

**Potassium *tert*-Butoxide Mediated Aerobic Hydroxylation of Arylboronic
Acids to Phenols: An Application towards the Synthesis of (*E*)-Phenoxy
Acrylates**

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Supporting Information

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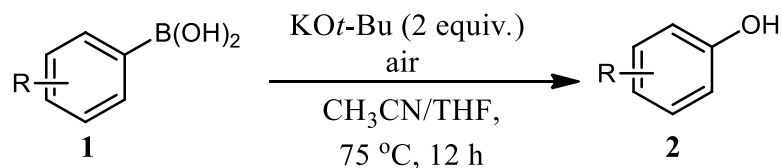
Page S6 – S16 ¹H NMR, ¹³C NMR and HRMS data

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Experimental Section:

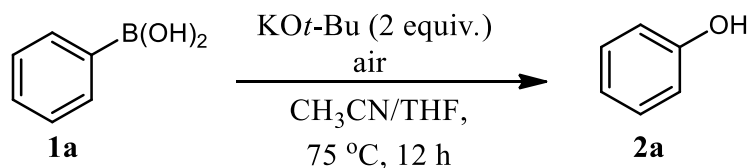
All reactions were carried out under aerobic condition unless otherwise specified. Commercially available chemicals including **1** and **3** were purchased from Aldrich, Avra synthesis, SRL and Thomas Baker were used as received without additional purification. The progress of all reactions was monitored by thin-layer chromatography (TLC). TLC was performed on pre-coated silica gel plates (Merck 60 F254, 0.2 mm thickness). The plates were visualized first with short wavelength UV light followed by KMnO₄ staining solution and heating where necessary. Proton nuclear magnetic resonance (¹H NMR) and Carbon nuclear magnetic resonance (¹³C NMR) spectra were determined in CDCl₃ and DMSO on a Bruker BBFO (500 MHz) spectrometer at room temperature and tetramethylsilane (TMS) served as an internal standard ($\delta_{\text{H}} = 0.00$ ppm). The residual solvent signals were used as references and the chemical shifts converted to the TMS scale (CDCl₃: $\delta_{\text{H}} = 7.25\text{-}7.30$ ppm, DMSO-d₆: $\delta_{\text{H}} = 2.49$ ppm). Spin multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), dt (doublet of triplets), td (triplets of doublets), qd (quartet of doublets), dtd (doublet of triplet of doublet), ddd (doublet of doublet of doublets), ddm (doublet of doublet of multiplets), m (multiplet) and br (broad). Coupling constants (*J*) are given in hertz (Hz).

General procedure for the synthesis of 2a-n



To a round bottom (RB) flask (100 mL) containing arylboronic acid (1.0 mmol, 1.0 equiv.) and KO t Bu (2.0 mmol, 2.0 equiv.), a mixture of CH₃CN/THF (2 mL in a ratio of 4:1) was added. Then, the round bottom flask was fitted with a condenser and was placed in a preheated oil bath at 75 °C. The reaction mixture was stirred for 12 h. The progress of the reaction was monitored by TLC. Upon completion, the reaction mixture was cooled to room temperature. Water (5 mL) was added to the reaction mixture and the pH of the reaction mixture was adjusted to 6 with 10% HCL acid solution. The reaction mixture was extracted with ethyl acetate (5 mL x 3), dried with anhydrous sodium sulphate and concentrated under vacuum. The residue was subjected to column chromatography to isolate the product **2**.

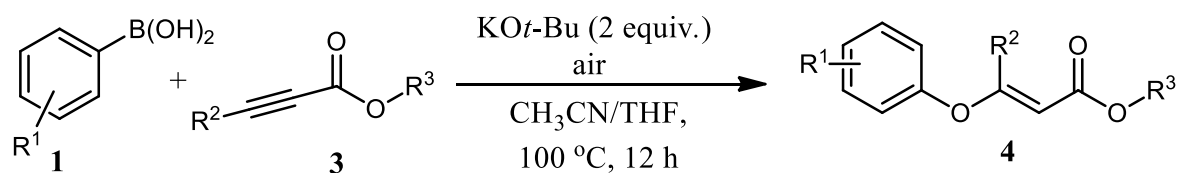
Procedure for the synthesis of phenol (2a)



To a round bottom flask (100 mL) containing arylboronic acid **1a** (121.93 mg, 1 mmol, 1 equiv.) and KO t Bu (224.43 mg, 2 mmol, 2 equiv.), a mixture of CH₃CN/THF (2 mL in a ratio of 4:1) was added. Then, the round bottom flask was fitted with a condenser and was placed in a preheated oil bath at 75 °C. The reaction mixture was stirred for 12 h. The progress of the reaction was monitored by TLC. Upon completion, the reaction mixture was cooled to room temperature. Water (5 mL)

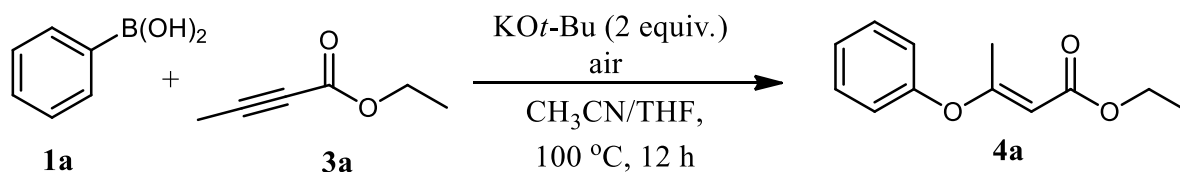
was added to the reaction mixture and the pH of the reaction mixture was adjusted to 6 with 10% HCL acid solution. The reaction mixture was extracted with ethyl acetate (5 mL x 3), dried with anhydrous sodium sulphate and concentrated under vacuum. The residue was subjected to column chromatography to isolate the product **2a** (74 mg; 79% yield).

General procedure for the synthesis of **4a-u**



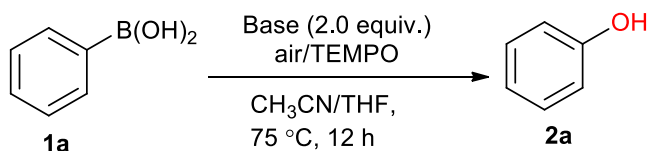
To a round bottom flask (100 mL) containing arylboronic acid (1.0 mmol) and $KOtBu$ (2.0 mmol), a mixture of CH_3CN/THF (2 mL in a ratio of 4:1) was added, followed by addition of alkyne (0.5 mmol). Then, the round bottom flask was fitted with a condenser and was placed in a preheated oil bath at $100\text{ }^\circ\text{C}$. The reaction mixture was stirred for 12 h. The progress of the reaction was monitored by TLC. Upon completion, the reaction mixture was cooled to room temperature. Water (5 mL) was added to the reaction mixture and extracted with ethyl acetate (5 mL x 3), and concentrated under vacuum. The concentrated crude reaction mixture was subjected to column chromatography to isolate the product **4**.

Procedure for the synthesis of **4a**



To a round bottom flask (100 mL) containing arylboronic acid **1a** (121.93 mg, 1.0 mmol) and KO t Bu (224.43 mg, 2.0 mmol), mixture of CH₃CN/THF (2 mL in a ratio of 4:1) was added and then followed by addition of ethyl but-2-ynoate **3a** (56 mg, 0.5 mmol). Then, the round bottom flask containing reaction mixture was fitted with the condenser and was placed in a preheated oil bath at 100 °C for 12 h with constant stirring. The progress of the reaction was monitored by TLC. Upon completion, the reaction was cooled to room temperature. Water (5 mL) was added to the reaction mixture and extracted with ethyl acetate (5 mL x 3), and concentrated under vacuum. The concentrated crude reaction mixture was subjected to column chromatography to isolate the product **4a** (98.0 mg; 95% yield).

Results of radical trapping experiments

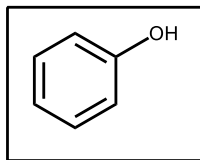


Entry	Base	Equivalent of TEMPO	Yield (%)
1	KOtBu	1.0 equiv.	27%
2	KOtBu	2.0 equiv.	<10%
3	KOtBu	2.5 equiv.	0%
4	KOH	2.5 equiv.	0%
5	Et ₃ N	2.5 equiv.	0%
6	K ₂ CO ₃	2.5 equiv.	0%

All reactions were carried out using phenyl boronic acid (**1a**) (1.0 equiv.), base (2.0 equiv.) and TEMPO (1.0-2.5 equiv.) in the presence of air for 24 h

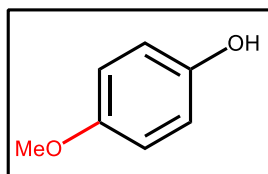
Spectral data of ^1H and ^{13}C NMR

Phenol (2a)



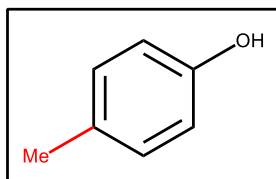
Colorless liquid (74 mg; 79% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.24 (t, $J = 6.6$ Hz, 2H), 6.93 (t, $J = 7.2$ Hz, 1H), 6.83 (d, $J = 7.6$ Hz, 2H), 4.92 (s, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 154.7, 129.6, 129.6, 120.9, 120.9, 115.3, 115.3; the spectroscopic data matched those reported in the literature.¹

4-Methoxyphenol (2b)



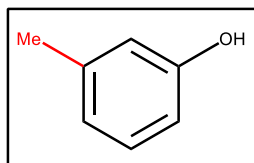
White solid (104 mg; 84% yield); ^1H NMR (500 MHz, CDCl_3) δ 6.84 – 6.71 (m, 4H), 5.11 (s, 1H), 3.77 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 153.4, 149.4, 116.1, 116.0, 114.9, 114.8, 55.8; the spectroscopic data matched those reported in the literature.¹

p-Cresol (2c)



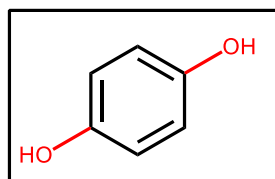
Colorless liquid (87 mg, 80% yield); ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 9.10 (s, 1H), 7.01 – 6.86 (m, 1H), 6.63 (dd, $J = 8.3, 1.6$ Hz, 1H); ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 155.5, 130.2, 127.7, 115.6, 20.9; the spectroscopic data matched those reported in the literature.⁸

***m*-Cresol (2d)**



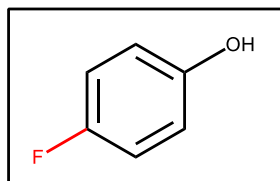
Colorless liquid (81 mg, 75% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.27 (d, $J = 6.9$ Hz, 1H), 6.92 (s, 1H), 6.86 (d, $J = 17.5$ Hz, 2H), 6.68 (s, 1H), 2.41 (s, 3H); ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 154.9, 139.9, 139.8, 129.4, 129.4, 129.4, 121.8, 121.7, 116.1, 112.4, 112.3, 21.2; the spectroscopic data matched those reported in the literature.¹

Hydroquinone (2e)



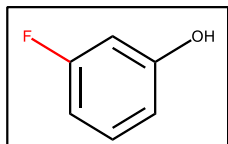
Brownish solid (80 mg; 73% yield); ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 6.62 (s, 4H), 4.10 (d, $J = 7.7$ Hz, 2H); ^{13}C NMR (126 MHz, $\text{DMSO-}d_6$) δ 150.0, 149.9, 116.2, 116.1; the spectroscopic data matched those reported in the literature.³

4-Fluorophenol (2f)



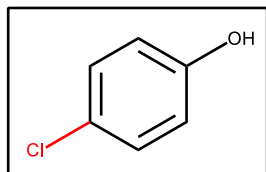
Colorless liquid (75 mg, 67% yield); ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 9.38 (s, 1H), 7.07 – 6.85 (m, 2H), 6.79 – 6.60 (m, 2H); ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 156.4, 154.1, 153.4, 115.9, 115.9, 115.6, 115.3; the spectroscopic data matched those reported in the literature.⁵

3-Fluorophenol (2g)



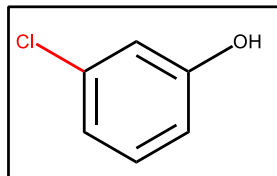
Colorless liquid (80 mg, 71% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.20 (q, $J = 7.4$ Hz, 1H), 6.77 – 6.52 (m, 3H), 6.34 (s, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 164.5, 162.5, 156.2, 156.1, 130.6, 130.6, 111.1, 108.1, 107.9, 103.3, 103.1; the spectroscopic data matched those reported in the literature.⁷

4-Chlorophenol (2h)



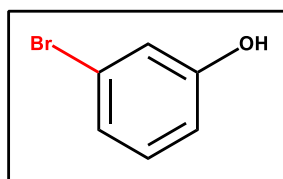
Yellowish liquid (100 mg, 78% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.12 (d, $J = 8.8$ Hz, 2H), 6.73 (d, $J = 8.7$ Hz, 2H), 5.61 (s, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 153.4, 129.4, 125.6, 116.5; the spectroscopic data matched those reported in the literature.¹

3-Chlorophenol (2i)



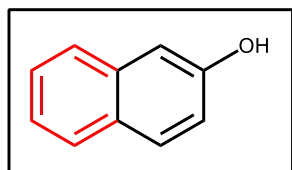
Colorless liquid (88 mg 68% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.17 (t, $J = 8.1$ Hz, 1H), 6.96 (d, $J = 8.0$ Hz, 1H), 6.89 (s, 1H), 6.76 (d, $J = 8.2$ Hz, 1H), 6.15 (s, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 155.5, 134.8, 130.5, 121.3, 115.8, 113.7; the spectroscopic data matched those reported in the literature.⁹

3-Bromophenol (2j)



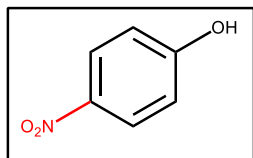
Yellowish liquid (113 mg 65% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.07 (tdd, $J = 7.9, 5.5, 2.3$ Hz, 2H), 7.04 – 7.00 (m, 1H), 6.78 (ddd, $J = 7.7, 2.4, 1.5$ Hz, 1H), 6.48 (s, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 156.2, 130.7, 123.8, 122.6, 118.7, 114.2; the spectroscopic data matched those reported in the literature.⁶

Naphthalen-2-ol (2k)



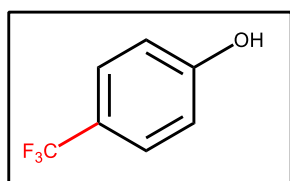
Brownish solid (103 mg, 71% yield); ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ 7.75 – 7.69 (m, 1H), 7.64 (d, $J = 8.3$ Hz, 1H), 7.35 (t, $J = 7.5$ Hz, 1H), 7.22 (t, $J = 7.5$ Hz, 1H), 7.18 (d, $J = 2.1$ Hz, 1H), 7.12 (dd, $J = 8.8, 2.4$ Hz, 1H), 4.01 (s, 1H); ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ 155.4, 135.0, 129.8, 128.2, 128.0, 126.6, 126.4, 123.2, 119.0, 118.9, 109.1, 109.1; the spectroscopic data matched those reported in the literature.²

4-Nitrophenol (2l)



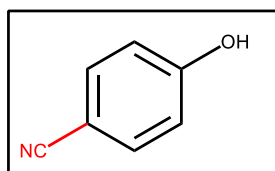
Yellowish solid (107 mg, 77% yield); ^1H NMR (500 MHz, DMSO- d_6) δ 8.04 (d, $J = 9.2$ Hz, 2H), 6.88 (d, $J = 9.2$ Hz, 2H), 3.93 (s, 1H); ^{13}C NMR (126 MHz, DMSO- d_6) δ 164.0, 140.0, 126.5, 116.0; the spectroscopic data matched those reported in the literature.⁴

4-(Trifluoromethyl)phenol (2m)



White solid (114 mg 70% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.51 (d, $J = 8.4$ Hz, 2H), 6.90 (d, $J = 8.4$ Hz, 2H), 5.40 (s, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 158.0, 127.2, 127.2, 127.2, 127.1, 125.4, 123.3, 123.3, 123.1, 115.4; the spectroscopic data matched those reported in the literature.⁵

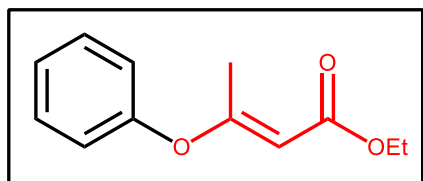
4-Hydroxybenzotrile (2n)



White solid (87 mg 73% yield); ^1H NMR (500 MHz, DMSO- d_6) δ 7.60 (d, $J = 8.2$ Hz, 2H), 6.88 (d, $J = 8.3$ Hz, 2H), 3.84 (s, 1H); ^{13}C NMR (126 MHz, DMSO- d_6) δ 161.7, 134.7, 120.0, 116.8, 101.44; the spectroscopic data matched those reported in the literature.²

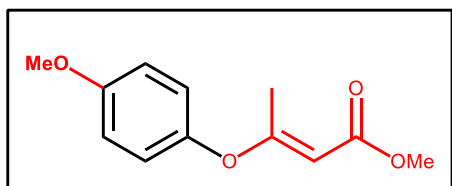
Spectral data of 4 (¹H NMR, ¹³C NMR and HRMS data)

(*E*)-Ethyl 3-phenoxybut-2-enoate (4a)



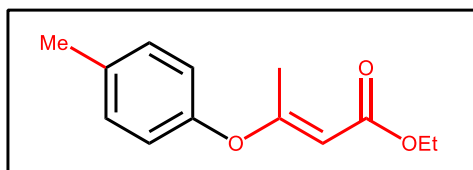
Colorless liquid. (98.0 mg, 95% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.43 – 7.35 (m, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.02 (d, *J* = 7.6 Hz, 2H), 4.86 (s, 1H), 4.09 (q, *J* = 7.2 Hz, 2H), 2.49 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 172.7, 167.6, 153.3, 129.9, 125.6, 121.6, 96.1, 59.5, 18.4, 14.3; HRMS (Q-TOF), *m/z*: (M+H)⁺ for C₁₂H₁₄O₃ calculated (207.1016) and obtained (207.1005).

(*E*)-Ethyl 3-(4-methoxyphenoxy)but-2-enoate (4b)



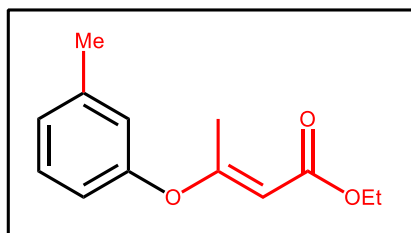
Colorless liquid (89.0 mg, 75% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.00 – 6.80 (m, 4H), 4.84 (s, 1H), 4.08 (q, *J* = 7.2 Hz, 2H), 3.81 (s, 3H), 2.47 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 173.3, 167.7, 157.1, 146.7, 122.4, 114.9, 95.5, 59.4, 55.6, 18.4, 14.3; HRMS (Q-TOF), *m/z*: (M+H)⁺ for C₁₃H₁₆O₄ calculated (237.1121) and obtained (237.1120).

(*E*)-Ethyl 3-(*p*-tolylloxy)but-2-enoate (4c)



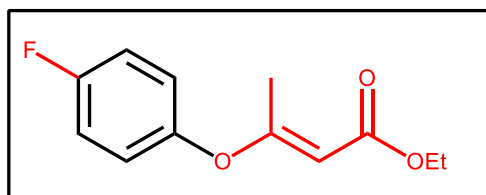
Yellowish brown liquid (95.0 mg, 86% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.07 (d, $J = 8.5$ Hz, 2H), 6.80 (d, $J = 8.4$ Hz, 2H), 4.77 (s, 1H), 3.99 (q, $J = 7.1$ Hz, 2H), 2.39 (s, 3H), 2.25 (s, 3H), 1.11 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 172.9, 167.7, 151.0, 135.2, 130.4, 121.2, 95.7, 59.4, 20.8, 18.4, 14.3; HRMS (Q-TOF), m/z : $(\text{M}+\text{H})^+$ for $\text{C}_{13}\text{H}_{16}\text{O}_3$ calculated (221.1272) and obtained (221.1238).

