

**Visible light-mediated radical fluoromethylation *via* halogen atom transfer
activation of fluoroiodomethane**

Supplementary Information

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Table of Contents

1. General information – S3
2. Optimization studies and control reactions – S4
3. General procedures – S6
4. Products of carbonyl fluoromethylative amination – S8
5. Products of hydrofluoromethylation – S31
6. NMR spectra – S35

1. General information

All reactions were performed in oven-dried glassware under an atmosphere of N₂ using standard techniques. Dichloromethane used as the solvent in the carbonyl fluoromethylative amination reaction was dried using beads of 4 Å molecular sieves (MS) that were activated prior to use by prolonged heating under high vacuum (overnight, 180 °C, < 1 mbar), then it was degassed via either the freeze-pump-thaw method (three cycles) or via sparging with N₂ (two hours) and stored in a Schlenk flask under an atmosphere of N₂. Powdered 4 Å MS used in the reaction were activated prior to use by heating under high vacuum (approx. 20 min, > 200 °C, < 1 mbar). Ethanol (99.5%, Extra Dry, absolute, AcroSeal™, ACROS Organics) used as the solvent in the alkene hydrofluoromethylation reaction was purchased from Fisher Scientific and used as supplied. Commercially available amines, aldehydes and alkenes were used as supplied if sufficiently pure, otherwise they were purified either by distillation or flash column chromatography and stored under an atmosphere of N₂. Fluoroiodomethane (CAS No: 373-53-5) was purchased from Apollo Scientific, ABCR or SynQuest Laboratories and used as supplied. Tris(trimethylsilyl)silane, *tert*-butyldimethylsilyl trifluoromethanesulfonate and trimethylsilyl trifluoromethanesulfonate were purchased from Sigma Aldrich or Fluorochem and used as supplied. All other commercially available reagents and solvents were used as supplied unless otherwise stated.

Irradiation of visible light-mediated reactions was achieved using a Kessil A160WE Tuna Blue aquarium light (40 W, spectral tuning: max actinic blue, intensity: max) at a distance of approximately 4 cm. The temperature of the reaction mixture was maintained below 30 °C using a desk fan positioned approximately 20 cm above the reaction vessel.

Analytical thin-layer chromatography (TLC) was performed on Merck Kieselgel 60 F₂₅₄ 0.20 mm pre-coated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance ($\lambda_{\text{max}} = 254 \text{ nm}$), and/or by staining with aqueous KMnO₄. Flash column chromatography was performed using a Teledyne ISCO CombiFlash NextGen 300 instrument with RediSep Rf pre-packed silica gel columns and the indicated solvent system. Strong cation exchange chromatography (SCX) was performed using Thermo Scientific HyperSep SCX cartridges (1000 mg) with methanol (10 mL) to elute non-amine components, then 3 N ammonia in methanol (10 mL) to elute amine products.

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance III HD (400 MHz), Avance NEO (400 MHz) or Avance II+ (700 MHz) spectrometer. Chemical shifts (δ) for ¹H NMR spectra are reported in parts per million (ppm) relative to tetramethylsilane with the solvent resonance as the internal standard (CDCl₃ = 7.26 ppm). Data is reported as follows: chemical shift (multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, m = multiplet, br = broad), coupling constant, integration]. ¹³C NMR spectra are reported in parts per million (ppm) relative to tetramethylsilane with the solvent resonance as the internal standard (CDCl₃ = 77.16 ppm). ¹⁹F {¹H} NMR spectra are reported in ppm from CFC₃ and are uncorrected. ¹H NMR analysis of crude reaction mixtures was determined with reference to 1,1,2,2-tetrachloroethane as an internal standard.

Infrared spectra (FT-IR) were recorded using a Nicolet Summit PRO FTIR spectrometer equipped with an ATR sampling accessory and analyzed as thin films, with absorption maxima (ν_{max}) quoted in wavenumbers (cm⁻¹).

High resolution mass spectra (HRMS) were recorded on a Micromass Q-TOF spectrometer or a Shimadzu Q-TOF LCMS-9030 spectrometer using electrospray ionization (ESI) techniques at the Department of Chemistry, University of Cambridge.

2. Optimization studies and control reactions

Table S1 | Optimization of reagent equivalents

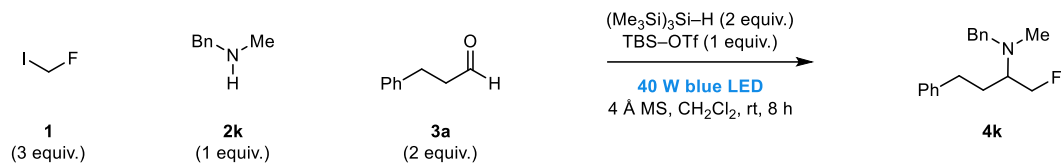
Entry	1 / equiv.	(Me ₃ Si) ₃ Si-H / equiv.	Additive (/ equiv.)	Yield ^a
1	1.0	2.0	TBS-OTf (1.0)	36%
2	1.5	2.0	TBS-OTf (1.0)	55%
3	2.0	2.0	TBS-OTf (1.0)	70%
4	2.5	2.0	TBS-OTf (1.0)	78%
5	3.0	2.0	TBS-OTf (1.0)	90%
6	3.0	1.5	TBS-OTf (1.0)	65%
7	3.0	1.0	TBS-OTf (1.0)	38%
8	3.0	2.0	TBS-OTf (2.0)	73%
9	3.0	2.0	TMS-OTf (1.0)	83%
10	3.0	2.0	TMS-OTf (2.0)	75%
11	3.0	2.0	—	65%

a) Yields determined by ¹H NMR analysis of crude reaction mixtures after work-up with 1,1,2,2-tetrachloroethane as internal standard.

Table S2 | Optimization of reaction time

Entry	Time / h	Yield ^a
1	2	28%
2	4	56%
3	6	77%
4	8	90%
5	14	89%

a) Yields determined by ¹H NMR analysis of crude reaction mixtures after work-up with 1,1,2,2-tetrachloroethane as internal standard.

Table S3 | Control reactions

Entry	Deviation from above	Yield ^a
1	none	90%
2	no 4 Å MS	47%
3	no light	0%
4	455 nm longpass filter	50%
5	420 nm longpass filter	67%
6 ^b	no light, AIBN, 70 °C	56%
7	TEMPO (3.0 equiv.)	0%

a) Yields determined by ¹H NMR analysis of crude reaction mixtures after work-up with 1,1,2,2-tetrachloroethane as internal standard. b) AIBN = azobisisobutyronitrile (0.2 equiv.)

3. General procedures

General procedure A – carbonyl fluoromethylative amination

An oven-dried glass vial (Biotage microwave reaction vial, 2.0–5.0 mL or 10–20 mL) was charged with a magnetic stir bar (PTFE, 12 mm) and freshly-activated powdered 4 Å MS (50 mg mL⁻¹ of solvent). In instances where solid amines or aldehydes were used, these were added at this stage. The vial was sealed with a gas-tight septum and was evacuated and backfilled with N₂ (three cycles). Dry dichloromethane (0.017–0.067 M) was added, followed by addition of amine (0.1–0.2 mmol, 1 equiv), aldehyde (1.2–3 equiv), fluoroiodomethane (3 equiv), tris(trimethylsilyl)silane (2–3 equiv) and *tert*-butyldimethylsilyl trifluoromethanesulfonate (1–3 equiv) via microsyringe. The reaction mixture was irradiated using a Kessil A160WE Tuna Blue aquarium light (40 W, spectral tuning: max actinic blue, intensity: max) at a distance of approximately 5 cm with vigorous stirring (800–1000 rpm) for 8 hours. A desk fan positioned approximately 20 cm above the reaction vessel was used for cooling. The reaction mixture was filtered through a sintered glass filter, washing with dichloromethane, and the filtrate was concentrated under vacuum. The resulting oily residue was washed with 40–60 °C petroleum ether (3 × 10 mL) to remove silane by-products, redissolved in dichloromethane (10 mL), and neutralized with NaOH (10 mL, 10% aq.). The resulting biphasic mixture was transferred to a separating funnel, the organic phase was collected, and the aqueous phase was further extracted with dichloromethane (2 × 10 mL). The combined organic phases were dried over anhydrous MgSO₄, filtered, and concentrated under vacuum. The crude material was purified by flash column chromatography on silica gel and/or strong cation exchange chromatography to afford the desired product.

Deviation A:

For some hindered amines or those containing proximal electron-withdrawing groups (where iminium formation is less favoured), pre-heating was employed. The amine, aldehyde and 4 Å MS were added to a microwave vial which was sealed with a gas-tight septum and evacuated and backfilled with N₂ (three cycles). Dichloromethane was added and the mixture heated at 80 °C for 3 hours. The vial was cooled to room temperature, the remaining reagents (fluoroiodomethane, silane, TBSOTf) were added via microsyringe and the reaction was irradiated as described above.

Deviation B:

Performed as described in the general procedure but without TBSOTf. This deviation was used when acid-sensitive moieties were present.

Deviation C:

Performed as described in the general procedure but without molecular sieves and using TMSOTf instead of TBSOTf. This deviation was used with benzaldehyde coupling partners.

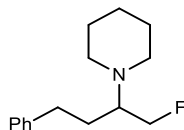
Deviation D:

For the synthesis of α -tertiary amino ester **4z**, pre-stirring with catalytic propionic acid was employed. The amine, α -keto ester and 4 Å MS were added to a microwave vial which was sealed with a gas-tight septum and evacuated and backfilled with N₂ (three cycles). Propionic acid (0.2 equiv) and dichloromethane were added, and the mixture was stirred at room temperature for 3 hours. The remaining reagents (fluoroiodomethane, silane, TBSOTf) were added via microsyringe and the reaction was irradiated as described above.

General procedure B – hydrofluoromethylation of electron-deficient alkenes

An oven-dried glass vial (Biotage microwave reaction vial, 0.5–2.0 mL or 2.0–5.0 mL) was charged with a magnetic stir bar (PTFE, 12 mm). In instances where solid alkene substrates were used, these were added at this stage. The vial was sealed with a gas-tight septum and was evacuated and backfilled with N₂ (three cycles). Dry ethanol or *tert*-butanol (0.2 M) was added, followed by addition of alkene (0.2 mmol, 1 equiv), fluoroiodomethane (2–3 equiv) and tris(trimethylsilyl)silane (2–3 equiv) via microsyringe. The reaction mixture was stirred vigorously (800–1000 rpm) and irradiated using a 40 W blue LED lamp (Kessil A160WE Tuna Blue) at a distance of approx. 5 cm for 8 h. A desk fan positioned approx. 20 cm above the reaction vessel was used for cooling. The reaction mixture was concentrated under vacuum and the crude material was purified by flash column chromatography on silica gel to afford the desired product.

4. Products of carbonyl fluoromethylative amination



1-(1-Fluoro-4-phenylbutan-2-yl)piperidine (4a). Prepared according to general procedure A using piperidine (20 μL , 0.2 mmol), hydrocinnamaldehyde (53 μL , 0.4 mmol), fluoroiodomethane (40 μL , 0.6 mmol), tris(trimethylsilyl)silane (123 μL , 0.4 mmol), *tert*-butyldimethylsilyl trifluoromethanesulfonate (92 μL , 0.4 mmol) and 4 Å MS (300 mg) in 12 mL dichloromethane. The crude reaction mixture was purified by flash column chromatography (0–30% ethyl acetate in 40–60 °C petroleum ether) to afford the product as a colourless oil (40 mg, 86%).

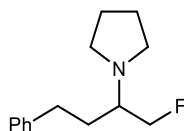
^1H NMR (400 MHz, CDCl_3) δ 7.33 – 7.25 (m, 2H), 7.24 – 7.14 (m, 3H), 4.63 – 4.40 (m, 2H), 2.79 – 2.57 (m, 5H), 2.49 (ddd, $J = 10.9, 6.7, 3.7$ Hz, 2H), 1.93 – 1.78 (m, 1H), 1.76 – 1.65 (m, 1H), 1.65 – 1.50 (m, 4H), 1.46 (q, $J = 5.4$ Hz, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 142.4, 128.6, 128.5, 128.4, 125.9, 83.7 (d, $J = 172.1$ Hz), 63.2 (d, $J = 17.5$ Hz), 50.5, 32.9, 32.9, 29.1 (d, $J = 6.6$ Hz), 26.9, 25.1.

^{19}F { ^1H } NMR (376 MHz, CDCl_3) δ –224.2.

IR (film, cm^{-1}) 3026, 2931, 2851, 2803, 1602, 1495, 1453, 1442, 1346, 1310, 1274, 1118, 1029, 960, 749, 699.

HRMS m/z (ESI) calcd for $\text{C}_{15}\text{H}_{23}\text{FN}$ [$\text{M}+\text{H}$] $^+$ 236.1809; found 236.1816.



1-(1-Fluoro-4-phenylbutan-2-yl)pyrrolidine (4b). Prepared according to general procedure A using pyrrolidine (17 μL , 0.2 mmol), hydrocinnamaldehyde (53 μL , 0.4 mmol), fluoroiodomethane (40 μL , 0.6 mmol), tris(trimethylsilyl)silane (123 μL , 0.4 mmol), *tert*-butyldimethylsilyl trifluoromethanesulfonate (46 μL , 0.2 mmol) and 4 Å MS (300 mg) in 6 mL dichloromethane. The crude reaction mixture was purified by flash column chromatography (0–20% ethyl acetate in 40–60 °C petroleum ether) to afford the product as a colourless oil (30 mg, 67%).

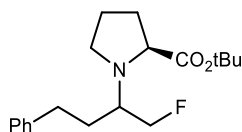
^1H NMR (400 MHz, CDCl_3) δ 7.33 – 7.26 (m, 2H), 7.21 (d, $J = 7.3$ Hz, 3H), 4.58 (dd, $J = 47.6, 4.3$ Hz, 2H), 2.78 (ddd, $J = 13.7, 10.2, 5.9$ Hz, 1H), 2.73 – 2.56 (m, 6H), 2.01 – 1.84 (m, 2H), 1.84 – 1.70 (m, 4H).

^{13}C NMR (101 MHz, CDCl_3) δ 142.2, 128.5, 128.4, 126.0, 84.1 (d, $J = 171.5$ Hz), 62.0 (d, $J = 17.9$ Hz), 51.0 (d, $J = 1.2$ Hz), 32.2, 30.9 (d, $J = 6.1$ Hz), 23.5.

^{19}F { ^1H } NMR (376 MHz, CDCl_3) δ –226.0.

IR (film, cm^{-1}) 3026, 2960, 2874, 2796, 1496, 1454, 1356, 1262, 1015, 748, 699.

HRMS m/z (ESI) calcd for $\text{C}_{14}\text{H}_{21}\text{FN}$ [$\text{M}+\text{H}$] $^+$ 222.1653; found 222.1657.



tert-Butyl (1-fluoro-4-phenylbutan-2-yl)-L-prolinate (4c). Prepared according to general procedure A, deviation A using *L*-proline *tert*-butyl ester hydrochloride (42 mg, 0.2 mmol), hydrocinnamaldehyde (53 μ L, 0.4 mmol), fluoroiodomethane (40 μ L, 0.6 mmol), tris(trimethylsilyl)silane (123 μ L, 0.4 mmol), *tert*-butyldimethylsilyl trifluoromethanesulfonate (92 μ L, 0.4 mmol) and 4 Å MS (300 mg) in 8 mL dichloromethane. The crude reaction mixture (4:1 d.r. by ^1H NMR) was purified by flash column chromatography (0–15% ethyl acetate in 40–60 °C petroleum ether) to afford the product as a colourless oil (39 mg, 60%, isolated as a single diastereomer).

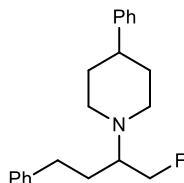
^1H NMR (400 MHz, CDCl_3) δ 7.32 – 7.25 (m, 2H), 7.23 – 7.15 (m, 3H), 4.74 – 4.35 (m, 2H), 3.71 – 3.48 (m, 1H), 3.25 – 2.97 (m, 2H), 2.89 – 2.61 (m, 3H), 2.12 – 1.97 (m, 1H), 1.98 – 1.86 (m, 2H), 1.86 – 1.71 (m, 3H), 1.45 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3) δ 174.1, 142.3, 128.4, 128.3, 125.8, 83.7 (d, J = 171.8 Hz), 80.4, 63.0 (d, J = 1.8 Hz), 58.3 (d, J = 17.4 Hz), 47.6, 32.6, 30.8 (d, J = 6.1 Hz), 29.9, 28.1, 23.7.

^{19}F $\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ –225.3.

IR (film, cm^{-1}) 3026, 2974, 2929, 2868, 1732, 1694, 1454, 1367, 1148, 844, 748, 699.

HRMS m/z (ESI) calcd for $\text{C}_{19}\text{H}_{29}\text{FNO}_2$ $[\text{M}+\text{H}]^+$ 322.2177; found 322.2176.



1-(1-fluoro-4-phenylbutan-2-yl)4-phenylpiperidine (4d). Prepared according to general procedure A using 4-phenylpiperidine (32 mg, 0.2 mmol), hydrocinnamaldehyde (53 μ L, 0.4 mmol), fluoroiodomethane (40 μ L, 0.6 mmol), tris(trimethylsilyl)silane (123 μ L, 0.4 mmol), *tert*-butyldimethylsilyl trifluoromethanesulfonate (92 μ L, 0.4 mmol) and 4 Å MS (300 mg) in 6 mL dichloromethane. The crude reaction mixture was purified by flash column chromatography (0–15% ethyl acetate in 40–60 °C petroleum ether) to afford the product as a colourless oil (45 mg, 72%).

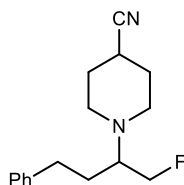
^1H NMR (700 MHz, CDCl_3) δ 7.39 – 7.32 (m, 4H), 7.32 – 7.27 (m, 4H), 7.27 – 7.22 (m, 2H), 4.67 – 4.60 (m, 1H), 4.60 – 4.52 (m, 1H), 3.07 – 3.01 (m, 1H), 2.94 (ddt, J = 11.4, 4.5, 2.2 Hz, 1H), 2.85 – 2.72 (m, 4H), 2.56 (tt, J = 12.1, 3.9 Hz, 1H), 2.50 (tt, J = 11.5, 2.3 Hz, 1H), 2.00 – 1.82 (m, 4H), 1.82 – 1.73 (m, 2H).

^{13}C NMR (176 MHz, CDCl_3) δ 146.7, 142.3, 128.6, 128.5, 128.5, 127.0, 126.2, 125.9, 83.6 (d, J = 172.5 Hz), 63.0 (d, J = 17.5 Hz), 52.6 (d, J = 1.5 Hz), 47.8, 43.2, 34.5, 34.3, 32.9, 29.1 (d, J = 6.7 Hz).

^{19}F $\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ –223.9.

IR (film, cm^{-1}) 3025, 2931, 2807, 1494, 1452, 1338, 1143, 1017, 750, 698.

HRMS m/z (ESI) calcd for $\text{C}_{21}\text{H}_{27}\text{FN}$ $[\text{M}+\text{H}]^+$ 312.2122; found 312.2129.



1-(1-fluoro-4-phenylbutan-2-yl)piperidine-4-carbonitrile (4e). Prepared according to general procedure A, deviation A using 4-cyanopiperidine (22 μL , 0.2 mmol), hydrocinnamaldehyde (53 μL , 0.4 mmol), fluoroiodomethane (40 μL , 0.6 mmol), tris(trimethylsilyl)silane (123 μL , 0.4 mmol), *tert*-butyldimethylsilyl trifluoromethanesulfonate (92 μL , 0.4 mmol) and 4 Å MS (300 mg) in 6 mL dichloromethane. The crude reaction mixture was purified by flash column chromatography (0–40% ethyl acetate in 40–60 °C petroleum ether) to afford the product as a colourless oil (27 mg, 52%).

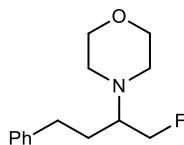
^1H NMR (400 MHz, CDCl_3) δ 7.29 (td, $J = 6.8, 1.5$ Hz, 2H), 7.24 – 7.15 (m, 3H), 4.48 (dd, $J = 47.7, 4.8$ Hz, 2H), 3.01 – 2.83 (m, 1H), 2.83 – 2.54 (m, 6H), 2.53 – 2.38 (m, 1H), 2.01 – 1.75 (m, 5H), 1.73 – 1.61 (m, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 141.9, 128.6, 128.5, 126.1, 122.0, 83.5 (d, $J = 172.9$ Hz), 62.9 (d, $J = 17.5$ Hz), 48.6, 46.8, 32.6, 29.7, 29.6, 28.7 (d, $J = 7.0$ Hz), 26.8.

^{19}F $\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ –224.0.

IR (film, cm^{-1}) 3026, 2951, 2928, 2854, 2816, 2239, 1495, 1453, 1144, 1029, 751, 701.

HRMS m/z (ESI) calcd for $\text{C}_{16}\text{H}_{22}\text{FN}_2$ $[\text{M}+\text{H}]^+$ 261.1762; found 261.1766.



1-(1-fluoro-4-phenylbutan-2-yl)piperidine-4-carbonitrile (4f). Prepared according to general procedure A, deviation A using morpholine (18 μL , 0.2 mmol), hydrocinnamaldehyde (53 μL , 0.4 mmol), fluoroiodomethane (40 μL , 0.6 mmol), tris(trimethylsilyl)silane (123 μL , 0.4 mmol), *tert*-butyldimethylsilyl trifluoromethanesulfonate (92 μL , 0.4 mmol) and 4 Å MS (300 mg) in 12 mL dichloromethane. The crude reaction mixture was purified by flash column chromatography (0–40% ethyl acetate in 40–60 °C petroleum ether) to afford the product as a colourless oil (29 mg, 62%).

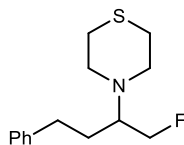
^1H NMR (400 MHz, CDCl_3) δ 7.33 – 7.24 (m, 2H), 7.24 – 7.16 (m, 3H), 4.53 (dd, $J = 47.7, 4.6$ Hz, 2H), 3.84 – 3.59 (m, 4H), 2.81 – 2.50 (m, 7H), 1.94 – 1.80 (m, 1H), 1.77 – 1.62 (m, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 142.0, 128.6, 128.5, 126.0, 83.4 (d, $J = 172.5$ Hz), 67.8, 62.8 (d, $J = 17.7$ Hz), 49.8, 32.6, 28.7 (d, $J = 6.6$ Hz).

^{19}F $\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ –223.5.

IR (film, cm^{-1}) 3025, 2953, 2852, 1495, 1453, 1117, 751, 700.

HRMS m/z (ESI) calcd for $\text{C}_{14}\text{H}_{21}\text{FNO}$ $[\text{M}+\text{H}]^+$ 238.1602; found 238.1606.



1-(1-fluoro-4-phenylbutan-2-yl)piperidine-4-carbonitrile (4g). Prepared according to general procedure A, deviation A using thiomorpholine (20 μL , 0.2 mmol), hydrocinnamaldehyde (53 μL , 0.4 mmol), fluoroiodomethane (40 μL , 0.6 mmol), tris(trimethylsilyl)silane (123 μL , 0.4 mmol), *tert*-butyldimethylsilyl trifluoromethanesulfonate (92 μL , 0.4 mmol) and 4 Å MS (300 mg) in 12 mL dichloromethane. The crude reaction mixture was purified by flash column chromatography (0–15% ethyl acetate in 40–60 °C petroleum ether) to afford the product as a colourless oil (29 mg, 58%).

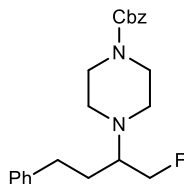
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.33 – 7.26 (m, 2H), 7.24 – 7.16 (m, 3H), 4.63 – 4.33 (m, 2H), 3.03 (ddd, $J = 10.9, 6.6, 3.1$ Hz, 2H), 2.89 – 2.78 (m, 2H), 2.77 – 2.57 (m, 7H), 1.91 – 1.77 (m, 1H), 1.76 – 1.59 (m, 1H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 142.0, 128.6, 128.5, 126.0, 83.6 (d, $J = 172.6$ Hz), 64.2 (d, $J = 17.6$ Hz), 51.9, 32.6, 28.9.

^{19}F $\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ –224.2.

IR (film, cm^{-1}) 3390, 3024, 2908, 2810, 1682, 1494, 1453, 1280, 1128, 980, 748, 698.

HRMS m/z (ESI) calcd for $\text{C}_{14}\text{H}_{21}\text{FN}$ $[\text{M}+\text{H}]^+$ 254.1373; found 254.1377.



Benzyl 4-(1-fluoro-4-phenylbutan-2-yl)piperazine-1-carboxylate (4h). Prepared according to general procedure A using 1-carbobenzoxypiperazine (39 μL , 0.2 mmol), hydrocinnamaldehyde (53 μL , 0.4 mmol), fluoroiodomethane (40 μL , 0.6 mmol), tris(trimethylsilyl)silane (123 μL , 0.4 mmol), *tert*-butyldimethylsilyl trifluoromethanesulfonate (92 μL , 0.4 mmol) and 4 Å MS (300 mg) in 6 mL dichloromethane. The crude reaction mixture was purified by flash column chromatography (0–60% ethyl acetate in 40–60 °C petroleum ether) to afford the product as a colourless oil (45 mg, 61%).

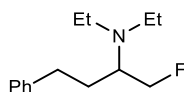
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.44 – 7.28 (m, 7H), 7.26 – 7.19 (m, 3H), 5.17 (s, 2H), 4.51 (dd, $J = 47.6, 4.7$ Hz, 2H), 3.67 – 3.38 (m, 4H), 2.86 – 2.64 (m, 5H), 2.57 (d, $J = 8.6$ Hz, 2H), 1.95 – 1.78 (m, 1H), 1.77 – 1.62 (m, 1H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 155.3, 141.9, 136.9, 128.6, 128.6, 128.5, 128.1, 128.0, 126.1, 83.4 (d, $J = 172.6$ Hz), 67.2, 62.7 (d, $J = 17.4$ Hz), 49.0, 44.6, 32.6, 28.7 (d, $J = 6.7$ Hz).

^{19}F $\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ –224.2.

IR (film, cm^{-1}) 3028, 2951, 2860, 1700, 1454, 1430, 1242, 1121, 753, 696.

HRMS m/z (ESI) calcd for $\text{C}_{22}\text{H}_{28}\text{FN}_2\text{O}_2$ $[\text{M}+\text{H}]^+$ 371.2129; found 371.2130.



***N,N*-Diethyl-1-fluoro-4-phenylbutan-2-amine (4i)**. Prepared according to general procedure A using diethylamine (21 μL , 0.2 mmol), hydrocinnamaldehyde (53 μL , 0.4 mmol), fluoroiodomethane (40 μL , 0.6 mmol), tris(trimethylsilyl)silane (123 μL , 0.4 mmol), *tert*-butyldimethylsilyl trifluoromethanesulfonate (92 μL , 0.4 mmol) and 4 Å MS (300 mg) in 6 mL dichloromethane. The crude reaction mixture was purified by strong cation exchange chromatography (methanol, then 3 N ammonia in methanol) to afford the product as a colourless oil (33 mg, 74%).

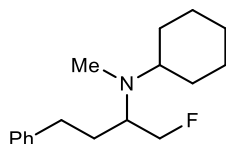
^1H NMR (400 MHz, CDCl_3) δ 7.37 – 7.16 (m, 5H), 4.65 – 4.36 (m, 2H), 3.02 – 2.87 (m, 1H), 2.87 – 2.77 (m, 1H), 2.77 – 2.52 (m, 5H), 1.90 – 1.69 (m, 2H), 1.07 (t, $J = 7.1$ Hz, 6H).

^{13}C NMR (101 MHz, CDCl_3) δ 142.5, 128.6, 128.5, 125.9, 84.4 (d, $J = 172.2$ Hz), 58.8 (d, $J = 17.7$ Hz), 44.2, 44.2, 33.1, 29.9 (d, $J = 5.2$ Hz), 14.8.

^{19}F $\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ -224.0.

IR (film, cm^{-1}) 3026, 2967, 2931, 2868, 2814, 1495, 1453, 1378, 1210, 1067, 1004, 749, 699.

HRMS m/z (ESI) calcd for $\text{C}_{14}\text{H}_{23}\text{FN}$ $[\text{M}+\text{H}]^+$ 224.1809; found 224.1818.



***N*-(1-Fluoro-4-phenylbutan-2-yl)-*N*-methylcyclohexanamine (4j)**. Prepared according to general procedure A, deviation A using *N*-methylcyclohexylamine (26 μL , 0.2 mmol), hydrocinnamaldehyde (53 μL , 0.4 mmol), fluoroiodomethane (40 μL , 0.6 mmol), tris(trimethylsilyl)silane (123 μL , 0.4 mmol), *tert*-butyldimethylsilyl trifluoromethanesulfonate (92 μL , 0.4 mmol) and 4 Å MS (300 mg) in 6 mL dichloromethane. The crude reaction mixture was purified by flash column chromatography (0–20% ethyl acetate in 40–60 °C petroleum ether) to afford the product as a colourless oil (38 mg, 73%).

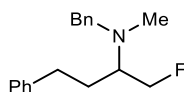
^1H NMR (700 MHz, CDCl_3) δ 7.29 (t, $J = 7.5$ Hz, 2H), 7.23 – 7.18 (m, 3H), 4.61 – 4.29 (m, 2H), 3.00 – 2.91 (m, 1H), 2.78 – 2.71 (m, 1H), 2.70 – 2.63 (m, 1H), 2.48 – 2.41 (m, 1H), 2.34 (s, 3H), 1.83 – 1.70 (m, 6H), 1.63 – 1.57 (m, 1H), 1.29 – 1.19 (m, 4H), 1.13 – 1.04 (m, 1H).

^{13}C NMR (176 MHz, CDCl_3) δ 142.6, 128.6, 128.5, 125.9, 84.8 (d, $J = 172.5$ Hz), 60.9, 58.9 (d, $J = 17.8$ Hz), 33.2, 33.2, 32.7, 32.7, 31.4, 31.3, 30.5 (d, $J = 5.4$ Hz), 26.3, 26.2, 26.2.

^{19}F $\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ -223.8.

IR (film, cm^{-1}) 3026, 2927, 2852, 2789, 1496, 1452, 1002, 891, 749, 699.

HRMS m/z (ESI) calcd for $\text{C}_{17}\text{H}_{27}\text{FN}$ $[\text{M}+\text{H}]^+$ 264.2122; found 264.2131.



***N*-Benzyl-1-fluoro-*N*-methyl-4-phenylbutan-2-amine (4k).** Prepared according to general procedure A using *N*-benzylmethylamine (26 μ L, 0.2 mmol), hydrocinnamaldehyde (53 μ L, 0.4 mmol), fluoriodomethane (40 μ L, 0.6 mmol), tris(trimethylsilyl)silane (123 μ L, 0.4 mmol), *tert*-butyldimethylsilyl trifluoromethanesulfonate (92 μ L, 0.4 mmol) and 4 Å MS (300 mg) in 6 mL dichloromethane. The crude reaction mixture was purified by flash column chromatography (0–10% ethyl acetate in 40–60 °C petroleum ether) to afford the product as a colourless oil (42 mg, 78%).

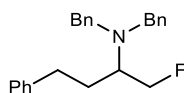
^1H NMR (600 MHz, CDCl_3) δ 7.43 – 7.20 (m, 10H), 4.72 – 4.48 (m, 2H), 3.83 (d, J = 13.6 Hz, 1H), 3.71 (d, J = 13.6 Hz, 1H), 3.00 – 2.83 (m, 2H), 2.81 – 2.72 (m, 1H), 2.34 (s, 3H), 1.99 – 1.87 (m, 1H), 1.80 – 1.70 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3): δ 142.3, 140.2, 128.7, 128.6, 128.5, 128.4, 127.0, 126.0, 83.8 (d, J = 172.4 Hz), 61.4 (d, J = 17.3 Hz), 58.8 (d, J = 1.8 Hz), 37.2 (d, J = 1.3 Hz), 32.9, 29.4 (d, J = 6.6 Hz).

^{19}F $\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ –224.6.

IR (film, cm^{-1}) 2953, 2855, 2790, 1602, 1494, 1453, 1357, 1320, 1215, 1126, 1074, 1027.

HRMS m/z calcd for $\text{C}_{18}\text{H}_{23}\text{FN}$ $[\text{M}+\text{H}]^+$ 272.1815; found 272.1814.



***N,N*-Dibenzyl-1-fluoro-4-phenylbutan-2-amine (4l).** Prepared according to general procedure A using dibenzylamine (39 μ L, 0.2 mmol), hydrocinnamaldehyde (53 μ L, 0.4 mmol), fluoriodomethane (40 μ L, 0.6 mmol), tris(trimethylsilyl)silane (123 μ L, 0.4 mmol), *tert*-butyldimethylsilyl trifluoromethanesulfonate (46 μ L, 0.2 mmol) and 4 Å MS (300 mg) in 6 mL dichloromethane. The crude reaction mixture was purified by flash column chromatography (0–10% ethyl acetate in 40–60 °C petroleum ether) to afford the product as a colourless oil (53 mg, 76%).

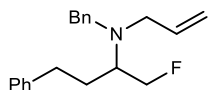
^1H NMR (400 MHz, CDCl_3): δ 7.68 – 7.05 (m, 15H), 4.64 (dd, J = 48.1, 5.5 Hz, 1H), 3.91 (d, J = 13.7 Hz, 1H), 3.82 – 3.34 (m, 3H), 3.09 – 2.76 (m, 2H), 2.75 – 2.42 (m, 2H), 2.07 – 1.66 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3): δ 142.3, 140.2, 129.1, 129.0, 128.7, 128.6, 128.5, 128.5, 128.4, 128.3, 127.0, 125.9, 125.7, 84.2 (d, J = 172.7 Hz), 58.4, 56.8 (d, J = 17.3 Hz), 54.6, 33.7, 33.2, 29.7 (d, J = 6.0 Hz), 29.0.

^{19}F $\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ –225.5.

IR (film, cm^{-1}) 3026, 2946, 2802, 1494, 1452, 1027, 743, 695.

HRMS m/z calcd for $\text{C}_{24}\text{H}_{27}\text{FN}$ $[\text{M}+\text{H}]^+$ 348.2122; found 348.2122.



***N*-Allyl-*N*-benzyl-1-fluoro-4-phenylbutan-2-amine (4m).** Prepared according to general procedure A using *N*-allylbenzylamine (31 μL , 0.2 mmol), hydrocinnamaldehyde (53 μL , 0.4 mmol), fluoroiodomethane (40 μL , 0.6 mmol), tris(trimethylsilyl)silane (123 μL , 0.4 mmol), *tert*-butyldimethylsilyl trifluoromethanesulfonate (92 μL , 0.4 mmol) and 4 Å MS (300 mg) in 6 mL dichloromethane. The crude reaction mixture was purified by flash column chromatography (0–30% dichloromethane in 40–60 °C petroleum ether) to afford the product as a colourless oil (27 mg, 60%).

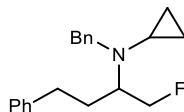
^1H NMR (400 MHz, CDCl_3) δ 7.43 – 7.15 (m, 11H), 5.93 – 5.78 (m, 1H), 5.21 (d, $J = 17.2, 1.6$ Hz, 1H), 5.12 (d, $J = 10.1$ Hz, 1H), 4.64 (d, $J = 4.9$ Hz, 1H), 4.52 (d, $J = 5.0$ Hz, 1H), 3.91 (d, $J = 14.0$ Hz, 1H), 3.69 (d, $J = 14.0$ Hz, 1H), 3.38 – 3.28 (m, 1H), 3.26 – 3.15 (m, 1H), 3.11 – 2.94 (m, 1H), 2.92 – 2.80 (m, 1H), 2.71 – 2.59 (m, 1H), 1.98 – 1.84 (m, 1H), 1.83 – 1.69 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 142.4, 140.5, 137.4, 128.8, 128.5, 128.5, 128.4, 126.9, 125.9, 116.9, 84.3 (d, $J = 172.5$ Hz), 57.6 (d, $J = 17.6$ Hz), 54.4, 54.4, 53.5, 53.5, 33.1, 29.8 (d, $J = 5.8$ Hz).

^{19}F $\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ –225.6.

IR (film, cm^{-1}) 3026, 2951, 2858, 2807, 1642, 1495, 1453, 1028, 994, 919, 736, 698.

HRMS m/z calcd for $\text{C}_{20}\text{H}_{25}\text{FN}$ $[\text{M}+\text{H}]^+$ 298.1966; found 298.1962.



***N*-Benzyl-*N*-(1-fluoro-4-phenylbutan-2-yl)cyclopropanamine (4n).** Prepared according to general procedure A using *N*-benzylcyclopropylamine (29 mg, 0.2 mmol), hydrocinnamaldehyde (53 μL , 0.4 mmol), fluoroiodomethane (40 μL , 0.6 mmol), tris(trimethylsilyl)silane (123 μL , 0.4 mmol), *tert*-butyldimethylsilyl trifluoromethanesulfonate (92 μL , 0.4 mmol) and 4 Å MS (300 mg) in 6 mL dichloromethane. The crude reaction mixture was purified by flash column chromatography (0–30% dichloromethane in 40–60 °C petroleum ether) then strong cation exchange chromatography (methanol, then 3 N ammonia in methanol) to afford the product as a colourless oil (26 mg, 44%).

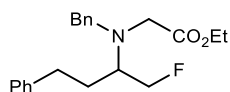
^1H NMR (700 MHz, CDCl_3) δ 7.34 – 7.24 (m, 7H), 7.23 – 7.19 (m, 1H), 7.16 (d, $J = 7.5$ Hz, 2H), 4.73 – 4.48 (m, 2H), 3.97 (d, $J = 13.7$ Hz, 1H), 3.85 (d, $J = 13.8$ Hz, 1H), 3.11 – 2.98 (m, 1H), 2.81 – 2.71 (m, 1H), 2.62 – 2.52 (m, 1H), 2.23 – 2.16 (m, 1H), 2.00 – 1.88 (m, 1H), 1.79 – 1.68 (m, 1H), 0.52 – 0.38 (m, 2H), 0.38 – 0.27 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 142.4, 140.8, 129.1, 128.5, 128.5, 128.2, 126.8, 125.9, 84.6 (d, $J = 172.4$ Hz), 60.5 (d, $J = 17.4$ Hz), 56.9, 56.9, 34.1, 34.1, 33.2, 29.9 (d, $J = 6.1$ Hz), 8.5, 6.8.

^{19}F $\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ –223.7.

IR (film, cm^{-1}) 3026, 2951, 2860, 1495, 1453, 1349, 1019, 750, 714, 698.

HRMS m/z calcd for $\text{C}_{20}\text{H}_{25}\text{FN}$ $[\text{M}+\text{H}]^+$ 298.1966; found 298.1974.



Ethyl *N*-benzyl-*N*-(1-fluoro-4-phenylbutan-2-yl)glycinate (4o). Prepared according to general procedure A, deviation A using *N*-benzylglycine ethyl ester (37 μ L, 0.2 mmol), hydrocinnamaldehyde (53 μ L, 0.4 mmol), fluoroiodomethane (40 μ L, 0.6 mmol), tris(trimethylsilyl)silane (123 μ L, 0.4 mmol), *tert*-butyldimethylsilyl trifluoromethanesulfonate (92 μ L, 0.4 mmol) and 4 Å MS (300 mg) in 6 mL dichloromethane. The crude reaction mixture was purified by flash column chromatography (0–10% ethyl acetate in 40–60 °C petroleum ether) then strong cation exchange chromatography (methanol, then 3 N ammonia in methanol) to afford the product as a colourless oil (43 mg, 62%).

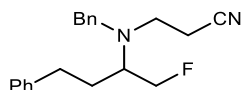
¹H NMR (700 MHz, CDCl₃) δ 7.44 (d, J = 7.5 Hz, 2H), 7.36 (t, J = 7.5 Hz, 2H), 7.33 – 7.27 (m, 3H), 7.24 – 7.16 (m, 3H), 4.69 – 4.49 (m, 2H), 4.16 (q, J = 7.2 Hz, 2H), 4.03 (d, J = 13.8 Hz, 1H), 3.89 (d, J = 13.8 Hz, 1H), 3.56 – 3.45 (m, 2H), 3.07 – 2.96 (m, 1H), 2.96 – 2.88 (m, 1H), 2.74 – 2.65 (m, 1H), 1.96 – 1.87 (m, 1H), 1.84 – 1.73 (m, 1H), 1.29 (t, J = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 172.3, 142.3, 139.4, 129.0, 128.5, 128.5, 128.4, 127.2, 125.9, 84.5 (d, J = 172.1 Hz), 60.5, 59.5 (d, J = 17.8 Hz), 55.6, 55.6, 52.1, 52.1, 32.8, 30.2 (d, J = 5.6 Hz), 14.3.

¹⁹F {¹H} NMR (376 MHz, CDCl₃) δ –225.9.

IR (film, cm^{–1}) 3026, 2952, 2904, 2861, 1744, 1495, 1454, 1373, 1185, 1153, 1029, 739, 699.

HRMS m/z calcd for C₂₁H₂₇FNO₂ [M+H]⁺ 344.2020; found 344.2029.



3-(Benzyl(1-fluoro-4-phenylbutan-2-yl)amino)propanenitrile (4p). Prepared according to general procedure A, deviation A using 3-(benzylamino)propanenitrile (52 mg, 0.2 mmol), hydrocinnamaldehyde (53 μ L, 0.4 mmol), fluoroiodomethane (40 μ L, 0.6 mmol), tris(trimethylsilyl)silane (123 μ L, 0.4 mmol), *tert*-butyldimethylsilyl trifluoromethanesulfonate (92 μ L, 0.4 mmol) and 4 Å MS (300 mg) in 6 mL dichloromethane. The crude reaction mixture was purified by flash column chromatography (0–40% dichloromethane in 40–60 °C petroleum ether) to afford the product as a colourless oil (45 mg, 72%).

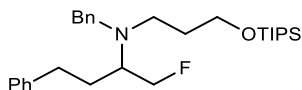
¹H NMR (700 MHz, CDCl₃) δ 7.29 (t, J = 7.5 Hz, 2H), 7.23 – 7.18 (m, 3H), 4.61 – 4.29 (m, 2H), 3.00 – 2.91 (m, 1H), 2.78 – 2.71 (m, 1H), 2.70 – 2.63 (m, 1H), 2.48 – 2.41 (m, 1H), 2.34 (s, 3H), 1.83 – 1.70 (m, 6H), 1.63 – 1.57 (m, 1H), 1.29 – 1.19 (m, 4H), 1.13 – 1.04 (m, 1H).

¹³C NMR (176 MHz, CDCl₃) δ 142.6, 128.6, 128.5, 125.9, 84.8 (d, J = 172.5 Hz), 60.9, 58.9 (d, J = 17.8 Hz), 33.2, 33.2, 32.7, 32.7, 31.4, 31.3, 30.5 (d, J = 5.4 Hz), 26.3, 26.2, 26.2.

¹⁹F {¹H} NMR (376 MHz, CDCl₃) δ –224.9.

IR (film, cm^{–1}) 3026, 2952, 2856, 1495, 1453, 1146, 1027, 732, 699.

HRMS m/z calcd for C₂₀H₂₄FN₂ [M+H]⁺ 311.1918; found 311.1922.



***N*-Benzyl-1-fluoro-4-phenyl-*N*-(3-((triisopropylsilyloxy)propyl)butan-2-amine (4q)**. Prepared according to general procedure A, deviation A using *N*-benzyl-3-((triisopropylsilyloxy)propyl)propan-1-amine (32 mg, 0.1 mmol), hydrocinnamaldehyde (26 μ L, 0.2 mmol), fluoroiodomethane (20 μ L, 0.3 mmol), tris(trimethylsilyl)silane (62 μ L, 0.2 mmol), *tert*-butyldimethylsilyl trifluoromethanesulfonate (23 μ L, 0.1 mmol) and 4 Å MS (150 mg) in 3 mL dichloromethane. The crude reaction mixture was purified by flash column chromatography (0–5% ethyl acetate in 40–60°C petroleum ether) to afford the product as a colourless oil (33 mg, 70%).

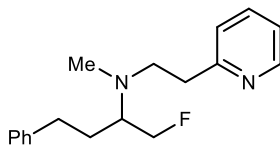
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.38 – 7.25 (m, 7H), 7.23 – 7.14 (m, 3H), 4.71 – 4.40 (m, 2H), 3.86 (d, $J = 14.0$ Hz, 1H), 3.78 – 3.60 (m, 3H), 3.05 – 2.89 (m, 1H), 2.89 – 2.52 (m, 4H), 1.95 – 1.80 (m, 1H), 1.80 – 1.61 (m, 3H), 1.11 – 1.02 (m, 21H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 142.4, 140.8, 128.8, 128.5, 128.5, 128.3, 126.9, 125.9, 84.4 (d, $J = 172.6$ Hz), 61.7, 58.5 (d, $J = 17.6$ Hz), 55.5, 55.5, 47.2, 47.2, 33.3, 32.6, 29.9 (d, $J = 5.8$ Hz), 18.2, 12.1.

^{19}F $\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ –225.1.

IR (film, cm^{-1}) 3027, 2942, 2891, 2864, 14945, 1454, 1382, 1256, 1100, 1013, 882, 733, 681, 658.

HRMS m/z calcd for $\text{C}_{29}\text{H}_{47}\text{FNOSi}$ $[\text{M}+\text{H}]^+$ 472.3405; found 472.3417.



1-fluoro-*N*-methyl-4-phenyl-*N*-(2-(pyridin-2-yl)ethyl)butan-2-amine (4r). Prepared according to general procedure A using *N*-methyl-*N*-(2-pyridin-2-ylethyl)amine (28 μ L, 0.2 mmol), hydrocinnamaldehyde (53 μ L, 0.4 mmol), fluoroiodomethane (40 μ L, 0.6 mmol), tris(trimethylsilyl)silane (123 μ L, 0.4 mmol), *tert*-butyldimethylsilyl trifluoromethanesulfonate (92 μ L, 0.4 mmol) and 4 Å MS (300 mg) in 6 mL dichloromethane. The crude reaction mixture was purified by flash column chromatography (0–100% ethyl acetate in 40–60 °C petroleum ether) to afford the product as a yellow oil (37 mg, 64%).

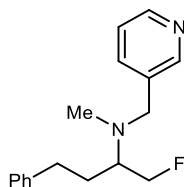
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.56 (d, $J = 4.8$ Hz, 1H), 7.60 (t, $J = 7.7$ Hz, 1H), 7.32 – 7.25 (m, 2H), 7.22 – 7.09 (m, 5H), 4.65 – 4.37 (m, 2H), 3.10 – 2.93 (m, 4H), 2.93 – 2.79 (m, 1H), 2.66 – 2.48 (m, 2H), 2.46 (s, 3H), 1.90 – 1.59 (m, 2H).

$^{13}\text{C NMR}$ (176 MHz, CDCl_3) δ 160.5, 149.3, 142.1, 136.3, 128.5, 128.4, 125.9, 123.5, 121.3, 83.5 (d, $J = 172.5$ Hz), 62.3 (d, $J = 17.4$ Hz), 54.4, 54.4, 37.5, 37.5, 37.2, 32.6, 29.1 (d, $J = 6.2$ Hz).

^{19}F $\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ –225.0.

IR (film, cm^{-1}) 3025, 2950, 2854, 2798, 1590, 1473, 1434, 1358, 1126, 1028, 993, 972, 748, 699.

HRMS m/z calcd for $\text{C}_{18}\text{H}_{24}\text{FN}_2$ $[\text{M}+\text{H}]^+$ 287.1918; found 287.1916.



1-Fluoro-*N*-methyl-4-phenyl-*N*-(pyridin-3-ylmethyl)butan-2-amine (4s). Prepared according to general procedure A using *N*-methyl-*N*-(3-pyridylmethyl)amine (25 μ L, 0.2 mmol), hydrocinnamaldehyde (53 μ L, 0.4 mmol), fluoroiodomethane (40 μ L, 0.6 mmol), tris(trimethylsilyl)silane (123 μ L, 0.4 mmol), *tert*-butyldimethylsilyl trifluoromethanesulfonate (92 μ L, 0.4 mmol) and 4 Å MS (300 mg) in 6 mL dichloromethane. The crude reaction mixture was purified by flash column chromatography (0–100% ethyl acetate in 40–60 °C petroleum ether) to afford the product as a colourless oil (15 mg, 28%).

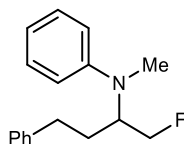
^1H NMR (400 MHz, CDCl_3) δ 8.56 (s, 1H), 8.50 (d, J = 4.7 Hz, 1H), 7.67 (d, J = 7.8 Hz, 1H), 7.31 – 7.27 (m, 2H), 7.19 (s, 4H), 4.66 – 4.45 (m, 2H), 3.79 (d, J = 13.9 Hz, 1H), 3.68 (d, J = 13.9 Hz, 1H), 2.95 – 2.76 (m, 2H), 2.75 – 2.68 (m, 1H), 2.27 (s, 3H), 1.93 – 1.81 (m, 1H), 1.76 – 1.68 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 150.3, 148.6, 142.0, 136.3, 135.6, 128.6, 128.5, 128.5, 126.1, 123.5, 83.8 (d, J = 172.6 Hz), 61.6 (d, J = 17.3 Hz), 56.4, 37.0, 32.9, 29.3 (d, J = 6.9 Hz).

^{19}F { ^1H } NMR (376 MHz, CDCl_3) δ –224.4.

IR (film, cm^{-1}) 3084, 3026, 2949, 2857, 2795, 1672, 1576, 1496, 1454, 1028, 752, 714, 700.

HRMS m/z calcd for $\text{C}_{17}\text{H}_{22}\text{FN}_2$ [$\text{M}+\text{H}$] $^+$ 273.1762; found 273.1751.



***N*-(1-Fluoro-4-phenylbutan-2-yl)-*N*-methylaniline (4t).** Prepared according to general procedure A using *N*-methylaniline (22 μ L, 0.2 mmol), hydrocinnamaldehyde (53 μ L, 0.4 mmol), fluoroiodomethane (40 μ L, 0.6 mmol), tris(trimethylsilyl)silane (123 μ L, 0.4 mmol), *tert*-butyldimethylsilyl trifluoromethanesulfonate (138 μ L, 0.6 mmol) and 4 Å MS (300 mg) in 6 mL dichloromethane. The crude reaction mixture was purified by flash column chromatography (0–30% dichloromethane in 40–60 °C petroleum ether) to afford the product as a colourless oil (20 mg, 38%).

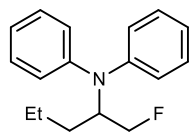
^1H NMR (700 MHz, CDCl_3) δ 7.32 – 7.20 (m, 5H), 7.16 (d, J = 7.5 Hz, 2H), 6.83 – 6.71 (m, 3H), 4.63 – 4.39 (m, 2H), 4.12 – 4.00 (m, 1H), 2.90 (s, 3H), 2.78 – 2.70 (m, 1H), 2.68 – 2.60 (m, 1H), 2.11 – 2.02 (m, 1H), 2.02 – 1.94 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 141.5, 129.6, 129.3, 128.6, 128.6, 128.6, 128.6, 126.2, 126.2, 118.0, 113.5, 84.2 (d, J = 173.7 Hz), 57.5, 52.4, 32.6, 30.2.

^{19}F { ^1H } NMR (376 MHz, CDCl_3) δ –225.0.

IR (film, cm^{-1}) 3025, 2949, 2863, 2814, 1598, 1504, 1318, 1030, 749, 697.

HRMS m/z calcd for $\text{C}_{17}\text{H}_{21}\text{FN}$ [$\text{M}+\text{H}$] $^+$ 258.1653; found 258.1647.



***N*-(1-Fluoropentan-2-yl)-*N*-phenylaniline (4u).** Prepared according to general procedure A using diphenylamine (34 mg, 0.2 mmol), butyraldehyde (36 μ L, 0.4 mmol), fluoroiodomethane (40 μ L, 0.6 mmol), tris(trimethylsilyl)silane (123 μ L, 0.4 mmol), *tert*-butyldimethylsilyl trifluoromethanesulfonate (138 μ L, 0.6 mmol) and 4 Å MS (300 mg) in 6 mL dichloromethane. The crude reaction mixture was purified by flash column chromatography (0–10% dichloromethane in 40–60 °C petroleum ether) to afford the product as a colourless oil (22 mg, 43%).

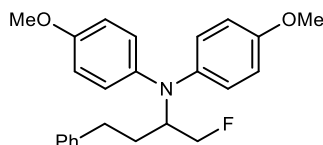
¹H NMR (700 MHz, CDCl₃) δ 7.32 – 7.28 (m, 4H), 7.03 (t, *J* = 7.3, 1.2 Hz, 2H), 6.93 (d, *J* = 8.1 Hz, 4H), 4.56 – 4.31 (m, 3H), 1.63 – 1.56 (m, 2H), 1.51 – 1.42 (m, 2H), 0.96 (t, *J* = 7.0 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 146.5, 129.4, 123.1, 122.2, 83.5 (d, *J* = 173.8 Hz), 57.4 (d, *J* = 19.1 Hz), 31.9 (d, *J* = 5.0 Hz), 20.1, 14.3.

¹⁹F {¹H} NMR (376 MHz, CDCl₃) δ –221.8.

IR (film, cm⁻¹) 3036, 2959, 2872, 1589, 1496, 1466, 1257, 1006, 746, 702, 692.

HRMS *m/z* calcd for C₁₇H₂₁FN [M+H]⁺ 258.1653; found 258.1654.



***N*-(1-Fluoro-4-phenylbutan-2-yl)-4-methoxy-*N*-(4-methoxyphenyl)aniline (4v).** Prepared according to general procedure A using *N*-methylaniline (26 μ L, 0.2 mmol), hydrocinnamaldehyde (53 μ L, 0.4 mmol), fluoroiodomethane (40 μ L, 0.6 mmol), tris(trimethylsilyl)silane (123 μ L, 0.4 mmol), *tert*-butyldimethylsilyl trifluoromethanesulfonate (138 μ L, 0.6 mmol) and 4 Å MS (300 mg) in 6 mL dichloromethane. The crude reaction mixture was purified by flash column chromatography (0–6% ethyl acetate in 40–60 °C petroleum ether) to afford the product as a colourless oil (38 mg, 50%).

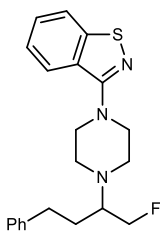
¹H NMR (700 MHz, CDCl₃) δ 7.29 (t, *J* = 7.6 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.17 – 7.13 (m, 2H), 6.84 (d, *J* = 1.0 Hz, 8H), 4.53 – 4.35 (m, 2H), 4.33 – 4.22 (m, 1H), 3.79 (s, 6H), 2.91 – 2.81 (m, 1H), 2.78 – 2.69 (m, 1H), 1.91 – 1.82 (m, 1H), 1.82 – 1.73 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 155.1, 141.6, 140.4, 128.6, 128.6, 126.2, 124.2, 114.8, 83.7 (d, *J* = 174.3 Hz), 57.1 (d, *J* = 19.1 Hz), 55.7, 32.9, 31.4 (d, *J* = 4.6 Hz).

¹⁹F {¹H} NMR (376 MHz, CDCl₃) δ –221.9.

IR (film, cm⁻¹) 3025, 2997, 2950, 2907, 2834, 1502, 1463, 1239, 1179, 1034, 819, 700.

HRMS *m/z* calcd for C₂₄H₂₇FNO₂ [M+H]⁺ 380.2020; found 380.2019.



3-(4-(1-Fluoro-4-phenylbutan-2-yl)piperazin-1-yl)benzo[*d*]isothiazole (4w). Prepared according to general procedure A using 3-(piperazin-1-yl)benzo[*d*]isothiazole (44 mg, 0.2 mmol), hydrocinnamaldehyde (53 μ L, 0.4 mmol), fluoroiodomethane (40 μ L, 0.6 mmol), tris(trimethylsilyl)silane (123 μ L, 0.4 mmol), *tert*-butyldimethylsilyl trifluoromethanesulfonate (92 μ L, 0.4 mmol) and 4 Å MS (300 mg) in 6 mL dichloromethane. The crude reaction mixture was purified by flash column chromatography (0–20% ethyl acetate in 40–60 °C petroleum ether) to afford the product as a colourless oil (43 mg, 58%).

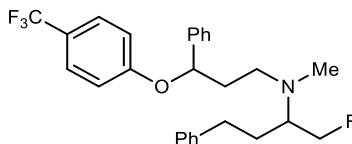
^1H NMR (400 MHz, CDCl_3) δ 7.95 (d, $J = 8.1$ Hz, 1H), 7.84 (d, $J = 8.1$ Hz, 1H), 7.49 (t, $J = 7.6$ Hz, 1H), 7.43 – 7.30 (m, 3H), 7.30 – 7.20 (m, 3H), 4.73 – 4.49 (m, 2H), 3.68 – 3.48 (m, 4H), 3.08 – 2.95 (m, 2H), 2.89 – 2.72 (m, 5H), 2.03 – 1.88 (m, 1H), 1.86 – 1.73 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 164.2, 152.9, 142.0, 128.6, 128.5, 128.2, 127.7, 126.1, 124.1, 124.0, 120.7, 83.5 (d, $J = 171.3$ Hz), 62.6 (d, $J = 17.3$ Hz), 50.9, 49.1, 49.0, 32.6, 28.8 (d, $J = 6.5$ Hz).

^{19}F { ^1H } NMR (376 MHz, CDCl_3) δ –223.1.

IR (film, cm^{-1}) 3025, 2950, 2837, 1492, 1450, 1380, 1260, 1138, 1023, 967, 736, 698.

HRMS m/z calcd for $\text{C}_{21}\text{H}_{25}\text{FN}_3\text{S}$ [$\text{M}+\text{H}$] $^+$ 370.1748; found 370.1733.



1-Fluoro-*N*-methyl-4-phenyl-*N*-(3-phenyl-3-(4-(trifluoromethyl)phenoxy)propyl)butan-2-amine (4x). Prepared according to general procedure A using fluoxetine (31 mg, 0.1 mmol), hydrocinnamaldehyde (27 μ L, 0.2 mmol), fluoroiodomethane (20 μ L, 0.3 mmol), tris(trimethylsilyl)silane (62 μ L, 0.2 mmol), *tert*-butyldimethylsilyl trifluoromethanesulfonate (46 μ L, 0.2 mmol) and 4 Å MS (150 mg) in 3 mL dichloromethane. The crude reaction mixture was purified by flash column chromatography (0–100% dichloromethane in 40–60 °C petroleum ether, then 2% ethyl acetate in dichloromethane) to afford the product as a colourless oil (39 mg, 84%, 1:1 d.r.).

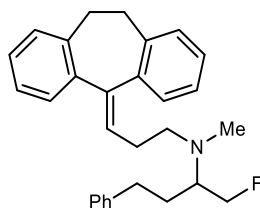
^1H NMR (400 MHz, CDCl_3) δ 7.45 (t, $J = 8.6$ Hz, 2H), 7.40 – 7.33 (m, 4H), 7.33 – 7.17 (m, 4H), 7.13 (d, $J = 7.5$ Hz, 2H), 6.94 (t, $J = 8.0$ Hz, 2H), 5.46 – 5.30 (m, 1H), 4.69 – 4.33 (m, 2H), 2.92 – 2.49 (m, 5H), 2.39 (d, $J = 12.7$ Hz, 3H), 2.23 – 2.08 (m, 1H), 2.08 – 1.92 (m, 1H), 1.87 – 1.59 (m, 2H).

^{13}C NMR (176 MHz, CDCl_3) δ 160.8, 160.7, 141.7 (d, $J = 76.2, 17.4$ Hz), 128.8, 128.4, 128.4, 128.3, 128.3, 127.7, 127.7, 126.8, 126.8, 126.7, 126.7, 126.7, 125.9, 125.8, 124.4 (q, $J = 271.0$ Hz), 115.7, 115.7, 83.4 (d, $J = 172.4$ Hz), 62.3 (d, $J = 58.5, 17.3$ Hz), 51.0, 49.7, 37.8, 37.6, 37.4, 36.3, 33.1, 32.9, 29.3, 29.2, 28.8, 28.8.

^{19}F { ^1H } NMR (376 MHz, CDCl_3) δ –62.5, –62.5, –224.3, –224.9.

IR (film, cm^{-1}) 2954, 1614, 1516, 1323, 1249, 1159, 1108, 1067, 835, 752, 699.

HRMS m/z calcd for $\text{C}_{27}\text{H}_{30}\text{F}_4\text{NO}$ [$\text{M}+\text{H}$] $^+$ 460.2258; found 460.2261.



***N*-(3-(10,11-Dihydro-5H-dibenzo[*a,d*][7]annulen-5-ylidene)propyl)-1-fluoro-*N*-methyl-4-phenylbutan-2-amine (4y).** Prepared according to general procedure A using nortriptyline (26 mg, 0.1 mmol), hydrocinnamaldehyde (27 μ L, 0.2 mmol), fluoroiodomethane (20 μ L, 0.3 mmol), tris(trimethylsilyl)silane (62 μ L, 0.2 mmol), *tert*-butyldimethylsilyl trifluoromethanesulfonate (46 μ L, 0.2 mmol) and 4 Å MS (150 mg) in 3 mL dichloromethane. The crude reaction mixture was purified by flash column chromatography (0–20% ethyl acetate in 40–60 °C petroleum ether) to afford the product as a colourless oil (31 mg, 76%).

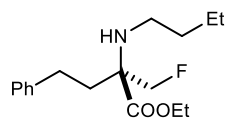
^1H NMR (400 MHz, CDCl_3) δ 7.33 – 7.26 (m, 2H), 7.25 – 7.10 (m, 10H), 7.08 – 7.00 (m, 1H), 5.91 (t, $J = 7.3$ Hz, 1H), 4.62 – 4.31 (m, 2H), 3.37 (d, $J = 49.2$ Hz, 2H), 3.12 – 2.87 (m, 1H), 2.87 – 2.50 (m, 6H), 2.27 (s, 5H), 1.76 (dd, $J = 11.2$, 5.4 Hz, 1H), 1.72 – 1.60 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 143.5, 142.2, 141.5, 140.3, 139.5, 137.2, 130.1, 129.9, 128.7, 128.5, 128.5, 128.4, 128.1, 127.5, 127.1, 126.1, 125.9, 125.8, 83.7 (d, $J = 172.2$ Hz), 62.1 (d, $J = 17.7$ Hz), 54.2 (d, $J = 43.5$ Hz), 37.5 (d, $J = 40.6$ Hz), 33.9, 32.9, 32.2, 29.2, 28.8.

^{19}F { ^1H } NMR (376 MHz, CDCl_3) δ –224.0.

IR (film, cm^{-1}) 3023, 2941, 2853, 2799, 1485, 1453, 1360, 1029, 1002, 973, 776, 754, 699.

HRMS m/z calcd for $\text{C}_{29}\text{H}_{33}\text{FN}$ [$\text{M}+\text{H}$] $^+$ 414.2592; found 414.2592.



Ethyl 2-(butylamino)-2-(fluoromethyl)-4-phenylbutanoate ((\pm)-4z) Prepared according to general procedure A, deviation D using *n*-butylamine (20 μ L, 0.2 mmol), ethyl 2-oxo-4-phenylbutyrate (76 μ L, 0.4 mmol), propionic acid (3 μ L, 0.04 mmol), fluoroiodomethane (40 μ L, 0.6 mmol), tris(trimethylsilyl)silane (185 μ L, 0.6 mmol), *tert*-butyldimethylsilyl trifluoromethanesulfonate (92 μ L, 0.4 mmol) and 4 Å MS (400 mg) in 8 mL dichloromethane. The crude reaction mixture was purified by flash column chromatography (0–20% ethyl acetate in 40–60 °C petroleum ether) to afford the product as a colourless oil (43 mg, 73%).

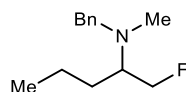
^1H NMR (400 MHz, CDCl_3) δ 7.31 (t, $J = 7.6$ Hz, 2H), 7.21 (t, $J = 8.2$ Hz, 3H), 4.67 (q, $J = 9.4$ Hz, 1H), 4.55 (q, $J = 9.4$ Hz, 1H), 4.25 (q, $J = 7.2$ Hz, 2H), 2.73 – 2.52 (m, 4H), 2.01 (t, $J = 8.5$ Hz, 2H), 1.80 (s, 1H), 1.62 – 1.48 (m, 2H), 1.48 – 1.37 (m, 2H), 1.36 – 1.30 (m, 3H), 0.96 (t, $J = 7.3$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 173.4, 173.3, 141.6, 128.6, 128.4, 126.2, 83.9 (d, $J = 174.8$ Hz), 65.1 (d, $J = 18.1$ Hz), 61.4, 42.8, 34.2, 34.2, 32.9, 29.8, 20.6, 14.4, 14.1.

^{19}F { ^1H } NMR (376 MHz, CDCl_3) δ –229.7.

IR (film, cm^{-1}) 3027, 2958, 2930, 2871, 1727, 1496, 1455, 1378, 1180, 1100, 1021, 745, 698.

HRMS m/z calcd for $\text{C}_{27}\text{H}_{27}\text{FNO}_2$ [$\text{M}+\text{H}$] $^+$ 296.2020; found 296.2017.



***N*-Benzyl-1-fluoro-*N*-methylpentan-2-amine (4aa).** Prepared according to general procedure A using *N*-benzylmethylamine (26 μL , 0.2 mmol), butyraldehyde (36 μL , 0.4 mmol), fluoroiodomethane (40 μL , 0.6 mmol), tris(trimethylsilyl)silane (123 μL , 0.4 mmol), *tert*-butyldimethylsilyl trifluoromethanesulfonate (46 μL , 0.2 mmol) and 4 Å MS (300 mg) in 6 mL dichloromethane. The crude reaction mixture was purified by flash column chromatography (0–10% ethyl acetate in 40–60 °C petroleum ether) to afford the product as a colourless oil (31 mg, 74%).

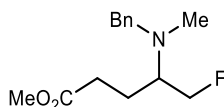
^1H NMR (700 MHz, CDCl_3) δ 7.37 – 7.28 (m, 4H), 7.24 (t, $J = 7.2$ Hz, 1H), 4.67 – 4.41 (m, 2H), 3.75 (d, $J = 13.6$ Hz, 1H), 3.67 (d, $J = 13.6$ Hz, 1H), 2.94 – 2.81 (m, 1H), 2.27 (s, 3H), 1.58 – 1.45 (m, 2H), 1.45 – 1.33 (m, 2H), 0.94 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (176 MHz, CDCl_3) δ 140.3, 128.6, 128.3, 126.9, 84.0 (d, $J = 171.8$ Hz), 61.8 (d, $J = 17.1$ Hz), 58.9 (d, $J = 1.8$ Hz), 37.2 (d, $J = 1.3$ Hz), 29.5 (d, $J = 6.8$ Hz), 20.0, 14.2.

^{19}F $\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ -224.3.

IR (film, cm^{-1}) 2028, 2958, 2933, 2872, 2793, 1494, 1454, 1362, 1028, 998, 733, 698.

HRMS m/z calcd for $\text{C}_{13}\text{H}_{21}\text{FN}$ $[\text{M}+\text{H}]^+$ 210.1653; found 210.1656.



Methyl 4-(benzyl(methyl)amino)-5-fluoropentanoate (4ab). Prepared according to general procedure A using *N*-benzylmethylamine (26 μL , 0.2 mmol), methyl 4-oxobutanoate (42 μL , 0.4 mmol), fluoroiodomethane (40 μL , 0.6 mmol), tris(trimethylsilyl)silane (123 μL , 0.4 mmol), *tert*-butyldimethylsilyl trifluoromethanesulfonate (46 μL , 0.2 mmol) and 4 Å MS (300 mg) in 6 mL dichloromethane. The crude reaction mixture was purified by flash column chromatography (0–20% ethyl acetate in 40–60 °C petroleum ether) to afford the product as a colourless oil (31 mg, 61%).

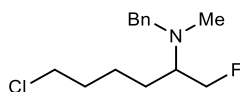
^1H NMR (400 MHz, CDCl_3) δ 7.44 – 7.11 (m, 5H), 4.67 – 4.40 (m, 2H), 3.75 (d, $J = 13.5$ Hz, 1H), 3.65 (d, $J = 8.7$ Hz, 4H), 2.97 – 2.80 (m, 1H), 2.58 – 2.35 (m, 2H), 2.22 (s, 3H), 1.90 – 1.75 (m, 1H), 1.76 – 1.63 (m, 1H).

^{13}C NMR (176 MHz, CDCl_3) δ 174.1, 140.0, 128.8, 128.4, 127.1, 83.6 (d, $J = 172.0$ Hz), 61.1 (d, $J = 17.6$ Hz), 59.4, 51.7, 36.7, 31.1, 22.9.

^{19}F $\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ -224.0.

IR (film, cm^{-1}) 3027, 2952, 2796, 1733, 1453, 1436, 1169, 1027, 1001, 969, 734, 698.

HRMS m/z calcd for $\text{C}_{14}\text{H}_{21}\text{FNO}_2$ $[\text{M}+\text{H}]^+$ 254.1551; found 254.1549.



N-Benzyl-6-chloro-1-fluoro-N-methylhexan-2-amine (4ac). Prepared according to general procedure A using *N*-benzylmethylamine (26 μL , 0.2 mmol), 5-chloropentanal (48 mg, 0.4 mmol), fluoroiodomethane (40 μL , 0.6 mmol), tris(trimethylsilyl)silane (123 μL , 0.4 mmol), *tert*-butyldimethylsilyl trifluoromethanesulfonate (46 μL , 0.2 mmol) and 4 Å MS (300 mg) in 6 mL dichloromethane. The crude reaction mixture was purified by flash column chromatography (0–5% ethyl acetate in 40–60 °C petroleum ether) to afford the product as a colourless oil (43 mg, 84%).

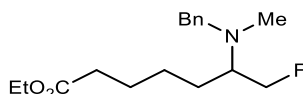
$^1\text{H NMR}$ (700 MHz, CDCl_3) δ 7.36 – 7.28 (m, 3H), 7.27 – 7.22 (m, 1H), 4.64 – 4.47 (m, 2H), 3.76 (d, $J = 13.5$ Hz, 1H), 3.66 (d, $J = 13.5$ Hz, 1H), 3.56 (t, $J = 6.6$ Hz, 2H), 2.90 – 2.83 (m, 1H), 2.27 (s, 3H), 1.85 – 1.71 (m, 2H), 1.68 – 1.60 (m, 1H), 1.61 – 1.48 (m, 2H), 1.47 – 1.38 (m, 1H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 128.7, 128.4, 127.0, 83.8 (d, $J = 172.3$ Hz), 61.7 (d, $J = 17.4$ Hz), 59.0 (d, $J = 1.7$ Hz), 45.1, 37.2, 32.7, 26.8, 26.8, 24.1.

^{19}F $\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ –223.8.

IR (film, cm^{-1}) 2951, 2872, 1630, 1458, 1215, 1078, 864, 762, 710, 568.

HRMS m/z calcd for $\text{C}_{14}\text{H}_{22}\text{ClFN}$ $[\text{M}+\text{H}]^+$ 258.1419; found 258.1428.



Ethyl 6-(benzyl(methyl)amino)-7-fluoroheptanoate (4ad). Prepared according to general procedure A using *N*-benzylmethylamine (26 μL , 0.2 mmol), ethyl 6-oxoheptanoate (63 mg, 0.4 mmol), fluoroiodomethane (40 μL , 0.6 mmol), tris(trimethylsilyl)silane (123 μL , 0.4 mmol), *tert*-butyldimethylsilyl trifluoromethanesulfonate (46 μL , 0.2 mmol) and 4 Å MS (300 mg) in 6 mL dichloromethane. The crude reaction mixture was purified by flash column chromatography (0–15% ethyl acetate in 40–60 °C petroleum ether) to afford the product as a colourless oil (46 mg, 77%).

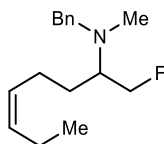
$^1\text{H NMR}$ (700 MHz, CDCl_3) δ 7.34 – 7.28 (m, 4H), 7.25 – 7.21 (m, 1H), 4.63 – 4.44 (m, 2H), 4.13 (t, $J = 7.1$ Hz, 2H), 3.75 (d, $J = 13.6$ Hz, 1H), 3.66 (d, $J = 13.5$ Hz, 1H), 2.90 – 2.82 (m, 1H), 2.32 (t, $J = 7.5$ Hz, 2H), 2.26 (s, 3H), 1.68 – 1.61 (m, 2H), 1.62 – 1.47 (m, 2H), 1.46 – 1.38 (m, 2H), 1.26 (t, $J = 7.1$ Hz, 3H).

$^{13}\text{C NMR}$ (176 MHz, CDCl_3) δ 173.7, 140.2, 128.7, 128.3, 126.9, 83.8 (d, $J = 172.3$ Hz), 61.9 (d, $J = 17.3$ Hz), 60.3, 59.0 (d, $J = 1.8$ Hz), 37.2, 34.4, 27.12, 26.4, 25.1, 14.4.

^{19}F $\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ –224.6.

IR (film, cm^{-1}) 3027, 2940, 2862, 2794, 1731, 1453, 1371, 1177, 1028, 734, 698.

HRMS m/z calcd for $\text{C}_{17}\text{H}_{27}\text{FNO}_2$ $[\text{M}+\text{H}]^+$ 296.2020; found 296.2021.



(Z)-N-Benzyl-1-fluoro-N-methyloct-5-en-2-amine (4ae). Prepared according to general procedure A using *N*-benzylmethylamine (26 μL , 0.2 mmol), *cis*-4-heptenal (53 μL , 0.4 mmol), fluoroiodomethane (40 μL , 0.6 mmol), tris(trimethylsilyl)silane (123 μL , 0.4 mmol), *tert*-butyldimethylsilyl trifluoromethanesulfonate (92 μL , 0.4 mmol) and 4 Å MS (300 mg) in 6 mL dichloromethane. The crude reaction mixture was purified by flash column chromatography (0–5% ethyl acetate in 40–60 °C petroleum ether) to afford the product as a colourless oil (38 mg, 76%).

