

Photoredox Catalysis in Alkene and Alkyne Alkylsulfonations: The Construction of Markovnikov Selective α -Sulfones

(Supporting Information)

Lingyi Lu,[†] Haoran wang,[†] Shanshan Huang, Biao Xiong, Xiaobao Zeng, Yong Ling and Xiaodong Qiu*

School of Pharmacy, Nantong Key Laboratory of Small Molecular Drug Innovation, Nantong University, 19 Qixiu Road, Nantong 226001, China

Email: qiuxiaodong@ntu.edu.cn

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1. General Information.

Unless otherwise noted, all reactions were performed under an nitrogen atmosphere using flame-dried glassware. MeCN, DMF, DMSO and DCM were purchased as anhydrous solvents and were used directly. All new compounds were fully characterized. NMR-spectra were recorded on Bruker ARX-400 MHz spectrometer. ^1H NMR spectra data were reported as δ values in ppm relative to chloroform (δ 7.26), methanol (δ 3.30), or DMSO (δ 2.50) if collected in CDCl_3 , CD_3OD , or DMSO-d^6 . ^{13}C NMR spectra data were reported as δ values in ppm relative to chloroform (δ 77.0) methanol (δ 49.0) or DMSO (δ 39.5) if collected in CDCl_3 (the carbon attached to B was not observed), CD_3OD , DMSO-d^6 . ^1H NMR coupling constants were reported in Hz, and multiplicity was indicated as follows: s (singlet); d (doublet); t (triplet); q (quartet); quint (quintet); m (multiplet); dd (doublet of doublets); ddd (doublet of doublet of doublets); dddd (doublet of doublet of doublet of doublets); dt (doublet of triplets); td (triplet of doublets); ddt (doublet of doublet of triplets); dq (doublet of quartets); app (apparent); br (broad). Mass spectra were conducted at Micromass Q-ToF instrument (ESI) and Agilent Technologies 5973N (EI). UV-visible spectroscopy was recorded on a AOE UV-1800PC UV-visible spectrophotometer. The fluorescence emission intensity of reaction solution was recorded on a SHIMADZU RF-6000 spectro fluorophotometer. The reactor was 3.0 cm from 8W blue LED strips, the power density of the incident light was recorded on a HPS350j spectral irradiance colorimeter (Zhejiang Hangpu Instrument Co., Ltd). Cyclic voltammetry was performed on a CH Instruments electrochemical workstation model CS300H. Photoredox reactions were carried out in flame-dried 10 mL Schlenk tubes with Teflon screw caps under nitrogen. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

2. The spectrum of our lamp and the visible-light irradiation instrument

All reactions have been studied in borosilicate glass vessels irradiated by a blue light LED strips purchased from www.taobao.com without using filters.

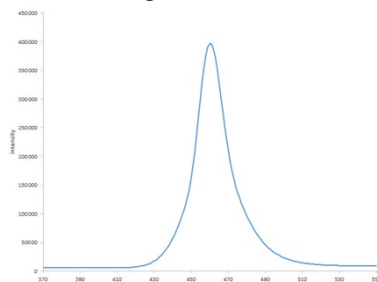


Figure S1. The spectrum of our blue LED. $\lambda_p = 460$ nm.

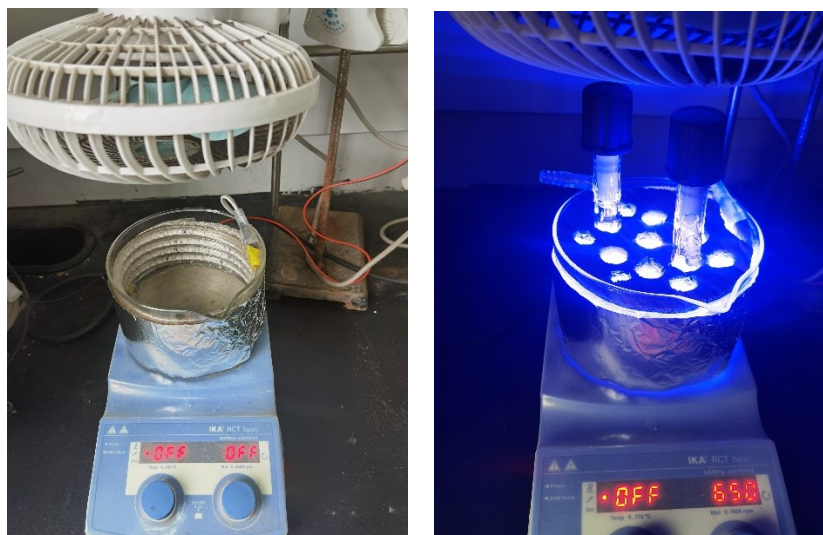
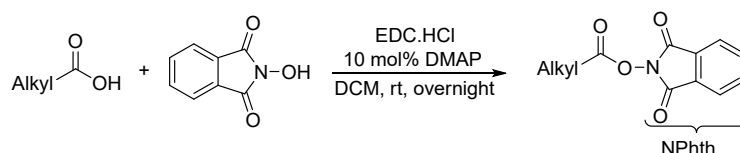


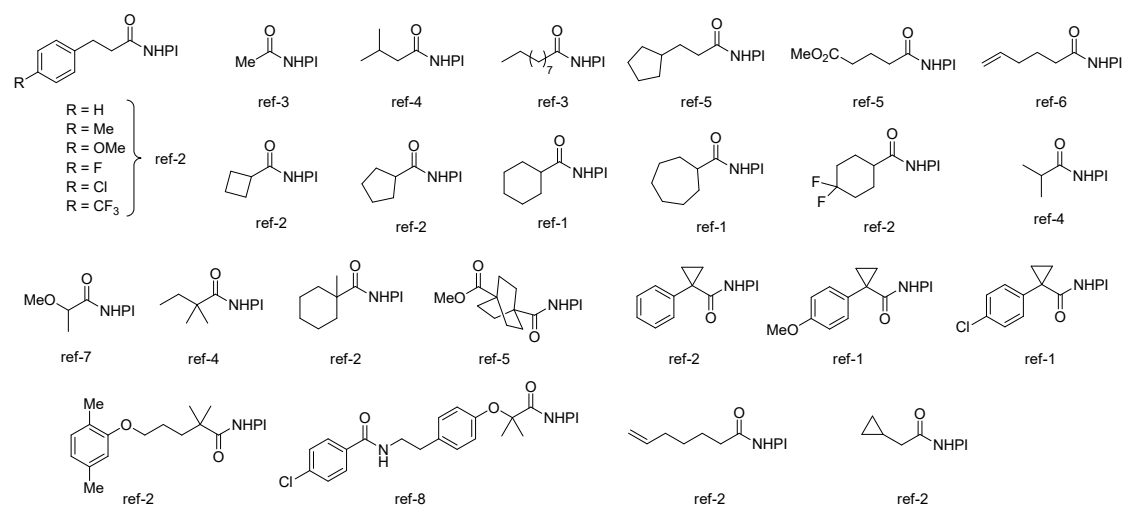
Figure S2. Photograph of the reaction setup

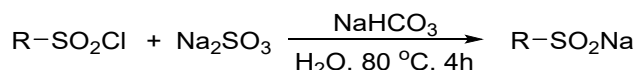
3. Experimental procedure for the synthesis of phthalimide esters and sodium sulfinates



General procedure for the synthesis of phthalimide esters. According to the reported procedure,¹ a round-bottom flask was charged with 5 mmol carboxylic acid, 1.05 eq. *N*-hydroxyphthalimide and 10 mol% of DMAP. 10 mL DCM was added and the mixture was stirred. Then, 1.1 eq. EDC·HCl (EDC= (1-ethyl-3-(3-dimethylaminopropyl)carbodiimide) dispersed in 5mL DCM was added slowly to the flask. During the addition, the solid *N*-hydroxyphthalimide was dissolved gradually. The reaction was left overnight. Afterwards, the reaction mixture was diluted with DCM and washed 3 times with H₂O. The organic phase was collected, dried over Na₂SO₄ and concentrated using an evaporator. The residual was separated on a silica gel column with hexane-EtOAc as eluent. The NMR data for the following NHPI esters (Table S1) could be found in the corresponding literature.¹⁻⁸

Table S1. Substrates of phthalimide esters

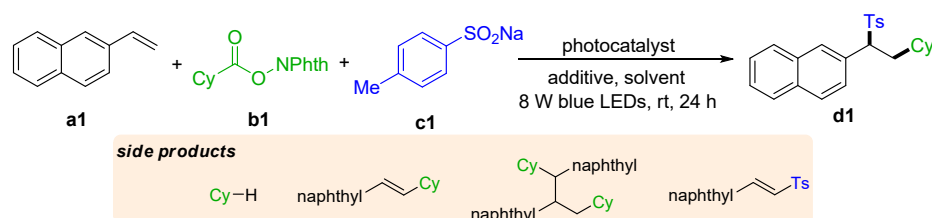




General procedure for the synthesis of sodium sulfonates. According to a known procedure,⁹ in a round-bottom flask was charged with sodium sulfite (2.5 g, 20 mmol, 2.0 equiv), sodium bicarbonate (1.68 g, 20 mmol, 2.0 equiv) and the corresponding sulfonyl chloride (10 mol), the mixture was dissolved in distilled water (9.6 mL). Then the reaction was stirred at 80 °C for 4h. After cooling to room temperature, the mixture was washed with ethyl acetate, the aqueous layer was removed under reduced pressure. Then, the obtained white solid was washed with ethanol (50 mL * 3). The combined organic layers were dried over anhydrous sodium sulfate, and was removed under reduced pressure to give the desired sodium sulfonates as white crystalline powder. **c5**, **c6**, **c7** were synthesized according to the above procedure.

4. Reaction optimization for alkene alkylsulfonylation

Table S2. Optimization of reaction conditions^a



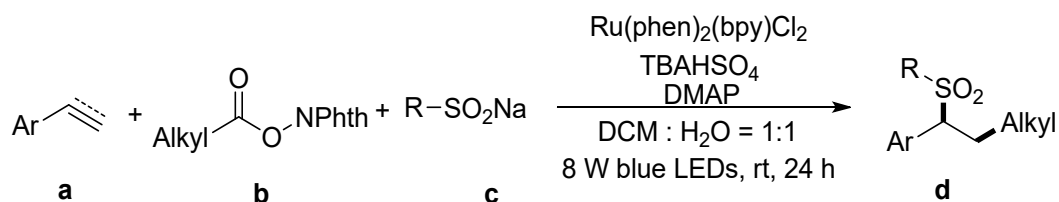
entry	Photocatalyst	additive	solvent	Yield (%) ^b
1	Ru(bpy) ₃ Cl ₂	-	MeCN	35
2	Ru(bpy) ₃ (PF ₆) ₂	-	MeCN	41
3	Eosin Y	-	MeCN	36
4	Ru(bpy) ₃ (PF ₆) ₂	-	DMF	33
5	Ru(bpy) ₃ (PF ₆) ₂	-	DMSO	25
6 ^c	Ru(bpy) ₃ (PF ₆) ₂	TBAHSO ₄	MeCN/H ₂ O	37
7 ^c	Ru(bpy) ₃ (PF ₆) ₂	TBAHSO ₄	DCM/H ₂ O	56
8 ^c	Ru(bpy) ₃ (PF ₆) ₂	TBAHSO ₄	EA/H ₂ O	51
9 ^c	Ru(phen) ₂ (bpy)(PF ₆) ₂	TBAHSO ₄	DCM/H ₂ O	60
10 ^c	Ru(phen) ₂ (bpy)Cl ₂	TBAHSO ₄	DCM/H ₂ O	62
11^{c,d}	Ru(phen)₂(bpy)Cl₂	TBAHSO₄, DMAP	DCM/H₂O	66
12 ^c	-	TBAHSO ₄ , DMAP	DCM/H ₂ O	0
13 ^{c,e}	Ru(phen) ₂ (bpy)Cl ₂	TBAHSO ₄ , DMAP	DCM/H ₂ O	0

^aReaction conditions: **a1** (0.4 mmol), **b1** (0.2 mmol), **c1** (0.6 mmol), photocatalyst (0.004 mmol), solvent (2 mL), at room temperature, 8 W blue LEDs, 24 h. ^bIsolated yields. ^cTBAHSO₄ (0.08 mmol), 4 mL mixed solvent (v/v = 1/1) were used. ^dDMAP (0.16 mmol) was added. ^eReaction in the dark.

We began our investigation using phthalimide ester **b1** and sodium *p*-methylbenzene sulfinate (**c1**) as the alkylation and sulfonylation reagents, and using 2-vinylnaphthalene (**a1**) as the model substrate for the convenience in observation and isolation of the product (Table S2). Some photocatalysts were initially tested to show the feasibility of this three-component reaction. To our delight, Ru(bpy)₃Cl₂ and

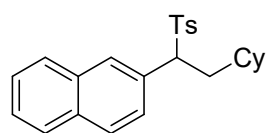
$\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$ were effective for this alkylsulfonylation process and α -sulfone product **d1** was obtained in 35% and 41% yield (entry 1 and 2). Eosin Y was also enabled to give 36% yield of **d1** (entry 3). Besides alkylsulfonylation, phthalimide ester decomposition, two-component coupling and further dimerization were detected as the main side-reactions (side-products were shown in Table 1), which showed challenge in improving the catalytic efficiency. Considering that the minor dissolvability of sulfinate in MeCN might restrict the generation of **d1**, we change the solvent to DMF or DMSO but inferior results were obtained (entries 4 and 5). Mixed solvent was then applied (entries 6-8), and we were glad to find that in DCM/ H_2O system, the yield of **d1** increased to 56% in the addition of phase transfer catalyst (PTC) tetrabutylammonium bisulfate (TBAHSO_4). Further screening of ruthenium catalysts disclosed that $\text{Ru}(\text{phen})_2(\text{bpy})(\text{PF}_6)_2$ and $\text{Ru}(\text{phen})_2(\text{bpy})\text{Cl}_2$ (phen = 1,10-phenanthroline) were more efficient catalysts. 60% and 62% yield were obtained respectively (entries 9 and 10). Yield of **d1** eventually increased to 66% after the addition of DMAP (4-dimethylaminopyridine) which could restrain the generation of dimeric by-product (entry 11). In addition, no reaction was observed in the absence of photocatalyst or in dark conditions (entries 12 and 13).

5. General procedure for alkylsulfonylation of alkenes or alkynes



A flame dried 10 mL Schlenk tube was charged with $\text{Ru}(\text{phen})_2(\text{bpy})\text{Cl}_2$ (0.004 mmol, 2.6 mg), **a** (0.4 mmol), **b** (0.2 mmol), **c** (0.6 mmol), TBAHSO_4 (0.08 mmol, 27.2 mg), and DMAP (0.16 mmol, 19.5 mg, not add when alkyne substrate was used), the tube was vacuumed and inflated with nitrogen gas three times. After that, DCM (2.0 mL) and H_2O (2.0 mL) were added through syringe under nitrogen atmosphere. The tube was screwed and the mixture was stirred at room temperature under blue light irradiation with a cooling fan. After 24 h, the mixture was diluted with DCM (5.0 mL) and the aqueous phase was separated and discarded. The organic phase was vacuumed to remove the solvent and the crude mixture was purified through silica gel column with ethyl acetate/petroleum ether as the eluent.

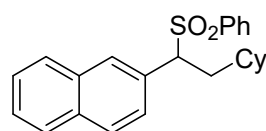
2-(2-Cyclohexyl-1-tosylethyl)naphthalene (**d1**)



d1

Compound **d1** was obtained as a white solid in 66% yield (51.6 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.85 – 7.77 (m, 1H), 7.77 – 7.67 (m, 2H), 7.55 – 7.43 (m, 3H), 7.37 (d, $J = 8.2$ Hz, 2H), 7.28 – 7.20 (m, 1H), 7.10 (d, $J = 8.1$ Hz, 2H), 4.37 – 4.25 (m, 1H), 2.34 (s, 3H), 2.23 (dd, $J = 8.8, 5.8$ Hz, 2H), 1.71 – 1.47 (m, 5H), 1.14 – 0.88 (m, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 144.3, 134.3, 133.1, 132.9, 130.0, 129.7, 129.2, 129.0, 128.1, 128.0, 127.6, 126.8, 126.5, 126.2, 69.5, 34.5, 34.3, 34.1, 31.5, 26.2, 25.9, 25.7, 21.5. HRMS m/z (ESI) calcd for $\text{C}_{25}\text{H}_{27}\text{O}_2\text{S}$ (M-H) $^-$ 391.1737, found 391.1736.

2-(2-Cyclohexyl-1-(phenylsulfonyl)ethyl)naphthalene (**d2**)

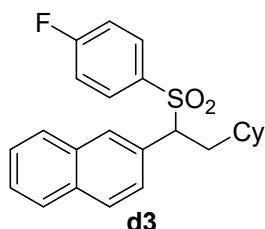


d2

Compound **d2** was obtained as a white solid in 62% yield (46.8 mg). ^1H

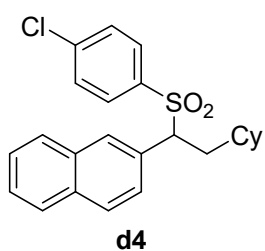
NMR (400 MHz, CDCl₃) δ 7.84 – 7.77 (m, 1H), 7.76 – 7.66 (m, 2H), 7.54 – 7.43 (m, 6H), 7.30 (t, J = 7.8 Hz, 2H), 7.24 (dd, J = 8.6, 1.8 Hz, 1H), 4.38 – 4.28 (m, 1H), 2.32 – 2.20 (m, 2H), 1.71 – 1.48 (m, 5H), 1.15 – 0.87 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 137.2, 133.3, 133.1, 132.9, 129.9, 129.8, 129.0, 128.5, 128.1, 128.0, 127.6, 126.8, 126.5, 126.2, 69.5, 34.3, 34.1, 31.5, 26.2, 25.9, 25.6. HRMS m/z (ESI) calcd for C₂₄H₂₅O₂S (M-H)⁻ 377.1581, found 377.1579.

2-(2-Cyclohexyl-1-((4-fluorophenyl)sulfonyl)ethyl)naphthalene (d3)



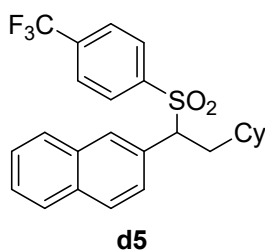
Compound **d3** was obtained as a white solid in 69% yield (54.5 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.90 – 7.64 (m, 3H), 7.61 – 7.39 (m, 5H), 7.22 (d, J = 8.4 Hz, 1H), 6.97 (t, J = 8.6 Hz, 2H), 4.37 – 4.26 (m, 1H), 2.26 (dd, J = 8.7, 5.8 Hz, 2H), 1.76 – 1.47 (m, 5H), 1.20 – 0.86 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 165.6 (d, J = 256.2 Hz), 133.3 (d, J = 3.0 Hz), 133.2, 132.9, 131.8 (d, J = 9.6 Hz), 129.8, 129.7, 128.3, 128.0, 127.6, 126.7, 126.7, 126.4, 115.8 (d, J = 22.5 Hz), 69.7, 34.3, 34.3, 34.1, 31.6, 26.2, 25.9, 25.6. ¹⁹F NMR (376 MHz, CDCl₃) δ -103.8. HRMS m/z (ESI) calcd for C₂₄H₂₄FO₂S (M-H)⁻ 395.1487, found 395.1484.

2-(1-((4-Chlorophenyl)sulfonyl)-2-cyclohexylethyl)naphthalene (d4)



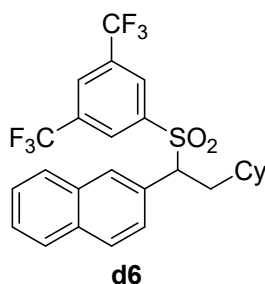
Compound **d4** was obtained as a white solid in 63% yield (51.7 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.86 – 7.79 (m, 1H), 7.78 – 7.69 (m, 2H), 7.56 – 7.46 (m, 3H), 7.43 – 7.37 (m, 2H), 7.30 – 7.25 (m, 2H), 7.22 (d, J = 8.5 Hz, 1H), 4.37 – 4.26 (m, 1H), 2.25 (p, J = 7.4 Hz, 2H), 1.72 – 1.49 (m, 5H), 1.17 – 0.83 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 140.1, 135.8, 133.2, 132.9, 130.4, 129.8, 129.6, 128.8, 128.3, 128.0, 127.6, 126.7, 126.7, 126.4, 69.6, 34.3, 34.1, 31.5, 26.2, 25.9, 25.6. HRMS m/z (ESI) calcd for C₂₄H₂₄ClO₂S (M-H)⁻ 411.1191, found 411.1190.

2-(2-Cyclohexyl-1-((4-(trifluoromethyl)phenyl)sulfonyl)ethyl)naphthalene (d5)



Compound **d5** was obtained as a white solid in 72% yield (64.3 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, J = 8.2 Hz, 1H), 7.75 (d, J = 8.1 Hz, 1H), 7.67 (d, J = 7.3 Hz, 1H), 7.51 (t, J = 7.8 Hz, 2H), 7.43 (d, J = 8.2 Hz, 2H), 7.33 (dd, J = 13.1, 7.7 Hz, 3H), 7.28 – 7.21 (m, 1H), 5.20 (dd, J = 10.9, 4.3 Hz, 1H), 2.49 – 2.32 (m, 2H), 1.67 – 1.47 (m, 5H), 1.24 – 0.82 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 140.7, 134.7 (q, J = 33.0 Hz), 133.4, 132.3, 129.6, 129.5, 128.9, 127.8, 127.2, 126.6, 125.5, 125.2, 125.1 (q, J = 3.7 Hz), 122.9 (q, J = 274.7 Hz), 121.3, 62.7, 34.6, 34.5, 34.1, 32.1, 26.1, 25.9, 25.6. ¹⁹F NMR (376 MHz, CDCl₃) δ -63.4. HRMS m/z (ESI) calcd for C₂₅H₂₄F₃O₂S (M-H)⁻ 445.1455, found 445.1452.

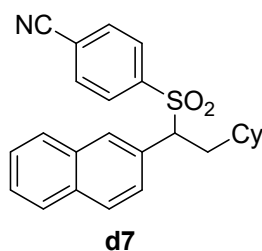
2-(1-((3,5-Bis(trifluoromethyl)phenyl)sulfonyl)-2-cyclohexylethyl)naphthalene (d6)



Compound **d6** was obtained as a colorless oil in 71% yield (72.8 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.90 (s, 1H), 7.85 – 7.74 (m, 4H), 7.65 (d, J = 7.5 Hz, 1H), 7.50 (pd, J = 6.9, 1.3 Hz, 2H), 7.42 (s, 1H), 7.22 (d, J = 8.3 Hz, 1H), 4.40 – 4.31 (m, 1H), 2.38 – 2.27 (m, 2H), 1.75 – 1.51 (m, 5H), 1.25 – 0.89 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 139.9, 133.4, 132.8, 132.2 (q, J = 34.6 Hz), 129.9, 129.3, 129.2, 128.9, 127.7, 127.6, 127.1, 126.8, 126.7 (q, J

= 3.4 Hz), 125.9, 122.1 (q, $J = 273.6$ Hz), 70.3, 34.5, 34.1, 33.5, 31.7, 26.1, 25.9, 25.6. ^{19}F NMR (376 MHz, CDCl_3) δ -63.2. HRMS m/z (ESI) calcd for $\text{C}_{26}\text{H}_{23}\text{F}_6\text{O}_2\text{S}$ (M-H^-) 513.1328, found 513.1325.

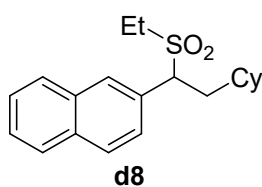
4-((2-Cyclohexyl-1-(naphthalen-2-yl)ethyl)sulfonyl)benzonitrile (d7)



402.1532.

Compound **d7** was obtained as a white solid in 58% yield (46.5 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.82 (d, $J = 7.0$ Hz, 1H), 7.77 – 7.67 (m, 2H), 7.61 – 7.45 (m, 7H), 7.20 (d, $J = 8.3$ Hz, 1H), 4.34 (t, $J = 7.7$ Hz, 1H), 2.33 – 2.23 (m, 2H), 1.73 – 1.50 (m, 5H), 1.18 – 0.82 (m, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 141.6, 133.2, 132.8, 132.2, 129.8, 129.6, 129.0, 128.5, 127.9, 127.7, 127.0, 126.7, 126.4, 117.1, 117.0, 69.7, 34.3, 34.1, 34.0, 31.5, 26.1, 25.9, 25.6. HRMS m/z (ESI) calcd for $\text{C}_{25}\text{H}_{24}\text{NO}_2\text{S}$ (M-H^-) 402.1533, found

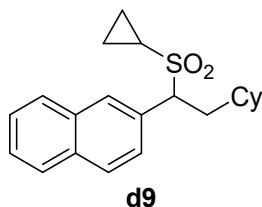
2-((2-Cyclohexyl-1-(ethylsulfonyl)ethyl)naphthalene (d8)



127.7, 126.8, 126.6, 126.1, 65.8, 45.0, 34.13, 34.10, 34.0, 31.6, 26.2, 25.9, 25.7, 6.1. HRMS m/z (ESI) calcd for $\text{C}_{20}\text{H}_{25}\text{O}_2\text{S}$ (M-H^-) 329.1581, found 329.1580.

Compound **d8** was obtained as a colorless oil in 61% yield (40.3 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.94 – 7.82 (m, 4H), 7.58 – 7.51 (m, 3H), 4.38 – 4.28 (m, 1H), 2.80 – 2.58 (m, 2H), 2.23 (dd, $J = 8.6, 5.6$ Hz, 2H), 1.78 (d, $J = 11.1$ Hz, 1H), 1.70 – 1.52 (m, 4H), 1.25 (t, $J = 7.5$ Hz, 3H), 1.16 – 0.91 (m, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 133.4, 133.2, 130.8, 129.1, 129.0, 128.0,

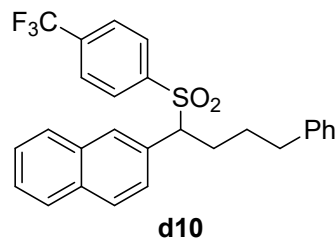
2-((2-Cyclohexyl-1-(cyclopropylsulfonyl)ethyl)naphthalene (d9)



26.0, 25.7, 4.8, 4.7. HRMS m/z (ESI) calcd for $\text{C}_{21}\text{H}_{25}\text{O}_2\text{S}$ (M-H^-) 341.1581, found 341.1580.

Compound **d9** was obtained as a colorless oil in 58% yield (39.7 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.98 – 7.81 (m, 4H), 7.61 – 7.49 (m, 3H), 4.33 (dd, $J = 10.5, 4.9$ Hz, 1H), 2.34 – 2.17 (m, 2H), 1.95 (tt, $J = 8.1, 4.9$ Hz, 1H), 1.76 (d, $J = 10.8$ Hz, 1H), 1.69 – 1.52 (m, 3H), 1.19 – 0.93 (m, 8H), 0.91 – 0.70 (m, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 133.3, 133.1, 130.7, 129.5, 128.6, 128.0, 127.7, 126.7, 126.6, 126.5, 67.1, 34.1, 34.1, 31.6, 27.8, 26.2,

2-((4-phenyl-1-((4-(trifluoromethyl)phenyl)sulfonyl)butyl)naphthalene (d10)

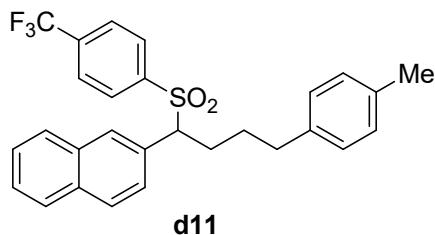


125.6 (q, $J = 3.7$ Hz), 123.0 (q, $J = 273.2$ Hz), 71.6, 35.3, 28.4, 26.8. ^{19}F NMR (376 MHz, CDCl_3) δ -63.2. HRMS m/z (ESI) calcd for $\text{C}_{27}\text{H}_{22}\text{F}_3\text{O}_2\text{S}$ (M-H^-) 467.1298, found 467.1293.

Compound **d10** was obtained as a white solid in 66% yield (61.8 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.85 – 7.79 (m, 1H), 7.74 (d, $J = 8.5$ Hz, 1H), 7.70 – 7.65 (m, 1H), 7.64 – 7.42 (m, 7H), 7.25 – 7.12 (m, 4H), 7.09 – 7.00 (m, 2H), 4.28 – 4.15 (m, 1H), 2.72 – 2.45 (m, 3H), 2.40 – 2.25 (m, 1H), 1.64 – 1.50 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 141.1, 140.8, 135.0 (q, $J = 33.2$ Hz), 133.2, 132.9, 129.8, 129.6, 128.8, 128.5, 128.4, 128.3, 127.9, 127.6, 126.9, 126.6, 126.4, 126.0,

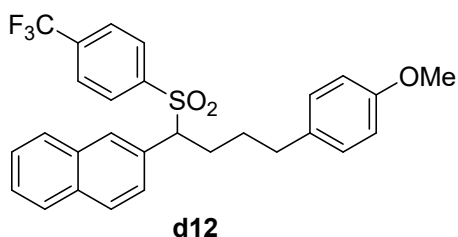
2-((4-(p-Tolyl)-1-((4-(trifluoromethyl)phenyl)sulfonyl)butyl)naphthalene (d11)

Compound **d11** was obtained as a white solid in 68% yield (65.3 mg). ^1H NMR (400 MHz, CDCl_3) δ



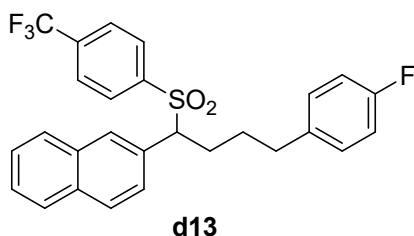
7.81 (d, $J = 7.4$ Hz, 1H), 7.73 (d, $J = 8.5$ Hz, 1H), 7.66 (d, $J = 7.3$ Hz, 1H), 7.63 – 7.54 (m, 4H), 7.54 – 7.45 (m, 2H), 7.43 (s, 1H), 7.19 (dd, $J = 8.5, 1.4$ Hz, 1H), 7.02 (d, $J = 7.8$ Hz, 2H), 6.92 (d, $J = 7.9$ Hz, 2H), 4.20 (dd, $J = 11.7, 3.7$ Hz, 1H), 2.66 – 2.43 (m, 3H), 2.37 – 2.23 (m, 4H), 1.57 – 1.47 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 140.8, 138.0, 135.5, 135.0 (q, $J = 33.3$ Hz), 133.3, 132.9, 129.8, 129.6, 129.0, 128.8, 128.5, 128.2, 127.9, 127.6, 126.9, 126.6, 126.4, 125.6 (q, $J = 3.6$ Hz), 123.0 (q, $J = 273.1$ Hz), 71.6, 34.8, 28.5, 26.7, 20.9. ^{19}F NMR (376 MHz, CDCl_3) δ -63.2. HRMS m/z (ESI) calcd for $\text{C}_{28}\text{H}_{24}\text{F}_3\text{O}_2\text{S}$ (M-H) $^-$ 481.1455, found 481.1451.

2-(4-(4-Methoxyphenyl)-1-((4-(trifluoromethyl)phenyl)sulfonyl)butyl)naphthalene (d12)



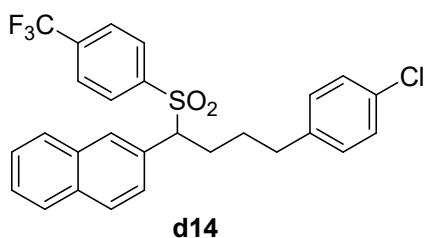
Compound **d12** was obtained as a white solid in 66% yield (65.6 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.83 – 7.78 (m, 1H), 7.73 (d, $J = 8.5$ Hz, 1H), 7.69 – 7.64 (m, 1H), 7.58 (q, $J = 8.5$ Hz, 4H), 7.54 – 7.45 (m, 2H), 7.43 (s, 1H), 7.18 (dd, $J = 8.5, 1.5$ Hz, 1H), 6.95 (d, $J = 8.6$ Hz, 2H), 6.76 (d, $J = 8.6$ Hz, 2H), 4.20 (dd, $J = 11.6, 3.7$ Hz, 1H), 3.76 (s, 3H), 2.65 – 2.44 (m, 3H), 2.37 – 2.24 (m, 1H), 1.57 – 1.47 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 157.8, 140.8, 135.0 (q, $J = 32.9$ Hz), 133.3, 133.1, 132.9, 129.8, 129.6, 129.2, 128.9, 128.5, 127.9, 127.6, 126.9, 126.6, 126.4, 125.6 (q, $J = 3.6$ Hz), 123.0 (q, $J = 273.1$ Hz), 113.8, 71.7, 55.2, 34.4, 28.6, 26.7. ^{19}F NMR (376 MHz, CDCl_3) δ -63.2. HRMS m/z (ESI) calcd for $\text{C}_{28}\text{H}_{24}\text{F}_3\text{O}_3\text{S}$ (M-H) $^-$ 497.1404, found 497.1402.

2-(4-(4-Fluorophenyl)-1-((4-(trifluoromethyl)phenyl)sulfonyl)butyl)naphthalene (d13)



Compound **d13** was obtained as a white solid in 67% yield (65.3 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.81 (d, $J = 7.4$ Hz, 1H), 7.74 (d, $J = 8.5$ Hz, 1H), 7.69 – 7.64 (m, 1H), 7.58 (q, $J = 8.5$ Hz, 4H), 7.54 – 7.46 (m, 2H), 7.44 (s, 1H), 7.22 – 7.15 (m, 1H), 6.99 (dd, $J = 8.4, 5.6$ Hz, 2H), 6.90 (t, $J = 8.7$ Hz, 2H), 4.20 (dd, $J = 11.6, 3.7$ Hz, 1H), 2.69 – 2.46 (m, 3H), 2.38 – 2.23 (m, 1H), 1.59 – 1.46 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 161.3 (d, $J = 243.9$ Hz), 140.8, 136.7 (d, $J = 3.2$ Hz), 135.1 (q, $J = 33.1$ Hz), 133.3, 132.9, 129.8, 129.7, 129.6, 128.8, 128.5, 127.9, 127.6, 126.9, 126.6, 126.3, 125.7 (q, $J = 3.7$ Hz), 123.0 (q, $J = 272.9$ Hz), 115.1 (d, $J = 21.1$ Hz), 71.6, 34.5, 28.5, 26.6. ^{19}F NMR (376 MHz, CDCl_3) δ -63.2, -117.3. HRMS m/z (ESI) calcd for $\text{C}_{27}\text{H}_{21}\text{F}_4\text{O}_2\text{S}$ (M-H) $^-$ 485.1204, found 485.1200.

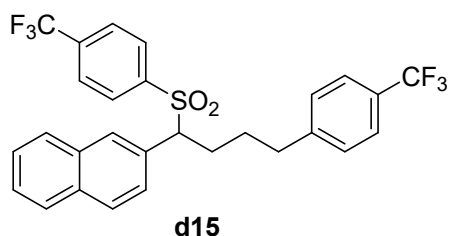
2-(4-(4-Chlorophenyl)-1-((4-(trifluoromethyl)phenyl)sulfonyl)butyl)naphthalene (d14)



Compound **d14** was obtained as a white solid in 63% yield (63.3 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.81 (d, $J = 7.4$ Hz, 1H), 7.73 (d, $J = 8.5$ Hz, 1H), 7.66 (d, $J = 7.3$ Hz, 1H), 7.62 – 7.45 (m, 6H), 7.43 (s, 1H), 7.18 (d, $J = 8.2$ Hz, 3H), 6.97 (d, $J = 8.3$ Hz, 2H), 4.19 (dd, $J = 11.6, 3.7$ Hz, 1H), 2.69 – 2.46 (m, 3H), 2.37 – 2.23 (m, 1H), 1.60 – 1.45 (m, 2H). ^{13}C NMR (101

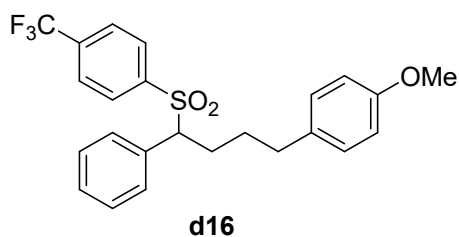
MHz, CDCl₃) δ 140.8, 139.5, 135.1 (q, $J = 33.0$ Hz), 133.3, 132.8, 131.8, 129.8, 129.6, 129.6, 128.8, 128.6, 128.5, 127.9, 127.6, 126.9, 126.6, 126.2, 125.7 (q, $J = 3.5$ Hz), 123.0 (q, $J = 273.3$ Hz), 71.6, 34.6, 28.3, 26.6. ¹⁹F NMR (376 MHz, CDCl₃) δ -63.2. HRMS m/z (ESI) calcd for C₂₇H₂₁ClF₃O₂S (M-H)⁻ 501.0908, found 501.0905.

2-(4-(4-(Trifluoromethyl)phenyl)-1-((4-(trifluoromethyl)phenyl)sulfonyl)butyl)naphthalene (d15)



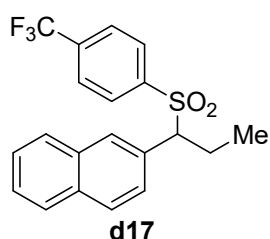
Compound **d15** was obtained as a white solid in 70% yield (75.0 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, $J = 7.5$ Hz, 1H), 7.73 (d, $J = 8.5$ Hz, 1H), 7.66 (d, $J = 7.4$ Hz, 1H), 7.57 (q, $J = 8.6$ Hz, 4H), 7.53 – 7.45 (m, 4H), 7.43 (s, 1H), 7.16 (t, $J = 8.9$ Hz, 3H), 4.20 (dd, $J = 11.5, 3.7$ Hz, 1H), 2.78 – 2.61 (m, 2H), 2.61 – 2.49 (m, 1H), 2.39 – 2.25 (m, 1H), 1.69 – 1.48 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 145.2, 140.7, 135.1 (q, $J = 33.0$ Hz), 133.3, 132.8, 129.7, 129.6, 128.8, 128.6, 127.9, 127.6, 127.0, 126.9 (q, $J = 274.2$ Hz), 126.7, 126.2, 125.7 (q, $J = 3.7$ Hz), 125.3 (q, $J = 3.8$ Hz), 123.0 (q, $J = 274.1$ Hz), 71.6, 35.2, 28.2, 26.7. ¹⁹F NMR (376 MHz, CDCl₃) δ -62.4, -63.3. HRMS m/z (ESI) calcd for C₂₈H₂₁F₆O₂S (M-H)⁻ 535.1172, found 535.1168.

1-Methoxy-4-(4-phenyl-4-((4-(trifluoromethyl)phenyl)sulfonyl)butyl)benzene (d16)



Compound **d16** was obtained as a white solid in 61% yield (54.8 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.66 – 7.55 (m, 4H), 7.33 – 7.25 (m, 1H), 7.22 (t, $J = 7.4$ Hz, 2H), 7.00 (dd, $J = 25.2, 7.9$ Hz, 4H), 6.78 (d, $J = 8.4$ Hz, 2H), 4.03 (dd, $J = 11.5, 3.5$ Hz, 1H), 3.77 (s, 3H), 2.64 – 2.38 (m, 3H), 2.26 – 2.12 (m, 1H), 1.51 (p, $J = 7.6$ Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 157.9, 140.9, 135.0 (q, $J = 32.8$ Hz), 133.2, 131.6, 129.8, 129.6, 129.2, 129.1, 128.7, 125.6 (q, $J = 3.6$ Hz), 123.1 (q, $J = 273.1$ Hz), 113.8, 71.5, 55.2, 34.4, 28.7, 26.6. ¹⁹F NMR (376 MHz, CDCl₃) δ -63.2. HRMS m/z (ESI) calcd for C₂₄H₂₂F₃O₃S (M-H)⁻ 447.1247, found 447.1244.

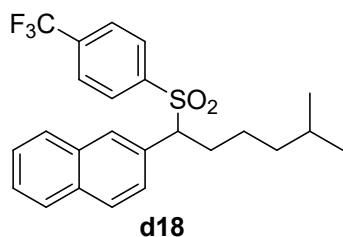
2-(1-((4-(Trifluoromethyl)phenyl)sulfonyl)propyl)naphthalene (d17)



Compound **d17** was obtained as a white solid in 65% yield (49.3 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, $J = 7.4$ Hz, 1H), 7.76 (d, $J = 8.5$ Hz, 1H), 7.72 – 7.67 (m, 1H), 7.66 – 7.55 (m, 4H), 7.55 – 7.45 (m, 3H), 7.22 – 7.27 (m, 1H), 4.15 (dd, $J = 11.6, 3.7$ Hz, 1H), 2.63 – 2.50 (m, 1H), 2.36 – 2.21 (m, 1H), 0.91 (t, $J = 7.4$ Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 140.9, 135.1 (q, $J = 33.2$ Hz), 133.3, 132.9, 129.9, 129.6, 128.8, 128.5, 127.9, 127.6, 126.8, 126.6, 126.4, 125.7 (q, $J = 3.7$ Hz), 123.0 (q, $J = 273.1$ Hz), 73.3, 20.9, 11.5. ¹⁹F NMR (376 MHz, CDCl₃) δ -63.2. HRMS m/z (ESI) calcd for C₂₀H₁₆F₃O₂S (M-H)⁻ 377.0828, found 377.0825.

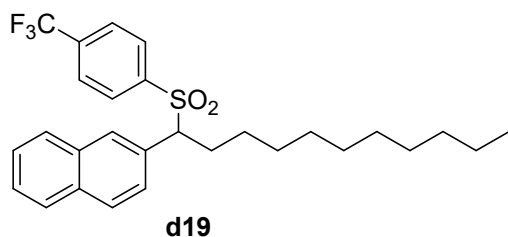
2-(5-Methyl-1-((4-(trifluoromethyl)phenyl)sulfonyl)hexyl)naphthalene (d18)

Compound **d18** was obtained as a white solid in 72% yield (62.4 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, $J = 7.3$ Hz, 1H), 7.75 (d, $J = 8.5$ Hz, 1H), 7.69 (d, $J = 7.3$ Hz, 1H), 7.65 – 7.54 (m, 4H), 7.54 –



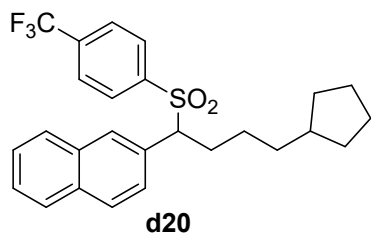
7.45 (m, 3H), 7.26 – 7.21 (m, 1H), 4.22 (dd, $J = 11.6, 3.6$ Hz, 1H), 2.52 – 2.41 (m, 1H), 2.83 – 2.21 (m, 1H), 1.49 – 1.37 (m, 1H), 1.27 – 1.14 (m, 4H), 0.82 – 0.71 (m, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 140.9, 135.0 (q, $J = 33.0$ Hz), 133.2, 132.9, 129.8, 129.6, 129.1, 128.5, 127.9, 127.6, 126.8, 126.6, 126.4, 125.6 (q, $J = 3.5$ Hz), 123.0 (q, $J = 273.0$ Hz), 71.9, 38.3, 27.6, 27.3, 24.6, 22.6, 22.2. ^{19}F NMR (376 MHz, CDCl_3) δ -63.2. HRMS m/z (ESI) calcd for $\text{C}_{24}\text{H}_{24}\text{F}_3\text{O}_2\text{S}$ (M-H)⁻ 433.1454, found 433.1450.

2-(1-(4-(Trifluoromethyl)phenyl)sulfonyl)undecyl)naphthalene (d19)



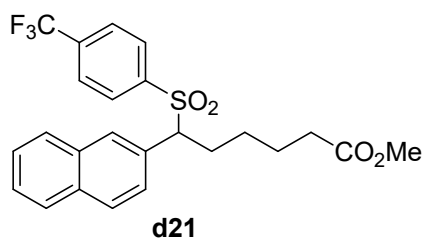
Compound **d19** was obtained as a colorless oil in 61% yield (59.7 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.81 (d, $J = 7.3$ Hz, 1H), 7.75 (d, $J = 8.5$ Hz, 1H), 7.71 – 7.66 (m, 1H), 7.62 (d, $J = 8.4$ Hz, 2H), 7.57 (d, $J = 8.4$ Hz, 2H), 7.54 – 7.45 (m, 3H), 7.23 (dd, $J = 8.5, 1.5$ Hz, 1H), 4.21 (dd, $J = 11.7, 3.6$ Hz, 1H), 2.54 – 2.43 (m, 1H), 2.34 – 2.21 (m, 1H), 1.35 – 1.11 (m, 16H), 0.85 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 140.9, 135.0 (q, $J = 33.2$ Hz), 133.2, 132.9, 129.8, 129.6, 129.1, 128.5, 127.9, 127.6, 126.8, 126.5, 126.4, 125.6 (q, $J = 3.5$ Hz), 123.0 (q, $J = 273.4$ Hz), 71.9, 31.8, 29.44, 29.39, 29.2, 29.14, 29.07, 27.1, 26.7, 22.6, 14.1. ^{19}F NMR (376 MHz, CDCl_3) δ -63.2. HRMS m/z (ESI) calcd for $\text{C}_{28}\text{H}_{32}\text{F}_3\text{O}_2\text{S}$ (M-H)⁻ 489.2080, found 489.2078.

2-(4-Cyclopentyl-1-(4-(trifluoromethyl)phenyl)sulfonyl)butyl)naphthalene (d20)



Compound **d20** was obtained as a colorless oil in 66% yield (60.6 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.84 – 7.79 (m, 1H), 7.75 (d, $J = 8.5$ Hz, 1H), 7.72 – 7.66 (m, 1H), 7.65 – 7.54 (m, 4H), 7.54 – 7.44 (m, 3H), 7.24 (dd, $J = 8.5, 1.5$ Hz, 1H), 4.22 (dd, $J = 11.7, 3.6$ Hz, 1H), 2.53 – 2.42 (m, 1H), 2.35 – 2.21 (m, 1H), 1.69 – 1.57 (m, 3H), 1.55 – 1.36 (m, 4H), 1.35 – 1.17 (m, 4H), 1.02 – 0.86 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 140.9, 135.0 (q, $J = 33.2$ Hz), 133.2, 132.9, 129.8, 129.6, 129.1, 128.4, 127.9, 127.6, 126.8, 126.5, 126.4, 125.6 (t, $J = 3.7$ Hz), 123.0 (q, $J = 273.0$ Hz), 71.9, 39.6, 35.5, 32.6, 32.4, 27.3, 25.9, 25.04, 25.01. ^{19}F NMR (376 MHz, CDCl_3) δ -63.2. HRMS m/z (ESI) calcd for $\text{C}_{26}\text{H}_{26}\text{F}_3\text{O}_2\text{S}$ (M-H)⁻ 459.1611, found 459.1610.

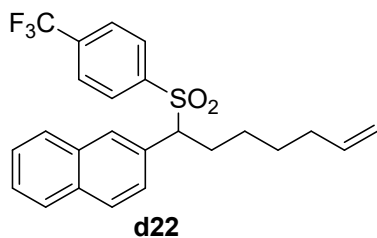
Methyl 6-(naphthalen-2-yl)-6-(4-(trifluoromethyl)phenyl)sulfonyl)hexanoate (d21)



Compound **d21** was obtained as a colorless oil in 60% yield (55.6 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.81 (d, $J = 7.4$ Hz, 1H), 7.75 (d, $J = 8.5$ Hz, 1H), 7.69 (d, $J = 7.3$ Hz, 1H), 7.65 – 7.54 (m, 4H), 7.55 – 7.44 (m, 3H), 7.25 – 7.19 (m, 1H), 4.22 (dd, $J = 11.6, 3.7$ Hz, 1H), 3.58 (s, 3H), 2.57 – 2.45 (m, 1H), 2.37 – 2.14 (m, 3H), 1.75 – 1.54 (m, 2H), 1.35 – 1.19 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 173.6, 140.8, 135.1 (q, $J = 33.2$ Hz), 133.3, 132.9, 129.8, 129.6, 128.9, 128.5, 127.9, 127.6, 126.9, 126.6, 126.3, 125.7 (q, $J = 3.7$ Hz),

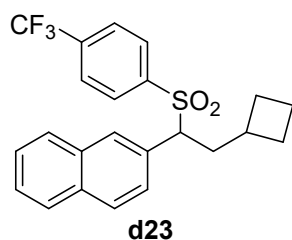
123.0 (q, $J = 273.4$ Hz), 71.5, 51.5, 33.5, 26.9, 26.2, 24.3. ^{19}F NMR (376 MHz, CDCl_3) δ -63.2. HRMS m/z (ESI) calcd for $\text{C}_{24}\text{H}_{22}\text{F}_3\text{O}_4\text{S}$ (M-H^-) 463.1196, found 463.1194.

2-(1-(4-(Trifluoromethyl)phenyl)sulfonyl)hept-6-en-1-yl)naphthalene (d22)



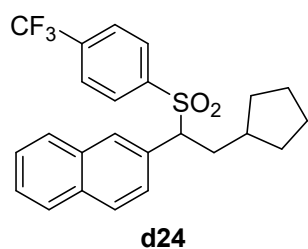
Compound **d22** was obtained as a colorless oil in 55% yield (47.4 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.82 (d, $J = 7.5$ Hz, 1H), 7.75 (d, $J = 8.5$ Hz, 1H), 7.69 (d, $J = 8.2$ Hz, 1H), 7.62 (d, $J = 8.3$ Hz, 2H), 7.57 (d, $J = 8.4$ Hz, 2H), 7.54 – 7.44 (m, 3H), 7.23 (d, $J = 8.5$ Hz, 1H), 5.75 – 5.63 (m, 1H), 4.97 – 4.83 (m, 2H), 4.21 (dd, $J = 11.6, 3.6$ Hz, 1H), 2.56 – 2.44 (m, 1H), 2.36 – 2.23 (m, 1H), 2.03 – 1.89 (m, 2H), 1.48 – 1.33 (m, $J = 6.4$ Hz, 2H), 1.30 – 1.17 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 140.9, 138.2, 135.0 (q, $J = 32.6$ Hz), 133.2, 132.9, 129.8, 129.6, 129.0, 128.5, 127.9, 127.6, 126.9, 126.6, 126.4, 125.6 (q, $J = 3.5$ Hz), 123.0 (q, $J = 274.0$ Hz), 114.7, 71.8, 33.2, 28.3, 27.0, 26.2. ^{19}F NMR (376 MHz, CDCl_3) δ -63.2. HRMS m/z (ESI) calcd for $\text{C}_{24}\text{H}_{22}\text{F}_3\text{O}_2\text{S}$ (M-H^-) 431.1298, found 431.1294.

2-(2-Cyclobutyl-1-(4-(trifluoromethyl)phenyl)sulfonyl)ethyl)naphthalene (d23)



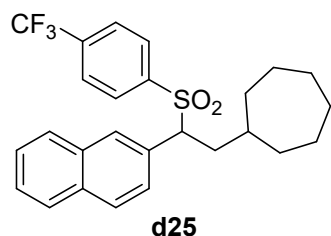
Compound **d23** was obtained as a white solid in 68% yield (56.7 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.85 – 7.77 (m, 1H), 7.73 (d, $J = 8.5$ Hz, 1H), 7.71 – 7.65 (m, 1H), 7.62 (d, $J = 8.3$ Hz, 2H), 7.56 (d, $J = 8.4$ Hz, 2H), 7.54 – 7.43 (m, 3H), 7.22 (d, $J = 8.5$ Hz, 1H), 4.12 (dd, $J = 11.6, 3.6$ Hz, 1H), 2.53 (ddd, $J = 13.3, 9.7, 3.6$ Hz, 1H), 2.47 – 2.36 (m, 1H), 2.16 – 2.04 (m, 1H), 1.95 – 1.59 (m, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 140.9, 135.0 (q, $J = 33.1$ Hz), 133.2, 132.8, 129.7, 129.6, 129.2, 128.4, 127.9, 127.6, 126.8, 126.5, 126.4, 125.6 (q, $J = 3.8$ Hz), 123.0 (q, $J = 272.9$ Hz), 70.2, 34.0, 33.0, 28.4, 27.4, 18.3. ^{19}F NMR (376 MHz, CDCl_3) δ -63.2. HRMS m/z (ESI) calcd for $\text{C}_{23}\text{H}_{20}\text{F}_3\text{O}_2\text{S}$ (M-H^-) 417.1142, found 417.1140.

2-(2-Cyclopentyl-1-(4-(trifluoromethyl)phenyl)sulfonyl)ethyl)naphthalene (d24)



Compound **d24** was obtained as a white solid in 74% yield (63.8 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.81 (d, $J = 7.4$ Hz, 1H), 7.74 (d, $J = 8.5$ Hz, 1H), 7.69 (d, $J = 7.5$ Hz, 1H), 7.65 – 7.54 (m, 4H), 7.54 – 7.44 (m, 3H), 7.25 (d, $J = 10.7$ Hz, 1H), 4.26 (dd, $J = 11.8, 3.6$ Hz, 1H), 2.47 (td, $J = 12.8, 12.3, 4.3$ Hz, 1H), 2.34 (ddd, $J = 13.3, 9.8, 3.5$ Hz, 1H), 1.70 – 1.49 (m, 5H), 1.45 – 1.32 (m, 2H), 1.20 – 1.07 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 140.9, 135.0 (q, $J = 33.1$ Hz), 133.2, 132.9, 129.8, 129.6, 129.3, 128.4, 127.9, 127.6, 126.8, 126.6, 126.5, 125.6 (q, $J = 3.7$ Hz), 123.0 (q, $J = 273.2$ Hz), 71.4, 37.0, 33.2, 33.1, 31.3, 25.0, 24.8. ^{19}F NMR (376 MHz, CDCl_3) δ -63.2. HRMS m/z (ESI) calcd for $\text{C}_{24}\text{H}_{22}\text{F}_3\text{O}_2\text{S}$ (M-H^-) 431.1298, found 431.1294.

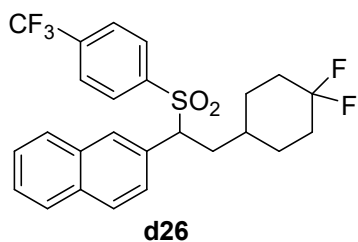
2-(2-Cycloheptyl-1-(4-(trifluoromethyl)phenyl)sulfonyl)ethyl)naphthalene (d25)



Compound **d25** was obtained as a white solid in 71% yield (65.4 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.82 (d, $J = 7.4$ Hz, 1H), 7.74 (d, $J = 8.5$ Hz, 1H), 7.71 – 7.66 (m, 1H), 7.60 (d, $J = 8.4$ Hz, 2H), 7.58 –

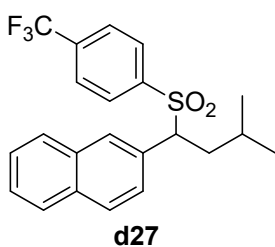
7.45 (m, 5H), 7.23 (d, $J = 8.4$ Hz, 1H), 4.30 (dd, $J = 11.6, 3.8$ Hz, 1H), 2.39 – 2.21 (m, 2H), 1.68 – 1.50 (m, 4H), 1.42 (brs, 4H), 1.36 – 1.24 (m, 3H), 1.25 – 1.11 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 140.9, 135.0 (q, $J = 33.1$ Hz), 133.2, 132.9, 129.9, 129.6, 129.2, 128.4, 127.9, 127.6, 126.8, 126.53, 126.49, 125.6 (q, $J = 3.7$ Hz), 123.0 (q, $J = 273.0$ Hz), 70.2, 35.7, 35.6, 34.5, 32.4, 28.4, 28.3, 26.0, 25.6. ^{19}F NMR (376 MHz, CDCl_3) δ -63.2. HRMS m/z (ESI) calcd for $\text{C}_{26}\text{H}_{26}\text{F}_3\text{O}_2\text{S}$ (M-H) $^-$ 459.1611, found 459.1610.

2-(2-(4,4-Difluorocyclohexyl)-1-((4-(trifluoromethyl)phenyl)sulfonyl)ethyl)naphthalene (d26)



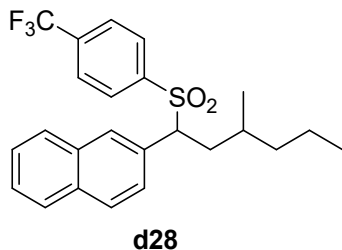
Compound **d26** was obtained as a white solid in 65% yield (62.5 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.82 (d, $J = 7.5$ Hz, 1H), 7.75 (d, $J = 8.5$ Hz, 1H), 7.69 (d, $J = 7.9$ Hz, 1H), 7.62 – 7.44 (m, 7H), 7.21 (d, $J = 8.4$ Hz, 1H), 4.34 – 4.24 (m, 1H), 2.41 – 2.32 (m, 2H), 2.07 – 1.93 (m, 2H), 1.80 – 1.65 (m, 2H), 1.56 – 1.27 (m, 5H). ^{13}C NMR (101 MHz, CDCl_3) δ 140.6, 135.2 (q, $J = 32.8$ Hz), 133.3, 132.8, 129.8, 129.6, 128.8, 128.7, 127.9, 127.7, 127.1, 126.8, 126.2, 125.7 (q, $J = 3.7$ Hz), 125.5, 123.1 (dd, $J = 240.6, 243.2$ Hz), 123.0 (q, $J = 273.0$ Hz), 69.8, 33.1 (dd, $J = 23.1, 25.6$ Hz), 32.9 (dd, $J = 23.3, 25.6$ Hz), 32.7, 29.7 (d, $J = 9.5$ Hz), 27.5 (d, $J = 9.7$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -63.2, -92.2 (d, $J = 235.6$ Hz), -102.3 (d, $J = 235.9$ Hz). HRMS m/z (ESI) calcd for $\text{C}_{25}\text{H}_{22}\text{F}_5\text{O}_2\text{S}$ (M-H) $^-$ 481.1266, found 481.1262.

2-(3-Methyl-1-((4-(trifluoromethyl)phenyl)sulfonyl)butyl)naphthalene (d27)



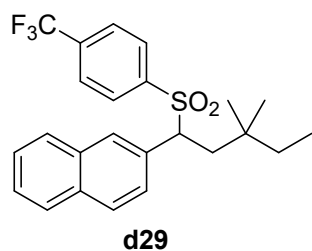
Compounds **d27** was obtained as a white solid in 63% yield (51.1 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.81 (d, $J = 7.4$ Hz, 1H), 7.74 (d, $J = 8.5$ Hz, 1H), 7.68 (d, $J = 8.4$ Hz, 1H), 7.64 – 7.54 (m, 4H), 7.53 – 7.44 (m, 3H), 7.23 (d, $J = 8.4$ Hz, 1H), 4.31 (dd, $J = 11.9, 3.7$ Hz, 1H), 2.40 – 2.28 (m, 1H), 2.25 – 2.16 (m, 1H), 1.49 – 1.37 (m, 1H), 0.92 (d, $J = 6.6$ Hz, 3H), 0.84 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 140.9, 135.0 (q, $J = 33.0$ Hz), 133.2, 132.8, 129.9, 129.6, 129.1, 128.4, 127.9, 127.6, 126.9, 126.6, 126.4, 125.6 (q, $J = 3.7$ Hz), 123.0 (q, $J = 274.7$ Hz), 70.4, 35.4, 25.2, 23.5, 20.7. ^{19}F NMR (376 MHz, CDCl_3) δ -63.2. HRMS m/z (ESI) calcd for $\text{C}_{22}\text{H}_{20}\text{F}_3\text{O}_2\text{S}$ (M-H) $^-$ 405.1142, found 405.1139.

2-(4-Methyl-1-(4-(trifluoromethyl)phenyl)heptan-2-yl)naphthalene (d28)



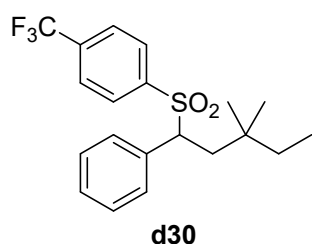
Compounds **d28** were obtained as a mixture in 69% total yield (59.8 mg, dr = 52:48, colorless oil). ^1H NMR (400 MHz, CDCl_3) δ 7.81 (d, $J = 7.7$ Hz, 1H), 7.77 – 7.72 (m, 1H), 7.71 – 7.65 (m, 1H), 7.64 – 7.44 (m, 7H), 7.24 (d, $J = 8.5$ Hz, 1H), 4.34 (t, $J = 3.6$ Hz, 0.48H), 4.31 (t, $J = 3.1$ Hz, 0.52H), 2.50 – 2.31 (m, 1H), 2.27 – 2.07 (m, 1H), 1.35 – 1.15 (m, 4H), 1.13 – 1.02 (m, 1H), 0.90 – 0.73 (m, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 140.9, 135.00 (q, $J = 33.2, 32.4$ Hz), 134.99 (q, $J = 32.9$ Hz), 133.21, 133.19, 132.9, 130.0, 129.8, 129.61, 129.60, 129.5, 128.9, 128.44, 128.40, 127.88, 127.86, 127.6, 126.85, 126.83, 126.5, 126.4, 125.6 (q, $J = 3.3$ Hz), 70.24, 70.19, 39.9, 37.2, 34.3, 33.3, 29.9, 29.4, 20.3, 19.9, 19.3, 18.4, 14.2, 14.1. ^{19}F NMR (376 MHz, CDCl_3) δ -63.21, -63.22. HRMS m/z (ESI) calcd for $\text{C}_{24}\text{H}_{24}\text{F}_3\text{O}_2\text{S}$ (M-H) $^-$ 433.1454, found 433.1450.

2-(3,3-Dimethyl-1-((4-(trifluoromethyl)phenyl)sulfonyl)pentyl)naphthalene (d29)



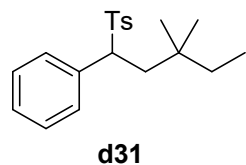
Compound **d29** was obtained as a white solid in 76% yield (65.8 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.80 (d, $J = 7.4$ Hz, 1H), 7.74 – 7.63 (m, 2H), 7.61 – 7.43 (m, 7H), 7.30 – 7.19 (m, 1H), 4.26 (d, $J = 10.1$ Hz, 1H), 2.53 (d, $J = 14.1$ Hz, 1H), 2.26 (dd, $J = 14.2, 10.5$ Hz, 1H), 1.26 – 1.10 (m, 2H), 0.79 – 0.68 (m, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 140.8, 134.9 (q, $J = 33.1$ Hz), 133.1, 132.8, 131.1, 129.9, 129.6, 129.1, 128.3, 127.9, 127.6, 126.8, 126.5, 125.5 (q, $J = 3.7$ Hz), 123.0 (q, $J = 273.1$ Hz), 69.4, 37.8, 34.5, 33.9, 27.0, 26.9, 8.2. ^{19}F NMR (376 MHz, CDCl_3) δ -63.2. HRMS m/z (ESI) calcd for $\text{C}_{24}\text{H}_{24}\text{F}_3\text{O}_2\text{S}$ (M-H) $^-$ 433.1454, found 433.1450.

1-((3,3-Dimethyl-1-phenylpentyl)sulfonyl)-4-(trifluoromethyl)benzene (d30)



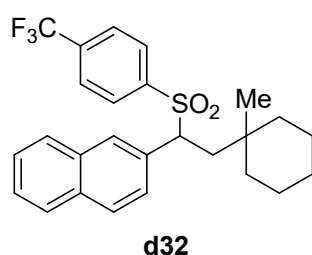
Compound **d30** was obtained as a white solid in 65% yield (49.8 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.64 – 7.55 (m, 4H), 7.30 – 7.23 (m, 1H), 7.20 (t, $J = 7.4$ Hz, 2H), 7.15 – 7.04 (m, 2H), 4.08 (dd, $J = 10.6, 1.7$ Hz, 1H), 2.45 (dd, $J = 14.2, 1.7$ Hz, 1H), 2.14 (dd, $J = 14.2, 10.5$ Hz, 1H), 1.25 – 1.08 (m, 2H), 0.81 – 0.67 (m, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 141.0, 134.9 (q, $J = 32.9$ Hz), 133.8, 130.1, 129.6, 128.8, 128.5, 125.5 (q, $J = 3.6$ Hz), 123.1 (q, $J = 273.1$ Hz), 69.2, 37.6, 34.5, 33.8, 27.0, 26.9, 8.1. ^{19}F NMR (376 MHz, CDCl_3) δ -63.2. HRMS m/z (ESI) calcd for $\text{C}_{20}\text{H}_{22}\text{F}_3\text{O}_2\text{S}$ (M-H) $^-$ 383.1298, found 383.1295.

1-((3,3-Dimethyl-1-phenylpentyl)sulfonyl)-4-methylbenzene (d31)



Compound **d31** was obtained as a colorless oil in 61% yield (40.4 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.36 (d, $J = 8.2$ Hz, 2H), 7.26 – 7.17 (m, 3H), 7.14 (d, $J = 7.9$ Hz, 4H), 4.04 (dd, $J = 10.5, 1.3$ Hz, 1H), 2.45 – 2.33 (m, 4H), 2.10 (dd, $J = 14.2, 10.5$ Hz, 1H), 1.23 – 1.05 (m, 2H), 0.77 – 0.65 (m, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 144.1, 134.45, 134.42, 130.1, 129.1, 129.0, 128.4, 128.2, 69.0, 38.0, 34.5, 33.7, 27.0, 26.8, 21.6, 8.1. HRMS m/z (ESI) calcd for $\text{C}_{20}\text{H}_{25}\text{O}_2\text{S}$ (M-H) $^-$ 329.1581, found 329.1578.

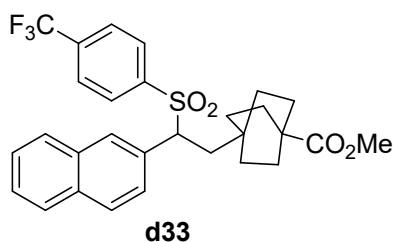
2-(2-(1-Methylcyclohexyl)-1-((4-(trifluoromethyl)phenyl)sulfonyl)ethyl)naphthalene (d32)



Compound **d32** was obtained as a colorless oil in 74% yield (68.0 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.83 – 7.76 (m, 1H), 7.69 (dd, $J = 16.0, 7.4$ Hz, 2H), 7.58 (d, $J = 8.3$ Hz, 2H), 7.55 – 7.42 (m, 5H), 7.37 – 7.16 (m, 1H), 4.34 – 4.23 (m, 1H), 2.56 (dd, $J = 14.2, 1.3$ Hz, 1H), 2.30 (dd, $J = 14.2, 10.4$ Hz, 1H), 1.50 – 1.16 (m, 8H), 1.05 (t, $J = 5.5$ Hz, 2H), 0.73 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 140.8, 134.9 (q, $J = 33.1$ Hz), 133.1, 132.8, 131.3, 129.9, 129.6, 128.2, 127.9, 127.6, 126.8, 126.5, 125.5 (q, $J = 3.7$ Hz), 123.0 (q, $J = 273.0$ Hz), 68.9, 38.6, 38.2, 37.9, 33.8, 26.0, 25.0, 21.75, 21.66. ^{19}F NMR (376 MHz, CDCl_3) δ -63.2. HRMS m/z (ESI) calcd for $\text{C}_{26}\text{H}_{26}\text{F}_3\text{O}_2\text{S}$ (M-H) $^-$ 459.1611, found 459.1608.

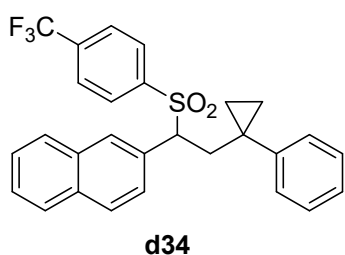
Methyl 4-(2-((4-(trifluoromethyl)phenyl)sulfonyl)-2-(naphthalen-2-yl)ethyl)bicyclo[2.2.2]octane-

1-carboxylate (d33)



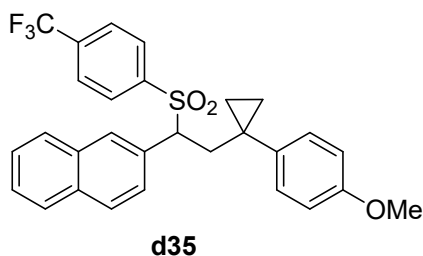
Compound **d33** was obtained as a white solid in 56% yield (59.5 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.80 (d, $J = 7.5$ Hz, 1H), 7.68 (dd, $J = 17.4, 7.8$ Hz, 2H), 7.59 – 7.38 (m, 7H), 7.19 (brs, 1H), 4.25 (d, $J = 10.3$ Hz, 1H), 3.57 (s, 3H), 2.45 (d, $J = 14.2$ Hz, 1H), 2.22 (dd, $J = 14.2, 10.6$ Hz, 1H), 1.65 (t, $J = 7.9$ Hz, 6H), 1.40 – 1.18 (m, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 178.0, 140.6, 135.0 (q, $J = 33.1$ Hz), 133.1, 132.8, 130.8, 129.9, 129.6, 128.4, 127.9, 127.6, 126.9, 126.6, 125.5 (q, $J = 3.6$ Hz), 123.0 (q, $J = 273.0$ Hz), 68.7, 51.6, 38.6, 37.7, 31.5, 30.7, 28.2. ^{19}F NMR (376 MHz, CDCl_3) δ -63.2. HRMS m/z (ESI) calcd for $\text{C}_{29}\text{H}_{28}\text{F}_3\text{O}_4\text{S}$ (M-H) $^-$ 529.1666, found 529.1661.

2-(2-(1-Phenylcyclopropyl)-1-((4-(trifluoromethyl)phenyl)sulfonyl)ethyl)naphthalene (d34)



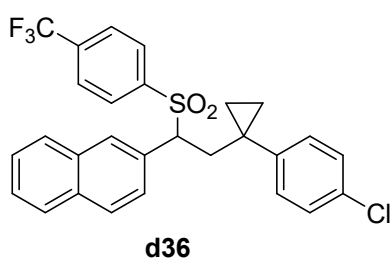
Compound **d34** was obtained as a white solid in 74% yield (71.5 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.87 – 7.78 (m, 1H), 7.70 (dd, $J = 16.6, 8.0$ Hz, 2H), 7.60 – 7.37 (m, 7H), 7.25 – 7.11 (m, 4H), 7.11 – 7.03 (m, 2H), 4.09 (dd, $J = 11.3, 2.6$ Hz, 1H), 3.19 (dd, $J = 14.1, 1.8$ Hz, 1H), 2.20 (dd, $J = 14.1, 11.3$ Hz, 1H), 0.81 – 0.69 (m, 1H), 0.67 – 0.57 (m, 2H), 0.36 – 0.23 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 142.6, 140.9, 134.9 (q, $J = 33.1$ Hz), 133.2, 132.8, 130.4, 129.3, 129.2, 129.0, 128.4, 128.2, 127.9, 127.6, 126.8, 126.6, 126.4, 125.6 (q, $J = 3.7$ Hz), 123.0 (q, $J = 273.1$ Hz), 70.0, 37.8, 23.4, 12.9, 12.5. ^{19}F NMR (376 MHz, CDCl_3) δ -63.2. HRMS m/z (ESI) calcd for $\text{C}_{28}\text{H}_{22}\text{F}_3\text{O}_2\text{S}$ (M-H) $^-$ 479.1298, found 479.1292.

2-(2-(1-(4-Methoxyphenyl)cyclopropyl)-1-((4-(trifluoromethyl)phenyl)sulfonyl)ethyl)naphthalene (d35)



Compound **d35** was obtained as a white solid in 70% yield (71.3 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.82 (d, $J = 7.6$ Hz, 1H), 7.69 (dd, $J = 16.9, 8.1$ Hz, 2H), 7.57 – 7.44 (m, 6H), 7.40 (brs, 1H), 7.19 (d, $J = 8.5$ Hz, 1H), 6.98 (d, $J = 8.6$ Hz, 2H), 6.70 (d, $J = 8.6$ Hz, 2H), 4.09 (dd, $J = 11.4, 2.5$ Hz, 1H), 3.74 (s, 3H), 3.12 (d, $J = 12.6$ Hz, 1H), 2.19 (dd, $J = 14.1, 11.4$ Hz, 1H), 0.75 – 0.66 (m, 1H), 0.62 – 0.51 (m, 2H), 0.33 – 0.23 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 158.1, 140.9, 134.9 (q, $J = 33.1$ Hz), 134.6, 133.2, 132.8, 130.4, 130.1, 129.4, 129.3, 128.1, 127.9, 127.6, 126.9, 126.8, 126.4, 125.6 (q, $J = 3.6$ Hz), 123.0 (q, $J = 273.1$ Hz), 113.7, 70.1, 55.2, 37.9, 22.8, 12.71, 12.66. ^{19}F NMR (376 MHz, CDCl_3) δ -63.2. HRMS m/z (ESI) calcd for $\text{C}_{29}\text{H}_{24}\text{F}_3\text{O}_3\text{S}$ (M-H) $^-$ 509.1404, found 509.1400.

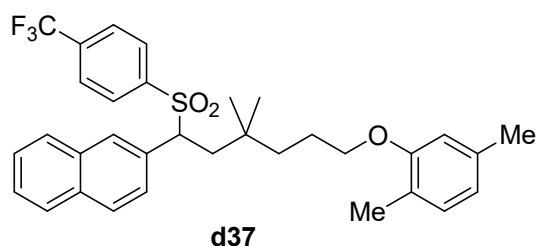
2-(2-(1-(4-Chlorophenyl)cyclopropyl)-1-((4-(trifluoromethyl)phenyl)sulfonyl)ethyl)naphthalene (d36)



Compound **d36** was obtained as a white solid in 72% yield (74.1 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.82 (s, 1H), 7.68 (dd, $J = 19.7, 8.2$ Hz, 2H), 7.50 (d, $J = 9.1$ Hz, 6H), 7.36 (brs, 1H), 7.13 (d, $J = 8.4$ Hz, 3H), 7.00 (d, $J = 8.4$ Hz, 2H), 4.03 (dd, $J = 11.3, 2.5$ Hz, 1H), 3.15 (dd, $J = 14.2, 2.6$ Hz, 1H), 2.25 (dd, $J =$

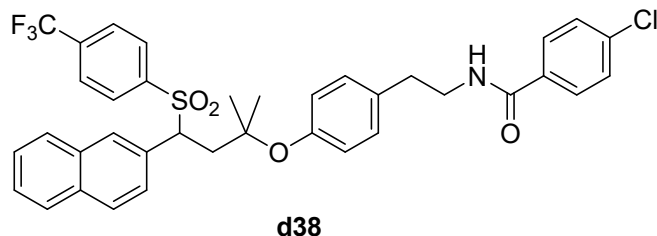
14.2, 11.4 Hz, 1H), 0.82 – 0.72 (m, 1H), 0.66 – 0.54 (m, 2H), 0.41 – 0.31 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 141.2, 140.7, 135.0 (q, *J* = 33.1 Hz), 133.2, 132.7, 132.3, 130.4, 130.3, 129.4, 129.1, 128.5, 128.3, 127.8, 127.6, 126.9, 126.65, 126.57, 125.6 (q, *J* = 3.7 Hz), 123.0 (q, *J* = 273.1 Hz), 70.1, 37.4, 23.0, 12.9. ¹⁹F NMR (376 MHz, CDCl₃) δ -63.2. HRMS *m/z* (ESI) calcd for C₂₈H₂₁ClF₃O₂S (M-H)⁻ 513.0908, found 513.0904.

2-((4-(trifluoromethyl)phenyl)sulfonyl)-6-(2,5-dimethylphenoxy)-3,3-dimethylhexyl)naphthalene (d37)



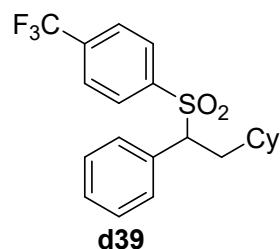
Compound **d37** was obtained as a white solid in 62% yield (70.3 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.83 – 7.76 (m, 1H), 7.69 (dd, *J* = 20.1, 7.2 Hz, 2H), 7.63 – 7.41 (m, 7H), 7.38 – 7.12 (m, 1H), 7.01 (d, *J* = 7.5 Hz, 1H), 6.67 (d, *J* = 7.4 Hz, 1H), 6.51 (s, 1H), 4.30 (d, *J* = 9.5 Hz, 1H), 3.79 – 3.67 (m, 2H), 2.67 – 2.56 (m, 1H), 2.40 – 2.25 (m, 4H), 2.15 (s, 3H), 1.85 – 1.71 (m, 1H), 1.70 – 1.56 (m, 1H), 1.43 (td, *J* = 13.0, 4.6 Hz, 1H), 1.27 (td, *J* = 13.2, 4.2 Hz, 1H), 0.83 (s, 3H), 0.80 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 156.8, 140.7, 136.5, 134.9 (q, *J* = 33.1 Hz), 133.1, 132.8, 130.9, 130.2, 129.9, 129.6, 128.3, 127.8, 127.6, 126.8, 126.6, 125.5 (q, *J* = 3.7 Hz), 123.4, 123.0 (q, *J* = 273.1 Hz), 120.6, 111.9, 69.3, 68.0, 38.2, 37.8, 33.6, 27.7, 27.5, 24.0, 21.4, 15.8. ¹⁹F NMR (376 MHz, CDCl₃) δ -63.2. HRMS *m/z* (ESI) calcd for C₃₃H₃₄F₃O₃S (M-H)⁻ 567.2186, found 567.2181.

4-Chloro-N-(4-((2-methyl-4-(naphthalen-2-yl)-4-((4-(trifluoromethyl)phenyl)sulfonyl)butan-2-yl)oxy)phenethyl)benzamide (d38)



Compound **d38** was obtained as a white solid in 48% yield (65.3 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 7.2 Hz, 1H), 7.73 (d, *J* = 8.6 Hz, 1H), 7.68 (d, *J* = 7.0 Hz, 1H), 7.65 – 7.56 (m, 5H), 7.56 – 7.45 (m, 4H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 9.3 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 6.05 (brs, 1H), 4.78 (d, *J* = 8.9 Hz, 1H), 3.66 (q, *J* = 6.6 Hz, 2H), 3.07 (d, *J* = 14.1 Hz, 1H), 2.86 (t, *J* = 6.9 Hz, 2H), 2.61 (dd, *J* = 14.3, 10.5 Hz, 1H), 1.25 (s, 3H), 0.93 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.3, 153.3, 140.72, 140.70, 137.6, 135.0 (q, *J* = 33.4 Hz), 133.9, 133.1, 132.93, 132.89, 130.7, 130.1, 129.6, 129.3, 128.8, 128.4, 128.2, 127.9, 127.6, 126.9, 126.6, 125.6 (q, *J* = 3.5 Hz), 124.6 (q, *J* = 272.1 Hz), 123.9, 79.1, 68.4, 41.2, 39.2, 34.9, 28.0, 27.3. ¹⁹F NMR (376 MHz, CDCl₃) δ -63.2. HRMS *m/z* (ESI) calcd for C₃₇H₃₂ClF₃NO₄S (M-H)⁻ 678.1698, found 678.1697.

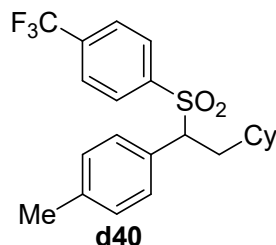
1-((2-Cyclohexyl-1-phenylethyl)sulfonyl)-4-(trifluoromethyl)benzene (d39)



Compound **d39** was obtained as a colorless oil in 67% yield (alkyne used, 53.2 mg) or 57% yield (alkene used, 45.2 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.66 – 7.54 (m, 4H), 7.30 (t, *J* = 7.3 Hz, 1H), 7.23 (t, *J* = 7.3 Hz, 2H), 7.07 (d, *J* = 7.2 Hz, 2H), 4.17 (dd, *J* = 11.2, 4.2 Hz, 1H), 2.26 – 2.10 (m, 2H),

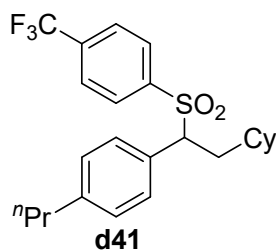
1.69 – 1.58 (m, 4H), 1.16 – 0.81 (m, 7H). ¹³C NMR (101 MHz, CDCl₃) δ 141.0, 135.0 (q, *J* = 32.9 Hz), 131.9, 129.8, 129.6, 129.0, 128.6, 125.6 (q, *J* = 3.7 Hz), 123.1 (q, *J* = 273.0 Hz), 69.6, 34.3, 34.1, 34.0, 31.6, 26.2, 26.0, 25.7. ¹⁹F NMR (376 MHz, CDCl₃) δ -63.2. HRMS *m/z* (ESI) calcd for C₂₁H₂₂F₃O₂S (M-H)⁻ 395.1298, found 395.1295.

1-(2-Cyclohexyl-1-((4-(trifluoromethyl)phenyl)sulfonyl)ethyl)-4-methylbenzene (d40)



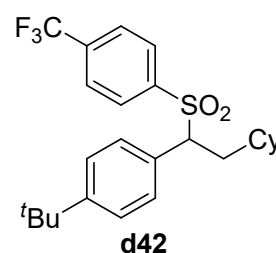
Compound **d40** was obtained as a colorless oil in 64% yield (alkyne used, 52.4 mg) or 54% yield (alkene used, 44.2 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.67 – 7.55 (m, 4H), 7.04 (d, *J* = 7.8 Hz, 2H), 6.95 (d, *J* = 7.8 Hz, 2H), 4.14 (dd, *J* = 11.0, 4.4 Hz, 1H), 2.32 (s, 3H), 2.21 – 2.06 (m, 2H), 1.67 – 1.50 (m, 5H), 1.18 – 0.93 (m, 5H), 0.91 – 0.80 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 141.1, 138.9, 134.9 (q, *J* = 33.1 Hz), 129.7, 129.6, 129.3, 128.6, 125.5 (q, *J* = 3.7 Hz), 123.1 (q, *J* = 273.1 Hz), 69.2, 34.2, 34.1, 34.0, 31.5, 26.2, 26.0, 25.6, 21.2. ¹⁹F NMR (376 MHz, CDCl₃) δ -63.1. HRMS *m/z* (ESI) calcd for C₂₂H₂₄F₃O₂S (M-H)⁻ 409.1454, found 409.1452.

1-(2-Cyclohexyl-1-((4-(trifluoromethyl)phenyl)sulfonyl)ethyl)-4-propylbenzene (d41)



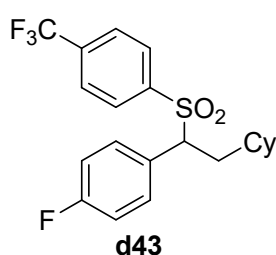
Compound **d41** was obtained as a colorless oil in 66% yield (alkyne used, 57.6 mg) or 57% yield (alkene used, 49.7 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.58 (brs, 4H), 7.02 (d, *J* = 7.9 Hz, 2H), 6.95 (d, *J* = 7.9 Hz, 2H), 4.15 (dd, *J* = 11.0, 4.4 Hz, 1H), 2.54 (t, *J* = 7.5 Hz, 2H), 2.24 – 2.08 (m, 2H), 1.69 – 1.52 (m, 7H), 1.17 – 0.83 (m, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 143.7, 141.1, 134.8 (q, *J* = 33.0 Hz), 129.6, 129.6, 128.9, 128.7, 125.4 (q, *J* = 3.7 Hz), 123.1 (q, *J* = 273.2 Hz), 69.4, 37.5, 34.3, 34.1, 33.9, 31.6, 26.2, 26.0, 25.7, 24.3, 13.6. ¹⁹F NMR (376 MHz, CDCl₃) δ -63.2. HRMS *m/z* (ESI) calcd for C₂₄H₂₈F₃O₂S (M-H)⁻ 437.1768, found 437.1763.

1-(tert-Butyl)-4-(2-cyclohexyl-1-((4-(trifluoromethyl)phenyl)sulfonyl)ethyl)benzene (d42)



Compound **d42** was obtained as a colorless oil in 70% yield (alkyne used, 63.4 mg) or 63% yield (alkene used, 57.1 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.57 (brs, 4H), 7.22 (d, *J* = 8.1 Hz, 2H), 6.96 (d, *J* = 8.1 Hz, 2H), 4.16 (dd, *J* = 9.4, 5.9 Hz, 1H), 2.22 – 2.06 (m, 2H), 1.70 – 1.53 (m, 5H), 1.28 (s, 9H), 1.20 – 0.96 (m, 5H), 0.93 – 0.82 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 152.2, 141.1, 134.8 (q, *J* = 33.1 Hz), 129.5, 129.4, 128.6, 125.5, 125.4 (q, *J* = 3.6 Hz), 123.1 (q, *J* = 273.1 Hz), 69.4, 34.6, 34.2, 34.1, 33.9, 31.6, 31.2, 26.2, 25.9, 25.6. ¹⁹F NMR (376 MHz, CDCl₃) δ -63.2. HRMS *m/z* (ESI) calcd for C₂₅H₃₀F₃O₂S (M-H)⁻ 451.1924, found 451.1922.

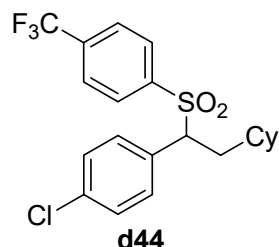
1-(2-Cyclohexyl-1-((4-(trifluoromethyl)phenyl)sulfonyl)ethyl)-4-fluorobenzene (d43)



Compound **d43** was obtained as a white solid in 65% yield (alkyne used, 53.7 mg) or 42% yield (alkene used, 34.7 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.71 – 7.58 (m, 4H), 7.11 – 7.03 (m, 2H), 6.95 (t, *J* = 8.5 Hz, 2H), 4.16 (dd, *J* = 11.6, 3.9 Hz, 1H), 2.24 – 2.03 (m, 2H), 1.69 – 1.51 (m, 5H), 1.16 – 0.78 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 162.9 (d, *J* = 249.4 Hz), 140.9,

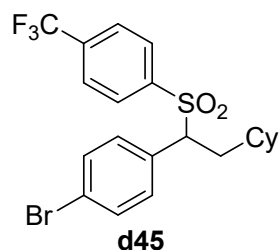
135.1 (q, $J = 33.1$ Hz), 131.5 (d, $J = 8.4$ Hz), 129.6, 127.7 (d, $J = 3.3$ Hz), 125.7 (q, $J = 3.7$ Hz), 123.0 (q, $J = 273.1$ Hz), 115.8 (d, $J = 21.6$ Hz), 68.6, 34.3, 34.1, 34.0, 31.5, 26.1, 25.9, 25.6. ^{19}F NMR (376 MHz, CDCl_3) δ -63.2, -111.7. HRMS m/z (ESI) calcd for $\text{C}_{21}\text{H}_{21}\text{F}_4\text{O}_2\text{S}$ (M-H^-) 413.1204, found 413.1202.

1-Chloro-4-(2-cyclohexyl-1-((4-(trifluoromethyl)phenyl)sulfonyl)ethyl)benzene (d44)



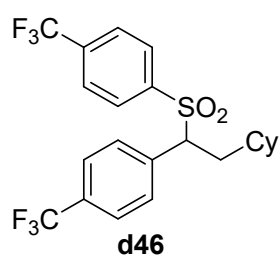
Compound **d44** was obtained as a white solid in 58% yield (alkyne used, 49.8 mg) or 55% yield (alkene used, 47.2 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.73 – 7.59 (m, 4H), 7.28 – 7.20 (m, 2H), 7.03 (d, $J = 8.4$ Hz, 2H), 4.15 (dd, $J = 11.6, 3.9$ Hz, 1H), 2.23 – 2.03 (m, 2H), 1.69 – 1.48 (m, 5H), 1.16 – 0.77 (m, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 140.8, 135.2 (q, $J = 33.1$ Hz), 135.1, 131.1, 130.4, 129.6, 128.9, 125.8 (q, $J = 3.7$ Hz), 123.0 (q, $J = 273.2$ Hz), 68.7, 34.3, 34.1, 34.0, 31.5, 26.1, 25.9, 25.6. ^{19}F NMR (376 MHz, CDCl_3) δ -63.2. HRMS m/z (ESI) calcd for $\text{C}_{21}\text{H}_{21}\text{ClF}_3\text{O}_2\text{S}$ (M-H^-) 429.0908, found 429.0905.

1-Bromo-4-(2-cyclohexyl-1-((4-(trifluoromethyl)phenyl)sulfonyl)ethyl)benzene (d45)



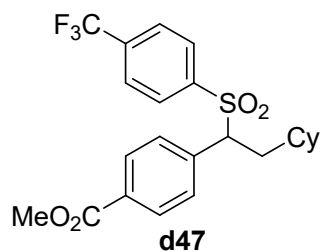
Compound **d45** was obtained as a white solid in 60% yield (alkyne used, 57.1 mg) or 51% yield (alkene used, 48.5 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.72 – 7.61 (m, 4H), 7.40 (d, $J = 8.3$ Hz, 2H), 6.97 (d, $J = 8.4$ Hz, 2H), 4.14 (dd, $J = 11.6, 3.9$ Hz, 1H), 2.22 – 2.02 (m, 2H), 1.69 – 1.48 (m, 5H), 1.15 – 0.81 (m, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 140.8, 135.2 (q, $J = 33.1$ Hz), 131.9, 131.4, 130.9, 129.6, 125.8 (q, $J = 3.6$ Hz), 123.3, 123.0 (q, $J = 273.1$ Hz), 68.8, 34.2, 34.1, 34.0, 31.5, 26.1, 25.9, 25.6. ^{19}F NMR (376 MHz, CDCl_3) δ -63.1. HRMS m/z (ESI) calcd for $\text{C}_{21}\text{H}_{21}\text{BrF}_3\text{O}_2\text{S}$ (M-H^-) 473.0403, found 473.0399.

1-(2-Cyclohexyl-1-((4-(trifluoromethyl)phenyl)sulfonyl)ethyl)-4-(trifluoromethyl)benzene (d46)



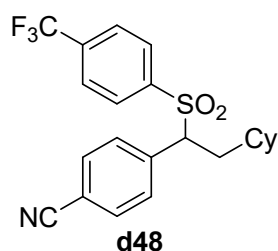
Compound **d46** was obtained as a white solid in 48% yield (alkyne used, 44.6 mg) or 50% yield (alkene used, 46.5 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.73 – 7.62 (m, 4H), 7.53 (d, $J = 8.2$ Hz, 2H), 7.24 (d, $J = 8.2$ Hz, 2H), 4.24 (dd, $J = 11.0, 4.5$ Hz, 1H), 2.24 – 2.09 (m, 2H), 1.68 – 1.52 (m, 5H), 1.14 – 0.94 (m, 5H), 0.92 – 0.80 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 140.7, 136.1, 135.4 (q, $J = 33.2$ Hz), 131.2 (q, $J = 32.8, 32.4$ Hz), 130.2, 129.6, 125.9 (q, $J = 3.7$ Hz), 125.6 (q, $J = 3.7$ Hz), 124.7 (q, $J = 65.4, 59.5$ Hz), 122.0 (q, $J = 70.8$ Hz), 69.0, 34.3, 34.0, 31.5, 26.1, 25.9, 25.6. ^{19}F NMR (376 MHz, CDCl_3) δ -62.8, -63.2. HRMS m/z (ESI) calcd for $\text{C}_{22}\text{H}_{21}\text{F}_6\text{O}_2\text{S}$ (M-H^-) 463.1172, found 463.1171.

Methyl 4-(2-cyclohexyl-1-((4-(trifluoromethyl)phenyl)sulfonyl)ethyl)benzoate (d47)



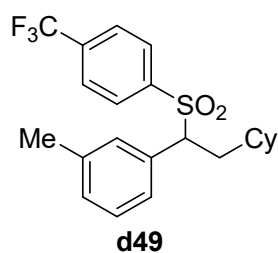
Compound **d47** was obtained as a white solid in 58% yield (alkyne used, 52.7 mg) or 52% yield (alkene used, 47.2 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.92 (d, $J = 8.0$ Hz, 2H), 7.68 – 7.58 (m, 4H), 7.18 (d, $J = 8.0$ Hz, 2H), 4.24 (dd, $J = 11.4, 4.1$ Hz, 1H), 3.92 (s, 3H), 2.28 – 2.08 (m, 2H), 1.68 – 1.51 (m, 5H), 1.15 – 0.80 (m, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 166.4, 140.7, 137.0, 135.2 (q, $J = 33.2$ Hz), 130.7, 129.9, 129.7, 129.6, 125.8 (q, $J = 3.7$ Hz), 123.0 (q, $J = 273.1$ Hz), 69.2, 52.3, 34.4, 34.1, 34.0, 31.5, 26.1, 25.9, 25.6. ^{19}F NMR (376 MHz, CDCl_3) δ -63.2. HRMS m/z (ESI) calcd for $\text{C}_{23}\text{H}_{24}\text{F}_3\text{O}_4\text{S}$ (M-H) $^-$ 453.1353, found 453.1351.

4-(2-Cyclohexyl-1-((4-(trifluoromethyl)phenyl)sulfonyl)ethyl)benzonitrile (d48)



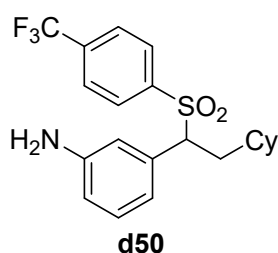
Compound **d48** was obtained as a white solid in 46% yield (alkyne used, 38.8 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.74 – 7.63 (m, 4H), 7.58 (d, $J = 8.1$ Hz, 2H), 7.25 (d, $J = 8.0$ Hz, 2H), 4.23 (dd, $J = 11.2, 4.2$ Hz, 1H), 2.24 – 2.07 (m, 2H), 1.68 – 1.51 (m, 5H), 1.16 – 0.79 (m, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 140.5, 137.4, 135.6 (q, $J = 33.0$ Hz), 132.3, 130.6, 129.5, 126.0 (q, $J = 3.5$ Hz), 122.9 (q, $J = 273.2$ Hz), 118.0, 113.0, 69.1, 34.4, 34.3, 34.0, 31.5, 26.0, 25.9, 25.6. ^{19}F NMR (376 MHz, CDCl_3) δ -63.2. HRMS m/z (ESI) calcd for $\text{C}_{22}\text{H}_{21}\text{F}_3\text{NO}_2\text{S}$ (M-H) $^-$ 420.1250, found 420.1250.

1-(2-Cyclohexyl-1-((4-(trifluoromethyl)phenyl)sulfonyl)ethyl)-3-methylbenzene (d49)



Compound **d49** was obtained as a colorless oil in 65% yield (alkyne used, 53.3 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.66 – 7.54 (m, 4H), 7.15 – 7.05 (m, 2H), 6.90 – 6.77 (m, 2H), 4.12 (dd, $J = 10.8, 4.6$ Hz, 1H), 2.25 – 2.08 (m, 5H), 1.69 – 1.52 (m, 5H), 1.17 – 0.81 (m, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 141.0, 138.3, 134.9 (q, $J = 33.4$ Hz), 131.7, 130.6, 129.7, 129.6, 128.4, 126.8, 125.5 (q, $J = 3.7$ Hz), 123.1 (q, $J = 273.1$ Hz), 69.6, 34.3, 34.1, 33.9, 31.6, 26.2, 26.0, 25.7, 21.2. ^{19}F NMR (376 MHz, CDCl_3) δ -63.2. HRMS m/z (ESI) calcd for $\text{C}_{22}\text{H}_{24}\text{F}_3\text{O}_2\text{S}$ (M-H) $^-$ 409.1454, found 409.1453.

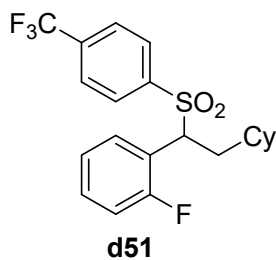
3-(2-Cyclohexyl-1-((4-(trifluoromethyl)phenyl)sulfonyl)ethyl)aniline (d50)



Compound **d50** was obtained as a colorless oil in 68% yield (alkyne used, 55.9 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.70 – 7.59 (m, 4H), 6.94 (t, $J = 7.8$ Hz, 1H), 6.59 (dd, $J = 8.0, 2.3$ Hz, 1H), 6.51 (s, 1H), 6.30 (d, $J = 7.6$ Hz, 1H), 4.06 (dd, $J = 11.2, 4.1$ Hz, 1H), 3.70 (brs, 2H), 2.22 – 2.02 (m, 2H), 1.72 – 1.48 (m, 5H), 1.20 – 0.93 (m, 5H), 0.93 – 0.80 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 146.6, 141.1, 134.9 (q, $J = 33.0$ Hz), 132.9, 129.6, 129.3, 125.5 (q, $J = 3.6$ Hz), 123.1 (q, $J = 273.0$ Hz), 120.3, 115.8, 115.6, 69.6, 34.2, 34.1, 34.0, 31.6, 26.2, 26.0, 25.7. ^{19}F NMR (376 MHz, CDCl_3) δ -63.1. HRMS m/z (ESI) calcd for $\text{C}_{21}\text{H}_{23}\text{F}_3\text{NO}_2\text{S}$ (M-H) $^-$ 410.1407, found 410.1406.

