

Supplementary Information

Hydroalkoxylation of 2-vinylaniline enabled by light-induced proton transfer

Xinyuan He, Mengyao Yuan and Zhigang Chai*

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General information

All the chemicals were commercially available and used without further purification.

High-performance liquid chromatography (HPLC) analysis was conducted on Agilent 1200 with a variable wavelength detector (VWD) and a refractive index detector (RID). A ZORBAX SB-Aq column and acetonitrile/water eluent were used for the analysis, and the wavelength value set for the VWD was 210 nm. Conversion of reactants and yields of the products was determined by external standard method.

Power of the LED irradiation was measured by a power meter (PM125D with a S425C detector, THORLABS).

Flash column chromatography was performed using silica gel (200 mesh). ^1H and ^{13}C NMR spectra were recorded on AscendTM400 spectrometer (400 MHz, 101 MHz). Internal solvent signals (CDCl_3 : ^1H 7.26 ppm, ^{13}C 77.16 ppm; CD_3OD : ^1H 3.31 ppm, ^{13}C 49.00 ppm) or tetramethylsilane (TMS, ^1H 0 ppm) were chosen as reference. ^1H NMR data are reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), and numbers of protons. ^{13}C NMR data are reported in terms of chemical shift (ppm). When ^{13}C coupling to heteronuclei (e.g. ^{19}F) is observed, ^{13}C NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constant (Hz).

Experimental procedures

Optimization of reaction conditions: Typically, an oven-dried Schlenk tube (10 mL) equipped with a magnetic stir bar was charged with 2-vinylaniline (0.2 mmol), trifluoroacetic acid (0.2 mmol, 1 equiv.), acetonitrile (MeCN, 2 mL) and ethanol (2 mL). The Schlenk tube was sealed with a rubber septum, and the solution was degassed via three freeze-pump-thaw cycles. The Schlenk tube was then back-filled with N_2 and sealed at atmospheric pressure (1 atm). The reaction mixture was stirred and irradiated with a 365 nm LED (5 W) for 2 h at 25 °C. Conversion and yield were determined by HPLC.

Investigation of scope of substrates:

General procedure A:

Typically, an oven-dried Schlenk tube (10 mL) equipped with a magnetic stir bar was charged with 2-vinylaniline (0.6 mmol), trifluoroacetic acid (0.6 mmol, 1 equiv.), acetonitrile (MeCN, 2 mL) and alcohol (2 mL). The Schlenk tube was sealed with a rubber septum, and the reaction mixture was degassed via three freeze-pump-thaw cycles. The Schlenk tube was then back-filled with N_2 and sealed at atmospheric pressure (1 atm). The reaction mixture was stirred and irradiated with a 365 nm LED (5 W) for 2 h at 25 °C.

General procedure B:

Typically, an oven-dried Schlenk tube (10 mL) equipped with a magnetic stir bar was charged with 2-vinylaniline (0.6 mmol, 0.15 M), trifluoroacetic acid (0.6 mmol, 1 equiv.), alcohol (6 mmol, 10 equiv.), and dichloromethane. The Schlenk tube was sealed with a rubber septum, and the reaction mixture was degassed via three freeze-pump-thaw cycles. The Schlenk tube was then back-filled with N_2 and sealed at atmospheric pressure (1 atm). The reaction mixture was stirred and irradiated with a 365 nm LED (5 W) for 2.5 h at 25 °C.

Work-up: after reaction, triethylamine (0.9 mmol) was added to the reaction mixture, and the new mixture was concentrated *in vacuo*. The residue was purified by column chromatography on silica gel using a mixture of EtOAc, *n*-hexane and triethylamine (0.1 % vol) as an eluent. The silica gel was immersed in a *n*-hexane/triethylamine mixture (98:2, v/v) for 0.5 h prior to use.

The gram-scale experiment:

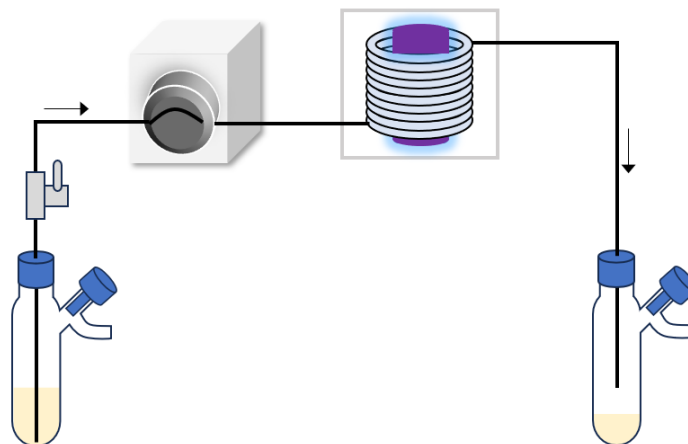


Figure S1. A schematic illustration of the continuous flow setup

The gram-scale experiment was conducted in continuous flow. The continuous flow system (Figure S1) consists of a peristaltic pump, a temperature-controlled coil-shaped photoreactor (FEP tubing, O.D. 3 mm, I.D. 2 mm, internal volume: 28.5 mL), a shutoff valve, and two Schlenk tubes (connected to Schlenk line). The system was degassed and backfilled with N_2 prior to the irradiation.

An oven-dried Schlenk tube (50 mL) equipped with a magnetic stir bar was charged with 2-vinylaniline (9 mmol, 0.3 M), trifluoroacetic acid (9 mmol, 1 equiv.), ethanol/MeCN (1:1, v/v, 30 mL). The reaction mixture was stirred for 5 min and then degassed via three freeze-pump-thaw cycles. After the Schlenk tube was back-filled with N_2 (1 atm), the reaction mixture was pumped into the temperature-controlled coil-shaped photoreactor and irradiated by 365 nm LEDs (80 W in total) at 25 °C. The residence time is 1.25 h.

Work-up: after reaction (total reaction time: 2.8 h), triethylamine (13.5 mmol) was added to the reaction mixture, and the new mixture was concentrated *in vacuo*. The product was isolated as a light-yellow oil (1.100 g, 74% yield) by silica gel column chromatography described above.

Mechanistic investigations

Intermittent irradiation experiment

An oven-dried Schlenk tube (10 mL) equipped with a magnetic stir bar was charged with 2-vinylaniline (0.2 mmol), trifluoroacetic acid (0.2 mmol, 1 equiv.), MeCN (2 mL) and ethanol (2 mL). The Schlenk tube was sealed with a rubber septum, and the solution was degassed via three freeze-pump-thaw cycles. The Schlenk tube was then back-filled with N_2 and sealed at atmospheric pressure (1 atm). The reaction mixture was stirred and irradiated with a 365 nm LED (5 W) at 25 °C. The reaction mixture was sampled every 5 min and analyzed by HPLC.

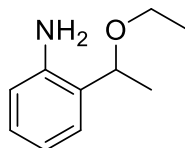
Supplementary Tables

Table S1. The influence of wavelength of irradiation on the reaction^a

Entry	Wavelength nm	Power of the irradiation W	Photon flux ^b	Reaction time h	Conv. of 1 %	Yield of 2 %
1 ^c	311	0.07	1.1×10^{17}	15	98	86
2	365	1.7	3.1×10^{18}	1	100	94
3	405	1.6	3.2×10^{18}	1	5	0
4	455	1.4	3.2×10^{18}	1	3	0

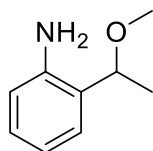
^a 2-vinylaniline (0.2 mmol, 50 mM), TFA (0.2 mmol, 1 equiv.), EtOH (2 mL), CH₃CN (2 mL), N₂ atmosphere, 25 °C, LED irradiation. ^b Number of incident photons per second. ^c A gas-tight quartz tube (O.D. 22 mm) was used to ensure high transmittance of the incident light.

Characterization of products



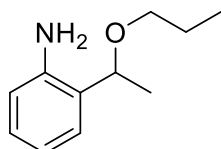
2-(1-ethoxyethyl)aniline

According to the general procedure A, 2-vinylaniline (0.6 mmol), trifluoroacetic acid (0.6 mmol, 1 equiv.), MeCN (2 mL) and ethanol (2 mL) were used (reaction time: 2 h). The product was isolated by silica gel column chromatography as a light-yellow oil (84 mg, 85% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.11 – 6.91 (m, 2H), 6.72 – 6.52 (m, 2H), 4.47 (q, $J = 6.7$ Hz, 1H), 3.49 – 3.29 (m, 2H), 1.53 (d, $J = 6.7$ Hz, 3H), 1.20 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 145.04, 128.57, 128.41, 126.26, 117.86, 116.43, 79.01, 63.86, 20.25, 15.61.



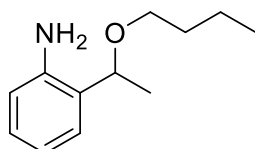
2-(1-methoxyethyl)aniline

According to the general procedure A, 2-vinylaniline (0.6 mmol), trifluoroacetic acid (0.6 mmol, 1 equiv.), MeCN (2 mL) and methanol (2 mL) were used (reaction time: 2 h). The product was isolated by silica gel column chromatography as a light-yellow oil (86 mg, 95% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.14 – 6.90 (m, 2H), 6.77 – 6.52 (m, 2H), 4.39 (q, $J = 6.7$ Hz, 1H), 3.27 (s, 3H), 1.53 (d, $J = 6.7$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 145.02, 128.73, 128.55, 125.58, 117.92, 116.45, 80.78, 56.19, 19.96.



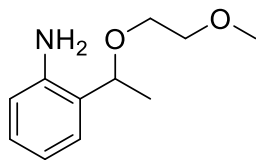
2-(1-propoxyethyl)aniline

According to the general procedure A, 2-vinylaniline (0.6 mmol), trifluoroacetic acid (0.6 mmol, 1 equiv.), MeCN (2 mL) and propan-1-ol (2 mL) were used (reaction time: 3 h). The product was isolated by silica gel column chromatography as a light-yellow oil (95 mg, 88% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.11 – 6.93 (m, 2H), 6.72 – 6.58 (m, 2H), 4.46 (q, $J = 6.7$ Hz, 1H), 3.36 – 3.24 (m, 2H), 1.60 (h, $J = 7.2$ Hz, 2H), 1.53 (d, $J = 6.7$ Hz, 3H), 0.90 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 144.87, 128.58, 128.42, 126.48, 118.00, 116.55, 79.22, 70.37, 23.32, 20.19, 10.85.



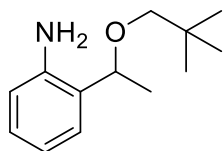
2-(1-butoxyethyl)aniline

According to the general procedure A, 2-vinylaniline (0.6 mmol), trifluoroacetic acid (0.6 mmol, 1 equiv.), MeCN (2 mL) and butan-1-ol (2 mL) were used (reaction time: 2 h). The product was isolated by silica gel column chromatography as a light-yellow oil (93 mg, 80% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.11 – 6.93 (m, 2H), 6.73 – 6.57 (m, 2H), 4.45 (q, $J = 6.7$ Hz, 1H), 3.40 – 3.26 (m, 2H), 1.62 – 1.49 (m, 5H), 1.41 – 1.29 (m, 2H), 0.89 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 145.16, 128.56, 128.38, 126.30, 117.77, 116.36, 79.22, 68.45, 32.26, 20.14, 19.61, 14.08.



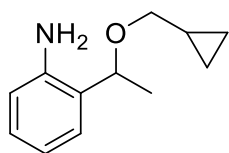
2-(1-(2-methoxyethoxy)ethyl)aniline

According to the general procedure A, 2-vinyylaniline (0.6 mmol), trifluoroacetic acid (0.6 mmol, 1 equiv.), MeCN (2 mL) and 2-methoxyethan-1-ol (2 mL) were used (reaction time: 2 h). The product was isolated by silica gel column chromatography as a light-yellow oil (111 mg, 95% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.10 – 6.98 (m, 2H), 6.72 – 6.63 (m, 2H), 4.54 (q, J = 6.7 Hz, 1H), 3.56 – 3.49 (m, 4H), 3.37 (s, 3H), 1.56 (d, J = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 145.25, 128.60, 128.50, 125.79, 117.86, 116.60, 79.26, 72.13, 67.49, 59.11, 19.88.



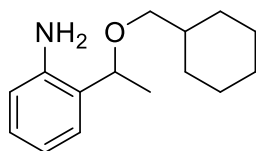
2-(1-(neopentyloxy)ethyl)aniline

According to the general procedure A, 2-vinyylaniline (0.6 mmol), trifluoroacetic acid (0.6 mmol, 1 equiv.), MeCN (2 mL) and 2,2-dimethylpropan-1-ol (2 mL) were used (reaction time: 2 h). The product was isolated by silica gel column chromatography as a light-yellow oil (82 mg, 66% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.10 – 7.03 (m, 1H), 6.99 – 6.93 (m, 1H), 6.71 – 6.60 (m, 2H), 4.40 (q, J = 6.7 Hz, 1H), 3.04 (d, J = 8.7 Hz, 1H), 2.94 (d, J = 8.7 Hz, 1H), 1.52 (d, J = 6.7 Hz, 3H), 0.91 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 144.78, 128.55, 128.36, 126.75, 117.99, 116.55, 80.03, 79.39, 31.98, 26.94, 20.04.



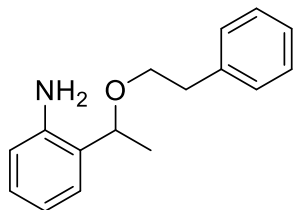
2-(1-(cyclopropylmethoxy)ethyl)aniline

According to the general procedure A, 2-vinyylaniline (0.6 mmol), trifluoroacetic acid (0.6 mmol, 1 equiv.), MeCN (2 mL) and cyclopropylmethanol (2 mL) were used (reaction time: 2 h). The product was isolated by silica gel column chromatography as a light-yellow oil (94 mg, 82% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.09 – 6.94 (m, 2H), 6.70 – 6.60 (m, 2H), 4.51 (q, J = 6.7 Hz, 1H), 3.26 (dd, J = 10.1, 6.5 Hz, 1H), 3.09 (dd, J = 10.1, 7.4 Hz, 1H), 1.55 (d, J = 6.7 Hz, 3H), 1.13 – 0.99 (m, 1H), 0.54 – 0.47 (m, 2H), 0.18 – 0.10 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 145.04, 128.63, 128.45, 126.03, 117.84, 116.43, 78.93, 73.31, 20.24, 10.94, 3.17, 3.11.



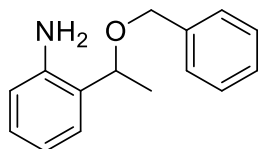
2-(1-(cyclohexylmethoxy)ethyl)aniline

According to the general procedure B, 2-vinyylaniline (0.6 mmol), trifluoroacetic acid (0.6 mmol, 1 equiv.), cyclohexylmethanol (6 mmol, 10 equiv.) were used (reaction time: 2.5 h). The product was isolated by silica gel column chromatography as a light-yellow oil (82 mg, 59% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.10 – 6.94 (m, 2H), 6.72 – 6.59 (m, 2H), 4.42 (q, J = 6.7 Hz, 1H), 3.18 – 3.08 (m, 2H), 1.80 – 1.55 (m, 6H), 1.52 (d, J = 6.7 Hz, 3H), 1.30 – 1.06 (m, 3H), 0.98 – 0.82 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 145.00, 128.57, 128.38, 126.45, 117.87, 116.44, 79.47, 74.61, 38.37, 30.40, 30.25, 26.73, 26.04, 25.99, 20.09.



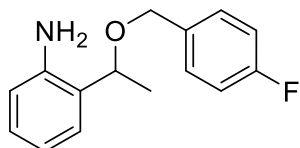
2-(1-phenethoxyethyl)aniline

According to the general procedure B, 2-vinylaniline (0.6 mmol), trifluoroacetic acid (0.6 mmol, 1 equiv.), 2-phenylethan-1-ol (6 mmol, 10 equiv.) were used (reaction time: 2.5 h). The product was isolated by silica gel column chromatography as a light-yellow oil (107 mg, 74% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.29 – 7.15 (m, 5H), 7.07 – 6.91 (m, 2H), 6.68 – 6.52 (m, 2H), 4.46 (q, $J = 6.7$ Hz, 1H), 3.56 (t, $J = 6.5$ Hz, 2H), 2.88 (t, $J = 7.2$ Hz, 2H), 1.51 (d, $J = 6.7$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 145.22, 139.36, 129.15, 128.59, 128.48, 128.42, 126.32, 125.90, 117.77, 116.46, 79.36, 69.35, 36.71, 19.91.



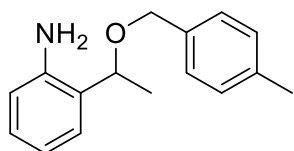
2-(1-(benzyloxy)ethyl)aniline

According to the general procedure B, 2-vinylaniline (0.6 mmol), trifluoroacetic acid (0.6 mmol, 1 equiv.), phenylmethanol (6 mmol, 10 equiv.) were used (reaction time: 2.5 h). The product was isolated by silica gel column chromatography as a light-yellow oil (114 mg, 84% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.38 – 7.25 (m, 5H), 7.14 – 6.95 (m, 2H), 6.75 – 6.60 (m, 2H), 4.58 (q, $J = 6.7$ Hz, 1H), 4.49 (d, $J = 11.6$ Hz, 1H), 4.33 (d, $J = 11.6$ Hz, 2H), 1.58 (d, $J = 6.7$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 145.23, 138.47, 128.89, 128.64, 128.53, 128.02, 127.74, 125.56, 117.88, 116.48, 78.63, 70.34, 20.19.



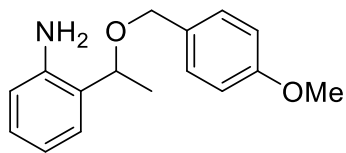
2-(1-(4-fluorobenzyl)oxy)ethyl)aniline

According to the general procedure B, 2-vinylaniline (0.6 mmol), trifluoroacetic acid (0.6 mmol, 1 equiv.), (4-fluorophenyl)methanol (6 mmol, 10 equiv.) were used (reaction time: 2.5 h). The product was isolated by silica gel column chromatography as a light-yellow oil (78 mg, 53% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.31 – 7.24 (m, 2H), 7.16 – 7.07 (m, 1H), 7.05 – 6.94 (m, 3H), 6.74 – 6.62 (m, 2H), 4.56 (q, $J = 6.7$ Hz, 1H), 4.43 (d, $J = 11.5$ Hz, 1H), 4.29 (d, $J = 11.5$ Hz, 1H), 1.57 (d, $J = 6.7$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 162.45 (d, $J = 245.5$ Hz), 145.15, 134.21, 129.79 (d, $J = 8.2$ Hz), 128.86, 128.71, 125.38, 117.92, 116.49, 115.37 (d, $J = 21.5$ Hz), 78.61, 69.64, 20.19.



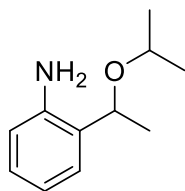
2-(1-(4-methylbenzyl)oxy)ethyl)aniline

According to the general procedure B, 2-vinylaniline (0.6 mmol), trifluoroacetic acid (0.6 mmol, 1 equiv.), *p*-tolylmethanol (6 mmol, 10 equiv.) were used (reaction time: 2.5 h). The product was isolated by silica gel column chromatography as a light-yellow oil (117 mg, 81% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.23 – 7.06 (m, 5H), 7.02 – 6.94 (m, 1H), 6.75 – 6.59 (m, 2H), 4.56 (q, $J = 6.7$ Hz, 1H), 4.44 (d, $J = 11.4$ Hz, 1H), 4.28 (d, $J = 11.4$ Hz, 1H), 2.34 (s, 3H), 1.56 (d, $J = 6.7$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 145.26, 137.46, 135.40, 129.21, 128.89, 128.59, 128.17, 125.64, 117.84, 116.45, 78.43, 70.19, 21.30, 20.19.



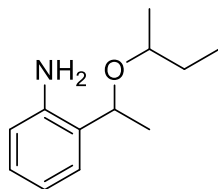
2-(1-((4-methoxybenzyl)oxy)ethyl)aniline

According to the general procedure B, 2-vinylaniline (0.6 mmol), trifluoroacetic acid (0.6 mmol, 1 equiv.), (4-methoxyphenyl)methanol (6 mmol, 10 equiv.) were used (reaction time: 2.5 h). The product was isolated by silica gel column chromatography as a light-yellow oil (133 mg, 86% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.25 – 7.21 (m, 2H), 7.13 – 7.06 (m, 1H), 7.02 – 6.95 (m, 1H), 6.89 – 6.85 (m, 2H), 6.74 – 6.63 (m, 2H), 4.56 (q, $J = 6.7$ Hz, 1H), 4.41 (d, $J = 11.2$ Hz, 1H), 4.26 (d, $J = 11.2$ Hz, 1H), 3.80 (s, 3H), 1.55 (d, $J = 6.7$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 159.32, 145.12, 130.52, 129.71, 128.89, 128.60, 125.72, 117.93, 116.52, 113.93, 78.28, 69.99, 55.41, 20.22.



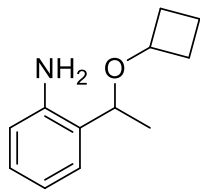
2-(1-isopropoxyethyl)aniline

According to the general procedure A, 2-vinylaniline (0.6 mmol), trifluoroacetic acid (0.6 mmol, 1 equiv.), MeCN (2 mL) and propan-2-ol (2 mL) were used (reaction time: 2 h). The product was isolated by silica gel column chromatography as a light-yellow oil (85 mg, 79% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.10 – 7.02 (m, 1H), 7.00 – 6.93 (m, 1H), 6.71 – 6.57 (m, 2H), 4.59 (q, $J = 6.7$ Hz, 1H), 3.58 (hept, $J = 6.1$ Hz, 1H), 1.51 (d, $J = 6.7$ Hz, 3H), 1.14 (t, $J = 5.6$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 145.28, 128.66, 128.35, 126.65, 117.77, 116.49, 76.14, 68.53, 23.47, 21.24, 20.65.



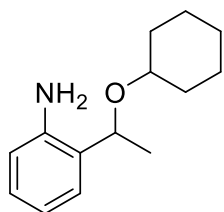
2-(1-(sec-butoxy)ethyl)aniline

According to the general procedure A, 2-vinylaniline (0.6 mmol), trifluoroacetic acid (0.6 mmol, 1 equiv.), MeCN (2 mL) and butan-2-ol (2 mL) were used (reaction time: 2 h). The product was isolated by silica gel column chromatography as a light-yellow oil (67 mg, 58% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.11 – 6.93 (m, 2H), 6.72 – 6.60 (m, 2H), 4.63 – 4.52 (m, 1H), 3.47 – 3.38 (m, 1H), 3.38 – 3.28 (m, 0H), 1.62 – 1.38 (m, 5H), 1.21 – 1.04 (m, 3H), 0.97 – 0.76 (m, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 145.23, 128.76, 128.55, 128.35, 128.31, 127.20, 126.65, 117.83, 116.59, 116.50, 75.91, 74.18, 73.59, 30.30, 28.25, 20.62, 20.45, 20.15, 18.50, 10.13, 9.39.