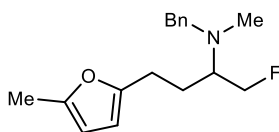
^1H NMR (700 MHz, CDCl_3) δ 7.37 – 7.28 (m, 4H), 7.24 (t, $J = 7.3$ Hz, 1H), 5.57 – 5.23 (m, 2H), 4.70 – 4.36 (m, 2H), 3.76 (dd, $J = 13.6, 9.0$ Hz, 1H), 3.66 (dd, $J = 13.7, 4.0$ Hz, 1H), 2.94 – 2.84 (m, 1H), 2.26 (d, $J = 3.5$ Hz, 3H), 2.24 – 1.95 (m, 4H), 1.61 (dt, $J = 14.3, 6.3$ Hz, 1H), 1.48 – 1.40 (m, 1H), 0.96 (td, $J = 7.4, 3.5$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 140.3, 132.9, 132.5, 128.7, 128.3, 126.9, 83.9 (d, $J = 169.2$ Hz), 61.6 (dd, $J = 35.6, 17.2$ Hz), 58.94 (dd, $J = 13.0, 1.7$ Hz), 37.30 (d, $J = 14.8$ Hz), 29.69, 27.55 (d, $J = 6.6$ Hz), 27.33 (d, $J = 6.8$ Hz), 25.74, 24.39, 20.71, 14.52, 14.08.

^{19}F $\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ –223.6.

IR (film, cm^{-1}) 2963, 1704, 1500, 1372, 1180, 1017, 938, 754, 696, 605.

HRMS m/z calcd for $\text{C}_{16}\text{H}_{25}\text{FN}$ $[\text{M}+\text{H}]^+$ 250.1966; found 250.1973.



***N*-Benzyl-1-fluoro-*N*-methyl-4-(5-methylfuran-2-yl)butan-2-amine (4af).** Prepared according to general procedure A using *N*-benzylmethylamine (13 μL , 0.1 mmol), 3-(5-methylfuran-2-yl)propanal (27 μL , 0.2 mmol), fluoroiodomethane (20 μL , 0.3 mmol), tris(trimethylsilyl)silane (62 μL , 0.2 mmol), *tert*-butyldimethylsilyl trifluoromethanesulfonate (46 μL , 0.2 mmol) and 4 Å MS (150 mg) in 3 mL dichloromethane. The crude reaction mixture was purified by flash column chromatography (0–5% ethyl acetate in 40–60 °C petroleum ether) to afford the product as a colourless oil (22 mg, 81%).

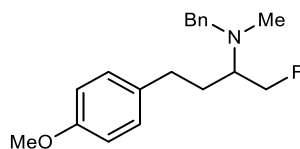
^1H NMR (700 MHz, CDCl_3) δ 7.36 – 7.29 (m, 4H), 7.28 – 7.23 (m, 1H), 5.87 – 5.83 (m, 2H), 4.65 – 4.49 (m, 2H), 3.78 (s, 1H), 3.68 (d, $J = 13.5$ Hz, 1H), 2.97 – 2.88 (m, 1H), 2.84 – 2.77 (m, 1H), 2.73 – 2.66 (m, 1H), 2.28 (s, 3H), 2.26 (s, 3H), 1.93 – 1.82 (m, 1H), 1.78 – 1.67 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 154.0, 150.5, 140.2, 128.7, 128.4, 127.0, 106.0, 105.7, 83.8 (d, $J = 172.4$ Hz), 61.4 (d, $J = 17.4$ Hz), 59.1 (d, $J = 1.9$ Hz), 37.0, 26.2 (d, $J = 6.7$ Hz), 25.3, 13.7.

^{19}F $\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ –223.7.

IR (film, cm^{-1}) 3028, 2951, 2922, 2849, 2795, 1714, 1570, 1453, 1356, 1218, 1021, 782, 735, 699.

HRMS m/z calcd for $\text{C}_{17}\text{H}_{23}\text{FNO}$ $[\text{M}+\text{H}]^+$ 276.1758; found 276.1768.



***N*-Benzyl-1-fluoro-4-(4-methoxyphenyl)-*N*-methylbutan-2-amine (4ag).** Prepared according to general procedure A using *N*-benzylmethylamine (13 μ L, 0.1 mmol), 3-(4-methoxyphenyl)propanal (32 μ L, 0.2 mmol), fluoroiodomethane (20 μ L, 0.3 mmol), tris(trimethylsilyl)silane (62 μ L, 0.2 mmol), *tert*-butyldimethylsilyl trifluoromethanesulfonate (46 μ L, 0.2 mmol) and 4 Å MS (150 mg) in 3 mL dichloromethane. The crude reaction mixture was purified by flash column chromatography (0–10% ethyl acetate in 40–60 °C petroleum ether) to afford the product as a colourless oil (22 mg, 74%).

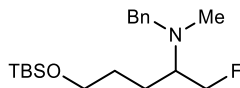
^1H NMR (700 MHz, CDCl_3) δ 7.37 – 7.30 (m, 4H), 7.28 – 7.23 (m, 1H), 7.13 – 7.09 (m, 2H), 6.85 – 6.81 (m, 2H), 4.64 – 4.48 (m, 2H), 3.81 – 3.76 (m, 4H), 3.66 (d, J = 13.6 Hz, 1H), 2.92 – 2.84 (m, 1H), 2.79 – 2.72 (m, 1H), 2.71 – 2.63 (m, 1H), 2.28 (s, 2H), 1.90 – 1.81 (m, 1H), 1.75 – 1.60 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 158.0, 140.2, 134.4, 129.5, 128.7, 128.4, 123.0, 114.0, 83.9 (d, J = 172.4 Hz), 61.4 (d, J = 17.3 Hz), 58.9 (d, J = 1.8 Hz), 55.4, 37.3, 32.0, 29.7, 29.6.

^{19}F $\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ –223.6.

IR (film, cm^{-1}) 3028, 2950, 2835, 2796, 1512, 1246, 1035, 824, 735, 699.

HRMS m/z calcd for $\text{C}_{19}\text{H}_{25}\text{FNO}$ $[\text{M}+\text{H}]^+$ 302.1915; found 302.1912.



***N*-Benzyl-5-((*tert*-butyldimethylsilyl)oxy)-1-fluoro-*N*-methylpentan-2-amine (4ah).** Prepared according to general procedure A using *N*-benzylmethylamine (13 μ L, 0.1 mmol), 4-((*tert*-butyldimethylsilyl)oxy)butanal (40 mg, 0.2 mmol), fluoroiodomethane (20 μ L, 0.3 mmol), tris(trimethylsilyl)silane (62 μ L, 0.2 mmol), *tert*-butyldimethylsilyl trifluoromethanesulfonate (46 μ L, 0.2 mmol) and 4 Å MS (150 mg) in 3 mL dichloromethane. The crude reaction mixture was purified by flash column chromatography (0–10% ethyl acetate in 40–60 °C petroleum ether) to afford the product as a colourless oil (21 mg, 63%).

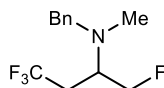
^1H NMR (700 MHz, CDCl_3) δ 7.36 – 7.28 (m, 4H), 7.23 (t, J = 7.2 Hz, 1H), 4.66 – 4.42 (m, 2H), 3.75 (d, J = 13.5 Hz, 1H), 3.67 (d, J = 13.9 Hz, 1H), 3.65 – 3.58 (m, 2H), 2.96 – 2.80 (m, 1H), 2.26 (s, 3H), 1.71 (t, J = 7.6 Hz, 1H), 1.64 – 1.54 (m, 2H), 1.50 – 1.41 (m, 1H), 0.90 (s, 9H), 0.05 (s, 6H).

^{13}C NMR (101 MHz, CDCl_3) δ 140.3, 140.3, 128.8, 128.3, 127.0, 84.0 (d, J = 172.0 Hz), 63.1, 61.9 (d, J = 17.3 Hz), 59.0 (d, J = 1.8 Hz), 37.2, 30.1, 26.1, 23.7, 23.6, 18.5, –5.1.

^{19}F $\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ –223.4.

IR (film, cm^{-1}) 2953, 2928, 2856, 2797, 1263, 1255, 1098, 836, 775, 698.

HRMS m/z calcd for $\text{C}_{19}\text{H}_{35}\text{FNOSi}$ $[\text{M}+\text{H}]^+$ 340.2466; found 340.2474.



***N*-Benzyl-1,4,4,4-tetrafluoro-*N*-methylbutan-2-amine (4ai).** Prepared according to general procedure A using *N*-benzylmethylamine (26 μL , 0.2 mmol), 3,3,3-trifluoropropanal (34 μL , 0.4 mmol), fluoroiodomethane (40 μL , 0.6 mmol), tris(trimethylsilyl)silane (123 μL , 0.4 mmol), *tert*-butyldimethylsilyl trifluoromethanesulfonate (92 μL , 0.4 mmol) and 4 Å MS (300 mg) in 6 mL dichloromethane. The crude reaction mixture was purified by flash column chromatography (0–10% ethyl acetate in 40–60 °C petroleum ether) to afford the product as a colourless oil (31 mg, 62%).

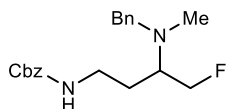
^1H NMR (700 MHz, CDCl_3) δ 7.36 – 7.29 (m, 4H), 7.29 – 7.23 (m, 1H), 4.74 – 4.46 (m, 2H), 3.69 (s, 2H), 3.34 – 3.18 (m, 1H), 2.49 – 2.31 (m, 2H), 2.29 (s, 3H).

^{13}C NMR (176 MHz, CDCl_3) δ 138.9, 128.5, 128.3, 127.2, 126.6 (q, $J = 276.5$ Hz), 82.9 (d, $J = 174.4$ Hz), 58.8 (d, $J = 1.9$ Hz), 56.7 (dq, $J = 18.4, 2.3$ Hz), 37.3 (d, $J = 1.9$ Hz), 31.2 (qd, $J = 28.2, 6.8$ Hz).

^{19}F $\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ -64.7, -226.6.

IR (film, cm^{-1}) 3030, 2961, 2801, 1454, 1368, 1327, 1253, 1214, 1176, 1138, 1054, 1014, 737, 698.

HRMS m/z calcd for $\text{C}_{12}\text{H}_{16}\text{F}_4\text{N}$ $[\text{M}+\text{H}]^+$ 250.1213; found 250.1212.



Benzyl (3-(benzyl(methyl)amino)-4-fluorobutyl)carbamate (4aj). Prepared according to general procedure A using *N*-benzylmethylamine (26 μL , 0.2 mmol), benzyl (3-oxopropyl)carbamate (83 mg, 0.4 mmol), fluoroiodomethane (40 μL , 0.6 mmol), tris(trimethylsilyl)silane (123 μL , 0.4 mmol), *tert*-butyldimethylsilyl trifluoromethanesulfonate (46 μL , 0.2 mmol) and 4 Å MS (300 mg) in 6 mL dichloromethane. The crude reaction mixture was purified by flash column chromatography (0–10% ethyl acetate in 40–60 °C petroleum ether) to afford the product as a colourless oil (37 mg, 54%).

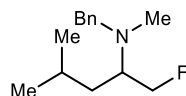
^1H NMR (400 MHz, CDCl_3) δ 7.41 – 7.18 (m, 10H), 5.45 (s, 1H), 5.09 (s, 2H), 4.72 – 4.37 (m, 2H), 3.79 (d, $J = 13.2$ Hz, 1H), 3.68 (d, $J = 13.2$ Hz, 1H), 3.44 – 3.21 (m, 2H), 3.03 – 2.89 (m, 1H), 2.29 (s, 3H), 1.80 – 1.65 (m, 1H), 1.64 – 1.48 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 156.5, 139.4, 136.9, 128.9, 128.6, 128.5, 128.2, 128.1, 127.3, 83.3 (d, $J = 172.9$ Hz), 66.6, 59.9 (d, $J = 17.5$ Hz), 59.5, 39.4, 36.7, 27.2, 27.1.

^{19}F $\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ -224.3.

IR (film, cm^{-1}) 3335, 3030, 2952, 2798, 1704, 1517, 1454, 1252, 1134, 1027, 735, 698.

HRMS m/z calcd for $\text{C}_{20}\text{H}_{26}\text{FN}_2\text{O}_2$ $[\text{M}+\text{H}]^+$ 345.1973; found 345.1970.



***N*-Benzyl-1-fluoro-*N*,4-dimethylpentan-2-amine (4ak).** Prepared according to general procedure A using *N*-benzylmethylamine (26 μ L, 0.2 mmol), isovaleraldehyde (43 μ L, 0.4 mmol), fluoroiodomethane (40 μ L, 0.6 mmol), tris(trimethylsilyl)silane (123 μ L, 0.4 mmol), *tert*-butyldimethylsilyl trifluoromethanesulfonate (92 μ L, 0.4 mmol) and 4 Å MS (300 mg) in 6 mL dichloromethane. The crude reaction mixture was purified by flash column chromatography (0–15% ethyl acetate in 40–60 °C petroleum ether) to afford the product as a colourless oil (33 mg, 73%).

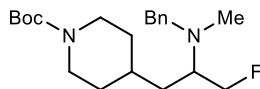
$^1\text{H NMR}$ (700 MHz, CDCl_3) δ 7.36 – 7.29 (m, 4H), 7.24 (t, $J = 7.2$ Hz, 1H), 4.64 – 4.44 (m, 2H), 3.76 (d, $J = 13.6$ Hz, 1H), 3.68 (d, $J = 13.6$ Hz, 1H), 3.02 – 2.93 (m, 1H), 2.26 (s, 3H), 1.86 – 1.77 (m, 1H), 1.51 – 1.45 (m, 1H), 1.19 – 1.12 (m, 1H), 0.93 (d, $J = 6.7$ Hz, 3H), 0.90 (d, $J = 6.5$ Hz, 3H).

$^{13}\text{C NMR}$ (176 MHz, CDCl_3) δ 140.4, 128.7, 128.3, 126.9, 84.2 (d, $J = 172.1$ Hz), 60.0 (d, $J = 16.9$ Hz), 59.0 (d, $J = 1.8$ Hz), 37.0 (d, $J = 1.2$ Hz), 36.5 (d, $J = 6.7$ Hz), 24.9, 23.3, 22.4.

^{19}F $\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ –223.6.

IR (film, cm^{-1}) 3028, 2954, 2868, 2793, 1454, 1007, 733, 698.

HRMS m/z calcd for $\text{C}_{14}\text{H}_{23}\text{FN}$ $[\text{M}+\text{H}]^+$ 224.1809; found, 224.1815.



***tert*-Butyl 4-(2-(benzyl(methyl)amino)-3-fluoropropyl)piperidine-1-carboxylate (4al).** Prepared according to general procedure A, deviation B using *N*-benzylmethylamine (26 μ L, 0.2 mmol), *tert*-butyl 4-(2-oxoethyl)piperidine-1-carboxylate (91 mg, 0.4 mmol), fluoroiodomethane (40 μ L, 0.6 mmol), tris(trimethylsilyl)silane (123 μ L, 0.4 mmol) and 4 Å MS (300 mg) in 6 mL dichloromethane. The crude reaction mixture was purified by flash column chromatography (0–30% ethyl acetate in 40–60 °C petroleum ether) to afford the product as a colourless oil (47 mg, 65%).

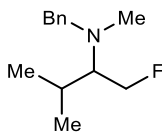
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.30 (d, $J = 4.3$ Hz, 4H), 7.26 – 7.20 (m, 1H), 4.68 – 4.35 (m, 2H), 4.06 (s, 2H), 3.76 (d, $J = 13.5$ Hz, 1H), 3.67 (d, $J = 13.5$ Hz, 1H), 3.07 – 2.90 (m, 1H), 2.68 (q, $J = 14.4, 13.9$ Hz, 2H), 2.28 (s, 3H), 1.68 – 1.49 (m, 4H), 1.46 (s, 9H), 1.20 – 1.08 (m, 2H), 1.05 – 0.92 (m, 1H).

$^{13}\text{C NMR}$ (176 MHz, CDCl_3) δ 155.0, 140.1, 128.7, 128.4, 127.0, 84.0 (d, $J = 172.7$ Hz), 79.3, 59.2, 59.2, 58.3 (d, $J = 17.2$ Hz), 36.9, 34.2, 34.2, 32.7, 28.6.

^{19}F $\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ –224.0.

IR (film, cm^{-1}) 2973, 2928, 2848, 1689, 1422, 1365, 1278, 1244, 1171, 1009, 735, 699.

HRMS m/z calcd for $\text{C}_{21}\text{H}_{34}\text{FN}_2\text{O}_2$ $[\text{M}+\text{H}]^+$ 365.2599; found 365.2602.



***N*-Benzyl-1-fluoro-*N*,3-dimethylbutan-2-amine (4am)**. Prepared according to general procedure A, deviation A using *N*-benzylmethylamine (26 μL , 0.2 mmol), isobutyraldehyde (55 μL , 0.6 mmol), fluoroiodomethane (40 μL , 0.6 mmol), tris(trimethylsilyl)silane (123 μL , 0.4 mmol), *tert*-butyldimethylsilyl trifluoromethanesulfonate (46 μL , 0.2 mmol) and 4 Å MS (300 mg) in 6 mL dichloromethane. The crude reaction mixture was purified by flash column chromatography (0–10% ethyl acetate in 40–60 °C petroleum ether) to afford the product as a colourless oil (24 mg, 58%).

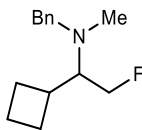
^1H NMR (700 MHz, CDCl_3) δ 7.36 – 7.28 (m, 4H), 7.23 (t, $J = 7.3$ Hz, 1H), 4.80 – 4.59 (m, 2H), 3.83 (d, $J = 13.7$ Hz, 1H), 3.63 (d, $J = 13.7$ Hz, 1H), 2.44 – 2.32 (m, 1H), 2.25 (s, 3H), 1.99 – 1.86 (m, 1H), 1.09 (d, $J = 6.6$ Hz, 3H), 0.96 (d, $J = 6.6$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 140.5, 128.5, 128.1, 126.7, 81.8 (d, $J = 170.8$ Hz), 68.9, 68.7, 59.4 (d, $J = 2.1$ Hz), 37.4, 37.4, 27.1 (d, $J = 6.8$ Hz), 21.0, 20.2.

^{19}F $\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ –226.6.

IR (film, cm^{-1}) 3029, 2960, 928, 2853, 2794, 1704, 1494, 1453, 1366, 1051, 1027, 736, 699.

HRMS m/z calcd for $\text{C}_{13}\text{H}_{21}\text{FN}$ $[\text{M}+\text{H}]^+$ 210.1653; found 210.1651.



***N*-Benzyl-1-cyclobutyl-2-fluoro-*N*-methylethan-1-amine (4an)**. Prepared according to general procedure A using *N*-benzylmethylamine (26 μL , 0.2 mmol), cyclobutanecarbaldehyde (36 μL , 0.4 mmol), fluoroiodomethane (40 μL , 0.6 mmol), tris(trimethylsilyl)silane (123 μL , 0.4 mmol), *tert*-butyldimethylsilyl trifluoromethanesulfonate (46 μL , 0.2 mmol) and 4 Å MS (300 mg) in 6 mL dichloromethane. The crude reaction mixture was purified by flash column chromatography (0–10% ethyl acetate in 40–60 °C petroleum ether) to afford the product as a colourless oil (31 mg, 71%).

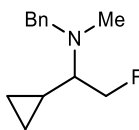
^1H NMR (400 MHz, CDCl_3) δ 7.40 – 7.17 (m, 5H), 4.70 – 4.30 (m, 2H), 3.78 (d, $J = 13.6$ Hz, 1H), 3.65 (d, $J = 13.6$ Hz, 1H), 2.94 – 2.73 (m, 1H), 2.64 – 2.48 (m, 1H), 2.27 (s, 3H), 2.20 – 2.08 (m, 1H), 2.08 – 1.87 (m, 3H), 1.86 – 1.69 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 140.5, 128.7, 128.3, 126.9, 81.9 (d, $J = 171.4$ Hz), 68.4, 68.2, 59.1, 59.1, 38.0, 37.9, 34.3, 34.2, 27.7, 27.7, 27.1, 18.7.

^{19}F $\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ –225.9.

IR (film, cm^{-1}) 3027, 2956, 2857, 2793, 1452, 1026, 987, 734, 698.

HRMS m/z calcd for $\text{C}_{14}\text{H}_{21}\text{FN}$ $[\text{M}+\text{H}]^+$ 222.1653; found 222.1652.



***N*-Benzyl-1-cyclopropyl-2-fluoro-*N*-methylethan-1-amine (4ao).** Prepared according to general procedure A, deviation B using *N*-benzylmethylamine (26 μL , 0.2 mmol), cyclopropanecarbaldehyde (30 μL , 0.4 mmol), fluoroiodomethane (40 μL , 0.6 mmol), tris(trimethylsilyl)silane (123 μL , 0.4 mmol) and 4 Å MS (300 mg) in 6 mL dichloromethane. The crude reaction mixture was purified by flash column chromatography (0–15% ethyl acetate in 40–60 °C petroleum ether) to afford the product as a colourless oil (18 mg, 42%).

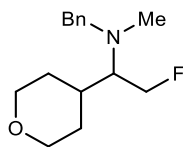
^1H NMR (700 MHz, CDCl_3) δ 7.35 (d, $J = 7.6$ Hz, 2H), 7.31 (t, $J = 7.5$ Hz, 2H), 7.23 (t, $J = 7.3$ Hz, 1H), 4.72 – 4.52 (m, 2H), 3.85 – 3.72 (m, 2H), 2.38 (s, 3H), 2.12 – 2.02 (m, 1H), 0.93 – 0.84 (m, 1H), 0.69 – 0.62 (m, 1H), 0.57 – 0.49 (m, 1H), 0.40 – 0.34 (m, 1H), 0.17 – 0.10 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3): δ 140.1, 128.8, 128.3, 127.0, 84.7 (d, $J = 172.3$ Hz), 67.5 (d, $J = 17.4$ Hz), 59.3 (d, $J = 1.7$ Hz), 38.5 (d, $J = 1.4$ Hz), 8.4 (d, $J = 8.7$ Hz), 4.8, 2.5.

^{19}F $\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ –227.4.

IR (film, cm^{-1}) 3027, 2956, 2849, 2793, 1677, 1453, 1019, 737, 699.

HRMS m/z calcd for $\text{C}_{13}\text{H}_{19}\text{FN}$ $[\text{M}+\text{H}]^+$ 208.1496; found 208.1497.



***N*-benzyl-2-fluoro-*N*-methyl-1-(tetrahydro-2H-pyran-4-yl)ethan-1-amine (4ap).** Prepared according to general procedure A using *N*-benzylmethylamine (26 μL , 0.2 mmol), tetrahydro-2H-pyran-4-carbaldehyde (63 μL , 0.6 mmol), fluoroiodomethane (40 μL , 0.6 mmol), tris(trimethylsilyl)silane (123 μL , 0.4 mmol), *tert*-butyldimethylsilyl trifluoromethanesulfonate (46 μL , 0.2 mmol) and 4 Å MS (300 mg) in 6 mL dichloromethane. The crude reaction mixture was purified by flash column chromatography (0–20% ethyl acetate in 40–60 °C petroleum ether) to afford the product as a colourless oil (26 mg, 52%).

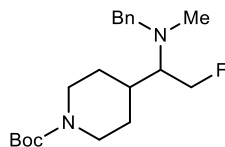
^1H NMR (700 MHz, CDCl_3) δ 7.31 (d, $J = 4.4$ Hz, 4H), 7.26 – 7.20 (m, 1H), 4.83 – 4.69 (m, 1H), 4.69 – 4.56 (m, 1H), 4.00 (dd, $J = 34.7, 11.6, 4.3$ Hz, 2H), 3.84 (d, $J = 13.7$ Hz, 1H), 3.61 (d, $J = 13.7$ Hz, 1H), 3.39 (q, $J = 11.5$ Hz, 2H), 2.48 (d, $J = 29.1, 6.6$ Hz, 1H), 2.27 (s, 3H), 2.09 (d, $J = 13.9, 2.0$ Hz, 1H), 1.90 (q, $J = 11.1$ Hz, 1H), 1.68 – 1.59 (m, 1H), 1.40 – 1.28 (m, 2H).

^{13}C NMR (176 MHz, CDCl_3) δ 140.1, 128.6, 128.4, 127.0, 80.3, 68.6, 67.7, 67.1, 67.0, 59.5, 37.6, 34.0, 33.9, 31.1, 30.8.

^{19}F $\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ –228.0.

IR (film, cm^{-1}) 3028, 2950, 2914, 2843, 2795, 1719, 1676, 1494, 1452, 1388, 1273, 1093, 987, 868, 739, 699.

HRMS m/z calcd for $\text{C}_{15}\text{H}_{23}\text{FNO}$ $[\text{M}+\text{H}]^+$ 252.1758; found 252.1759.



tert-Butyl 4-(1-(benzyl(methyl)amino)-2-fluoroethyl)piperidine-1-carboxylate (4aq). Prepared according to general procedure A, deviation B using *N*-benzylmethylamine (26 μL , 0.2 mmol), *tert*-butyl 4-formylpiperidine-1-carboxylate (85 mg, 0.4 mmol), fluoroiodomethane (40 μL , 0.6 mmol), tris(trimethylsilyl)silane (123 μL , 0.4 mmol) and 4 Å MS (300 mg) in 6 mL dichloromethane. The crude reaction mixture was purified by flash column chromatography (0–30% ethyl acetate in 40–60 °C petroleum ether) to afford the product as a colourless oil (26 mg, 37%).

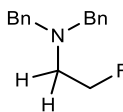
^1H NMR (700 MHz, CDCl_3) δ 7.30 (d, $J = 4.5$ Hz, 4H), 7.25 – 7.21 (m, 1H), 4.82 – 4.69 (m, 1H), 4.69 – 4.55 (m, 1H), 4.12 (s, 2H), 3.82 (d, $J = 13.7$ Hz, 1H), 3.61 (d, $J = 13.7$ Hz, 1H), 2.69 (s, 2H), 2.54 – 2.40 (m, 1H), 2.26 (s, 3H), 2.21 – 2.12 (m, 1H), 1.82 – 1.73 (m, 1H), 1.70 (d, $J = 12.8$ Hz, 1H), 1.46 (s, 9H), 1.23 – 1.06 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 155.0, 140.1, 128.7, 128.4, 127.0, 81.0 (d, $J = 172.0$ Hz), 79.4, 66.7, 59.6, 37.6, 37.6, 35.1, 35.0, 30.1, 29.7, 28.6.

^{19}F $\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ –227.7.

IR (film, cm^{-1}) 2973, 2852, 2796, 1690, 1424, 1365, 1247, 1160, 738, 699.

HRMS m/z calcd for $\text{C}_{20}\text{H}_{32}\text{FN}_2\text{O}_2$ $[\text{M}+\text{H}]^+$ 351.2442; found 351.2443.



***N,N*-Dibenzyl-2-fluoroethan-1-amine (4ar).** Prepared according to general procedure A, deviation A using dibenzylamine (39 μL , 0.2 mmol), paraformaldehyde (18 mg, 0.6 mmol), fluoroiodomethane (40 μL , 0.6 mmol), tris(trimethylsilyl)silane (123 μL , 0.4 mmol), *tert*-butyldimethylsilyl trifluoromethanesulfonate (46 μL , 0.2 mmol) and 4 Å MS (300 mg) in 6 mL dichloromethane. The crude reaction mixture was purified by flash column chromatography (0–5% ethyl acetate in 40–60 °C petroleum ether) to afford the product as a colourless oil (22 mg, 44%).

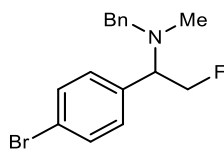
^1H NMR (400 MHz, CDCl_3) δ 7.39 (d, $J = 7.1$ Hz, 4H), 7.36 – 7.29 (m, 4H), 7.29 – 7.22 (m, 2H), 4.58 (t, $J = 5.2$ Hz, 1H), 4.46 (t, $J = 5.2$ Hz, 1H), 3.70 (s, 4H), 2.81 (dt, $J = 25.7, 5.2$ Hz, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 139.5, 128.9, 128.9, 128.4, 128.4, 127.3, 127.1, 83.0 (d, $J = 167.6$ Hz), 59.0, 59.0, 58.9, 53.2, 53.0.

^{19}F $\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ –219.9.

IR (film, cm^{-1}) 3028, 2951, 2799, 1494, 1453, 1027, 745, 698.

HRMS m/z calcd for $\text{C}_{16}\text{H}_{19}\text{FN}$ $[\text{M}+\text{H}]^+$ 244.1496; found 244.1495.



***N*-Benzyl-1-(4-bromophenyl)-2-fluoro-*N*-methylethan-1-amine (4as).** Prepared according to general procedure A, deviation C using *N*-benzylmethylamine (26 μL , 0.2 mmol), 4-bromobenzaldehyde (44 mg, 0.24 mmol), fluoroiodomethane (40 μL , 0.6 mmol), tris(trimethylsilyl)silane (185 μL , 0.6 mmol) and trimethylsilyl trifluoromethanesulfonate (97 μL , 0.5 mmol) in 2 mL dichloromethane. The crude reaction mixture was purified by flash column chromatography (0–30% dichloromethane in 40–60 $^{\circ}\text{C}$ petroleum ether) to afford the product as a colourless oil (26 mg, 41%).

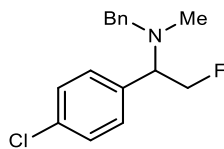
^1H NMR (400 MHz, CDCl_3) δ 7.59 – 7.45 (m, 2H), 7.39 – 7.20 (m, 7H), 4.91 – 4.56 (m, 2H), 3.88 – 3.73 (m, 1H), 3.67 (d, $J = 13.5$ Hz, 1H), 3.45 (d, $J = 13.4$ Hz, 1H), 2.26 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 139.2, 137.7, 137.6, 131.8, 130.2, 128.8, 128.4, 127.2, 121.8, 84.2 (d, $J = 175.1$ Hz), 67.2 (d, $J = 19.1$ Hz), 59.5, 59.5, 39.1, 39.1.

^{19}F $\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ –220.2.

IR (film, cm^{-1}) 3027, 2968, 2793, 1487, 1453, 1072, 1008, 821, 737, 697.

HRMS m/z calcd for $\text{C}_{16}\text{H}_{18}\text{BrFN}$ $[\text{M}+\text{H}]^+$ 322.0601; found 322.0607.



***N*-Benzyl-1-(4-chlorophenyl)-2-fluoro-*N*-methylethan-1-amine (4at).** Prepared according to general procedure A, deviation C using *N*-benzylmethylamine (26 μL , 0.2 mmol), 4-chlorobenzaldehyde (34 mg, 0.24 mmol), fluoroiodomethane (40 μL , 0.6 mmol), tris(trimethylsilyl)silane (185 μL , 0.6 mmol) and trimethylsilyl trifluoromethanesulfonate (97 μL , 0.5 mmol) in 2 mL dichloromethane. The crude reaction mixture was purified by flash column chromatography (0–40% dichloromethane in 40–60 $^{\circ}\text{C}$ petroleum ether) to afford the product as a colourless oil (26 mg, 47%).

^1H NMR (700 MHz, CDCl_3) δ 7.45 – 7.15 (m, 9H), 4.85 – 4.60 (m, 2H), 3.89 – 3.72 (m, 1H), 3.64 (d, $J = 13.5$ Hz, 1H), 3.43 (d, $J = 13.4$ Hz, 1H), 2.23 (s, 3H).

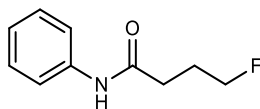
^{13}C NMR (176 MHz, CDCl_3) δ 139.3, 137.1, 133.6, 129.9, 128.8, 128.8, 128.4, 127.2, 84.3 (d, $J = 175.1$ Hz), 67.2, 67.1, 59.5, 59.5, 39.1, 39.1.

^{19}F $\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ –220.2.

IR (film, cm^{-1}) 3062, 3027, 2970, 2948, 2794, 1595, 1492, 1453, 1091, 1042, 1014, 827, 738, 698, 535.

HRMS m/z calcd for $\text{C}_{16}\text{H}_{18}\text{ClFN}$ $[\text{M}+\text{H}]^+$ 278.1112; found 278.1121.

5. Products of hydrofluoromethylation



4-fluoro-*N*-phenylbutanamide (6a). Prepared according to general procedure B using *N*-phenylacrylamide (29 mg, 0.2 mmol), fluoroiodomethane (27 μ L, 0.4 mmol) and tris(trimethylsilyl)silane (123 μ L, 0.4 mmol) in 1 mL ethanol. The crude reaction mixture was purified by flash column chromatography (0–30% ethyl acetate in 40–60 °C petroleum ether) to afford the product as a white solid (29 mg, 81%).

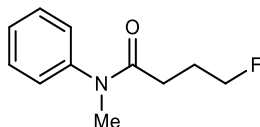
^1H NMR (400 MHz, CDCl_3) δ 7.50 (d, $J = 7.9$ Hz, 2H), 7.41 (s, 1H), 7.31 (t, $J = 7.7$ Hz, 2H), 7.11 (t, $J = 7.4$ Hz, 1H), 4.53 (dt, $J = 47.3, 5.7$ Hz, 2H), 2.51 (t, $J = 7.3$ Hz, 2H), 2.12 (dq, $J = 26.6, 6.6$ Hz, 2H).

^{13}C NMR (176 MHz, CDCl_3) δ 170.4, 137.9, 129.1, 124.5, 120.0, 83.3 (d, $J = 164.6$ Hz), 33.1 (d, $J = 4.3$ Hz), 26.3 (d, $J = 19.9$ Hz).

^{19}F $\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ -221.6.

IR (film, cm^{-1}) 3299, 2971, 2901, 1656, 1601, 1538, 1440, 1032, 897, 756, 692.

HRMS m/z calcd for $\text{C}_{10}\text{H}_{13}\text{FNO}$ $[\text{M}+\text{H}]^+$ 182.0976; found 182.0981.



4-Fluoro-*N*-methyl-*N*-phenylbutanamide (6b). Prepared according to general procedure B using *N*-methyl-*N*-phenylacrylamide (32 mg, 0.2 mmol), fluoroiodomethane (40 μ L, 0.6 mmol) and tris(trimethylsilyl)silane (185 μ L, 0.6 mmol) in 1 mL ethanol. The crude reaction mixture was purified by flash column chromatography (0–30% ethyl acetate in 40–60 °C petroleum ether) to afford the product as a white solid (29 mg, 73%).

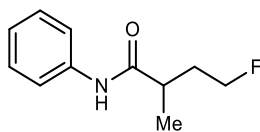
^1H NMR (400 MHz, CDCl_3) δ 7.41 (dd, $J = 8.3, 6.7$ Hz, 2H), 7.21 – 7.12 (m, 2H), 4.40 (dt, $J = 47.3, 5.8$ Hz, 2H), 3.26 (s, 3H), 2.19 (t, $J = 7.3$ Hz, 2H), 2.03 – 1.90 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 172.1, 144.0, 129.9, 128.0, 127.4, 83.5 (d, $J = 164.3$ Hz), 37.4, 29.9 (d, $J = 4.7$ Hz), 26.3 (d, $J = 19.9$ Hz).

^{19}F $\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ -220.1.

IR (film, cm^{-1}) 2967, 1651, 1595, 1496, 1420, 1383, 1027, 773, 699.

HRMS m/z calcd for $\text{C}_{11}\text{H}_{15}\text{FNO}$ $[\text{M}+\text{H}]^+$ 196.1132; found 196.1133.



4-Fluoro-2-methyl-N-phenylbutanamide (6c). Prepared according to general procedure B using *N*-phenylmethacrylamide (32 mg, 0.2 mmol), fluoroiodomethane (27 μ L, 0.4 mmol) and tris(trimethylsilyl)silane (123 μ L, 0.4 mmol) in 1 mL ethanol. The crude reaction mixture was purified by flash column chromatography (0–30% ethyl acetate in 40–60 °C petroleum ether) to afford the product as a white solid (32 mg, 83%).

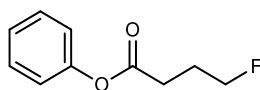
$^1\text{H NMR}$ (700 MHz, CDCl_3) δ 7.53 (d, $J = 7.9$ Hz, 2H), 7.32 (t, $J = 7.8$ Hz, 3H), 7.11 (t, $J = 7.4$ Hz, 1H), 4.62 – 4.43 (m, 2H), 2.61 (sext, $J = 6.9$ Hz, 1H), 2.19 – 2.05 (m, 1H), 1.94 – 1.82 (m, 1H), 1.29 (d, $J = 7.0$ Hz, 3H).

$^{13}\text{C NMR}$ (176 MHz, CDCl_3) δ 174.0, 137.9, 129.1, 124.5, 120.1, 82.2 (d, $J = 164.0$ Hz), 38.5 (d, $J = 3.4$ Hz), 34.8 (d, $J = 19.5$ Hz), 18.0.

^{19}F $\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ –220.5.

IR (film, cm^{-1}) 3249, 2973, 1659, 1597, 1541, 1441, 1249, 752, 693.

HRMS m/z calcd for $\text{C}_{11}\text{H}_{15}\text{FNO}$ $[\text{M}+\text{H}]^+$ 196.1132; found 196.1138.



Phenyl 4-fluorobutanoate (6d). Prepared according to general procedure B using phenyl acrylate (28 μ L, 0.2 mmol), fluoroiodomethane (27 μ L, 0.4 mmol) and tris(trimethylsilyl)silane (123 μ L, 0.4 mmol) in 1 mL *tert*-butanol. The crude reaction mixture was purified by flash column chromatography (0–100% dichloromethane in 40–60 °C petroleum ether) to afford the product as a colourless oil (31 mg, 84%).

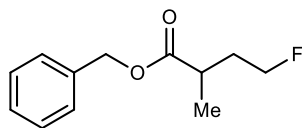
$^1\text{H NMR}$ (700 MHz, CDCl_3) δ 7.39 (t, $J = 7.9$ Hz, 2H), 7.24 (t, $J = 7.4$ Hz, 1H), 7.09 (d, $J = 7.9$ Hz, 2H), 4.57 (dt, $J = 47.1$, 5.8 Hz, 2H), 2.74 (t, $J = 7.3$ Hz, 2H), 2.19 – 2.11 (m, 2H).

$^{13}\text{C NMR}$ (176 MHz, CDCl_3) δ 171.5, 150.7, 129.5, 126.0, 121.6, 82.9 (d, $J = 165.5$ Hz), 30.3 (d, $J = 4.9$ Hz), 25.9 (d, $J = 20.3$ Hz).

^{19}F $\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ –220.8.

IR (film, cm^{-1}) 3065, 2972, 2907, 1753, 1593, 1493, 1194, 1162, 1140, 1035, 941, 751, 690.

HRMS m/z calcd for $\text{C}_{10}\text{H}_{12}\text{FO}_2$ $[\text{M}+\text{H}]^+$ 183.0816; found 183.0822.



Benzyl 4-fluoro-2-methylbutanoate (6e). Prepared according to general procedure B using benzyl methacrylate (34 μL , 0.2 mmol), fluoroiodomethane (27 μL , 0.4 mmol) and tris(trimethylsilyl)silane (123 μL , 0.4 mmol) in 1 mL *tert*-butanol. The crude reaction mixture was purified by flash column chromatography (0–100% dichloromethane in 40–60 °C petroleum ether) to afford the product as a colourless oil (37 mg, 87%).

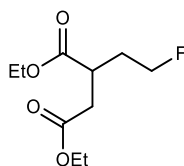
$^1\text{H NMR}$ (700 MHz, CDCl_3) δ 7.40 – 7.29 (m, 5H), 5.13 (s, 2H), 4.56 – 4.40 (m, 2H), 2.72 (sext, $J = 7.1$ Hz, 1H), 2.18 – 2.07 (m, 1H), 1.87 – 1.76 (m, 1H), 1.24 (d, $J = 7.1$ Hz, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 175.9, 136.1, 128.7, 128.4, 128.2, 82.0 (d, $J = 164.8$ Hz), 66.5, 36.0 (d, $J = 4.3$ Hz), 34.2 (d, $J = 19.9$ Hz), 17.2.

^{19}F $\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ –220.9.

IR (film, cm^{-1}) 3034, 2974, 2908, 1734, 1498, 1456, 1384, 1171, 1136, 1047, 751, 698.

HRMS m/z calcd for $\text{C}_{12}\text{H}_{16}\text{FO}_2$ $[\text{M}+\text{H}]^+$ 211.1129; found 211.1121.



Diethyl 2-(2-fluoroethyl)succinate (6f). Prepared according to general procedure B using *N*-phenylacrylamide (29 mg, 0.2 mmol), fluoroiodomethane (27 μL , 0.4 mmol) and tris(trimethylsilyl)silane (123 μL , 0.4 mmol) in 1 mL ethanol. The crude reaction mixture was purified by flash column chromatography (0–30% ethyl acetate in 40–60 °C petroleum ether) to afford the product as a colourless oil (38 mg, 86%).

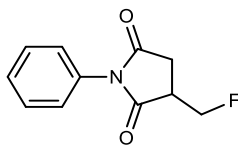
$^1\text{H NMR}$ (700 MHz, CDCl_3) δ 4.58 – 4.42 (m, 2H), 4.22 – 4.04 (m, 4H), 2.99 (tt, $J = 8.1, 5.8$ Hz, 1H), 2.73 (dd, $J = 16.6, 8.5$ Hz, 1H), 2.52 (dd, $J = 16.6, 5.6$ Hz, 1H), 2.14 – 2.02 (m, 1H), 1.99 – 1.85 (m, 1H), 1.28 – 1.22 (m, 6H).

$^{13}\text{C NMR}$ (176 MHz, CDCl_3) δ 174.1, 171.6, 81.8 (d, $J = 165.9$ Hz), 61.0, 60.8, 38.1 (d, $J = 3.9$ Hz), 36.1, 32.3 (d, $J = 20.2$ Hz), 14.3, 14.2.

^{19}F $\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ –219.1.

IR (film, cm^{-1}) 2981, 2940, 1728, 1374, 1159, 1096, 1027, 858.

HRMS m/z calcd for $\text{C}_{10}\text{H}_{18}\text{FO}_4\text{Na}$ $[\text{M}+\text{Na}]^+$ 243.1009; found 243.1018.



3-(Fluoromethyl)-1-phenylpyrrolidine-2,5-dione (6g). Prepared according to general procedure B using *N*-phenylmaleimide (35 mg, 0.2 mmol), fluoriodomethane (40 μ L, 0.6 mmol) and tris(trimethylsilyl)silane (185 μ L, 0.6 mmol) in 1 mL ethanol. The crude reaction mixture was purified by flash column chromatography (0–10% ethyl acetate in 40–60 °C petroleum ether) to afford the product as a colourless oil (43 mg, 79%).

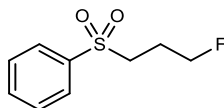
^1H NMR (700 MHz, CDCl_3) δ 7.48 (t, $J = 7.7$ Hz, 2H), 7.40 (t, $J = 7.3$ Hz, 1H), 7.28 (d, $J = 7.9$ Hz, 2H), 5.00 (ddd, $J = 46.4, 9.4, 3.3$ Hz, 1H), 4.66 (ddd, $J = 46.8, 9.4, 2.9$ Hz, 1H), 3.25 – 3.14 (m, 1H), 3.04 (dd, $J = 18.2, 9.6$ Hz, 1H), 2.94 (dd, $J = 18.2, 5.2$ Hz, 1H).

^{13}C NMR (176 MHz, CDCl_3) δ 175.6 (d, $J = 5.2$ Hz), 174.8, 131.8, 129.3, 128.8, 126.5, 81.5 (d, $J = 172.4$ Hz), 41.5 (d, $J = 21.3$ Hz), 30.9 (d, $J = 4.0$ Hz).

^{19}F $\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ –231.3.

IR (film, cm^{-1}) 3028, 2952, 2795, 1714, 1570, 1453, 1356, 1218, 1021, 782, 735, 699.

HRMS m/z calcd for $\text{C}_{11}\text{H}_{11}\text{FNO}_2$ $[\text{M}+\text{H}]^+$ 208.0768; found 208.0771.



((3-Fluoropropyl)sulfonyl)benzene (6h). Prepared according to general procedure B using phenyl vinyl sulfone (34 mg, 0.2 mmol), fluoriodomethane (27 μ L, 0.4 mmol) and tris(trimethylsilyl)silane (123 μ L, 0.4 mmol) in 1 mL ethanol. The crude reaction mixture was purified by flash column chromatography (0–30% ethyl acetate in 40–60 °C petroleum ether) to afford the product as a colourless oil (31 mg, 76%).

^1H NMR (700 MHz, CDCl_3) δ 7.93 – 7.88 (m, 2H), 7.69 – 7.63 (m, 1H), 7.61 – 7.54 (m, 2H), 4.50 (dt, $J = 46.9, 5.7$ Hz, 2H), 3.29 – 3.14 (m, 2H), 2.17 – 2.06 (m, 2H).

^{13}C NMR (176 MHz, CDCl_3) δ 139.0, 134.0, 129.5, 128.1, 81.6 (d, $J = 167.8$ Hz), 52.6 (d, $J = 4.2$ Hz), 24.2 (d, $J = 20.8$ Hz).

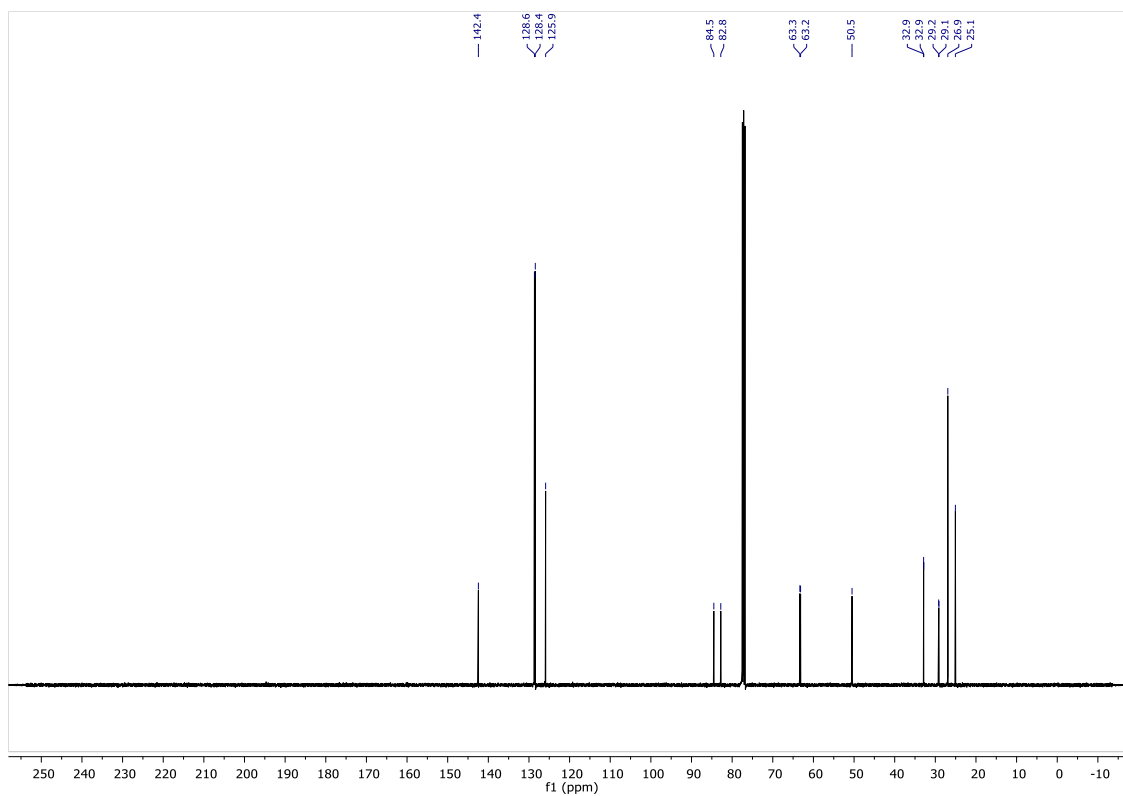
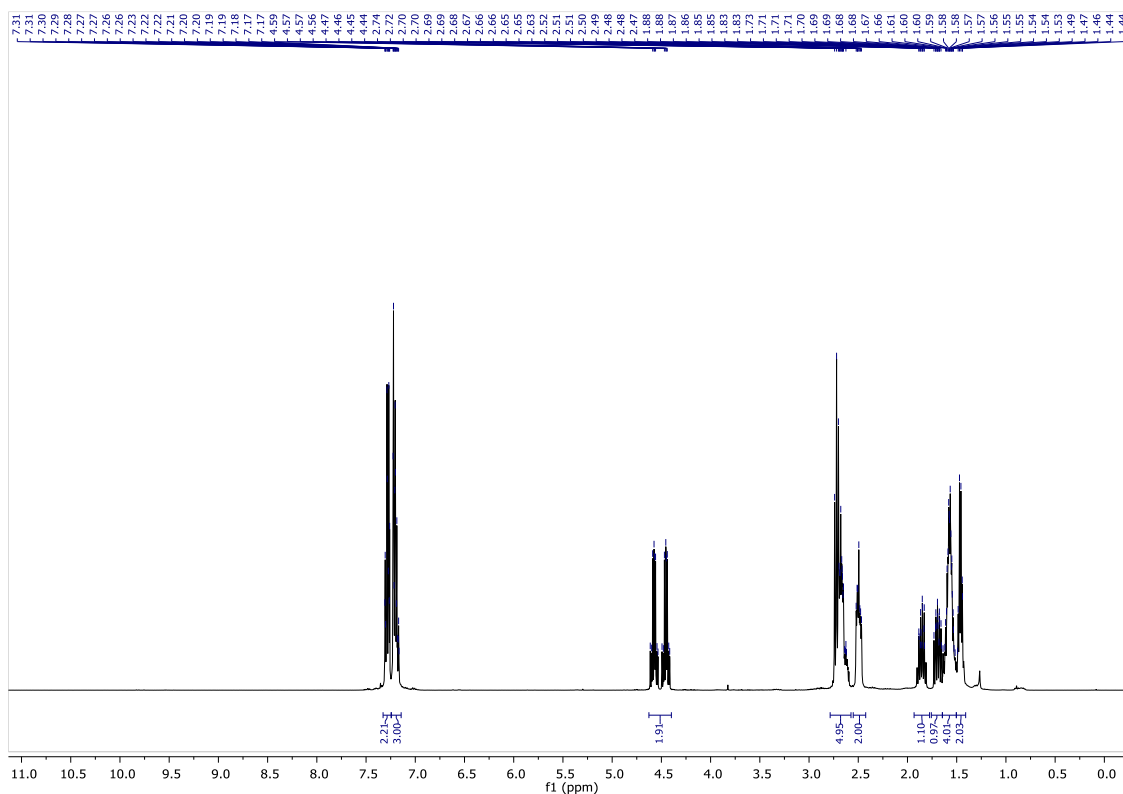
^{19}F $\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ –220.5.

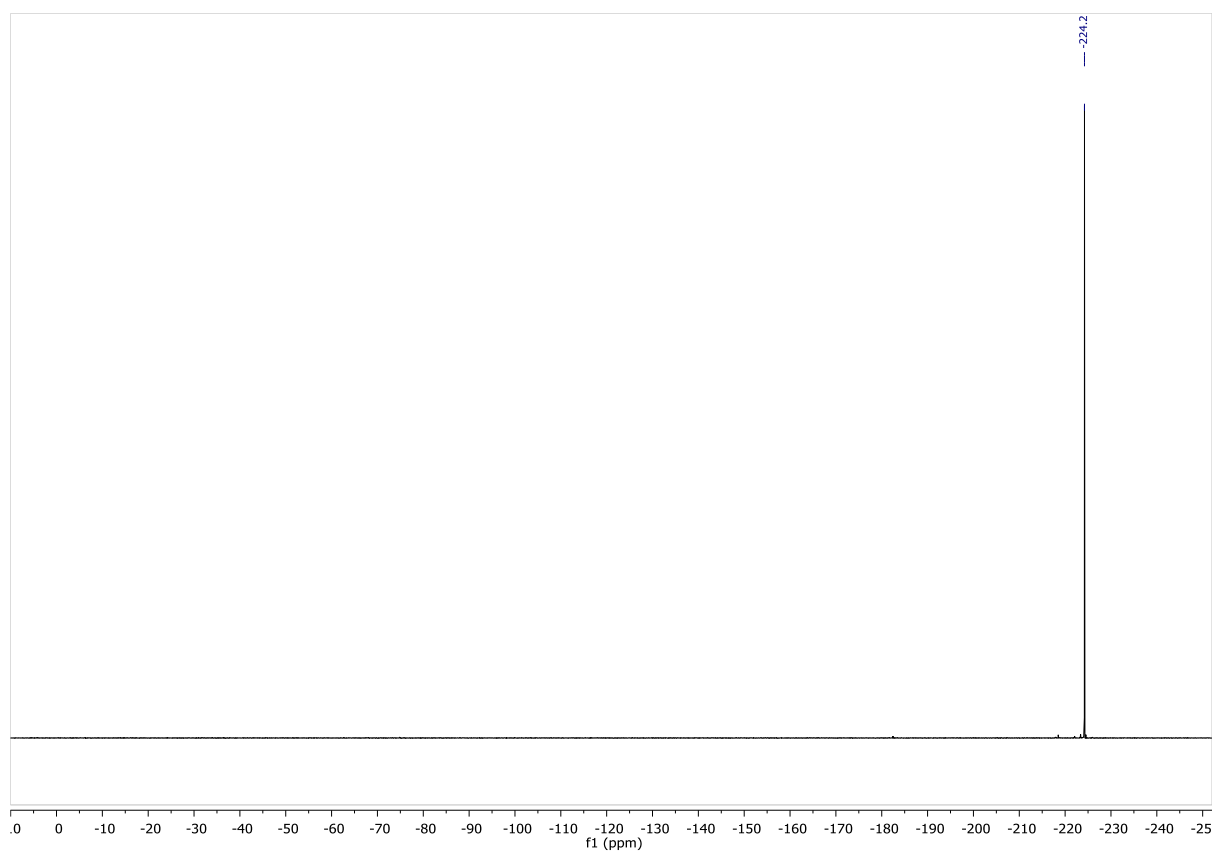
IR (film, cm^{-1}) 2973, 2911, 1447, 1306, 1264, 1141, 1087, 1023, 889, 732, 689.

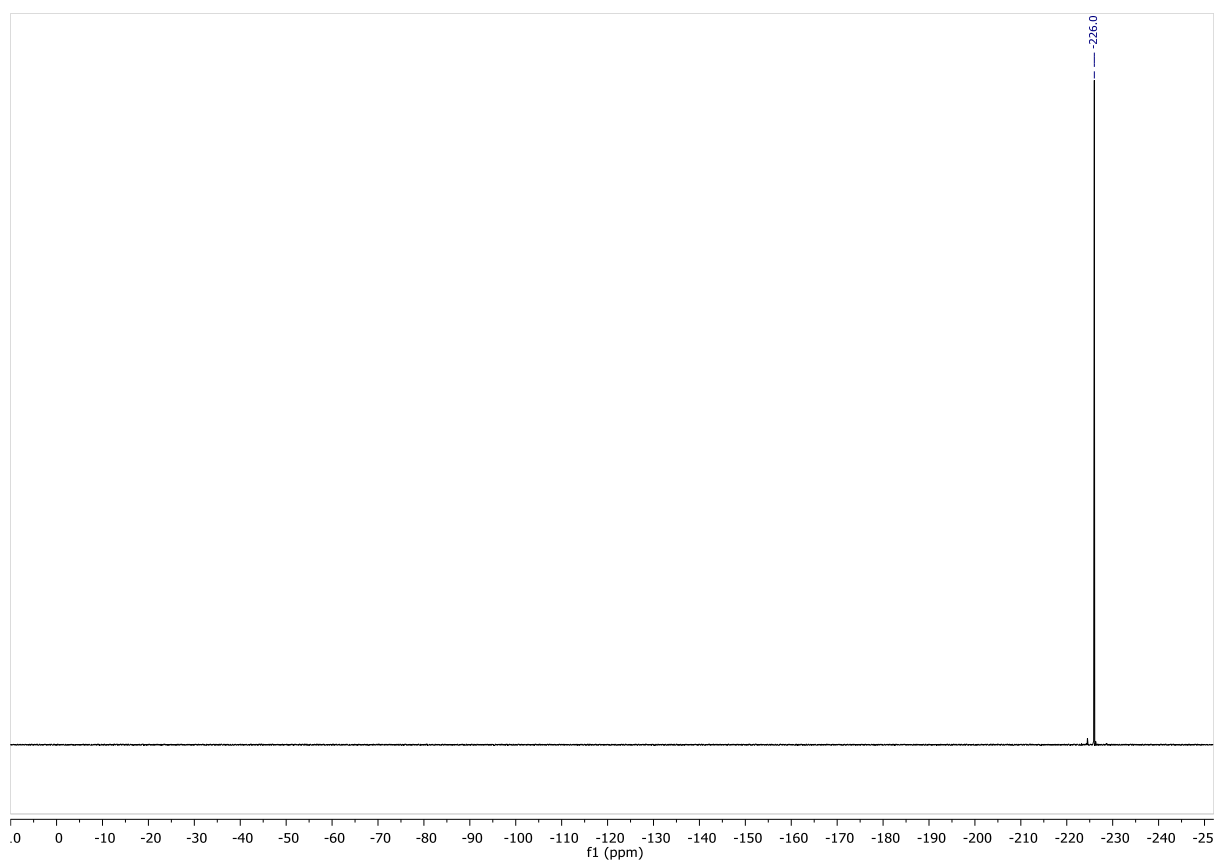
HRMS m/z calcd for $\text{C}_9\text{H}_{12}\text{FO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 203.0537; found 203.0544.

6. NMR Spectra

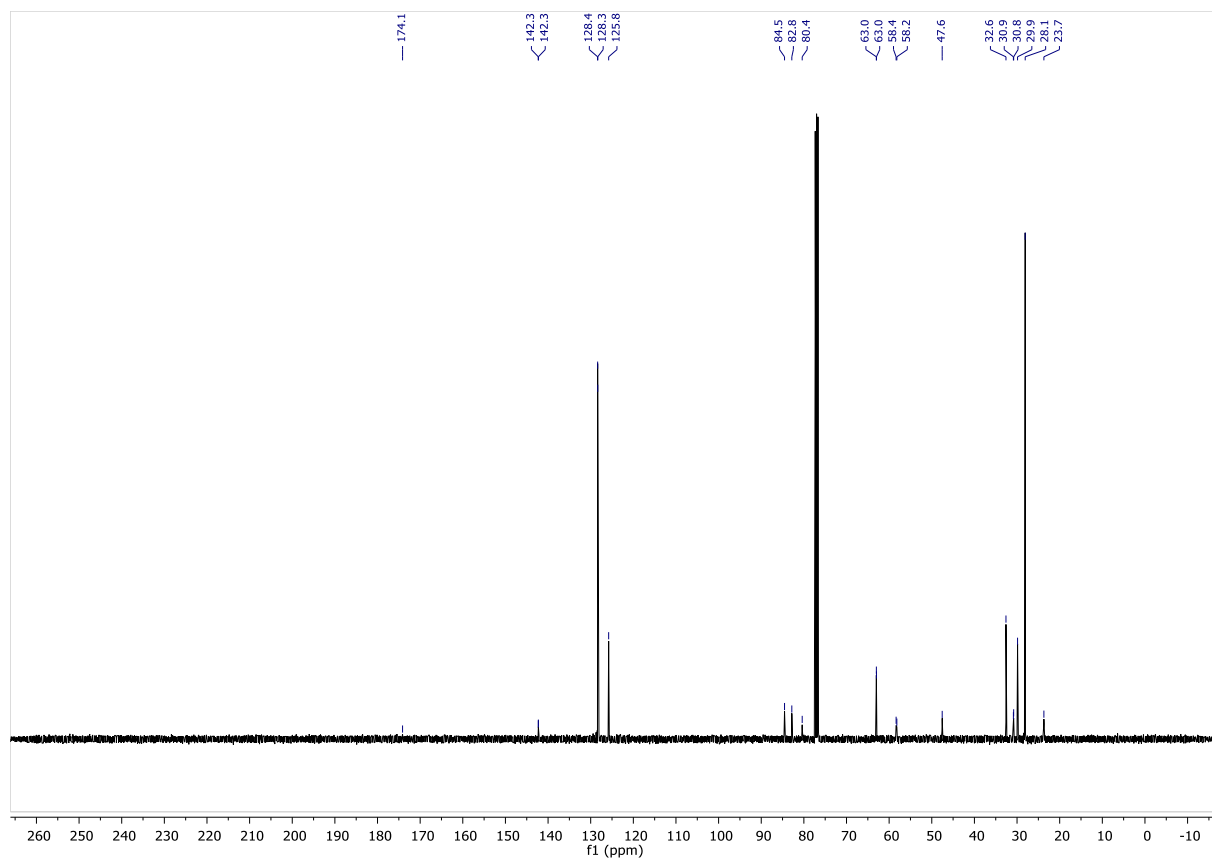
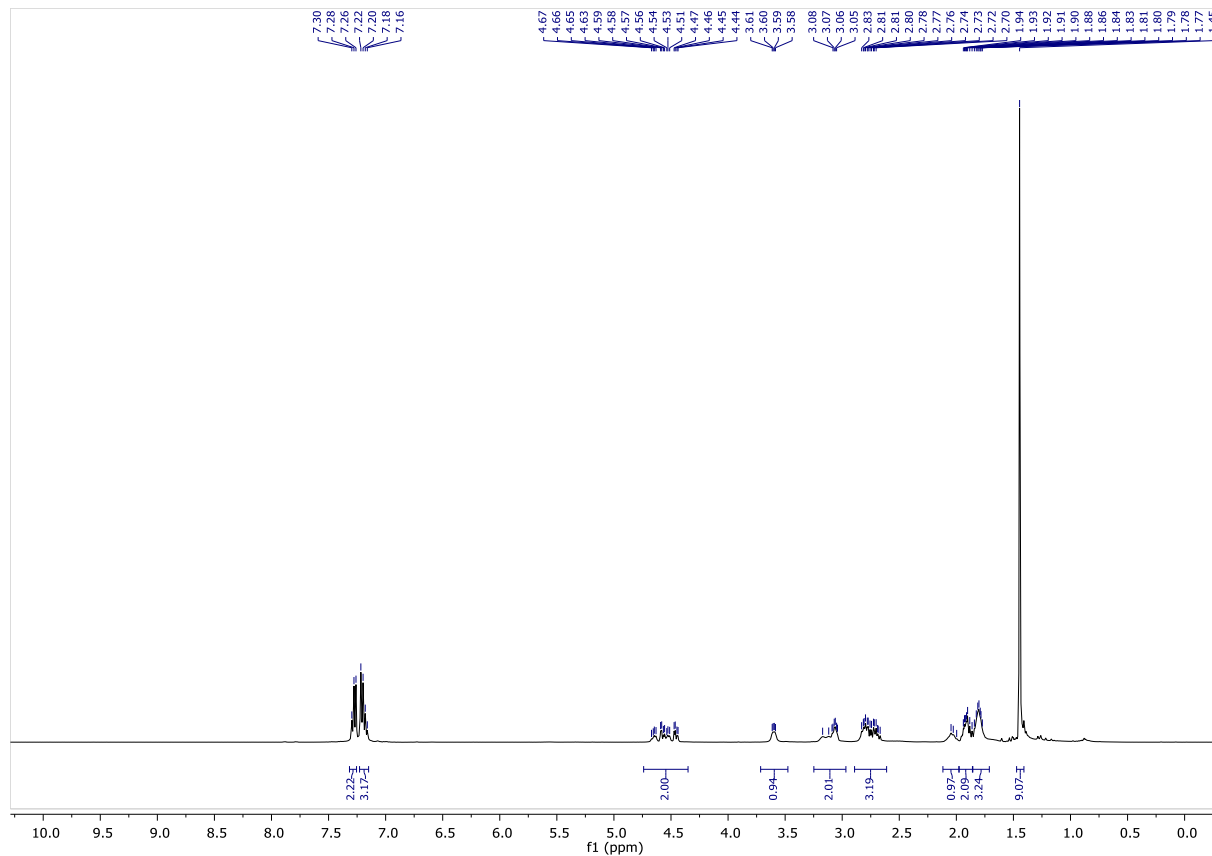
4a

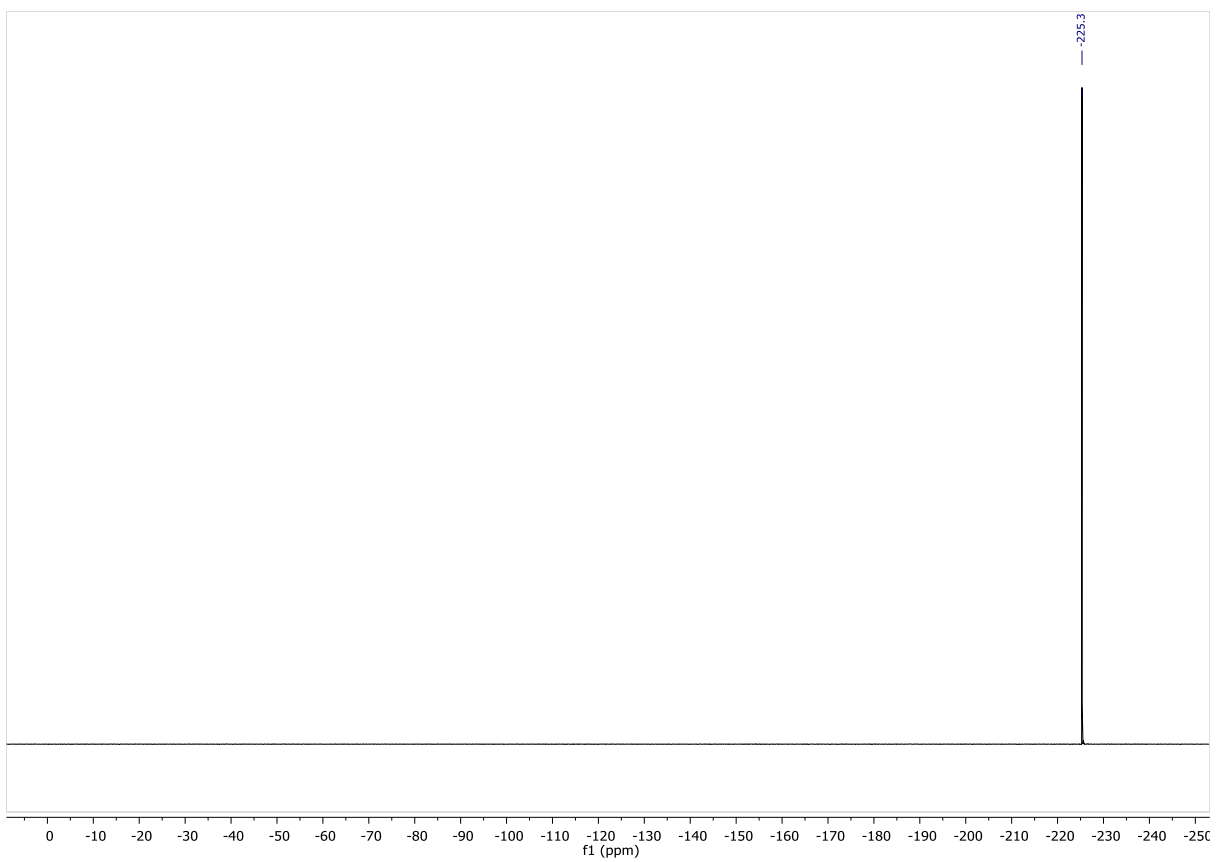




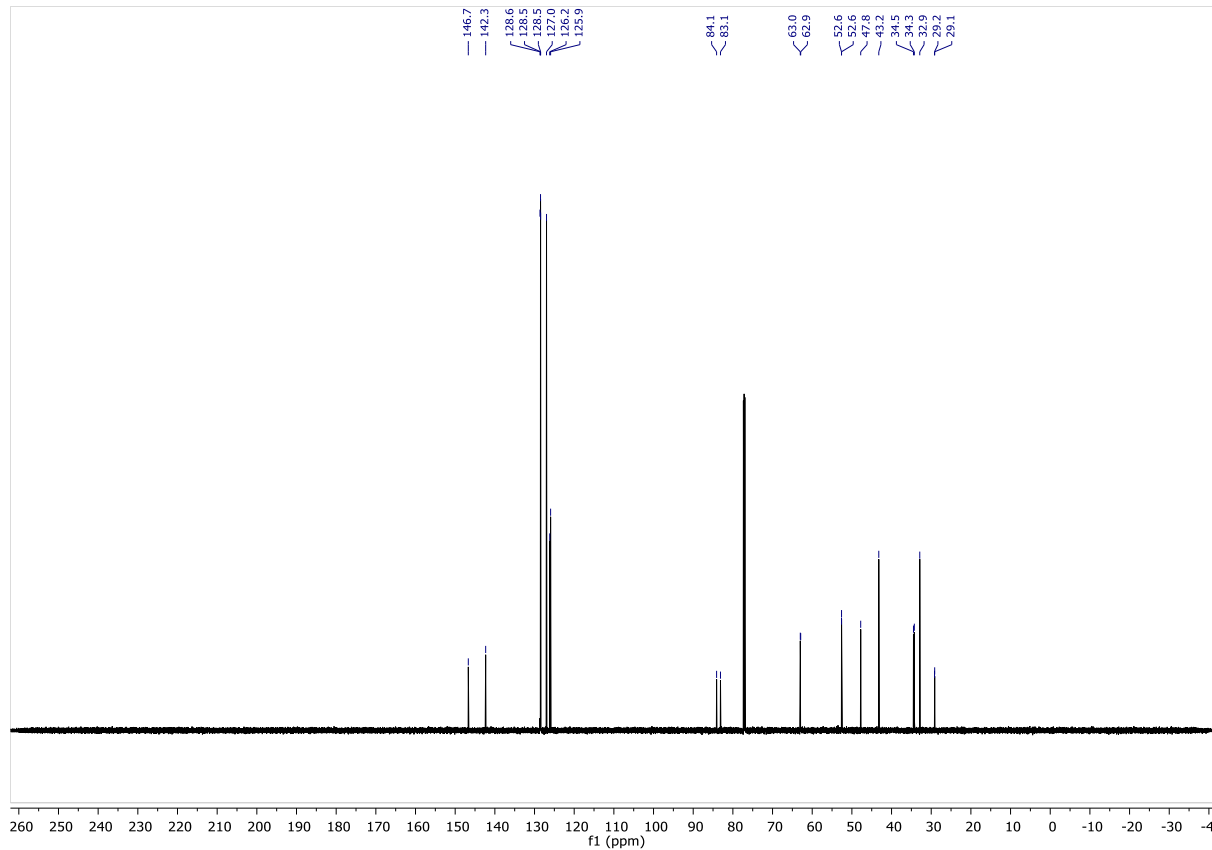
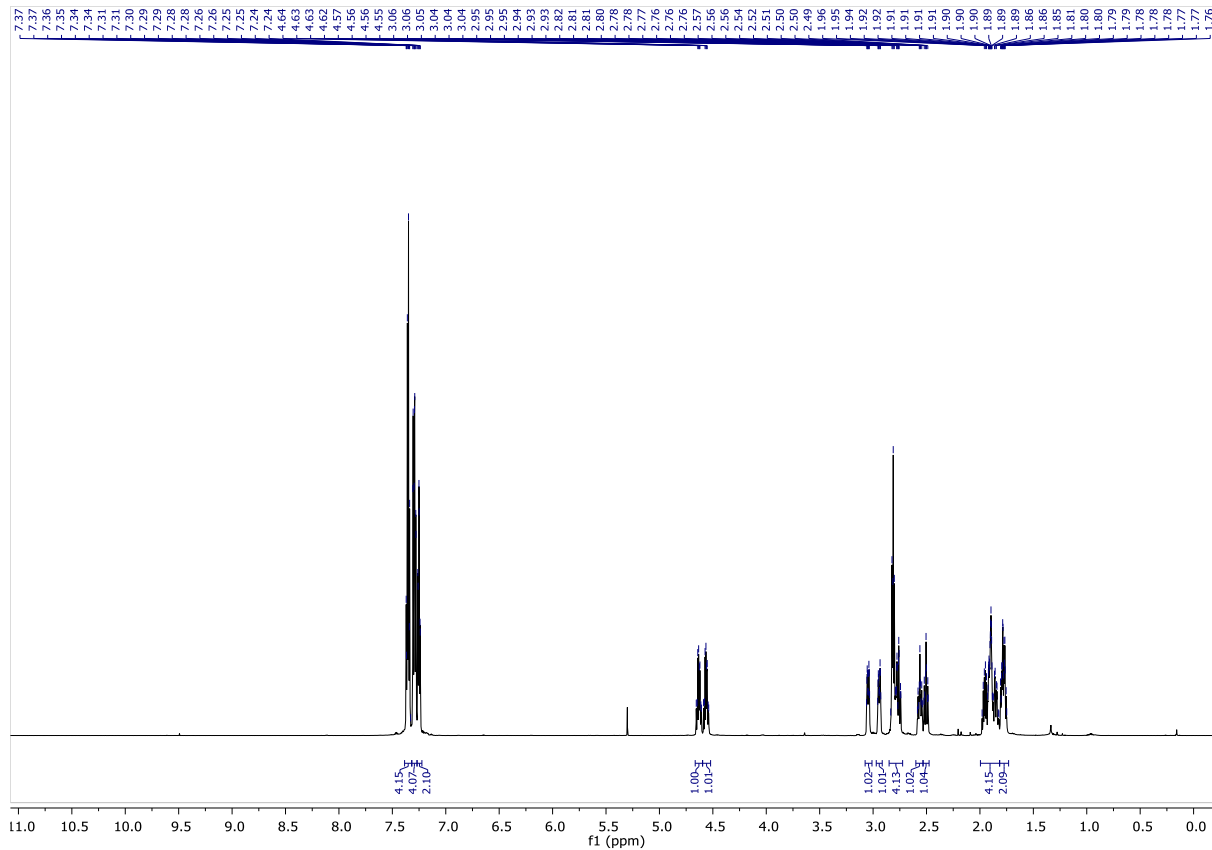