1-(2-Cyclohexyl-1-((4-(trifluoromethyl)phenyl)sulfonyl)ethyl)-2-fluorobenzene (d51)

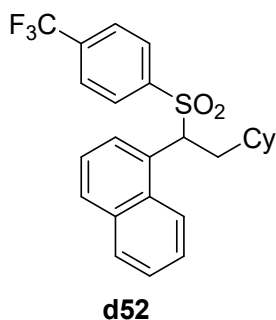
Compound **d51** was obtained as a colorless oil in 62% yield (alkyne used, 51.4 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.69 – 7.59 (m, 4H), 7.52 (t, $J = 7.1$ Hz, 1H), 7.33 – 7.24 (m, 1H), 7.19 (t, $J = 7.6$ Hz,



413.1202.

1H), 6.80 (t, $J = 8.8$ Hz, 1H), 4.70 (dd, $J = 11.4, 4.1$ Hz, 1H), 2.30 – 2.12 (m, 2H), 1.71 – 1.50 (m, 5H), 1.18 – 0.79 (m, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 161.0 (d, $J = 248.2$ Hz), 141.1, 135.1 (q, $J = 33.1$ Hz), 130.7 (d, $J = 8.6$ Hz), 129.7, 129.4, 125.6 (q, $J = 3.7$ Hz), 124.6 (d, $J = 3.6$ Hz), 123.1 (q, $J = 273.0$ Hz), 119.5 (d, $J = 13.3$ Hz), 115.2 (d, $J = 22.7$ Hz), 60.2, 34.5, 34.0, 33.4, 31.5, 26.2, 26.0, 25.7. ^{19}F NMR (376 MHz, CDCl_3) δ -63.2, -113.3. HRMS m/z (ESI) calcd for $\text{C}_{21}\text{H}_{21}\text{F}_4\text{O}_2\text{S}$ (M-H) $^-$ 413.1204, found

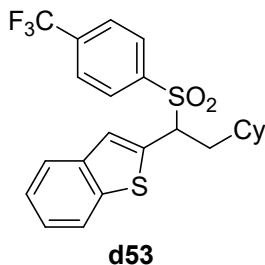
1-(2-Cyclohexyl-1-((4-(trifluoromethyl)phenyl)sulfonyl)ethyl)naphthalene (d52)



-63.4. HRMS m/z (ESI) calcd for $\text{C}_{25}\text{H}_{24}\text{F}_3\text{O}_2\text{S}$ (M-H) $^-$ 445.1454, found 445.1452.

Compound **d52** was obtained as a white solid in 47% yield (alkyne used, 41.8 mg) or 70% yield (alkene used, 62.3 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.82 (d, $J = 8.2$ Hz, 1H), 7.75 (d, $J = 8.1$ Hz, 1H), 7.67 (d, $J = 7.3$ Hz, 1H), 7.51 (t, $J = 7.8$ Hz, 2H), 7.43 (d, $J = 8.2$ Hz, 2H), 7.38 – 7.29 (m, 3H), 7.28 – 7.20 (m, 1H), 5.20 (dd, $J = 10.9, 4.3$ Hz, 1H), 2.49 – 2.31 (m, 2H), 1.68 – 1.47 (m, 5H), 1.24 – 0.82 (m, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 140.7, 134.7 (q, $J = 33.0$ Hz), 133.4, 132.3, 129.6, 129.5, 128.9, 127.8, 127.2, 126.6, 125.5, 125.2, 125.1 (q, $J = 3.7$ Hz), 122.9 (q, $J = 273.2$ Hz), 121.3, 62.7, 34.6, 34.5, 34.1, 32.1, 26.1, 25.9, 25.6. ^{19}F NMR (376 MHz, CDCl_3) δ

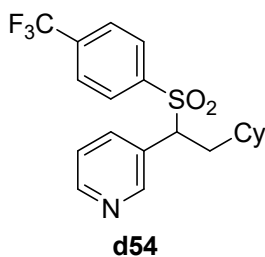
2-(1-((4-(Trifluoromethyl)phenyl)sulfonyl)-2-cyclohexylethyl)benzo[b]thiophene (d53)



25.9, 25.6. ^{19}F NMR (376 MHz, CDCl_3) δ -63.2. HRMS m/z (ESI) calcd for $\text{C}_{23}\text{H}_{22}\text{F}_3\text{O}_2\text{S}_2$ (M-H) $^-$ 451.1019, found 451.1017.

Compound **d53** was obtained as a white solid in 54% yield (alkene used, 48.7 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.76 (d, $J = 8.0$ Hz, 3H), 7.71 – 7.59 (m, 3H), 7.41 – 7.31 (m, 2H), 7.05 (s, 1H), 4.52 (dd, $J = 11.9, 3.2$ Hz, 1H), 2.27 (ddd, $J = 13.4, 10.1, 3.2$ Hz, 1H), 2.18 – 2.05 (m, 1H), 1.77 – 1.52 (m, 5H), 1.33 – 0.82 (m, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 140.4, 140.0, 138.7, 135.6 (q, $J = 32.9$ Hz), 135.1, 129.7, 126.3, 125.8 (q, $J = 3.7$ Hz), 125.0, 124.6, 123.8, 123.0 (q, $J = 273.2$ Hz), 122.3, 65.7, 35.7, 34.4, 34.0, 31.6, 26.1,

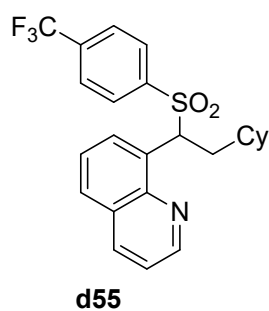
3-(1-((4-(Trifluoromethyl)phenyl)sulfonyl)-2-cyclohexylethyl)pyridine (d54)



25.6. ^{19}F NMR (376 MHz, CDCl_3) δ -63.2. HRMS m/z (ESI) calcd for $\text{C}_{20}\text{H}_{21}\text{F}_3\text{NO}_2\text{S}$ (M-H) $^-$ 396.1250, found 396.1248.

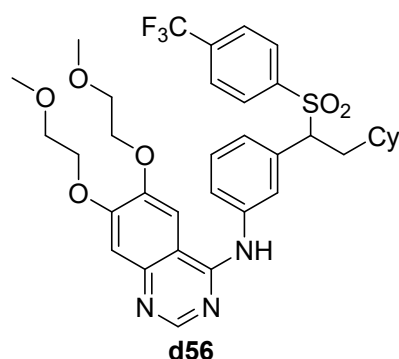
Compound **d54** was obtained as a white solid in 69% yield (alkyne used, 54.8 mg) or 58% yield (alkene used, 46.0 mg). ^1H NMR (400 MHz, CDCl_3) δ 8.57 (d, $J = 4.6$ Hz, 1H), 8.15 (s, 1H), 7.73 – 7.61 (m, 5H), 7.30 (dd, $J = 8.0, 4.8$ Hz, 1H), 4.21 (dd, $J = 11.6, 3.9$ Hz, 1H), 2.29 – 2.07 (m, 2H), 1.68 – 1.50 (m, 5H), 1.17 – 0.80 (m, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 151.0, 150.3, 140.5, 136.8, 135.5 (q, $J = 33.4$ Hz), 129.5, 128.1, 126.0 (q, $J = 3.7$ Hz), 123.6, 122.9 (q, $J = 273.2$ Hz), 66.8, 34.3, 34.0, 33.8, 31.4, 26.1, 25.9,

8-(1-((4-(Trifluoromethyl)phenyl)sulfonyl)-2-cyclohexylethyl)quinoline (d55)



Compound **d55** was obtained as a colorless oil in 74% yield (alkene used, 66.2 mg). ^1H NMR (400 MHz, CDCl_3) δ 8.51 (dd, $J = 4.1, 1.5$ Hz, 1H), 8.05 – 7.94 (m, 2H), 7.77 (dd, $J = 8.2, 1.3$ Hz, 1H), 7.62 (t, $J = 7.7$ Hz, 1H), 7.49 (d, $J = 8.1$ Hz, 2H), 7.29 – 7.23 (m, 2H), 7.21 (dd, $J = 8.3, 4.1$ Hz, 1H), 6.33 (dd, $J = 11.6, 4.0$ Hz, 1H), 2.52 – 2.31 (m, 2H), 1.77 – 1.45 (m, 5H), 1.20 – 0.98 (m, 4H), 0.97 – 0.80 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 149.5, 146.2, 141.6, 136.0, 134.2 (q, $J = 33.0$ Hz), 131.0, 129.8, 129.4, 128.7, 127.7, 126.2, 124.6 (q, $J = 3.7$ Hz), 123.0 (q, $J = 273.0$ Hz), 120.9, 60.0, 34.8, 34.1, 33.9, 31.9, 26.2, 26.0, 25.7. ^{19}F NMR (376 MHz, CDCl_3) δ -63.4. HRMS m/z (ESI) calcd for $\text{C}_{24}\text{H}_{23}\text{F}_3\text{NO}_2\text{S}$ (M-H) $^-$ 448.1553, found 448.1544.

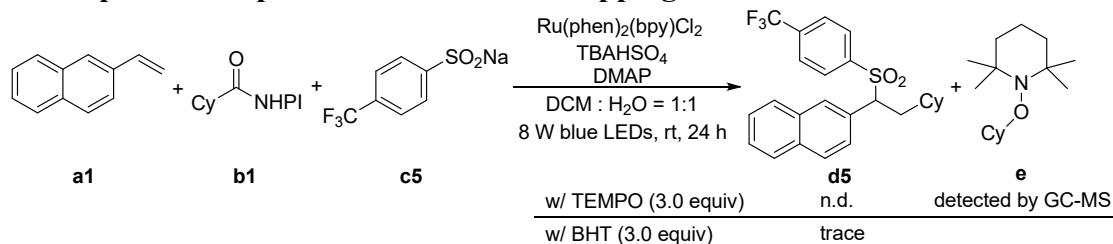
N-(3-(1-((4-(Trifluoromethyl)phenyl)sulfonyl)-2-cyclohexylethyl)phenyl)-6,7-bis(2-methoxyethoxy)quinazolin-4-amine (d56)



Compound **d56** was obtained as a yellow solid in 49% yield (alkyne used, 67.4 mg). ^1H NMR (400 MHz, CDCl_3) δ 8.58 (s, 1H), 7.94 (d, $J = 8.3$ Hz, 1H), 7.74 – 7.61 (m, 4H), 7.51 (s, 1H), 7.34 – 7.14 (m, 4H), 6.66 (d, $J = 7.5$ Hz, 1H), 4.38 – 4.16 (m, 5H), 3.93 – 3.74 (m, 4H), 3.51 – 3.39 (m, 6H), 2.20 – 2.03 (m, 2H), 1.69 – 1.50 (m, 4H), 1.30 – 0.91 (m, 5H), 0.91 – 0.79 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 156.0, 154.5, 153.2, 148.9, 140.9, 139.2, 135.1 (q, $J = 33.1$ Hz), 132.4, 129.6, 129.0, 125.7 (q, $J = 3.4$ Hz), 125.5, 123.0 (q, $J = 273.0$ Hz), 122.24, 122.20, 109.1, 108.5, 102.1, 70.8, 70.4, 69.3, 69.1, 68.3, 59.3, 59.2, 34.3, 34.1, 34.1, 31.5, 26.1, 25.9, 25.6. ^{19}F NMR (376 MHz, CDCl_3) δ -63.1. HRMS m/z (ESI) calcd for $\text{C}_{35}\text{H}_{39}\text{F}_3\text{N}_3\text{O}_6\text{S}$ (M-H) $^-$ 686.2517, found 686.2512.

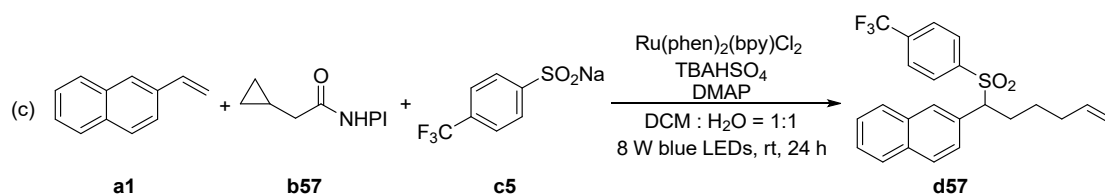
6. Mechanistic studies

6.1. Experimental procedure for radical trapping reaction



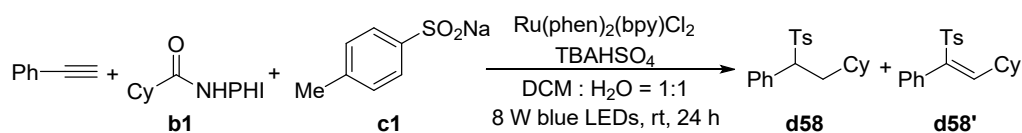
A flame dried 10 mL Schlenk tube was charged with $\text{Ru}(\text{phen})_2(\text{bpy})\text{Cl}_2$ (0.004 mmol, 2.6 mg), **a1** (0.4 mmol, 61.6 mg), **b1** (0.2 mmol, 54.6 mg), **c5** (0.6 mmol, 139.2 mg), TBAHSO₄ (0.08 mmol, 27.2 mg), and DMAP (0.16 mmol, 19.5 mg). TEMPO (0.6 mmol, 93.6 mg) or BHT (0.6 mmol, 132 mg) was then added to the mixture. The tube was vacuumed and inflated with nitrogen gas three times. After that, DCM (2.0 mL) and H₂O (2.0 mL) were added through syringe under nitrogen atmosphere. The tube was screwed and the mixture was stirred at room temperature under blue light irradiation with a cooling fan. After 24 h, the mixture was diluted with DCM (5.0 mL) and the reaction results was detected by GC-MS.

6.2. Experimental procedure for radical clock reaction



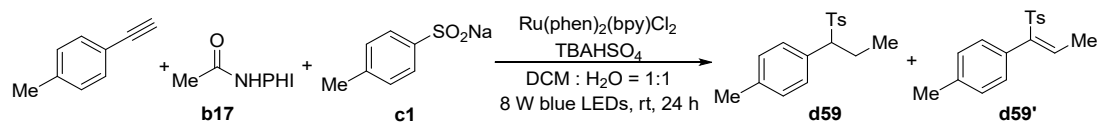
A flame dried 10 mL Schlenk tube was charged with $\text{Ru}(\text{phen})_2(\text{bpy})\text{Cl}_2$ (0.004 mmol, 2.6 mg), **a1** (0.4 mmol, 61.6 mg), **b57** (0.2 mmol, 49.0 mg), **c5** (0.6 mmol, 139.2 mg), TBAHSO₄ (0.08 mmol, 27.2 mg), and DMAP (0.16 mmol, 19.5 mg). The tube was vacuumed and inflated with nitrogen gas three times. After that, DCM (2.0 mL) and H₂O (2.0 mL) were added through syringe under nitrogen atmosphere. The tube was screwed and the mixture was stirred at room temperature under blue light irradiation with a cooling fan. After 24 h, the mixture was diluted with DCM (5.0 mL) and the aqueous phase was separated and discarded. The organic phase was vacuumed to remove the solvent and the crude mixture was purified through silica gel column with ethyl acetate/petroleum ether as the eluent. Compound **d57** was obtained as a colorless oil in 65% yield (54.2 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, $J = 7.5$ Hz, 1H), 7.75 (d, $J = 8.5$ Hz, 1H), 7.69 (d, $J = 7.4$ Hz, 1H), 7.65 – 7.54 (m, 4H), 7.54 – 7.45 (m, 3H), 7.24 (d, $J = 8.5$ Hz, 1H), 5.73 – 5.60 (m, 1H), 5.00 – 4.89 (m, 2H), 4.22 (dd, $J = 11.6, 3.6$ Hz, 1H), 2.57 – 2.45 (m, 1H), 2.35 – 2.23 (m, 1H), 2.14 – 1.97 (m, $J = 7.2$ Hz, 2H), 1.41 – 1.26 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 140.9, 137.4, 135.1 (q, $J = 33.0$ Hz), 133.3, 132.9, 129.8, 129.6, 129.0, 128.5, 127.9, 127.6, 126.9, 126.6, 126.3, 125.7 (q, $J = 3.7$ Hz), 123.0 (q, $J = 273.0$ Hz), 115.5, 71.7, 33.1, 26.6, 26.0. ¹⁹F NMR (376 MHz, CDCl₃) δ -63.2. HRMS m/z (ESI) calcd for C₂₃H₂₀F₃O₂S (M-H)⁻ 417.1142, found 417.1140.

6.3. Experimental procedure for alkyne alkylsulfonation with sodium 4-methylbenzenesulfinate



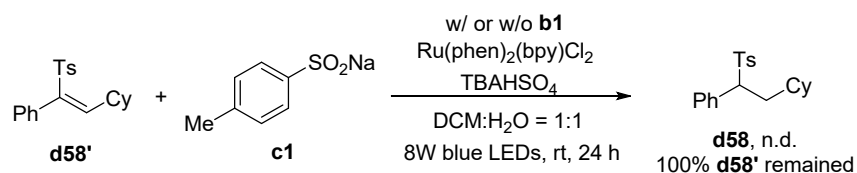
A flame dried 10 mL Schlenk tube was charged with $\text{Ru}(\text{phen})_2(\text{bpy})\text{Cl}_2$ (0.004 mmol, 2.6 mg), **b1** (0.2 mmol, 54.6 mg), **c1** (0.6 mmol, 106.8 mg), and TBAHSO₄ (0.08 mmol, 27.2 mg). The tube was vacuumed and inflated with nitrogen gas three times. After that, DCM (2.0 mL), H₂O (2.0 mL) and phenylacetylene (0.4 mmol, 40.8 mg) were added through syringe under nitrogen atmosphere. The tube was screwed and the mixture was stirred at room temperature under blue light irradiation with a cooling fan. After 24 h, the mixture was diluted with DCM (5.0 mL) and the aqueous phase was separated and discarded. GC-MS results showed that the ratio of product **d58** and **d58'** was 40:60. The organic phase was vacuumed to remove the solvent and the crude mixture was purified through silica gel column with ethyl acetate/petroleum ether as the eluent. Compound **d58** were obtained as a white solid in 24% yield (16.4 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.35 (d, $J = 8.2$ Hz, 2H), 7.31 – 7.19 (m, 3H), 7.15 (d, $J = 8.0$ Hz, 2H), 7.08 (d, $J = 7.0$ Hz, 2H), 4.13 (dd, $J = 10.8, 4.7$ Hz, 1H), 2.38 (s, 3H), 2.23 – 2.05 (m, 2H), 1.70 – 1.49 (m, 5H), 1.14 – 0.76 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 144.2, 134.4, 132.5, 129.9, 129.1, 129.0, 128.5, 128.3, 69.3, 34.31, 34.29, 34.1, 31.5, 26.2, 26.0, 25.7, 21.6. Compound **d58'** were obtained as a white solid in 38% yield (25.8 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.36 (d, $J = 8.2$ Hz, 2H), 7.29 –

7.22 (m, 1H), 7.22 – 7.15 (m, 2H), 7.10 (d, $J = 8.1$ Hz, 2H), 6.96 – 6.85 (m, 3H), 2.31 (s, 3H), 1.93 – 1.80 (m, 1H), 1.65 – 1.55 (m, 2H), 1.49 (brs, 2H), 1.24 – 0.93 (m, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 146.8, 143.8, 141.1, 136.1, 130.9, 130.6, 129.3, 128.7, 128.4, 128.1, 38.0, 31.9, 25.5, 25.0, 21.6.

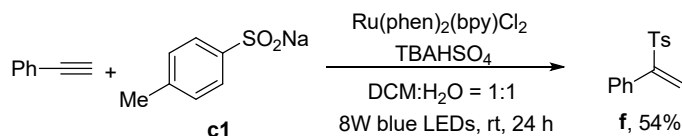


A flame dried 10 mL Schlenk tube was charged with $\text{Ru}(\text{phen})_2(\text{bpy})\text{Cl}_2$ (0.004 mmol, 2.6 mg), **b17** (0.2 mmol, 41.0 mg), **c1** (0.6 mmol, 106.8 mg), and TBAHSO₄ (0.08 mmol, 27.2 mg). The tube was vacuumed and inflated with nitrogen gas three times. After that, DCM (2.0 mL), H₂O (2.0 mL) and *p*-tolylacetylene (0.4 mmol, 46.4 mg) were added through syringe under nitrogen atmosphere. The tube was screwed and the mixture was stirred at room temperature under blue light irradiation with a cooling fan. After 24 h, the mixture was diluted with DCM (5.0 mL) and the aqueous phase was separated and discarded. GC-MS results showed that **d59'** was the major product and trace amount of **d59** was detected. The organic phase was vacuumed to remove the solvent and the crude mixture was purified through silica gel column with ethyl acetate/petroleum ether as the eluent. Compound **d59'** were obtained as a colorless oil in 62% yield (35.4 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.46 (d, $J = 8.1$ Hz, 2H), 7.23 (d, $J = 7.1$ Hz, 1H), 7.18 (d, $J = 8.0$ Hz, 2H), 7.08 (d, $J = 7.8$ Hz, 2H), 6.88 (d, $J = 8.0$ Hz, 2H), 2.38 (s, 3H), 2.33 (s, 3H), 1.70 (d, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.8, 143.7, 138.7, 137.5, 136.2, 130.4, 129.3, 129.0, 128.4, 127.4, 21.6, 21.3, 14.9. HRMS m/z (ESI) calcd for $\text{C}_{17}\text{H}_{17}\text{O}_2\text{S}$ (M-H)⁻ 287.1100, found 287.1095.

6.4. Control experiments in alkyne alkylsulfonylation

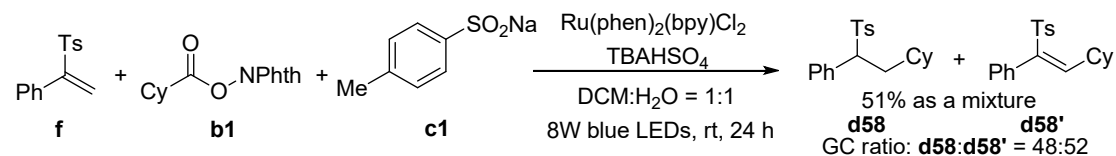


d58' was tested to verify whether it was the intermediate in alkyne alkylsulfonylation reaction. A flame dried 10 mL Schlenk tube was charged with $\text{Ru}(\text{phen})_2(\text{bpy})\text{Cl}_2$ (0.002 mmol, 1.3 mg), **d58'** (0.1 mmol, 34.0 mg), **c1** (0.3 mmol, 53.4 mg) and TBAHSO₄ (0.04 mmol, 13.6 mg). Compound **b1** (0.1 mmol, 27.3 mg) could be added or not. The tube was vacuumed and inflated with nitrogen gas three times. After that, DCM (1.0 mL) and H₂O (1.0 mL) were added through syringe under nitrogen atmosphere. The tube was screwed and the mixture was stirred at room temperature under blue light irradiation with a cooling fan. After 24 h, the mixture was diluted with DCM (5.0 mL) and the aqueous phase was separated and discarded. GC-MS results showed that **d58** was not detected and **d58'** was remained unreacted. This result indicated that **d58'** was hardly the reaction intermediate.

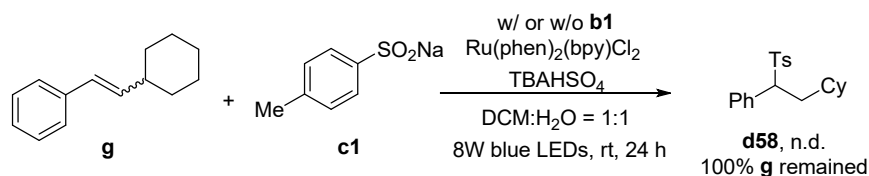


Phenylacetylene was direct reacted with **c1** under standard conditions. A flame dried 10 mL Schlenk tube was charged with $\text{Ru}(\text{phen})_2(\text{bpy})\text{Cl}_2$ (0.004 mmol, 2.6 mg), **c1** (0.6 mmol, 106.8 mg) and

TBAHSO₄ (0.08 mmol, 27.2 mg). The tube was vacuumed and inflated with nitrogen gas three times. After that, DCM (2.0 mL), H₂O (2.0 mL) and phenylacetylene (0.2 mmol, 20.4 mg) were added through syringe under nitrogen atmosphere. The tube was screwed and the mixture was stirred at room temperature under blue light irradiation with a cooling fan. After 24 h, the mixture was diluted with DCM (5.0 mL) and the aqueous phase was separated and discarded. The organic phase was vacuumed to remove the solvent and the crude mixture was purified through silica gel column with ethyl acetate/petroleum ether as the eluent. Compound **f** were obtained as a colorless oil in 54% yield (27.8 mg). The spectroscopic data was consistent with the reported literature.¹⁰ ¹H NMR (400 MHz, CDCl₃) δ 7.56 (d, *J* = 8.2 Hz, 2H), 7.37 – 7.30 (m, 3H), 7.30 – 7.23 (m, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.61 (s, 1H), 5.93 (s, 1H), 2.37 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 151.0, 144.3, 135.6, 132.5, 129.5, 129.2, 129.1, 128.4, 128.2, 125.5, 21.6.

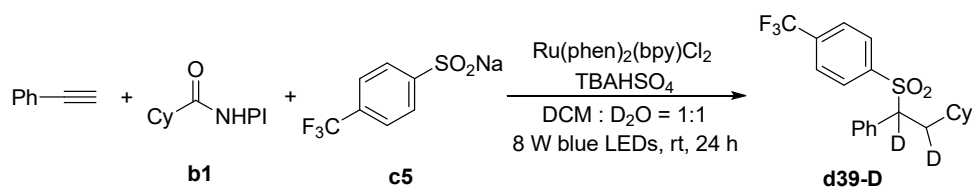


Then we tested whether compound **f** was the intermediate in the alkyne alkylsulfonylation reaction. A flame dried 10 mL Schlenk tube was charged with Ru(phen)₂(bpy)Cl₂ (0.002 mmol, 1.3 mg), **b1** (0.1 mmol, 106.8 mg), **c1** (0.3 mmol, 53.4 mg) and TBAHSO₄ (0.04 mmol, 13.6 mg). The tube was vacuumed and inflated with nitrogen gas three times. After that, DCM (1.0 mL) and H₂O (1.0 mL) were added through syringe under nitrogen atmosphere. The tube was screwed and the mixture was stirred at room temperature under blue light irradiation with a cooling fan. After 24 h, the mixture was diluted with DCM (5.0 mL) and the aqueous phase was separated and discarded. The organic phase was vacuumed to remove the solvent and the crude mixture was purified through silica gel column with ethyl acetate/petroleum ether as the eluent. **d58** and **d58'** were isolated as a mixture in totally 51% yield (17.4 mg). The ratio (**d58:d58'** = 48:52) was tested through GC-MS. This result indicated that compound **f** was probably the actual

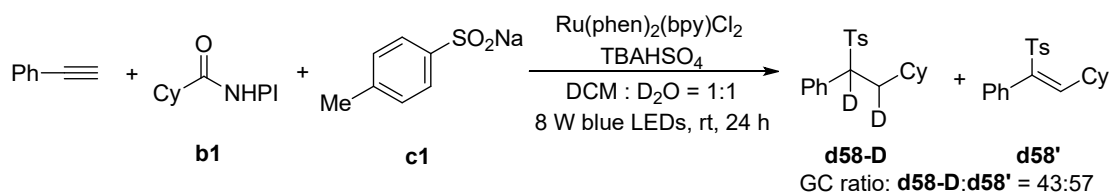


Later, we also tested whether compound **g**¹¹ could be the reaction intermediate. A flame dried 10 mL Schlenk tube was charged with Ru(phen)₂(bpy)Cl₂ (0.002 mmol, 1.3 mg), **c1** (0.3 mmol, 53.4 mg) and TBAHSO₄ (0.04 mmol, 13.6 mg). Compound **b1** (0.1 mmol, 27.3 mg) could be added or not. The tube was vacuumed and inflated with nitrogen gas three times. After that, DCM (1.0 mL), H₂O (1.0 mL) and **g** (0.1 mmol, 18.6 mg) were added through syringe under nitrogen atmosphere. The tube was screwed and the mixture was stirred at room temperature under blue light irradiation with a cooling fan. After 24 h, the mixture was diluted with DCM (5.0 mL) and the aqueous phase was separated and discarded. GC-MS results showed that **d58** was not detected and **g** was remained unreacted. Compound **g** was not the reaction intermediate either.

6.5. Deuterium experiment of alkyne substrate



A flame dried 10 mL Schlenk tube was charged with $\text{Ru(phen)}_2\text{(bpy)Cl}_2$ (0.004 mmol, 2.6 mg), **b1** (0.2 mmol, 54.6 mg), **c5** (0.6 mmol, 139.2 mg), and TBAHSO₄ (0.08 mmol, 27.2 mg). The tube was vacuumed and inflated with nitrogen gas three times. After that, DCM (2.0 mL), D₂O (2.0 mL) and phenylacetylene (0.4 mmol, 40.8 mg) were added through syringe under nitrogen atmosphere. The tube was screwed and the mixture was stirred at room temperature under blue light irradiation with a cooling fan. After 24 h, the mixture was diluted with DCM (5.0 mL) and the aqueous phase was separated and discarded. The organic phase was vacuumed to remove the solvent and the crude mixture was purified through silica gel column with ethyl acetate/petroleum ether as the eluent. Compound **d39-D** was obtained as a colorless oil and was absolutely deuterated in 64% yield (51.4 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.68 – 7.55 (m, 4H), 7.33 – 7.20 (m, 3H), 7.07 (d, *J* = 7.1 Hz, 2H), 2.17 (dd, *J* = 18.6, 6.8 Hz, 1H), 1.70 – 1.51 (m, 5H), 1.18 – 0.80 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 141.0, 134.9 (q, *J* = 33.0 Hz), 131.8, 129.8, 129.5, 128.9, 128.6, 125.5 (q, *J* = 3.7 Hz), 123.1 (q, *J* = 273.1 Hz), 69.1 (dd, *J* = 20.9, 20.9 Hz), 34.2, 34.0, 33.5 (dd, *J* = 19.6, 19.6 Hz), 31.5, 26.2, 25.9, 25.6. ¹⁹F NMR (376 MHz, CDCl₃) δ -63.2. HRMS *m/z* (ESI) calcd for C₂₁H₂₀D₂F₃O₂S (M-H)⁻ 397.1424 and C₂₁H₂₁DF₃O₂S (M-D)⁻ 396.1361, found 397.1424 and 396.1359.



Deuterium experiment using **c1** as the sulfonylation reagent was also carried out. A flame dried 10 mL Schlenk tube was charged with $\text{Ru(phen)}_2\text{(bpy)Cl}_2$ (0.004 mmol, 2.6 mg), **b1** (0.2 mmol, 54.6 mg), **c1** (0.6 mmol, 106.8 mg), and TBAHSO₄ (0.08 mmol, 27.2 mg). The tube was vacuumed and inflated with nitrogen gas three times. After that, DCM (2.0 mL), D₂O (2.0 mL) and phenylacetylene (0.4 mmol, 40.8 mg) were added through syringe under nitrogen atmosphere. The tube was screwed and the mixture was stirred at room temperature under blue light irradiation with a cooling fan. After 24 h, the mixture was diluted with DCM (5.0 mL) and the aqueous phase was separated and discarded. GC-MS results showed that, just like the above experiment with **c5** as the sulfonylation reagent, **d58-D** was generated under the reaction conditions. The ratio of **d58-D** and **d58'** was 43:57.

The above experiments indicated that water was the hydrogen source in alkyne alkylsulfonation.

6.6. UV-visible absorption experiment

UV-visible spectroscopy of photocatalyst solution was recorded on a AOE UV-1800PC UV-visible spectrophotometer. Photocatalyst $\text{Ru(phen)}_2\text{(bpy)Cl}_2$ (8.2 mg) was dissolved in DMF in a 25 mL volumetric flask to set the concentration to be 0.5 mM. The resulting 1.0 mM solution of $\text{Ru(phen)}_2\text{(bpy)Cl}_2$ (20 μL) was added to cuvette. Then the solution was diluted to a volume of 2.0 mL by adding further solvent (DMF) to prepare a 5.0 μM solution of $\text{Ru(phen)}_2\text{(bpy)Cl}_2$. The resulting mixture was sparged with nitrogen for 3 minutes and then irradiated from 200 nm to 800 nm. The UV-

visible spectroscopy indicated that the maximum absorption wavelength of reaction solution was found to be 435 nm. The absorption was collected and the result was listed in Figure S3.

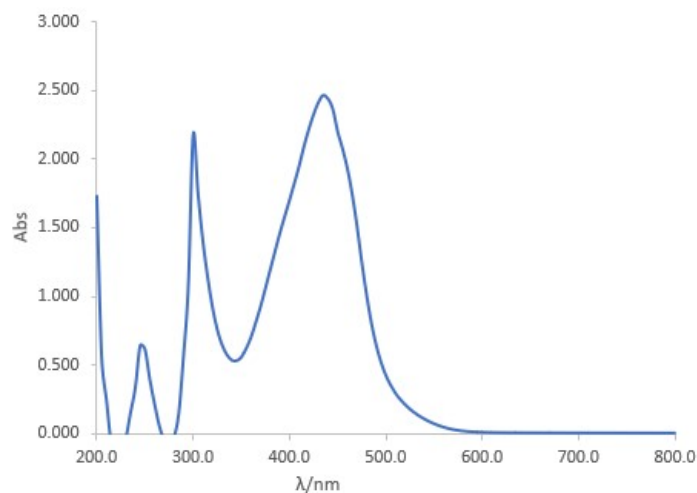


Figure S3. UV-Vis spectra of Ru(phen)₂(bpy)Cl₂.

6.7. Stern-Volmer fluorescence quenching experiments

The fluorescence emission intensities were recorded on a SHIMADZU RF-6000 spectro fluorophotometer. The excitation wavelength was fixed at 460 nm.

Formulation solution: Photocatalyst Ru(phen)₂(bpy)Cl₂ (1.6 mg) was dissolved in DMF in a 25 mL volumetric flask to set the concentration to be 0.1 mM. 2-Vinylnaphthalene **a1** (192.5 mg) was dissolved in DMF in a 25 mL volumetric flask to set the concentration to be 0.05 M. 1,3-Dioxoisindolin-2-yl cyclohexanecarboxylate **b1** (341.3 mg) was dissolved in DMF in a 25 mL volumetric flask to set the concentration to be 0.05 M. Sodium 4-trifluoromethylbenzenesulfinate **c5** (290.0 mg) was dissolved in DMF in a 25 mL volumetric flask to set the concentration to be 0.05 M. TBAHSO₄ (425.0 mg) was dissolved in DMF in a 25 mL volumetric flask to set the concentration to be 0.05 M. DMAP (152.5 mg) was dissolved in DMF in a 25 mL volumetric flask to set the concentration to be 0.05 M.

Experimental procedure: The resulting 0.1 mM solution of Ru(phen)₂(bpy)Cl₂ (60 μL) was added to cuvette. 0 μL, 30 μL, 60 μL, 90 μL, 120 μL, and 150 μL solution of 2-vinylnaphthalene (0.05 M) were added to the cuvette in six separate measurements. Then the solution was diluted to a volume of 3.0 mL by adding further solvent (DMF) to prepare a 2.0 μM solution of Ru(phen)₂(bpy)Cl₂ as well as solution of 2-vinylnaphthalene in different concentrations (0 M, 0.5 mM, 1.0 mM, 1.5 mM, 2.0 mM and 2.5 mM). The resulting mixture was sparged with nitrogen for 3 minutes and then irradiated at 460 nm. Fluorescence emission spectra were recorded (3 trials per sample). Follow this method and the Stern-Volmer relationships of **b1**, **c5**, TBAHSO₄ and DMAP with Ru(phen)₂(bpy)Cl₂ were recorded in turn.

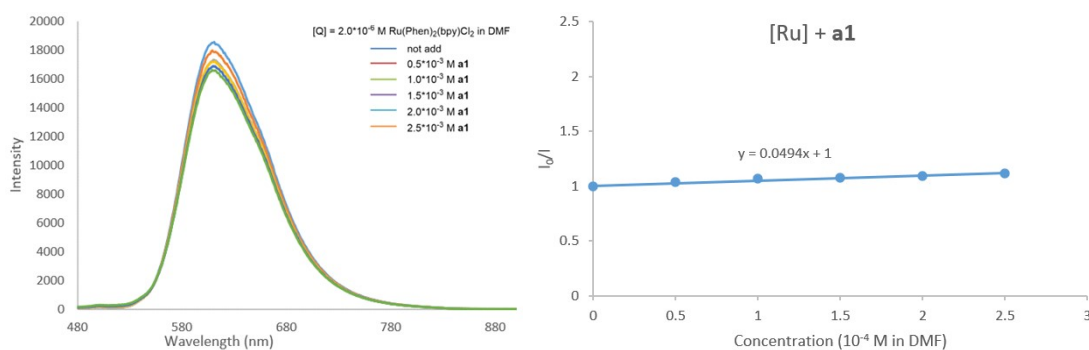


Figure S4. Ru(phen)₂(bpy)Cl₂ quenched by 2-vinylnaphthalene (**a1**) in DMF. Linear quenching is not observed.

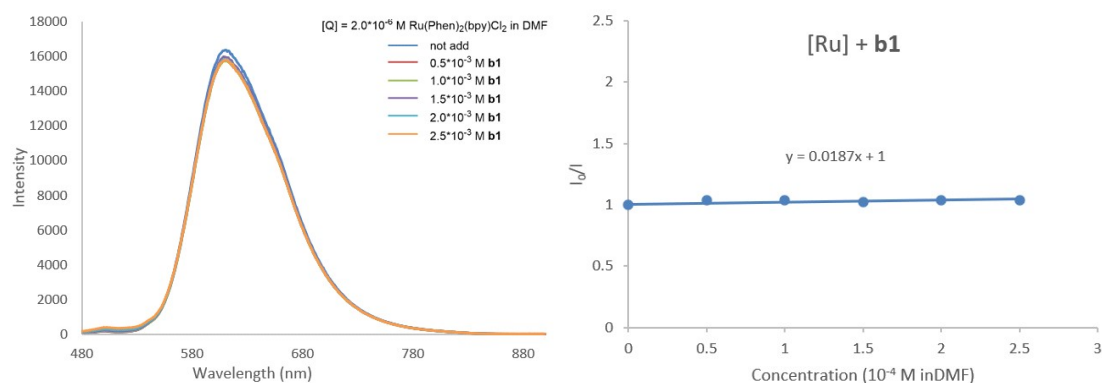


Figure S5. Ru(phen)₂(bpy)Cl₂ quenched by 1,3-dioxisoindolin-2-yl cyclohexanecarboxylate (**b1**) in DMF. Linear quenching is not observed.

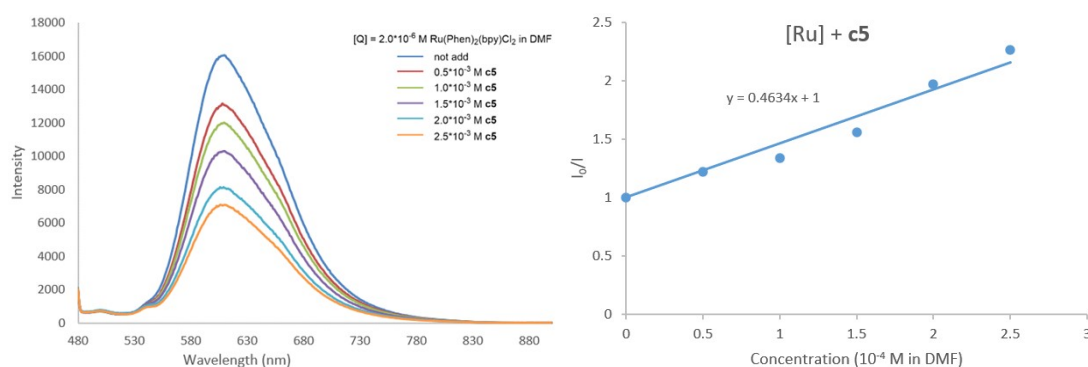


Figure S6. Ru(phen)₂(bpy)Cl₂ quenched by sodium 4-trifluoromethylbenzenesulfonate (**c5**) in DMF.

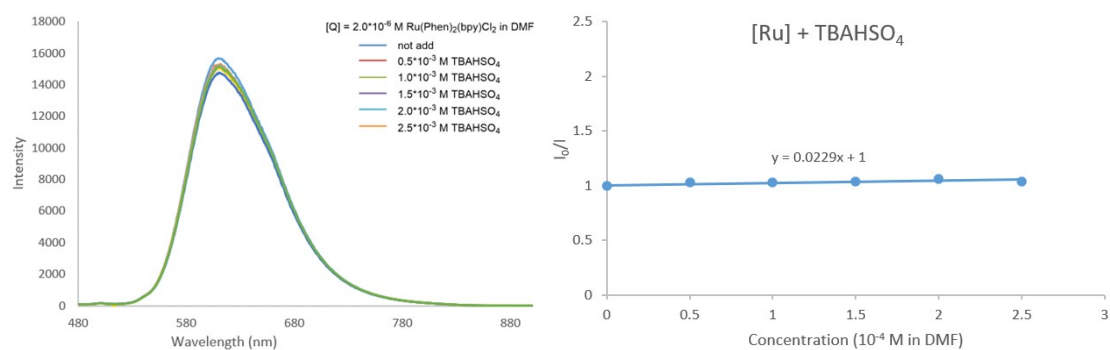


Figure S7. Ru(phen)₂(bpy)Cl₂ quenched by TBAHSO₄ in DMF. Linear quenching is not observed.

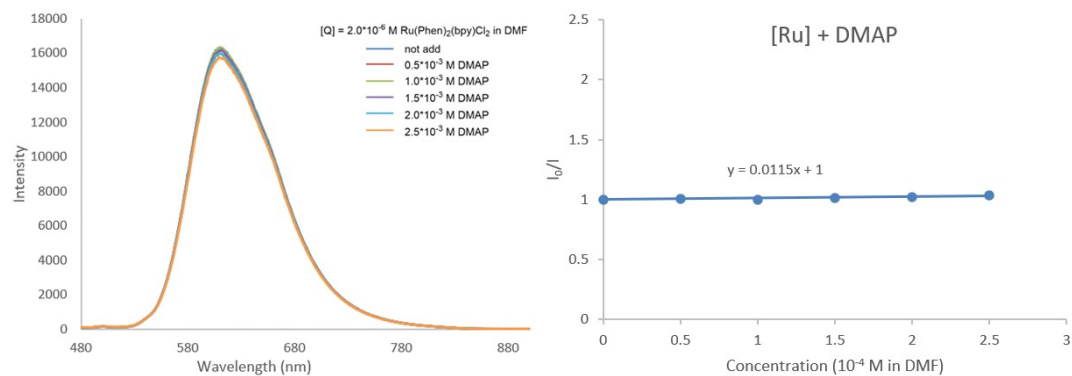


Figure S8. Ru(phen)₂(bpy)Cl₂ quenched by DMAP in DMF. Linear quenching is not observed.

6.8. Cyclic voltammetry measurements

Cyclic voltammograms were taken on a CHI660D electrochemical analyzer/workstation (Shanghai S13 Chen Hua Instrument Co., Ltd) in DMF at room temperature using a glass carbon working electrode, a platinum auxiliary electrode and 0.1 M NBu₄BF₄ as supporting electrolyte. All potentials are referenced against the SCE (saturated calomel electrode). The solution was prepared in DMF and degassed with nitrogen bubbling for 3 min prior to voltammetric studies. The scan rate was 50 mV/s.

6.8.1 Cyclic voltammetry measurement of Ru(phen)₂(bpy)Cl₂

The concentration of photocatalyst was 0.5 mM (in DMF). The scan direction was positive and sensitivity was 1*10⁻⁵.

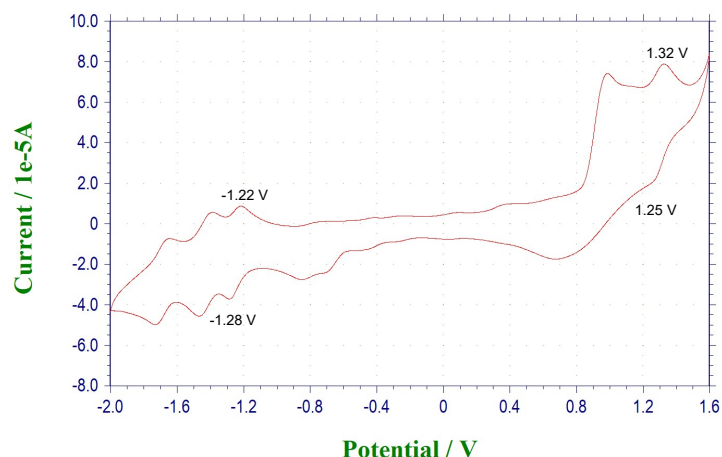


Figure S9. Cyclic Voltammogram of Ru(phen)₂(bpy)Cl₂. $E_{1/2}$ (Ru^{III}/Ru^{II}) = (1.32 + 1.25)/2 = 1.29 V (vs SCE). $E_{1/2}$ (Ru^{II}/Ru^I) = (-1.22-1.28)/2 = -1.25 V (vs SCE).

6.8.2 Cyclic voltammetry measurement of **b1**

The concentration of **b1** was 10.0 mM (in DMF). The scan direction was positive and sensitivity was 1*10⁻⁵.

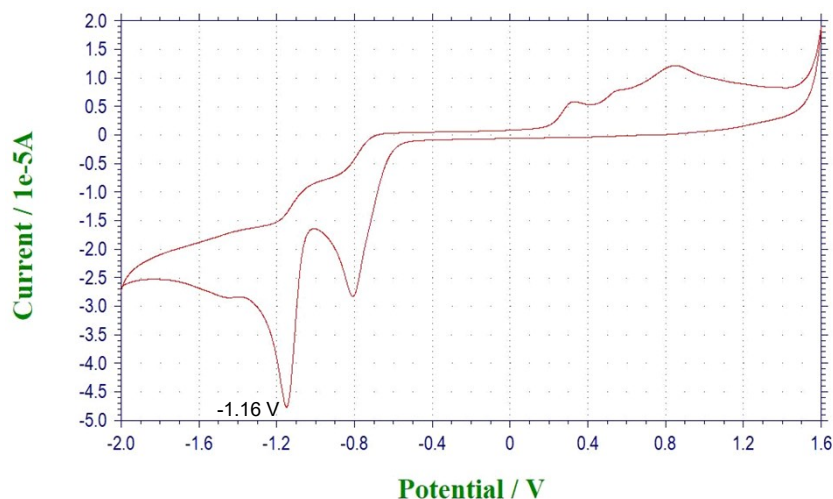


Figure S10. Cyclic Voltammogram of **b1**. E_p = -1.16 V (vs SCE).

6.8.3 Cyclic voltammetry measurement of **c5**

The concentration of **c5** was 10.0 mM (in DMF). The scan direction was positive and sensitivity was 1*10⁻⁵.

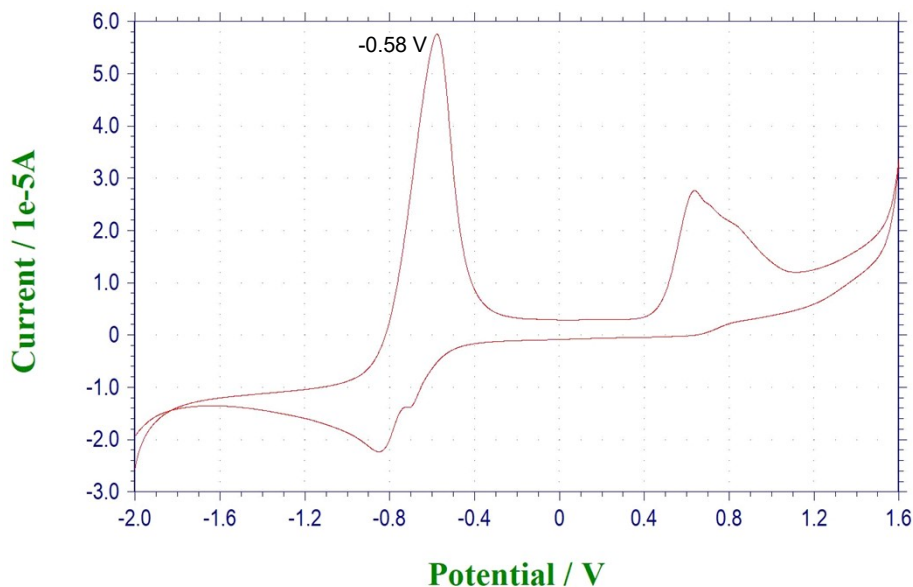


Figure S11. Cyclic Voltammogram of **c5**. $E_p = -0.58$ V (vs SCE).

According to the UV-visible spectra and the emission spectra of $\text{Ru}(\text{phen})_2(\text{bpy})\text{Cl}_2$, the maximum absorption was at 435 nm, the maximum emission wavelength is 610 nm. The triplet energy E_T is 2.44 eV (calculated from the intersection of emission wavelength and excitation wavelength), and the $E_{1/2}(\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}) = 1.29$ V (vs SCE). $E_{1/2}(\text{Ru}^{\text{II}}/\text{Ru}^{\text{I}}) = 0.82$ V (vs SCE). Excited state oxidation and reduction potentials were calculated by the following approximating formulas:

$$E_{1/2}(\text{M}^*/\text{M}^-) = E_{1/2}(\text{M}/\text{M}^-) + E_T \text{ and } E_{1/2}(\text{PC}^+/\text{PC}^*) = E_{1/2}(\text{PC}^+/\text{PC}) - E_T$$

Then:

[Ru]	$E_{1/2}(\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}*})$ [V (vs SCE)]	$E_{1/2}(\text{Ru}^{\text{II}*}/\text{Ru}^{\text{I}})$ [V (vs SCE)]	$E_{1/2}(\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}})$ [V (vs SCE)]	$E_{1/2}(\text{Ru}^{\text{II}}/\text{Ru}^{\text{I}})$ [V (vs SCE)]	E_T
	-1.15	+1.19	+1.29	-1.25	2.44

For **b1**. $E_p^{\text{red}} = -1.16$ V (vs SCE), for **c5**. $E_p^{\text{ox}} = -0.58$ V (vs SCE).

6.9. Light on/off experiments

The reaction between **a1**, **b1** and **c5** was conducted under the standard conditions on a 0.2 mmol scale. The mixture was subjected to sequential periods of stirring under visible light irradiation (8 W blue LEDs) followed by stirring in the absence of light. At each time point, one reaction system was suspended, which was then purified with chromatography column on silica gel (EtOAc: petroleum ether = 1:10) to give the corresponding products **d1**. The yield of **d1** was measured by weight of the product.

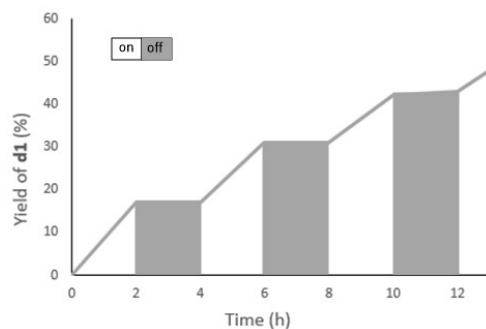


Figure S12. Blue Light Irradiation on/off experiment

6.10. Calculation of apparent quantum efficiency (A. Q. E)

$$E_{\text{photon}} = \frac{hc}{\lambda_{\text{inc}} (460\text{nm})} = \frac{6.63 \times 10^{-34} \text{ J}\cdot\text{s} \times 3 \times 10^8 \text{ m}\cdot\text{s}^{-1}}{460 \times 10^{-9} \text{ m}} = 4.37 \times 10^{-19} \text{ J}$$

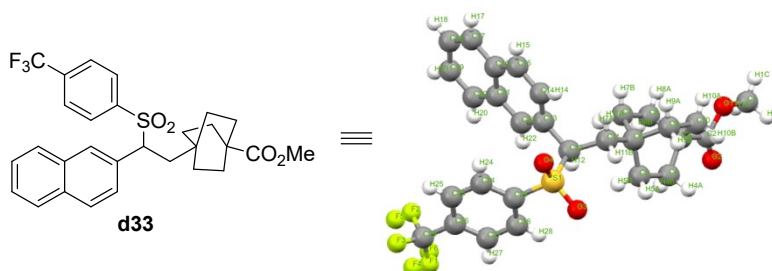
$$E_{\text{total}} = PSt = 1.97 \times 10^{-3} \text{ W}\cdot\text{cm}^{-2} \times 11.93 \text{ cm}^2 \times 24 \times 3600 \text{ s} = 1.86 \times 10^3 \text{ J}$$

$$\text{Number of incident photons} = \frac{E_{\text{total}}}{E_{\text{photon}}} = \frac{1.86 \times 10^3 \text{ J}}{4.37 \times 10^{-19} \text{ J}} = 4.26 \times 10^{21} = 7.08 \text{ mmol}$$

$$\text{A.Q.Y (\%)} = \frac{\text{Number of product}}{\text{Number of incident photons}} = \frac{0.132 \text{ mmol}}{7.08 \text{ mmol}} = 1.86\% < 1$$

Where h (J·s) is Planck's constant, c (m·s⁻¹) is the speed of light and λ_{inc} (m) is the wavelength of the incident light. P (W·cm⁻²) is the power density of the incident light, S (cm²) is the irradiation area and t (s) is the photoreaction time.

7. Crystallographic data



S(1)-O(3)	1.436(2)	C(7)-C(6)-C(9)	107.8(3)
S(1)-O(4)	1.436(3)	C(5)-C(6)-C(7)	108.7(3)
S(1)-C(23)	1.772(3)	C(5)-C(6)-C(9)	107.0(3)
S(1)-C(12)	1.803(3)	C(28)-C(23)-S(1)	118.2(2)
O(1)-C(2)	1.326(4)	C(28)-C(23)-C(24)	121.1(3)
O(1)-C(1)	1.442(4)	C(24)-C(23)-S(1)	120.8(3)
O(2)-C(2)	1.206(4)	C(13)-C(12)-S(1)	110.4(2)
C(13)-C(12)	1.515(4)	C(13)-C(12)-C(11)	116.5(3)
C(13)-C(14)	1.415(4)	C(11)-C(12)-S(1)	108.4(2)
C(13)-C(22)	1.365(5)	C(22)-C(21)-C(16)	118.7(3)
C(6)-C(11)	1.528(4)	C(20)-C(21)-C(22)	122.2(3)
C(6)-C(7)	1.534(5)	C(20)-C(21)-C(16)	119.1(3)
C(6)-C(9)	1.540(4)	C(15)-C(14)-C(13)	120.5(3)
C(6)-C(5)	1.529(4)	C(6)-C(11)-C(12)	114.4(3)
C(23)-C(28)	1.378(5)	C(27)-C(28)-C(23)	119.5(3)
C(23)-C(24)	1.395(4)	C(2)-C(3)-C(8)	108.5(3)
C(12)-C(11)	1.543(4)	C(2)-C(3)-C(10)	112.5(3)
C(21)-C(22)	1.419(5)	C(2)-C(3)-C(4)	110.7(3)
C(21)-C(16)	1.421(5)	C(10)-C(3)-C(8)	108.2(3)
C(21)-C(20)	1.410(5)	C(4)-C(3)-C(8)	108.5(3)
C(14)-C(15)	1.373(5)	C(4)-C(3)-C(10)	108.3(3)

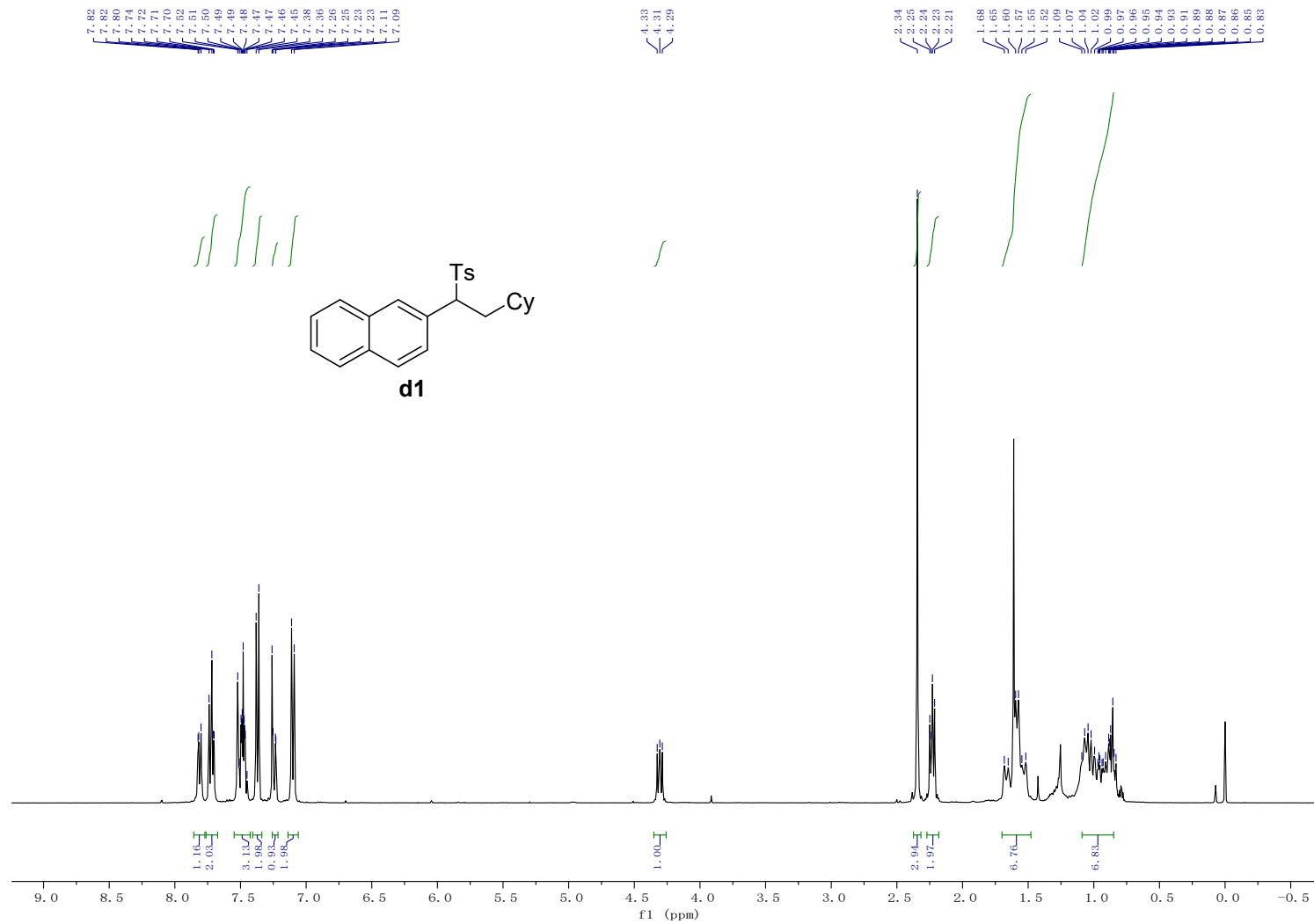
C(28)-C(27)	1.375(5)	O(1)-C(2)-C(3)	112.4(3)
C(3)-C(2)	1.513(5)	O(2)-C(2)-O(1)	122.1(3)
C(3)-C(8)	1.528(5)	O(2)-C(2)-C(3)	125.5(3)
C(3)-C(10)	1.526(5)	C(13)-C(22)-C(21)	121.7(3)
C(3)-C(4)	1.523(5)	C(25)-C(26)-C(29)	119.3(3)
C(26)-C(25)	1.387(5)	C(27)-C(26)-C(25)	121.0(3)
C(26)-C(27)	1.375(5)	C(27)-C(26)-C(29)	119.8(4)
C(26)-C(29)	1.496(5)	C(14)-C(15)-C(16)	121.2(3)
C(15)-C(16)	1.407(5)	C(15)-C(16)-C(21)	118.7(3)
C(16)-C(17)	1.417(5)	C(15)-C(16)-C(17)	122.8(3)
C(7)-C(8)	1.525(5)	C(17)-C(16)-C(21)	118.5(3)
C(25)-C(24)	1.378(5)	C(8)-C(7)-C(6)	110.2(3)
C(9)-C(10)	1.534(5)	C(24)-C(25)-C(26)	119.6(3)
C(5)-C(4)	1.526(5)	C(28)-C(27)-C(26)	119.8(3)
C(20)-C(19)	1.366(5)	C(25)-C(24)-C(23)	119.0(3)
C(17)-C(18)	1.359(6)	C(10)-C(9)-C(6)	111.5(3)
C(18)-C(19)	1.404(6)	C(4)-C(5)-C(6)	110.8(3)
C(29)-F(1)	1.324(6)	C(19)-C(20)-C(21)	120.6(4)
C(29)-F(2)	1.396(6)	C(7)-C(8)-C(3)	111.3(3)
C(29)-F(3)	1.263(6)	C(18)-C(17)-C(16)	120.9(4)
C(29)-F(4)	1.434(12)	C(17)-C(18)-C(19)	120.5(4)
C(29)-F(5)	1.253(11)	C(20)-C(19)-C(18)	120.3(4)
C(29)-F(6)	1.315(8)	C(3)-C(10)-C(9)	109.6(3)
		C(3)-C(4)-C(5)	110.8(3)
O(3)-S(1)-C(23)	106.90(15)	F(1)-C(29)-C(26)	113.5(4)
O(3)-S(1)-C(12)	107.77(15)	F(1)-C(29)-F(2)	100.8(5)
O(4)-S(1)-O(3)	118.33(16)	F(2)-C(29)-C(26)	108.8(4)
O(4)-S(1)-C(23)	108.76(15)	F(3)-C(29)-C(26)	116.0(4)
O(4)-S(1)-C(12)	109.96(15)	F(3)-C(29)-F(1)	111.5(5)
C(23)-S(1)-C(12)	104.16(15)	F(3)-C(29)-F(2)	104.5(5)
C(2)-O(1)-C(1)	116.4(3)	F(4)-C(29)-C(26)	104.3(6)
C(14)-C(13)-C(12)	121.2(3)	F(5)-C(29)-C(26)	118.9(7)
C(22)-C(13)-C(12)	119.6(3)	F(5)-C(29)-F(4)	101.6(8)
C(22)-C(13)-C(14)	119.2(3)	F(5)-C(29)-F(6)	113.3(10)
C(11)-C(6)-C(7)	111.9(3)	F(6)-C(29)-C(26)	114.0(12)
C(11)-C(6)-C(9)	108.9(3)	F(6)-C(29)-F(4)	101.8(9)
C(11)-C(6)-C(5)	112.3(3)		

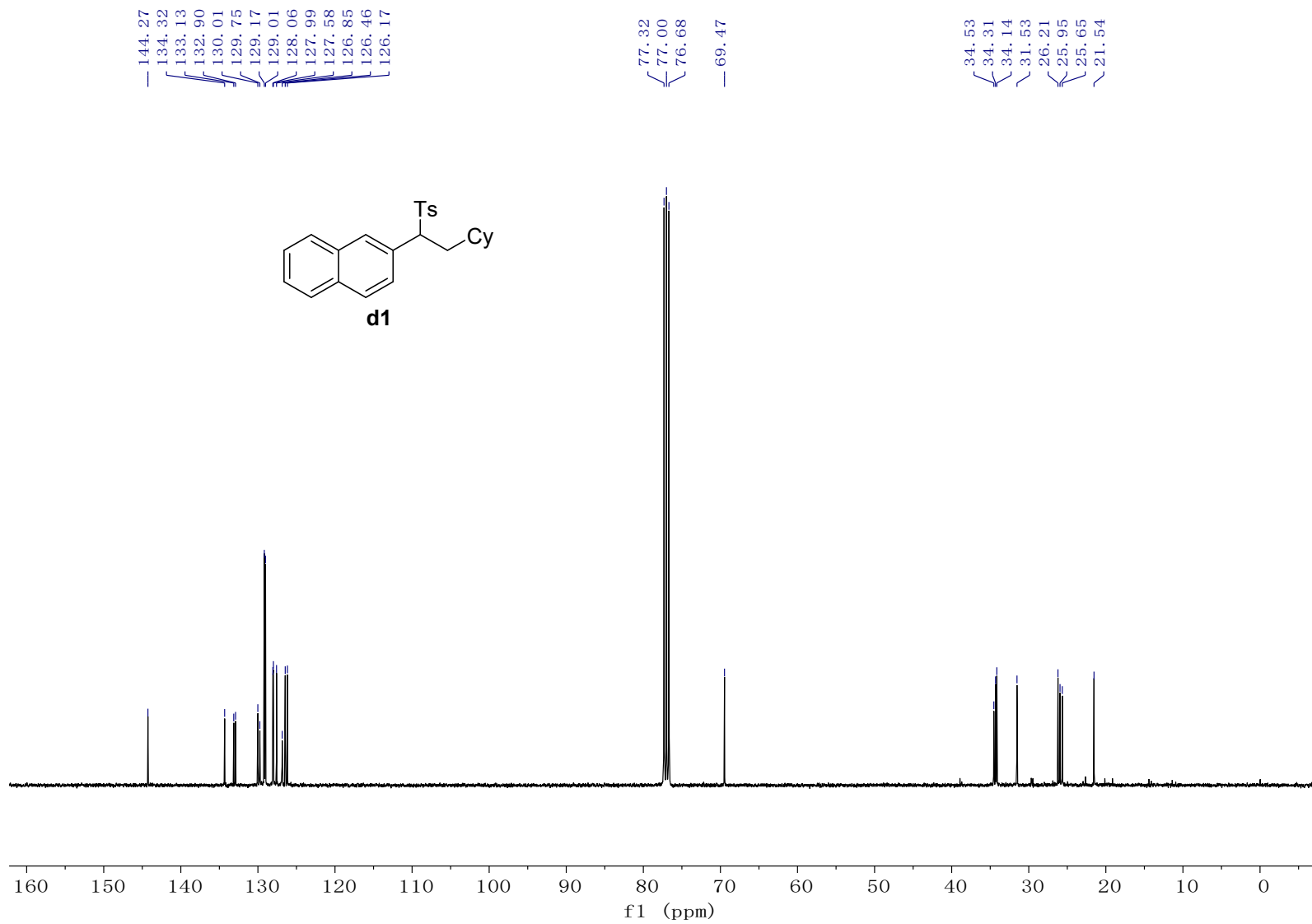
8. Reference

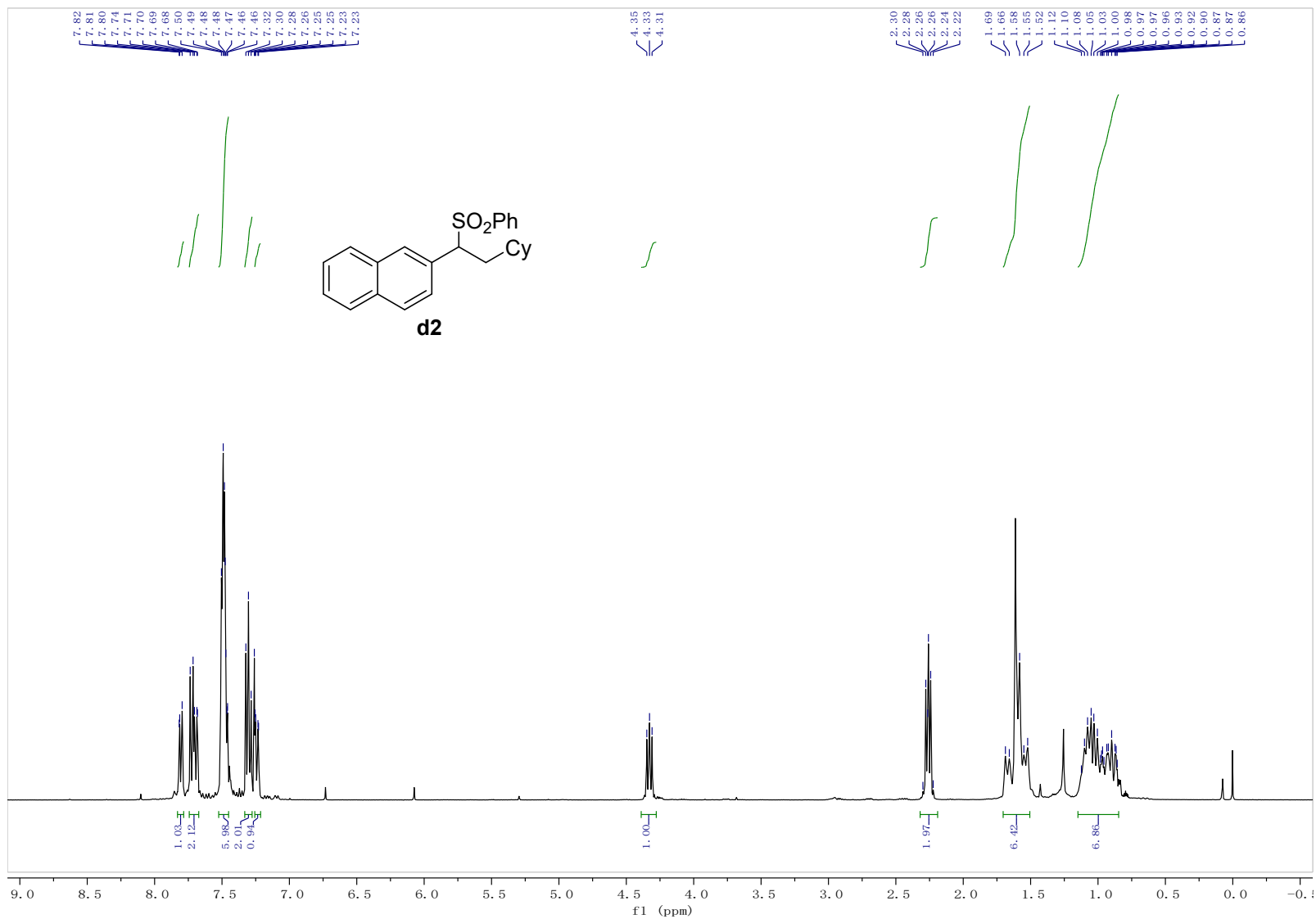
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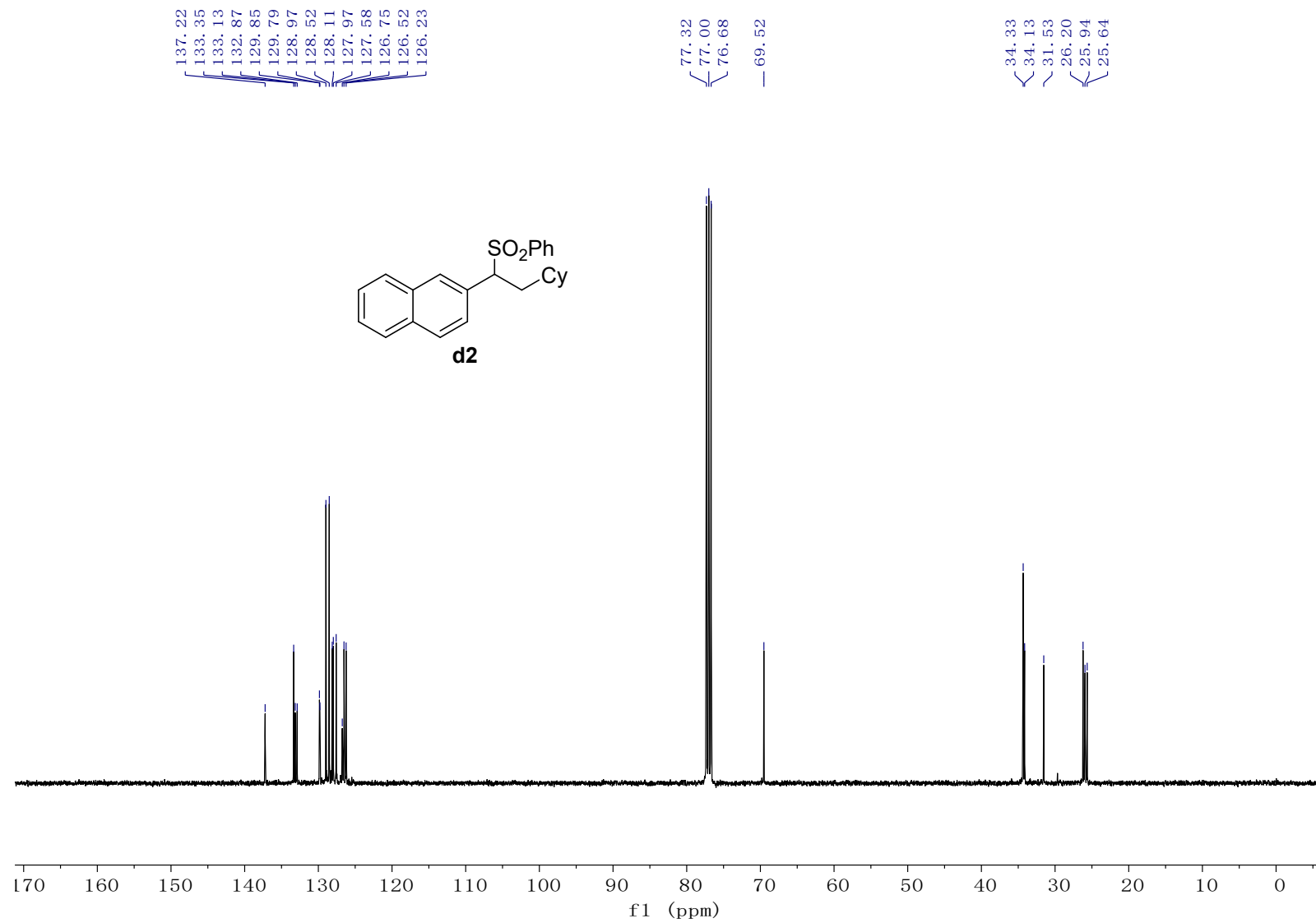
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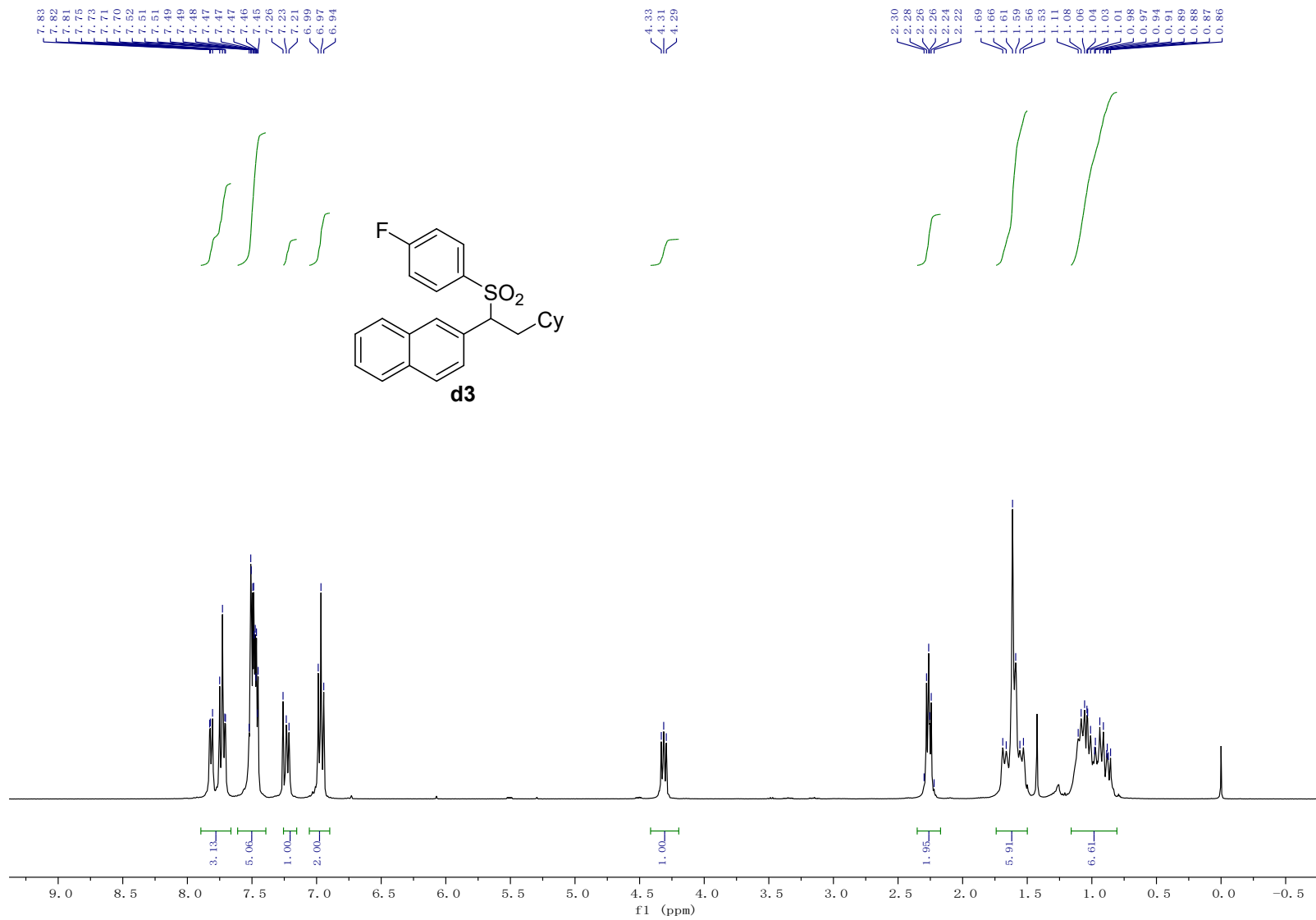
9. Spectroscopic data

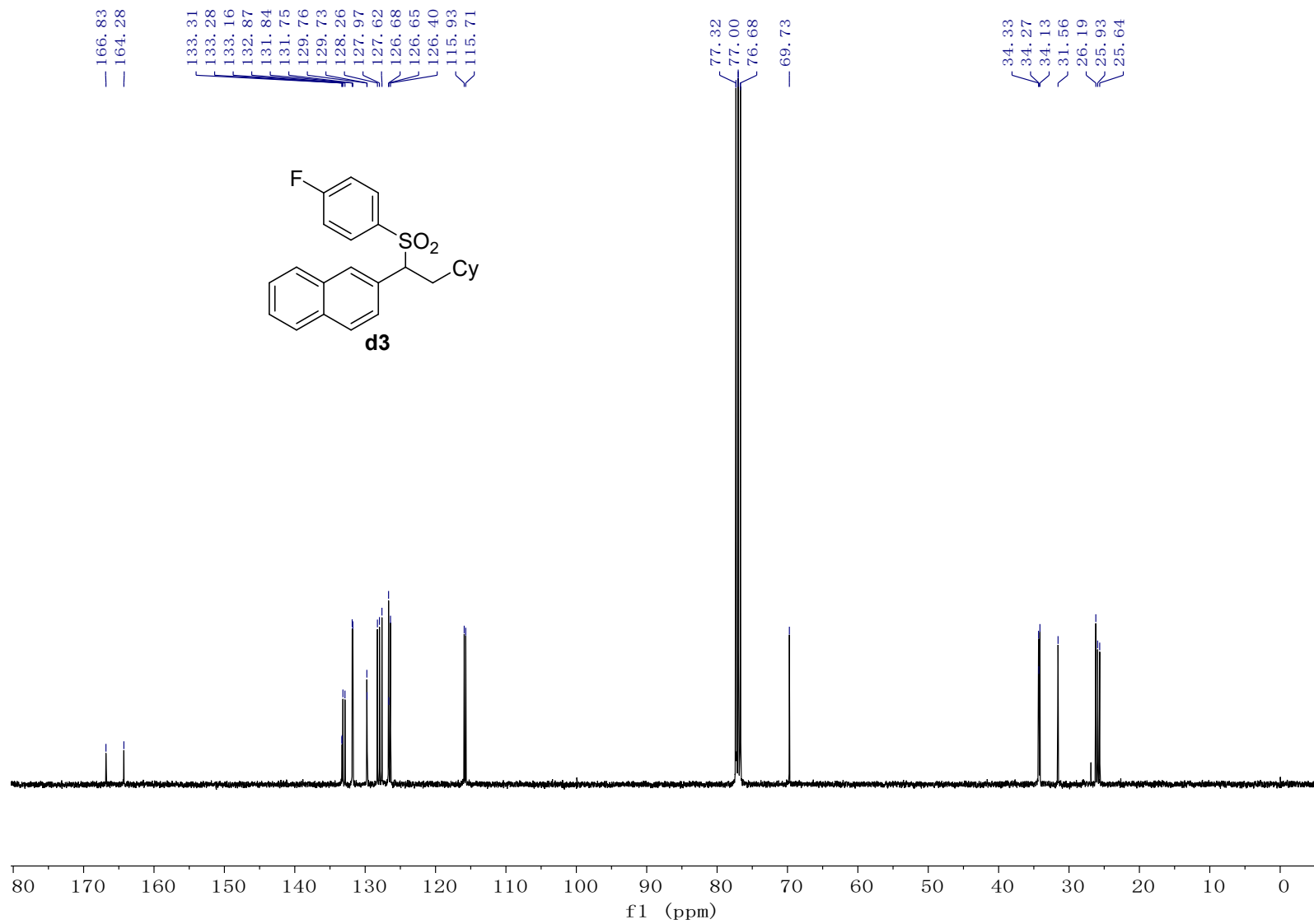


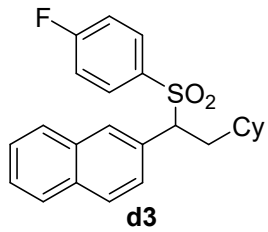




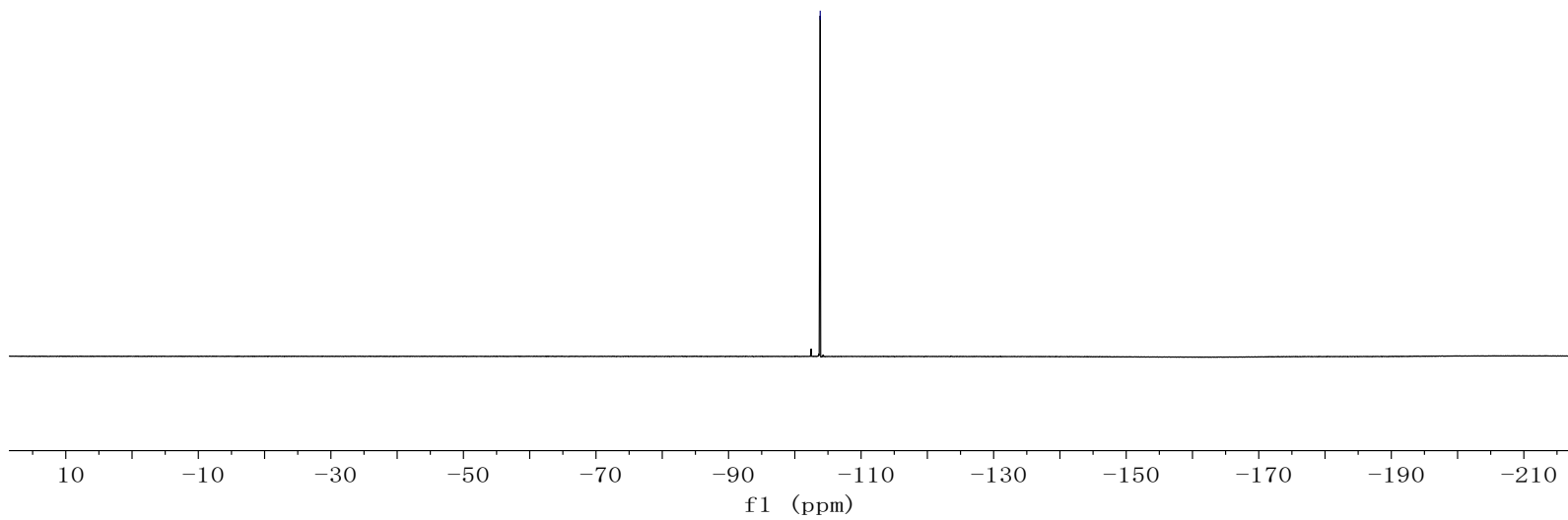


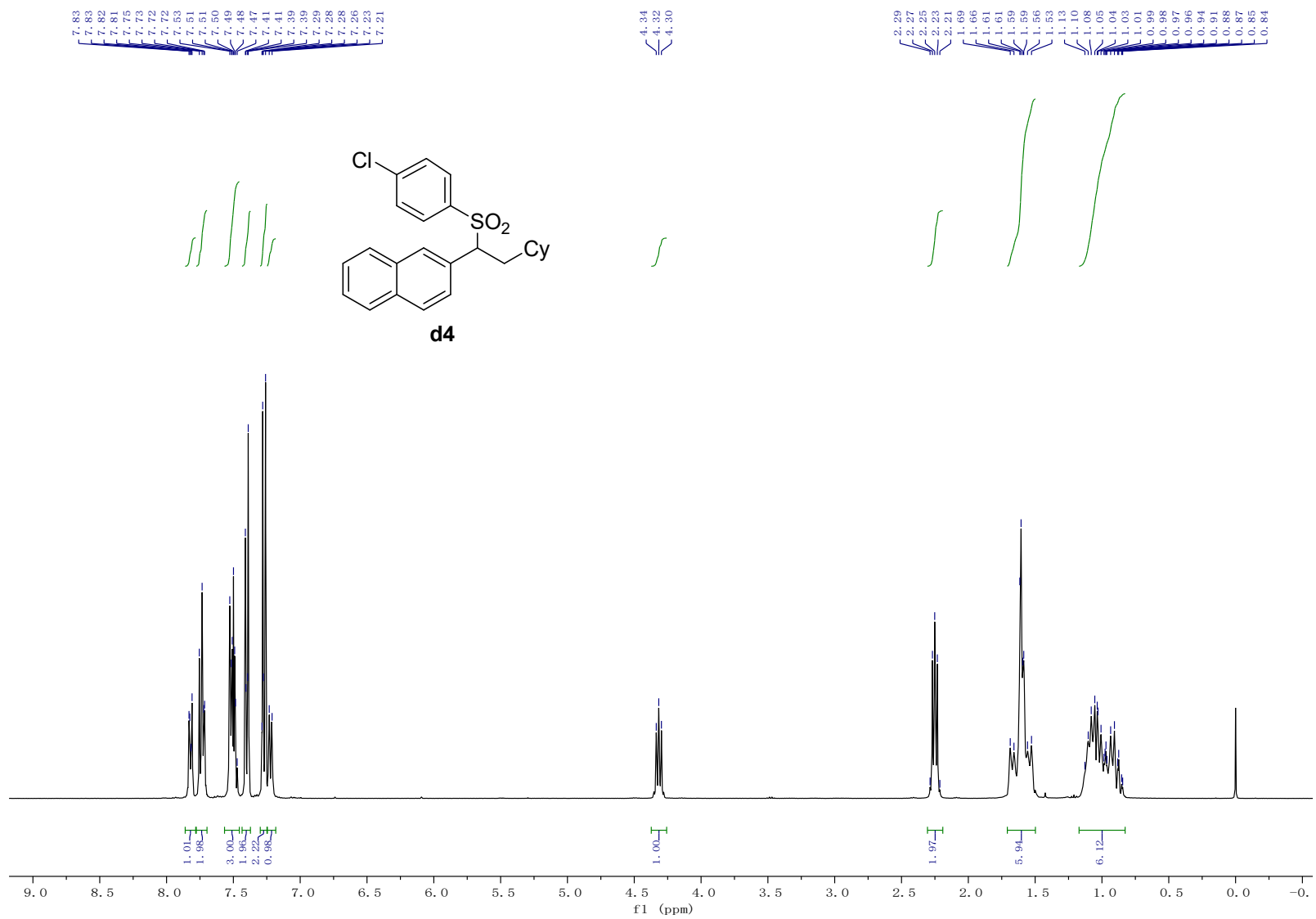


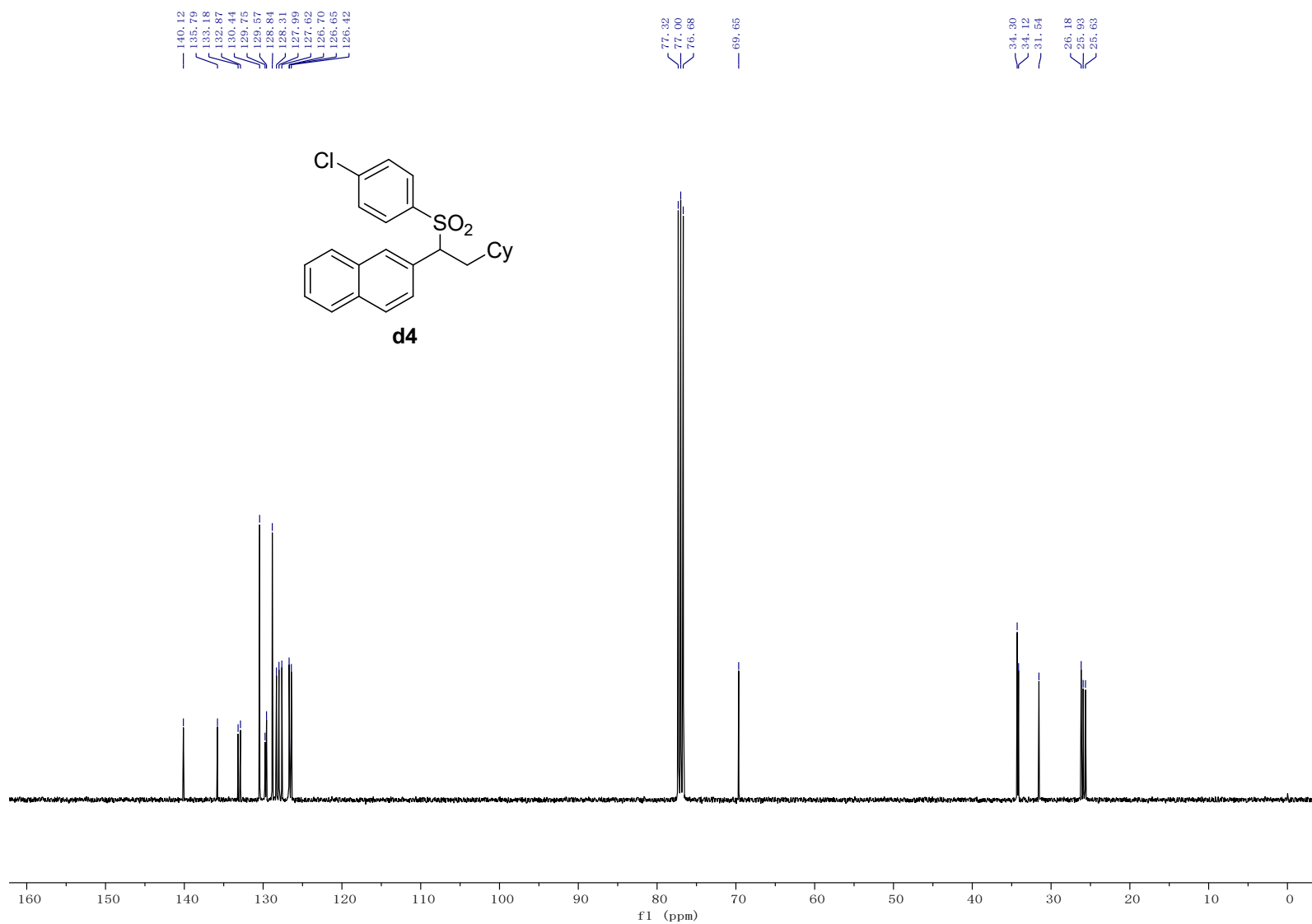


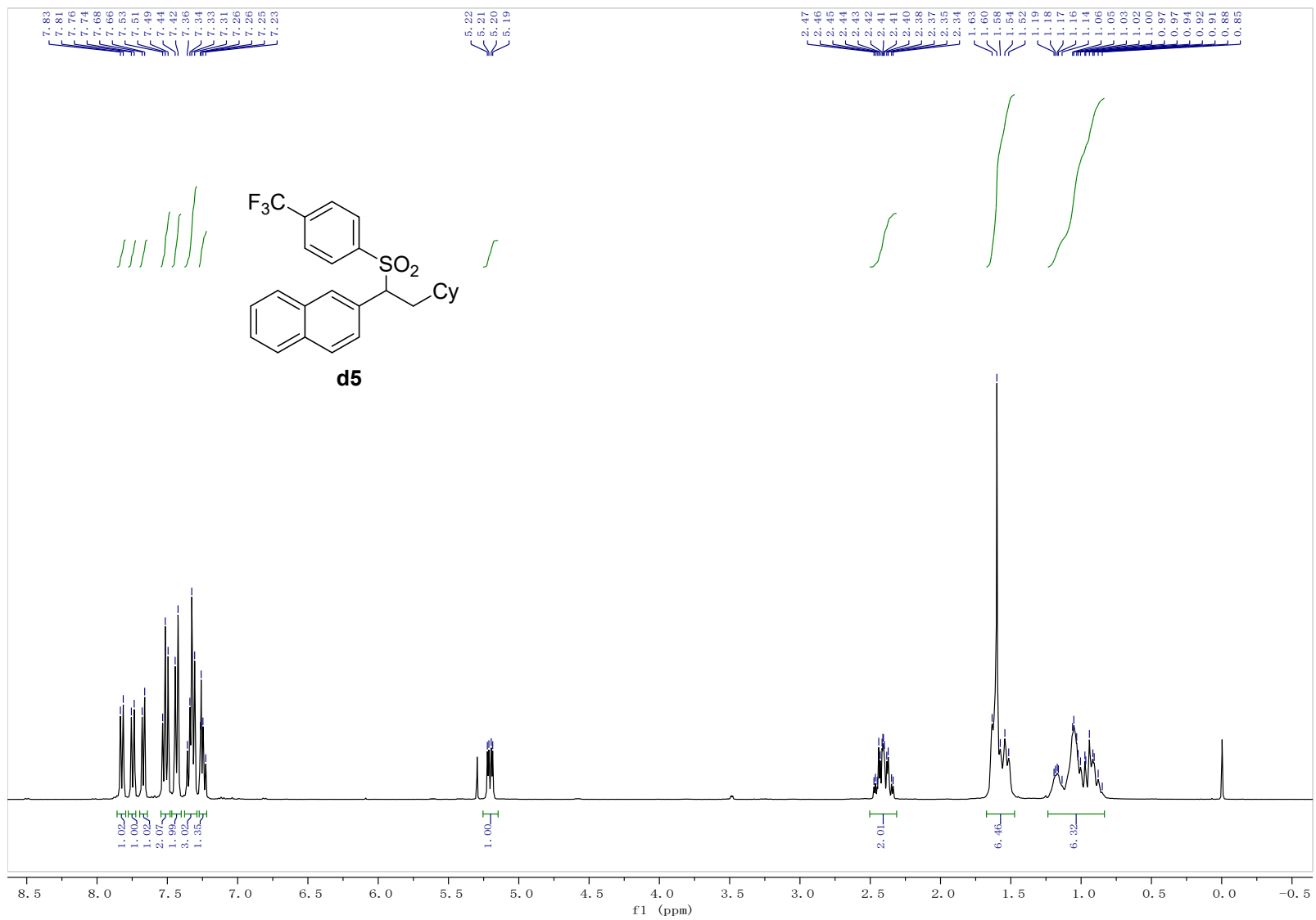


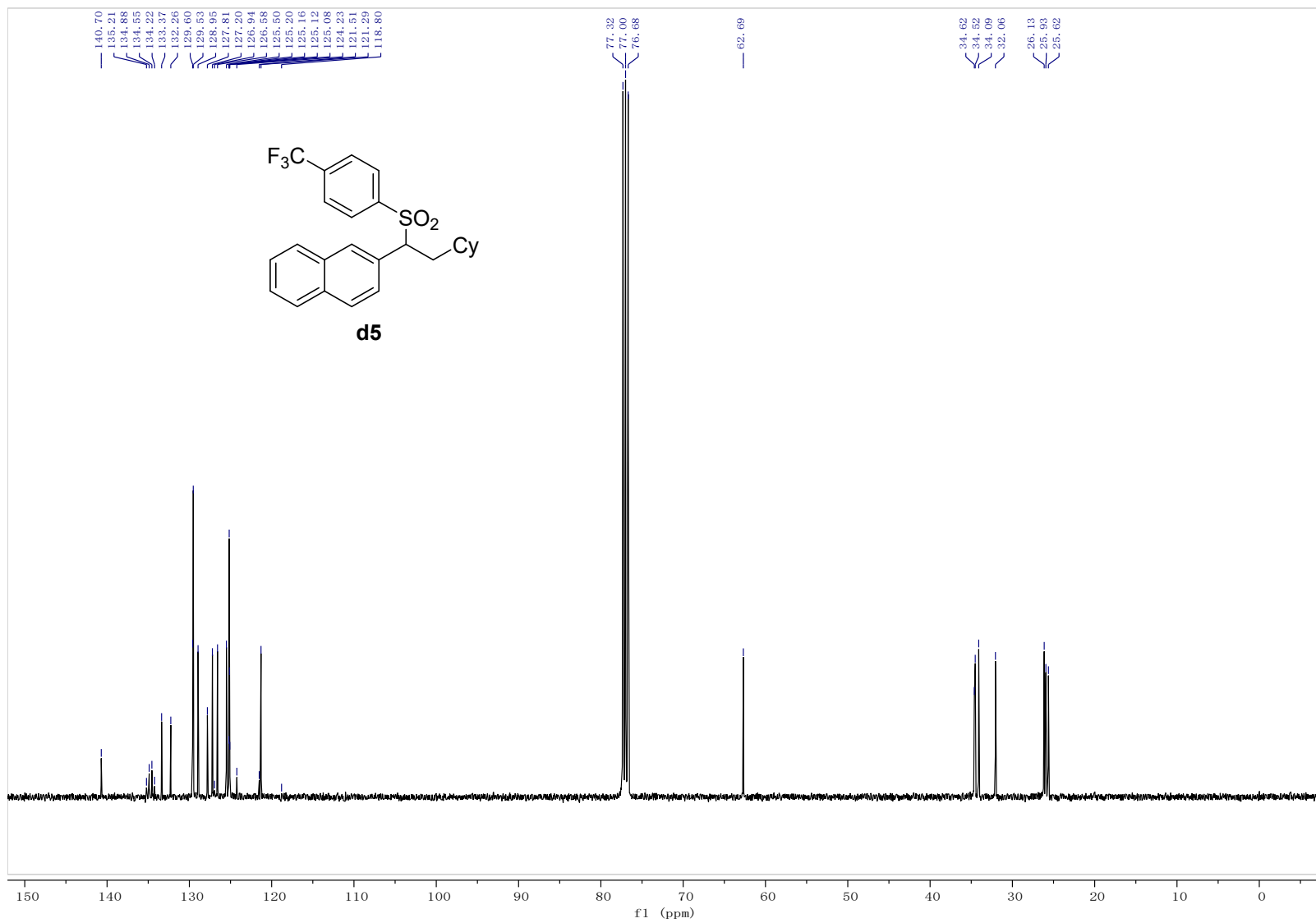
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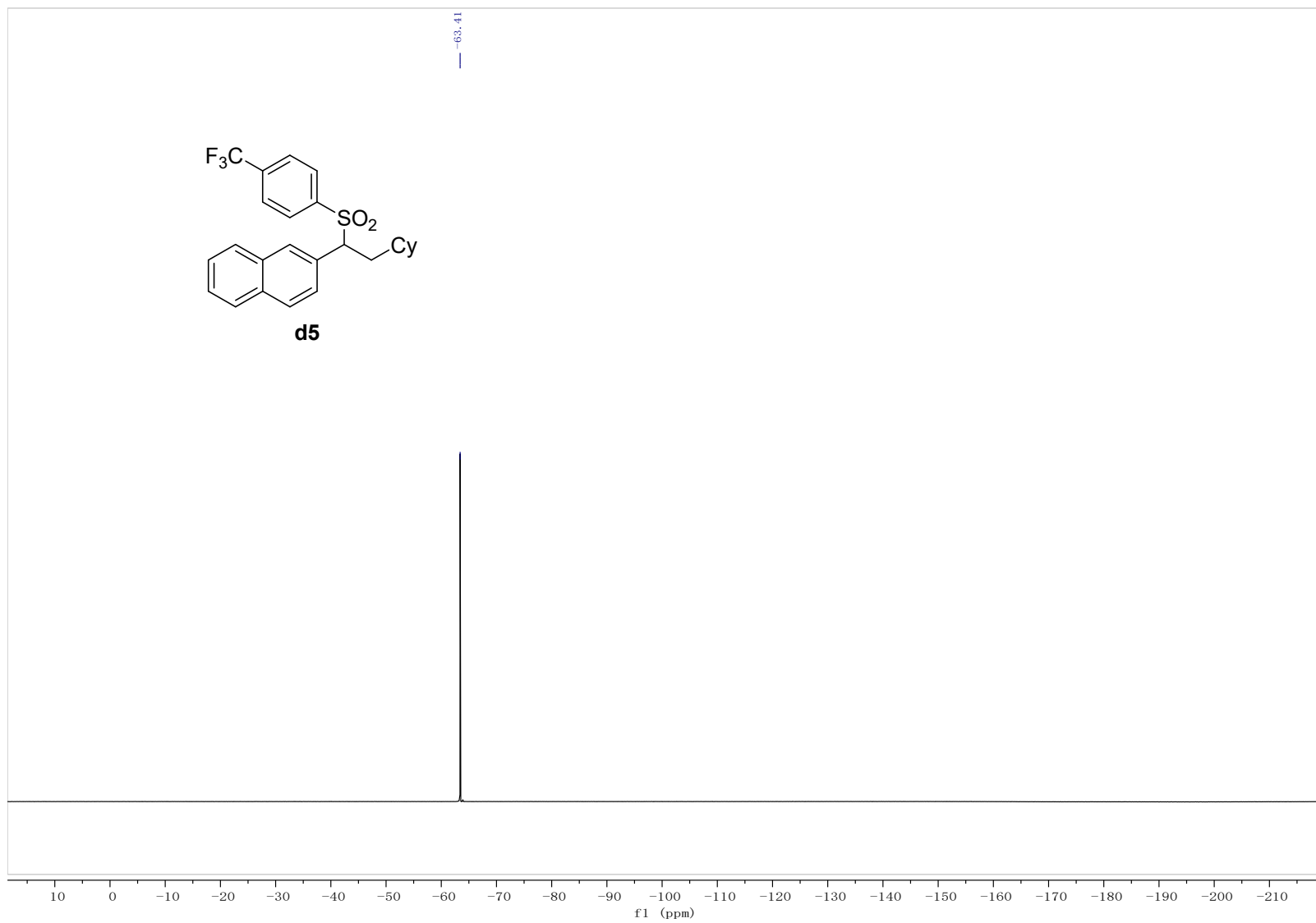


