

Supporting Information

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General Considerations

All reactions described were performed at ambient temperature and atmosphere unless otherwise specified. Column chromatography was carried out with 230-400 mesh silica gel (E. Merck, Silica Gel 60). Concentration and removal of trace solvents was done via an IKA rotary evaporator using an IKA RC2 Green Basic circulating cooler and an IKA VacStar pump. Electrochemical reactions were carried on IKA's ElectraSyn 2.0 instrument.

Nuclear magnetic resonance (NMR) spectra were recorded using deuteriochloroform (CDCl₃) or deuterioacetonitrile (CD₃CN) as the solvent. Signal positions (δ) are given in parts per million from tetramethylsilane (δ 0) and were measured relative to the signal of the solvent (**¹H NMR:** CDCl₃: δ 7.26; CD₃CN: δ 1.96; acetone-d₆: δ 2.05; **¹³C NMR:** CDCl₃: δ 77.16, acetone-d₆: 29.84, dmsod₆: 39.5). Coupling constants (*J* values) are given in Hertz (Hz) and are reported to the nearest 0.1 Hz. ¹H NMR spectral data are tabulated in the order: multiplicity (*s*, singlet; *d*, doublet; *t*, triplet; *q*, quartet; *sept*, septet; *m*, multiplet; *br* broad), coupling constants, number of protons. NMR spectra were recorded on either 400 or 500 MHz spectrometers.

High-resolution mass spectra were recorded using either electron impact (EI) or electrospray ionization (ESI) techniques by the mass spec lab at the University of Alberta.

Starting Materials

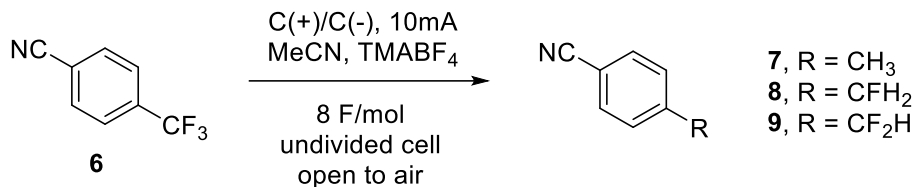
Starting materials for **7**, **11**, **12**, **13**, **16**, **17**, **18**, **19**, **20**, and **21** are commercially available. Starting materials for **14**¹ and **15**² were prepared using literature procedures.

General Procedure for Electrochemical Hydrodefluorination (e-HDF) Reaction

A 5 mL ElectraSyn vial was charged with trifluoromethyl(hetero)arene (0.20 mmol, 1.0 equiv.), tetramethylammonium tetrafluoroborate (0.20 mmol, 1.0 equiv.), and triethylsilane (0.60 mmol, 3.0 equiv.) in dry acetonitrile (2.7 mL, 0.075 M). The vial was then capped with an ElectraSyn vial cap equipped with two graphite electrodes and the reaction mixture was stirred until the solution became homogenous. The reaction mixture was then electrolyzed under a constant current of 10 mA for 8 F/mol. Following electrolysis, the ElectraSyn vial cap was removed and the graphite electrodes were rinsed with dichloromethane (ca. 2 mL). The reaction mixture was then transferred to a separatory funnel, dilute with 10 mL of dichloromethane, and washed with deionized water (twice, ca. 3 mL per wash). The aqueous layers were combined and extracted twice with dichloromethane. The organic layers were then combined, dried over Na₂SO₄, filtered, concentrated under reduced pressure, and the crude product was purified by flash chromatography as indicated.

Optimization

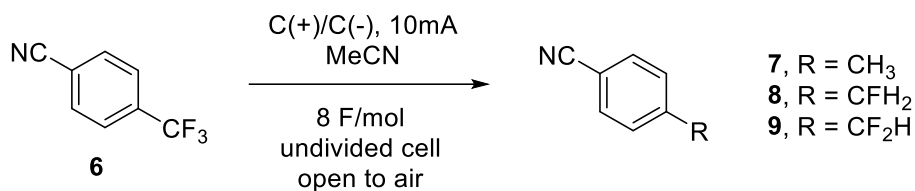
Silane additive screening



Entry ^[a]	Variation from above	7/8/9 ^[b]	Yield ^[c]
1	Added Ph ₃ SiH (3 eq.)	100/0/0	33%
2	Added Ph ₂ SiH ₂ (3 eq.)	100/0/0	51%
3	Added (EtO) ₃ SiH (3 eq.)	100/0/0	65%
4	Added (TMS) ₃ SiH (3 eq.)	N.D.	0%
5	Added Et ₃ SiH (3 eq.)	100/0/0	76%

Table S1. ^aConditions: **6** (1 equiv.), TMABF₄ (1 equiv.), and MeCN (0.075 M);^b ratio of products determined from ¹H NMR analysis of crude reaction mixture using CH₂Br₂ as an internal standard; ^c ¹H NMR yield **7**.

Electrolyte screening

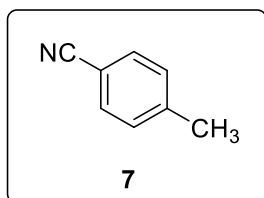


Entry ^[a]	Variation from above	7/8/9 ^[b]	Yield ^[c]
1	TEABF ₄ (1 eq.)	100/0/0	60%
2	TMAPF ₆ (1 eq.)	100/0/0	51%
3	TMABF ₄ (1 eq.)	100/0/0	76%
4	LiClO ₄ (1 eq.)	100/0/0	8%
5	LiFSI (1 eq.)	2/1/3.5	3%
6	TMABF ₄ (2 eq.)	100/0/0	63%

Table S2. ^aConditions: **6** (1 equiv.), Et₃SiH (3 equiv.), and MeCN (0.075 M);^b ratio of products determined from ¹H NMR analysis of crude reaction mixture using CH₂Br₂ as an internal standard; ^c ¹H NMR yield **7**.

Preparation and characterization of hydrodefluorination products

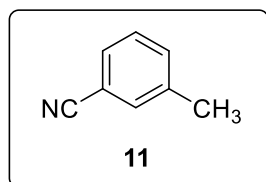
Preparation of **7**



Following the General Procedure, a solution of 4-(trifluoromethyl)benzonitrile (34.2 mg, 0.200 mmol), TMABF₄ (32.2 mg, 0.200 mmol), and triethylsilane (96 μ L, 0.600 mmol) in acetonitrile (2.7 mL) was electrolyzed for 8 F/mol with a 10 mA current. The ¹H NMR yield of the crude product was determined to be 76% where dibromomethane was used as an internal standard (8.0 μ L). Purification of the crude product **7** by flash chromatography (0 \rightarrow 5 % \rightarrow 10% EtOAc in hexanes and 2.5% triethylamine) afforded **7** (16.8 mg, 72 % yield) as a light yellow liquid. The spectral data matched those from previous reports.³

Data for **7**: ¹H NMR (500 MHz, CDCl₃): δ 7.54 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 2.42 (s, 3H); ¹³C NMR (125 MHz, (CDCl₃): δ 143.8, 132.2, 130.0, 119.4, 109.6, 21.9.

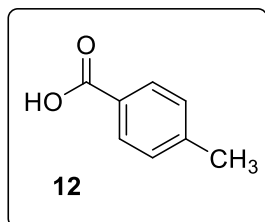
Preparation of **11**



Following the General Procedure, a solution of 3-(trifluoromethyl)benzonitrile (34.2 mg, 0.200 mmol), TMABF₄ (32.2 mg, 0.200 mmol), and triethylsilane (96 μ L, 0.600 mmol) in acetonitrile (2.7 mL) was electrolyzed for 8 F/mol with a 10 mA current. The ¹H NMR yield of the crude product was determined to be 53% where dibromomethane was used as an internal standard (8.0 μ L). Purification of the crude product **11** by flash chromatography (0 \rightarrow 5 % \rightarrow 10% EtOAc in hexanes and 2.5% triethylamine) afforded **11** (11.9 mg, 51 % yield) as a colourless oil. The spectral data matched those from previous reports.⁴

Data for **11**: $^1\text{H NMR}$ (600 MHz, CDCl_3): δ 7.44-7.47 (m, 2H), 7.41 (d, $J = 8.2$ Hz, 1H), 7.35 (dd, $J = 7.8, 7.8$ Hz, 1H), 2.39 (s, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 139.4, 133.8, 132.7, 129.4, 129.1, 119.2, 112.4, 21.3.

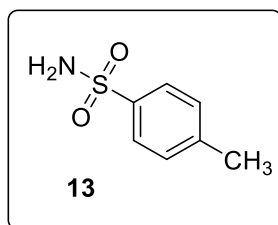
Preparation of **12**



Following the General Procedure, a solution of 4-(trifluoromethyl)benzoic acid (38.0 mg, 0.200 mmol), TBABF_4 (65.8 mg, 0.200 mmol), sodium bicarbonate (16.8 mg, 0.200 mmol) and triethylsilane (96 μL , 0.600 mmol) in NMP (2.7 mL) was electrolyzed for 8 F/mol with a 10 mA current. The $^1\text{H NMR}$ yield of the crude product was determined to be 56% where dibromomethane was used as an internal standard (8.0 μL). Purification of the crude product **12** by flash chromatography (pentane:EtOAc – 1:1) afforded **12** (14.1 mg, 52 % yield) as a white solid. The spectral data matched those from previous reports.¹The spectral data matched those from previous reports.⁵

Data for **12**: $^1\text{H NMR}$ (500 MHz, $(\text{CD}_3)_2\text{CO}$): δ 7.92 (d, $J = 8.2$ Hz, 2H), 7.31 (d, $J = 8.2$ Hz, 2H), 2.40 (s, 3H); $^{13}\text{C NMR}$ (125 MHz, $(\text{CD}_3)_2\text{CO}$): δ 168.8, 145.4, 131.6, 131.0, 130.1, 22.7.

Preparation of **13**

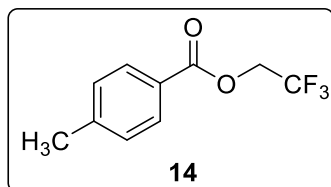


Following the General Procedure, a solution of 4-(trifluoromethyl)benzenesulfonamide (50.4 mg, 0.200 mmol), TMABF_4 (64.4 mg, 0.400 mmol), and triethylsilane (96 μL , 0.600 mmol) in acetonitrile (2.7 mL) was electrolyzed for 10 F/mol with a 8 mA current. The $^1\text{H NMR}$ yield of the crude product was determined to be 46% where dibromomethane was used as an internal

standard (8.0 μL). Purification of the crude product **13** by flash chromatography (20 \rightarrow 50% EtOAc in hexanes) afforded **13** (17.1 mg, 41%) as a white solid. The spectral data matched those from previously reports.⁶

Data for **17**: $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.82 (d, $J = 8.3$ Hz, 2H), 7.32 (d, $J = 8.3$ Hz), 4.79 (br s, 1H), 2.43 (s, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 143.8, 139.2, 129.9, 126.6, 21.7.

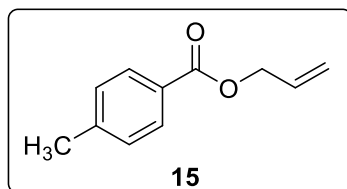
Preparation of **14**



Following the General Procedure, a solution of 2,2,2-trifluoroethyl 4-(4-methylphenyl)benzoate (54.4 mg, 0.200 mmol), TMABF_4 (32.2 mg, 0.200 mmol), and triethylsilane (96 μL , 0.600 mmol) in acetonitrile (2.7 mL) was electrolyzed for 8 F/mol with a 6.5 mA current. The $^1\text{H NMR}$ yield of the crude product was determined to be 33% where dibromomethane was used as an internal standard (8.0 μL). Purification of the crude product **14** by flash chromatography (0 \rightarrow 10% \rightarrow 20% EtOAc in hexanes) afforded **14** (13.5 mg, 31 % yield) as a colourless oil. The spectral data matched those from previously reports.⁷

Data for **14**: $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.96 (d, $J = 8.4$ Hz, 2H), 7.27 (d, $J = 8.4$ Hz, 2H), 4.68 (q, $J = 8.3$ Hz, 2H), 2.43 (s, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 165.1, 144.9, 130.2, 129.5, 125.8, 123.3 (q, $J = 278$ Hz), 60.8 (q, $J = 36.7$ Hz), 21.9; $^{19}\text{F NMR}$ (470 MHz, CDCl_3): δ -73.9

Preparation of **15**

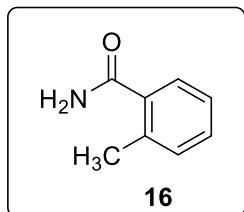


Following the General Procedure, a solution of allyl 4-(4-methylphenyl)benzoate (46.0 mg, 0.200 mmol), TMABF_4 (32.2 mg, 0.200 mmol), and triethylsilane (96 μL , 0.600 mmol) in acetonitrile (2.7 mL) was electrolyzed for 8 F/mol with a 10 mA current. The $^1\text{H NMR}$ yield of the crude product was determined to be 54% where dibromomethane was used as an internal standard (8.0

μL). Purification of the crude product **15** by flash chromatography (0 \rightarrow 10% EtOAc in hexanes) afforded **15** (18.6 mg, 53 % yield) as an inseparable mixture with starting material. The spectral data matched those from previously reports.⁸

Data for **15**: $^1\text{H NMR}$ (600 MHz, CDCl_3): δ 7.95 (d, $J = 8.2$ Hz, 2H), 7.24 (d, $J = 8.2$ Hz, 2H), 6.04 (m, 1H), 5.40 (m, 1H), 5.28 (m, 1H), 4.81 (dt, $J = 5.6, 1.4, 1.4$ Hz, 2H), 2.41 (s, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 166.5, 143.8, 132.5, 129.9, 129.2, 127.6, 118.2, 65.6, 21.8.

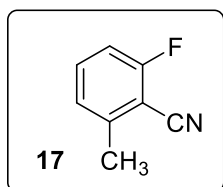
Preparation of 16



Following the General Procedure, a solution of 2-(trifluoromethyl)benzamide (37.8 mg, 0.200 mmol), TMABF_4 (64.4 mg, 0.400 mmol), and triethylsilane (96 μL , 0.600 mmol) in acetonitrile (2.7 mL) was electrolyzed for 6 F/mol with a 8 mA current. The $^1\text{H NMR}$ yield of the crude product was determined to be 57% where dibromomethane was used as an internal standard (8.0 μL). Purification of the crude product **16** by flash chromatography (hexanes:EtOAc – 1:1) afforded **16** as a white solid. The spectral data matched those from previously reports.⁹

Data for **16**: $^1\text{H NMR}$ (500 MHz, $(\text{CD}_3)_2\text{CO}$): δ 7.43 (dd, $J = 7.5, 1.2$ Hz, 1H), 7.34 (ddd, $J = 7.5, 7.5, 1.4$ Hz, 1H), 7.24 – 7.16 (m, 2H), 2.43 (s, 3H); $^{13}\text{C NMR}$ (125 MHz, $(\text{CD}_3)_2\text{CO}$): δ 172.9, 138.8, 137.9, 132.6, 131.3, 129.0, 127.3, 21.3

Preparation of 17

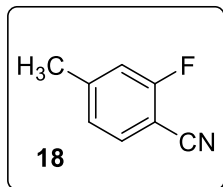


Following the General Procedure (10 mL ElectraSyn vial was used instead of the standard 5 mL), a solution of 2-fluoro-6-trifluoromethylbenzonitrile (75.6 mg, 0.400 mmol), TMABF_4 (64.4 mg, 0.400 mmol), and triethylsilane (192 μL , 1.20 mmol) in acetonitrile (5.4 mL) was electrolyzed for

10 F/mol with a 8 mA current. The ^1H NMR yield of the crude product was determined to be 77% where dibromomethane was used as an internal standard (8.0 μL). Purification of the crude product **17** by flash chromatography (0 \rightarrow 5 % \rightarrow 10% EtOAc in hexanes and 2.5% triethylamine) afforded **17** (39.4 mg, 73%) as a white solid.

Data for **17**: ^1H NMR (500 MHz, CDCl_3): δ 7.46 (m, 1H), 7.11 (d, (J = 7.8 Hz, 1H), 7.02 (dd, J = 8.5, 8.5 Hz, 1H), 2.56 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 163.7 (d, J = 258 Hz), 144.4, 134.2 (d, J = 8.9 Hz), 125.9 (d, J = 3.2 Hz), 113.4 (d, J = 19.9 Hz), 113.4, 102.4 (d, J = 15.2 Hz), 20.5 (d, J = 2.2 Hz); ^{19}F NMR (470 MHz, CDCl_3): δ -106.5

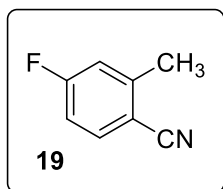
Preparation of **18**



Following the General Procedure, a solution of 2-fluoro-4-(trifluoromethyl)benzonitrile (37.8 mg, 0.200 mmol), TEABF_4 (43.4 mg, 0.200 mmol), and triethylsilane (96 μL , 0.600 mmol) in dry acetonitrile (2.7 mL) was electrolyzed for 8 F/mol with a 10 mA current. The ^1H NMR yield of the crude product was determined to be 55% where dibromomethane was used as an internal standard (8.0 μL). Purification of the crude product **18** by flash chromatography (0 \rightarrow 5 % \rightarrow 10% EtOAc in hexanes and 2.5% triethylamine) afforded **18** (13.7 mg, 51%) as a white solid. The spectral data matched those from previous reports.¹⁰

Data for **18**: ^1H NMR (500 MHz, CDCl_3): δ 7.50 (dd, J = 7.6, 7.1 Hz, 1H), 7.01-7.06 (m, 2H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 163.3 (d, J = 258 Hz), 147.0 (d, J = 8.3 Hz), 133.2 (d, J = 0.7 Hz), 125.8 (d, J = 3.2 Hz), 117.1 (d, J = 19.3 Hz), 114.4, 98.6 (d, J = 15.4 Hz), 22.0 (d, J = 1.7 Hz); ^{19}F NMR (470 MHz, CDCl_3): -107.3.