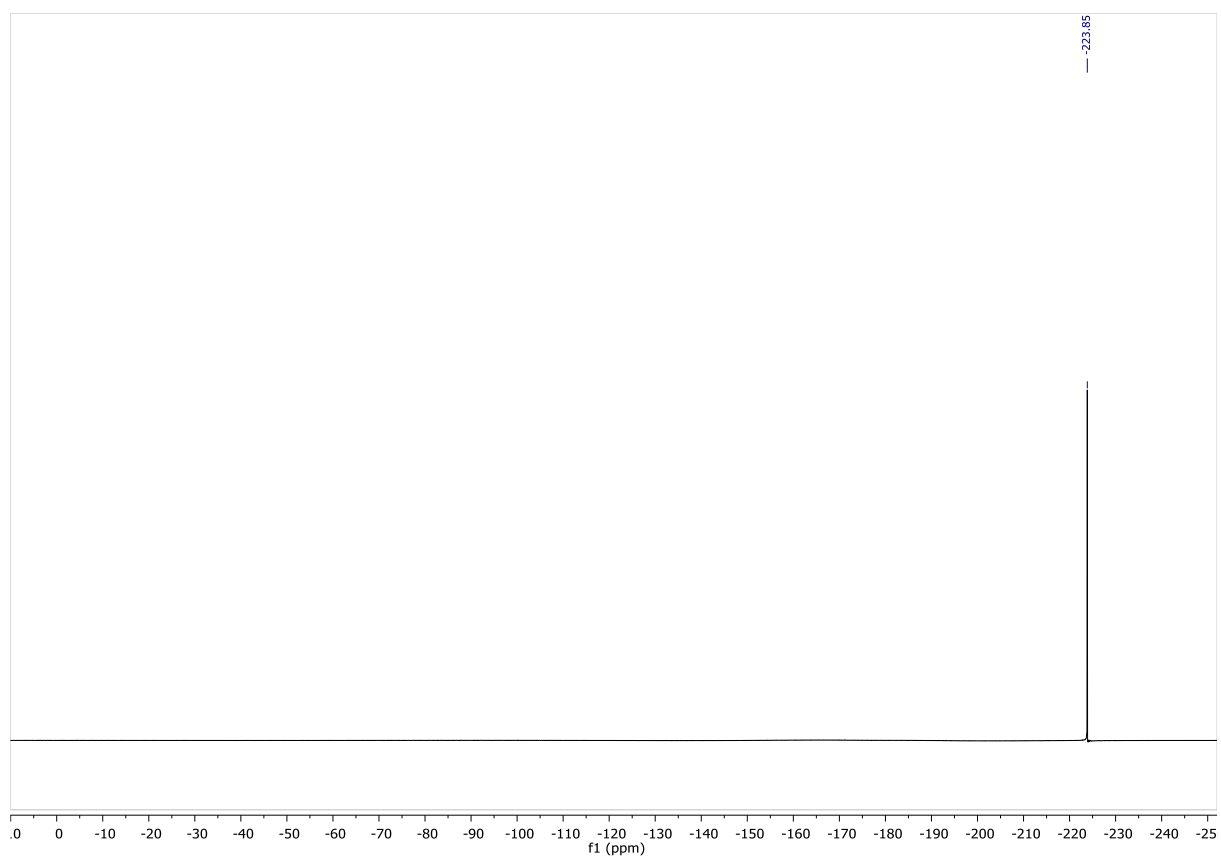
4c

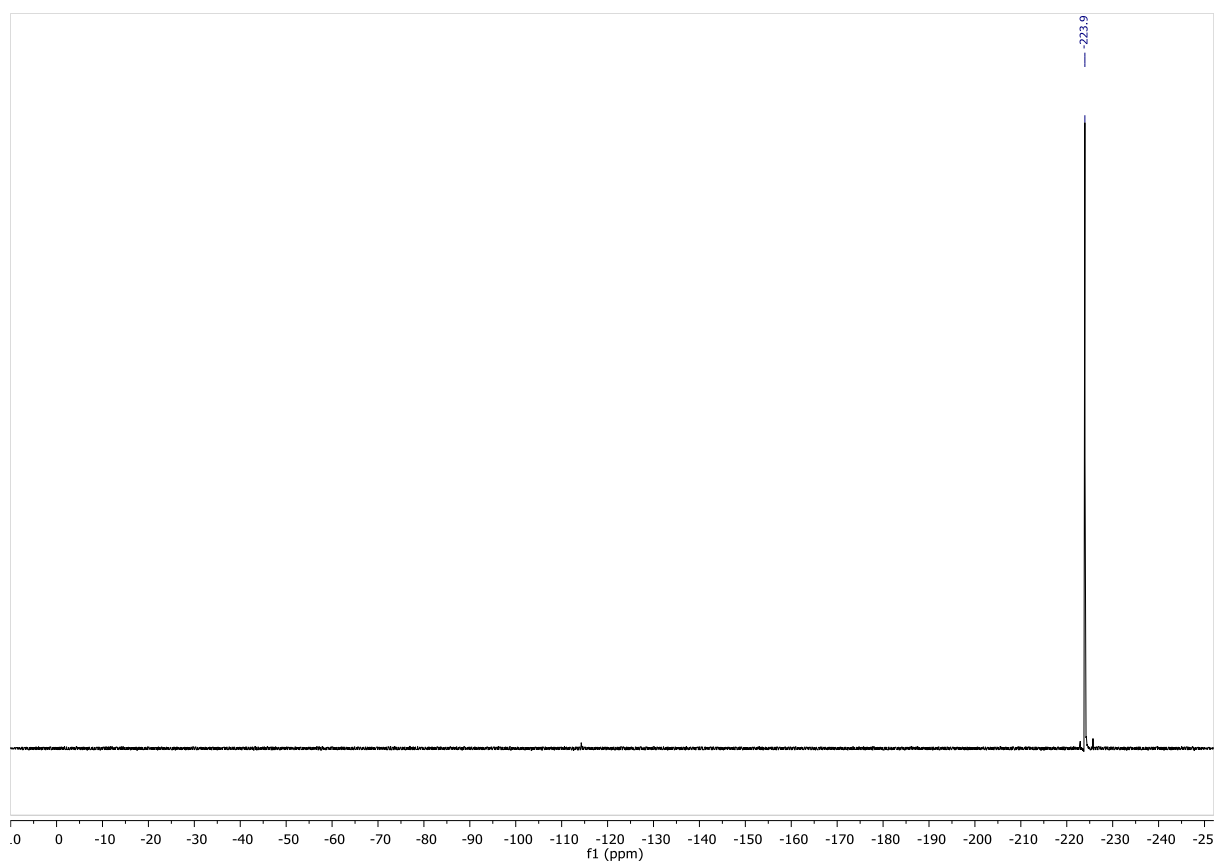




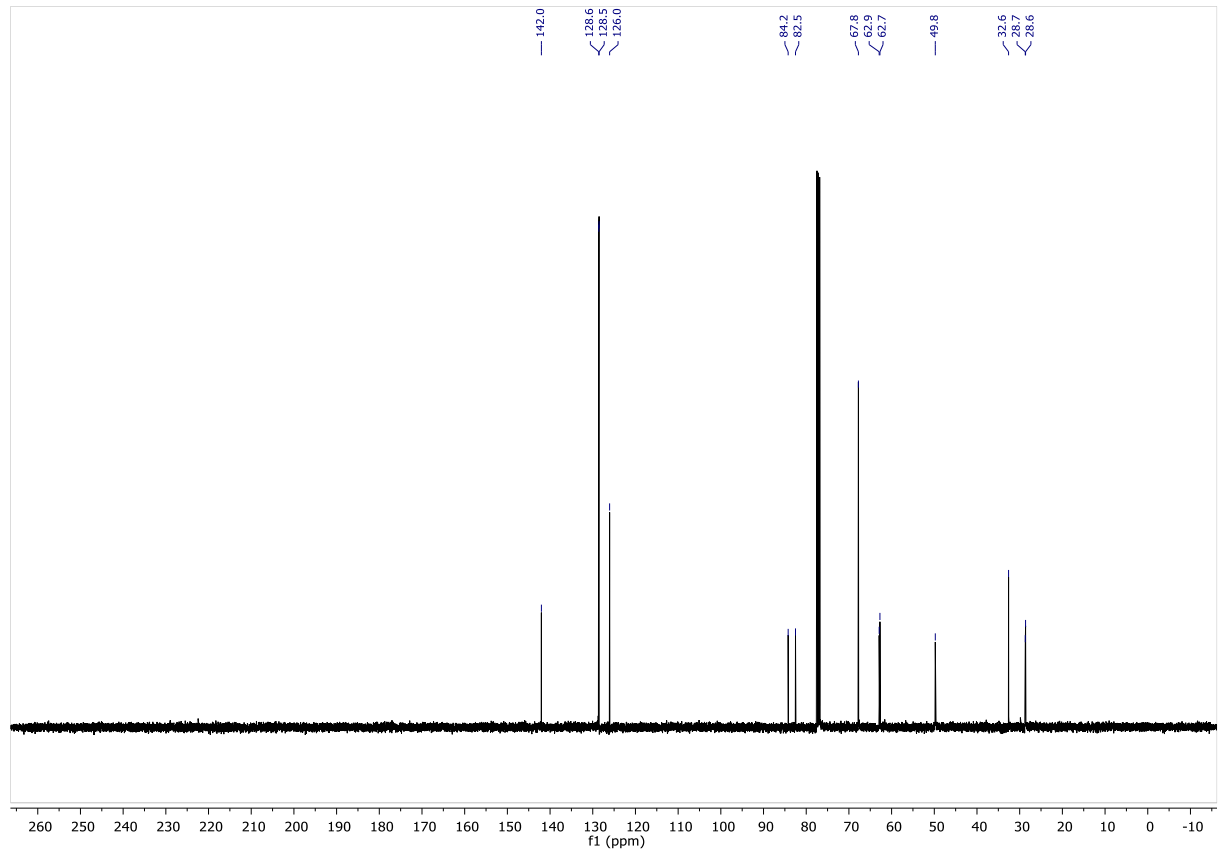
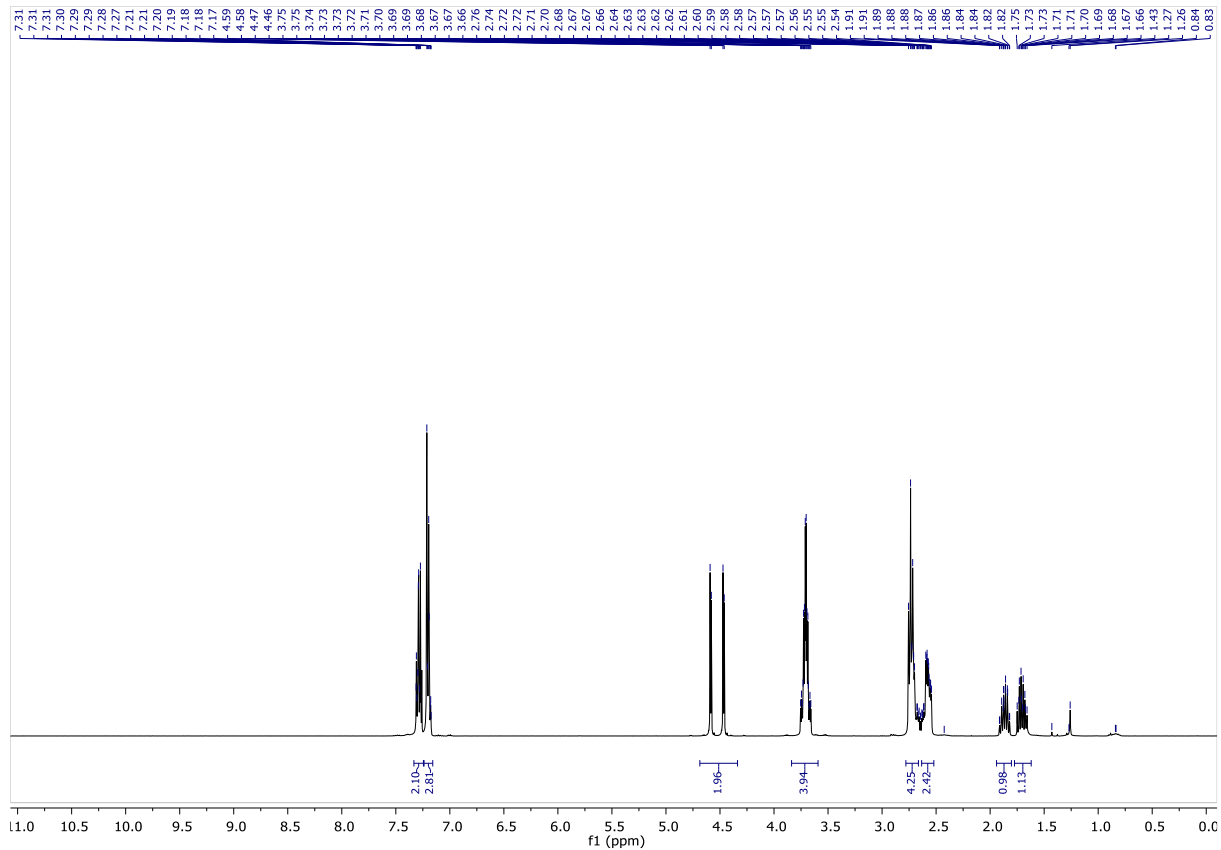
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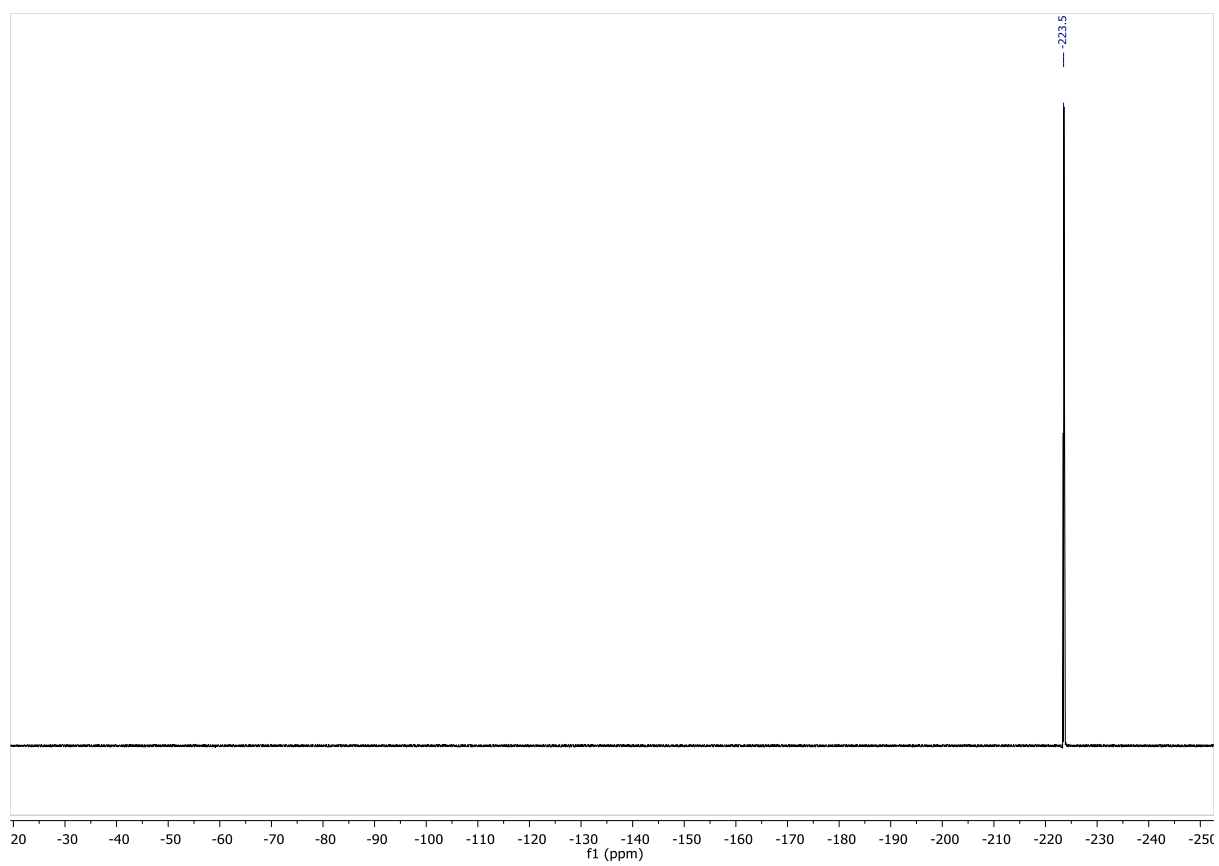




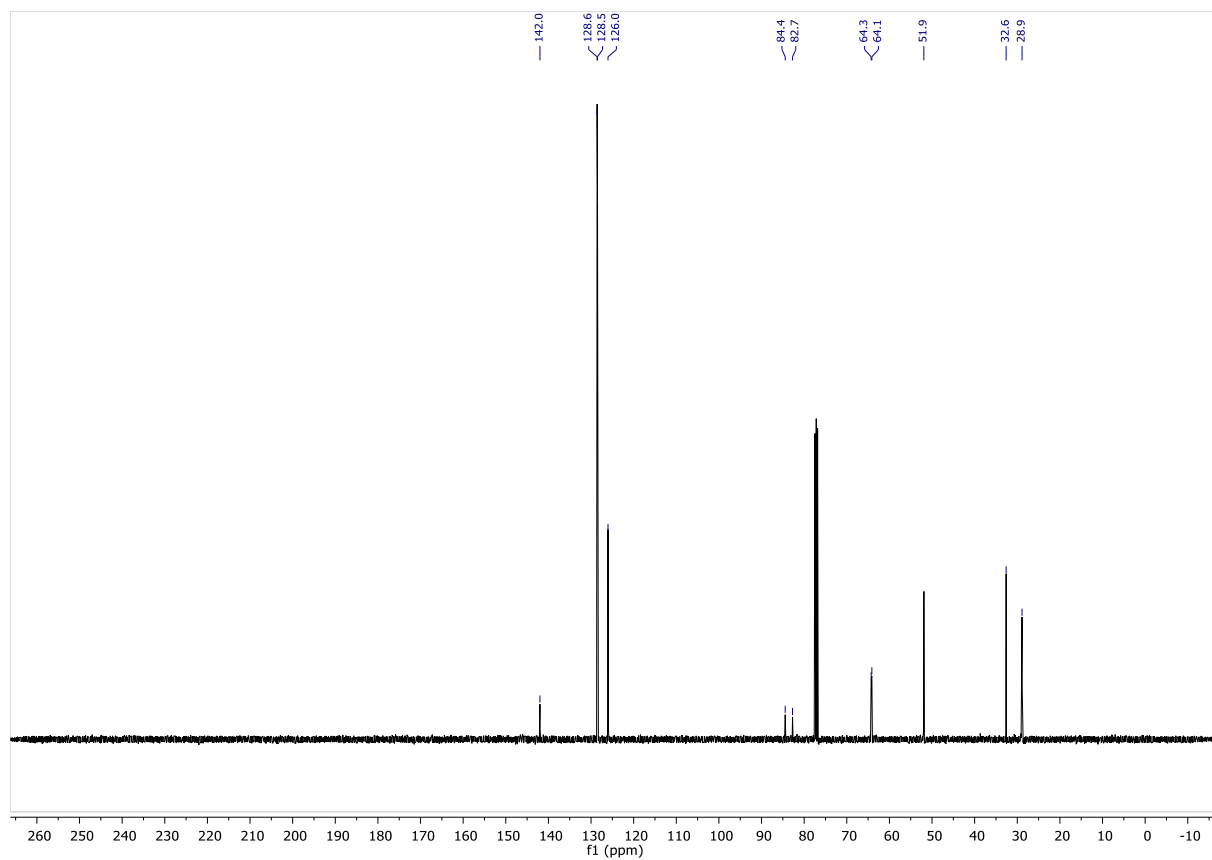
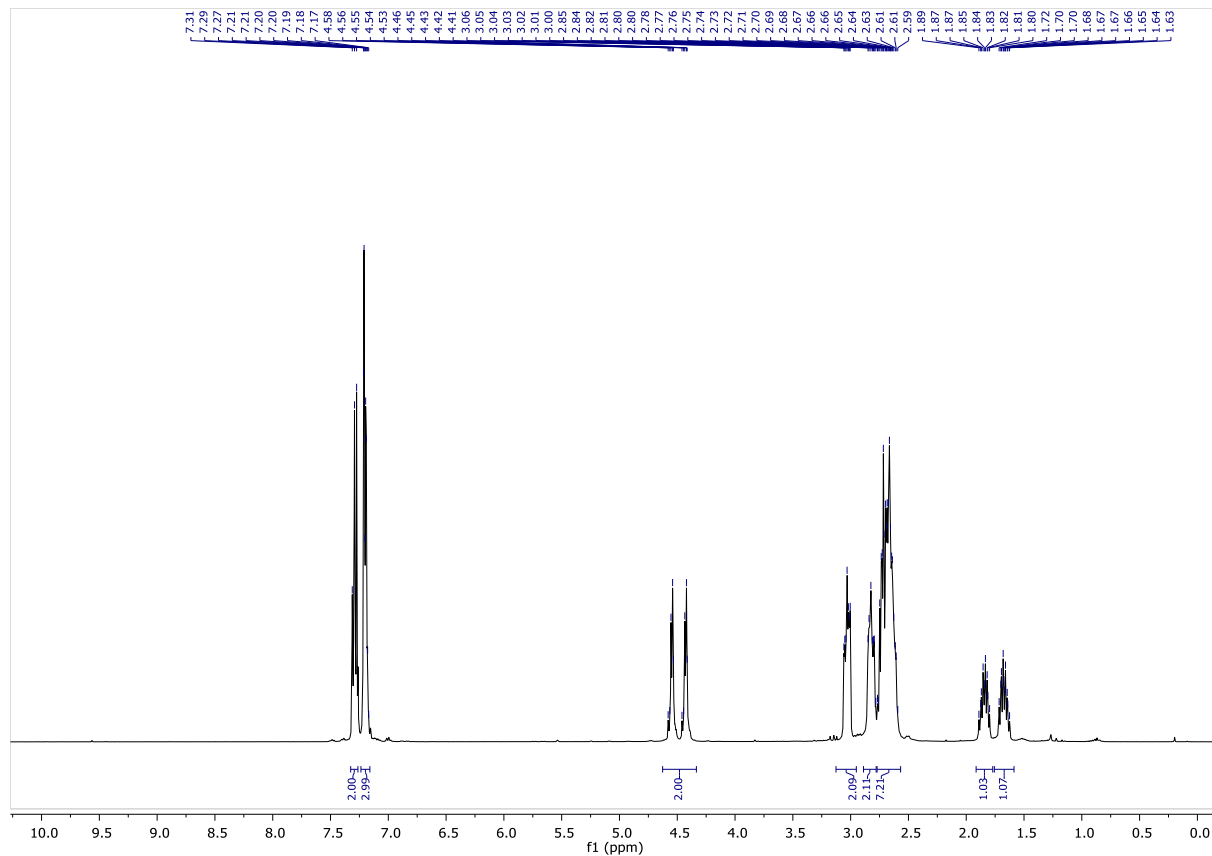


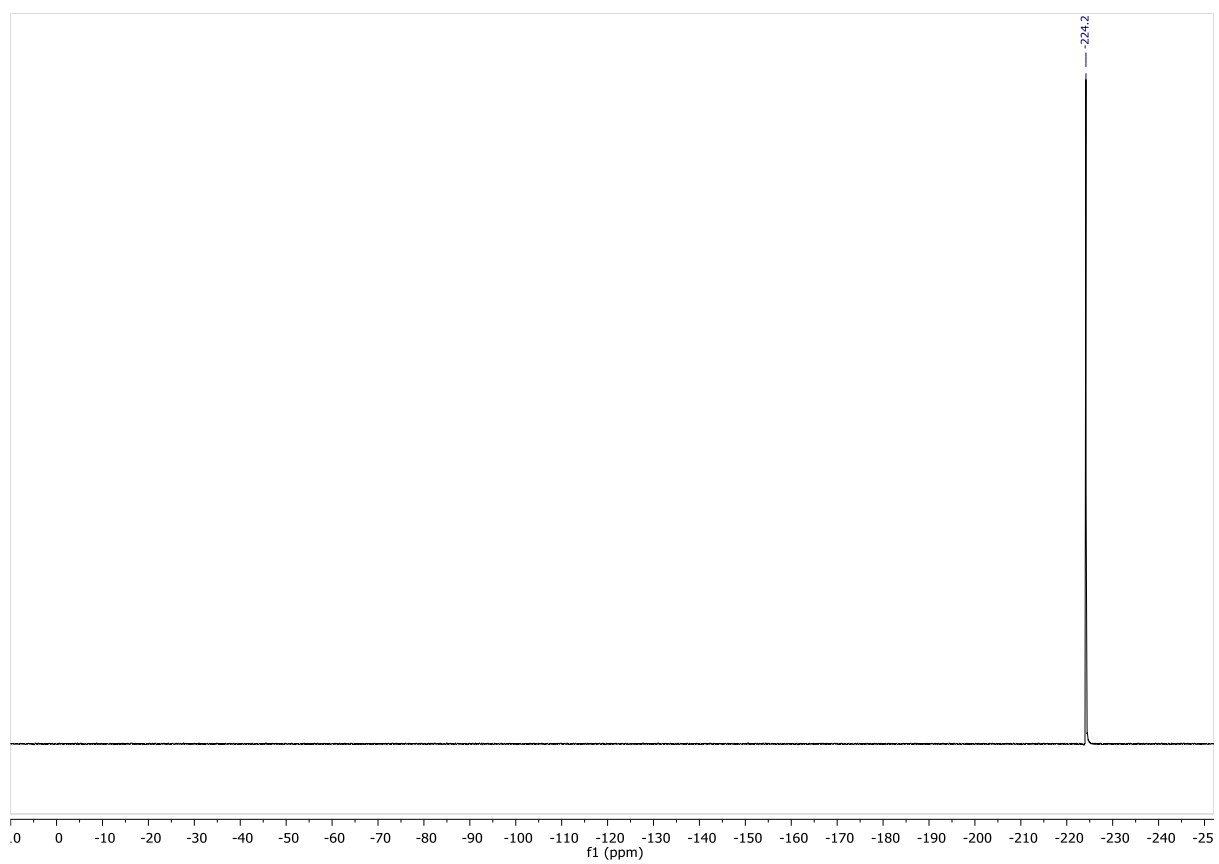
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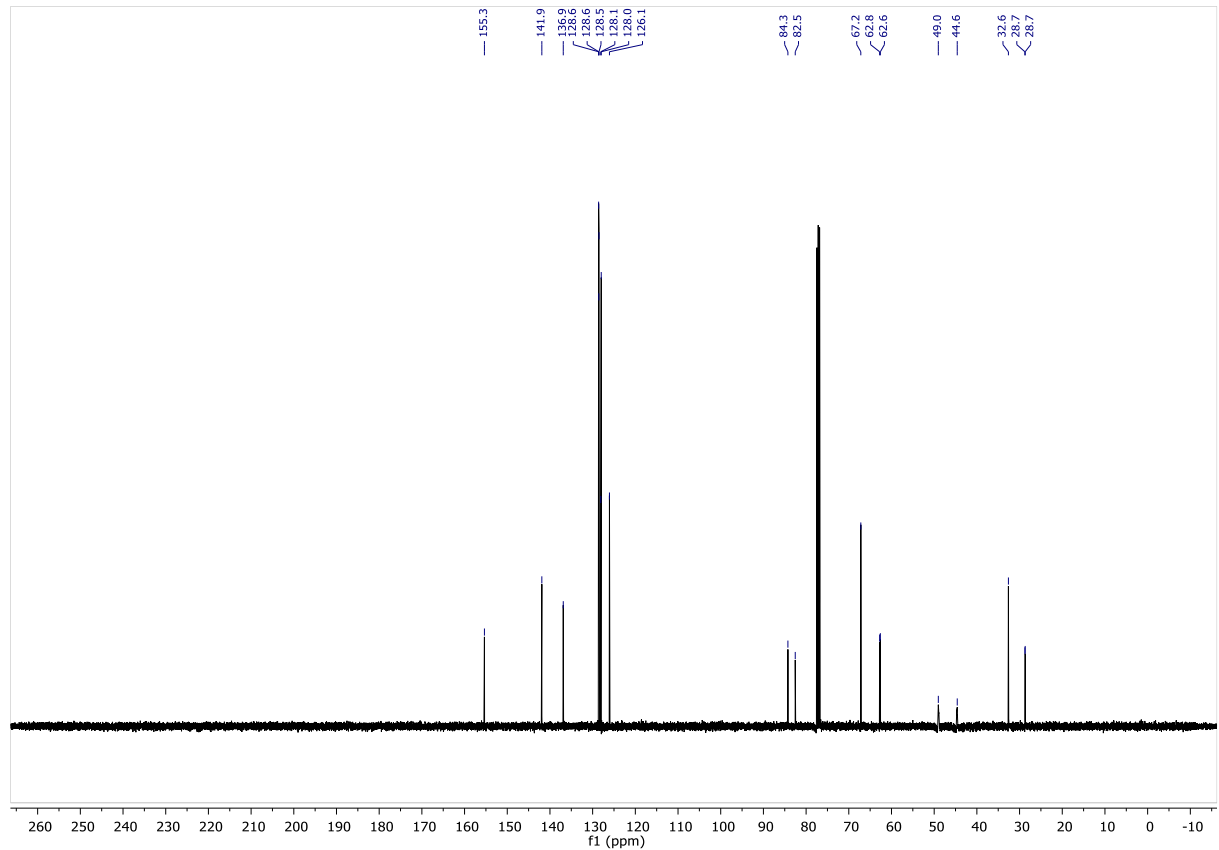
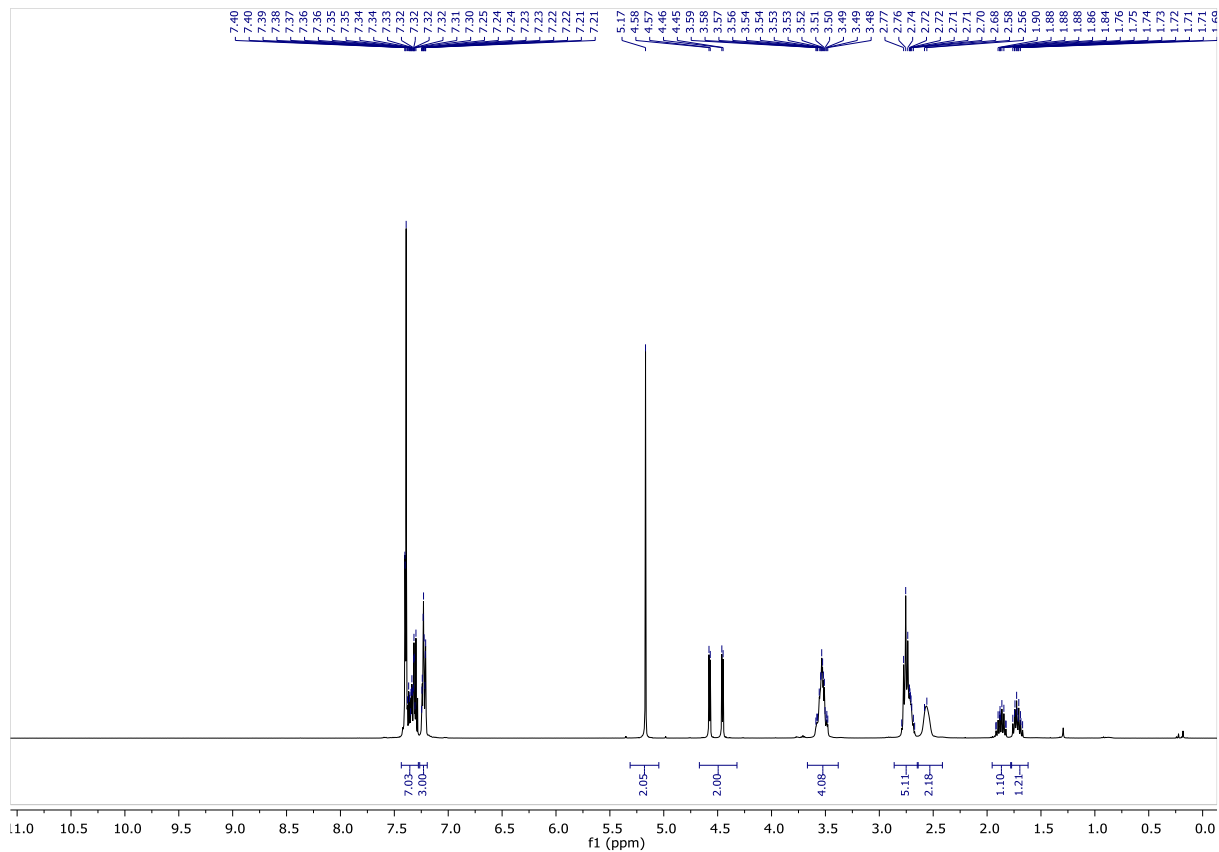


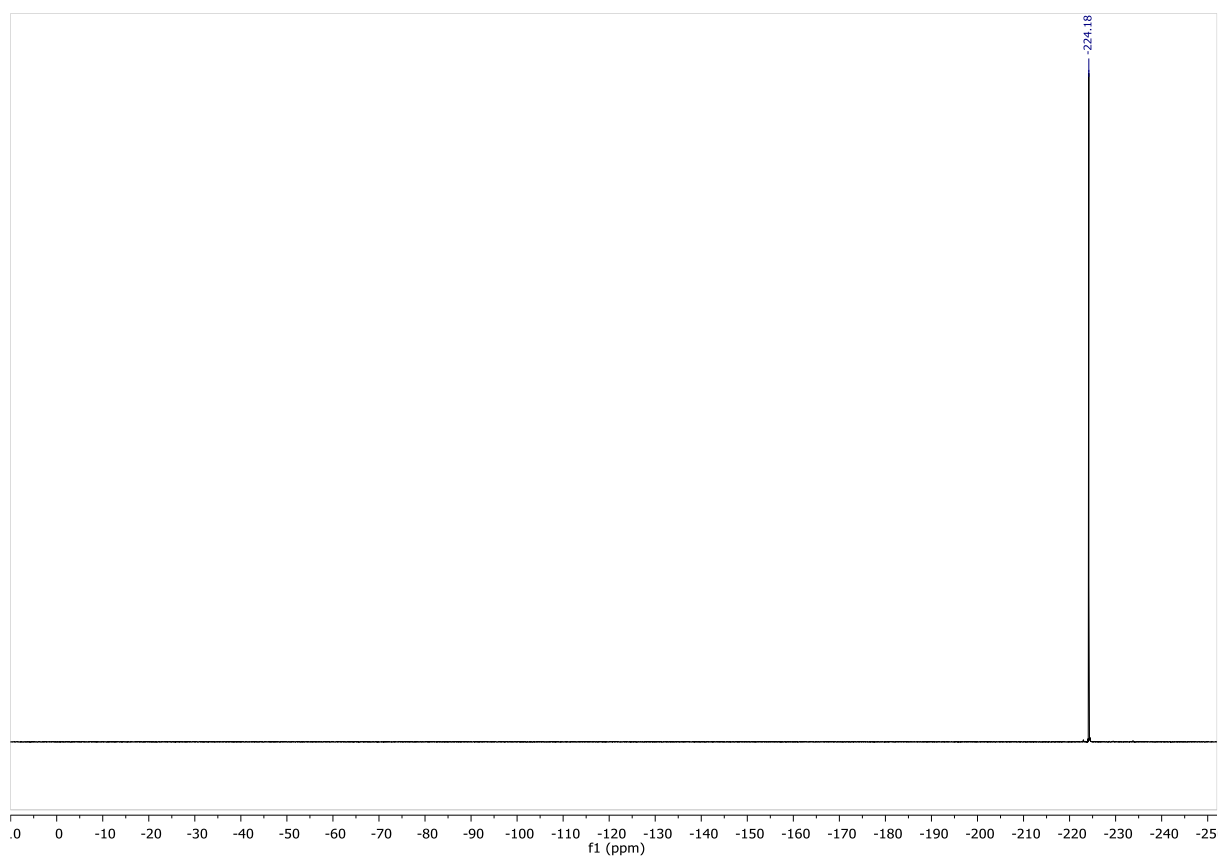
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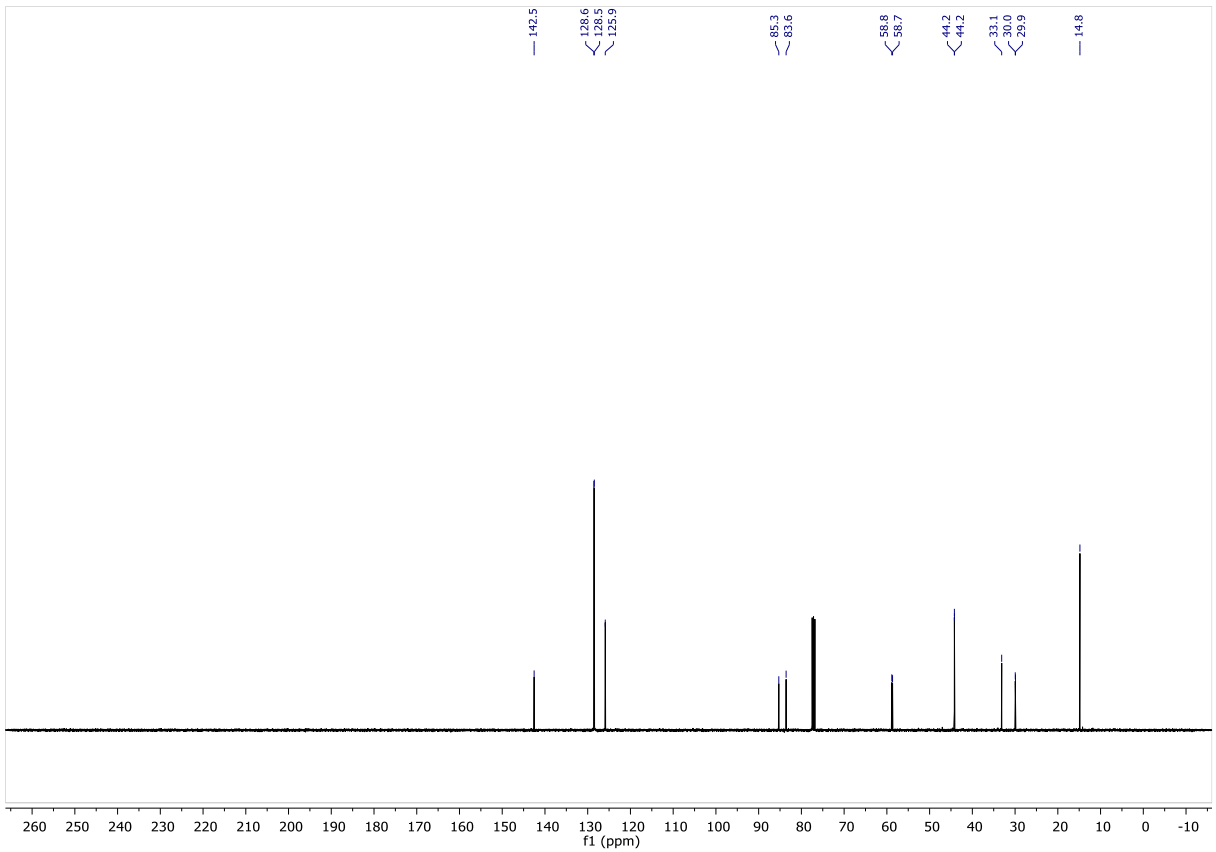
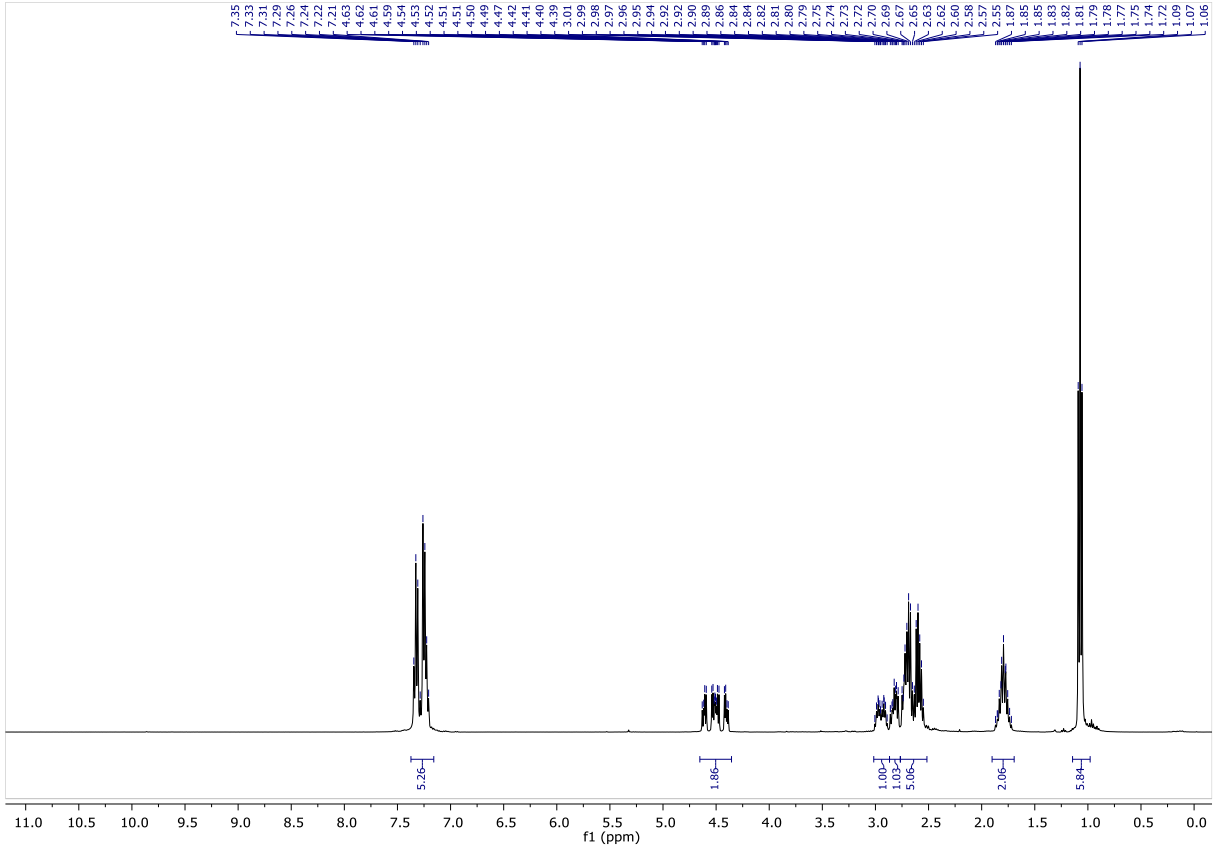


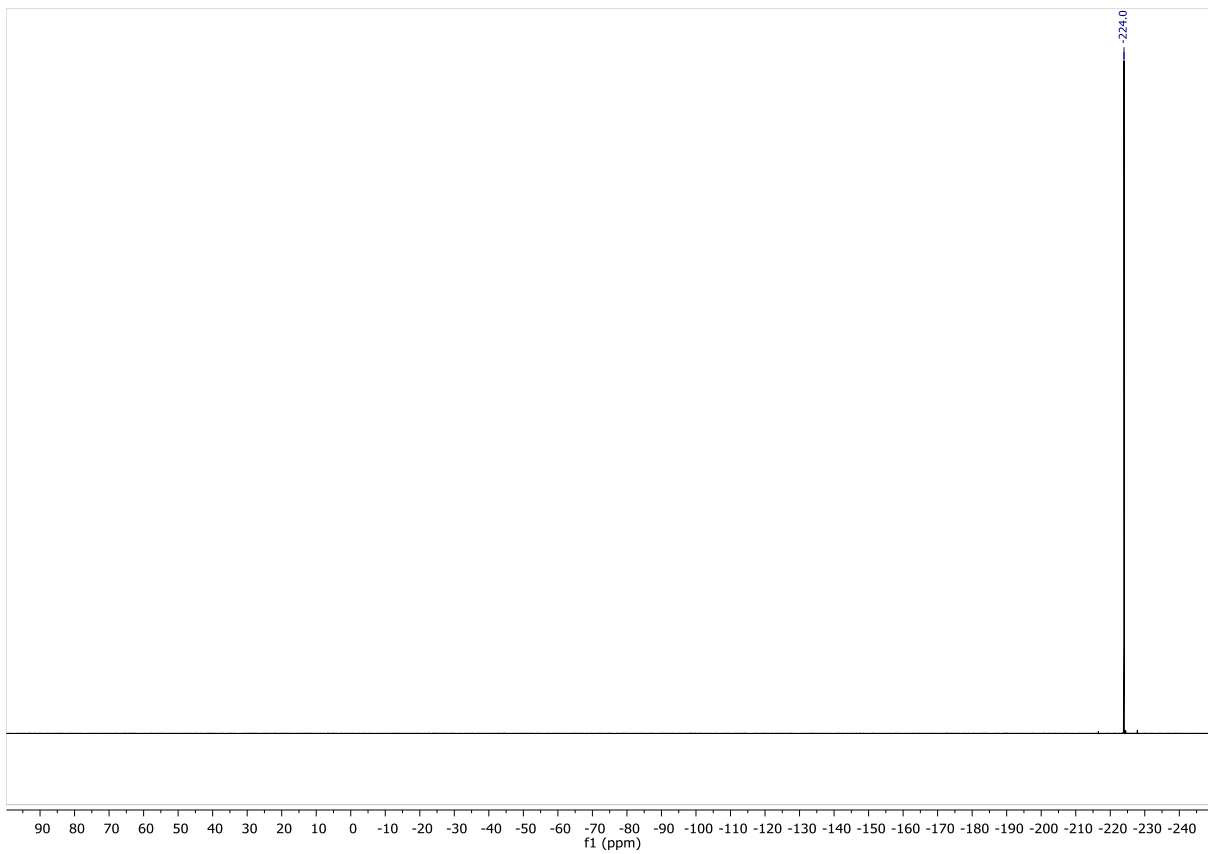
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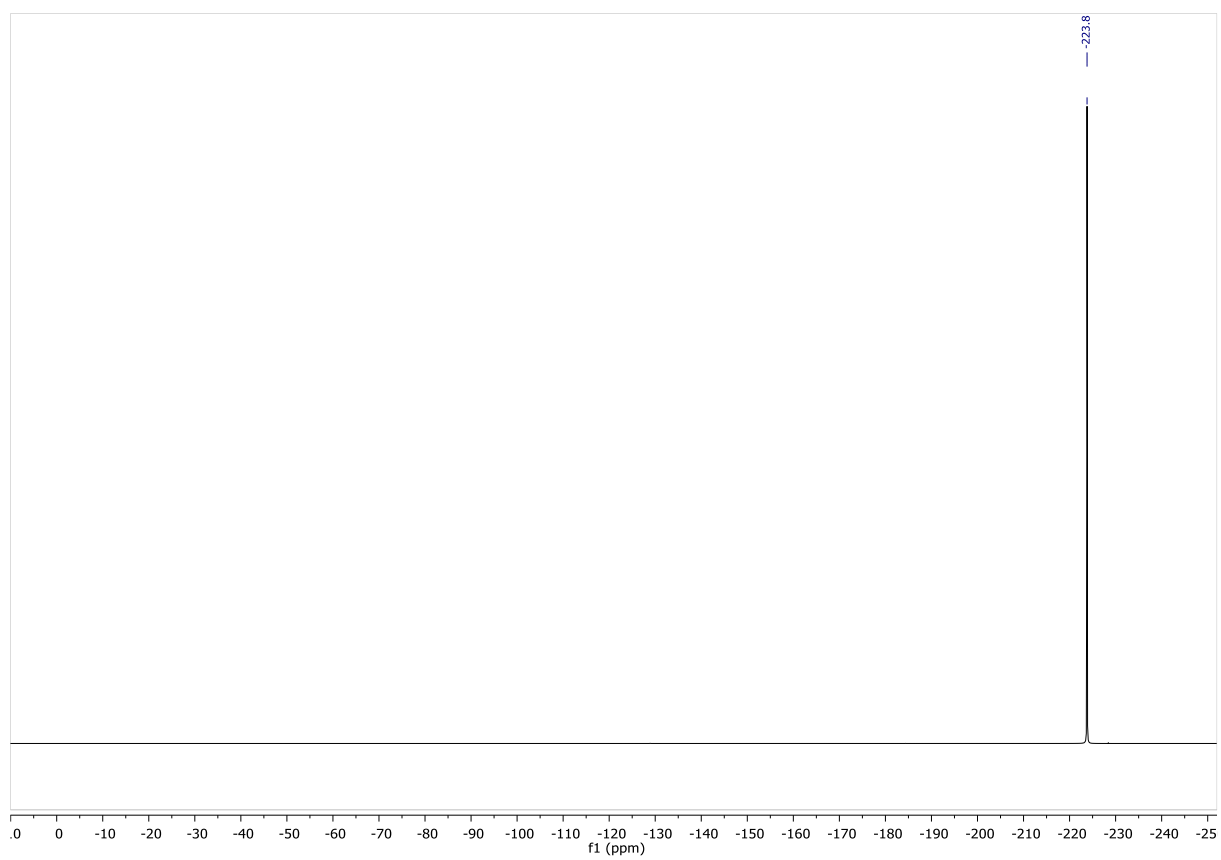




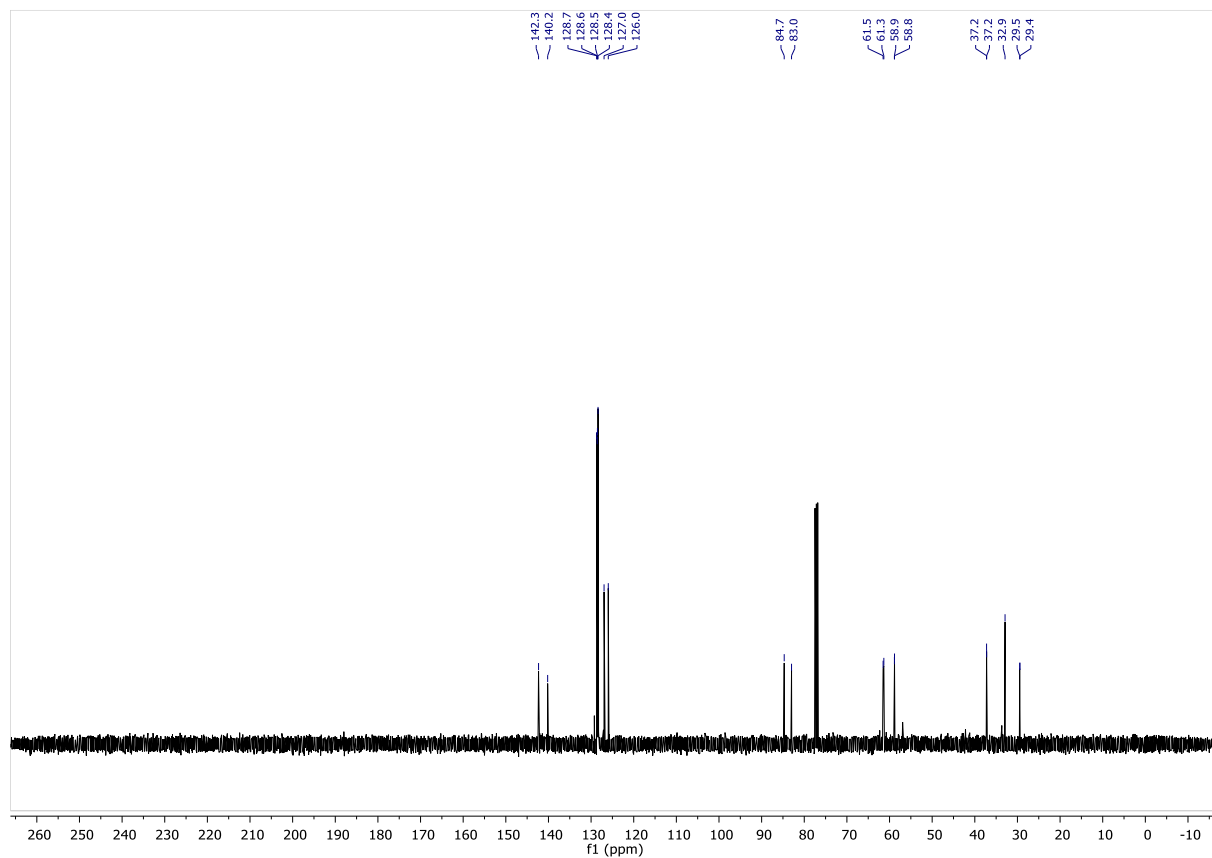
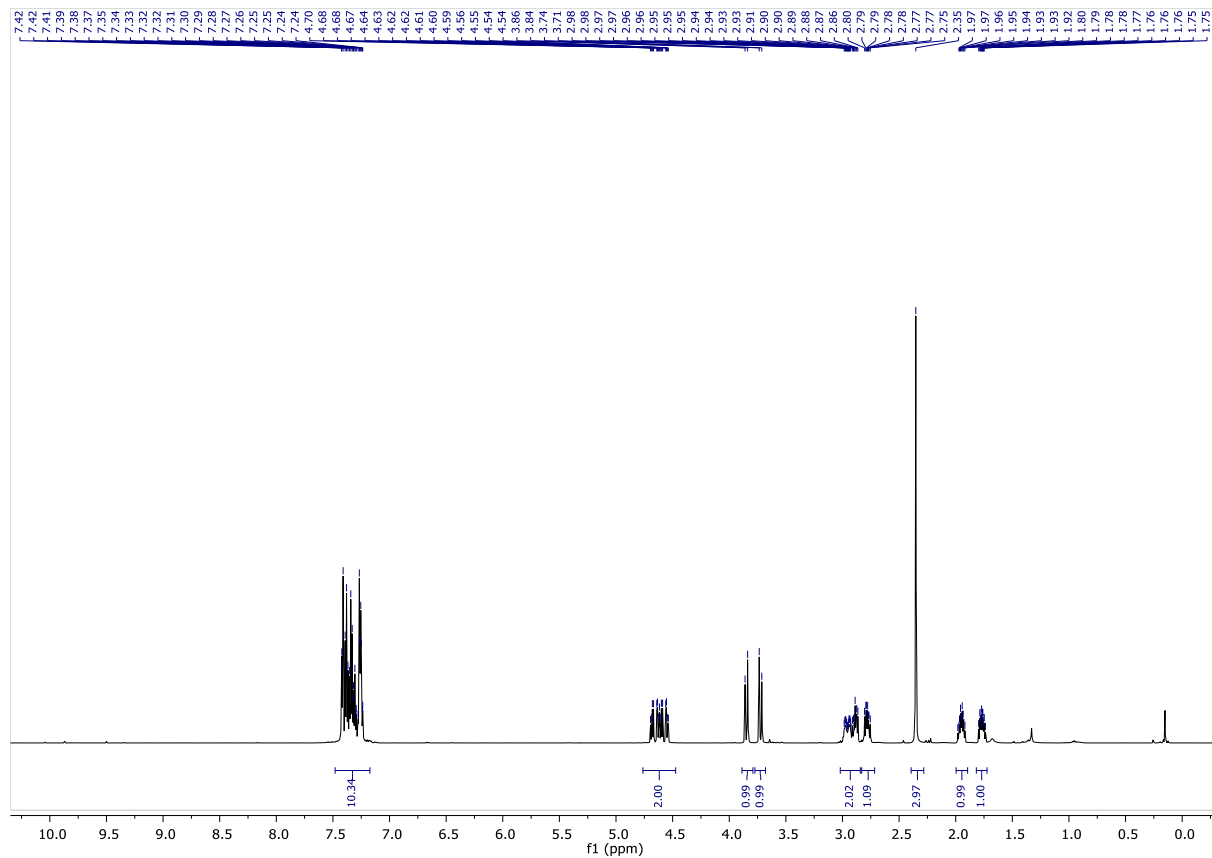
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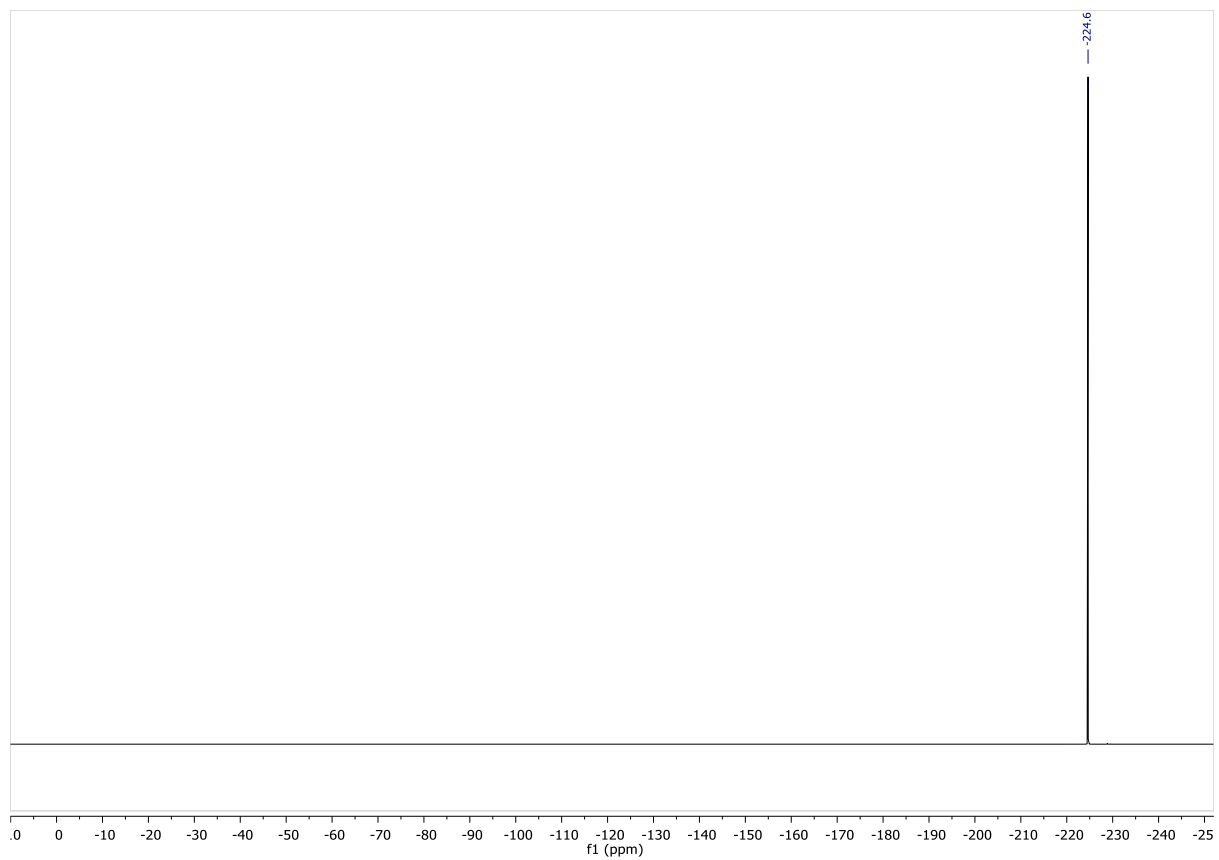


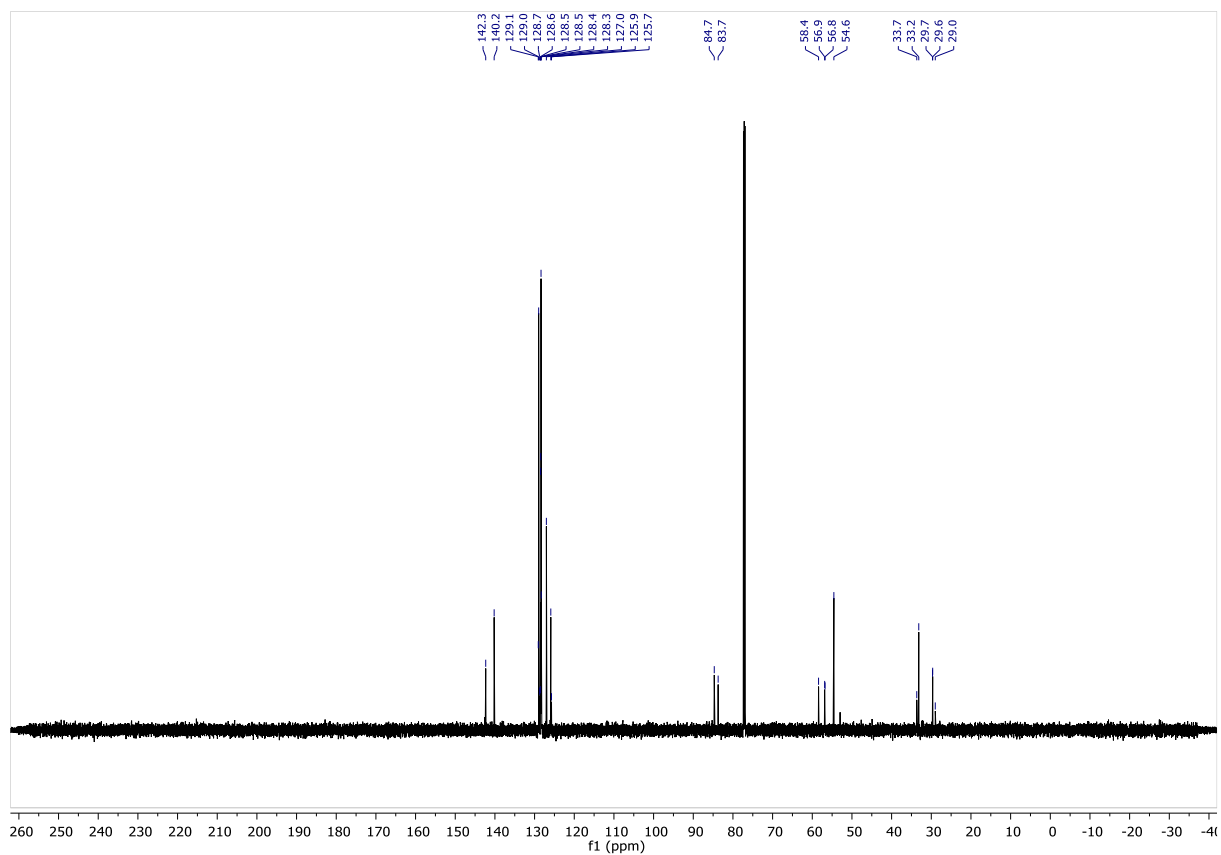
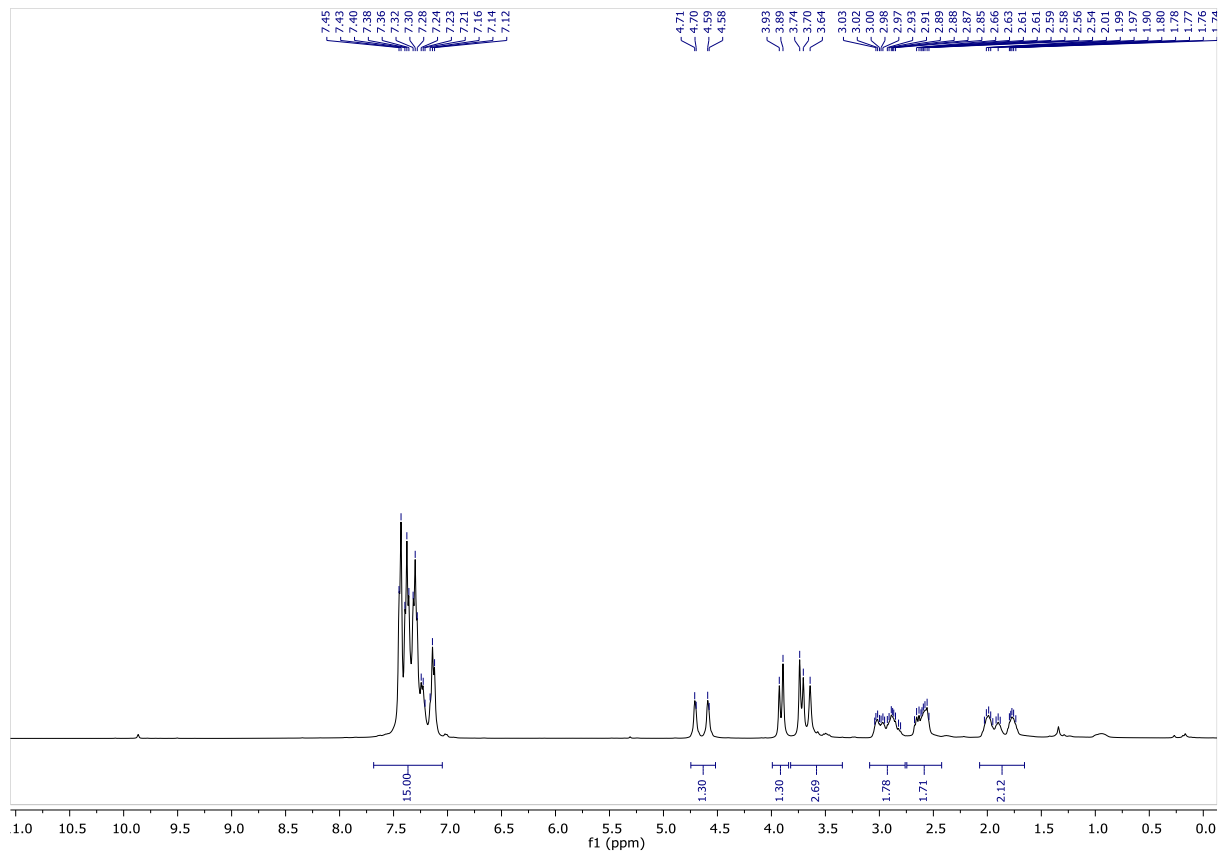


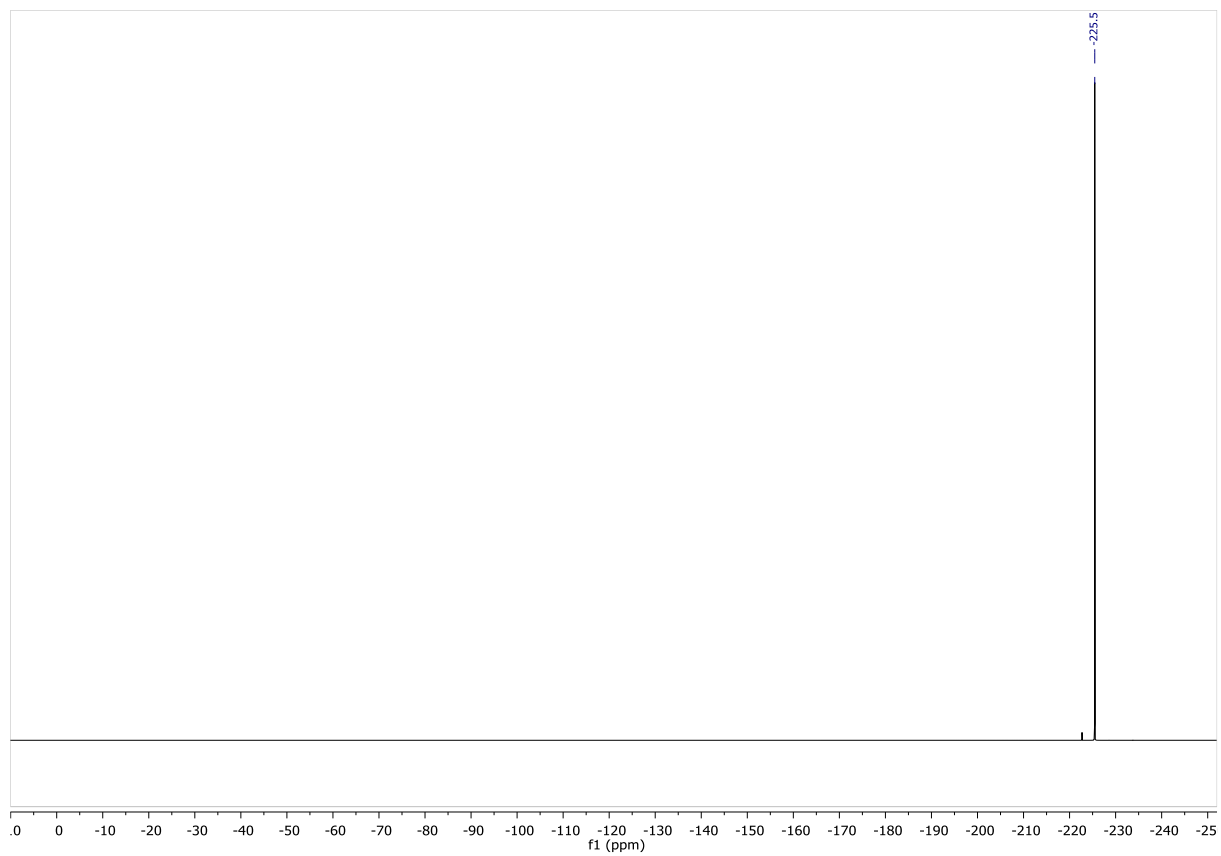


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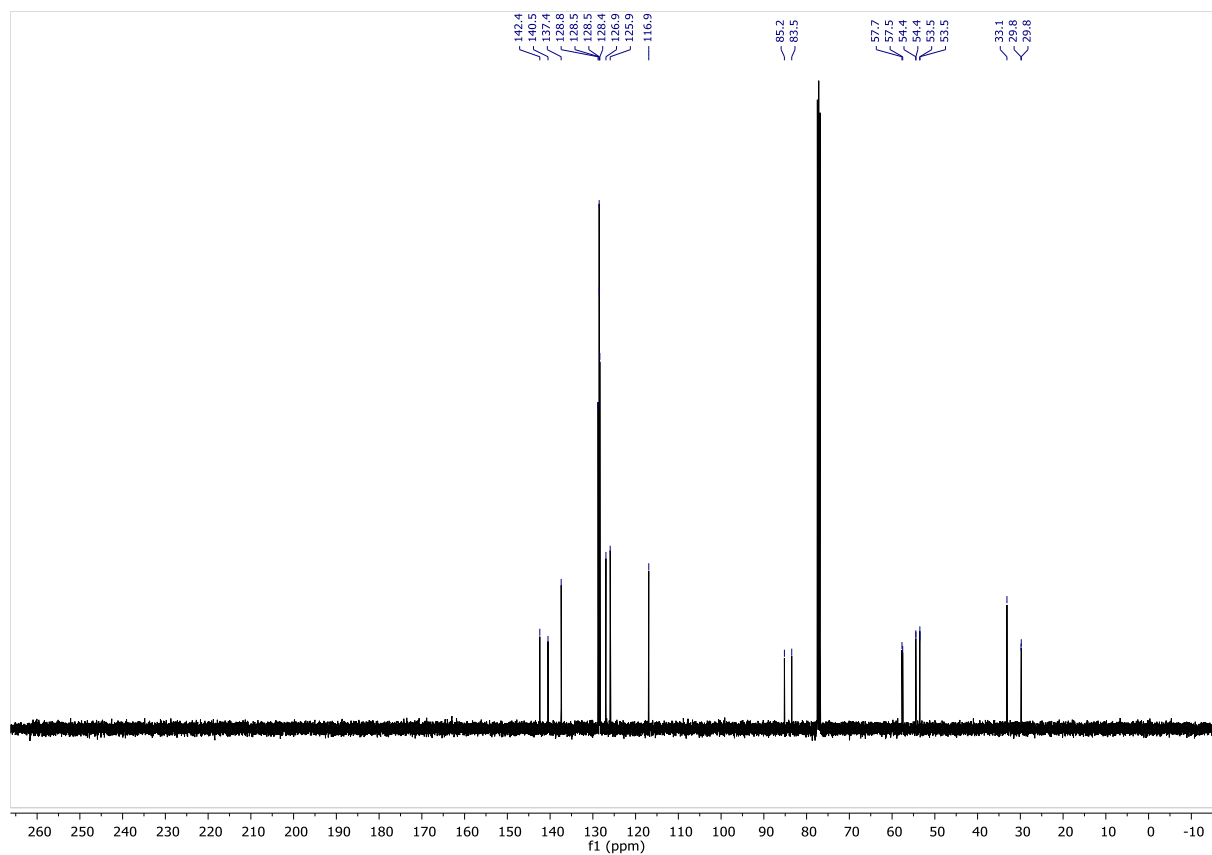
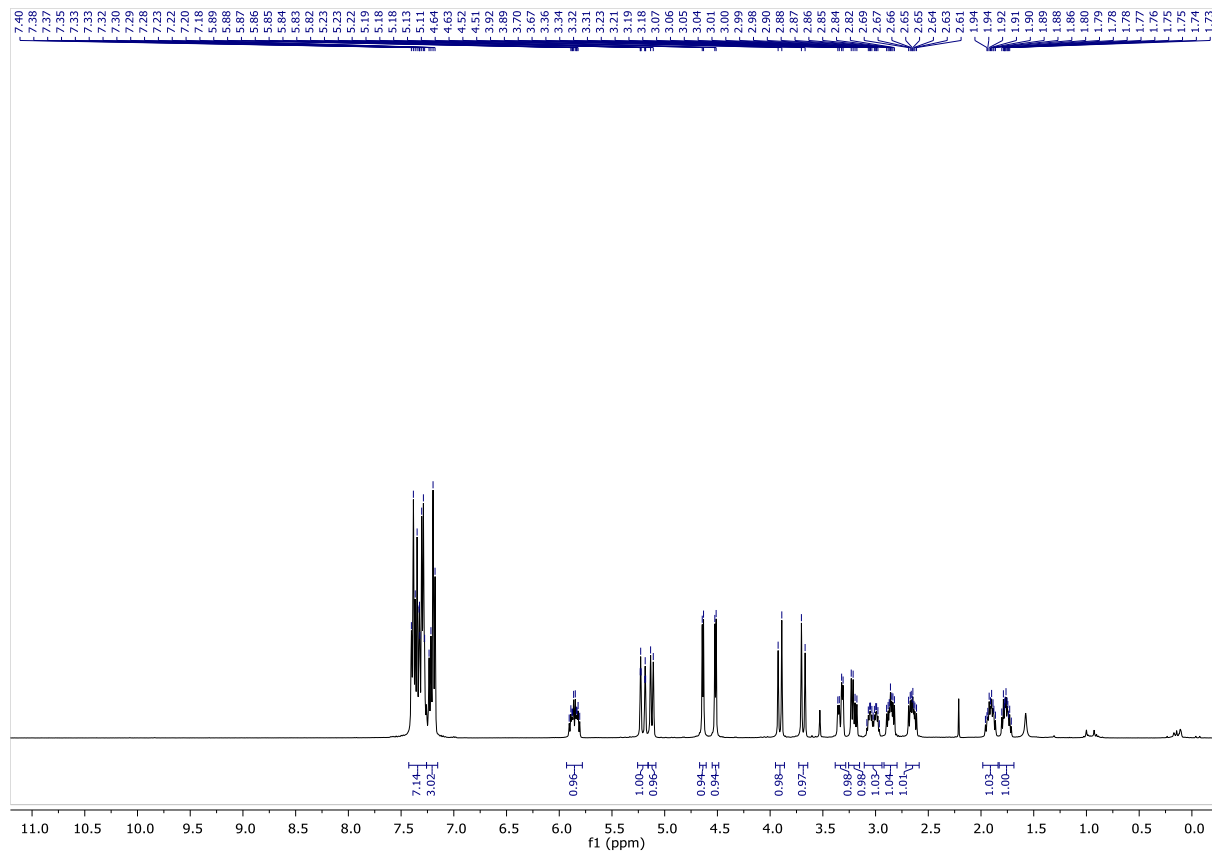