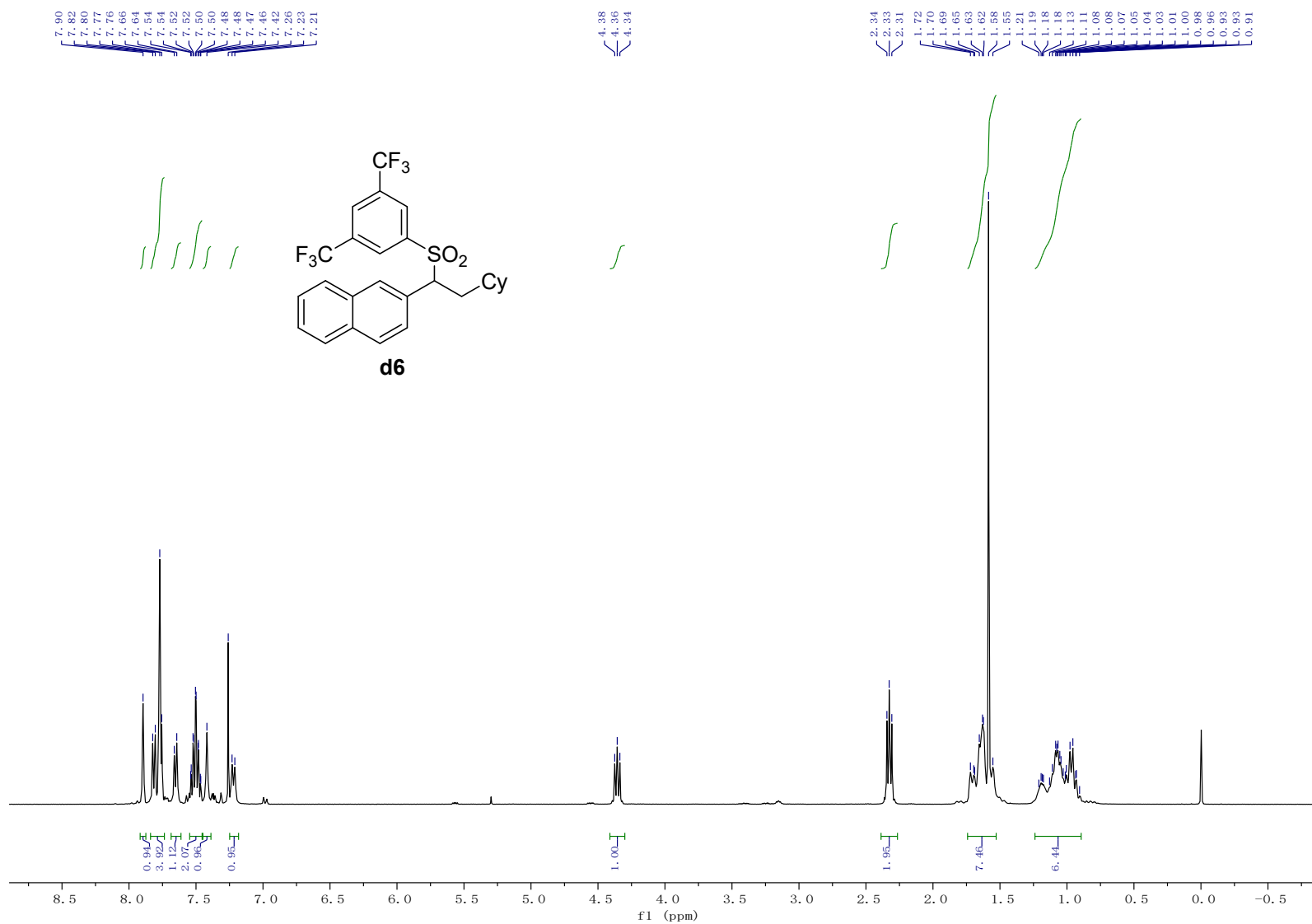


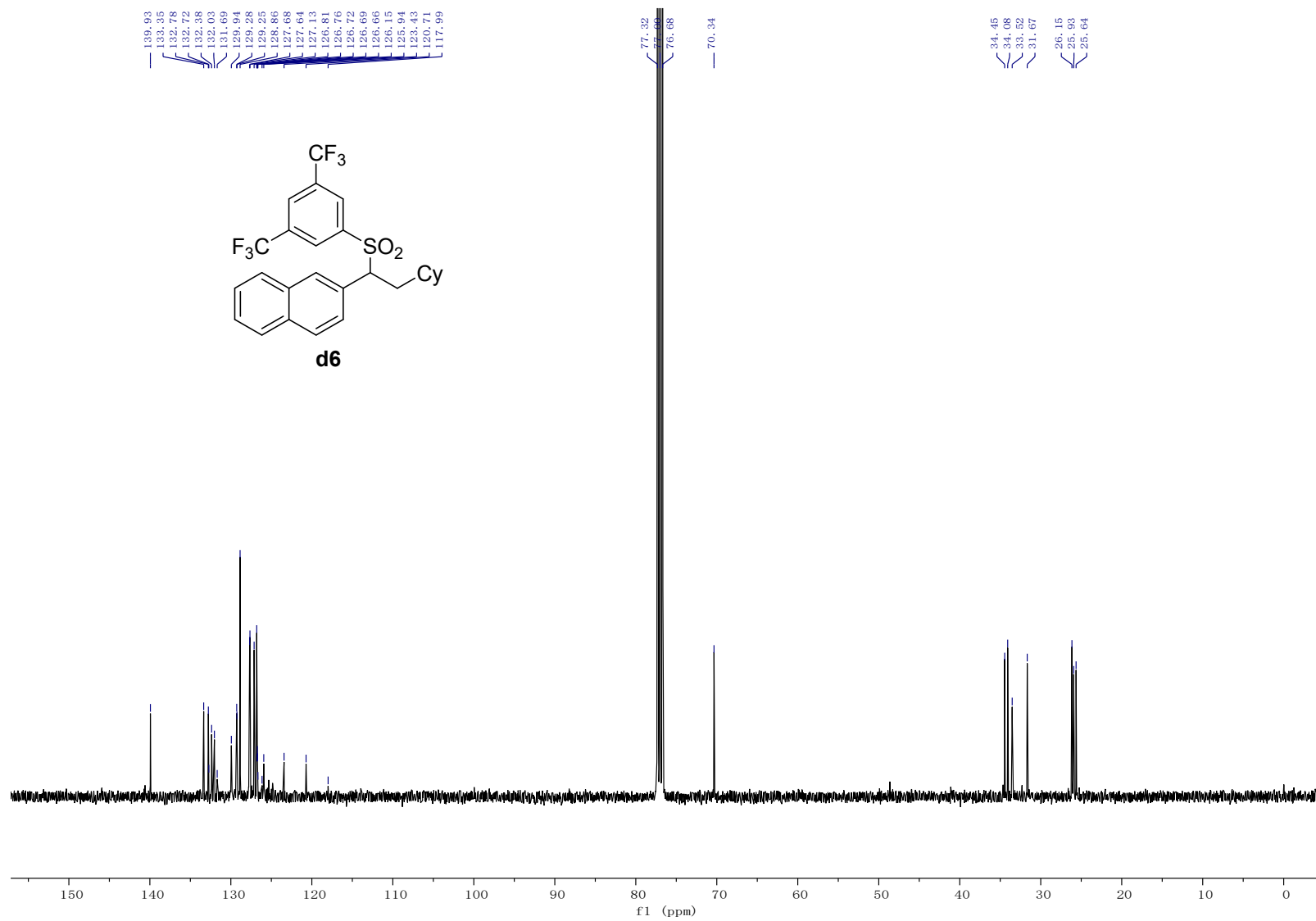


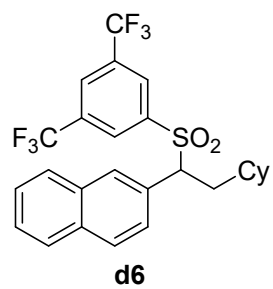




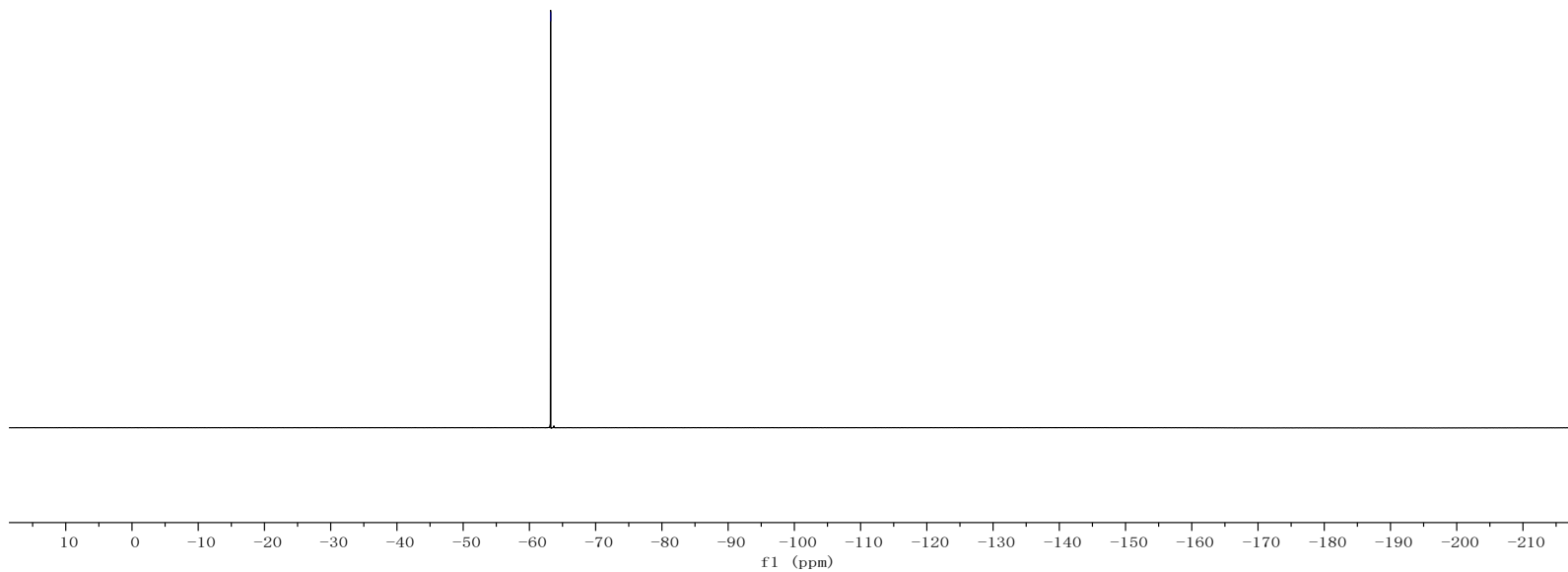


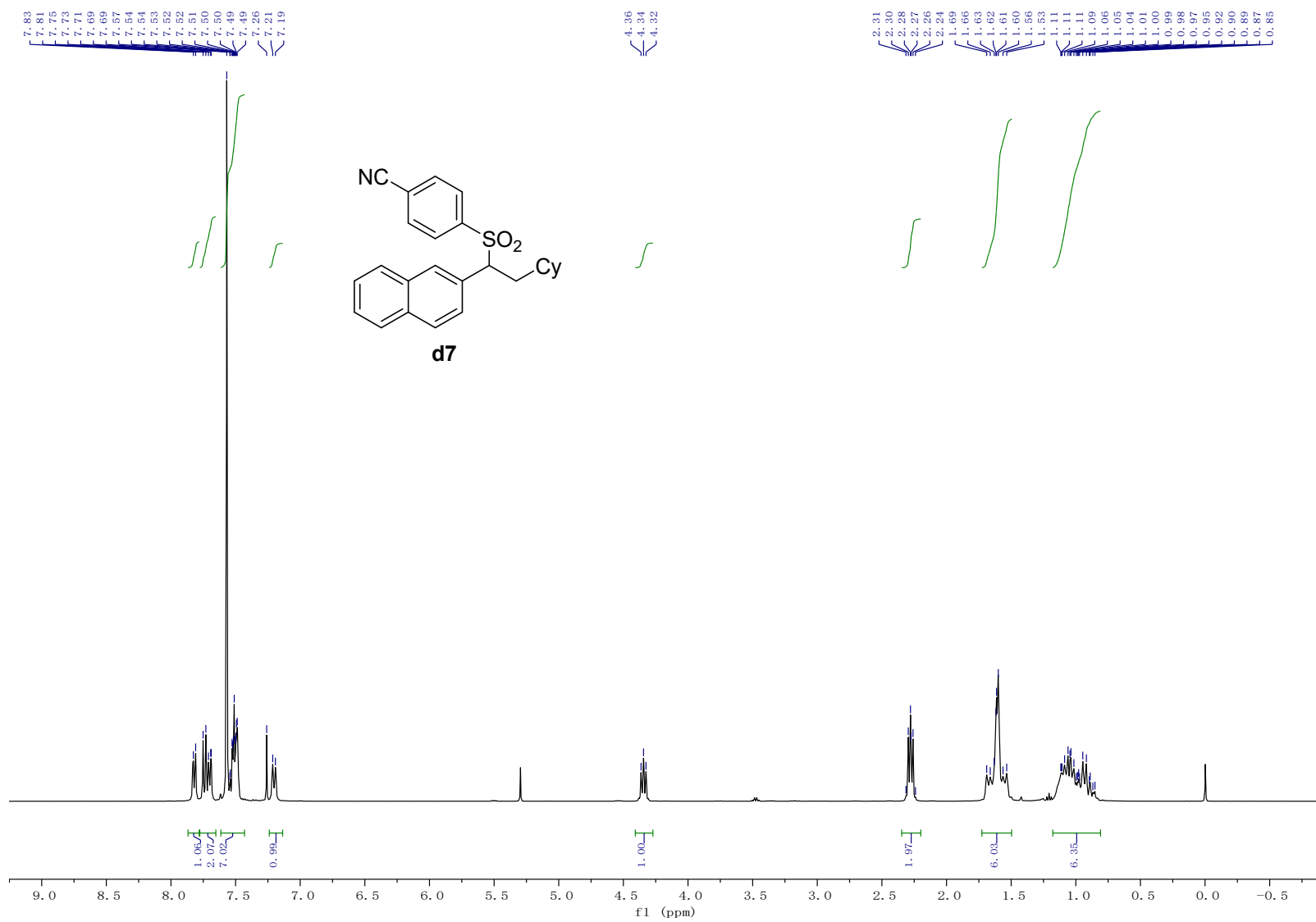






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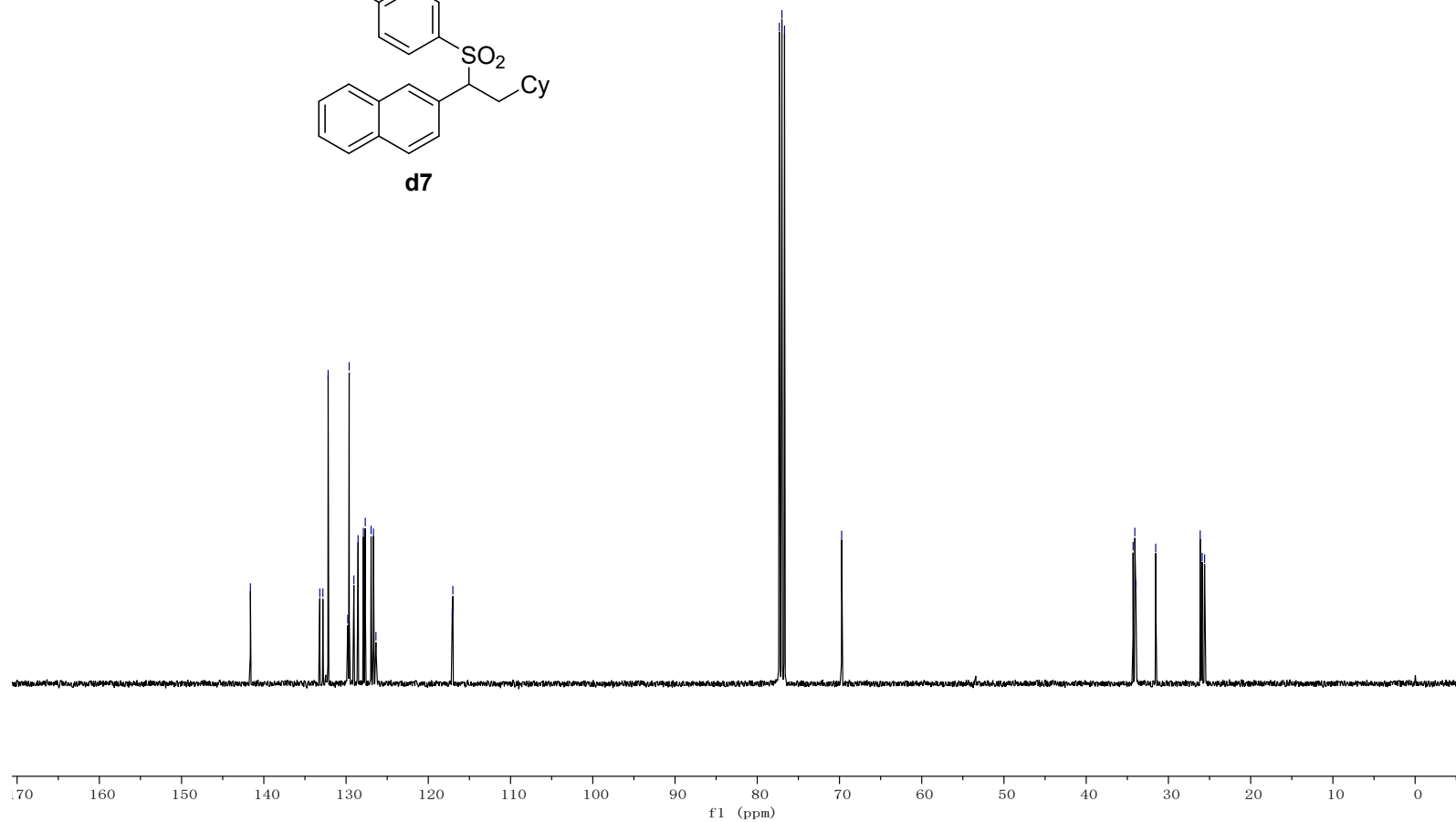
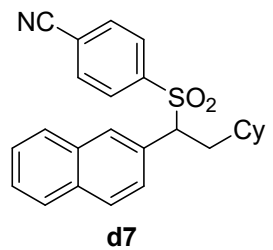


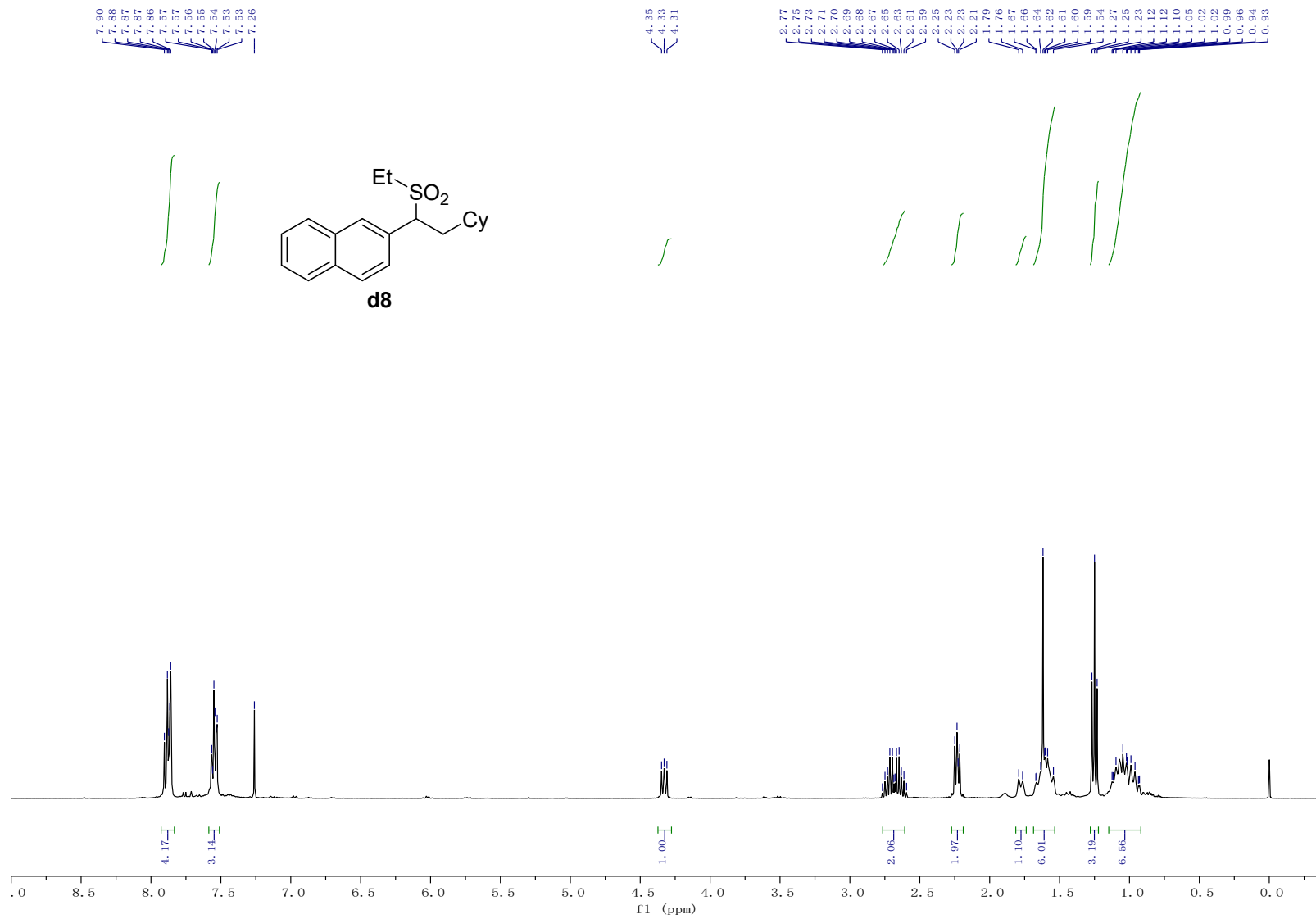


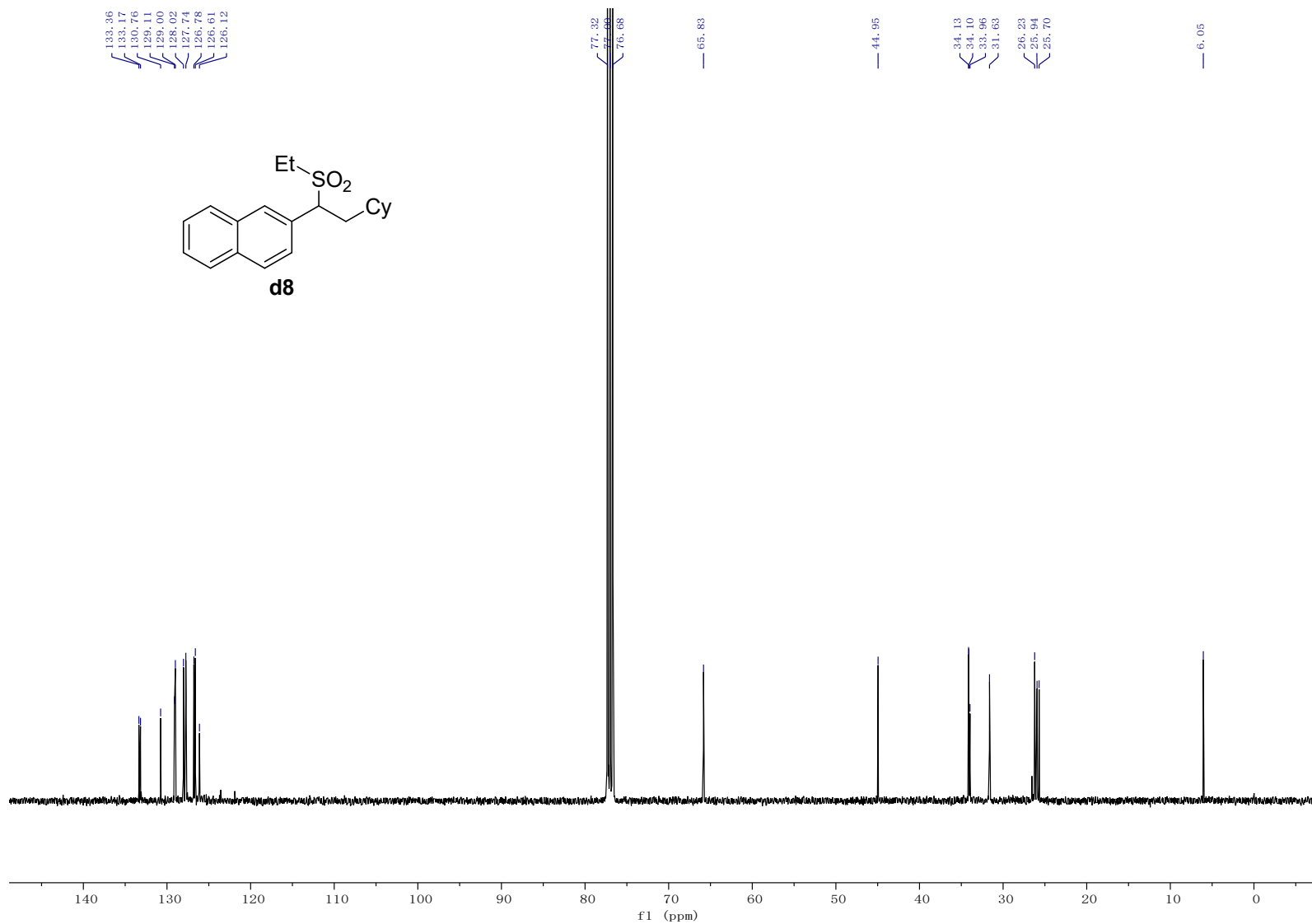
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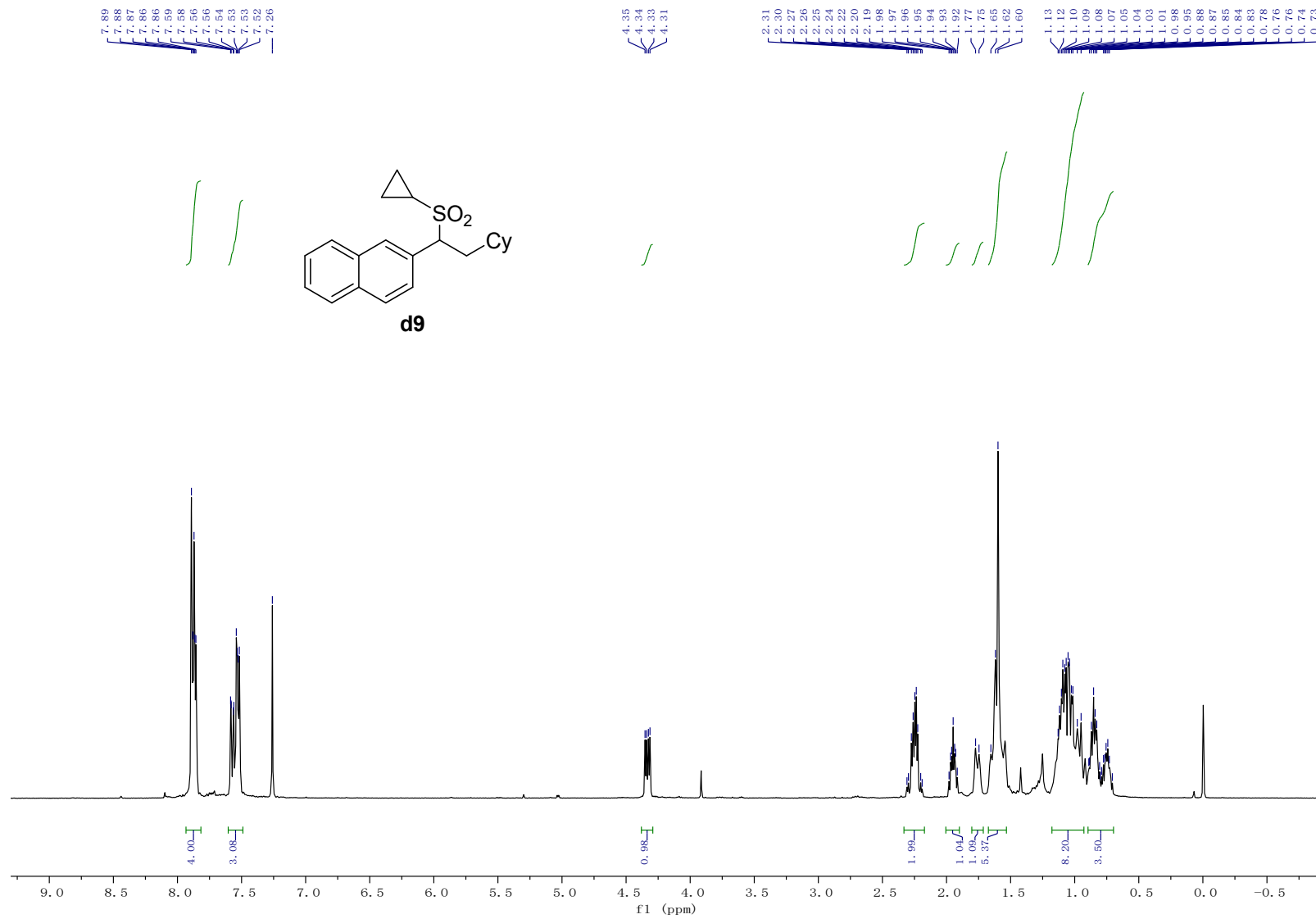
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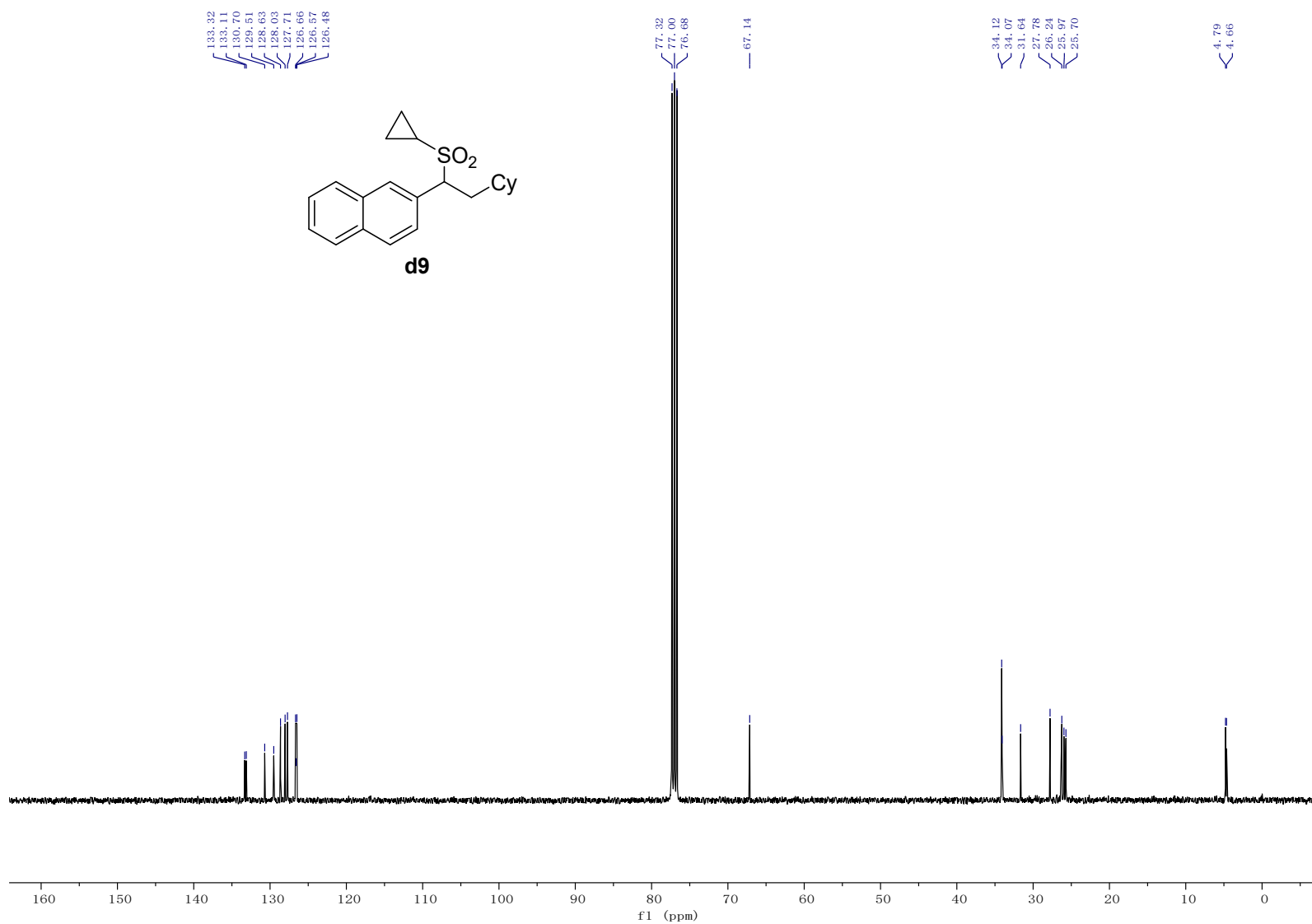
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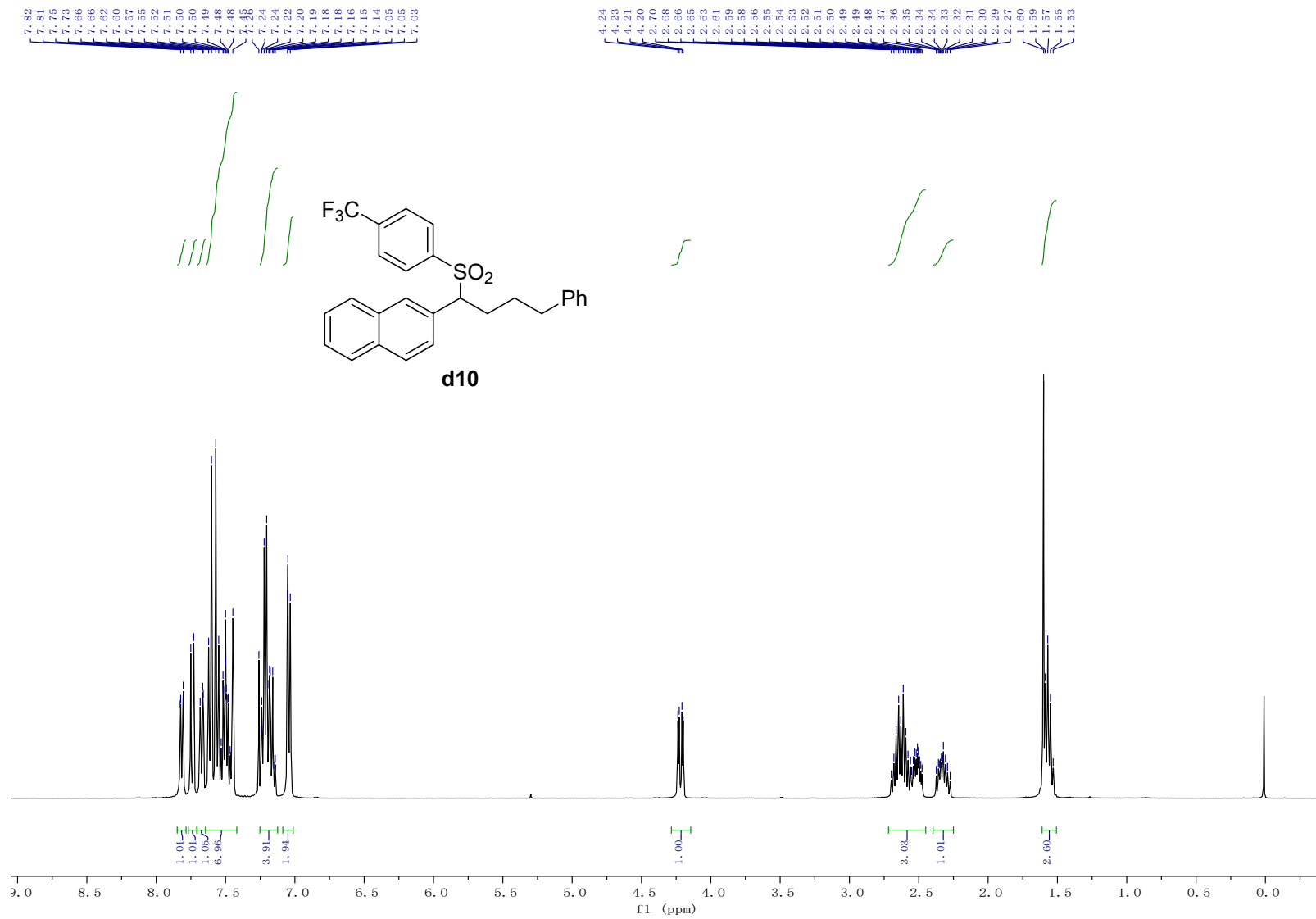


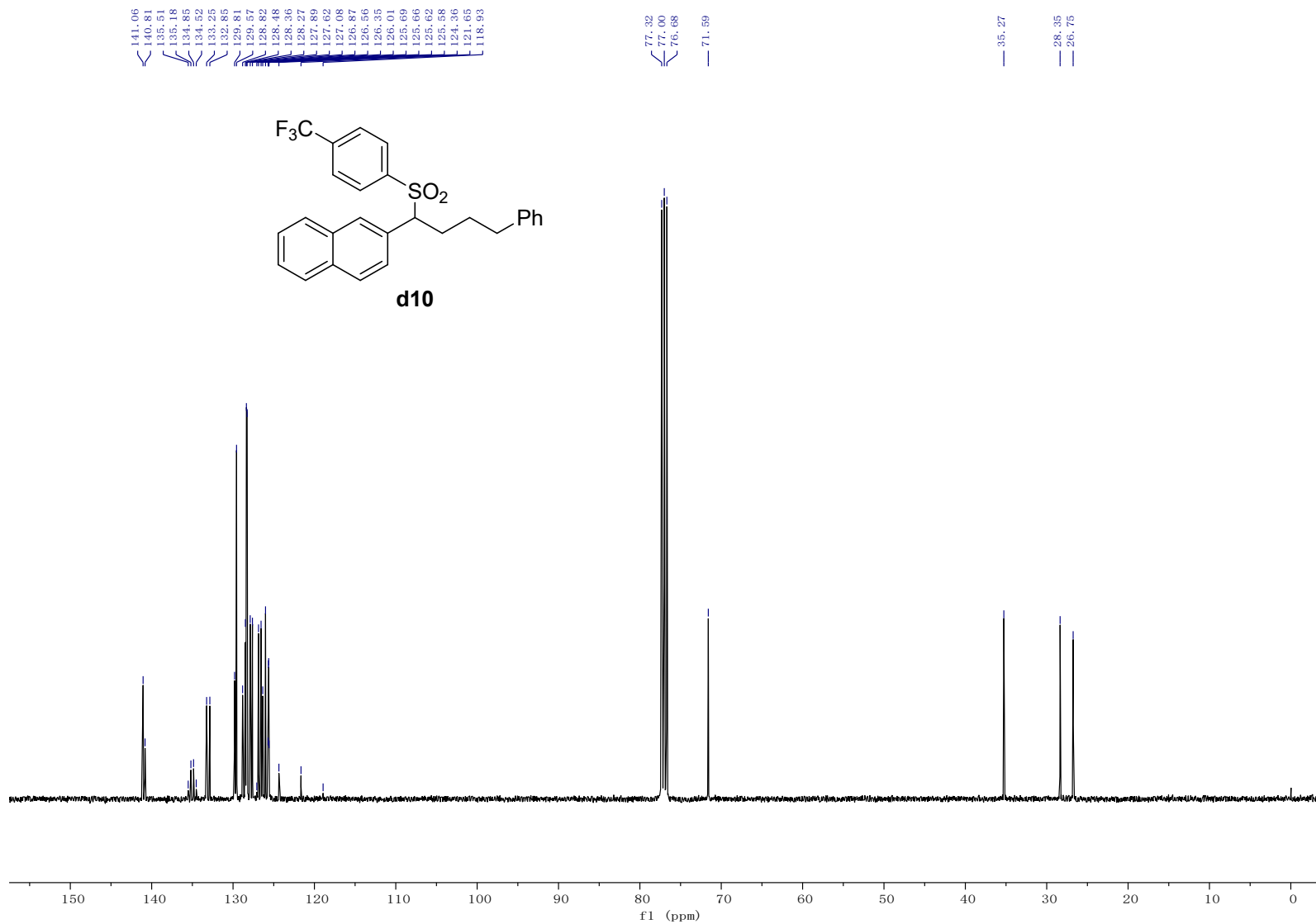


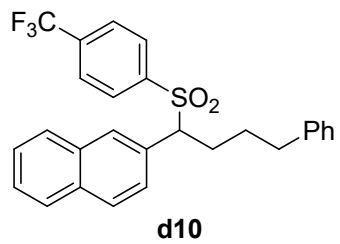




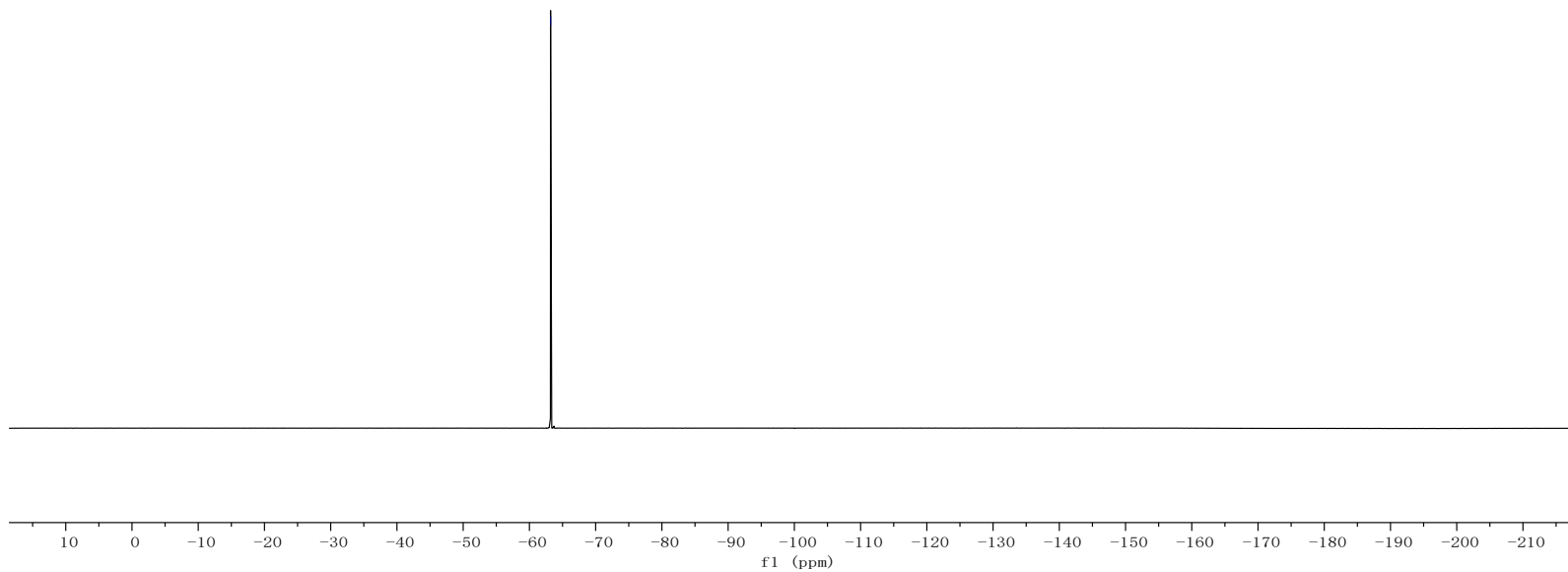


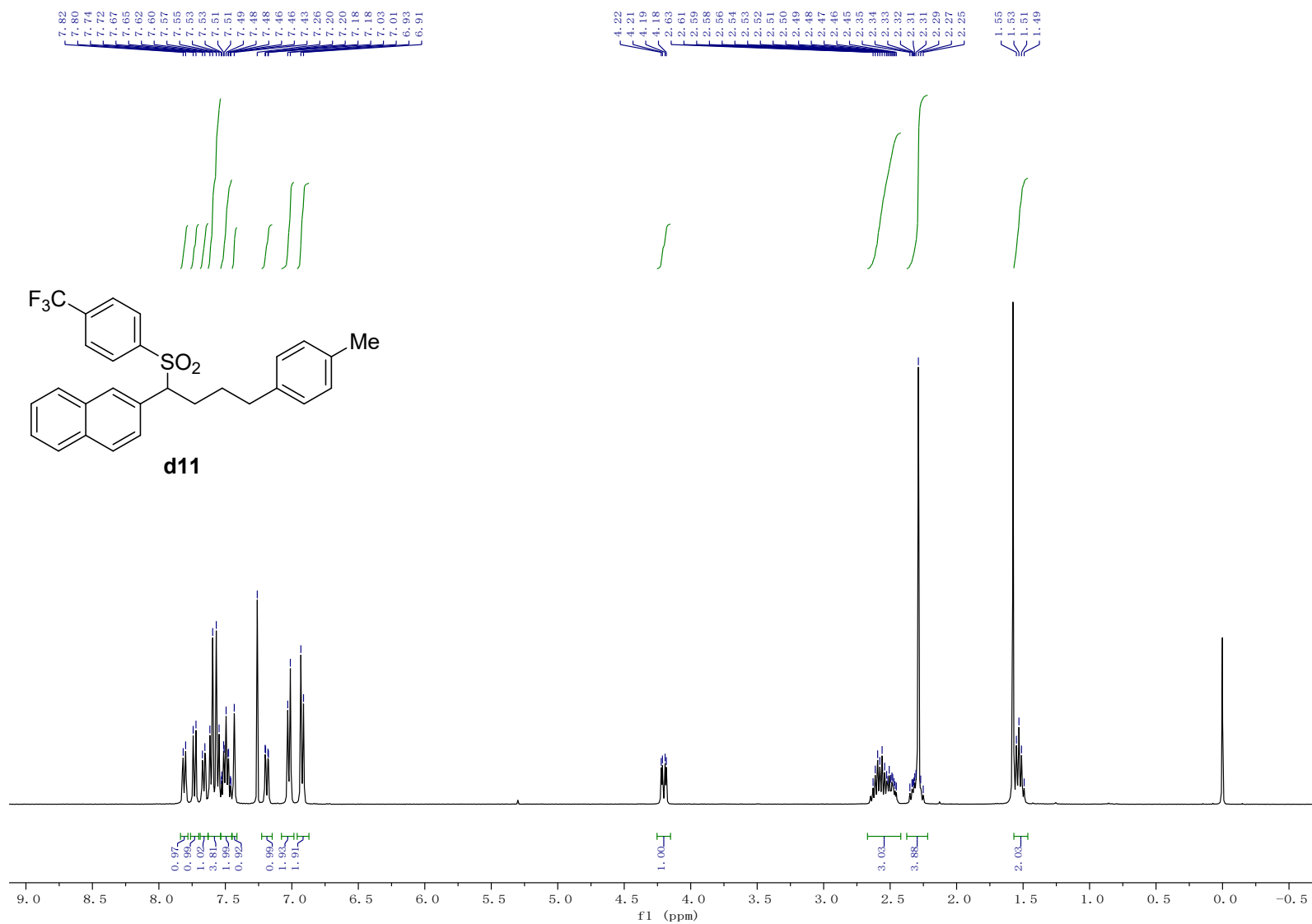


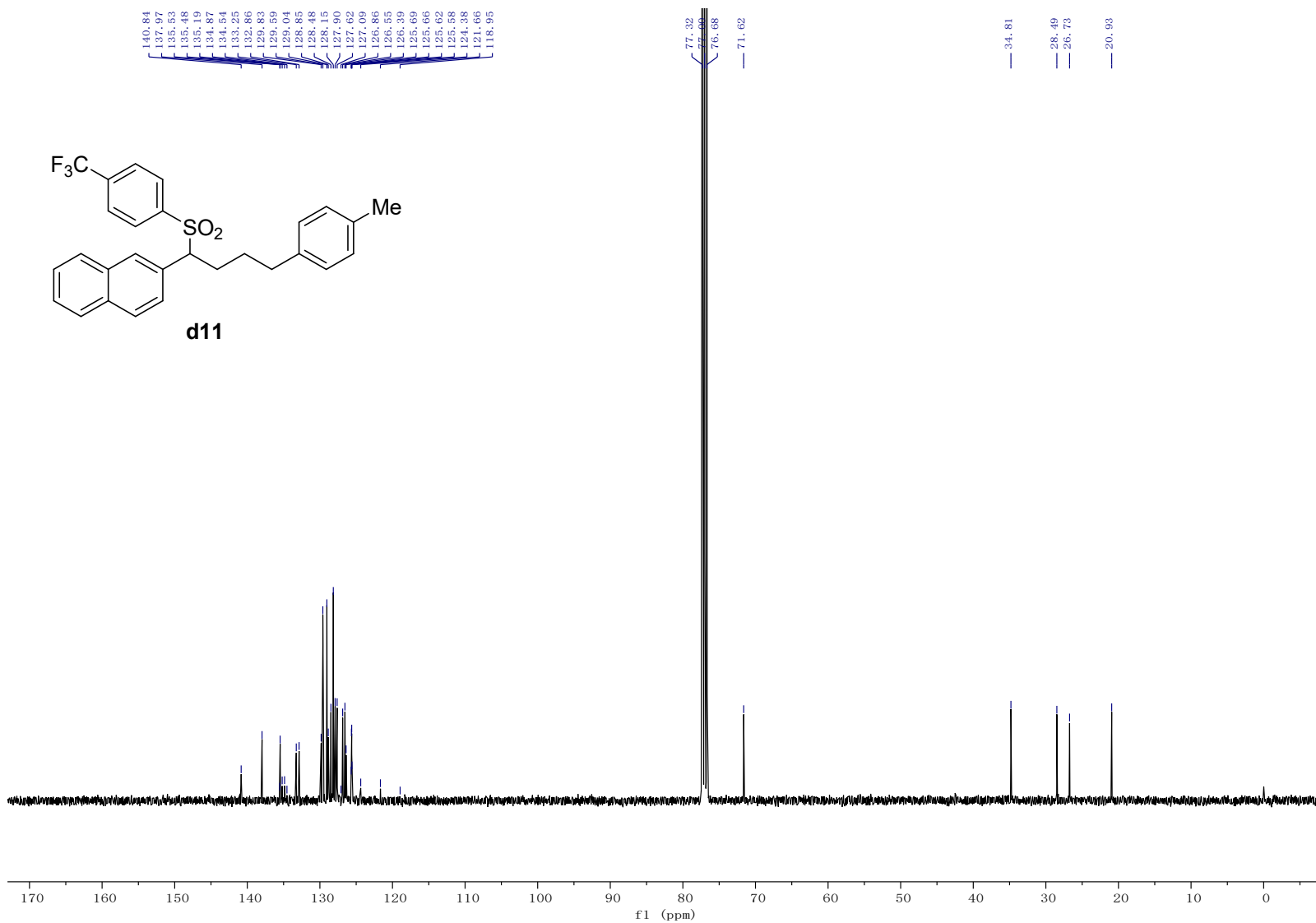


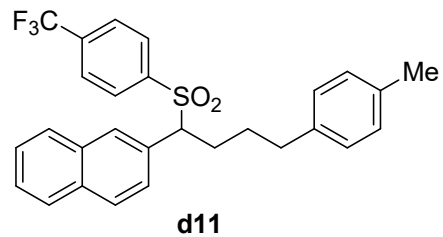


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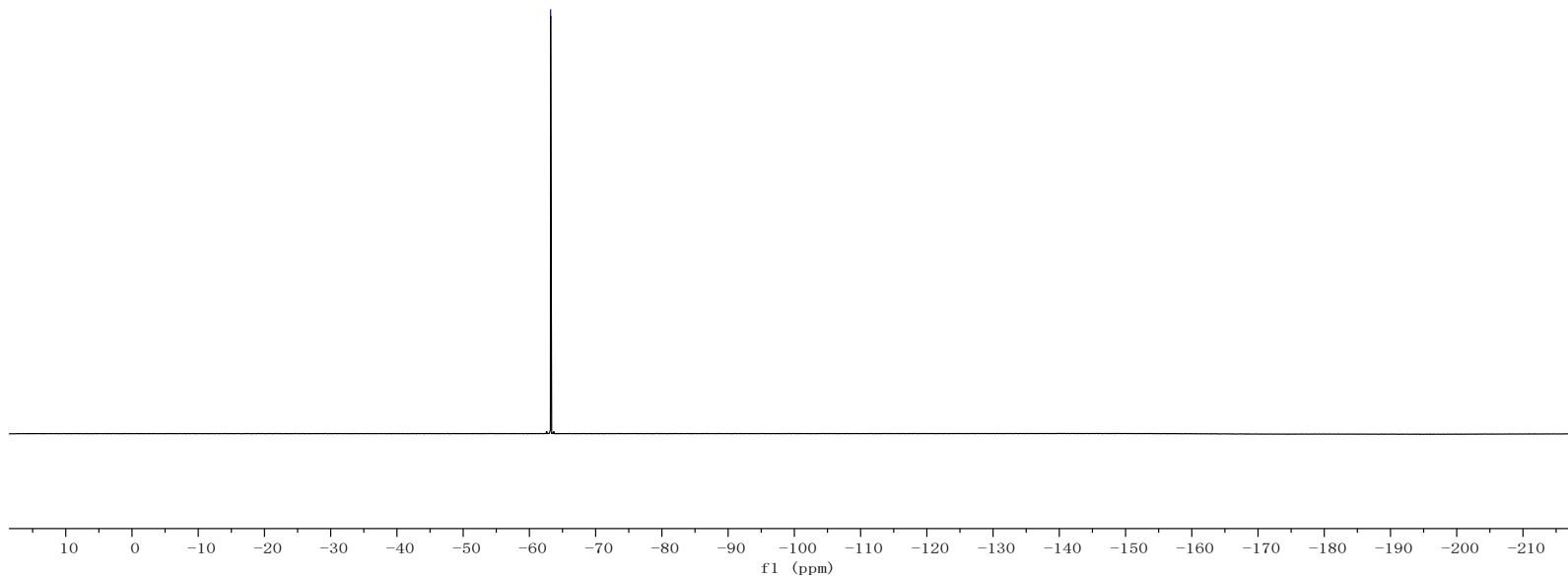


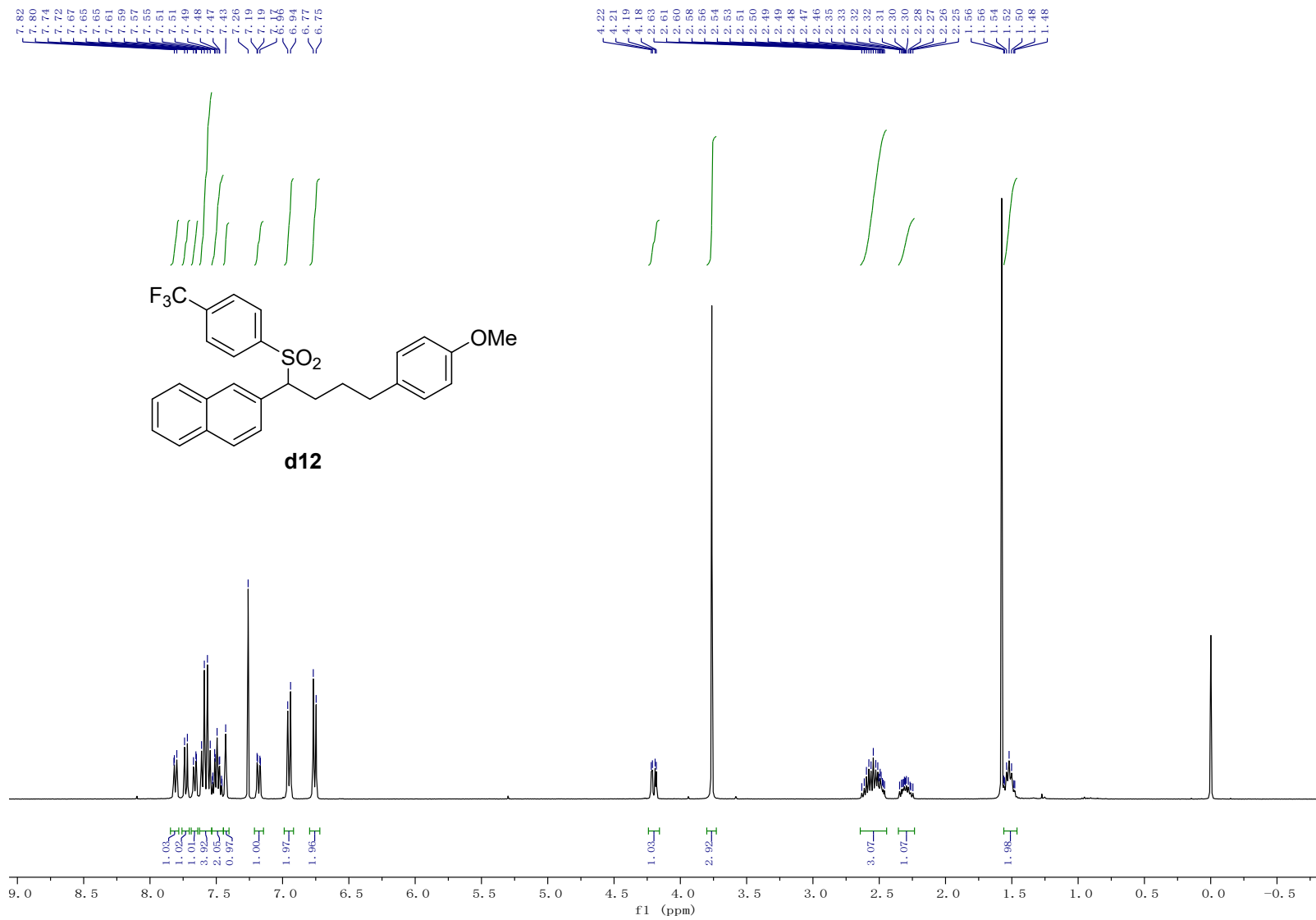


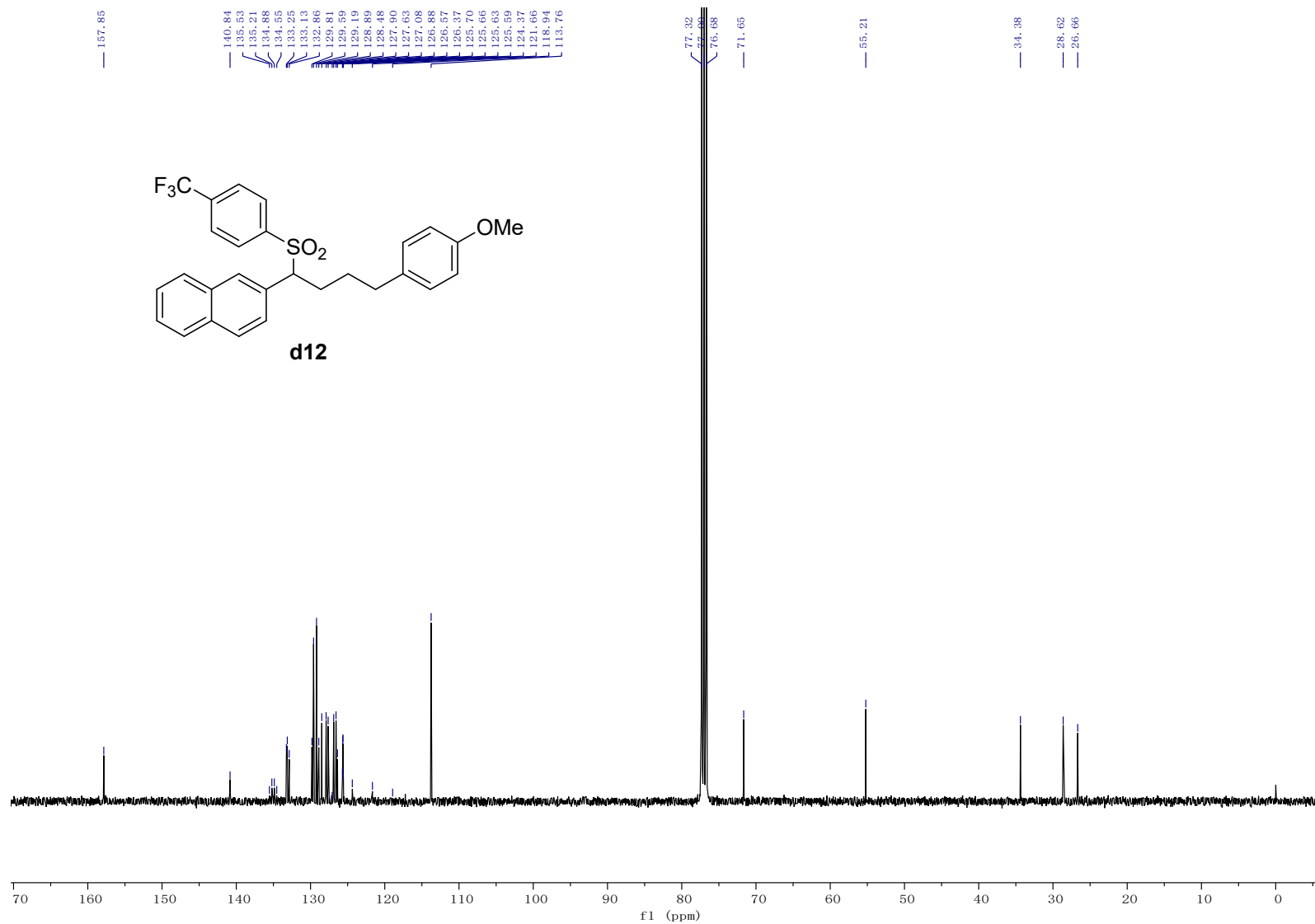


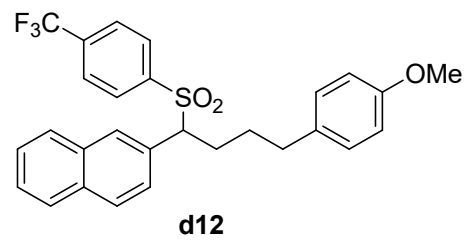


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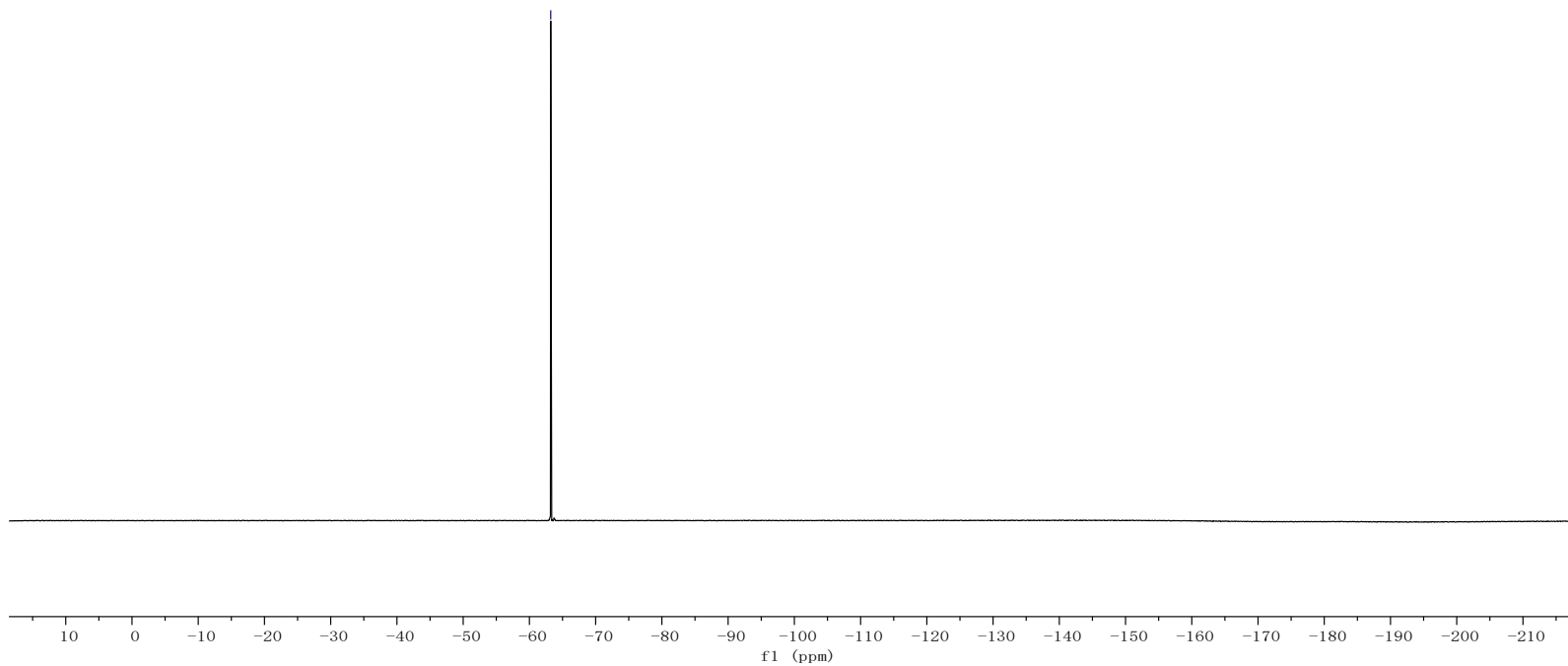






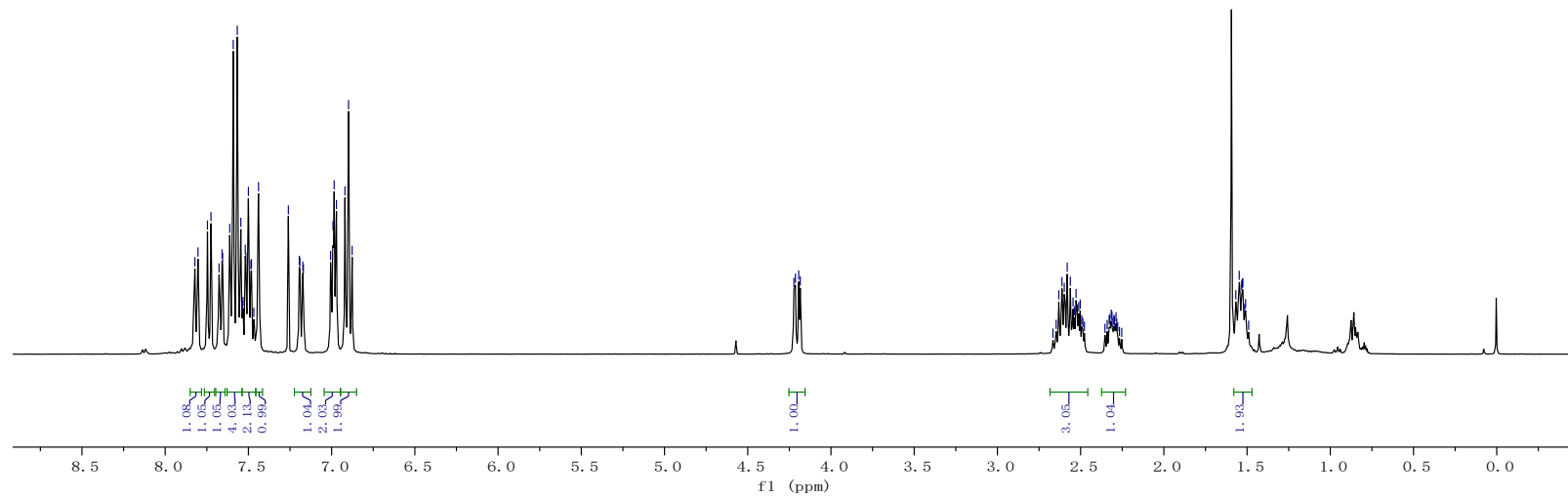
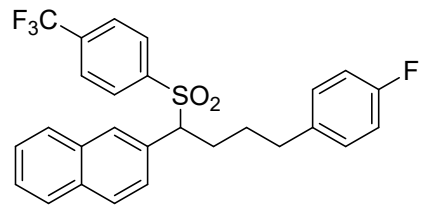


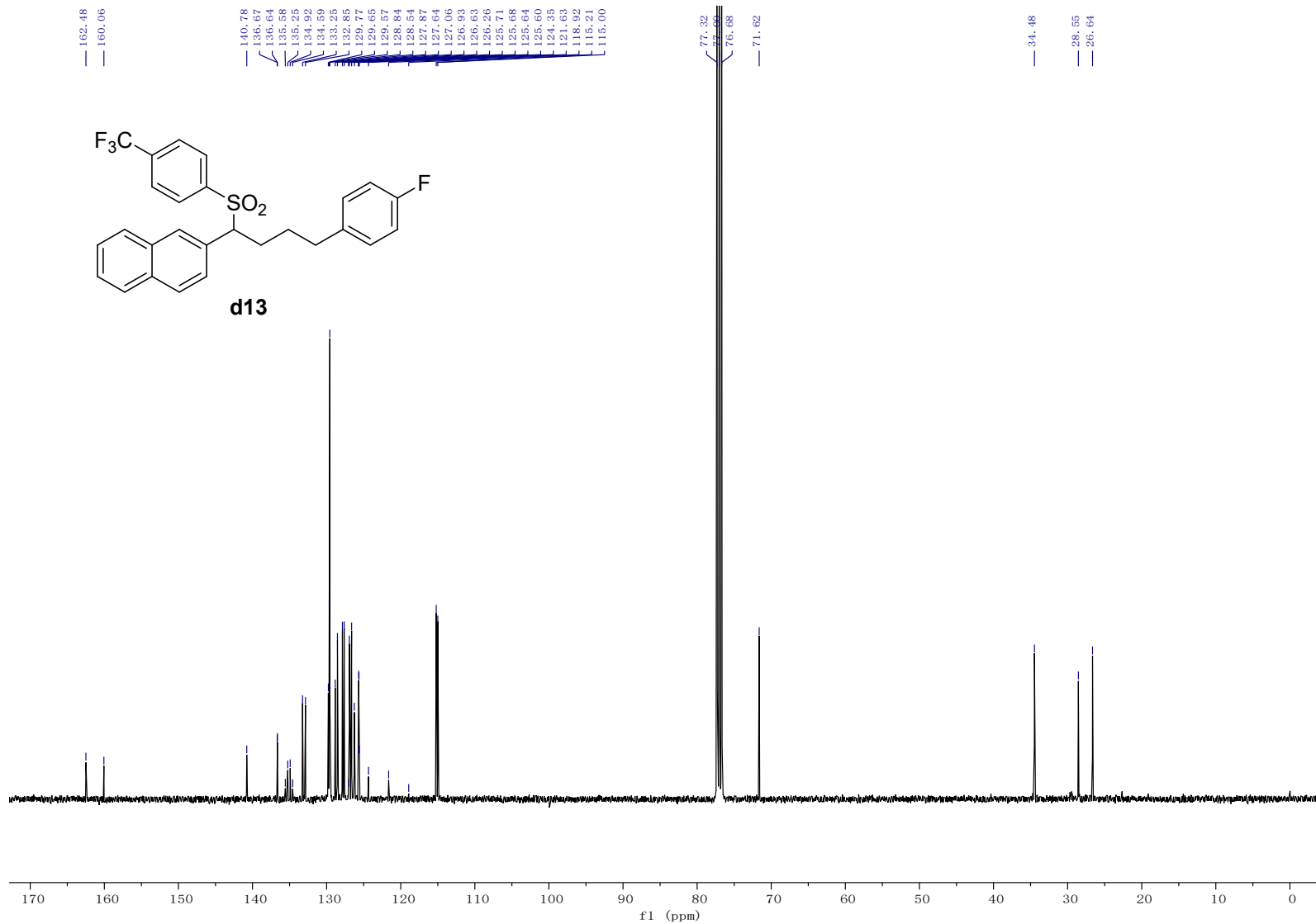
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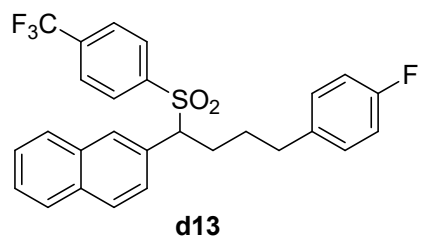


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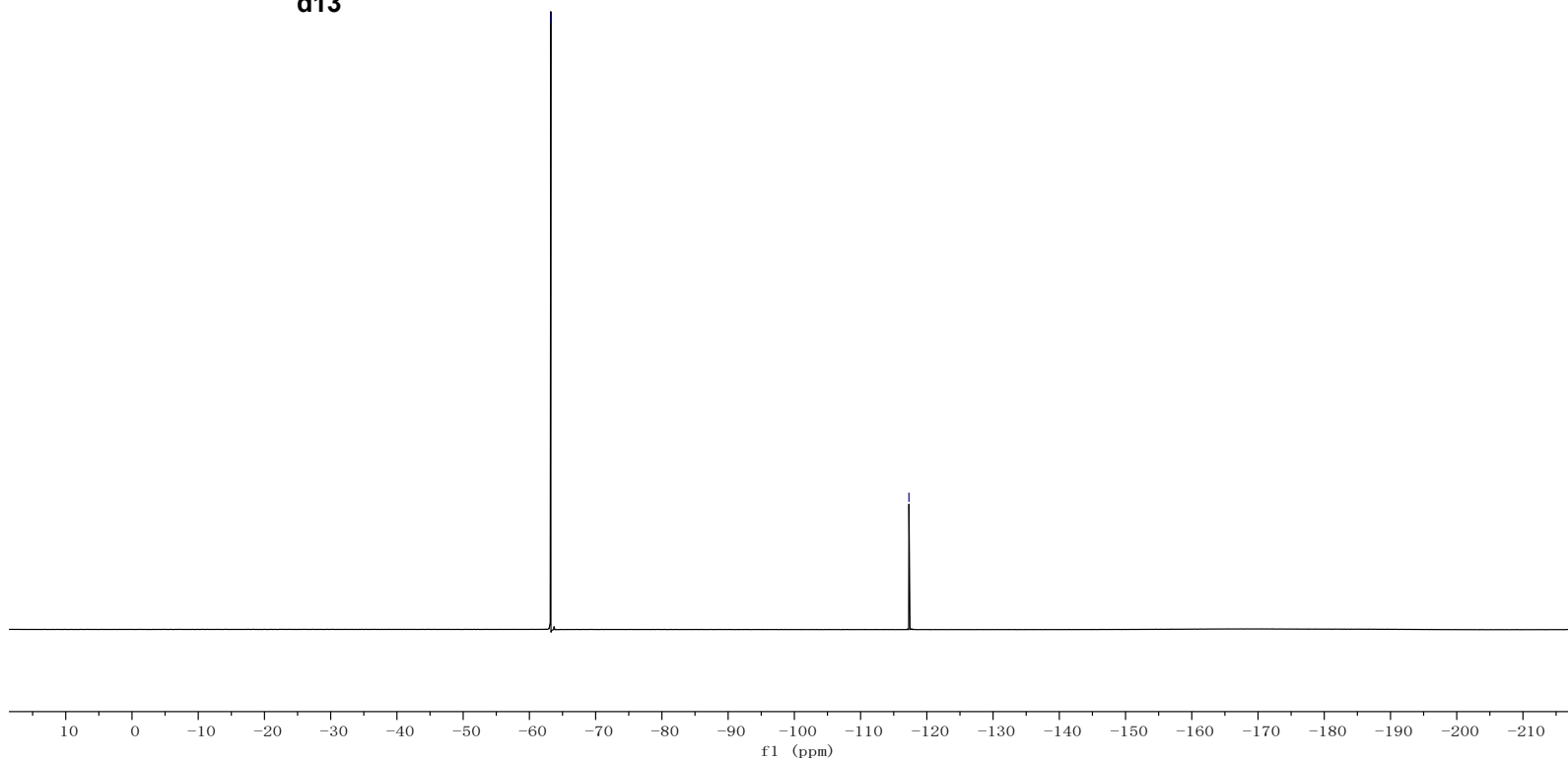






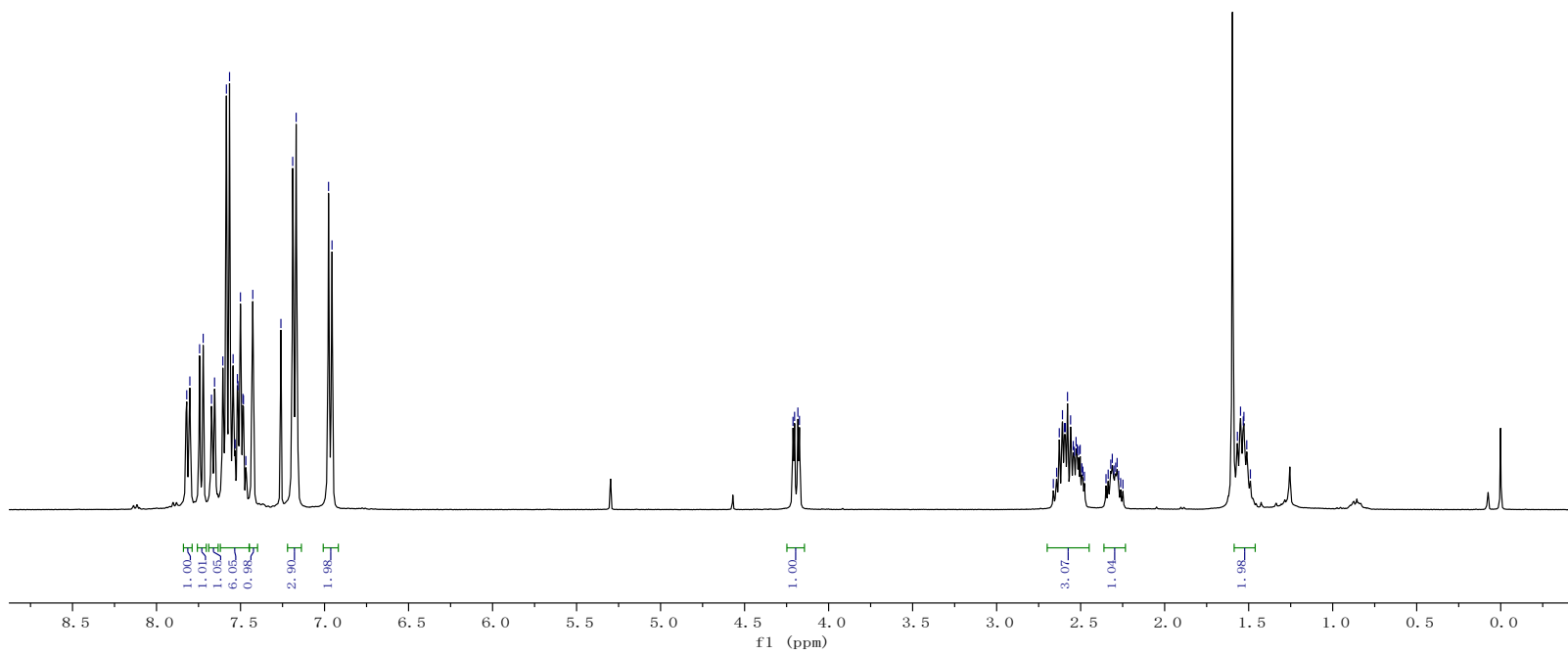
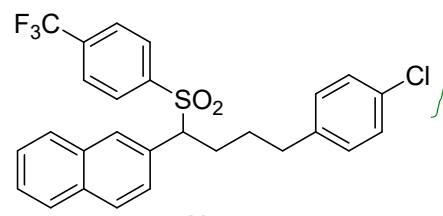
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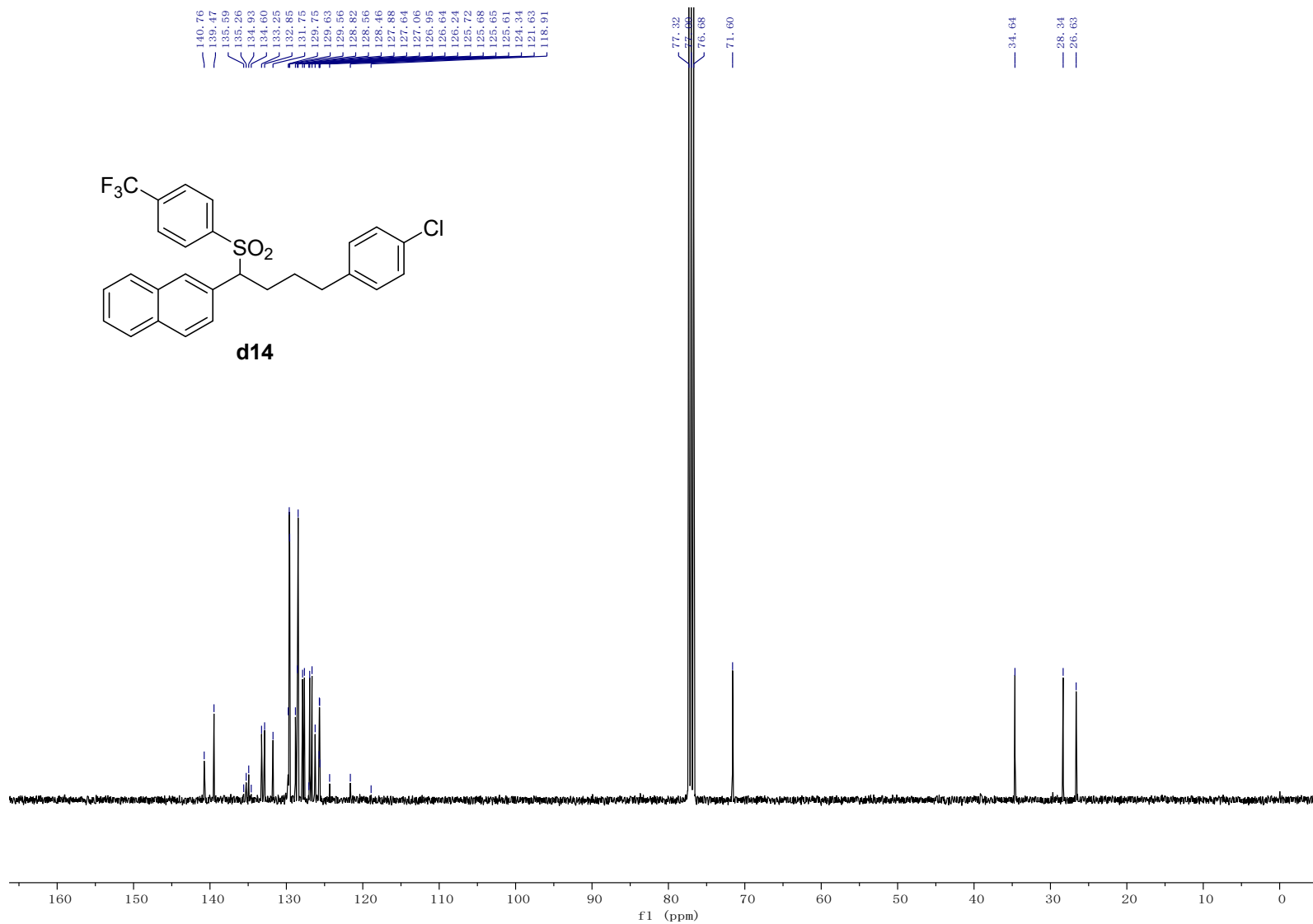
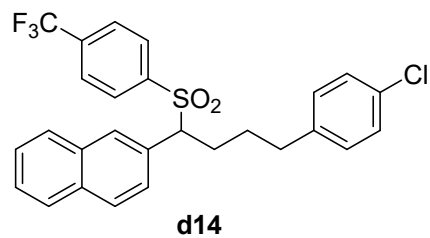
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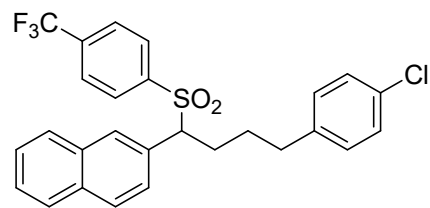


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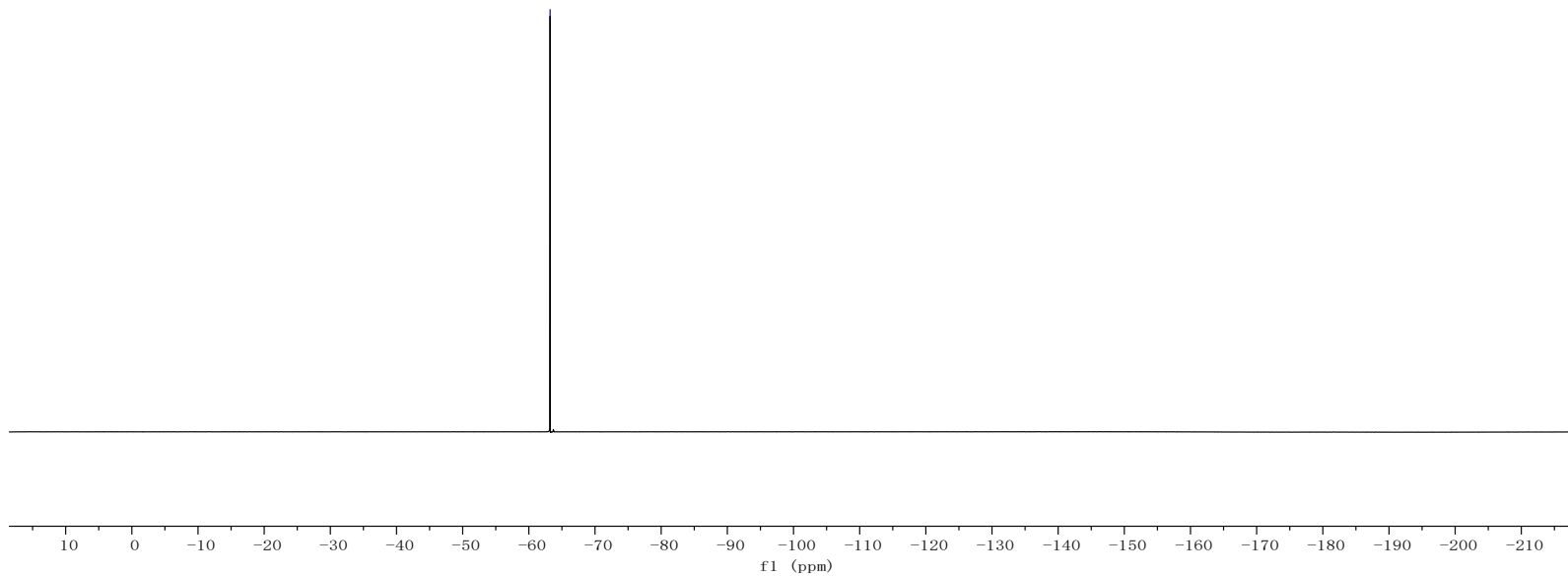


