Electronic Supplementary Material (ESI) for Medicinal Chemistry Communications

A facile synthesis of oroidin and its congeners through imidazo[1, 2-*a*]pyrimidine chemistry

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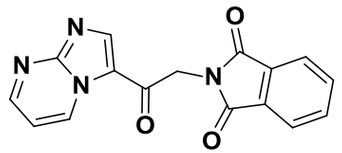
Supporting Information

General Information. All dry reactions were carried out in flame-dried glassware. Anhydrous THF, diethyl ether, dichloromethane, DMSO solvents were purchased from Aldrich and used directly. Thin-layer chromatography (TLC) was carried out on Silicycle F254 precoated, glass silica gel plates which were visualized with either ultraviolet light and stained with PMA. ^{1}H and ^{13}C NMR spectra were recorded on 300 MHz Bruker AC (Tecmag DSPECT-F12 data acquisition system) spectrometers. Chemical shifts are reported in ppm with reference to tetramethylsilane [^{1}H-NMR: CDCl3 (0.00 δ)] or residual protio solvent signals [^{1}H-NMR:CDCl3 (7.26 δ); ^{13}C-NMR: CDCl3 (77.27 δ). Signal patterns are indicated as br (broad peak); s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet). Infrared spectral data were obtained using Perkin-Elmer Spectrum 100 FT-IR spectrometer with diamond ATR accessory as thin film. HRMS data was obtained on Q-Tof instrument using ESI mode.

2-(2-(imidazo[1,2-a]pyrimidin-3-yl)-2-oxoethyl)isoindoline-1,3-dione (2 A)



A mixture of *N*, *N*-dimethyl-*N*-pyrimidylformamidine (15.00 g, 0.1mol) and 2-(4-bromo-3-oxobutyl)isoindoline-1,3-dione (31.29 g, 0.11mol) in ethanol (40 ml) was stirred under reflux for 2h. After the completion of the reaction as monitored by TLC, the reaction mixture was cooled to room temperature and the resulting precipitate was collected by filtration and successively washed with cold ethanol (3 x 30 mL) to give title compound **2 A** as a pale white solid (21.31 g, 69 %).

Melting point: 255-260 ^{o}C

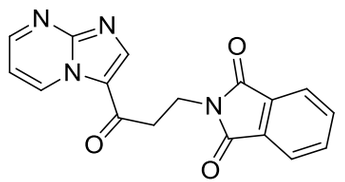
IR (neat): 3028, 2970, 2028, 1688, 1629, 1512, 1413, 1370, 1152, 840, 758 cm^{-1}

^{1}H NMR (CDCl$_3$): δ 9.74 (dd, *J* = 6.0, 3.0 Hz, 1H), 8.81 (dd, *J* = 4.1, 3.0 Hz, 1H), 8.69 (s, 1H), 7.92 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.77 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.19 (s, 1H), 7.17 (dd, *J* = 6.8, 4.1 Hz, 1H), 5.12 (s, 2H)

^{13}CNMR (CDCl$_3$) δ: 186.1, 160.1, 154.0, 150.6, 144.0, 136.3, 126.4, 121.6, 120.0, 111.9, 95.0, 45.4.

HRMS (ES+) *m/z* calc. for [$C_{16}H_{11}N_4O_3$+H^+]: 307.0822; found: 307.0831

2-(3-(imidazo[1,2-a]pyrimidin-3-yl)-3-oxopropyl)isoindoline-1,3-dione (2 B)



A mixture of *N*,*N*-dimethyl-*N*-pyrimidylformamidine (25.00 g, 0.16 mol) and 2-(4-bromo-3-oxobutyl)isoindoline-1,3-dione (49.29 g, 0.16 mmol) in ethanol (60 ml) was stirred under reflux for 2h. After the completion of the reaction as monitored by TLC, the reaction mixture was cooled to room temperature and the resulting precipitate was collected by filtration and successively washed with cold ethanol (3 x 30 mL) to give title compound **2 B** as a pale white solid (37.31 g, 70 %).

Melting point: 220-225 ^{o}C

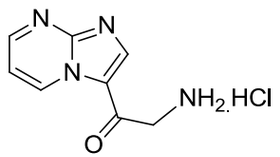
IR (neat): 3039, 2974, 2039, 1683, 1639, 1520, 1403, 1360, 1152, 840, 768 cm^{-1}

^{1}H NMR ($CDCl_3$): δ 9.87 (dd, *J* = 6.8, 2.0 Hz, 1H), 8.80 (dd, *J* = 4.1, 2.0 Hz, 1H), 8.52 (s, 1H), 7.84 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.72 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.26 (s, 1H), 7.18 (dd, *J* = 6.8, 4.1 Hz, 1H), 4.18 (t, *J* = 7.0 Hz, 2H), 3.39 (t, *J* = 7.0 Hz, 2H).

^{13}CNMR ($CDCl_3$, 75 MHz) δ: 200.3, 187.8, 168.3, 154.2, 143.3, 138.0, 136.8, 134.3, 132.1, 123.6, 111.9, 37.6, 33.7.

HRMS (ES+) *m/z* calc. for [$C_{17}H_{12}N_4O_3$+H^+]: 321.0981; found: 321.0988.

2-amino-1-(imidazo[1,2-a]pyrimidin-3-yl)ethanone hydrochloride (3 A)



Compound **2 A** (21.00 g, 0.07 mol) was dissolved in 6N hydrochloric acid (100 ml) and the reaction mixture was heated at reflux for 24h. After completion, reaction mixture was cooled to room temperature and solid was filtered. The filtrate was extracted with dichloromethane and the aqueous layer was concentrated under reduced pressure. The resulting solid was recrystallized in ethanol to give **3 A** (13.15 g, 94 %) as a brown solid.

Melting point: 210-215 ^{o}C

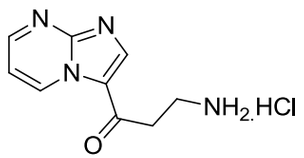
IR (ATR): 3439, 2899, 2642, 2038, 1685, 1640, 1525, 1355, 1325, 1147, 936, 820, 721, 659cm^{-1}.

^{1}H NMR (D_2O, 300 MHz): δ 9.94 (dd, *J* = 6.9, 1.5 Hz, 1H), 9.08 (s, 1H), 8.98 (dd, *J* = 4.2, 6.9 Hz, 1H), 7.72 (dd, *J* = 4.2, 6.9 Hz, 1H), 4.70 (s, 2H)

^{13}C NMR (D_2O + DMSO, 75 MHz): 183.8, 161.0, 146.2, 140.3, 135.3, 122.5, 117.4, 46.0.

HRMS (ES+) *m/z* calc. for [C_8H_8O+H^+]: 173.0773; found: 173.0776

3-amino-1-(imidazo[1,2-a]pyrimidin-3-yl)propan-1-one hydrochloride (3 B)



Compound **2 B** (30 g, 93.66 mmol) was dissolved in 6N hydrochloric acid (125 ml) and the reaction mixture was heated at reflux for 24h. After completion, reaction mixture was cooled to room temperature and solid was filtered. The filtrate was extracted with dichloromethane and the aqueous layer was concentrated under reduced pressure. The residue was recrystalised using ethanol to give **3 B** (20.15 g, 95 %) as a brown solid.

Melting point: 206-210 ^{o}C

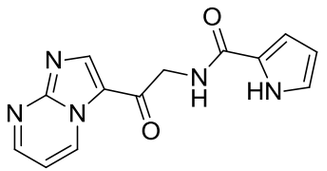
IR (ATR): 3434, 3039, 2889, 2642, 2023, 1710, 1685, 1640, 1618, 1525, 1433, 1355, 1147, 930, 827, 779 cm^{-1}.

^{1}H NMR (D_2O, 300 MHz) : δ 10.00 (dd, *J* = 6.9, 1.5 Hz 1H), 9.12 (dd, *J* = 4.2, 1.5 Hz, 1H), 9.06 (s, 1H), 7.80 (dd, *J* = 4.2, 6.9 Hz, 1H), 3.57 (t, *J* = 6.2 Hz, 2H), 3.47 (t, *J* = 6.2 Hz, 2H).

^{13}C NMR (D_2O + DMSO, 75 MHz): 190.1, 161.3, 146.3, 140.7, 133.6, 122.6, 117.4, 37.4, 35.4.

HRMS (ES+) *m/z* calc. for [$C_9H_{10}N_4O$+H^+]+: 191.0933; found: 191.0933

_N_-(2-(imidazo[1,2-a]pyrimidin-3-yl)-2-oxoethyl)-1_H_-pyrrole-2-carboxamide (4 A_1)



To a stirred solution of **3 A** (2.10 g, 0.01 mol) in anhydrous DMF (10 ml), anhydrous sodium carbonate (4.9 g, 47.16 mmol) was added and the reaction mixture was stirred for 10 min and 2,2,2-trichloro-1-(1*H*-pyrrol-2-yl)ethanone (2.96 g, 14.14 mmol) was added and reaction mixture was stirred at 55 ^{o}C for 2h. After completion of reaction (TLC) solvent was removed. The residue was purified by flash chromatography using methanol:dichloromethane as eluent to obtain condensed compound **4 A_1** (1.33 g, 50 %).

Melting point: 195-198 ^{o}C

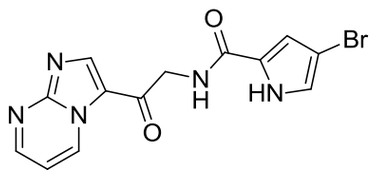
IR (ATR): 3226, 3103, 1642, 1628, 1614, 1514, 1476, 1403, 1327, 1275, 1182, 912,775 cm^{-1}.

^{1}H NMR (DMSO d_6, 300 MHz) : δ 11.49 (s, 1H), 9.76 (dd, *J* = 6.8, 1.9 Hz, 1H), 8.94 (s, 1H), 8.85 (dd, *J* = 4.0, 1.9 Hz, 1H), 8.50 (t, *J* = 5.4 Hz, 1H), 7.42 (dd, *J* = 6.8, 4.0 Hz, 1H), 7.01 – 6.71 (m, 2H), 6.12 (d, *J* = 3.1 Hz, 1H), 4.67 (d, *J* = 5.4 Hz, 2H).

^{13}CNMR (DMSO d_6, 75 MHz): δ 186.6, 161.04, 154.0, 150.6, 143.9, 136.3, 125.7, 121.7, 120.1, 111.9, 110.4, 108.7, 45.5.

HRMS (ES+) *m/z* calc. for [$C_{13}H_{11}N_5O_2$+H^+] 270.0988; found: 270.0991.

4-bromo-*N*-(2-(imidazo[1,2-a]pyrimidin-3-yl)-2-oxoethyl)-1*H*-pyrrole-2-carboxamide (4 A_2)



To a stirred solution of **3 A** (2.10 g, 0.01 mol) in anhydrous DMF (10 ml), anhydrous sodium carbonate (4.9 g, 47.12 mmol) was added and the reaction mixture was stirred for 10 min and 1-(4-bromo-1*H*-pyrrol-2-yl)-2,2,2-trichloroethanone (4.10 g, 14.14 mmol) was added and reaction mixture was stirred at 55 ^{o}C for 2h. After completion of reaction (TLC) solvent was removed. The residue was purified by flash chromatography using methanol:dichloromethane (1:9) as eluent to obtain condensed compound **4 A_2** (1.75 g, 51 %).

Melting point: 200-205 ^{o}C

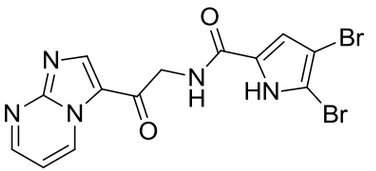
IR (ATR): 3228, 3113, 1648, 1628, 1614, 1514, 1475, 1413, 1327, 1275, 1182, 912,775 cm^{-1}.

^{1}H NMR (DMSO d_6, 300 MHz) : δ 11.88 (s, 1H), 9.75 (d, *J* = 6.8 Hz, 1H), 8.93 (s, 1H), 8.85 – 8.74 (m, 1H), 8.62 (t, *J* = 5.6 Hz, 1H), 7.43 – 7.29 (m, 1H), 7.02 (s, 1H), 6.95 (s, 1H), 4.68 (d, *J* = 6.0 Hz, 2H)

^{13}CNMR (DMSO d_6, 75 MHz): δ 186.1, 160.0, 154.0, 150.6, 144.0, 136.3, 126.4, 121.6, 120.08, 111.9, 95.1, 45.4.

HRMS (ES+) *m/z* calc. for [$C_{13}H_{10}N_5O_2Br+H^+$] 347.0018; found: 347.0096

4,5-dibromo-*N*-(2-(imidazo[1,2-a]pyrimidin-3-yl)-2-oxoethyl)-1*H*-pyrrole-2-carboxamide (4 A_3)



To a stirred solution of **3 A** (2.10 g, 0.01 mol) in anhydrous DMF (10 ml), anhydrous sodium carbonate (4.9 g, 47.12 mmol) was added and the reaction mixture was stirred for 10 min and 2,2,2-trichloro-1-(4,5-dibromo-1*H*-pyrrol-2-yl)ethanone (5.63 g, 14.14 mmol) was added and reaction mixture was stirred at 55 ^{o}C for 2 h. After completion of reaction (TLC) solvent was removed. The residue was purified by flash chromatography using methanol:dichloromethane (1:9) as eluent to obtain condensed compound **4 A_3** ((2.25 g, 52 %).

Melting point: 198-201^{o}C

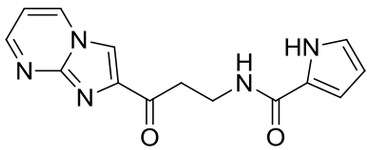
IR (ATR): 3214, 3102, 1649, 1621, 1618, 1517, 1475, 1413, 1327, 1275, 1181, 912,775 cm^{-1}.

^{1}H NMR (DMSO d_6, 300 MHz) : δ 12.77 (s, 1H), 9.76 (d, *J* = 6.8, 1H), 8.94 (s, 1H), 8.93 – 8.74 (m, 1H), 8.67 (t, *J* = 5.8, 1H), 7.43 (dd, *J* = 6.8, 3.6 Hz, 1H), 7.04 (s, 1H), 4.70 (d, *J* = 5.8 Hz, 2H).

^{13}CNMR (DMSO d_6, 75 MHz): δ 184.7, 158.0, 152.9, 149.3, 142.9, 135.1, 126.4, 118.8, 111.93, 110.6, 103.8, 96.7, 44.1.

HRMS (ES+) *m/z* calc. for [$C_{13}H_9N_5O_2Br_2$+H^+] 424.9123; found:

_N_-(3-(imidazo[1,2-a]pyrimidin-2-yl)-3-oxopropyl)-1_H_-pyrrole-2-carboxamide (4 B_1)



To a stirred solution of **3 B** (2.26 g, 0.01 mol) in anhydrous DMF (10 ml), anhydrous sodium carbonate (5.1 g, 0.05 mol) was added and the reaction mixture was stirred for 10 min and 2,2,2-trichloro-1-(1*H*-pyrrol-2-yl)ethanone (3.22 g, 0.015mol) was added and reaction mixture was stirred at 55 ^{o}C for 2h. After completion of reaction (TLC) solvent was removed. The residue was purified by flash chromatography using methanol:dichloromethane as eluent to obtain condensed compound **4 B_1** (1.33 g, 49 %).

Melting point: 220-225 ^{o}C

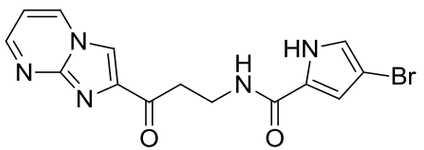
IR (ATR): 3226, 3104, 1660, 1628, 1614, 1514, 1476, 1403, 1327, 1285, 1182, 932, 778, 759cm^{-1}.

^{1}H NMR (DMSO d_6, 300 MHz) : δ 11.43 (s, 1H), 9.78 (dd, *J* = 6.8, 2.0 Hz, 1H), 8.82 (dd, *J* = 4.2, 2.0 Hz, 1H), 8.77 (s, 1H), 8.14 (t, *J* = 5.5 Hz, 1H), 7.39 (dd, *J* = 6.8, 4.3 Hz, 1H), 6.83 (dd, *J* = 2.1, 3.9 Hz, 1H), 6.70 (dd, *J* = 2.1, 4.8, 1H), 6.04 (dd, *J* = 2.4, 5.7 Hz, 1H), 3.61 (q, *J* = 6.4 Hz, 2H), 3.21 (t, *J* = 6.4 Hz, 2H).

^{13}CNMR (DMSO d_6, 75 MHz): δ 189.1, 160.9, 153.9, 150.6, 144.4, 136.5, 126.2, 121.8, 121.4, 111.8, 109.9, 108.6, 39.1, 35.0.

HRMS (ES+) *m/z* calc. for [$C_{14}H_{13}N_5O_2$+H^+]: 284.1155; found: 284.1147.

4-bromo-*N*-(3-(imidazo[1,2-a]pyrimidin-2-yl)-3-oxopropyl)-1*H*-pyrrole-2-carboxamide (4 B_2)



To a stirred solution of **3 B** (2.26 g, 0.01 mol) in anhydrous DMF (10 ml), anhydrous sodium carbonate (5.1 g, 0.05 mol) was added and the reaction mixture was stirred for 10 min and 1-(4-bromo-1*H*-pyrrol-2-yl)-2,2,2-trichloroethanone (4.43 g, 0.015 mol) was added and reaction mixture was stirred at 55 ^{o}C for 2h. After completion of reaction (TLC) solvent was removed. The residue was purified by flash chromatography using methanol:dichloromethane (1:9) as eluent to obtain condensed compound **4 B_2** (2.02 g, 55 %).

Melting point: 205-210 ^{o}C

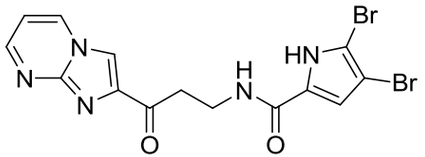
IR (ATR): 33332, 3099, 2582, 1646, 1625, 1515, 1407, 1315, 1261, 1176, 1133, 956, 917, 778, 765 cm^{-1}.

^{1}H NMR (DMSO d_6, 300 MHz) : 11.83 (s, 1H), 9.79 (dd, *J* = 6.8, 2.0 Hz, 1H), 8.83 (dd, *J* = 4.2, 2.0 Hz, 1H), 8.77 (s, 1H), 8.23 (t, *J* = 5.4 Hz, 2H), 7.40 (dd, *J* = 6.8, 4.2 Hz, 1H), 6.96 (s, 1H), 6.79 (s, 1H), 3.62 (q, *J* = 6.4 Hz, 2H), 3.22 (t, *J* = 6.4 Hz, 2H).

^{13}CNMR (DMSO d_6, 75 MHz): δ 189.0, 160.8, 153.9, 150.6, 144.3, 136.4, 126.2, 121.2, 111.8, 109.9, 108.5, 94.9, 39.1, 34.9.

HRMS (ES+) *m/z* calc. for [$C_{14}H_{12}N_5O_2Br+H^+$]: 362.0247; found: 362.0253.

4,5-dibromo-*N*-(3-(imidazo[1,2-a]pyrimidin-2-yl)-3-oxopropyl)-1*H*-pyrrole-2-carboxamide (4 B_3)



To a stirred solution of **3 B** (2.26 g, 0.01 mol) in anhydrous DMF (10 ml), anhydrous sodium carbonate (5.1 g, 0.05 mol) was added and the reaction mixture was stirred for 10 min and 2,2,2-trichloro-1-(4,5-dibromo-1*H*-pyrrol-2-yl)ethanone (5.63 g, 0.015 mol) was added and reaction mixture was stirred at 55 ^{o}C for 2h. After completion of reaction (TLC) solvent was removed. The residue was purified by flash chromatography using methanol:dichloromethane (1:9) as eluent to obtain condensed compound **4 B_3** ((2.4 g, 55 %).

Melting point: 195-200 ^{o}C

IR (ATR): 3227, 3103, 2100, 1647, 1628, 1613, 1514, 1476, 1403, 1326, 1284, 1182, 1136, 1000 cm^{-1}.

^{1}H NMR (DMSO d_6, 300 MHz) : δ 12.68 (s, 1H), 9.79 (dd, *J* = 6.0, 2.1 Hz, 1H), 8.82 (dd, *J* = 4.2, 2.1 Hz, 1H), 8.76 (s, 1H), 8.23 (t, *J* = 5.4 Hz, 1H), 7.38 (dd, *J* = 6.0, 4.2 Hz, 1H), 6.86 (s, 1H), 3.60 (q, *J* = 6.6 Hz, 2H), 3.20 (t, *J* = 6.6 Hz, 2H).

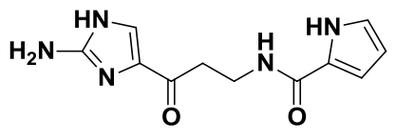
^{13}CNMR (DMSO d_6, 75 MHz): δ 188.7, 158.9, 153.9, 150.59, 144.3, 136.4, 128.0, 121.7, 112.6, 111.8, 104.5, 97.7, 38.7, 34.9.

HRMS (ES+) *m/z* calc. for [$C_{14}H_{11}N_5O_2Br_2$+H^+]: 439.9359; found: 439.9358.

General procedure for synthesis of 5 B_1 - 5 B_3

To the respective keto compound (0.14 mmol) was added hydrazine hydrate (2 mL) and reaction mixture was stirred for 10-30 min at room temp. After completion of reaction (monitored by TLC), hydrazine was removed at rt under reduced pressure in the fume hood. Compound was purified by preparative chromatography using methanol: dichloromethane: NH_4OH (1:9:0.001) to obtain deprotected compound.

N-(3-(2-amino-1H-imidazol-4-yl)-3-oxopropyl)-1*H*-pyrrole-2-carboxamide (5 B_1)

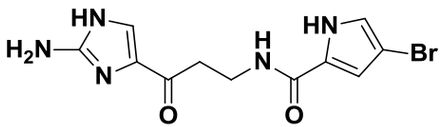


IR (ATR): 3212, 2162, 1608, 1551, 1537, 1419, 1334, 1176, 916, 827, 739, 658 cm^{-1}.

^{1}H NMR (DMSO d_6) : δ 11.55 (s, 1H), 10.87 (s, 1H), 8.30 (t, *J* = 6.0 Hz, 1H), 7.08 (s, 1H), 6.91 (s, 1H), 6.72 (t, *J* = 6.0 Hz, 1H), 6.09 (t, *J* =3.0 Hz, 1H), 5.81 (s, 1H), 3.47 (q, *J* = 6.4 Hz, 2H), 2.92 (t, *J* = 6.4 Hz, 2H).

^{13}C NMR (DMSO-d_6): δ160.8, 153.1, 130.7, 126.0, 125.5, 121.3, 109.8, 108.7, 37.4, 28.9

_N_-(3-(2-amino-1_H_-imidazol-4-yl)-3-oxopropyl)-4-bromo-1_H_-pyrrole-2-carboxamide (5 B_2)

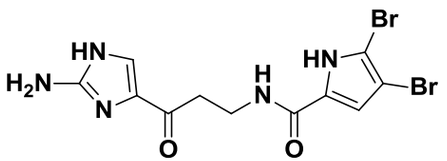


IR (ATR): 3222, 2102, 1608, 1560, 1530, 1519, 1334, 1318, 1235, 1174, 1096, 1000, 827, 739, 655 cm^{-1}.

^{1}H NMR (DMSO d_6): δ 11.92 (s, 1H), 10.87 (s, 1H), 8.49 (s, 1H), 7.17 (s, 2H), 6.81 (s, 1H), 5.81 (s, 2H), 3.47 (q, *J* = 6.4 Hz, 2H), 2.90 (t, *J* = 6.4 Hz, 2H).

^{13}C NMR (DMSO-d_6): δ 190.9, 165.1, 158.4, 136.3, 132.0, 130.6, 126.6, 116.8, 100.4, 42.8, 32.0.

_N_-(3-(2-amino-1_H_-imidazol-4-yl)-3-oxopropyl)-4,5-dibromo-1_H_-pyrrole-2-carboxamide (5 B_3)

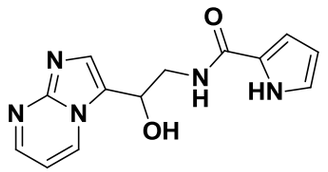


IR (ATR): 3207, 2113, 1610, 1507, 1419, 1394, 1330, 1173, 1198, 1026, 974, 834, 740 cm^{-1}.

^{1}H NMR (DMSO d_6,): δ 8.01 (s, 1H), 6.64 (s, 2H), 6.57 (s, 1H), 6.20 (s, 1H), 5.20 (s, 2H), 3.24 (q, *J* = 6.4 Hz, 2H), 2.57 (t, *J* = 6.4 Hz, 2H).

^{13}C NMR (DMSO-d_6): δ 191.5, 164.4, 158.7, 158.2, 133.4, 131.3, 118.0, 110.0, 103.2, 42.9, 33.8.

***N*-(2-hydroxy-2-(imidazo[1,2-a]pyrimidin-3-yl)ethyl)-1*H*-pyrrole-2-carboxamide (6 A_1) :**



To a well stirred solution of keto compound **4 A_1** (0.47g, 1.76 mmol) in THF:H_2O (9:1) 15 mL was added $NaBH_4$ (0.032g, 0.88 mmol) portion wise at 0 °C and the reaction mixture was continued to stir at room temp. After completion of reaction (30 min), it was quenched using acetic acid. The pH was adjusted to 6.5 and solvent was removed by rotary evaporation under reduced pressure. The resultant residue was purified by flash column chromatography (SiO_2) eluting with dichloromethane:methanol (1:9) to deliver the hydroxyl compound **6 A_1** (0.39, 79%).

Melting point: 240-245 ^oC

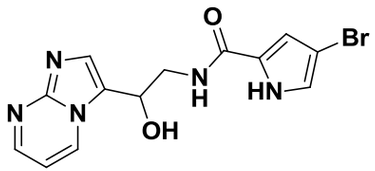
IR (Diamond-ATR, neat): νmax: 3030, 2972, 1634, 1626, 1535, 1350, 1145 cm^{-1}.

^{1}H NMR (DMSO d_6, 300 MHz) : δ 11.84 (s, 1H), 8.95 (d, *J* = 6.8 Hz, 2H), 8.73 (t, *J* = 5.0 Hz, 1H), 8.65 – 8.42 (m, 1H), 7.80 – 7.57 (m, 1H), 7.20 – 6.97 (m, 1H), 6.82 (d, *J* = 6.2 Hz, 1H), 6.05 (d, *J* = 6.2 Hz, 1H), 5.14 (t, *J* = 6.7 Hz, 1H), 3.90 – 3.70 (m, 1H), 3.58 (dt, *J* = 14.2, 6.6 Hz, 1H).

^{13}CNMR (DMSO d_6, 75 MHz): δ 160.87, 149.47, 148.14, 133.92, 131.48, 126.25, 124.24, 121.28, 110.64, 108.25, 63.33, 43.08.

HRMS (ES+) *m/z* calc. for [$C_{13}H_{13}N_5O_2$+H^+]: 272.1147; found: 272.1149

4-bromo-*N*-(2-hydroxy-2-(imidazo[1,2-a]pyrimidin-3-yl)ethyl)-1*H*-pyrrole-2-carboxamide (6 A_2) :



To a well stirred solution of keto compound **4 A_2** (0.44 g, 1.25 mmol) in THF:H_2O (9:1) 15 mL was added $NaBH_4$ (0.025g, 0.68 mmol) portionwise at 0 ^oC and the reaction mixture was continued to stir at room temp. After completion of reaction (30 min), it was quenched using acetic acid. The pH was adjusted to 6.5 and solvent was removed by rotary evaporation under reduced pressure. The resultant residue was purified by flash column chromatography (SiO_2) eluting with dichloromethane:methanol (1:9) to deliver the hydroxyl compound **6 A_2** (0.37g, 90%).

Melting point: 238-241 ^oC

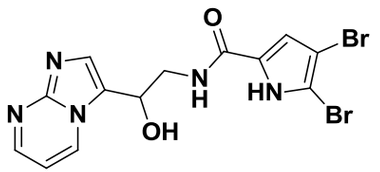
IR (Diamond-ATR, neat): νmax: 3220, 2943, 1606, 1569, 1526, 1327, 1135, 940 cm^{-1}.