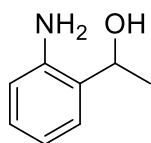
2-(1-cyclobutoxyethyl)aniline

According to the general procedure A, 2-vinylaniline (0.6 mmol), trifluoroacetic acid (0.6 mmol, 1 equiv.), MeCN (2 mL) and cyclobutanol (2 mL) were used (reaction time: 2 h). The product was isolated by silica gel column chromatography as a light-yellow oil (88 mg, 77% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.11 – 7.02 (m, 1H), 6.99 – 6.93 (m, 1H), 6.73 – 6.58 (m, 2H), 4.47 (q, $J = 6.7$ Hz, 1H), 3.95 – 3.83 (m, 1H), 2.22 – 1.82 (m, 4H), 1.72 – 1.55 (m, 1H), 1.51 (d, $J = 6.7$ Hz, 3H), 1.46 – 1.31 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 145.03, 128.43, 126.63, 118.00, 116.57, 76.57, 71.19, 30.99, 30.95, 20.30, 12.82.



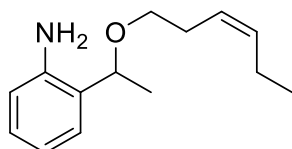
2-(1-(cyclohexyloxy)ethyl)aniline

According to the general procedure B, 2-vinylaniline (0.6 mmol), trifluoroacetic acid (0.6 mmol, 1 equiv.), cyclohexanol (6 mmol, 10 equiv.) were used (reaction time: 2.5 h). The product was isolated by silica gel column chromatography as a light-yellow oil (64 mg, 49% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.12 – 6.92 (m, 2H), 6.70 – 6.57 (m, 2H), 4.63 (q, $J = 6.7$ Hz, 1H), 3.32 – 3.21 (m, 1H), 2.01 – 1.90 (m, 1H), 1.84 – 1.62 (m, 3H), 1.54 – 1.46 (m, 4H), 1.38 – 1.13 (m, 5H). ^{13}C NMR (101 MHz, CDCl_3) δ 145.37, 128.55, 128.26, 126.94, 117.72, 116.47, 75.77, 74.63, 33.55, 31.55, 25.92, 24.36, 24.12, 20.76.



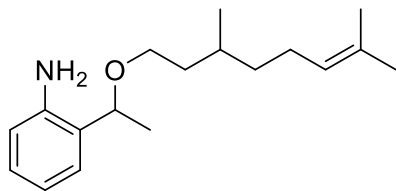
1-(2-aminophenyl)ethan-1-ol

According to the general procedure A, 2-vinylaniline (0.6 mmol), trifluoroacetic acid (0.6 mmol, 1 equiv.), MeCN (2 mL) and H_2O (2 mL) were used (reaction time: 2 h). The product was isolated by silica gel column chromatography as a light-yellow solid (77 mg, 94% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.12 – 6.99 (m, 2H), 6.75 – 6.59 (m, 2H), 4.86 (q, $J = 6.6$ Hz, 1H), 1.55 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 145.07, 128.62, 128.56, 126.64, 118.29, 116.80, 69.59, 21.62.



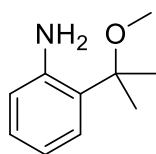
(Z)-2-(1-(hex-3-en-1-yloxy)ethyl)aniline

According to the general procedure A, 2-vinylaniline (0.6 mmol), trifluoroacetic acid (0.6 mmol, 1 equiv.), MeCN (2 mL) and (Z)-hex-3-en-1-ol (2 mL) were used (reaction time: 2 h). The product was isolated by silica gel column chromatography as a yellow oil (89 mg, 68% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.11 – 6.94 (m, 2H), 6.71 – 6.59 (m, 2H), 5.49 – 5.40 (m, 1H), 5.36 – 5.27 (m, 1H), 4.48 (q, $J = 6.7$ Hz, 1H), 3.40 – 3.30 (m, 2H), 2.37 – 2.28 (m, 2H), 2.08 – 1.99 (m, 2H), 1.53 (d, $J = 6.7$ Hz, 3H), 0.94 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 145.12, 133.87, 128.61, 128.46, 126.12, 125.18, 117.82, 116.44, 79.25, 68.18, 28.13, 20.75, 20.04, 14.38.



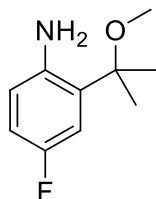
2-(1-((3,7-dimethyloct-6-en-1-yl)oxy)ethyl)aniline

According to the general procedure A, 2-vinylaniline (0.6 mmol), trifluoroacetic acid (0.6 mmol, 1 equiv.), MeCN (2 mL) and 3,7-dimethyloct-6-en-1-ol (2 mL) were used (reaction time: 2 h). The product was isolated by silica gel column chromatography as a yellow oil (86 mg, 52% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.10 – 7.03 (m, 1H), 7.00 – 6.94 (m, 1H), 6.73 – 6.58 (m, 2H), 5.12 – 5.03 (m, 1H), 4.45 (q, J = 6.7 Hz, 1H), 3.45 – 3.29 (m, 2H), 2.05 – 1.85 (m, 2H), 1.68 (d, J = 1.5 Hz, 3H), 1.66 – 1.60 (m, 1H), 1.59 (s, 3H), 1.52 (dd, J = 6.7, 0.9 Hz, 3H), 1.44 – 1.36 (m, 1H), 1.35 – 1.25 (m, 1H), 1.20 – 1.06 (m, 1H), 0.87 – 0.82 (m, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 145.08, 131.31, 128.58, 128.53, 128.39, 126.32, 124.90, 117.82, 116.39, 79.27, 66.98, 66.92, 37.40, 37.21, 37.14, 29.70, 25.86, 25.56, 20.17, 19.78, 19.62, 17.77.



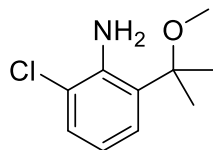
2-(2-methoxypropan-2-yl)aniline

According to the general procedure A, 2-(prop-1-en-2-yl)aniline (0.6 mmol), trifluoroacetic acid (0.6 mmol, 1 equiv.), MeCN (2 mL) and methanol (2 mL) were used (reaction time: 10 h). The product was isolated by silica gel column chromatography as a light-yellow oil (74 mg, 75% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.11 – 7.00 (m, 2H), 6.71 – 6.56 (m, 2H), 3.10 (s, 3H), 1.60 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 145.68, 128.46, 127.65, 127.03, 117.47, 116.57, 78.99, 50.45, 26.02.



4-fluoro-2-(2-methoxypropan-2-yl)aniline

According to the general procedure A, 4-fluoro-2-(prop-1-en-2-yl)aniline (0.6 mmol), trifluoroacetic acid (0.6 mmol, 1 equiv.), MeCN (2 mL) and methanol (2 mL) were used (reaction time: 2.5 h). The product was isolated by silica gel column chromatography as a light-yellow oil (85 mg, 77% yield). ^1H NMR (400 MHz, CDCl_3) δ 6.84 – 6.74 (m, 2H), 6.59 – 6.51 (m, 1H), 3.10 (s, 3H), 1.58 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 155.78 (d, J = 234.2 Hz), 128.57 (d, J = 5.2 Hz), 117.23 (d, J = 7.5 Hz), 114.69 (d, J = 22.0 Hz), 114.36 (d, J = 23.2 Hz), 78.63, 50.57, 25.83.

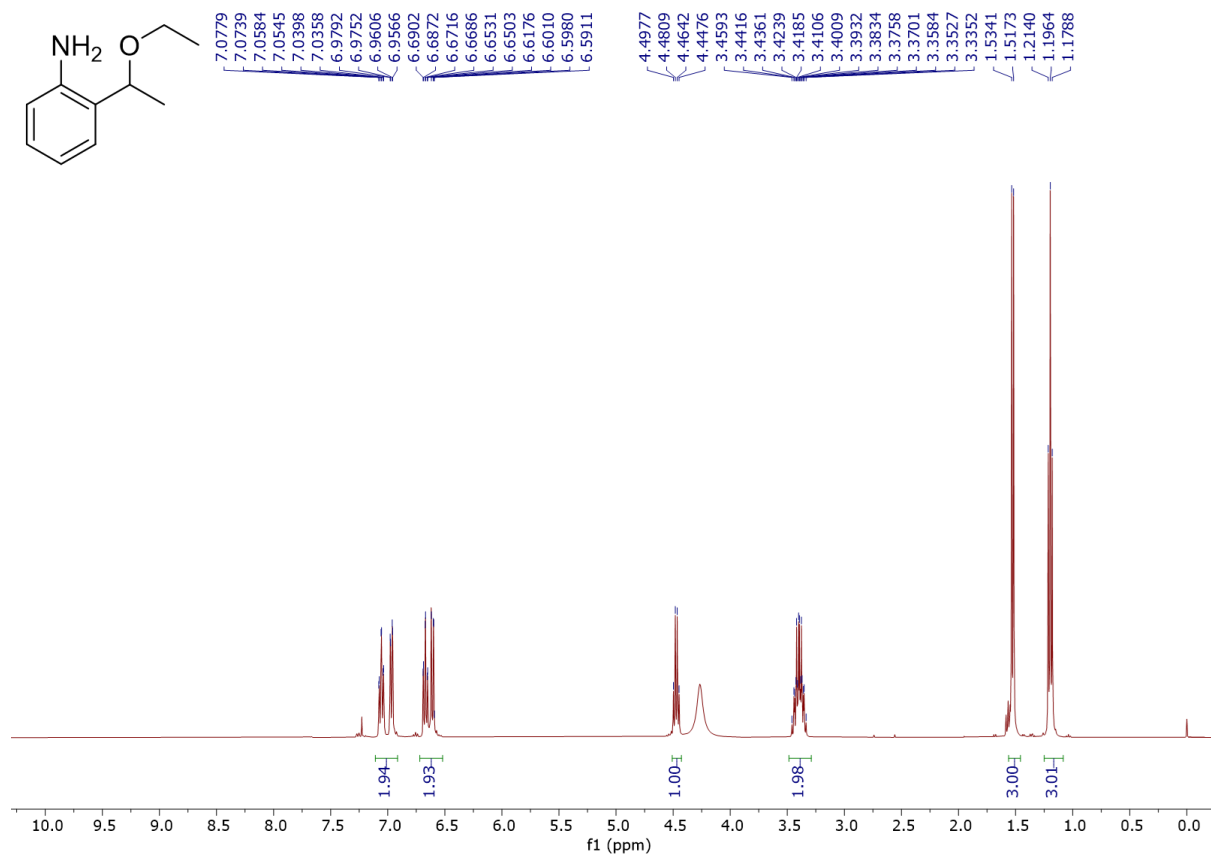


2-chloro-6-(2-methoxypropan-2-yl)aniline

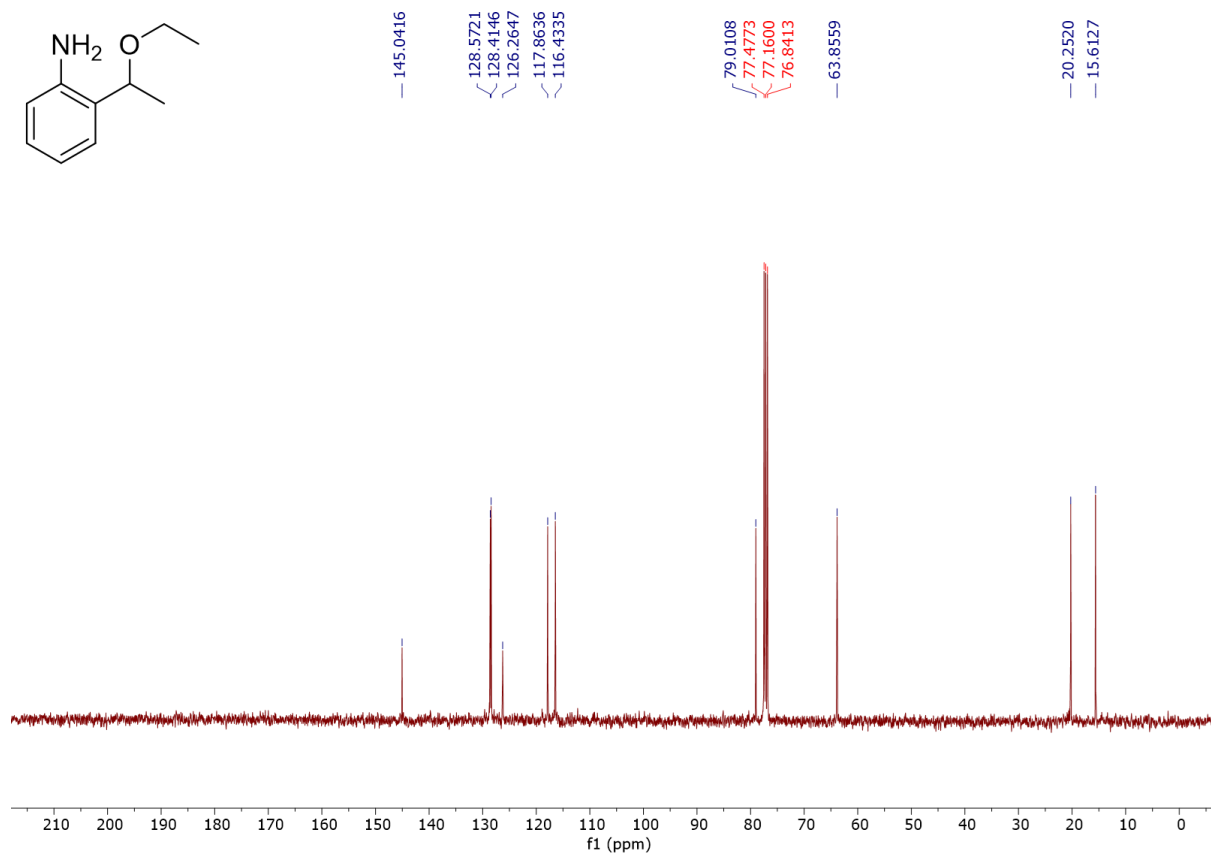
According to the general procedure A, 2-chloro-6-(prop-1-en-2-yl)aniline (0.6 mmol), trifluoroacetic acid (0.6 mmol, 1 equiv.), MeCN (2 mL) and methanol (2 mL) were used (reaction time: 13 h). The product was isolated by silica gel column chromatography as a light-yellow oil (78 mg, 65% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.20 (dd, J = 7.9, 1.5 Hz, 1H), 6.98 (dd, J = 7.8, 1.5 Hz, 1H), 6.59 (t, J = 7.9 Hz, 1H), 3.09 (s, 3H), 1.60 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 141.99, 128.61, 128.40, 126.16, 120.25, 117.01, 79.16, 50.62, 26.00.

