Electronic Supplementary Material (ESI) for ChemComm.

Supporting information

Alkenes as synthetic equivalents of alkynes: combining cyclizations and fragmentation to design one-pot synthesis of quinolines from o-alkenyl arylisocyanides

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1. General Information

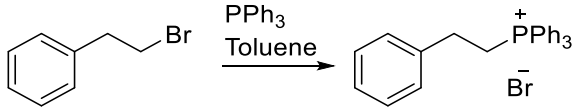
Unless otherwise noted, all ^{1}H NMRs were run on 400 MHz and 600 MHz spectrometer in $CDCl_3$ and all ^{13}C NMR were run on 100 MHz and 150 MHz spectrometer in $CDCl_3$. Proton chemical shifts are given relative to the residual proton signal of $CDCl_3$ (7.26 ppm). Carbon chemical shifts were internally referenced to $CDCl_3$ (77.23 ppm) signal. Data are reported as follows: chemical shift in ppm(δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), coupling constant (Hz), and integration. Infrared spectra (IR) were obtained on a Perkin Elmer Lambda 950 or Perkin Elmer Spectrum 100; absorptions are reported in reciprocal centimeters. High resolution mass spectra (HRMS) were obtained on a JEOL TheMSroute JMS-600H with Agilent 6890 Series GC System.

2. Materials

Acetonitrile, Toluene and THF were obtained from a SPS-4 Solvent Purification System. Hexanes for column chromatography and preparatory thin layer chromatography were distilled prior to use. Dichloromethane was dried using 4 Å molecular sieves and stored under N_2 prior to use. All other solvents were used as purchased. Column chromatography was performed using silica gel (60 Å) and preparatory thin layer chromatography was performed using a 1000 μm glass backed plate containing UV dye. Phenylboronic acid(Acros Organics), 4-tolylphenylboronic acid(Matrix), isobutylboronic acid(Matrix), 4-cyanophenylboronic acid(Matrix), 4-flourophenylboronic acid(Matrix), thiophen-2-ylboronic acid(Matrix), pyridine-4-boronic acid(Matrix), 3,5-dimethoxyphenylboronic acid(Aldrich), 2-bromophenylboronic acid(Matrix), naphthalen-1-ylboronic acid(Matrix), were commercially available and used as received. $Mn(acac)_3$(Aldrich), $Mn(OAc)_3 \cdot 2H_2O$(Acros Organics), were obtained from commercial suppliers and used as received.

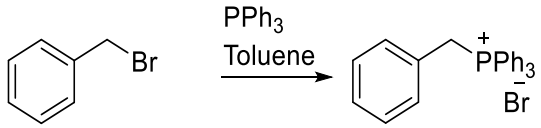
3. Synthesis of Isocyanides

Preparation of Wittig salt – phenethyltriphenylphosphoniumbromide, W1



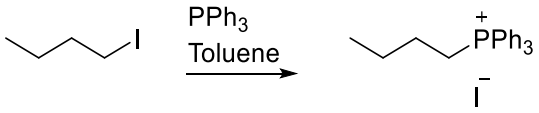
(2-bromoethyl)benzene (10.0mmol) was added dropwise into a solution of triphenylphosphine (10.0mmol) in toluene at room temperature. The solution was stirred for 48 hours in refluxing toluene. The resulting oily substance was collected and washed with hexane. Product was obtained as off white solid. Yield: 92%.

Preparation of Wittig salt – phenethyltriphenylphosphoniumbromide, W2



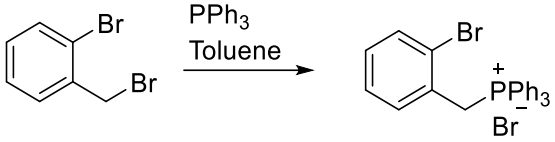
Benzyl bromide (10.0mmol) was added dropwise into a solution of triphenylphosphine (10.0mmol) in toluene at room temperature. The solution was stirred for 48 hours in refluxing toluene. The separated solid was filtered through a Buchner funnel and the residue was washed with hexane. The product was obtained as off white solid. Yield: 88%.

Preparation of Wittig salt – butyltriphenylphosphonium iodide, W3

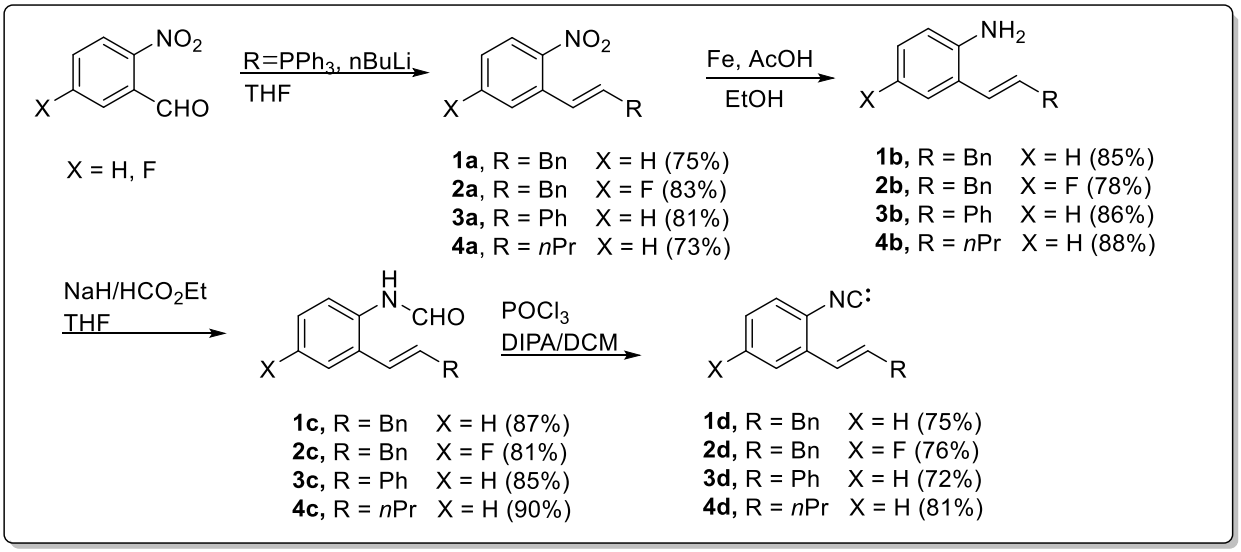


Iodobutane (12.0mmol) was added dropwise into a solution of triphenylphosphine (10.0mmol) in toluene in a pressure tube at room temperature. It was stirred for 48 hours at 120 ◦C. The separated solid was filtered through a Buchner funnel and the residue was washed with hexane. The product was obtained as off white solid. Yield: 85%.

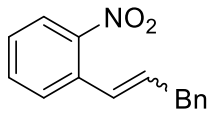
Preparation of Wittig salt – (2-bromobenzyl)triphenylphosphonium bromide, W4



(2-bromoethyl)benzene (10.0mmol) was added dropwise into a solution of triphenylphosphine (10.0mmol) in toluene in a pressure tube at room temperature. It was stirred for 48 hours at 120 ◦C. The separated solid was filtered through a Buchner funnel and the residue was washed with hexane. The product was obtained as off white solid. Yield: 89%.

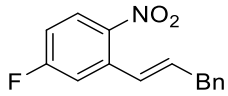


Synthesis of 1-nitro-2-(3-phenylprop-1-enyl)benzene, 1a



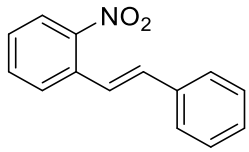
To a solution of the Wittig salt W**1** (3.5 mmol) in anhydrous THF (10mL) at -78 °C was added slowly n-BuLi (3 mL of a 1.5M solution in hexane, 3.0 mmol). After 45 min, a solution of 2-nitrobenzaldehyde(3.5 mmol) in THF (10 mL) was added dropwise. The resulting solution was stirred for 1 h at -78 °C and then at room temperature for 12 h and quenched with saturated NH_4Cl solution. The aqueous phase was extracted with Et_2O (3 × 30 mL), and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The crude was purified by column chromatography(hexane) on silica gel affording (E : Z = 1:3 ,75%) as dark yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.05 (m, 3H), 7.96 – 7.90 (m, 1H), 7.65 – 7.58 (m, 4H), 7.58 – 7.55 (m, 1H), 7.50 – 7.19 (m, 27H), 6.98 (t, *J* = 10.4 Hz, 1H), 6.92 (d, *J* = 11.4 Hz, 3H), 6.39 (dt, *J* = 15.5, 7.0 Hz, 1H), 6.08 (dt, *J* = 11.4, 7.7 Hz, 3H), 3.64 (dd, *J* = 7.0, 1.0 Hz, 2H), 3.50 (dd, *J* = 7.7, 0.8 Hz, 6H). Spectral data match those previously reported[1]. HRMS (ESI): Calcd for $C_{15}H_{13}NNaO_2$ 262.0844, Found: 262.0845

Synthesis of 4-fluoro-1-nitro-2-(3-phenylprop-1-en-1-yl)benzene(E:Z, 1:3), 2a



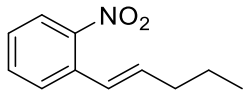
Substrate **2a** was synthesized following the procedure for **1a** from 5-fluro-2-nitrobenzaldehyde and Wittig salt **W1**. The crude product was purified by flash chromatography (Hexanes:EtOAc, 10:1) to give the title compound (E:Z = 1:3, 83%) as a light brown oil. R_f = 0.44 (hexanes/EtOAc 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (dd, *J* = 8.7, 5.1 Hz, 1H), 8.00 (dd, *J* = 9.1, 5.2 Hz, 1H), 6.37 (d, *J* = 15.5 Hz, 1H), 6.09 (dt, *J* = 11.4, 7.7 Hz, 1H), 3.62 (d, *J* = 6.7 Hz, 1H), 3.48 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 163.2, 139.5, 136.2, 136.0, 135.9, 132.9, 128.8, 128.8, 128.8, 128.3, 127.8, 127.7, 126.7, 126.5, 126.2, 126.0, 118.7, 118.5, 115.3, 115.1, 39.6, 34.5. HRMS (ESI): Calcd for $C_{15}H_{12}FNNaO_2$ 280.0742, Found: 280.0744

Synthesis of 1-nitro-2-styrylbenzene, 3a



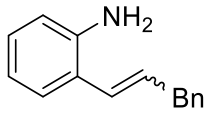
Substrate **3a** was synthesized following the procedure for **1a** from 2-nitrobenzaldehyde and Wittig salt **W2**. The crude product was purified by flash chromatography (Hexanes:EtOAc, 10:1) to give (E:Z = 0.7:1, 81%) of the title compound as a light brown oil. R_f = 0.44 (hexanes/EtOAc 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.06 (m, 1H), 7.97 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.78 (d, *J* = 7.5 Hz, 1H), 7.64 – 7.52 (m, 3H), 7.45 – 7.24 (m, 11H), 7.21 – 7.15 (m, 3H), 7.13 – 7.04 (m, 3H), 6.91 (d, *J* = 12.1 Hz, 1H), 6.78 (d, *J* = 12.1 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 136.6, 136.0, 134.0, 134.0, 133.8, 133.8, 133.2, 133.2, 132.4, 132.0, 129.3, 129.0, 128.8, 128.7, 128.6, 128.4, 128.3, 128.2, 128.1, 127.7, 127.2, 126.6, 126.0, 124.9, 124.8, 123.7. HRMS (ESI): Calcd for $C_{14}H_{11}NO_2$ 225.0790, Found: 225.0801

Synthesis of 1-nitro-2-(pent-1-en-1-yl)benzene, 4a



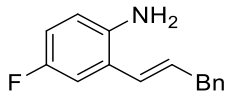
Substrate **4a** was synthesized following the procedure for **1a** from 2-nitrobenzaldehyde and Wittig salt **W3**. The crude product was purified by flash chromatography (Hexanes:EtOAc, 10:1) to give (E:Z = 1:2, 73%) of the title compound as a light brown oil. R_f = 0.73 (hexanes/EtOAc 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.86 – 7.76 (m, 1H), 7.60 – 7.43 (m, 2H), 7.41 – 7.24 (m, 3H), 6.80 (d, *J* = 15.7 Hz, 1H), 6.66 (d, *J* = 11.6 Hz, 1H), 6.20 (dt, *J* = 15.6, 6.9 Hz, 1H), 5.78 (dt, *J* = 11.6, 7.5 Hz, 1H), 2.20 (qd, *J* = 7.3, 1.5 Hz, 1H), 2.03 (qd, *J* = 7.5, 1.7 Hz, 2H), 1.57 – 1.43 (m, 1H), 1.42 – 1.31 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 2H), 0.83 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.6, 134.5, 133.3, 132.8, 132.8, 132.6, 131.9, 128.3, 127.6, 127.3, 125.1, 125.0, 124.3, 124.3, 35.2, 30.4, 22.7, 22.2, 13.6, 13.6. HRMS (ESI): Calcd for $C_{11}H_{12}NO_2$ 191.0946, Found: 191.0942

Synthesis of 2-(3-phenylprop-1-en-1-yl)aniline, 1b



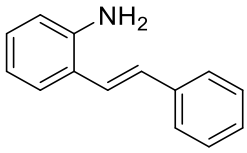
Aniline **1b** was prepared by reduction of nitro group following a method reported by Bowman and co-workers[2]. To a solution of **1a**(1.5 g, 6.2mmol) in 20 ml of absolute ethanol was added 20 ml of glacial acetic acid and of iron powder (1.8 g, 31 mmol). The mixture was heated to reflux. After 6 h, the crude mixture was cooled and filtered through a pad of Celite. The filtrate was concentrated in *vacuo*. Purification by flash chromatography on silica gel (Hexanes:EtOAc) afforded **1b** as a dark brown oil 1.1 g (E:Z = 1:3 , 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.04 (m, 31H), 6.81 – 6.69 (m, 7H), 6.67 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.49 (d, *J* = 15.5 Hz, 1H), 6.44 (d, *J* = 11.1 Hz, 3H), 6.24 (dt, *J* = 15.5, 6.9 Hz, 1H), 5.99 (dt, *J* = 11.1, 7.5 Hz, 3H), 3.69 (s, 6H), 3.58 (d, *J* = 7.0 Hz, 3H), 3.52 (d, *J* = 7.5 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) 144.8, 143.4, 136.2,133.4, 130.2, 129.8, 128.9, 128.8, 128.6, 126.9, 126.5, 123.0, 121.0, 120.5, 56.6, 35.5, 31.5, 21.6. HRMS (ESI): Calcd for $C_{15}H_{15}N$ 209.1250, Found: 209.1260 Spectral data match those previously reported[3].

Synthesis of 4-fluoro-2-(3-phenylprop-1-en-1-yl)aniline, 2b



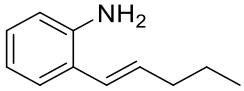
Substrate **2b** was synthesized following the procedure for **1b** from **2a**. The crude product was purified by flash chromatography (Hexanes:EtOAc, 10:1) to give (E:Z = 1:3, 78%) of the title compound as a brown oil. R_f = 0.44 (hexanes/EtOAc 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (dt, *J* = 9.5, 3.2 Hz, 1H), 6.67 (ddd, *J* = 8.4, 4.8, 1.4 Hz, 1H), 6.64 – 6.58 (m, 1H), 6.45 (d, *J* = 15.2 Hz, 1H), 6.40 (d, *J* = 11.4 Hz, 1H), 6.32 – 6.20 (m, 1H), 6.09 – 5.96 (m, 1H), 3.52 (d, *J* = 7.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.1, 154.8, 140.4, 133.8, 132.4, 128.8, 128.7, 128.7, 128.7, 1n28.5, 128.5, 126.4, 126.3, 126.1, 125.3, 124.0, 123.9, 116.2, 116.1, 115.9, 114.9, 114.7, 39.7, 34.8. HRMS (ESI): Calcd for $C_{15}H_{15}FN$ 228.1188, Found: 228.1199

Synthesis of 2-styrylaniline, 3b



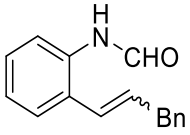
Substrate **3b** was synthesized following the procedure for **1b** from **3a**. The crude product was purified by flash chromatography (Hexanes:EtOAc, 10:1) to give (E:Z = 0.7:1, 86%) of the title compound as a dark oil. R_f = 0.44 (hexanes/EtOAc 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.64 – 7.58 (m, 1H), 7.54 (t, *J* = 7.6 Hz, 2H), 7.45 (dd, *J* = 7.7, 1.6 Hz, 2H), 7.41 – 7.25 (m, 6H), 7.18 (d, *J* = 16.1 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.92 – 6.85 (m, 1H), 6.85 – 6.78 (m, 3H), 6.68 (d, *J* = 12.1 Hz, 1H), 3.84 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0, 143.7, 137.5, 136.6, 131.5, 130.0, 129.5, 128.7, 128.7, 128.7, 128.6, 128.6, 128.4, 128.2, 127.5, 127.4, 127.1, 126.4, 126.4, 124.2, 123.6, 123.0, 119.0, 118.3, 116.2, 115.4. HRMS (ESI): Calcd for $C_{14}H_{14}N$ 196.1126, Found: 196.1141

Synthesis of 2-(pent-1-en-1-yl)aniline, 4b



Substrate **4b** was synthesized following the procedure for **1b** from **4a**. The crude product was purified by flash chromatography (Hexanes:EtOAc, 10:1) to give (E:Z = 1:2, 88%) of the title compound as a light brown oil. R_f = 0.44 (hexanes/EtOAc 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 1H), 7.21 – 7.04 (m, 1H), 6.90 – 6.65 (m, 1H), 6.54 – 6.42 (m, 1H), 6.35 (d, *J* = 11.3 Hz, 1H), 6.14 (dtd, *J* = 9.1, 6.9, 2.2 Hz, 1H), 5.85 (dtd, *J* = 9.5, 7.4, 2.1 Hz, 1H), 3.71 (s, 1H), 2.38 – 2.05 (m, 1H), 1.66 – 1.40 (m, 1H), 1.21 – 0.85 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0, 143.4, 134.8, 133.1, 129.8, 128.0, 127.9, 127.4, 125.5, 125.0, 124.5, 123.4, 119.0, 118.0, 116.0, 115.6, 115.1, 35.6, 30.7, 23.0, 22.7, 13.9, 13.8. HRMS (ESI): Calcd for $C_{11}H_{16}N$ 162.1282, Found: 162.1295

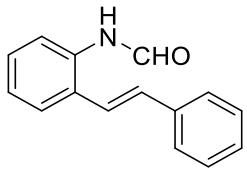
Synthesis of N-(2-(3-phenylprop-1-en-1-yl)phenyl)formamide, 1c



A solution of aniline **1b** (1.3 g, 6.4 mmol) and ethyl formate (3 ml) in anhydrous THF (10 ml) was added dropwise to a suspension of NaH (60% in mineral oil, 0.5 g, 14 mmol) in anhydrous THF (5 ml). The resulting mixture was stirred at r.t. for 24 h, then the reaction was quenched with cold water (5 mL). The solvents were removed under reduced pressure, and the residue was dissolved in ethyl acetate/water (20/5 mL). The aqueous phase was extracted with ethyl acetate (3 x 20 mL), the combined organic extracts were dried over anhydrous Na_2SO_4 and evaporated. The residue was washed thoroughly with hexane (3 x 30 mL) and dried in vacuo to give 1.3 g (E : Z = 1:3, 87%) of the title compound as a dark yellow liquid that slowly crystallized. ^{1}H NMR ($CDCl_3$, 400 MHz, inseparable mixture of rotamers & E:Z isomers): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 11.3 Hz, 1H), 8.49 (d, *J* = 11.2 Hz, 1H), 8.39 (dd, *J* = 6.6, 1.7 Hz, 1H), 8.36 – 8.26 (m, 2H), 7.99 (d, *J* = 10.9 Hz, 1H), 7.91 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.81 (s, 1H), 7.56 (d, *J* = 4.8 Hz, 1H), 7.50 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.43 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.39 – 7.08 (m, 24H), 6.63

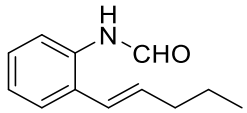
(dd, *J* = 23.0, 15.6 Hz, 1H), 6.51 (dd, *J* = 11.2, 4.6 Hz, 2H), 6.40 – 6.24 (m, 1H), 6.12 (ddt, *J* = 17.2, 11.2, 7.6 Hz, 2H), 3.49 (d, *J* = 7.6 Hz, 2H), 3.44 (d, *J* = 7.6 Hz, 2H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8, 159.2, 139.8, 135.1, 134.6, 134.6, 134.5, 130.4, 129.5, 128.6, 128.5, 128.3, 128.2, 127.0, 126.4, 126.3, 125.3, 125.1, 125.0, 124.4, 121.5, 119.5, 119.3, 77.5, 77.2, 76.9, 39.7, 34.7, 34.6.. HRMS (ESI): Calcd for $C_{16}H_{15}NNaO$ 260.1051, Found: 260.1057. Spectral data match those previously reported[4].

Synthesis of N-(2-styrylphenyl)formamide, 3c



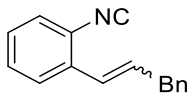
Substrate **3c** was synthesized following the procedure for **1c** from **3b**. The crude product was purified by flash chromatography (Hexanes:EtOAc, 10:1) to give (E:Z = 0.7:1, 85%) of the title compound as an off white solid. R_f = 0.41 (hexanes/EtOAc 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.07 (d, *J* = 11.0 Hz, 1H), 8.55 – 8.43 (m, 2H), 8.43 – 8.35 (m, 2H), 8.19 (d, *J* = 7.9 Hz, 1H), 8.14 (d, *J* = 1.9 Hz, 1H), 8.03 (d, *J* = 11.0 Hz, 1H), 7.90 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.70 – 7.60 (m, 2H), 7.55 (ddd, *J* = 5.6, 4.2, 0.9 Hz, 3H), 7.49 (dd, *J* = 7.9, 0.9 Hz, 2H), 7.40 – 6.92 (m, 40H), 6.73 (dd, *J* = 12.1, 3.0 Hz, 3H), 6.51 (dd, *J* = 12.1, 5.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1, 162.8, 160.1, 159.2, 136.9, 136.8, 135.9, 135.8, 134.1, 134.0, 133.9, 133.8, 133.5, 133.4, 131.9, 131.8, 130.8, 130.4, 129.8, 129.4, 129.3, 128.7, 128.7, 128.6, 128.6, 128.5, 128.4, 128.4, 128.3, 128.2, 128.2, 128.1, 128.0, 127.8, 126.8, 126.7, 126.6, 126.4, 126.3, 125.6, 125.5, 125.1, 124.8, 124.8, 123.9, 123.3, 122.7, 122.2, 121.9, 119.9. HRMS (ESI): Calcd for $C_{15}H_{13}NNaO$ 246.0895, Found: 246.0868.

Synthesis of N-(2-(pent-1-en-1-yl)phenyl)formamide, 4c



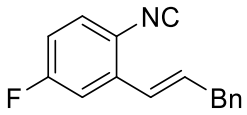
Substrate **4c** was synthesized following the procedure for **1c** from **4b**. The crude product was purified by flash chromatography (Hexanes:EtOAc, 4:1) to give (E:Z = 1:2, 90%) of the title compound as a light brown oil. R_f = 0.5 (hexanes/EtOAc 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 11.4 Hz, 1H), 8.48 (d, *J* = 11.2 Hz, 1H), 8.40 (dd, *J* = 5.6, 1.3 Hz, 1H), 8.23 (d, *J* = 8.2 Hz, 1H), 8.00 – 7.83 (m, 1H), 7.60 (s, 1H), 7.46 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.38 (d, *J* = 7.7 Hz, 1H), 7.30 – 7.05 (m, 1H), 6.50 (t, *J* = 14.7 Hz, 1H), 6.34 (d, *J* = 11.4 Hz, 1H), 6.15 (ddt, *J* = 22.6, 15.6, 6.9 Hz, 1H), 5.97 – 5.77 (m, 1H), 2.27 – 2.14 (m, 1H), 2.12 – 1.98 (m, 1H), 1.50 (ddd, *J* = 14.7, 7.4, 4.6 Hz, 1H), 1.39 (dq, *J* = 14.7, 7.4 Hz, 1H), 0.95 (td, *J* = 7.4, 4.1 Hz, 1H), 0.87 (td, *J* = 7.4, 4.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.8 162.8, 159.1, 144.1, 137.1, 136.6, 135.3, 134.5, 134.3, 133.3, 131.4, 130.5, 129.5, 129.2, 128.1, 127.8, 127.8, 127.5, 127.3, 127.0, 126.3, 125.4, 125.0, 124.6, 124.3, 124.2, 124.1, 123.9, 123.4, 121.9, 121.2, 119.0, 35.4, 35.4, 30.6, 30.6, 22.6, 22.4, 22.4, 13.8, 13.8. HRMS (ESI) Calcd for $C_{12}H_{16}NO$ 190.1279, Found: 190.1261.

Synthesis of 1-isocyano-2-(3-phenylprop-1-en-1-yl)benzene, 1d



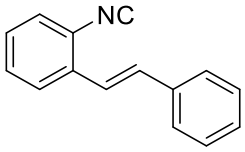
To a solution of N-formyl amide **6b** (0.35 g, 1.4 mmol) in anhydrous CH_2Cl_2 (3.0 mL) was added at 0 °C diisopropylamine (0.5 ml, 3.5 mmol), then dropwise over a period of 5 min $POCl_3$ (0.2 mL, 1.9 mmol) was added. The mixture was stirred at 0 °C for 1 h, then a saturated solution of Na_2CO_3 (2mL) was added slowly. The mixture was transferred into a separatory funnel, diluted with CH_2Cl_2 (20mL), the organic phase was washed with a half-saturated solution of Na_2CO_3(10mL) and brine(10mL), then dried over anhydrous Na_2SO_4 and evaporated. The crude product was purified by flash chromatography (Hexanes:EtOAc, 10:1) to give 0.24 g (E : Z = 1:3, 75%) of the title compound as a brown oil. R_f = 0.53 (hexanes/EtOAc 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.7 Hz, 1H), 7.48 – 7.22 (m, 8H), 6.86 (d, *J* = 15.8 Hz, 1H), 6.74 (d, *J* = 11.5 Hz, 3H), 6.57 – 6.44 (m, 1H), 6.15 (d, *J* = 11.5 Hz, 3H), 3.66 (d, *J* = 7.1 Hz, 2H), 3.62 (d, *J* = 7.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 139.6, 139.2, 134.0, 133.9, 133.9, 133.7, 129.6, 129.2, 128.9, 128.6, 128.5, 128.5, 128.4, 128.2, 127.8, 127.6, 126.9, 126.8, 126.3, 126.2, 125.7, 124.9, 124.9, 39.5, 34.6. HRMS (ESI) calculated for $C_{16}H_{13}N$ 219.1048, found 219.1052.

Synthesis of 4-fluoro-1-isocyano-2-(3-phenylprop-1-en-1-yl)benzene, 2d



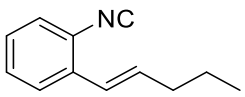
Substrate **2d** was synthesized following the procedure for **1d**. The crude product was purified by flash chromatography (Hexanes:EtOAc, 10:1) to give (E:Z = 1:3, 76%) of the title compound as a light brown oil. R_f = 0.44 (hexanes/EtOAc 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.4 Hz, 1H), 7.49 – 7.23 (m, 12H), 6.93 – 6.82 (m, 1H), 6.76 (d, *J* = 11.5 Hz, 1H), 6.55 (t, *J* = 11.4 Hz, 1H), 6.17 (dt, *J* = 11.5, 7.6 Hz, 1H), 3.68 (d, *J* = 7.1 Hz, 1H), 3.64 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 139.8, 139.3, 134.1, 134.0, 129.7, 129.3, 129.0, 128.7, 128.6, 128.5, 128.3, 128.1, 127.9, 127.7, 127.1, 127.0, 126.5, 126.3, 126.2, 125.8, 125.1, 125.0, 77.5, 77.2, 76.9, 34.7. HRMS (ESI): Calcd for $C_{15}H_{12}FN$ 237.0952, Found: 237.0960

Synthesis of 1-isocyano-2-styrylbenzene, 3d

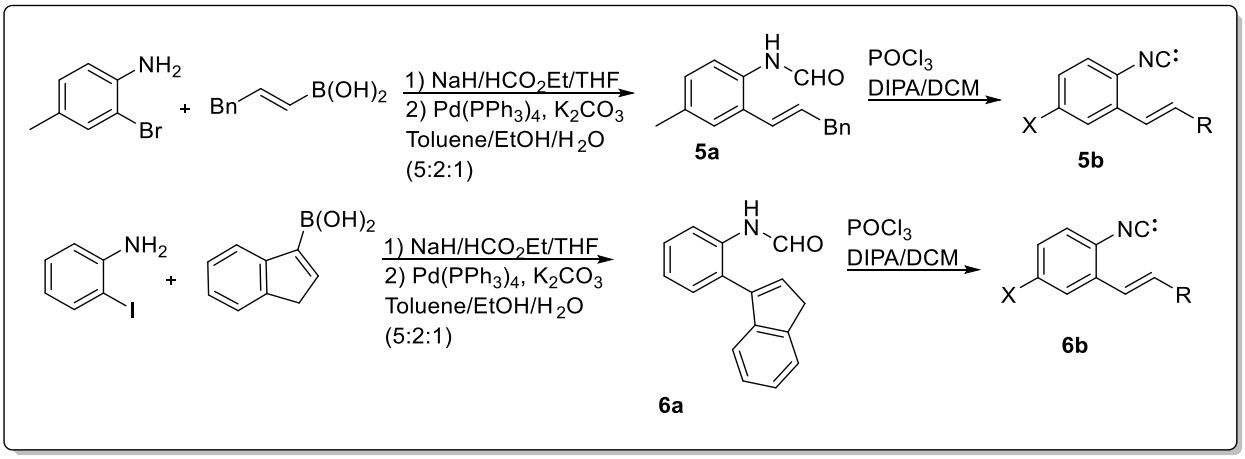


Substrate **3d** was synthesized following the procedure for **1d** from **3c**. The crude product was purified by flash chromatography (Hexanes:EtOAc, 10:1) to give (E:Z = 0.7:1, 76%) of the title compound as a light brown oil. R_f = 0.44 (hexanes/EtOAc 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.9 Hz, 1H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.46 – 7.13 (m, 15H), 6.83 (d, *J* = 12.2 Hz, 1H), 6.68 (d, *J* = 12.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 166.7, 136.4, 136.1, 134.5, 133.7, 133.6, 132.6, 130.0, 129.4, 128.8, 128.8, 128.8, 128.6, 128.3, 128.3, 128.3, 128.0, 128.0, 127.7, 127.2, 127.0, 126.9, 125.4, 124.5, 122.0, 49.0, 49.0, 21.6, 21.5. HRMS (ESI): Calcd for $C_{15}H_{11}N$ 205.0891, Found: 205.0844

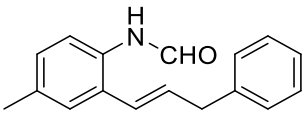
Synthesis of 1-isocyano-2-(pent-1-en-1-yl)benzene, 4d



Substrate **4d** was synthesized following the procedure for **1d** from **4c**. The crude product was purified by flash chromatography (Hexanes:EtOAc, 10:1) to give (E:Z = 1:2, 81%) of the title compound as a light brown oil. R_f = 0.44 (hexanes/EtOAc 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.0 Hz, 1H), 7.33 (dd, *J* = 6.8, 2.5 Hz, 1H), 7.31 – 7.26 (m, 1H), 7.26 – 7.14 (m, 1H), 6.67 (d, *J* = 15.8 Hz, 1H), 6.50 (dd, *J* = 11.6, 1.5 Hz, 1H), 6.34 (dt, *J* = 15.7, 7.0 Hz, 1H), 5.88 (dt, *J* = 11.6, 7.4 Hz, 1H), 2.21 (dqd, *J* = 22.2, 7.3, 1.5 Hz, 1H), 1.57 – 1.39 (m, 1H), 0.92 (dt, *J* = 24.1, 7.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 166.3, 136.4, 135.7, 134.5, 134.2, 129.8, 129.2, 128.8, 127.4, 127.3, 126.9, 126.7, 125.6, 124.0, 123.8, 35.3, 30.7, 22.7, 22.3, 13.7, 13.7. HRMS (ESI): Calcd for $C_{12}H_{13}N$ 171.1048, Found: 171.1061

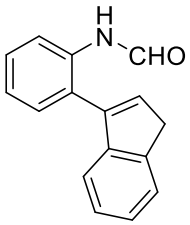


Synthesis of N-(4-methyl-2-(3-phenylprop-1-en-1-yl)phenyl)formamide, 5a



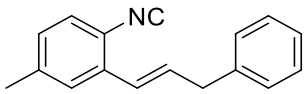
Following the same procedure described above for the synthesis of formylamine **1c**, the corresponding N-(2-bromo-4-methylphenyl)formamide was prepared and used in a procedure outlined by Bin Li and co-workers[4]. To a solution of trans-3-phenyl-1-propen-1-ylboronic acid (0.365g, 2.25mmol), $Pd(PPh_3)_4$ (0.173g, 0.15mmol) and K_2CO_3 (0.828g, 6mmol) in 20 mL of toluene, 8 mL of absolute ethanol, and 4 mL of H_2O was added N-(2-bromo-4-methylphenyl)formamide (0.310g, 1.5mmol). The mixture was then purged with N_2 and refluxed for 24 h. The reaction was then cooled to room temperature and 20 mL of H_2O were added and the resulting phases were separated. The resulting aqueous phase was extracted with 3 x 10 mL ethyl acetate. The resulting organic phases were then washed with water (1 x 20 mL) followed by a saturated solution of brine (1 x 20 mL). The resulting organic phase was then dried using Na_2SO_4 and filtered. The solvent was removed under reduced pressure in vacuo and the crude product was purified using flash chromatography on silica gel (n-hexane/EtOAc 5:1 as eluent) to give the desired products **5a** (60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (dd, *J* = 28.2, 6.3 Hz, 1H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.39 – 7.28 (m, 2H), 7.28 – 7.19 (m, 2H), 7.11 – 6.94 (m, 1H), 6.58 (dd, *J* = 30.3, 15.6 Hz, 1H), 6.38 – 6.21 (m, 1H), 3.56 (t, *J* = 7.1 Hz, 1H), 2.31 (d, *J* = 15.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1, 139.7, 136.2, 135.4, 133.1, 131.1, 131.0, 128.8, 128.7, 128.6, 128.6, 128.6, 127.7, 127.4, 126.4, 125.5, 122.5, 39.7, 39.6, 21.0, 21.0. HRMS (ESI): Calcd for $C_{17}H_{17}NNaO$ 274.1207, Found: 274.1216

Synthesis of N-(2-(1H-inden-3-yl)phenyl)formamide, 6a



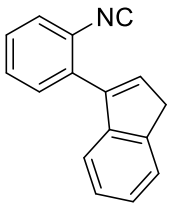
Following the same procedure described above for the synthesis of formylamine **1c**, the corresponding N-(2-iodo-phenyl)formamide was prepared and used in a procedure similar to that outlined by Bin Li and co-workers[4]. To a solution of (1H-inden-3-yl)boronic acid (0.490g, 3.04mmol), $Pd(PPh_3)_4$ (0.233g, 0.20mmol) and K_2CO_3 (1.12g, 8.08mmol) in 20 mL of toluene, 8 mL of absolute ethanol, and 4 mL of H_2O was added N-(2-iodo-phenyl)formamide (0.500g, 2.02mmol). The mixture was then purged with N_2 and refluxed for 24 h. The reaction was then cooled to room temperature and 20 mL of H_2O were added and the resulting phases were separated. The resulting aqueous phase was extracted with 3 x 10 mL ethylacetate. The resulting organic phases were then washed with water (1 x 20 mL) followed by a saturated solution of brine (1 x 20 mL). The resulting organic phase was then dried using Na_2SO_4 and filtered. The solvent was removed under reduced pressure in vacuo and the crude product was purified using flash chromatography on silica gel (n-hexane/EtOAc 5:1 as eluent) to give the desired products **6a** (64%) as a brown oil that slowly crystallized. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.62 (dd, *J* = 11.3, 2.2 Hz, 1H), 8.45 (d, *J* = 8.0 Hz, 1H), 8.24 – 8.10 (m, 1H), 7.77 – 7.67 (m, 1H), 7.63 – 7.52 (m, 1H), 7.48 (s, 1H), 7.44 – 7.37 (m, 1H), 7.37 – 7.28 (m, 2H), 7.26 – 7.12 (m, 1H), 6.61 (dt, *J* = 20.2, 1.9 Hz, 1H), 3.60 (dd, *J* = 7.8, 1.5 Hz, 1H).^{13}C NMR (151 MHz, $CDCl_3$) δ 161.9, 159.1, 144.1, 144.1, 143.9, 143.8, 141.5, 140.9, 134.7, 134.5, 134.0, 133.9, 130.7, 129.8, 129.0, 128.8, 126.6, 126.6, 125.6, 125.6, 125.1, 124.5, 124.3, 124.2, 121.3, 120.5, 120.2, 118.0, 38.8. HRMS (ESI): Calcd for $C_{16}H_{13}NNaO$ 258.0894, Found: 258.0896

Synthesis of 1-isocyano-4-methyl-2-(3-phenylprop-1-en-1-yl)benzene, 5b



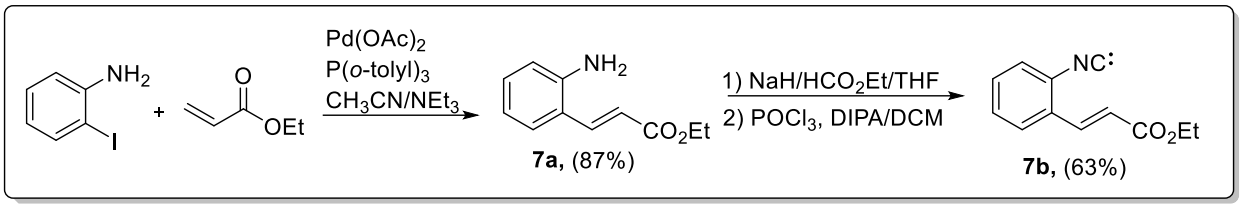
Substrate **5b** was synthesized following the procedure for **1d** from **5a,** (79%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 1H), 7.26 – 7.18 (m, 1H), 7.00 (dd, *J* = 8.1, 1.0 Hz, 1H), 6.76 (d, *J* = 15.7 Hz, 1H), 6.44 (dt, *J* = 15.7, 7.1 Hz, 1H), 3.60 (d, *J* = 7.1 Hz, 1H), 2.32 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.6, 139.5, 133.6, 133.6, 128.7, 128.7, 128.7, 128.6, 126.9, 126.5, 126.3, 125.2, 39.7, 21.7. HRMS (ESI): Calcd for $C_{17}H_{15}N$ 233.1204, Found: 233.1216

Synthesis of 3-(2-isocyanophenyl)-1H-indene, 6b

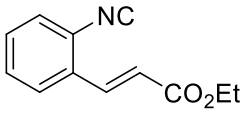


Substrate **6b** was synthesized following the procedure for **1d** from **6a**, (78%)**.** ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 – 7.56 (m, 1H), 7.54 (dd, *J* = 10.6, 3.9 Hz, 1H), 7.48 (dd, *J* = 12.0, 4.4 Hz, 1H), 7.41 (dd, *J* = 10.7, 4.6 Hz, 1H), 7.34 – 7.27 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.0, 143.7, 140.1, 134.8,

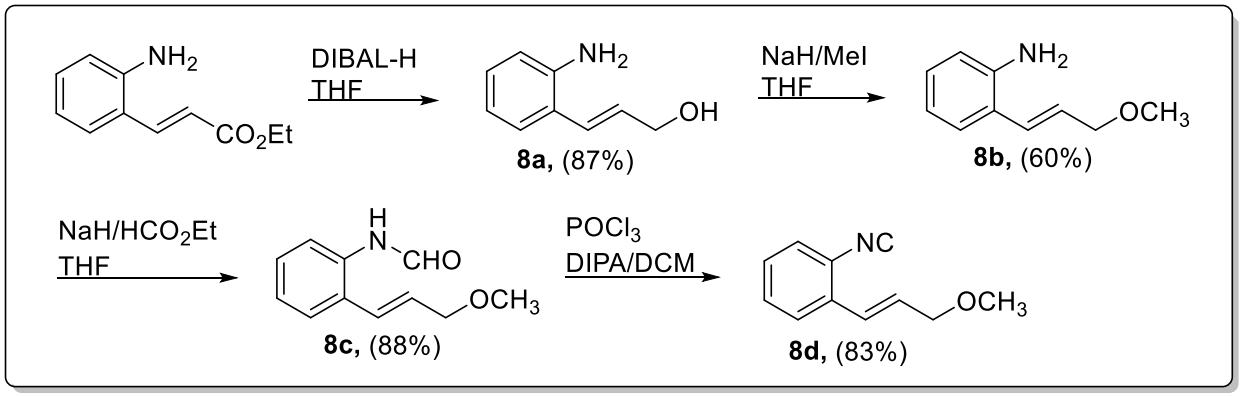
133.4, 130.1, 129.4, 128.5, 128.0, 126.3, 125.3, 124.3, 120.3, 38.9. HRMS (ESI): Calcd for $C_{16}H_{11}N$ 217.0891, Found: 217.0885



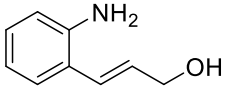
Synthesis of ethyl-3-(2-isocyanophenyl)acrylate, 7b



To prepare substrate **7a**, to a one neck round bottom flask was added a magnetic stir bar, 2-iodoaniline (9.636g, 44mmol), ethyl acrylate (17.6g, 176mmol), $Pd(OAc)_2$ (1g, 4.45mmol), P(*o*-tolyl)$_3$ (2.7g, 8.9mmol), Triethylamine (15 mL), and CH_3CN. The mixture was then purged with N_2 and refluxed for 24 h. The reaction was then cooled to room temperature and 20 mL of H_2O were added and the resulting phases were separated. The resulting aqueous phase was extracted with 3 x 10 mL ethyl acetate. The resulting organic phases were then washed with water (1 x 20 mL) followed by a saturated solution of brine (1 x 20 mL). The resulting organic phase was then dried using Na_2SO_4 and filtered. The solvent was removed under reduced pressure in vacuo and the crude product was purified using flash chromatography on silica gel (n-hexane/EtOAc 10:1 as eluent) to give the desired products **7a** (92%) as a dark yellow oil that slowly crystallized. Substrate **7b (63%)** was prepared by formylation followed by subsequent dehydration of Aniline **7a** following the method described above for substrate **1c, 1d.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 16.1 Hz, 1H), 7.77 – 7.56 (m, 1H), 7.50 – 7.31 (m, 1H), 6.51 (d, *J* = 16.0 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 1H), 1.41 – 1.25 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 166.1, 137.7, 130.9, 130.8, 129.7, 127.8, 127.0, 122.6, 77.5, 77.2, 76.9, 61.0, 14.4. HRMS (EI): Calcd for $C_{12}H_{11}NO_2$ 201.0790, Found: 201.0796

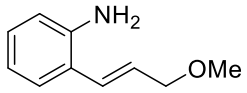


3-(2-aminophenyl)prop-2-en-1-ol, 8a



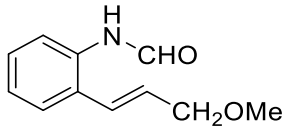
Substrate **8a** was prepared by DIBAL reduction of substrate **7a**. To a flame dried round bottom flask was added aniline **7a** (3.06g, 16mmol), magnetic stirbar and dry THF (20 mL). The resulting mixture was placed into an ice bath under an inert atmosphere of N_2. To the resulting solution was added drop wise diisobutyl aluminum hydride (37 mL, 1M solution). The resulting mixture was allowed to stir for 8 h under N_2. Upon completion of the reaction, MeOH and H_2O were added (10 mL) and allowed to stir for another 2 h. The resulting mixture was then filtered and the resulting phases were separated. The aqueous phase was extracted with 3 x 10 mL ethyl acetate. The resulting organic phases were then washed with water (1 x 20 mL) followed by a saturated solution of brine (1 x 20 mL). The resulting organic phase was then dried using Na_2SO_4 and filtered. The solvent was removed under reduced pressure in vacuo and the crude product was purified using flash chromatography on silica gel (n-hexane/EtOAc 6:1 as eluent) to give the desired products **8a** (87%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.08 (td, *J* = 7.9, 1.4 Hz, 1H), 6.84 – 6.72 (m, 1H), 6.70 – 6.57 (m, 2H), 6.17 (dt, *J* = 15.7, 5.3 Hz, 1H), 4.23 (d, *J* = 5.4 Hz, 2H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 130.2, 128.5, 127.2, 125.9, 123.2, 119.1, 116.4, 77.5, 77.2, 76.9, 63.2. HRMS (EI): Calcd for (2M + Na) $C_{18}H_{22}N_2O_2Na$ 321.1413, Found: 321.1399

2-(3-methoxyprop-1-en-1-yl)aniline, 8b



Substrate **8b** was obtained by treating **8a** (0.110g, 0.737mmols) with NaH (0.02g, 0.8mmol) in dry THF (10 mL). This solution was allowed to stir in an ice bath for 30 min. Then to the solution was added MeI (0.115g, 0.81mmol). The solution was allowed to stir for 1 h, and was monitored by TLC. Upon completion, 5 mL of water was added. The aqueous phase was separated and washed with ethyl acetate (1 x 20 mL). The organic phases were collected and washed with water (1 x 20 mL) followed by saturated solution of brine (1 x 20 mL). The organic phases were separated and dried using Na_2SO_4 and filtered. The solvent was removed under reduced pressure in vacuo and the crude product was purified using flash chromatography on silica gel (n-hexane/EtOAc, 10:1 as eluent) to give the desired product **8b** (60%) as a crème colored oil that slowly crystallized. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.14 – 7.03 (m, 1H), 6.76 (ddd, *J* = 7.6, 1.1, 0.6 Hz, 1H), 6.72 – 6.54 (m, 1H), 6.17 (dt, *J* = 15.8, 6.0 Hz, 1H), 4.10 (dd, *J* = 6.0, 1.5 Hz, 1H), 3.75 (s, 1H), 3.41 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 128.7, 128.1, 127.5, 127.5, 123.0, 118.9, 116.1, 77.5, 77.2, 76.9, 73.3, 58.0. HRMS(ESI) calculated for $C_{10}H_{13}NO$ 163..0997, found 163.1003.

