Palladium(0)-Catalyzed Cyclopropane C-H Bond Functionalization: Synthesis of Quinoline and Tetrahydroquinoline Derivatives

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Supporting Information

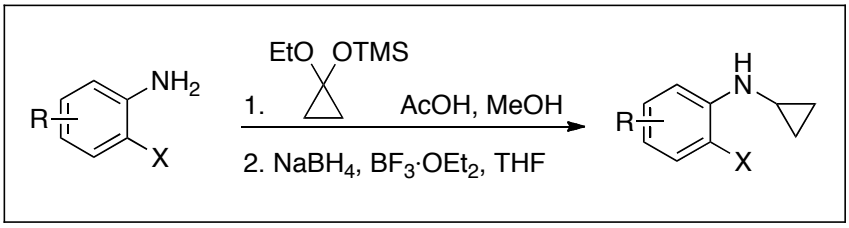
General Considerations

Reactions were set-up on the bench top and carried out under an argon atmosphere unless otherwise noted. HPLC Grade THF and toluene were dried and purified via solvent purification system. DCE was purchased from Aldrich in Sure-Seal bottles and used without further purification. Mesitylene was purchased from Aldrich, stored over molecular sieves and used without further purification. $Pd(OAc)_2$, $PCy_3{\cdot}HBF_4$, $PtBu_2Me{\cdot}HBF_4$, Cs_2CO_3 and CsOPiv were stored in a dessicator and were weighed to air. K_3PO_4, NaOtBu and KOtBu were stored in a glovebox and small quantities were removed prior to their use. Cyclopropylamine was distilled and stored under argon. All other reagents and solvents were used without further purification.

New compounds (starting materials and products) were characterized by ^1H NMR and ^{13}C NMR using 300 MHz or 400 MHz spectrometers. Copies of the ^1H and ^{13}C spectra can be found at the end of the supporting information. Spectra were calibrated according to residual solvent peaks ($CDCl_3$). ^{13}C NMR spectra were obtained with ^1H decoupling. For most starting materials, spectra were obtained at 55 °C (due to rotamers). IR spectra, melting point (when applicable) and, in most cases, HRMS were also obtained.

Synthesis and Characterization of Cyclopropylaniline Starting Materials

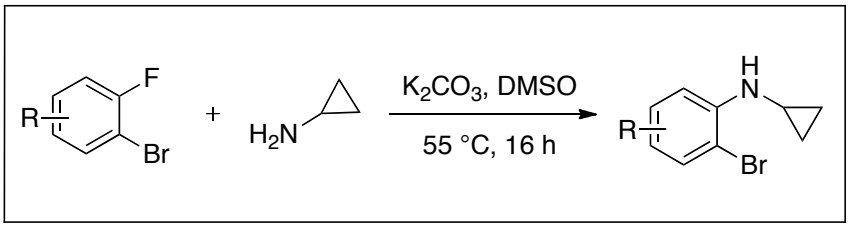
General Procedure A for the Preparation of *N*-Cyclopropylbenzenamines



Step 1. To a solution of the desired 2-haloaniline (1.00 equiv) in AcOH (3.00 equiv) and MeOH (1.5M) at room temperature under argon was added (1-ethoxycyclopropoxy)trimethylsilane (1.20 equiv) dropwise. The mixture was stirred at reflux for 24 h then concentrated under reduced pressure.

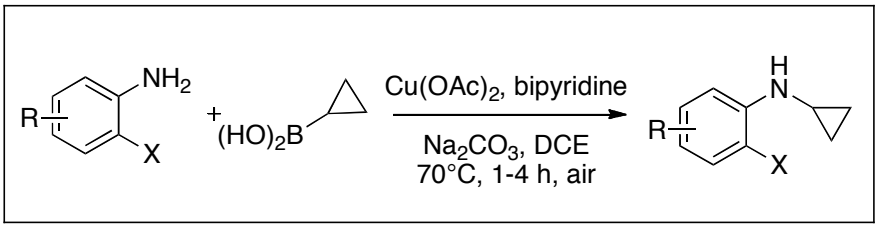
Step 2. To a solution of $NaBH_4$ (2.00 equiv) in THF (0.50 M) at 0 °C was added $BF_3{\cdot}OEt_2$ (2.00 equiv) dropwise. The resulting mixture was stirred for 1 h after which time the crude concentrated mixture from Step 1 was added dropwise as a solution in a minimal amount of THF. The solution was brought to room temperature and then stirred at reflux for 24 h. The reaction was quenched by the slow addition of H_2O and the crude product was extracted with Et_2O (x3), washed with brine, dried with $MgSO_4$ and concentrated under reduced pressure. The product was purified by silica gel flash chromatography.

General Procedure B for the Preparation of *N*-Cyclopropylbenzenamines



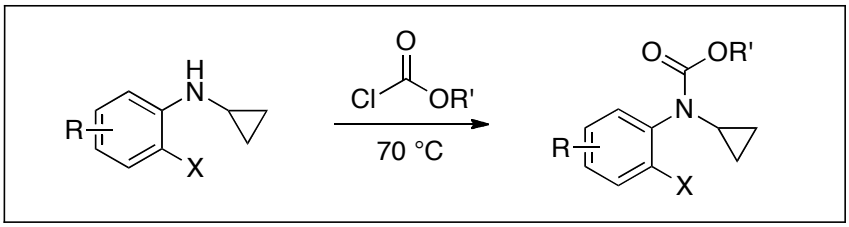
To a solution of the desired 1-bromo-2-fluoroarene (1.00 equiv) and K_2CO_3 (1.10 equiv) in DMSO (0.45 M) was added cyclopropylamine (3.00 equiv). The resulting mixture was heated at 55 °C for 16 h. The crude product was extracted with Et_2O (x3), washed with brine, dried with $MgSO_4$ and concentrated under reduced pressure. The product was purified by silica gel flash chromatography.

General Procedure C for the Preparation of *N*-Cyclopropylbenzenamines

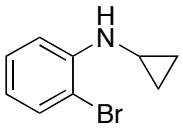


Prepared according to a literature procedure.[1] A solution of $Cu(OAc)_2$ (1.00 equiv) and bipyridine (1.00 equiv) in DCE (0.12 M) at 70 °C was added to a room temperature suspension of the desired 2-haloaniline (1.00 equiv), cyclopropylboronic acid (2.00 equiv) and Na_2CO_3 (2.00 equiv) in DCE (0.6 M). The mixture was heated at 70 °C until the reaction was judged to be complete by TLC (1-4 hours). After cooling to room temperature, an aqueous solution of NH_4OH (25%) was added. The organic layer was separated and the aqueous layer was extracted with DCM (x3). The combined organic layers were washed with brine, dried with $MgSO_4$ and concentrated under reduced pressure. The product was purified by silica gel flash chromatography.

General Procedure for the Protection of *N*-Cyclopropylbenzenamines

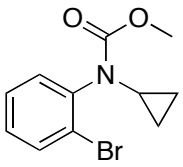


A solution of *N*-cyclopropylbenzenamine (1.00 equiv) in the desired chloroformate (0.4 M) was heated at 70 °C for 2.5 to 24 h (until judged complete by TLC). The reaction was slowly poured over H_2O and the crude product was extracted with $CHCl_3$ (x3), dried with $MgSO_4$ and concentrated under reduced pressure. The product was purified by silica gel flash chromatography.



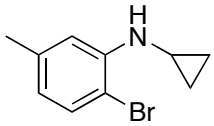
2-Bromo-*N*-cyclopropylbenzenamine *General procedure A for the preparation of N-cyclopropylbenzenamines* was followed using 2-bromoaniline (3.44 g, 20.0 mmol, 1.00 equiv). The product was purified by silica gel flash chromatography (100% petroleum ether) to afford 2.49 g (59% yield) of an orange oil.

^{1}H NMR (400 MHz, $CDCl_3$, 293K, TMS) δ 7.41 (dd, J = 7.9, 1.5 Hz, 1H), 7.21 (ddd, J = 8.1, 7.3, 1.4 Hz, 1H), 7.07 (dd, J = 8.1, 1.5 Hz, 1H), 6.61 (ddd, J = 7.6, 7.6, 1.5 Hz, 1H), 4.73 (br s, 1H), 2.45 (tt, J = 6.7, 3.4 Hz, 1H), 0.85-0.73 (m, 2H), 0.64-0.53 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$, 293K, TMS)** δ 145.7, 132.3, 128.4, 118.3, 112.8, 109.3, 25.3, 7.6. **HRMS** Calculated for $C_9H_{10}NBr$ (M^+) 210.9997, Found 210.9969. **IR (ν_{max}/cm^{-1})** 3400, 3287, 3072, 2971, 1499, 668 cm^{-1}. **R_f** 0.34 (100% petroleum ether).



Methyl 2-bromophenylcyclopropylcarbamate (1a) *General procedure for the protection of N-cyclopropylbenzenamines* was followed using 2-bromo-*N*-cyclopropylbenzenamine (1.27 g, 5.97 mmol, 1.00 equiv) and methyl chloroformate (15 mL, 0.40 M). The product was purified by silica gel flash chromatography (20% Et_2O in petroleum ether) to afford 1.42 g (88% yield) of a pale yellow oil.

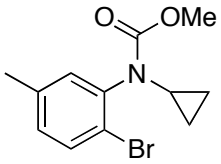
^{1}H NMR (400 MHz, $CDCl_3$, 293K, TMS) δ 7.61 (dd, J = 8.0, 1.4 Hz, 1H), 7.31 (ddd, J = 7.6, 7.6, 1.5 Hz, 1H), 7.16 (ddd, J = 7.9, 7.5, 1.7 Hz, 1H), 7.11 (br d, J = 7.7 Hz, 1H), 3.65 (br s, 3H), 3.15-3.09 (m, 1H), 0.74 (d, J = 5.8 Hz, 2H), 0.63-0.58 (m, 2H). **^{13}C NMR (75 MHz, $CDCl_3$, 328K, TMS)** δ 156.7, 141.1, 133.3, 130.4, 128.8, 128.2, 124.2, 53.0, 31.2, 7.6. **HRMS** Calculated for $C_{11}H_{12}NO_2Br$ (M^+) 271.0031, Found 271.0029. **IR (ν_{max}/cm^{-1})** 3091, 3013, 2953, 1720, 1340, 1212 cm^{-1}. **R_f** 0.23 (20% Et_2O in petroleum ether).



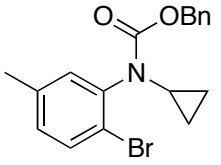
2-Bromo-*N*-cyclopropyl-5-methylbenzenamine *General procedure A for the preparation of N-cyclopropylbenzenamines* was followed using 2-bromo-5-methylaniline (0.67 mL, 5.4 mmol, 1.0 equiv). The product was purified by silica gel flash chromatography (100% petroleum ether) to afford 963 mg (66% yield) of an orange oil.

^{1}H NMR (400 MHz, $CDCl_3$, 293K, TMS) δ 7.27 (d, J = 8.0 Hz, 1H), 6.88 (dd, J = 2.1, 0.5 Hz, 1H), 6.44 (ddd, J = 8.0, 2.1, 0.6 Hz, 1H), 4.66 (br s, 1H), 2.43 (tt, J = 6.7, 3.4 Hz, 1H), 2.31 (s, 3H), 0.85-0.72 (m, 2H), 0.64-0.52 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$, 293K, TMS)** δ 145.4, 138.5, 132.0, 119.3,

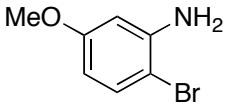
113.6, 106.2, 25.3, 21.7, 7.6. **HRMS** Calculated for $C_{10}H_{12}NBr$ (M^+) 225.0153, Found 225.0132. **IR (ν_{max}/cm^{-1})** 3410, 3008, 2972, 2921, 1598, 1502, 1305, 1017 cm^{-1}. **R_f** 0.60 (100% petroleum ether).



Methyl 2-bromo-5-methylphenylcyclopropylcarbamate (1b) *General procedure for the protection of N-cyclopropylbenzenamines* was followed using 2-bromo-*N*-cyclopropyl-5-methylbenzenamine (300 mg, 1.33 mmol, 1.00 equiv) and methyl chloroformate (3.3 mL, 0.40 M). The product was purified by silica gel flash chromatography (25% Et_2O in petroleum ether) to afford 291 mg (77% yield) of a clear oil. **^{1}H NMR (300 MHz, $CDCl_3$, 328K, TMS)** δ 7.46 (d, J = 8.1 Hz, 1H), 6.96 (d, J = 8.2 Hz, 1H), 6.93 (s, 1H), 3.70 (s, 3H), 3.15-3.08 (m, 1H), 2.31 (s, 3H), 0.75-0.71 (m, 2H), 0.65-0.58 (m, 2H). **^{13}C NMR (75 MHz, $CDCl_3$, 328K, TMS)** δ 156.7, 140.7, 138.4, 132.9, 131.0, 129.7, 120.7, 53.0, 31.3, 20.9, 7.6. **HRMS** Calculated for $C_{11}H_{11}NOBr$ (M^+ - OCH_3) 252.0024, Found 252.0027. **IR (ν_{max}/cm^{-1})** 3014, 2953, 1718, 1442, 1340, 1091, 1021 cm^{-1}. **R_f** 0.35 (30% Et_2O in petroleum ether).



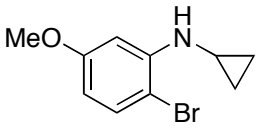
Benzyl 2-bromo-5-methylphenylcyclopropylcarbamate (1b') *General procedure for the protection of N-cyclopropylbenzenamines* was followed using 2-bromo-*N*-cyclopropyl-5-methylbenzenamine (300 mg, 1.33 mmol, 1.00 equiv) and benzyl chloroformate (3.3 mL, 0.40 M). The product was purified by silica gel flash chromatography (60% CH_2Cl_2 in petroleum ether) to afford 323 mg (68% yield) of a yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$, 328K, TMS)** δ 7.47 (d, J = 8.0 Hz, 1H), 7.32-7.23 (m, 5H), 6.98-6.93 (m, 2H), 5.18 (s, 2H), 3.20-3.12 (m, 1H), 2.30 (s, 3H), 0.77-0.61 (m, 4H). **^{13}C NMR (75 MHz, $CDCl_3$, 328K, TMS)** δ 156.2, 140.7, 138.4, 137.0, 132.9, 131.1, 129.8, 128.5, 127.9, 127.7, 120.7, 67.5, 31.2, 20.9, 7.7. **HRMS** Calculated for $C_{11}H_{11}NO_2Br$ (M^+ - $CH_2C_6H_5$) 267.9973, Found 267.9941. **IR (ν_{max}/cm^{-1})** 3033, 2959, 1717, 1477, 1329, 1088 cm^{-1}. **R_f** 0.32 (70% CH_2Cl_2 in petroleum ether).



2-Bromo-5-methoxybenzenamine Prepared according to a modified literature procedure.[2] To a mixture of concentrated HCl (0.15 M, 17 mL) and glacial acetic acid (0.15 M, 17 mL) at 0 °C was added 1-bromo-4-methoxy-2-nitrobenzene (600 mg, 2.59 mmol, 1.00 equiv). Zinc powder (4.31 g) was then added portionwise over 1h after which point the reaction mixture was stirred for an additional 15 minutes at 0 °C and then quenched by addition of concentrated ammonium hydroxide until slightly

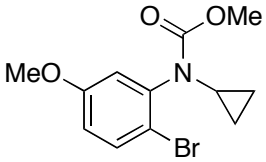
basic. The crude product was extracted with CH_2Cl_2 (x3), washed with brine, dried with $MgSO_4$ and concentrated under reduced pressure. The product was purified by silica gel flash chromatography (15% Et_2O in petroleum ether) to afford 522 mg (80% yield) of a brown oil.

^{1}H NMR (400 MHz, $CDCl_3$, 293K, TMS) δ 7.27 (d, J = 8.8 Hz, 1H), 6.33 (d, J = 2.8 Hz, 1H), 6.23 (dd, J = 8.8, 2.8 Hz, 1H), 3.89 (br s, 1H), 3.74 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$, 293K, TMS)** δ 160.0, 144.8, 132.9, 105.6, 101.3, 100.5, 55.4. **HRMS** Calculated for C_7H_8NOBr (M^+) 200.9789, Found 200.9773. **IR (ν_{max}/cm^{-1})** 3481, 3374, 3006, 2943, 1492, 1301, 1210 cm^{-1}. **R_f** 0.25 (15% Et_2O in petroleum ether).



2-Bromo-*N*-cyclopropyl-5-methoxybenzenamine *General procedure A for the preparation of N-cyclopropylbenzenamines* was followed using 2-bromo-5-methoxyaniline (400 mg, 1.98 mmol, 1.00 equiv). The product was purified by silica gel flash chromatography (3% Et_2O in petroleum ether) to afford 318 mg (66% yield) of a pale pink oil.

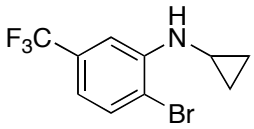
^{1}H NMR (400 MHz, $CDCl_3$, 293K, TMS) δ 7.28 (d, J = 8.7 Hz, 1H), 6.64 (d, J = 2.9 Hz, 1H), 6.20 (dd, J = 8.7, 2.9 Hz, 1H), 4.69 (br , 1H), 3.80 (s, 3H), 2.43 (tt, J = 6.7, 3.4 Hz, 1H), 0.81-0.72 (m, 2H), 0.64-0.55 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$, 293K, TMS)** δ 160.2, 146.6, 132.5, 103.3, 100.6, 99.5, 55.5, 25.2, 7.6. **HRMS** Calculated for C_9H_9NOBr (M^+ - CH_3) 227.9847, Found 227.9837. **IR (ν_{max}/cm^{-1})** 3397, 3091, 2961, 1600, 1215, 1016 cm^{-1}. **R_f** 0.47 (4% Et_2O in petroleum ether).



Methyl 2-bromo-5-methoxyphenylcyclopropylcarbamate (1c) *General procedure for the protection of N-cyclopropylbenzenamines* was followed using 2-bromo-*N*-cyclopropyl-5-methoxybenzenamine (200 mg, 0.826 mmol, 1.00 equiv) and methyl chloroformate (2.1 mL, 0.40 M). The product was purified by silica gel flash chromatography (40% Et_2O in petroleum ether) to afford 190 mg (77% yield) of a white solid.

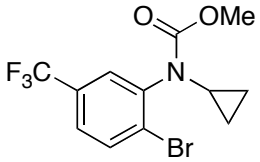
^{1}H NMR (300 MHz, $CDCl_3$, 328K, TMS) δ 7.47 (d, J = 8.8 Hz, 1H), 6.73 (dd, J = 8.8, 3.0 Hz, 1H), 6.67 (d, J = 3.0 Hz, 1H), 3.79 (s, 3H), 3.71 (s, 3H), 3.11 (tt, J = 7.1, 3.7 Hz, 1H), 0.76-0.72 (m, 2H), 0.67-0.61 (m, 2H). **^{13}C NMR (75 MHz, $CDCl_3$, 328K, TMS)** δ 159.7, 156.7, 141.8, 133.4, 116.4, 114.8, 114.7, 55.8, 53.1, 31.3, 7.7. **HRMS** Calculated for $C_{12}H_{14}NO_3Br$ (M^+) 301.0114, Found 301.0137. **IR (ν_{max}/cm^{-1})** 3012, 2954, 2838, 1718, 1593, 1340, 1230 cm^{-1}. **R_f** 0.18 (30% Et_2O in petroleum ether).

Melting point 64-66 ºC



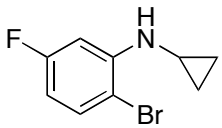
2-Bromo-*N*-cyclopropyl-5-(trifluoromethyl)benzenamine *General procedure A for the preparation of N-cyclopropylbenzenamines* was followed using 2-bromo-5-(trifluoromethyl)aniline (0.60 mL, 4.2 mmol, 1.0 equiv). The product was purified by silica gel flash chromatography (100% petroleum ether) to afford 710 mg (61% yield) of a clear oil.

^{1}H NMR (400 MHz, $CDCl_3$, 293K, TMS) δ 7.49 (dd, J = 8.2, 0.7 Hz, 1H), 7.24 (d, J = 2.0 Hz, 1H), 6.85-6.82 (m, 1H), 4.90 (br s, 1H), 2.51-2.45 (m, 1H), 0.88-0.79 (m, 2H), 0.62-0.58 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$, 293K, TMS)** δ 146.0, 132.6, 130.9 (q, J_F = 32.1 Hz), 124.3 (q, J_F = 271 Hz), 114.6 (q, J_F = 3.8 Hz), 112.5, 108.9 (q, J_F = 3.7 Hz), 25.1, 7.7. **HRMS** Calculated for $C_{10}H_9NBrF_3$ (M^+) 278.9870, Found 278.9861. **IR (ν_{max}/cm^{-1})** 3419, 3096, 3010, 2978, 1600, 1437, 1334, 1276, 1128, 1081 cm^{-1}. **R_f** 0.48 (100% petroleum ether).



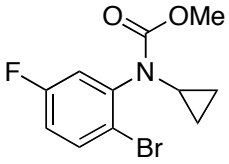
Methyl 2-bromo-5-(trifluoromethyl)phenylcyclopropylcarbamate (1d) *General procedure for the protection of N-cyclopropylbenzenamines* was followed using 2-bromo-*N*-cyclopropyl-5-(trifluoromethyl)benzenamine (550 mg, 1.96 mmol, 1.00 equiv) and methyl chloroformate (5.0 mL, 0.40 M). The product was purified by silica gel flash chromatography (15% Et_2O in petroleum ether) to afford 575 mg (87% yield) of a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$, 328K) δ 7.75 (d, J = 8.2 Hz, 1H), 7.41 (br d, J = 8.3 Hz, 1H), 7.39 (br s, 1H), 3.73 (br s, 3H), 3.14 (tt, J = 7.2, 3.8 Hz, 1H), 0.81-0.76 (m, 2H), 0.62 (br s, 2H). **^{13}C NMR (100 MHz, $CDCl_3$, 328K)** δ 156.1, 141.8, 133.9, 130.9 (q, J_F = 33.2 Hz), 128.2, 127.1 (q, J_F = 3.6 Hz), 125.3 (q, J_F = 3.7 Hz), 123.4 (q, J_F = 271 Hz), 53.0, 31.0, 7.7. **HRMS** Calculated for $C_{11}H_8NOBrF_3$ (M^+-OCH_3) 305.9741, Found 305.9757. **IR (ν_{max}/cm^{-1})** 3017, 2956, 1727, 1607, 1443, 1335, 1131, 1078, 1016, 822 cm^{-1}. **R_f** 0.21 (10% Et_2O in petroleum ether).



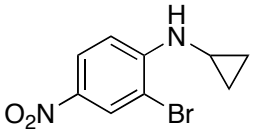
2-Bromo-*N*-cyclopropyl-5-fluorobenzenamine *General procedure A for the preparation of N-cyclopropylbenzenamines* was followed using 2-bromo-5-fluoroaniline (1.00 g, 5.26 mmol, 1.00 equiv). The product was purified by silica gel flash chromatography (100% petroleum ether) to afford 696 mg (57% yield) of a clear oil.

^{1}H NMR (400 MHz, $CDCl_3$, 293K, TMS) δ 7.32 (dd, J = 8.7, 6.0 Hz, 1H), 6.77 (dd, J = 11.3, 2.9 Hz, 1H), 6.33 (ddd, J = 8.7, 8.1, 2.9 Hz, 1H), 4.80 (br s, 1H), 2.45-2.40 (m, 1H), 0.87-0.75 (m, 2H), 0.65-0.53 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$, 293K, TMS)** δ 163.3 (d, J_F = 241 Hz), 147.1 (d, J_F = 11.2 Hz), 132.8 (d, J_F = 9.7 Hz), 104.9 (d, J_F = 23.2 Hz), 103.2 (d, J_F = 2.8 Hz), 100.1 (d, J_F = 27.6 Hz), 25.2, 7.6. **HRMS** Calculated for C_9H_9NBrF (M^+) 228.9902, Found 228.9891. **IR (ν_{max}/cm^{-1})** 3407, 3090, 3007, 2974, 1613, 1503, 1176, 1029 cm^{-1}. **R_f** 0.46 (100% petroleum ether).



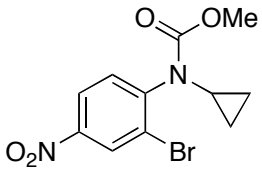
Methyl 2-bromo-5-fluorophenylcyclopropylcarbamate (1e) *General procedure for the protection of N-cyclopropylbenzenamines* was followed using 2-bromo-*N*-cyclopropyl-5-fluorobenzenamine (550 mg, 2.39 mmol, 1.00 equiv) and methyl chloroformate (6.0 mL, 0.40 M). The product was purified by silica gel flash chromatography (15% Et_2O in petroleum ether) to afford 586 mg (85% yield) of a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$, 328K) δ 7.55 (dd, J = 8.7, 5.8 Hz, 1H), 6.93-6.87 (m, 2H), 3.71 (br s, 3H), 3.11 (tt, J = 7.1, 3.8 Hz, 1H), 0.78-0.75 (m, 2H), 0.62 (br s, 2H). **^{13}C NMR (100 MHz, $CDCl_3$, 328K)** δ 161.9 (d, J_F = 247 Hz), 156.2, 147.1 (d, J_F = 9.8 Hz), 133.8 (d, J_F = 8.7 Hz), 118.5 (d, J_F = 3.8 Hz), 117.6 (d, J_F = 22.6 Hz), 115.9 (d, J_F = 22.1 Hz), 53.0, 31.0, 7.6. **HRMS** Calculated for $C_{10}H_8NO_2BrF$ (M^+ - CH_3) 271.9722, Found 271.9727. **IR (ν_{max}/cm^{-1})** 3010, 2955, 1724, 1474, 1442, 1339, 1219, 1084 cm^{-1}. **R_f** 0.18 (10% Et_2O in petroleum ether).



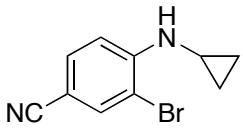
2-Bromo-*N*-cyclopropyl-4-nitrobenzenamine *General procedure B for the preparation of N-cyclopropylbenzenamines* was followed using 2-bromo-1-fluoro-4-nitrobenzene (1.00 g, 4.55 mmol, 1.00 equiv). The product was purified by silica gel flash chromatography (10% Et_2O in petroleum ether) to afford 1.05 g (90% yield) of a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$, 293K, TMS) δ 8.34 (d, J = 2.5 Hz, 1H), 8.12 (dd, J = 9.1, 2.5 Hz, 1H), 7.02 (d, J = 9.1 Hz, 1H), 5.39 (br s, 1H), 2.56 (ttd, J = 6.8, 3.4, 1.3 Hz, 1H), 0.95-0.90 (m, 2H), 0.67-0.63 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$, 293K, TMS)** δ 150.8, 138.4, 128.7, 125.2, 110.7, 107.5, 25.2, 7.9. **HRMS** Calculated for $C_9H_9N_2O_2Br$ (M^+) 257.9827, Found 257.9889. **IR (ν_{max}/cm^{-1})** 3391, 3086, 1593, 1323 cm^{-1}. **R_f** 0.24 (10% Et_2O in petroleum ether). **Melting point** 91 ºC



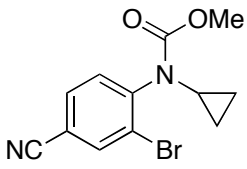
Methyl 2-bromo-4-nitrophenylcyclopropylcarbamate (1f) *General procedure for the protection of N-cyclopropylbenzenamines* was followed using 2-bromo-*N*-cyclopropyl-4-nitrobenzenamine (800 mg, 3.11 mmol, 1.00 equiv) and methyl chloroformate (8.0 mL, 0.40 M). The product was purified by silica gel flash chromatography (gradient from 20% to 30% EtOAc in petroleum ether) to afford 358 mg (37% yield) of a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$, 293K, TMS) δ 8.49 (d, J = 2.5 Hz, 1H), 8.19 (dd, J = 8.7, 2.6 Hz, 1H), 7.32 (d, J = 8.7 Hz, 1H), 3.72 (br s, 3H), 3.13 (tt, J = 7.0, 3.6 Hz, 1H), 0.82-0.80 (m, 2H), 0.59 (br s, 2H). **^{13}C NMR (75 MHz, $CDCl_3$, 293K, TMS)** δ 155.8, 147.2, 147.1, 130.6, 128.8, 124.7, 123.3, 53.4, 31.2, 8.1. **HRMS** Calculated for $C_{10}H_8N_2O_3Br$ (M^+ - OCH_3) 284.9698, Found 284.9680. **IR (ν_{max}/cm^{-1})** 3099, 3014, 295, 1729, 1527, 1345 cm^{-1}. **R_f** 0.24 (20% EtOAc in petroleum ether). **Melting point** 87-89 °C



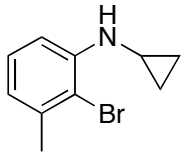
3-Bromo-4-(cyclopropylamino)benzonitrile *General procedure B for the preparation of N-cyclopropylbenzenamines* was followed using 3-bromo-4-fluorobenzonitrile (1.00 g, 4.55 mmol, 1.00 equiv). The product was purified by silica gel flash chromatography (10% Et_2O in petroleum ether) to afford 0.954 g (89% yield) of a white solid.

^{1}H NMR (400 MHz, $CDCl_3$, 293K, TMS) δ 7.64 (s, 1H), 7.46 (d, J = 8.5 Hz, 1H), 7.03 (d, J = 8.5 Hz, 1H), 5.18 (br s, 1H), 2.52-2.47 (m, 1H), 0.93-0.81 (m, 2H), 0.67-0.55 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$, 293K, TMS)** δ 149.1, 135.7, 132.8, 119.1, 112.1, 108.3, 100.3, 24.9, 7.8. **HRMS** Calculated for $C_{10}H_9N_2Br$ (M^+) 235.9949, Found 235.9924. **IR (ν_{max}/cm^{-1})** 3404, 3091, 3007, 2221, 1596, 1334, 1192, 815 cm^{-1}. **R_f** 0.28 (10% Et_2O in petroleum ether). **Melting point** 100-101 °C



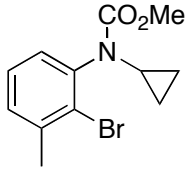
Methyl 2-bromo-4-cyanophenylcyclopropylcarbamate (1g) *General procedure for the protection of N-cyclopropylbenzenamines* was followed using 3-bromo-4-(cyclopropylamino)benzonitrile (700 mg, 2.95 mmol, 1.00 equiv) and methyl chloroformate (7.0 mL, 0.40 M). The product was purified by silica gel flash chromatography (25% EtOAc in petroleum ether) to afford 674 mg (77% yield) of a white solid.

^{1}H NMR (400 MHz, $CDCl_3$, 293K, TMS) δ 7.92 (d, J = 1.8 Hz, 1H), 7.63 (dd, J = 8.1, 1.9 Hz, 1H), 7.26 (d, J = 8.4 Hz, 1H), 3.71 (br s, 3H), 3.11 (tt, J = 7.1, 3.6 Hz, 1H), 0.81-0.79 (m, 2H), 0.57 (br s, 2H). **^{13}C NMR (75 MHz, $CDCl_3$, 328K, TMS)** δ 155.9, 145.7, 136.9, 131.9, 131.0, 124.9, 116.9, 112.9, 53.3, 31.2, 30.9, 8.0. **HRMS** Calculated for $C_{11}H_8N_2OBr$ (M^+ - OCH_3) 264.9800, Found 264.9767. **IR (ν_{max}/cm^{-1})** 3529, 3096, 3014, 2955, 2233, 1725, 1442, 1340, 1214, 534 cm^{-1}. **R_f** 0.28 (25% EtOAc in petroleum ether).



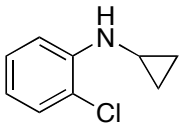
2-Bromo-*N*-cyclopropyl-3-methylaniline *General procedure C for the preparation of N-cyclopropylbenzenamines* was followed using 2-bromo-3-methylaniline (0.37 mL, 3.0 mmol, 1.0 equiv). The product was purified by silica gel flash chromatography (100% hexanes) to afford 350 mg (52% yield) of a clear oil.

^{1}H NMR (400 MHz, $CDCl_3$, 293K) δ 7.09 (dd, J = 7.8, 7.8 Hz, 1H), 6.91 (d, J = 8.0 Hz, 1H), 6.62 (d, J = 7.4 Hz, 1H), 4.89 (br s, 1H), 2.45-2.40 (m, 1H), 2.35 (s, 3H), 0.78-0.70 (m, 2H), 0.62-0.56 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$, 293K)** δ 145.8, 138.2, 127.5, 119.4, 111.9, 110.1, 25.4, 23.6, 7.5. **IR (ν_{max}/cm^{-1})** 3404, 2922, 1595, 1469, 1323, 1016, 766 cm^{-1}. **R_f** 0.36 (100% hexanes).



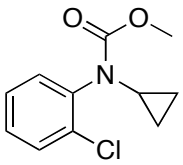
Methyl (2-bromo-3-methylphenyl)(cyclopropyl)carbamate (1h) *General procedure for the protection of N-cyclopropylbenzenamines* was followed using 2-bromo-*N*-cyclopropyl-3-methylaniline (590 mg, 2.61 mmol, 1.00 equiv) and methyl chloroformate (5.2 mL, 0.50 M). The product was purified by silica gel flash chromatography (10% EtOAc in hexanes) to afford 632 mg (85% yield) of a white solid.

^{1}H NMR (400 MHz, $CDCl_3$, 328K) δ 7.22-7.16 (m, 2H), 6.94 (dd, J = 6.8, 2.6 Hz, 1H), 3.70 (br s, 3H), 3.15 (tt, J = 7.2, 3.8 Hz, 1H), 2.46 (s, 3H), 0.78-0.68 (m, 2H), 0.65-0.60 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$, 328K)** δ 156.7, 141.1, 139.6, 129.6, 127.6, 127.2, 126.7, 52.8, 31.0, 23.7, 7.4. **IR (ν_{max}/cm^{-1})** 3013, 2953, 1722, 1469, 1442, 1340, 1217, 1087, 550 cm^{-1}. **R_f** 0.18 (10% EtOAc in hexanes). **Melting point** 66-68 °C



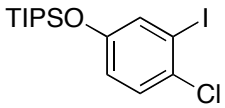
2-Chloro-*N*-cyclopropylbenzenamine *General procedure A for the preparation of N-cyclopropylbenzenamines* was followed using 2-chloroaniline (2.1 mL, 20 mmol, 1.0 equiv). The product was purified by silica gel flash chromatography (100% petroleum ether) to afford 2.0 g (60% yield) of a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$, 293K, TMS) δ 7.23 (dd, J = 7.9, 1.5 Hz, 1H), 7.16 (ddd, J = 8.1, 7.3, 1.5 Hz, 1H), 7.08 (dd, J = 8.1, 1.6 Hz, 1H), 6.66 (ddd, J = 7.6, 7.6, 1.6 Hz, 1H), 4.72 (s, 1H), 2.44 (tt, J = 6.7, 3.4 Hz, 1H), 0.84-0.71 (m, 2H), 0.63-0.51 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$, 293K, TMS)** δ 144.7, 129.1, 127.8, 118.9, 117.8, 112.7, 25.1, 7.6. **HRMS** Calculated for $C_9H_{10}NCl$ (M^+) 167.0502, Found 167.0500. **IR (ν_{max}/cm^{-1})** 3408, 3288, 2957, 2898, 1595, 1036, 747cm^{-1}. **R_f** 0.35 (100% petroleum ether).



Methyl 2-chlorophenylcyclopropylcarbamate (1i) *General procedure for the protection of N-cyclopropylbenzenamines* was followed using 2-chloro-*N*-cyclopropylbenzenamine (175 mg, 1.04 mmol, 1.00 equiv) and methyl chloroformate (4.7 mL, 0.22 M). The product was purified by silica gel flash chromatography (20% Et_2O in petroleum ether) to afford 219 mg (93% yield) of a pale yellow oil.

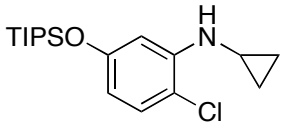
^{1}H NMR (400 MHz, $CDCl_3$, 328K, TMS) δ 7.48-7.44 (m, 1H), 7.32-7.22 (m, 2H), 7.17-7.13 (m, 1H), 3.73 (s, 3H), 3.15 (tt, J = 7.1, 3.6 Hz, 1H), 0.81-0.74 (m, 2H), 0.65-0.59 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$, 293K, TMS)** δ 156.8, 139.2, 133.3, 130.1, 130.0, 128.5, 127.4, 53.0, 31.0, 7.5. **HRMS** Calculated for $C_{10}H_9NOCl$ (M^+ - OCH_3) 194.0373, Found 194.0354. **IR (ν_{max}/cm^{-1})** 3100, 3018, 2956, 1719, 1442, 1341, 753 cm^{-1}. **R_f** 0.30 (20% Et_2O in petroleum ether).



(4-Chloro-3-iodophenoxy)triisopropylsilane To a solution of 4-chloro-2-iodophenol (1.00 g, 3.93 mmol, 1.00 equiv) and imidazole (401 mg, 5.90 mmol, 1.50 equiv) in DMF (20 mL, 0.20 M) at room temperature was added triisopropylsilyl chloride (1.7 mL, 7.9 mmol, 2.0 equiv) via syringe. The resulting solution was stirred at room temperature for four hours. The crude reaction mixture was then diluted with H_2O and extracted with Et_2O (x3). The combined organic layers were washed with brine, dried with $MgSO_4$ and concentrated under reduced pressure. The product was purified by silica gel flash chromatography (gradient 0 to 5% EtOAc in hexanes) to afford 1.49 g (93% yield) of a clear oil.

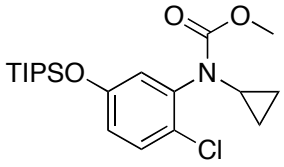
^{1}H NMR (400 MHz, $CDCl_3$, 293K) δ 7.36 (d, J = 2.8 Hz, 1H), 7.23 (d, J = 8.7 Hz, 1H), 6.77 (dd, J = 8.7, 2.8 Hz, 1H), 1.26-1.17 (m, 3H), 1.07 (d, J = 6.8 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$,**

293K) δ 154.9, 131.3, 130.3, 129.1, 120.9, 97.7, 17.8, 12.6. **IR (ν_{max}/cm^{-1})** 3063, 2946, 2867, 1579, 1461, 1283, 1230, 932, 883, 686 cm^{-1}. **R$_f$** 0.60 (100% hexanes).



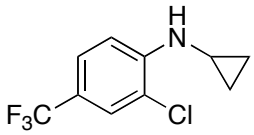
2-Chloro-N-cyclopropyl-5-((triisopropylsilyl)oxy)aniline An oven-dried test tube equipped with a magnetic stir bar and a teflon septum was charged with BrettPhos Palladacycle Precatalyst[3] (24.3 mg, 0.0304 mmol, 1.00 mol%), BrettPhos[3] (16.3 mg, 0.0304 mmol, 1.00 mol%) and NaOtBu (351 mg, 3.65 mmol, 1.2 equiv). The test tube was evacuated and backfilled with argon (x3). (4-Chloro-3-iodophenoxy)triisopropylsilane (1.25g, 3.04 mmol, 1.00 equiv) was then added as a solution in toluene (3.0 mL, 1.0 M) followed by cyclopropylamine (0.25 mL, 3.7 mmol, 1.2 equiv). The resulting mixture was stirred at room temperature for 12 hours after which point it was diluted with EtOAc. After addition of H_2O, the organic layer was separated and the aqueous layer was extracted with EtOAc (x3). The combined organic layers were washed with brine, dried with $MgSO_4$ and concentrated under reduced pressure. The product was purified by silica gel flash chromatography (gradient 0 to 2% EtOAc in hexanes) to afford 508 mg (49% yield) of a yellow oil.

^{1}H NMR (400 MHz, CDCl$_3$, 293K) δ 7.04 (d, J = 8.6 Hz, 1H), 6.66 (d, J = 2.8 Hz, 1H), 6.22 (dd, J = 8.5, 2.8 Hz, 1H), 4.64 (br s, 1H), 2.44-2.38 (m, 1H), 1.31-1.22 (m, 3H), 1.12 (d, J = 7.0 Hz, 18H), 0.83-0.70 (m, 2H), 0.63-0.55 (m, 2H). **^{13}C NMR (100 MHz, CDCl$_3$, 293K)** δ 155.8, 145.2, 129.0, 110.9, 109.4, 104.6, 24.9, 17.9, 12.7, 7.3. **IR (ν_{max}/cm^{-1})** 3417, 3089, 2945, 2867, 1599, 1505, 1464, 1426, 1308, 1196, 1009, 883, 686 cm^{-1}. **R$_f$** 0.27 (100% hexanes).



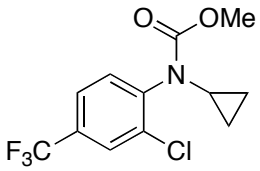
Methyl (2-chloro-5-((triisopropylsilyl)oxy)phenyl)(cyclopropyl)carbamate (1j) *General procedure for the protection of N-cyclopropylbenzenamines* was followed using 2-chloro-*N*-cyclopropyl-5-((triisopropylsilyl)oxy)aniline (450 mg, 1.32 mmol, 1.00 equiv) and methyl chloroformate (3.0 mL, 0.44 M). The product was purified by silica gel flash chromatography (10% EtOAc in hexanes) to afford 398 mg (76% yield) of a clear oil.

^{1}H NMR (400 MHz, CDCl$_3$, 328K) δ 7.24 (d, J = 8.8 Hz, 1H), 6.77 (dd, J = 8.7, 2.8 Hz, 1H), 6.65 (d, J = 2.8 Hz, 1H), 3.69 (br s, 3H), 3.10 (tt, J = 7.2, 3.8 Hz, 1H), 1.29-1.20 (m, 3H), 1.11 (d, J = 7.1 Hz, 18H), 0.77-0.72 (m, 2H), 0.61-0.57 (m, 2H). **^{13}C NMR (100 MHz, CDCl$_3$, 328K)** δ 156.6, 155.3, 139.7, 130.0, 125.2, 121.9, 120.1, 52.8, 31.0, 17.8, 12.7, 7.3. **IR (ν_{max}/cm^{-1})** 2947, 2868, 1728, 1595, 1480, 1337, 1259 cm^{-1}. **R$_f$** 0.32 (10% EtOAc in hexanes).



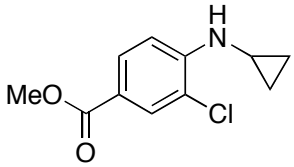
2-Chloro-*N*-cyclopropyl-4-(trifluoromethyl)benzenamine *General procedure A for the preparation of N-cyclopropylbenzenamines* was followed using 2-chloro-4-(trifluoromethyl)aniline (0.57 mL, 4.1 mmol, 1.0 equiv). The product was purified by silica gel flash chromatography (100% petroleum ether) to afford 0.56 mg (29% yield) of a clear oil.

^{1}H NMR (400 MHz, $CDCl_3$, 293K, TMS) δ 7.31 (dd, J = 8.2, 0.7 Hz, 1H), 7.26 (d, J = 2.6 Hz, 1H), 6.91 (ddt, J = 8.2, 1.4, 0.7 Hz, 1H), 4.88 (br s, 1H), 2.47 (tt, J = 6.7, 3.4 Hz, 1H), 0.87-0.82 (m, 2H), 0.61-0.57 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$, 293K, TMS)** δ 145.0, 130.2 (q, J_F = 32 Hz), 129.3, 124.2 (q, J_F = 270 Hz), 122.0, 114.2 (q, J_F = 4.2 Hz), 108.9 (q, J_F = 4.1 Hz), 24.9, 7.7. **HRMS** Calculated for $C_{10}H_9NF_3Cl$ (M^+) 235.0376, Found 235.0353. **IR (ν_{max}/cm^{-1})** 3422, 3097, 2981, 1511, 1278 cm^{-1}. **R_f** 0.39 (100% petroleum ether).



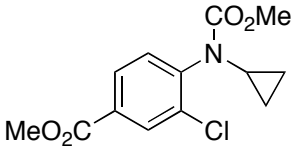
Methyl 2-chloro-4-(trifluoromethyl)phenylcyclopropylcarbamate (1k) *General procedure for the protection of N-cyclopropylbenzenamines* was followed using 2-chloro-*N*-cyclopropyl-4-(trifluoromethyl)benzenamine (450 mg, 1.91 mmol, 1.00 equiv) and methyl chloroformate (3.8 mL, 0.50 M). The product was purified by silica gel flash chromatography (10% Et_2O in petroleum ether) to afford 350 mg (62% yield) of a clear oil.

^{1}H NMR (400 MHz, $CDCl_3$, 293K, TMS) δ 7.56 (d, J = 8.4 Hz, 1H), 7.51-7.48 (m, 1H), 7.40 (br s, 1H), 3.70 (br s, 3H), 3.10 (tt, J = 7.1, 3.6 Hz, 1H), 0.80-0.77 (m, 2H), 0.61-0.55 (m, 2H). **^{13}C NMR (75 MHz, $CDCl_3$, 328K, TMS)** δ 156.5, 140.4, 137.6, 130.8, 130.4 (q, J_F = 33 Hz), 127.4 (q, J_F = 3.6 Hz), 125.3 (q, J_F = 4.0 Hz), 123.5 (q, J_F = 271 Hz), 53.3, 31.2, 8.0. **HRMS** Calculated for $C_{11}H_8NOF_3Cl$ (M^+ - OCH_3) 264.0217, Found 264.0204. **IR (ν_{max}/cm^{-1})** 3024, 2958, 1727, 1646, 1336, 1131 cm^{-1}. **R_f** 0.25 (10% Et_2O in petroleum ether).



Methyl 3-chloro-4-(cyclopropylamino)benzoate *General procedure C for the preparation of N-cyclopropylbenzenamines* was followed using methyl 4-amino-3-chlorobenzoate (742 mg, 4.00 mmol, 1.00 equiv). The product was purified by silica gel flash chromatography (10% EtOAc in hexanes) to afford 427 mg (47% yield) of a white solid.

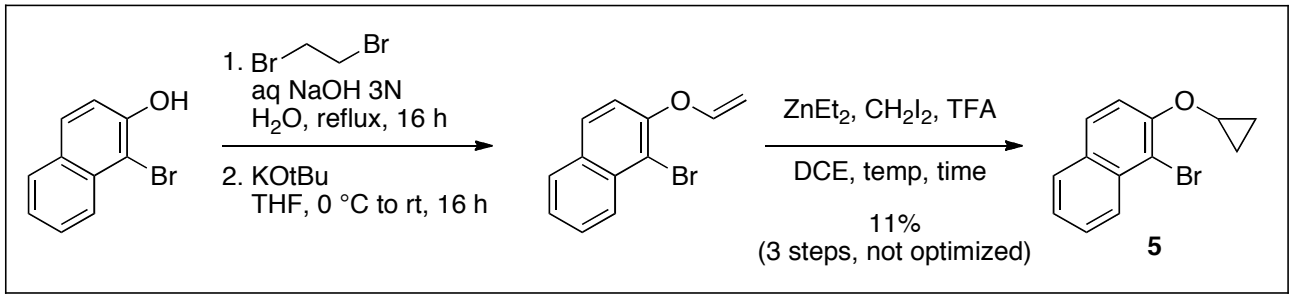
^{1}H NMR (400 MHz, $CDCl_3$, 293K) δ 7.91 (d, J = 2.0 Hz, 1H), 7.83 (dd, J = 8.6, 2.0 Hz, 1H), 7.02 (d, J = 8.6 Hz, 1H), 5.08 (br s, 1H), 3.84 (s, 3H), 2.52-2.47 (m, 1H), 0.86-0.81 (m, 2H), 0.61-0.57 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$, 293K)** δ 166.4, 148.2, 130.5, 129.8, 119.2, 118.0, 111.3, 51.8, 24.7, 7.6. **IR (ν_{max}/cm^{-1})** 3411, 3374, 3090, 2992, 2950, 1712, 1603, 1281, 1114, 764 cm^{-1}. **R_f** 0.26 (10% EtOAc in hexanes). **Melting point** 51-52 °C

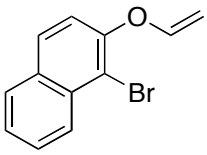


Methyl 3-chloro-4-(cyclopropyl(methoxycarbonyl)amino)benzoate (1l) *General procedure for the protection of N-cyclopropylbenzenamines* was followed using methyl 3-chloro-4-(cyclopropylamino)benzoate (563 mg, 2.50 mmol, 1.00 equiv) and methyl chloroformate (5.0 mL, 0.50 M). The product was purified by silica gel flash chromatography (20% EtOAc in hexanes) to afford 472 mg (67% yield) of a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$, 328K) δ 8.09 (d, J = 2.0 Hz, 1H), 7.92 (dd, J = 8.2, 1.9 Hz, 1H), 7.20 (d, J = 8.2 Hz, 1H), 3.92 (s, 3H), 3.70 (br s, 3H), 3.14-3.08 (m, 1H), 0.78-0.69 (m, 2H), 0.63-0.55 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$, 328K)** δ 165.3, 156.2, 143.4, 133.6, 131.3, 130.5, 130.0, 128.5, 52.9, 52.3, 30.9, 7.6. **IR (ν_{max}/cm^{-1})** 3093, 3014, 2955, 2852, 1726, 1339, 1288, 760 cm^{-1}. **R_f** 0.19 (20% EtOAc in hexanes). **Melting point** 78-79 °C

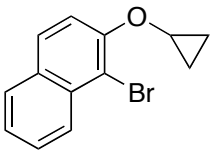
Synthesis and Characterization of Starting Materials 5, 7a, 8 and 10





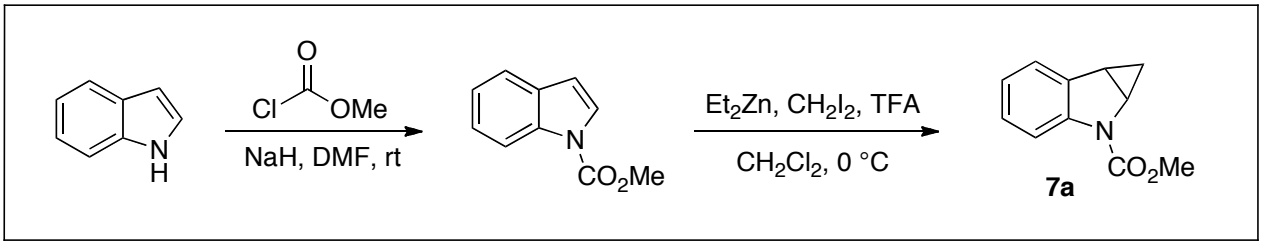
1-Bromo-2-(vinyloxy)naphthalene. Prepared according to a modified literature procedure.[4] A solution of 1-bromonaphthalen-2-ol (5.59 g, 24.0 mmol, 1.00 equiv) and 1,2-dibromoethane (3.1 mL, 36 mmol, 1.5 equiv) in water (20 mL) was stirred under reflux for 30 min. A 3N aqueous solution of sodium hydroxide (10.4 mL, 31.2 mmol, 1.30 equiv) was then added dropwise via an addition funnel.

