Electronic Supplementary Material (ESI) for ChemComm.


# Supporting information

# Double C-H Amination by Consecutive SET Oxidations

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1. General Information

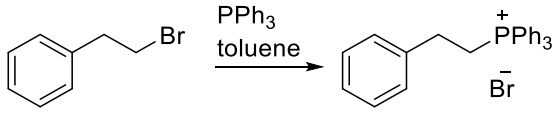
Unless otherwise noted, all $^{1}H$ NMRs were run on 400 MHz and 600 MHz spectrometer in $CDCl_3$ and all $^{13}C$ NMR were run on 100 MHz and 150 MHz spectrometer in $CDCl_3$. Proton chemical shifts are given relative to the residual proton signal of $CDCl_3$ (7.26 ppm). Carbon chemical shifts were internally referenced to $CDCl_3$ (77.23 ppm) signal. Data are reported as follows: chemical shift in ppm($\delta$), 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, benzene, diethyl-ether, dichloromethane, toluene and tetrahydrofuran (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. N-butyl Lithium was purchased from SigmaAldrich as a 2.5M solution in hexanes. $AlCl_3$ was purchased from AlfaAesar and freshly sublimed before use. $Pd(PPh_3)_4$ was purchased from SigmaAldrich and stored under Ar at -25°C.Triphenylphospine was purchased from SigmaAldrich. Trimethoxyborane was purchased from SigmaAldrich. Phenethyl-bromide, 4-methyl-phenethyl-bromide, 4-methoxy-phenethyl-bromide, 1-(2-bromoethyl)naphthalene, iodo-butane, 2-bromo-benzylbromide, pyrrolidine were all purchased from SigmaAldrich. Phenylboronic acid (Acros Organics), 4-tolylphenylboronic acid (Matrix).

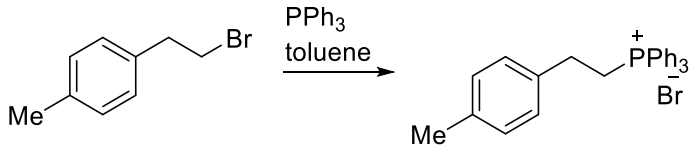
3. Synthesis of Wittig Salts

Preparation of Wittig salt – phenethyltriphenylphosphoniumbromide, **W1**



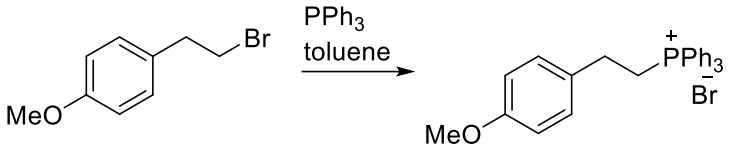

(2-bromoethyl)benzene (10.0 mmol) was added dropwise into a solution of triphenylphosphine (10.0 mmol) in toluene at room temperature. The solution was stirred for 48 hours in refluxing toluene. The resulting oily substance was collected and washed with hexane. Product was obtained as off white glassy substance and was used without further purification. Yield: 92%.[1]

Preparation of Wittig salt – (4-methylphenethyl)triphenylphosphonium bromide, **W2**



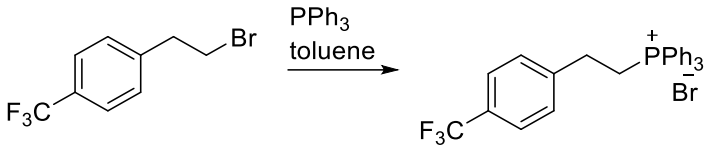

1-(2-bromoethyl)-4-methylbenzene (10.0 mmol) was added dropwise into a solution of triphenylphosphine (10.0 mmol) in toluene at room temperature. The solution was stirred for 48 hours in refluxing toluene. The resulting oily substance was collected and washed with hexane. The product was obtained as slightly yellow glass substance and was used without further purification. Yield: 86%.

Preparation of Wittig salt – (4-methoxyphenethyl)triphenylphosphonium bromide, **W3**



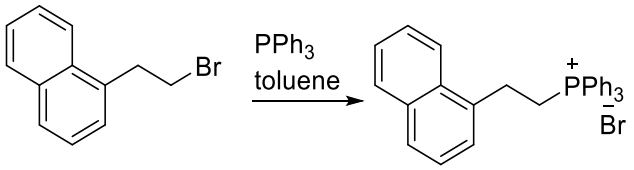

1-(2-bromoethyl)-4-methoxyybenzene (10.0 mmol) was added dropwise into a pressure tube containing triphenylphosphine (10.0 mmol) at room temperature. The solution was stirred for 48 hours in refluxing toluene. The resulting oily substance was collected and washed with hexane. The product was obtained as a light brown glassy substance and was used without further purification. Yield: 81%.

Preparation of Wittig salt – triphenyl(4-(trifluoromethyl)phenethyl)phosphonium bromide, **W4**



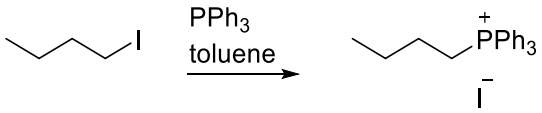

1-(2-bromoethyl)-4-trifluoromethylbenzene (10.0 mmol) was added dropwise into a solution of triphenylphosphine (10.0 mmol) in toluene at room temperature. The solution was stirred for 48 hours in refluxing toluene. The resulting oily substance was collected and washed with hexane. Product was obtained as off white glassy substance and was used without further purification. Yield: 87%.

Preparation of Wittig salt - (2-(naphthalen-1-yl)ethyl)triphenylphosphonium bromide, **W5**




1-(2-bromoethyl)-4-methylbenzene (10.0 mmol) was added dropwise into a solution of triphenylphosphine (10.0 mmol) 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 an off white solid and was used without further purification. Yield: 88%.

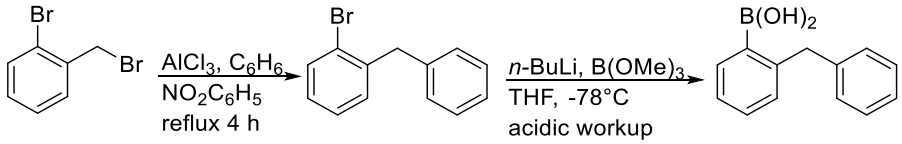
Preparation of Wittig salt – butyltriphenylphosphonium iodide, **W6**




Iodobutane (12.0 mmol) was added dropwise into a solution of triphenylphosphine (10.0 mmol) in toluene in a pressure tube at room temperature. It 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 and was used without further purification. Yield: 85%.

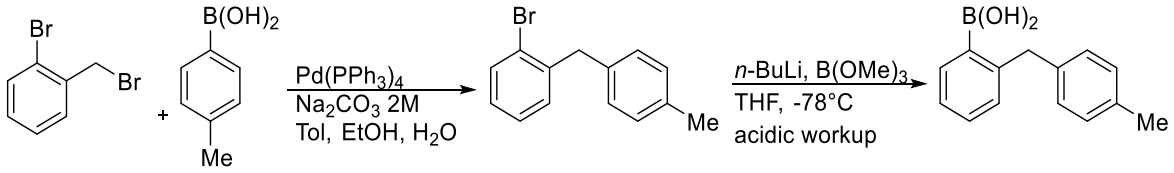
4. Synthesis of boronic acids:

Preparation of boronic acid - (2-benzylphenyl)boronic acid, **B1**




Boronic acid **B1**: Following a procedure by Dine et al.; To a flame dried 1 neck round bottom flask containing a solution of 2-bromobenzylbromide (1g, 4 mmol) in 12 mL of benzene was added a magnetic stir bar and $AlCl_3$ (336.6 mg, 4 mmol) dissolved in 5 mL of nitrobenzene all conducted under a stream of $N_2$. The mixture was then allowed to reflux for 6 h. Upon completion the mixture was allowed to cool to room temperature and was extracted with $Et_2O$ (3 x 15 mL), dried over $Na_2SO_4$, and evaporated under reduced pressure. The crude residue was purified via column chromatography with silica gel and hexane as the eluent to afford benzyl-2-bromobenzene (0.79 g, 3.2 mmol, 80%). Benzyl-2-bromobenzene (0.750 g, 3.0 mmol) was then added to a flame dried one neck round bottom flask equipped with a magnetic stir bar and kept under a stream of $N_2$. To this flask was added dry THF (15 mL) and the vessel was then added to a dewer containing dry ice and acetone. To this flask was added dropwise *n*-BuLi (1.24 mL, 2.5M) and the solution was allowed to stir for 1.5 hours, while maintaining inert atmosphere at -78°C. After the 1.5 hours, $B(OMe)_3$ (3.0 mL, 27mmol) was added over the course of 15 minutes. The resulting solution was allowed to stir for 8 hours. After the allotted time, $H_2O$ (15 mL) was added to the solution slowly followed by HCl (15 mL, 2M) and the solution was allowed to stir for an additional 1 h. This mixture was then neutralized with $Na_2CO_3$ and extracted with ether (3 x 15 mL). The resulting organic solution was dried with $Na_2SO_4$ and the solution was concentrated under reduced vacuum. The resulting oil was dissolved in $CH_2Cl_2$ (2 mL) and then hexane was added (15 mL) and the solution was placed in the freezer (-25°C) overnight. The resulting solid was filtered to afford **B1** as an off-white crystalline solid, (0.382 g, 1.8 mmol, 60%) which was used without further purification.[2]

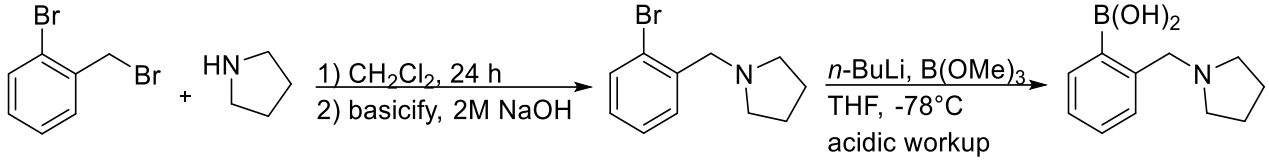
Preparation of boronic acid - (2-(4-methylbenzyl)phenyl)boronic acid, **B2**




Boron acid **B2**: Following a procedure by Anselmi et al.;To a 1 neck round bottom flask equipped with a magnetic stirring bar and reflux condenser was added 2-bromobenzyl bromide (1g, 4 mmol), 4-methylphenylboronic acid (544 mg, 4 mmol), $Na_2CO_3$ (4.5 mL, 1.5M), toluene (8 mL) EtOH (4 mL). This solution was allowed to stir and was outgassed with argon for 0.5 h, then the outlet needle was removed and the solution was kept under inert atmosphere for the remainder of the reaction. To this solution was then added $Pd(PPh_3)_4$ (140 mg, 3 mol%). The reaction was allowed to stir at 90°C for 8 h. Upon completion the mixture was diluted with ethyl acetate (10mL) and $H_2O$ (10 mL) and added to a separatory funnel. The aqueous layer was washed with ethyl acetate (1 x 15mL). The organic layers were collected and washed with $H_2O$ (2 x 15 mL) followed by brine (1 x 20 mL). The resulting organic solution was dried over $Na_2SO_4$, and concentrated under reduced pressure to afford a dark colored oil. This oil was then subjected to column chromatography (hexanes) to afford 1-bromo-2-(4-methylbenzyl)benzene as a light yellow oil (0.868 g, 3 mmol, 75%). 1-bromo-2-(4-methylbenzyl)benzene (0.78 g, 2.7 mmol) was then added to a flame dried one neck round bottom flask equipped with a magnetic stir bar and kept under a stream of $N_2$. To this flask was added dry THF (15 mL) and the vessel was then added to a dewer containing dry ice and acetone. To this flask was added *n*-BuLi (1.2 mL, 2.5M) and the solution was allowed to stir for 1.5 hours, while maintaining inert atmosphere as well as -78°C. After the 1.5 hours, $B(OMe)_3$ (2.86 mL, 25.7 mmol) was added over the course of 15 minutes. The resulting solution was allowed to stir for 8 hours. After the allotted time, $H_2O$ (15 mL) was added to the solution slowly followed by HCl (15 mL, 2M) and the solution was allowed to stir for an

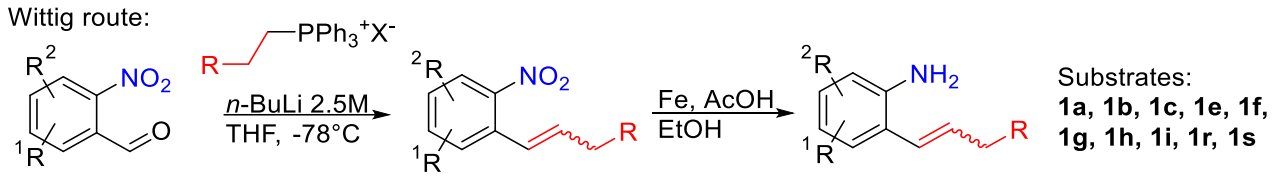
additional 1 h. This mixture was then neutralized with $Na_2CO_3$ and extracted with ether (3 x 15 mL). The resulting organic solution was dried with $Na_2SO_4$ and the solution was concentrated under reduced pressure. The resulting oil was dissolved in $CH_2Cl_2$ (2 mL) and then hexane was added (15 mL) and the solution was placed in the freezer (-25°C) overnight. The resulting solid was filtered to afford **B2** (0.397 g, 1.8 mmol, 65%) as an off white crystalline solid, which was used without further purification.[3]

Preparation of boronic acid - (2-(pyrrolidin-1-ylmethyl)phenyl)boronic acid, **B3**




Boron acid B3: Following a procedure by Wilson et al.; 2-bromobenzylbromide (1 g, 4 mmol) was added to a flask containing and pyrollidine (0.299 g, 4.2 mmol). To this solution was added dry methylene chloride (5 mL). After addition of solvent the mixture was allowed to stir for 24 h. To the solution was added NaOH (15 mL, 2M) and allowed to stir for an additional 30 minutes. Upon completion the mixture was diluted with ethyl acetate (15 mL) and $H_2O$ (15 mL) and added to a separatory funnel. The aqueous layer was washed with ethyl acetate (1 x 15mL). The organic layers were collected and washed with $H_2O$ (2 x 15 mL) followed by brine (1 x 20 mL). The resulting organic solution was dried over $Na_2SO_4$, and concentrated under reduced pressure to yield 1-(2-bromobenzyl)pyrrolidine (0.826 g, 3.44 mmol, 86%) which was used in next step without further purification. 1-(2-bromobenzyl)pyrrolidine (0.800 g, 3.3 mmol) was then added to a flame dried one neck round bottom flask equipped with a magnetic stir bar and kept under a stream of $N_2$. To this flask was added dry THF (12 mL) and the vessel was then added to a dewer containing dry ice and acetone. To this flask was added *n*-BuLi (1.5 mL, 2.5M) and the solution was allowed to stir for 1.5 hours, while maintaining inert atmosphere as well as -78C. After the 1.5 hours, $B(OMe)_3$ (3.5 mL, 31 mmol) was added over the course of 15 minutes. The resulting solution was allowed to stir for 8 hours. After the allotted time, $H_2O$ (15 mL) was added to the solution slowly followed by HCl (15 mL, 2M) and the solution was allowed to stir for an additional 1 h. This mixture was then neutralized with $Na_2CO_3$ and extracted with ether (3 x 15 mL). The resulting organic solution was dried with $Na_2SO_4$ and the solution was concentrated under reduced pressure to afford **B3** (0.515 g, 2.51 mmol, 76%) as a light yellow oil, which was used without further purification.[4]

5. Synthesis of substrates via Wittig, Grignard or Suzuki routes:




General procedure (A) for Wittig reaction:

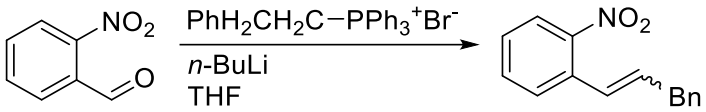
To a solution of the Wittig salt (1.2 equiv) in anhydrous THF (10mL) at -78°C was added slowly n-BuLi (1.5M solution in hexane, 1.2 equiv). After 45 min, a solution of desired aldehyde (1 equiv) in THF (10 mL) was added dropwise. The resulting solution was stirred for 1 h at -78 °C and then at room temperature 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:EtOAc) on silica gel affording desired alkene. The alkenes are reported as a mixture of E:Z isomers that were unable to be separated.

General procedure (B) for iron reduction of nitro group:

To a solution of nitro compound (1 equiv) in 15 ml of absolute ethanol was added 15 ml of glacial acetic acid and iron powder (5 equiv). The mixture was heated to reflux. After 6 h, the crude mixture was cooled and filtered

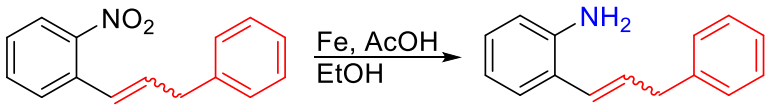
through a pad of Celite. The filtrate was concentrated in *vacuo*. Purification by flash chromatography on silica gel (Hexanes:EtOAc) afforded desired aniline.

Synthesis of 1-nitro-2-(3-phenylprop-1-enyl)benzene, **S1a**



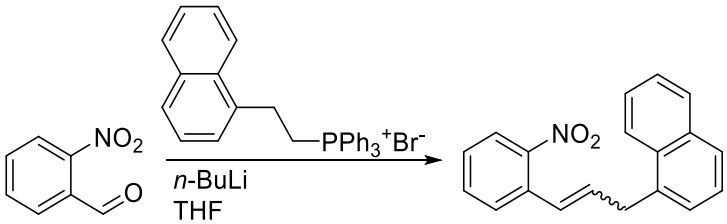

**S1a** was prepared following general procedure (A) using 2-nitrobenzaldehyde and Wittig salt **W1**. The crude was purified by column chromatography (hexane) on silica gel affording 1-nitro-2-(3-phenylprop-1-enyl)benzene in an inseparable mixture of isomers (E : Z = 1:3 ,75%) as dark yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.05 (m, 3H), 7.96 – 7.90 (m, 0.3H), 7.58 – 7.55 (m, 0.3H), 7.50 – 7.19 (m, 9H), 6.98 (t, *J* = 10.4 Hz, 0.6H), 6.92 (d, *J* = 11.4 Hz, 1H), 6.39 (dt, *J* = 15.5, 7.0 Hz, 0.3H), 6.08 (dt, *J* = 11.4, 7.7 Hz, 1H), 3.64 (dd, *J* = 7.0, 1.0 Hz, 0.6H), 3.50 (dd, *J* = 7.7, 0.8 Hz, 2H). HRMS (ESI): Calcd for $C_{15}H_{13}NNaO_2$ 262.0844, Found: 262.0845. Spectral data match those previously reported.[1]

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



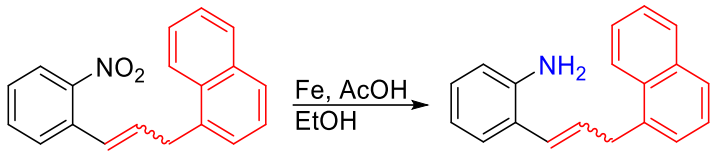

Aniline **1a** was prepared following general procedure (B). Purification by flash chromatography on silica gel (Hexanes:EtOAc) afforded **1b** in an inseparable mixture of isomers as a dark brown oil 1.1 g (E:Z = 1:3 , 85%). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.04 (m, 6H), 6.81 – 6.69 (m, 2H), 6.67 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.49 (d, *J* = 15.5 Hz, 1H), 6.44 (d, *J* = 11.1 Hz, 1H), 6.24 (dt, *J* = 15.5, 6.9 Hz, 0.3H), 5.99 (dt, *J* = 11.1, 7.5 Hz, 1H), 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. [1]

1-(3-(2-nitrophenyl)allyl)naphthalene, **S1f**



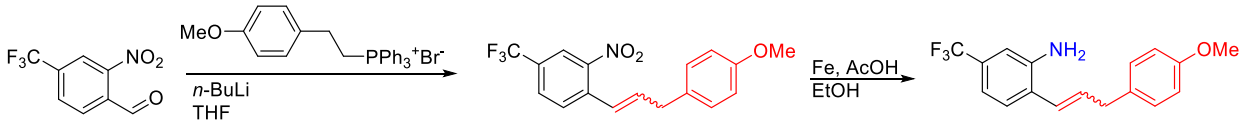

**S1f** was prepared following the general procedure (A) from 2-nitro-benzaldehyde and Wittig salt **W5**. The crude product was purified by flash chromatography (Hexanes:EtOAc, 10:1) to give the title compound **S1f** in an inseparable mixture of isomers (E:Z = 0.4:1, 83%) as a brown oil. $R_f$ = 0.43 (hexanes/EtOAc 10:1). $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.16 (dd, *J* = 8.5, 1.1 Hz, 0.5H), 8.10 (dd, *J* = 8.2, 1.3 Hz, 1H), 8.00 – 7.73 (m, 4H), 7.71 – 7.37 (m, 10H), 7.30 (ddd, *J* = 8.5, 7.2, 1.5 Hz, 0.5H), 7.07 (d, *J* = 15.7 Hz, 0.5H), 6.99 (d, *J* = 11.4 Hz, 1H), 6.46 (dt, *J* = 15.6, 6.7 Hz, 0.4H), 6.18 (dt, *J* = 11.4, 7.5 Hz, 1H), 4.08 (dd, *J* = 6.7, 1.6 Hz, 1H), 4.01 – 3.87 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 148.3, 147.6, 134.5, 133.9, 133.8, 132.9, 132.9, 132.3, 131.9, 131.9, 131.8, 131.7, 128.8, 128.8, 128.6, 128.1, 127.7, 127.4, 127.2, 126.8, 126.7, 126.5, 126.1, 126.0, 125.7, 125.7, 125.7, 125.7, 125.5, 124.7, 124.4, 123.9, 123.6, 36.8, 31.9. HRMS (ESI): Calcd for $C_{19}H_{15}NNaO_2$ 311.1000, Found: 311.0996

2-(3-(naphthalen-1-yl)prop-1-en-1-yl)aniline, **1f**



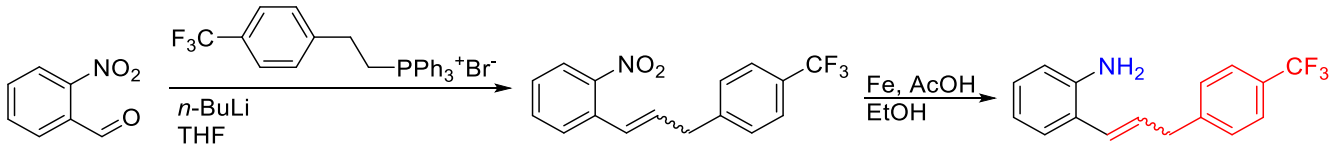

Aniline **1f** was prepared by reduction of nitro group following procedure (B). Purification by flash chromatography on silica gel (Hexanes:EtOAc, 7:1) afforded **1f** in an inseparable mixture of isomers as a dark brown oil 1.1 g (E:Z = 0.4:1 , 85%). $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.25 – 8.19 (m, 0.3H), 8.05 – 7.94 (m, 3H), 7.86 (ddd, *J* = 9.7, 7.9, 1.6 Hz, 2H), 7.70 – 7.44 (m, 6H), 7.36 (dd, *J* = 7.7, 1.6 Hz, 0.5H), 7.33 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.26 (td, *J* = 7.7, 1.6 Hz, 1H), 7.16 (td, *J* = 7.6, 1.6 Hz, 0.4H), 6.91 (td, *J* = 7.4, 1.2 Hz, 1H), 6.85 (ddd, *J* = 8.0, 5.2, 1.2 Hz, 1H), 6.71 (dd, *J* = 7.9, 1.2 Hz, 0.4H), 6.64 – 6.55 (m, 2H), 6.48 (dt, *J* = 15.7, 6.3 Hz, 0.4H), 6.15 (dt, *J* = 11.2, 7.3 Hz, 1H), 4.11 (dd, *J* = 6.3, 1.4 Hz, 0.8H), 4.07 (dd, *J* = 7.3, 1.7 Hz, 2H), 3.75 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 144.3, 136.8, 136.3, 133.9, 133.9, 132.4, 132.0, 132.0, 130.7, 129.8, 128.8, 128.7, 128.4, 128.2, 127.4, 127.2, 127.1, 127.0, 126.4, 126.2, 126.0, 125.9, 125.7, 125.7, 125.7, 125.7, 125.6, 124.1, 123.9, 122.6, 118.9, 118.2, 116.0, 115.3, 36.8, 32.3. IR (neat, $cm^{-1}$): 3464, 3372, 3042, 3008, 2954, 2922, 2853, 1927, 1614, 1575, 1508, 1490, 1454, 1394, 1302, 1262, 1214, 1157, 1140, 1077, 1017, 969, 935, 857, 790, 776, 748, 699. HRMS (ESI): Calcd for $C_{19}H_{17}N$ 259.1395, Found: 259.1390

2-(3-(4-methoxyphenyl)prop-1-en-1-yl)-5-(trifluoromethyl)aniline, **1g**




Aniline **1g** was prepared by following the general procedure (A) to prepare the nitro compound above. The nitro compound was subsequently reduced to the aniline following procedure (B), which yielded **1g** in an inseparable mixture of isomers as a dark brown oil (E:Z, 0.45:1, 73%). $^1$H NMR (600 MHz, Chloroform-*d*) δ 7.32 (d, *J* = 8.0 Hz, 0.45H), 7.21 – 7.15 (m, 2H), 7.09 (dd, *J* = 8.8, 0.7 Hz, 2H), 6.99 (d, *J* = 8.5 Hz, 1H), 6.98 – 6.90 (m, 2H), 6.88 (d, *J* = 8.7 Hz, 1H), 6.87 – 6.84 (m, 2H), 6.43 (d, *J* = 15.6 Hz, 0.46H), 6.38 (d, *J* = 11.2 Hz, 1H), 6.30 (dt, *J* = 15.5, 6.8 Hz, 0.44H), 6.05 (dt, *J* = 11.1, 7.5 Hz, 1H), 4.03 (s, 3H), 3.81 (s, 2H), 3.80 (s, 3H), 3.56 – 3.51 (m, 1H), 3.42 (dd, *J* = 7.6, 1.7 Hz, 2H). $^{13}$C NMR (150 MHz, $CDCl_3$) δ 158.4, 158.2, 144.4, 134.9, 134.2, 132.3, 131.8, 130.6, 130.2, 129.7, 129.5, 129.4, 127.9, 126.1, 125.3, 124.7, 115.7, 114.8, 114.7, 114.2, 114.2, 114.0, 111.7, 111.7, 100.1, 55.4, 38.9, 34.0. HRMS (ESI): Calcd for $C_{17}H_{16}F_3NO$ 307.1218, Found: 307.1215.

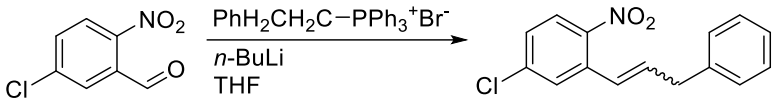
2-(3-(4-(trifluoromethyl)phenyl)prop-1-en-1-yl)aniline, **1i**




Aniline **1i** was prepared following the general procedure (A) to acquire the nitro substrate above (70%). The nitro compound was successfully reduced following general procedure (B). Purification by flash chromatography on silica gel (Hexanes:EtOAc, 5:1) afforded **1i** in an inseparable mixture of isomers as a brown oil (1.1 g, 3.9 mmol, 85%, E:Z = 1:3). (E:Z = 0.24:1). $^1$H NMR (600 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 8.1 Hz, 1H), 7.55 (d, *J* = 8.1 Hz, 3H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.14 (td, *J* = 7.6, 1.5 Hz, 2H), 7.09

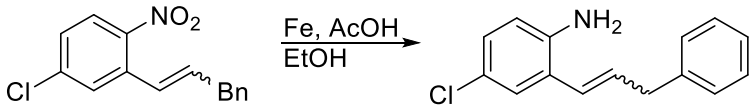
(dd, *J* = 7.9, 1.3 Hz, 1H), 6.83 – 6.69 (m, 3H), , 6.56 – 6.46 (m, 2H), 6.22 (dt, *J* = 15.6, 6.9 Hz, 0.24H), 5.96 (dt, *J* = 11.1, 7.4 Hz, 1H), 3.73 (s, 3H), 3.63 (d, *J* = 6.9 Hz, 1H), 3.58 (dd, *J* = 7.5, 1.4 Hz, 2H). $^{13}$C NMR (150 MHz, $CDCl_3$) δ 144.9, 144.3, 131.7, 130.4, 130.0, 129.7, 129.1, 128.8, 128.6, 128.0, 127.6, 127.1, 127.1, 126.4, 126.4, 125.6, 125.6, 125.6, 125.5, 125.5, 122.4, 119.2, 118.3, 116.2, 116.1, 115.4, 34.7, 29.9. HRMS (ESI): Calcd for $C_{16}H_{14}F_3N$ 277.1112, Found: 277.1107

Synthesis of 4-chloro-1-nitro-2-(3-phenylprop-1-en-1-yl)benzene, **S1j**



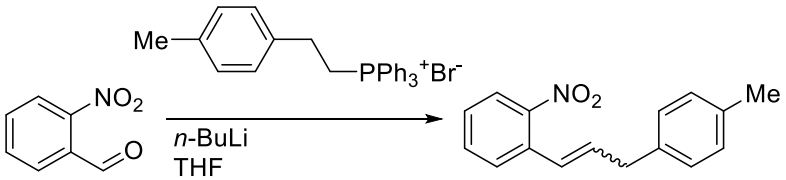

**S1j** was prepared following general procedure (A) using 5-chloro-2-nitrobenzaldehyde and Wittig Salt **W1** which was purified using column chromatography (Hexanes:EtOAc, 15:1) to afford desired compound (0.4 g, 1.5 mmol, 74%). E:Z, 0.3:1 isomer: $^1$H NMR (400 MHz, Chloroform-d) δ 8.16 (dd, J = 9.0, 5.1 Hz, 1H), 8.02 (dd, J = 9.0, 5.2 Hz, 0.3H), 7.61 – 7.55 (m, 0.3H), 7.40 – 7.22 (m, 5H), 7.22 – 7.06 (m, 4H), 7.05 – 6.97 (m, 0.3H), 7.02(m, 1H), 6.38 (dt, J = 15.6, 7.0 Hz, 0.3H), 6.10 (dt, J = 11.4, 7.7 Hz, 1H), 3.64 (dd, J = 6.9, 1.5 Hz, 0.6H), 3.49 (dd, J = 7.7, 1.6 Hz, 2H). E isomer: $^1$H NMR (400 MHz, Chloroform-d) δ 8.06 (d, J = 9.3 Hz, 1H), 7.47 – 7.40 (m, 2H), 7.39 – 7.32 (m, 2H), 7.30 – 7.25 (m, 1H), 7.23 – 7.16 (m, 2H), 6.87 (d, J = 11.5 Hz, 1H), 6.12 (dt, J = 11.5, 7.7 Hz, 1H), 3.50 (d, J = 7.7 Hz, 2H). $^{13}$C NMR (100 MHz, CDCl3) δ 146.6, 139.4, 139.2, 134.4, 133.2, 131.7, 128.8, 128.3, 128.2, 126.5, 126.3, 125.5, 34.6. HRMS (ESI): Calcd for $C_{15}H_{12}ClNO_2$ 275.0527. Found: 275.0523

Synthesis of 4-chloro-2-(3-phenylprop-1-en-1-yl)aniline, **1j**




Aniline **1j** was prepared by reduction of nitro group following general procedure (B). Purification by flash chromatography on silica gel (Hexanes:EtOAc, 6:1) afforded **1j** as a dark brown oil (1.1 g, 4.5 mmol, 85%, E:Z = 1:3). (E:Z = 1:10 , 85%). $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.33 (m, 2H), 7.32 – 7.21 (m, 4H), 7.20 – 7.03 (m, 2H), 6.68 (d, *J* = 8.2 Hz, 1H), 6.39 (d, *J* = 11.3 Hz, 1H), 6.12 – 5.99 (m, 1H), 3.74 (s, 2H), 3.58 – 3.48 (m, 2H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 142.8, 140.3, 134.0, 129.2, 128.6, 128.4, 128.0, 126.2, 124.8, 124.0, 122.5, 116.3, 34.8. HRMS (ESI): Calcd for $C_{15}H_{14}ClN$ 245.0785, Found: 245.0783

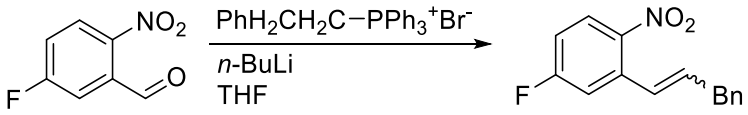
1-nitro-2-(3-(p-tolyl)prop-1-en-1-yl)benzene, **S1k**




**S1k** was prepared following general procedure (A) using 2-nitrobenzaldehyde and Wittig salt **W2**. The crude product was purified by flash chromatography (Hexanes:EtOAc, 10:1) to give the title compound as a brown oil (0.3 g, 1.1 mmol, 78%, E:Z = 0.4:1). $R_f$ = 0.48 (hexanes/EtOAc 10:1). $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.05 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.90 (dd, *J* = 8.2, 1.3 Hz, 0.36H), 7.62 – 7.55 (m, 2H), 7.55 – 7.49 (m, 0.5H), 7.48 – 7.40 (m, 2H), 7.35 (ddd, *J* = 8.6, 6.1, 1.5 Hz, 0.5H), 7.16 (s, 1H), 7.12 (d, *J* = 7.9 Hz, 2H), 7.07 (d, *J* = 8.1 Hz, 2H), 6.94 (d, *J* = 15.6 Hz, 0.45H), 6.91 – 6.84 (m, 1H), 6.34 (dt, *J* = 15.6, 7.0 Hz, 0.4H), 6.03 (dt, *J* = 11.4, 7.7 Hz, 1H), 3.57 (dd, *J* = 6.9, 1.5 Hz,

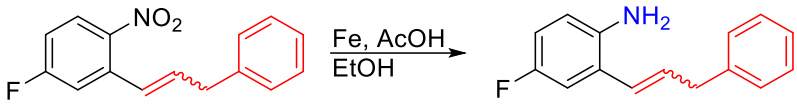
0.7H), 3.46 – 3.38 (m, 2H), 2.35 (s, 1H), 2.33 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 136.8, 136.3, 136.1, 135.9, 135.3, 133.3, 133.0, 132.9, 132.6, 132.5, 131.9, 129.4, 129.4, 128.7, 128.2, 128.1, 127.7, 126.4, 126.2, 124.8, 124.6, 39.3, 34.1, 21.1. HRMS (ESI): Calcd for $C_{16}H_{15}NNaO_2$ 276.1000, Found: 276.1002

Synthesis of 4-fluoro-1-nitro-2-(3-phenylprop-1-en-1-yl)benzene, **S1l**



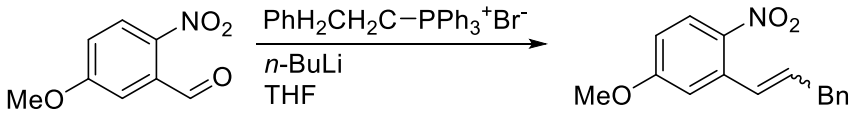

**S1l** was prepared following general procedure (A) using 5-fluoro-2-nitrobenzaldehyde and Wittig salt **W1**. The crude product was purified by flash chromatography (Hexanes:EtOAc, 10:1) to give the title compound (1.7 g, 6.0 mmol, 83%, E:Z = 1:3) as a light brown oil. $R_f$ = 0.6 (hexanes/EtOAc 10:1). $^1$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 (100 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[1]

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



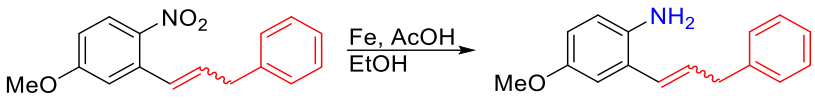

Aniline **1l** was prepared following general procedure (B). Purification by flash chromatography on silica gel (Hexanes:EtOAc) afforded **1l** as a dark brown oil (1.1 g, 4.8 mmol, 85%, E:Z = 1:3). The crude product was purified by flash chromatography (Hexanes:EtOAc, 10:1) to give (E:Z = 1:3, 78%) of the title compound as a brown oil. $R_f$ = 0.44 (hexanes/EtOAc 7:1). $^1$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 (100 MHz, Chloroform-*d*) δ 157.1, 154.8, 140.4, 133.8, 132.4, 128.8, 128.7, 128.7, 128.7, 128.5, 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 $C_{15}H_{15}FN$ 227.1188, Found: 227.1199. Spectral data match those previously reported. [1]

Synthesis of 4-methoxy-1-nitro-2-(3-phenylprop-1-en-1-yl)benzene, **S1m**



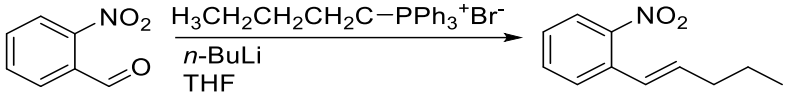

**S1m** was prepared following general procedure (A) using 5-methoxy-2-nitrobenzaldehyde and Wittig salt **W1**. The crude product was purified by flash chromatography (Hexanes:EtOAc, 10:1) to give the title compound (2.0 g, 7.4 mmol, 83%, E:Z = 0.6:1) as a dark brown oil. $R_f$ = 0.4 (hexanes/EtOAc 10:1). $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.12 (d, *J* = 8.9 Hz, 1H), 7.98 (d, *J* = 9.2 Hz, 0.5H), 7.42 – 7.29 (m, 4H), 7.28 – 7.16 (m, 4H), 7.09 (d, *J* = 15.5 Hz, 1H), 7.00 – 6.92 (m, 2H), 6.90 – 6.82 (m, 2H), 6.79 (dd, *J* = 9.1, 2.8 Hz, 1H), 6.32 (dt, *J* = 15.5, 6.9 Hz, 1H), 6.03 (dt, *J* = 11.4, 7.8 Hz, 1H), 3.82 (s, 1.5H), 3.77 (s, 3H), 3.70 – 3.57 (m, 1H), 3.49 (dd, *J* = 7.7, 1.6 Hz, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 162.8, 162.6, 140.7, 140.2, 139.7, 139.1, 136.0, 135.0, 134.1, 130.8, 128.3, 128.0, 127.9, 127.4, 127.2, 127.1, 127.0, 126.1, 125.9, 116.1, 113.1, 112.7, 112.4, 55.4, 39.1, 34.1. HRMS (ESI): Calcd for $C_{15}H_{15}NNaO_3$ 269.1052, Found: 269.1049

2-(3-methoxyprop-1-en-1-yl)aniline, **1m**



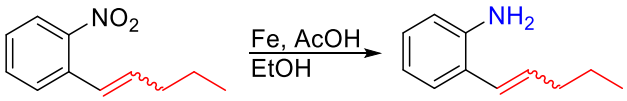

Aniline **1m** was prepared following general procedure (B). Purification by flash chromatography on silica gel (Hexanes:EtOAc) afforded **1m** as a dark brown oil (1.2 g, 5.0 mmol, 85%, E:Z = 0.6:1). $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.25 (m, 9H), 6.99 (d, *J* = 2.9 Hz, 1H), 6.85 (t, *J* = 2.0 Hz, 1H), 6.82 (d, *J* = 2.9 Hz, 1H), 6.79 (dd, *J* = 8.6, 2.9 Hz, 1H), 6.75 (dd, *J* = 8.3, 0.7 Hz, 1H), 6.69 (d, *J* = 8.6 Hz, 1H), 6.61 (d, *J* = 15.6 Hz, 0.6H), 6.54 (dd, *J* = 11.1, 1.7 Hz, 1H), 6.36 (dt, *J* = 15.6, 6.9 Hz, 1H), 6.08 (dt, *J* = 11.1, 7.5 Hz, 1H), 3.82 (s, 2H)3.80 (s, 3H), 3.66 (td, *J* = 7.4, 1.5 Hz, 4H), 3.55 (s, 3H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 152.8, 152.1, 140.5, 137.9, 137.2, 132.6, 131.0, 128.5, 128.5, 128.3, 126.6, 126.0, 126.0, 124.8, 123.7, 117.4, 116.4, 114.9, 114.3, 114.0, 112.0, 77.5, 77.2, 76.9, 55.6, 55.6, 39.6, 34.7. IR (neat, cm$^{-1}$): 3446, 3372, 2910, 2860, 1630, 1500, 1033, HRMS (ESI): Calcd for $C_{16}H_{17}NO$ 239.1344, Found: 239.1340.

Synthesis of 1-nitro-2-(pent-1-en-1-yl)benzene, **S1c**



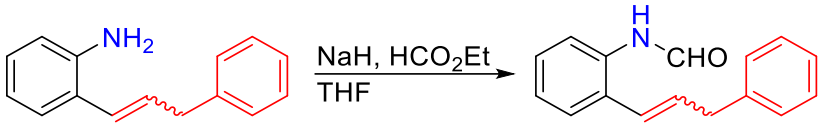

**S1c** was prepared following general procedure (A) using 2-nitrobenzaldehyde and Wittig salt **W6** The crude product was purified by flash chromatography (Hexanes:EtOAc, 10:1) to give the title compound as a light brown oil (0.5 g, 2.6 mmol, 73%, E:Z = 1:2). $R_f$ = 0.73 (hexanes/EtOAc 10:1). $^1$H 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 (100 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. Spectral data match those previously reported.[1]

Synthesis of 2-(pent-1-en-1-yl)aniline, **1c**



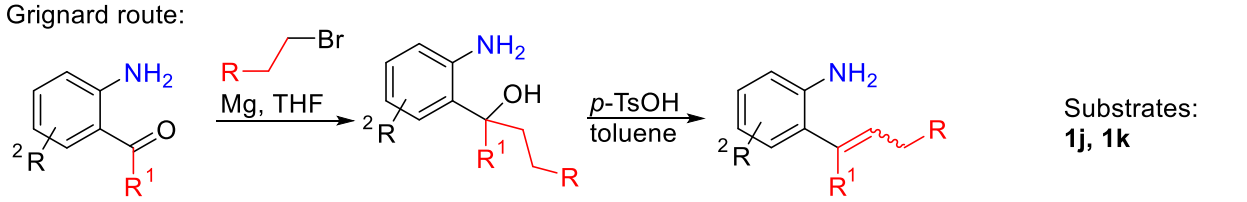

Substrate **1c** was prepared following general procedure (B) for nitro reduction. The crude product was purified by flash chromatography (Hexanes:EtOAc, 10:1) to give of the title compound as a light brown oil (0.1 g, 0.6 mmol, 88%, E:Z = 1:2). $R_f$ = 0.44 (hexanes/EtOAc 10:1). $^1$H NMR (400 MHz, Chloroform-*d*) 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 (100 MHz, Chloroform-*d*) 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. Spectral data match those previously reported. [1]

Synthesis of N-(2-(3-phenylprop-1-en-1-yl)phenyl)formamide, **1a'**




A solution of aniline **1a** (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 (400 MHz, Chloroform-*d*, 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 (100 MHz, Chloroform-*d*) 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.[1]

Grignard route:




Substrates:
**1j, 1k**

Substrate synthesis via Grignard route:

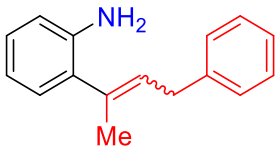
General procedure (C) for Grignard reaction:

Following a procedure by Chen et al.; To a $N_2$ purged, flame dried round bottom flask equipped with a magnetic stir bar and reflux condenser was charged Mg turnings (1.5 equiv). To the Mg turnings was added dry THF (20 mL) and a single crystal of $I_2$ and the solution was allowed to stir at 50°C for 1 h. The solution was allowed to cool to room temperature. To the solution was added dropwise, alkyl-bromide (1 equiv). This solution was then heated to 50°C and allowed to stir for 1.5 h. The generated Grignard reagent was then added dropwise to a round bottom flask containing carbonyl species (0.4 equiv) in THF (10 mL). This solution was then allowed to stir at 50°C overnight. To this mixture was then stirred with HCl 2M for 0.5 h, where upon the mixture was then washed with Brine (2 x 10 mL) and extracted with $Et_2O$ (3 x 15 mL) and dried over $Na_2SO_4$. Column chromatography using silica gel and EtOAc: Hexanes as eluent afforded the desired product.[5]

General procedure (D) for dehydration reaction:

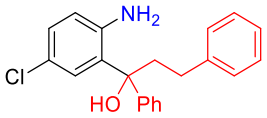
To a flask equipped with reflux condenser and magnetic stir bar was added desired tertiary alcohol (1 equiv), *p*-TsOH (20 mol%), toluene (15 mL). This mixture was allowed to stir at reflux for 24 h. The solution was then washed with $H_2O$ (3 x 15 mL), Brine (2 x 15 mL) and extracted with $Et_2O$ (3 x 15 mL) and dried over $Na_2SO_4$. The crude residue was purified via column chromatography using EtOAc:Hexanes as the eluent to afford the desired olephin.

2-(4-phenylbut-2-en-2-yl)aniline, **1n**



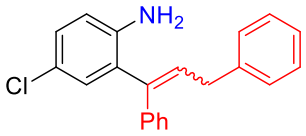

**1n** was prepared following the general procedure (C) to afford a crude dark brown oil which was subsequently subjected to general procedure (D) to afford a dark crude oil that was purified via flash chromatography (Hexanes:EtOAc, 8:1) to afford **1j** as a light brown oil (0.201 g, .0.9 mmol, 65%). $^1$H NMR (600 MHz, Chloroform-*d*) δ 7.54 – 7.48 (m, 2H), 7.45 – 7.40 (m, 1H), 7.39 (ddd, *J* = 7.6, 1.3, 0.6 Hz, 2H), 7.35 (ddd, *J* = 8.0, 7.3, 1.6 Hz, 1H), 7.27 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.04 (td, *J* = 7.4, 1.2 Hz, 1H), 6.93 (dd, *J* = 8.0, 1.1 Hz, 1H), 6.05 – 6.00 (m, 1H), 3.84 (s, 2H), 3.44 (d, *J* = 7.5 Hz, 2H), 2.26 (s, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$) δ 142.93, 141.15, 134.67, 128.84, 128.44, 128.41, 128.07, 127.95, 127.21, 125.88, 118.35, 115.10, 35.56, 24.57. IR (neat, cm$^{-1}$) 3070, 3033, 2956, 2821, 1643, 1599, 1550, 1300, 1250, 1248, 1143, 1100, 1059, 1011. HRMS (ESI): Calcd for $C_{16}H_{17}N$ 223.1395, Found: 223.1391. Spectral data match those previously reported.[6]

1-(2-amino-5-chlorophenyl)-1,3-diphenylpropan-1-ol, **S10**



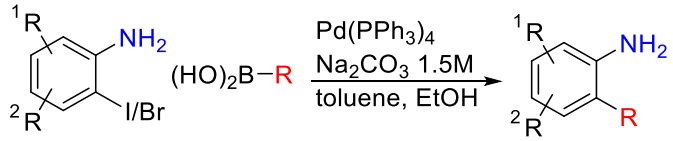

**S10** was prepared following the general procedure (C). Purification via flash chromotagraphy (Hexanes:EtOAc, 5:1) yielded the desired product as a brown/black oil (70%). $^1$H NMR (600 MHz, Chloroform-d) δ 7.48 – 7.40 (m, 3H), 7.35 (dd, J = 8.4, 6.9 Hz, 2H), 7.28 (tt, J = 8.1, 1.6 Hz, 3H), 7.20 (d, J = 7.4 Hz, 1H), 7.18 – 7.14 (m, 2H), 7.09 (dd, J = 8.4, 2.4 Hz, 1H), 6.54 (d, J = 8.4 Hz, 1H), 3.75 (s, 4H), 2.93 – 2.74 (m, 1H), 2.55 (ddd, J = 14.2, 12.6, 4.4 Hz, 1H), 2.50 – 2.35 (m, 2H). $^{13}$C NMR (150 MHz, CDCl3) δ 144.9, 142.3, 128.6, 128.4, 128.4, 127.3, 126.6, 126.0, 125.9, 120.2, 78.0, 44.3, 29.9. HRMS (ESI): Calcd for $C_{21}H_{20}ClNO$ 339.1204, Found 339.1203.

