Electronic Supplementary Information

Rhodium-Catalyzed Intermolecular C–H Amination of Simple Hydrocarbons Using the Shelf-Stable Nonafluorobutanesulfonyl Azide

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General Methods: Proton and carbon-13 nuclear magnetic resonance (^{1}H NMR, ^{13}C NMR) spectra were recorded on a BRUKER AMX-300 (300 and 75 MHz), or Varian INOVA 300 (300 and 75 MHz) spectrometers, ^{19}F spectra were recorded on a Mercury 400 (375 MHz) spectrometer. Chemical shifts are expressed in parts per million (δ scale) downfield from tetramethylsilane and are referenced to residual peaks of the deuterated NMR solvent used for ^{1}H NMR and ^{13}C NMR or to fluorotrichloromethane as an external reference for ^{19}F NMR. Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, quintet = quintuplet, m = multiplet and/or multiple resonances, br = broad), integration, and coupling constants in hertz (Hz). Thin layer chromatography (TLC) was performed on Merck Silica Gel 60 F254 plates. The chromatograms were viewed under UV light and/or by treatment with a solution of ammonium molybdate (50 g) and cerium(IV) sulphate (1 g) in 5 % aqueous H_2SO_4 (1 L) followed by charring on a hot plate. Column chromatography was performed with Merck silica gel, grade 60, and 230–400 mesh. High resolution mass spectra (APCI or ESI-HRMS) were recorded on an Agilent 6520 Q-TOF instrument. Melting points were measured with a Reichert Jung Thermovar micro-melting apparatus. All solvents were of HPLC grade and were used as provided.

Sulfamination reaction. The reaction was carried out in a Schlenk tube (5 mL) under argon. The hydrocarbon substrate (0.60 mmol), nonafluorobutanesulfonyl azide (0.235 g, 0.72 mmol), 4Å MS (20 mg), and $Rh_2(OAc)_4$ (13 mg, 0.03 mmol, 5 mole%) were added to

dry $ClCH_2CH_2Cl$ (3 mL, in the case of **4**, **9**, **10** and **11**; toluene, cyclohexane, cycloheptane, and cycloctane were used as solvents) and stirred at 90 ºC for 12 h. The reaction mixture was filtered through a pad of Celite, rinsing with $ClCH_2CH_2Cl$, and concentrated. The residue was purified by silica column chromatography (hexane/AcOEt 9:1 v/v) to afford the corresponding sulfamination product.

***N*-(2,3-dihydro-1*H*-inden-1-yl)-1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonamide (1):** White powder. Mp: 87–90 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 1.90-2.02 (m, 1H), 2.56-2.69 (m, 1H), 2.78-2.89 (m, 1H), 2.95-3.04 (m, 1H), 5.05-5.13 (m, 1H), 5.26 (d, J = 9.2 Hz, 1H), 7.22-7.35 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 29.9 (CH_2), 35.0 (CH_2), 61.1 (CH), 124.3 (CH), 125.2 (CH), 127.4 (CH), 129.2 (CH), 140.6 (C), 143.1 (C). **^{19}F NMR** (375 MHz, $CDCl_3$): δ -126.6 (CF_2), -121.7 (CF_2), -113.1 (CF_2), -81.4 (CF_3). **HRMS** (APCI) $[M+H]^+$ calcd for $C_{13}H_9F_9NO_2S$: 414.0210, found: 414.0286.

1,1,2,2,3,3,4,4,4-nonafluoro-*N*-(1,2,3,4-tetrahydronaphthalen-1-yl)butane-1-sulfonamide (2): White powder. Mp: 98–101 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 1.84-1.92 (m, 2H), 1.98-2.19 (m, 2H), 2.71-2.90 (m, 2H), 4.81-4.87 (m, 1H), 5.18 (d, J = 8.6 Hz, 1H), 7.10-7.14 (m, 1H), 7.20-7.24 (m, 2H), 7.37-7.42 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 19.3 (CH_2), 28.9 (CH_2), 31.6 (CH_2), 54.7 (CH), 126.9 (CH), 128.5 (CH), 129.0 (CH), 129.7 (CH), 136.1 (C), 137.8 (C). **^{19}F NMR** (375 MHz, $CDCl_3$): δ -126.4 (CF_2), -121.5 (CF_2), -112.8 (CF_2), -81.2 (CF_3). **HRMS** (APCI) $[M+H]^+$ calcd for $C_{14}H_{11}F_9NO_2S$: 428.0372, found: 428.0398.

1,1,2,2,3,3,4,4,4-nonafluoro-*N*-(isochroman-1-yl)butane-1-sulfonamide (3): White powder. Mp: 154–157 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 2.71 (dt, J = 12.0, 3.3 Hz, 1H), 2.92-3.02 (m, 1H), 3.93-4.07 (m, 2H), 6.02 (d, J = 8.5 Hz, 1H), 6.13 (d, J = 8.5 Hz, 1H), 7.15 (d, J = 6.8 Hz, 1H), 7.23-7.31 (m, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 27.5 (CH_2), 59.7 (CH_2), 80.8 (CH), 126.9 (CH), 127.2 (CH), 129.3 (2 × CH), 131.3 (C), 134.9 (C). **^{19}F NMR** (375 MHz, $CDCl_3$): δ -128.4– -124.7 (m, CF_2), -121.4 (CF_2), -114.5– -110.8 (m, CF_2), -81.2 (CF_3). **HRMS** (ESI) $[M+NH_4]^+$ calcd for $C_{13}H_{14}F_9N_2O_3S$: 449.0576, found: 449.0635.

***N*-benzyl-1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonamide (4):** White powder. Mp: 85–88 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 4.48 (d, *J* = 5.8 Hz, 2H), 5.20 (t, *J* = 5.8 Hz, 1H), 7.32-7.43 (m, 5H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 48.8 (CH_2), 128.1 (2 × CH), 128.9 (CH), 129.3 (2 × CH), 135.3 (C). **^{19}F NMR** (375 MHz, $CDCl_3$): δ -126.8 (CF_2), -121.7 (CF_2), -112.7 (CF_2), -81.2 (CF_3). **HRMS** (ESI) $[M+K]^+$ calcd for $C_{11}H_8F_9KNO_2S$: 427.9764, found: 427.9744.

1,1,2,2,3,3,4,4,4-Nonafluoro-*N*-(1-phenylethyl)butane-1-sulfonamide (5): White powder. Mp: 96–99 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 1.54 (d, *J* = 6.9 Hz, 3H), 4.71-4.80 (m, 1H), 5.62 (d, *J* = 8.6 Hz, 1H), 7.22-7.32 (m, 5H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 23.6 (CH_3), 55.9 (CH), 126.0 (2 × CH), 128.5 (CH), 129.2 (2 × CH), 141.3 (C). **^{19}F NMR** (375 MHz, $CDCl_3$): δ -126.6 (CF_2), -121.6 (CF_2), -113.2 (CF_2), -81.3 (CF_3). **HRMS** (ESI) $]M+NH_4]^+$ calcd for $C_{12}H_{14}F_9N_2O_2S$: 421.0627, found: 421.0681.

1,1,2,2,3,3,4,4,4-Nonafluoro-*N*-(1-(4-methoxyphenyl)ethyl)butane-1-sulfonamide (6): White powder. Mp: 89–92 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 1.63 (d, *J* = 6.9 Hz, 3H), 3.82 (s, 3H), 4.76-4.86 (m, 1H), 5.44 (d, *J* = 8.3 Hz, 1H), 6.90 (d, *J* = 8.8 Hz, 2H), 7.25 (d, *J* = 8.8 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 23.5 (CH_3), 55.4 (CH_3 and CH), 114.5 (2 × CH), 127.4 (2 × CH), 133.4 (C), 159.6 (C). **^{19}F NMR** (375 MHz, $CDCl_3$): δ -126.4 (CF_2), -121.6 (CF_2), -113.1 (CF_2), -81.2 (CF_3). **HRMS** (ESI) $]M+NH_4]^+$ calcd for $C_{13}H_{16}F_9N_2O_3S$: 451.0732, found: 451.0741.

***N*-(1-(4-Chlorophenyl)ethyl)-1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonamide (7)**: White powder. Mp: 93–95 °C **^{1}H NMR** (300 MHz, $CDCl_3$): δ 1.63 (d, *J* = 6.9 Hz, 3H), 4.78-4.88 (m, 1H), 5.26 (d, *J* = 8.3 Hz, 1H), 7.26 (d, *J* = 8.6 Hz, 2H), 7.37 (d, *J* = 8.6 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 23.5 (CH_3), 55.2 (CH), 127.5 (2 × CH), 129.4 (2 × CH), 134.5 (C), 139.7 (C). **^{19}F NMR** (375 MHz, $CDCl_3$): δ -126.4 (CF_2), -121.5 (CF_2), -113.0 (CF_2), -81.1 (CF_3). **HRMS** (ESI) $]M-H]^+$ calcd for $C_{12}H_8ClF_9NO_2S$: 435.9826, found: 435.9846.

1,1,2,2,3,3,4,4,4-Nonafluoro-*N*-(2-phenylpropan-2-yl)butane-1-sulfonamide (8): White powder. Mp: 73–76 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 1.83 (s, 6H), 5.13 (br s, 1H), 7.31-7.50 (m, 5H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 29.8 (2 × CH_3), 62.7 (C), 125.1 (2 × CH), 128.2 (CH), 129.0 (2 × CH), 145.4 (C). **^{19}F NMR** (375 MHz, $CDCl_3$): δ -126.3 (CF_2), -121.4 (CF_2), -112.1 (CF_2), -81.1 (CF_3). **HRMS** (ESI) $[M+NH_4]^+$ calcd for $C_{13}H_{16}F_9N_2O_2S$: 435.0783, found: 435.0787.

***N*-(9H-Fluoren-9-yl)-1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonamide (9):** White powder. Mp: 115–118 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 5.09 (d, J = 9.6 Hz, 1H), 5.60 (d, J = 9.6 Hz, 1H), 7.34-7.476 (m, 4H), 7.64-7.67 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 60.3 (CH), 120.4 (2 × CH), 125.4 (2 × CH), 128.5 (2 × CH), 129.9 (2 × CH), 140.4 (2 × C), 141.7 (2 × C). **^{19}F NMR** (375 MHz, $CDCl_3$): δ -126.2 (CF_2), -121.2 (CF_2), -112.2 (CF_2), -81.0 (CF_3). **HRMS** (APCI) $[M+H]^+$ calcd for $C_{17}H_9F_9NO_2S$: 462.0216, found: 462.0217.

***N*-Benzhydryl-1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonamide (10):** White powder. Mp: 118–121 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 5.56 (d, J = 8.8 Hz, 1H), 5.85 (d, J = 8.8 Hz, 1H), 7.17-7.34 (m, 10H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 63.0 (CH), 127.3 (4 × CH), 128.5 (2 × CH), 129.1 (4 × CH), 139.8 (2 × C). **^{19}F NMR** (375 MHz, $CDCl_3$): δ -126.4 (CF_2), -121.4 (CF_2), -112.7 (CF_2), -81.1 (CF_3). **HRMS** (ESI) $[M+NH_4]^+$ calcd for $C_{17}H_{16}F_9N_2O_2S$: 483.0783, found: 483.0802.

***N*-Cyclohexyl-1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonamide (11):** White powder. M.p.= 58-61 ºC. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 1.15-1.43 (m, 5H), 1.58-1.78 (m. 3H), 2.01-2.04 (m, 2H), 3.47-3.58 (m, 1H), 4.96 (d, J = 8.5 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 24.9 (2 × CH_2), 25.0 (CH_2), 34.7 (2 × CH_2), 55.4 (CH). **^{19}F NMR** (375 MHz, $CDCl_3$): δ -126.5 (CF_2), -121.6 (CF_2), -113.4 (CF_2), -81.2 (CF_3). **HRMS** (APCI) $[M+H]^+$ calcd for $C_{10}H_{11}F_9NO_2S$: 380.2505, found: 380.2563.

***N*-Cycloheptyl-1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonamide (12):** White powder. M.p.= 159-162 ºC. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 1.46-1.65 (m, 10H), 2.00-2.08 (m, 2H),

3.67-3.79 (m, 1H), 5.17 (d, J = 8.9 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 23.5 (2 × CH_2), 27.9 (2 × CH_2), 36.7 (2 × CH_2), 57.7 (CH). **^{19}F NMR** (375 MHz, $CDCl_3$): δ -126.5 (CF_2), -121.7 (CF_2), -113.5 (CF_2), -81.3 (CF_3). **HRMS** (APCI) $[M+H]^+$ calcd for $C_{11}H_{13}F_9NO_2S$: 394.0529, found: 394.0511.

***N*-Cyclooctyl-1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonamide (13):** White powder. M.p.= 75-78 ºC. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 1.54-1.70 (m, 12H), 1.93-2.01 (m, 2H), 3.72-3.83 (m, 1H), 5.14 (d, J = 8.8 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 23.3 (2 × CH_2), 25.1 (CH_2), 27.1 (2 × CH_2), 33.6 (2 × CH_2), 56.9 (CH). **^{19}F NMR** (375 MHz, $CDCl_3$): δ -126.5 (CF_2), -121.7 (CF_2), -113.5 (CF_2), -82.2 (CF_3). **HRMS** (APCI) $[M+H]^+$ calcd for $C_{12}H_{15}F_9NO_2S$: 408.0685, found: 408.0680.

***N*-(Adamantan-1-yl)-1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonamide (14):** White powder. M.p.= 94-97 ºC. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 1.67 (s, 6H), 2.00 (s, 6H), 2.14 (s, 3H), 5.01 (s, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 29.9 (3 × CH_2), 35.8 (3 × CH_2), 43.4 (3 × CH), 59.2 (C). **^{19}F NMR** (375 MHz, $CDCl_3$): δ -126.7 (CF_2), -121.7 (CF_2), -112.8 (CF_2), -82.5 (CF_3). **HRMS** (ESI) $[M+NH_4]^+$ calcd for $C_{14}H_{20}F_9N_2O_2S$: 451.1096, found: 451.1083.

Compound 15: Mixture of 2 unassigned isomers in 1.0 : 1.4 ratio. White powder. M.p.= 112-115 ºC. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 0.85-1.37 (m, 16H, both isomers), 1.54-1.83 (m, 10H, both isomers), 1.93-2.14 (m, 6H, both isomers), 3.11-3.24 (m, 1H, isomer 1), 3.45-3.56 (m, 1H, isomer 2), 4.89 (d, J = 9.3 Hz, 1H, isomer 1), 5.01 (d, J = 8.7 Hz, 1H, isomer 2). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 24.7, 26.2, 26.5, 29.5, 32.5, 33.2, 33.6, 33.9, 34.9, 35.5, 41.9, 42.0, 42.4, 48.8, 55.7, 60.2. **HRMS** (ESI) $[M+NH_4]^+$ calcd for $C_{14}H_{22}F_9N_2O_2S$: 451.1258, found: 451.1889.

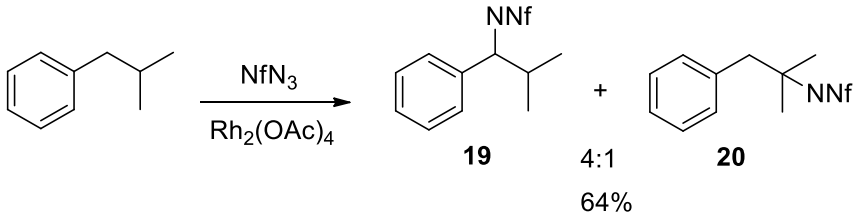
Compound 16: Mixture of 3 unassigned isomers in 3.3 : 1.9 : 1.0 ratio. White powder. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 1.26-2.08 (m, 48H), 3.44-3.54 (m, 1H, one isomer of **16a**), 3.62-3.72 (m, 2H, one isomer of **16a** and **16b**), 5.03 (s, 1H, **16b**), 5.16 (d, J = 8.6 Hz, 1H, one isomer of **16a**), 5.21 (d, J = 9.1 Hz, 1H, one isomer of **16a**). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 19.4, 20.8, 21.1, 24.0, 25.1, 25.3, 25.5, 26.2, 26.7, 28.5, 29.4, 30.9, 31.6, 31.7,

34.3, 34.4, 34.9, 35.4, 36.4, 41.1, 42.1, 42.8, 52.2, 56.6, 59.1. **HRMS** (ESI) $[M+NH_4]^+$ calcd for $C_{14}H_{22}F_9N_2O_2S$: 451.1258, found: 451.1882.

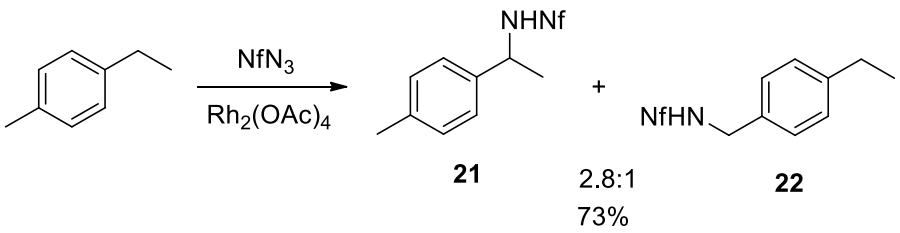
Compound 17: Mixture of 2 unassigned isomers in 1.0 : 0.15 ratio. White powder. Spectrum dates for the major isomer **17a**. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 0.92 (d, *J* = 6.5 Hz, 3H), 1.05 (d, *J* = 6.3 Hz, 3H), 1.13-1.26 (m, 2H), 1.36-1.67 (m, 3H), 1.80 (dd, *J* = 13.2, 3.2 Hz, 1H), 1.94-2.09 (m, 2H), 3.13 (ddd, *J* = 13.8, 11.6, 4.1 Hz, 1H), 4.84 (s, 1H isomer **17c**), 4.91 (d, *J* = 9.2 Hz, 1H, isomer **17a**). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 18.9 (CH_3), 22.1 (CH_3), 32.4 (CH_2), 34.1 (2 × CH_2), 38.6 (CH), 43.8 (CH), 61.9 (CH_2). **HRMS** (ESI) $[M-H]^+$ calcd for $C_{12}H_{15}F_9NO_2S$: 408.0685, found: 408.0690.

Compound 18: Mixture of 3 unassigned isomers in 1.0 : 1.2 : 3.1 ratio. White powder. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 0.90-0.98 (m, 11H), 1.04-1.16 (m, 7H), 1.26-1.44 (m, 11H), 1.55-1.72 (m, 12H), 1.88-1.92 (m, 4H), 3.44 (ddd, *J* = 11.7, 8.6, 4.0 Hz, 1H, one isomer of **18a/b**), 3.63-3.74 (m, 2H, one isomer of **18a/b** and **18c**), 4.99 (s, 1H, **18c**), 5.15 (d, *J* = 6.3 Hz, 1H, one isomer of **18a/b**), 5.18 (d, *J* = 7.9 Hz, 1H, one isomer of **18a/b**). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 11.2, 18.5, 19.4, 21.7, 22.2, 23.6, 27.6, 27.9, 28.0, 29.7, 31.2, 31.4, 31.7, 32.7, 36.7, 37.3, 38.6, 57.9, 58.1, 61.1.

Amination of isobutylbenzene and 4-ethyltoluene. The reaction was carried out following the general sufamidation conditions described above.



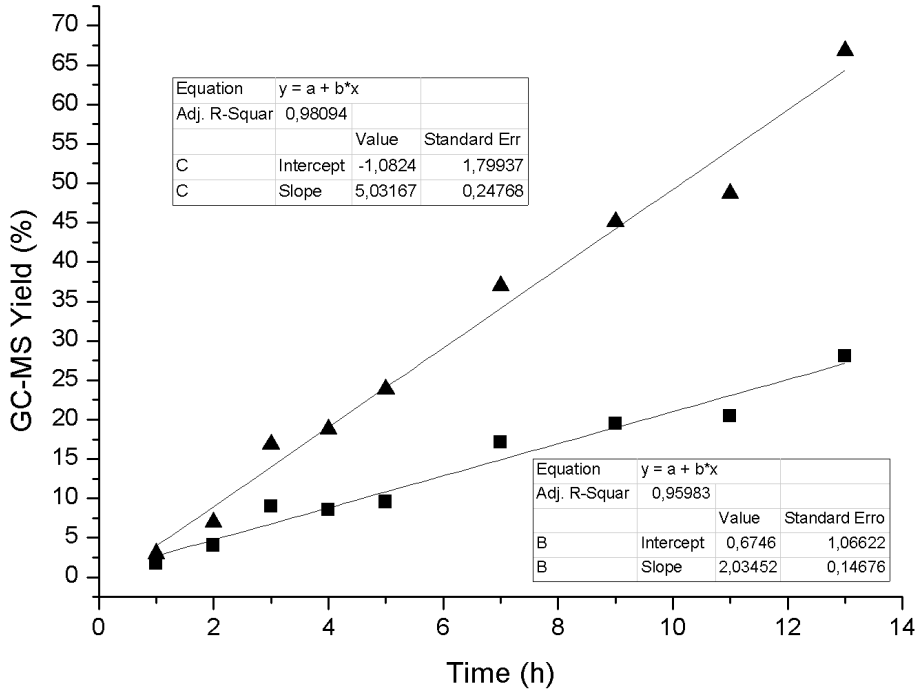
^{1}H NMR (300 MHz, $CDCl_3$): δ 0.86 (d, *J* = 6.7 Hz, 3H, for **19**), 1.04 (d, *J* = 6.7 Hz, 3H, for **19**), 1.44 (s, 6H, for **20**), 1.99-2.10 (m, 1H, for **19**), 2.94 (s, 2H, for **20**), 4.34 (dd, *J* = 9.2, 7.9 Hz, 1H, for **19**), 4.72 (s, 1H, for **20**), 5.60 (d, *J* = 9.3 Hz, 1H, for **19**), 7.17-7.39 (m, 10H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 18.2, 19.6, 27.9, 35.0, 49.4, 60.1, 66.3, 71.5, 126.6, 127.5, 128.2, 128.8, 128.9, 135.6, 138.8.



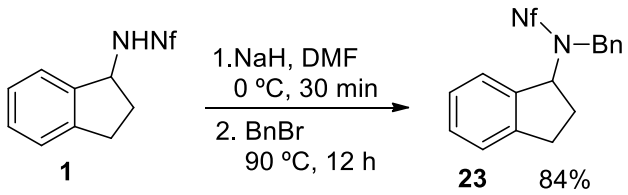
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.27 (t, *J* = 7.6 Hz, 3H, for **22**), 1.65 (d, *J* = 6.9 Hz, 3H, for **21**), 2.38 (s, 3H, for **21**), 2.69 (q, *J* = 7.6 Hz, 2H, for **22**), 4.48 (d, *J* = 5.7 Hz, 2H, for **22**), 4.79-4.90 (m, 1H, for **21**), 5.33 (t, *J* = 5.0 Hz, 1H, for **22**), 5.43 (d, *J* = 8.4 Hz, 1H, for **21**), 7.01-7.30 (m, 10H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 15.6 (CH_3, for **22**), 21.2 (CH_3, for **21**), 23.6 (CH_3, for **21**), 28.7 (CH_2, for **22**), 48.7 (CH_2, for **22**), 55.7 (CH, for **21**), 126.0 (2 × CH, for **21**), 128.2 (2 × CH, for **22**), 128.8 (2 × CH, for **22**), 129.8 (2 × CH, for **21**), 132.5 (C, for **22**), 138.2 (C, for **21**), 138.4 (C, for **21**), 145.2 (C, for **22**).

Determination of Kinetic Deuterium Isotope Effects. To a stirred solution of nonafluorobutanesulfonyl azide (130 mg, 0.4 mmol) in a mixture of cyclohexane (200 μL) and cyclohexane-d_{12} (200 μL), was added $Rh_2(OAc)_4$ (5 mg, 3 mole% with respect to NfN_3) and methyl trichloroacetate (28 μL, 0.2 mmol), which was used as internal standard. The mixture was heated at 90 ºC. Aliquots (10 μL) of the reaction mixture were taken after 0, 1, 2, 3, 4, 5, 7, 9, 11, and 13 hours. The aliquots were immediately quenched by addition to 20 μL of a solution of PPh_3 (2M in CH_2Cl_2) and diluted with CH_2Cl_2 to 1.0 mL. The so treated aliquots were analyzed by GC-MS (see graph).

$$k_H/k_D = 5.03167/2.03452 = 2.47$$



Synthesis of *N*-benzyl-*N*-(2,3-dihydro-1*H*-inden-1-yl)-1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonamide (23). To a solution of compound **1** (150 mg, 0.36 mmol) in dry DMF (1.0 mL) was added NaH (30 mg, 60% dispersion in mineral oil) at 0 ºC. After stirring the reaction mixture at this temperature for 30 min, benzyl bromide (0.05 mL, 0.432 mmol) was added and the reaction mixture was stirred at 90 ºC for 12 h. The mixture was concentrated under reduced pressure, Et_2O (5 mL) was added, and the resultant solution was washed with a saturated aqueous solution of NaCl (3×5 mL). The organic layer was separated, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (hexane/EtOAc 10:1) to afford **23** as a colorless oil (157 mg, 84% yield).



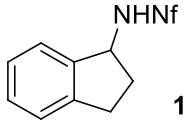
^{1}H NMR (300 MHz, $CDCl_3$, *T* = 25 ºC, mixture of rotamers): δ 1.67 (br s, 1H), 2.01 (br s, 1H), 2.34 (br s, 2H), 2.52 (br s, 2H), 2.93 (br s, 1H), 3.07 (br s, 1H), 3.94 (d, *J* = 16.5 Hz, 1H), 4.57 (s, 2H), 4.83 (d, *J* = 16.5 Hz, 1H), 5.67 (br s, 2H), 6.93-7.38 (m, 18H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 28.8, 30.1, 33.0, 50.0, 65.3, 66.0, 72.1, 125.7, 127.1, 127.8, 127.9, 128.3, 128.7, 129.4, 139.0, 137.3, 138.3, 146.0. **HRMS** (ESI) $[M+NH_4]^+$ calcd for $C_{20}H_{20}F_9N_2O_2S$: 523.1096, found: 523.1091.

***N*-Benzyl-2,3-dihydro-1*H*-inden-1-amine (24).** To a stirred solution of sulfonamide **23** (0.2 mmol) in dry toluene (1.0 mL) was added dropwise a solution of Red-Al ($NaAlH_2(OCH_2CH_2OCH_3)_2$, 0.3 mL, 5 eq., 65% wt in toluene). The mixture was refluxed for 3 h and then cooled. Excess Red-Al was decomposed by addition of water (3.5 mL), aqueous NaOH (3.5 mL, 15% w/v) and the organic layer was extracted with Et_2O (3×5 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (hexane/EtOAc 6:1) to afford **24** as a colorless oil (41 mg, 91% yield), with ^{1}H NMR and ^{13}C NMR in agreement with those reported in the literature.[1]

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.62 (br s, 1H), 1.78-1.90 (m, 1H), 2.33-2.42 (m, 1H), 2.72-2.82 (m, 1H), 2.93-3.02 (m, 1H), 3.87 (AB system, *J* = 4.3 Hz, 2H), 4.26 (apparent t, *J* = 6.6 Hz, 1H), 7.14-7.36 (m, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$): 30.2 (CH_2), 33.8 (CH_2), 51.3 (CH_2), 62.9 (CH), 124.3 (CH), 124.9 (CH), 126.4 (CH), 127.0 (CH), 127.5 (CH), 128.3 (2 × CH), 128.5 (2 × CH), 140.8 (C), 143.8 (C), 145.5 (C). **HRMS** (ESI) $[M+H]^+$ calcd for $C_{16}H_{18}N_2$: 224.1434, found: 224.1431.

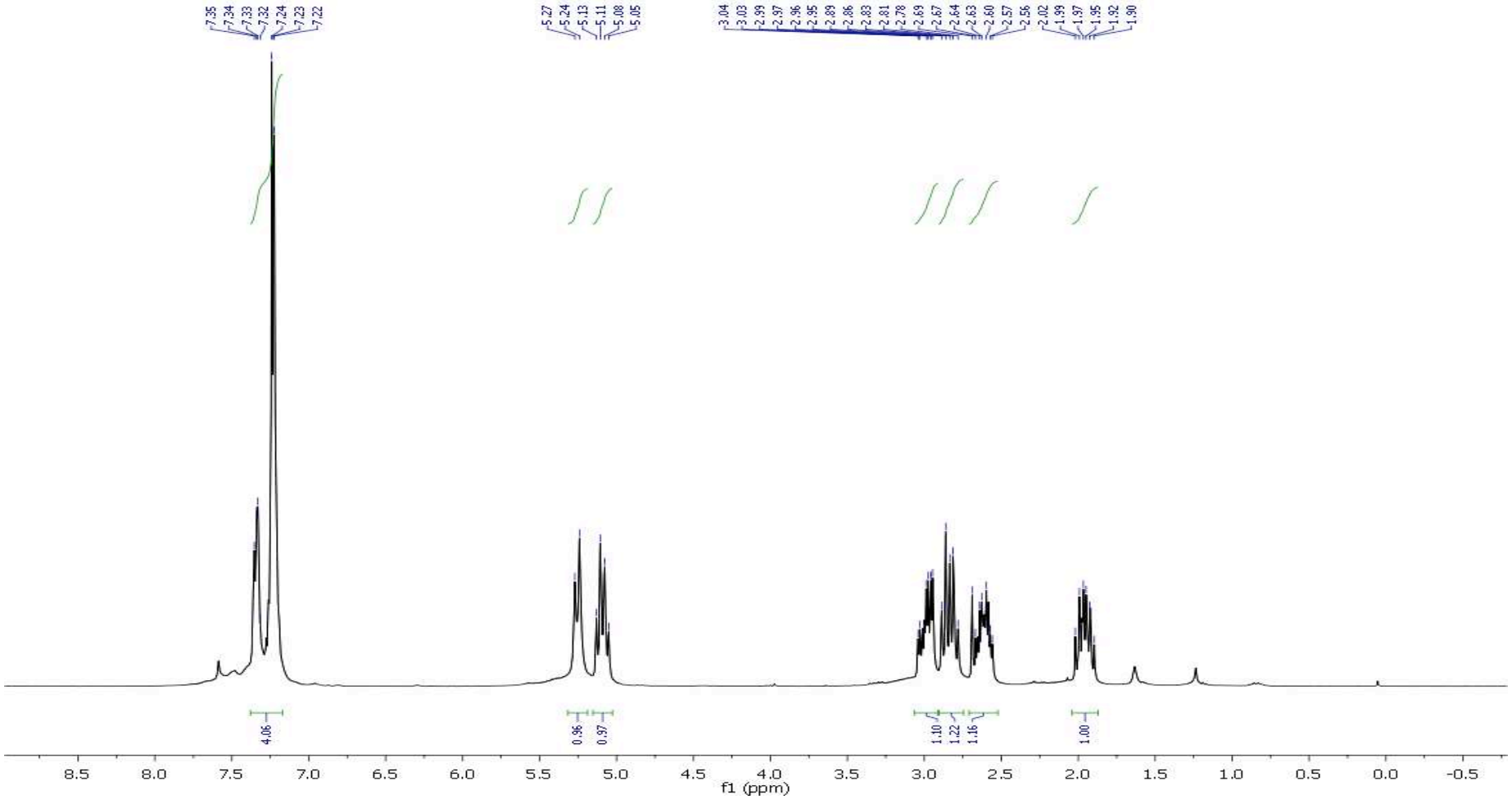
References:

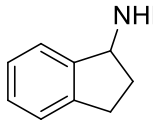
1) Lee, O.-H.; Kaw, K.-L.; Yan, D. *Org. Lett.* **2009**, *11*, 3302-3305.