^{1}H NMR (DMSO d_6, 300 MHz) : δ 11.78 (s, 1H), 8.93 (dd, *J* = 6.6, 1.2 Hz, 1H), 8.63 – 8.44 (m, 383H), 8.27 (t, *J* = 4.8 Hz, 1H), 7.68 (s, 1H), 7.08 (dd, *J* = 6.2, 4.0 Hz, 1H), 6.95 (s, 1H), 6.80 (s, 1H), 5.90 (s, 1H), 5.11 (t, *J* = 6.1 Hz, 1H), 3.88 – 3.74 (m, 1H), 3.67 – 3.49 (m, 1H).

^{13}CNMR (DMSO d_6, 75 MHz): δ 159.96, 149.59, 148.24, 133.92, 131.75, 126.87, 123.91, 121.53, 111.64, 108.31, 94.82, 63.41, 42.85.

HRMS (ES+) *m/z* calc. for [$C_{13}H_{13}N_5BrO_2$+H^+]: 350.0253; found: 350.0251

4,5-dibromo-*N*-(2-hydroxy-2-(imidazo[1,2-a]pyrimidin-3-yl)ethyl)-1*H*-pyrrole-2-carboxamide (6 A_3) :



To a well stirred solution of keto compound **4 A_3** (0.53 g, 1.25 mmol) in THF:H_2O (9:1) 15 mL was added $NaBH_4$ (0.032 g, 0.88 mmol) portion wise at 0 °C and the reaction mixture was continue to stir at room temp. After completion of reaction (30 min), it was quenched using acetic acid. The pH was adjusted to 6.5 with acetic acid and the solvent was removed by rotary evaporation under reduced pressure. The resulting residue was purified by flash column chromatography (SiO_2) eluting with dichloromethane:methanol (1:9) to deliver the hydroxyl compound **6 A_3** (0.42 g, 80%).

Melting point: 234-238 ^oC

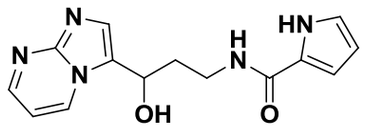
IR (Diamond-ATR, neat): νmax: 3228, 1630, 1614, 1520, 1403, 1327, 1135, 921, 773 cm^{-1}.

^{1}H NMR (DMSO d_6, 300 MHz): δ 12.71 (s, 1H), 8.95 (d, *J* = 6.6 Hz, 1H), 8.57 (d, *J* = 3.8 Hz, 1H), 8.42 – 8.27 (m, 1H), 7.70 (s, 1H), 7.17 – 7.02 (m, 1H), 6.92 (s, 1H), 5.89 (d, *J* = 5.5 Hz, 1H), 5.13 (dd, *J* = 3.7, 2.6 Hz, 1H), 3.94 – 3.73 (m, 1H), 3.60 (dt, *J* = 12.3, 6.7 Hz, 1H).

^{13}CNMR (DMSO d_6, 75 MHz): δ 159.05, 149.59, 148.24, 133.97, 131.94, 127.88, 123.77, 112.66, 108.34, 104.69, 97.76, 63.36, 42.80.

HRMS (ES+) *m/z* calc. for [$C_{14}H_{11}N_5O_2Br_2$+H^+]:427.9358 obsd.: 427.9352

_N_-(3-hydroxy-3-(imidazo[1,2-_a_]pyrimidin-2-yl)propyl)-1_H_-pyrrole-2-carboxamide (6 B_1)



To a well stirred solution of keto compound **4 B_1** (500mg, 1.76 mmol) in THF:H_2O (9:1) 15 mL was added $NaBH_4$ (0.032g, 0.88 mmol) portion wise at 0 °C and the reaction mixture was continued to stir at room temp. After completion of reaction (30 min), it was quenched using acetic acid. The pH was adjusted to 6.5 and solvent was removed by rotary evaporation under reduced pressure. The resultant residue was purified by flash column chromatography (SiO_2) eluting with dichloromethane:methanol (1:9) to deliver the hydroxyl compound **6 B_1** (0.40 g, 80%).

Melting point: 90-95 °C

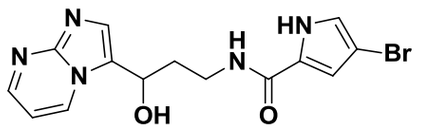
IR (Diamond-ATR, neat): vmax: 3039, 2975, 1635, 1621, 1520, 1403, 1350, 1152, 827, cm^{-1}.

^{1}H NMR (DMSO-D_6): δ 10.82 (s, 1H), 8.27 (dd, *J* = 6.9, 2.1 Hz, 1H), 7.95 (dd, *J* = 2.1, 4.2 Hz, 1H), 7.46 (t, *J* = 5.5 Hz, 1H), 7.11 (s, 1H), 6.48 (dd, *J* = 6.9, 4.2 Hz, 1H), 6.23 (dd, *J* = 1.5, 4.7 Hz, 1H), 6.13 (dd, *J* = 1.5, 2.4 Hz, 1H), 5.46 (dd, *J* = 2.4, 4.7 Hz, 1H), 4.94 (d, *J* = 6.3 Hz, 1H), 4.44 (q, *J* = 6.3 Hz, 1H), 2.78 (q, *J* = 5.4 Hz, 1H), 1.49 – 1.63 (m, 2H).

^{13}CNMR (DMSO-D_6): δ 154.4, 142.4, 140.4, 126.7, 125.9, 122.1, 117.5, 113.4, 101.3, 100.7, 100.5, 53.9, 27.6, 26.2.

HRMS (ES+) *m/z* calc. for [$C_{14}H_{15}N_5O_2$+H^+]: 286.1295, obsd.: 286.1304.

4-bromo-*N*-(3-hydroxy-3-(imidazo[1,2-*a*]pyrimidin-2-yl)propyl)-1*H*-pyrrole-2-carboxamide (6 B_2)



To a well stirred solution of keto compound **6 B_2** (0.5 g, 1.37 mmol) in THF:H_2O (9:1) 15 mL was added $NaBH_4$ (0.025g, 0.68 mmol) portionwise at 0 ^oC and the reaction mixture was continued to stir at room temp. After completion of reaction (30 min), it was quenched using acetic acid. The pH was adjusted to 6.5 and solvent was removed by rotary evaporation under reduced pressure. The resultant residue was purified by flash column chromatography (SiO_2) eluting with dichloromethane:methanol (1:9) to deliver the hydroxyl compound **6 B_2** (0.41g, 82%).

Melting point: 201-205 °C

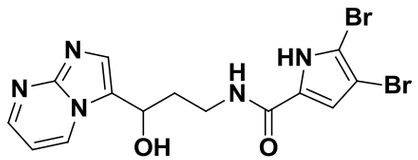
IR (Diamond-ATR, neat): vmax: 3228, 2948, 1604, 1561, 1516, 1403, 1327, 1135, 921, 773 cm^{-1}.

^{1}H NMR (DMSO-D_6): δ 11.85 (s, 1H), 8.88 (dd, *J* = 6.8, 1.9 Hz, 1H), 8.55 (dd, *J* = 4.0, 1.9 Hz, 1H), 8.20 (t, *J* = 5.4 Hz, 1H), 7.72 (s, 1H), 7.08 (dd, *J* = 6.8, 4.0 Hz, 1H), 6.97 (d, *J* = 1.5 Hz, 1H), 6.82 (d, *J* = 1.5 Hz, 1H), 5.54 (d, *J* = 7.5 Hz, 1H), 5.00 – 5.04 (m, 1H), 3.38 (q, *J* = 6.6 Hz, 2H), 2.08 – 2.22 (m, 2H).

^{13}CNMR (DMSO-D_6): δ 158.4, 148.3, 146.9, 132.6, 129.9, 125.5, 124.3, 119.8, 110.0, 107.0, 93.6, 60.1, 34.3, 33.2.

HRMS (ES+) *m/z* calc. for [$C_{14}H_{14}N_5O_2Br+H^+$]: 364.0412, obsd.: 364.0409.

4,5-dibromo-*N*-(3-hydroxy-3-(imidazo[1,2-a]pyrimidin-2-yl)propyl)-1*H*-pyrrole-2-carboxamide (6 B_3)



To a well stirred solution of keto compound **4 B_3**(0.54 g, 1.2 mmol) in THF:H_2O (9:1) 15 mL was added $NaBH_4$ (0.032 g, 0.88 mmol) portion wise at 0 °C and the reaction mixture was continue to stir at room temp. After completion of reaction (30 min), it was quenched using acetic acid. The pH was adjusted to 6.5 with acetic acid and the solvent was removed by rotary evaporation under reduced pressure. The resulting residue was purified by flash column chromatography (SiO_2) eluting with dichloromethane:methanol (1:9) to deliver the hydroxyl compound **6 B_3** (0.42 g, 83%).

Melting point: 200-204 °C

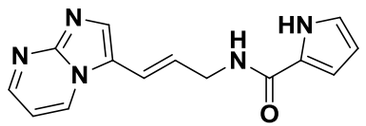
IR (Diamond-ATR, neat): νmax: 3228, 1630, 1614, 1520, 1403, 1327, 1135, 921, 773 cm^{-1}.

^{1}H NMR (DMSO-D_6): δ 12.69 (s, 1H), 8.86 (dd, *J* = 6.8, 1.9 Hz, 1H), 8.55 (dd, *J* = 4.0, 1.9 Hz, 1H), 8.20 (t, *J* = 5.4 Hz, 1H), 7.70 (s, 1H), 7.09 (dd, *J* = 6.8, 4.0 Hz, 1H), 6.90 (s, 1H), 5.53 (d, *J* = 6.0 Hz, 1H), 5.02 (q, *J* = 6.3 Hz, 1H), 3.37 (q, *J* = 5.5 Hz, 2H), 2.09-2.21 (m, 2H).

^{13}CNMR (DMSO-D_6): 159.0, 149.6, 148.1, 133.9, 131.2, 128.1, 125.5, 112.4, 108.3, 104.4, 97.7, 61.3, 35.7, 34.4.

HRMS (ES+) *m/z* calc. for [$C_{14}H_{13}N_5O_2Br_2$+H^+]: 441.9505, obsd.: 441.9514.

(*E*)-*N*-(3-(imidazo[1,2-a]pyrimidin-2-yl)allyl)-1*H*-pyrrole-2-carboxamide (7 B_1)



A solution of compound **6 B_1** (0.350 mmol) in acetic acid (5 mL) was heated at 70 ^{o}C for 8 h. After completion of reaction, acetic acid was removed by evaporation under reduced pressure and compound was purified by using flash chromatography using methanol:dichloromethane (1:9) as eluent to obtain olefin compound **7 B_1** (0.046 g, 50%).

Melting point: 216-220 °C

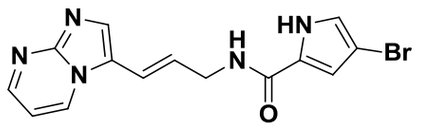
IR (Diamond-ATR, neat): νmax: 3295, 2930, 1632, 1512, 1434, 1170, 1157, 970, 919, 770, 749 cm^{-1}.

^{1}H NMR (DMSO-D_6): δ 11.55 (s, 1H), 9.04 (dd, *J* = 6.9, 2.4 Hz, 1H), 8.52 (dd, *J* = 4.2, 2.4 Hz, 1H), 8.38 (t, *J* = 5.7 Hz, 1H), 8.02 (s, 1H), 7.12 (dd, *J* = 6.9, 4.2 Hz, 1H), 6.77 – 6.92 (m, 1H), 6.40 (dt, *J* = 15.8, 5.8 Hz, 1H), 6.09 (dd, *J* = 2.1, 4.2 Hz, 1H), 4.09 (t, *J* = 5.4 Hz, 2H).

^{13}CNMR (DMSO-D_6): 160.5, 149.4, 148.0, 132.8, 132.3, 127.9, 126.2, 121.6, 121.3, 115.4, 110.1, 109.0, 108.5, 40.7.

HRMS (ES+) *m/z* calc. for [$C_{14}H_{13}N_5O+H^+$]: 268.1188, obsd.: 268.1198.

(*E*)-4-bromo-*N*-(3-(imidazo[1,2-a]pyrimidin-2-yl)allyl)-1*H*-pyrrole-2-carboxamide (7 B_2)



A solution of compound **6 B_2** (0.1 g, 0.274 mmol) in acetic acid (5 mL) was heated at 70 ^{o}C for 8 h. After completion of the reaction acetic acid was removed by evaporation under reduced pressure and the crude compound was purified by flash column chromatography using methanol:dichloromethane (1:9) as eluent to obtain olefin **7 B_2** (0.052 g, 55%).

Melting point: 210-214 °C

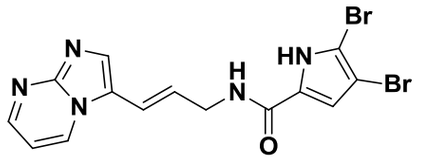
IR (Diamond-ATR, neat): νmax: 3290, 2918, 1629, 1582, 1513, 1434, 11285, 1157, 970, 919, 770, 749 cm^{-1}.

^{1}H NMR (DMSO-D_6): δ 11.87 (s, 1H), 9.03 (dd, *J* = 6.7, 1.5 Hz, 1H), 8.50 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.42 (t, *J* = 6.0 Hz, 1H), 8.01 (s, 1H), 7.10 (dd, *J* = 6.7, 4.0 Hz, 2H), 6.99 (s, 1H), 6.91 (s, 1H), 6.86 (d, *J* = 16.0 Hz, 1H), 6.38 (dt, *J* = 16.0, 5.4 Hz, 1H), 4.08 (t, *J* = 5.4 Hz, 2H).

^{13}CNMR (DMSO-D_6): δ 159.4, 149.4, 148.1, 132.8, 132.3, 127.5, 126.7, 121.5, 121.2, 115.5, 111.6, 109.1, 94.9, 40.7.

HRMS (ES+) *m/z* calc. for [$C_{14}H_{13}N_5OBr+H^+$]: 346.0301 obsd.: 346.0303

(*E*)-4,5-dibromo-*N*-(3-(imidazo[1,2-a]pyrimidin-2-yl)allyl)-1*H*-pyrrole-2-carboxamide (7 B_3)



A solution of compound **6 B_3** (100 mg, 0.226 mmol) in acetic acid (5 mL)was heated at 70 ^{o}C for 8 h. After completion of the reaction acetic acid was removed by rotary evaporation under reduced pressure and the residue was purified by flash column chromatography using methanol:dichloromethane (1:9) as eluent to obtain olefin **7 B_3** (0.053 g, 55%)

Melting point: 185-190 °C

IR (Diamond-ATR, neat): vmax: 3103, 2936, 2851, 1621, 1562, 1509, 1304, 1151, 973, 947, 795, 762 cm^{-1}.

^{1}H NMR (DMSO-D_6): δ 12.76 (s, 1H), 9.08 (dd, *J* = 6.9, 2.1 Hz, 1H), 8.55 (dd, *J* = 4.2, 2.1 Hz, 1H), 8.48 (t, *J* = 5.4 Hz, 1H), 8.06 (s, 1H), 7.16 (dd, *J* = 6.9, 4.2 Hz, 1H), 7.01 (s, 1H), 6.90 (d, *J* = 16.0 Hz, 1H), 6.40 (dt, *J* = 16.0, 5.8 Hz, 1H), 4.08 (t, *J* = 5.4 Hz, 2H).

^{13}CNMR (DMSO-D_6): δ 158.7, 149.8, 147.7, 133.0, 131.5, 128.1, 127.6, 121.7, 115.4, 112.8, 109.3, 104.7, 97.9, 40.3.

HRMS (ES+) *m/z* calc. for [$C_{14}H_{11}N_5O_2Br_2$+H^+]: 423.9407, obsd.: 423.9409.

X-ray Structural data for 2-(2-(imidazo[1,2-a]pyrimidin-3-yl)-2-oxoethyl)isoindoline-1,3-dione (2 A)

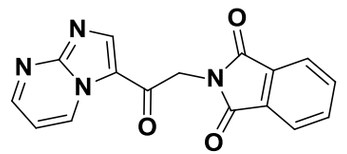


Table 1. Crystal data and structure refinement for GOL09C.

Identification code	gol09c (keene)	
Empirical formula	C16 H10 N4 O3	
Formula weight	306.28	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 6.8351(10) Å	α= 90°.
	b = 14.195(2) Å	β= 96.596(16)°.
	c = 27.980(7) Å	γ = 90°.
Volume	2696.8(9) $Å^3$	
Z	8	
Density (calculated)	1.509 Mg/m^3	
Absorption coefficient	0.109 mm^{-1}	
F(000)	1264	
Crystal size	0.45 x 0.08 x 0.08 mm^3	
Theta range for data collection	3.22 to 27.88°.	
Index ranges	-8<=h<=8, -18<=k<=18, -36<=l<=35	

Reflections collected	24937
Independent reflections	6394 [R(int) = 0.0720]
Completeness to theta = 25.00°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9914 and 0.9527
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6394 / 0 / 415
Goodness-of-fit on F^2	1.030
Final R indices [I>2sigma(I)]	R1 = 0.0626, wR2 = 0.1186
R indices (all data)	R1 = 0.1217, wR2 = 0.1478
Largest diff. peak and hole	0.190 and -0.247 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for GOL09C. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	489(3)	4958(2)	7142(1)	41(1)
C(2)	-173(3)	5275(1)	7603(1)	37(1)
C(3)	-652(3)	4758(2)	7990(1)	45(1)
C(4)	-1177(3)	5255(2)	8382(1)	52(1)
C(5)	-1208(3)	6223(2)	8384(1)	51(1)
C(6)	-749(3)	6744(2)	7993(1)	44(1)
C(7)	-239(3)	6247(1)	7603(1)	36(1)
C(8)	340(3)	6584(2)	7138(1)	40(1)
C(9)	1562(3)	5813(2)	6430(1)	52(1)
C(10)	69(3)	5980(2)	5996(1)	40(1)
C(11)	922(3)	6120(2)	5556(1)	42(1)
C(12)	2857(4)	6188(2)	5464(1)	60(1)
C(13)	1220(4)	6388(2)	4780(1)	53(1)
C(14)	-2095(3)	6272(2)	4954(1)	46(1)
C(15)	-2655(4)	6423(2)	4482(1)	57(1)
C(16)	-1222(5)	6551(2)	4172(1)	66(1)
C(17)	5278(3)	7505(2)	7167(1)	44(1)
C(18)	4700(3)	7887(2)	7623(1)	38(1)
C(19)	4147(3)	7426(2)	8020(1)	47(1)
C(20)	3677(3)	7978(2)	8397(1)	52(1)
C(21)	3756(3)	8943(2)	8377(1)	51(1)

C(22)	4331(3)	9406(2)	7980(1)	44(1)
C(23)	4800(3)	8860(1)	7604(1)	37(1)
C(24)	5490(3)	9126(2)	7139(1)	42(1)
C(25)	6613(3)	8215(2)	6453(1)	56(1)
C(26)	5214(3)	8385(1)	6006(1)	40(1)
C(27)	6187(3)	8497(2)	5578(1)	40(1)
C(28)	8144(3)	8476(2)	5510(1)	51(1)
C(29)	6688(4)	8789(2)	4819(1)	49(1)
C(30)	3296(3)	8814(2)	4954(1)	46(1)
C(31)	2864(4)	9023(2)	4484(1)	59(1)
C(32)	4393(5)	9116(2)	4196(1)	67(1)
N(1)	740(3)	5779(1)	6882(1)	45(1)
N(2)	3064(3)	6346(2)	5000(1)	70(1)
N(3)	-139(3)	6252(1)	5106(1)	40(1)
N(4)	674(4)	6538(2)	4310(1)	67(1)
N(5)	5732(3)	8281(1)	6898(1)	46(1)
N(6)	8477(3)	8646(2)	5056(1)	60(1)
N(7)	5231(3)	8698(1)	5123(1)	39(1)
N(8)	6275(4)	9002(2)	4353(1)	65(1)
O(1)	832(2)	4176(1)	7003(1)	57(1)
O(2)	494(2)	7378(1)	6988(1)	56(1)
O(3)	-1702(2)	5984(1)	6022(1)	54(1)
O(4)	5387(2)	6699(1)	7033(1)	63(1)
O(5)	5835(2)	9893(1)	6981(1)	58(1)
O(6)	3431(2)	8421(1)	6009(1)	56(1)

Table 3. Bond lengths [Å] and angles [°] for GOL09C.

C(1)-O(1)	1.209(2)
C(1)-N(1)	1.396(3)
C(1)-C(2)	1.484(3)
C(2)-C(3)	1.377(3)
C(2)-C(7)	1.381(3)
C(3)-C(4)	1.388(3)
C(3)-H(3A)	0.9300
C(4)-C(5)	1.375(3)
C(4)-H(4A)	0.9300
C(5)-C(6)	1.386(3)
C(5)-H(5A)	0.9300
C(6)-C(7)	1.378(3)
C(6)-H(6A)	0.9300
C(7)-C(8)	1.480(3)
C(8)-O(2)	1.212(2)
C(8)-N(1)	1.393(3)
C(9)-N(1)	1.441(3)
C(9)-C(10)	1.513(3)
C(9)-H(9A)	0.9700
C(9)-H(9B)	0.9700
C(10)-O(3)	1.221(2)
C(10)-C(11)	1.435(3)
C(11)-N(3)	1.392(3)
C(11)-C(12)	1.379(3)
C(12)-N(2)	1.341(3)

C(12)-H(12A)	0.9300
C(13)-N(2)	1.339(3)
C(13)-N(4)	1.343(3)
C(13)-N(3)	1.387(3)
C(14)-C(15)	1.350(3)
C(14)-N(3)	1.356(3)
C(14)-H(14A)	0.9300
C(15)-C(16)	1.392(4)
C(15)-H(15A)	0.9300
C(16)-N(4)	1.309(3)
C(16)-H(16A)	0.9300
C(17)-O(4)	1.209(2)
C(17)-N(5)	1.390(3)
C(17)-C(18)	1.480(3)
C(18)-C(19)	1.379(3)
C(18)-C(23)	1.383(3)
C(19)-C(20)	1.381(3)
C(19)-H(19A)	0.9300
C(20)-C(21)	1.372(3)
C(20)-H(20A)	0.9300
C(21)-C(22)	1.386(3)
C(21)-H(21A)	0.9300
C(22)-C(23)	1.374(3)
C(22)-H(22A)	0.9300
C(23)-C(24)	1.485(3)
C(24)-O(5)	1.208(2)

C(24)-N(5)	1.395(3)
C(25)-N(5)	1.445(3)
C(25)-C(26)	1.505(3)
C(25)-H(25A)	0.9700
C(25)-H(25B)	0.9700
C(26)-O(6)	1.220(2)
C(26)-C(27)	1.444(3)
C(27)-C(28)	1.373(3)
C(27)-N(7)	1.391(3)
C(28)-N(6)	1.339(3)
C(28)-H(28A)	0.9300
C(29)-N(6)	1.337(3)
C(29)-N(8)	1.338(3)
C(29)-N(7)	1.388(3)
C(30)-C(31)	1.347(3)
C(30)-N(7)	1.363(3)
C(30)-H(30A)	0.9300
C(31)-C(32)	1.398(4)
C(31)-H(31A)	0.9300
C(32)-N(8)	1.320(3)
C(32)-H(32A)	0.9300
O(1)-C(1)-N(1)	124.0(2)
O(1)-C(1)-C(2)	130.4(2)
N(1)-C(1)-C(2)	105.62(18)
C(3)-C(2)-C(7)	121.5(2)
C(3)-C(2)-C(1)	130.1(2)

C(7)-C(2)-C(1)	108.38(19)
C(2)-C(3)-C(4)	117.2(2)
C(2)-C(3)-H(3A)	121.4
C(4)-C(3)-H(3A)	121.4
C(5)-C(4)-C(3)	121.1(2)
C(5)-C(4)-H(4A)	119.5
C(3)-C(4)-H(4A)	119.5
C(4)-C(5)-C(6)	121.8(2)
C(4)-C(5)-H(5A)	119.1
C(6)-C(5)-H(5A)	119.1
C(7)-C(6)-C(5)	116.9(2)
C(7)-C(6)-H(6A)	121.5
C(5)-C(6)-H(6A)	121.5
C(6)-C(7)-C(2)	121.5(2)
C(6)-C(7)-C(8)	130.4(2)
C(2)-C(7)-C(8)	108.11(19)
O(2)-C(8)-N(1)	123.6(2)
O(2)-C(8)-C(7)	130.3(2)
N(1)-C(8)-C(7)	106.04(18)
N(1)-C(9)-C(10)	114.43(18)
N(1)-C(9)-H(9A)	108.7
C(10)-C(9)-H(9A)	108.7
N(1)-C(9)-H(9B)	108.7
C(10)-C(9)-H(9B)	108.7
H(9A)-C(9)-H(9B)	107.6
O(3)-C(10)-C(11)	123.68(19)

O(3)-C(10)-C(9)	122.3(2)
C(11)-C(10)-C(9)	114.04(18)
N(3)-C(11)-C(12)	103.5(2)
N(3)-C(11)-C(10)	125.05(18)
C(12)-C(11)-C(10)	131.4(2)
N(2)-C(12)-C(11)	113.7(2)
N(2)-C(12)-H(12A)	123.1
C(11)-C(12)-H(12A)	123.1
N(2)-C(13)-N(4)	126.8(2)
N(2)-C(13)-N(3)	111.0(2)
N(4)-C(13)-N(3)	122.3(2)
C(15)-C(14)-N(3)	117.9(2)
C(15)-C(14)-H(14A)	121.0
N(3)-C(14)-H(14A)	121.0
C(14)-C(15)-C(16)	119.3(2)
C(14)-C(15)-H(15A)	120.3
C(16)-C(15)-H(15A)	120.3
N(4)-C(16)-C(15)	123.9(2)
N(4)-C(16)-H(16A)	118.1
C(15)-C(16)-H(16A)	118.1
O(4)-C(17)-N(5)	123.7(2)
O(4)-C(17)-C(18)	130.3(2)
N(5)-C(17)-C(18)	105.98(19)
C(19)-C(18)-C(23)	121.5(2)
C(19)-C(18)-C(17)	130.2(2)
C(23)-C(18)-C(17)	108.32(19)

C(18)-C(19)-C(20)	117.1(2)
C(18)-C(19)-H(19A)	121.4
C(20)-C(19)-H(19A)	121.4
C(21)-C(20)-C(19)	121.5(2)
C(21)-C(20)-H(20A)	119.3
C(19)-C(20)-H(20A)	119.3
C(20)-C(21)-C(22)	121.5(2)
C(20)-C(21)-H(21A)	119.3
C(22)-C(21)-H(21A)	119.3
C(23)-C(22)-C(21)	117.2(2)
C(23)-C(22)-H(22A)	121.4
C(21)-C(22)-H(22A)	121.4
C(22)-C(23)-C(18)	121.2(2)
C(22)-C(23)-C(24)	130.8(2)
C(18)-C(23)-C(24)	107.98(19)
O(5)-C(24)-N(5)	123.9(2)
O(5)-C(24)-C(23)	130.2(2)
N(5)-C(24)-C(23)	105.85(18)
N(5)-C(25)-C(26)	114.63(18)
N(5)-C(25)-H(25A)	108.6
C(26)-C(25)-H(25A)	108.6
N(5)-C(25)-H(25B)	108.6
C(26)-C(25)-H(25B)	108.6
H(25A)-C(25)-H(25B)	107.6
O(6)-C(26)-C(27)	123.77(19)
O(6)-C(26)-C(25)	122.8(2)

C(27)-C(26)-C(25)	113.47(18)
C(28)-C(27)-N(7)	103.95(19)
C(28)-C(27)-C(26)	131.4(2)
N(7)-C(27)-C(26)	124.64(18)
N(6)-C(28)-C(27)	113.7(2)
N(6)-C(28)-H(28A)	123.2
C(27)-C(28)-H(28A)	123.2
N(6)-C(29)-N(8)	126.5(2)
N(6)-C(29)-N(7)	111.3(2)
N(8)-C(29)-N(7)	122.2(2)
C(31)-C(30)-N(7)	117.4(2)
C(31)-C(30)-H(30A)	121.3
N(7)-C(30)-H(30A)	121.3
C(30)-C(31)-C(32)	119.3(3)
C(30)-C(31)-H(31A)	120.3
C(32)-C(31)-H(31A)	120.3
N(8)-C(32)-C(31)	124.1(2)
N(8)-C(32)-H(32A)	117.9
C(31)-C(32)-H(32A)	117.9
C(8)-N(1)-C(1)	111.82(19)
C(8)-N(1)-C(9)	122.98(19)
C(1)-N(1)-C(9)	124.71(19)
C(13)-N(2)-C(12)	104.7(2)
C(14)-N(3)-C(13)	120.2(2)
C(14)-N(3)-C(11)	132.71(19)
C(13)-N(3)-C(11)	107.13(19)