4-chloro-2-(1,3-diphenylprop-1-en-1-yl)aniline, **10**




Following the general procedure (D) using 1-(2-amino-5-chlorophenyl)-1,3-diphenylpropan-1-ol (0.54 g, 1.6 mmol), substrate **10** was prepared as a deep brown oil(0.42 g, 1.3 mmol, 83%). (E:Z = 1:0.8) $^1$H NMR (600 MHz, Chloroform-*d*) δ 7.51 – 7.43 (m, 2H), 7.42 – 7.26 (m, 11H), 7.25 – 7.20 (m, 7H), 7.16 (d, *J* = 2.5 Hz, 1H), 7.13 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.59 (d, *J* = 8.5 Hz, 1H), 6.56 (t, *J* = 7.5 Hz, 1H), 6.14 (t, *J* = 7.7 Hz, 1H), 3.73 (m, 5H), 3.48 (d, *J* = 7.5 Hz, 2H). $^{13}$C NMR (150 MHz, Chloroform-*d*) δ 143.0, 142.7, 140.6, 140.3, 139.7, 139.3, 138.5, 137.6, 131.7, 130.9, 130.5, 130.4, 130.4, 129.5, 129.1, 128.7, 128.7, 128.7, 128.6, 128.6, 128.5, 128.4, 128.2, 127.8, 127.7, 126.4, 126.3, 126.2, 126.1, 122.8, 122.8, 117.0, 116.6, 77.4, 77.2, 77.0, 36.2, 35.5. IR (neat, cm$^{-1}$): 3351, 3060, 3030, 1680, 1590, 1484, 1448, 1357, 1264, 1156, 1077, 1028. HRMS (ESI): Calcd for $C_{21}H_{18}ClN$ 321.1098, Found: 321.1100.

Suzuki route:



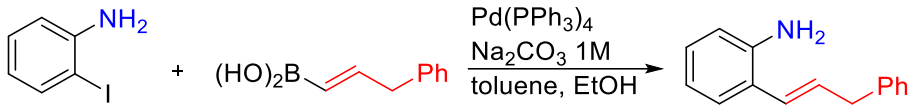

Substrates:
**1aE, 1l, 1m, 1n, 1o, 1q**

General procedure (E) for Suzuki coupling:

To a round bottom flask equipped with a magnetic stirring bar and reflux condenser was added 2-haloaniline (1 equiv), boronic acid (1.2 equiv), $Na_2CO_3$ (4 equiv, 1.5M), toluene (8 mL), EtOH (4 mL). This solution was allowed

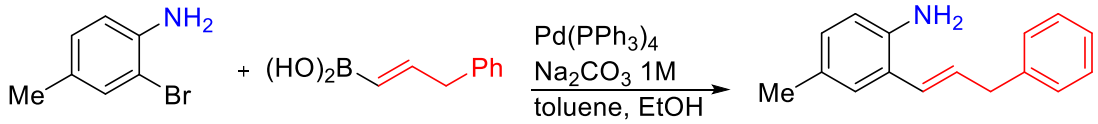
to stir and was outgassed with argon for 0.5 h, then the outlet needle was removed and the solution was kept under inert atmosphere for the remainder of the reaction. To this solution was then added $Pd(PPh_3)_4$ (5 mol%). The reaction was allowed to stir at reflux for 8 h. Upon completion the mixture was diluted with ethyl acetate (10mL) and $H_2O$ (10 mL) and added to a separatory funnel. The aqueous layer was washed with ethyl acetate (1 x 15mL). The organic layers were collected and washed with $H_2O$ (2 x 15 mL) followed by brine (1 x 20 mL). The resulting organic solution was dried over $Na_2SO_4$, and concentrated under reduced pressure. The residue was then subjected to column chromatography (hexanes:EtOAc) to afford desired product.

(E)-2-(3-phenylprop-1-en-1-yl)aniline, **1aE**



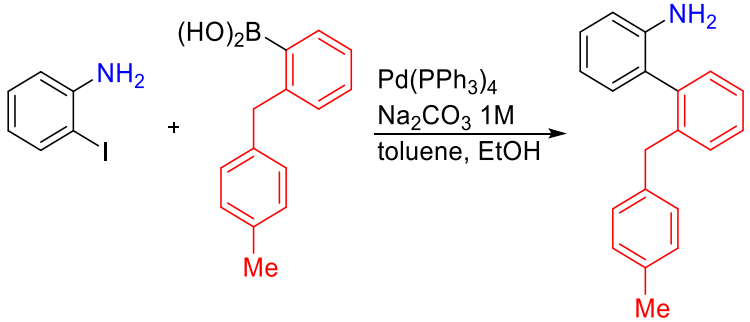

Following the general procedure (E) using 2-iodoaniline (0.2 g, 0.91 mmol) and (E)-(3-phenylprop-1-en-1-yl)boronic acid (0.178 g, 1.1 mmol), substrate **1aE** was synthesized as a dark brown oil (0.162 g, 0.77 mmol, 85%). $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.33 (m, 2H), 7.33 – 7.21 (m, 4H), 7.21 – 7.07 (m, 2H), 6.68 (d, *J* = 8.2 Hz, 1H), 6.39 (d, *J* = 11.2 Hz, 1H), 6.13 – 5.99 (m, 1H), 3.74 (s, 3H), 3.59 – 3.48 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 142.8, 140.3, 134.0, 129.2, 128.6, 128.4, 128.0, 126.2, 124.8, 124.0, 122.5, 116.3, 34.8. HRMS (ESI): Calcd for $C_{15}H_{15}N$ 209.1250, Found: 209.1260. Spectral data match those previously reported.[7]

4-methyl-2-(3-phenylprop-1-en-1-yl)aniline, **5h**




Following the general procedure (E) using 2-iodoaniline (0.2 g, 1.07 mmol) and (E)-(3-phenylprop-1-en-1-yl)boronic acid (0.208 g, 1.28 mmol), substrate **1h** was obtained as a dark yellow oil (0.205 g, 0.92 mmol, 86%). $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.37 (m, 3H), 7.37 – 7.27 (m, 4H), 7.17 (d, *J* = 2.0 Hz, 1H), 6.95 (dd, *J* = 8.0, 2.1 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 1H), 6.56 (d, *J* = 15.6 Hz, 1H), 6.31 (dt, *J* = 15.6, 6.9 Hz, 1H), 3.65 (dd, *J* = 6.9, 1.4 Hz, 4H), 2.31 (s, 3H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 141.0, 140.3, 130.8, 128.9, 128.7, 128.6, 128.2, 127.8, 126.8, 126.3, 123.9, 116.3, 39.8, 20.6. HRMS (ESI): Calcd for C16H17N 223.1395, Found: 223.1400. IR (neat, $cm^{-1}$) 3060, 3026, 2920, 2860, 1686, 1626, 1600, 1494, 1452, 1294, 1268, 1159, 1107, 1073, 1029. HRMS (ESI): Calcd for $C_{16}H_{17}N$ 223.1395, Found 223.1397. Spectral data match those previously reported. [1]

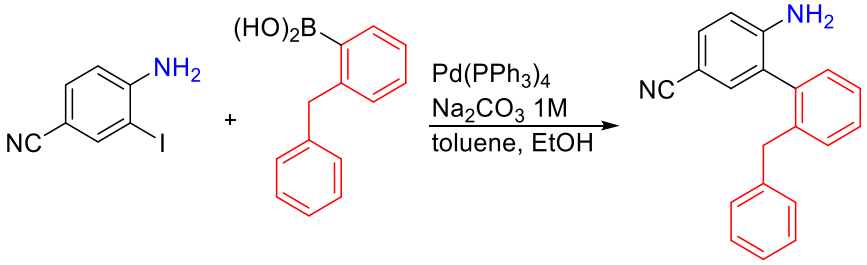
2'-(4-methylbenzyl)-[1,1'-biphenyl]-2-amine, **1p**




Following the general procedure (E) using 2-iodoaniline (0.19 g, 0.87 mmol) and boronic acid **B2** (0.235 g, 1.04 mmol), substrate **1p** was obtained as a brown oil (0.219 g, 0.8 mmol, 92%). $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.50 – 7.38 (m, 4H), 7.34 (tdd, *J* = 8.2, 2.6, 1.3 Hz, 1H), 7.18 (ddt, *J* = 6.3, 5.0, 2.2 Hz, 3H), 7.07 (dd, *J* = 8.0, 3.7 Hz,

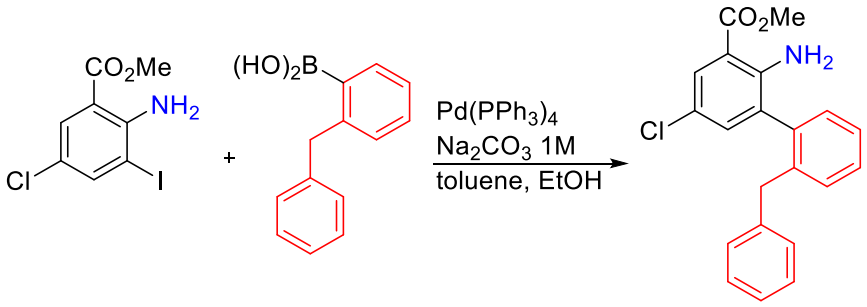
2H), 7.01 – 6.93 (m, 1H), 6.87 (dd, *J* = 7.9, 1.3 Hz, 1H), 4.01 (qd, *J* = 15.2, 3.8 Hz, 2H), 3.51 (s, 2H), 2.46 (s, 3H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 143.9, 140.5, 138.5, 138.0, 135.2, 130.5, 130.1, 129.0, 128.9, 128.5, 128.0, 127.1, 126.6, 126.6, 118.2, 115.2, 38.6, 21.1. IR (neat, cm$^{-1}$): 3461, 3376, 3049, 3019, 2919, 2857, 1613, 1499, 1478, 1444, 1296, 1183, 1156, 1115, 1047, 1005. HRMS (ESI): Calcd for $C_{20}H_{19}N$ 273.1517, Found: 273.1520.

6-amino-2'-benzyl-[1,1'-biphenyl]-3-carbonitrile, **1q**



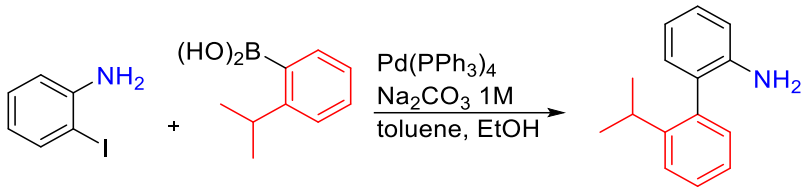

Following the general procedure (E) using 2-iodoaniline (0.2 g, 0.82 mmol) and boronic acid **B1** (0.209 g, 0.98 mmol), substrate **1q** was obtained as a dark yelllow oil (0.203 g, 0.71 mmol, 87%).$^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.41 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.39 – 7.34 (m, 1H), 7.34 (s, 1H), 7.33 – 7.28 (m, 1H), 7.23 – 7.09 (m, 5H), 7.01 – 6.81 (m, 2H), 6.68 (d, *J* = 8.4 Hz, 1H), 3.87 (s, 2H), 3.86 – 3.69 (m, 2H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 148.3, 140.5, 136.1, 134.6, 132.9, 130.8, 130.5, 128.9, 128.9, 128.4, 127.3, 126.7, 126.2, 120.2, 114.7, 100.0, 39.5. IR (neat, cm$^{-1}$): 3480, 3366, 3215, 3027, 2919, 2217, 1617, 1502, 1452, 1414, 1316, 1154, 1074, 1026. HRMS (ESI): Calcd for $C_{20}H_{16}N_2$ 284.1313, Found: 284.1310.

methyl 2-amino-2'-benzyl-5-chloro-[1,1'-biphenyl]-3-carboxylate, **1r**



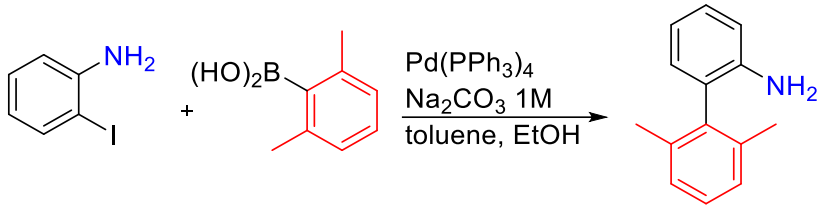

Following the general procedure (E) using methyl 2-amino-5-chloro-3-iodobenzoate(0.2 g, 0.64 mmol) and boronic acid **B1** (0.163 g, 0.77 mmol), substrate **1r** was obtained as a light brown oil (0.193 g, 0.55 mmol, 86%).$^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 2.6 Hz, 1H), 7.39 – 7.27 (m, 3H), 7.23 – 7.10 (m, 4H), 6.95 (d, *J* = 2.6 Hz, 1H), 6.94 – 6.90 (m, 2H), 5.60 (s, 2H), 3.89 (s, 3H), 3.87 – 3.69 (m, 2H). $^{13}$C NMR (150 MHz, Chloroform-*d*) δ 168.0, 147.1, 140.5, 140.5, 136.3, 135.0, 130.7, 130.6, 129.9, 129.8, 129.1, 129.0, 128.4, 127.3, 126.2, 120.2, 111.4, 52.0, 39.4. IR (KBr, cm$^{-1}$): 3485, 3364, 3061, 3026, 2950, 2844, 1693, 1604, 1556, 1494, 1436, 1303, 1221, 1127, 1090, 1030. HRMS (ESI): Calcd for $C_{21}H_{18}ClNO_2$ 351.1026, Found: 351.1022.

2'-isopropyl-[1,1'-biphenyl]-2-amine, **1s**



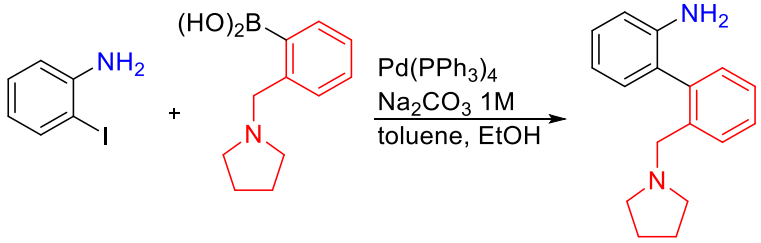

Following the general procedure (E) using 2-iodoaniline (0.139g, 0.63mmol) and 2-isopropylphenylboronic acid (0.135 g, 0.82mmol), substrate **1p** was obtained as a light brown oil (0.11 g, 0.52mmol, 82%).$^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.49 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.44 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.30 (td, *J* = 7.3, 1.5 Hz, 1H), 7.27 – 7.21 (m, 2H), 7.09 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.87 (td, *J* = 7.4, 1.2 Hz, 1H), 6.81 (dd, *J* = 7.9, 1.2 Hz, 1H), 3.48 (s, 2H), 2.93 (p, *J* = 6.9 Hz, 1H), 1.27 (d, *J* = 6.9 Hz, 1H), 1.16 (d, *J* = 6.9 Hz, 1H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 147.9, 144.0, 137.5, 130.5, 130.3, 128.4, 128.3, 127.3, 126.1, 125.9, 118.1, 115.0, 30.0, 24.8, 23.6. Spectral data match those previously reported.[8]

2',6'-dimethyl-[1,1'-biphenyl]-2-amine, **1b**



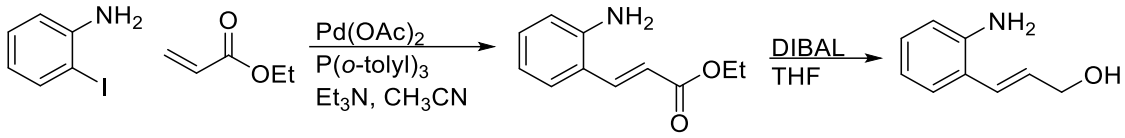

Following the general procedure (E) using 2-iodoaniline (0.2 g, 0.91 mmol) and 2,6-dimethylphenylboronic acid (0.164 g, 1.1 mmol), substrate **1q** was obtained as a brown oil (0.142 g, 0.72mmol, 79%).$^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.22 – 7.11 (m, 4H), 6.93 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.84 (dd, *J* = 7.4, 1.2 Hz, 1H), 6.79 (dd, *J* = 7.9, 1.2 Hz, 1H), 3.43 (s, 2H), 2.06 (s, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 143.5, 137.0, 136.9, 134.8, 129.9, 128.4, 128.0, 126.1, 118.4, 114.9, 20.1 . Spectral data match those previously reported.[9]

2'-(pyrrolidin-1-ylmethyl)-[1,1'-biphenyl]-2-amine, **1e**



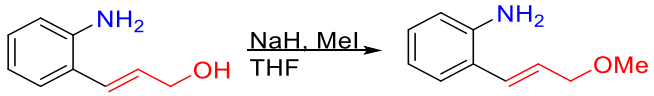

Following the general procedure (E) using 2-iodoaniline (0.2 g, 0.91 mmol) and boronic acid **B3** (0.225 g, 1.1 mmol), substrate **1o** was obtained as a light brown oil (0.202 g, 0.8 mmol, 88%).$^{1}$H NMR (400 MHz, Chloroform*d*) δ 7.67 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.42 (td, *J* = 7.5, 1.6 Hz, 1H), 7.37 (td, *J* = 7.4, 1.5 Hz, 1H), 7.28 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.23 (td, *J* = 7.6, 1.6 Hz, 1H), 7.08 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.86 (td, *J* = 7.4, 1.2 Hz, 1H), 6.79 (dd, *J* = 8.0, 1.2 Hz, 1H), 3.83 (s, 2H), 3.56 (dd, *J* = 105.1, 13.6 Hz, 2H), 2.52 (dtd, *J* = 9.3, 4.8, 2.7 Hz, 4H), 1.86 – 1.69 (m, 4H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 144.4, 138.6, 138.2, 130.5, 130.3, 129.4, 128.3, 127.6, 127.3, 127.0, 118.0, 115.3, 57.1, 54.0, 23.5. IR (neat, $cm^{-1}$): 3462, 3374, 3191, 3058, 3021, 2962, 2928, 2907, 2873, 2789, 2734, 2684, 1613, 1479, 1447, 1375, 1347, 1295, 1240, 1197, 1127, 1095, 1049, 1005. HRMS (ESI): Calcd for $C_{17}H_{20}N_2$ 252.1626, Found: 252.1629.

3-(2-aminophenyl)prop-2-en-1-ol, **1d'**



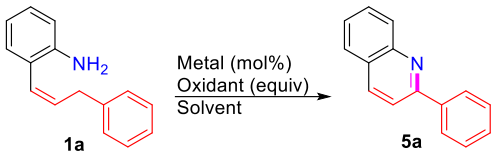

To prepare substrate **1d'**, a one neck round bottom flask was equipped with a magnetic stir bar, 2-iodoaniline (9.636g, 44mmol), ethyl acrylate (17.6g, 176mmol), $Pd(OAc)_2$ (1g, 4.45mmol), P(*o*-tolyl)$_3$ (2.7g, 8.9mmol), Triethylamine (15 mL), and $CH_3CN$ (30 mL). The mixture was then purged with $N_2$ 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 of ethyl acetate. The resulting oranic 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 ester product (92%) as a dark yellow oil that slowly crystallized. 1s' was prepared by DIBAL reduction of ester substrate. To a flame dried round bottom flask was added ester-aniline (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 **1s'** (87%) as a yellow oil. $^1$H NMR (400 MHz, Chloroform-*d*) 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 (100 MHz, Chloroform-*d*) 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. Spectral data match those previously reported. [1]

2-(3-methoxyprop-1-en-1-yl)aniline, **1d**




Substrate 1s was obtained by treating **1d'** (0.11 g, 0.7 mmol) 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 **1d** (60%) as a crème colored oil that slowly crystallized. $^1$H NMR (400 MHz, Chloroform-*d* ) 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 (100 MHz, Chloroform-*d*) 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. Spectral data match those previously reported.[1]

6. Optimization Studies

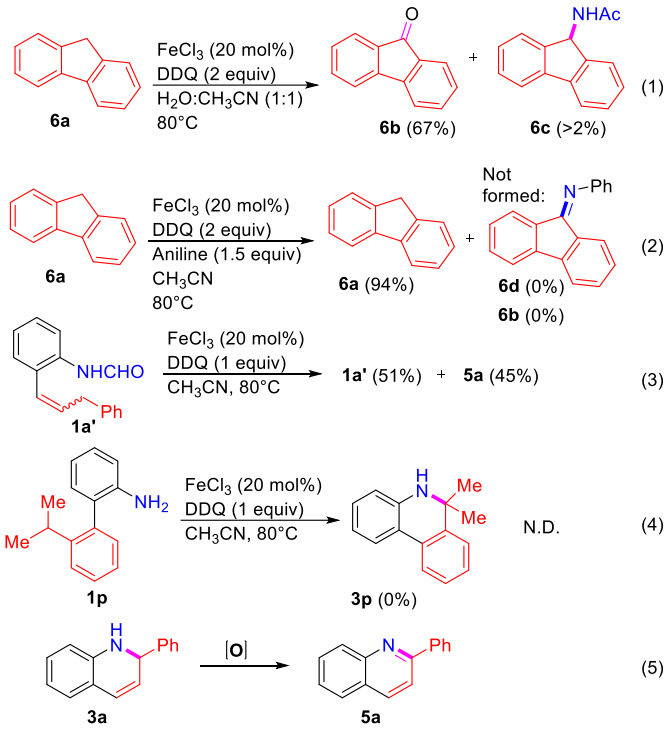


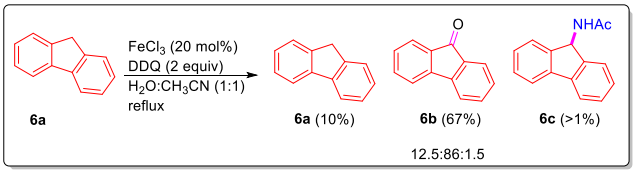

| Entry | Metal | Oxidant | Solvent | Temp. (°C) | Yield%[g] |
|---|---|---|---|---|---|
| 1 | $Co(acac)_2$[a] | DDQ[c] | $CH_3CN$ | 80 | trace |
| 2 | $TiCl_4$[a] | DDQ[c] | $CH_3CN$ | 80 | 20 |
| 3 | CuI[a] | DDQ[c] | $CH_3CN$ | 80 | 60 |
| 4 | $ZnCl_2$[a] | DDQ[c] | $CH_3CN$ | 80 | 0 |
| 5 | $FeCl_2$[a] | DDQ[c] | $CH_3CN$ | 80 | 66 |
| 6 | $FeCl_3 \bullet 6H_2O$[a] | DDQ[c] | $CH_3CN$ | 80 | 60 |
| 7 | $Fe(acac)_3$[a] | DDQ[c] | $CH_3CN$ | 80 | 62 |
| 8 | $FeCl_3$[a] | DDQ[c] | $CH_3CN$ | 80 | 69 |
| 9 | $FeCl_3$[a] | TBHP[c] | $CH_3CN$ | 80 | 61 |
| 10 | $FeCl_3$[a] | DTBP[c] | $CH_3CN$ | 80 | 59 |
| 11 | $FeCl_3$[a] | BPO[c] | $CH_3CN$ | 80 | 51 |
| 12 | $FeCl_3$[a] | $Na_2S_2O_8$[c] | $CH_3CN$ | 80 | 40 |
| 13 | $FeCl_3$[b] | DDQ[c] | $CH_3CN$ | 80 | 86 |
| 14 | None | DDQ[c] | $CH_3CN$ | 80 | 31 |
| 15 | $FeCl_3$[b] | DDQ[d] | $CH_3CN$ | 80 | 81 |
| 16 | $FeCl_3$[b] | DDQ[e] | $CH_3CN$ | 80 | 45 |
| 17 | $FeCl_3$[b] | None | $CH_3CN$ | 80 | trace |
| 18 | $FeCl_3$[b] | DDQ[c] | $ClC_6H_6$ | 80 | 78 |
| 19 | $FeCl_3$[b] | DDQ[c] | $C_6H_6$ | reflux | 75 |
| 20 | $FeCl_3$[b] | DDQ[c] | DMF | 80 | 14 |
| 21 | $FeCl_3$[b] | DDQ[c] | EtOH | Reflux | trace |
| 22 | $FeCl_3$[b] | DDQ[c] | $CH_3CN$ | rt | 5 |
| 23 | $FeCl_3$[b] | DDQ[c] | $CH_3CN$ | 50 | 61 |
| 24 | $FeCl_3$[b] | DDQ[c] | $CH_3CN$ | reflux | 85 |

Reaction conditions: **1a** (1 eq.), specified amount of metal ([a] 100 mol%, [b] 20 mol%) and oxidant; [c] 2 eq., [d] 3 eq., [e] 1 eq.) in 4 mL of solvent. Reactions were allowed to stir for 4 hours with heating bath set to 80°C. [g] NMR yield based on **1a** and determined by internal standard ($Ph_3CH$).

Our first attempt using $FeCl_3$ (1 eq.), *t*ert-butylhydroperoxide (TBHP, 4 eq.) in acetonitrile (80°C) with **1a** yielded **5a** in 56% (see SI for full details). Encouraged by this result, we tested other oxidants in this reaction (DDQ (0.05 V vs. $Fc/Fc^+$), TBHP (0.07 V), DTBP (-0.1 V))[10] and found that DDQ outperformed other oxidants. Two equivalents of DDQ were needed for full conversion of **1a**. We next tested first row transition metals that have been shown to undergo similar TMM-SET oxidation reactions.[7] For the other Lewis acids such as $Ti^{IV}$, $Zn^{II}$, $Cu^{I}$ and $Co^{II}$ salts, the observed conversions/yields were poor. However, $Fe^{II}$ and $Fe^{III}$ salts facilitated the desired transformation and provided high yields of the C-H amination product. $FeCl_3$ provided slightly higher yields over $FeCl_2$ (entries 8 and 5 in Table 2). Other $Fe^{III}$ salts ($Fe(acac)_3$, $FeCl_3 \bullet 6H_2O$) provide comparable yields of 62% and 60%, respectively. Aprotic solvents were favored with acetonitrile providing highest yields. At room temperature, only trace amounts of **5a** were observed. Elevated temperatures were needed to achieve full conversion (see SI for full details). We found that sub-stoichiometric quantities (20 mol%, entry 12) were sufficient for driving reaction to completion. Under the optimal conditions, i.e, $FeCl_3$ (20 mol%), DDQ (2 eq.) in acetonitrile at 80°C gave the target product in 86% yield.

7. Mechanistic Studies



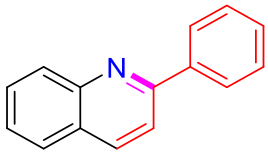

9H-fluoren-9-one was prepared using general procedure (F) below using fluorene and instead of dry acetonitrile a 1:1 mixture of $H_2O$:$CH_3CN$ was used. $^1$H NMR (600 MHz, Chloroform-*d*) δ 7.66 (dt, *J* = 7.3, 1.0 Hz, 2H), 7.53 (dt, *J* = 7.4, 1.0 Hz, 2H), 7.49 (td, *J* = 7.4, 1.1 Hz, 2H), 7.30 (td, *J* = 7.3, 1.1 Hz, 2H). 13C NMR (150 MHz, Chloroform-*d*) δ 144.6, 134.9, 129.2, 124.5, 120.5.

8. General procedure (F) for iron-catalyzed intramolecular C-H amination:

To a flame dried 10 mL round bottom flask purged with $N_2$ was equipped a magnetic stirring bar, vigreux column and was charged with aniline substrate (1 equiv), DDQ (2 equiv) and $FeCl_3$ (20 mol%) under a gentle stream of $N_2$. To the flask was then added 2-3 mL of dry acetonitrile and the mixture was allowed to stir at 80°C for 4-6 hours. The resulting mixture was directly filtered through a pad of basic alumina with EtOAc (20 mL). The resulting solution was concentrated under reduced pressure to afford the desired product without the need for column chromatography.

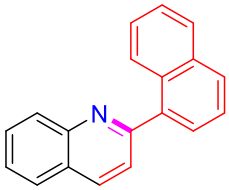
9. Spectroscopic data for products:

2-Phenylquinoline, **5a**



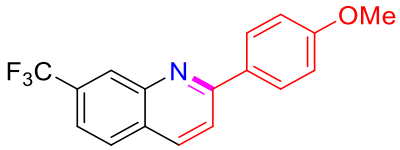
Following the general procedure (F) using substrate **1a** (30 mg, 0.143 mmol) afforded desired product **5a** (24 mg, 0.119 mmol, 83%). $^1$H NMR (600 MHz, Chloroform-*d*) δ 8.25 – 8.15 (m, 4H), 7.88 (d, *J* = 8.5 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.74 (t, *J* = 7.6 Hz, 1H), 7.59 – 7.51 (m, 3H), 7.48 (t, *J* = 7.3 Hz, 1H). $^{13}$C NMR (150 MHz, Chloroform-*d*) 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.[1]

2-(naphthalen-1-yl)quinoline, **5f**



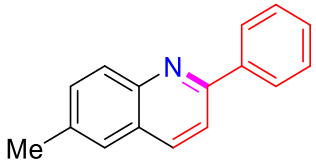
Following the general procedure (F) using substrate **1b** (50 mg, 0.193 mmol) afforded desired product **5b** (39 mg, 0.154 mmol, 80%). $^1$H NMR (400 MHz, Chloroform-*d*) δ: 7.47 (t, J = 7.6 Hz, 1H), 7.52 (t, J = 6.9 Hz, 1H), 7.60 (t, J = 7.6 Hz, 2H), 7.72 (t, J =6.8 Hz, 2H), 7.78 (t, J = 7.1 Hz, 1H), 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 (100 MHz, Chloroform-*d*) 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.[116]

2-(4-methoxyphenyl)-7-(trifluoromethyl)quinoline, **5g**



Following the general procedure (F) using substrate **1c** (35 mg, 0.114 mmol) afforded desired product **5c** (29 mg, 0.095 mmol, 83%) as light yellow crystals. Mp: 143-146°C. $^1$H NMR (600 MHz, Chloroform-*d*) δ 8.57 (s, 1H), 8.29 (d, *J* = 8.6 Hz, 1H), 8.21 (d, *J* = 8.3 Hz, 2H), 7.98 (dd, *J* = 21.4, 8.5 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.10 (d, *J* = 8.7 Hz, 2H), 3.93 (s, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$) δ 158.0, 129.3, 129.2, 129.2, 128.6, 128.2, 124.8, 123.0, 121.7, 120.4, 114.4, 99.9, 55.4. IR (neat, cm$^{-1}$): 3900, 3847, 3835, 3826, 3800, 3748, 3735, 3712, 3693, 3669, 3644, 3636, 3570, 1867, 1767, 1720, 1706, 1677, 1645, 1600, 1550, 1547, 1515, 1486, 1472, 1452, 1427, 1347, 1243, 1164, 1028. HRMS (ESI): Calcd for $C_{17}H_{12}F_3NO$ 303.0871, Found: 303.0868.

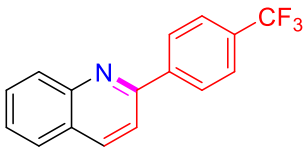
6-methyl-2-phenylquinoline, **5h**



Following the general procedure (F) using substrate **1d** (47mg, 0.21 mmol) afforded desired product **5d** (21 mg, 0.095mmol, 45%). $^1$H NMR (600 MHz, Chloroform-*d*) δ 8.14 (dd, *J* = 7.9, 4.1 Hz, 1H), 8.06 (d, *J* = 8.6 Hz, 1H), 7.84

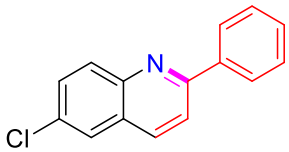
(d, *J* = 8.5 Hz, 1H), 7.59 (s, 1H), 7.56 (d, *J* = 8.6 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.46 (d, *J* = 7.0 Hz, 1H), 7.42 (d, *J* = 3.7 Hz, 1H), 2.55 (s, 1H). $^{13}$C NMR (150 MHz, Chloroform-*d*) δ 136.3, 132.1, 129.6, 129.3, 129.2, 129.0, 128.0, 128.0, 127.6, 127.4, 126.5, 125.7, 119.2, 21.8. Spectral data match those previously reported.[1]

2-(4-(trifluoromethyl)phenyl)quinoline, **5i**



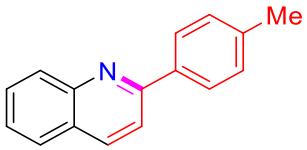

Following the general procedure (F) using substrate **1e** (57mg, 0.21mmol) afforded desired product **5e** (44 mg, 0.16 mmol, 77%). $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 8.25 (d, J= 8.3 Hz, 2H), 8.21 (d, J= 8.6 Hz, 1H), 8.17 (d, J= 8.3 Hz, 1H), 7.85-7.69 (m, 5H), 7.51 (t, J= 7.5 Hz, 1H). $^{13}$C NMR (100 MHz, Chloroform-*d*): δ = 118.6, 124.2, 125.6, 126.8, 127.4, 127.5, 127.7, 129.8, 129.9, 131.0 (q, J = 30.3 Hz), 137.0, 142.8, 148.2, 155.5. Spectral data match those previously reported.[12]

6-chloro-2-phenylquinoline, **5j**



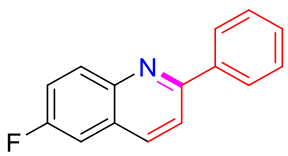

Following the general procedure (F) using substrate **1f** (45mg, 0.18 mmol) afforded desired product **5f** (35 mg, 0.14 mmol, 78%). $^{1}$H NMR (600 MHz, Chloroform-*d*) δ 8.20 (d, *J* = 7.9 Hz, 3H), 7.95 (d, *J* = 8.6 Hz, 1H), 7.86 (s, 1H), 7.71 (d, *J* = 9.1 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 3H), 7.53 (d, *J* = 7.3 Hz, 1H). Spectral data match those previously reported.

2-(4-Methylphenyl)quinoline, **5k**



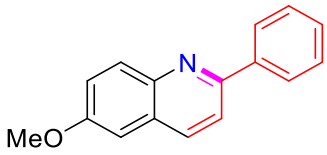

Following the general procedure (F) using substrate **1g** (53 mg, 0.24 mmol) afforded desired product **5g** (43 mg, 0.19 mmol, 82%). $^{1}$H NMR (400 MHz, Chloroform-*d*): δ 2.36 (s, 3H), 7.25,c (d, J = 8.3 Hz, 2H), 7.35-7.45, (m, 1H), 7.60-7.75, (m, 3H), 8.00-8.05 (m, 3H), 8.15 (d, J = 4.4 Hz, 1H); $^{13}$C NMR (100 MHz, Chloroform-*d*): 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.[1]

6-fluoro-2-phenylquinoline, **5l**



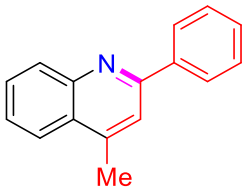
Following the general procedure (F) using substrate **1h** (63 mg, 0.28 mmol) afforded desired product **5h** (49 mg, 0.22 mmol, 79%). $^1$H NMR (600 MHz, Chloroform-*d*) δ 8.21 – 8.11 (m, 4H), 7.90 (d, *J* = 8.7 Hz, 1H), 7.50 (dddd, *J* = 21.6, 19.9, 9.1, 5.1 Hz, 5H). $^{13}$C NMR (150 MHz, Chloroform-*d*) 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. Spectral data match those previously reported. [1]

6-methoxy-2-phenylquinoline, **5m**



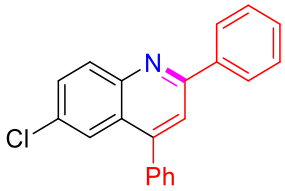

Following the general procedure (F) using substrate **1i** (51 mg, 0.21 mmol) afforded desired product **5i** (35 mg, 0.15 mmol, 71%). $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.20 – 8.12 (m, 4H), 7.92 (d, *J* = 8.7 Hz, 1H), 7.51 (dddd, *J* = 21.4, 20.0, 9.2, 5.0 Hz, 5H). $^{13}$C NMR (150 MHz, Chloroform-*d*) 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. Spectral data match those previously reported.[13]

4-methyl-2-phenylquinoline, **5n**



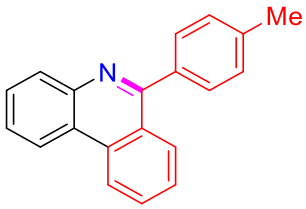

Following the general procedure (F) using substrate **1j** (72 mg, 0.32 mmol) afforded desired product **5j** (59 mg, 0.27 mmol, 84%). $^1$H NMR (600 MHz, Chloroform-*d*) δ 8.18 (dd, *J* = 8.6, 1.3 Hz, 1H), 8.15 (dt, *J* = 6.6, 1.4 Hz, 1H), 8.01 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.75 – 7.70 (m, 1H), 7.57 – 7.55 (m, 1H), 7.55 – 7.51 (m, 1H), 7.48 – 7.44 (m, 1H), 2.78 (d, *J* = 1.0 Hz, 3H). $^{13}$C NMR (150 MHz, Chloroform-*d*) δ 157.3, 148.3, 145.0, 140.0, 130.5, 129.5, 129.3, 128.9, 127.7, 127.4, 126.2, 123.8, 120.0, 19.2. Spectral data match those previously reported
[14]

2,4-diphenylquinoline, **5o**



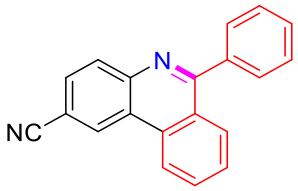

Following the general procedure (F) using substrate **1k** (100 mg, 0.31 mmol) afforded desired product **5k** (85 mg, 0.26 mmol, 86%). $^1$H NMR (600 MHz, Chloroform-d) δ 8.18-8.21 (m, 3H), 7.86 (d, J = 2.0 Hz, 1 H), 7.85 (s, 7.85), 7.67 (dd, 1J = 9.0 Hz, 2J = 2.2 Hz, 1H), 7.48-7.60 (m, 7 H).13C NMR (150 MHz, Chloroform-d) δ 157.2, 148.7, 147.33, 139.3, 137.9, 132.4, 131.8, 130.7, 129.8, 129.6, 129.1, 129.0, 128.9, 127.7, 126.7, 124.7, 120.2. Spectral data match those previously reported.

6-(p-tolyl)phenanthridine, **5p**



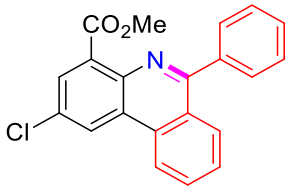

Following the general procedure (F) using substrate **1l** (100 mg, 0.37 mmol) afforded desired product **5l** (82 mg, 0.3 mmol, 83%). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.69 (1H, d, J = 8.0 Hz), 8.61 (1H, d, J = 8.4 Hz), 8.26 (1H, d, J = 8.4 Hz), 8.14 (1H, d, J = 8.4 Hz), 7.87 (1H, dd, J = 8.0, 8.4 Hz), 7.76 (1H, dd, J = 8.4, 8.4 Hz), 7.59-7.70 (4H, m), 7.38 (2H, d, J = 7.9 Hz), 2.49 (3H, s). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 161.3, 143.7, 138.6, 136.8, 133.4, 130.5, 130.2, 129.7, 129.1, 129.1, 129.0, 128.8, 127.1, 126.8, 123.7, 122.2, 121.9, 21.4. Spectral data match those previously reported.

6-phenylphenanthridine-2-carbonitrile, **5q**



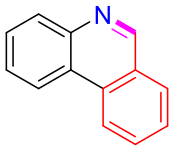

Following the general procedure (F) using substrate **1m** (50 mg, 0.18 mmol) afforded desired product **5m** (43 mg, 0.15 mmol, 88%). $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.96 (d, *J* = 1.8 Hz, 1H), 8.74 – 8.63 (m, 1H), 8.30 (dd, *J* = 8.4, 0.6 Hz, 1H), 8.18 (ddd, *J* = 8.3, 1.3, 0.7 Hz, 1H), 8.01 – 7.90 (m, 2H), 7.82 – 7.69 (m, 3H), 7.65 – 7.53 (m, 3H). $^{13}$C NMR (150 MHz, Chloroform-*d*) δ 164.3, 145.4, 138.9, 132.4, 131.6, 131.4, 130.4, 129.6, 129.3, 128.5, 127.7, 125.5, 123.8, 122.1, 119.1, 110.1. Spectral data match those previously reported.

methyl 2-chloro-6-phenylphenanthridine-4-carboxylate, **5r**




Following the general procedure (F) using substrate **1n** (30mg, 0.08 mmol) afforded desired product **5n** (25 mg, 0.07 mmol, 84%) as an off white solid. mp: 180-184°C. $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.67 (d, *J* = 2.4 Hz, 1H), 8.62 (d, *J* = 8.3 Hz, 1H), 8.27 (d, *J* = 8.3 Hz, 1H), 7.97 – 7.87 (m, 2H), 7.87 – 7.80 (m, 2H), 7.71 (t, *J* = 7.7 Hz, 1H), 7.55 (d, *J* = 6.3 Hz, 3H), 4.02 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 167.7, 161.3, 139.8, 139.2, 134.5, 132.2, 131.9, 130.9, 130.4, 129.1, 129.0, 128.9, 128.2, 128.2, 125.1, 125.0, 124.1, 122.4, 52.6. IR (neat, $cm^{-1}$): IR (neat): 3910, 3840, 3830, 3805, 3671, 3642, 3559, 2946, 1870, 1720, 1676, 1650, 1611, 1557, 1540, 1523, 1510, 1490, 1475, 1457, 1434, 1401, 1365, 1280, 1103, 1021. HRMS (ESI): Calcd for $C_{21}H_{14}ClNO_2$ 347.0713, Found: 347.0710.

Phenanthridine, **5e**

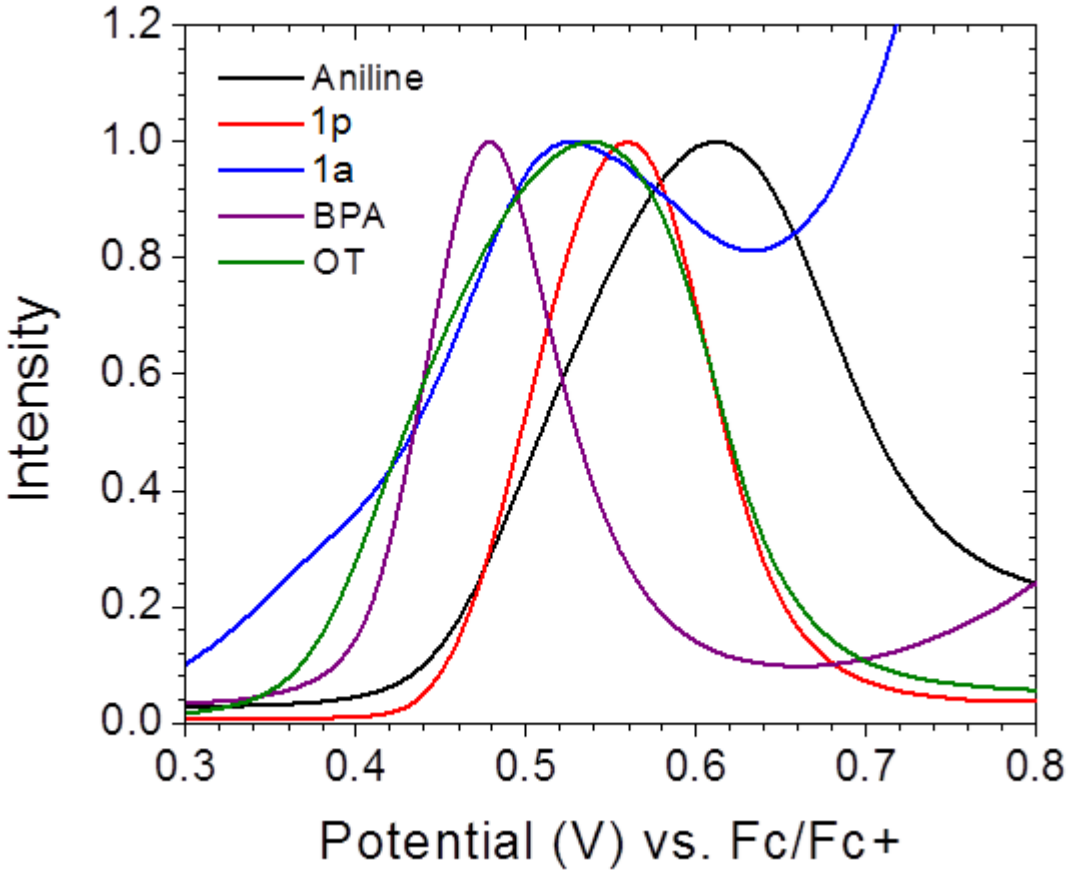


Following the general procedure (F) using substrate **10** (90 mg, 0.36 mmol) afforded desired product **50** (52 mg, 0.29 mmol, 81%). $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 9.30 (d, *J* = 0.8 Hz, 1H), 8.62 (ddd, *J* = 13.4, 8.2, 1.2 Hz, 2H), 8.24 – 8.17 (m, 1H), 8.07 (ddd, *J* = 7.9, 1.4, 0.7 Hz, 1H), 7.88 (ddd, *J* = 8.4, 7.1, 1.4 Hz, 1H), 7.80 – 7.67 (m, 3H). $^{13}$C NMR (100 MHz, Chloroform-*d)* 153.7, 144.6, 132.7, 131.2, 130.3, 129.0, 128.9, 127.7, 127.3, 126.6, 124.3, 122.4, 122.1. Spectral data match those previously reported.[15]

10. Differential Pulse Voltammetry.

*Differential Pulse Voltammetry*. Data were collected using a CH Instruments CHI630E electrochemical analyzer using a three-electrode configuration (glassy carbon working, Pt counter, Ag reference). The samples were measured by scanning in the positive direction at a scan rate of 0.1 V/s. Oxidation potentials were calculated using Fc/Fc+ as an internal standard.