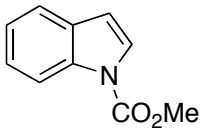
The reaction mixture was then stirred at reflux for 16 h, cooled to room temperature, extracted with CH_2Cl_2, washed with water and brine, dried with $MgSO_4$ and concentrated under reduced pressure. The resulting crude product was then dissolved in dry THF (20 mL) and slowly added via syringe to a solution of potassium *tert*-butoxide (2.69 g, 24.0 mmol, 1.00 equiv) in THF (60 mL) at 0 °C under argon. The reaction mixture was stirred at room temperature for 16 h, quenched with water, extracted with EtOAc, washed with water and brine, dried with $MgSO_4$ and concentrated under reduced pressure. The residue was passed over a plug of silica gel to provide 1.1 g of crude 1-bromo-2-(vinyloxy)naphthalene (Rf = 0.39, 100% petroleum ether).



1-Bromo-2-cyclopropoxynaphthalene (5) To a solution of diethylzinc (1M in hexanes, 8.0 mL, 8.0 mmol, 2.0 equiv) in dichloroethane (20 mL) at -5 °C under argon was added dropwise, and very slowly, a solution of trifluoroacetic acid (592 μL, 8.00 mmol, 2.00 equiv) in dichloroethane (10 mL). The reaction mixture was stirred for 20 min then a solution of diiodomethane (643 μL, 8.00 mmol, 2.00 equiv) in dichloroethane (10 mL) was added dropwise. The reaction mixture was again stirred for 20 min then a solution of 1-bromo-2-(vinyloxy)naphthalene (1.00 g, 4.00 mmol, 1.00 equiv) in dichloroethane (10 mL) was added dropwise. The mixture was allowed to warm to room temperature and then stirred until the reaction was judged to be complete by TLC. The reaction was then quenched at 0 °C by addition of a saturated solution of NH_4Cl (stir for 1 h). The crude product was then extracted with CH_2Cl_2, washed with water and brine, dried with $MgSO_4$, concentrated under reduced pressure and purified by silica gel flash chromatography to give 613 mg of **5**.

^{1}H NMR (400 MHz, $CDCl_3$, 293K, TMS) δ 8.21 (dd, J = 8.6, 0.8 Hz, 1H), 7.79 (dd, J = 9.1, 9.1 Hz, 2H), 7.60 (d, J = 9.0 Hz, 1H), 7.55 (ddd, J = 8.5, 7.0, 1.4 Hz, 1H), 7.39 (ddd, J = 8.1, 6.9, 1.2 Hz, 1H), 3.99-3.94 (m, 1H), 0.95-0.90 (m, 2H), 0.89-0.83 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$, 293K, TMS)** δ 153.4, 133.1, 129.9, 128.6, 128.0, 127.6, 126.1, 124.3, 115.3, 108.4, 52.5, 6.7. **HRMS** Calculated for $C_{13}H_{11}OBr$ (M^+) 261.9993, Found 261.9988. **R_f** 0.44 (5% Et_2O in petroleum ether).

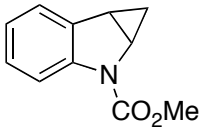




Methyl 1H-indole-1-carboxylate Prepared according to a literature procedure.[5] To a solution of indole (1.17 g, 10.0 mmol, 1.00 equiv) in DMF (33 mL, 0.30 M) at room temperature under an atmosphere of argon was added NaH (0.505 g, 20.0 mmol, 2.00 equiv). The resulting mixture was stirred at room temperature for 30 min after which point methyl chloroformate (1.16 mL, 15.0 mmol, 1.50 equiv) was added via syringe. The mixture was allowed to stir until the reaction was judged to be complete by TLC. The reaction was quenched by the slow addition of H_2O. The crude product was extracted with EtOAc (x3), washed with brine, dried with $MgSO_4$ and concentrated under reduced pressure. The product was purified by silica gel flash chromatography (5% EtOAc in hexanes) to afford 1.52 g (87% yield) of a clear oil.

^{1}H NMR (400 MHz, $CDCl_3$, 293K) δ 8.21 (d, J = 7.6 Hz, 1H), 7.62 (d, J = 3.6 Hz, 1H), 7.59 (dd, J = 7.8, 0.6 Hz, 1H), 7.36 (dd, J = 7.8, 7.8 Hz, 1H), 7.27 (ddd, J = 7.5, 7.5, 0.4 Hz, 1H), 6.62 (d, J = 3.7 Hz, 1H), 4.06 (s, 3H).

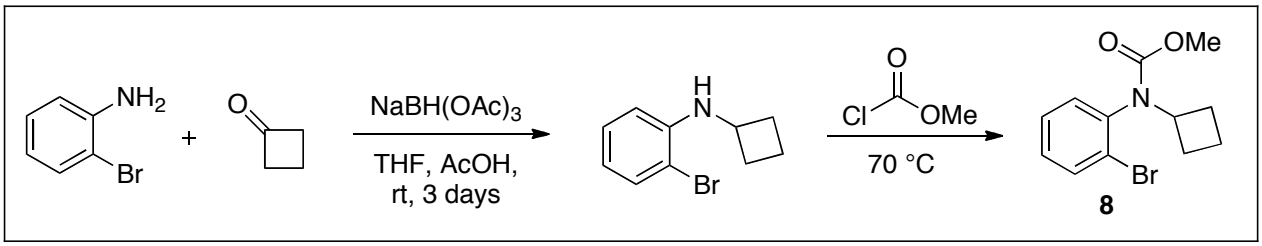
Exhibited spectral data identical to a previous report.[6]

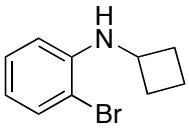


Methyl 1,6b-dihydrocyclopropa[b]indole-2(1aH)-carboxylate (7a) To a solution of diethylzinc (1M in hexanes, 5.0 mL, 5.0 mmol, 2.0 equiv) in dichloromethane (5.0 mL) at 0 °C under argon was added dropwise, and very slowly, a solution of trifluoroacetic acid (0.37 mL, 5.0 mmol, 2.0 equiv) in dichloromethane (2.5 mL). The reaction mixture was stirred for 20 min then a solution of diiodomethane (0.40 mL, 5.0 mmol, 2.0 equiv) in dichloromethane (2.5 mL) was added dropwise. The reaction mixture was again stirred for 20 min then a solution of methyl 1H-indole-1-carboxylate (0.438 g, 2.50 mmol, 1.00 equiv) in dichloromethane (2.5 mL) was added dropwise. The mixture was allowed to warm to room temperature and then stirred until the reaction was judged to be complete by TLC. The reaction was then quenched at 0 °C by addition of a saturated solution of NH_4Cl (stir for 30 min). The crude product was then extracted with CH_2Cl_2 (x3), washed with water and brine, dried with $MgSO_4$, concentrated under reduced pressure and purified by silica gel flash chromatography (50% CH_2Cl_2 in hexanes) to give 180 mg (38% yield) of a white solid.

^{1}H NMR (400 MHz, $CDCl_3$, 293K) δ 7.86 (br s, 1H), 7.32 (d, J = 7.5 Hz, 1H), 7.18 (dd, J = 7.7, 7.7 Hz, 1H), 6.98 (ddd, J = 7.5, 7.5, 1.1 Hz, 1H), 4.18 (br s, 1H), 3.90 (br s, 3H), 2.65 (ddd, J = 8.6, 6.6, 4.0 Hz, 1H), 1.09-1.07 (m, 1H), 0.29-0.28 (m, 1H).

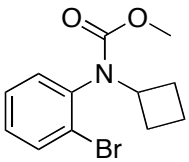
Exhibited spectral data identical to a previous report.[7]





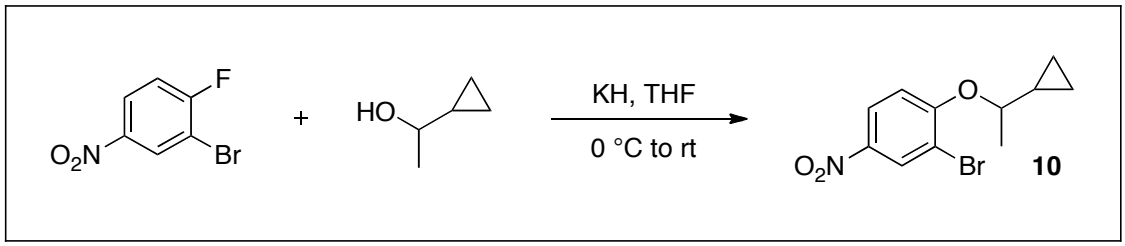
2-Bromo-*N*-cyclobutylaniline Prepared according to a literature procedure.[8] To a solution of 2-bromoaniline (2.70 g, 15.7 mmol, 1.10 equiv) in THF at room temperature under an atmosphere of argon was added cyclobutanone (1.00 g, 14.3 mmol, 1.00 equiv) via syringe followed by $NaBH(OAc)_3$ (4.54 g, 21.4 mmol, 1.50 equiv), portionwise. AcOH (0.82 mL, 14.3 mmol, 1.00 equiv) was then added via syringe. The resulting mixture was stirred at room temperature for 3 days. The crude product was extracted with Et_2O (x3), washed with brine, dried with $MgSO_4$ and concentrated under reduced pressure. The product was purified by silica gel flash chromatography (100% hexanes) to afford 1.63 g (50% yield) of a clear oil.

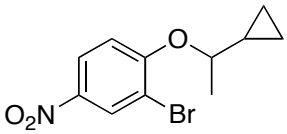
^{1}H NMR (400 MHz, $CDCl_3$, 293K) δ 7.45 (dd, J = 7.7, 1.5 Hz, 1H), 7.19 (ddd, J = 7.5, 7.5, 1.4 Hz, 1H), 6.61-6.57 (m, 2H), 4.47 (br s, 1H), 3.97 (sextuplet, J = 6.7 H, 1Hz), 2.53-2.46 (m, 2H), 2.00-1.78 (m, 4H). **^{13}C NMR (100 MHz, $CDCl_3$, 293K)** δ 144.0, 132.3, 128.4, 117.6, 111.6, 109.3, 48.7, 31.0, 15.3. **IR (ν_{max}/cm^{-1})** 3406, 3066, 2980, 2935, 1595, 1507, 1319, 1170, 1017, 741 cm^{-1}. **R_f** 0.47 (100% hexanes).



Methyl (2-bromophenyl)(cyclobutyl)carbamate (8) *General procedure for the protection of N-cyclopropylbenzenamines* was followed using 2-bromo-*N*-cyclobutylaniline (1.50 g, 6.63 mmol, 1.00 equiv) and methyl chloroformate (13.0 mL, 0.51 M). The product was purified by silica gel flash chromatography (10% EtOAc in hexanes) to afford 1.60 g (85% yield) of a white solid.

^{1}H NMR (400 MHz, $CDCl_3$, 328K) δ 7.65 (dd, J = 7.8, 1.0 Hz, 1H), 7.35 (ddd, J = 7.6, 7.6, 0.7 Hz, 1H), 7.22-7.16 (m, 2H), 4.72 (br s, 1H), 3.66 (br s, 3H), 2.22-2.15 (m, 2H), 1.95 (quintet, J = 10.0 Hz, 1H), 1.83 (quintet, J = 10.1 Hz, 1H), 1.66-1.51 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$, 328K)** δ 155.4, 138.7, 133.4, 131.6, 129.1, 128.0, 125.8, 52.9, 52.8, 29.7, 28.7, 15.1. **IR (ν_{max}/cm^{-1})** 2988, 2951, 1714, 1442, 1322, 1293, 1039 cm^{-1}. **R_f** 0.24 (10% EtOAc in hexanes). **Melting point** 46-47 °C



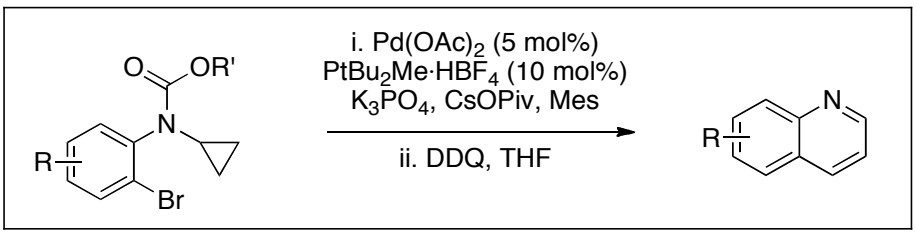


2-Bromo-1-(1-cyclopropylethoxy)-4-nitrobenzene (10) 1-Cyclopropylethanol (0.37 mL, 3.8 mmol, 1.1 equiv) was added dropwise via syringe to a solution of KH (0.500 g, 3.75 mmol, 1.10 equiv) in THF (23 mL, 0.15 M) at 0 °C under an atmosphere of argon. The resulting mixture was stirred for 10 minutes after which time 2-bromo-1-fluoro-4-nitrobenzene (0.750 g, 3.41 mmol, 1.00 equiv) was added and the solution was brought to room temperature. Once judged complete by TLC, the reaction was quenched by slow addition of water. The crude product was extracted with CH_2Cl_2 (x3), washed with brine, dried with $MgSO_4$ and concentrated under reduced pressure. The product was purified by silica gel flash chromatography (3% Et_2O in petroleum ether) to afford 0.819 g (84% yield) of a pale yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$, 328K) δ 8.46 (d, J = 2.8 Hz, 1H), 8.15 (dd, J = 9.1, 2.8 Hz, 1H), 6.92 (dd, J = 9.2, 0.5 Hz, 1H), 4.13 (quintet, J = 6.4 Hz, 1H), 1.46 (d, J = 6.2 Hz, 3H), 1.21 (tdt, J = 8.3, 6.9, 5.1 Hz, 1H), 0.65-0.56 (m, 2H), 0.48-0.32 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$, 328K)** δ 160.0, 141.1, 129.3, 124.4, 113.3, 113.2, 80.0, 19.5, 16.5, 3.5, 2.1. **R_f** 0.27 (3% Et_2O in petroleum ether).

General Procedures and Characterization for Arylation Products

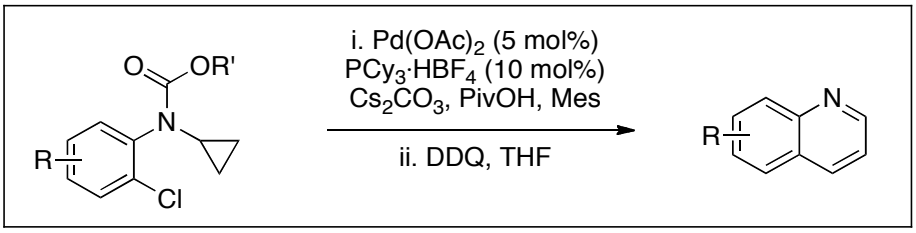
General Procedure A for Arylation at sp^3 C–H Bonds of Cyclopropanes – Quinoline Synthesis



A 4 mL screw-cap vial equipped with a magnetic stir bar and a teflon septum was charged with the starting material (if a solid, 1.00 equiv), $Pd(OAc)_2$ (5.00 mol%), $PtBu_2Me{\cdot}HBF_4$ (10.0 mol%), K_3PO_4 (1.50 equiv) and CsOPiv (30.0 mol%). The vial was purged with argon. The starting material (if a liquid, 1.00 equiv) was added as a solution in mesitylene (0.20 M). The resulting mixture was placed in a preheated bath and stirred for the indicated time. The reaction was then cooled to 0 °C and diluted with THF (0.20 M) after which point DDQ (1.20 equiv) was added. The mixture was then brought to room

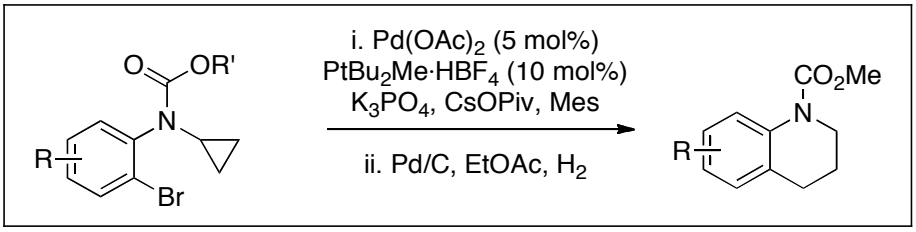
temperature and stirred until the reaction was judged complete by TLC. The crude product was extracted with CH_2Cl_2 (x3), dried with $MgSO_4$ and concentrated under reduced pressure. The product was purified by silica gel flash chromatography.

General Procedure B for Arylation at sp^3 C–H Bonds of Cyclopropanes – Quinoline Synthesis



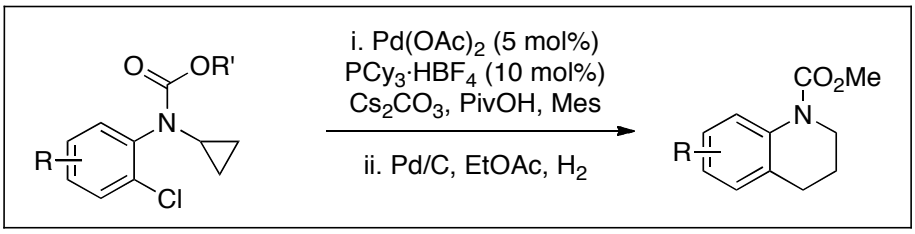
A 4 mL screw-cap vial equipped with a magnetic stir bar and a teflon septum was charged with the starting material (if a solid, 1.00 equiv), $Pd(OAc)_2$ (5.00 mol%), $PCy_3{\cdot}HBF_4$ (10.0 mol%), Cs_2CO_3 (1.50 equiv) and PivOH (30.0 mol%). The vial was purged with argon. The starting material (if a liquid, 1.00 equiv) was added as a solution in mesitylene (0.20 M). The resulting mixture was placed in a preheated bath and stirred for the indicated time. The reaction was then cooled to 0 °C and diluted with THF (0.20 M) after which point DDQ (1.20 equiv) was added. The mixture was then brought to room temperature and stirred until the reaction was judged complete by TLC. The crude product was extracted with CH_2Cl_2 (x3), dried with $MgSO_4$ and concentrated under reduced pressure. The product was purified by silica gel flash chromatography.

General Procedure C for Arylation at sp^3 C–H Bonds of Cyclopropanes – Tetrahydroquinoline Synthesis

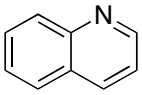


A 4 mL screw-cap vial equipped with a magnetic stir bar and a teflon septum was charged with the starting material (if a solid, 1.00 equiv), $Pd(OAc)_2$ (5.00 mol%), $PtBu_2Me{\cdot}HBF_4$ (10.0 mol%), K_3PO_4 (1.50 equiv) and CsOPiv (30.0 mol%). The vial was purged with argon. The starting material (if a liquid, 1.00 equiv) was added as a solution in mesitylene (0.20 M). The resulting mixture was placed in a preheated bath and stirred for the indicated time. The reaction was then cooled to room temperature and diluted with EtOAc (0.20 M) after which point Pd/C (10 mol%) was added. The mixture was then vigorously stirred under H_2 bubbling for 10 minutes after which point the reaction was stirred under an atmosphere of H_2 (no bubbling) until judged complete by TLC. The crude product was filtered over celite and concentrated under reduced pressure. The product was purified by silica gel flash chromatography.

General Procedure D for Arylation at sp^3 C–H Bonds of Cyclopropanes – Tetrahydroquinoline Synthesis



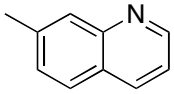
A 4 mL screw-cap vial equipped with a magnetic stir bar and a teflon septum was charged with the starting material (if a solid, 1.00 equiv), $Pd(OAc)_2$ (5.00 mol%), $PCy_3{\cdot}HBF_4$ (10.0 mol%), Cs_2CO_3 (1.50 equiv) and PivOH (30.0 mol%). The vial was purged with argon. The starting material (if a liquid, 1.00 equiv) was added as a solution in mesitylene (0.20 M). The resulting mixture was placed in a preheated bath and stirred for the indicated time. The reaction was then cooled to room temperature and diluted with EtOAc (0.20 M) after which point Pd/C (10 mol%) was added. The mixture was then vigorously stirred under H_2 bubbling for 10 minutes after which point the reaction was stirred under an atmosphere of H_2 (no bubbling) until judged complete by TLC. The crude product was filtered over celite and concentrated under reduced pressure. The product was purified by silica gel flash chromatography.



Quinoline (3a) Synthesized according to *General Procedure A* using methyl 2-bromophenylcyclopropylcarbamate **1a** (110 mg, 0.409 mmol, 1.00 equiv) at 90 °C for 16 h (DDQ oxidation at room temperature for 3.5 h). The product was purified by silica gel flash chromatography (40% Et_2O in petroleum ether) to afford 46 mg (87% yield) of an orange oil. Synthesized according to *General Procedure B* using methyl 2-chlorophenylcyclopropylcarbamate **1i** (92.3 mg, 0.409 mmol, 1.00 equiv) at 140 °C for 4 h (DDQ oxidation at room temperature for 3.5 h). The product was purified by silica gel flash chromatography (40% Et_2O in petroleum ether) to afford 40 mg (76% yield) of an orange oil.

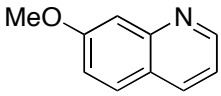
^{1}H NMR (400 MHz, $CDCl_3$, 293K, TMS) δ 8.93 (dd, J = 4.1, 1.4 Hz, 1H), 8.16 (d, J = 8.3 Hz, 1H), 8.12 (d, J = 8.6 Hz, 1H), 7.82 (d, J = 8.1 Hz, 1H), 7.72 (ddd, J = 8.4, 7.0, 1.4 Hz, 1H), 7.58-7.52 (m, 1H), 7.40 (dd, J = 8.3, 4.2 Hz, 1H).

Commercially available - CAS#: 91-22-5.



7-Methylquinoline (3b) Synthesized according to *General Procedure A* using methyl 2-bromo-5-methylphenylcyclopropylcarbamate **1b** (128 mg, 0.450 mmol, 1.00 equiv) at 90 °C for 16 h (DDQ oxidation at room temperature for 3.5 h). The product was purified by silica gel flash chromatography (40% Et_2O in petroleum ether) to afford 43 mg (67% yield) of an orange oil. Synthesized according to *General Procedure A* using benzyl 2-bromo-5-methylphenylcyclopropylcarbamate **1b'** (162 mg, 0.450 mmol, 1.00 equiv) at 90 °C for 16 h (DDQ oxidation at room temperature for 3.5 h). The product was purified by silica gel flash chromatography (40% Et_2O in petroleum ether) to afford 38 mg (59% yield) of an orange oil.

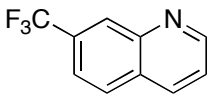
^{1}H NMR (400 MHz, $CDCl_3$, 293K, TMS) δ 8.87 (dd, J = 4.2, 1.5 Hz, 1H), 8.10 (dd, J = 8.2, 1.1 Hz, 1H), 7.88 (d, J = 0.7 Hz, 1H), 7.71 (d, J = 8.3 Hz, 1H), 7.38 (dd, J = 8.3, 1.6 Hz, 1H), 7.32 (dd, J = 8.2, 4.2 Hz, 1H), 2.57 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$, 293K, TMS)** δ 150.5, 148.7, 139.9, 135.8, 128.9, 128.6, 127.5, 126.5, 120.4, 22.0. **HRMS** Calculated for $C_{10}H_9N$ (M^+) 143.0735, Found 143.0727. **IR (ν_{max}/cm^{-1})** 3048, 2924, 1627, 1503 cm^{-1}. **R_f** 0.20 (30% Et_2O in petroleum ether).



7-Methoxyquinoline (3c) Synthesized according to *General Procedure A* using methyl 2-bromo-5-methoxyphenylcyclopropylcarbamate **1c** (150 mg, 0.500 mmol, 1.00 equiv) at 110 °C for 16 h (DDQ oxidation at room temperature for 3.5 h). The product was purified by silica gel flash chromatography (70% Et_2O in petroleum ether) to afford 73 mg (91% yield) of a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$, 293K, TMS) δ 8.83 (d, J = 3.1 Hz, 1H), 8.06 (dd, J = 8.2, 1.3 Hz, 1H), 7.69 (d, J = 9.0 Hz, 1H), 7.42 (d, J = 2.4 Hz, 1H), 7.26 (dd, J = 7.8, 4.7 Hz, 1H), 7.20 (dd, J = 9.0, 2.5 Hz, 1H), 3.95 (s, 3H).

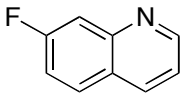
Exhibited spectral data identical to a previous report.[9]



7-(Trifluoromethyl)quinoline (3d) Synthesized according to *General Procedure A* using methyl 2-bromo-5-(trifluoromethyl)phenylcyclopropylcarbamate **1d** (169 mg, 0.500 mmol, 1.00 equiv) at 110 °C for 16 h (DDQ oxidation at room temperature for 20 h). The product was purified by silica gel flash chromatography (15% EtOAc and 15% toluene in hexanes) to afford 77 mg (78% yield) of a white solid.

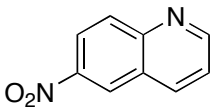
^{1}H NMR (400 MHz, $CDCl_3$, 293K) δ 9.01 (d, J = 3.1 Hz, 1H), 8.41 (br s, 1H), 8.21 (d, J = 8.3 Hz, 1H), 7.94 (d, J = 8.4 Hz, 1H), 7.71 (dd, J = 8.5, 1.6 Hz, 1H), 7.51 (dd, J = 8.3, 4.2 Hz, 1H).

Exhibited spectral data identical to a previous report.[10]



7-Fluoroquinoline (3e) Synthesized according to *General Procedure A* using methyl 2-bromo-5-fluorophenylcyclopropylcarbamate **1e** (144 mg, 0.500 mmol, 1.00 equiv) at 110 °C for 16 h (DDQ oxidation at room temperature for 2 h). The product was purified by silica gel flash chromatography (15% EtOAc and 15% toluene in hexanes) to afford 54 mg (73% yield) of a yellow oil.

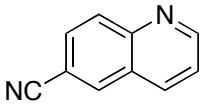
^{1}H NMR (400 MHz, $CDCl_3$, 293K) δ 8.89 (dd, J = 4.2, 1.6 Hz, 1H), 8.13 (dd, J = 8.3, 1.0 Hz, 1H), 7.79 (dd, J = 9.0, 6.0 Hz, 1H), 7.71 (dd, J = 10.1, 2.5 Hz, 1H), 7.37-7.29 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$, 293K)** δ 162.9 (d, J_F = 249 Hz), 151.3, 149.1 (d, J_F = 12 Hz), 136.0, 129.8 (d, J_F = 10 Hz), 125.3 (d, J_F = 1 Hz), 120.4 (d, J_F = 3 Hz), 117.2 (d, J_F = 26 Hz), 113.0 (d, J_F = 20 Hz). **IR (ν_{max}/cm^{-1})** 3055, 3005, 2927, 1630, 1507, 1322, 1258, 1108 cm^{-1}. **R_f** 0.19 (15% EtOAc and 15% toluene in hexanes).



6-Nitroquinoline (3f) Synthesized according to *General Procedure A* using methyl 2-bromo-4-nitrophenylcyclopropylcarbamate **1f** (129 mg, 0.409 mmol, 1.00 equiv) at 110 °C for 16 h (DDQ oxidation at room temperature for 8 h). The product was purified by silica gel flash chromatography (40% EtOAc in petroleum ether) to afford 44 mg (61% yield) of a yellow solid.

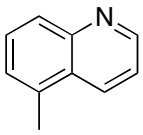
^{1}H NMR (400 MHz, $CDCl_3$, 293K, TMS) δ 9.11 (dd, J = 4.2, 1.7 Hz, 1H), 8.81 (d, J = 2.5 Hz, 1H), 8.49 (dd, J = 9.3, 2.5 Hz, 1H), 8.38-8.36 (m, 1H), 8.25 (d, J = 9.3 Hz, 1H), 7.59 (dd, J = 8.4, 4.2 Hz, 1H).

Exhibited spectral data identical to a previous report.[11]



Quinoline-6-carbonitrile (3g) Synthesized according to *General Procedure A* using methyl 2-bromo-4-cyanophenylcyclopropylcarbamate **1g** (133 mg, 0.450 mmol, 1.00 equiv) at 110 °C for 16 h (DDQ oxidation at room temperature for 3.5 h). The product was purified by silica gel flash chromatography (45% EtOAc in petroleum ether) to afford 45 mg (65% yield) of a beige solid.

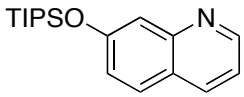
^{1}H NMR (400 MHz, $CDCl_3$, 293K, TMS) δ 9.05 (dd, J = 4.2, 1.5 Hz, 1H), 8.24-8.21 (m, 2H), 8.19 (d, J = 8.8 Hz, 1H), 7.86 (dd, J = 8.7, 1.8 Hz, 1H), 7.54 (dd, J = 8.3, 4.2 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$, 293K, TMS)** δ 153.4, 149.3, 136.5, 134.2, 131.2, 130.3, 127.7, 122.9, 118.6, 110.5. **HRMS** Calculated for $C_{10}H_6N_2$ (M^+) 154.0531, Found 154.0529. **IR (ν_{max}/cm^{-1})** 3050, 2230, 1496, 1321, 1216, 838, 755 cm^{-1}. **R_f** 0.24 (45% EtOAc in petroleum ether). **Melting point** 131-132 ºC



5-Methylquinoline (3h) Synthesized according to *General Procedure A* using methyl (2-bromo-3-methylphenyl)(cyclopropyl)carbamate **1h** (142 mg, 0.500 mmol, 1.00 equiv) at 110 °C for 16 h (DDQ oxidation at room temperature for 3.5 h). The product was purified by silica gel flash chromatography (30% EtOAc in hexanes) to afford 62 mg (87% yield) of an orange oil.

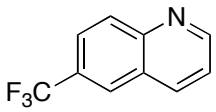
^{1}H NMR (400 MHz, $CDCl_3$, 293K) δ 8.90 (d, J = 3.1 Hz, 1H), 8.31 (d, J = 8.5 Hz, 1H), 7.95 (d, J = 8.5 Hz, 1H), 7.58 (dd, J = 7.1, 7.1 Hz, 1H), 7.40 (dd, J = 8.5, 4.2 Hz, 1H), 7.35 (d, J = 7.0 Hz, 1H), 2.67 (s, 3H).

Exhibited spectral data identical to a previous report.[12]



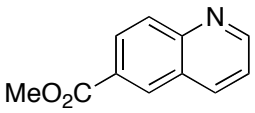
7-((Triisopropylsilyl)oxy)quinoline (3j) Synthesized according to *General Procedure B* using methyl (2-chloro-5-((triisopropylsilyl)oxy)phenyl)(cyclopropyl)carbamate **1j** (128 mg, 0.322 mmol, 1.00 equiv) at 140 °C for 3.5 h (DDQ oxidation at room temperature for 2 h). The product was purified by silica gel flash chromatography (5% EtOAc in hexanes) to afford 83 mg (85% yield) of a red oil.

^{1}H NMR (400 MHz, $CDCl_3$, 293K) δ 8.83 (dd, J = 4.3, 1.7 Hz, 1H), 8.07 (dd, J = 8.3, 1.2 Hz, 1H), 7.69 (d, J = 8.8 Hz, 1H), 7.50 (d, J = 2.4 Hz, 1H), 7.25 (dd, J = 8.2, 4.3 Hz, 1H), 7.20 (dd, J = 8.8, 2.4 Hz, 1H), 1.40-1.29 (m, 3H), 1.14 (d, J = 7.4 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$, 328K)** δ 157.2, 150.5, 149.7, 135.7, 128.7, 123.7, 123.0, 119.0, 115.7, 17.9, 12.7. **IR (ν_{max}/cm^{-1})** 3062, 2945, 2868, 1619, 1499, 1322, 1271, 1211, 1072, 969, 836 cm^{-1}. **R_f** 0.13 (5% EtOAc in hexanes).



6-(Trifluoromethyl)quinoline (3k) Synthesized according to *General Procedure B* using methyl 2-chloro-4-(trifluoromethyl)phenylcyclopropylcarbamate **1k** (120 mg, 0.409 mmol, 1.00 equiv) at 140 °C for 8 h (DDQ oxidation at room temperature for 2.5 h). The product was purified by silica gel flash chromatography (30% Et_2O in petroleum ether) to afford 42 mg (52% yield) of a yellow solid.

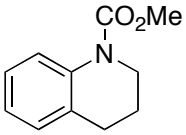
^{1}H NMR (400 MHz, $CDCl_3$, 293K, TMS) δ 9.03 (dd, J = 4.2, 1.7 Hz, 1H), 8.43 (d, J = 0.8 Hz, 1H), 8.23 (dd, J = 8.4, 0.9 Hz, 1H), 7.96 (d, J = 8.6 Hz, 1H), 7.73 (dd, J = 8.5, 1.8 Hz, 1H), 7.53 (dd, J = 8.3, 4.2 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$, 293K, TMS)** δ 151.9, 147.4, 136.1, 131.4 (q, J_F = 32.4 Hz), 129.8, 129.2, 127.5 (q, J_F = 4.4 Hz), 124.1 (q, J_F = 271 Hz), 123.1, 122.4 (q, J_F = 3.1 Hz). **HRMS** Calculated for $C_{10}H_6NF_3$ (M^+) 197.0452, Found 197.0456. **IR (ν_{max}/cm^{-1})** 3060, 1510, 1321, 1153, 1145, 1117, 933, 842 cm^{-1}. **R_f** 0.26 (30% Et_2O in petroleum ether). **Melting point** 60-62 °C



Methyl quinoline-6-carboxylate (3l) Synthesized according to *General Procedure B* using methyl 3-chloro-4-(cyclopropyl(methoxycarbonyl)amino)benzoate **1l** (143 mg, 0.500 mmol, 1.00 equiv) at 140 °C for 3 h (DDQ oxidation at room temperature for 3 h). The product was purified by silica gel flash chromatography (50% EtOAc in hexanes) to afford 77 mg (82% yield) of an orange solid.

^{1}H NMR (400 MHz, $CDCl_3$, 293K) δ 8.98 (dd, J = 4.2, 1.7 Hz, 1H), 8.57 (d, J = 1.8 Hz, 1H), 8.27 (dd, J = 8.8, 1.9 Hz, 1H), 8.24 (d, J = 8.3 Hz, 1H), 8.12 (d, J = 8.8 Hz, 1H), 7.45 (dd, J = 8.3, 4.2 Hz, 1H), 3.97 (s, 3H).

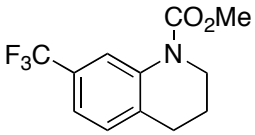
Exhibited spectral data identical to a previous report.[13]



Methyl 3,4-dihydroquinoline-1(2H)-carboxylate (4a) Synthesized according to *General Procedure C* using methyl 2-bromophenylcyclopropylcarbamate **1a** (135 mg, 0.500 mmol, 1.00 equiv) at 110 °C for 13 h. The product was purified by silica gel flash chromatography (10% EtOAc in hexanes) to afford 78 mg (82% yield) of a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$, 293K) δ 7.65 (br d, J = 7.9 Hz, 1H), 7.16-7.12 (m, 1H), 7.08-7.06 (m, 1H), 6.99 (ddd, J = 7.4, 7.4, 1.2 Hz, 1H), 3.78 (s, 3H), 3.76-3.73 (m, 2H), 2.76 (t, J = 6.6 Hz, 2H), 1.93 (tt, J = 6.4, 6.4 Hz, 2H).

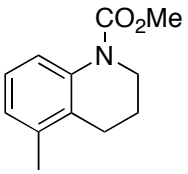
Exhibited spectral data identical to a previous report.[14]



Methyl 7-(trifluoromethyl)-3,4-dihydroquinoline-1(2H)-carboxylate (4d) Synthesized according to *General Procedure C* using methyl 2-bromo-5-(trifluoromethyl)phenylcyclopropylcarbamate **1d** (84.5 mg, 0.250 mmol, 1.00 equiv) at 110 °C for 15 h. The product was purified by silica gel flash chromatography (10% EtOAc in hexanes) to afford 29 mg (45% yield) of a yellow oil.

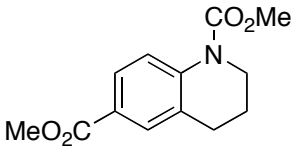
^{1}H NMR (400 MHz, $CDCl_3$, 293K) δ 8.07 (br s, 1H), 7.25 (dd, J = 7.9, 1.1 Hz, 1H), 7.19 (d, J = 8.0 Hz, 1H), 3.83 (s, 3H), 3.81-3.78 (m, 2H), 2.82 (t, J = 6.5 Hz, 2H), 1.98 (dd, J = 12.6, 6.3 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$, 293K) δ 155.1, 138.5, 133.4, 129.0, 128.5 (q, J_F = 32.1 Hz), 124.1 (q, J_F = 271 Hz), 120.7 (q, J_F = 3.7 Hz), 119.9 (q, J_F = 3.7 Hz), 53.1, 44.8, 27.5, 23.0. **IR (ν_{max}/cm^{-1})** 2957, 1714, 1511, 1435, 1328, 1122, 1079 cm^{-1}. **R_f** 0.19 (10% EtOAc in hexanes).



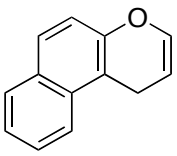
Methyl 5-methyl-3,4-dihydroquinoline-1(2H)-carboxylate (4h) Synthesized according to *General Procedure C* using methyl (2-bromo-3-methylphenyl)(cyclopropyl)carbamate **1h** (142 mg, 0.500 mmol, 1.00 equiv) at 110 °C for 13 h. The product was purified by silica gel flash chromatography (10% EtOAc in hexanes) to afford 102 mg (99% yield) of a clear oil.

^{1}H NMR (400 MHz, $CDCl_3$, 293K) δ 7.43 (d, J = 7.9 Hz, 1H), 7.06 (dd, J = 7.8, 7.8 Hz, 1H), 6.91 (d, J = 7.4 Hz, 1H), 3.76 (s, 3H), 3.75-3.72 (m, 2H), 2.65 (t, J = 6.9 Hz, 2H), 2.21 (s, 3H), 2.00-1.93 (m, 2H). Exhibited spectral data identical to a previous report.[14]



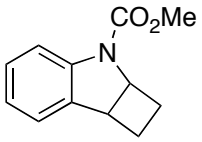
Dimethyl 3,4-dihydroquinoline-1,6(2H)-dicarboxylate (4l) Synthesized according to *General Procedure D* using methyl 3-chloro-4-(cyclopropyl(methoxycarbonyl)amino)benzoate **1l** (143 mg, 0.500 mmol, 1.00 equiv) at 140 °C for 3 h. The product was purified by silica gel flash chromatography (15% EtOAc in hexanes) to afford 119 mg (95% yield) of a clear oil.

^{1}H NMR (400 MHz, $CDCl_3$, 293K) δ 7.83 (br s, 2H), 7.79 (br s, 1H), 3.90 (s, 3H), 3.84-3.78 (m, 2H), 3.83 (s, 3H), 2.82 (t, J = 6.5 Hz, 2H), 1.96 (dt, J = 12.5, 6.3 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$, 293K)** δ 166.8, 155.1, 142.4, 130.2, 129.4, 127.5, 124.7, 123.1, 53.1, 51.9, 45.2, 27.5, 23.0. **IR (ν_{max}/cm^{-1})** 2953, 2847, 1717, 1611, 1440, 1283, 1192, 1109 cm^{-1}. **R_f** 0.27 (20% EtOAc in hexanes).

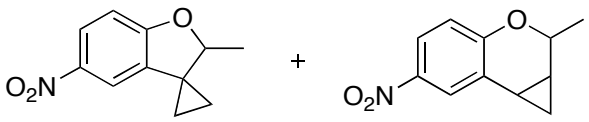


1*H*-benzo[*f*]chromene (6) A 4 mL screw-cap vial equipped with a magnetic stir bar and a teflon septum was charged with 1-bromo-2-cyclopropoxynaphthalene **5** (148 mg, 0.563 mmol, 1.00 equiv), $Pd(OAc)_2$ (6.3 mg, 2.82 x 10^{-2} mmol, 5.00 mol%), $PCy_3{\cdot}HBF_4$ (20.7 mg, 5.63 x 10^{-2} mmol, 10.0 mol%), Cs_2CO_3 (275 mg, 0.845 mmol, 1.50 equiv) and PivOH (17.3 mg, 0.169 mmol, 30.0 mol%). The vial was purged with argon. Mesitylene (2.8 mL, 0.2 M) was then added and the resulting mixture was placed in a preheated oil bath at 110 °C and stirred for 16 h. The reaction was then cooled to room temperature and the crude product was extracted with CH_2Cl_2 (x3), dried with $MgSO_4$ and concentrated under reduced pressure. The product was purified by silica gel flash chromatography (100% petroleum ether) to afford 91 mg (91% yield) of a pale yellow solid.

^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS) δ 7.81 (dd, J = 8.1, 1.3 Hz, 1H), 7.72-7.66 (m, 2H), 7.54 (ddd, J = 8.4, 6.9, 1.5 Hz, 1H), 7.43 (ddd, J = 8.1, 6.9, 1.2 Hz, 1H), 7.09 (d, J = 8.8 Hz, 1H), 6.61 (dt, J = 6.3, 2.0 Hz, 1H), 5.15 (dt, J = 6.3, 3.5 Hz, 1H), 3.69 (dd, J = 3.4, 2.0 Hz, 2H).
Exhibited spectral data identical to a previous report.[15]



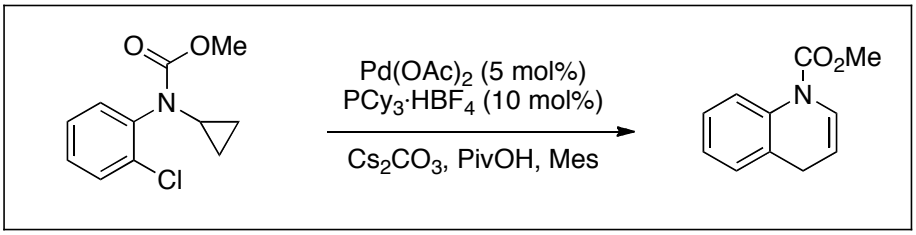
Methyl 2,2a-dihydro-1H-cyclobuta[b]indole-3(7bH)-carboxylate (9) A 4 mL screw-cap vial equipped with a magnetic stir bar and a teflon septum was charged with methyl (2-bromophenyl)(cyclobutyl)carbamate **8** (142 mg, 0.500 mmol, 1.00 equiv), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 5.0 mol%), $PCy_3{\cdot}HBF_4$ (18.4 mg, 0.050 mmol, 10.0 mol%), Cs_2CO_3 (244 mg, 0.750 mmol, 1.50 equiv) and PivOH (15.3 mg, 0.150 mmol, 30.0 mol%). The vial was evacuated and backfilled with argon. This procedure was repeated 3 times. Mesitylene (2.5 mL, 0.2 M) was then added and the resulting mixture was placed in a preheated oil bath at 140 °C and stirred for 16 h. The reaction was then cooled to room temperature and the crude product was extracted with CH_2Cl_2 (x3), dried with $MgSO_4$ and concentrated under reduced pressure. The product was purified by silica gel flash chromatography (5% EtOAc in hexanes) to afford 66 mg (65% yield) of an orange oil.
^{1}H NMR (400 MHz, $CDCl_3$, 328K) δ 7.86 (br s, 1H), 7.22 (dd, J = 7.7, 7.7 Hz, 1H), 7.14 (d, J = 7.4 Hz, 1H), 7.00 (ddd, J = 7.4, 7.4, 0.9 Hz, 1H), 4.86 (br s, 1H), 3.98-3.93 (m, 1H), 3.83 (s, 3H), 2.66-2.49 (m, 2H), 2.29-2.21 (m, 1H), 2.06-1.98 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$, 293K)** δ 153.1, 143.6, 135.6, 127.8, 124.5, 122.9, 115.2, 58.4, 52.4, 40.9, 29.3, 26.6. **IR (ν_{max}/cm^{-1})** 2989, 2949, 1715, 1602, 1383, 1067, 762 cm^{-1}. **R_f** 0.24 (5% EtOAc in hexanes).

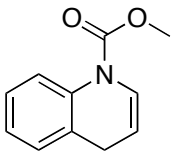


2-Methyl-5-nitro-2H-spiro[benzofuran-3,1'-cyclopropane] (11) and **2-methyl-6-nitro-1,1a,2,7b-tetrahydrocyclopropa[c]chromene (12)** A 4 mL screw-cap vial equipped with a magnetic stir bar and a teflon septum was charged with 2-bromo-1-(1-cyclopropylethoxy)-4-nitrobenzene **10** (150 mg, 0.524 mmol, 1.00 equiv), $Pd(OAc)_2$ (5.9 mg, 0.0262 mmol, 5.00 mol%), $PCy_3{\cdot}HBF_4$ (19.3 mg, 0.0524 mmol, 10.0 mol%), Cs_2CO_3 (188 mg, 0.577 mmol, 1.10 equiv) and PivOH (16.1 mg, 0.157 mmol, 30.0 mol%). The vial was evacuated and backfilled with argon. This procedure was repeated 3 times. Mesitylene (3.1 mL, 0.17 M) was then added and the resulting mixture was placed in a preheated oil bath at 140 °C and stirred for 16 h. The reaction was then cooled to room temperature and the crude product was extracted with CH_2Cl_2 (x3), dried with $MgSO_4$ and concentrated under reduced pressure. The

product was purified by silica gel flash chromatography (gradient from 3% to 4% Et_2O in petroleum ether) to afford 72 mg (67% yield) of a yellow solid as an inseparable mixture of **11** and **12** in a 3:1 ratio. **^{1}H NMR (400 MHz, $CDCl_3$, 328K, TMS)** δ 8.14 (d, J = 2.4 Hz, 1H, **12**), 8.07 (dd, J = 8.8, 2.4 Hz, 1H, **11**), 7.96 (dd, J = 8.8, 2.4 Hz, 1H, **12**), 7.55 (d, J = 2.4 Hz, 1H, **11**), 6.83 (d, J = 8.8 Hz, 1H, **12**), 6.79 (d, J = 8.8 Hz, 1H, **11**), 4.98 (q, J = 6.4 Hz, 1H, **11**), 4.65 (qd, J = 6.5, 0.8 Hz, 1H, **12**), 2.07 (td, J = 8.5, 4.4 Hz, 1H, **12**), 1.67 (tdd, J = 8.3, 5.6, 1.2 Hz, 1H, **12**), 1.35 (d, J = 6.4 Hz, 3H, **11**), 1.31-0.93 (m, remaining 9H, **11** and **12**). **^{13}C NMR (100 MHz, $CDCl_3$, 293K, TMS)** Product **11**: δ 165.0, 142.0, 134.7, 125.0, 115.3, 108.6, 85.7, 28.4, 18.1, 15.4, 13.8. Product **12**: δ 156.0, 141.7, 128.1, 123.9, 122.4, 118.3, 69.6, 22.6, 20.5, 12.0, 11.8.

Characterization of the 1,2-Dihydroquinoline Intermediate





Methyl quinoline-1(4*H*)-carboxylate (2a) A 4 mL screw-cap vial equipped with a magnetic stir bar and a teflon septum was charged $Pd(OAc)_2$ (3.9 mg, 1.7 x 10^{-2} mmol, 5.0 mol%), $PCy_3{\cdot}HBF_4$ (12.7 mg, 3.47 x 10^{-2} mmol, 10.0 mol%), Cs_2CO_3 (124 mg, 0.380 mmol, 1.10 equiv) and PivOH (10.6 mg, 0.104 mmol, 30.0 mol%). The vial was purged with argon. Methyl 2-chlorophenylcyclopropylcarbamate **1i** (78.0 mg, 0.346 mmol, 1.00 equiv) was then added as a 0.2 M solution in mesitylene and the resulting mixture was placed in a preheated oil bath at 140 °C and stirred for 16 h. The reaction was then cooled to room temperature and the crude product was extracted with CH_2Cl_2 (x3), dried with $MgSO_4$ and concentrated under reduced pressure. The product was purified by silica gel flash chromatography (4% Et2O in petroleum ether) to afford 53 mg (82% yield) of a pale yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$, 293K, TMS) δ 7.93 (d, J = 8.3 Hz, 1H), 7.21 (t, J = 7.6 Hz, 1H), 7.12-7.06 (m, 2H), 6.94 (d, J = 7.6 Hz, 1H), 5.33 (dt, J = 7.8, 4.0 Hz, 1H), 3.87 (d, J = 0.6 Hz, 3H), 3.34 (d, J = 3.7 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$, 293K, TMS)** δ 153.4, 136.8, 128.3, 128.0, 127.0, 126.4, 125.0, 121.7, 109.6, 53.3, 27.6. **IR (ν_{max}/cm^{-1})** 3028, 2959, 1730 1667, 1460, 1334 cm^{-1}. **R_f** 0.29 (5% Et_2O in petroleum ether).

Experimental References

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(14) T. Watanabe, S. Oishi, N. Fujii and H. Ohno, *Org. Lett.*, 2007, **9**, 4821.