(E)-Ethyl 3-(m-tolyloxy)but-2-enoate (4d)



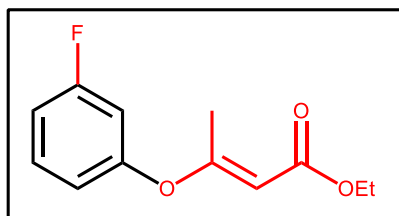
Yellowish brown liquid. (97.0 mg, 88% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.16 (t, $J = 7.8$ Hz, 1H), 6.93 (d, $J = 7.6$ Hz, 1H), 6.73 (dd, $J = 5.9, 5.0$ Hz, 2H), 4.79 (s, 1H), 4.00 (q, $J = 7.1$ Hz, 2H), 2.40 (s, 3H), 2.26 (s, 3H), 1.12 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 172.7, 167.7, 153.3, 140.1, 129.6, 126.4, 122.1, 118.4, 96.0, 59.4, 21.2, 18.4, 14.3; HRMS (Q-TOF), m/z : $(\text{M}+\text{H})^+$ for $\text{C}_{13}\text{H}_{16}\text{O}_3$ calculated (221.1172) and obtained (221.1167).

(E)-Ethyl 3-(4-fluorophenoxy)but-2-enoate (4e)



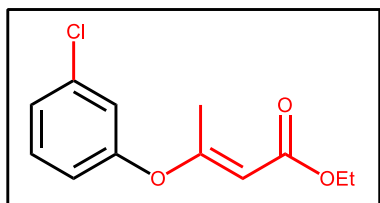
Colorless liquid. (62 mg, 55% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.00 (t, $J = 8.2$ Hz, 2H), 6.91 (dd, $J = 7.1, 4.6$ Hz, 2H), 4.75 (s, 1H), 4.01 (q, $J = 7.0$ Hz, 2H), 2.40 (s, 3H), 1.14 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 171.7, 166.4, 160.0, 158.1, 148.1, 148.1, 122.0, 121.9, 115.7, 115.5, 95.1, 58.5, 17.3, 13.2; HRMS (Q-TOF), m/z : $(\text{M}+\text{H})^+$ for $\text{C}_{12}\text{H}_{13}\text{FO}_3$ calculated (225.0921) and obtained (225.0912).

(E)-Ethyl 3-(3-fluorophenoxy)but-2-enoate (4f)



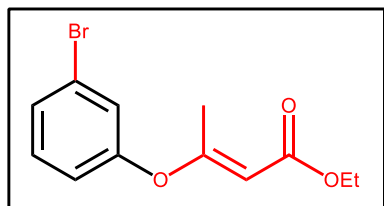
Colorless liquid; 101.0 mg, 90% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.26 (td, $J = 8.2, 6.6$ Hz, 1H), 6.85 (td, $J = 8.3, 2.5$ Hz, 1H), 6.74 (dd, $J = 8.3, 1.9$ Hz, 1H), 6.68 (dt, $J = 9.4, 2.3$ Hz, 1H), 4.83 (s, 1H), 4.02 (q, $J = 7.1$ Hz, 2H), 2.39 (s, 3H), 1.13 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 171.9, 167.3, 164.3, 162.3, 154.3, 154.2, 130.8, 130.7, 117.3, 112.7, 112.6, 109.5, 109.4, 96.9, 59.6, 18.2, 14.2; HRMS (Q-TOF), m/z : $(\text{M}+\text{H})^+$ for $\text{C}_{12}\text{H}_{13}\text{FO}_3$ calculated (225.0921) and obtained (225.0933).

(E)-Ethyl 3-(3-chlorophenoxy)but-2-enoate (4g)



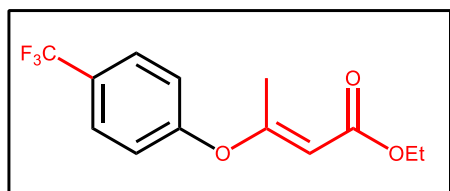
Colorless liquid; 96.0 mg, 80% yield; ^1H NMR (500 MHz, CDCl_3) δ 7.32 (t, $J = 8.1$ Hz, 1H), 7.23 – 7.19 (m, 1H), 7.05 (t, $J = 2.1$ Hz, 1H), 6.96 – 6.91 (m, 1H), 4.89 (s, 1H), 4.10 (q, $J = 7.1$ Hz, 2H), 2.47 (s, 3H), 1.22 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 172.0, 167.3, 153.9, 135.2, 130.7, 125.9, 122.2, 119.9, 97.0, 59.7, 18.3, 14.3; HRMS (Q-TOF), m/z : $(\text{M}+\text{H})^+$ for $\text{C}_{12}\text{H}_{13}\text{ClO}_3$ calculated (241.0626) and obtained (241.0621).

(E)-Ethyl 3-(3-bromophenoxy)but-2-enoate (4h)



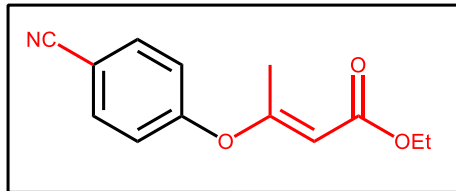
Yellowish liquid. (102.0 mg, 72% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.29 (d, $J = 8.0$ Hz, 1H), 7.18 (t, $J = 7.9$ Hz, 1H), 7.13 (s, 1H), 6.90 (d, $J = 8.1$ Hz, 1H), 4.80 (s, 1H), 4.03 (q, $J = 7.1$ Hz, 2H), 2.39 (s, 3H), 1.15 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 172.0, 167.3, 153.9, 131.0, 128.8, 125.0, 122.9, 120.3, 97.1, 59.6, 18.2, 14.2; HRMS (Q-TOF), m/z : $(\text{M}+\text{H})^+$ for $\text{C}_{12}\text{H}_{13}\text{BrO}_3$ calculated (285.0121) and obtained (285.0140).

(E)-Ethyl 3-(4-(trifluoromethyl)phenoxy)but-2-enoate (4i)



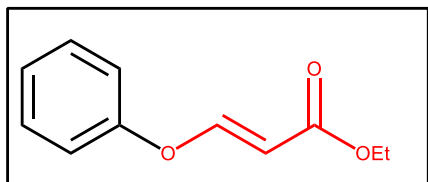
Colorless liquid. (96.0 mg, 70% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.59 (d, $J = 8.5$ Hz, 2H), 7.07 (d, $J = 8.4$ Hz, 2H), 4.82 (s, 1H), 4.03 (q, $J = 7.1$ Hz, 2H), 2.42 (d, $J = 0.4$ Hz, 3H), 1.15 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 171.6, 167.1, 156.0, 127.9, 127.6, 127.4, 127.4, 127.4, 127.3, 124.9, 122.7, 121.8, 97.6, 59.7, 18.2, 14.2; HRMS (Q-TOF), m/z : $(\text{M}+\text{H})^+$ for $\text{C}_{13}\text{H}_{13}\text{FO}_3$ calculated (275.0890) and obtained (275.0883).

(E)-Ethyl 3-(4-cyanophenoxy)but-2-enoate (4j)



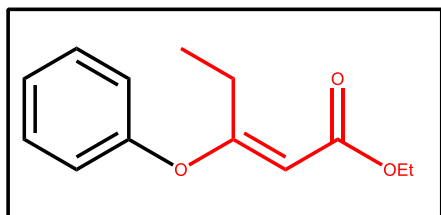
Yellowish liquid. (88.0 mg, 76% yield). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.69 – 7.48 (m, 2H), 7.17 – 6.90 (m, 2H), 4.87 (s, 1H), 4.04 (q, $J = 7.1$ Hz, 2H), 2.41 (s, 3H), 1.15 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 169.8, 165.8, 156.0, 133.3, 121.2, 117.1, 108.2, 97.8, 58.8, 17.1, 13.2; HRMS (Q-TOF), m/z : $(\text{M}+\text{H})^+$ for $\text{C}_{13}\text{H}_{13}\text{NO}_3$ calculated (232.0968) and obtained (232.0966).

(E)-Ethyl 3-phenoxyacrylate (4k)



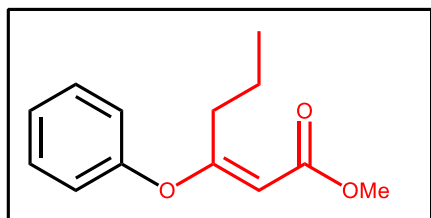
Colorless liquid. (70 mg, 72% yield); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.73 (d, $J = 12.2$ Hz, 1H), 7.34 – 7.28 (m, 2H), 7.12 (t, $J = 7.4$ Hz, 1H), 7.00 (d, $J = 7.7$ Hz, 2H), 5.48 (d, $J = 12.2$ Hz, 1H), 4.12 (q, $J = 7.1$ Hz, 2H), 1.22 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 167.2, 159.0, 155.8, 129.9, 124.9, 118.1, 102.1, 60.1, 14.3; HRMS (Q-TOF), m/z : $(\text{M}+\text{H})^+$ for $\text{C}_{11}\text{H}_{12}\text{O}_3$ calculated (193.0859) and obtained (193.0877).

(E)-Ethyl 3-phenoxybut-2-enoate (4l)



Colorless liquid (74.0 mg, 67% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.32 (t, $J = 7.7$ Hz, 2H), 7.15 (t, $J = 7.4$ Hz, 1H), 6.94 (d, $J = 8.5$ Hz, 2H), 4.70 (s, 1H), 4.01 (q, $J = 7.1$ Hz, 2H), 2.87 (q, $J = 7.5$ Hz, 2H), 1.21 (t, $J = 7.5$ Hz, 3H), 1.13 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 177.6, 167.3, 153.5, 129.9, 125.5, 121.5, 95.1, 59.4, 24.9, 14.2, 11.8; HRMS (Q-TOF), m/z : $(\text{M}+\text{H})^+$ for $\text{C}_{13}\text{H}_{16}\text{O}_3$ calculated (221.1172) and obtained (221.1174).

(E)-Methyl 3-phenoxyhex-2-enoate (4m)



Colorless liquid (72.0 mg, 65% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.31 (t, $J = 7.9$ Hz, 2H), 7.15 (t, $J = 7.4$ Hz, 1H), 6.93 (d, $J = 7.8$ Hz, 2H), 4.74 (s, 1H), 3.54 (s, 3H), 2.96 – 2.55 (m, 2H), 1.84 – 1.57 (m, 2H), 0.99 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 176.7, 167.8, 153.4, 129.9, 125.6, 121.5, 95.4, 50.8, 33.1, 20.8, 13.7; HRMS (Q-TOF) $(\text{M}+\text{H})^+$ for $\text{C}_{13}\text{H}_{16}\text{O}_3$ calculated (221.1172) and obtained (221.1174).

REFERENCES

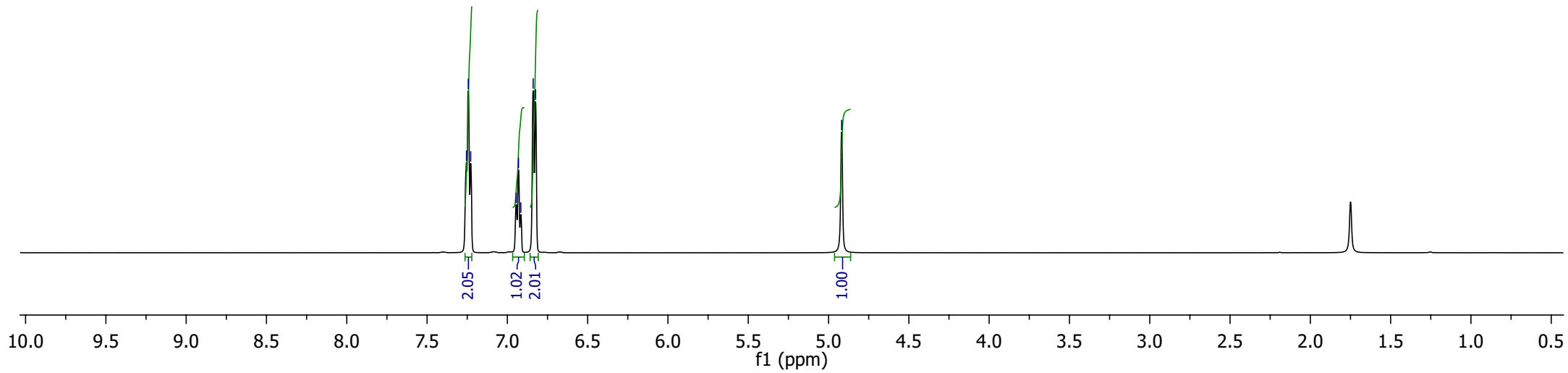
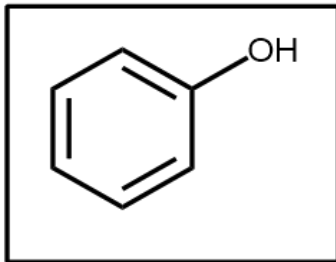
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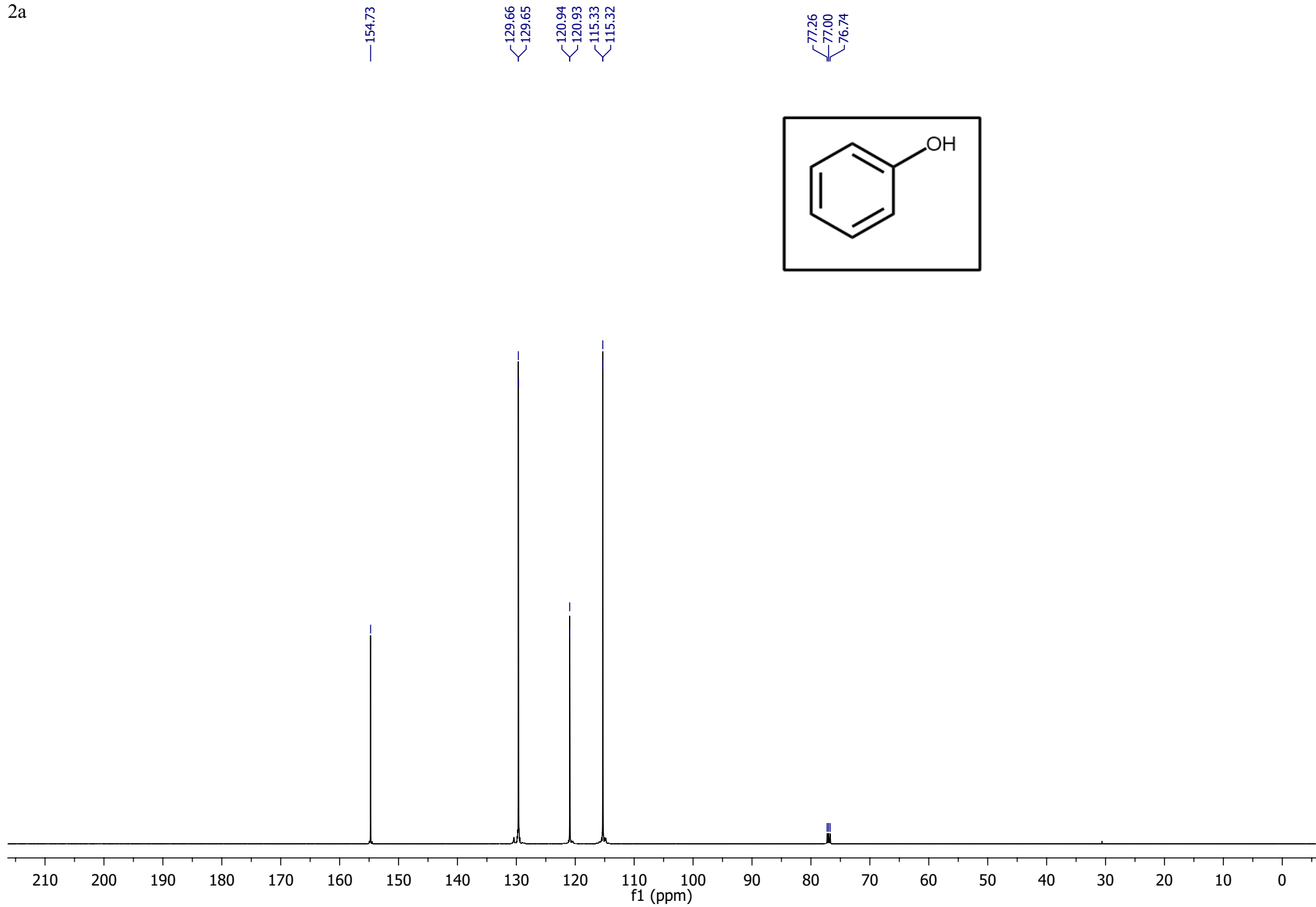
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7.25
7.24
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6.94
6.93
6.92
6.84
6.82

4.92



2a

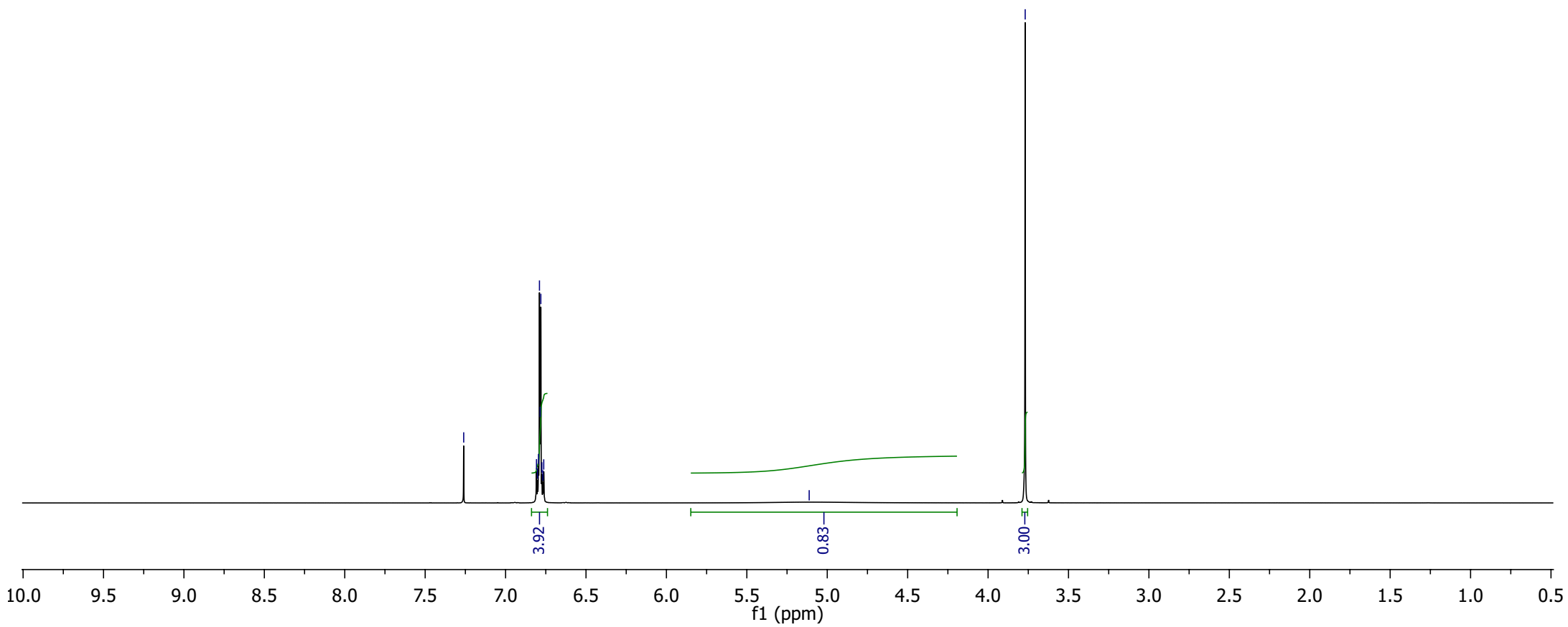
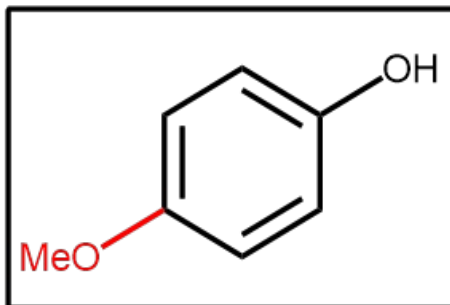