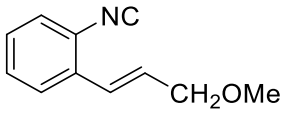
Synthesis of N-(2-(3-methoxyprop-1-en-1-yl)phenyl)formamide, 8c



Substrate **8c** was synthesized following the procedure described for **1c** using aniline **8b**. The crude residue was washed thoroughly with hexane (3 x 30 mL) and dried in vacuo to give (88%) of the title compound as a light orange liquid that slowly crystallized. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 – 8.33 (m, 11H), 7.85 (d, *J* = 8.0 Hz, 5H), 7.48 (dd, *J* = 7.5, 1.6 Hz, 4H), 7.39 (dd, *J* = 7.8, 1.1 Hz, 3H), 7.30 – 7.16 (m, 12H), 7.12 (t, *J* = 7.7 Hz, 7H), 6.81 – 6.66 (m, 7H), 6.30 – 6.11 (m, 7H), 4.08 (ddd, *J* = 4.8, 2.3, 1.0 Hz, 14H), 3.37 (t, *J* = 1.2 Hz, 21H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9, 159.8, 133.8, 133.5, 130.4, 130.0, 129.9,

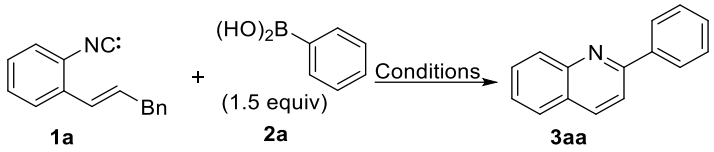
129.4, 128.7, 128.3, 127.4, 127.0, 126.6, 126.5, 125.7, 123.8, 122.3, 77.5, 76.9, 72.9, 72.9, 58.3, 58.2. HRMS(ESI) calculated for $C_{11}H_{13}NO_2Na$ 214.0844, found 214.0856.

Synthesis of 1-isocyano-2-(3-methoxyprop-1-en-1-yl)benzene, 8d



Substrate **8d** was synthesized following the procedure for **1a** using **8c**. The crude product was purified by flash chromatography (Hexanes:EtOAc, 10:1) to give (83%) of the title compound as a light brown oil. R_f = 0.44 (hexanes/EtOAc 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.45 – 7.33 (m, 2H), 6.94 (d, *J* = 15.9 Hz, 1H), 6.40 (dt, *J* = 15.9, 5.8 Hz, 1H), 4.25 – 4.03 (m, 2H), 3.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 133.3, 130.9, 129.5, 128.3, 127.3, 126.2, 77.5, 76.9, 72.9, 58.4, 29.8. 690cm^{-1}. HRMS(ESI) calculated for $C_{11}H_{11}NO$ 173.0841, found 173.0850.

4. Optimization Studies



1a **2a** **3aa**

Entry	Oxidant	$Mn(acac)_3$ (equiv)	Solvent	Temp, ◦C	Conv %[a]	Yield %[b]
1	$Mn(acac)_3$	(1)	C_7H_8	90	23	17
2	$Mn(acac)_3$	(2)	C_7H_8	90	67	64
3	$Mn(acac)_3$	(3)	C_7H_8	90	100	86
5	$Mn(acac)_3$	(3)	C_7H_8	Reflux	100	82
6	$Mn(acac)_3$	(3)	C_7H_8	rt	0	0
7	$Mn(acac)_3$	(3)	C_7H_8	50	64	59
8	$Mn(OAc)_3 \cdot 2H_2O$ (3)	(3)	C_7H_8	90	100	67
9	$Mn(OAc)_2$	(3)	C_7H_8	90	0	0
10	$Cu(OAc)_2$	(3)	C_7H_8	90	0	0
11	BPO	(1.2)	C_7H_8	90	0	0
12	TBHP	(2.5)	C_7H_8	90	0	0
13	$AgNO_3/Na_2S_2O_8$	0.2/5	DCM/H_2O	90	trace	0
14	$Mn(acac)_3$	(3)	MeCN	Reflux	100	79
15	$Mn(acac)_3$	(3)	C_6H_6	Reflux	100	84
16	$Mn(acac)_3$	(3)	DMF	90	trace	trace

[a] NMR yield based on **1a** using 1,2-dichloroethane as an internal standard. [b] Isolated yield based on **1a**.

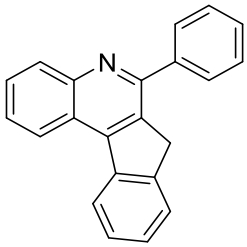
At the outset, we examined the reaction of isocyanide **1a** with phenylboronic acid(2a) in the presence of $Mn(OAc)_3 \cdot 2H_2O$ due to its known ability to generate carbon centered radical with organo boron reagents. The use of $Mn(OAc)_3 \cdot 2H_2O$ (3 equiv) gave quinoline **3aa** in 67% yield at 90 °C for 4 hours (entry 8). There was no other observed byproduct. The oxidant was then varied to $Mn(acac)_3$ (3 equiv) under similar reaction conditions gave quinoline **3aa** in 86% yield. It was then decided to screen conditions using $Mn(acac)_3$ as our preferred oxidant. The use of more than two equivalents of the manganese salt was required for the complete conversion of **1a** (entry 1, 2). Solvent screening showed a preference for non-polar aromatics, along with this reflux was not necessary with only mild heating to observe desired transformation.

5. General procedure for the Mn(III) Mediated radical cyclization with boronic acids

Preparation of the corresponding quinolines followed a similar method reported by Chatani, Tobisu and co-workers[5]. To an oven-dried 10 mL single neck flask, isocyanide (0.1 mmol), phenylboronic acid(0.15mmol), Mn(acac)3 (0.3 mmol) and toluene (3.0ml) were added sequentially under an inert atmosphere of nitrogen. The mixture was stirred at 90 °C for 4 h under a nitrogen atmosphere. The reaction mixture was then cooled to room temperature and purified by column chromatography on silica gel to afford the desired product.

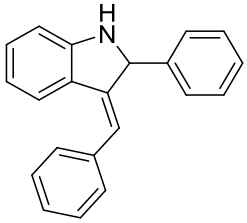
6. Spectroscopic data for products

6-phenyl-7H-indeno[2,1-c]quinoline, Q2



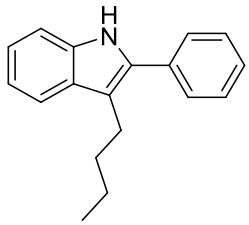
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.76 (d, *J* = 8.3 Hz, 1H), 8.49 (d, *J* = 7.8 Hz, 1H), 8.32 (d, *J* = 8.3 Hz, 1H), 7.94 (d, *J* = 7.3 Hz, 1H), 7.78 (t, *J* = 7.5 Hz, 1H), 7.69 (dd, *J* = 10.9, 7.6 Hz, 1H), 7.52 (ddd, *J* = 17.6, 14.4, 7.5 Hz, 3H), 4.18 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.5, 148.5, 145.7, 145.2, 141.0, 140.6, 134.5, 130.9, 129.0, 128.9, 128.9, 128.8, 128.4, 127.5, 126.8, 125.3, 124.5, 124.1, 123.6, 37.9. HRMS (EI): Calcd for $C_{22}H_{16}N$ 294.1282, Found: 294.1298

3-benzylidene-2-phenylindoline, Q3



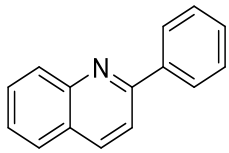
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.36 (d, *J* = 7.4 Hz, 3H), 7.28 (d, *J* = 8.1 Hz, 1H), 7.18 (dd, *J* = 6.2, 2.5 Hz, 2H), 7.08 (t, *J* = 6.3 Hz, 6H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.62 (t, *J* = 7.6 Hz, 1H), 5.32 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.6, 135.9, 133.4, 129.4, 129.2, 128.5, 128.3, 128.0, 127.8, 125.7, 122.0, 122.0, 121.1, 119.4, 114.9, 110.4, 50.0. HRMS (EI): Calcd for $C_{22}H_{16}N$ 294.1282, Found: 294.1298

3-butyl-2-phenyl-1H-indole, Q4



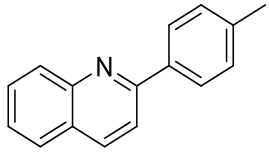
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.56 (dd, *J* = 8.1, 1.0 Hz, 2H), 7.47 (t, *J* = 7.7 Hz, 3H), 7.39 – 7.36 (m, 2H), 7.22 – 7.18 (m, 1H), 7.16 – 7.12 (m, 1H), 2.94 – 2.83 (m, 2H), 1.72 (dt, *J* = 15.4, 7.7 Hz, 2H), 1.48 – 1.38 (m, 3H), 0.93 (t, *J* = 7.4 Hz, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.9, 136.1, 134.2, 130.5, 129.5, 129.5, 129.0, 128.1, 127.6, 122.3, 119.6, 119.5, 114.3, 110.9, 33.4, 29.9, 24.5, 23.1. HRMS (EI): Calcd for $C_{18}H_{18}N$ 248.1439, Found: 248.1452

2-Phenylquinoline(Q1)



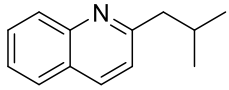
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.25 – 8.15 (m, 4H), 7.88 (d, *J* = 8.5 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.74 (t, *J* = 7.6 Hz, 1H), 7.59 – 7.51 (m, 3H), 7.48 (t, *J* = 7.3 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.5, 148.4, 139.8, 136.9, 129.9, 129.8, 129.5, 129.0, 127.7, 127.6, 127.3, 126.4, 119.2. Spectral data match those previously reported[6].

2-(4-Methylphenyl)quinoline(Q5)



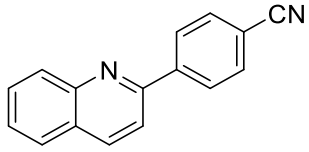
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.36 (s, 3H), 7.25, (d, J = 8.3 Hz, 2H), 7.35-7.45, (m, 1H), 7.60-7.75, (m, 3H), 8.00-8.05 (m, 3H), 8.15 (d, J = 4.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 21.1, 118.5, 125.8, 126.8, 127.2, 127.3, 128.0, 129.3, 129.4, 136.4, 136.6, 139.1, 148.0, 156.9. Spectral data match those previously reported[6].

2-isobutylquinoline(Q10)



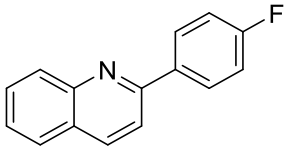
^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 8.06 (d, J = 8.4 Hz, 1H), 8.01 (d, J = 8.4 Hz, 1H), 7.74 (dd, J = 8.2, 0.8 Hz, 1H), 7.44-7.40 (m, 1H), 7.67-7.63 (m, 1H), 7.20 (d, J = 8.4 Hz, 1H), 2.81 (d, J = 7.4 Hz, 2H), 2.20 (q, J = 6.8 Hz, 1H), 0.95 (s, 6H). ^{13}C NMR ($CDCl_3$, 101 MHz) δ: 162.2, 148.0, 135.9, 129.2, 128.9, 127.5, 126.7, 125.6, 122.0, 48.3, 29.4, 22.6. Spectral data match those previously reported[7].

4-(quinolin-2-yl)benzonitrile(Q7)



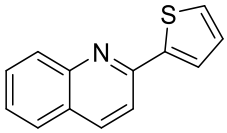
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 – 8.24 (m, 2H), 8.21 – 8.12 (m, 1H), 7.91 – 7.84 (m, 1H), 7.82 – 7.73 (m, 3H), 7.70 – 7.66 (m, 1H), 7.59 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 101 MHz) δ: 112.7, 118.5, 118.8, 127.1, 127.5, 128.0, 132.5, 137.2, 143.6, 148.2, 154.8. Spectral data match those previously reported[8].

2-(4-fluorophenyl)quinoline(Q6)



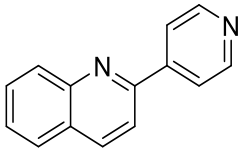
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.7 Hz, 1H), 8.20 – 8.14 (m, 1H), 7.83 (d, *J* = 8.6 Hz, 1H), 7.74 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.54 (ddd, *J* = 8.1, 6.9, 1.1 Hz, 1H), 7.22 (dd, *J* = 9.7, 7.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 163.8, 156.2, 148.2, 136.8, 135.8, 129.7, 129.4, 129.3, 127.4, 127.1, 126.3, 118.6, 115.7. Spectral data match those previously reported[7].

2-(2-Thienyl)quinoline(Q9)



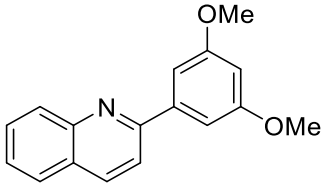
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11-7.18 (m, 1H), 7.42-7.47 (m, 2H), 7.61-7.74 (m, 4H), 8.05 (d, J = 8.1 Hz, 1H), 8.07 (d, J = 7.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 117.1, 125.7, 125.9, 127.0, 127.4, 128.0, 128.5, 129.0, 129.7, 136.5, 145.2, 147.9, 152.2. Spectral data match those previously reported[9].

2-(pyridin-4-yl)quinoline(Q13)



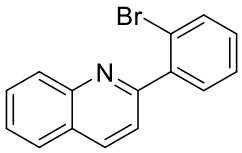
^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.80 (d, J = 5.7 Hz, 2H), 8.31 (d, J = 8.6 Hz, 1H), 8.21 (d, J = 8.5 Hz, 1H), 8.09 (d, J = 6.0 Hz, 2H), 7.93 (d, J = 8.6 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.76-7.80 (m, 1H), 7.61 (t, J = 7.5 Hz,1H). ^{13}C NMR ($CDCl_3$, 101 MHz) δ: 118.2, 121.4, 127.0, 127.4, 127.6, 129.8, 129.9, 137.0, 146.3, 148.1, 150.3, 154.1. Spectral data match those previously reported[7].

2-(3,5-dimethoxyphenyl)quinolone(Q8)



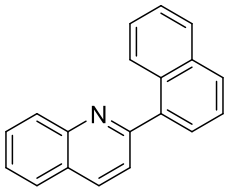
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.6 Hz, 1H), 8.18 (d, *J* = 8.5 Hz, 1H), 7.87 – 7.81 (m, 2H), 7.76 – 7.71 (m, 1H), 7.54 (dd, *J* = 11.0, 3.9 Hz, 1H), 7.33 (d, *J* = 2.2 Hz, 2H), 6.59 (t, *J* = 2.2 Hz, 1H), 3.91 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.3, 157.2, 148.3, 142.0, 136.9, 129.9, 129.8, 127.6, 127.5, 126.5, 119.3, 105.8, 101.8, 55.7. HRMS(ESI) calculated for $C_{17}H_{15}NO_2Na$ [M+Na]+m/z 288.0093, found 288.0103

2-(2-bromophenyl)quinoline(Q12)



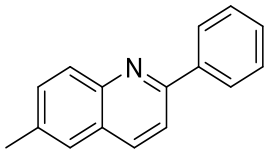
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 16.3, 8.4 Hz, 2H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.76 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H), 7.71 (dd, *J* = 8.3, 1.8 Hz, 2H), 7.64 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.62 – 7.56 (m, 1H), 7.46 (td, *J* = 7.4, 1.0 Hz, 1H), 7.31 (td, *J* = 7.7, 1.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 148.1, 141.8, 135.8, 133.4, 131.7, 130.1, 129.9, 129.8, 127.9, 127.7, 127.3, 127.2, 127.0, 122.9, 122.0, 120.0. Spectral data match those previously reported[9].

2-(naphthalen-1-yl)quinoline(Q11)



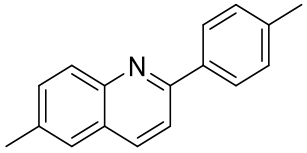
^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.47 (t, J = 7.6 Hz, 1H), 7.52 (t, J = 6.9 Hz, 1H), 7.60 (t, J = 7.6 Hz, 2H), 7.72 (t, J =6.8 Hz, 2H), 7.78 (t, J = 7.1 Hz, 1H), 7.91-7.96 (m, 3H), 8.14 (d, J = 8.4 Hz, 1H) , 8.23 (d, J = 8.3 Hz, 1H), 8.30 (d, J = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ: 123.2, 125.3, 125.9, 126.5, 127.0, 127.5, 127.7, 128.4, 129.1, 129.7, 131.3. Spectral data match those previously reported[6].

6-methyl-2-phenylquinoline, (Q17)



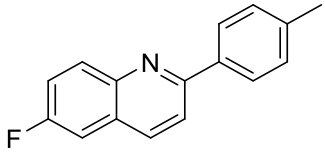
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (dd, *J* = 7.9, 4.1 Hz, 1H), 8.06 (d, *J* = 8.6 Hz, 1H), 7.84 (d, *J* = 8.5 Hz, 1H), 7.59 (s, 1H), 7.56 (d, *J* = 8.6 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.46 (d, *J* = 7.0 Hz, 1H), 7.42 (d, *J* = 3.7 Hz, 1H), 2.55 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.3, 132.1, 129.6, 129.3, 129.2, 129.0, 128.0, 128.0, 127.6, 127.4, 126.5, 125.7, 119.2, 21.8.

6-methyl-2-(p-tolyl)quinoline, (Q18)



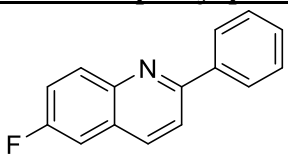
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.6 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 3H), 7.82 (d, *J* = 8.6 Hz, 1H), 7.57 (s, 1H), 7.55 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 2H), 2.54 (s, 3H), 2.43 (s, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.7, 147.0, 139.3, 137.1, 136.1, 136.1, 132.0, 129.7, 129.5, 127.5, 127.3, 126.5, 119.0, 21.8, 21.7.

6-fluoro-2-(p-tolyl)quinoline, (Q15)



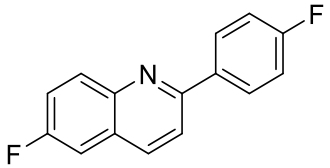
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 (dt, *J* = 4.9, 2.8 Hz, 1H), 8.05 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 8.7 Hz, 1H), 7.49 (td, *J* = 8.8, 2.8 Hz, 1H), 7.43 (dd, *J* = 8.8, 2.8 Hz, 1H), 7.34 (dd, *J* = 7.9, 0.5 Hz, 1H), 2.44 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.5, 139.7, 136.7, 136.2, 132.3, 132.2, 129.8, 129.8, 127.8, 127.5, 120.0, 119.8, 119.7, 110.7, 110.5, 21.5.

6-fluoro-2-phenylquinoline, (Q16)



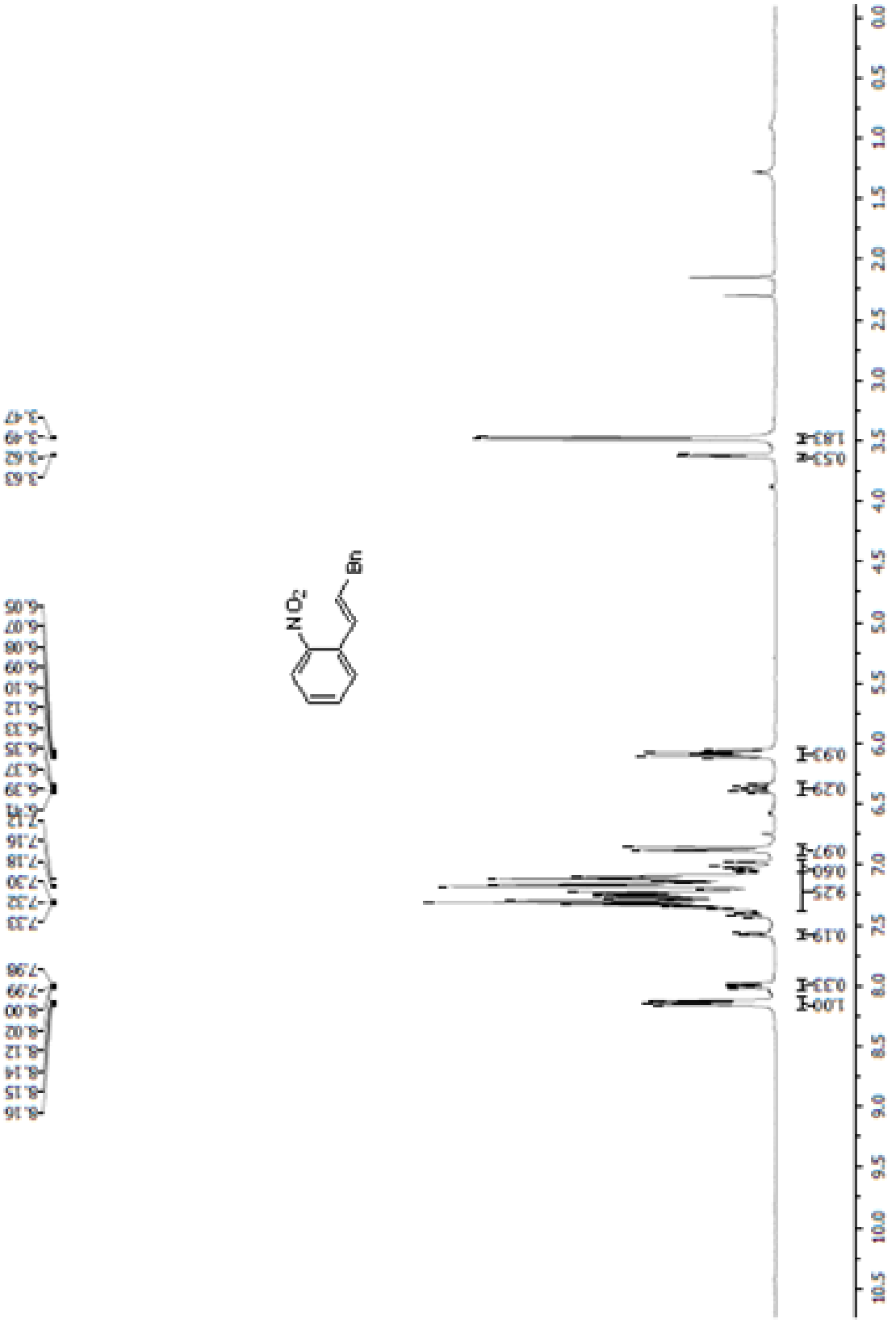
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 – 8.11 (m, 1H), 7.90 (d, *J* = 8.7 Hz, 1H), 7.50 (dddd, *J* = 21.6, 19.9, 9.1, 5.1 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.3, 156.9, 145.5, 139.5, 136.3, 132.4, 132.3, 129.6, 129.1, 127.9, 127.6, 120.1, 119.9, 110.7, 110.6.

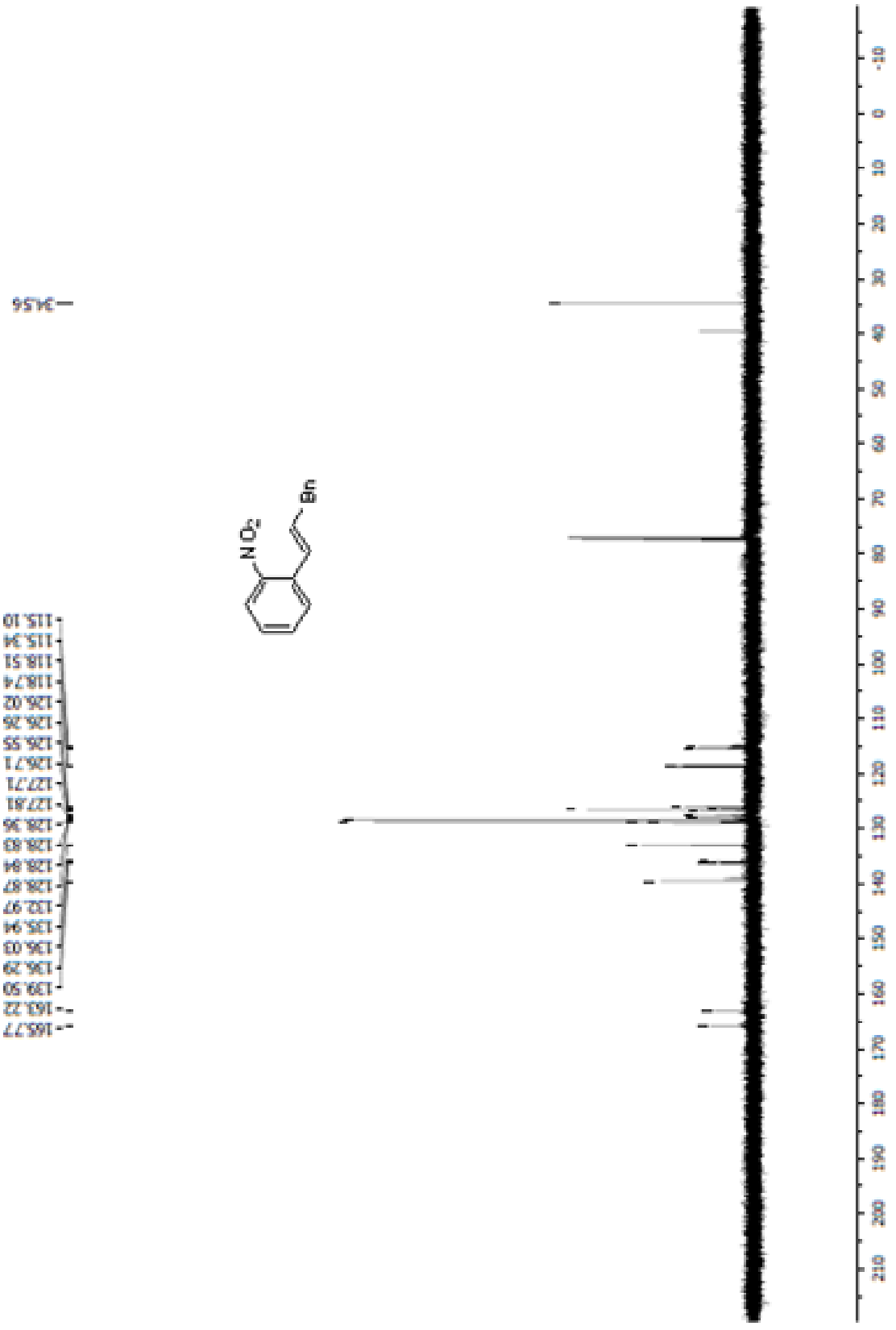
6-fluoro-2-(4-fluorophenyl)quinoline, (Q14)



^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 (ddd, *J* = 9.5, 7.6, 5.4 Hz, 3H), 7.85 (d, *J* = 8.6 Hz, 1H), 7.53 – 7.48 (m, 1H), 7.44 (dd, *J* = 8.7, 2.8 Hz, 1H), 7.25 – 7.18 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.8, 163.2, 161.4, 159.7, 155.8, 145.5, 136.4, 136.4, 135.7, 132.3, 132.2, 129.5, 129.4, 127.8, 127.7, 120.2, 120.1, 119.5, 116.1, 115.9, 110.7, 110.6.