1

^{1}H NMR (300 MHz, $CDCl_3$)





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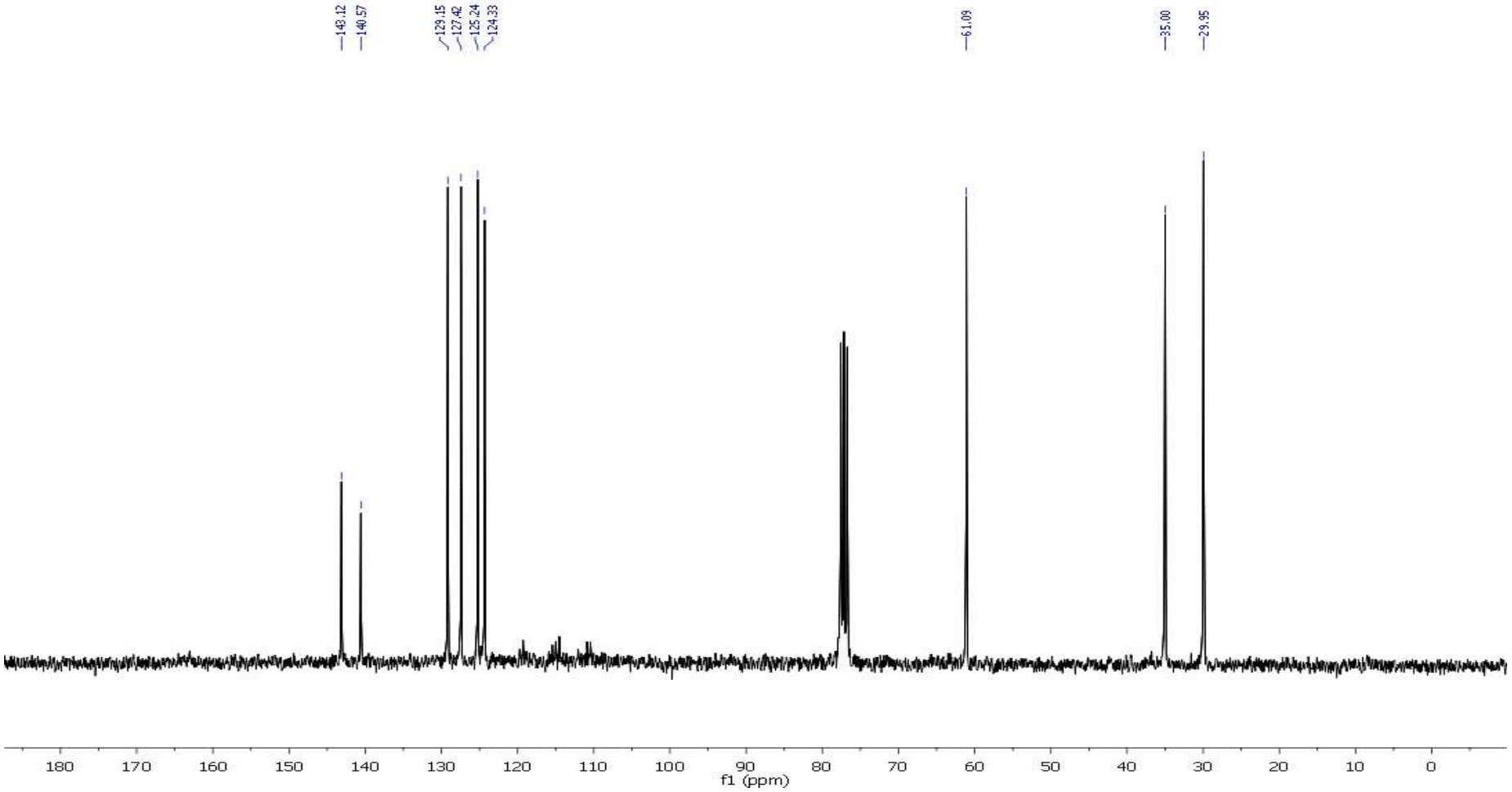
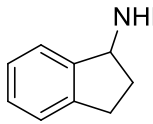
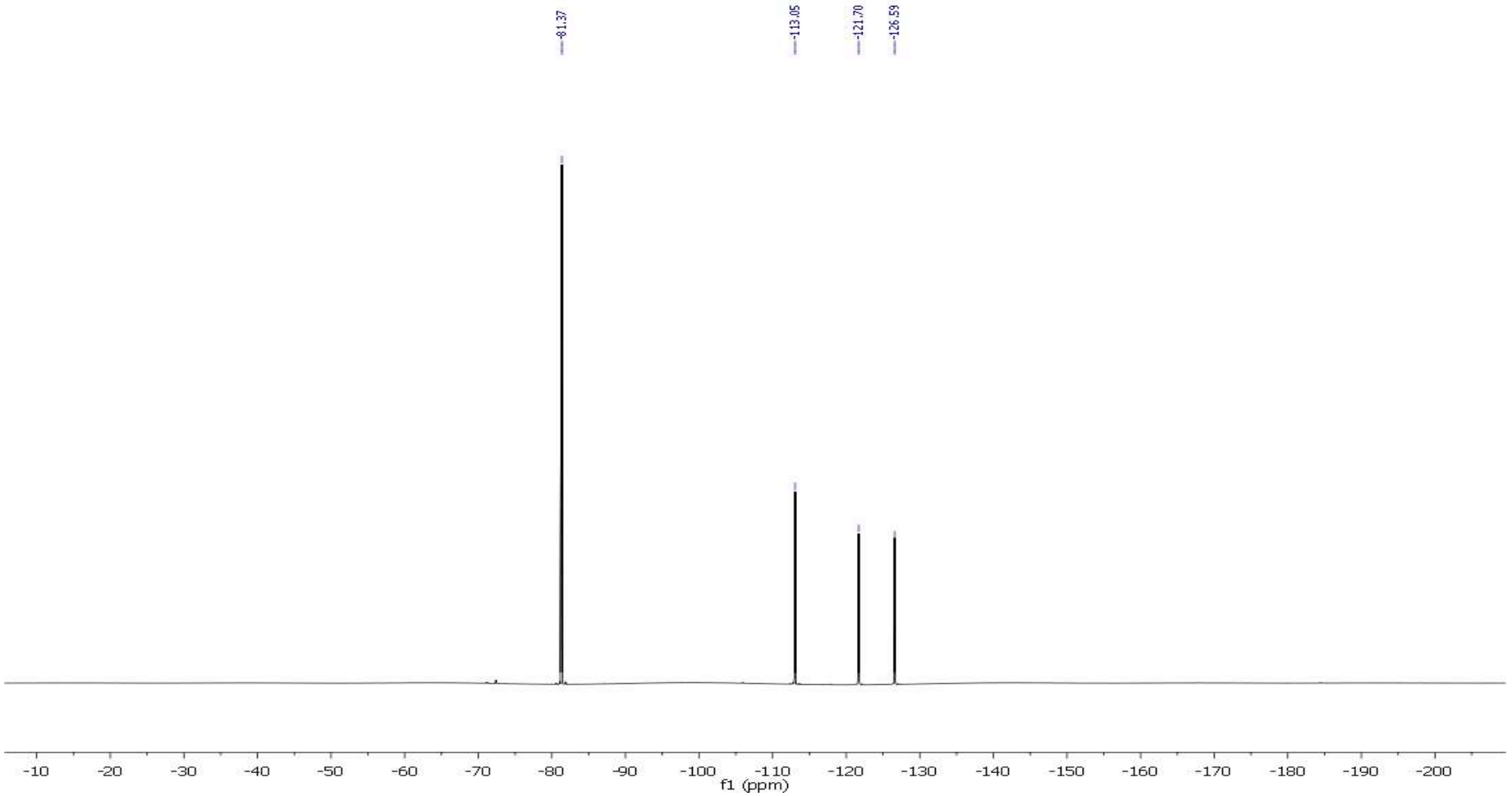
^{13}C NMR (75 MHz, $CDCl_3$)

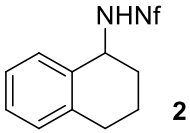




1

^{19}F NMR (375 MHz, $CDCl_3$)





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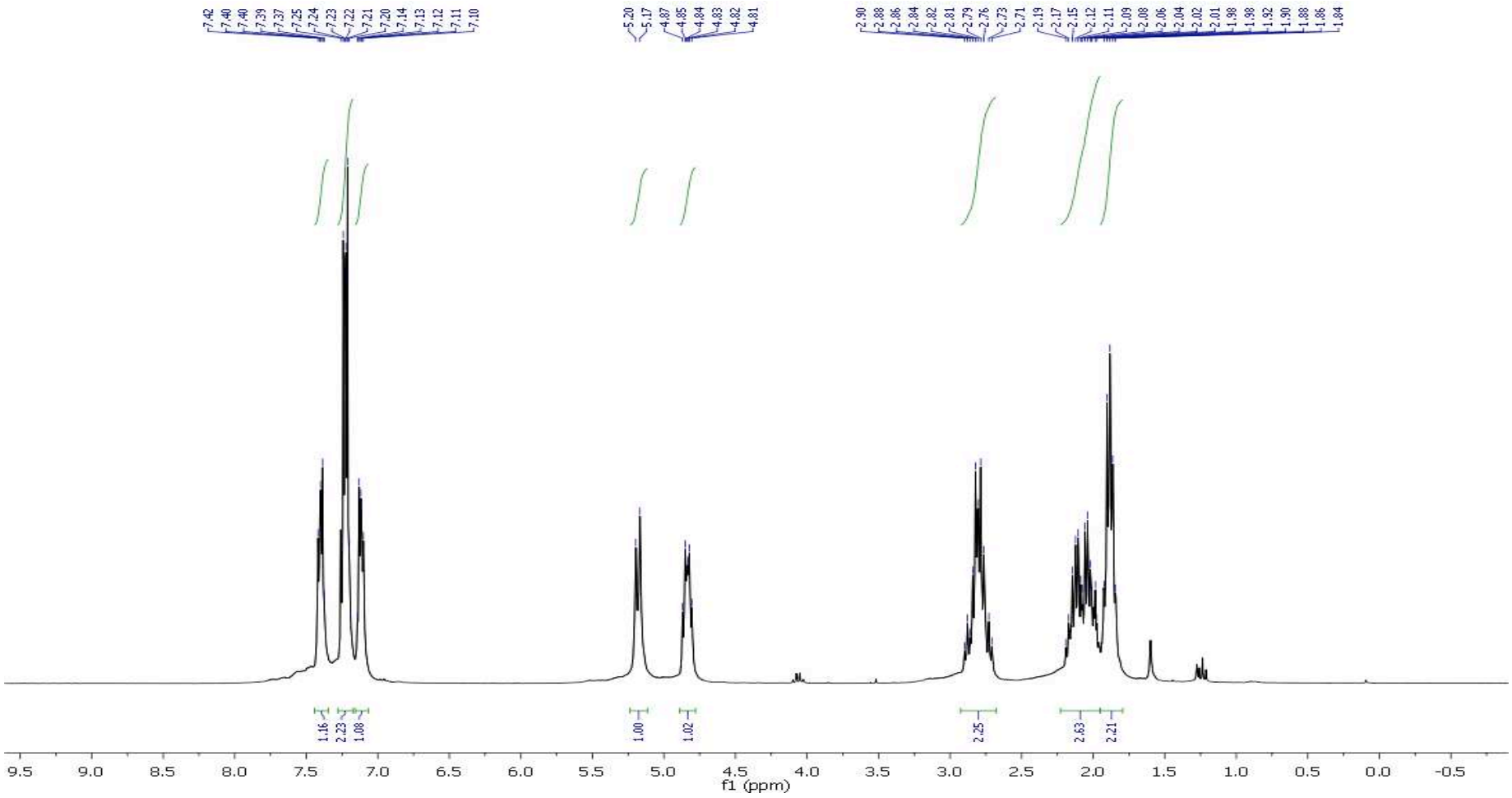
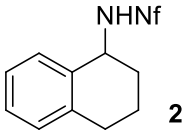
^{1}H NMR (300 MHz, $CDCl_3$)





2

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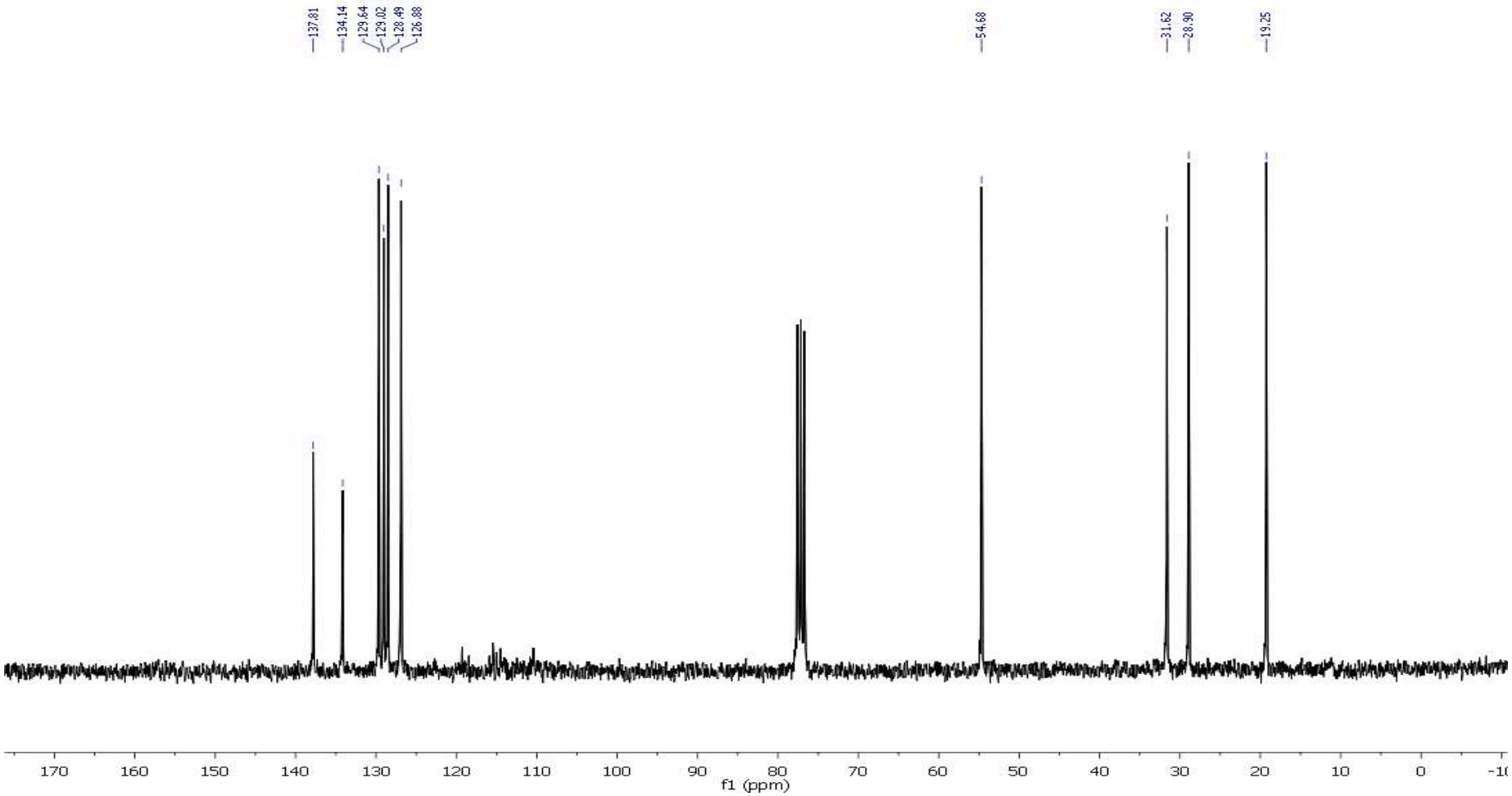

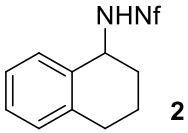

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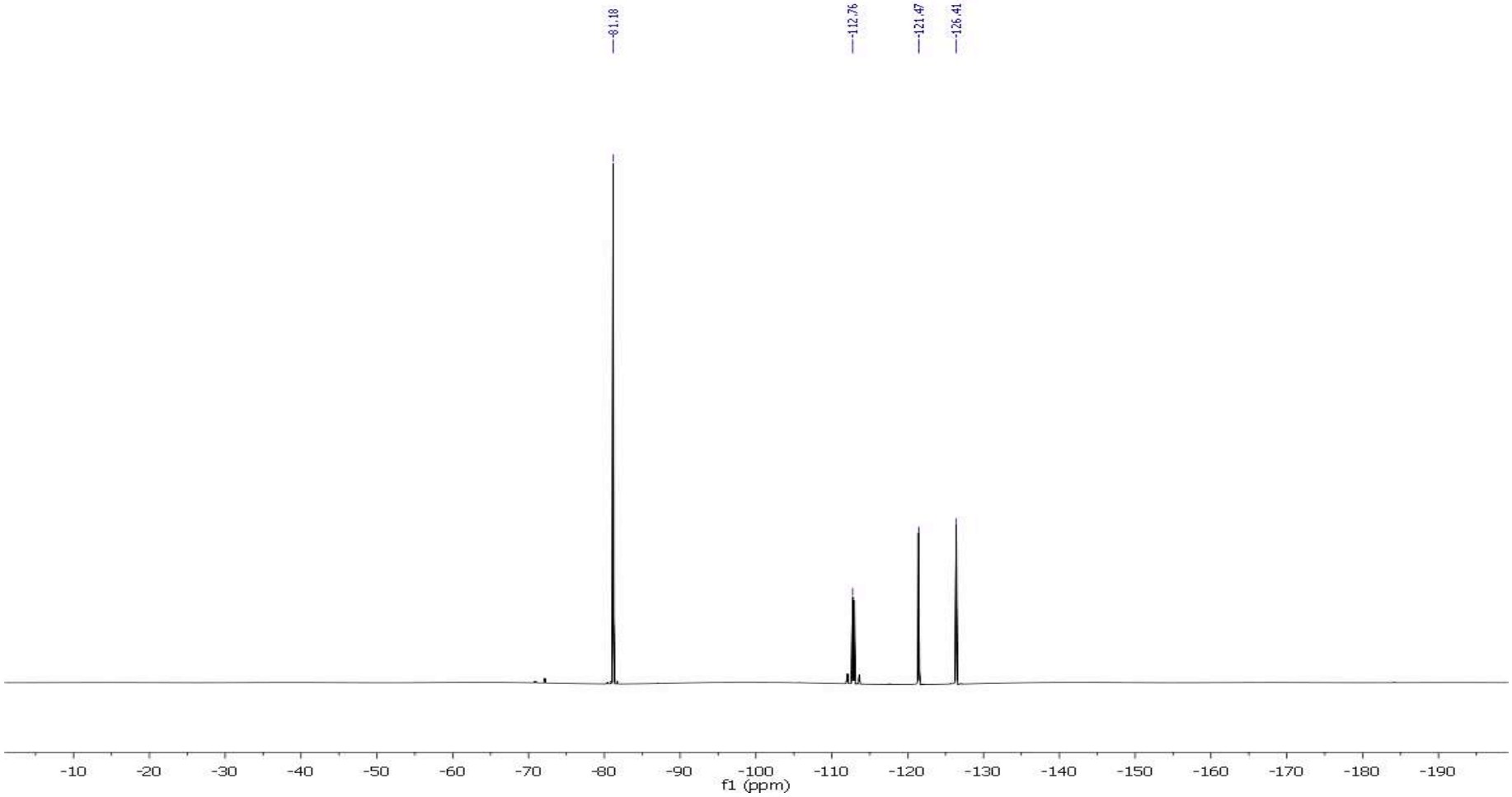

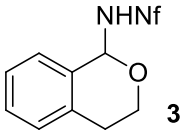

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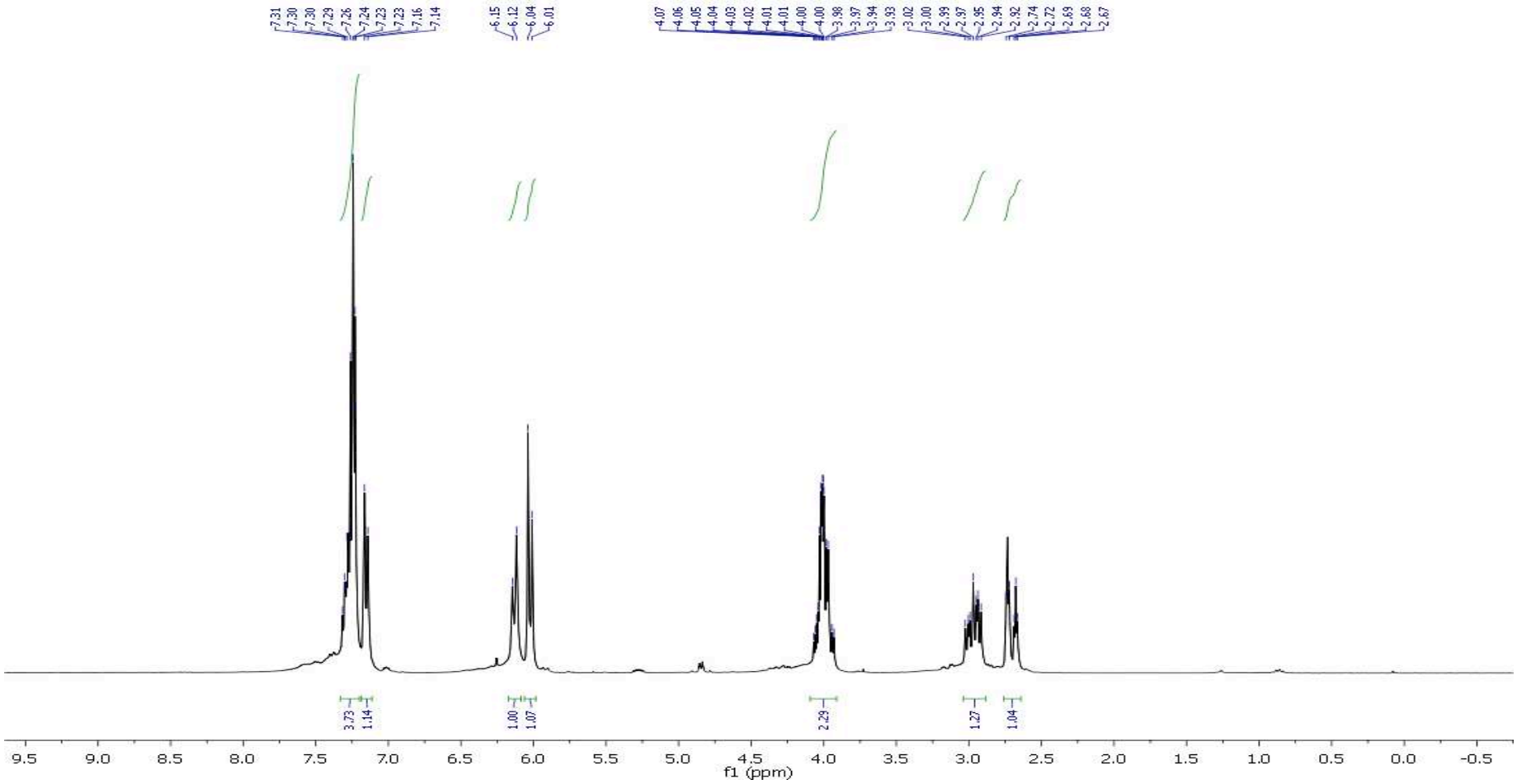
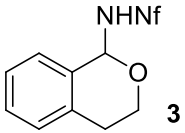
^{1}H NMR (300 MHz, $CDCl_3$)





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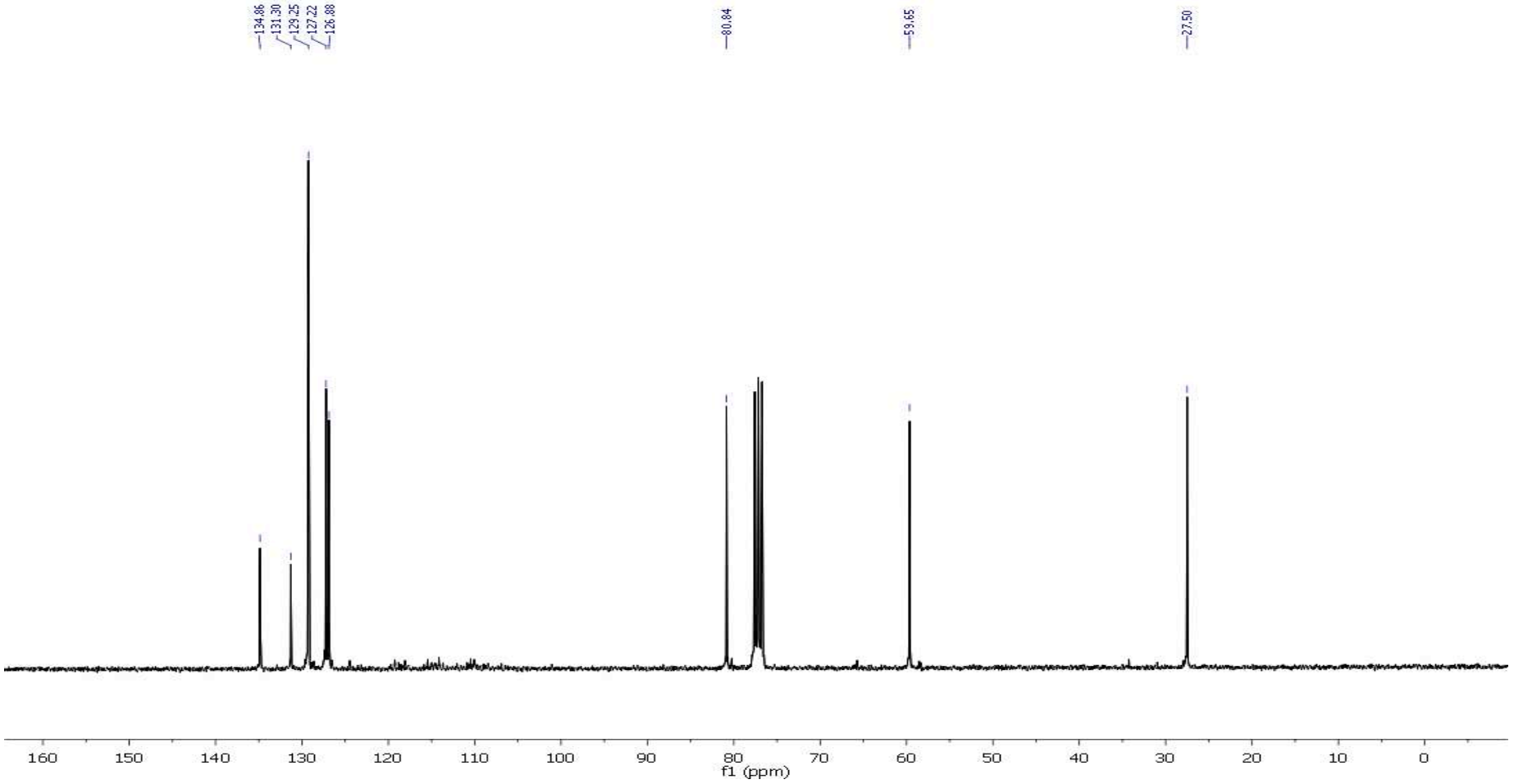

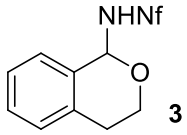

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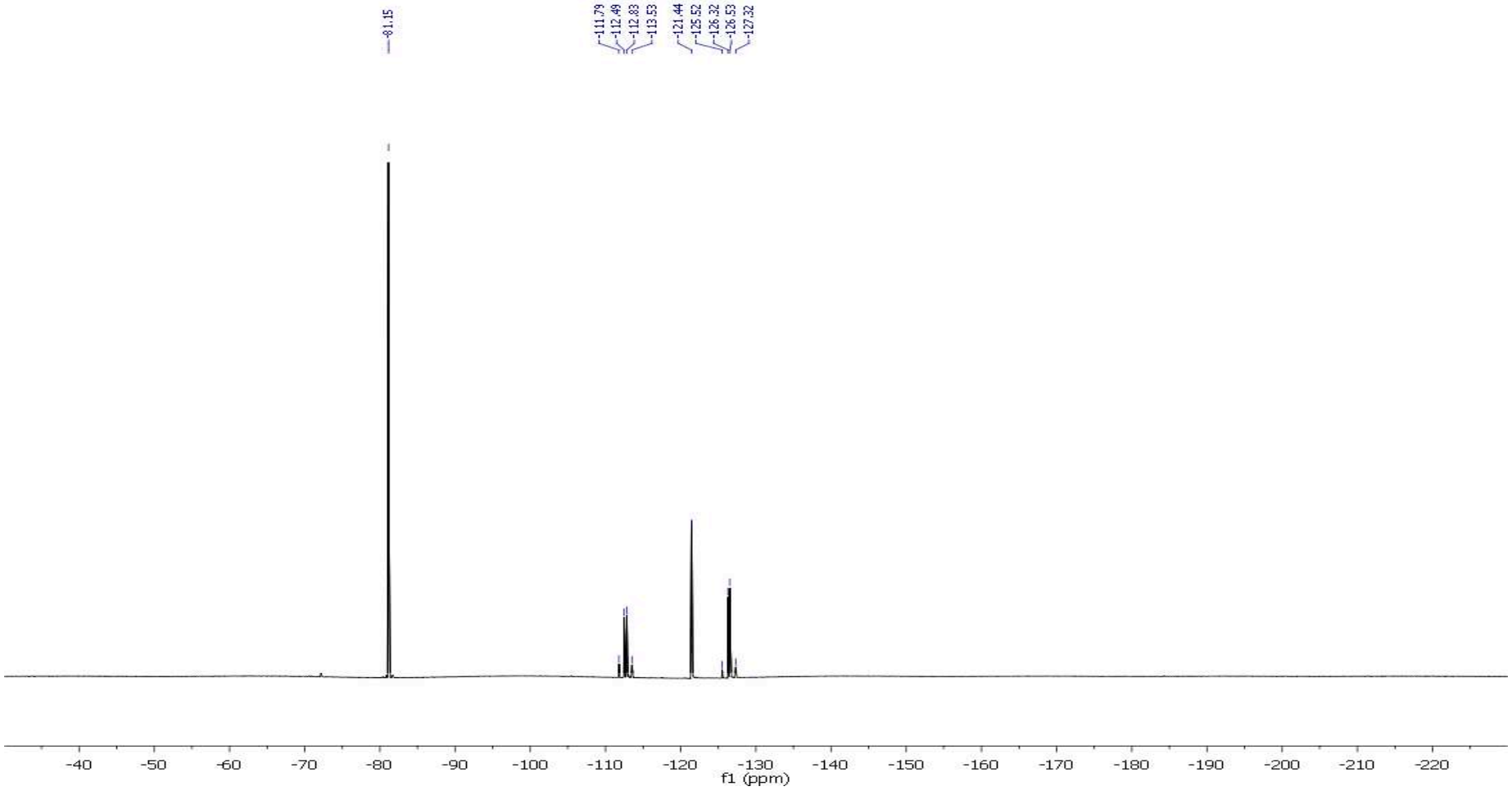