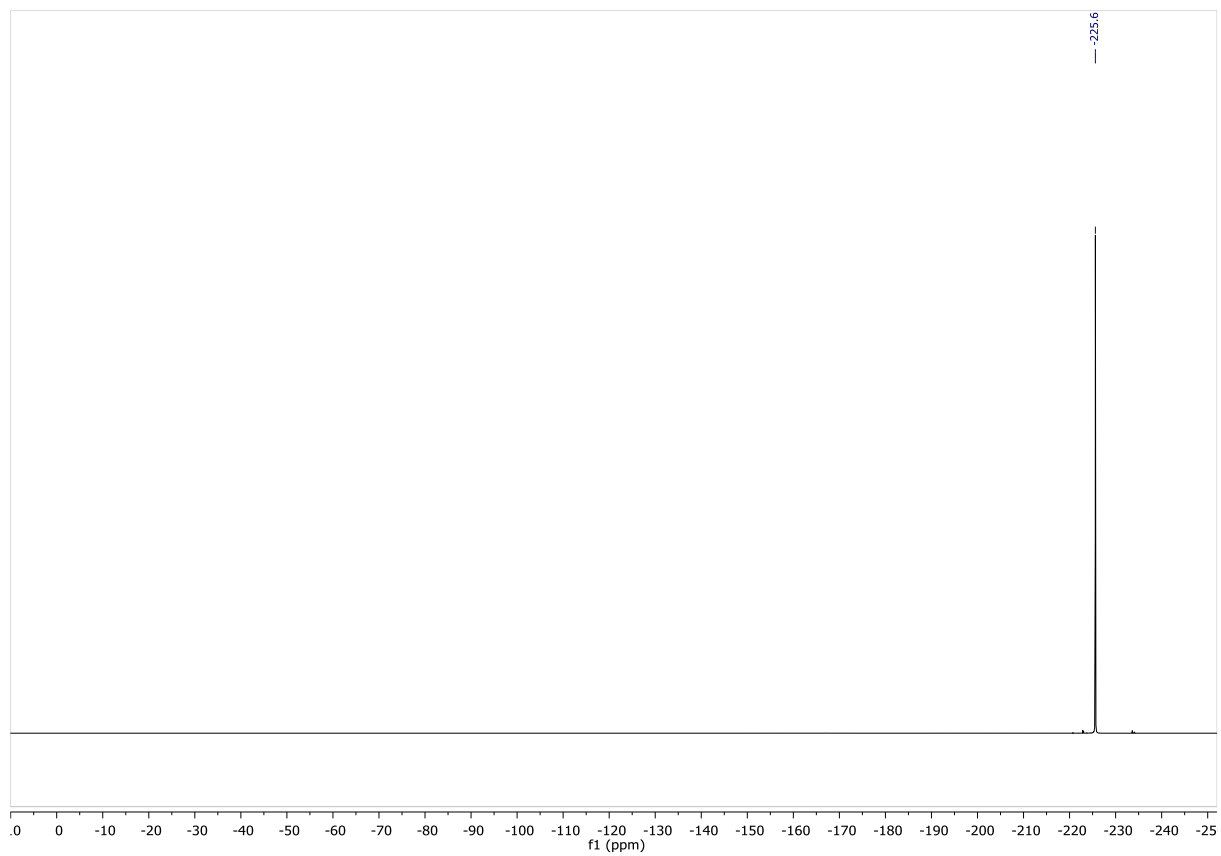




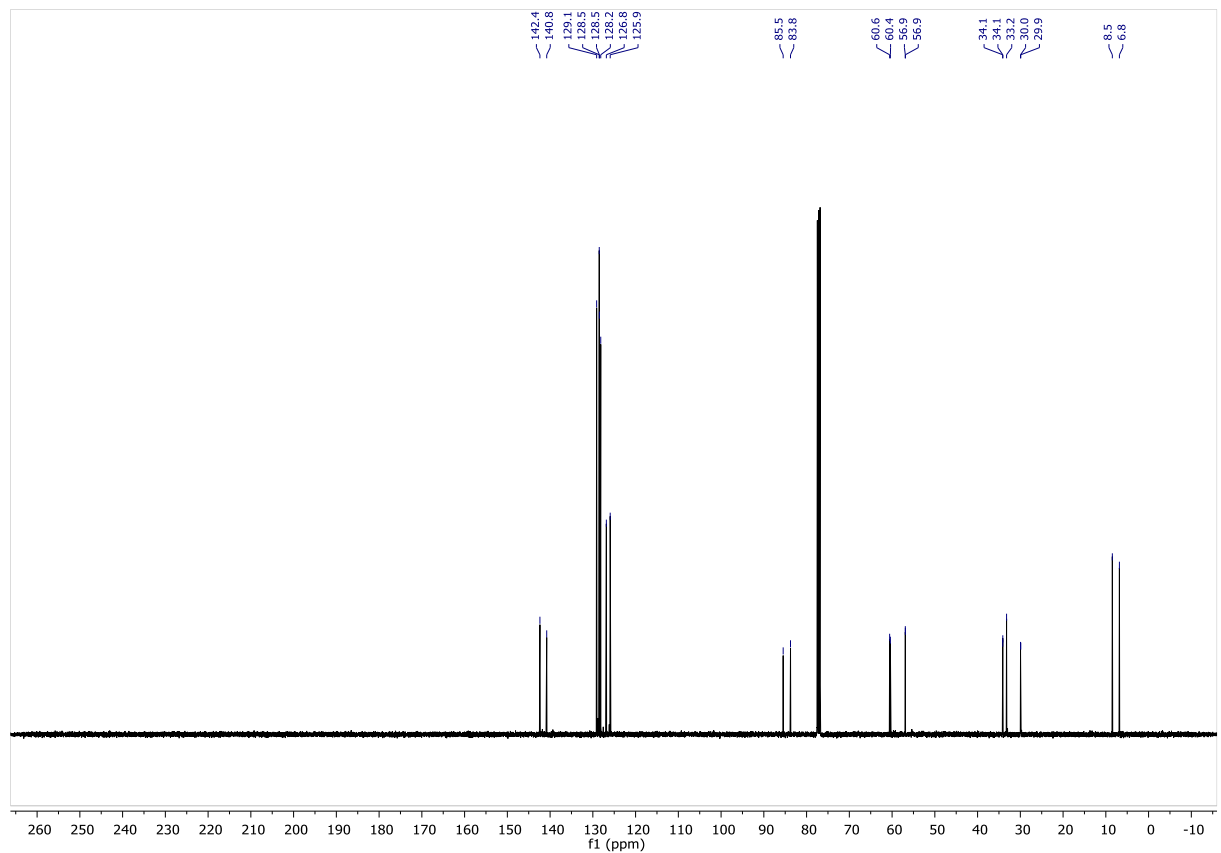
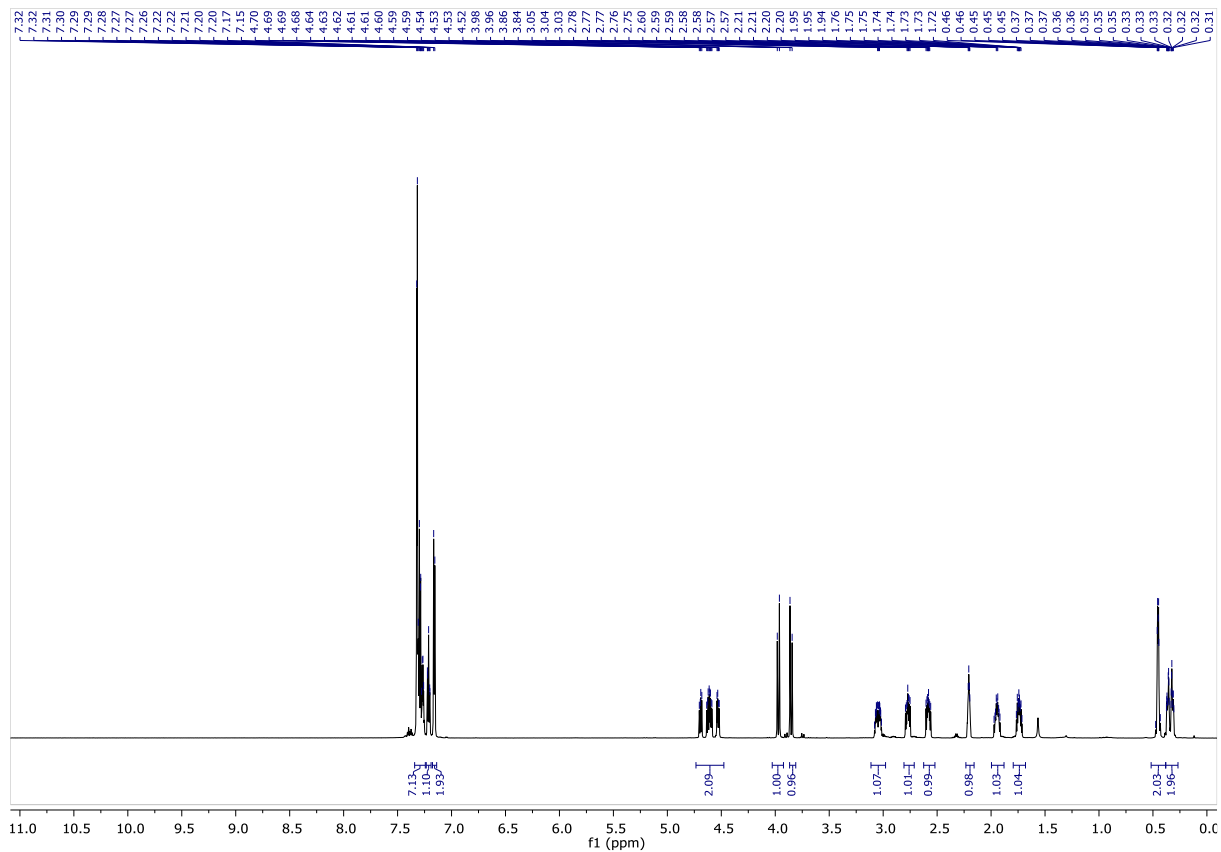


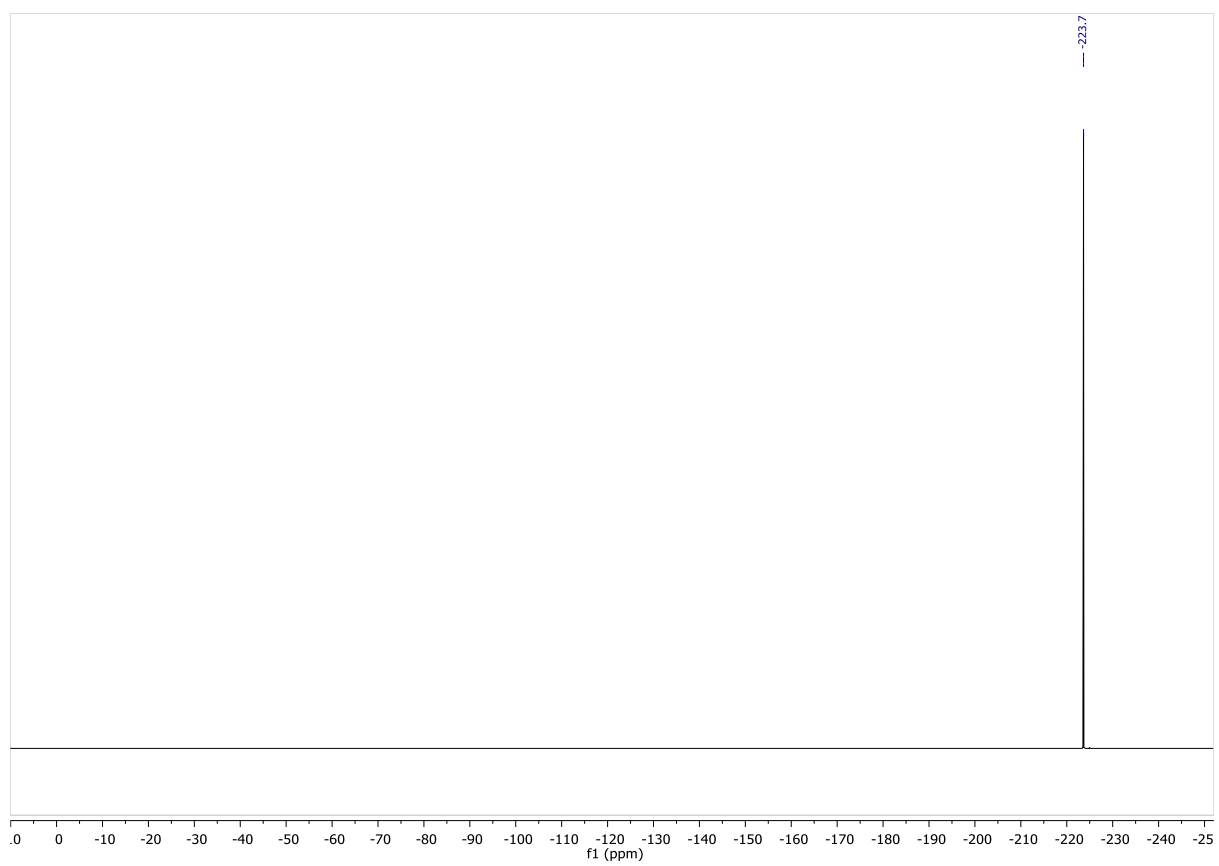
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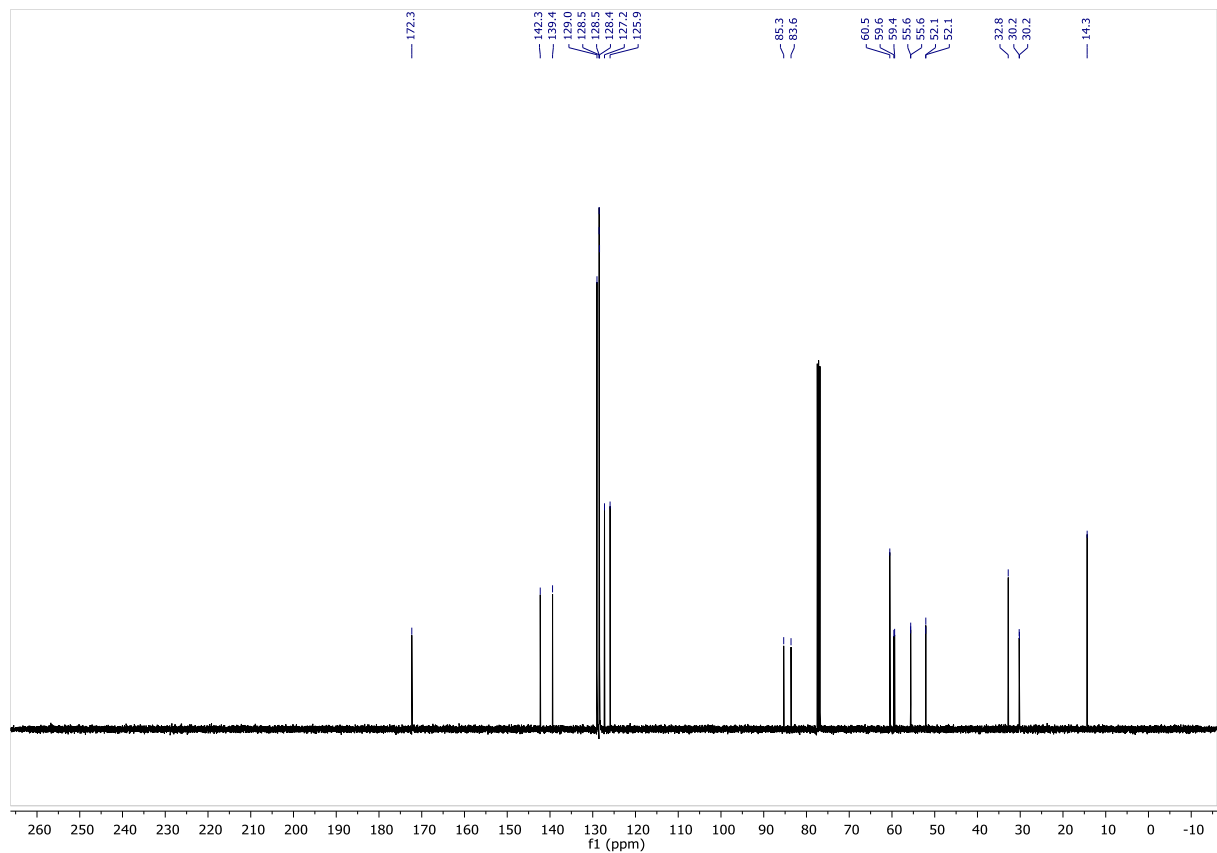
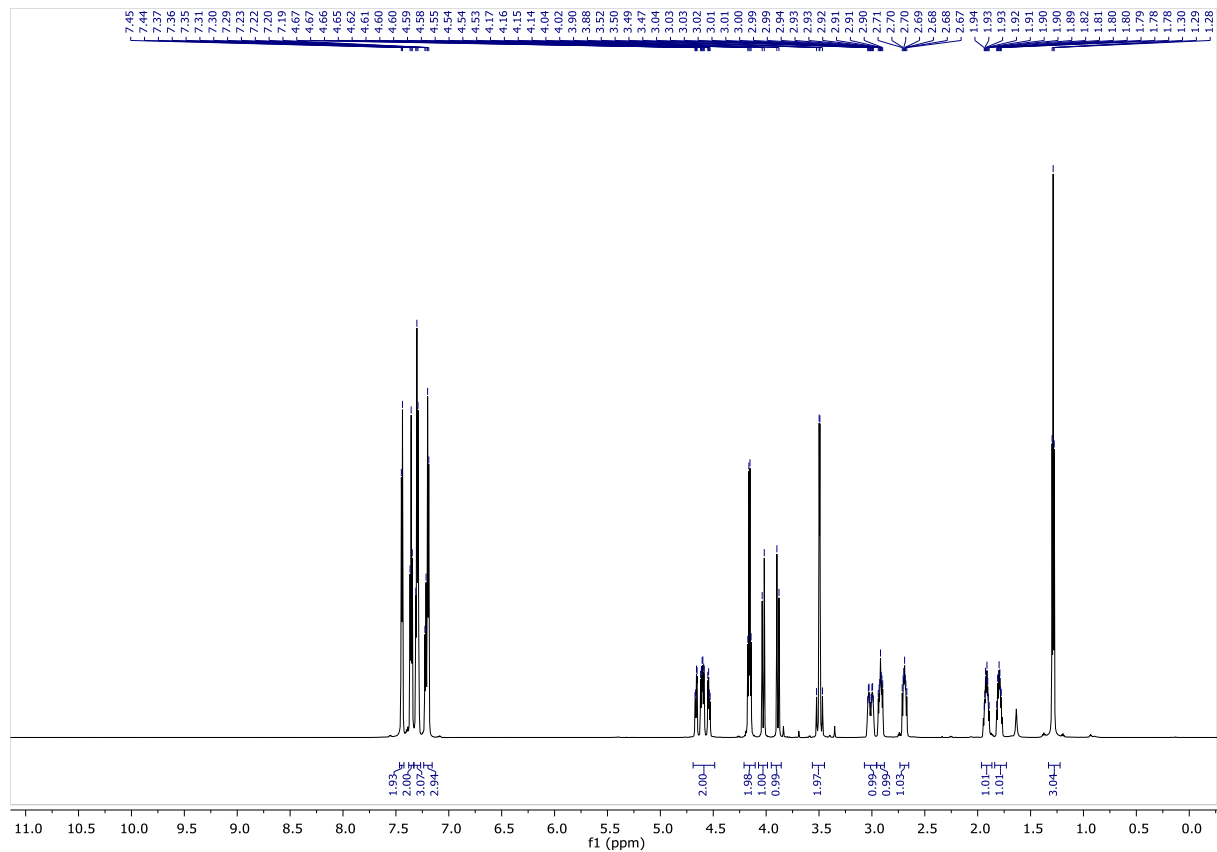


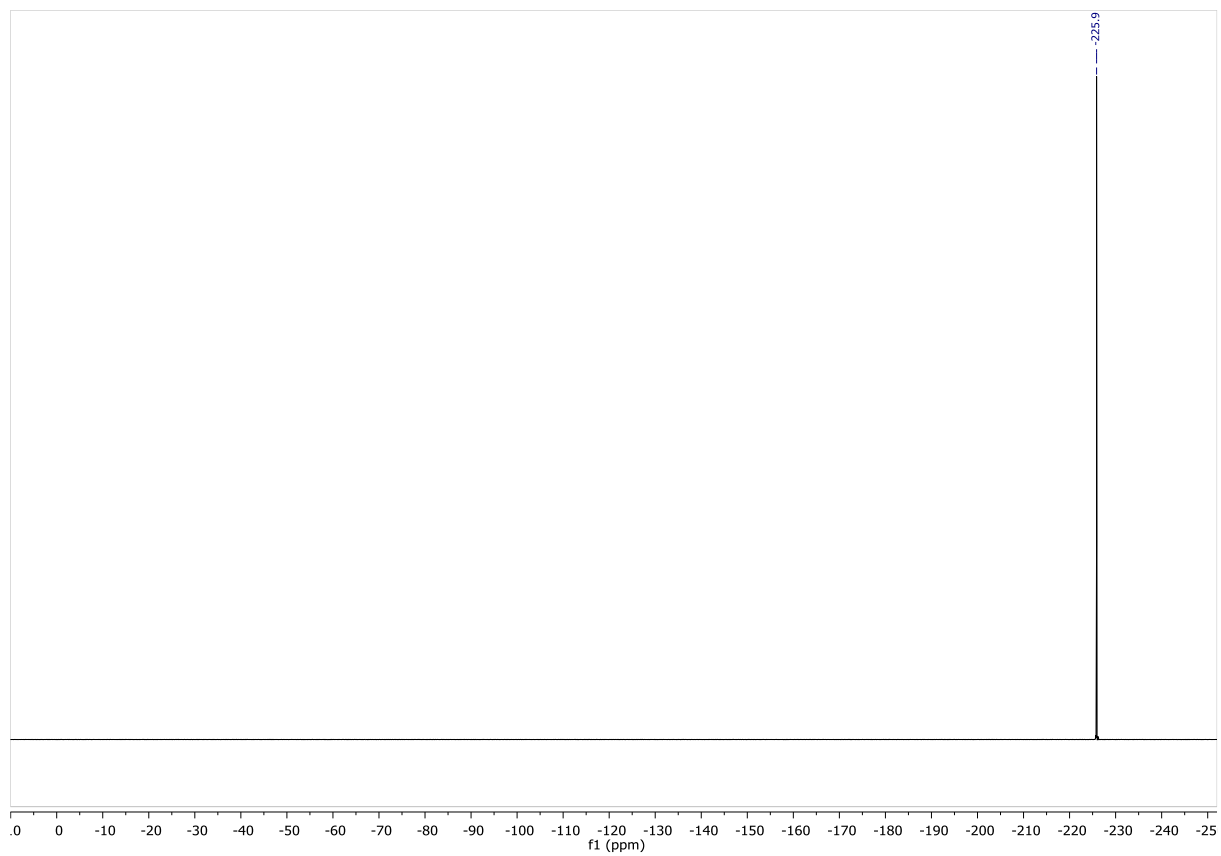


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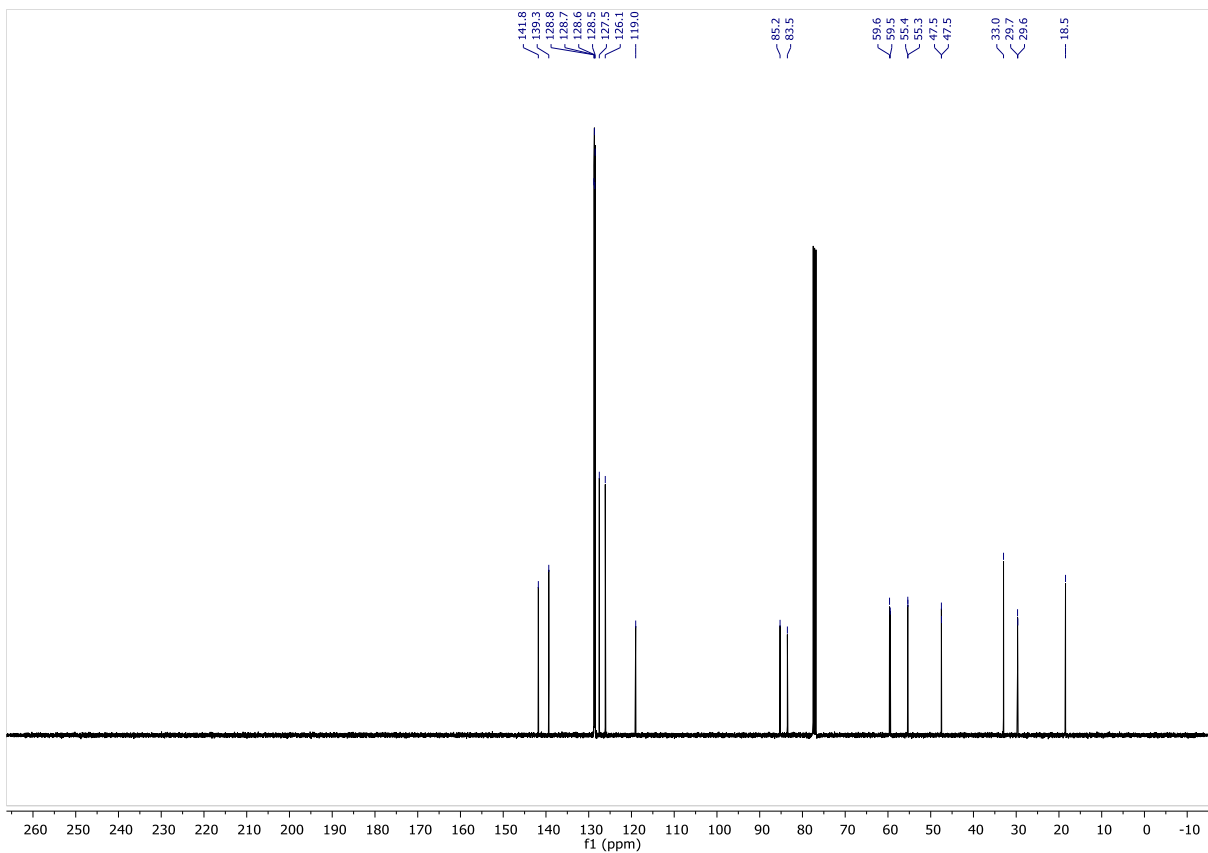
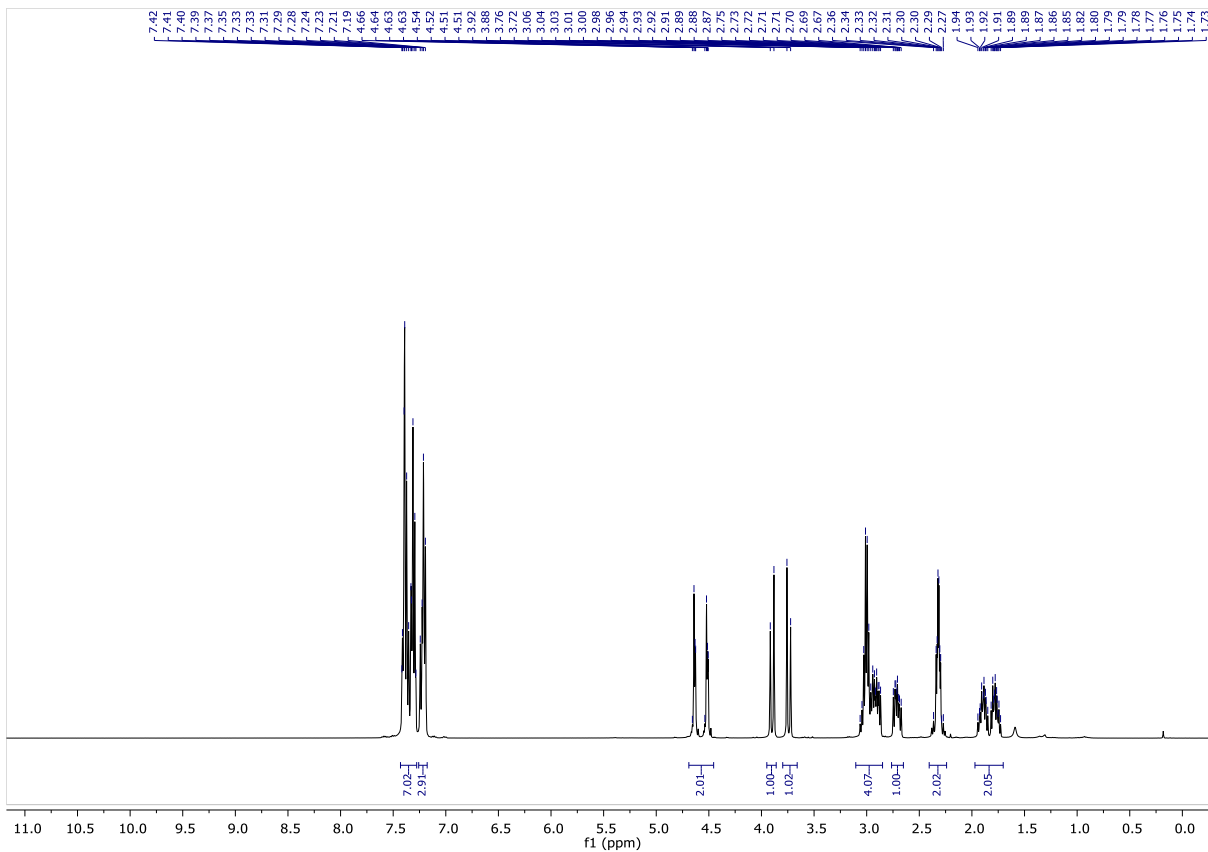


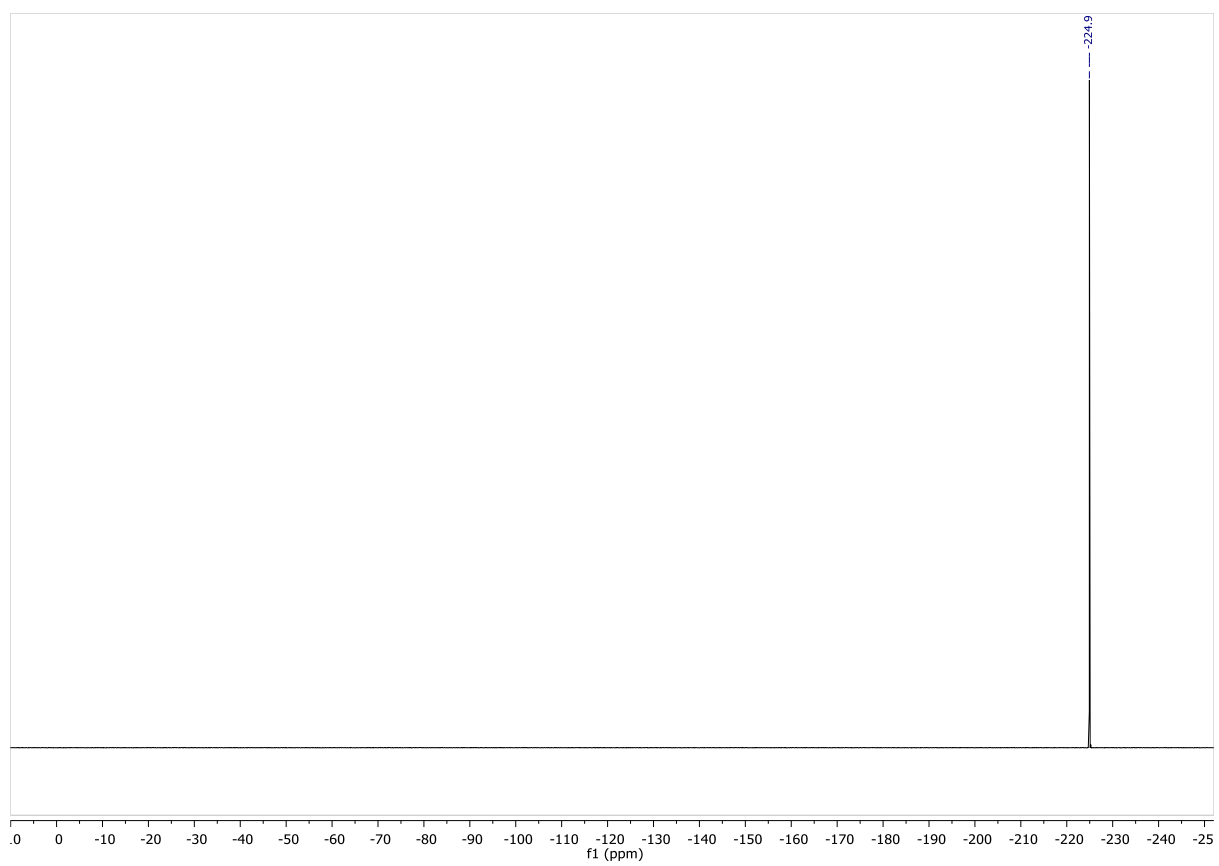




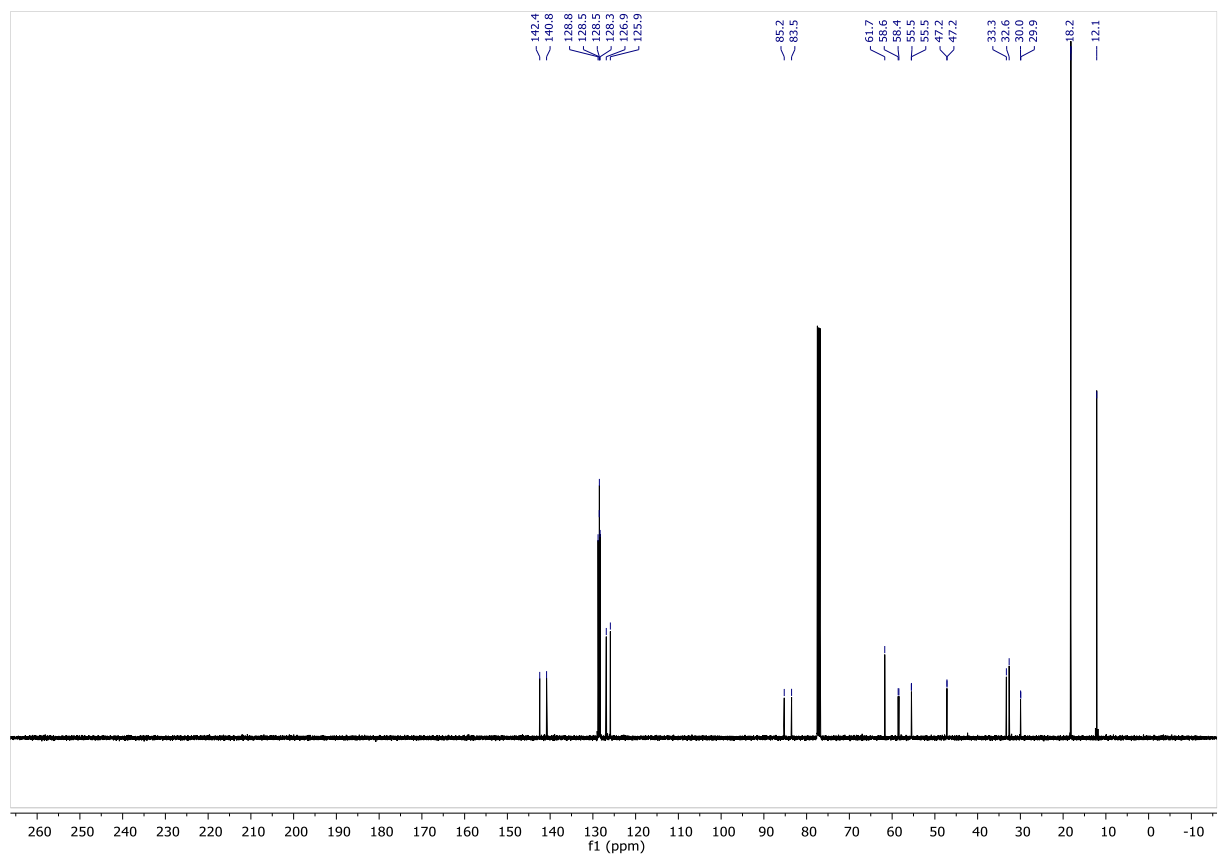
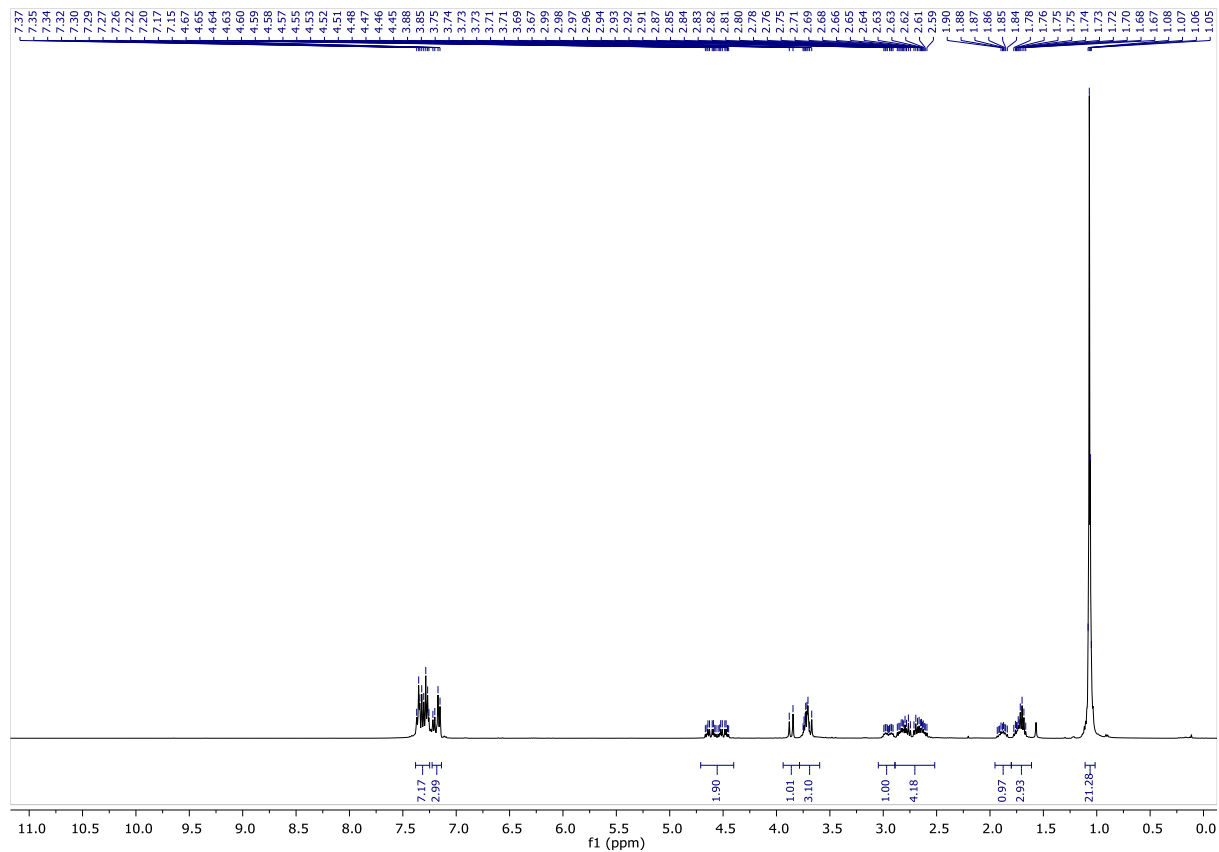


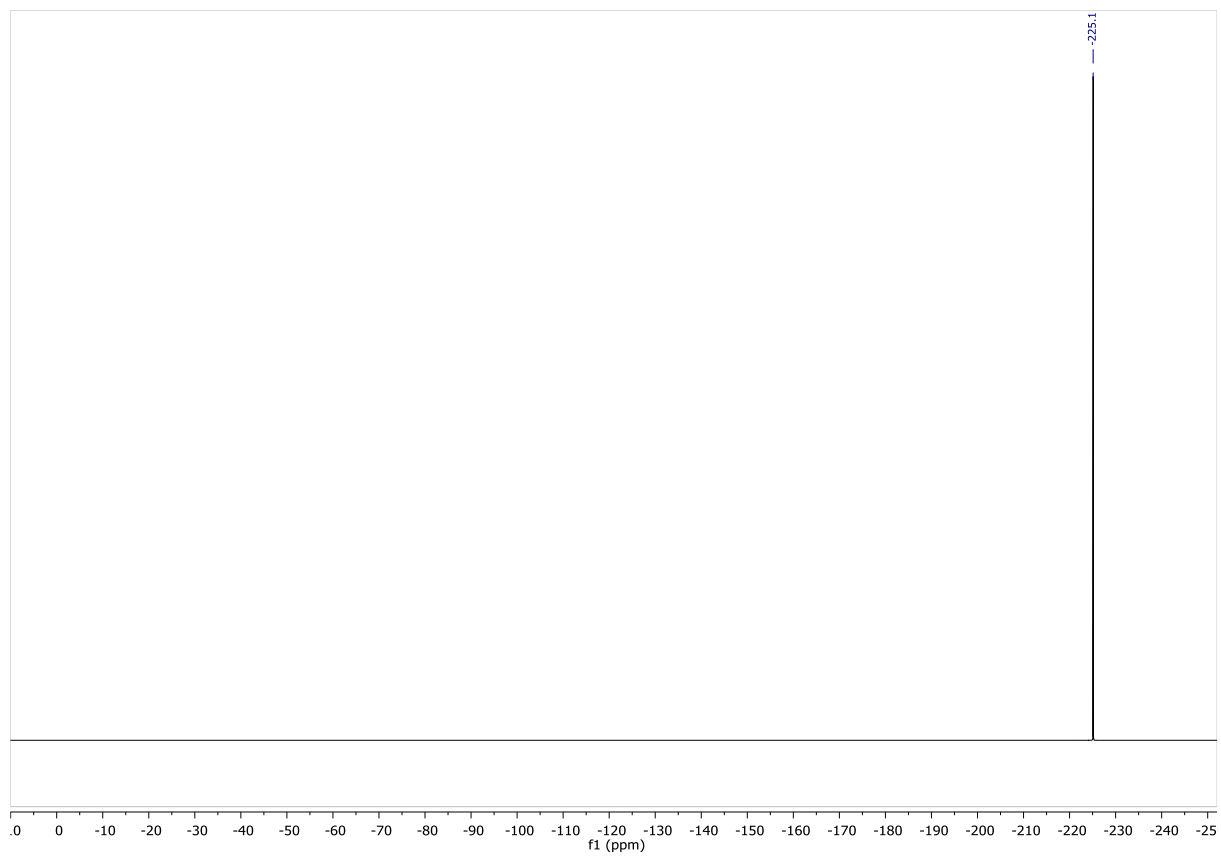
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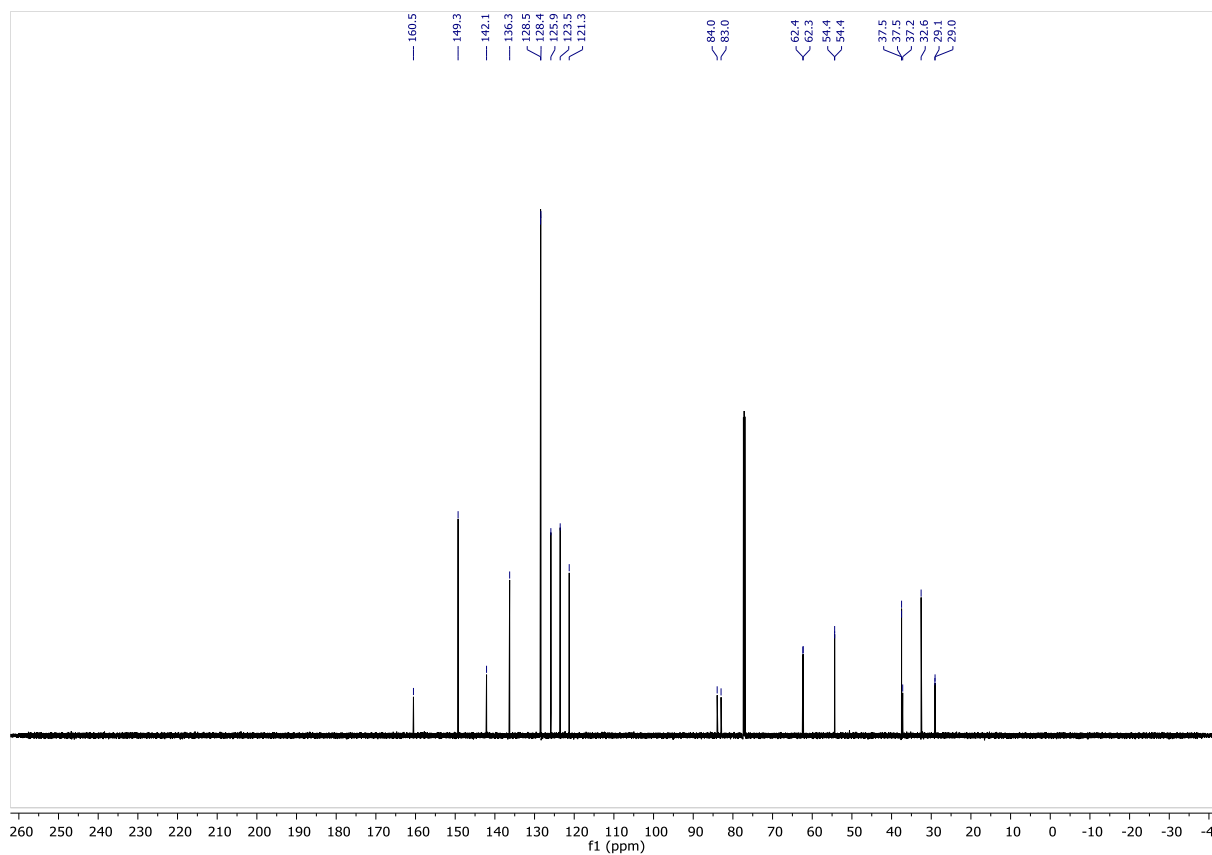
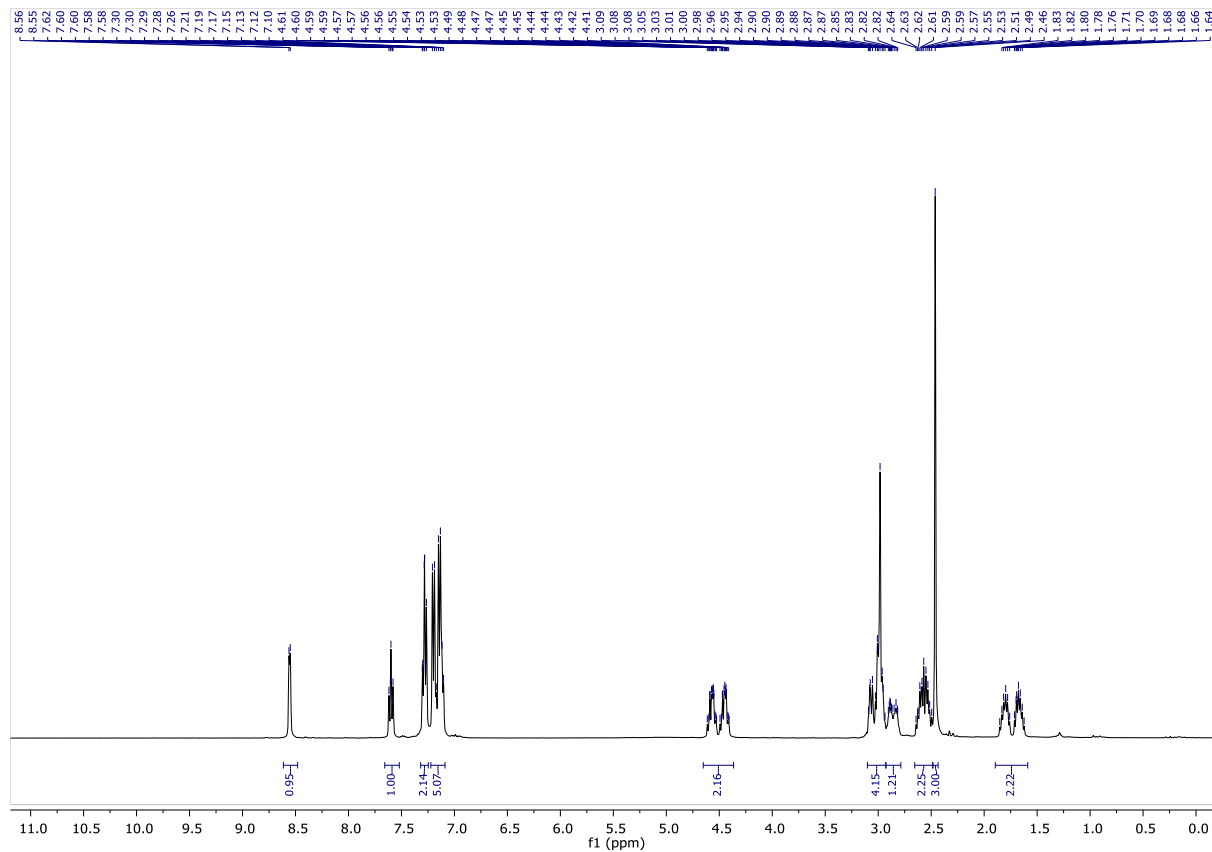


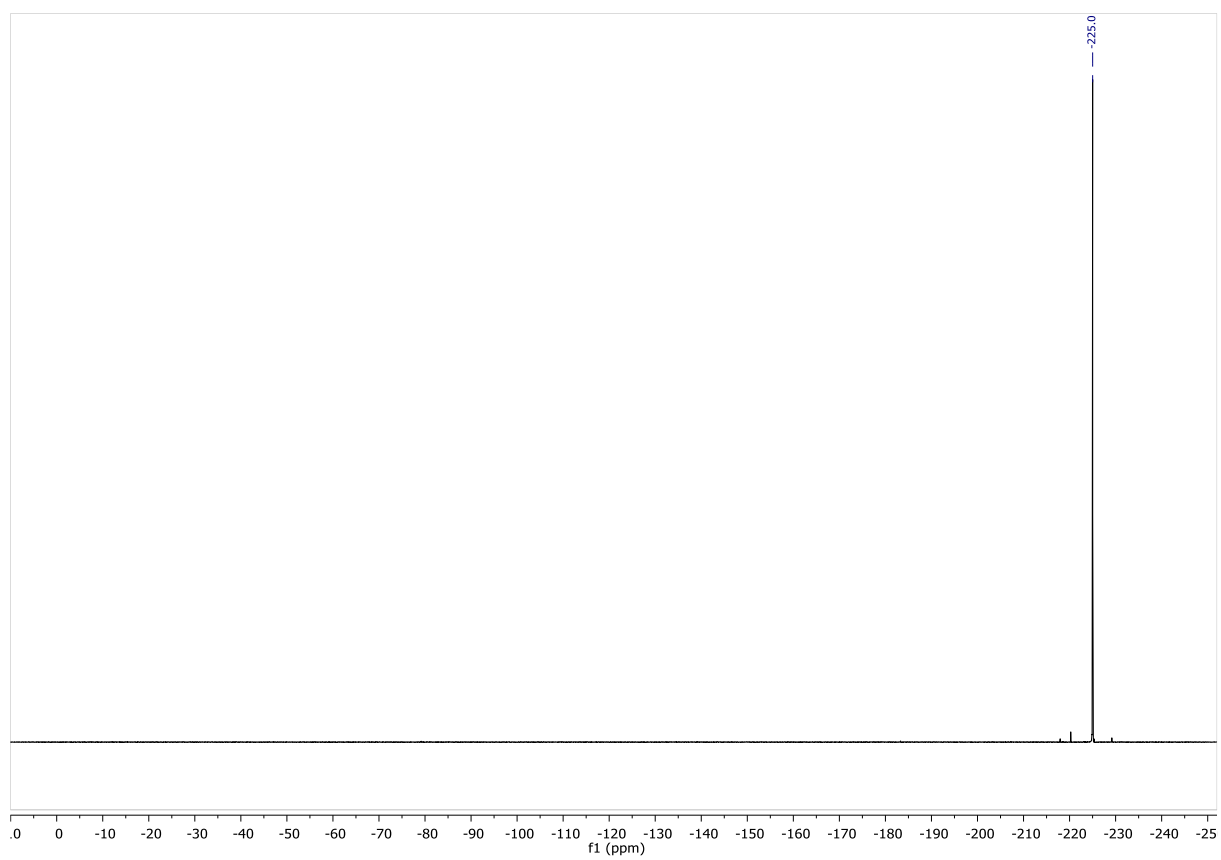
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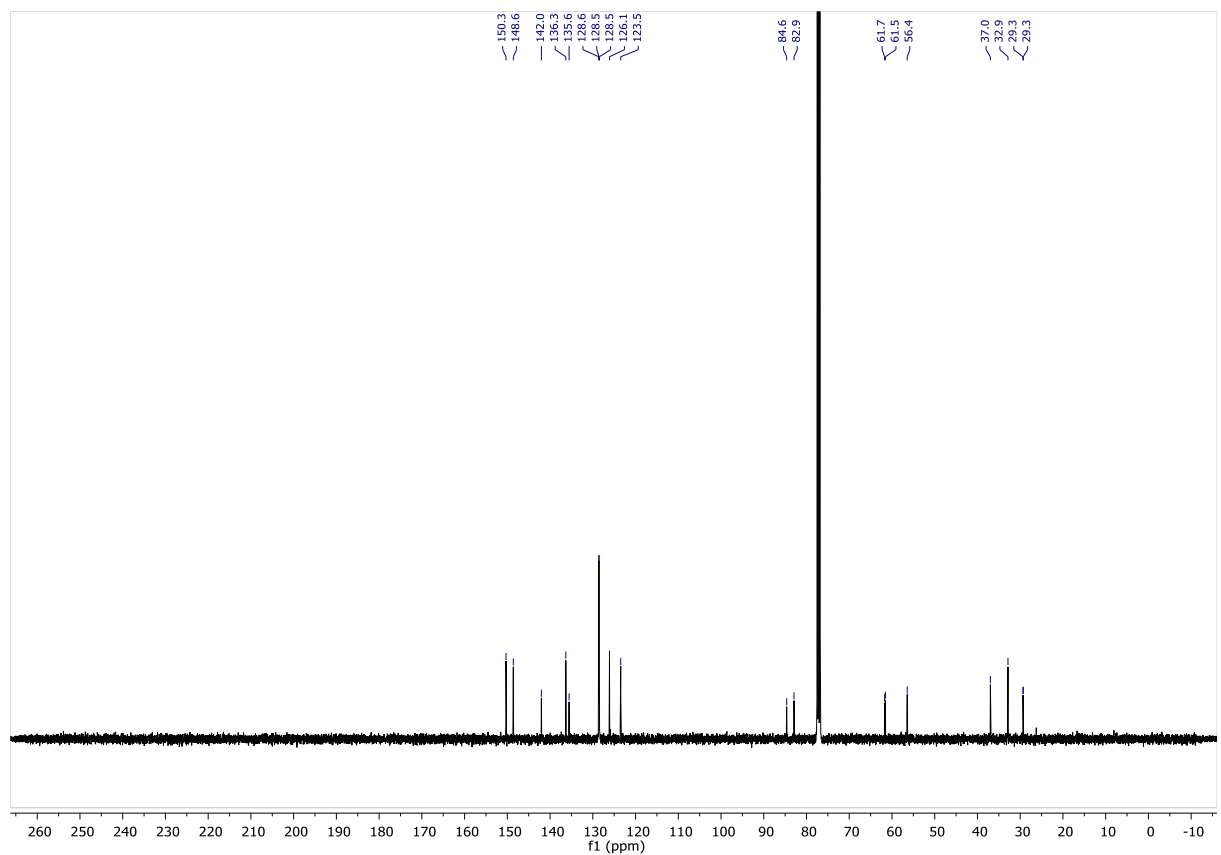
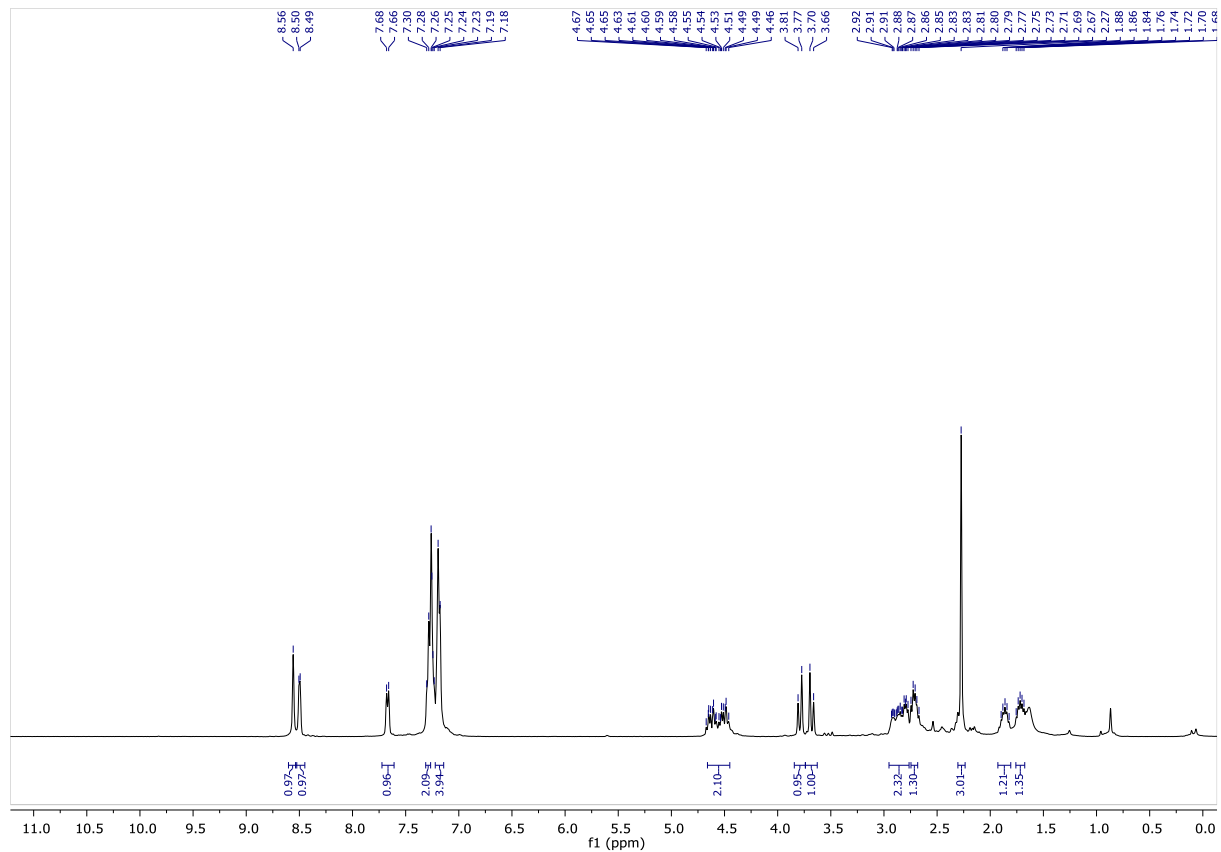


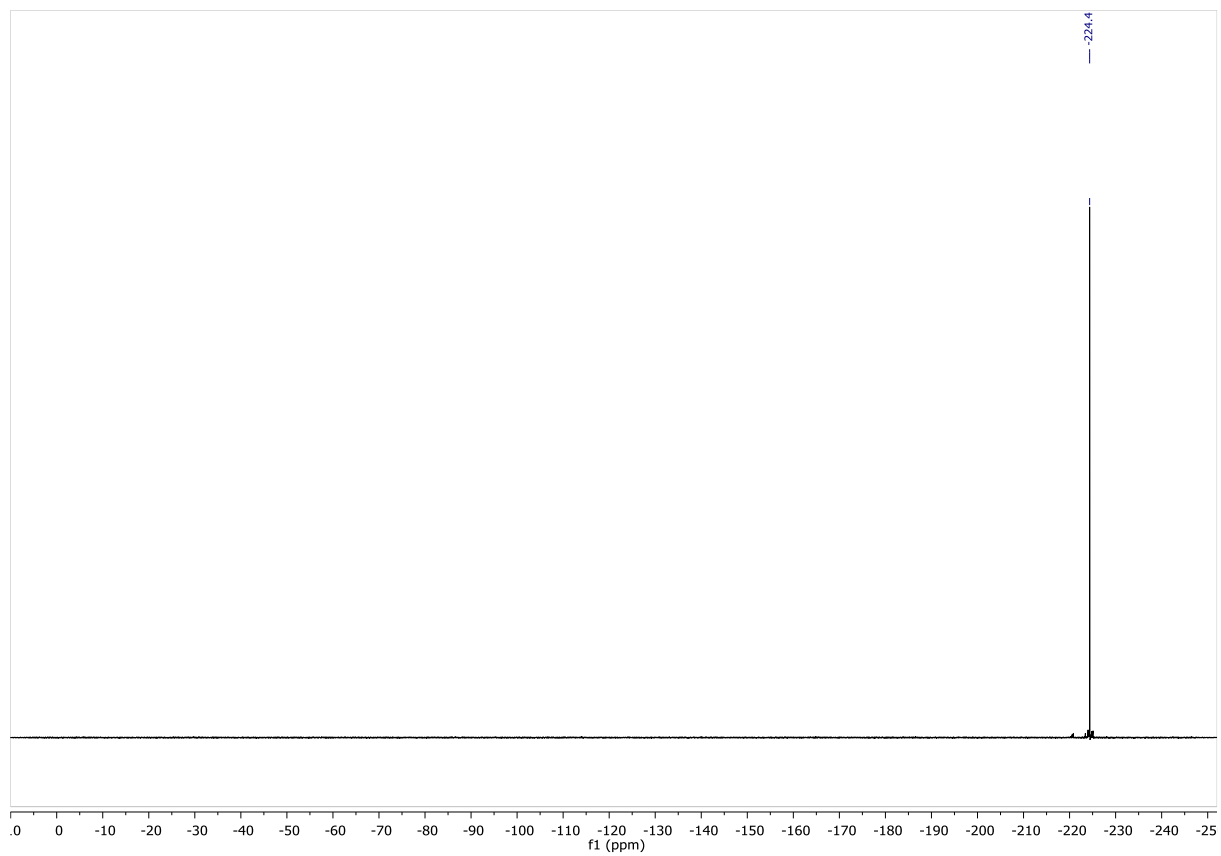
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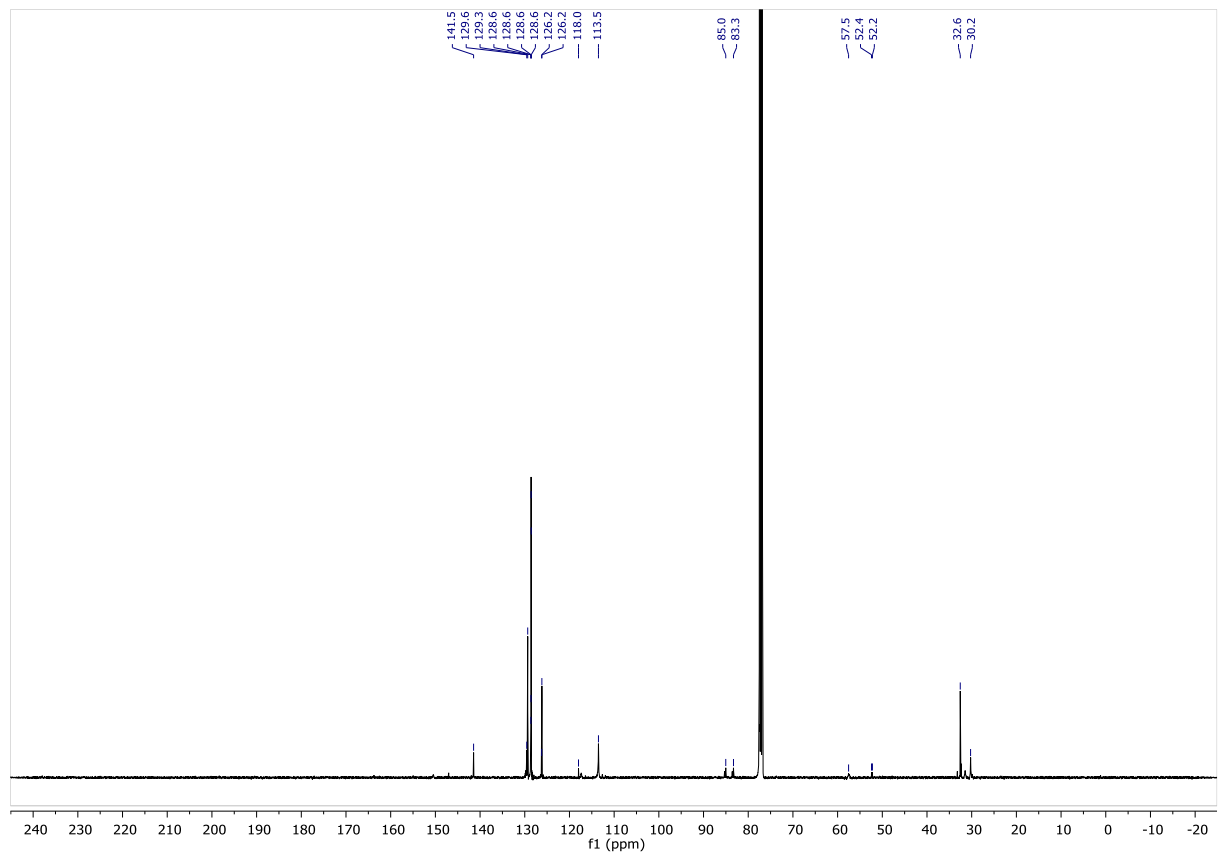
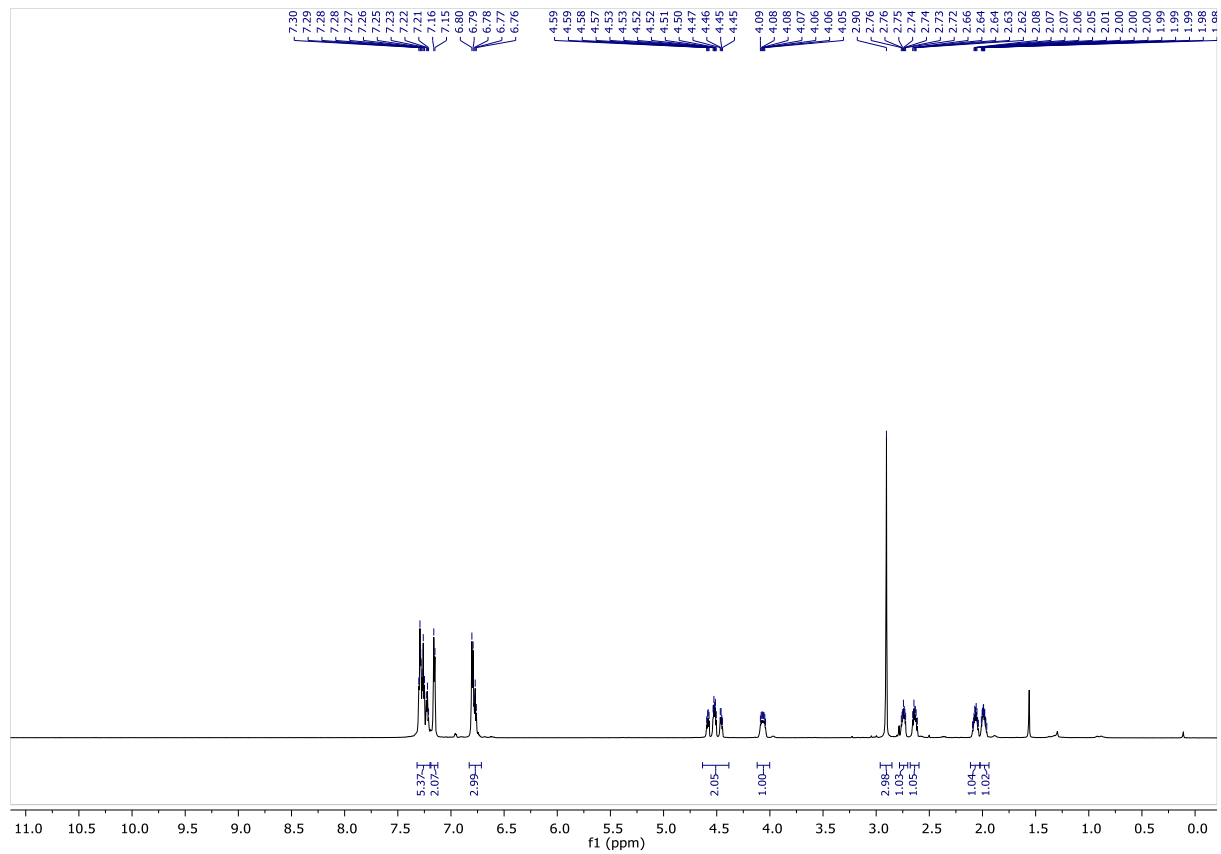