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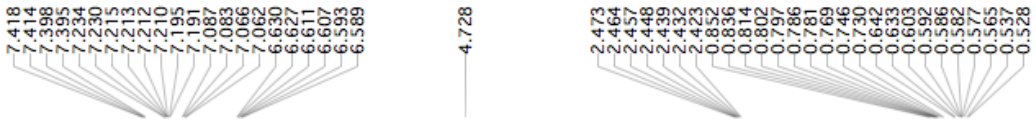
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7.062
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6.627
6.611
6.607
6.593
6.589
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2.439
2.432
2.423
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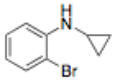
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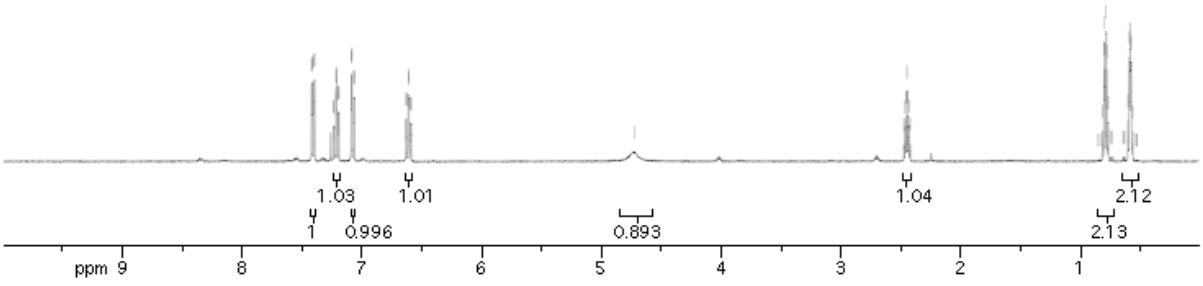
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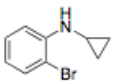
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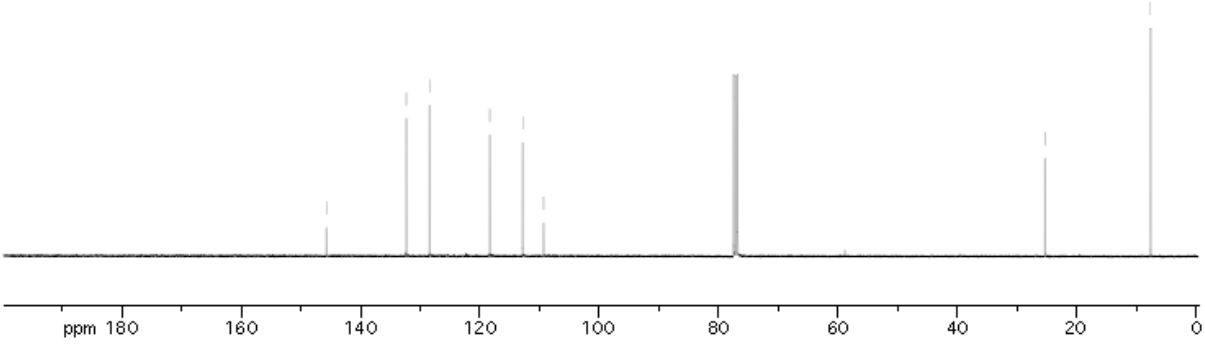
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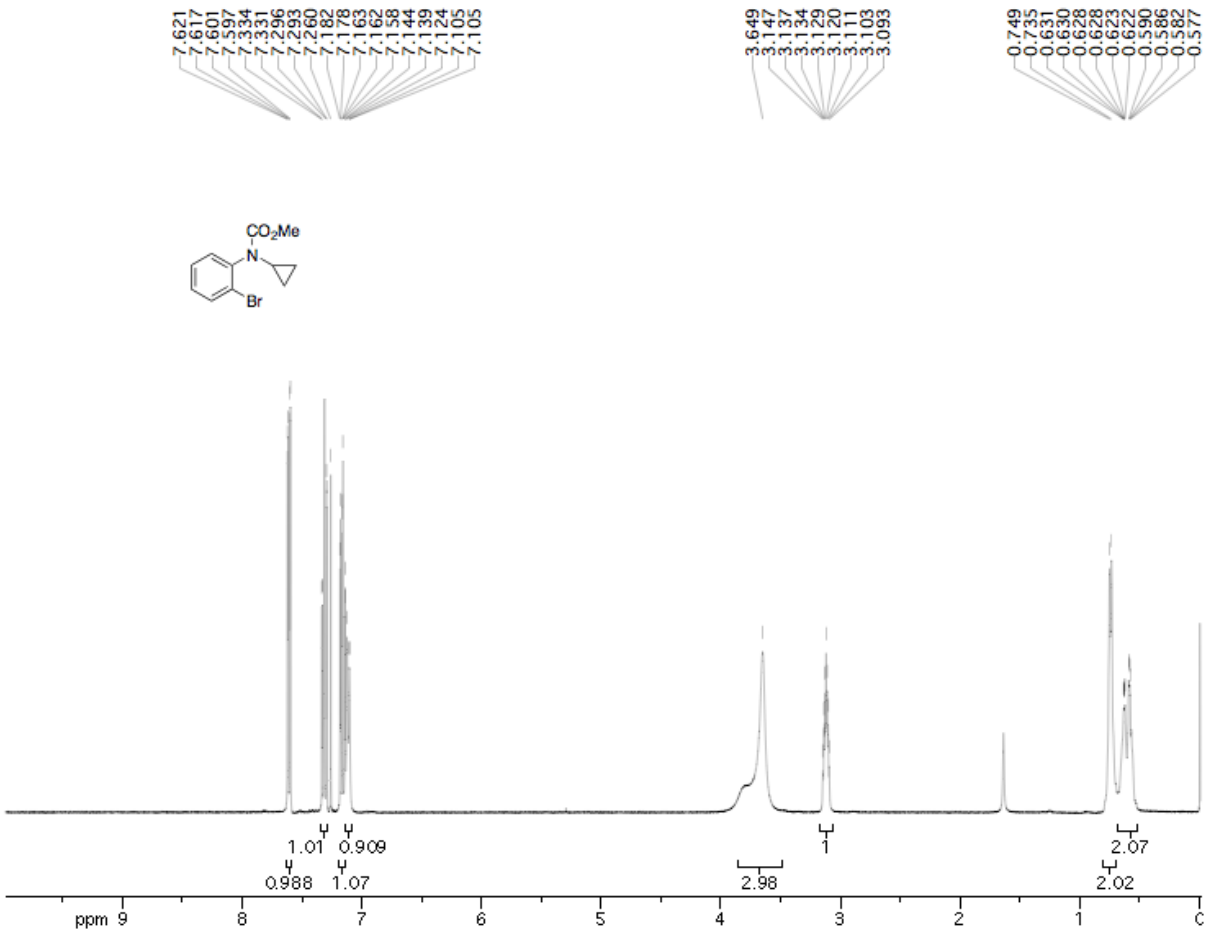
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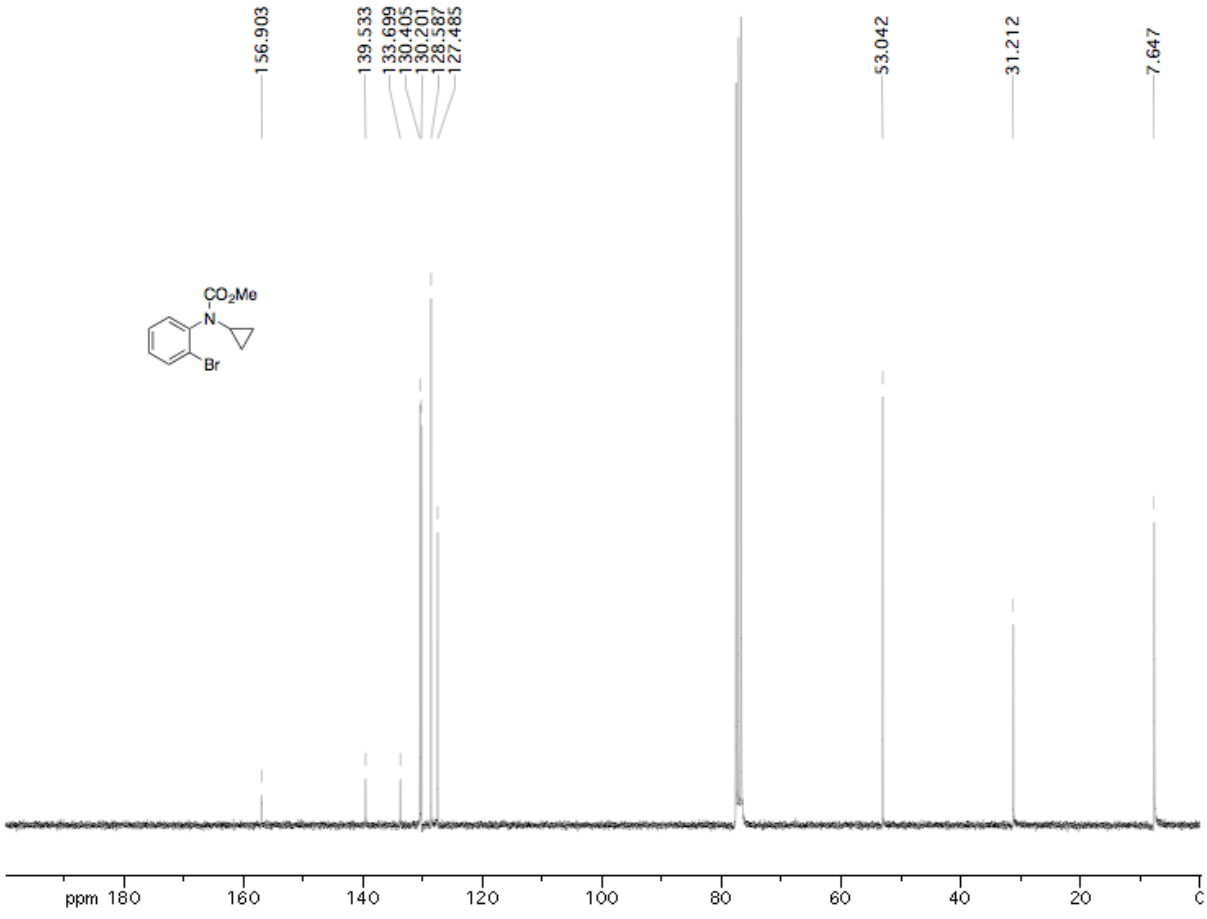
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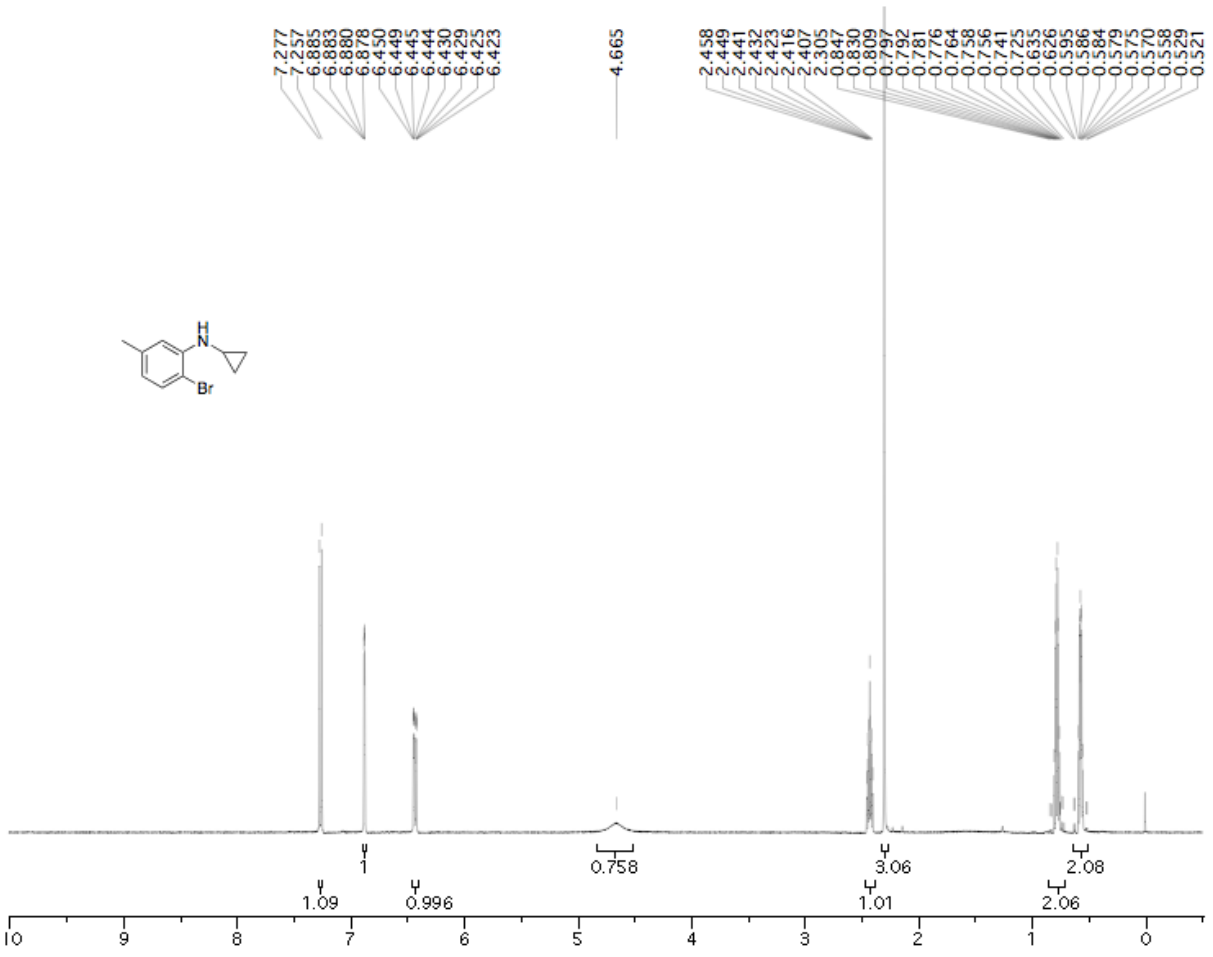
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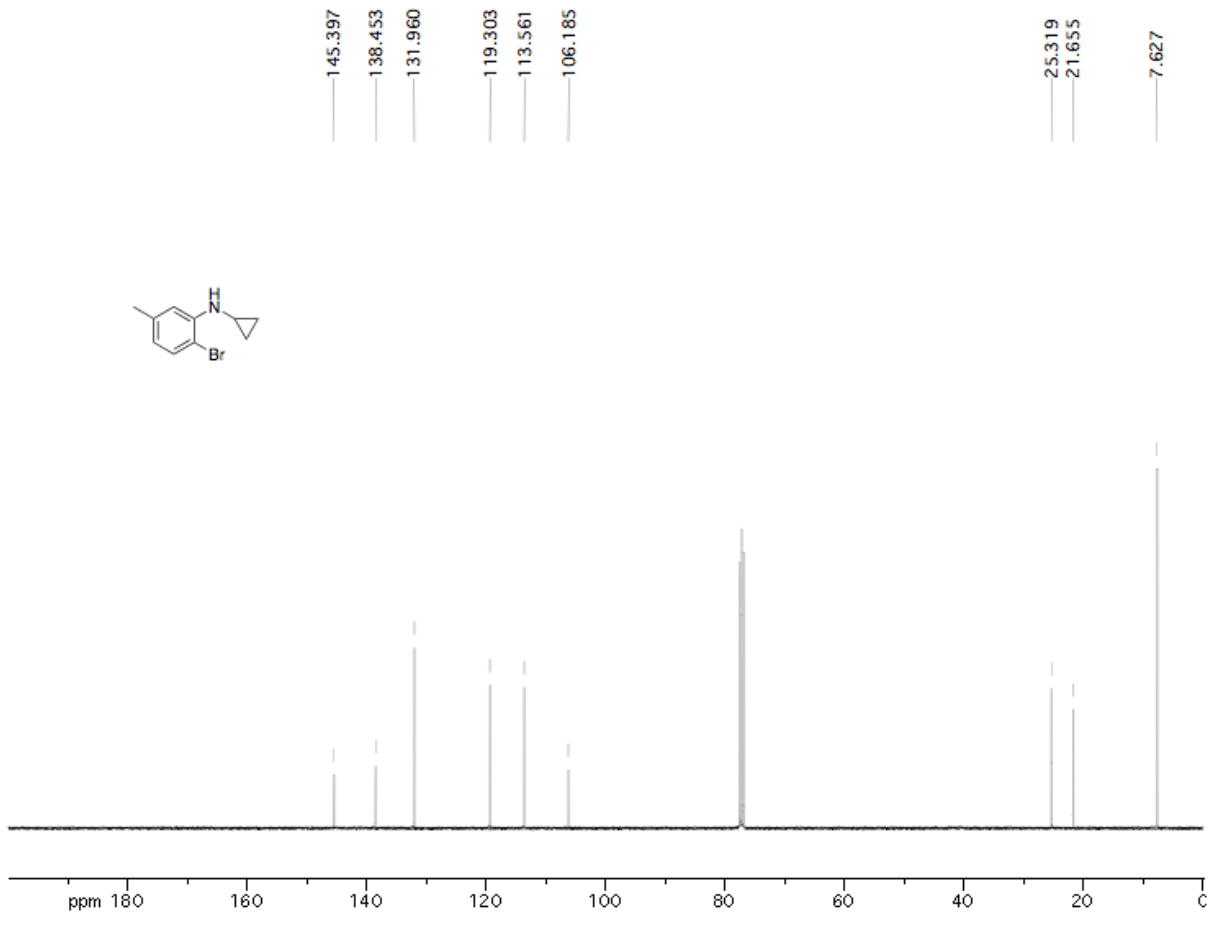
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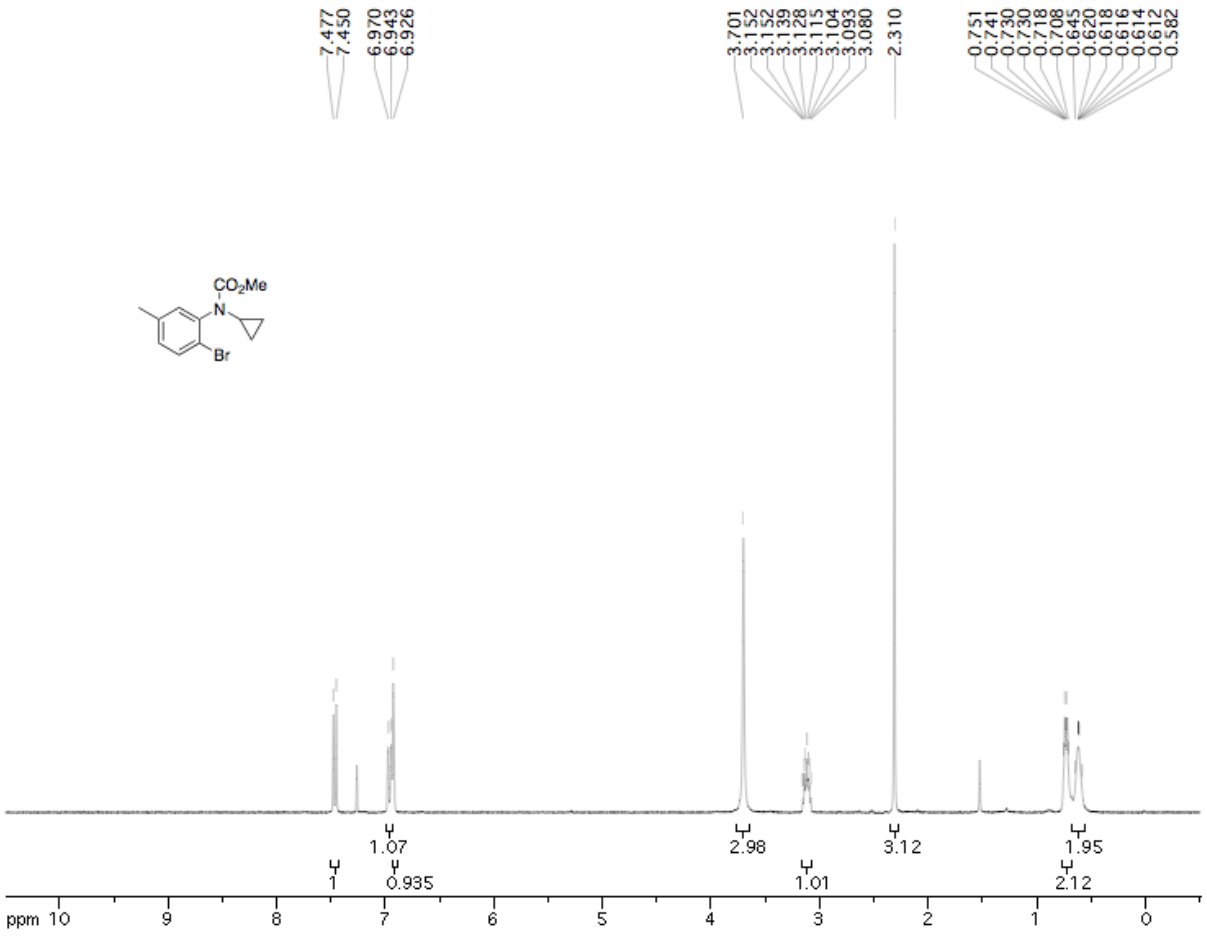
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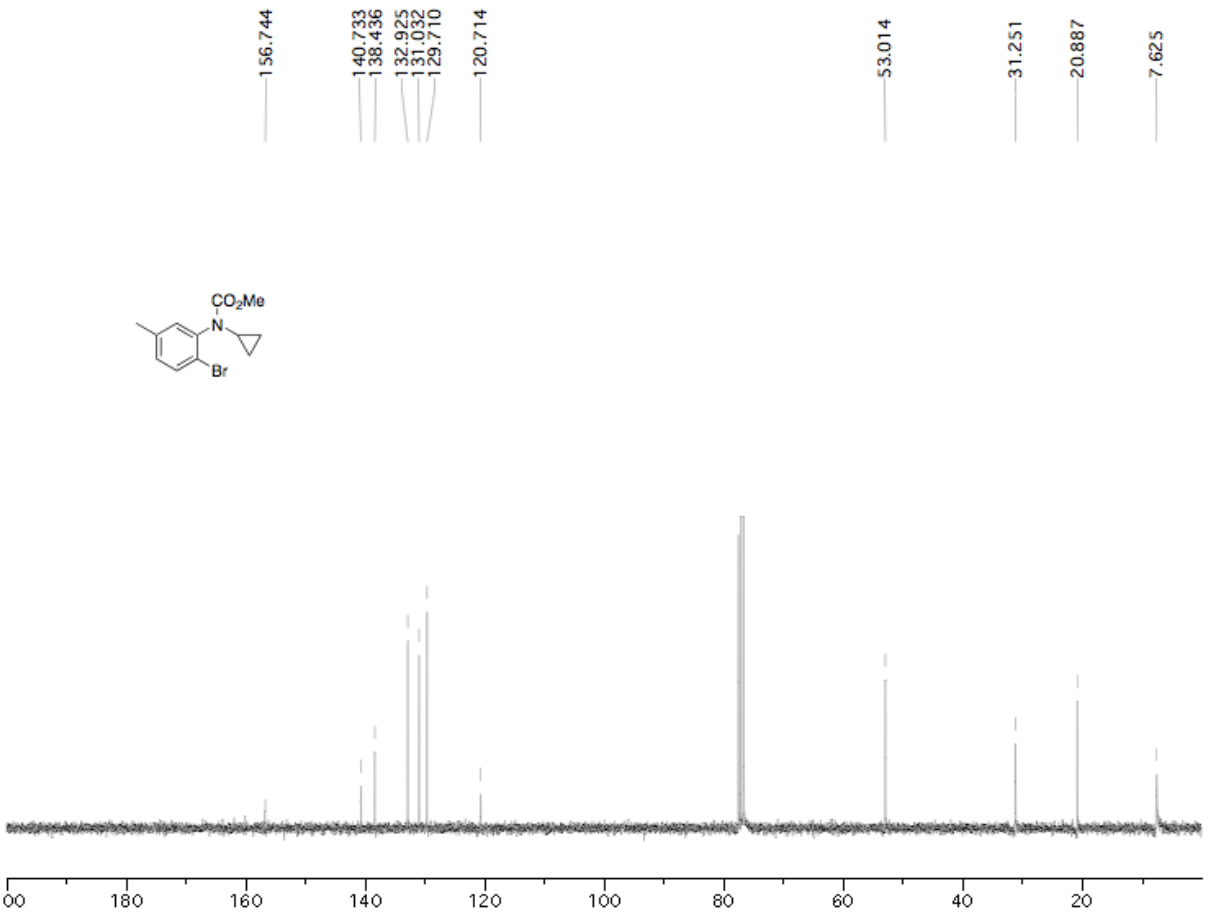
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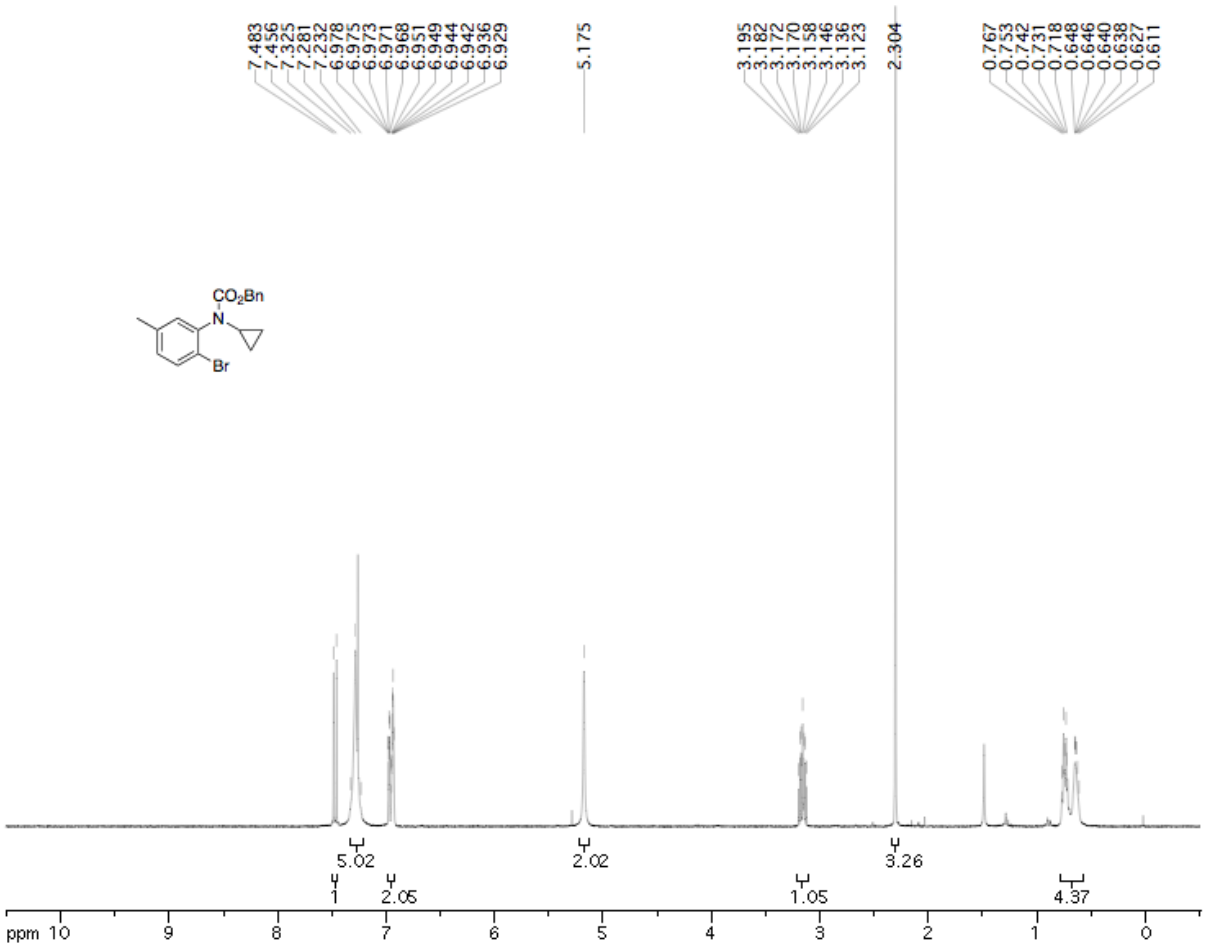

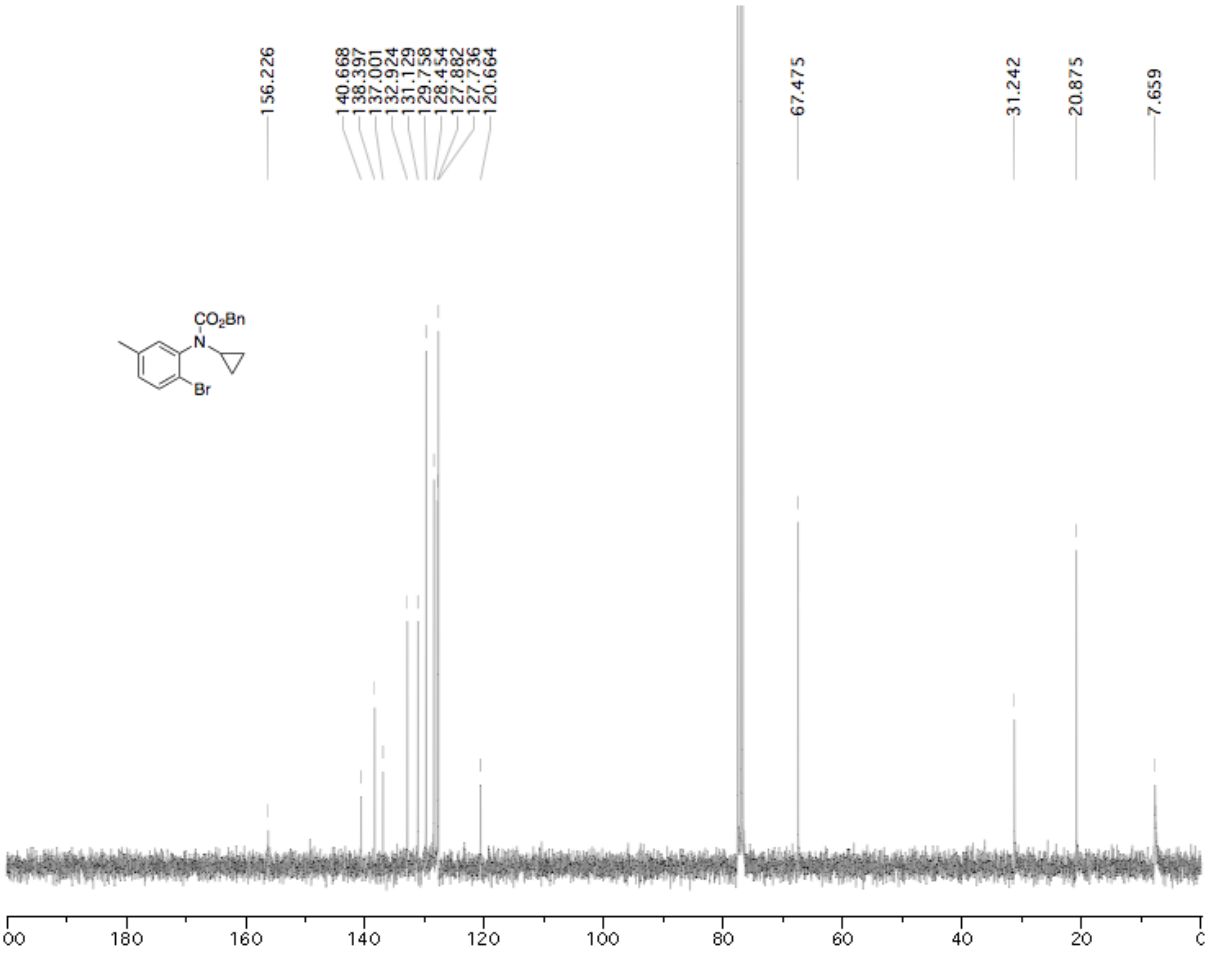

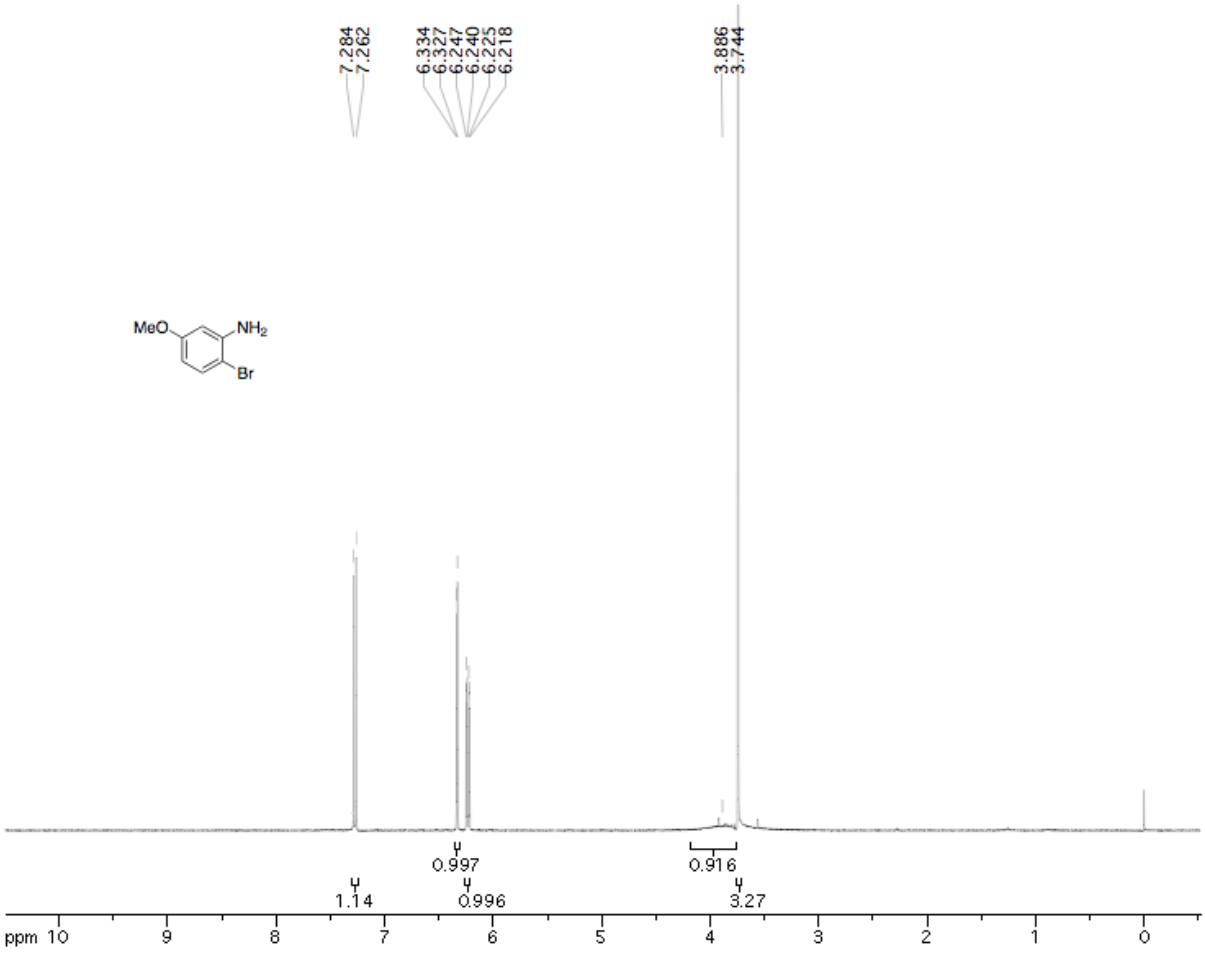
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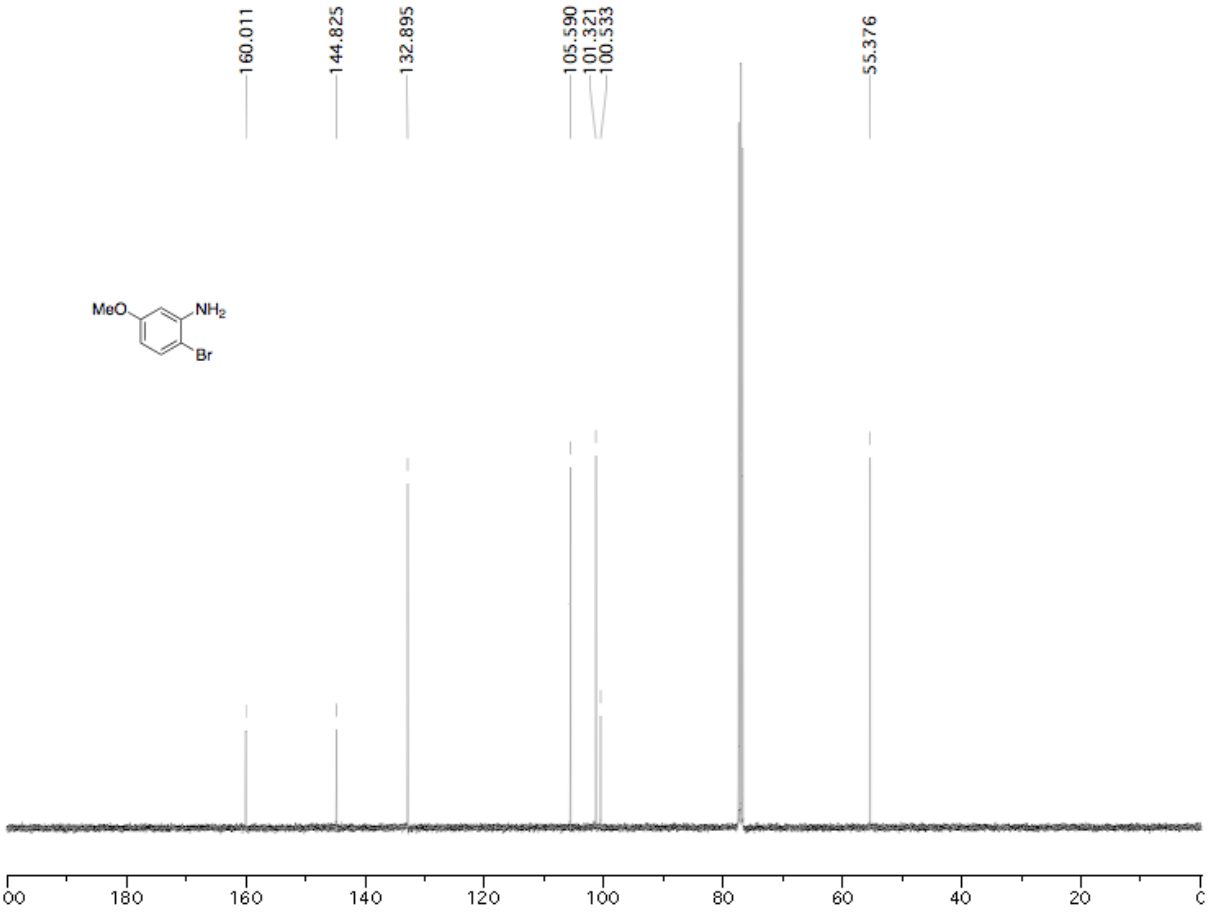
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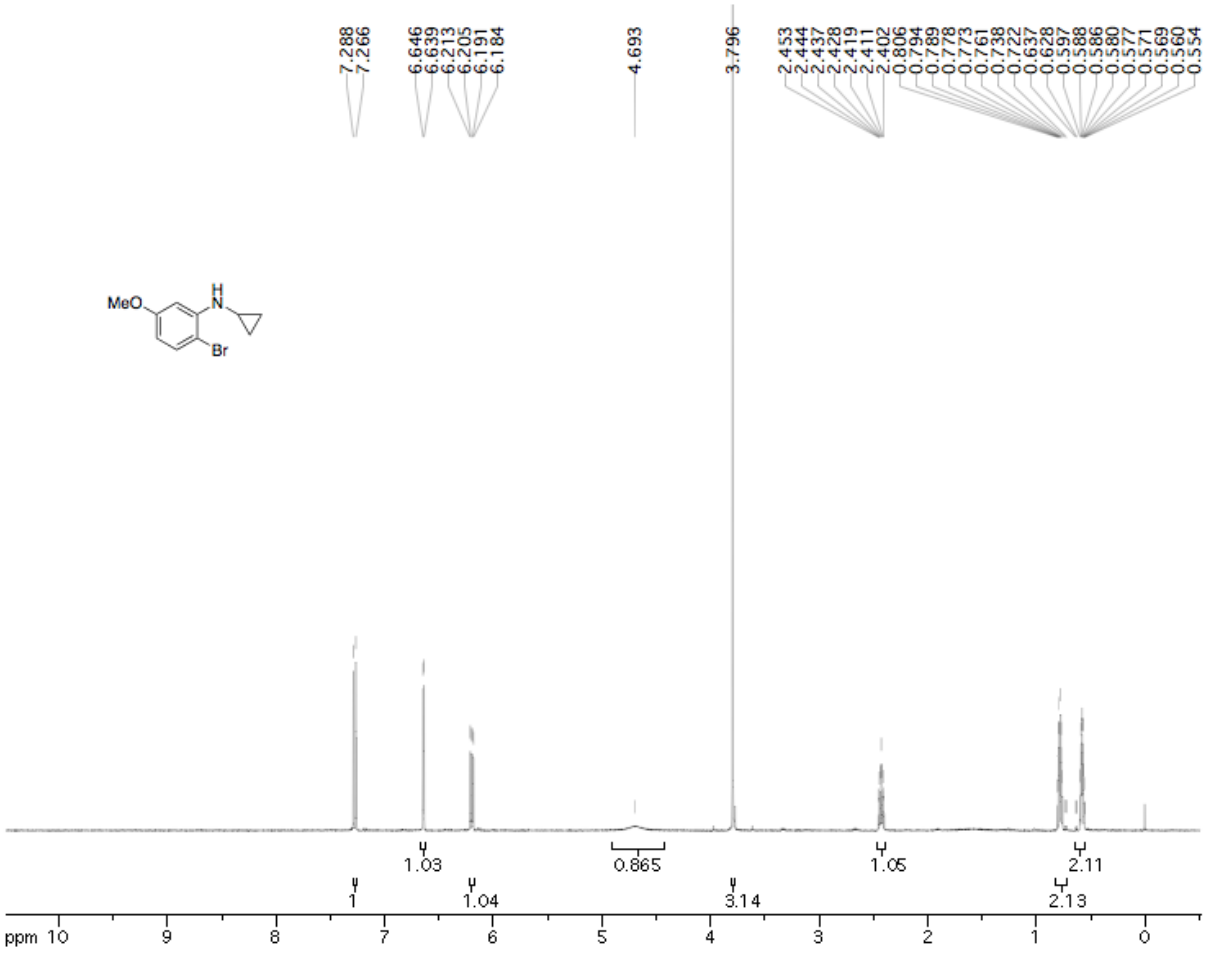
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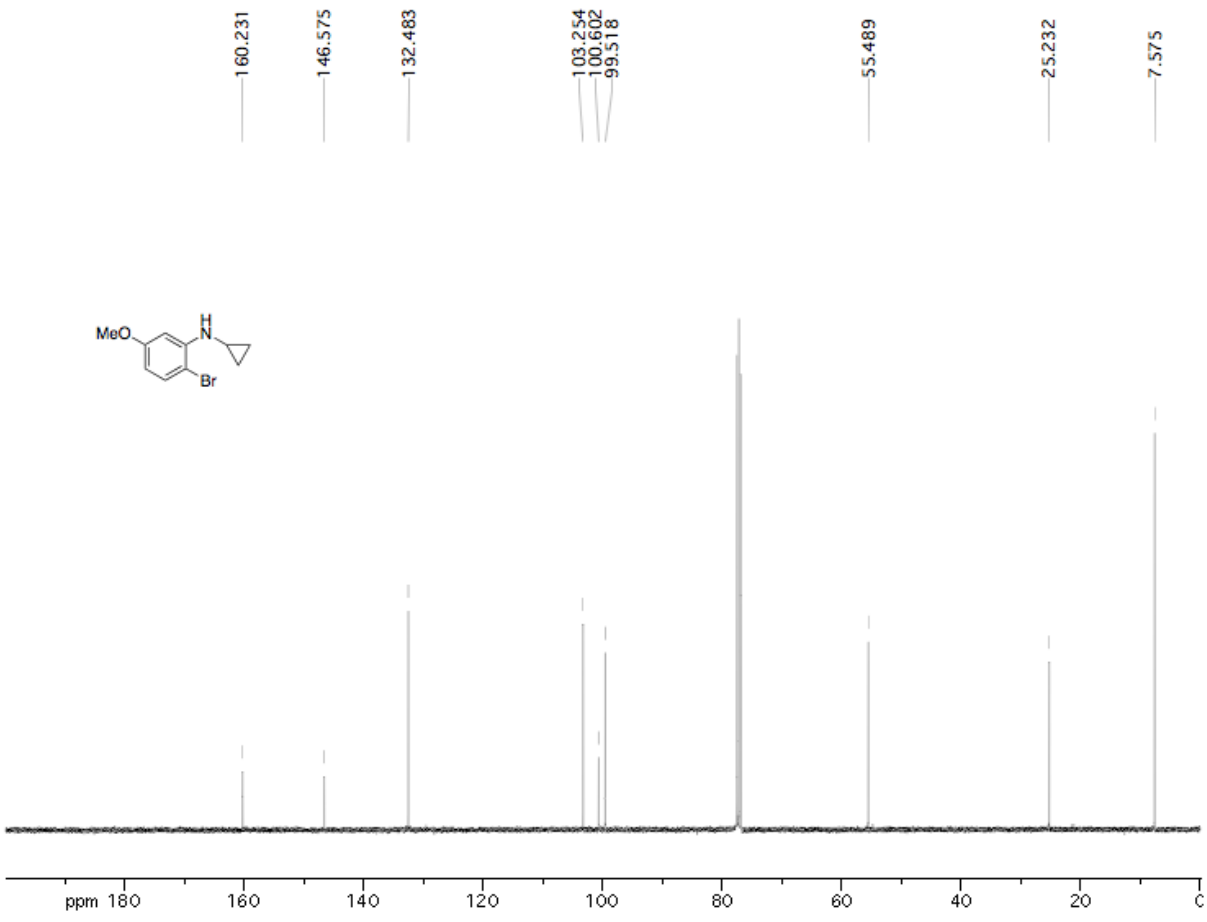
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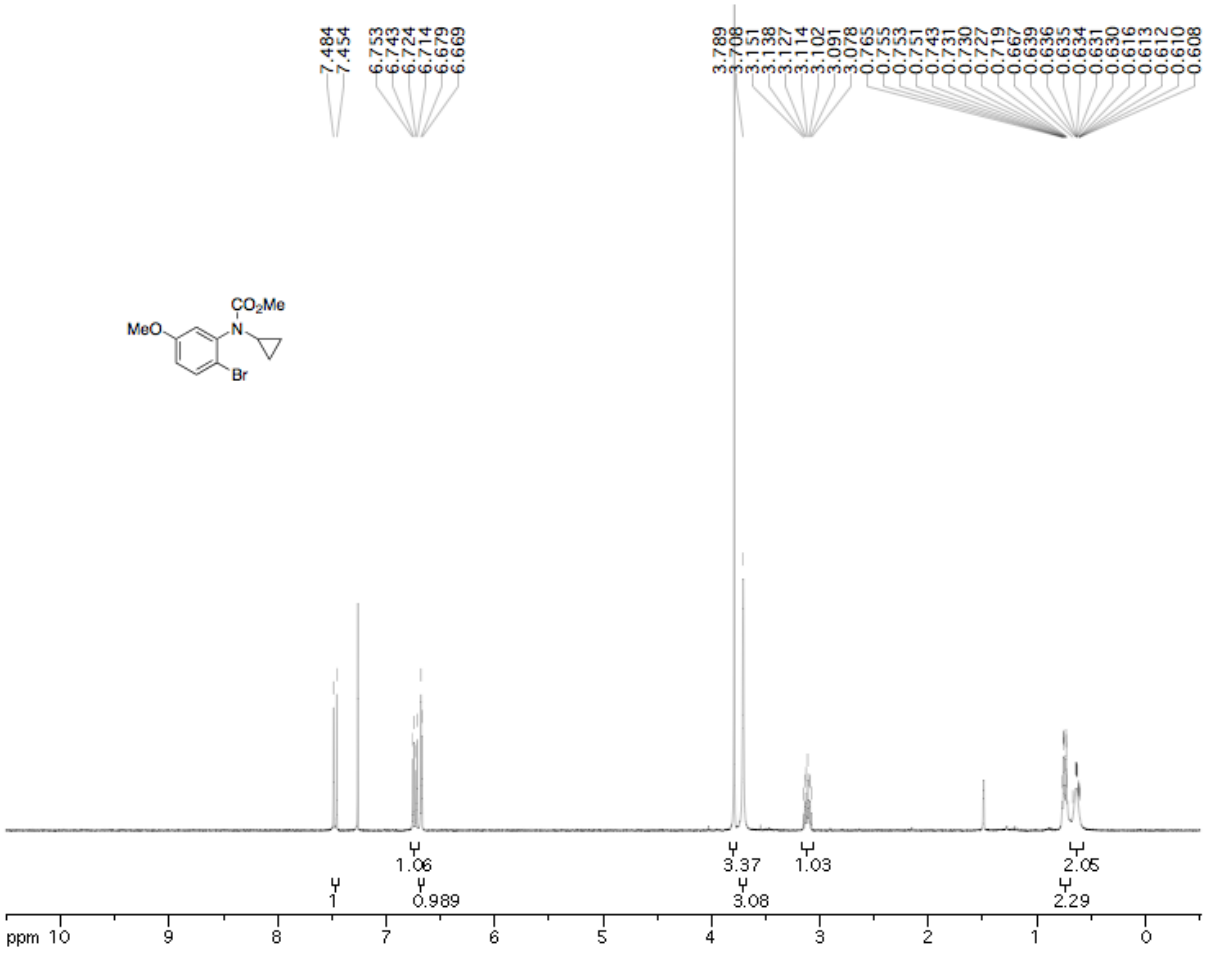
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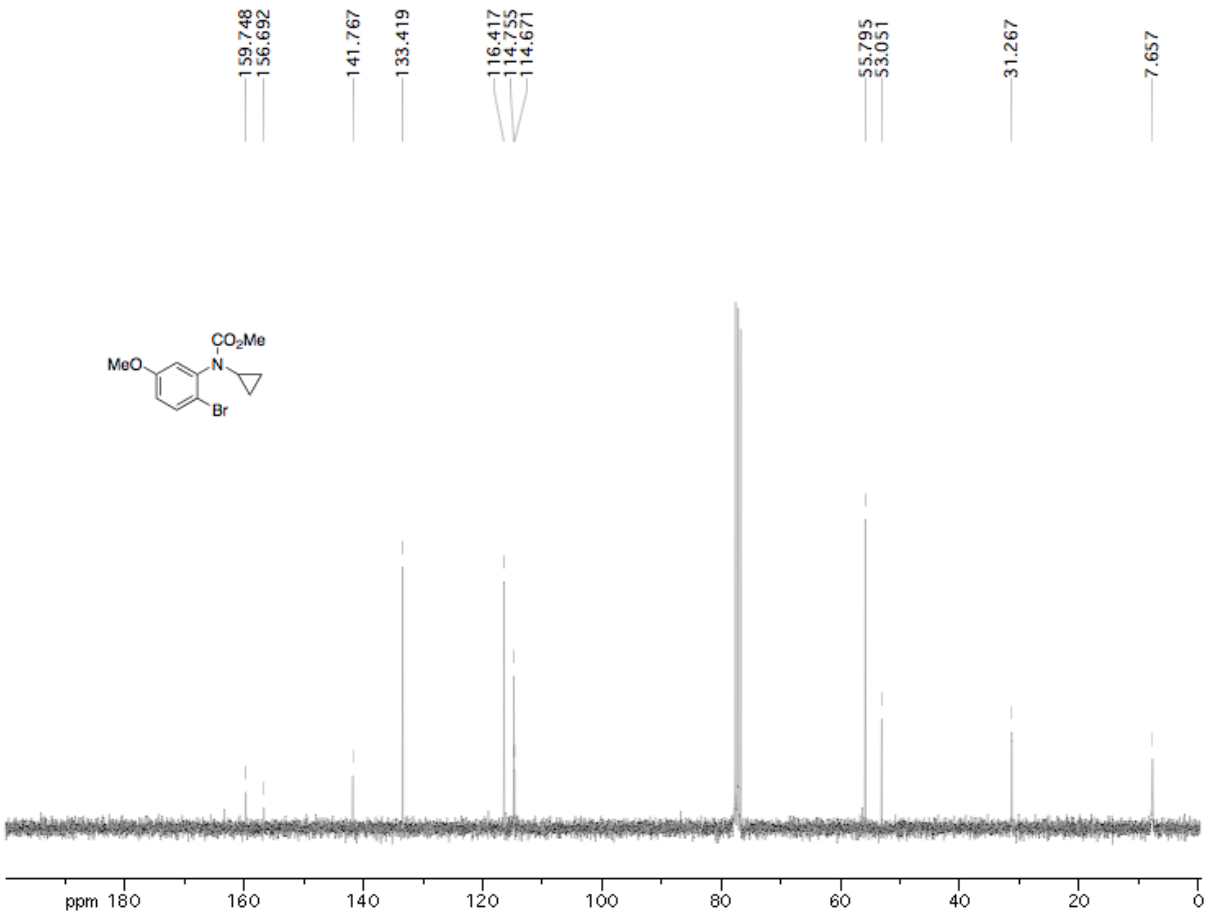
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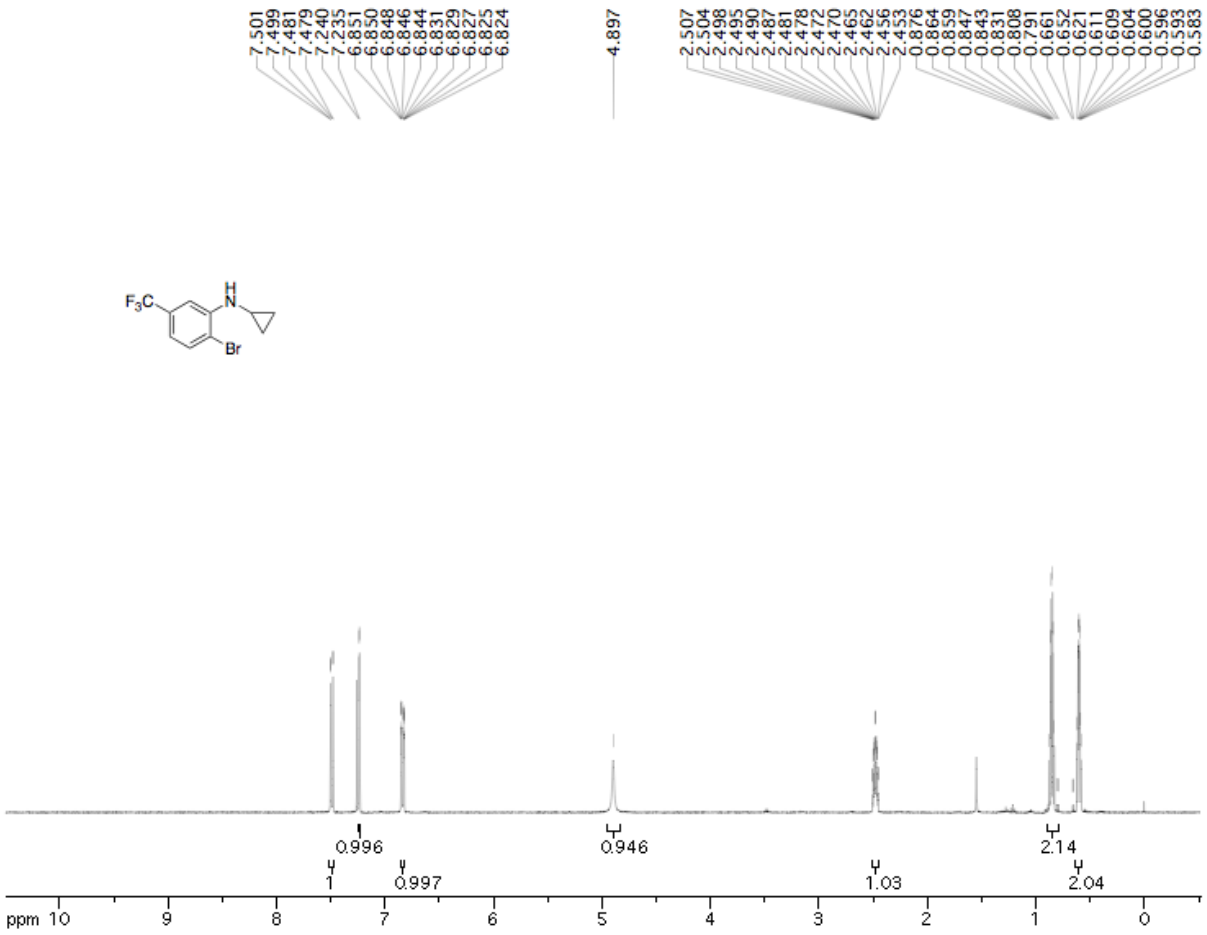
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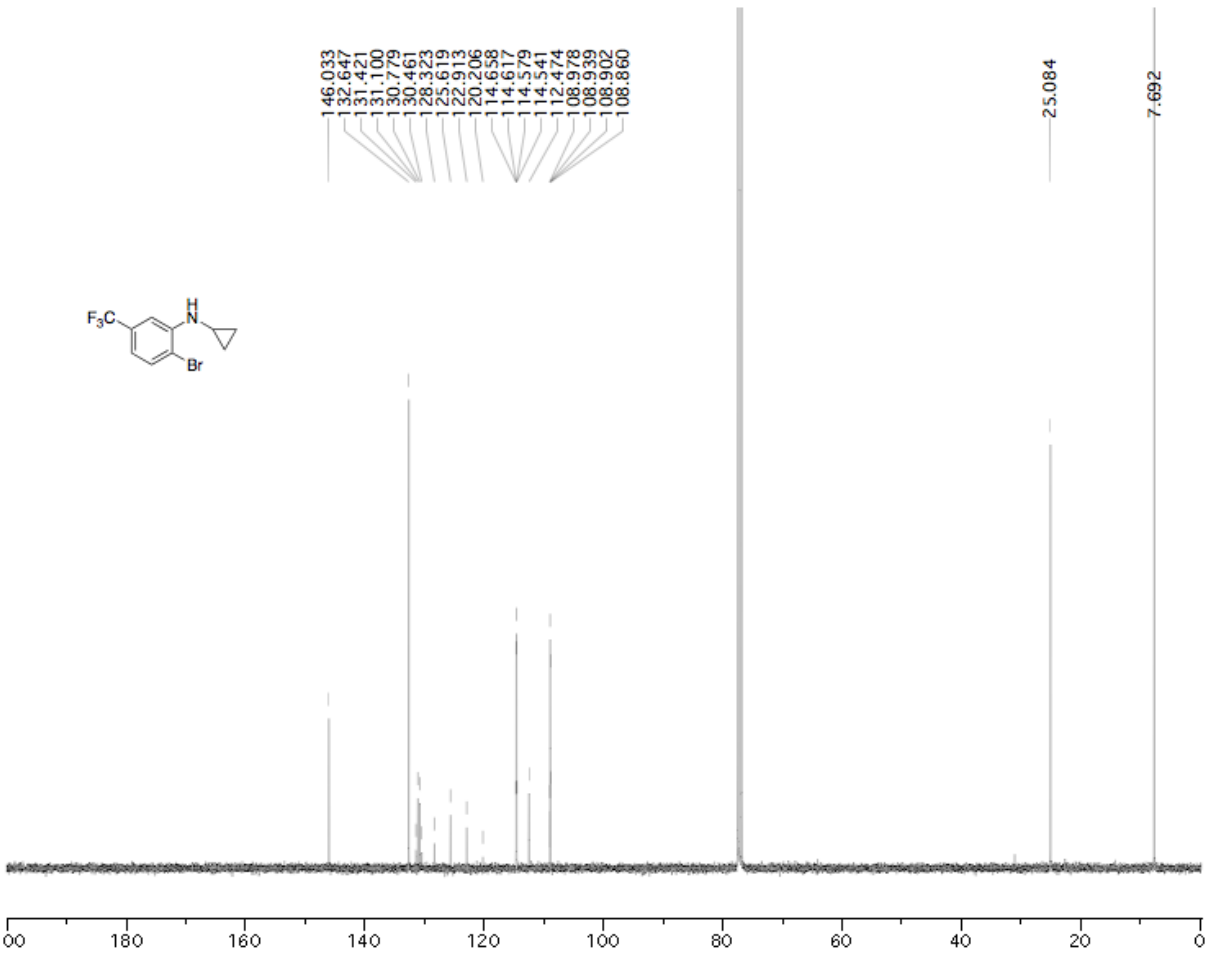
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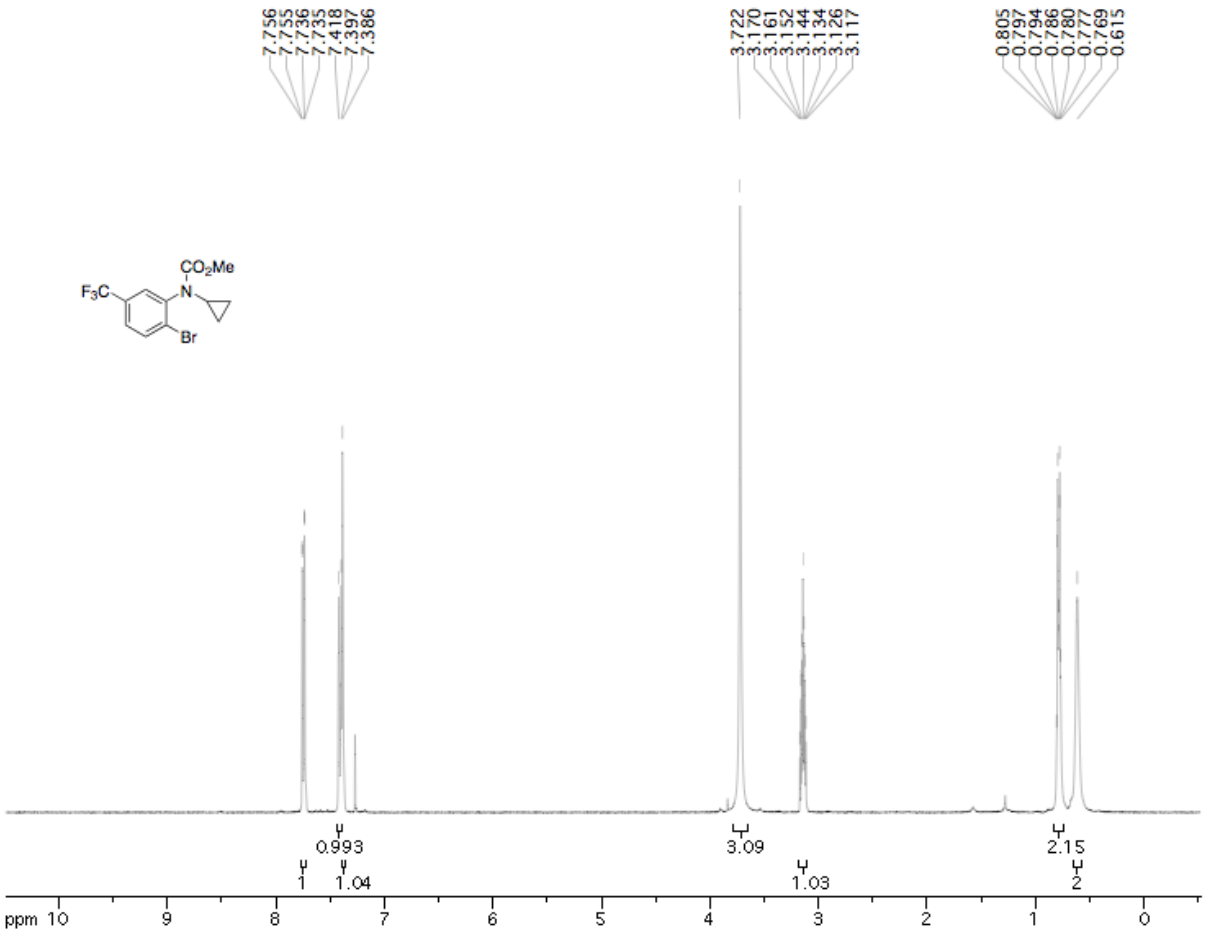
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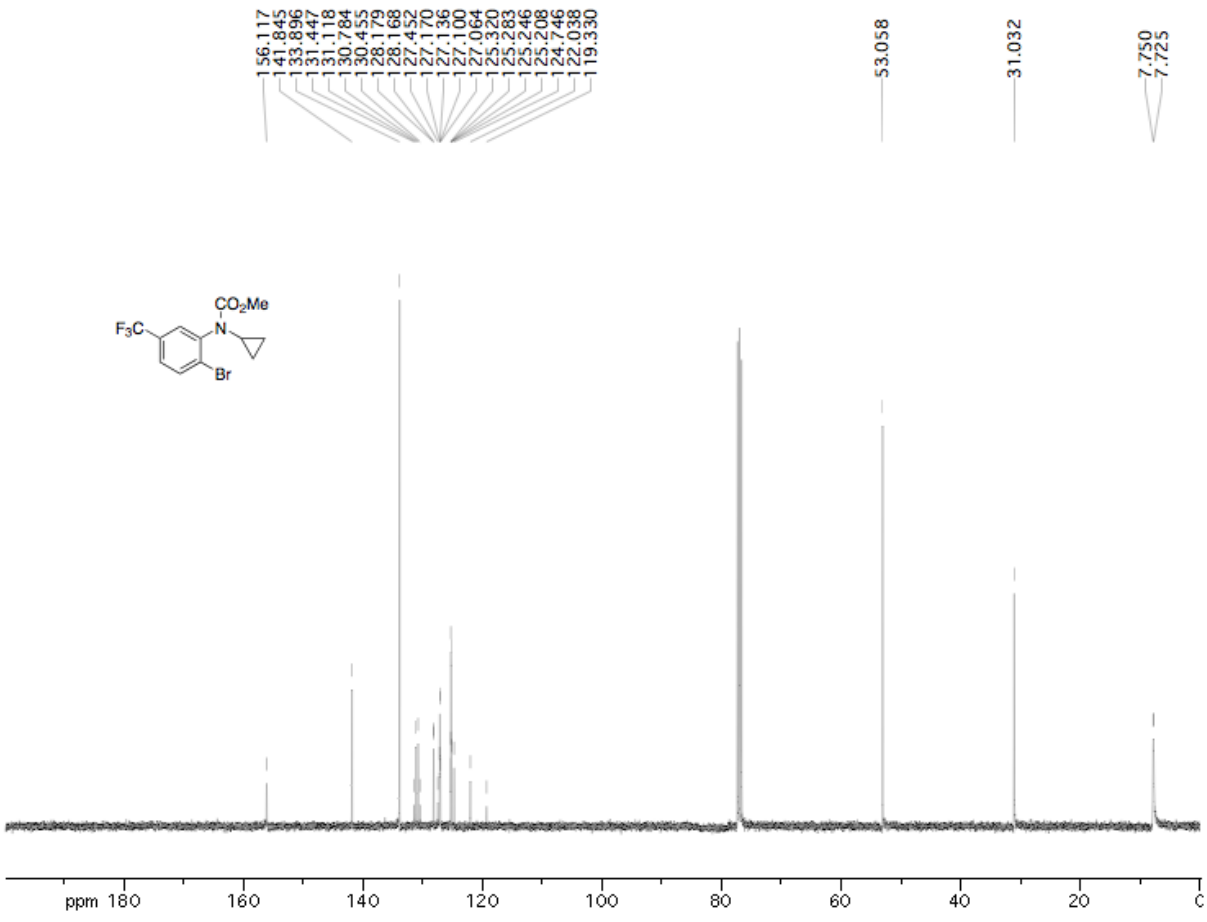
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125.246
125.208
124.746
122.038
119.330
53.058
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N
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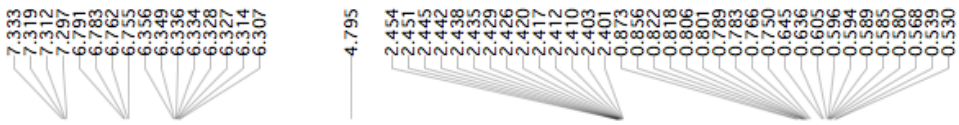
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6.314
6.307
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2.438
2.435
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2.426
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2.417
2.412
2.410
2.403
2.401
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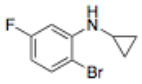
0.530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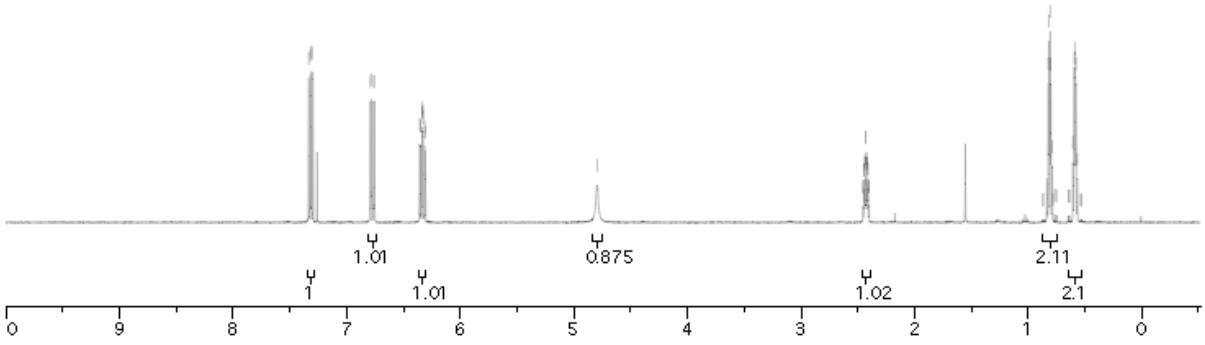
H
N
Br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2
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0