NMR spectra

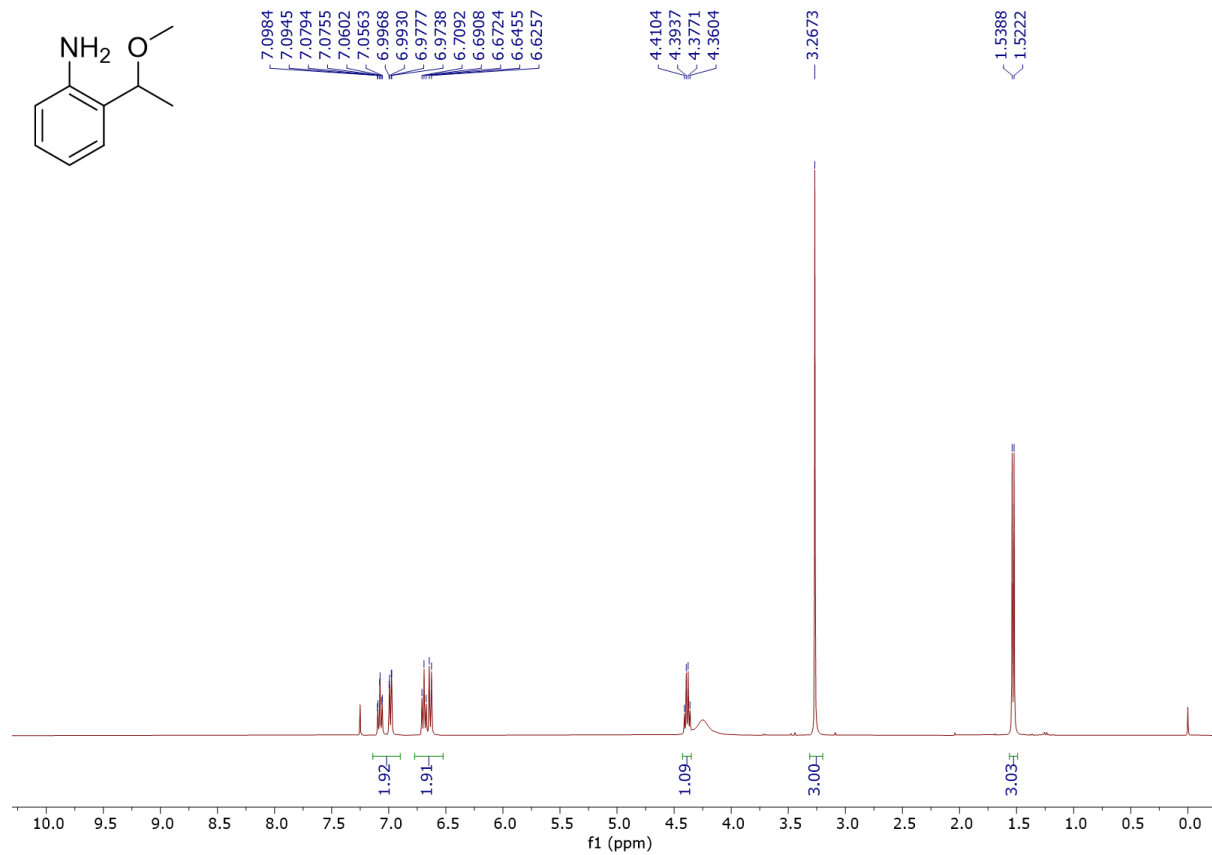
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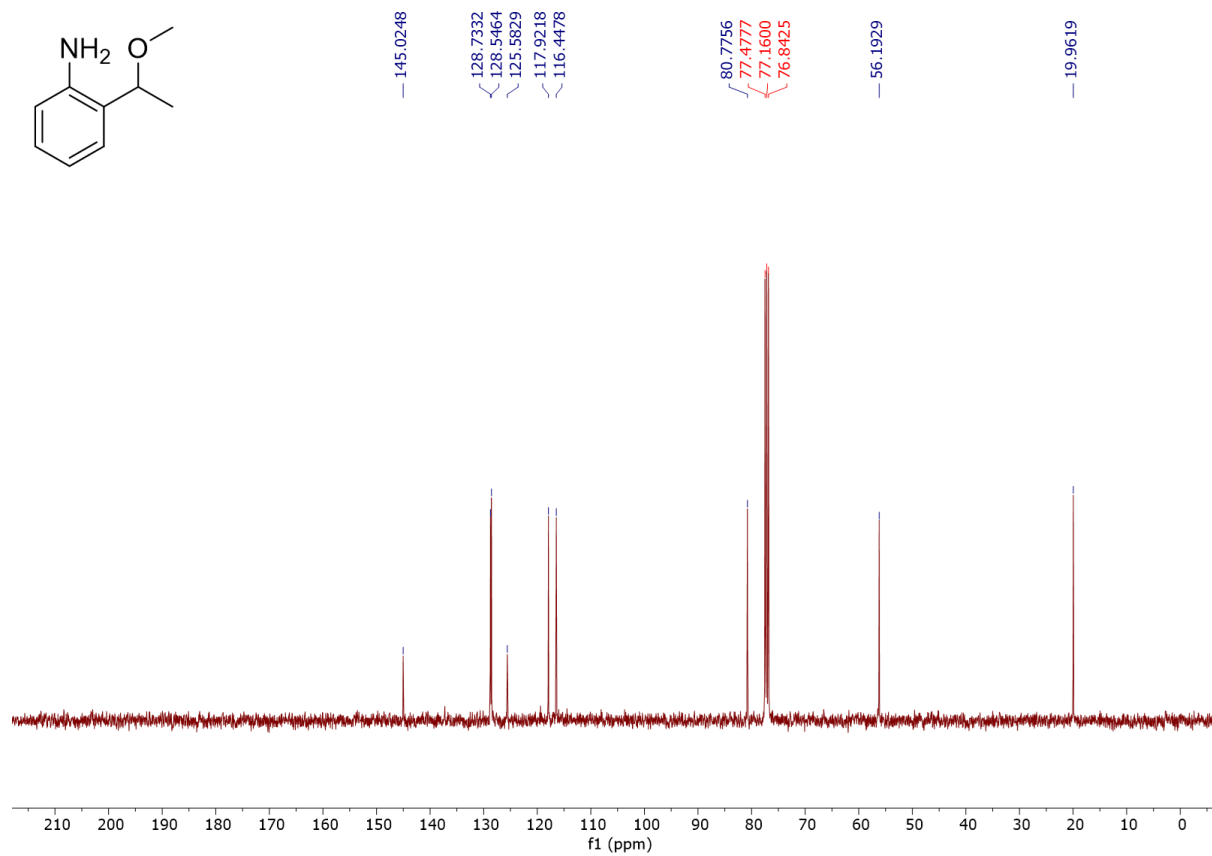
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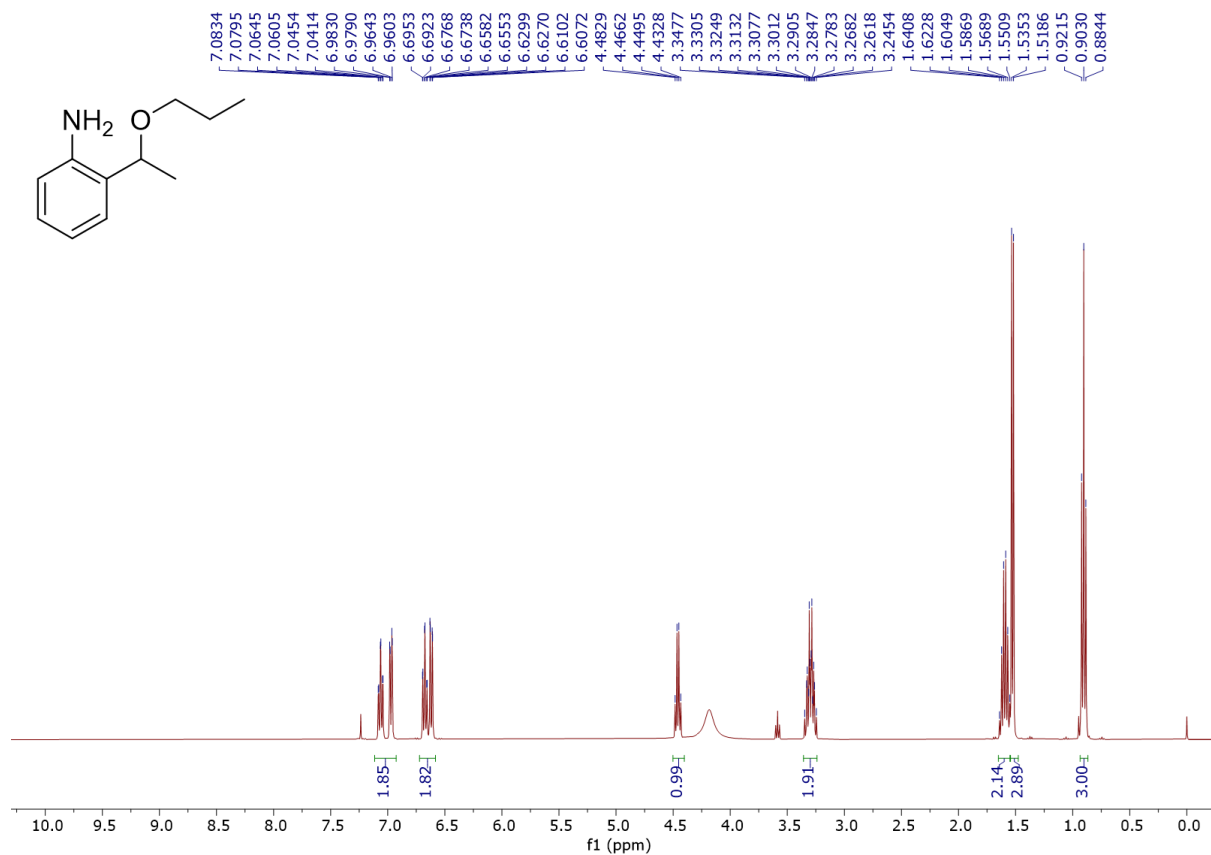
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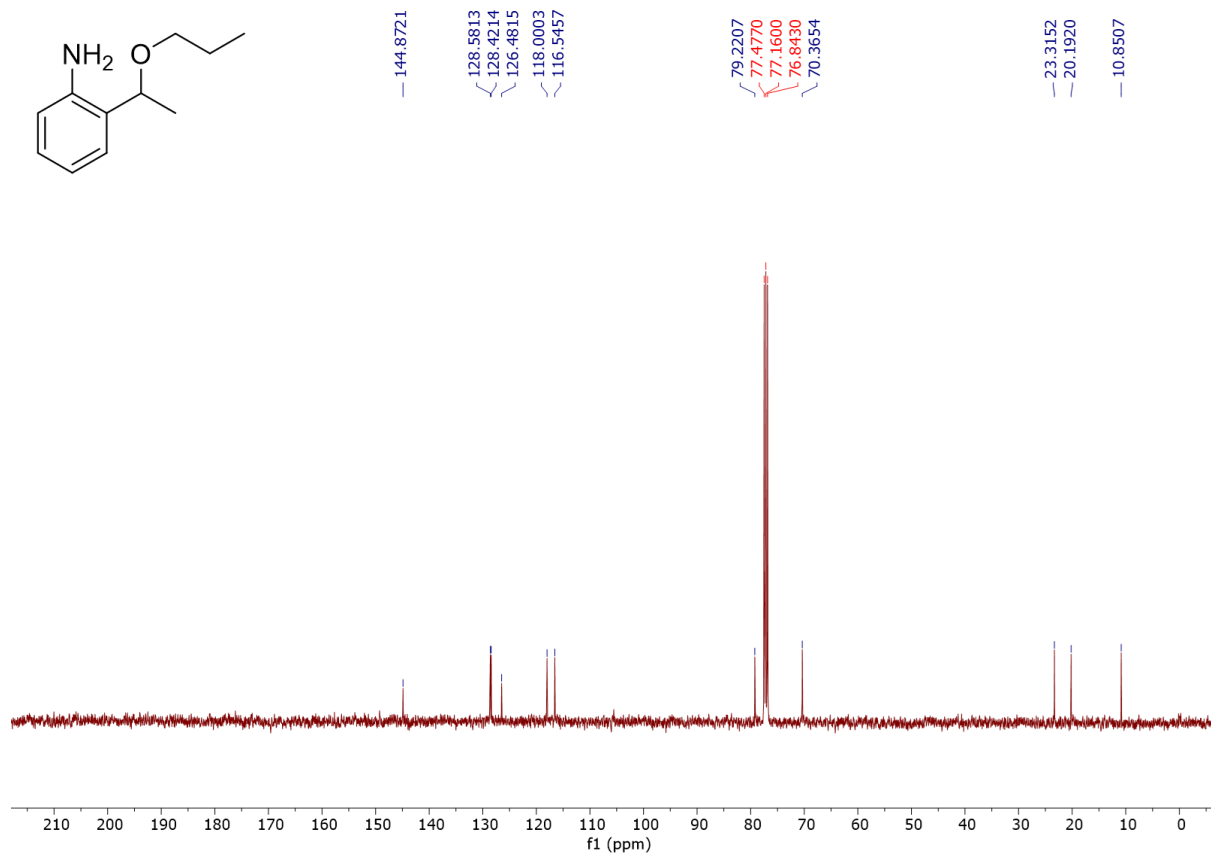
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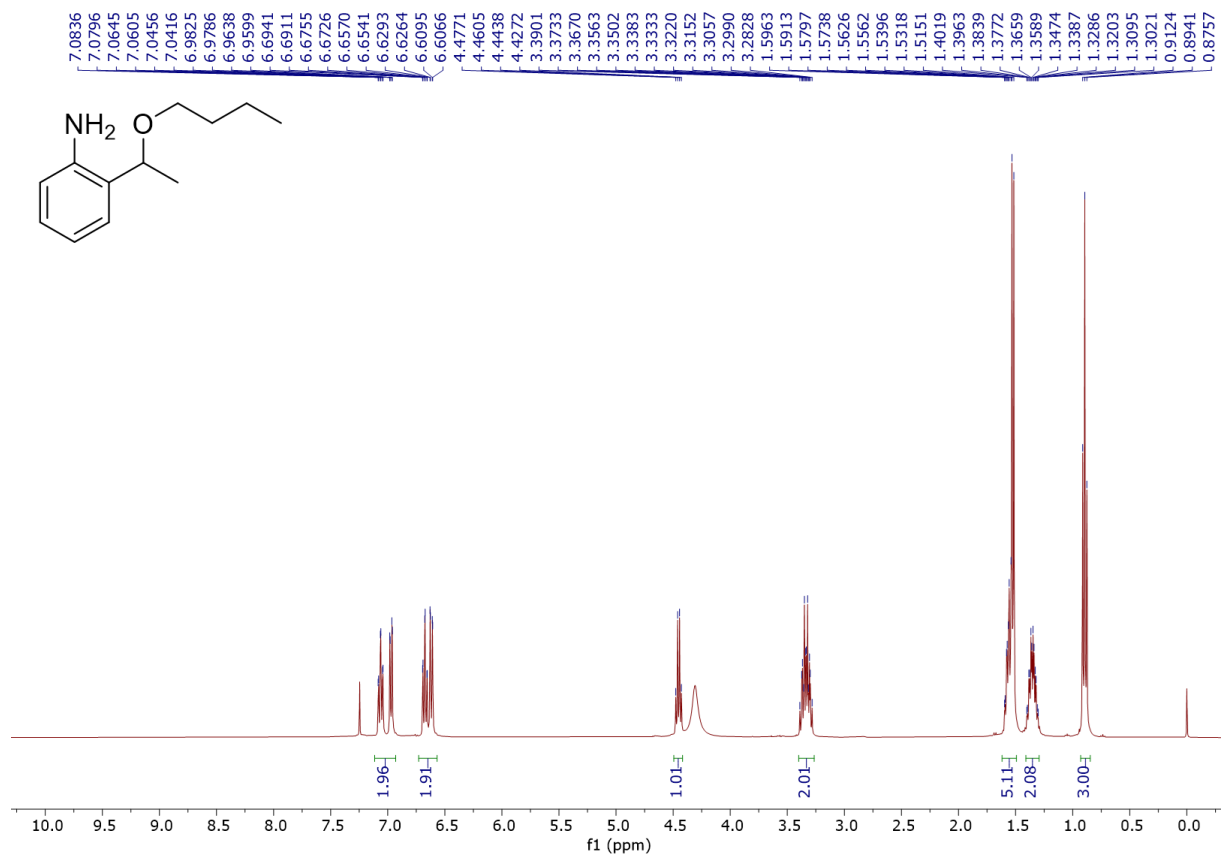
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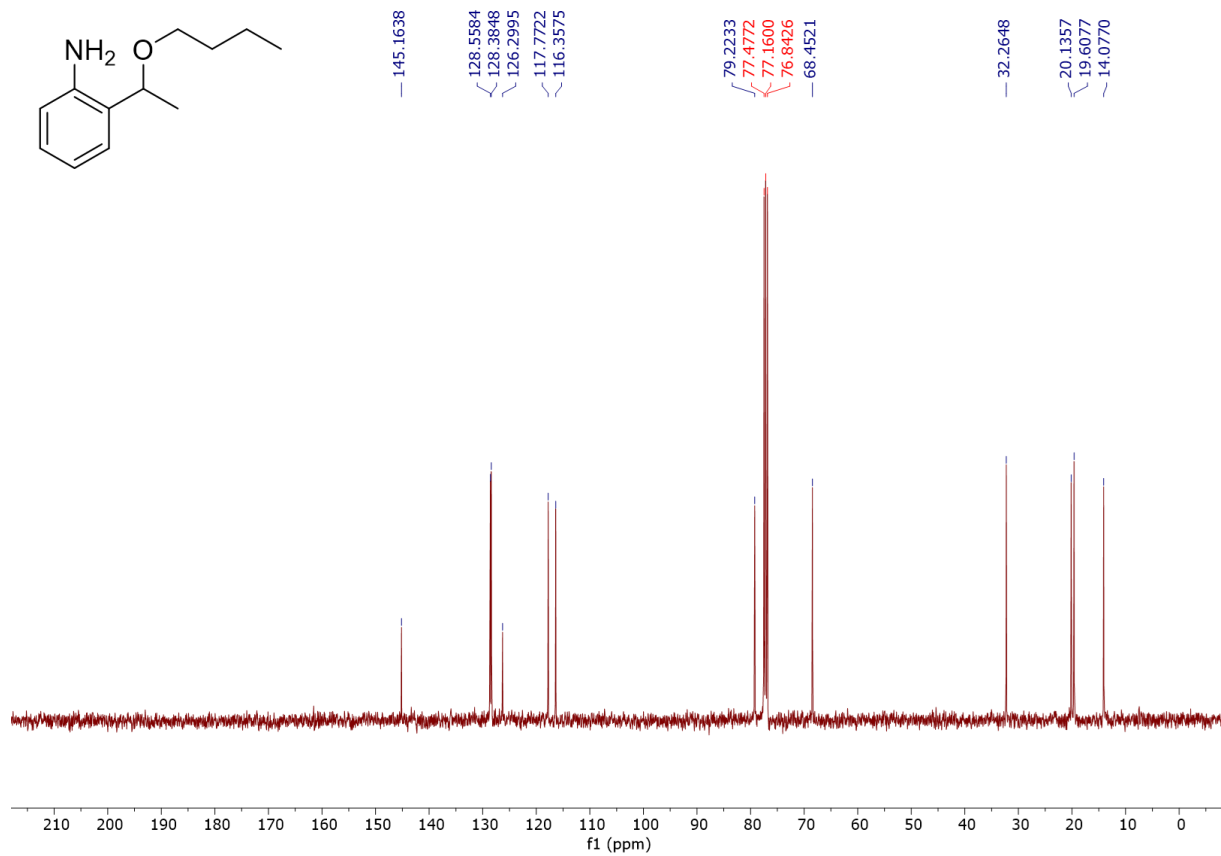
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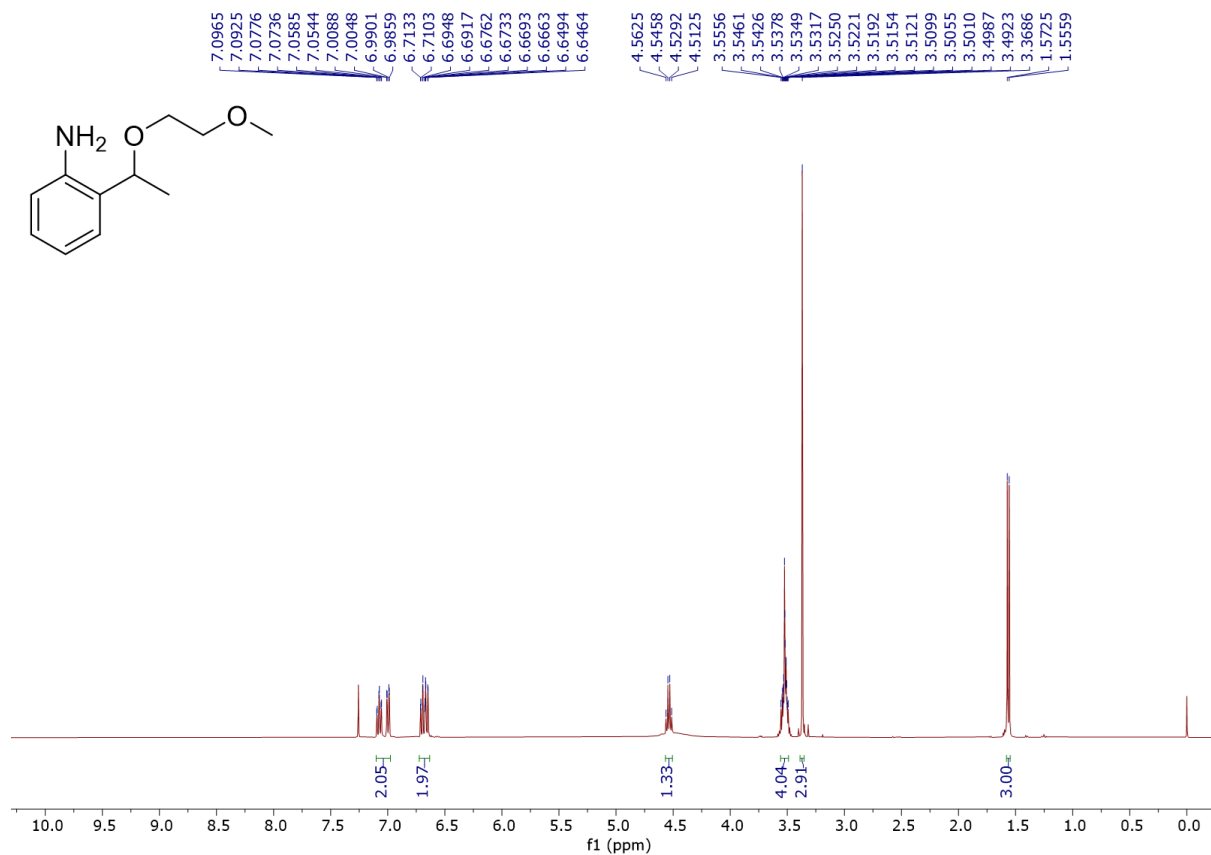
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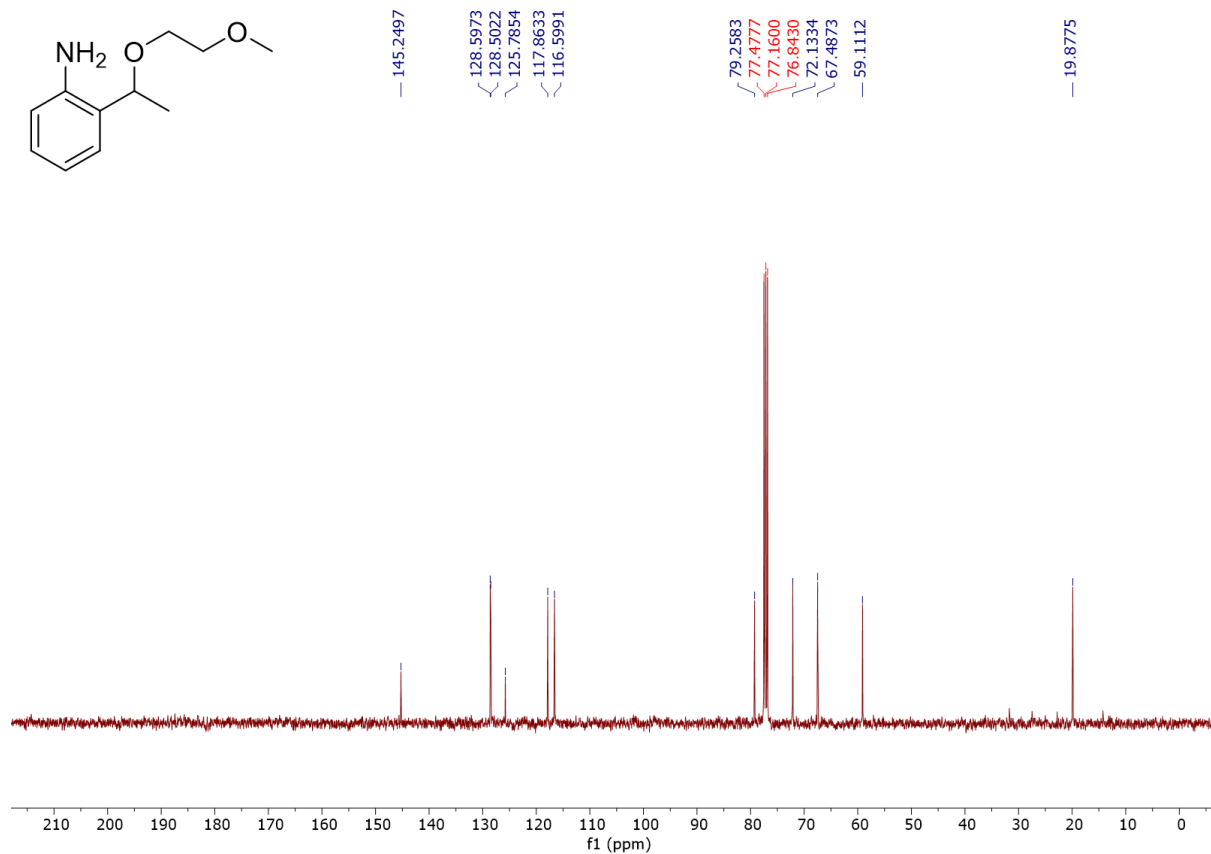