DPV Values:
Aniline = 0.605
**1p** = 0.555
**1a** = 0.525
BPA = 0.475
OT = 0.535

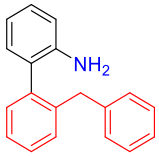



DPV spectra for aniline, **1p**, **1a**, BPA (4-aminobiphenyl), and OT (*o*-toluidine) in 0.1 M $TBAClO_4$ in MeCN at 0.1 V/s scan rate measured vs. an internal Fc/Fc+ standard.

11. Gaussian calculations for geometry optimization and frequency calculations neutral and radical cation species were performed at the UM06-2x/6-311+g(d,p) level of theory.[16]

Computational Detail:

Geometries

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| C | -0.15491 | 1.58626 | -0.73849 |
| C | -0.11358 | 2.81301 | -0.06224 |
| C | -0.09248 | 4.01227 | -0.78699 |
| C | -0.11271 | 3.98478 | -2.18797 |
| C | -0.15404 | 2.75803 | -2.86421 |
| H | -0.20669 | 0.62212 | -2.6558 |
| H | -0.06093 | 4.94892 | -0.27066 |
| H | -0.0966 | 4.90044 | -2.74133 |
| H | -0.16949 | 2.73704 | -3.9339 |
| C | -0.17809 | 0.26839 | 0.05794 |
| C | -0.21942 | -0.95836 | -0.61831 |
| C | -0.15786 | 0.29588 | 1.45892 |
| C | -0.24051 | -2.15762 | 0.10644 |
| C | -0.17895 | -0.90338 | 2.18366 |
| H | -0.1263 | 1.23253 | 1.97524 |
| C | -0.22028 | -2.13013 | 1.50742 |
| H | -0.27207 | -3.09427 | -0.40989 |
| H | -0.1635 | -0.88239 | 3.25334 |
| H | -0.23638 | -3.04579 | 2.06078 |
| C | -0.24166 | -0.98856 | -2.15785 |
| H | -0.92307 | -0.19743 | -2.39171 |
| H | 0.75431 | -0.68657 | -2.40634 |
| C | -0.55345 | -2.025 | -3.25337 |
| C | -0.42345 | -3.39346 | -2.98071 |
| C | -0.96719 | -1.59971 | -4.52297 |
| C | -0.70718 | -4.33662 | -3.97764 |
| H | -0.10756 | -3.71818 | -2.01135 |
| C | -1.25092 | -2.54287 | -5.5199 |
| H | -1.06645 | -0.55486 | -4.73115 |
| C | -1.12092 | -3.91132 | -5.24723 |
| H | -0.60792 | -5.38147 | -3.76945 |
| H | -1.56682 | -2.21814 | -6.48926 |
| H | -1.33755 | -4.63145 | -6.00841 |
| N | -0.09236 | 2.84184 | 1.40732 |
| H | 0.40465 | 3.65219 | 1.71768 |

H -1.02995 2.87289 1.75368
HF=-788.8886141
Sum of electronic and zero-point Energies= -788.579673
Sum of electronic and thermal Energies= -788.563284
Sum of electronic and thermal Enthalpies= -788.562340
Sum of electronic and thermal Free Energies= -788.626277
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5 C -0.328885
6 C -0.685807
7 H 0.223997
8 H 0.149911
9 H 0.155634
10 H 0.150648
11 C 1.337954
12 C 0.699666
13 C -0.232655
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27 C -0.234168
28 H 0.162673
29 C -0.581562
30 H 0.167449
31 C -0.212698
32 H 0.156164
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36 H 0.265722
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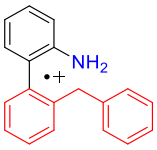
Sum of Mulliken atomic charges = 0.00000

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| C | -0.40848 | 1.32913 | -0.35444 |
| C | -0.48796 | 2.43337 | 0.50478 |
| C | -0.52315 | 3.731 | -0.02329 |
| C | -0.47885 | 3.92438 | -1.41057 |
| C | -0.39937 | 2.82014 | -2.26979 |
| H | -0.30349 | 0.6794 | -2.39775 |
| H | -0.58383 | 4.57411 | 0.63274 |
| H | -0.50571 | 4.91514 | -1.81377 |
| H | -0.36554 | 2.96779 | -3.32902 |
| C | -0.36981 | -0.09683 | 0.22586 |
| C | -0.29033 | -1.20107 | -0.63336 |
| C | -0.41411 | -0.29021 | 1.61315 |
| C | -0.25514 | -2.49869 | -0.10529 |
| C | -0.37892 | -1.58783 | 2.14121 |
| H | -0.47479 | 0.5529 | 2.26918 |
| C | -0.29943 | -2.69208 | 1.282 |
| H | -0.19446 | -3.34181 | -0.76132 |
| H | -0.41274 | -1.73549 | 3.20044 |
| H | -0.27256 | -3.68284 | 1.68519 |
| C | -0.24166 | -0.98856 | -2.15785 |
| H | -0.86754 | -0.15053 | -2.3834 |
| H | 0.77072 | -0.75725 | -2.41567 |
| C | -0.69074 | -2.15319 | -3.05983 |
| C | -0.62999 | -3.47049 | -2.58554 |
| C | -1.16014 | -1.8957 | -4.35493 |
| C | -1.03865 | -4.5303 | -3.40635 |
| H | -0.27159 | -3.66709 | -1.5967 |
| C | -1.5688 | -2.95551 | -5.17574 |
| H | -1.20653 | -0.88991 | -4.71706 |
| C | -1.50806 | -4.27281 | -4.70144 |
| H | -0.99227 | -5.53609 | -3.04421 |
| H | -1.92721 | -2.75891 | -6.16457 |
| H | -1.82008 | -5.082 | -5.32815 |
| N | -0.53443 | 2.23052 | 1.95998 |
| H | -0.11289 | 3.01248 | 2.41916 |
| H | -1.48625 | 2.1445 | 2.25432 |

HF= -788.6161082

Sum of electronic and zero-point Energies= -788.307303

Sum of electronic and thermal Energies= -788.291004
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Sum of electronic and thermal Free Energies= -788.353655
Mulliken atomic charges:
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6 C -0.427671
7 H 0.192958
8 H 0.190052
9 H 0.208358
10 H 0.212749
11 C 0.543742
12 C 0.292013
13 C -0.494138
14 C -0.260633
15 C -0.211673
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30 H 0.148199
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33 H 0.170044
34 H 0.174540
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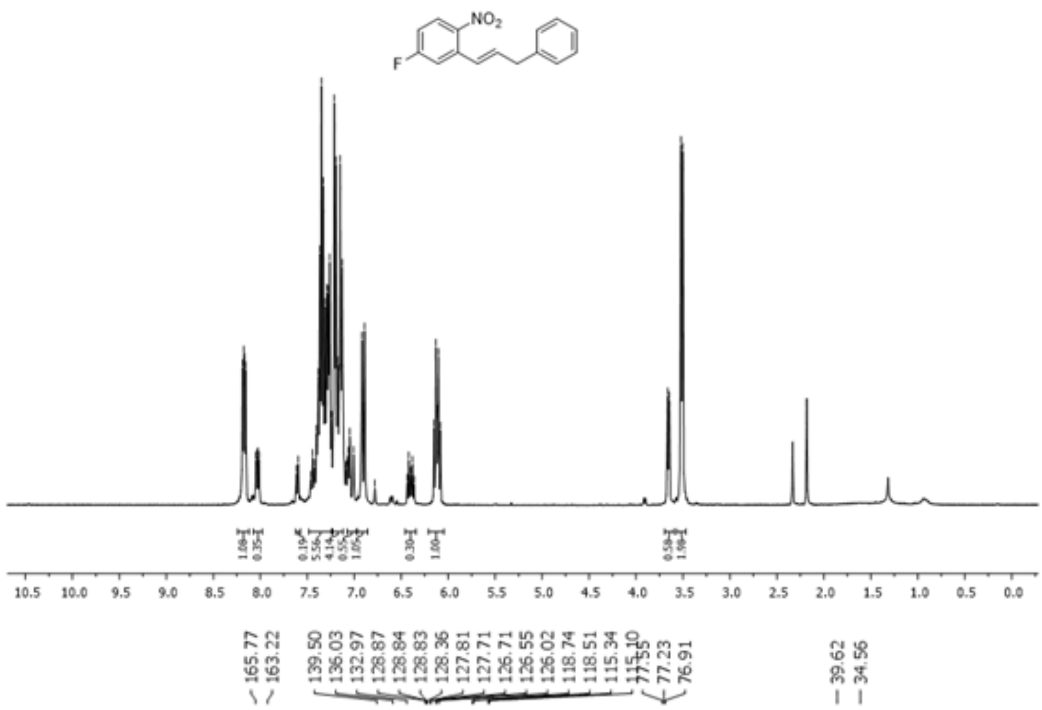
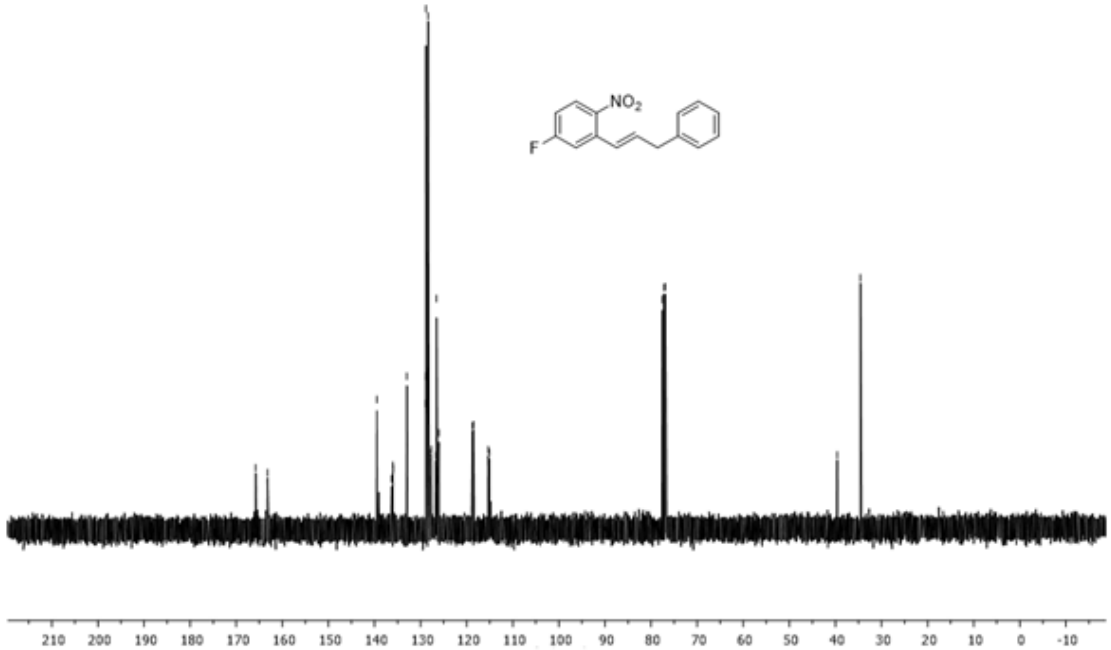
36 H 0.338919
37 H 0.332325
Sum of Mulliken atomic charges = 1.00000

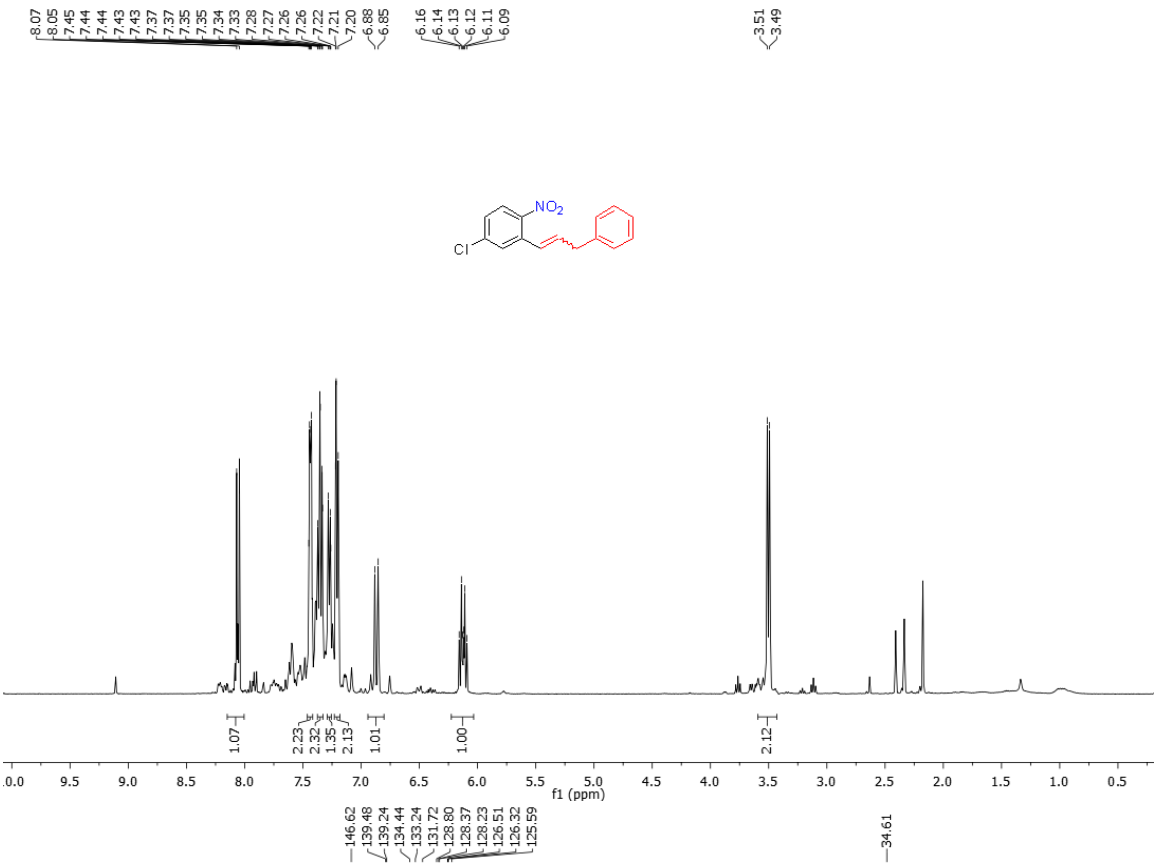
12. Copies of $^{1}H$ and $^{13}C$ NMR spectra





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7.21
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6.16
6.14
6.13
6.12
6.11
6.09
3.51
3.49
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Cl
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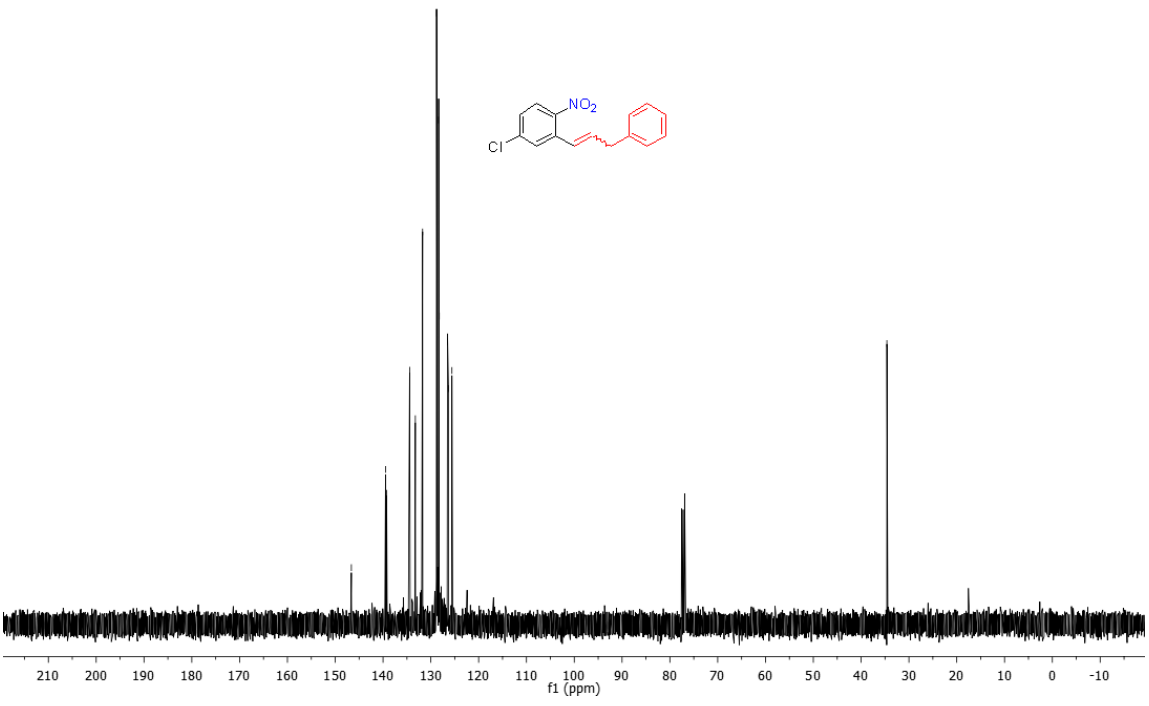
f1 (ppm)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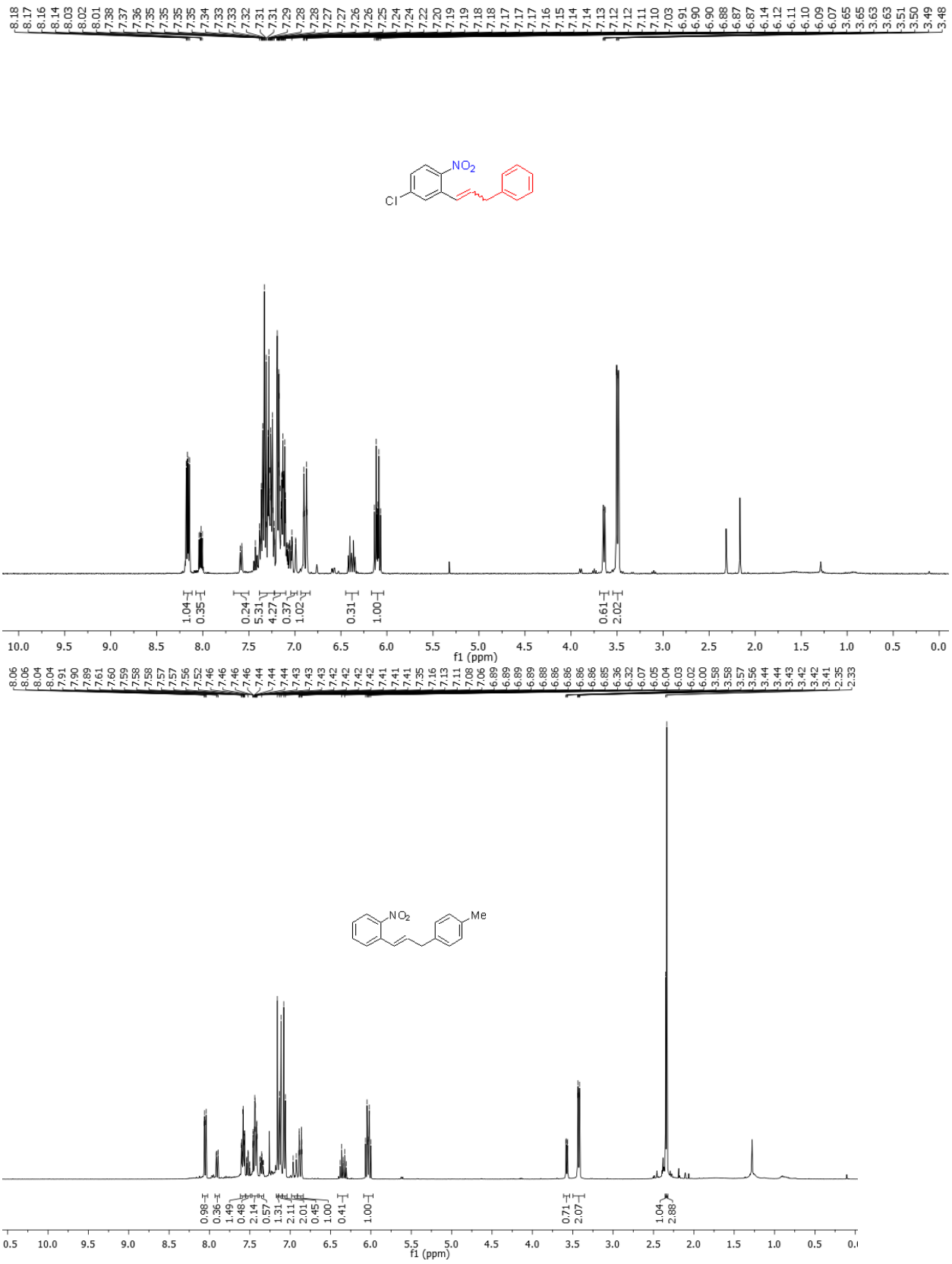
Cl
f1 (ppm)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Me
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2.14
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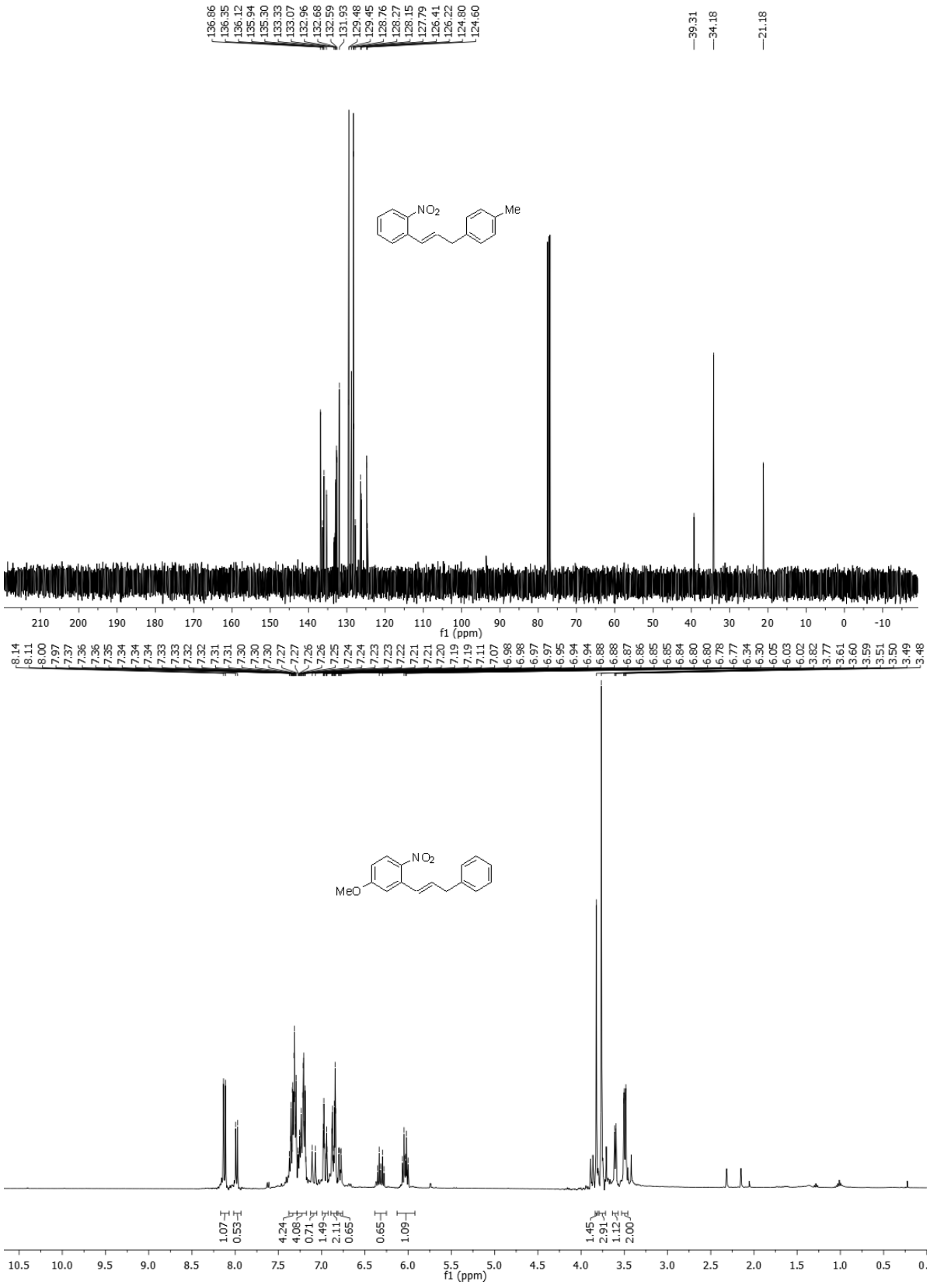
f1 (ppm)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Me
f1 (ppm)
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3.49
3.48
NO2
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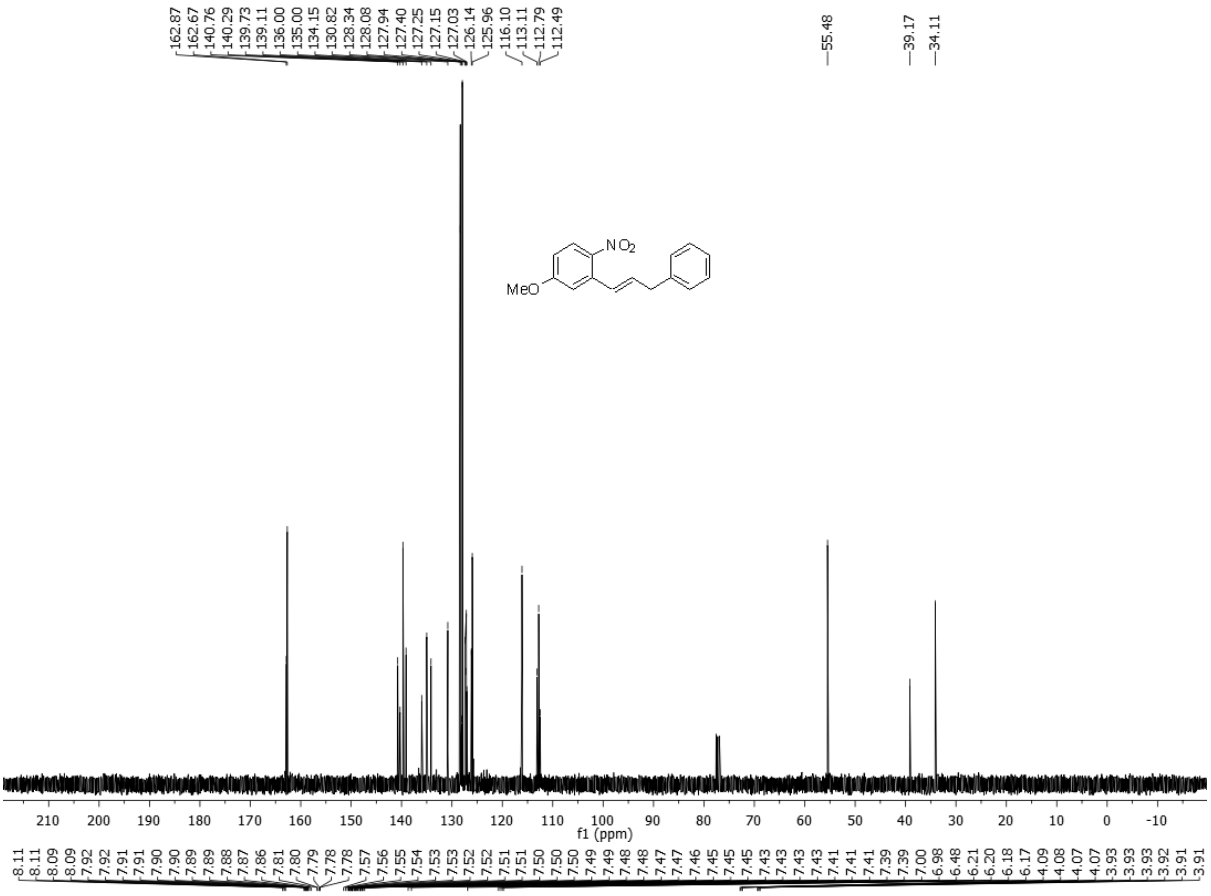
f1 (ppm)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127.25
127.15
127.03
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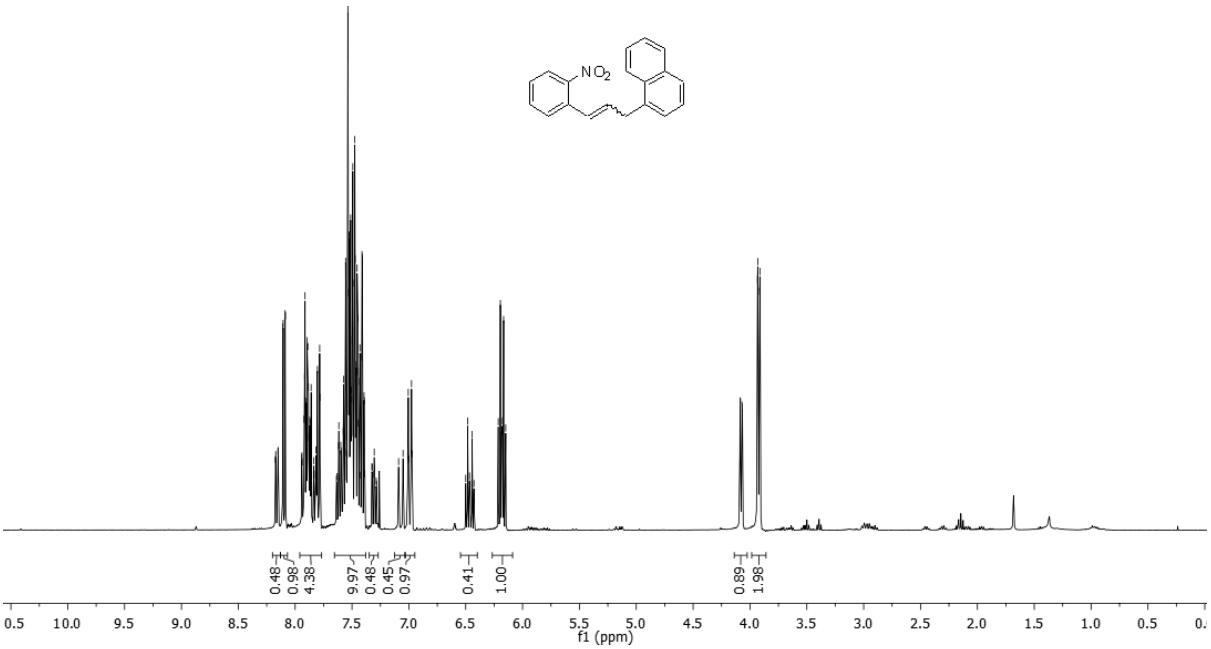
NO2
MeO
f1 (ppm)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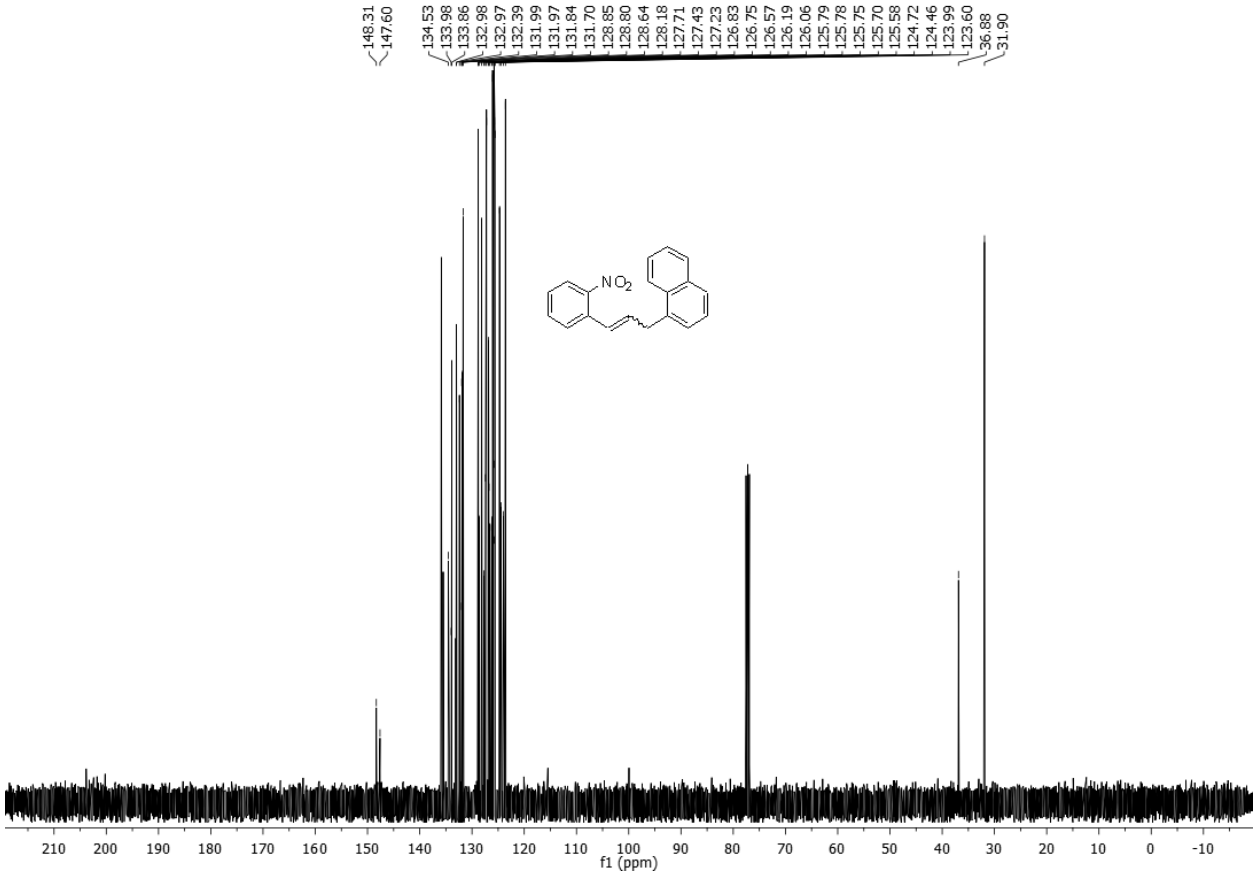
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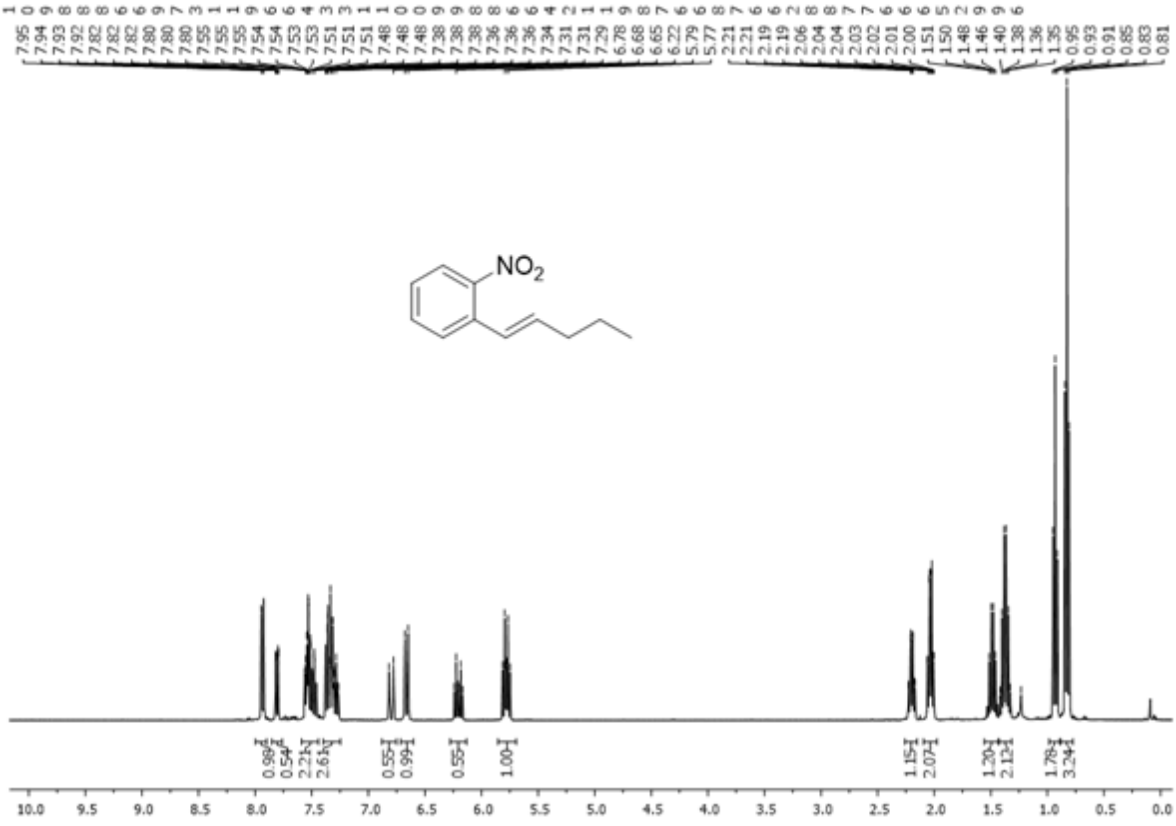
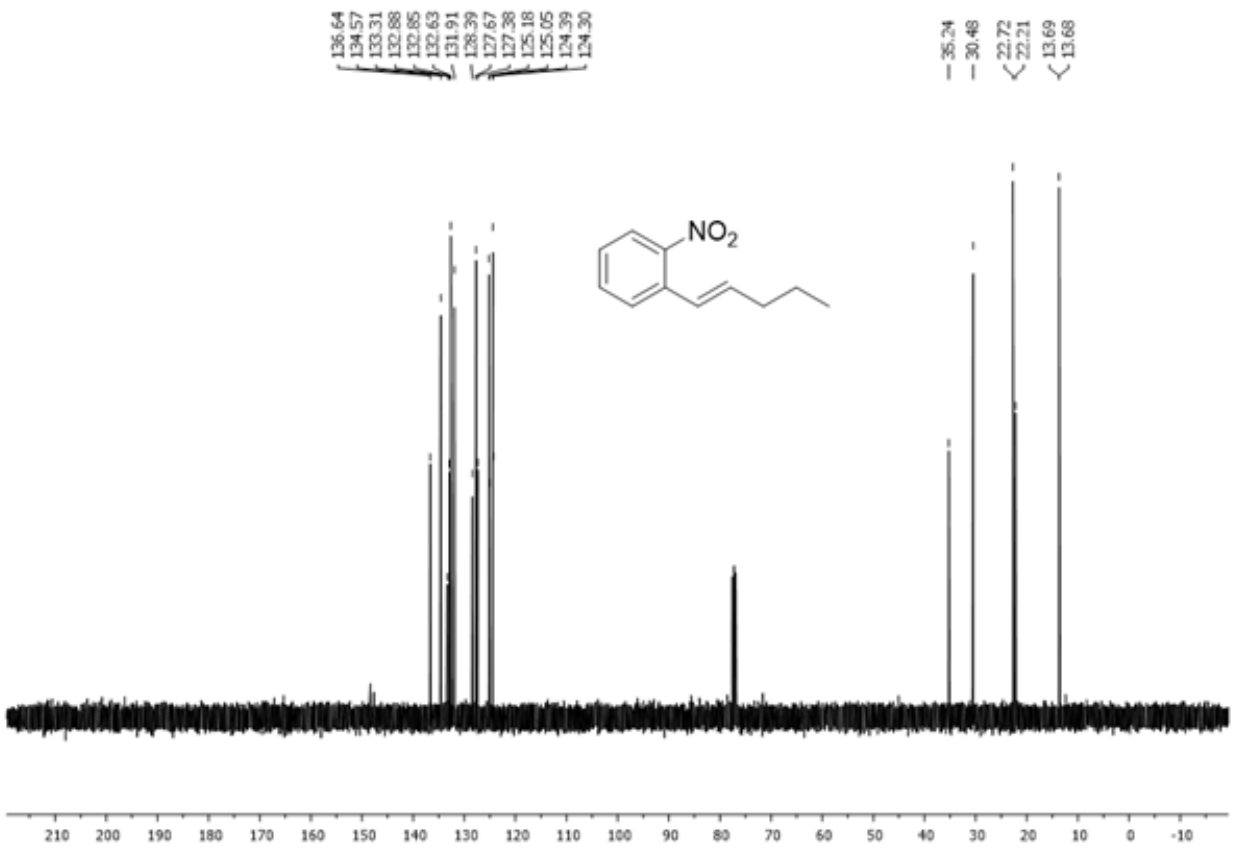
f1 (ppm)