7. Copies of ^{1}H and ^{13}C NMR spectra

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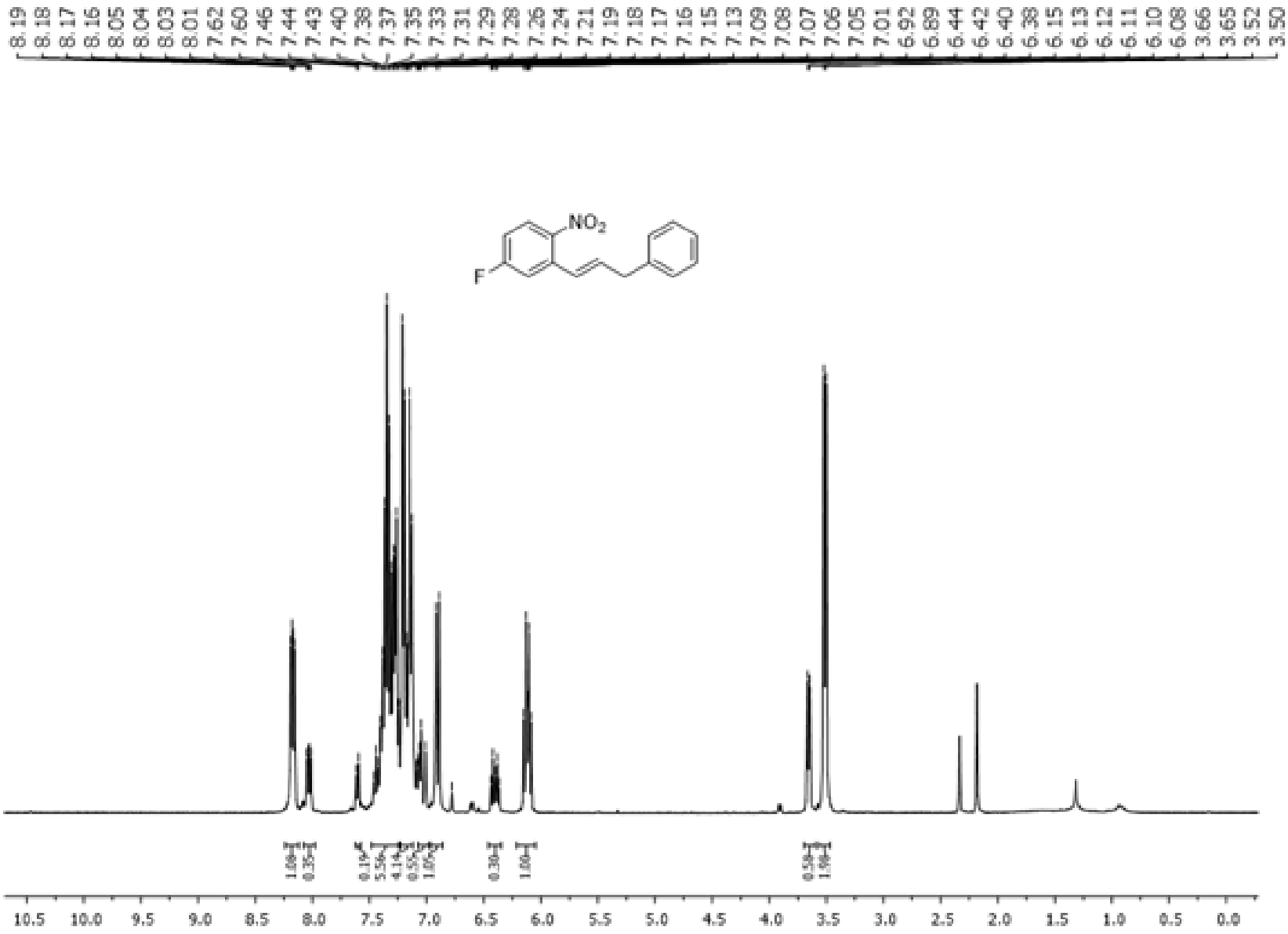
165.77
Bn
NO2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7.19
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7.17
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7.15
7.13
7.09
7.08
7.07
7.06
7.05
7.01
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6.40
6.38
6.15
6.13
6.12
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6.10
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3.52
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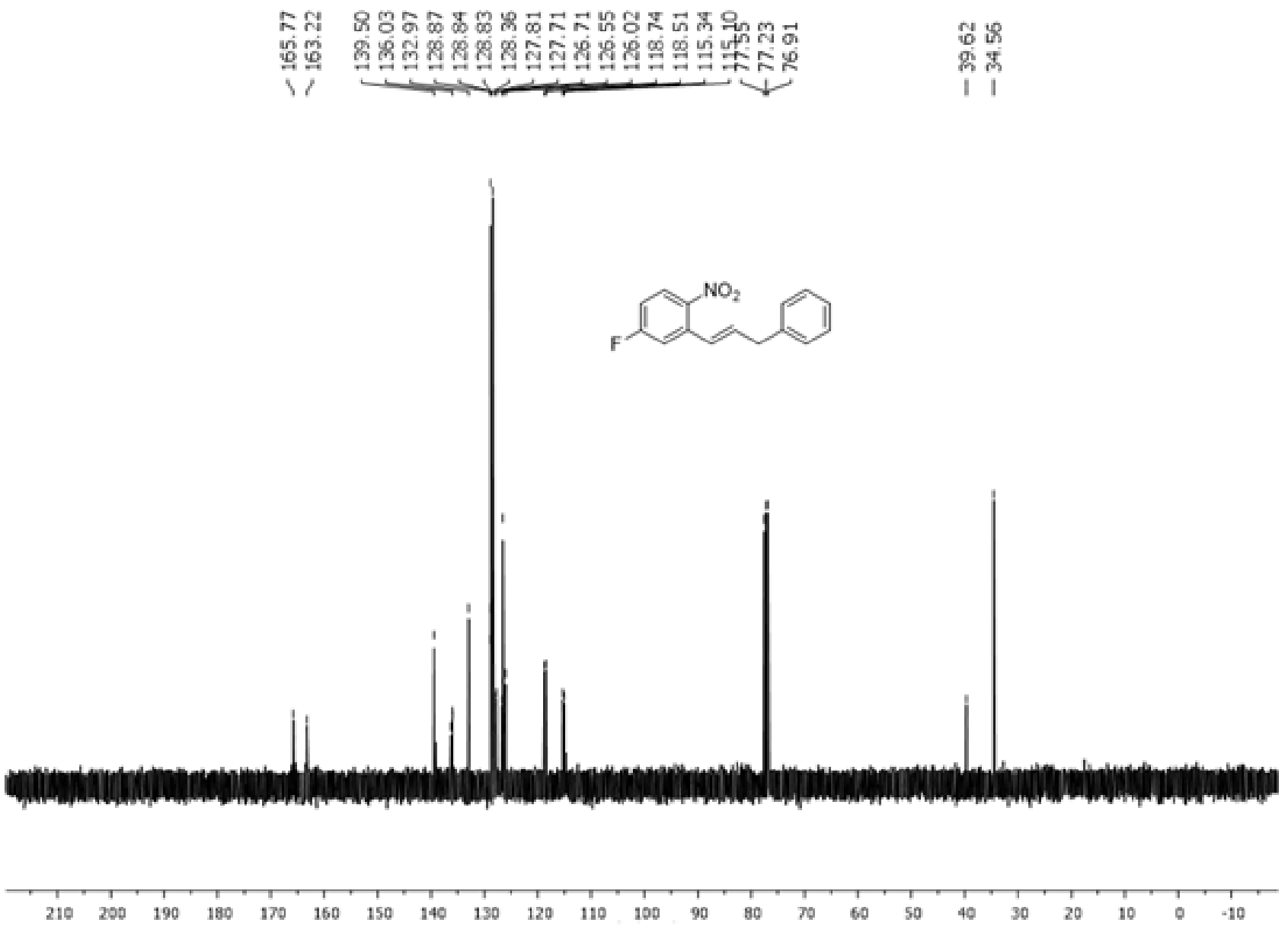
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76.91
39.62
34.56
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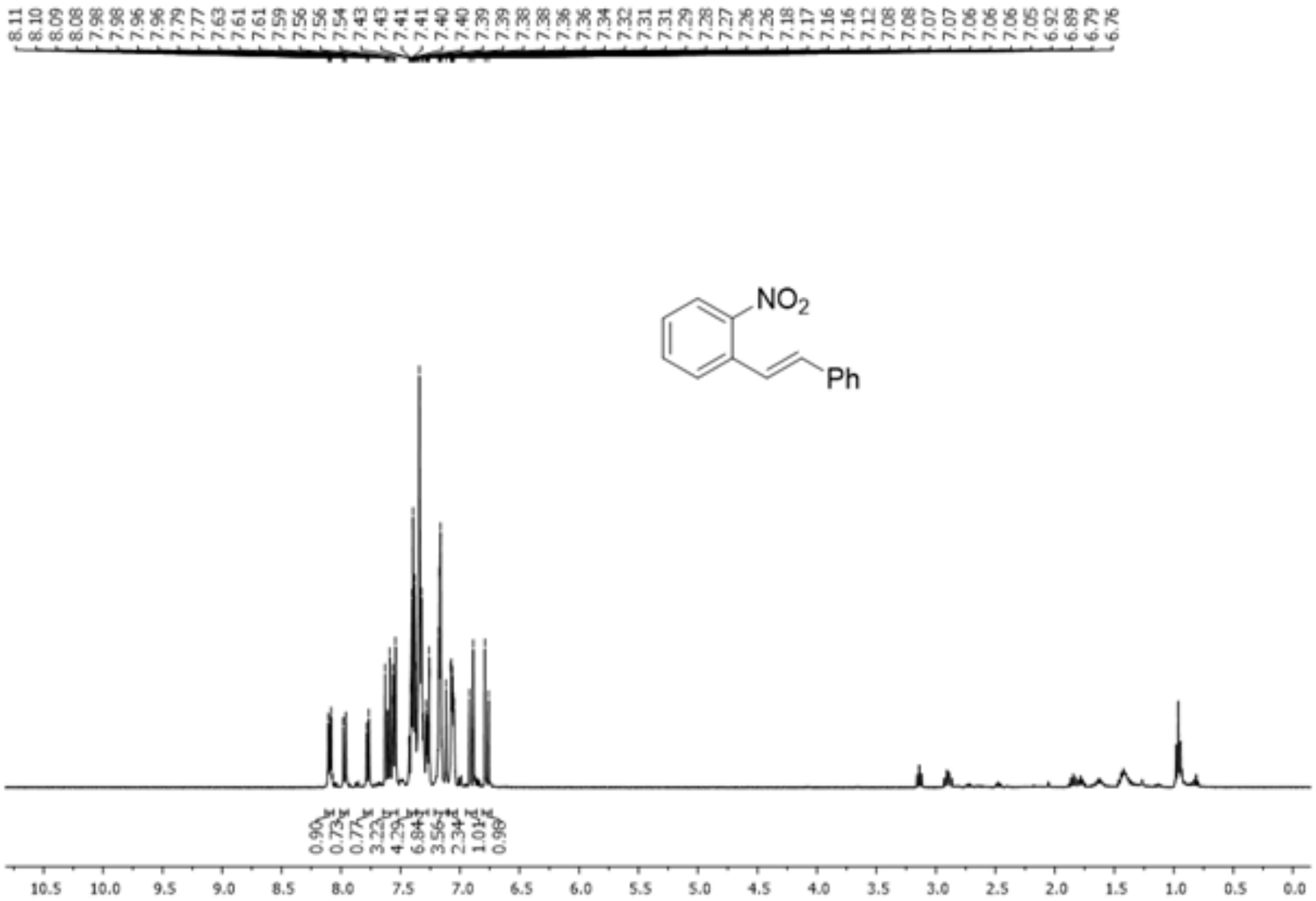
-10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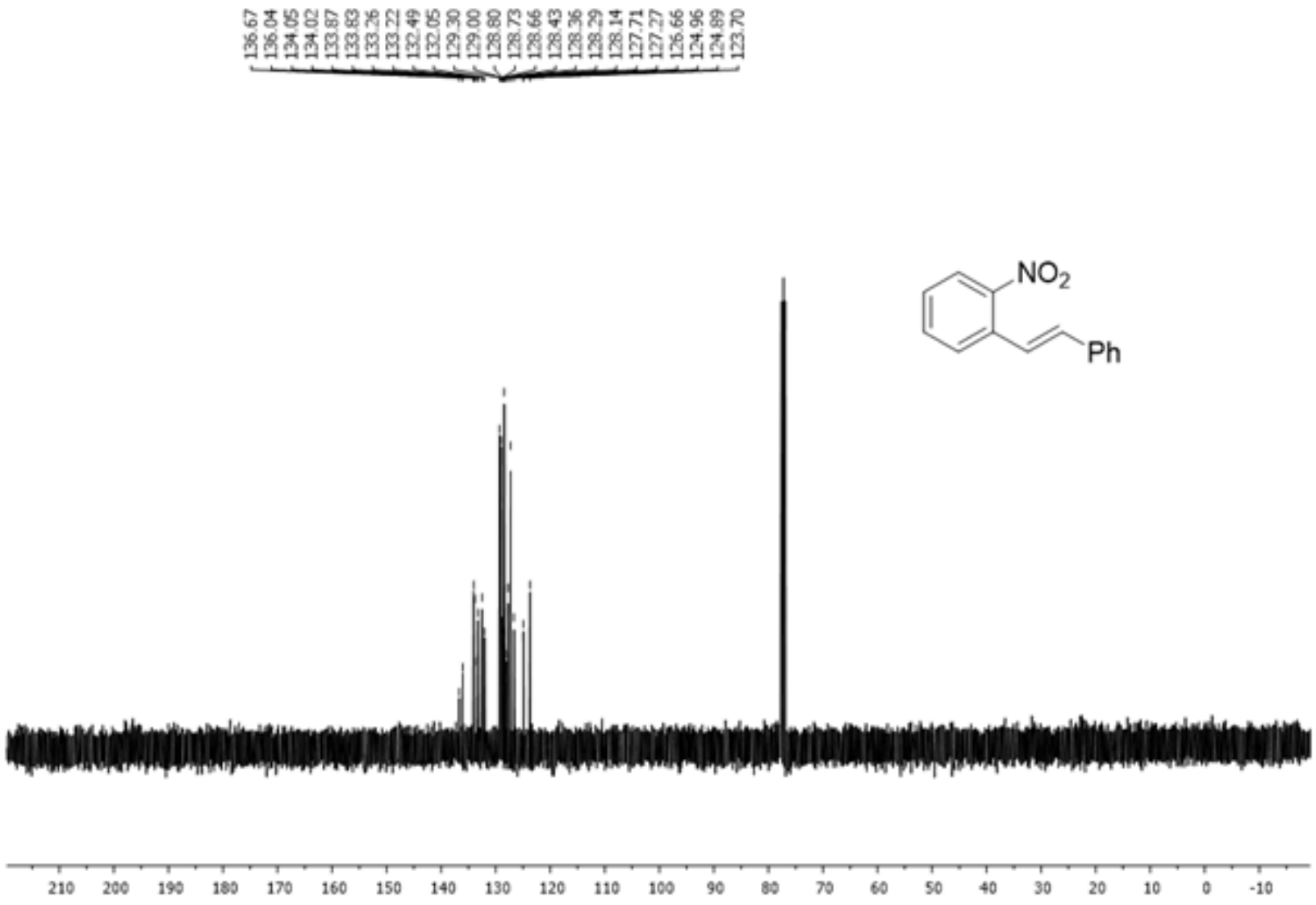
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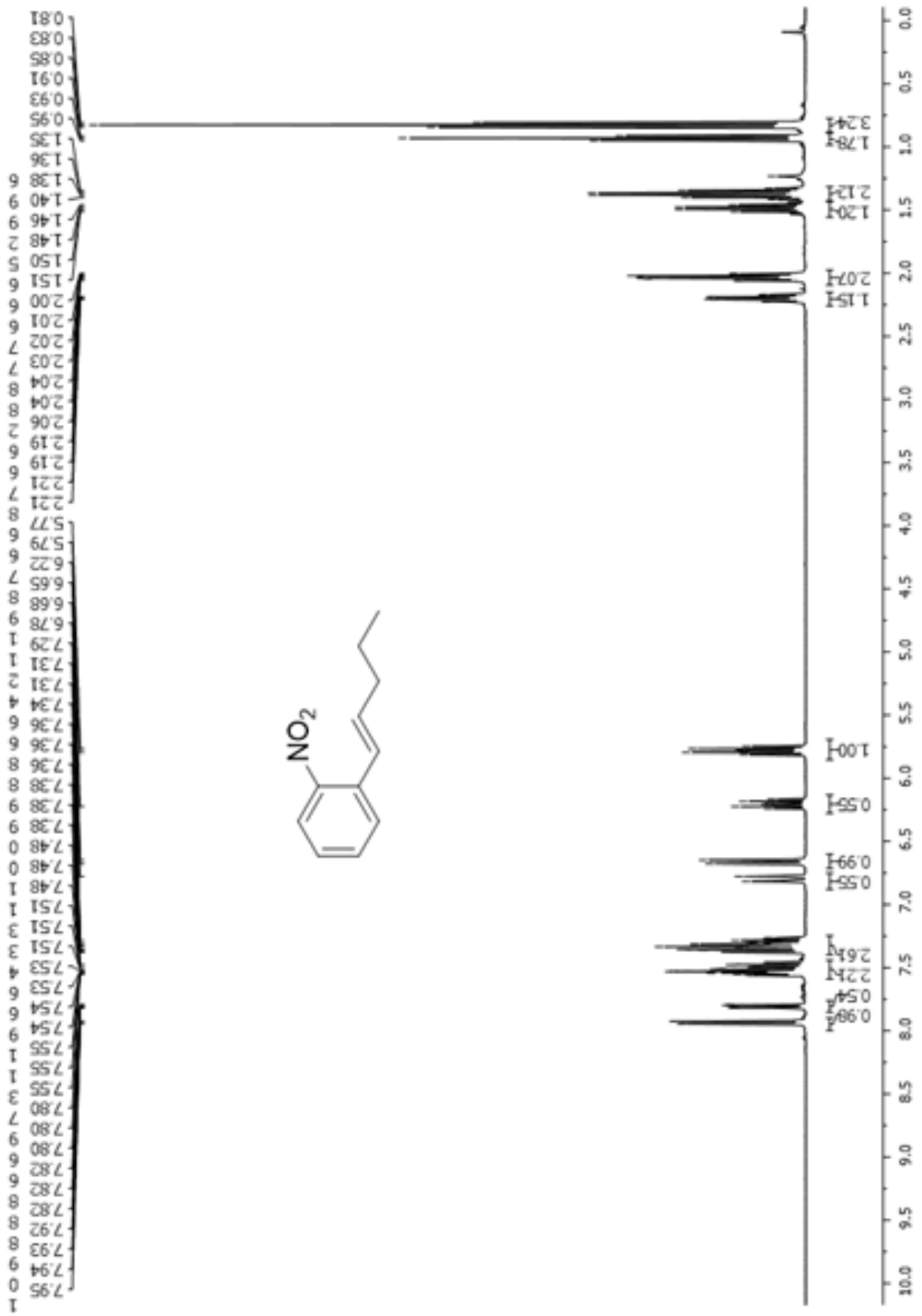
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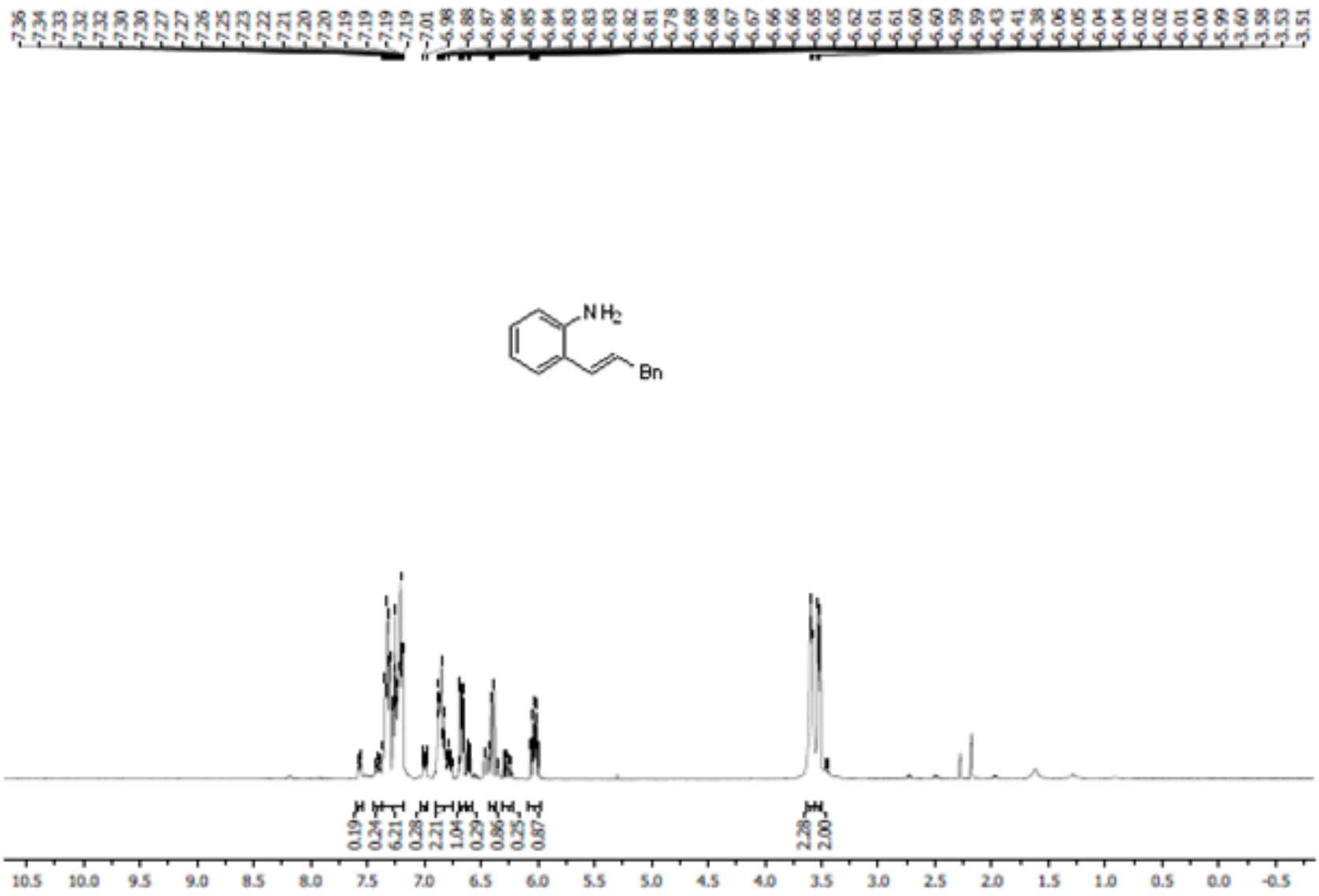
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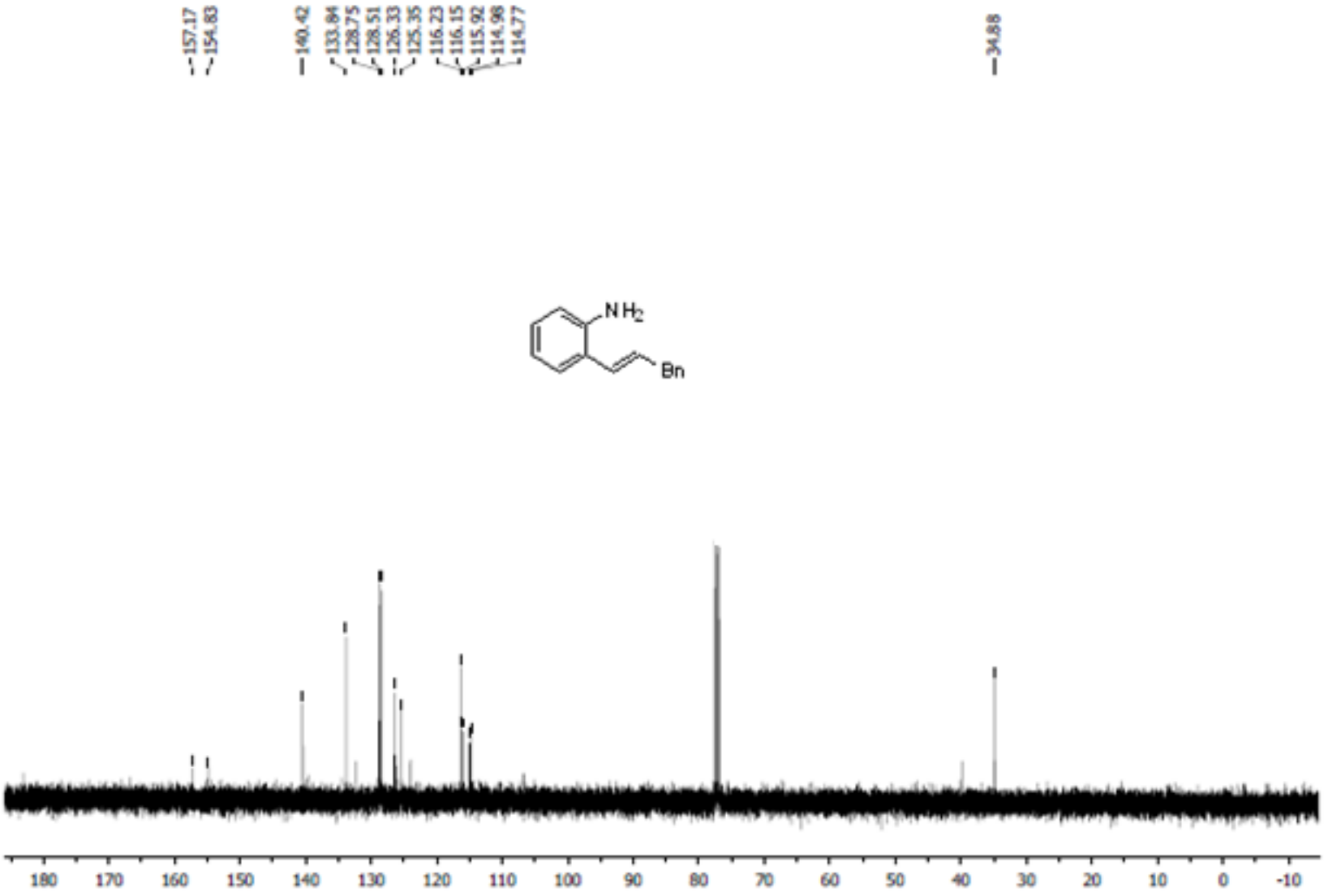
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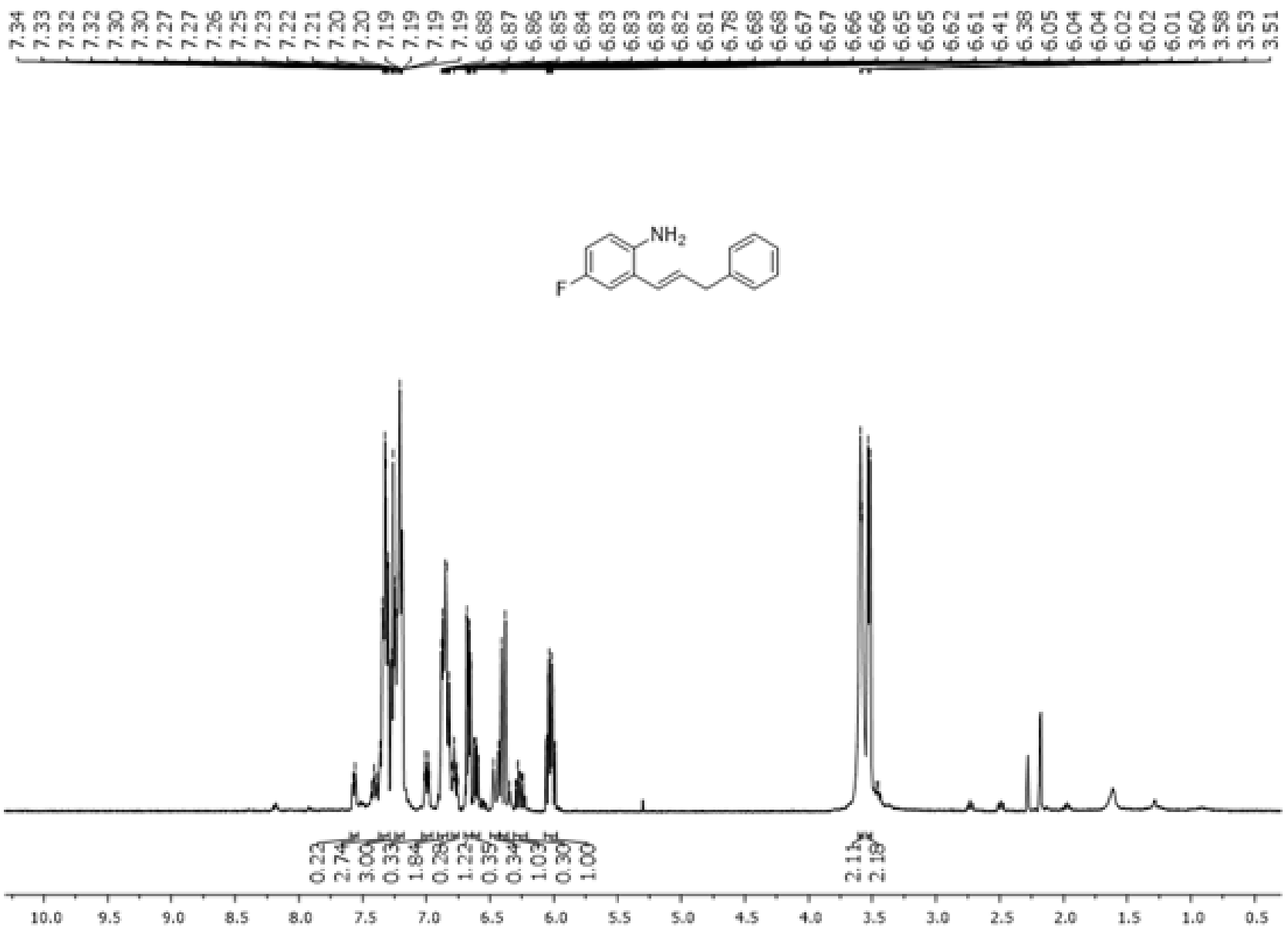
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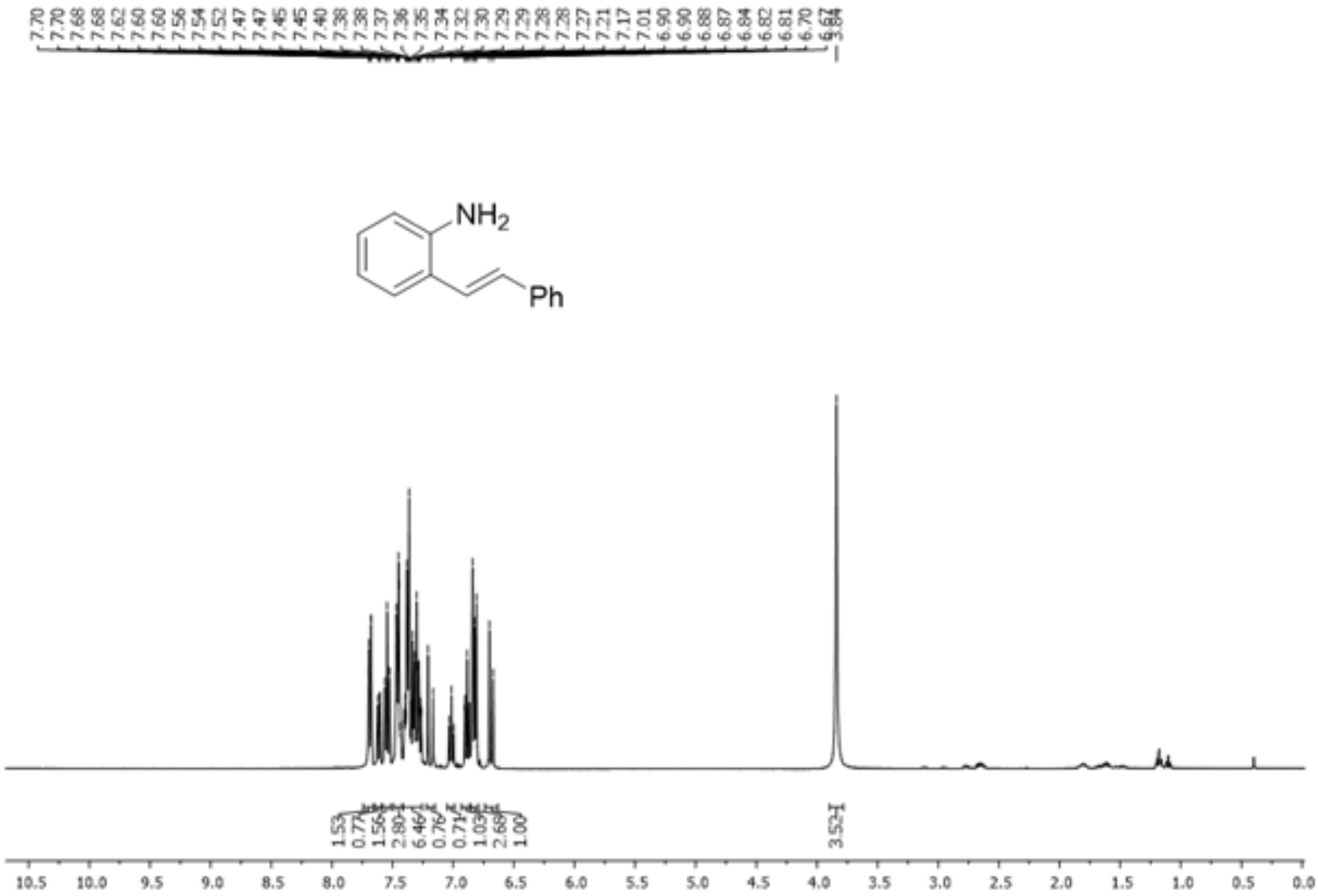
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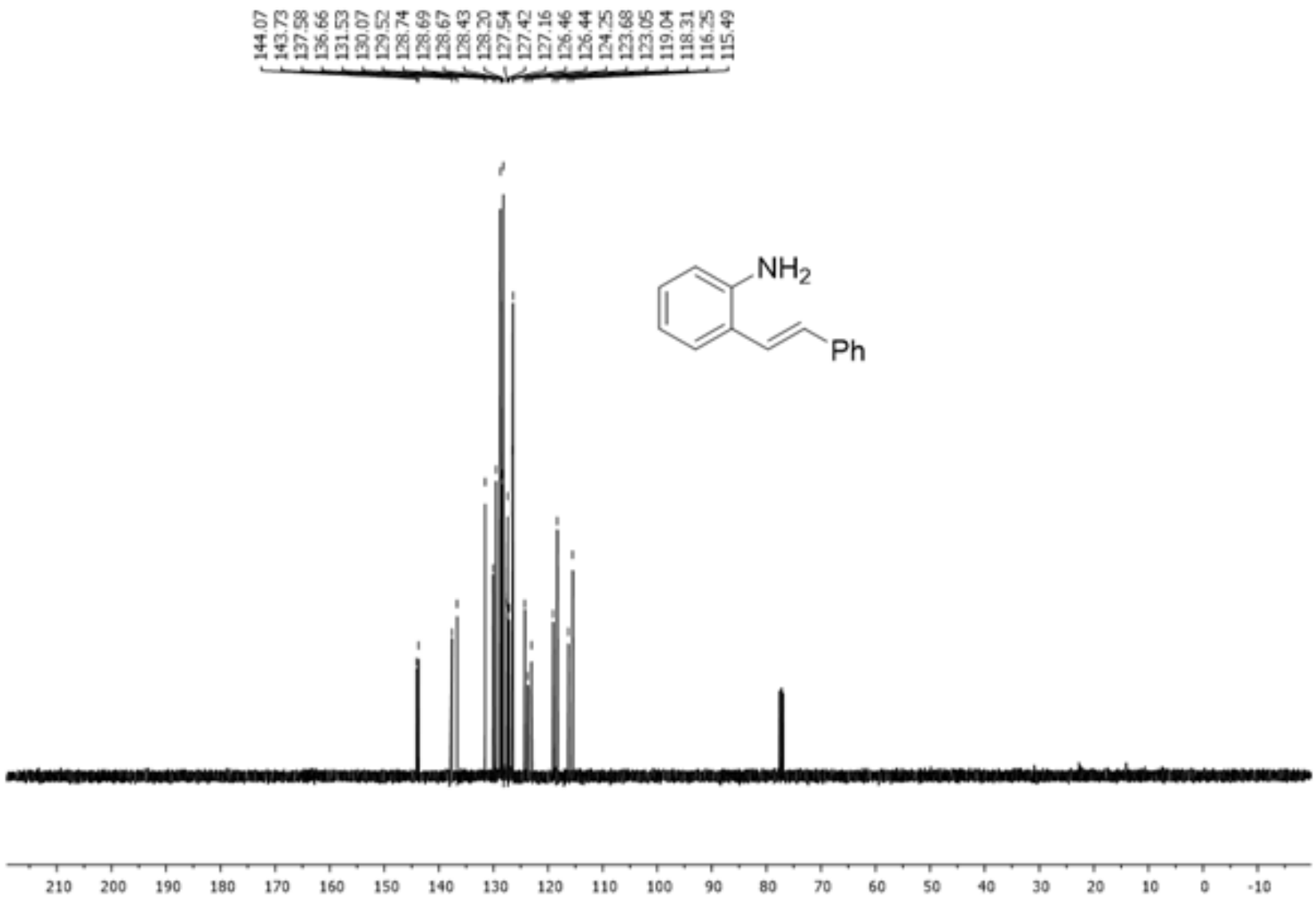
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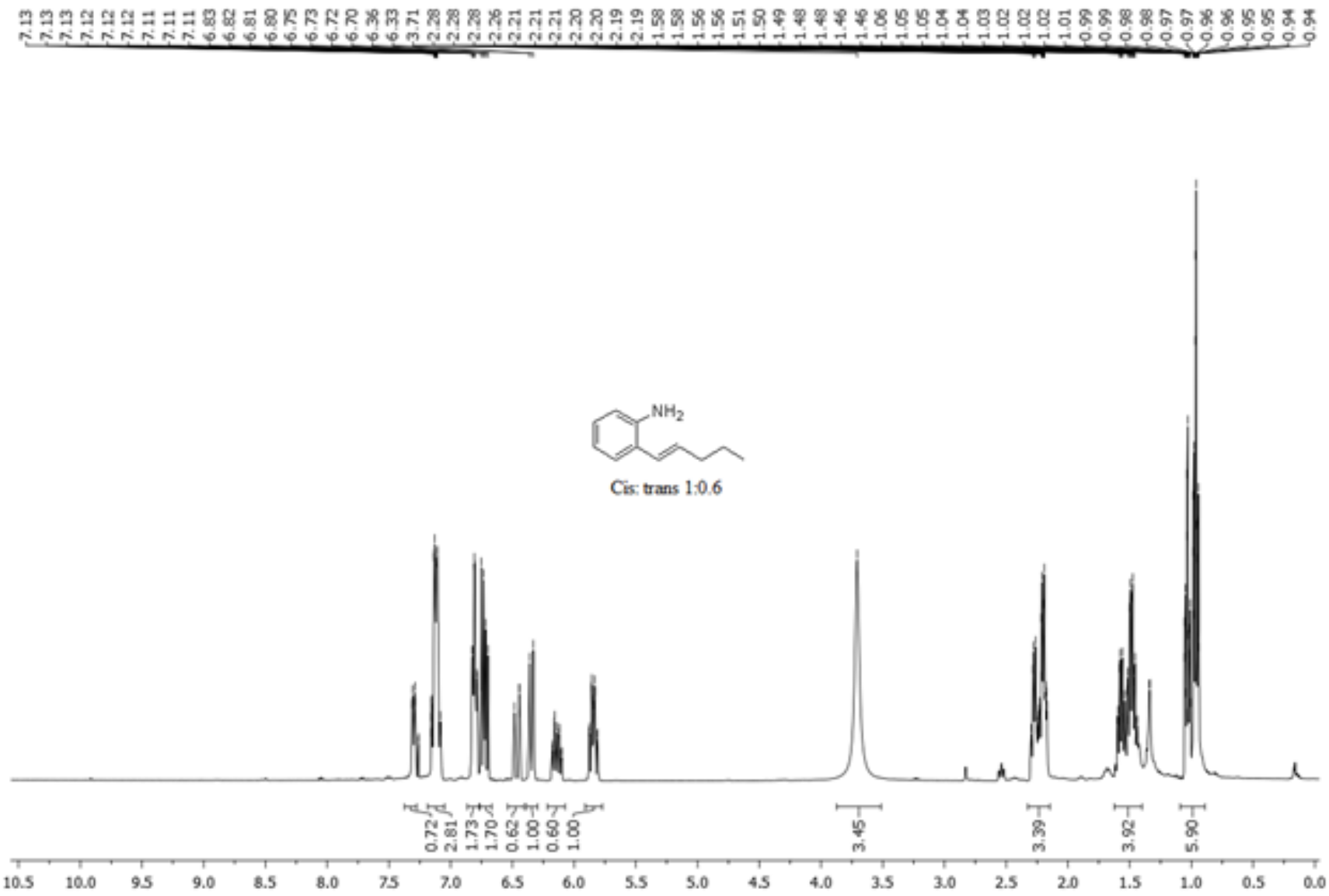
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NH2
Cis: trans 1:0.6
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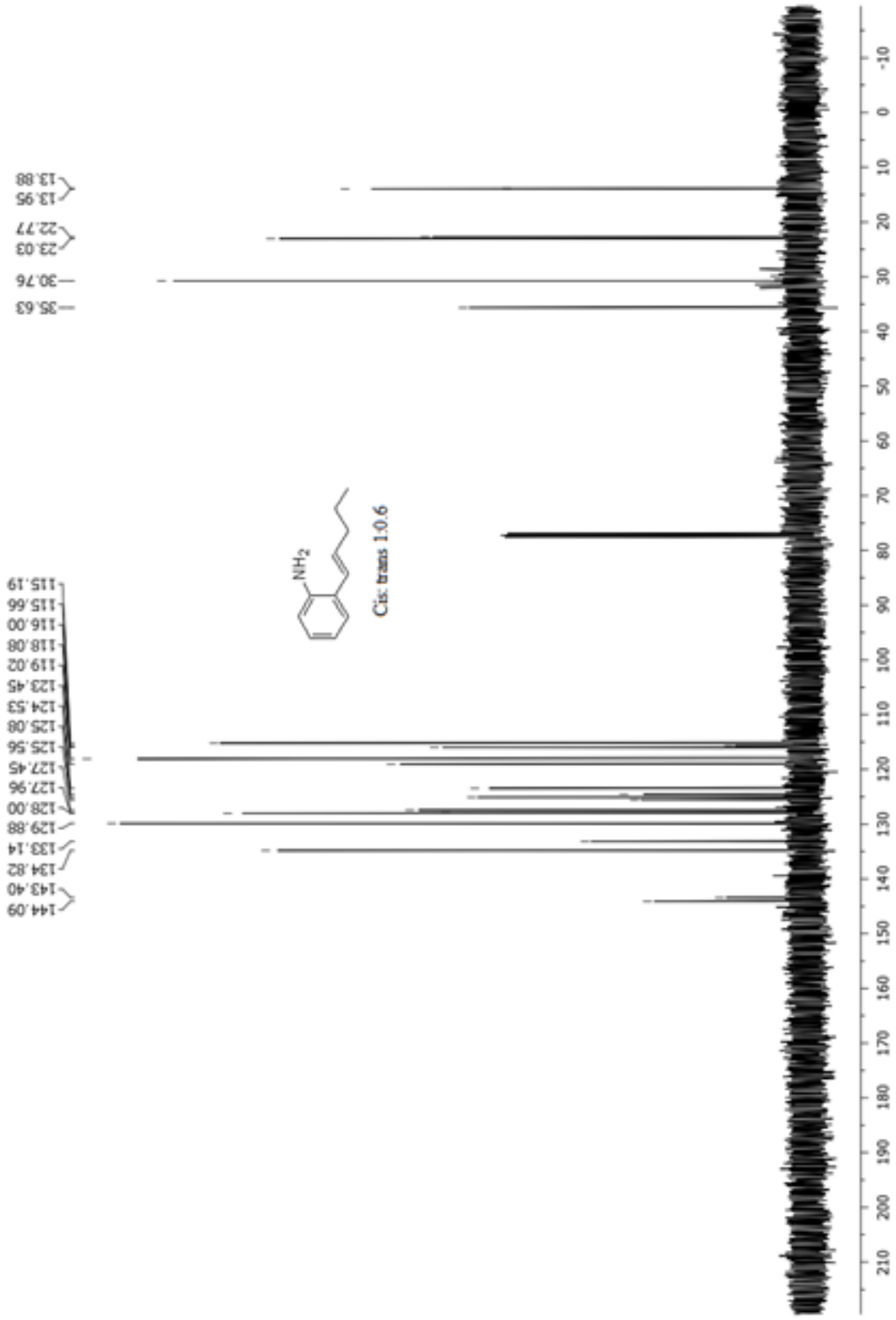
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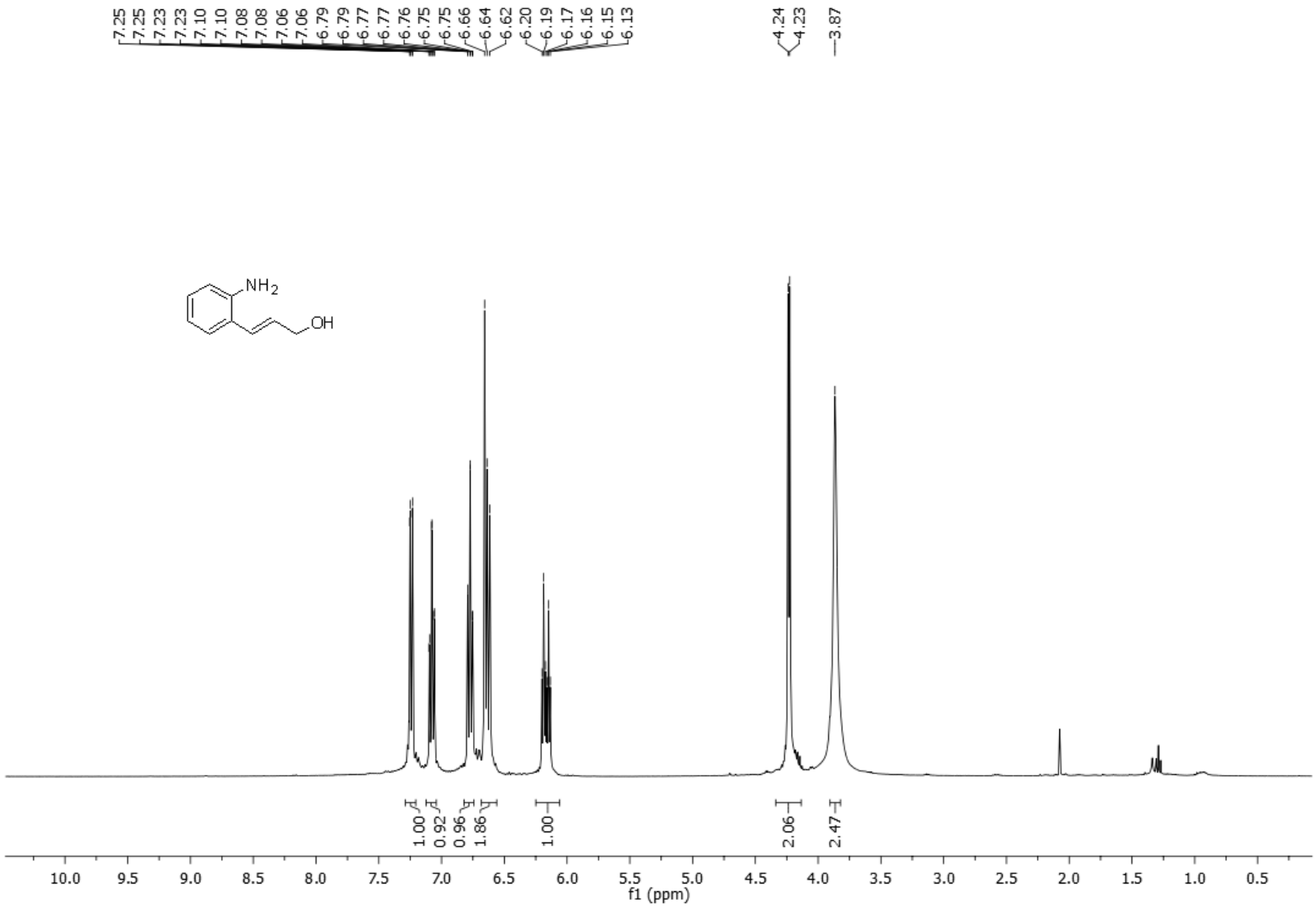
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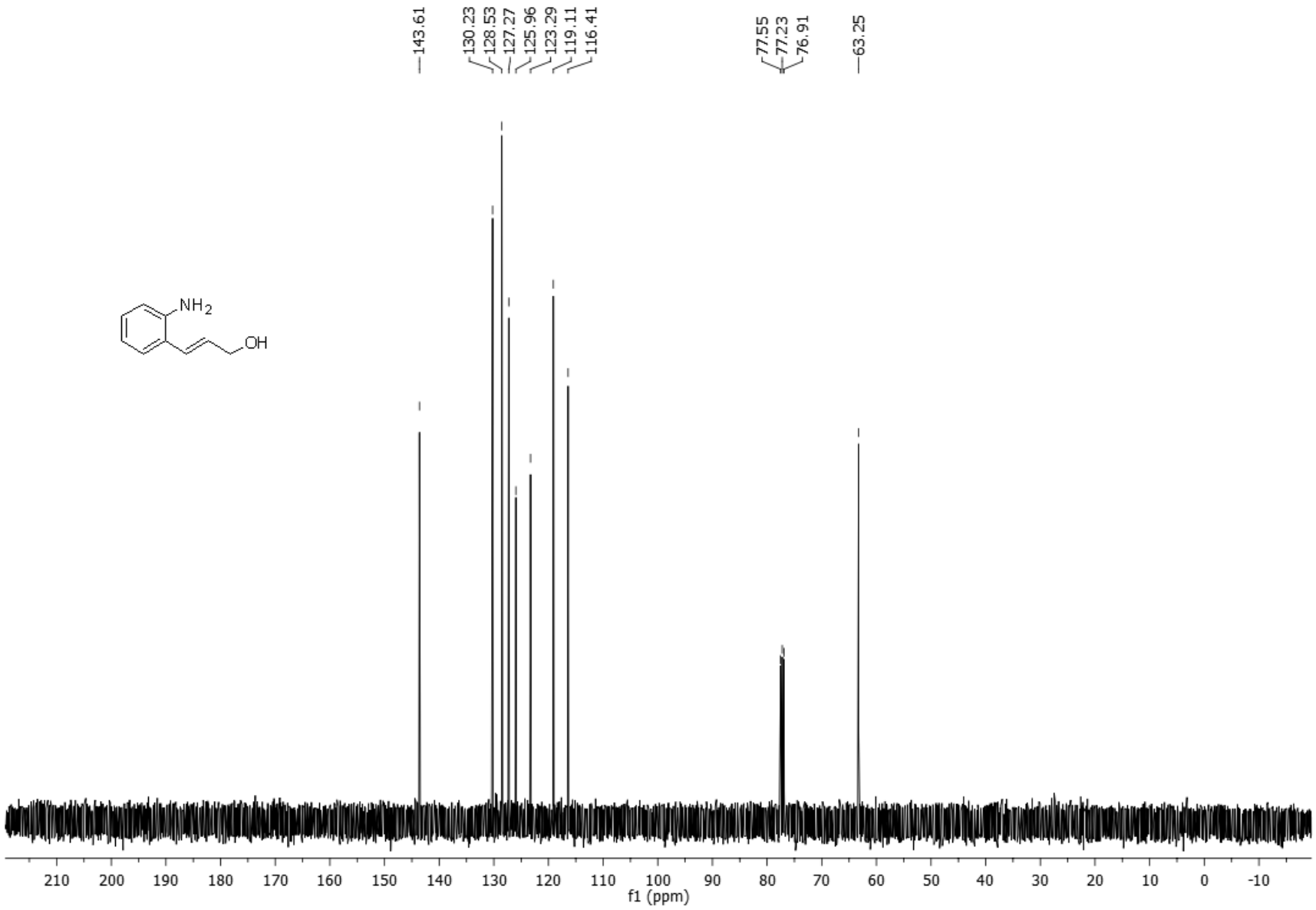
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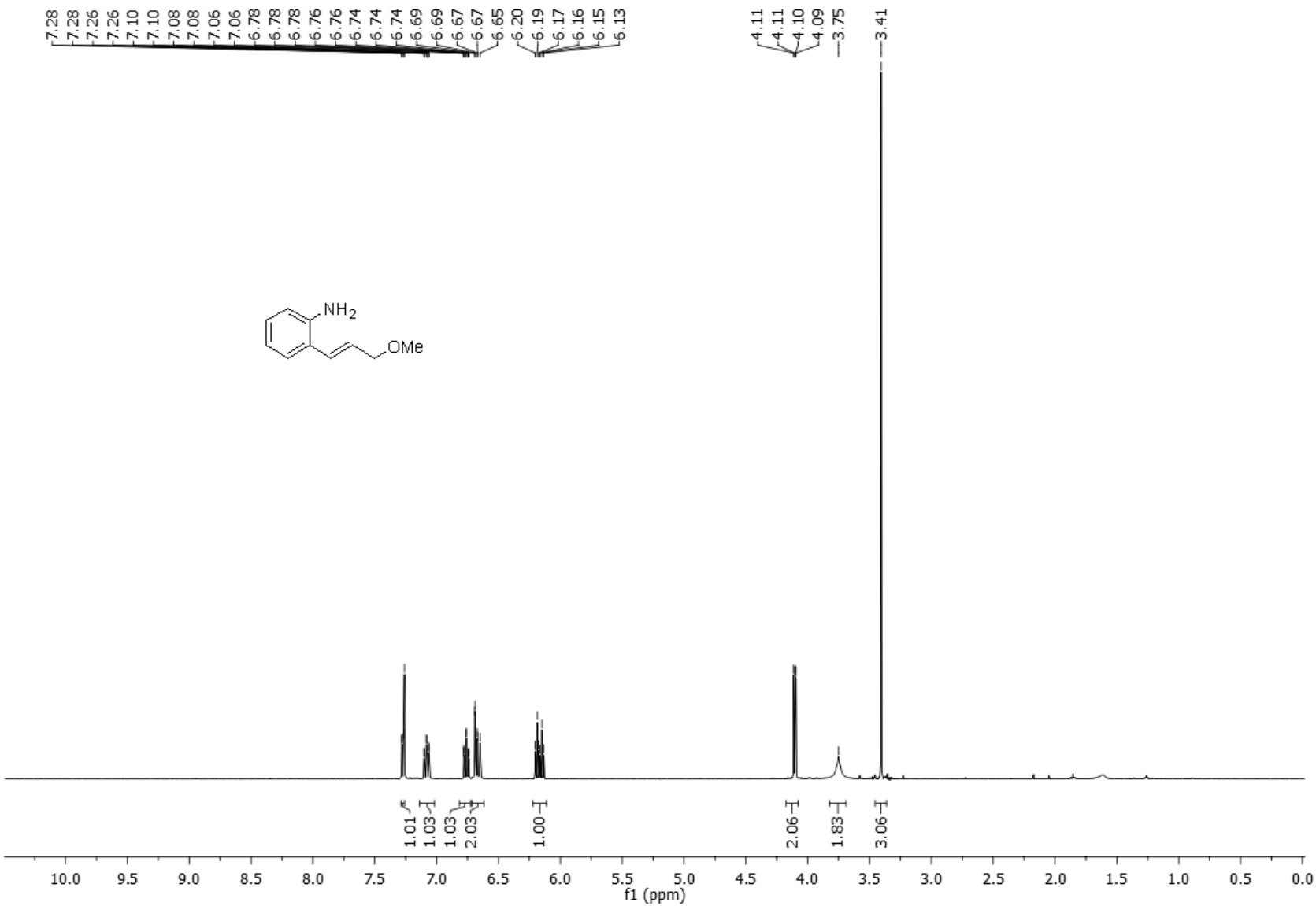
f1 (ppm)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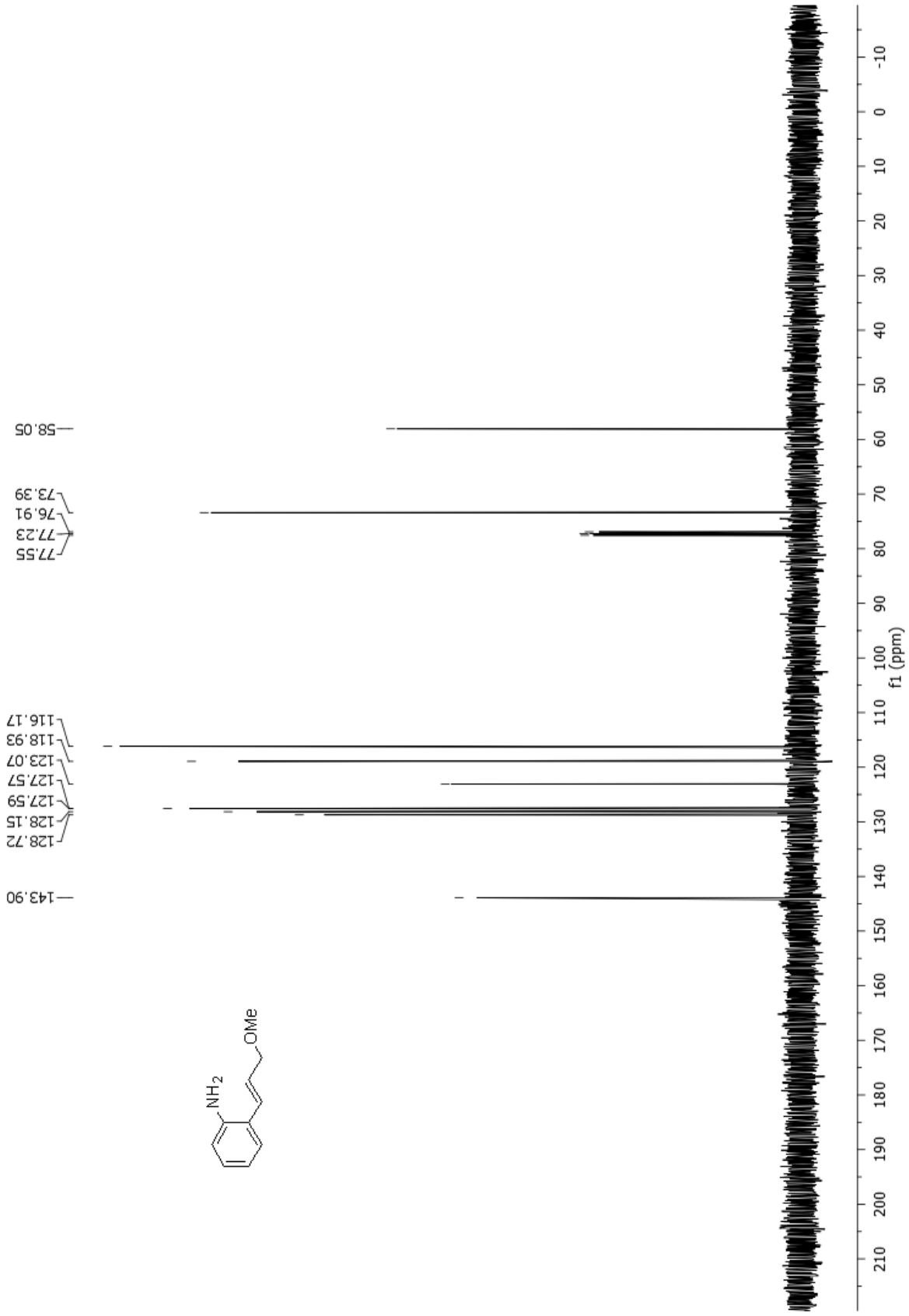
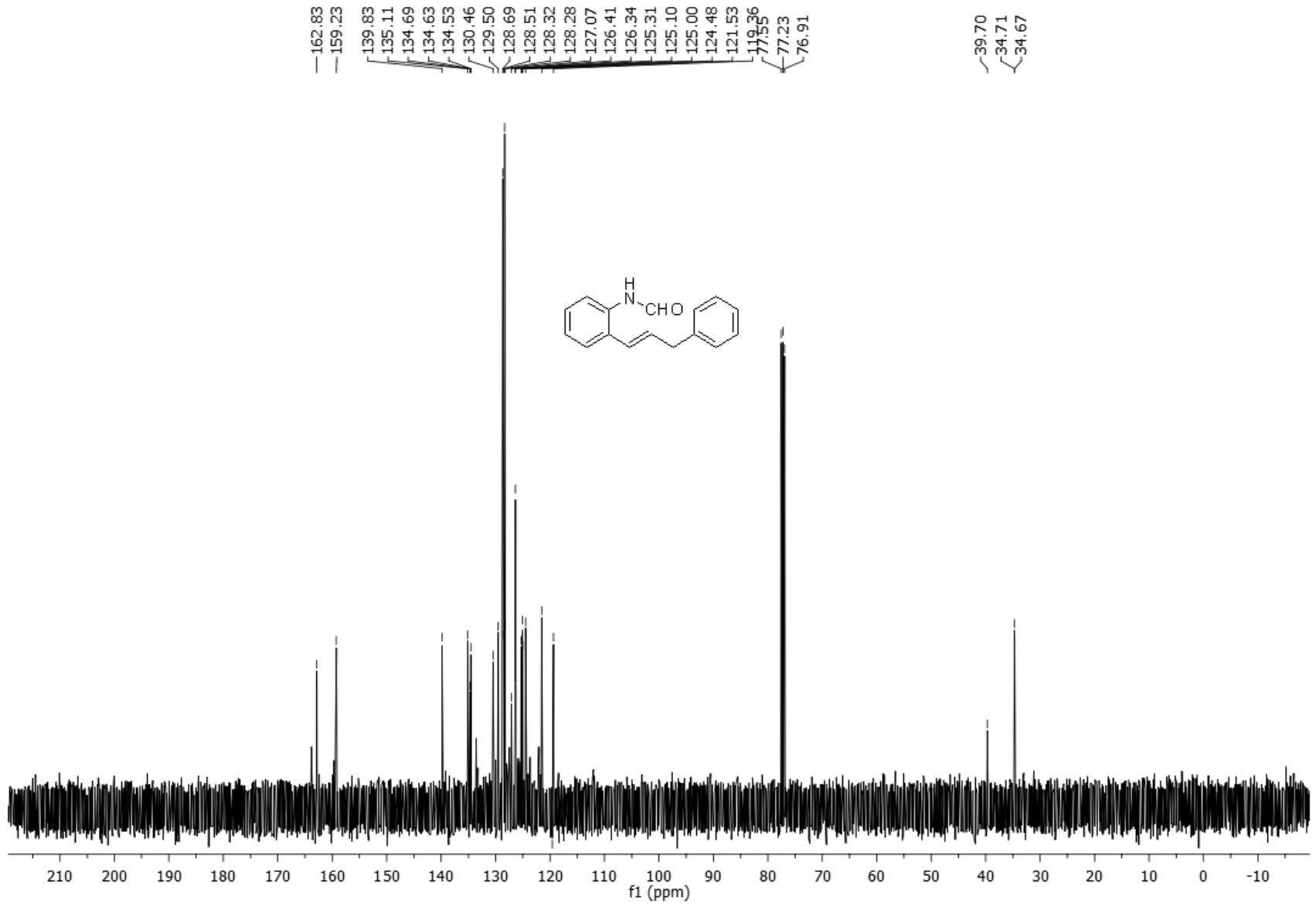
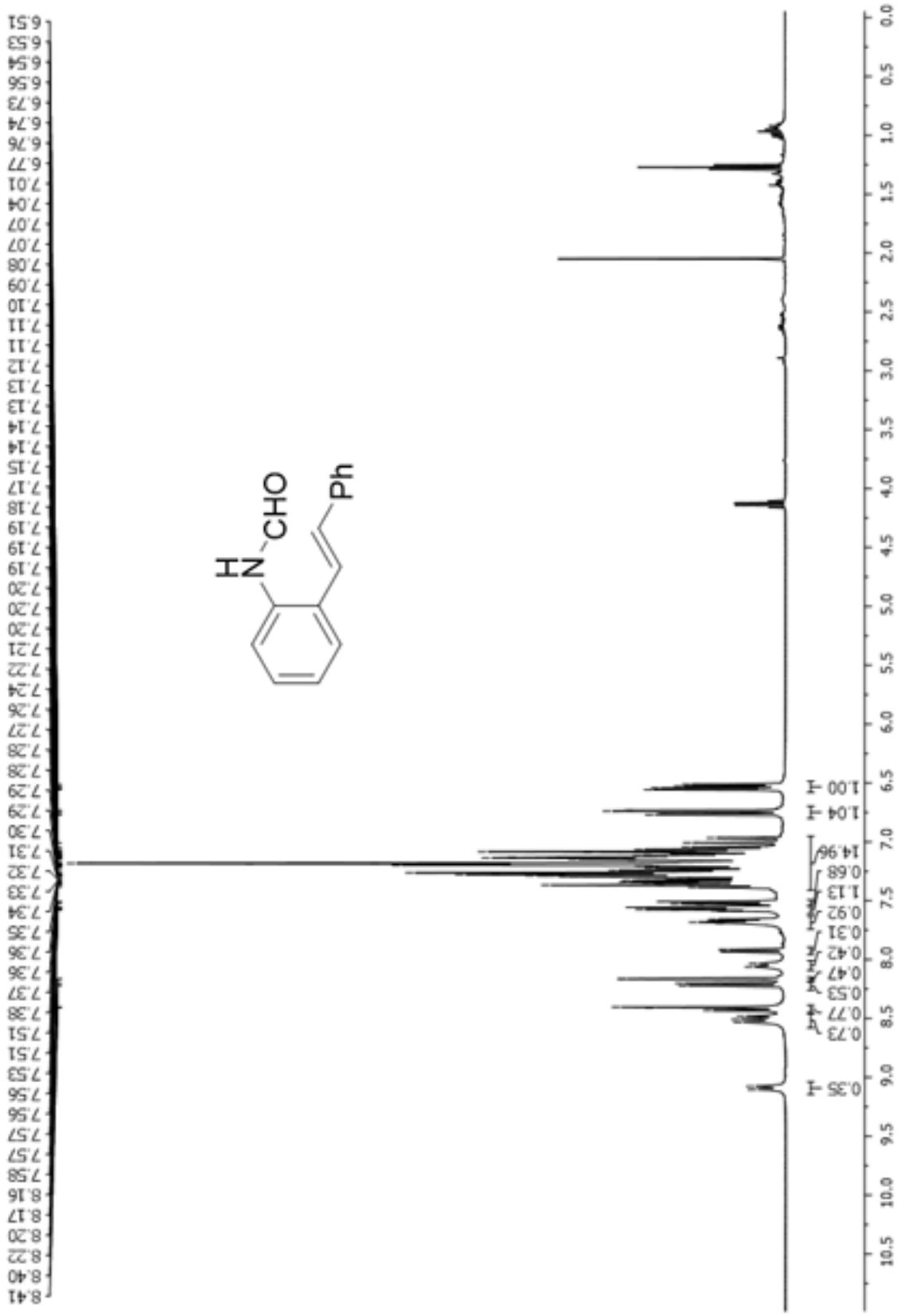
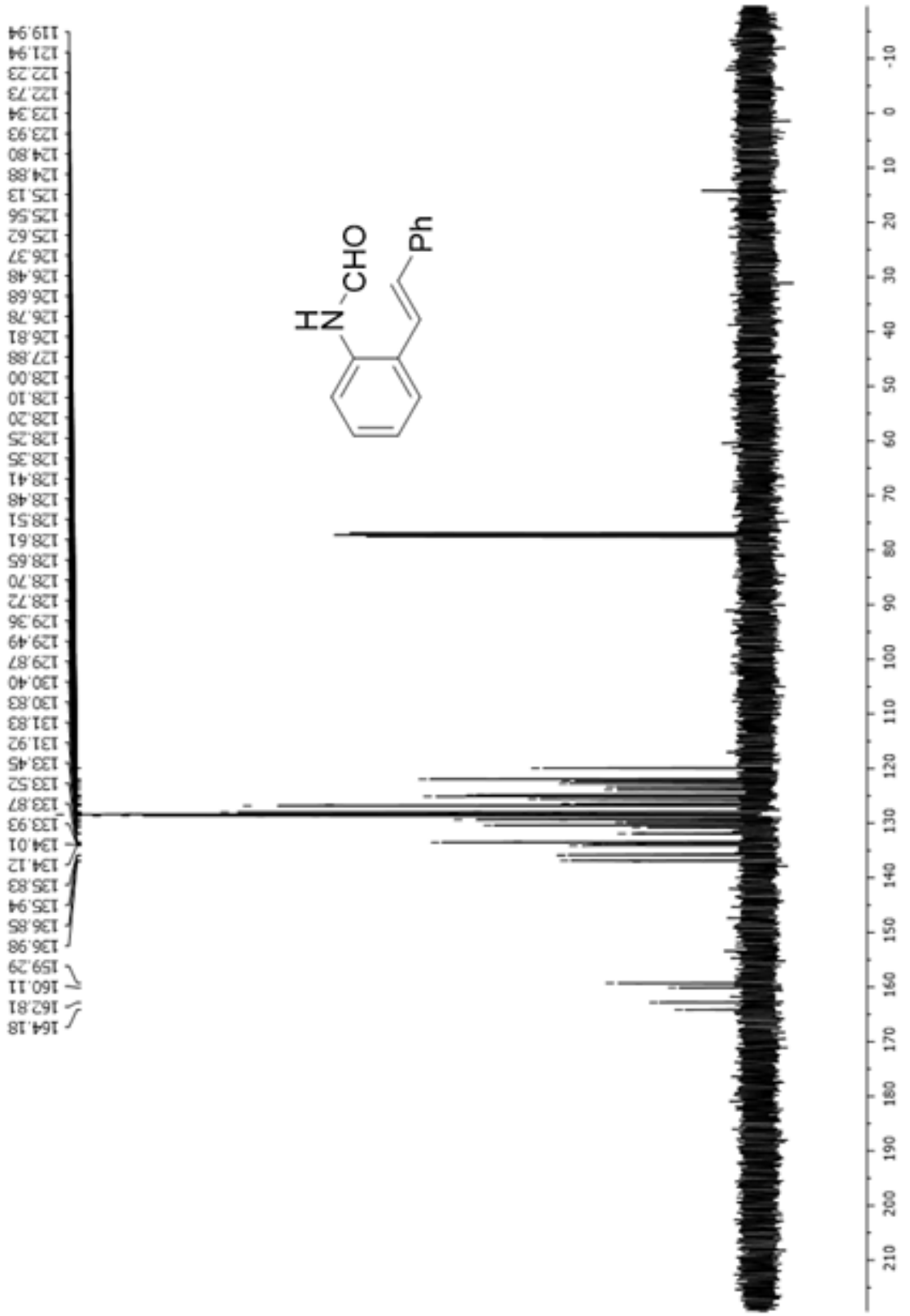
6.69
6.67
6.67
6.65
6.20
6.19
6.17
6.16
6.15
6.13
4.11
4.11
4.10
4.09
3.75
3.41
NH2
OMe
1.01
1.03
1.03
2.03
1.00
2.06
1.83
3.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