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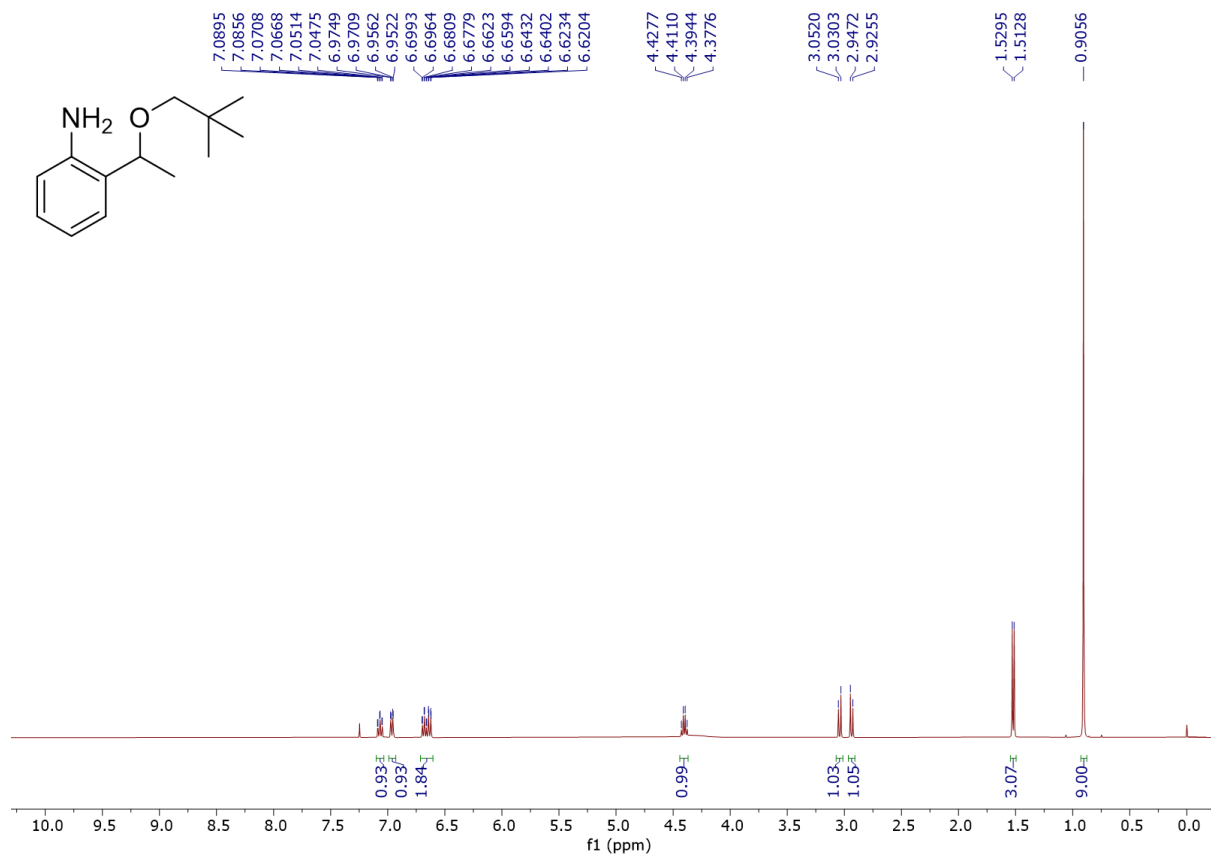
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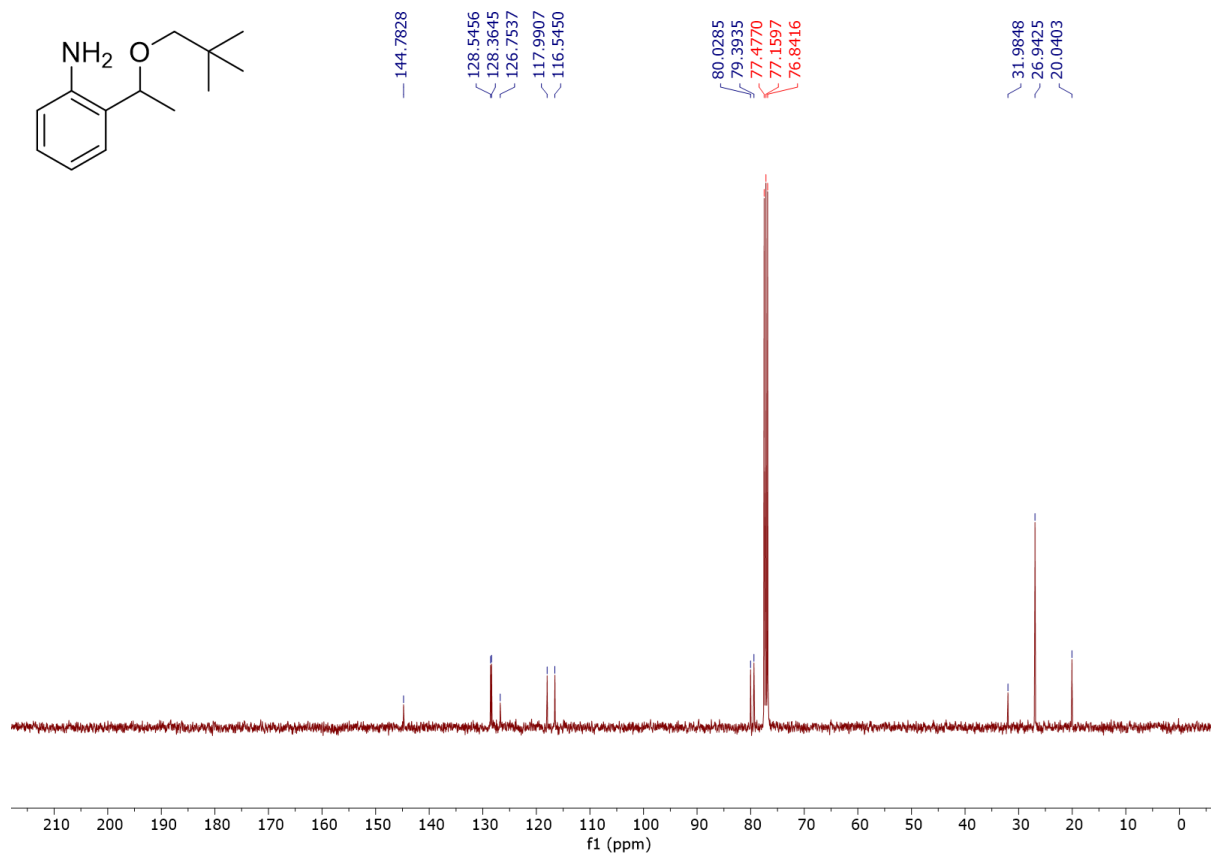
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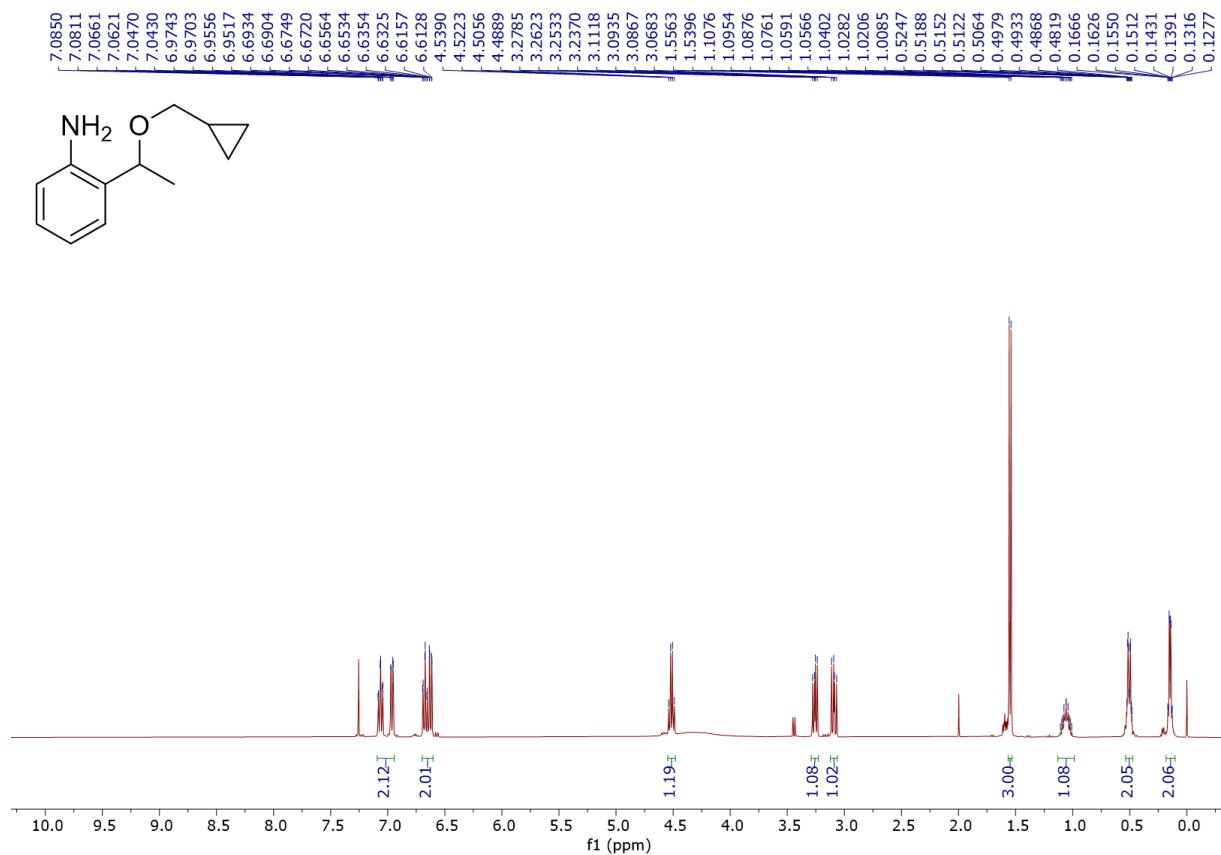
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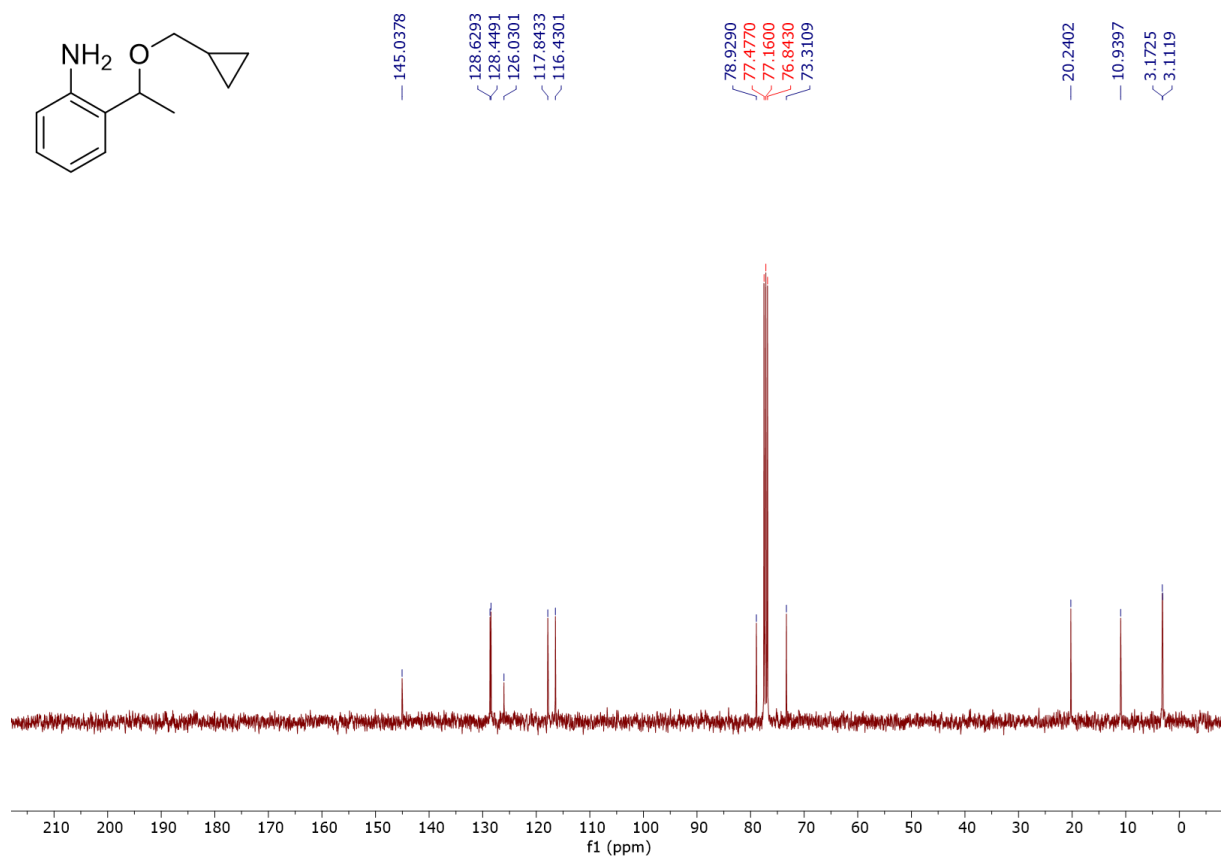
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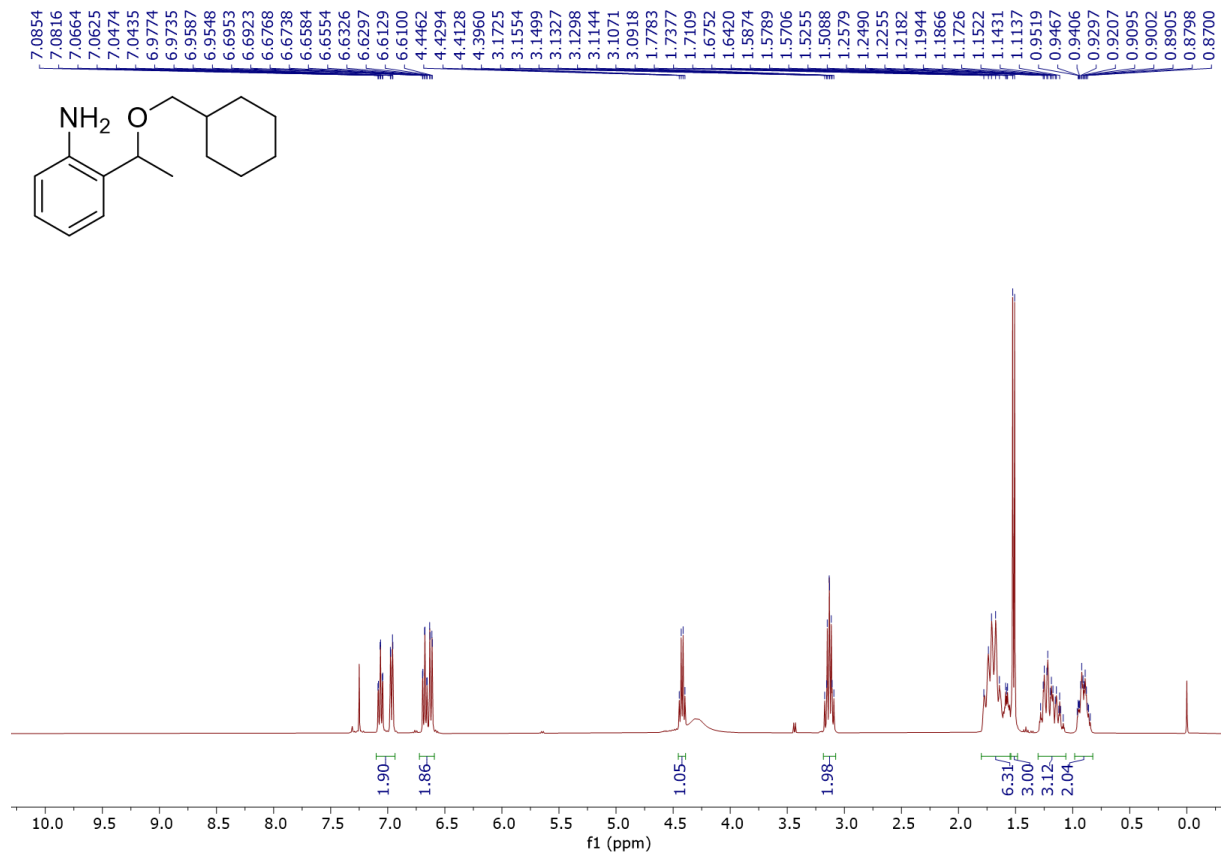
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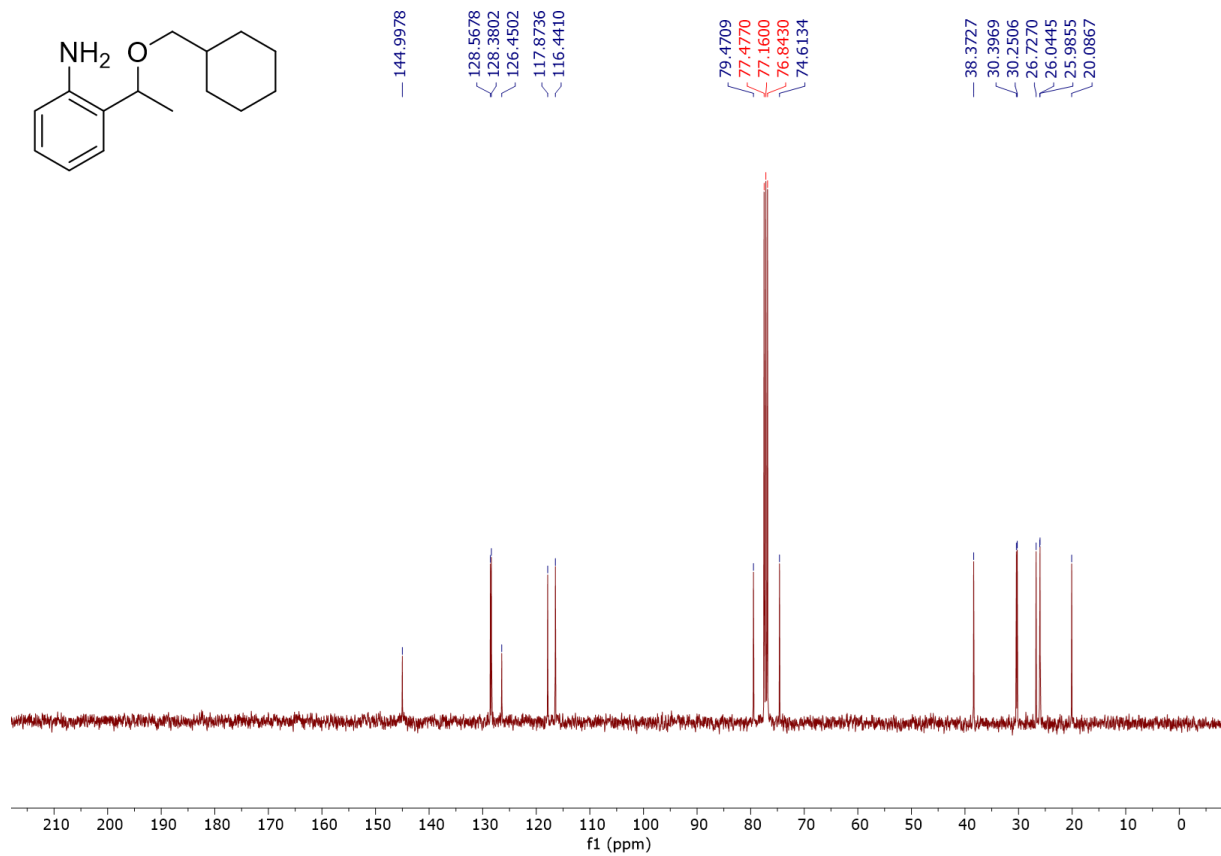
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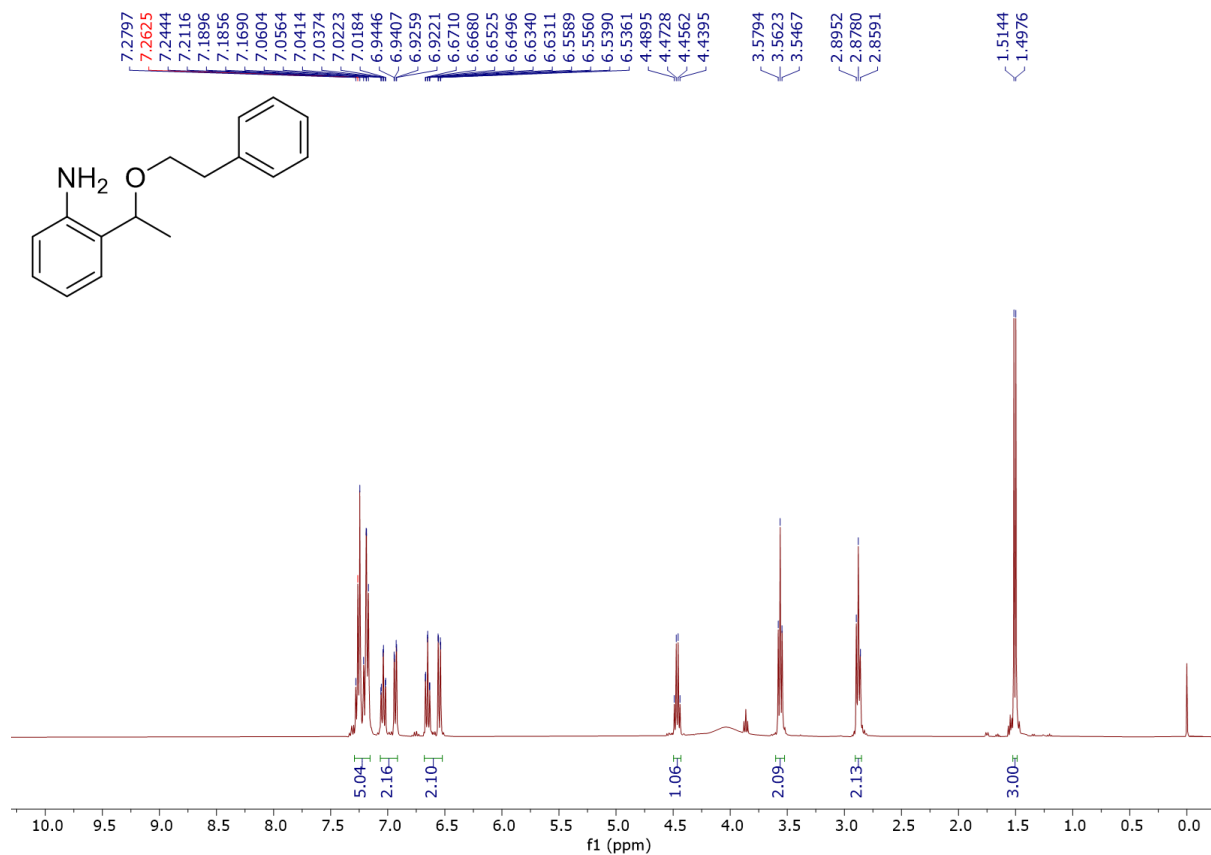