2b

7.26
6.81
6.80
6.80
6.79
6.78
6.78
6.77
6.76

5.11

3.77



2b

—153.48

—149.48

116.10

116.05

114.92

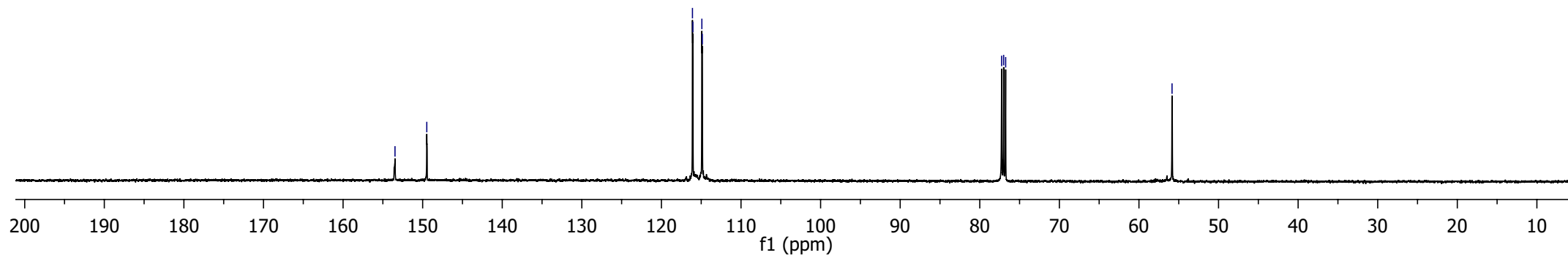
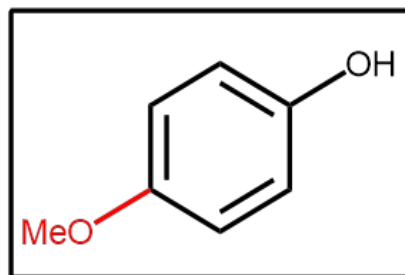
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77.25

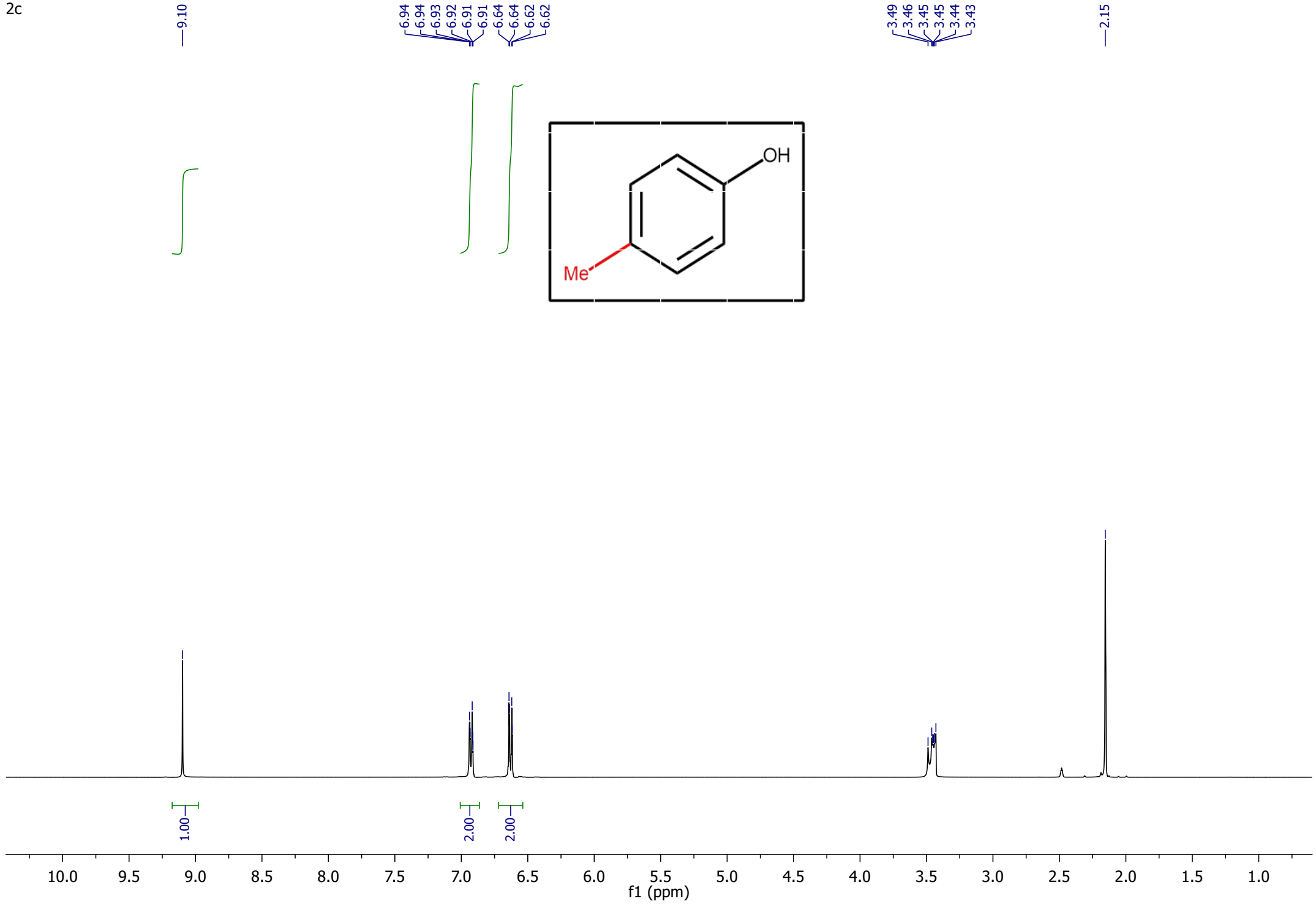
77.00

76.75

—55.84



2c



13C 2c

—155.50

—130.28

—127.73

—115.62

40.64

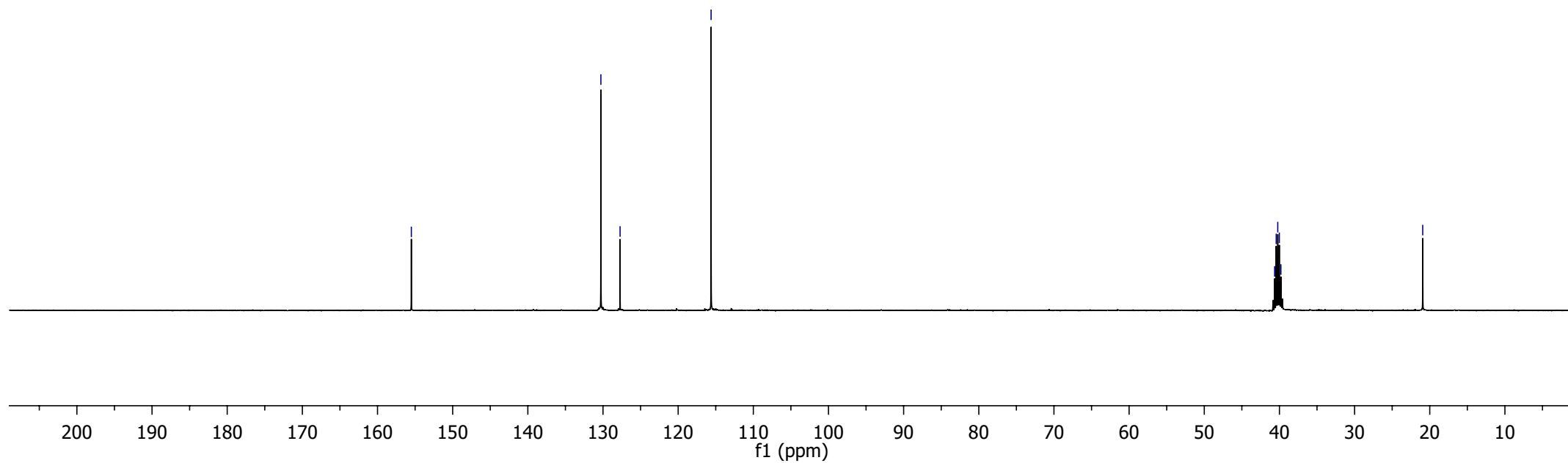
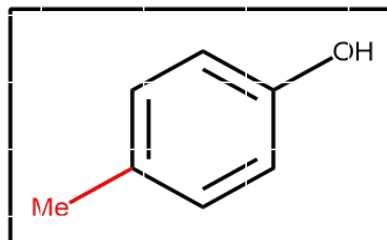
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40.22

40.01

39.81

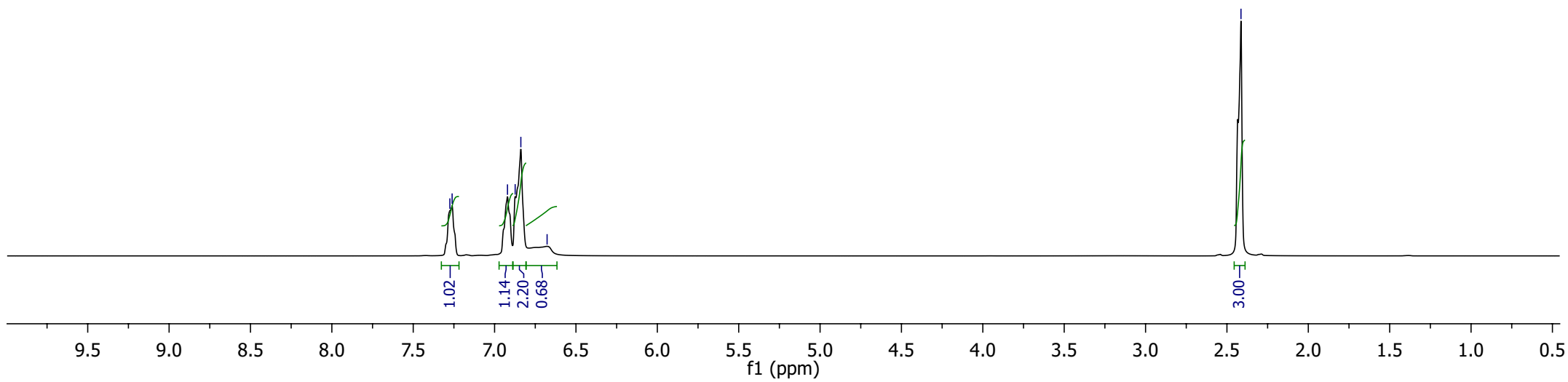
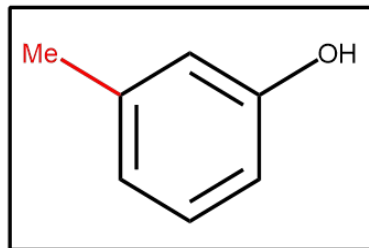
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2d

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6.84
6.68

2.41



2d

—154.93

139.90
139.82

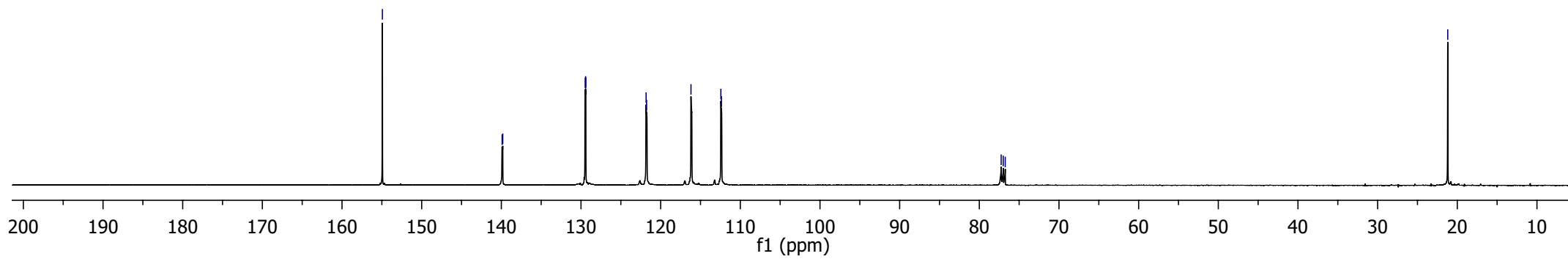
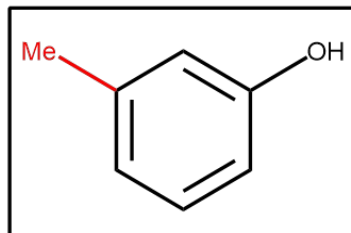
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121.77

116.19
112.44
112.37

77.25
77.00
76.75

—21.20

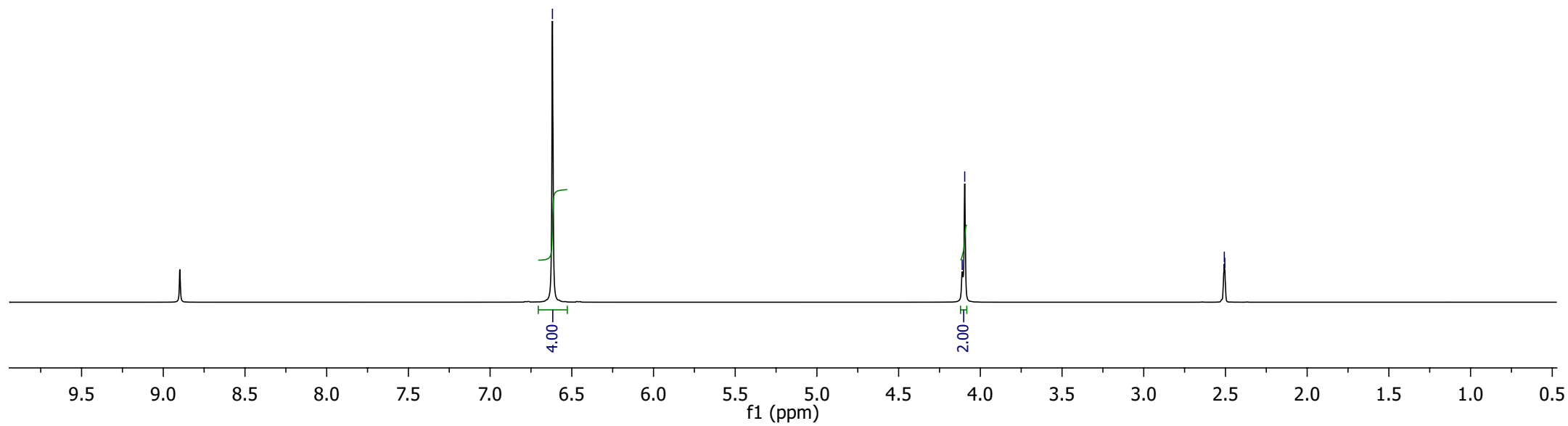
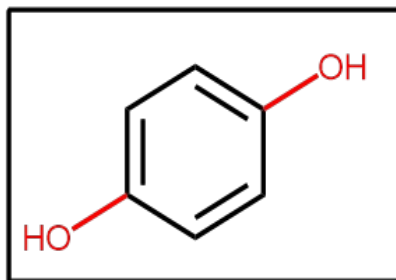


2e

6.62

4.11
4.10

2.51
2.50

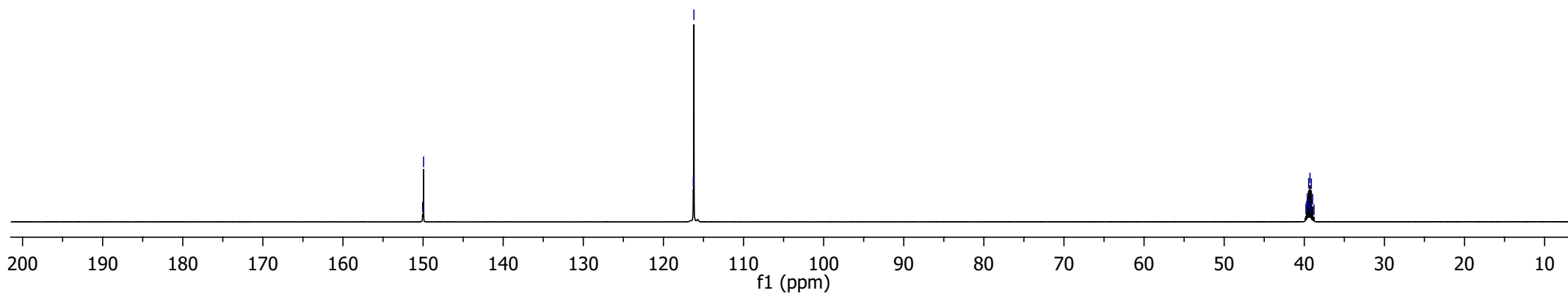
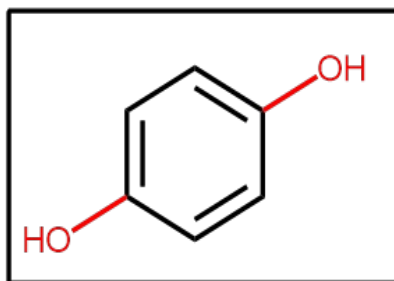


2e

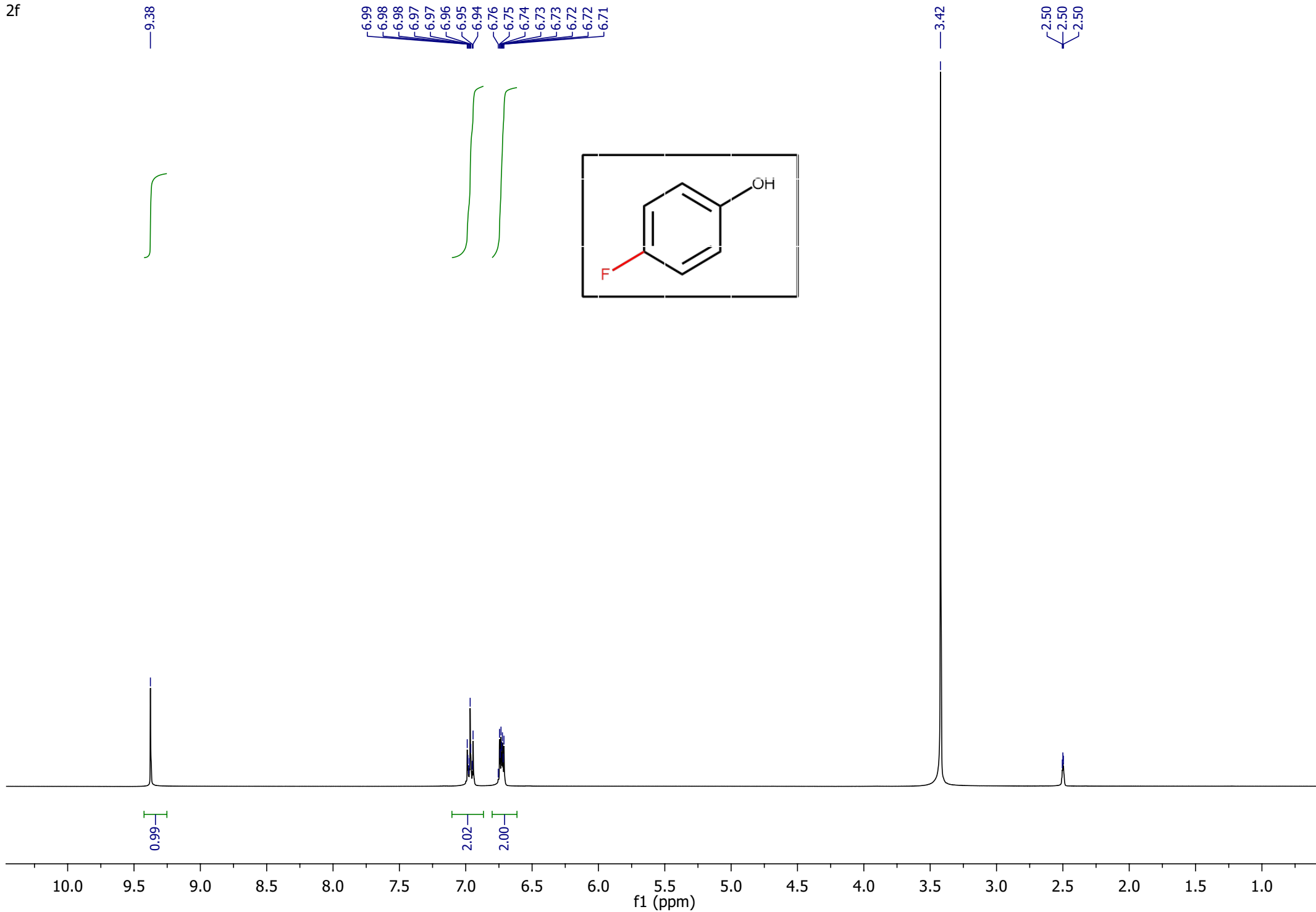
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116.19