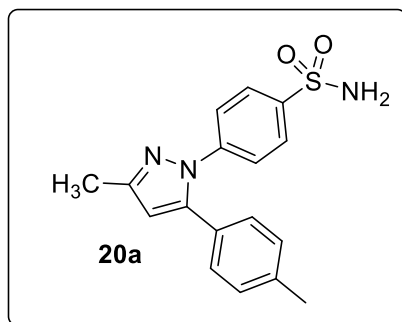
Preparation of 19



Following the General Procedure (10 mL ElectraSyn vial was used instead of the standard 5 mL), a solution of 4-fluoro-2-(trifluoromethyl)benzonitrile (76.0 mg, 0.400 mmol), TMABF₄ (64.4 mg, 0.400 mmol), and triethylsilane (0.192 μ L, 1.20 mmol) in dry acetonitrile (5.4 mL) was electrolyzed for 8 F/mol with a 10 mA current. The ¹H NMR yield of the crude product was determined to be 67% where dibromomethane was used as an internal standard (8.0 μ L). Purification of the crude product **19** by flash chromatography (0 \rightarrow 5 % \rightarrow 10% EtOAc in hexanes and 2.5% triethylamine) afforded **19** as a colourless oil (35.5 mg, 65%). The spectral data matched those from previously reports.¹¹

Data for **19**: ¹H NMR (500 MHz, CDCl₃): δ 7.61 (dd, J = 8.6, 5.6 Hz, 1H), 7.02 (dd, J = 9.3, 2.6 Hz, 1H), 6.98 (ddd, J = 8.6, 8.5, 2.6 Hz, 1H), 2.56 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 165.0 (d, J = 256.0 Hz), 145.5 (d, J = 9.3 Hz), 134.9 (d, J = 9.3 Hz), 117.7 (d, J = 22.5 Hz), 117.5, 114.2 (d, J = 22.6 Hz), 109.1 (d, J = 3.1 Hz), 20.7 (d, J = 1.4 Hz); ¹⁹F NMR (470 MHz, CDCl₃): -103.6.

Preparation of 20a



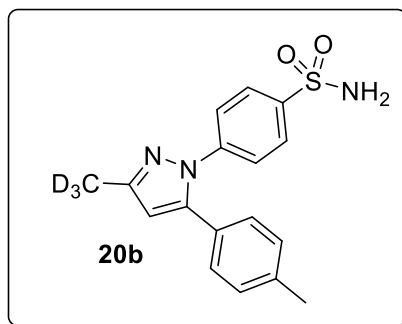
Following the General Procedure, a solution of celecoxib (76.4 mg, 0.200 mmol), TMABF₄ (32.2 mg, 0.200 mmol), and triethylsilane (96 μ L, 0.600 mmol) in acetonitrile (2.7 mL) was electrolyzed for 6 F/mol with a 8 mA current. The ¹H NMR yield of the crude product was determined to be 35% where dibromomethane was used as an internal standard (8.0 μ L). Purification of the crude

product **20a** by flash chromatography (hexanes:EtOAc – 35:65) afforded **20** (22.3 mg, 34 % yield) as a white solid. 25.0 mg of starting material was recovered.

Data for **20a**: $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.80 (d, $J = 8.3$ Hz, 2H), 7.37 (d, $J = 8.3$ Hz, 2H), 7.14 (d, $J = 8.6$ Hz, 2H), 7.09 (d, $J = 8.6$ Hz, 2H), 6.30 (s, 1H), 5.12 (br s, 1H), 5.08 (br s, 1H) 2.38 (s, 3H), 2.36 (s, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 150.9, 144.4, 143.6, 139.8, 138.9, 129.6, 127.4, 127.4, 124.8, 109.2, 21.4, 13.7.

HRMS (ESI): Expected mass ($\text{M}+\text{H}^+$): 328.1114; found: 328.1114

Preparation of **20b**

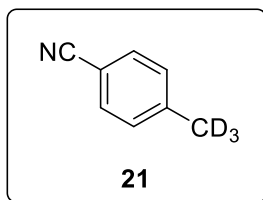


Following the General Procedure, a solution of celecoxib (76.4 mg, 0.200 mmol), TMABF_4 (32.2 mg, 0.200 mmol), and triethylsilane (96 μL , 0.600 mmol) in acetonitrile- d_3 (2.7 mL) was electrolyzed for 6 F/mol with a 8 mA current. The $^1\text{H NMR}$ yield of the crude product was determined to be 35% where dibromomethane was used as an internal standard (8.0 μL). Purification of the crude product **20b** by flash chromatography (hexanes:EtOAc – 35:65) afforded **20b** (22.5 mg, 34 % yield) as a white solid. 24.8 mg of starting material was recovered. Deuterium incorporation was determined by $^1\text{H NMR}$ spectroscopy to be 79% CD_3 , 16% CD_2H , and 4% CDH_2 .

Data for **20b**: $^1\text{H NMR}$ (500 MHz, CD_3CN): δ 7.80 (d, $J = 8.8$ Hz, 2H), 7.40 (d, $J = 8.8$ Hz, 2H), 7.20 (d, $J = 7.9$ Hz, 2H), 7.16 (d, $J = 7.9$ Hz, 2H), 6.38 (s, 1H), 5.70 (br s, 2H), 2.35 (s, 3H), 2.32 (s, $-\text{CH}_3$), 2.30 (t, CH_2D), 2.29 (quintet, CHD_2); $^{13}\text{C NMR}$ (125 MHz, $\text{DMSO}-\text{d}_6$): δ 149.3, 143.4, 142.1, 142.1, 138.0, 129.3, 128.3, 127.1, 126.5, 124.6, 108.6, 20.8.

HRMS (ESI): Expected mass ($\text{M}+\text{H}^+$): 331.1303; found: 331.1301.

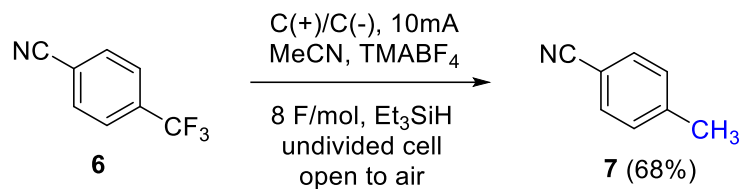
Preparation of 21



Following the General Procedure, a solution of 4-(trifluoromethyl)benzonitrile (34.2 mg, 0.200 mmol), TMABF₄ (32.2 mg, 0.200 mmol), and triethylsilane (96 μ L, 0.600 mmol) in acetonitrile- d_3 (2.7 mL) was electrolyzed for 8 F/mol with a 10 mA current. The ¹H NMR yield of the crude product was determined to be 70% where dibromomethane was used as an internal standard (8.0 μ L). Purification of the crude product **7** by flash chromatography (0 \rightarrow 5 % \rightarrow 10% EtOAc in hexanes and 2.5% triethylamine) afforded **7** (14.2 mg, 59 % yield) as a light yellow liquid. Deuterium incorporation was determined by ¹H NMR spectroscopy to be 50% CD₃, 31% CD₂H, and 16% CDH₂.

Data for **21**: ¹H NMR (500 MHz, CDCl₃): δ 7.54 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 2.42 (s, -CH₃), 2.40 (t, -CH₂D), 2.39 (quintet, -CHD₂); ¹³C NMR (125 MHz, (CDCl₃): δ 143.7, 132.2, 129.9, 119.3, 109.5, 21.4 (m).

Scale-up e-HDF reaction



A 20 mL ElectraSyn vial was charged with 4-(trifluoromethyl) benzonitrile (1.00 g, 5.85 mmol, 1.0 equiv.), tetramethylammonium tetrafluoroborate (0.942 g, 5.85 mmol, 1.0 equiv.), and triethylsilane (2.8 mL, 17.6 mmol, 3.0 equiv.) in dry acetonitrile (16 mL, 0.075 M). The vial was then capped with an ElectraSyn vial cap equipped with two graphite electrodes and the reaction mixture was stirred until the solution became homogenous. The reaction mixture was then electrolyzed under a constant current of 10 mA for 8 F/mol. Following electrolysis, the ElectraSyn vial cap was removed and the graphite electrodes were rinsed with dichloromethane (ca. 5 mL). The reaction mixture was then transferred to a separatory funnel, dilute with 50 mL of dichloromethane, and washed with deionized water (twice, ca. 20 mL per wash). The aqueous layers were combined and extracted twice with dichloromethane. The organic layers were then combined, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was purified by flash chromatography (0 → 10% EtOAc in hexanes) to afford a light yellow liquid (465.5 mg, 68%).

Graphical guide:

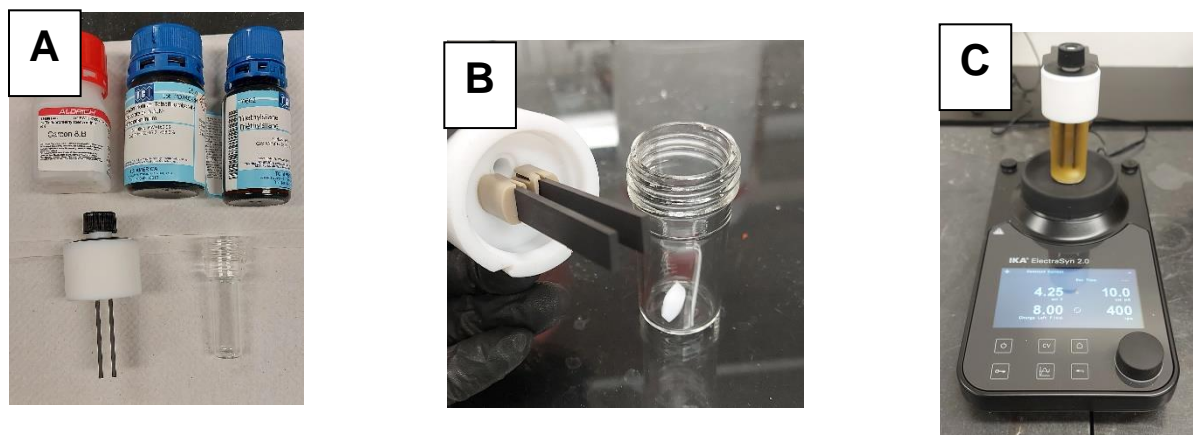
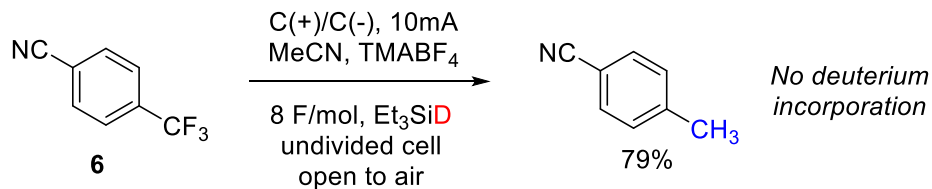


Figure S1: A) Reagents and small-scale setup; B) 20 mL reaction vial for 1 gram scale; C) Large scale experimental setup.

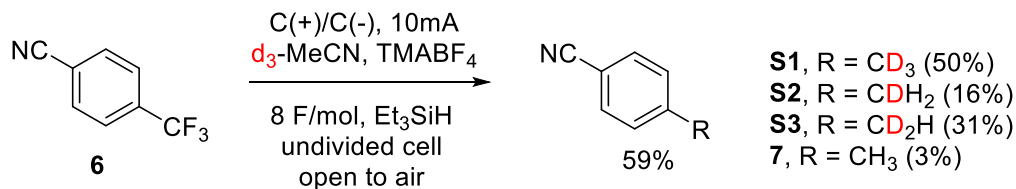
Mechanistic Investigations

Reaction with triethyl(silane-d)



A 5 mL ElectraSyn vial was charged with 4-(trifluoromethyl) benzonitrile (34.2 mg, 0.20 mmol, 1.0 equiv.), tetramethylammonium tetrafluoroborate (32.2 mg, 0.20 mmol, 1.0 equiv.), and triethyl(silane-d) (96 μ L, 0.60 mmol, 3.0 equiv.) in dry acetonitrile (2.7 mL, 0.075 M). The vial was then capped with an ElectraSyn vial cap equipped with two graphite electrodes and the reaction mixture was stirred until the solution became homogenous. The reaction mixture was then electrolyzed under a constant current of 10 mA for 8 F/mol. Following electrolysis, the ElectraSyn vial cap was removed and the graphite electrodes were rinsed with dichloromethane (ca. 2 mL). The reaction mixture was then transferred to a separatory funnel, dilute with 10 mL of dichloromethane, and washed with deionized water (twice, ca. 3 mL per wash). The aqueous layers were combined and extracted twice with dichloromethane. The organic layers were then combined, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was dissolved in CDCl₃ and dibromomethane (8.0 μ L) was added as an internal standard. The yield was determined by ¹H NMR spectroscopy to be 79%. No deuterium was incorporated into the product.

Reaction with d₃-MeCN



A 5 mL ElectraSyn vial was charged with 4-(trifluoromethyl) benzonitrile (34.2 mg, 0.20 mmol, 1.0 equiv.), tetramethylammonium tetrafluoroborate (32.2 mg, 0.20 mmol, 1.0 equiv.), and triethylsilane (96 μ L, 0.60 mmol, 3.0 equiv.) in acetonitrile-d₃ (2.7 mL, 0.075 M). The vial was

then capped with an ElectraSyn vial cap equipped with two graphite electrodes and the reaction mixture was stirred until the solution became homogenous. The reaction mixture was then electrolyzed under a constant current of 10 mA for 8 F/mol. Following electrolysis, the ElectraSyn vial cap was removed and the graphite electrodes were rinsed with dichloromethane (ca. 2 mL). The reaction mixture was then transferred to a separatory funnel, dilute with 10 mL of dichloromethane, and washed with deionized water (twice, ca. 3 mL per wash). The aqueous layers were combined and extracted twice with dichloromethane. The organic layers were then combined, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was dissolved in CDCl₃ and dibromomethane (8.0 μL) was added as an internal standard. The yield was determined by ¹H NMR spectroscopy to 59%. Deuterium incorporation was determined by ¹H NMR spectroscopy to be 50% CD₃, 31% CD₂H, and 16% CDH₂ (see Figure S2 for ¹H NMR spectrum of crude product in CDCl₃)

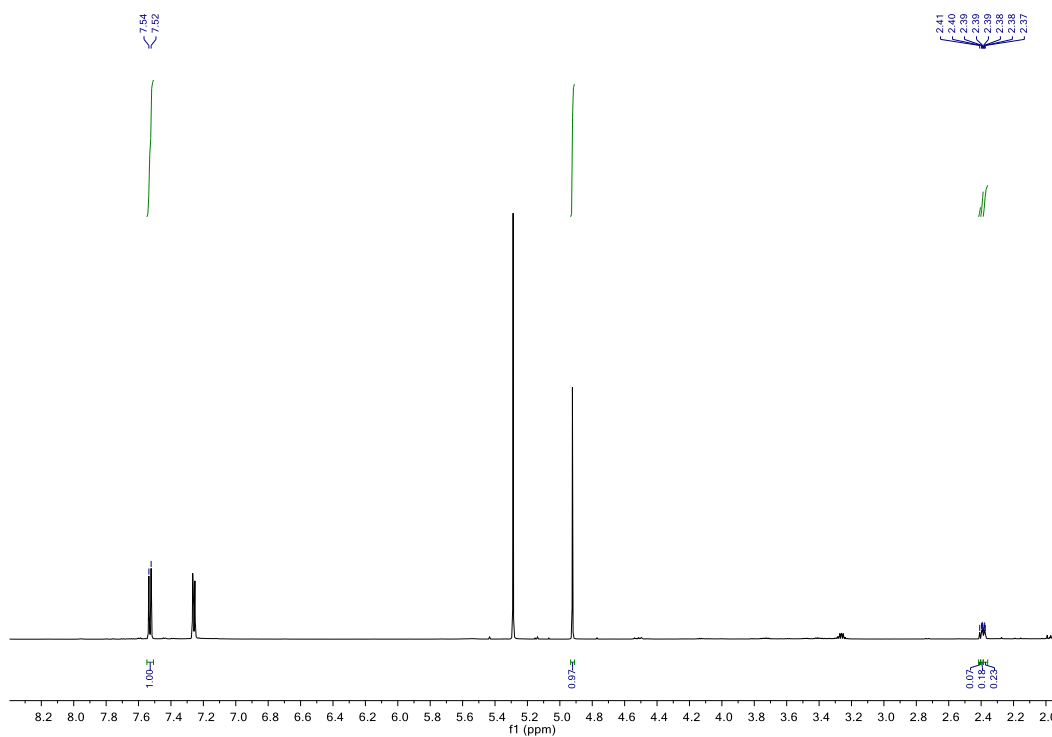


Figure S2: crude ¹H NMR spectrum of **21** in CDCl₃ showing deuterium incorporation.