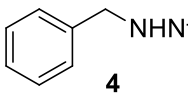

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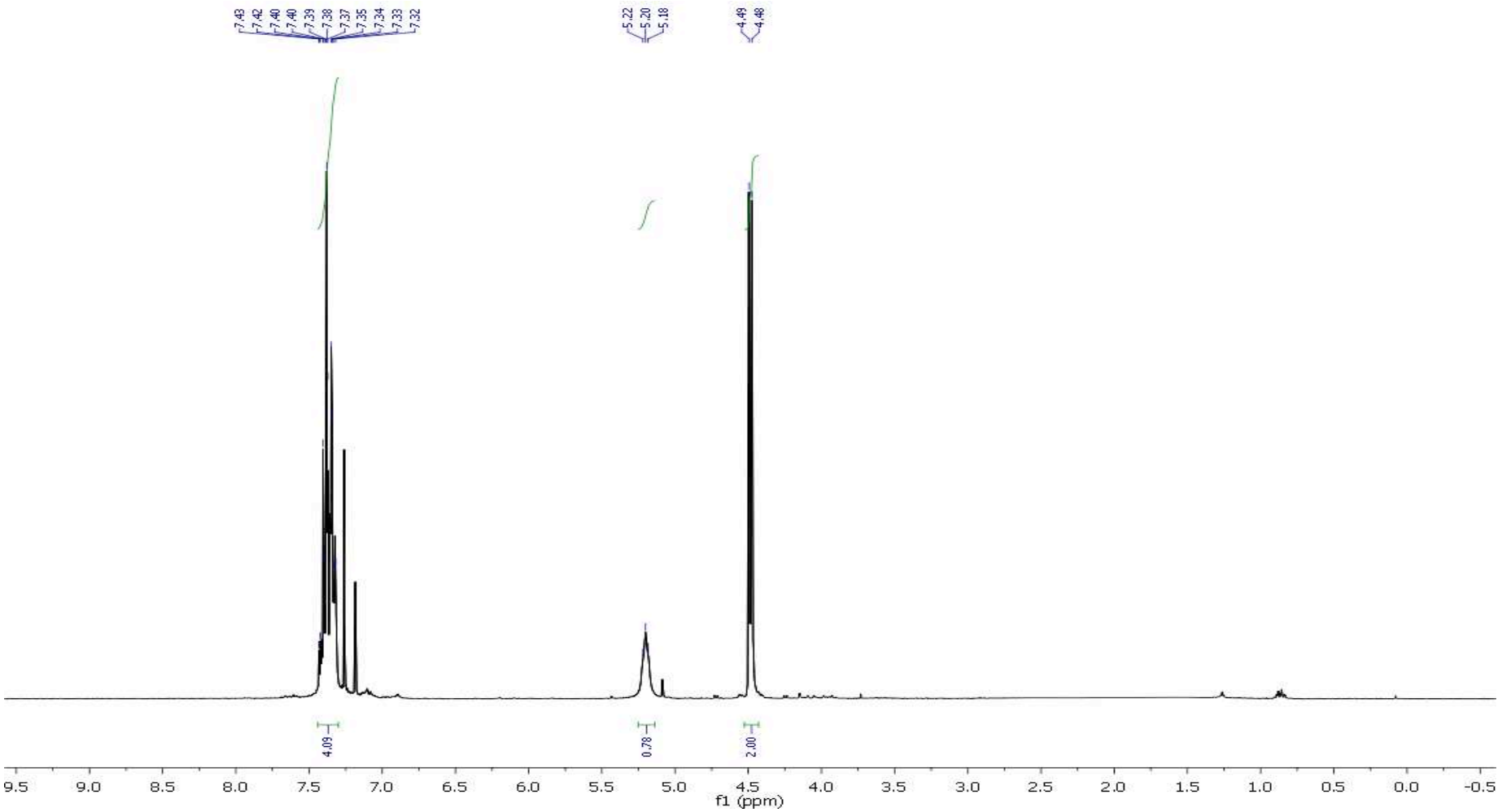

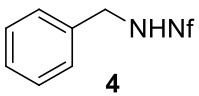

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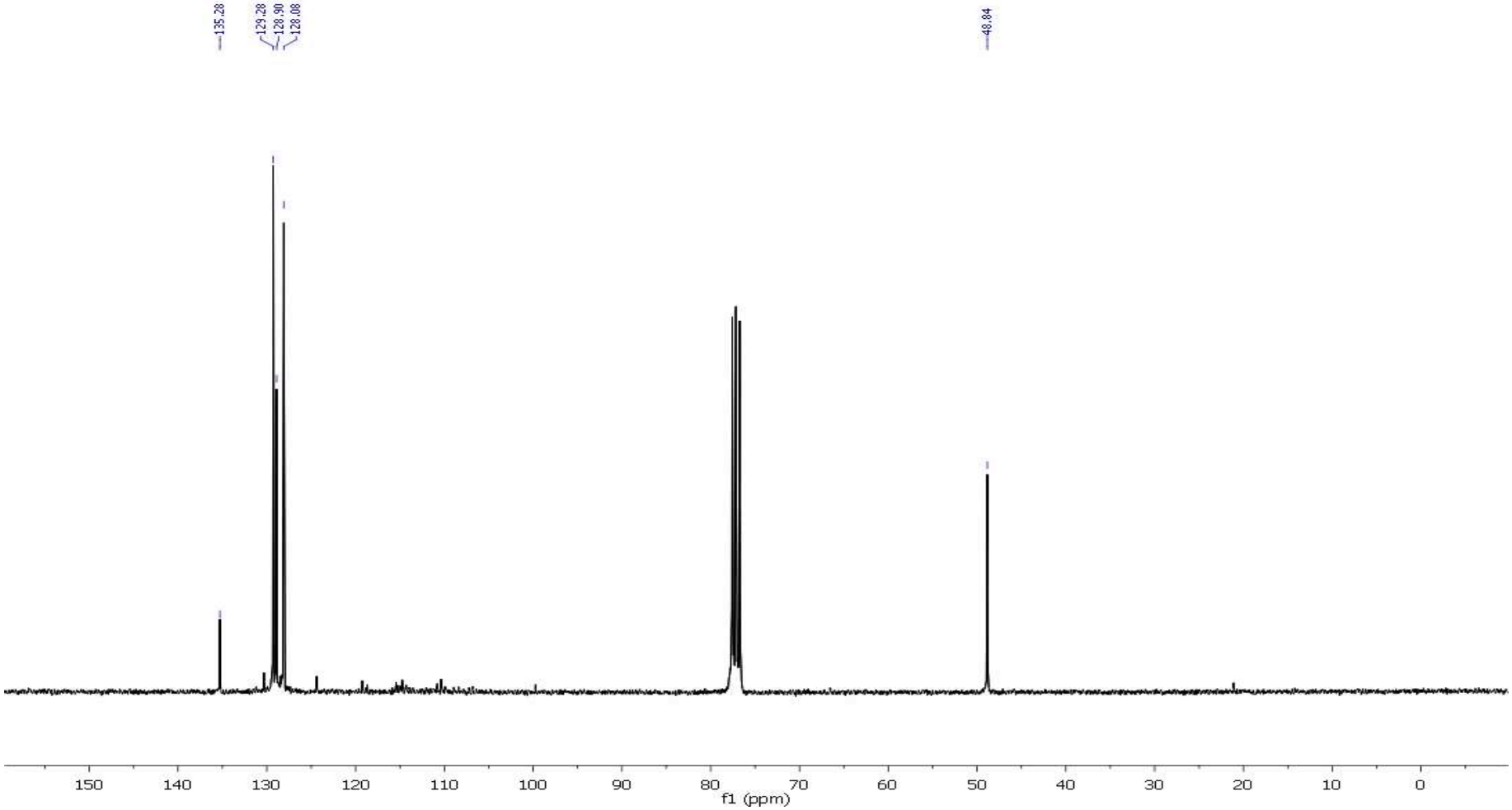

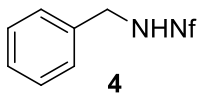

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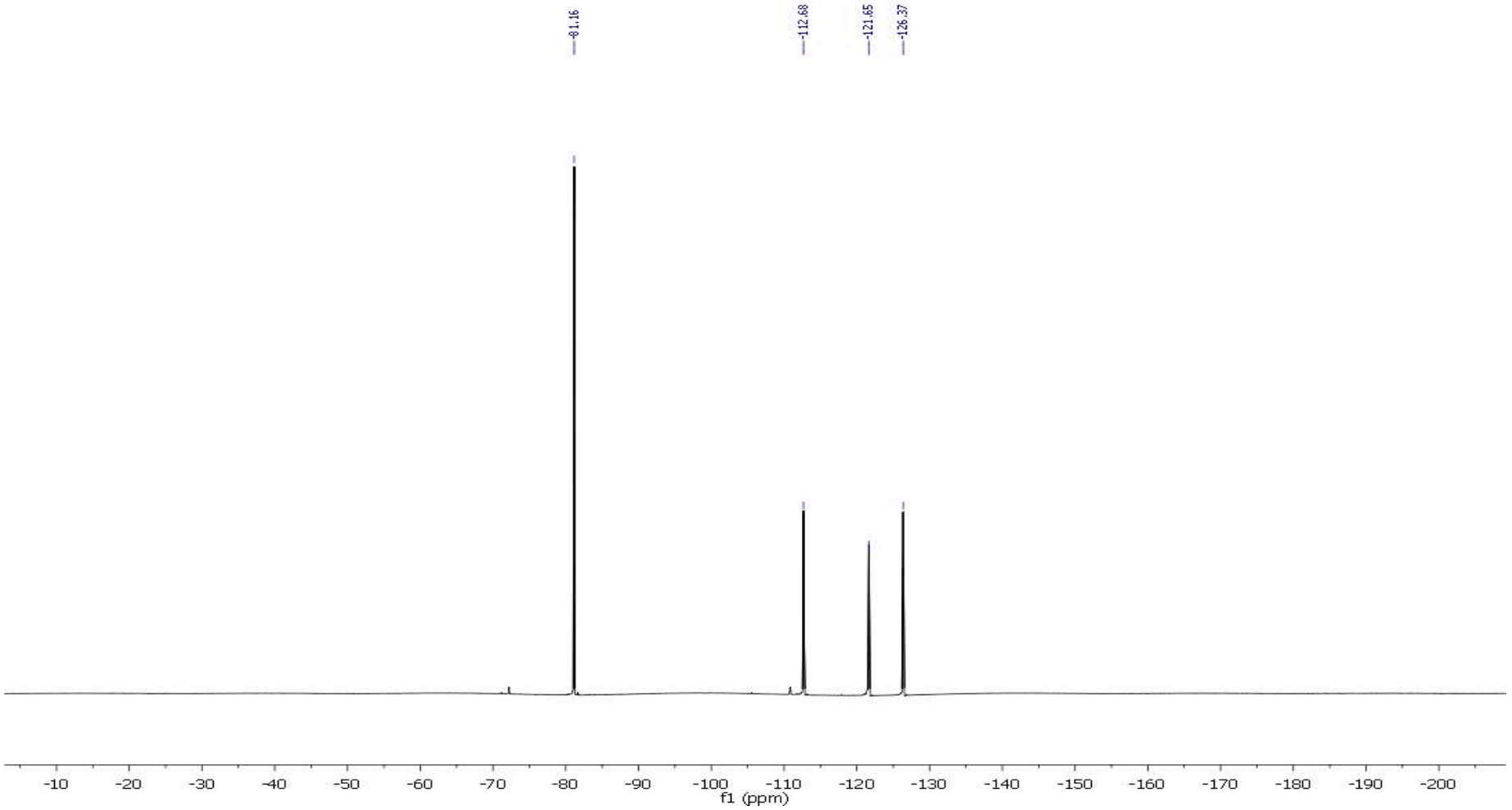

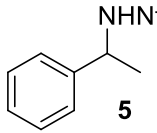

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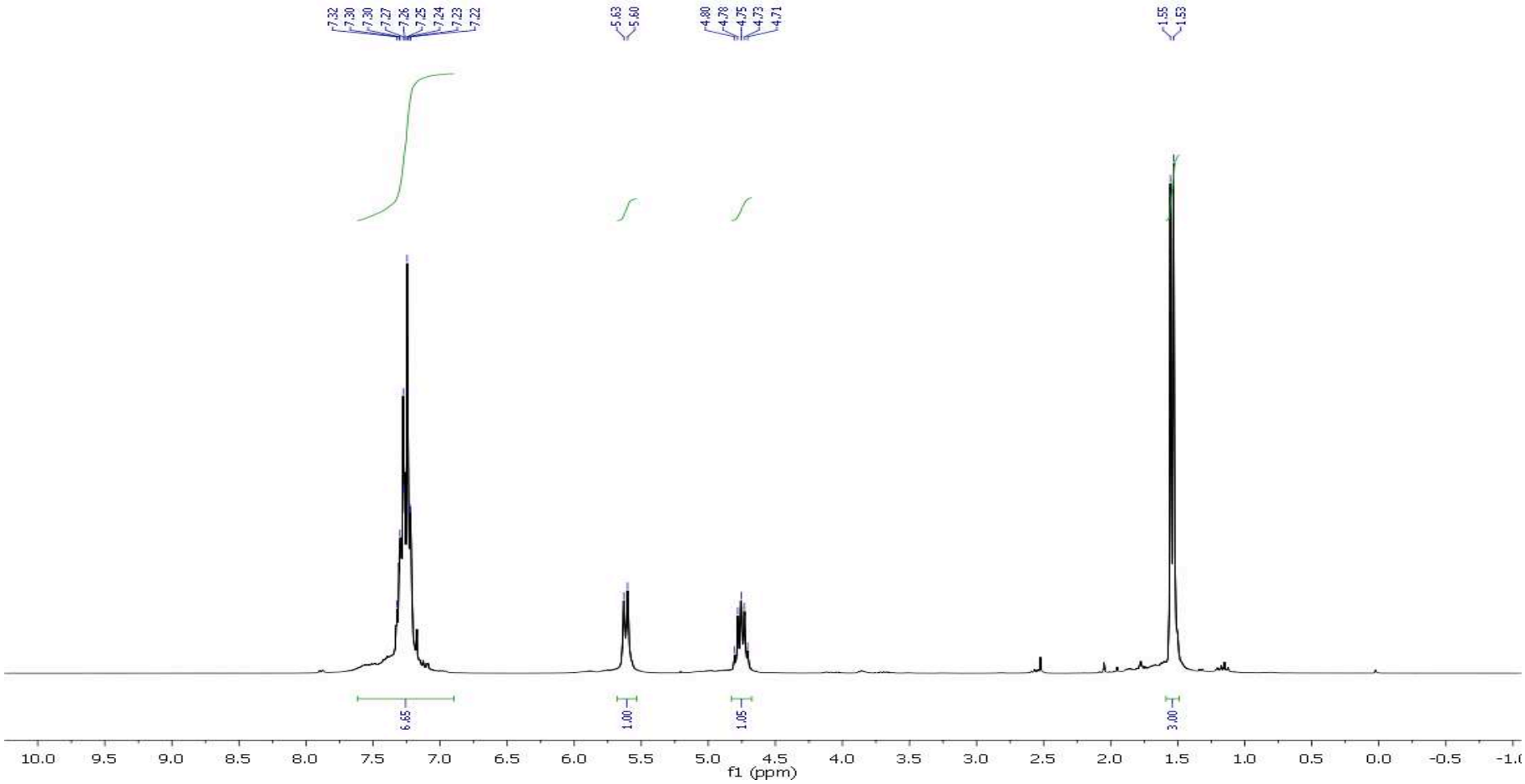

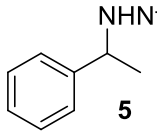

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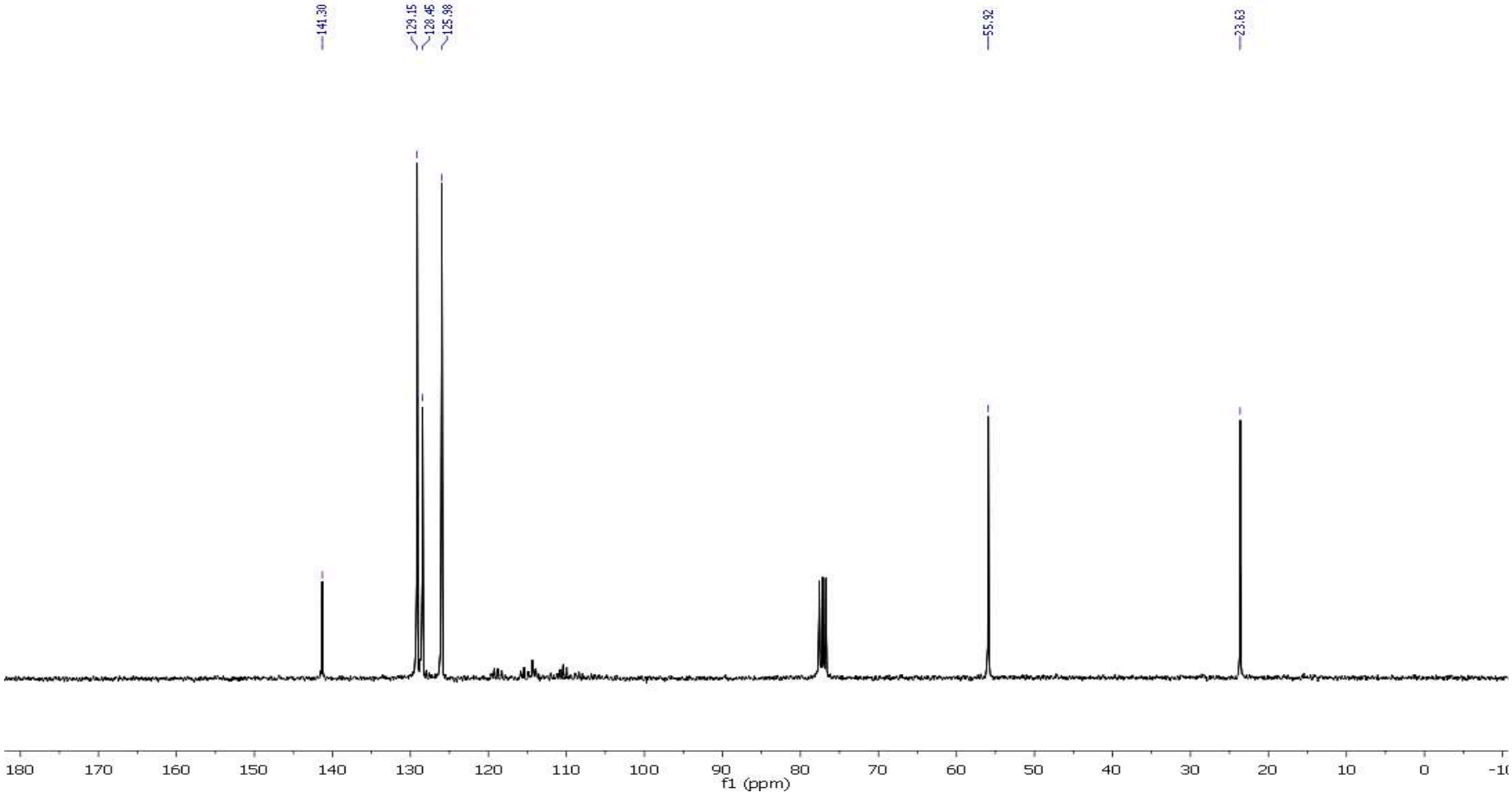

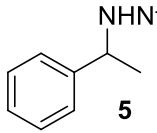

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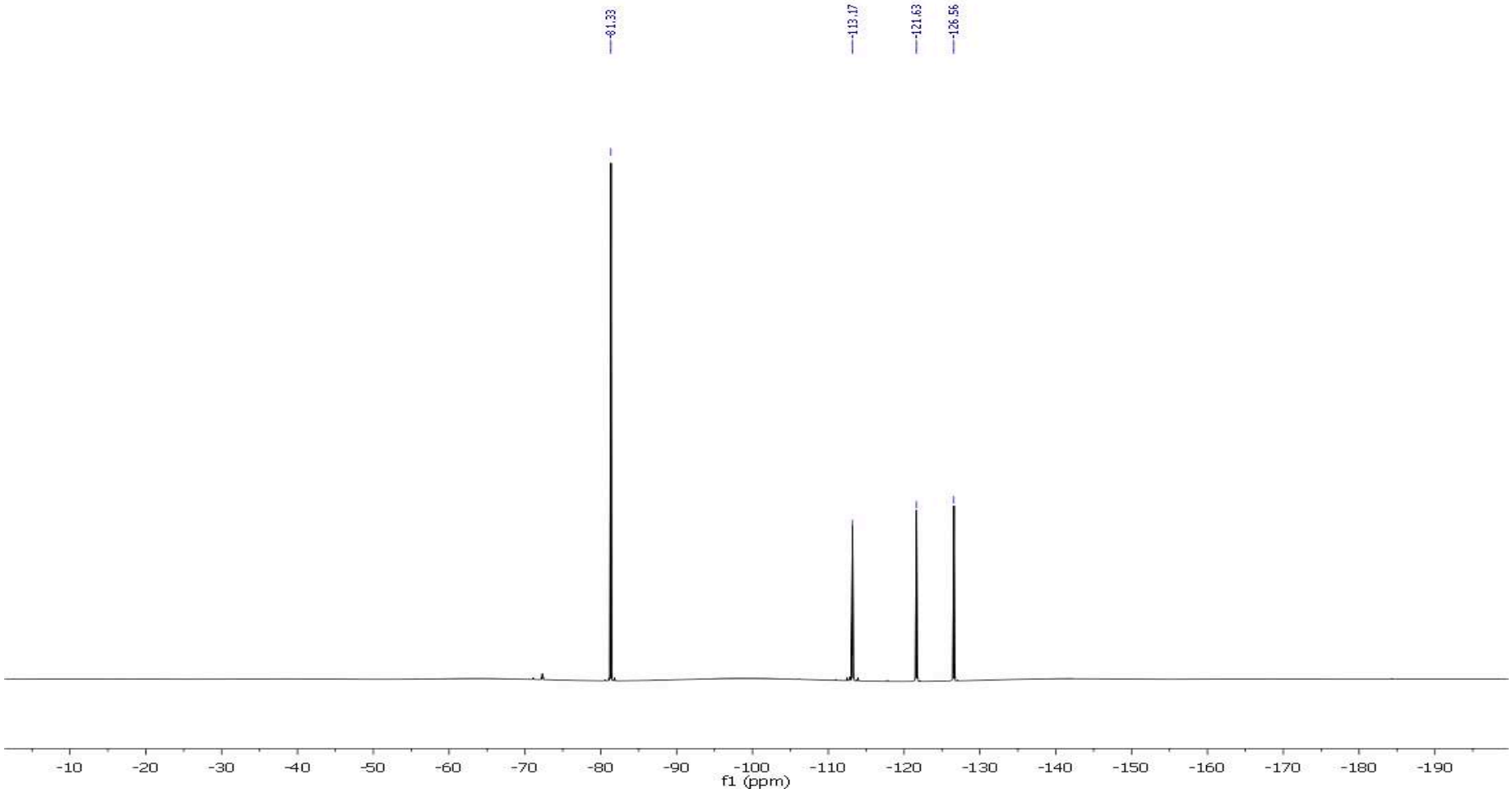
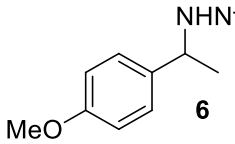
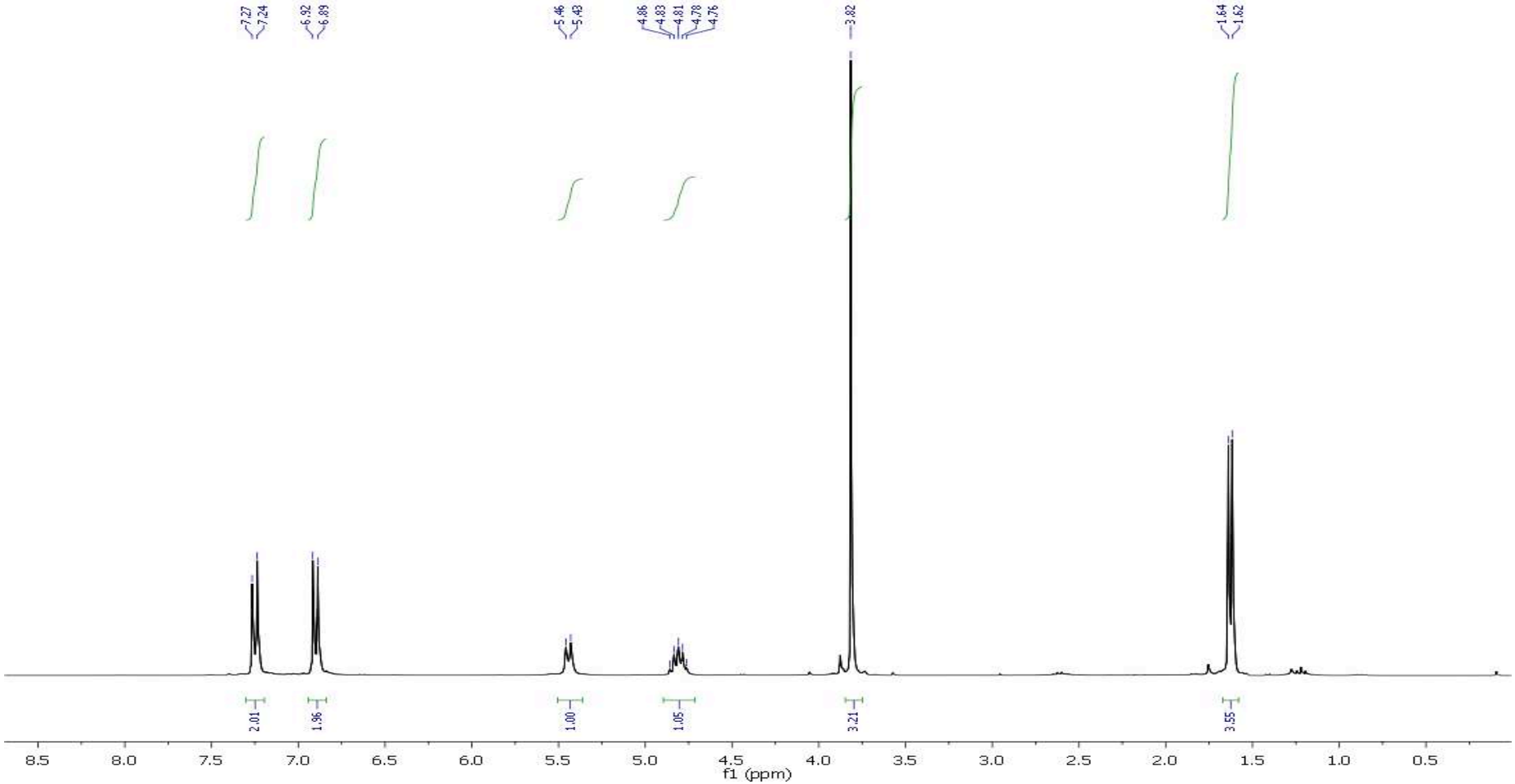
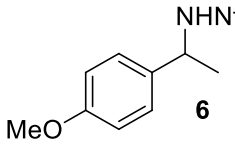




6

^{1}H NMR (300 MHz, $CDCl_3$)





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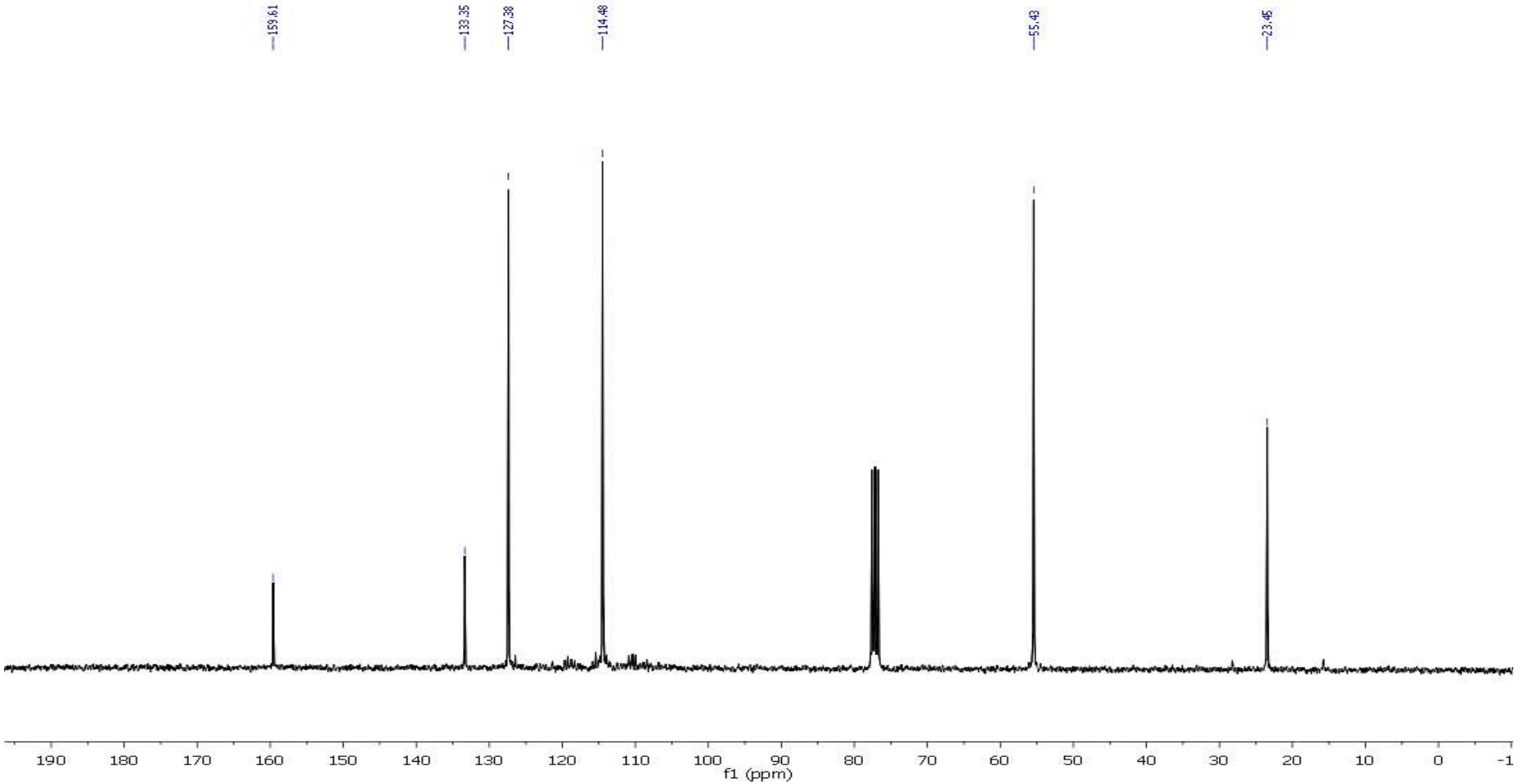

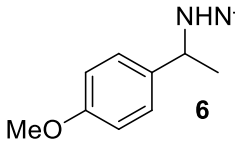

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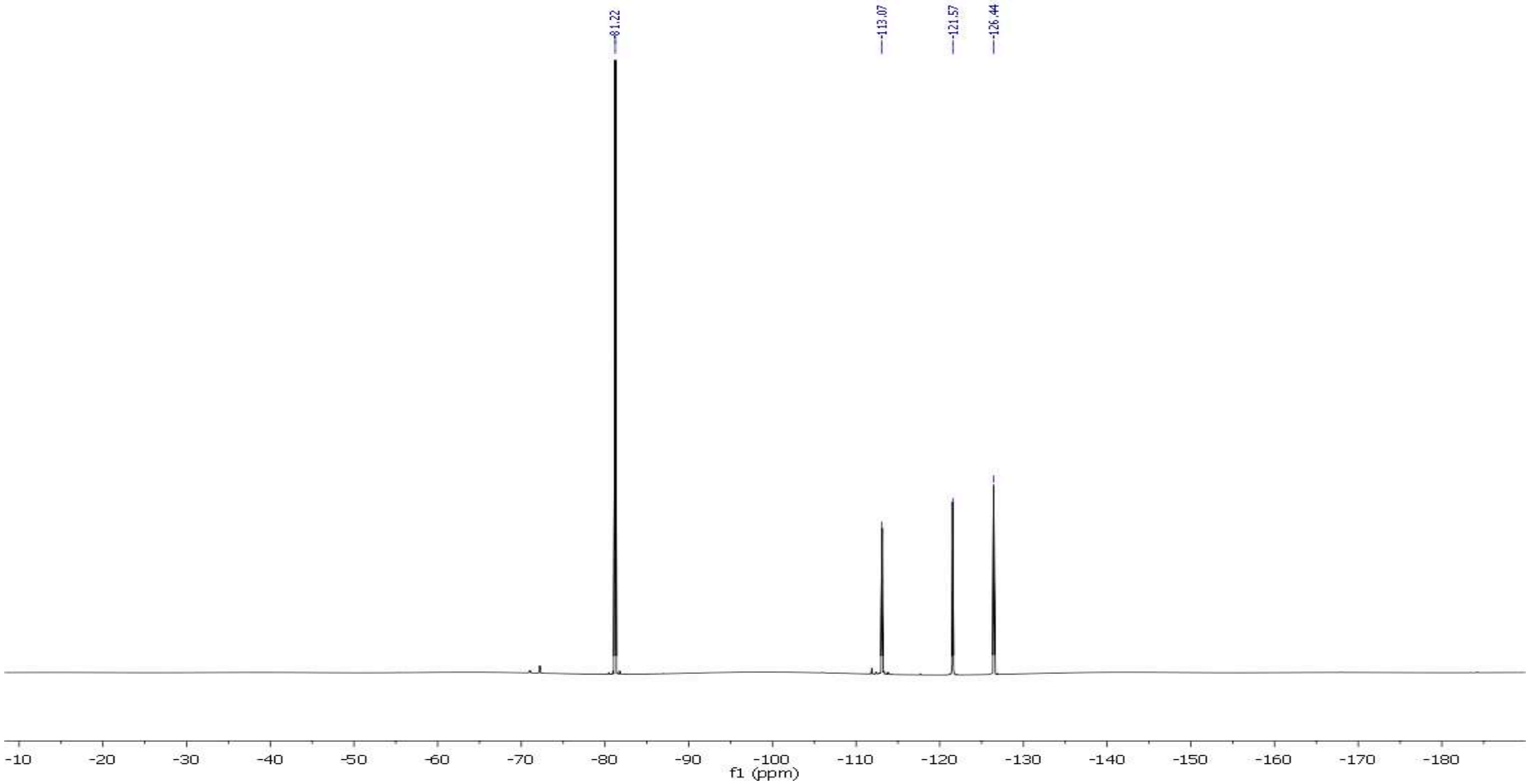