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39.29
39.20
39.12
38.95
38.79



2f

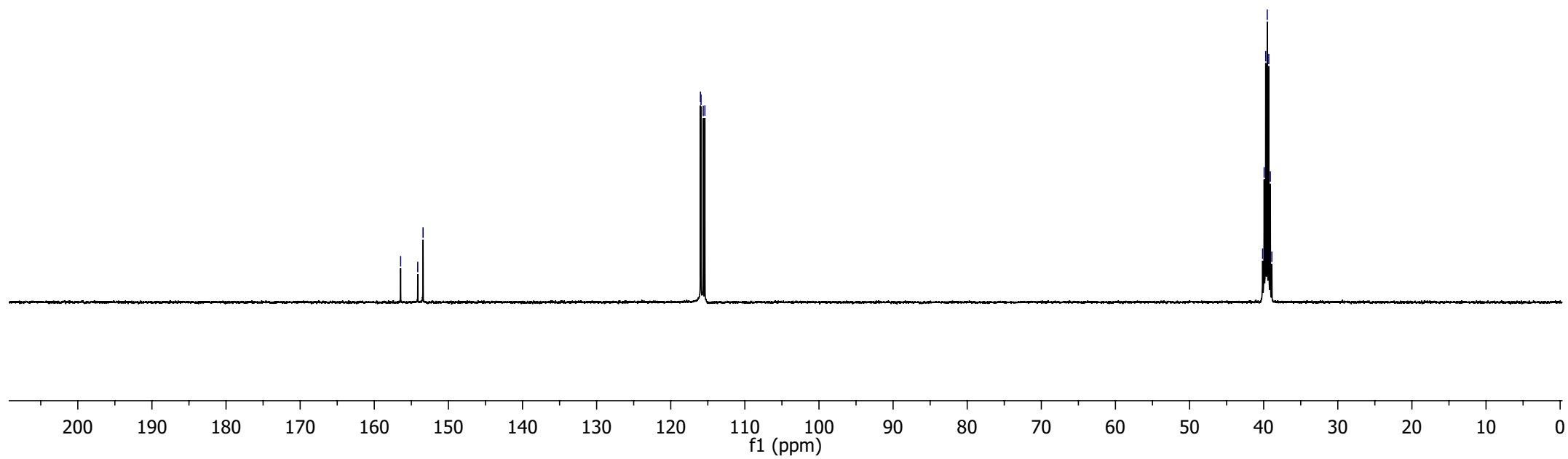
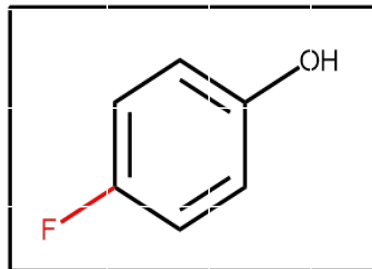


2f

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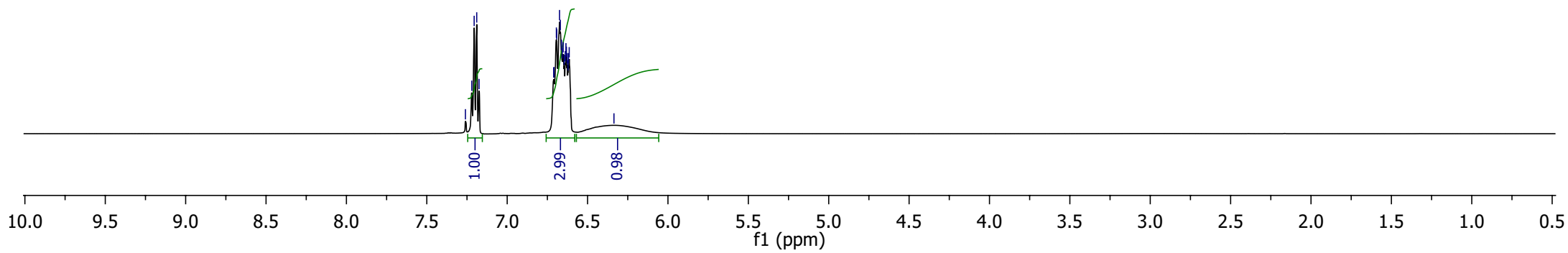
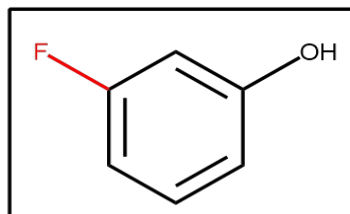
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115.91
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115.39

40.14
39.94
39.73
39.52
39.31
39.10
38.90



2g

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7.22
7.21
7.19
7.18
6.69
6.69
6.67
6.54



2g

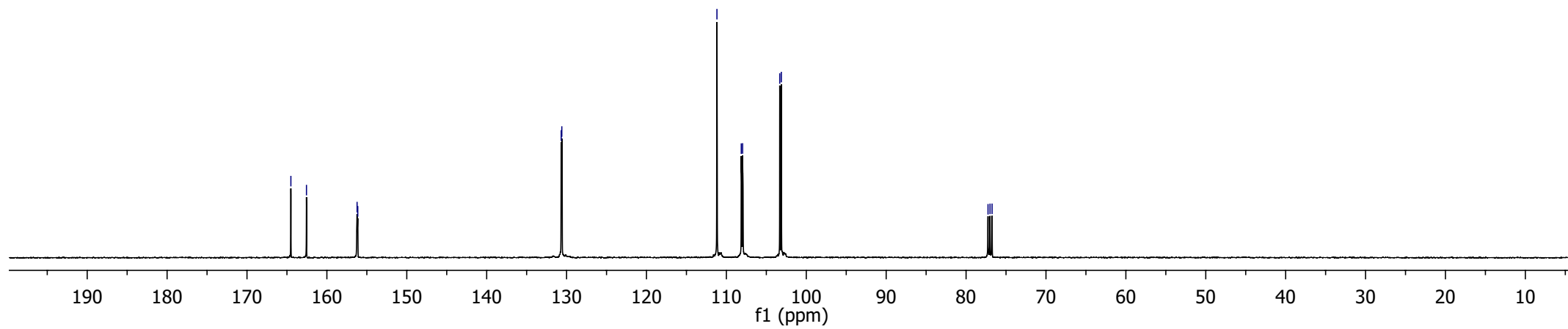
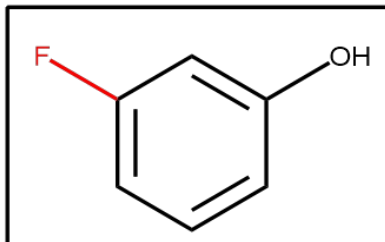
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108.14
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103.32
103.12

77.25
77.00
76.75

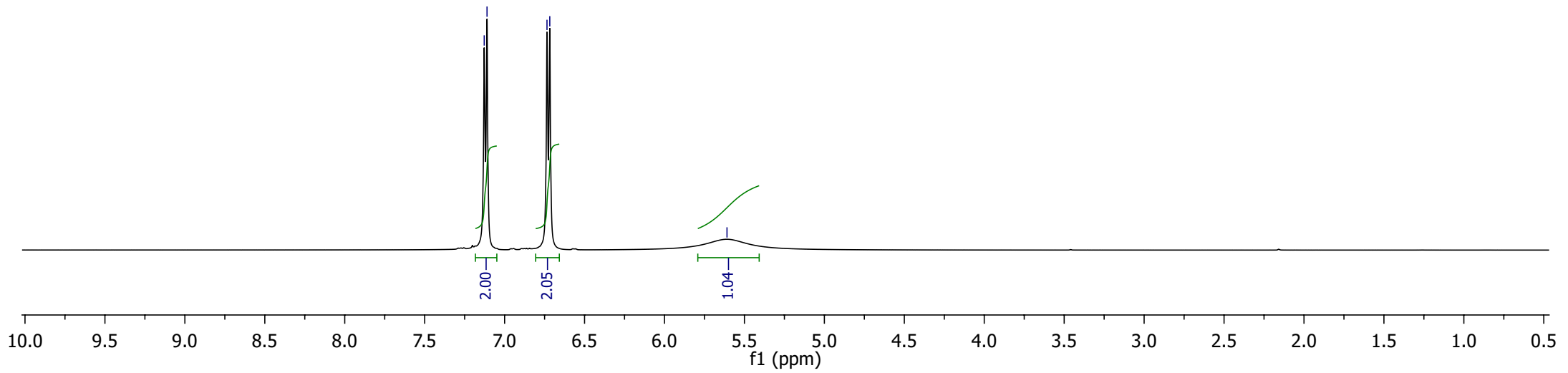
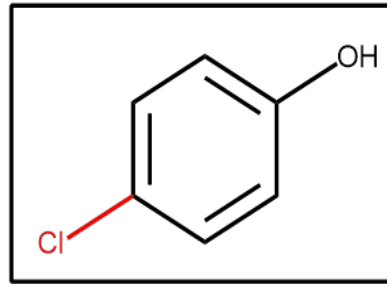


2h

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7.11

6.74
6.72

5.61



2h

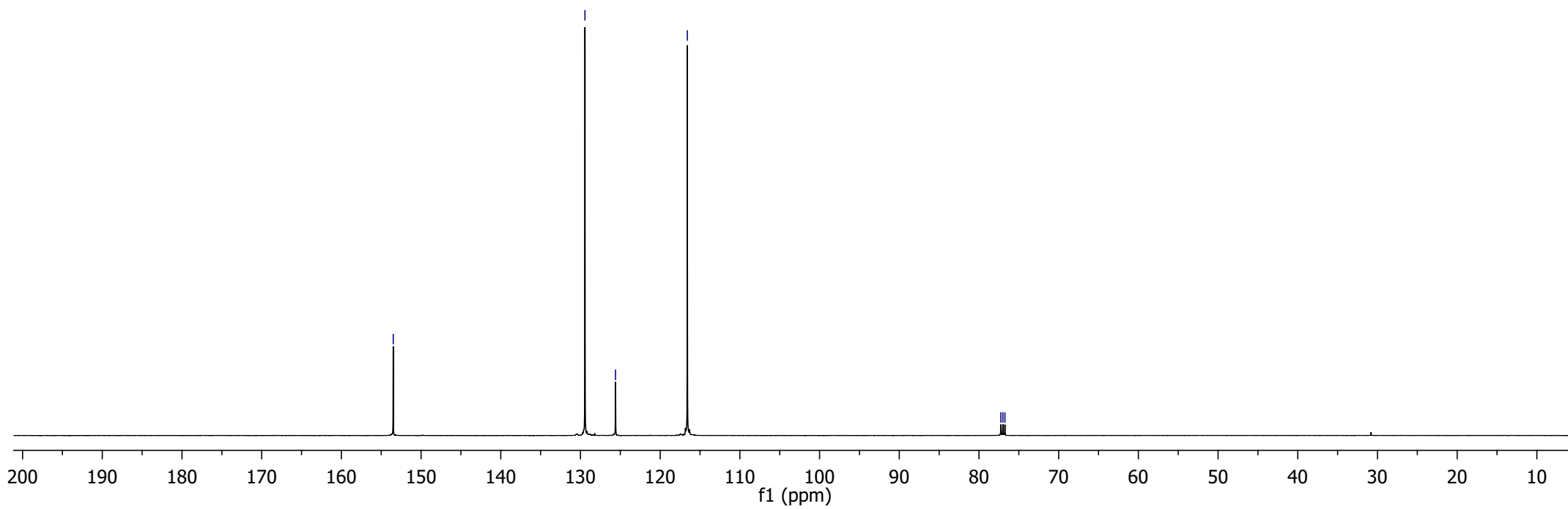
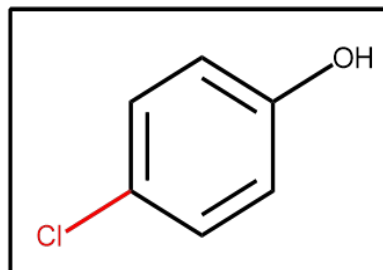
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—129.44

—125.60

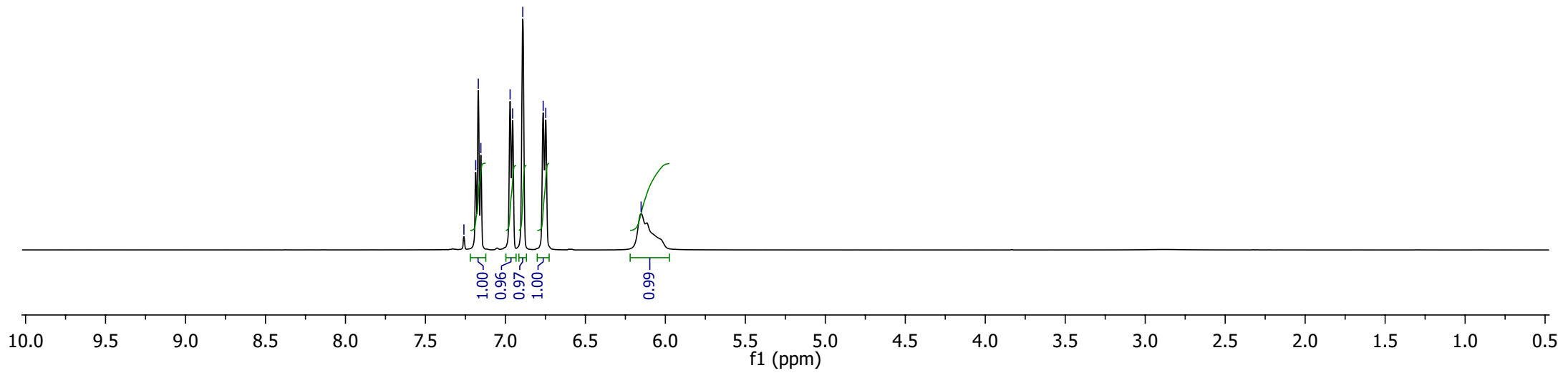
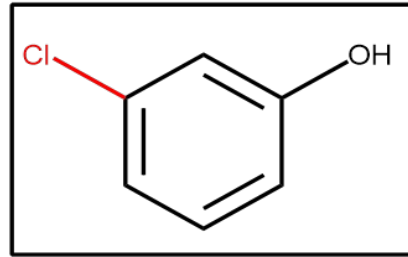
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77.00
76.74



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6.75

—6.15



—155.55

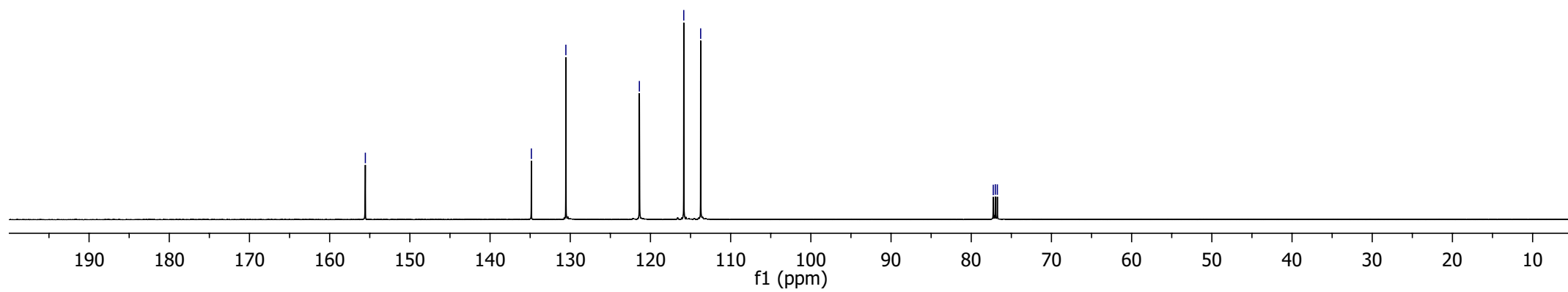
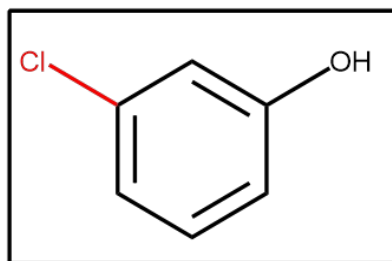
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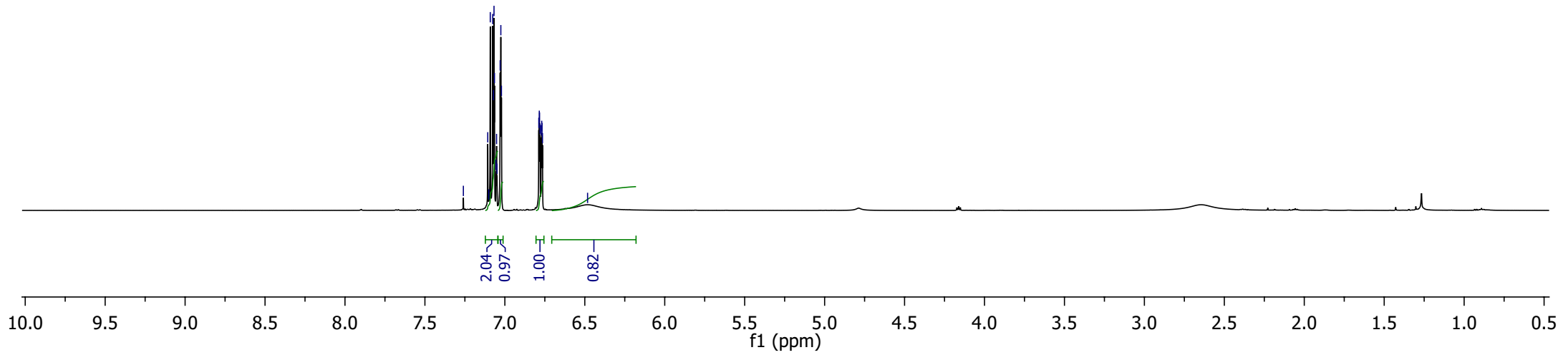
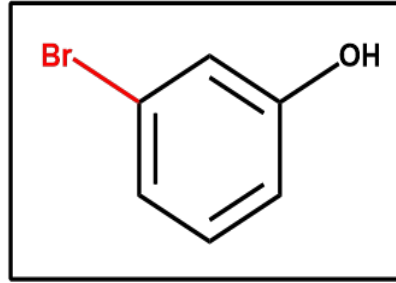
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—113.74

77.25
77.00
76.75

2j

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7.07
7.06
7.06
7.05
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6.48



2j

—156.25

—130.78

—123.85

—122.69

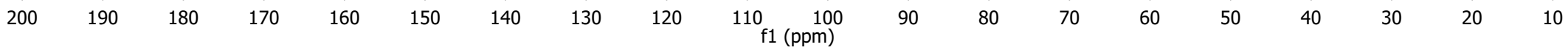
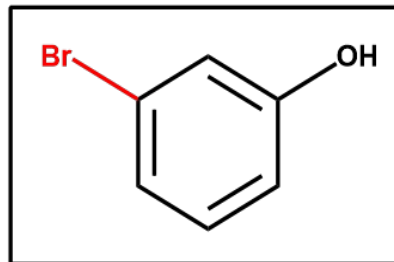
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—77.00