C(16)-N(4)-C(13)	116.5(2)
C(17)-N(5)-C(24)	111.9(2)
C(17)-N(5)-C(25)	123.8(2)
C(24)-N(5)-C(25)	123.8(2)
C(29)-N(6)-C(28)	104.6(2)
C(30)-N(7)-C(27)	132.7(2)
C(30)-N(7)-C(29)	120.8(2)
C(27)-N(7)-C(29)	106.54(18)
C(32)-N(8)-C(29)	116.1(2)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for GOL09C. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	33(1)	42(1)	46(1)	-3(1)	-3(1)	2(1)
C(2)	31(1)	40(1)	38(1)	0(1)	-6(1)	2(1)
C(3)	37(1)	42(1)	54(2)	10(1)	-3(1)	-4(1)
C(4)	47(1)	66(2)	44(2)	11(1)	4(1)	-8(1)
C(5)	49(1)	64(2)	42(1)	-4(1)	8(1)	0(1)
C(6)	44(1)	44(1)	43(1)	-4(1)	6(1)	1(1)
C(7)	33(1)	39(1)	35(1)	0(1)	-4(1)	2(1)
C(8)	40(1)	42(1)	36(1)	5(1)	-3(1)	2(1)
C(9)	47(1)	72(2)	37(1)	-3(1)	4(1)	7(1)
C(10)	43(1)	43(1)	34(1)	-2(1)	5(1)	2(1)
C(11)	42(1)	47(1)	38(1)	0(1)	9(1)	2(1)
C(12)	47(1)	75(2)	59(2)	6(1)	12(1)	2(1)
C(13)	61(2)	54(2)	49(2)	4(1)	27(1)	0(1)
C(14)	48(1)	50(1)	41(1)	-2(1)	8(1)	-1(1)
C(15)	70(2)	61(2)	38(1)	-1(1)	2(1)	-5(1)
C(16)	99(2)	61(2)	36(2)	2(1)	6(2)	-4(2)
C(17)	43(1)	45(1)	40(1)	0(1)	-6(1)	3(1)
C(18)	34(1)	42(1)	35(1)	2(1)	-3(1)	-2(1)
C(19)	44(1)	46(1)	50(2)	8(1)	1(1)	-2(1)
C(20)	47(1)	67(2)	41(1)	10(1)	5(1)	0(1)
C(21)	43(1)	65(2)	42(1)	-11(1)	-2(1)	7(1)

C(22)	38(1)	43(1)	48(1)	-6(1)	-4(1)	2(1)
C(23)	30(1)	42(1)	36(1)	4(1)	-3(1)	-1(1)
C(24)	35(1)	45(1)	46(1)	7(1)	-3(1)	-1(1)
C(25)	48(1)	82(2)	36(1)	2(1)	3(1)	5(1)
C(26)	43(1)	42(1)	35(1)	-3(1)	4(1)	2(1)
C(27)	41(1)	44(1)	36(1)	-3(1)	6(1)	1(1)
C(28)	44(1)	56(2)	54(2)	-4(1)	11(1)	2(1)
C(29)	62(2)	44(1)	43(1)	-5(1)	22(1)	0(1)
C(30)	48(1)	50(1)	40(1)	-2(1)	5(1)	-2(1)
C(31)	75(2)	58(2)	40(2)	1(1)	-4(1)	0(1)
C(32)	111(2)	55(2)	34(1)	-2(1)	7(2)	0(2)
N(1)	54(1)	48(1)	31(1)	-2(1)	2(1)	5(1)
N(2)	54(1)	94(2)	68(2)	11(1)	30(1)	1(1)
N(3)	48(1)	42(1)	33(1)	0(1)	13(1)	0(1)
N(4)	92(2)	71(2)	43(1)	7(1)	29(1)	-1(1)
N(5)	54(1)	52(1)	31(1)	-1(1)	3(1)	3(1)
N(6)	56(1)	68(2)	62(2)	-5(1)	26(1)	2(1)
N(7)	46(1)	41(1)	33(1)	-4(1)	12(1)	-2(1)
N(8)	95(2)	63(1)	42(1)	1(1)	29(1)	0(1)
O(1)	54(1)	46(1)	69(1)	-16(1)	2(1)	6(1)
O(2)	69(1)	46(1)	54(1)	12(1)	7(1)	2(1)
O(3)	44(1)	82(1)	38(1)	4(1)	9(1)	2(1)
O(4)	77(1)	46(1)	63(1)	-14(1)	2(1)	6(1)
O(5)	55(1)	50(1)	68(1)	18(1)	4(1)	-5(1)
O(6)	41(1)	86(1)	41(1)	2(1)	8(1)	-1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for GOL09C.

	x	y	z	U(eq)
H(3A)	-625	4103	7987	54
H(4A)	-1513	4928	8649	63
H(5A)	-1546	6537	8654	62
H(6A)	-784	7399	7994	52
H(9A)	2234	5222	6387	63
H(9B)	2539	6311	6446	63
H(12A)	3919	6129	5702	71
H(14A)	-3021	6185	5169	55
H(15A)	-3984	6441	4365	68
H(16A)	-1637	6652	3848	79
H(19A)	4094	6773	8033	56
H(20A)	3298	7689	8670	62
H(21A)	3416	9294	8636	61
H(22A)	4396	10060	7969	52
H(25A)	7183	7593	6433	67
H(25B)	7678	8669	6463	67
H(28A)	9145	8356	5757	61
H(30A)	2311	8752	5155	55
H(31A)	1563	9105	4353	70
H(32A)	4064	9267	3873	80

Table 6. Torsion angles [°] for GOL09C.

O(1)-C(1)-C(2)-C(3)	-2.9(4)
N(1)-C(1)-C(2)-C(3)	179.33(19)
O(1)-C(1)-C(2)-C(7)	176.3(2)
N(1)-C(1)-C(2)-C(7)	-1.5(2)
C(7)-C(2)-C(3)-C(4)	-0.9(3)
C(1)-C(2)-C(3)-C(4)	178.19(19)
C(2)-C(3)-C(4)-C(5)	-0.2(3)
C(3)-C(4)-C(5)-C(6)	1.0(3)
C(4)-C(5)-C(6)-C(7)	-0.6(3)
C(5)-C(6)-C(7)-C(2)	-0.5(3)
C(5)-C(6)-C(7)-C(8)	-179.39(19)
C(3)-C(2)-C(7)-C(6)	1.3(3)
C(1)-C(2)-C(7)-C(6)	-178.00(17)
C(3)-C(2)-C(7)-C(8)	-179.61(17)
C(1)-C(2)-C(7)-C(8)	1.1(2)
C(6)-C(7)-C(8)-O(2)	-0.4(4)
C(2)-C(7)-C(8)-O(2)	-179.5(2)
C(6)-C(7)-C(8)-N(1)	178.7(2)
C(2)-C(7)-C(8)-N(1)	-0.3(2)
N(1)-C(9)-C(10)-O(3)	-7.5(3)
N(1)-C(9)-C(10)-C(11)	173.25(19)
O(3)-C(10)-C(11)-N(3)	-1.7(4)
C(9)-C(10)-C(11)-N(3)	177.6(2)
O(3)-C(10)-C(11)-C(12)	176.0(2)

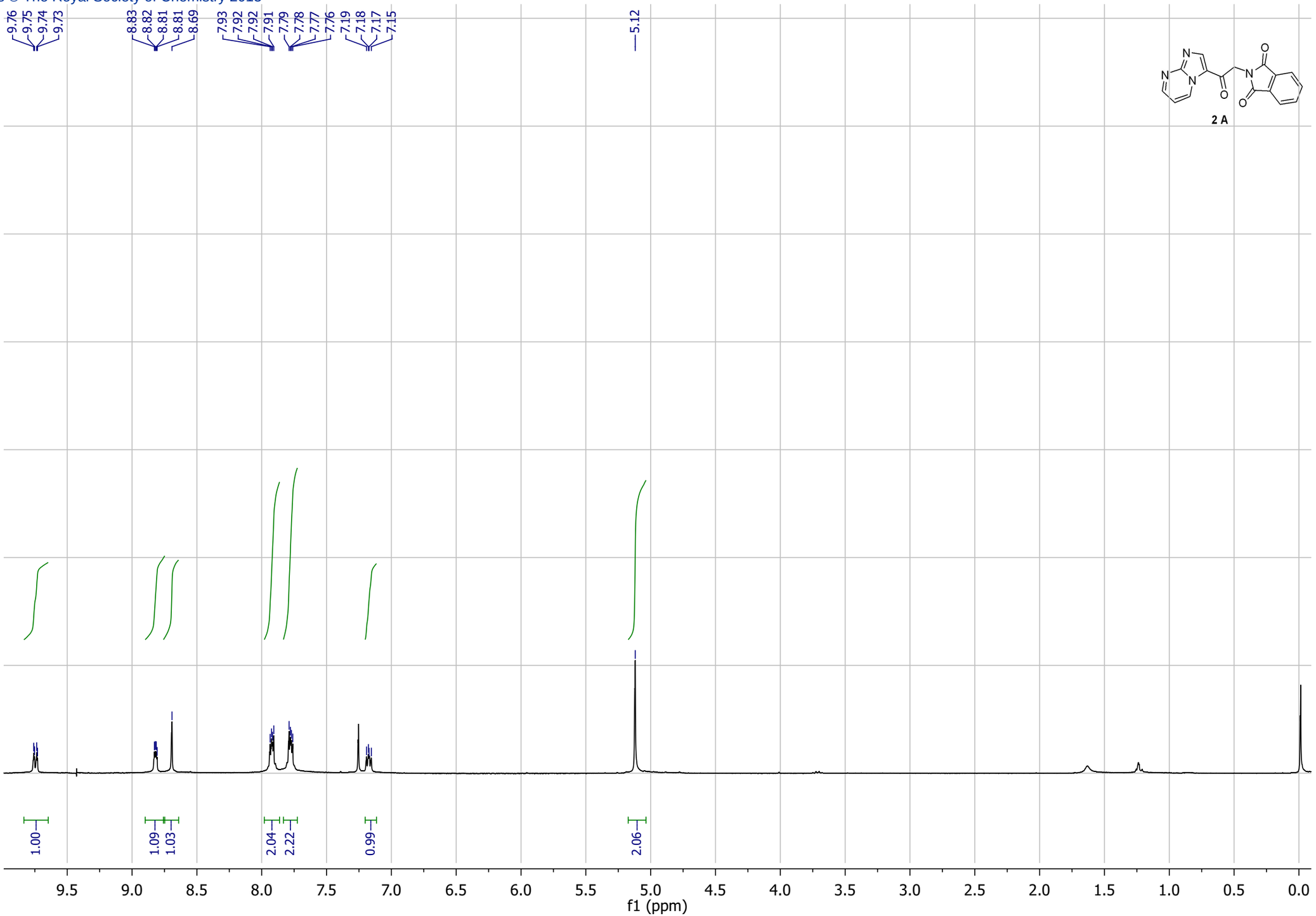
C(9)-C(10)-C(11)-C(12)	-4.7(4)
N(3)-C(11)-C(12)-N(2)	-0.2(3)
C(10)-C(11)-C(12)-N(2)	-178.3(2)
N(3)-C(14)-C(15)-C(16)	0.0(3)
C(14)-C(15)-C(16)-N(4)	-0.2(4)
O(4)-C(17)-C(18)-C(19)	0.7(4)
N(5)-C(17)-C(18)-C(19)	-178.7(2)
O(4)-C(17)-C(18)-C(23)	-179.7(2)
N(5)-C(17)-C(18)-C(23)	0.9(2)
C(23)-C(18)-C(19)-C(20)	0.7(3)
C(17)-C(18)-C(19)-C(20)	-179.78(19)
C(18)-C(19)-C(20)-C(21)	0.0(3)
C(19)-C(20)-C(21)-C(22)	-0.7(3)
C(20)-C(21)-C(22)-C(23)	0.6(3)
C(21)-C(22)-C(23)-C(18)	0.0(3)
C(21)-C(22)-C(23)-C(24)	-178.82(19)
C(19)-C(18)-C(23)-C(22)	-0.7(3)
C(17)-C(18)-C(23)-C(22)	179.68(17)
C(19)-C(18)-C(23)-C(24)	178.39(18)
C(17)-C(18)-C(23)-C(24)	-1.3(2)
C(22)-C(23)-C(24)-O(5)	1.2(4)
C(18)-C(23)-C(24)-O(5)	-177.7(2)
C(22)-C(23)-C(24)-N(5)	-179.9(2)
C(18)-C(23)-C(24)-N(5)	1.1(2)
N(5)-C(25)-C(26)-O(6)	-11.6(3)
N(5)-C(25)-C(26)-C(27)	168.63(19)

O(6)-C(26)-C(27)-C(28)	-179.9(2)
C(25)-C(26)-C(27)-C(28)	-0.1(3)
O(6)-C(26)-C(27)-N(7)	2.9(3)
C(25)-C(26)-C(27)-N(7)	-177.29(19)
N(7)-C(27)-C(28)-N(6)	0.0(3)
C(26)-C(27)-C(28)-N(6)	-177.6(2)
N(7)-C(30)-C(31)-C(32)	-0.3(3)
C(30)-C(31)-C(32)-N(8)	0.7(4)
O(2)-C(8)-N(1)-C(1)	178.55(19)
C(7)-C(8)-N(1)-C(1)	-0.6(2)
O(2)-C(8)-N(1)-C(9)	6.2(3)
C(7)-C(8)-N(1)-C(9)	-172.95(17)
O(1)-C(1)-N(1)-C(8)	-176.64(19)
C(2)-C(1)-N(1)-C(8)	1.3(2)
O(1)-C(1)-N(1)-C(9)	-4.5(3)
C(2)-C(1)-N(1)-C(9)	173.46(17)
C(10)-C(9)-N(1)-C(8)	-82.9(3)
C(10)-C(9)-N(1)-C(1)	105.7(2)
N(4)-C(13)-N(2)-C(12)	179.8(2)
N(3)-C(13)-N(2)-C(12)	-0.2(3)
C(11)-C(12)-N(2)-C(13)	0.3(3)
C(15)-C(14)-N(3)-C(13)	0.3(3)
C(15)-C(14)-N(3)-C(11)	179.8(2)
N(2)-C(13)-N(3)-C(14)	179.75(19)
N(4)-C(13)-N(3)-C(14)	-0.3(3)
N(2)-C(13)-N(3)-C(11)	0.2(3)

N(4)-C(13)-N(3)-C(11)	-179.9(2)
C(12)-C(11)-N(3)-C(14)	-179.5(2)
C(10)-C(11)-N(3)-C(14)	-1.3(4)
C(12)-C(11)-N(3)-C(13)	0.0(2)
C(10)-C(11)-N(3)-C(13)	178.3(2)
C(15)-C(16)-N(4)-C(13)	0.2(4)
N(2)-C(13)-N(4)-C(16)	180.0(3)
N(3)-C(13)-N(4)-C(16)	0.1(4)
O(4)-C(17)-N(5)-C(24)	-179.6(2)
C(18)-C(17)-N(5)-C(24)	-0.2(2)
O(4)-C(17)-N(5)-C(25)	-7.9(3)
C(18)-C(17)-N(5)-C(25)	171.54(17)
O(5)-C(24)-N(5)-C(17)	178.38(19)
C(23)-C(24)-N(5)-C(17)	-0.5(2)
O(5)-C(24)-N(5)-C(25)	6.6(3)
C(23)-C(24)-N(5)-C(25)	-172.28(17)
C(26)-C(25)-N(5)-C(17)	104.3(2)
C(26)-C(25)-N(5)-C(24)	-84.9(3)
N(8)-C(29)-N(6)-C(28)	178.7(2)
N(7)-C(29)-N(6)-C(28)	-0.7(3)
C(27)-C(28)-N(6)-C(29)	0.4(3)
C(31)-C(30)-N(7)-C(27)	179.0(2)
C(31)-C(30)-N(7)-C(29)	-0.3(3)
C(28)-C(27)-N(7)-C(30)	-179.7(2)
C(26)-C(27)-N(7)-C(30)	-1.9(4)
C(28)-C(27)-N(7)-C(29)	-0.4(2)

C(26)-C(27)-N(7)-C(29)	177.4(2)
N(6)-C(29)-N(7)-C(30)	-179.88(19)
N(8)-C(29)-N(7)-C(30)	0.7(3)
N(6)-C(29)-N(7)-C(27)	0.7(3)
N(8)-C(29)-N(7)-C(27)	-178.7(2)
C(31)-C(32)-N(8)-C(29)	-0.3(4)
N(6)-C(29)-N(8)-C(32)	-179.7(2)
N(7)-C(29)-N(8)-C(32)	-0.4(3)

Symmetry transformations used to generate equivalent atoms:



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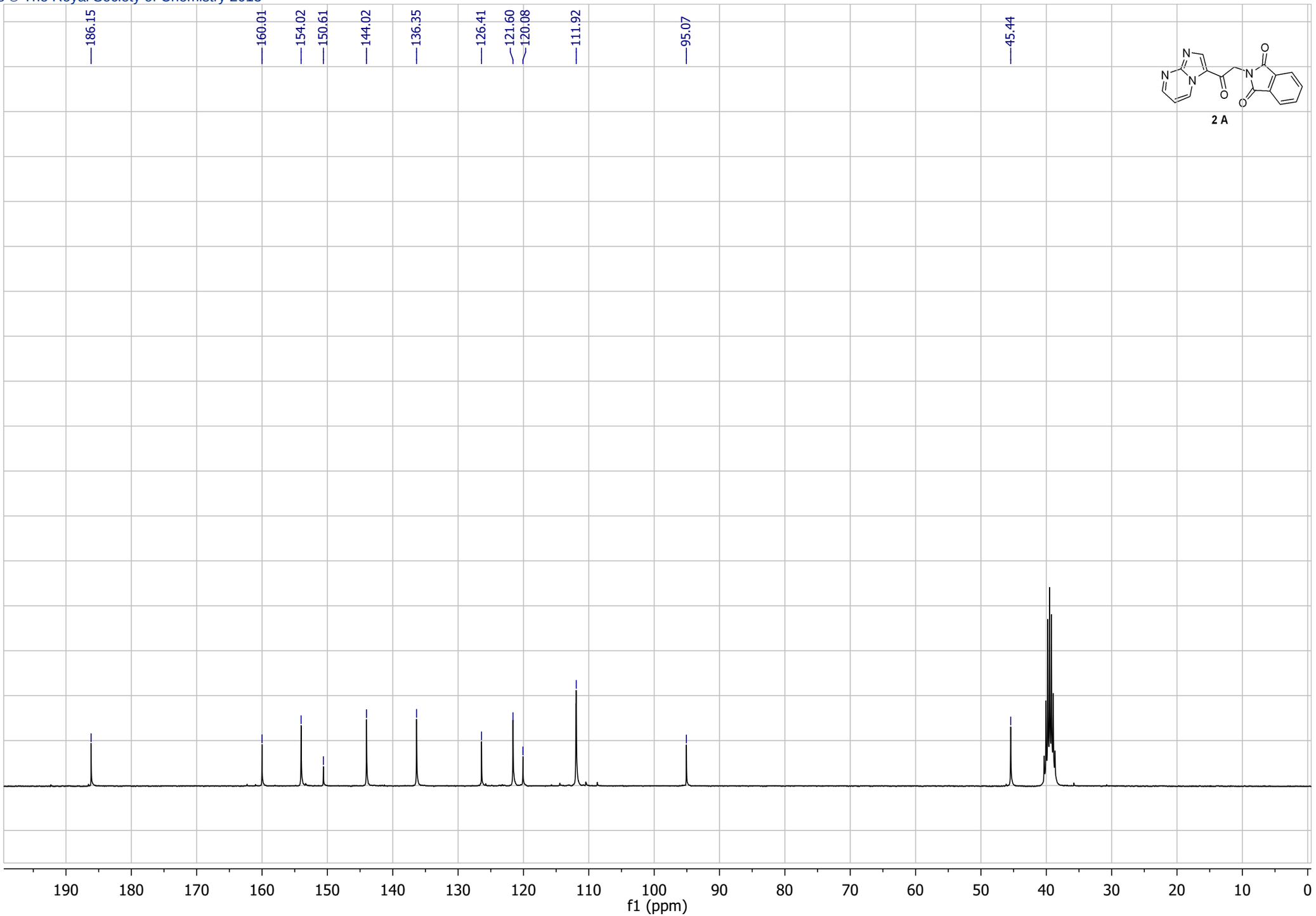

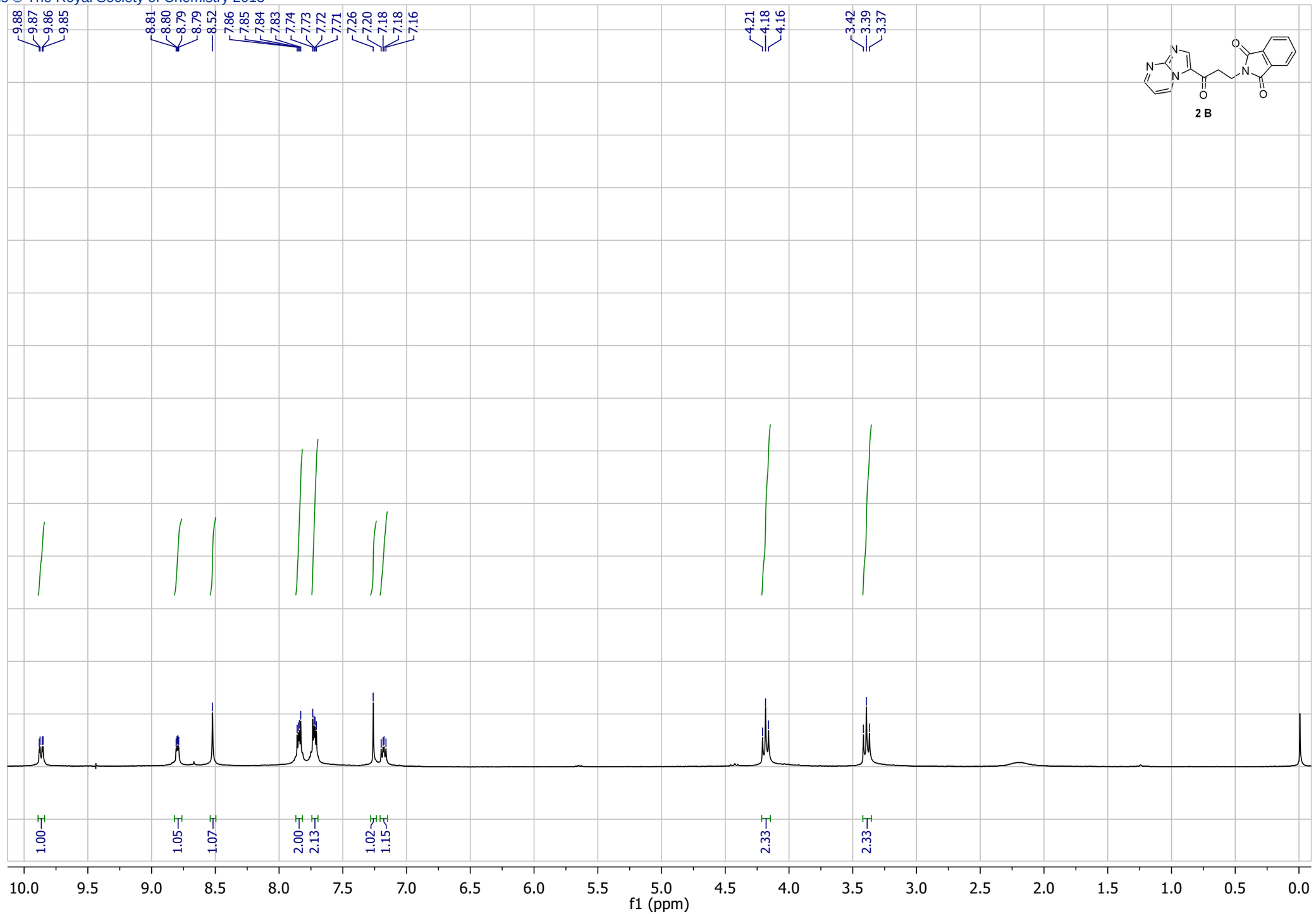

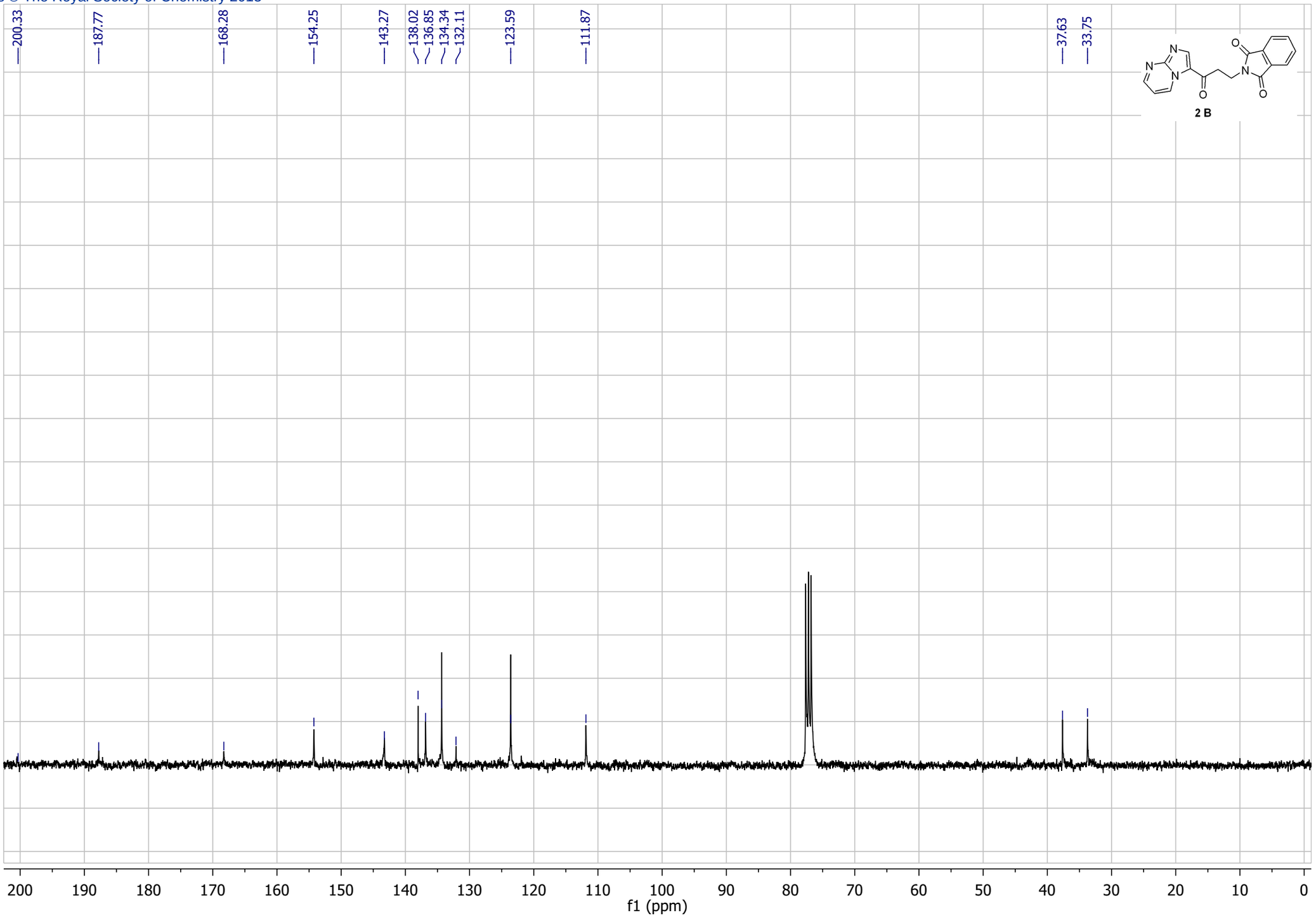

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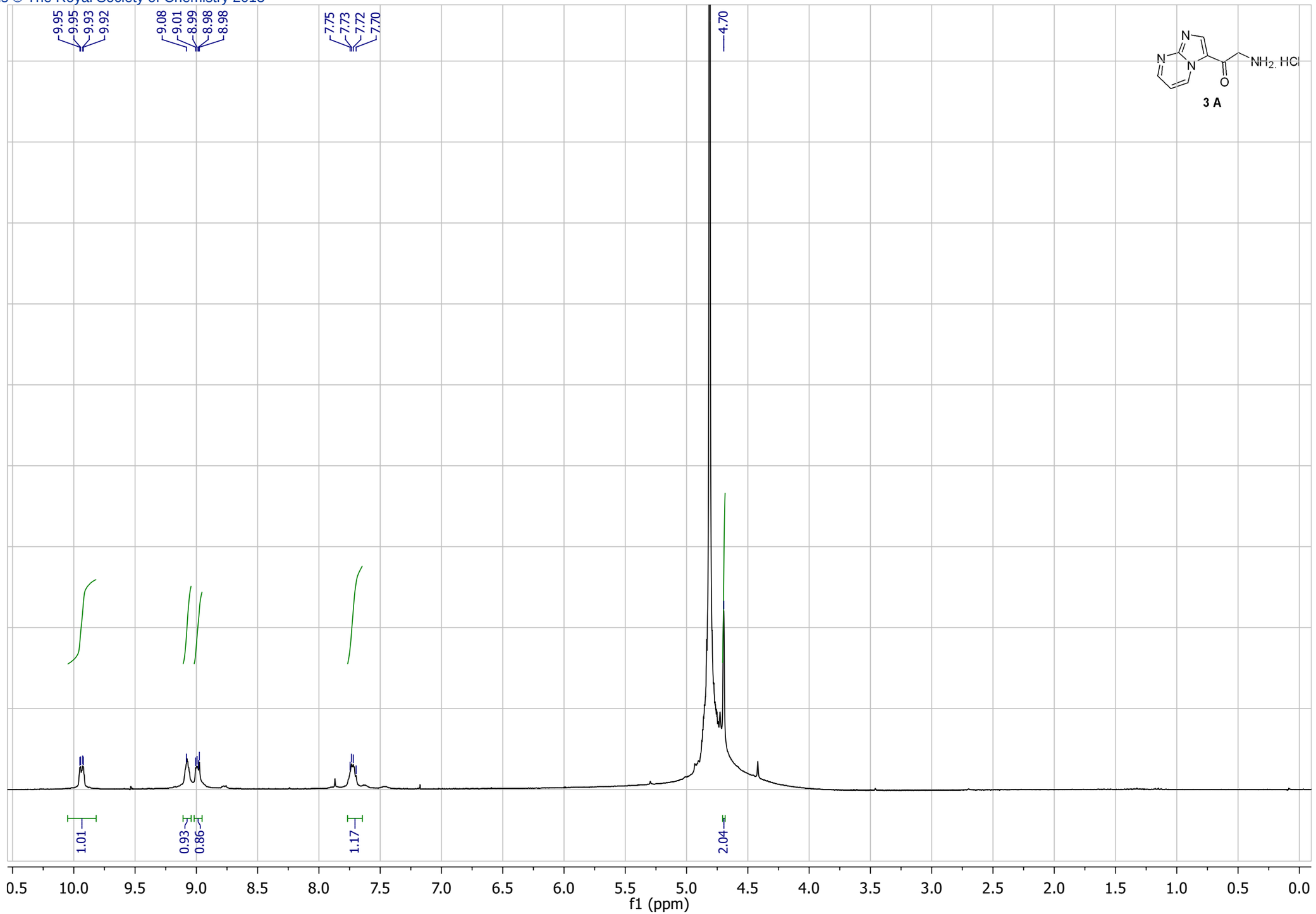