On/Off Electrolysis

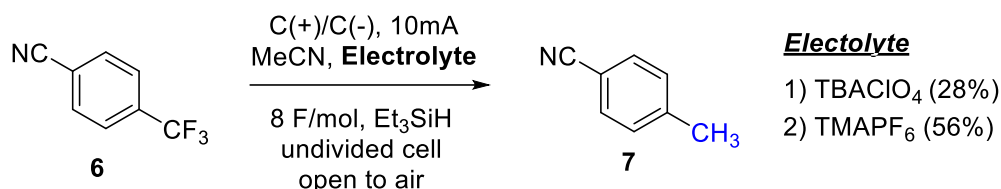
A 5 mL ElectraSyn vial was charged with tetramethylammonium tetrafluoroborate (32.2 mg, 0.20 mmol, 1.0 equiv.) and triethylsilane (96 μ L, 0.60 mmol, 3.0 equiv.) in dry acetonitrile (2.7 mL, 0.075 M). The vial was then capped with an ElectraSyn vial cap equipped with two graphite electrodes and the reaction mixture was stirred until the solution became homogenous. The reaction mixture was then electrolyzed under a constant current of 10 mA for 1.5 F/mol. Following electrolysis, 4-(trifluoromethyl) benzonitrile (0.20 mmol, 1.0 equiv.) was then added to the reaction mixture and the resulting reaction mixture was allowed to stir for 16 hours at room temperature (without electrolysis). The reaction mixture was then transferred to a separatory funnel, dilute with 10 mL of dichloromethane, and washed with deionized water (twice, ca. 3mL per wash). The aqueous layers were combined and extracted twice with dichloromethane. The organic layers were then combined, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was dissolved in CDCl₃ and dibromomethane (8.0 μ L) was added as an internal standard. The yield was determined by ¹H NMR spectroscopy to be 2%. This experiment was performed three times with the aforementioned yield being the average of the three runs.

Control experiment (no electrolysis)

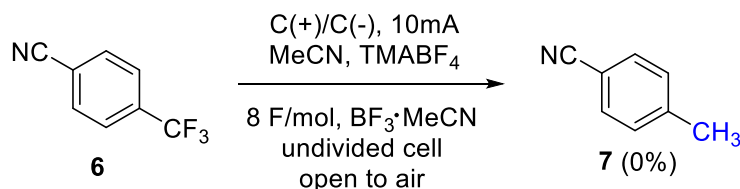
A 5 mL ElectraSyn vial was charged with 4-(trifluoromethyl)benzonitrile (34.2 mg, 0.20 mmol, 1.0 equiv.), tetramethylammonium tetrafluoroborate (32.2 mg, 0.20 mmol, 1.0 equiv.), and triethylsilane (96 μ L, 0.60 mmol, 3.0 equiv.) in dry acetonitrile (2.7 mL, 0.075 M). The vial was then capped with an ElectraSyn vial cap equipped with two graphite electrodes and the reaction mixture was stirred until the solution became homogenous. The reaction mixture was left to stir for 16 hrs at room temperature (without electrolysis). The ElectraSyn vial cap was removed and the graphite electrodes were rinsed with dichloromethane (ca. 2 mL). The reaction mixture was then transferred to a separatory funnel, dilute with 10 mL of dichloromethane, and washed with deionized water (twice, ca. 3 mL per wash). The aqueous layers were combined and extracted twice with dichloromethane. The organic layers were then combined, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was dissolved in CDCl₃ and

dibromomethane (8.0 μL) was added as an internal standard. The yield was determined by ^1H NMR spectroscopy to 0%. The experiment was performed twice.

Evaluating the role of BF_4^-



We had initially suspected that the TMABF₄ was playing a non-innocent role in the fluoride abstraction process where the silyl cation first abstracted a fluoride from BF₄⁻ to generate BF₃ in situ. We believed that BF₃ was the Lewis acid responsible for the mediating fluoride abstraction of the trifluoromethyl arenes. However, upon replacing TMABF₄ with other electrolytes (TBAClO₄ and TMAPF₆ – see above) and obtaining reasonable yields and high selectivity for exhaustive defluorination, it became evident that TMABF₄ was not involved in fluoride abstraction.



Additionally, we ran our eTHDF reaction using BF₃ (5 equiv. or 3 equiv.) in place of triethylsilane and did not observe any product in the ^1H NMR spectrum of the crude reaction. This further confirmed that BF₄⁻/BF₃ was not involved in the fluoride abstraction process.

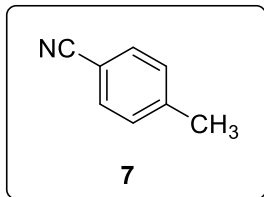
Protonation Experiment with D₂O

A 5 mL ElectraSyn vial was charged with 4-(trifluoromethyl) benzonitrile (34.2 mg, 0.20 mmol, 1.0 equiv.), tetramethylammonium tetrafluoroborate (32.2 mg, 0.20 mmol, 1.0 equiv.), and triethylsilane (96 μL , 0.60 mmol, 3.0 equiv.) in dry acetonitrile (2.7 mL, 0.075 M). 0.05 mL of D₂O was then added to the reaction mixture. The vial was then capped with an ElectraSyn vial cap equipped with two graphite electrodes and the reaction mixture was stirred until the solution

became homogenous. The reaction mixture was then electrolyzed under a constant current of 10 mA for 8 F/mol. Following electrolysis, the ElectraSyn vial cap was removed and the graphite electrodes were rinsed with dichloromethane (ca. 2 mL). The reaction mixture was then transferred to a separatory funnel, dilute with 10 mL of dichloromethane, and washed with deionized water (twice, ca. 3 mL per wash). The aqueous layers were combined and extracted twice with dichloromethane. The organic layers were then combined, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was dissolved in CDCl₃ and dibromomethane (8.0 μL) was added as an internal standard. The yield was determined by ¹H NMR spectroscopy to be 46%. CD₃ incorporation was found to be 29% by ¹H NMR.

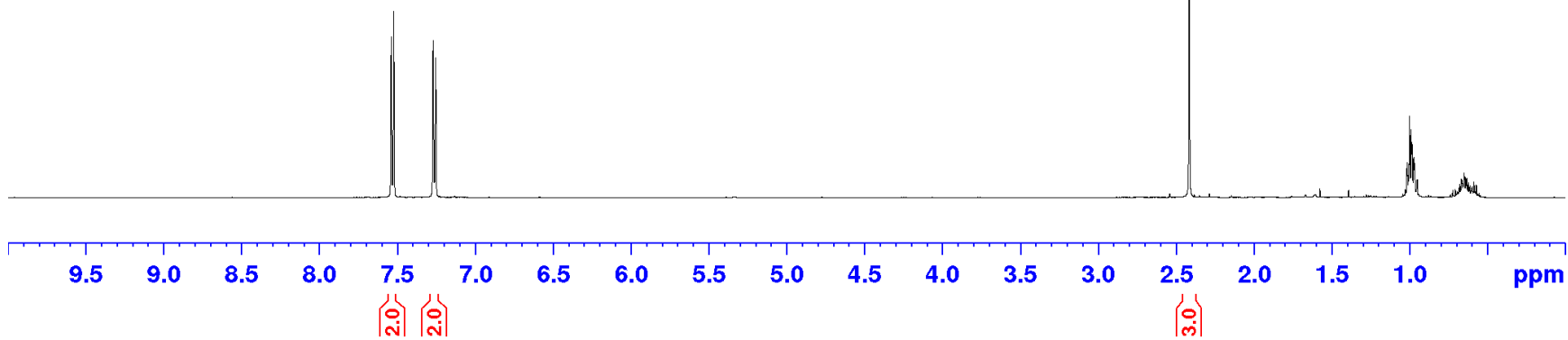
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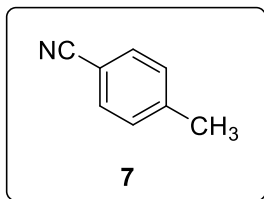
- 1) N. Mori and H. Togo, *Synlett* 2004, **5**, 880-882.
- 2) T. J. Deming and B. M. Novak, *J. Am. Chem. Soc.* 1993, **115**, 9101 -9111.
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- 8) Y. Wang and Q. Kang, *Org. Lett.* 2014, **16**, 4190-4193.
- 9) C. Song, S. Claessen, and E. V. Van der Eycken, *J. Org. Chem.* 2020, **85**, 8045-8054.
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- 11) W. Yin, C. Wang, and Y. Huang, *Org. Lett.* 2013, **15**, 1850-1853.



— 7.53
— 7.27

— 2.42





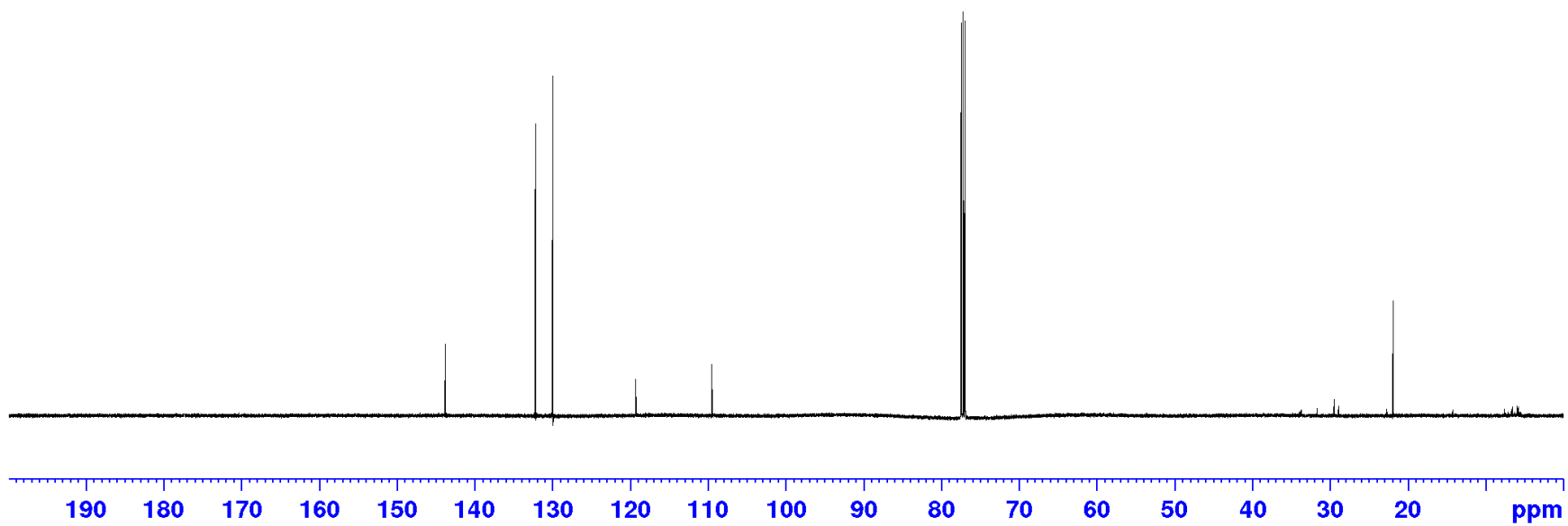
— 143.8

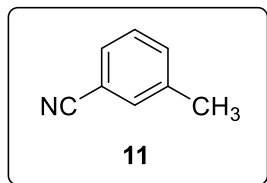
— 132.2
— 130.0

— 119.4

— 109.6

— 21.9

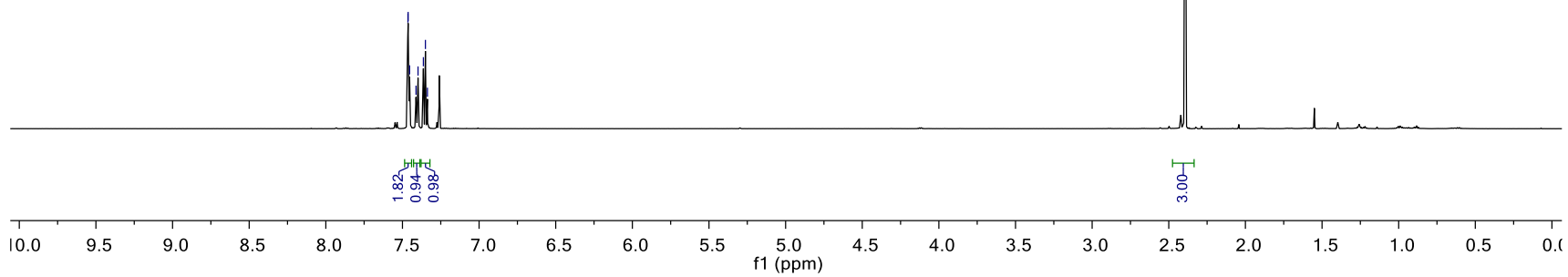


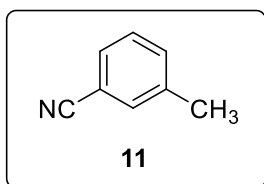


7.46
7.46
7.45
7.41
7.40
7.36
7.35
7.34



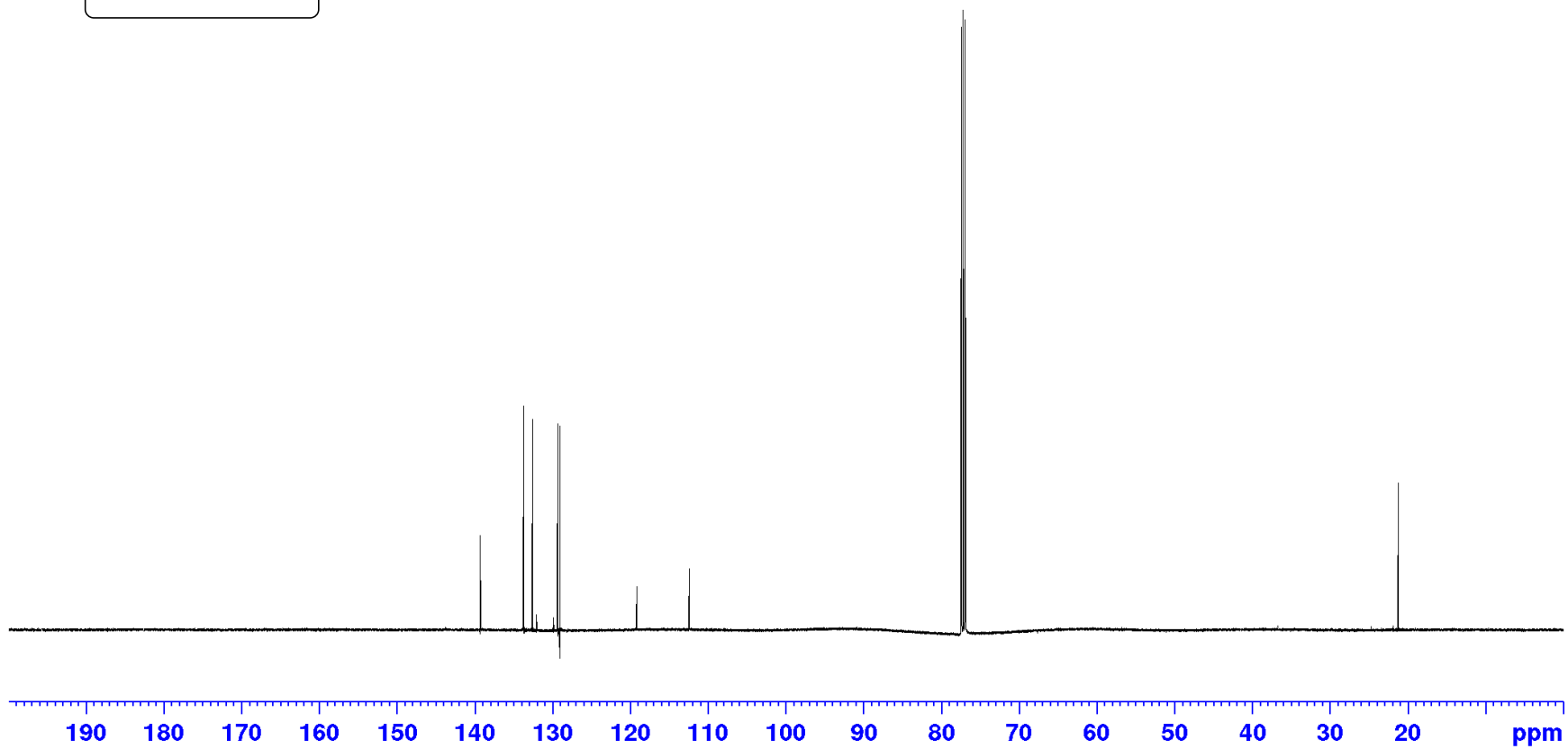
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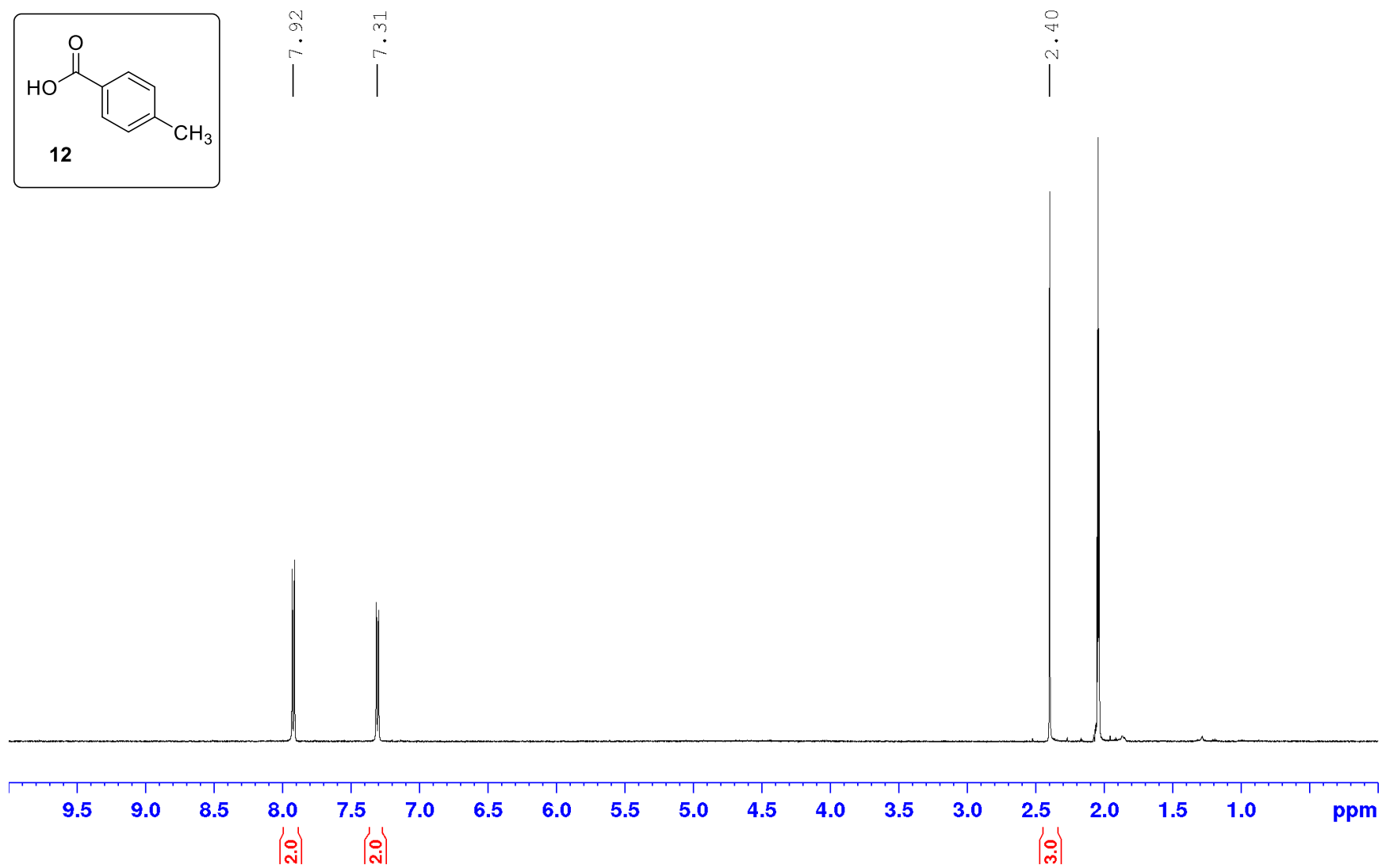
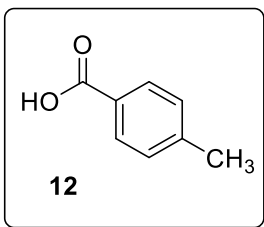