NO2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22.72
22.21
13.69
13.68
NO2
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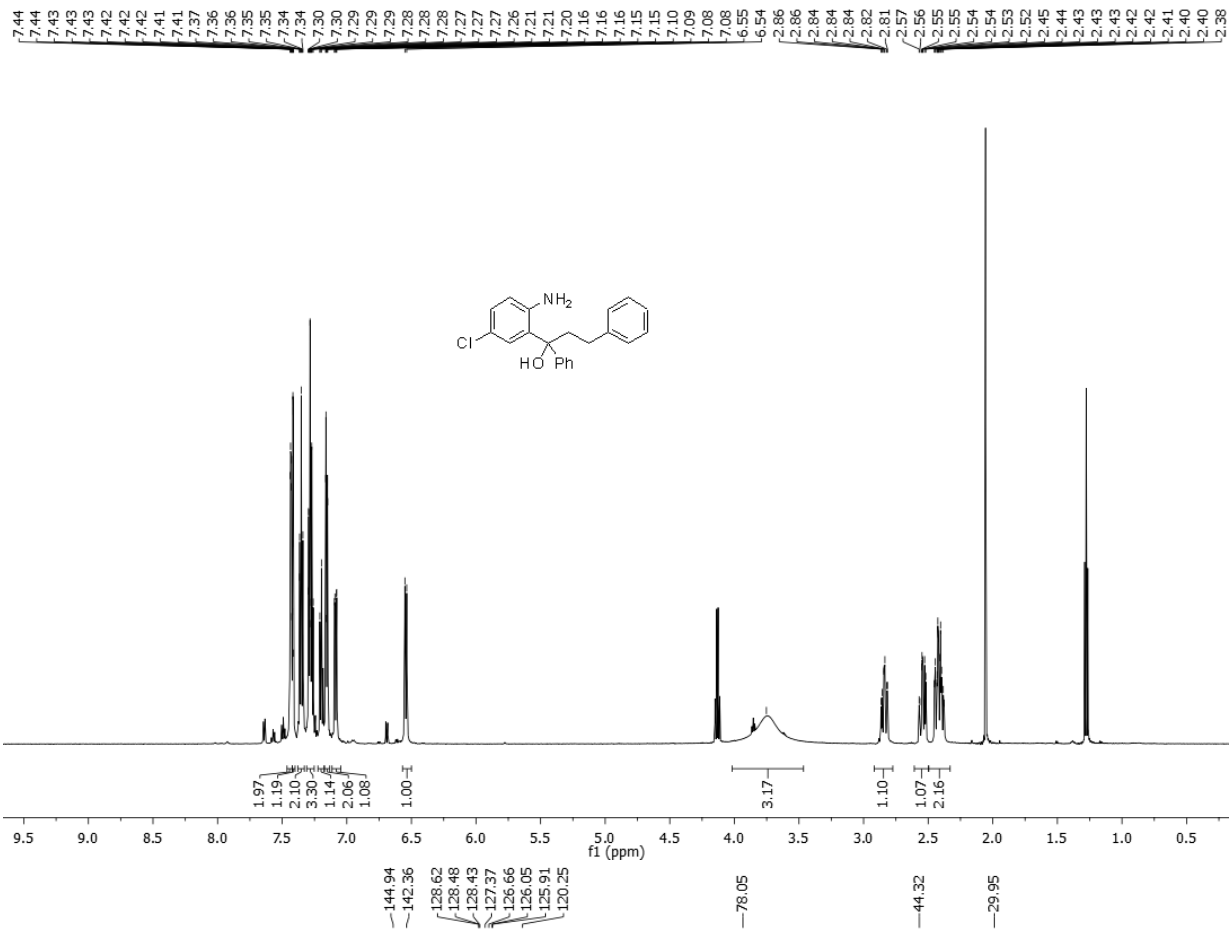
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NH2
Cl
HO Ph
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9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
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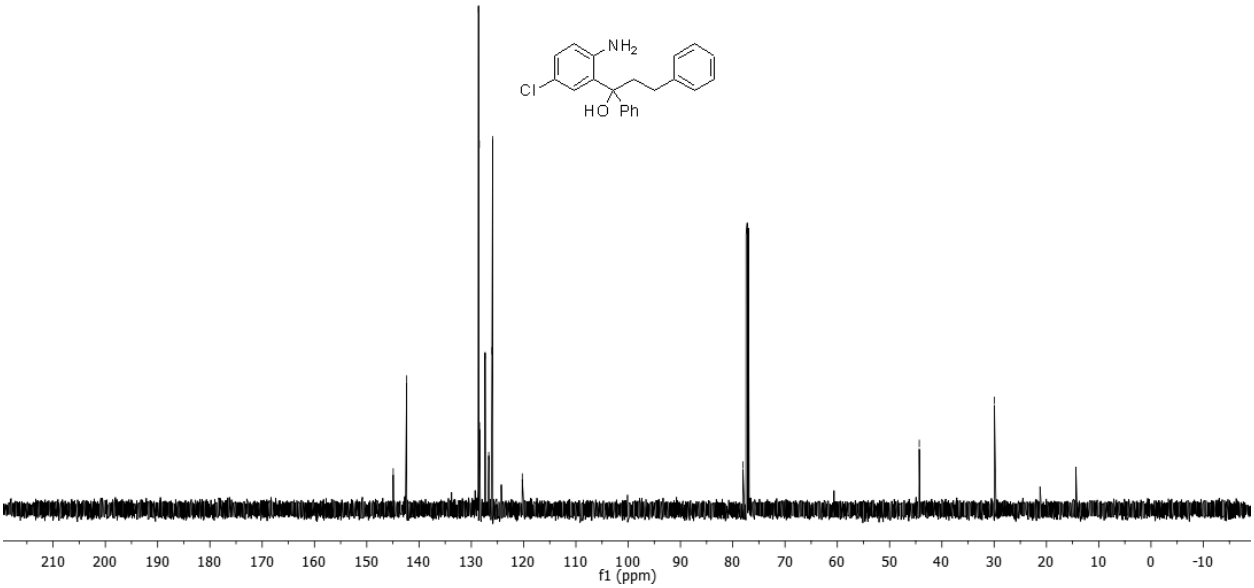
NH2
Cl
HO Ph
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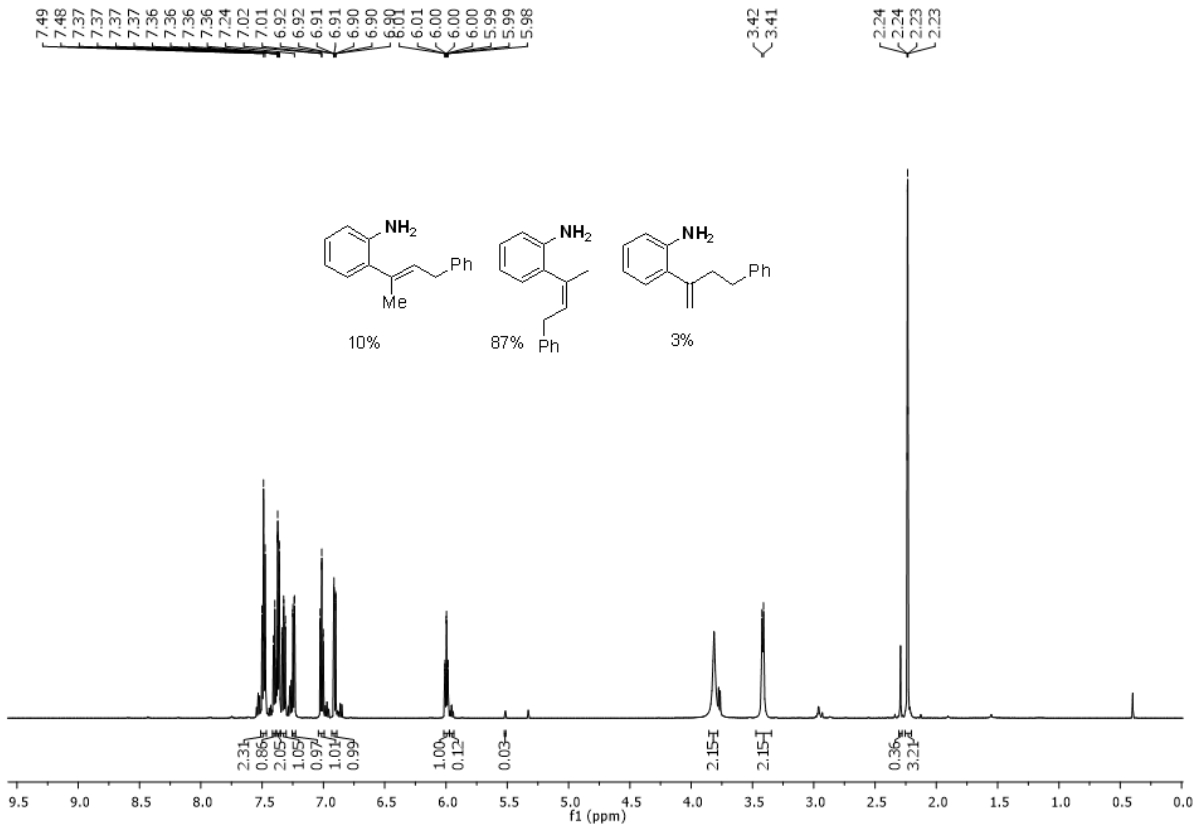
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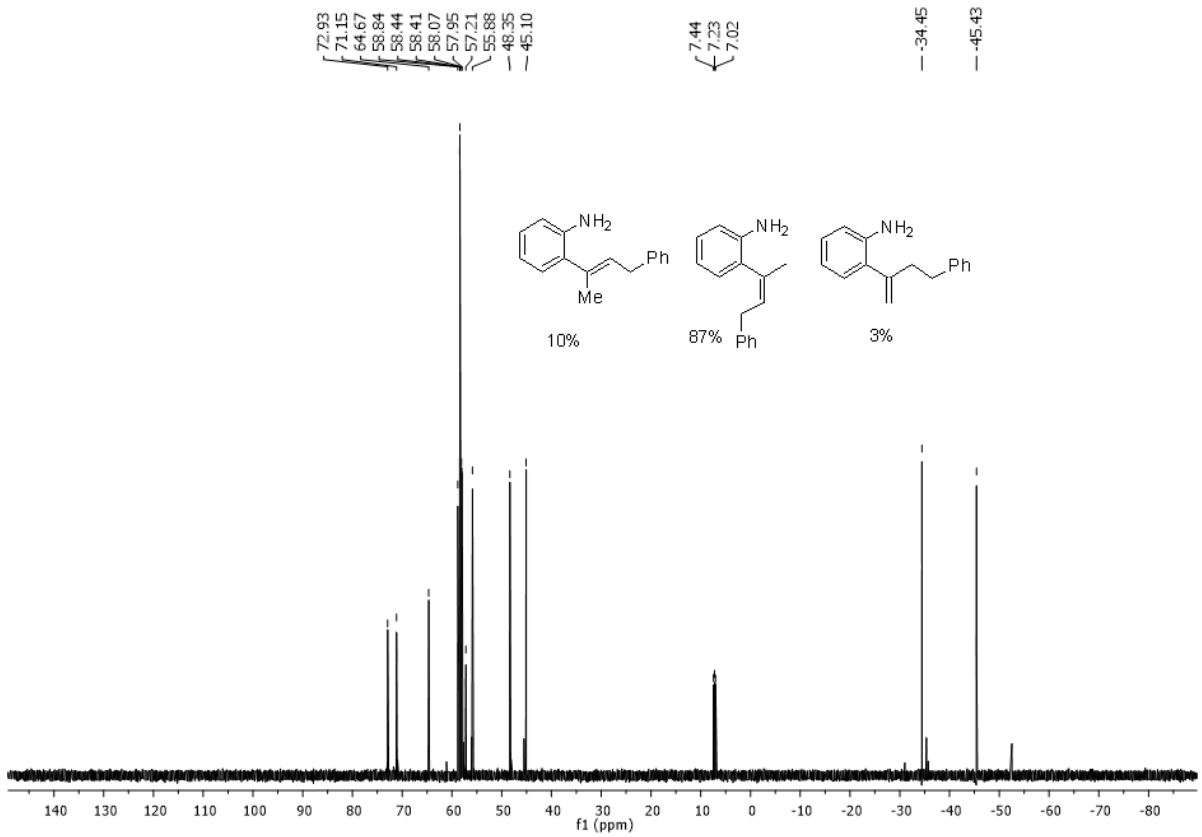
2.24
2.23
2.23
NH2
Ph
Me
10%
NH2
87%
Ph
NH2
Ph
3%
2.31
0.86
2.05
1.05
0.97
1.01
0.99
1.00
0.12
0.03
2.15
2.15
0.36
3.21
f1 (ppm)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58.41
58.07
57.95
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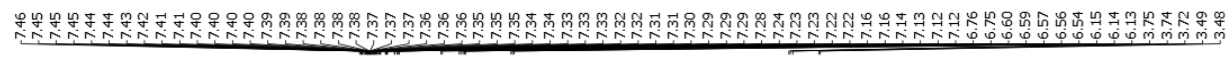
55.88
48.35
45.10
7.44
7.23
7.02
34.45
45.43
NH2
Ph
Me
10%
NH2
87%
Ph
NH2
Ph
3%
f1 (ppm)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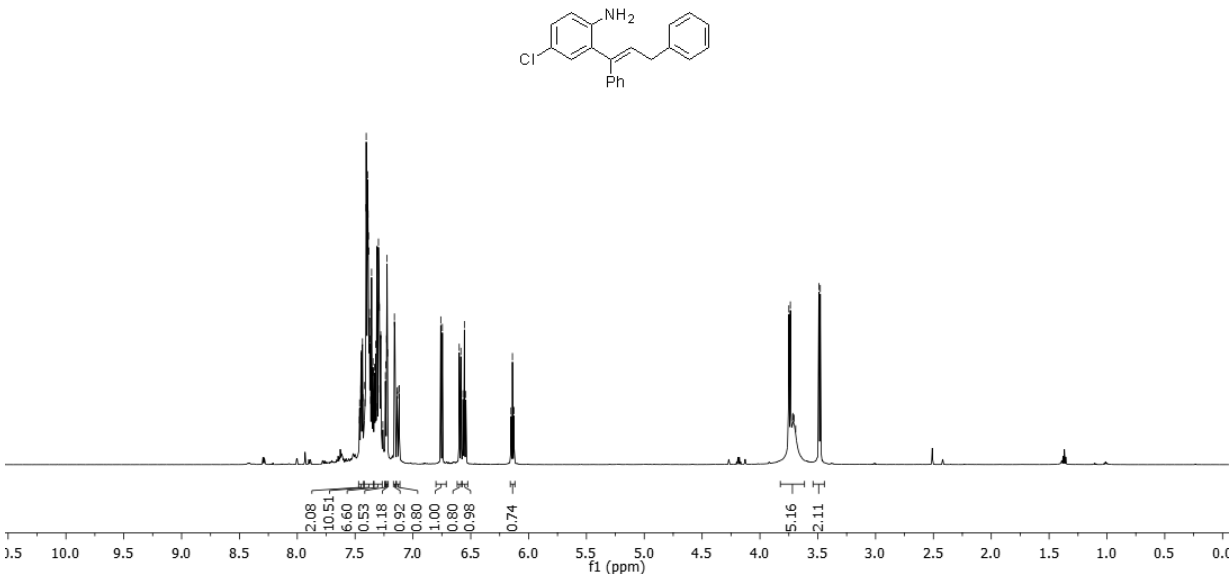
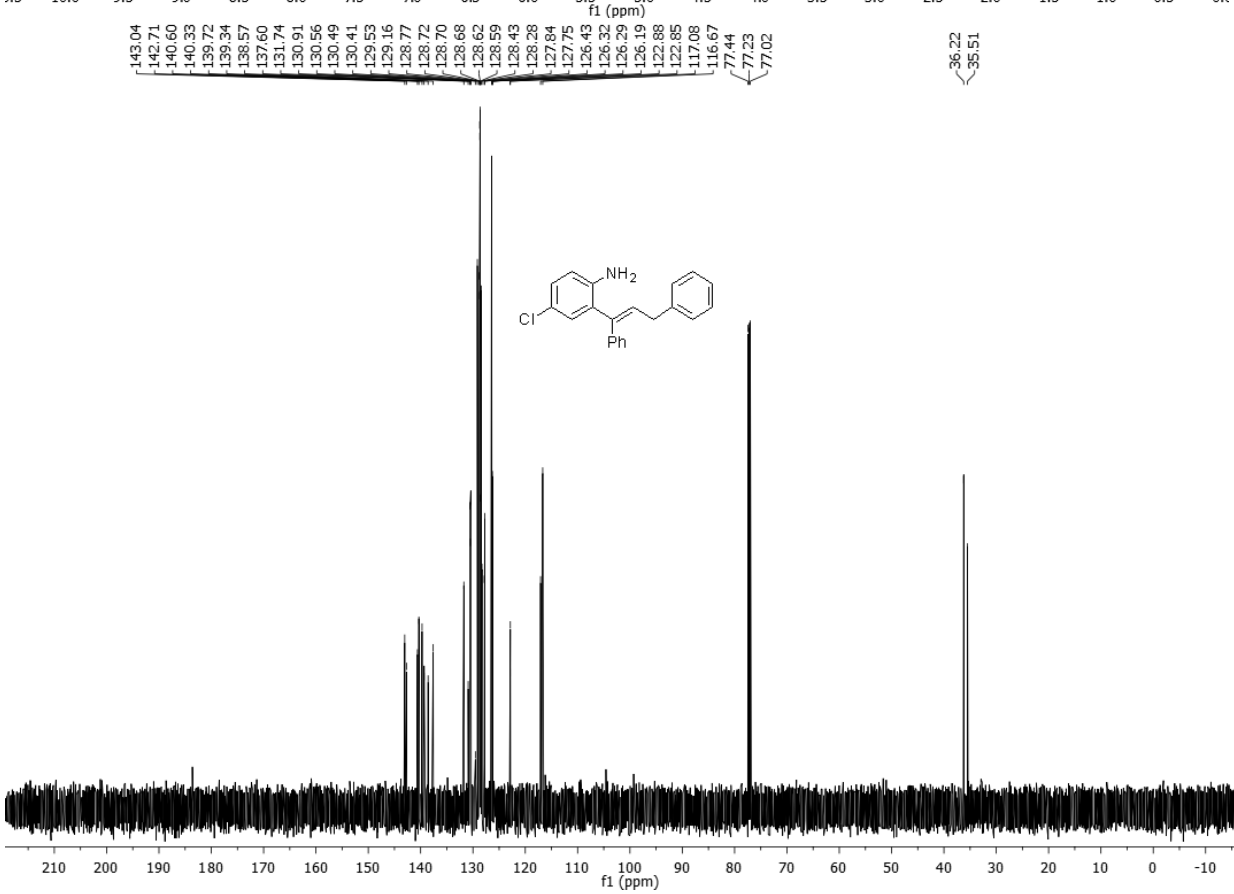
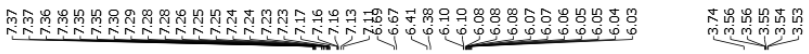

NH2
Cl
Ph
2.08 10.51 6.60 0.53 1.18 0.92 0.80 1.00 0.80 0.98 0.74 5.16 2.11
f1 (ppm)


143.04 142.71 140.60 140.33 139.72 139.34 138.57 137.60 131.74 130.91 130.56 130.49 130.41 129.53 129.16 128.77 128.72 128.70 128.68 128.62 128.59 128.43 128.28 127.84 127.75 126.43 126.32 126.29 126.19 122.88 122.85 117.08 116.67 77.44 77.23 77.02 36.22 35.51
NH2
Cl
Ph
f1 (ppm)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7.23
7.23
7.17
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7.16
7.13
6.67
6.41
6.38
6.10
6.10
6.08
6.08
6.08
6.07
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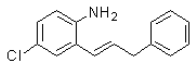
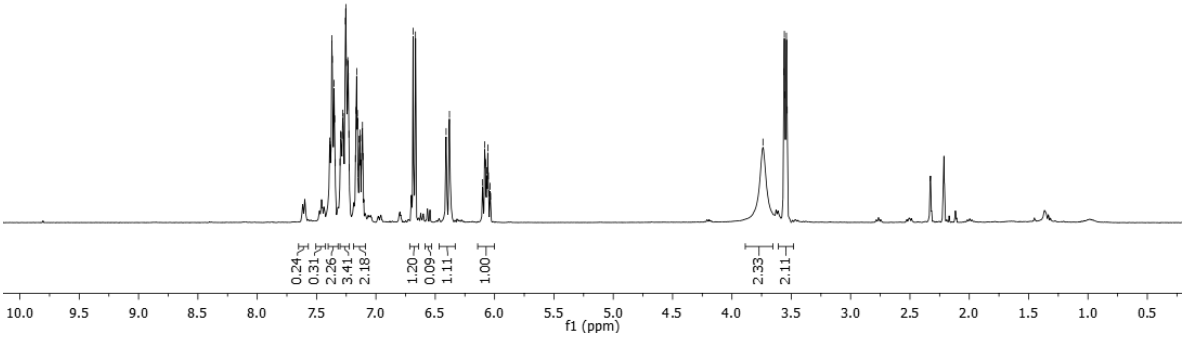
3.53


NH2
Cl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2.26
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0.09
1.11
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2.33
2.11
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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4.0
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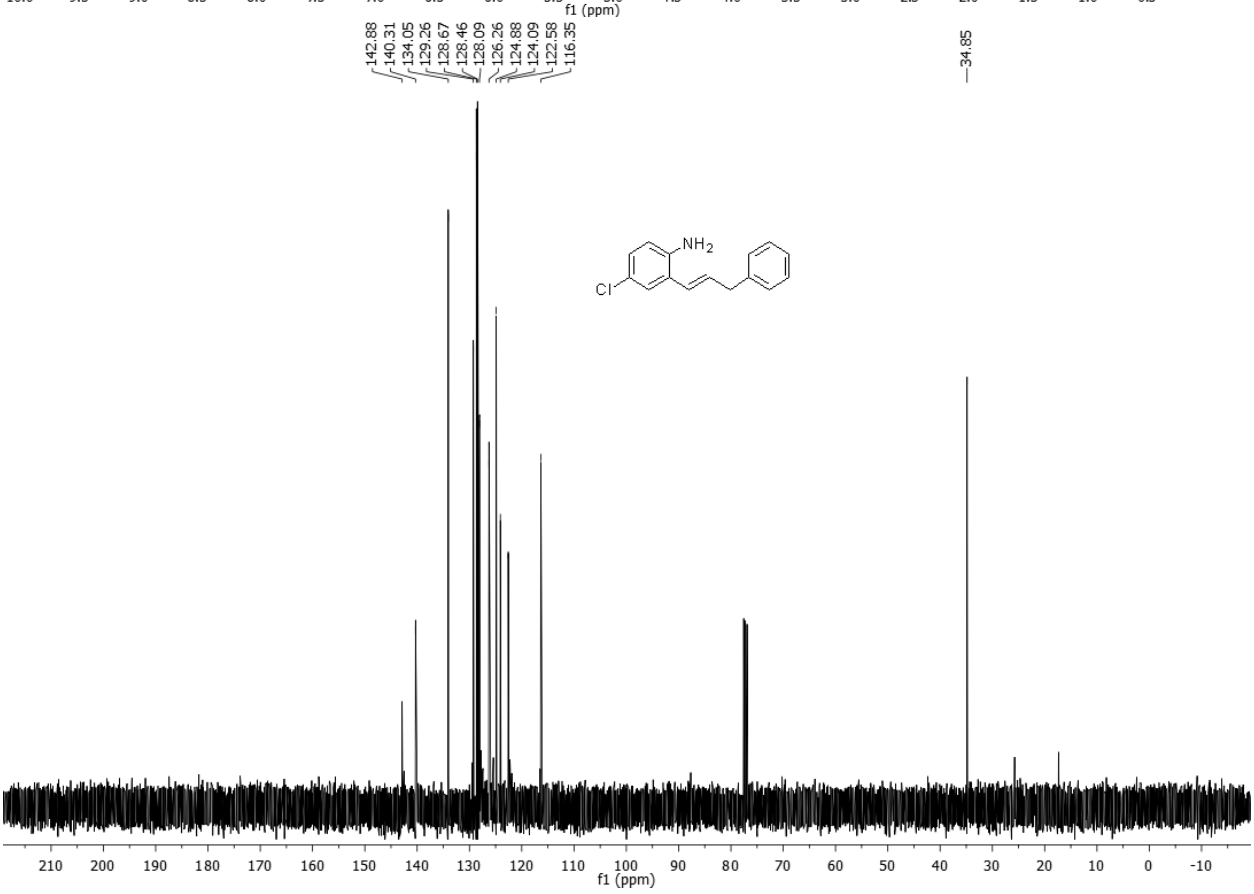
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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129.26
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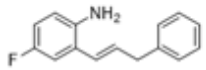
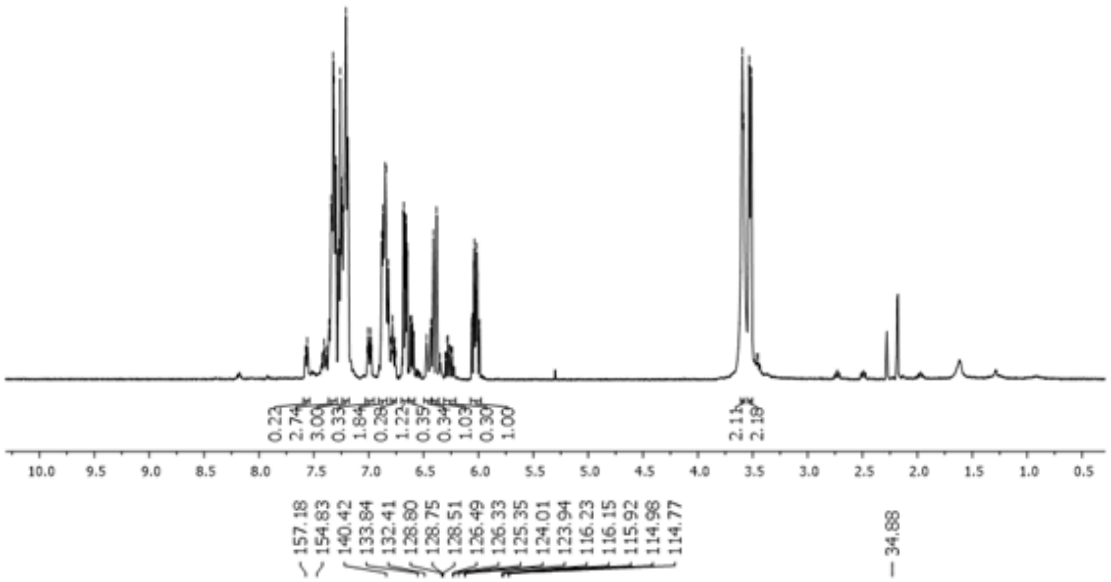
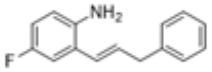
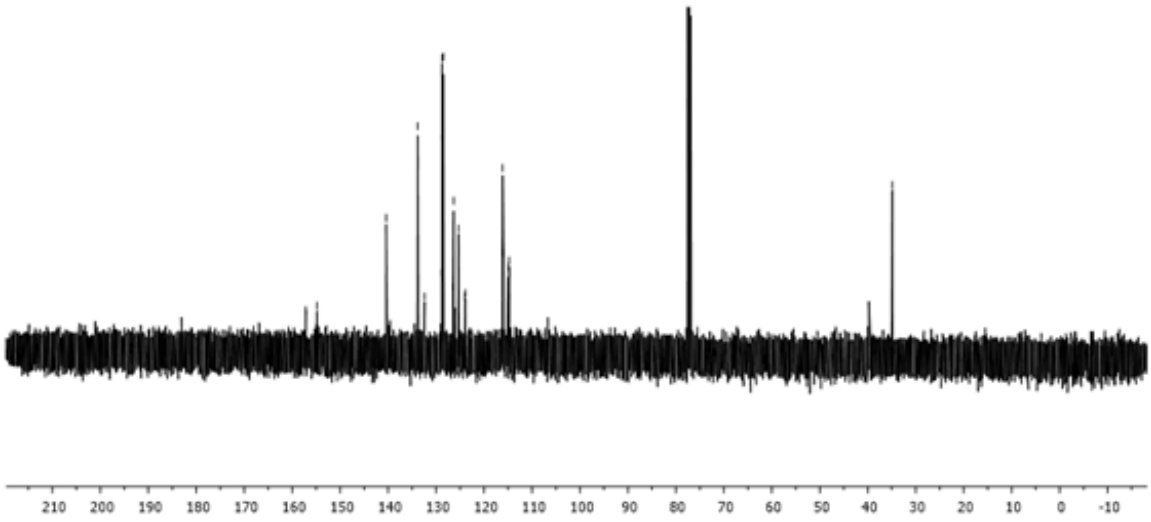
128.46
128.09
126.26
124.88
124.09
122.58
116.35
34.85
NH2
Cl
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

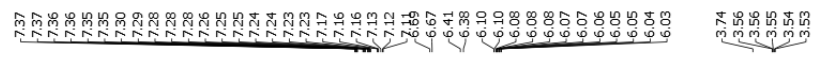

NH2
F






NH2
F

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7.12
7.11
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6.67
6.41
6.38
6.10
6.10
6.08
6.08
6.08
6.08
6.07
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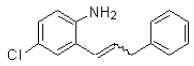
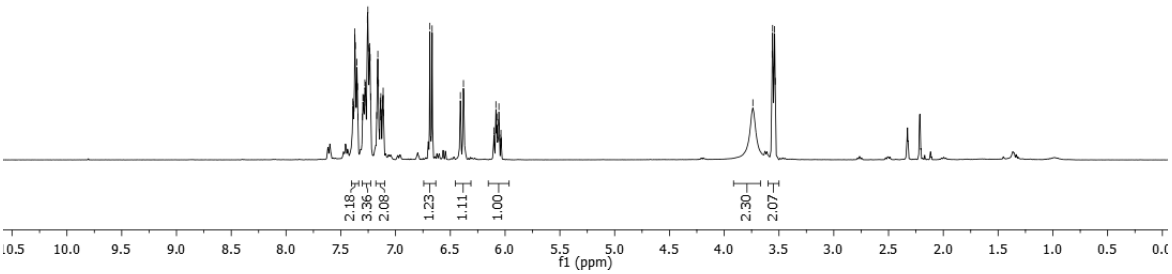
3.54
3.53


NH2
Cl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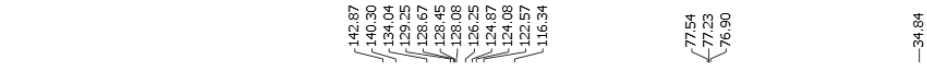
2.08
1.23
1.11
1.00
2.30
2.07
f1 (ppm)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140.30
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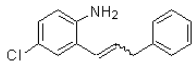
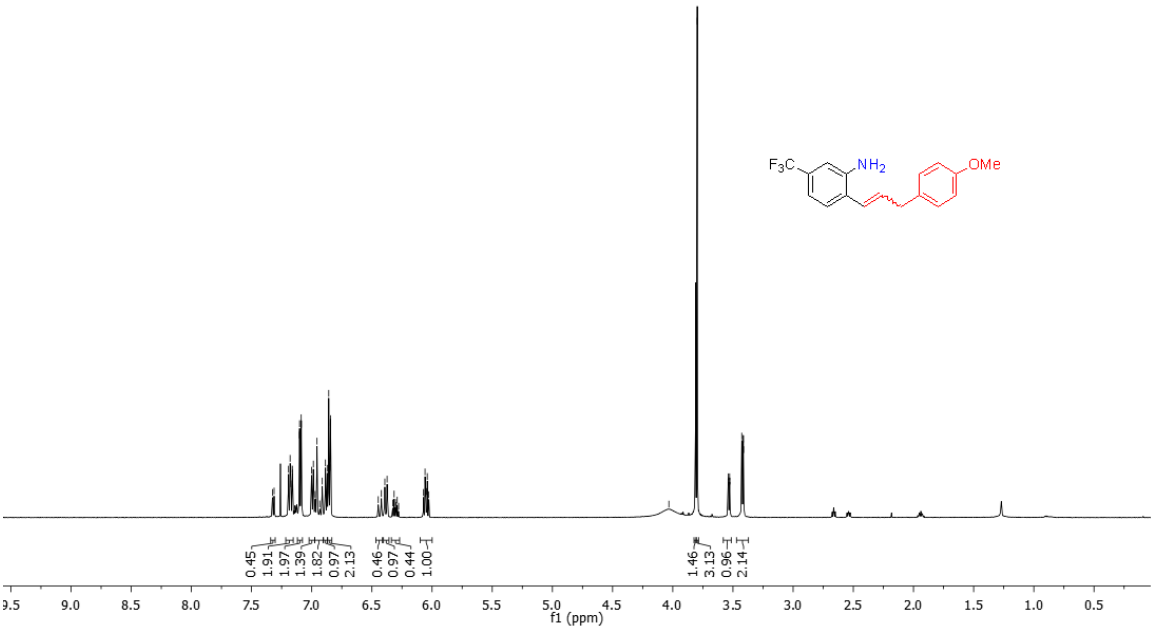
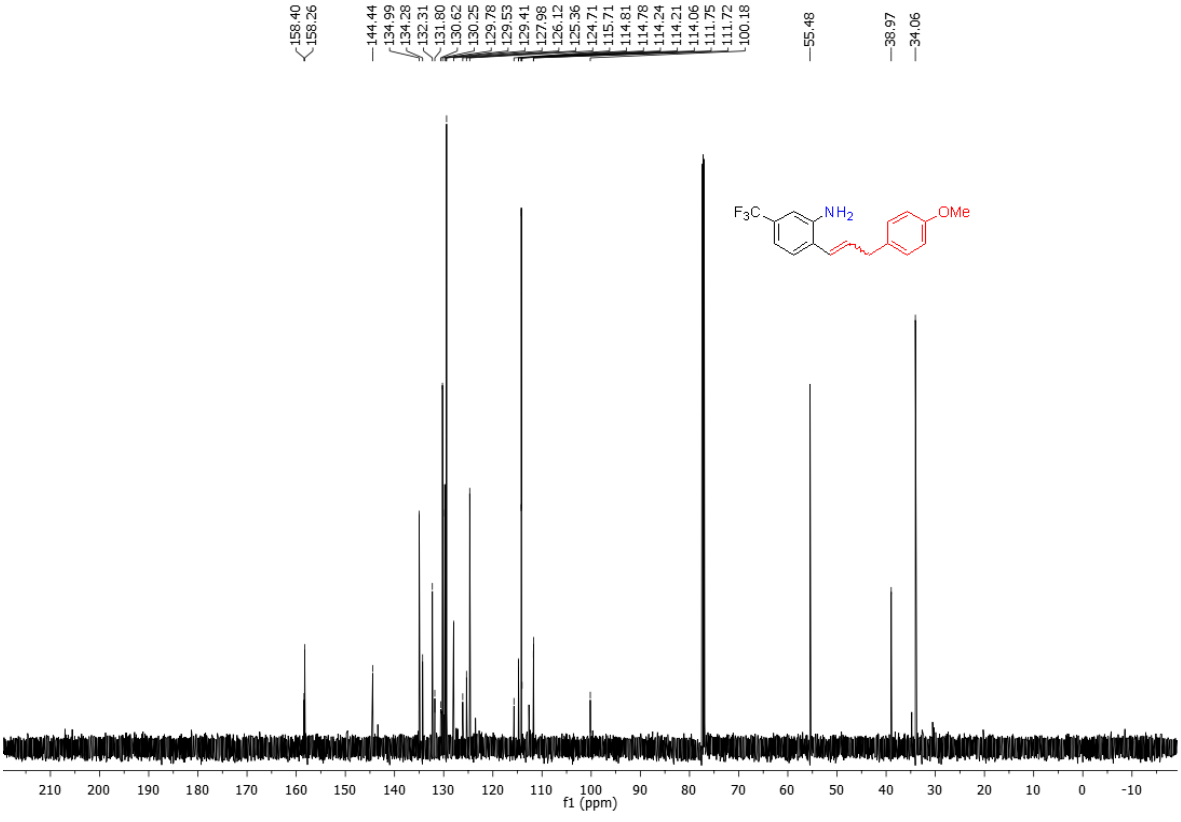
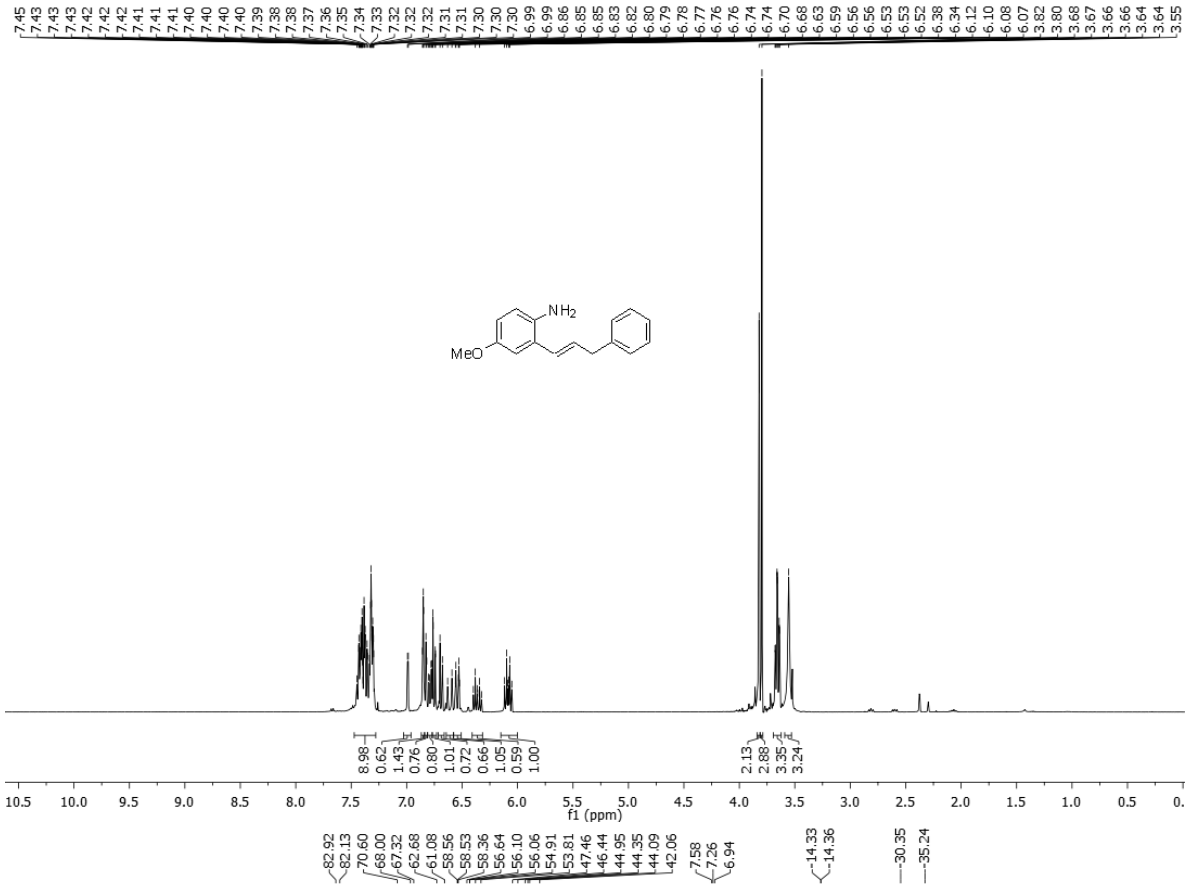
129.25
128.67
128.45
128.08
126.25
124.87
124.08
122.57
116.34
77.54
77.23
76.90
34.84

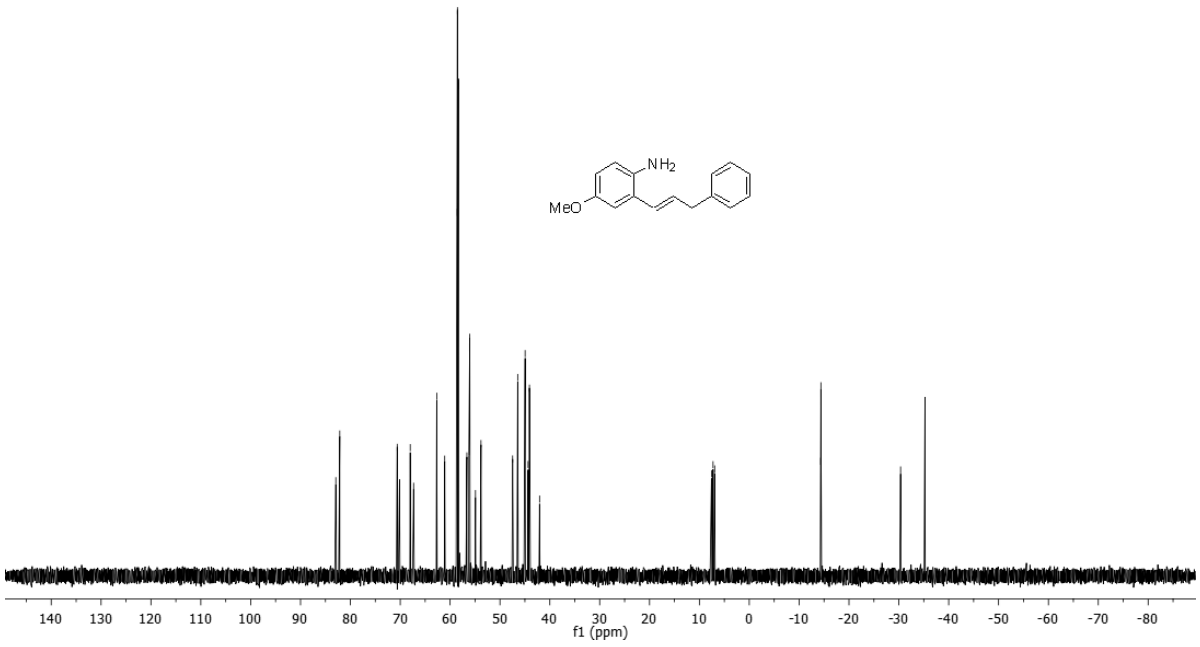

NH2
Cl

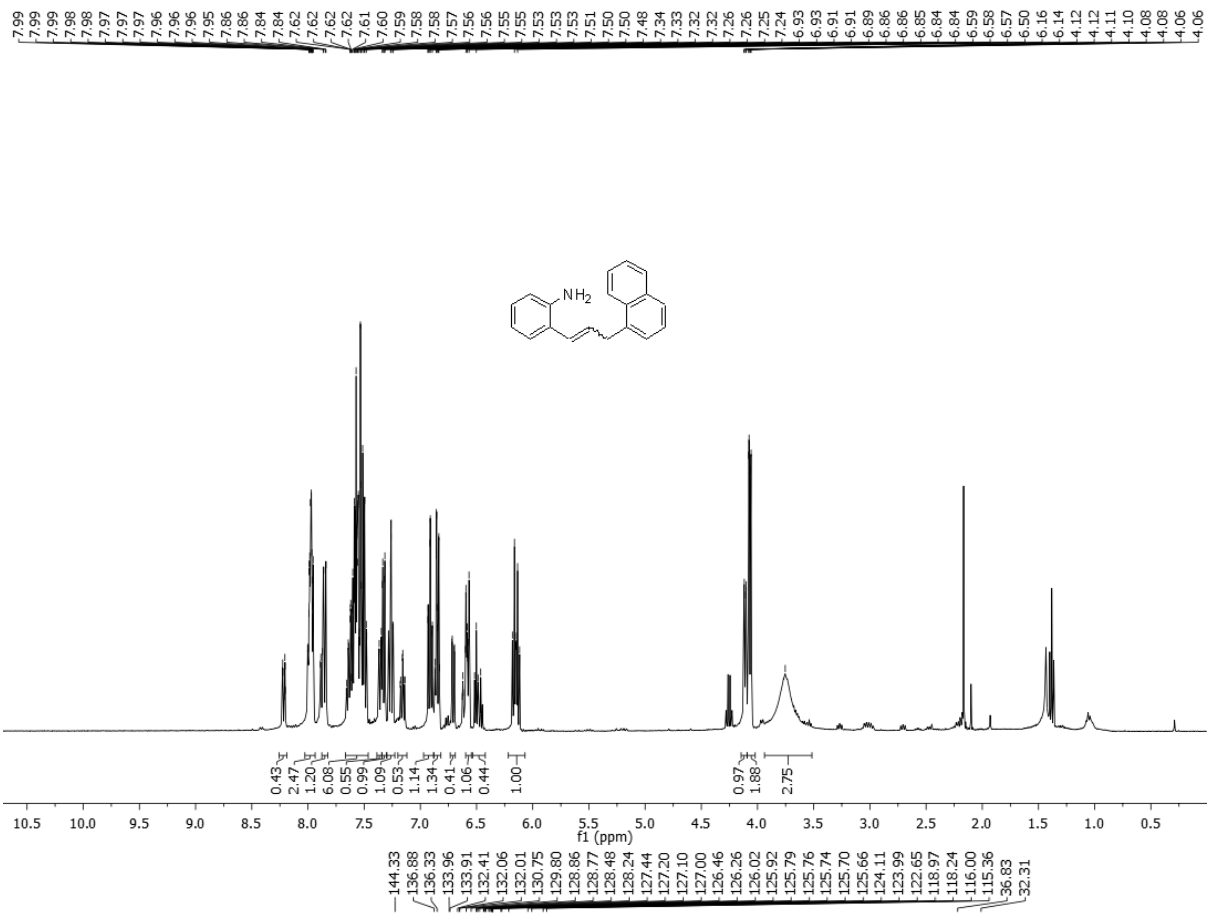

f1 (ppm)


F3C
NH2
OMe
f1 (ppm)


F3C
NH2
OMe
f1 (ppm)


NH2
MeO
f1 (ppm)


NH2
MeO
f1 (ppm)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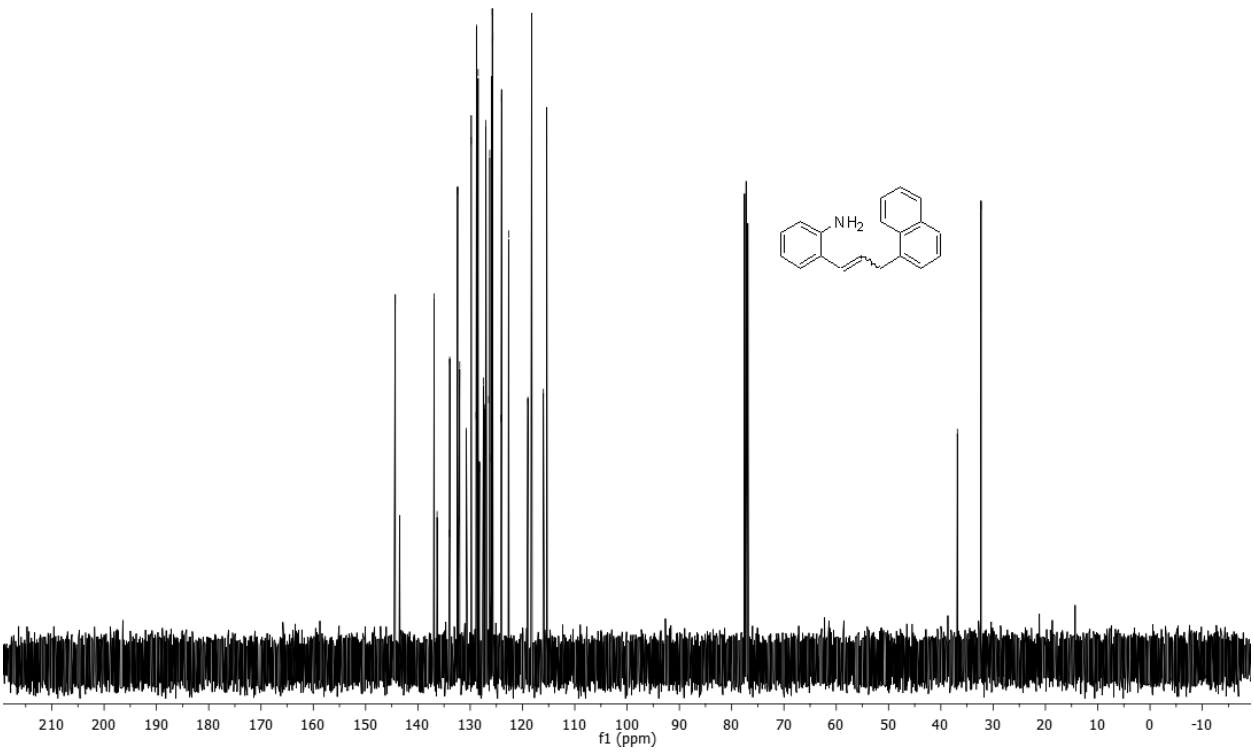
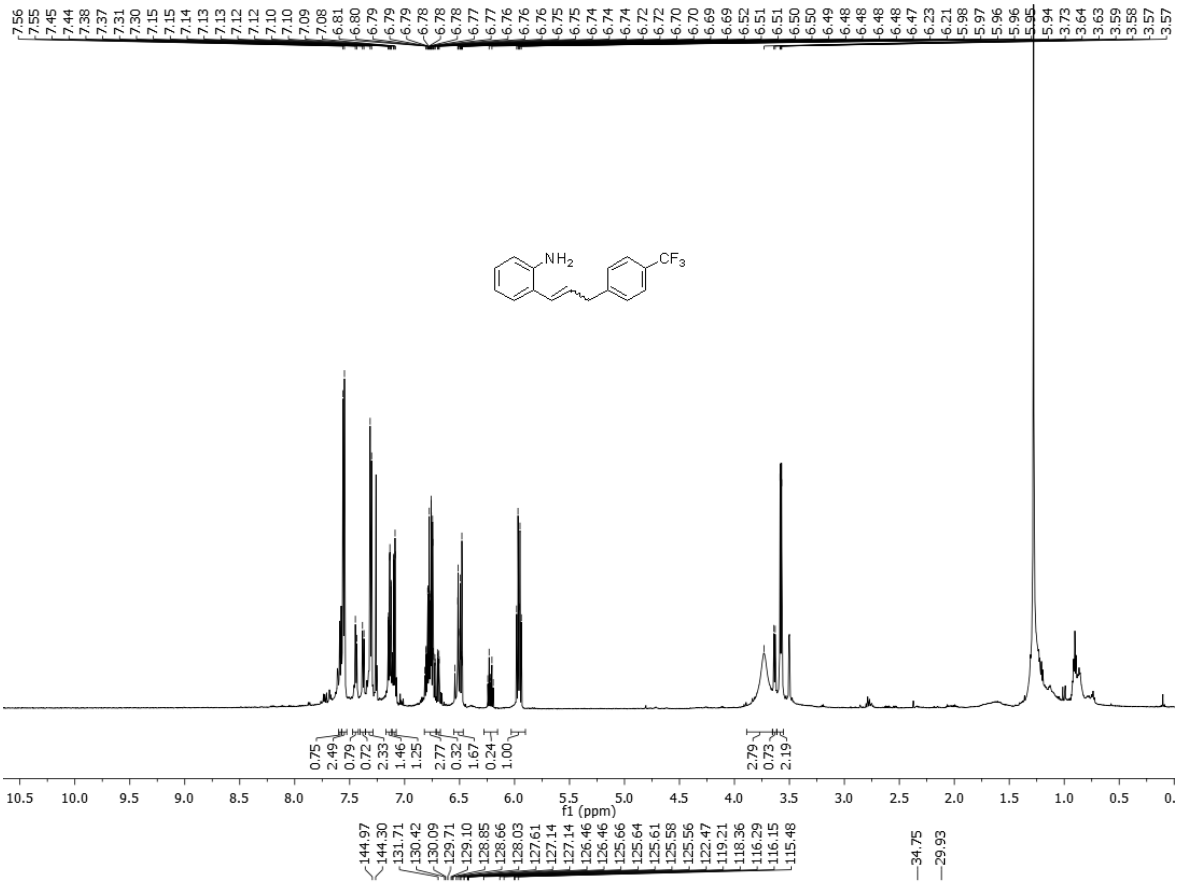
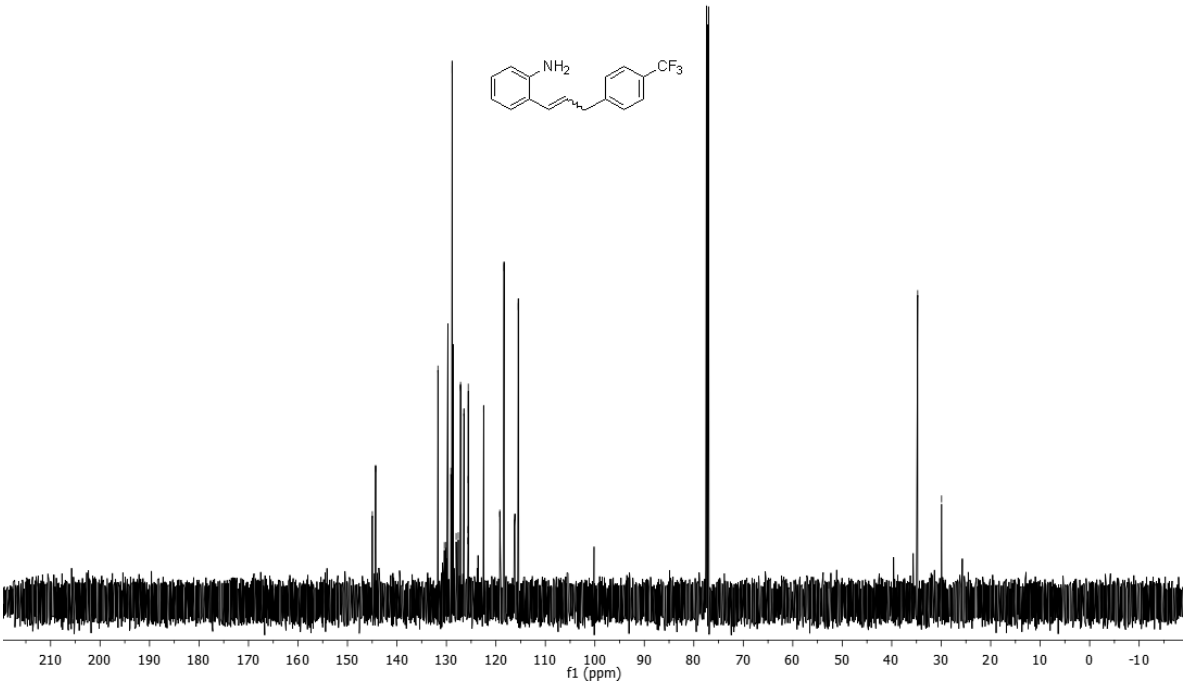
f1 (ppm)