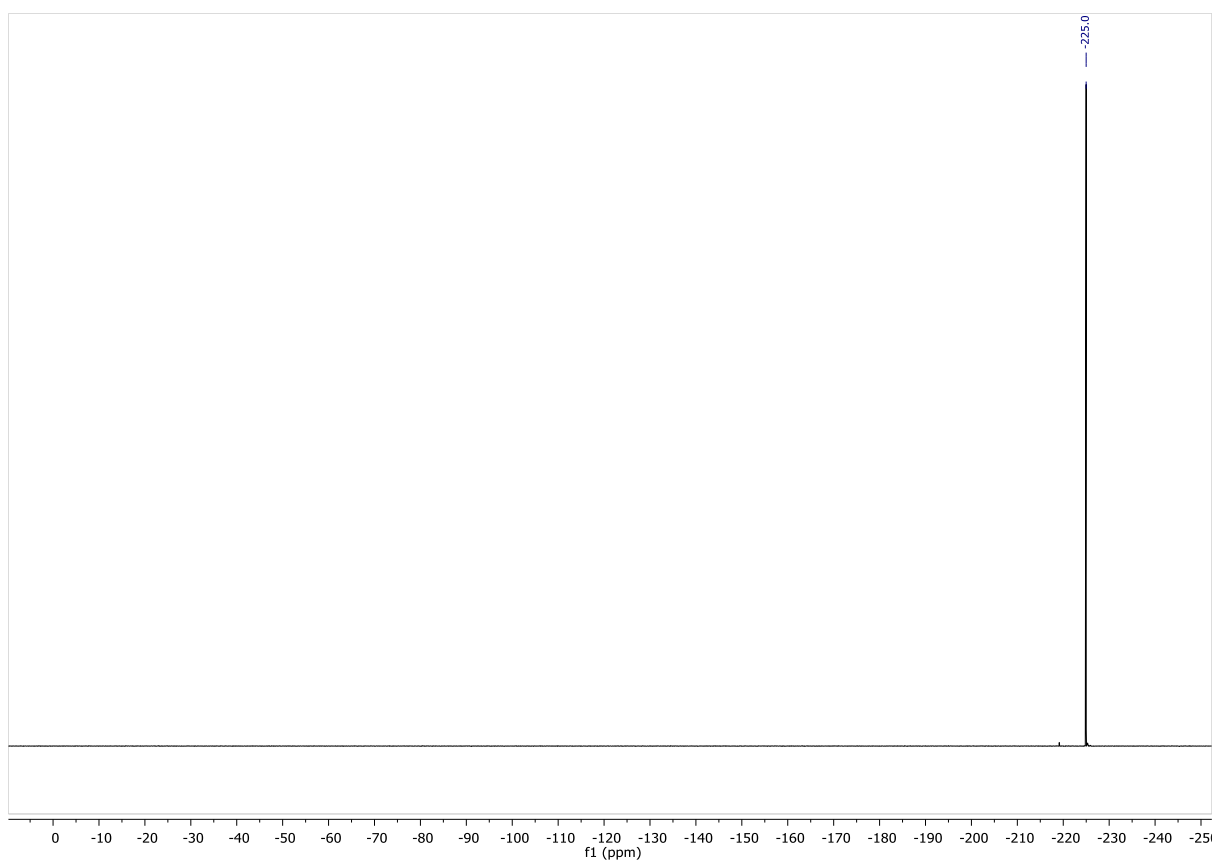
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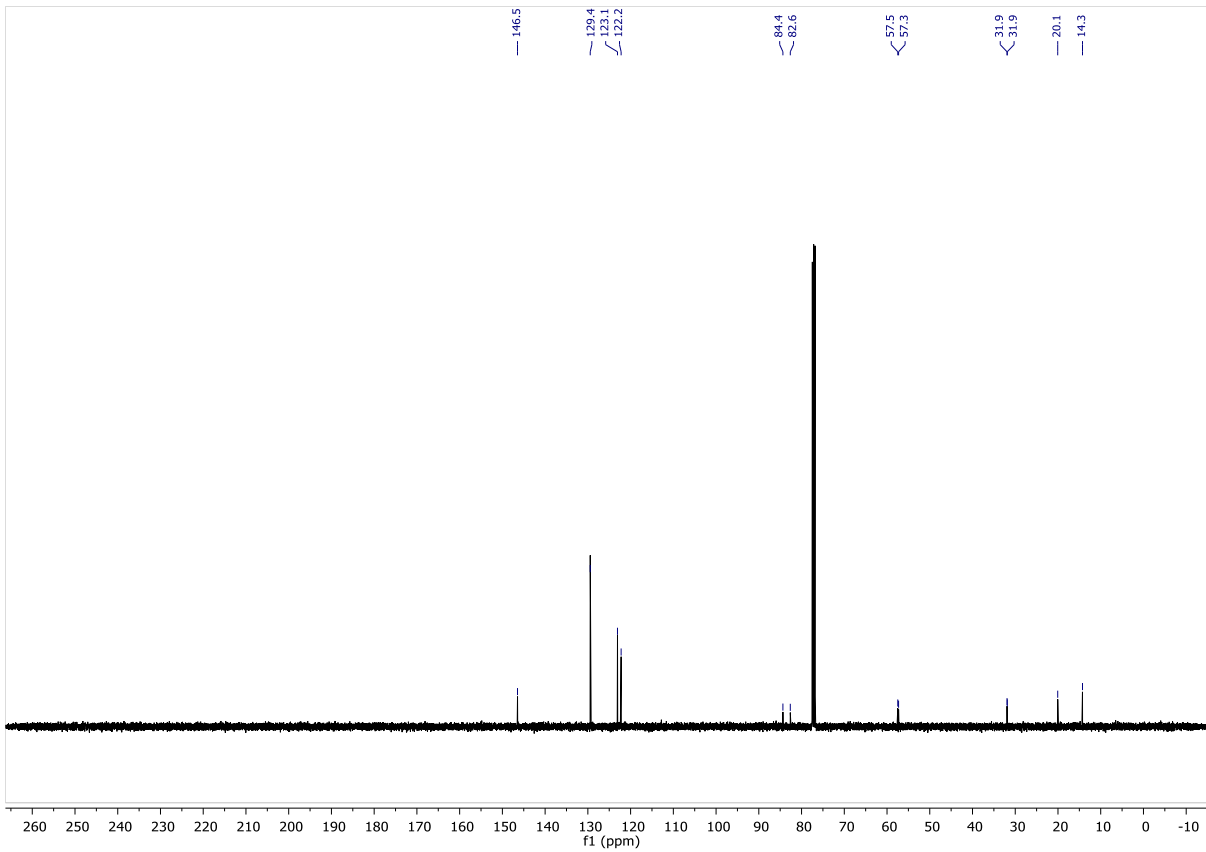
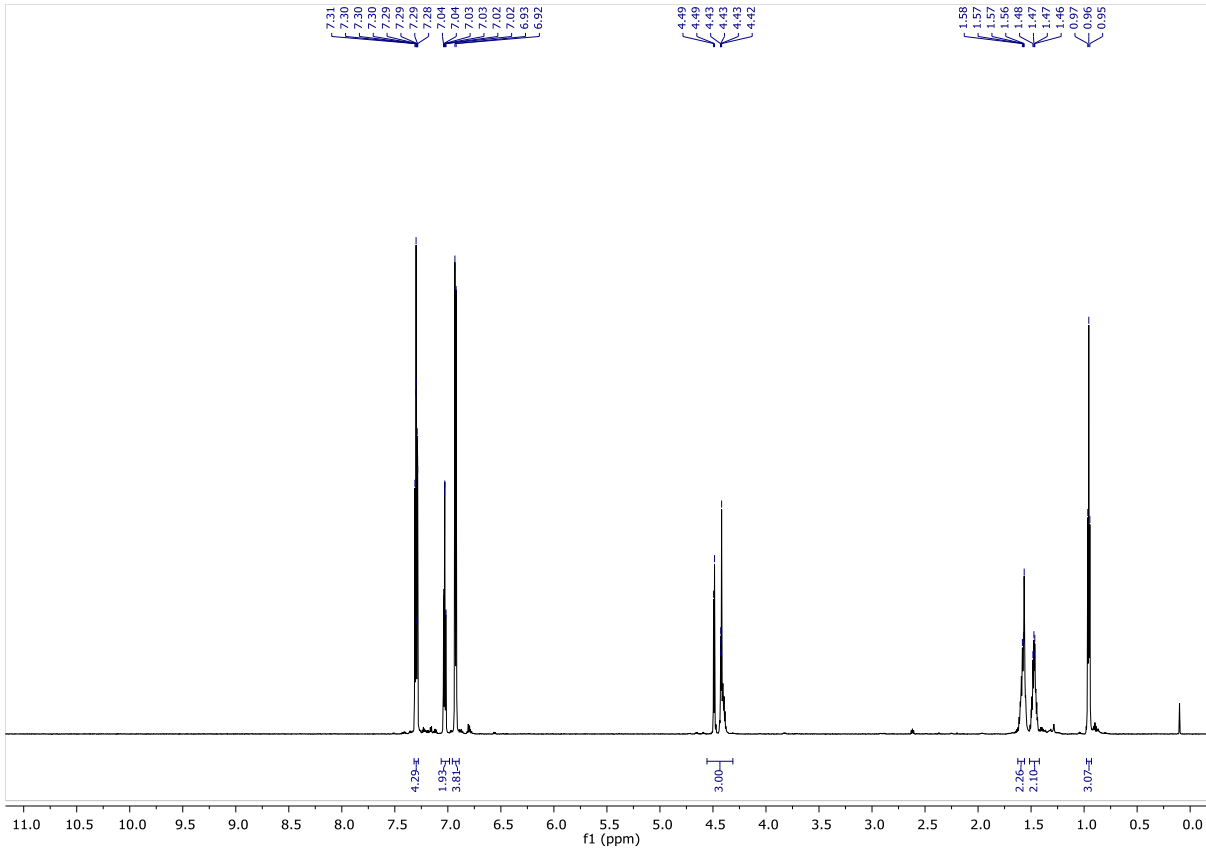


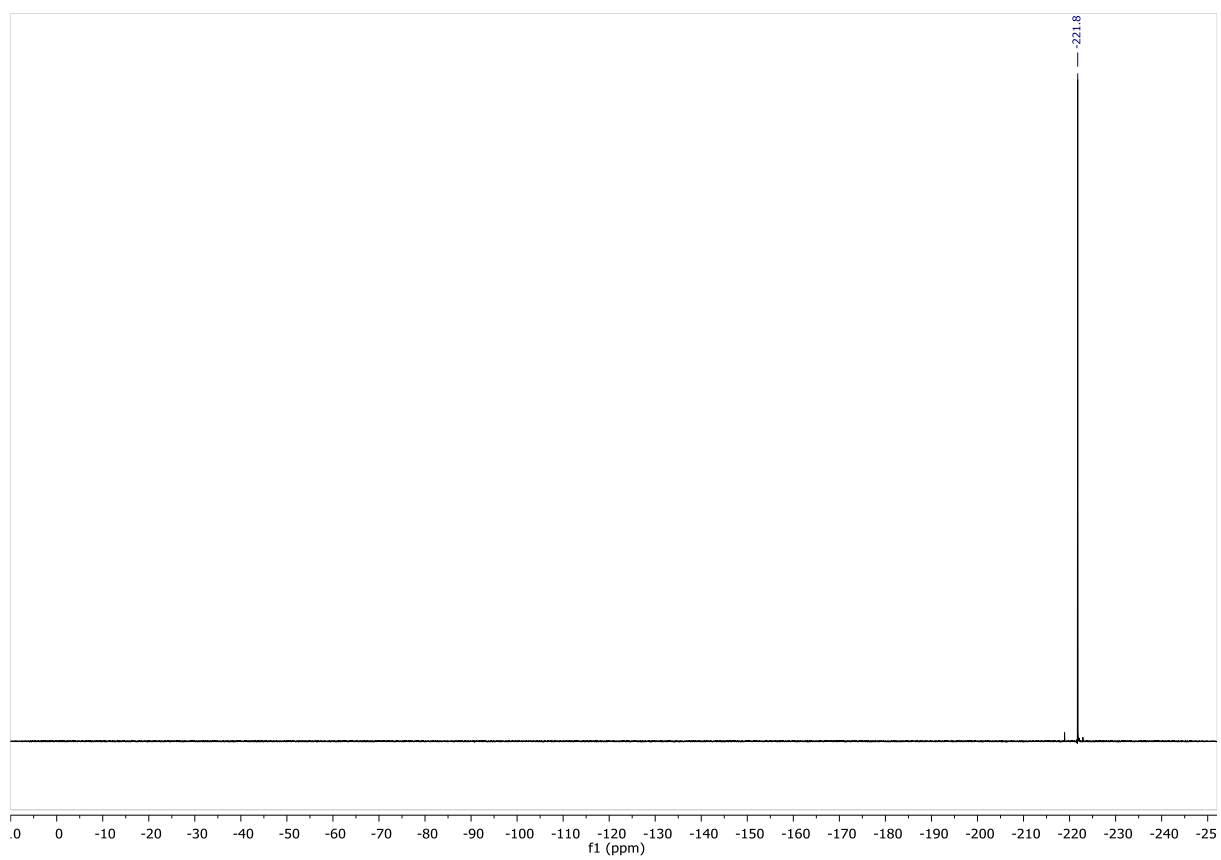
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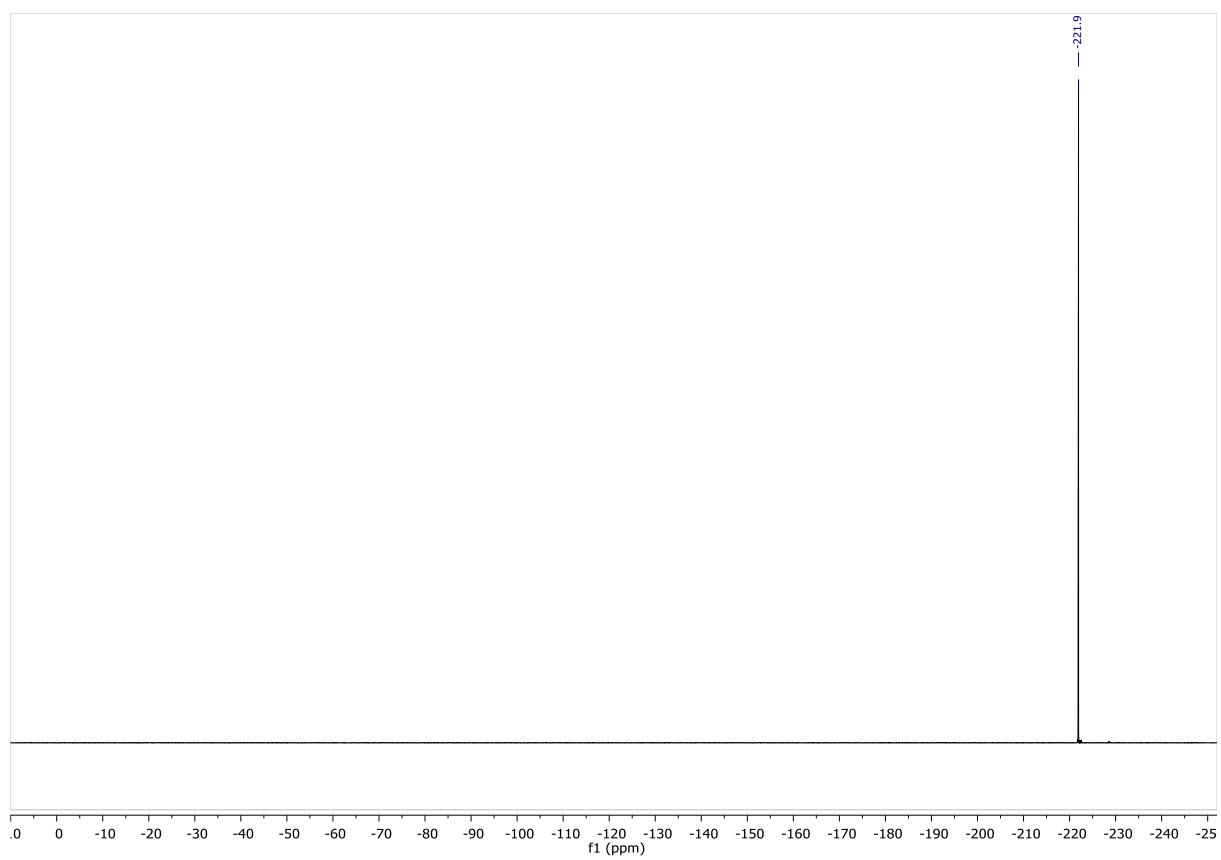




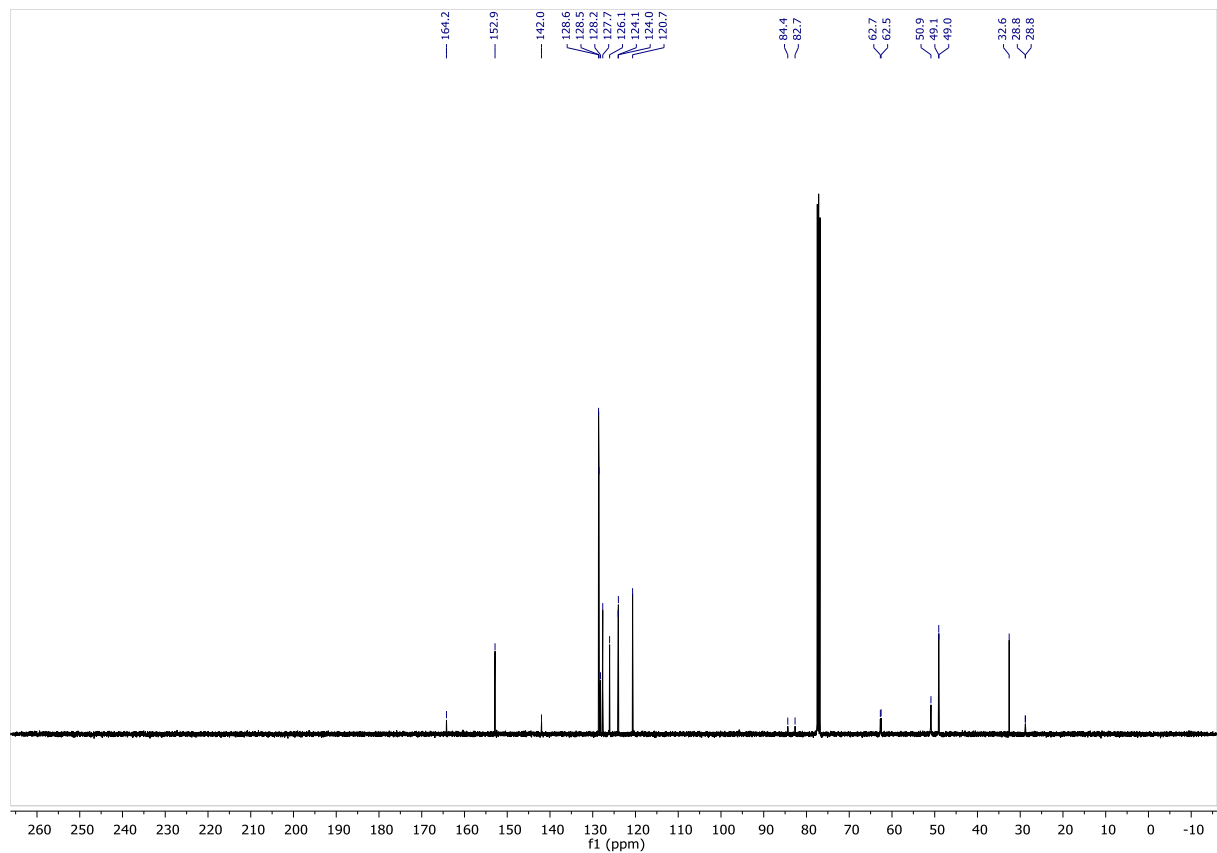
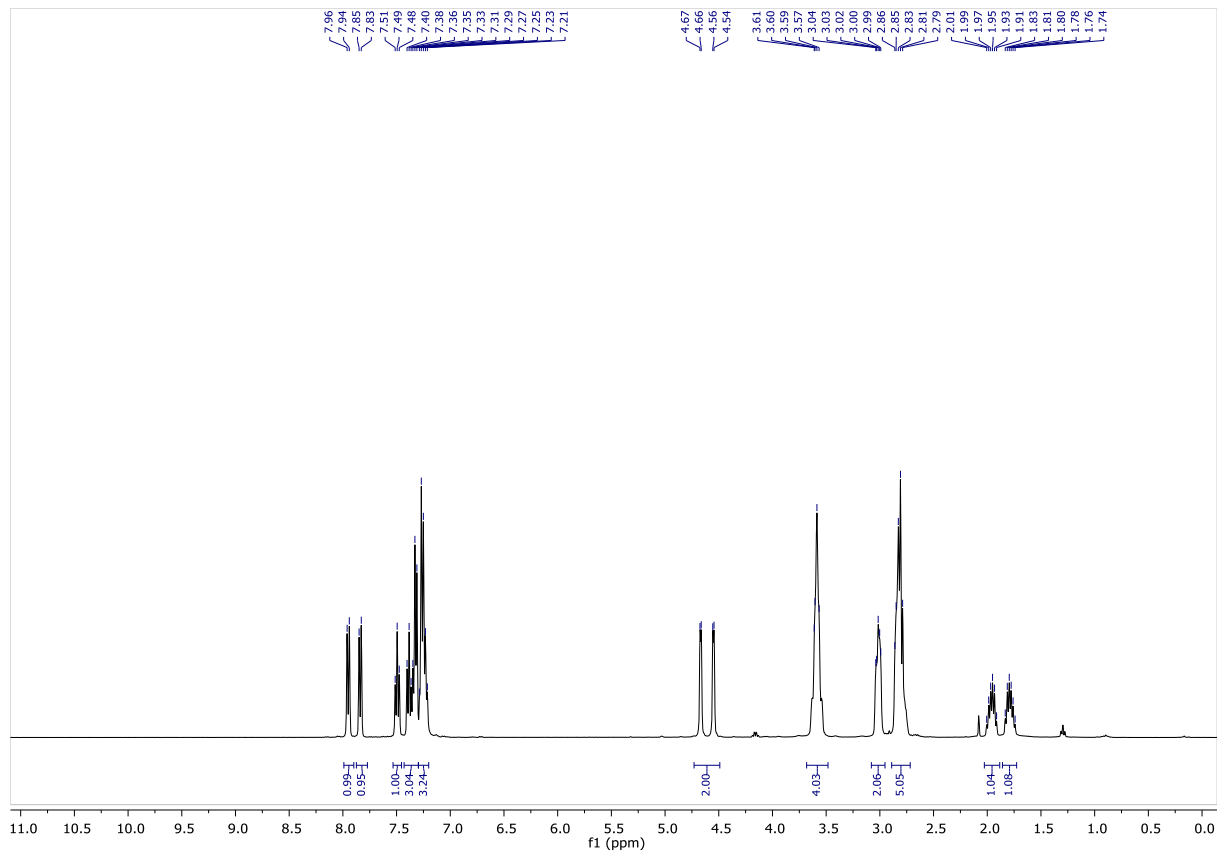
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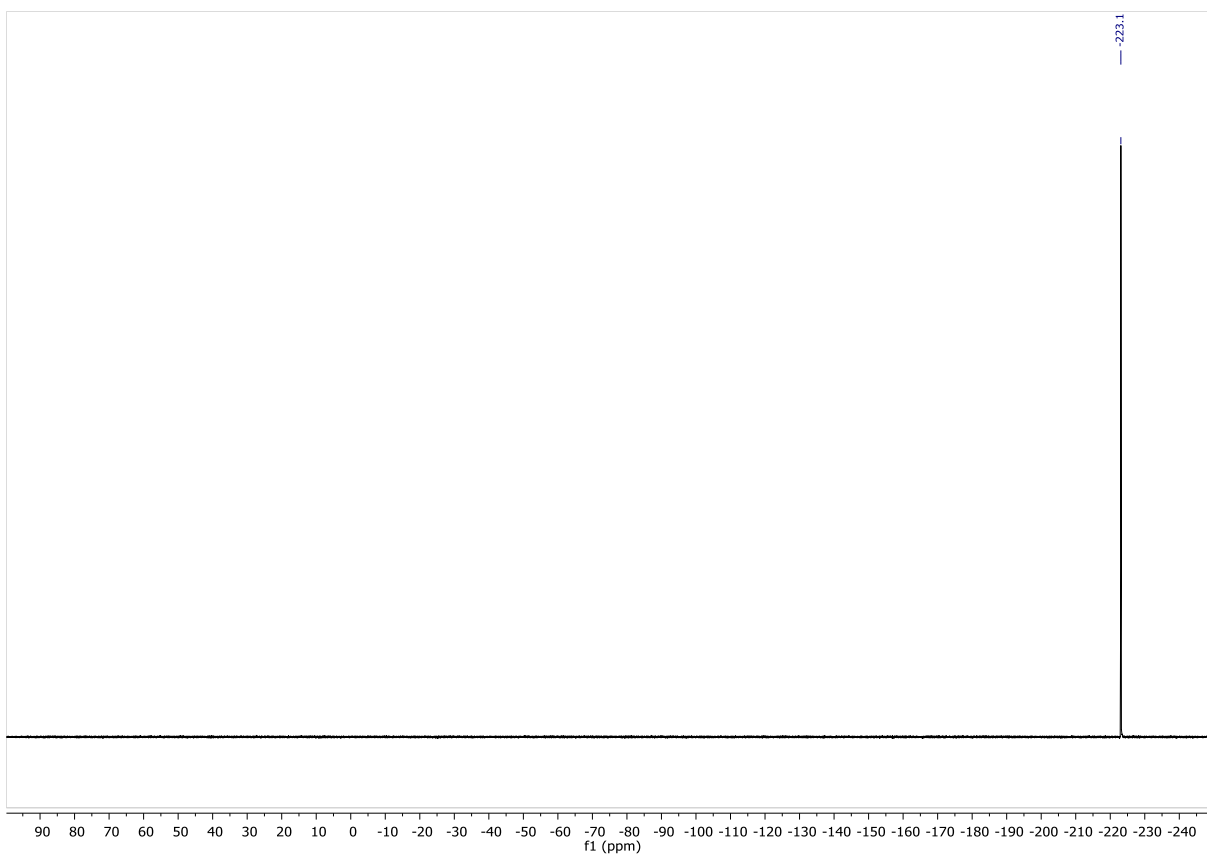




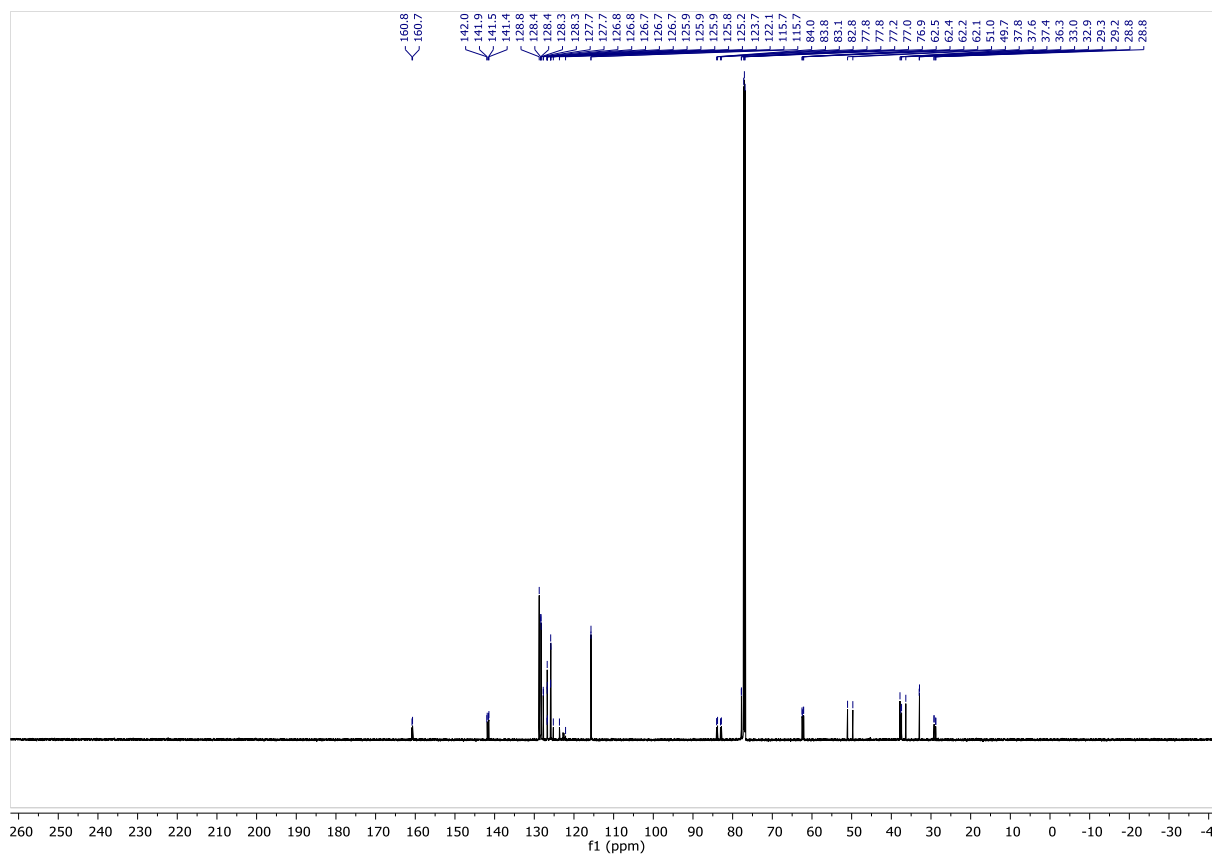
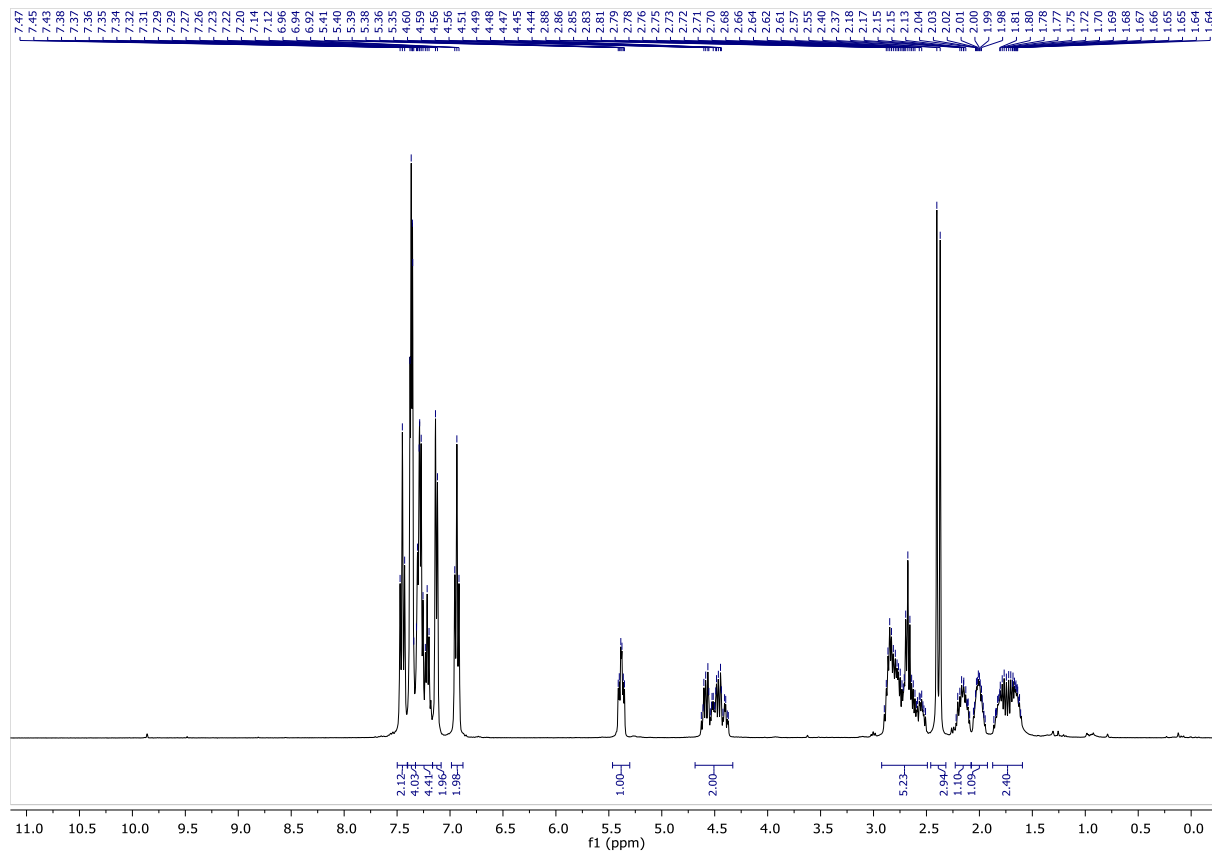


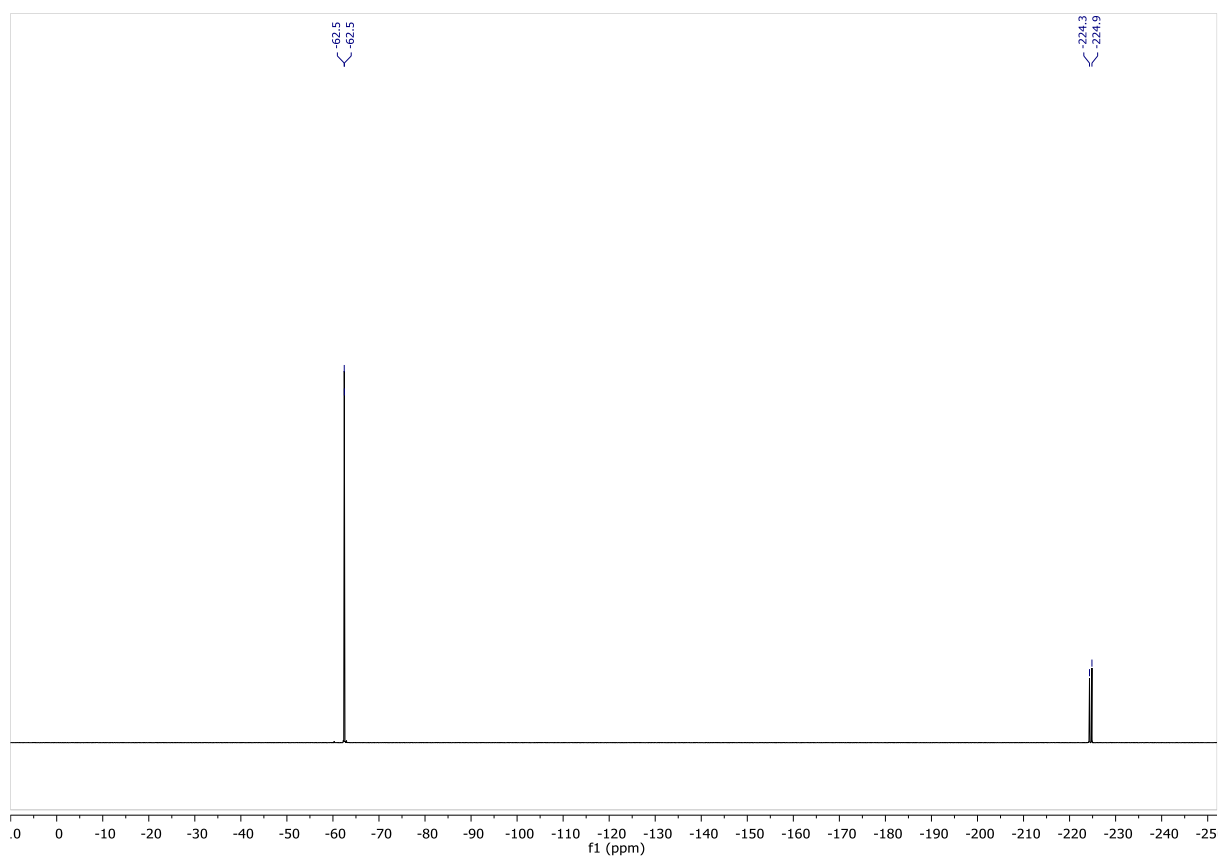
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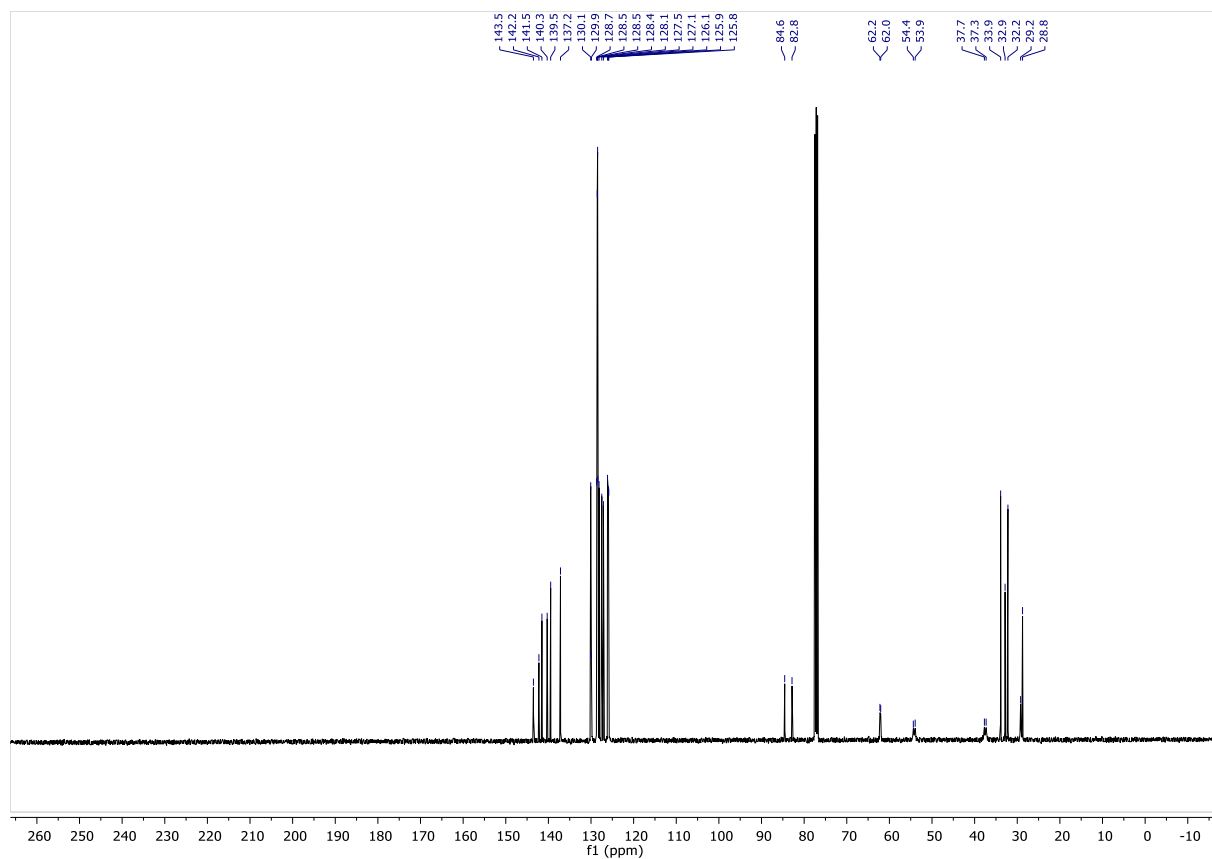
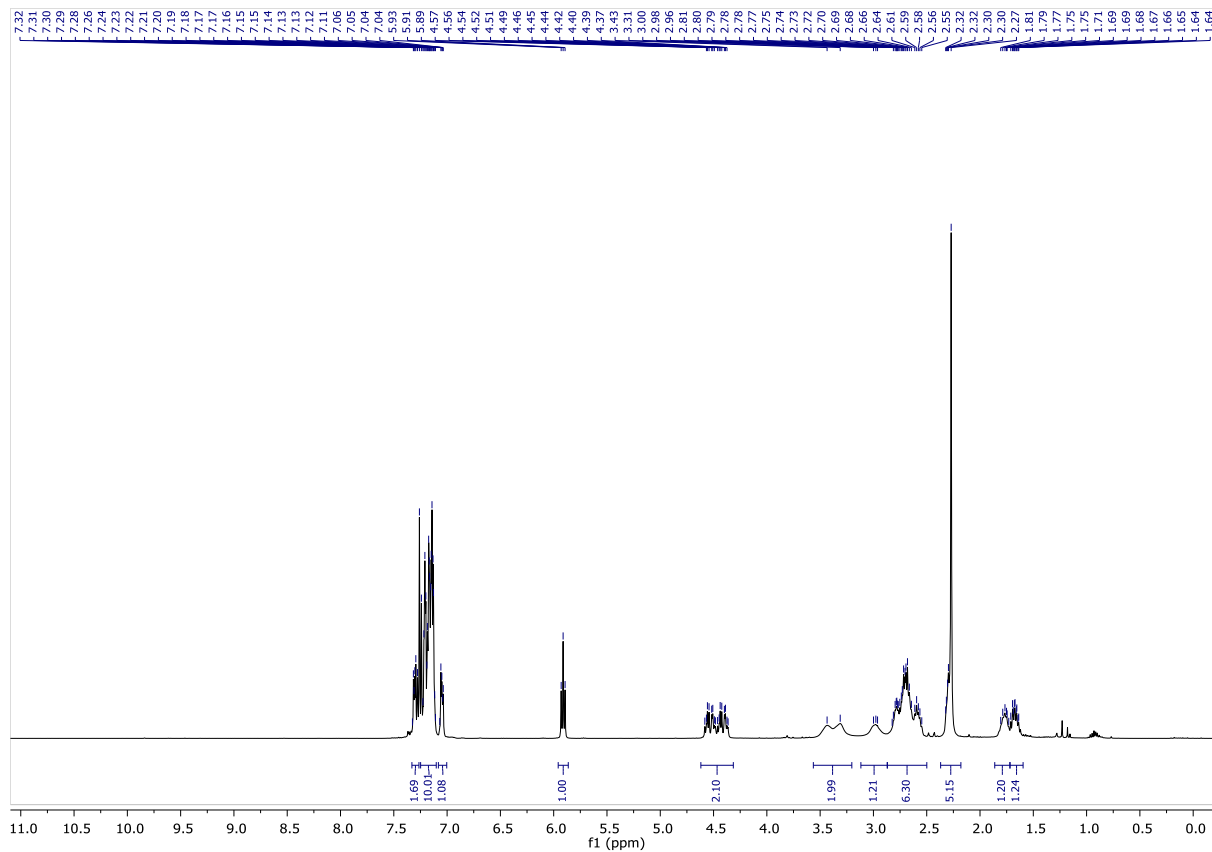


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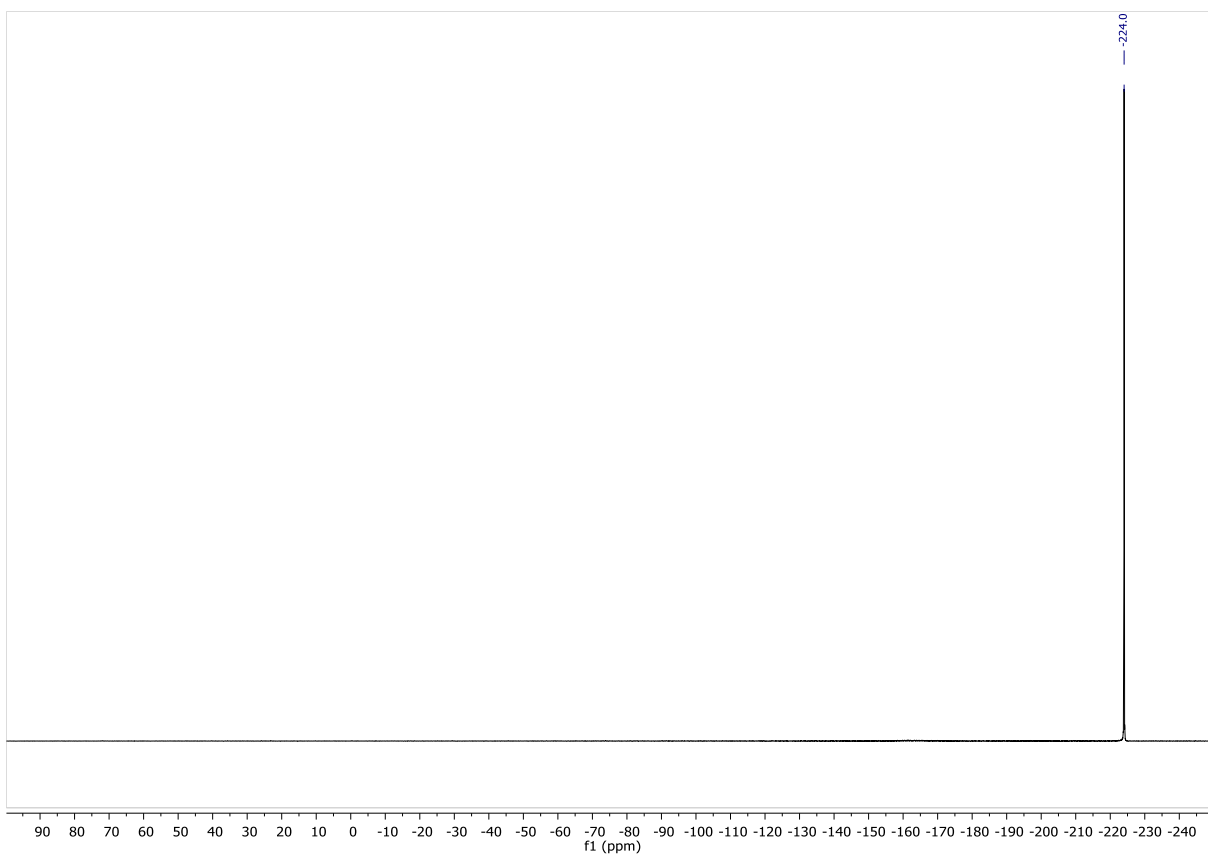




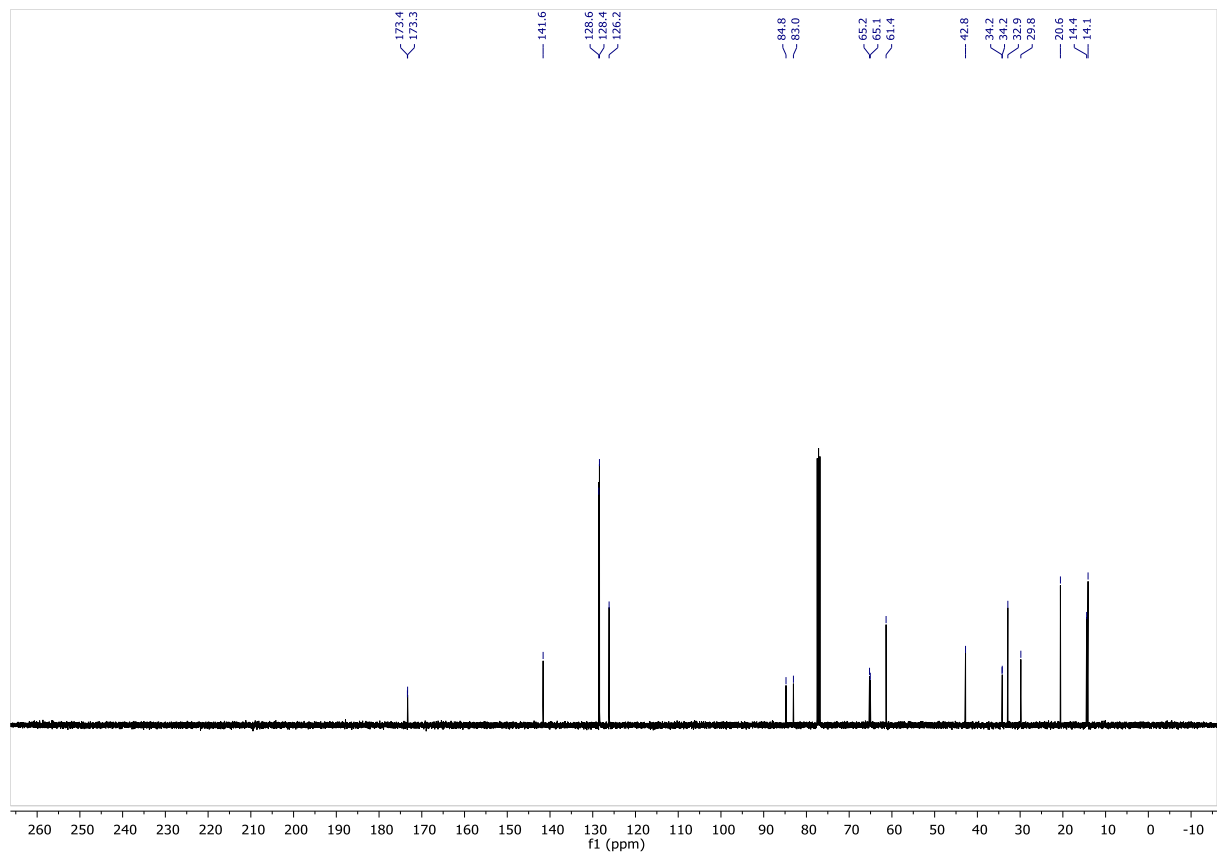
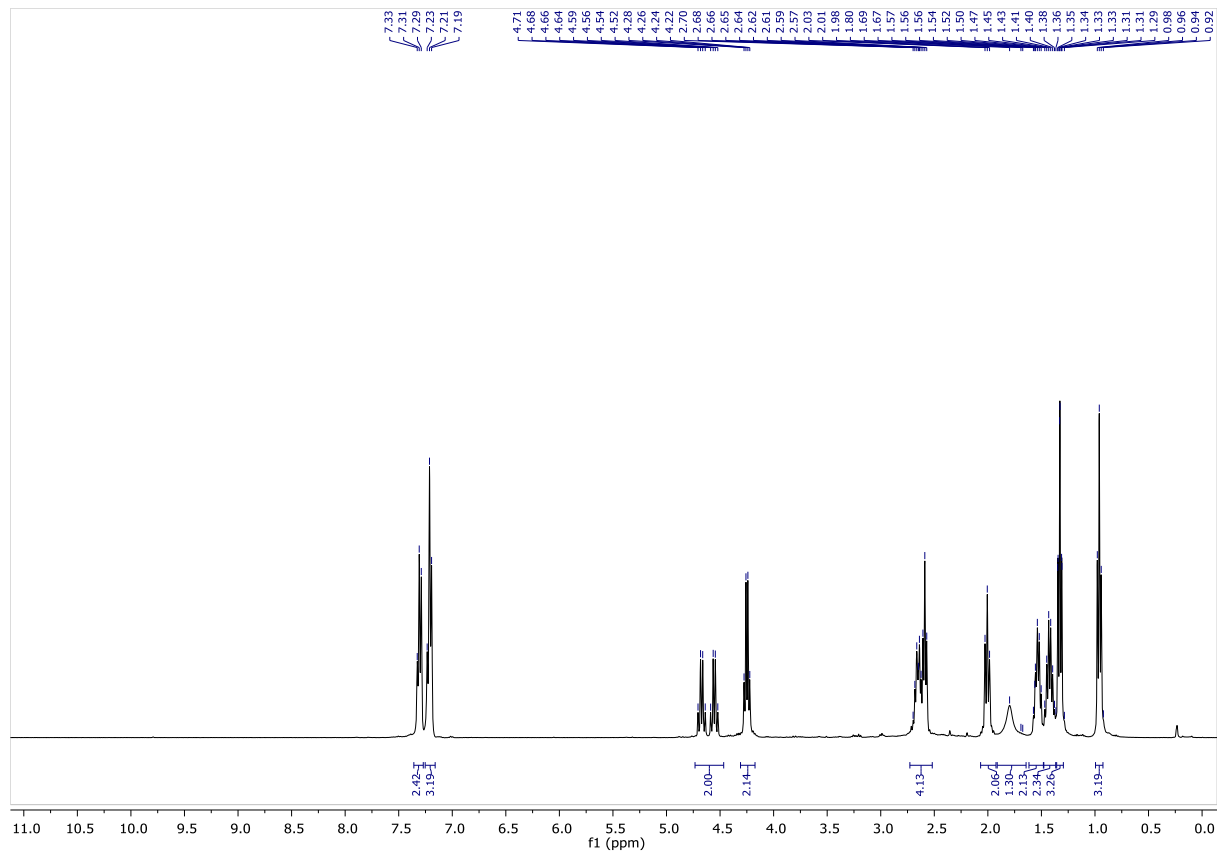
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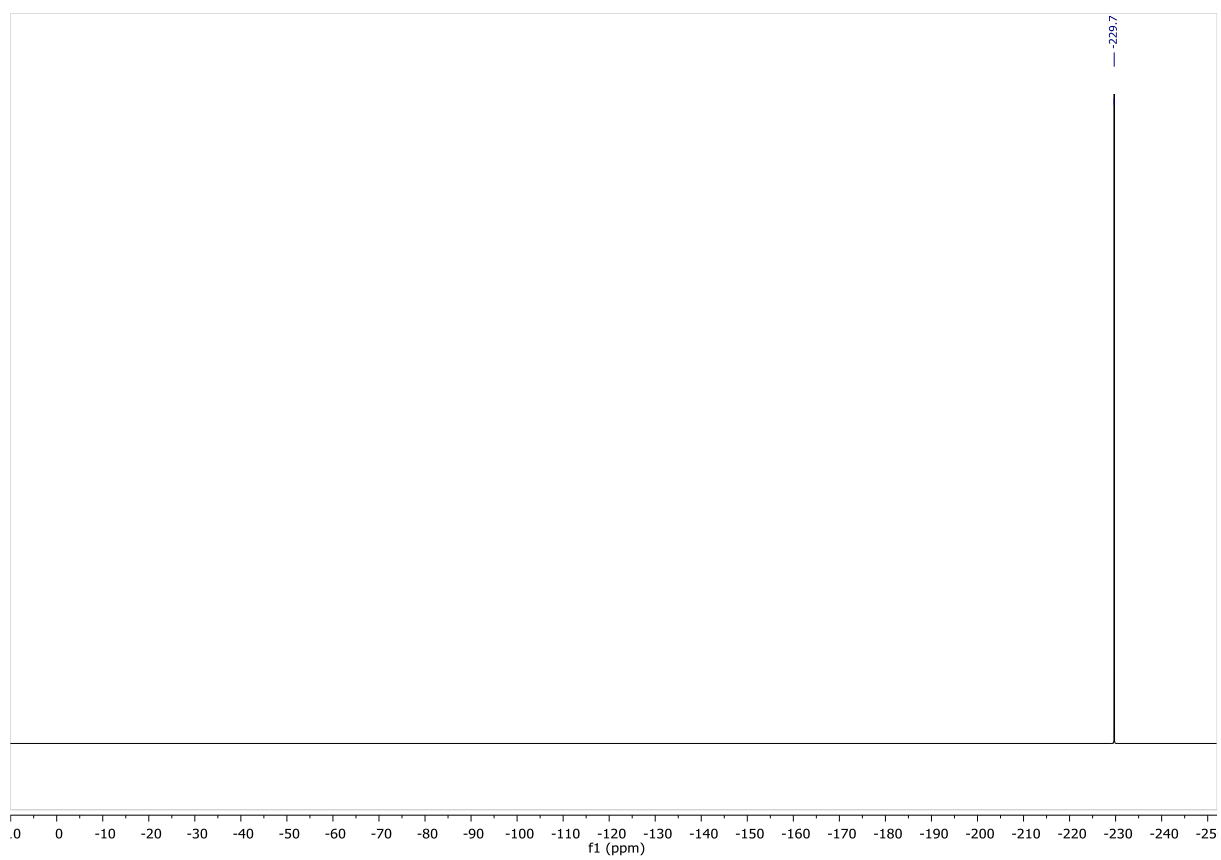


S83

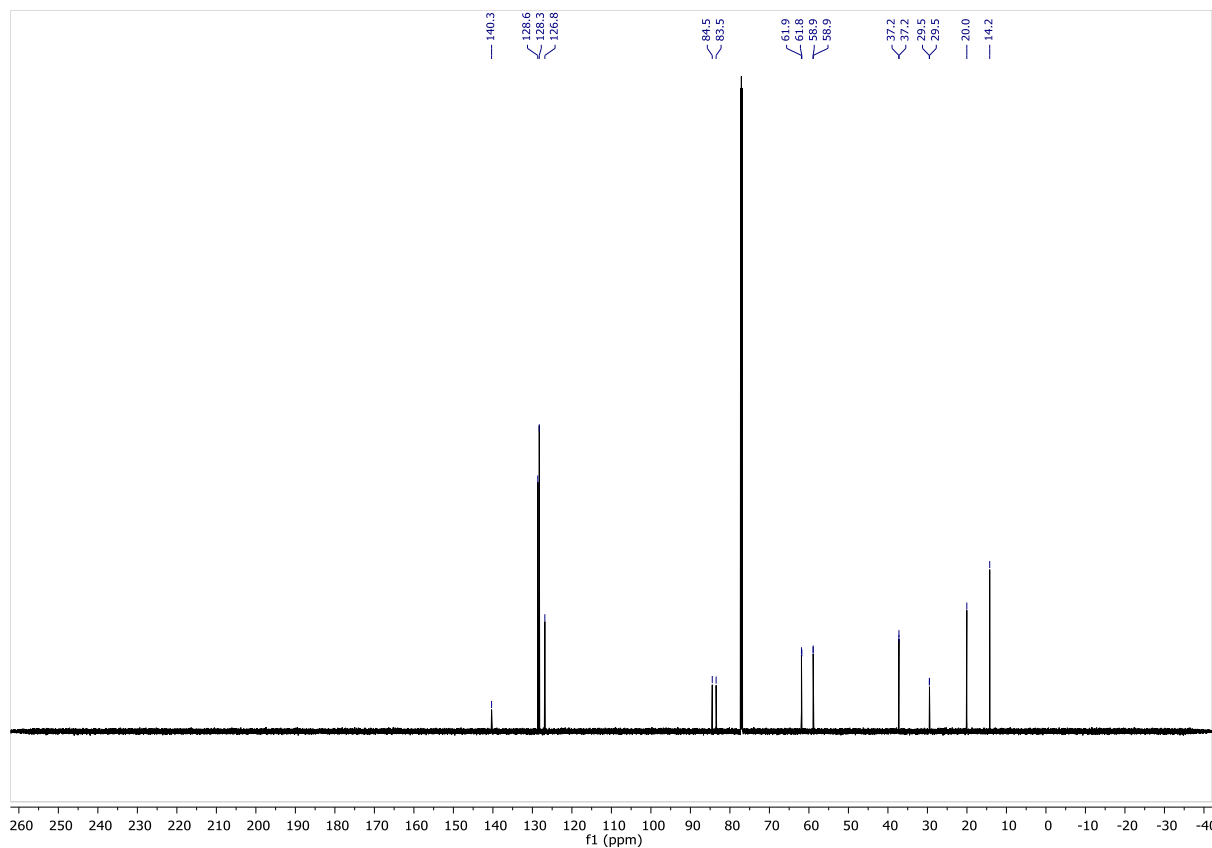
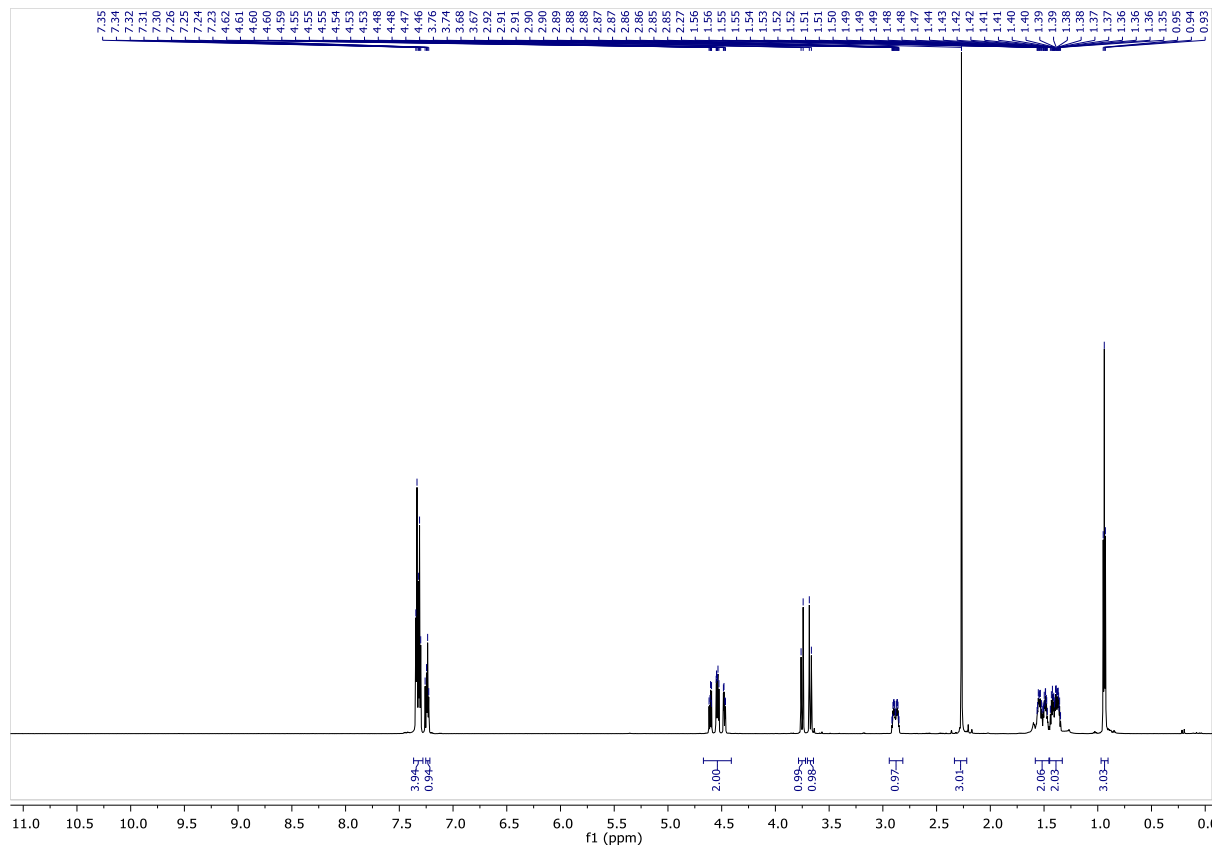


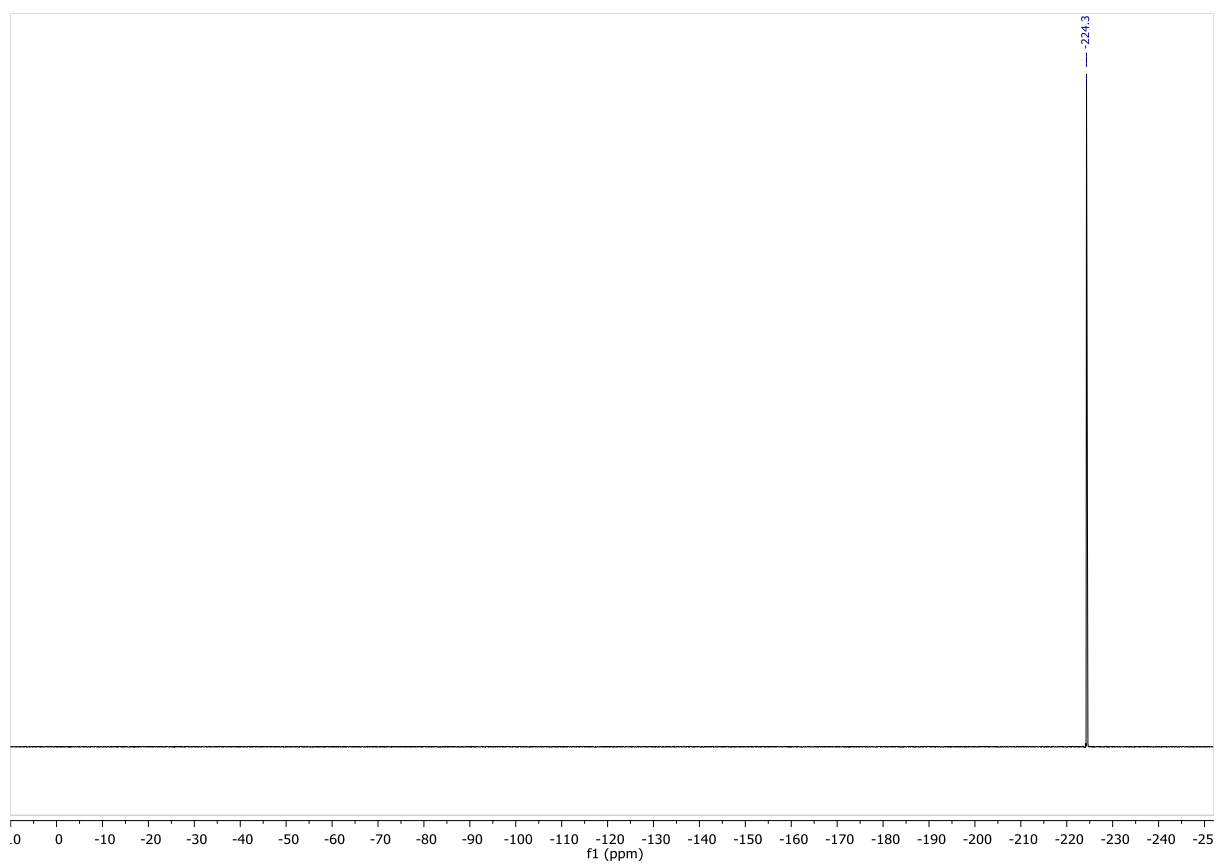
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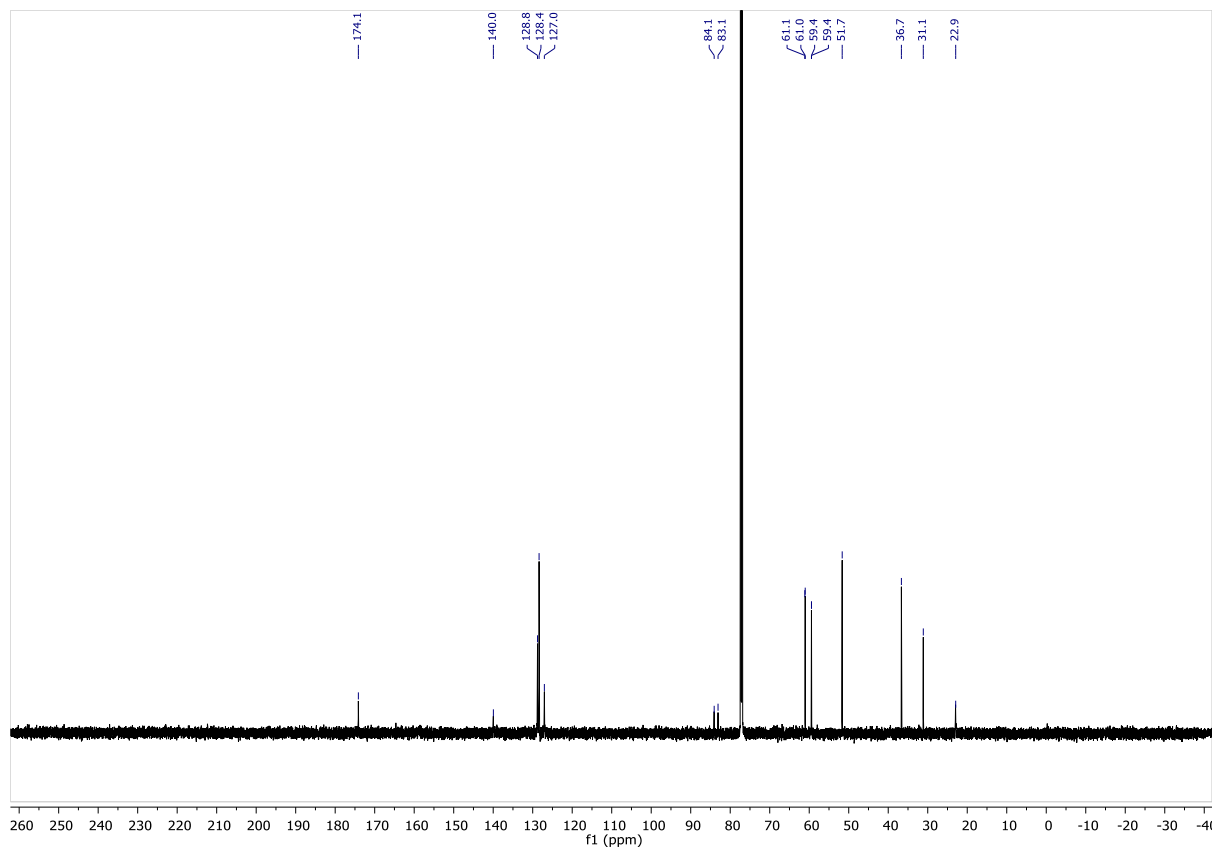
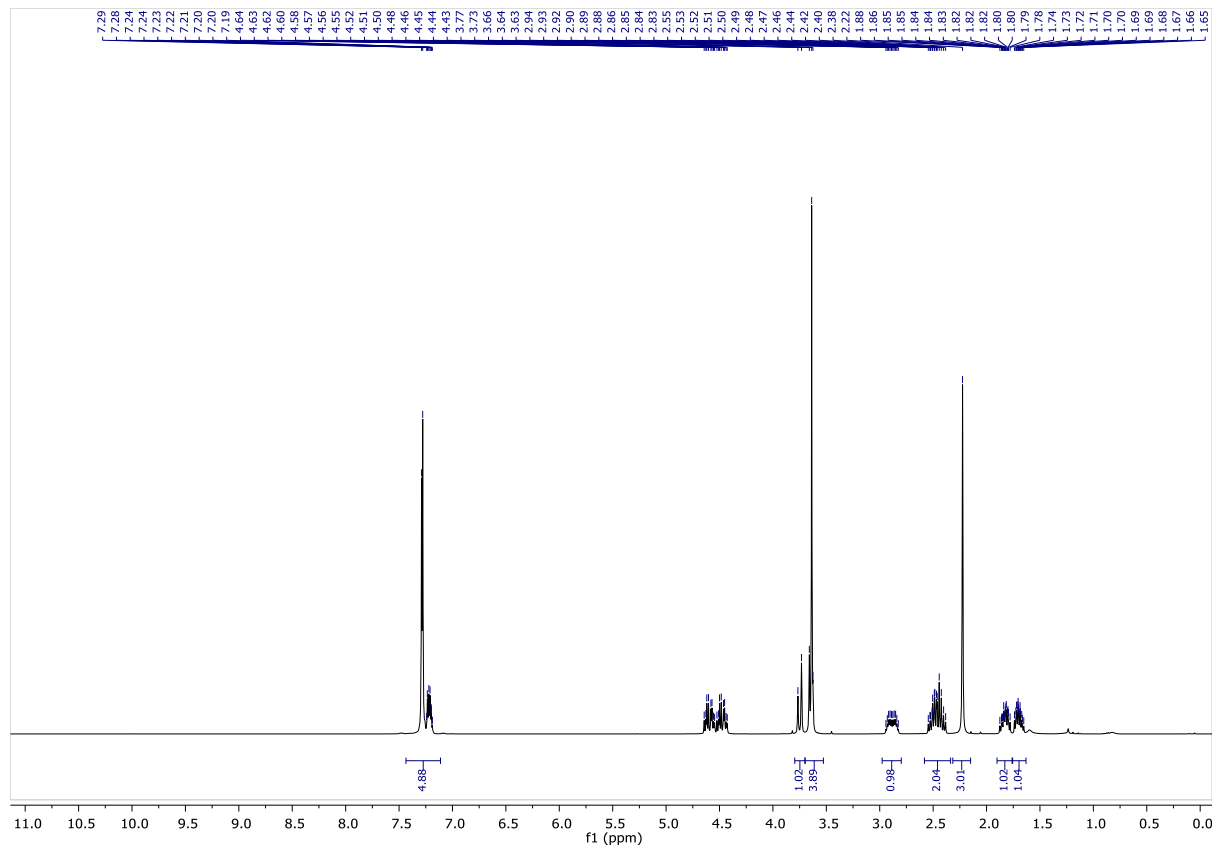


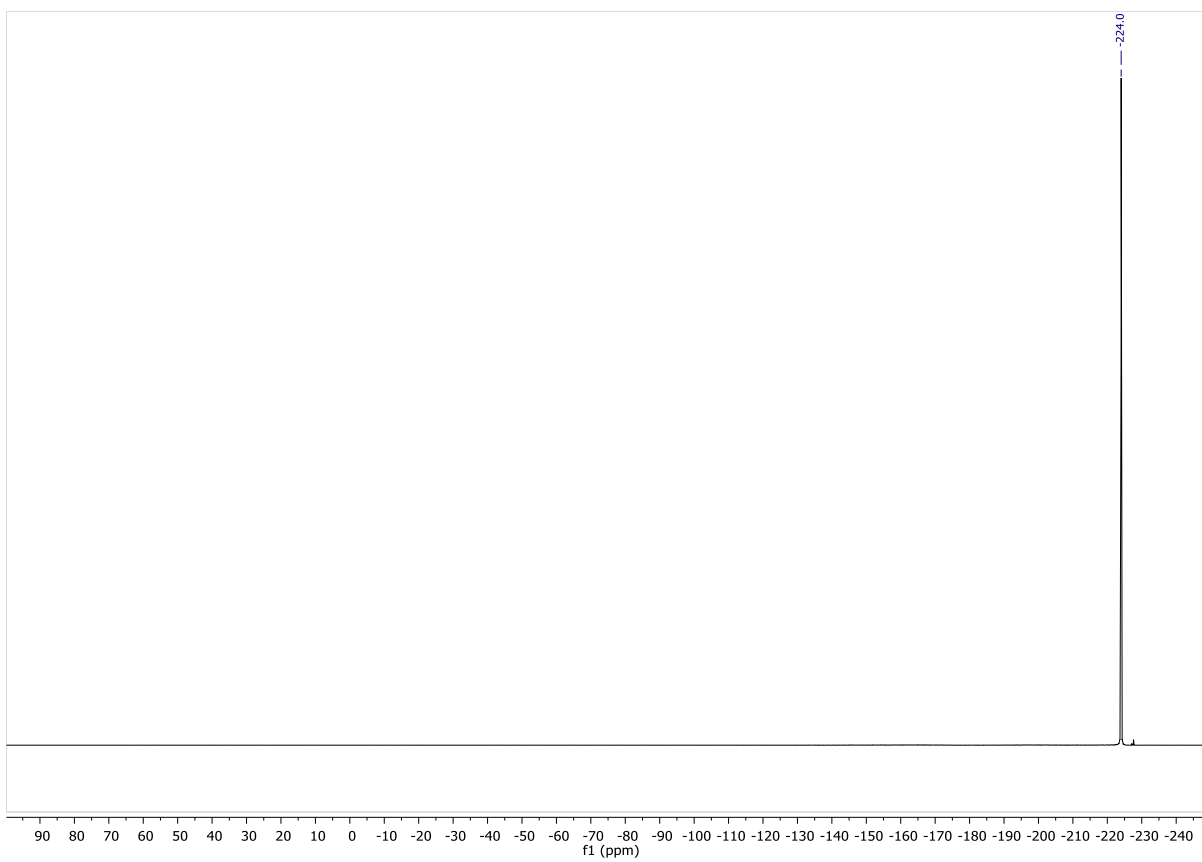
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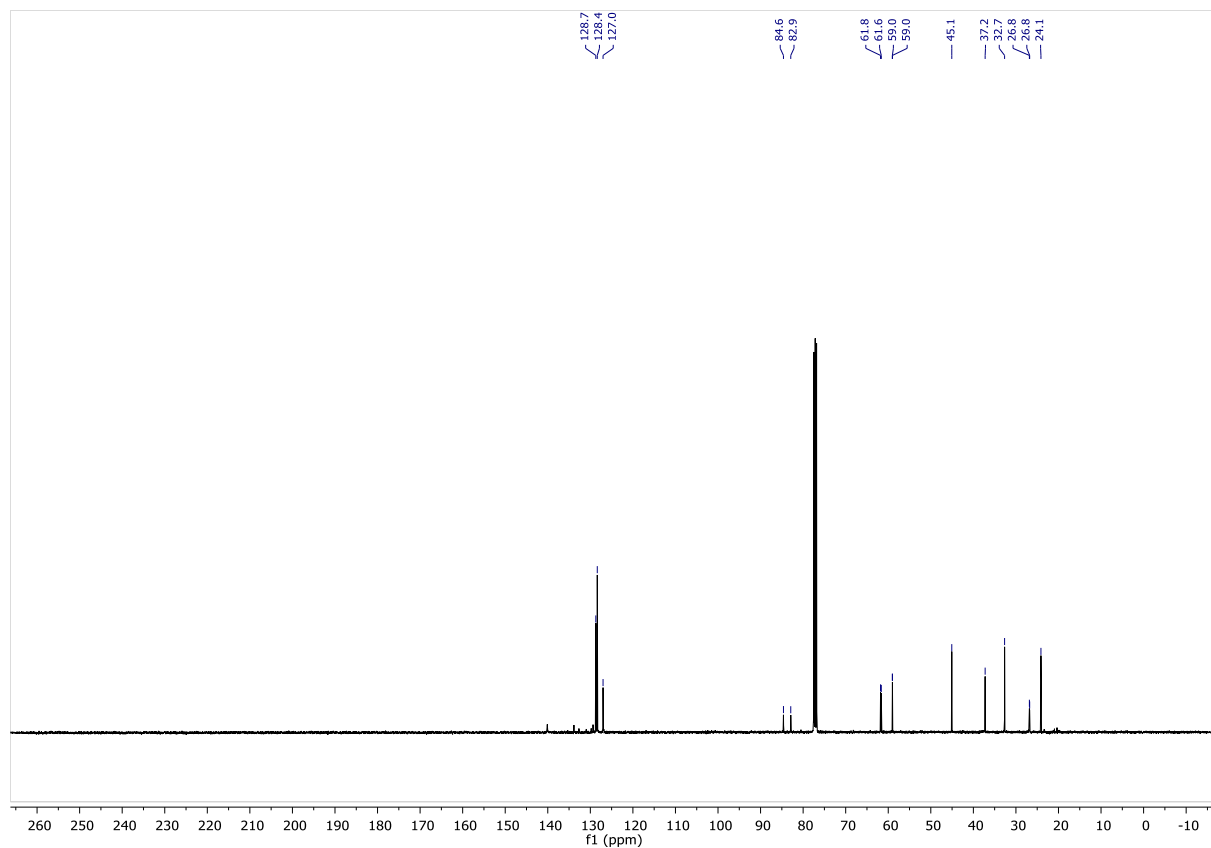
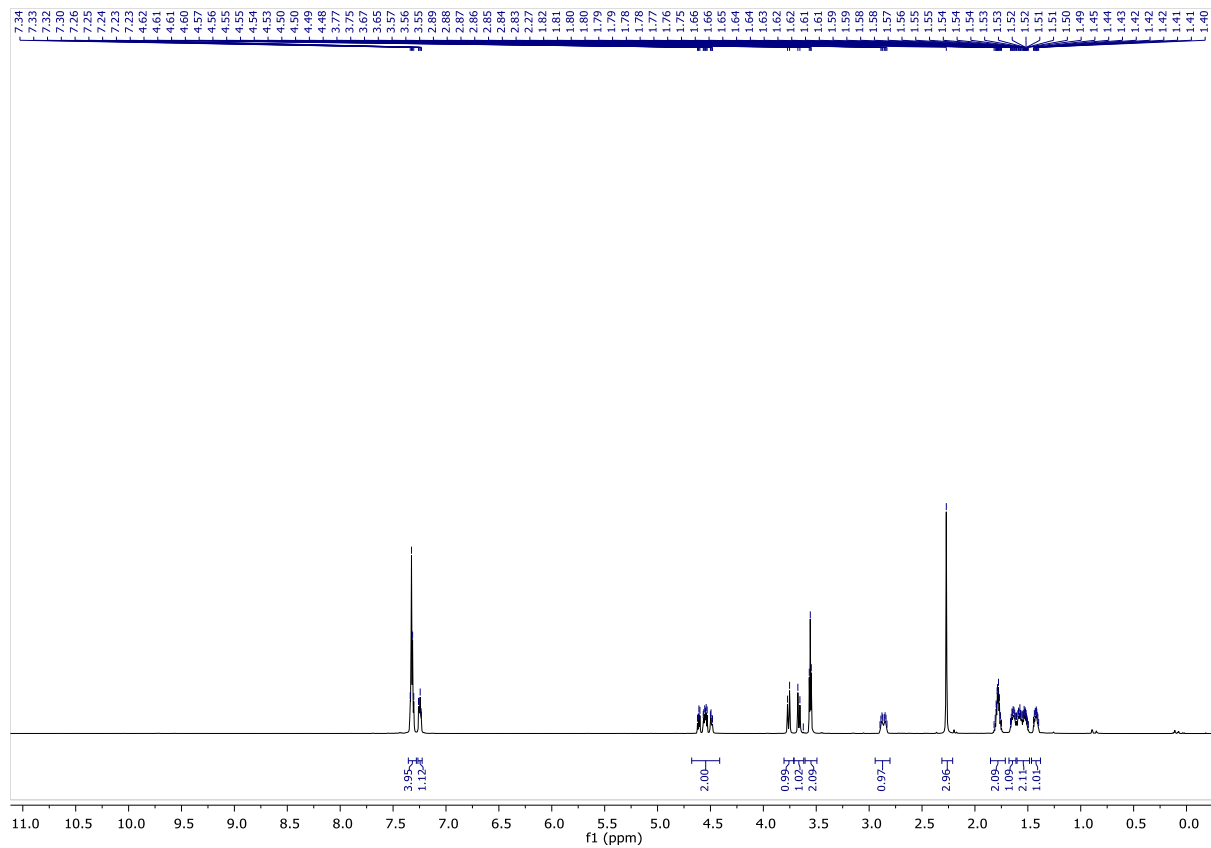