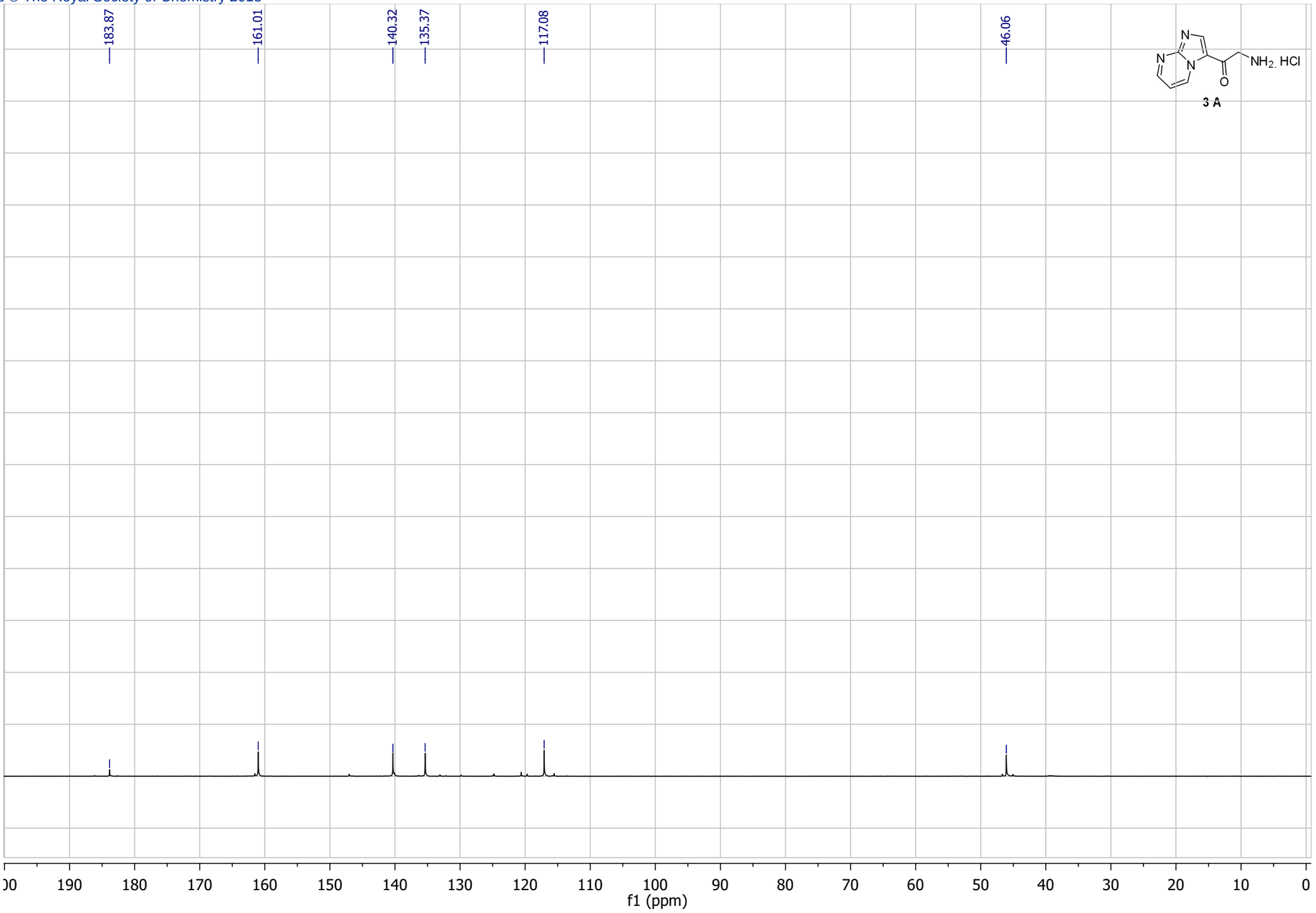

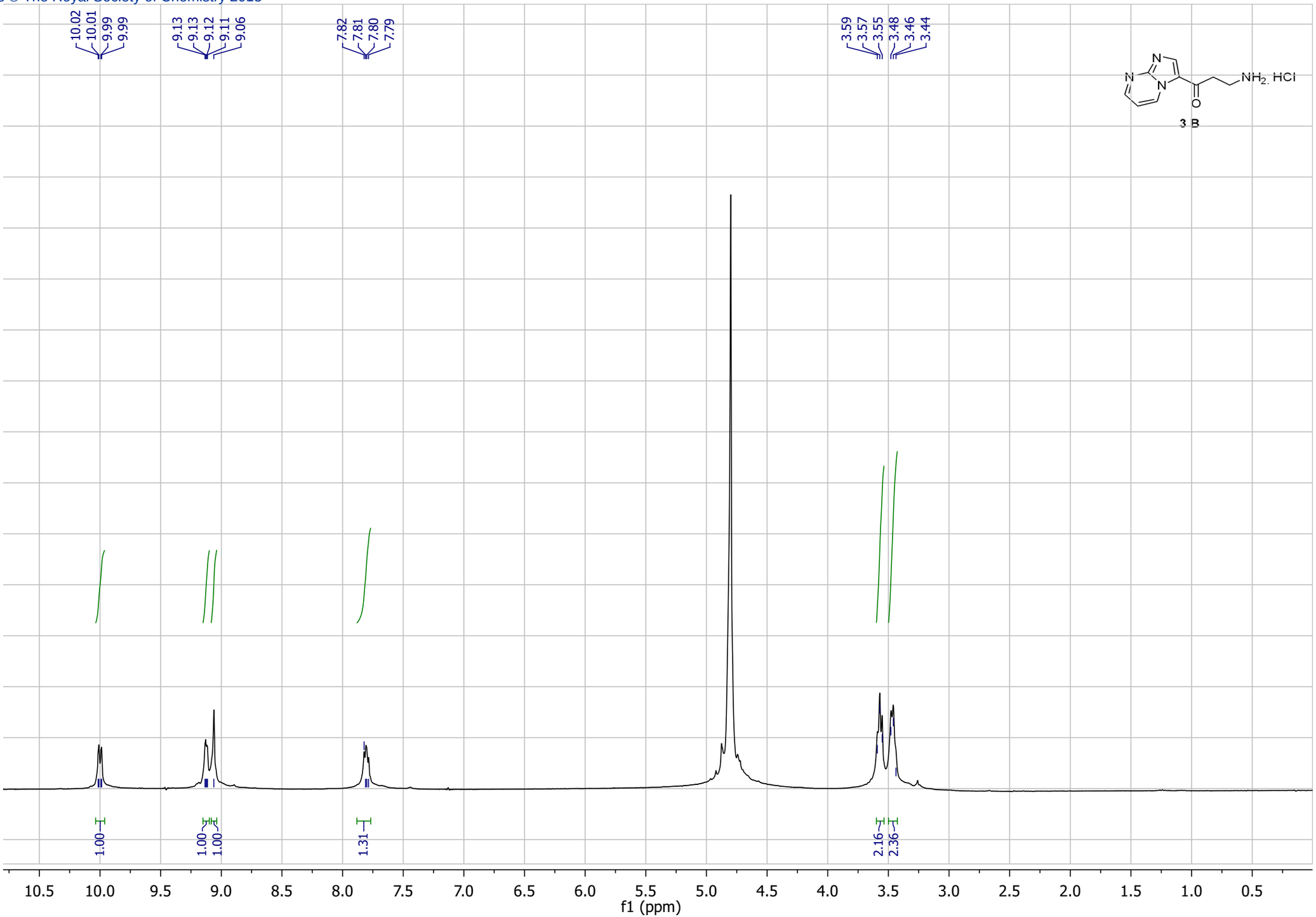

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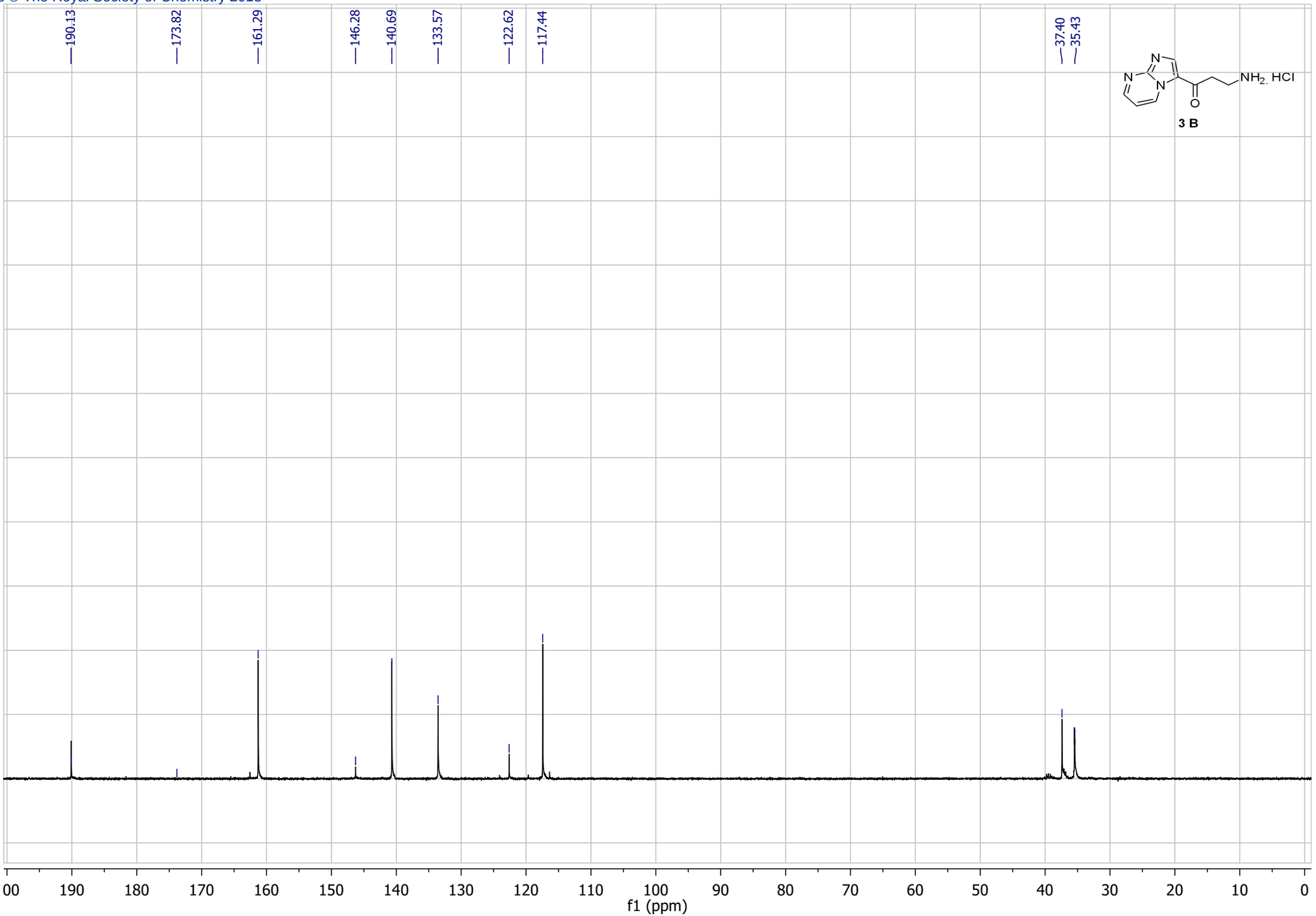
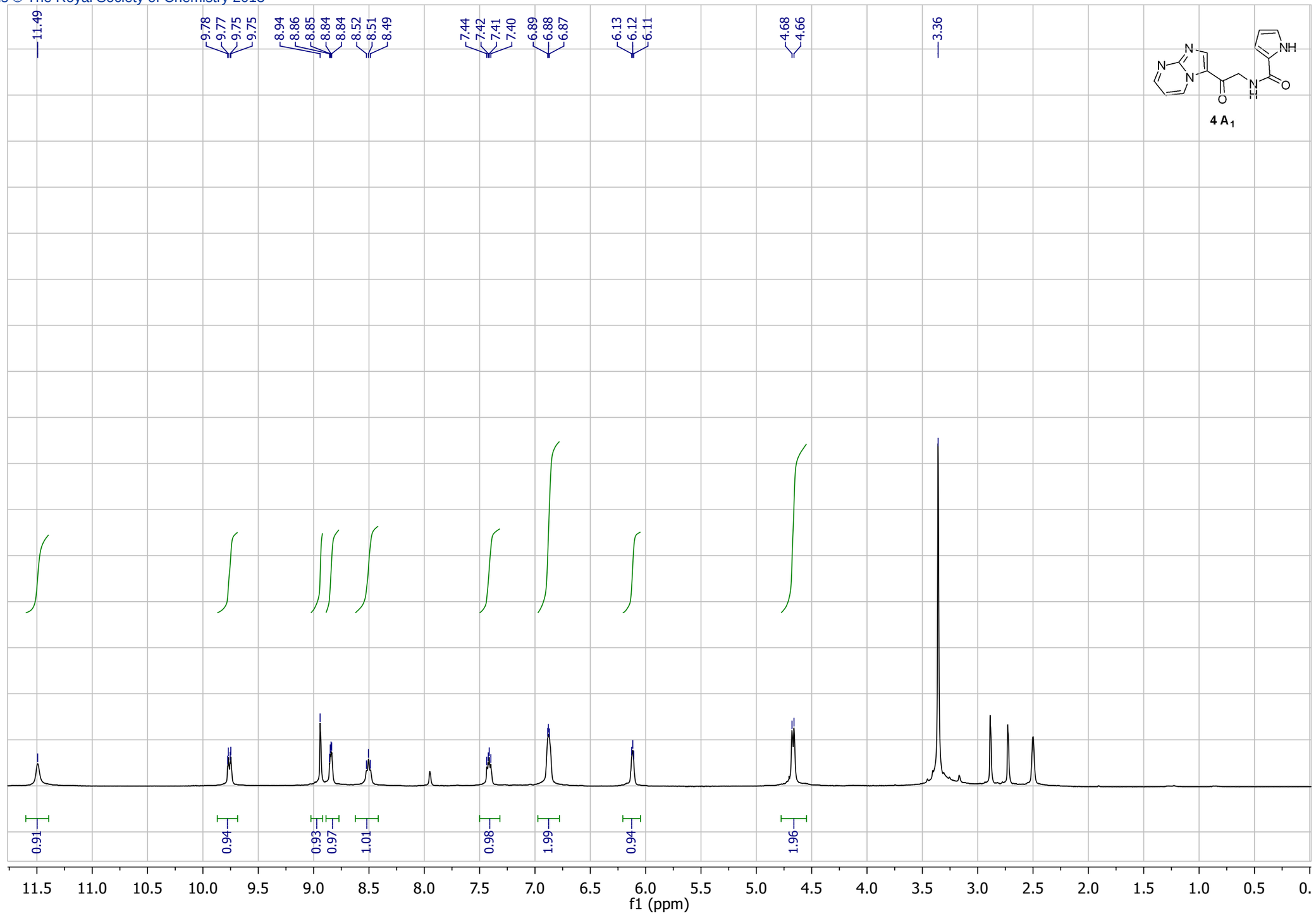
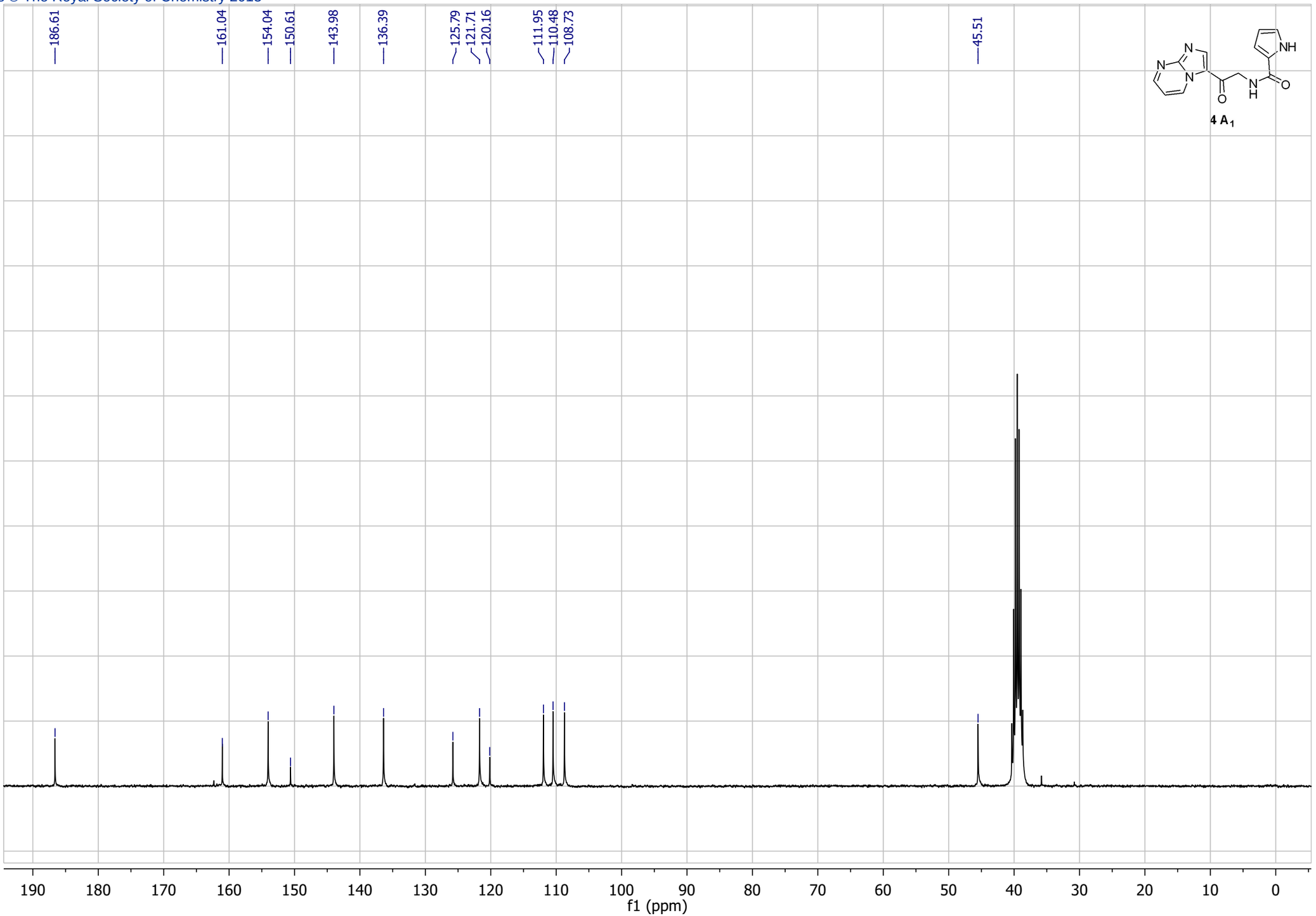
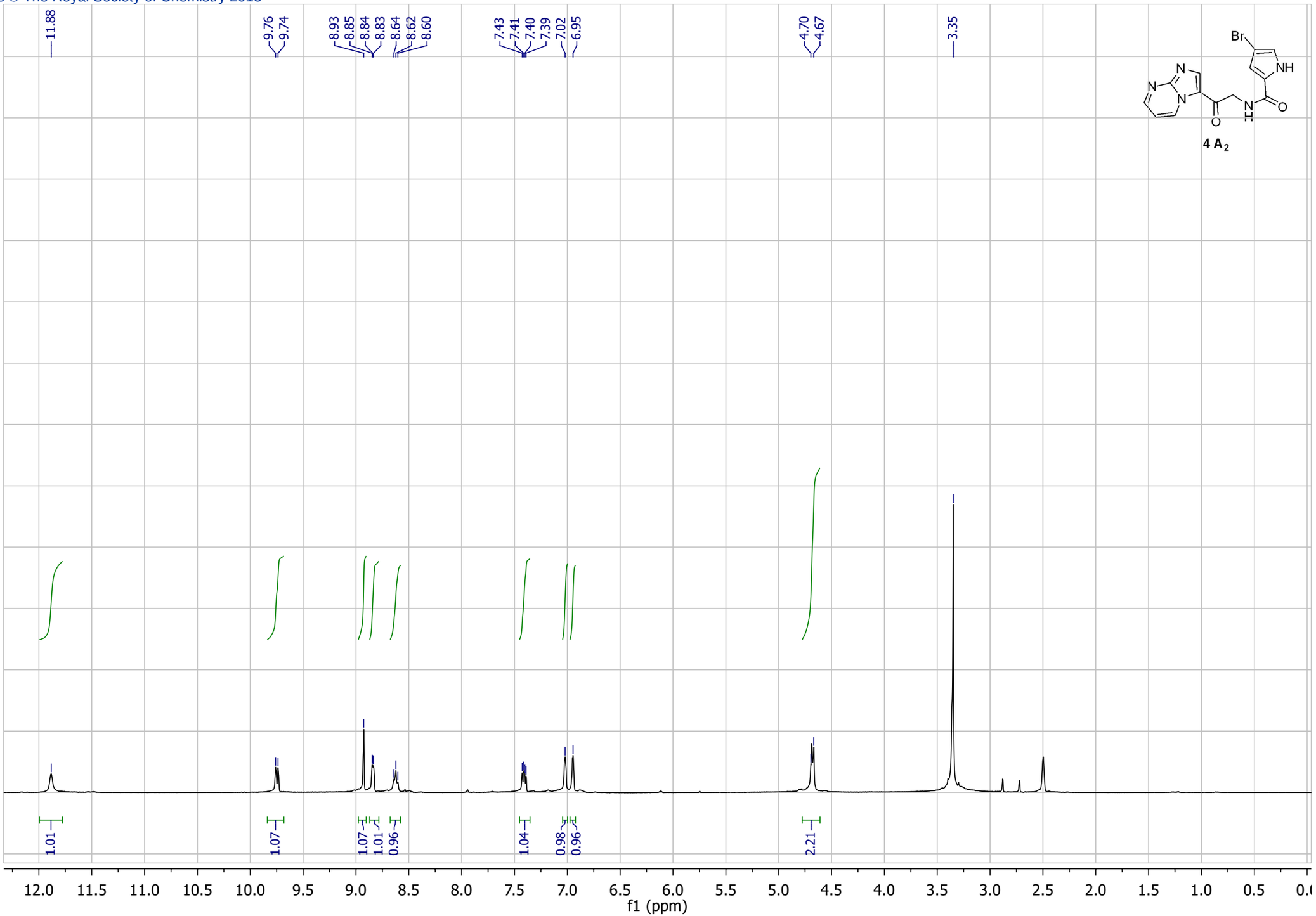




4 A$_1$





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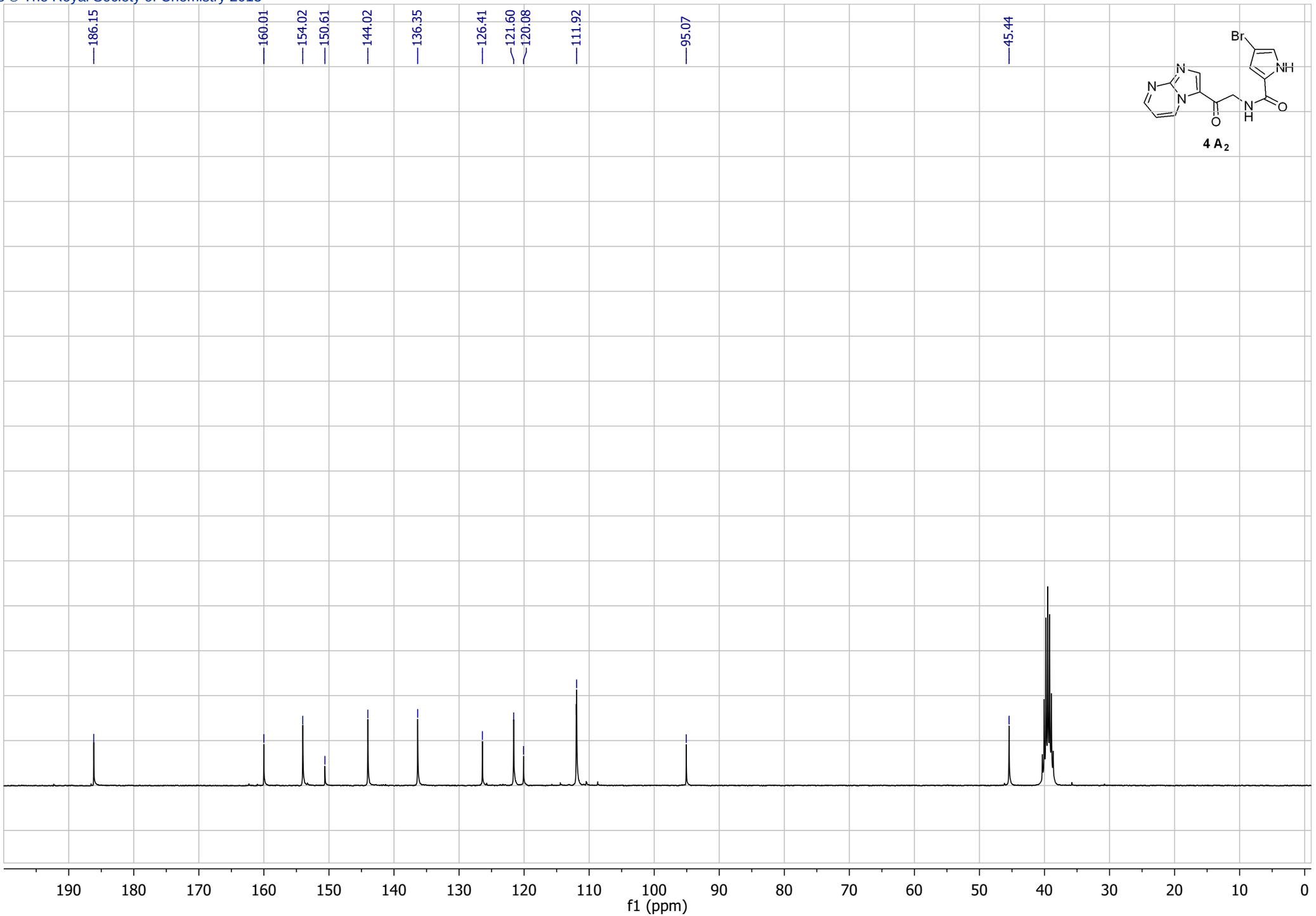