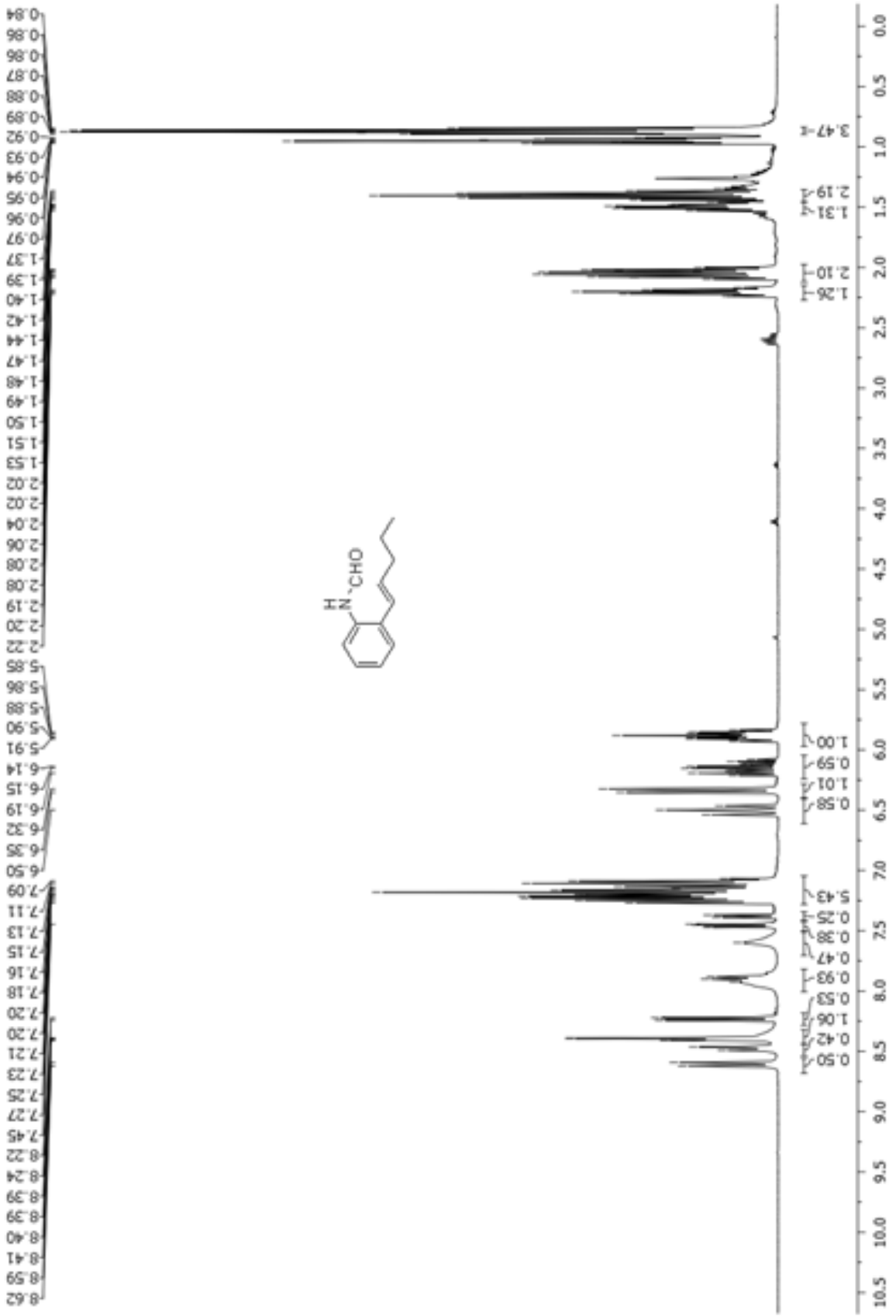

143.90
128.72
128.15
127.59
127.57
123.07
118.93
116.17
77.55
77.23
76.91
73.39
58.05
NH2
OMe
f1 (ppm)

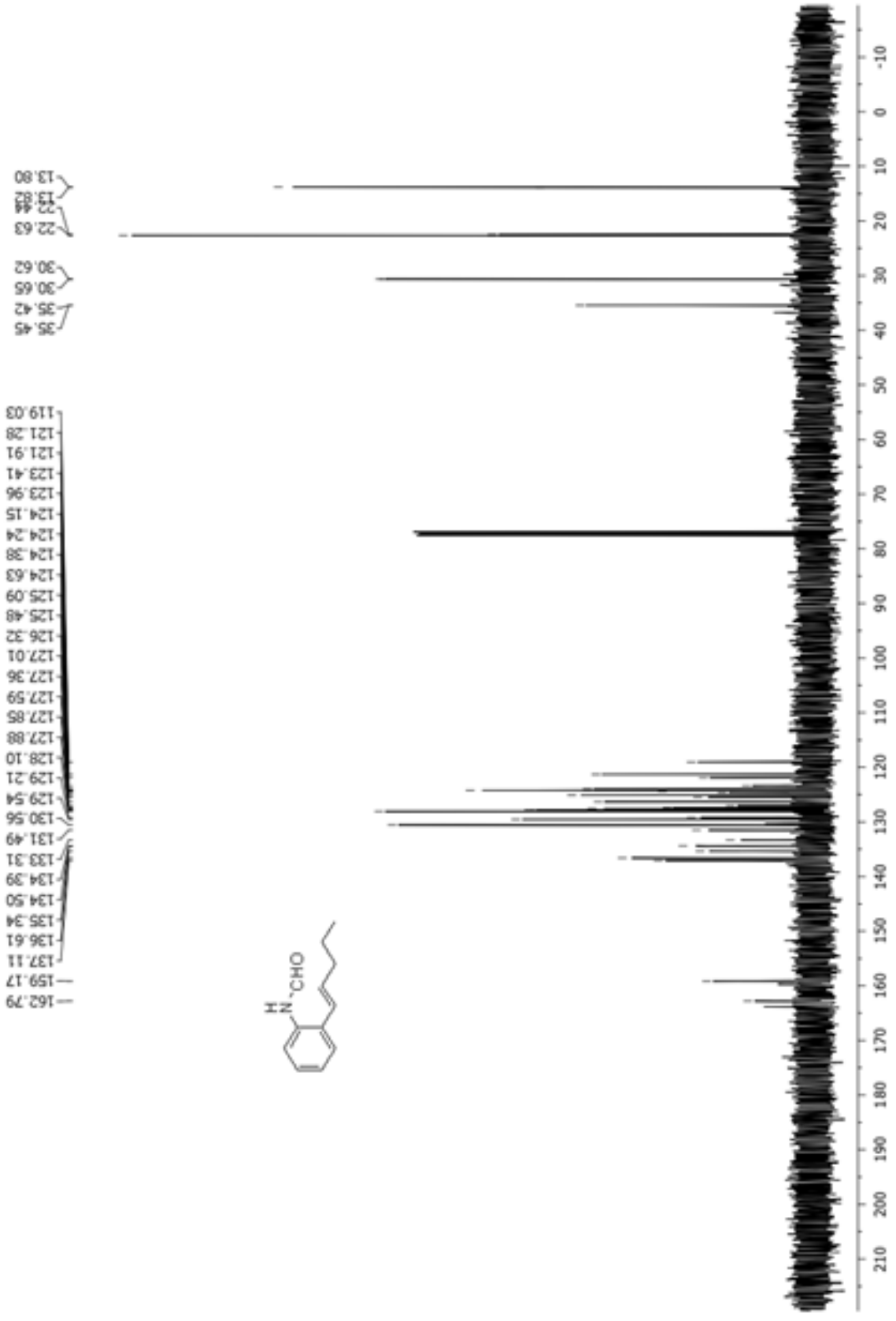
8.65
8.62
8.40
8.40
8.33
8.32
8.31
8.31
8.29
8.29
7.36
7.36
7.34
7.34
7.33
7.32
7.32
7.30
7.30
7.28
7.27
7.27
7.26
7.25
7.24
7.23
7.23
7.22
7.21
7.21
7.20
7.19
7.18
7.18
7.17
7.17
7.16
7.16
7.14
7.14
7.13
7.12
6.53
6.52
6.51
6.49
6.37
6.33
6.18
6.16
6.15
6.14
6.14
6.13
6.12
6.11
6.11
6.10
6.09
6.07
3.50
3.48
3.45
3.43
H
N
CHO
0.48
0.20
0.29
1.06
0.42
0.13
0.12
0.55
0.29
0.19
11.60
0.33
1.01
0.36
1.00
0.96
1.06
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

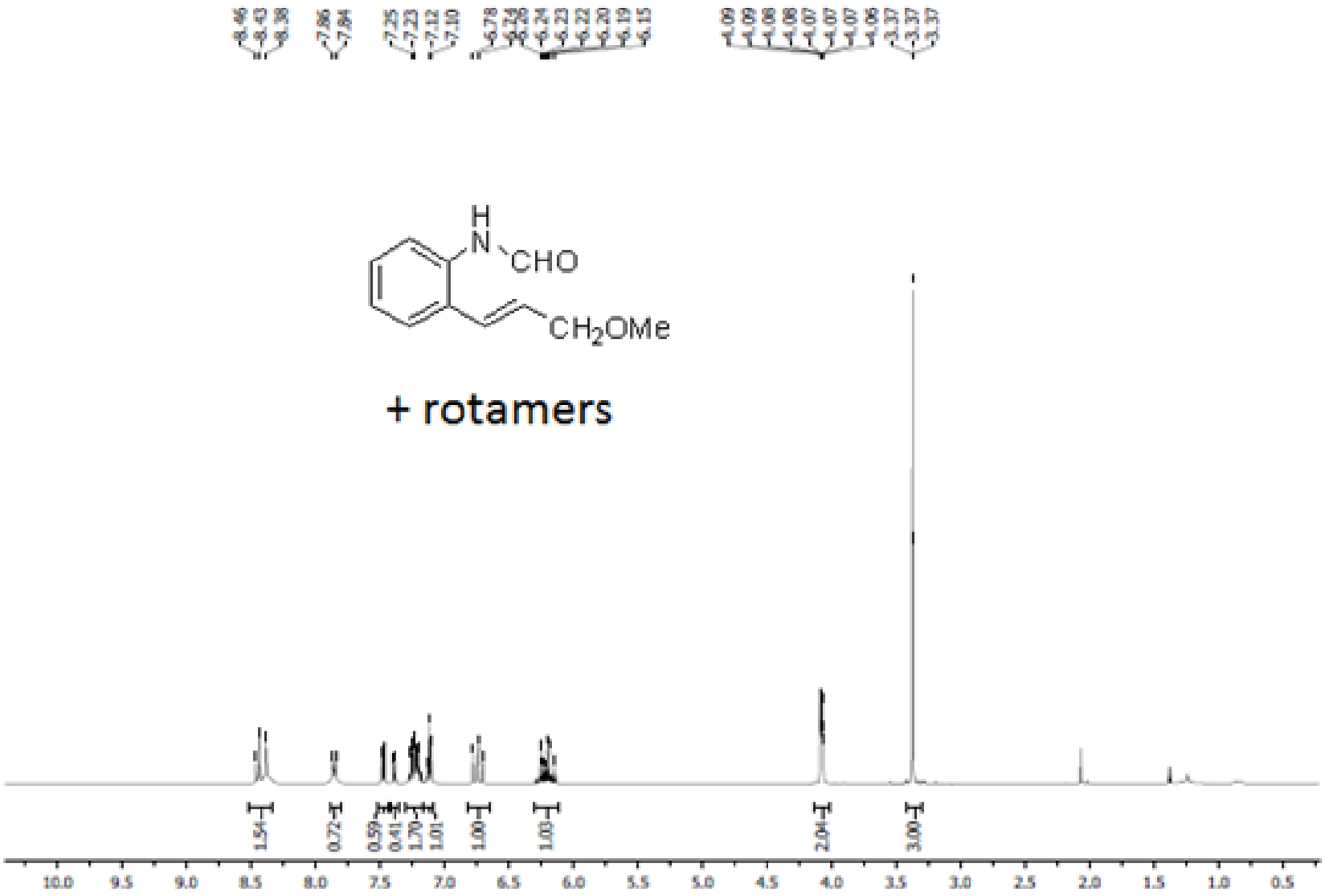

162.83
159.23
139.83
135.11
134.69
134.63
134.53
130.46
129.50
128.69
128.51
128.32
128.28
127.07
126.41
126.34
125.31
125.10
125.00
124.48
121.53
119.36
77.55
77.23
76.91
39.70
34.71
34.67
CHO
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

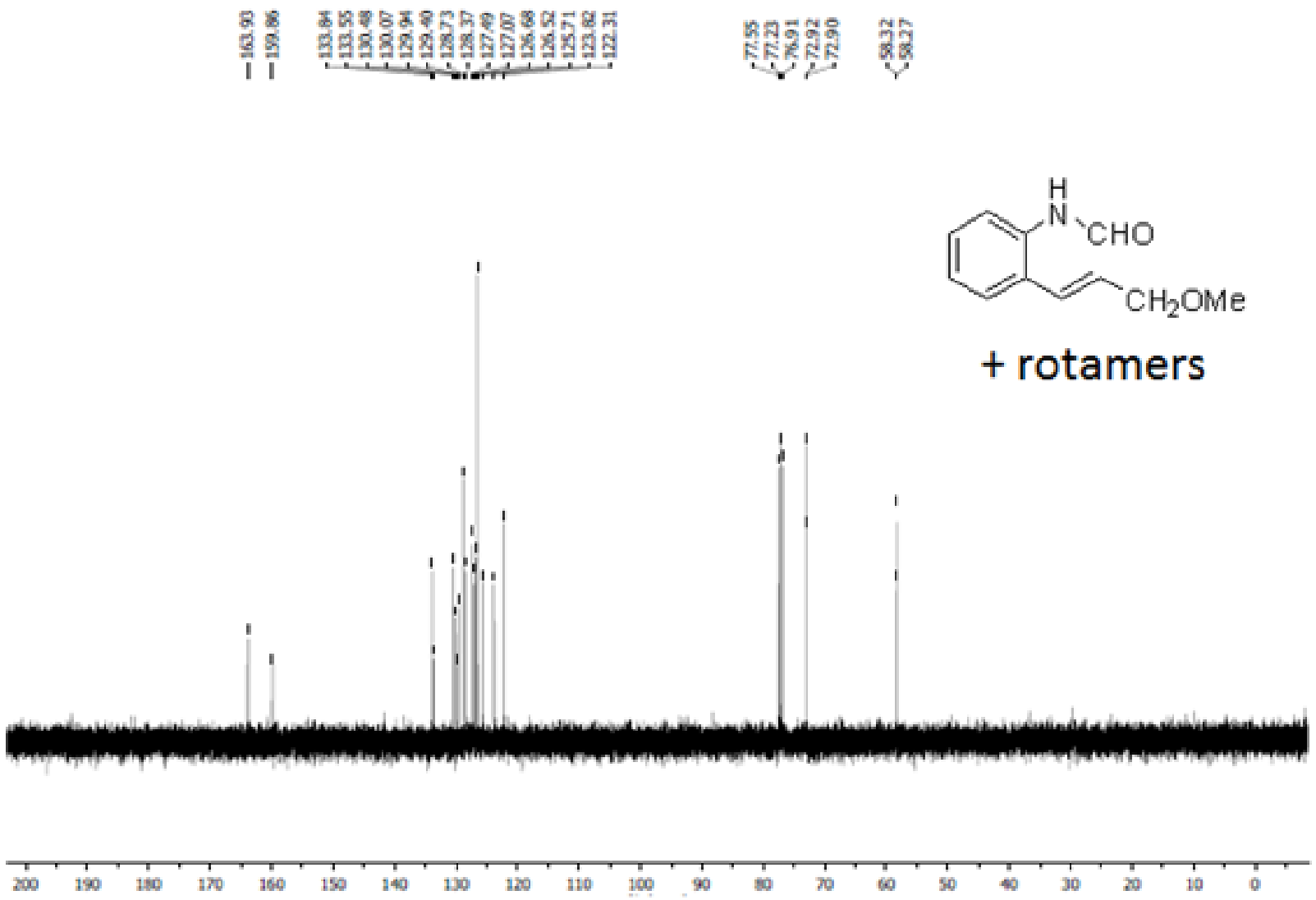

HN
CHO
Ph

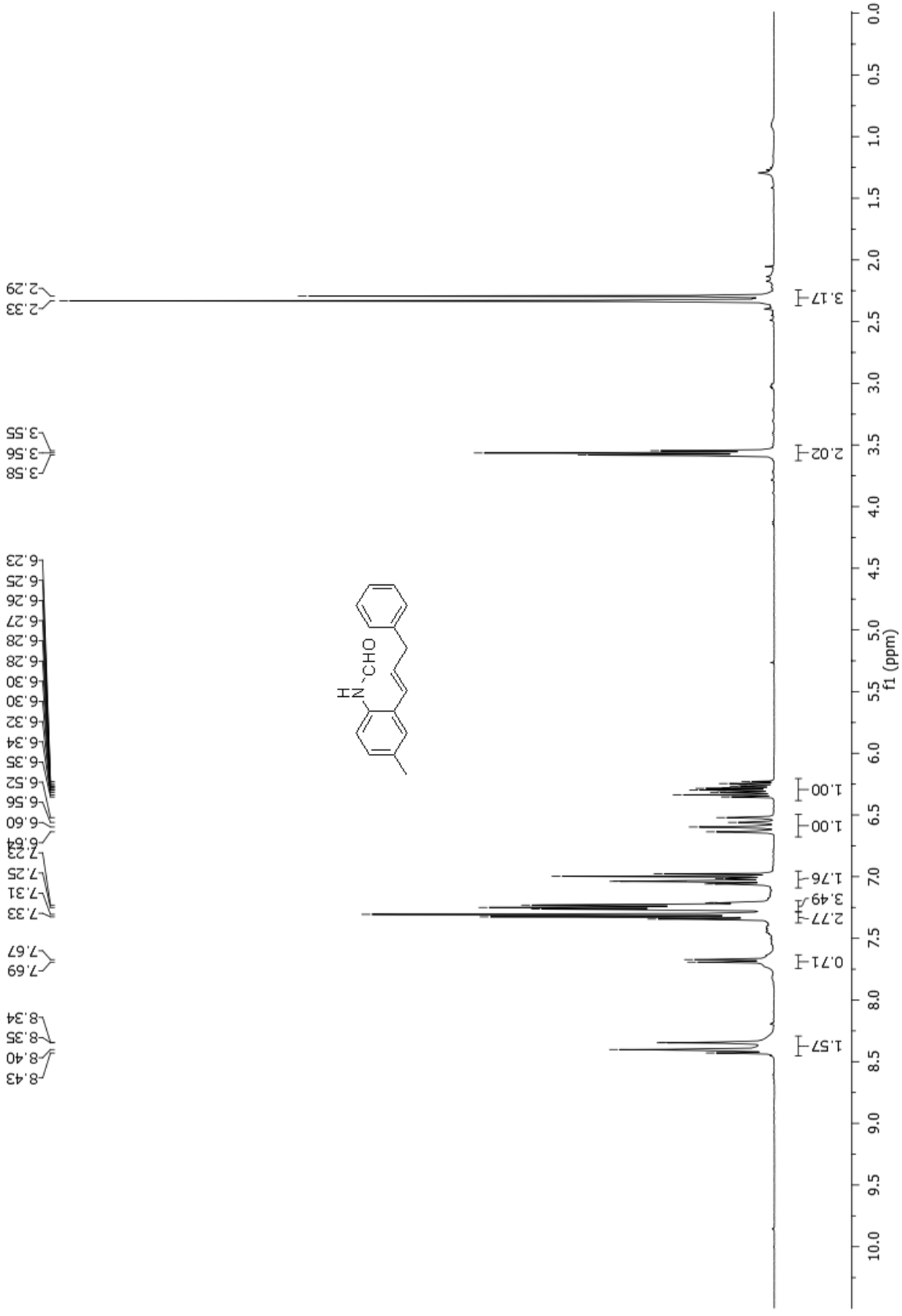

119.94
121.94
122.23
122.73
123.34
123.93
124.80
124.88
125.13
125.56
125.62
126.37
126.48
126.68
126.78
126.81
127.88
128.00
128.10
128.20
128.25
128.35
128.41
128.48
128.51
128.61
128.65
128.70
128.72
129.36
129.49
129.87
130.40
130.83
131.83
131.92
133.45
133.52
133.87
133.93
134.01
134.12
135.83
135.94
136.85
136.98
159.29
160.11
162.81
164.18
HN
CHO
Ph
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