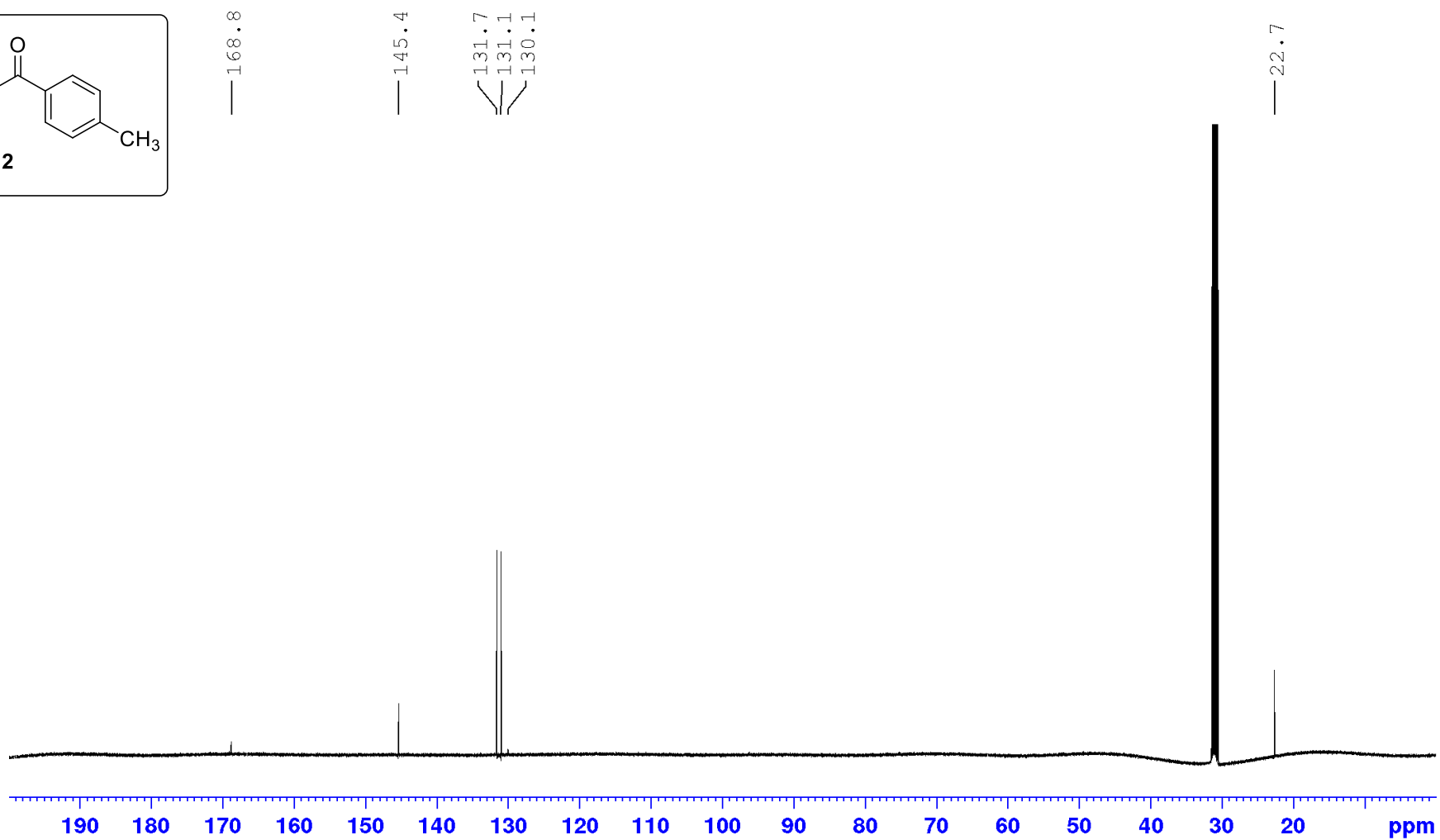
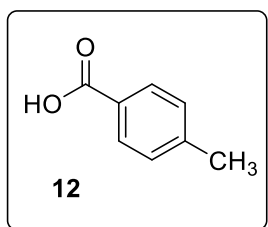


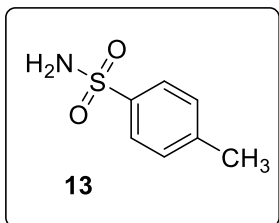
— 139.4
— 133.8
— 132.7
— 129.4
— 129.1
— 119.2
— 112.4

— 21.3









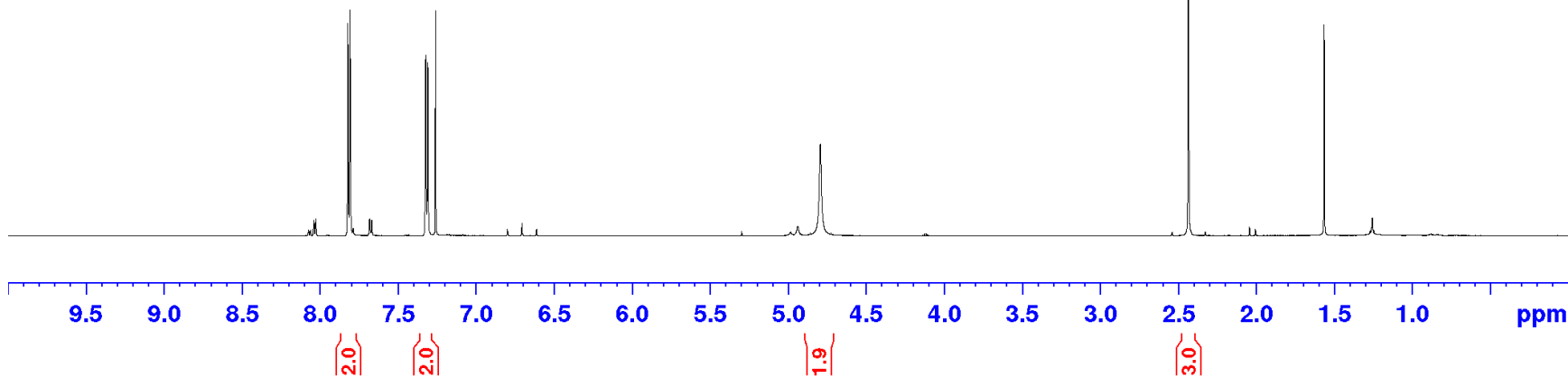
— 7.82

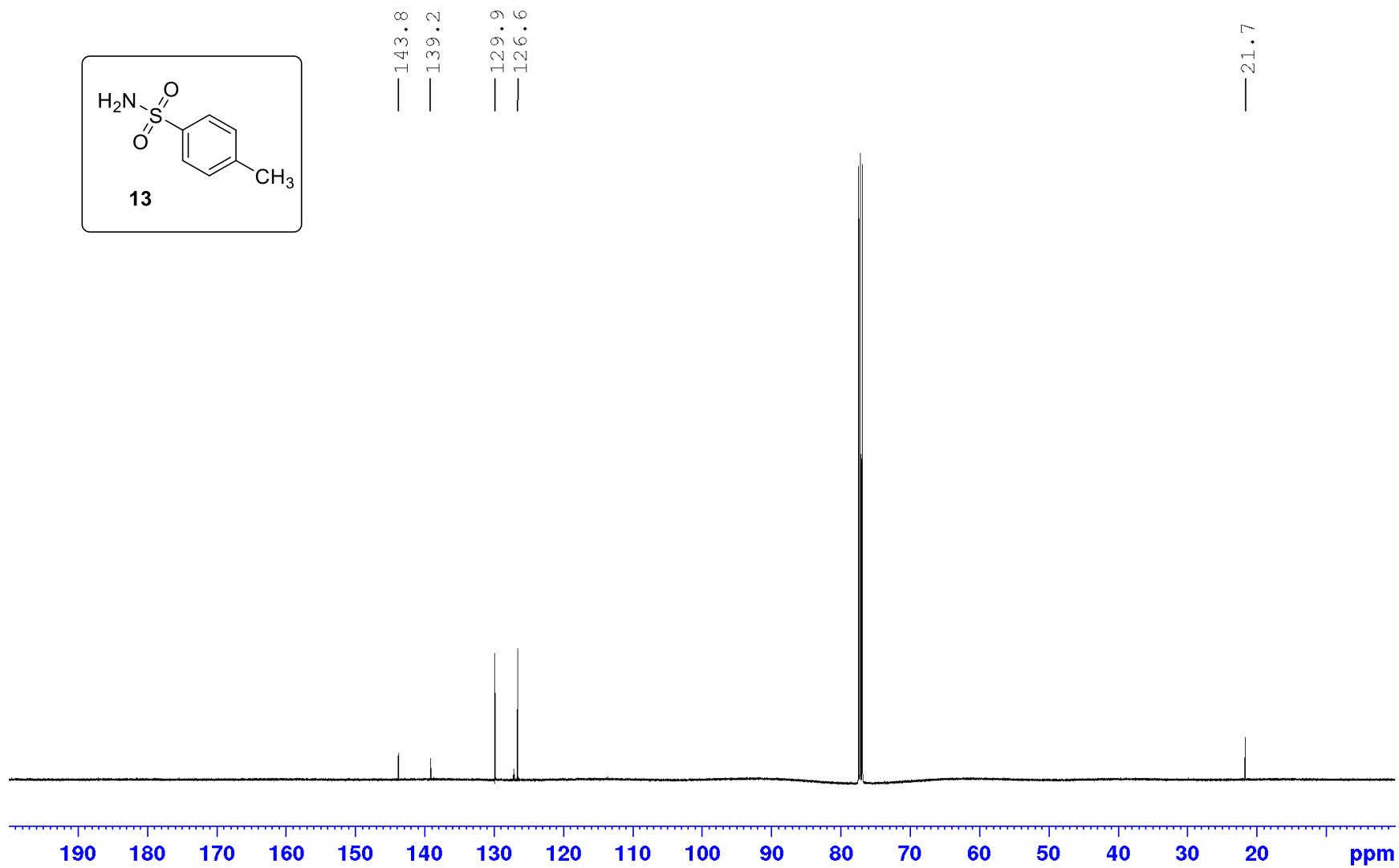
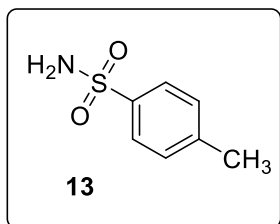
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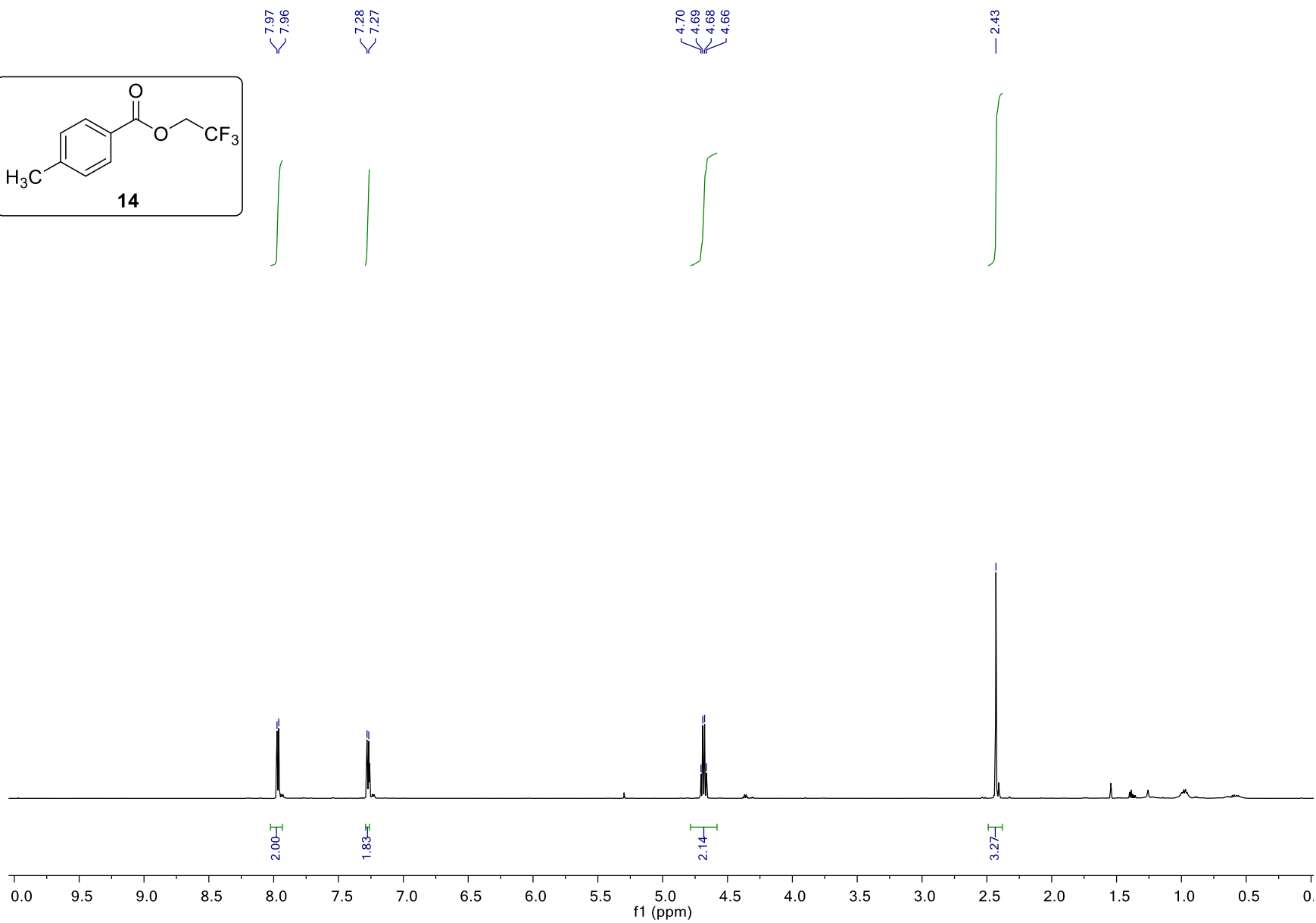
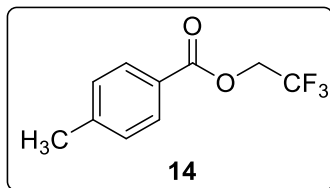
— 4.79