—76.75

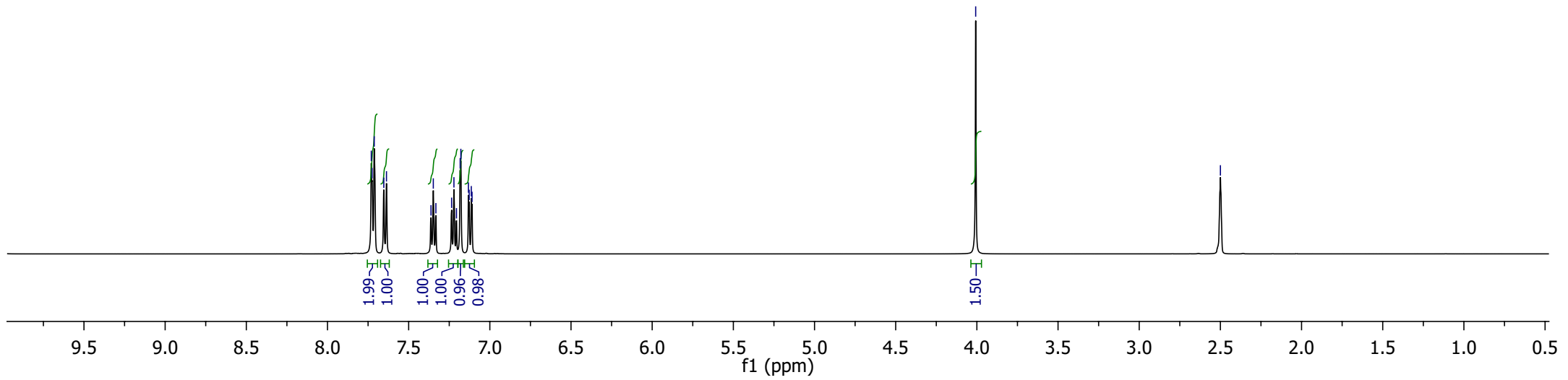
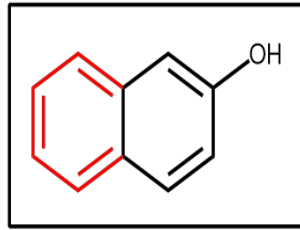


2k

7.73
7.73
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7.64
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7.11

4.01

2.50



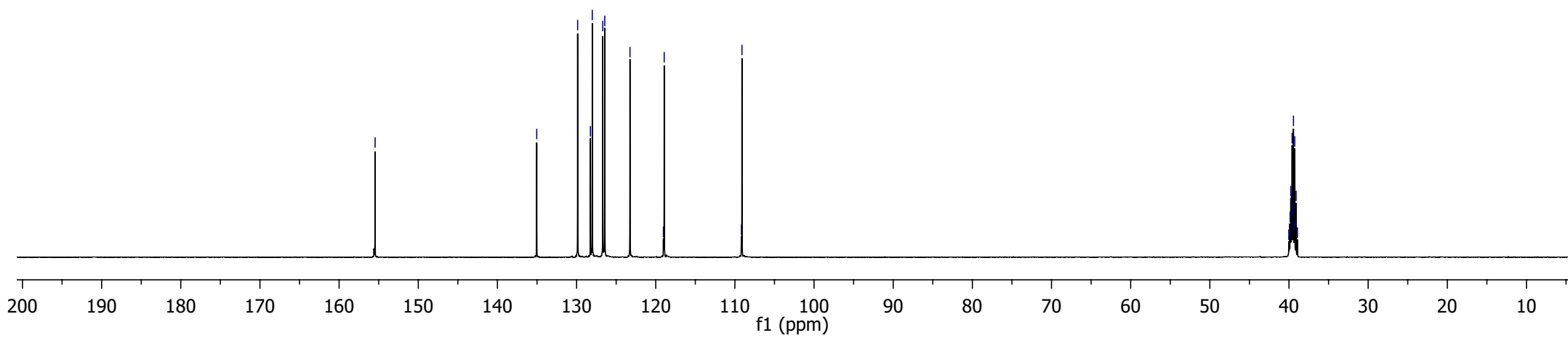
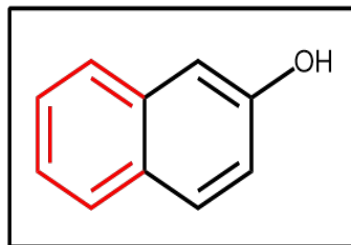
2k

—155.45

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—128.25
—128.02
—126.69
—126.44
—123.25
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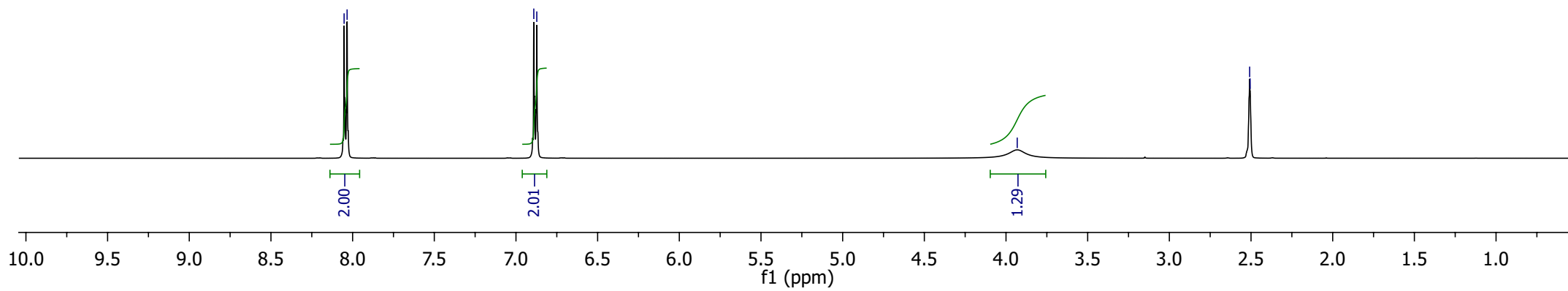
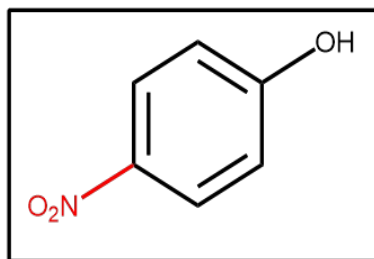
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39.10
38.94



8.05
8.036.89
6.87

— 3.93

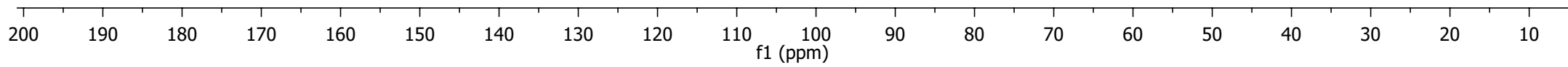
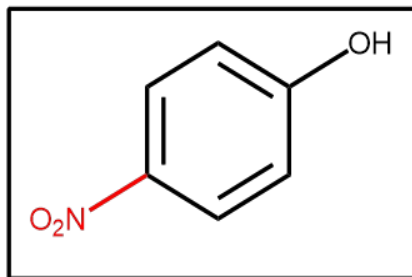
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2.51

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—140.06

—126.51

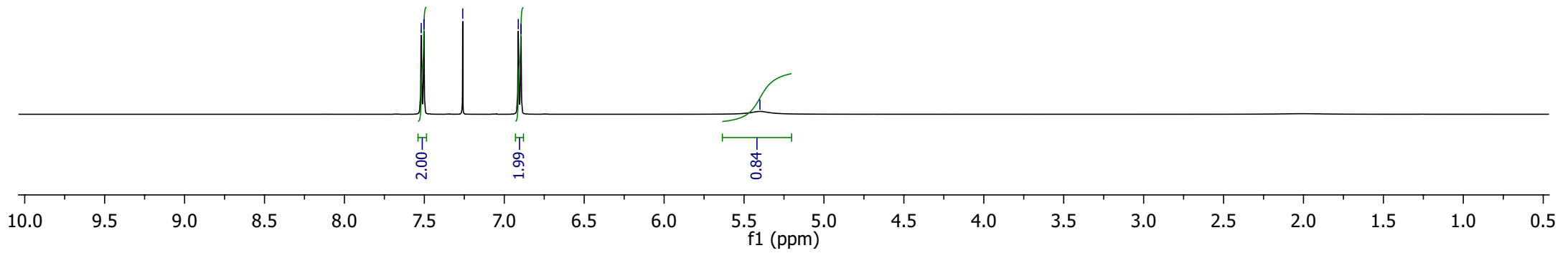
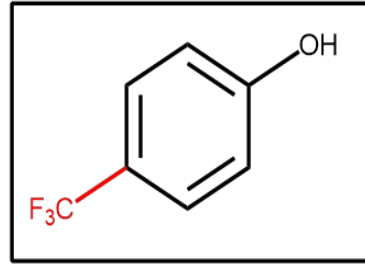
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39.31
39.23
39.06
38.89

2m

7.52
7.50
7.26
6.91
6.90

5.40

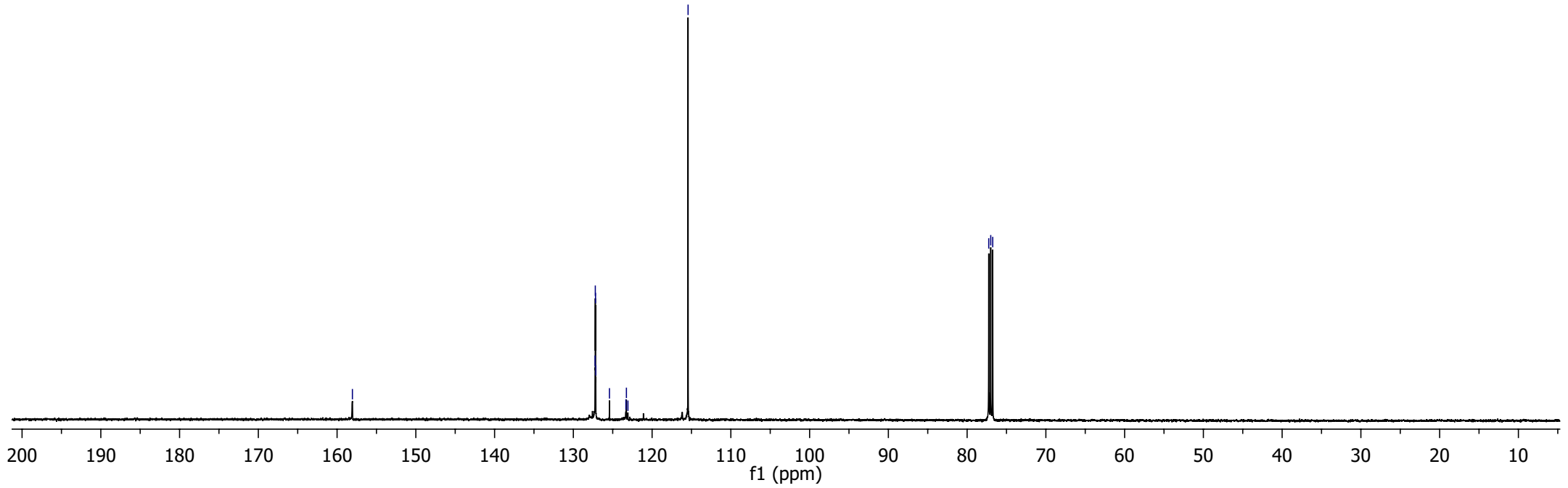
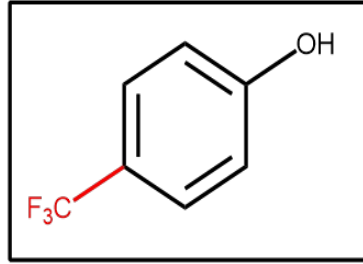


2m

—158.05

127.24
127.21
127.18
127.15
125.42
123.33
123.26
123.07
—115.43

77.25
77.00
76.75



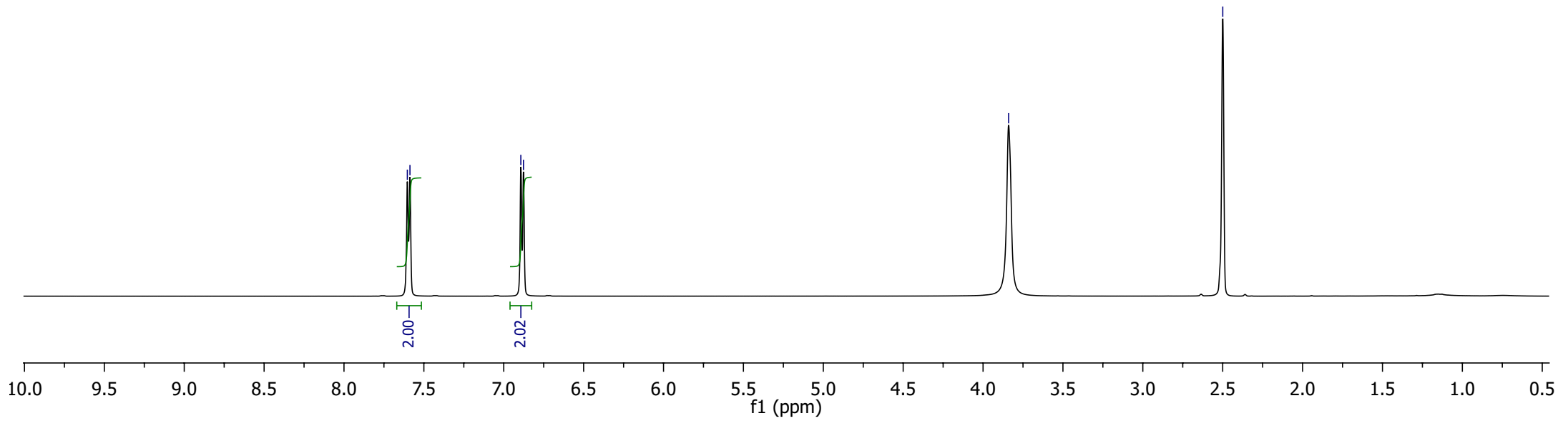
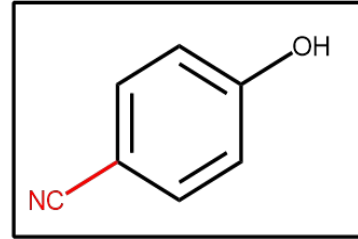
2n

7.60
7.59

6.89
6.88

3.84

2.50



2n

—161.77

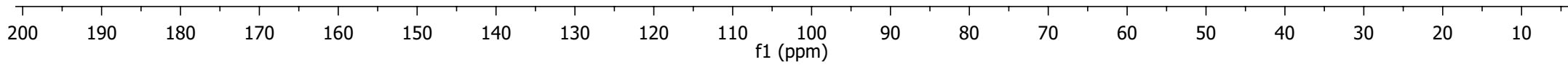
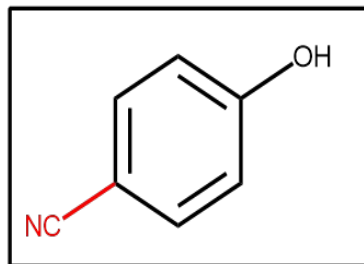
—134.72

—120.04

—116.80

—101.44

40.02
39.94
39.85
39.77
39.69
39.60
39.52
39.44
39.35
39.27
39.10
38.93



4a

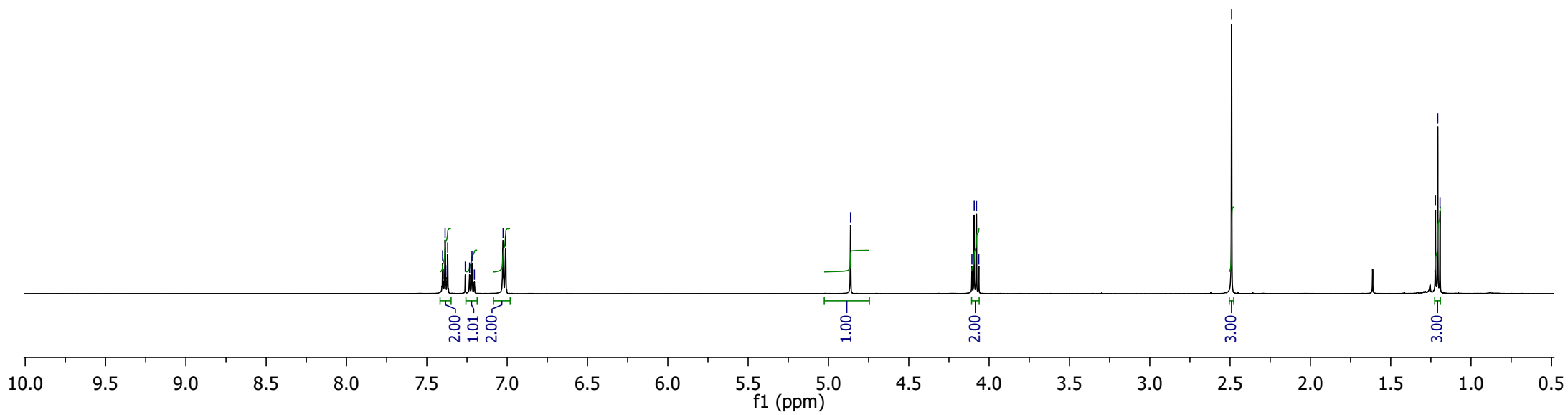
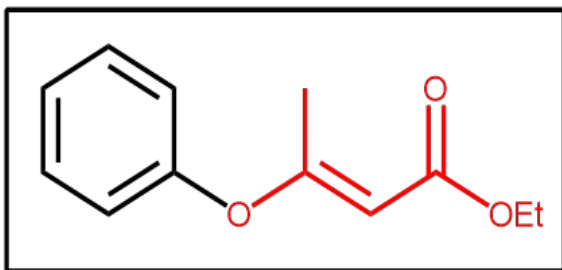
7.40
7.40
7.39
7.37
7.37
7.26
7.23
7.22
7.20
7.03
7.01

4.86

4.11
4.09
4.08
4.06

2.49

1.22
1.21
1.19



4a

—172.68

—167.65

—153.29

—129.94

—125.61

—121.56

—96.11

—77.25

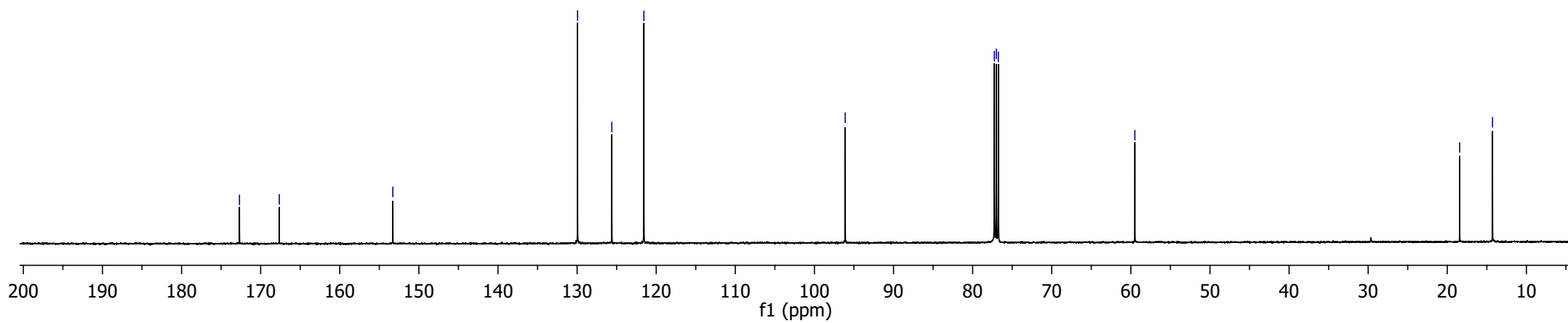
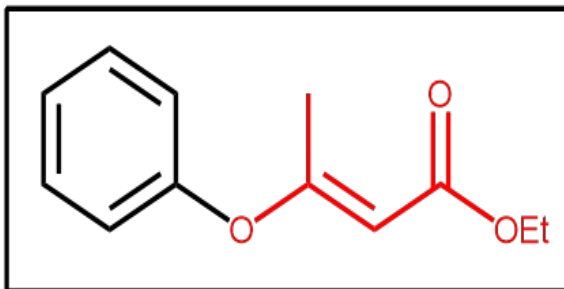
—77.00