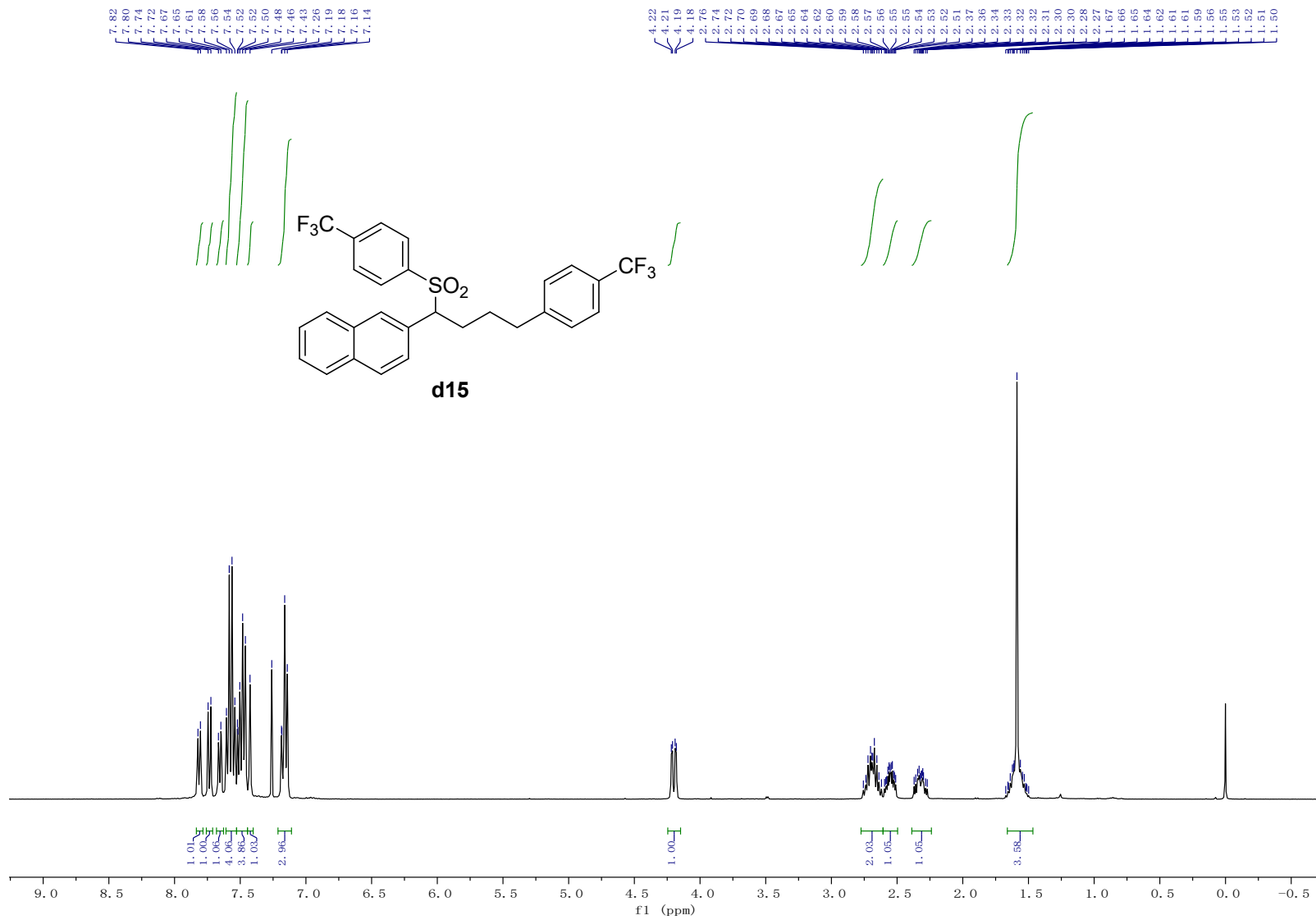


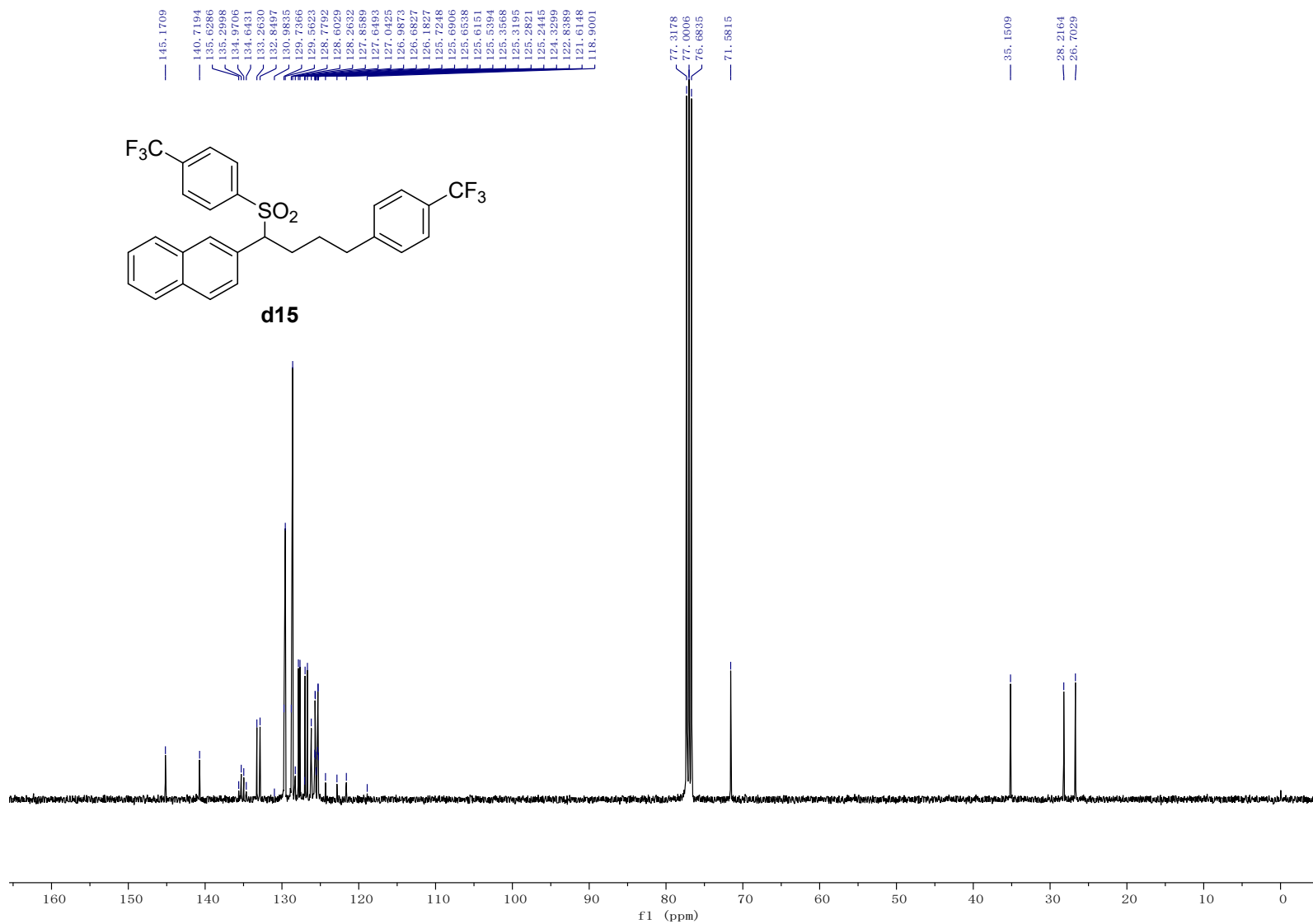


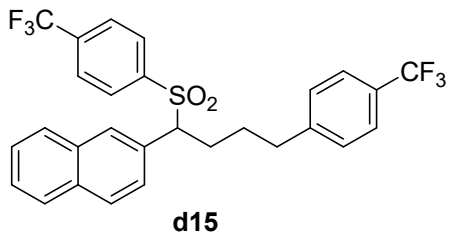
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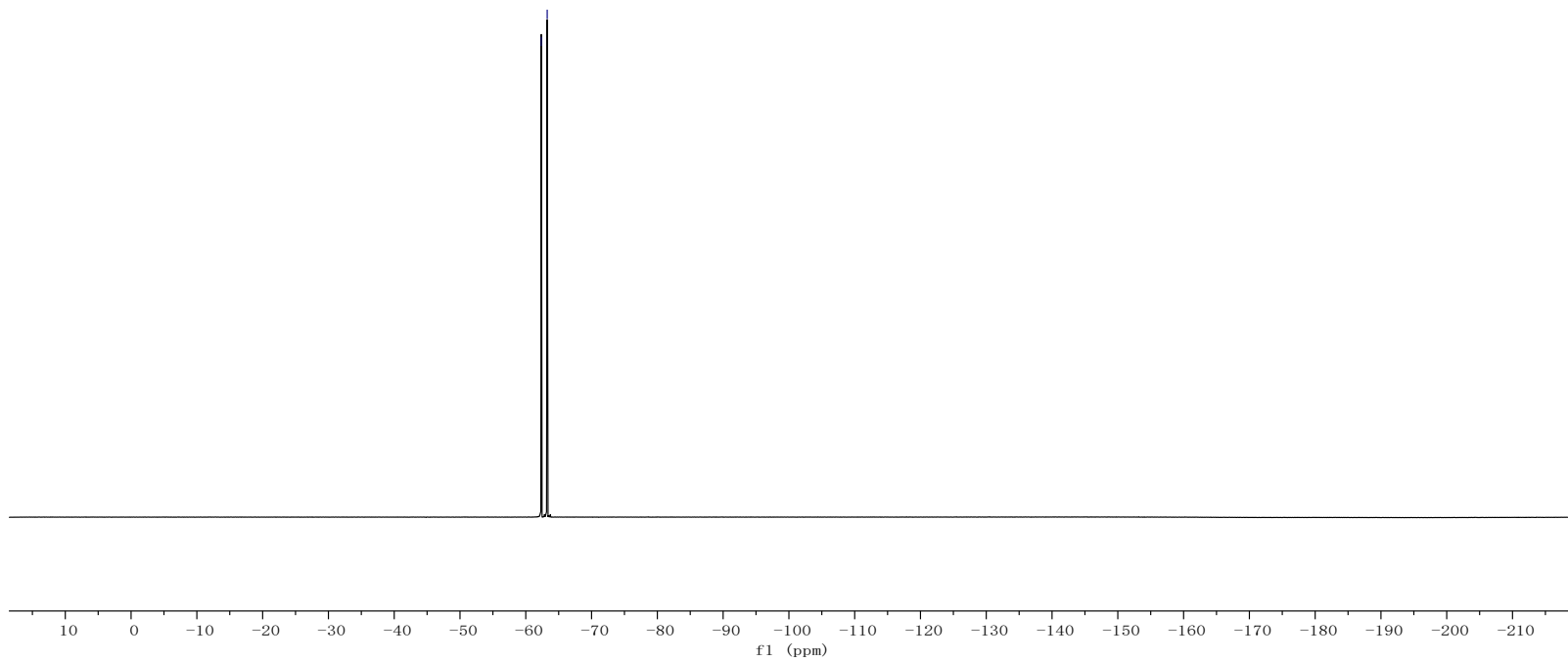


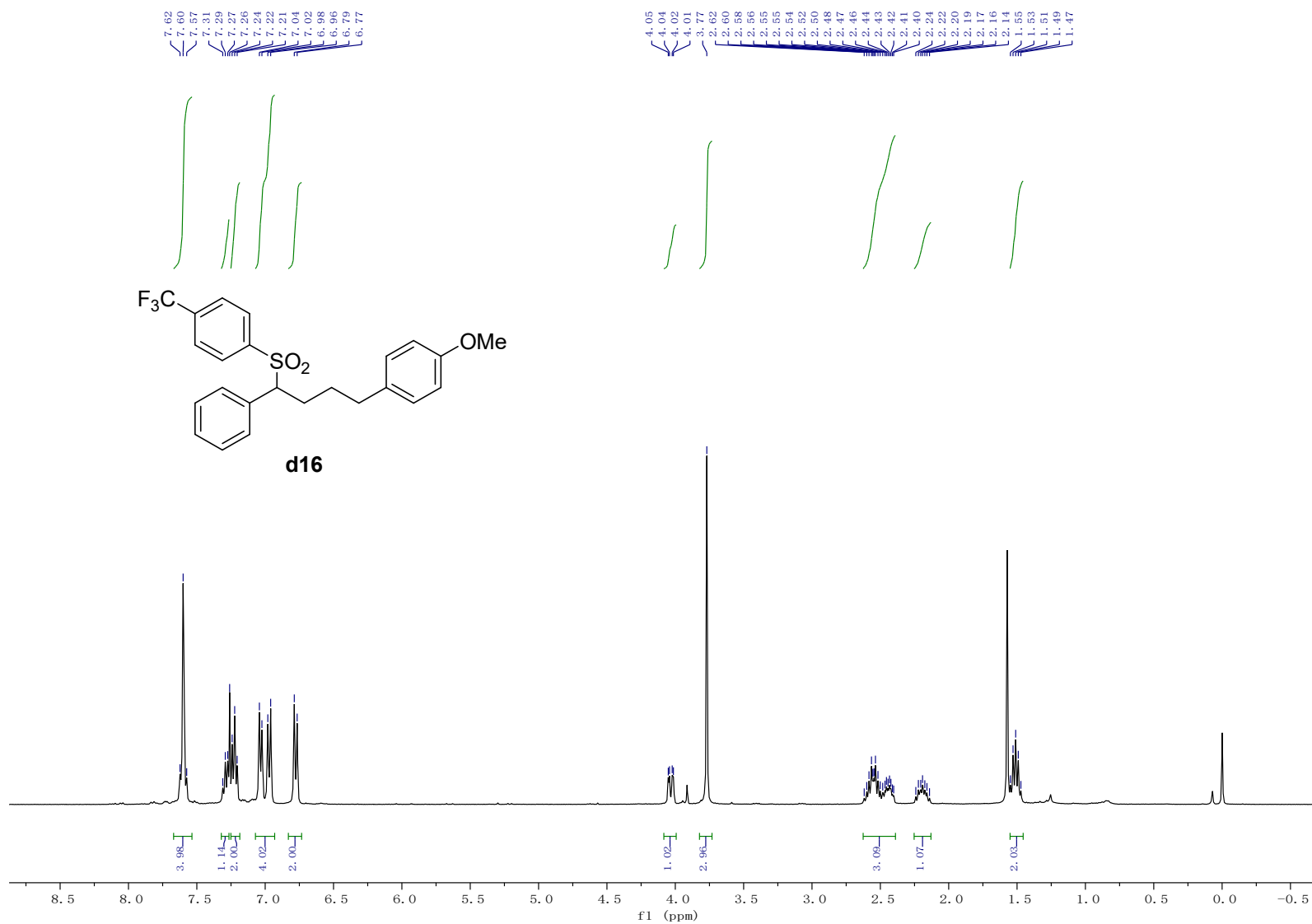


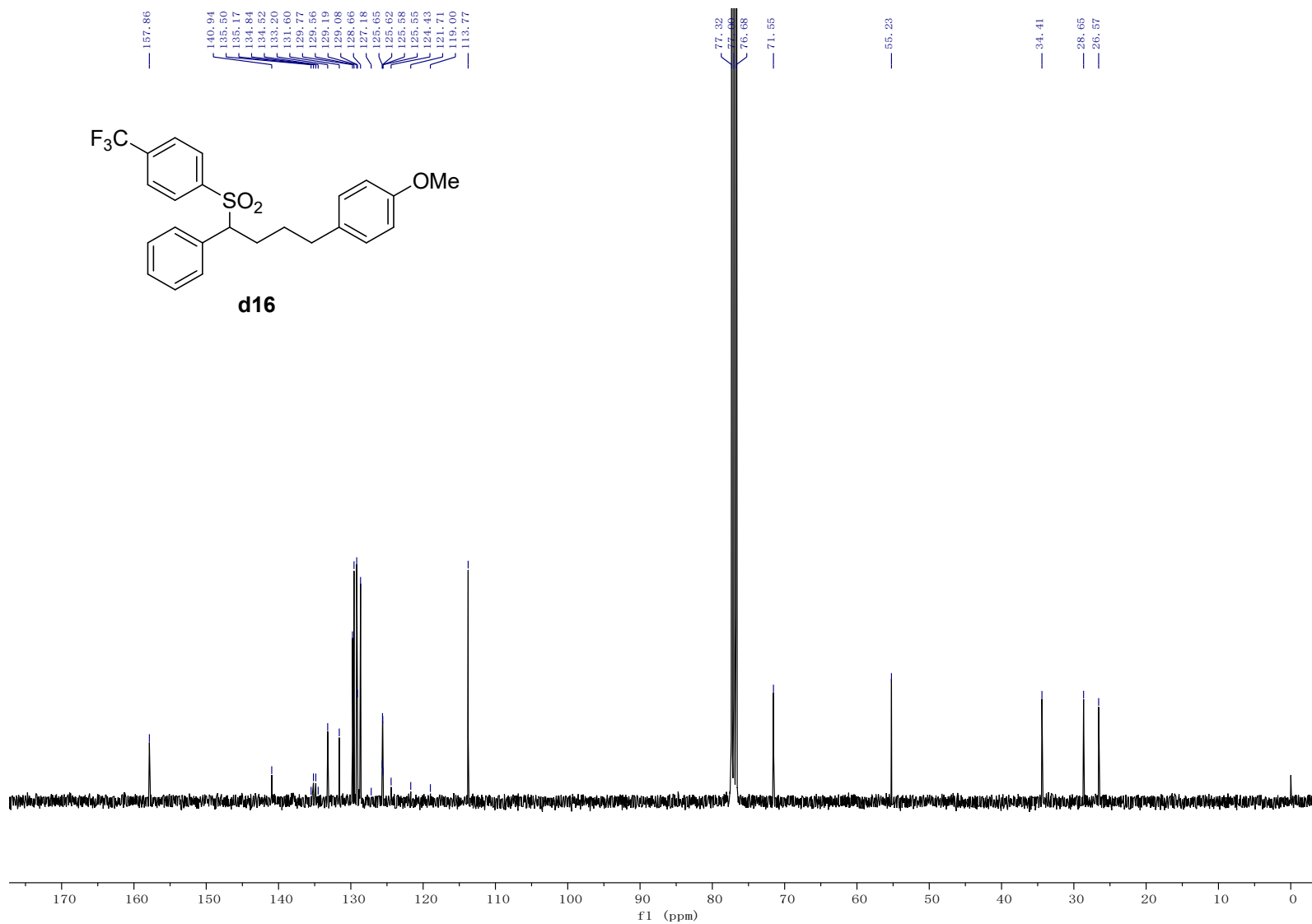
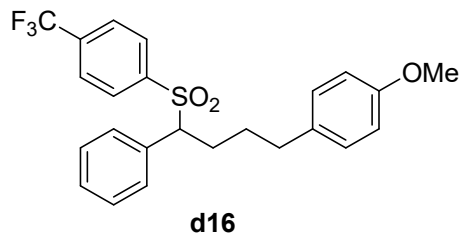


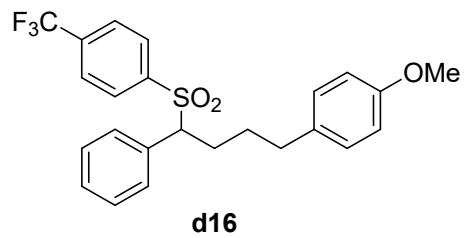


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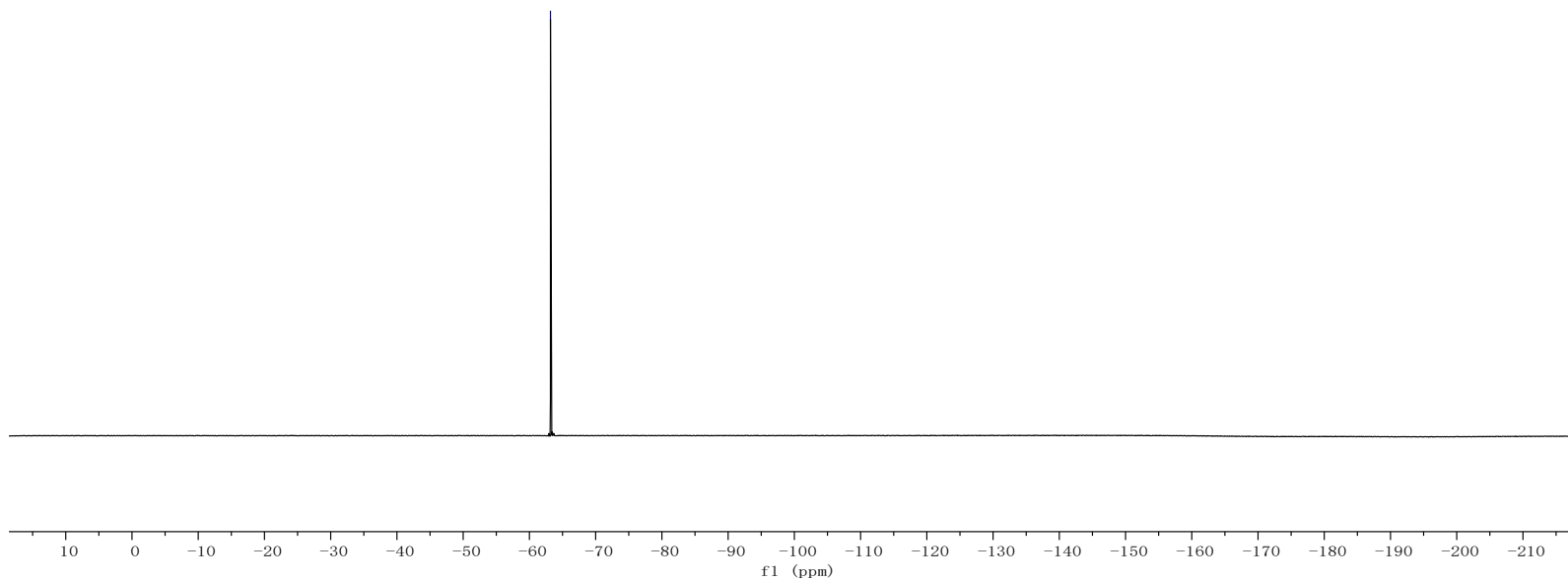


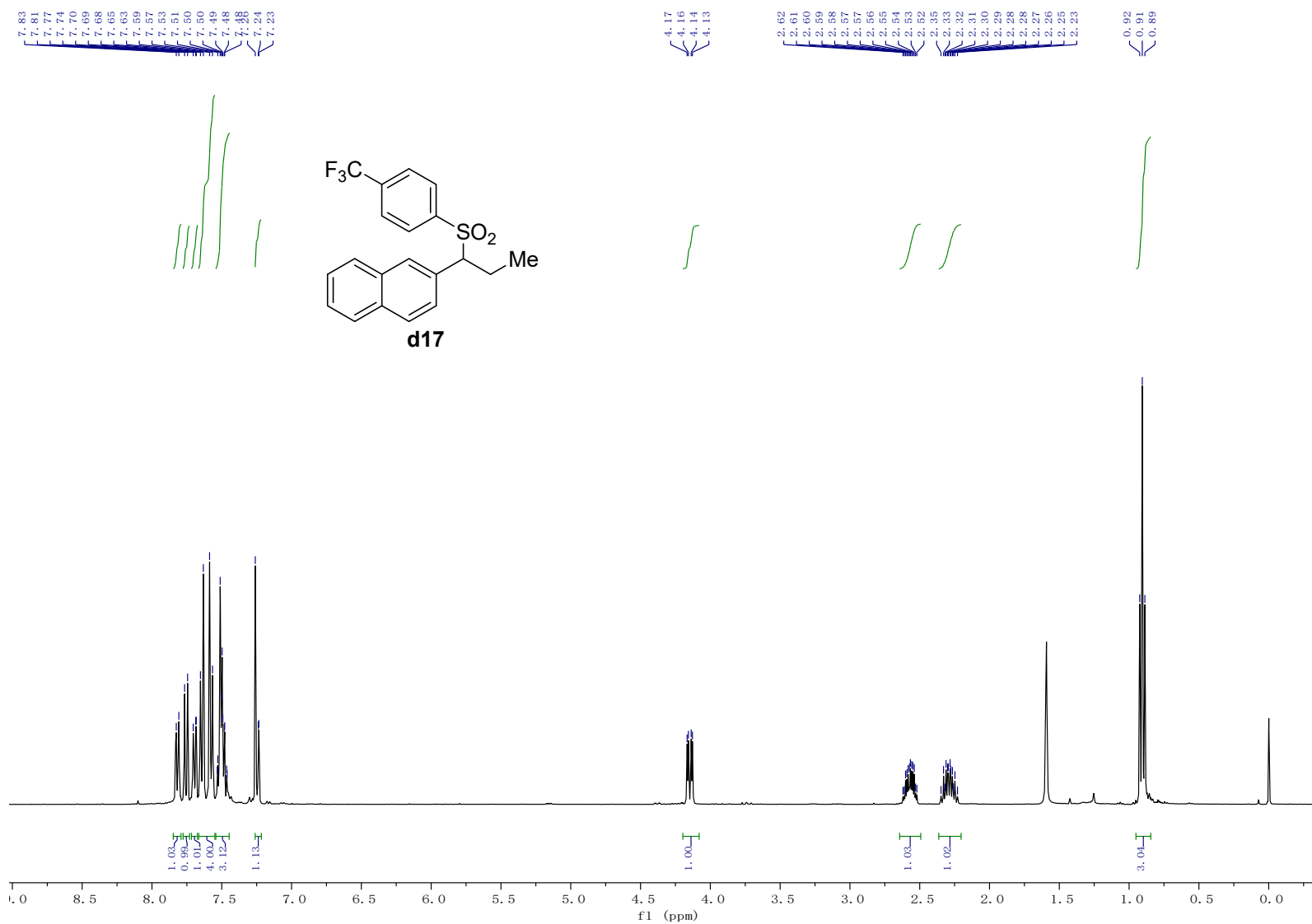


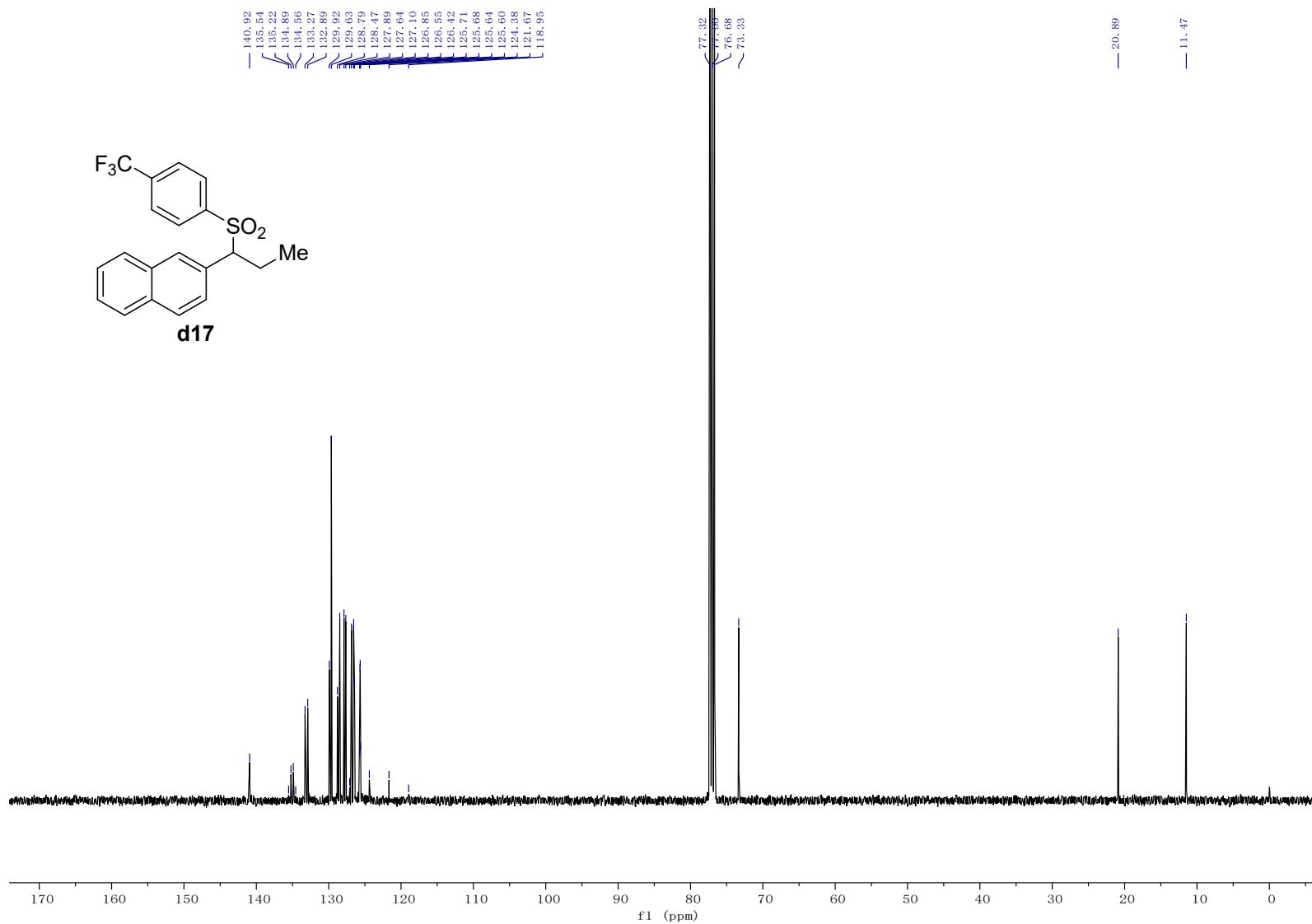
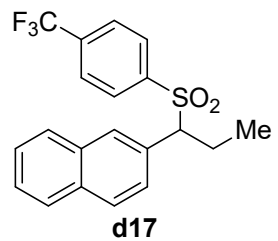


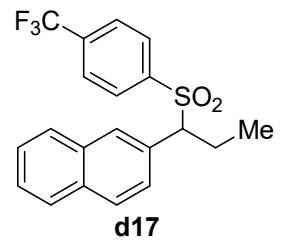


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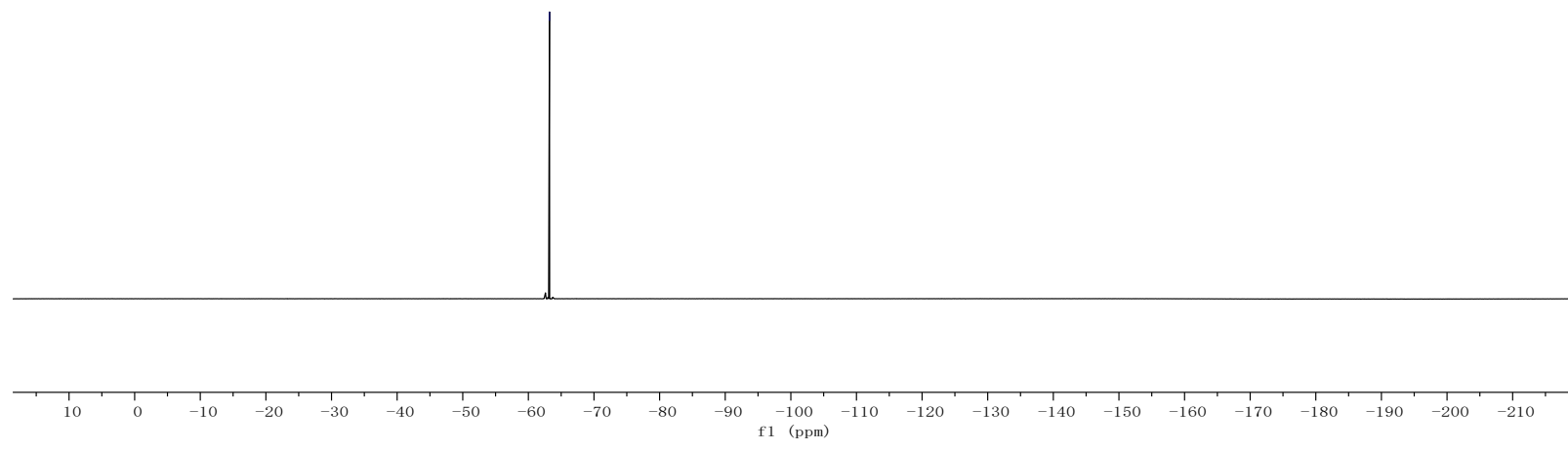








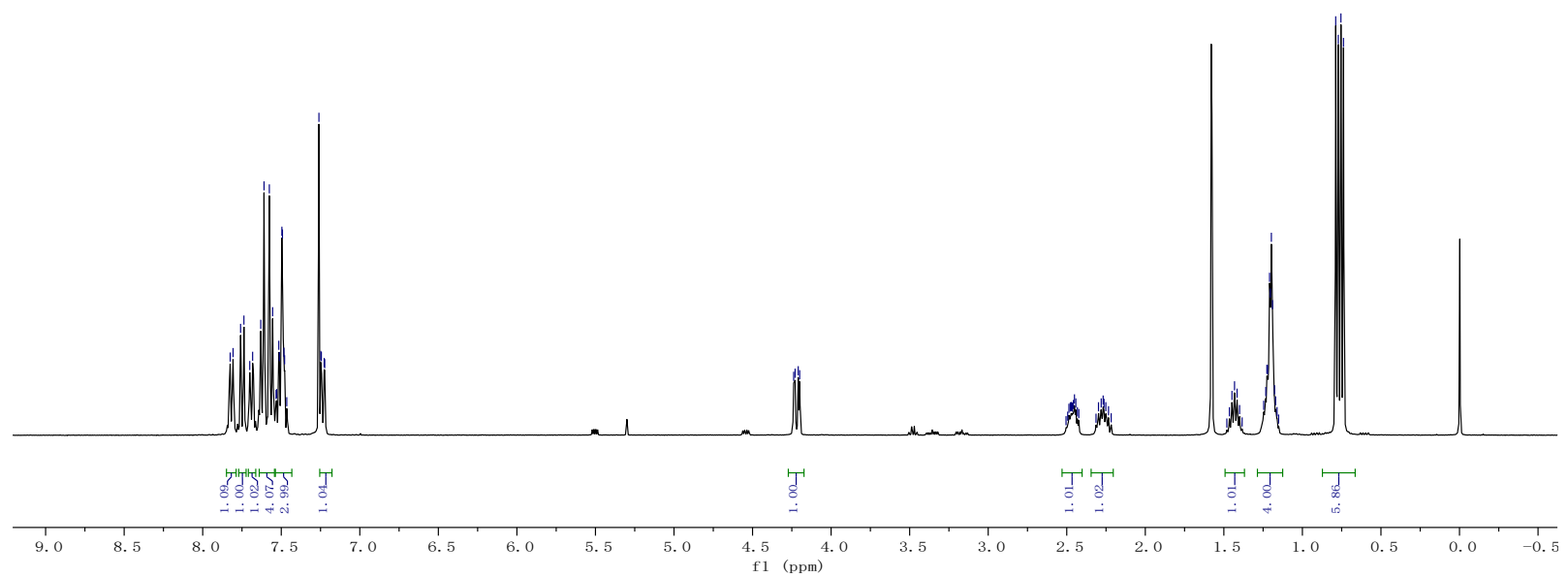
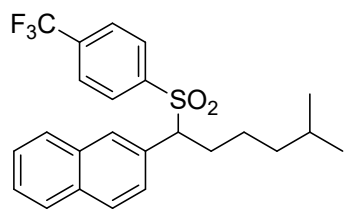
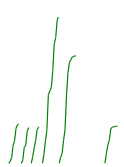
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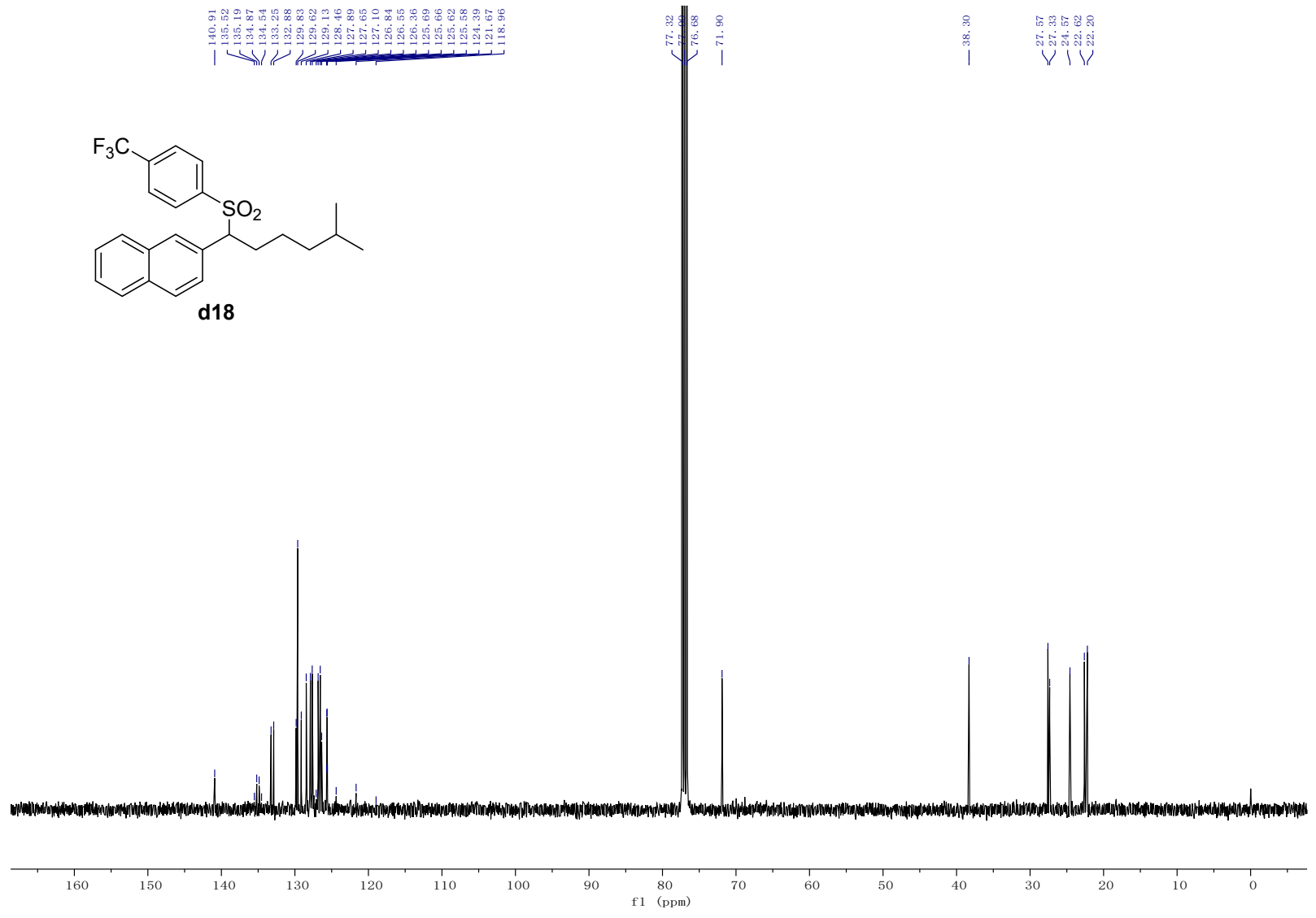
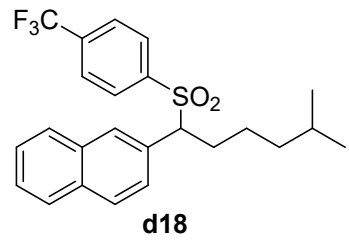


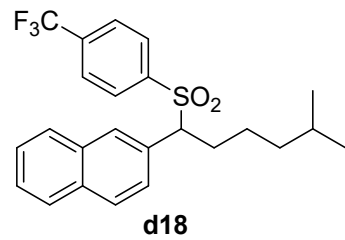
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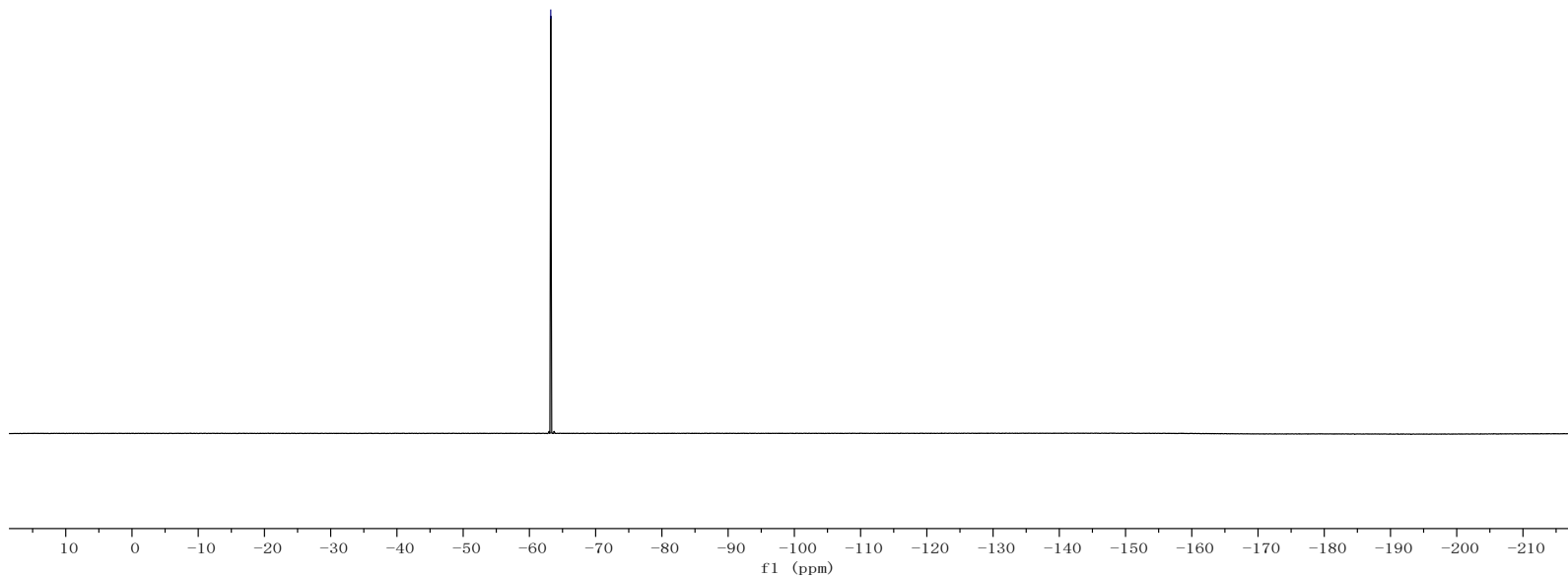
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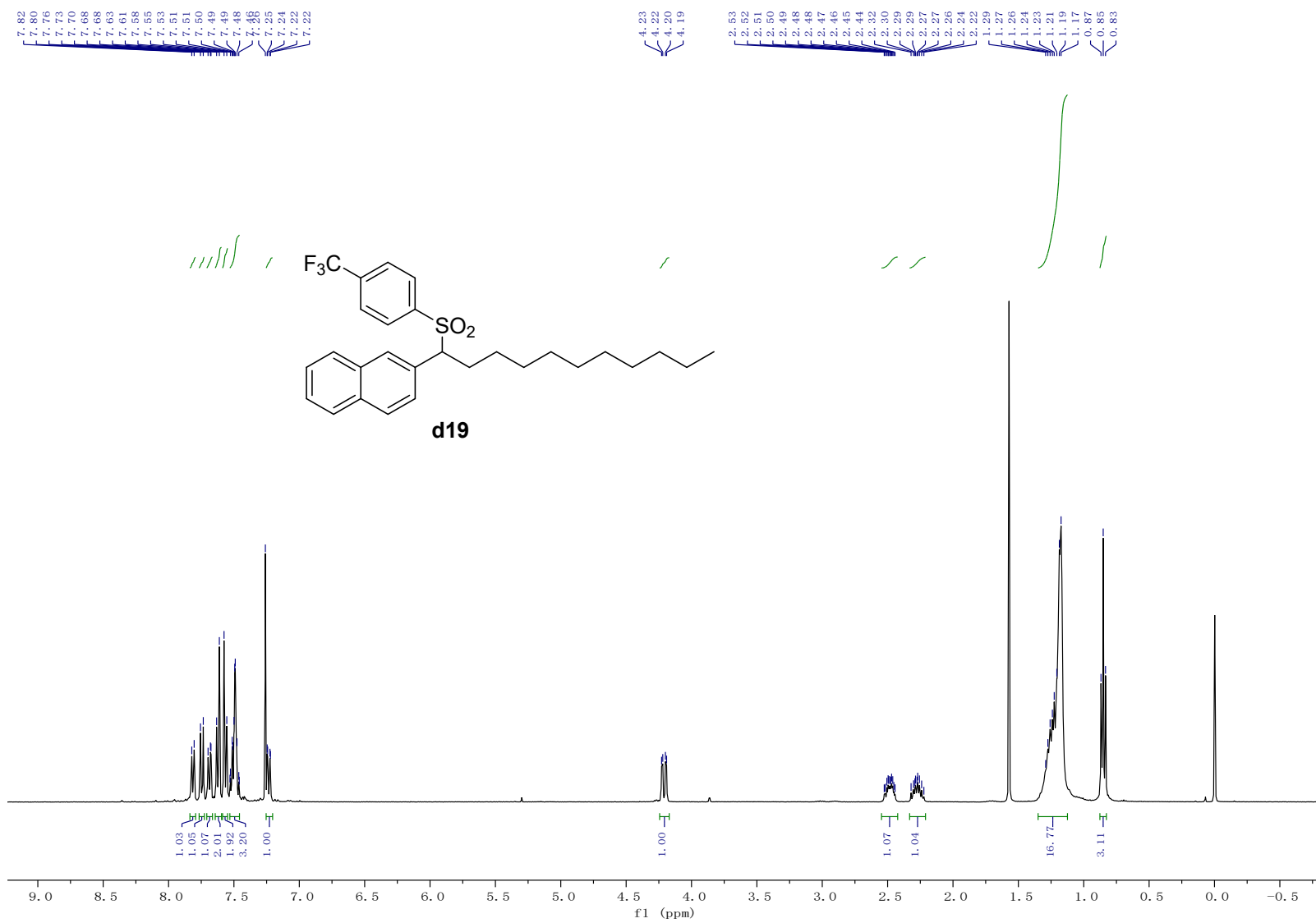


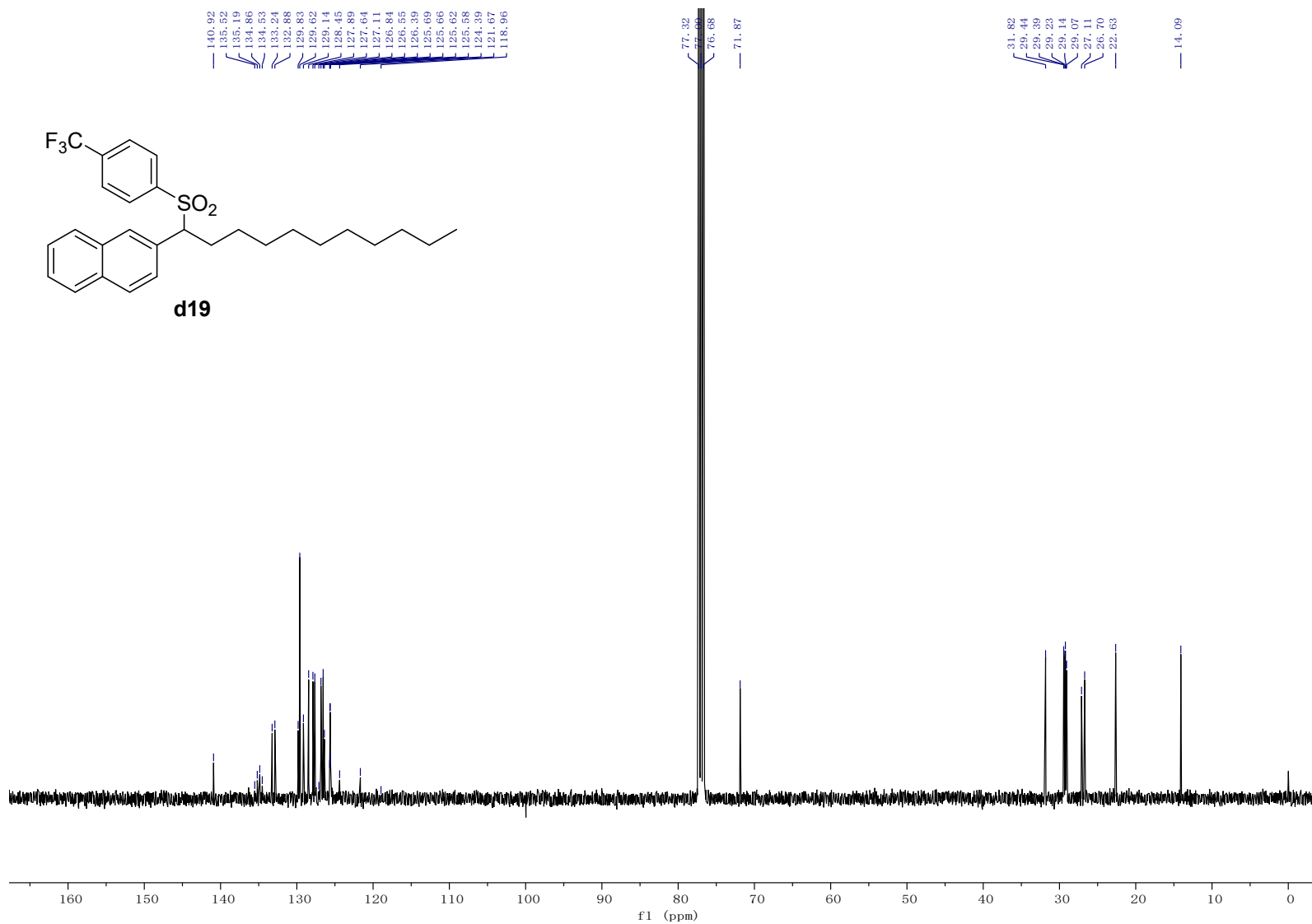


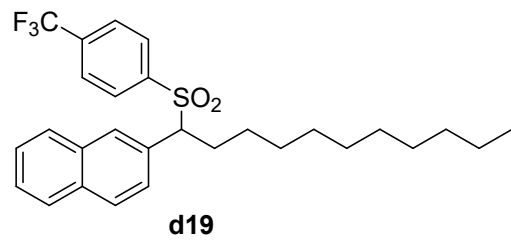


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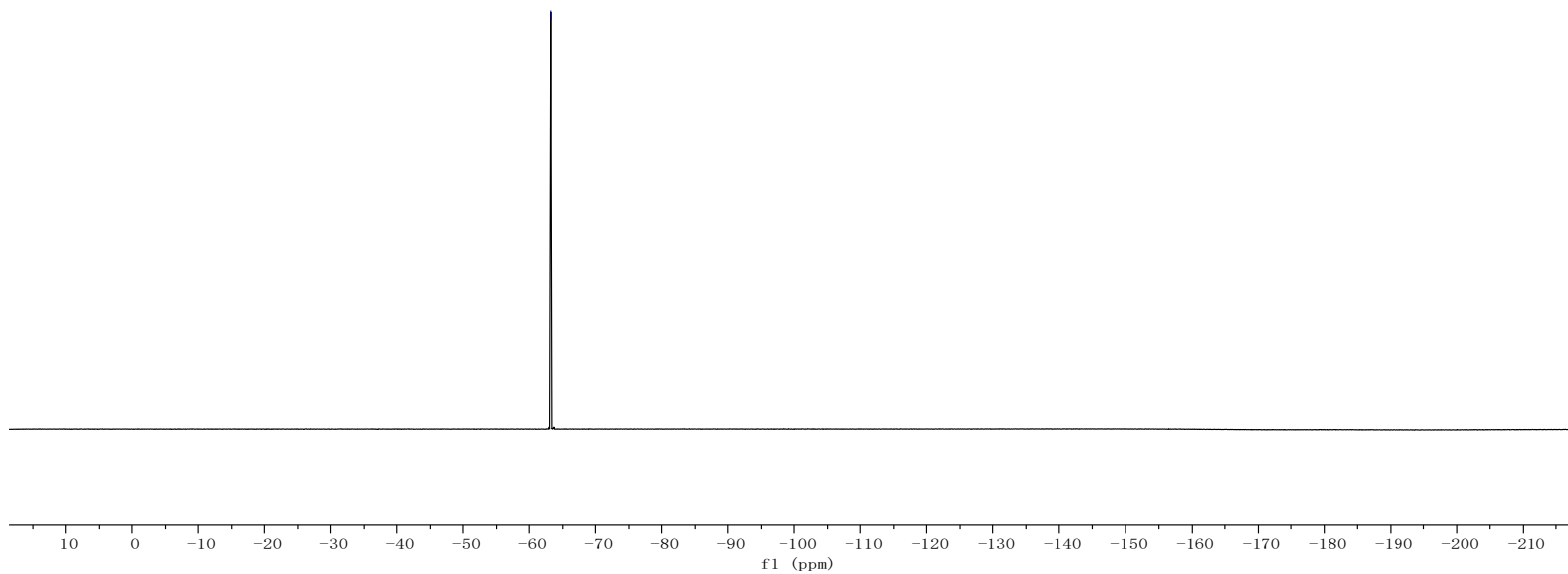


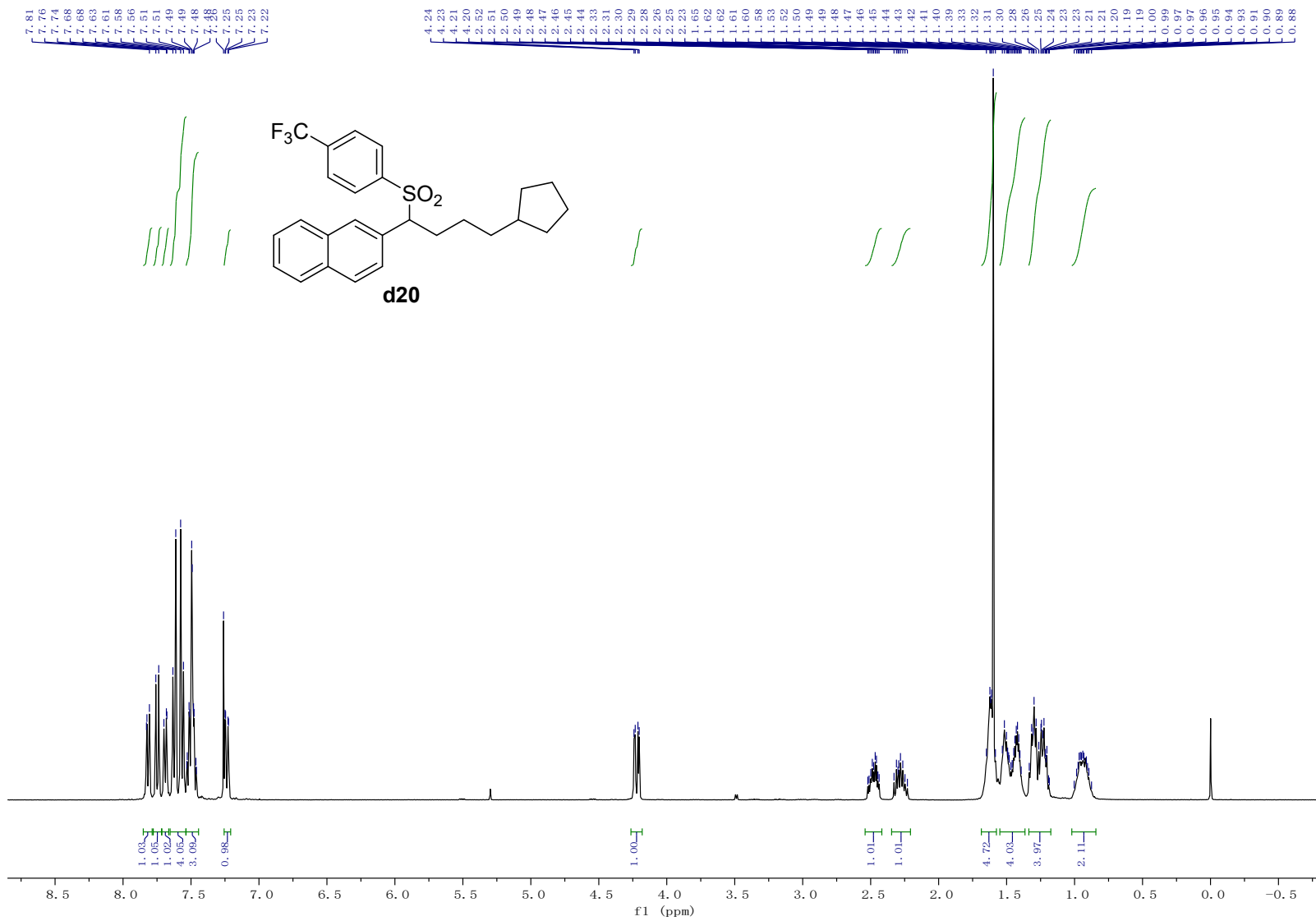


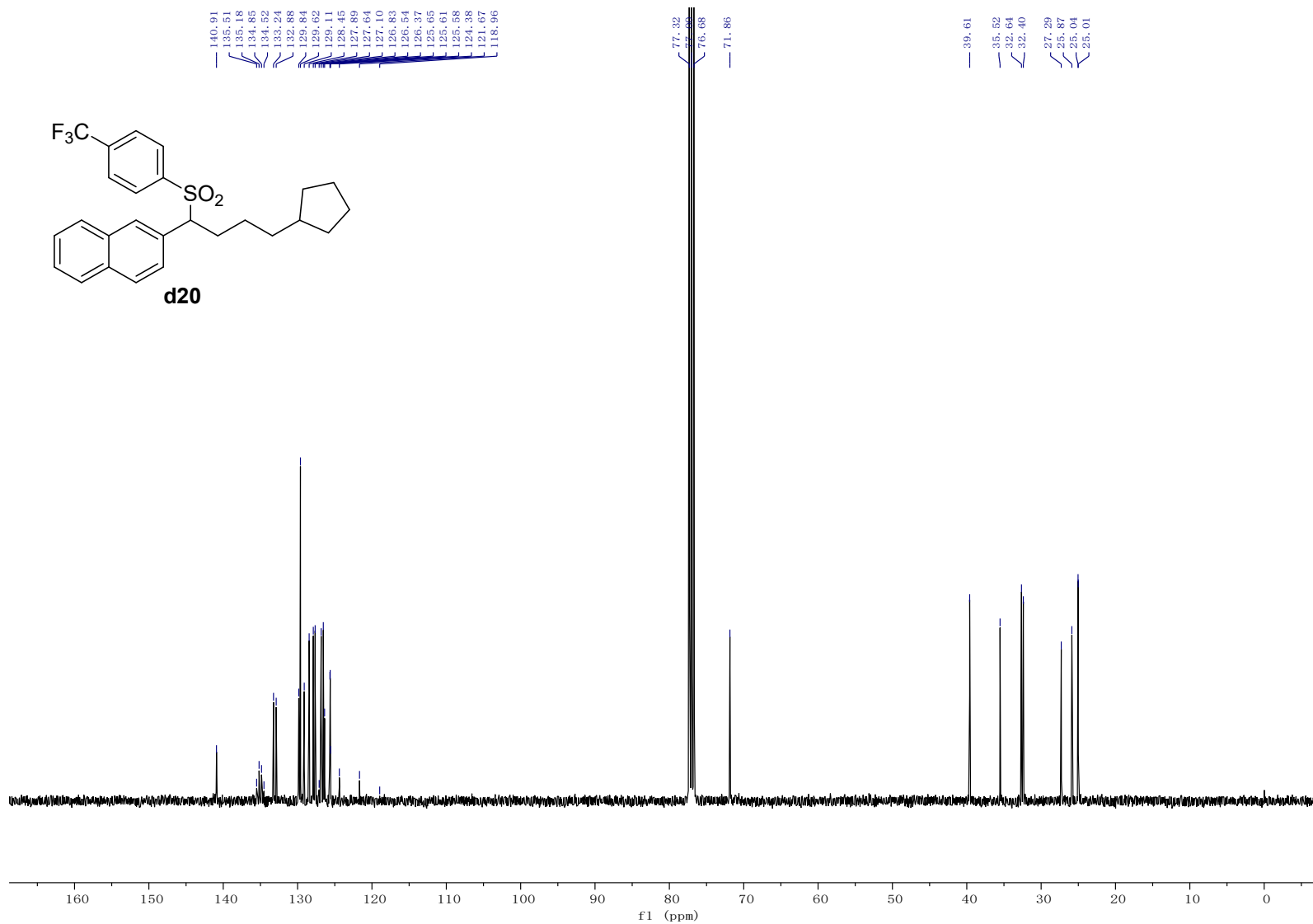
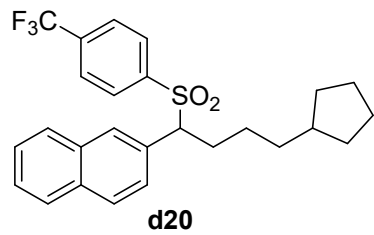


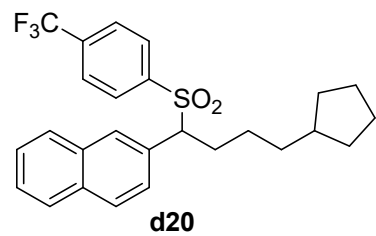


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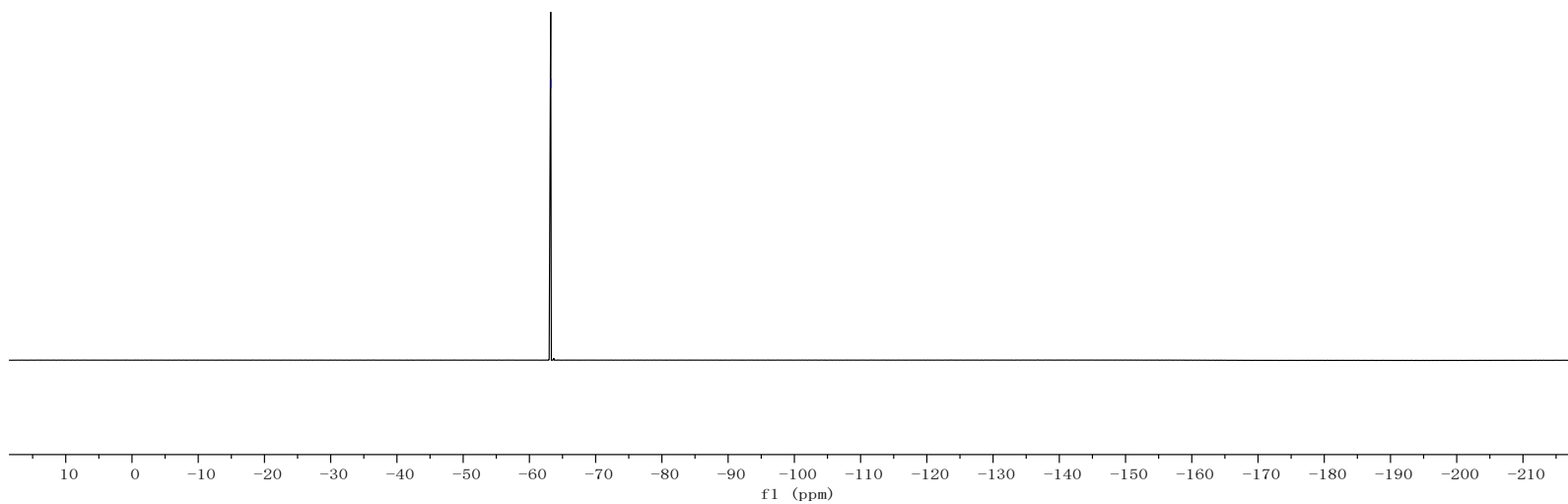


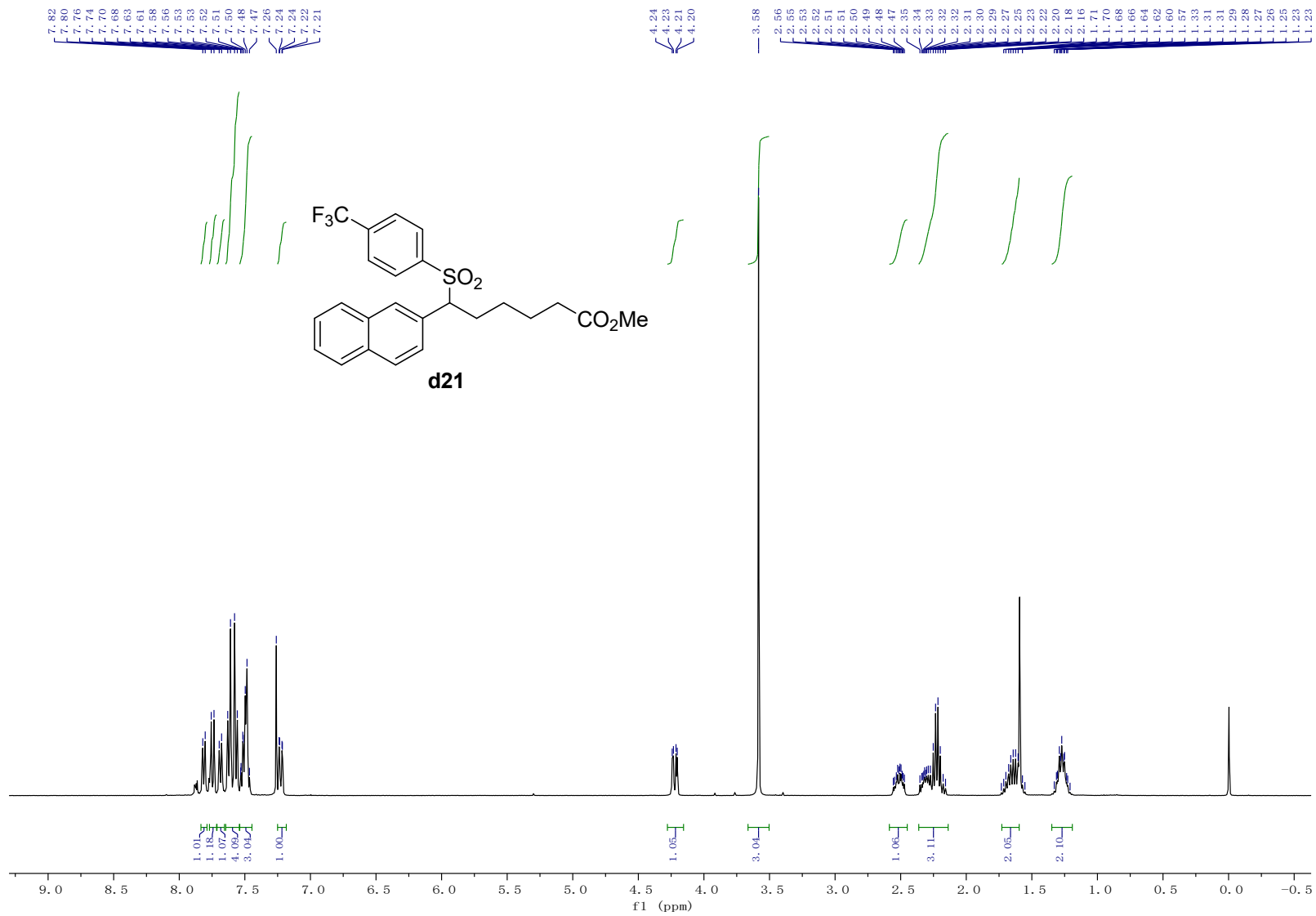


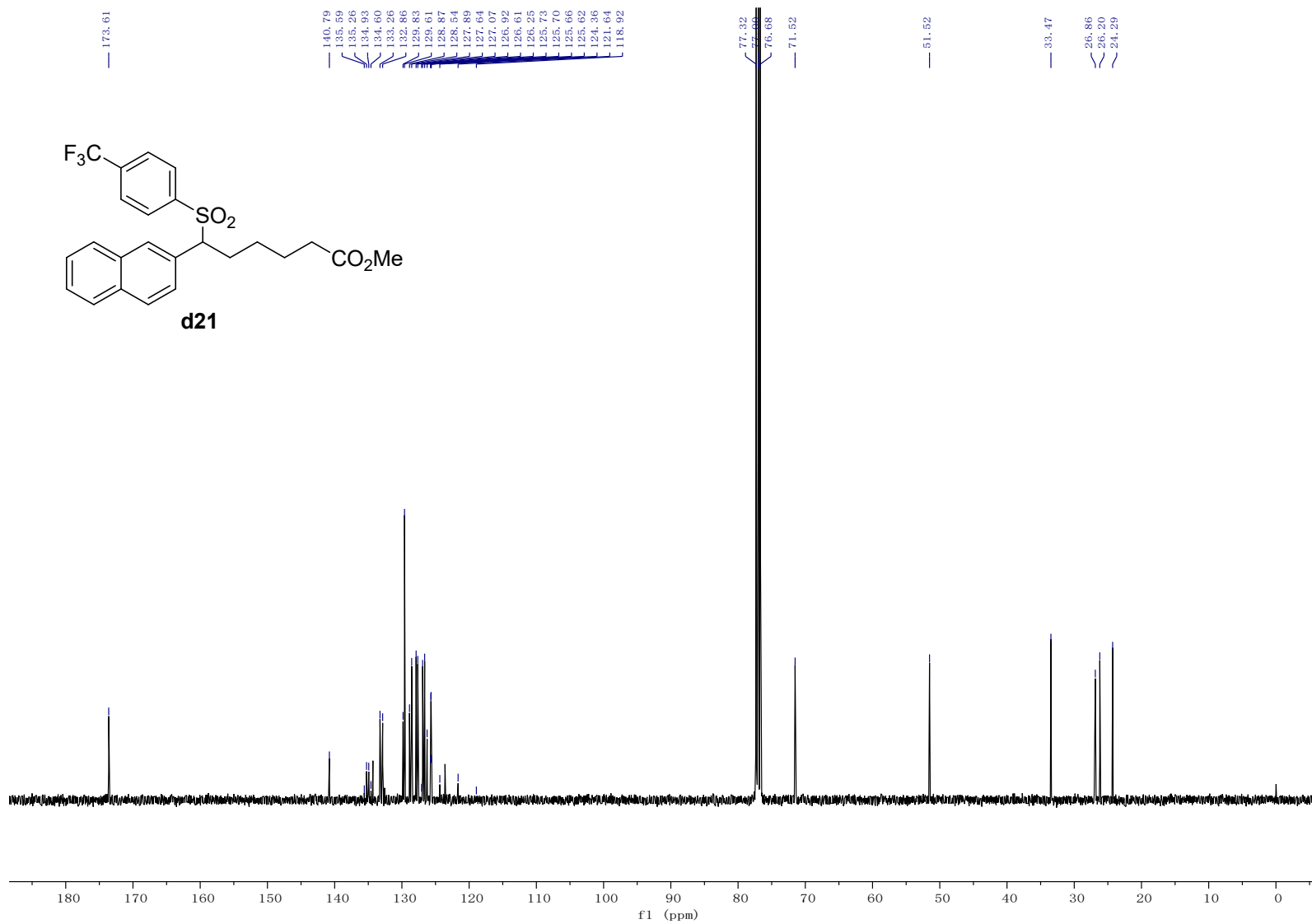
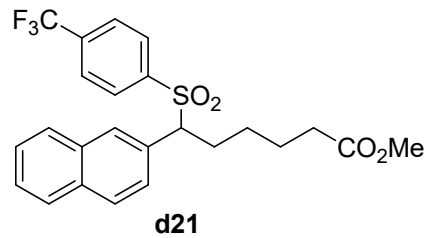


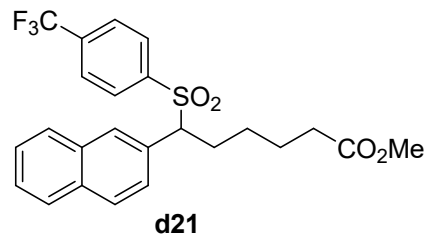


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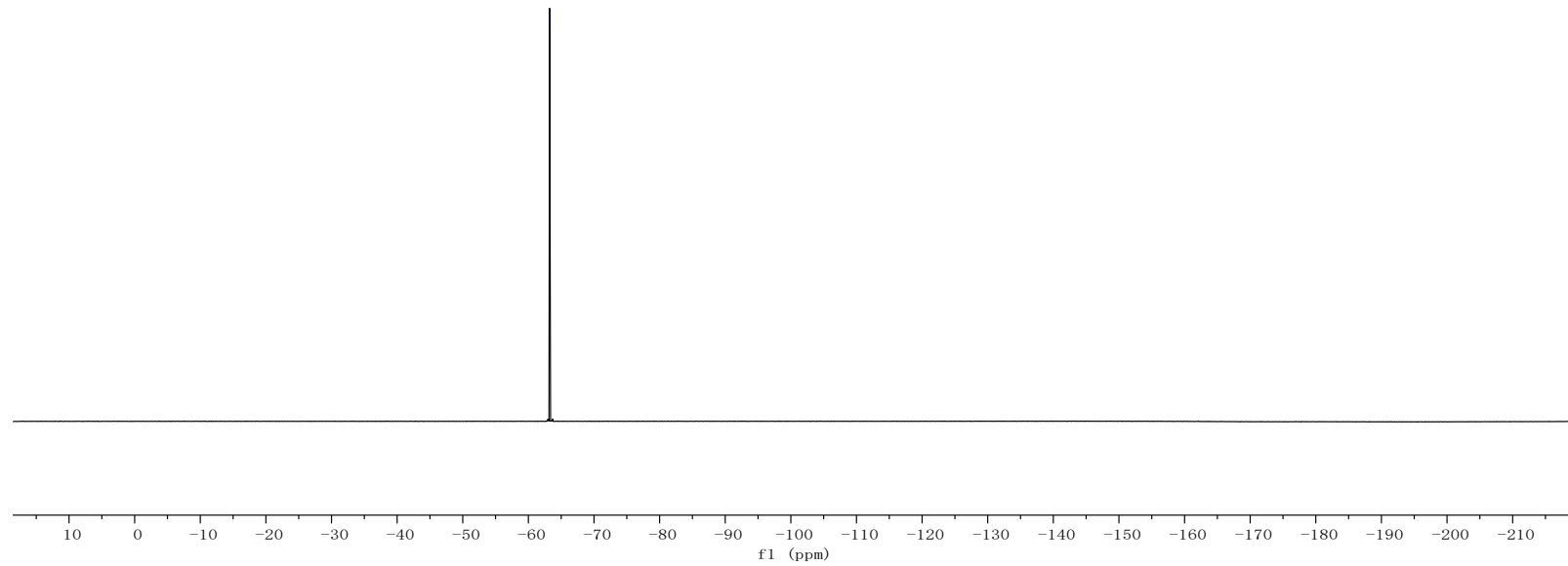


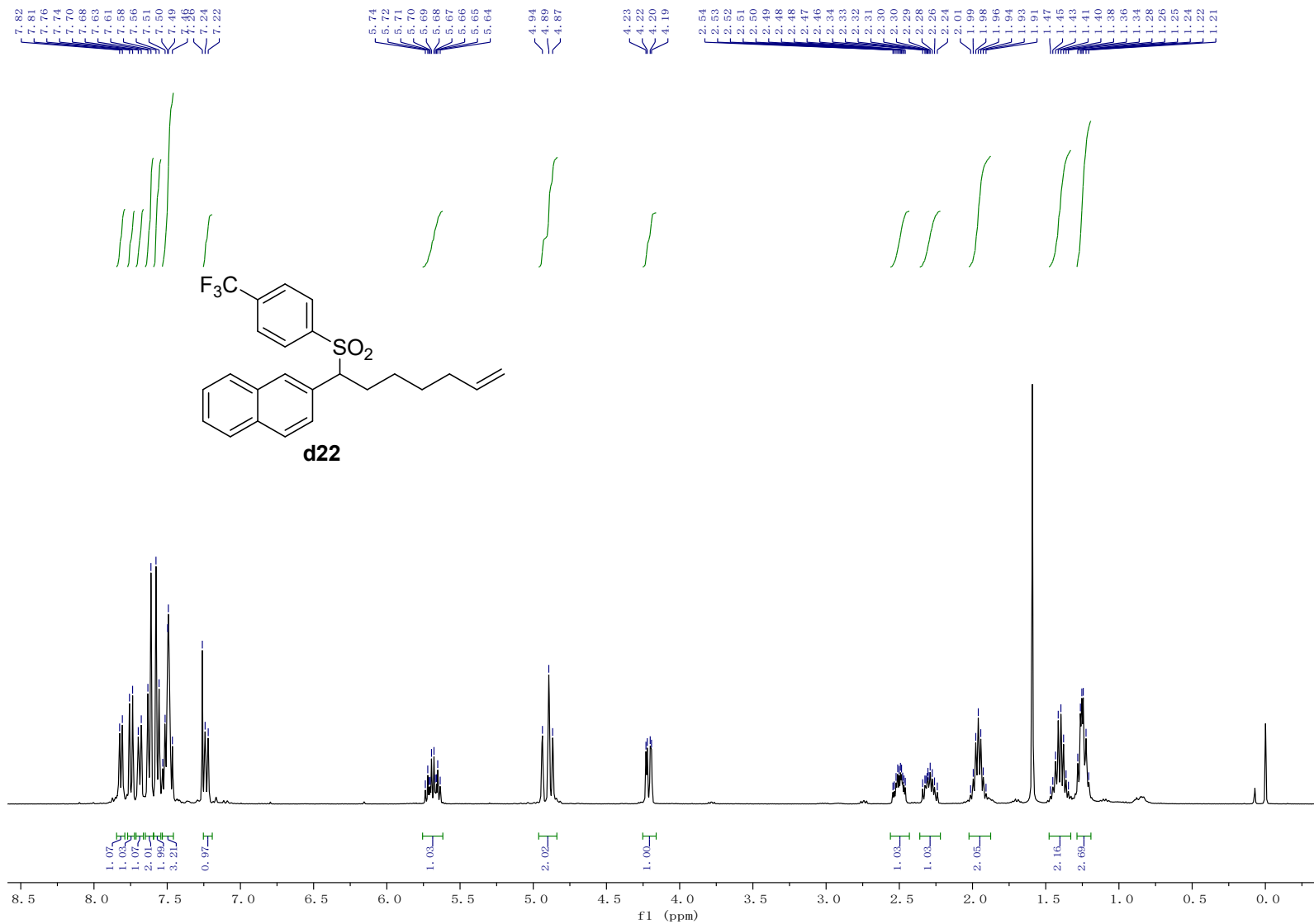


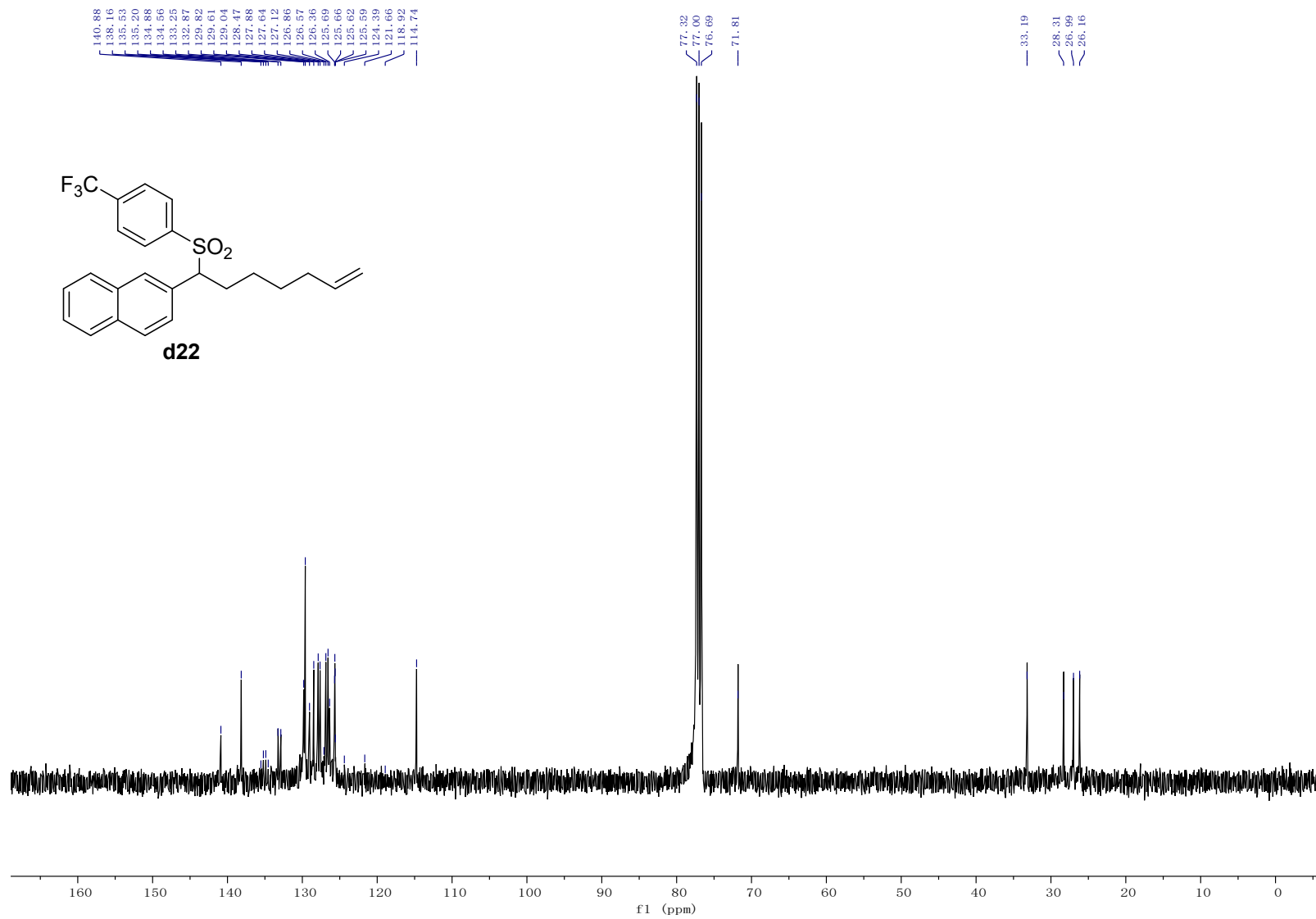


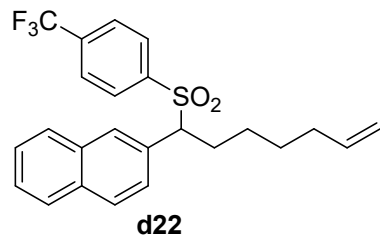


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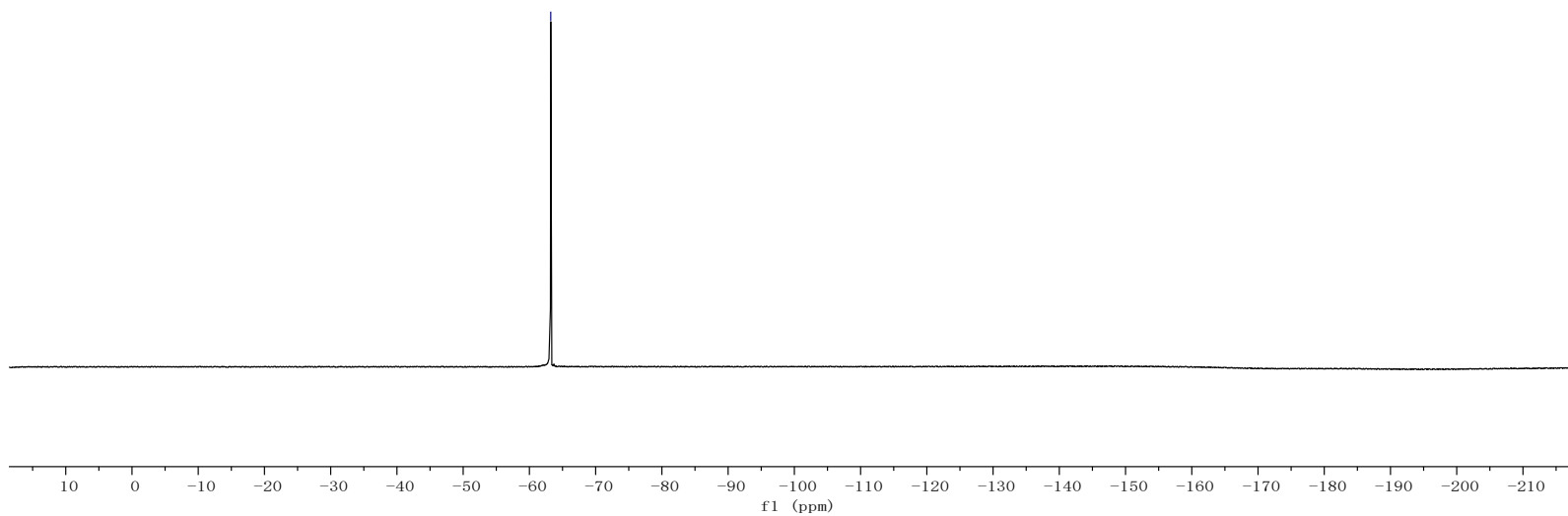


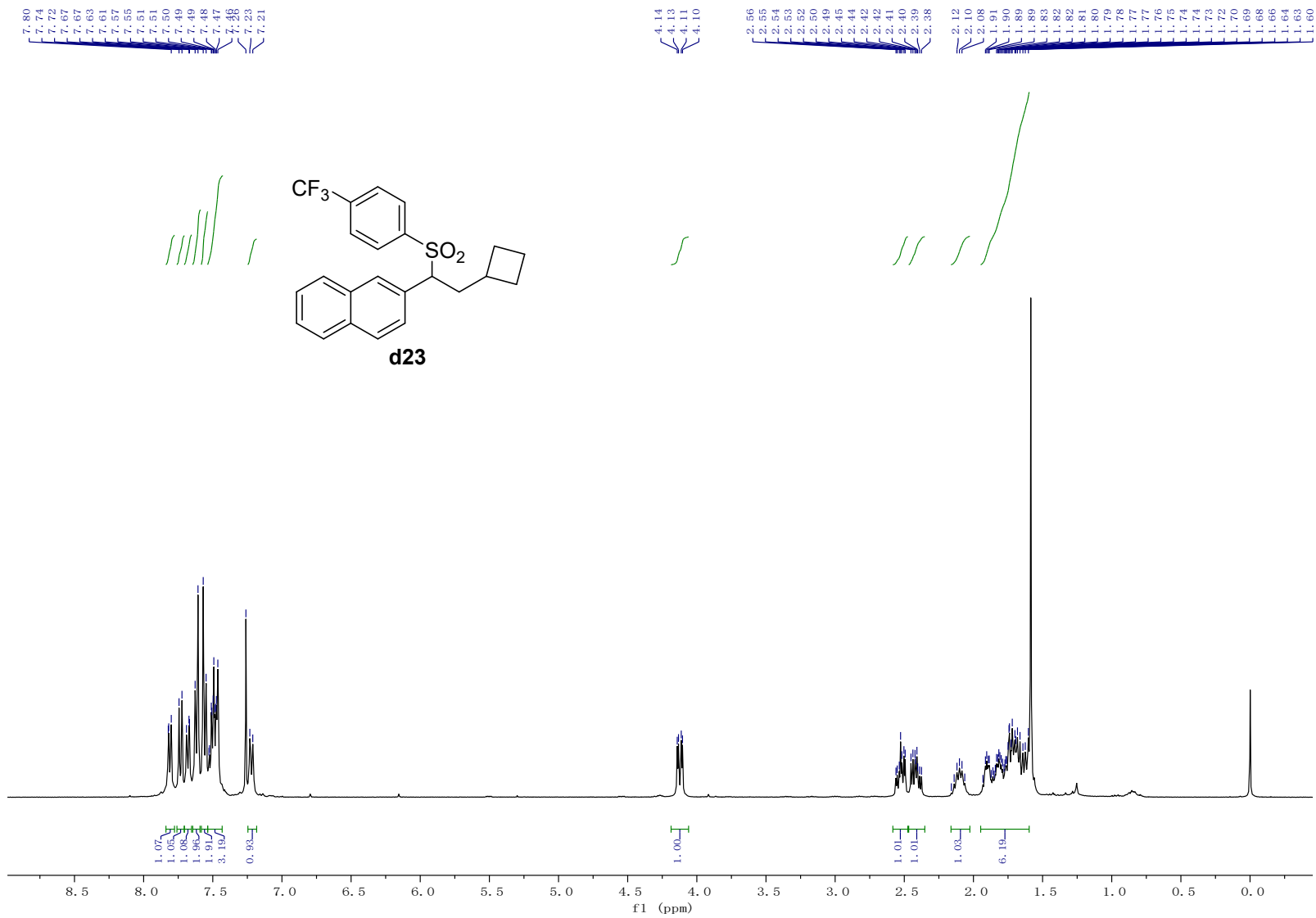


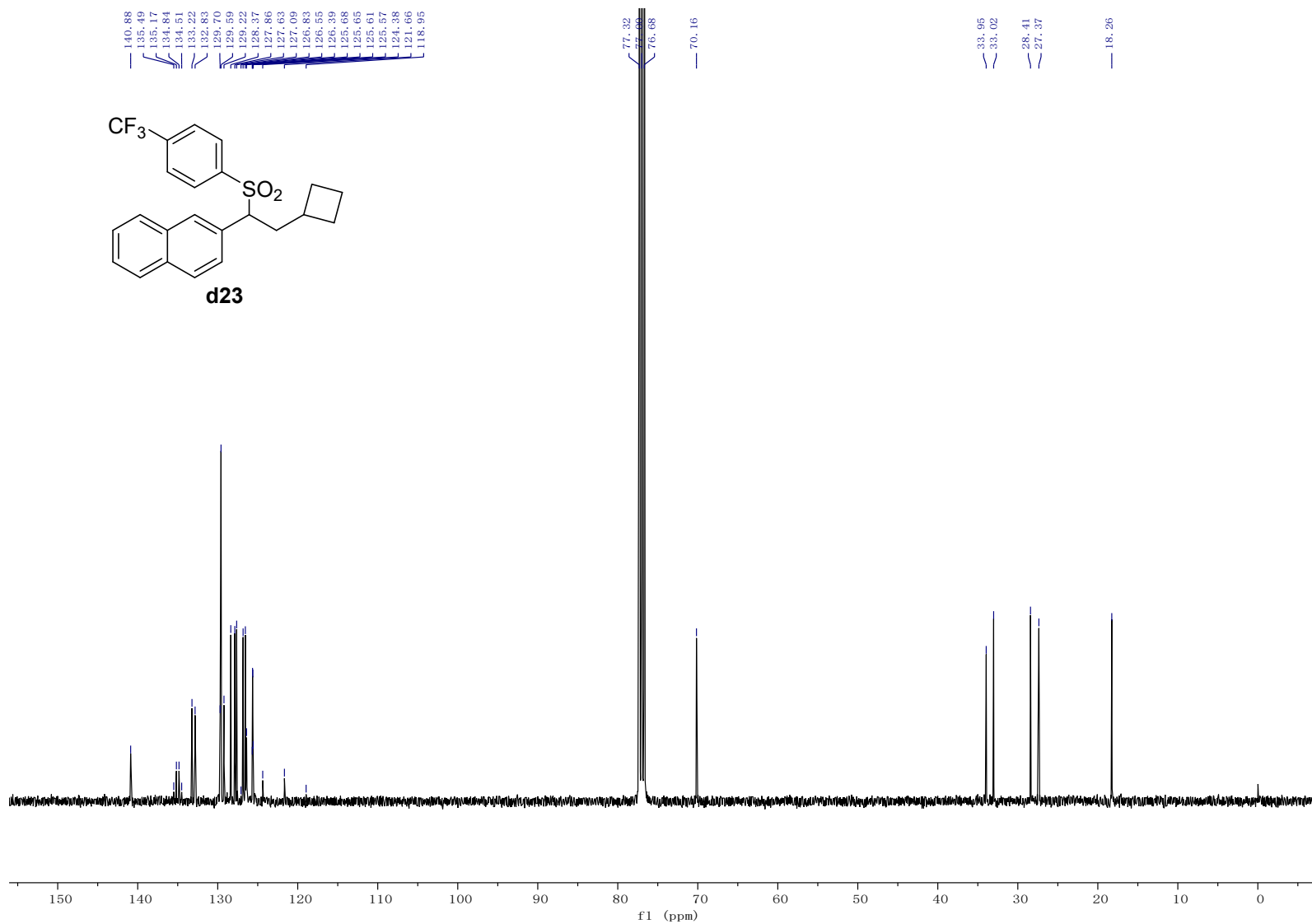


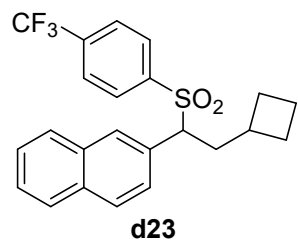


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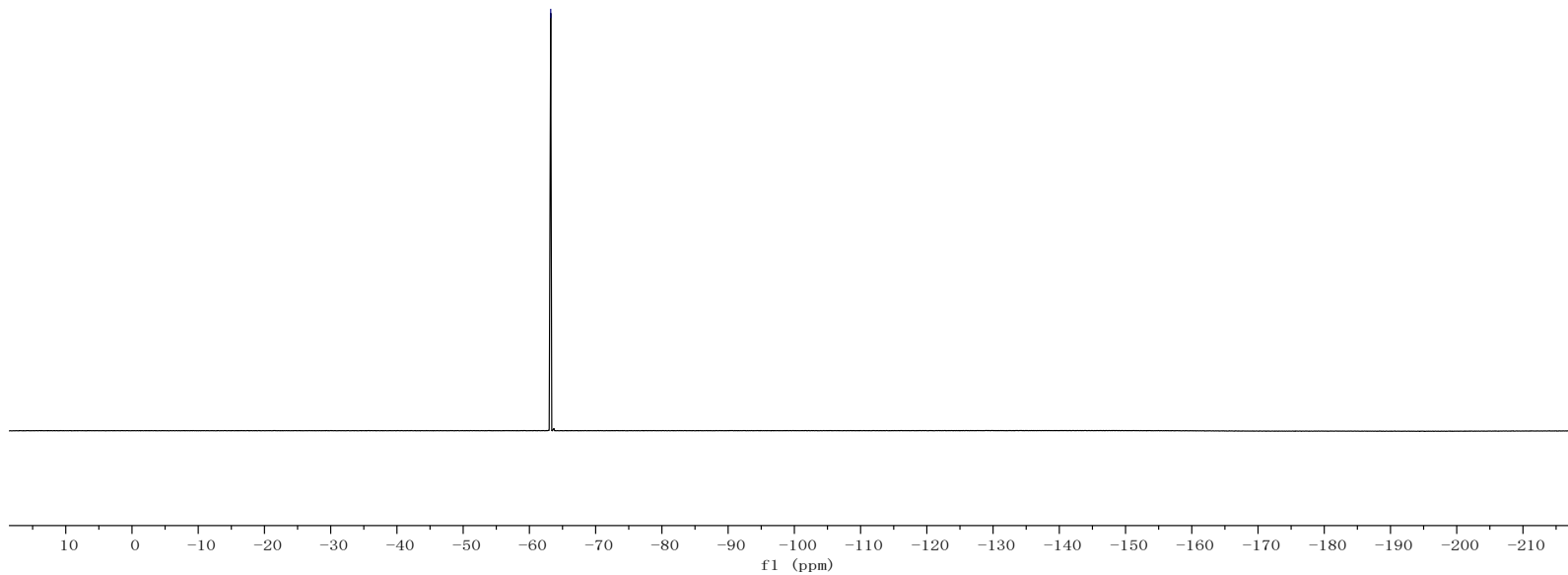


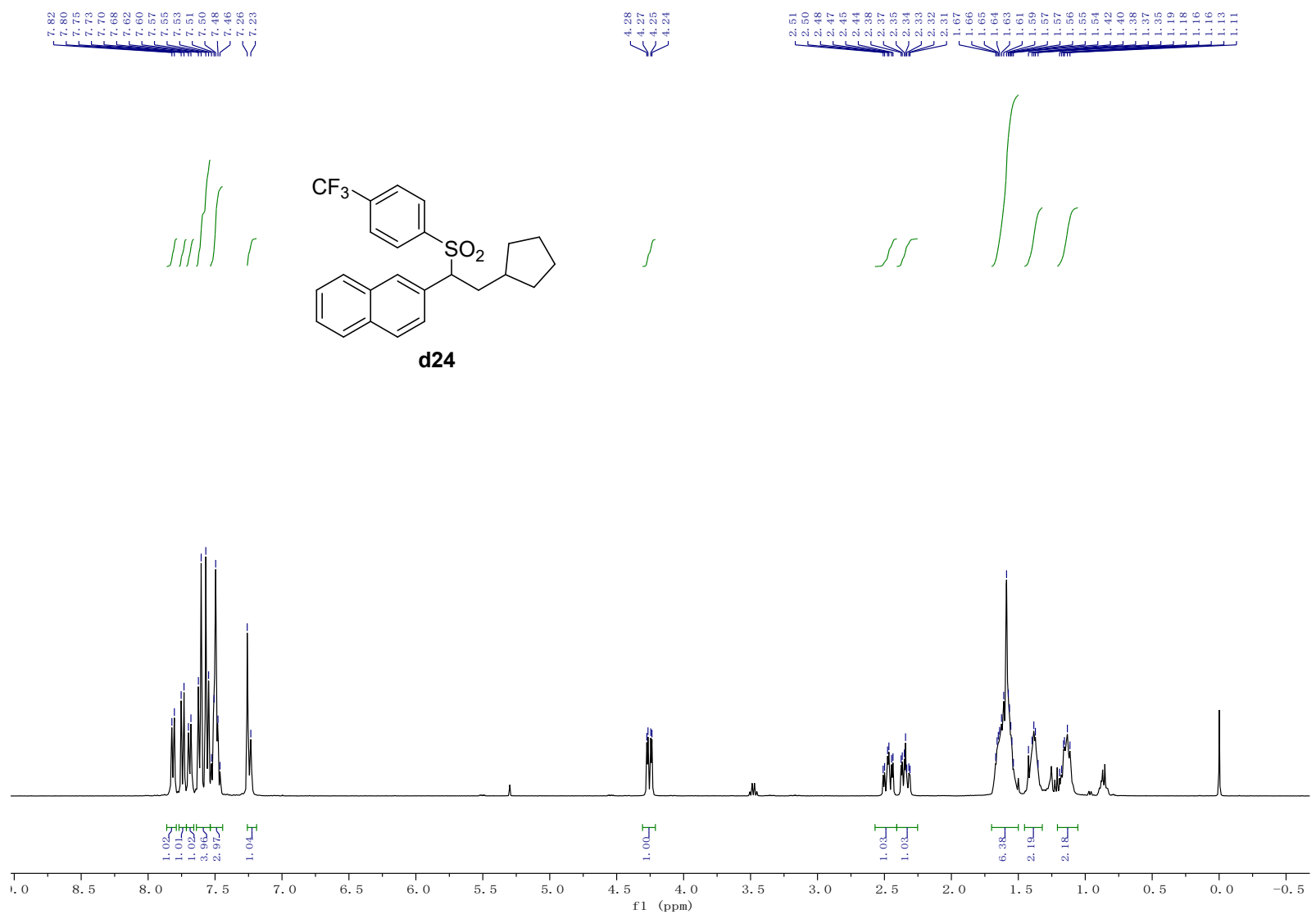


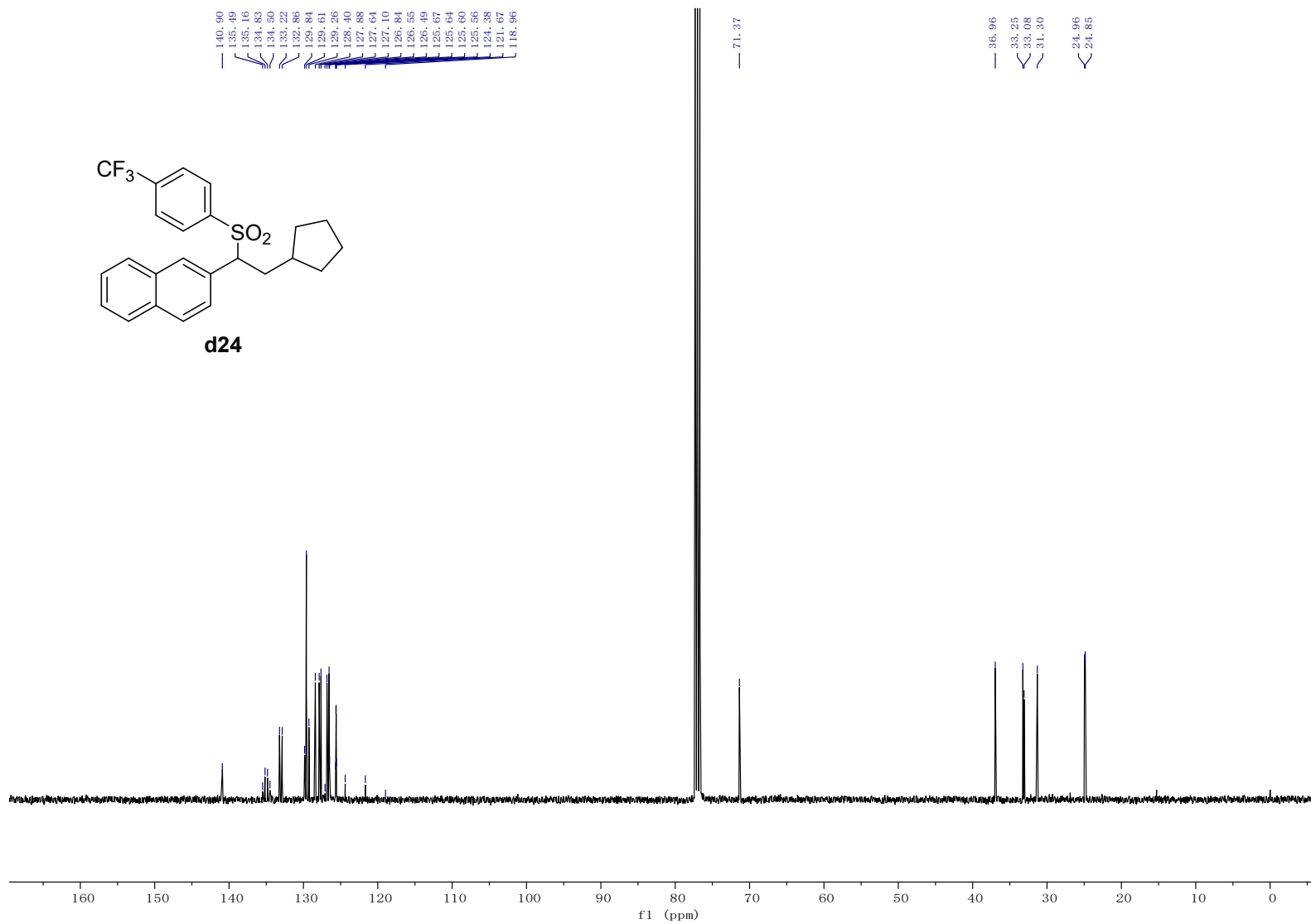
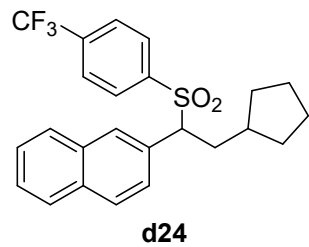