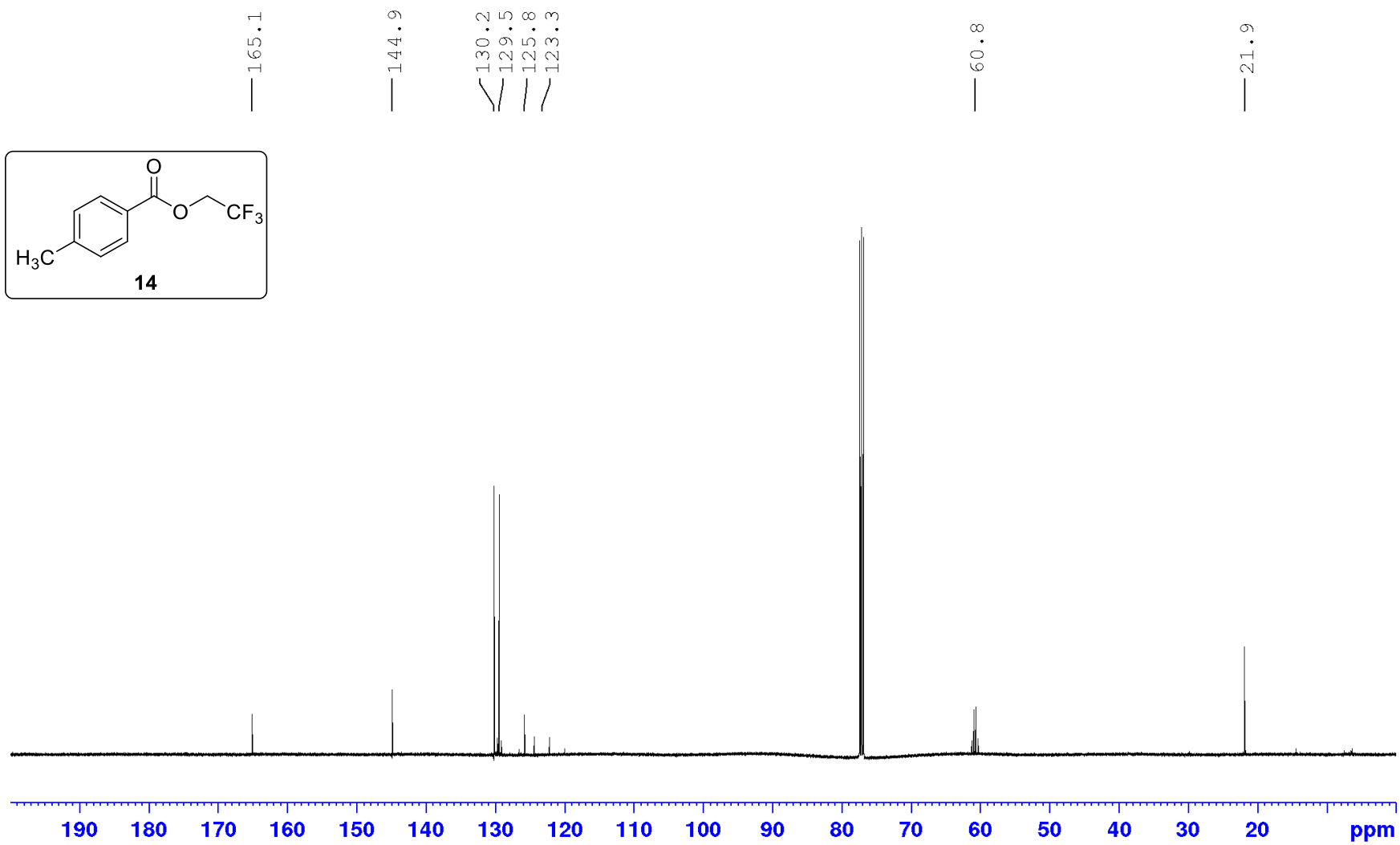
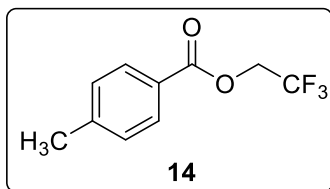
— 2.43

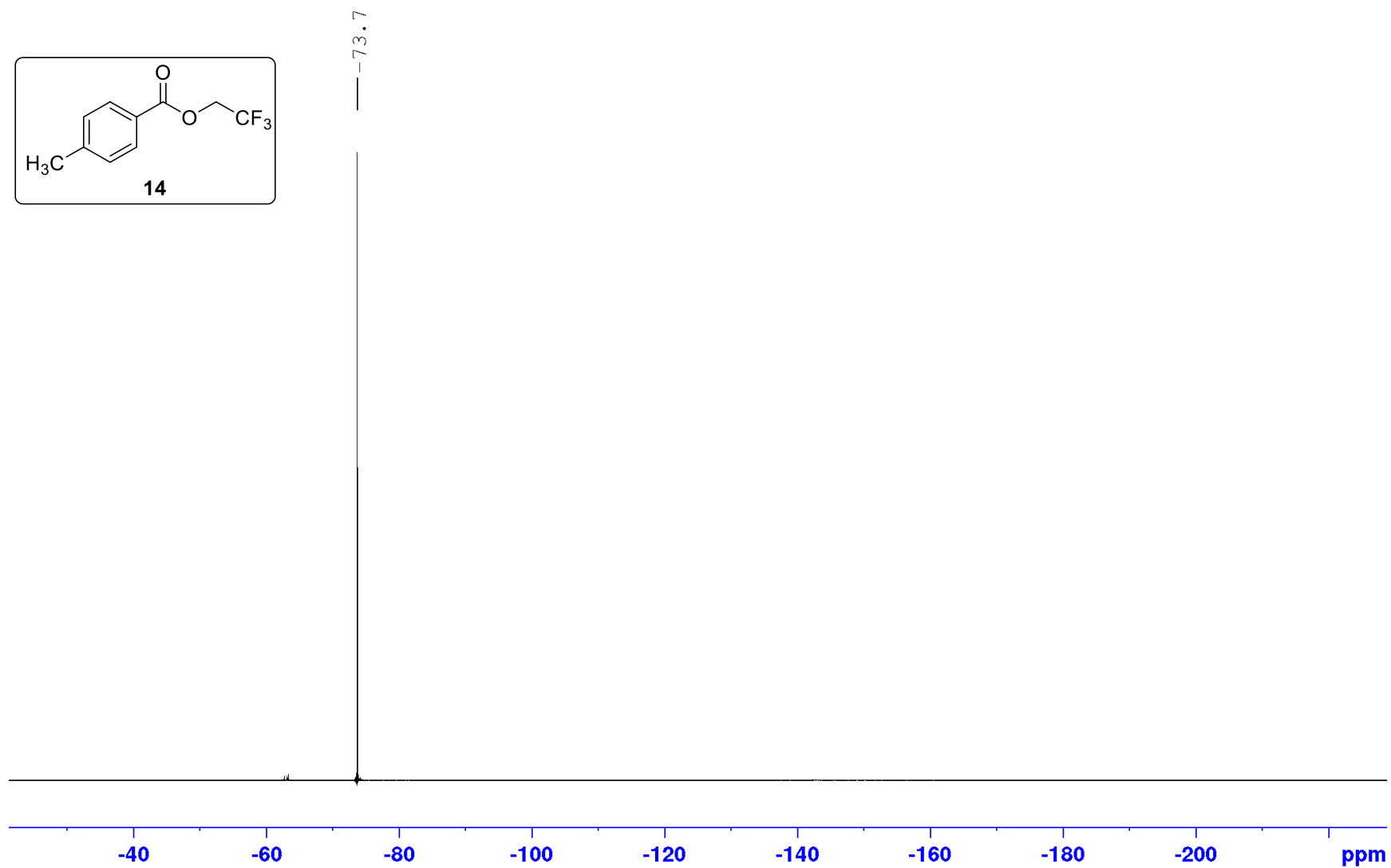
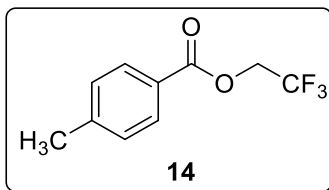
Inseparable difluorinated product
present (~8%)

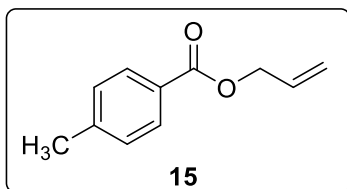












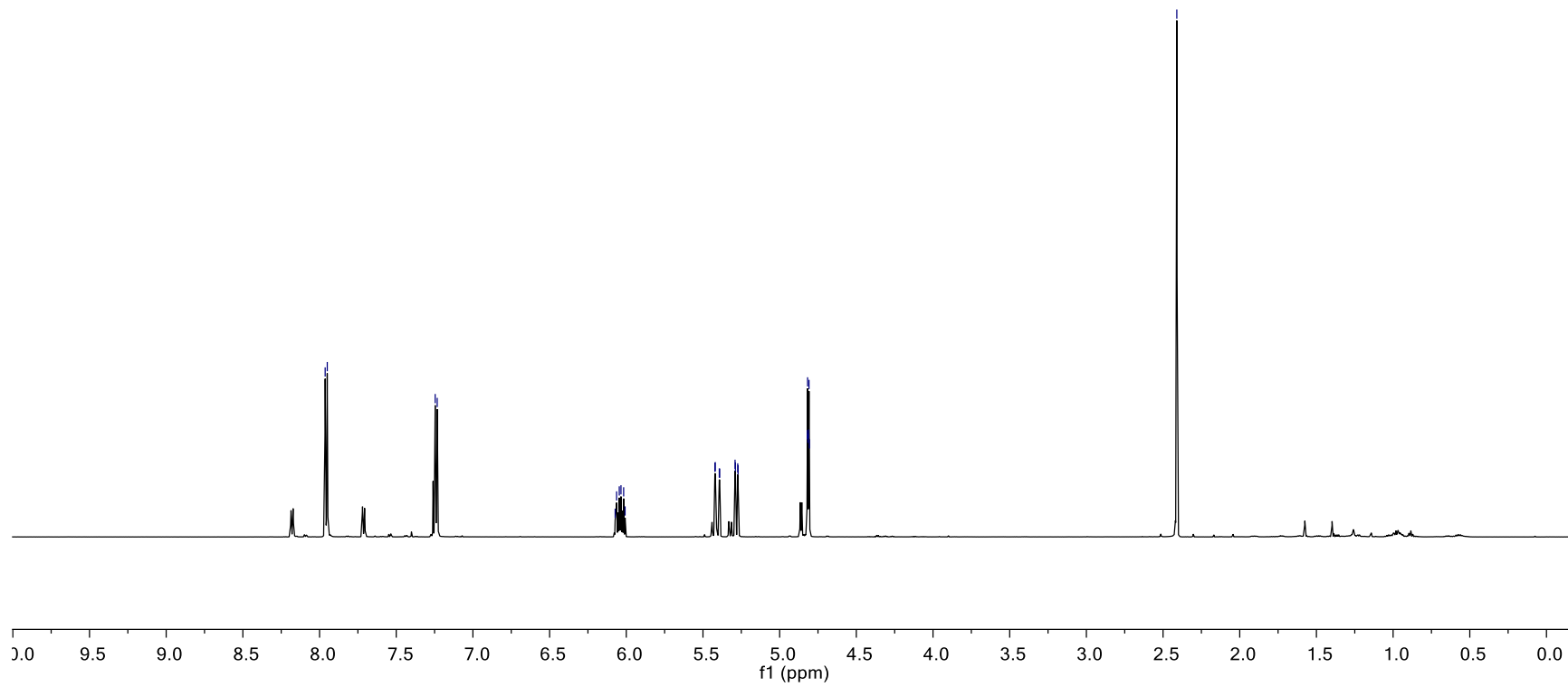
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7.95

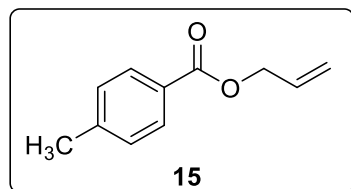
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7.23

6.07
6.06
6.05
6.03
6.02
6.01
5.42
5.42
5.39
5.39
5.29
5.29
5.27
5.27
4.82
4.82
4.81
4.81
4.81

2.41

3.3:1 mixture of **15** to starting material





— 166.5

— 143.8

132.5

129.8

129.2

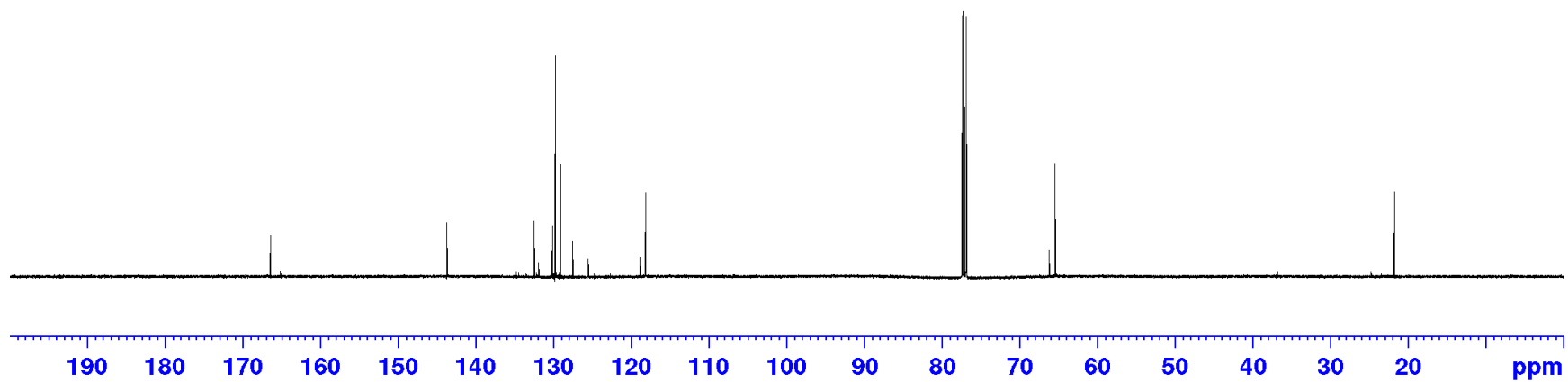
127.6

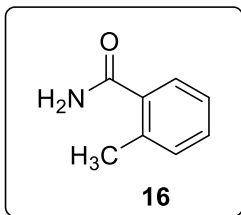
— 118.2

— 65.5

— 21.8

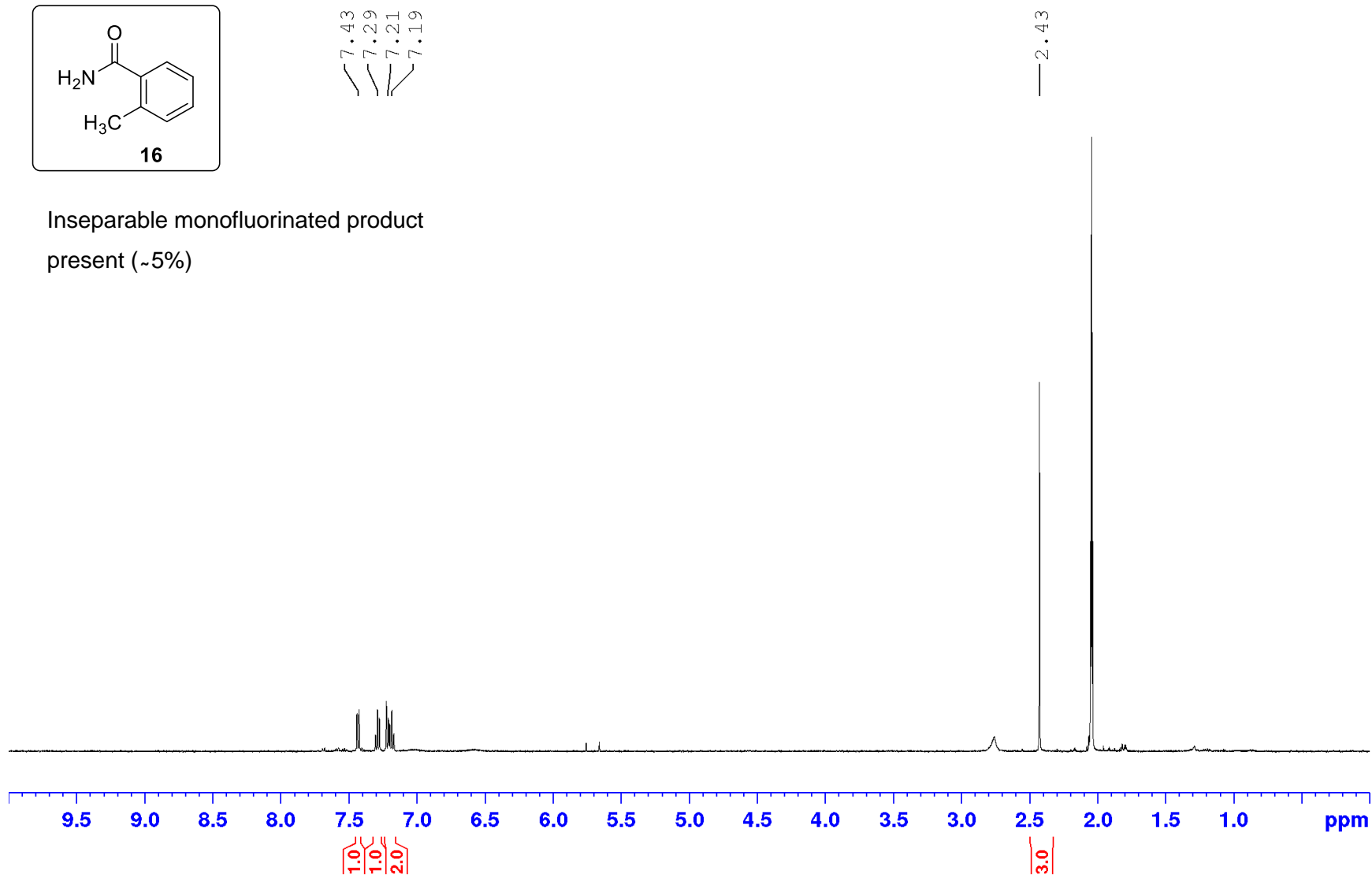
3.3:1 mixture of **15** to starting material