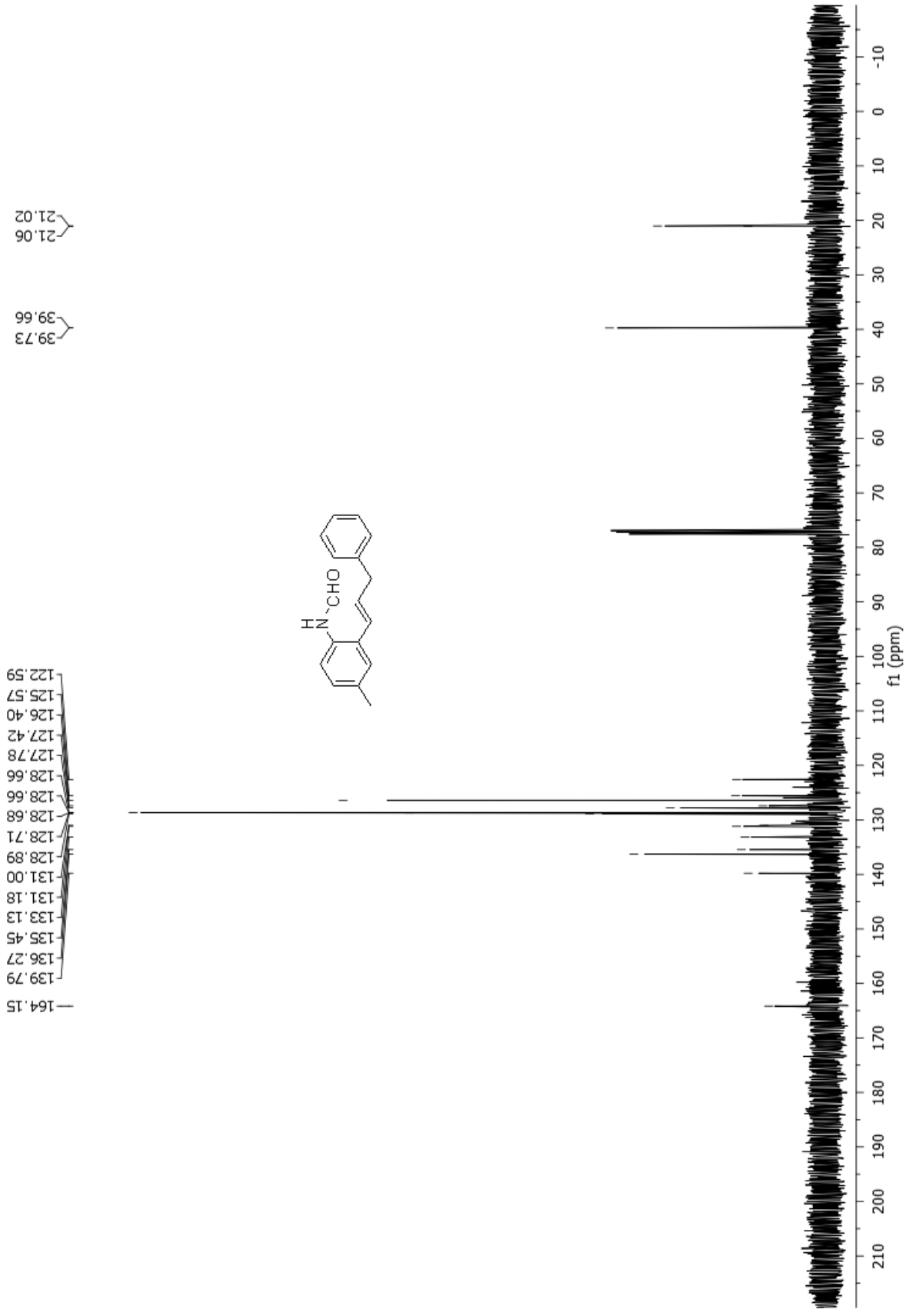


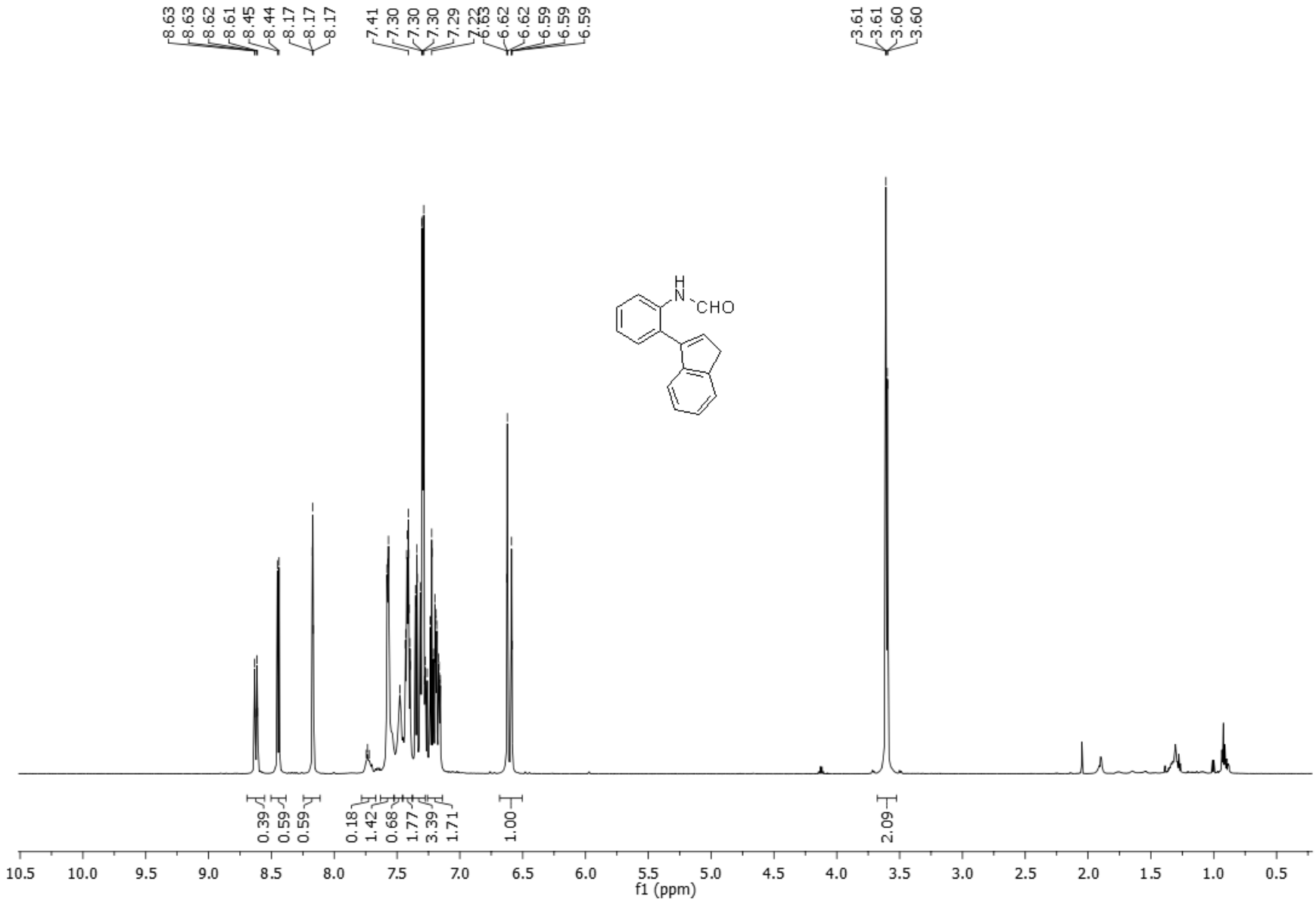

13.80
13.82
22.44
22.63
30.62
30.65
35.42
35.45
119.03
121.28
121.91
123.41
123.96
124.15
124.24
124.38
124.63
125.09
125.48
126.32
127.01
127.36
127.59
127.85
127.88
128.10
129.21
129.54
130.56
131.49
133.31
134.39
134.50
135.34
136.61
137.11
159.17
162.79
H
N
CHO

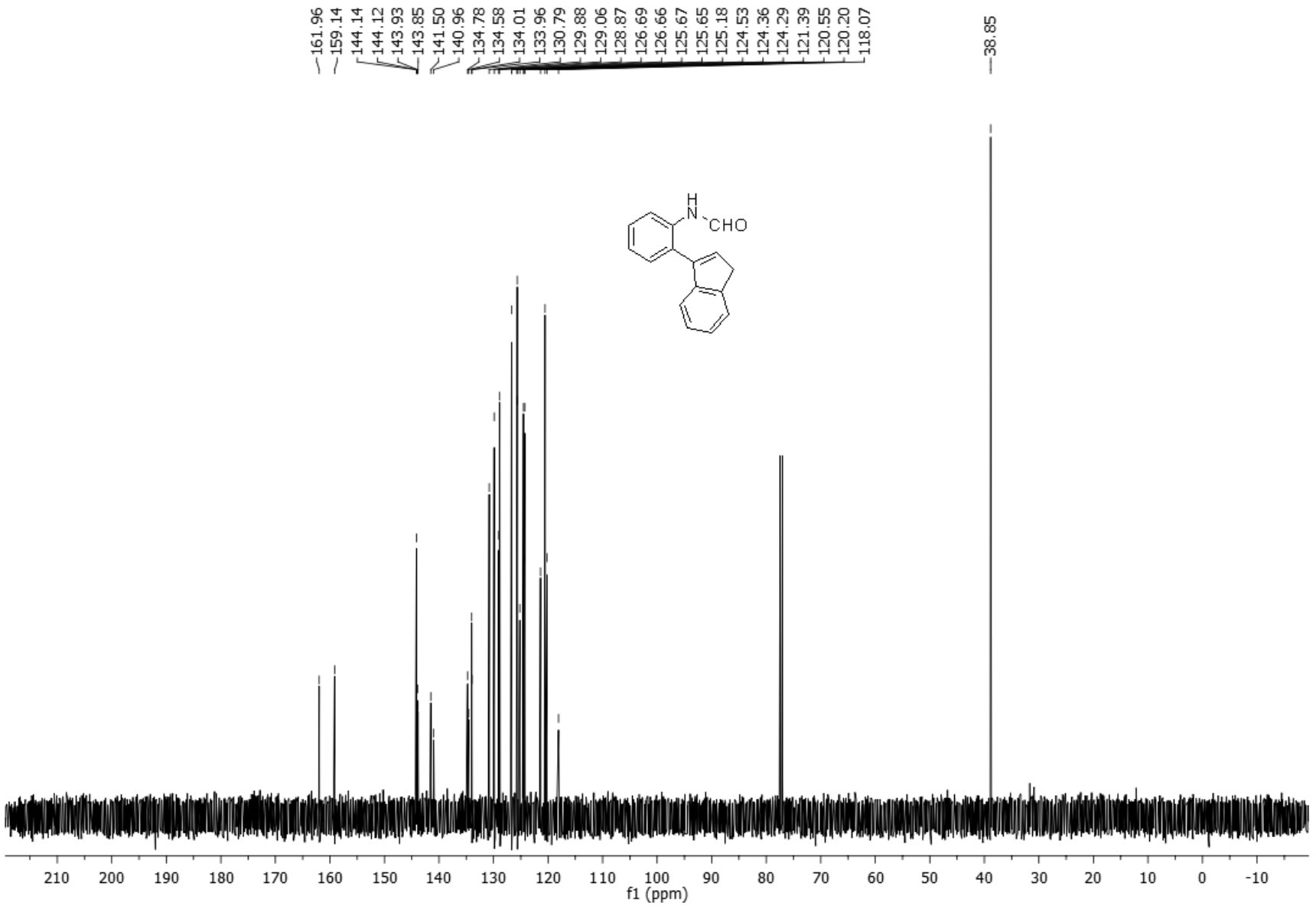

8.46
8.43
8.39
7.86
7.84
7.25
7.23
7.12
7.10
6.78
6.24
6.23
6.22
6.20
6.19
6.15
4.09
4.08
4.08
4.08
4.07
4.07
4.07
4.06
3.37
3.37
3.37
H
N
CHO
CH2OMe
+ rotamers
1.54
0.72
0.59
0.41
1.70
1.01
1.00
1.03
2.04
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

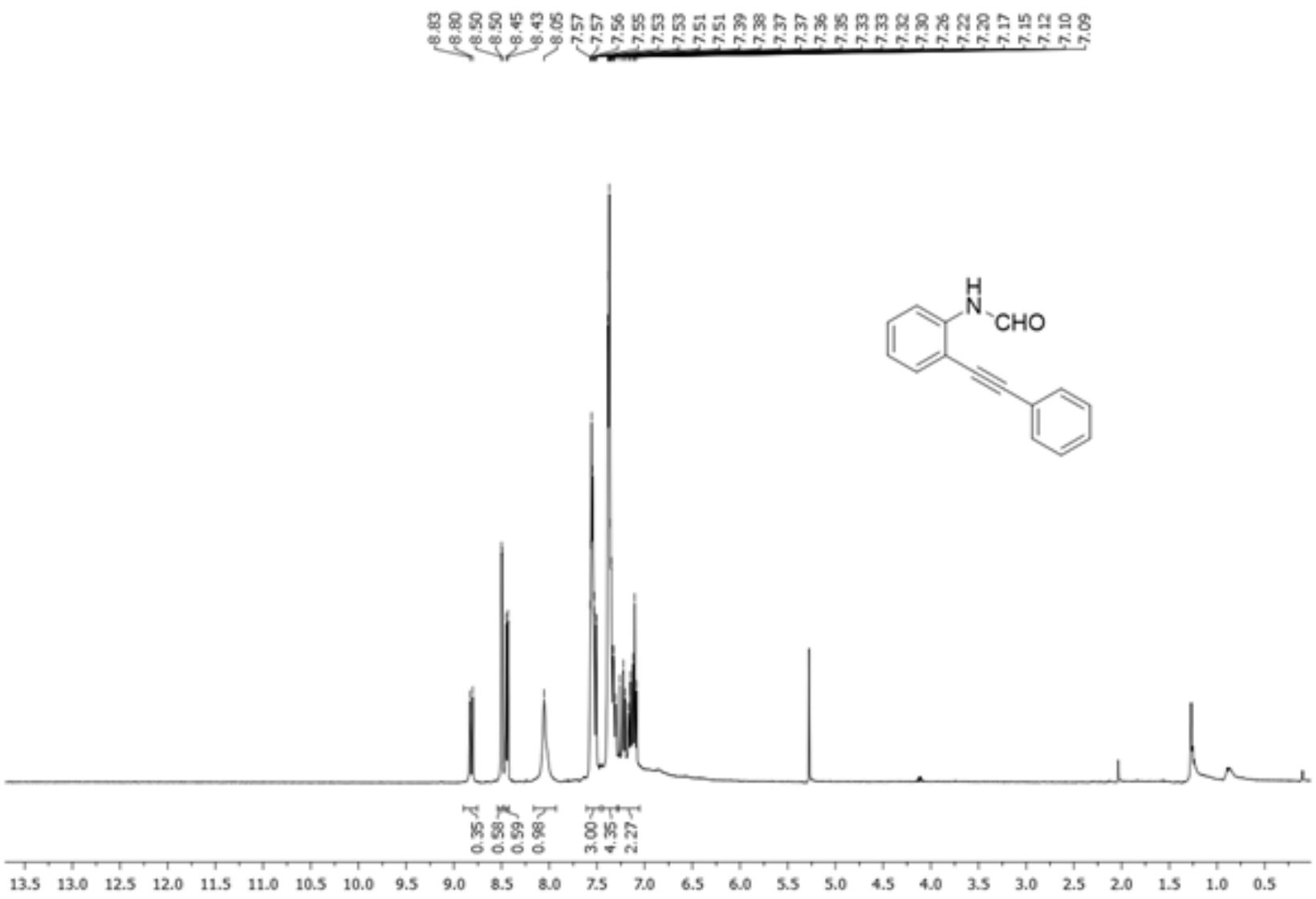

163.90
159.86
133.84
133.55
130.48
130.07
129.94
129.40
128.73
128.37
127.49
127.07
126.68
126.52
125.71
123.62
122.31
77.55
77.23
76.91
72.92
72.90
58.32
58.27
H
N
CHO
CH2OMe
+ rotamers
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

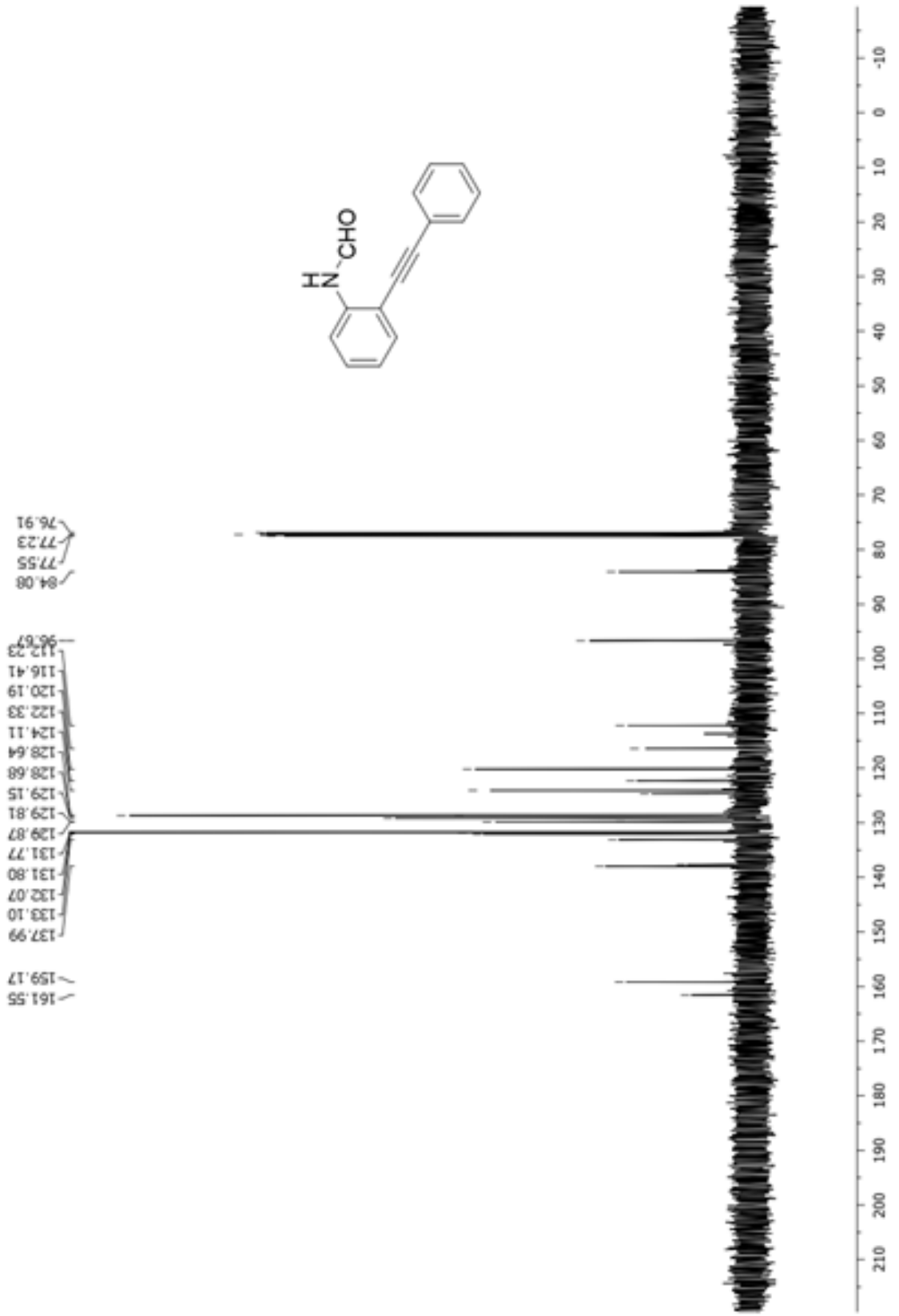

8.43
8.40
8.35
8.34
7.69
7.67
7.33
7.31
7.25
7.23
6.64
6.60
6.56
6.52
6.35
6.34
6.32
6.30
6.30
6.28
6.28
6.27
6.26
6.25
6.23
3.58
3.56
3.55
2.33
2.29
1.57
0.71
2.77
3.49
1.76
1.00
1.00
2.02
3.17
f1 (ppm)

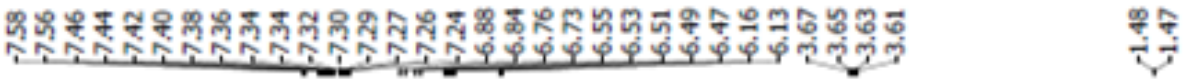

164.15
139.79
136.27
135.45
133.13
131.18
131.00
128.89
128.71
128.68
128.66
128.66
127.78
127.42
126.40
125.57
122.59
39.73
39.66
21.06
21.02
H
N
CHO
f1 (ppm)

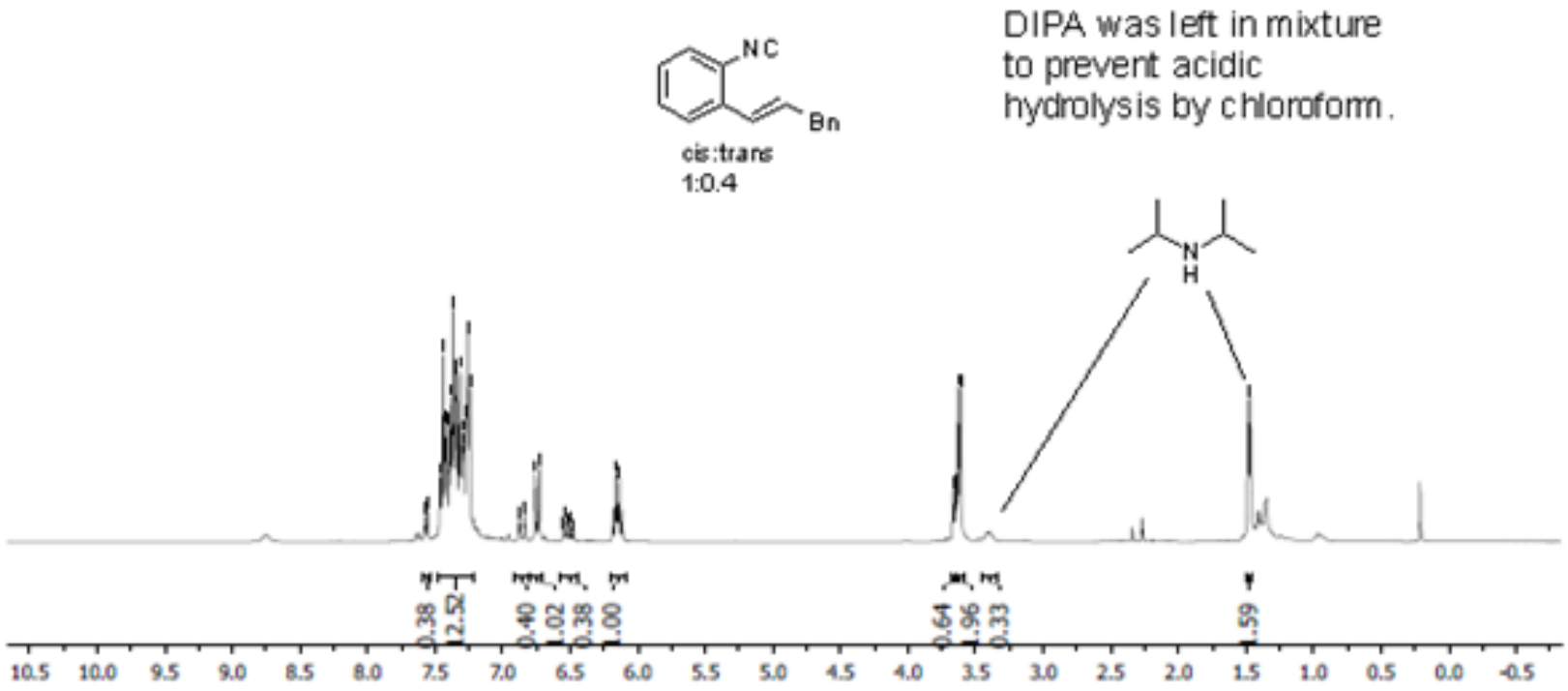

8.63
8.63
8.62
8.61
8.45
8.44
8.17
8.17
8.17
7.41
7.30
7.30
7.30
7.29
7.22
6.63
6.62
6.62
6.59
6.59
6.59
3.61
3.61
3.60
3.60
N
H
CHO
0.39
0.59
0.59
0.18
1.42
0.68
1.77
3.39
1.71
1.00
2.09
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

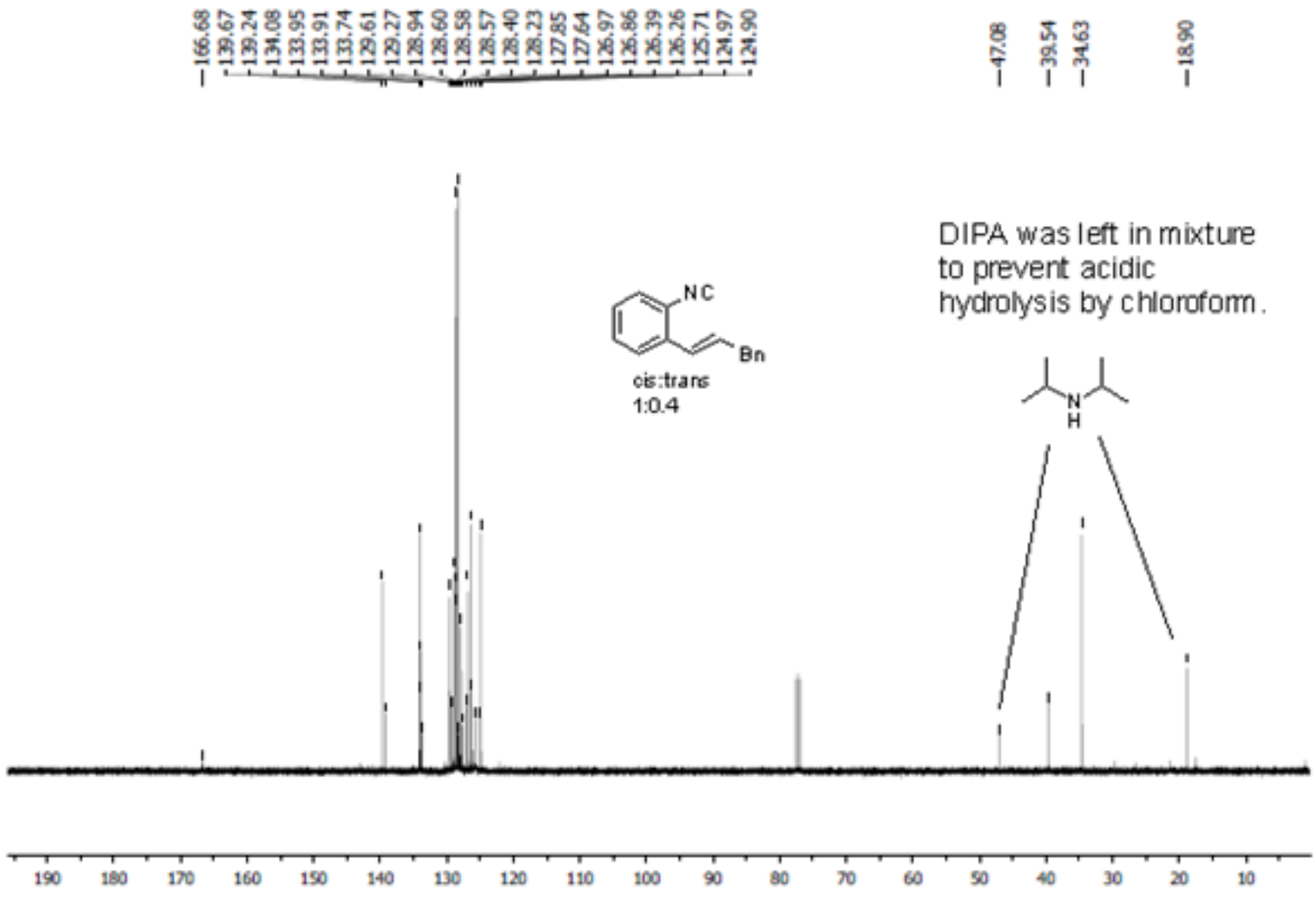

161.96
159.14
144.14
144.12
143.93
143.85
141.50
140.96
134.78
134.58
134.01
133.96
130.79
129.88
129.06
128.87
126.69
126.66
125.67
125.65
125.18
124.53
124.36
124.29
121.39
120.55
120.20
118.07
38.85
NH
CHO
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

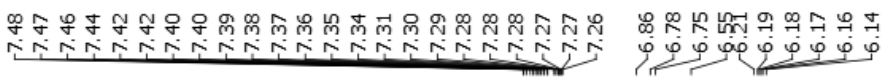

8.83
8.80
8.50
8.50
8.45
8.43
8.05
7.57
7.57
7.56
7.55
7.53
7.53
7.51
7.51
7.39
7.38
7.37
7.37
7.36
7.35
7.33
7.33
7.32
7.30
7.26
7.22
7.20
7.17
7.15
7.12
7.10
7.09
H
N
CHO
0.35
0.58
0.59
0.98
3.00
4.35
2.27
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

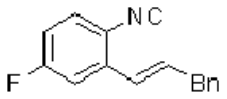

NH
CHO
161.55
159.17
137.99
133.10
132.07
131.80
131.77
129.87
129.81
129.15
128.68
128.64
124.11
122.33
120.19
116.41
112.23
96.67
84.08
77.55
77.23
76.91

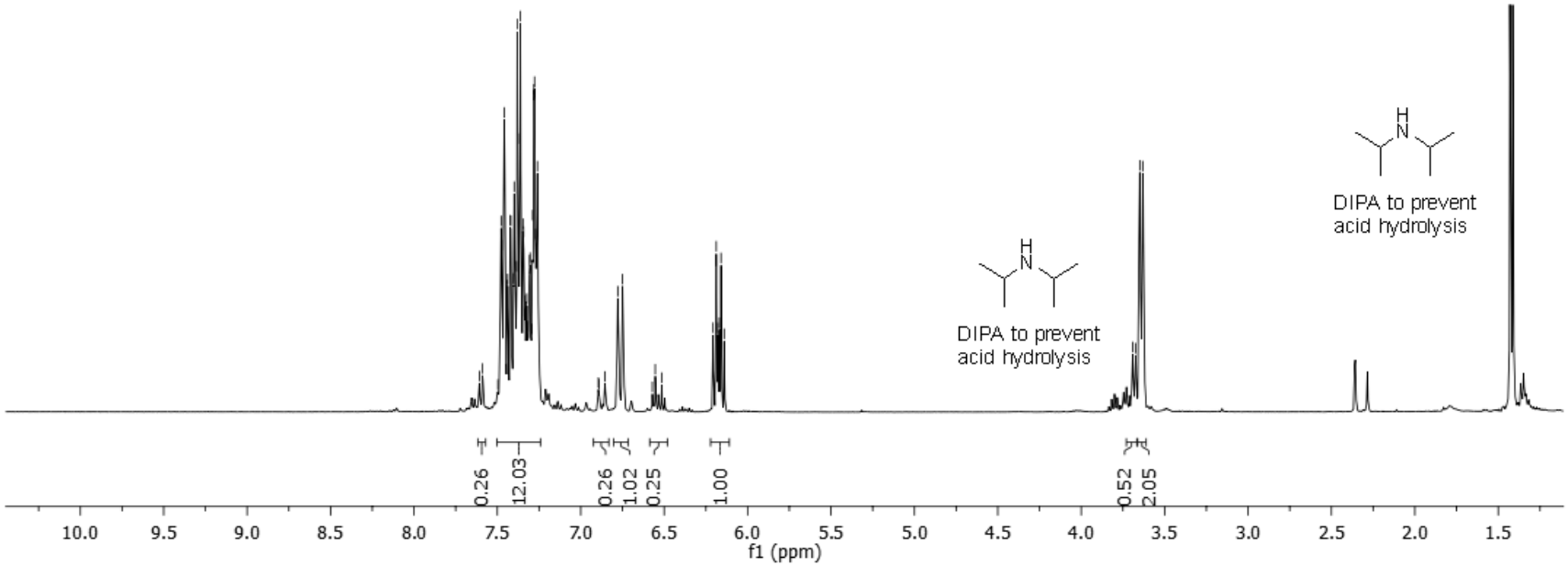

7.58
7.56
7.46
7.44
7.42
7.40
7.38
7.36
7.34
7.34
7.32
7.30
7.29
7.27
7.26
7.24
6.88
6.84
6.76
6.73
6.55
6.53
6.51
6.49
6.47
6.16
6.13
3.67
3.65
3.63
3.61
1.48
1.47

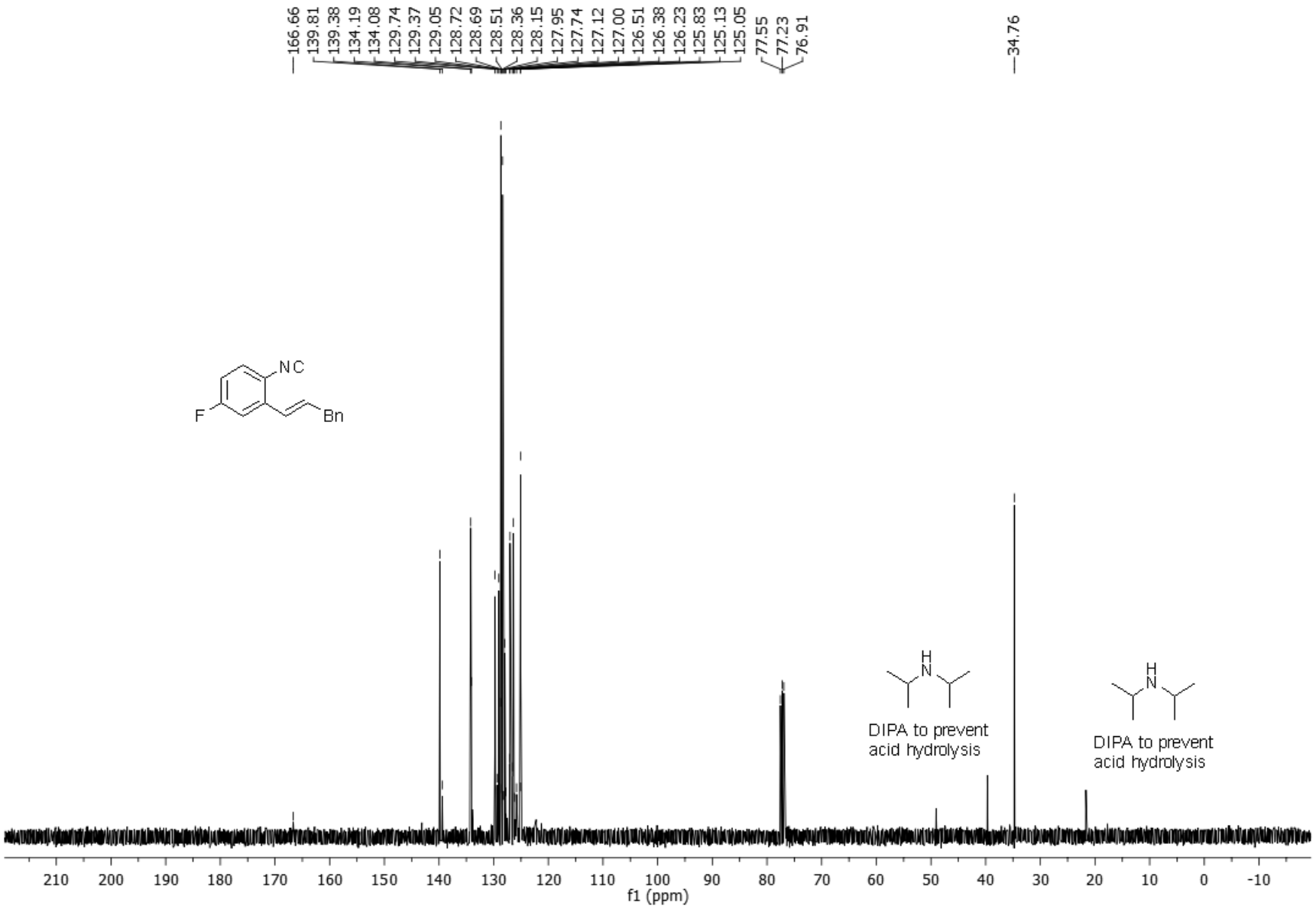

NC
Bn
cis:trans
1:0.4
DIPA was left in mixture to prevent acidic hydrolysis by chloroform.
N
H
0.38
2.52
0.40
1.02
0.38
1.00
0.64
1.96
0.33
1.59
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

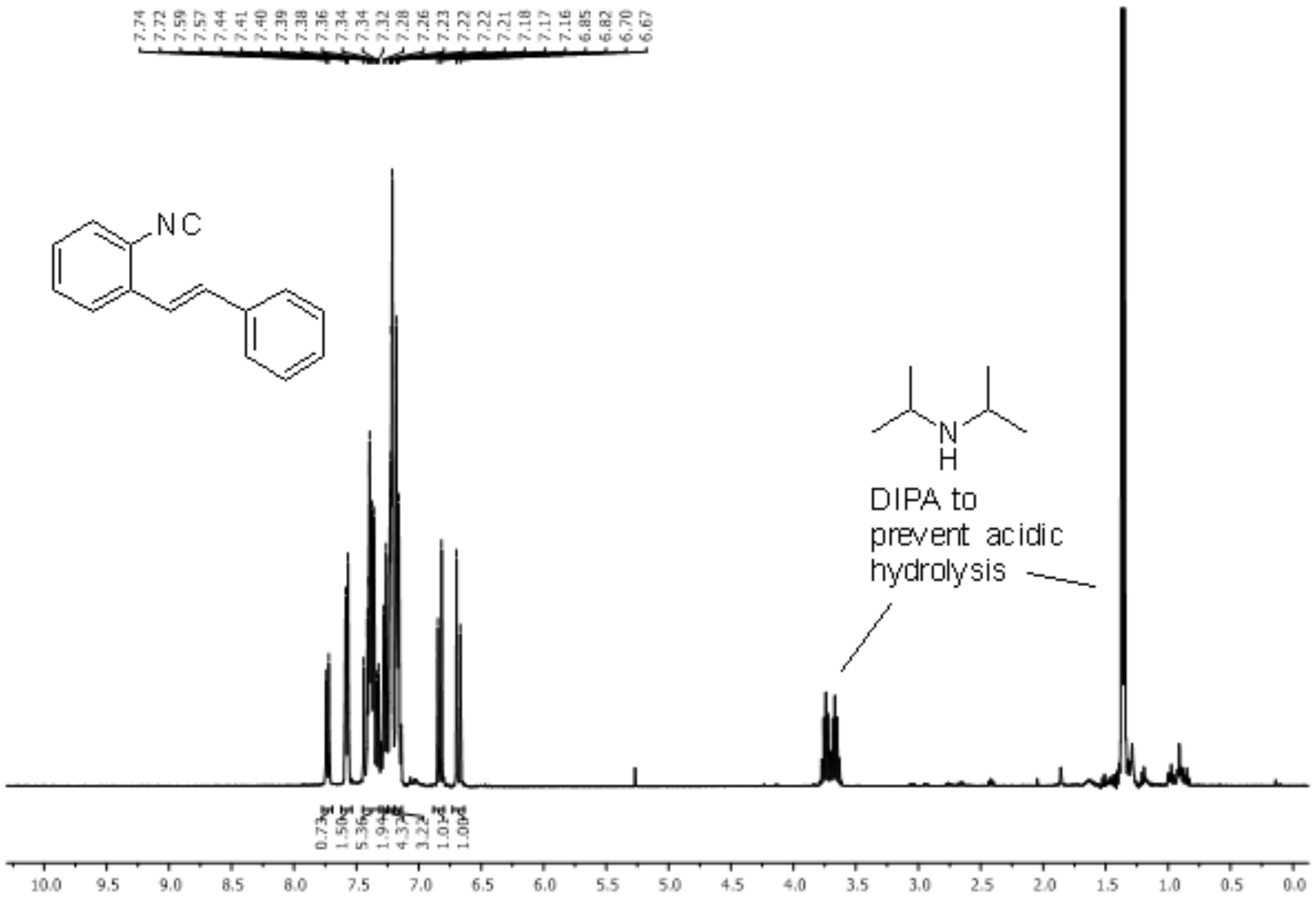

166.68
139.67
139.24
134.08
133.95
133.91
133.74
129.61
129.27
128.94
128.60
128.58
128.57
128.40
128.23
127.85
127.64
126.97
126.86
126.39
126.26
125.71
124.97
124.90
47.08
39.54
34.63
18.90
DIPA was left in mixture to prevent acidic hydrolysis by chloroform.
NC
Bn
cis:trans
1:0.4
N
H
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