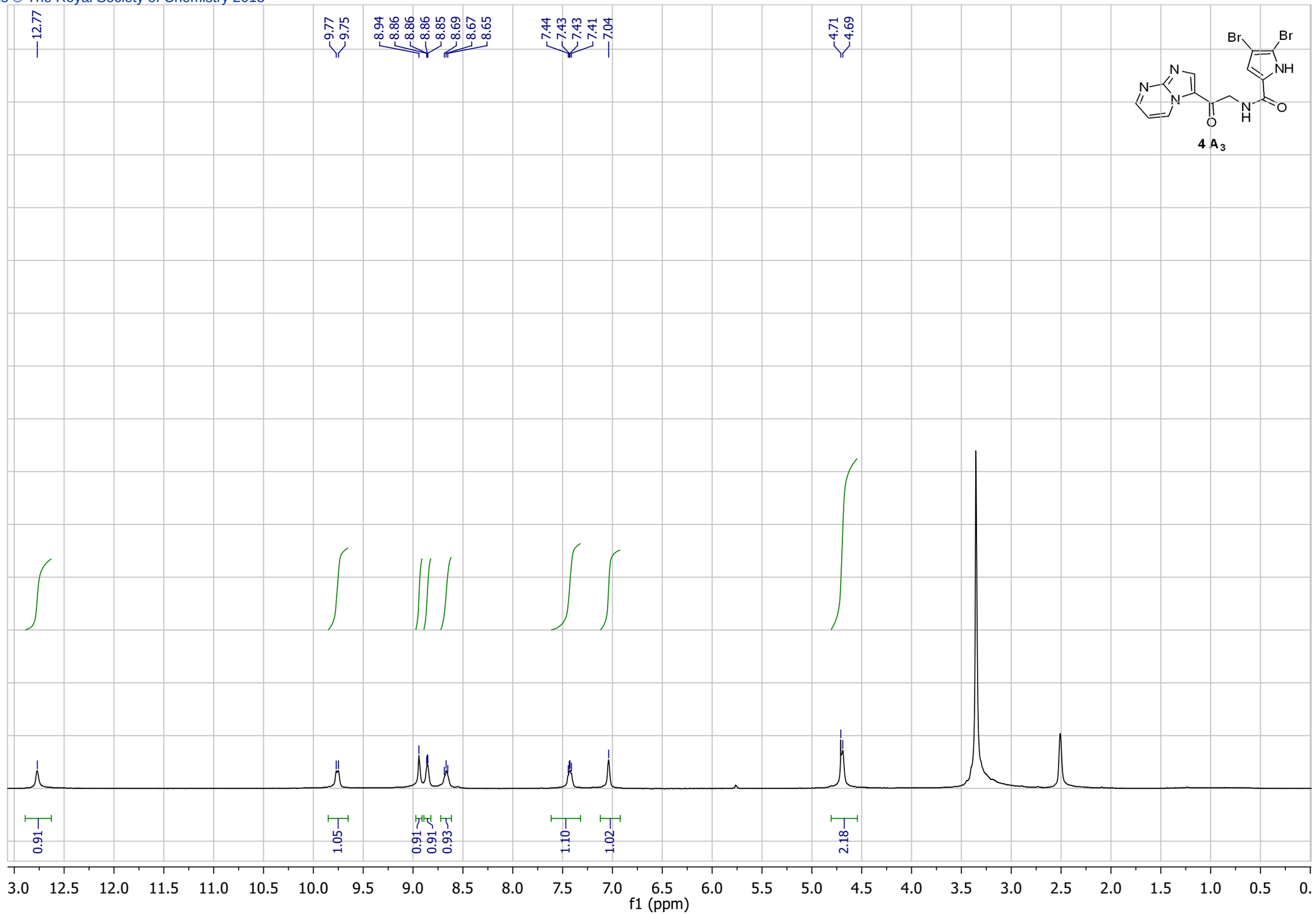

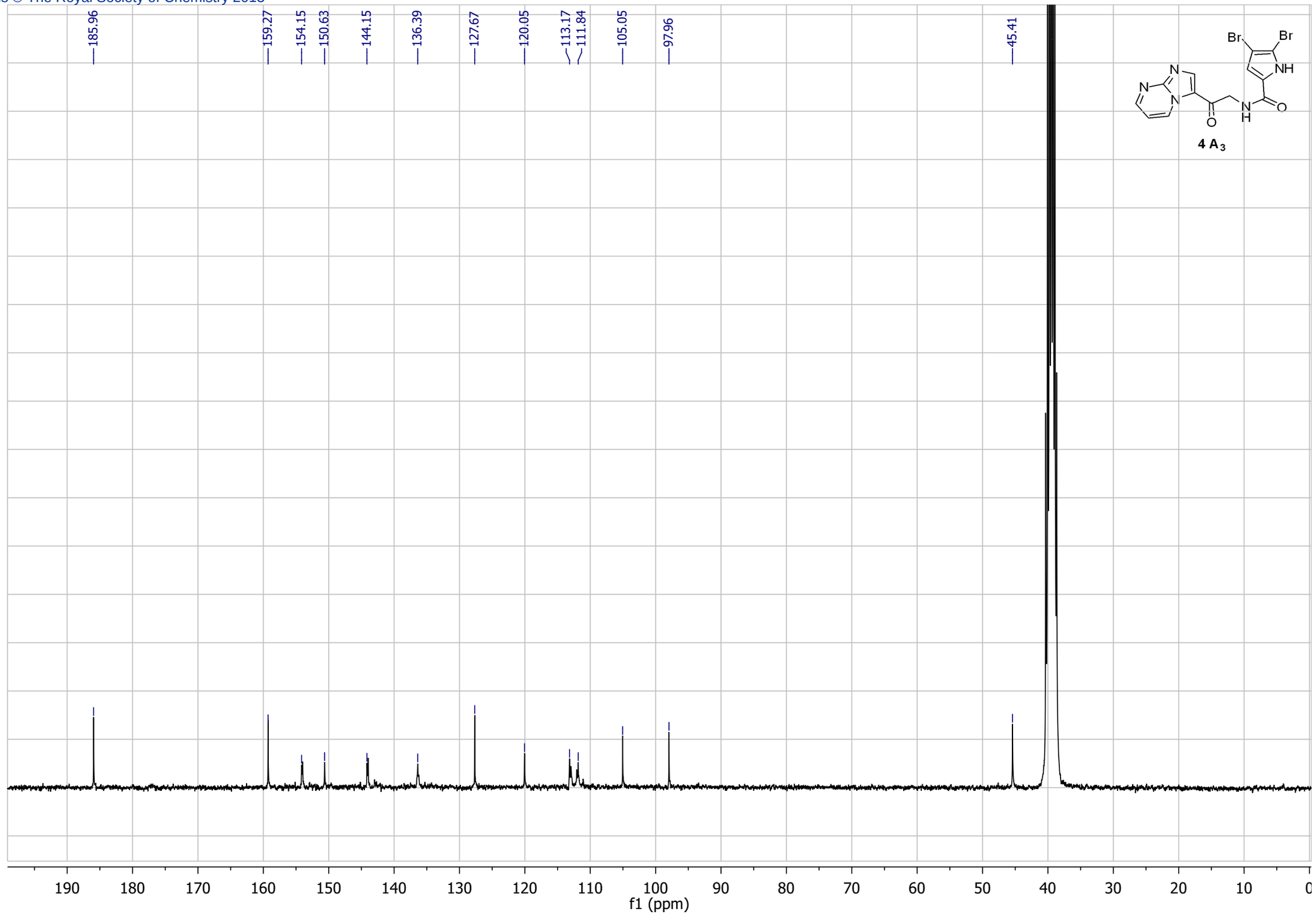

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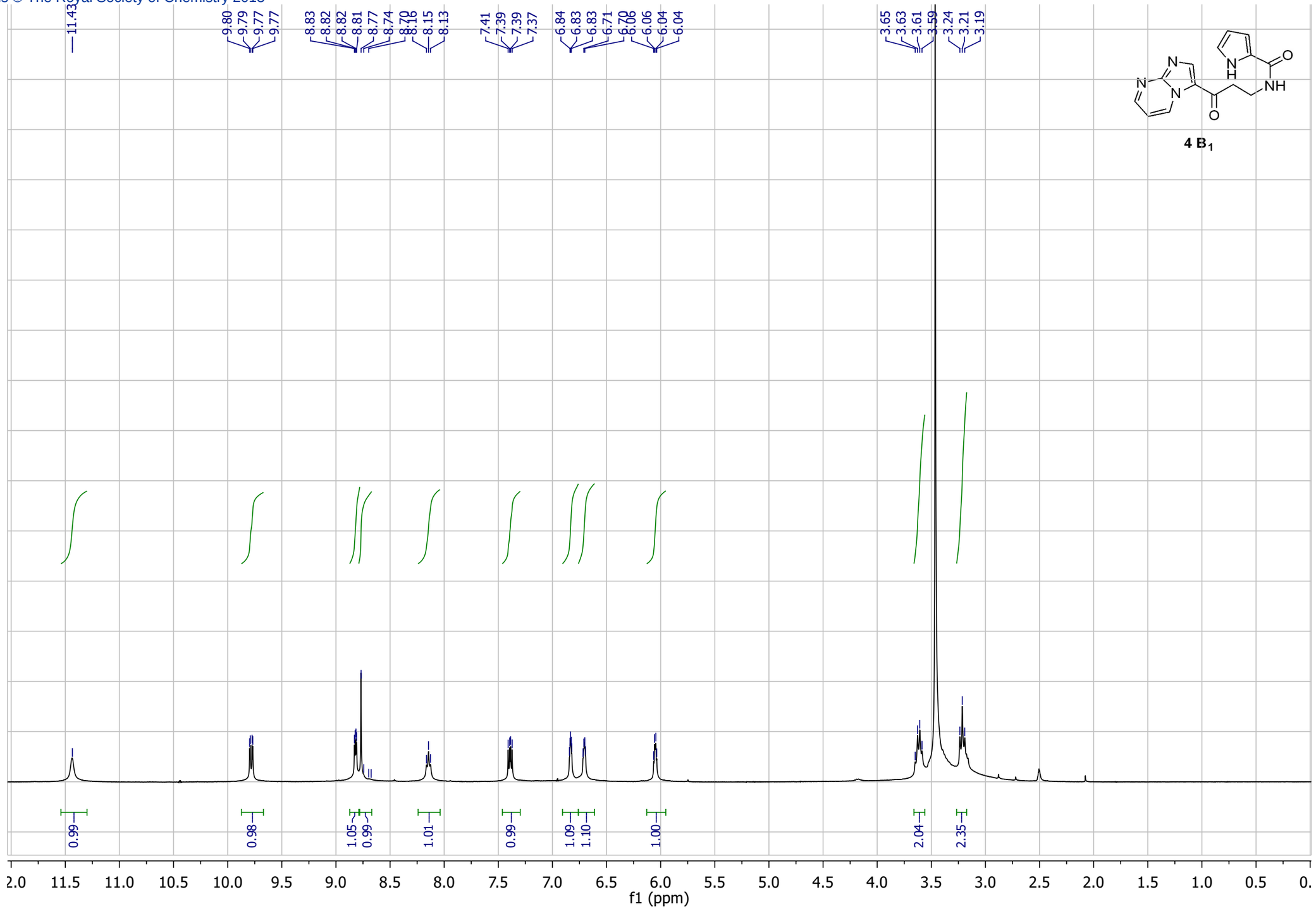
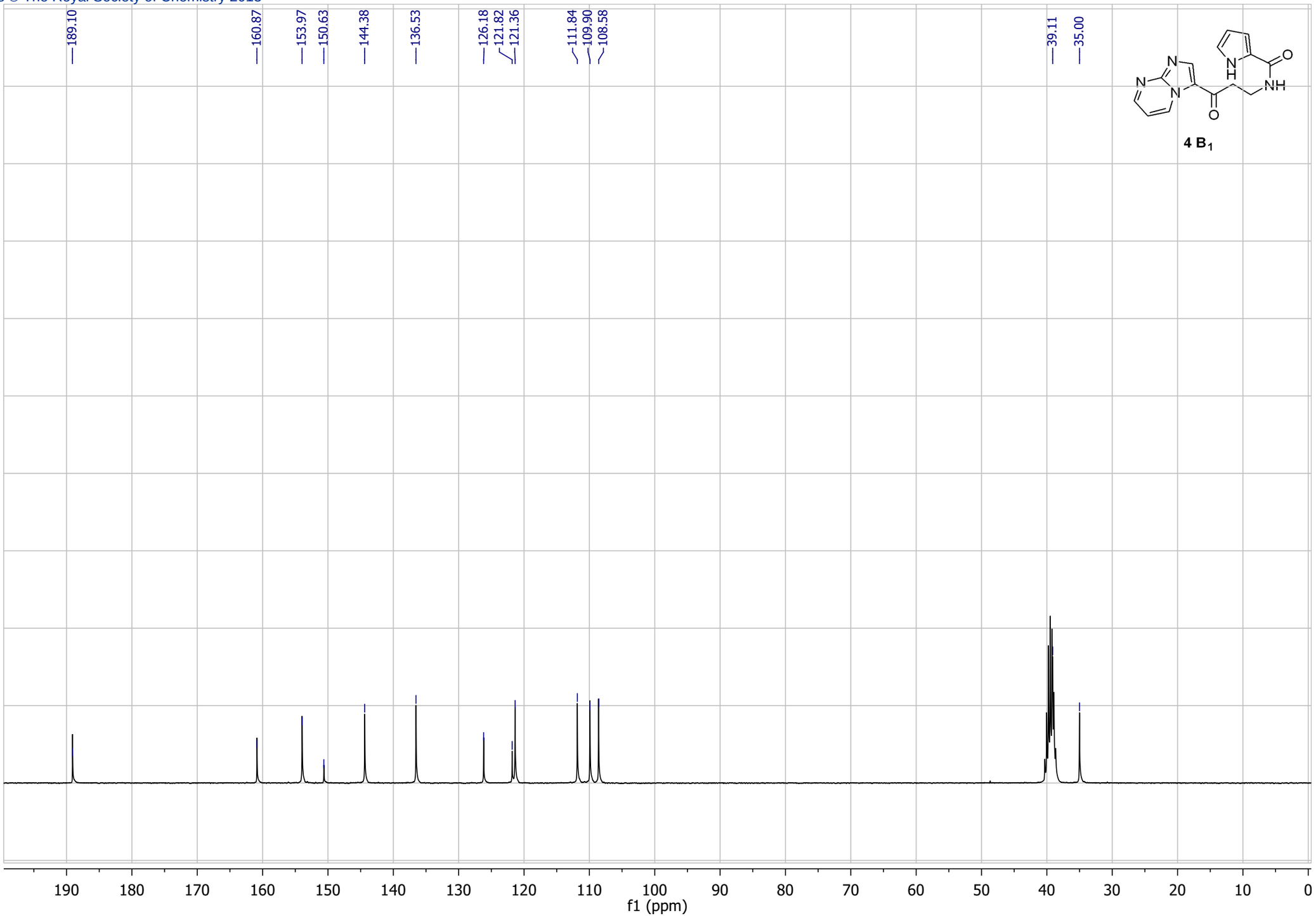
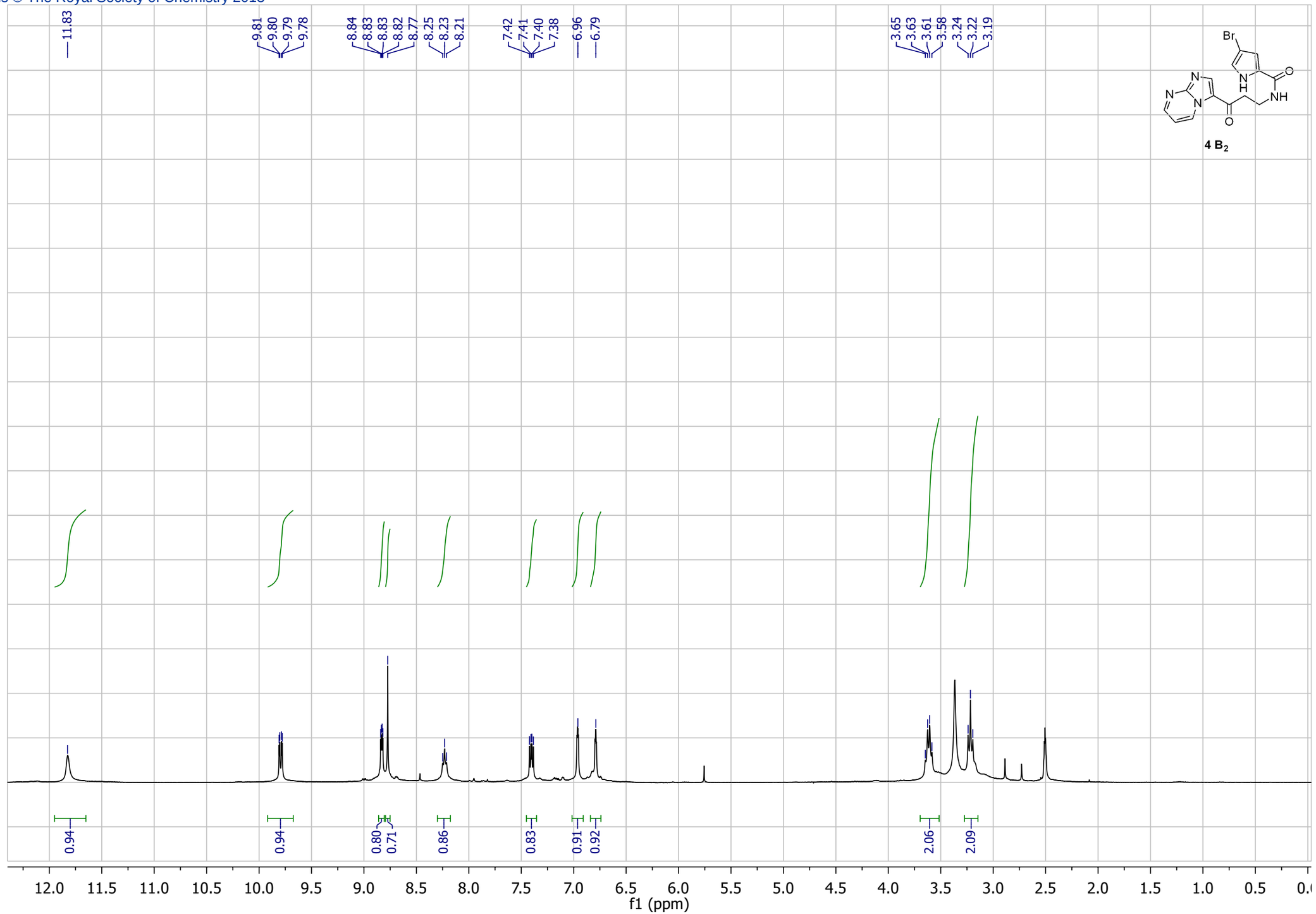
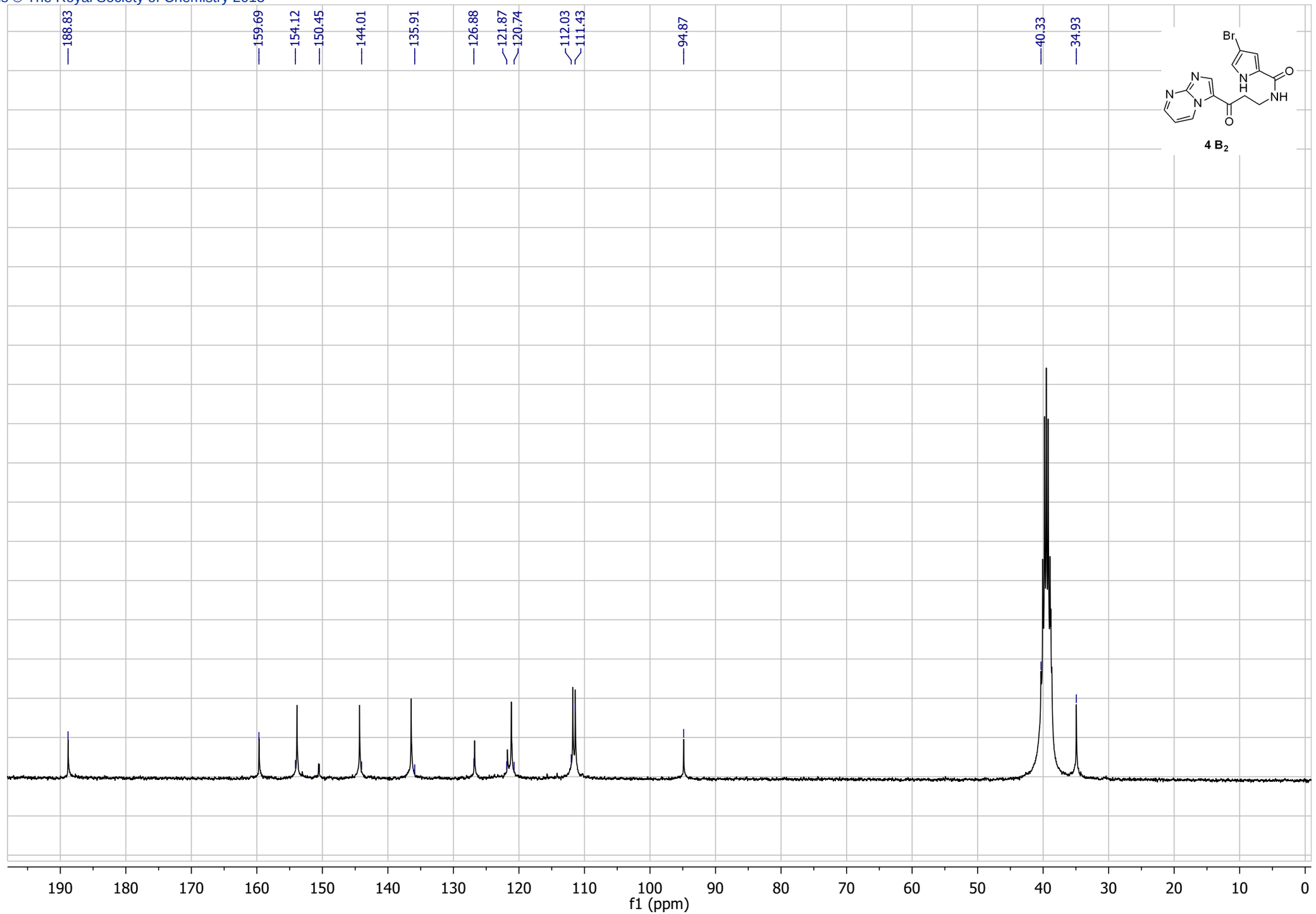
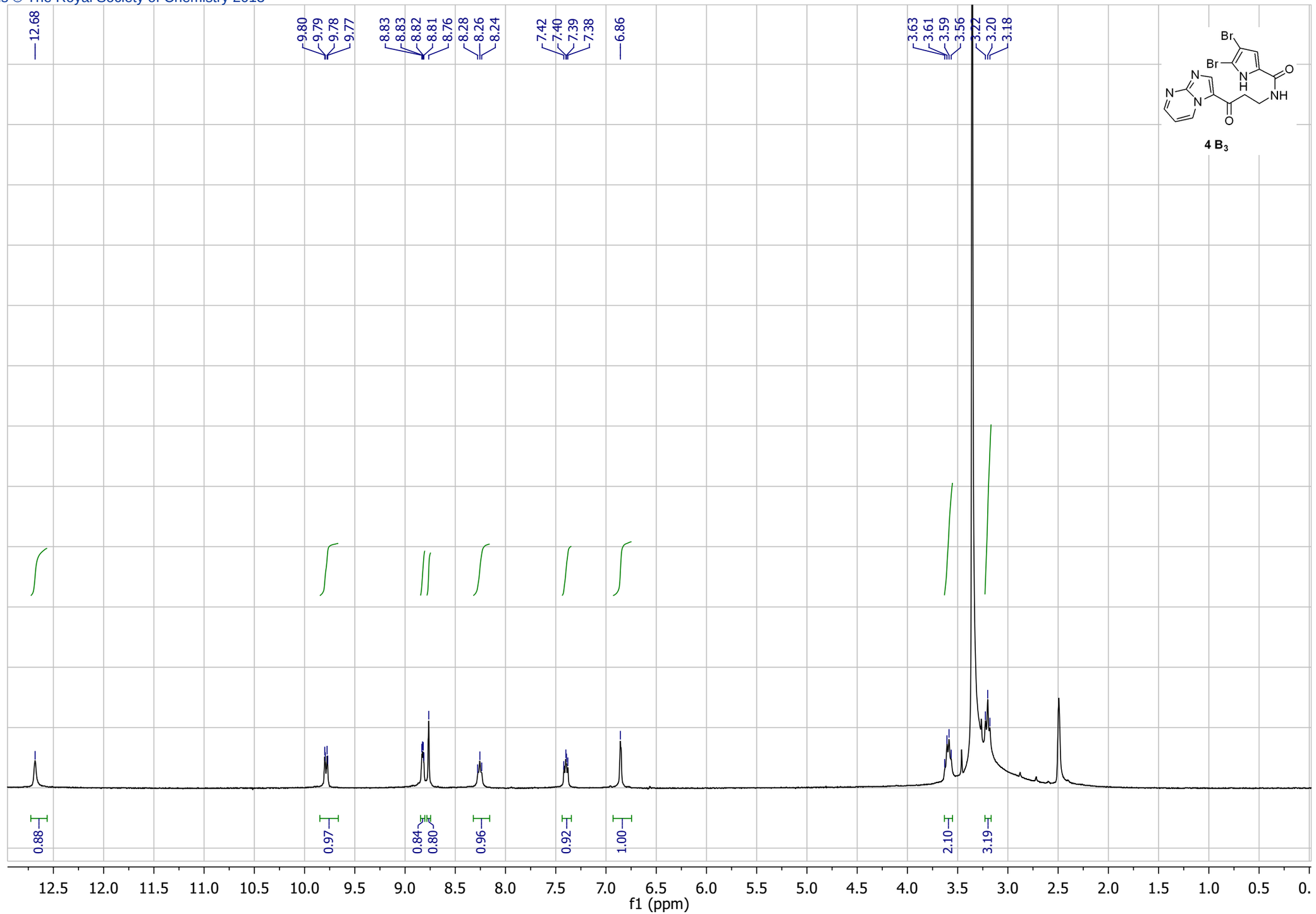