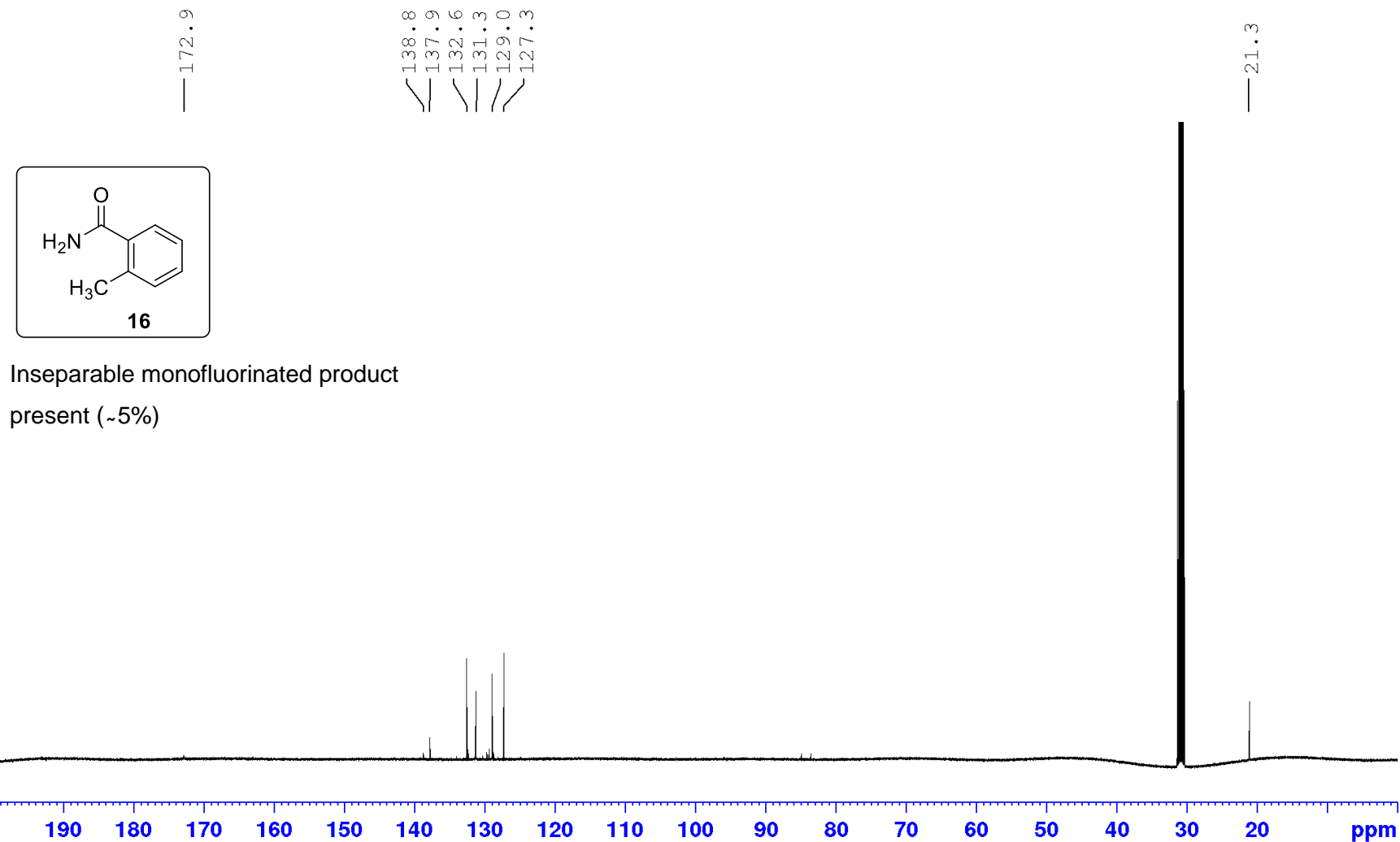
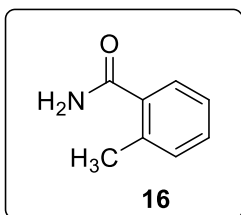




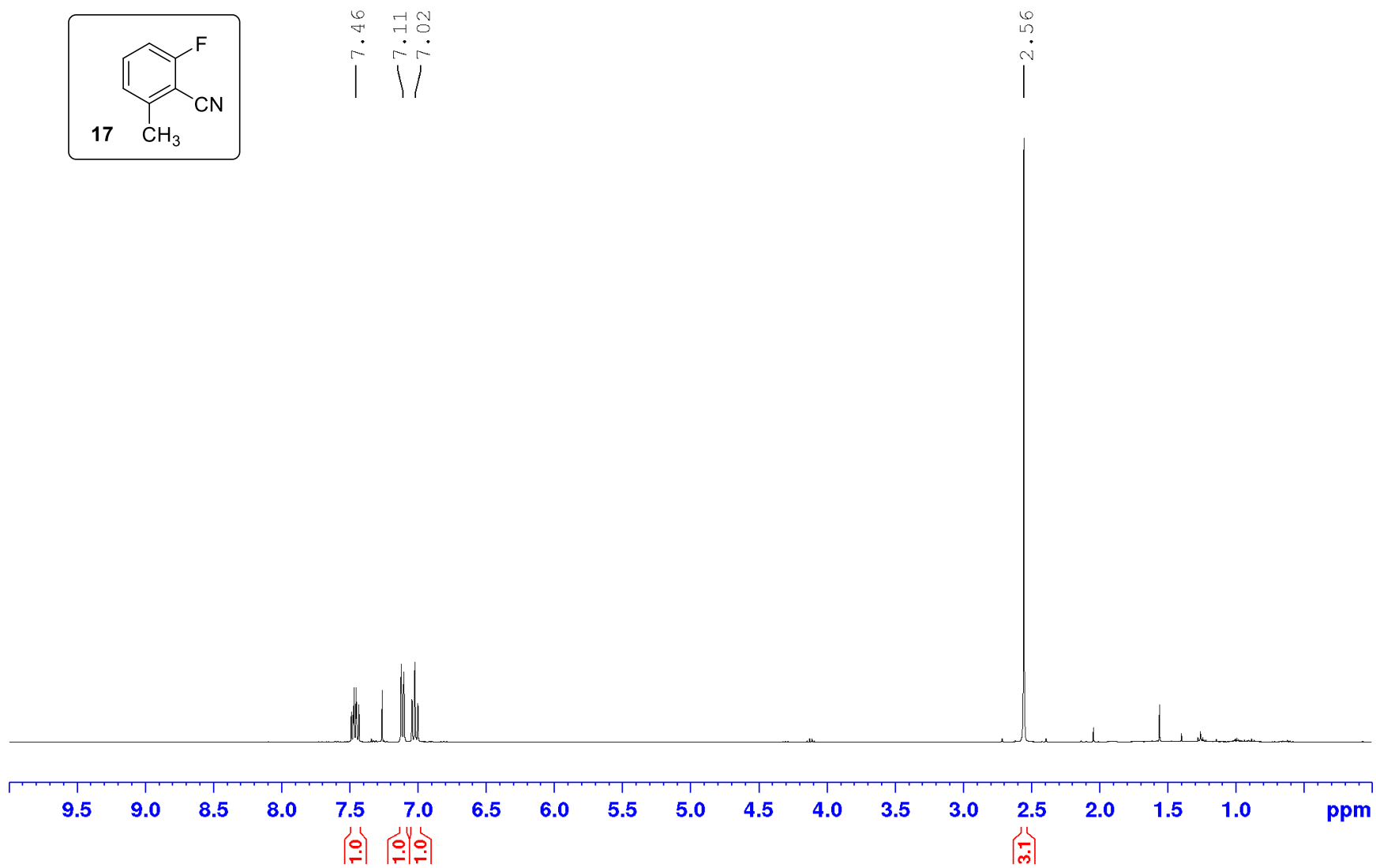
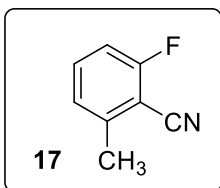
7.43
7.29
7.21
7.19

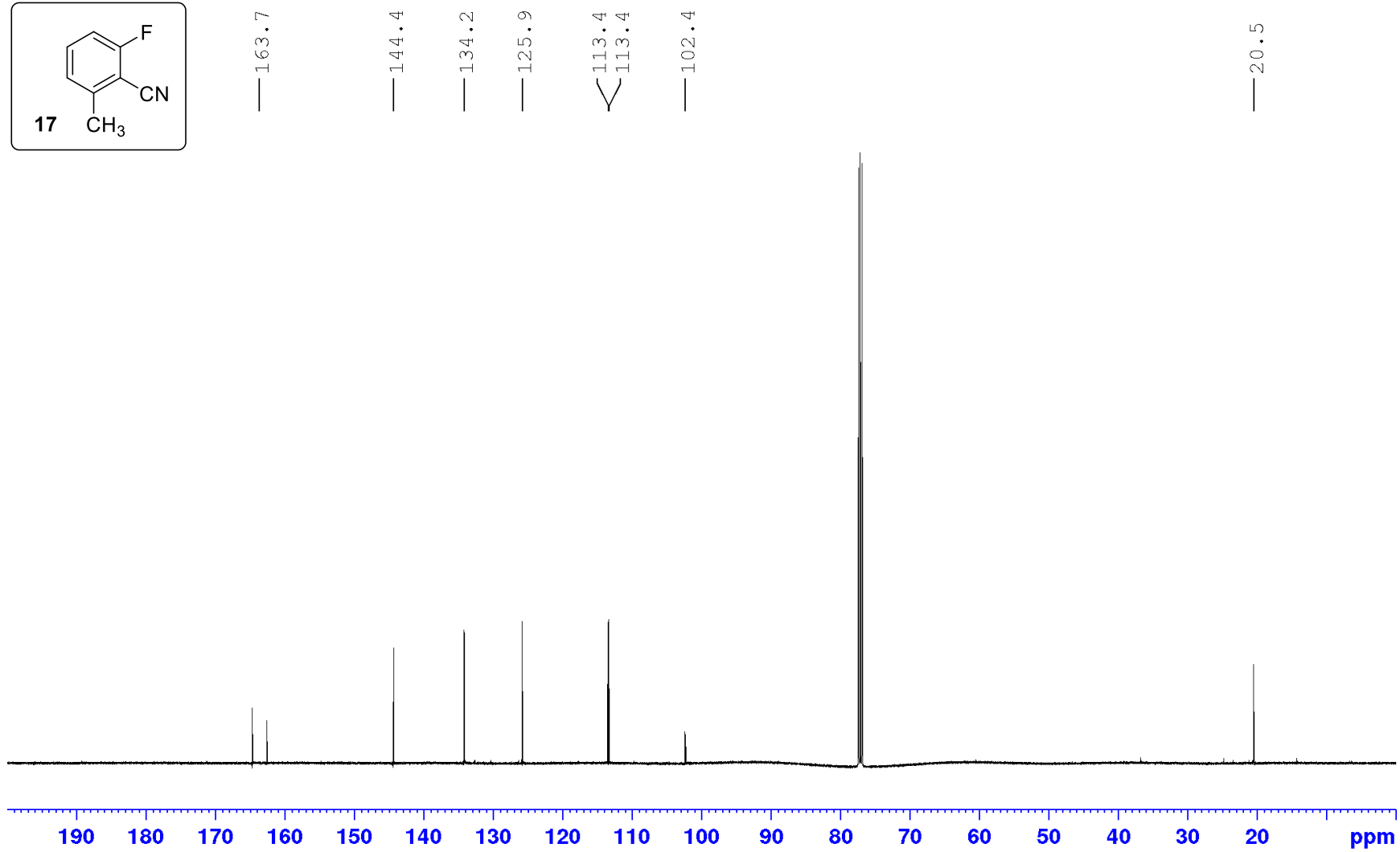
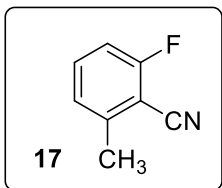
Inseparable monofluorinated product
present (~5%)

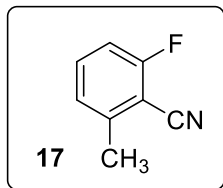




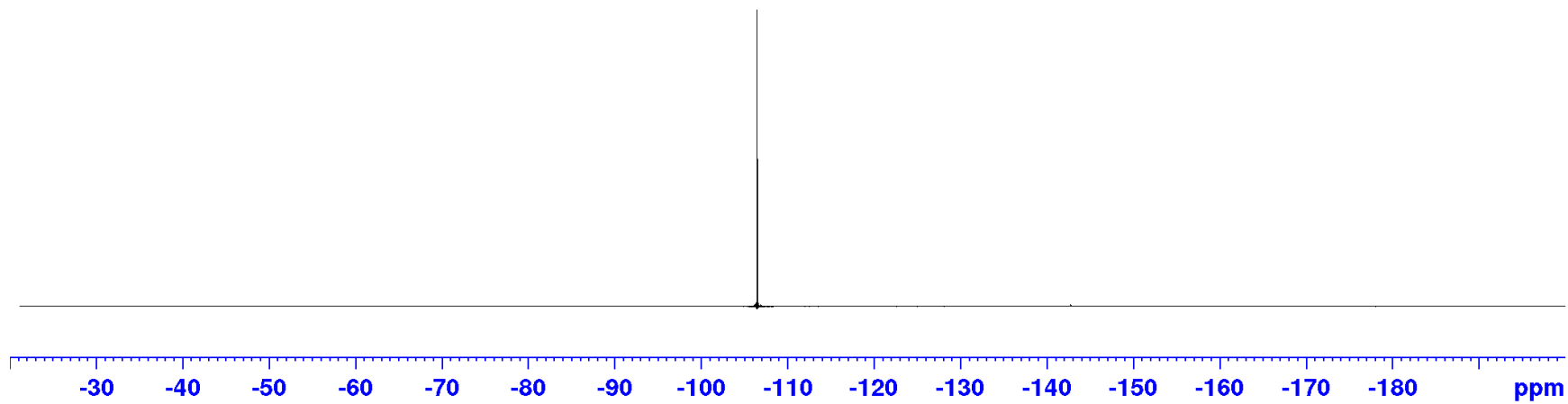
Inseparable monofluorinated product
present (~5%)

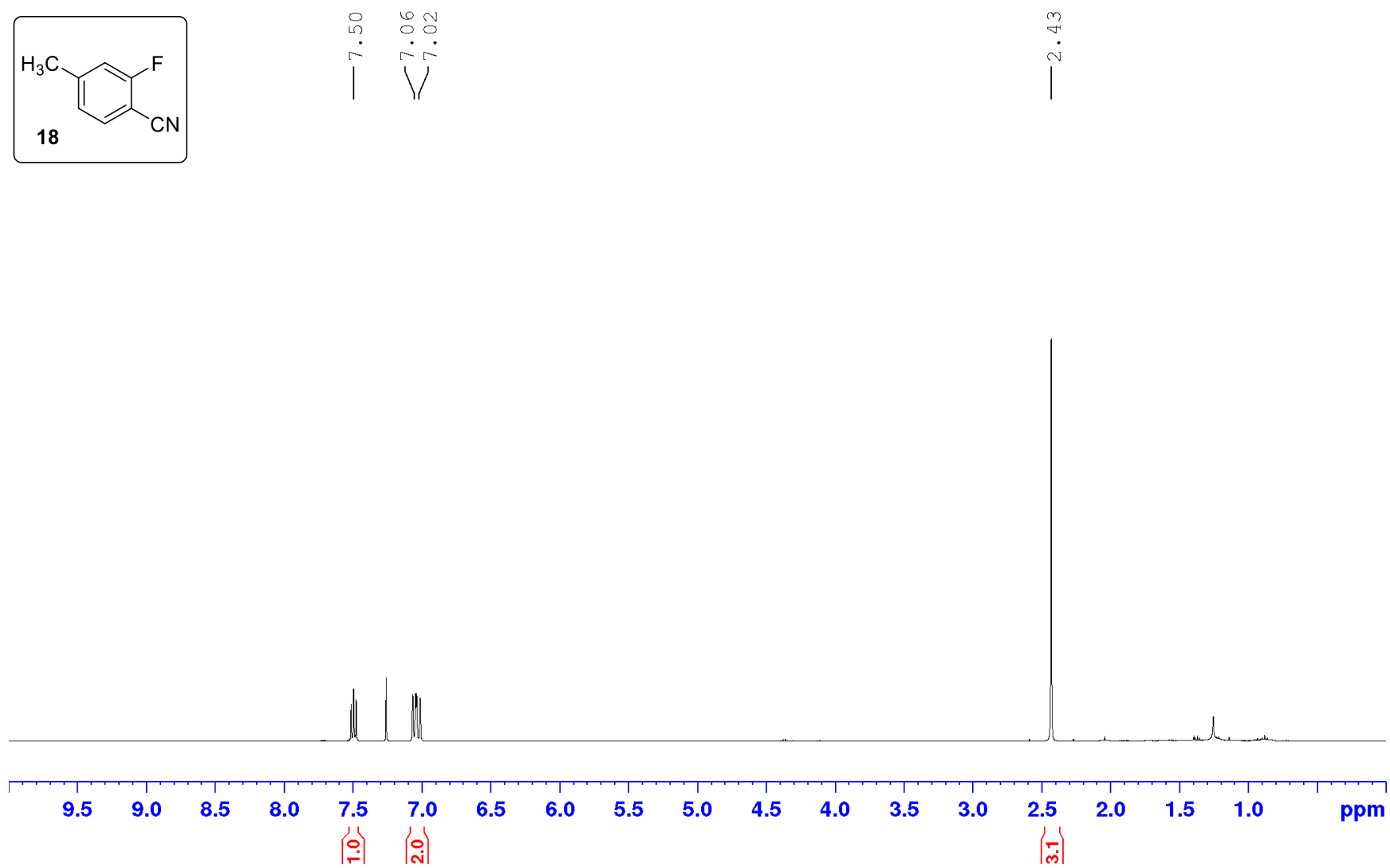
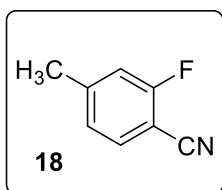