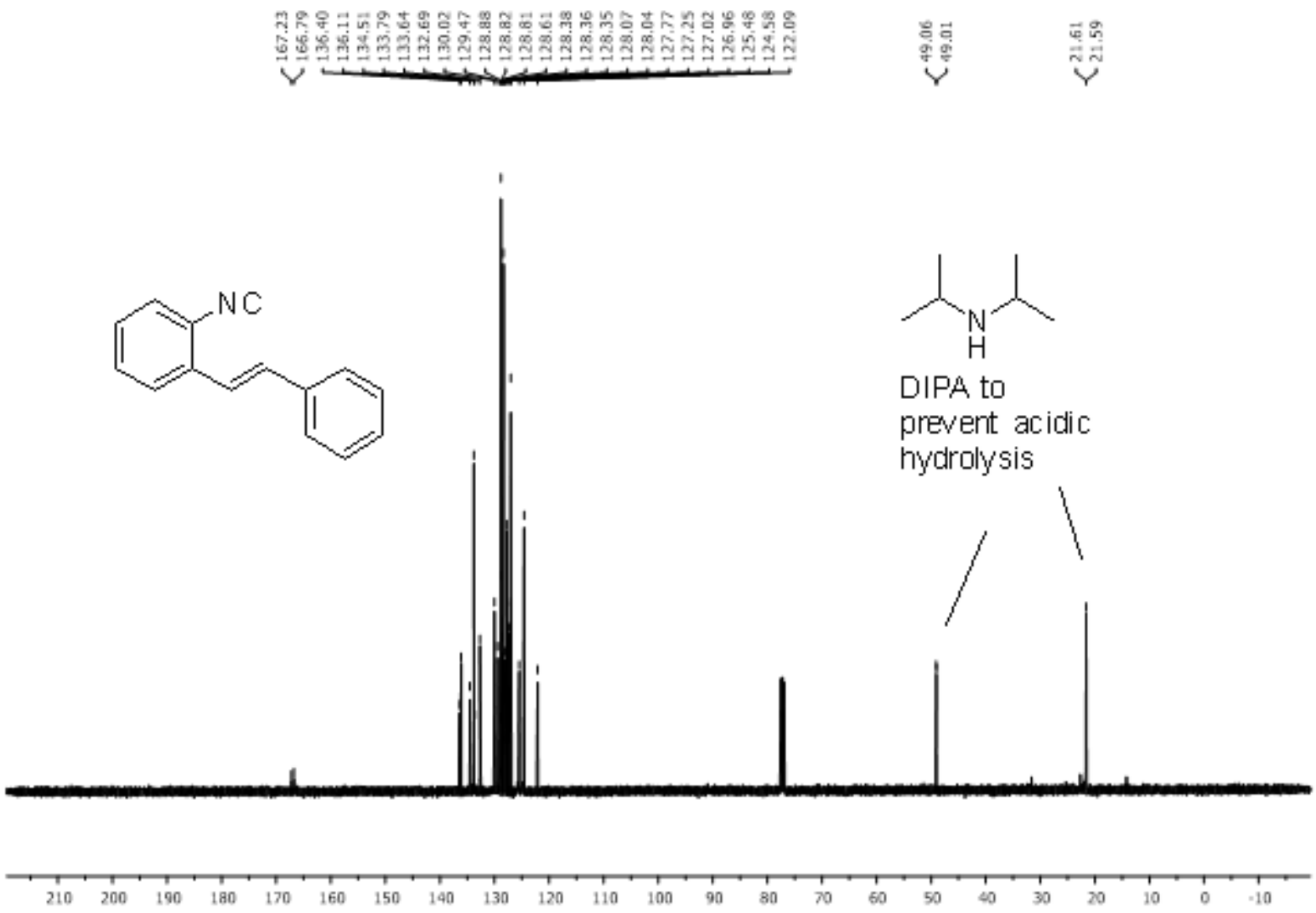

7.48
7.47
7.46
7.44
7.42
7.42
7.40
7.40
7.39
7.38
7.37
7.36
7.35
7.34
7.31
7.30
7.29
7.28
7.28
7.28
7.27
7.27
7.26
6.86
6.78
6.75
6.55
6.21
6.19
6.18
6.17
6.16
6.14
3.69
3.67
3.65
3.63

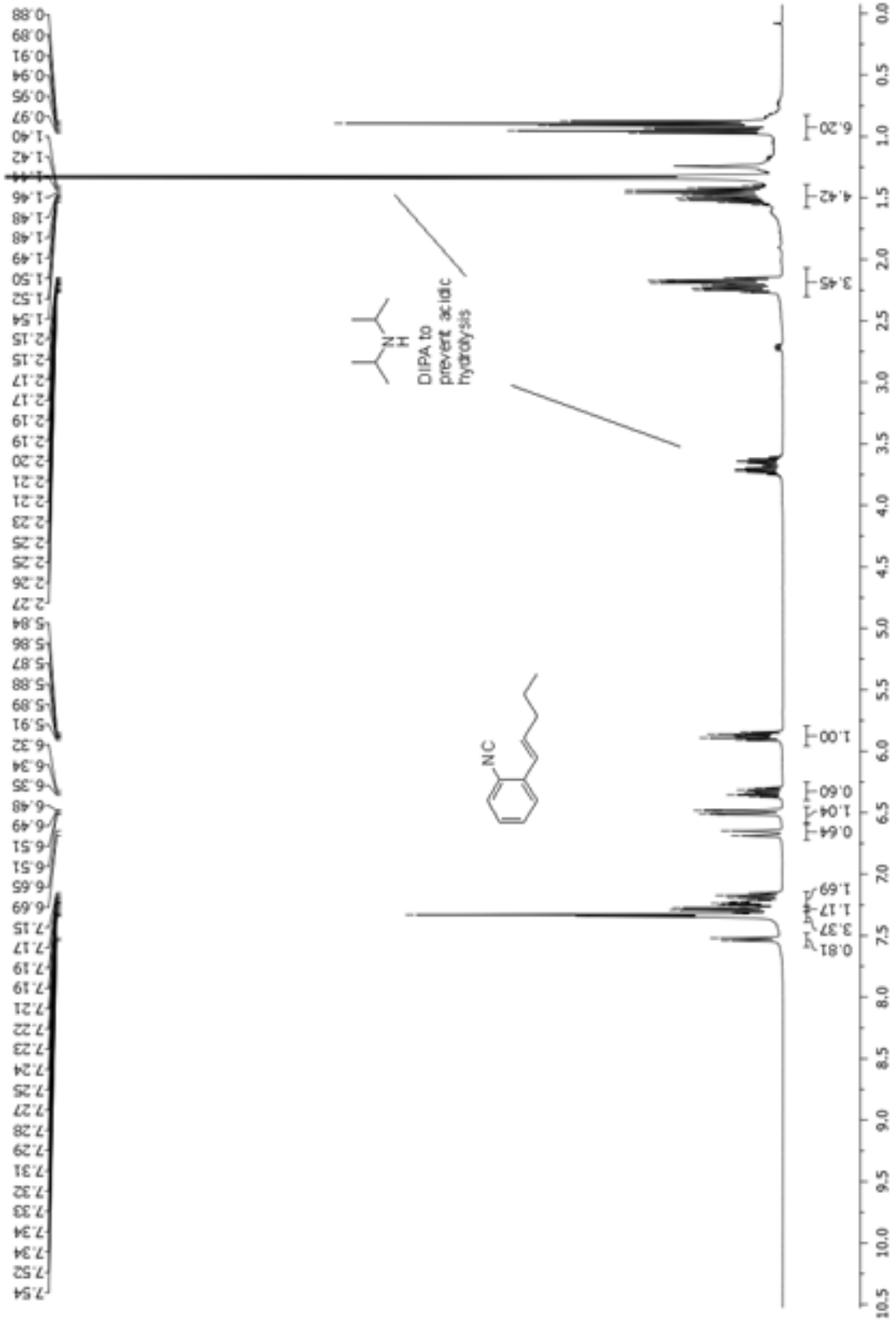

NC
F
Bn


DIPA to prevent
acid hydrolysis
DIPA to prevent
acid hydrolysis
0.26
12.03
0.26
1.02
0.25
1.00
0.52
2.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

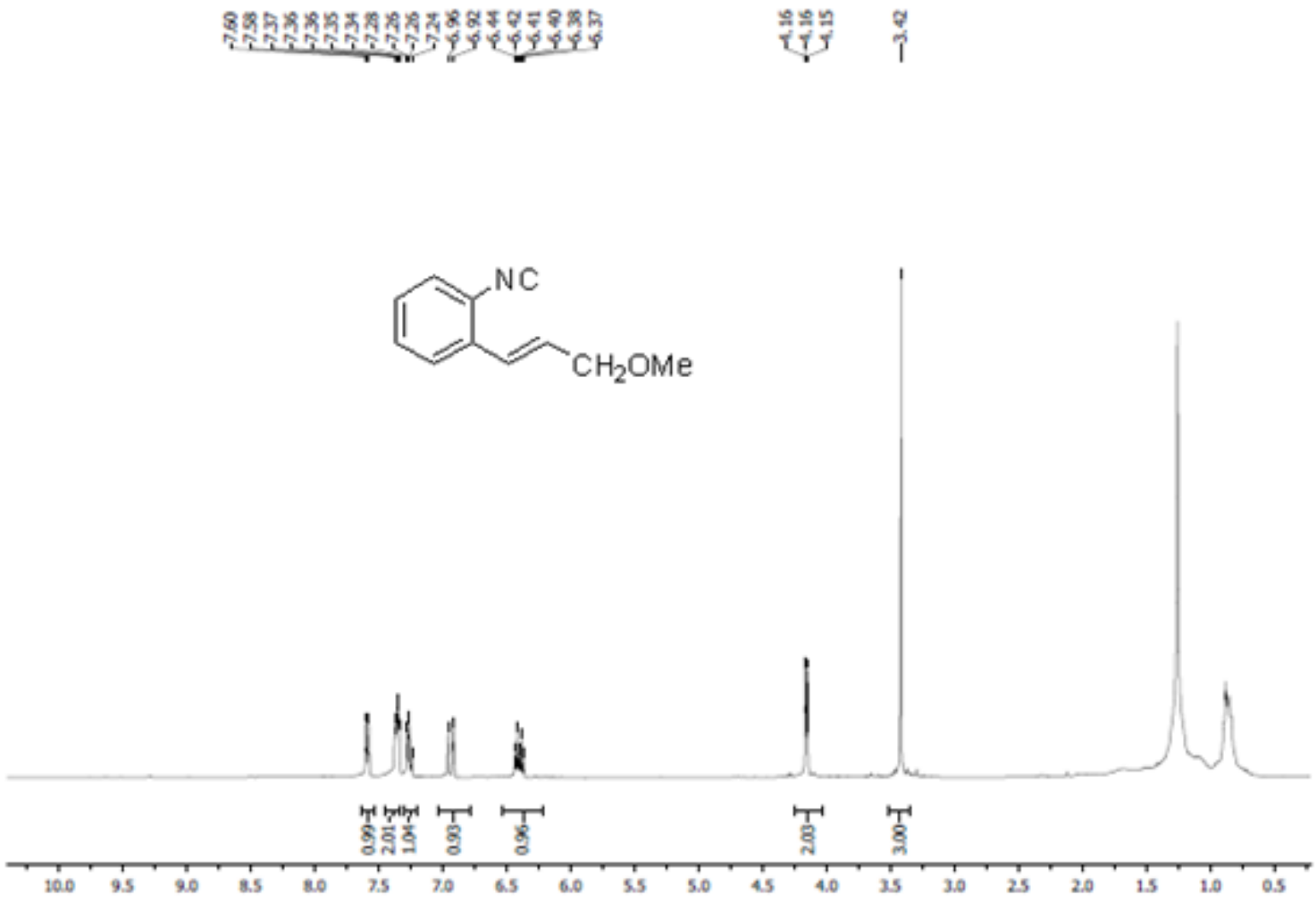

166.66
139.81
139.38
134.19
134.08
129.74
129.37
129.05
128.72
128.69
128.51
128.36
128.15
127.95
127.74
127.12
127.00
126.51
126.38
126.23
125.83
125.13
125.05
77.55
77.23
76.91
34.76
NC
F
Bn
DIPA to prevent acid hydrolysis
DIPA to prevent acid hydrolysis
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.74
7.72
7.59
7.57
7.44
7.41
7.40
7.39
7.38
7.36
7.34
7.34
7.32
7.28
7.26
7.23
7.22
7.22
7.21
7.18
7.17
7.16
6.85
6.82
6.70
6.67
NC
N
H
DIPA to
prevent acidic
hydrolysis
0.73
1.50
5.36
1.94
4.37
3.22
1.01
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


167.23
166.79
136.40
136.11
134.51
133.79
133.64
132.69
130.02
129.47
128.88
128.82
128.81
128.61
128.38
128.36
128.35
128.07
128.04
127.77
127.25
127.02
126.96
125.48
124.58
122.09
49.06
49.01
21.61
21.59
NC
N
H
DIPA to prevent acidic hydrolysis
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


DIPA to
prevent acidic
hydrolysis
NC
6.20
4.42
3.45
1.00
0.60
1.04
0.64
1.69
1.17
3.37
0.81

166.53
166.35
136.41
135.72
134.55
134.26
129.83
129.29
128.82
127.46
127.33
126.98
126.77
125.65
124.08
123.81
35.31
30.74
22.75
22.30
13.76
13.71
DIPA to prevent acidic hydrolysis
NC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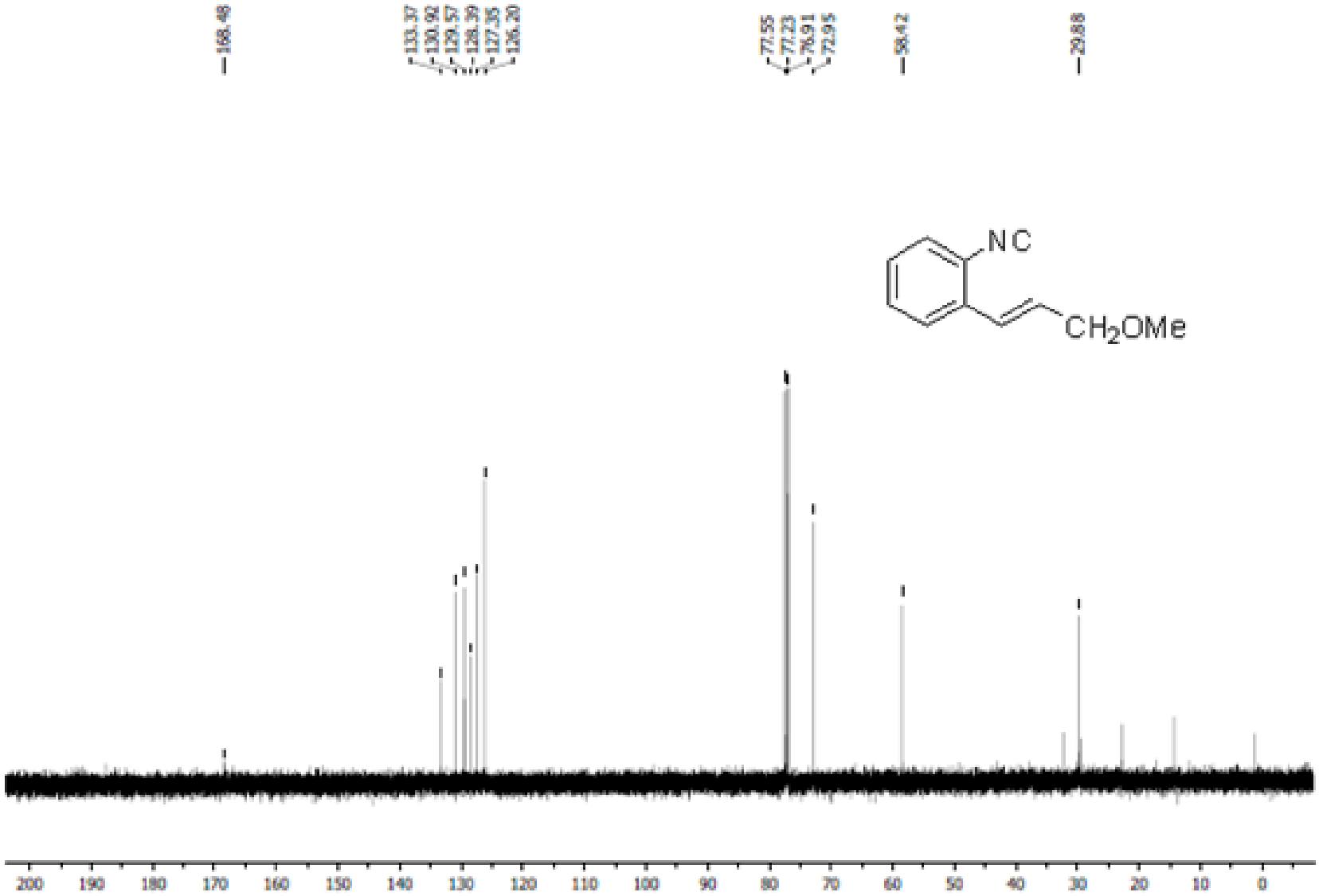
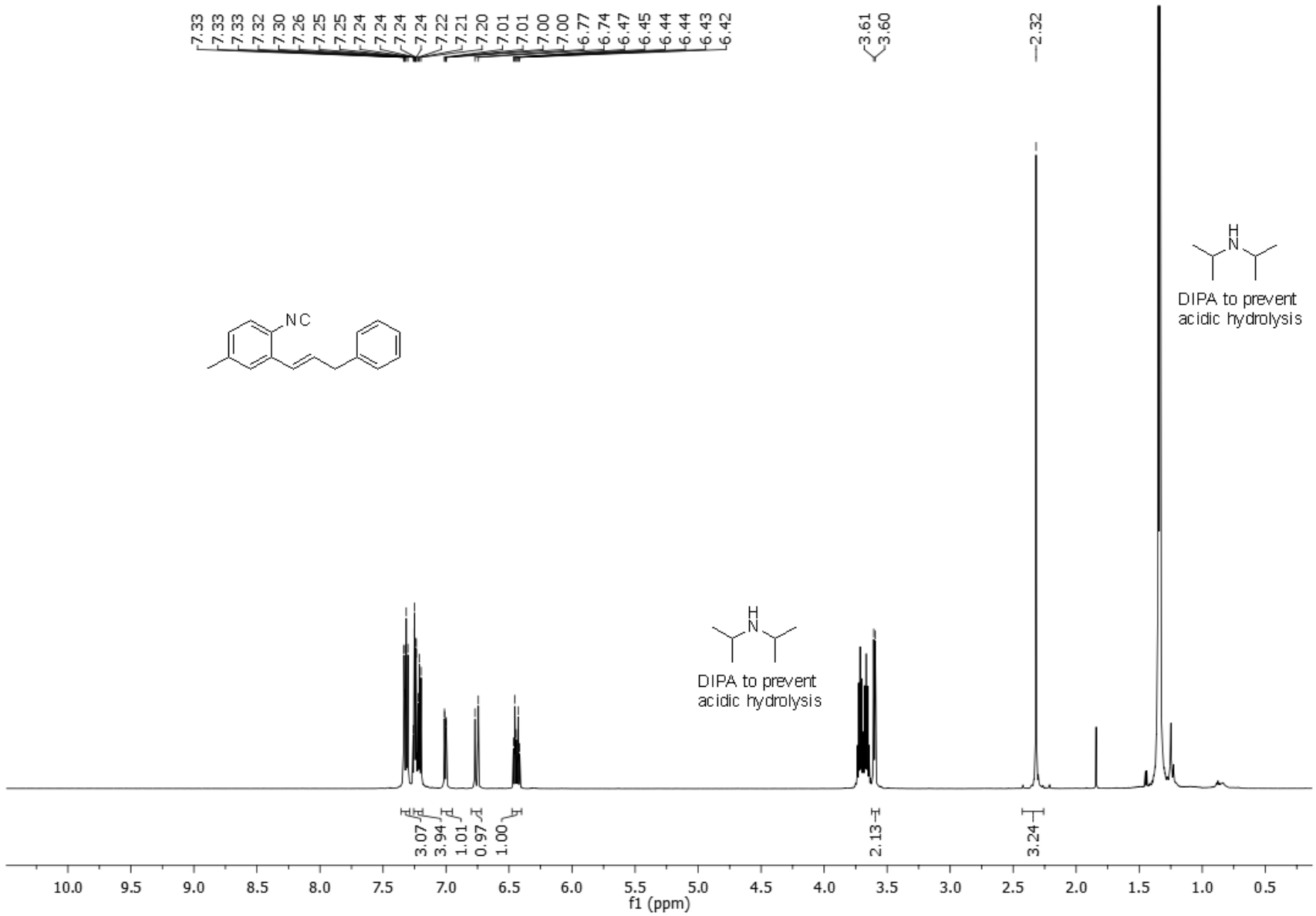
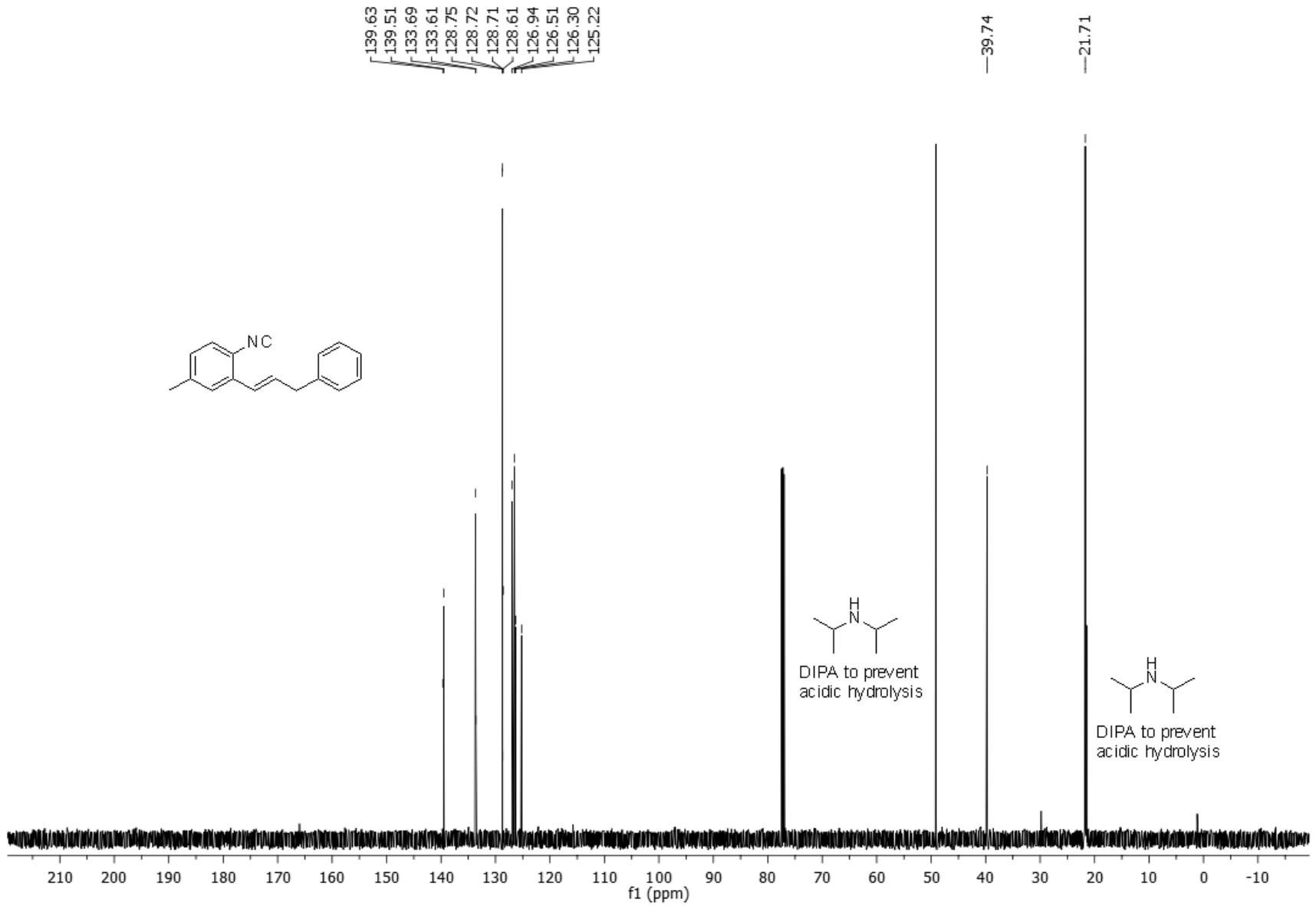
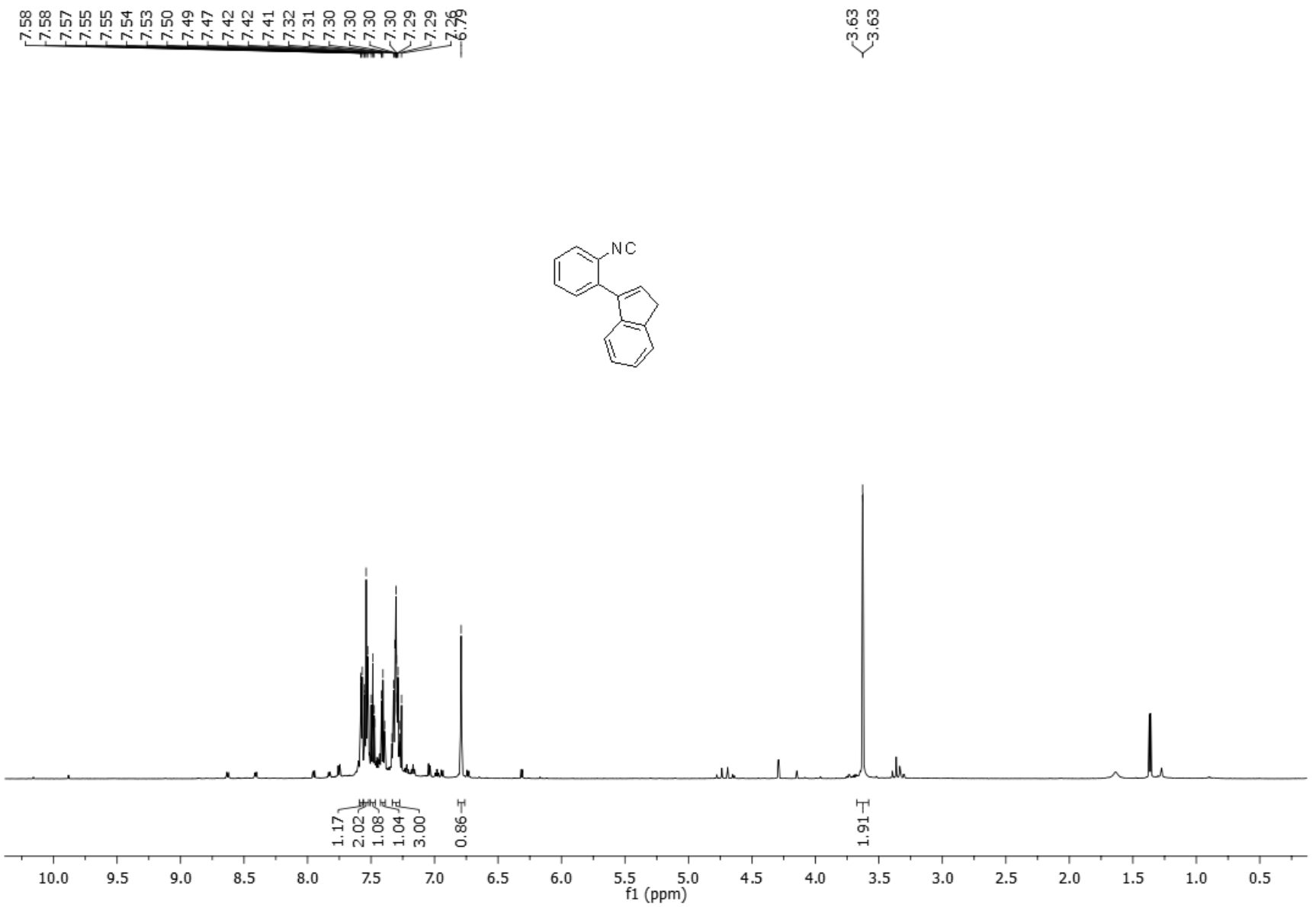
7.58
7.37
7.36
7.36
7.35
7.34
7.28
7.26
7.26
7.24
6.96
6.92
6.44
6.42
6.41
6.40
6.38
6.37
4.16
4.16
4.15
3.42
NC
CH2OMe
0.99
2.01
1.04
0.93
0.96
2.03
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


168.48
133.37
130.92
129.57
128.39
127.35
126.20
77.55
77.23
76.91
72.95
58.42
29.88
NC
CH2OMe
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

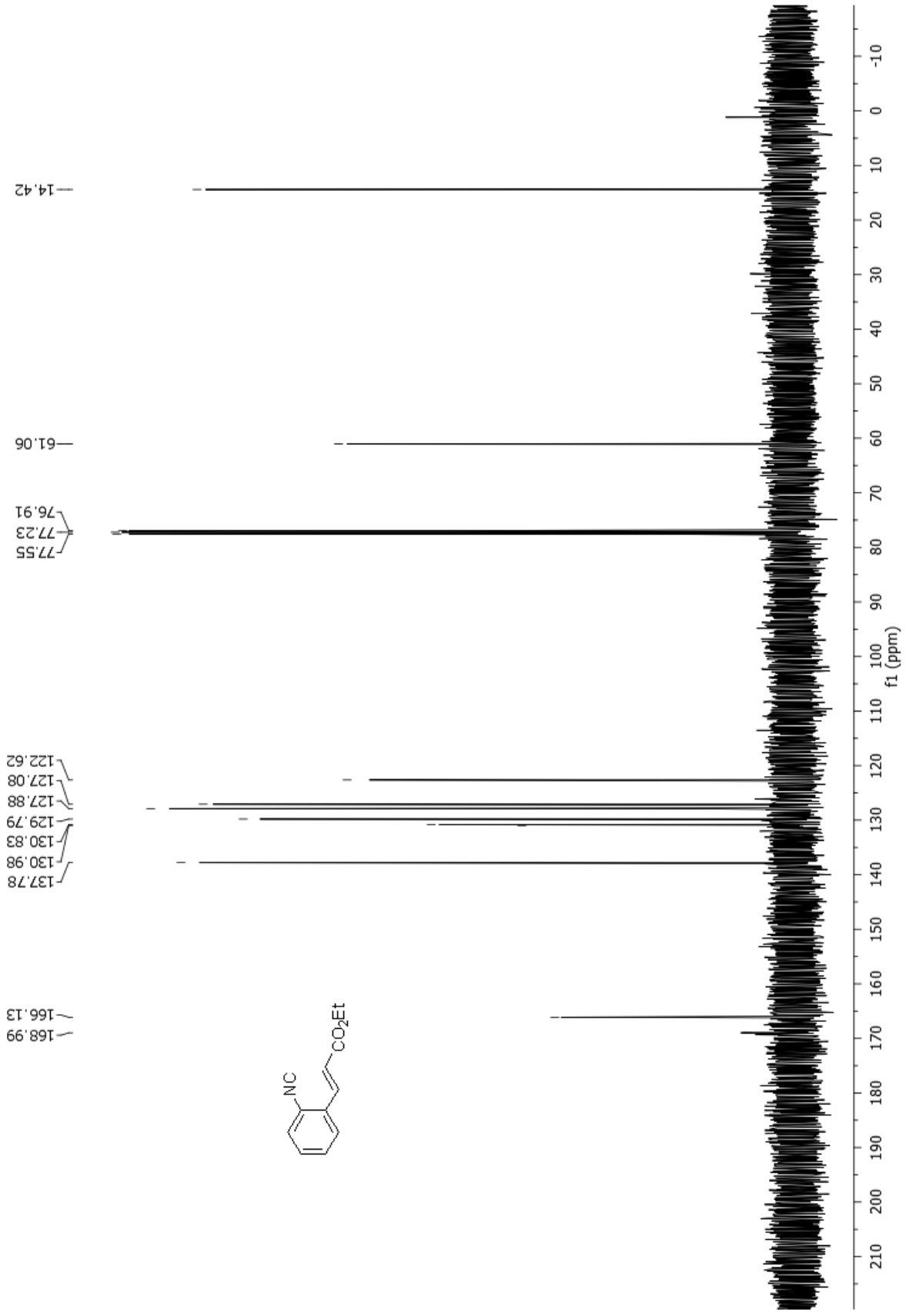

7.33
7.33
7.33
7.32
7.30
7.26
7.25
7.25
7.24
7.24
7.24
7.24
7.24
7.22
7.21
7.20
7.01
7.01
7.00
7.00
6.77
6.74
6.47
6.45
6.44
6.44
6.43
6.42
3.61
3.60
2.32
NC
DIPA to prevent acidic hydrolysis
DIPA to prevent acidic hydrolysis
3.07
3.94
1.01
0.97
1.00
2.13
3.24
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

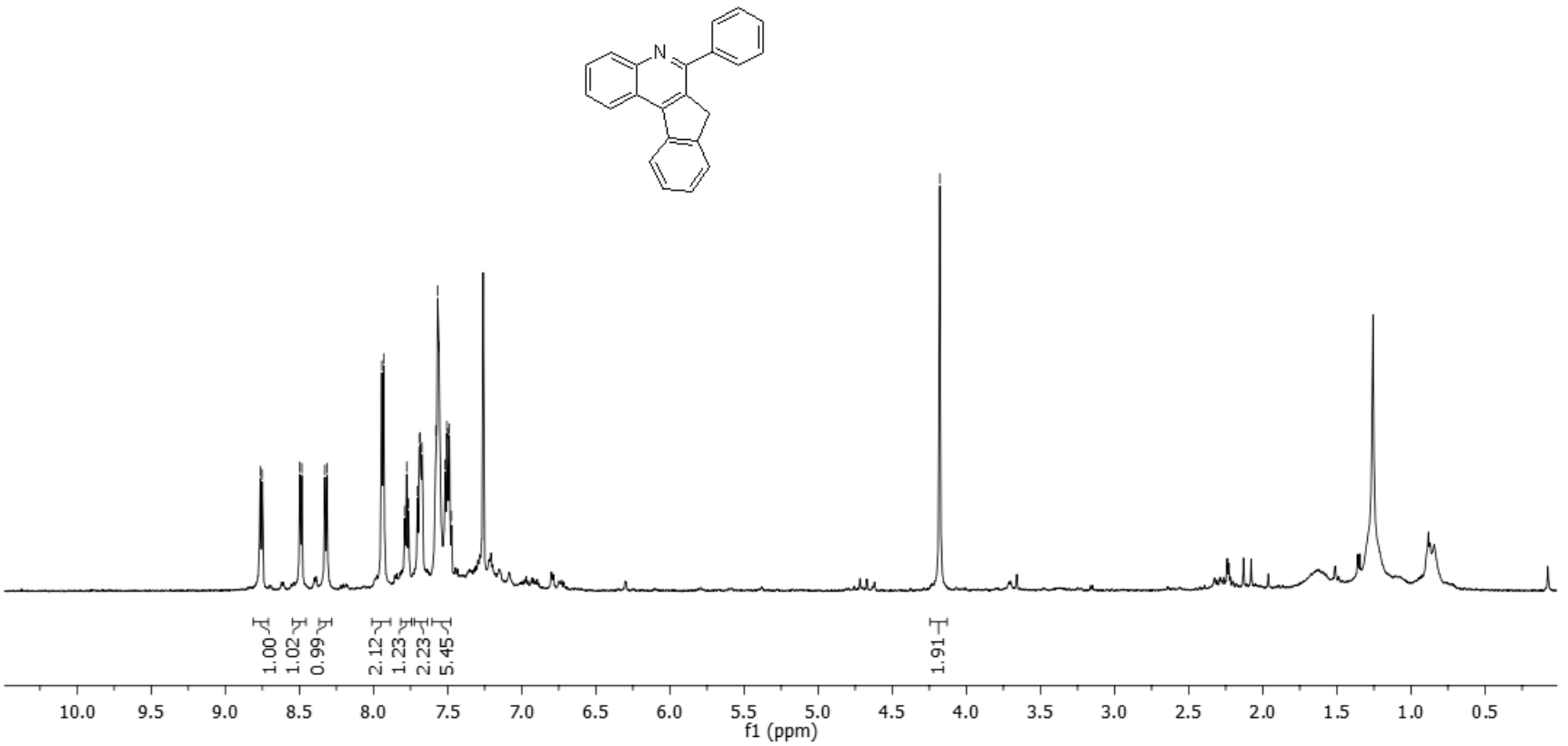

139.63
139.51
133.69
133.61
128.75
128.72
128.71
128.61
126.94
126.51
126.30
125.22
39.74
21.71
NC
DIPA to prevent acidic hydrolysis
DIPA to prevent acidic hydrolysis
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.58
7.58
7.57
7.55
7.55
7.54
7.53
7.50
7.49
7.47
7.42
7.42
7.41
7.32
7.31
7.30
7.30
7.30
7.30
7.29
7.29
7.26
6.79
3.63
3.63
NC
1.17
2.02
1.08
1.04
3.00
0.86
1.91
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

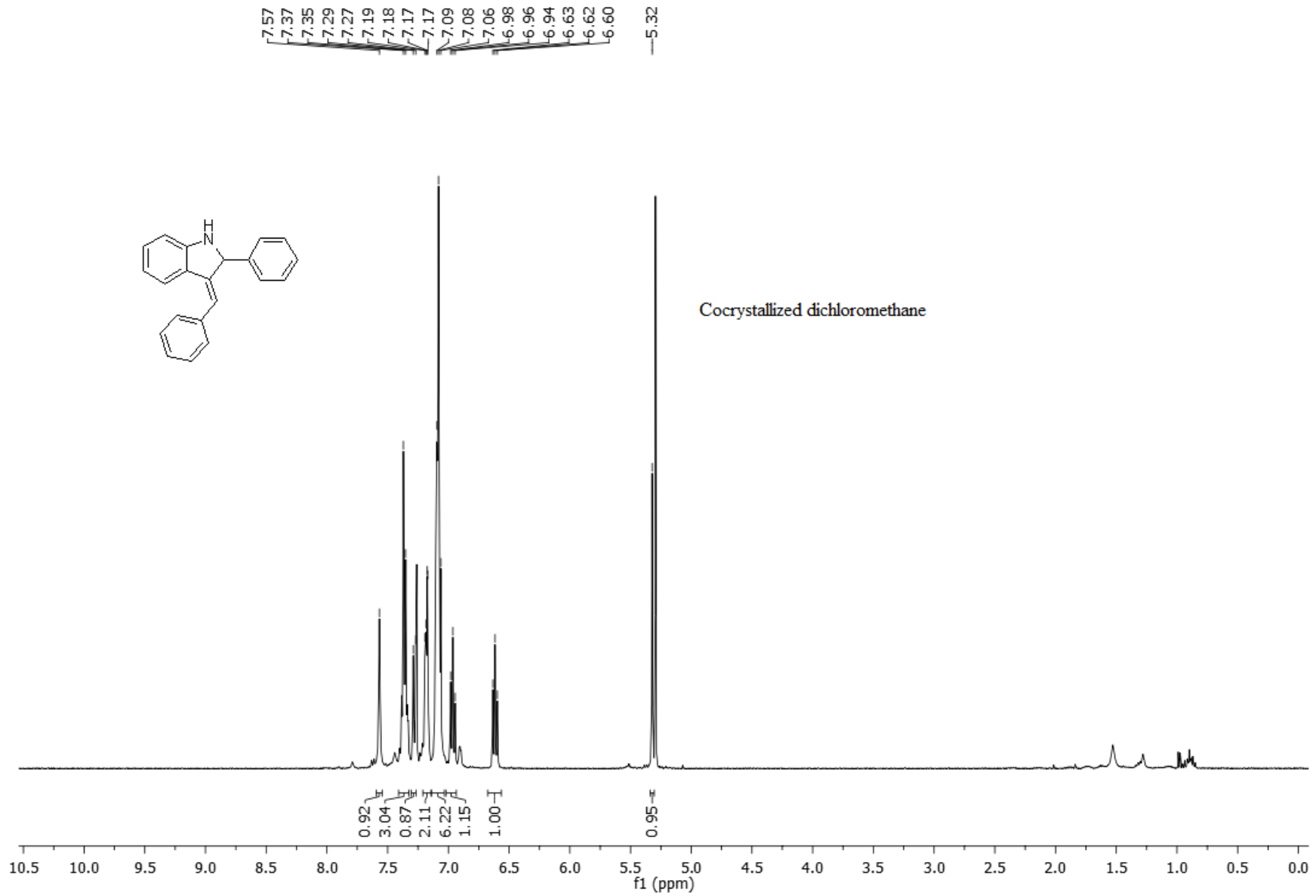
38.96
77.44
77.23
77.02
144.09
143.75
140.18
134.86
133.45
130.16
129.42
128.50
128.00
126.39
125.39
124.34
120.30
NC

1.31
1.32
1.33
1.33
1.34
4.24
4.26
4.28
4.29
6.49
6.53
7.26
7.39
7.39
7.40
7.40
7.40
7.41
7.41
7.42
7.43
7.43
7.63
7.63
7.64
7.64
7.65
7.65
7.66
7.92
7.96
NC
CO2Et
3.44
2.17
1.00
0.97
1.05
2.95
f1 (ppm)

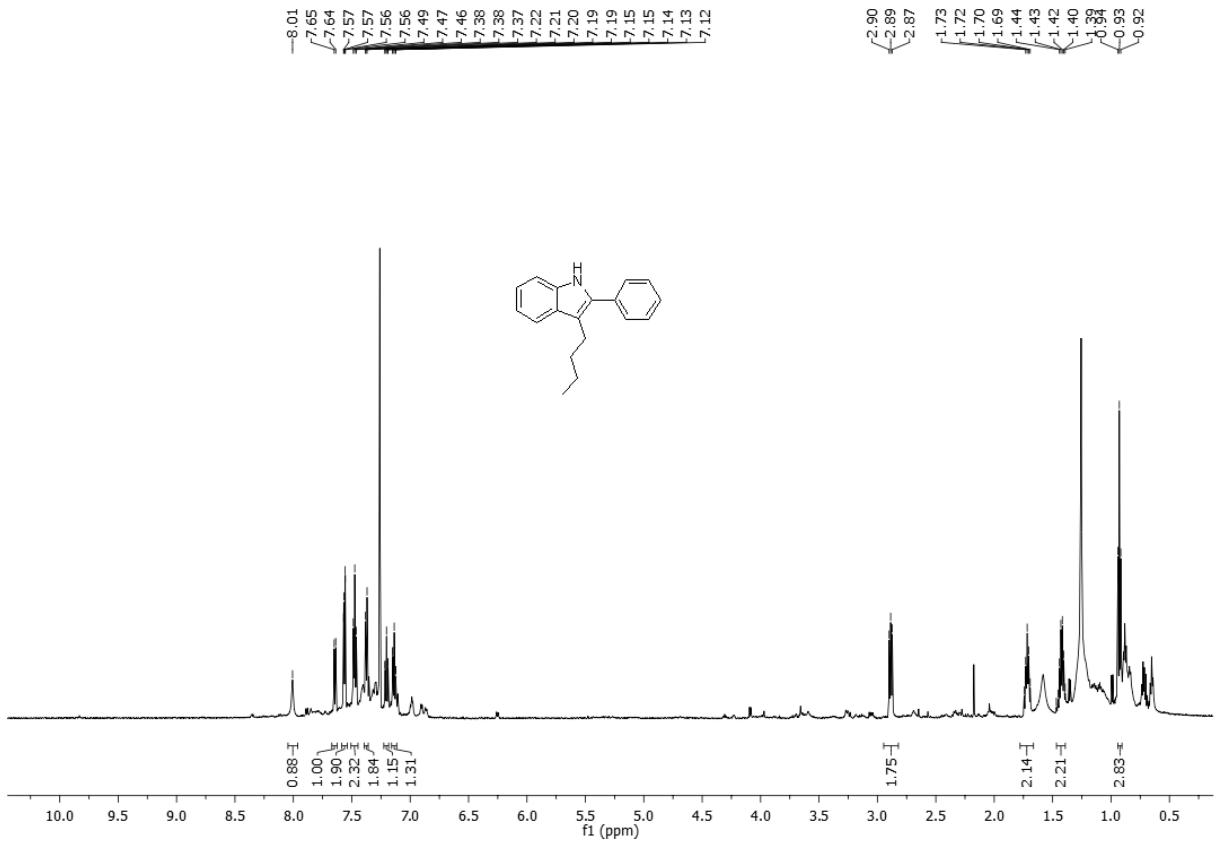

168.99
166.13
137.78
130.98
130.83
129.79
127.88
127.08
122.62
77.55
77.23
76.91
61.06
14.42
NC
CO2Et
f1 (ppm)