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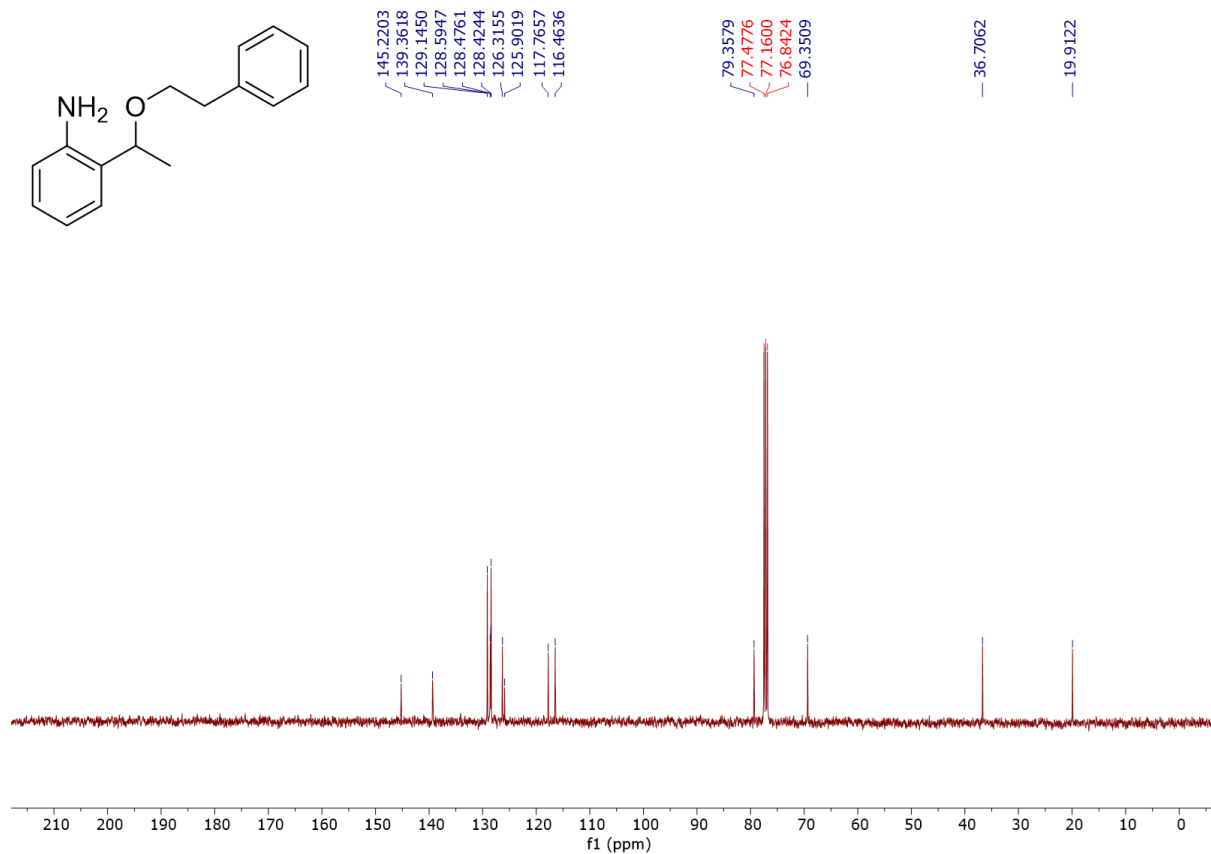
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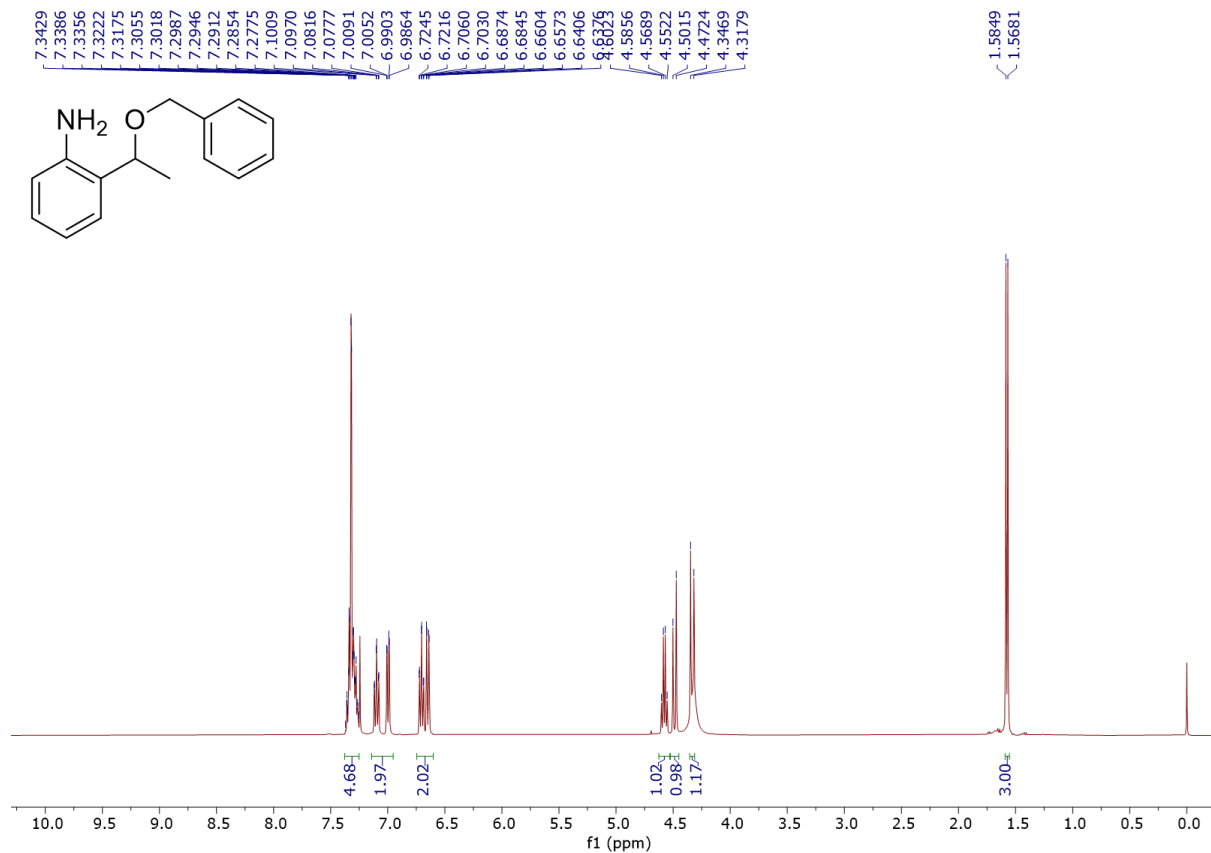
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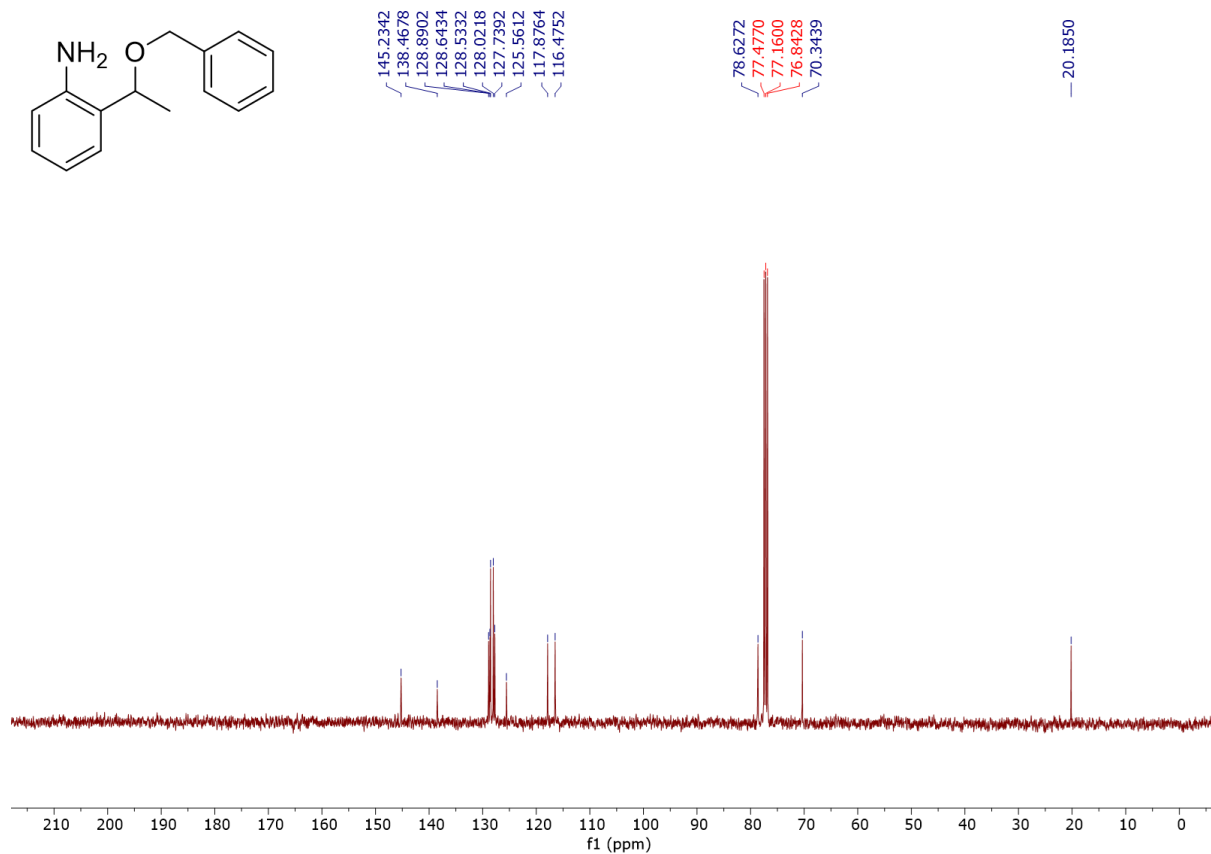
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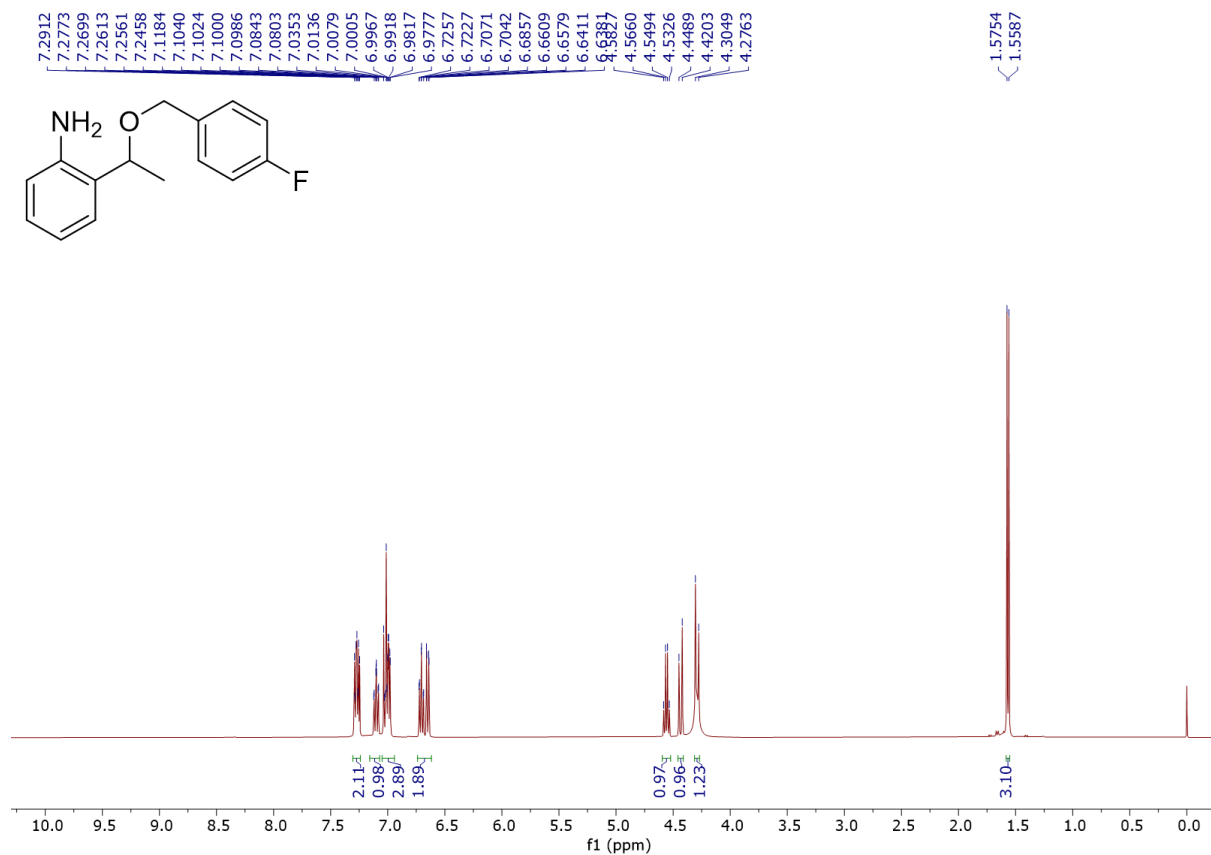
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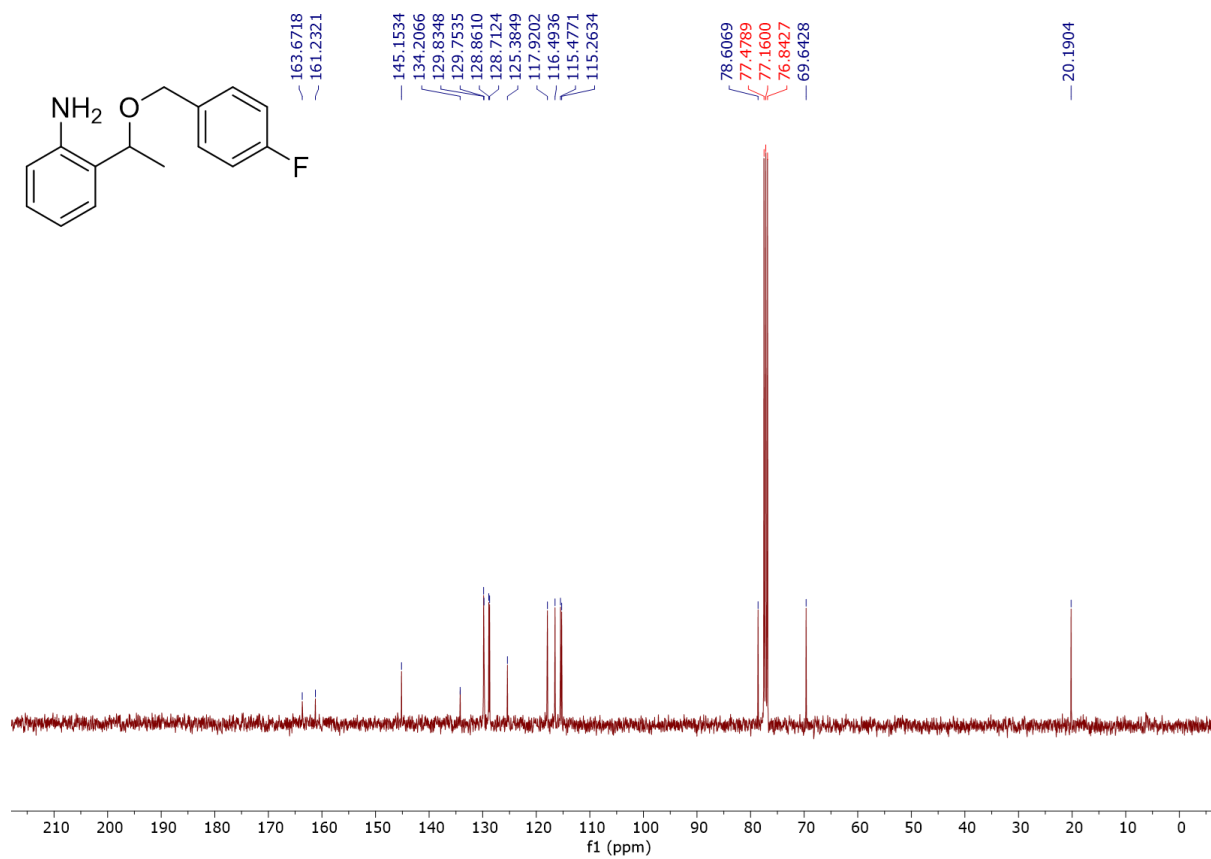
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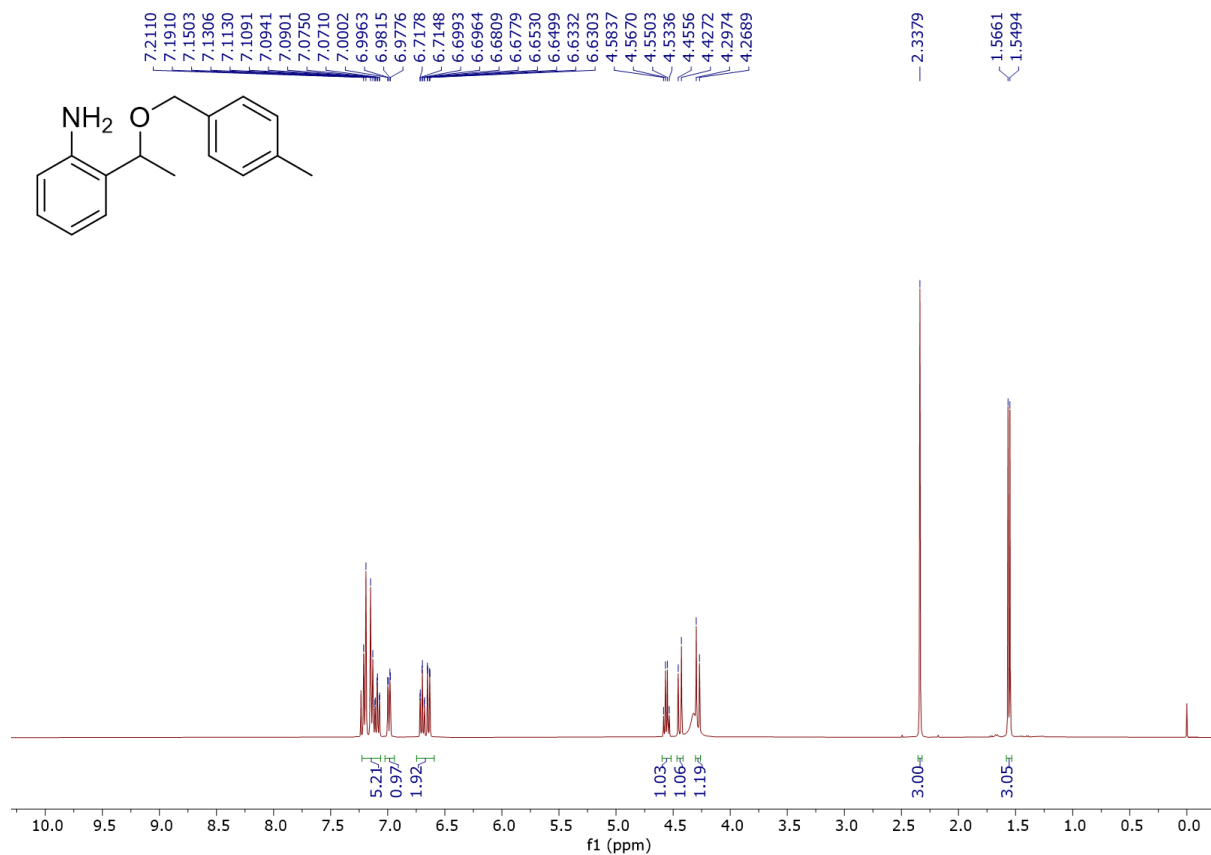
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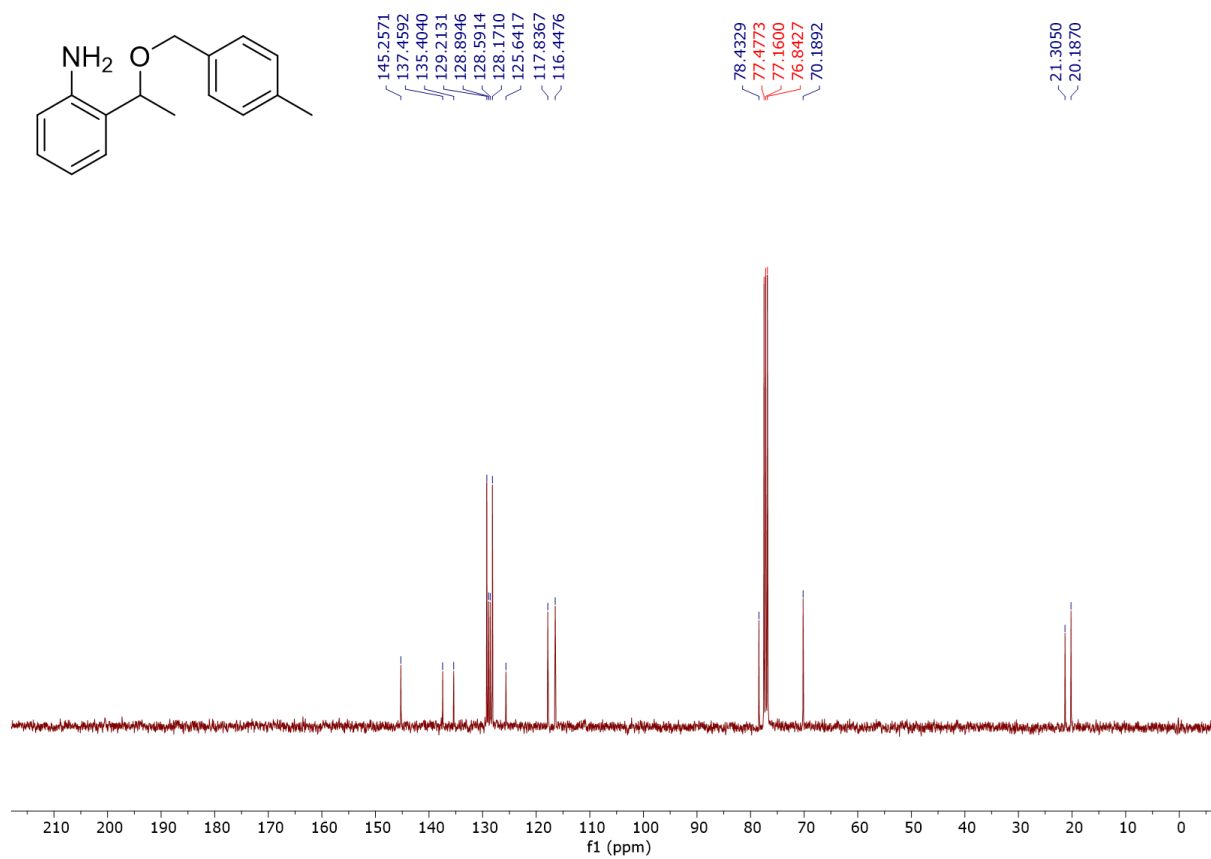