—76.75

—59.49

—18.44

—14.28



4b

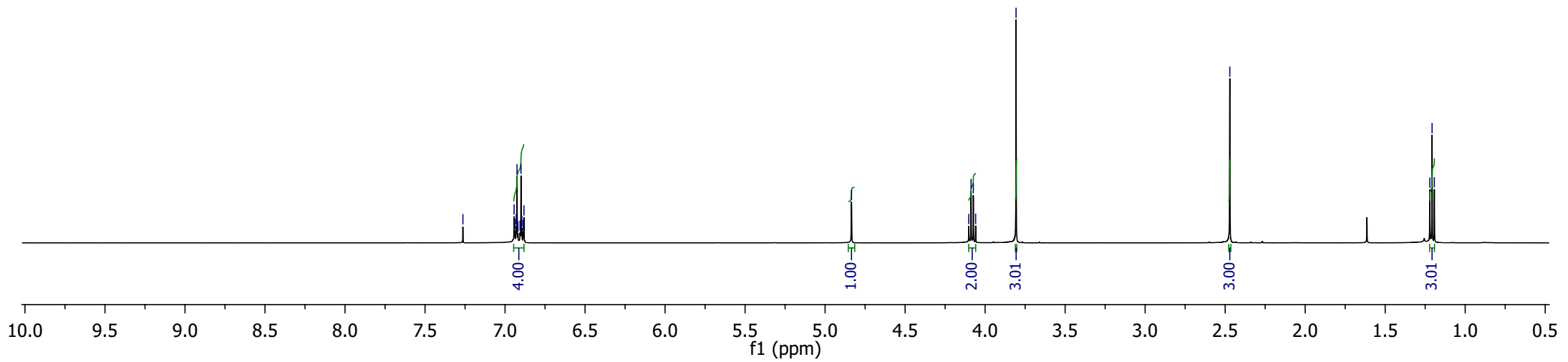
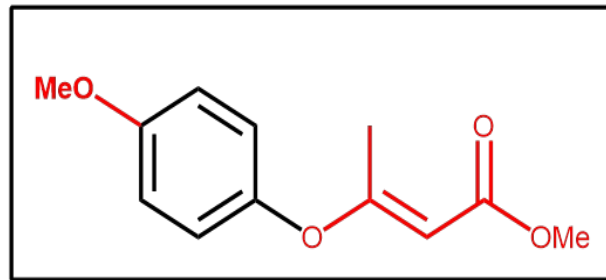
7.26
6.94
6.94
6.93
6.93
6.92
6.91
6.90
6.90
6.89
6.88

4.84

4.10
4.09
4.07
4.06
3.81

2.47

1.22
1.21
1.19



4b

—173.31

—167.75

—157.12

—146.67

—122.39

—114.90

—95.52

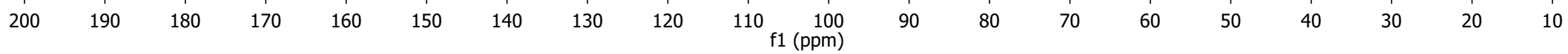
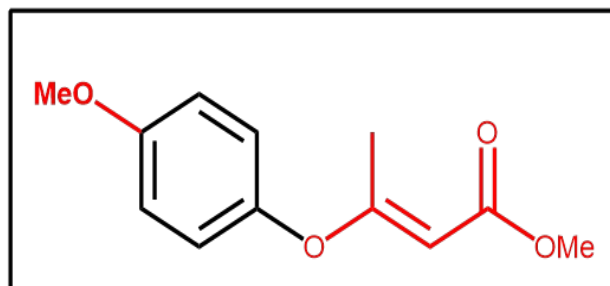
—77.25
—77.00
—76.75

—59.44

—55.56

—18.43

—14.30



4c

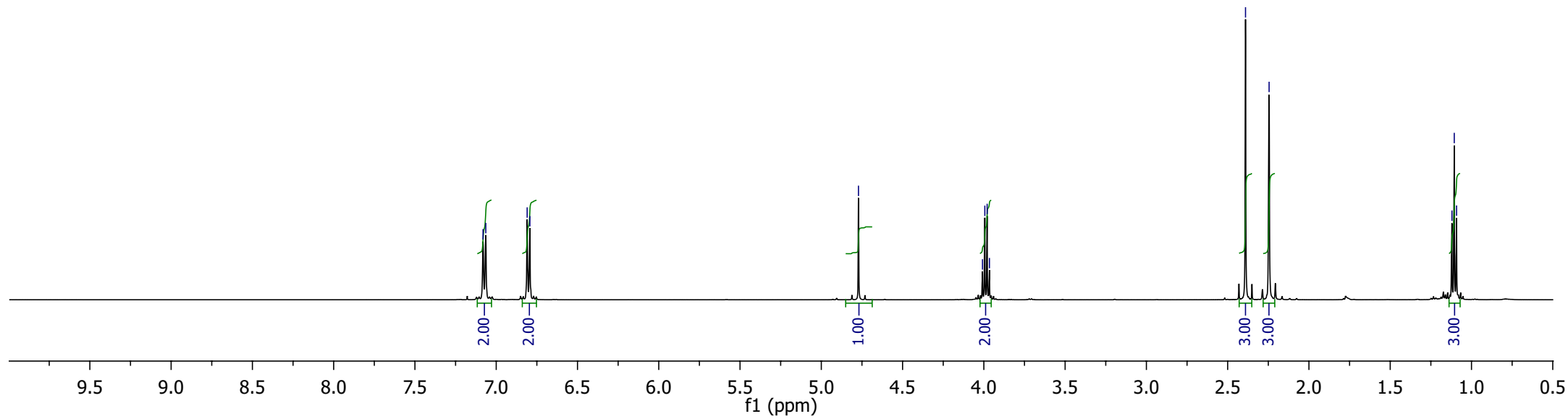
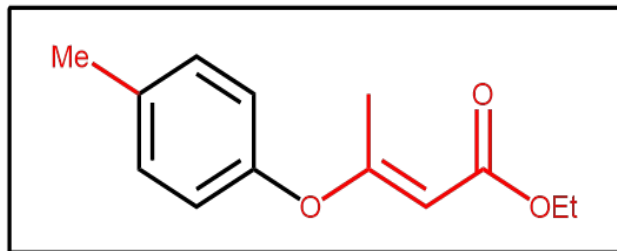
7.08
7.06
6.81
6.79

4.77

4.01
3.99
3.98
3.97

2.39
2.25

1.12
1.11
1.09



4c

—172.86

—167.59

—150.95

—135.13

—130.33

—121.17

—95.66

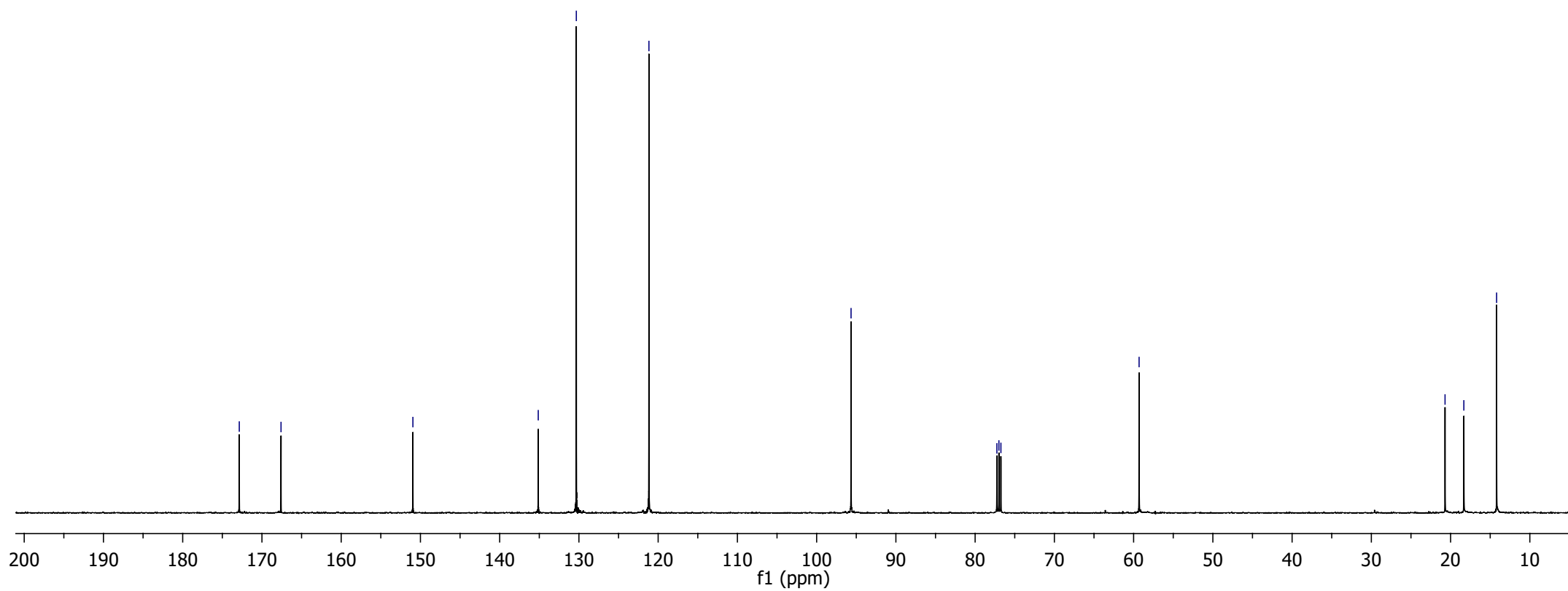
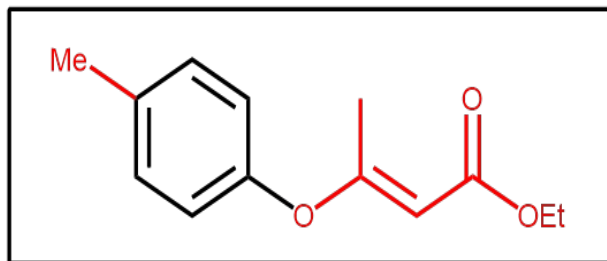
—77.25
—77.00
—76.75

—59.31

—20.70

—18.33

—14.19



4d

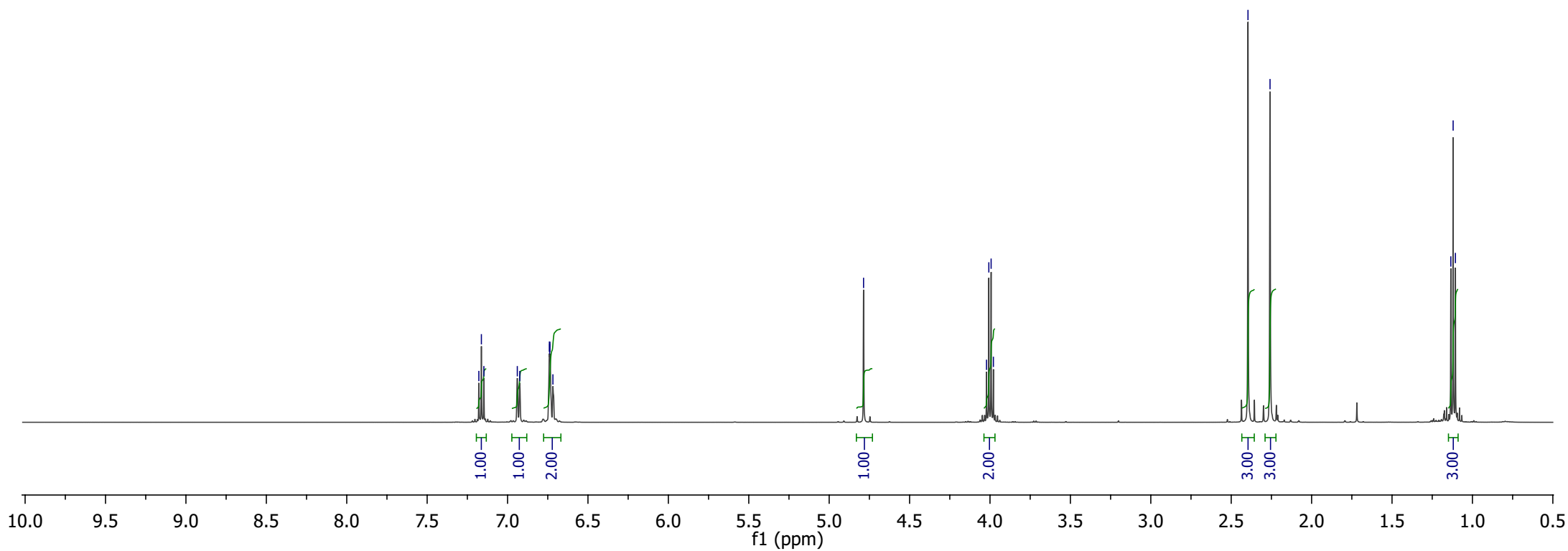
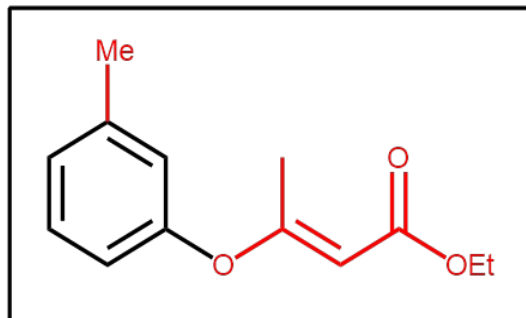
7.18
7.16
7.15
6.94
6.92
6.74
6.74
6.72

4.79

4.02
4.01
3.99
3.98

2.40
2.26

1.13
1.12
1.11



4d

—172.68

—167.61

—153.22

—140.10

—129.54

—126.32

—122.02

—118.40

—95.93

—77.25

—77.00

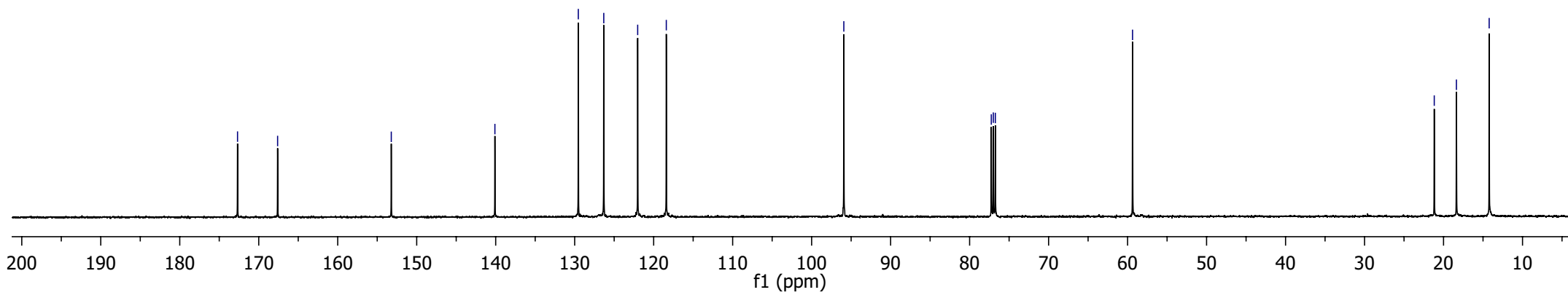
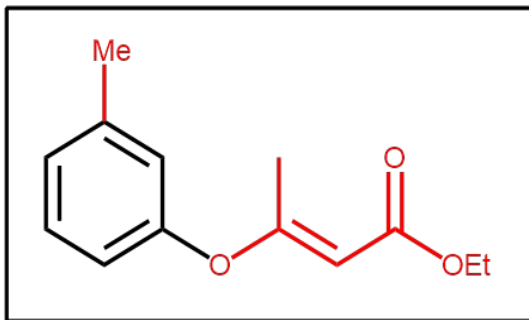
—76.75

—59.37

—21.17

—18.37

—14.22



4e

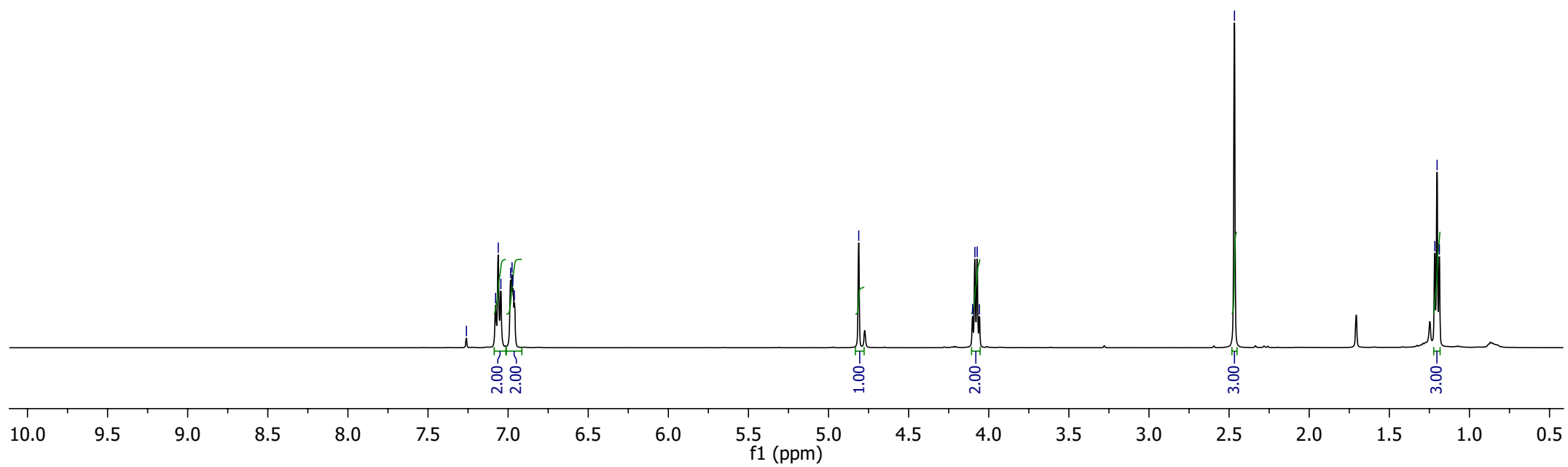
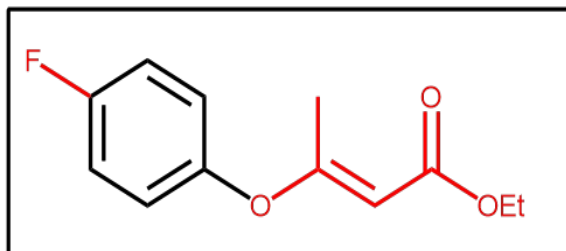
7.26
7.08
7.06
7.05
6.98
6.98
6.97
6.96

4.81

4.10
4.09
4.07
4.06

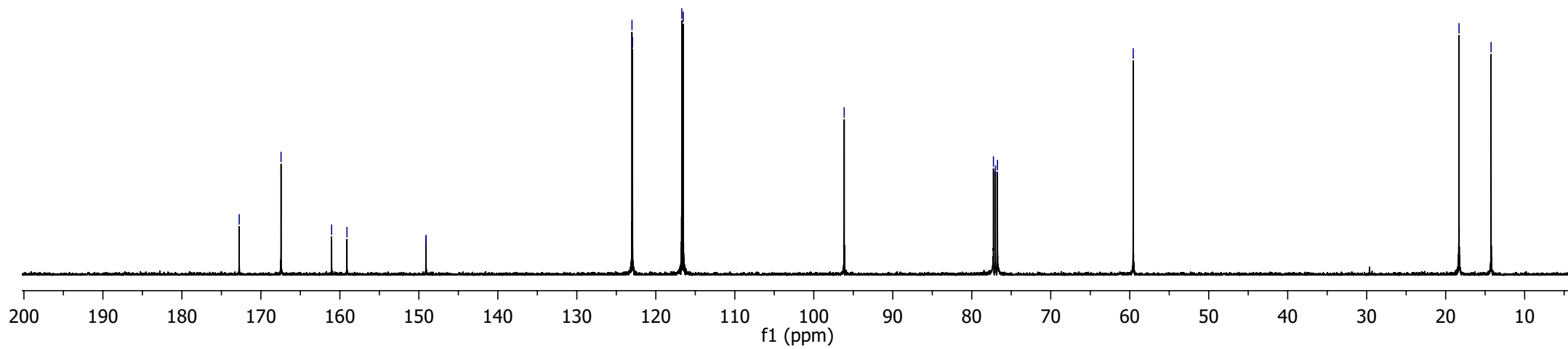
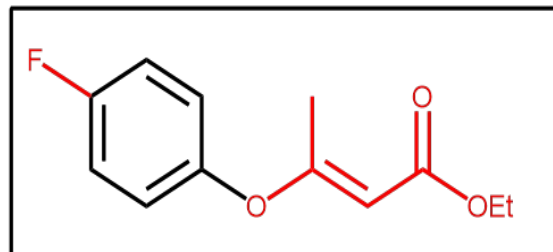
2.47