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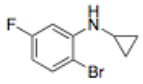
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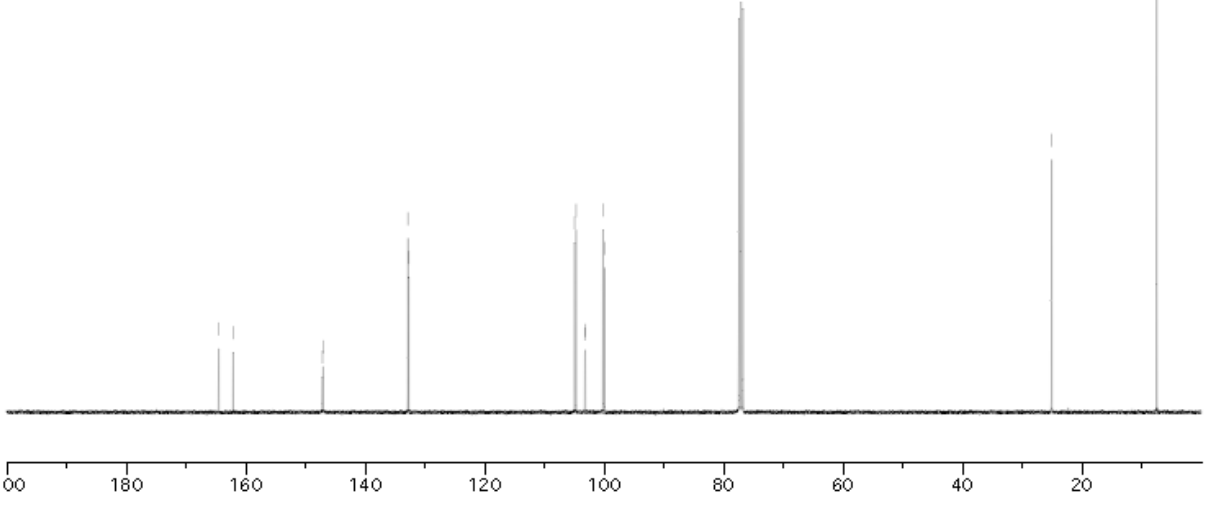
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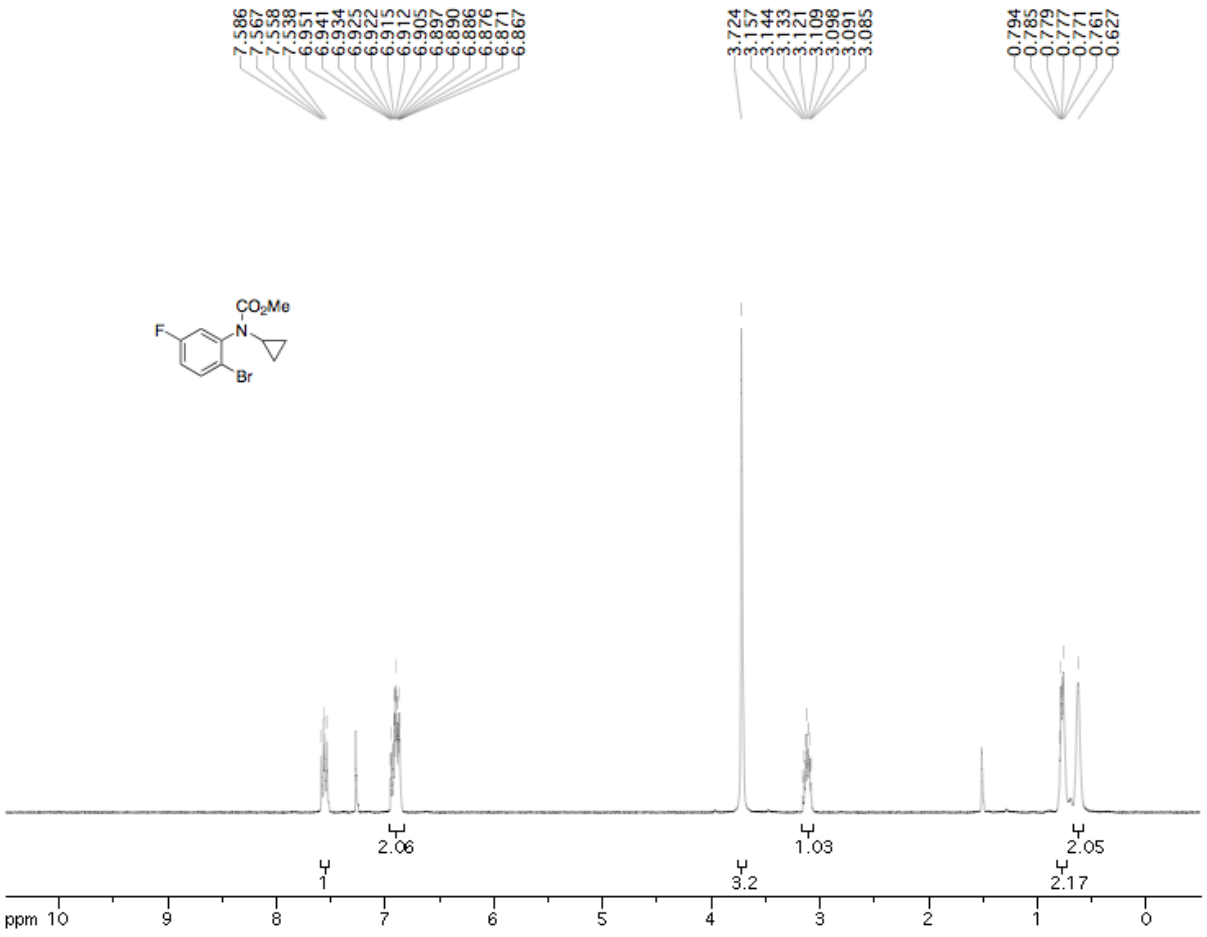
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6.890
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6.876
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3.144
3.133
3.121
3.109
3.098
3.091
3.085
0.794
0.785
0.779
0.777
0.771
0.761
0.627
CO2Me
F
N
Br
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1
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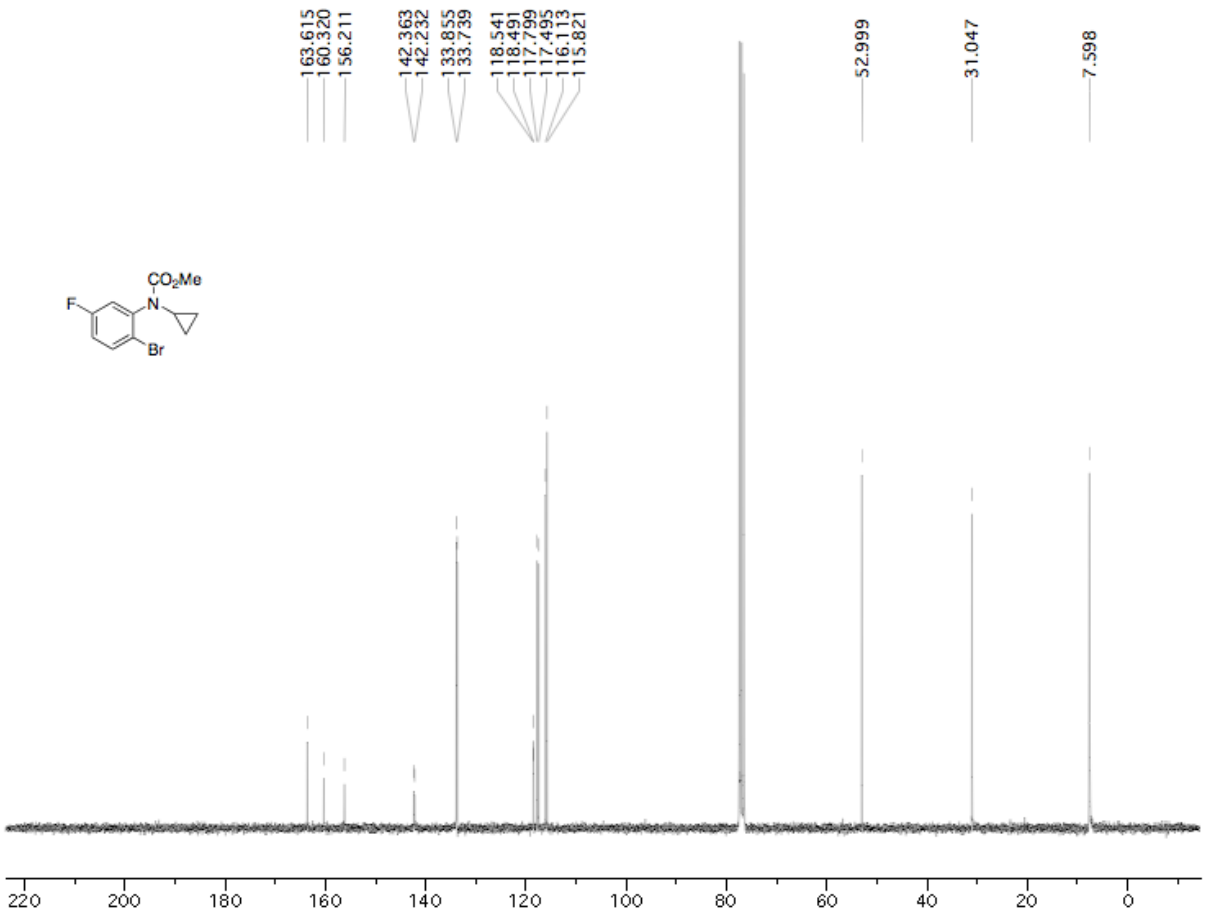
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52.999
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20
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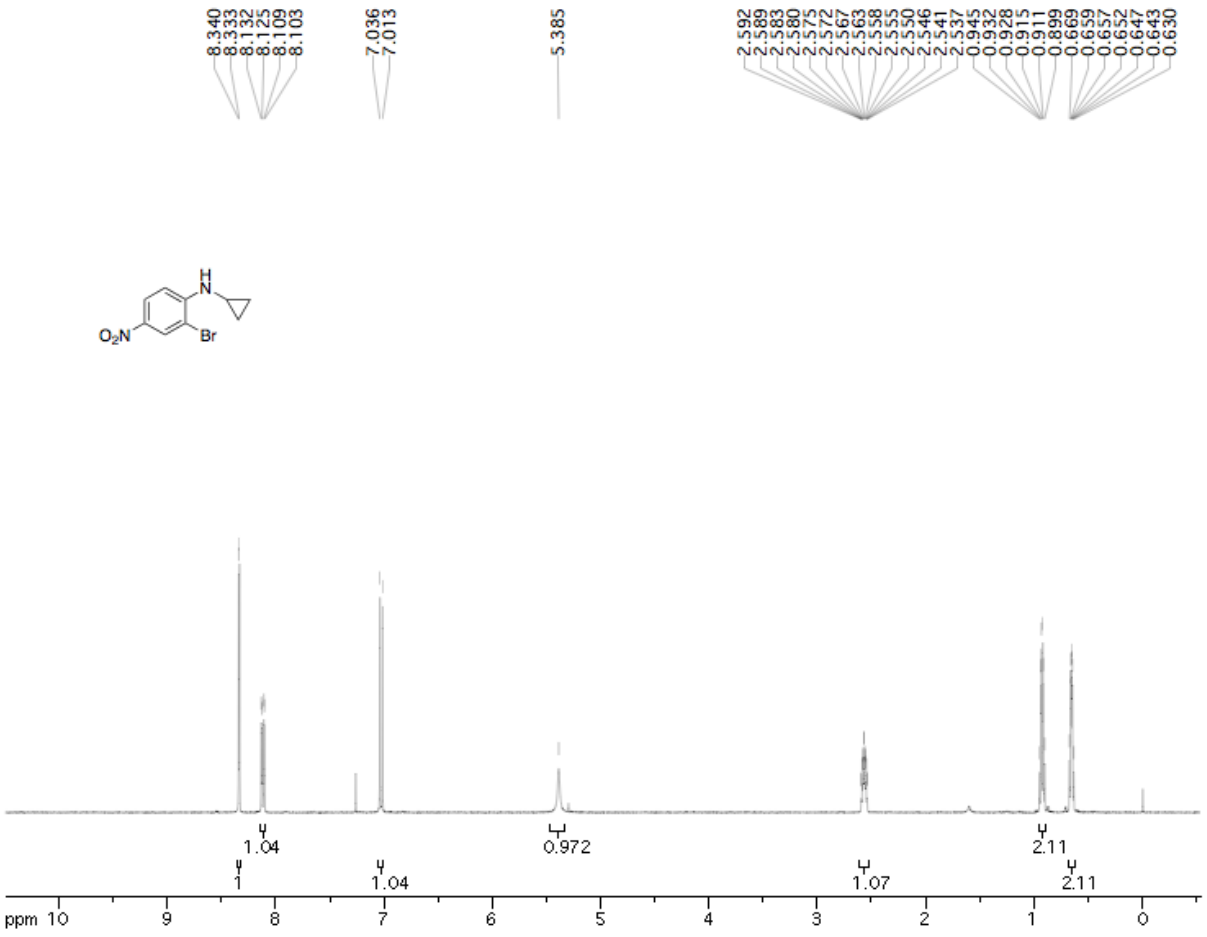
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2.575
2.572
2.567
2.563
2.558
2.555
2.550
2.546
2.541
2.537
0.945
0.932
0.928
0.915
0.911
0.899
0.669
0.659
0.657
0.652
0.647
0.643
0.630
H
N
O2N
Br
1.04
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1.04
1.07
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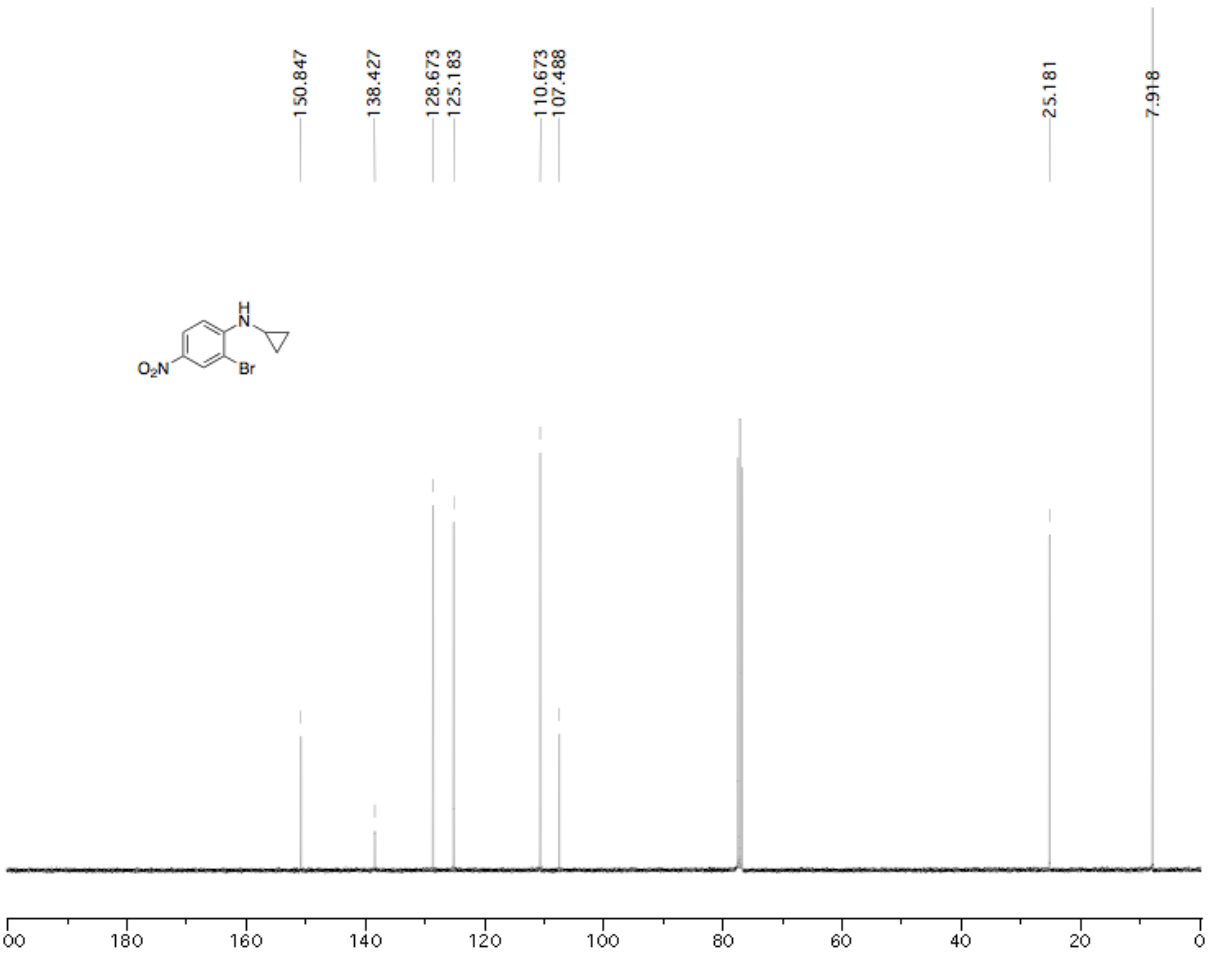
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N
O2N
Br
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140
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100
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60
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20
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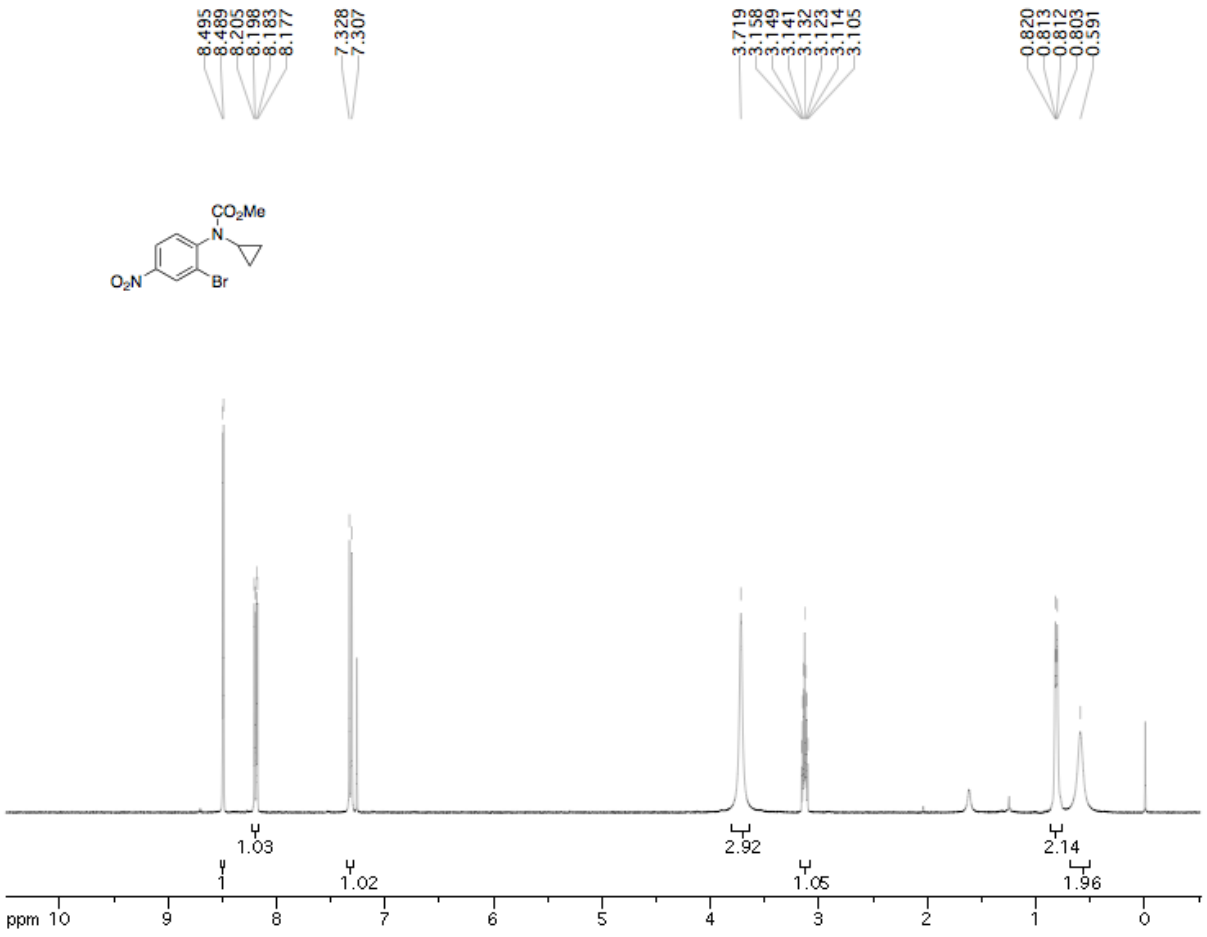