NH2
f1 (ppm)


NH2
CF3
f1 (ppm)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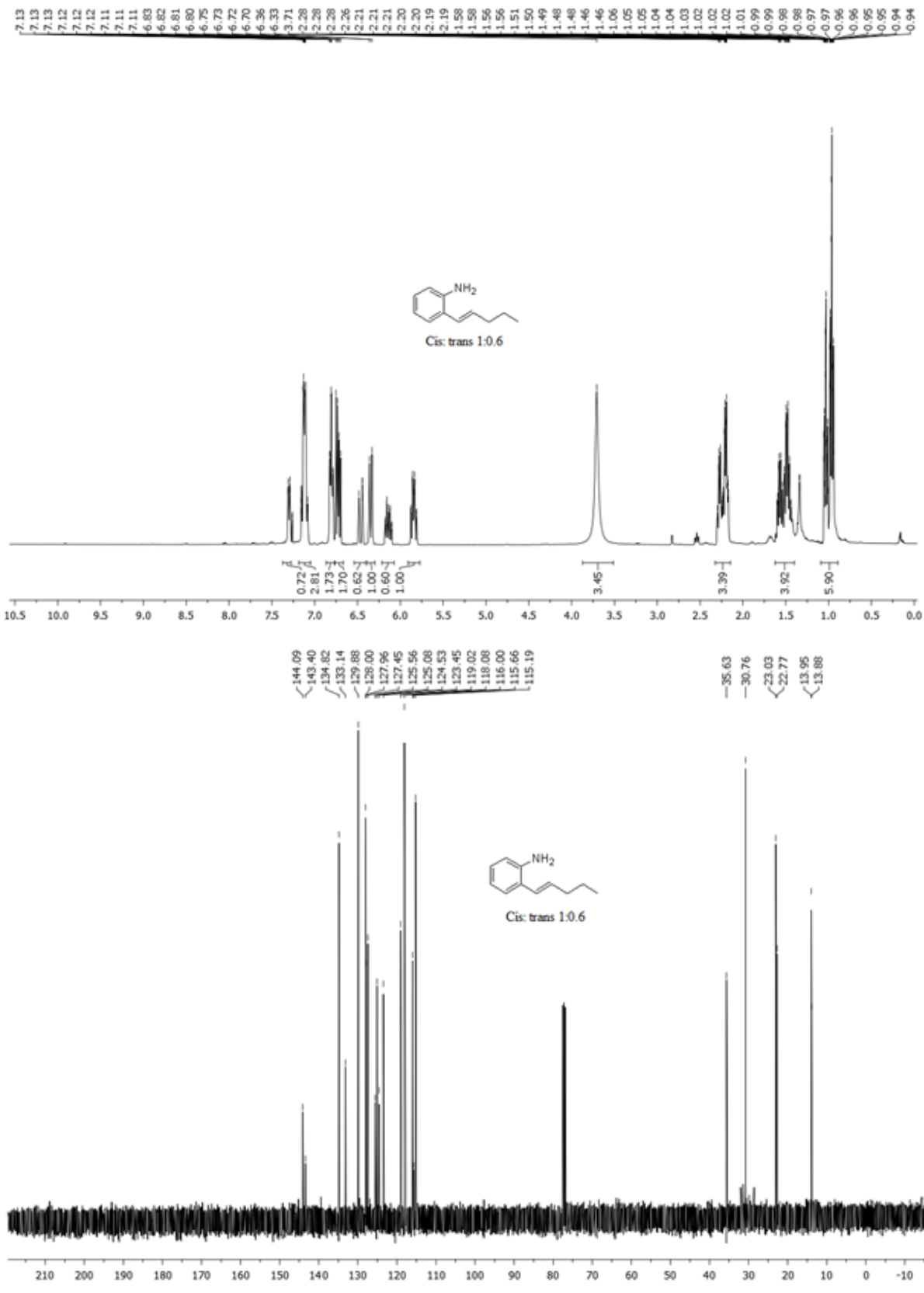
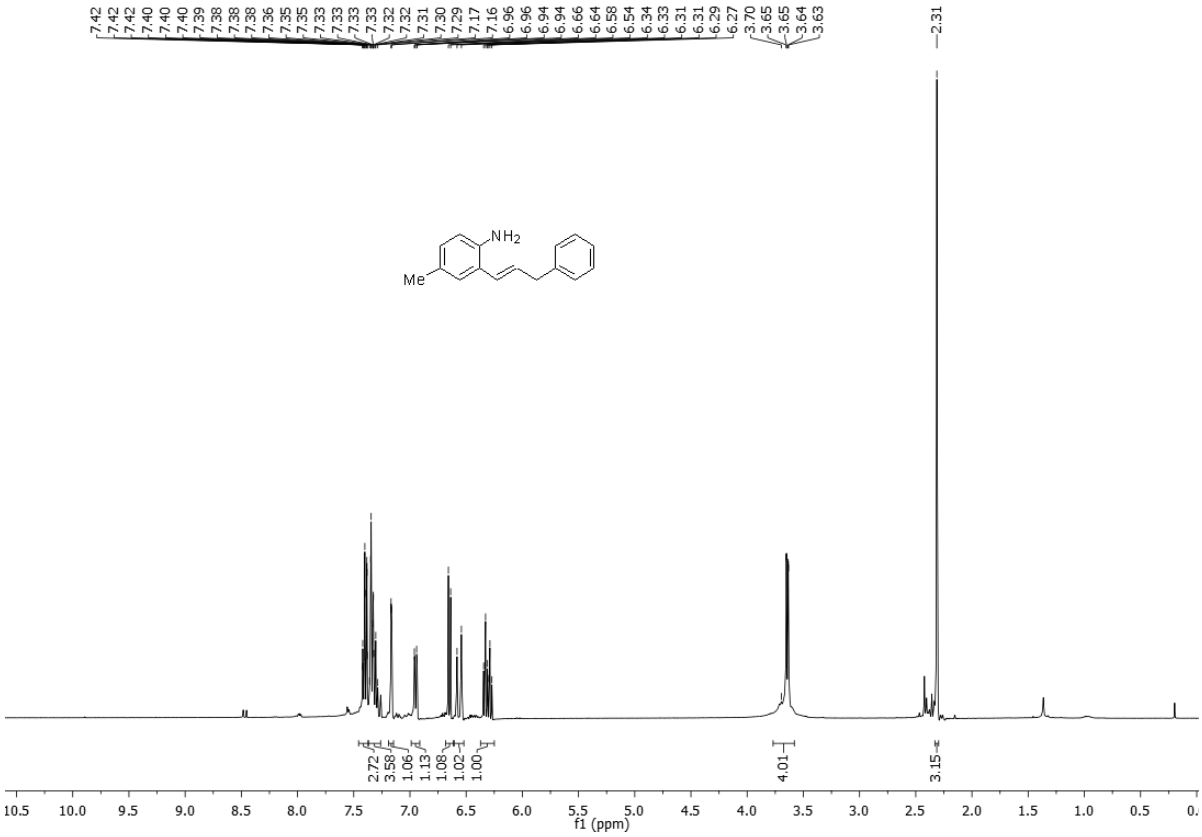
CF3
f1 (ppm)


NH2
Cis: trans 1:0.6
NH2
Cis: trans 1:0.6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6.54
6.34
6.33
6.31
6.31
6.29
6.27
3.70
3.65
3.65
3.64
3.63
2.31
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Me
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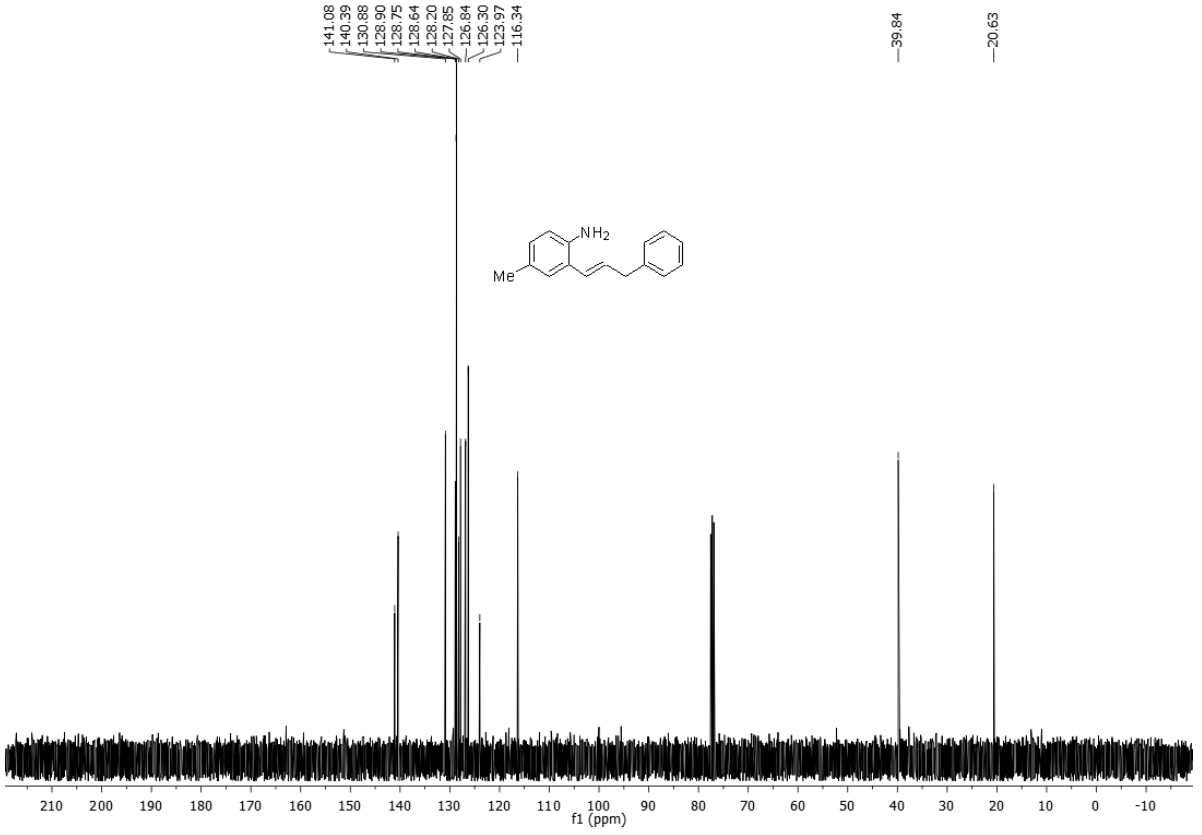
1.13
1.08
1.02
1.00
4.01
3.15
f1 (ppm)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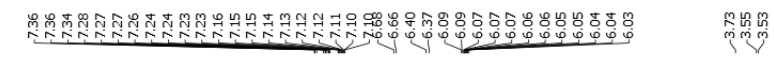
39.84
20.63
NH2
Me
f1 (ppm)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6.07
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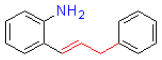
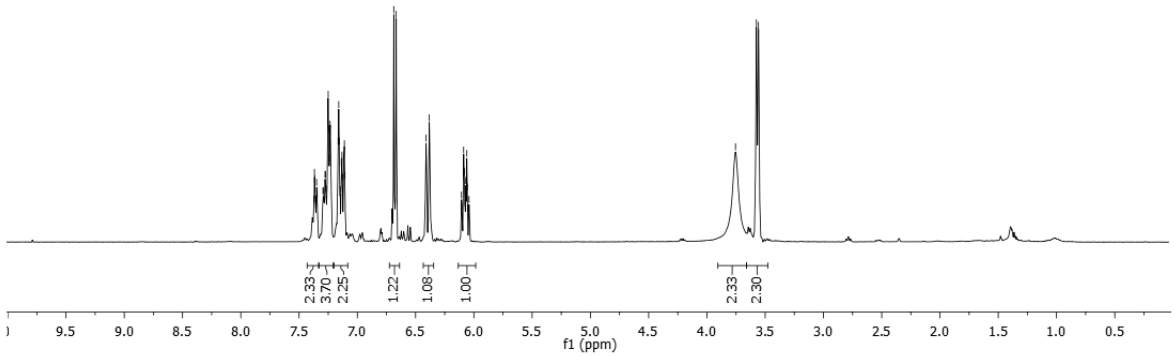
6.04
6.03
3.73
3.55
3.53


NH2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9.5
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8.5
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6.0
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2.5
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1.5
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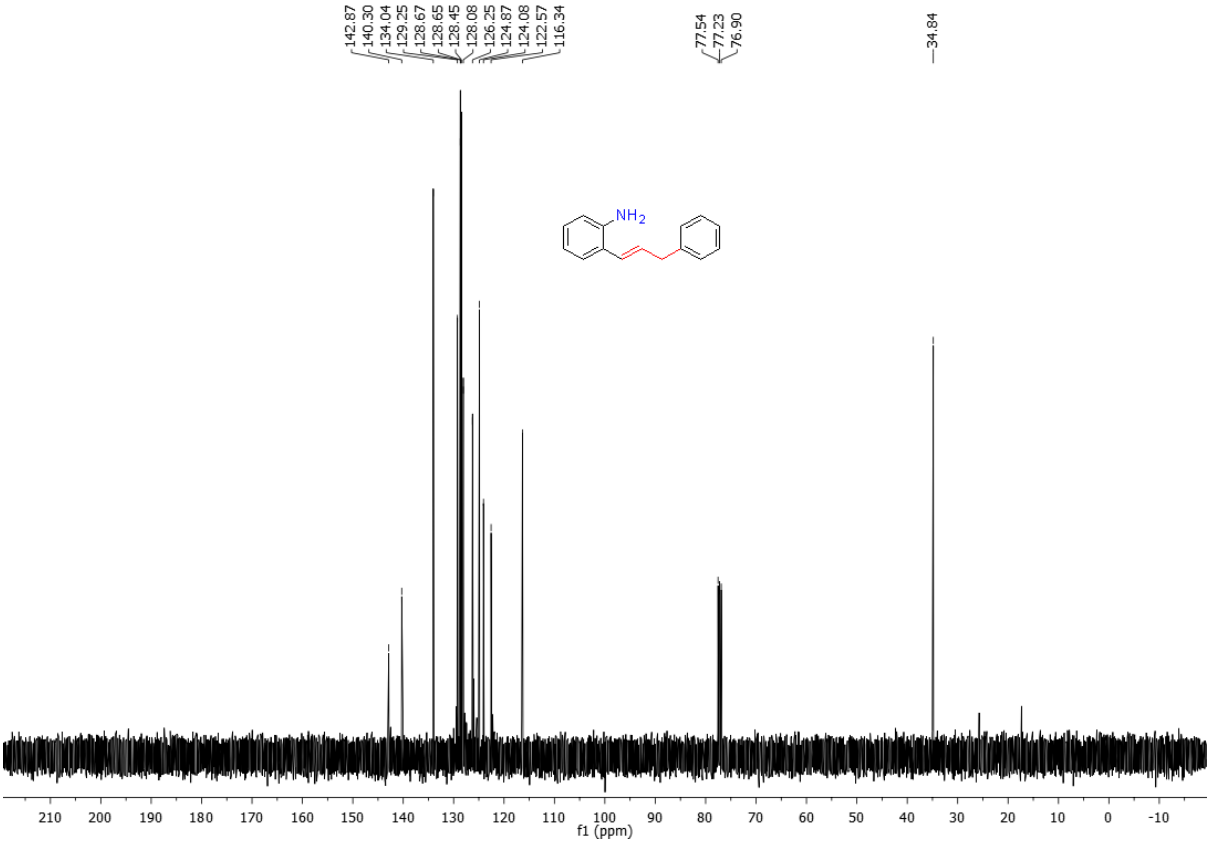
0.5
f1 (ppm)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122.57
116.34
77.54
77.23
76.90
34.84
NH2
210
200
190
180
170
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100
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80
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60
50
40
30
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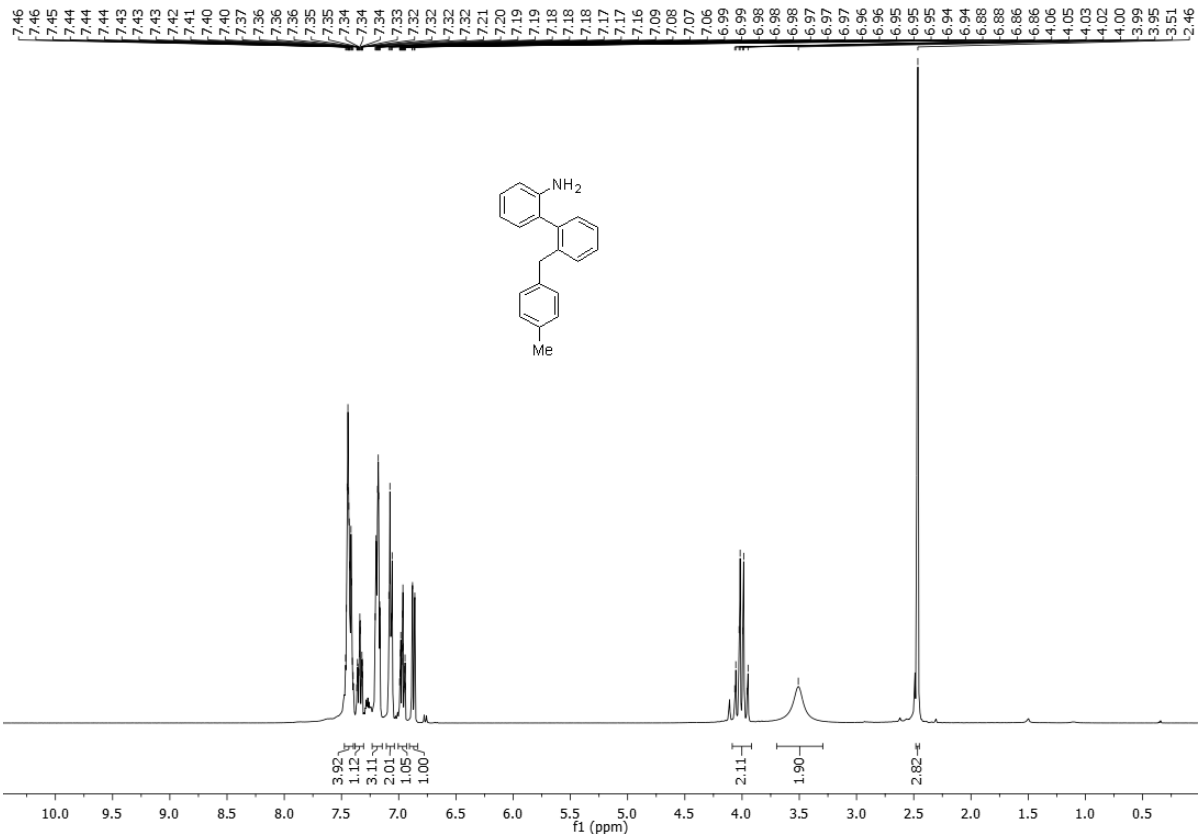
0
-10
f1 (ppm)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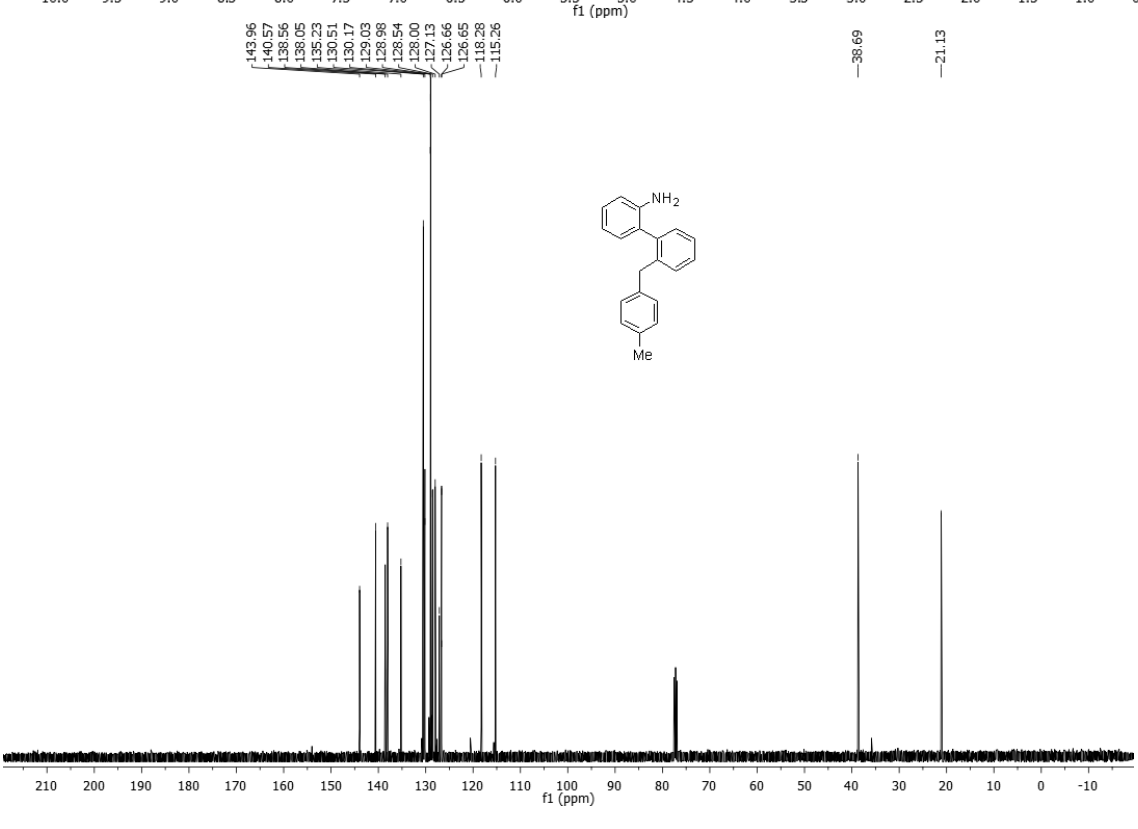
NH2
Me
3.92 1.12 3.11 2.01 1.05 1.00 2.11 1.90 2.82
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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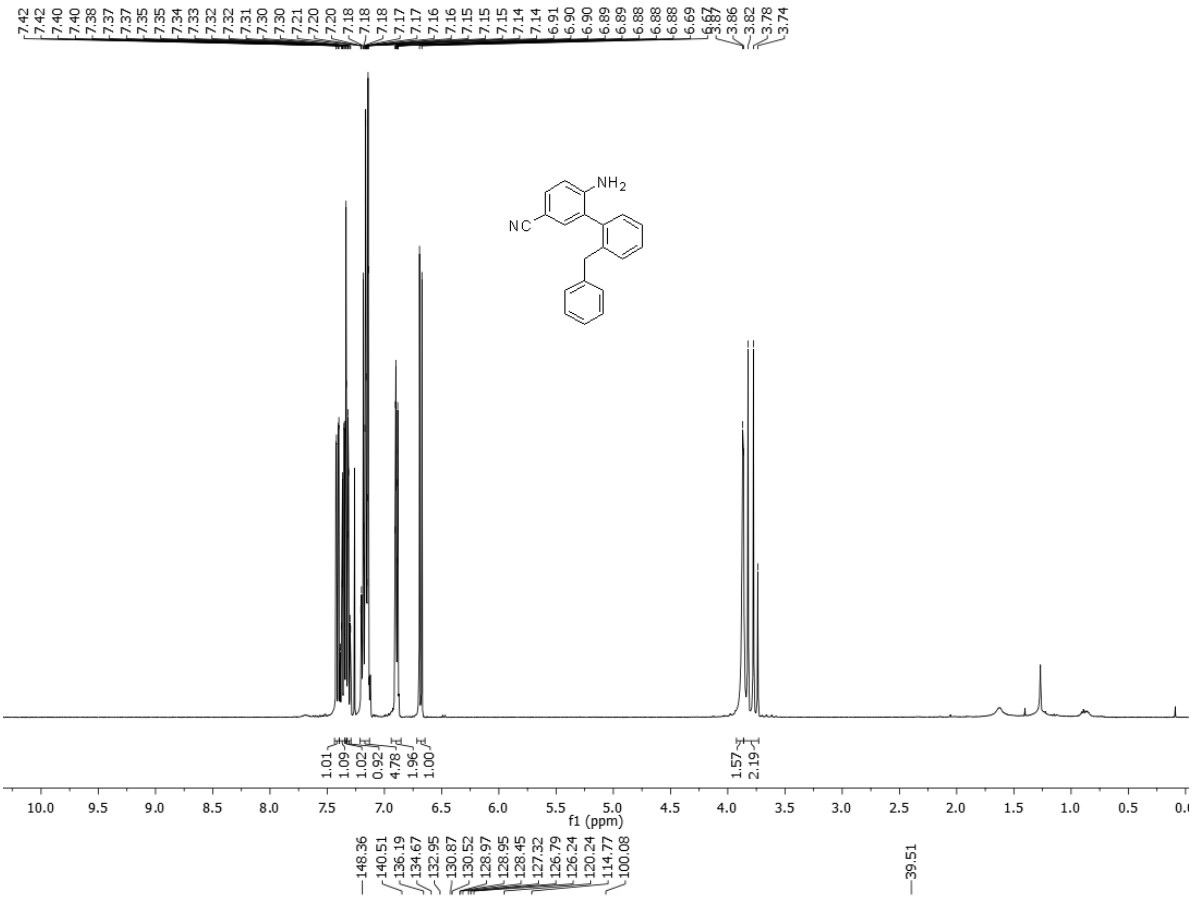
f1 (ppm)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6.88
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6.67
3.87
3.86
3.82
3.78
3.74
NH2
NC
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1.09
1.02
0.92
4.78
1.96
1.00
1.57
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9.5
9.0
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7.0
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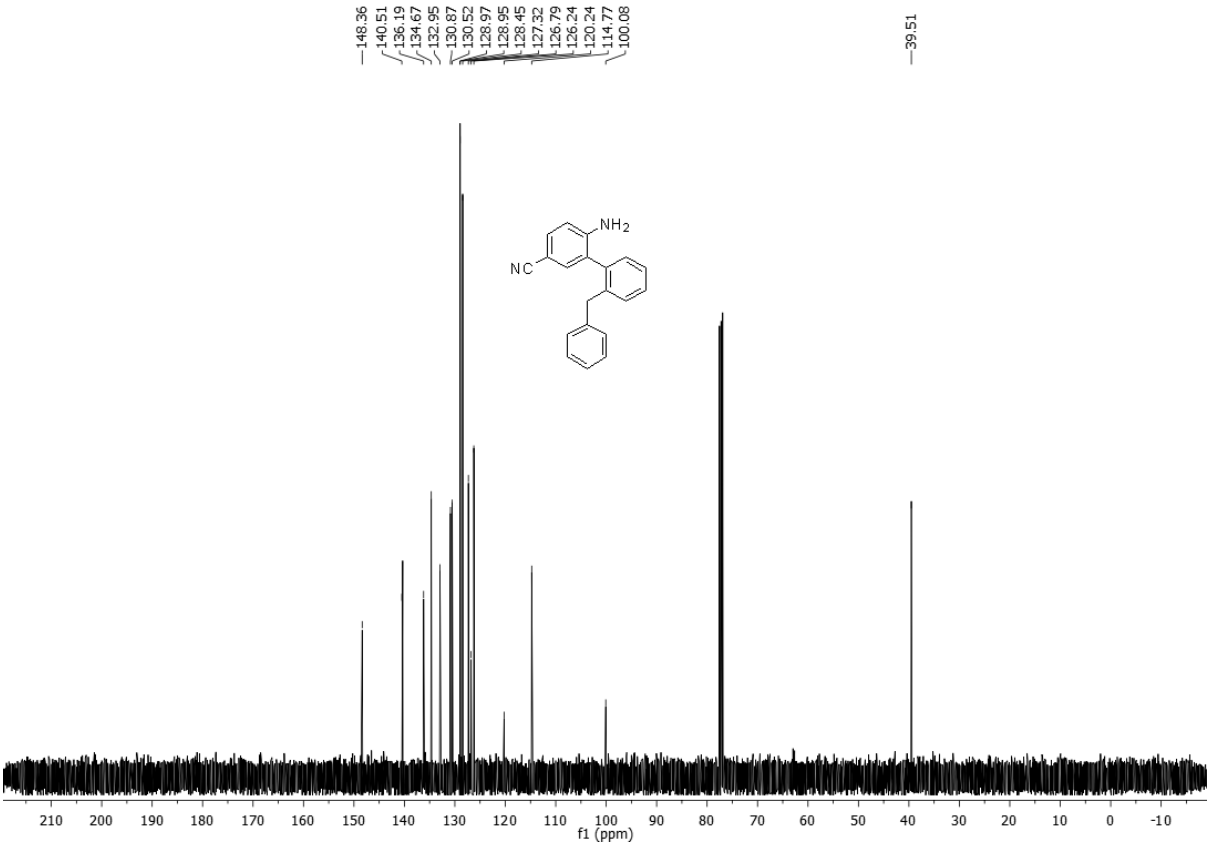
1.5
1.0
0.5
f1 (ppm)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130.52
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128.95
128.45
127.32
126.79
126.24
120.24
114.77
100.08
39.51
NH2
NC
210
200
190
180
170
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100
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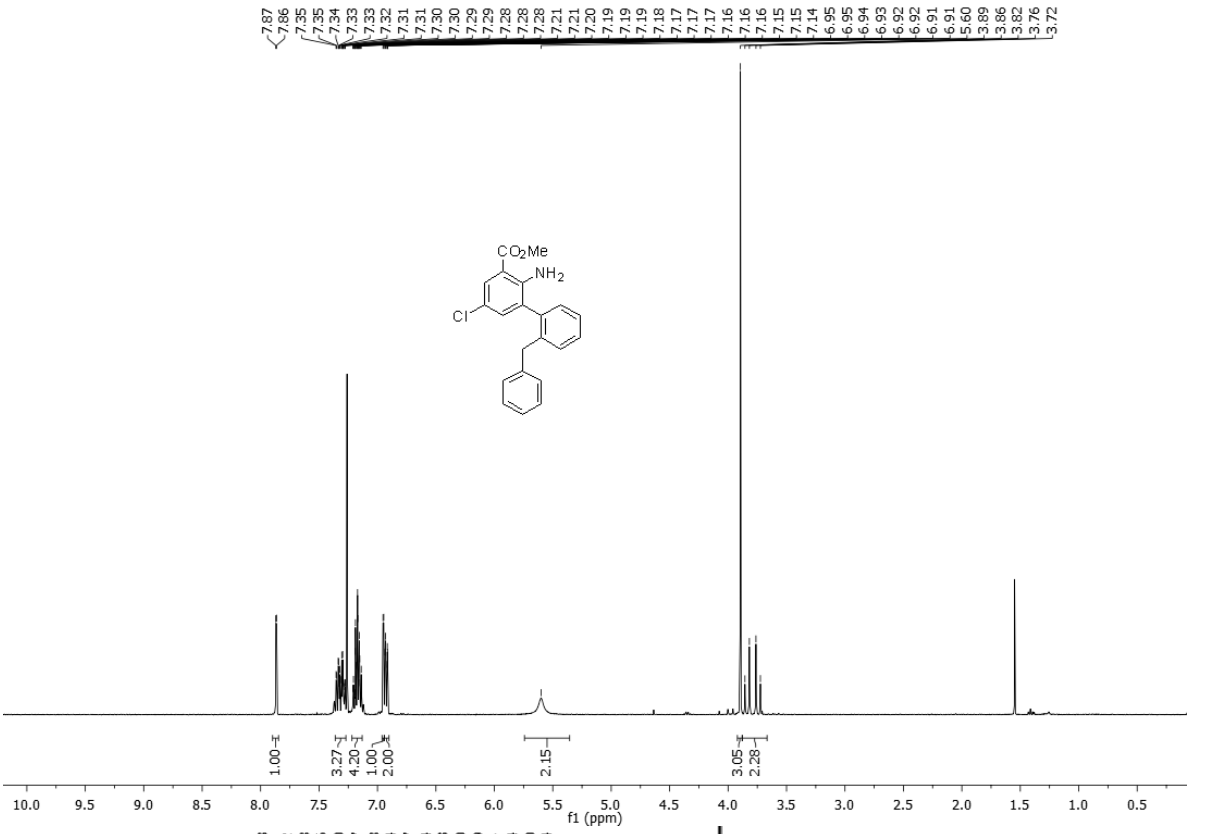
-10
f1 (ppm)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7.28
7.28
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7.19
7.19
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7.17
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6.95
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6.91
6.91
5.60
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3.86
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3.76
3.72
CO2Me
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Cl
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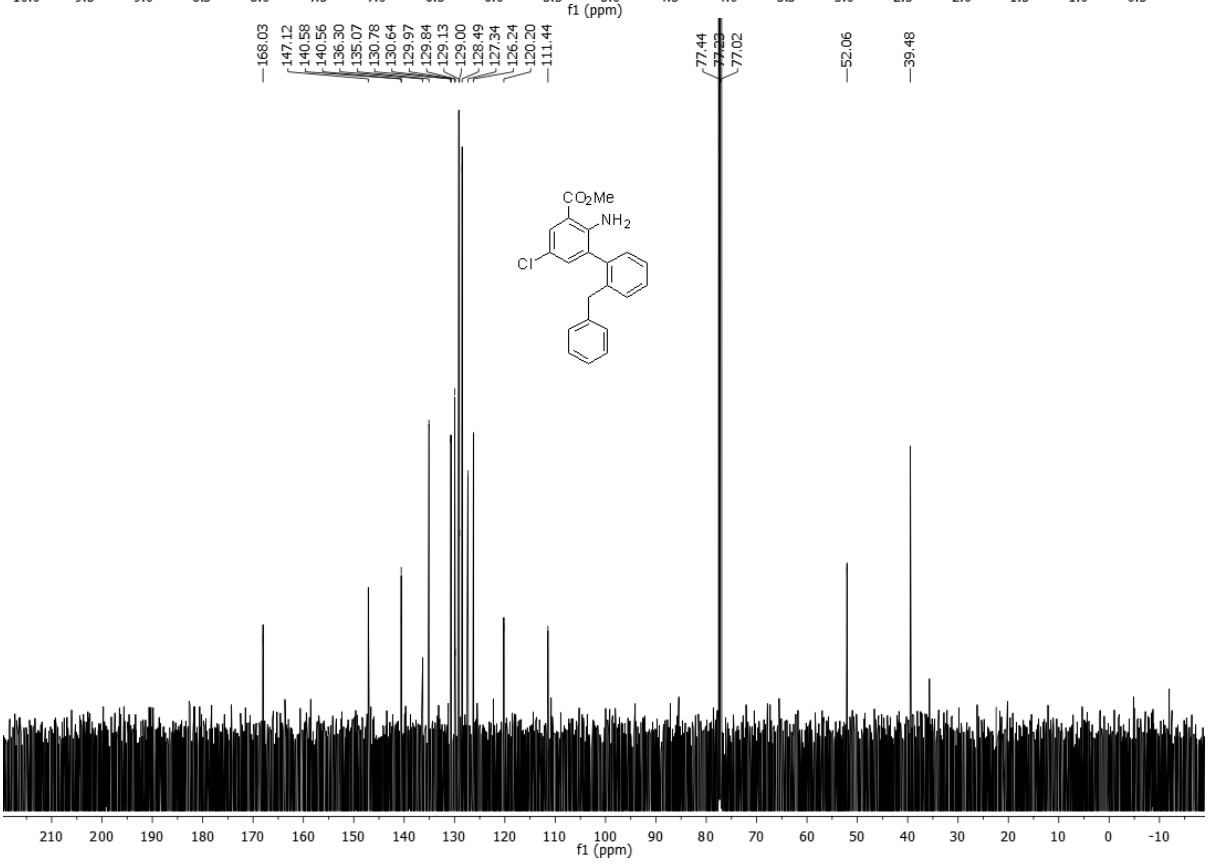
2.28
f1 (ppm)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128.49
127.34
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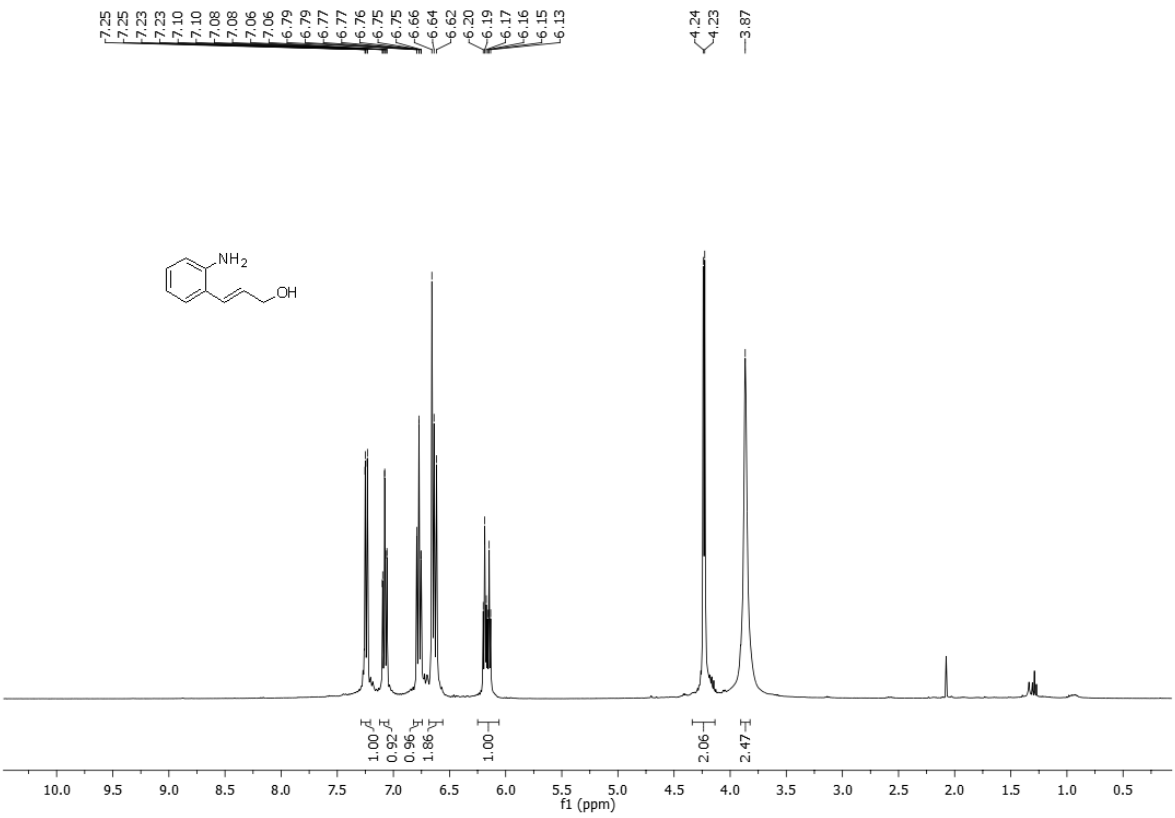
CO2Me
NH2
Cl
f1 (ppm)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6.77
6.77
6.76
6.75
6.75
6.66
6.64
6.62
6.20
6.19
6.17
6.16
6.15
6.13
4.24
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NH2
OH
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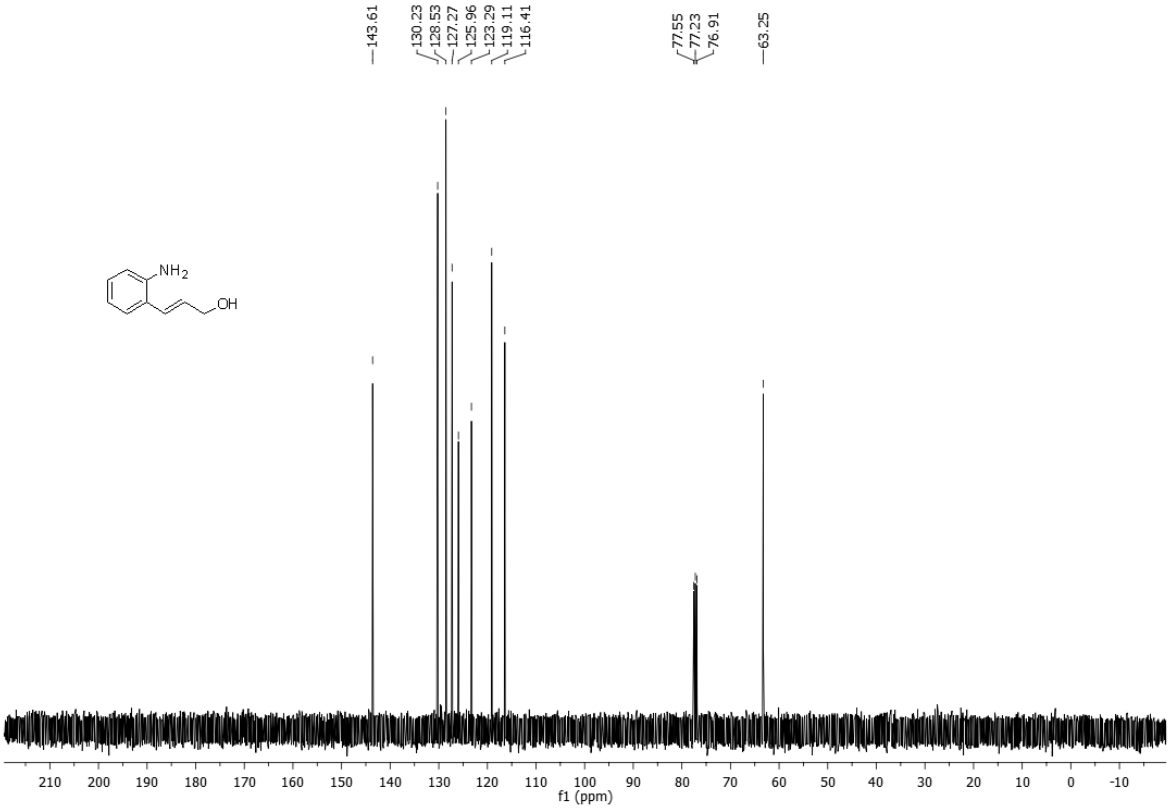
f1 (ppm)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119.11
116.41
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76.91
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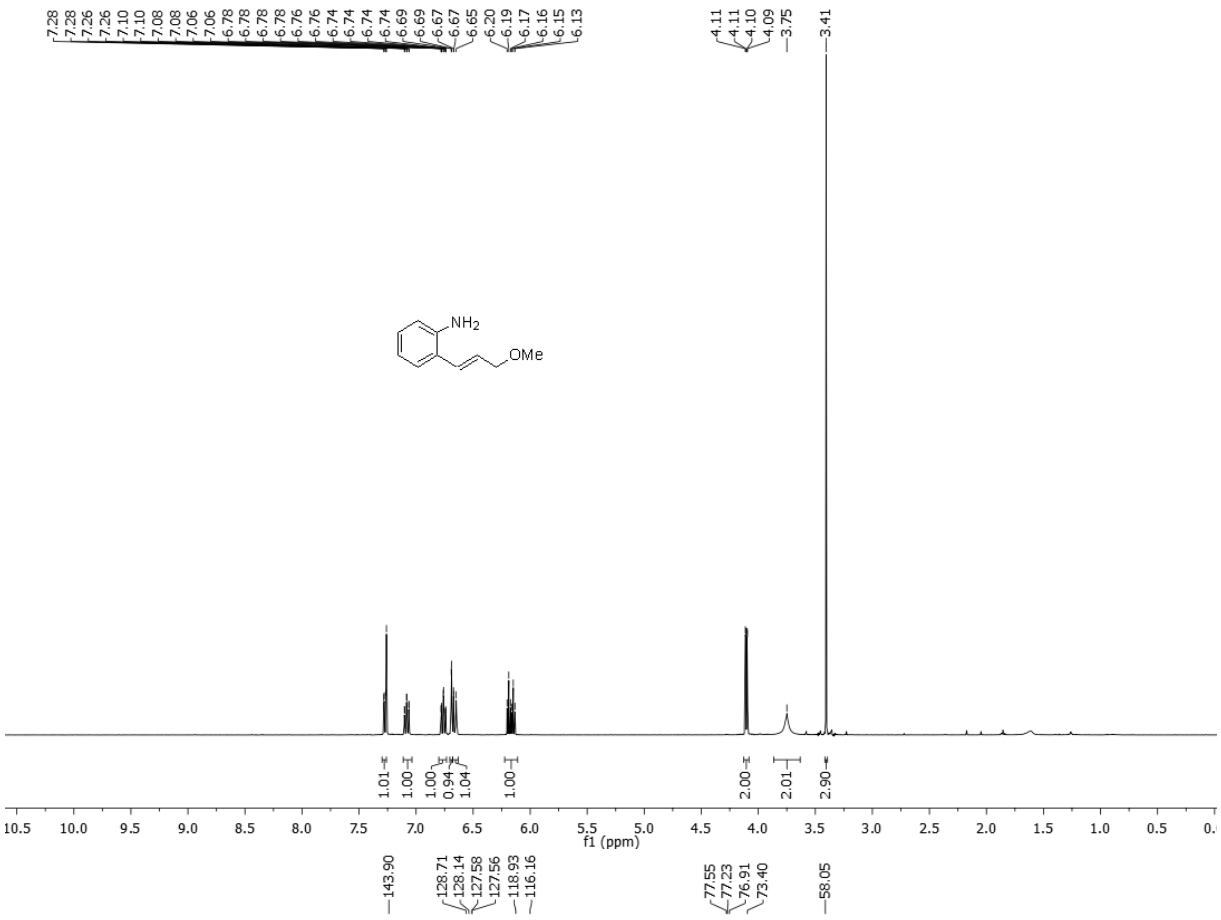
NH2
OH
f1 (ppm)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6.78
6.76
6.76
6.74
6.74
6.74
6.74
6.69
6.69
6.67
6.67
6.65
6.20
6.19
6.17
6.16
6.15
6.13
4.11
4.11
4.10
4.09
3.75
3.41
NH2
OMe
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1.00
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1.00
2.00
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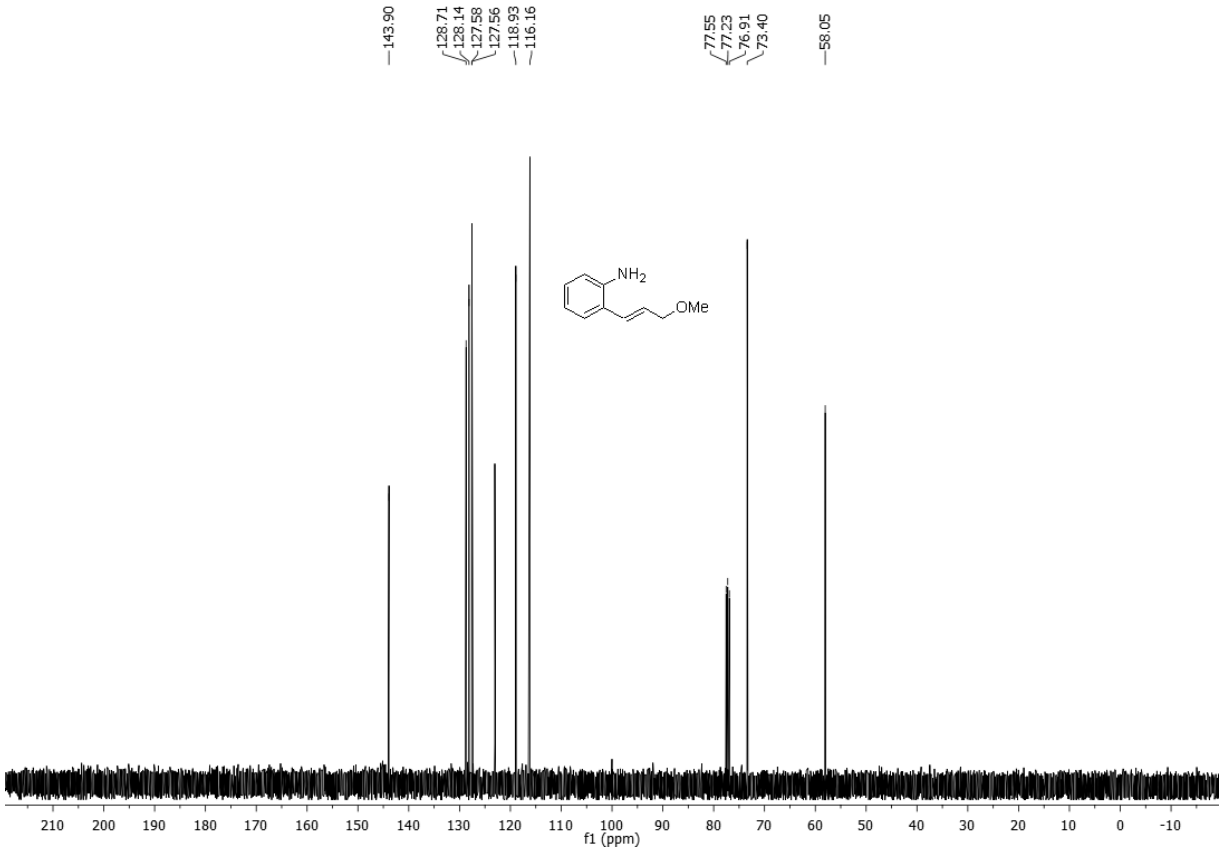
2.90
f1 (ppm)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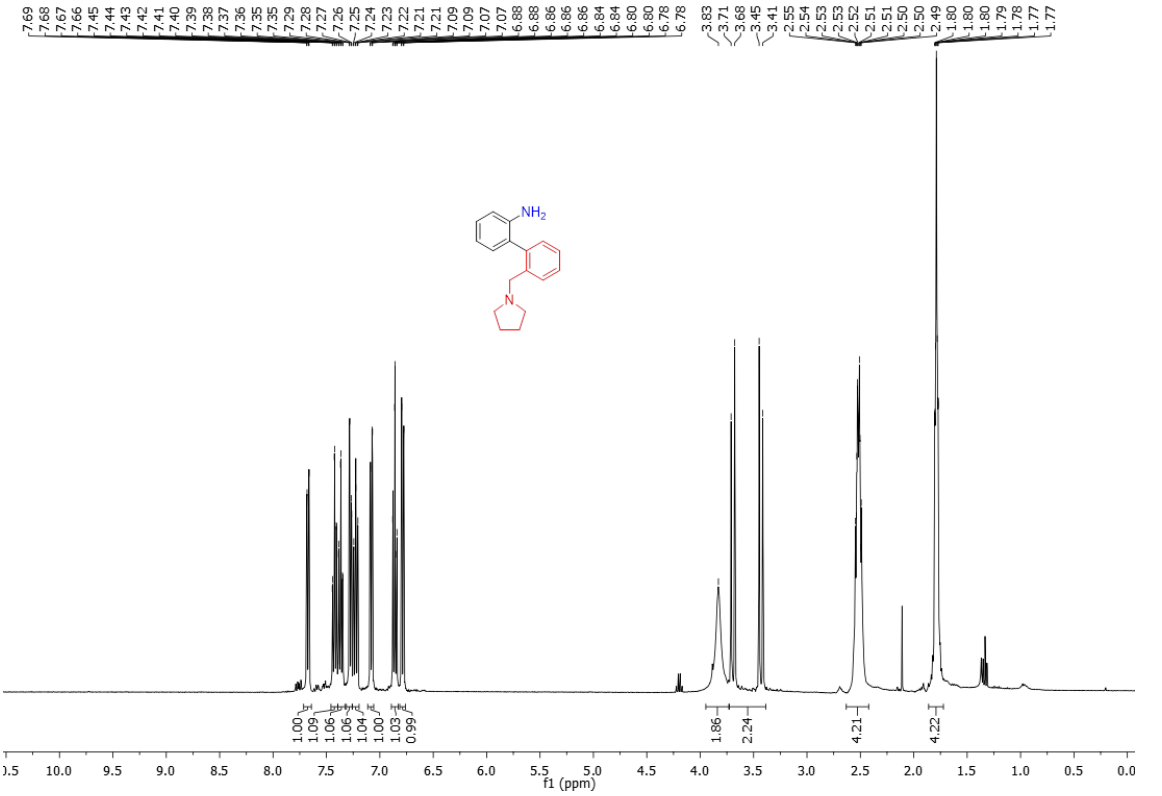
NH2
OMe
f1 (ppm)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3.83 3.71 3.68 3.45 3.41
2.55 2.54 2.53 2.53 2.52 2.51 2.51 2.50 2.50 2.49
1.80 1.80 1.80 1.79 1.78 1.77 1.77
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N
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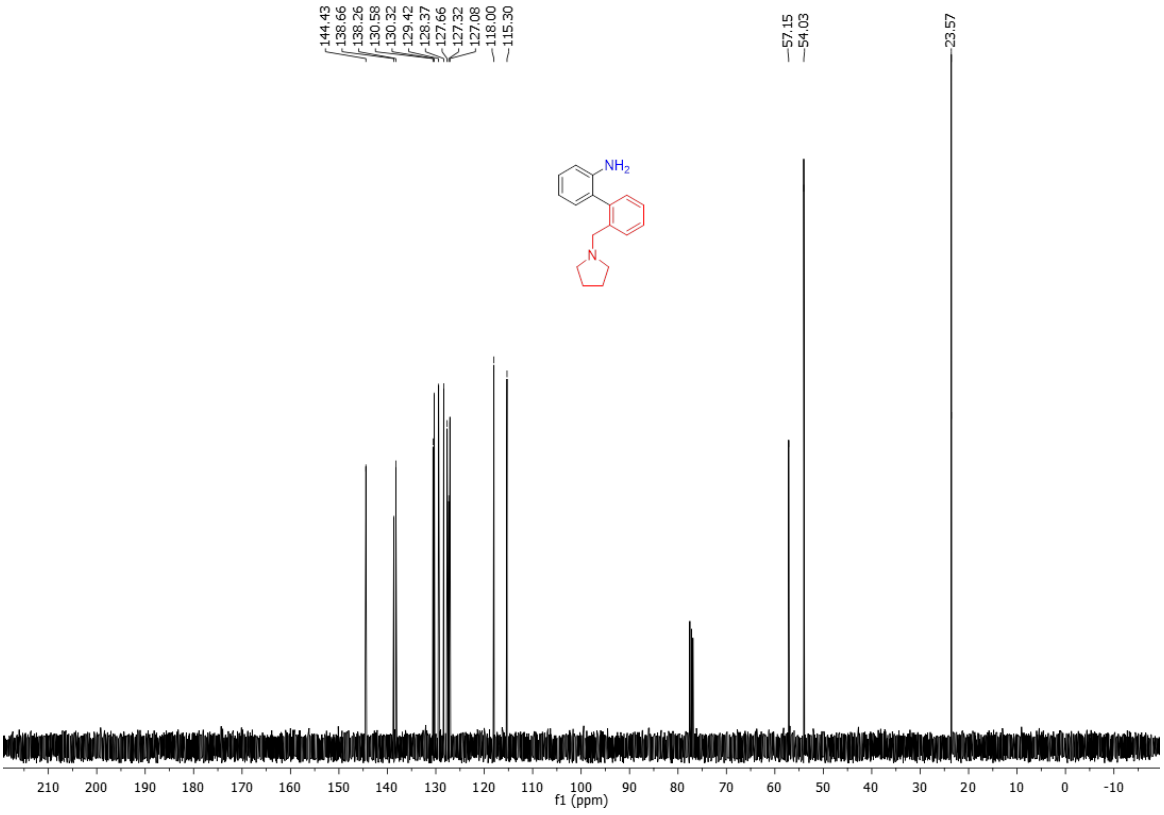
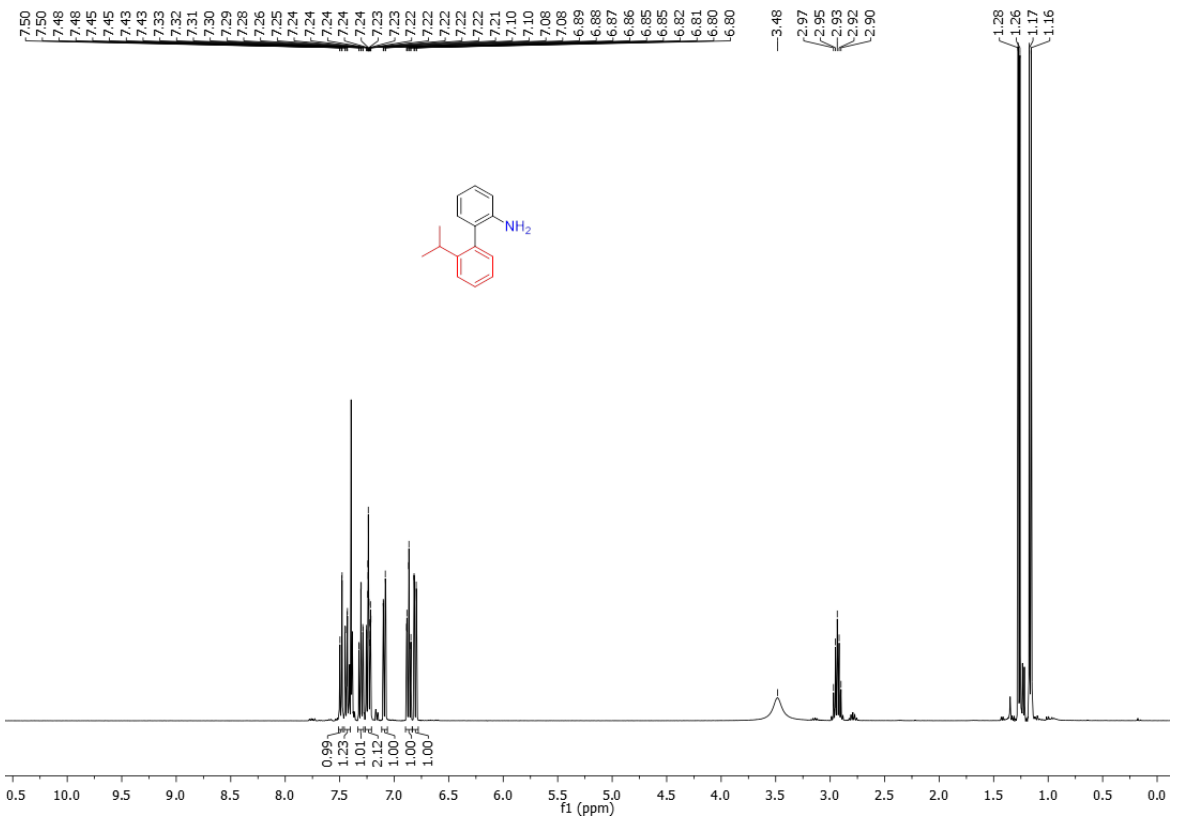
f1 (ppm)