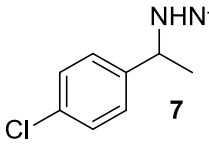

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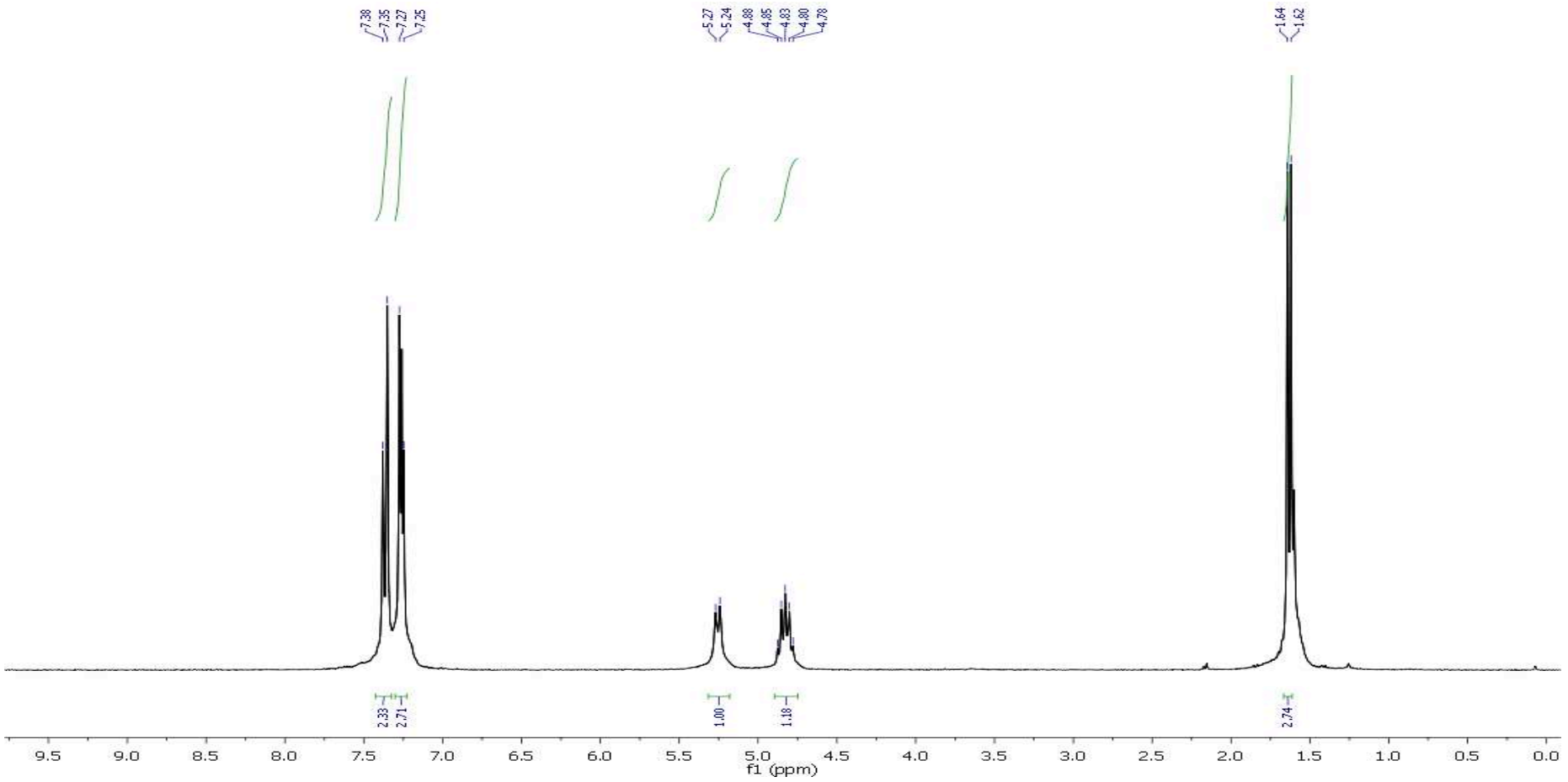
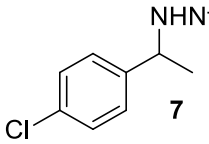
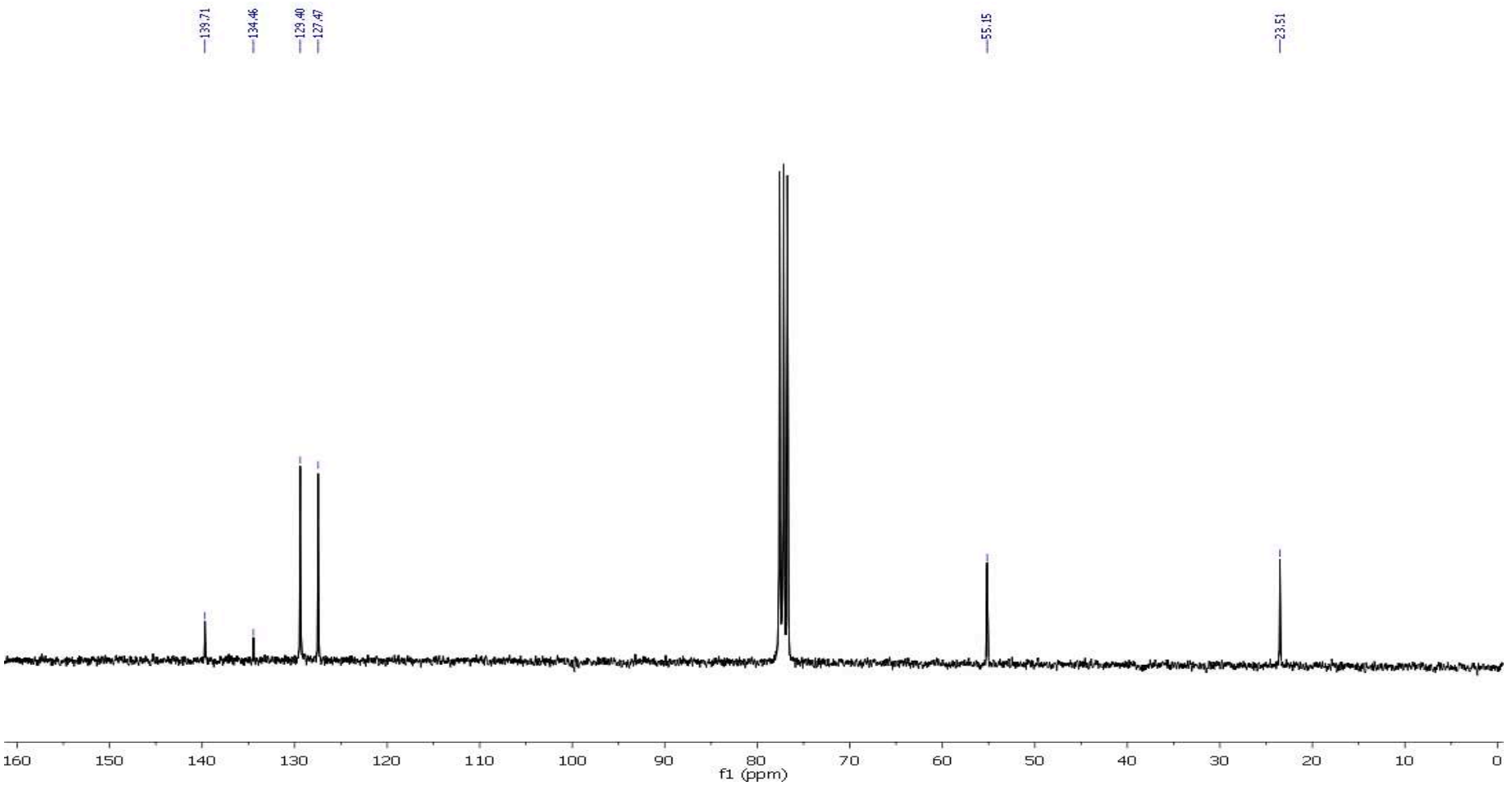
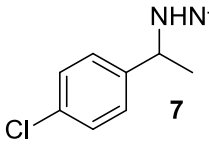




7

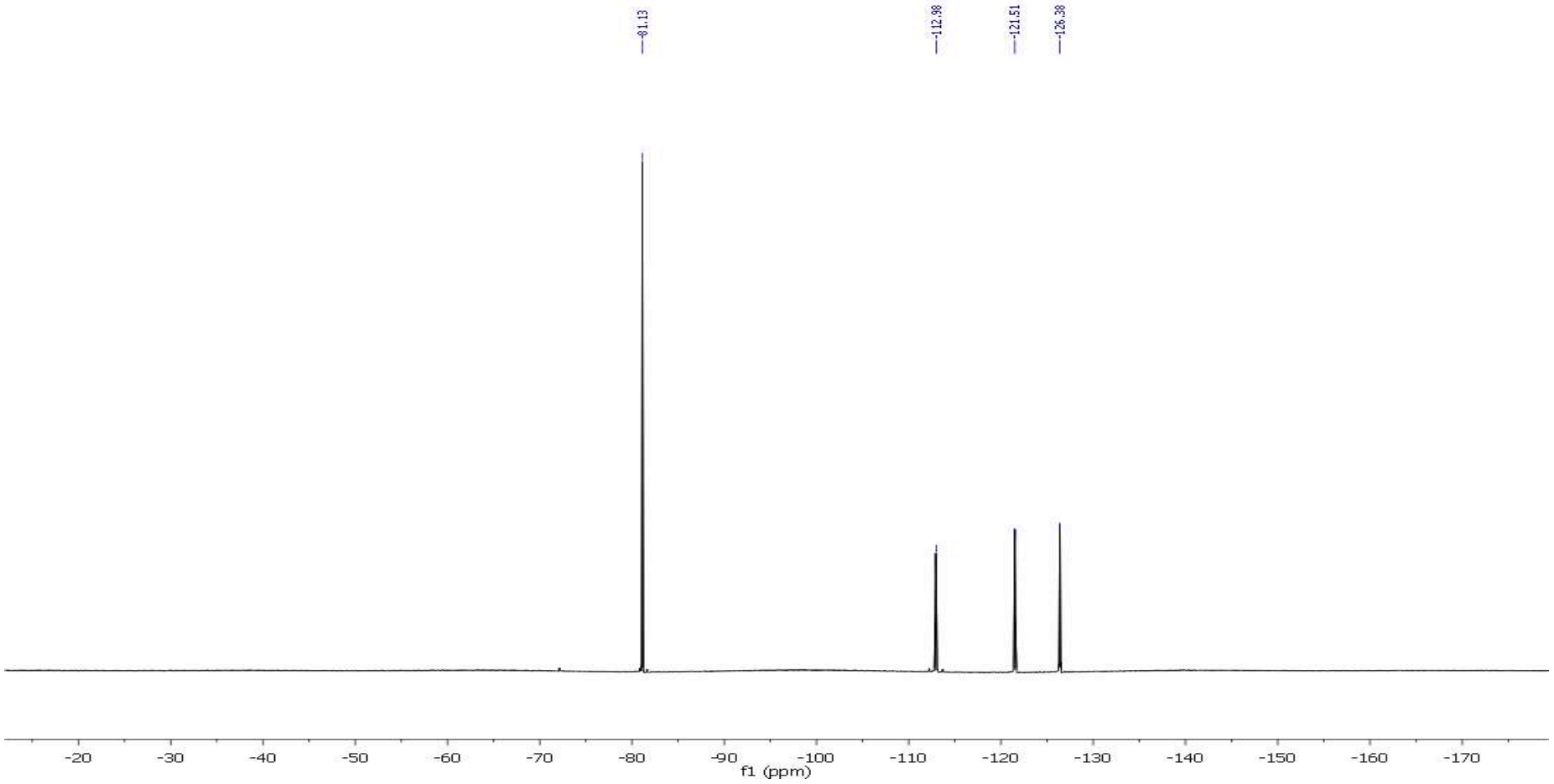
^{13}C NMR (75 MHz, $CDCl_3$)

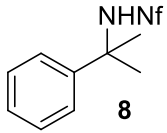




7

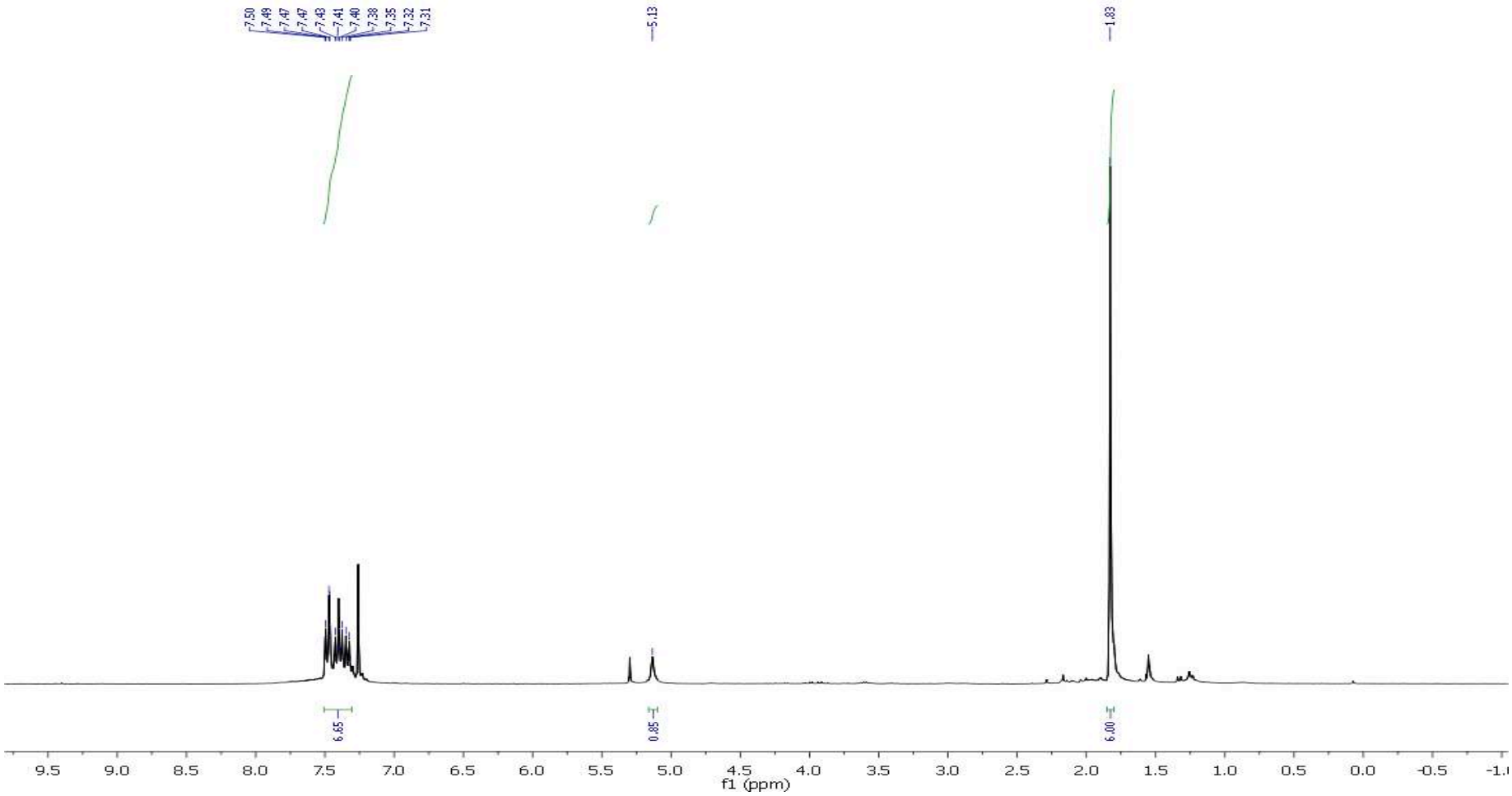
^{19}F NMR (375 MHz, $CDCl_3$)

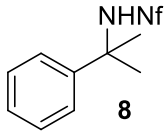




8

^{1}H NMR (300 MHz, $CDCl_3$)





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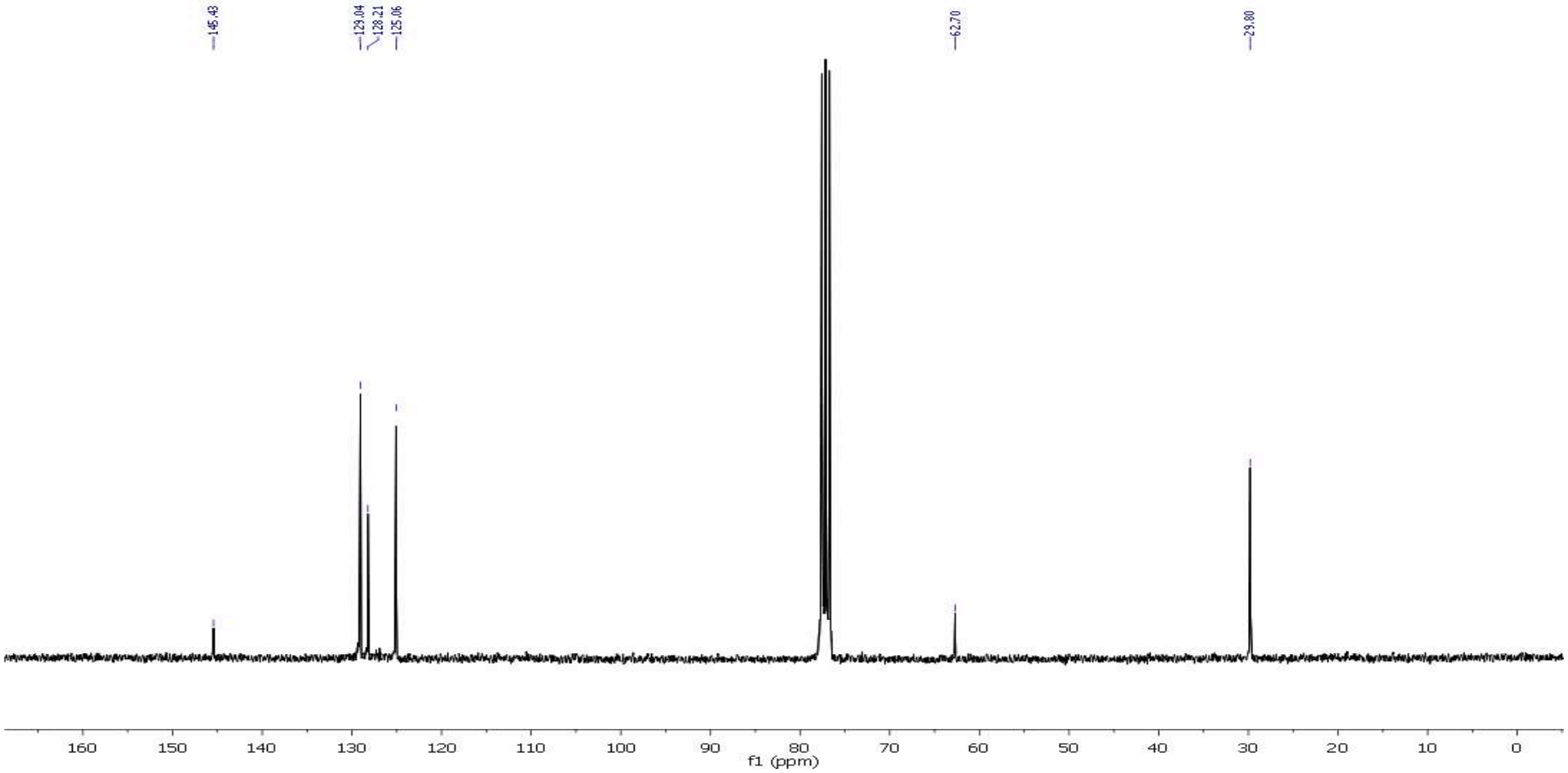

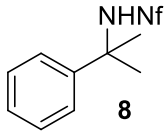

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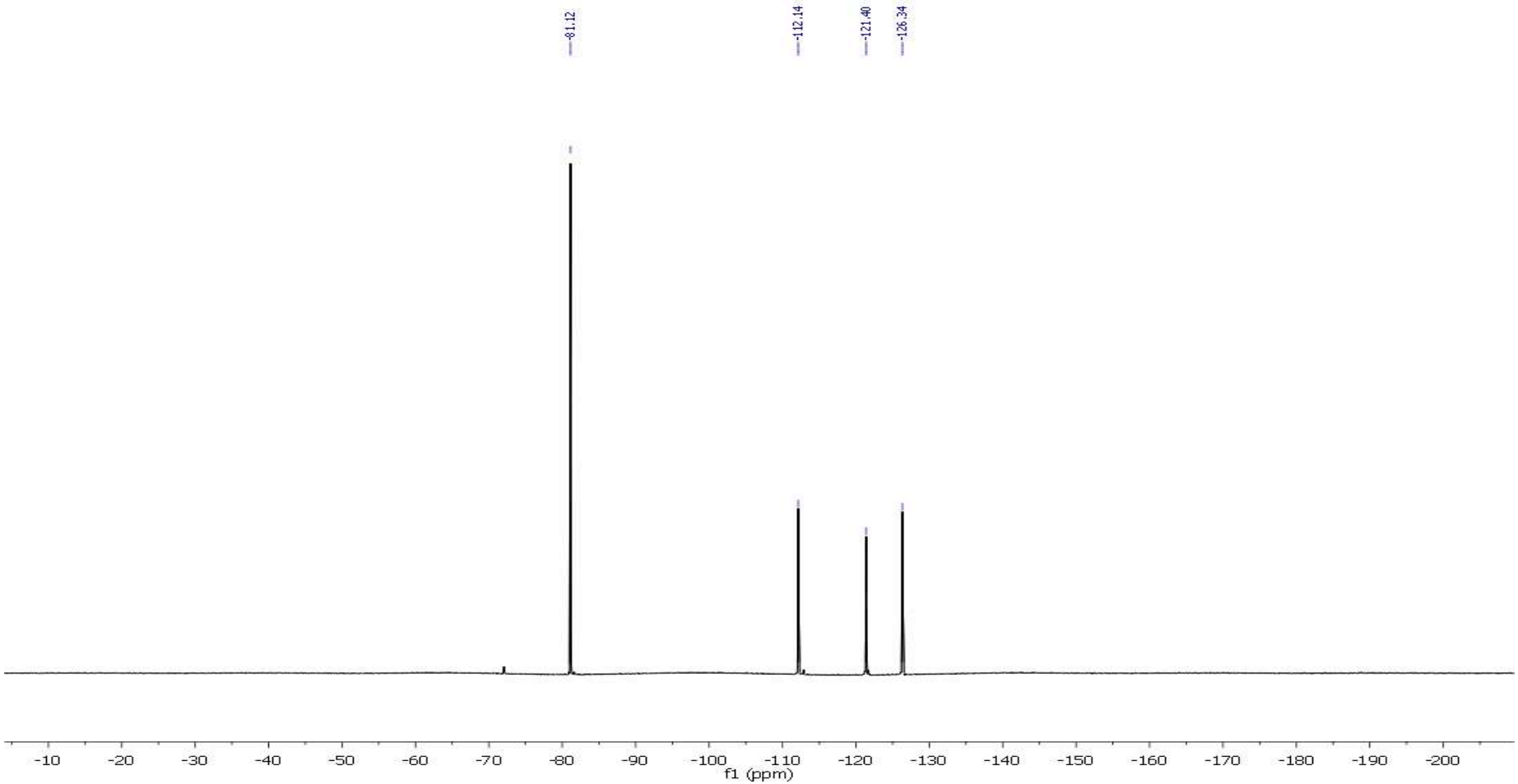
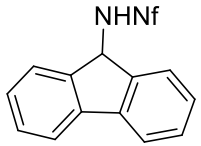
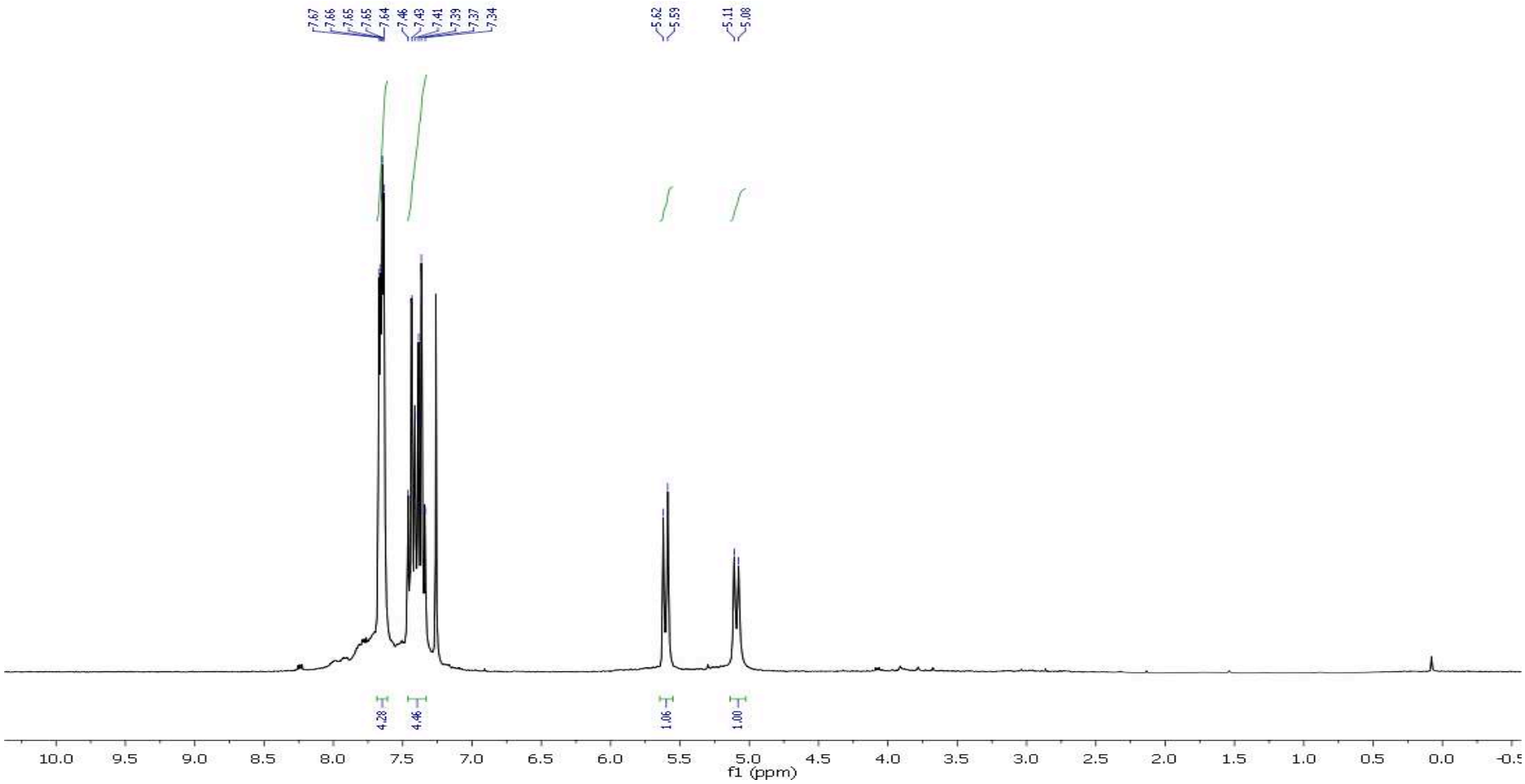
^{19}F NMR (375 MHz, $CDCl_3$)

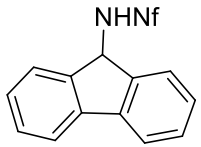




^{1}H NMR (300 MHz, $CDCl_3$)