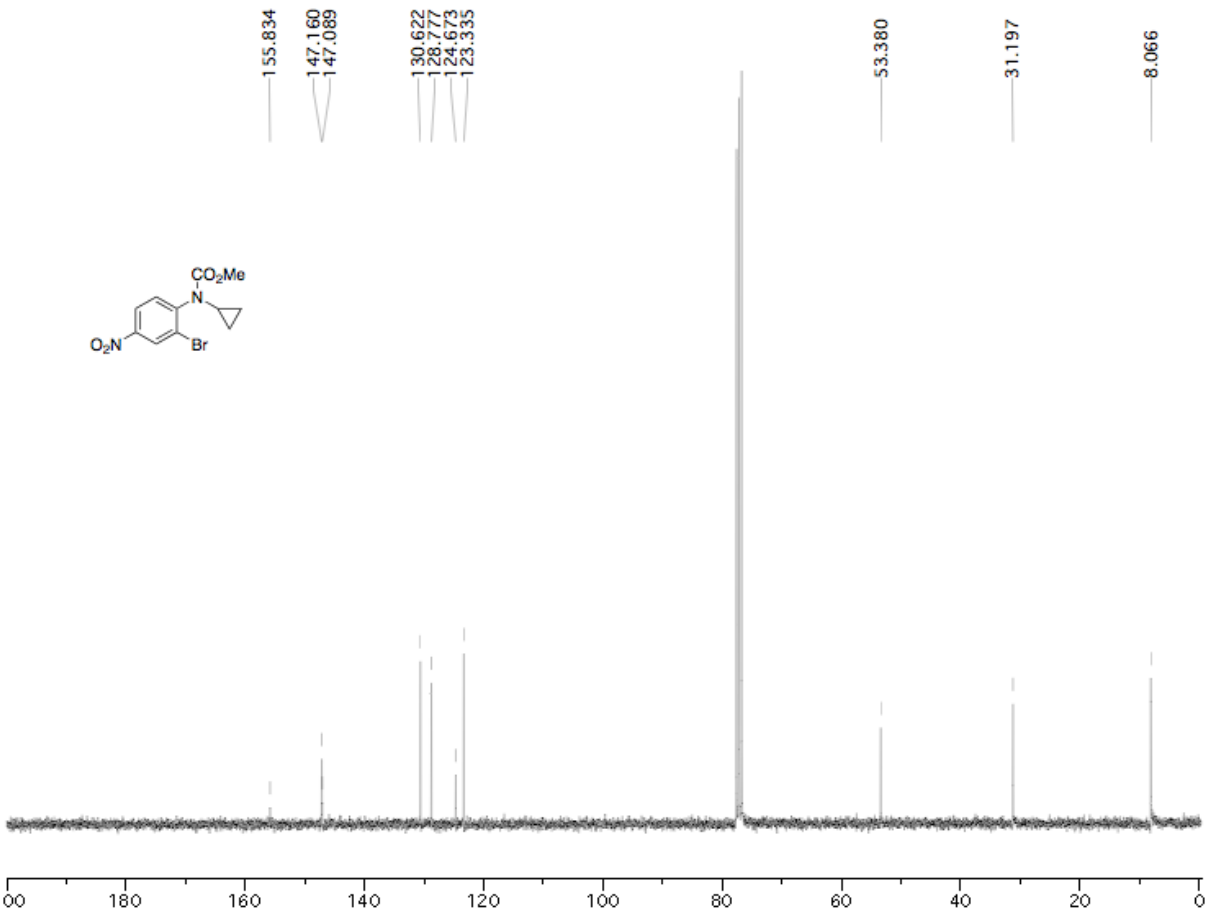

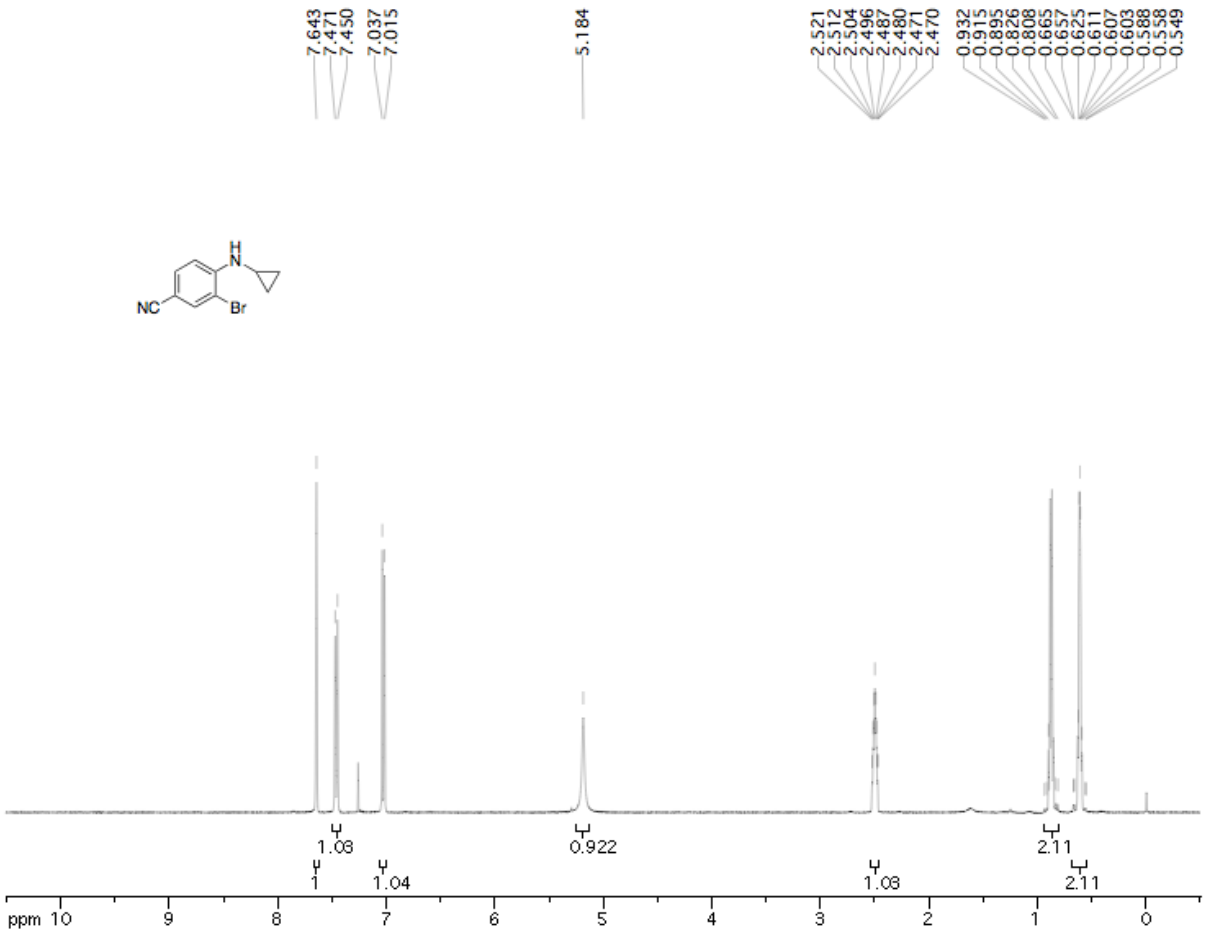

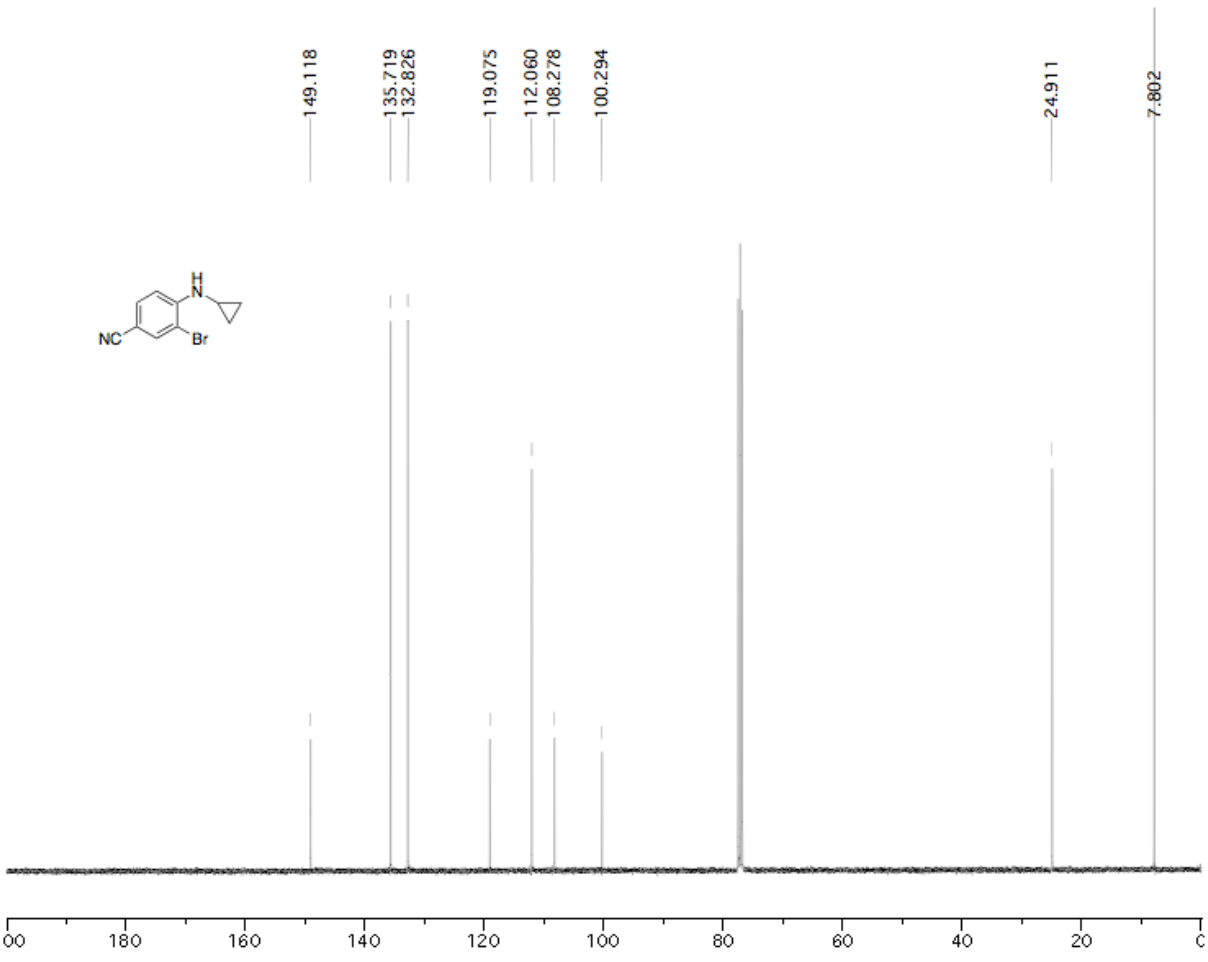

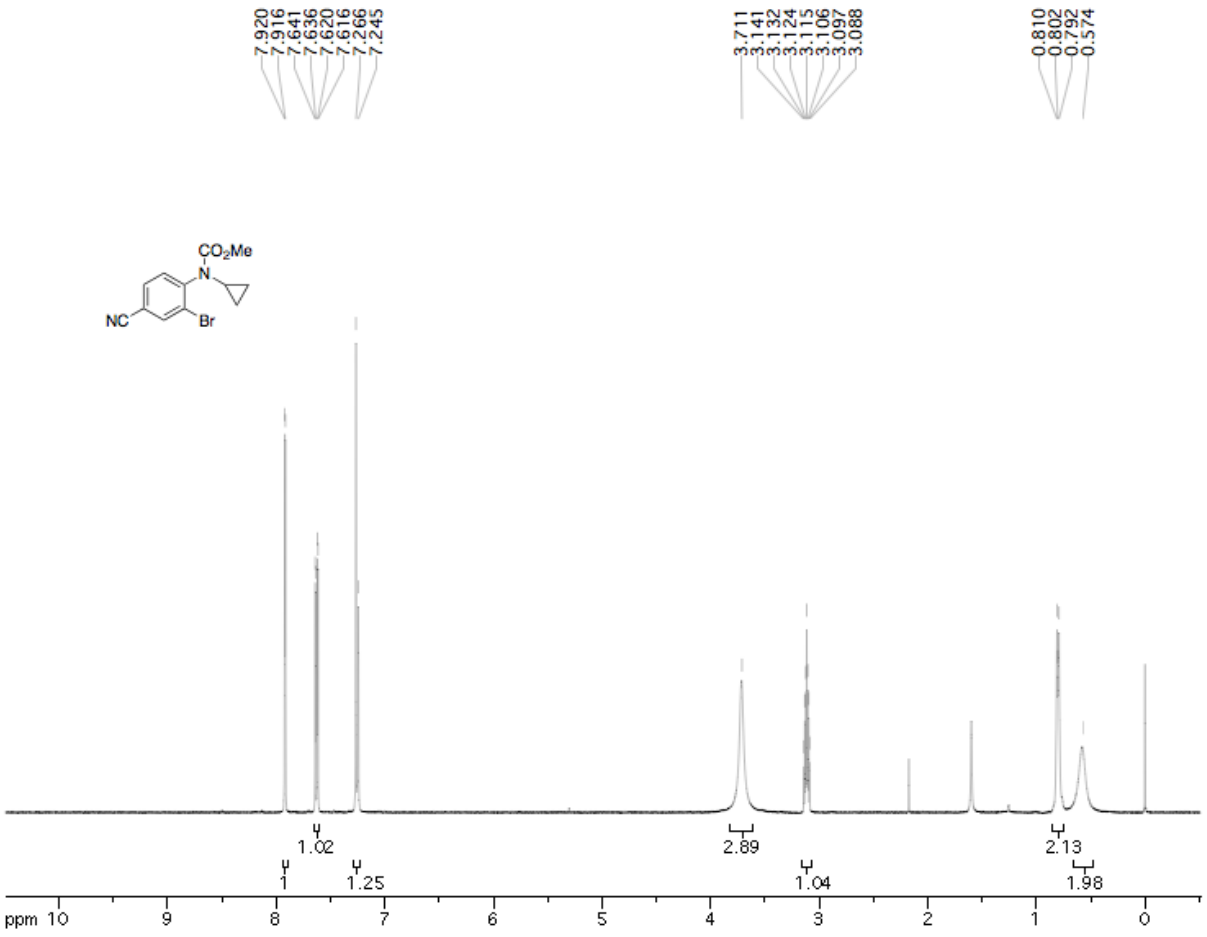

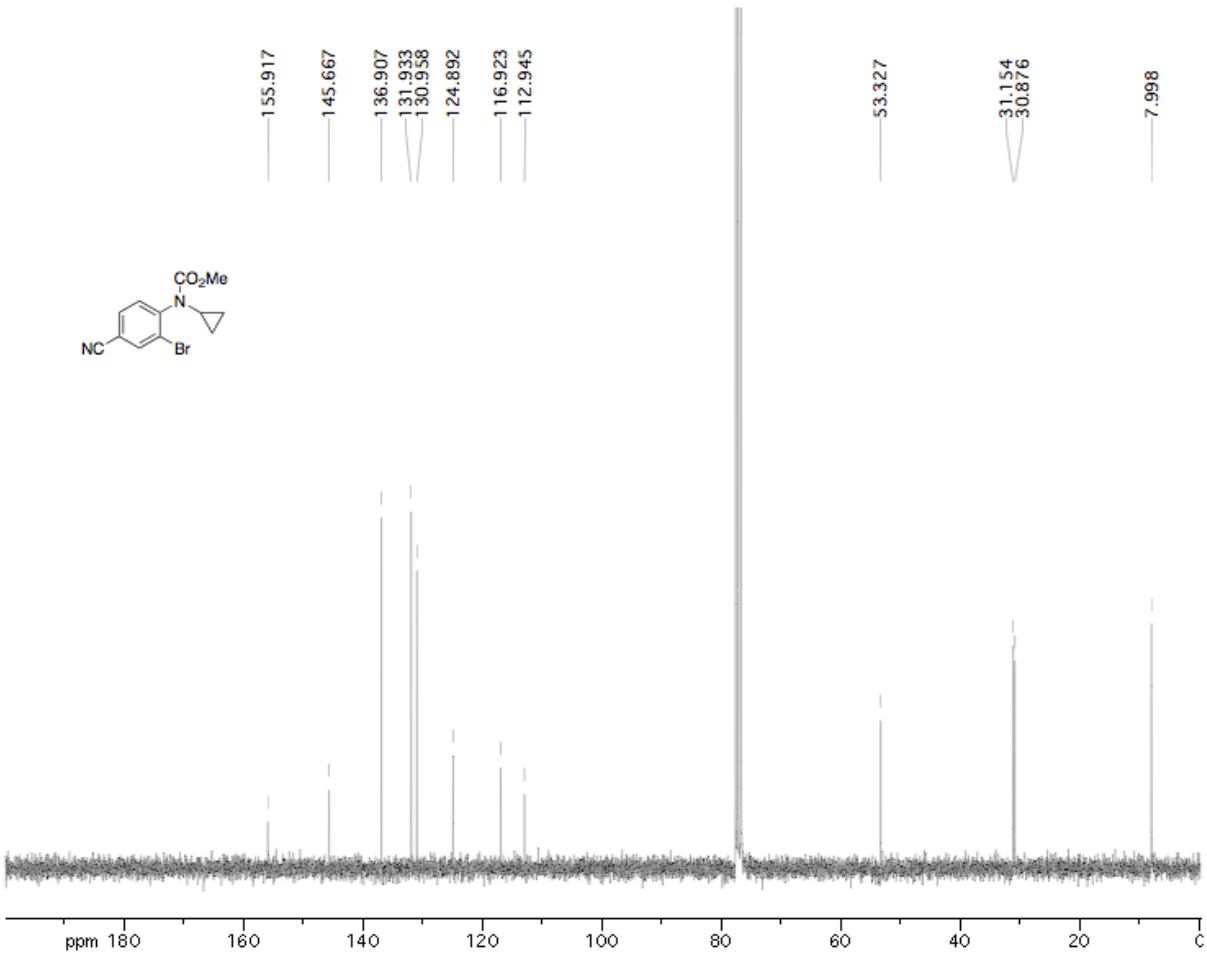

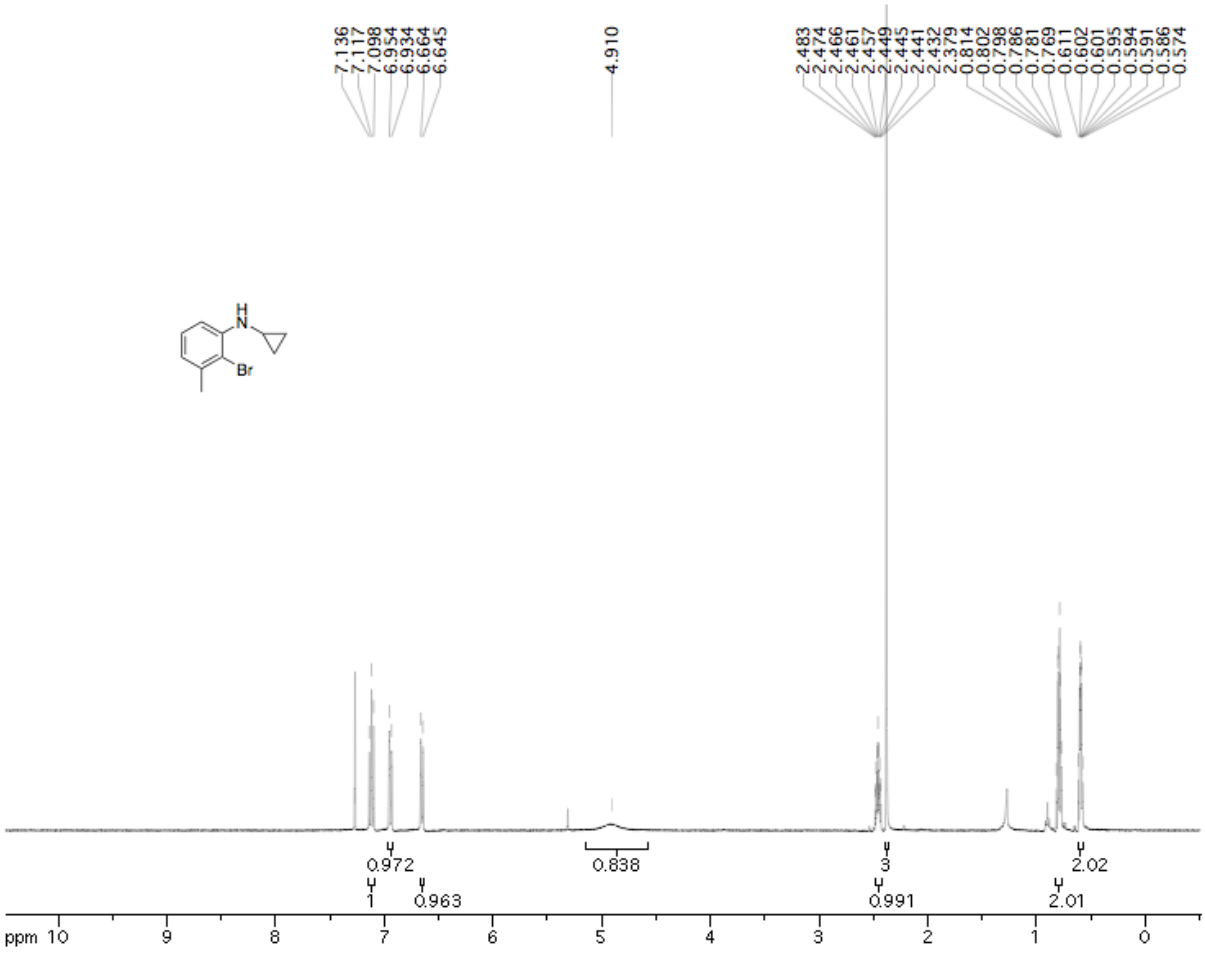
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2.461
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2.449
2.445
2.441
2.432
2.379
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0.798
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0.781
0.769
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0.594
0.591
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0.574
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Br
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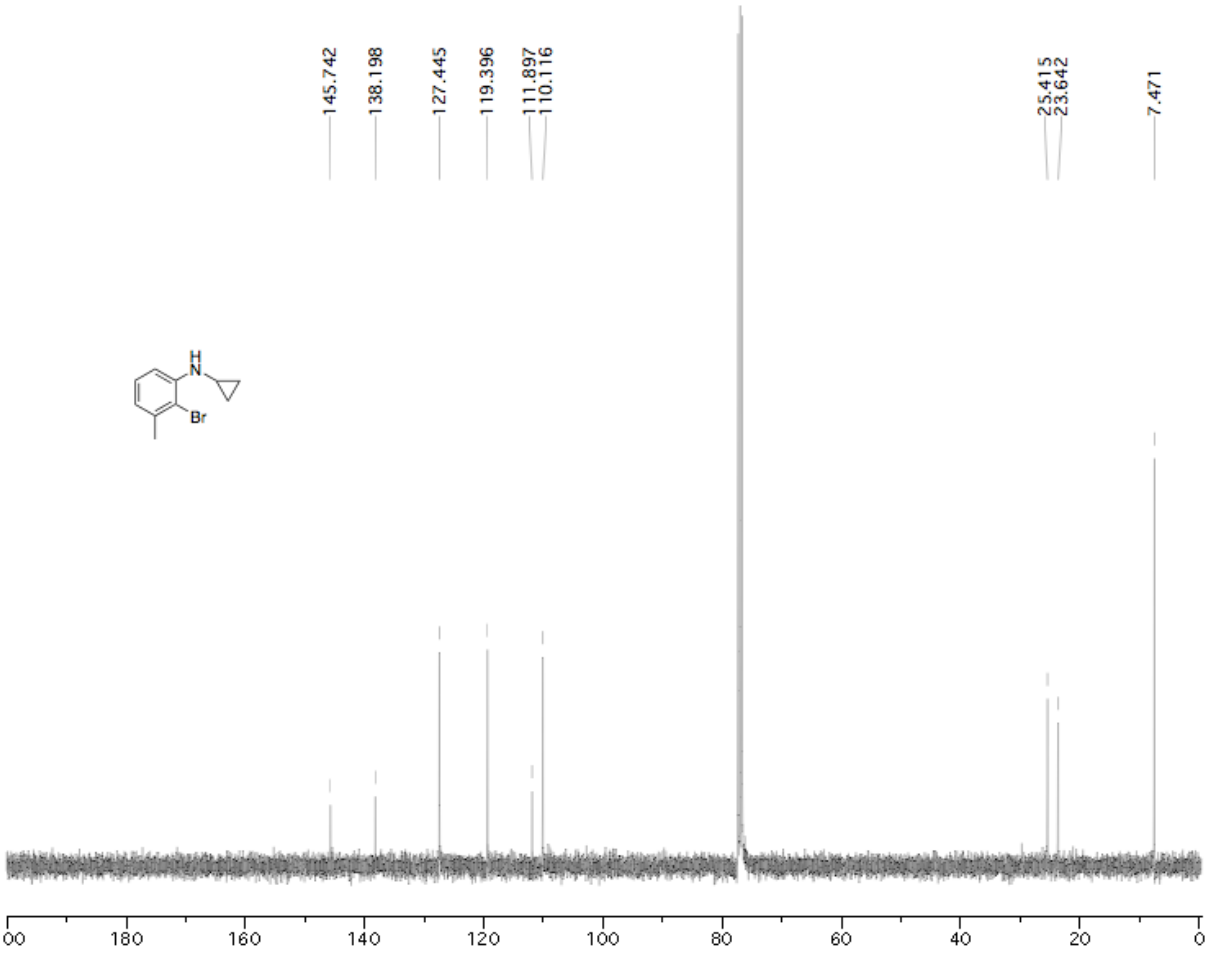
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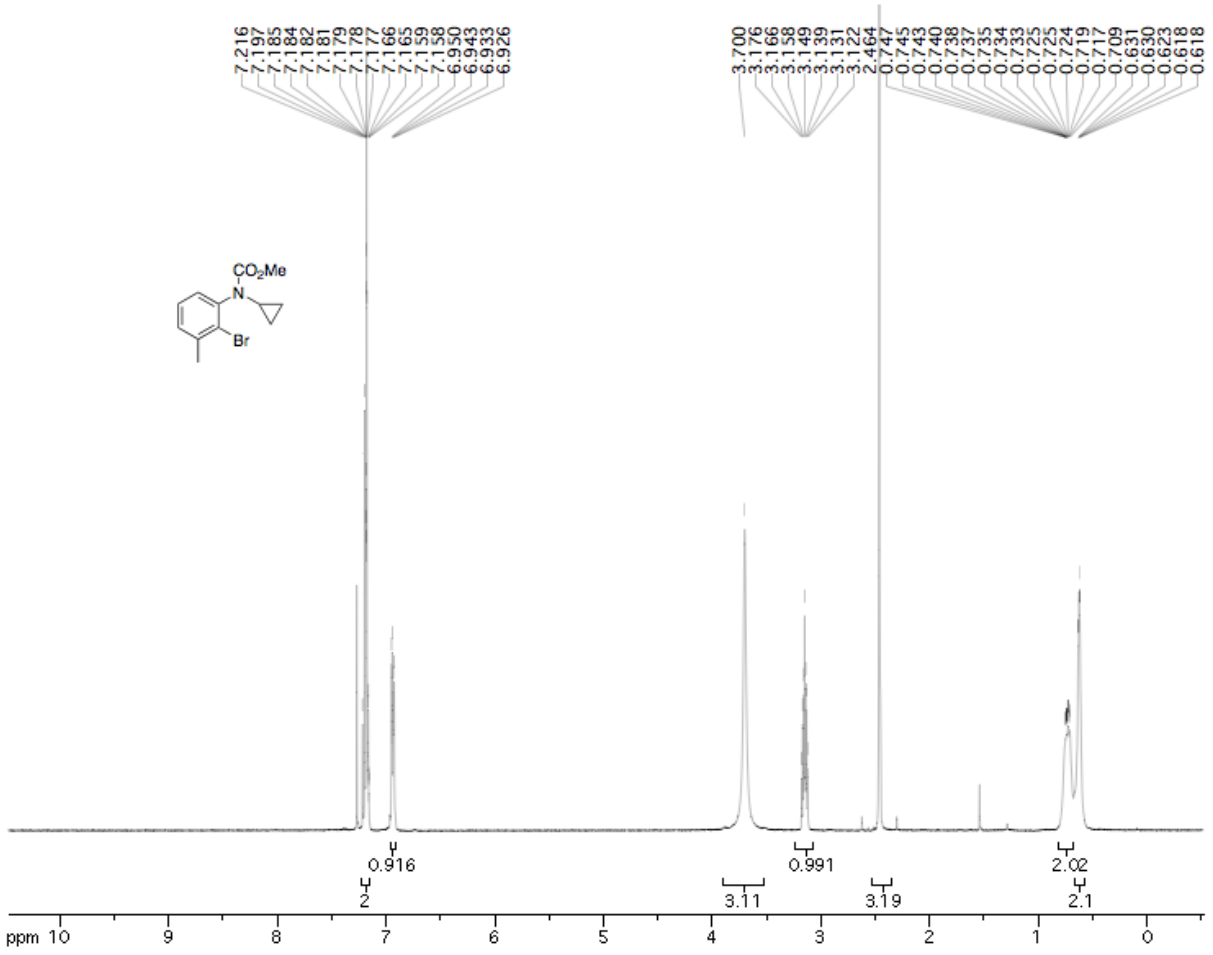
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6.933
6.926
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3.149
3.139
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0.735
0.734
0.733
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0.725
0.724
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0.630
0.623
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0.618
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Br
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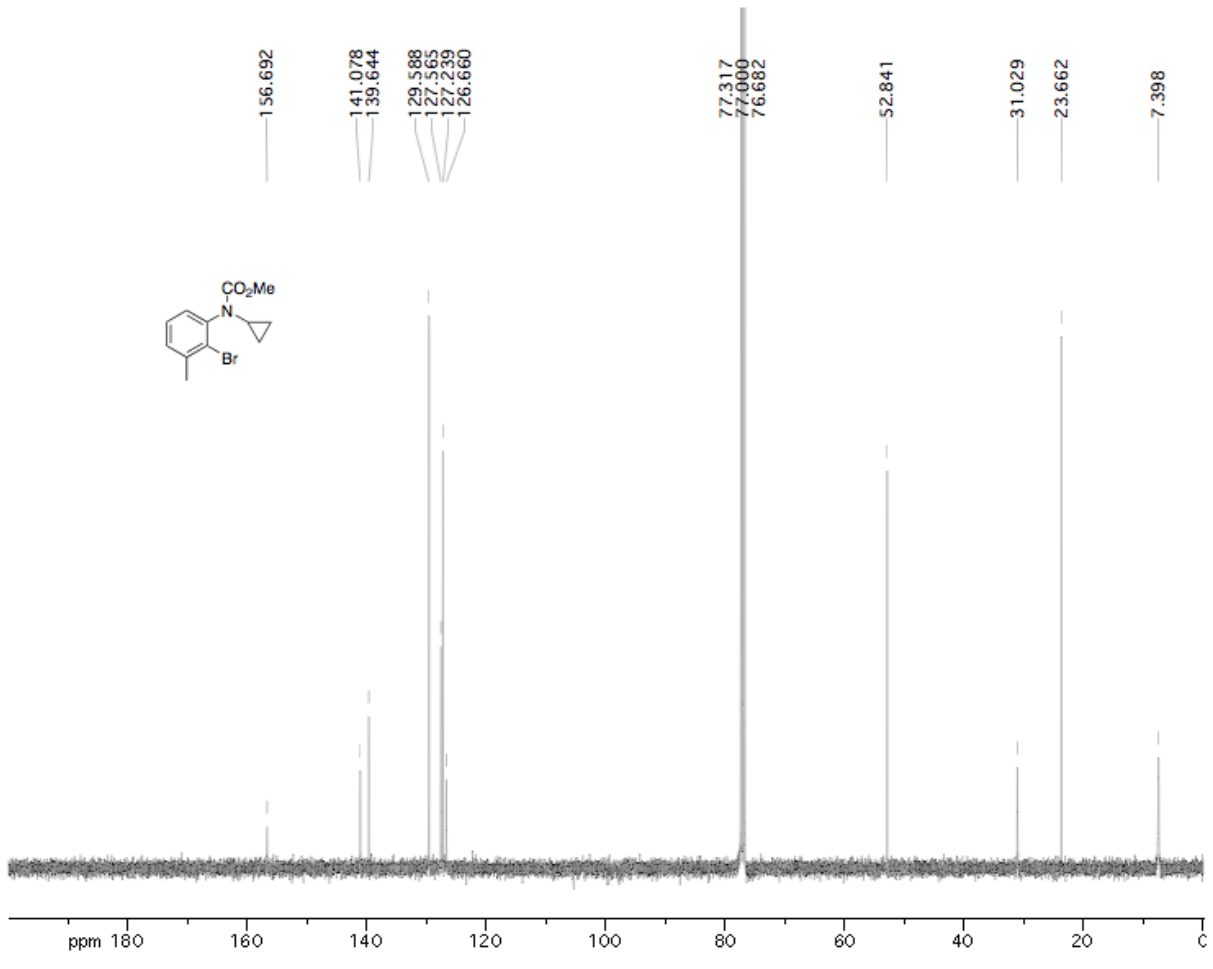
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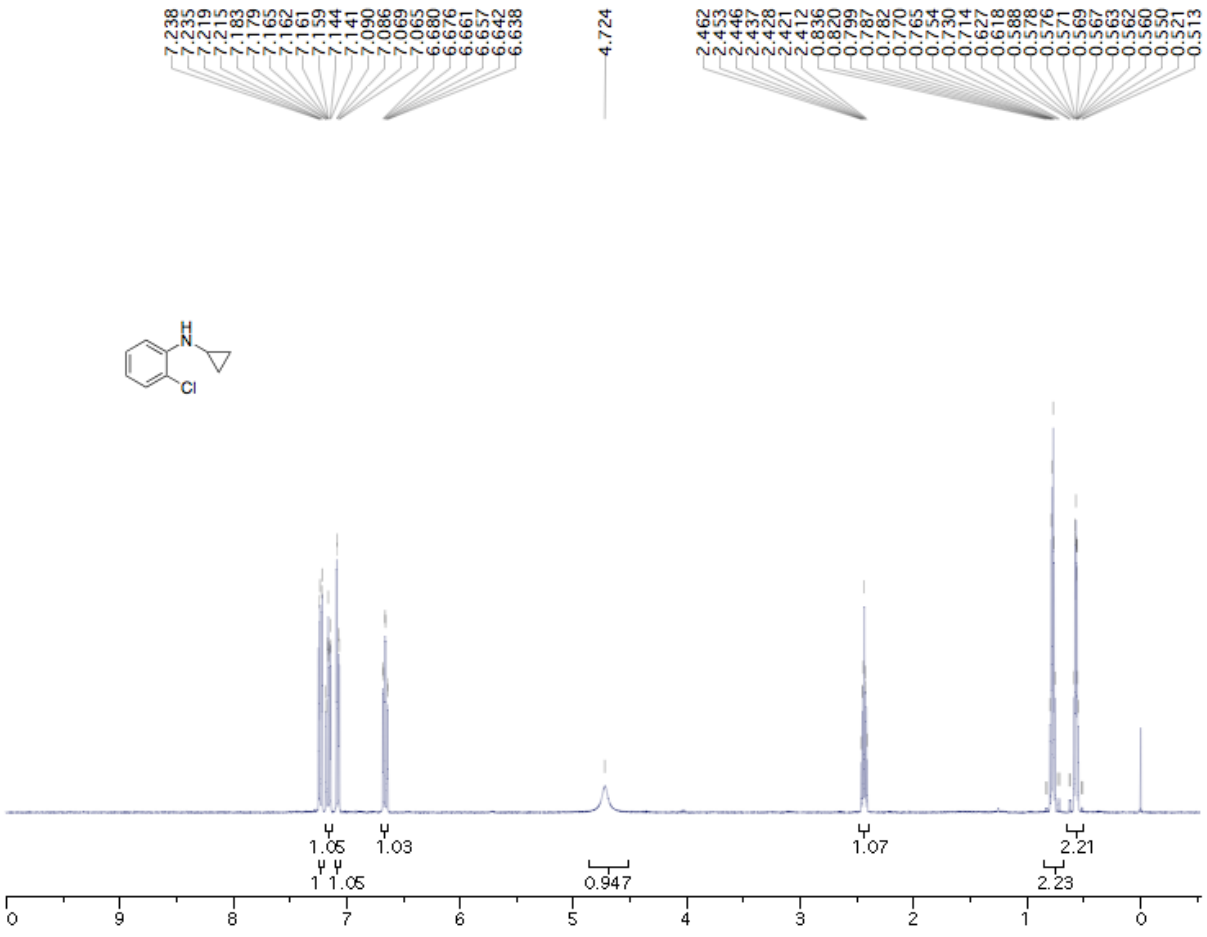
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7.086
7.069
7.065
6.680
6.676
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6.657
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4.724
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2.453
2.446
2.437
2.428
2.421
2.412
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0.820
0.799
0.787
0.782
0.770
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0.730
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0.627
0.618
0.588
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0.569
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0.563
0.562
0.560
0.550
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Cl
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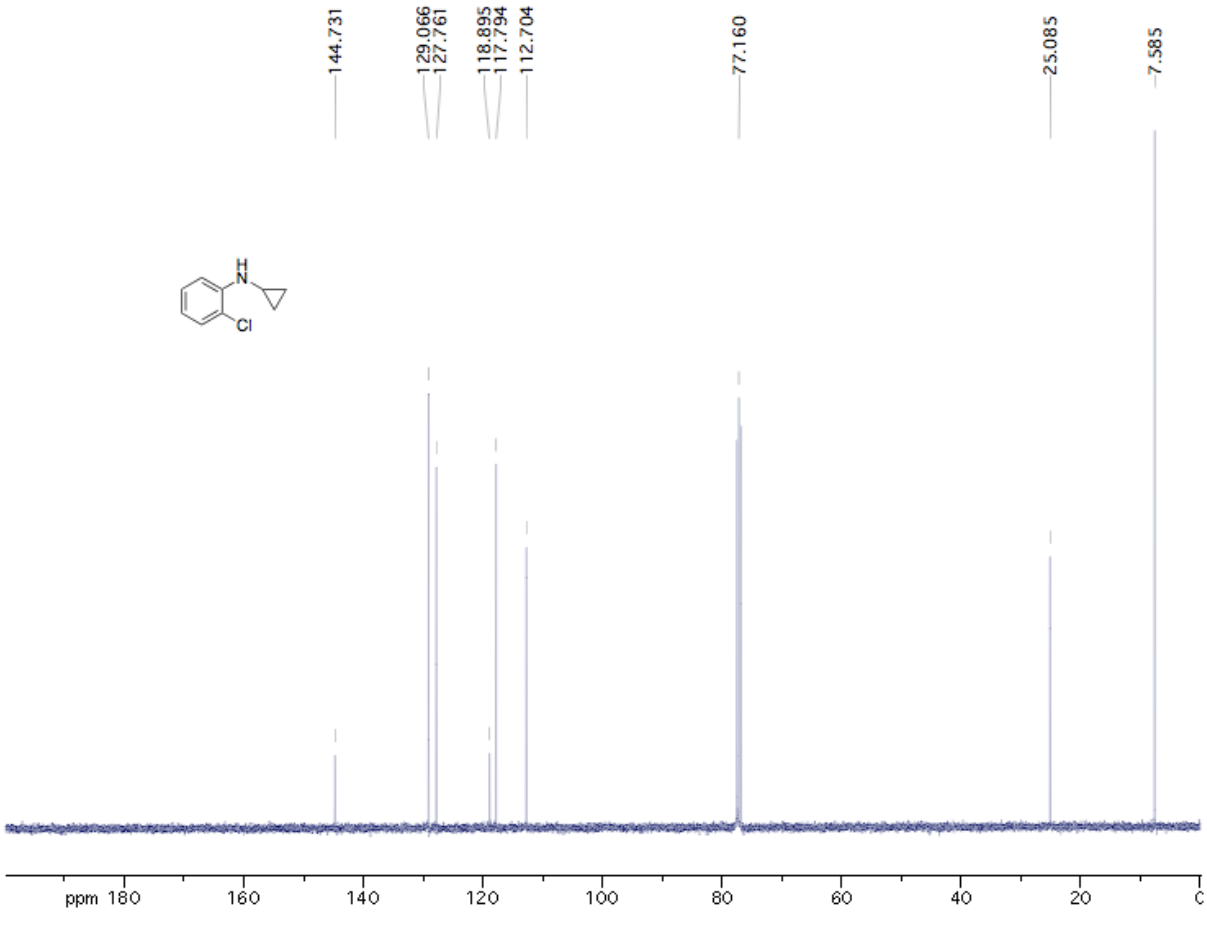
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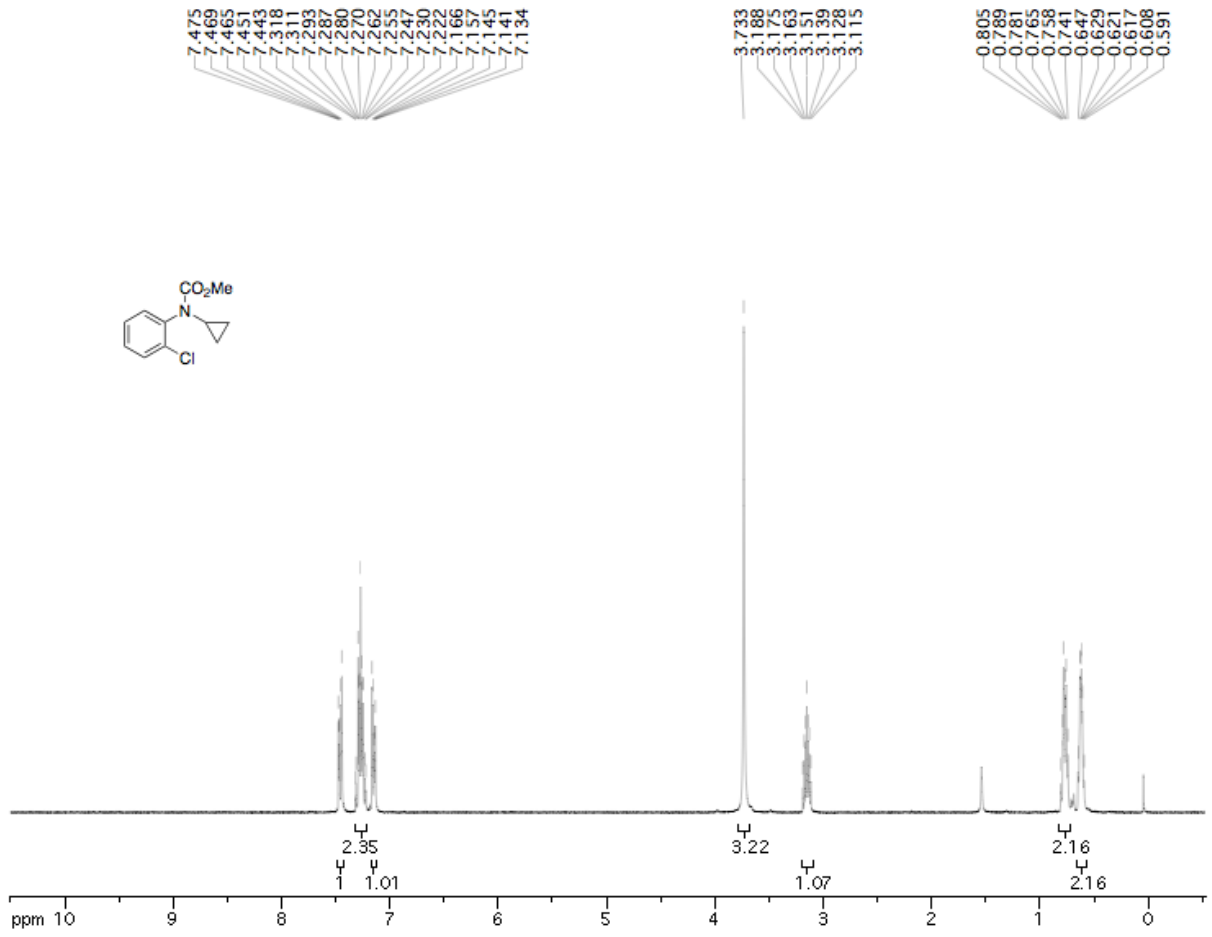
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7.222
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0.621
0.617
0.608
0.591
CO2Me
N
Cl
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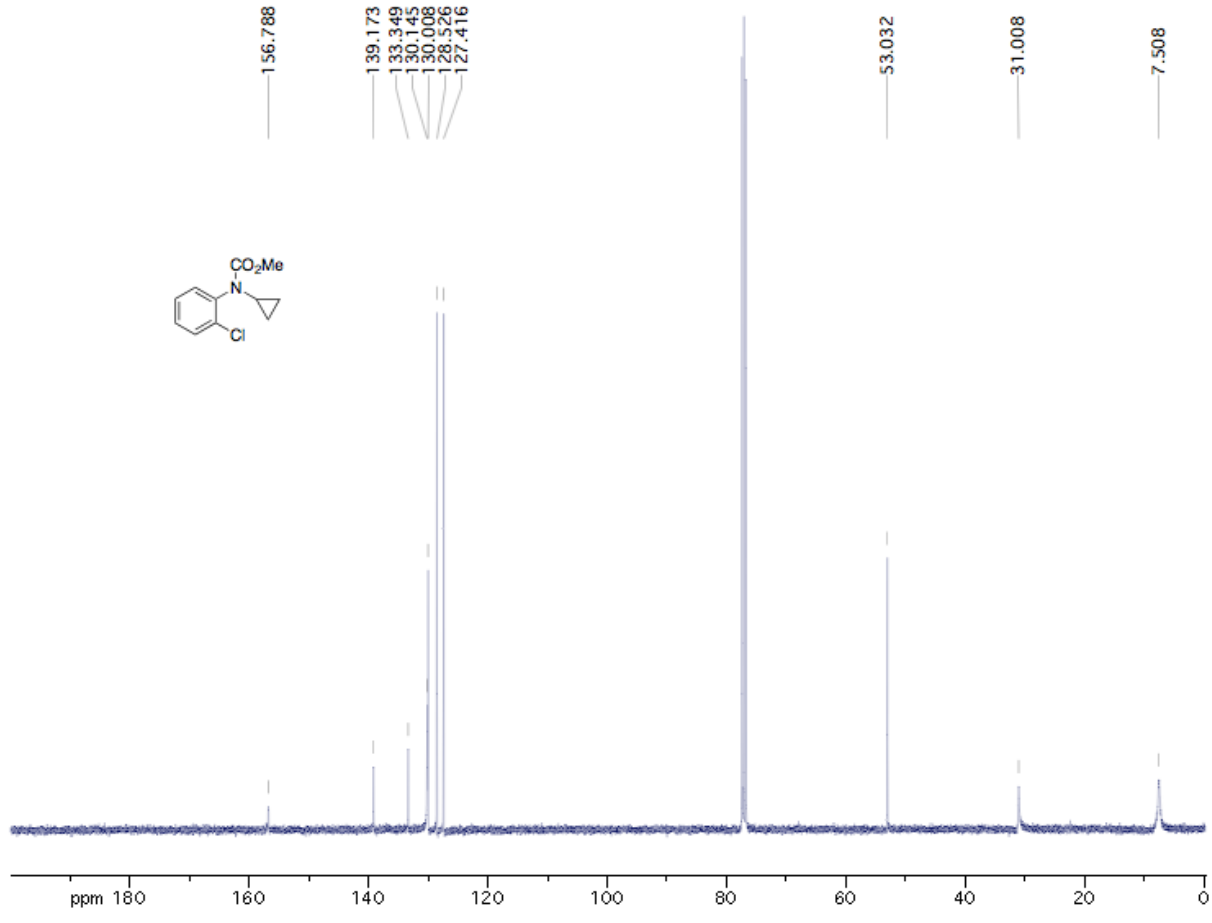
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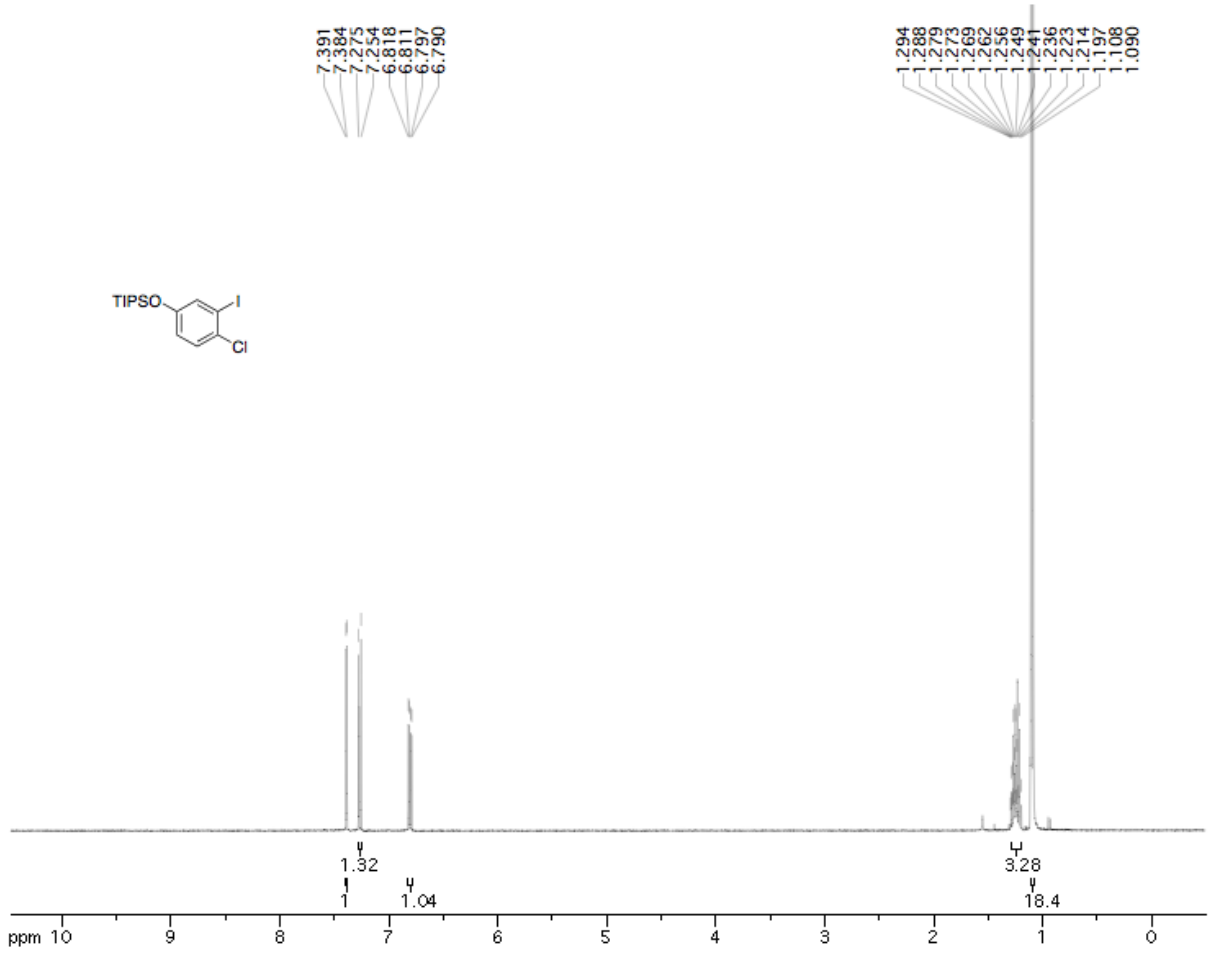
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1.256
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1.236
1.223
1.214
1.197
1.108
1.090
TIPSO
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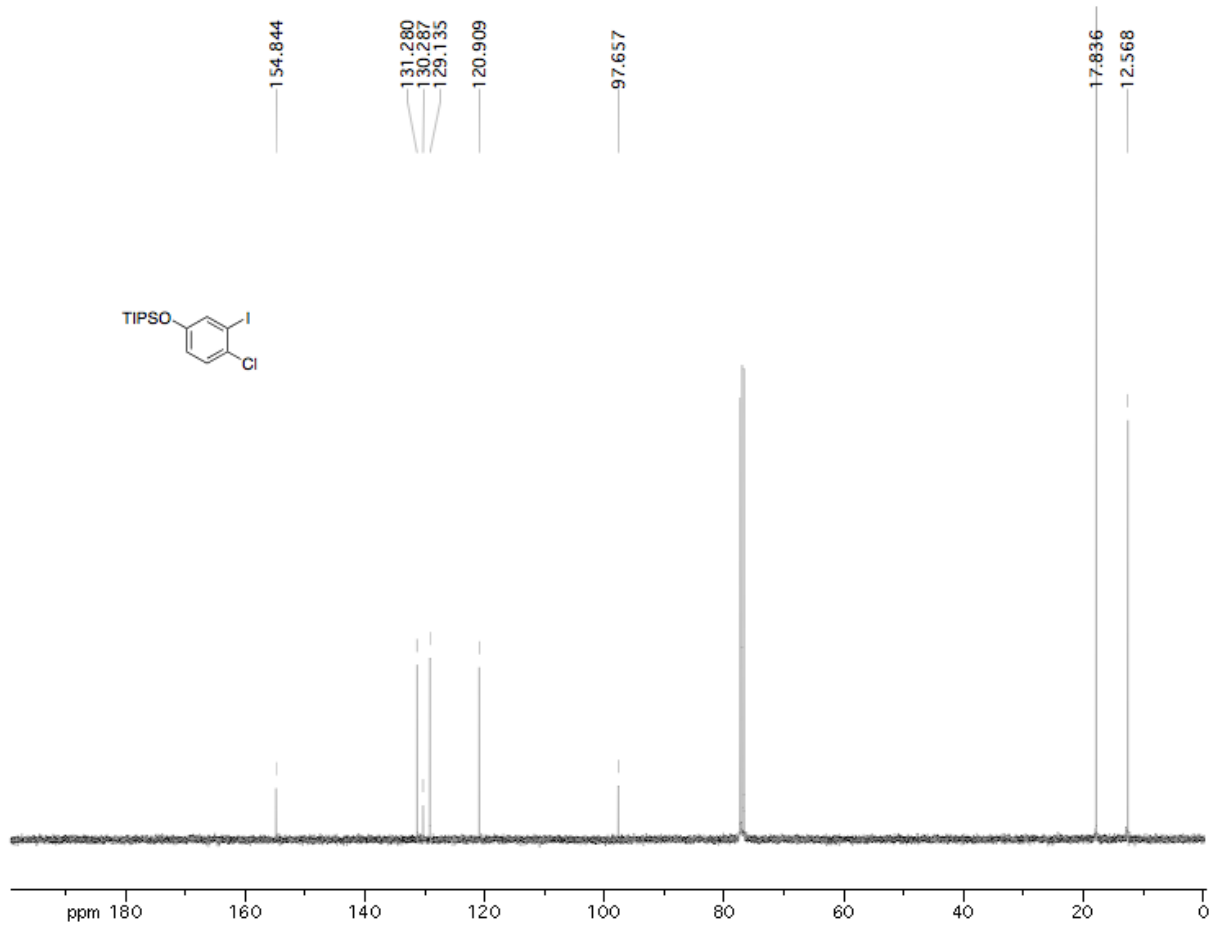
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120
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60
40
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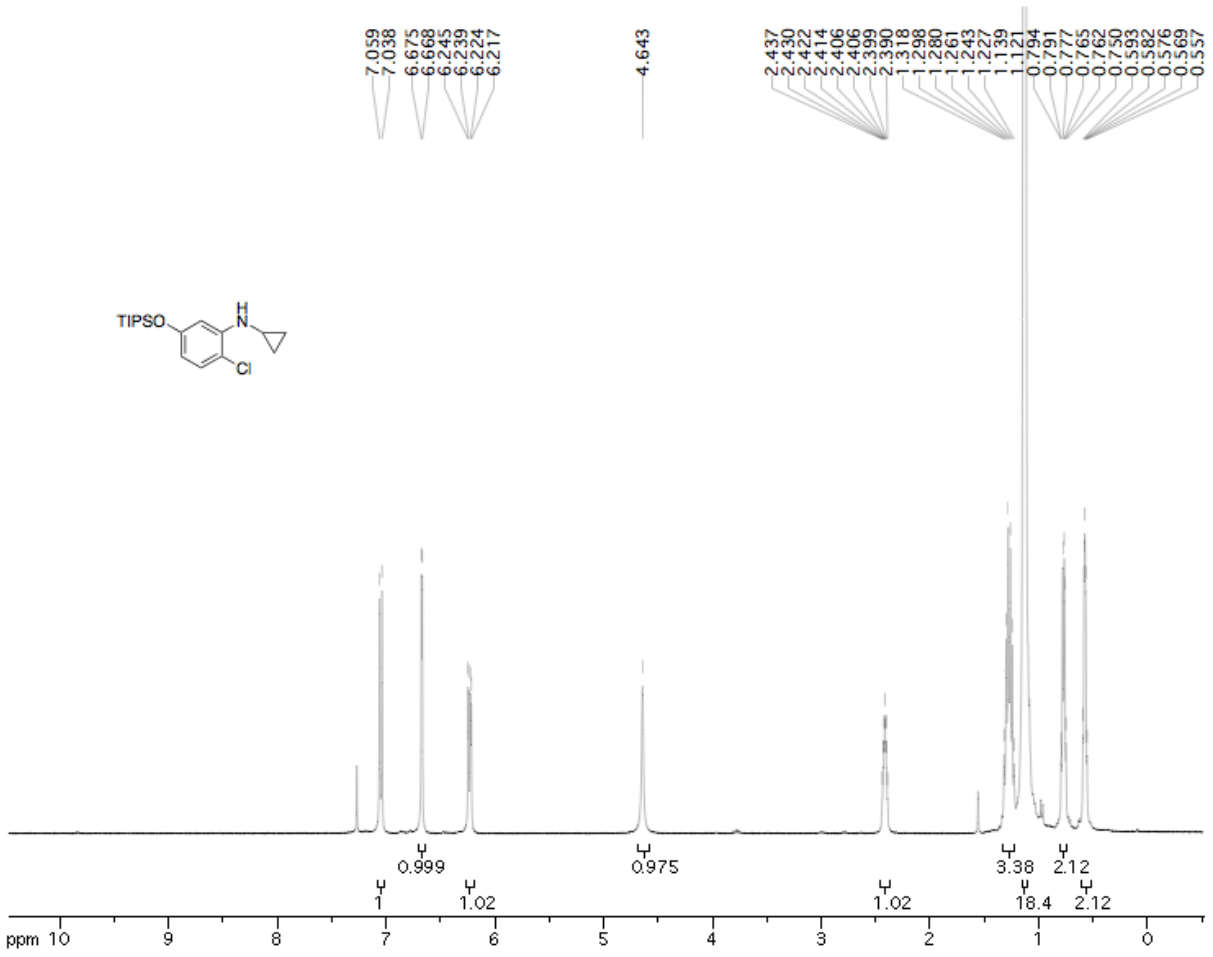