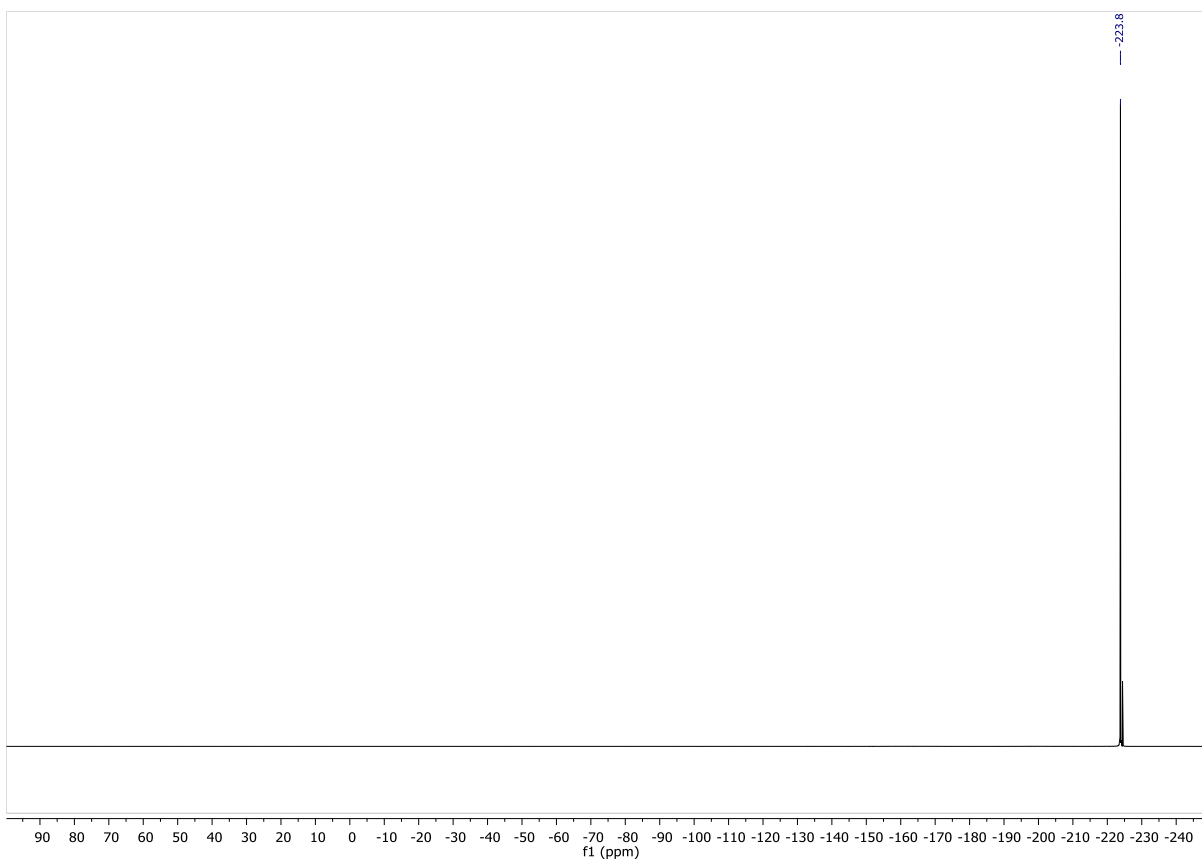
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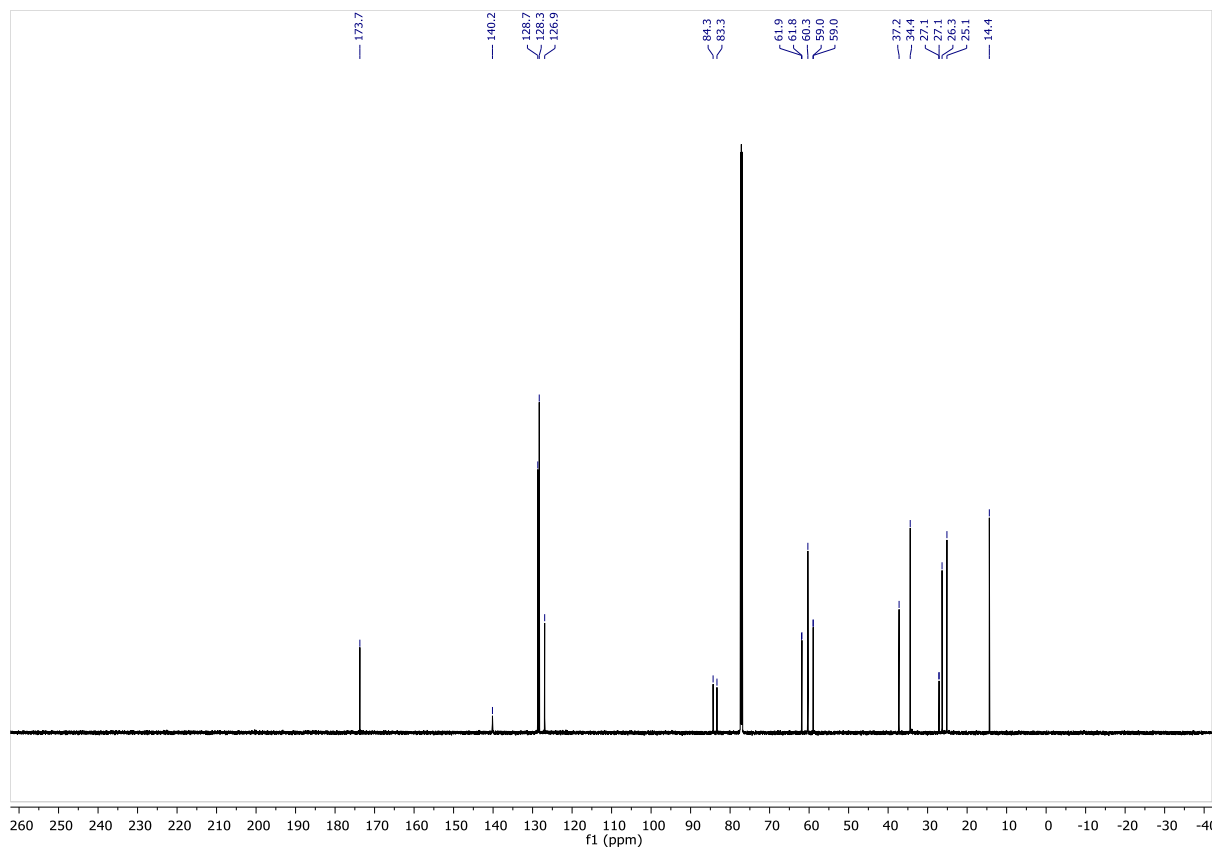
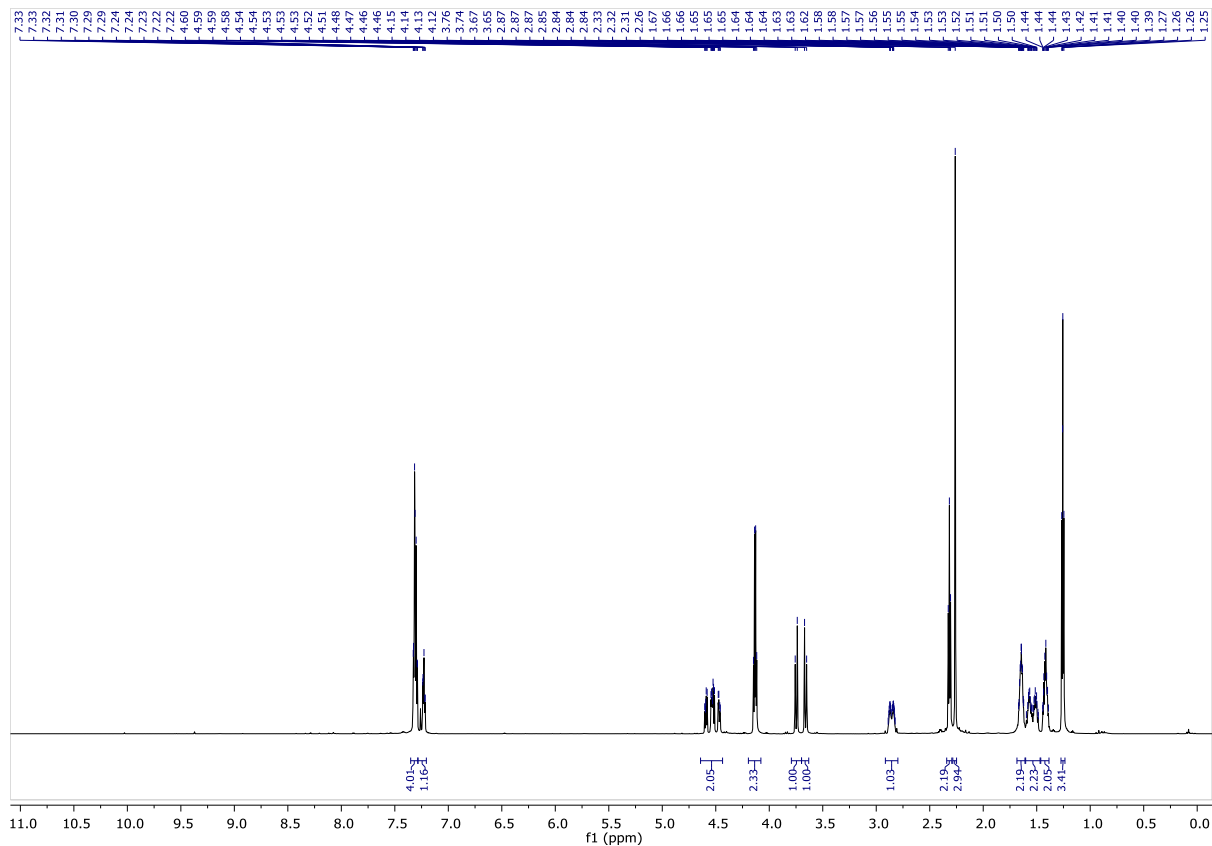


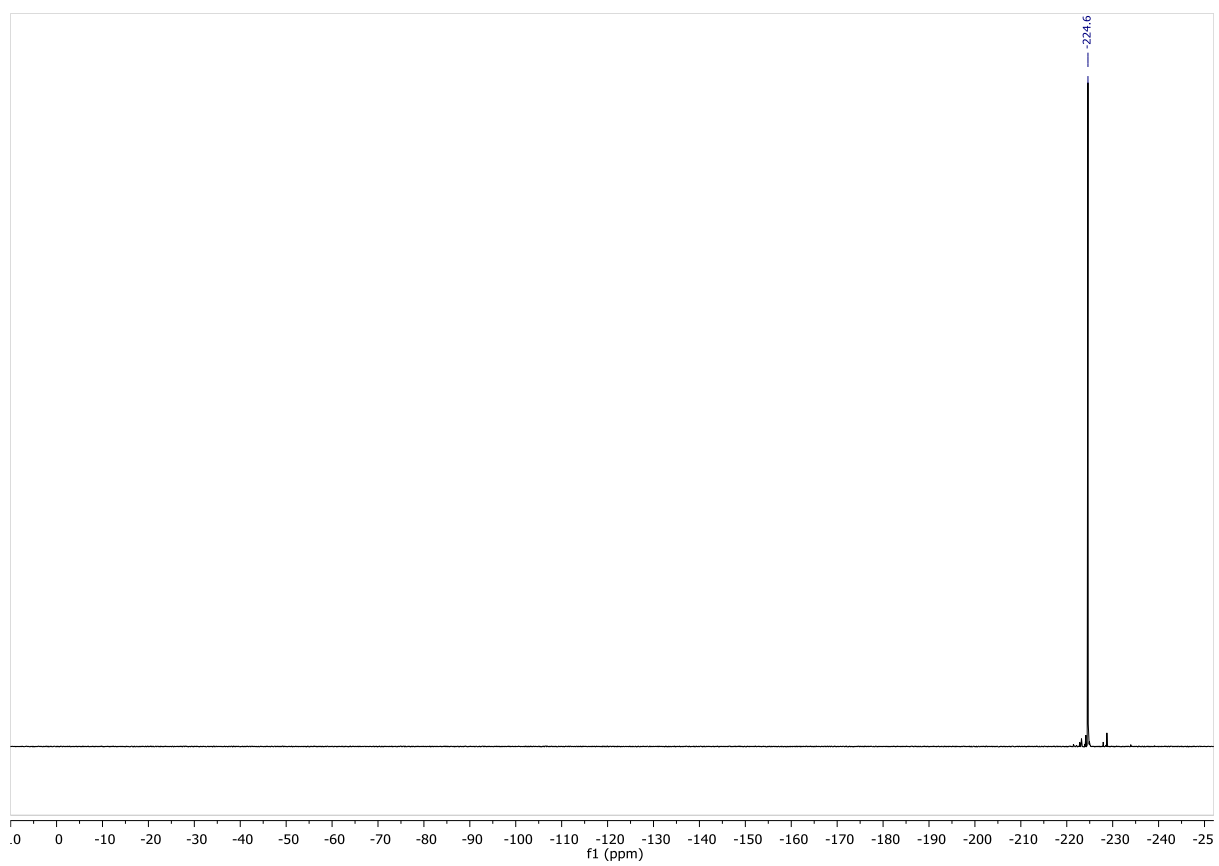
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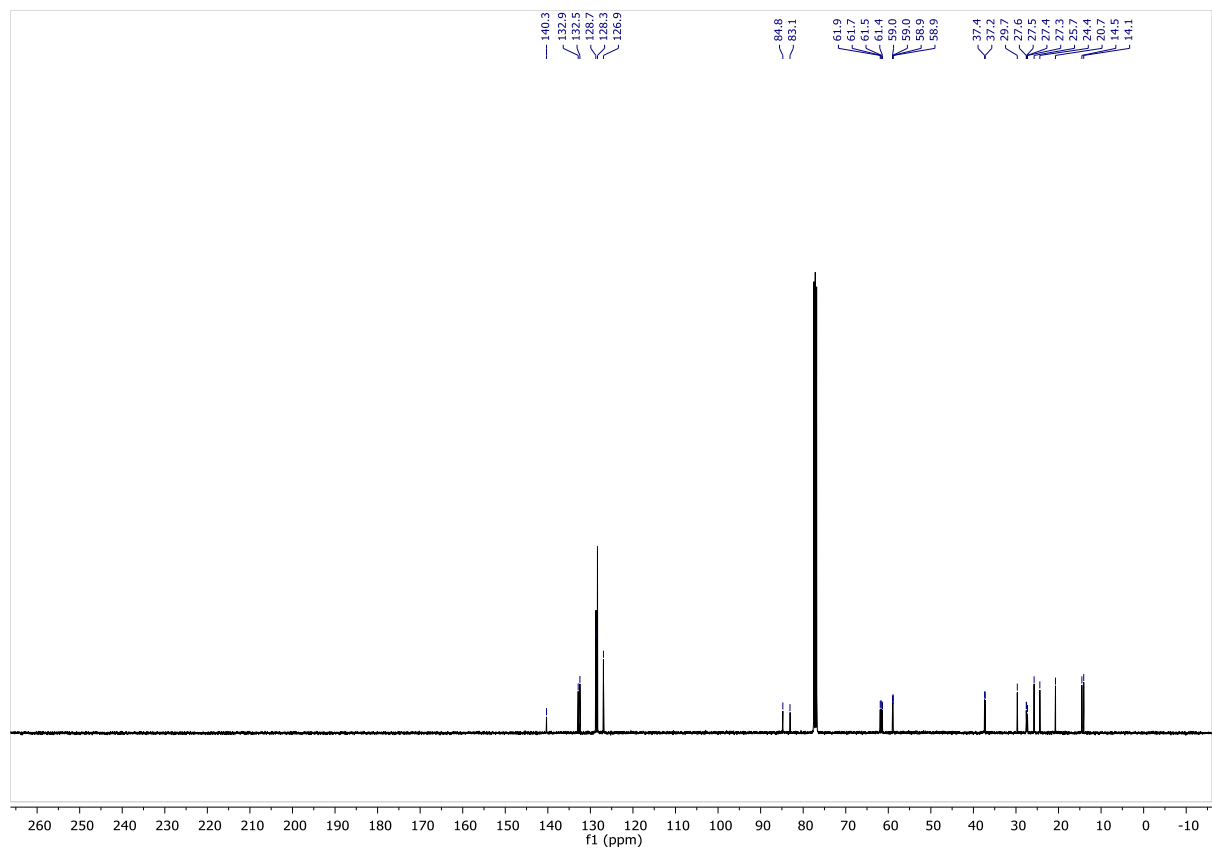
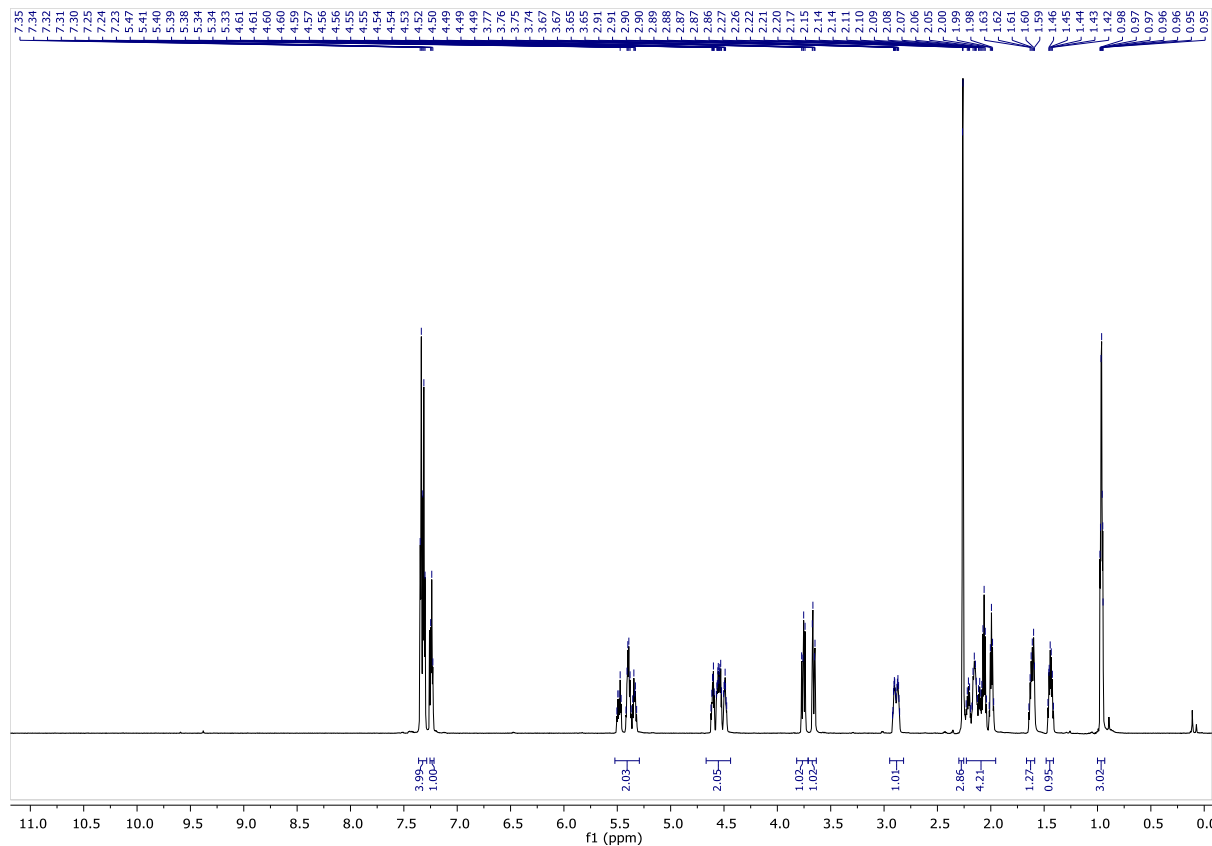


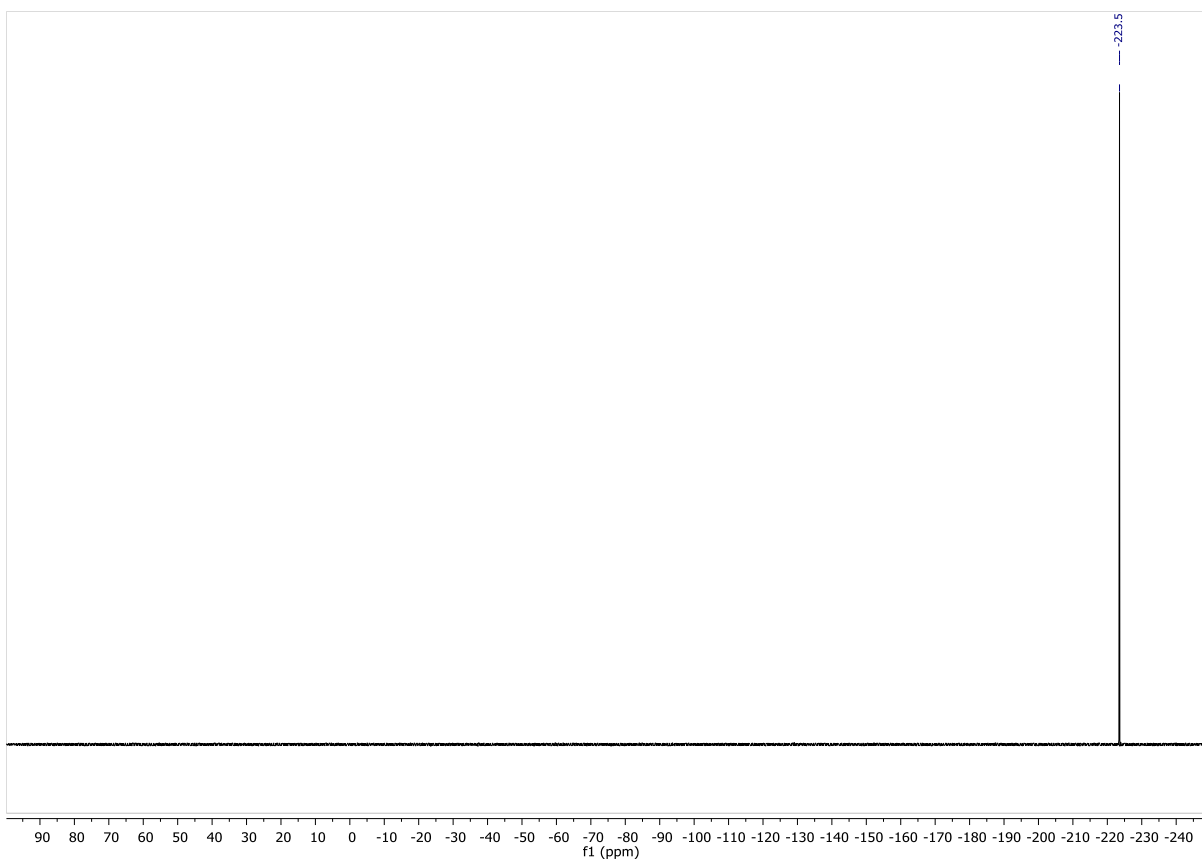
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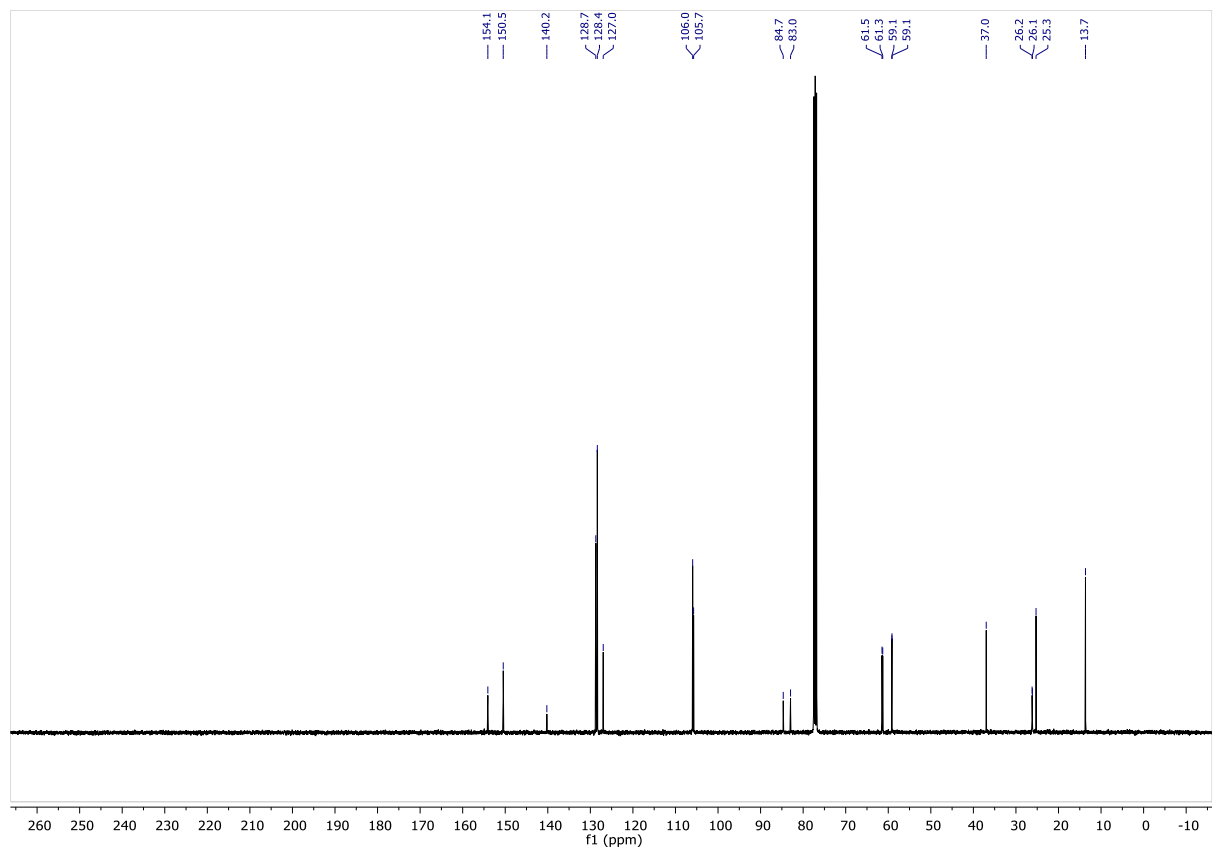
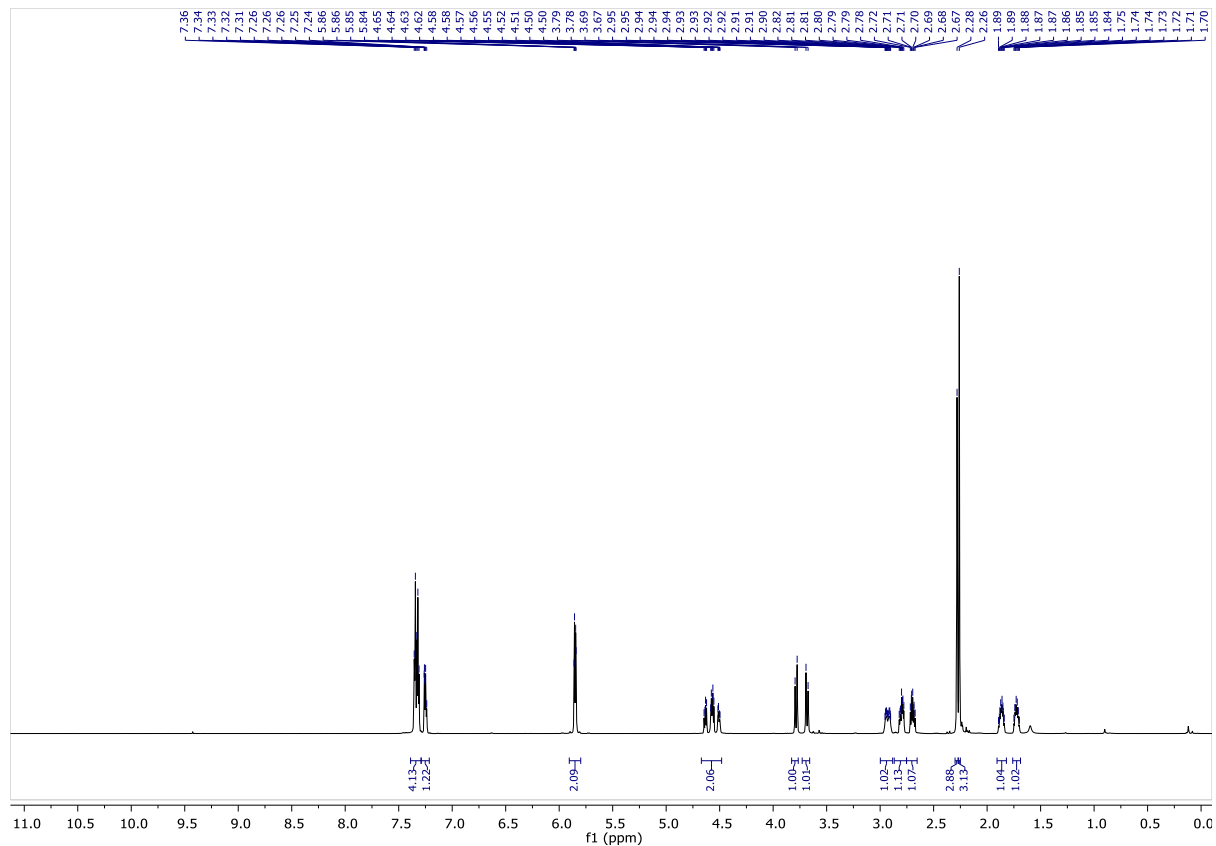


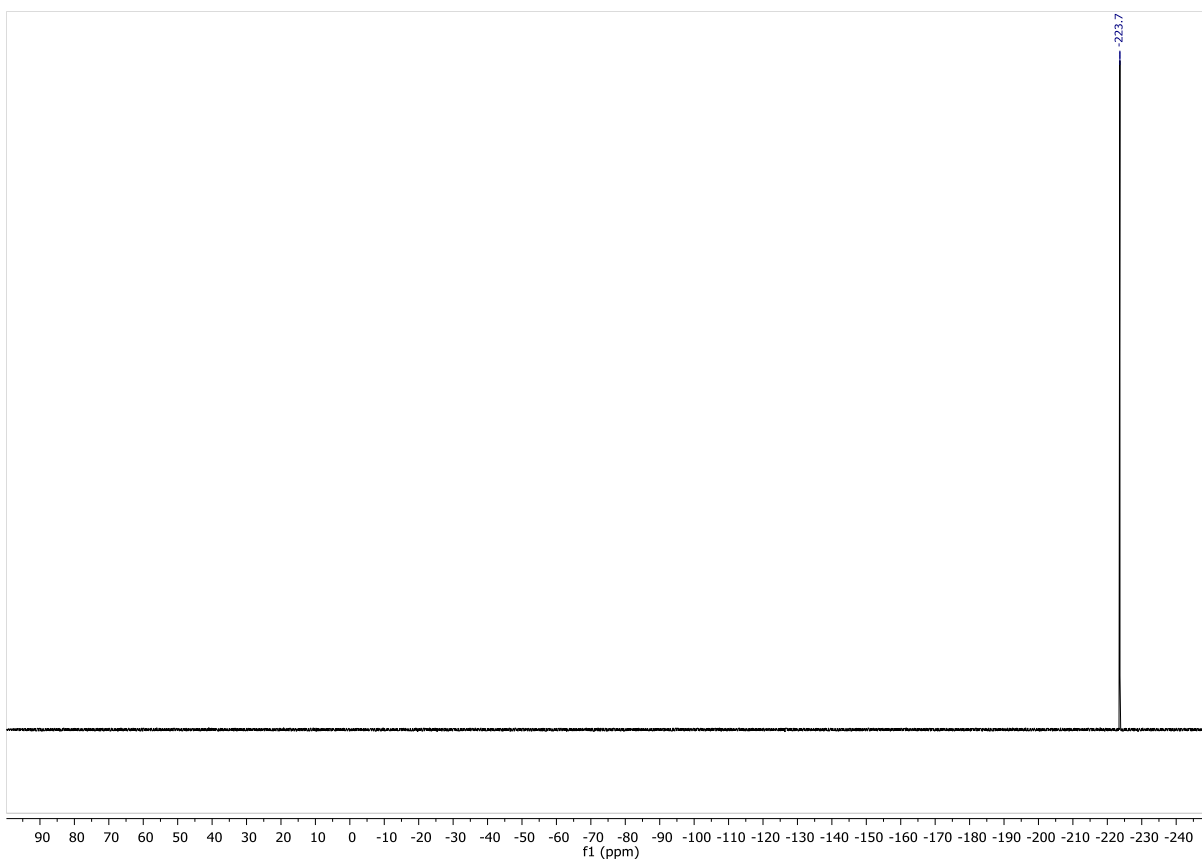
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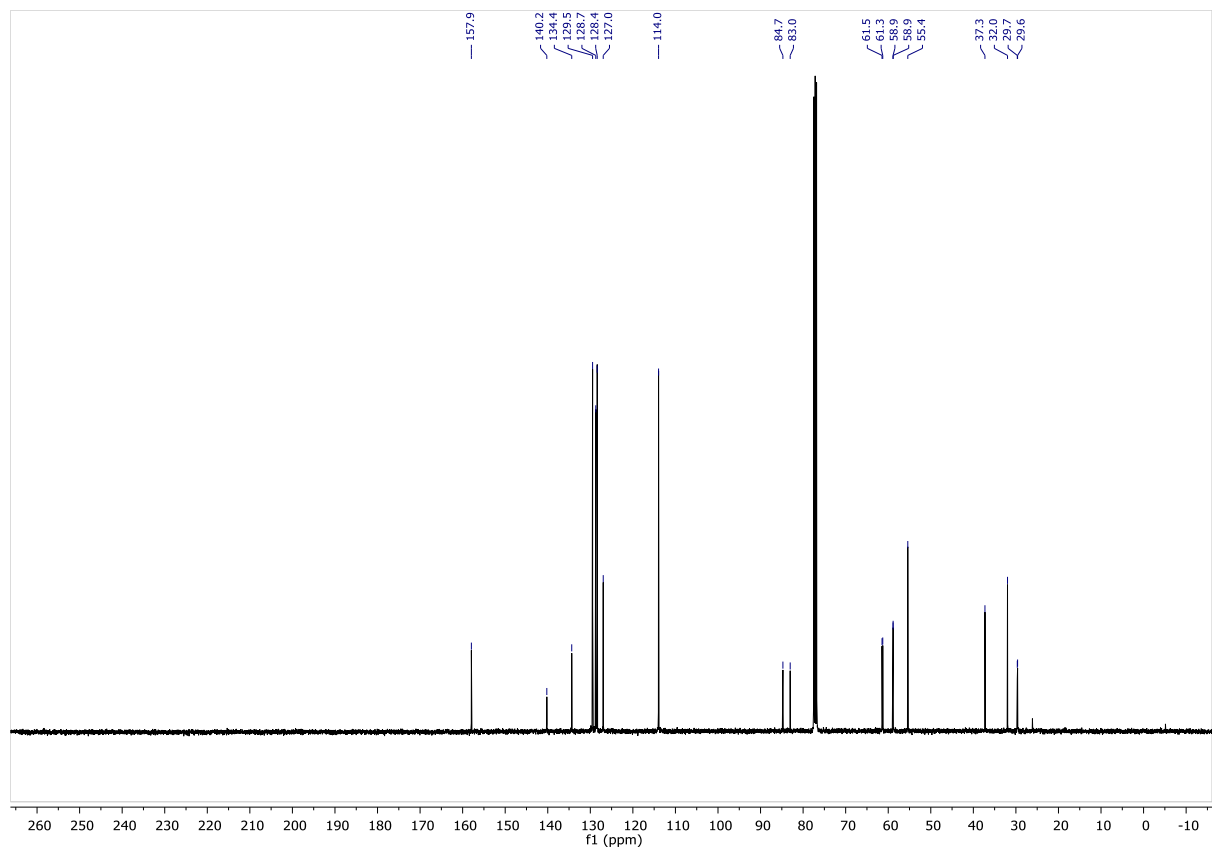
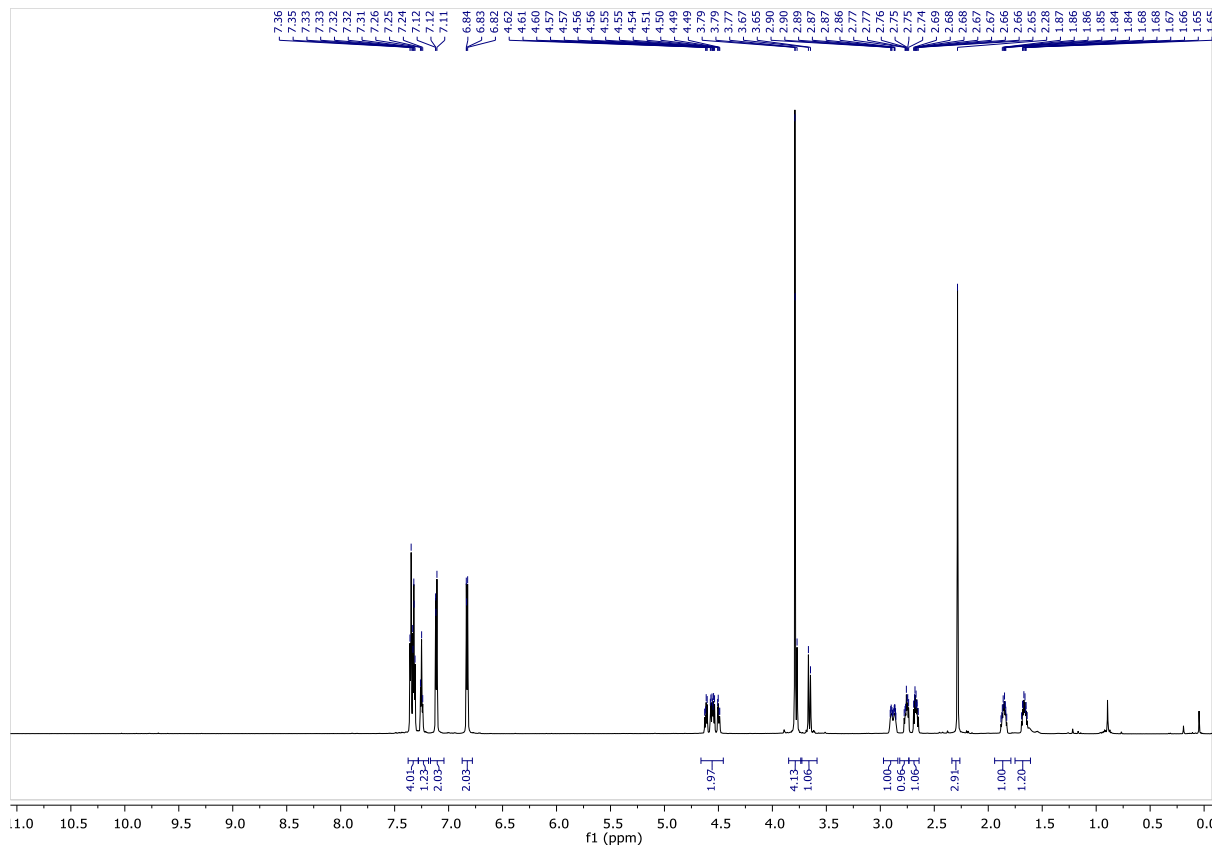


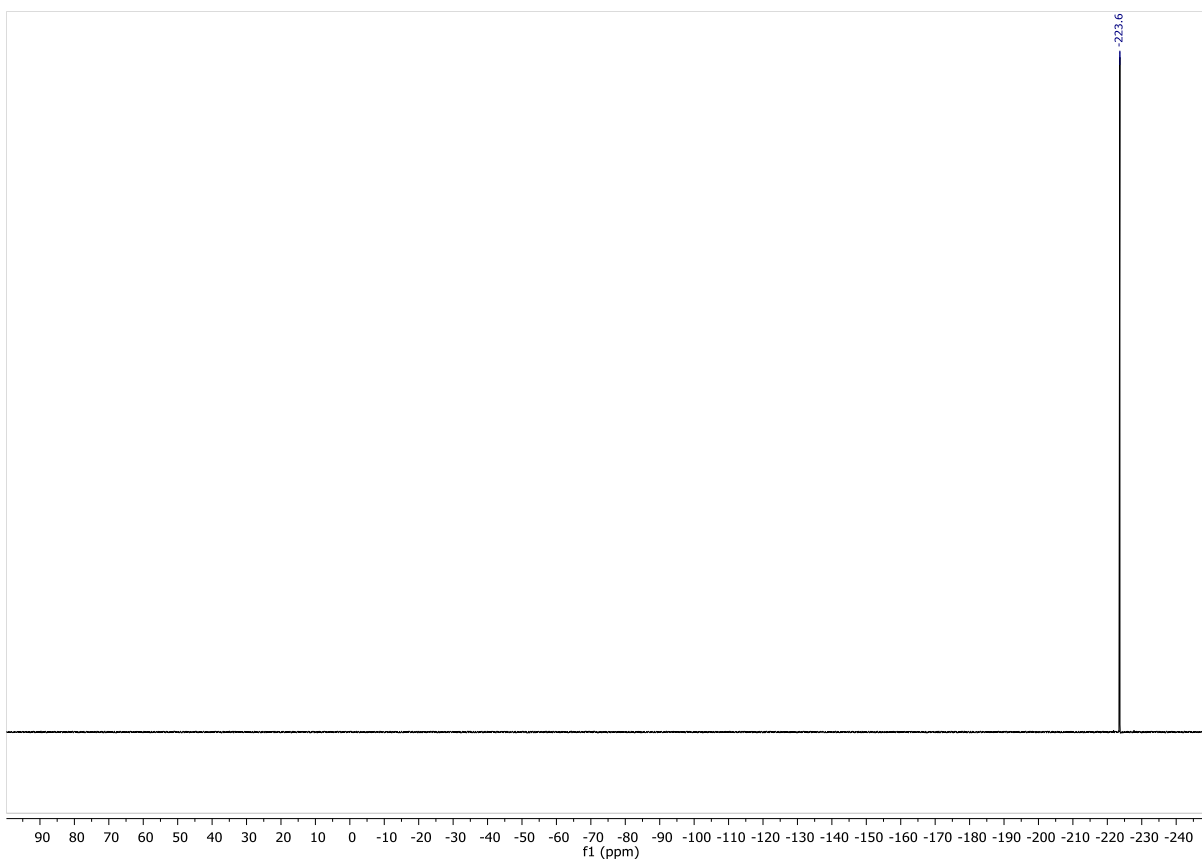
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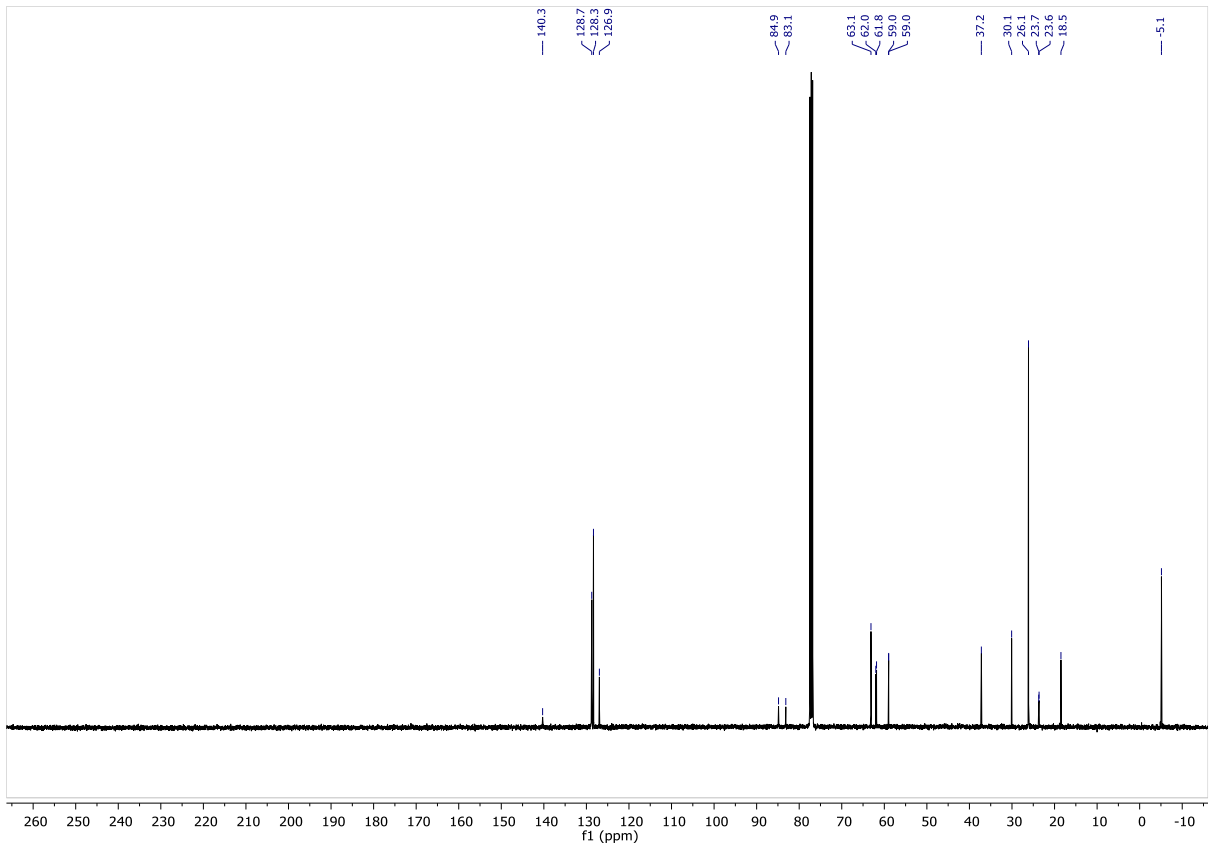
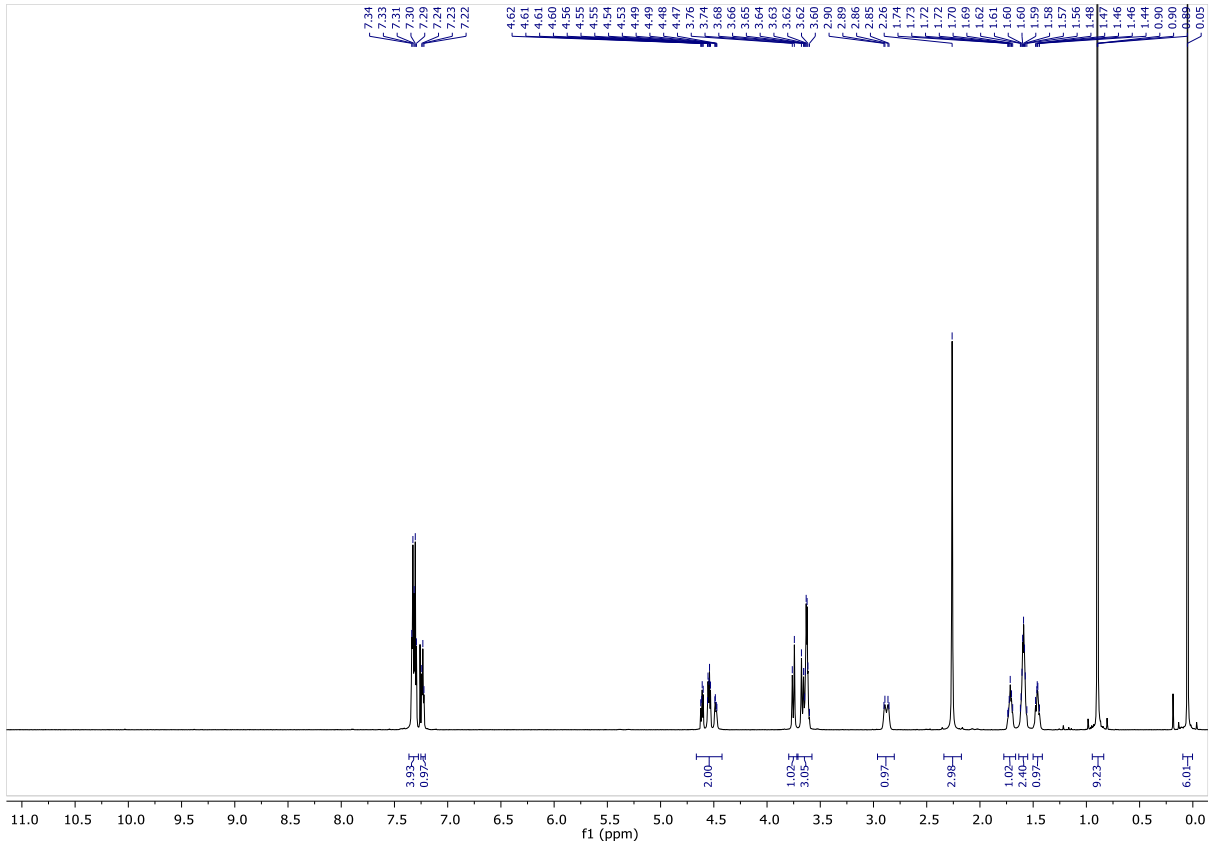


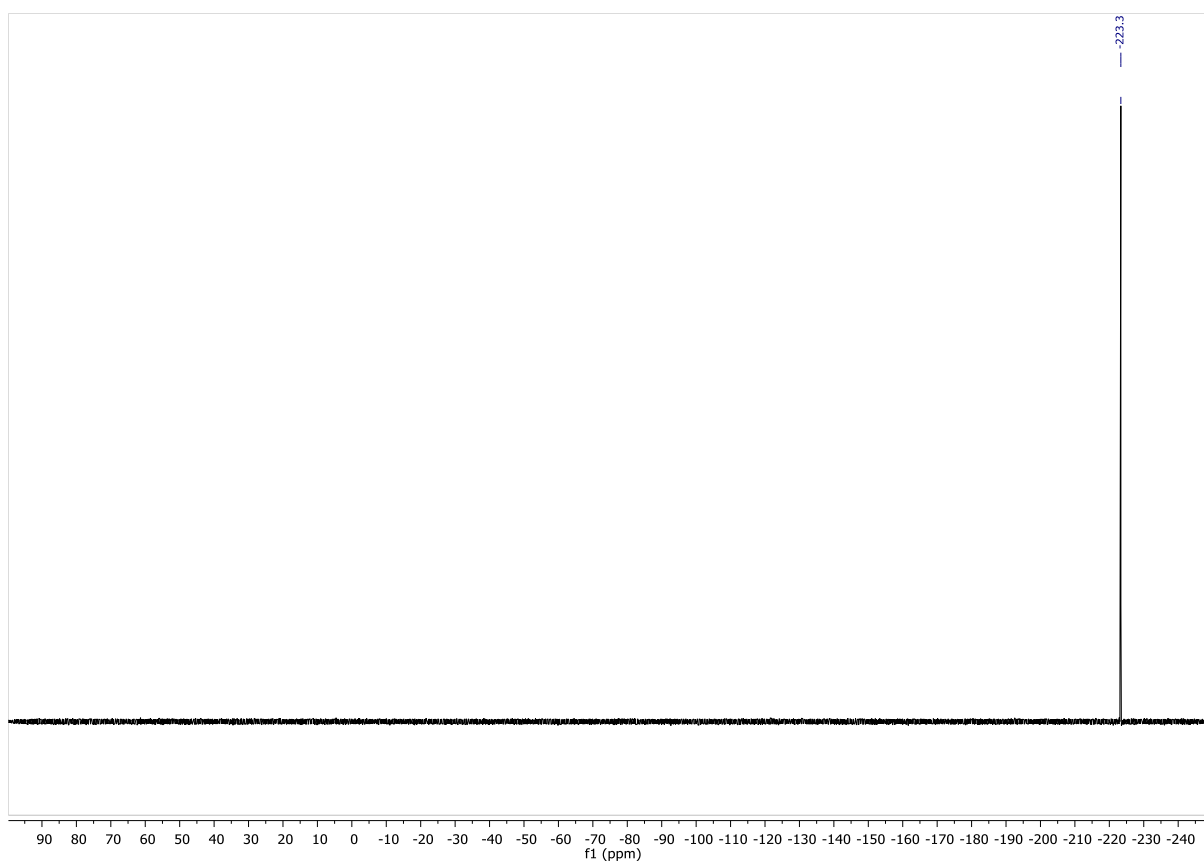
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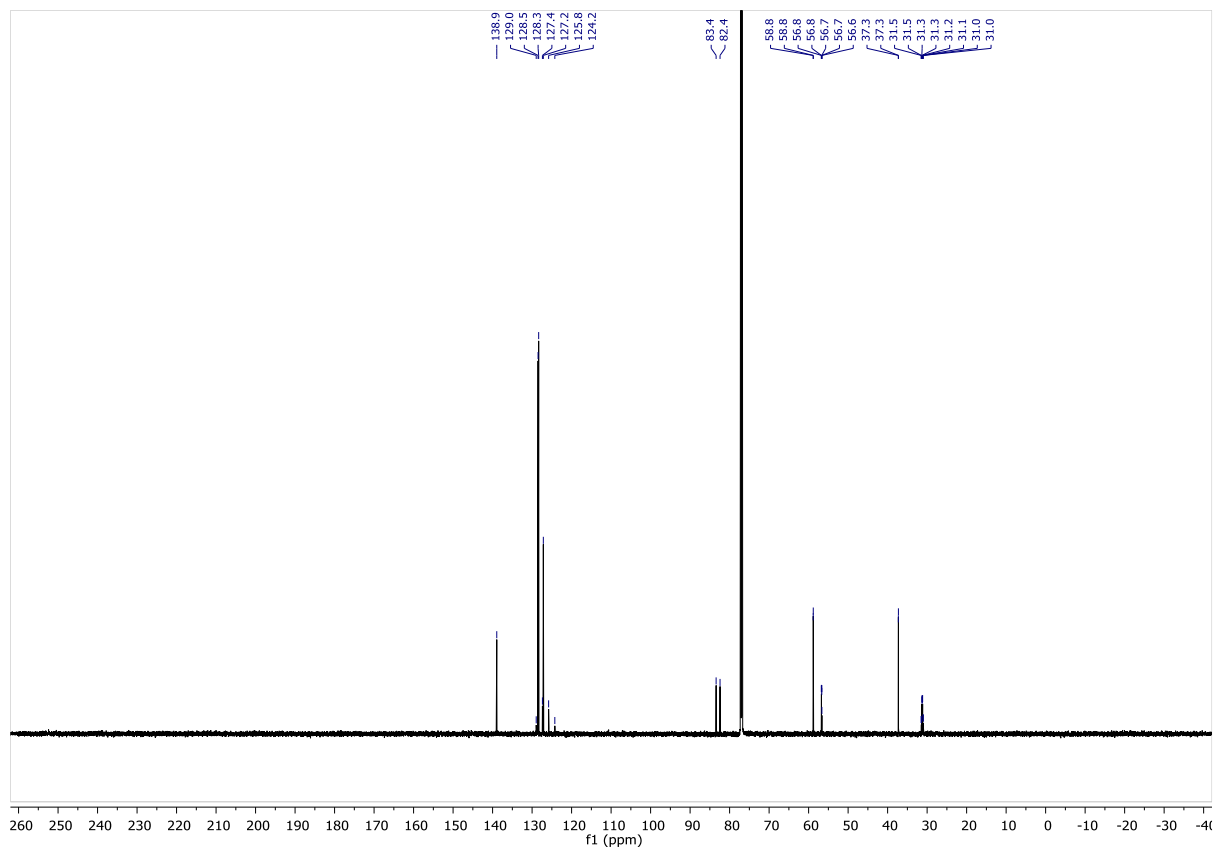
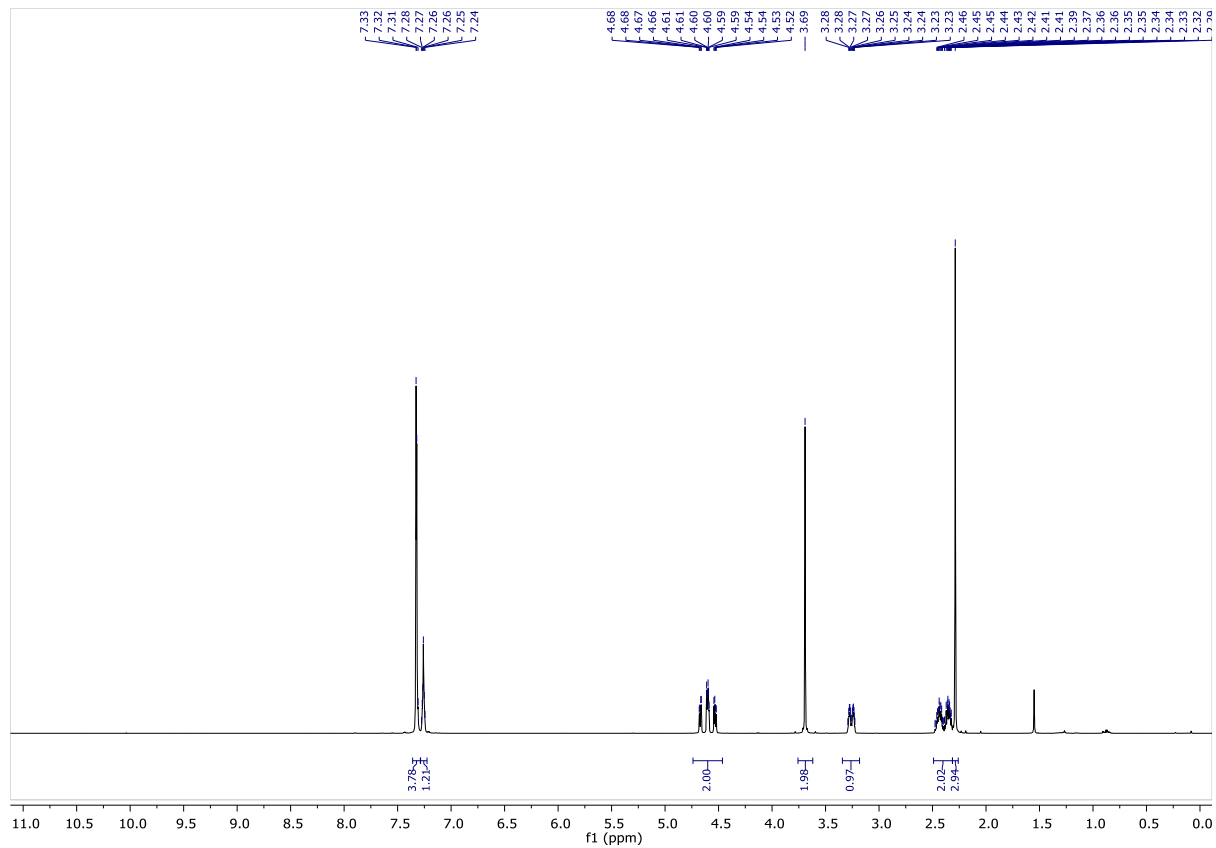


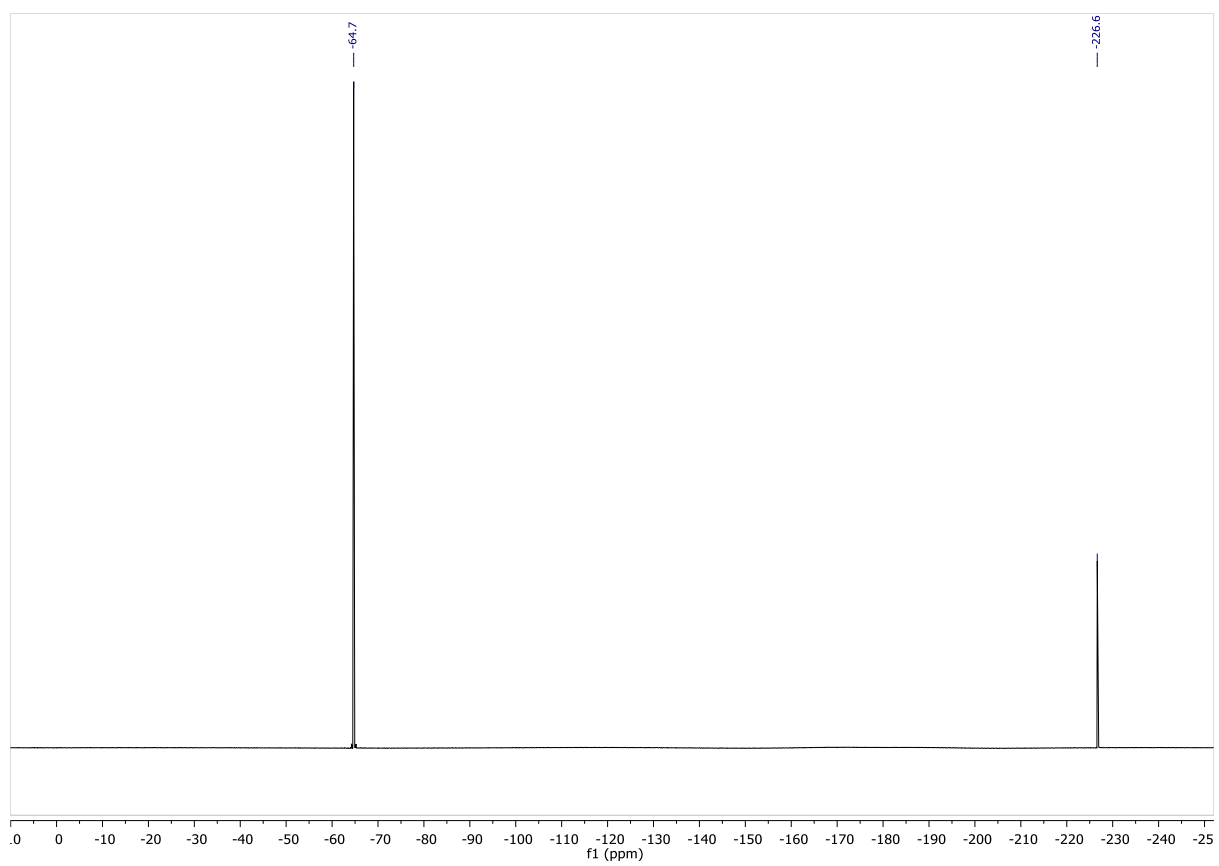
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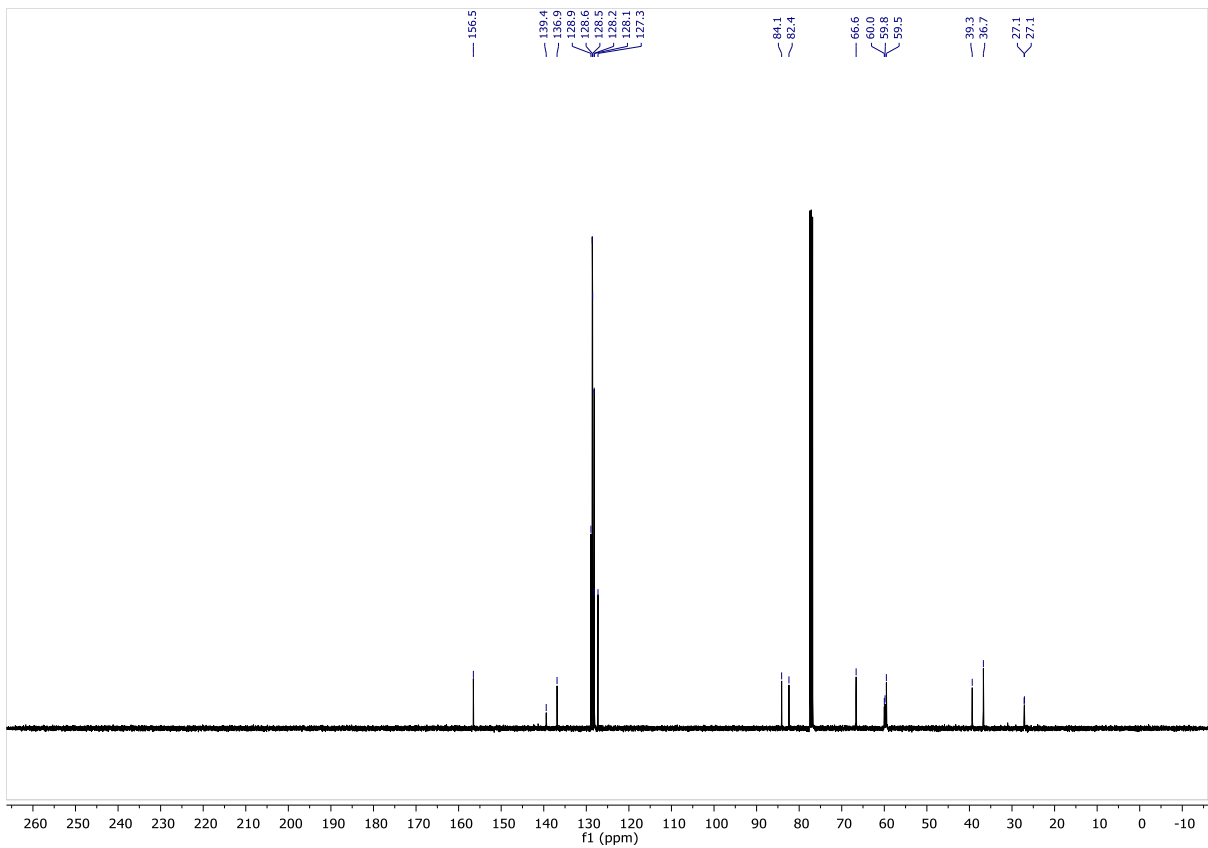
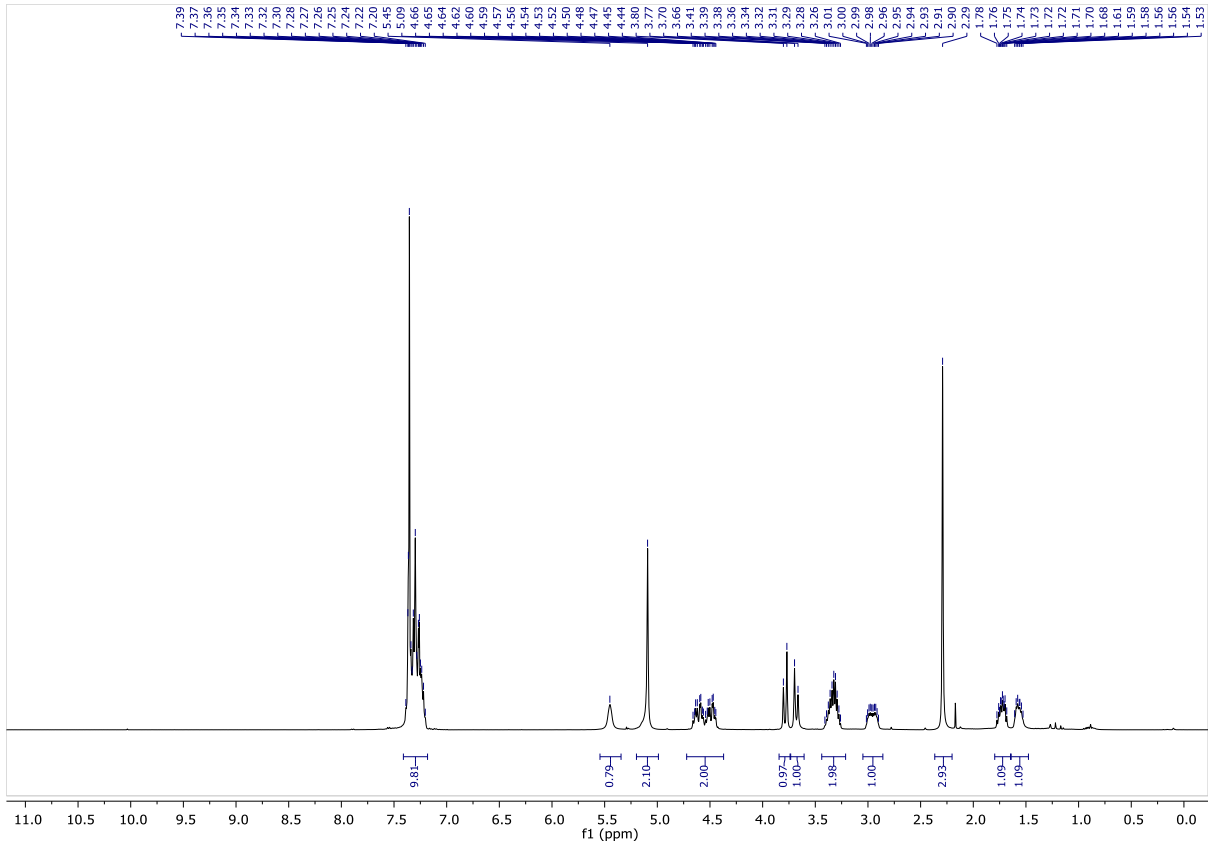