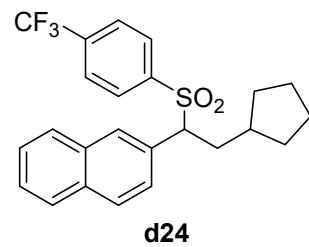


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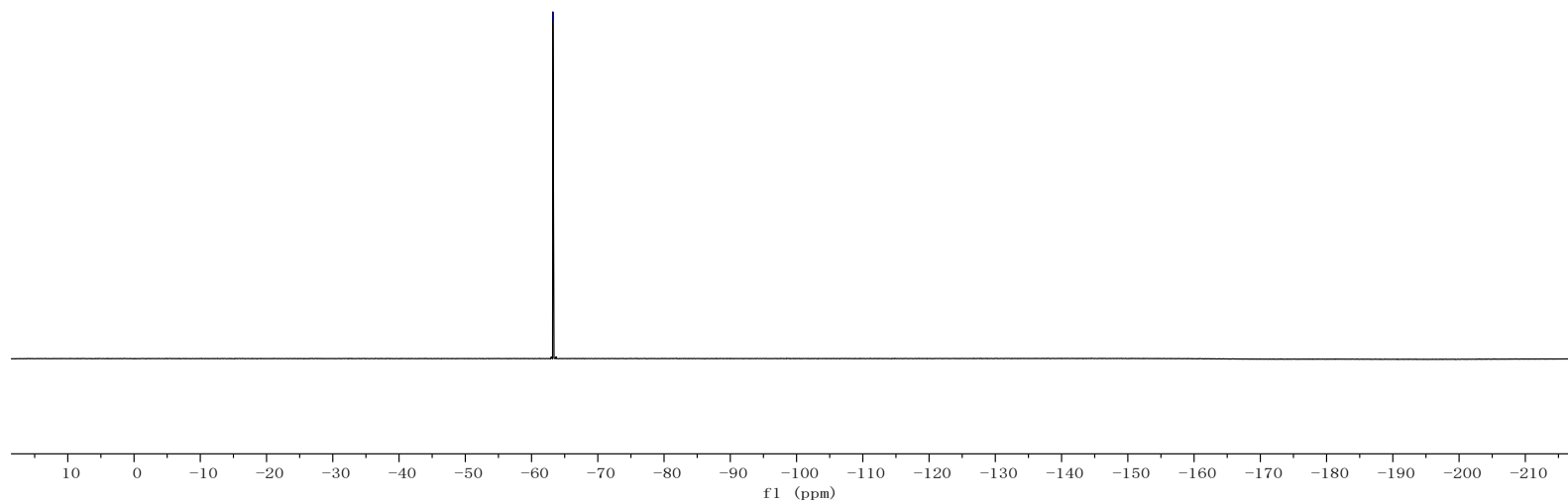


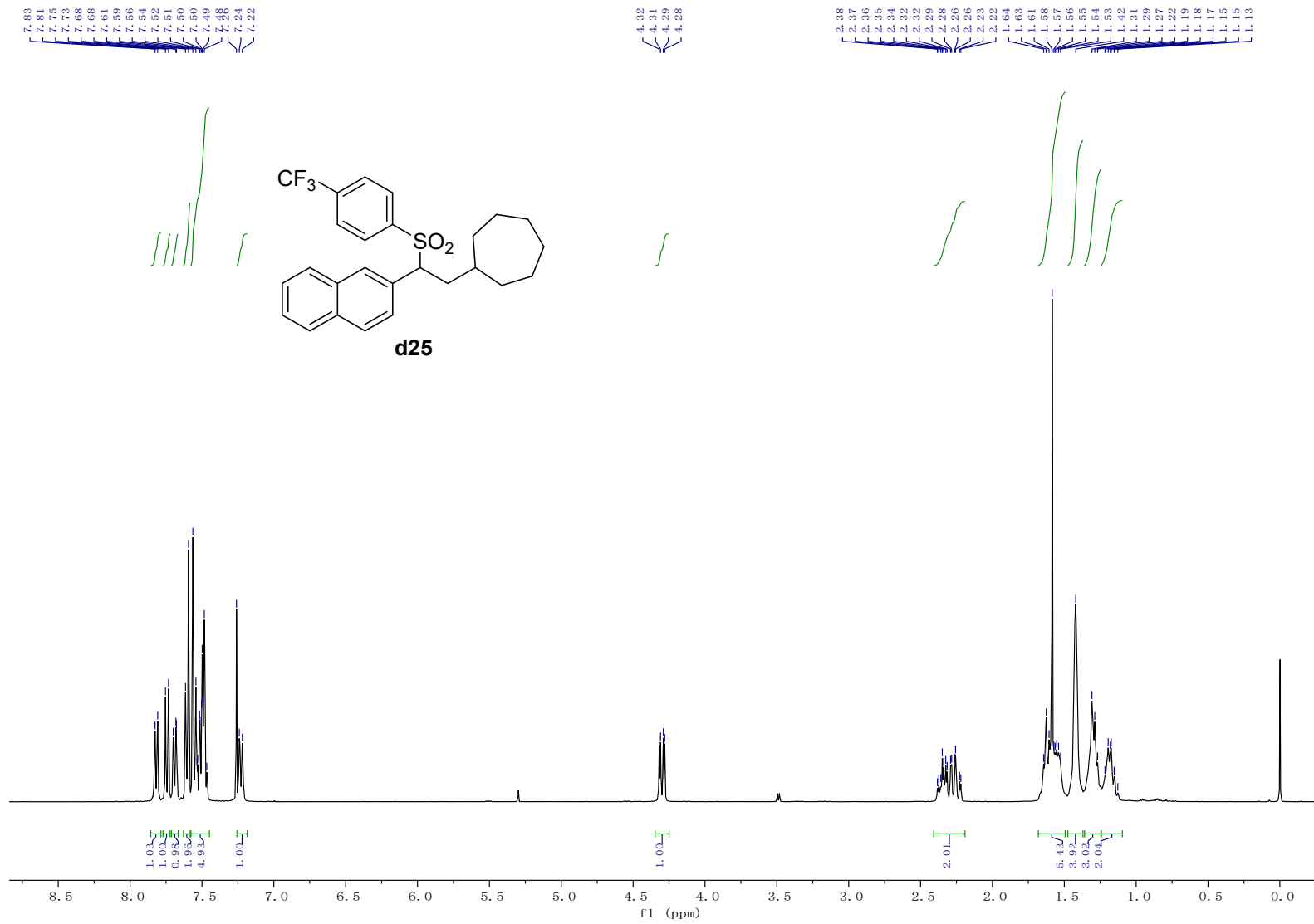


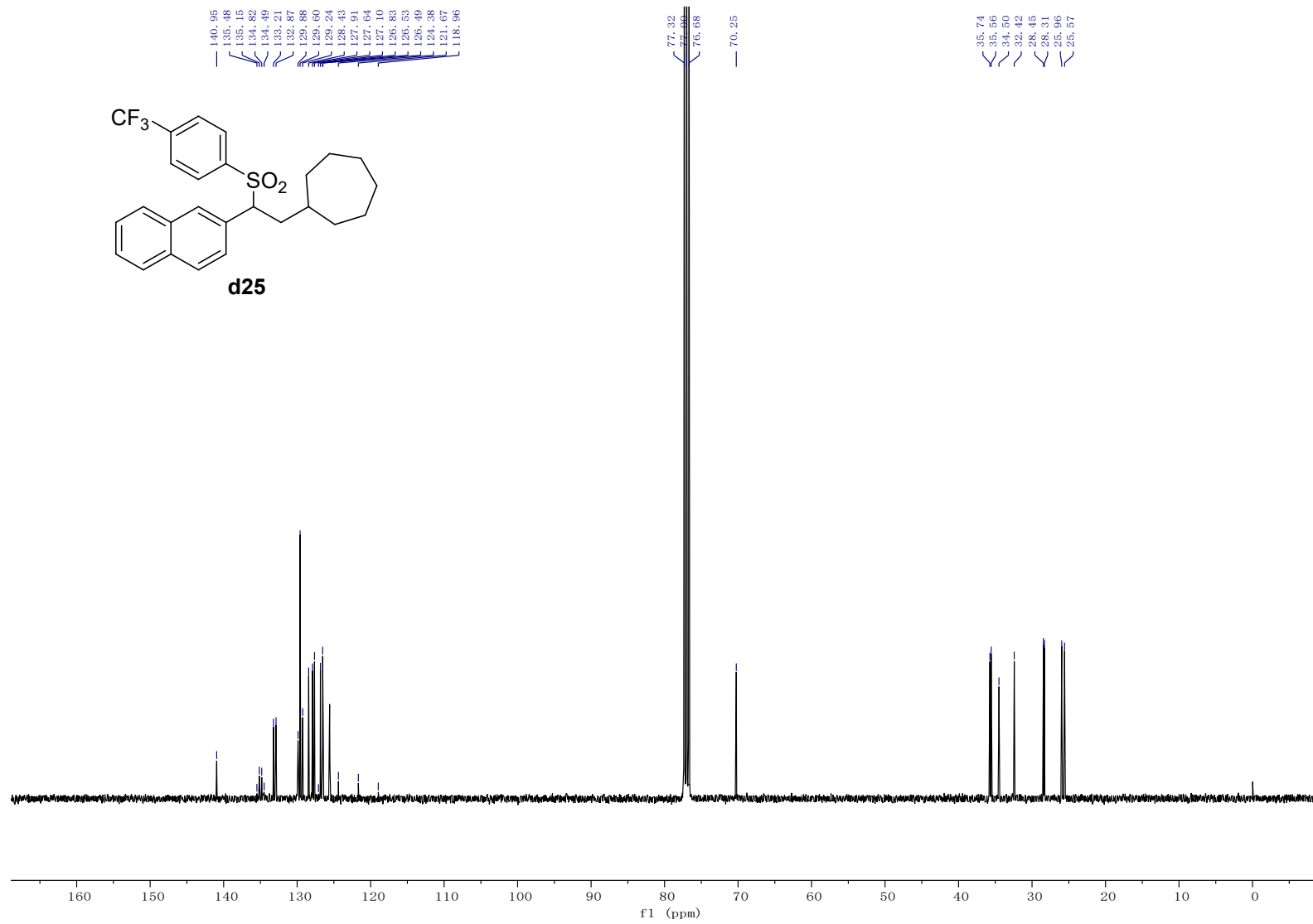
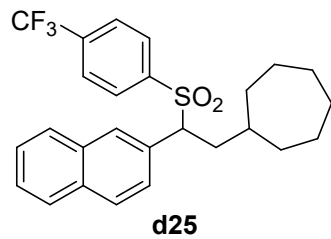


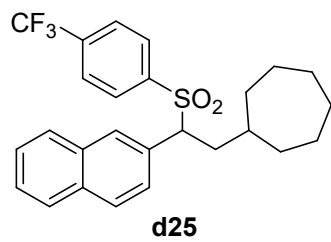


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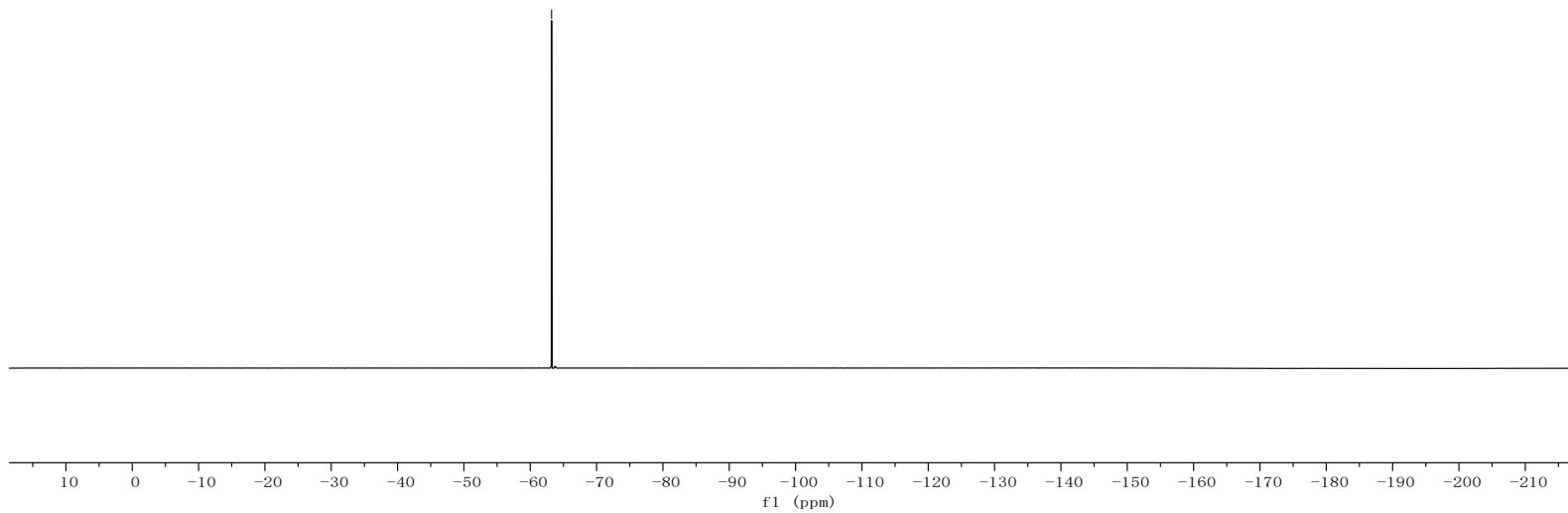








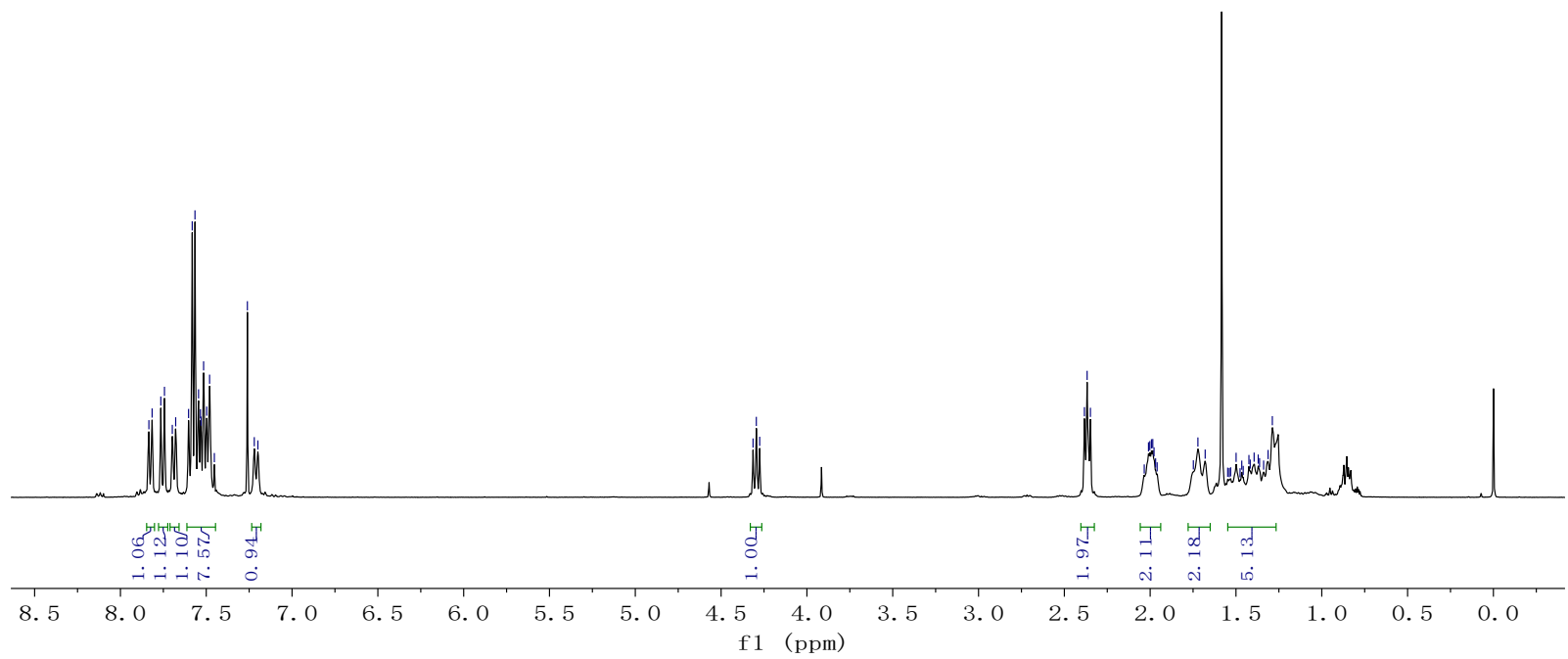
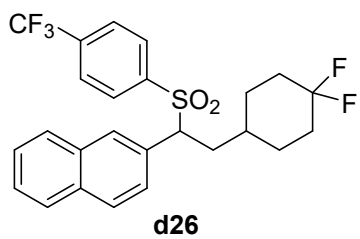
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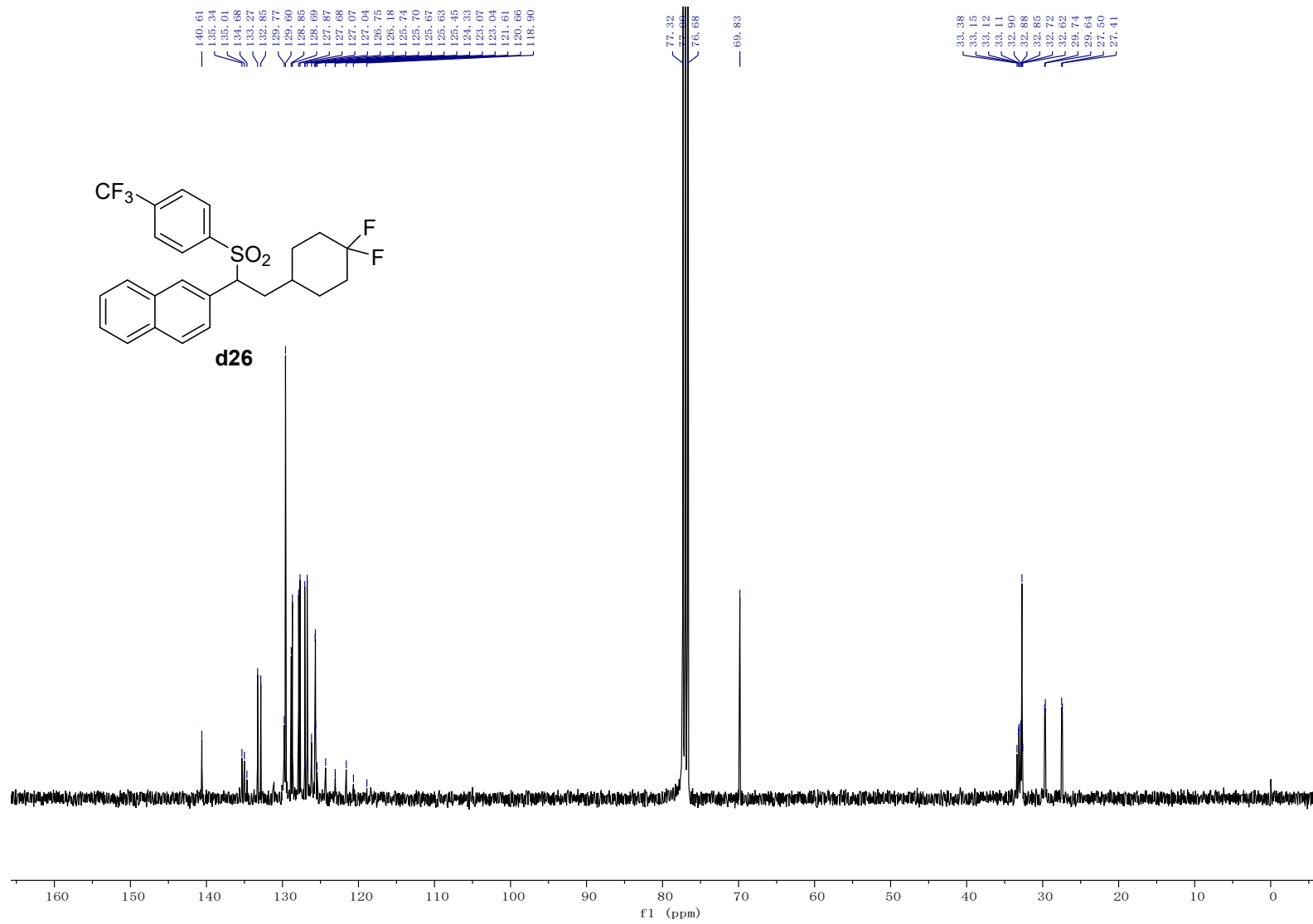


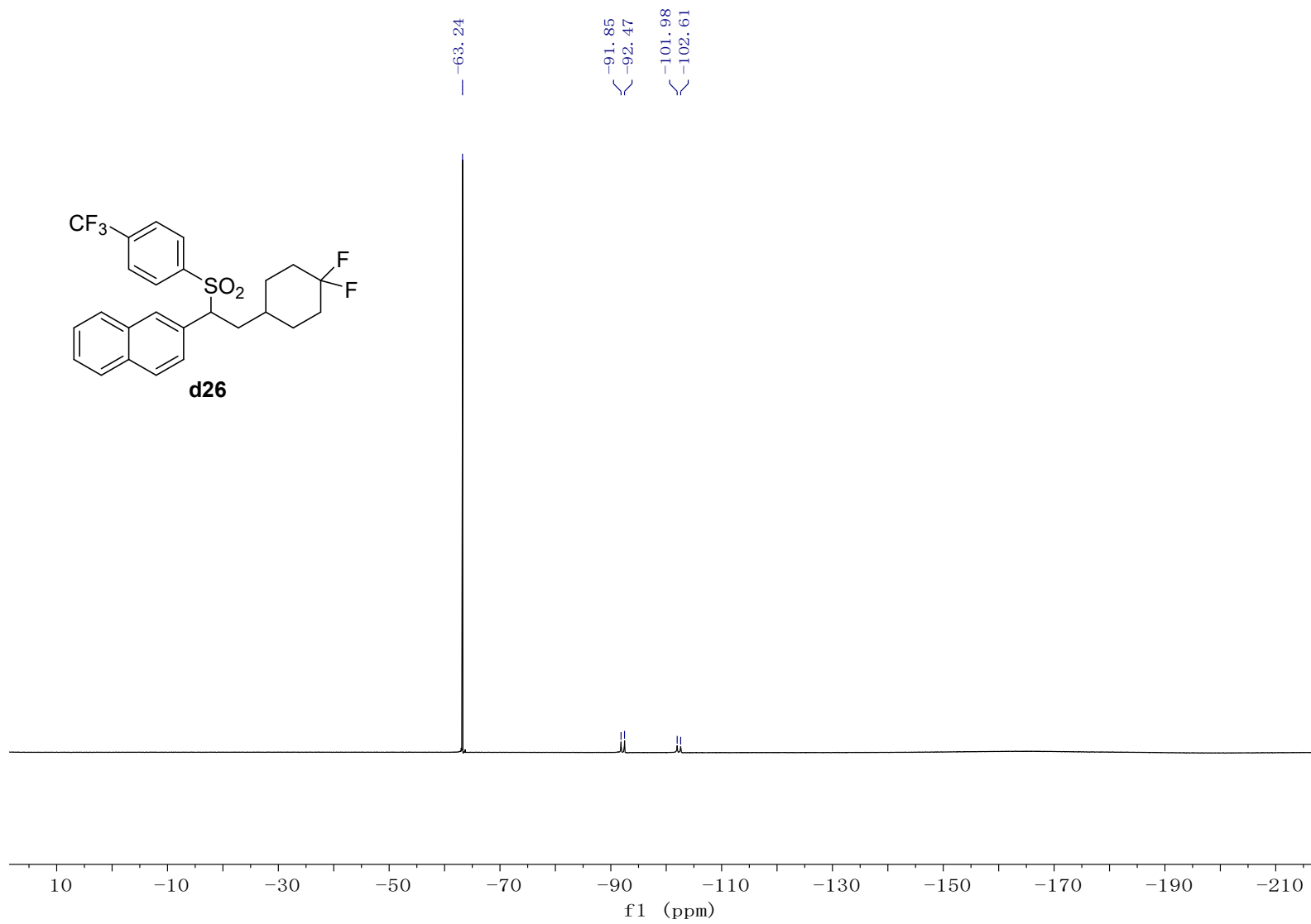
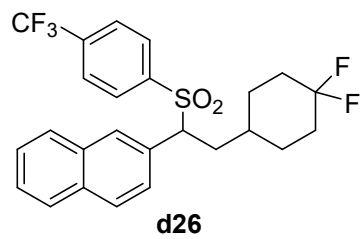
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4.31
4.29
4.28

2.38
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1.29



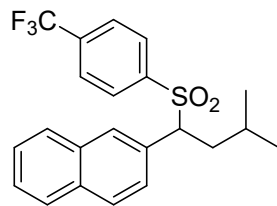




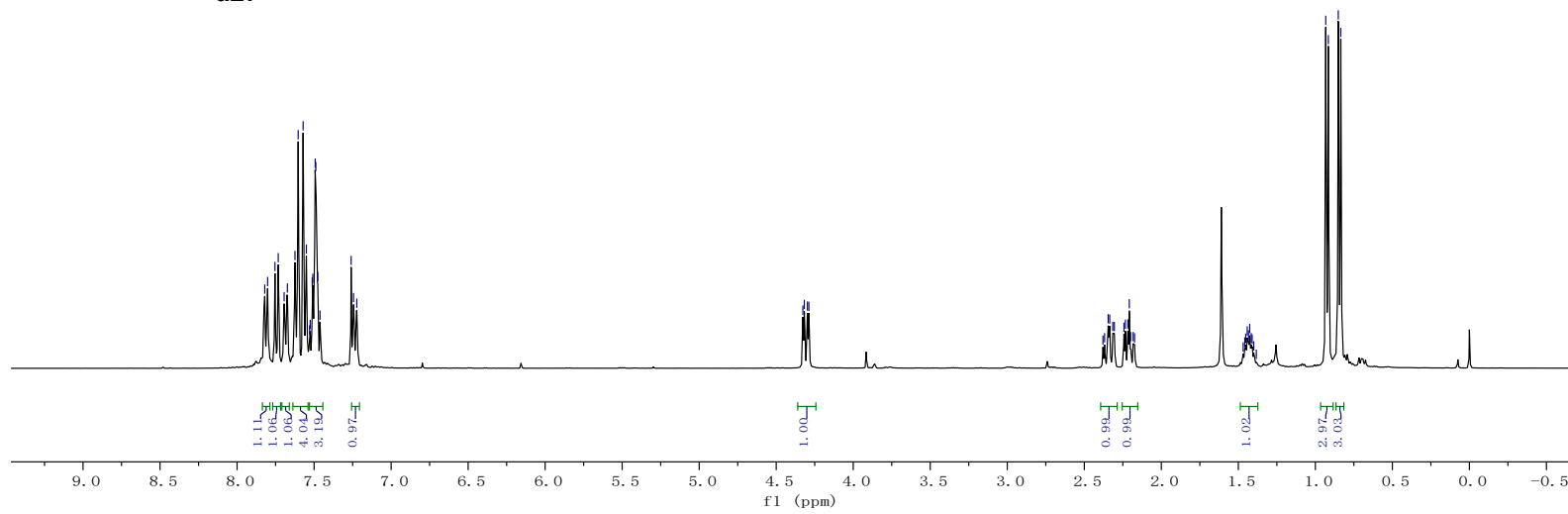
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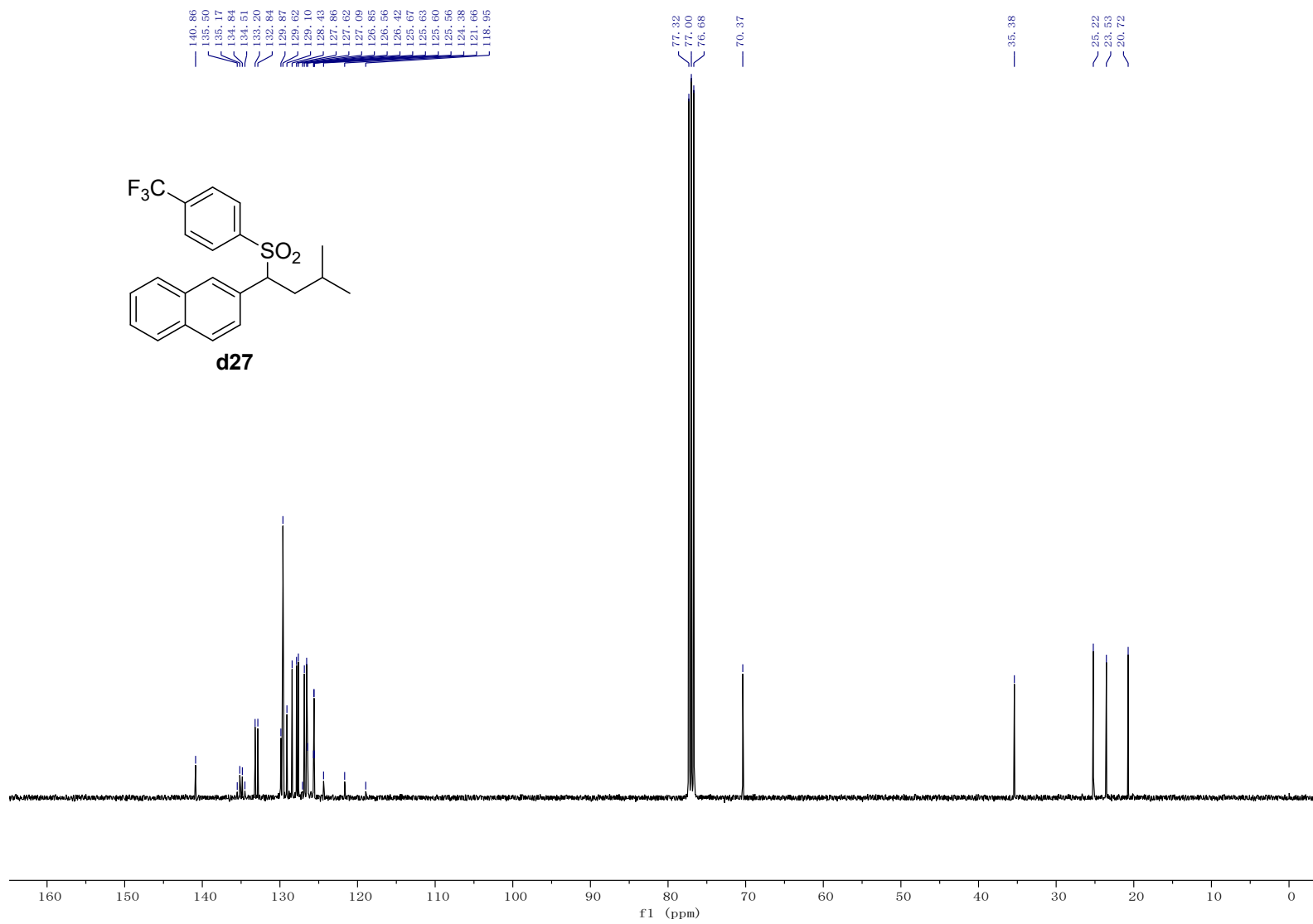
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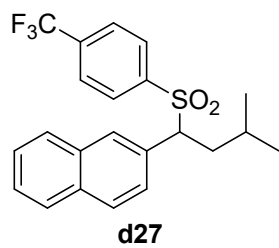
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0.83



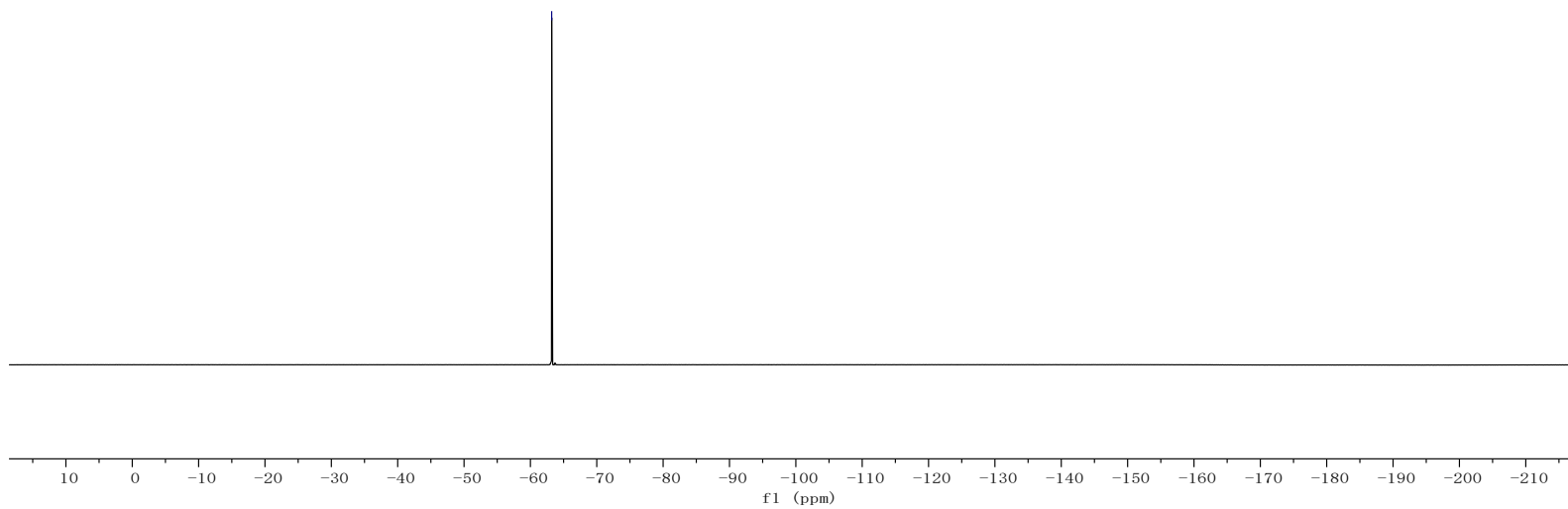
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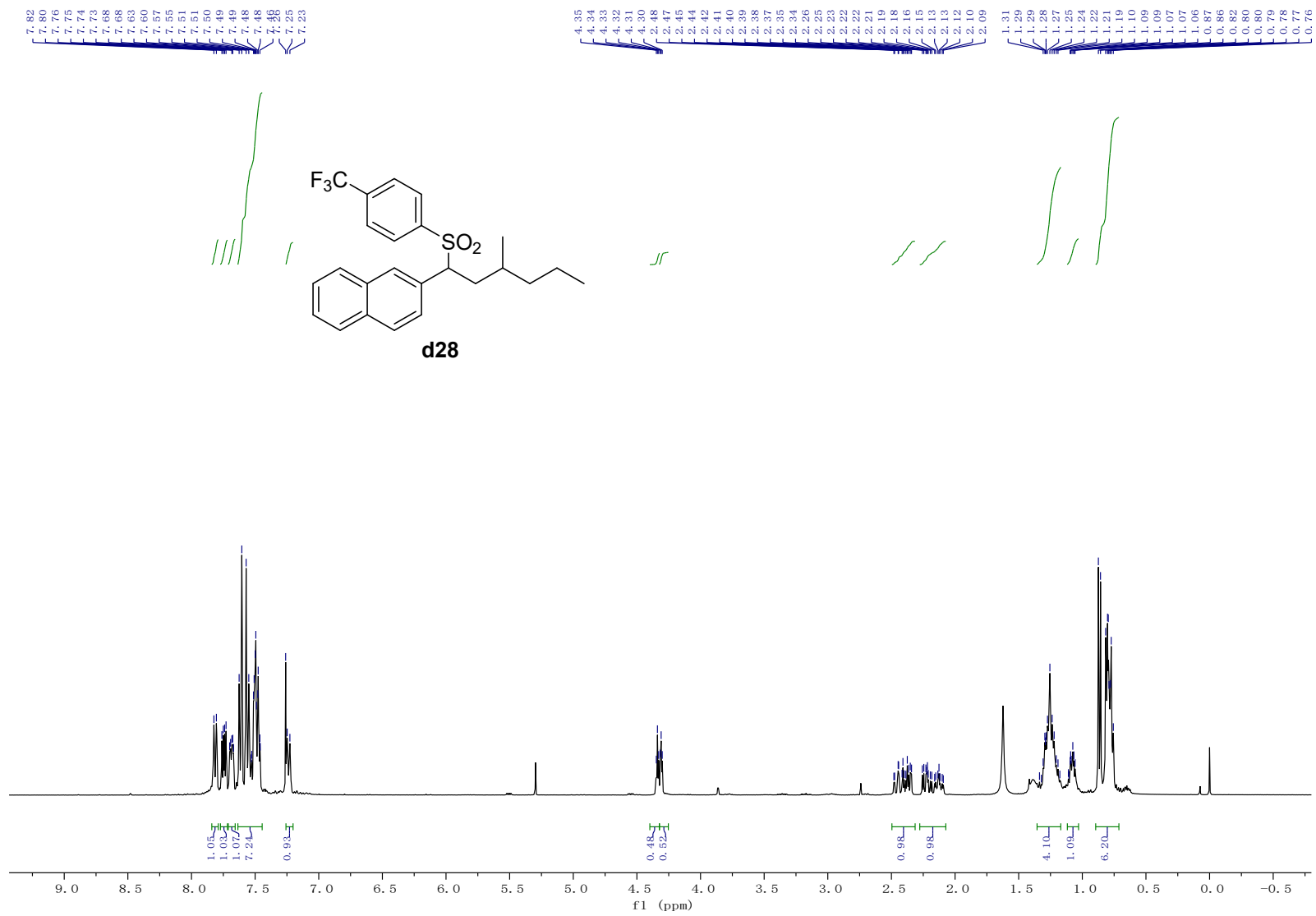


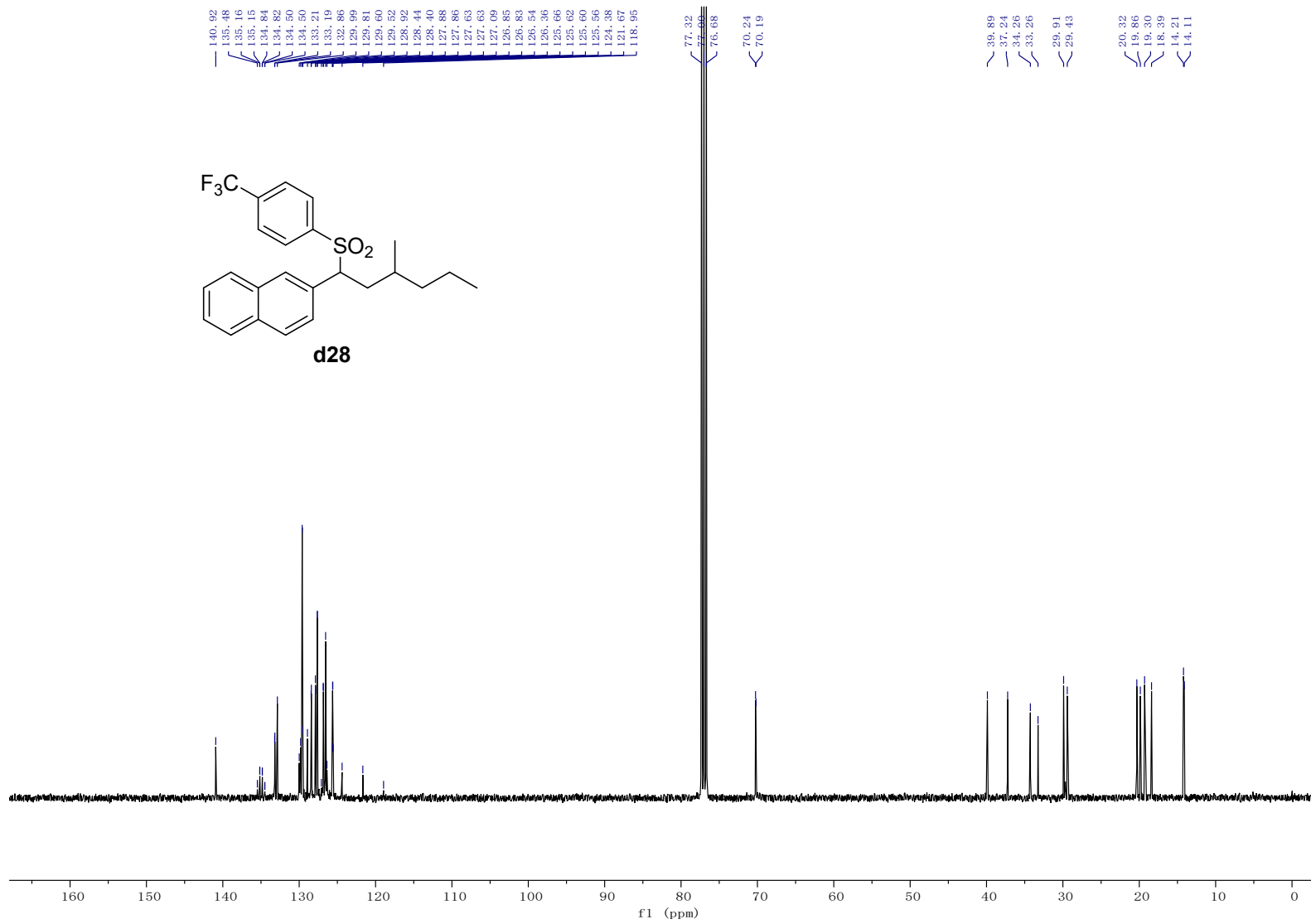


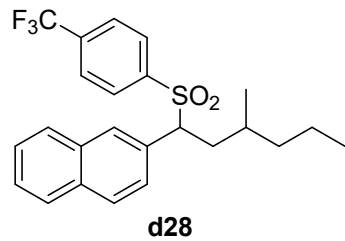


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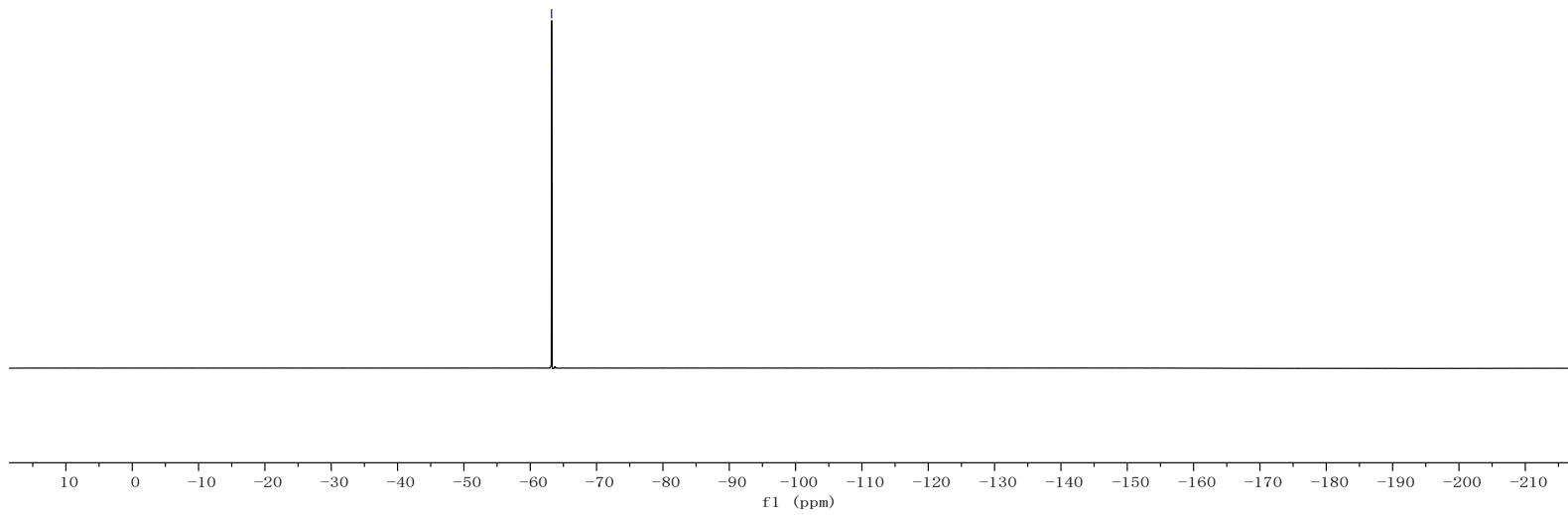


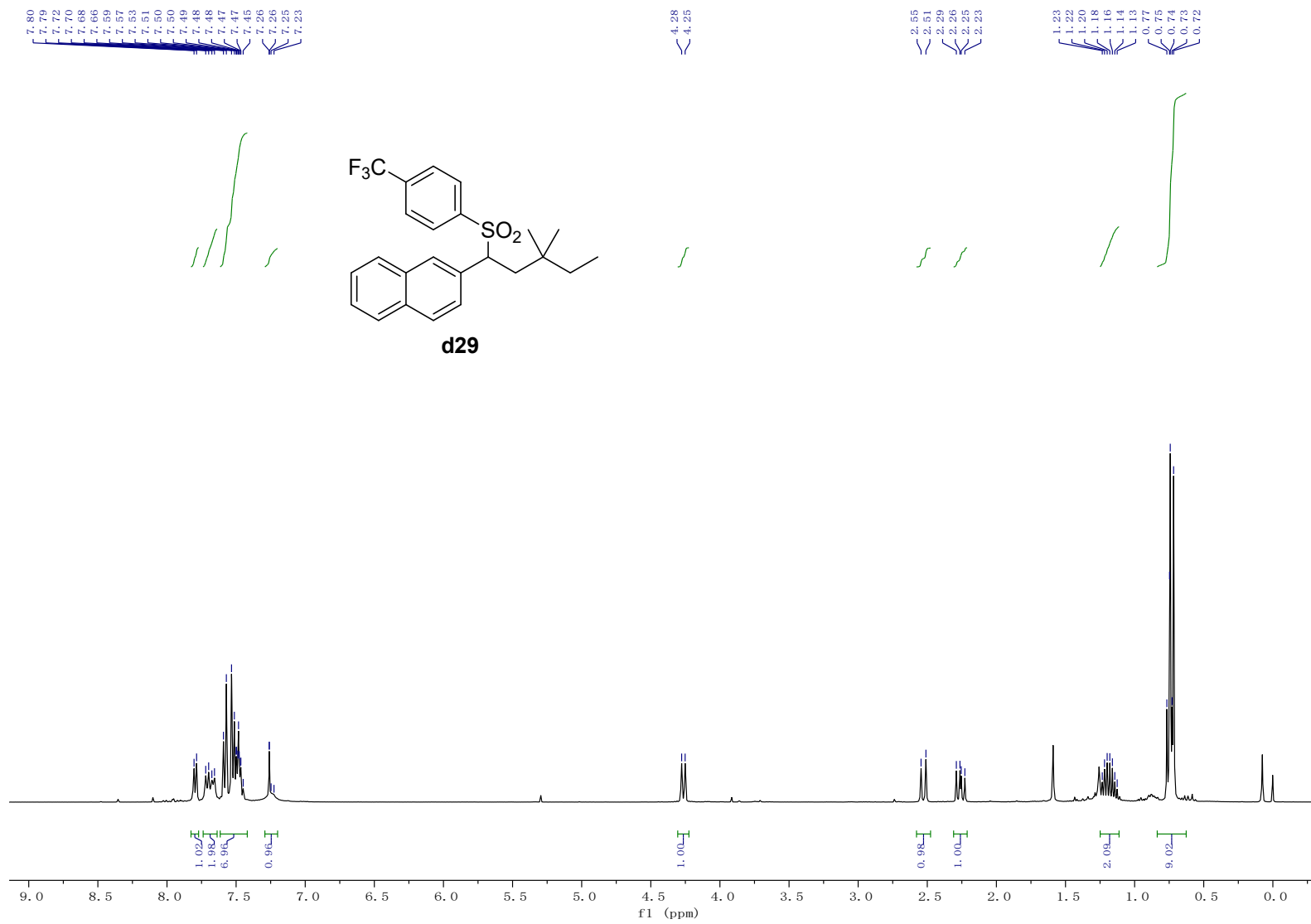


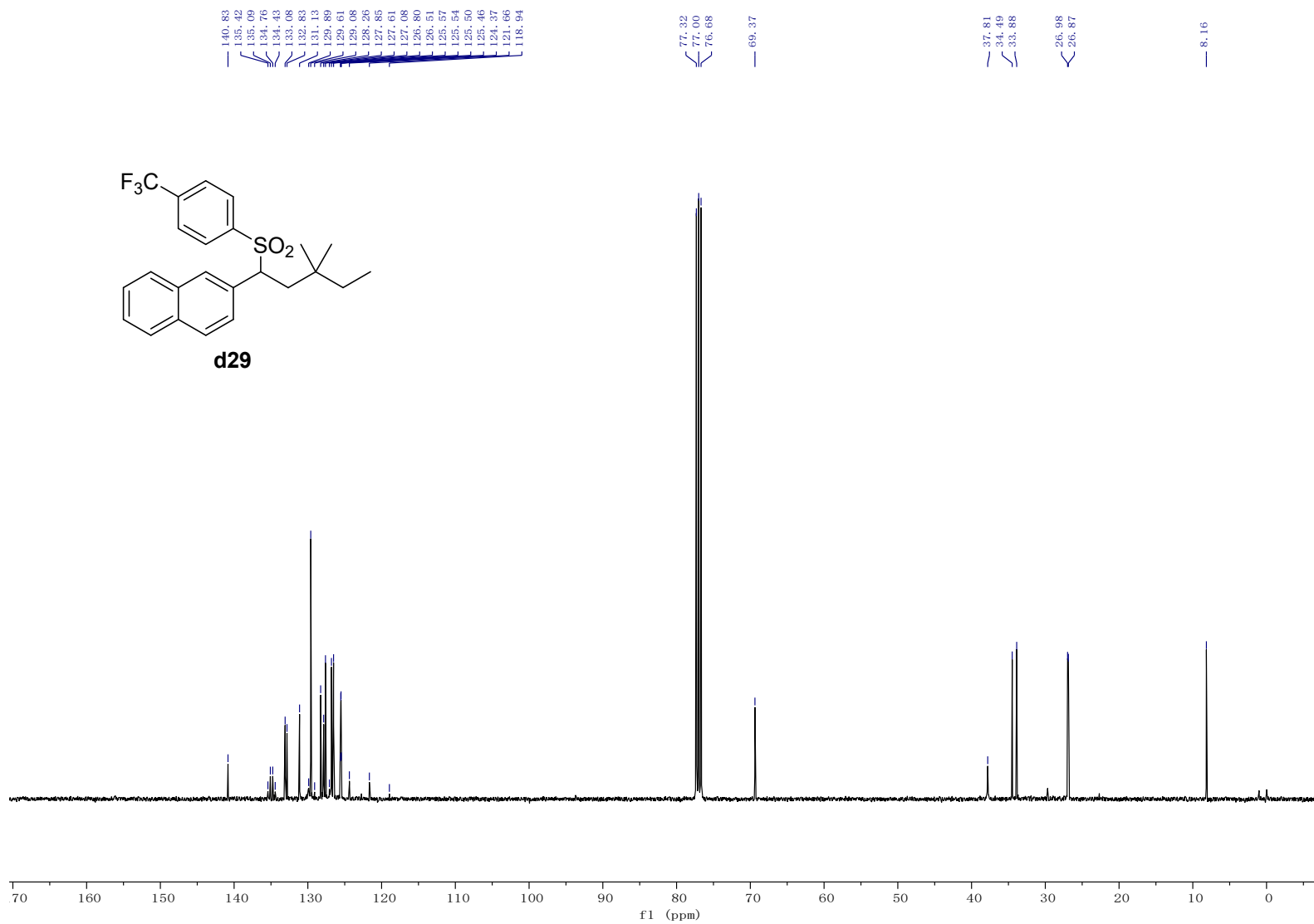
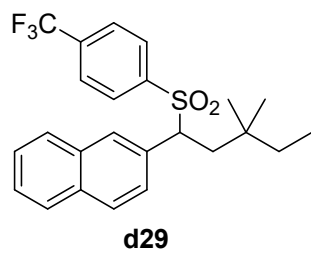


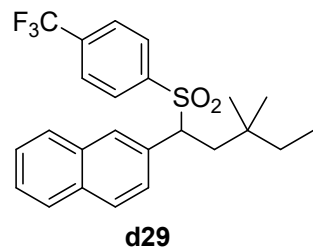


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-63.22

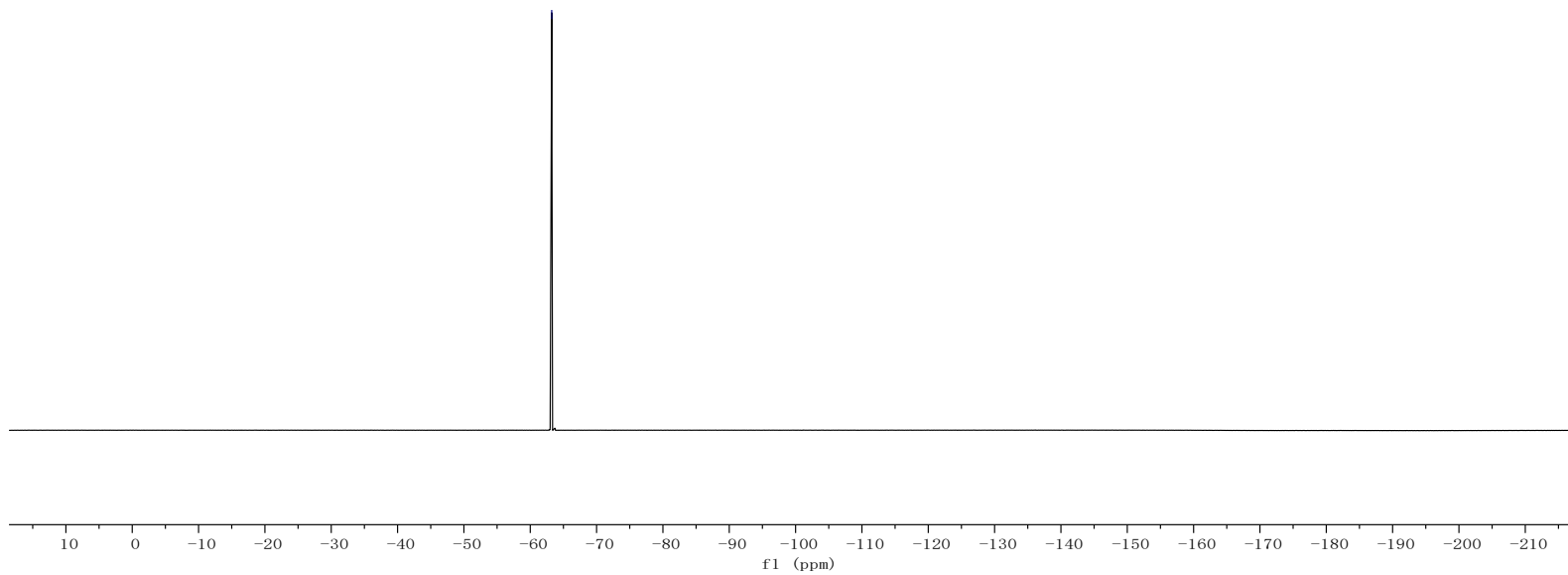


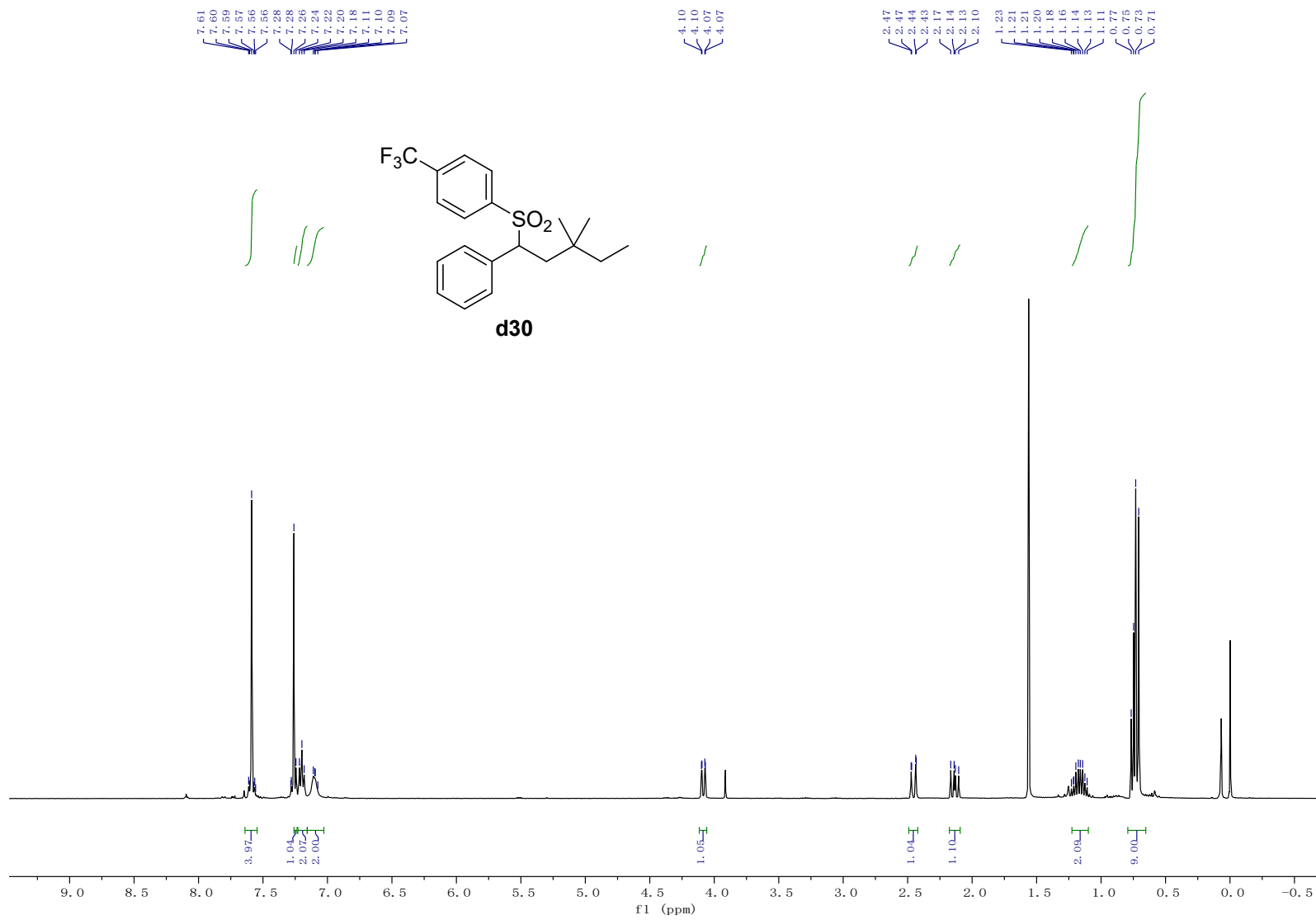


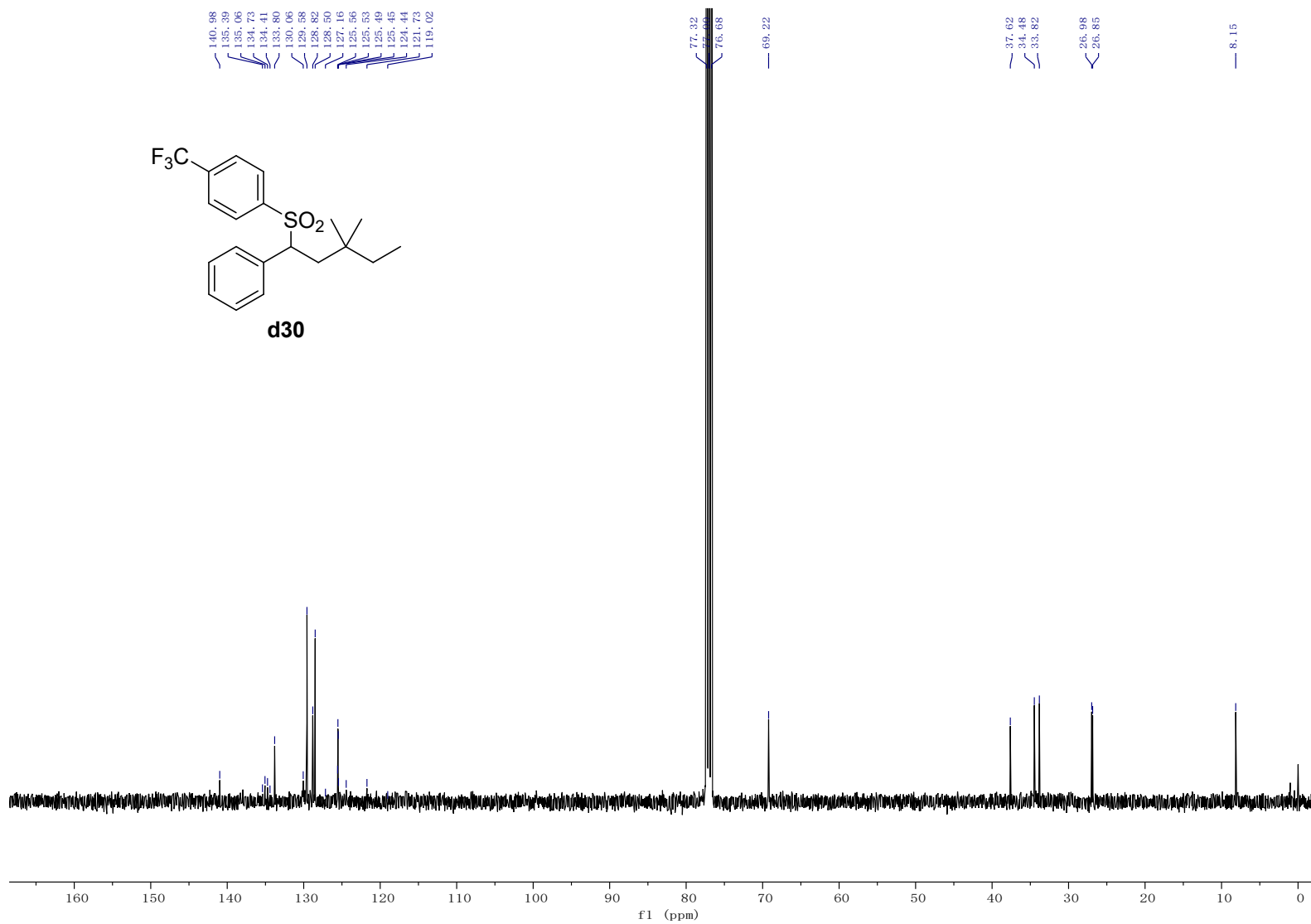
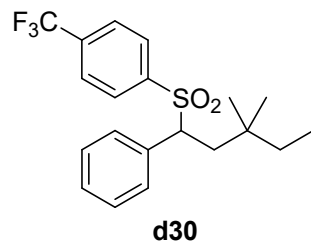


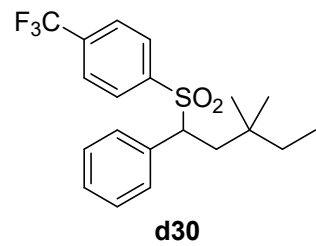


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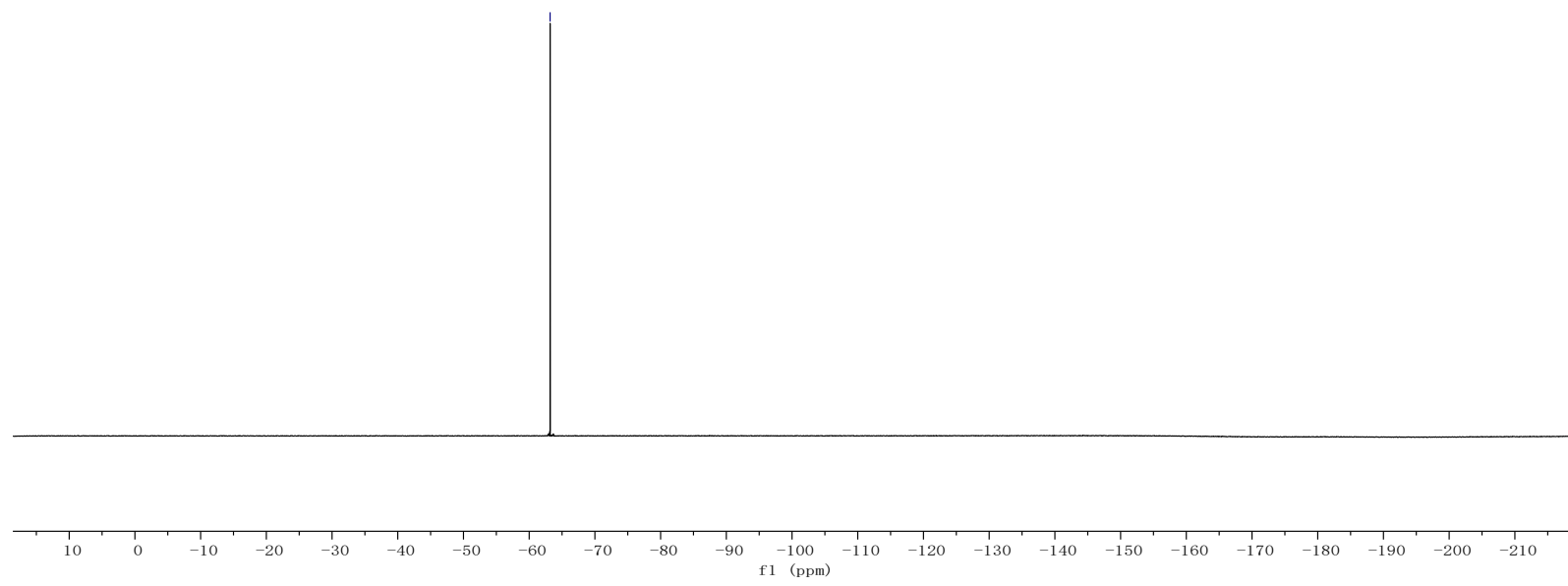


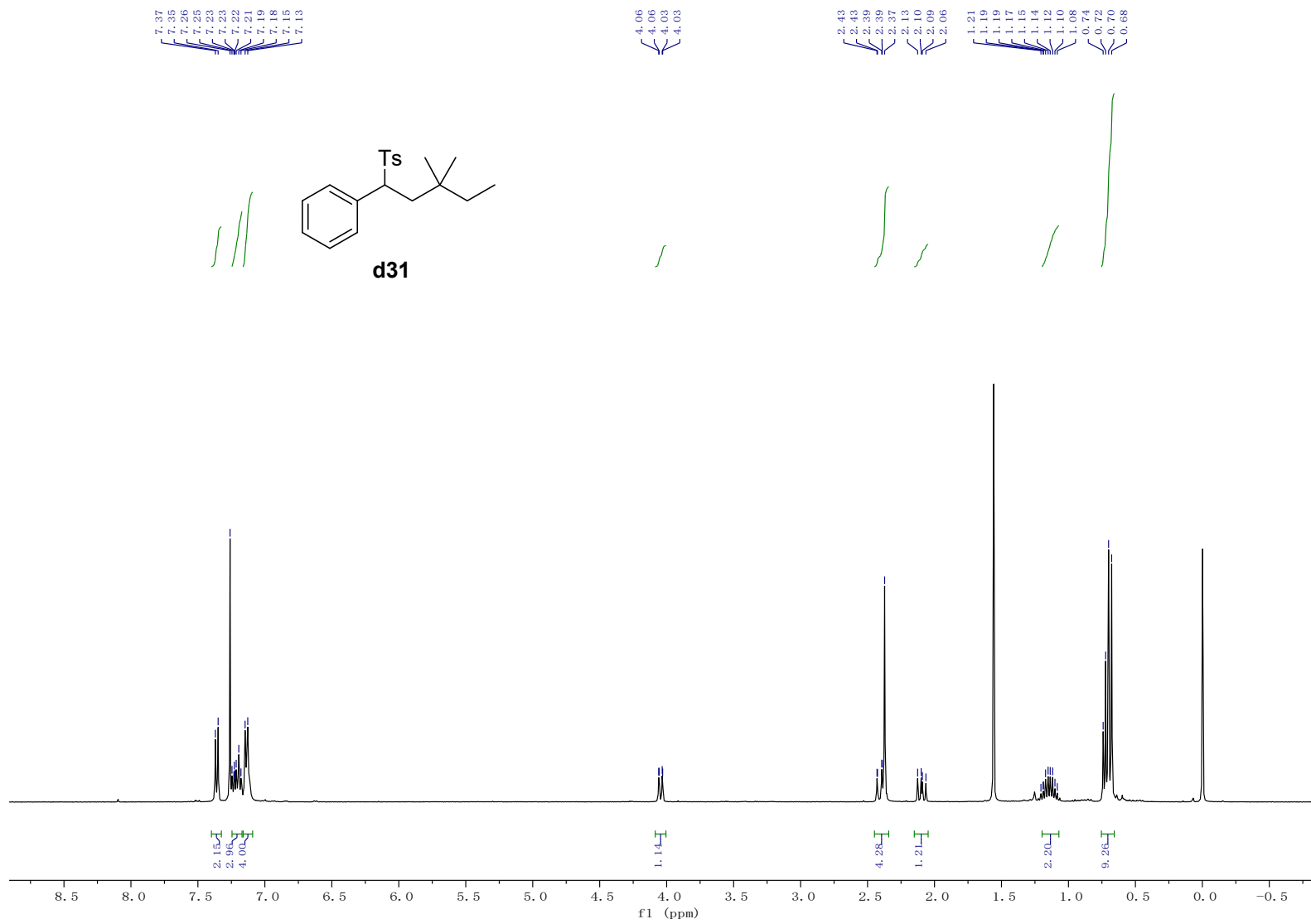


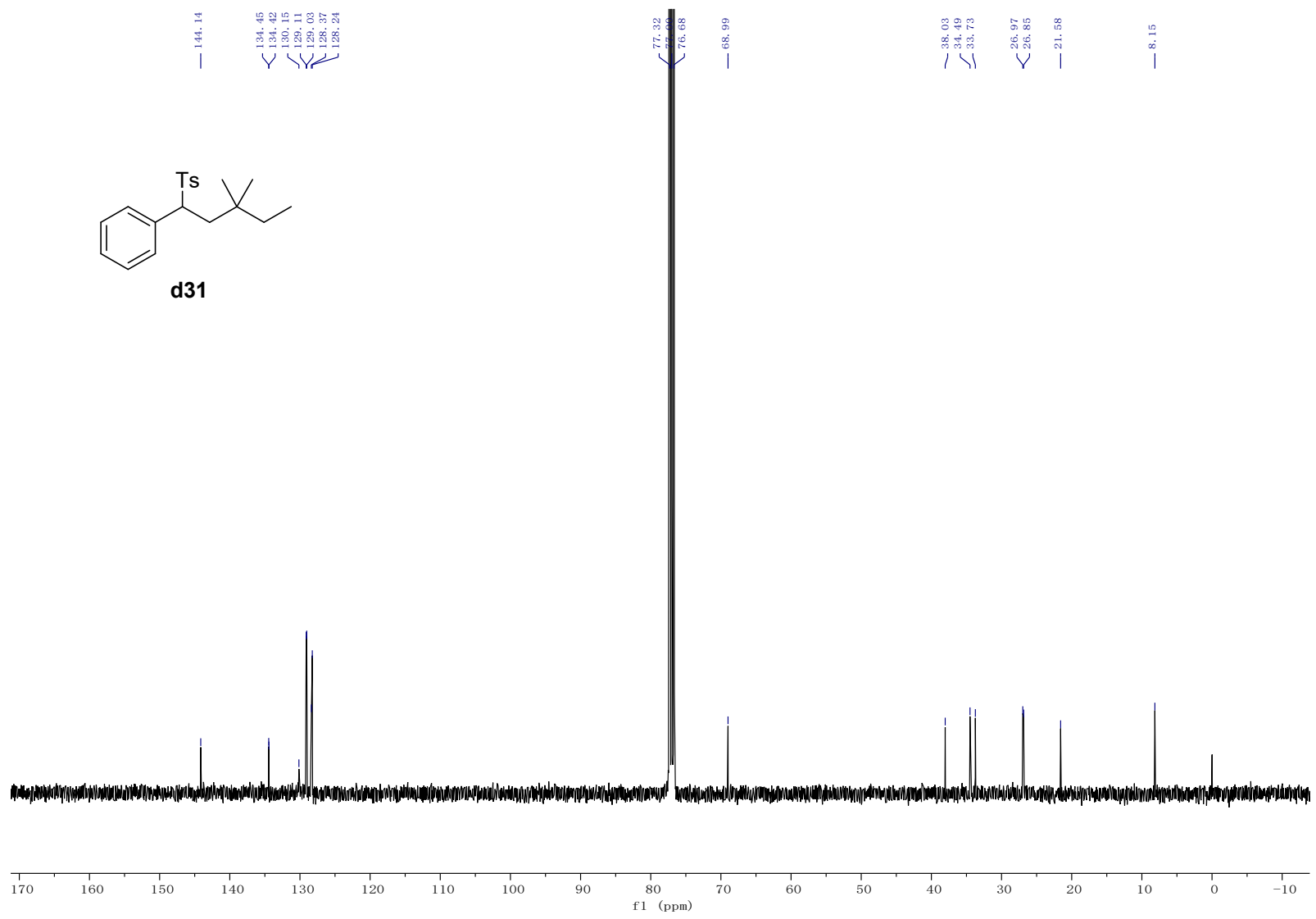
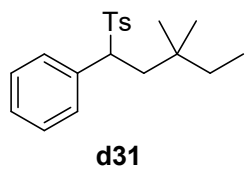


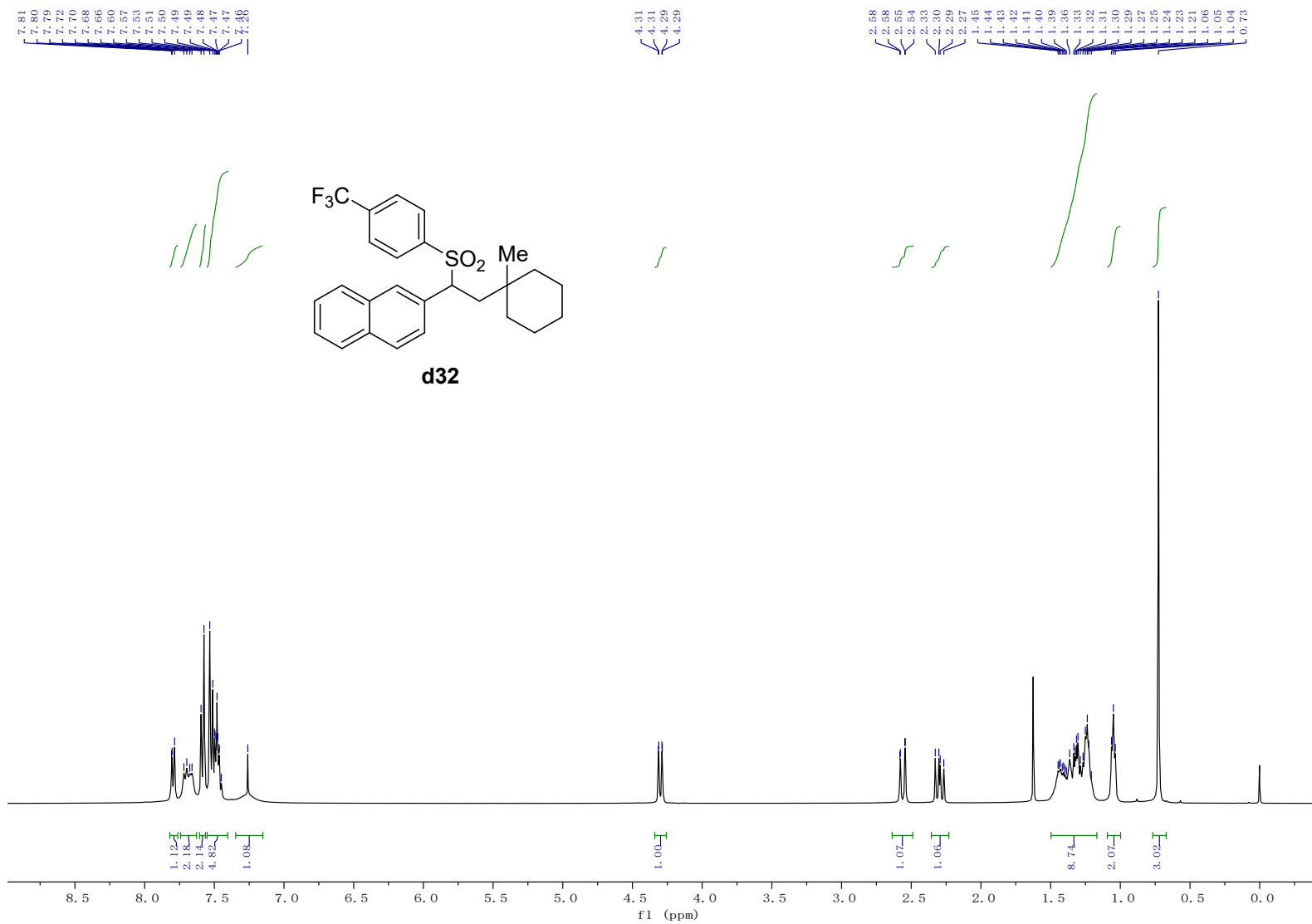


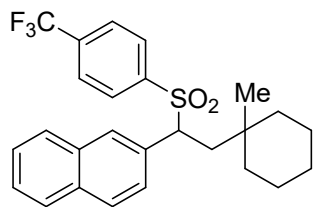
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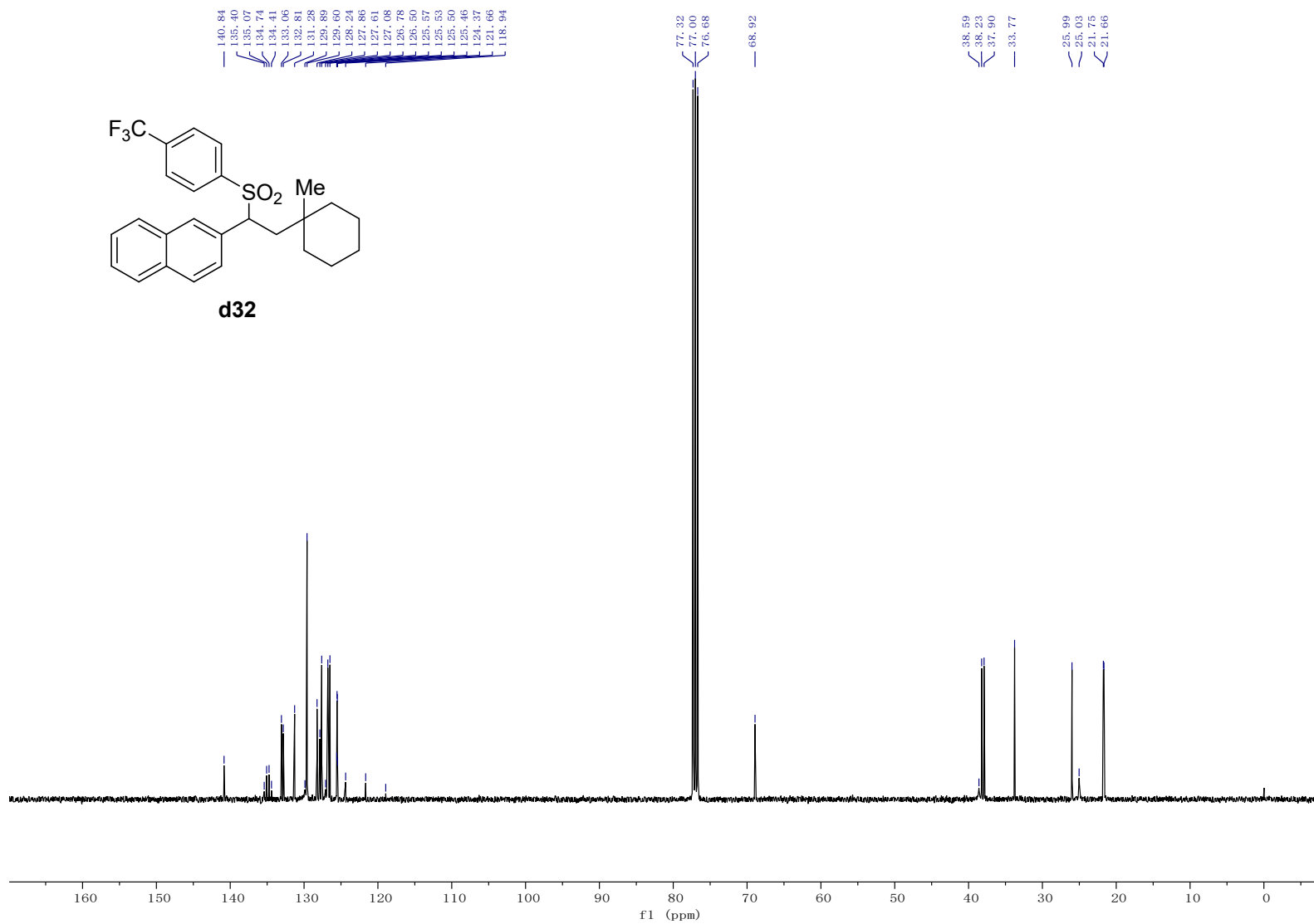


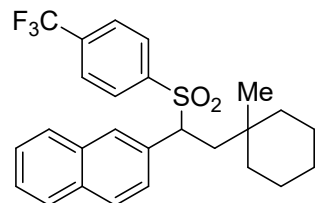






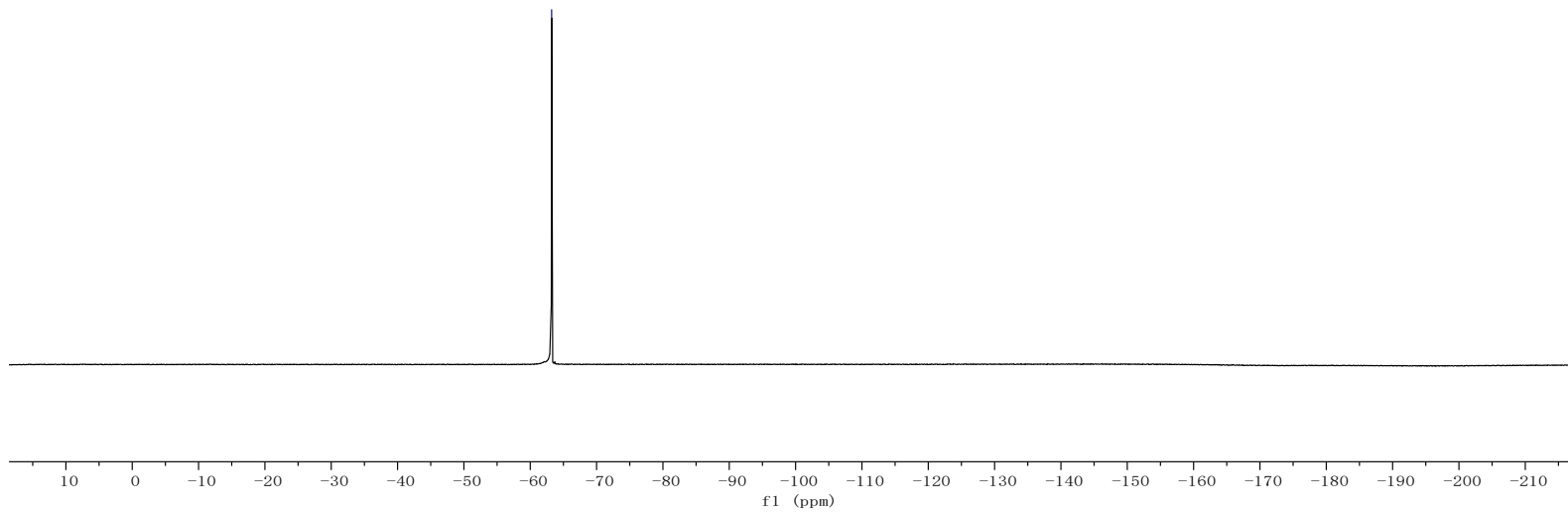
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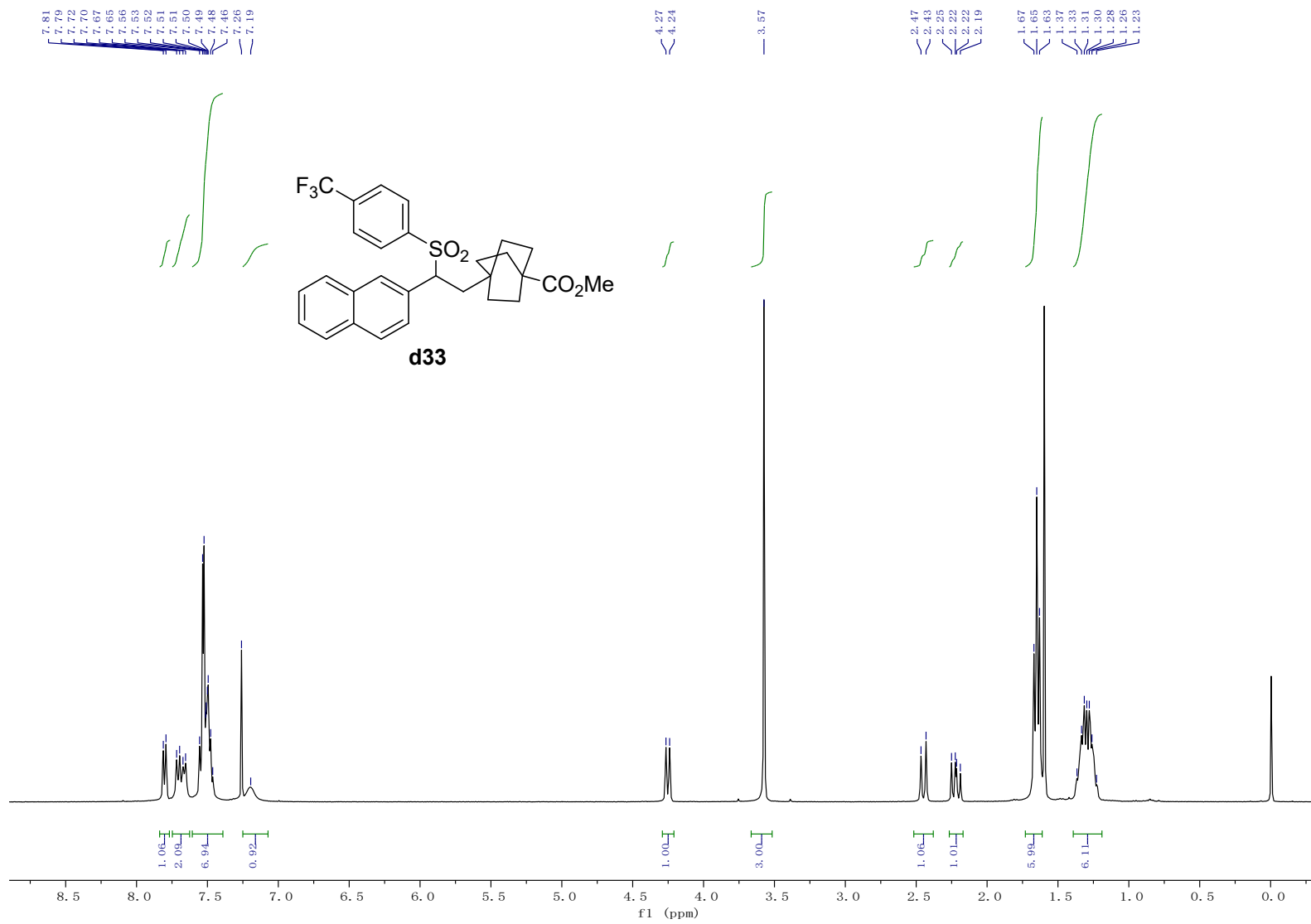


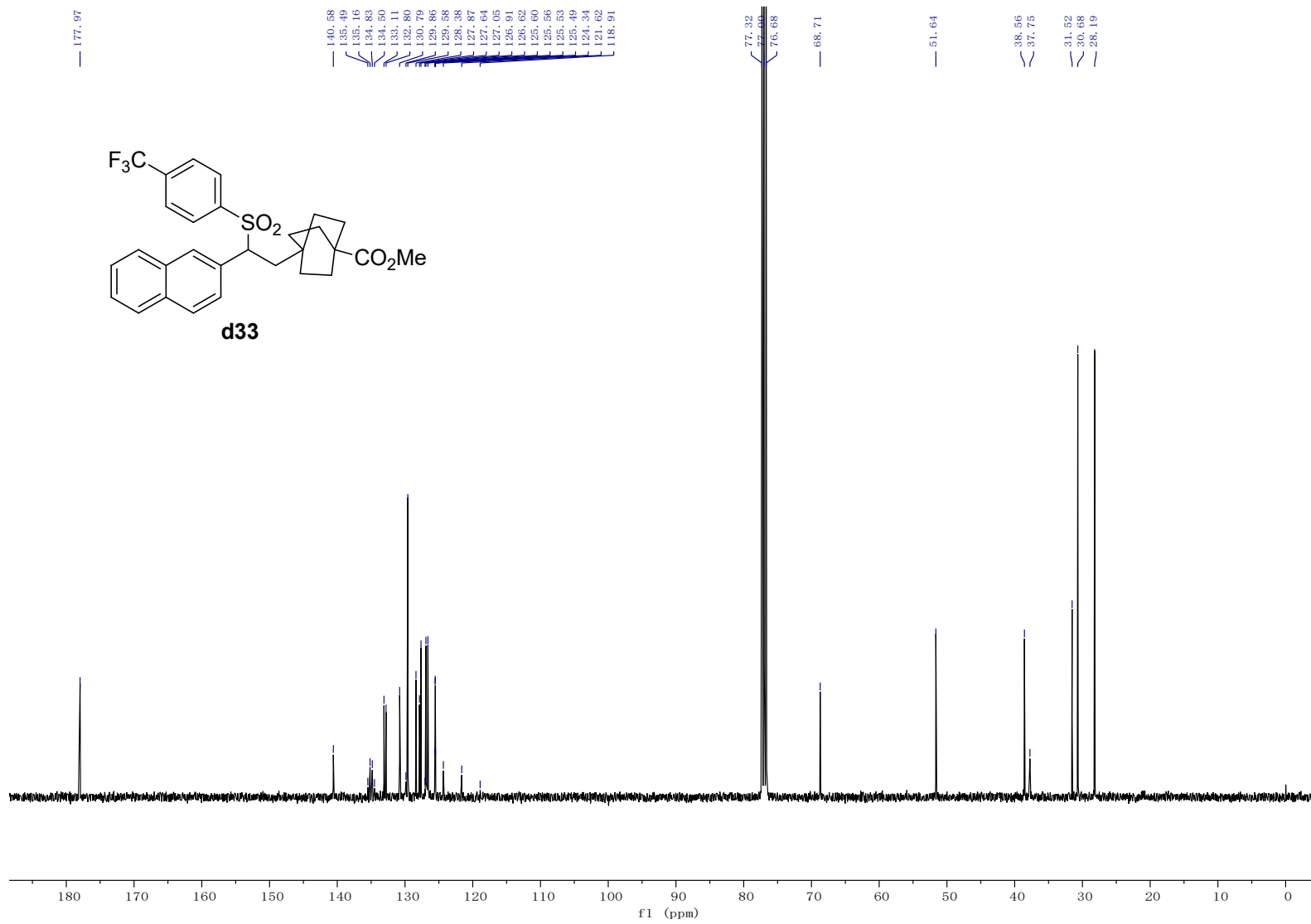


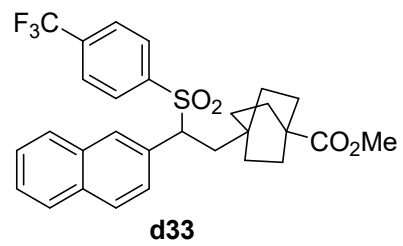
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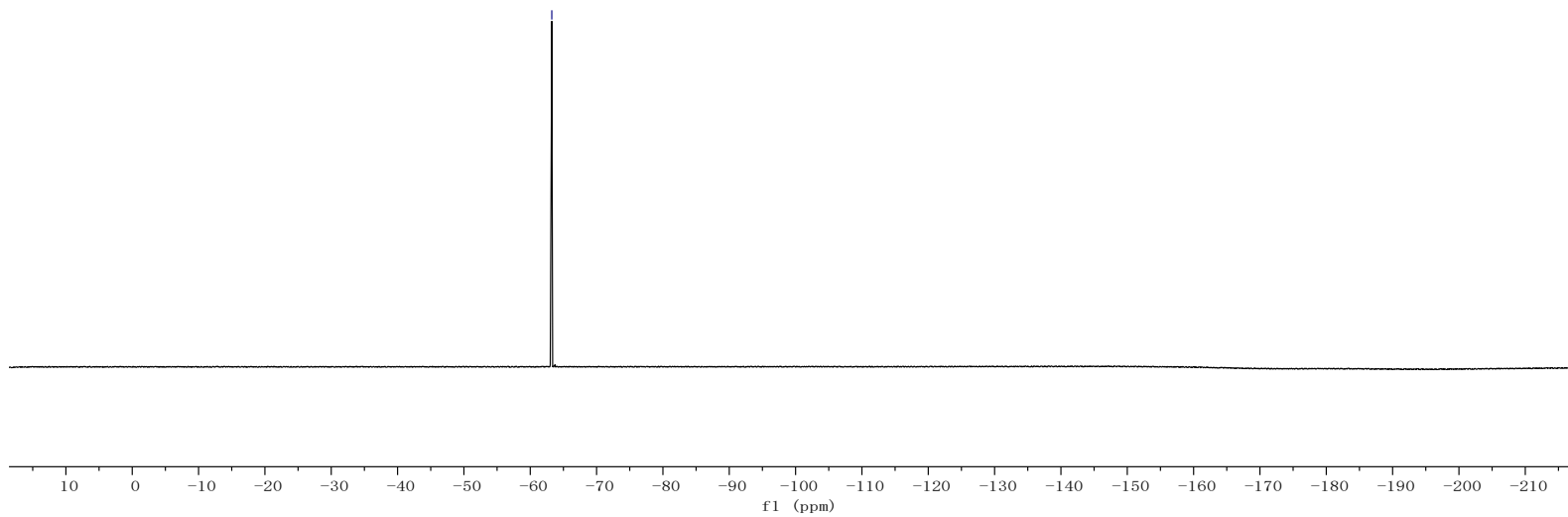