4 B$_1$

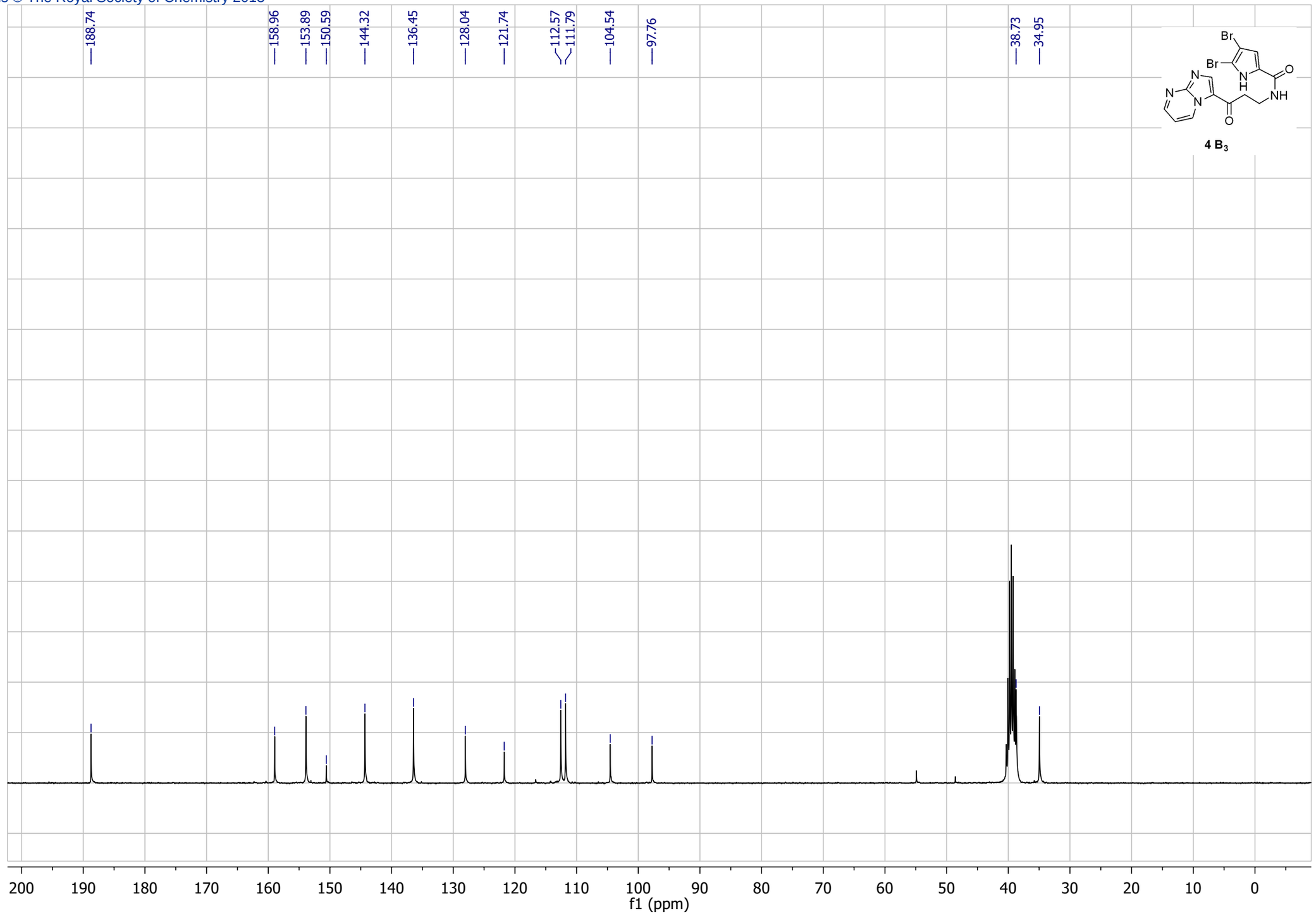








4 B_3



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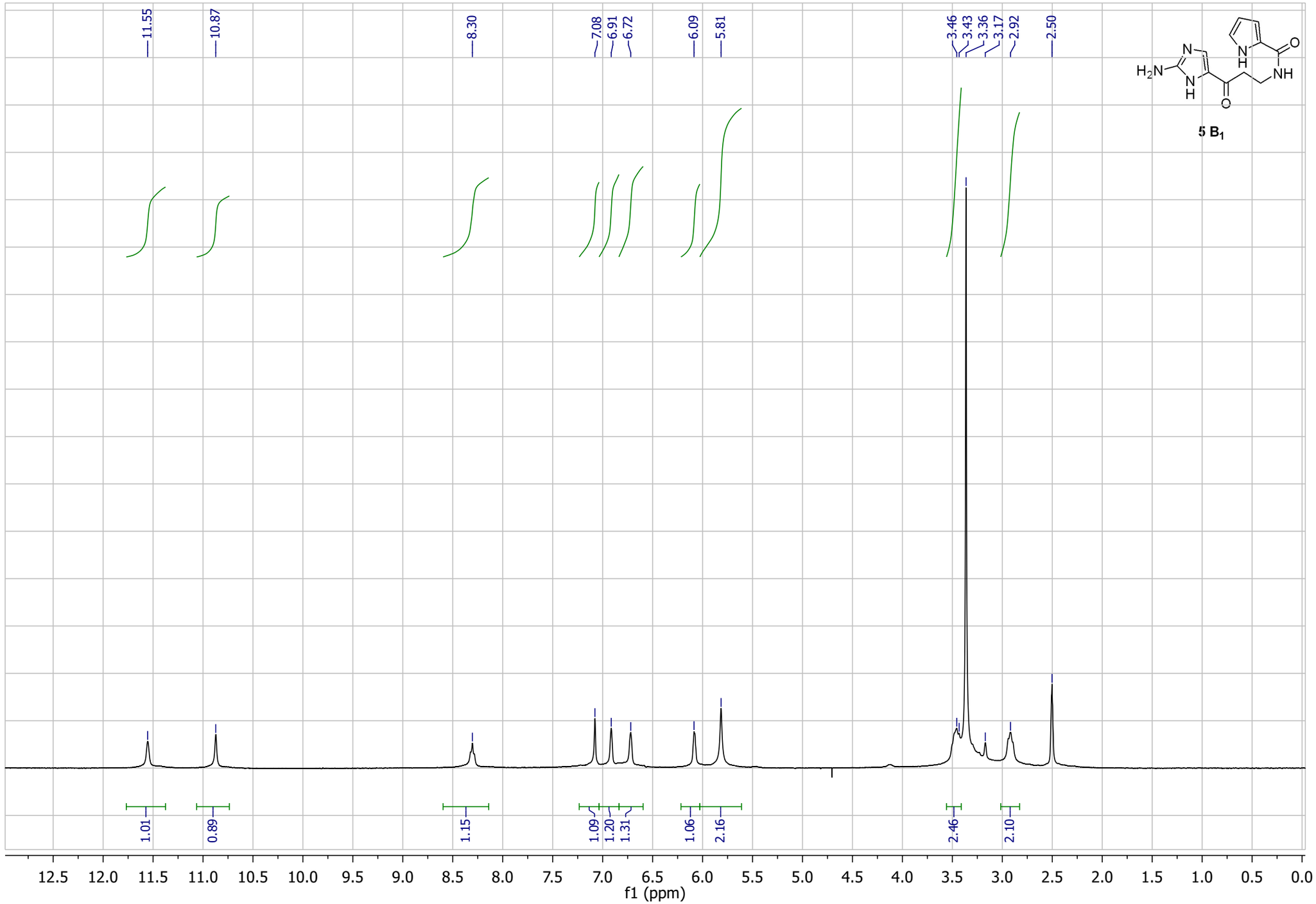
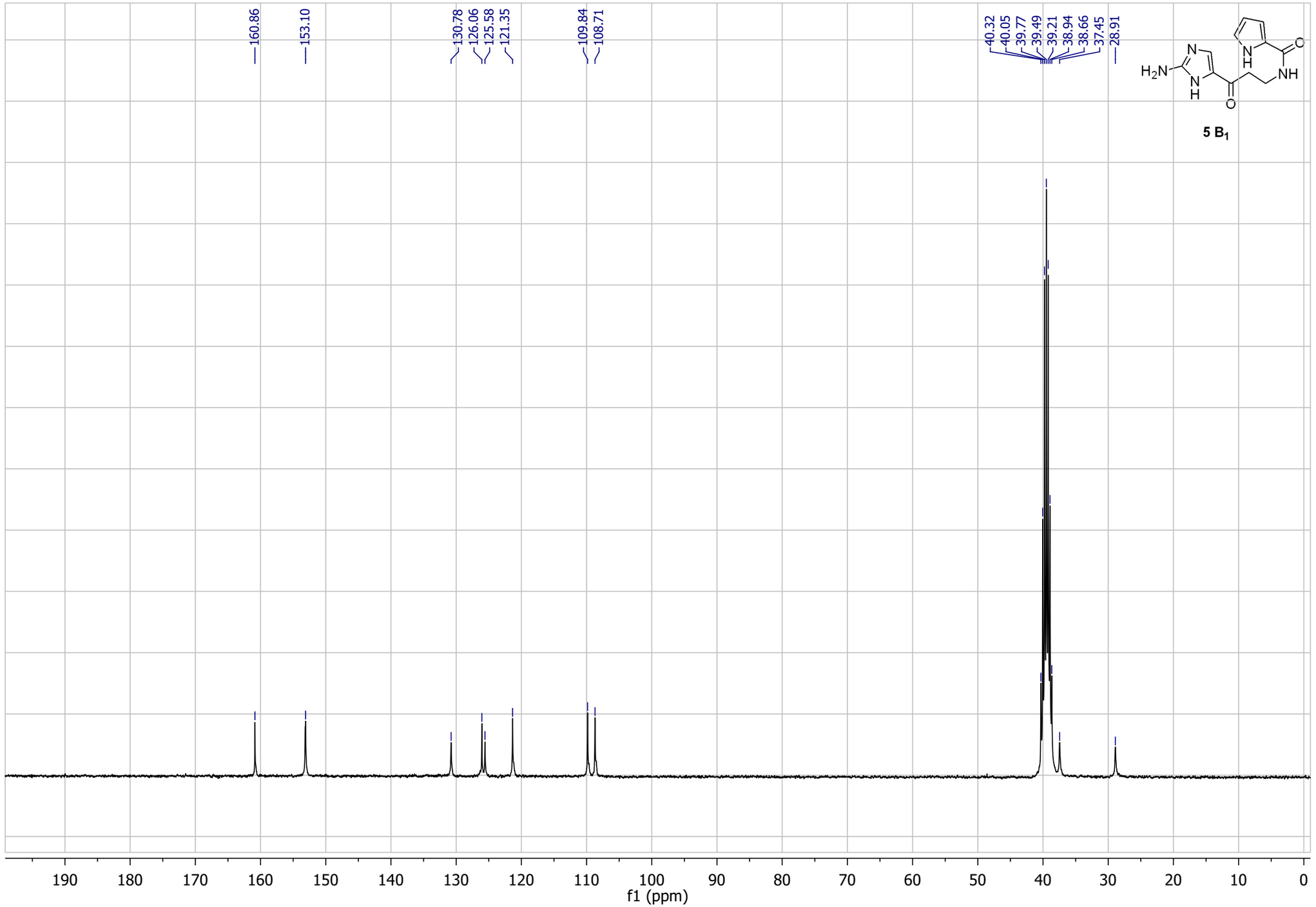


5 B_1



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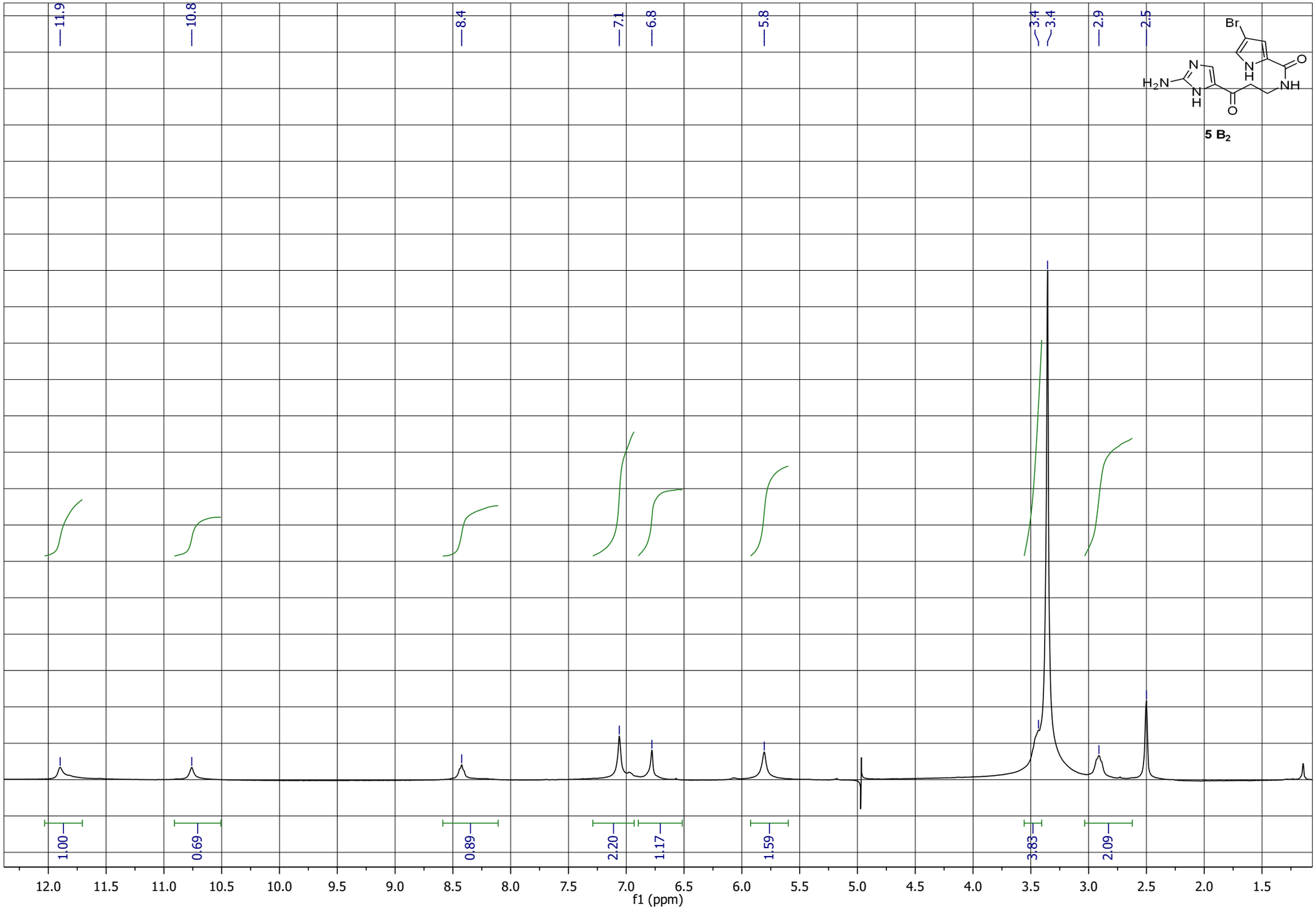
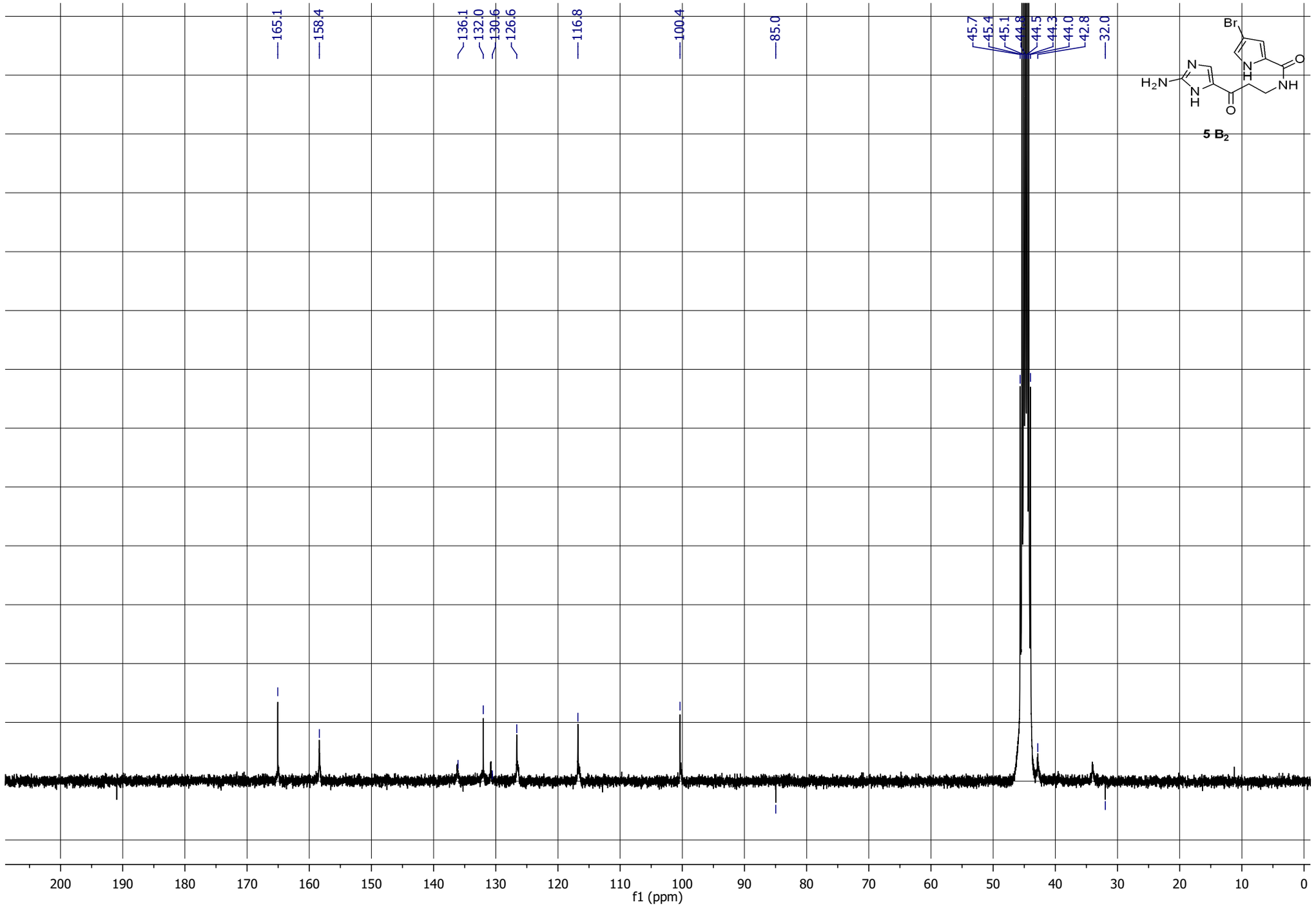
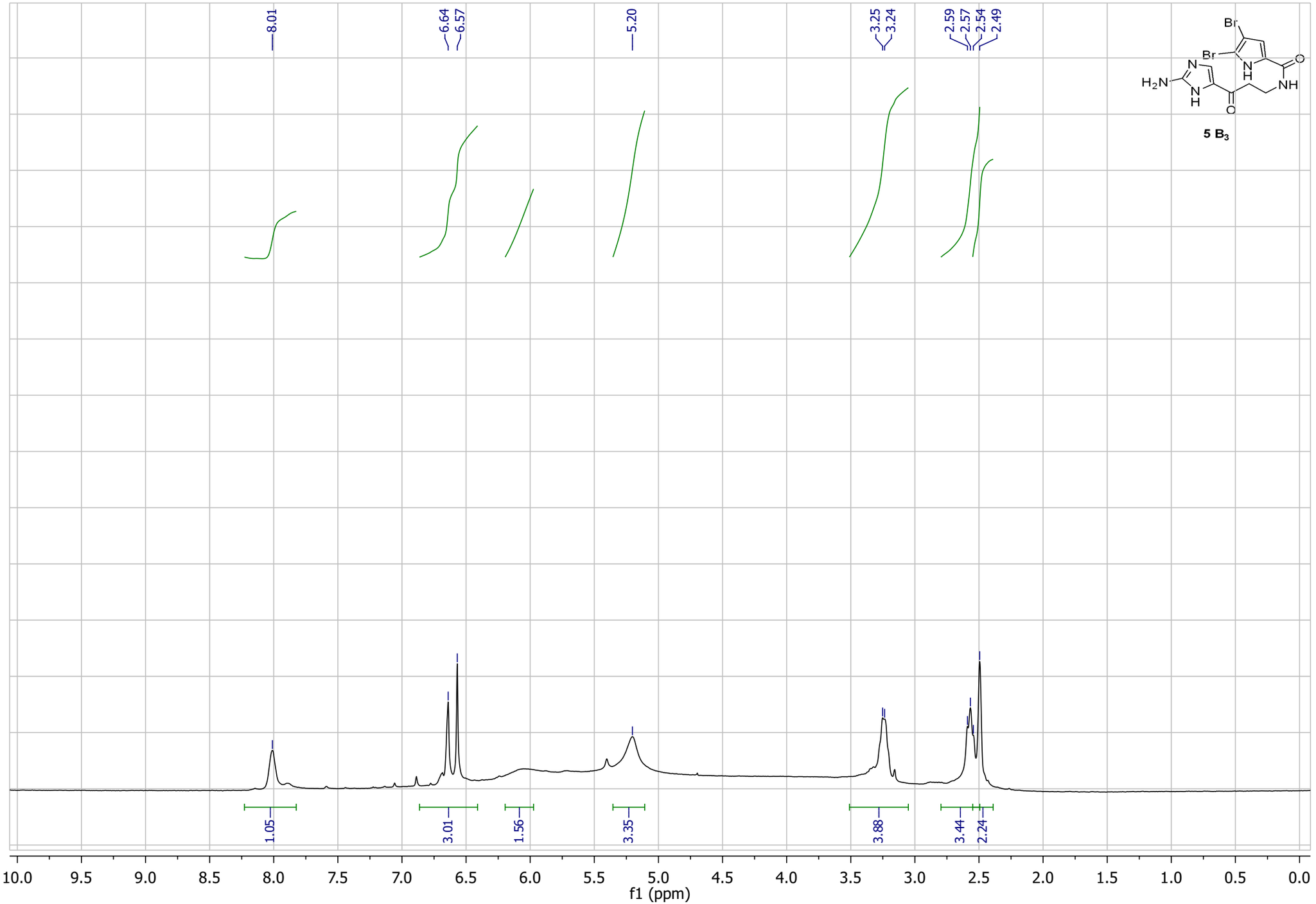
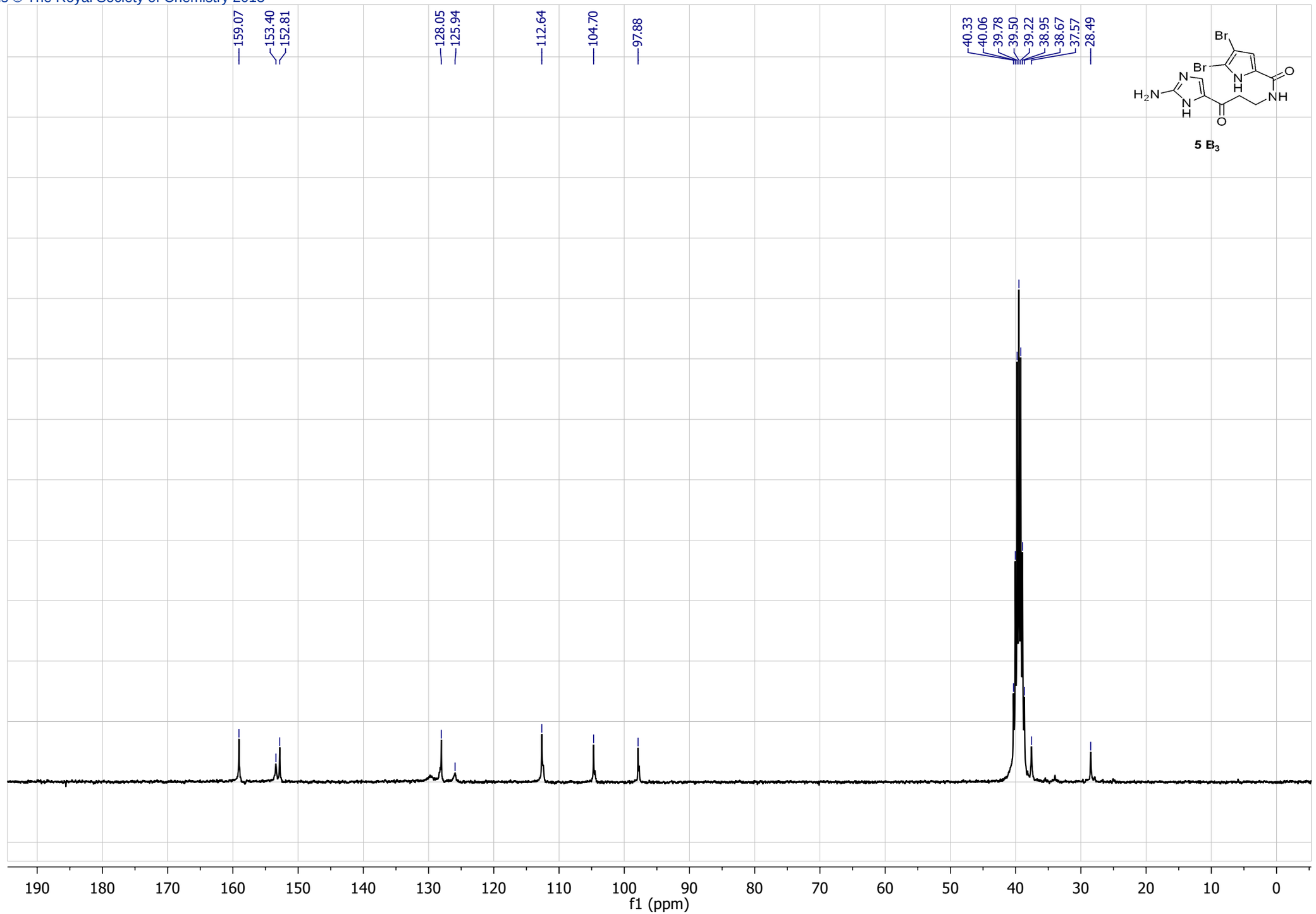
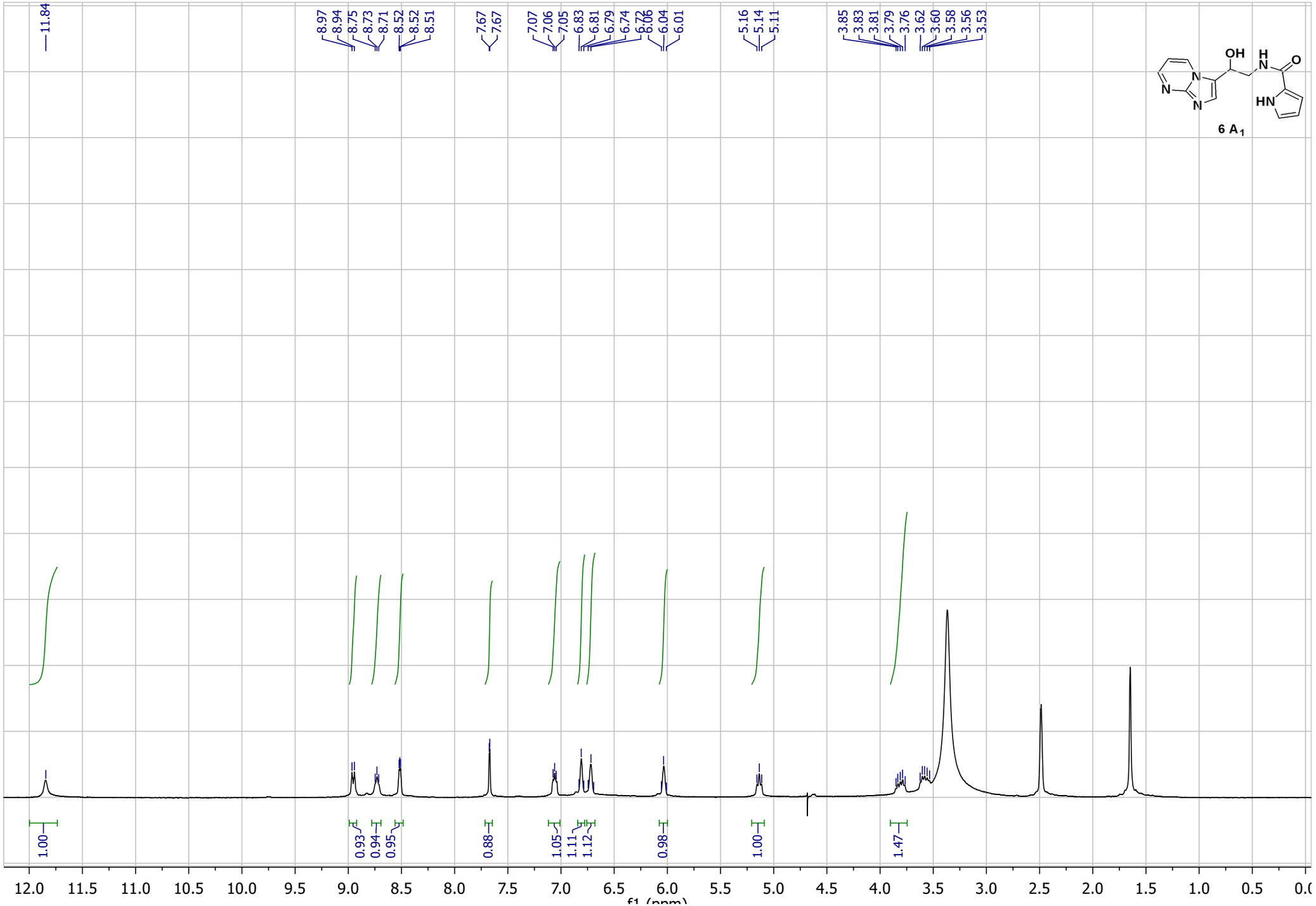