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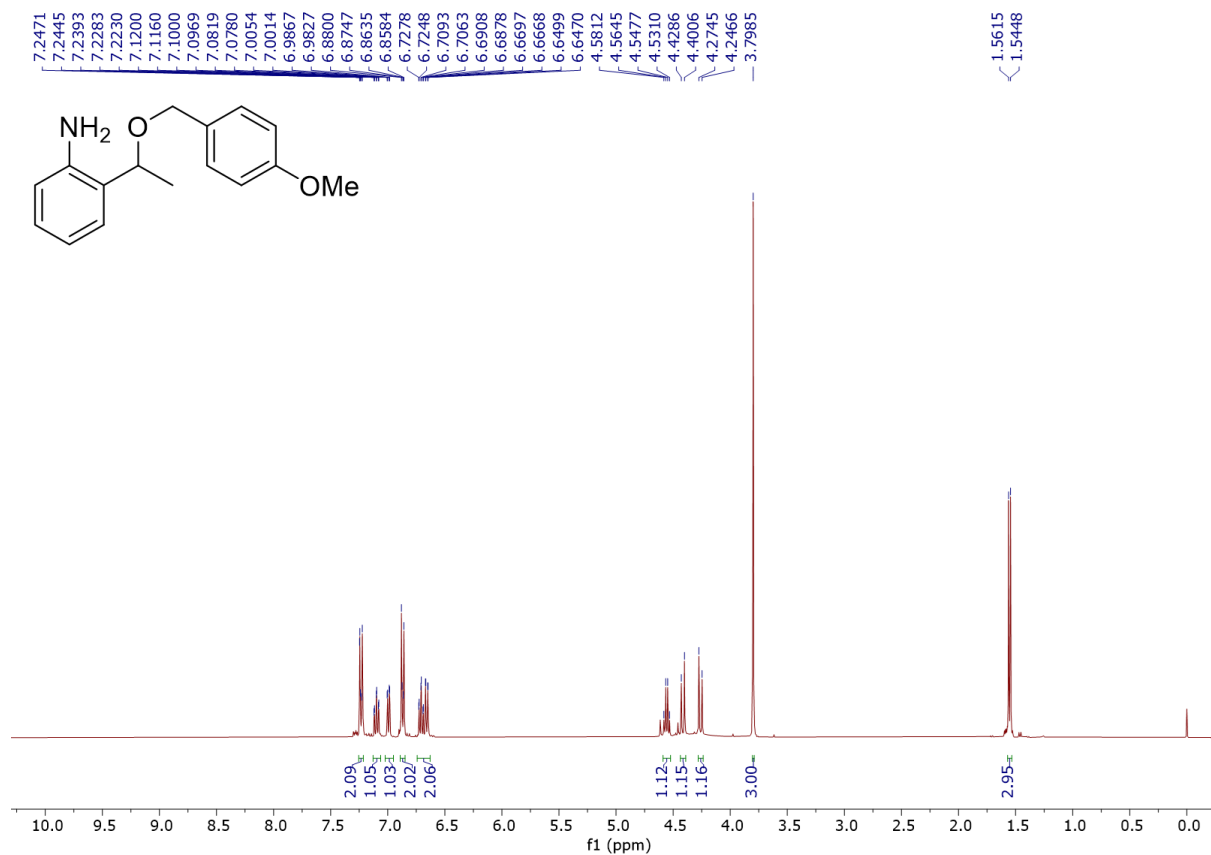
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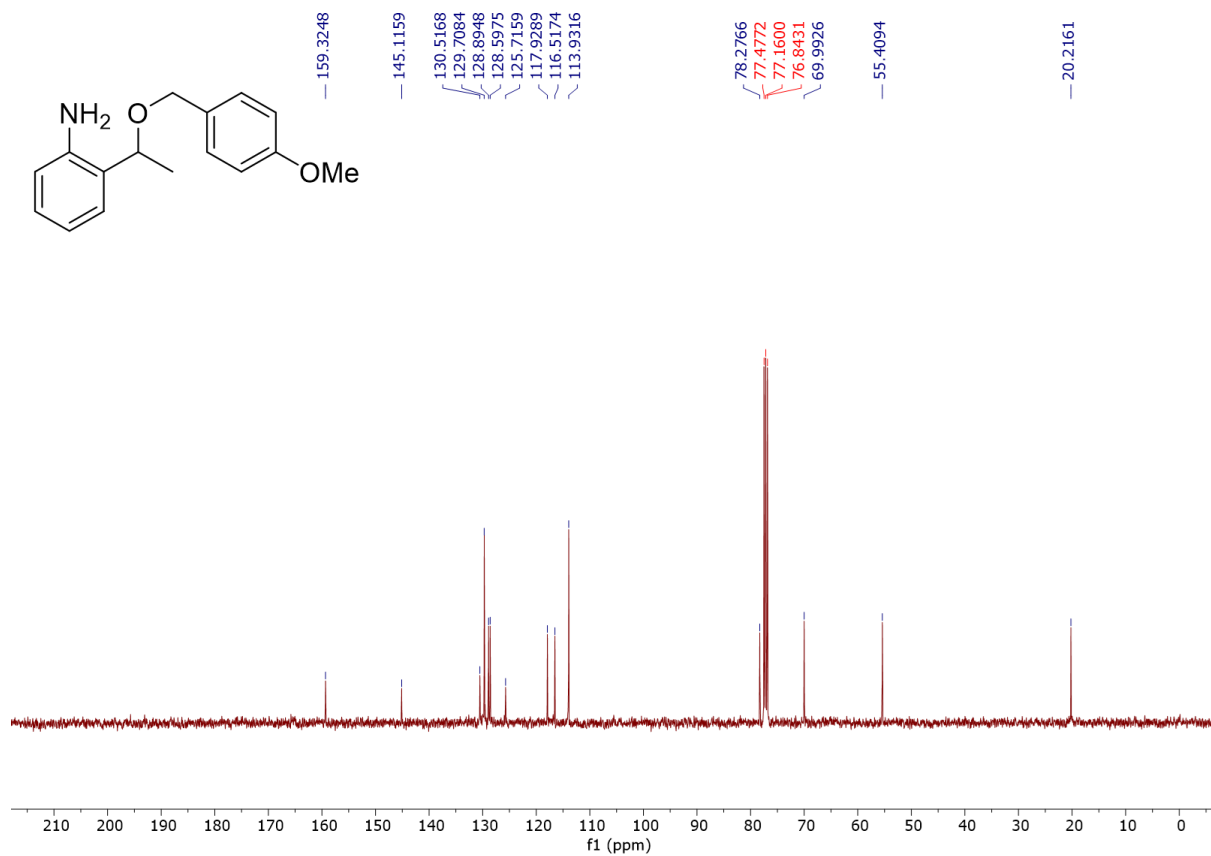
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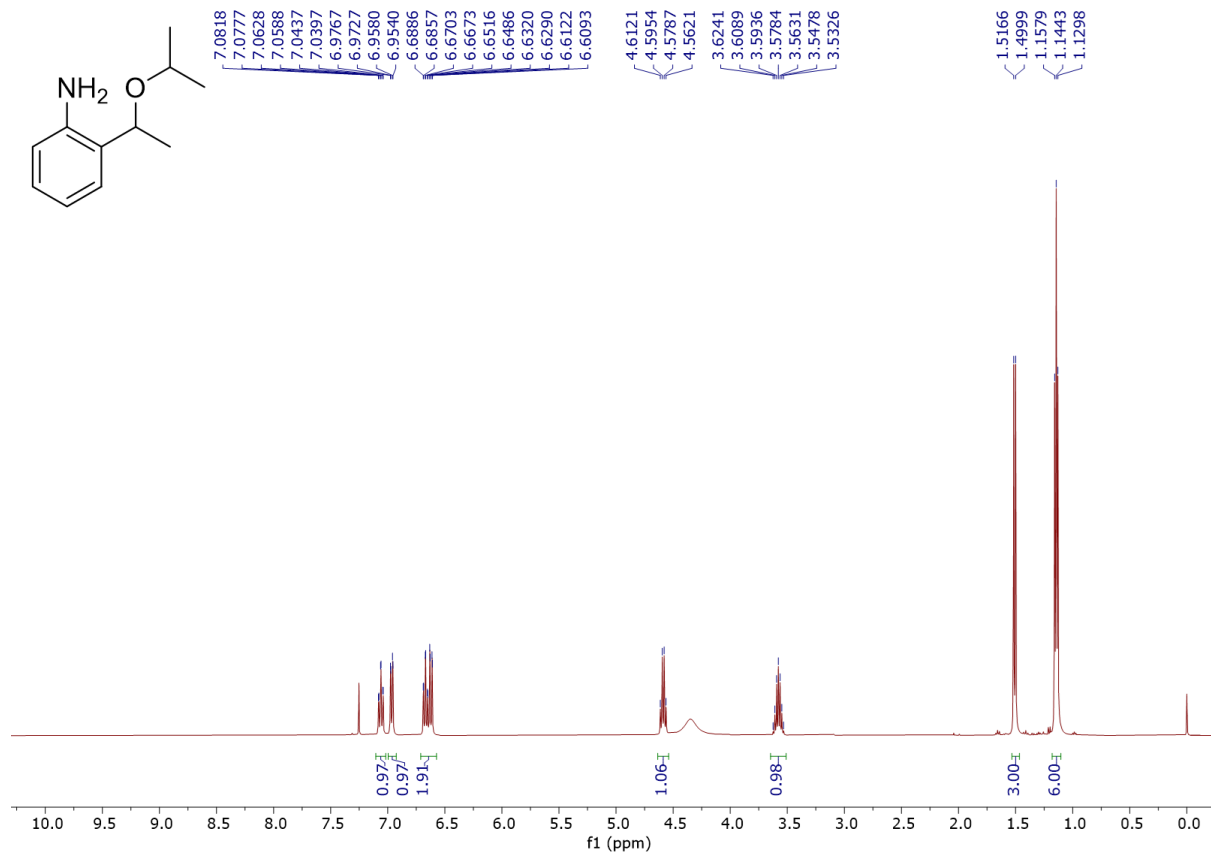
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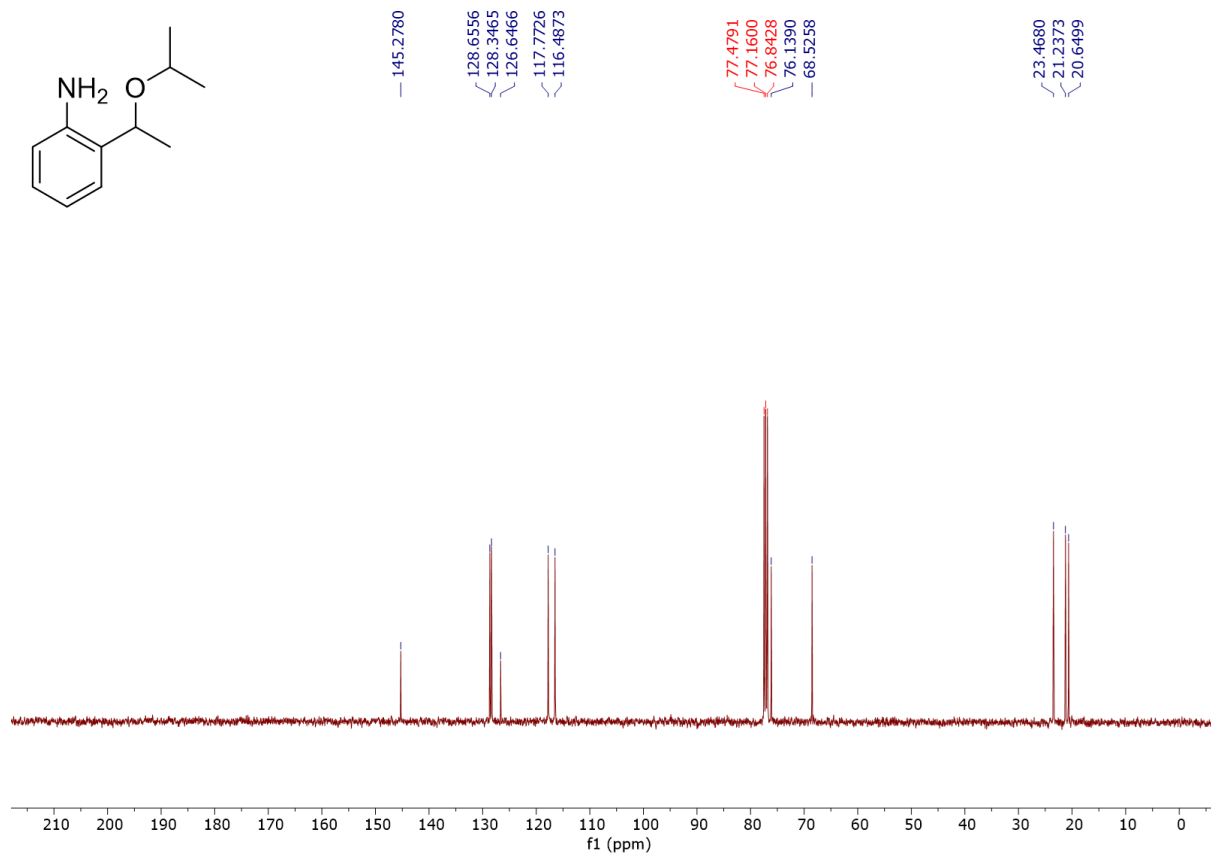
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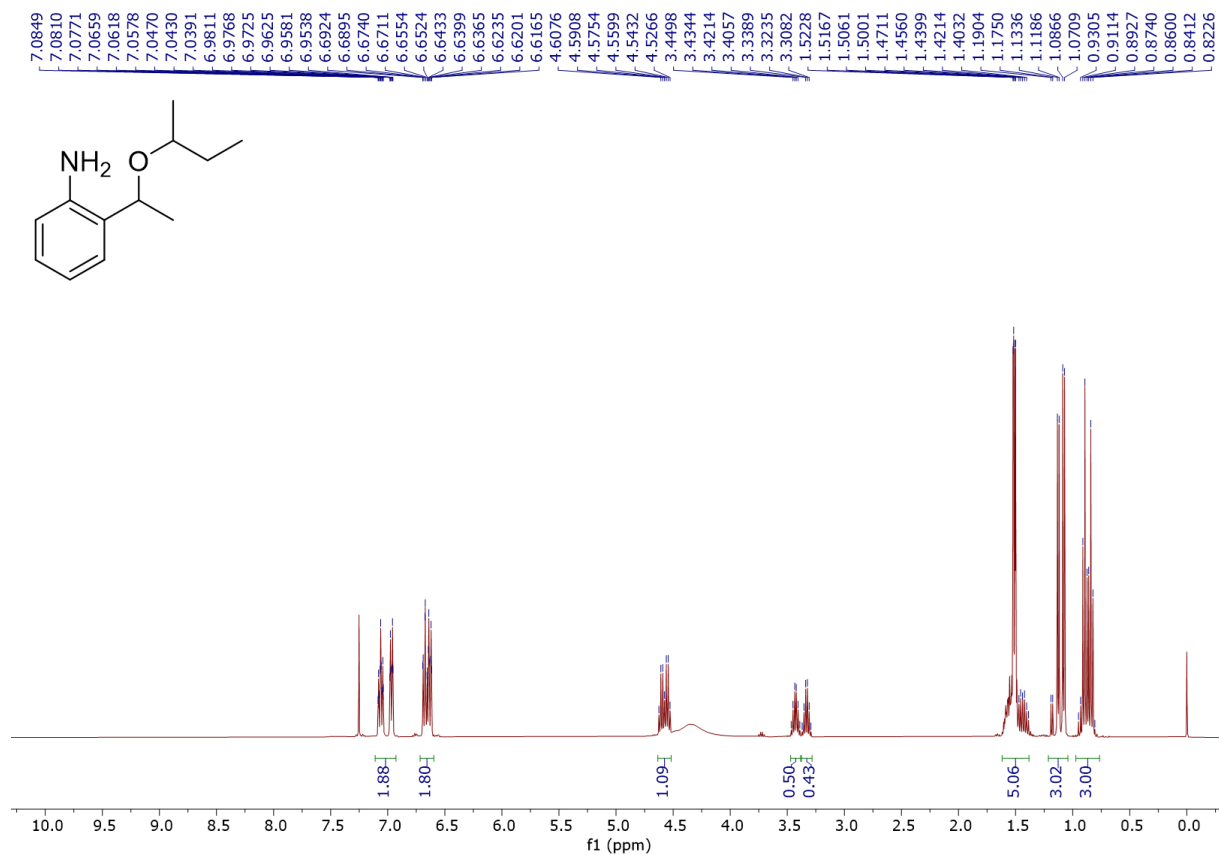
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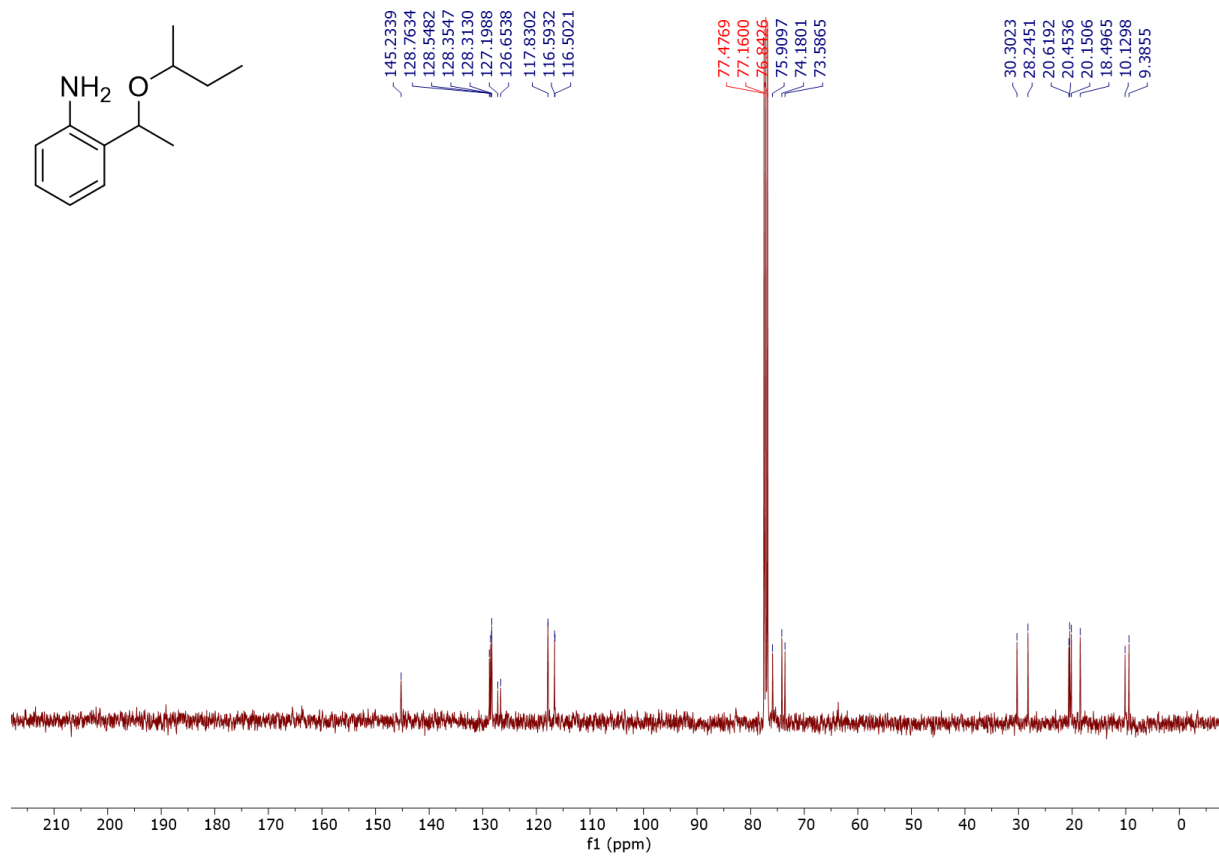
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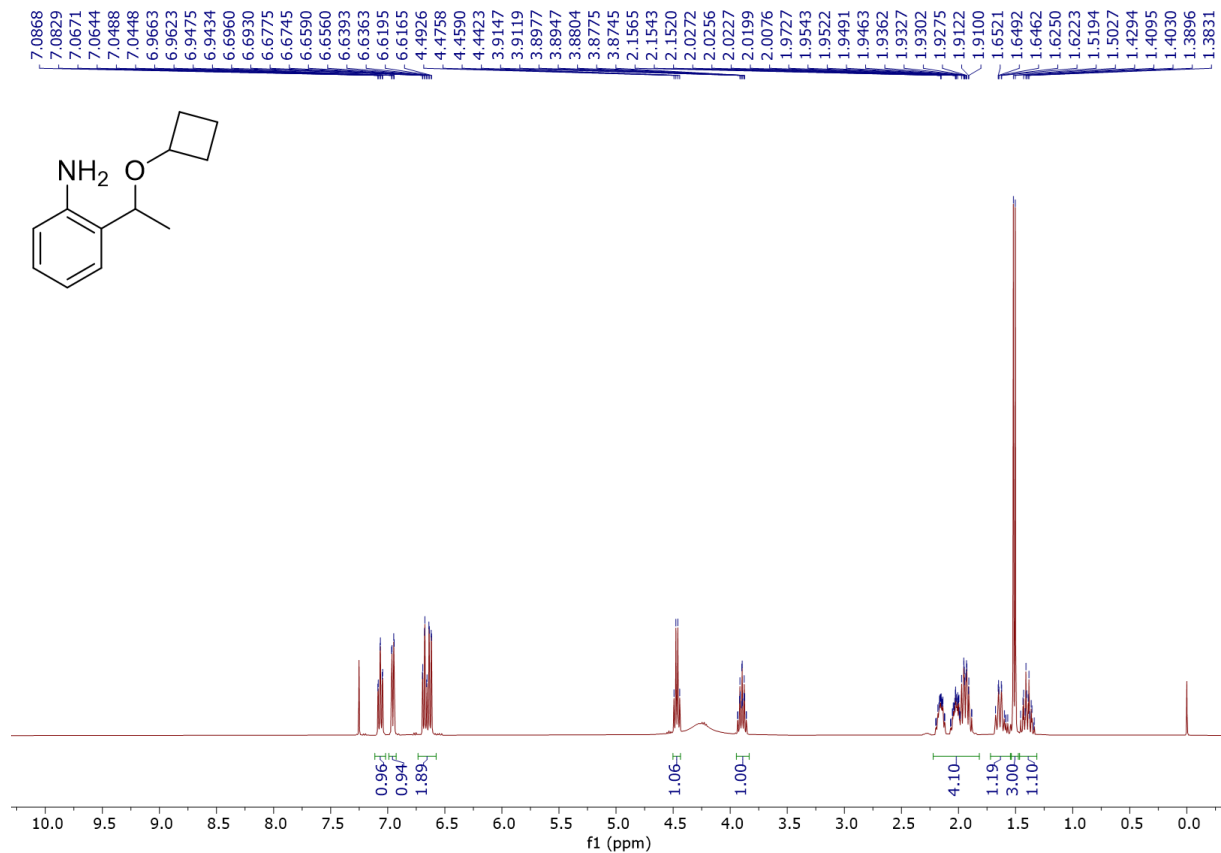
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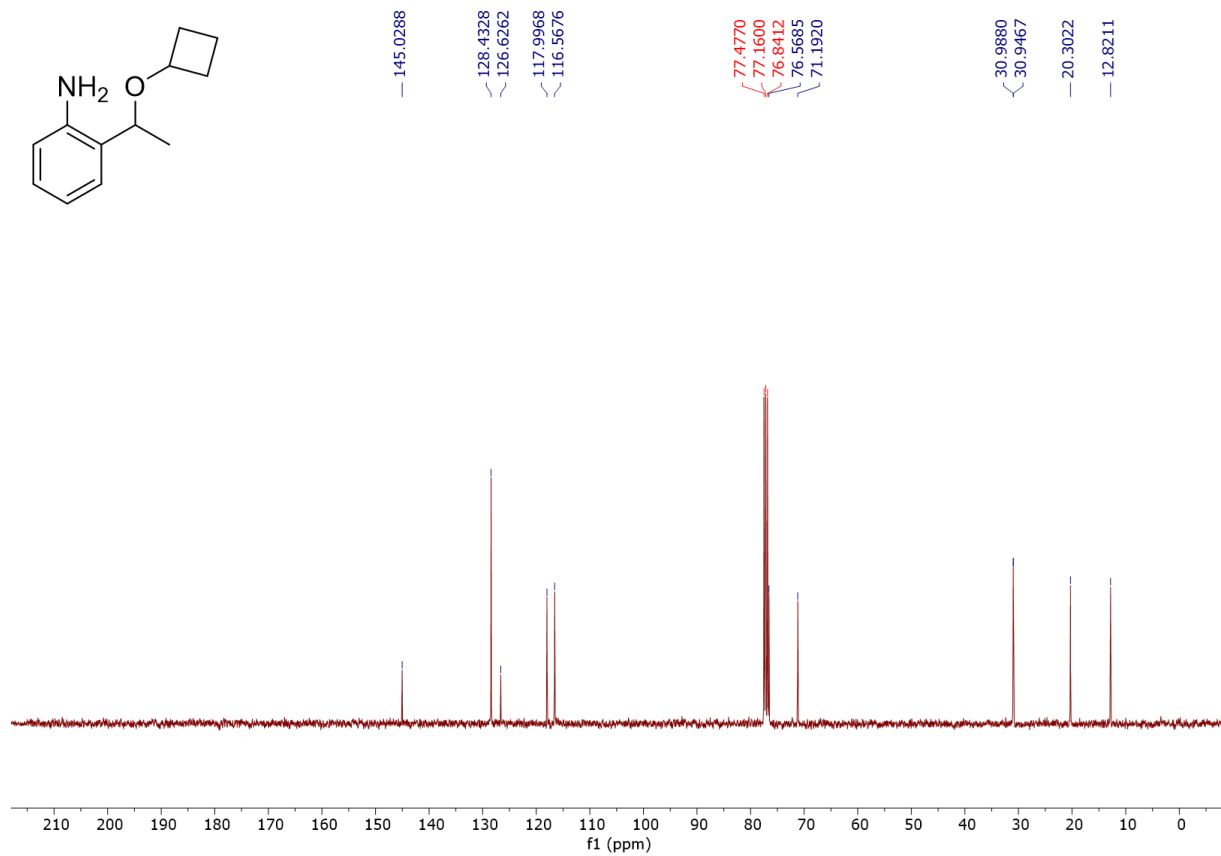