144.43 138.66 138.26 130.58 130.32 129.42 128.37 127.66 127.32 127.08 118.00 115.30
57.15 54.03
23.57
NH2
N
f1 (ppm)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7.10
7.10
7.08
7.08
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6.80
3.48
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2.95
2.93
2.92
2.90
1.28
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NH2
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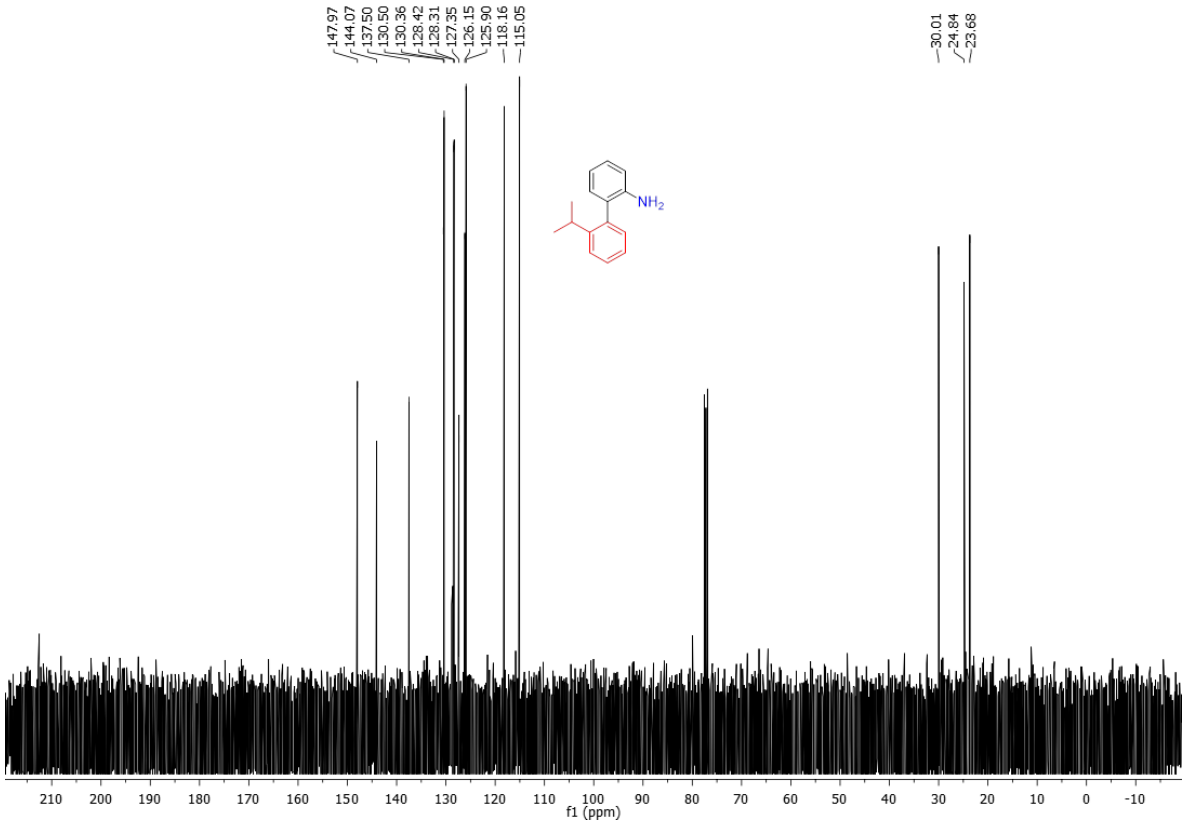
1.00
f1 (ppm)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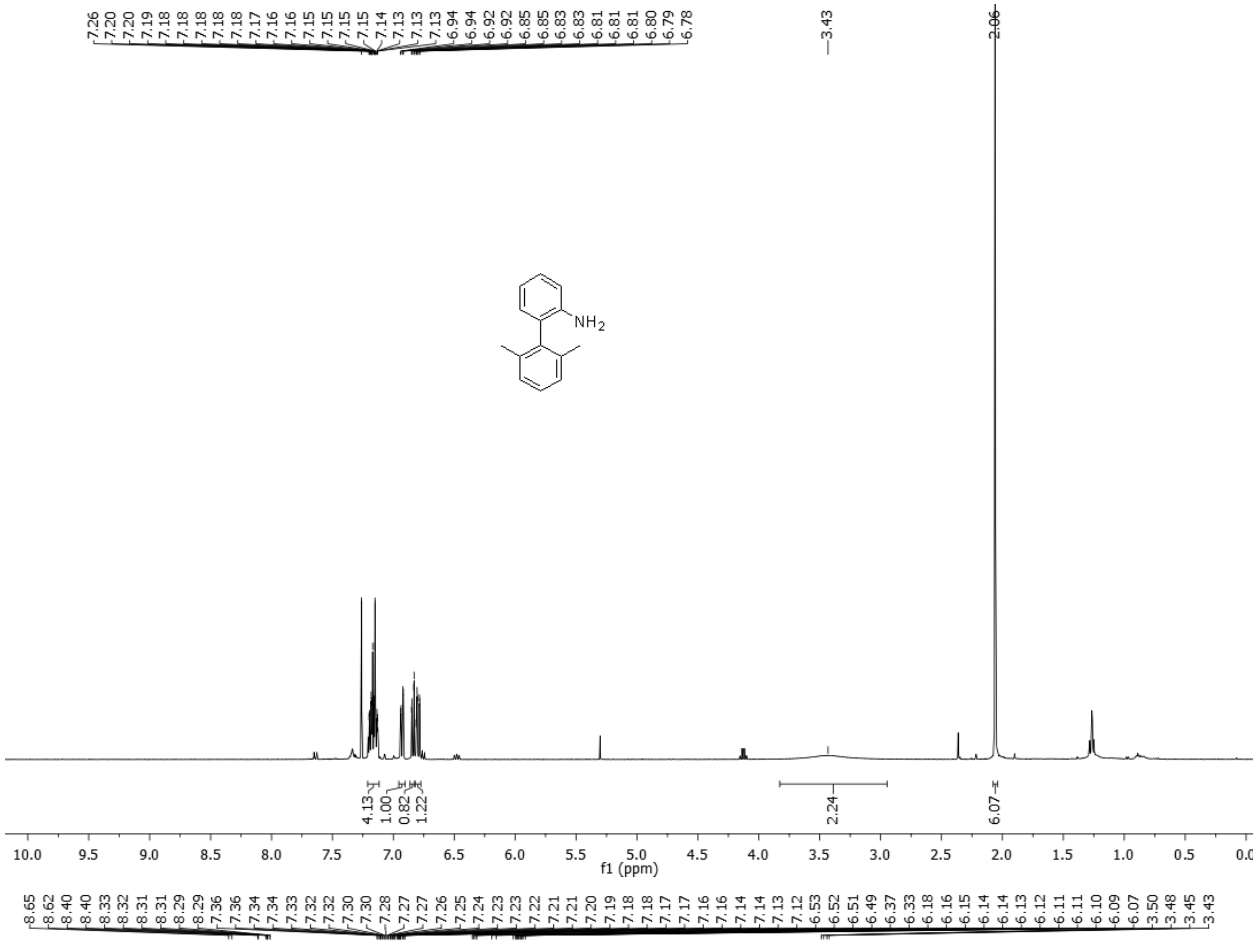
125.90
118.16
115.05
30.01
24.84
23.68
NH2
f1 (ppm)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7.15
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6.83
6.83
6.81
6.81
6.80
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NH2
4.13
1.00
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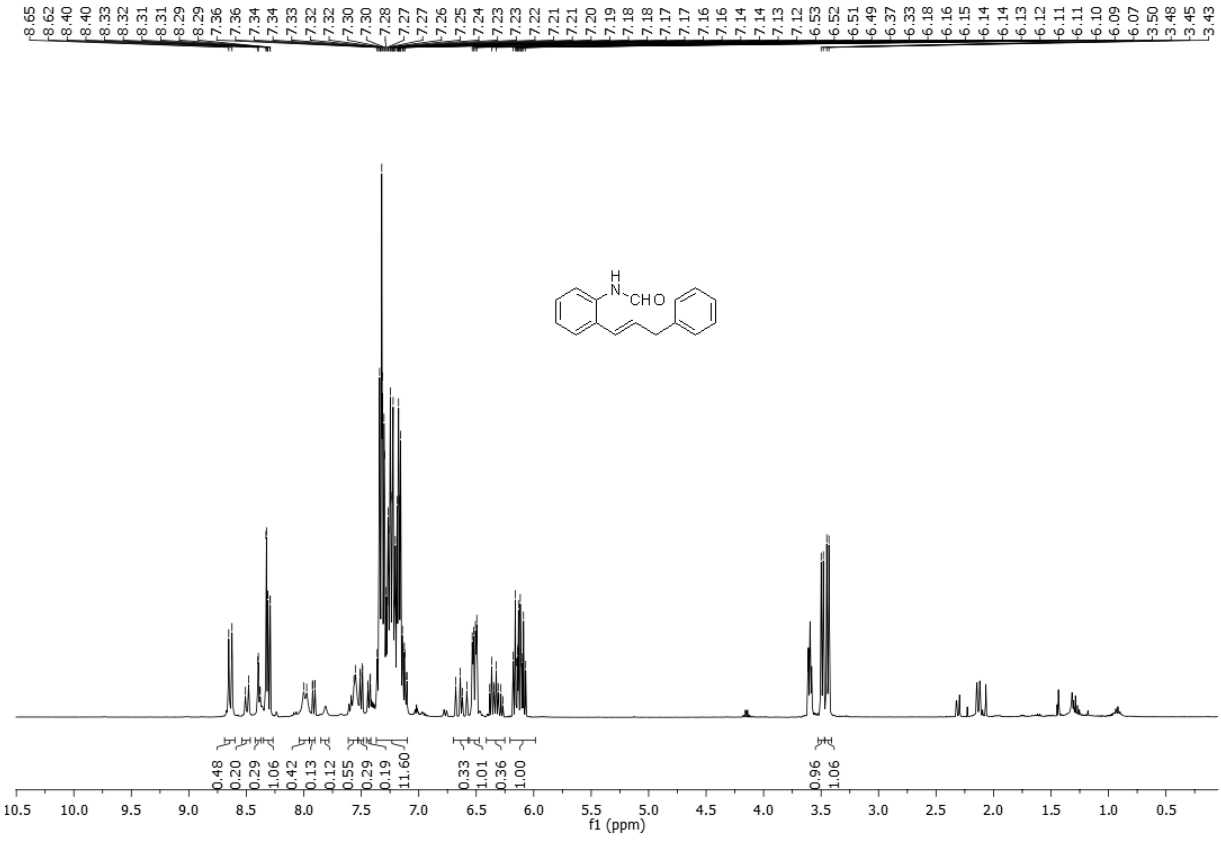
1.22
2.24
6.07
f1 (ppm)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7.12
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6.52
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6.49
6.37
6.33
6.18
6.16
6.15
6.14
6.14
6.13
6.12
6.11
6.11
6.10
6.09
6.07
3.50
3.48
3.45
3.43
H
N
CHO
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0.20
0.29
1.06
0.42
0.13
0.12
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0.19
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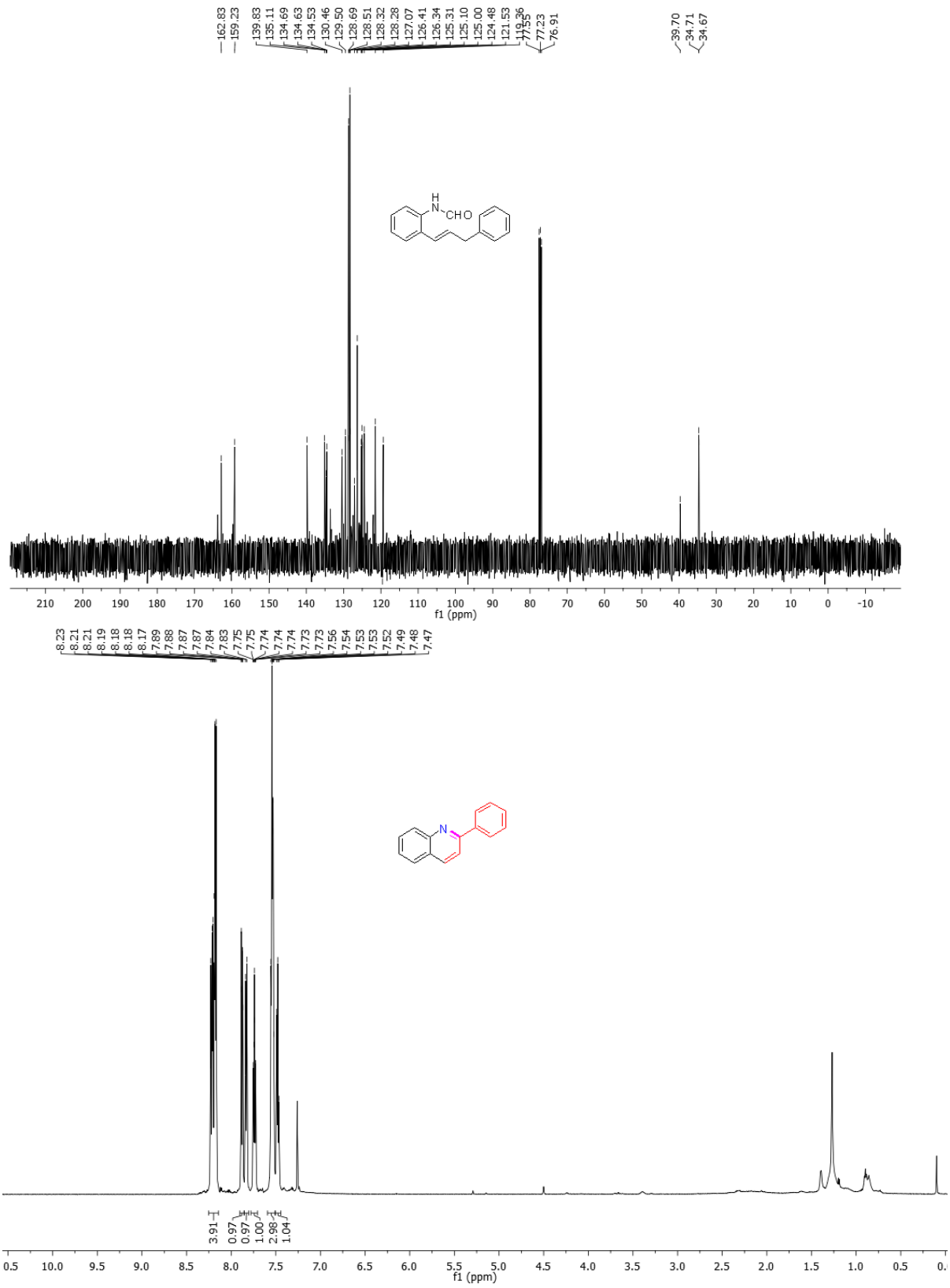
0.33
1.01
0.36
1.00
0.96
1.06
f1 (ppm)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128.28
127.07
126.41
126.34
125.31
125.10
125.00
124.48
121.53
119.36
77.55
77.23
76.91
39.70
34.71
34.67
CHO
f1 (ppm)
8.23
8.21
8.21
8.19
8.18
8.18
8.17
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7.87
7.87
7.84
7.83
7.75
7.75
7.74
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7.53
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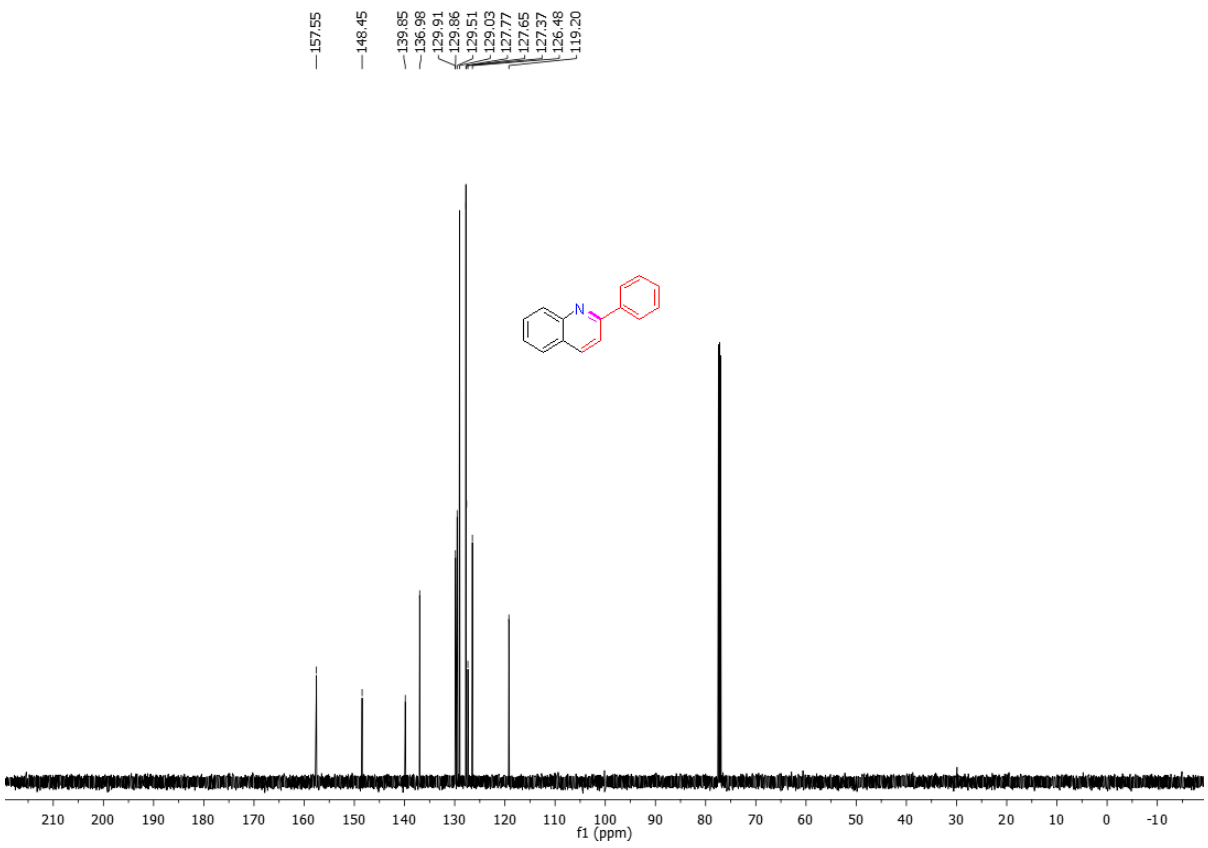
1.04
f1 (ppm)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127.37
126.48
119.20
N
210
200
190
180
170
160
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140
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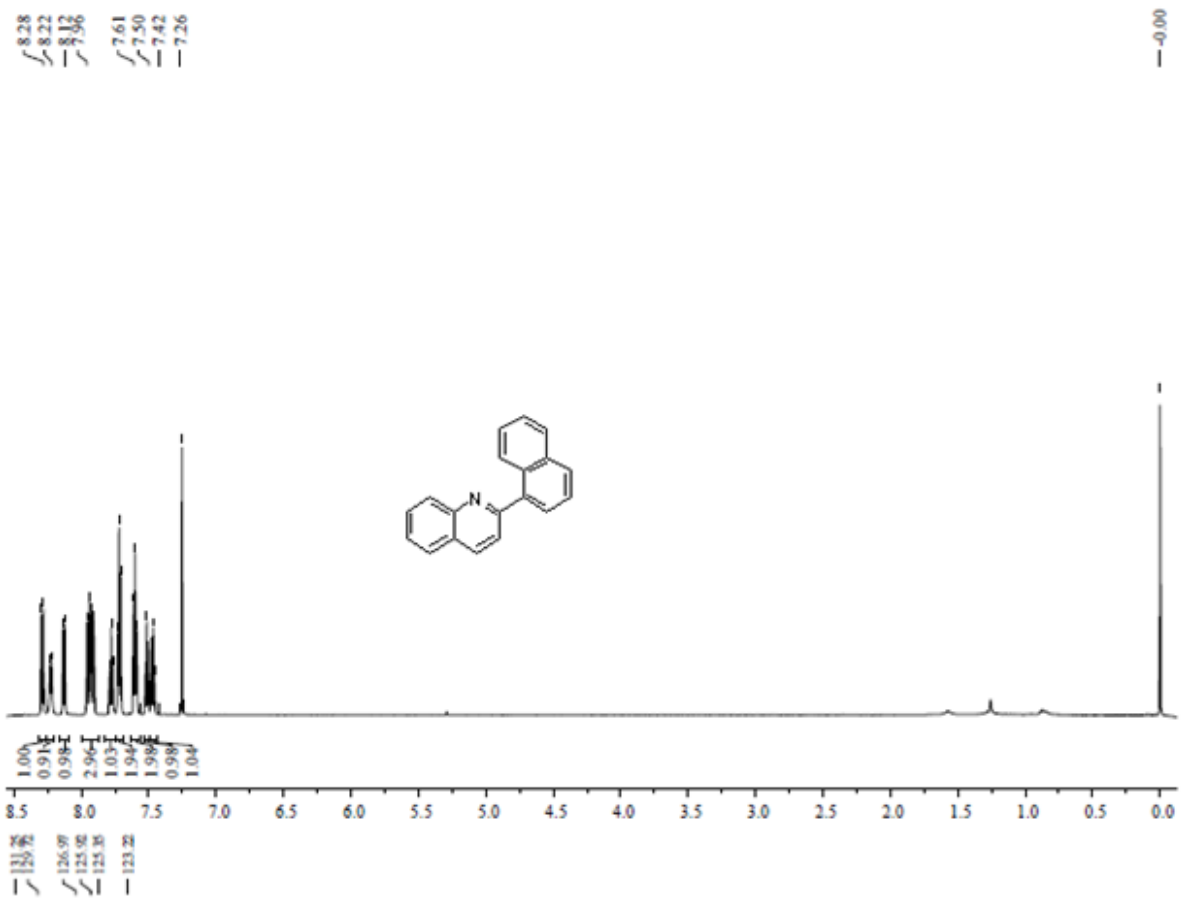
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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0.91
0.98
2.96
1.03
1.94
1.98
0.98
1.04
8.5
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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1.0
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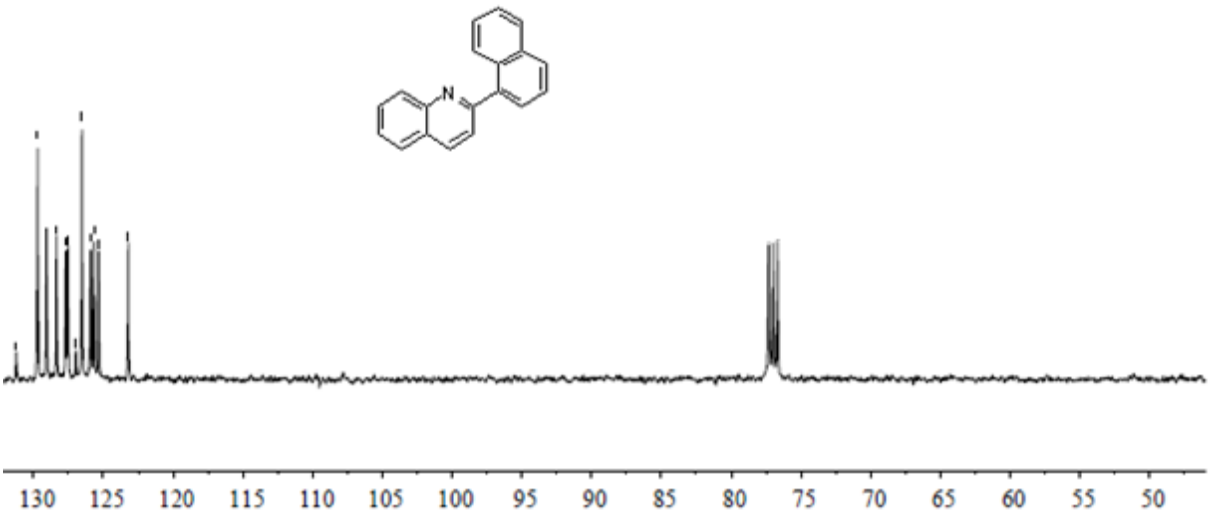
125.85
123.22
N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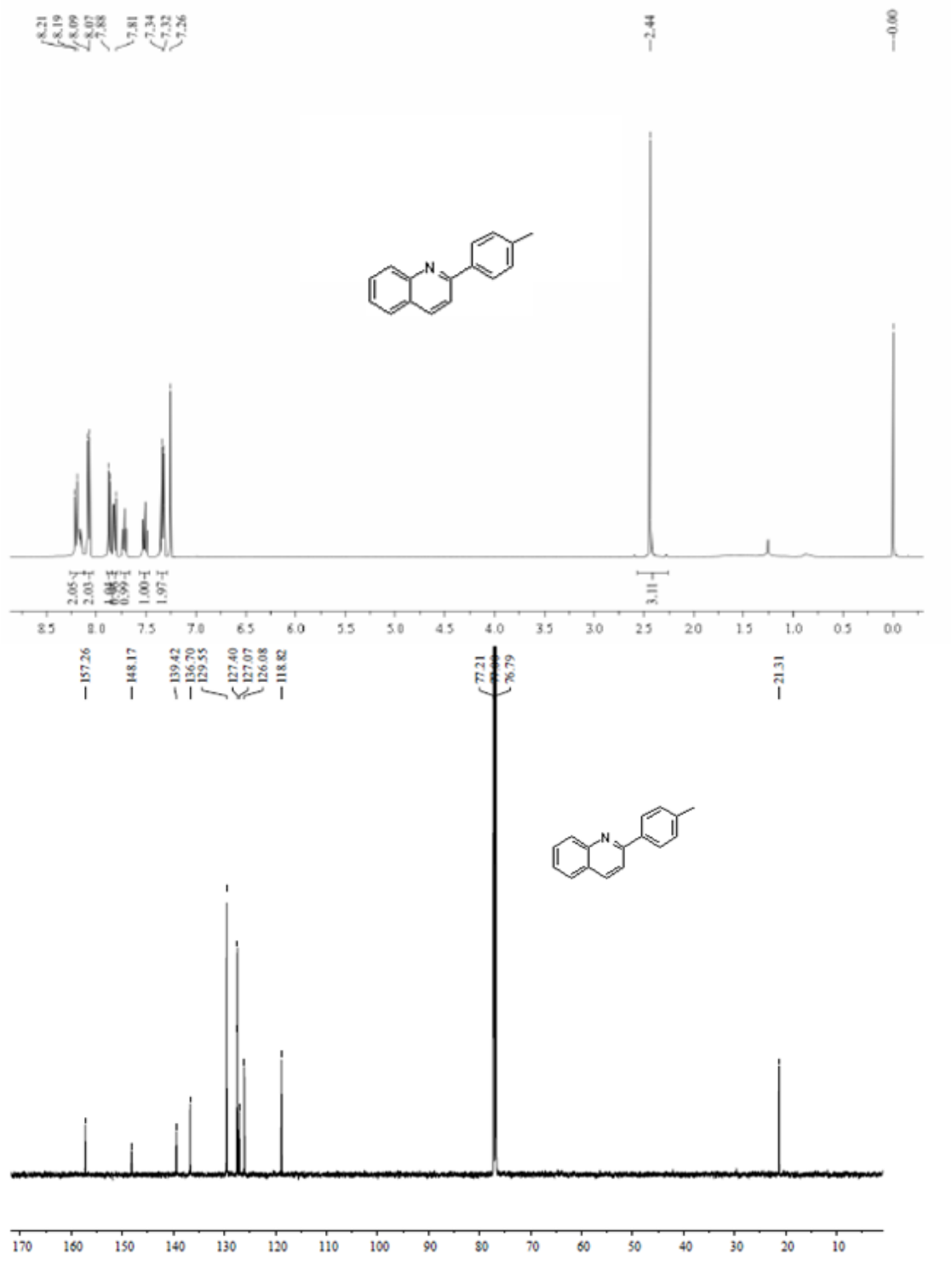
50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7.32
7.26
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2.05
2.03
1.00
1.97
3.11
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127.07
126.08
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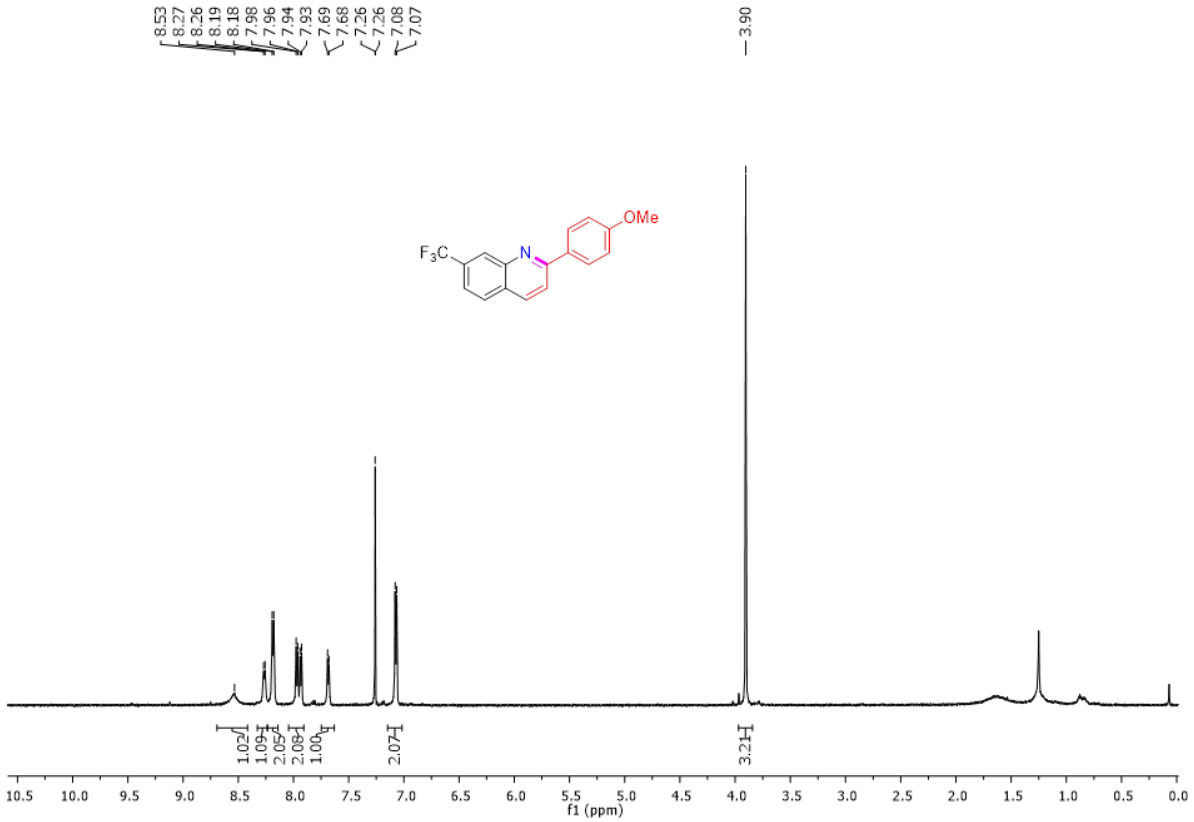
77.21
76.79
21.31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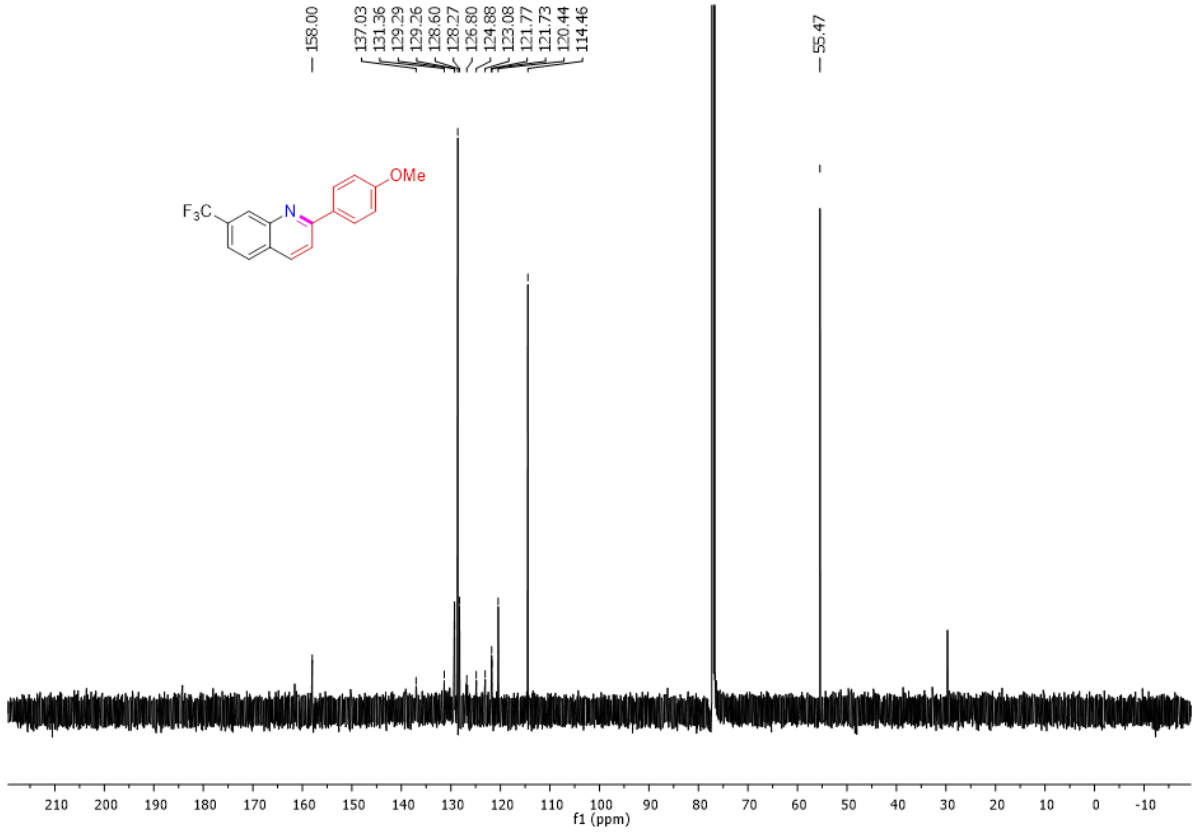
7.96
7.94
7.93
7.69
7.68
7.26
7.26
7.08
7.07
3.90
OMe
F3C
N
1.02
1.09
2.05
2.08
1.00
2.07
3.21
f1 (ppm)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121.77
121.73
120.44
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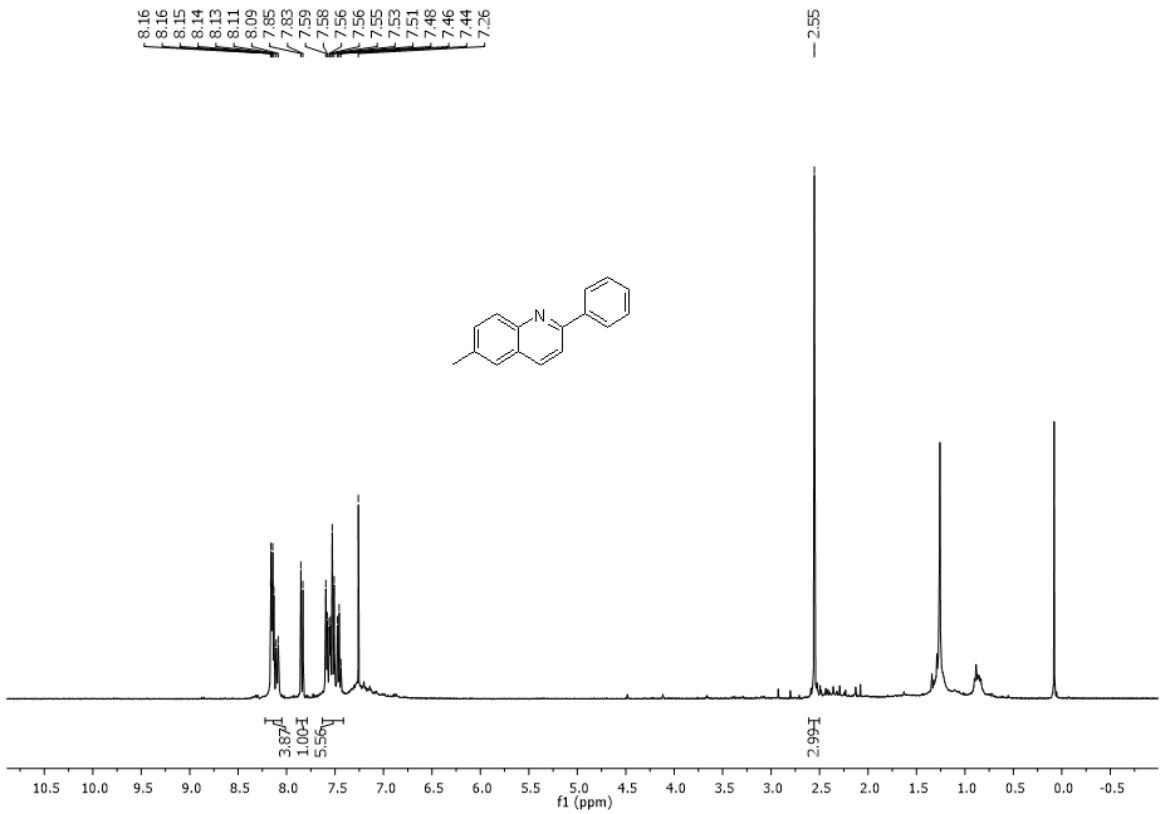
55.47
OMe
F3C
N
f1 (ppm)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7.56
7.55
7.53
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N
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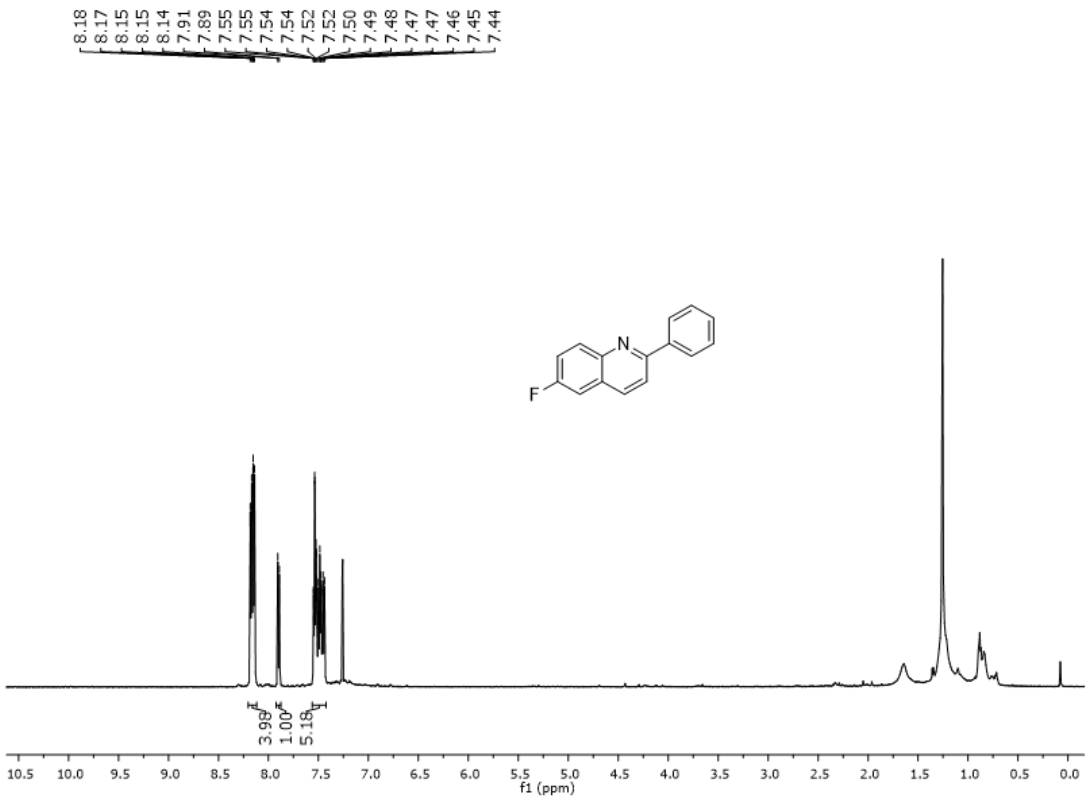
2.99
f1 (ppm)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7.50
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7.46
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F
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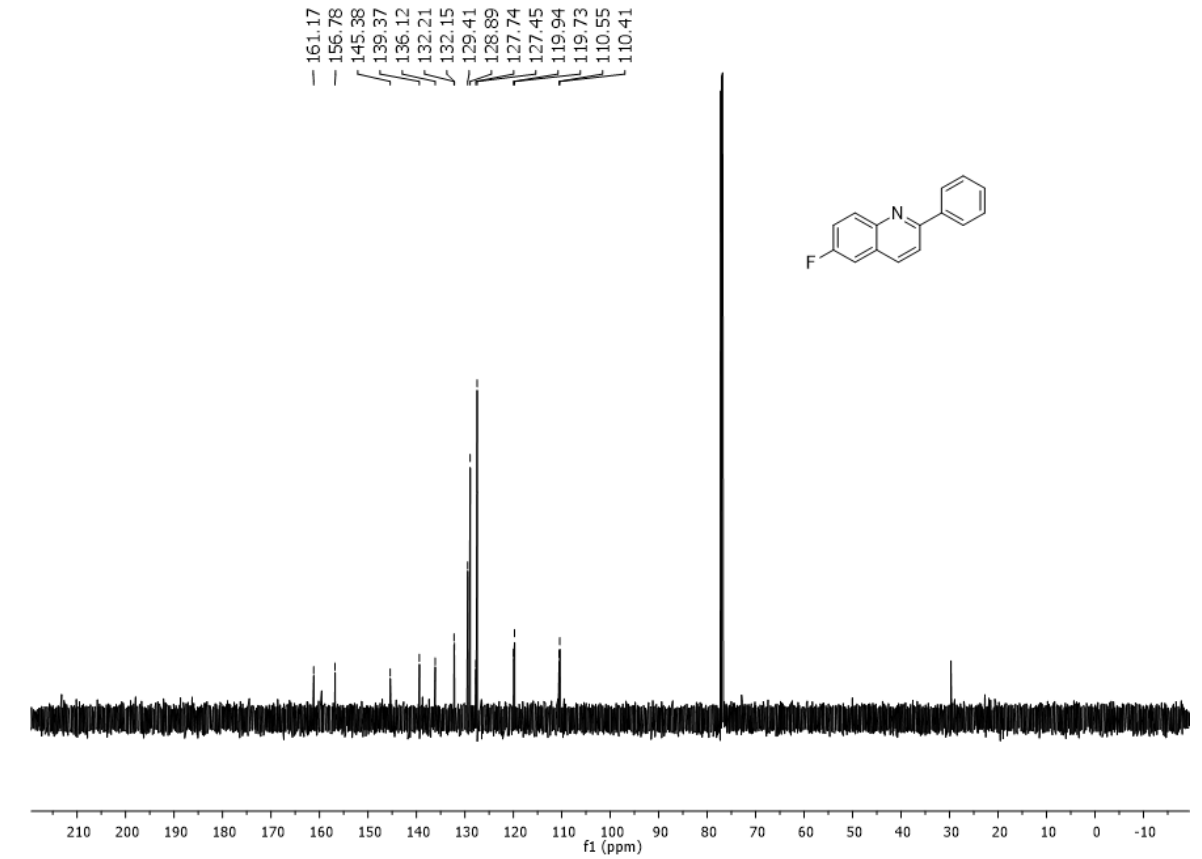
1.00
5.18
f1 (ppm)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127.74
127.45
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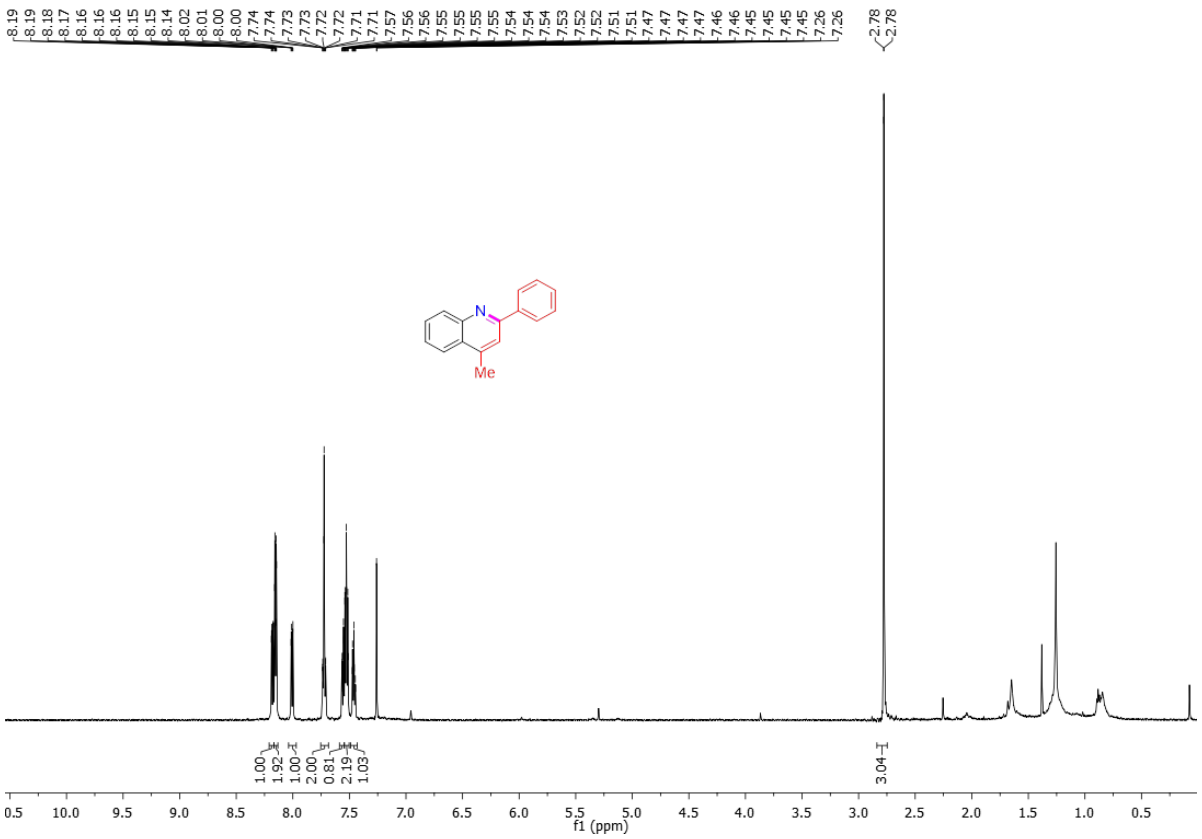
110.55
110.41
N
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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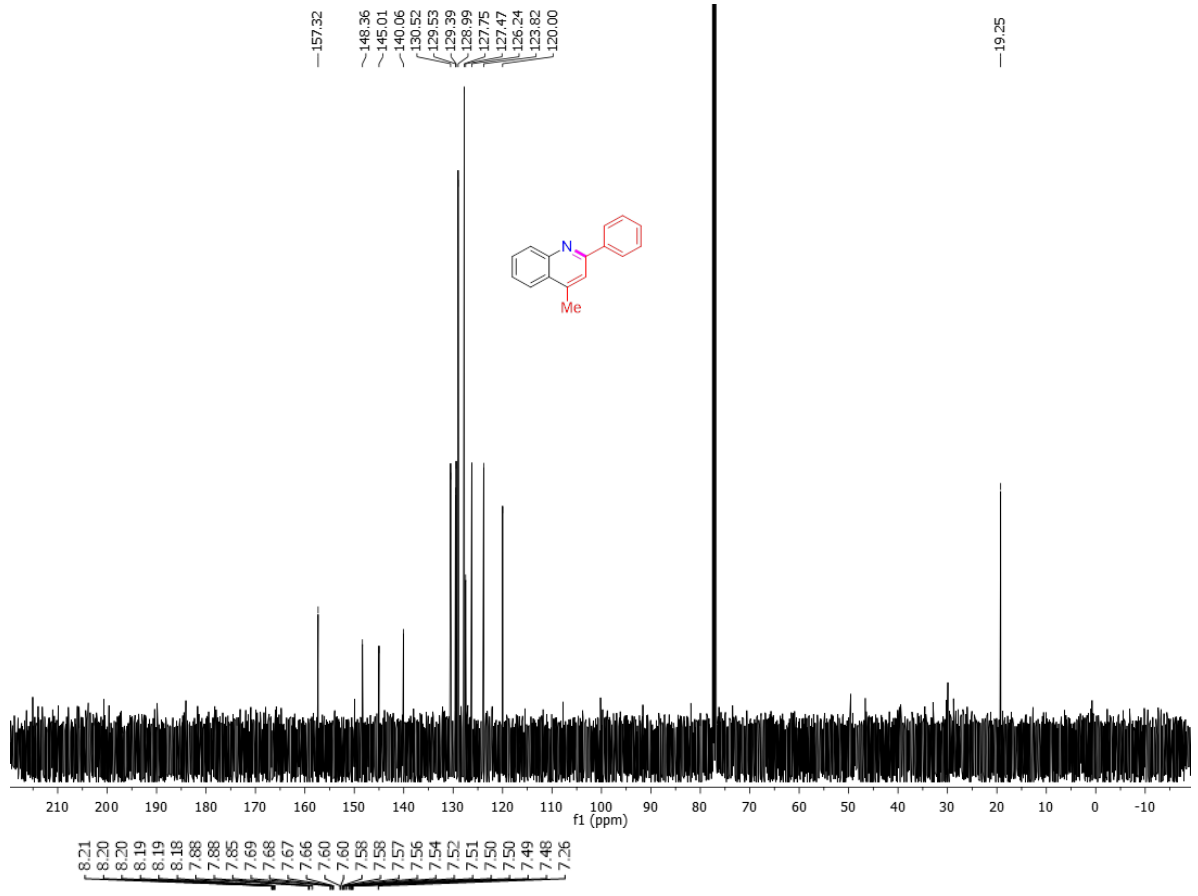
2.78 2.78
N
Me
1.00 1.92 1.00 2.00 0.81 2.19 1.03
3.04
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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129.39
128.99
127.75
127.47
126.24
123.82
120.00
19.25
N
Me
f1 (ppm)
8.21
8.20
8.20
8.19
8.19
8.18
7.88
7.88
7.85
7.69
7.68
7.67
7.66
7.60
7.60
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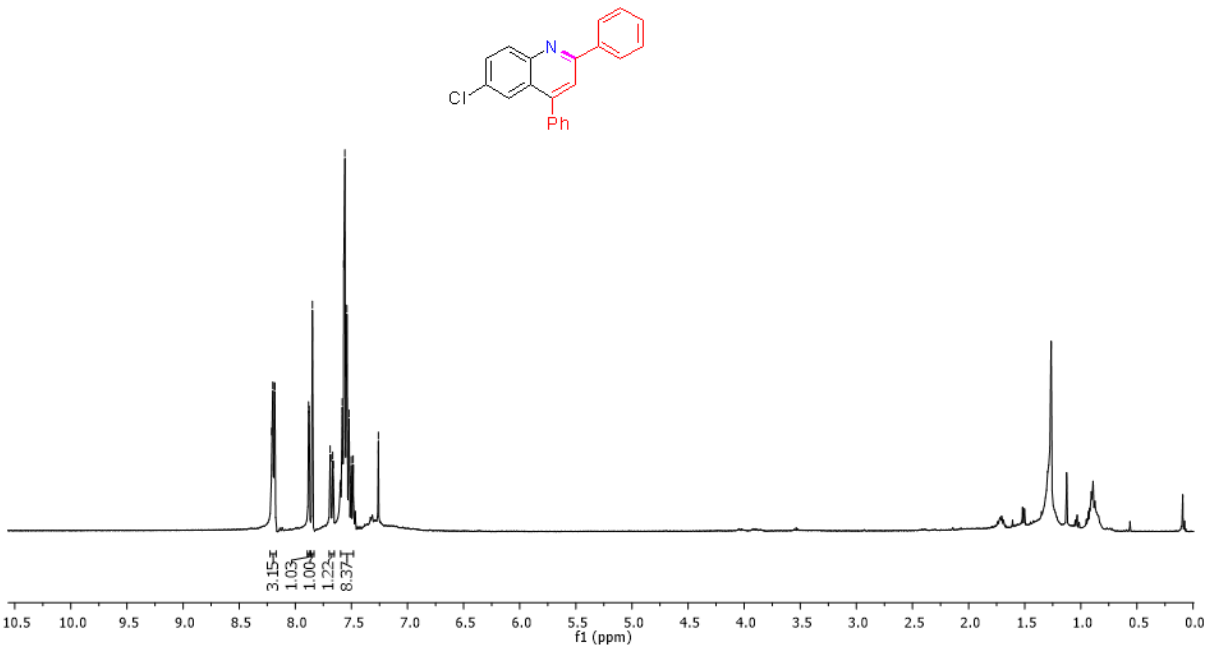
7.26