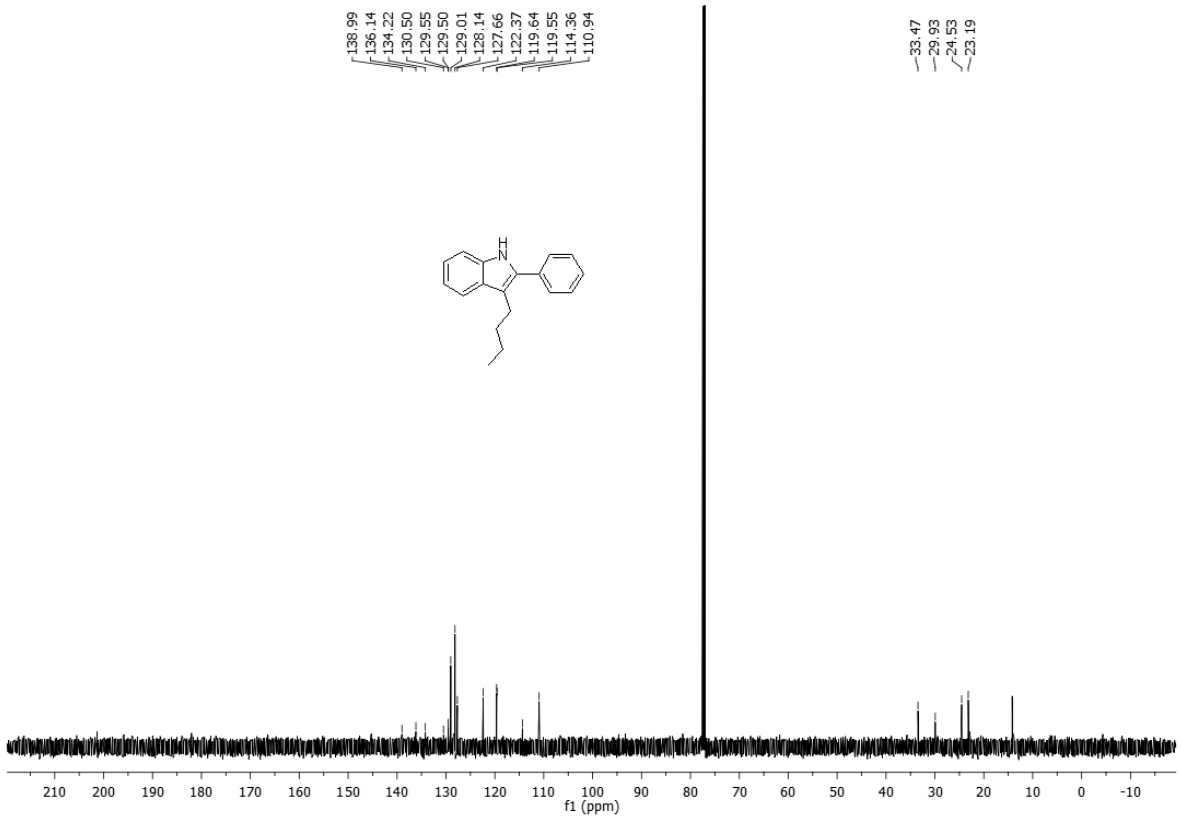

N
1.00
1.02
0.99
2.12
1.23
2.23
5.45
1.91
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

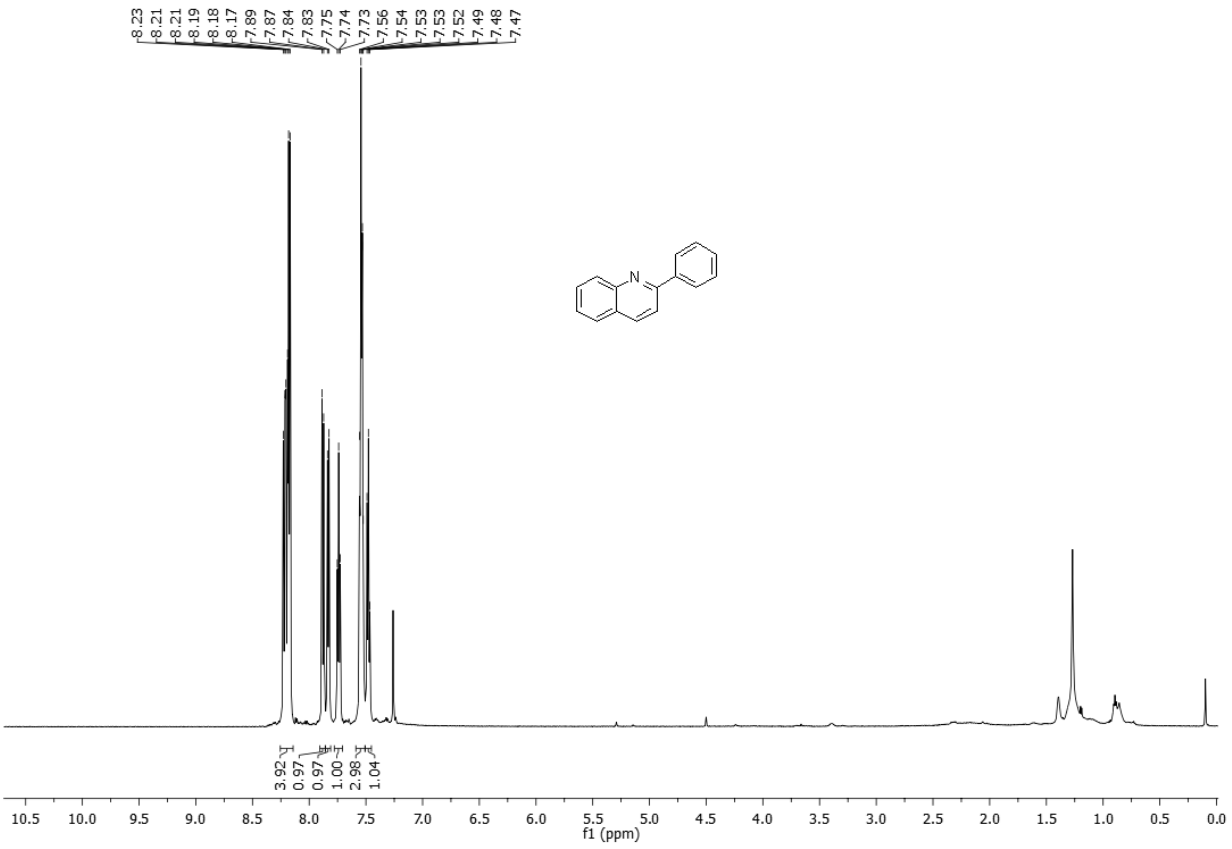
37.90
156.54
148.54
145.74
145.27
141.00
140.62
134.58
130.93
129.03
128.99
128.91
128.82
128.41
127.53
126.84
125.36
124.55
124.16
123.67
N
f1 (ppm)

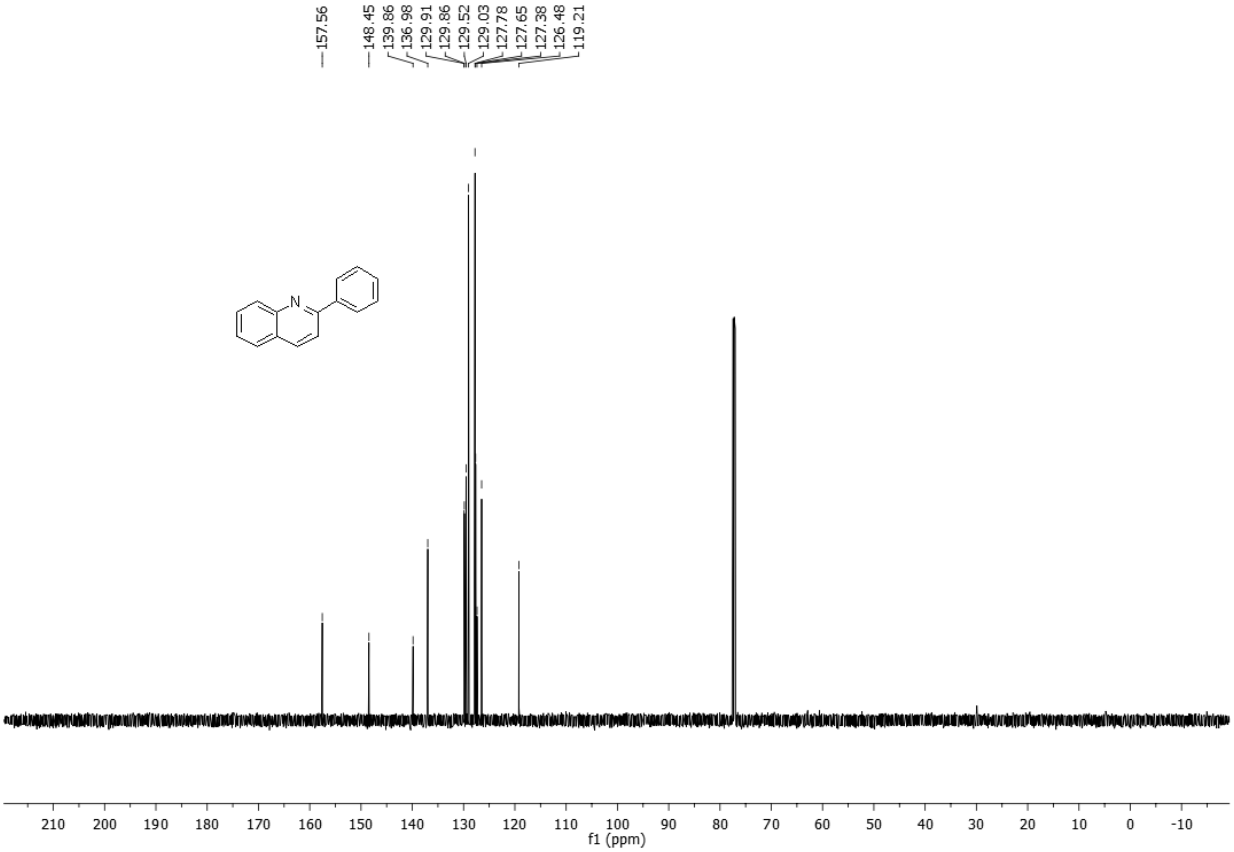

7.57
7.37
7.35
7.29
7.27
7.19
7.18
7.17
7.17
7.09
7.08
7.06
6.98
6.96
6.94
6.63
6.62
6.60
5.32
Cocrystallized dichloromethane
0.92
3.04
0.87
2.11
6.22
1.15
1.00
0.95
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

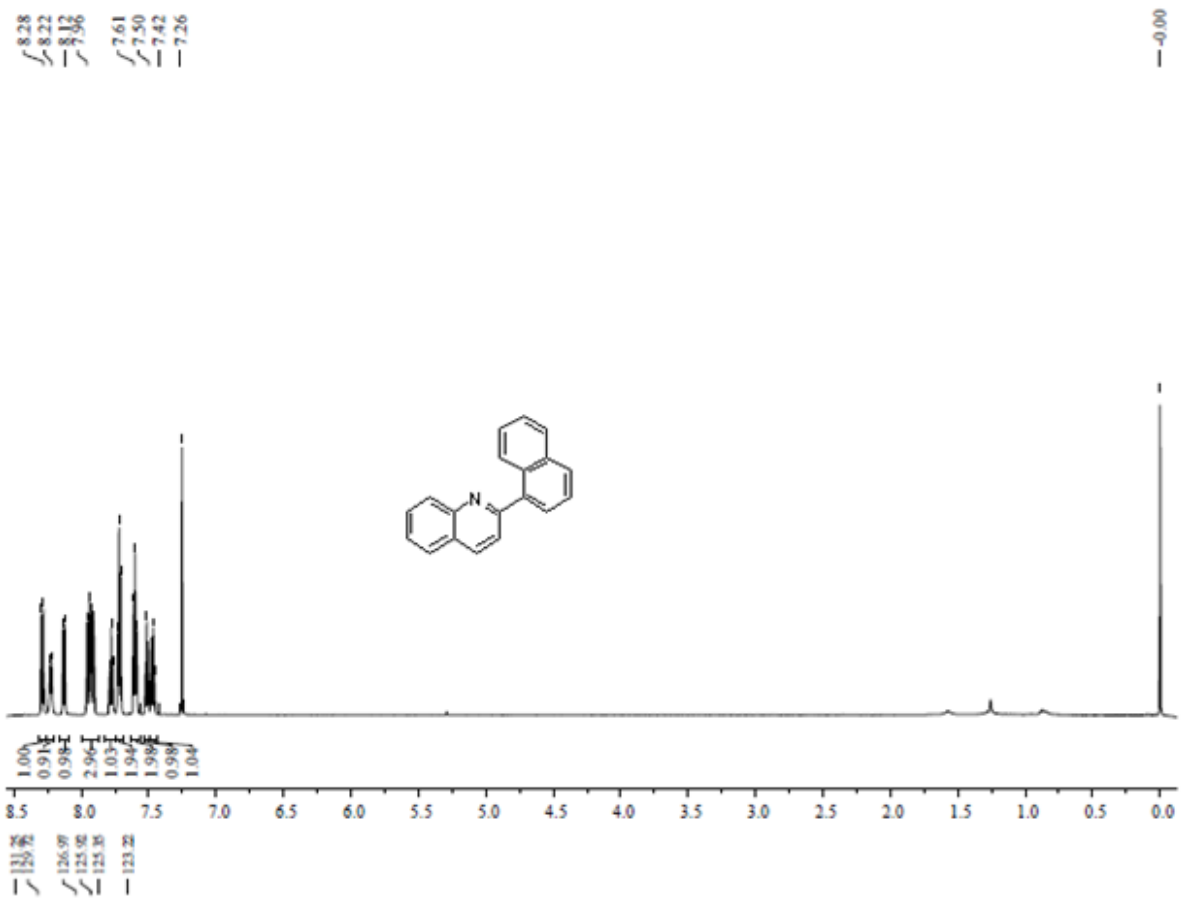
50.01
145.69
135.94
133.47
129.47
129.28
128.50
128.31
128.01
127.83
125.76
122.09
122.03
121.12
119.40
114.98
110.43
NH
f1 (ppm)

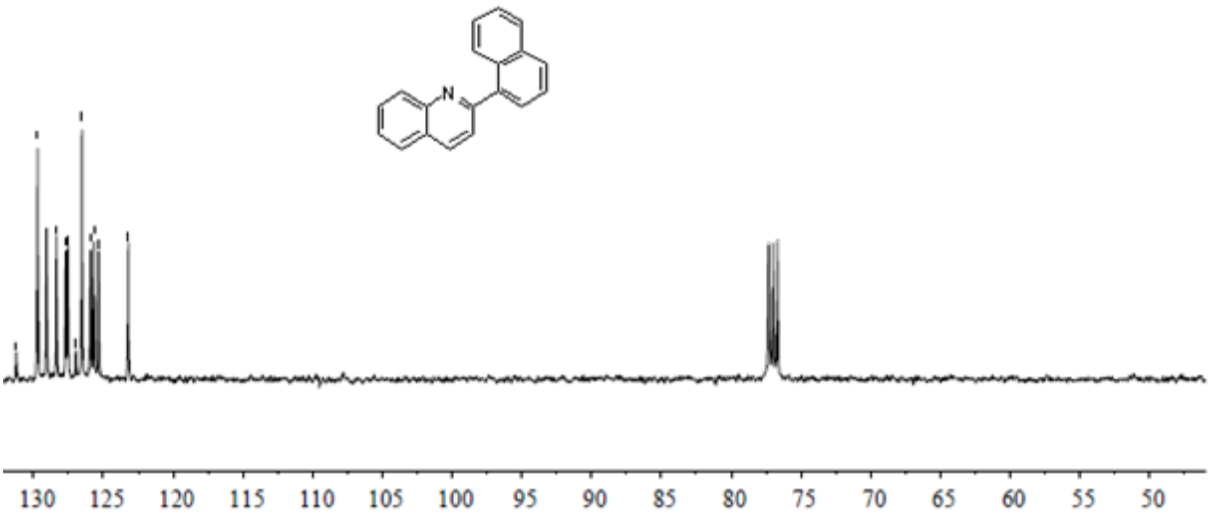

8.01
7.65
7.64
7.57
7.57
7.56
7.56
7.49
7.47
7.46
7.38
7.38
7.37
7.22
7.21
7.20
7.19
7.19
7.15
7.15
7.14
7.13
7.12
2.90
2.89
2.87
1.73
1.72
1.70
1.69
1.44
1.43
1.42
1.40
1.39
0.94
0.93
0.92
0.88
1.00
1.90
2.32
1.84
1.15
1.31
1.75
2.14
2.21
2.83
f1 (ppm)

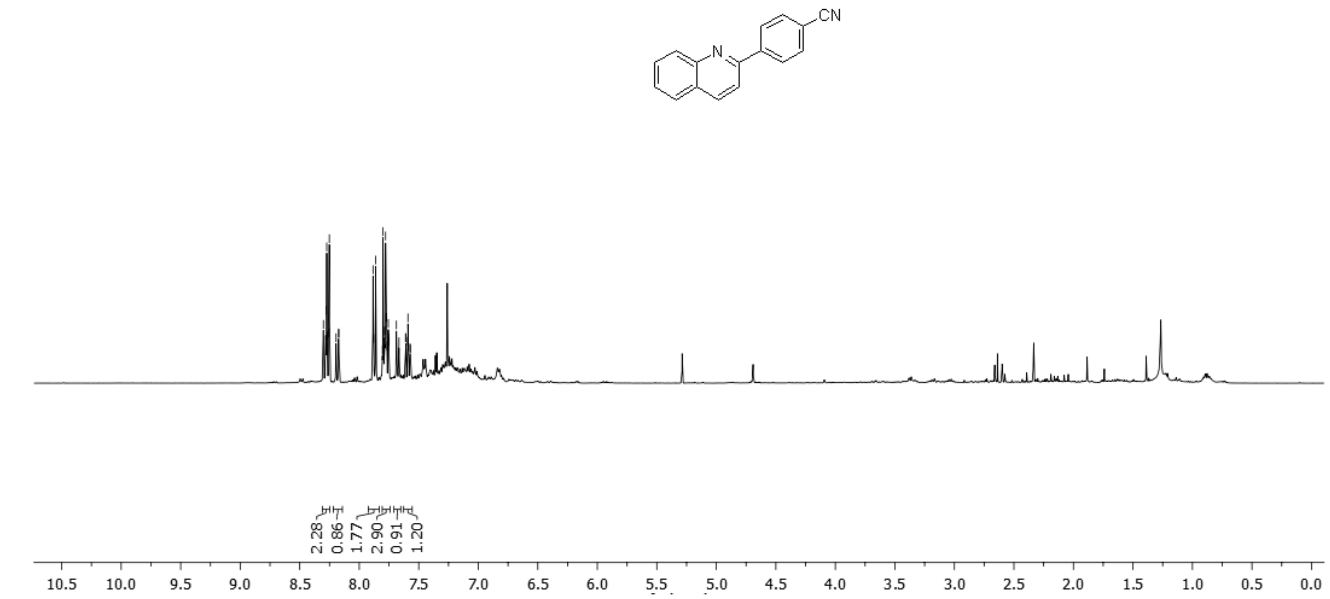

138.99
136.14
134.22
130.50
129.55
129.50
129.01
128.14
127.66
122.37
119.64
119.55
114.36
110.94
33.47
29.93
24.53
23.19
f1 (ppm)

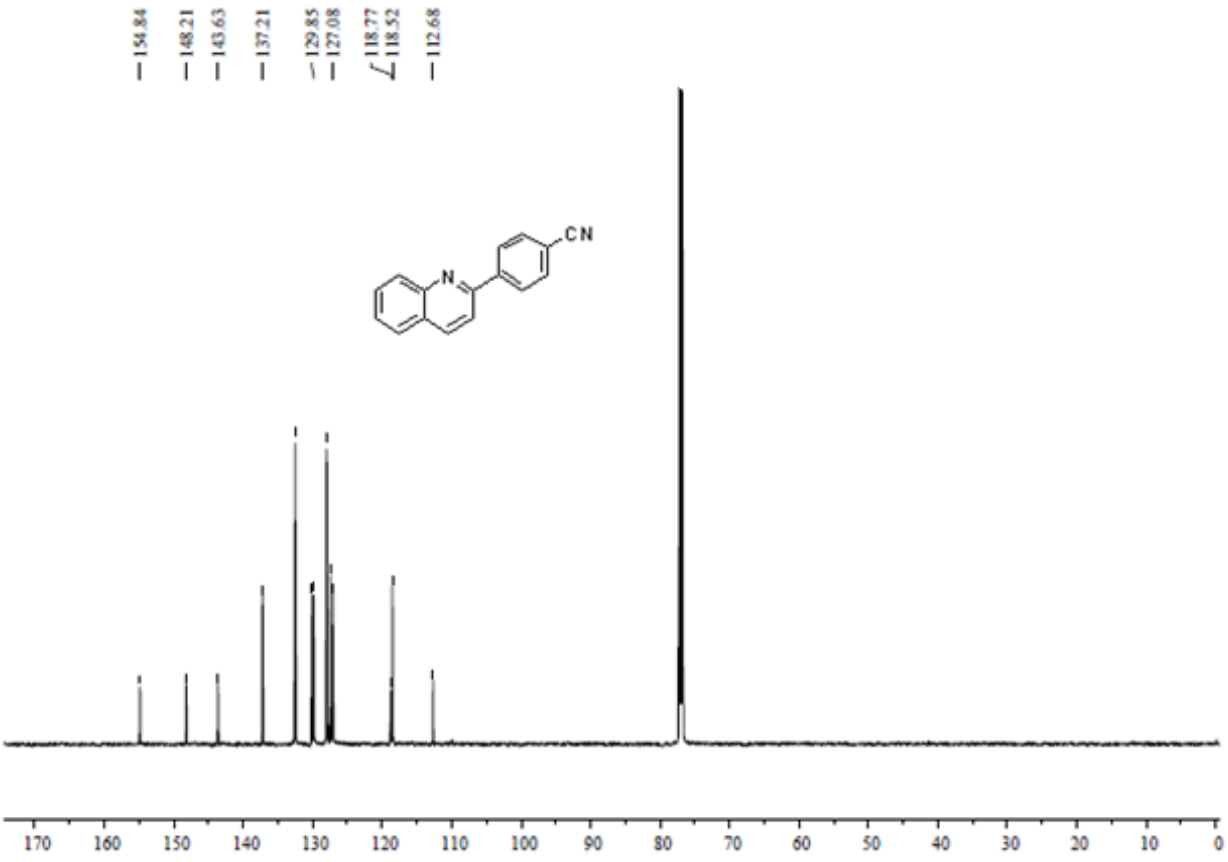

8.23
8.21
8.21
8.19
8.18
8.17
7.89
7.87
7.84
7.83
7.75
7.74
7.73
7.56
7.54
7.53
7.53
7.52
7.49
7.48
7.47
3.92
0.97
0.97
1.00
2.98
1.04
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
N

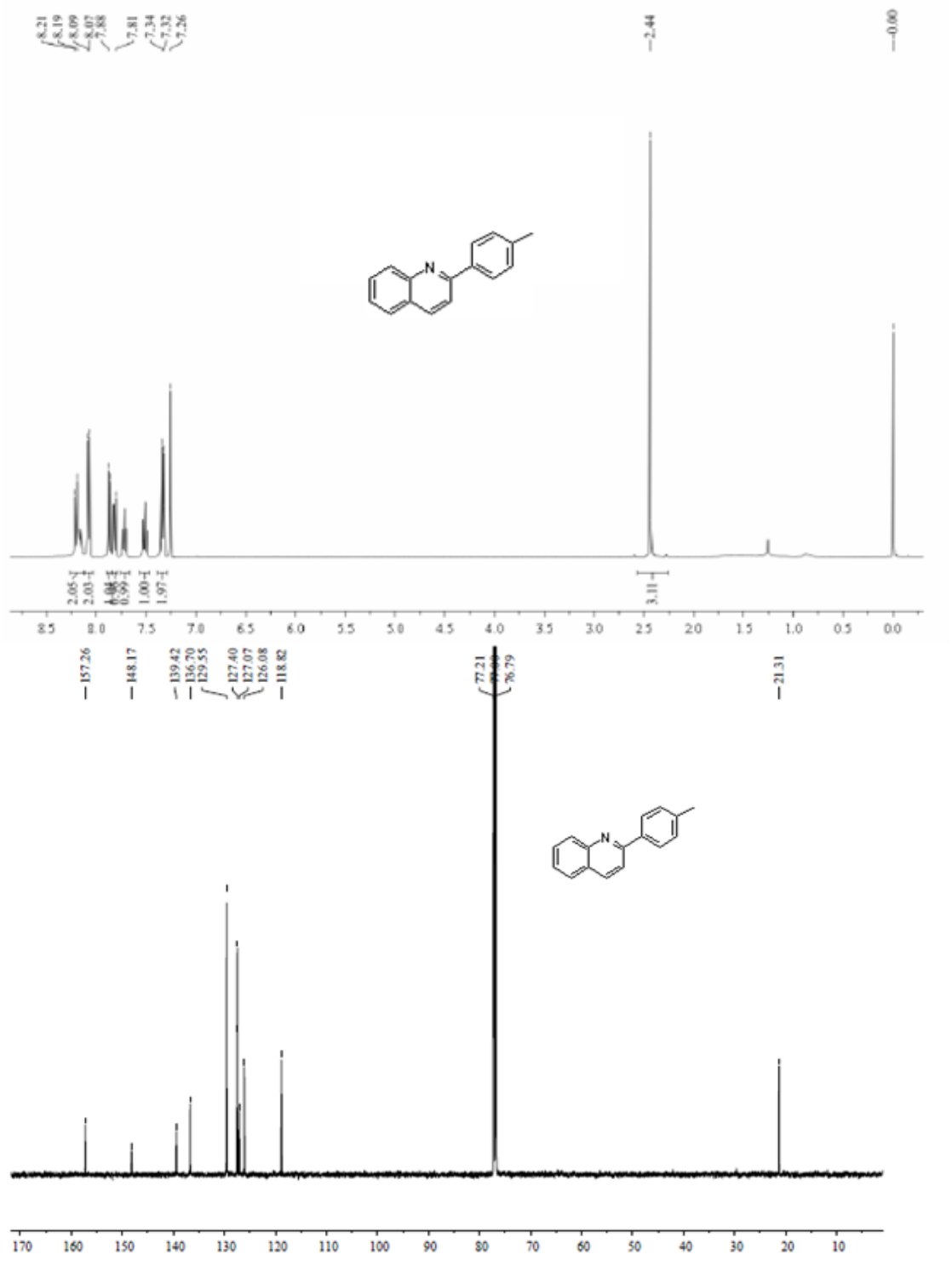

157.56
148.45
139.86
136.98
129.91
129.86
129.52
129.03
127.78
127.65
127.38
126.48
119.21
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
N

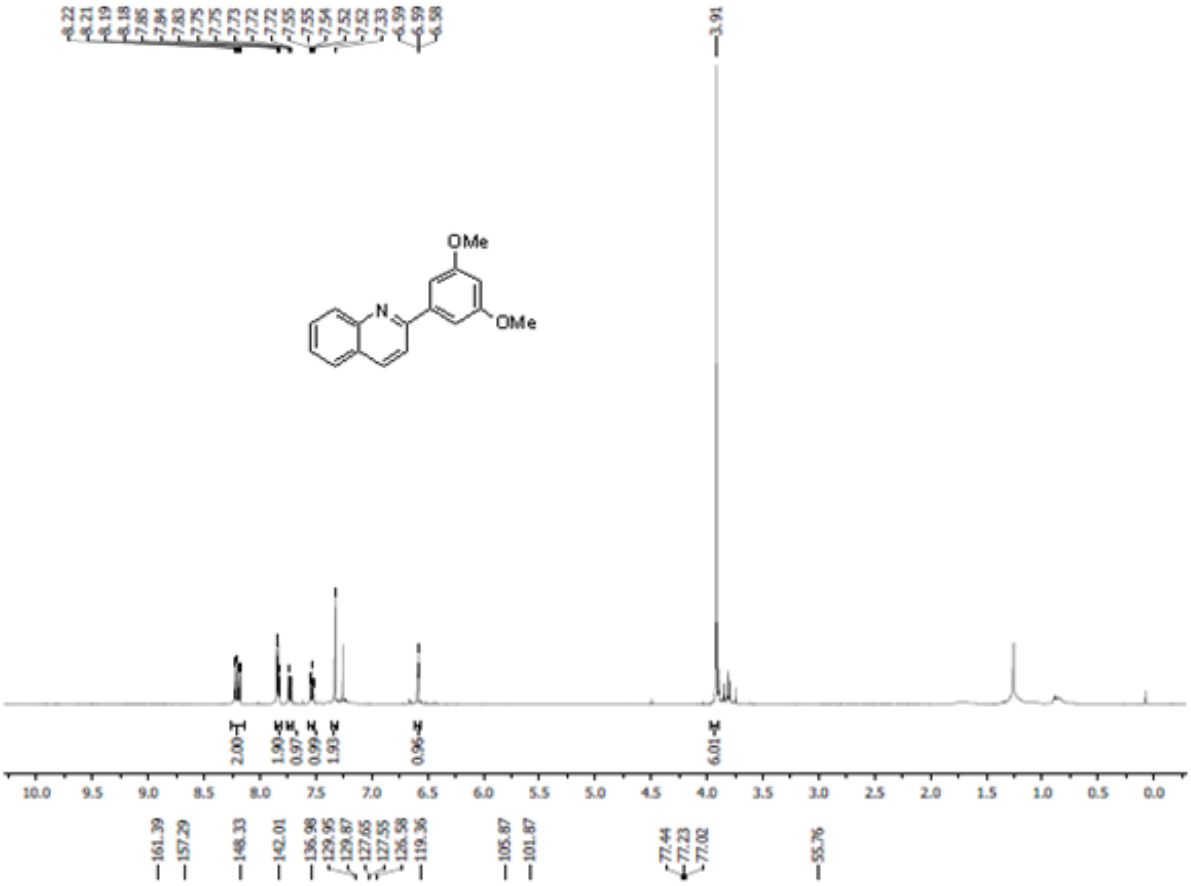

8.28
8.22
8.12
7.96
7.61
7.50
7.42
7.26
0.00
1.00
0.91
0.98
2.96
1.03
1.94
1.98
0.98
1.04
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
131.76
129.62
126.97
125.98
125.85
123.22

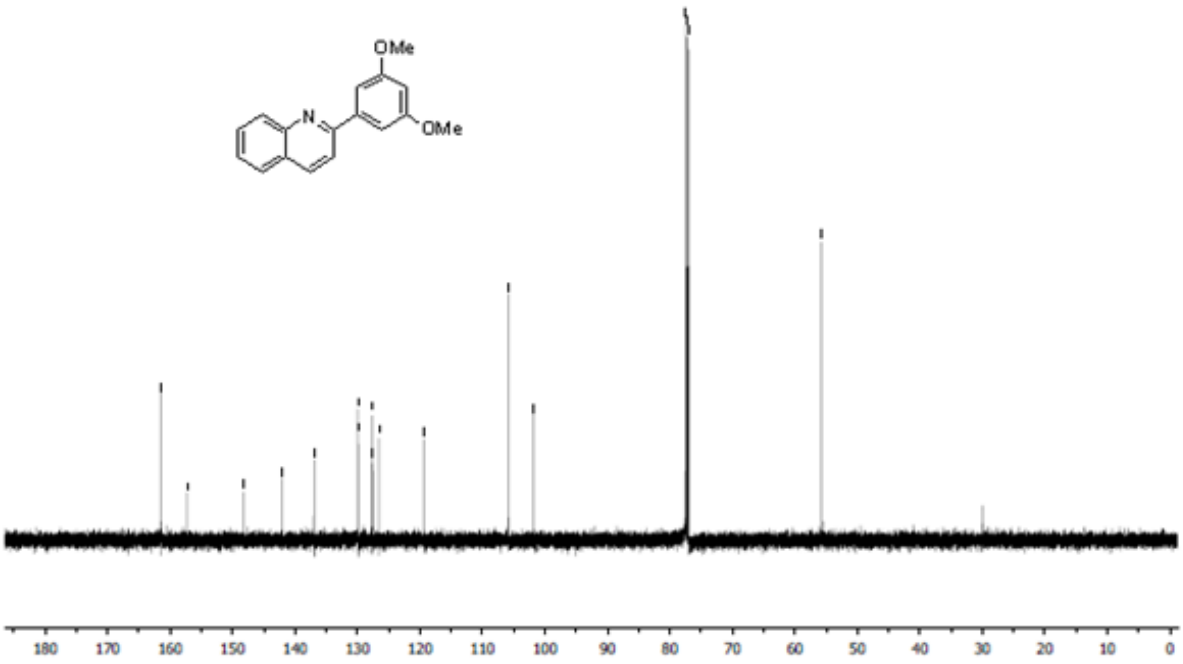

130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50

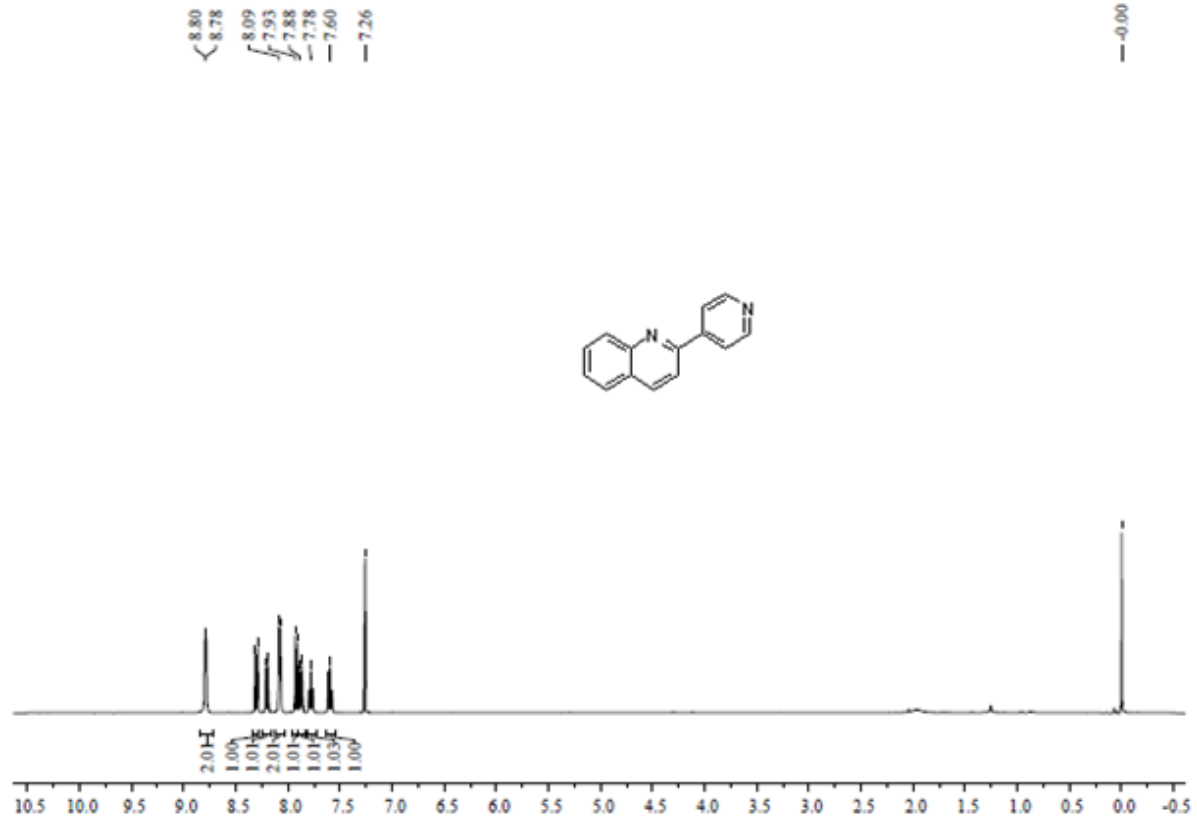

CN
N
2.28
0.86
1.77
2.90
0.91
1.20
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

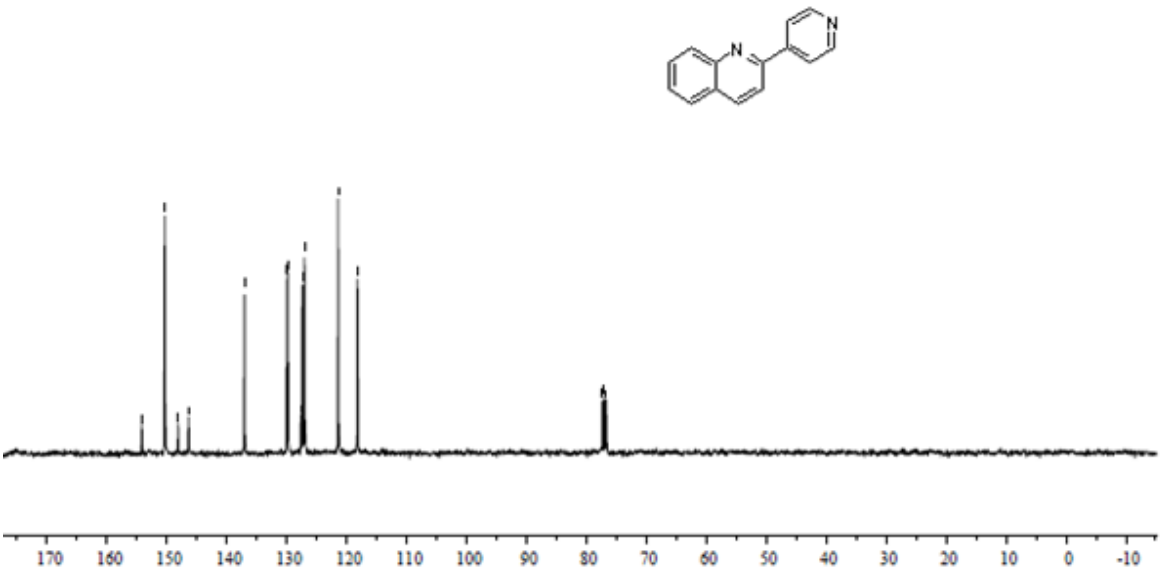

154.84
148.21
143.63
137.21
129.85
127.08
118.77
118.52
112.68
CN
N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


8.21
8.19
8.09
8.07
7.88
7.81
7.34
7.32
7.26
2.44
0.00
2.05
2.03
1.00
1.97
3.11
157.26
148.17
139.42
136.70
129.55
127.40
127.07
126.08
118.82
77.21
76.79
21.31

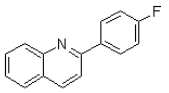

8.22
8.21
8.19
8.18
7.85
7.84
7.83
7.75
7.75
7.73
7.72
7.72
7.55
7.55
7.54
7.52
7.52
7.33
6.59
6.59
6.58
3.91
OMe
OMe
N
2.00
1.90
0.97
0.99
1.93
0.96
6.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

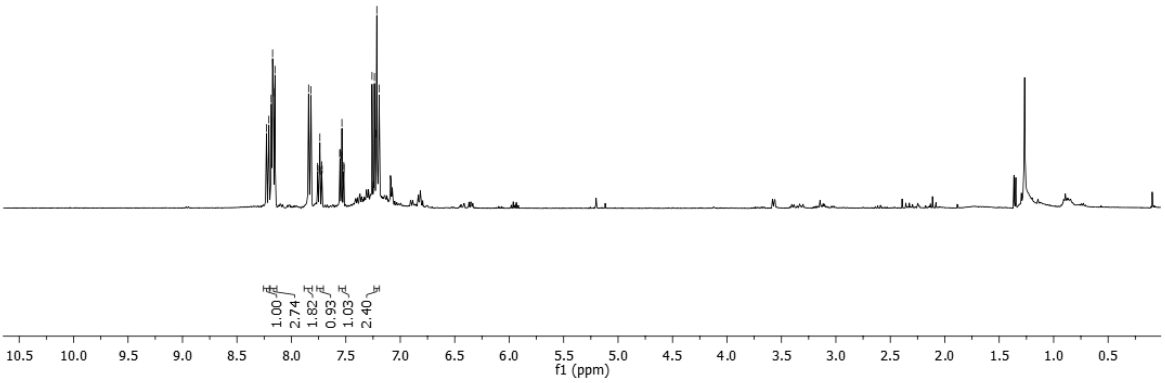

161.39
157.29
148.33
142.01
136.98
129.95
129.87
127.65
127.55
126.58
119.36
105.87
101.87
77.44
77.23
77.02
55.76
OMe
OMe
N
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