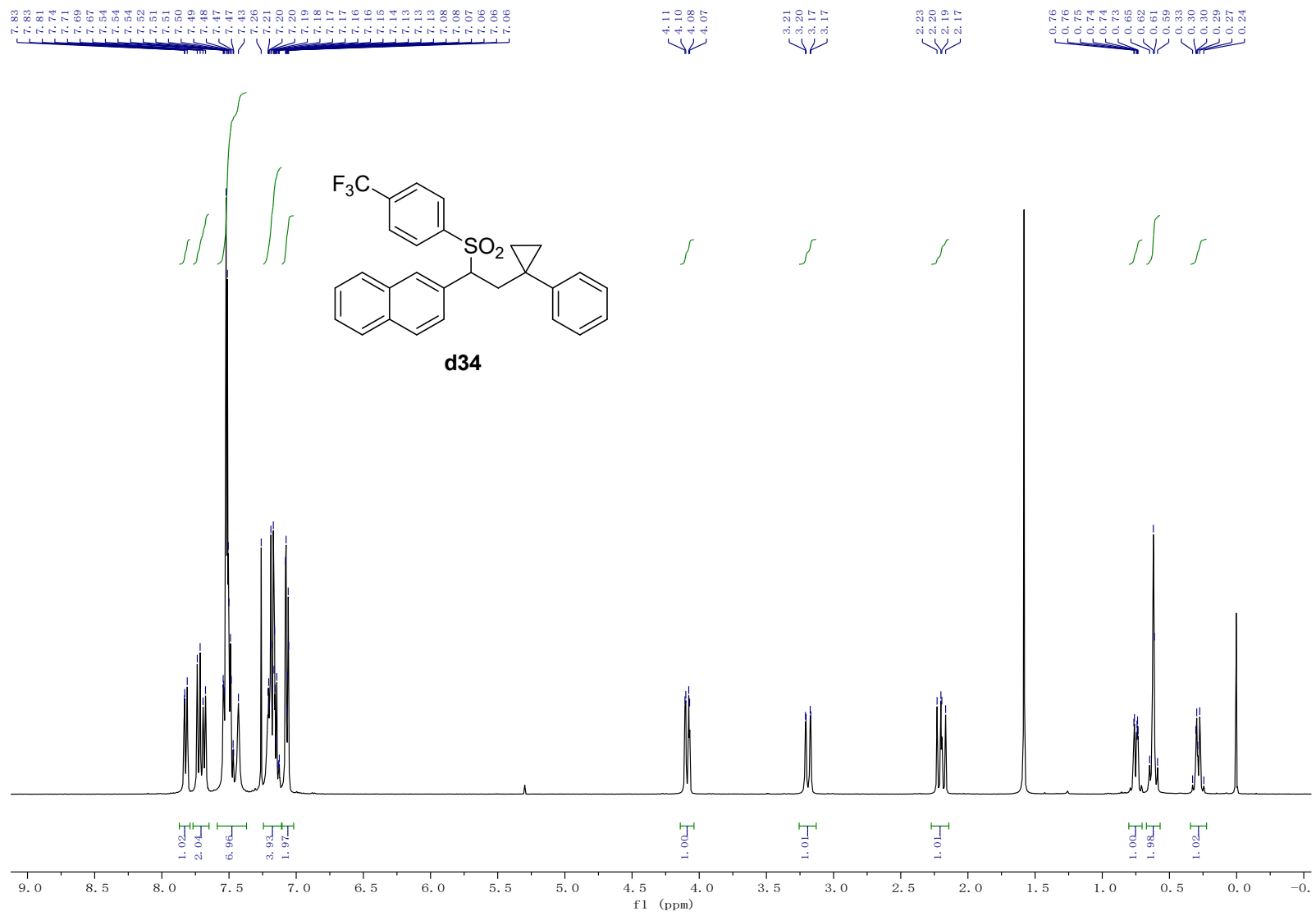


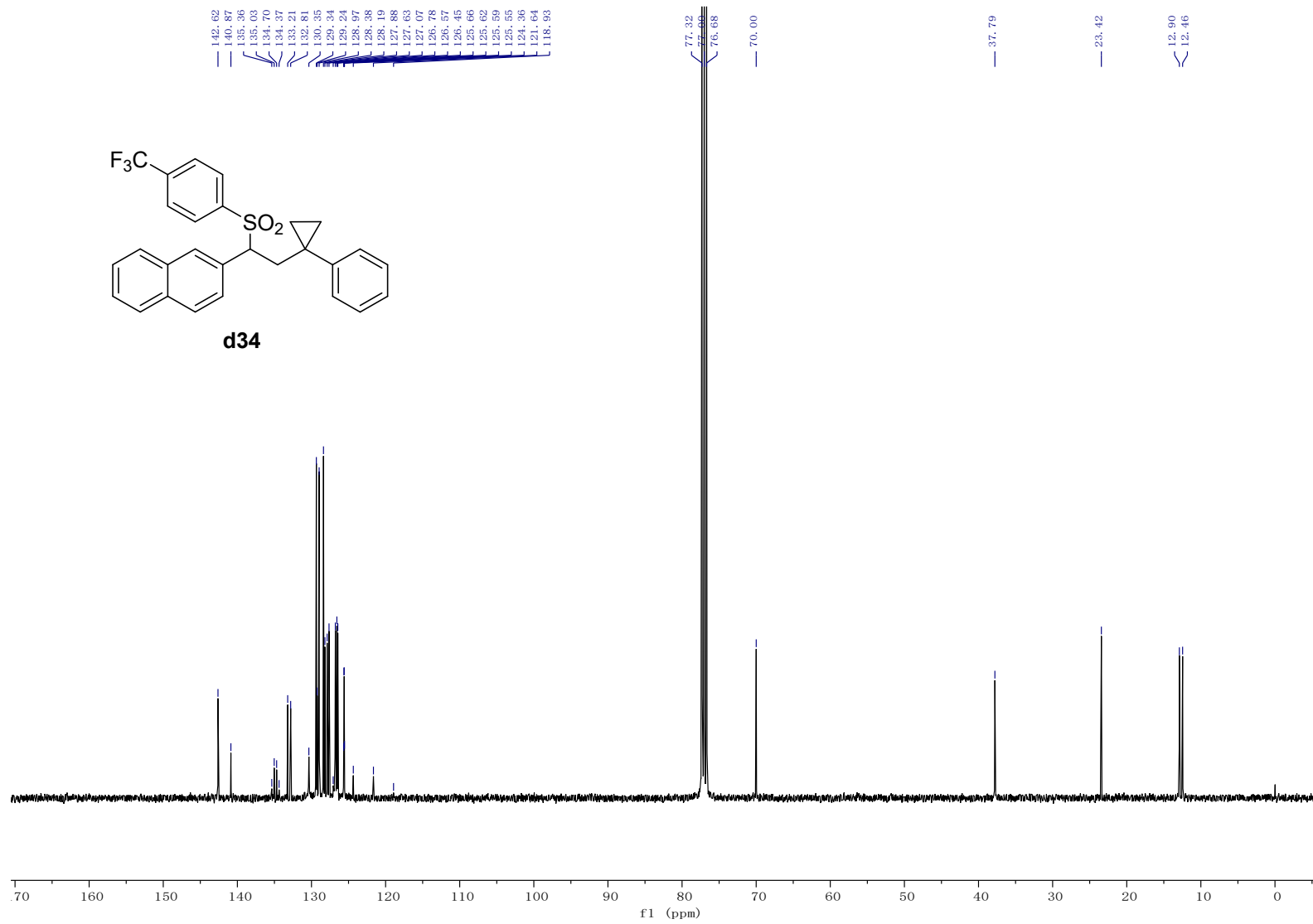


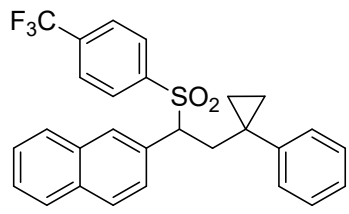


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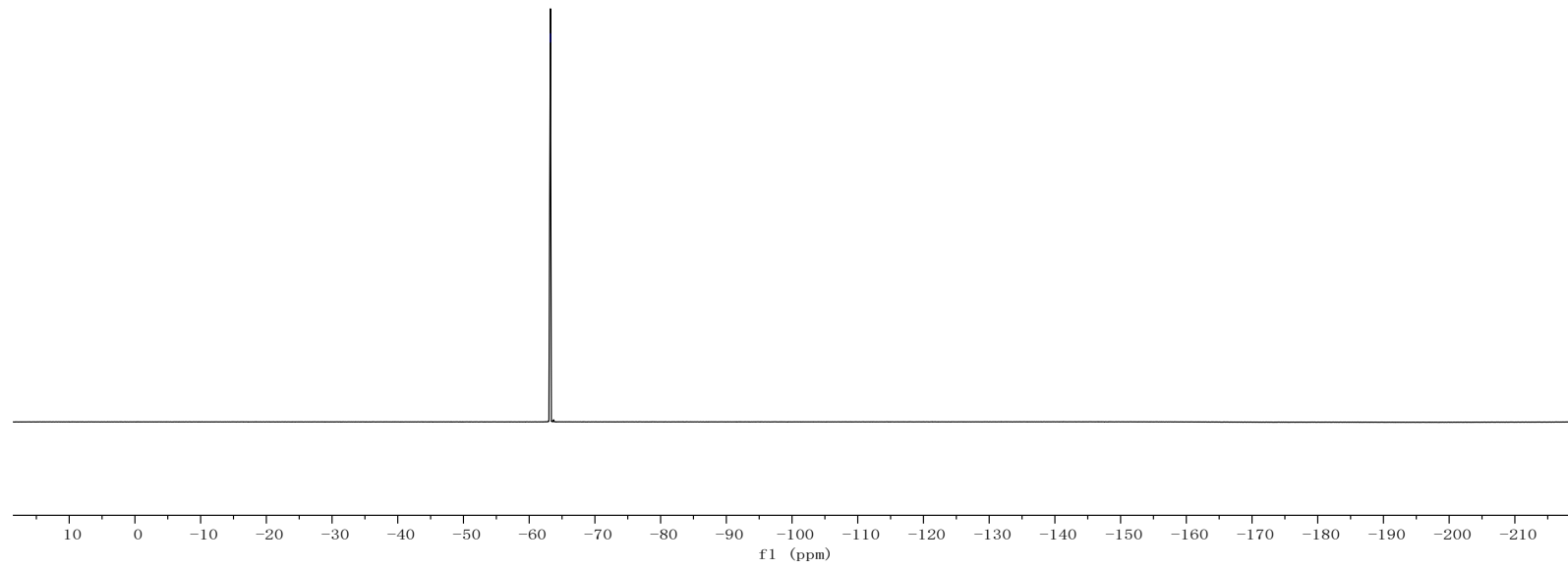


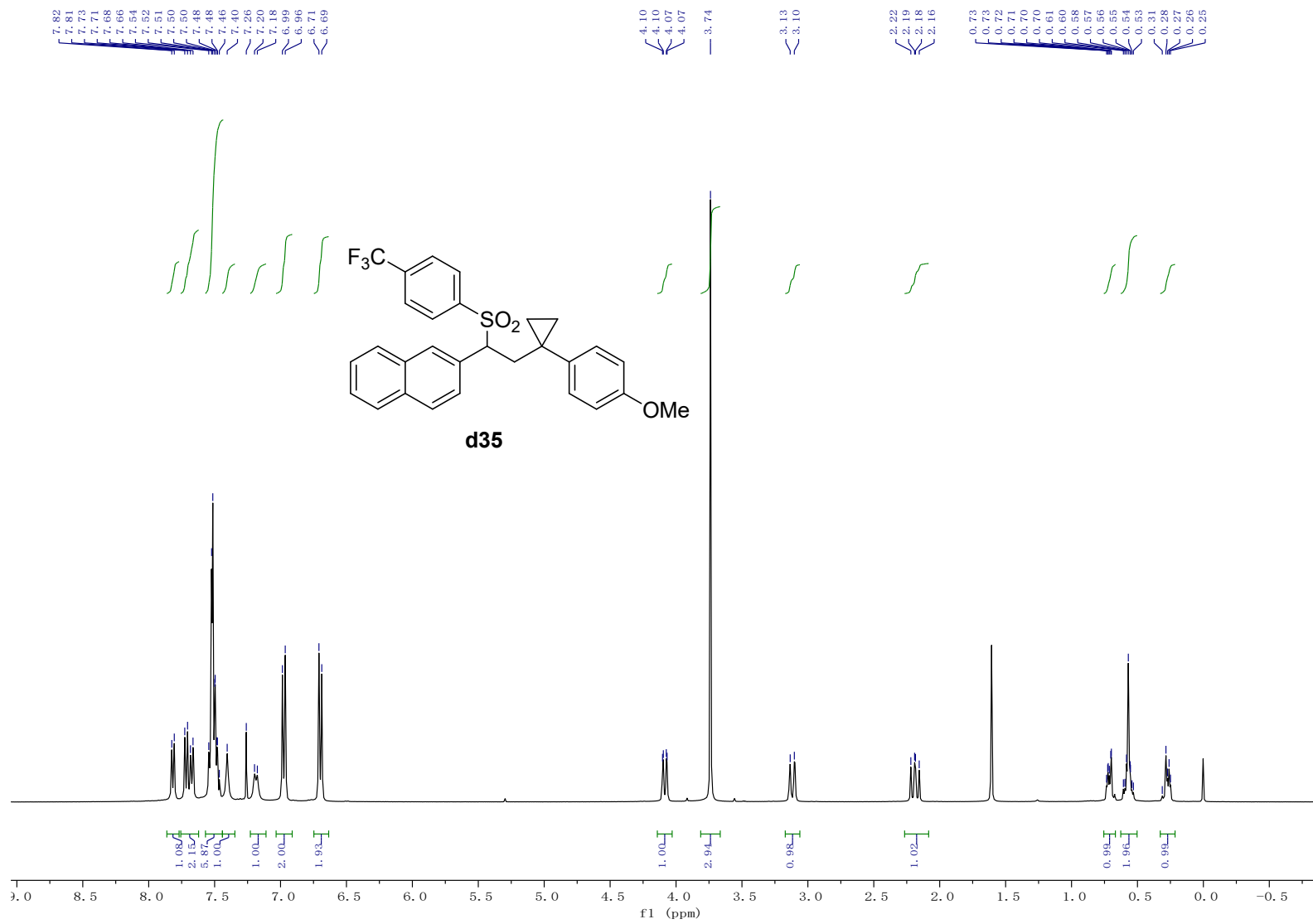


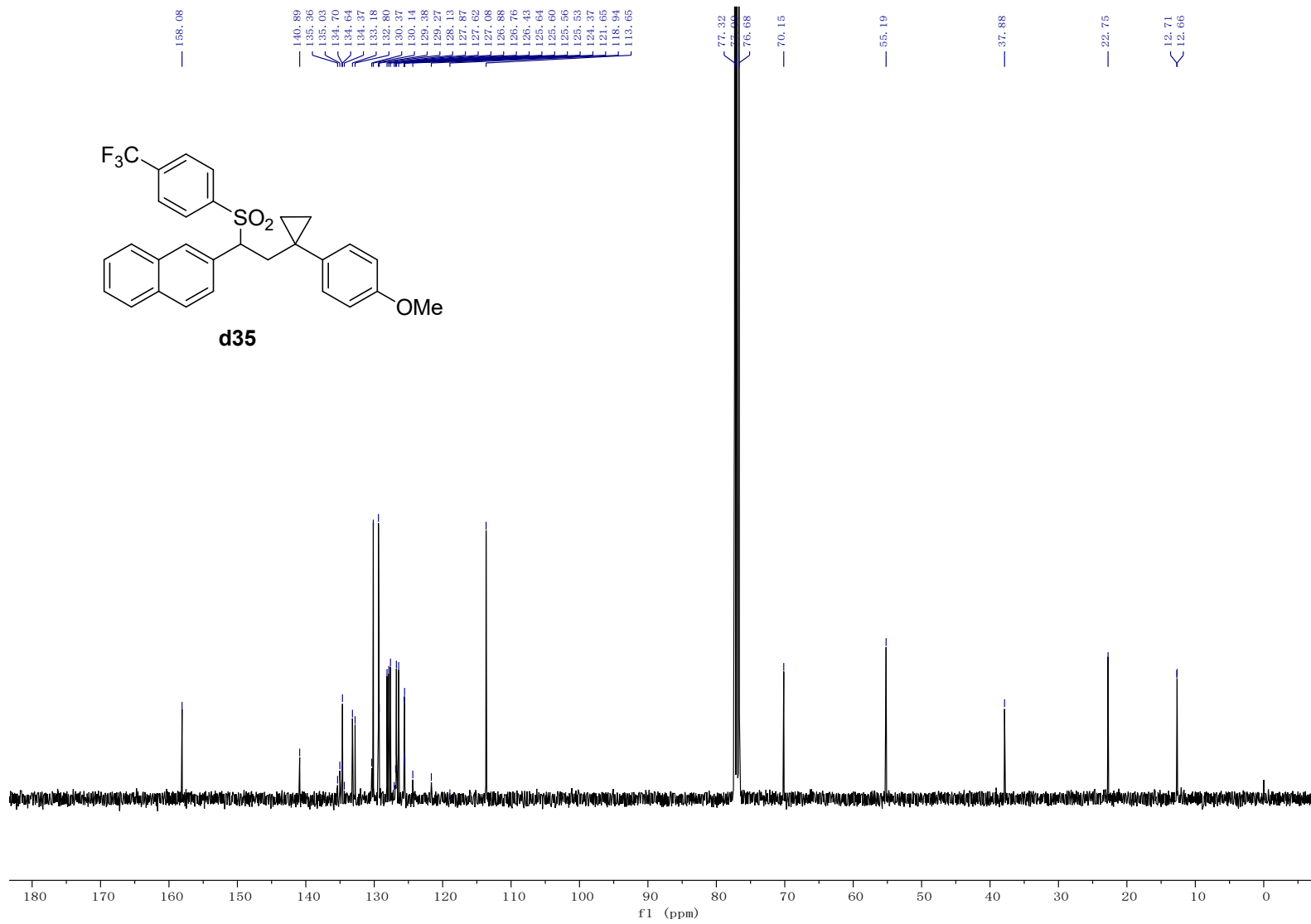


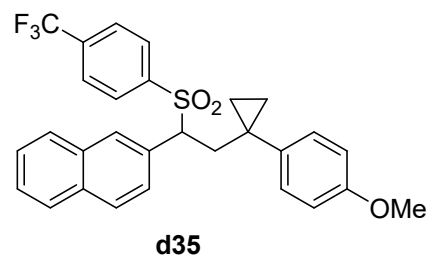
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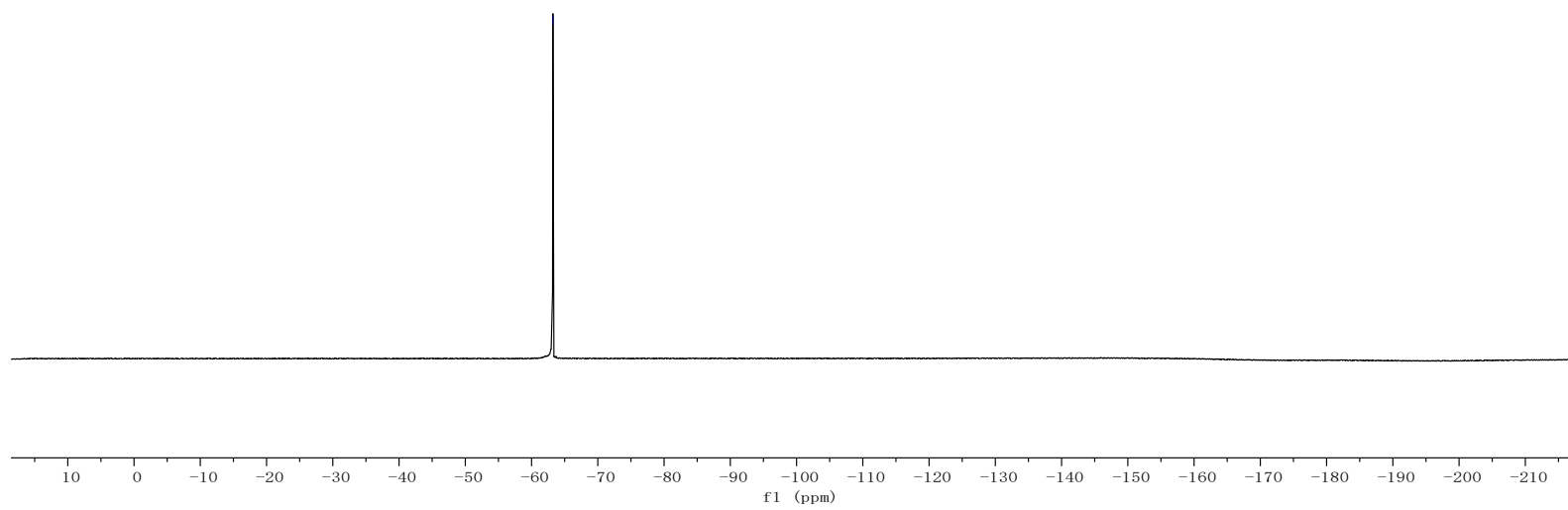


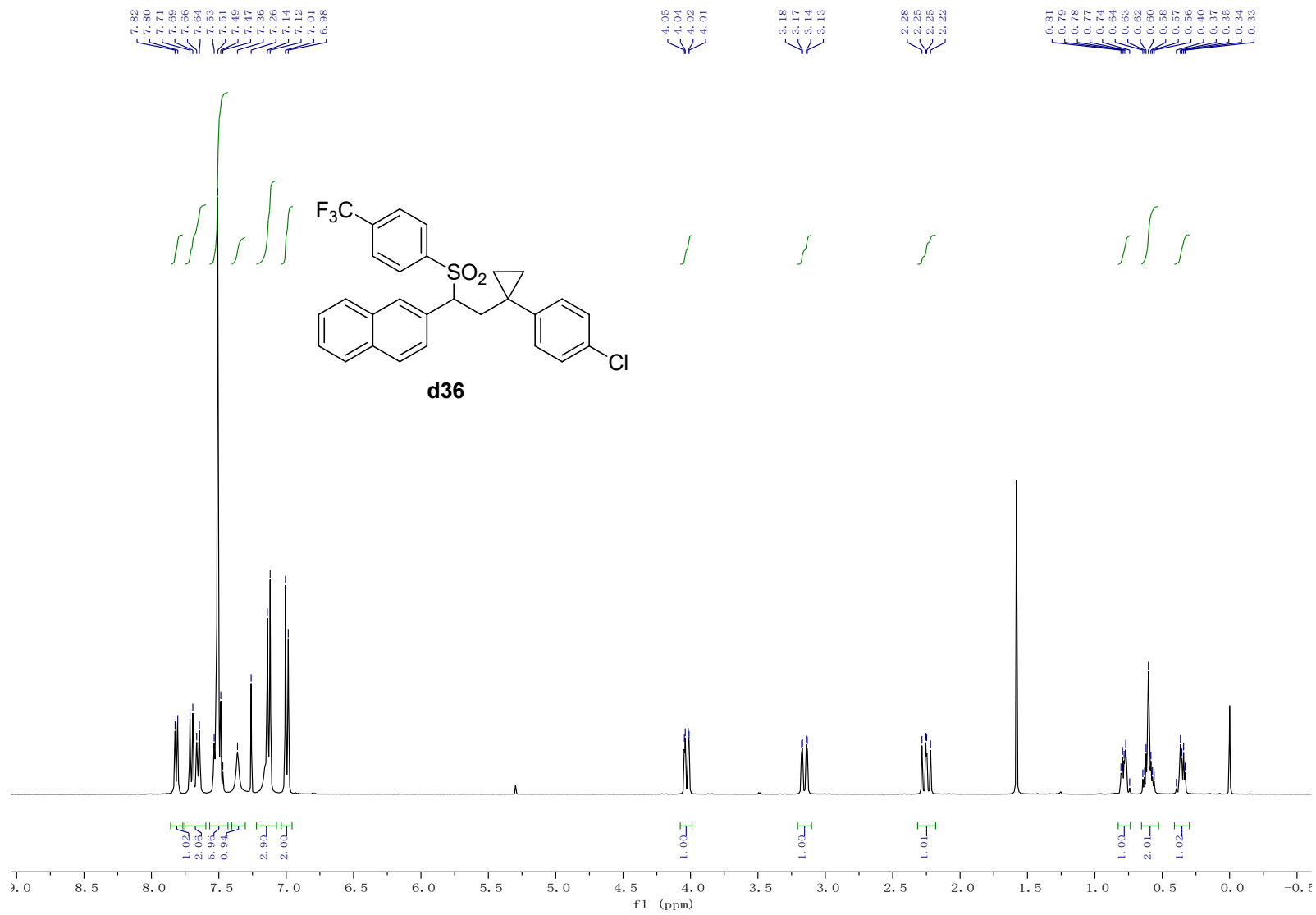


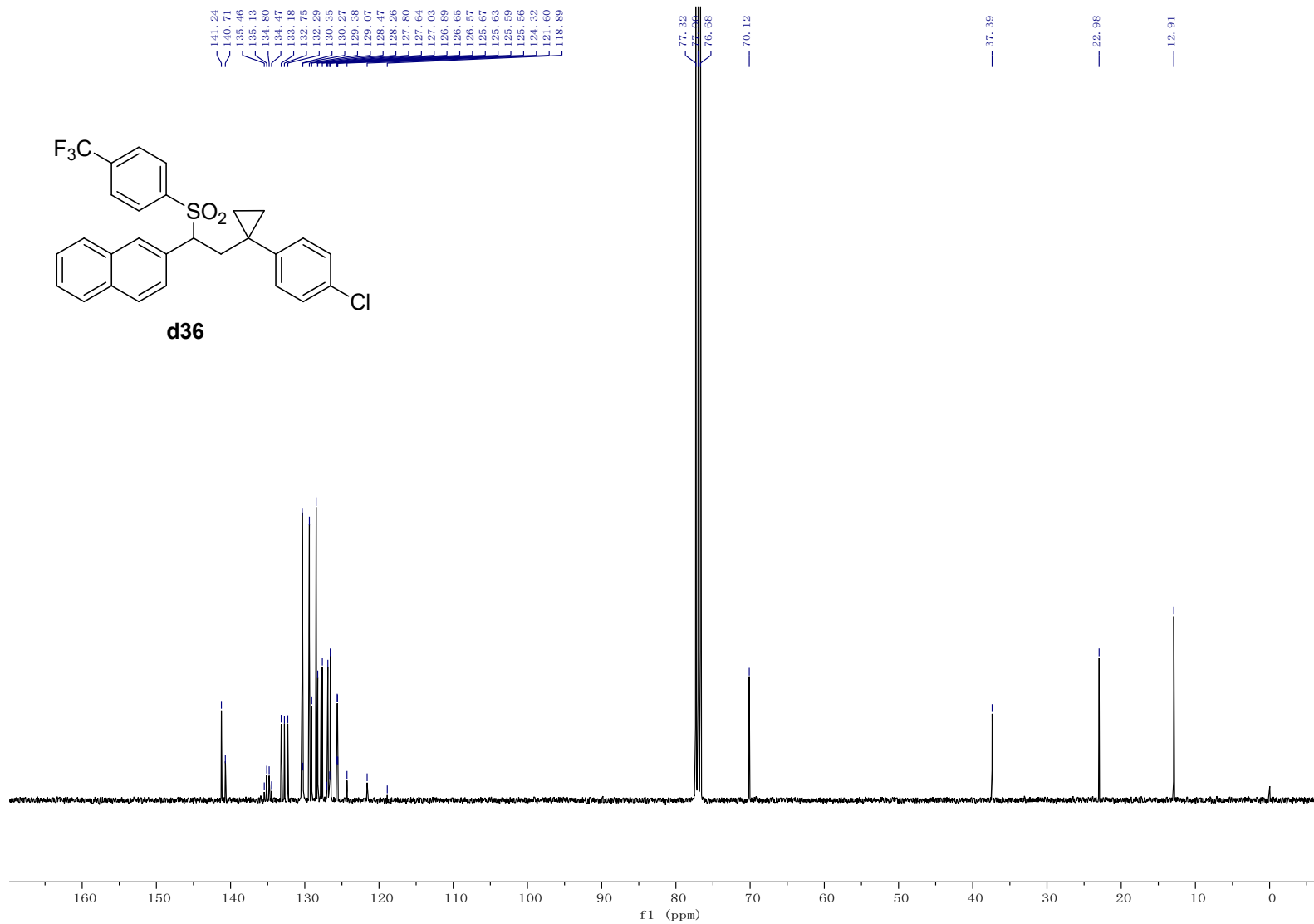
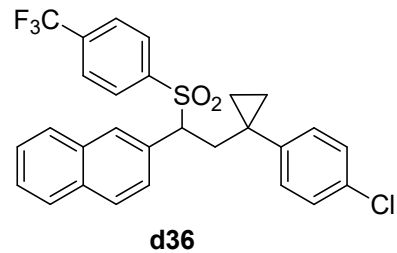


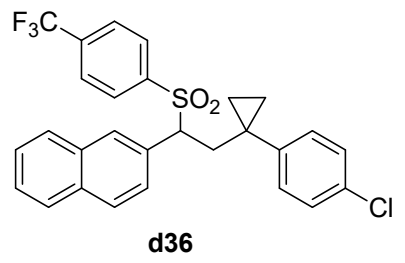


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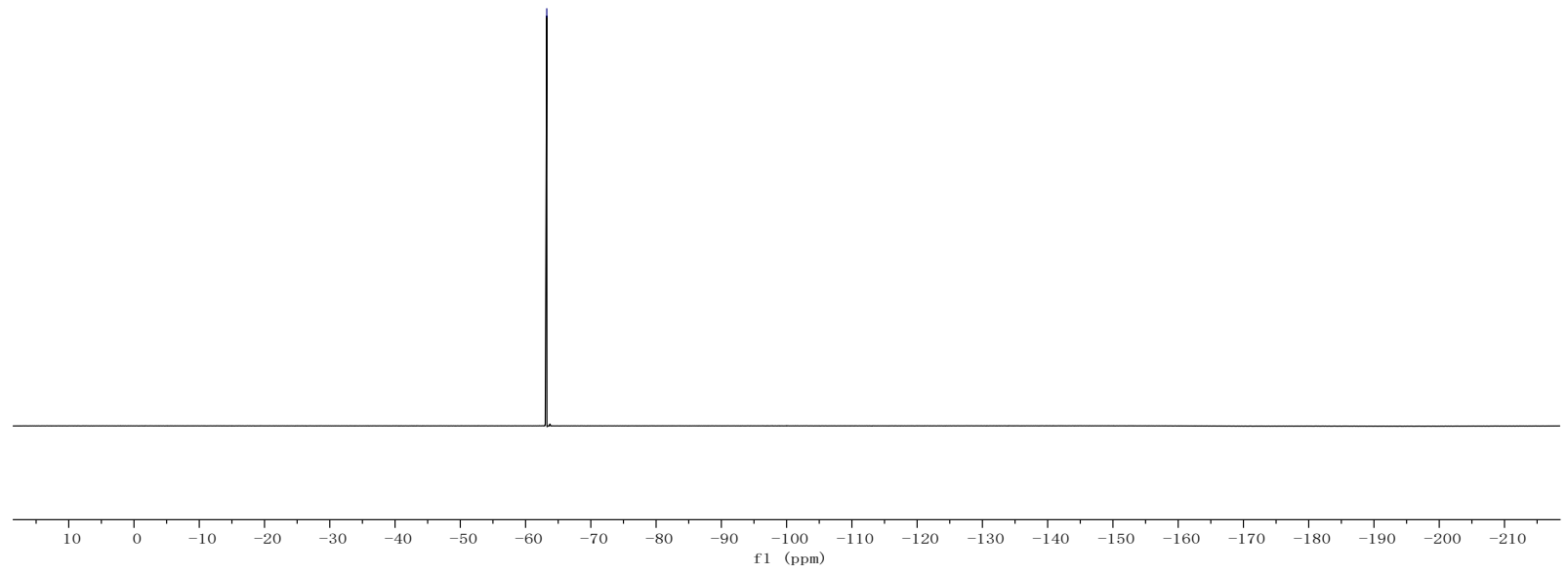


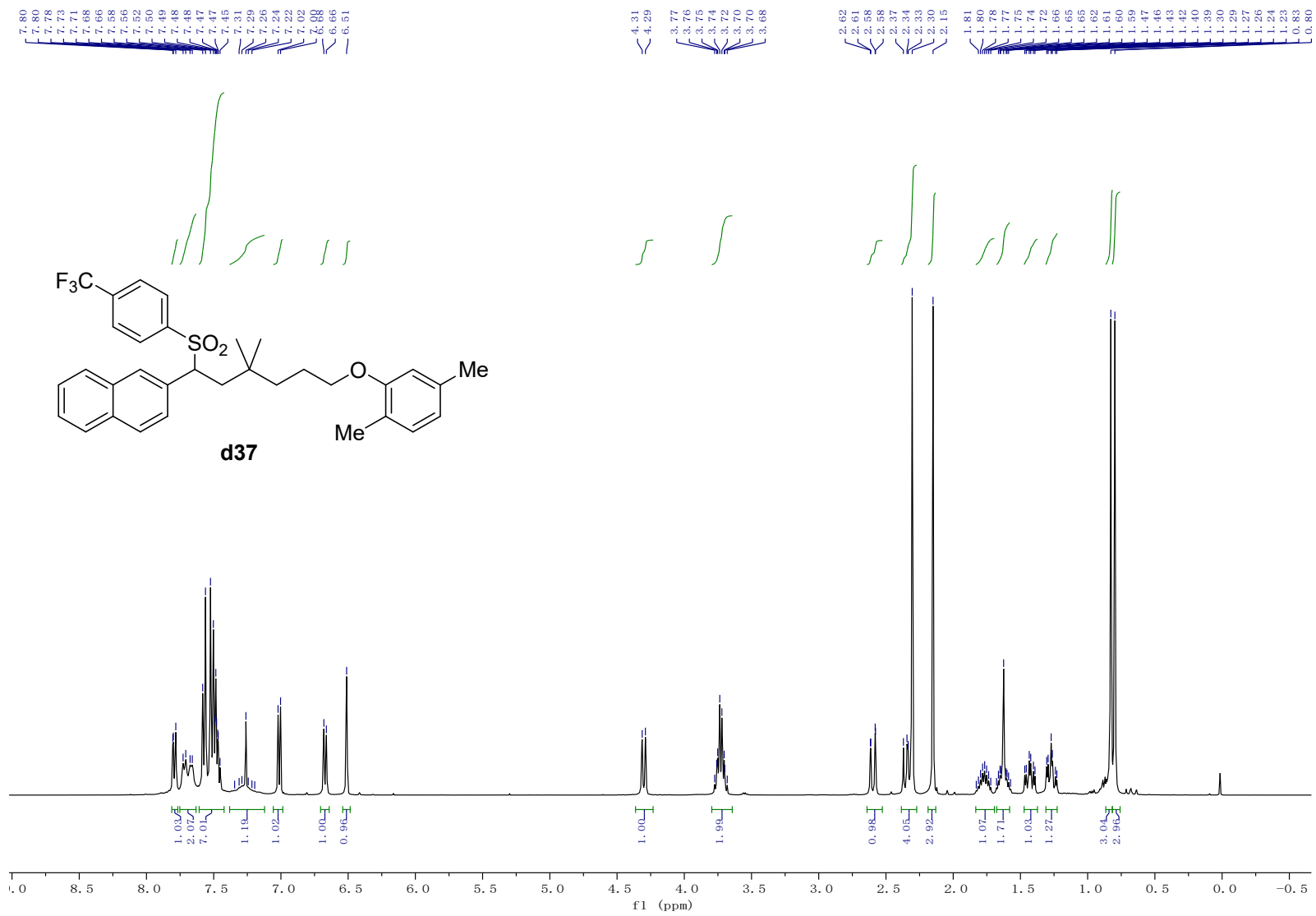


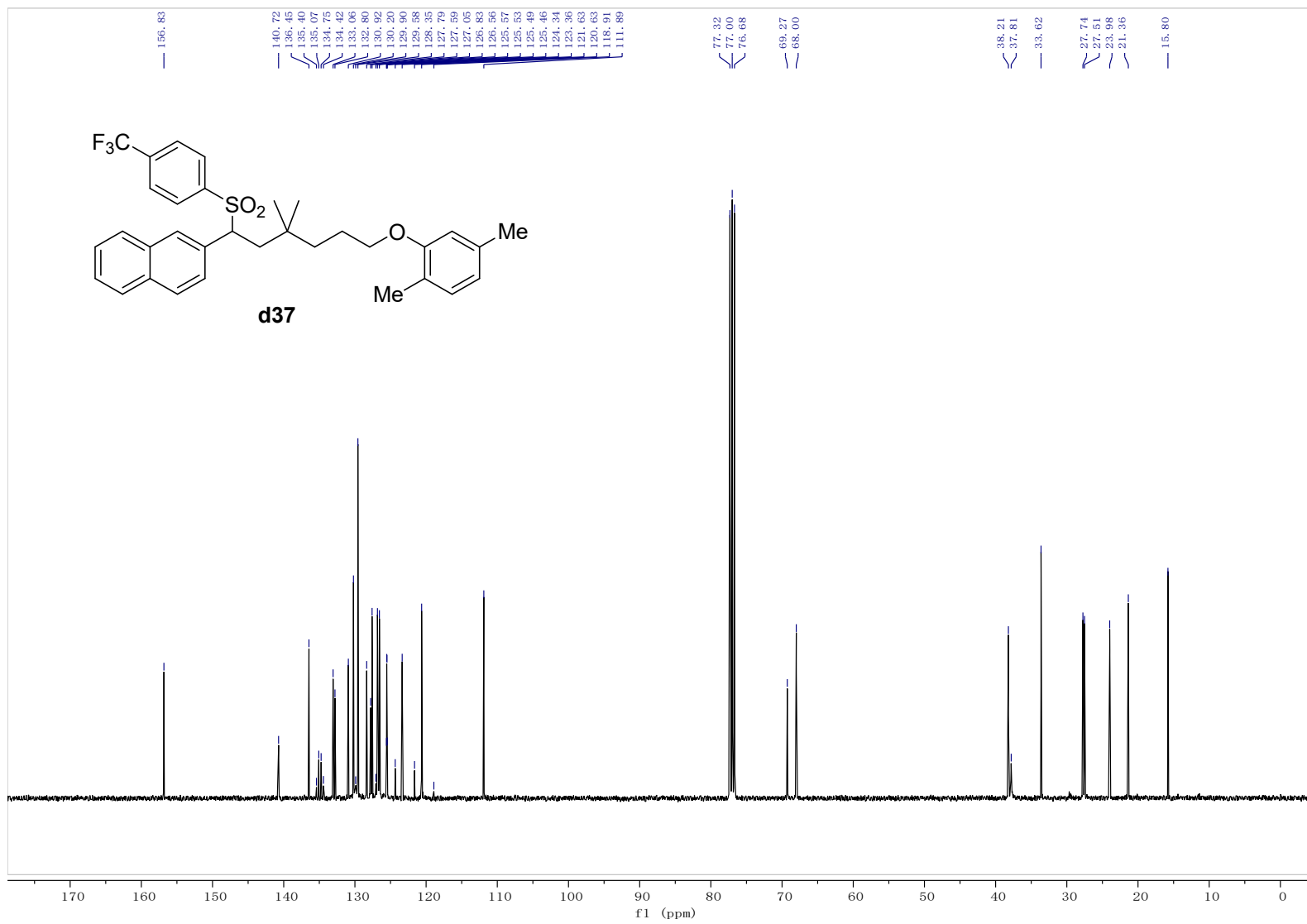


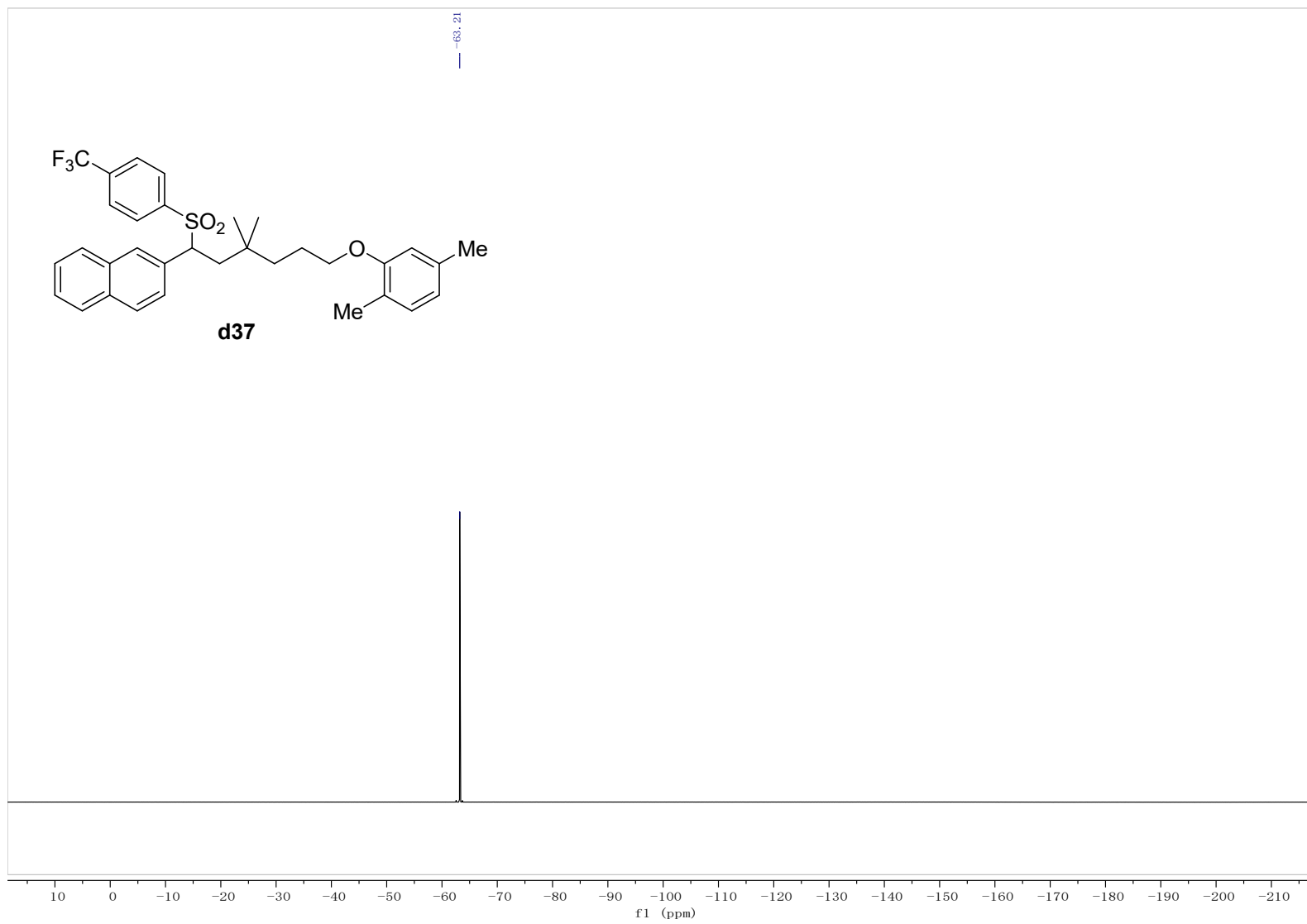


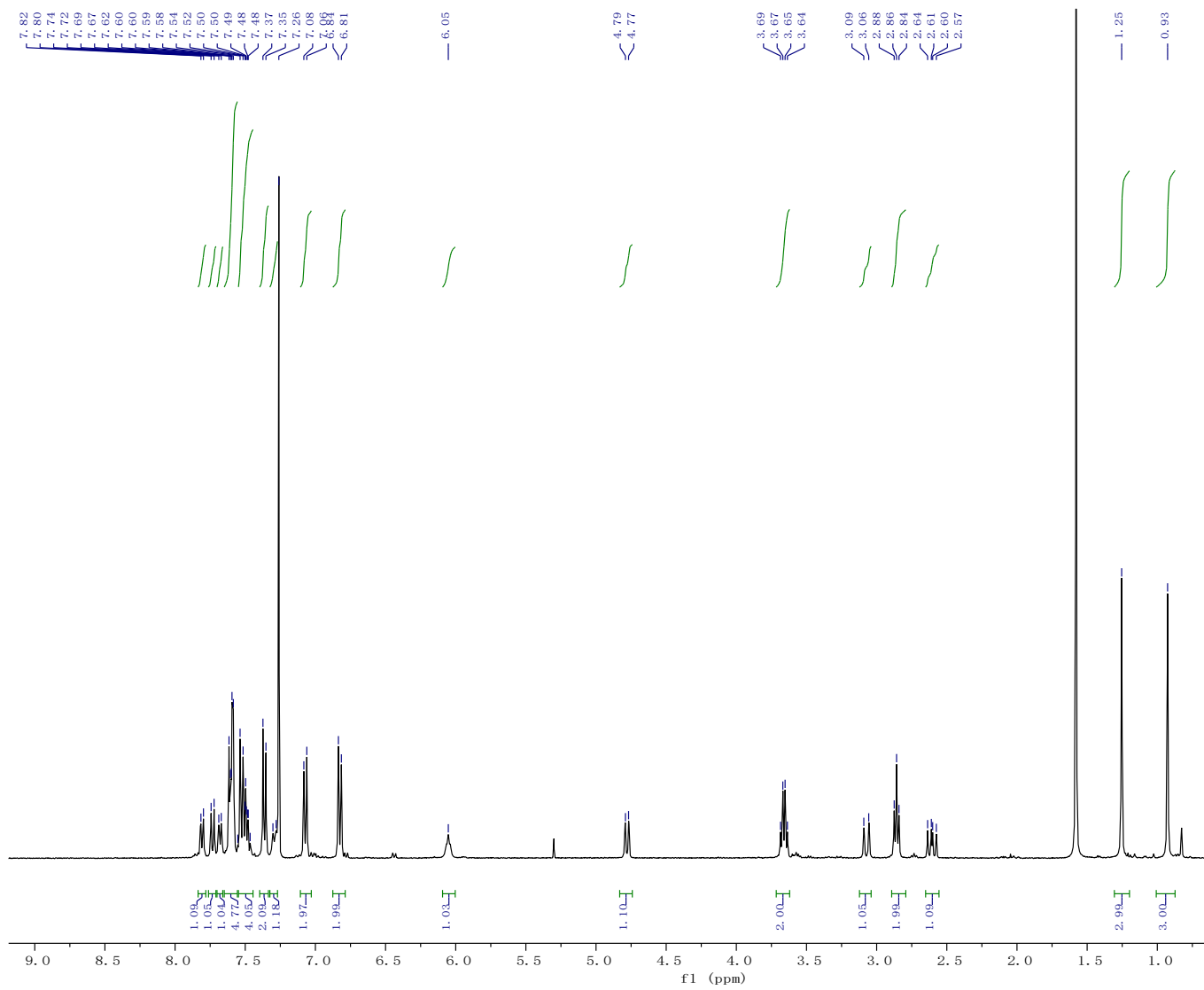
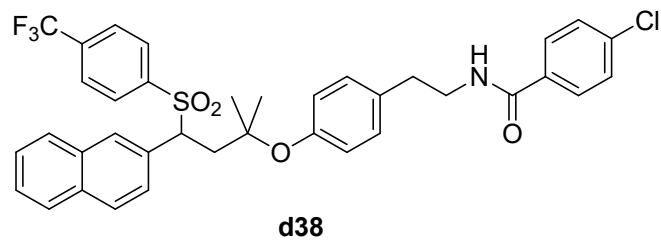
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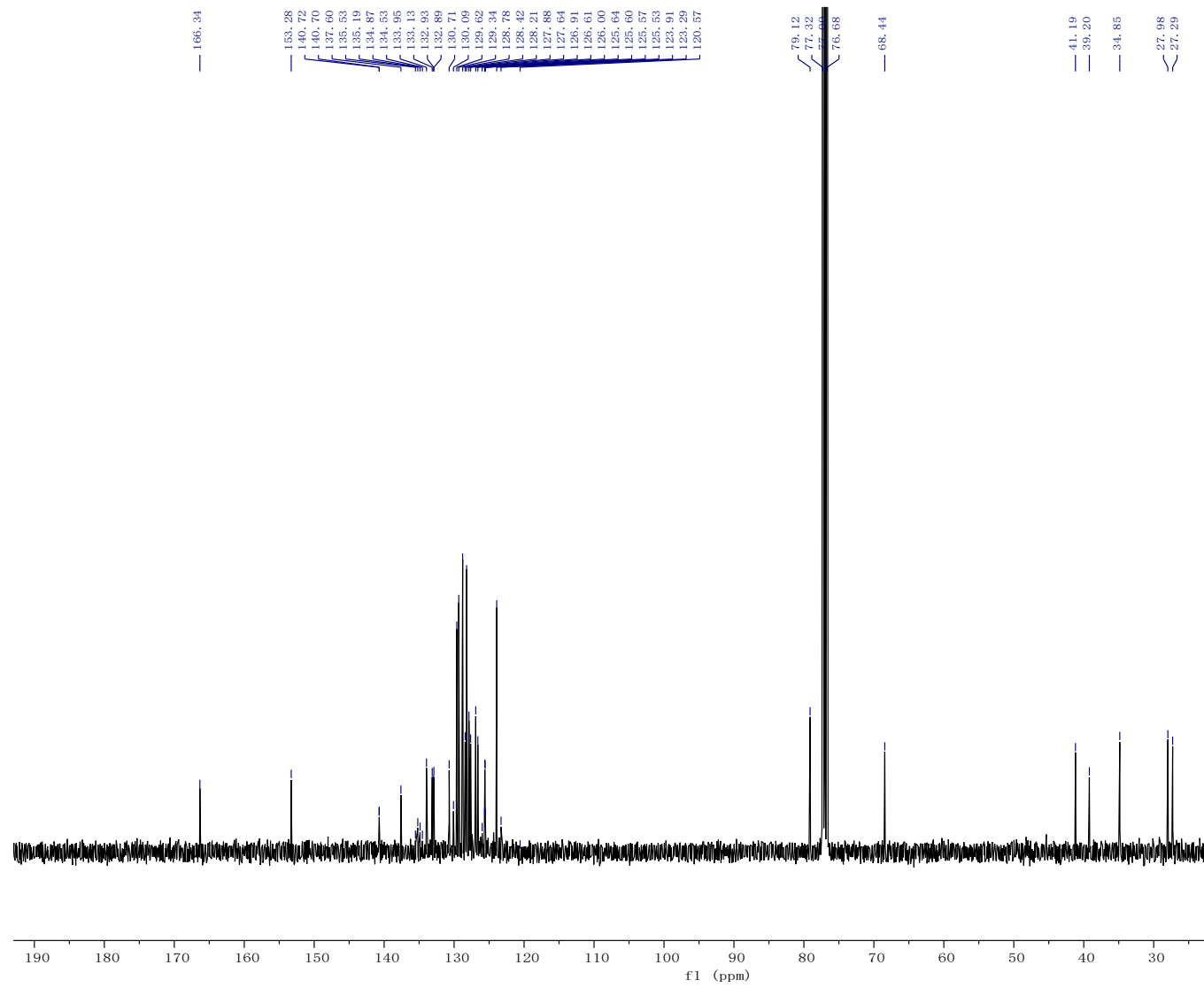
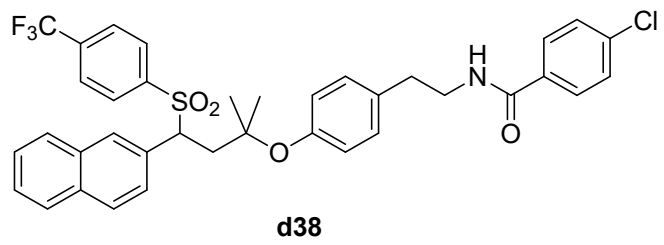


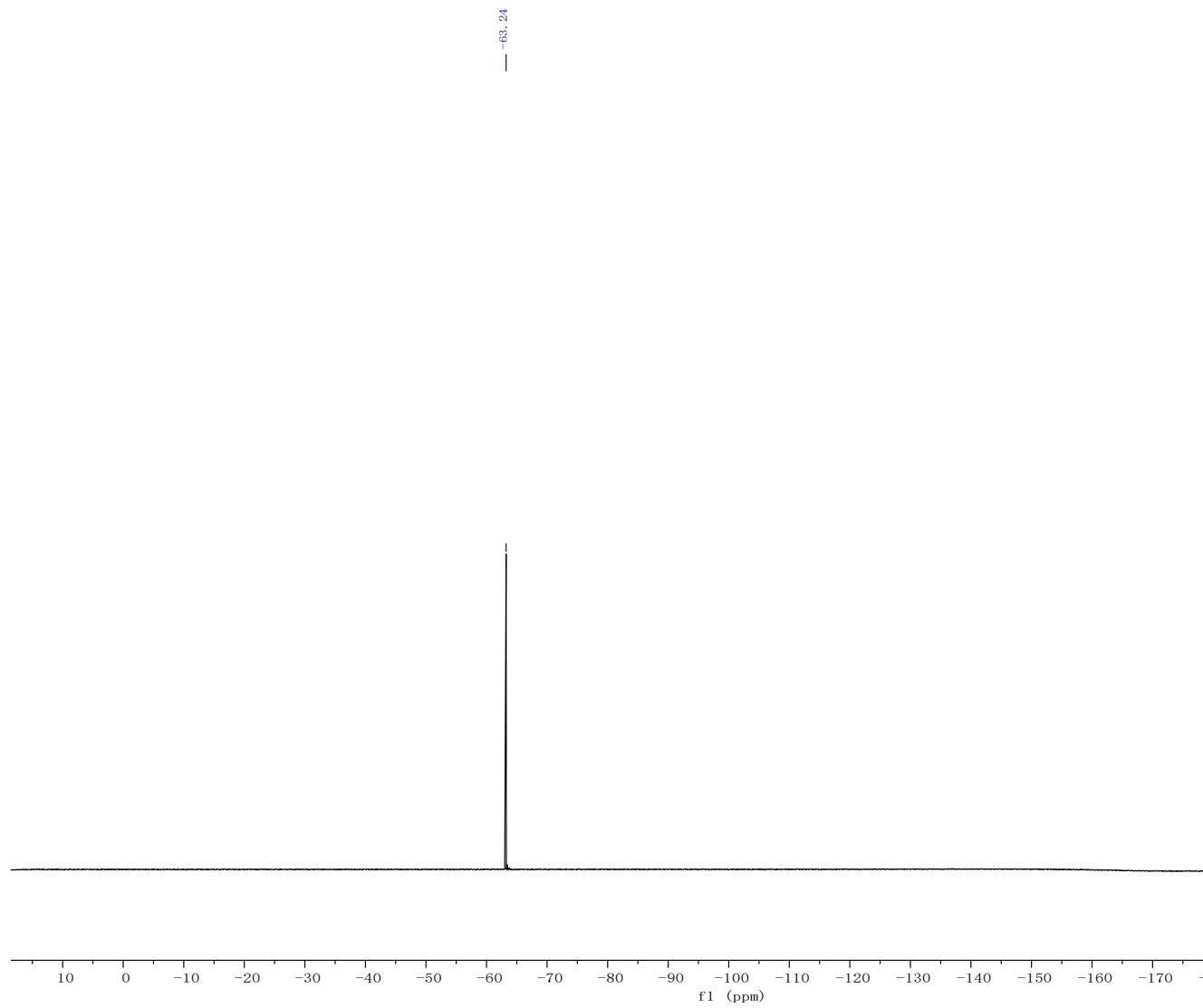
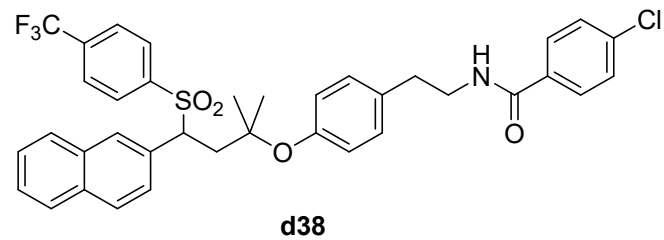


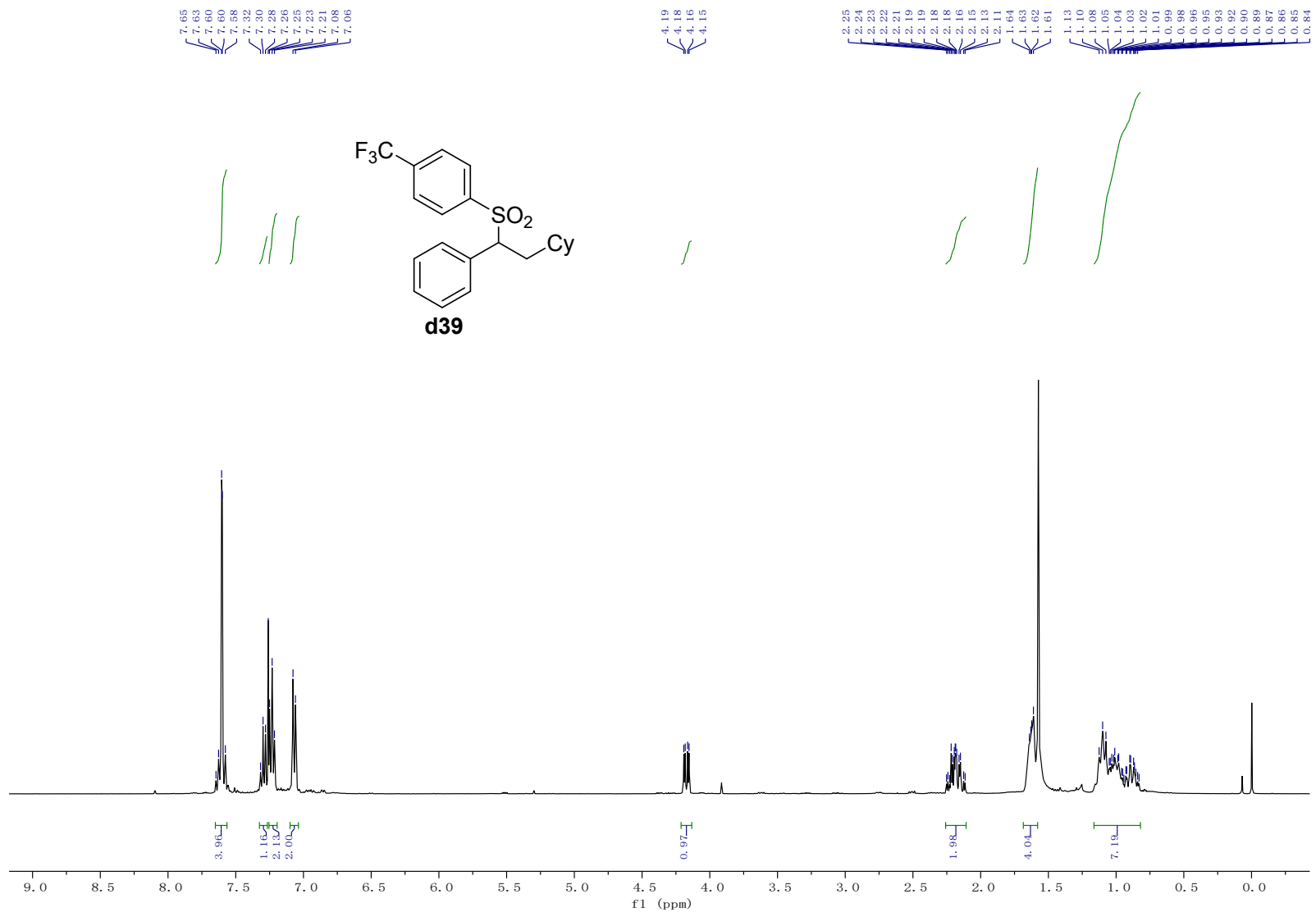


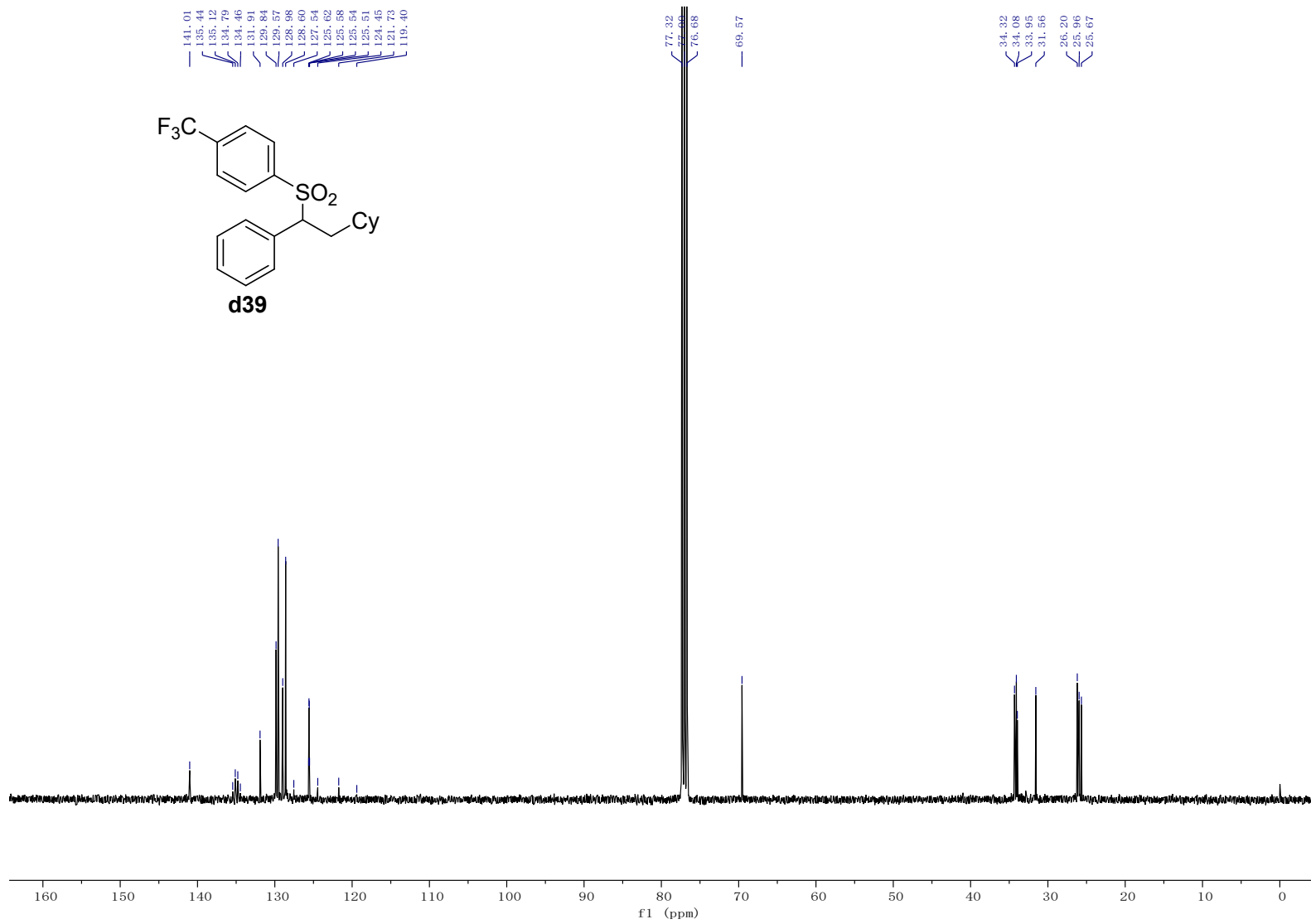


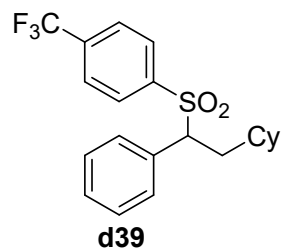




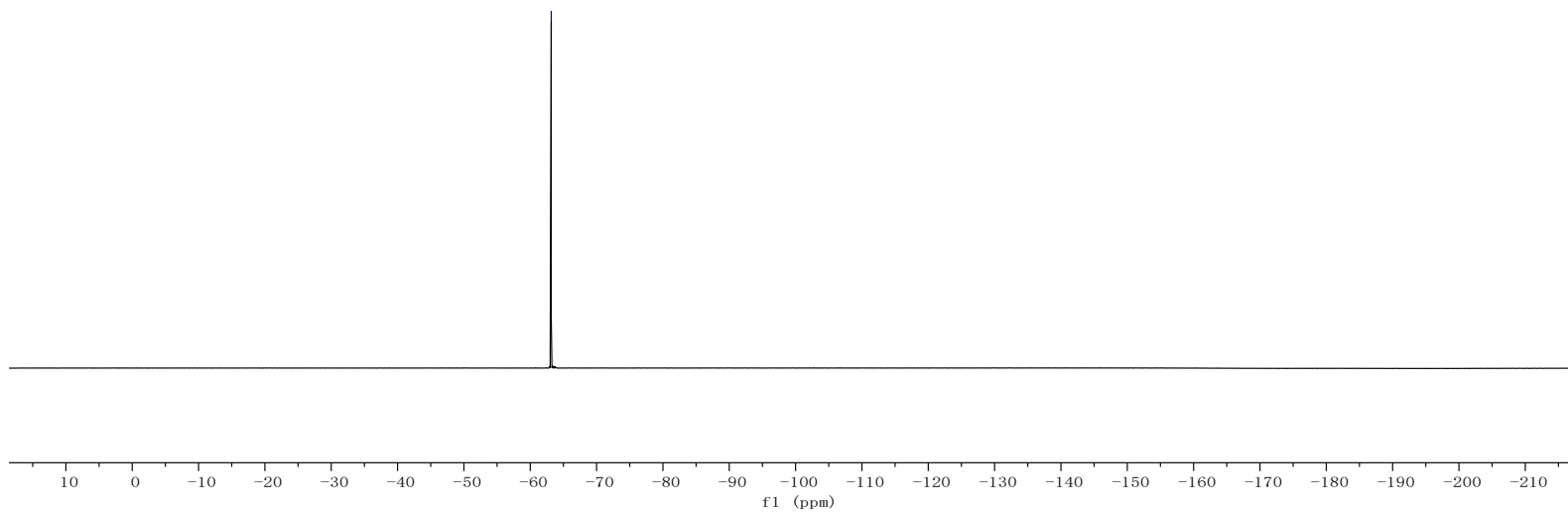


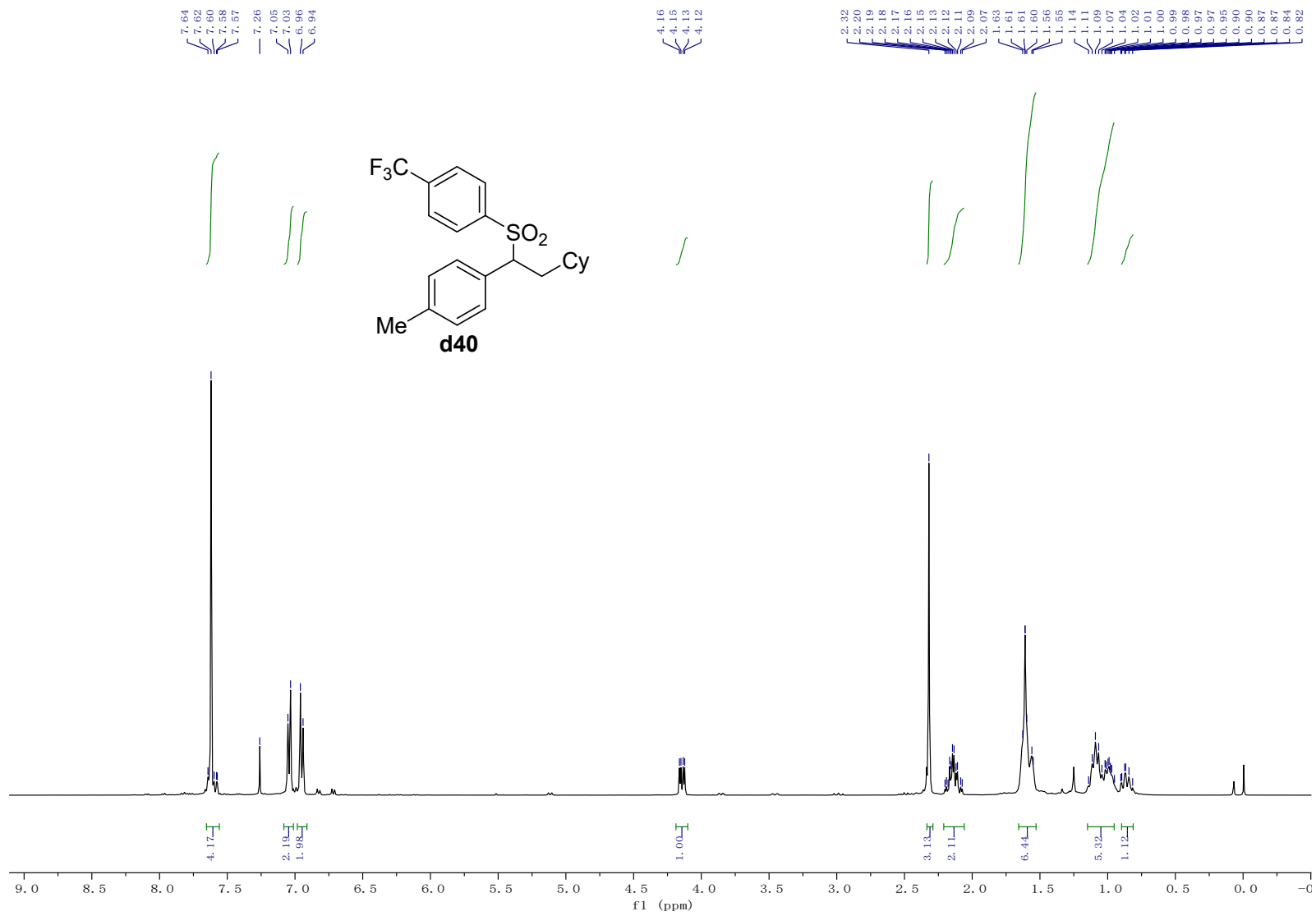


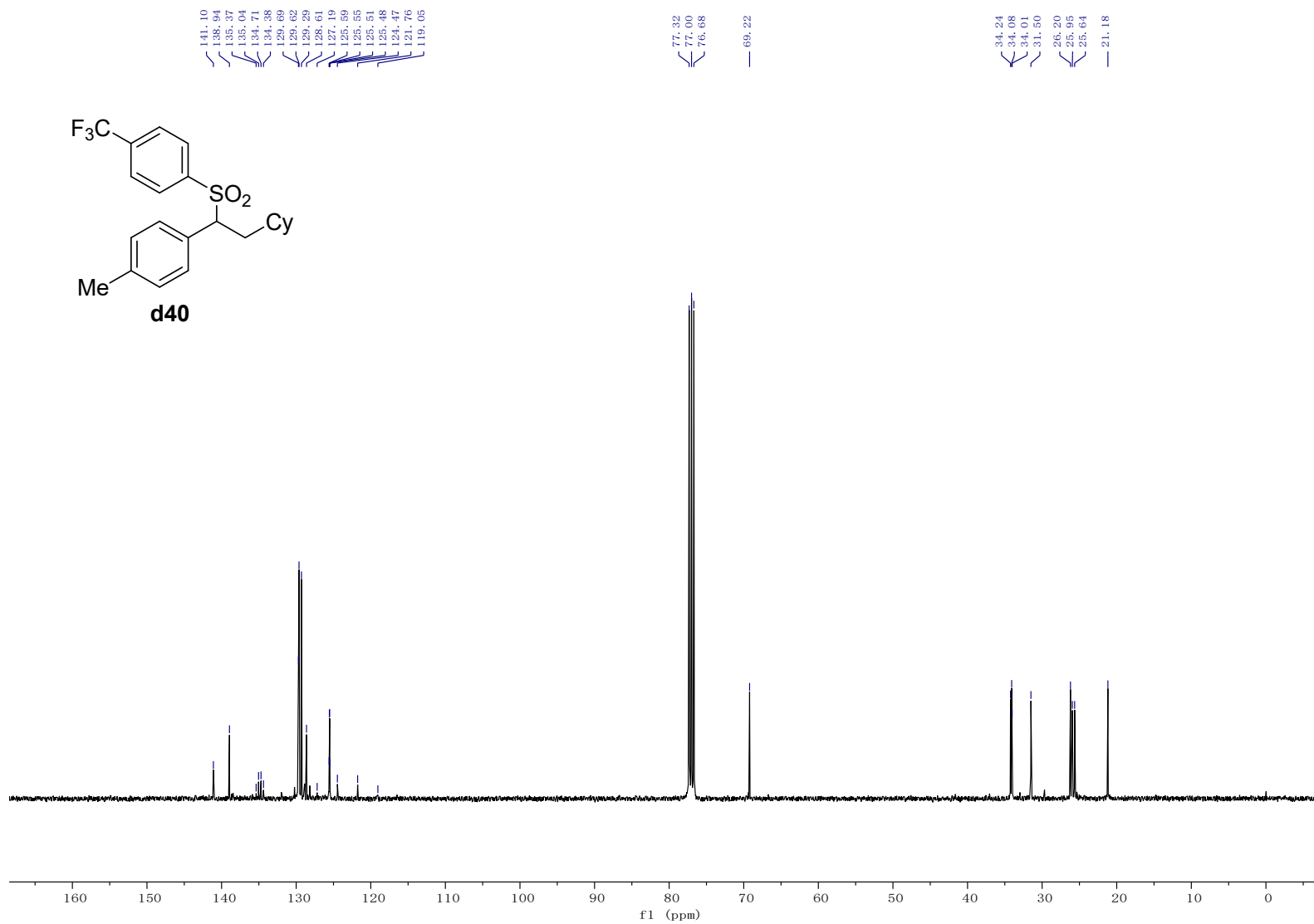
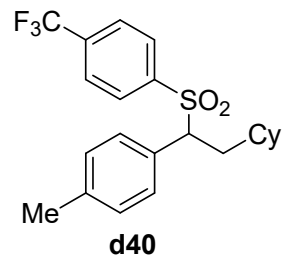


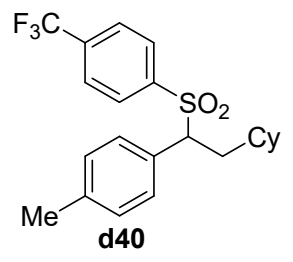


— 63.17

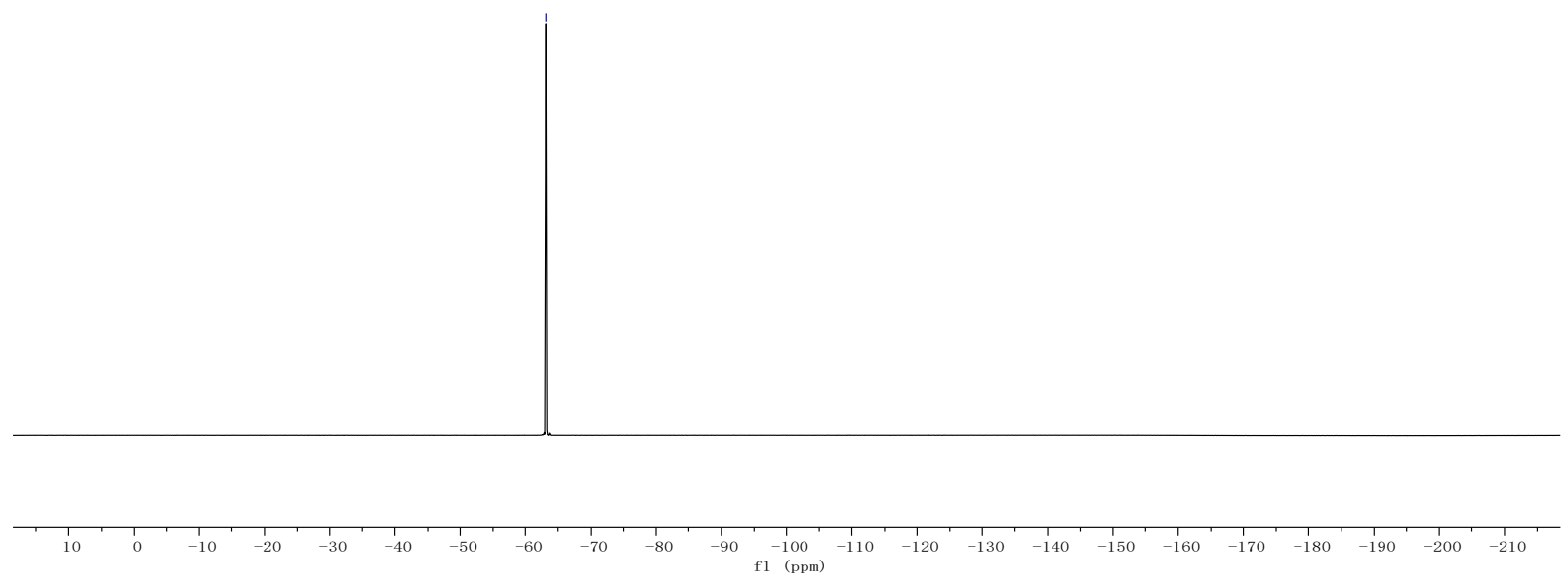


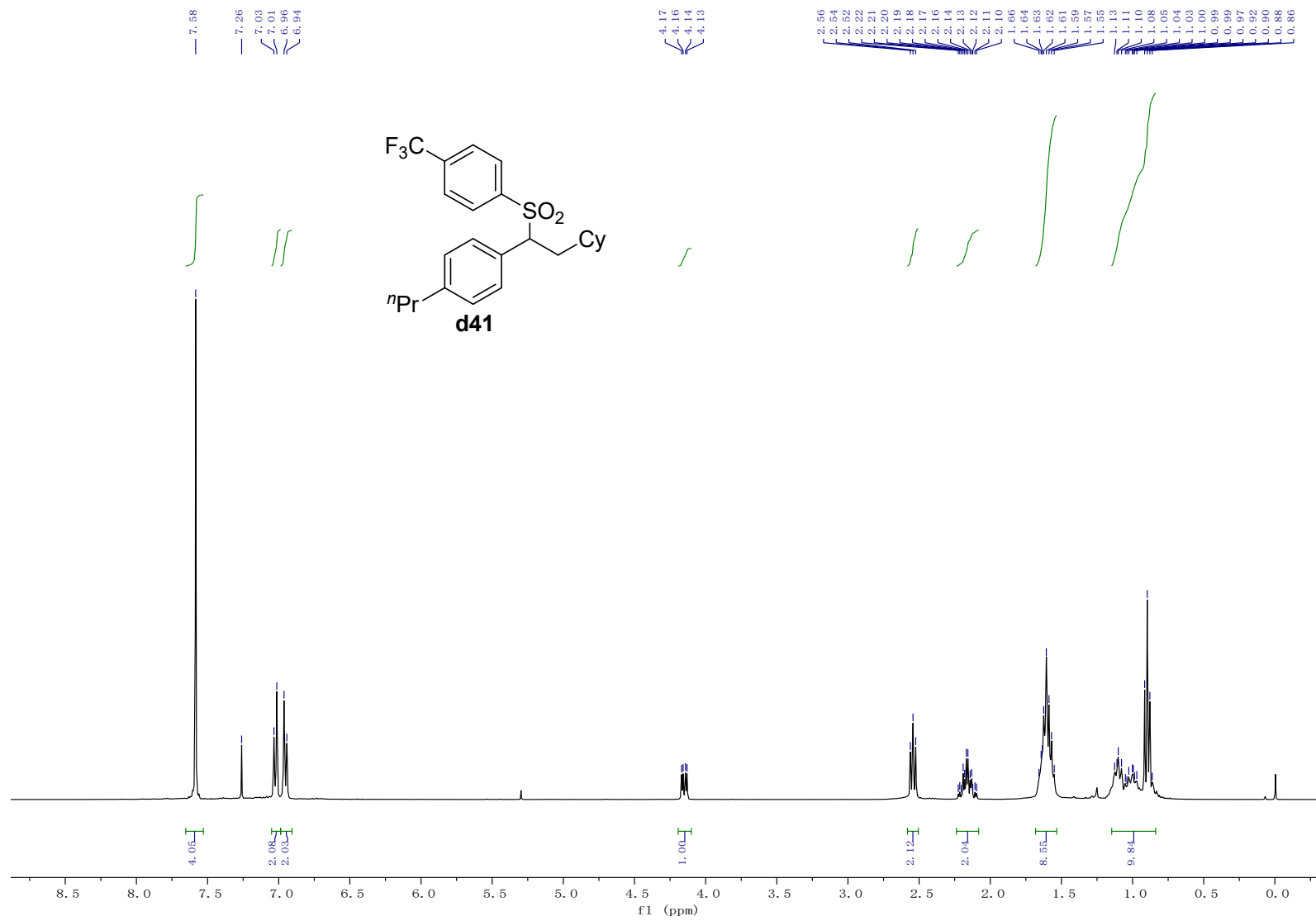


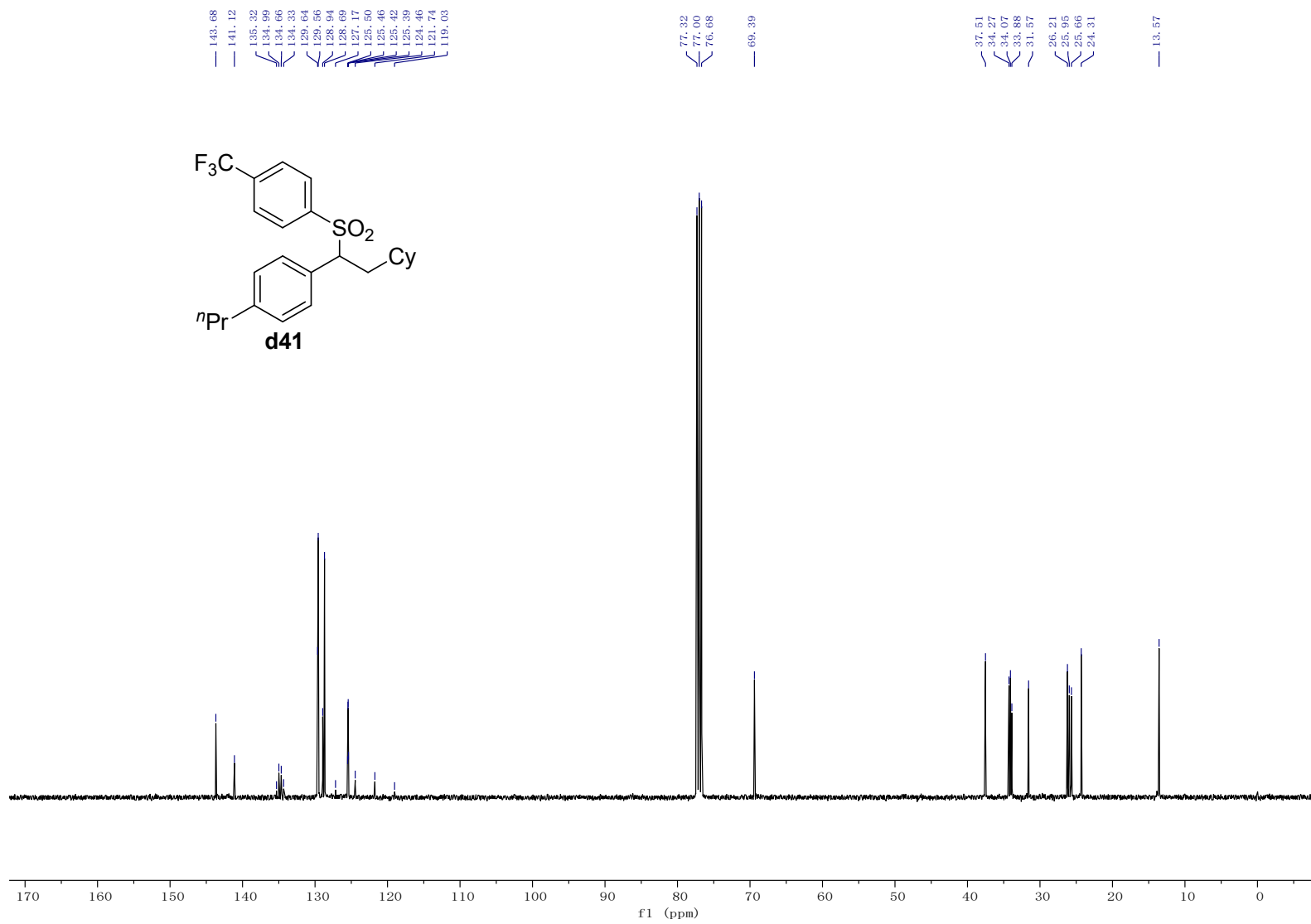


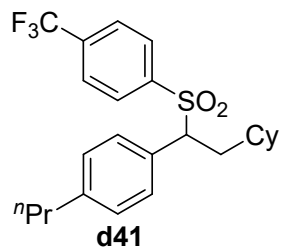


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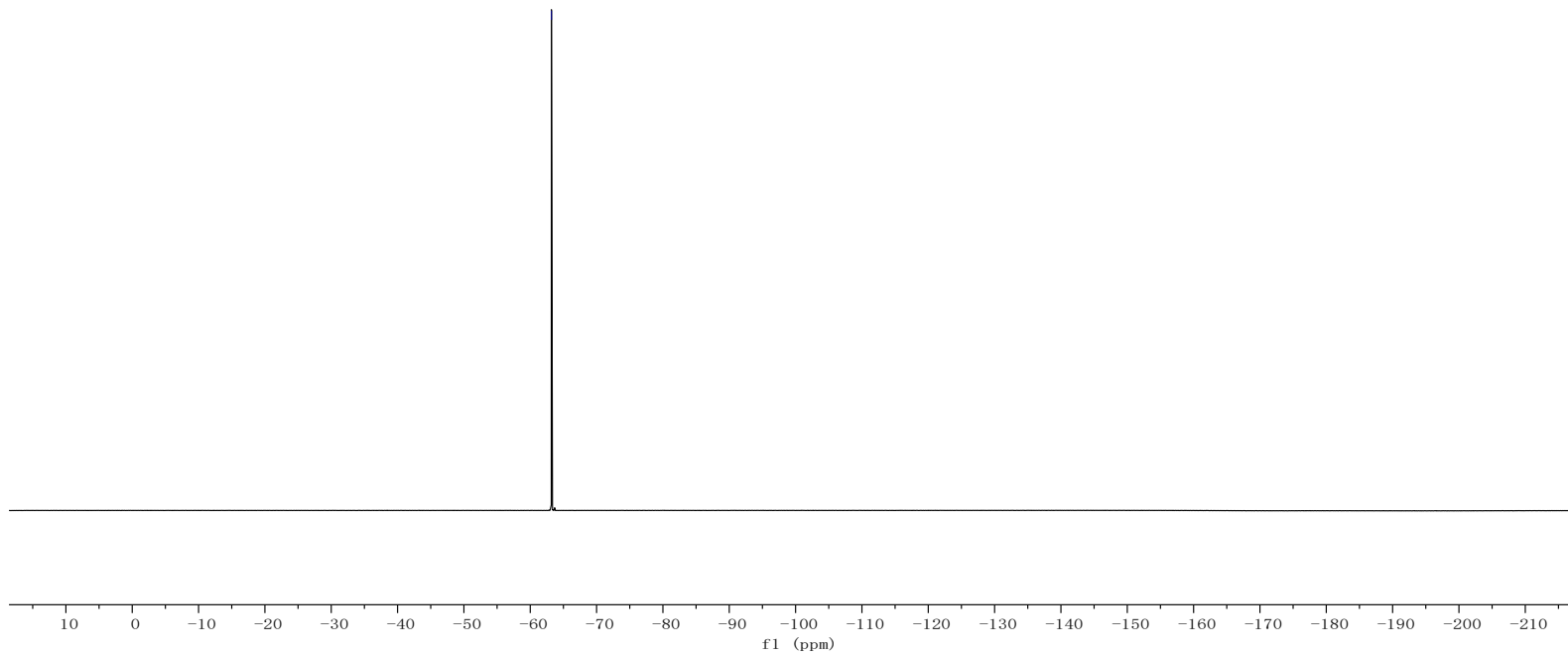


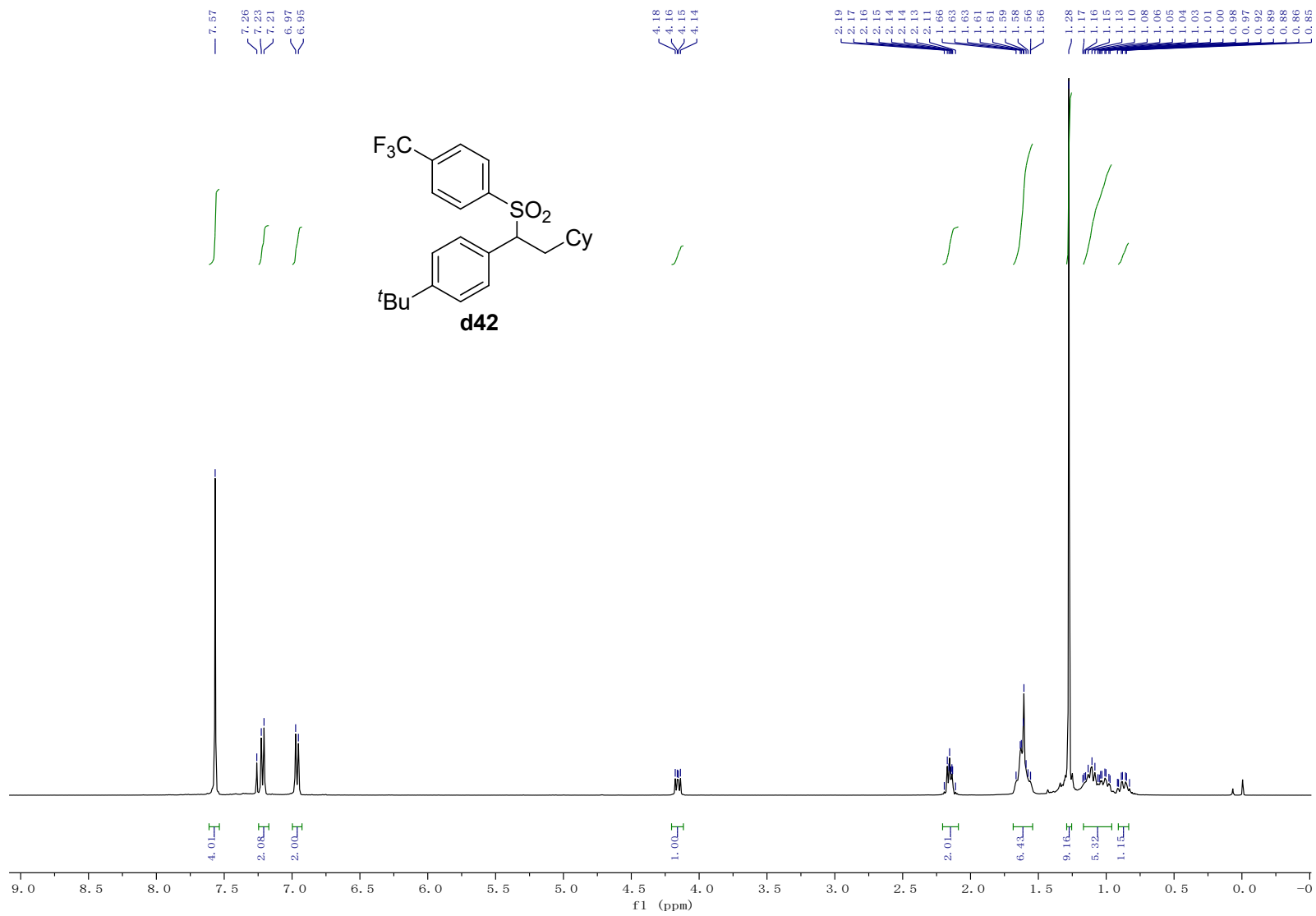


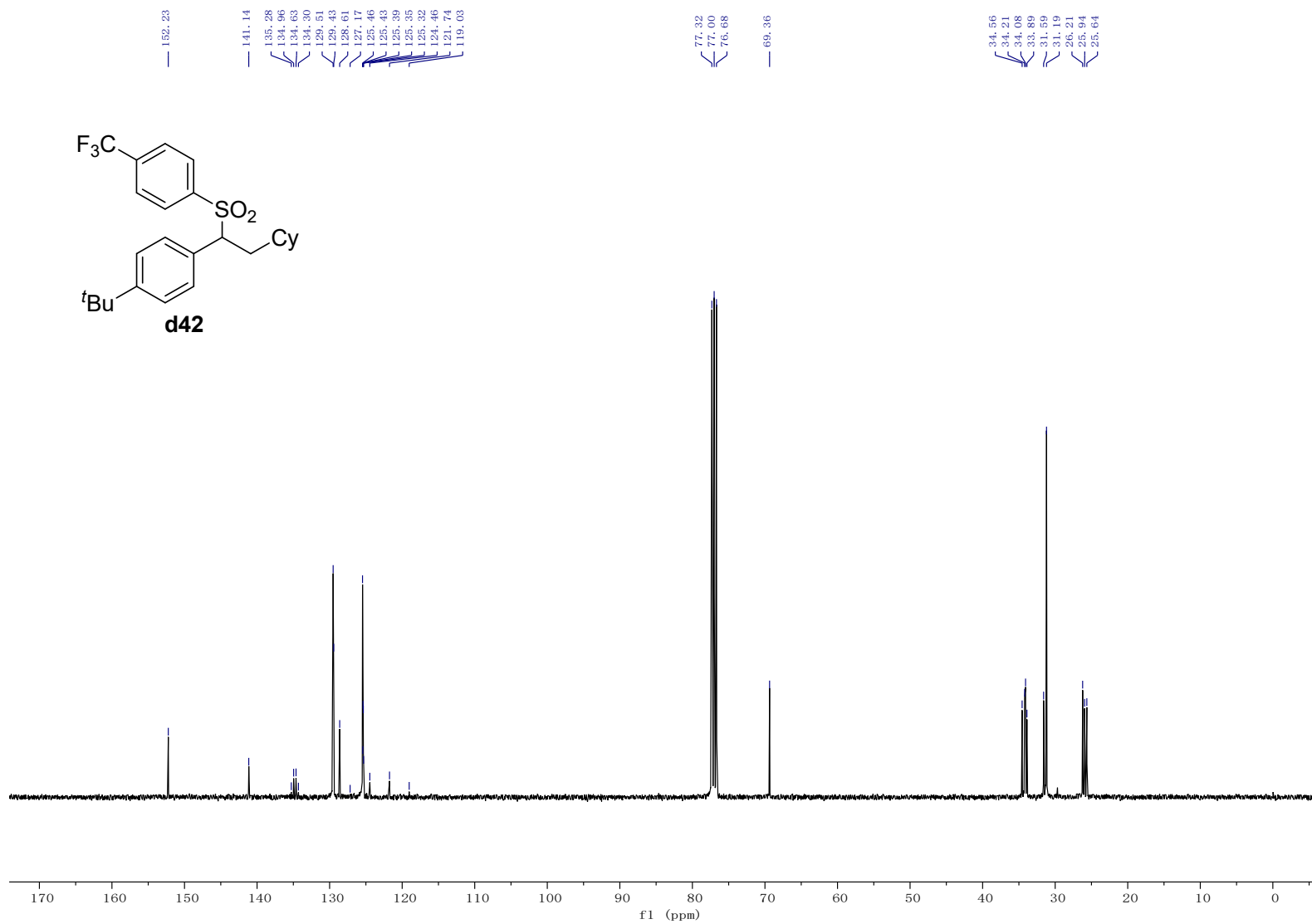
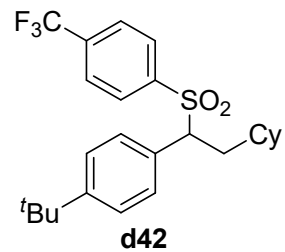