N
Cl
Ph
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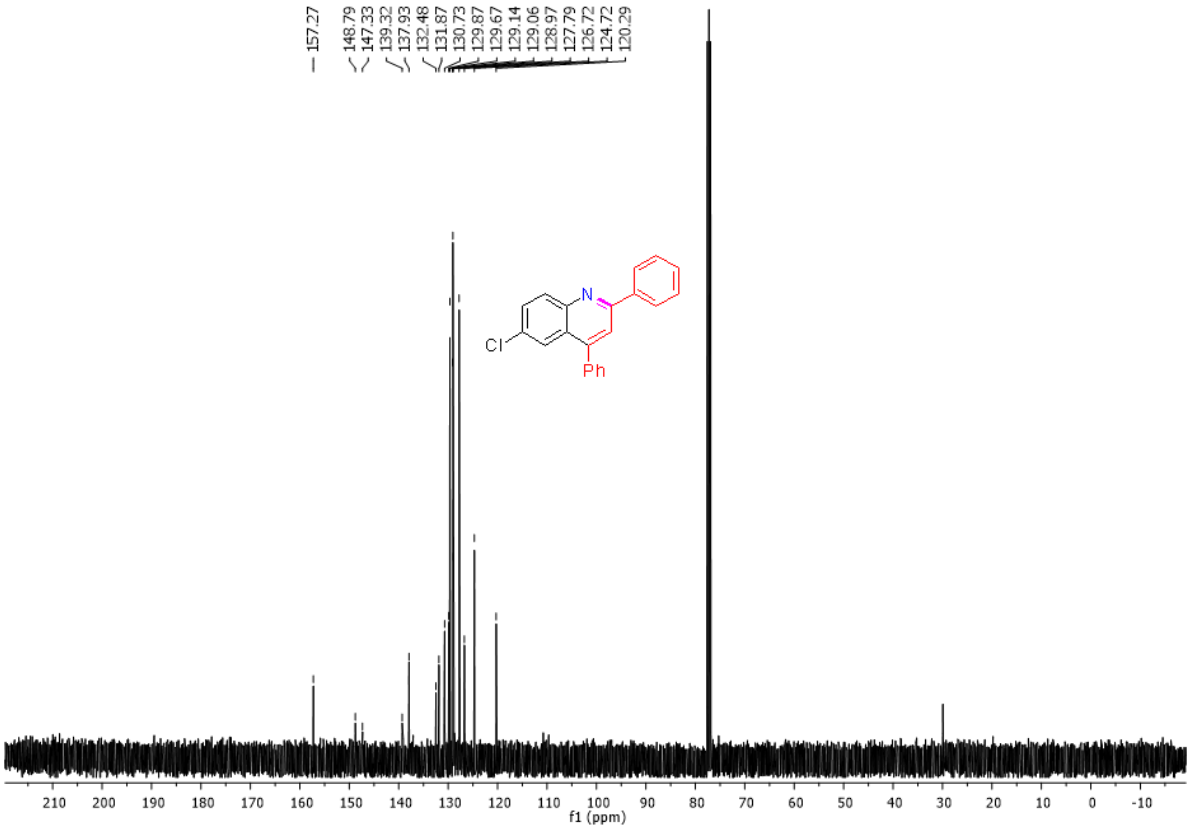
f1 (ppm)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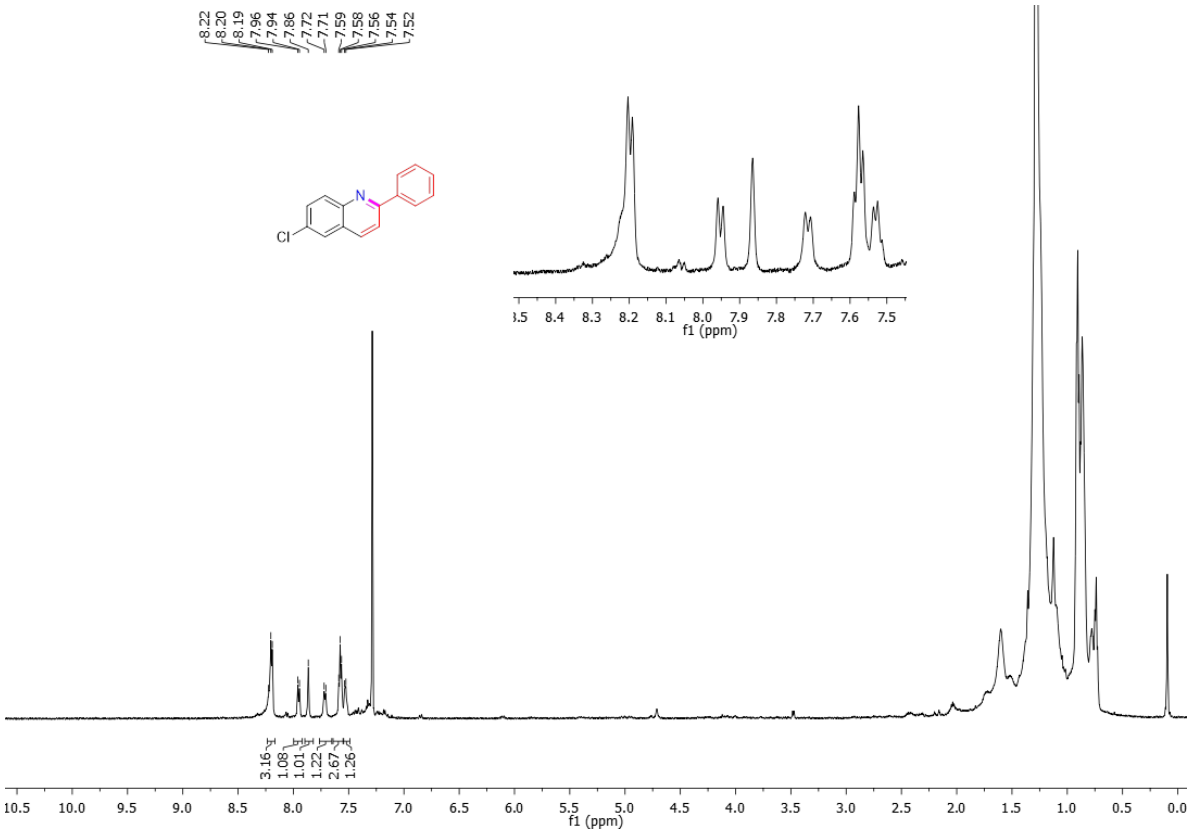
124.72
120.29
N
Cl
Ph
f1 (ppm)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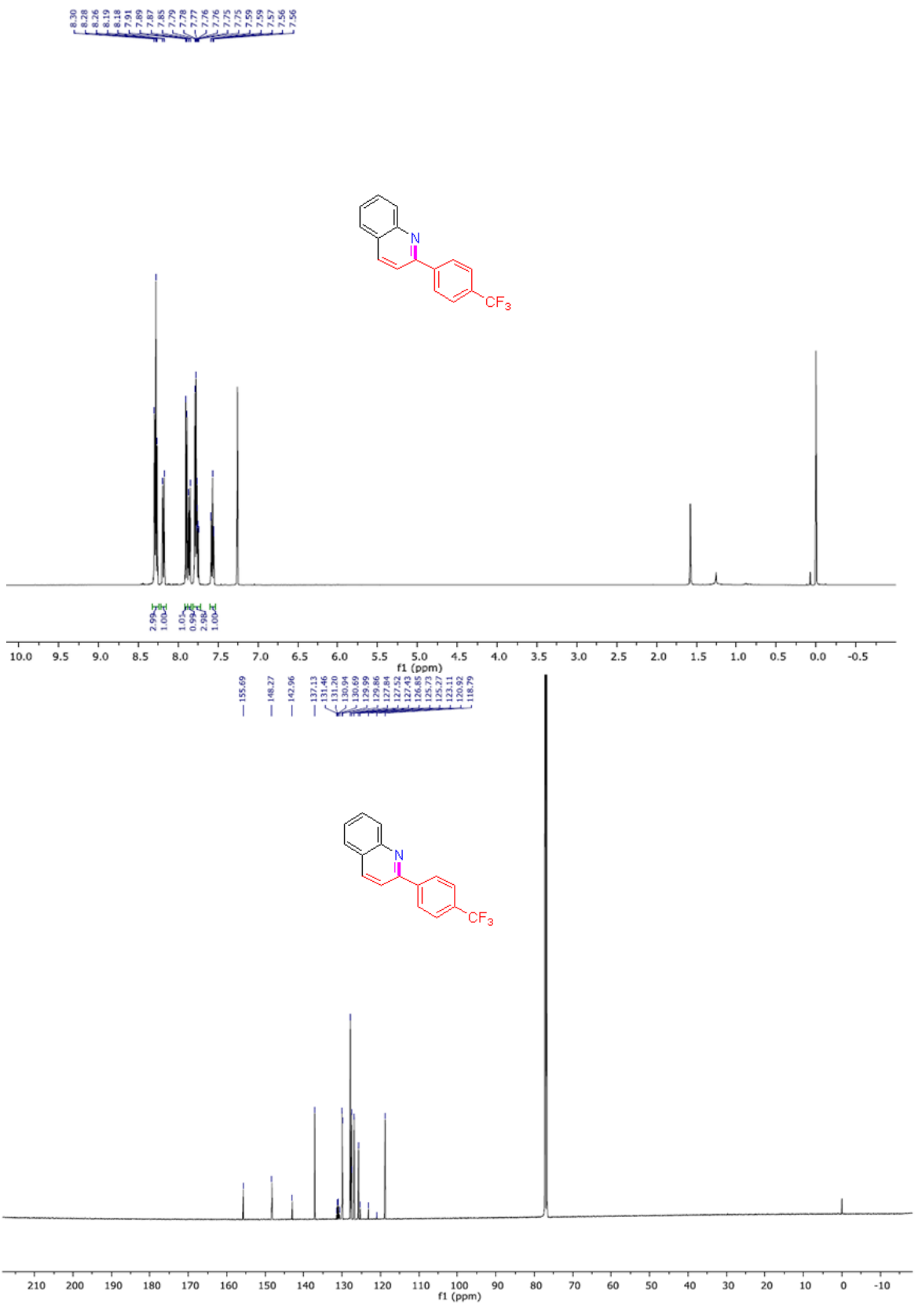
8.20
8.19
7.96
7.94
7.86
7.72
7.71
7.59
7.58
7.56
7.54
7.52
N
Cl
3.16
1.08
1.01
1.22
2.67
1.26
f1 (ppm)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8.26
8.19
8.18
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7.87
7.85
7.79
7.78
7.77
7.76
7.76
7.75
7.75
7.59
7.59
7.57
7.56
7.56
N
CF3
2.99
1.00
1.01
0.99
2.98
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 -0.5
f1 (ppm)
155.69
148.27
142.96
137.13
131.46
131.20
130.94
130.69
129.99
129.86
127.84
127.52
127.43
126.85
125.73
125.27
123.11
120.92
118.79
N
CF3
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)


8.96
8.96
8.69
8.68
8.67
8.66
8.31
8.31
8.29
8.29
8.20
8.20
8.19
8.19
8.19
8.18
8.18
8.17
8.17
7.98
7.98
7.97
7.96
7.96
7.95
7.94
7.94
7.93
7.92
7.77
7.76
7.76
7.76
7.75
7.75
7.74
7.74
7.73
7.73
7.73
7.71
7.71
7.62
7.61
7.61
7.60
7.60
7.60
7.59
7.59
7.58
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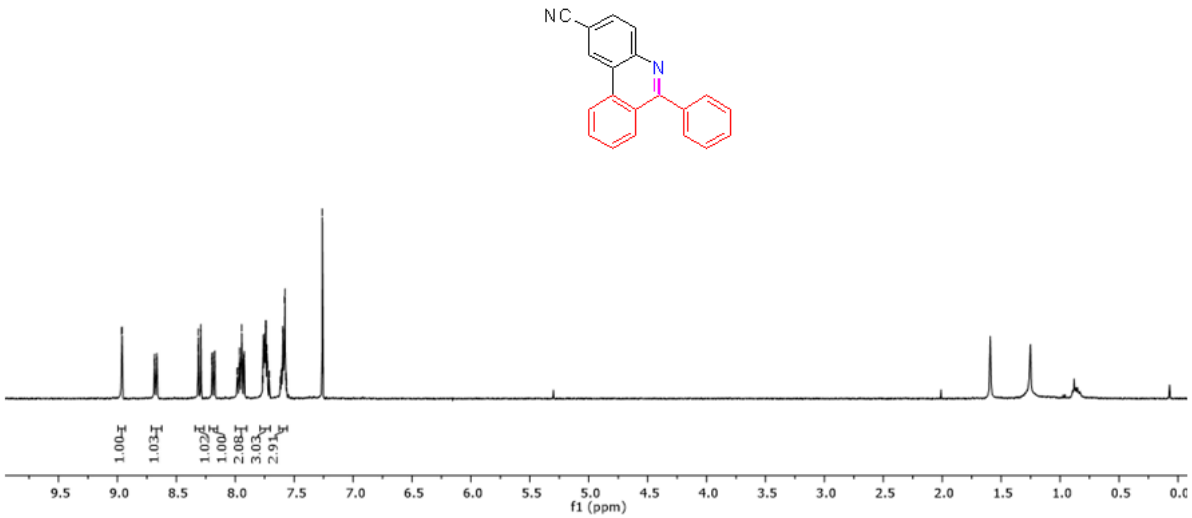
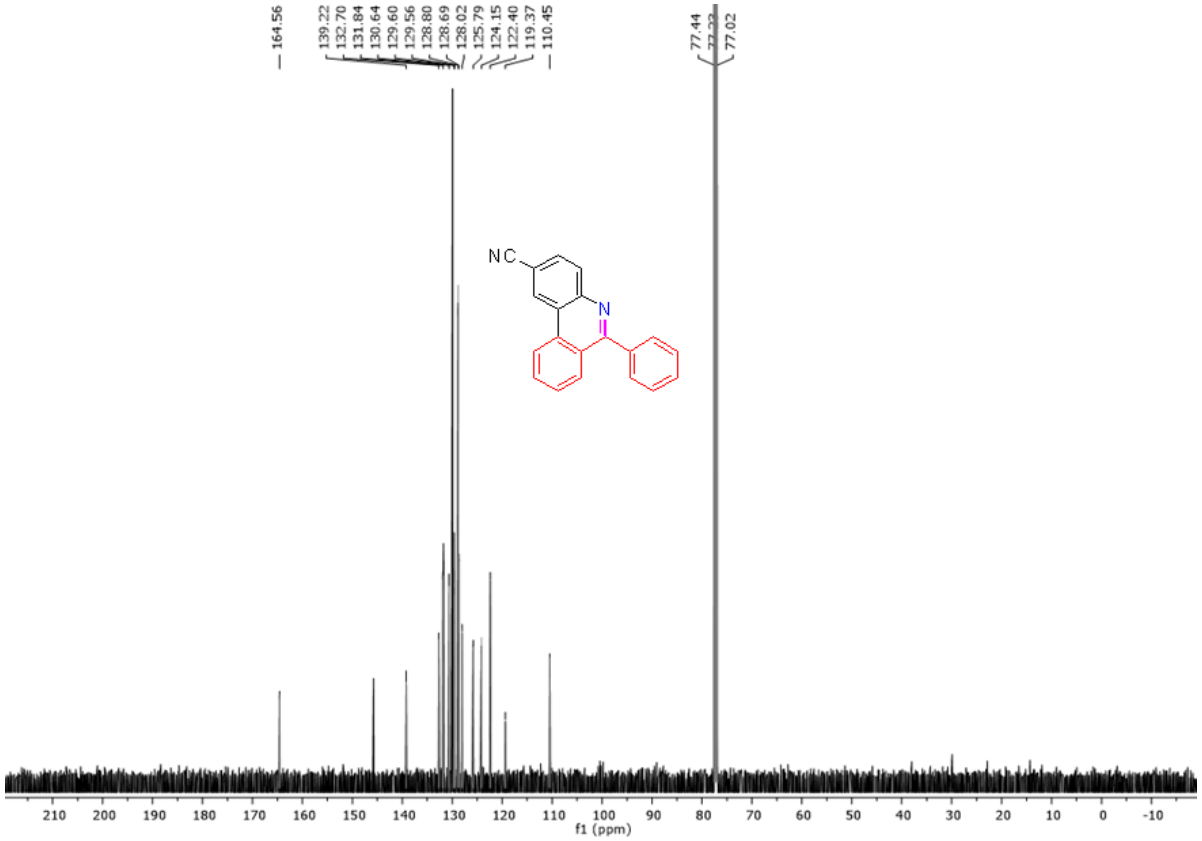
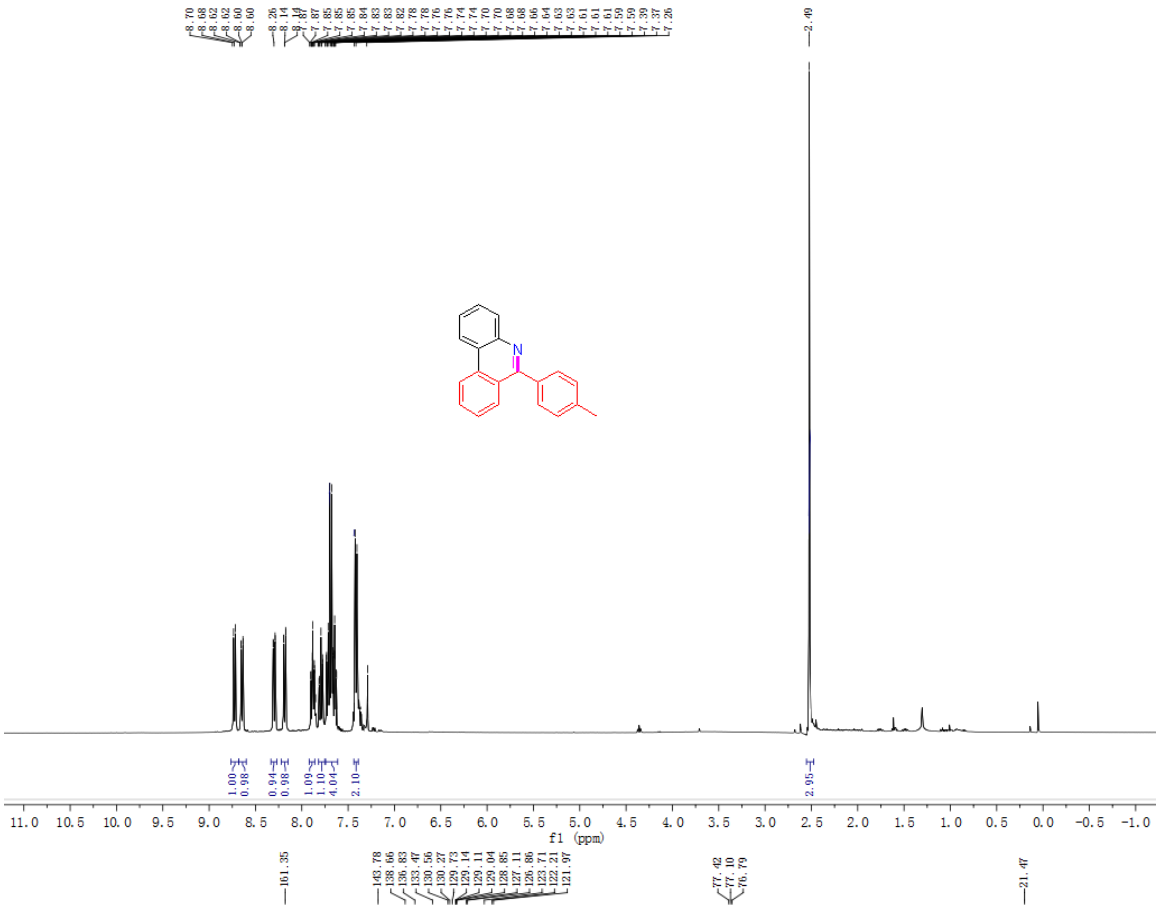
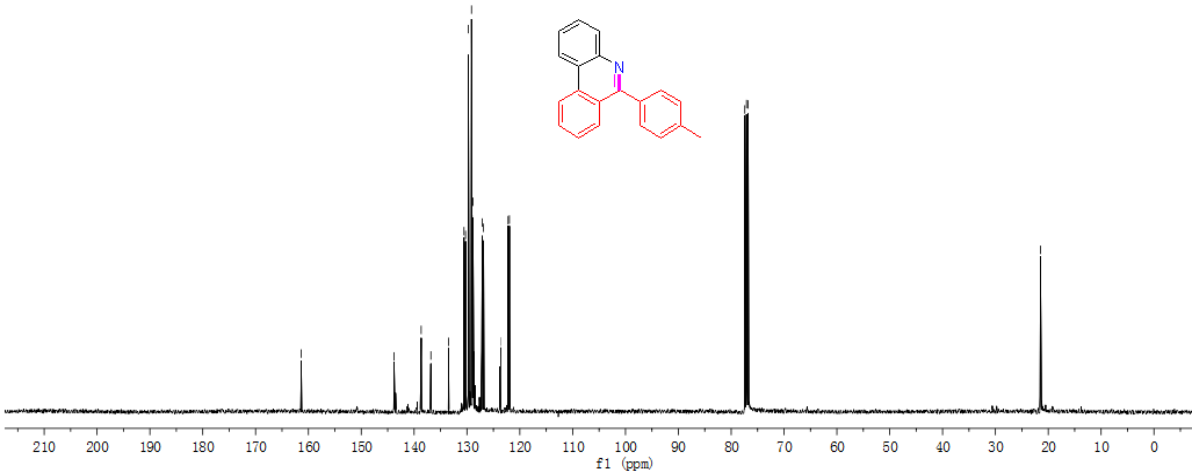
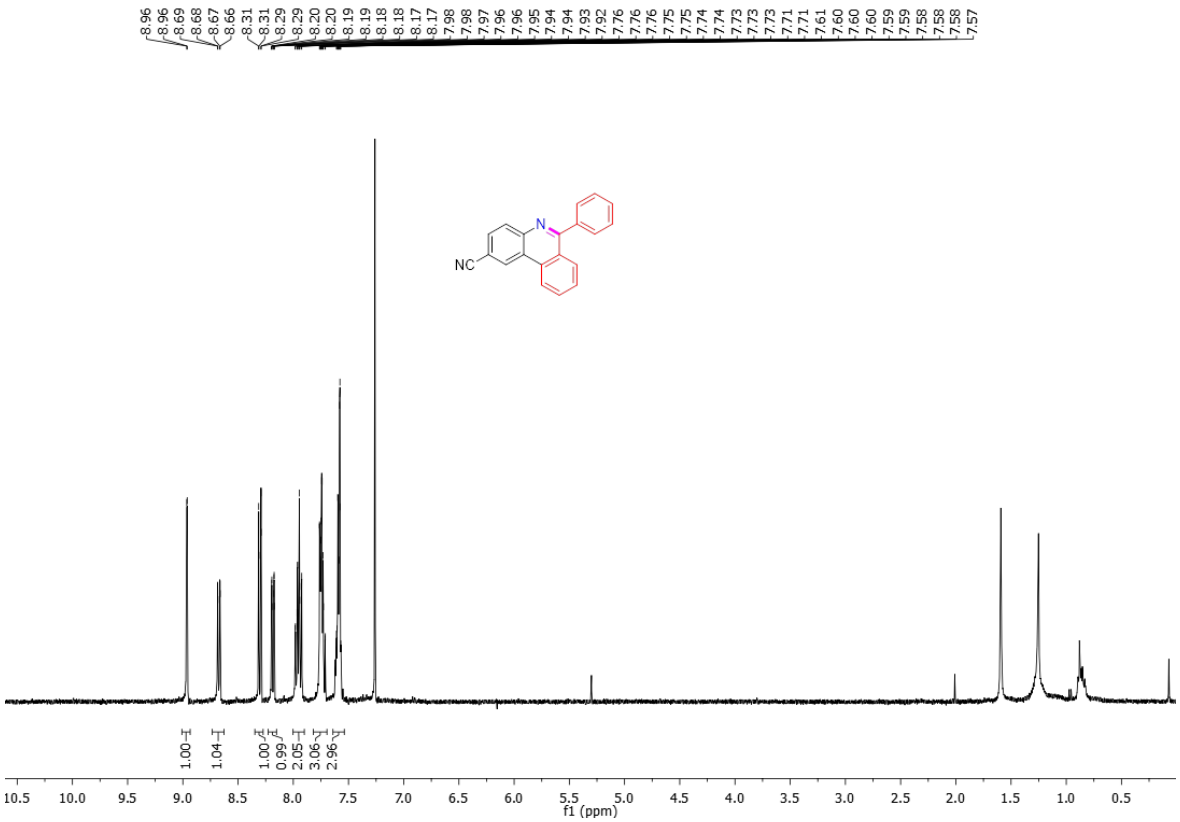
7.58
7.57
7.56
7.26
7.26
7.26

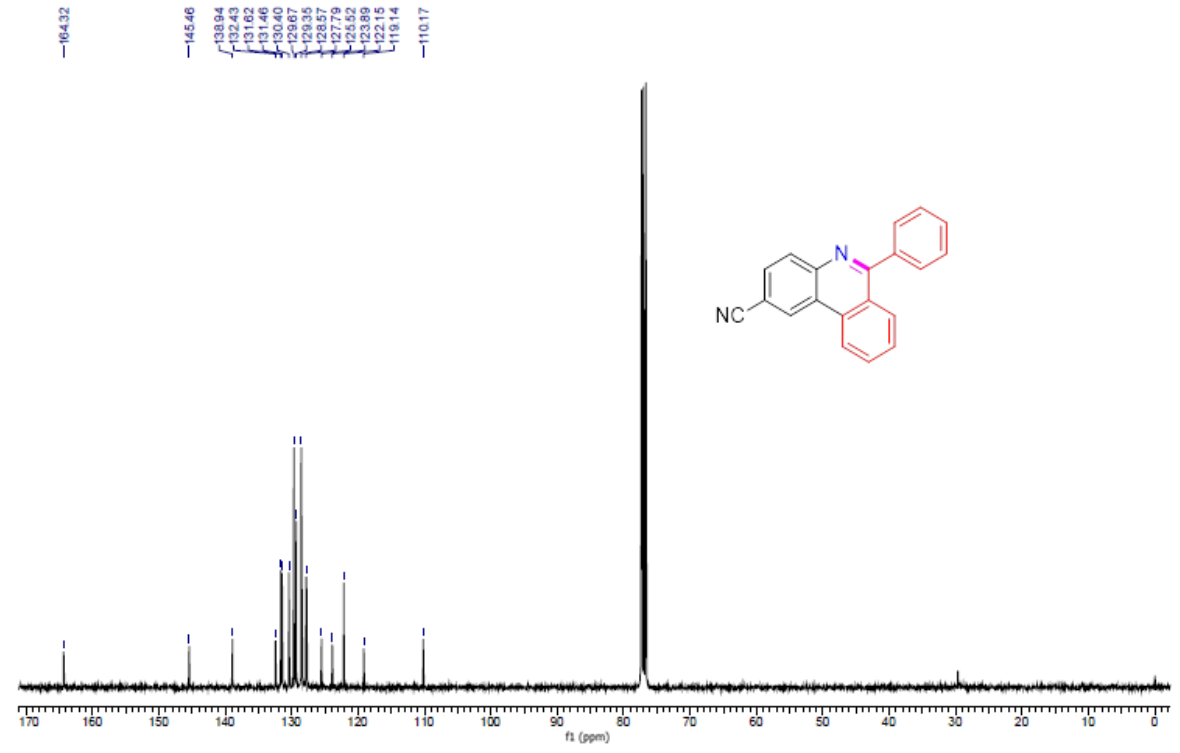

NC
N
1.00
1.03
1.02
1.00
2.08
3.03
2.91
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