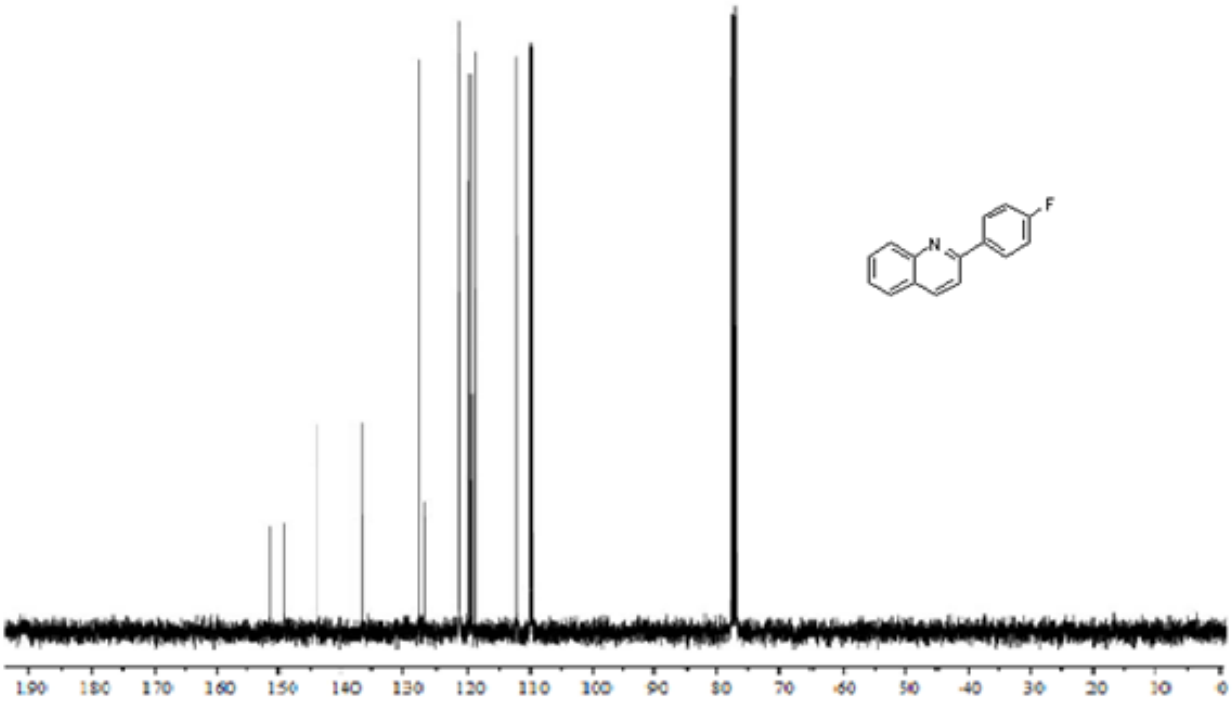

8.80
8.78
8.09
7.93
7.88
7.78
7.60
7.26
0.00
2.01
1.00
1.01
1.01
2.01
1.01
1.01
1.03
1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5


154.15
150.30
148.06
146.35
137.03
129.89
127.00
121.38
118.15
77.31
76.99
76.67
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

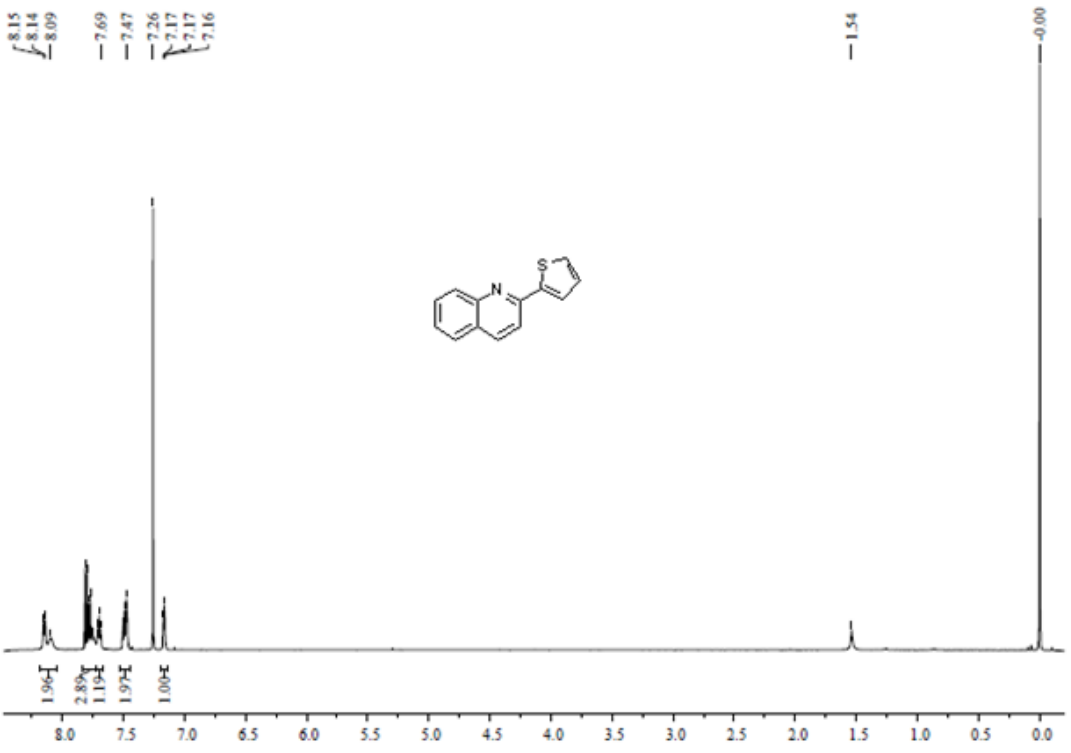

8.23
8.21
8.19
8.17
8.16
8.16
8.15
7.84
7.82
7.76
7.76
7.74
7.74
7.73
7.72
7.72
7.56
7.55
7.54
7.54
7.53
7.52
7.52
7.26
7.24
7.22
7.22
7.19

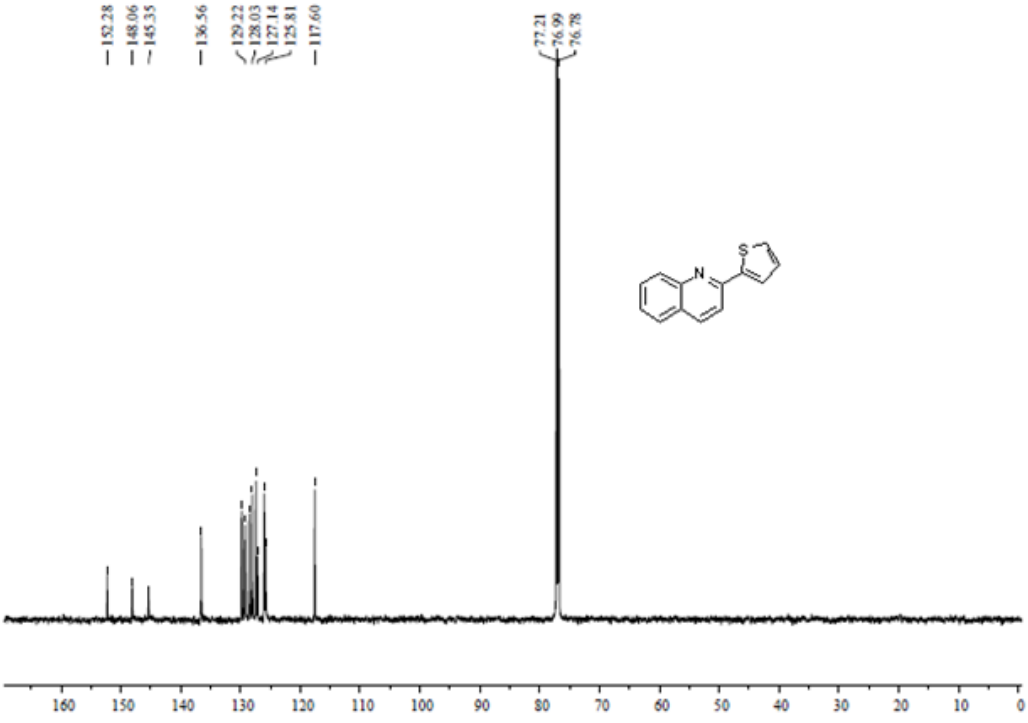

N
F


1.00
2.74
1.82
0.93
1.03
2.40
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

N
F


8.15
8.14
8.09
7.69
7.47
7.26
7.17
7.17
7.16
1.54
0.00
1.96
2.89
1.19
1.97
1.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
N
S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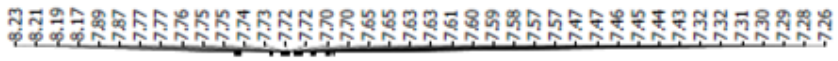
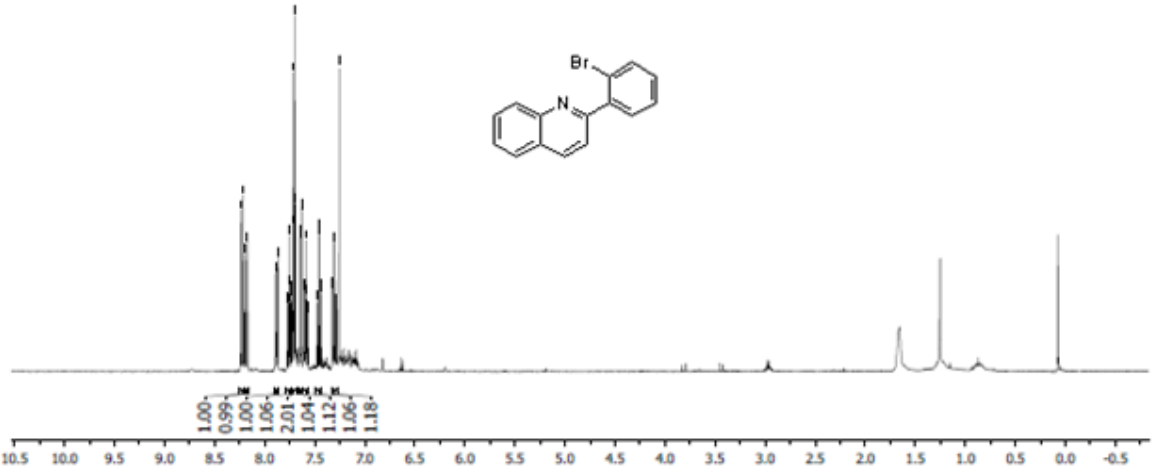
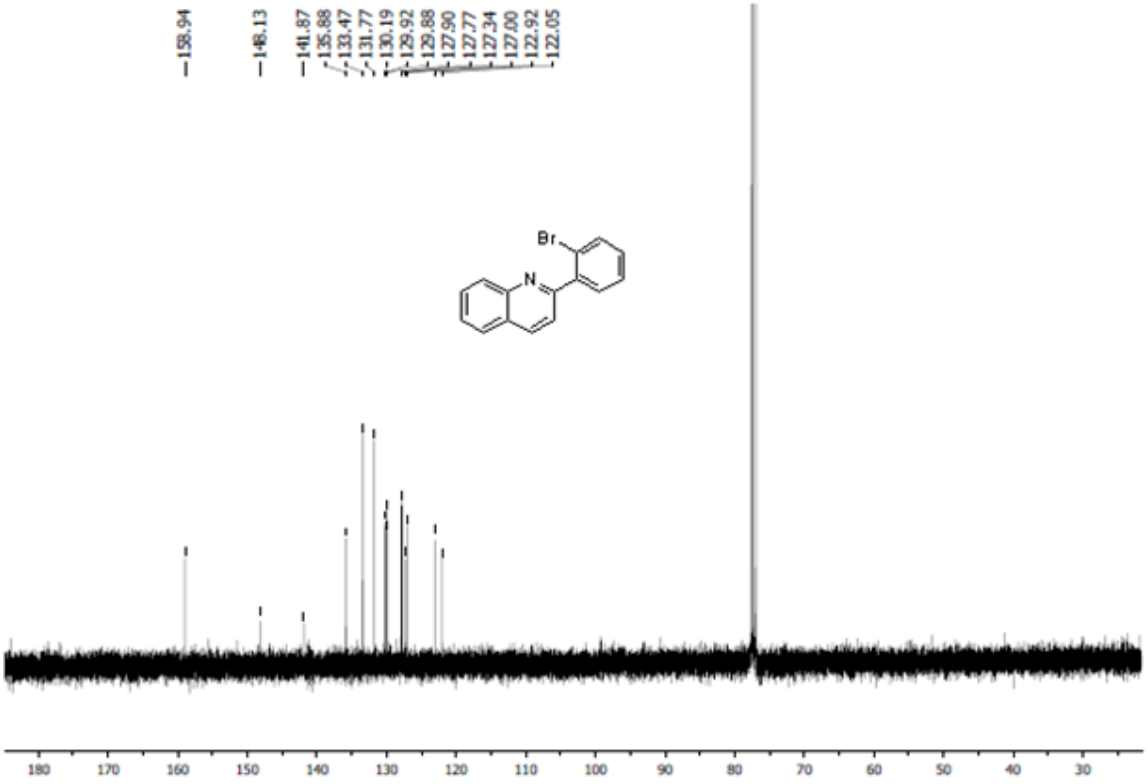
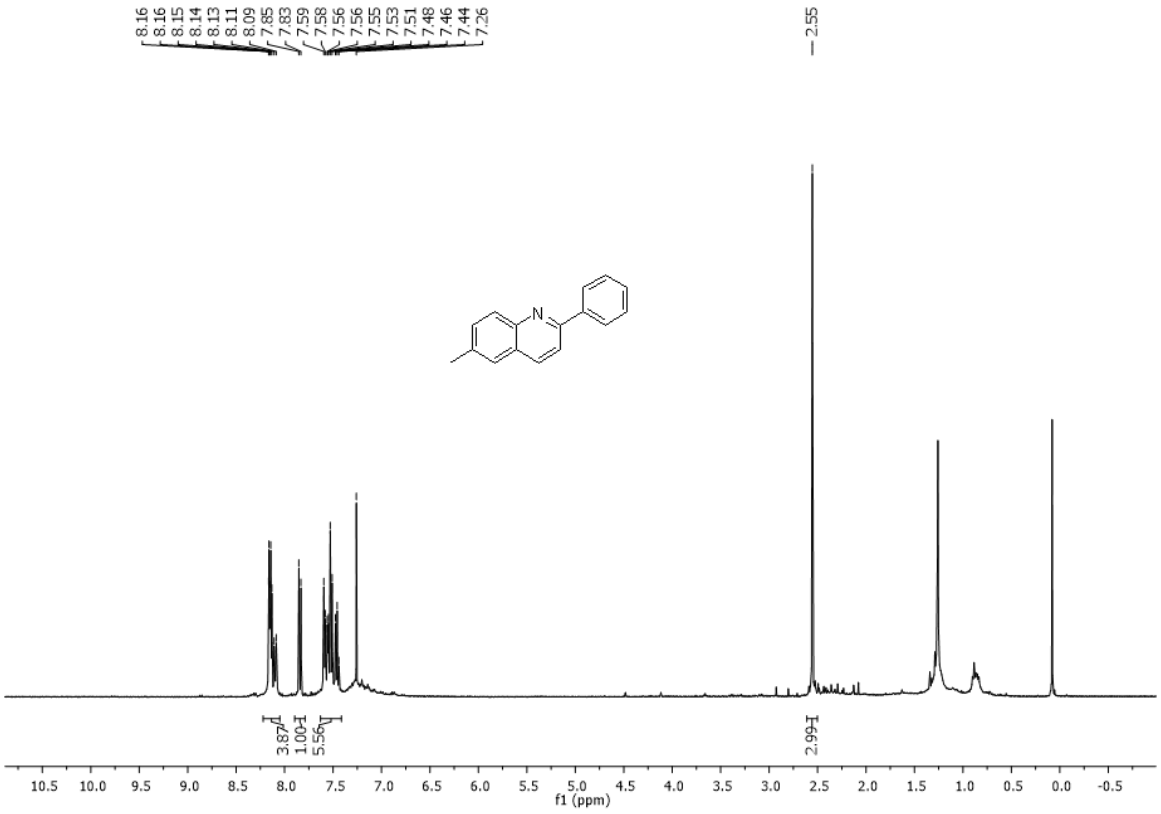
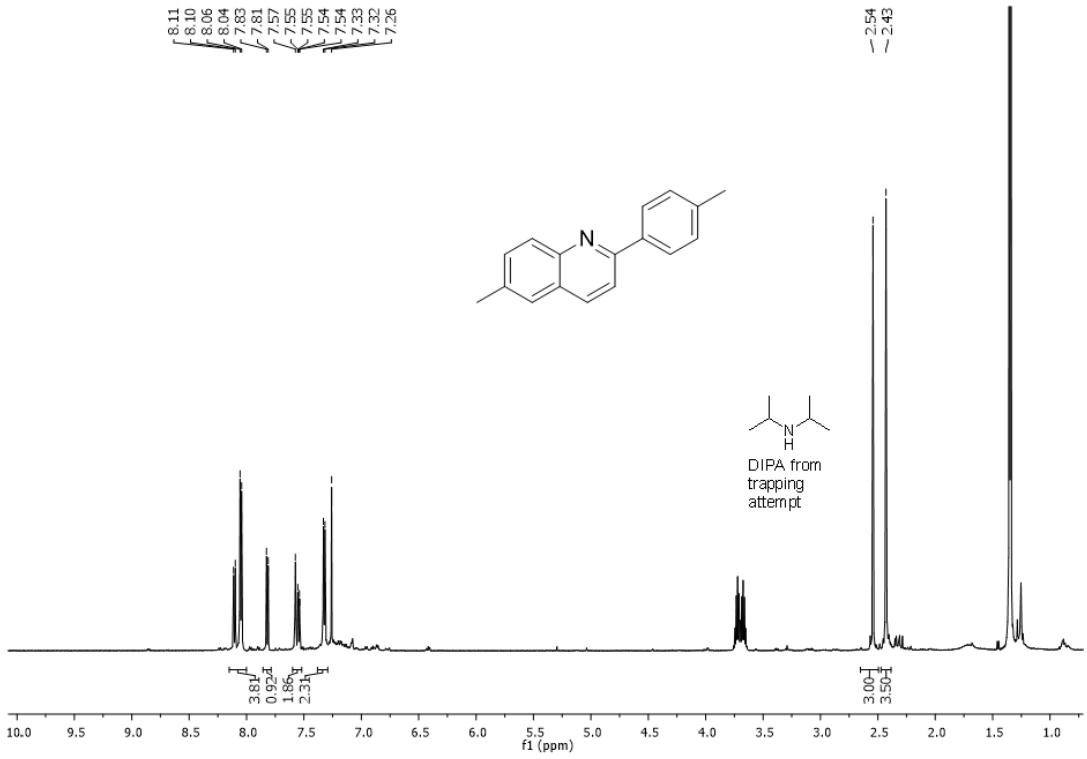
148.06
145.35
136.56
129.22
128.03
127.14
125.81
117.60
77.21
76.99
76.78
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
N
S

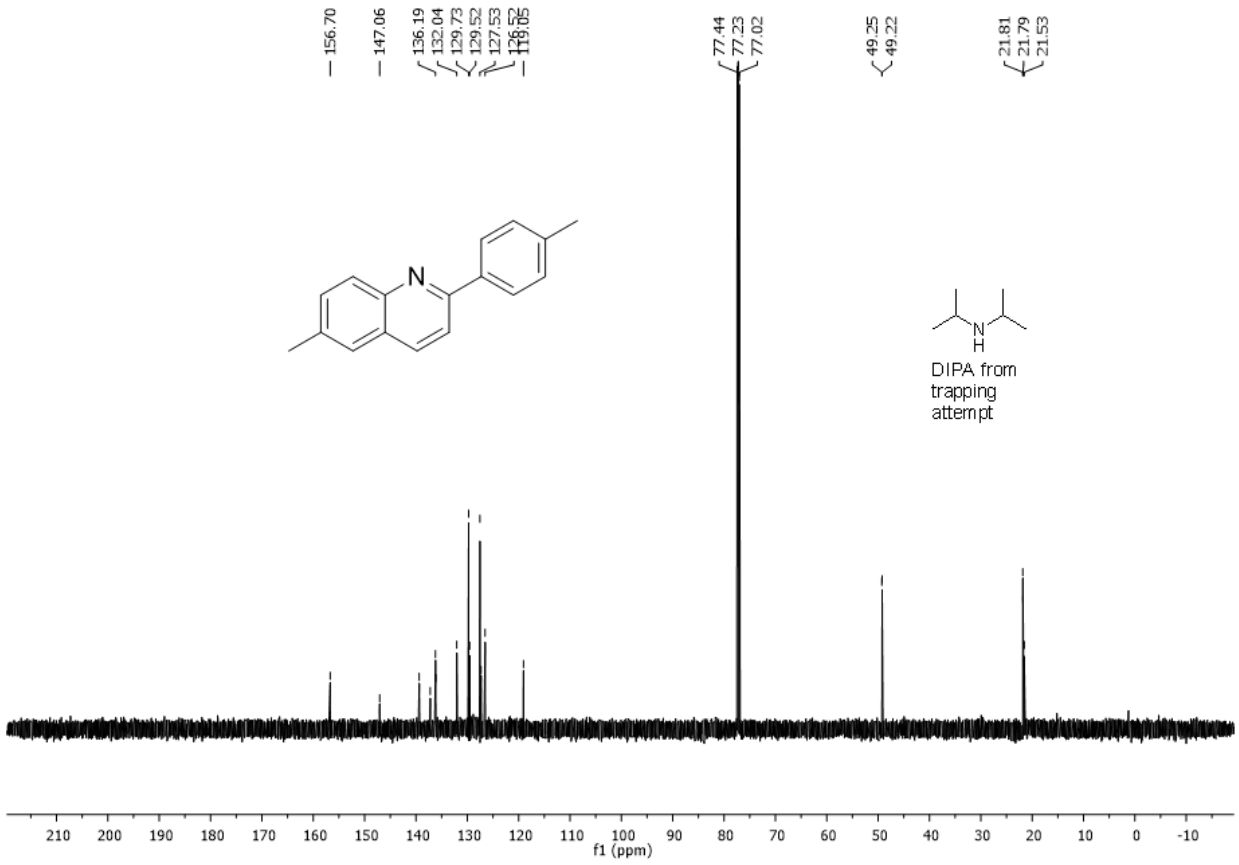

8.23
8.21
8.19
8.17
7.89
7.87
7.77
7.77
7.76
7.75
7.75
7.74
7.73
7.72
7.72
7.70
7.70
7.65
7.65
7.63
7.63
7.61
7.60
7.59
7.58
7.57
7.57
7.47
7.47
7.46
7.45
7.44
7.43
7.32
7.32
7.31
7.30
7.29
7.28
7.26

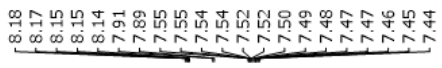

Br
N
1.00
0.99
1.00
1.06
2.01
1.04
1.12
1.06
1.18
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


158.94
148.13
141.87
135.88
133.47
131.77
130.19
129.92
129.88
127.90
127.77
127.34
127.00
122.92
122.05
Br
N
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30


8.16
8.16
8.15
8.14
8.13
8.11
8.09
7.85
7.83
7.59
7.58
7.56
7.56
7.55
7.53
7.51
7.48
7.46
7.44
7.26
2.55
N
3.87
1.00
5.56
2.99
f1 (ppm)


8.11
8.10
8.06
8.04
7.83
7.81
7.57
7.55
7.55
7.54
7.54
7.33
7.32
7.26
2.54
2.43
N
N
H
DIPA from
trapping
attempt
3.81
0.92
1.86
2.31
3.00
3.50
f1 (ppm)


156.70
147.06
136.19
132.04
129.73
129.52
127.53
126.52
119.05
77.44
77.23
77.02
49.25
49.22
21.81
21.79
21.53
N
N
H
DIPA from trapping attempt
f1 (ppm)


8.18
8.17
8.15
8.15
8.14
7.91
7.89
7.55
7.55
7.54
7.54
7.52
7.52
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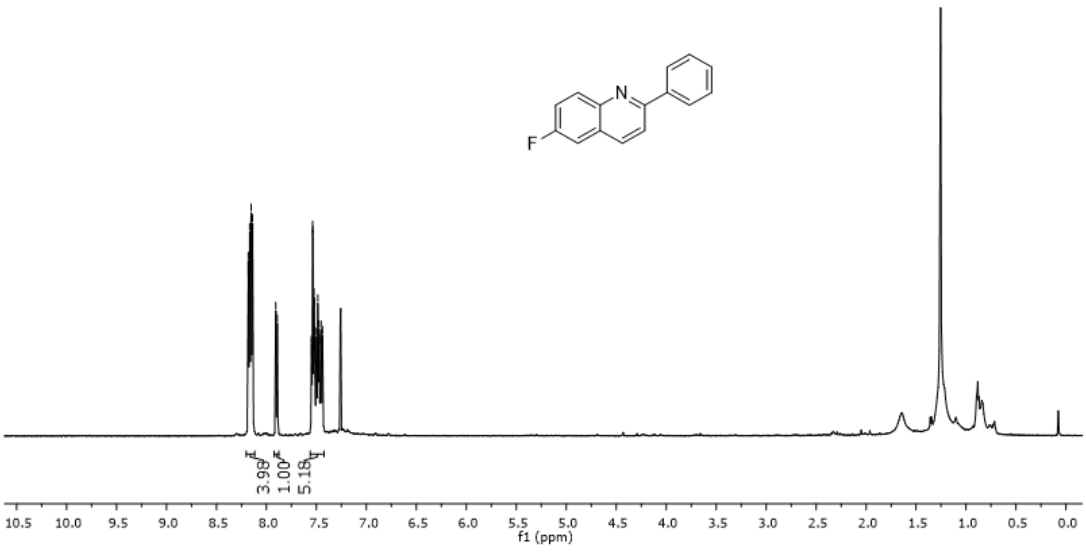
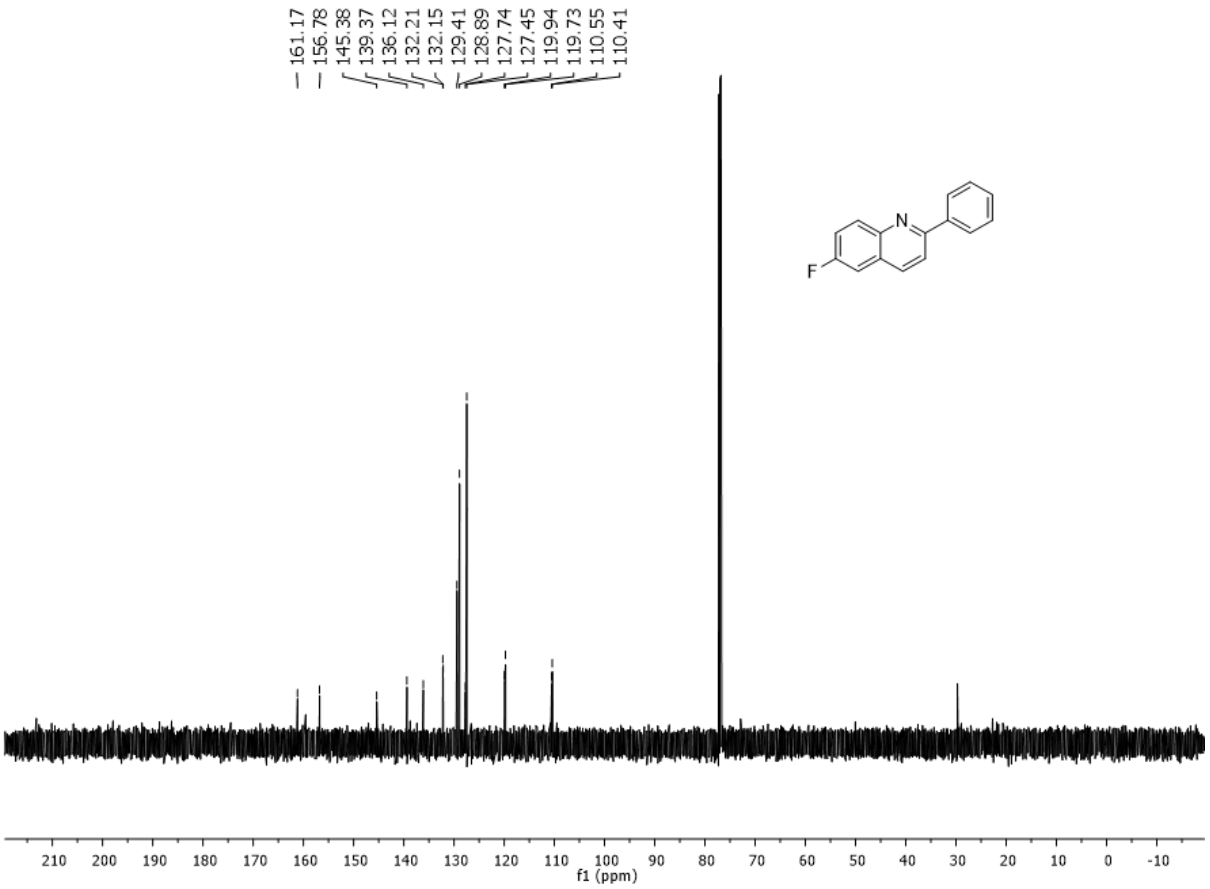
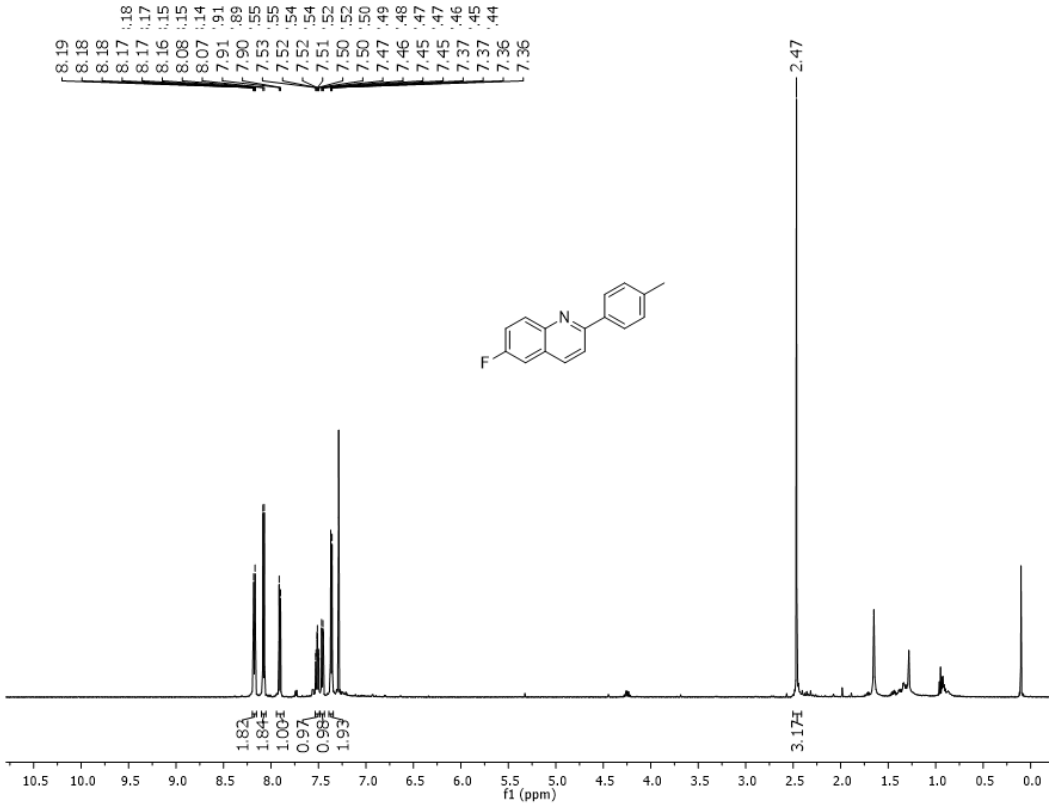
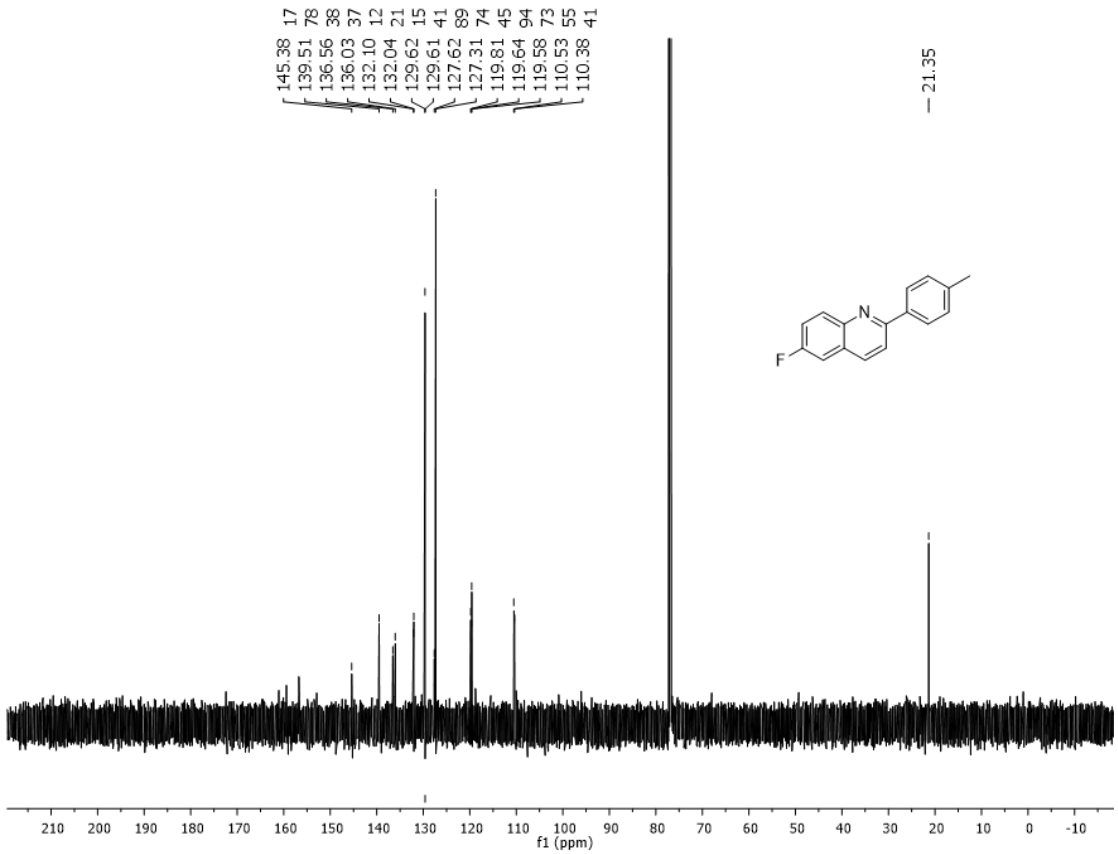
7.48
7.47
7.47
7.46
7.45
7.44

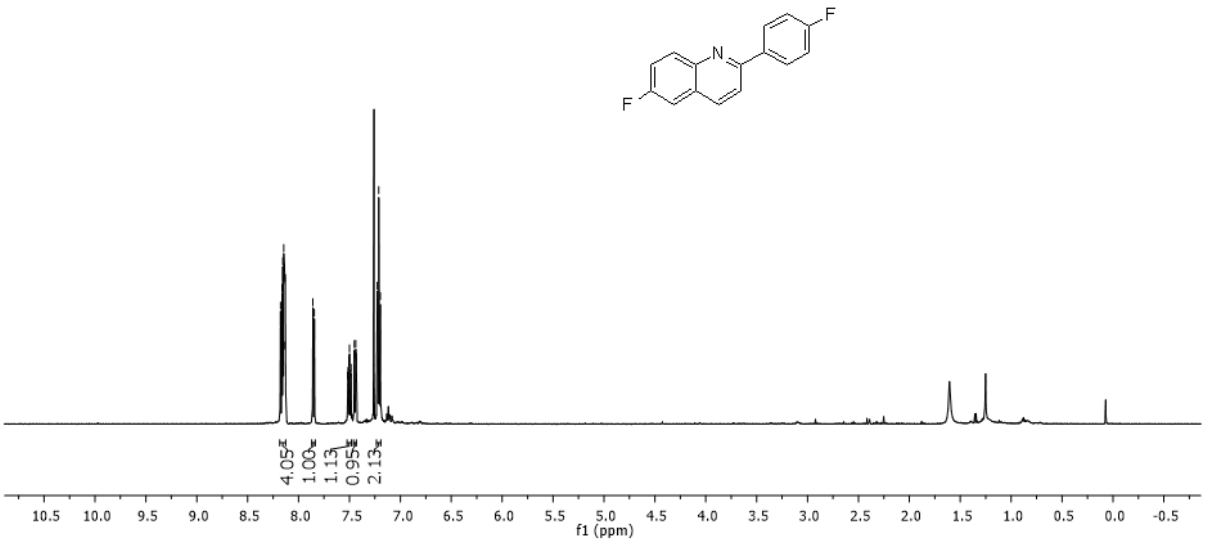

N
F
3.99
1.00
5.18
f1 (ppm)

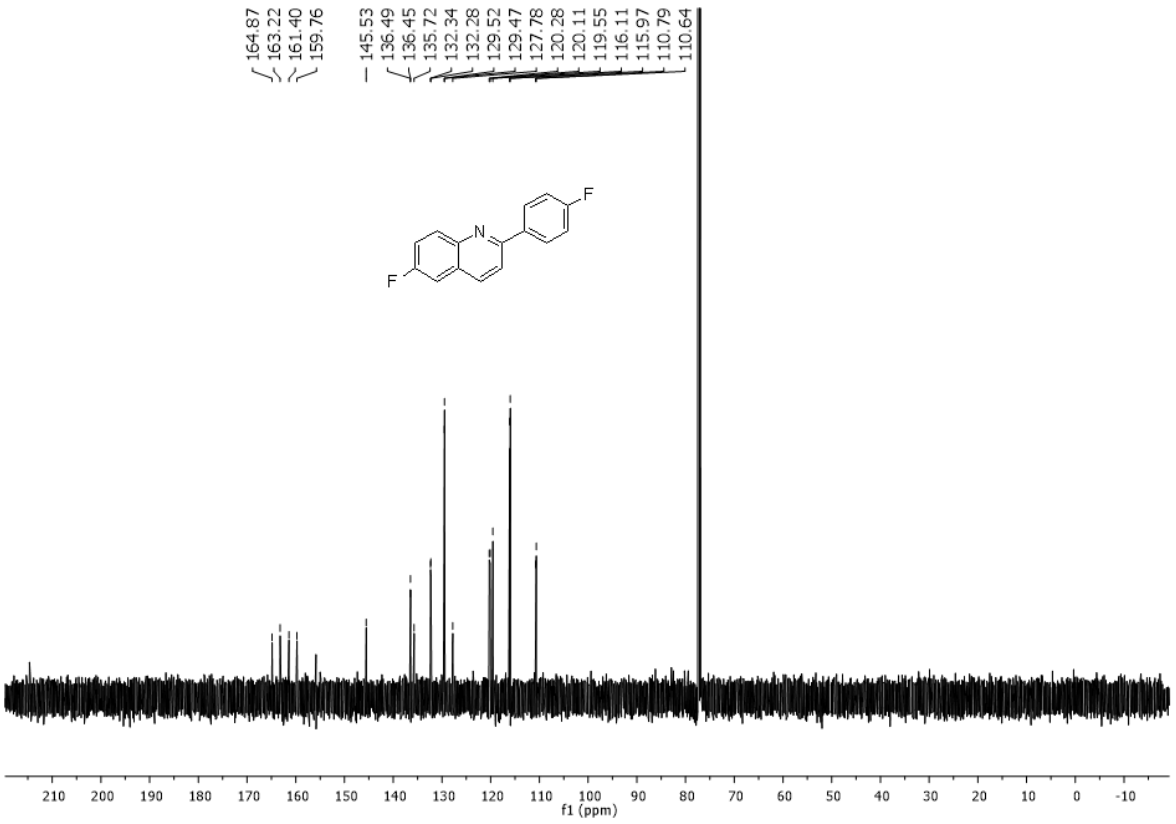

161.17
156.78
145.38
139.37
136.12
132.21
132.15
129.41
128.89
127.74
127.45
119.94
119.73
110.55
110.41
N
F
f1 (ppm)


8.19
8.18
8.18
8.17
8.17
8.16
8.08
8.07
7.91
7.90
7.53
7.52
7.52
7.51
7.50
7.50
7.47
7.46
7.45
7.45
7.37
7.36
7.36
2.47
N
F
1.82
1.84
1.00
0.97
0.98
1.93
3.17
f1 (ppm)


145.38 17
139.51 78
136.56 38
136.03 37
132.10 12
132.04 21
129.62 15
129.61 41
127.62 89
127.31 74
119.81 45
119.64 94
119.58 73
110.53 55
110.38 41
21.35
F
N
f1 (ppm)


8.18
8.16
8.15
8.15
8.14
8.14
8.13
8.13
7.86
7.85
7.52
7.51
7.50
7.50
7.50
7.49
7.48
7.45
7.45
7.44
7.43
7.23
7.21
7.20


F
F
N
4.05
1.00
1.13
0.95
2.13
f1 (ppm)



8. References

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