1.22
1.20
1.19

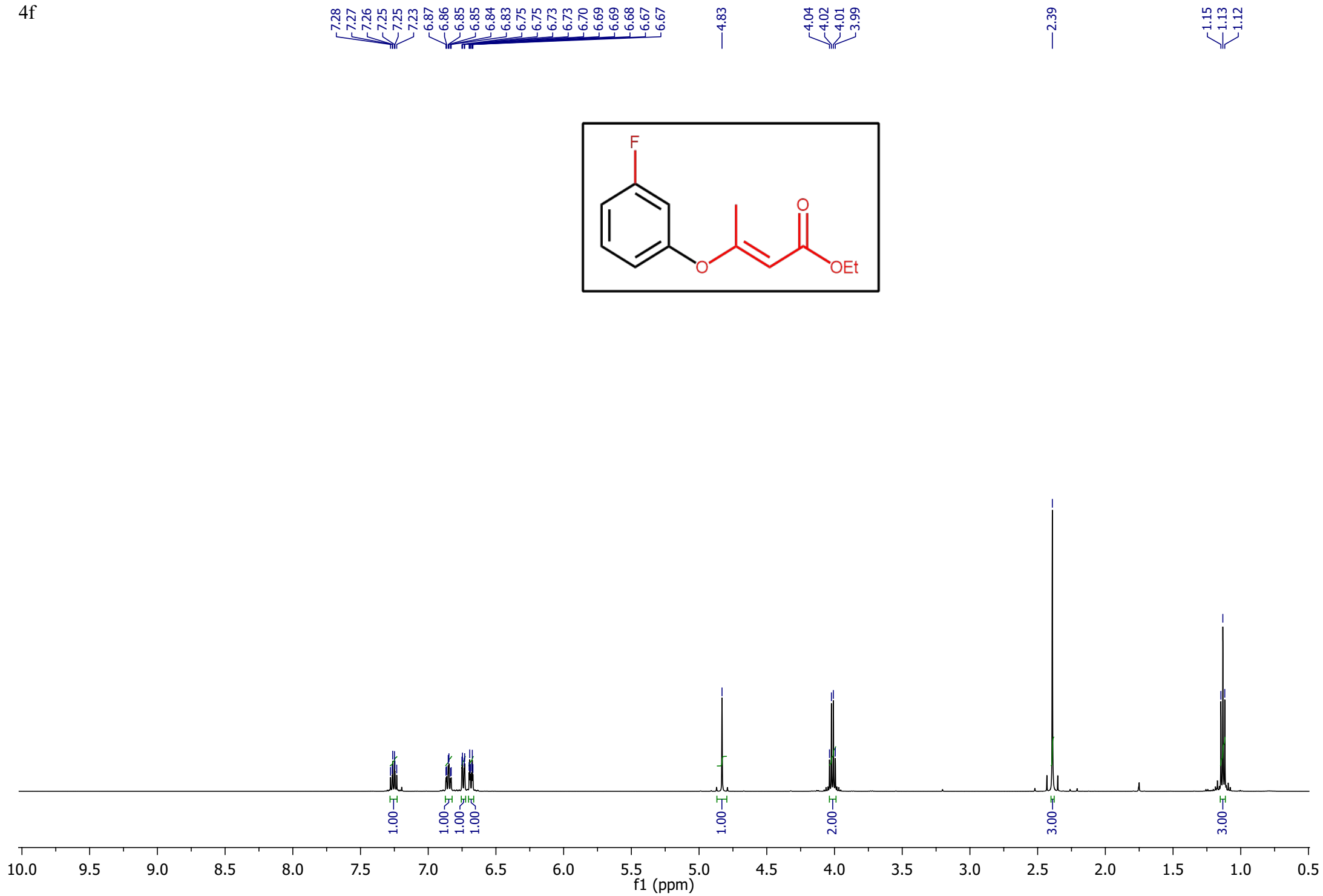


4e

—172.74
—167.45
—161.04
—159.10
—149.11
—149.09
—123.02
—122.95
—116.71
—116.53
—96.15
—77.25
—77.00
—76.75
—59.56
—18.31
—14.25



4f



4f

171.89
167.23
164.23
162.25

154.31
154.23

130.76
130.68

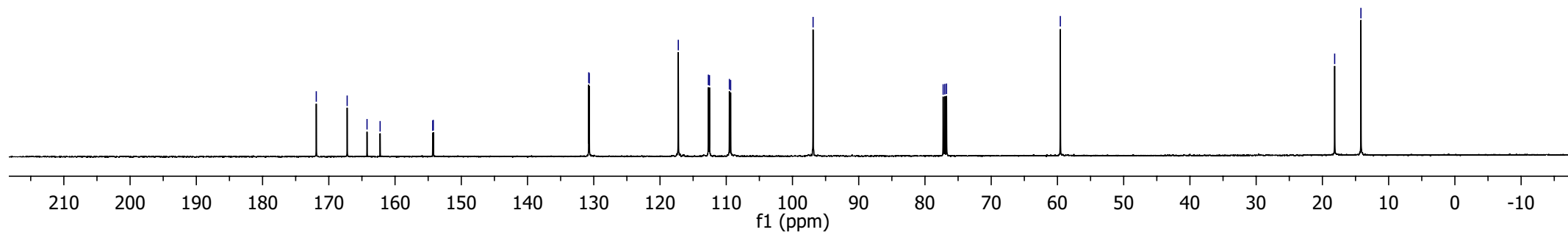
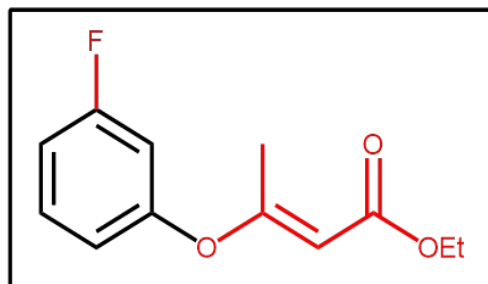
117.24
112.70
112.53
109.52
109.34

96.89

77.25
77.00
76.75

59.57

18.15
14.19



4g

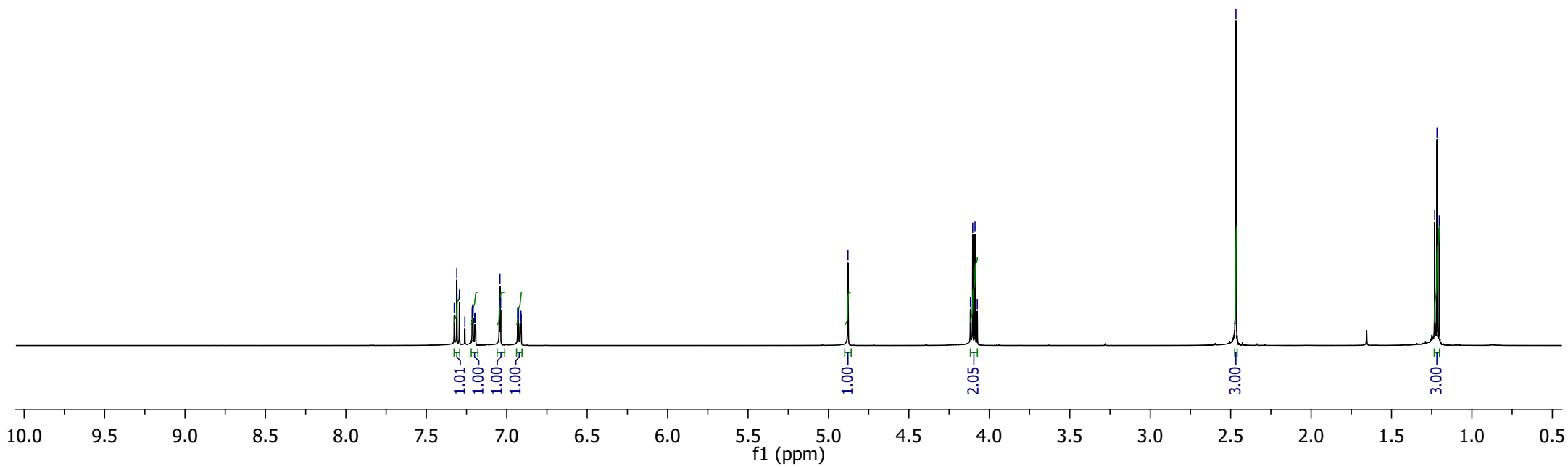
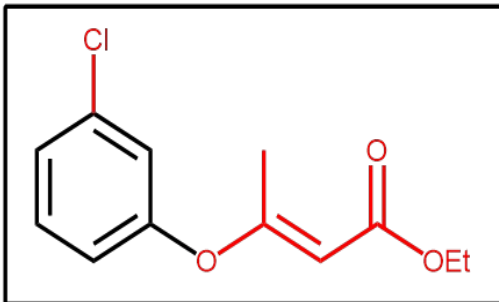
7.33
7.31
7.29
7.26
7.21
7.21
7.21
7.21
7.20
7.20
7.20
7.05
7.04
7.04
6.93
6.93
6.93
6.92
6.91
6.91
6.91

4.88

4.12
4.10
4.09
4.07

2.47

1.23
1.22
1.20



4g

—172.03

—167.28

—153.89

—135.18

—130.71

~125.92

~122.15

~119.89

—96.96

77.25

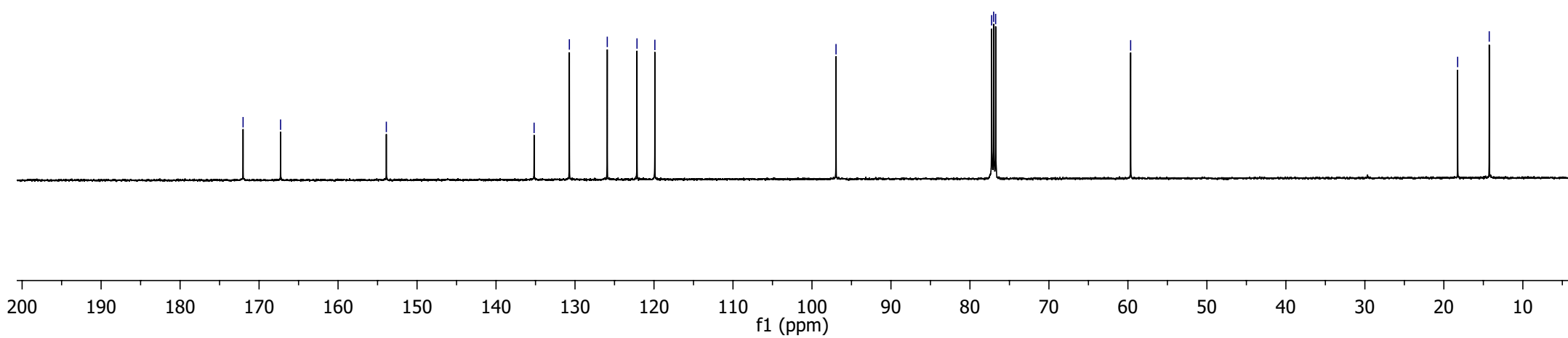
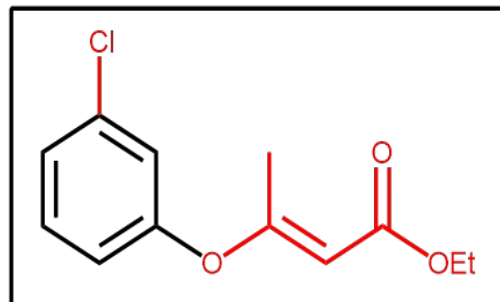
77.00

76.75

—59.65

—18.25

—14.25



4h

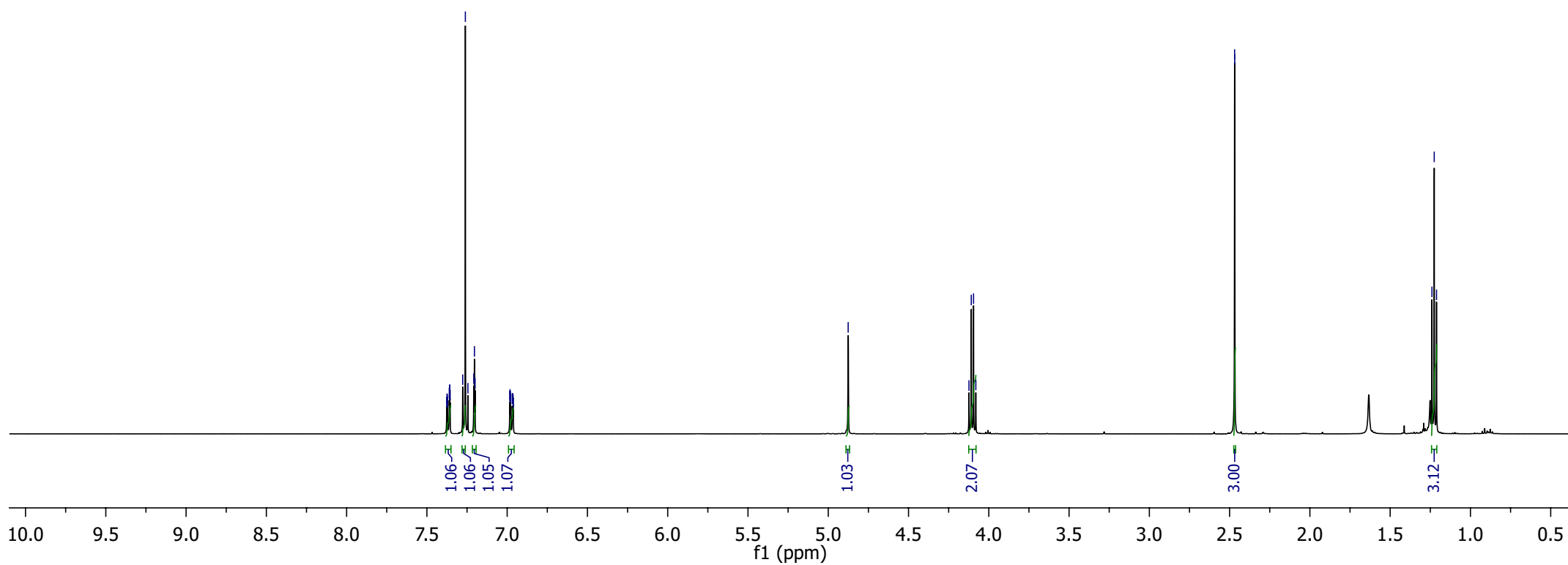
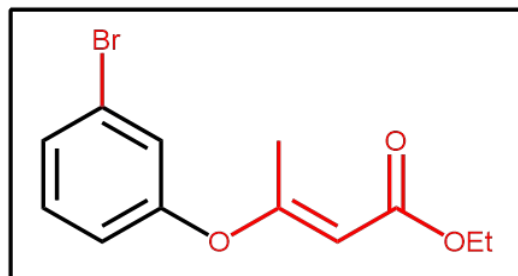
7.38
7.37
7.37
7.37
7.36
7.36
7.36
7.28
7.26
7.24
7.21
7.20
7.20
6.98
6.98
6.98
6.98
6.97
6.97
6.96
6.96

4.88

4.12
4.11
4.09
4.08

2.47
2.47

1.24
1.23
1.21



4h

—171.92

—167.12

—153.84

—130.93

—128.73

—124.91

—122.79

—120.27

—96.92

—77.25

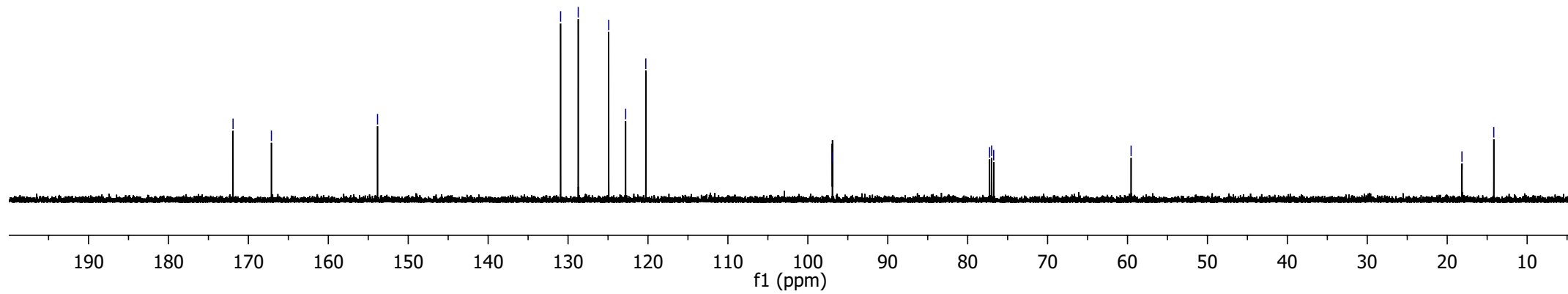
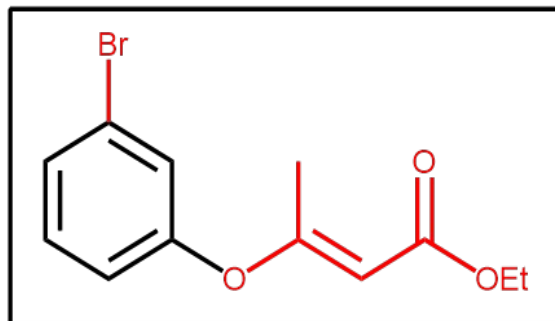
—77.00

—76.74

—59.55

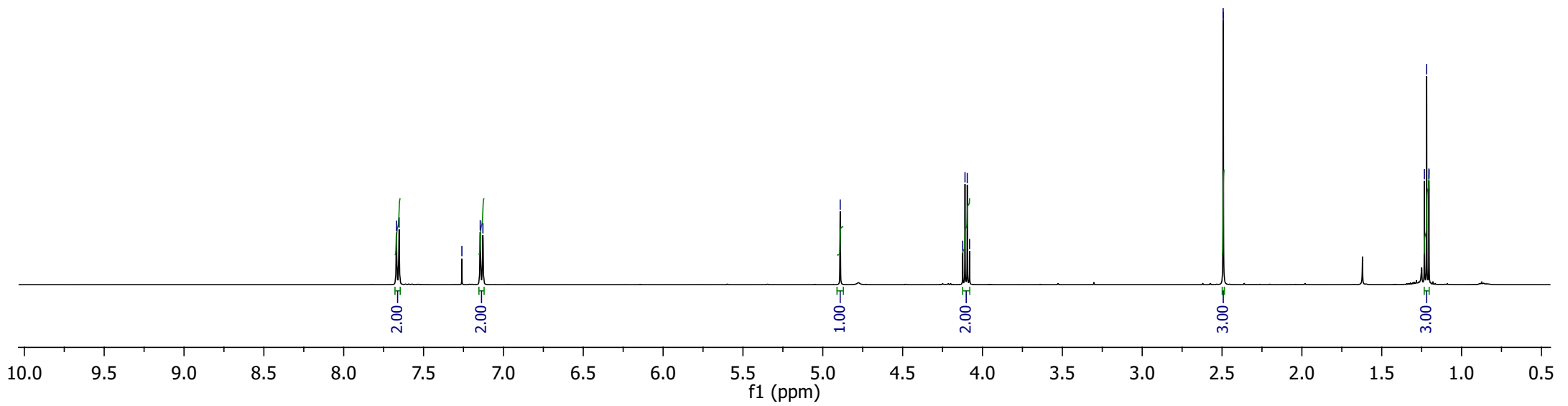
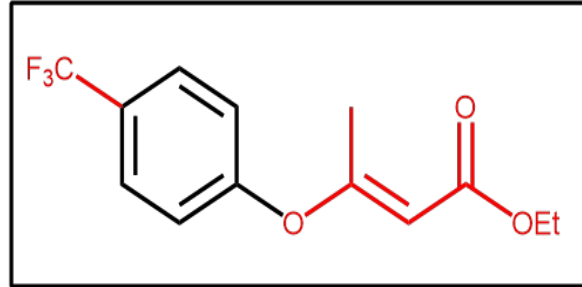
—18.16