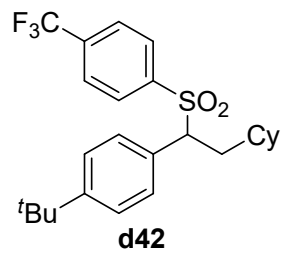


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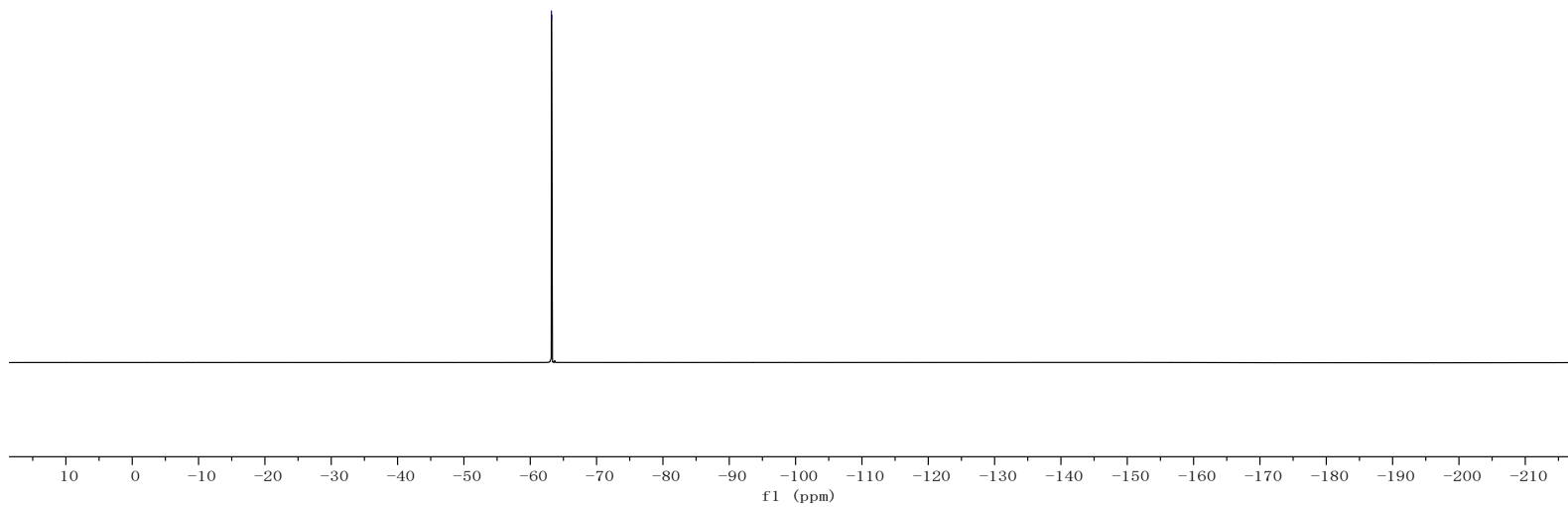


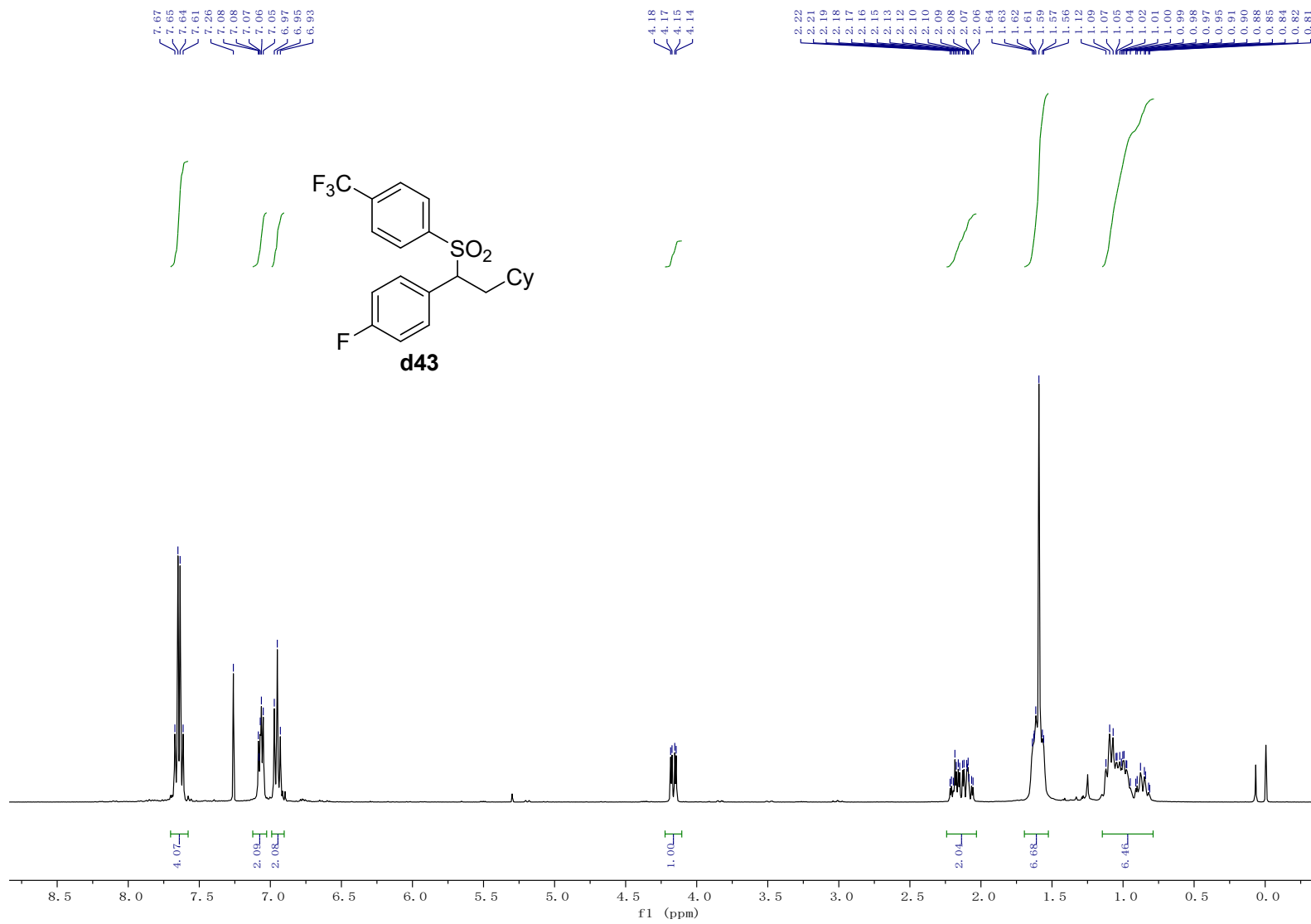


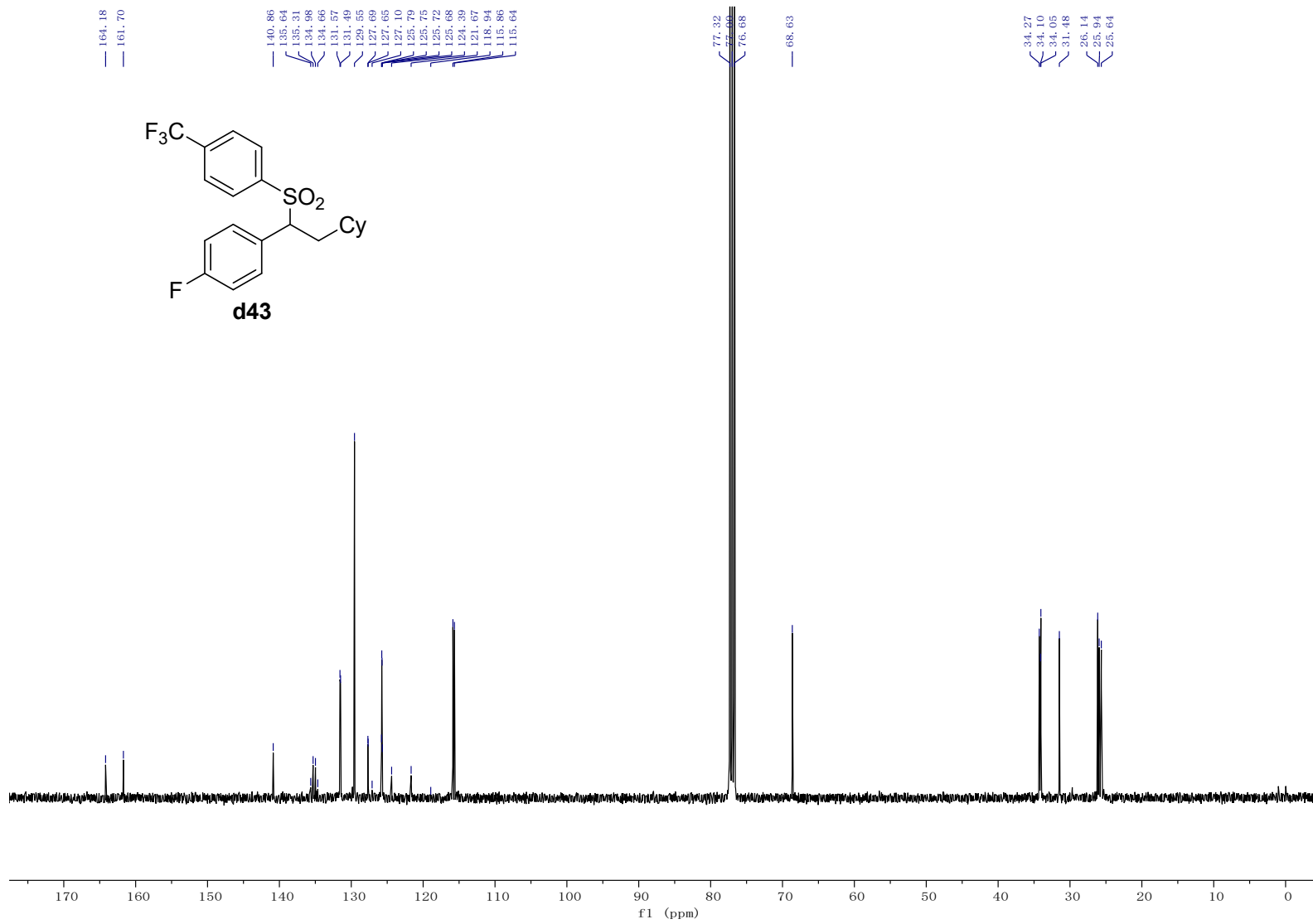


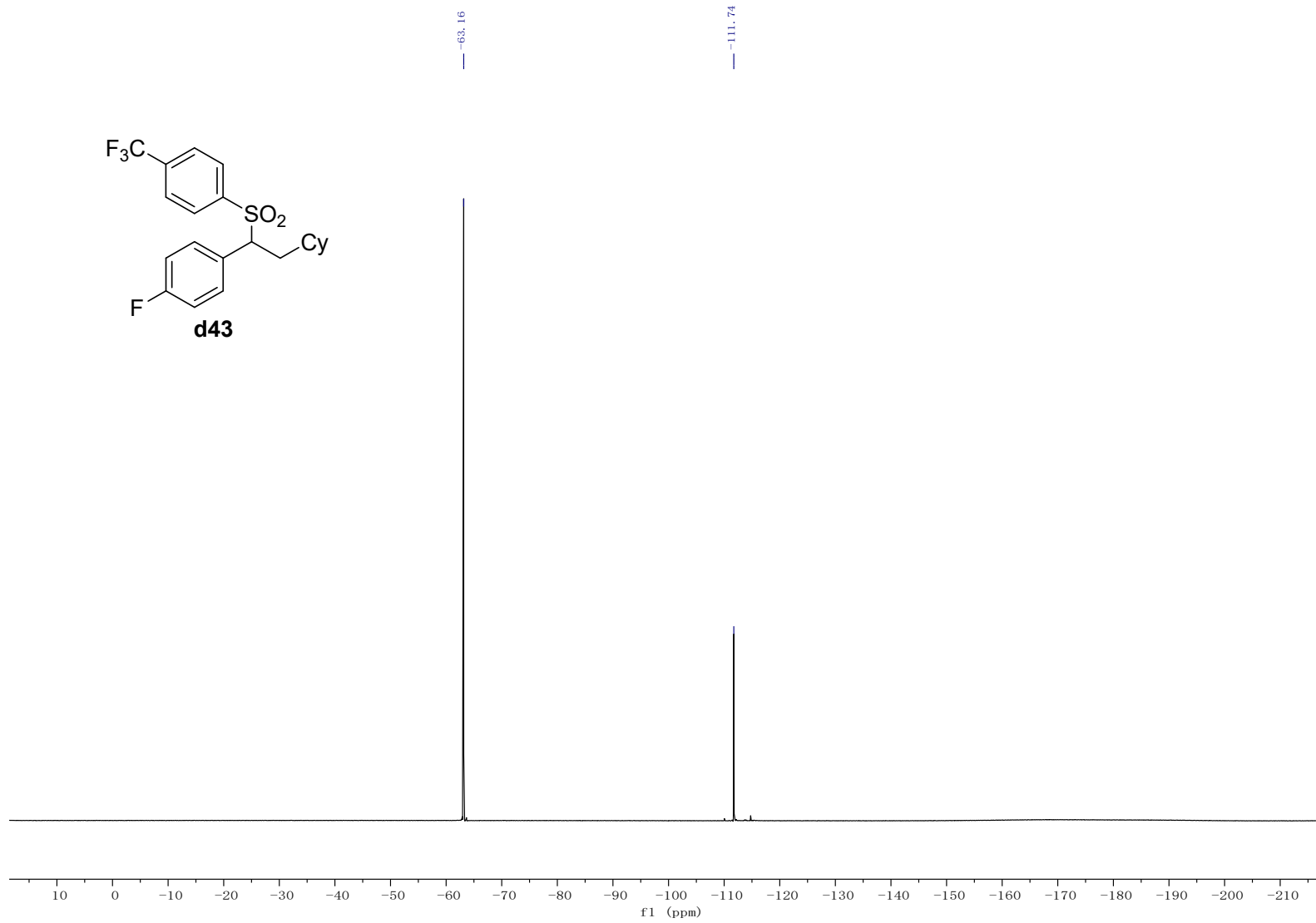
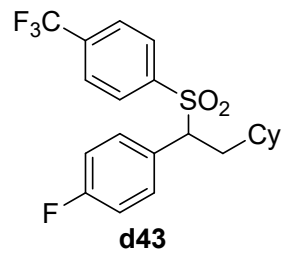


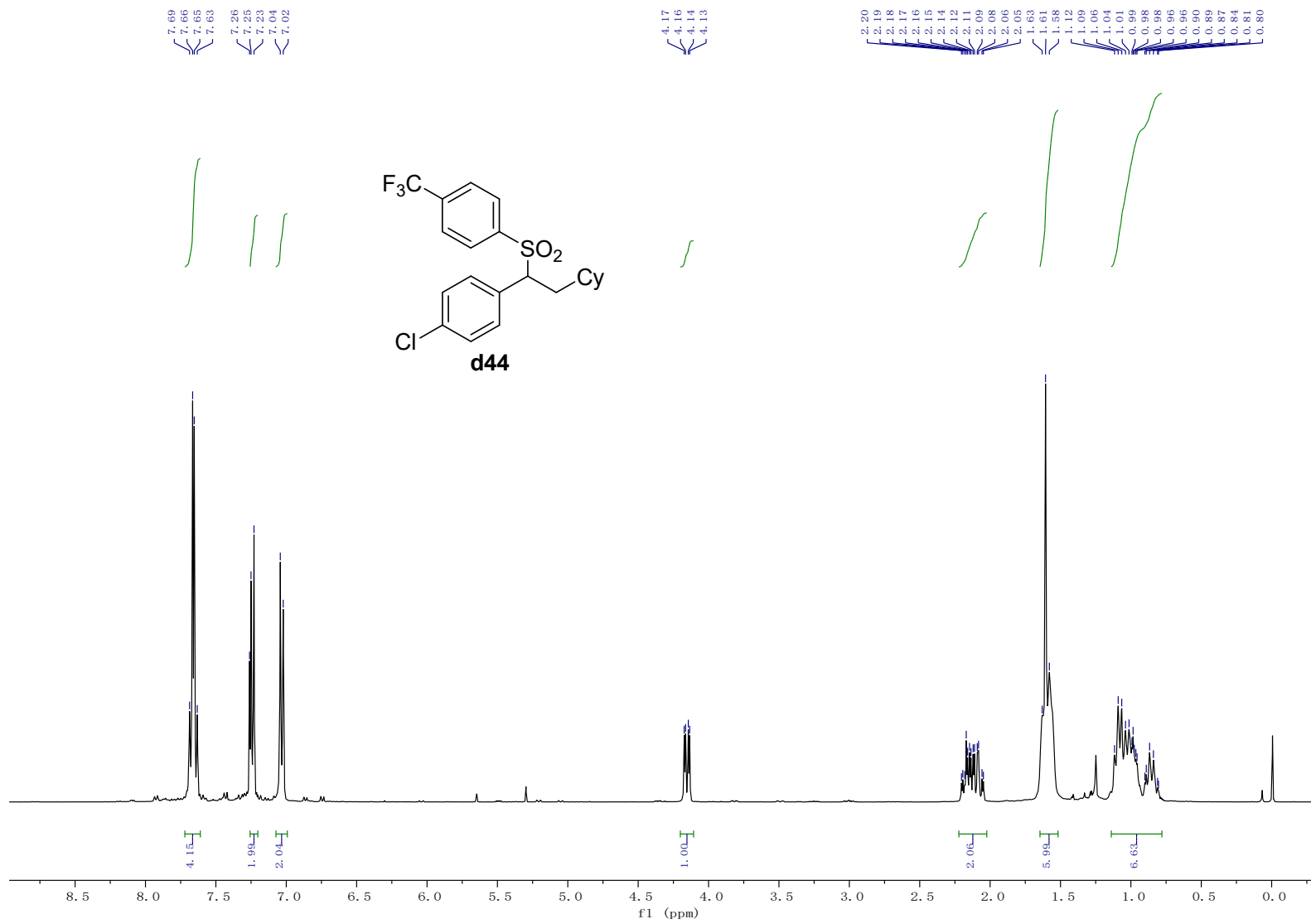
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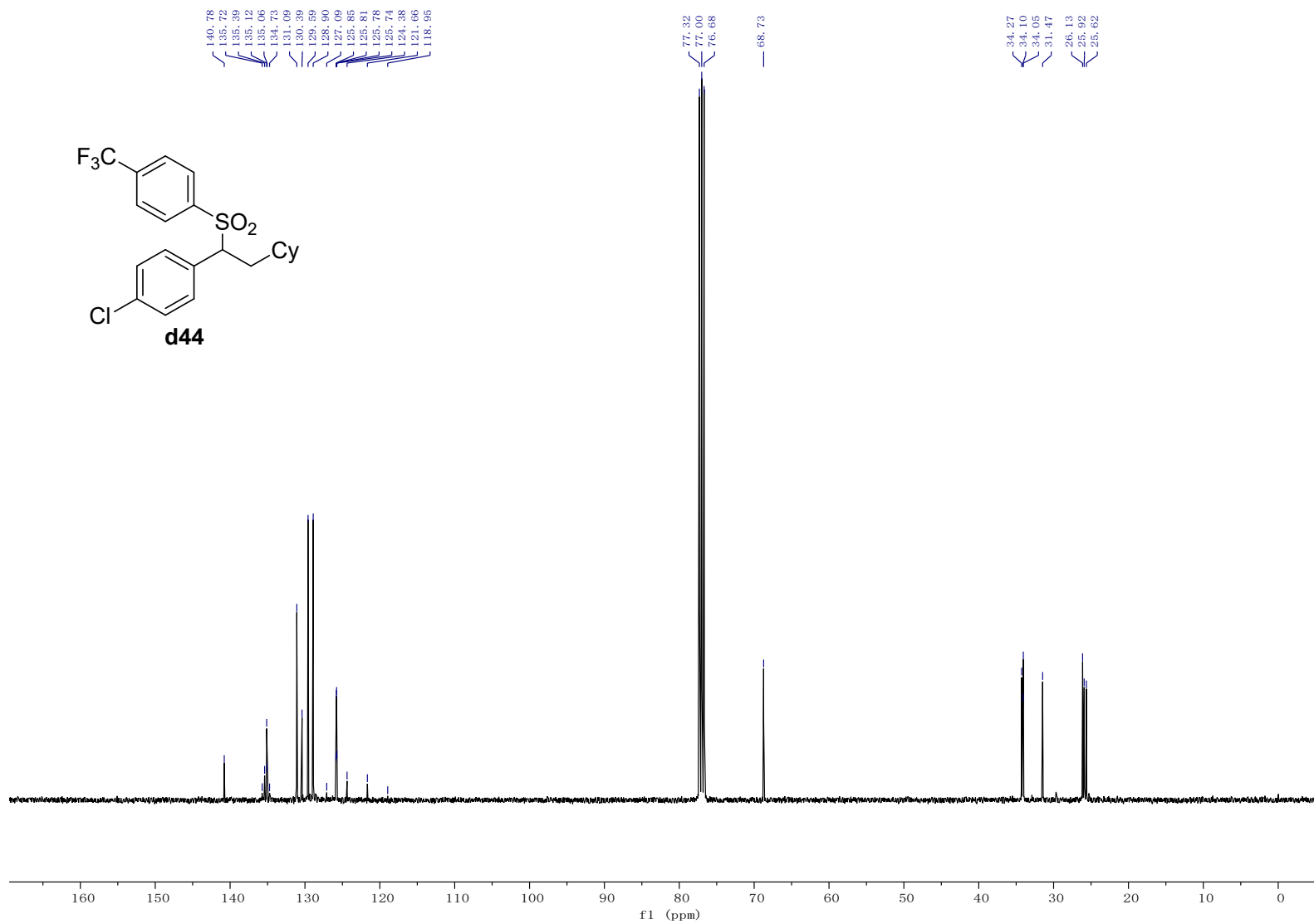
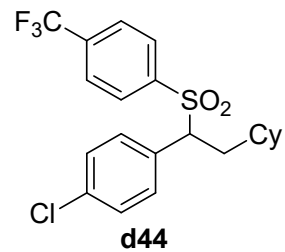


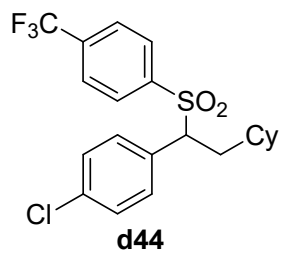




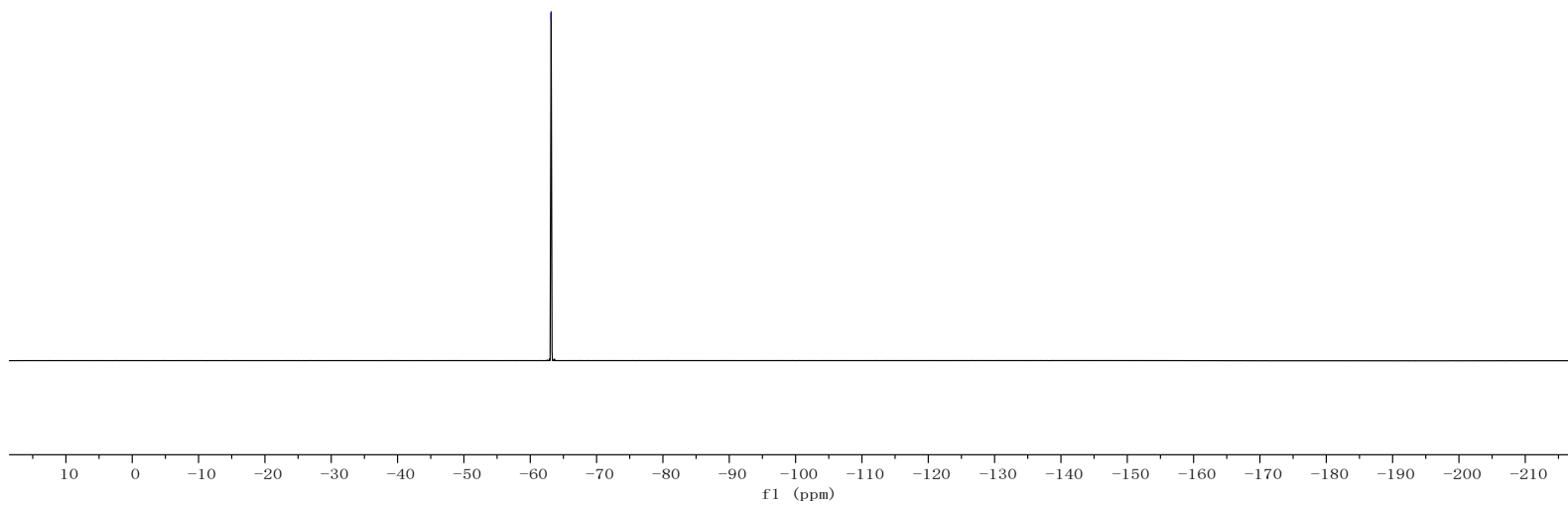


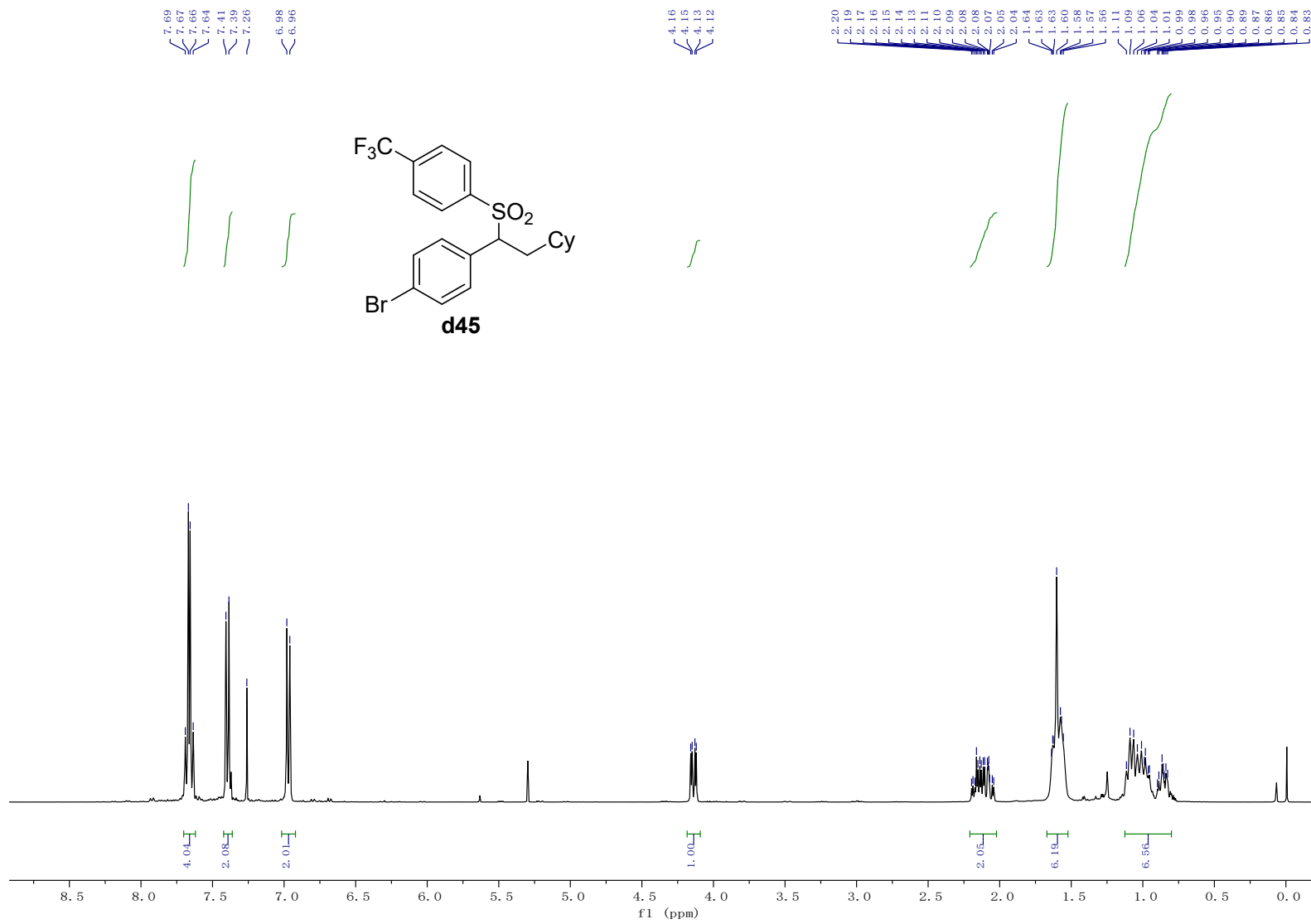


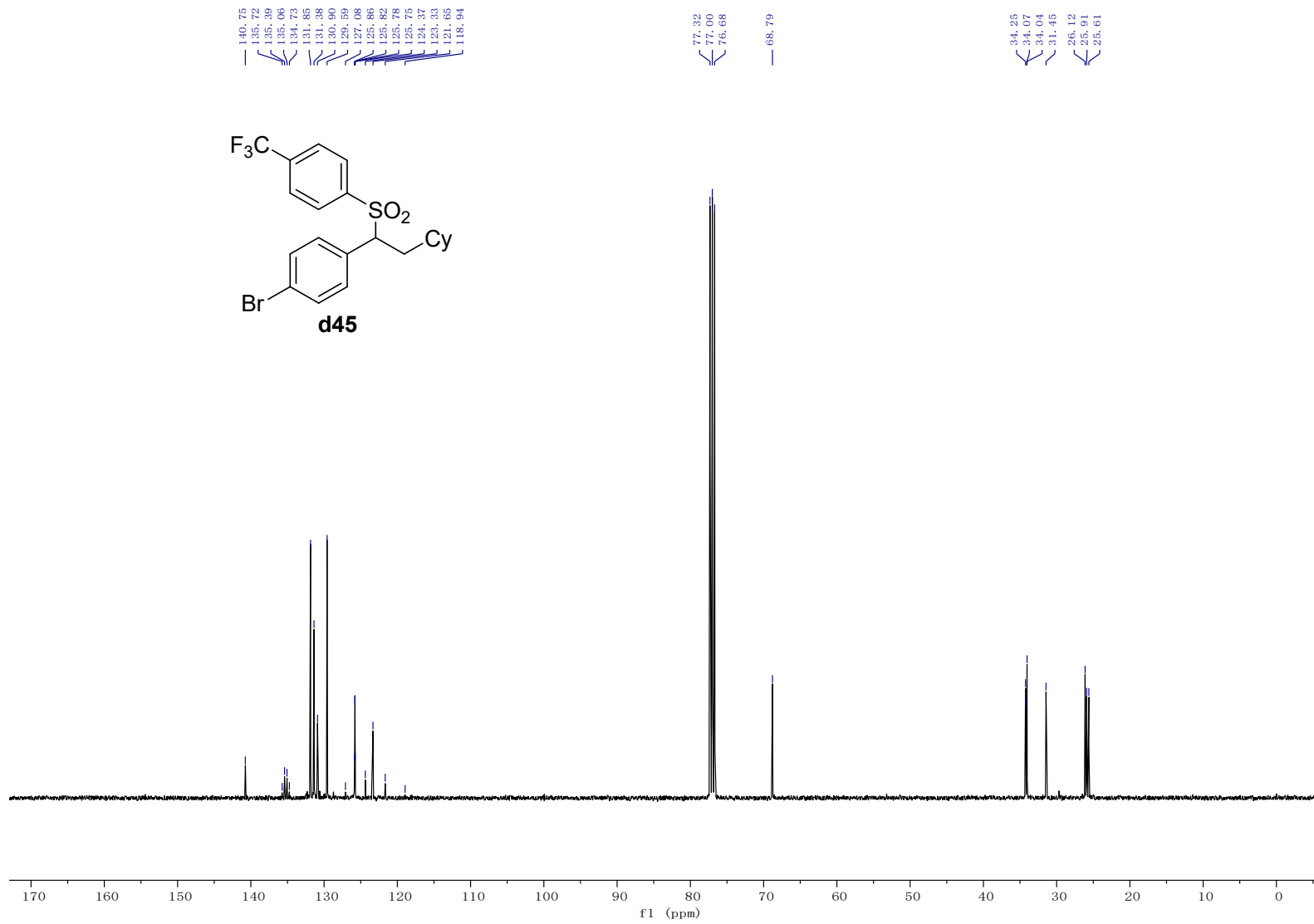


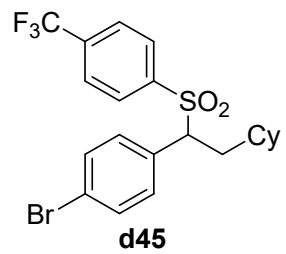


— 63.15

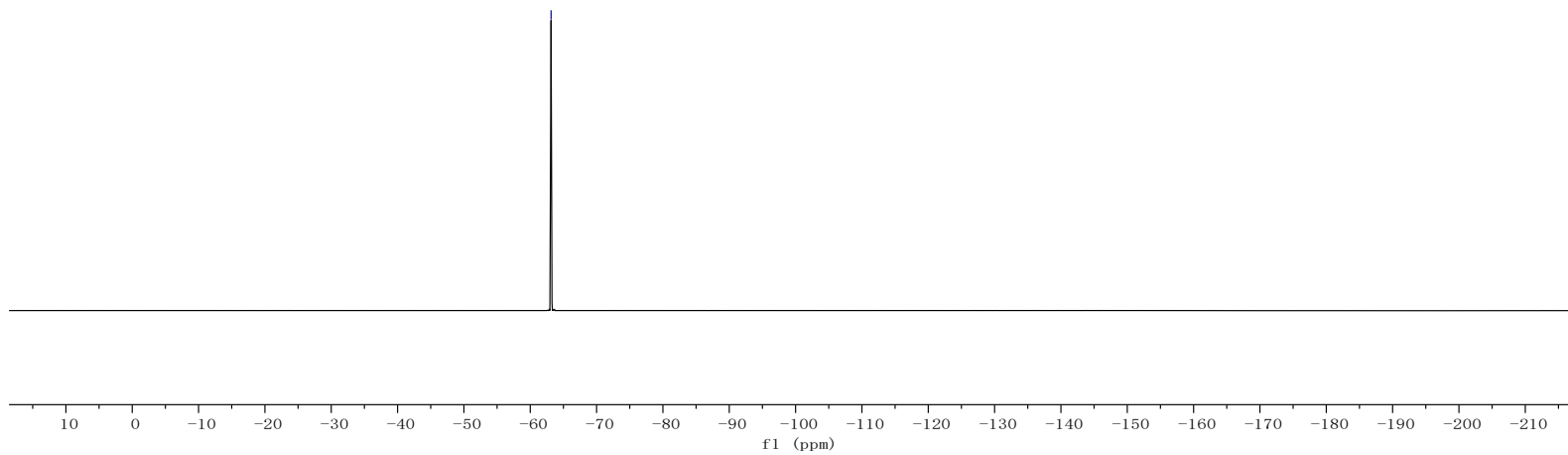


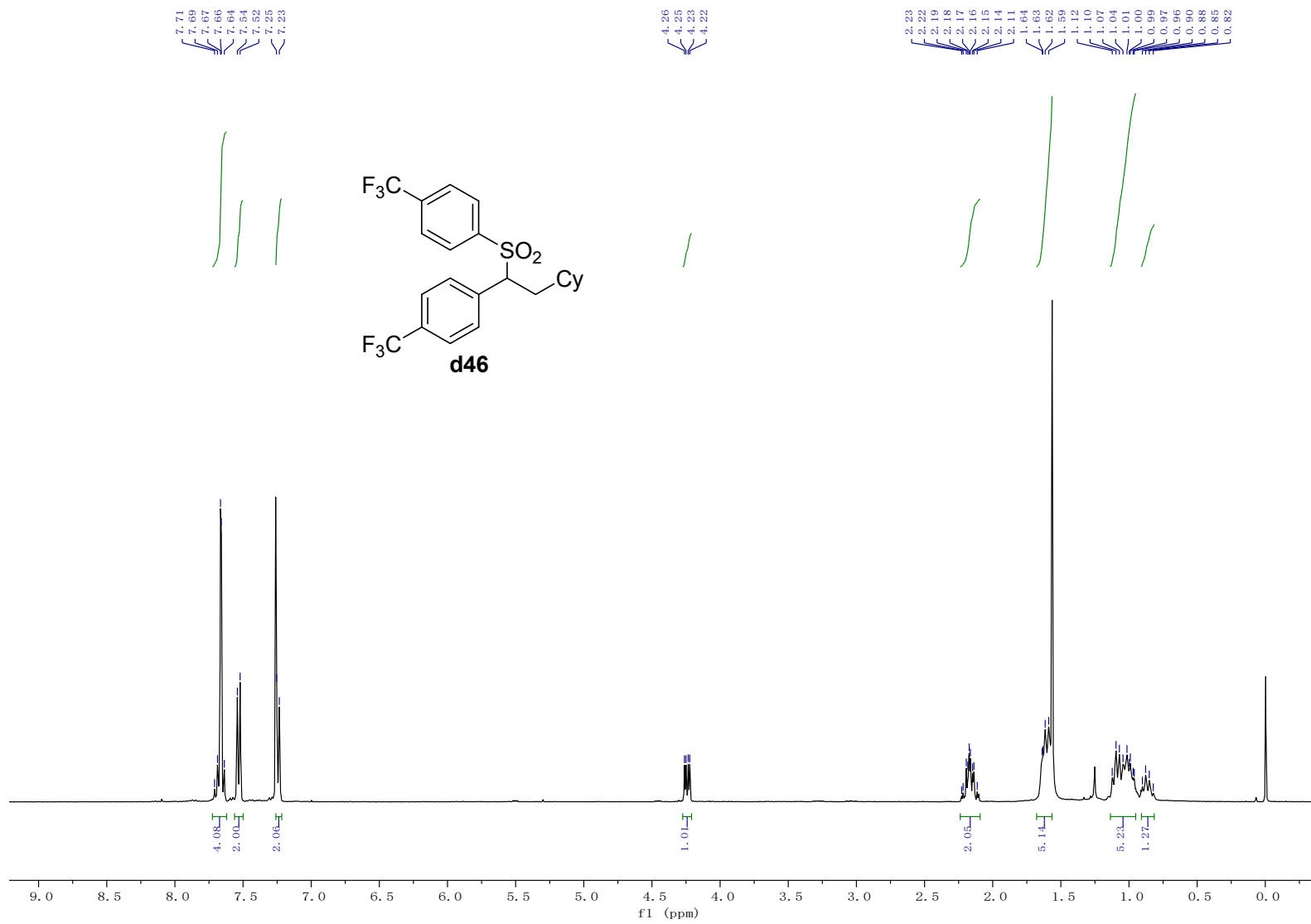


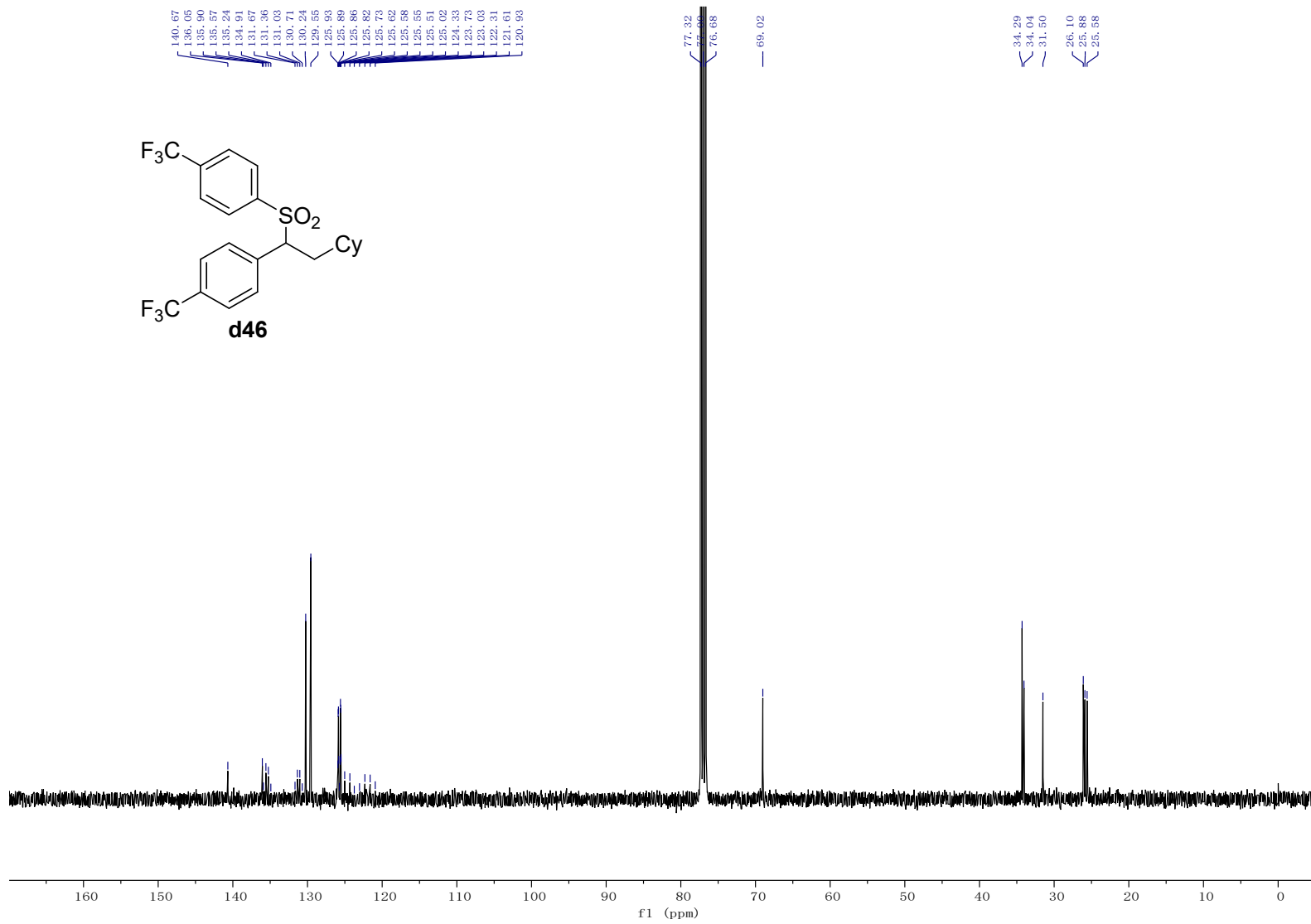


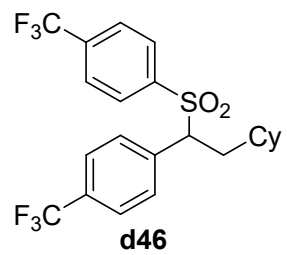


— 63.14

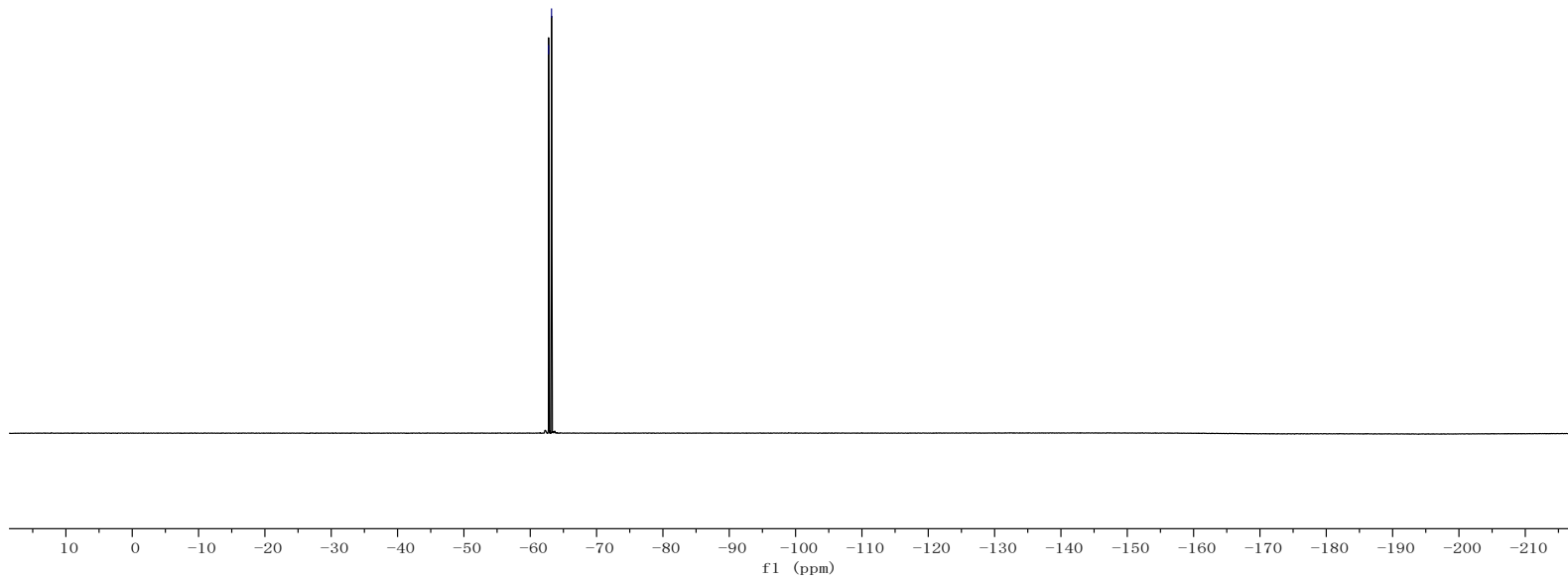


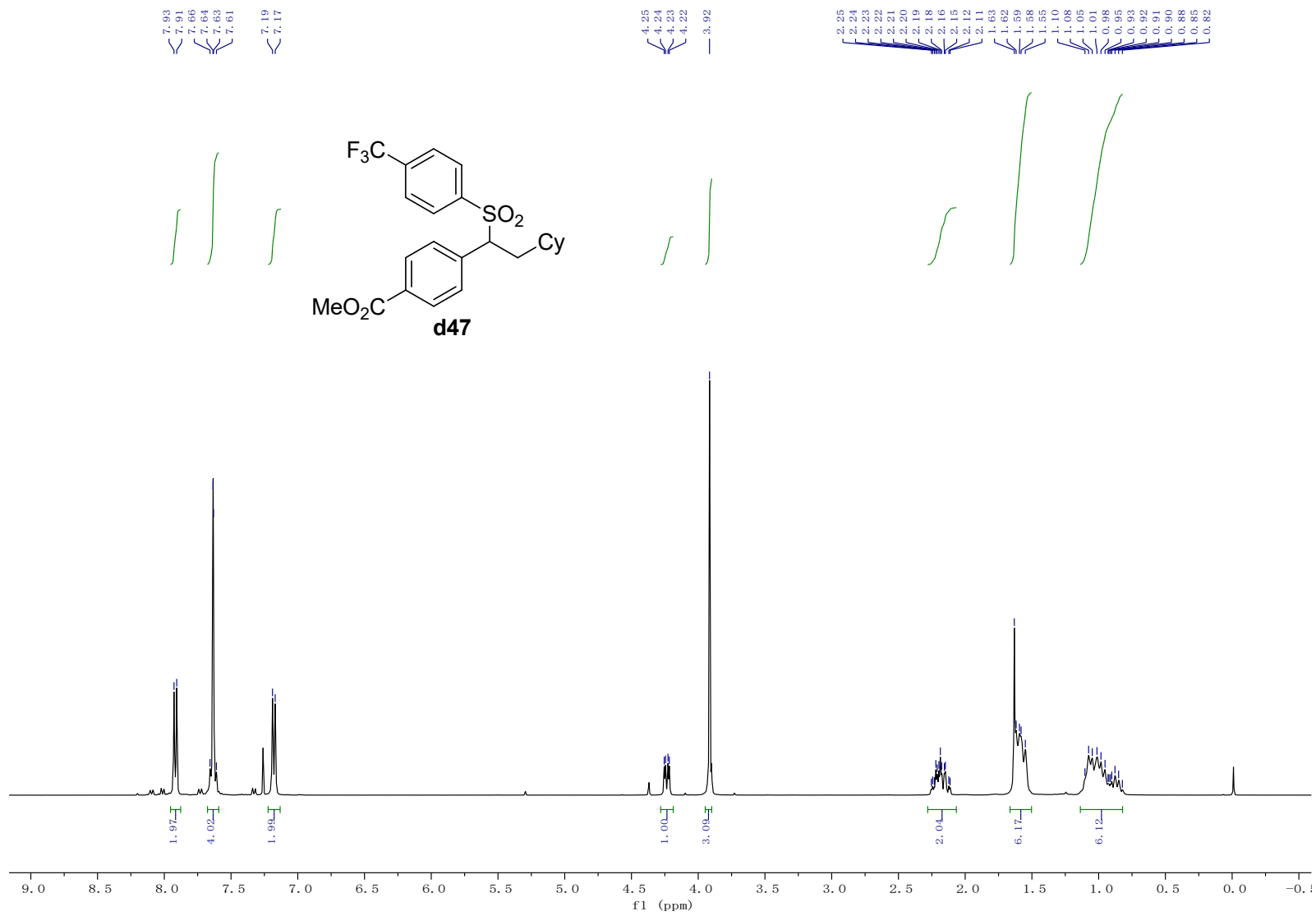


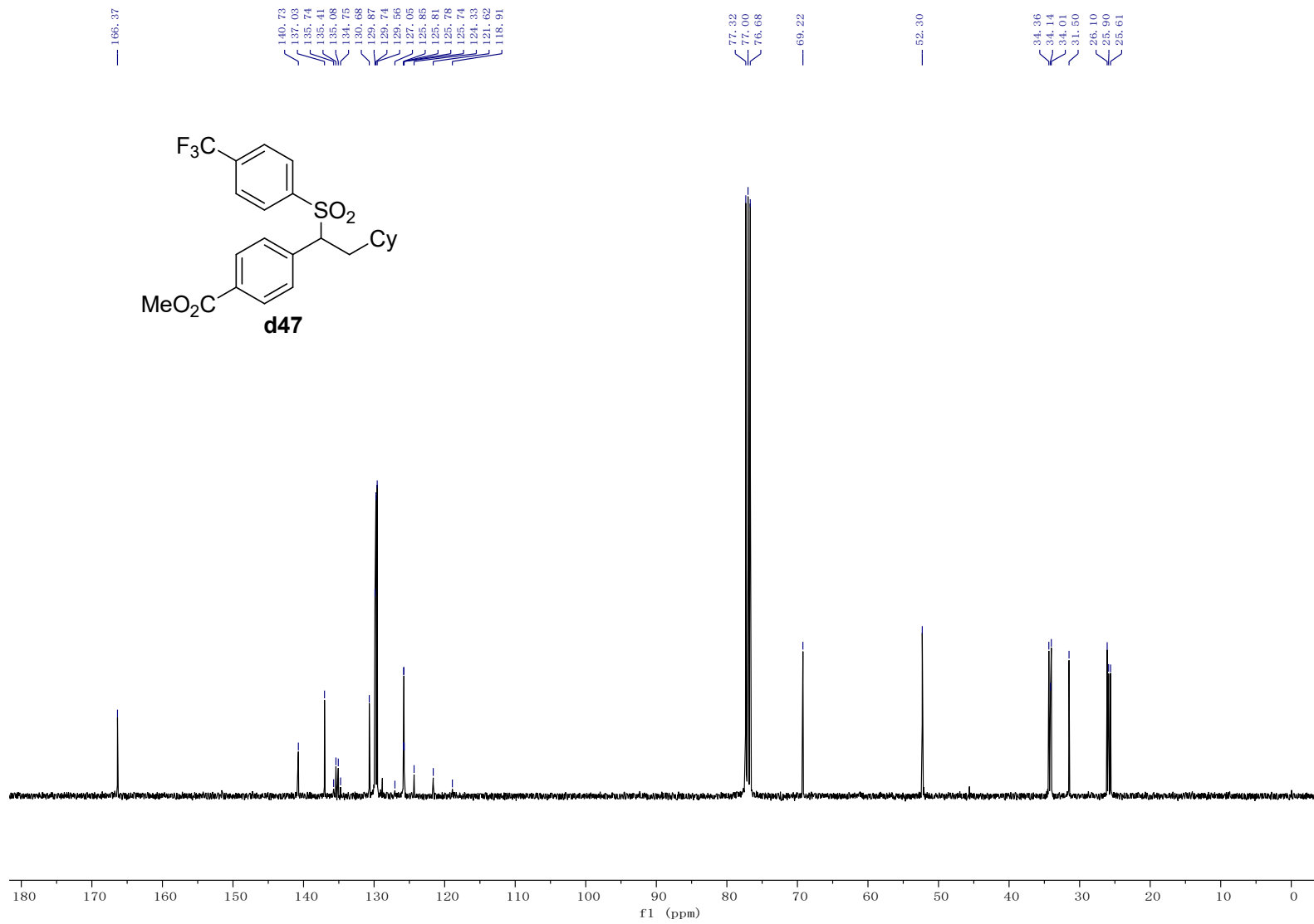


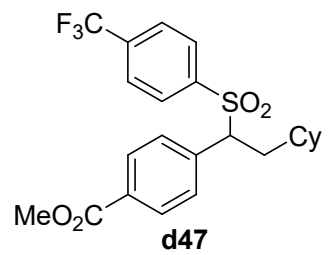


-62.77
-63.21

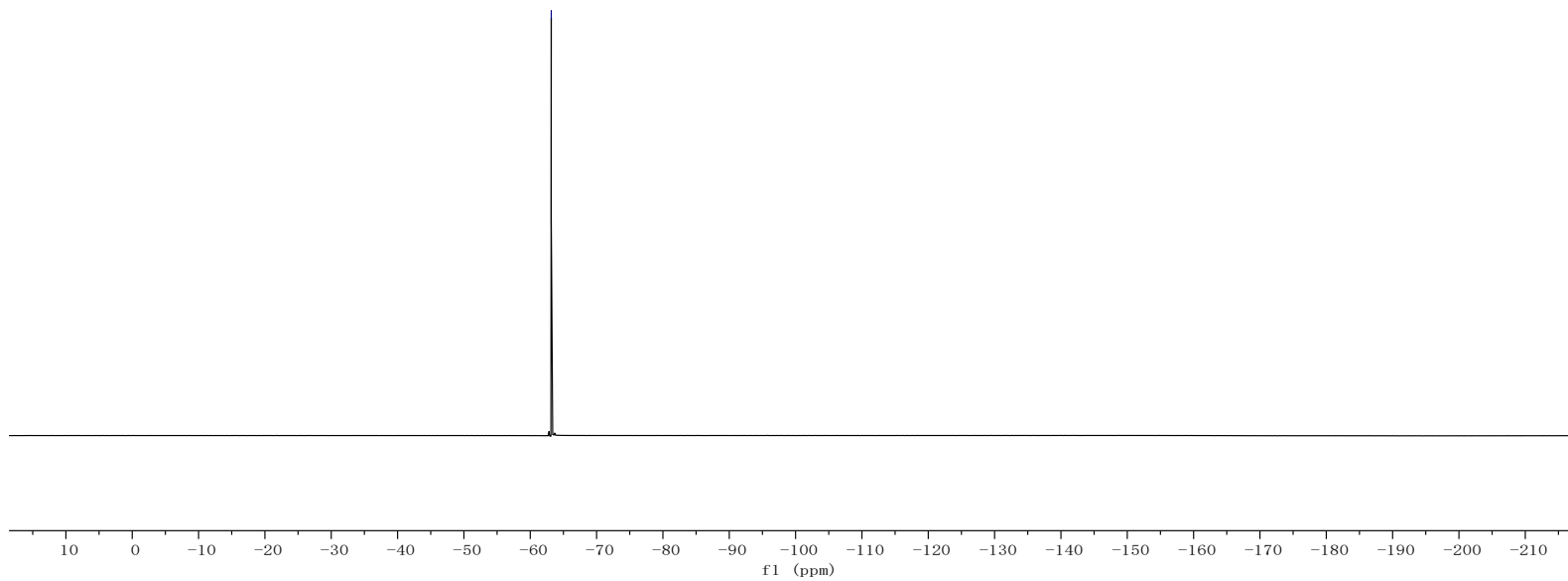


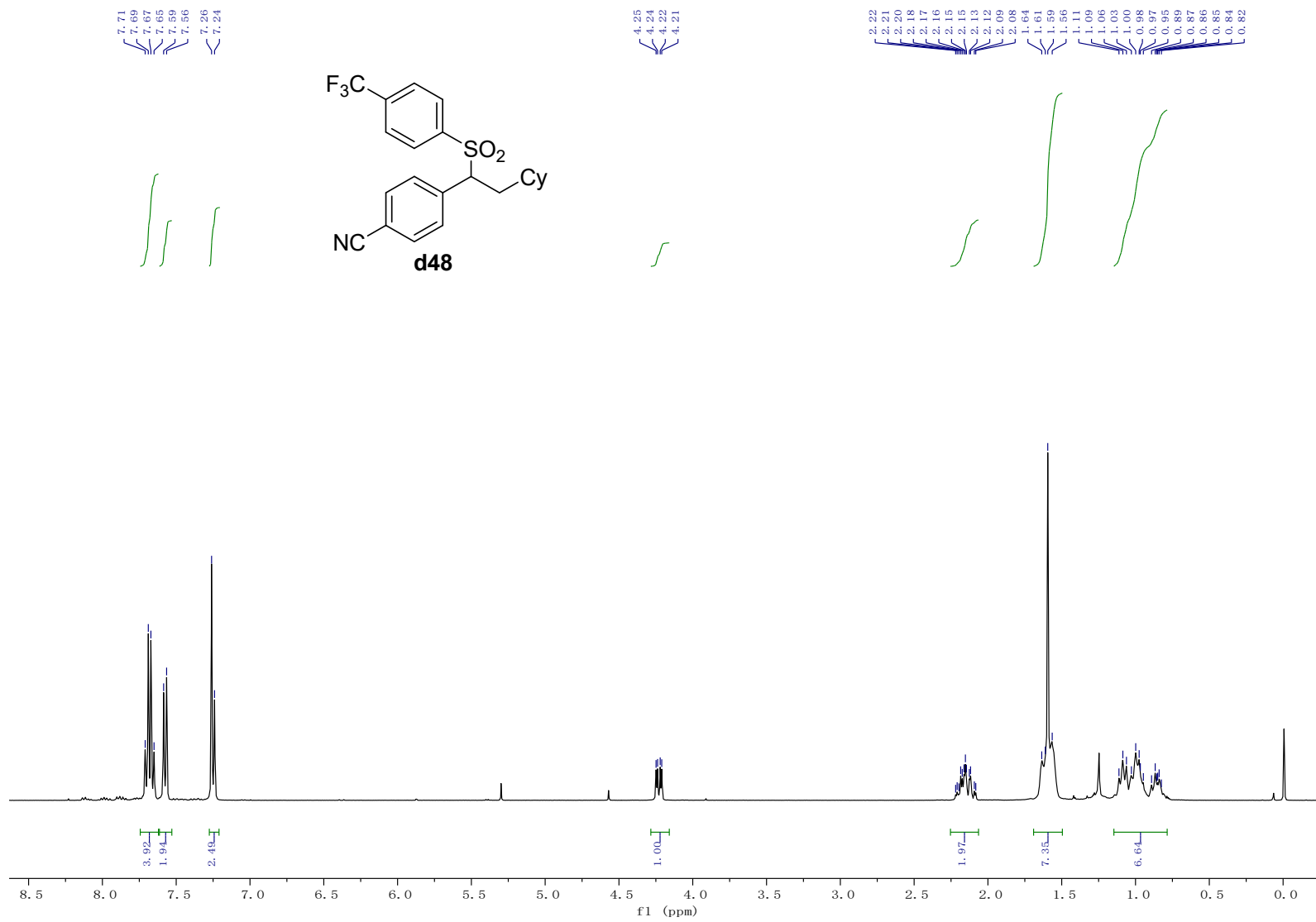


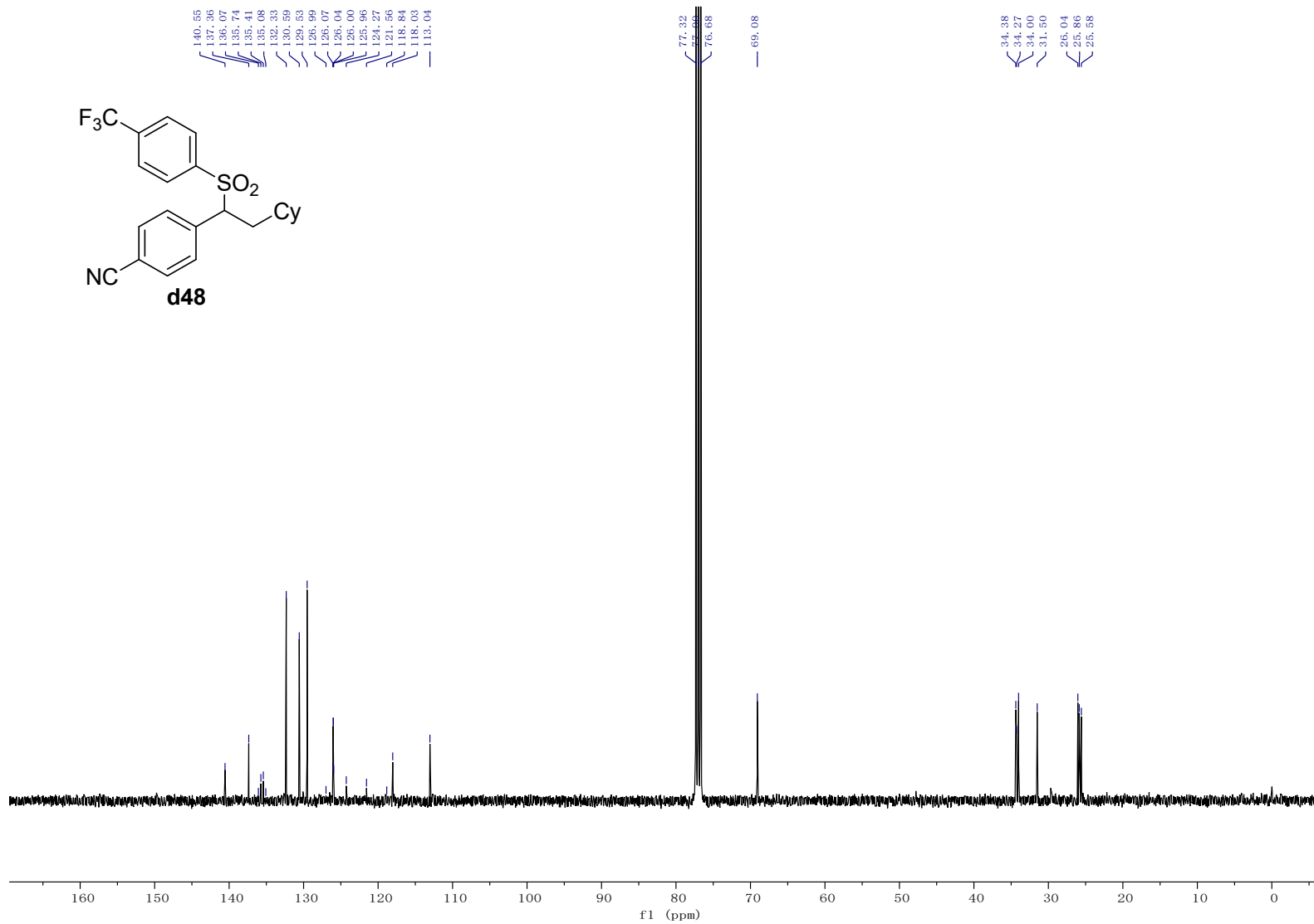
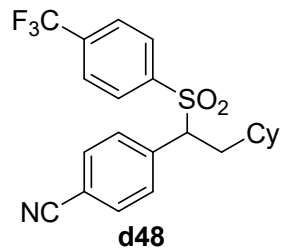


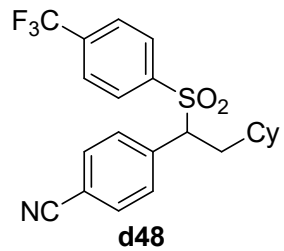


— 63.17

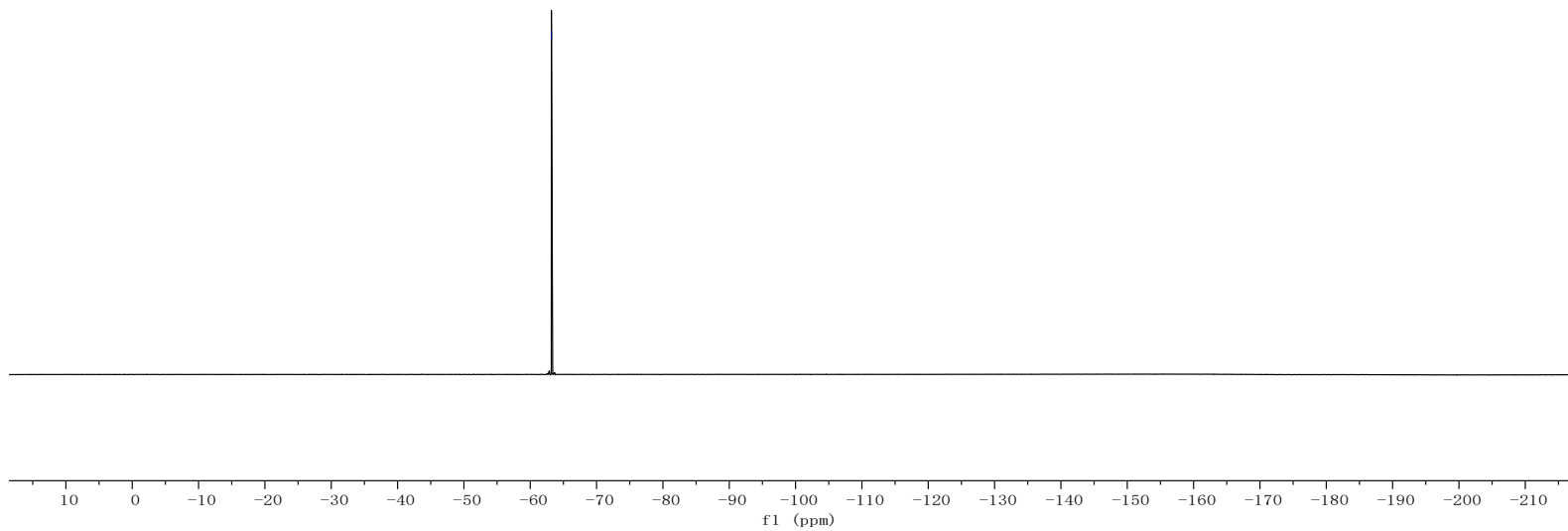


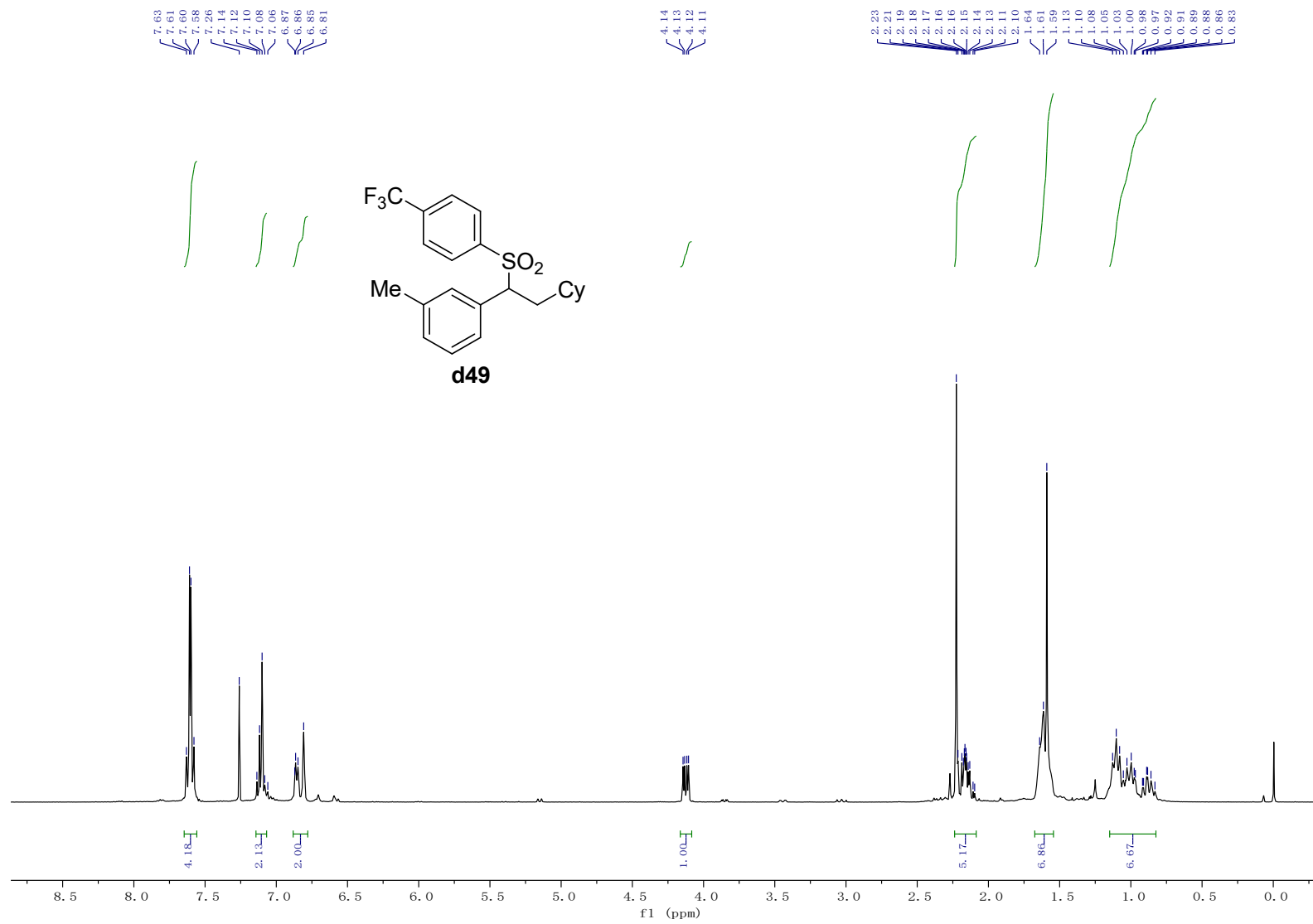


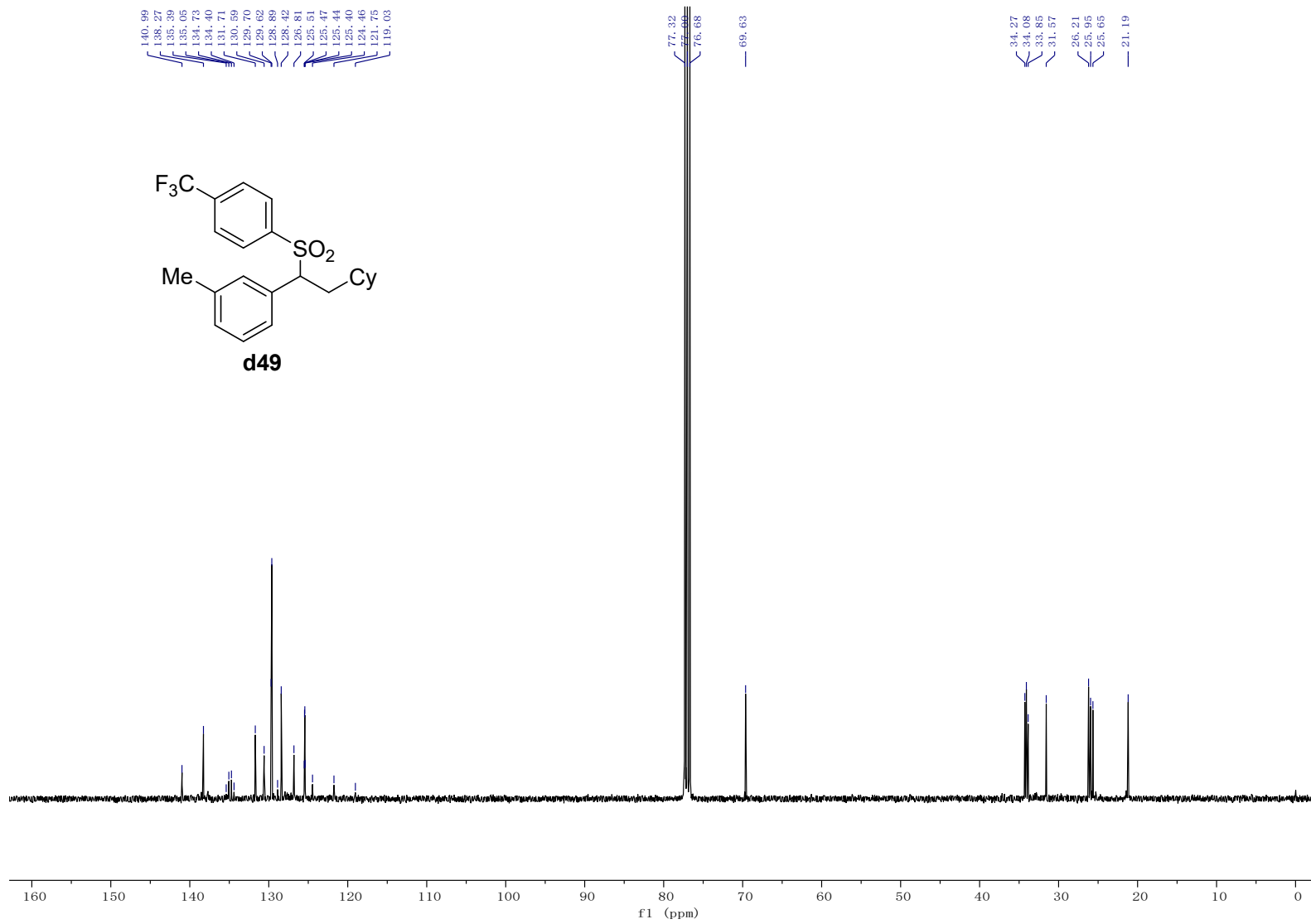


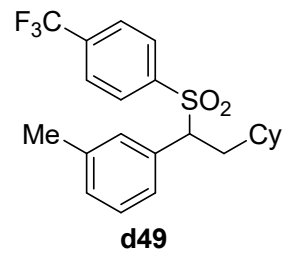


63.18

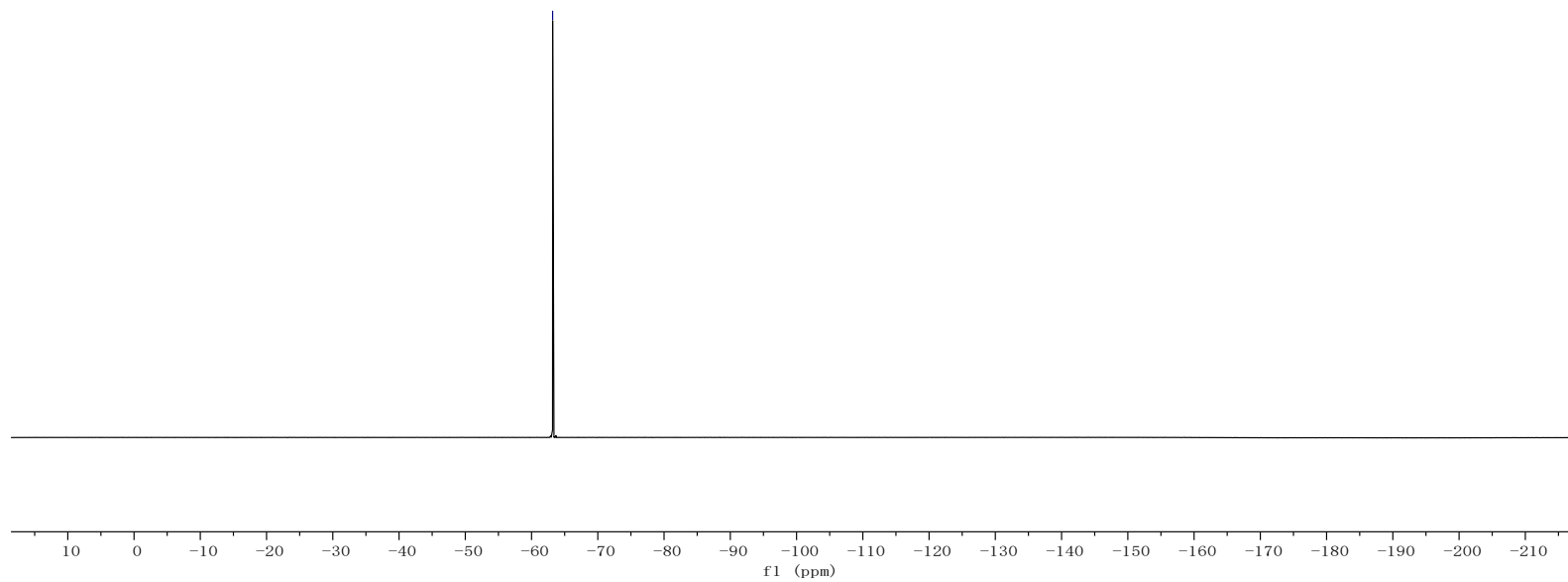


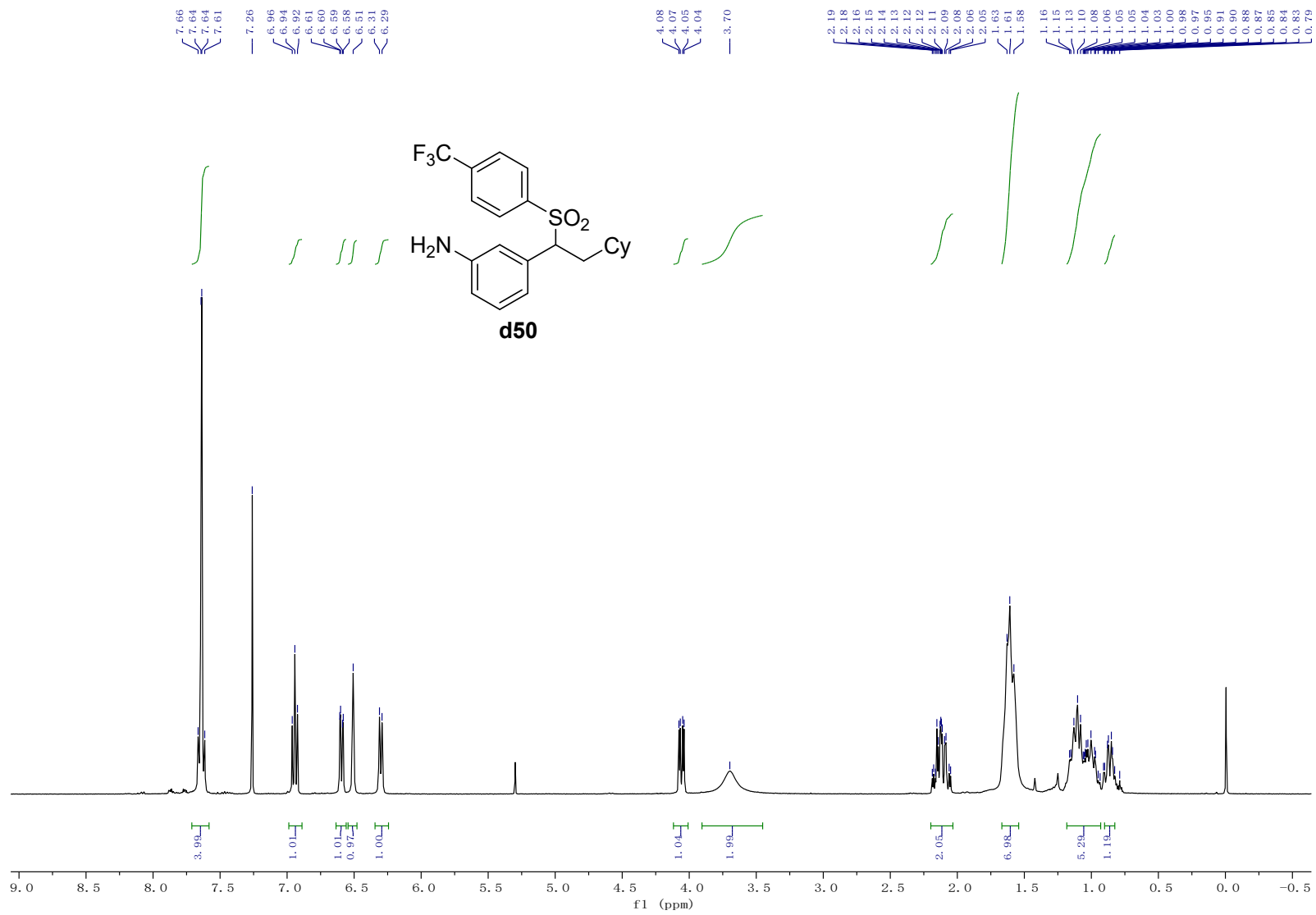


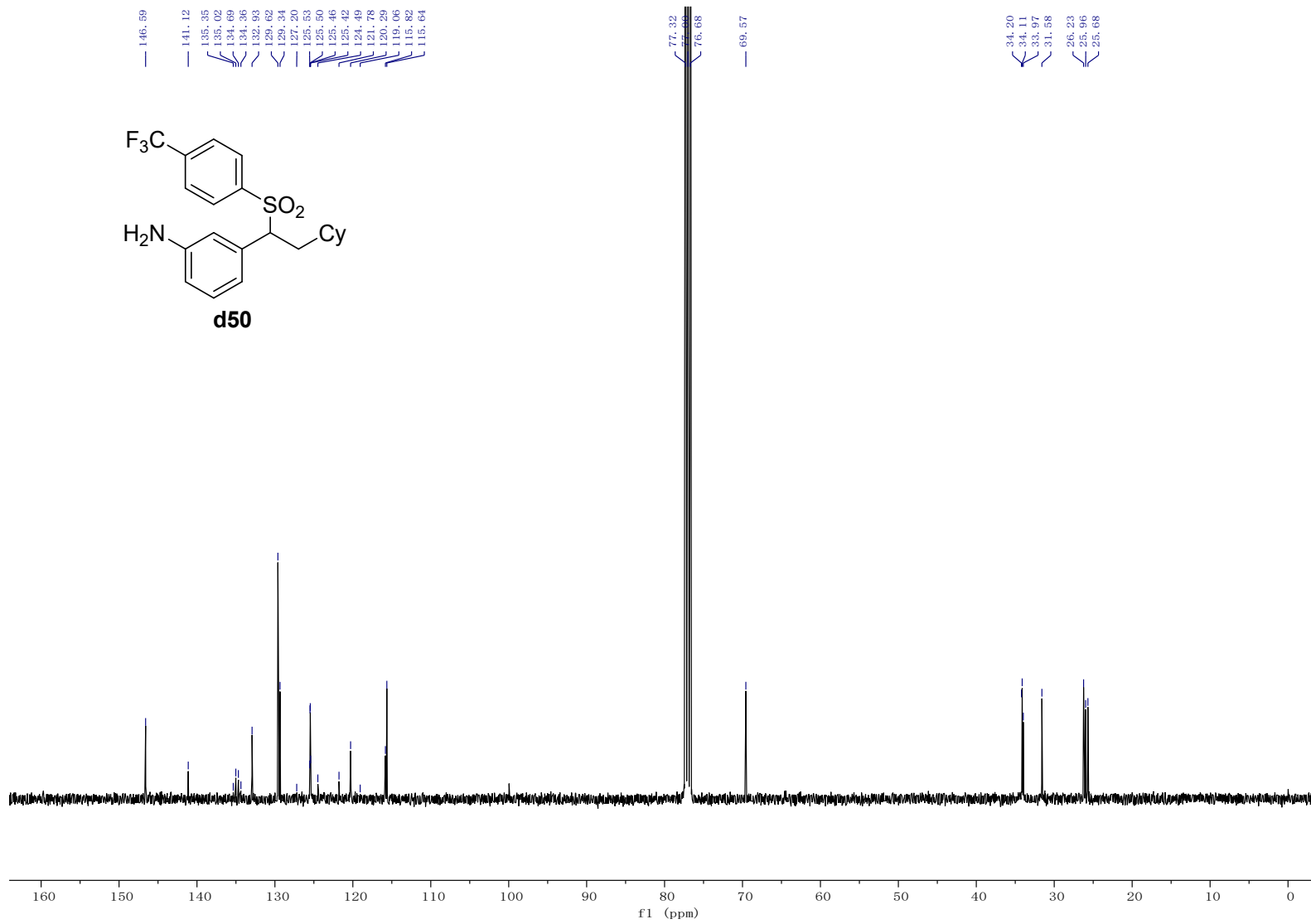


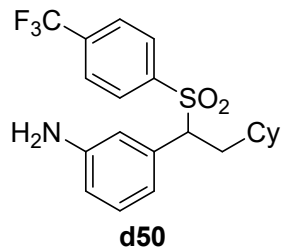


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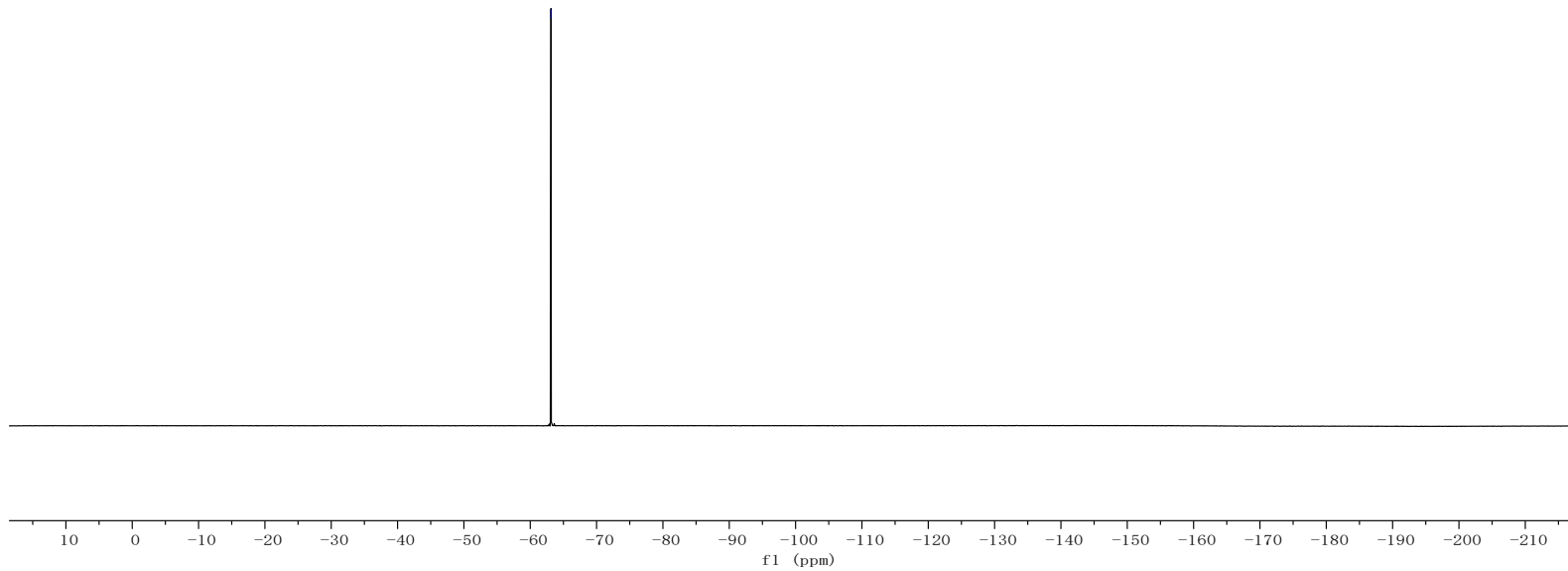


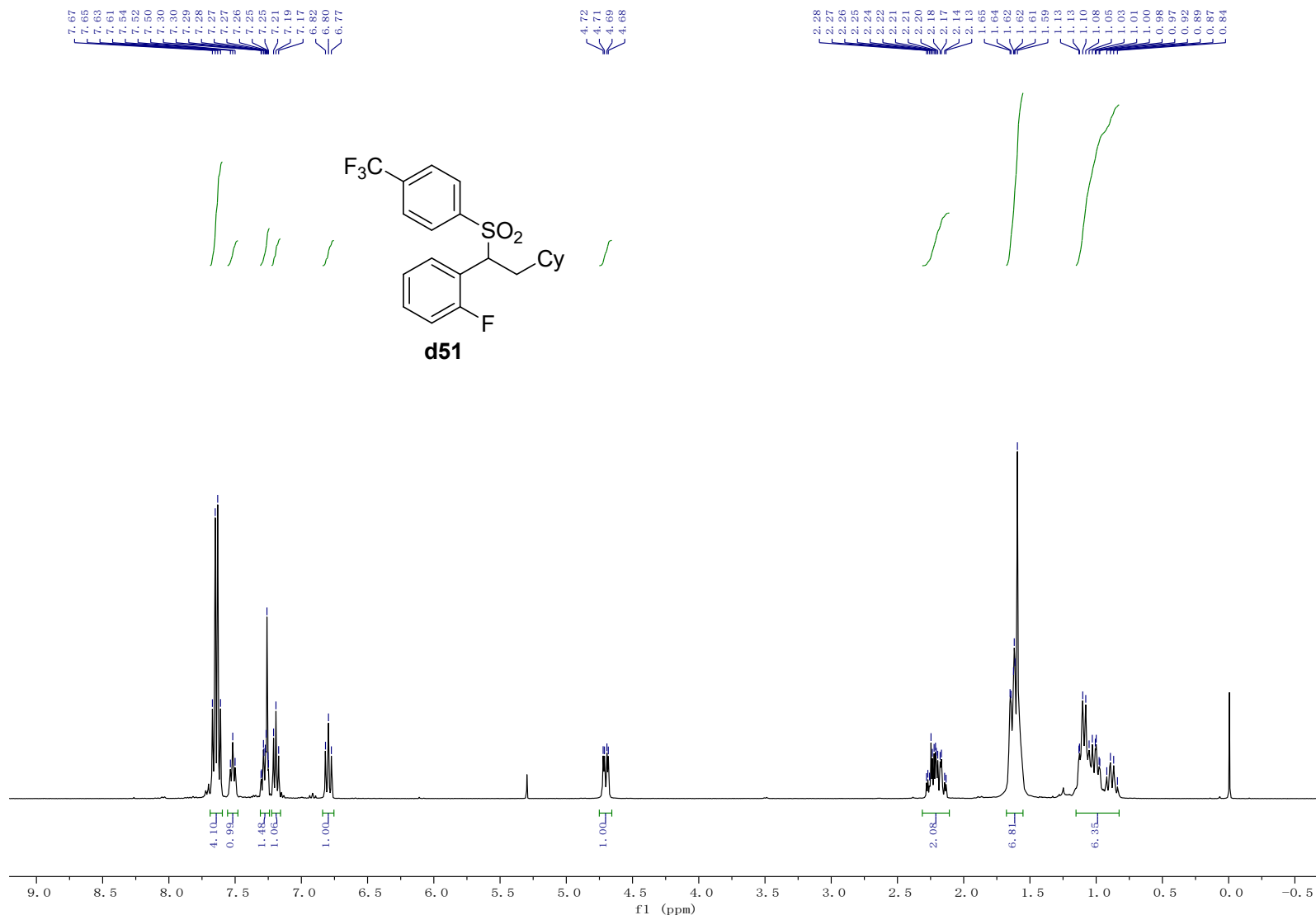


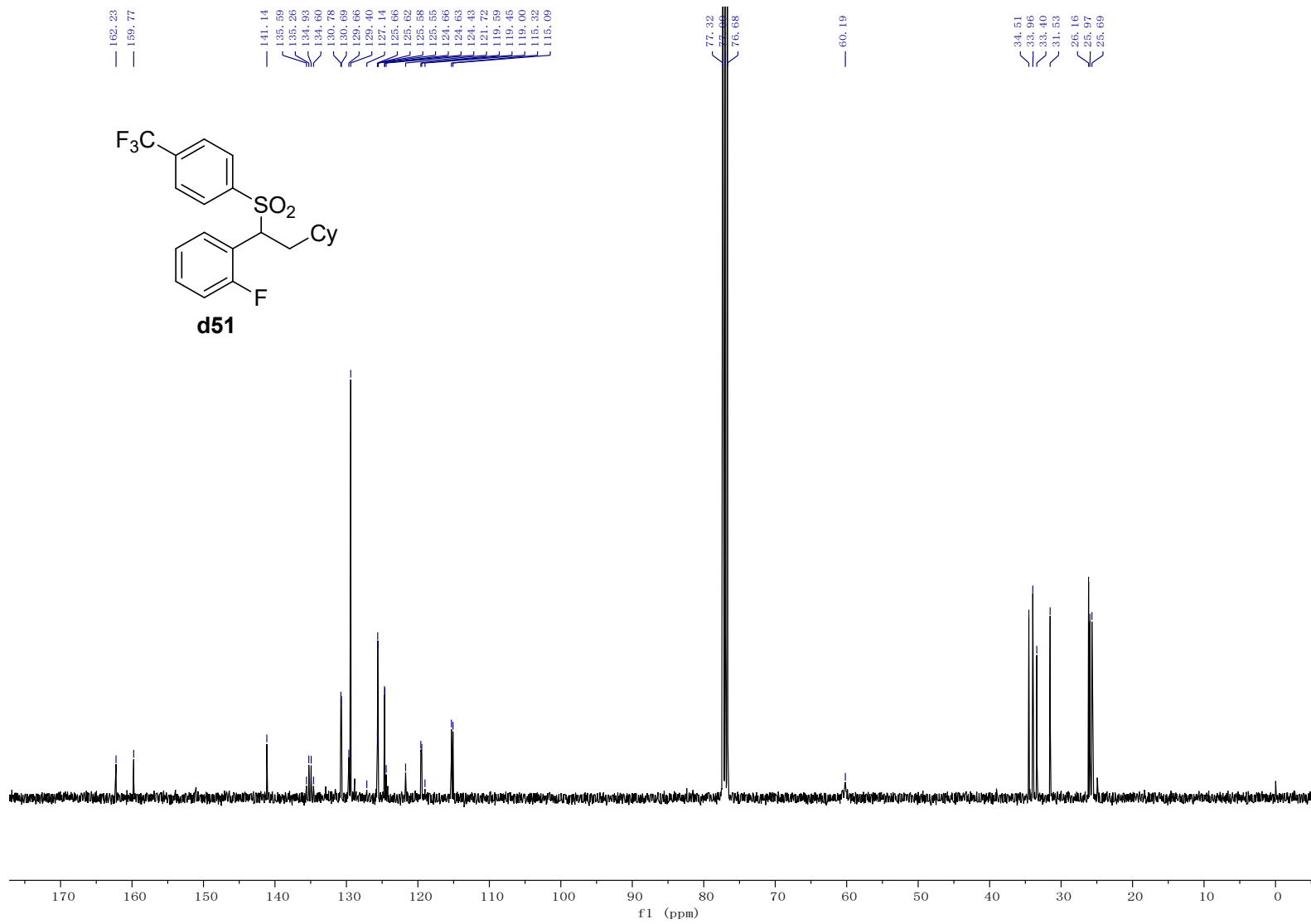


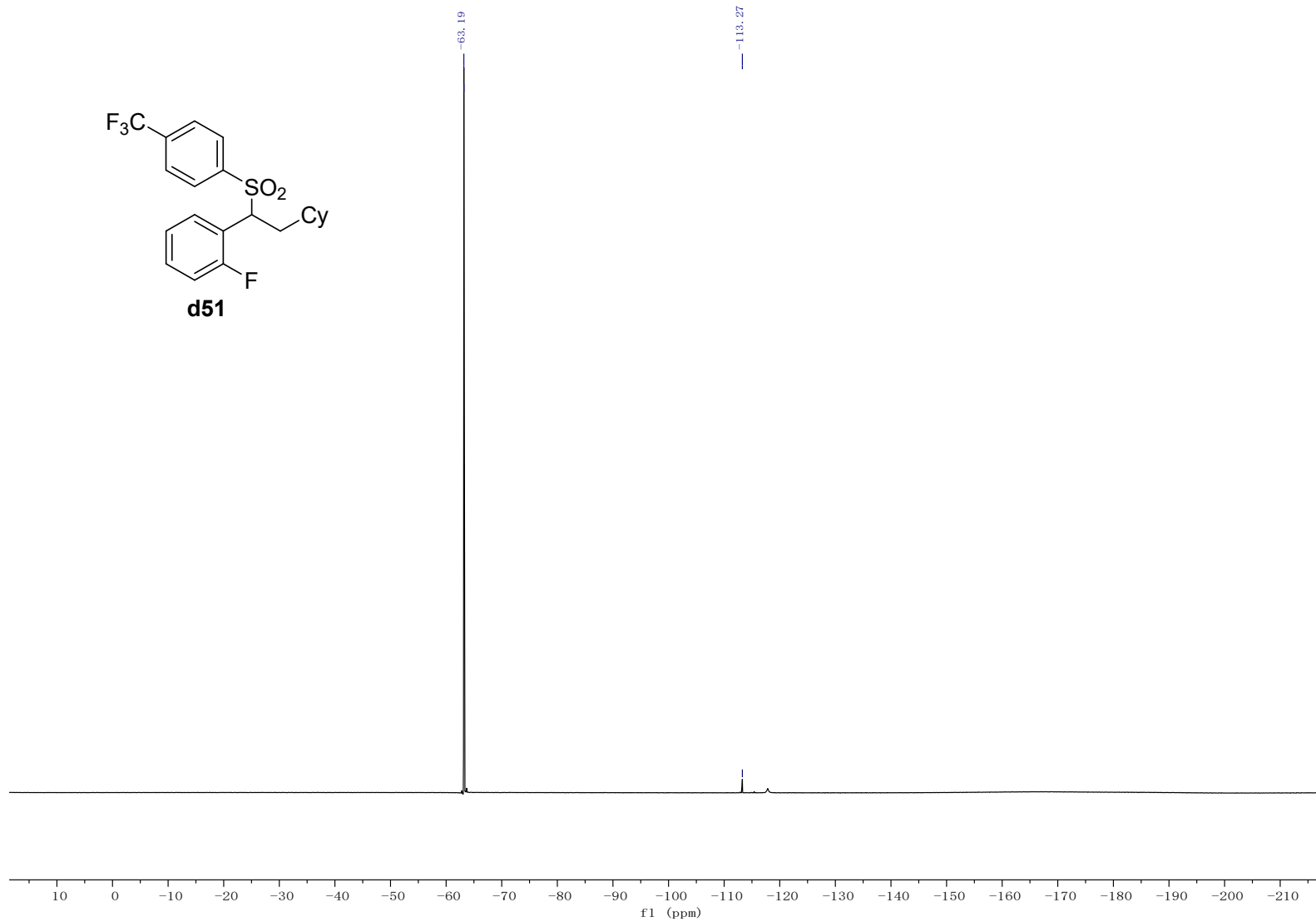
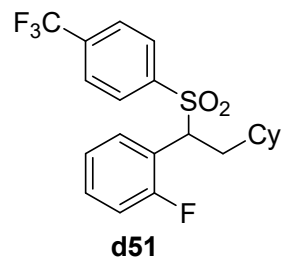