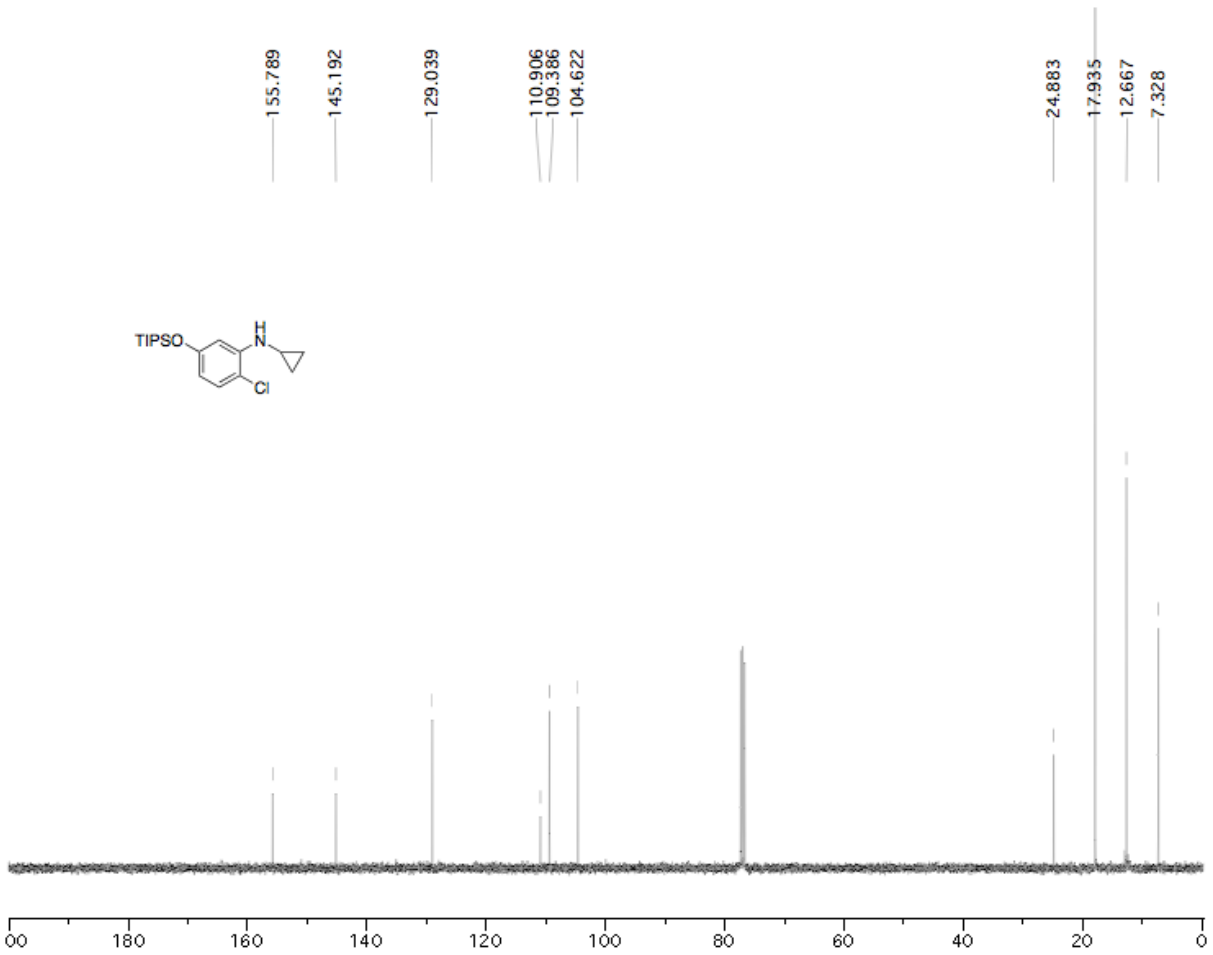

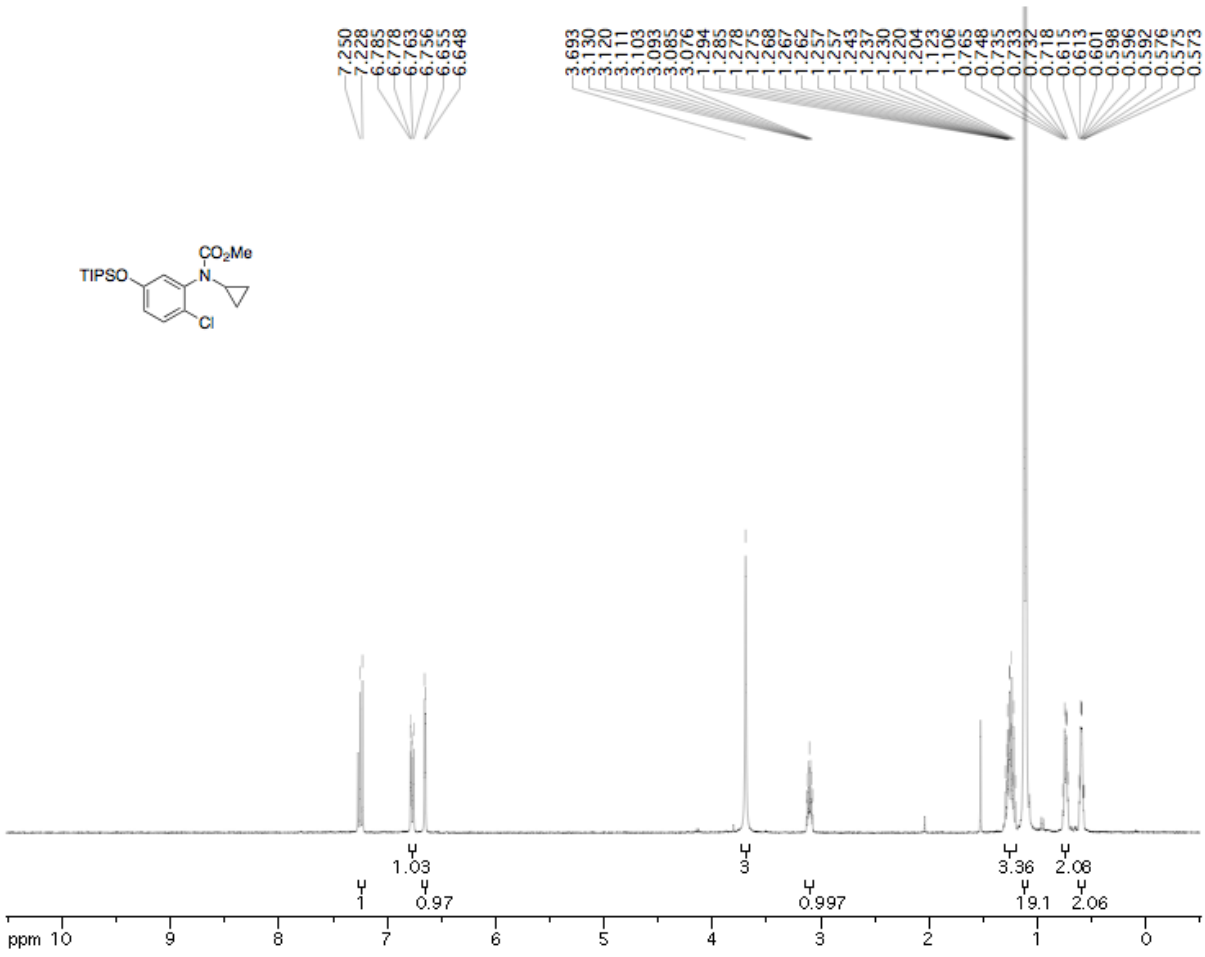
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3.085
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CO2Me
TIPSO
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Cl
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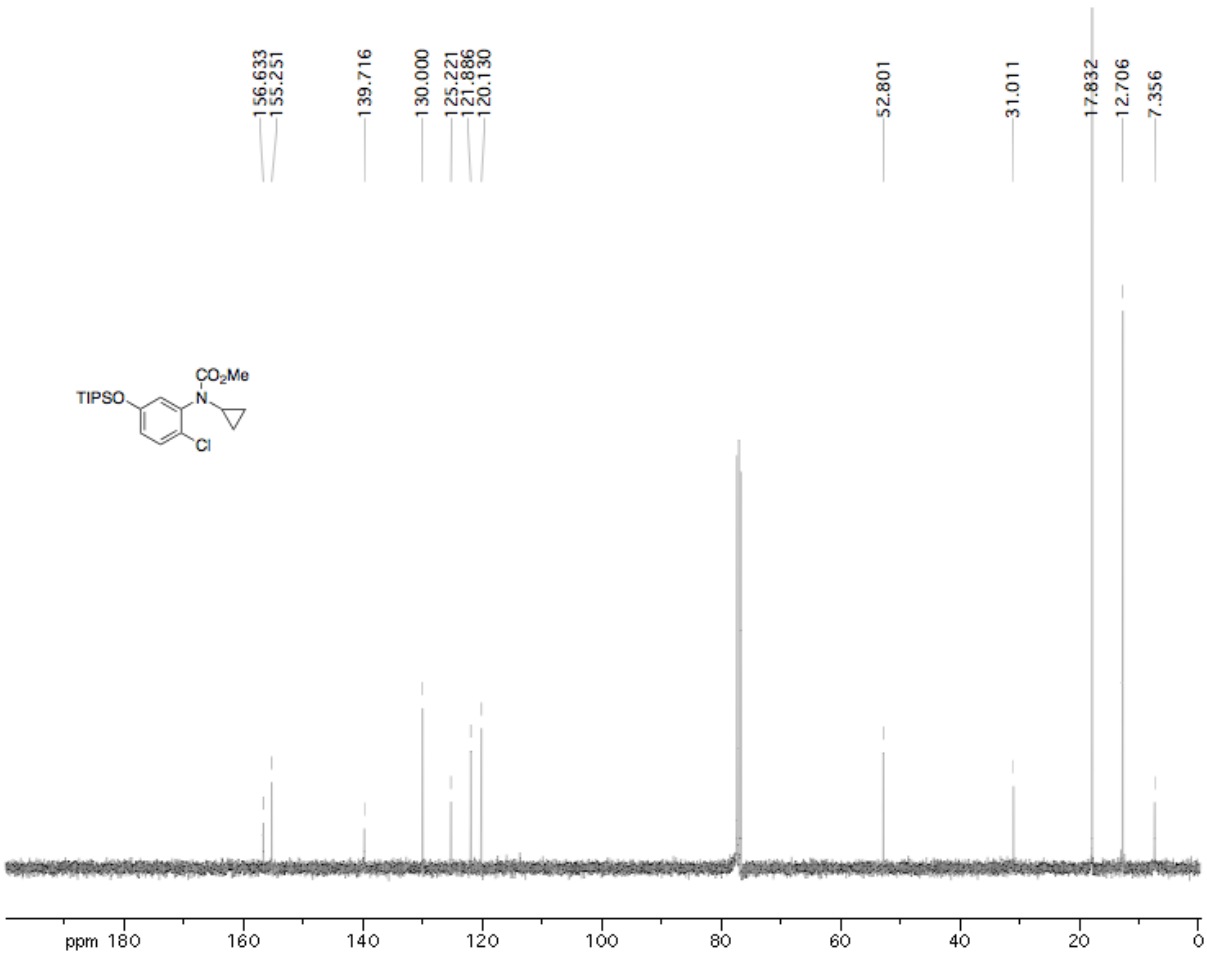
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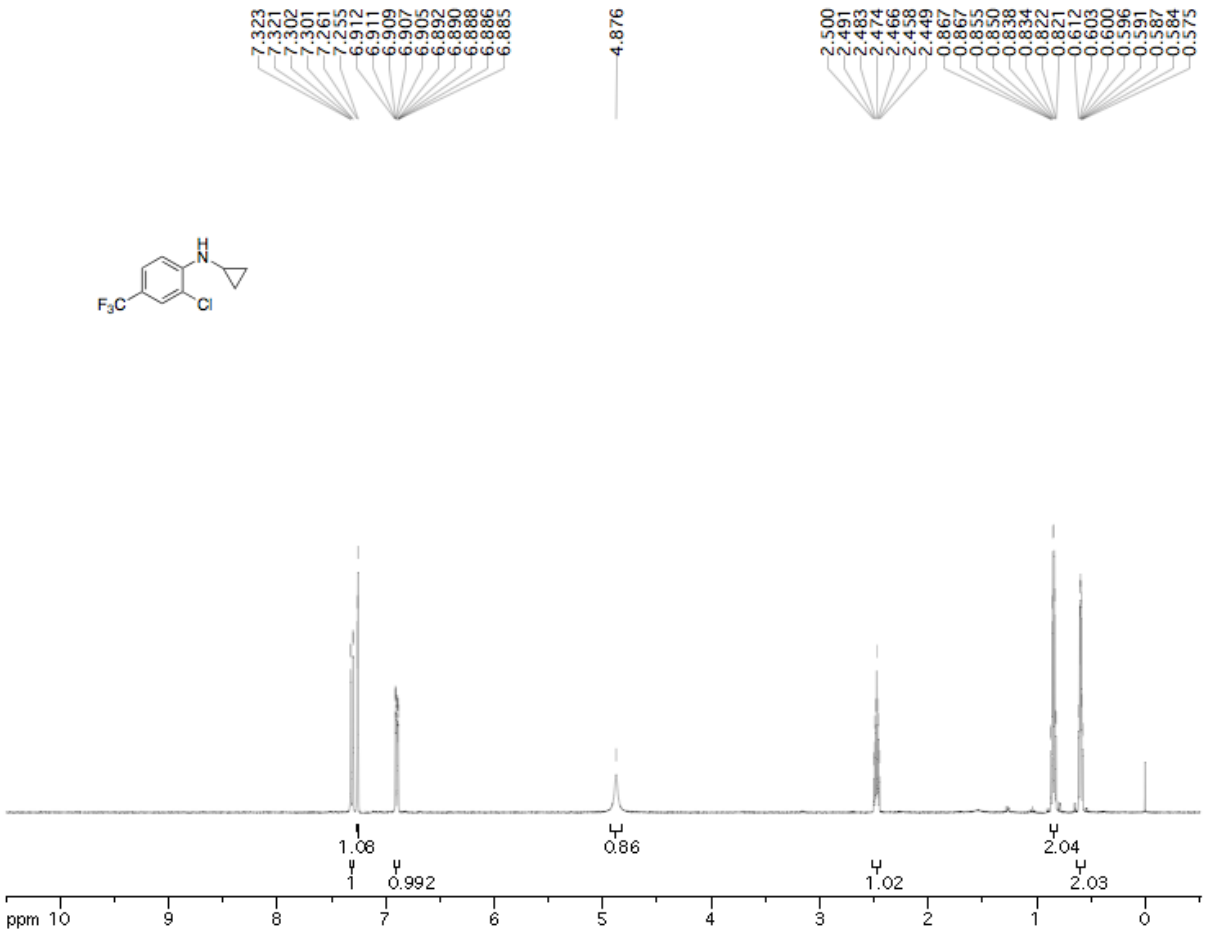
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6.911
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6.907
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6.890
6.888
6.886
6.885
4.876
2.500
2.491
2.483
2.474
2.466
2.458
2.449
0.867
0.855
0.850
0.838
0.834
0.822
0.821
0.612
0.603
0.600
0.596
0.591
0.587
0.584
0.575
H
N
F3C
Cl
1.08
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0.992
1.02
2.03
ppm 10
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7
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5
4
3
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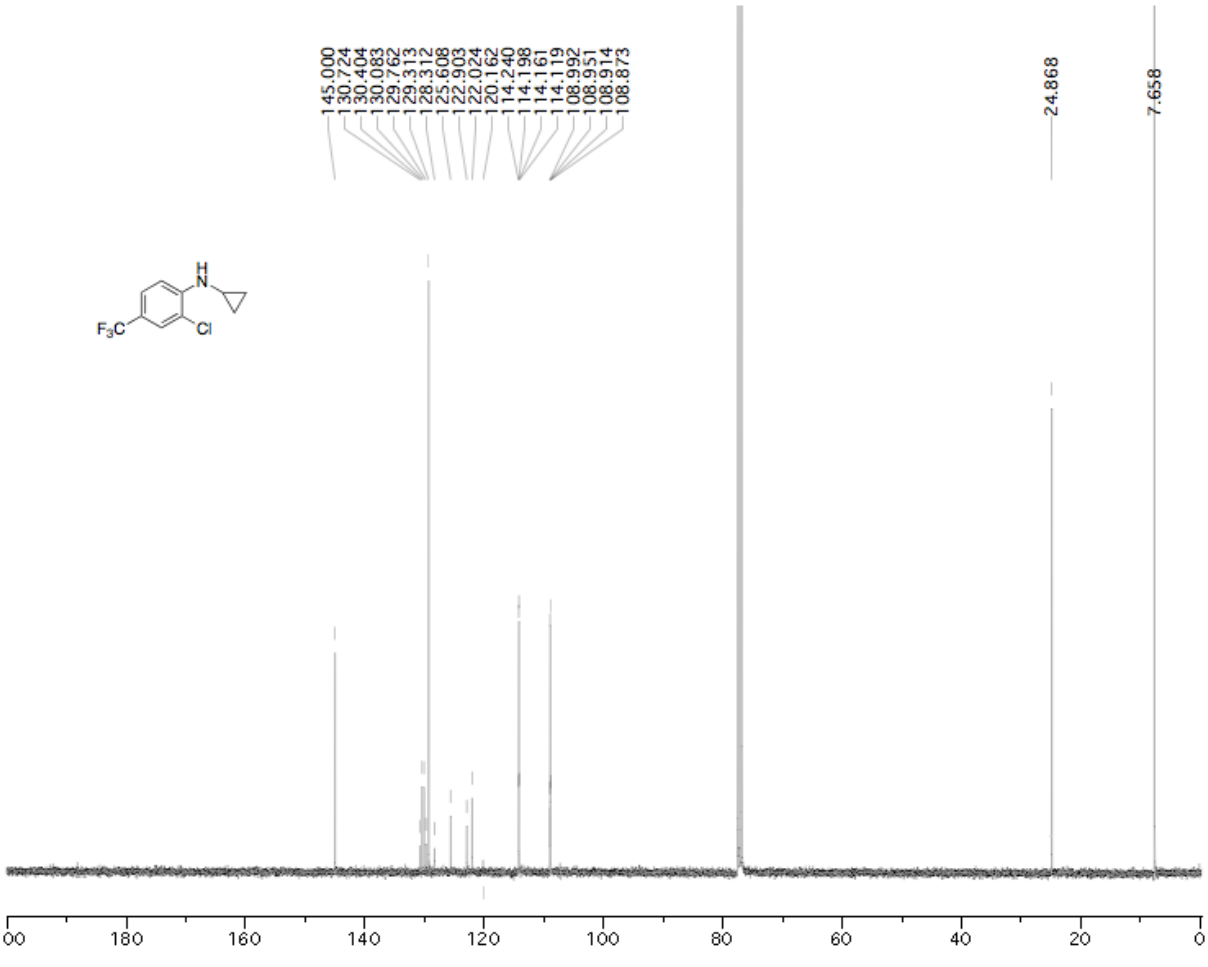
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114.198
114.161
114.119
108.992
108.951
108.914
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H
N
F3C
Cl
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180
160
140
120
100
80
60
40
20
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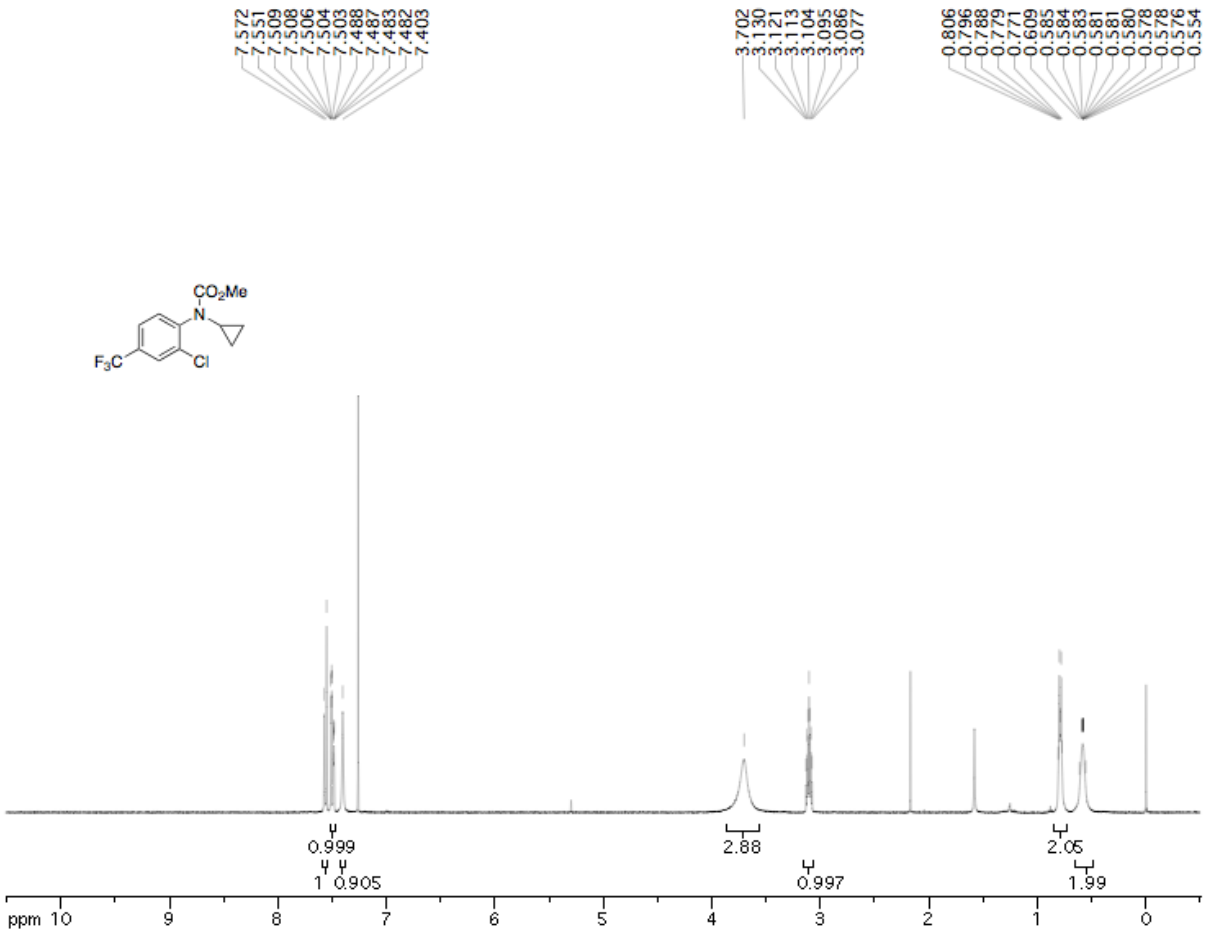
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7.509
7.508
7.506
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7.488
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7.482
7.403
3.702
3.130
3.121
3.113
3.104
3.095
3.086
3.077
0.806
0.796
0.788
0.779
0.771
0.609
0.585
0.584
0.583
0.581
0.581
0.580
0.578
0.578
0.576
0.554
CO2Me
N
F3C
Cl
0.999
1
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2.05
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7
6
5
4
3
2
1
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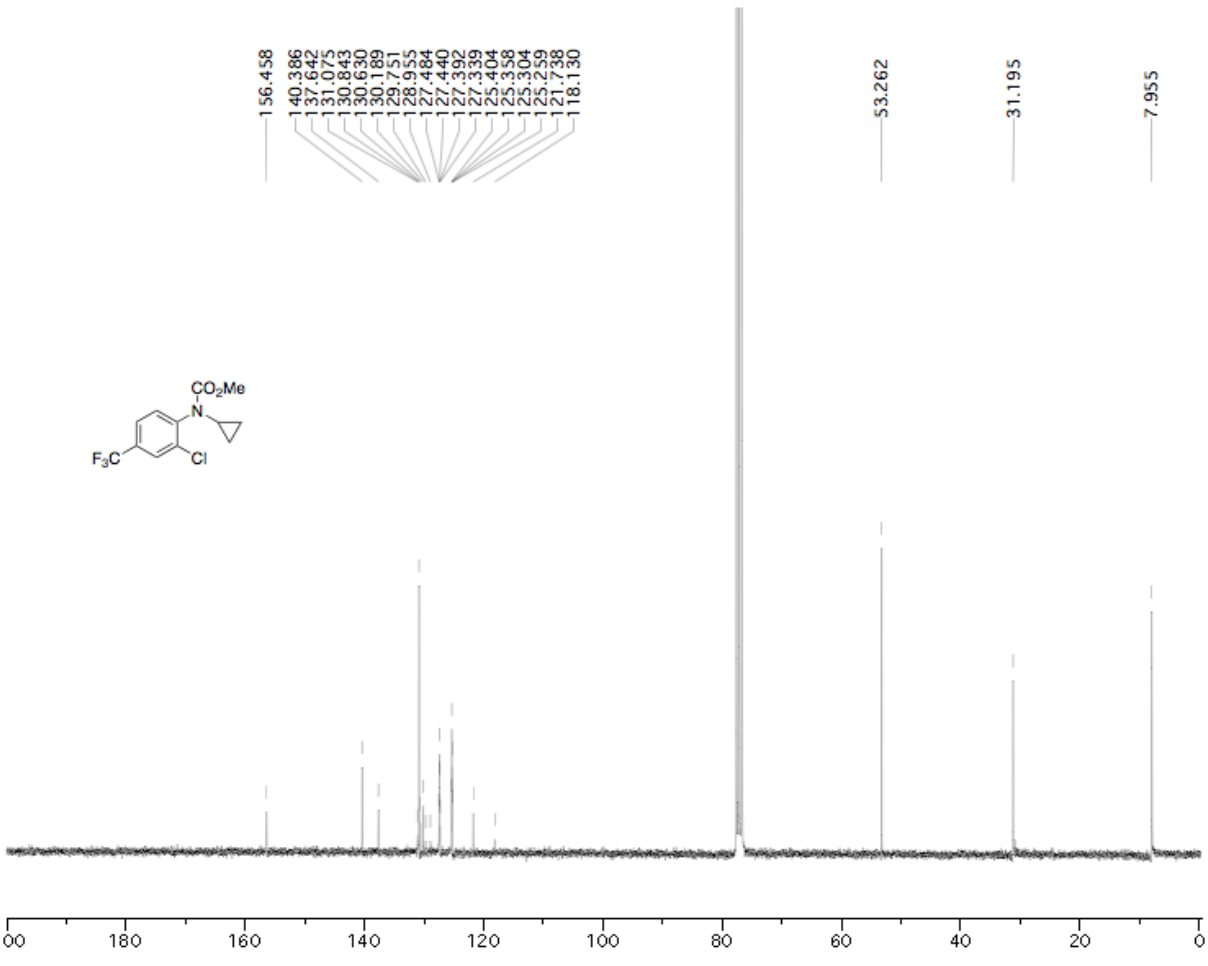
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137.642
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130.630
130.189
129.751
128.955
127.484
127.440
127.392
127.339
125.404
125.358
125.304
125.259
121.738
118.130
53.262
31.195
7.955
CO2Me
N
F3C
Cl
00
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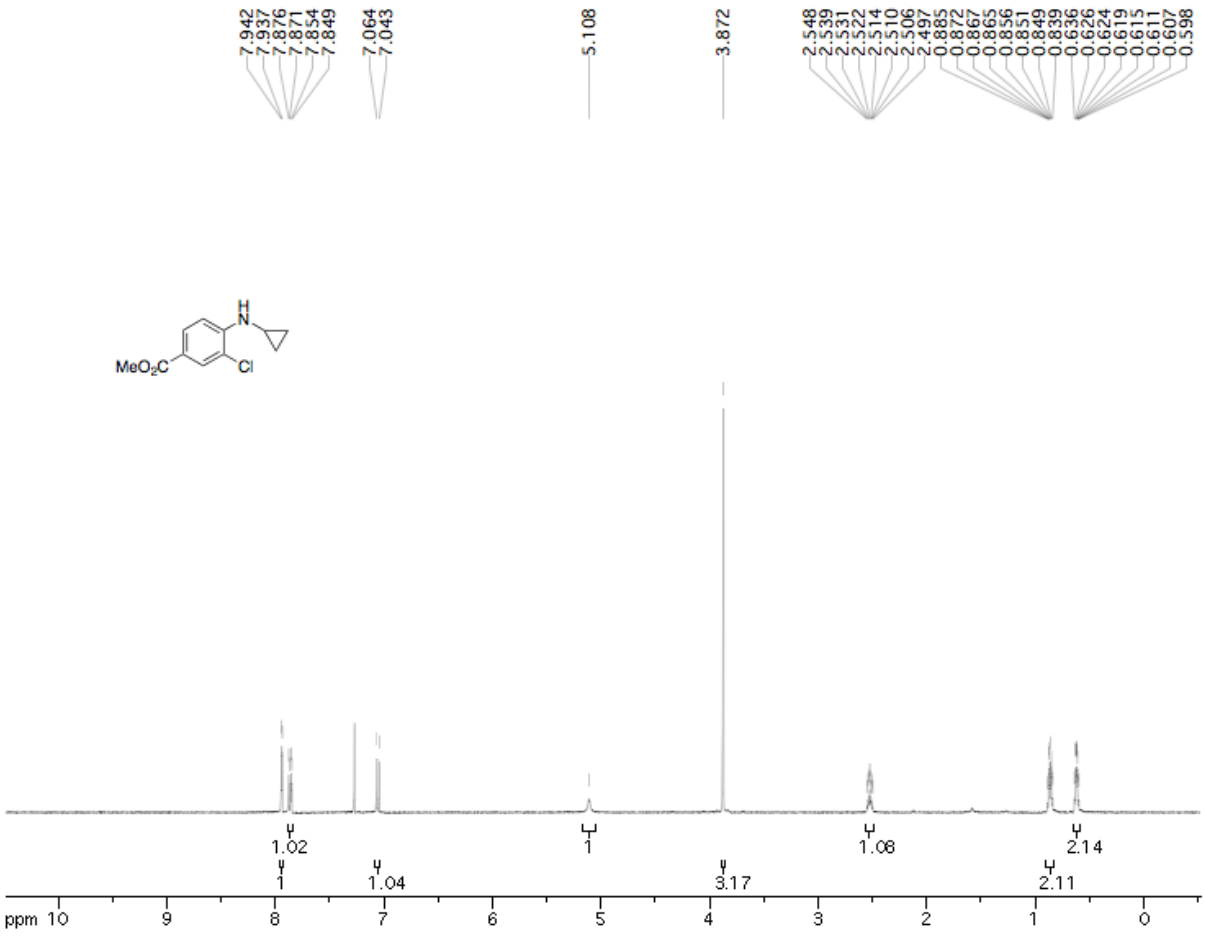
160
140
120
100
80
60
40
20
0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7.876
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7.043
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3.872
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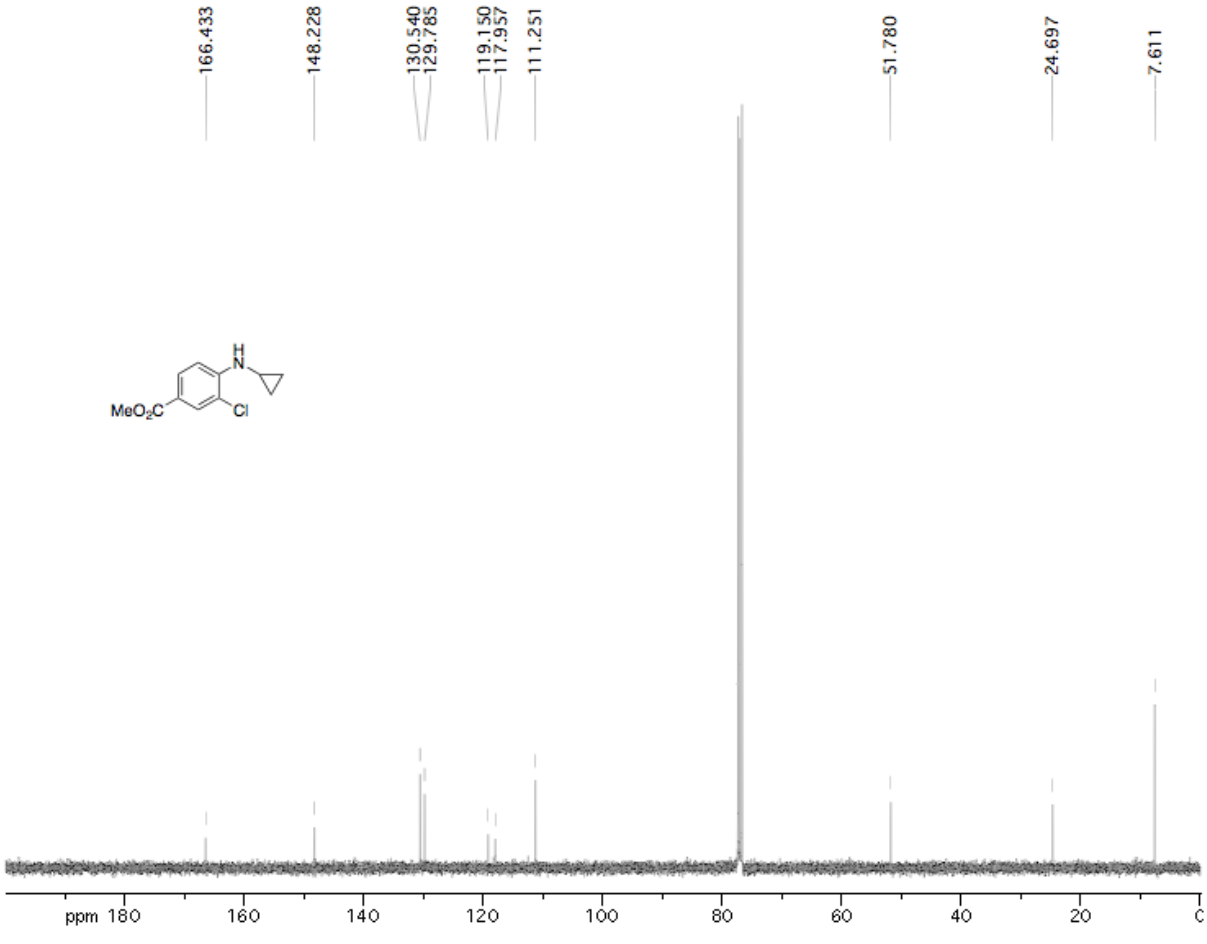
2.539
2.531
2.522
2.514
2.510
2.506
2.497
0.885
0.872
0.867
0.865
0.856
0.851
0.849
0.839
0.636
0.626
0.624
0.619
0.615
0.611
0.607
0.598
MeO2C
Cl
1.02
1
1.04
1
1.08
3.17
2.14
2.11
ppm 10
9
8
7
6
5
4
3
2
1
0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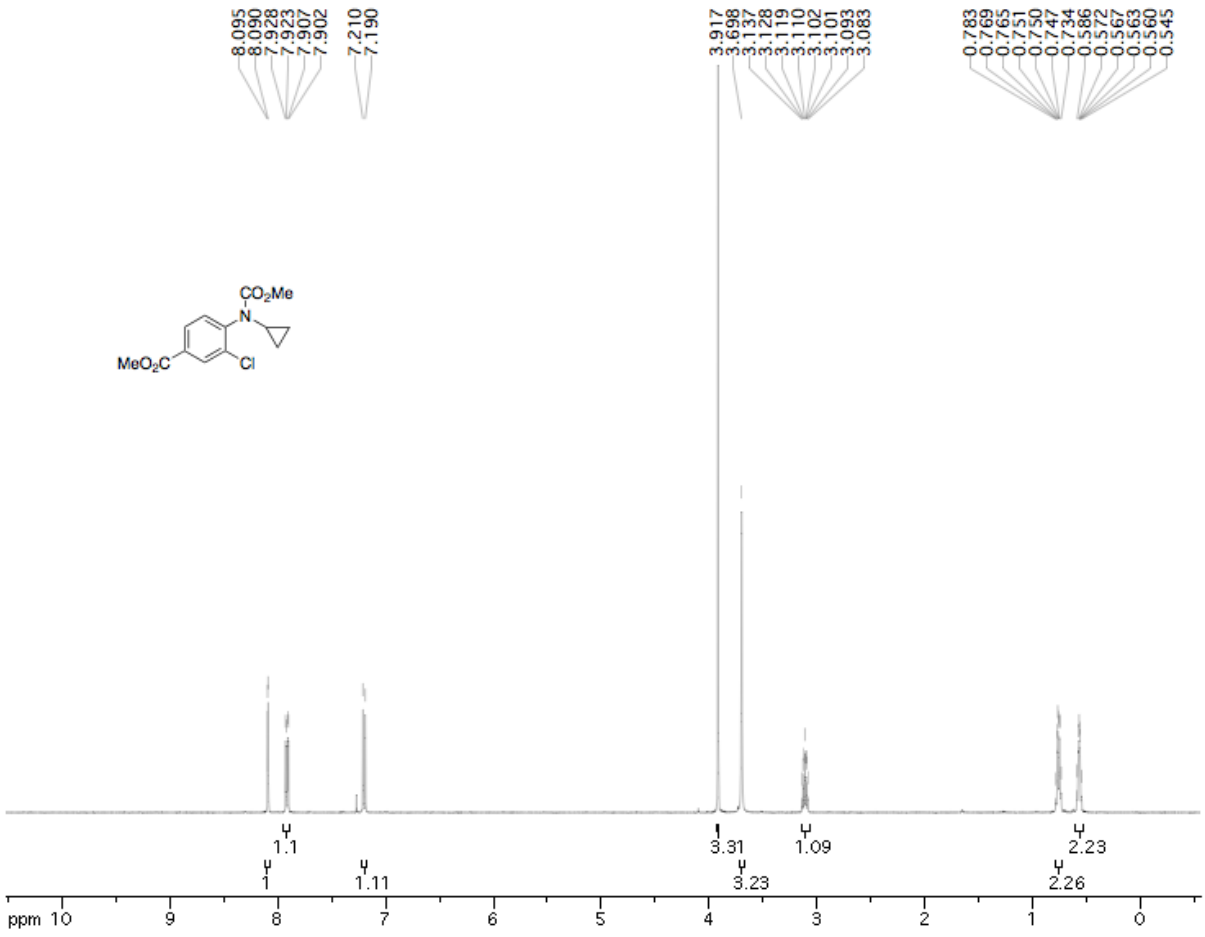
148.228
130.540
129.785
119.150
117.957
111.251
51.780
24.697
7.611
MeO2C
Cl
ppm 180
160
140
120
100
80
60
40
20
0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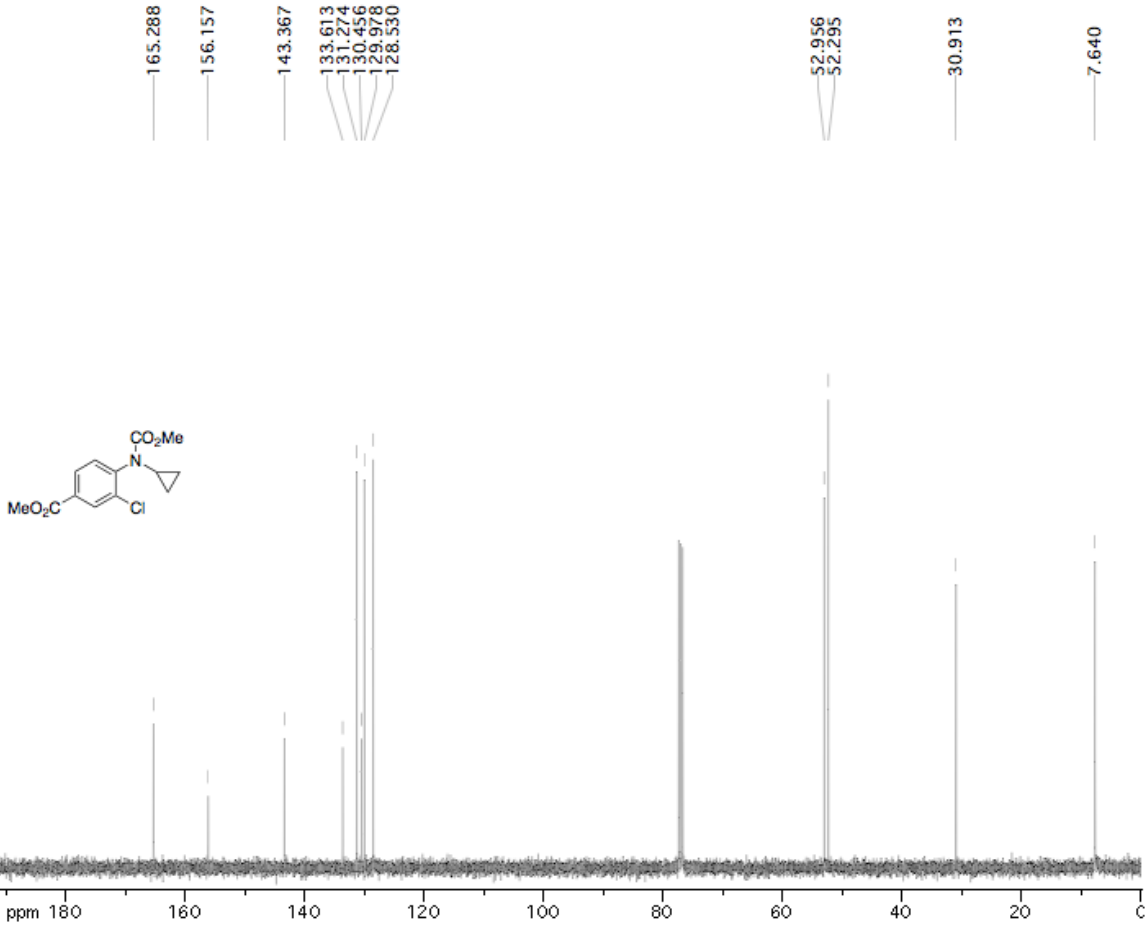
8.090
7.928
7.923
7.907
7.902
7.210
7.190
3.917
3.698
3.137
3.128
3.119
3.110
3.102
3.101
3.093
3.083
0.783
0.769
0.765
0.751
0.750
0.747
0.734
0.586
0.572
0.567
0.563
0.560
0.545
CO2Me
N
MeO2C
Cl
1.1
1
1.11
3.31
3.23
1.09
2.23
2.26
ppm 10
9
8
7
6
5
4
3
2
1
0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143.367
133.613
131.274
130.456
129.978
128.530
52.956
52.295
30.913
7.640
CO2Me
N
MeO2C
Cl
ppm 180
160
140
120
100
80
60
40
20
0


8.241
8.239
8.219
8.217
7.839
7.816
7.793
7.634
7.611
7.595
7.591
7.577
7.574
7.570
7.556
7.553
7.432
7.429
7.414
7.411
7.408
7.394
7.391
4.012
4.004
3.997
3.994
3.992
3.989
3.982
3.974
3.967
0.977
0.975
0.972
0.969
0.968
0.960
0.957
0.954
0.950
0.947
0.944
0.939
0.936
0.934
0.927
0.909
0.906
0.904
0.899
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0.891
0.889
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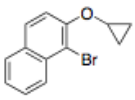
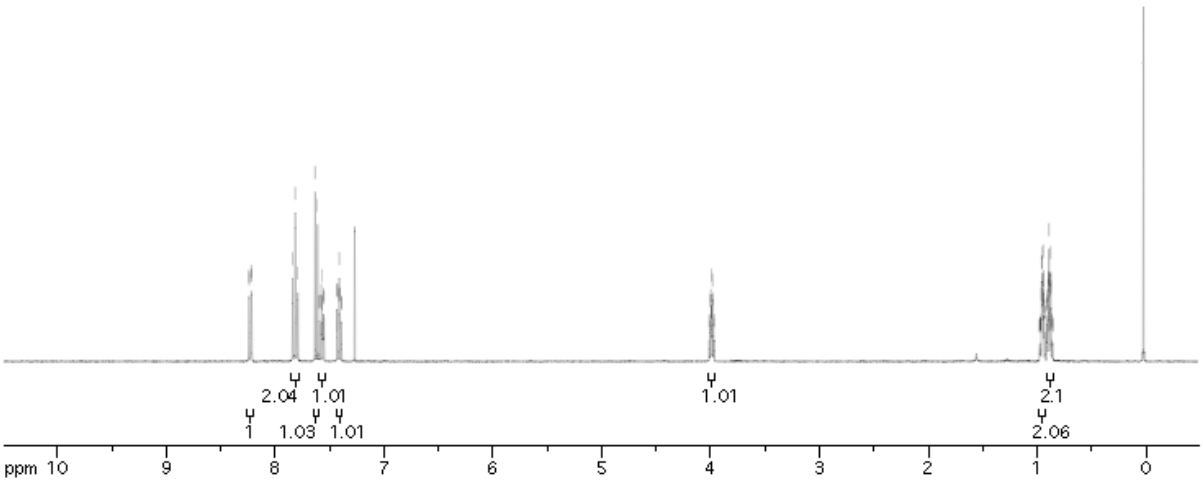
0.876
0.873
0.864
0.858
0.856


O
Br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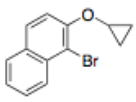
1.01
1.01
1
1.03
1.01
1.01
2.1
2.06
ppm 10
9
8
7
6
5
4
3
2
1
0


153.398
133.044
129.911
128.623
128.010
127.595
126.130
124.308
115.338
108.401
52.524
6.658


O
Br

00
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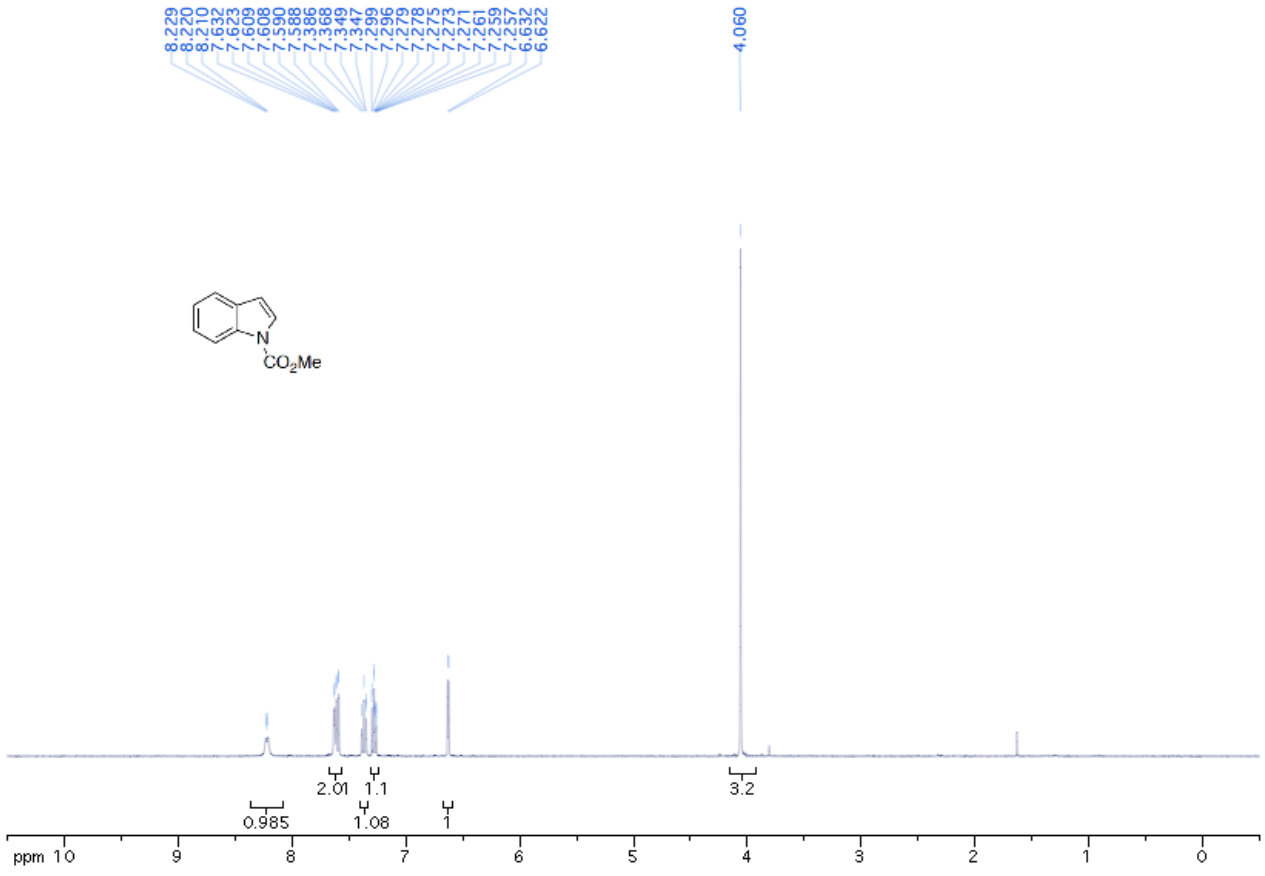
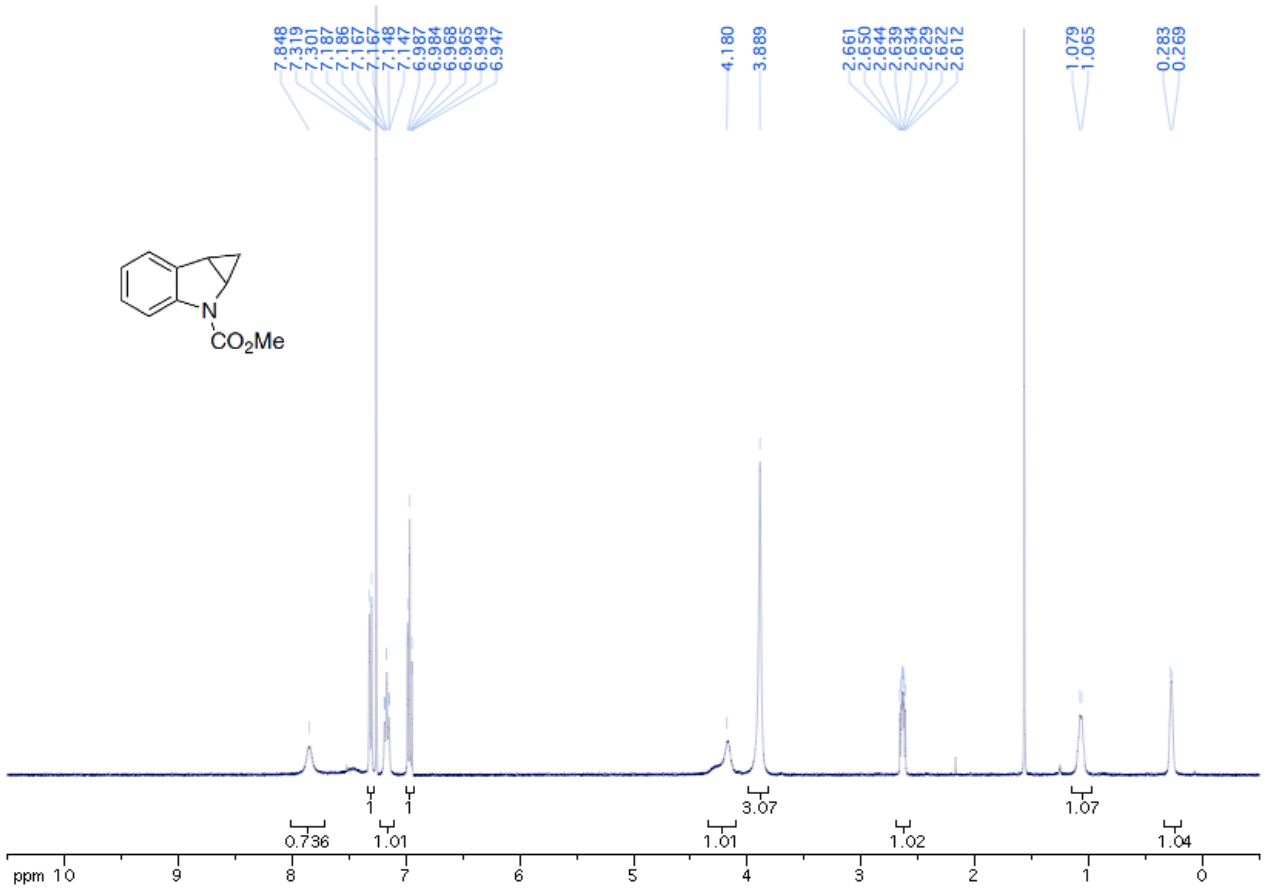
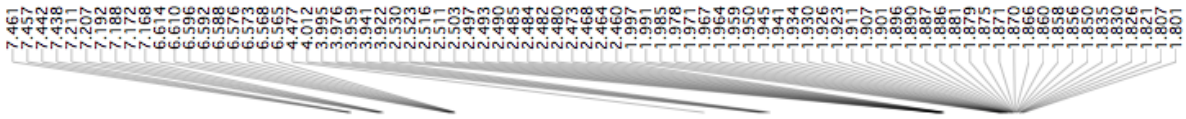
160
140
120
100
80
60
40
20
0



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7.192
7.188
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7.168
6.614
6.610
6.596
6.592
6.588
6.576
6.573
6.568
6.565
4.477
4.012
3.995
3.976
3.959
3.941
3.922
2.530
2.523
2.516
2.511
2.503
2.497
2.493
2.490
2.485
2.484
2.482
2.480
2.473
2.468
2.464
2.460
1.997
1.991
1.985
1.978
1.971
1.967
1.964
1.959
1.950
1.945
1.941
1.934
1.930
1.926
1.923
1.911
1.907
1.901
1.896
1.890
1.887
1.886
1.881
1.879
1.875
1.871
1.870
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1.826
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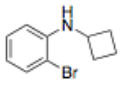
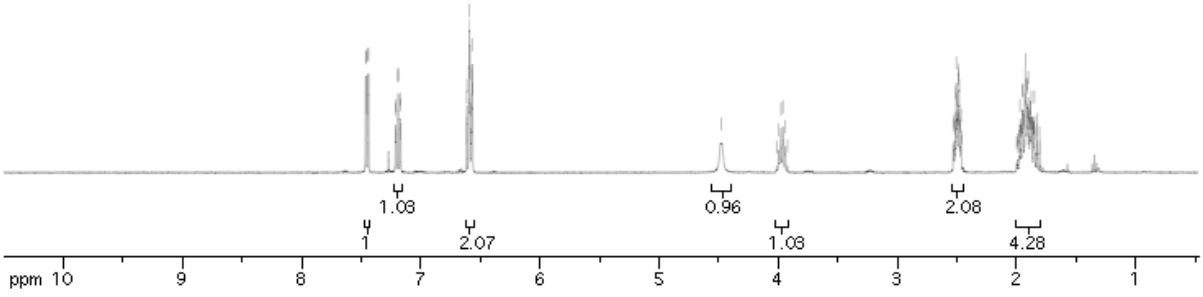
1.807
1.801


H
N
Br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0.96
2.08
1
2.07
1.03
4.28
ppm 10
9
8
7
6
5
4
3
2
1