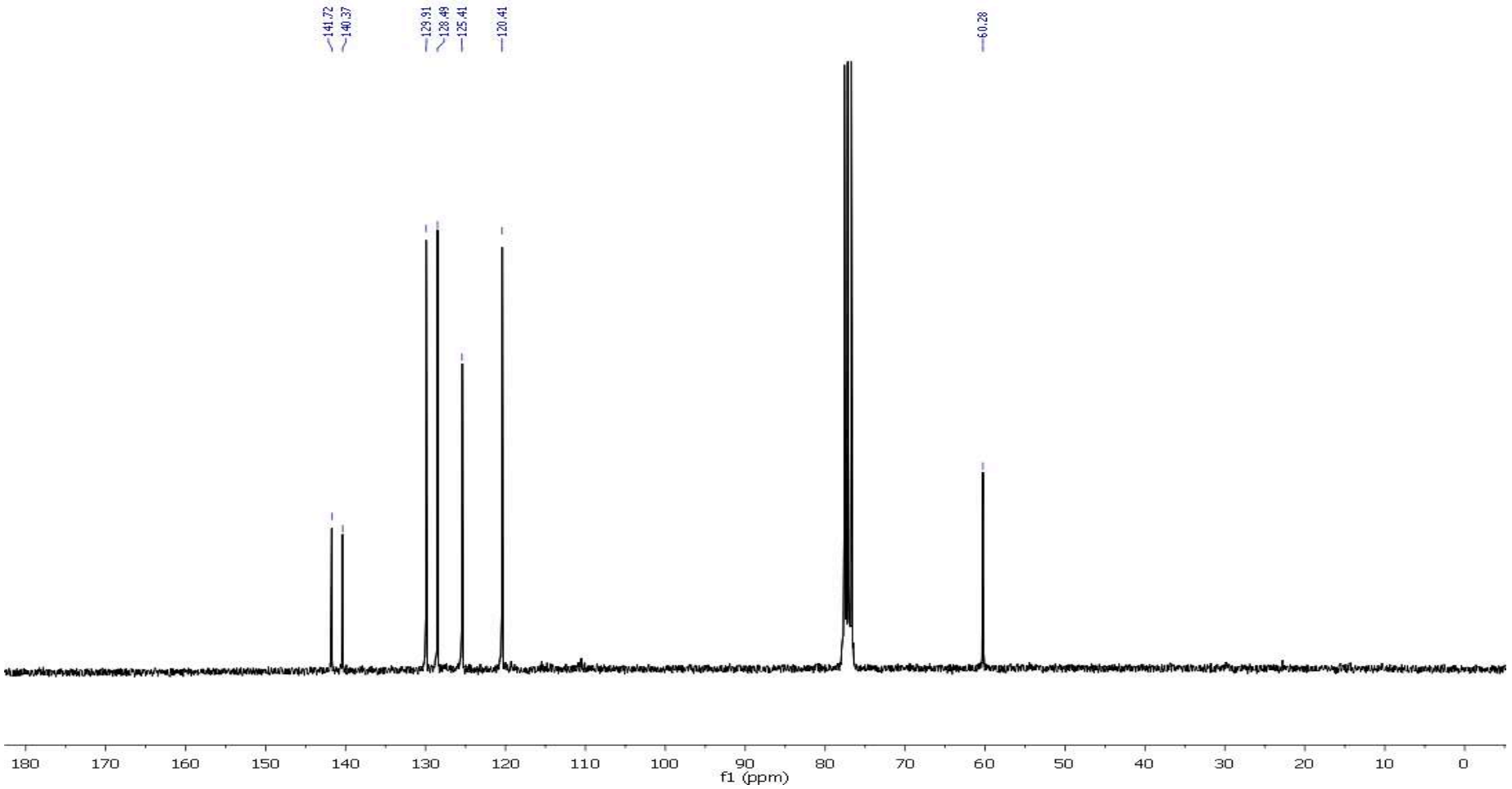
9

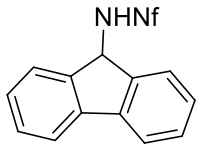




9

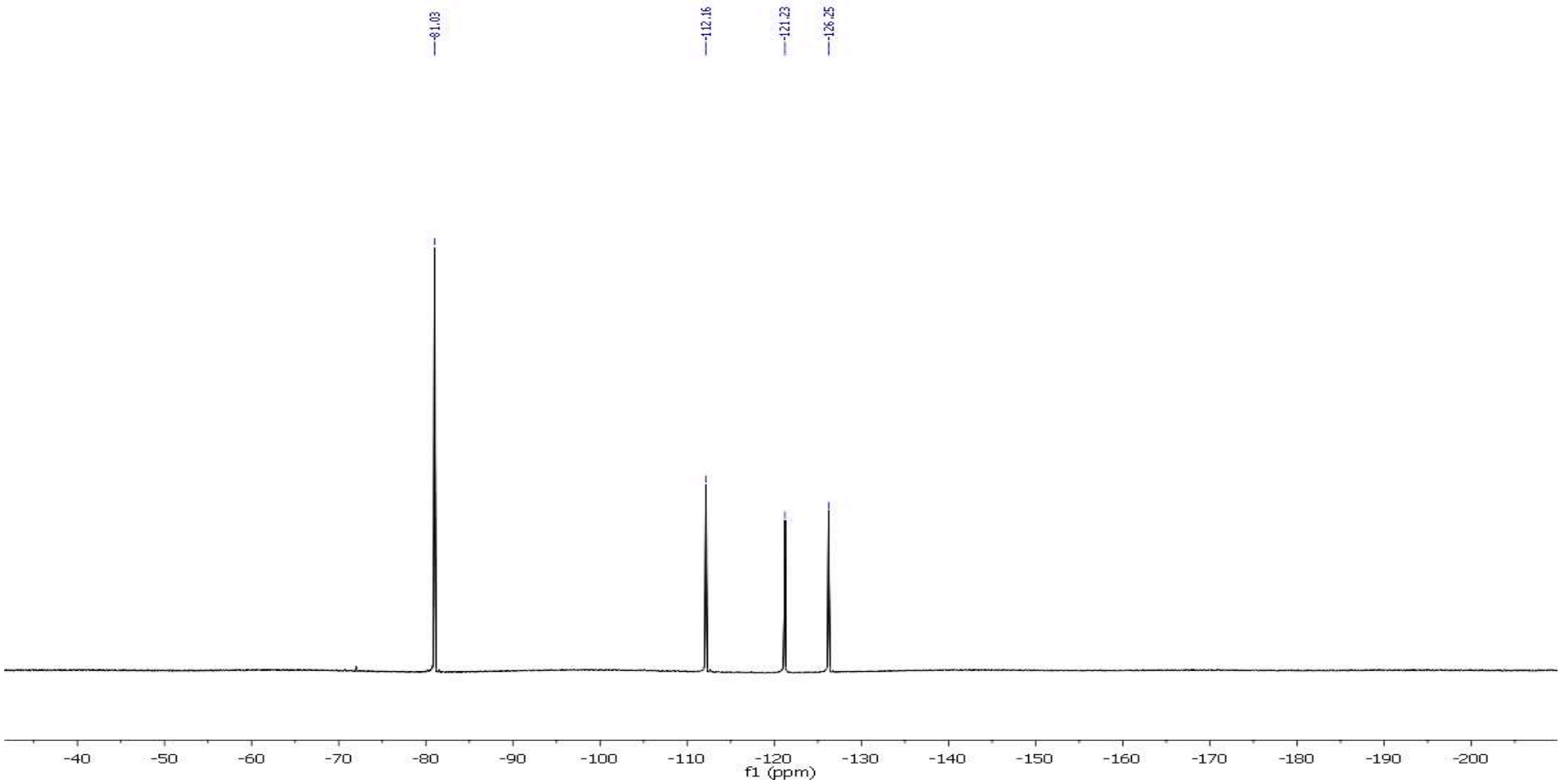
^{13}C NMR (75MHz, $CDCl_3$)

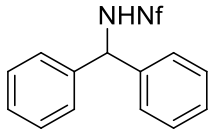




9

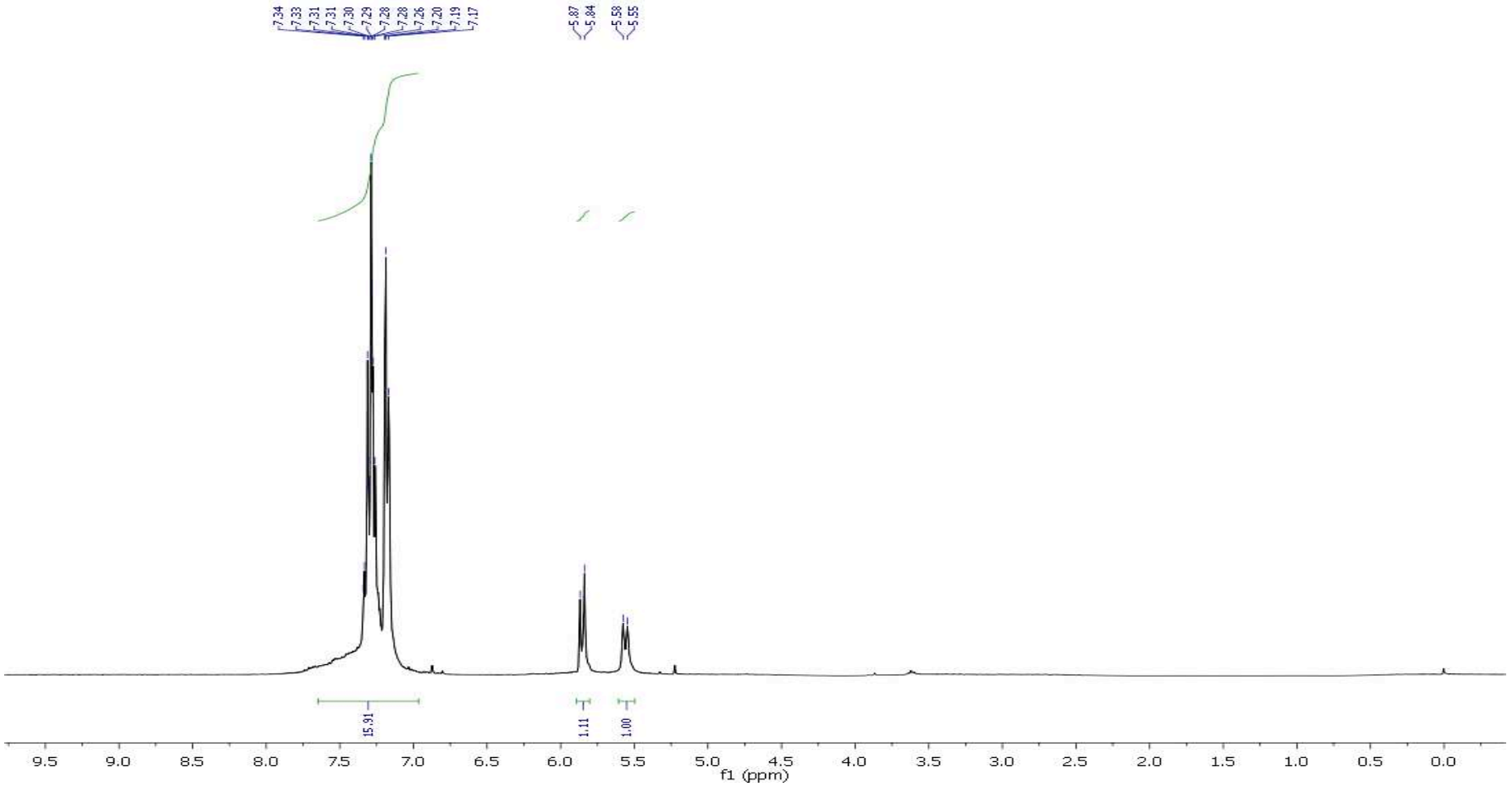
^{19}F NMR (375 MHz, $CDCl_3$)

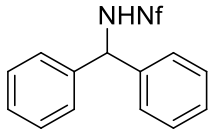




^{1}H NMR (300 MHz, $CDCl_3$)

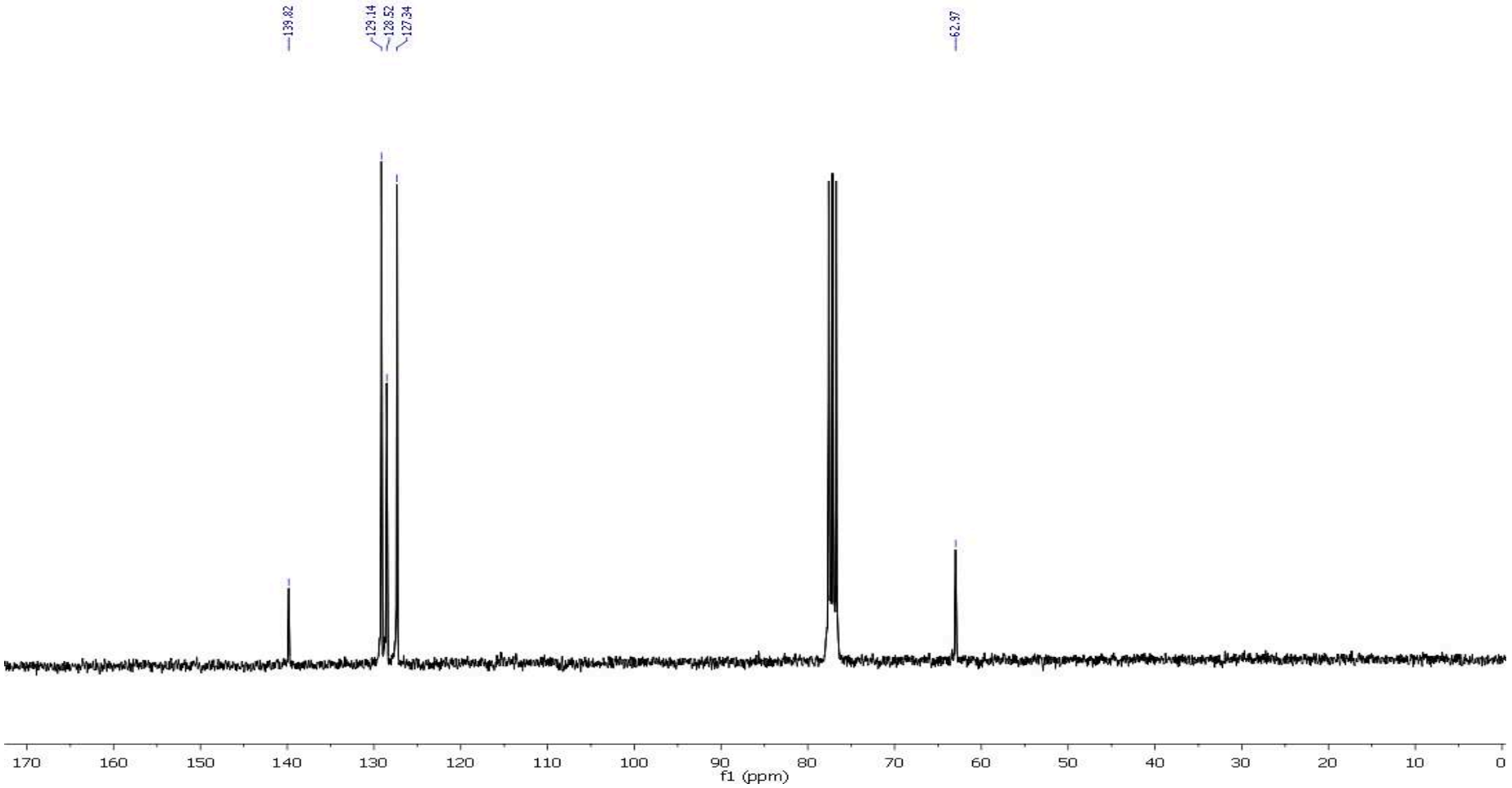
10

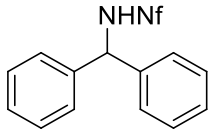




^{13}C NMR (75 MHz, $CDCl_3$)

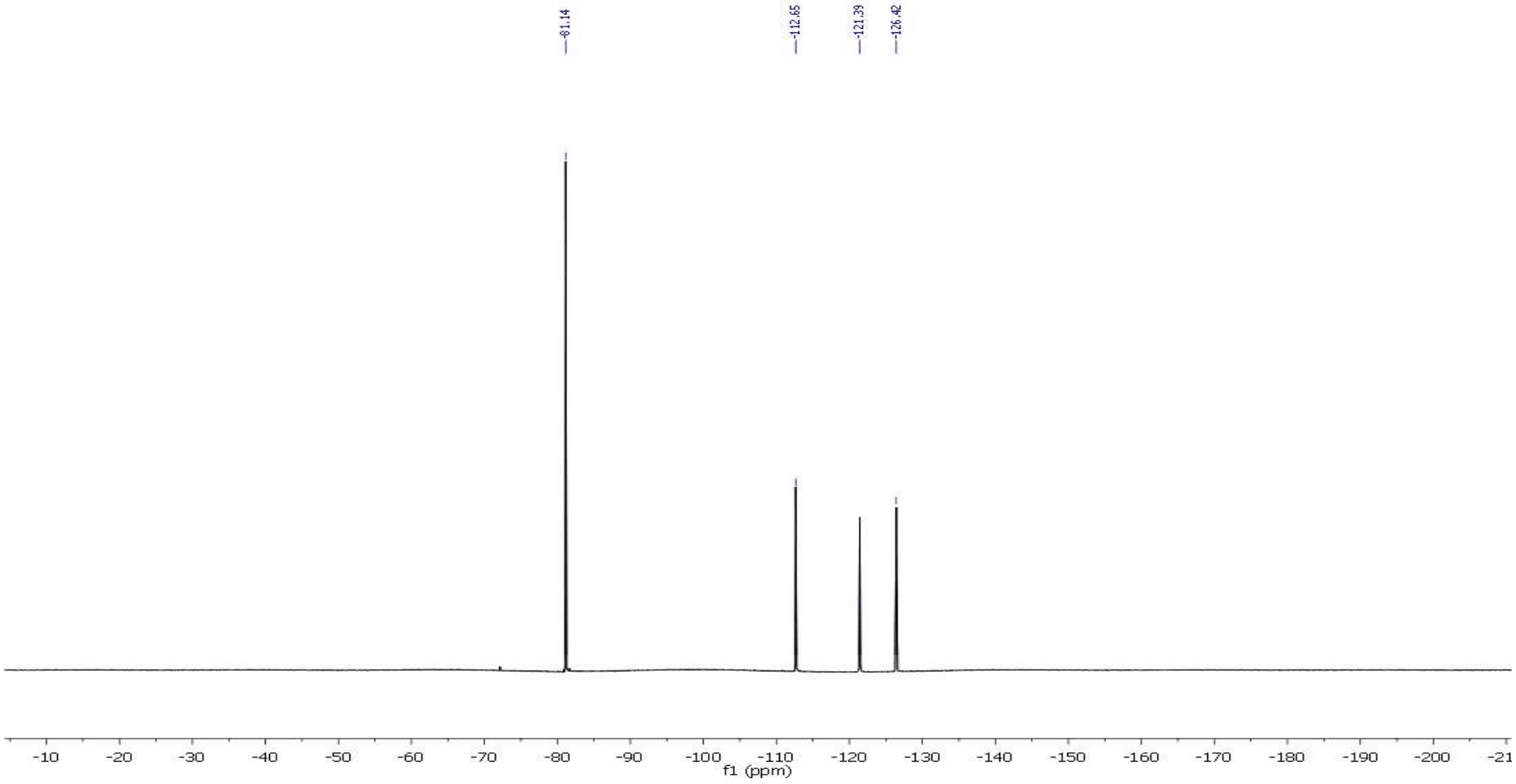
10

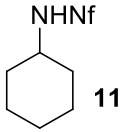




^{19}F NMR (375 MHz, $CDCl_3$)

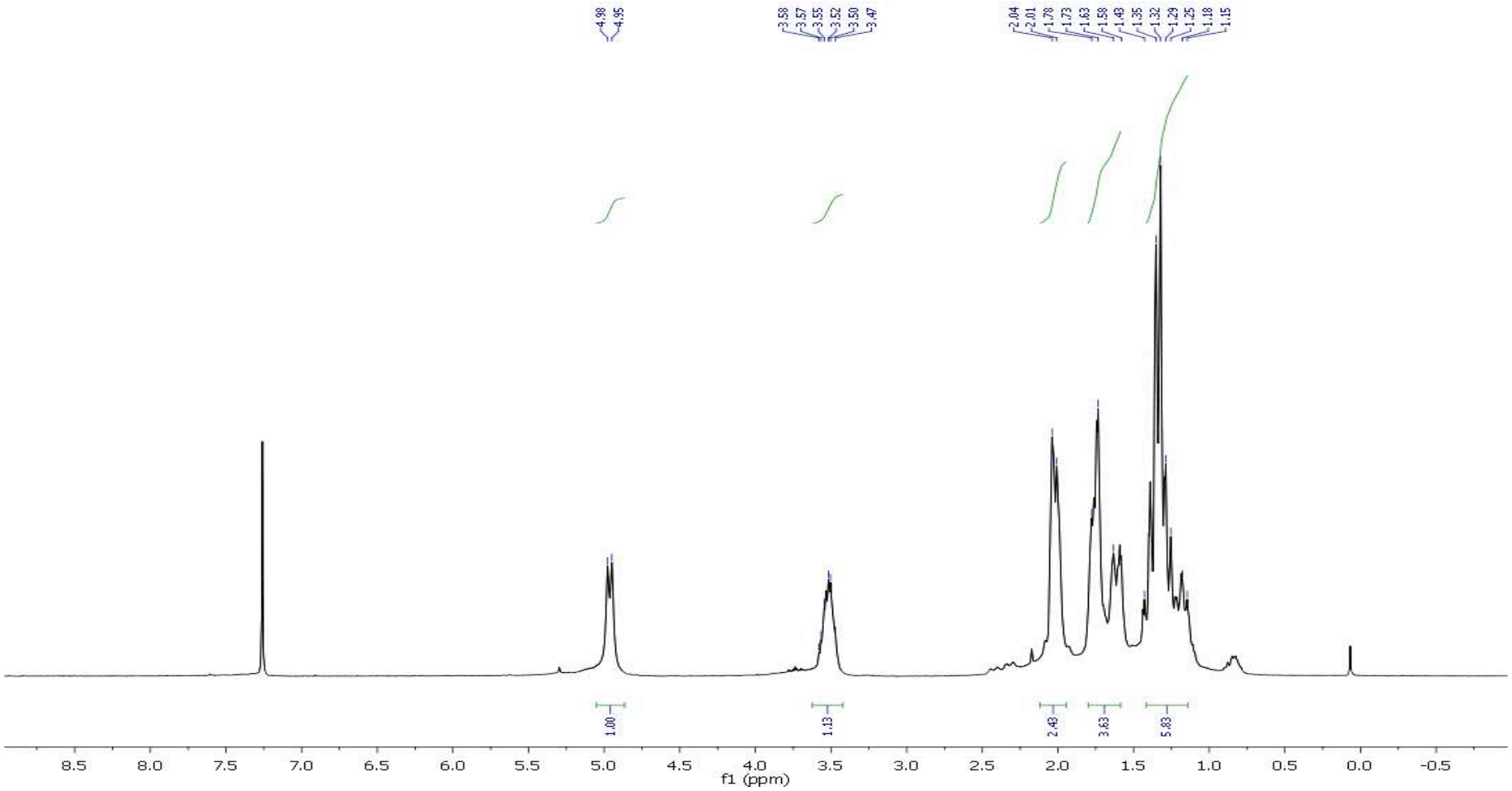
10

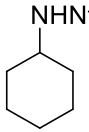




11

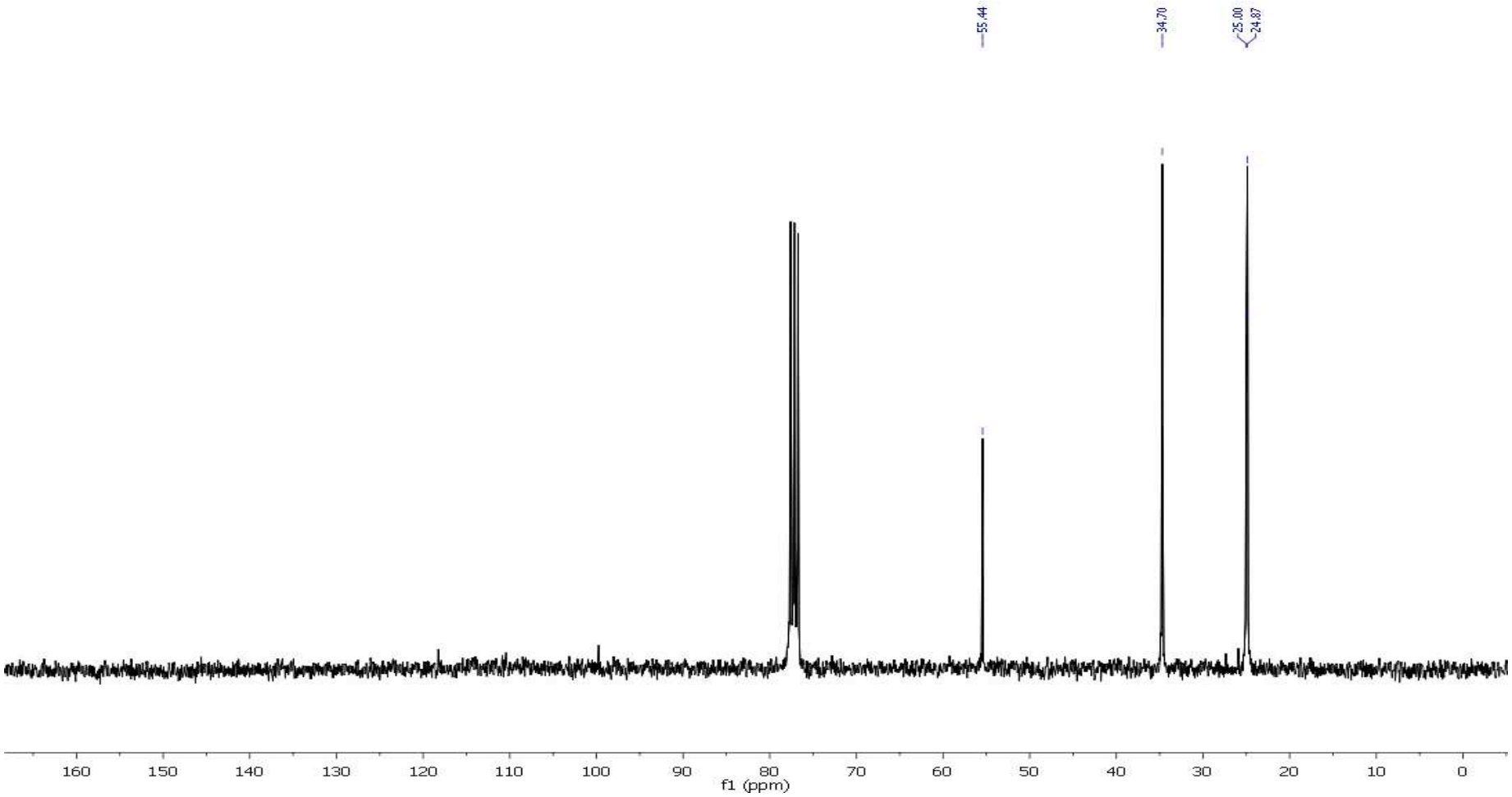
^{1}H NMR (300 MHz, $CDCl_3$)

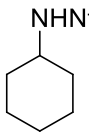




11

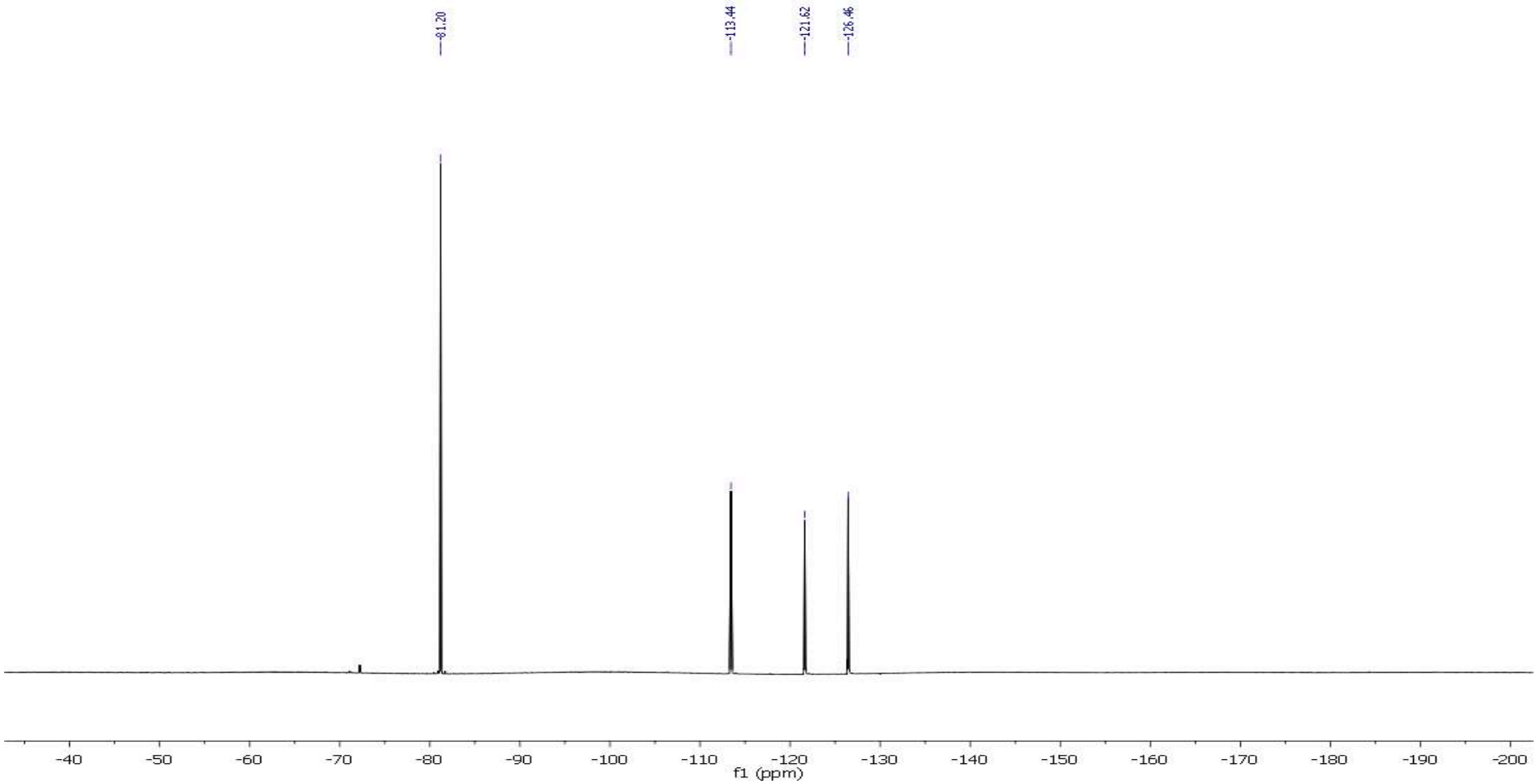
^{13}C NMR (75 MHz, $CDCl_3$)

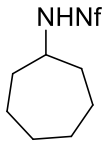




11

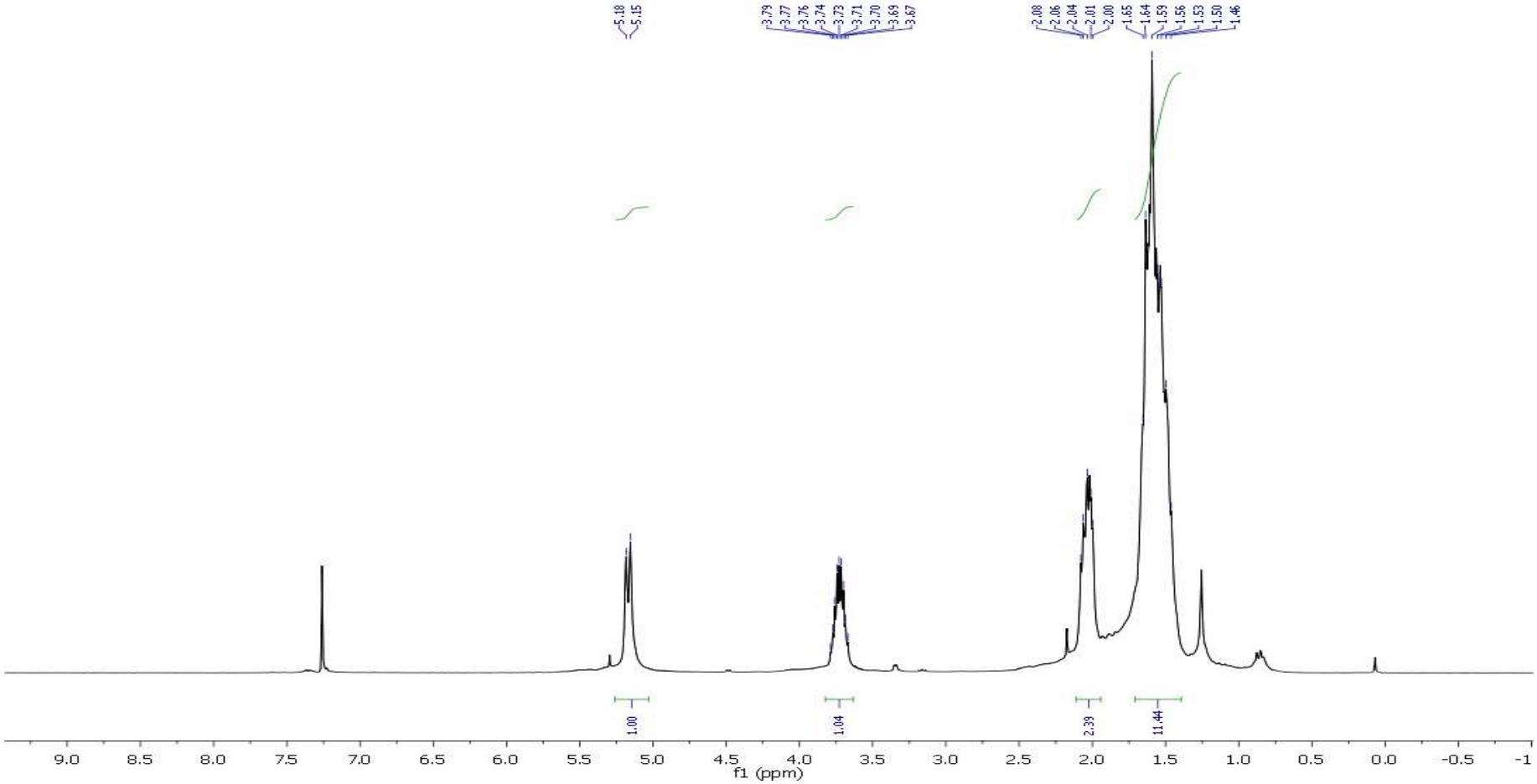
^{19}F NMR (375 MHz, $CDCl_3$)