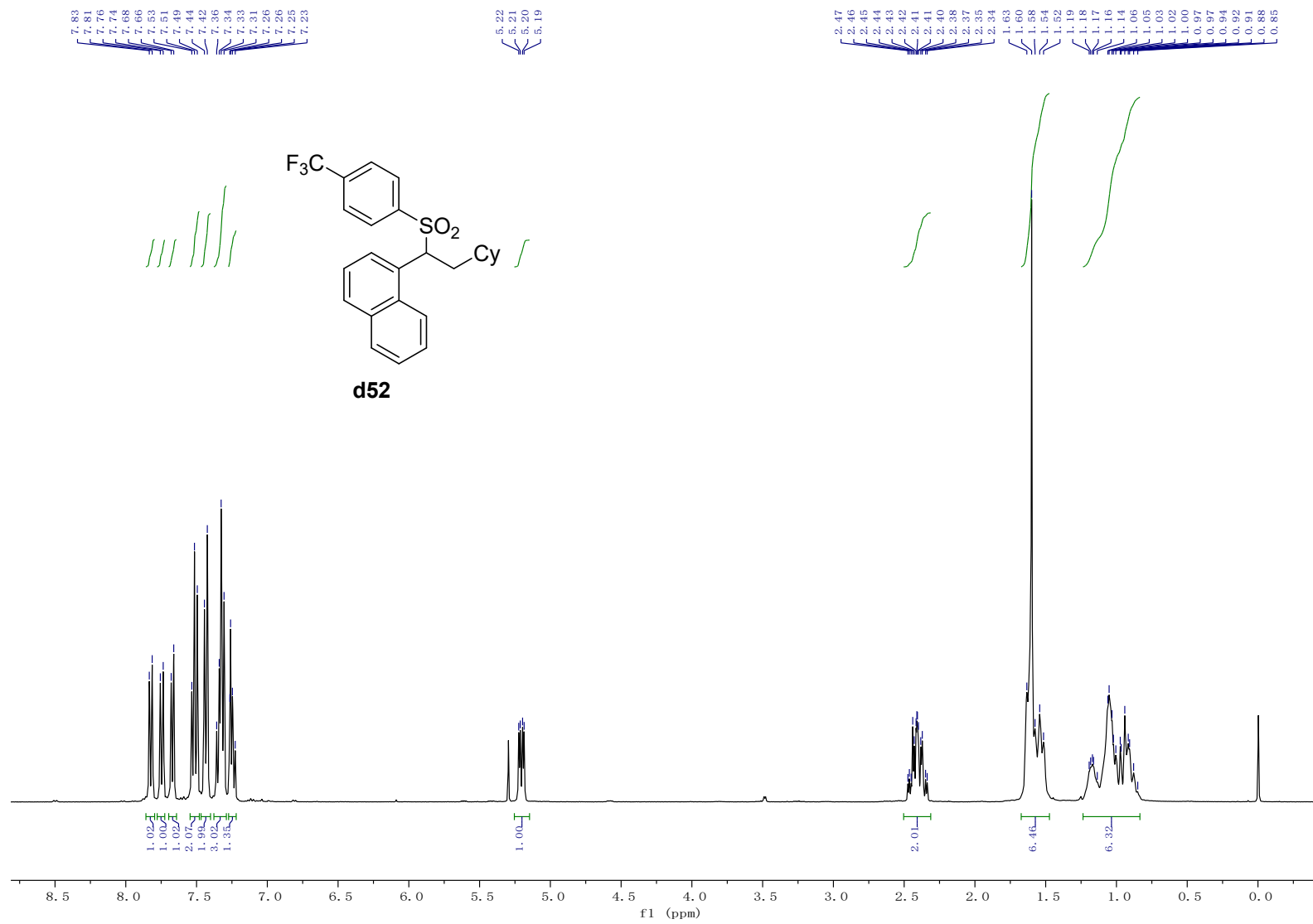
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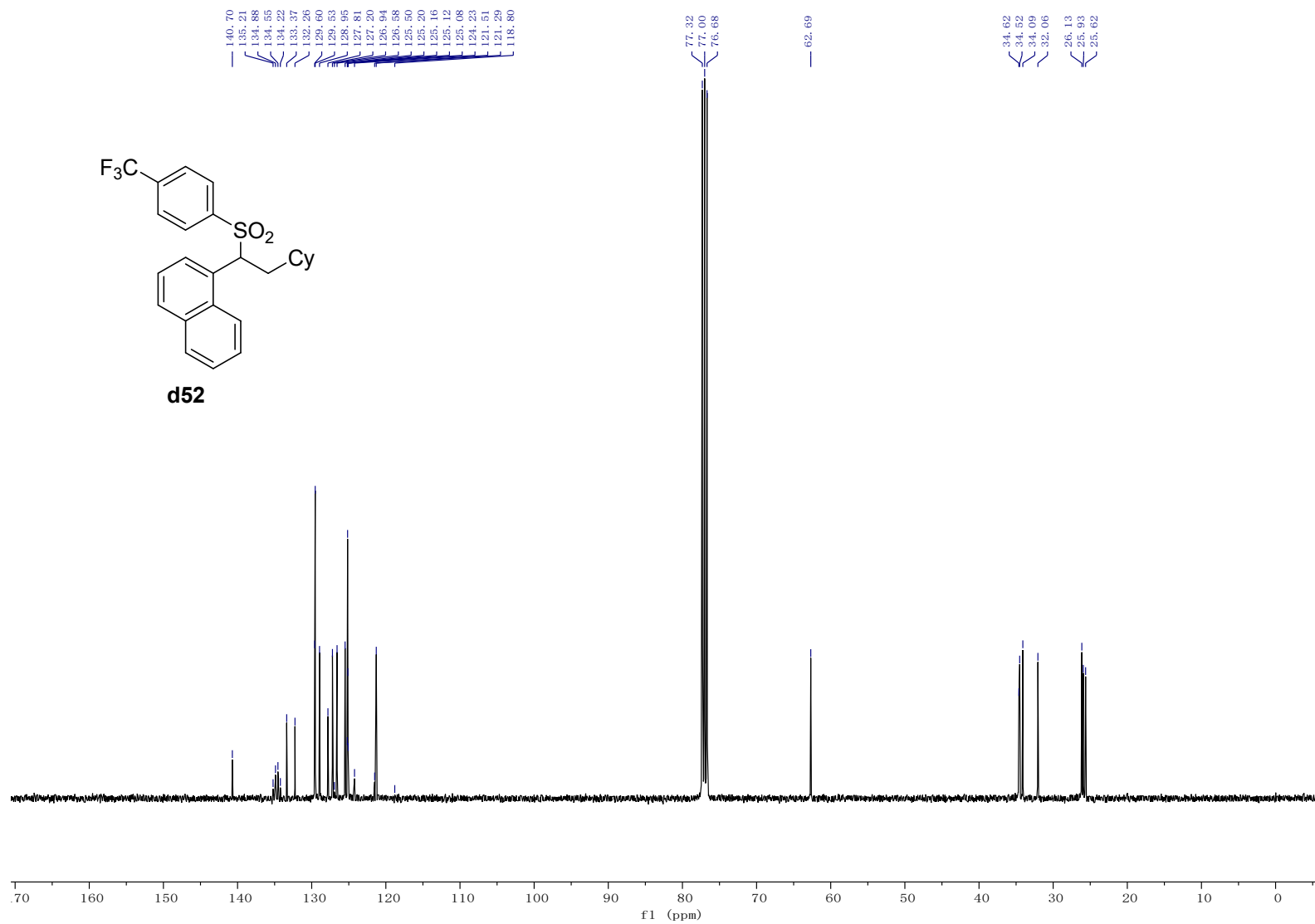
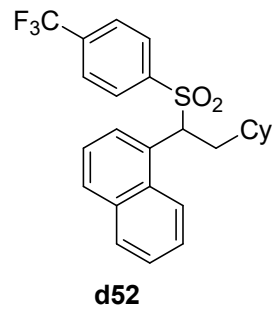


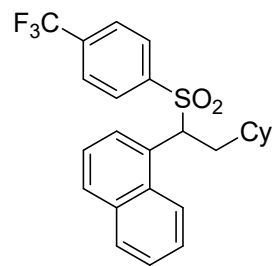






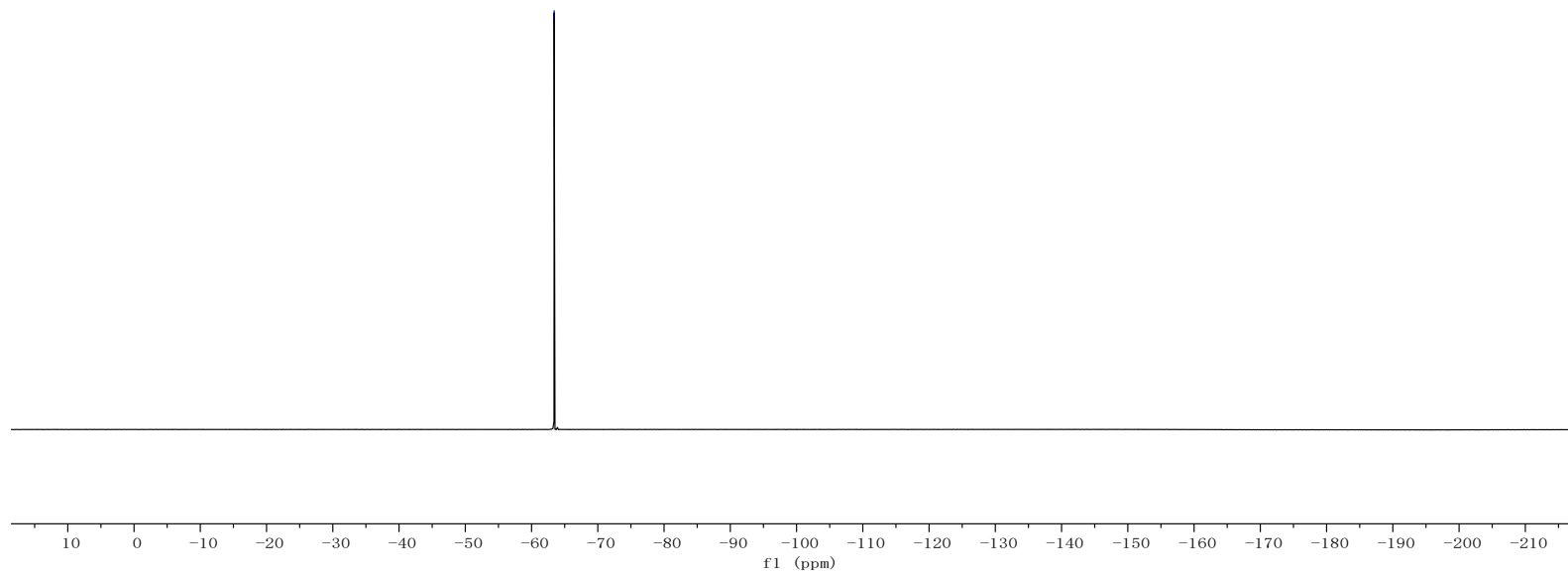


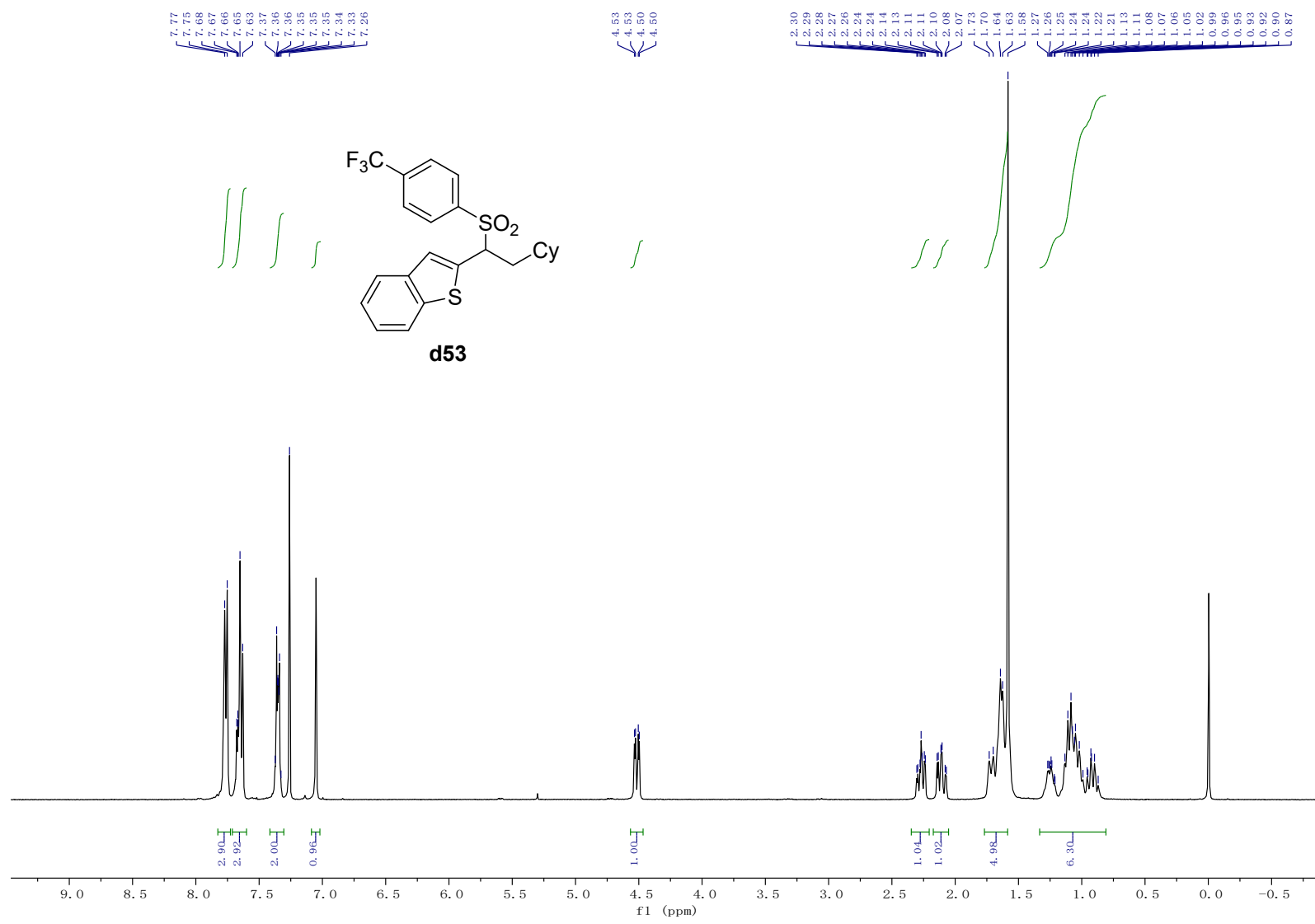


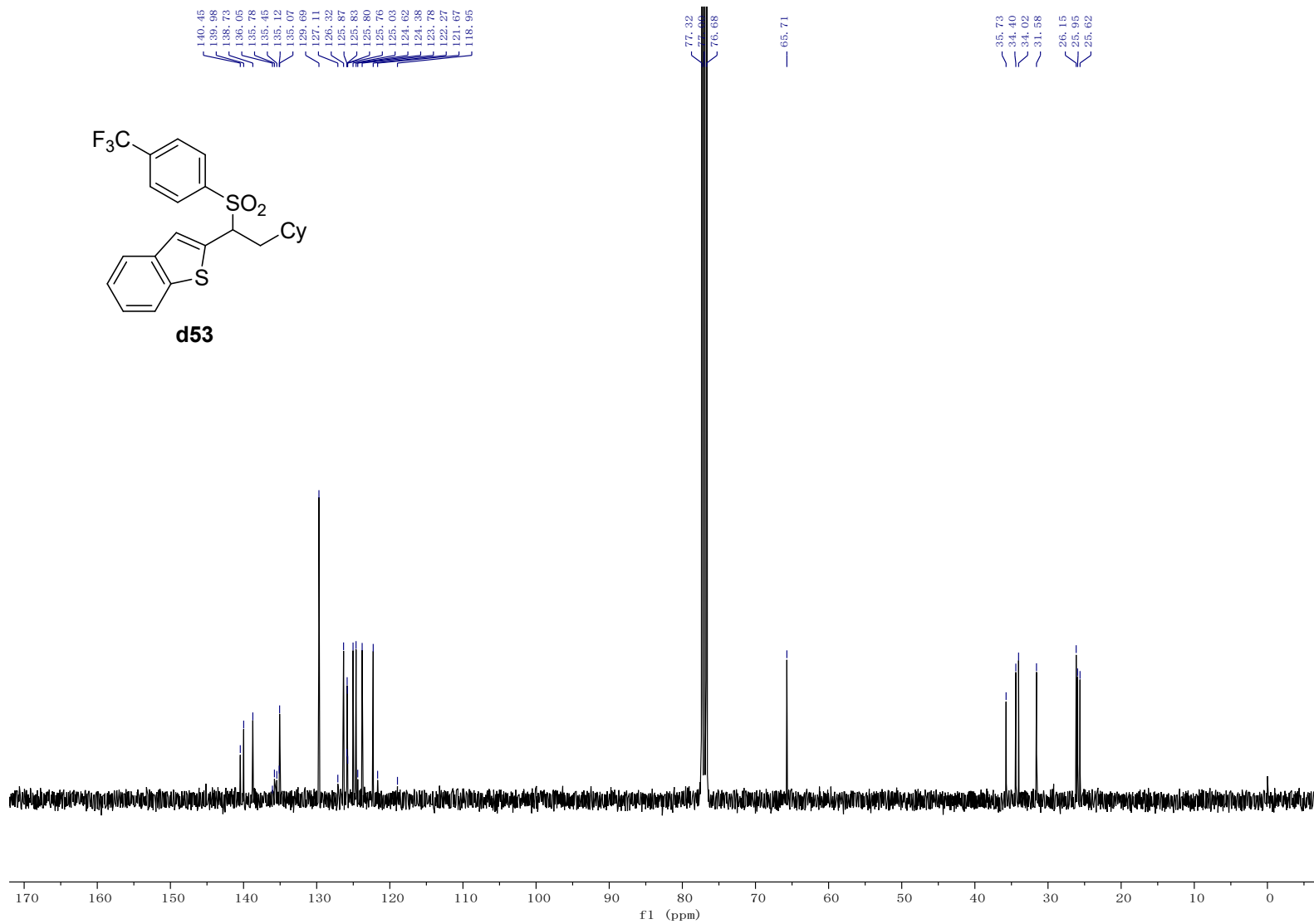
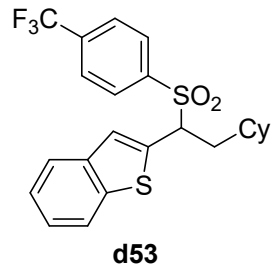


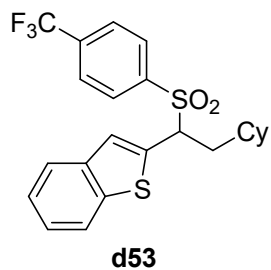
d52

— 63.41

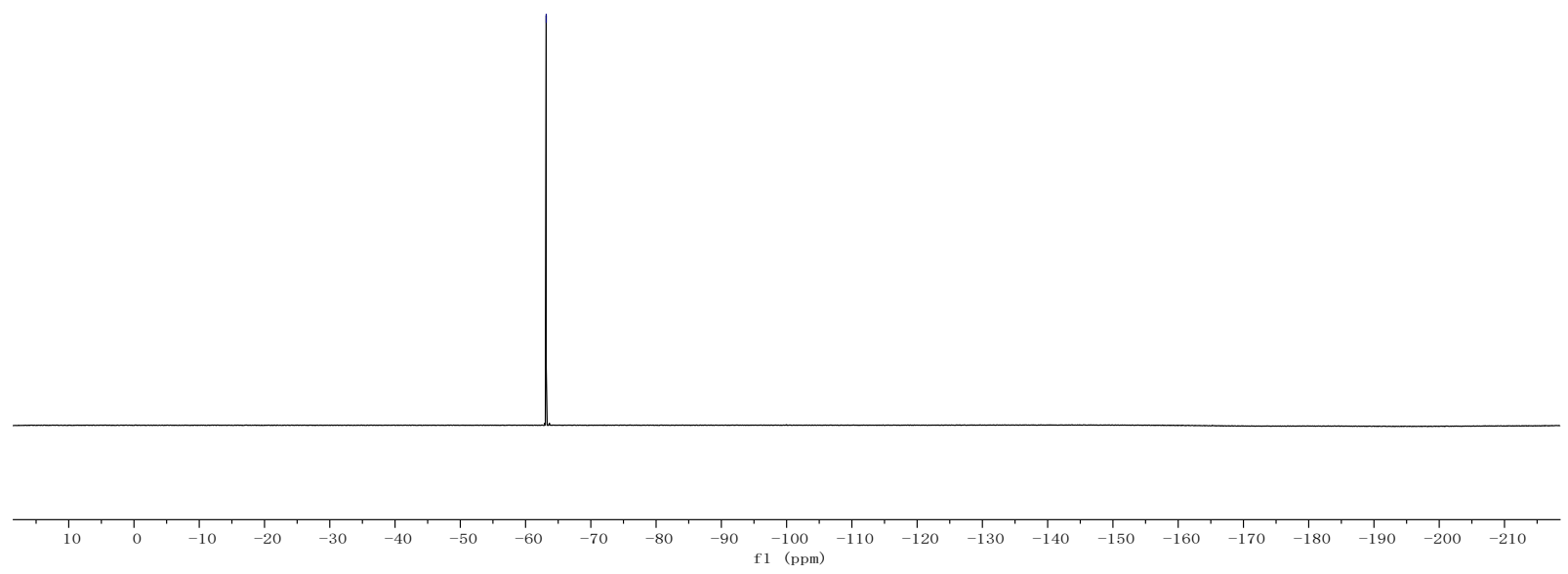


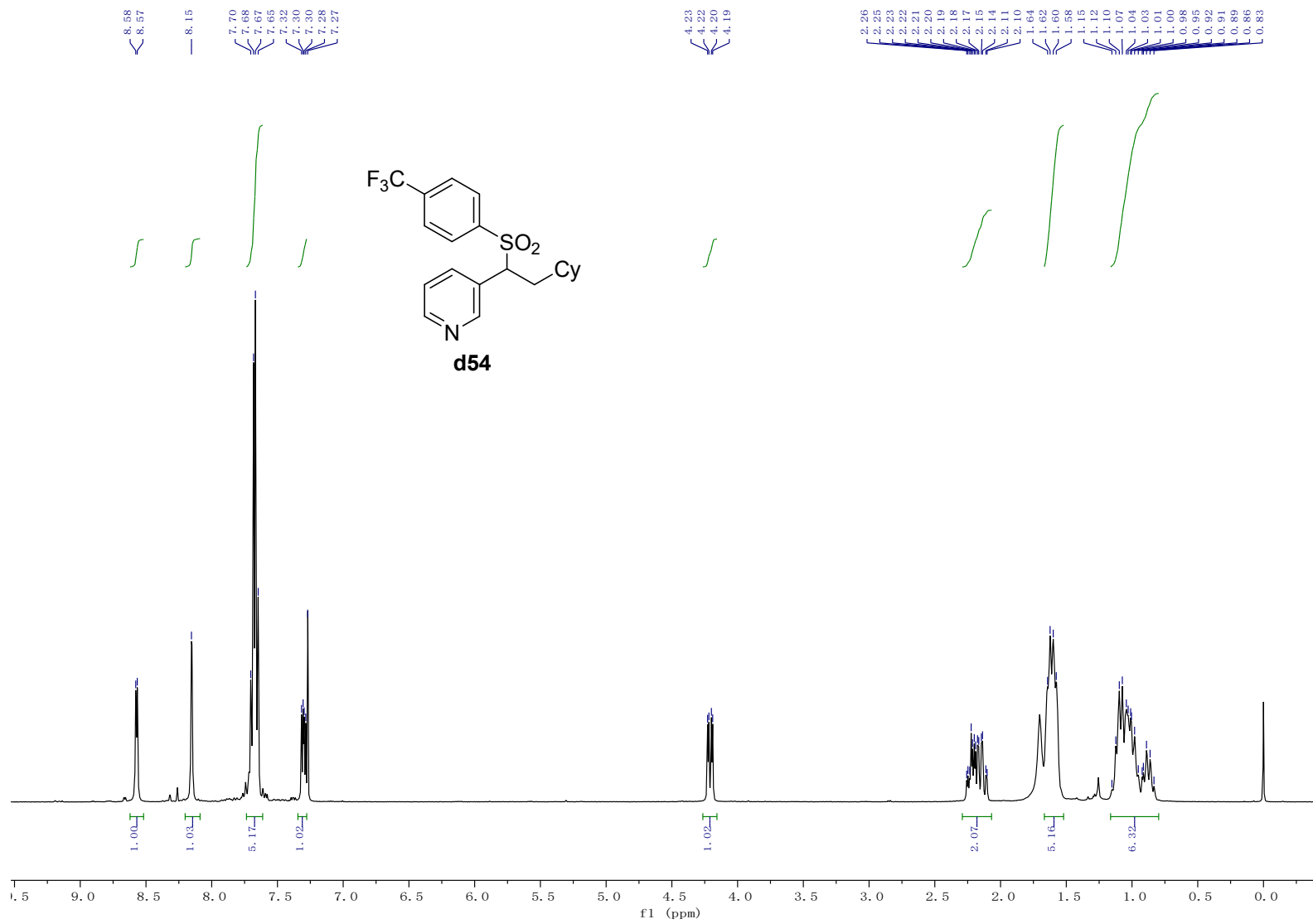


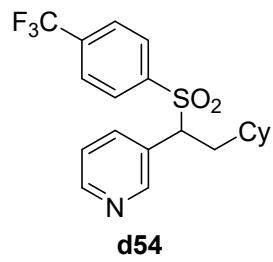




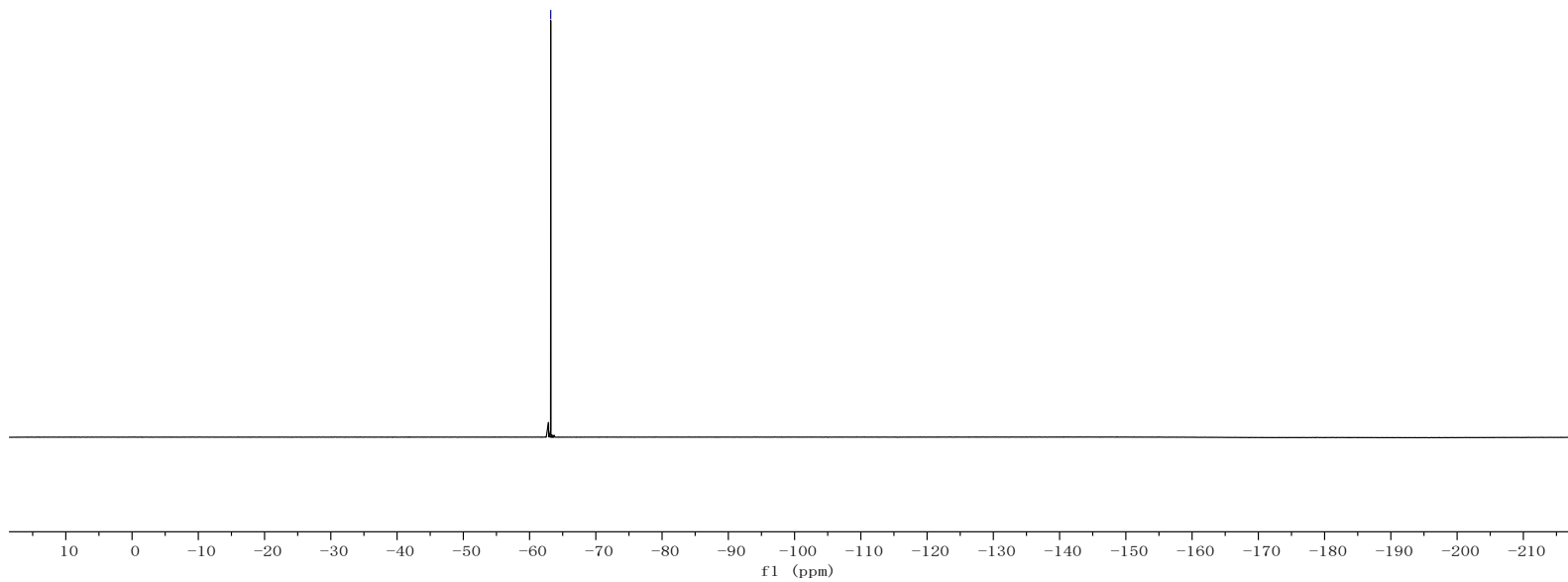
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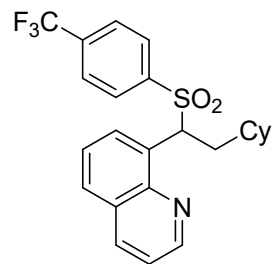
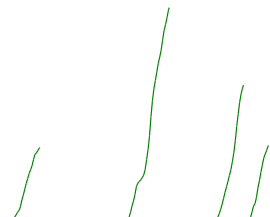
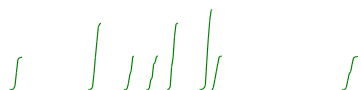


-63.19

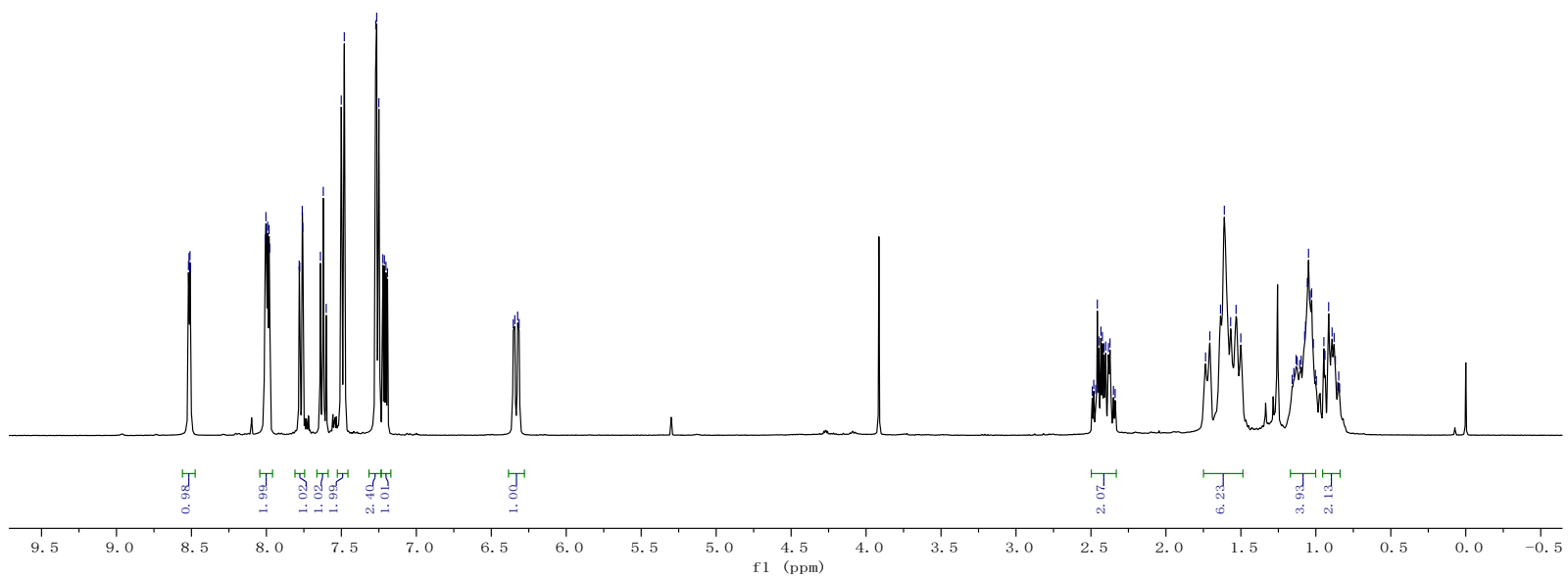


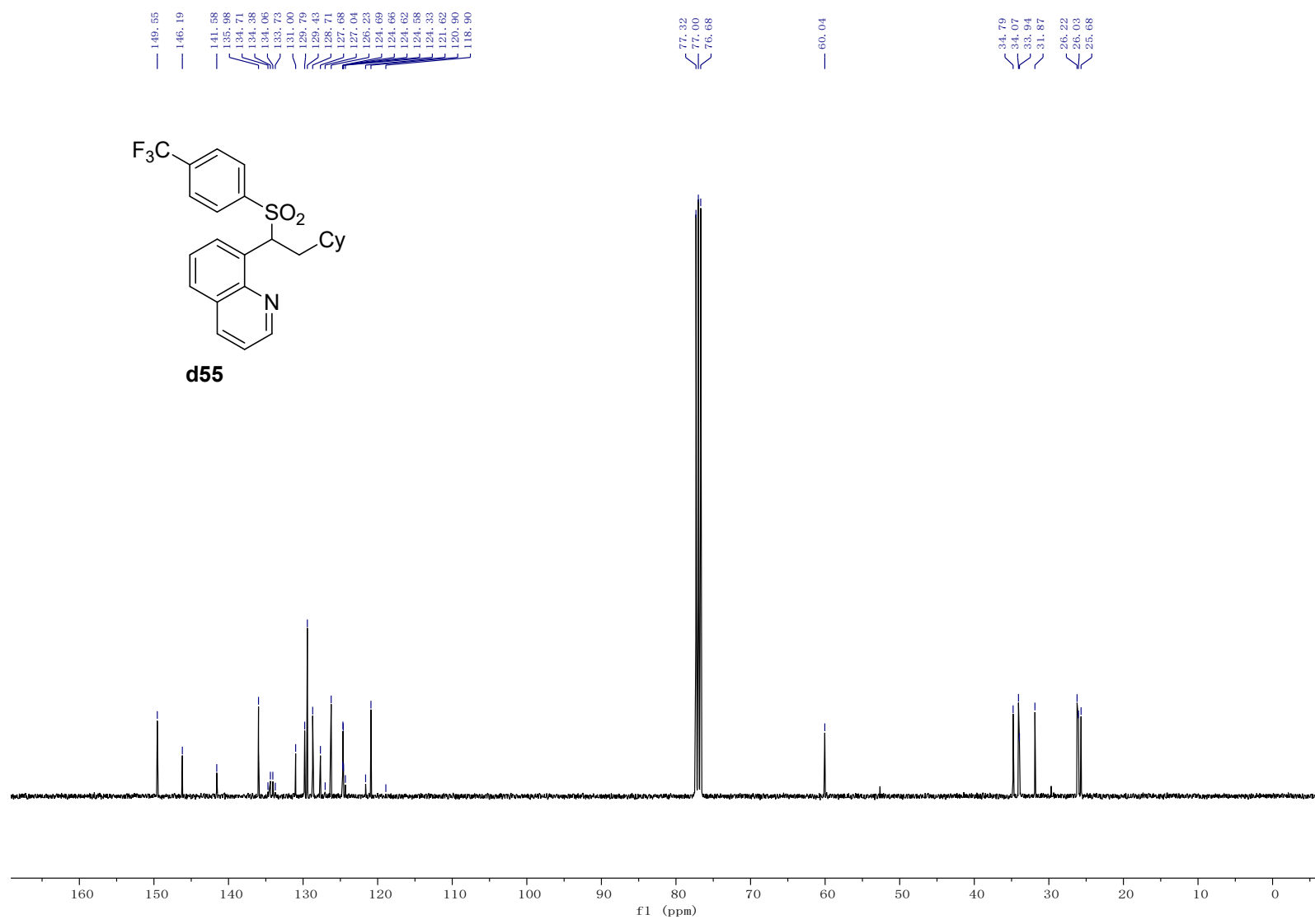
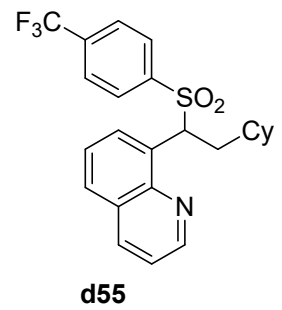
8.52
8.51
8.51
8.01
8.00
7.99
7.98
7.78
7.78
7.76
7.76
7.64
7.62
7.60
7.50
7.48
7.27
7.26
7.25
7.22
7.21
7.20
7.19
6.35
6.34
6.32
6.31

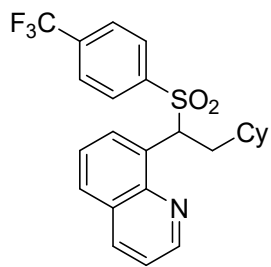
2.49
2.48
2.47
2.46
2.45
2.43
2.42
2.41
2.40
2.38
2.37
2.35
2.34
1.74
1.71
1.64
1.61
1.57
1.53
1.50
1.15
1.13
1.12
1.11
1.10
1.07
1.07
1.06
1.05
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1.03
1.02
1.00
0.95
0.94
0.91
0.89
0.88
0.87



d55

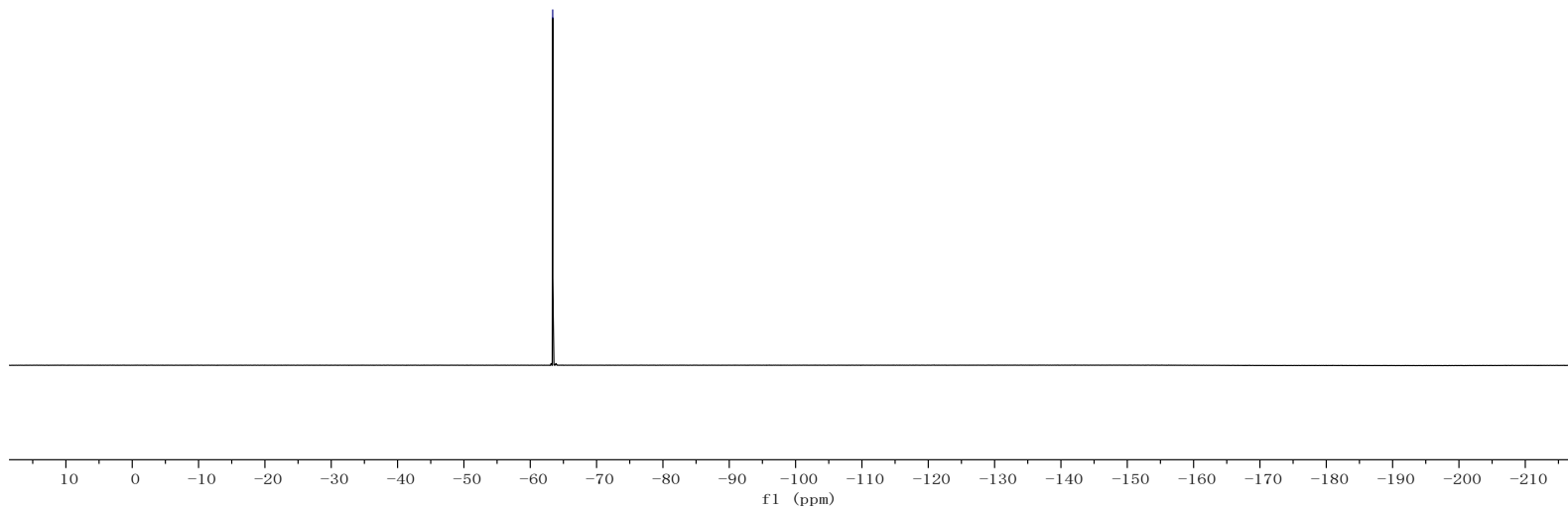


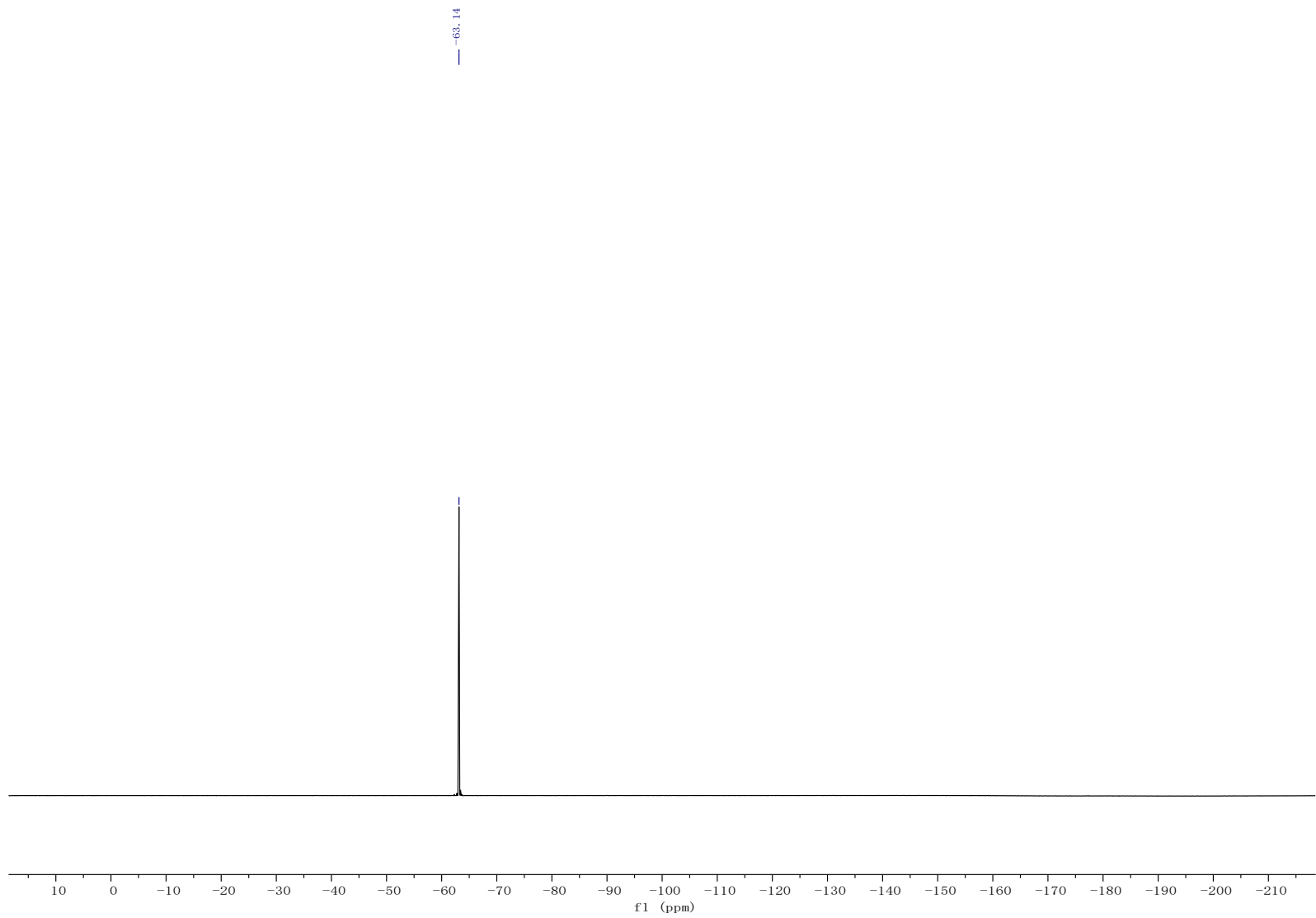
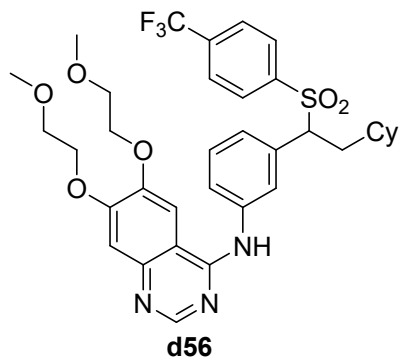


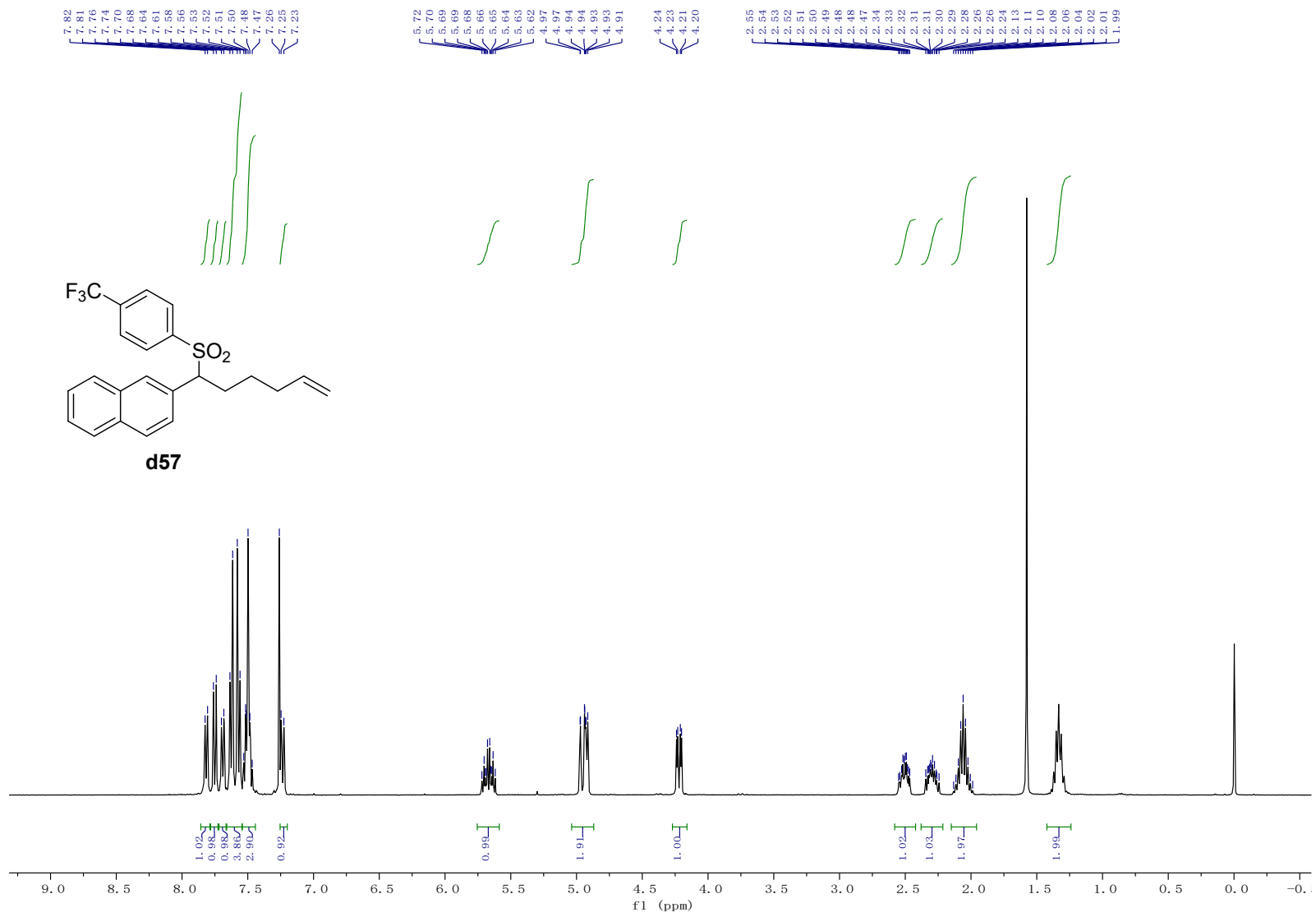


d55

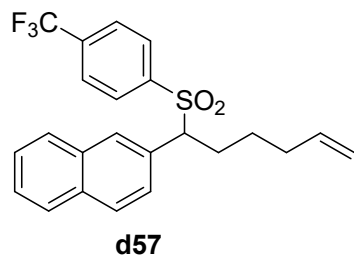
63.38





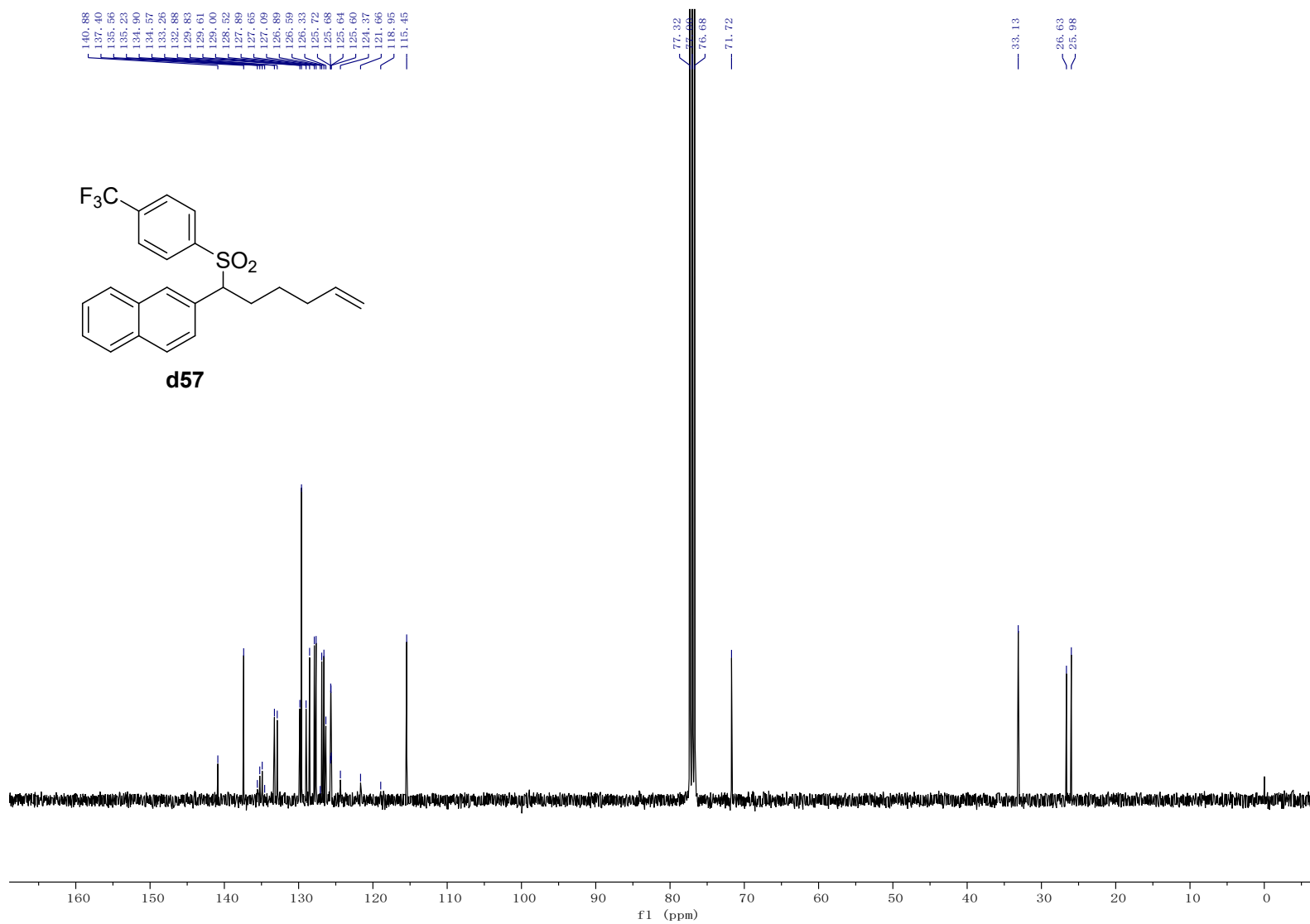


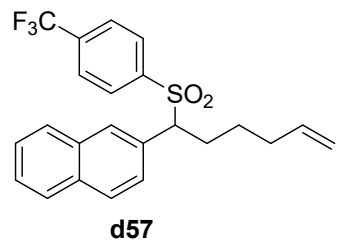
140.88
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135.23
134.90
134.57
133.26
132.88
129.83
129.61
129.00
128.52
127.89
127.65
127.09
126.89
126.39
125.33
125.72
125.64
125.60
124.37
121.66
118.95
115.45



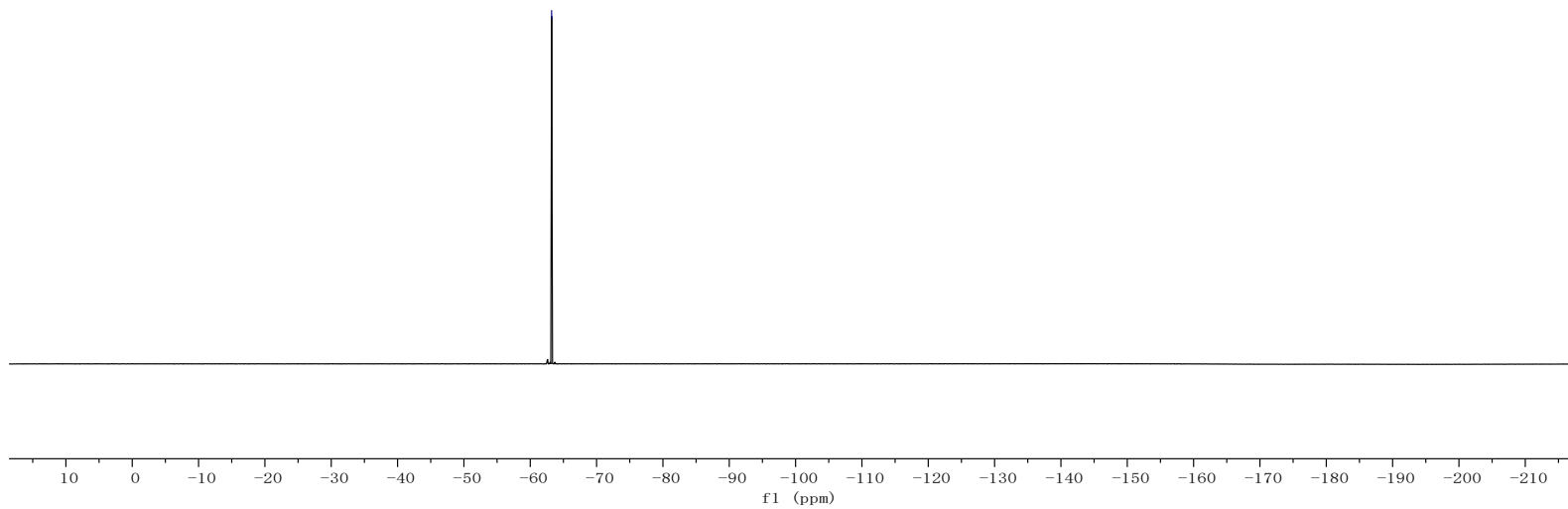
77.32
77.00
76.68
71.72

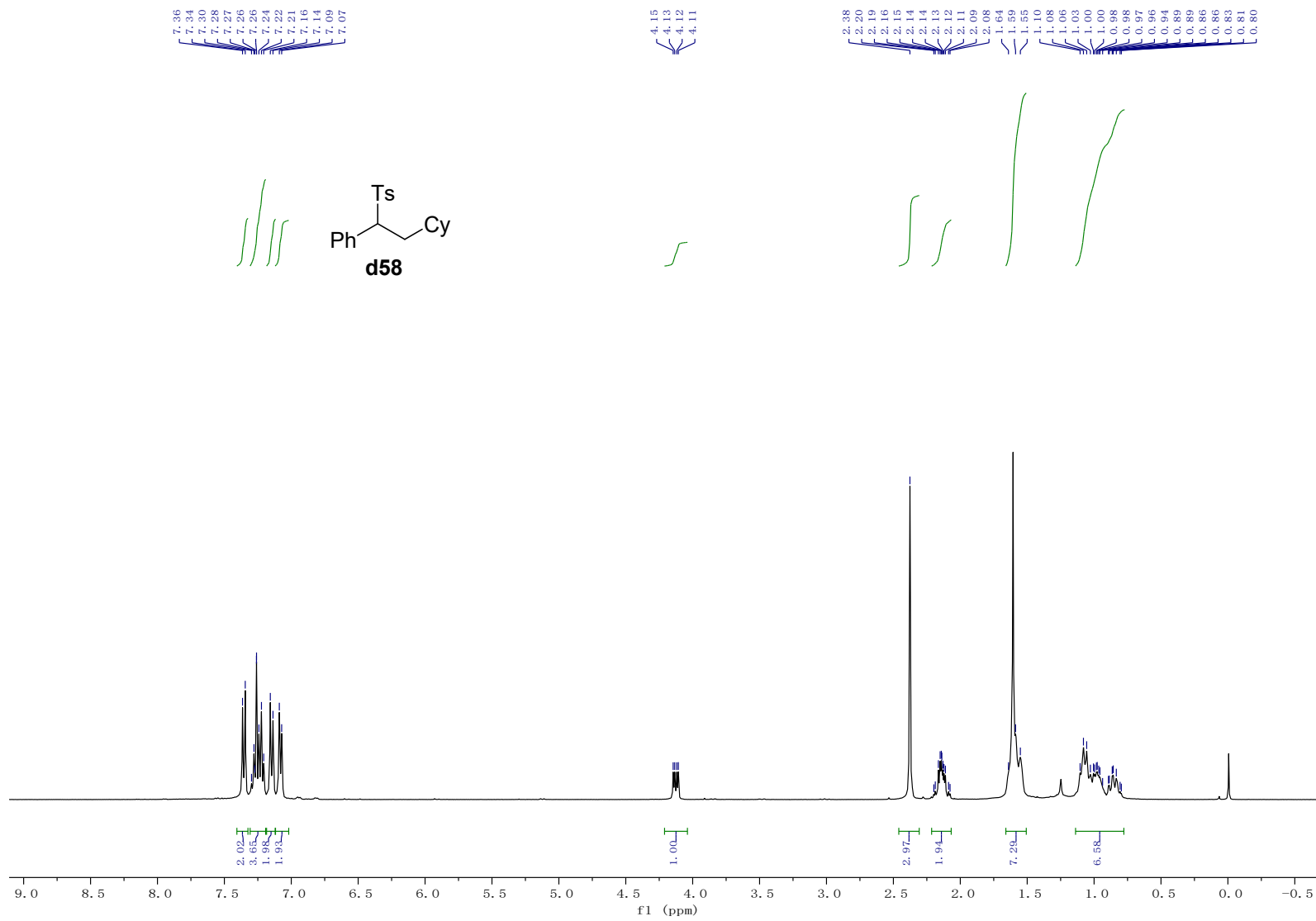
33.13
26.63
26.96

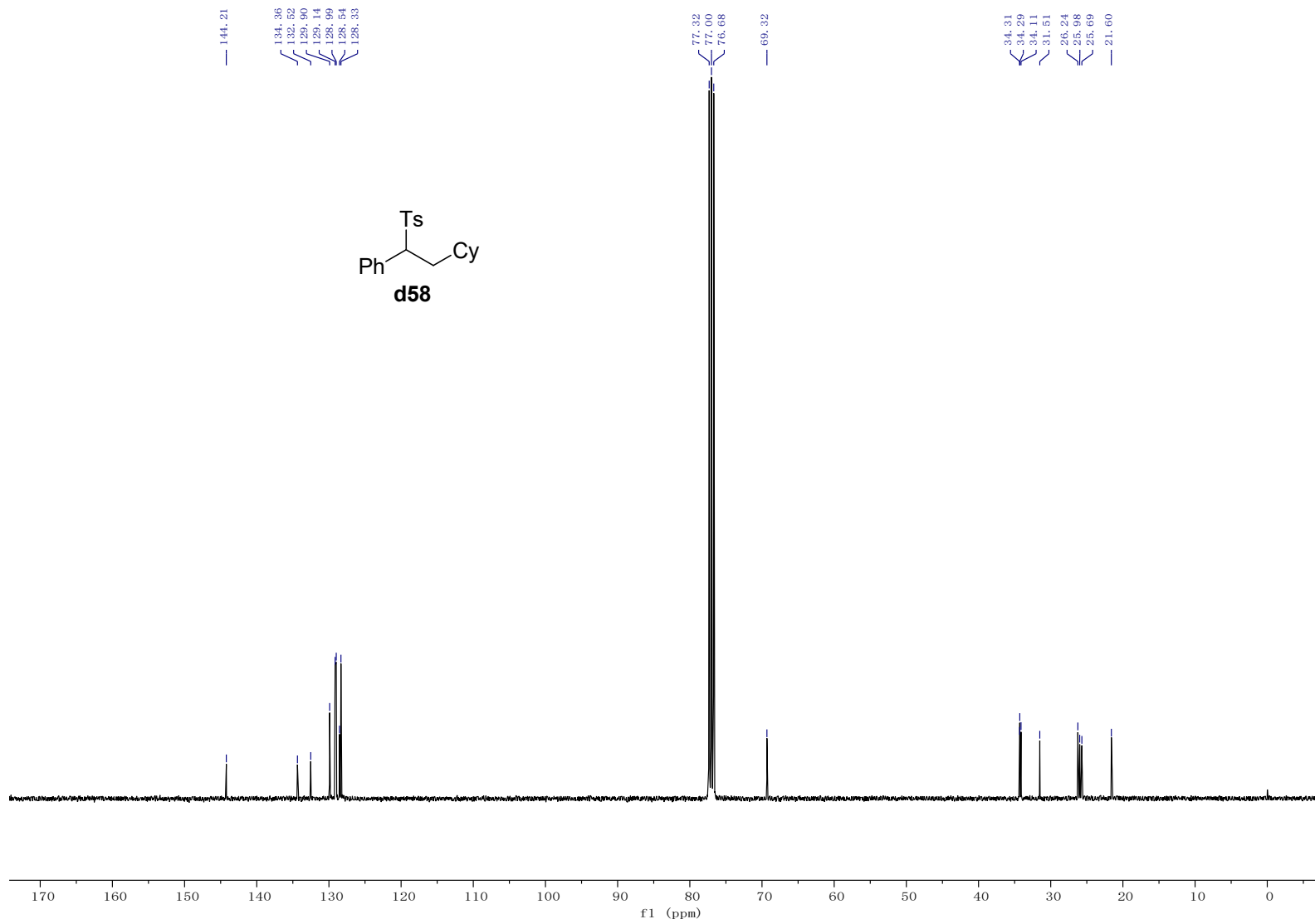


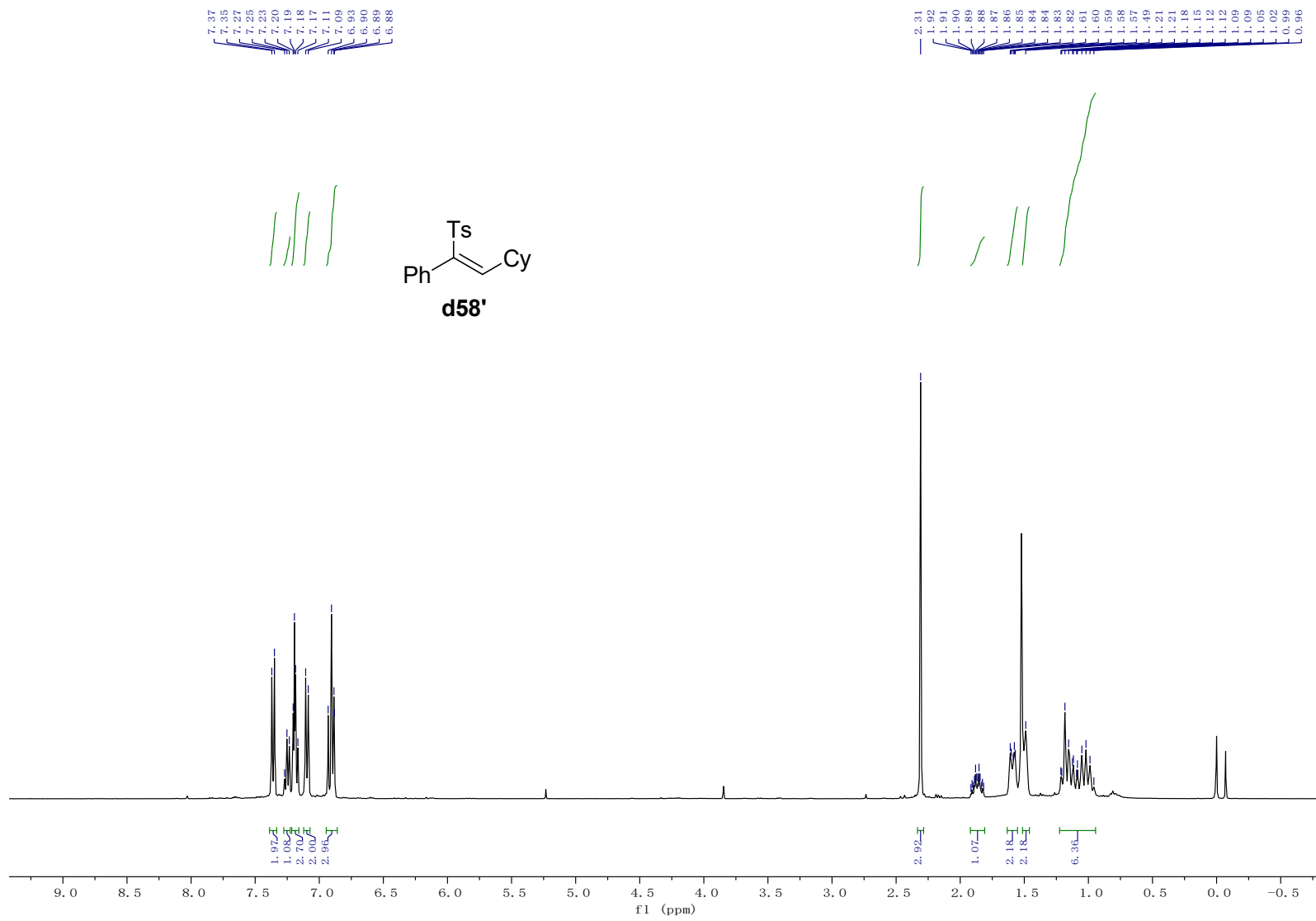


— 63.22









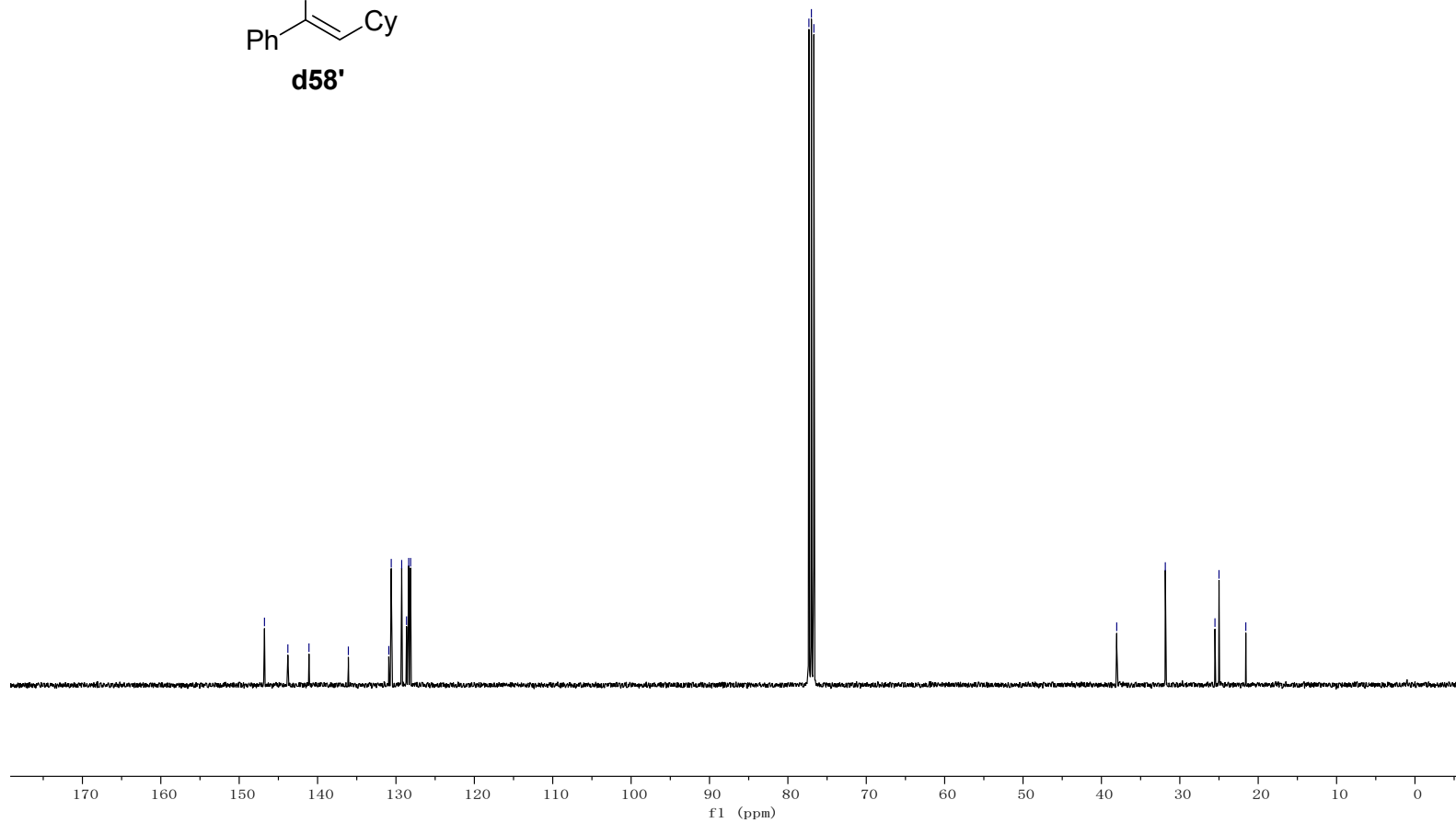
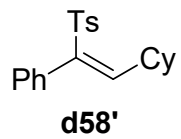
146.78
143.79
141.10
136.07
130.91
130.60
129.27
128.65
128.38
128.13

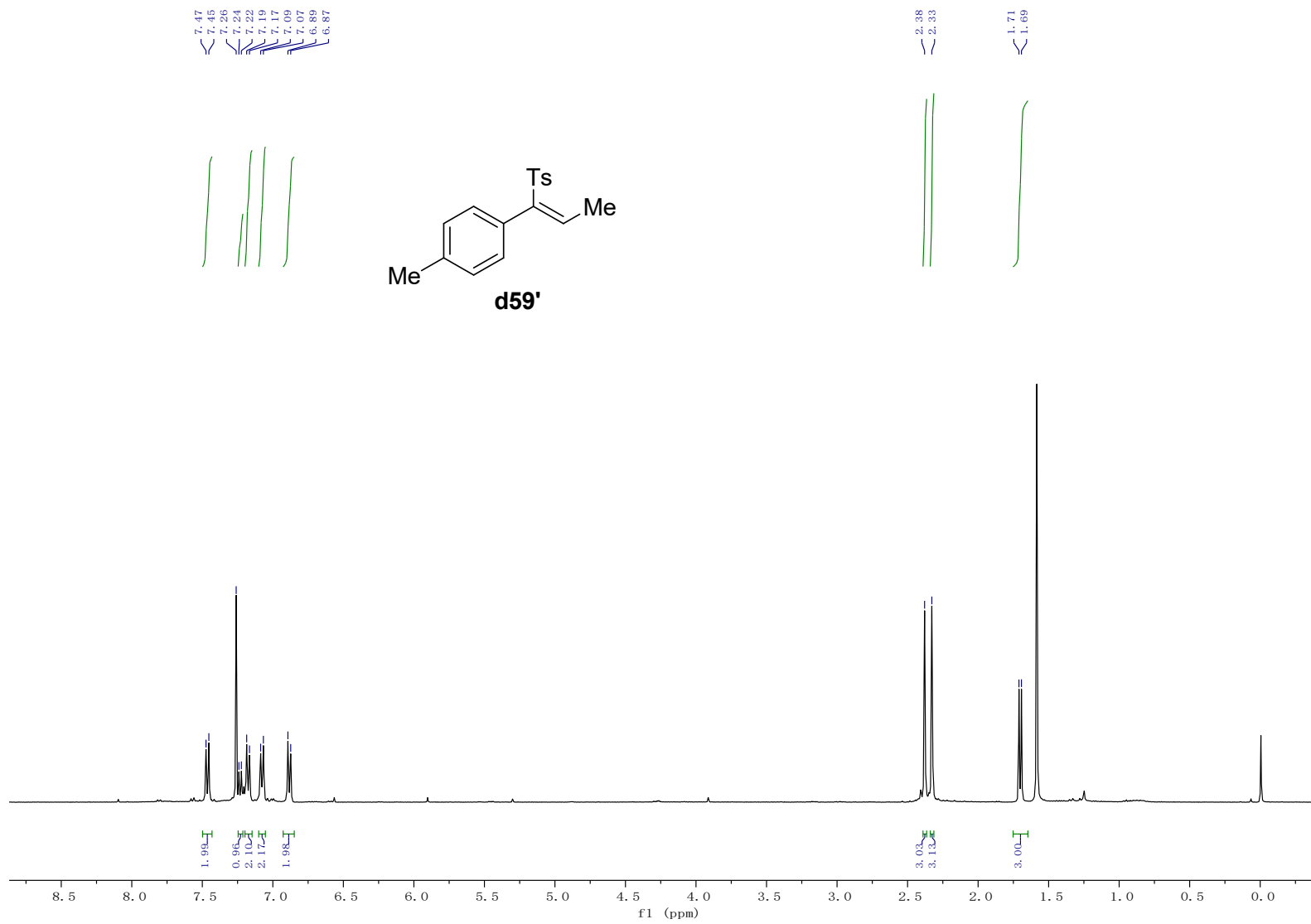
77.32
77.00
76.68

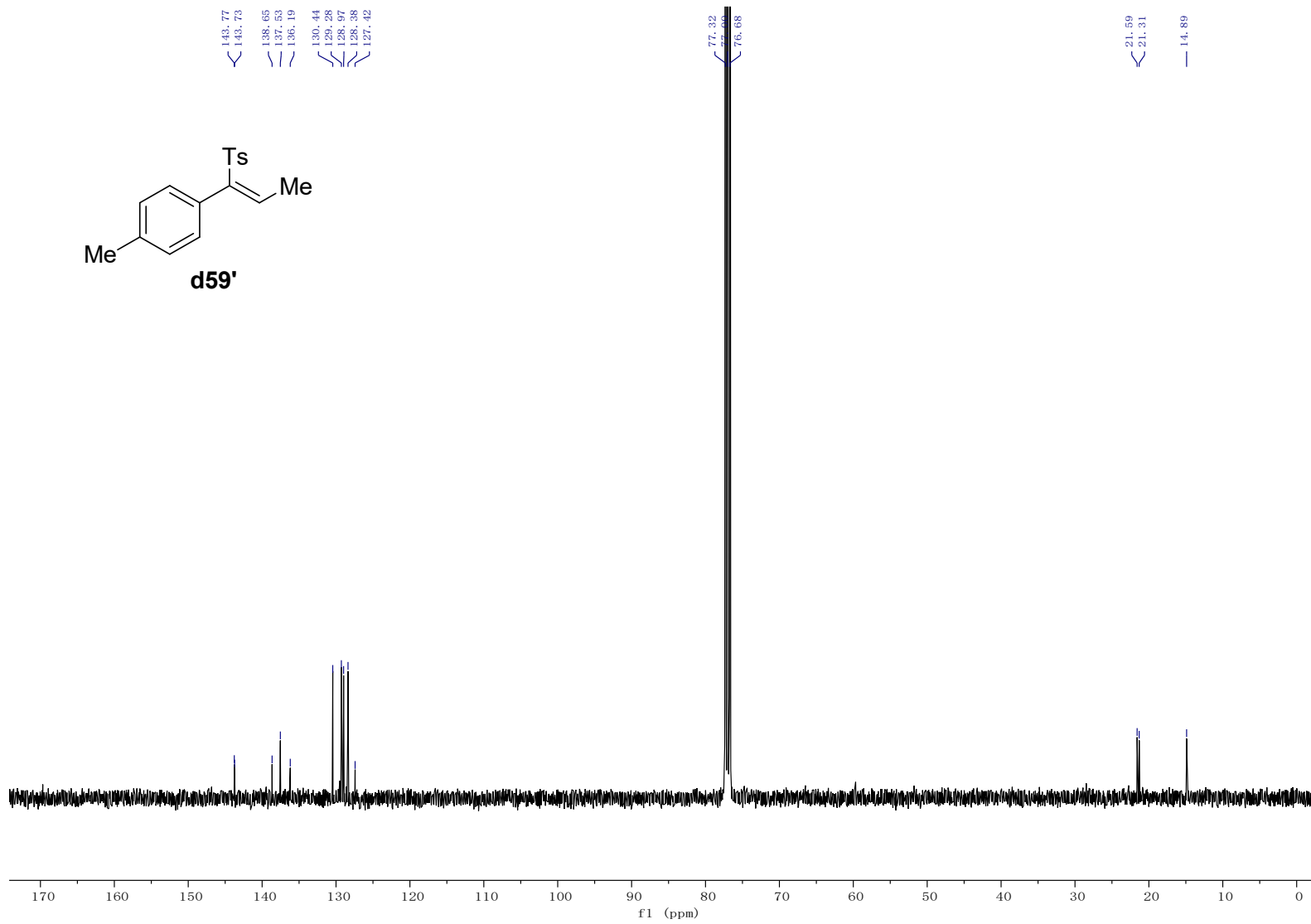
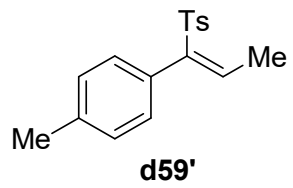
38.05

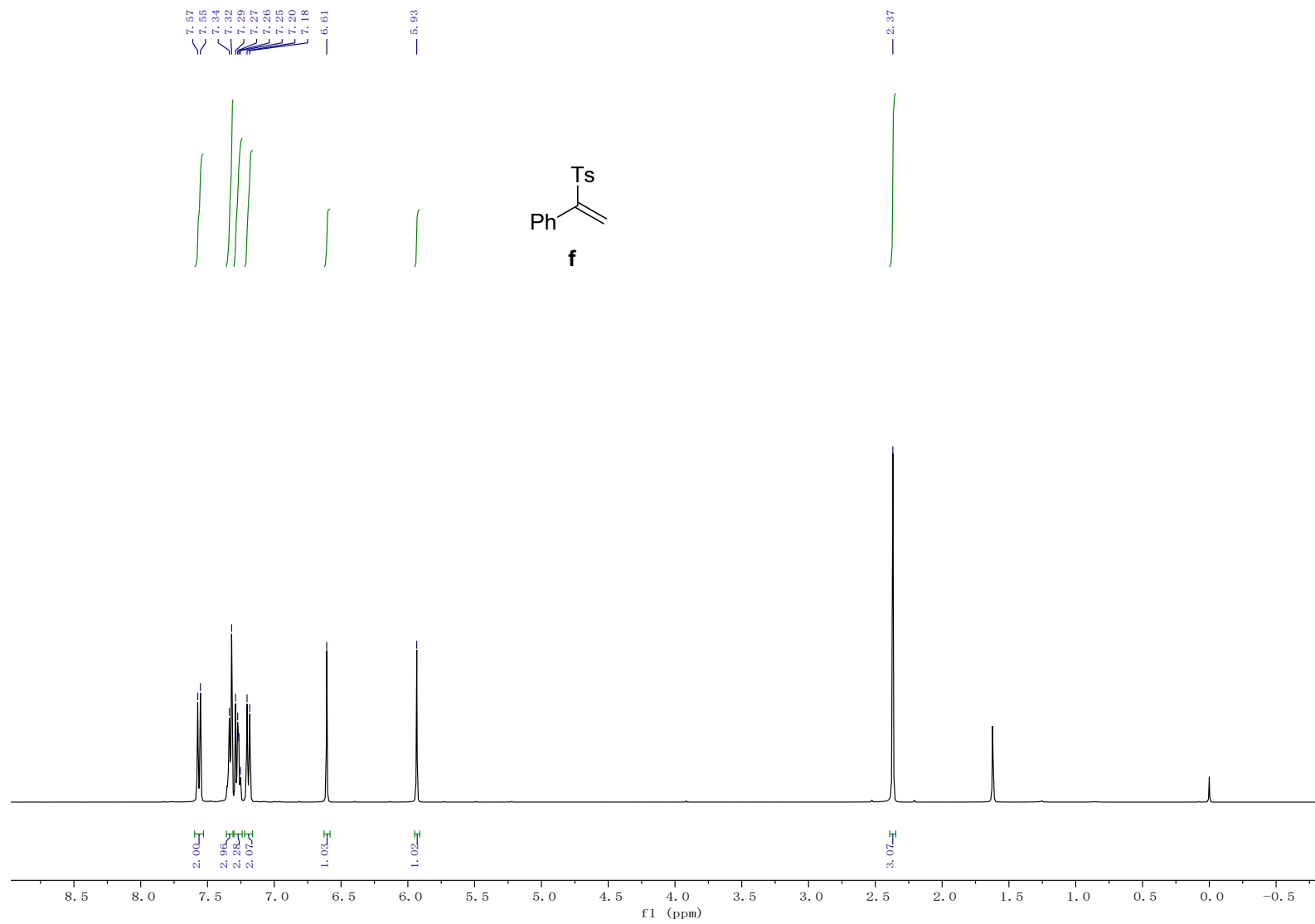
31.85

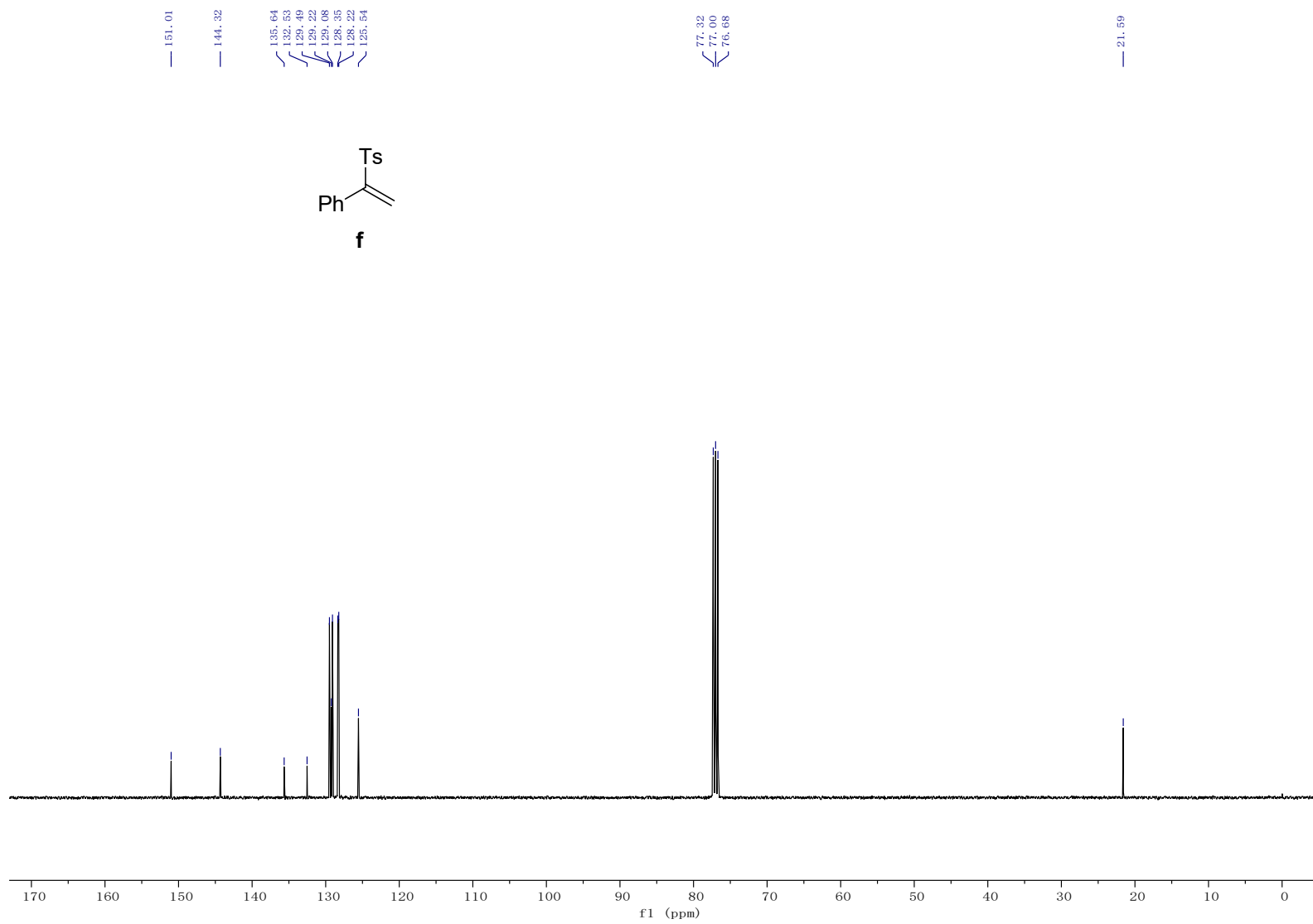
25.52
25.00
21.88

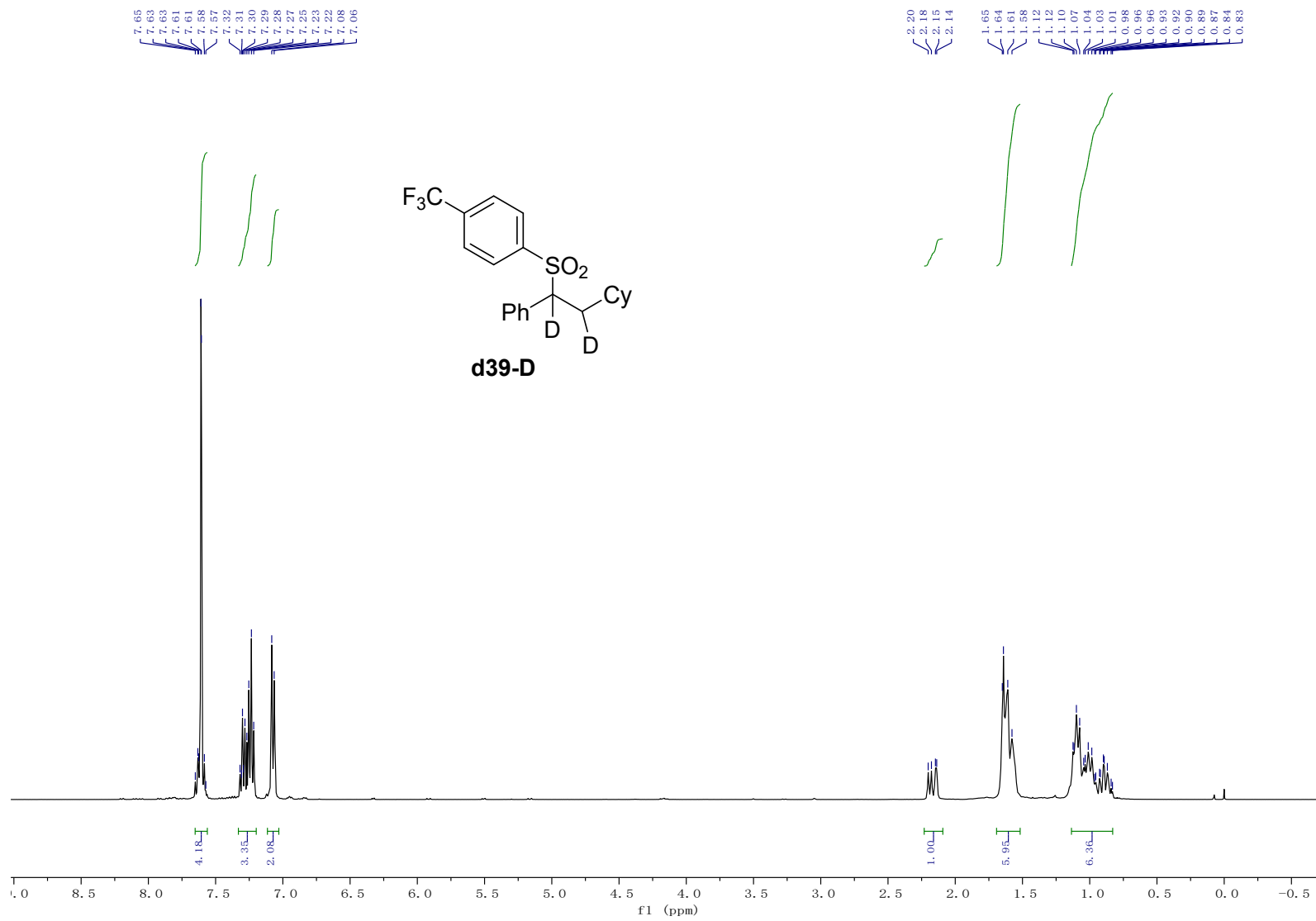


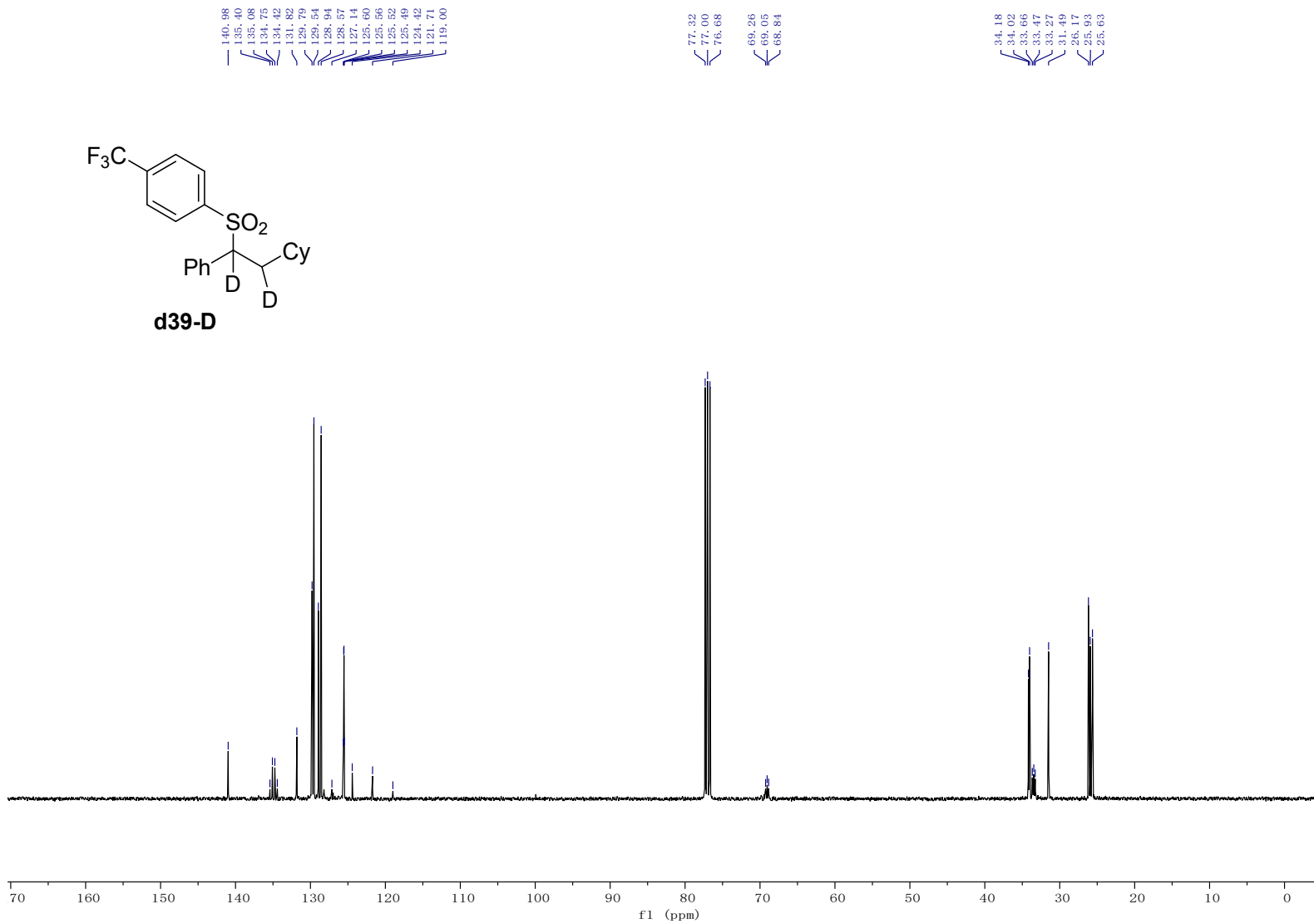
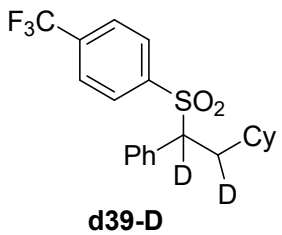


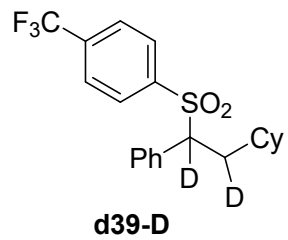












-63.17

