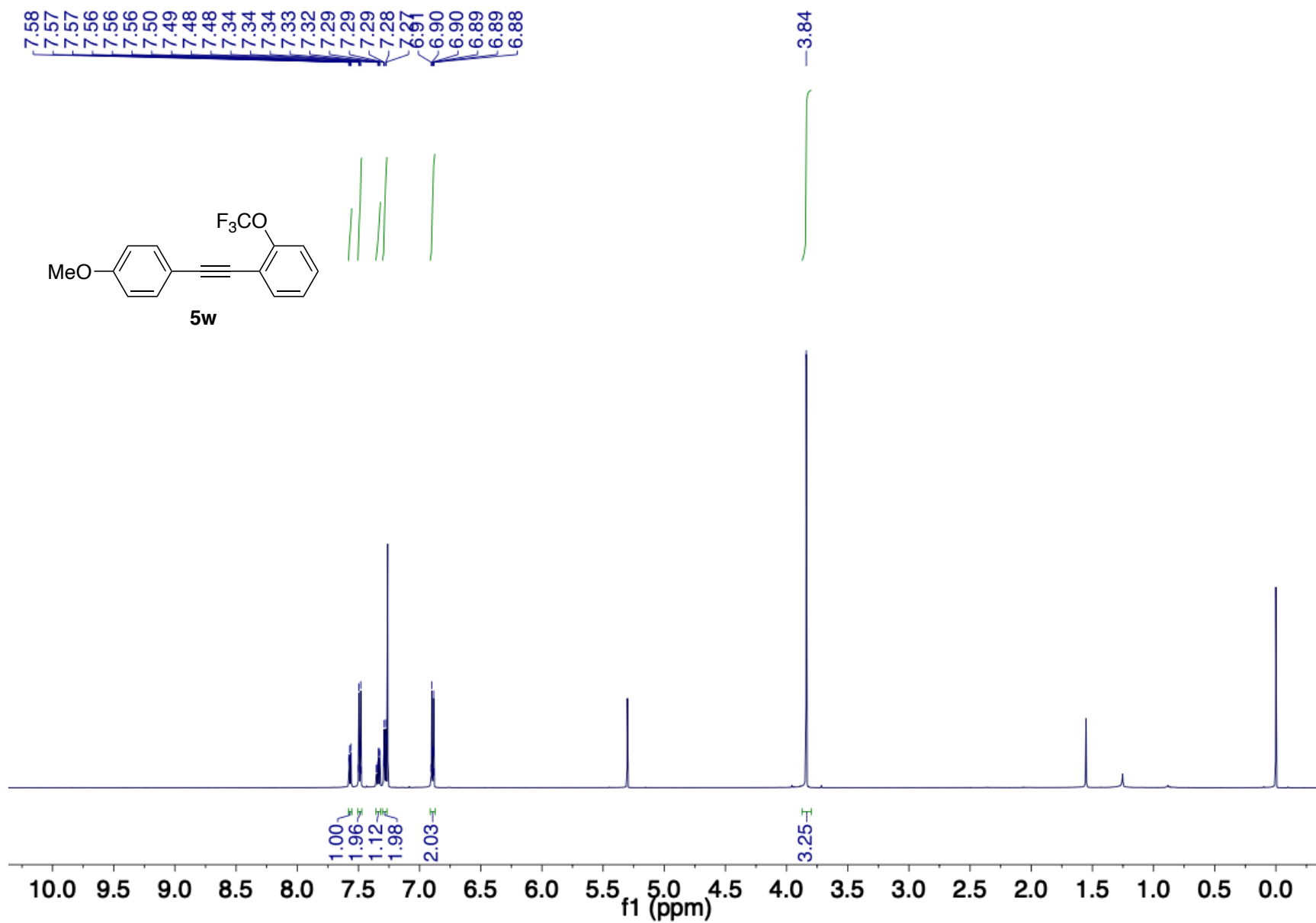


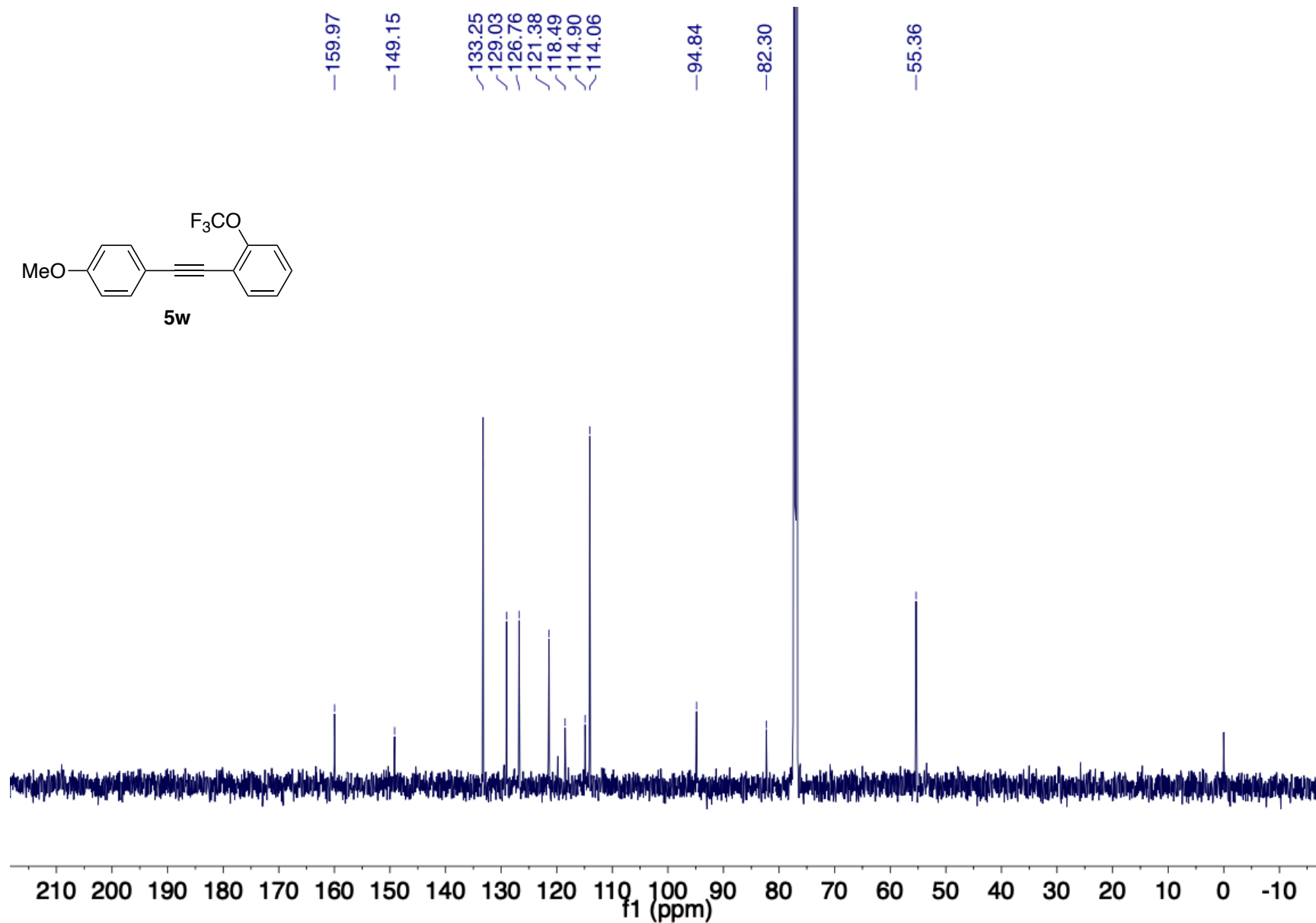
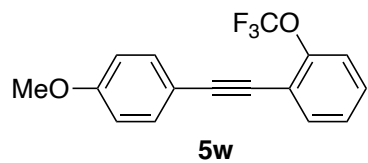


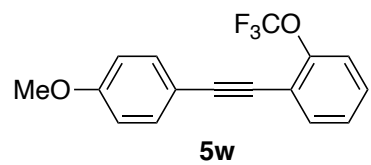


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