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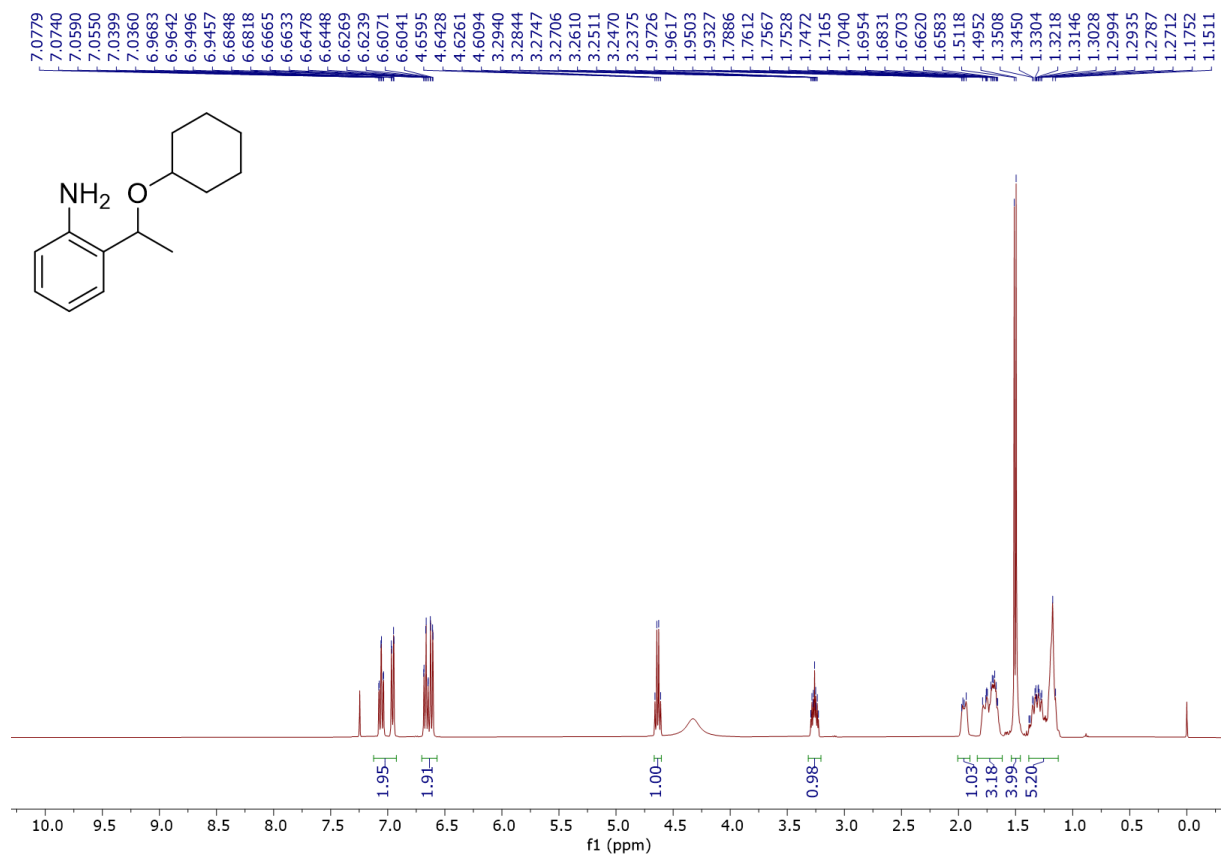
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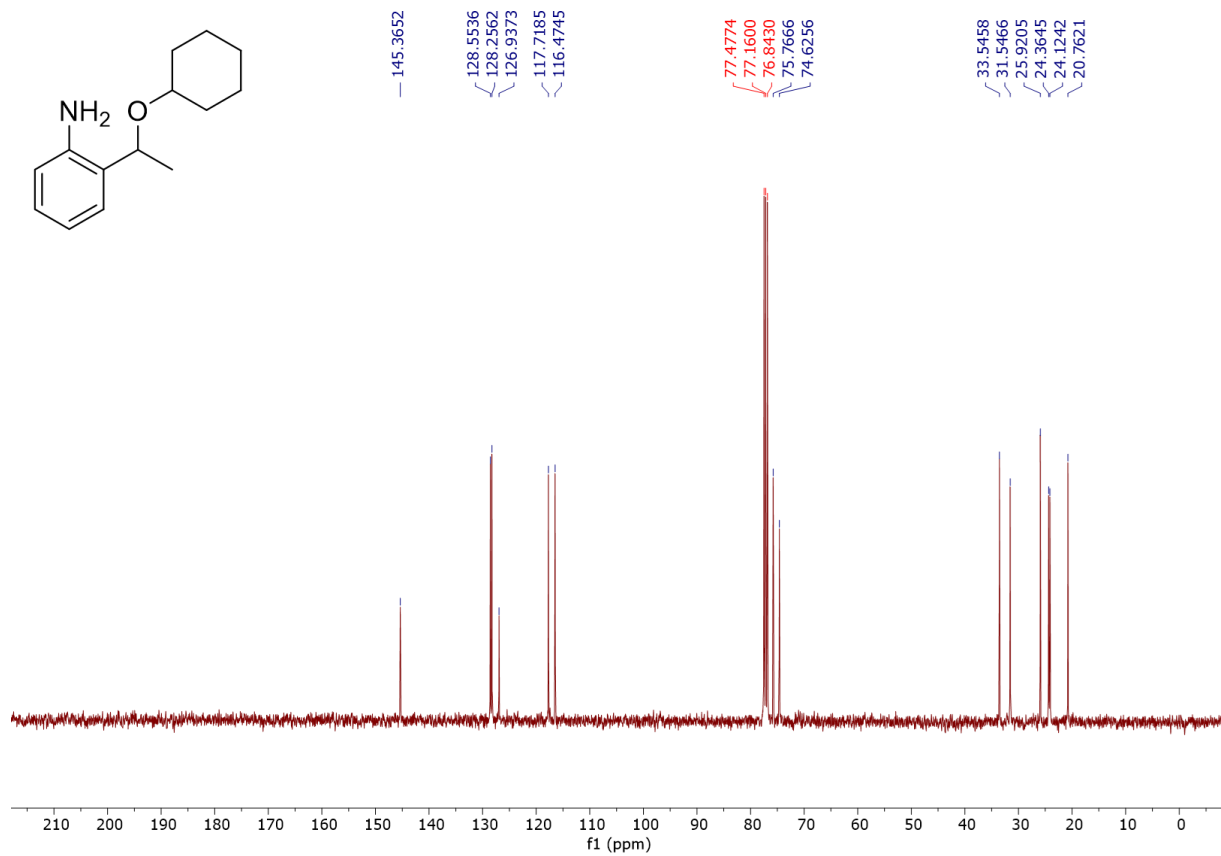
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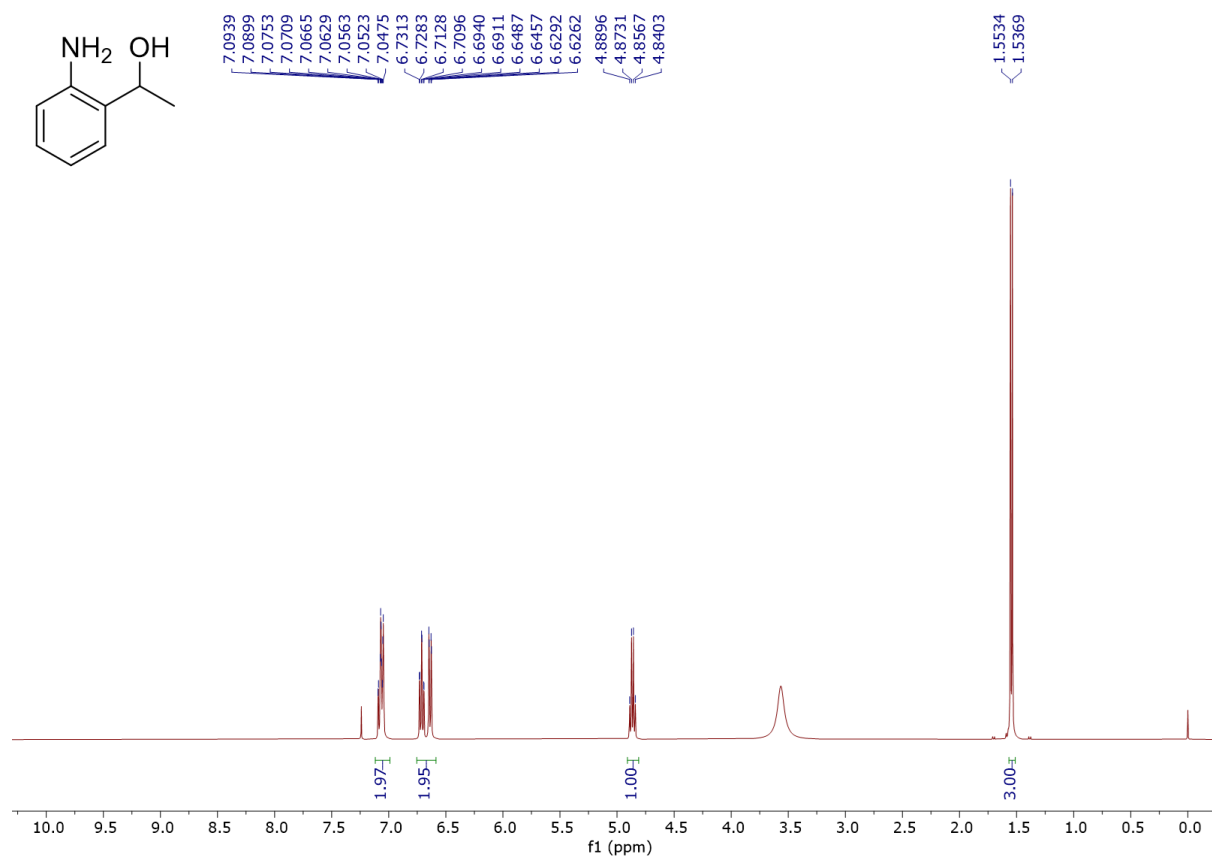
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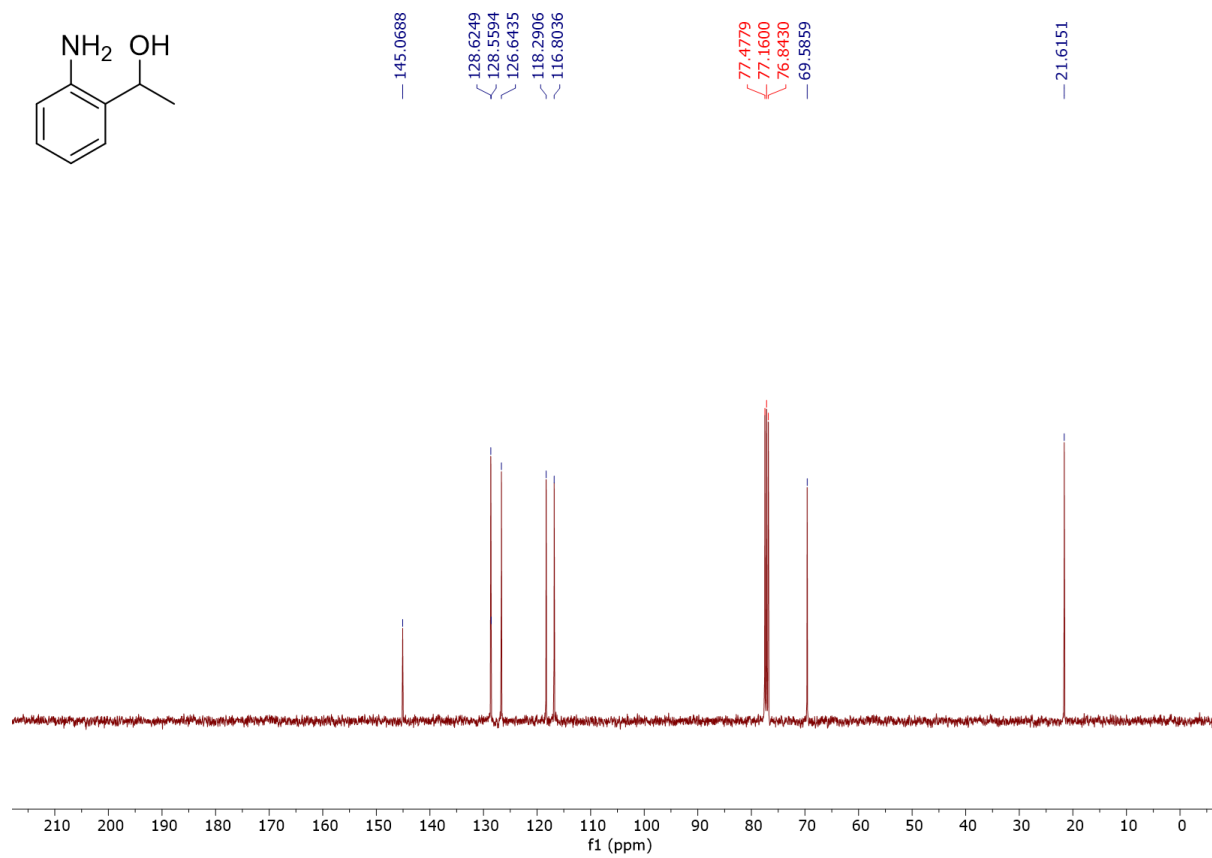
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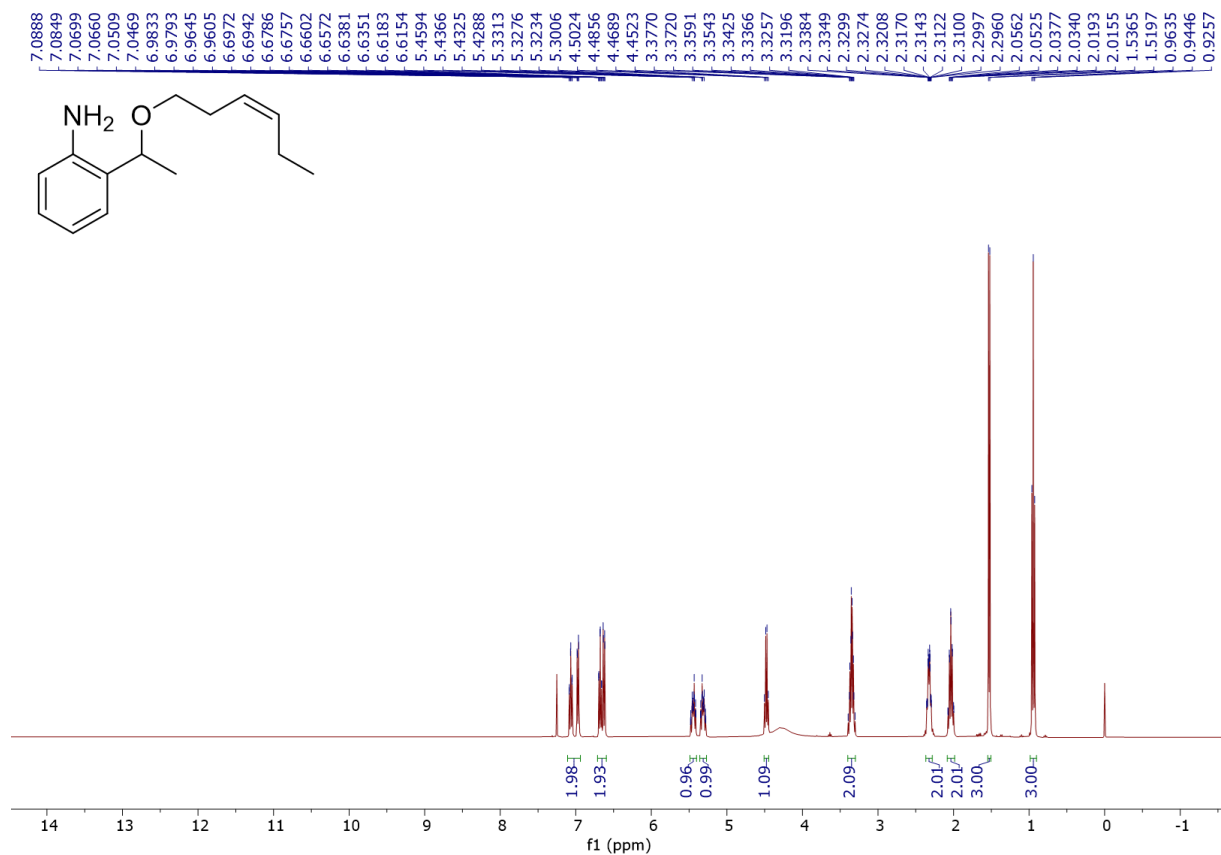
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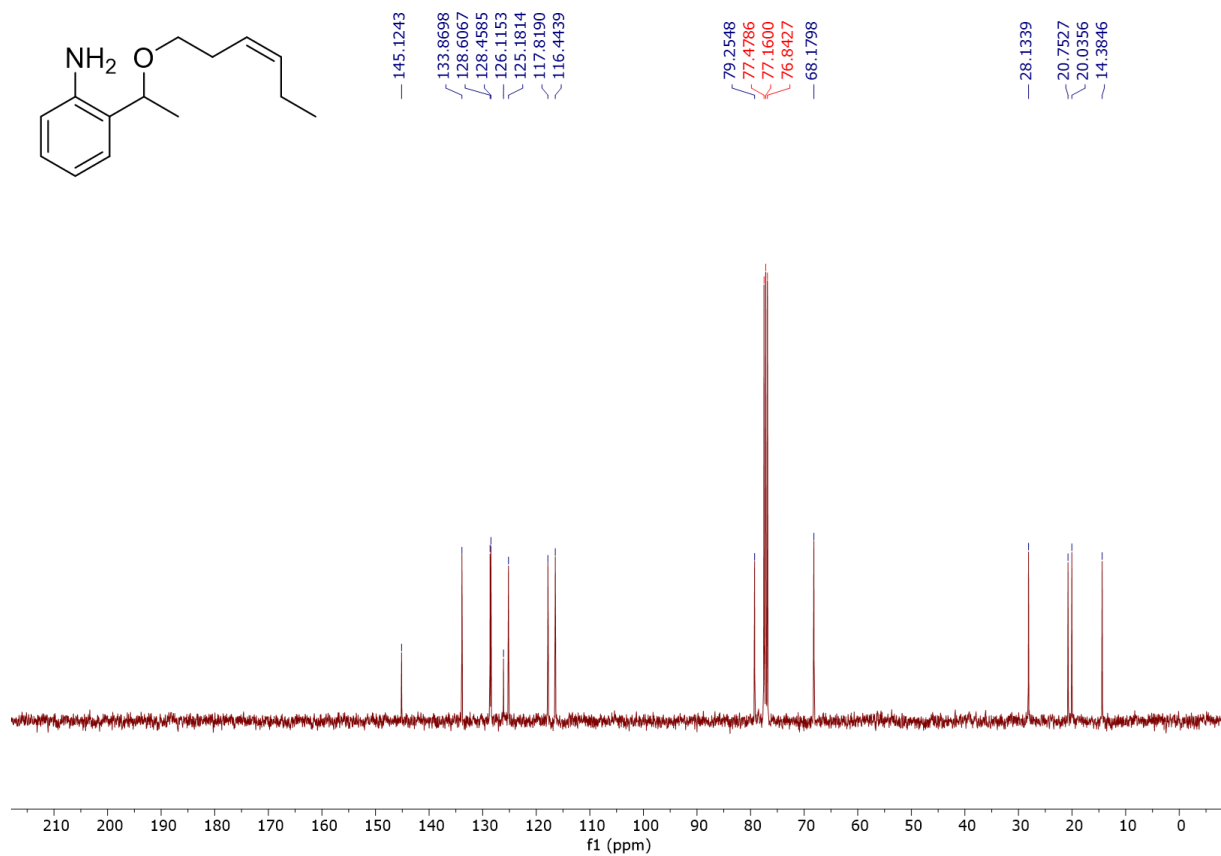
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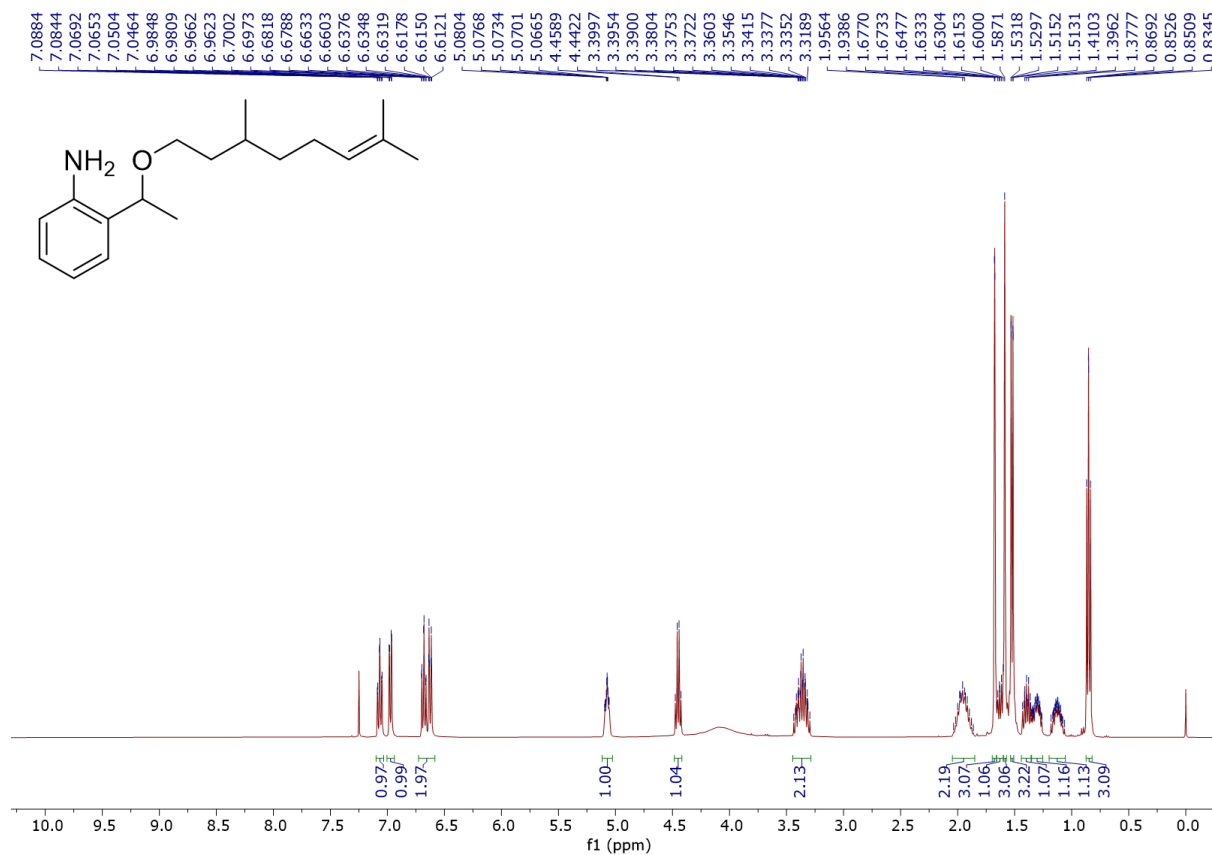