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128.387
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111.655
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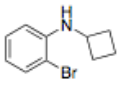
30.997
15.301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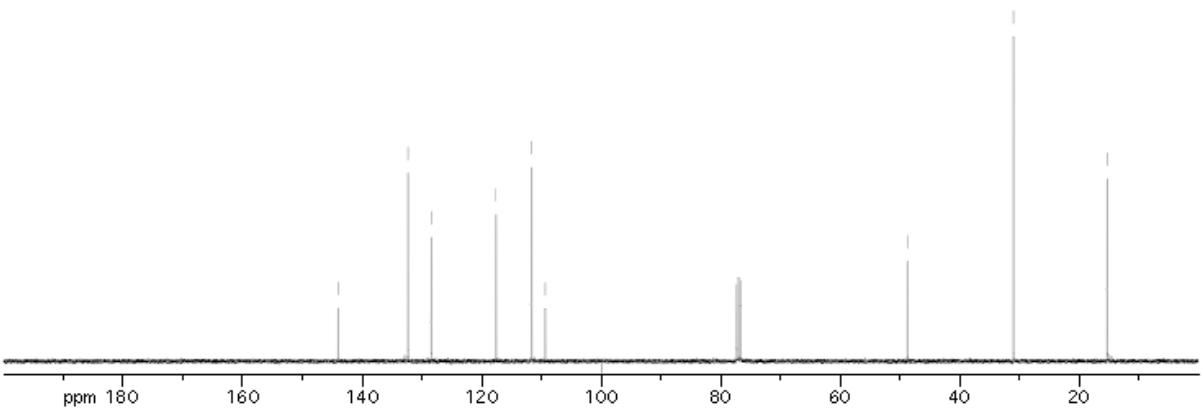
N
Br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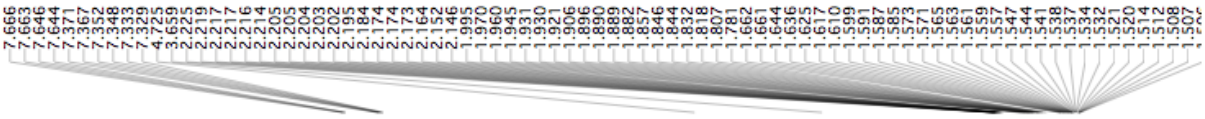
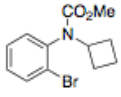
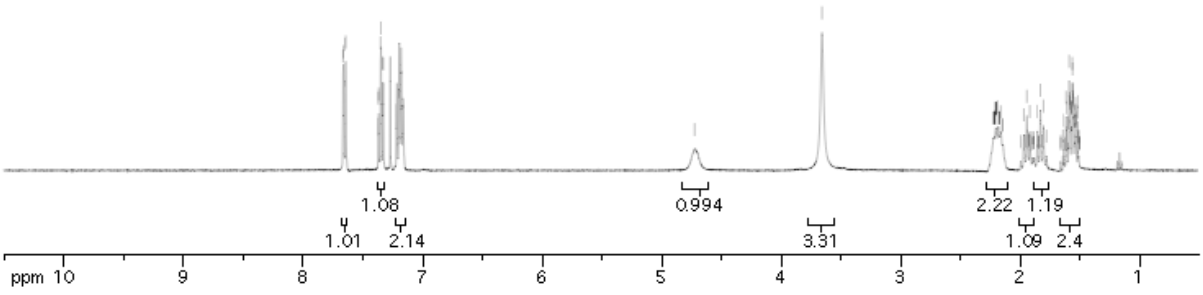
140
120
100
80
60
40
20




CO2Me
N
Br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1.09
2.4
ppm 10
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8
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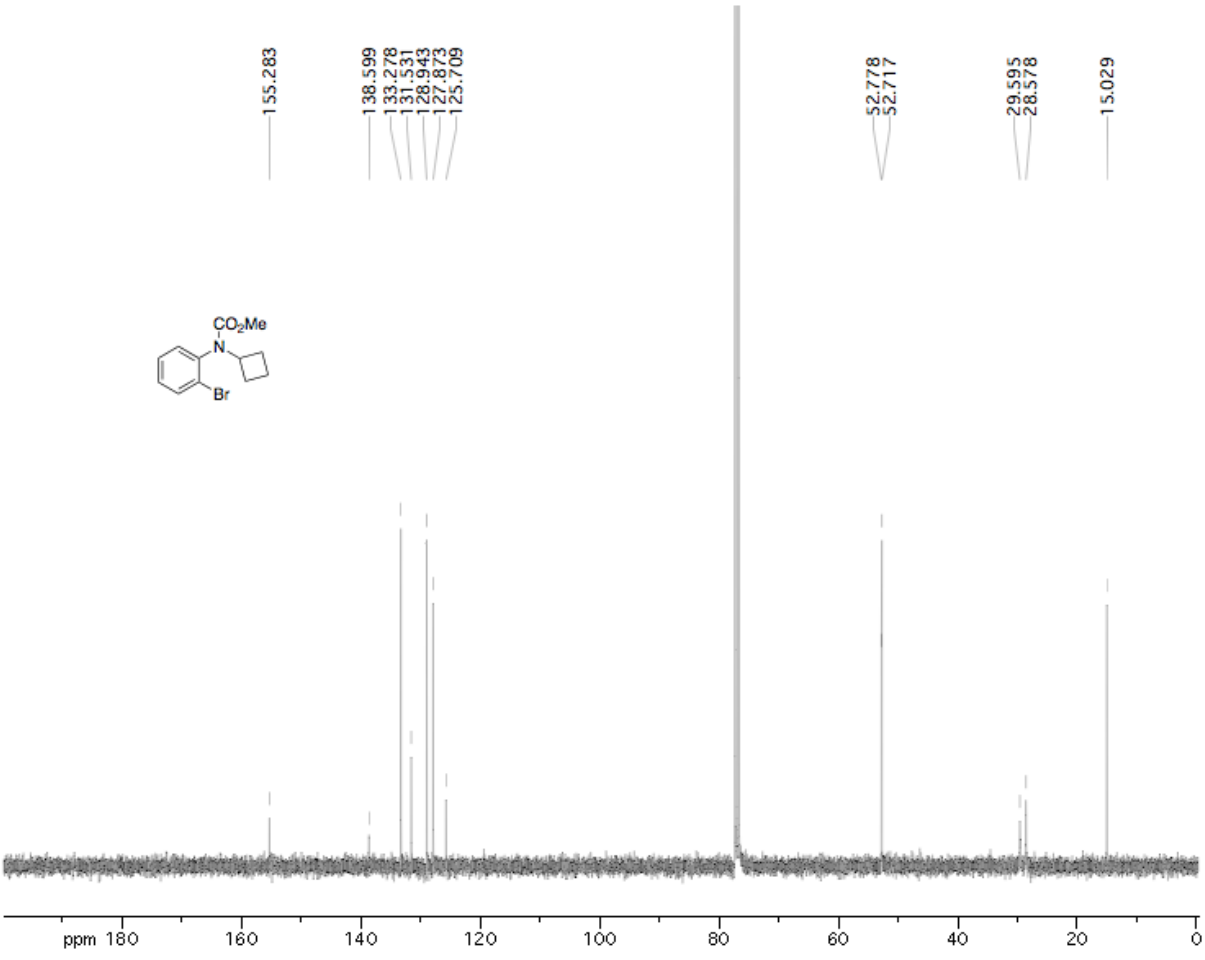
5
4
3
2
1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131.531
128.943
127.873
125.709
52.778
52.717
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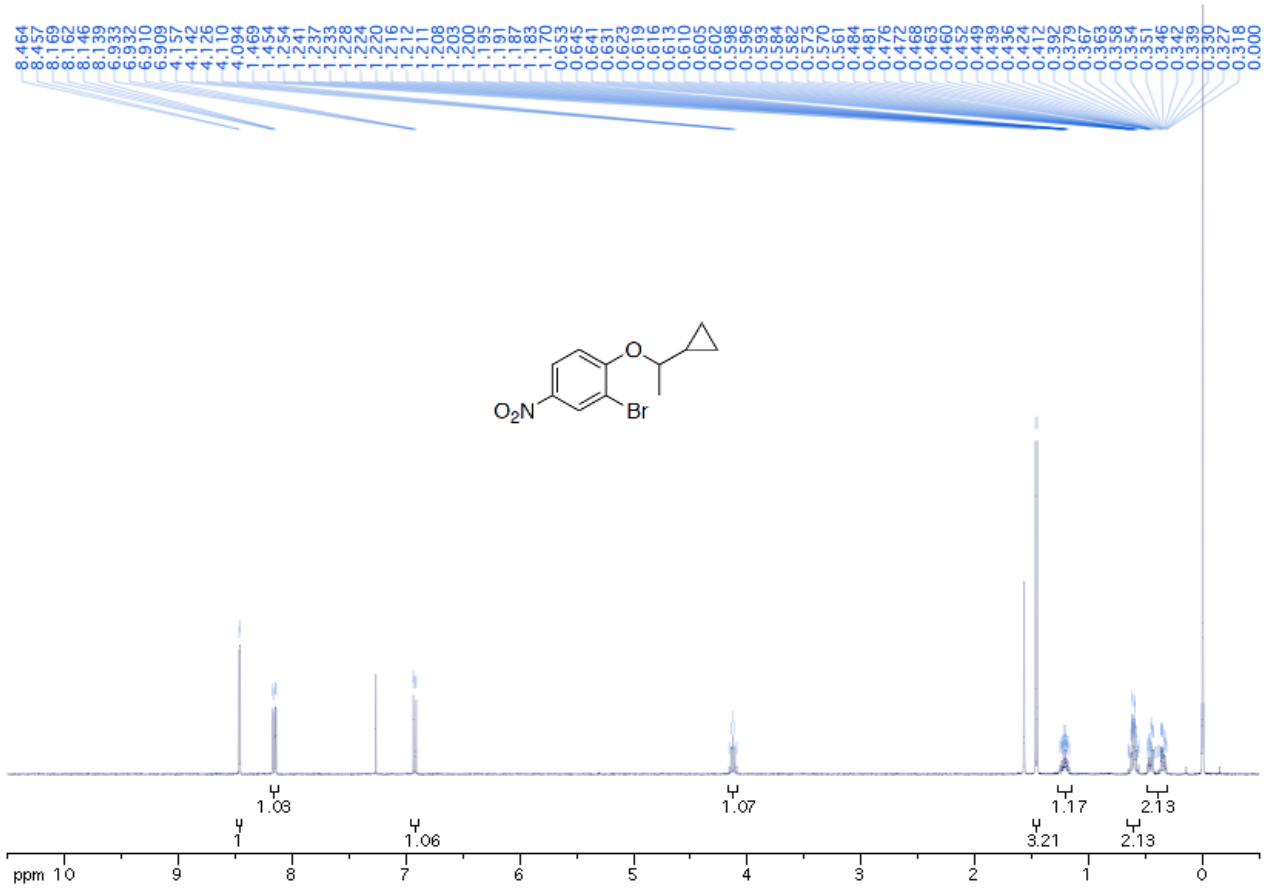
15.029
CO2Me
N
Br
ppm 180
160
140
120
100
80
60
40
20
0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8.139
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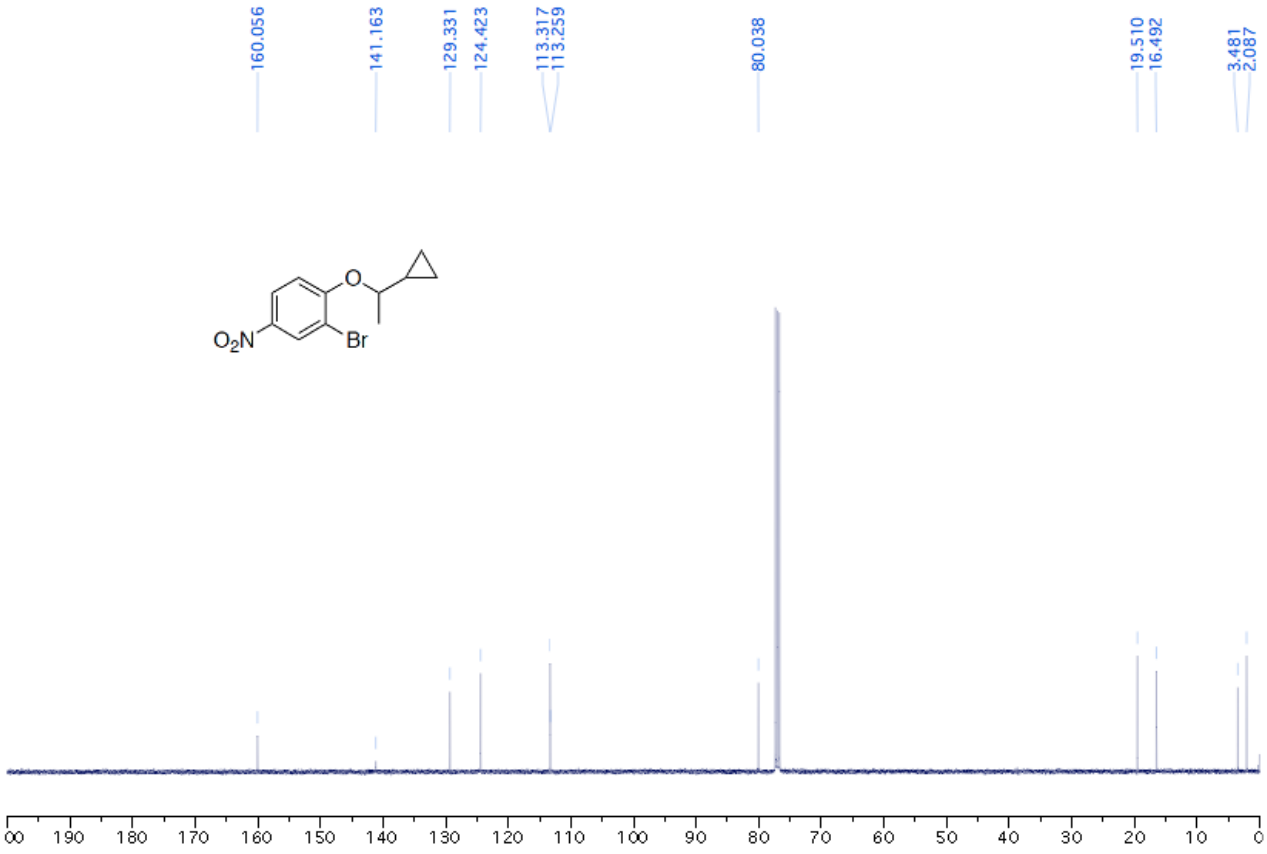
6.932
6.910
6.909
4.157
4.142
4.126
4.110
4.094
1.469
1.454
1.254
1.241
1.237
1.233
1.228
1.224
1.220
1.216
1.212
1.211
1.208
1.203
1.200
1.195
1.191
1.187
1.183
1.170
0.653
0.645
0.641
0.631
0.623
0.619
0.616
0.613
0.610
0.605
0.602
0.598
0.596
0.593
0.584
0.582
0.573
0.570
0.561
0.484
0.481
0.476
0.472
0.468
0.463
0.460
0.452
0.449
0.439
0.436
0.424
0.412
0.392
0.379
0.367
0.363
0.358
0.354
0.351
0.346
0.342
0.339
0.330
0.327
0.318
0.000
O
O2N
Br
1.08
1.07
1.17
2.13
1
1.06
3.21
2.13
ppm 10
9
8
7
6
5
4
3
2
1
0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113.317
113.259
80.038
19.510
16.492
3.481
2.087
O
O2N
Br
200
190
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60
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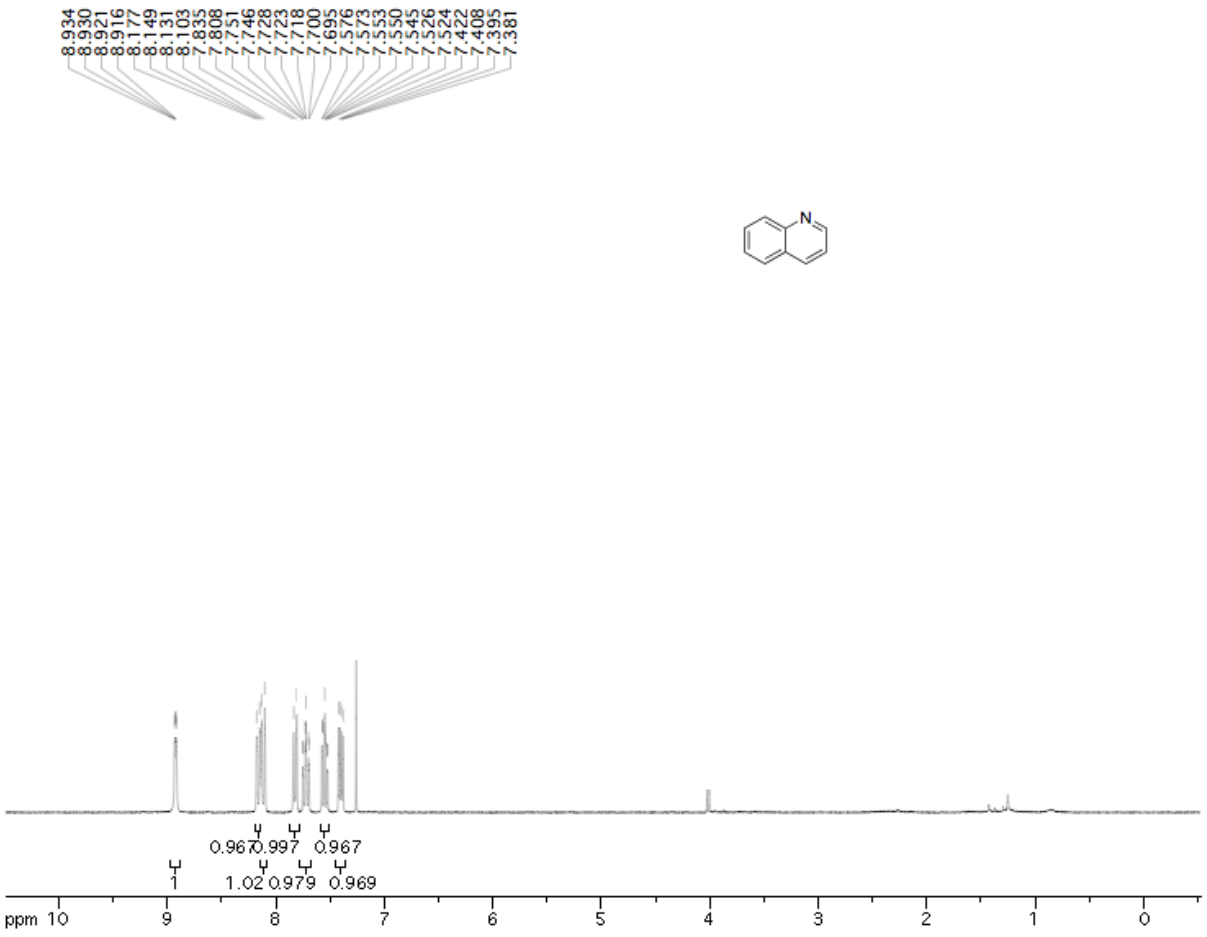
30
20
10
0

f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8.103
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7.808
7.751
7.746
7.728
7.723
7.718
7.700
7.695
7.576
7.573
7.553
7.550
7.545
7.526
7.524
7.422
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7.381
N
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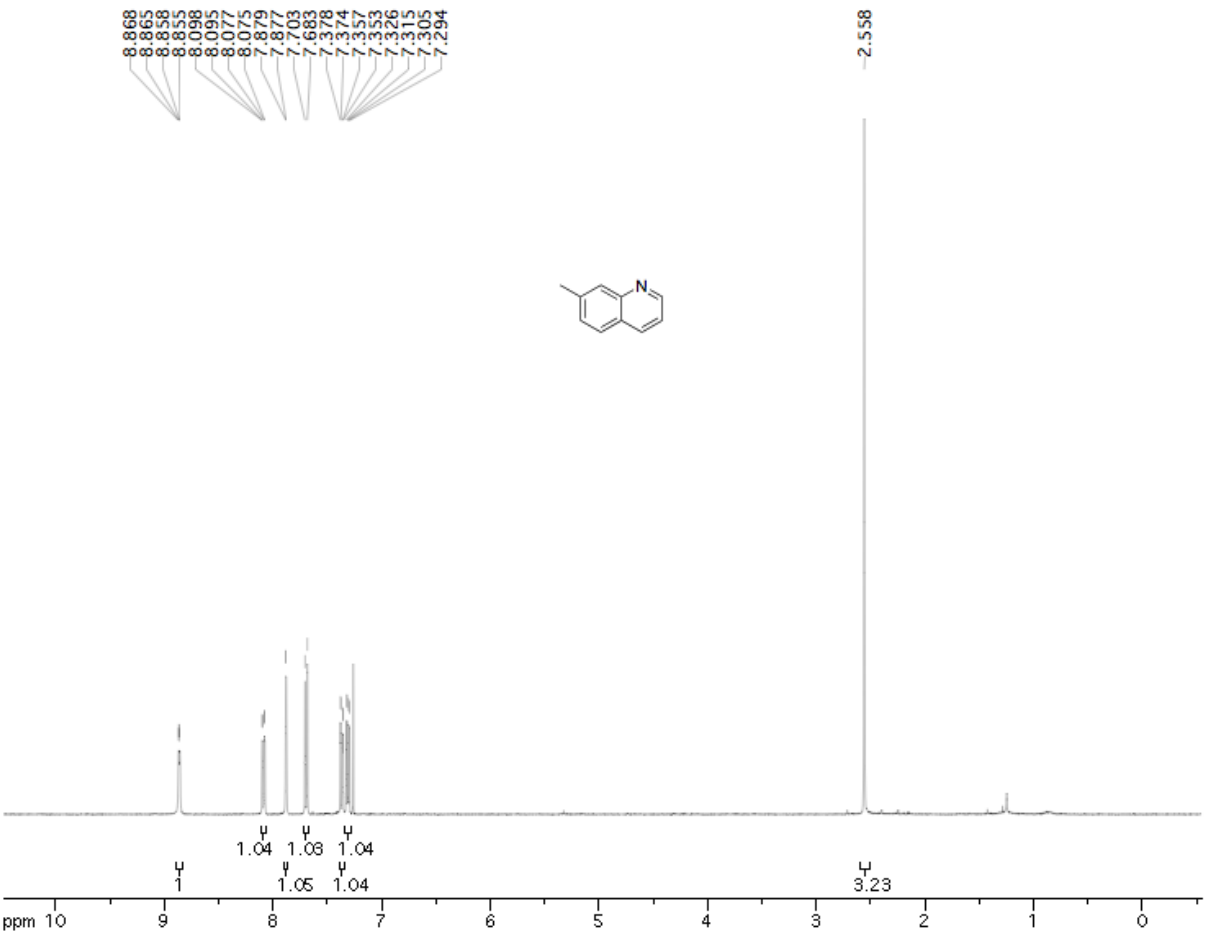
1 1.02 0.979 0.969
ppm 10 9 8 7 6 5 4 3 2 1 0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8.075
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7.877
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7.374
7.357
7.353
7.326
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2.558
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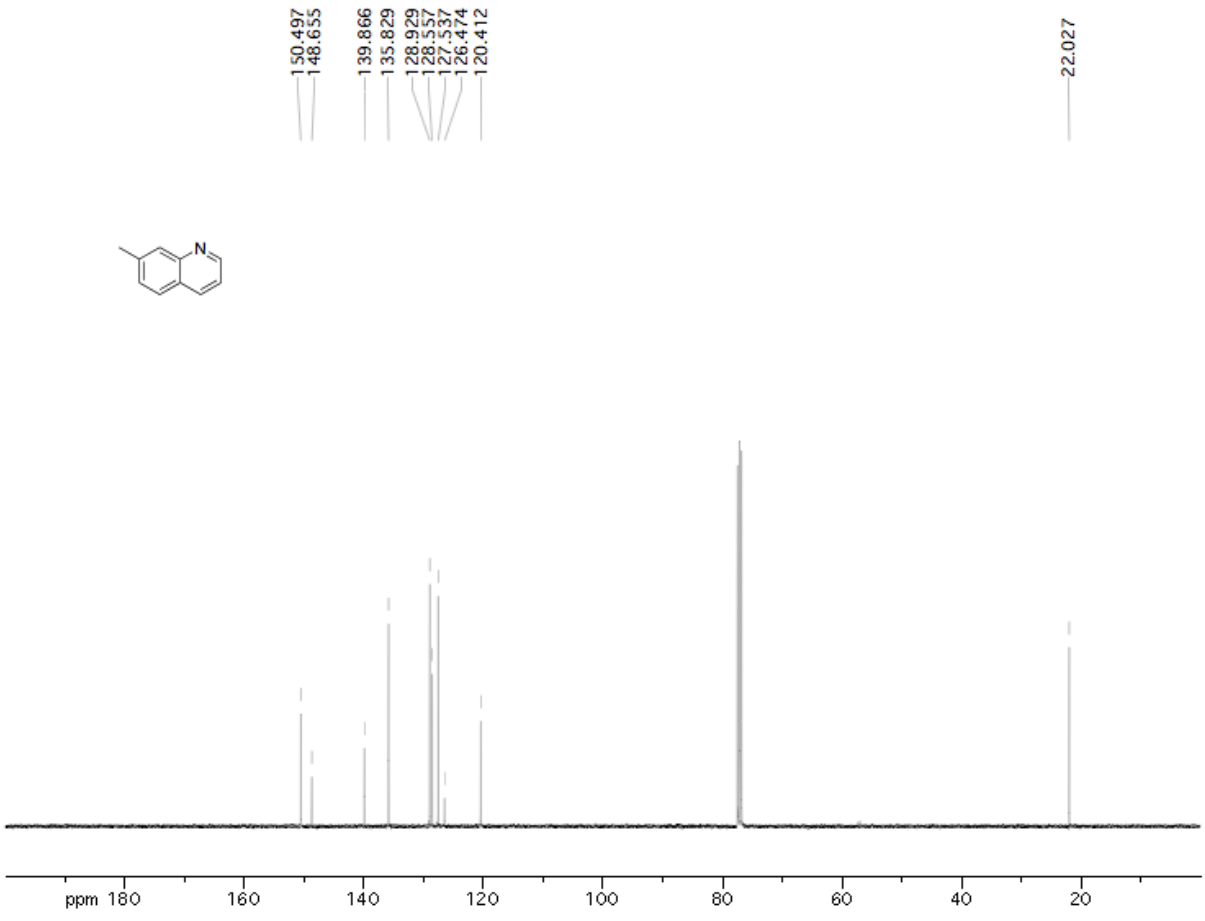
1.04 1.03 1.04
1 1.05 1.04 3.23
ppm 10 9 8 7 6 5 4 3 2 1 0


150.497
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139.866
135.829
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128.557
127.537
126.474
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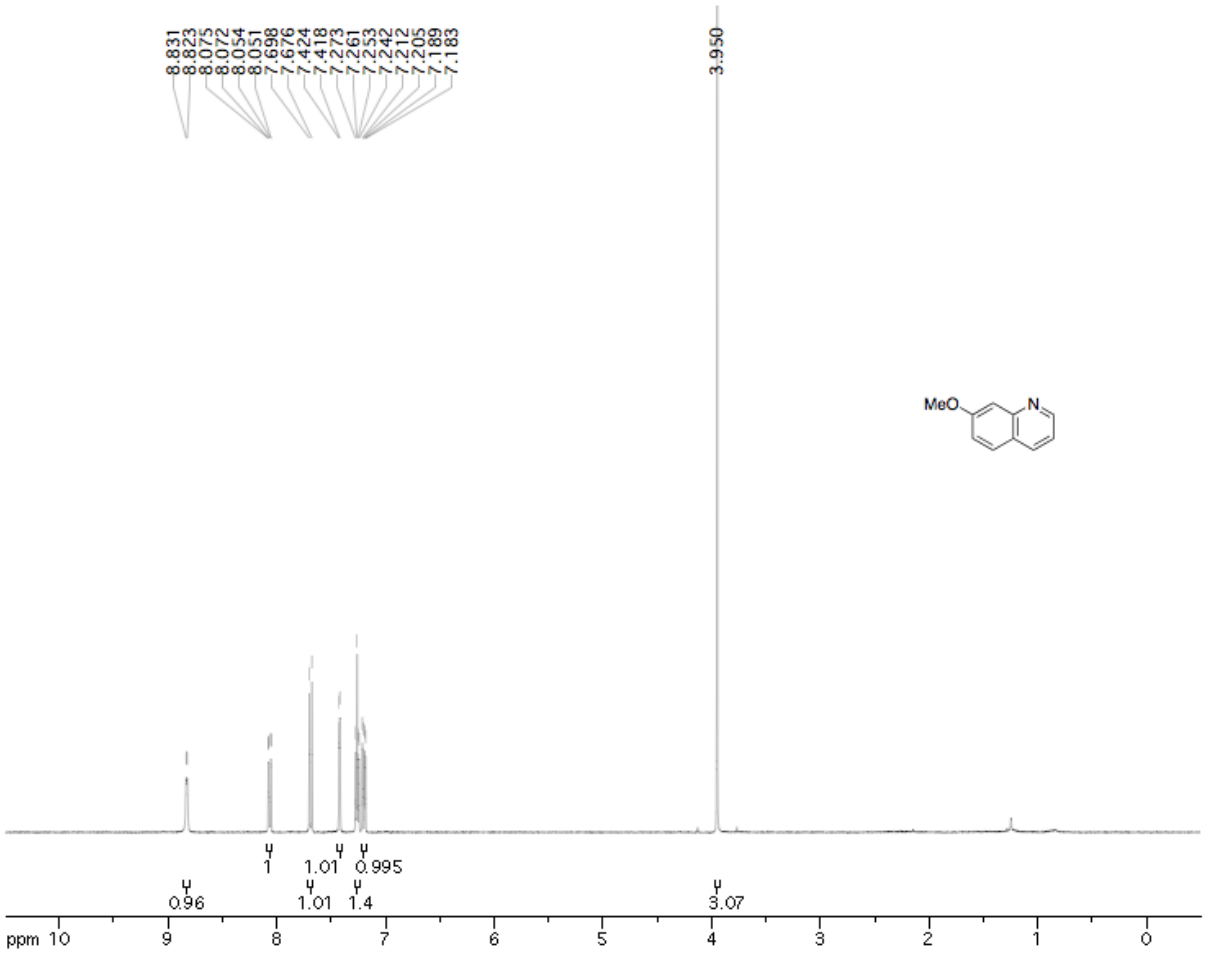
22.027
N
ppm 180
160
140
120
100
80
60
40
20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8.823
8.075
8.072
8.054
8.051
7.698
7.676
7.424
7.418
7.273
7.261
7.253
7.242
7.212
7.205
7.189
7.183
3.950
MeO
N
1
1.01
0.995
0.96
1.01
1.4
3.07
ppm 10
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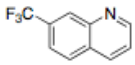
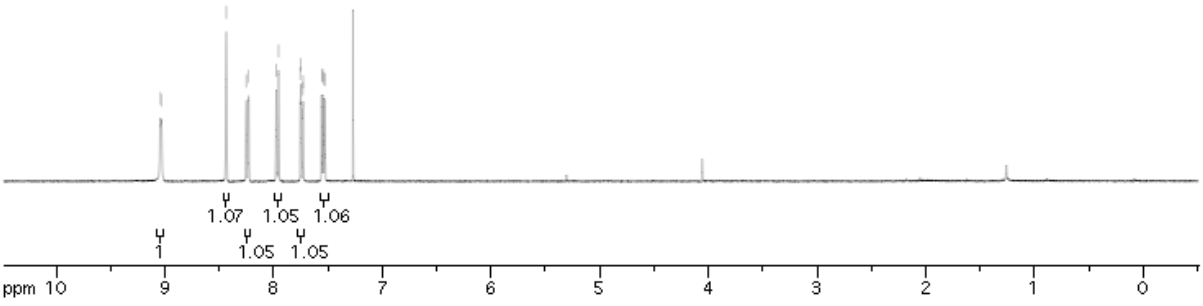
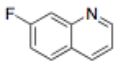
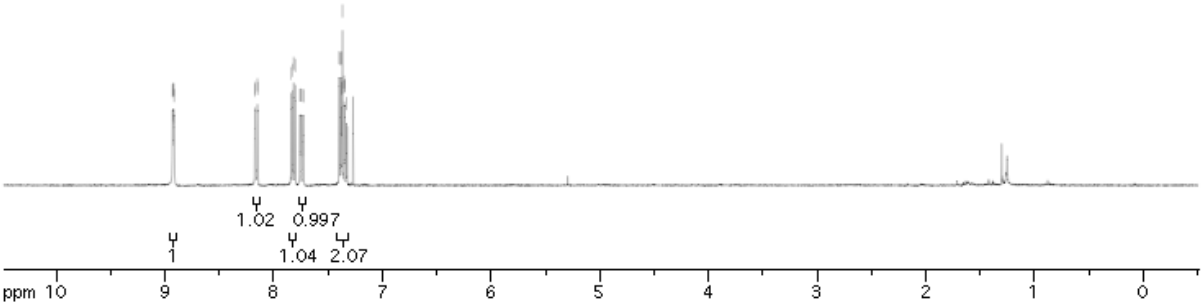
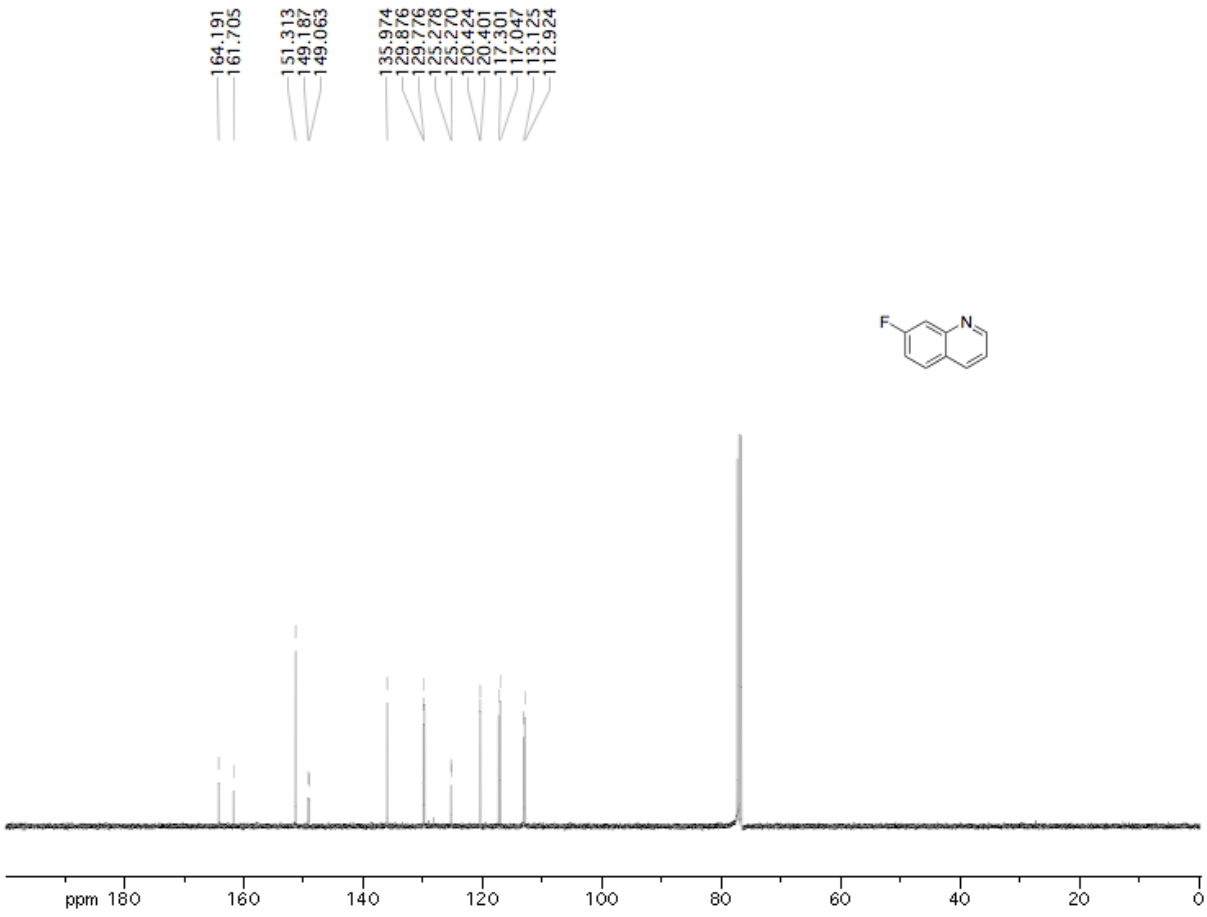
8
7
6
5
4
3
2
1
0







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129.776
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125.270
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113.125
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F
N
ppm 180
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20
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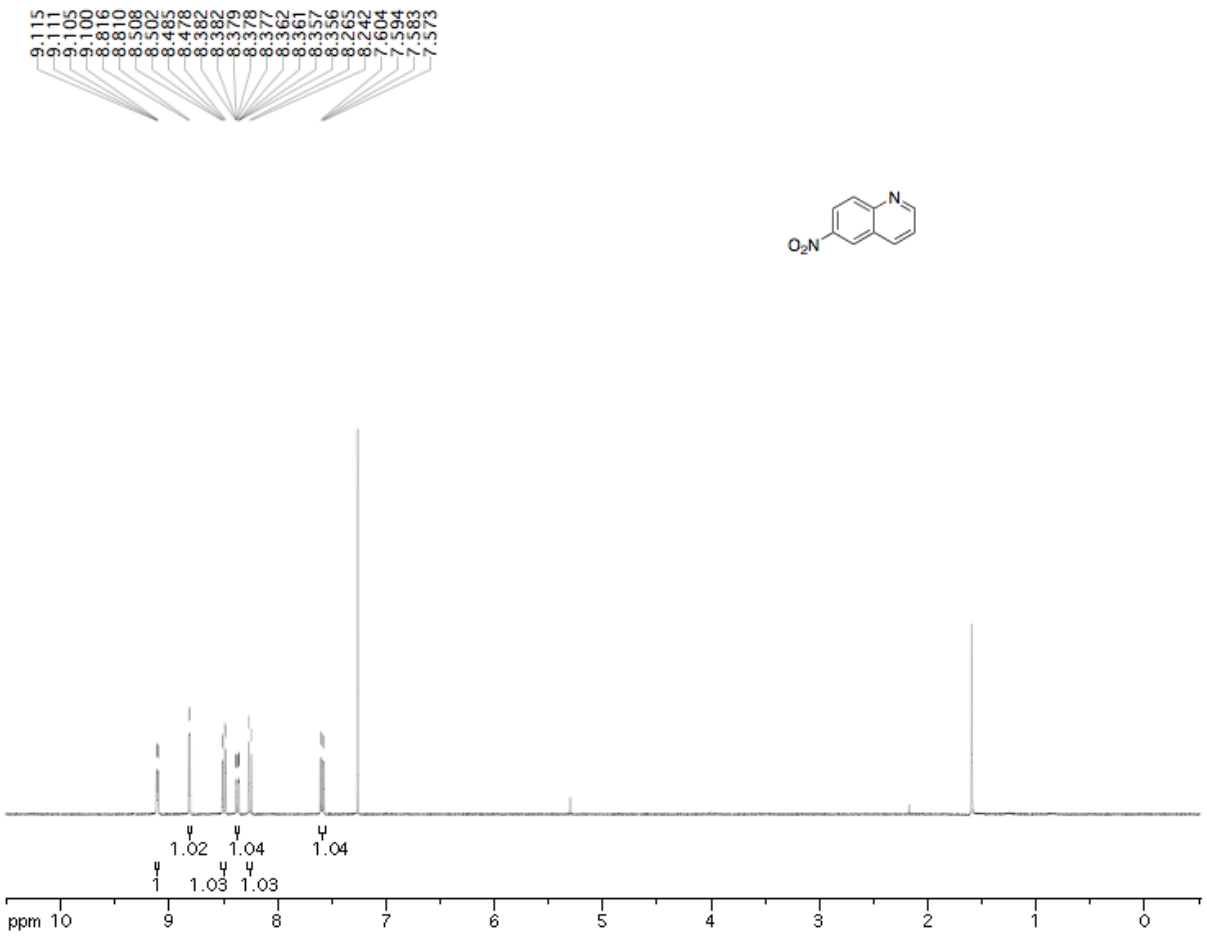
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8.502
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8.382
8.379
8.378
8.377
8.362
8.361
8.357
8.356
8.265
8.242
7.604
7.594
7.583
7.573
N
O2N
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1
1.03
1.03
ppm 10
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8
7
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4
3
2
1
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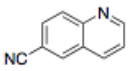