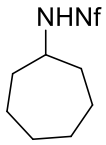




^{1}H NMR (300 MHz, $CDCl_3$)

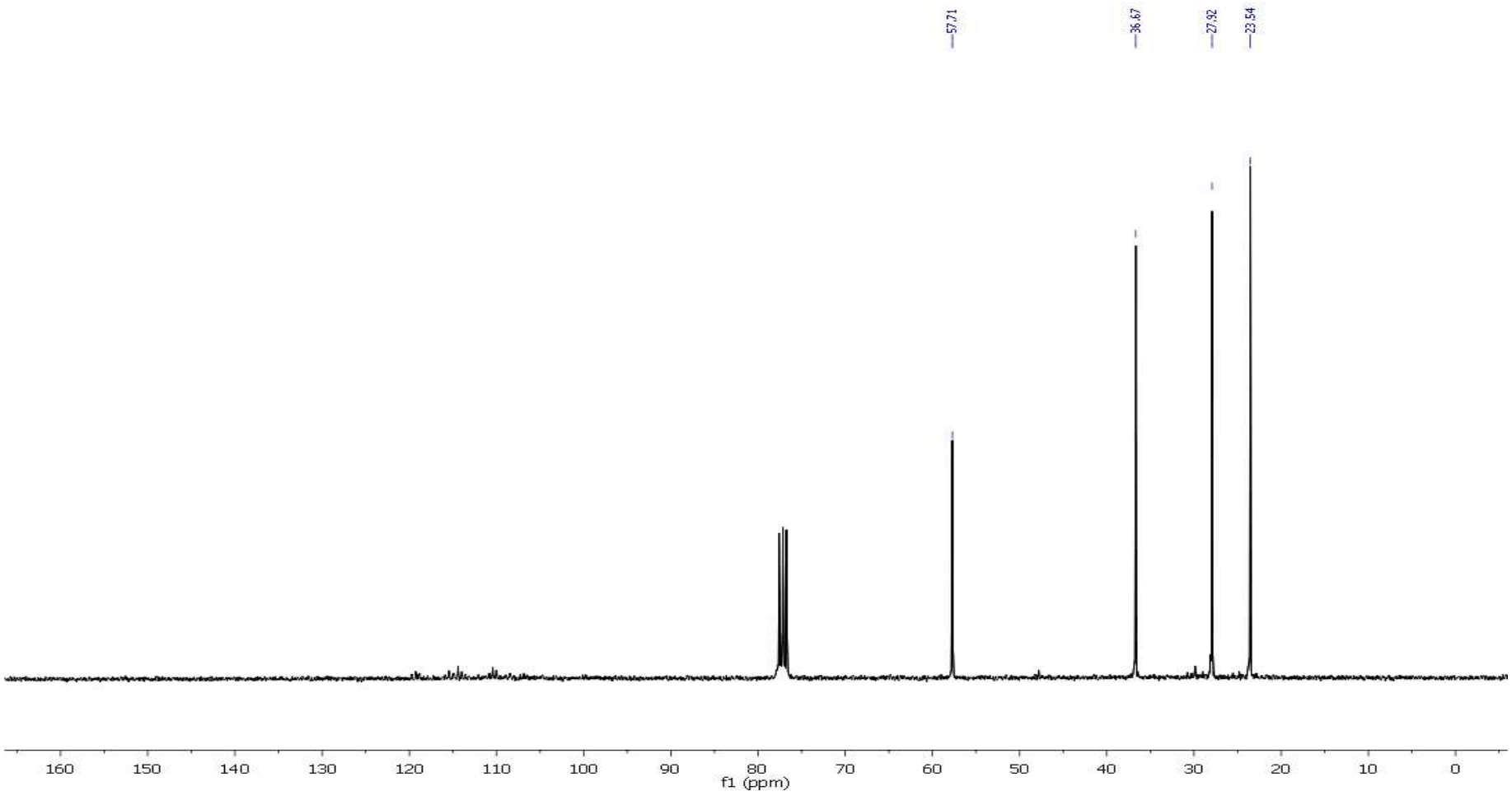
12

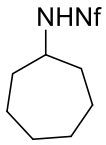




^{13}C NMR (75 MHz, $CDCl_3$)

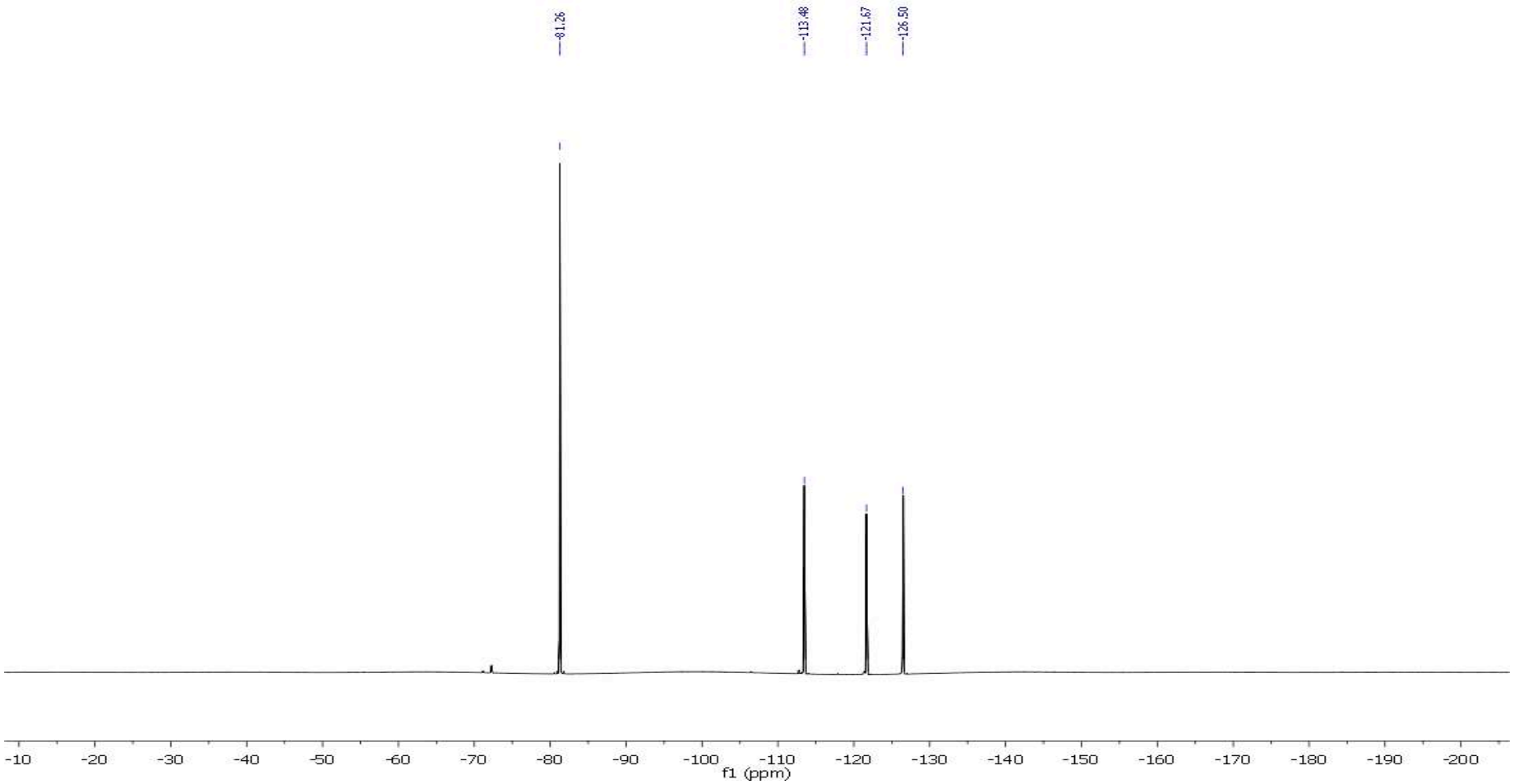
12

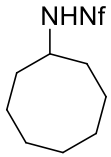




^{19}F NMR (375 MHz, $CDCl_3$)

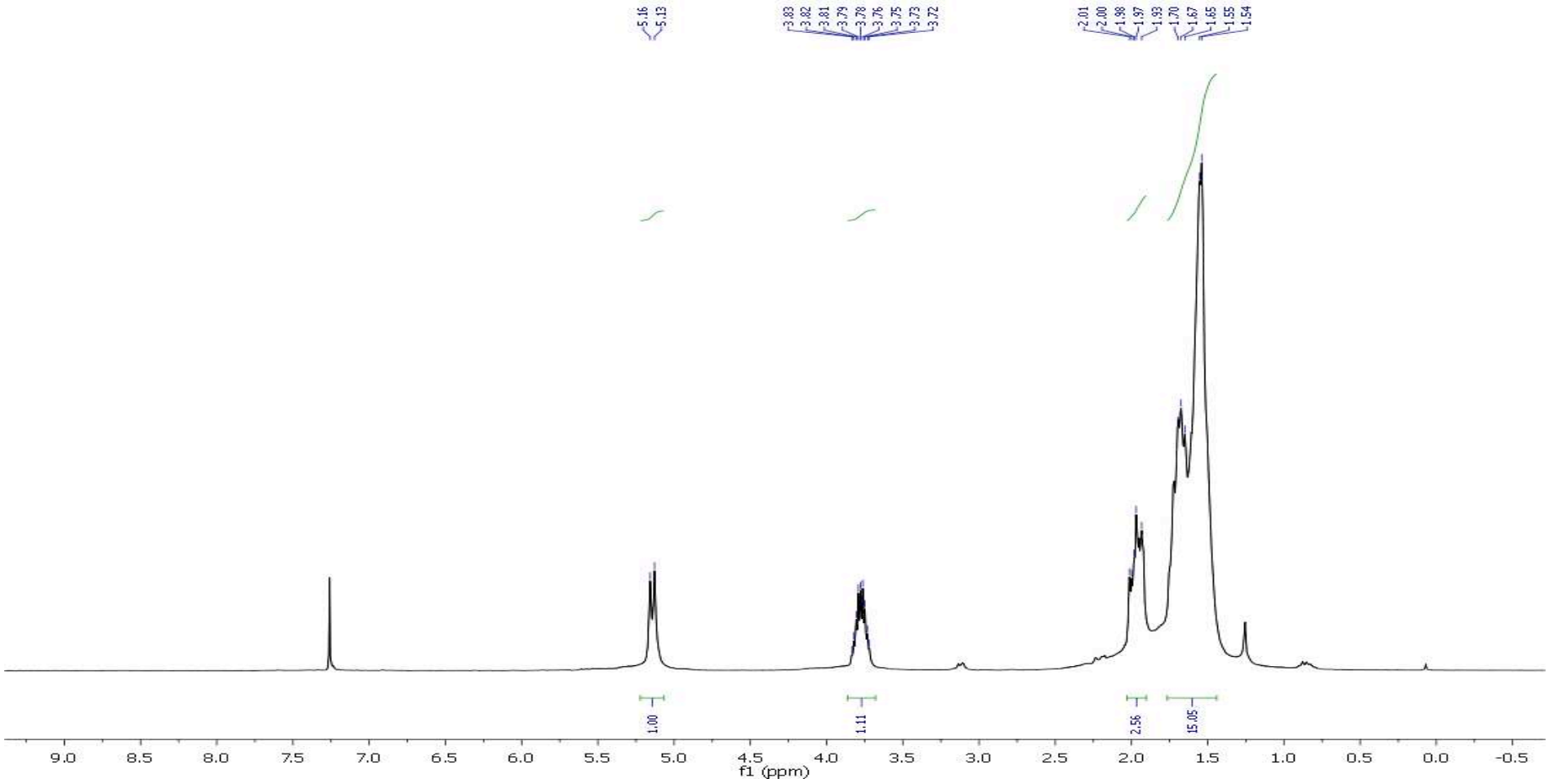
12

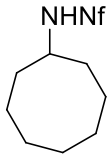




^{1}H NMR (300 MHz, $CDCl_3$)

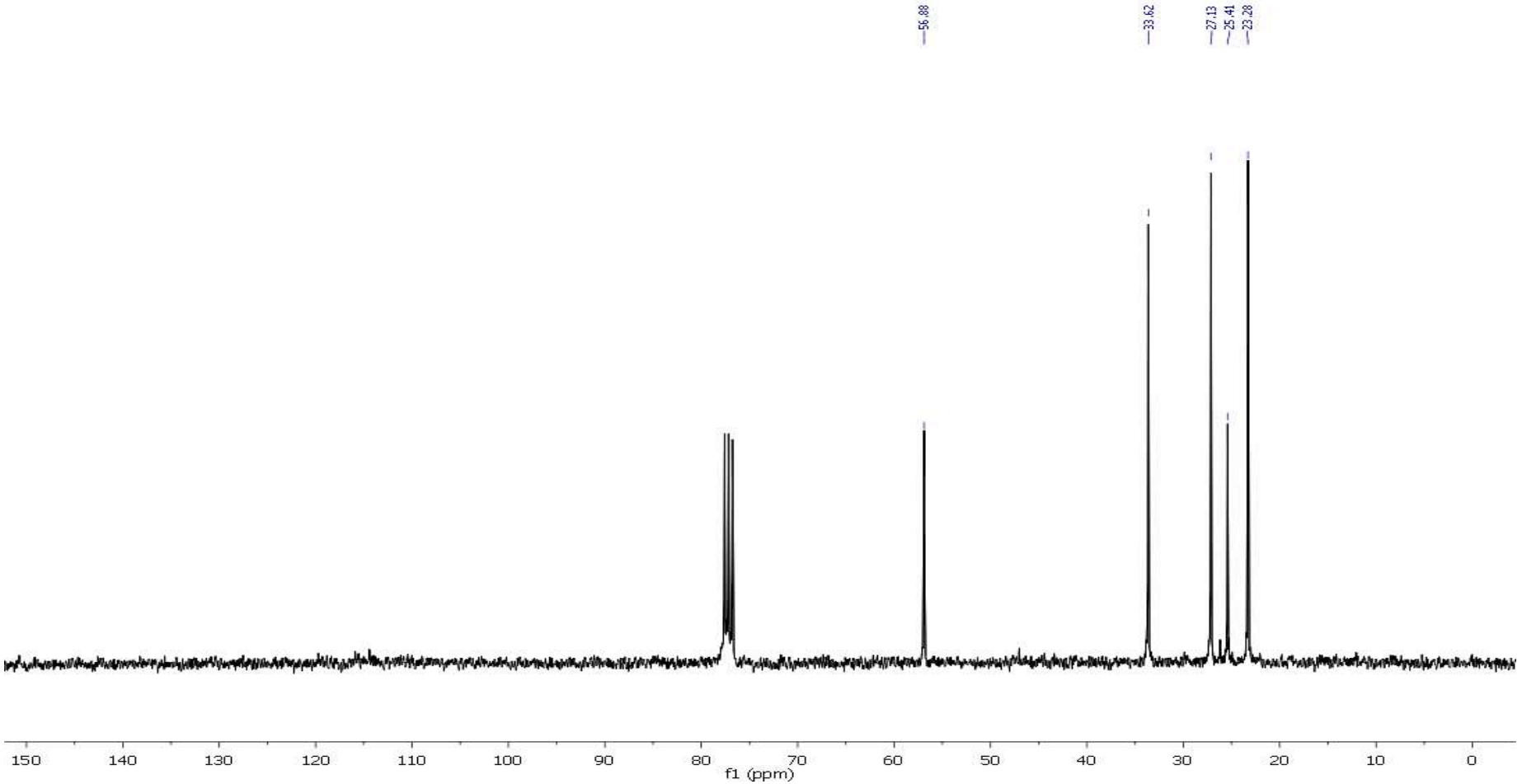
13

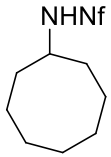




^{13}C NMR (75 MHz, $CDCl_3$)

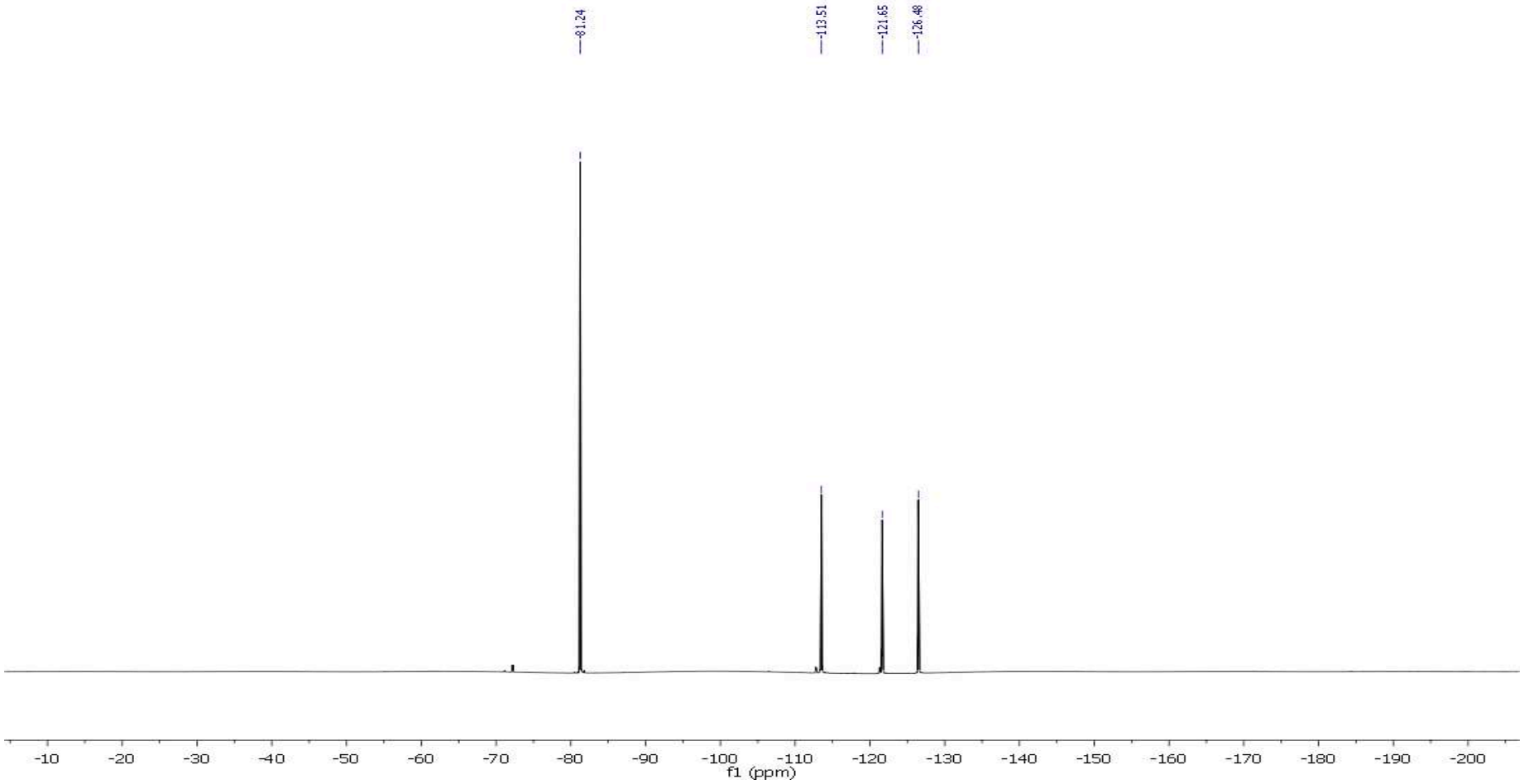
13

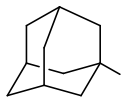




^{19}F NMR (375 MHz, $CDCl_3$)

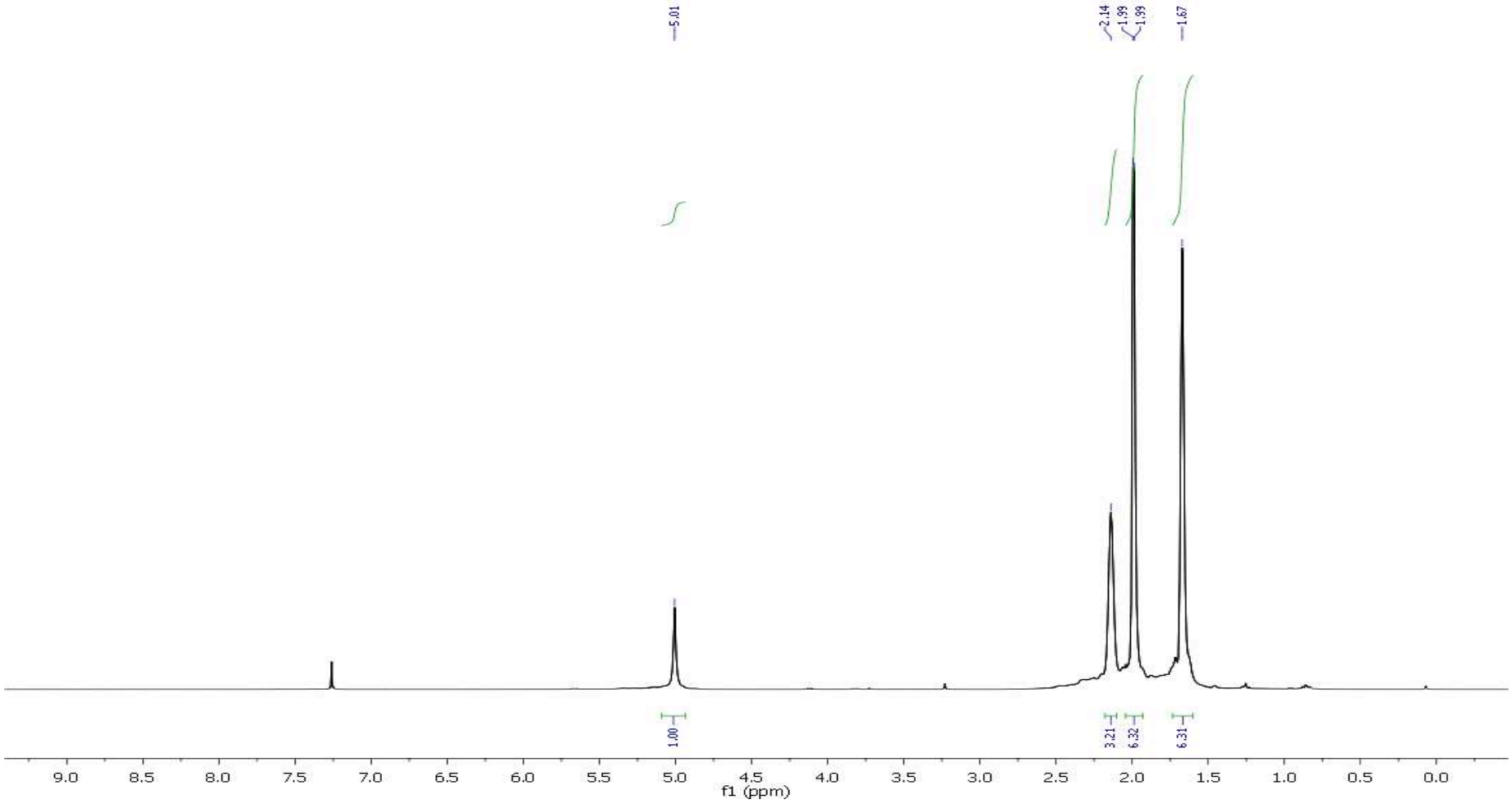
13

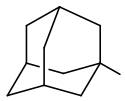




NHNf **14**

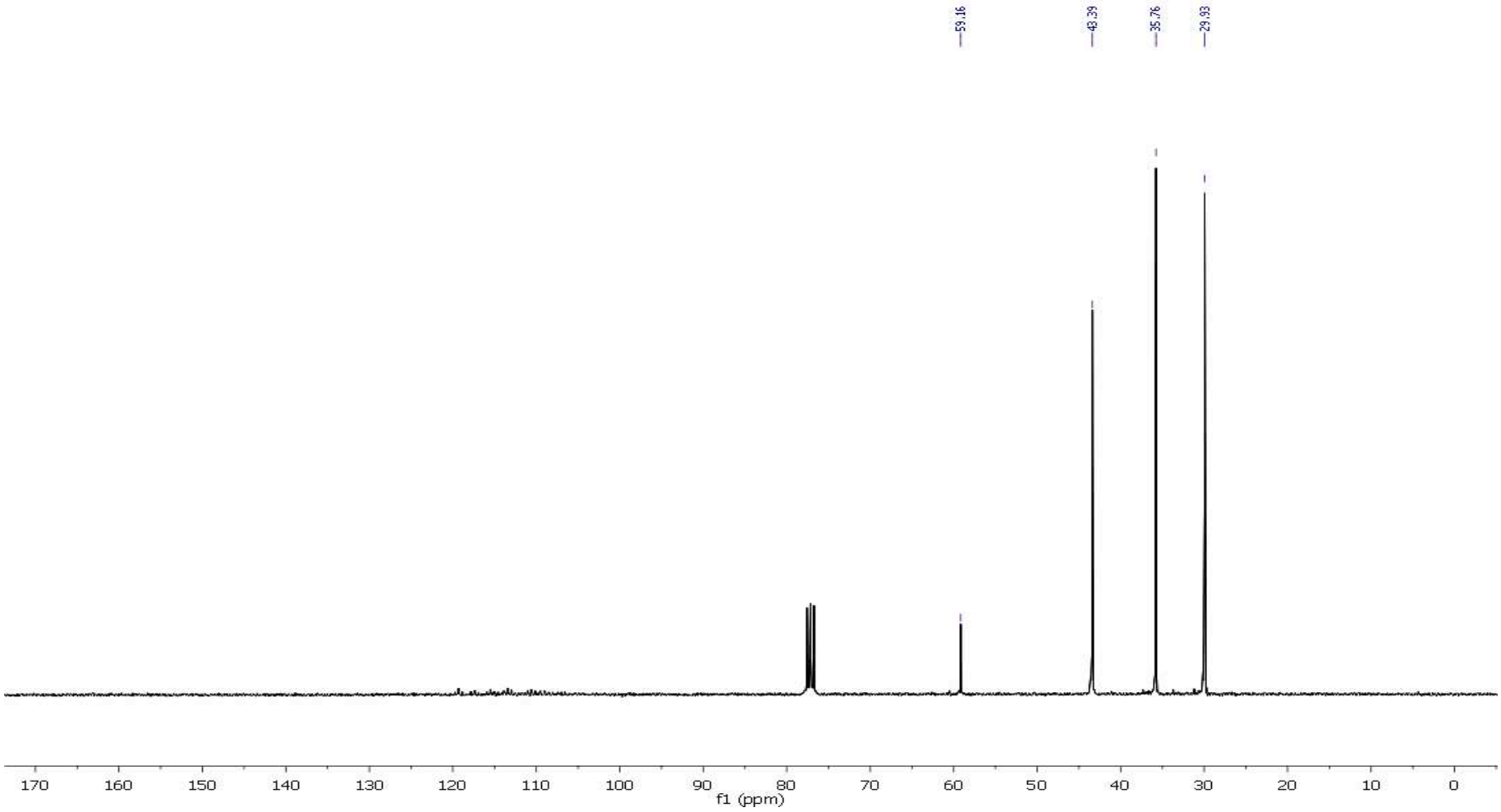
^{1}H NMR (300 MHz, $CDCl_3$)

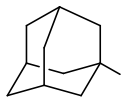




14

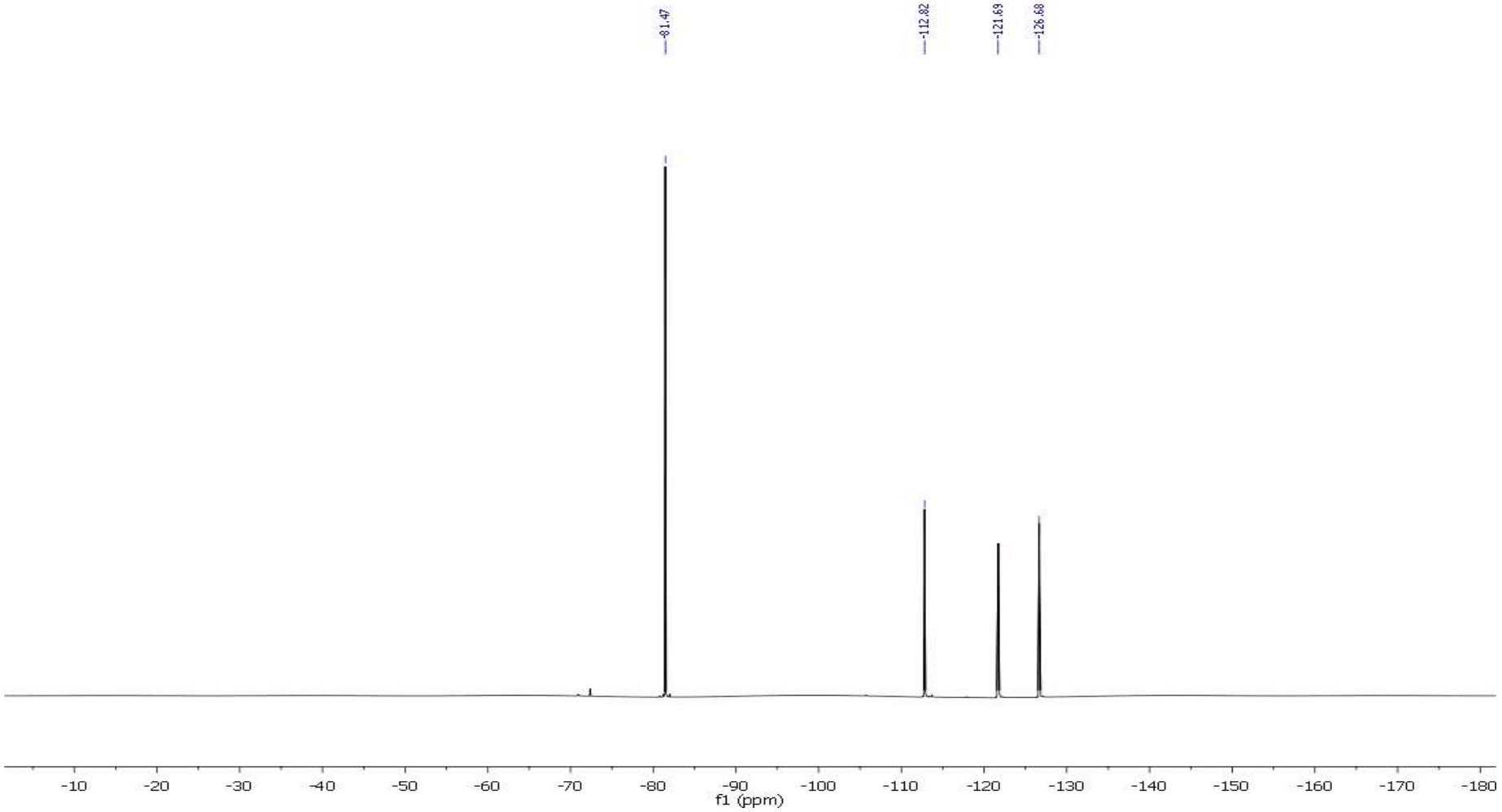
^{13}C NMR (75 MHz, $CDCl_3$)