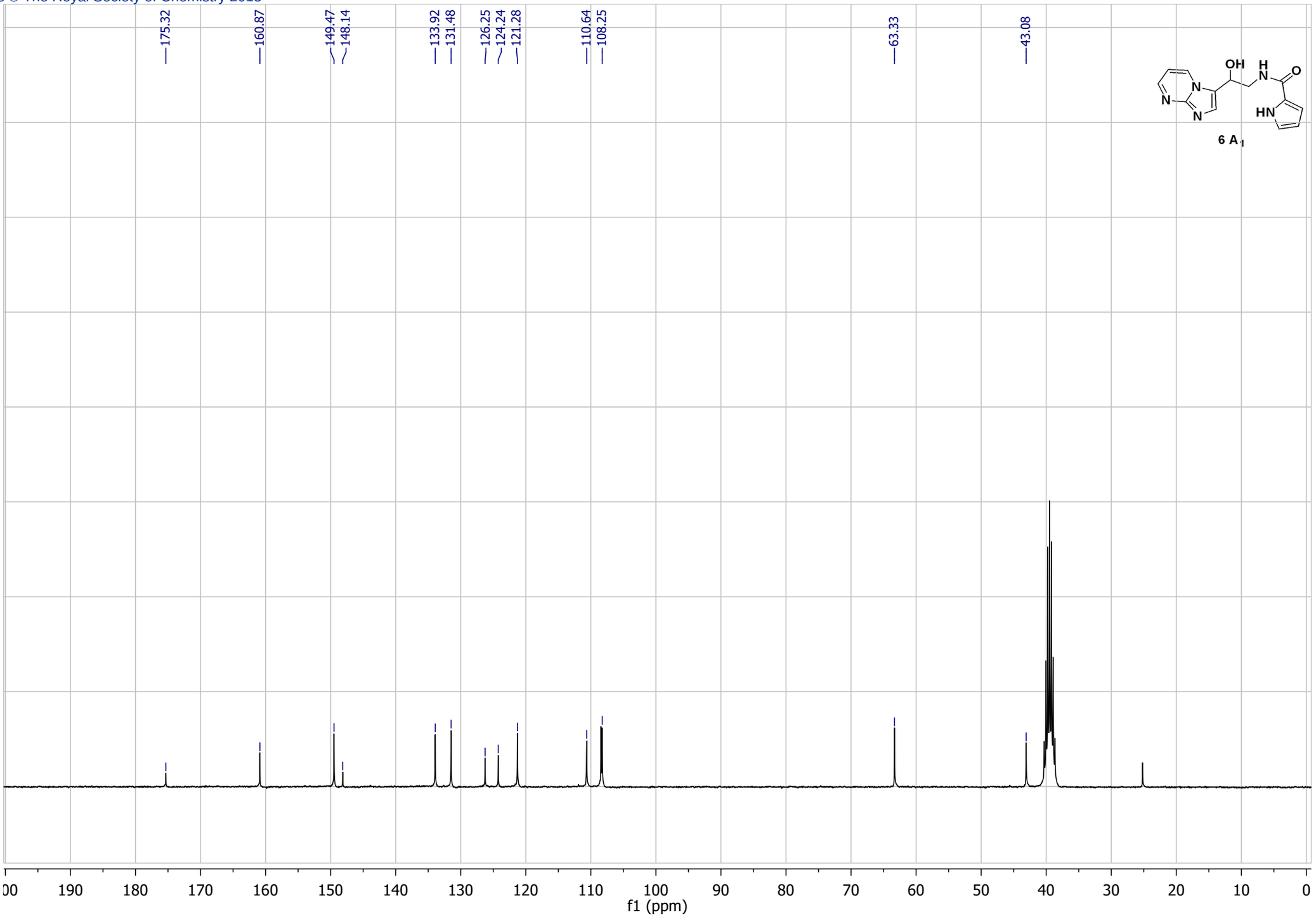


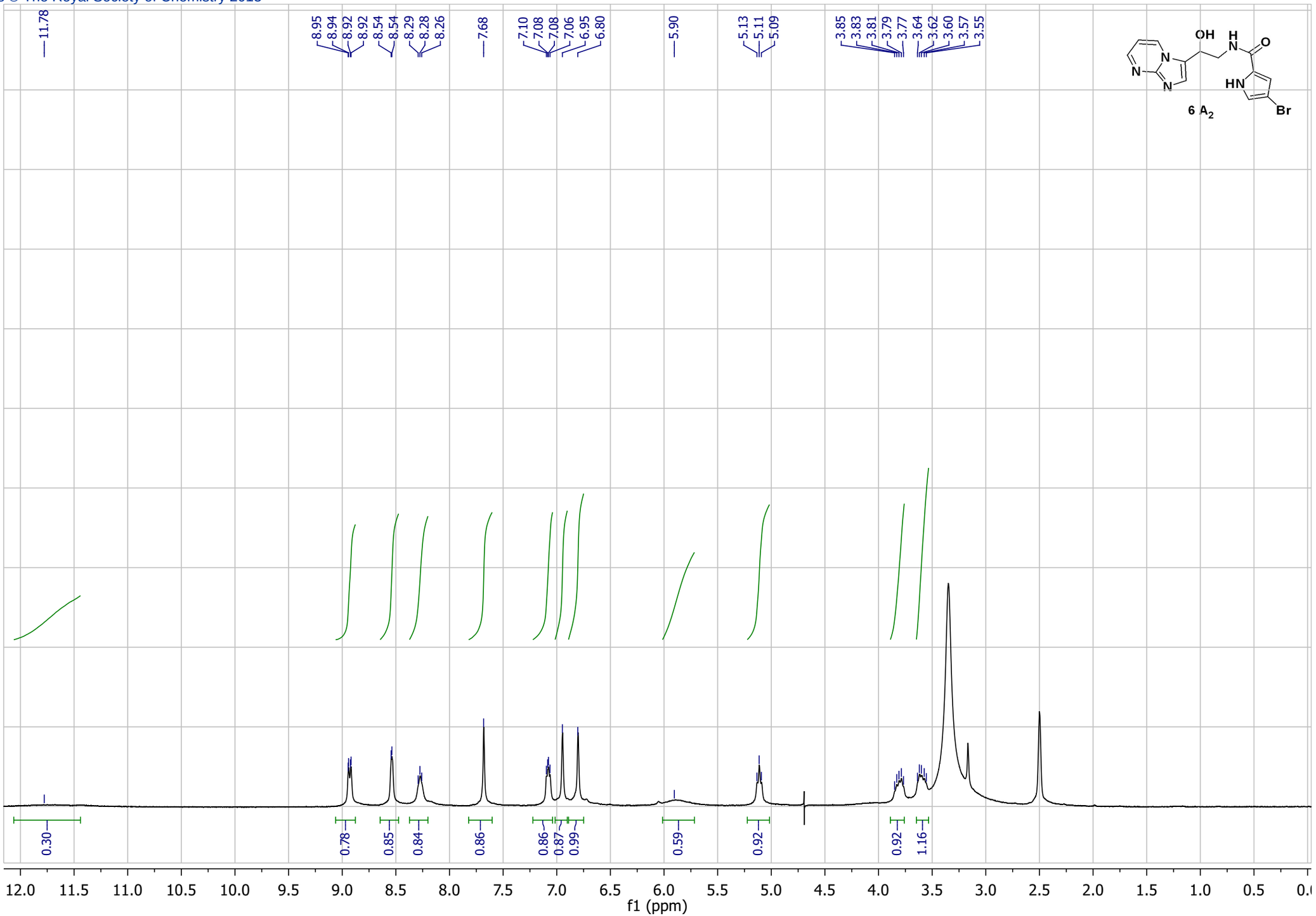


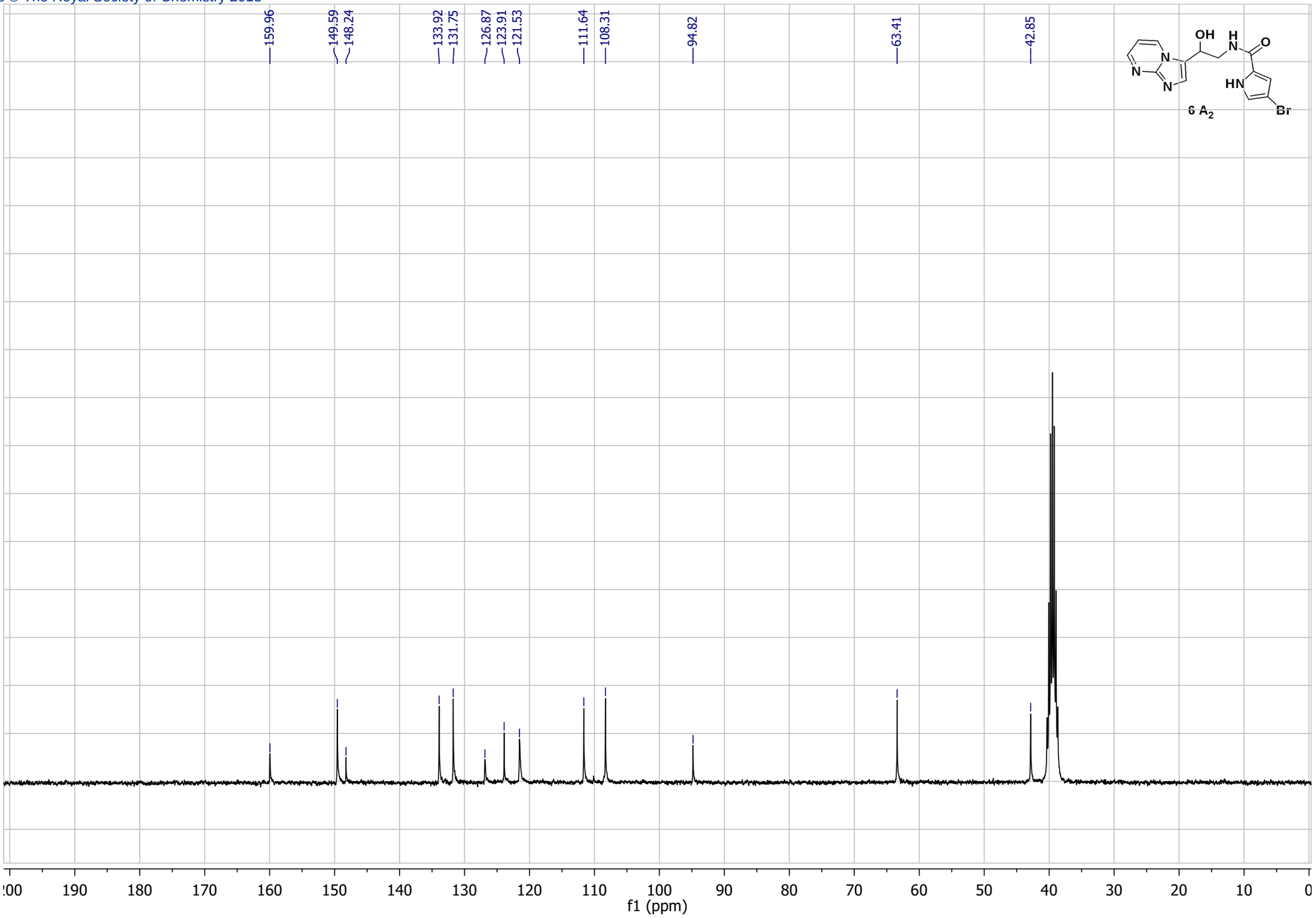
5 B_3

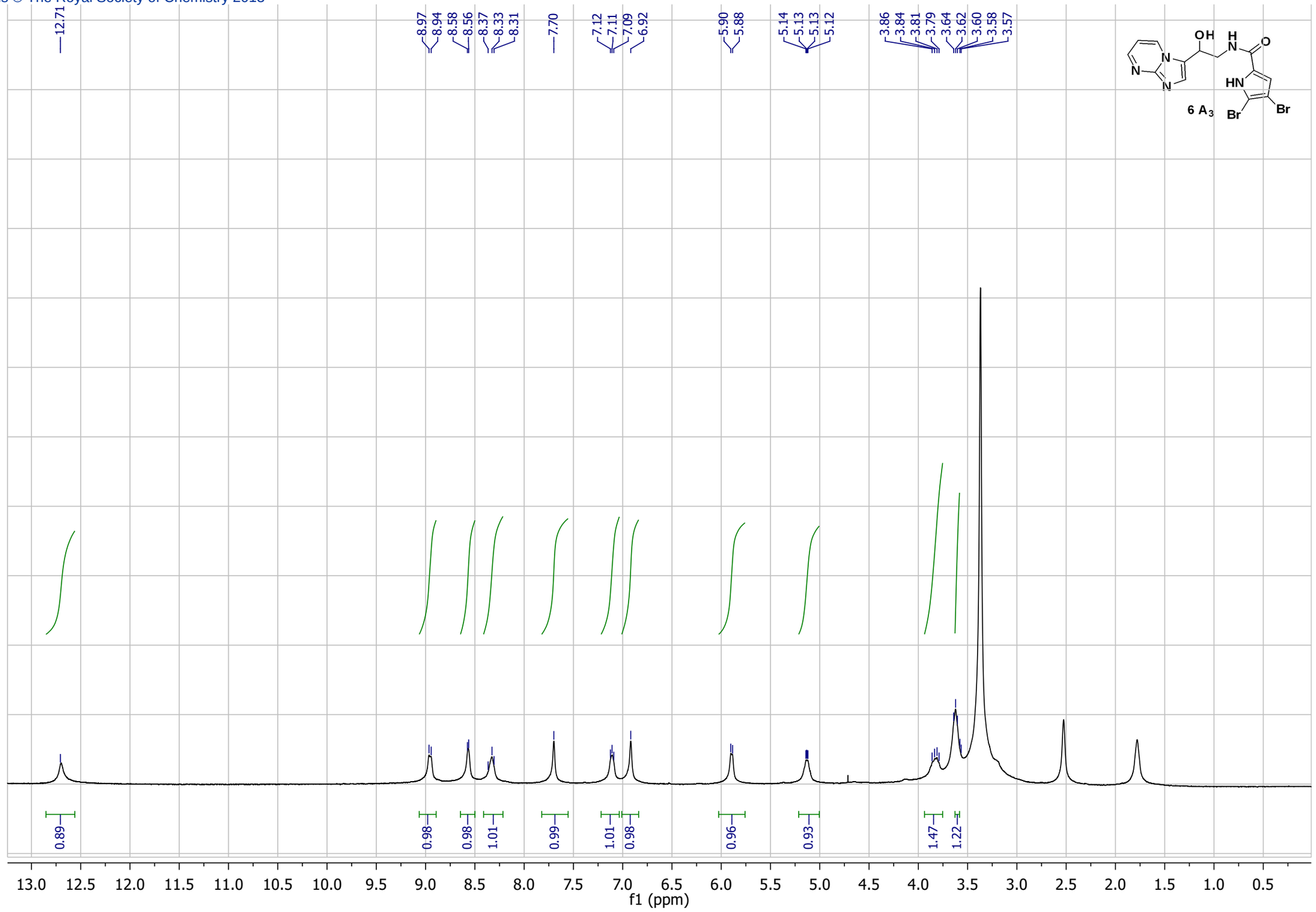


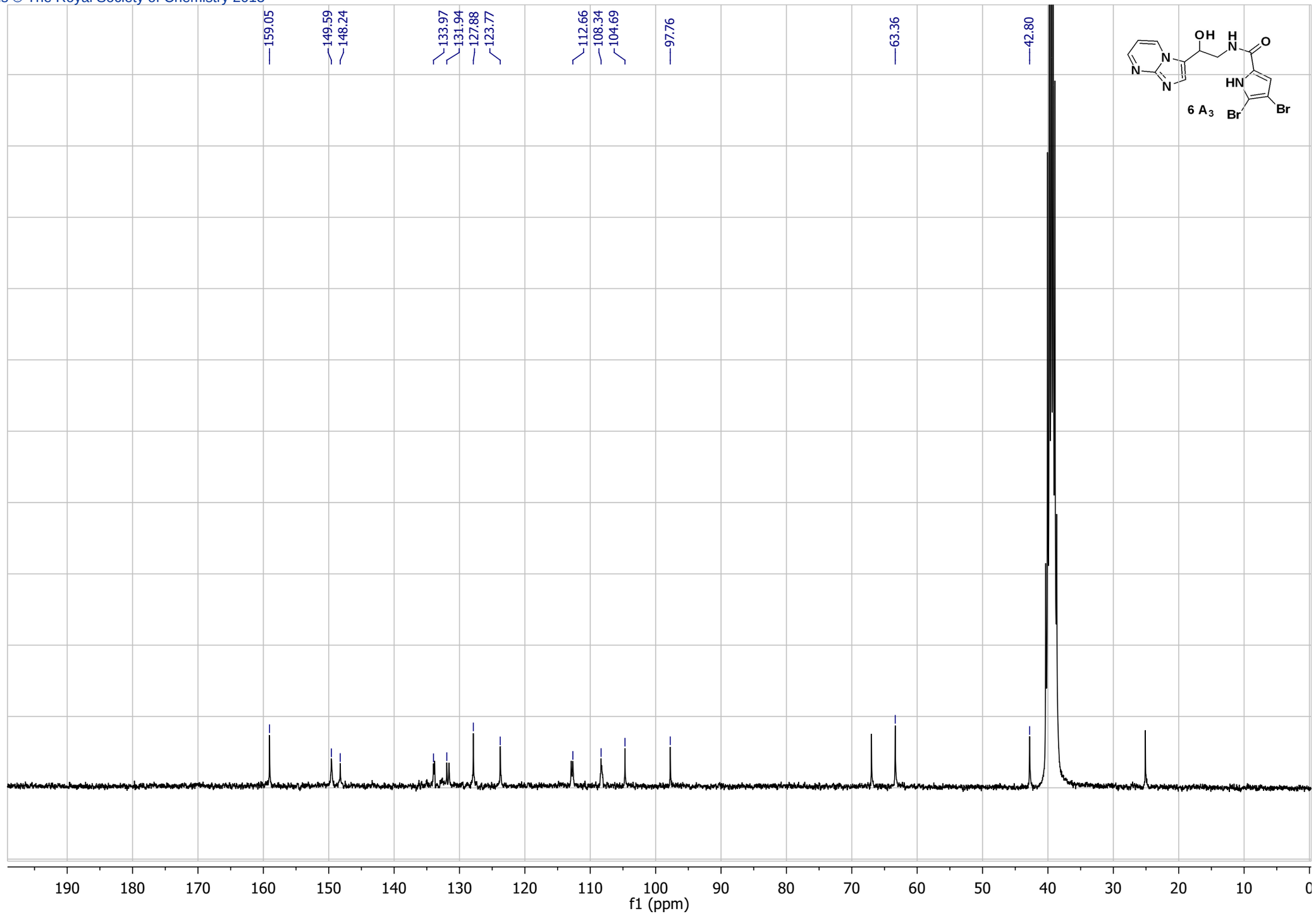


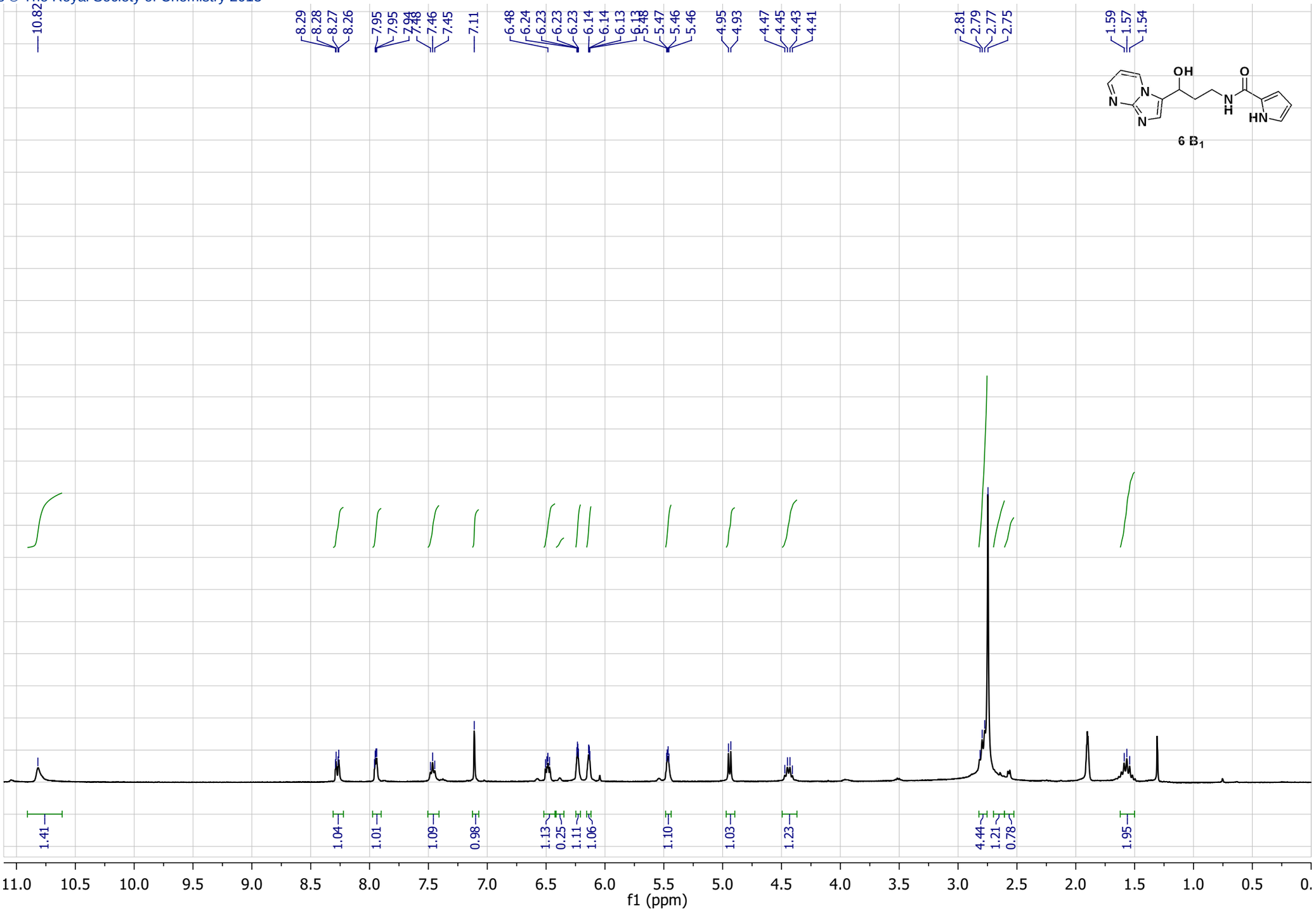


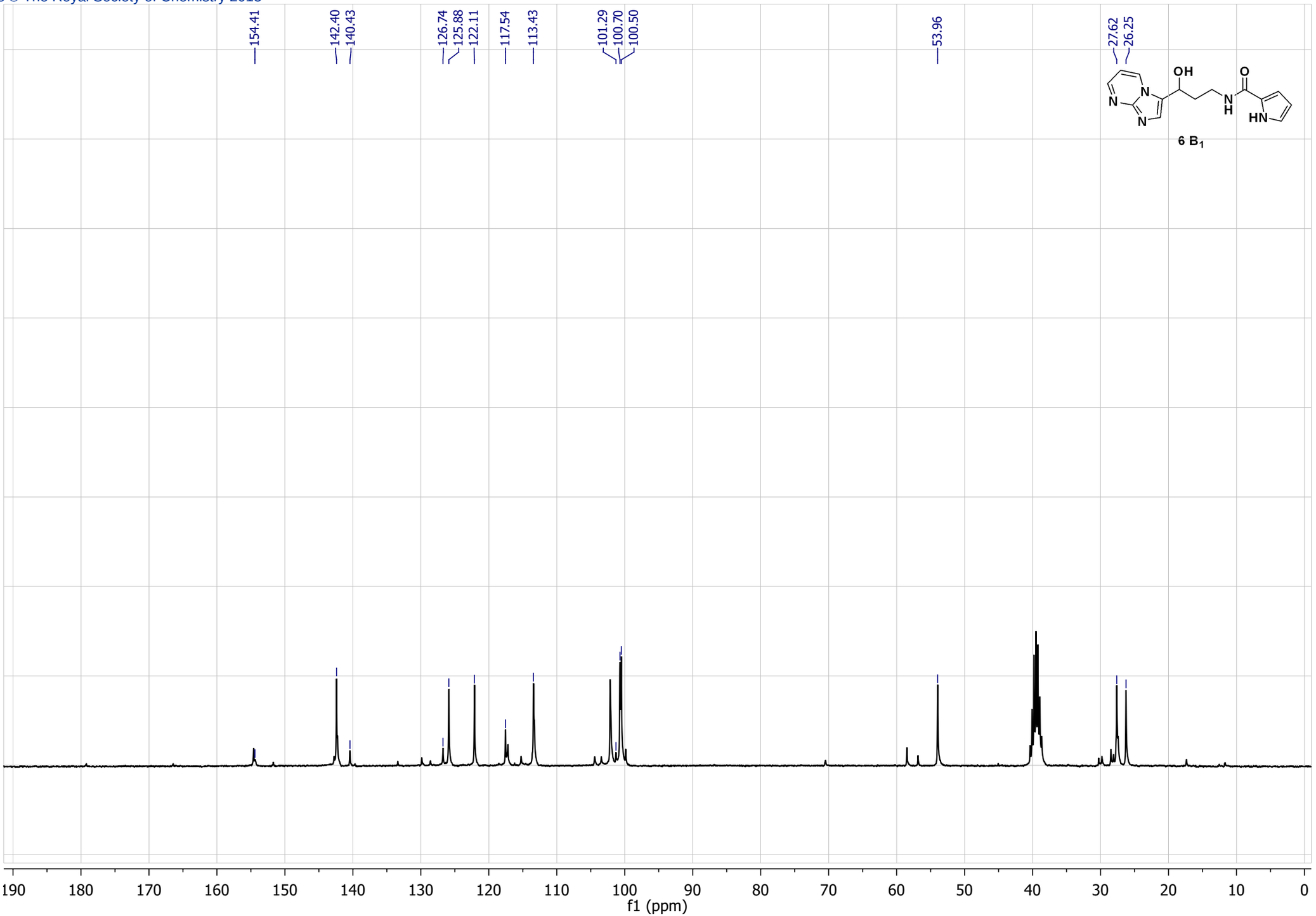


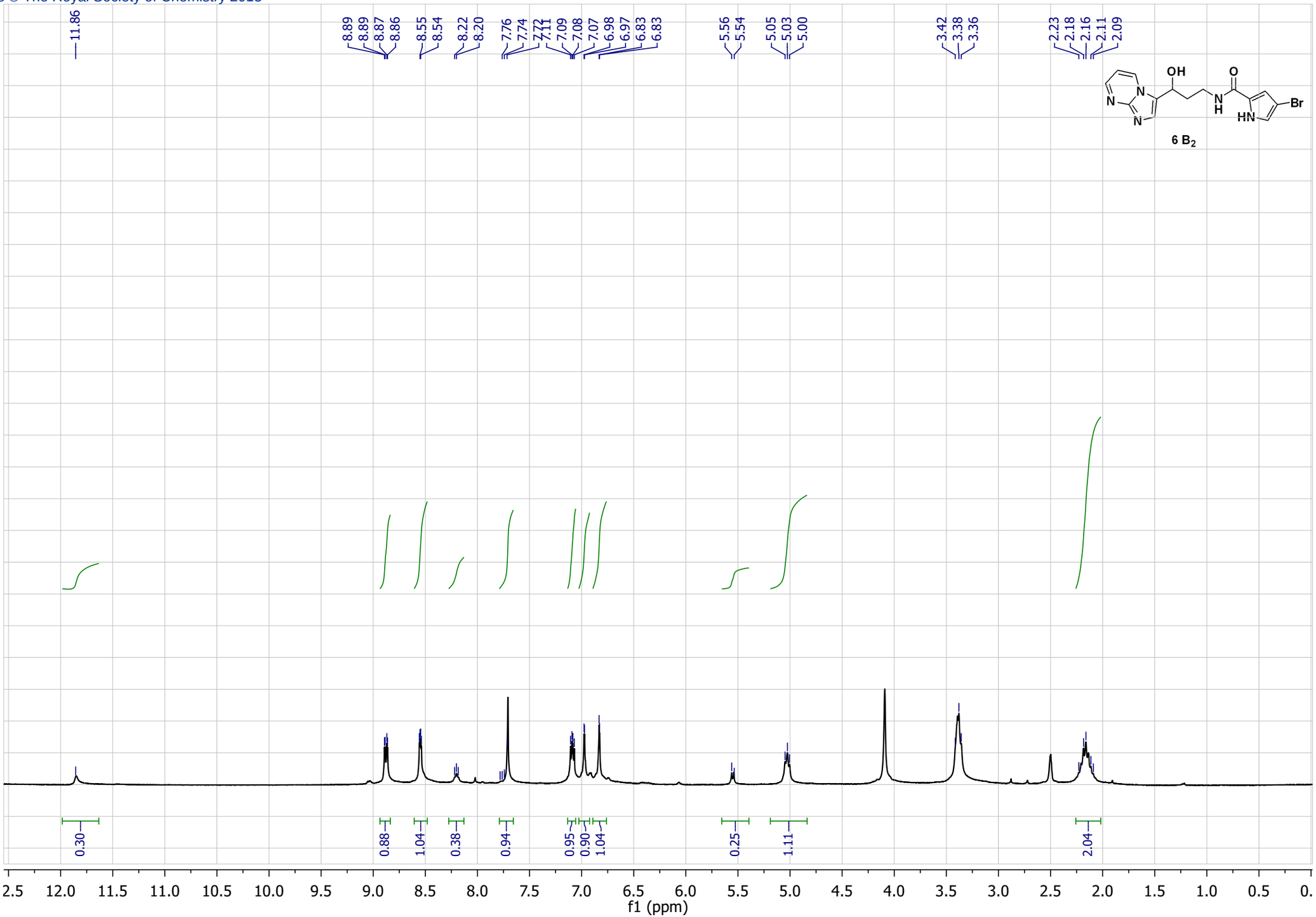