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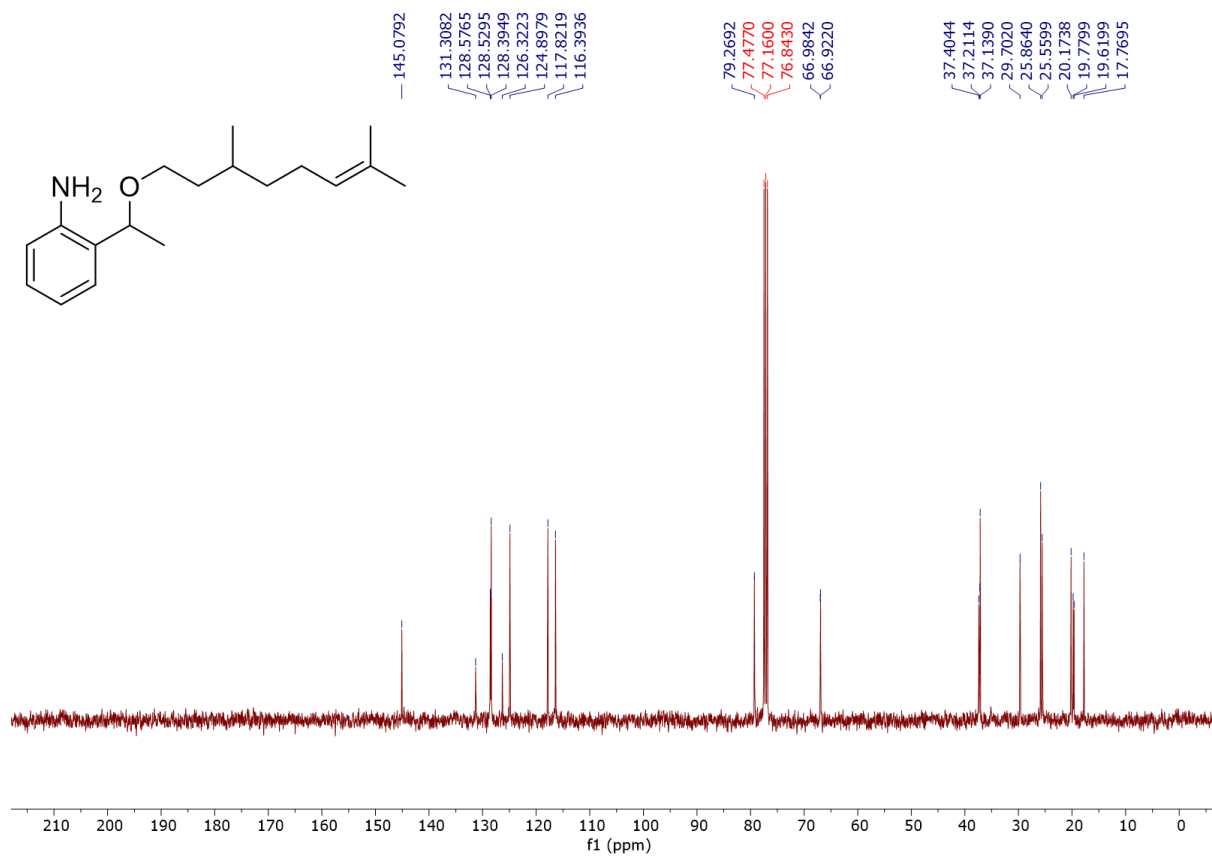
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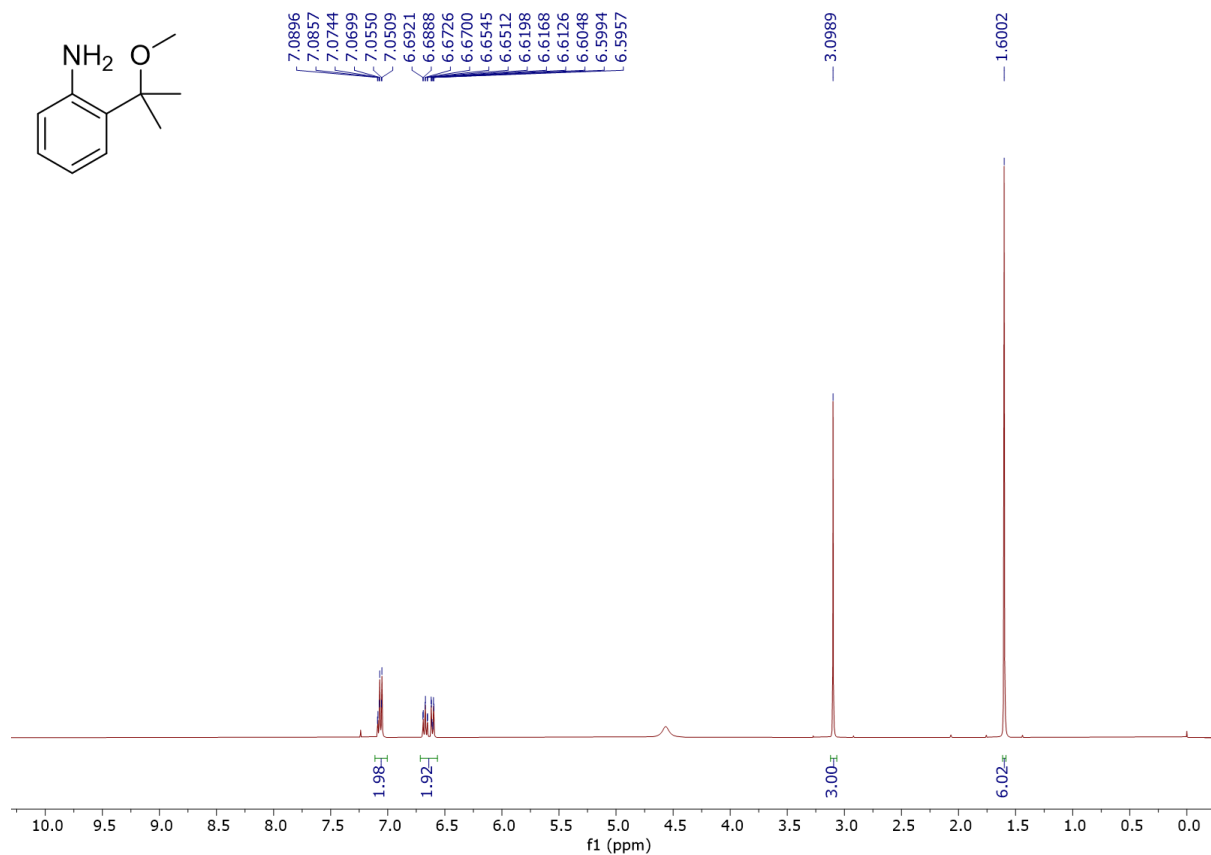
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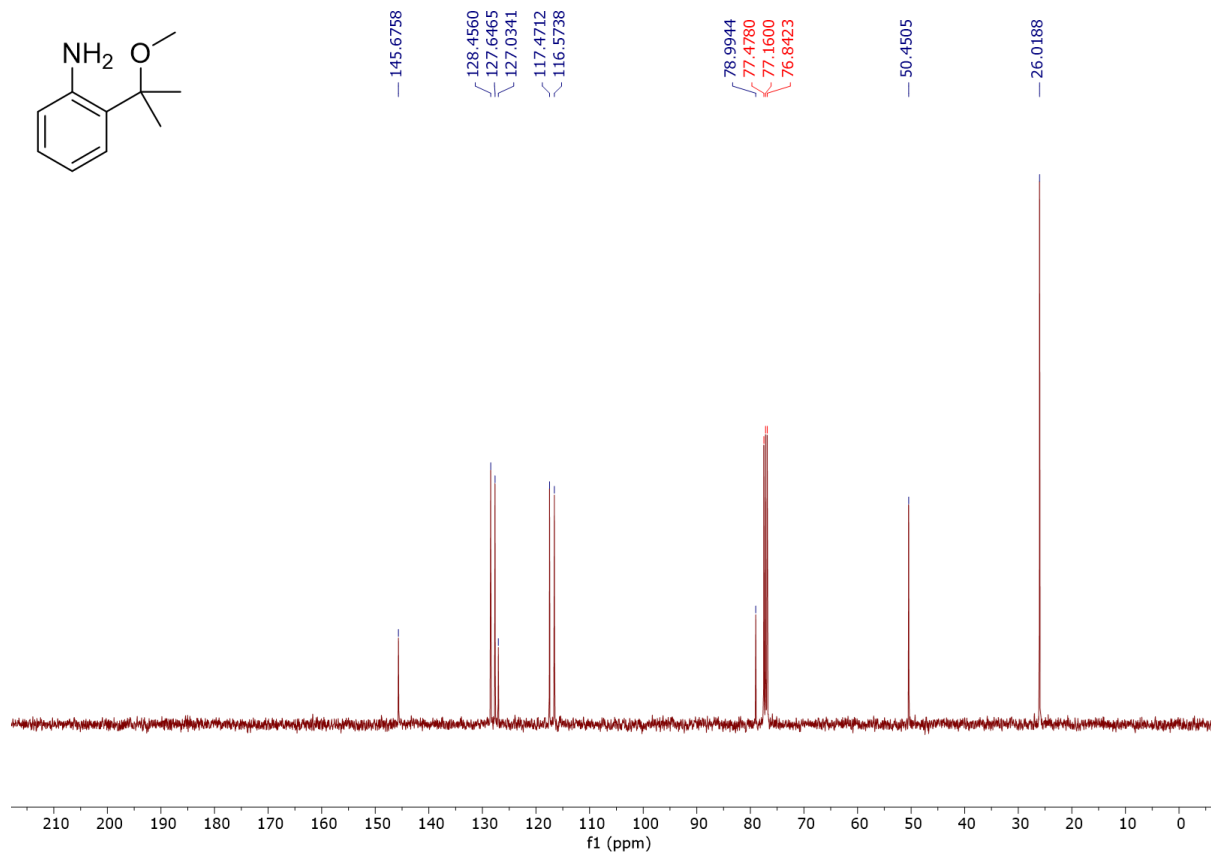
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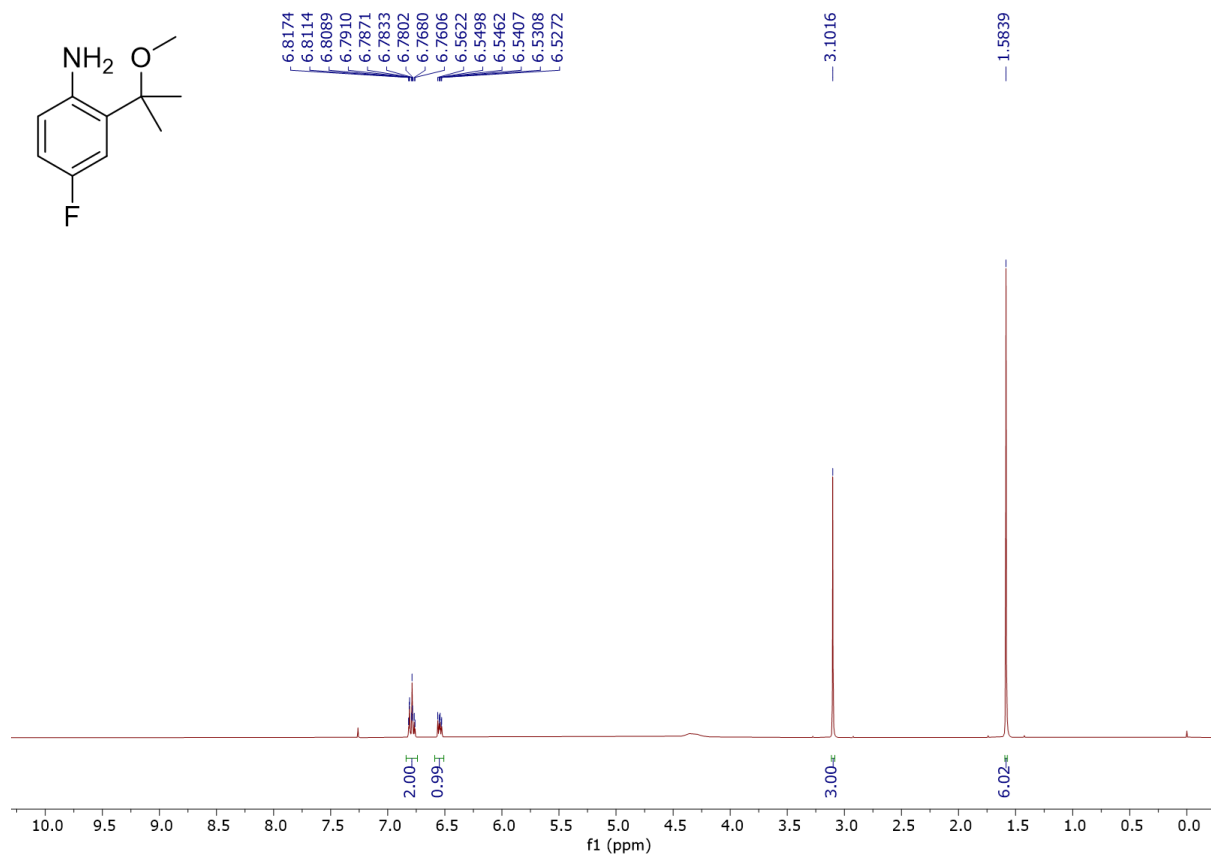
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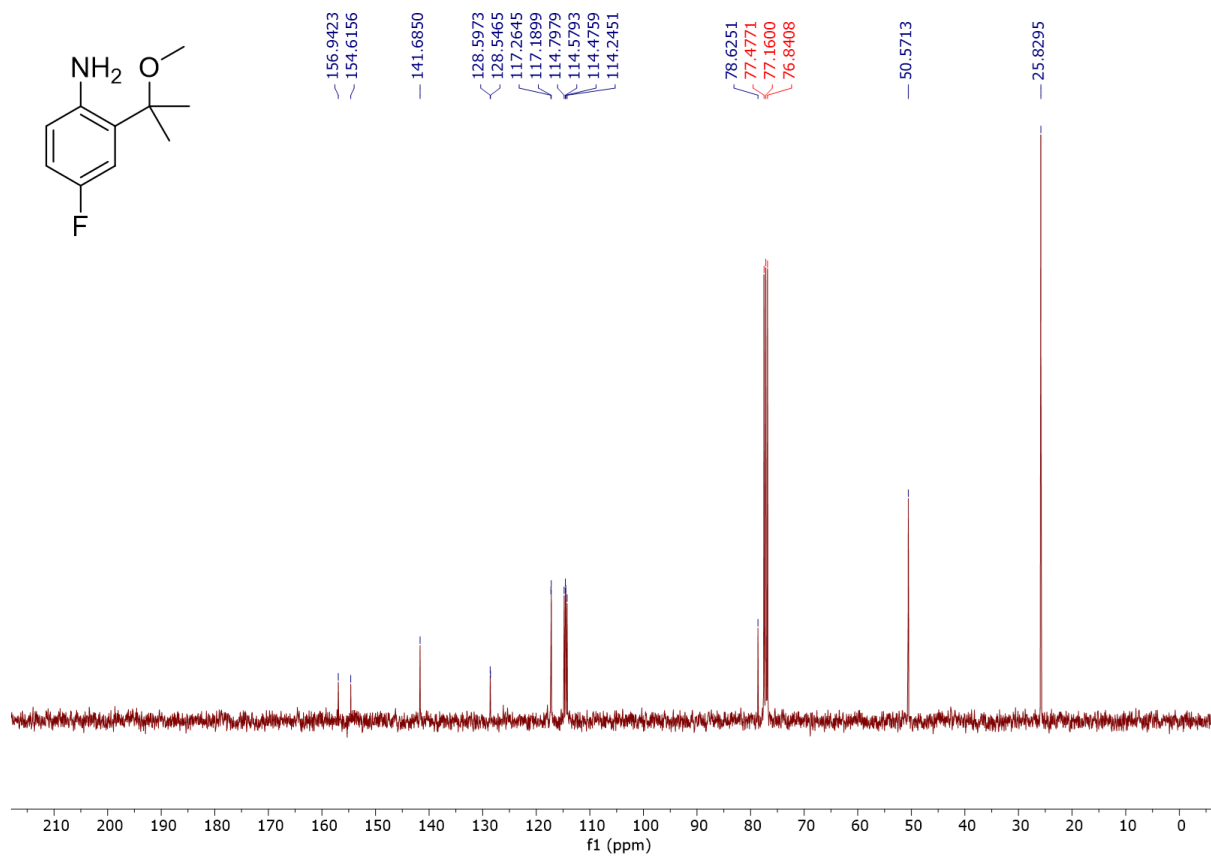
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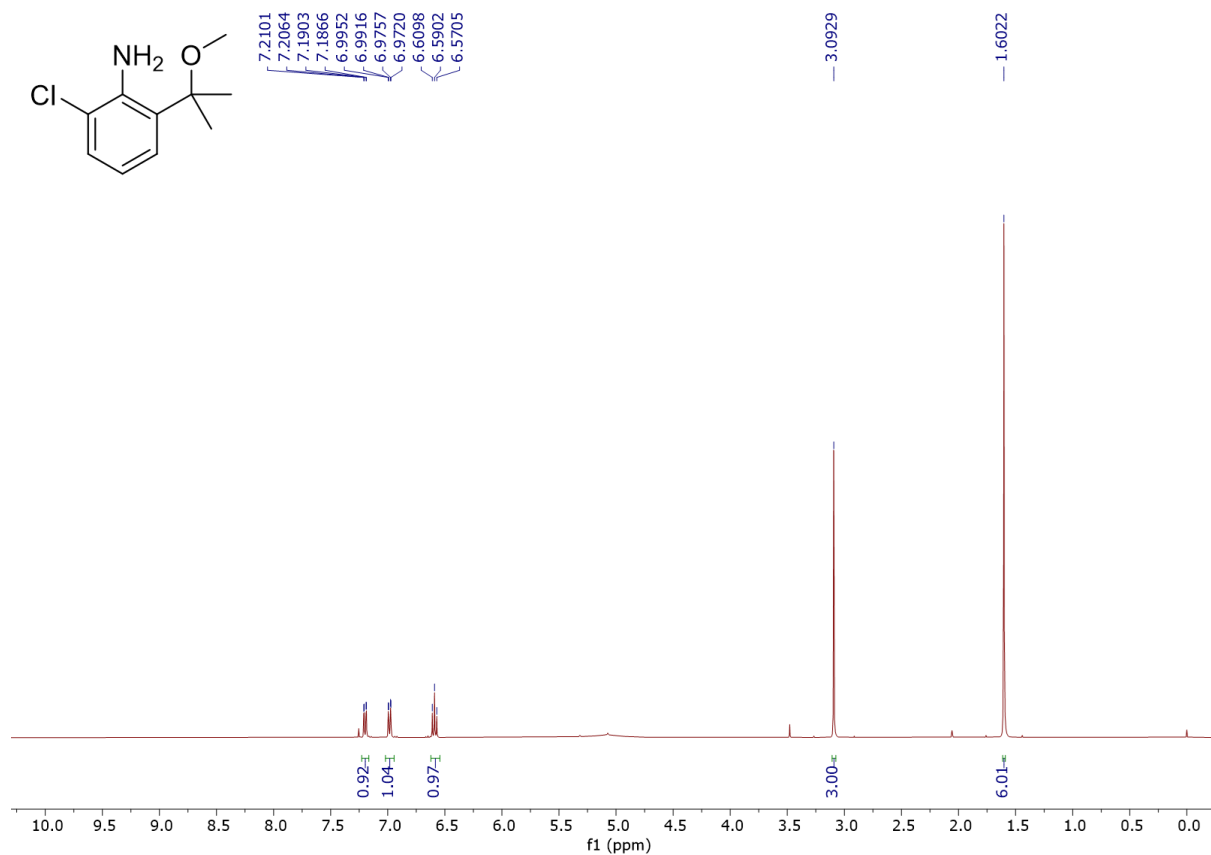
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¹³C NMR (101 MHz, CDCl₃)



¹H NMR (400 MHz, CDCl₃)



¹³C NMR (101 MHz, CDCl₃)