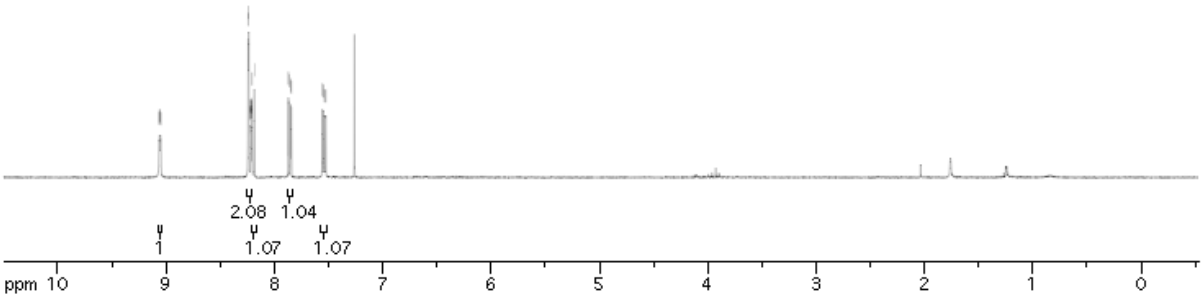

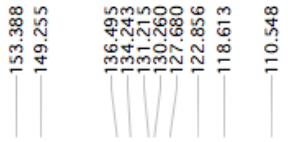

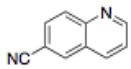

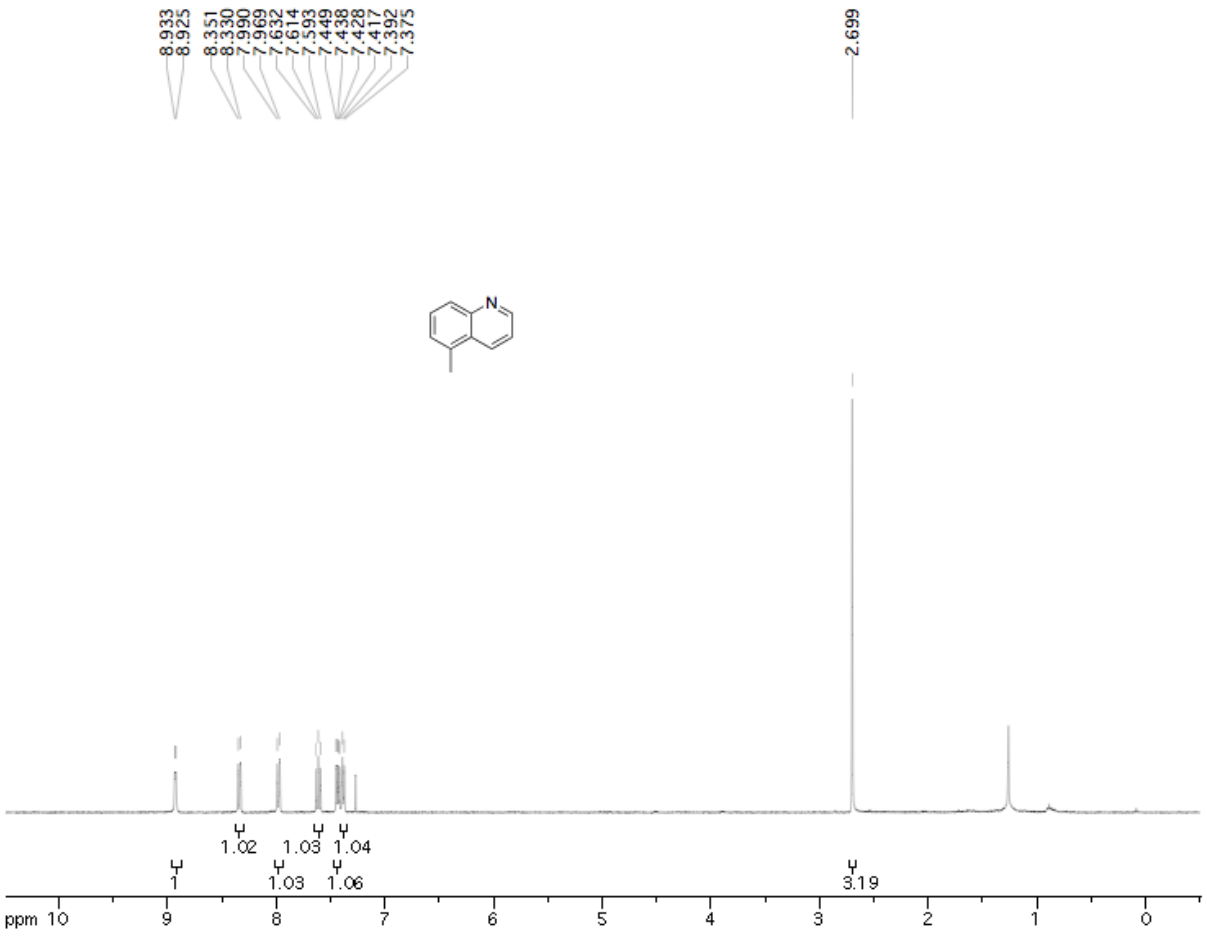

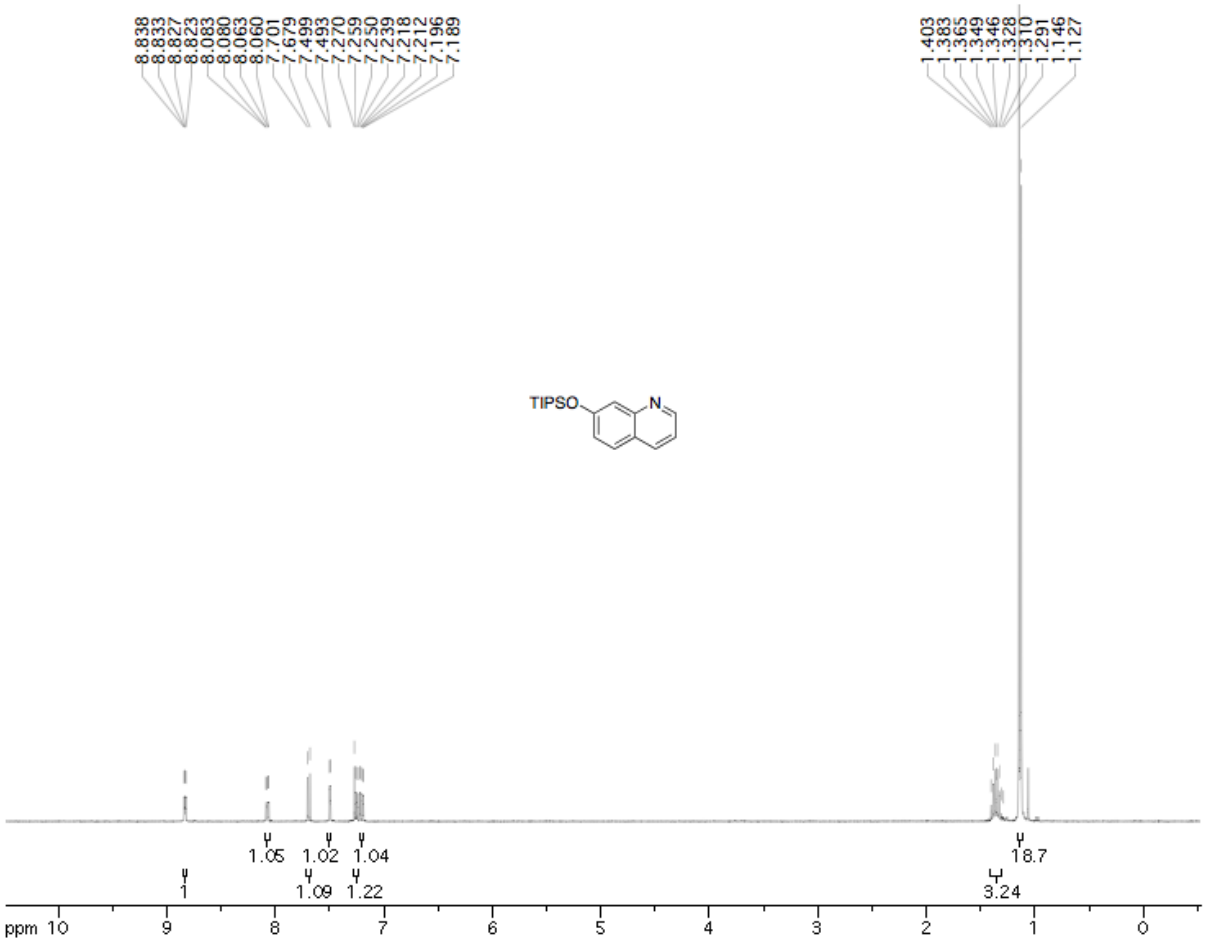

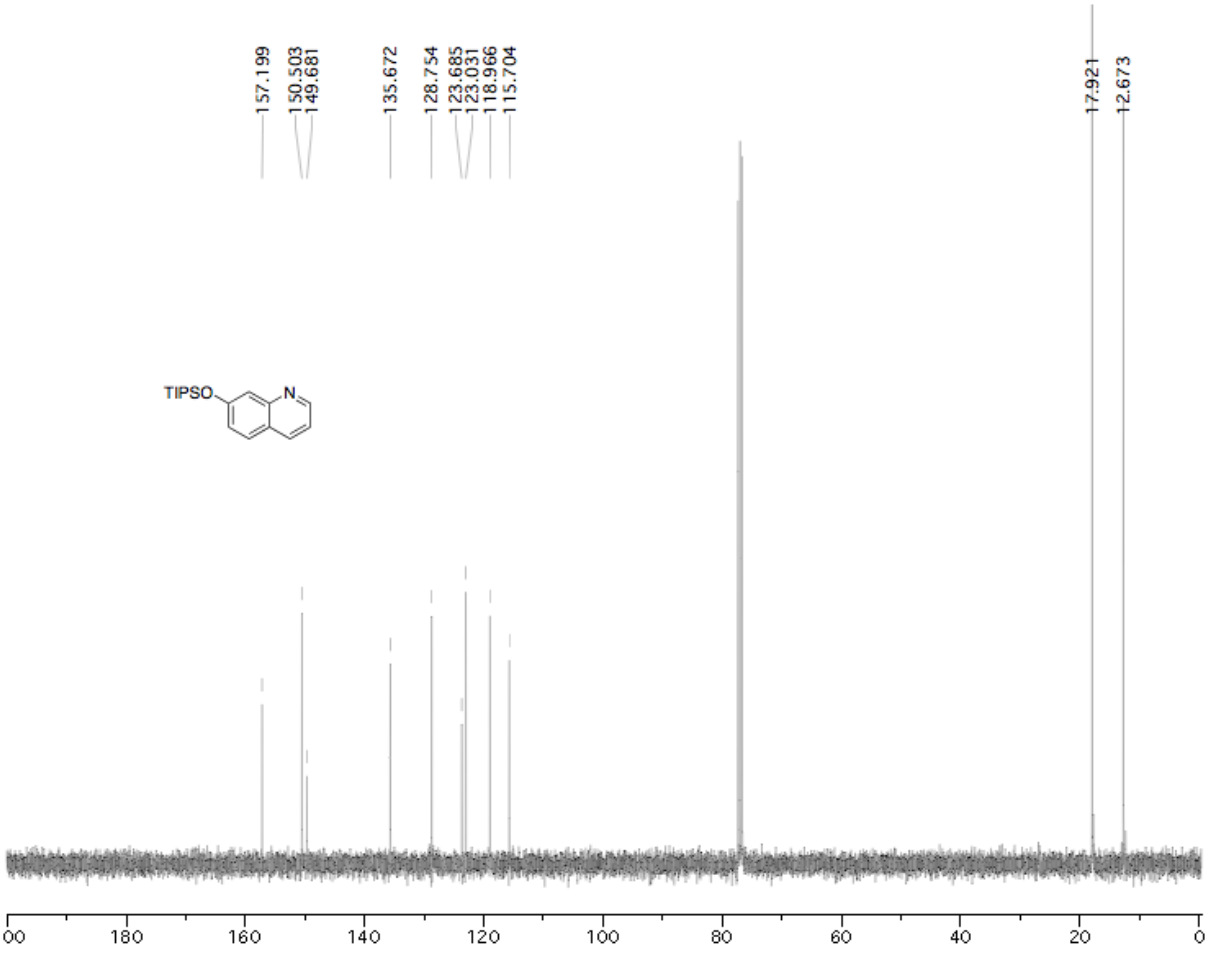
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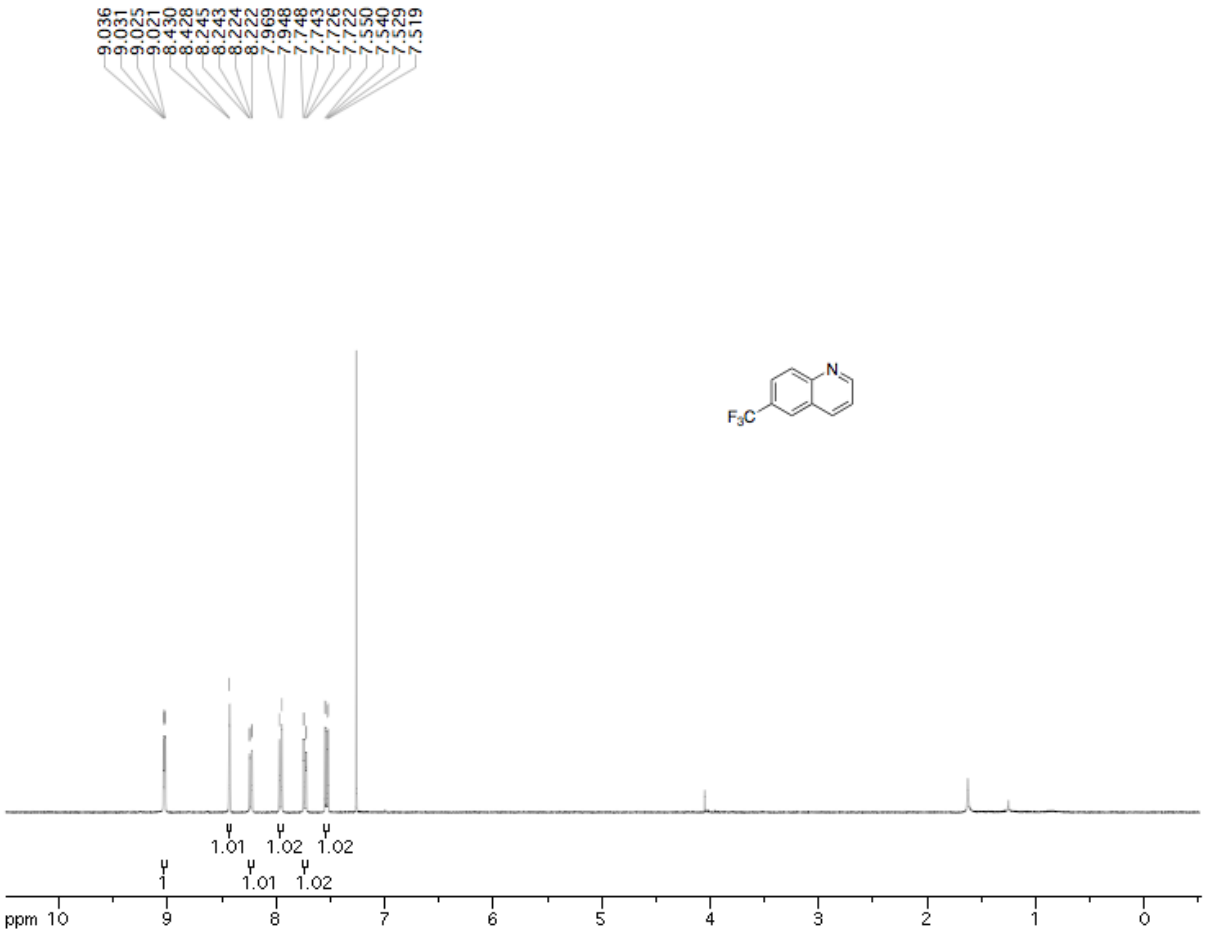
20
0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9.025
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8.243
8.224
8.222
7.969
7.948
7.748
7.743
7.726
7.722
7.550
7.540
7.529
7.519
N
F3C
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1.02
1.02
1
1.01
1.02
ppm 10
9
8
7
6
5
4
3
2
1
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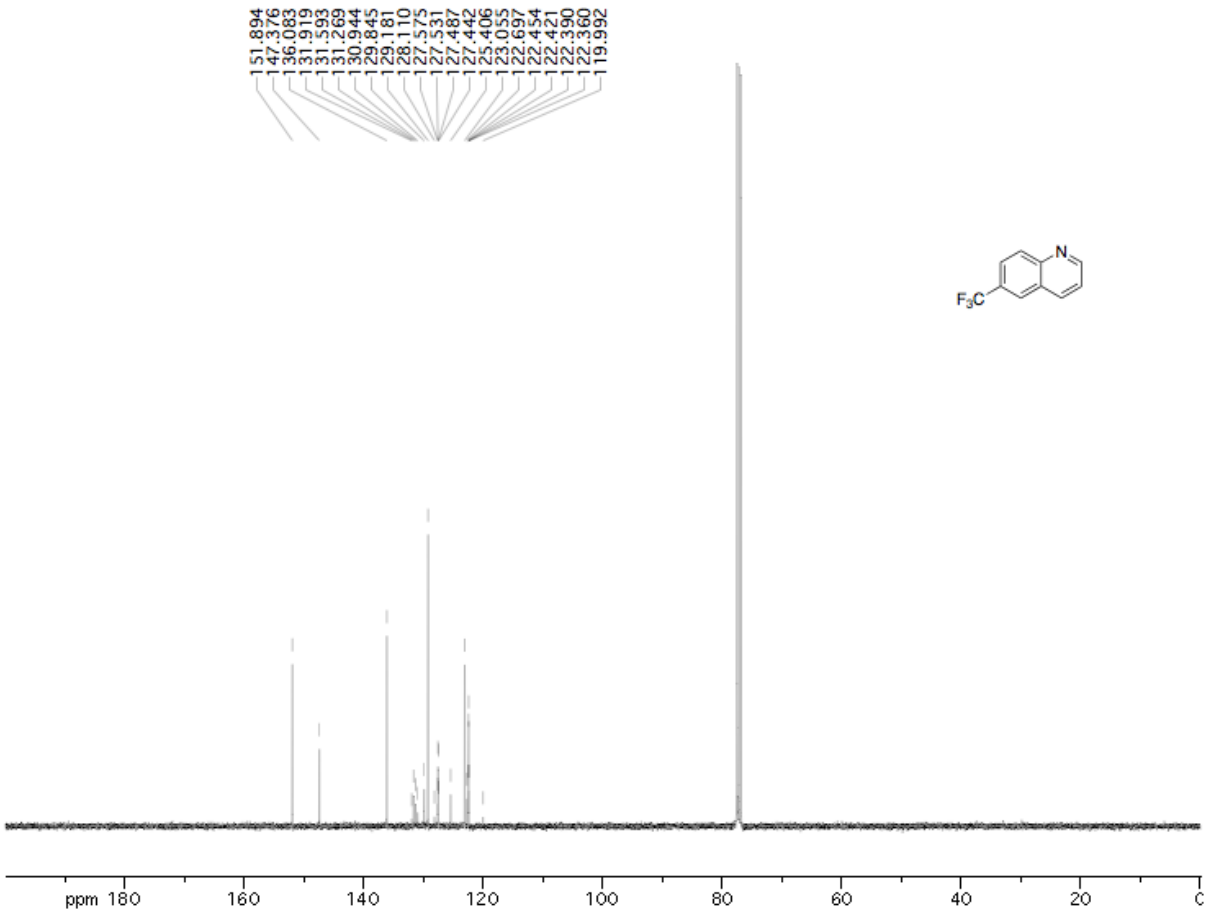
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127.487
127.442
125.406
123.055
122.697
122.454
122.421
122.390
122.360
119.992
N
F3C
ppm 180
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140
120
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20
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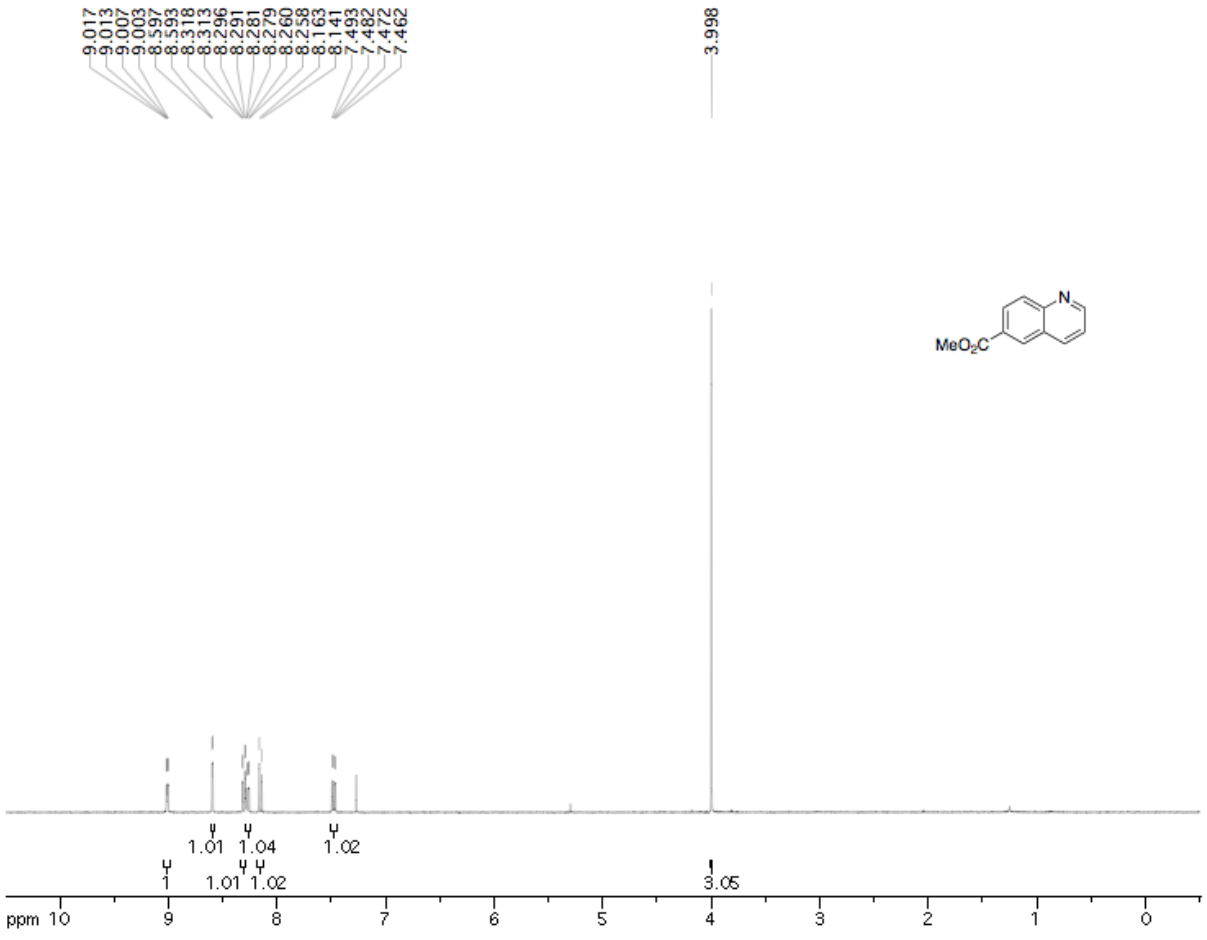
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8.313
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8.291
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8.279
8.260
8.258
8.163
8.141
7.493
7.482
7.472
7.462
3.998
N
MeO2C
1.01
1.04
1.02
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1.01
1.02
3.05
ppm 10
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8
7
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5
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2
1
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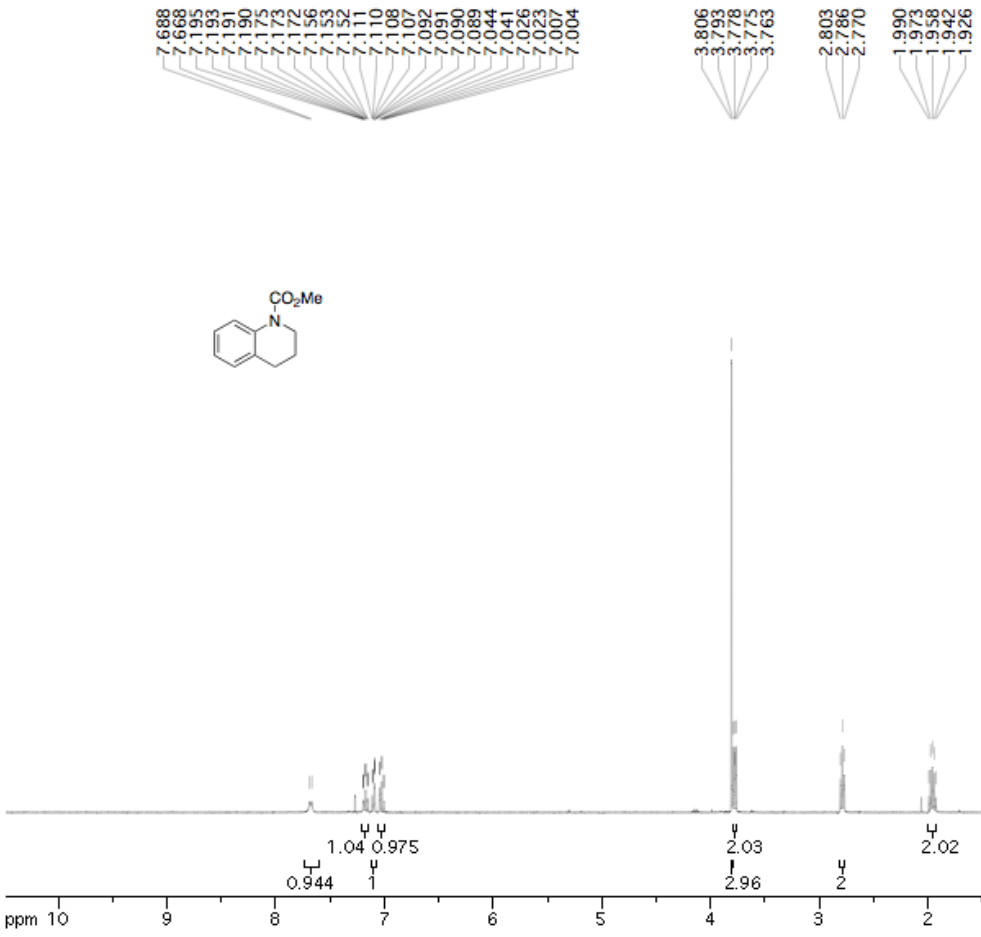
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7.173
7.172
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7.153
7.152
7.111
7.110
7.108
7.107
7.092
7.091
7.090
7.089
7.044
7.041
7.026
7.023
7.007
7.004
3.806
3.793
3.778
3.775
3.763
2.803
2.786
2.770
1.990
1.973
1.958
1.942
1.926
CO2Me
N
1.04
0.975
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2
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7
6
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1
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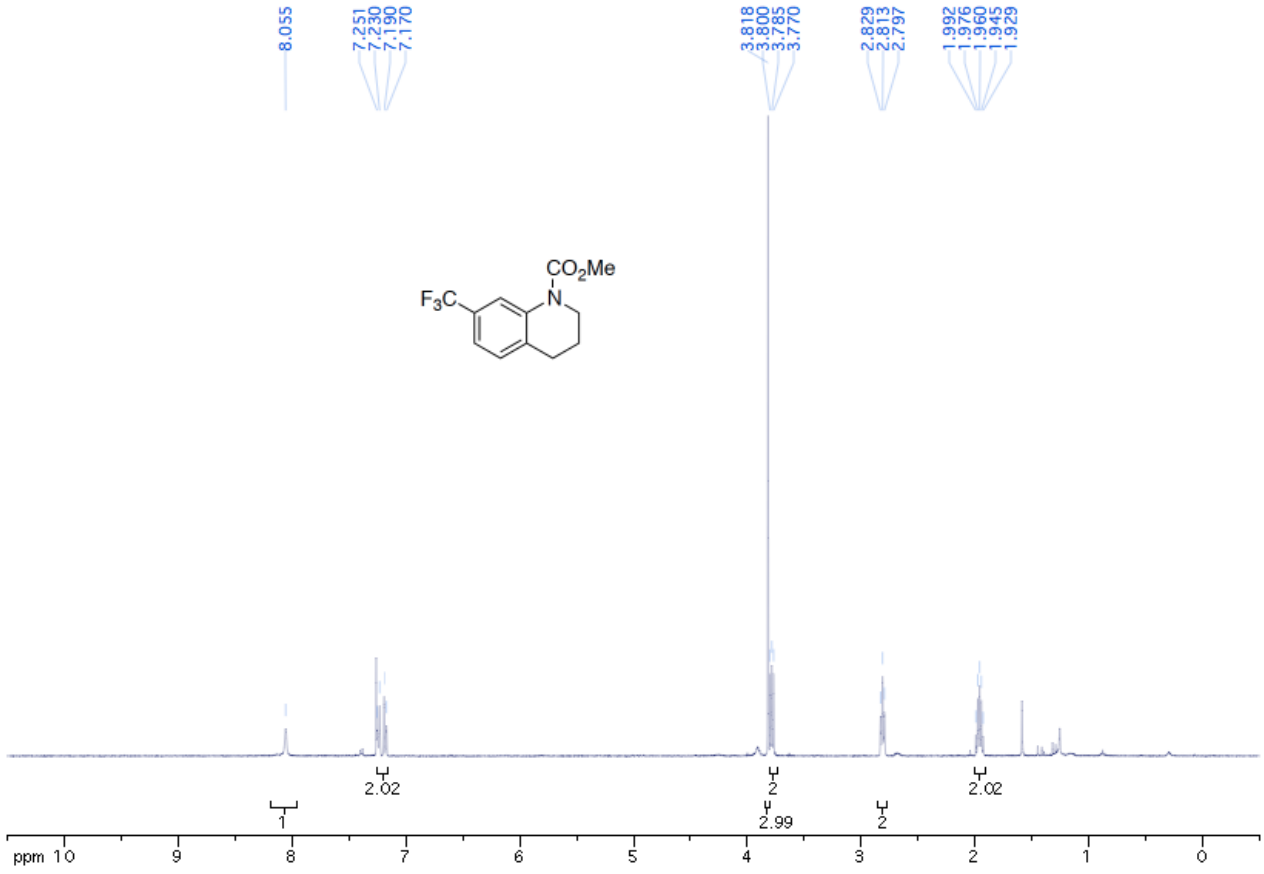
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3.785
3.770
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2.813
2.797
1.992
1.976
1.960
1.945
1.929
CO2Me
F3C
N
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2
2.02
1
2.99
2
ppm 10
9
8
7
6
5
4
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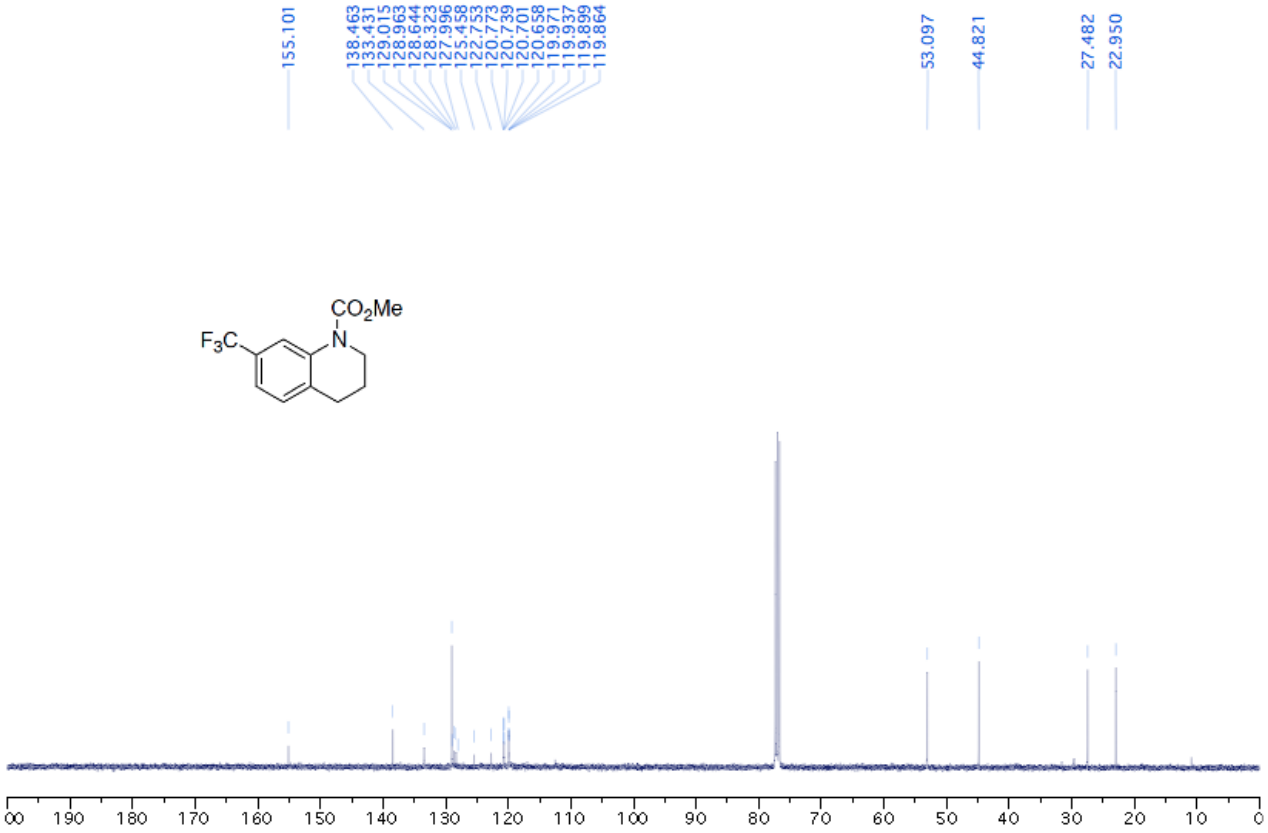
2
1
0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128.644
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122.753
120.773
120.739
120.701
120.658
119.977
119.937
119.899
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27.482
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CO2Me
F3C
N
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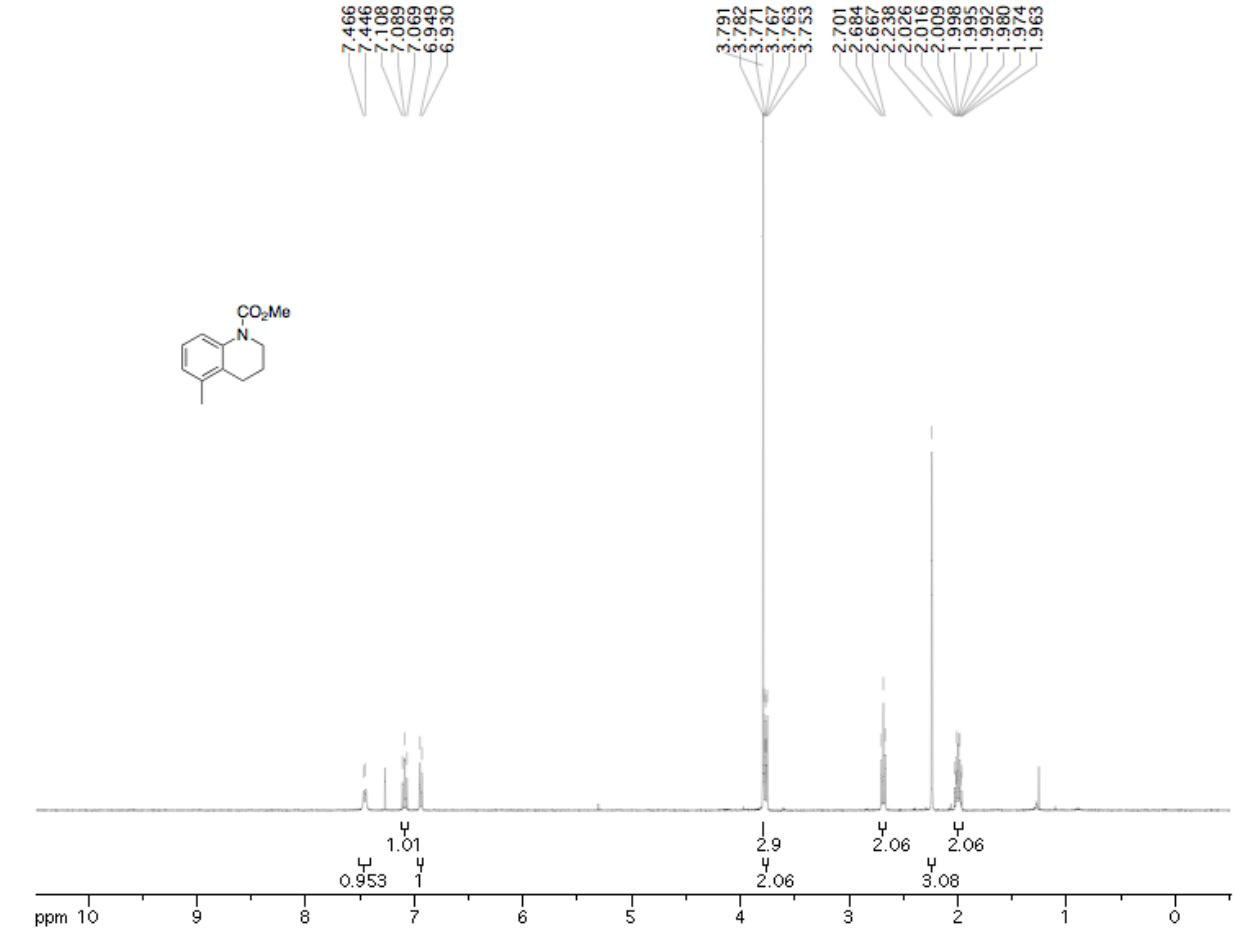
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3.763
3.753
2.701
2.684
2.667
2.238
2.026
2.016
2.009
1.998
1.995
1.992
1.980
1.974
1.963
CO2Me
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2.06
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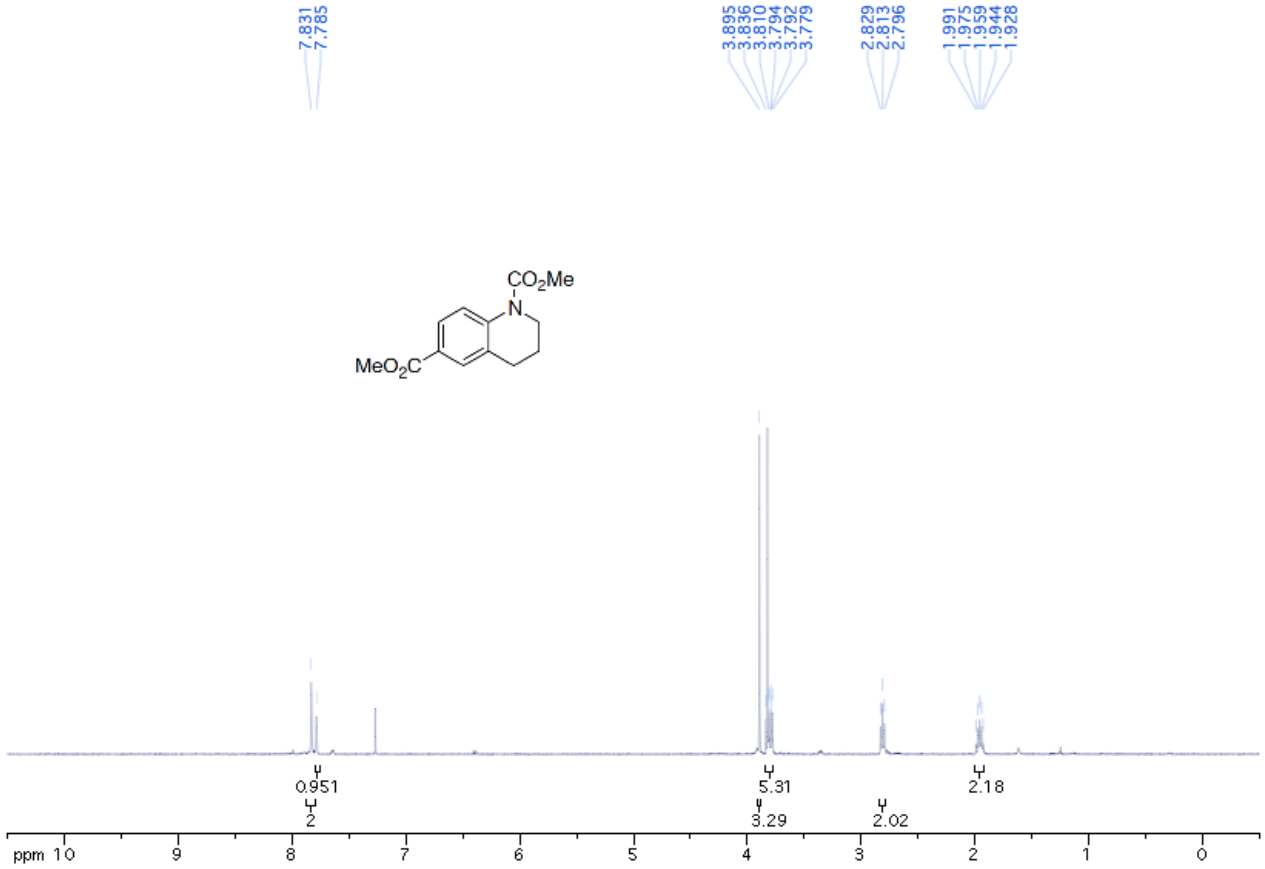
ppm 10 9 8 7 6 5 4 3 2 1 0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2.813
2.796
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1.975
1.959
1.944
1.928
CO2Me
N
MeO2C
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2.02
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6
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2
1
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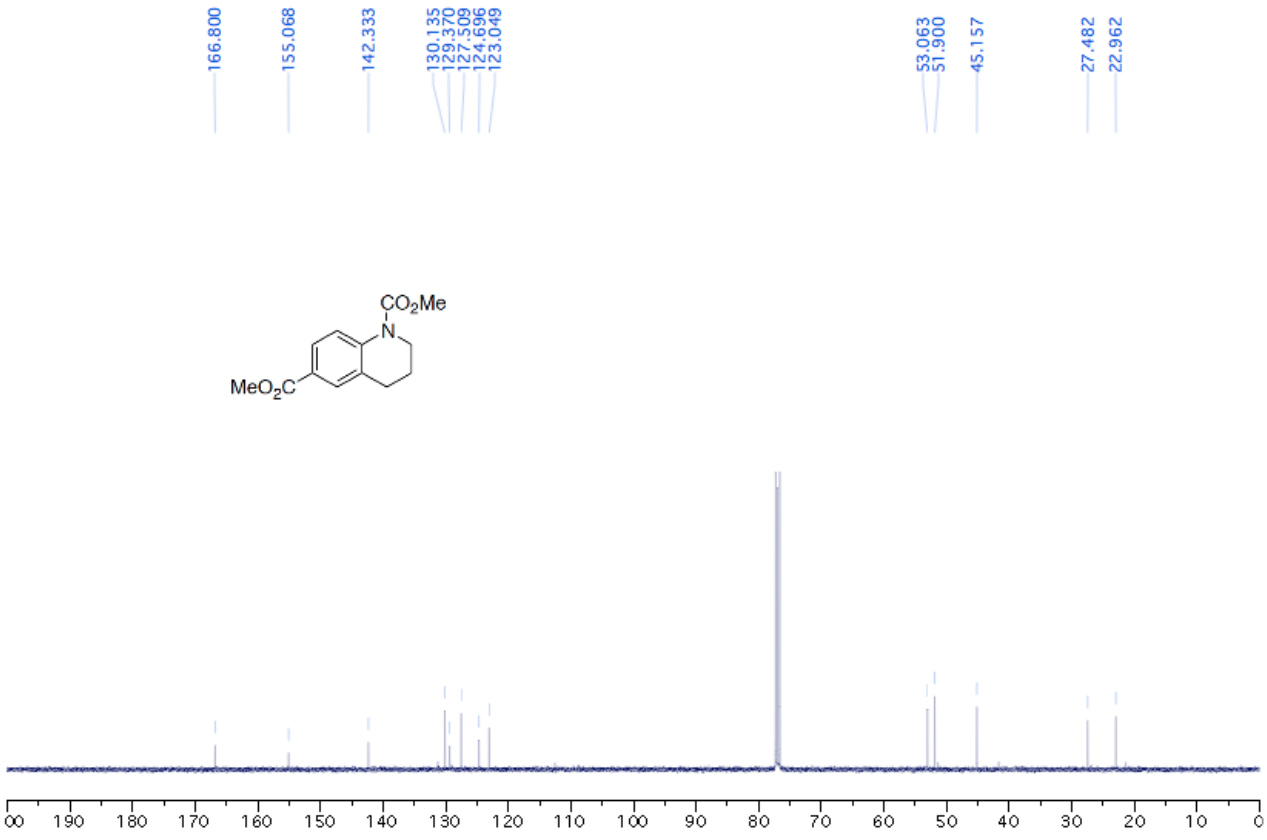
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123.049
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51.900
45.157
27.482
22.962
CO2Me
N
MeO2C
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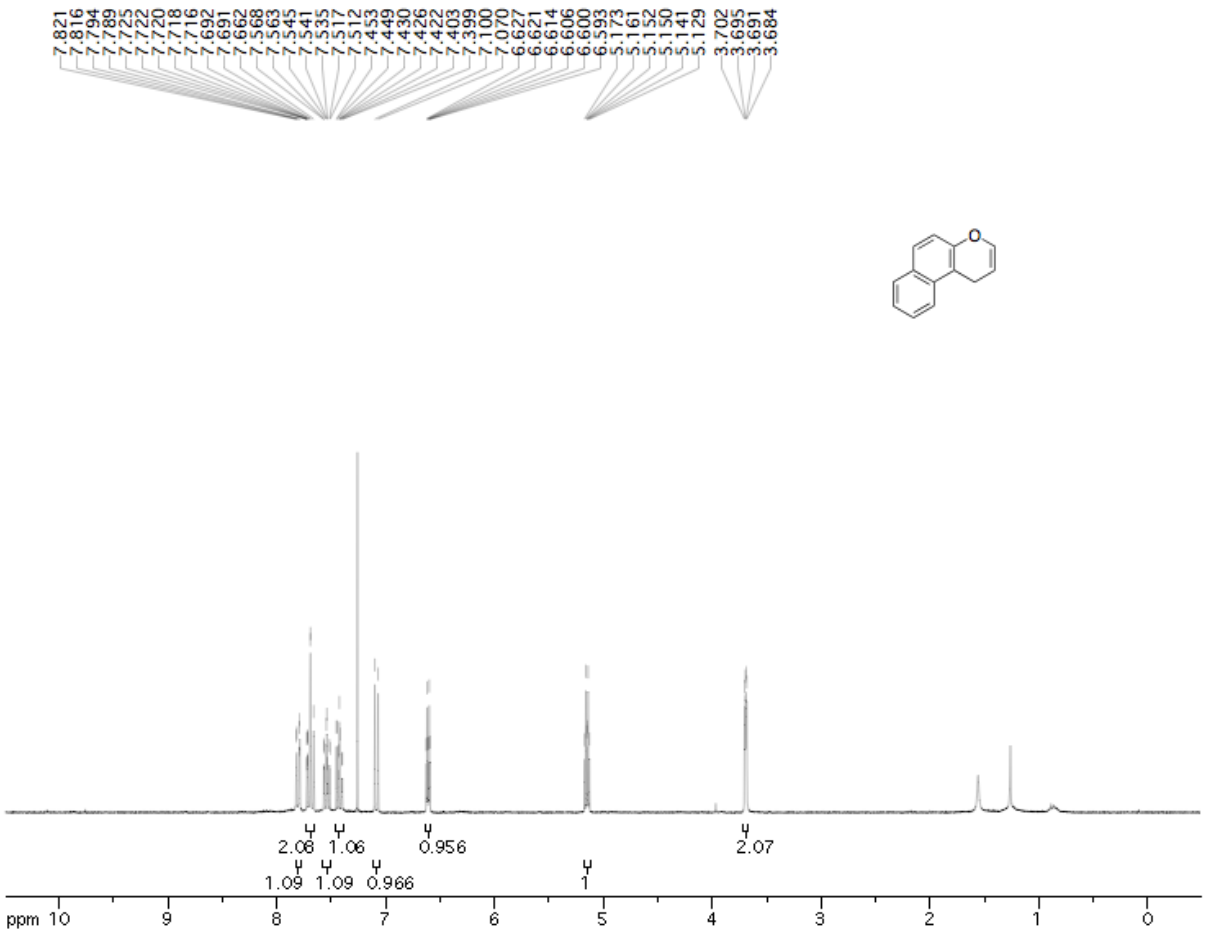

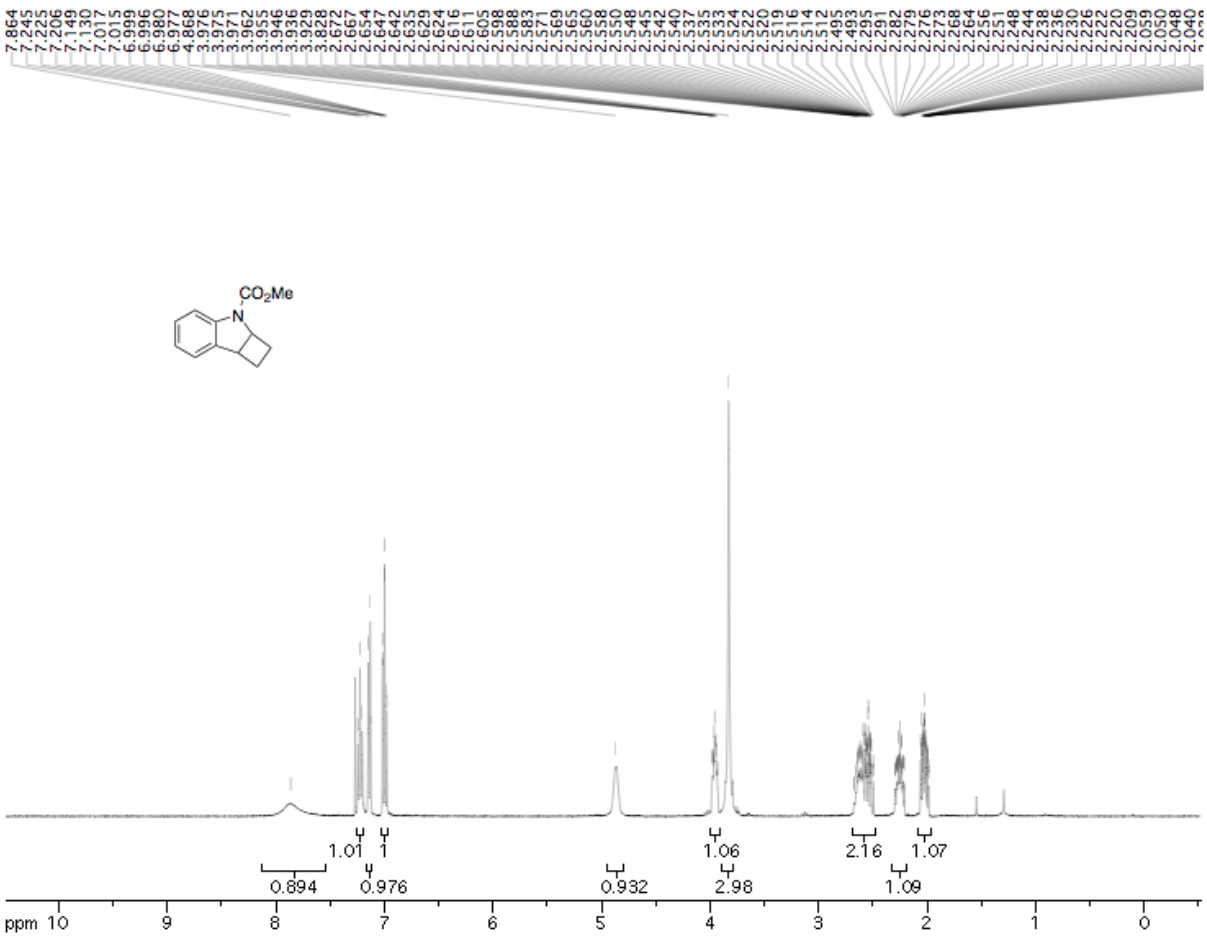

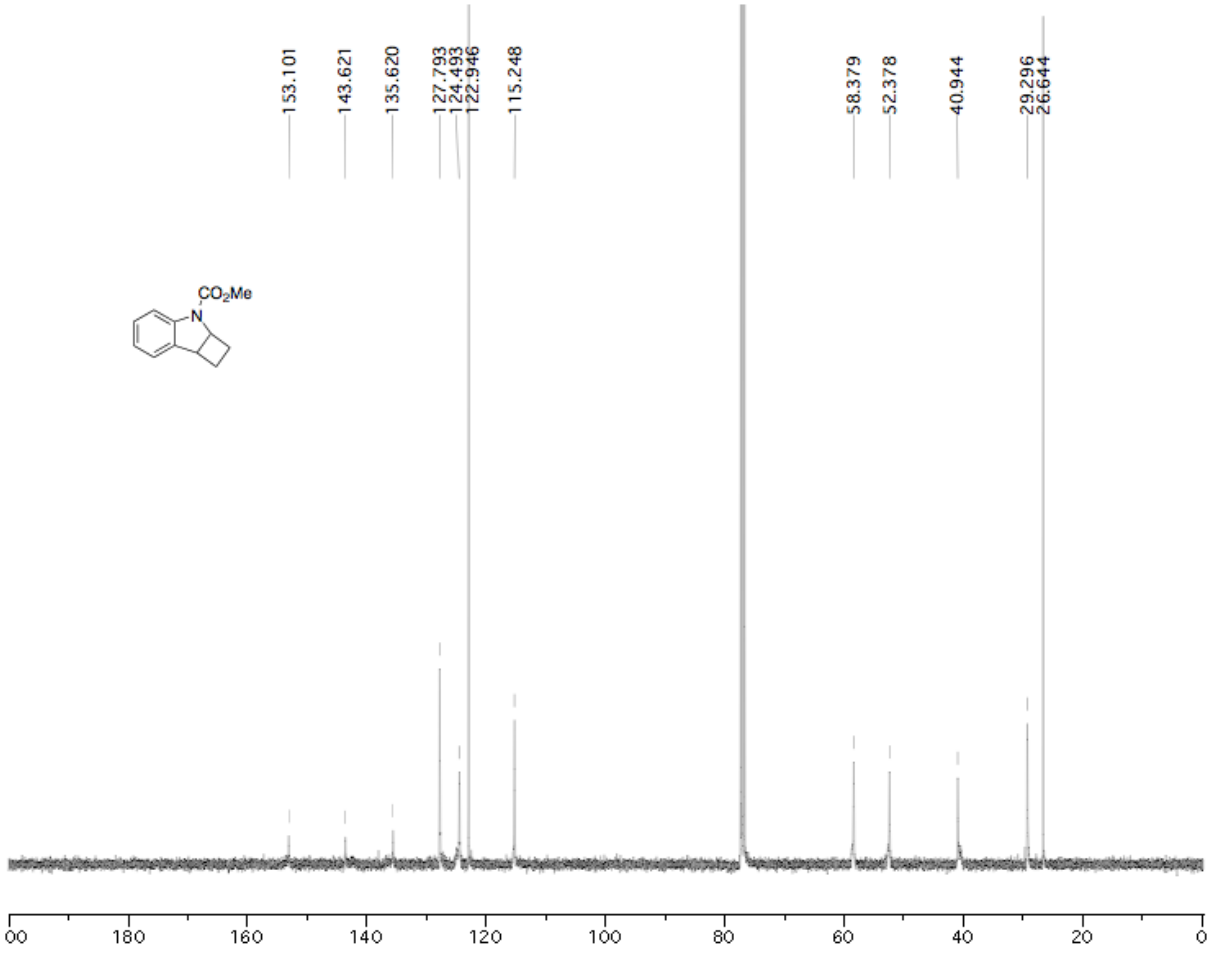
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122.946
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58.379
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26.644
CO2Me
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140
120
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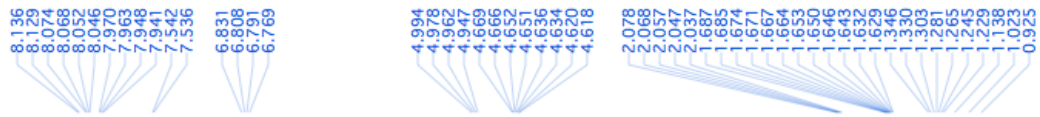
40
20
0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2.047
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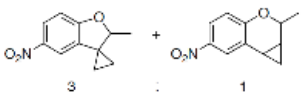
0.925


O2N
O2N
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:
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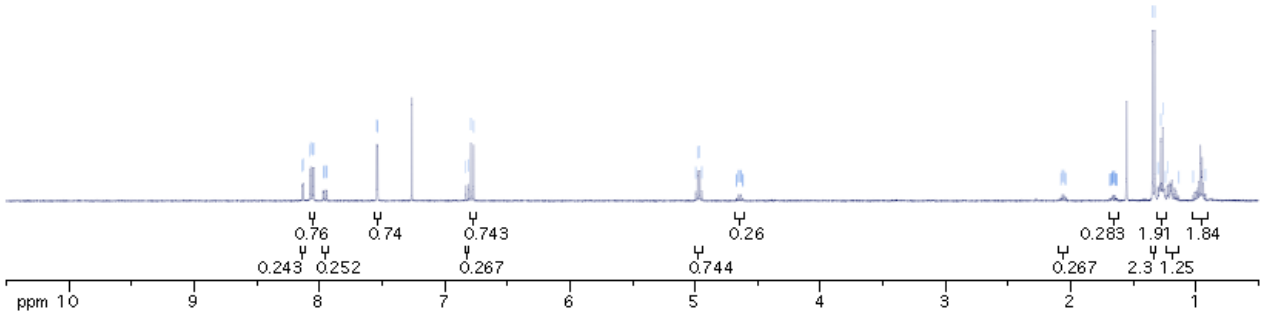
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8
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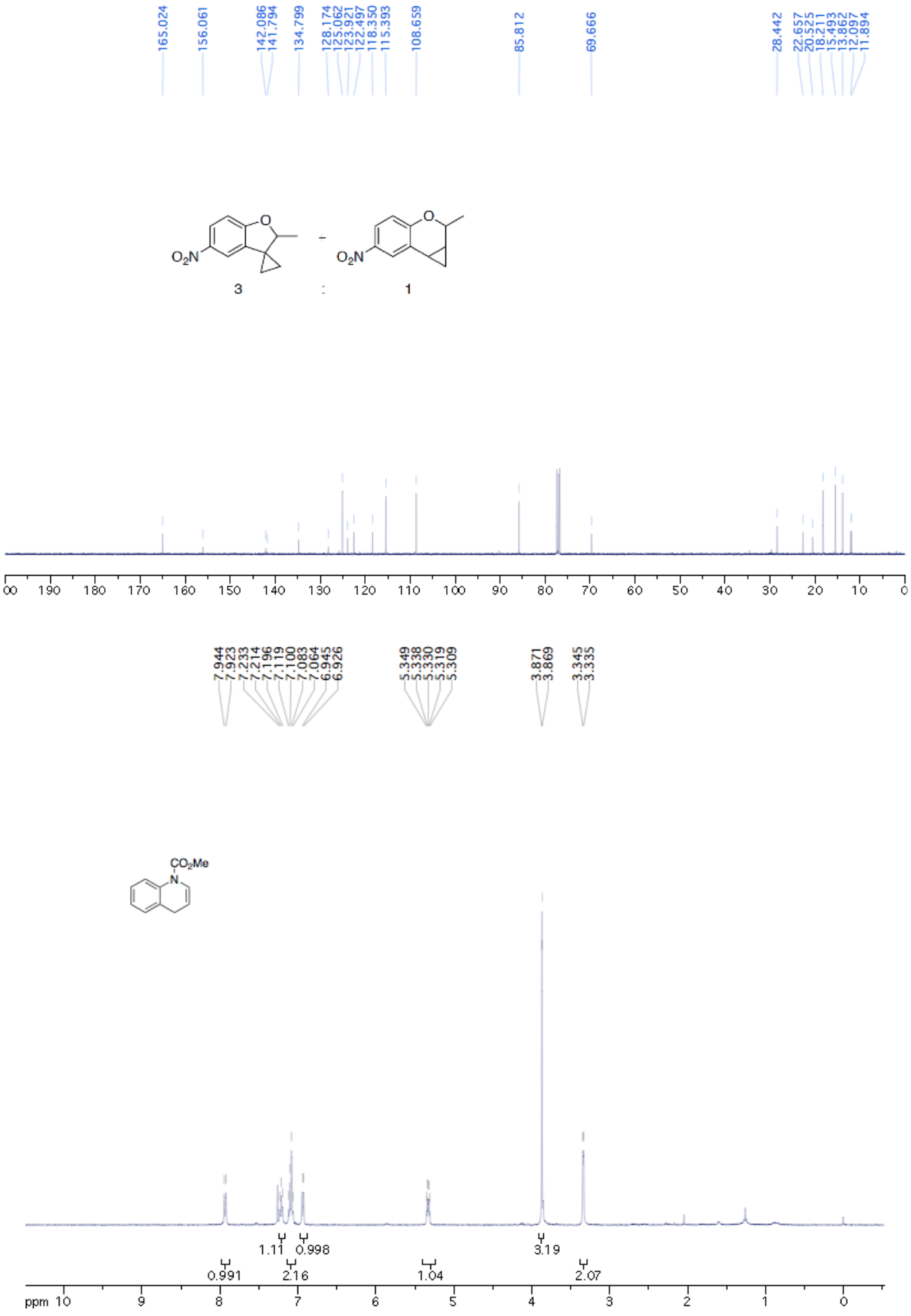
5
4
3
2
1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118.350
115.393
108.659
85.812
69.666
28.442
22.657
20.525
18.211
15.493
13.862
12.097
11.894
O2N
O
3
:
1
7.944
7.923
7.233
7.214
7.196
7.119
7.100
7.083
7.064
6.945
6.926
5.349
5.338
5.330
5.319
5.309
3.871
3.869
3.345
3.335
CO2Me
N
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0.998
3.19
0.991
2.16
1.04
2.07
ppm