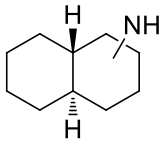




NHNf **14**

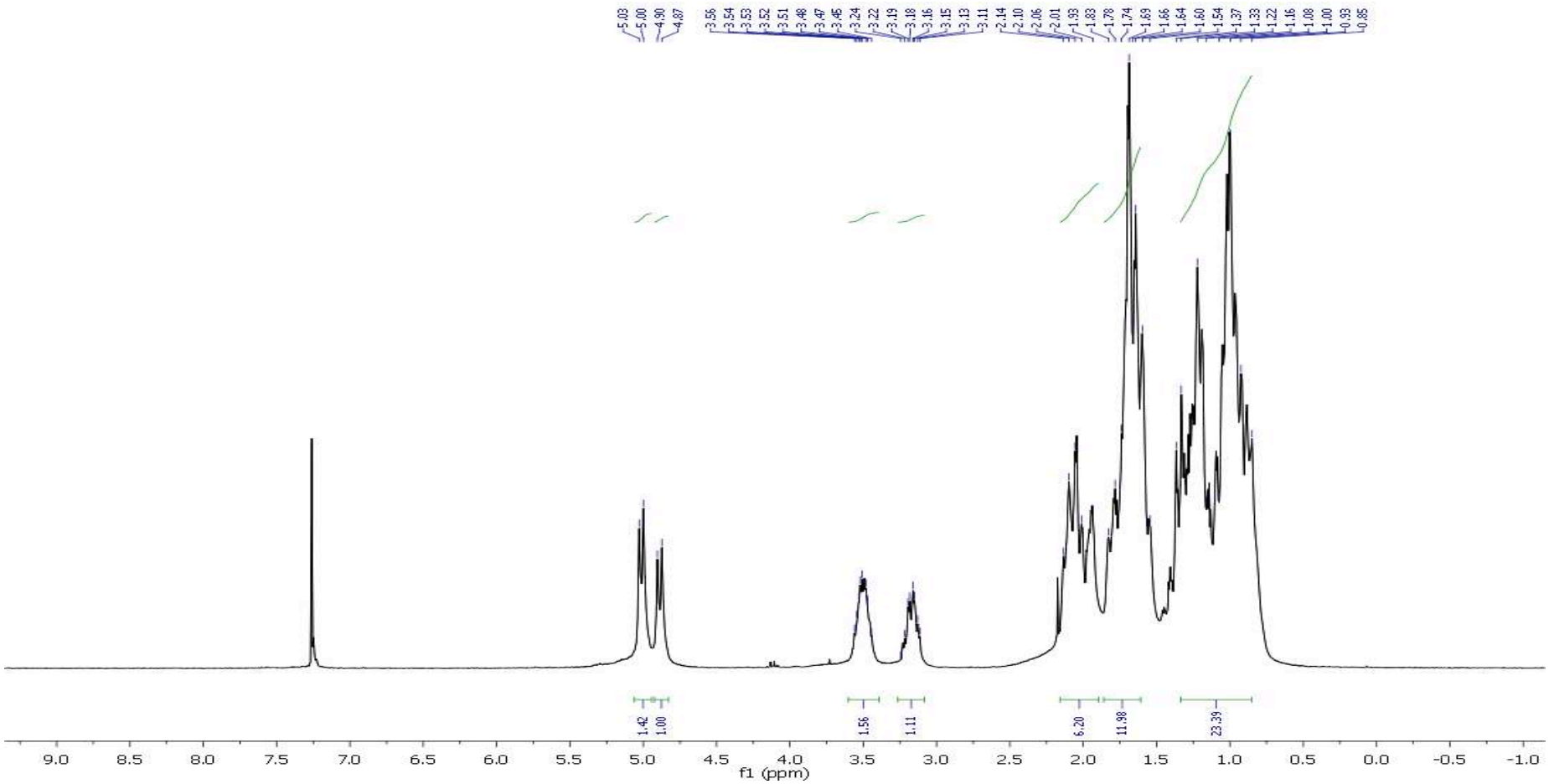
^{19}F NMR (375 MHz, $CDCl_3$)

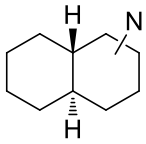




15

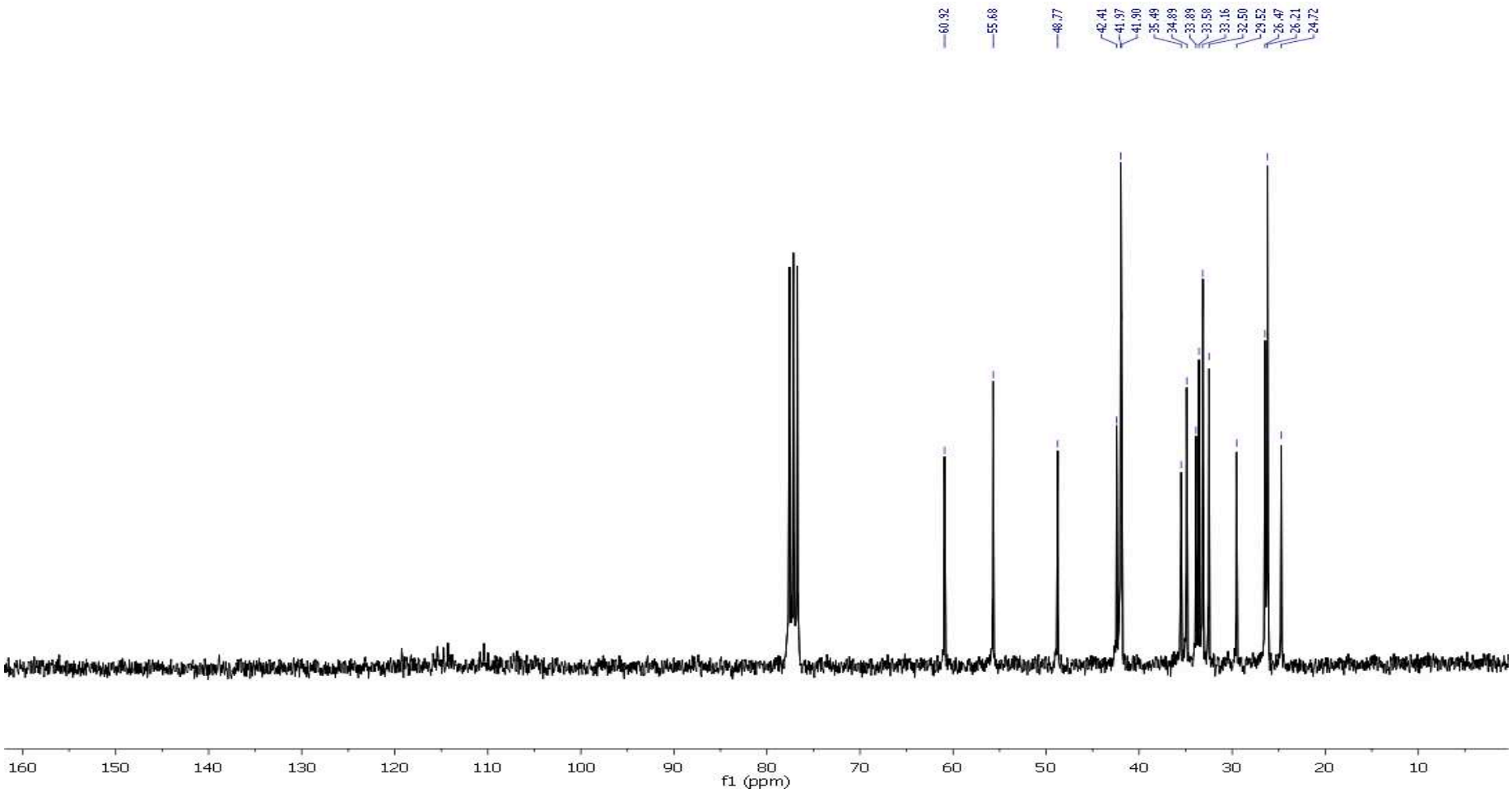
^{1}H NMR (300 MHz, $CDCl_3$)

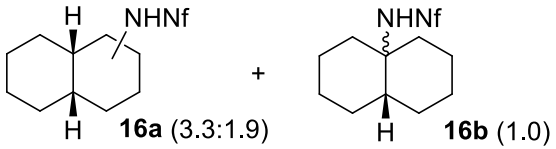




15

^{13}C NMR (75 MHz, $CDCl_3$)

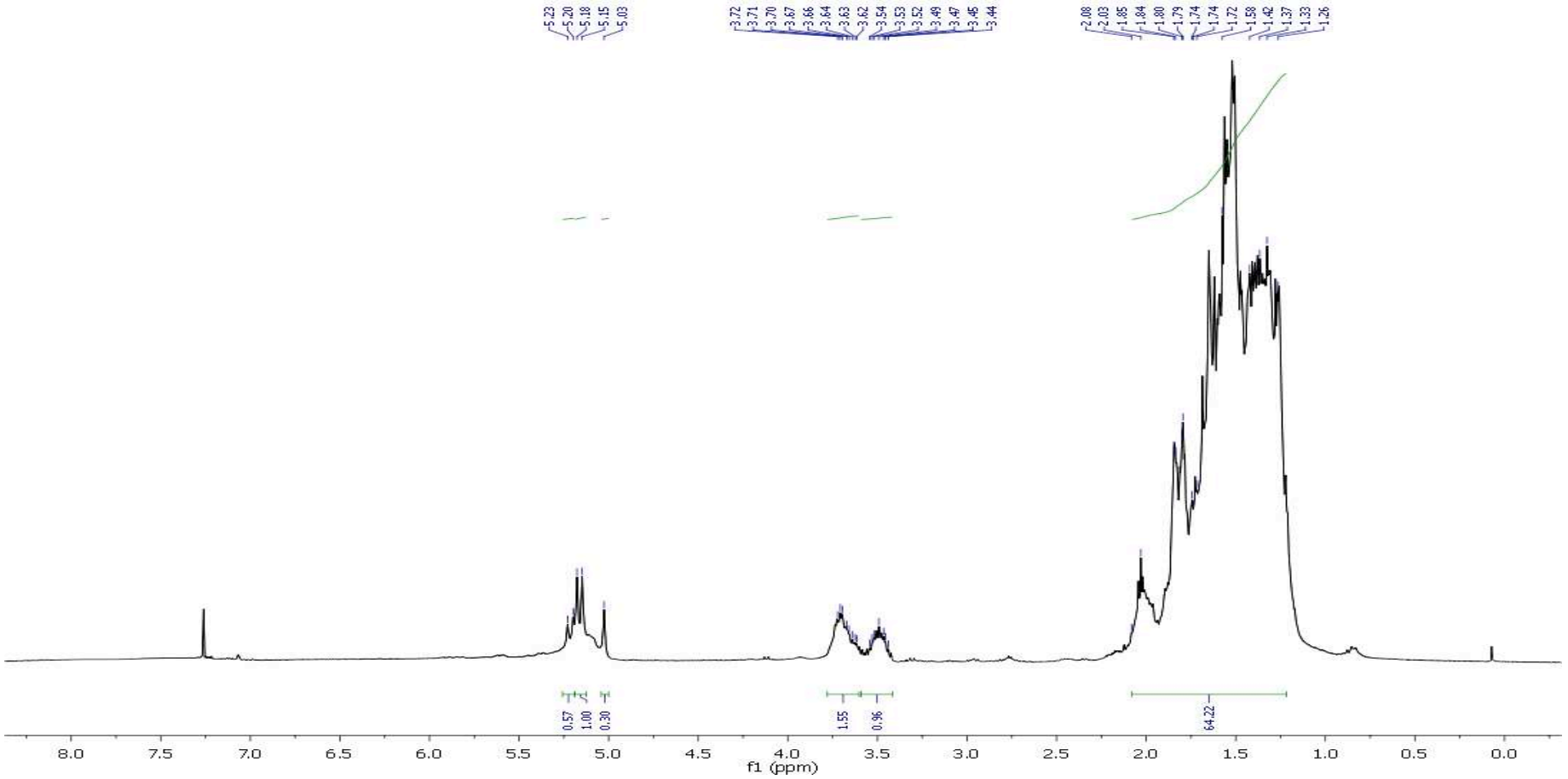


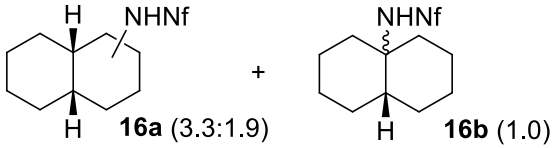


16a (3.3:1.9) +

16b (1.0)

^{1}H NMR (300 MHz, $CDCl_3$)

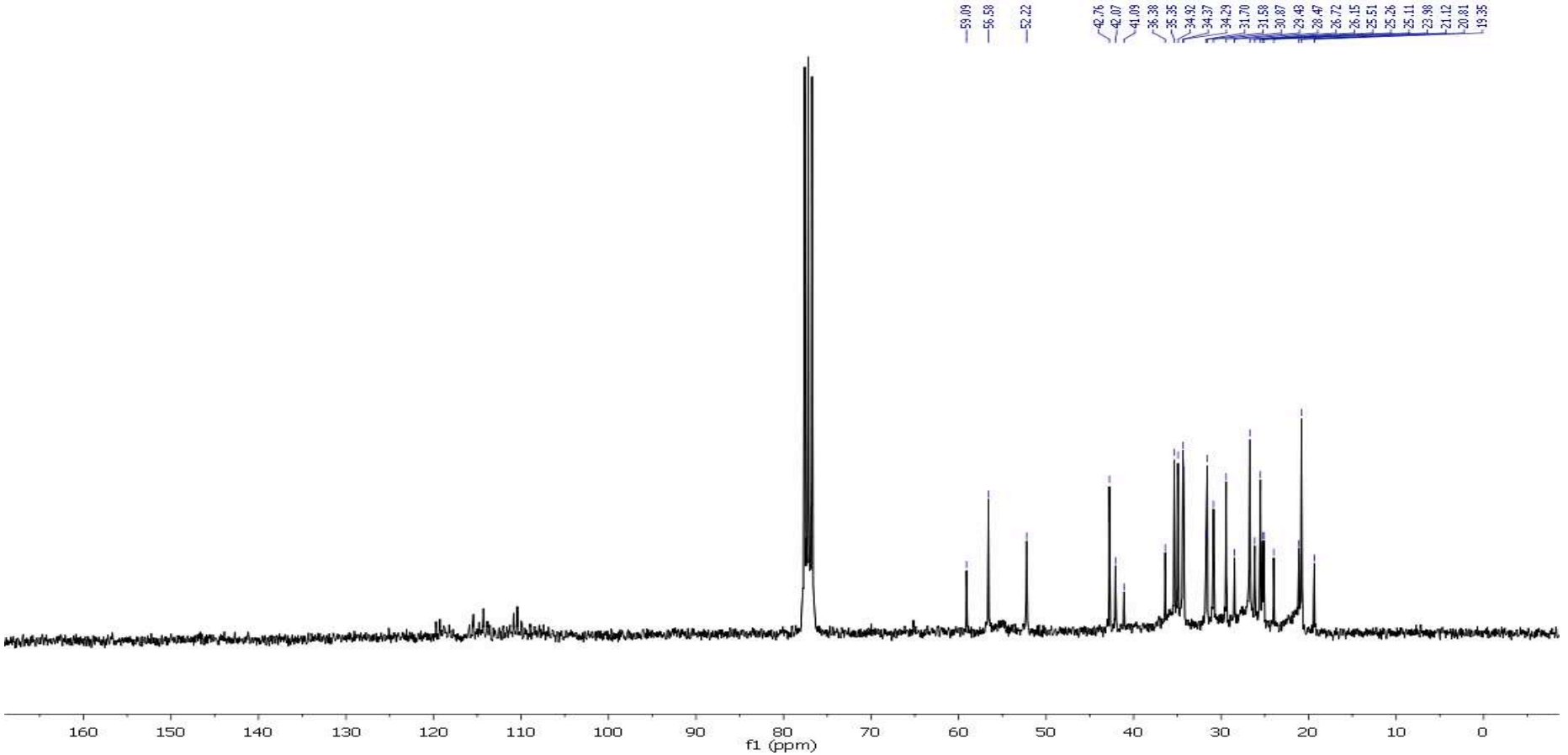


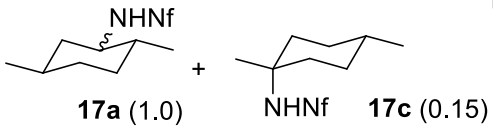


16a (3.3:1.9) +

16b (1.0)

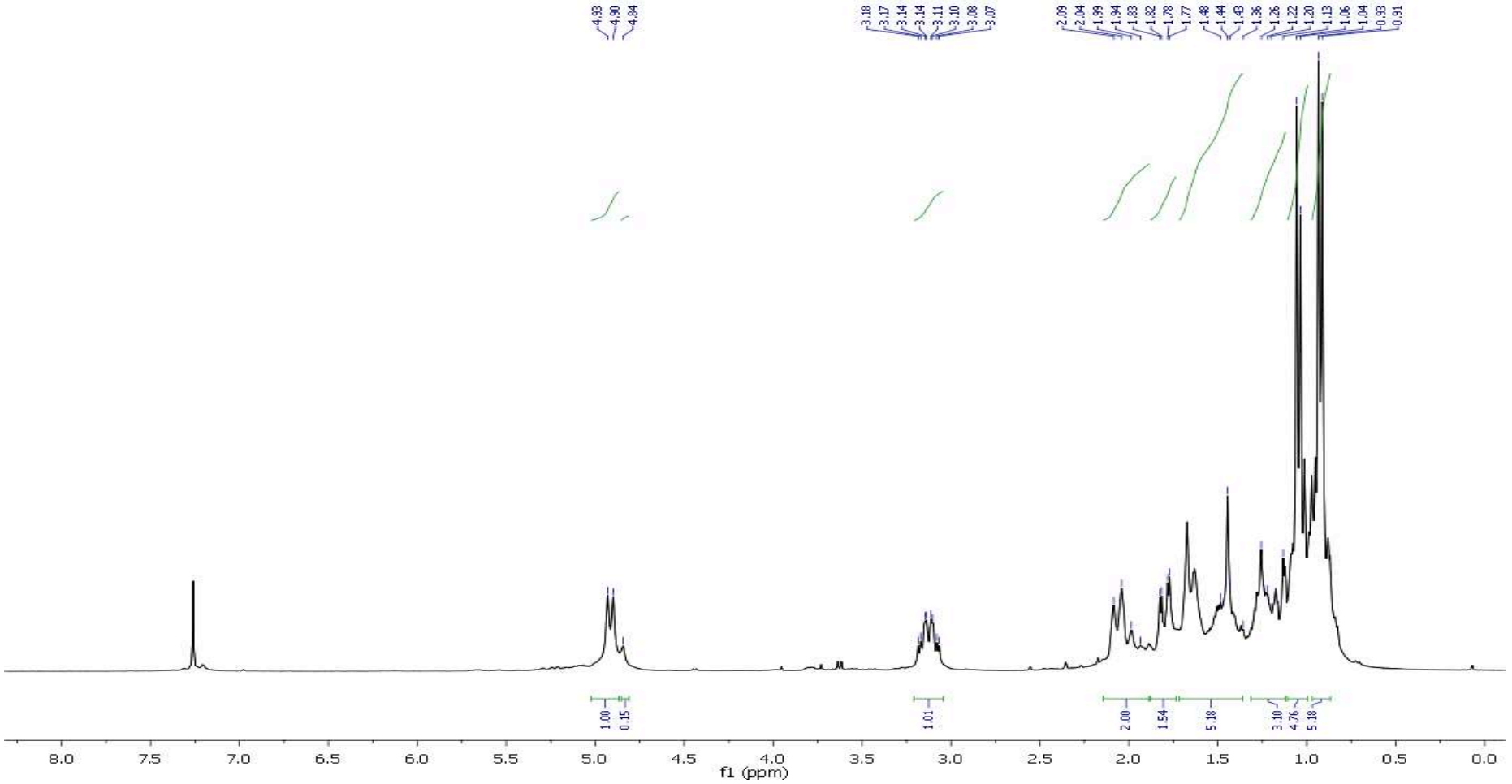
^{13}C NMR (75 MHz, $CDCl_3$)

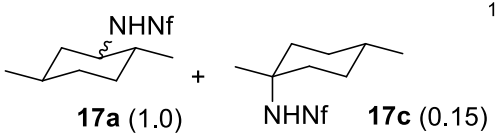




17a (1.0) **17c** (0.15)

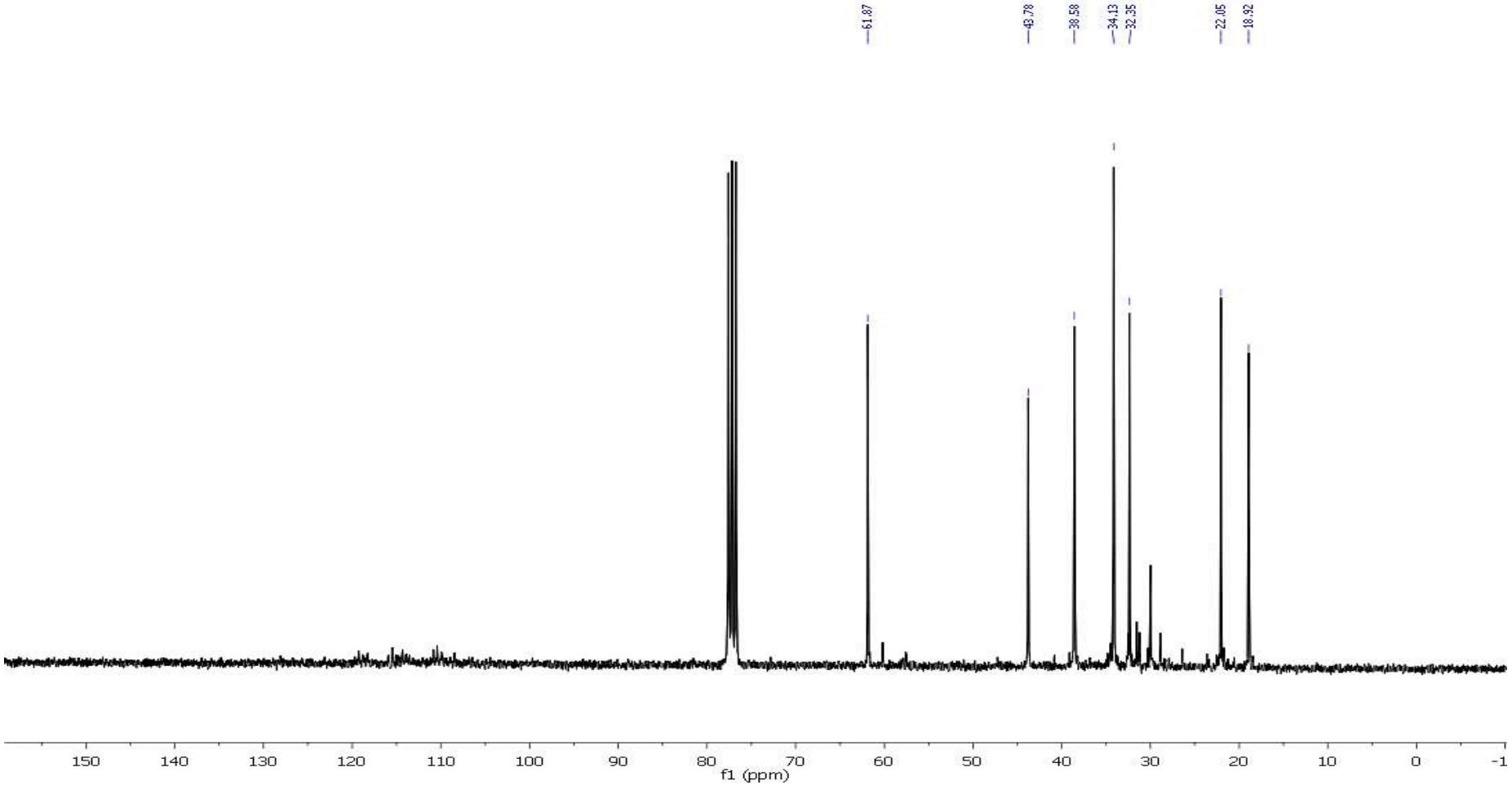
^{1}H NMR (300 MHz, $CDCl_3$)

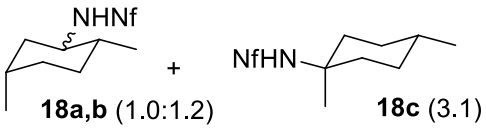




17a (1.0) **17c** (0.15)

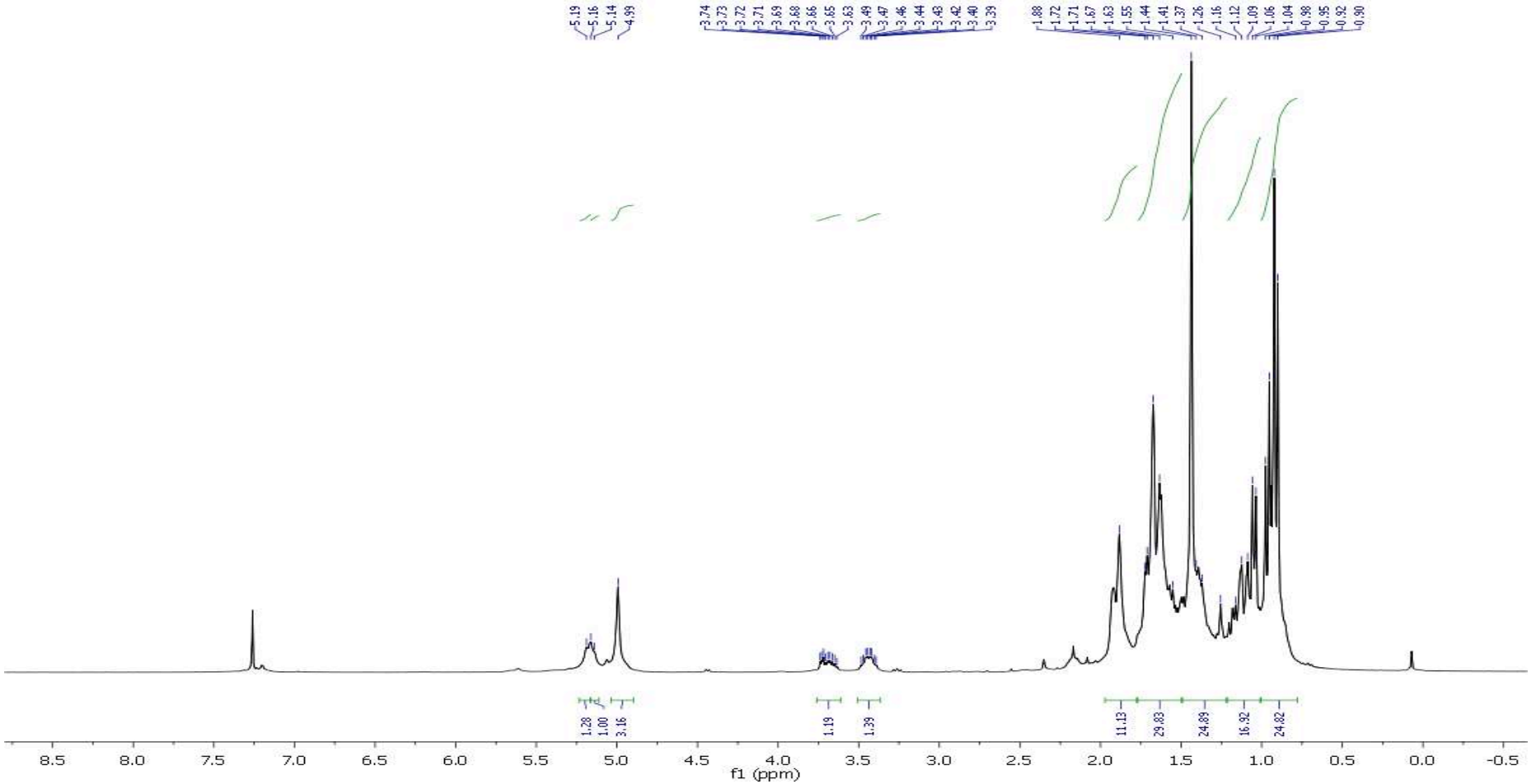
^{13}C NMR (75 MHz, $CDCl_3$)

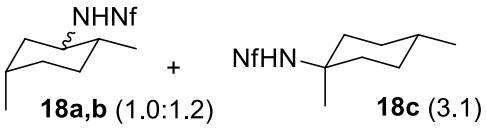




18a,b (1.0:1.2) **18c** (3.1)

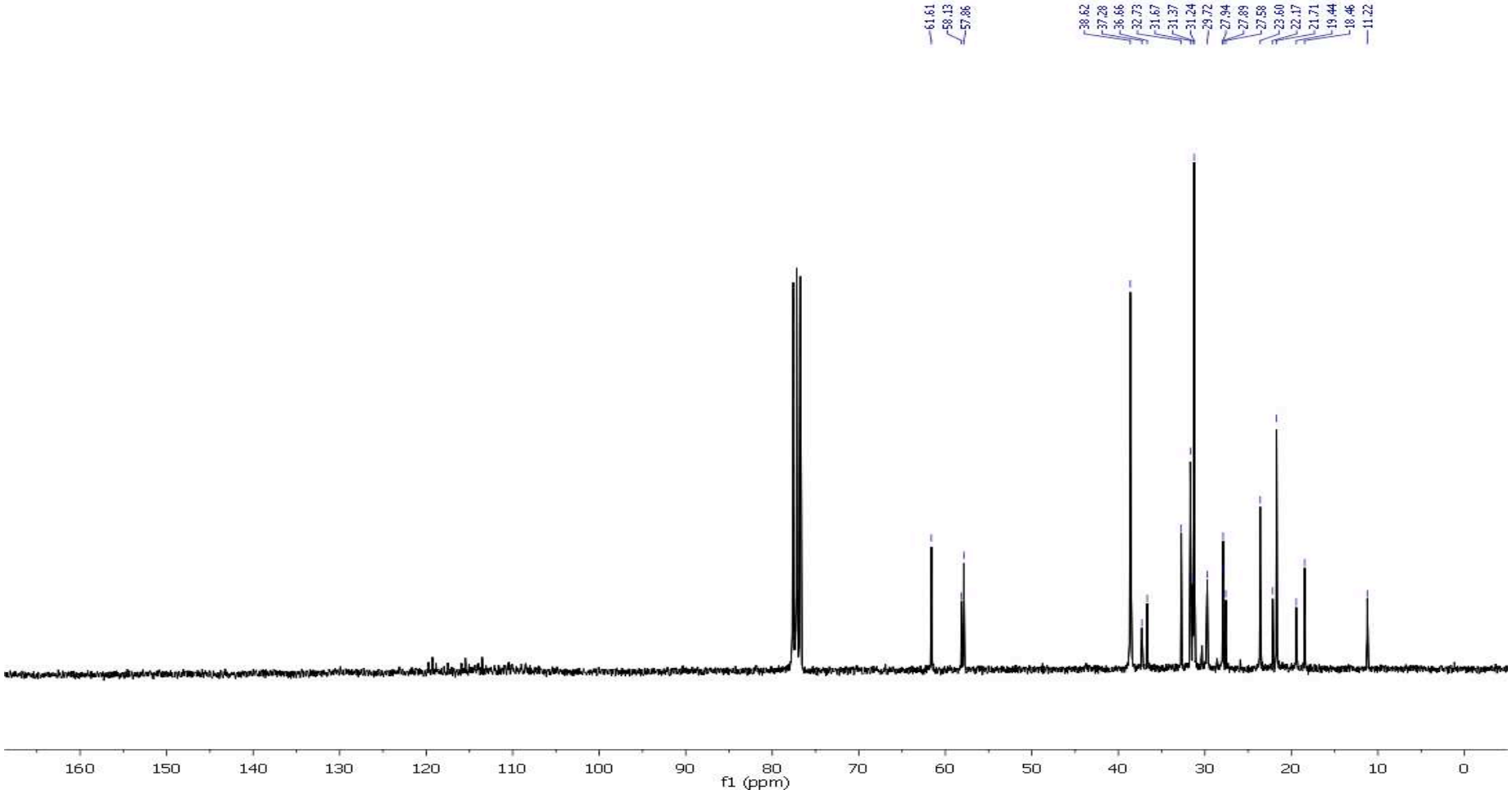
^{1}H NMR (300 MHz, $CDCl_3$)