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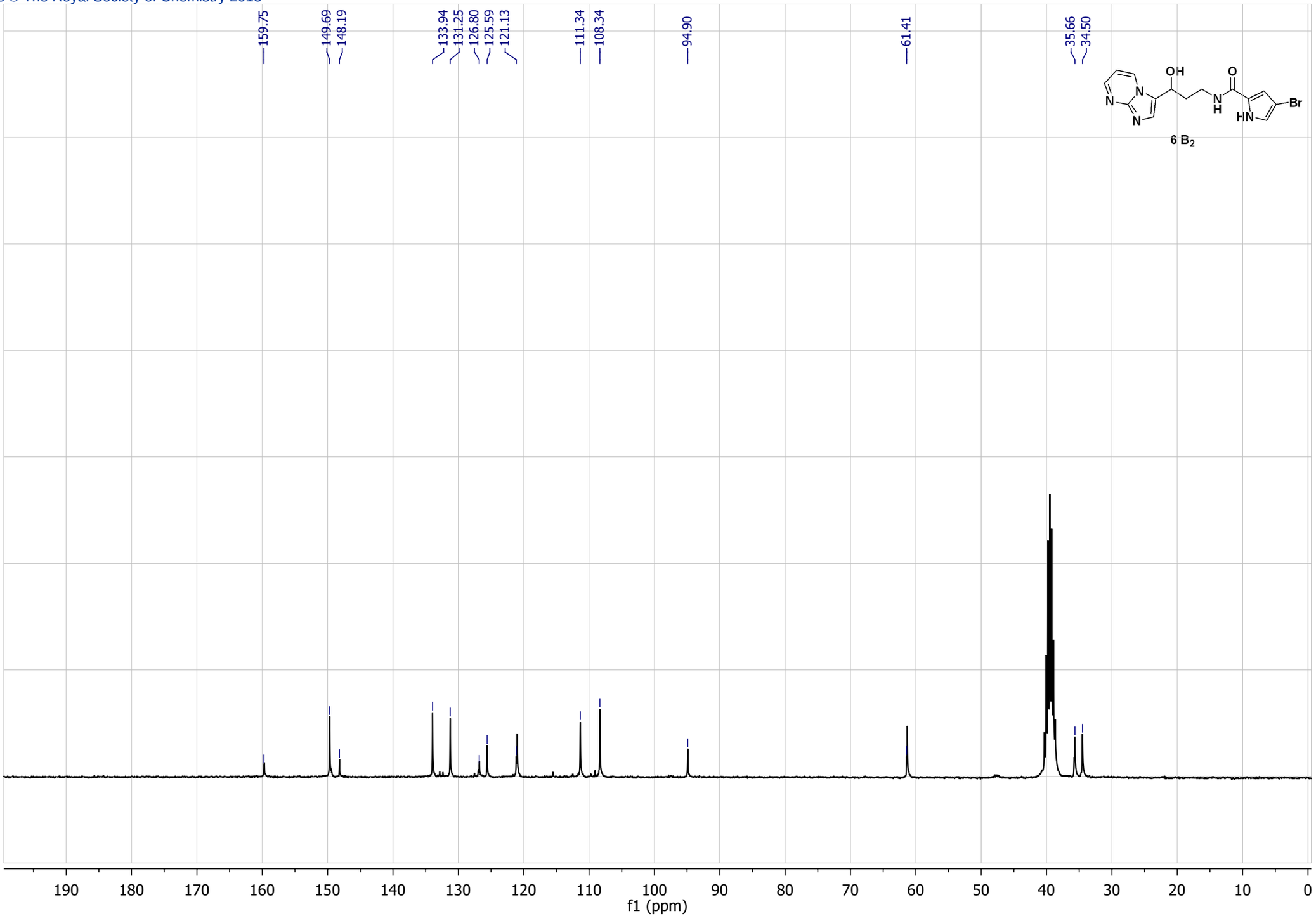

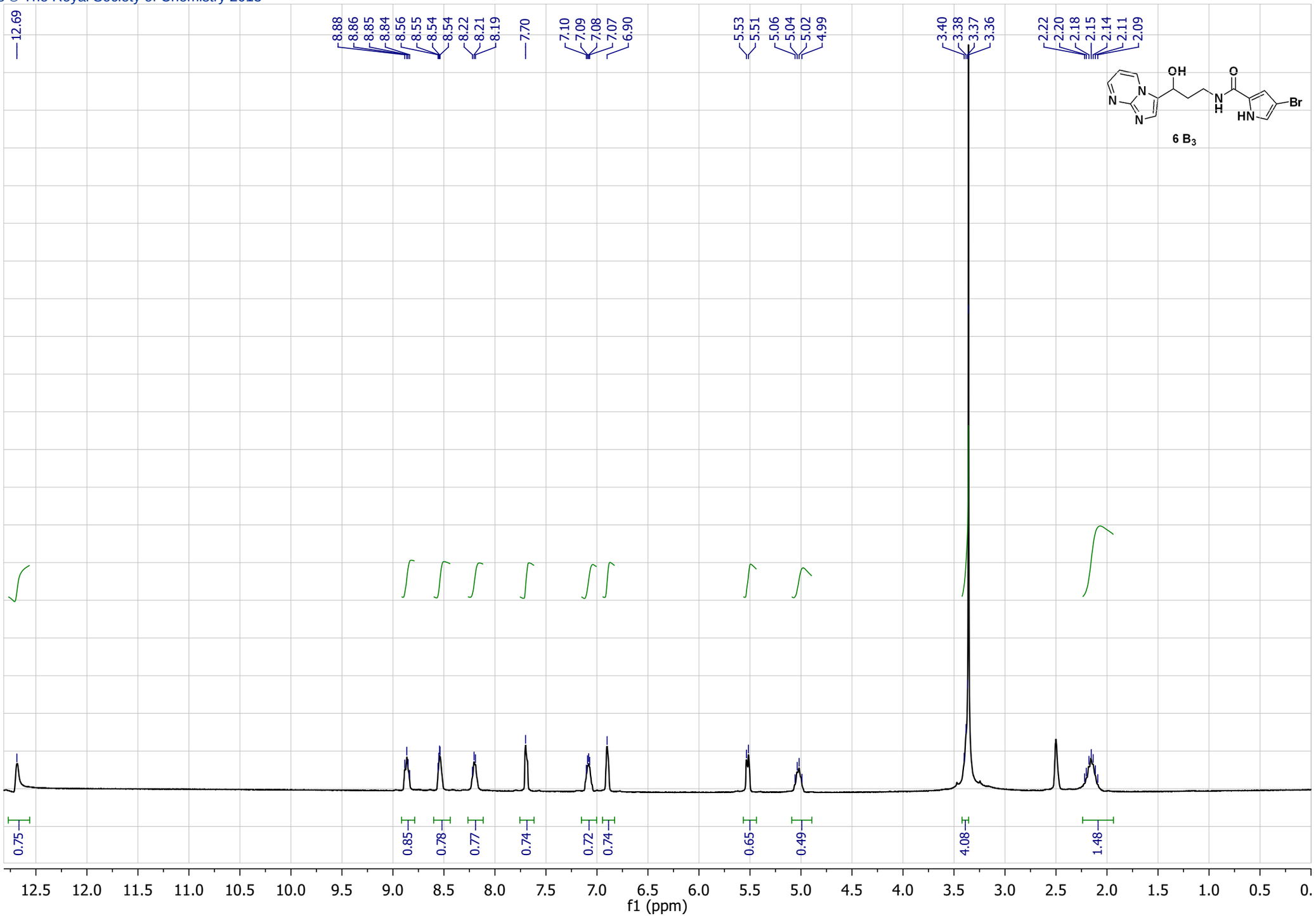

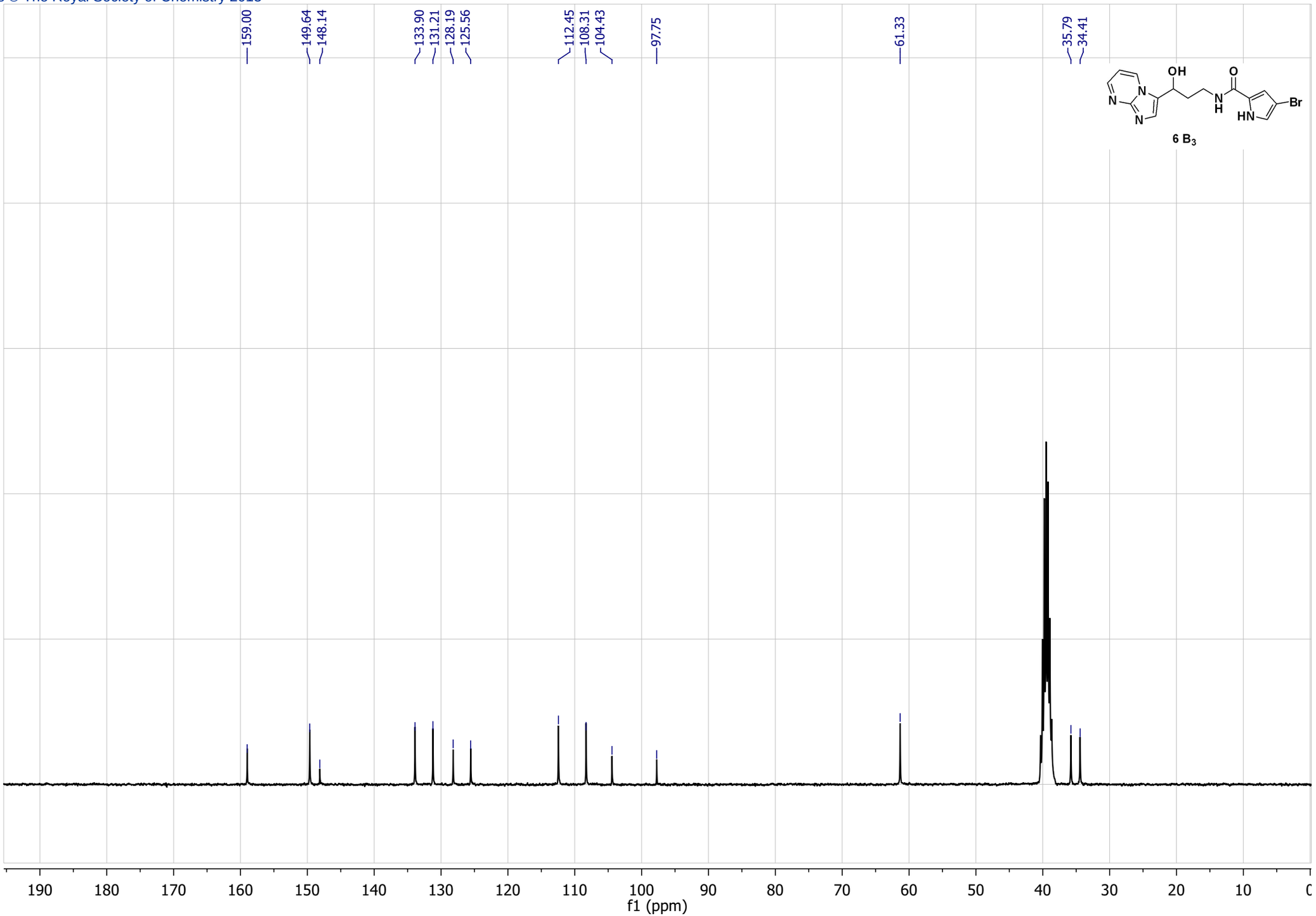

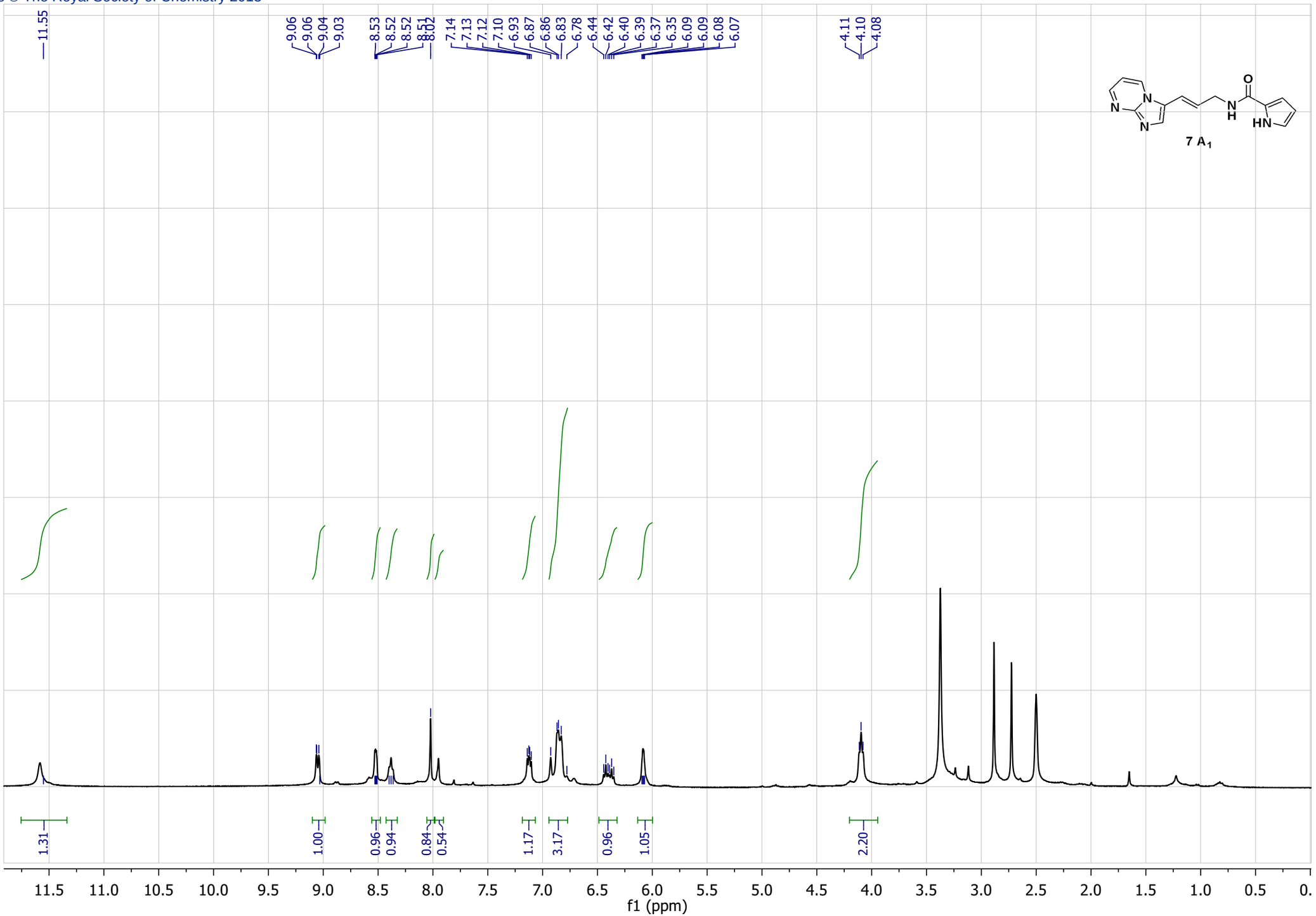

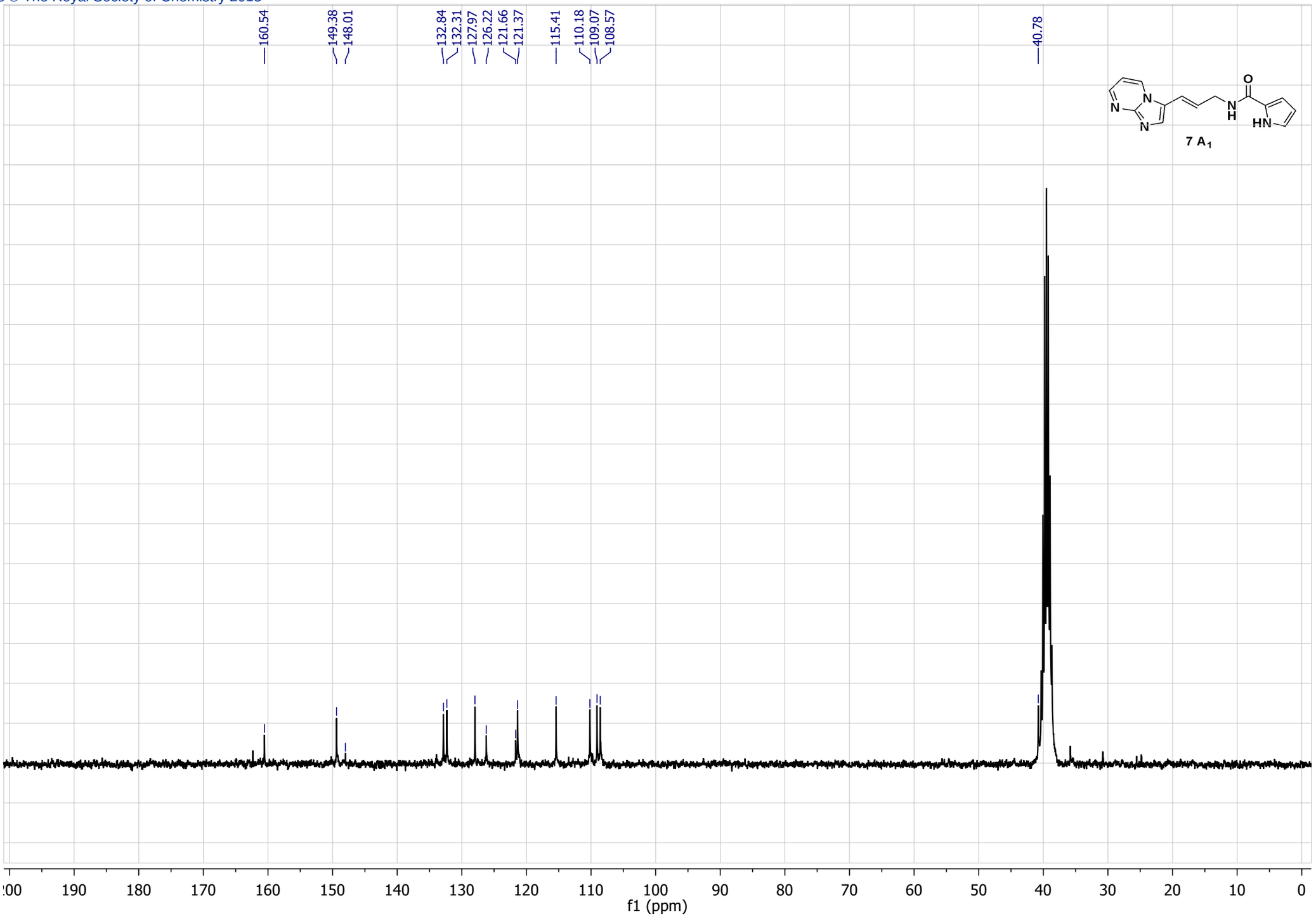

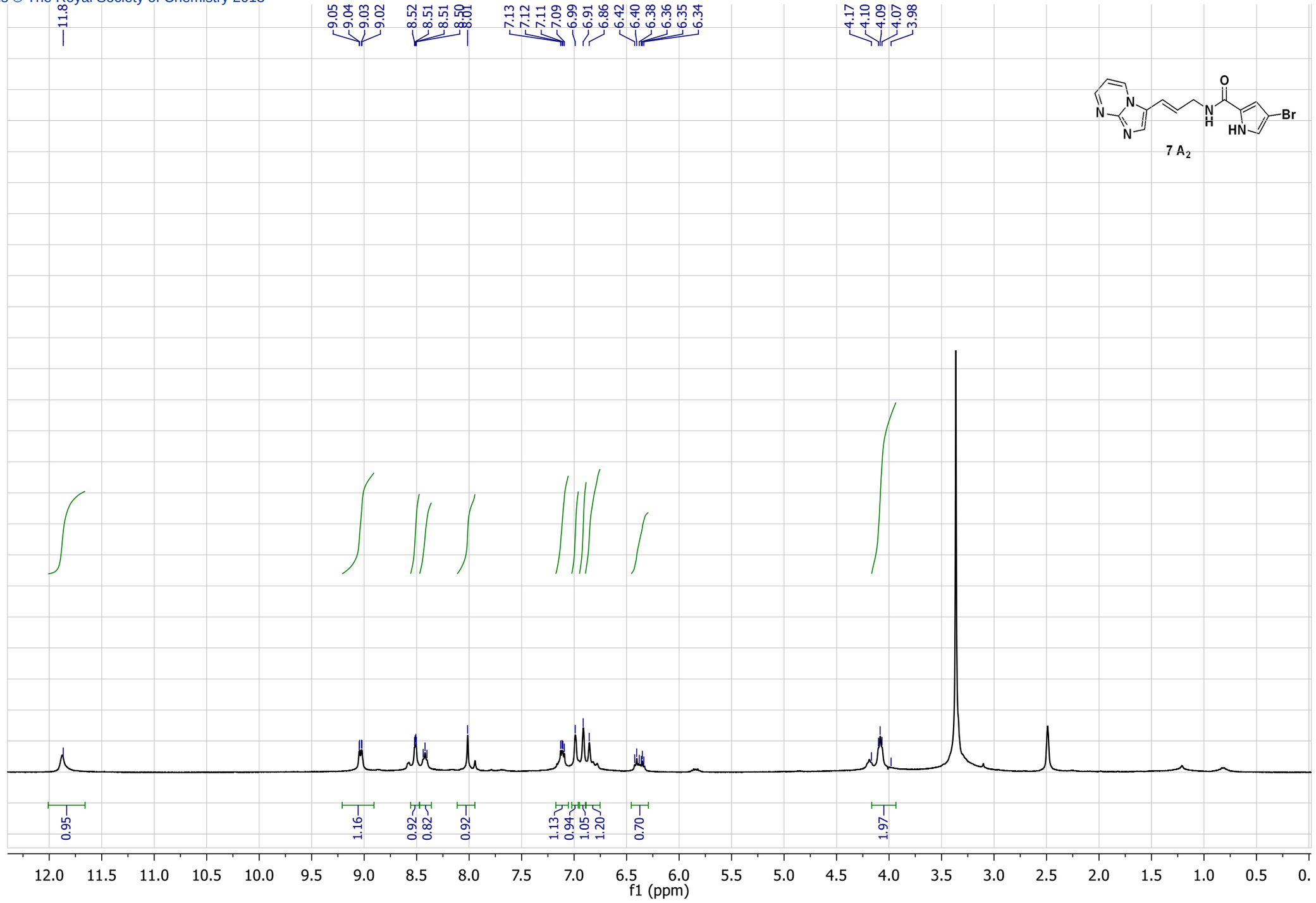

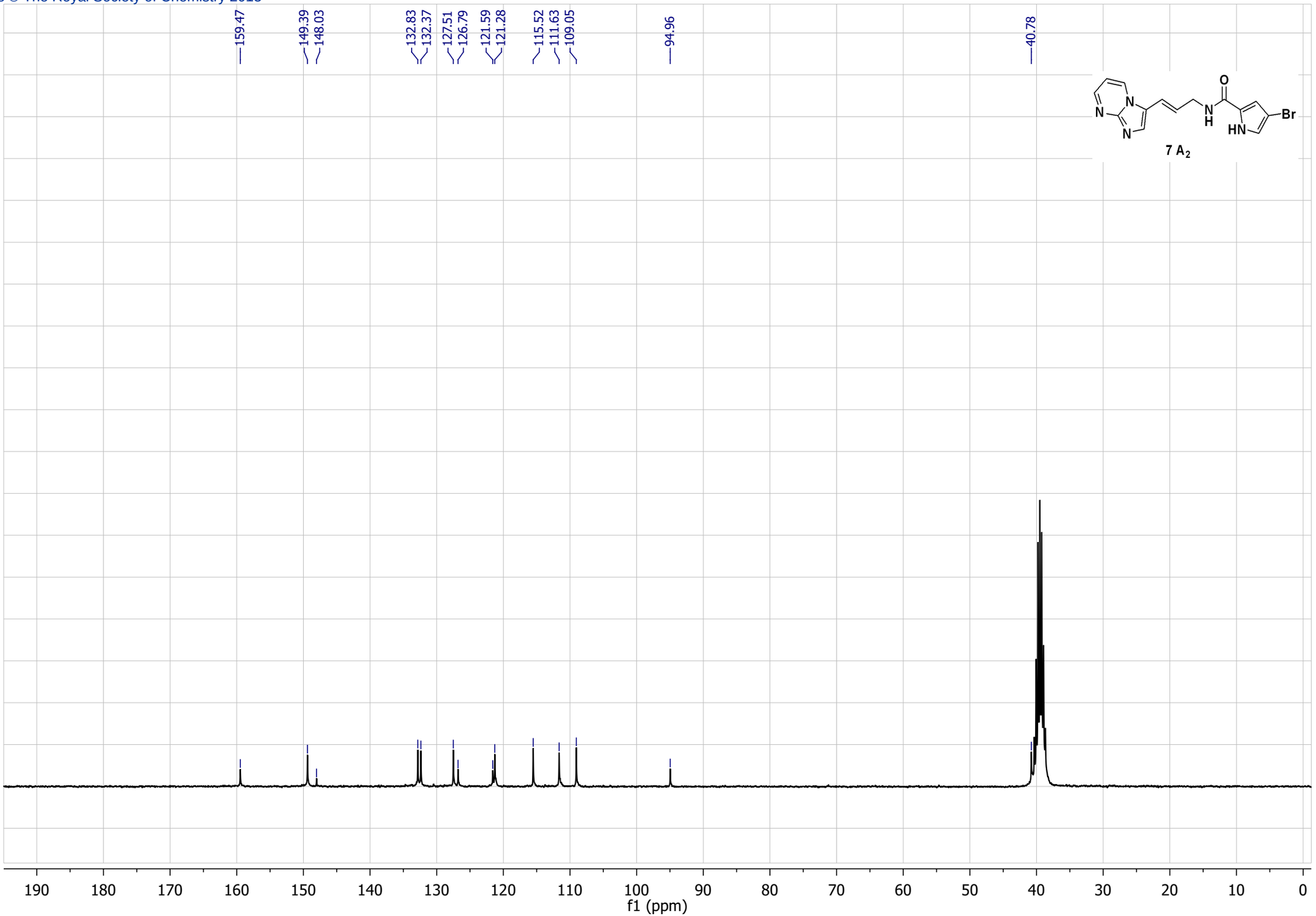

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