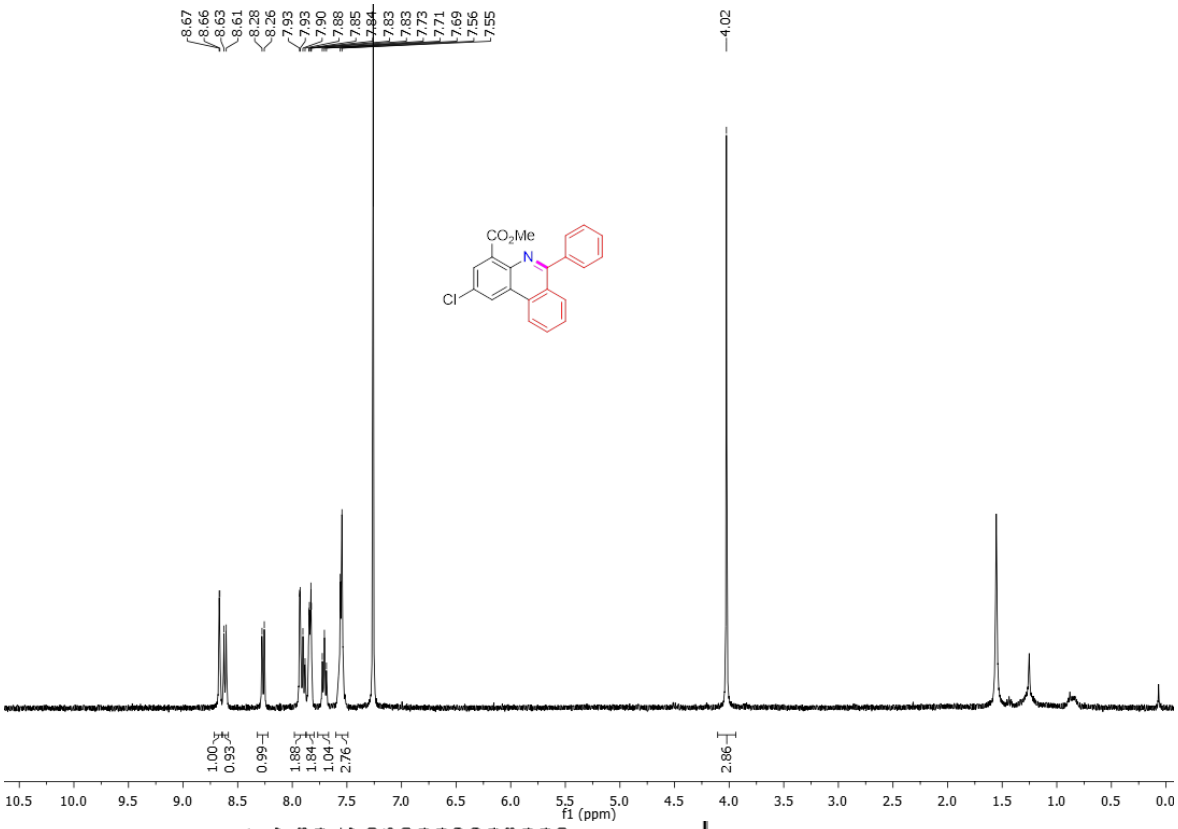

164.56
139.22
132.70
131.84
130.64
129.60
129.56
128.80
128.69
128.02
125.79
124.15
122.40
119.37
110.45
77.44
77.02
NC
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

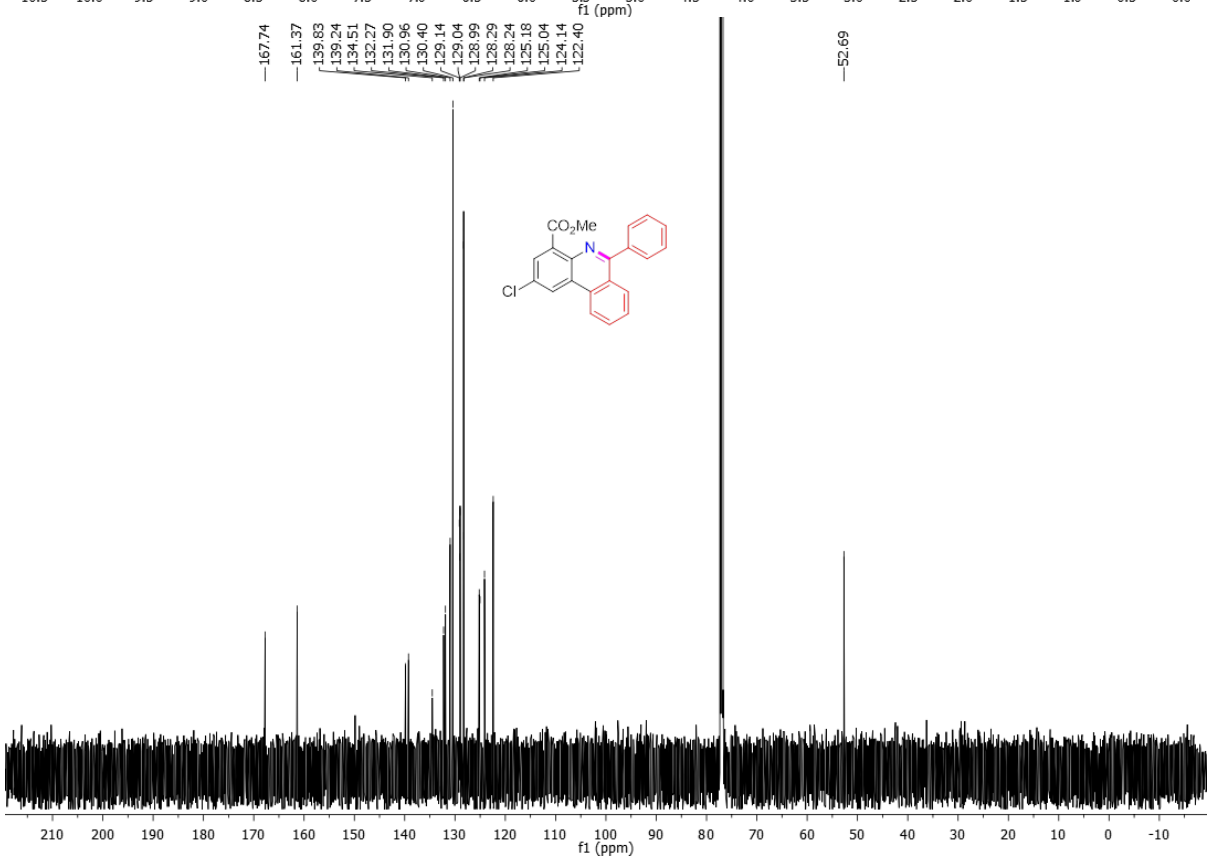


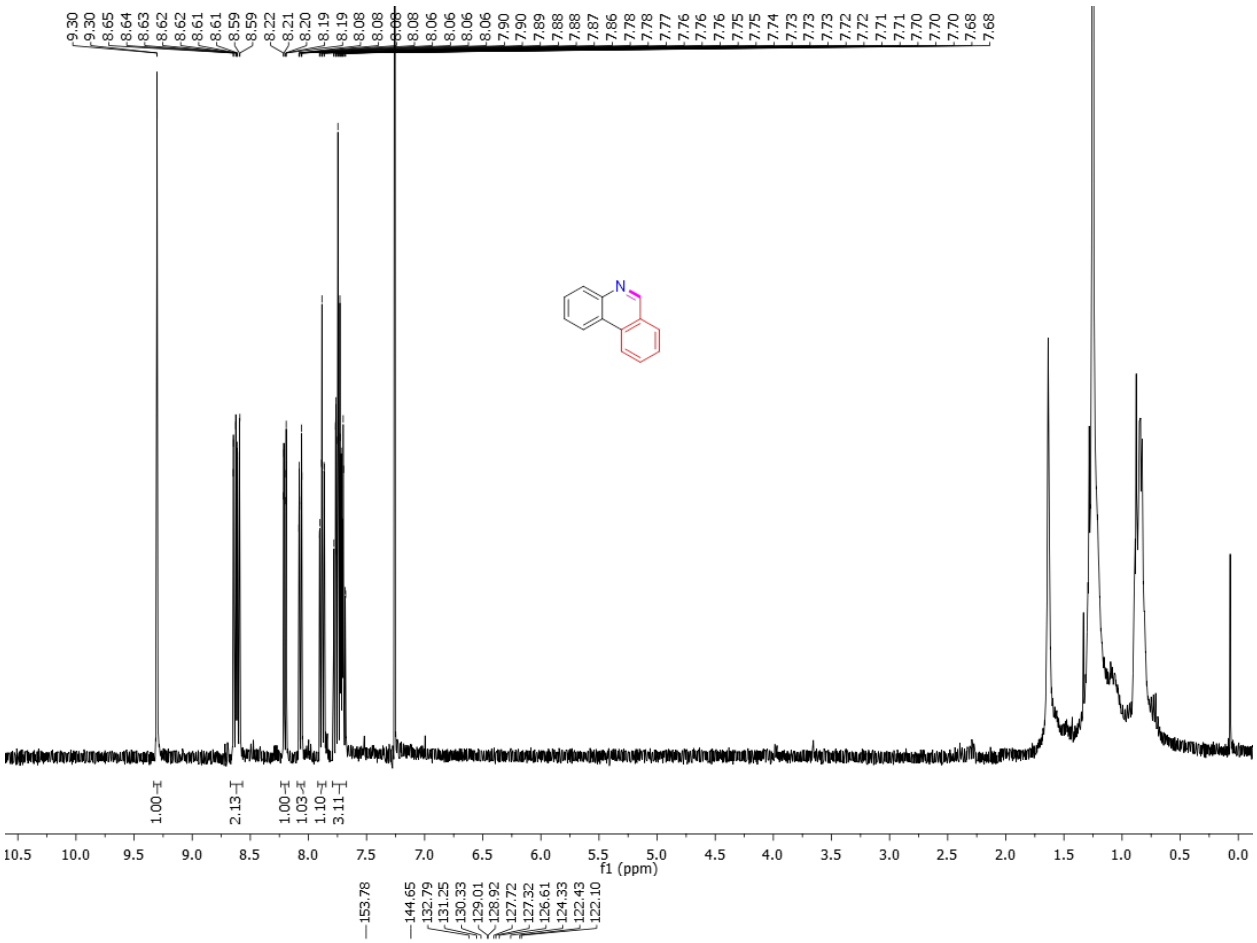



8.96
8.96
8.69
8.68
8.67
8.66
8.31
8.31
8.29
8.29
8.20
8.20
8.19
8.19
8.18
8.18
8.17
8.17
7.98
7.98
7.97
7.96
7.96
7.95
7.94
7.94
7.93
7.92
7.76
7.76
7.76
7.75
7.75
7.74
7.74
7.73
7.73
7.73
7.71
7.71
7.61
7.60
7.60
7.59
7.59
7.58
7.58
7.58
7.57
N
NC
1.00
1.04
1.00
0.99
2.05
3.06
2.96
10.5
10.0
9.5
9.0
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)

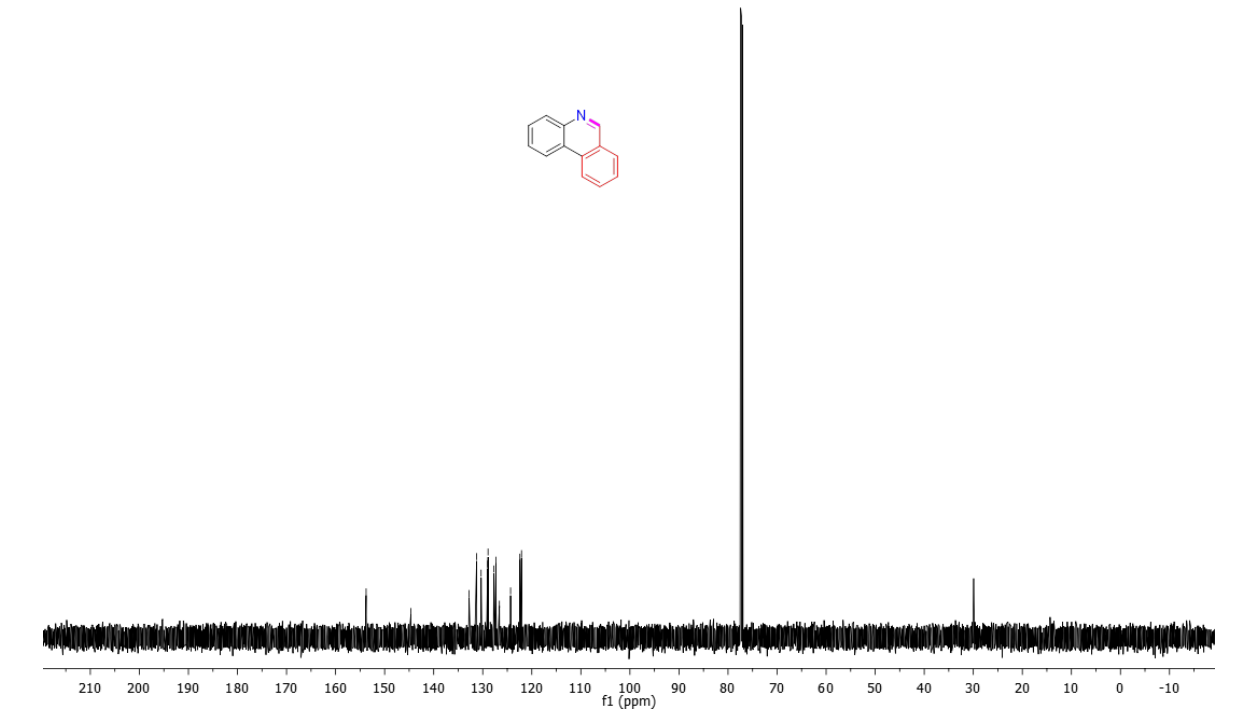

164.32
145.46
138.94
132.43
131.62
131.46
130.40
129.67
129.35
128.57
127.79
125.52
123.89
122.15
119.14
110.17
N
NC
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

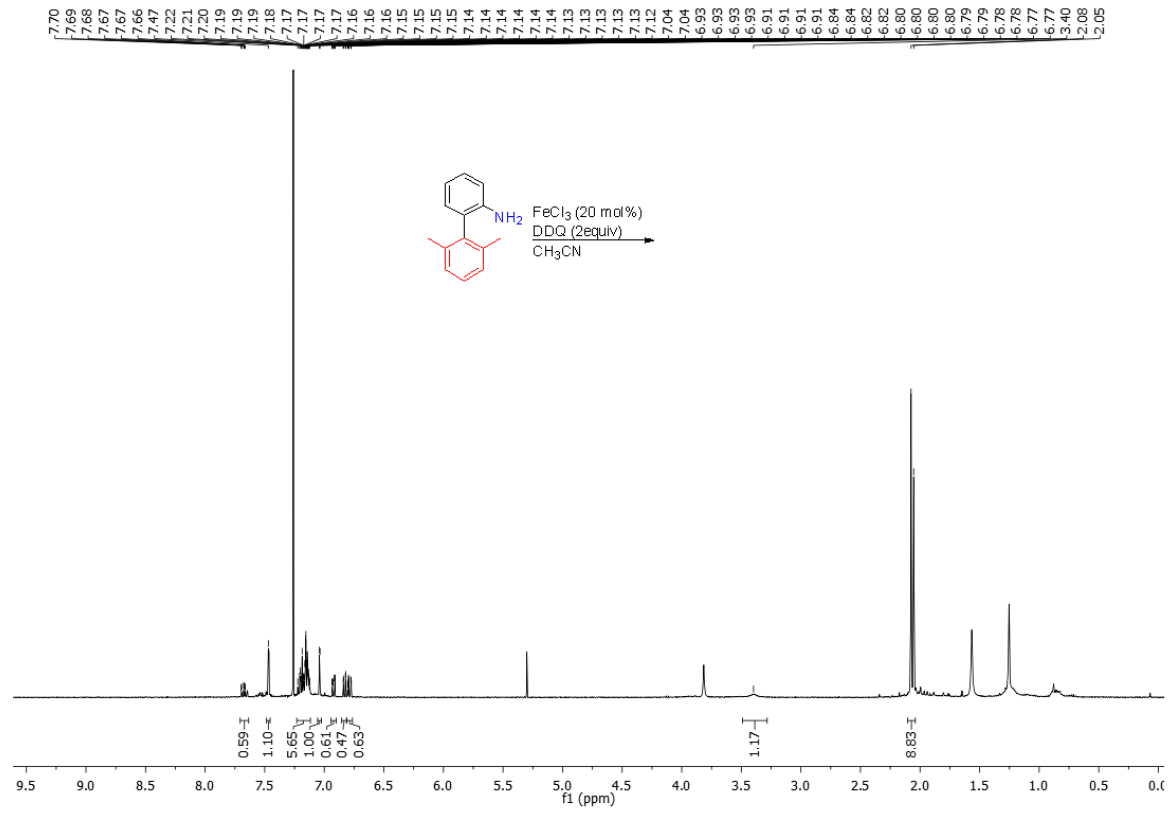

8.67
8.66
8.63
8.61
8.28
8.26
7.93
7.93
7.90
7.88
7.85
7.84
7.83
7.83
7.73
7.71
7.69
7.56
7.55
4.02
CO2Me
N
Cl
1.00
0.93
0.99
1.88
1.84
1.04
2.76
2.86
f1 (ppm)

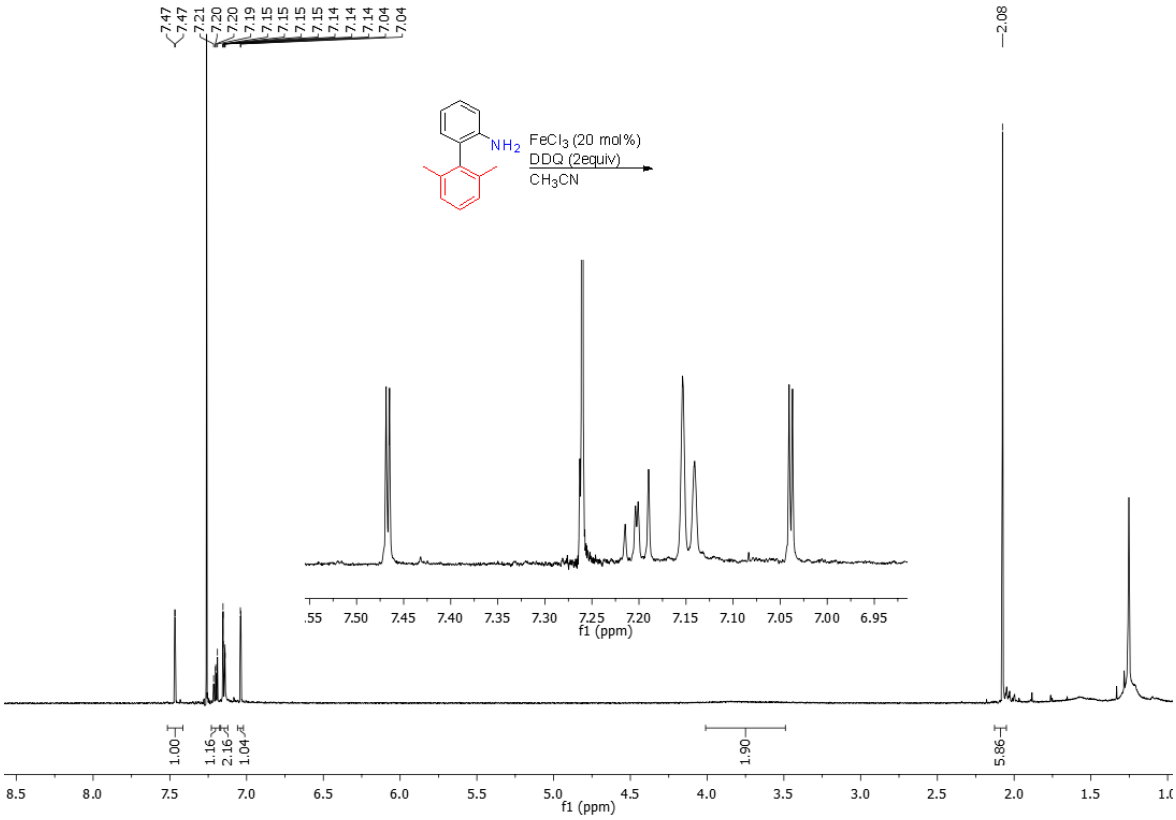

167.74
161.37
139.83
139.24
134.51
132.27
131.90
130.96
130.40
129.14
129.04
128.99
128.29
128.24
125.18
125.04
124.14
122.40
52.69
CO2Me
N
Cl
f1 (ppm)

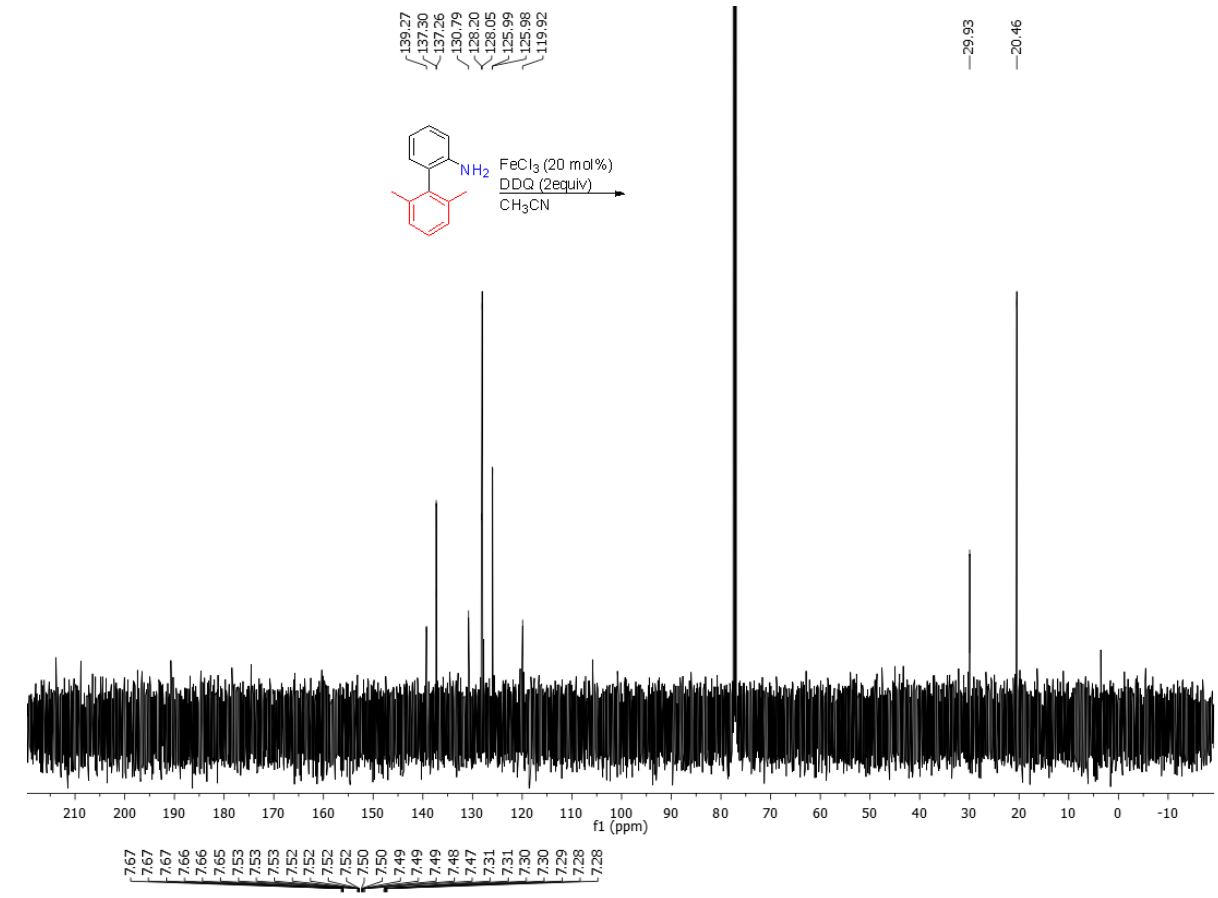

9.30
9.30
8.65
8.64
8.63
8.62
8.62
8.61
8.61
8.59
8.59
8.22
8.21
8.20
8.19
8.19
8.08
8.08
8.08
8.08
8.06
8.06
8.06
8.06
8.06
7.90
7.90
7.89
7.88
7.88
7.87
7.86
7.78
7.78
7.77
7.76
7.76
7.76
7.75
7.75
7.74
7.73
7.73
7.73
7.72
7.72
7.71
7.71
7.70
7.70
7.70
7.68
7.68
N
1.00
2.13
1.00
1.03
1.10
3.11
10.5 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)


153.78
144.65
132.79
131.25
130.33
129.01
128.92
127.72
127.32
126.61
124.33
122.43
122.10


N
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)


NH2
FeCl3 (20 mol%)
DDQ (2equiv)
CH3CN
f1 (ppm)


NH2
FeCl3 (20 mol%)
DDQ (2equiv)
CH3CN
f1 (ppm)


139.27
137.30
137.26
130.79
128.20
128.05
125.99
125.98
119.92
29.93
20.46
NH2
FeCl3 (20 mol%)
DDQ (2equiv)
CH3CN
f1 (ppm)
7.67
7.67
7.67
7.66
7.66
7.65
7.53
7.53
7.53
7.52
7.52
7.52
7.52
7.50
7.50
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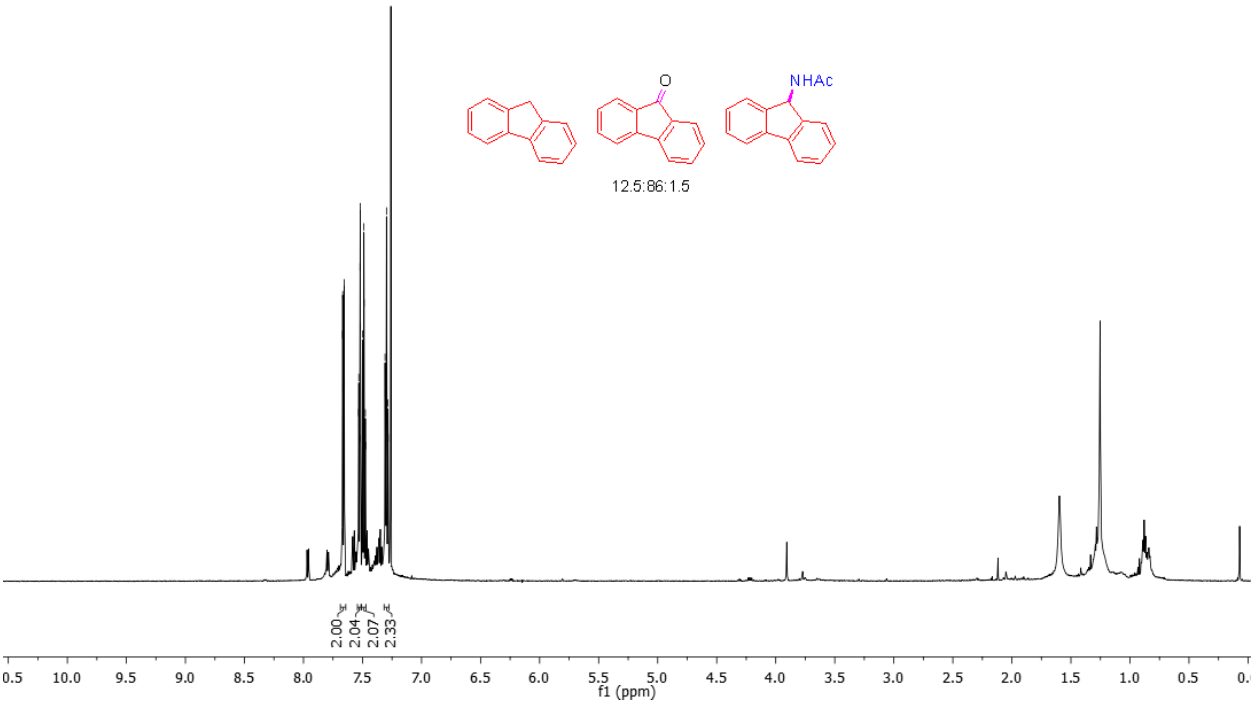
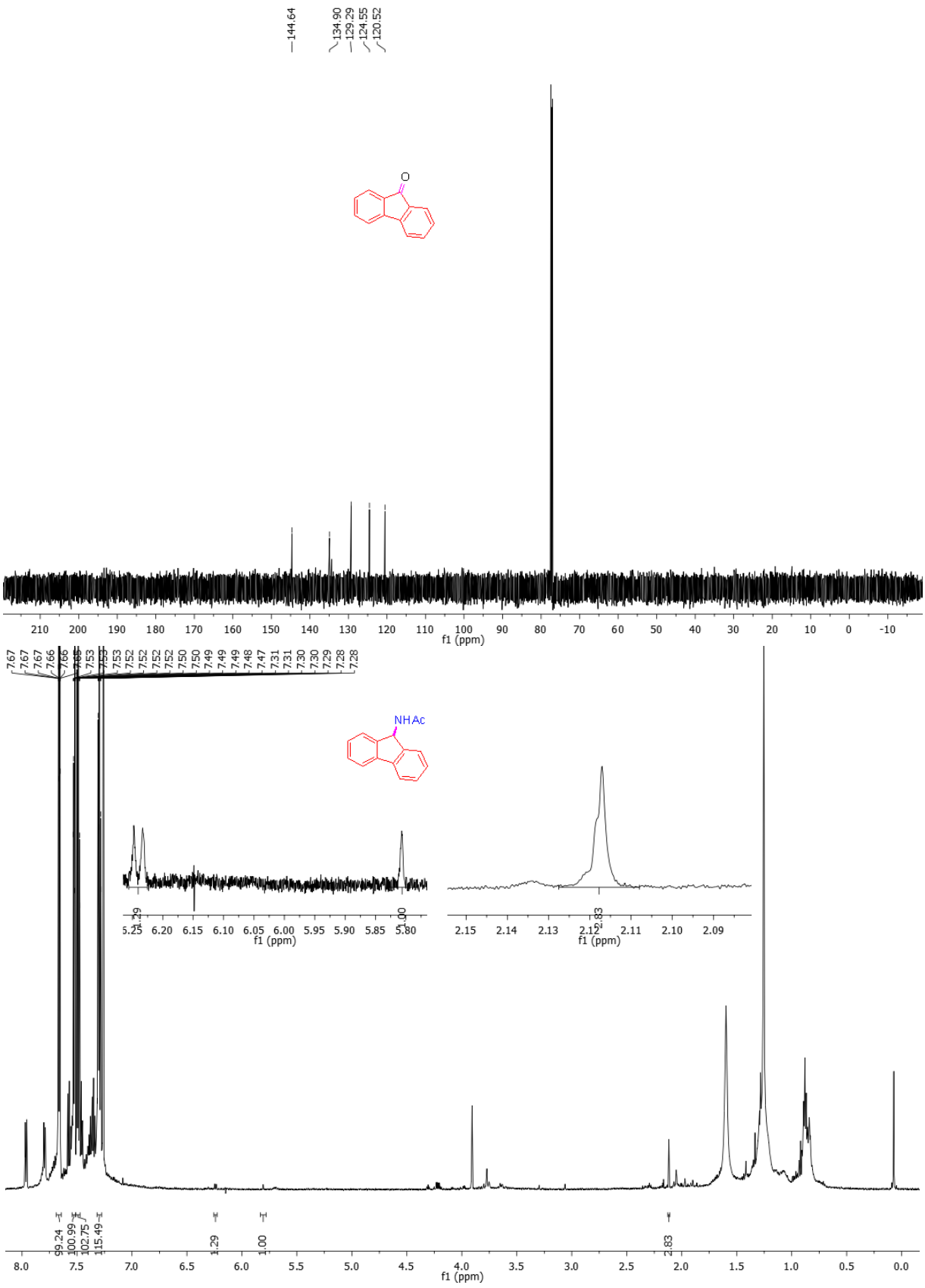
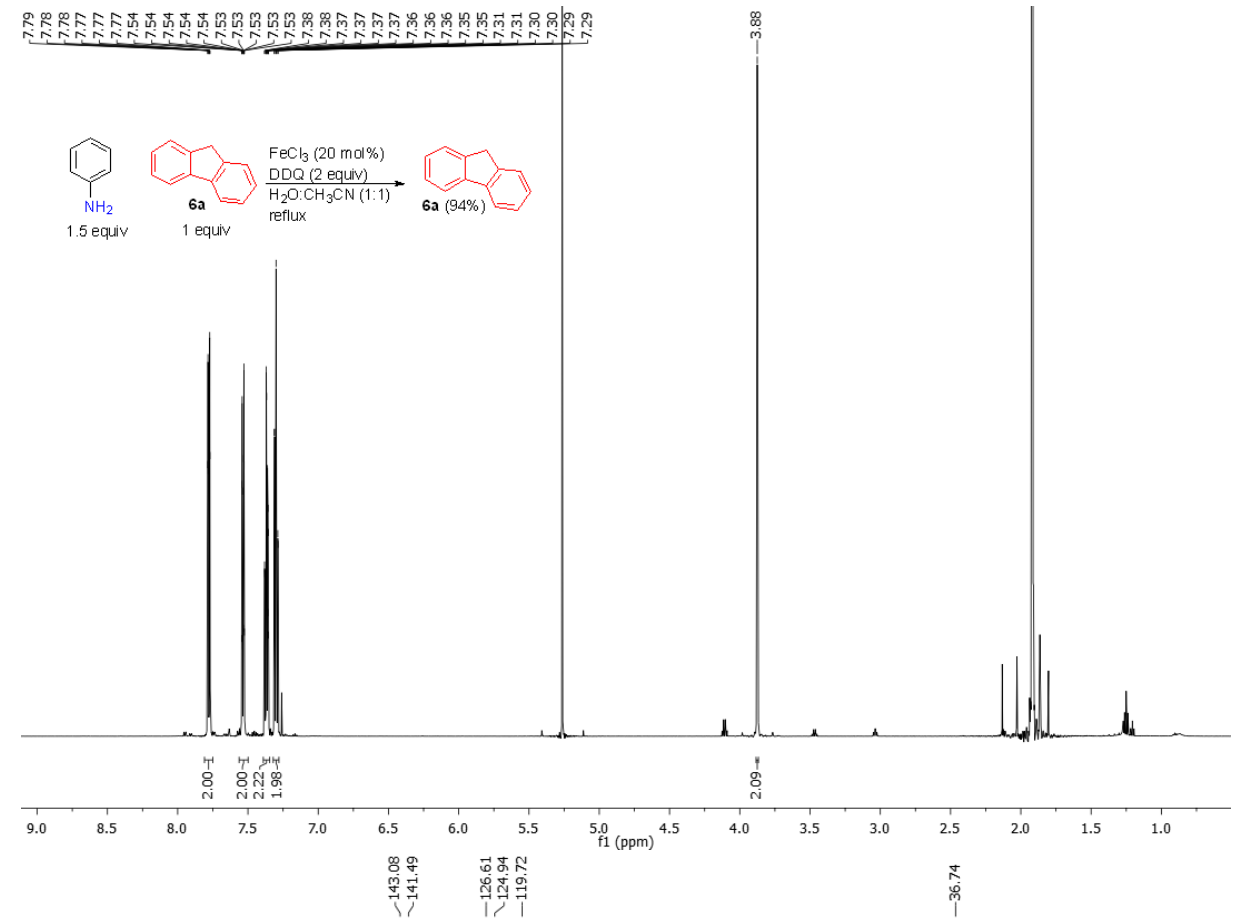
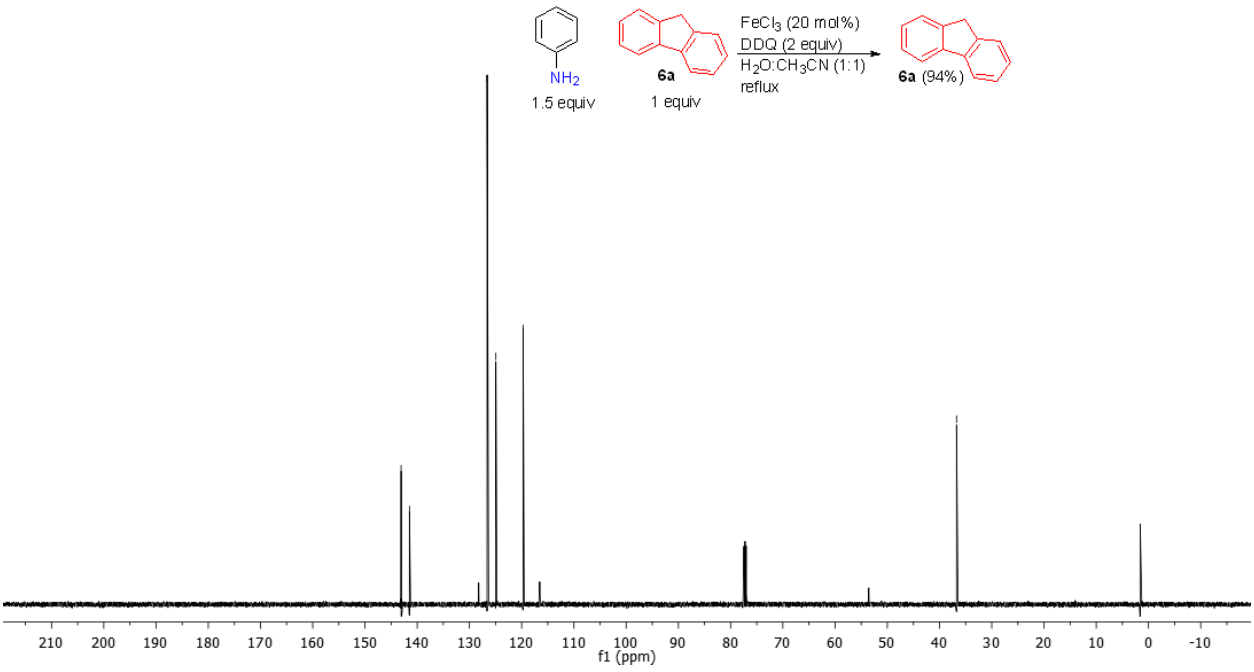
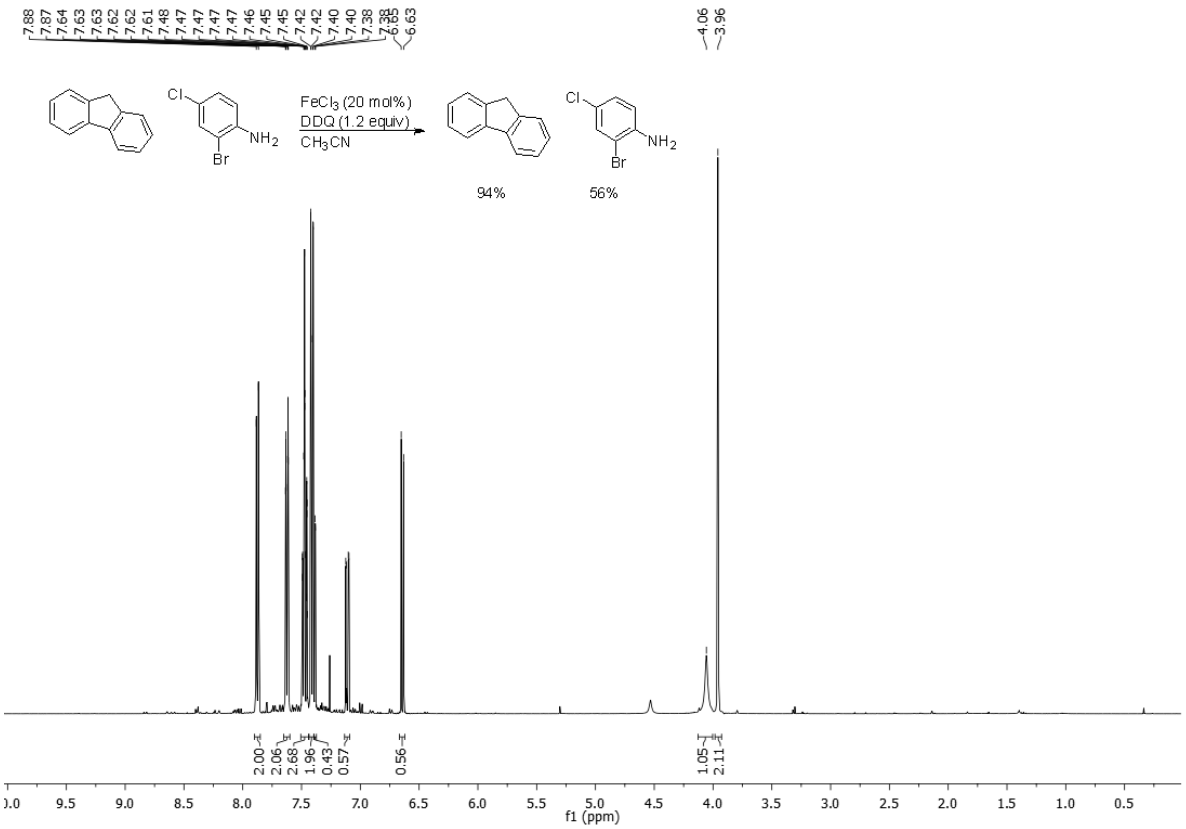
7.31
7.30
7.30
7.29
7.28
7.28

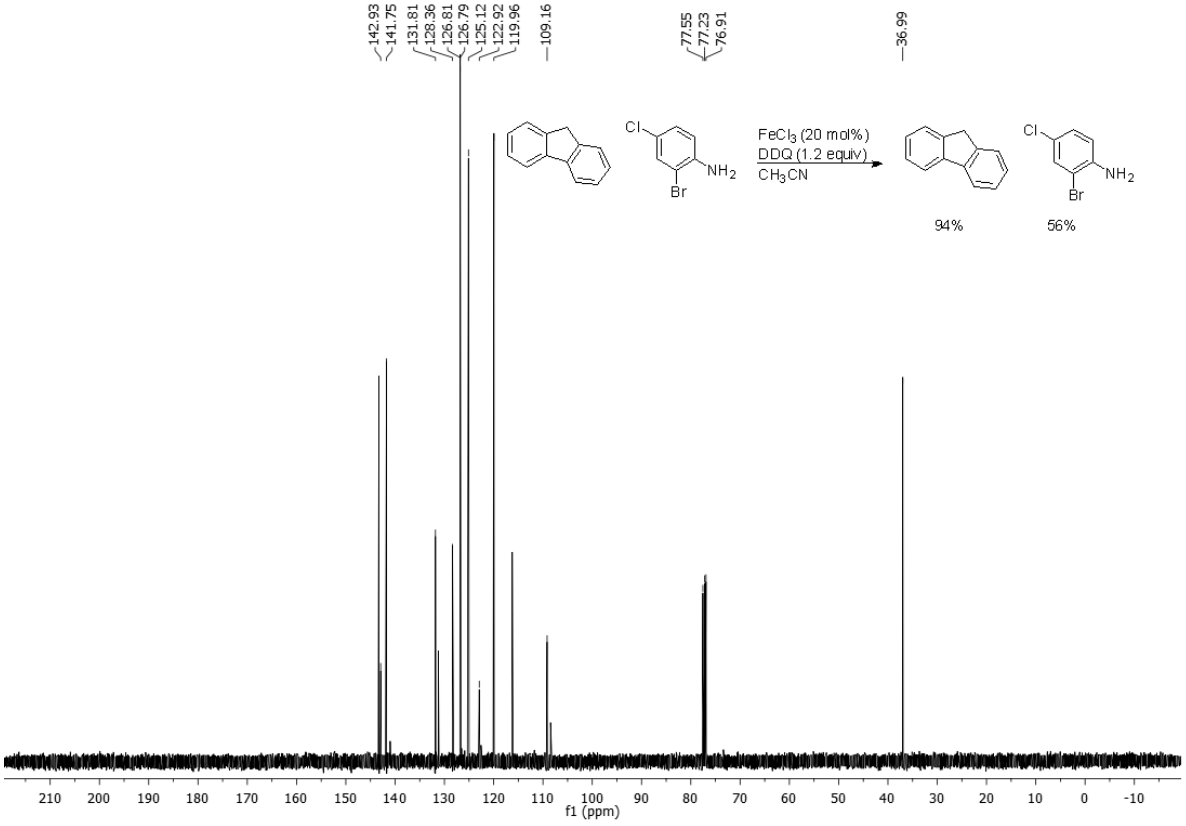

O
NHAc
12.5:86:1.5
2.00
2.04
2.07
2.33
f1 (ppm)


144.64
134.90
129.29
124.55
120.52
O
f1 (ppm)
NHAc
f1 (ppm)
f1 (ppm)
f1 (ppm)


7.79
7.78
7.78
7.77
7.77
7.77
7.54
7.54
7.54
7.54
7.53
7.53
7.53
7.53
7.53
7.38
7.38
7.37
7.37
7.37
7.37
7.37
7.36
7.36
7.36
7.35
7.35
7.31
7.30
7.30
7.29
7.29
7.29
3.88
NH2
1.5 equiv
6a
1 equiv
FeCl3 (20 mol%)
DDQ (2 equiv)
H2O:CH3CN (1:1)
reflux
6a (94%)
2.00
2.00
2.22
1.98
2.09
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
f1 (ppm)
143.08
141.49
126.61
124.94
119.72
36.74


NH2
1.5 equiv
6a
1 equiv
FeCl3 (20 mol%)
DDQ (2 equiv)
H2O:CH3CN (1:1)
reflux
6a (94%)
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)


7.88
7.87
7.64
7.63
7.63
7.62
7.62
7.61
7.48
7.47
7.47
7.47
7.47
7.46
7.45
7.45
7.42
7.42
7.40
7.40
7.38
7.38
6.65
6.63
4.06
3.96
FeCl3 (20 mol%)
DDQ (1.2 equiv)
CH3CN
Cl
NH2
Br
94%
56%
2.00
2.06
2.68
1.96
0.43
0.57
0.56
1.05
2.11
f1 (ppm)


142.93
141.75
131.81
128.36
126.81
126.79
125.12
122.92
119.96
109.16
77.55
77.23
76.91
36.99
FeCl3 (20 mol%)
DDQ (1.2 equiv)
CH3CN
Cl
NH2
Br
94%
56%
f1 (ppm)

## 13. References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