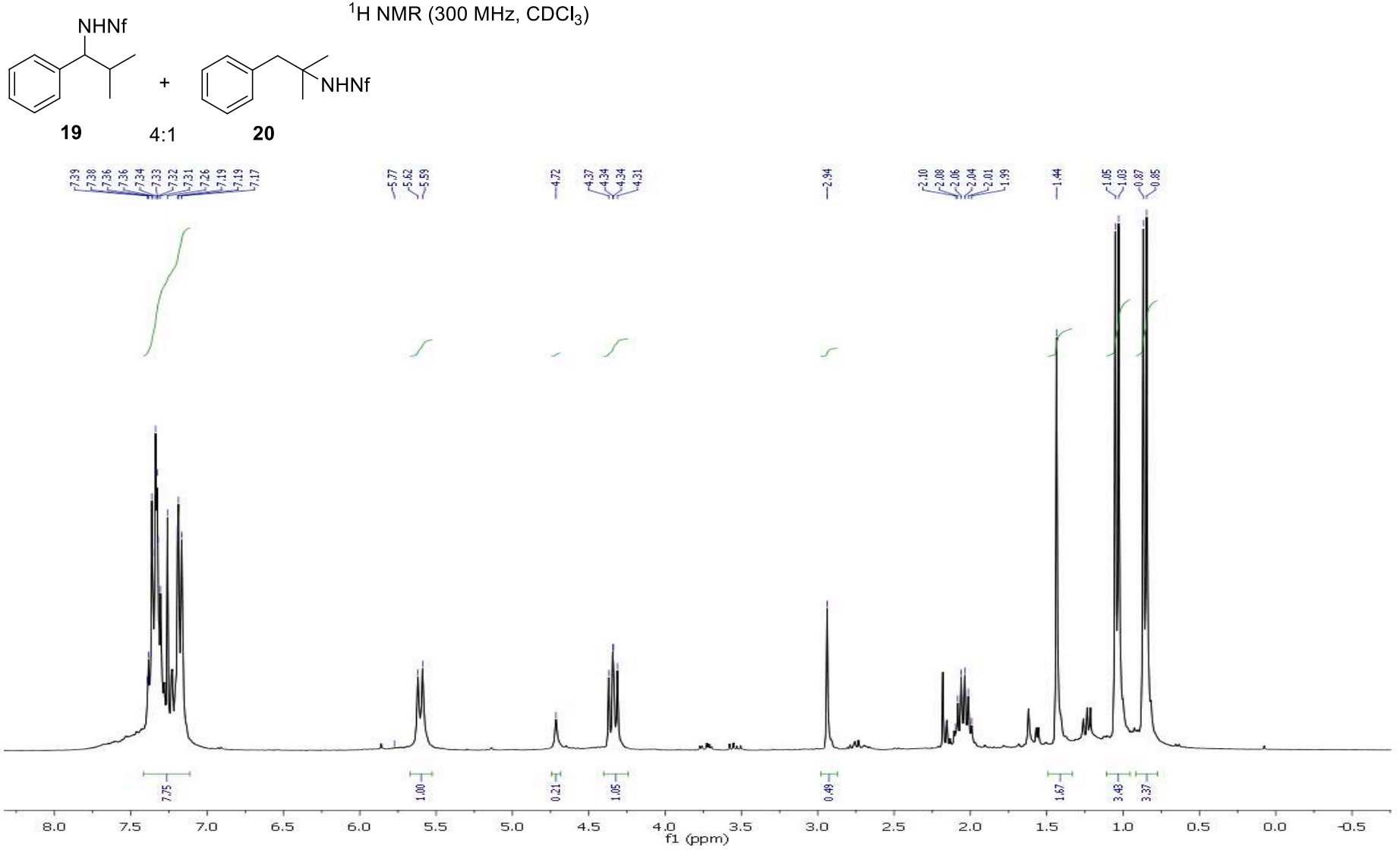


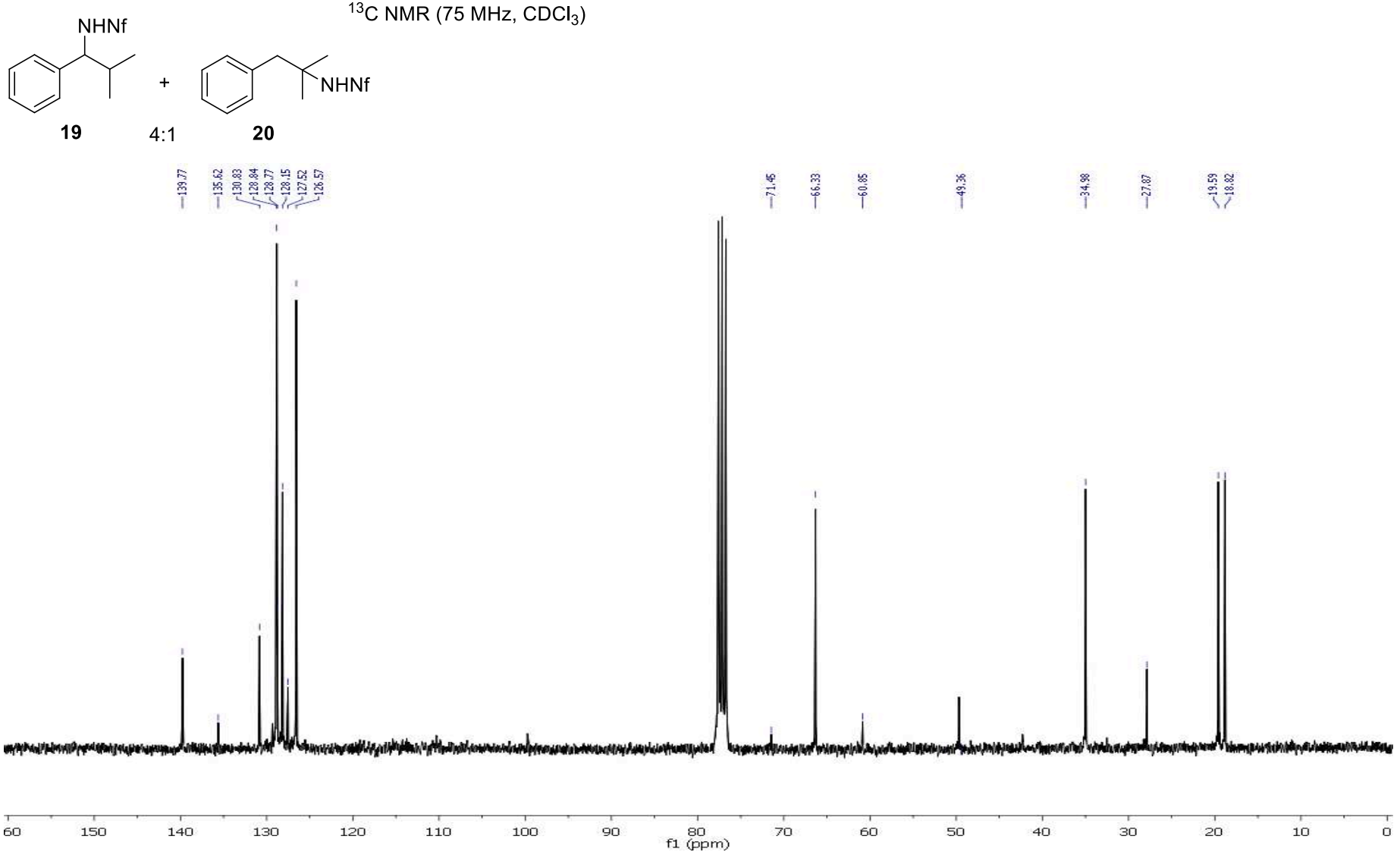


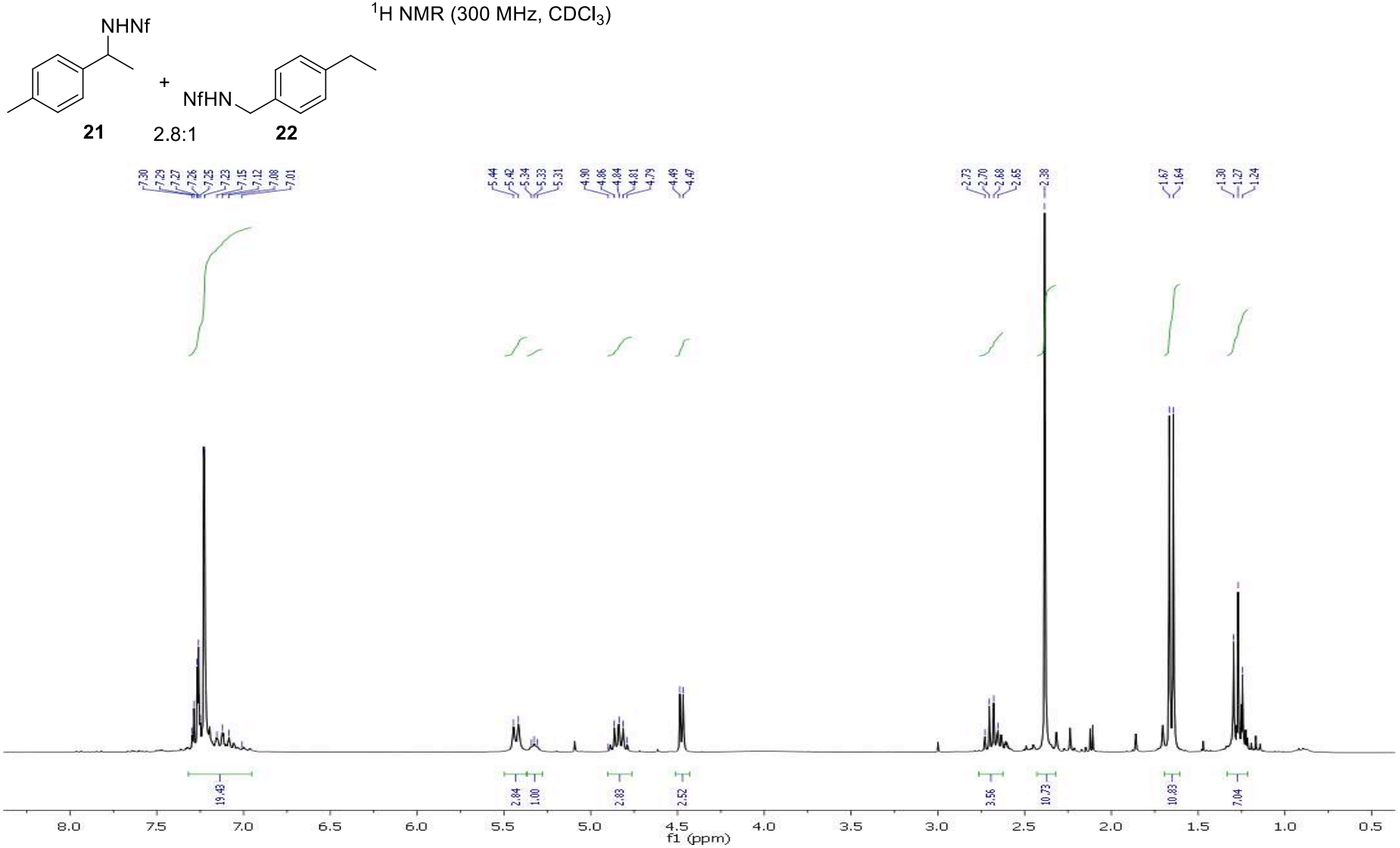
18a,b (1.0:1.2) **18c** (3.1)

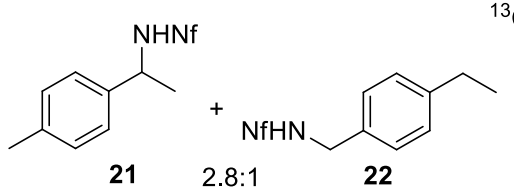
^{13}C NMR (75 MHz, $CDCl_3$)



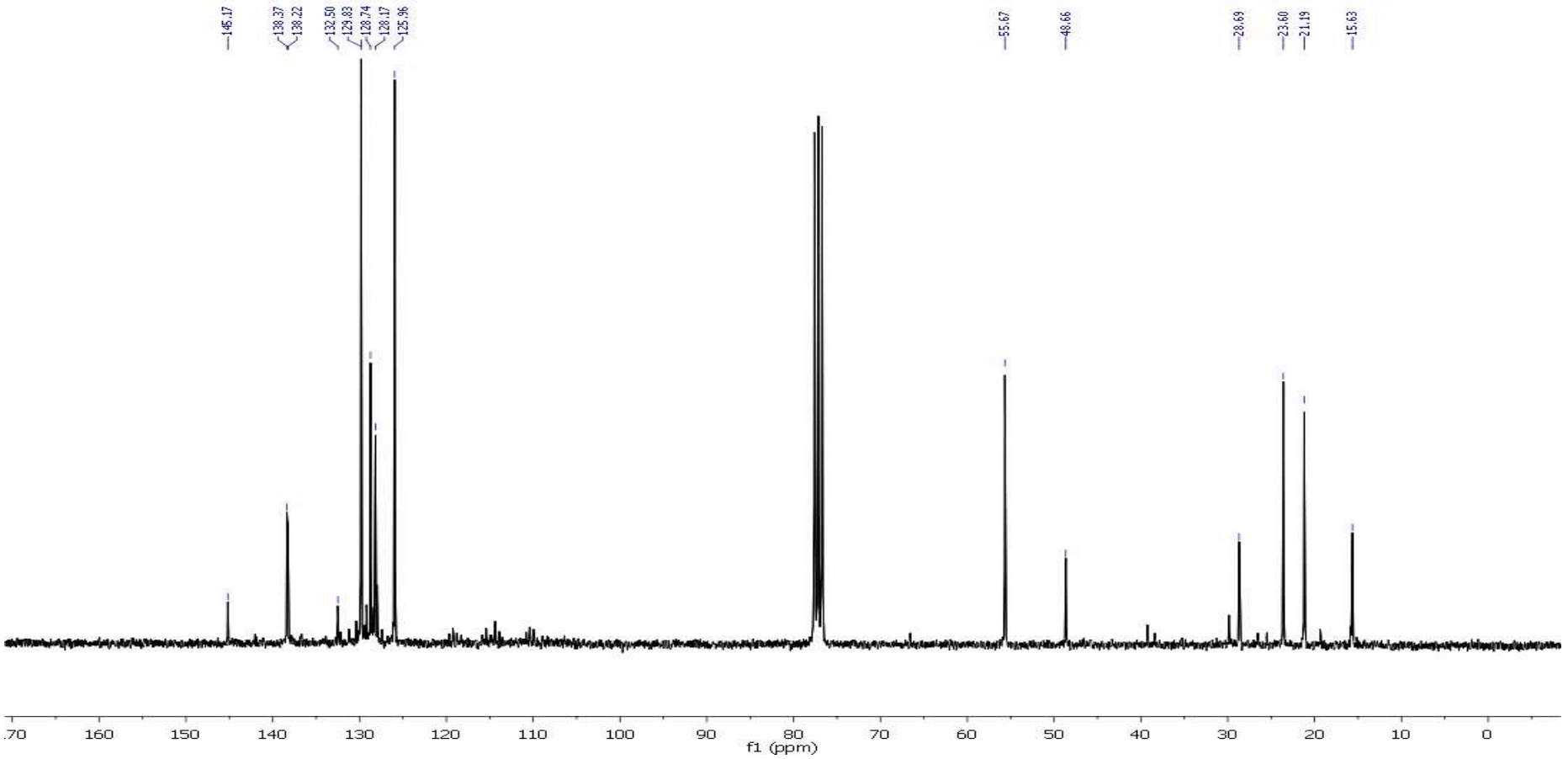


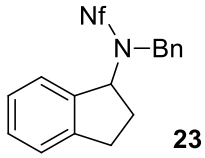






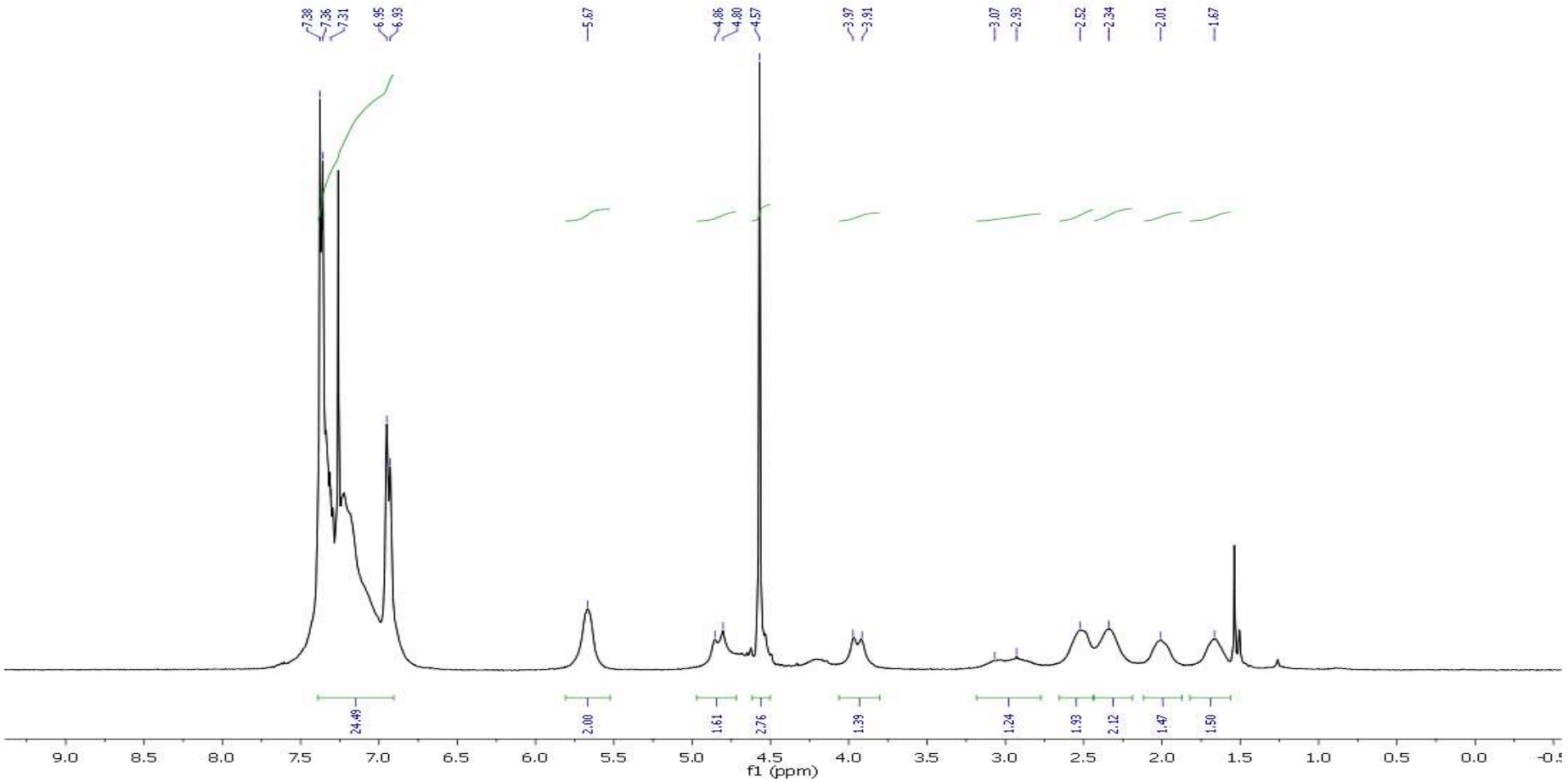
^{13}C NMR (75 MHz, $CDCl_3$)

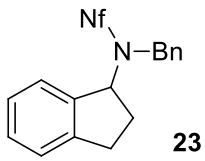




23

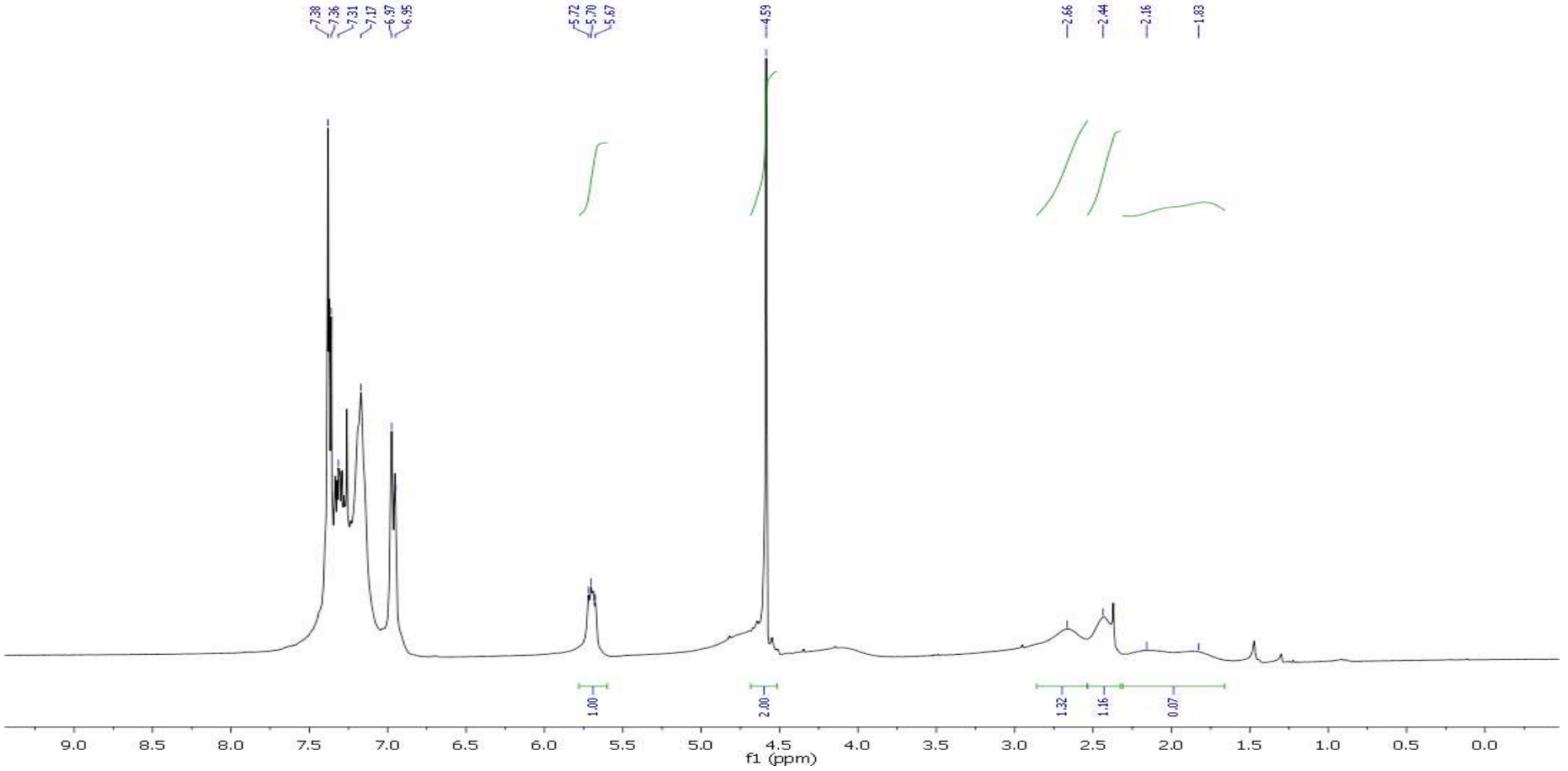
^{1}H NMR (300 MHz, $CDCl_3$ T= 25ºC)

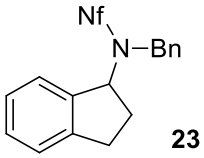




23

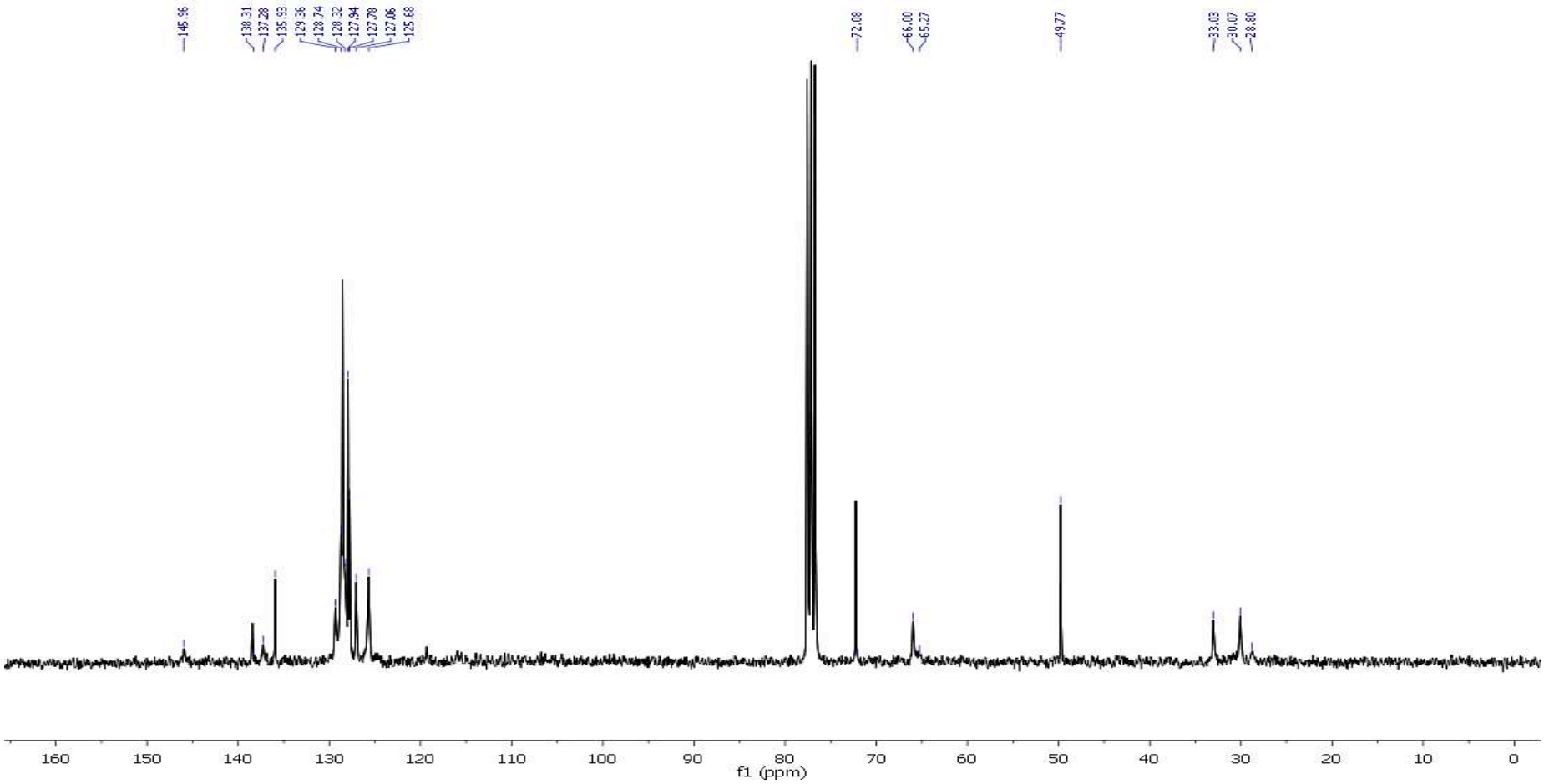
^{1}H NMR (300 MHz, $CDCl_3$, T= 50 ºC)



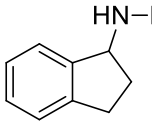


23

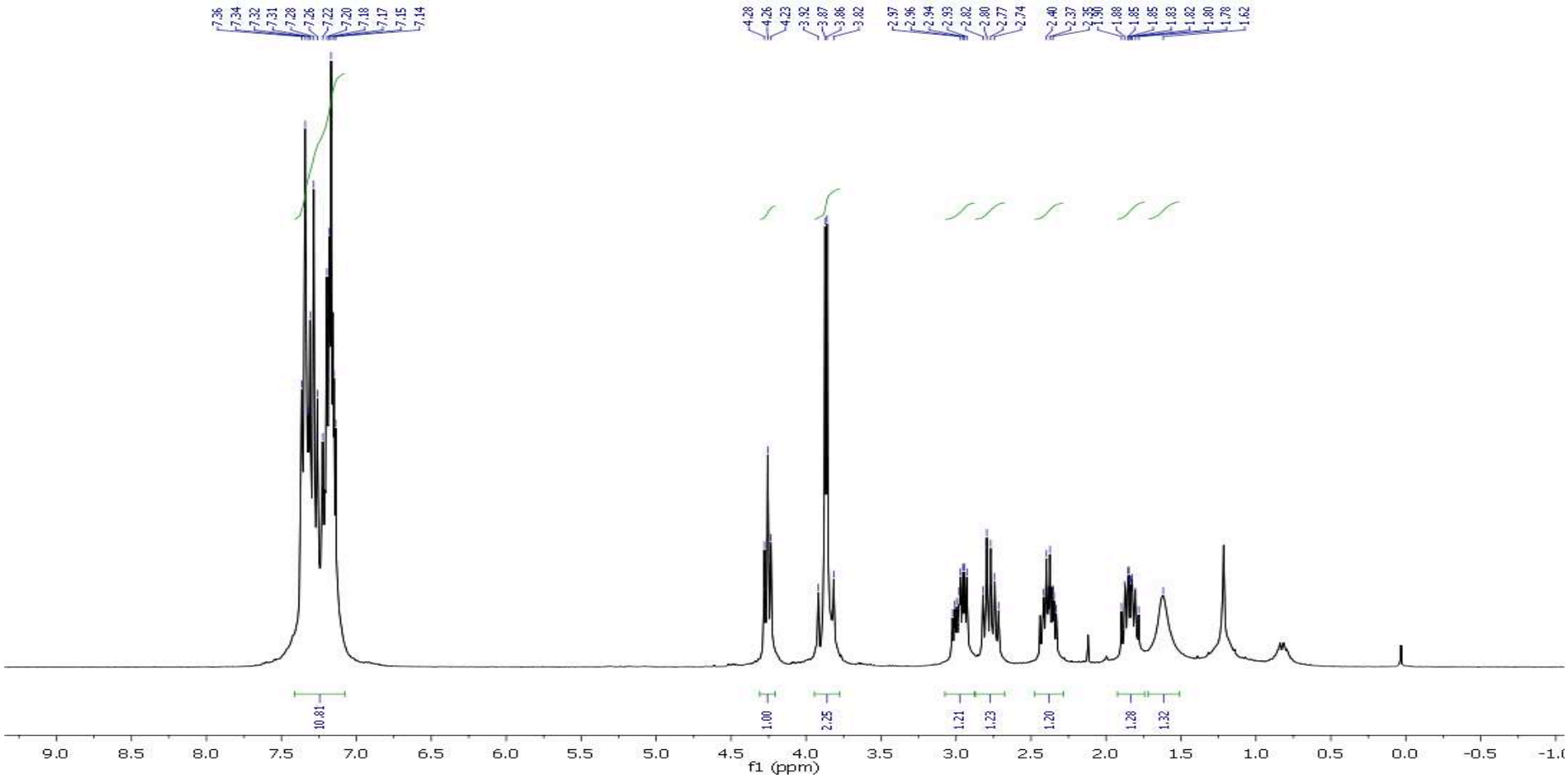
^{13}C NMR (75 MHz, $CDCl_3$ T= 25ºC)

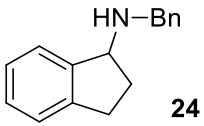


^{1}H NMR (300 MHz, $CDCl_3$)



24





24

^{13}C NMR (75 MHz, $CDCl_3$)