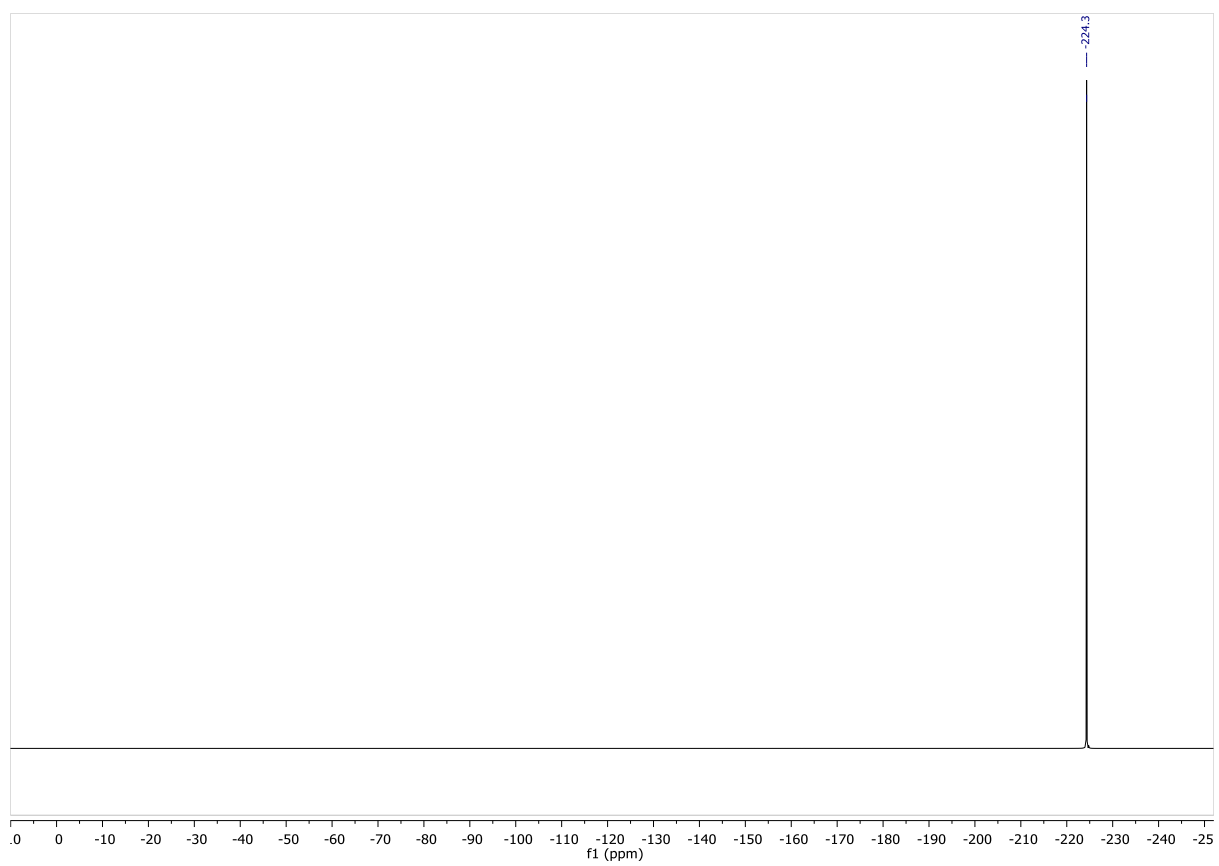
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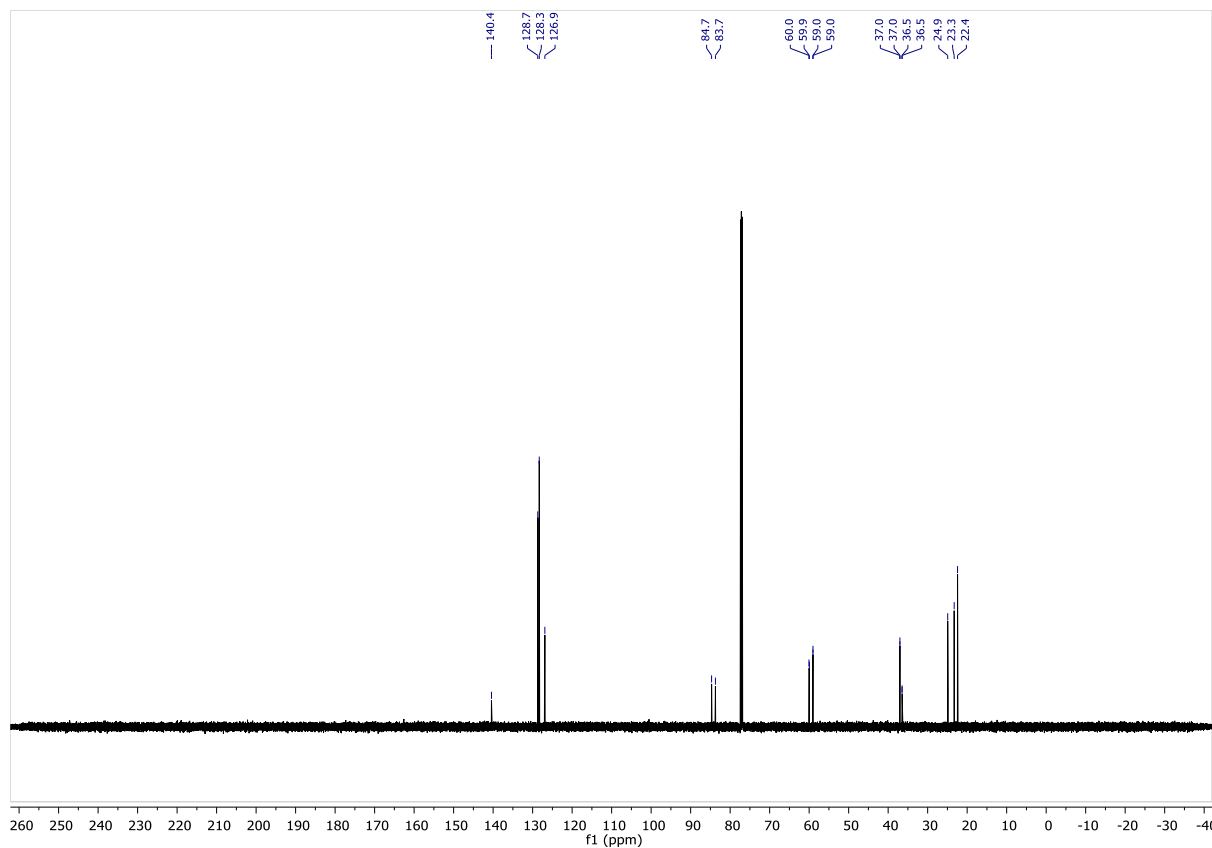
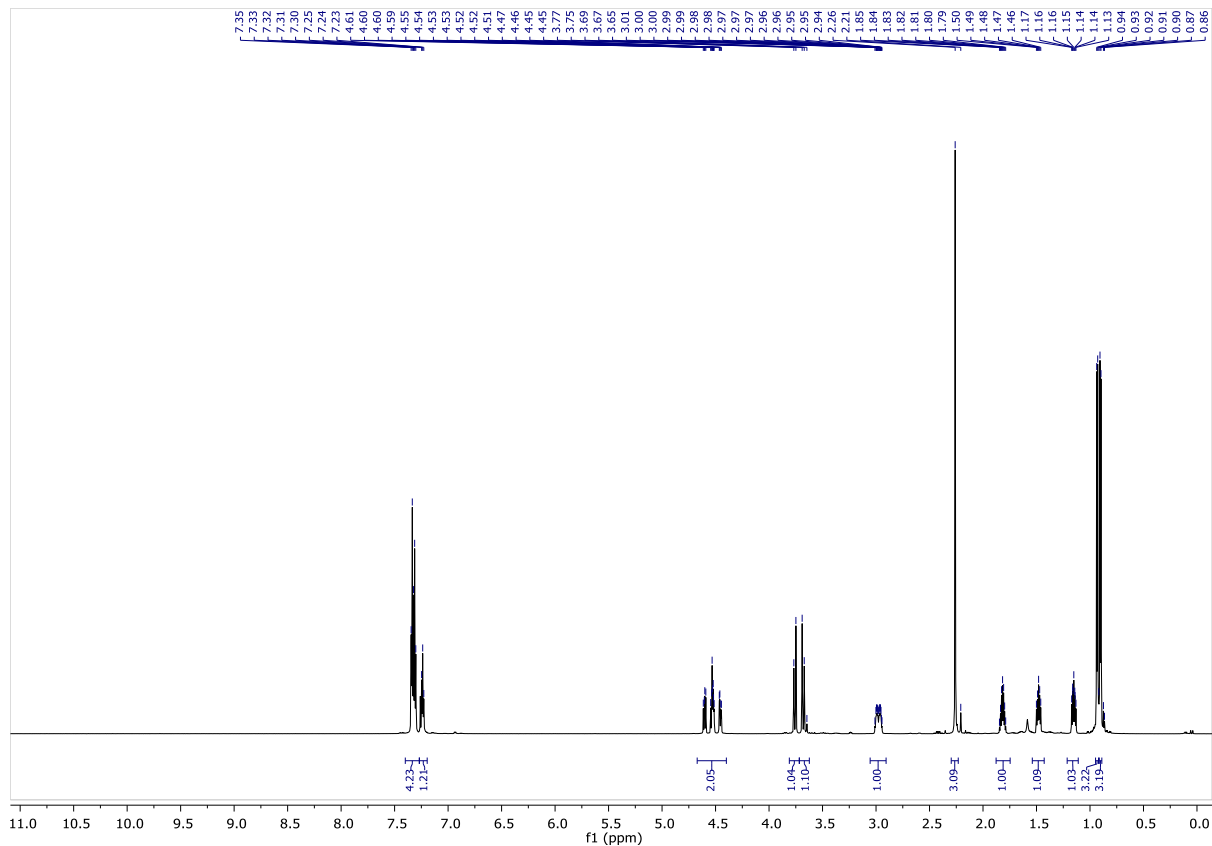


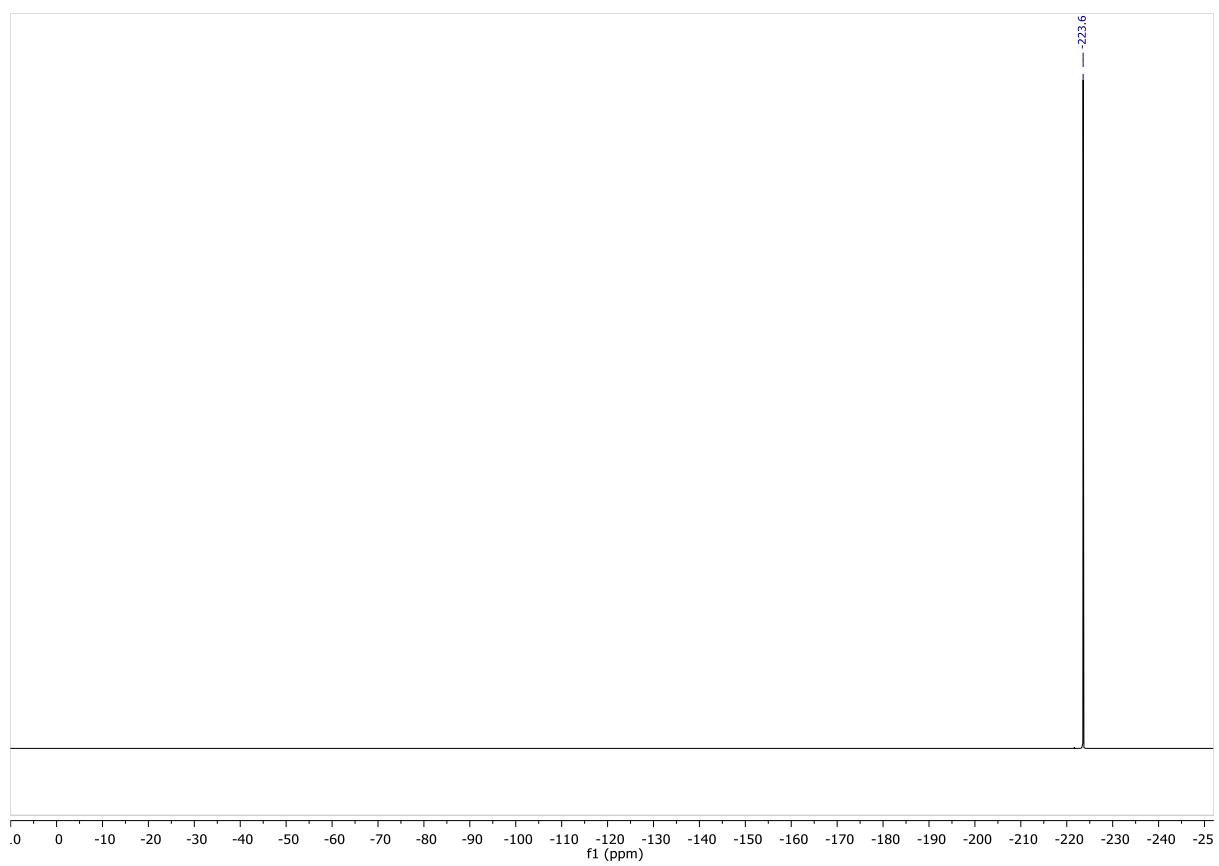
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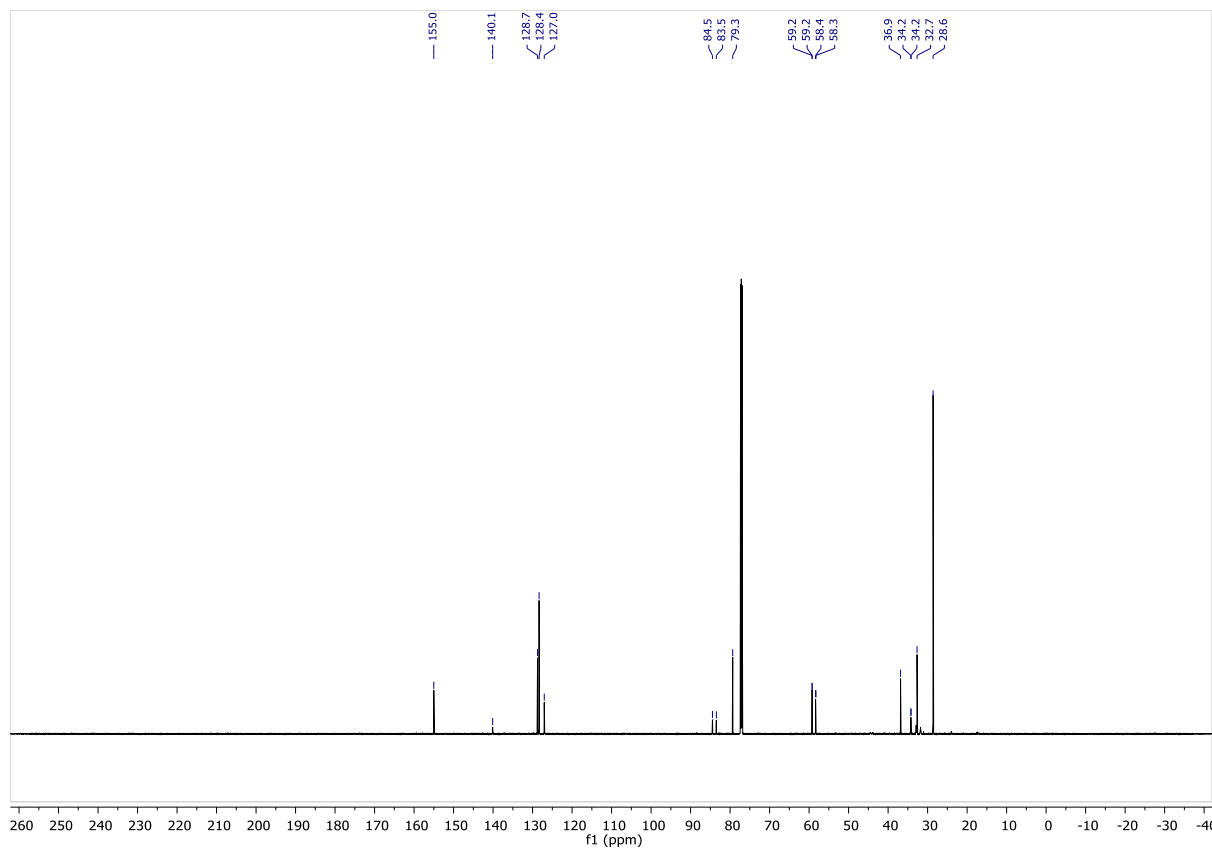
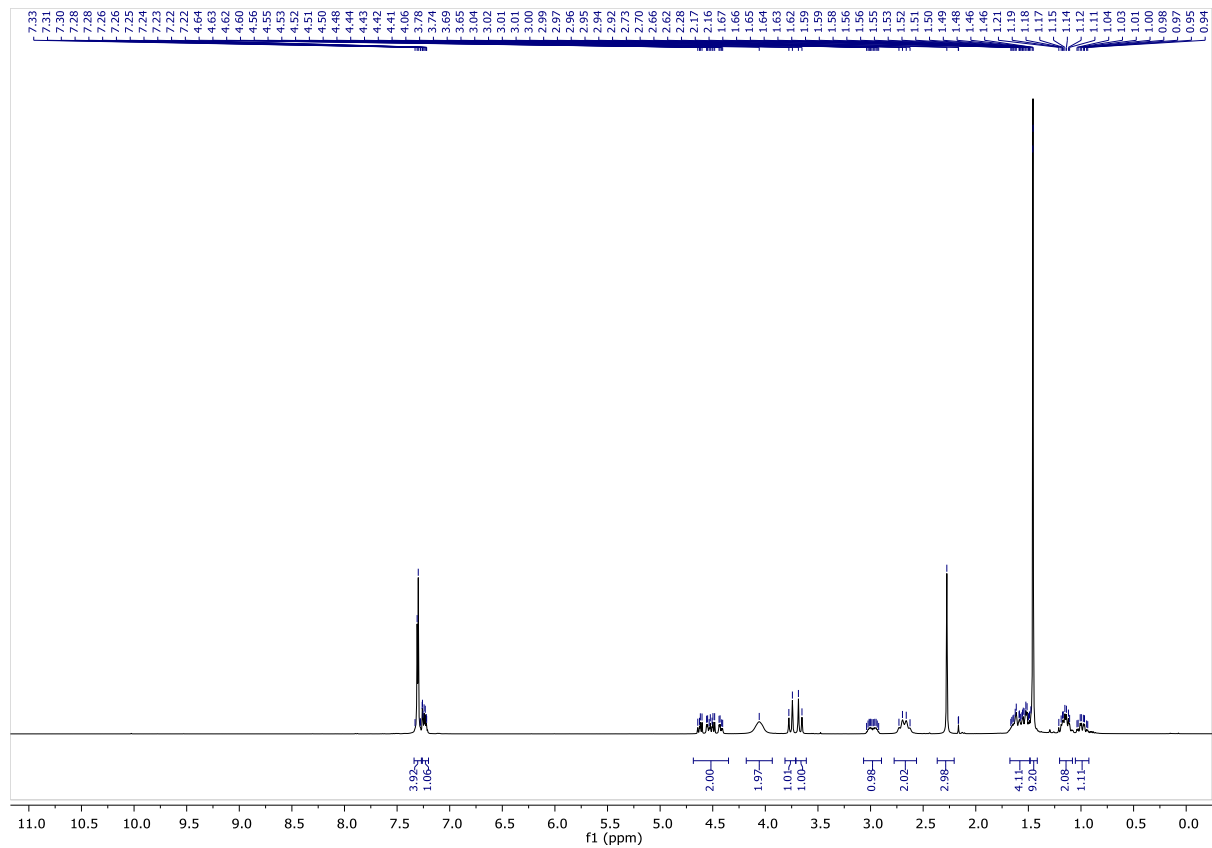


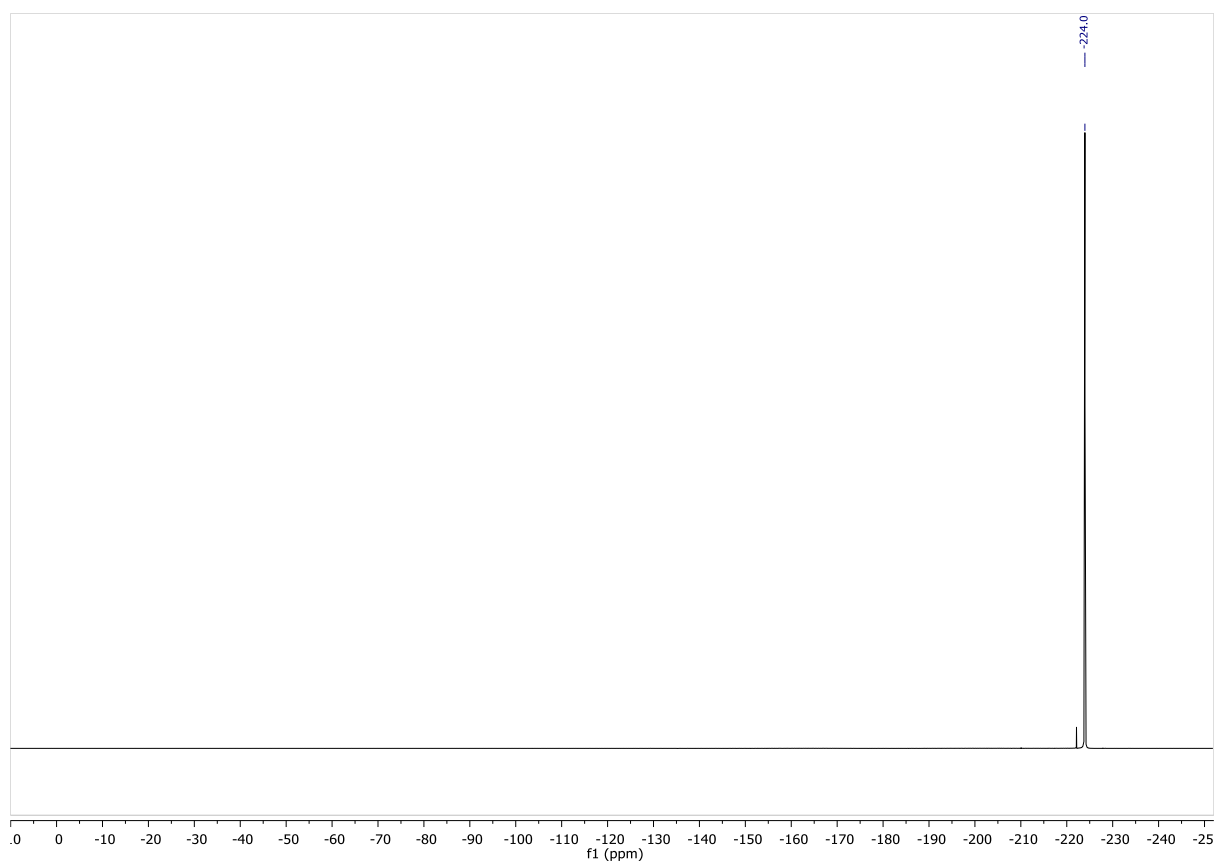
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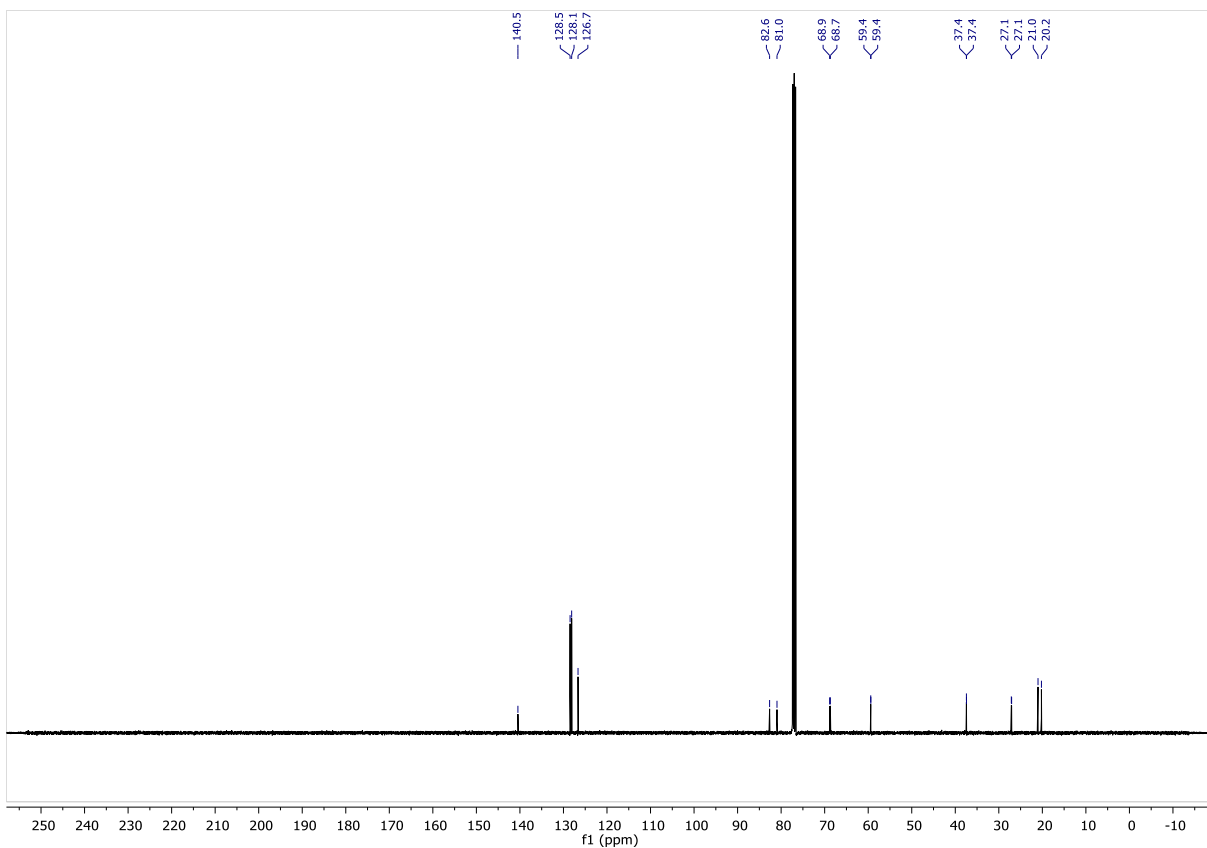
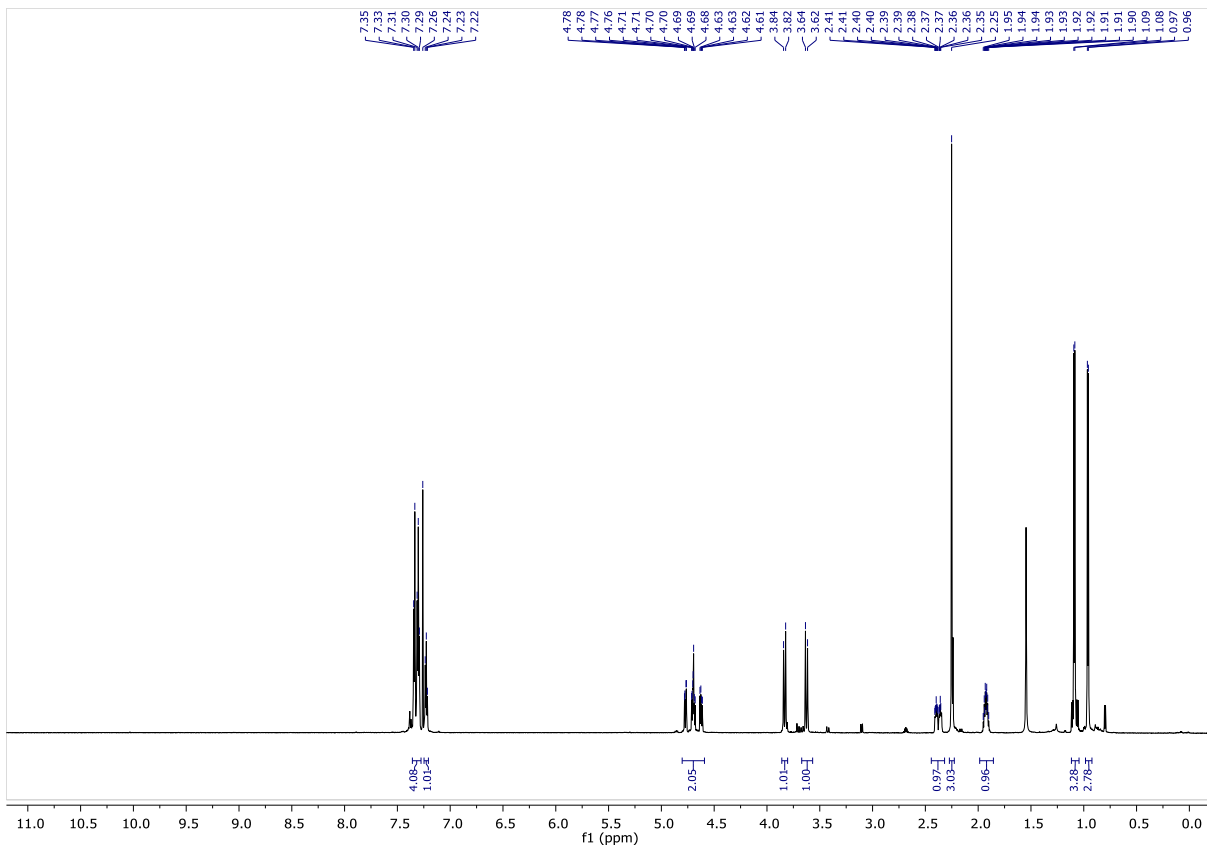


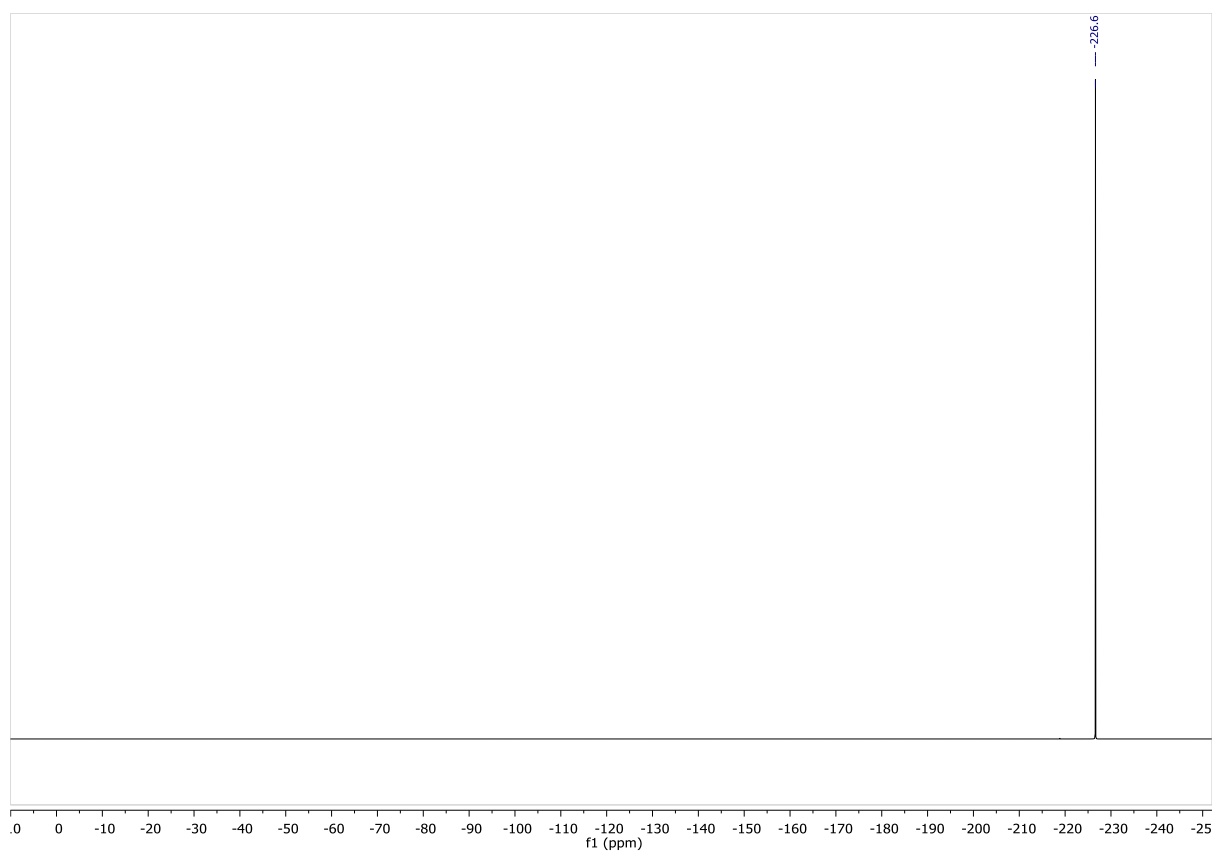
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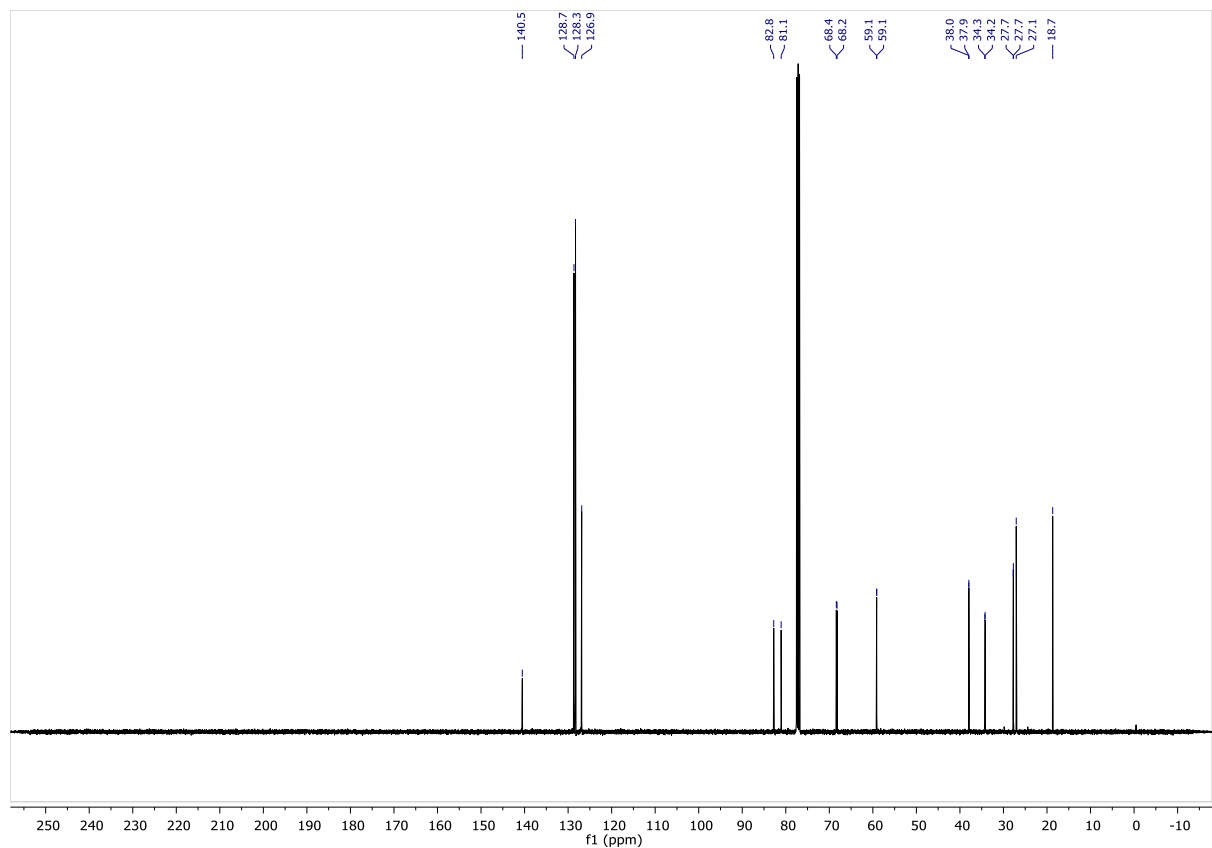
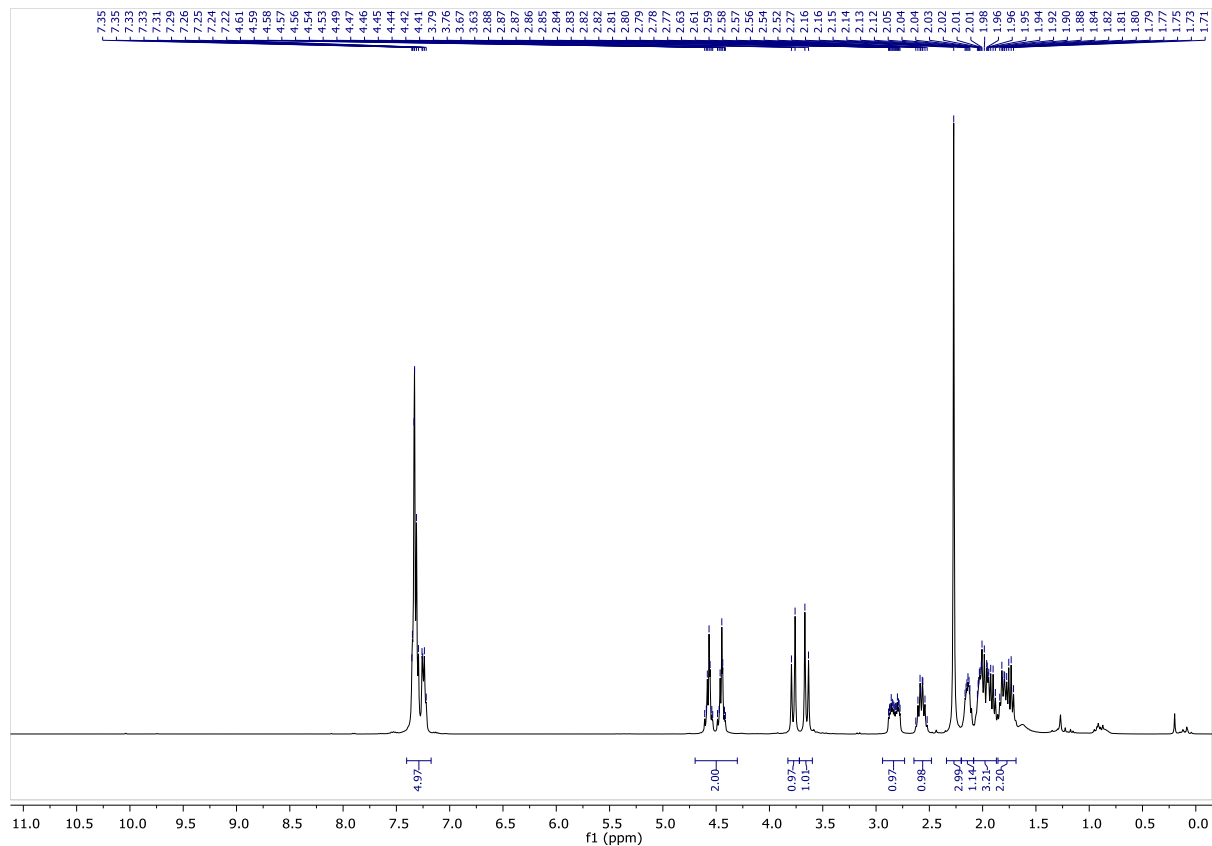


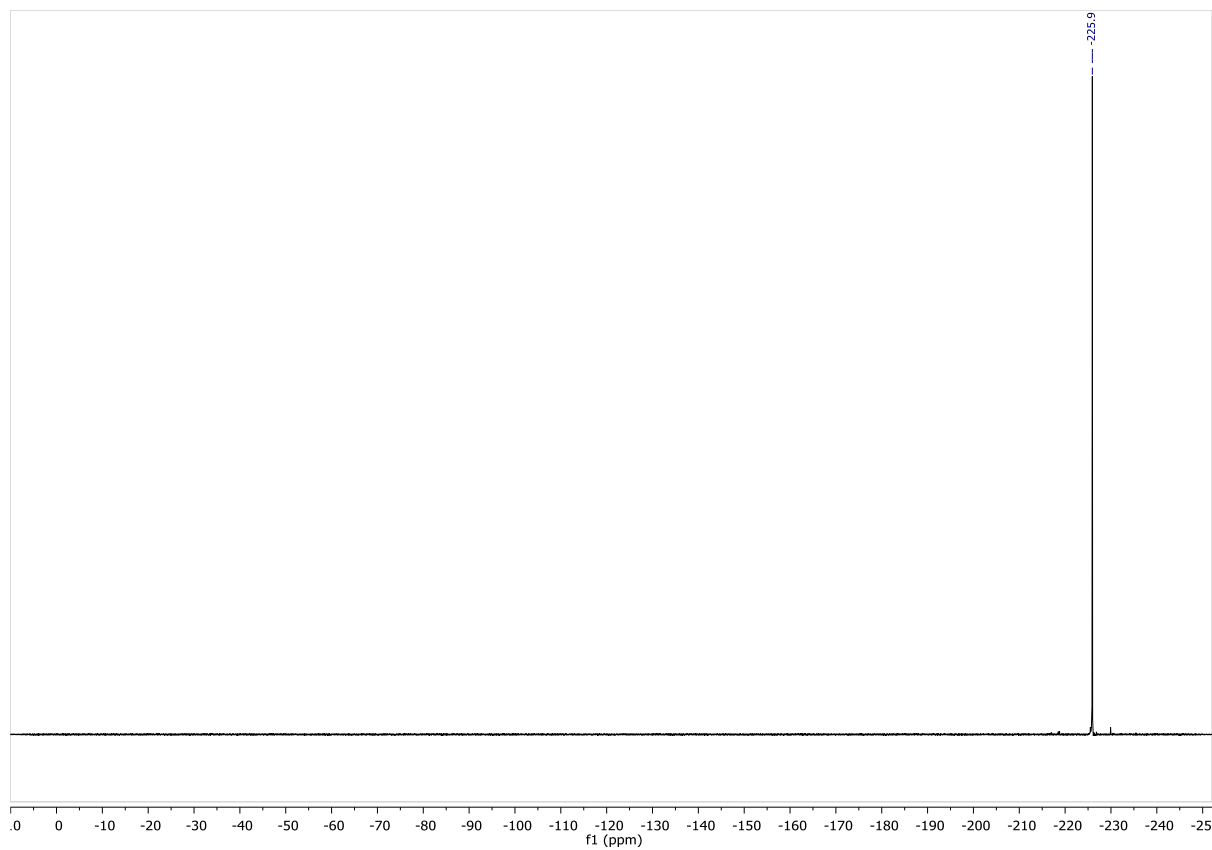
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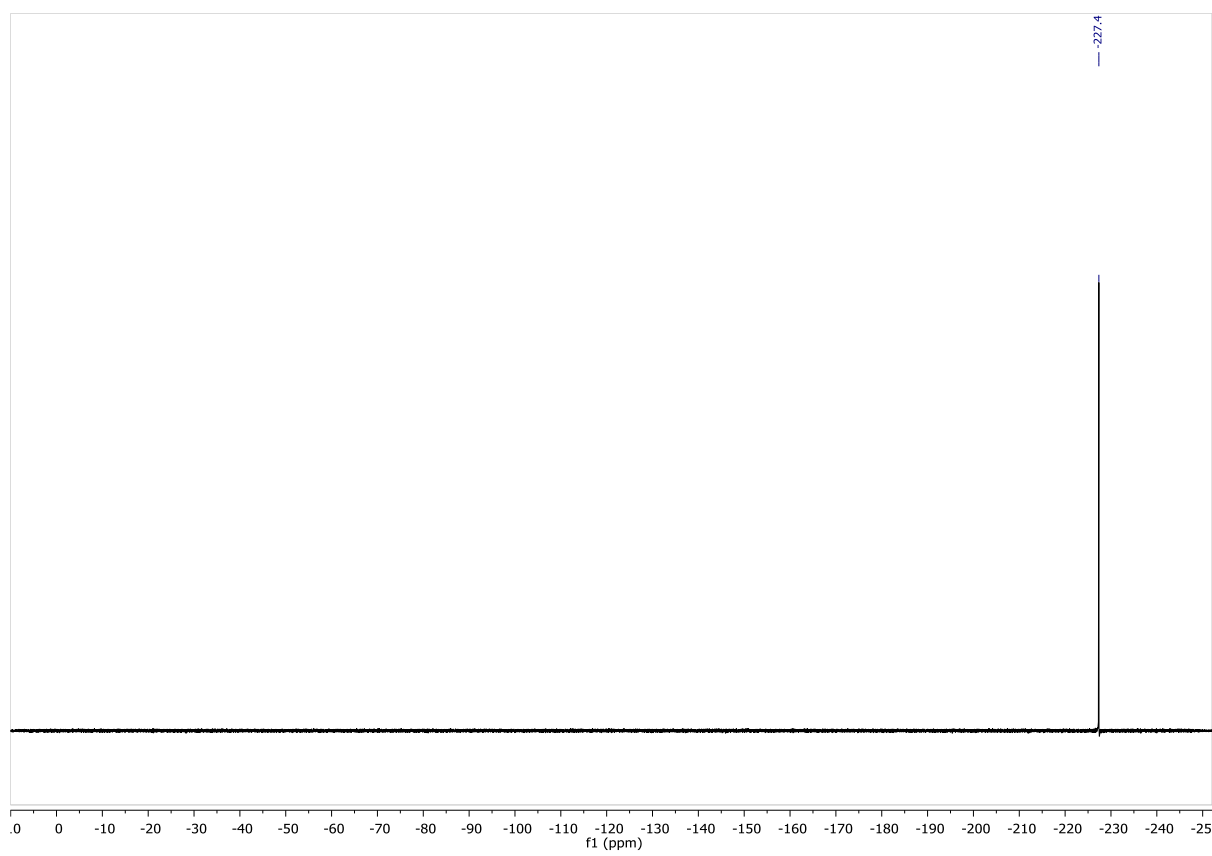


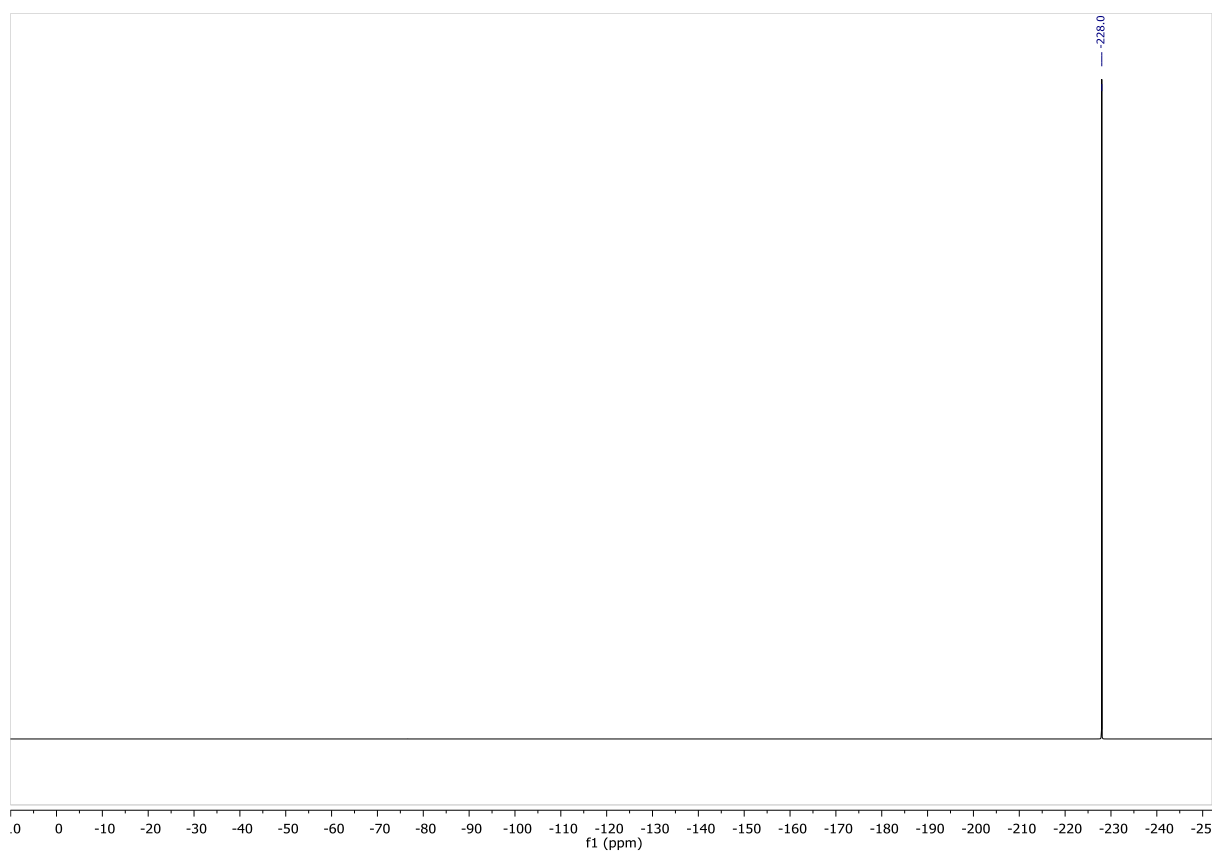


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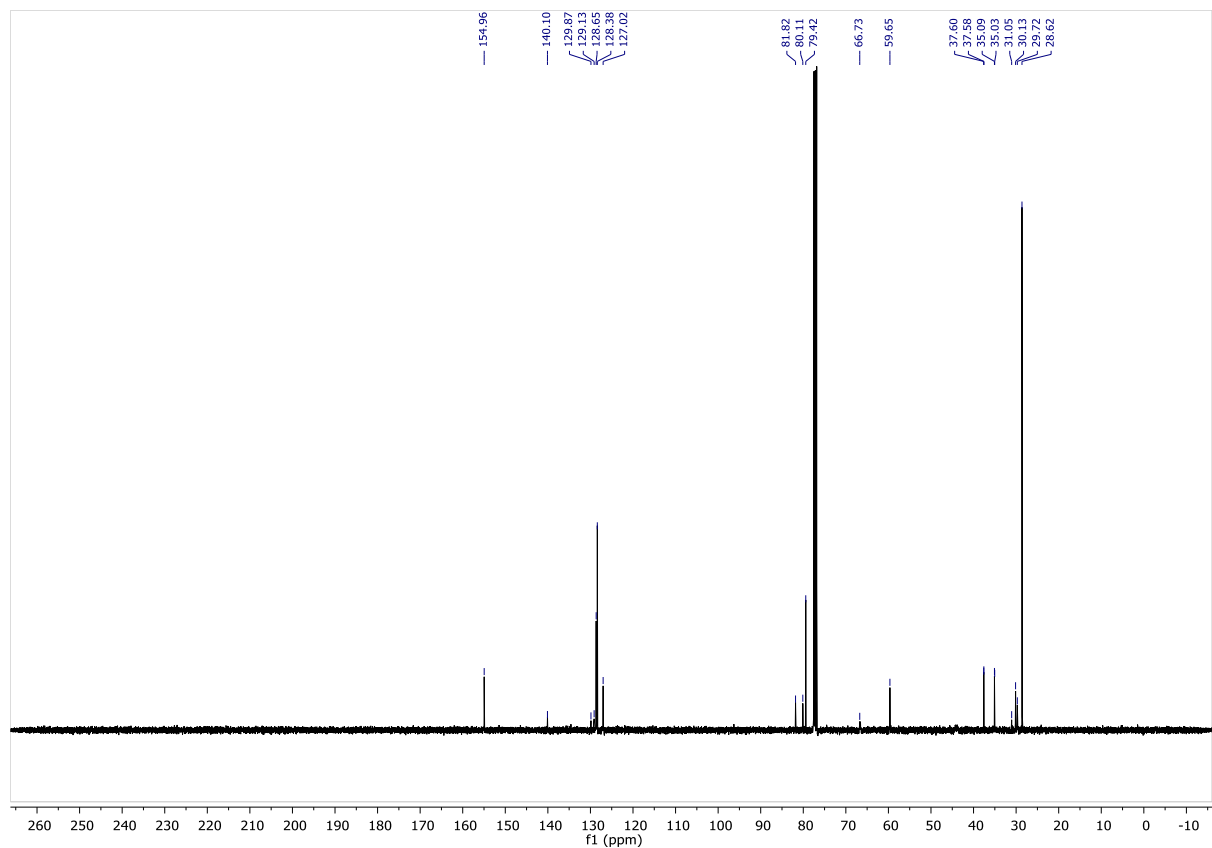
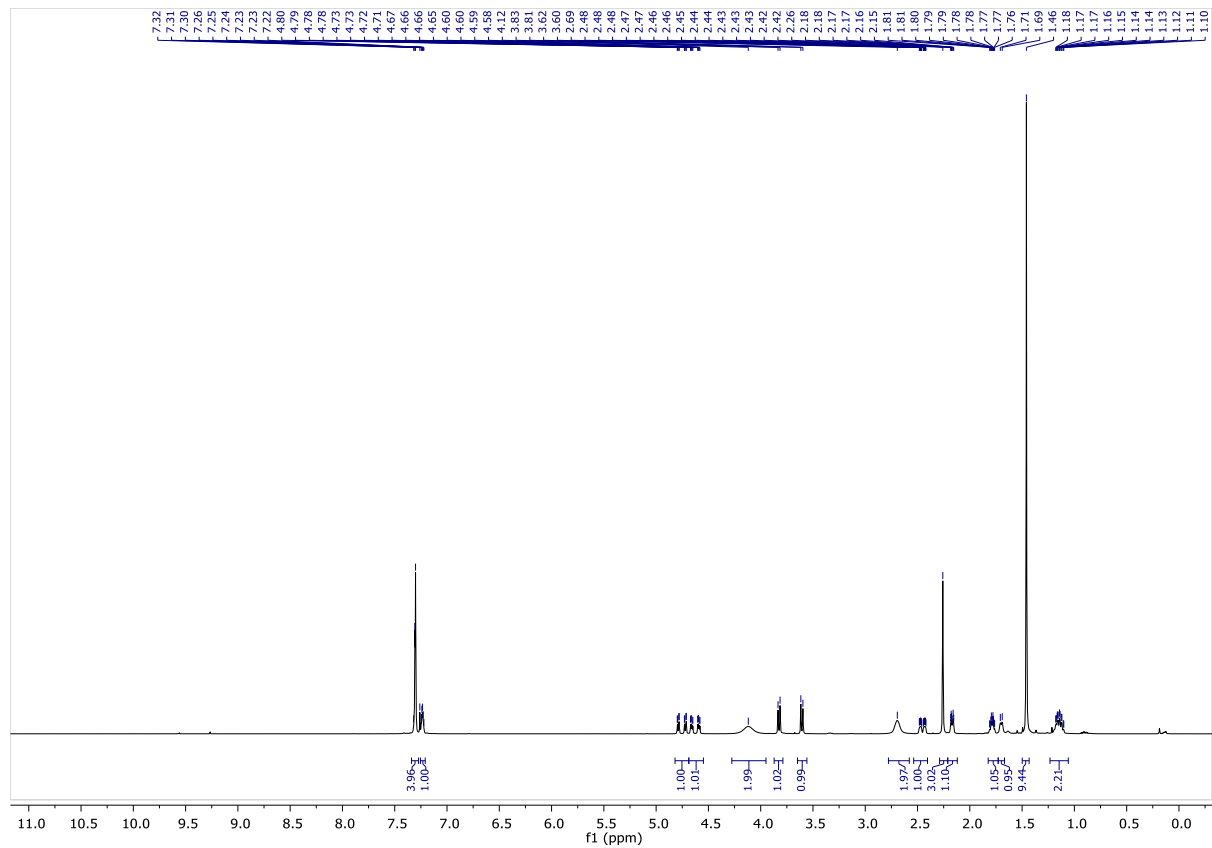


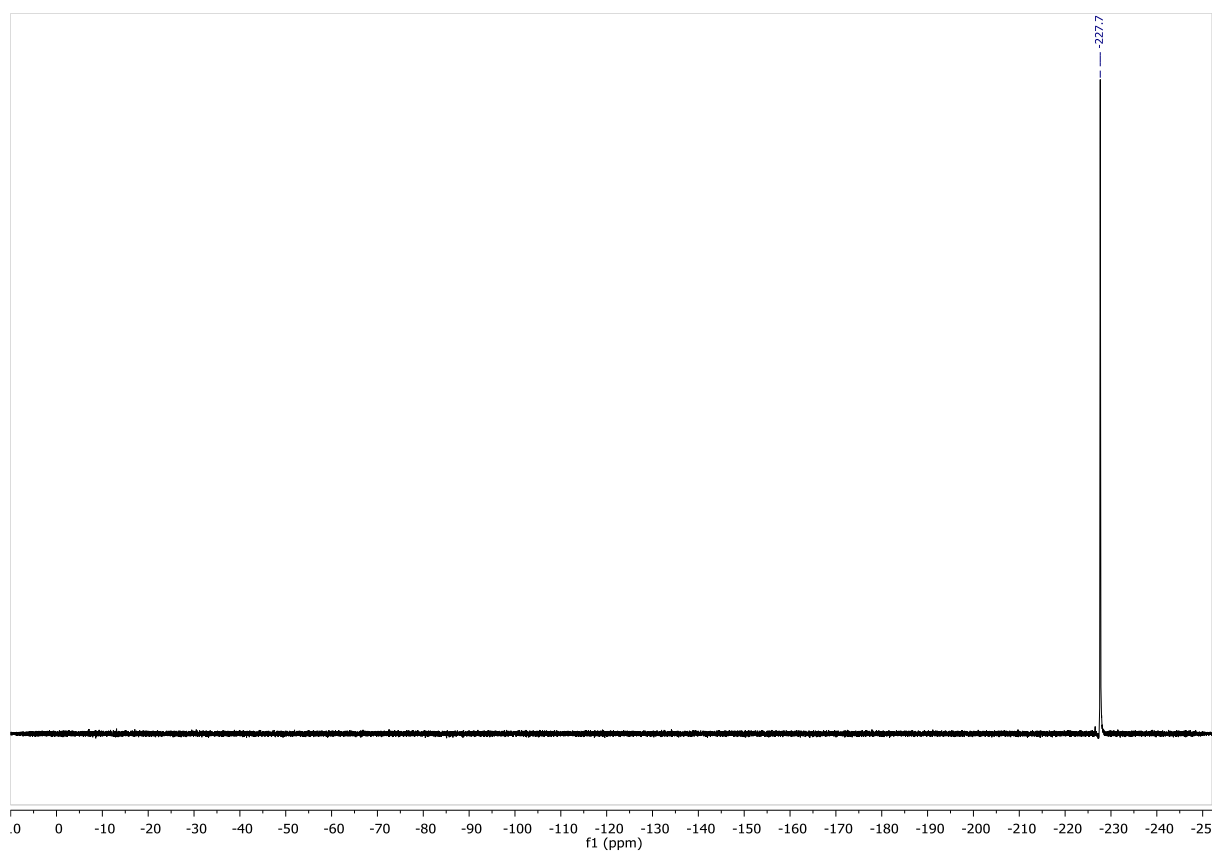




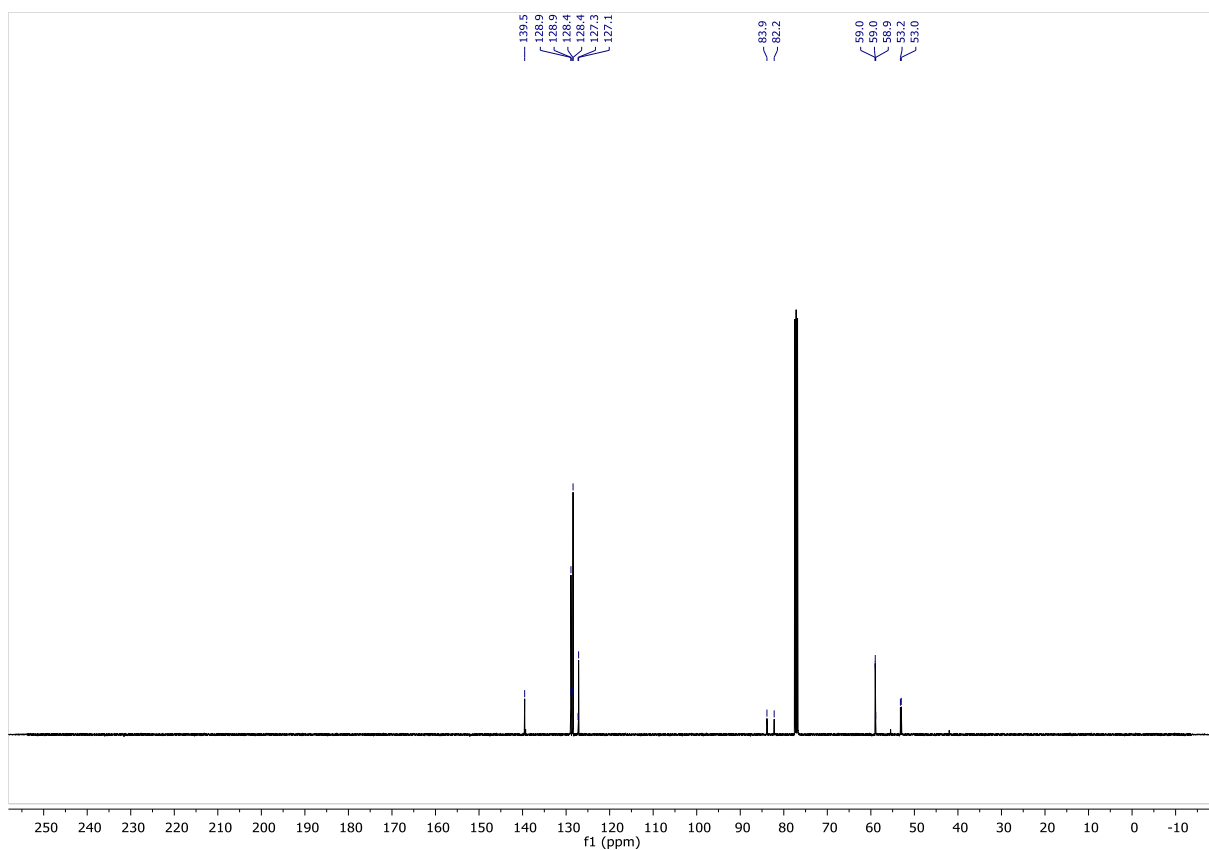
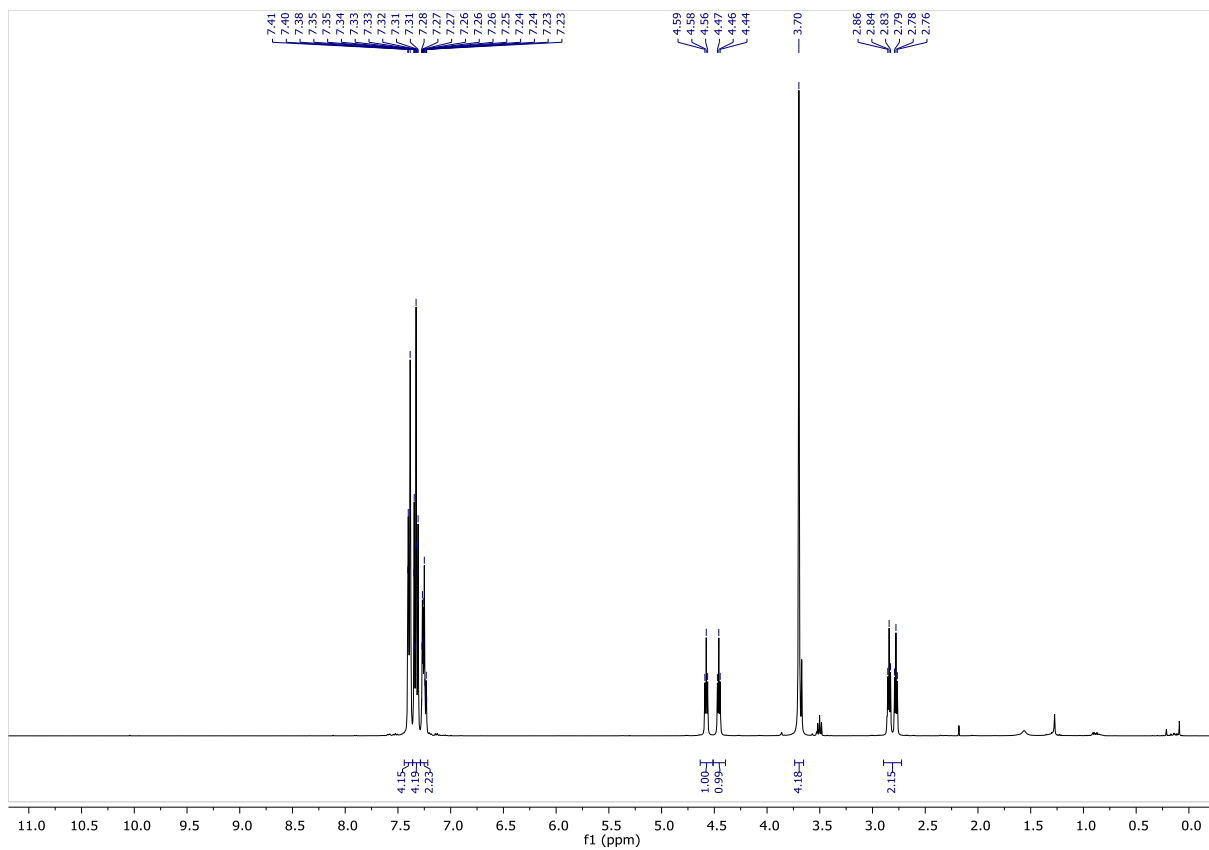


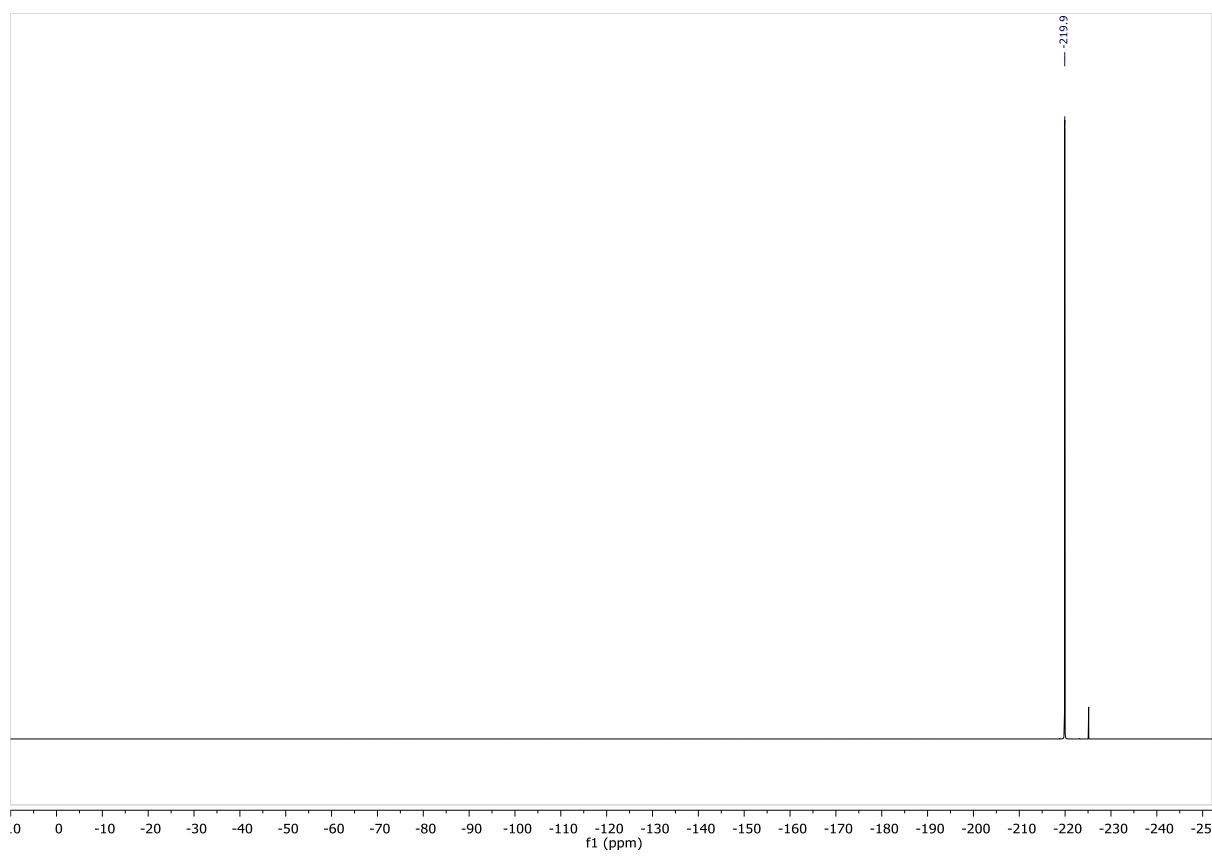
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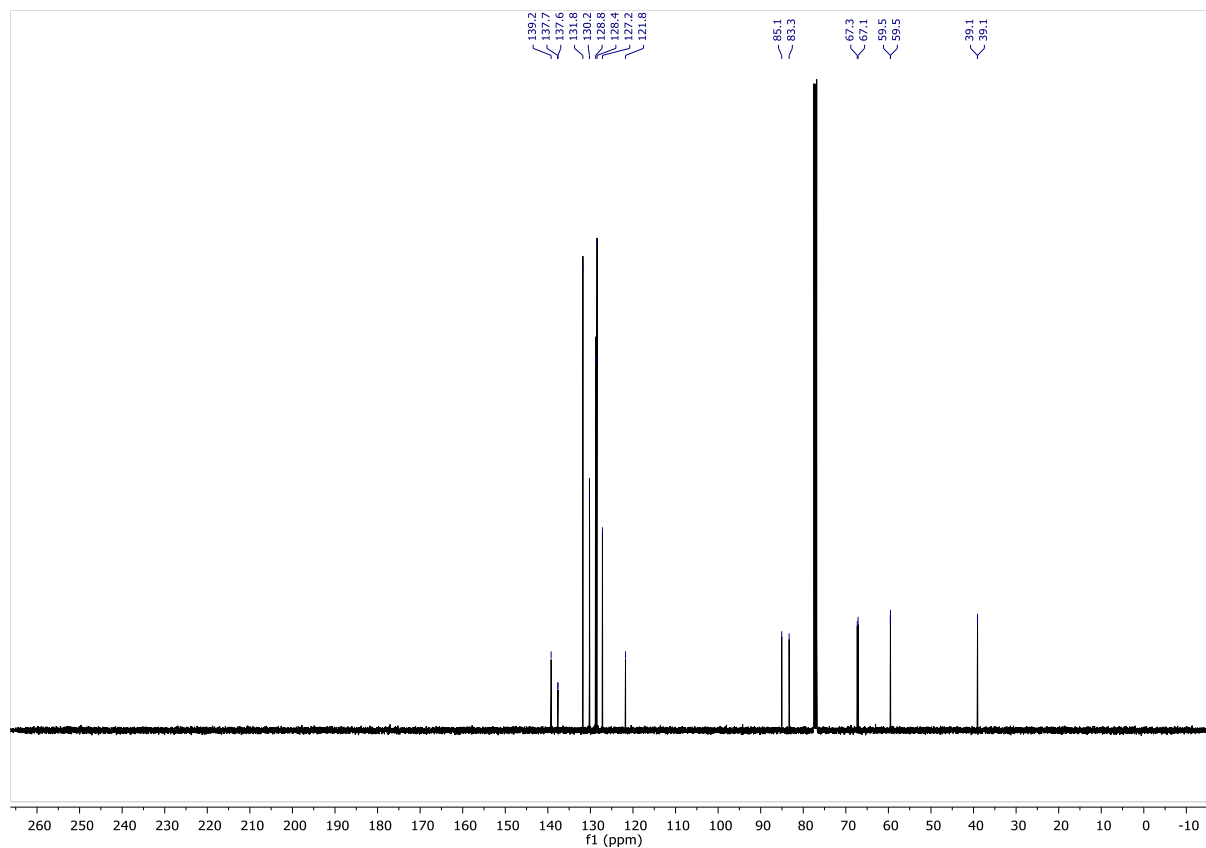
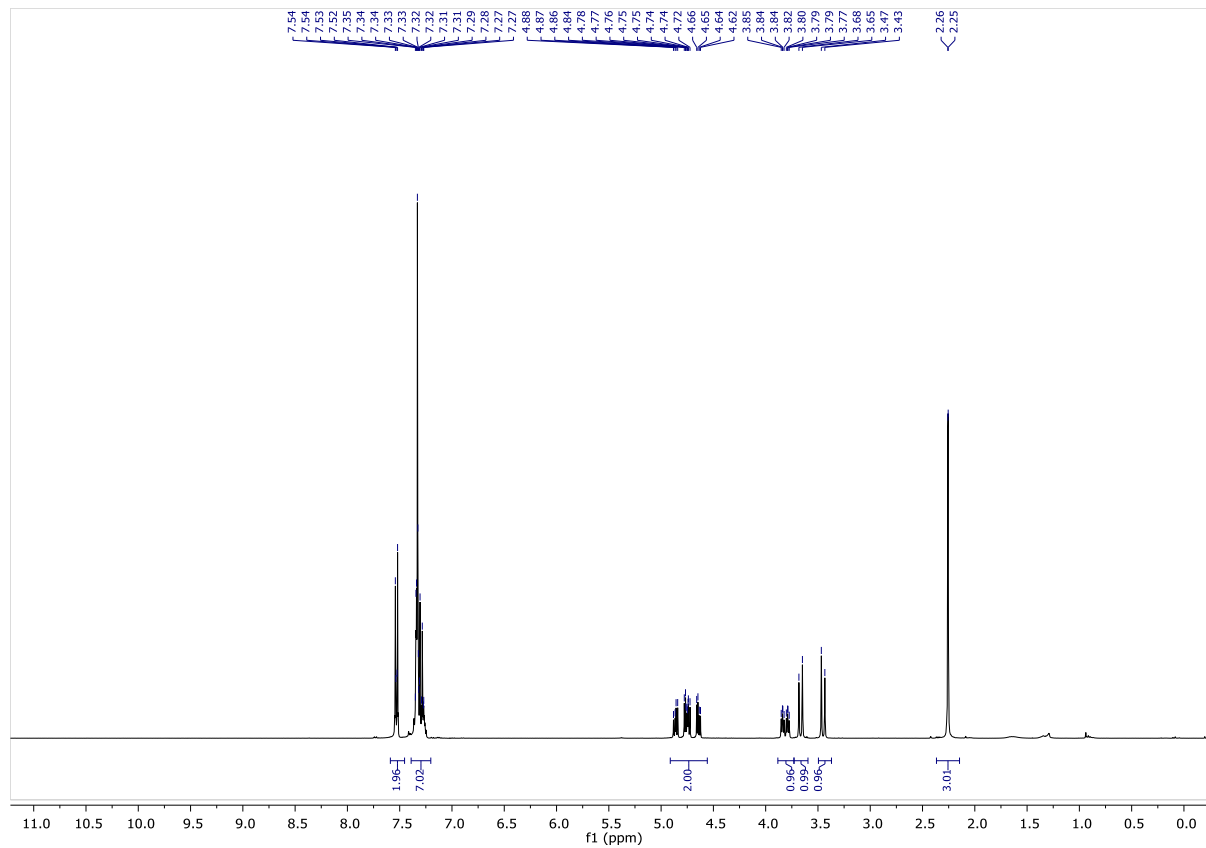