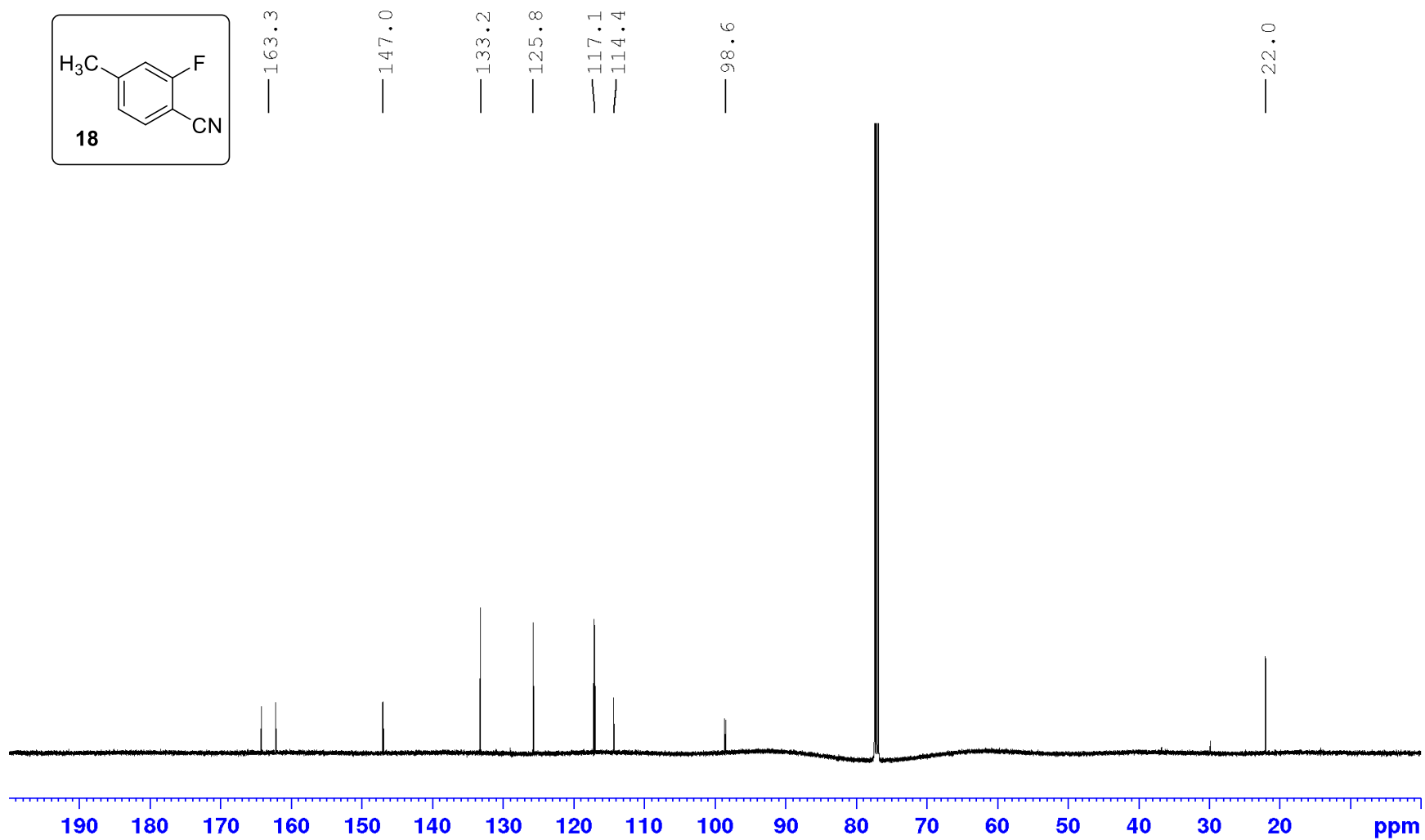
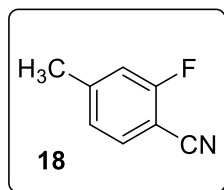


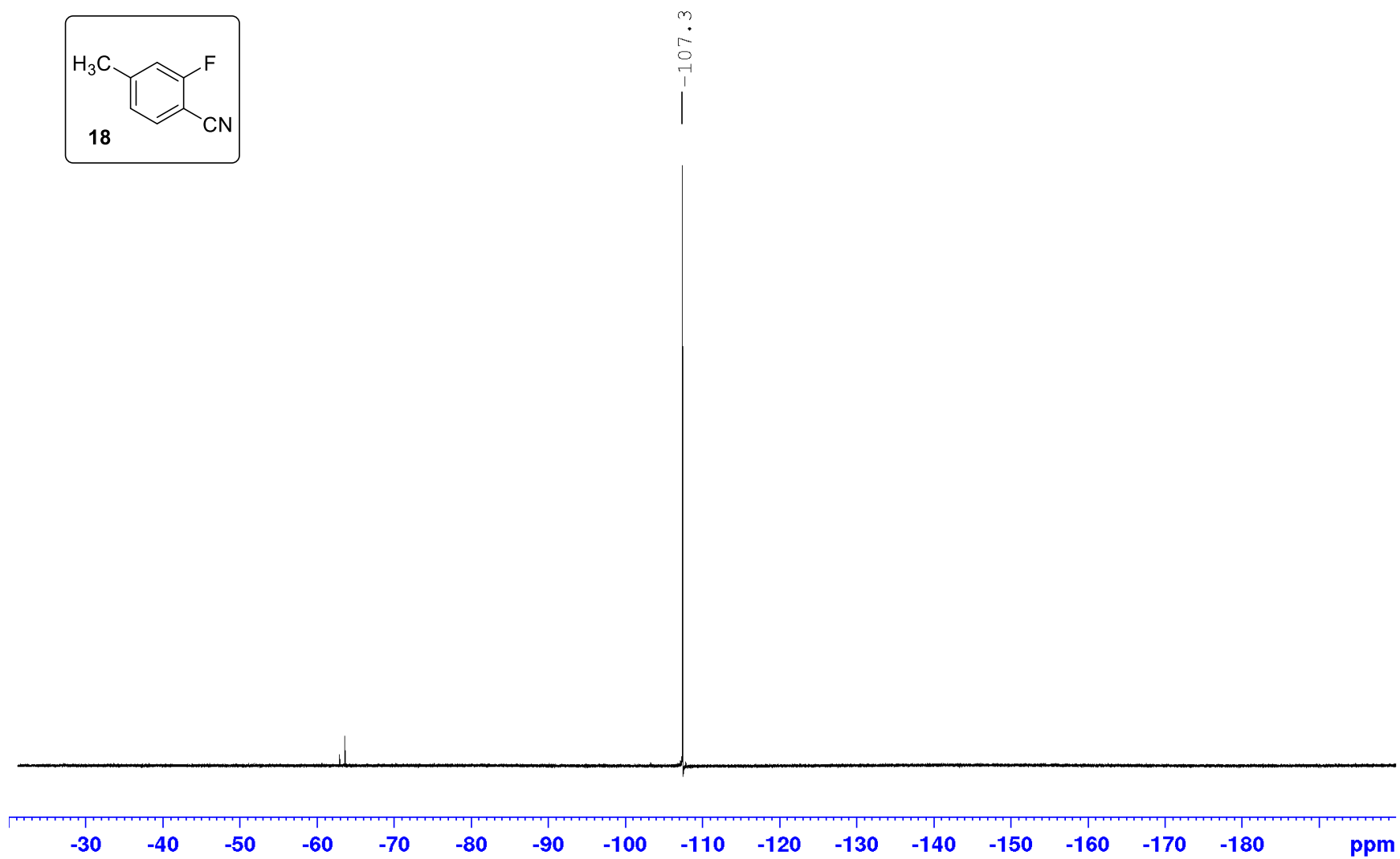
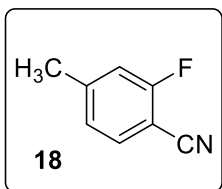


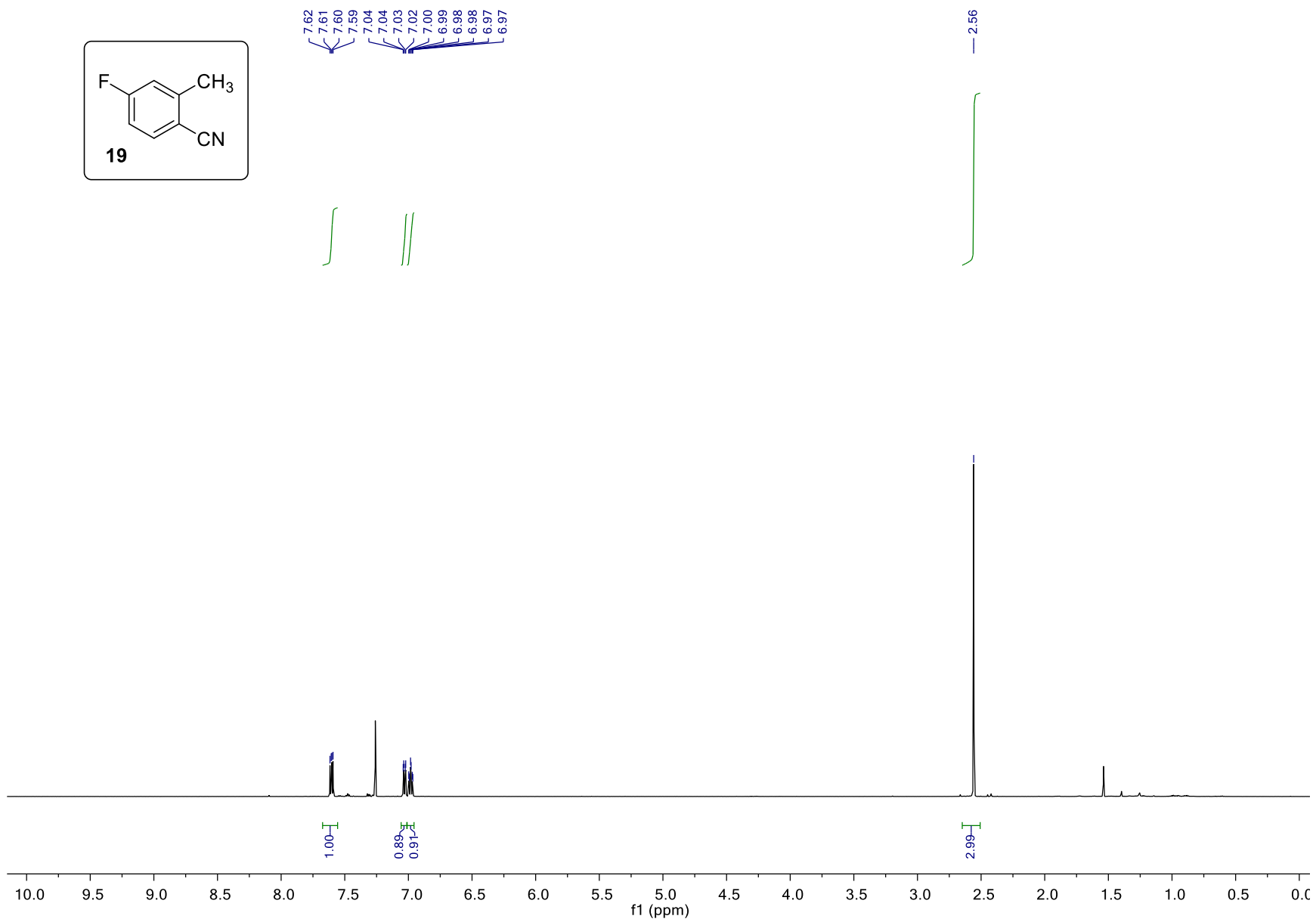
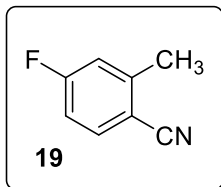
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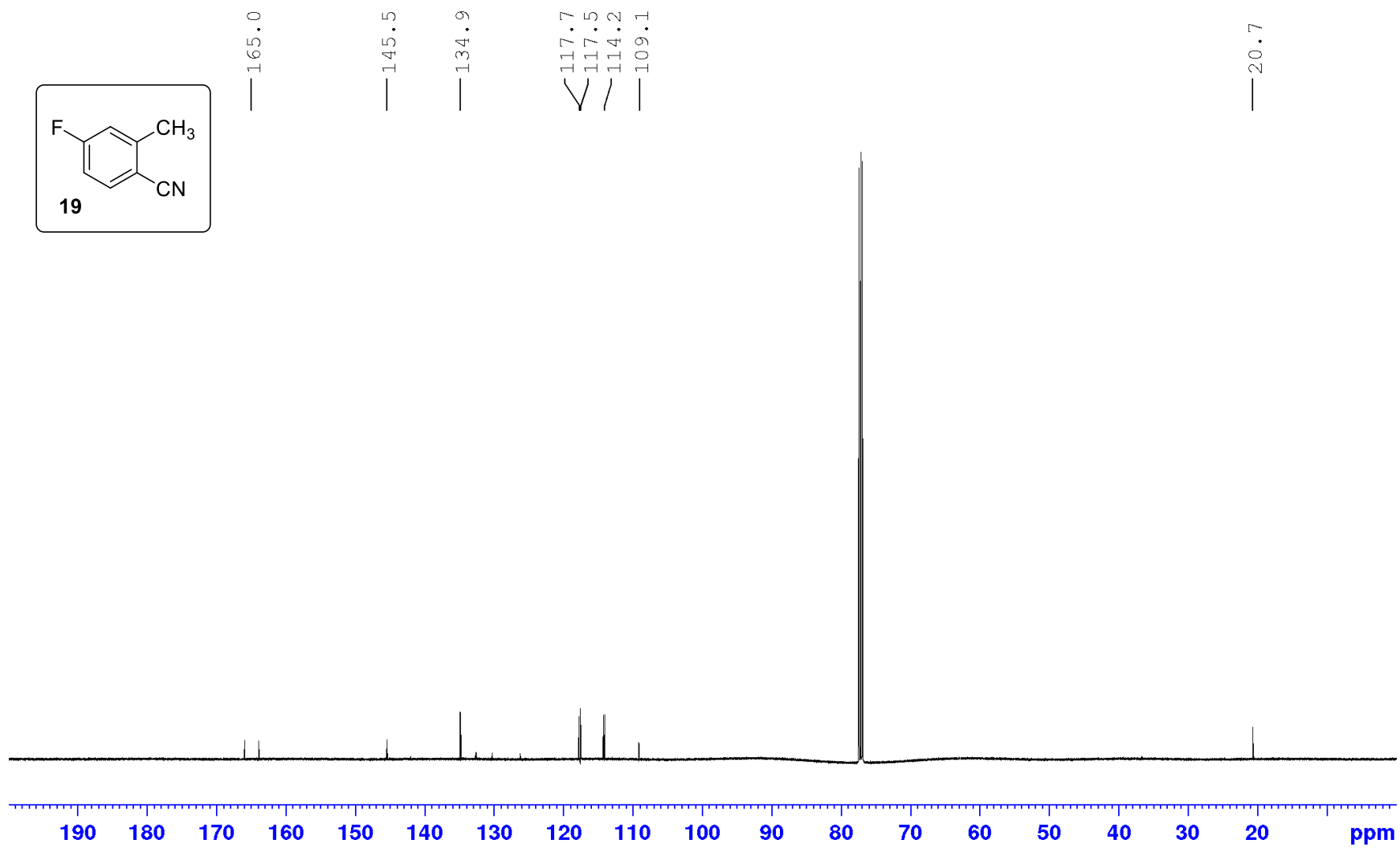
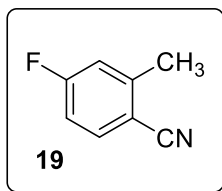


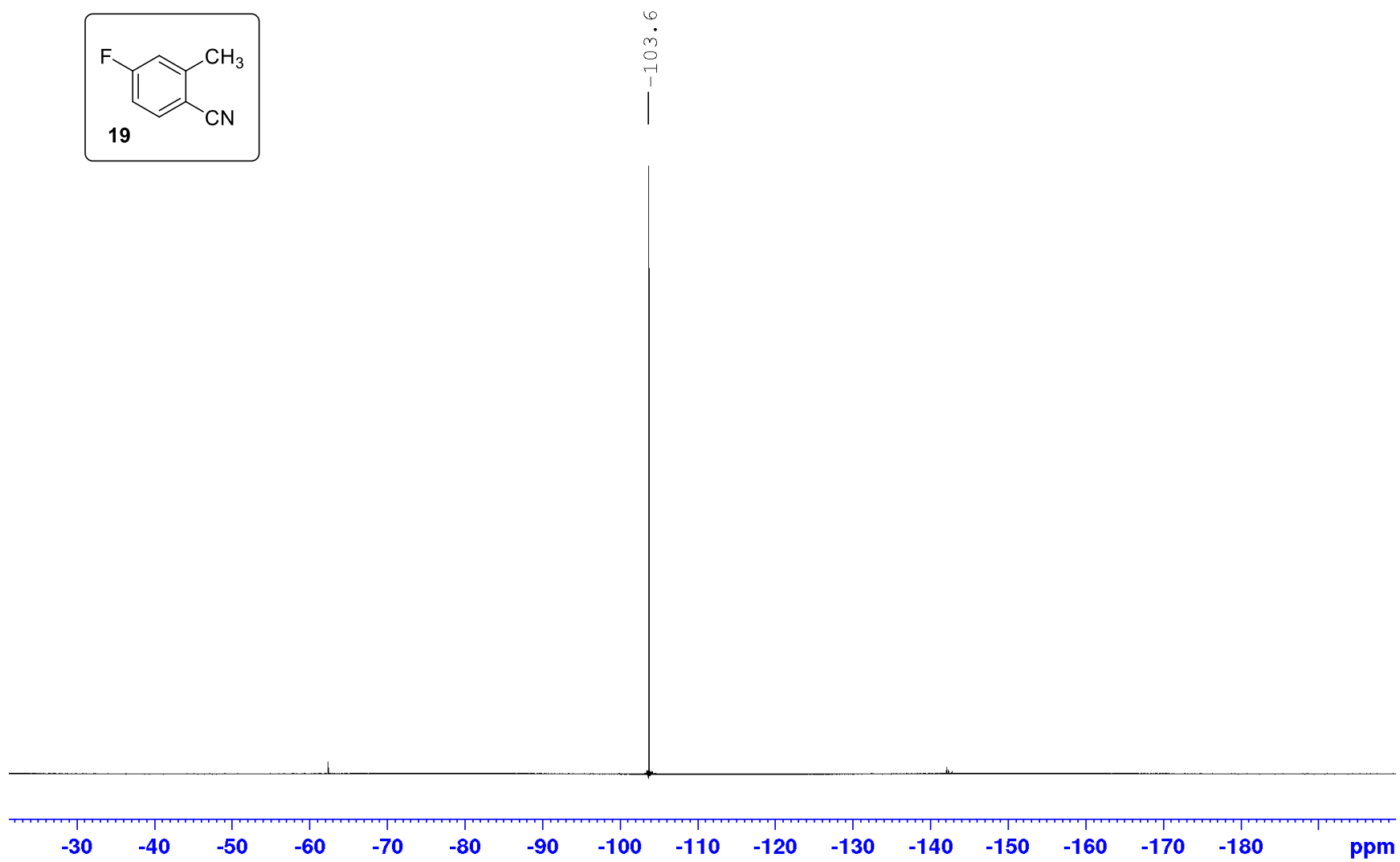
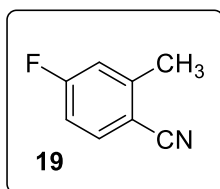