—14.17



7.67
7.657.26
7.15
7.13

4.89

4.12
4.11
4.10
4.082.49
2.491.23
1.22
1.20

—171.63

—167.14

—156.05

127.93

127.67

127.45

127.42

127.39

127.36

124.90

122.74

121.84

—97.67

77.25

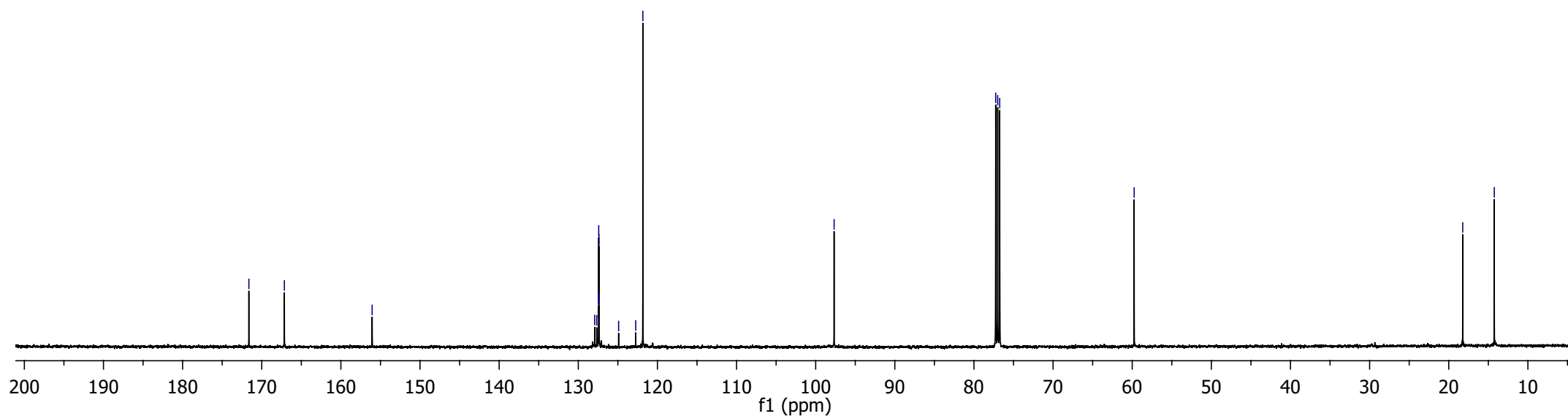
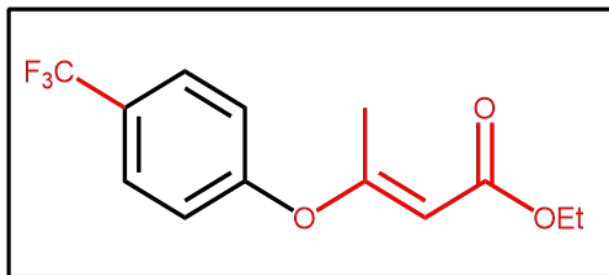
77.00

76.75

—59.75

—18.23

—14.25



4j

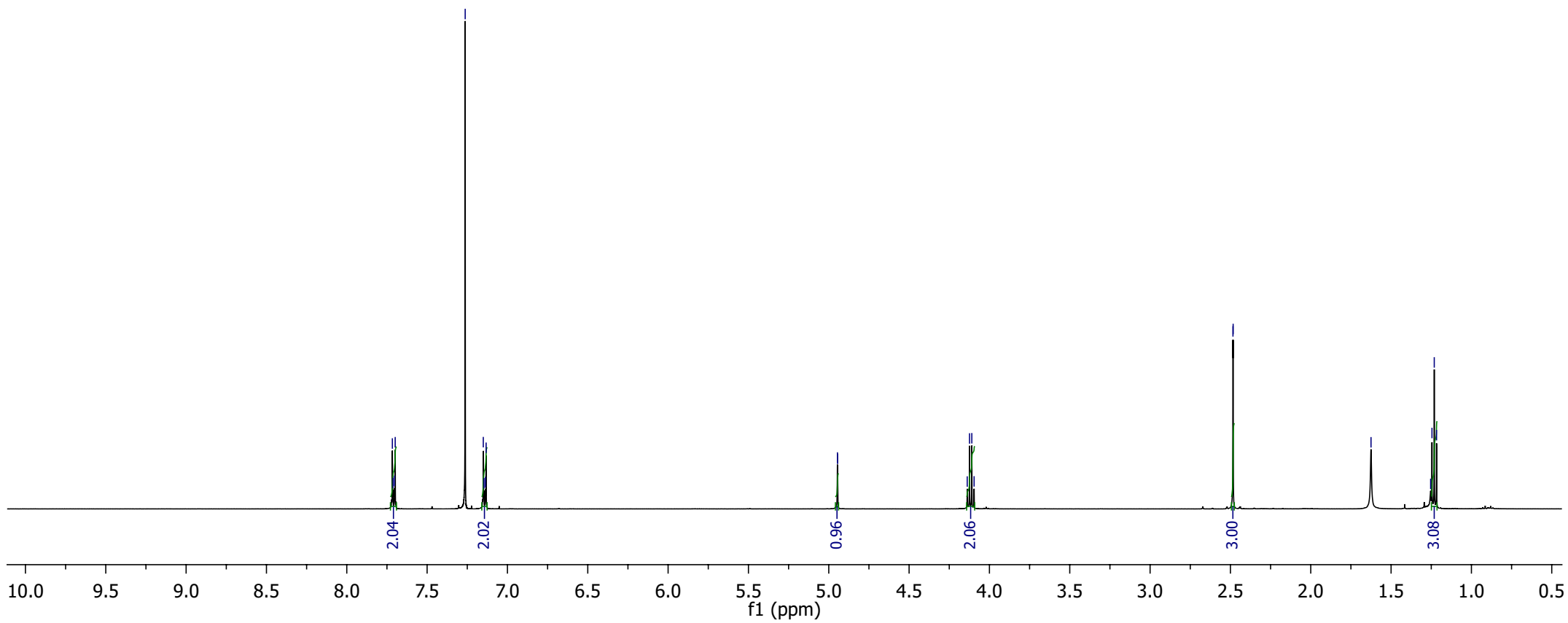
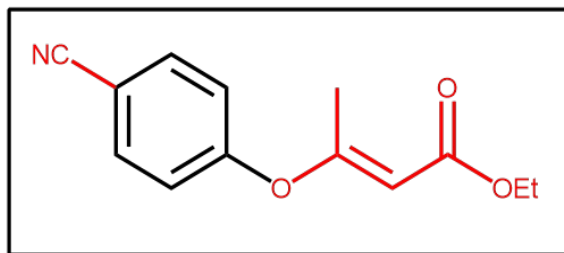
7.72
7.71
7.70
7.70
7.26
7.15
7.15
7.14
7.13

4.95
4.95

4.14
4.12
4.11
4.10

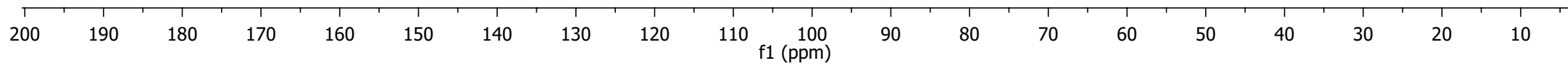
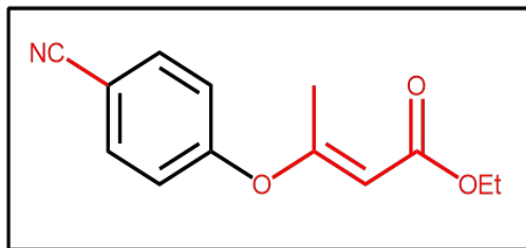
2.48
2.48

1.62
1.25
1.25
1.23
1.22



4j

—170.75 —166.71 —156.84 —134.20 —122.11 —118.03 —109.10 —98.66 —77.25 —77.00 —76.75 —59.74 —17.99 —14.11



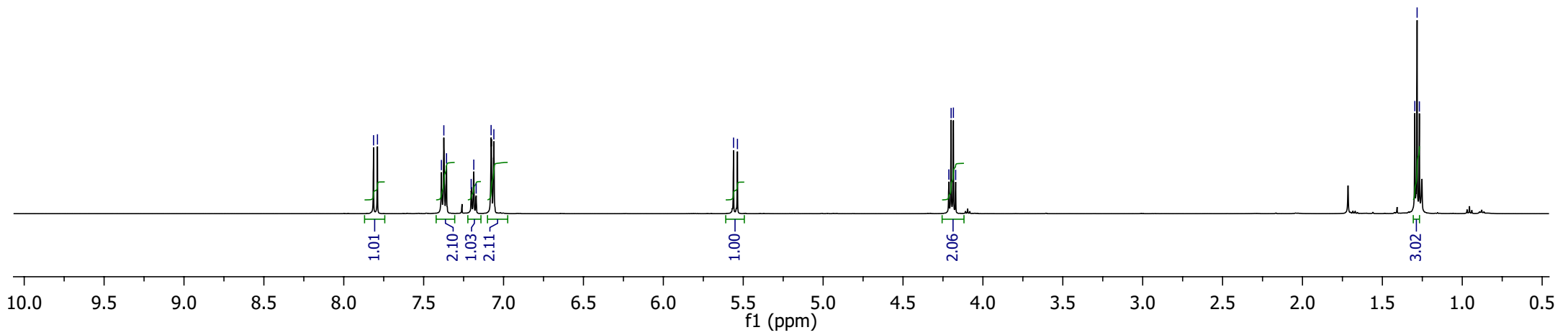
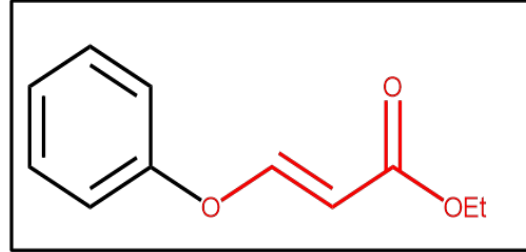
4k

7.81
7.79
7.39
7.37
7.36
7.20
7.19
7.17
7.08
7.06

5.56
5.54

4.21
4.20
4.18
4.17

1.30
1.28
1.27



4k

—167.27

—159.07

—155.87

—129.97

—124.98

—118.09

—102.17

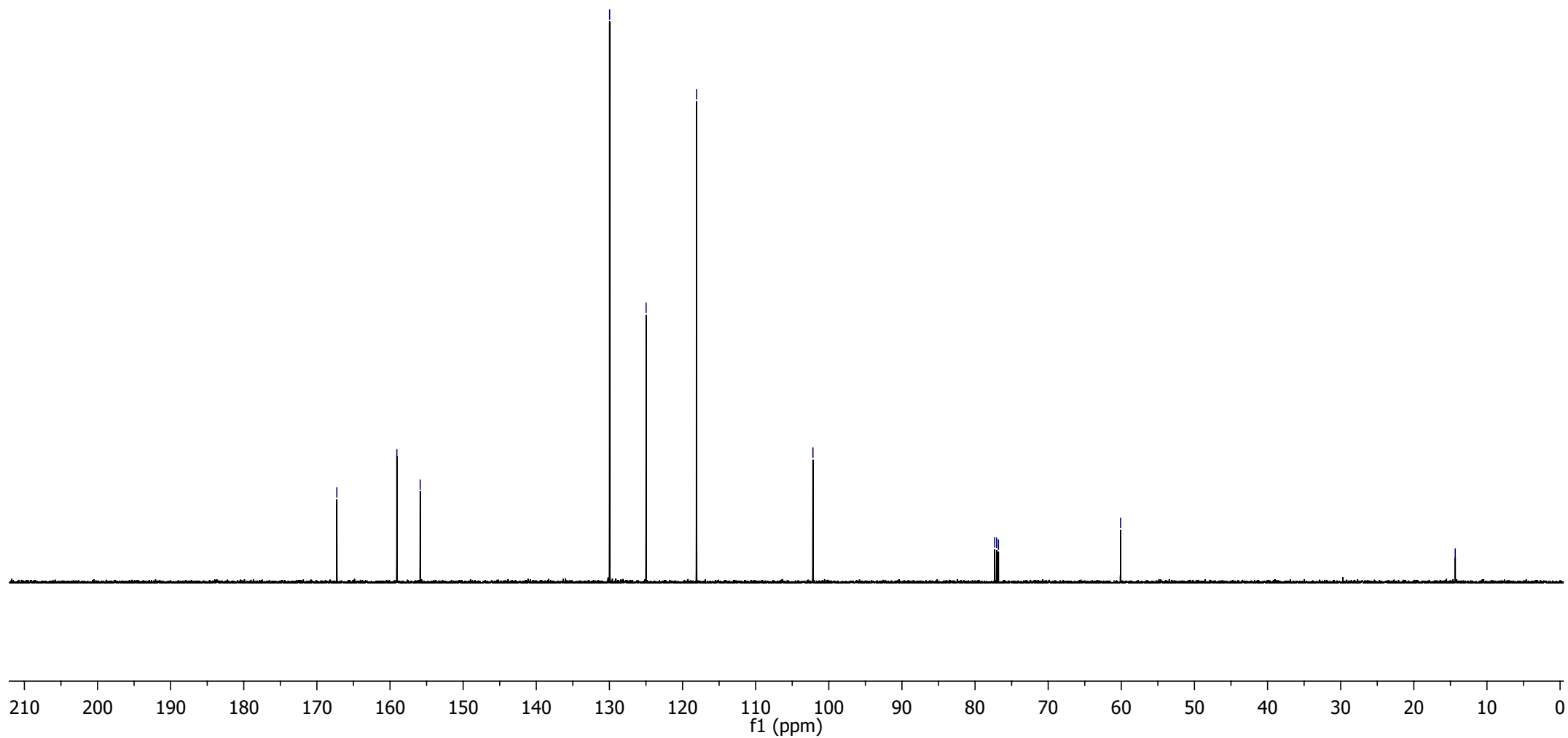
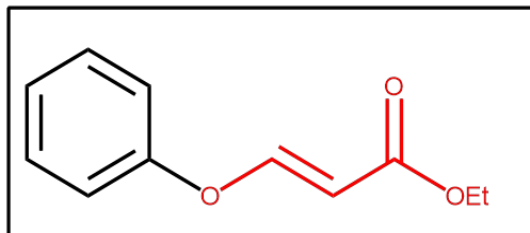
—77.31

—77.05

—76.80

—60.10

—14.34



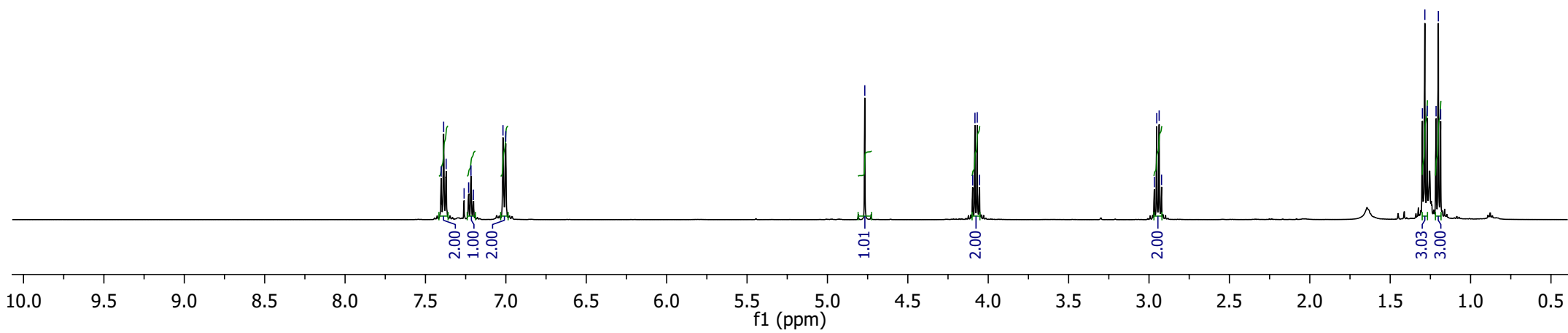
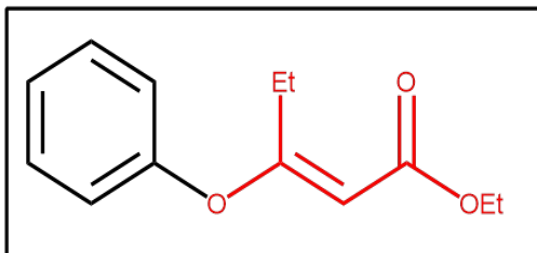
7.40
7.39
7.37
7.26
7.23
7.22
7.20
7.02
7.00

4.77

4.10
4.08
4.07
4.05

2.97
2.95
2.94
2.92

1.30
1.28
1.27
1.21
1.20
1.19



—177.65

—167.35

—153.50

—129.94

—125.55

—121.52

—95.13

—77.25

—77.00

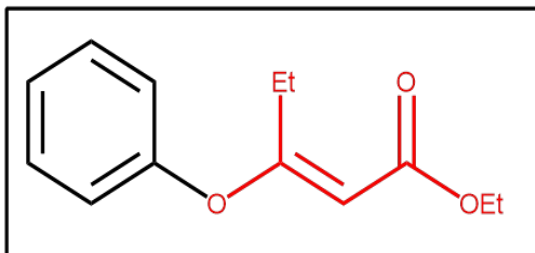
—76.75

—59.47

—24.90

—14.26

—11.84



200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

f1 (ppm)

4m

7.33
7.31
7.30
7.19
6.94
6.92

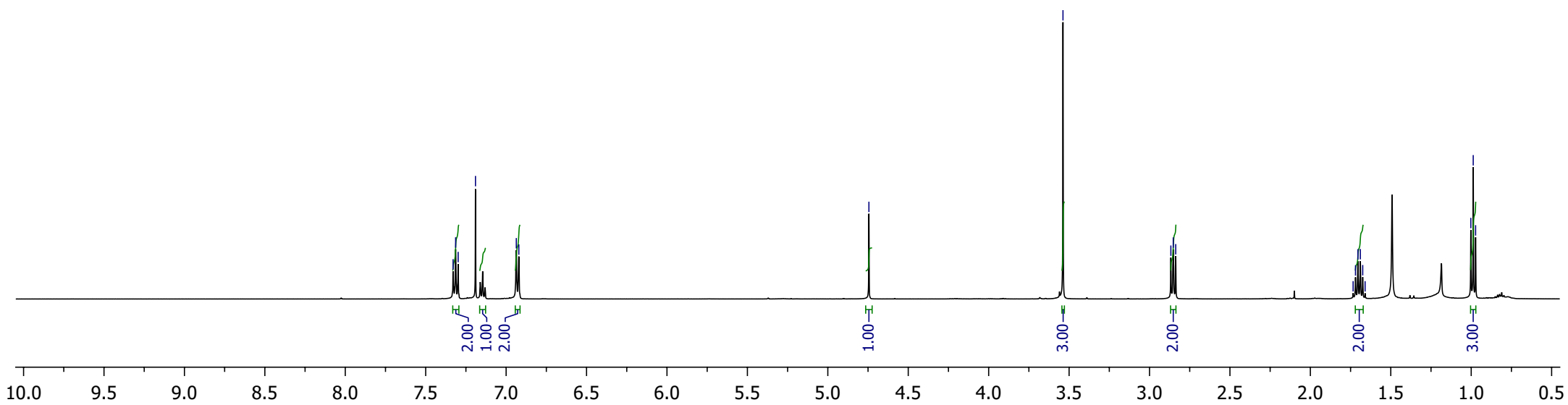
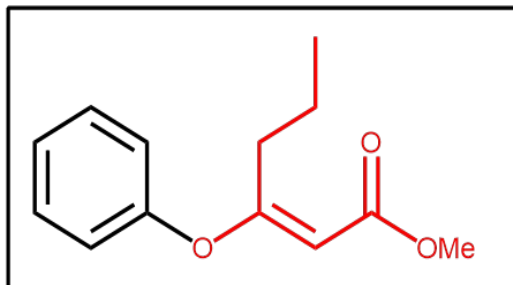
4.74

3.54

2.87
2.85
2.84

1.73
1.72
1.70
1.69
1.67
1.66

1.00
0.99
0.97



4m

—176.71

—167.82

—153.45

—129.99

—125.64

—121.56

—95.41

—77.28

—77.03

—76.78

—50.81

—33.11

—20.85

—13.78