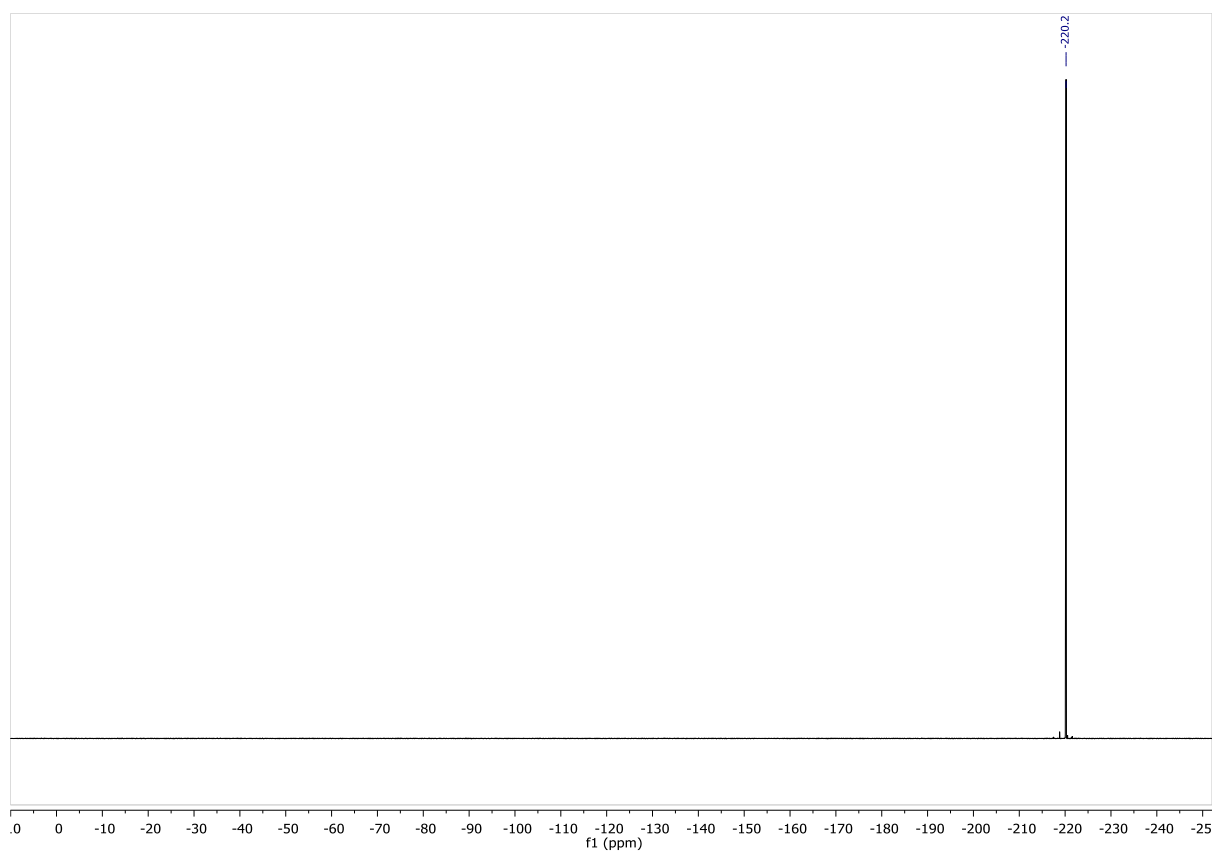
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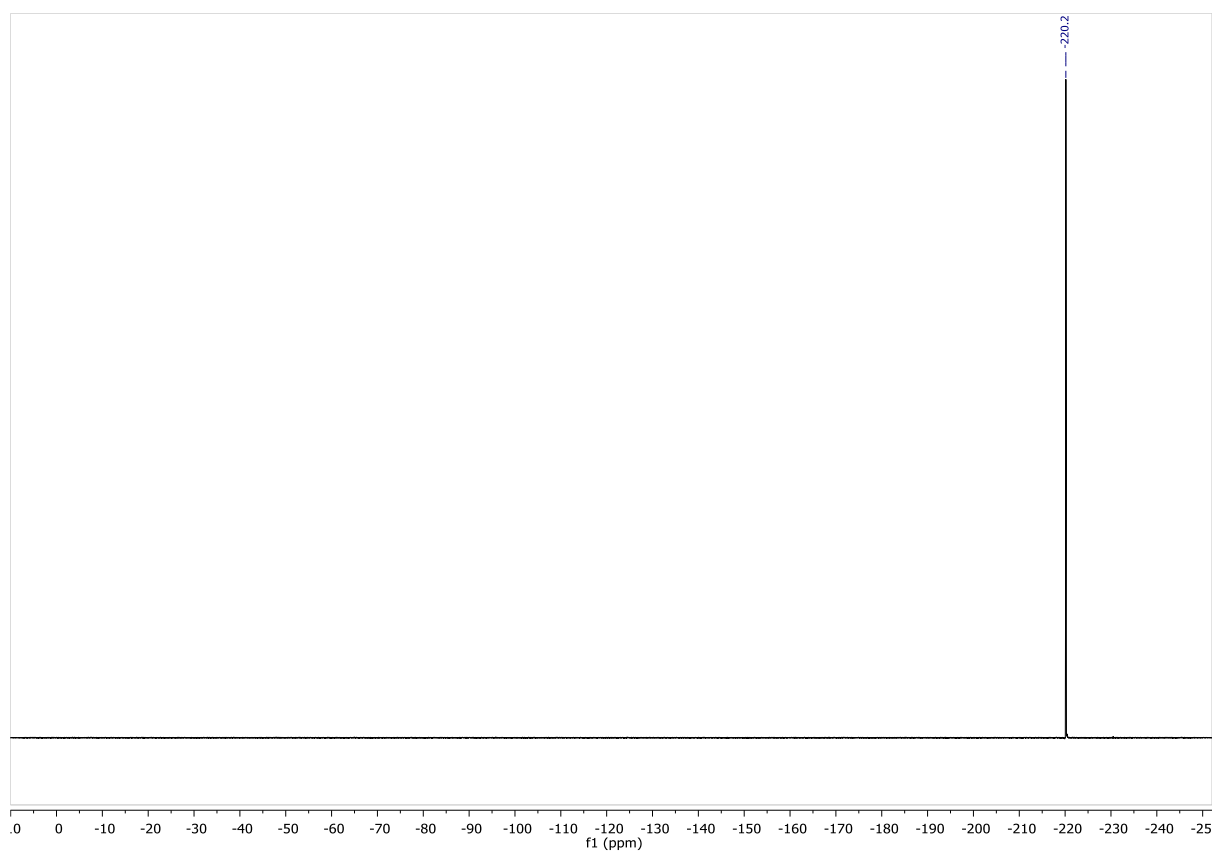




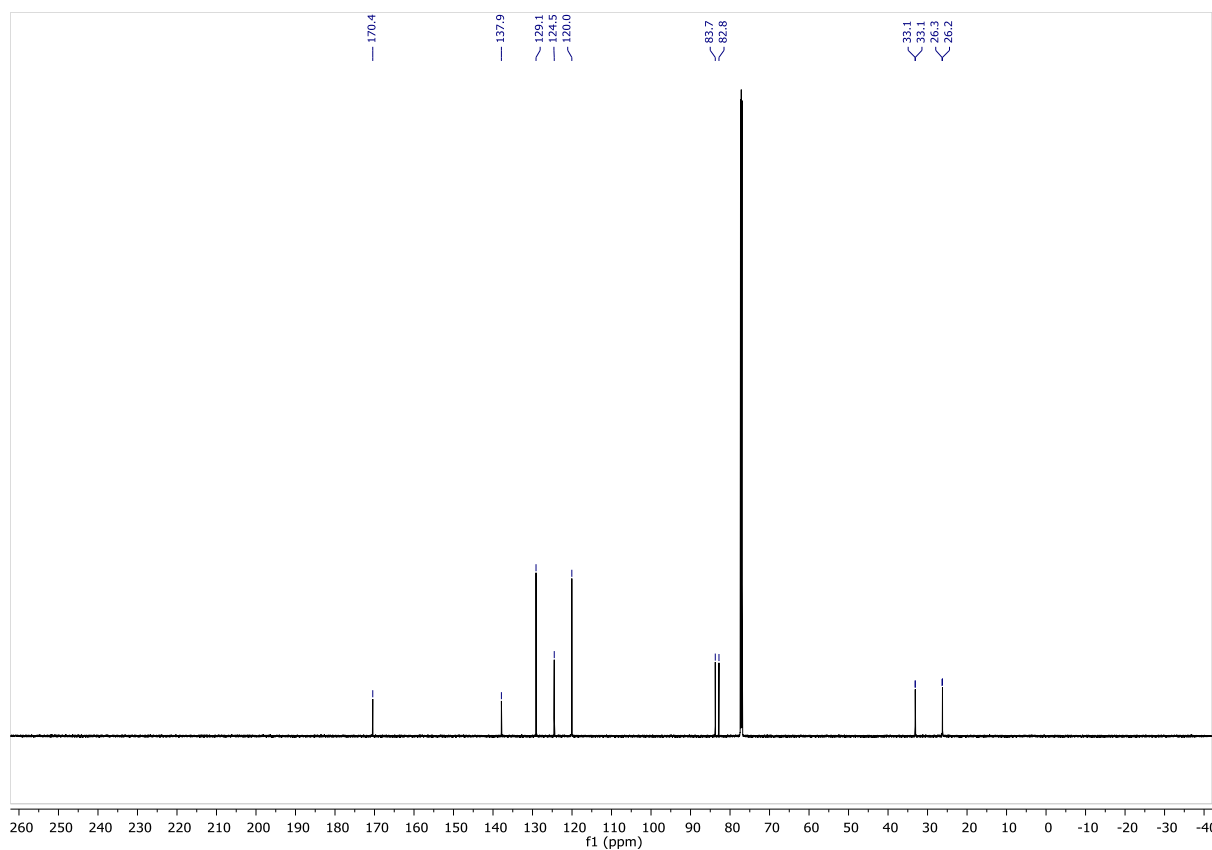
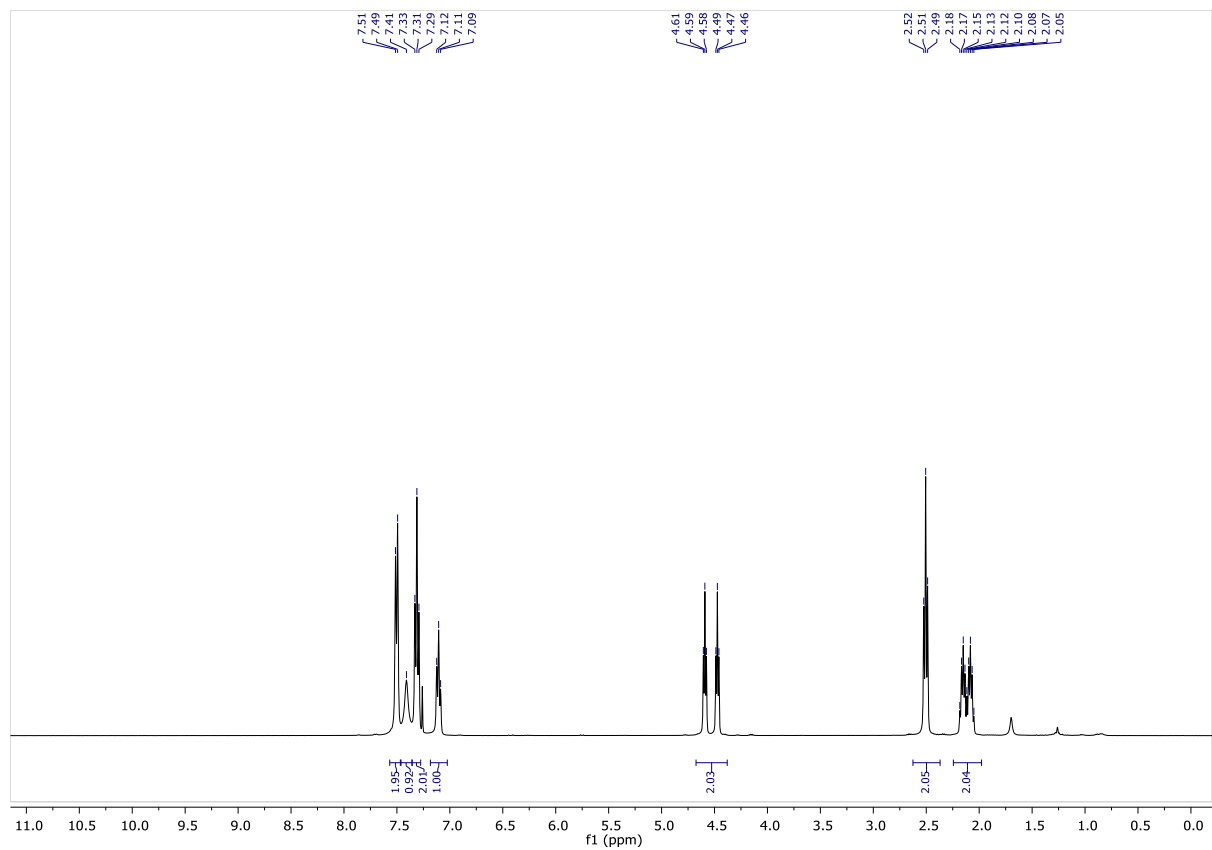
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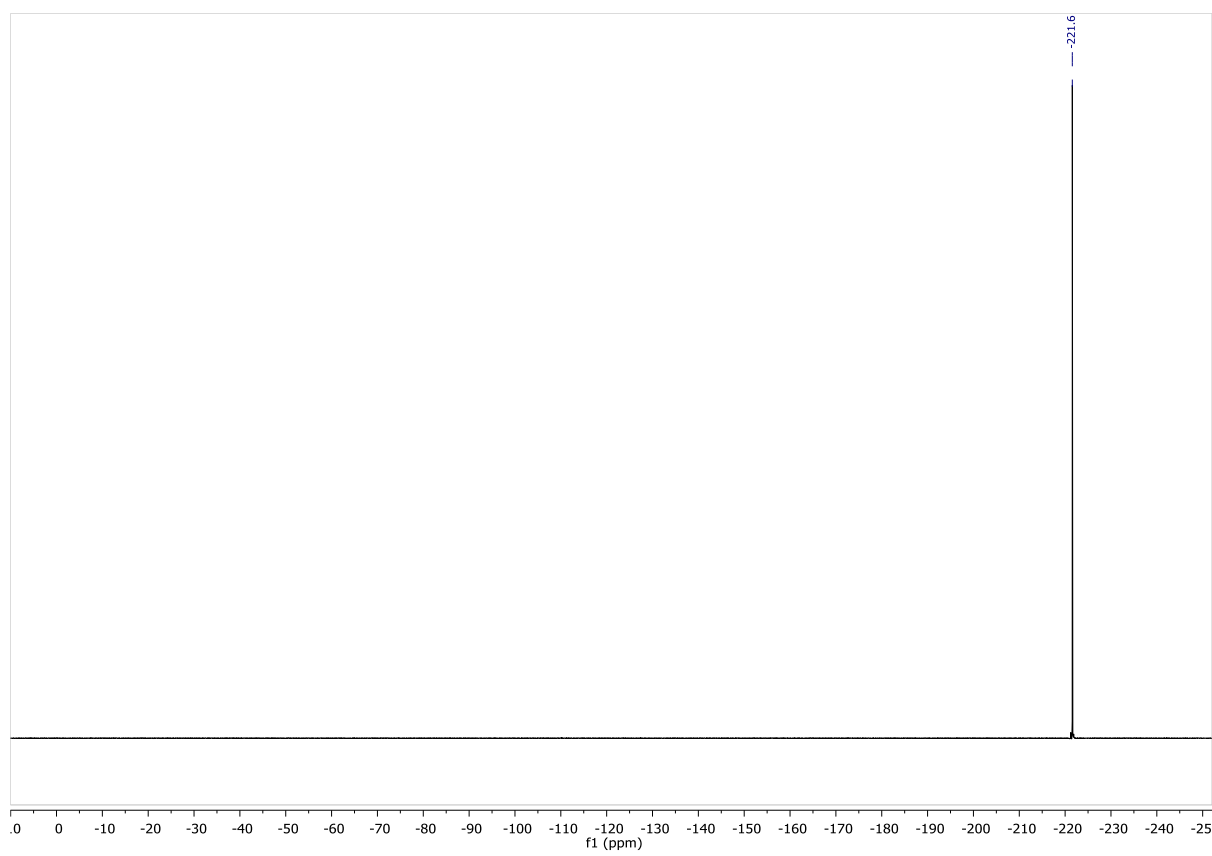




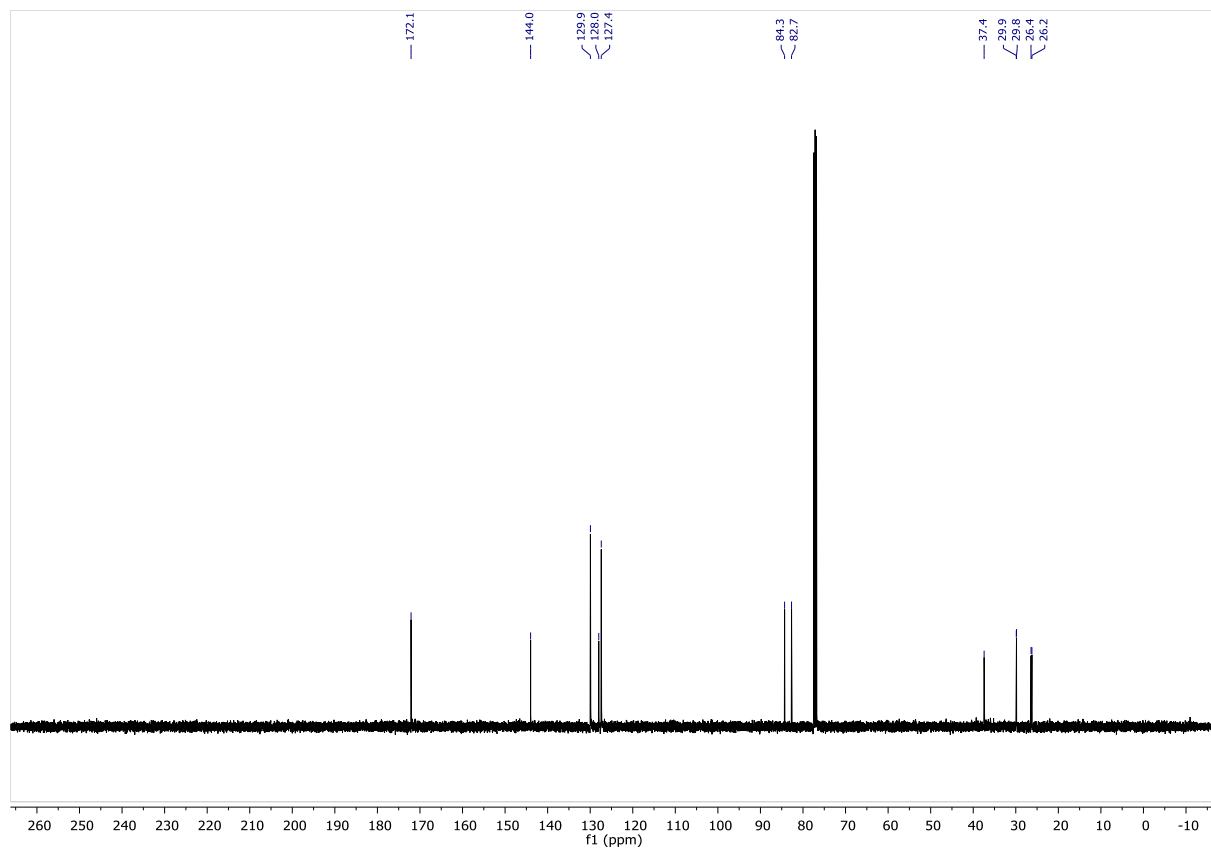
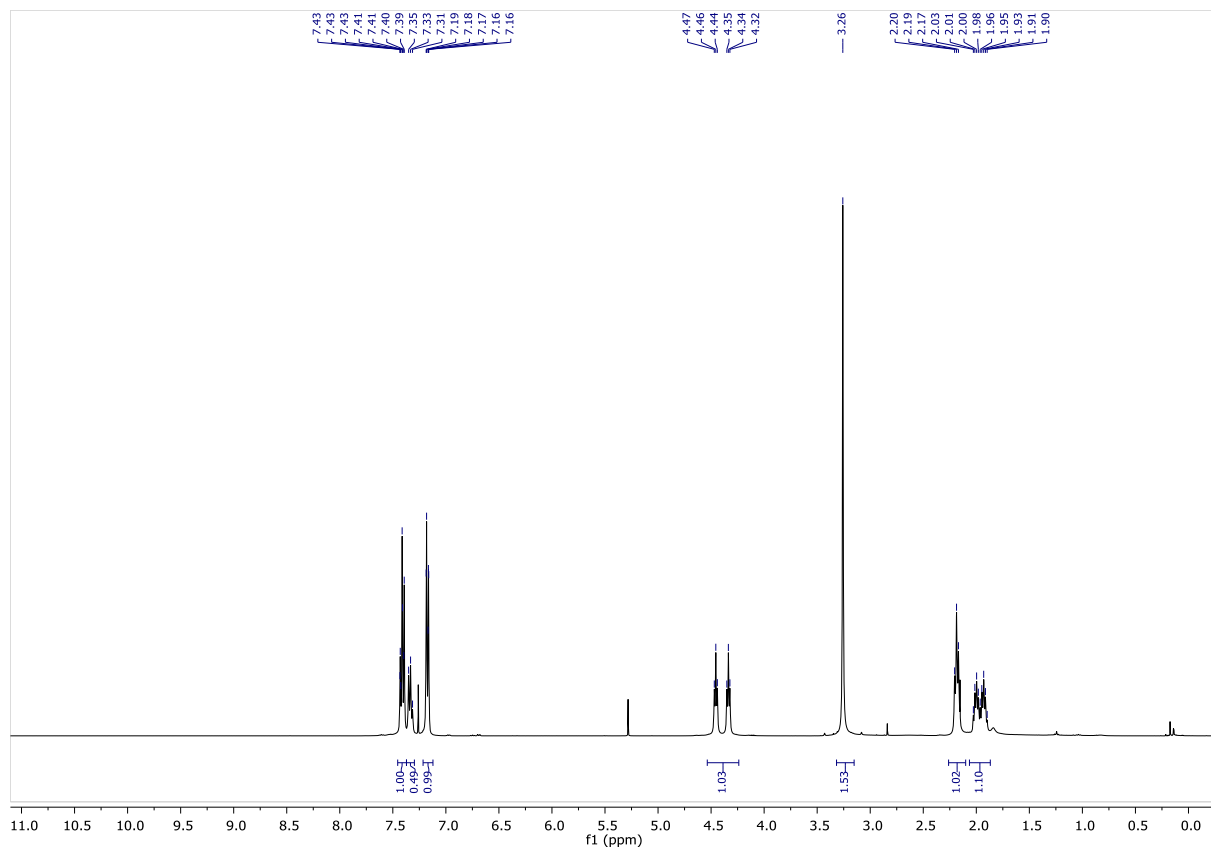


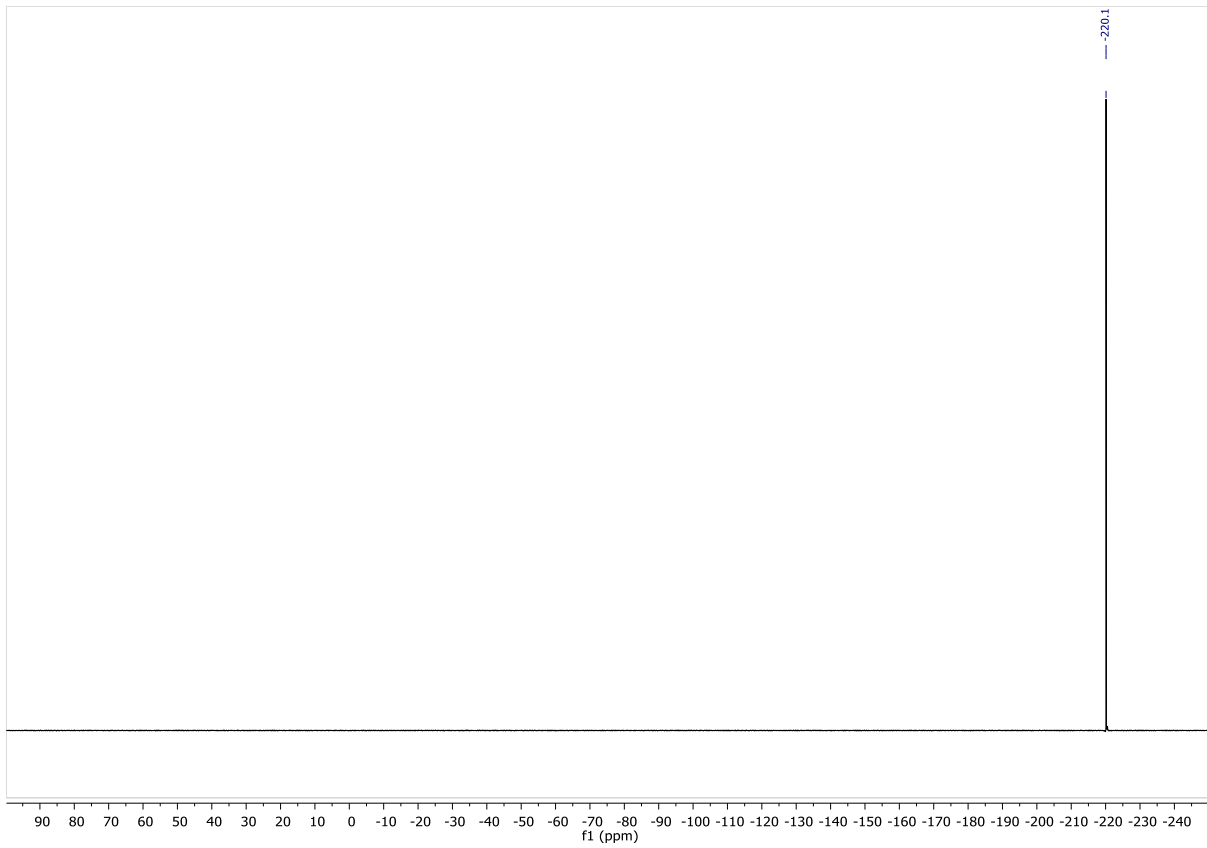
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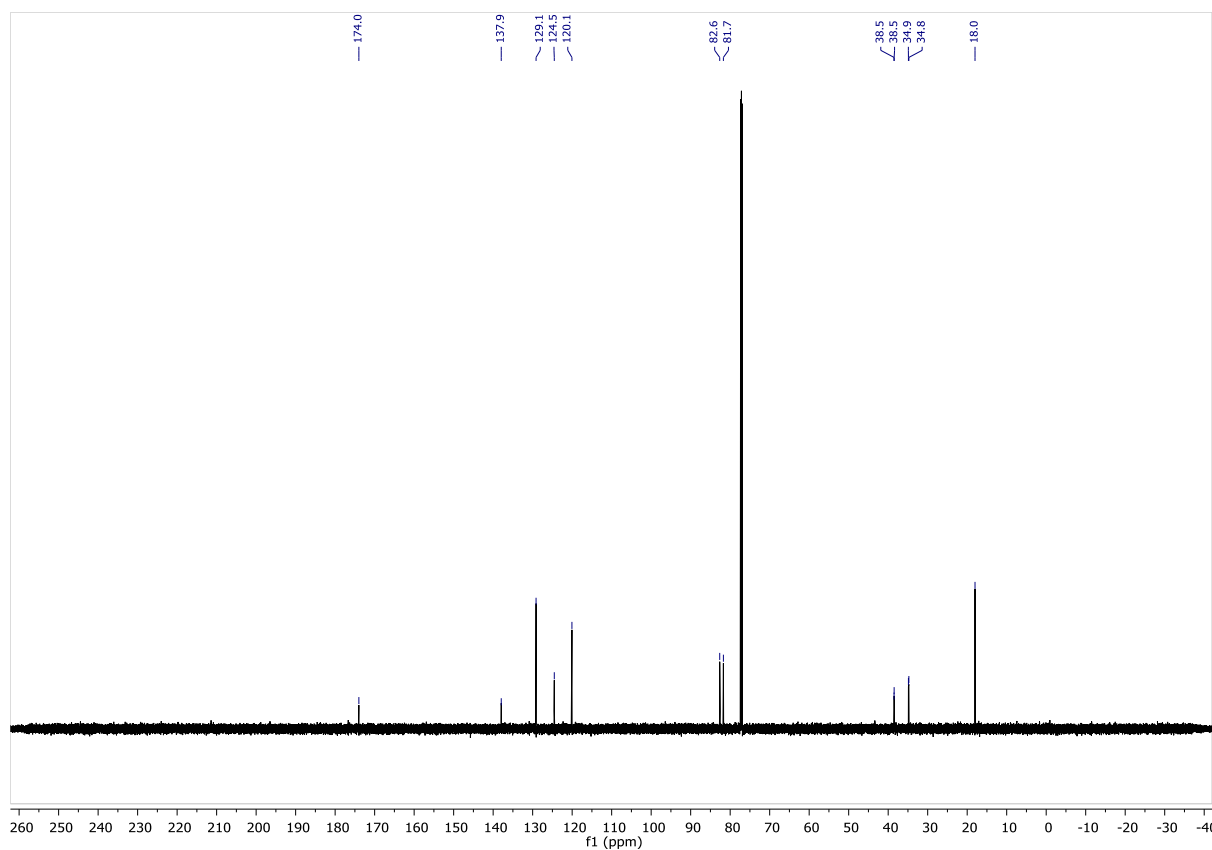
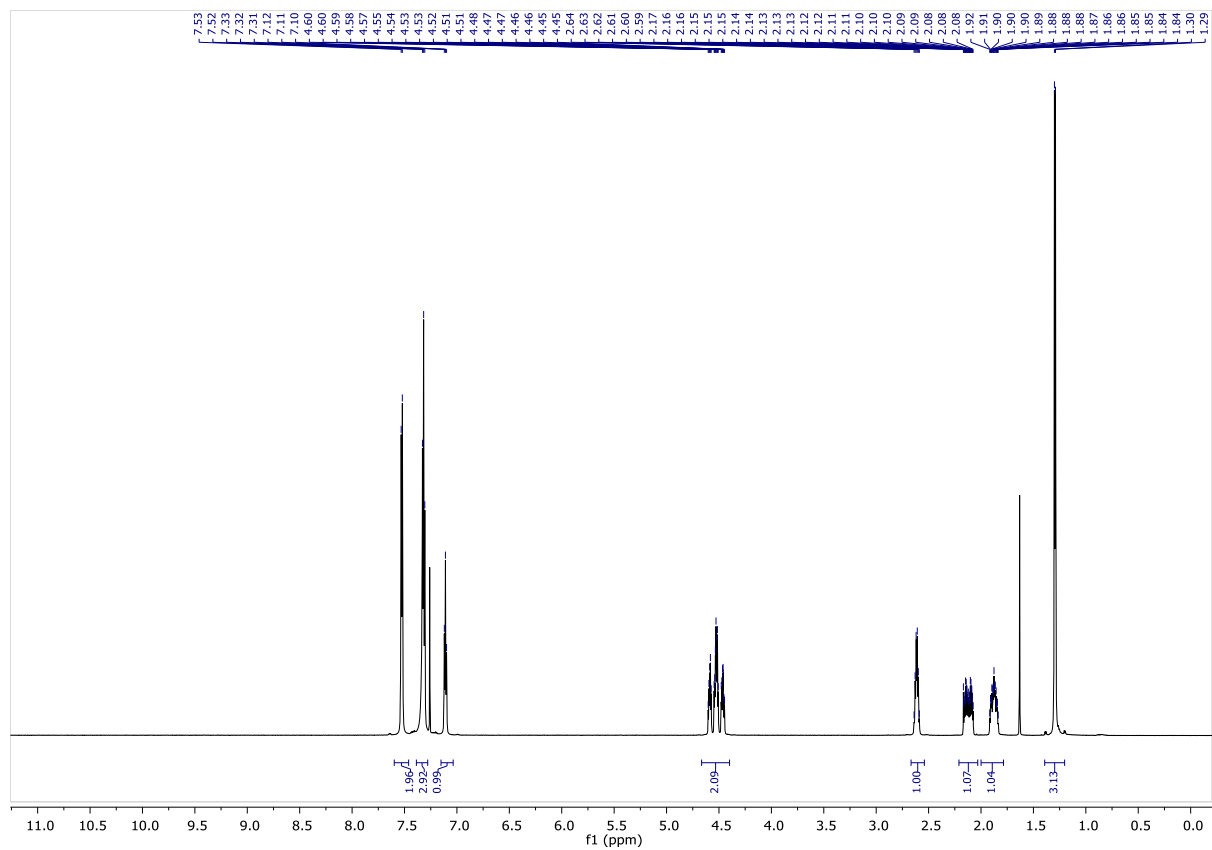


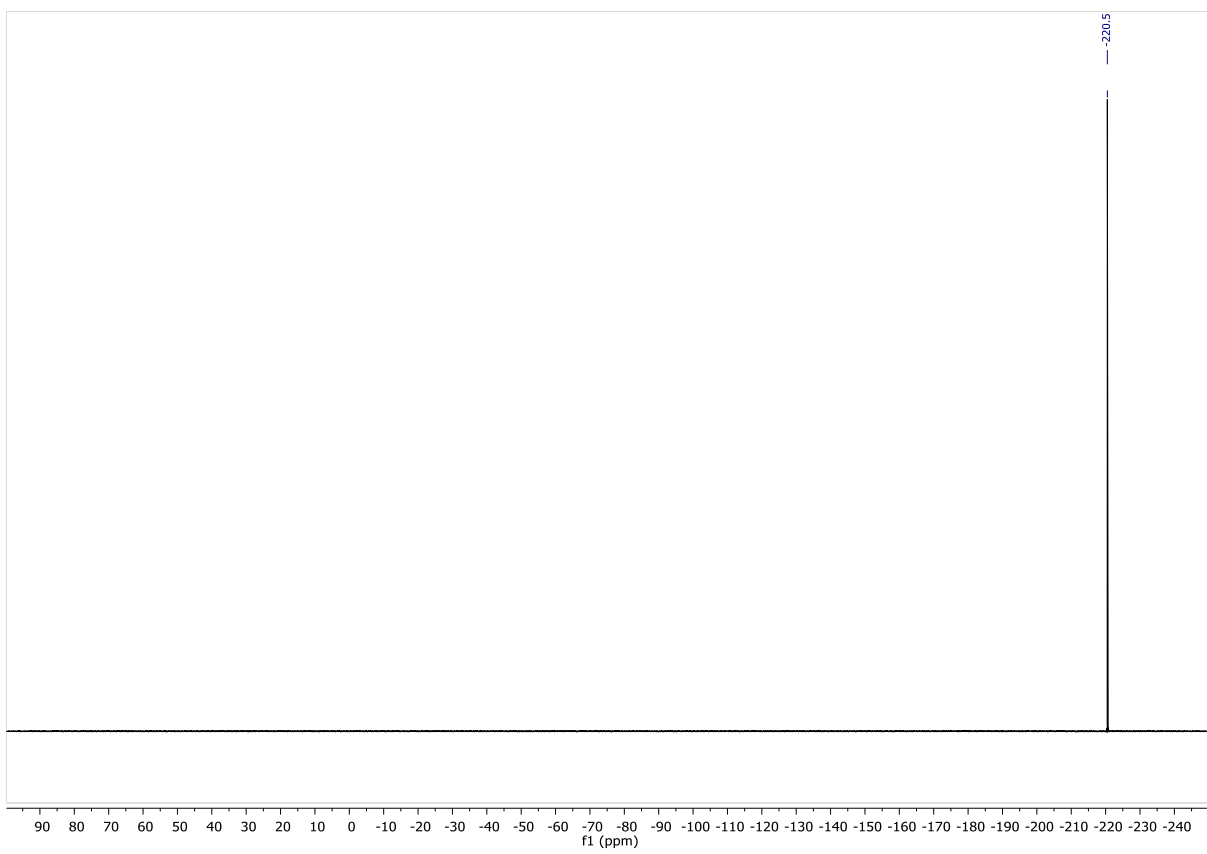
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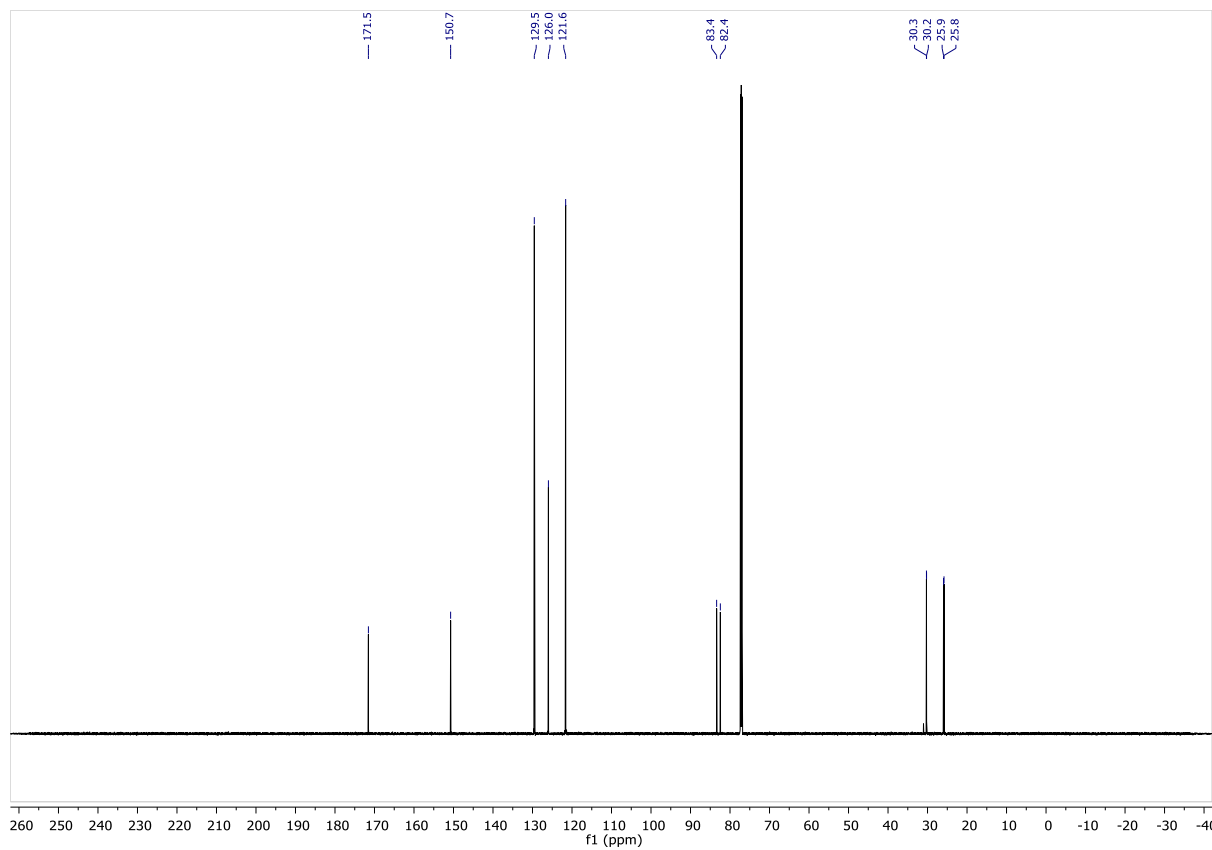
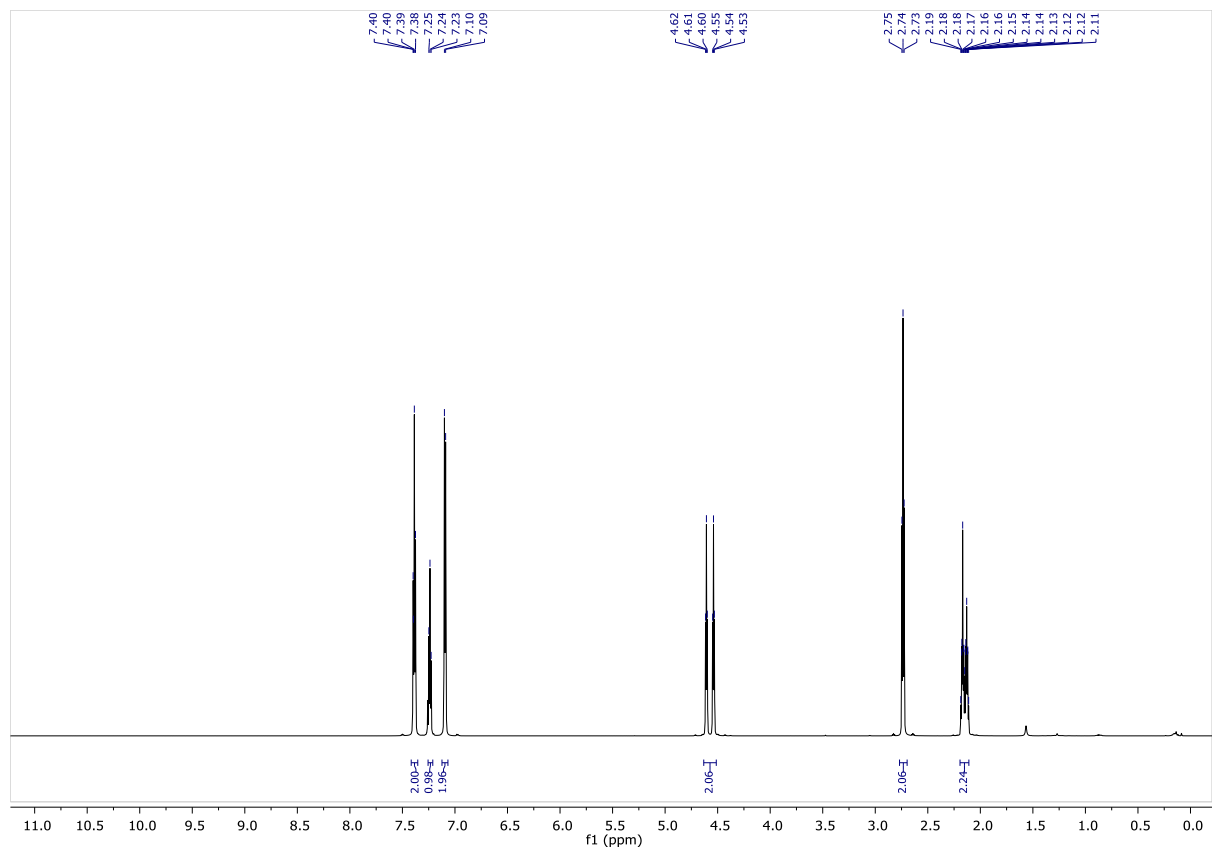


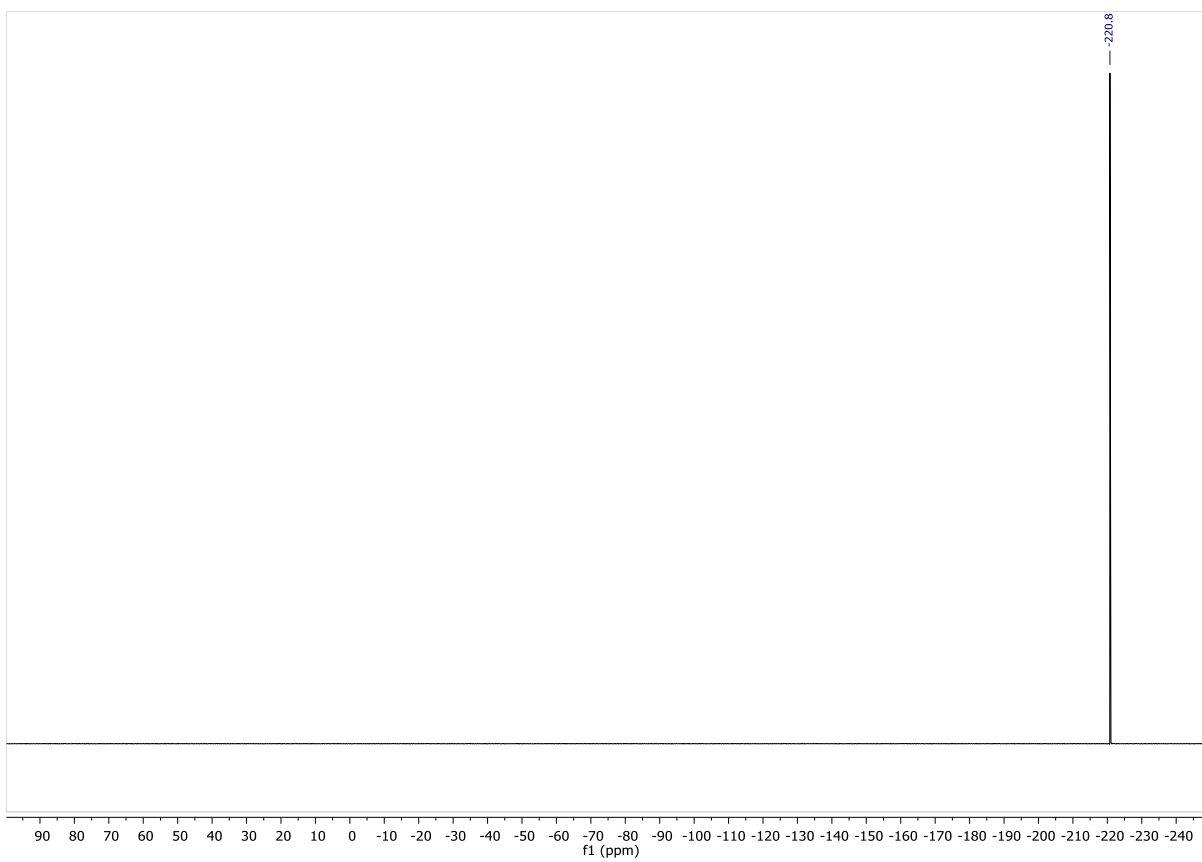
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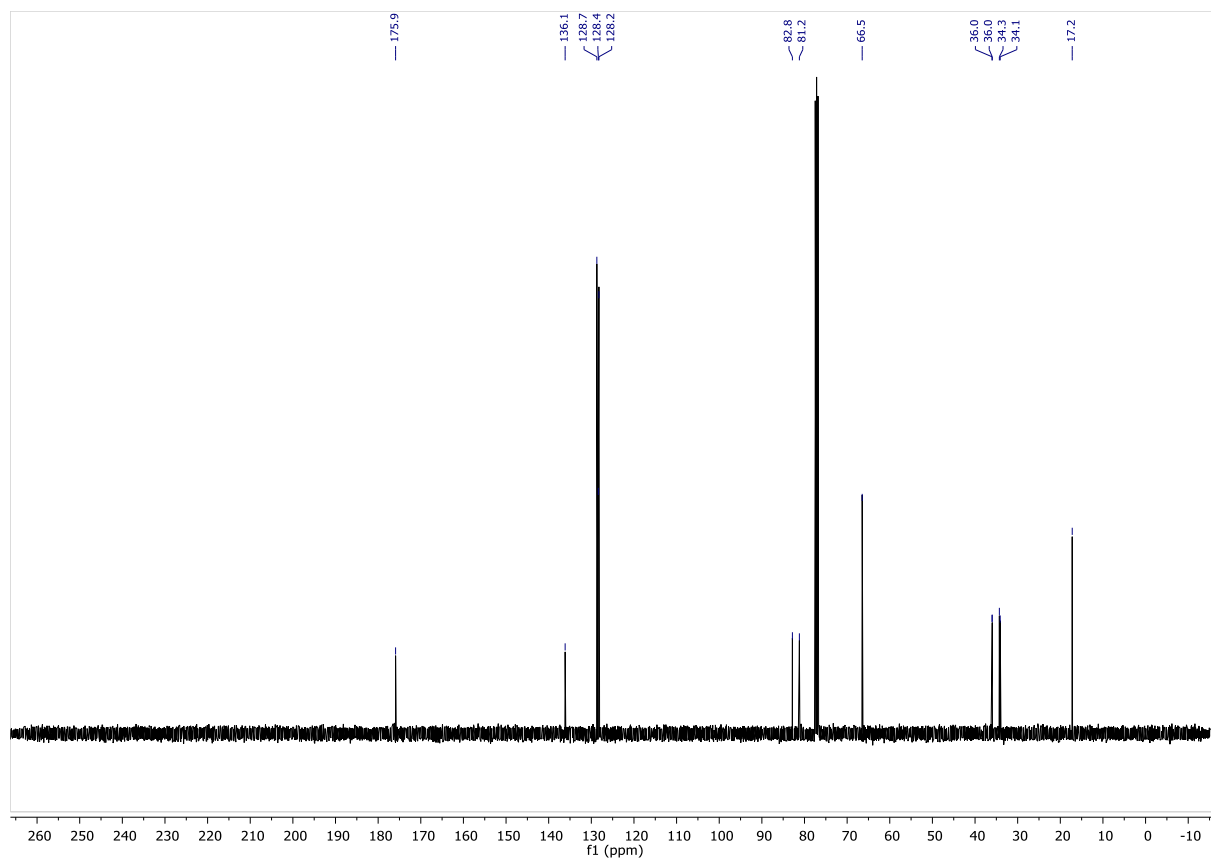
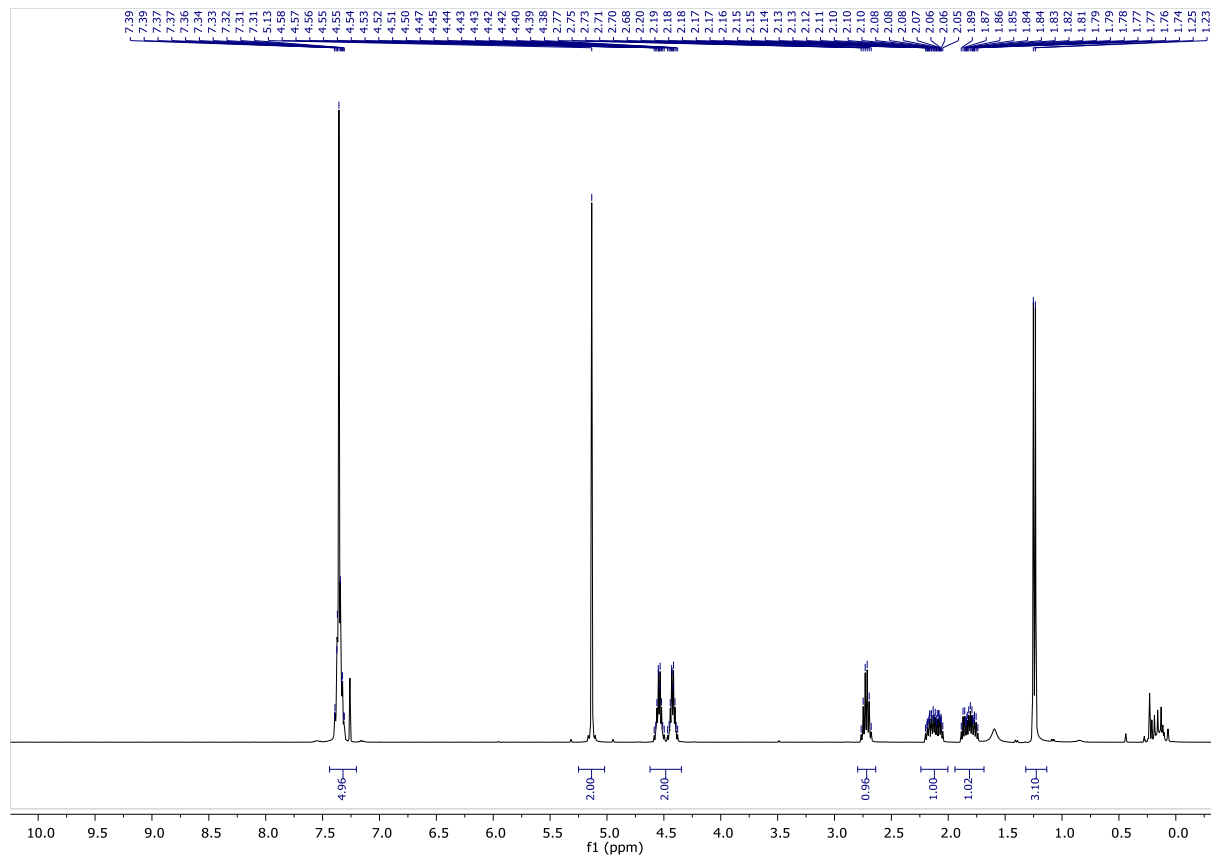


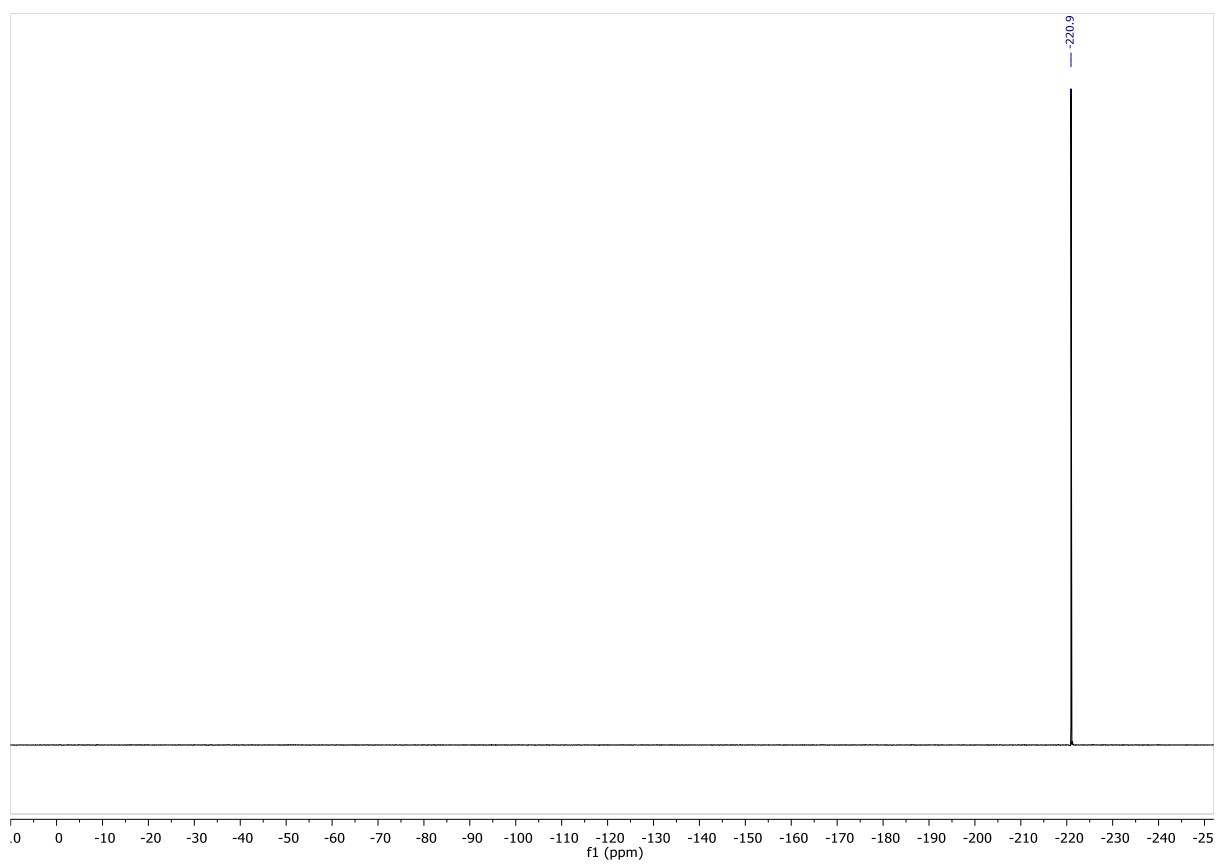
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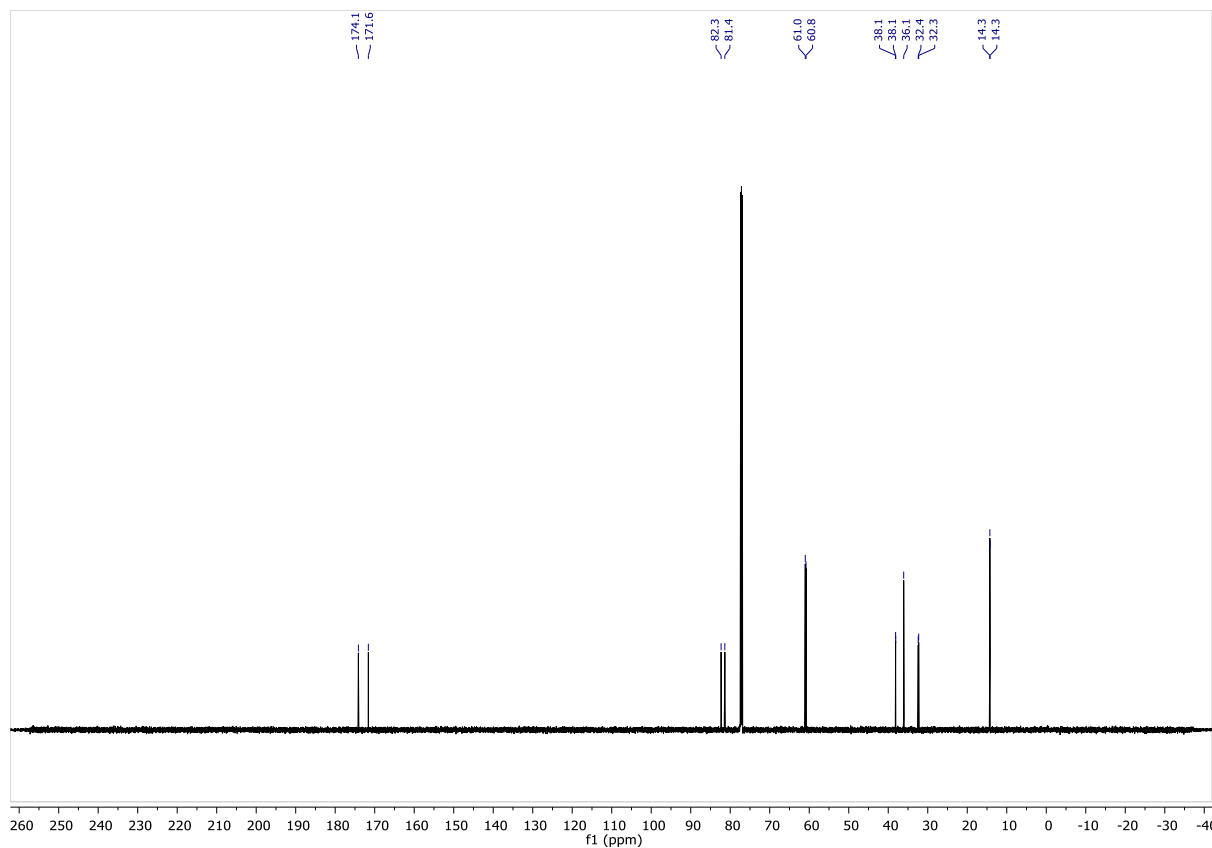
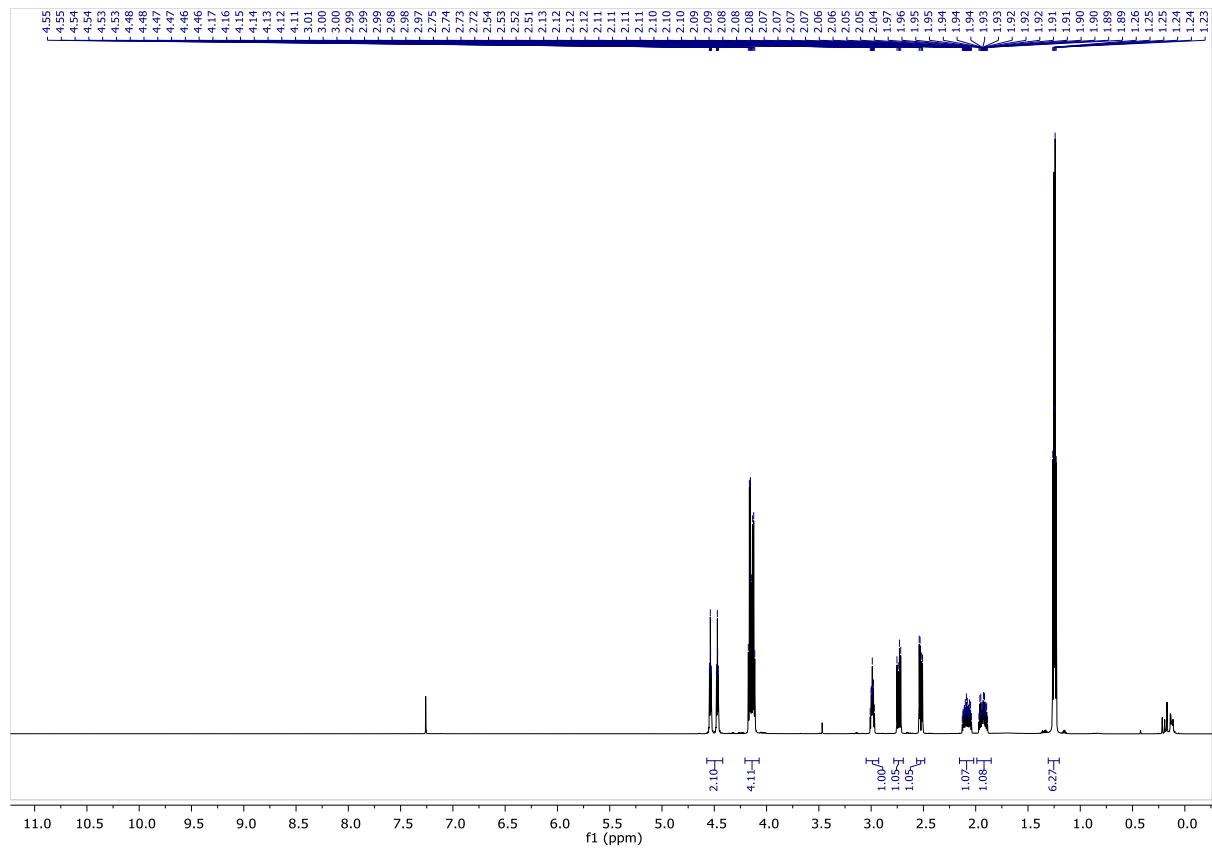


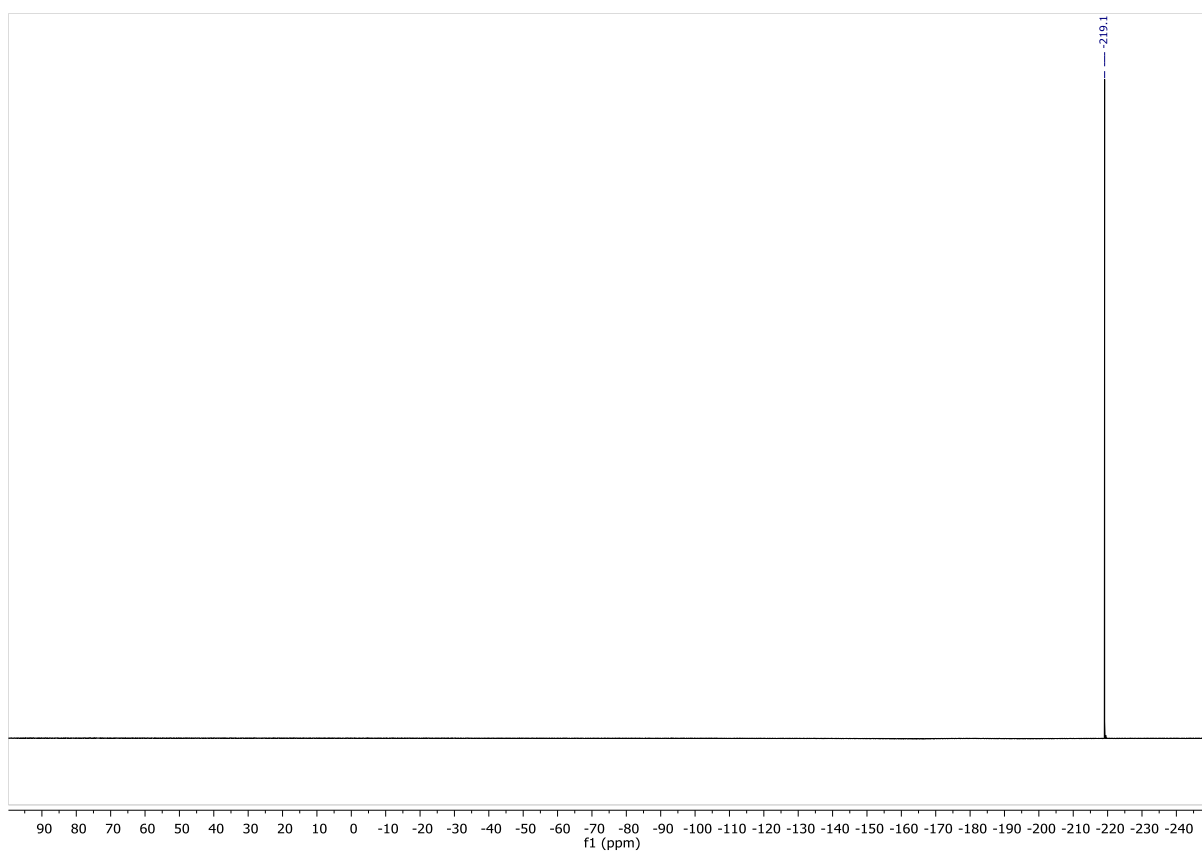
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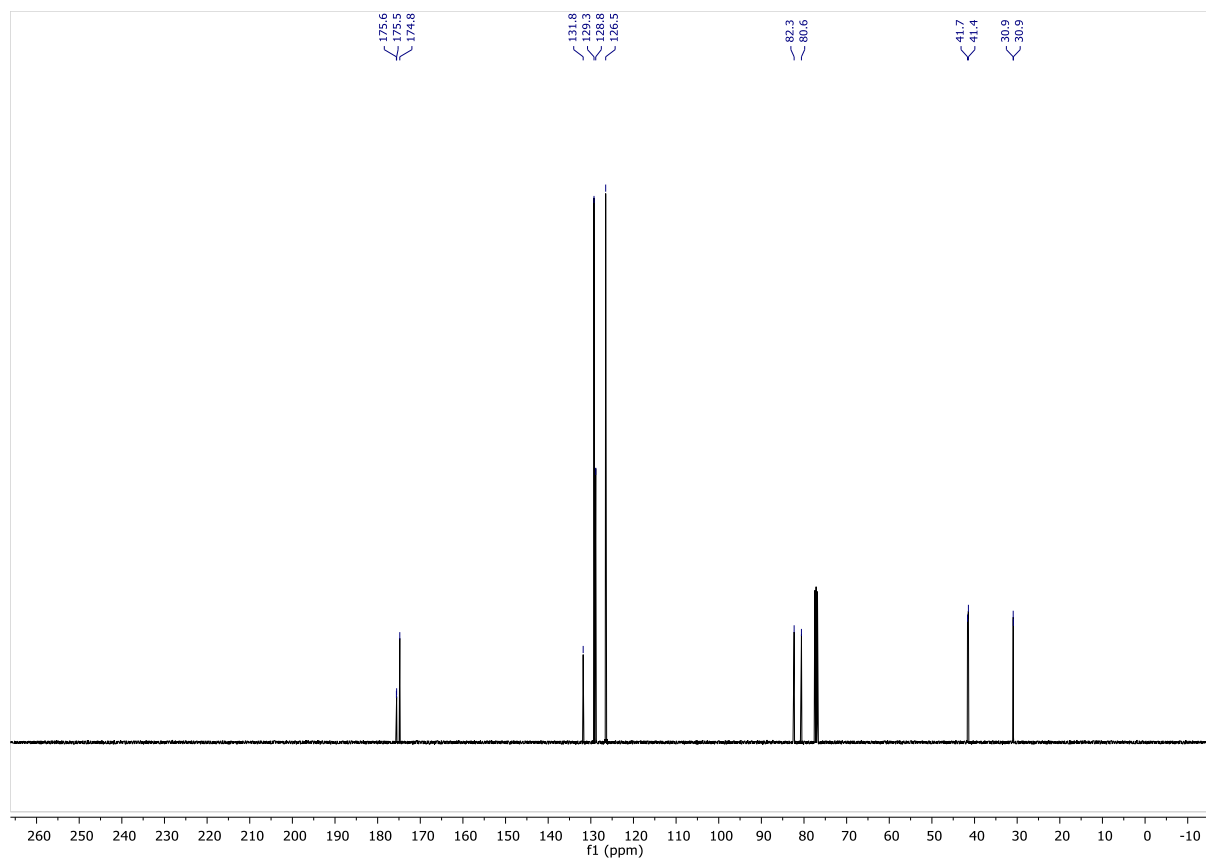
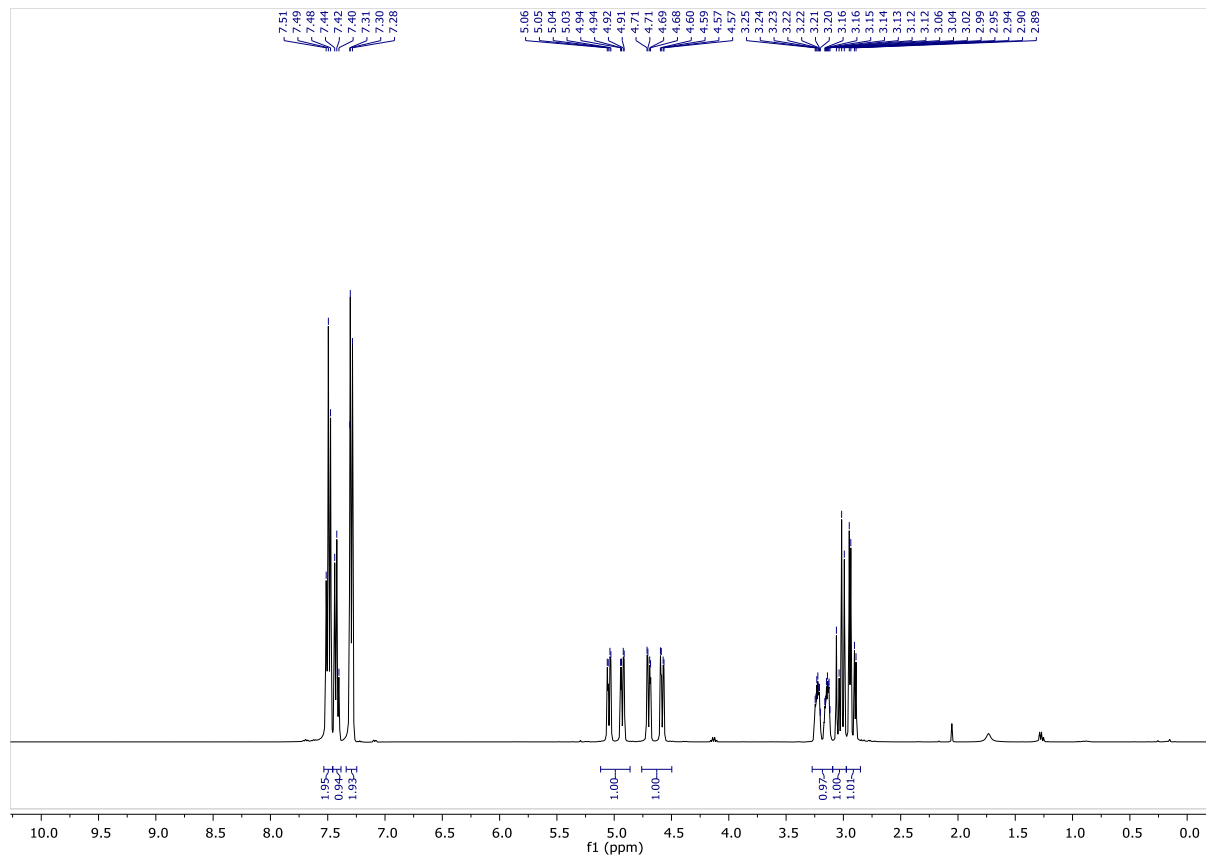


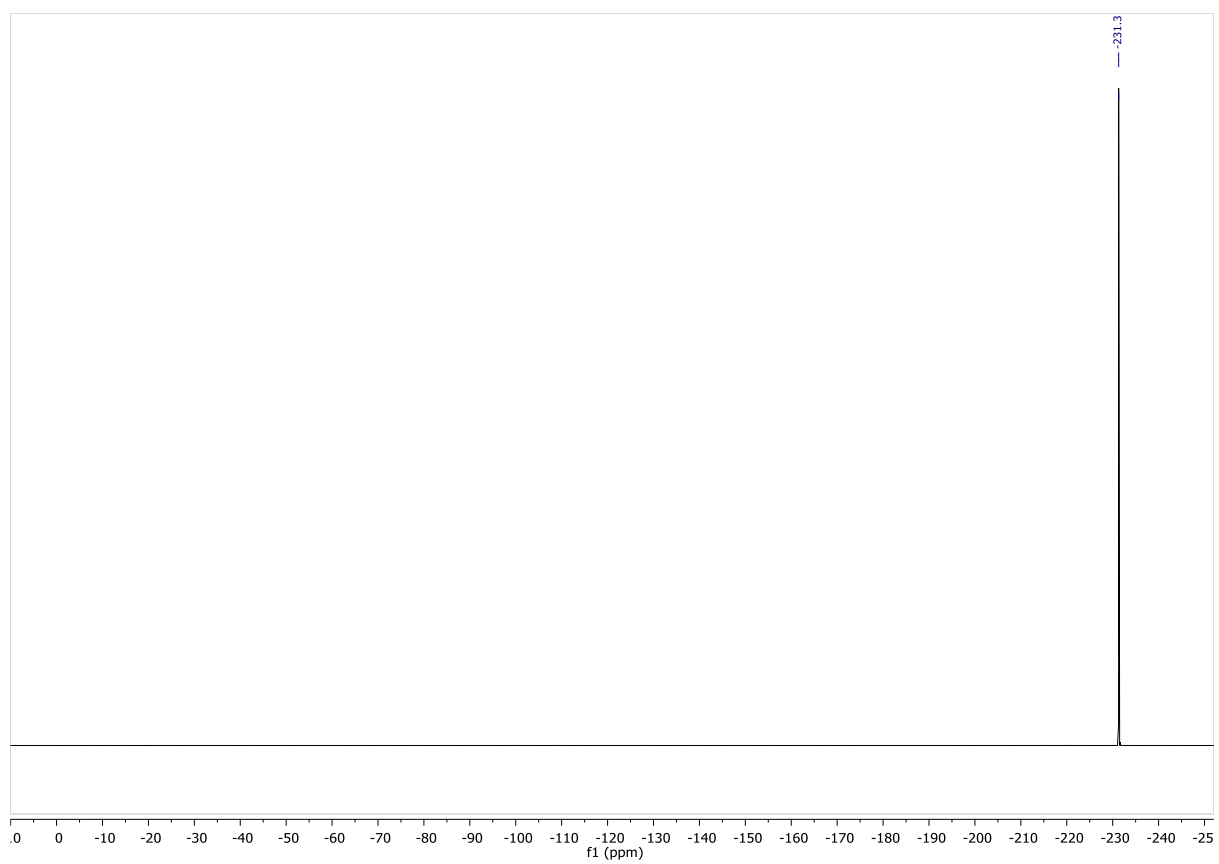
6f





6g





6h