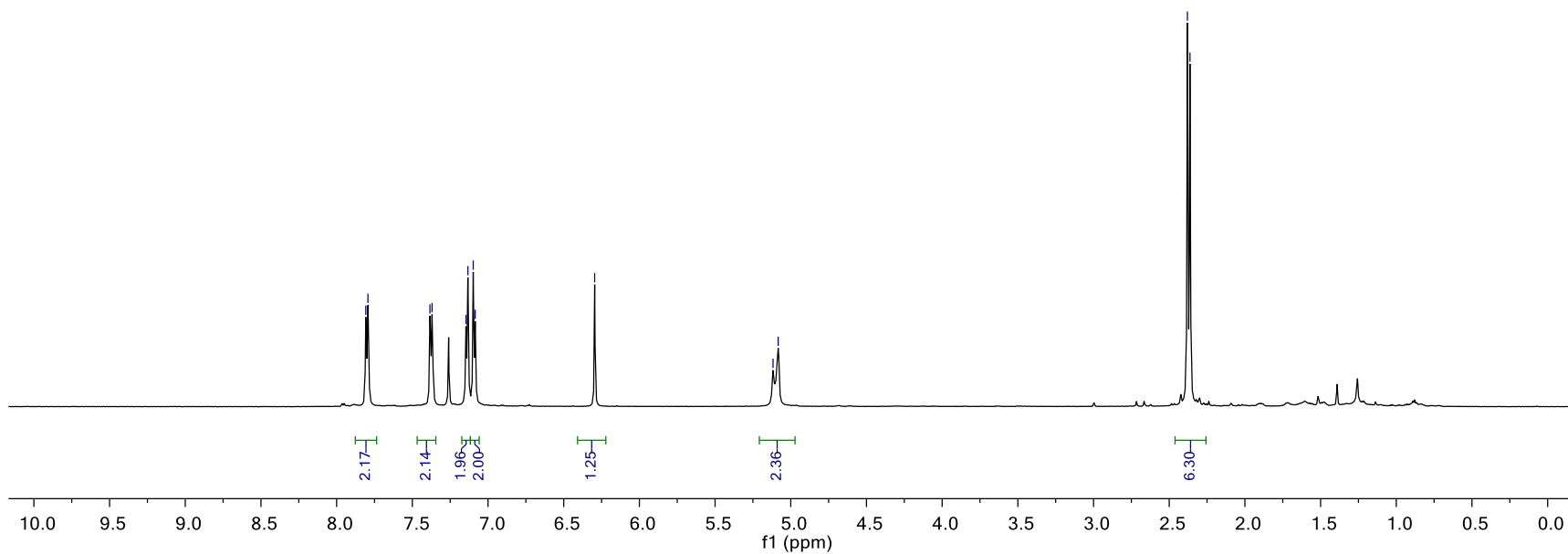
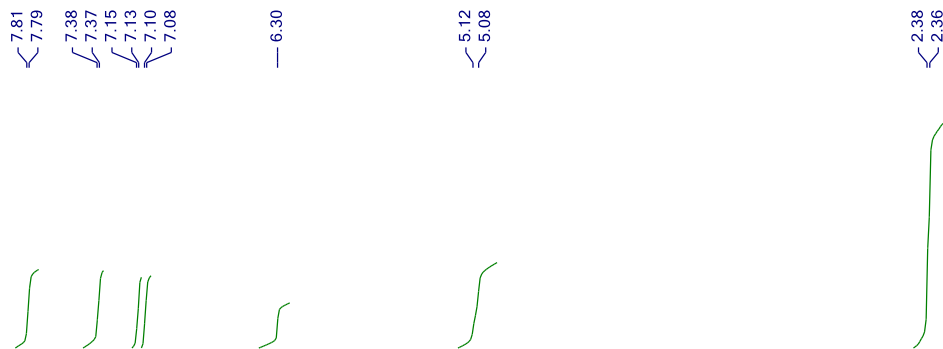
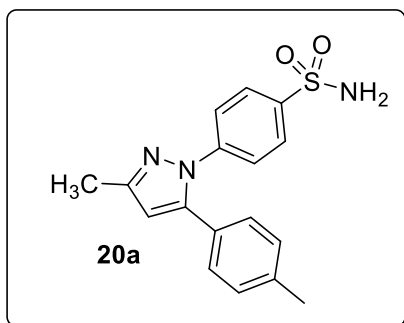


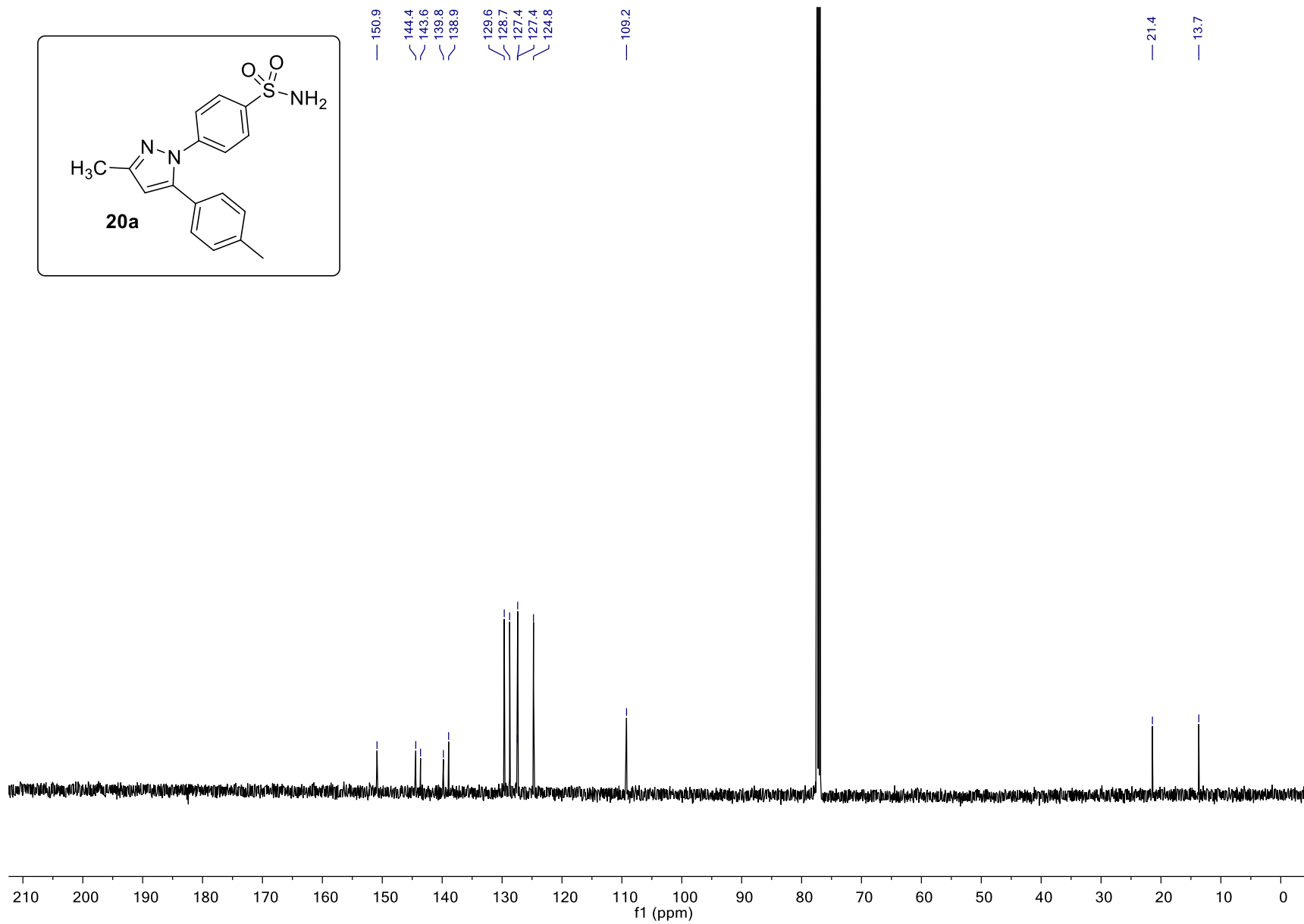
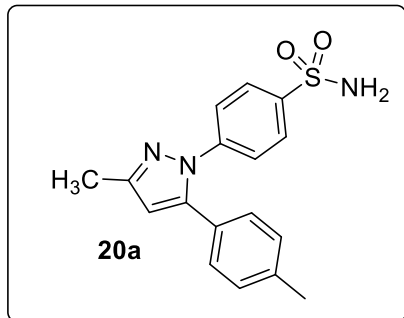


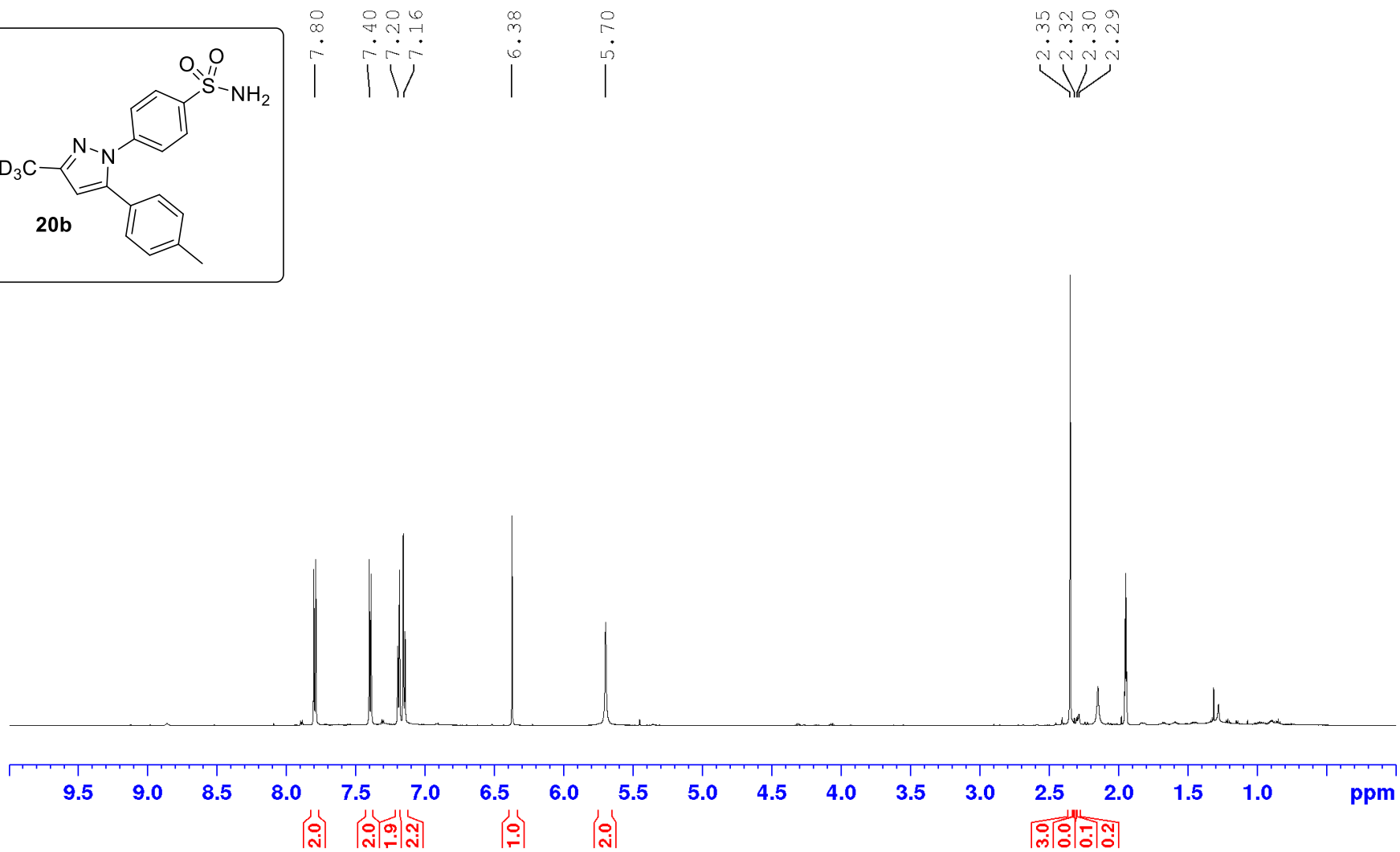
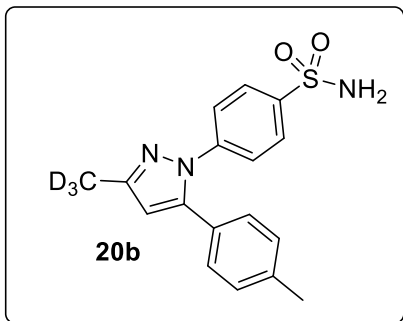


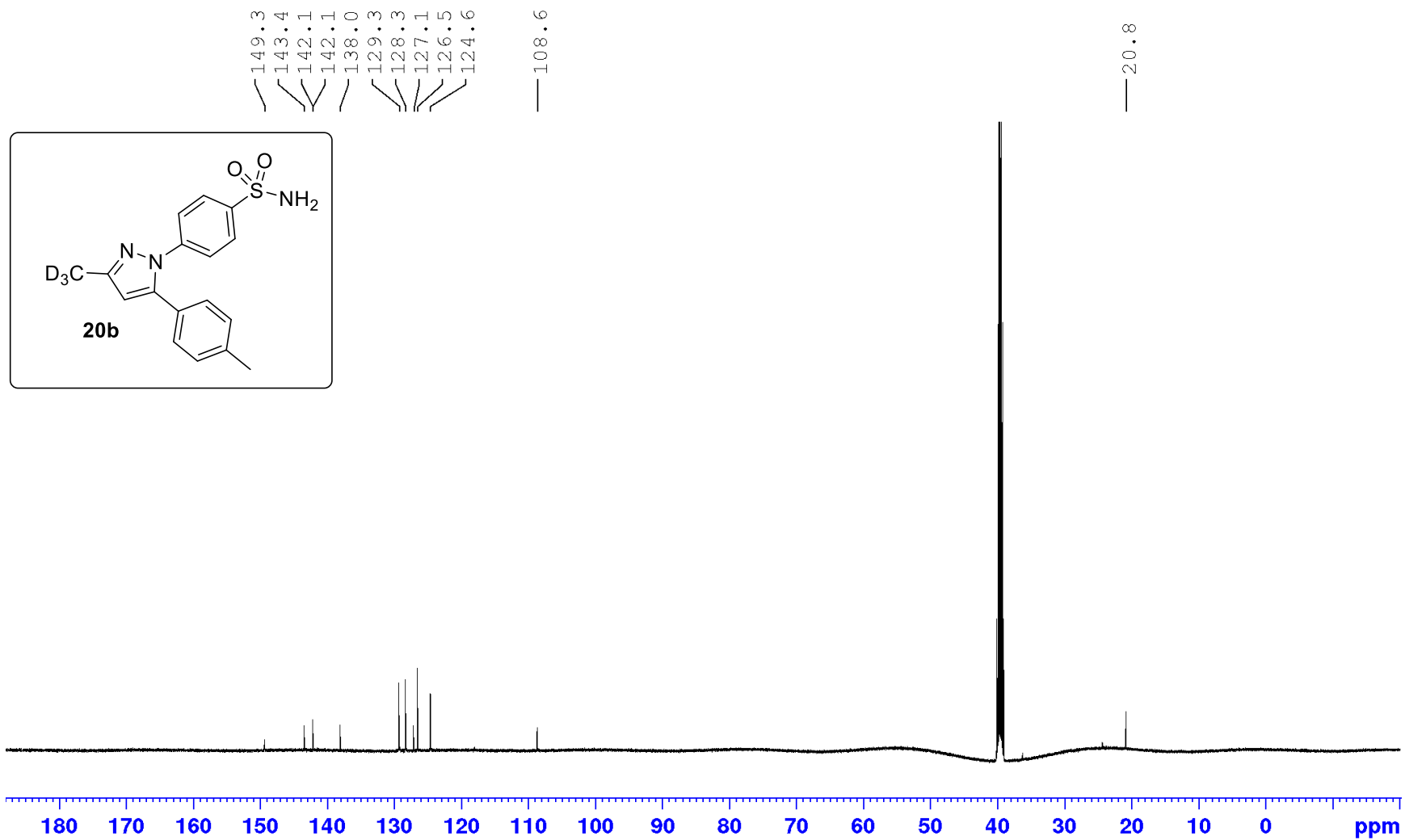


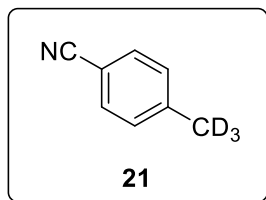












— 7.54
— 7.27

2.42
2.40
2.39

