Supporting Information

Employing Pd-Catalyzed C–H Arylation in Multicomponent-Multicatalyst Reactions $(MC)^2R$: One-Pot Synthesis of Dihydrobenzoquinolines

Fabian Lied, Helena Brodnik Žugelj, Bogdan Štefane, Frank Glorius*, and Mark Lautens*

Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster, Corrensstraße 40, 48149 Münster, Germany

Davenport Research Laboratories, Department of Chemistry, University of Toronto, 80 St. George St., Toronto, Ontario M5S 3H6, Canada

Faculty of Chemistry and Chemical Technology, University of Ljubljana, Večna pot 113, SI-1000 Ljubljana, Slovenia

mlautens@chem.utoronto.ca

glorius@uni-muenster.de

Table of Contents

General Information

Unless otherwise noted, all reactions were carried out under an atmosphere of argon in flamedried glassware. Reaction temperatures are reported as the temperature of the bath surrounding the vessel unless otherwise stated.

Münster:

Commercially available chemicals were obtained from Acros Organics, Aldrich Chemical Co., Strem Chemicals, Alfa Aesar, ABCR, TCI Europe and Combi-Blocks and used as received unless otherwise stated.

NMR-spectra were recorded on a Bruker ARX-300, AV-300, AV-400 MHz or a Varian Unity Plus 600 or 500 INOVA.

GC were recorded on an Agilent Technologies 7890A GC-system with an Agilent 5975C VL MSD or an Agilent 5975 inert Mass Selective Detector (EI) and a HP-5MS column (0.25 mm × 30 m, film: 0.25 µm). The methods used start with the injection temperature T0. After holding this temperature for 3 min, the column is heated to temperature T1 (ramp) and this temperature is held for an additional time t (method 50_40: T0 = 50 °C, T1 = 290 °C, ramp = 40 °C/min, t = 10 min).

ESI mass spectra were recorded on a Bruker Daltonics MicroTof.

Analytical thin layer chromatography was performed on Polygram SIL G/UV254 plates. Visualization was accomplished with short wave UV light and/or KMnO4 staining solution followed by gentle heating.

Flash column chromatography was performed on Merck silica gel (40-63 mesh) by using standard laboratory techniques. Solvents used for flash column chromatography were distilled before use.

Toronto:

Reactions were monitored using thin layer chromatography (TLC) with Silicycle™ normal phase glass plates (0.25 mm, 60-Å pore size, 230-400 mesh), visualised by UV light and/or stained with potassium permanganate, anisaldehyde or vanillin stains. Column chromatography was performed using Silicycle™ Ultra-Pure 230-400 mesh silica gel. Yields quoted are isolated yields unless otherwise stated.

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Varian Mercury 300, Varian Mercury 400, Varian VnmrS 400, or Bruker Avance III 400 at specified field

strengths. ^{1}H NMR, ^{19}F NMR, and ^{13}C NMR spectra were recorded in $CDCl_3$ and CD_2Cl_2.

Infrared (IR) spectra were obtained using a Perkin-Elmer Spectrum 1000 FT-IR spectrometer as thin films from dichloromethane or chloroform. High resolution mass spectra (HRMS) were obtained on a JEOL AccuTOF JMST1000LC mass spectrometer equipped with an IONICS® Direct Analysis in Real Time (DART) ion source or an ABI/Sciex Qstar mass spectrometer (ESI). The [M+H]+ peak in positive ionisation mode was observed. Melting points were taken on a Fisher-Johns melting point apparatus and are uncorrected.

Chemical shifts (δ) are quoted in ppm downfield of tetramethylsilane and were referenced to the solvent peak (for $CDCl_3$, ^{1}H NMR: 7.26 ppm, ^{13}C NMR: 77.16 ppm, for DMSO-d_6, ^{1}H NMR: 2.50 ppm, ^{13}C NMR: 39.52 ppm and for CD_2Cl_4, ^{1}H NMR 5.91 ppm). Coupling constants (*J*) are quoted in Hz. ^{1}H- and ^{13}C-peak attributions were determined by DEPT, ^{1}H-^{1}H gCOSY, ^{1}H-^{13}C gHSQC, ^{1}H-^{13}C gHMBC or by analogy. To describe the multiplicities of the signals, the following abbreviations were used: s: singlet, bs: broad signal, d: doublet, t: triplet, q: quartet, m: multiplet.

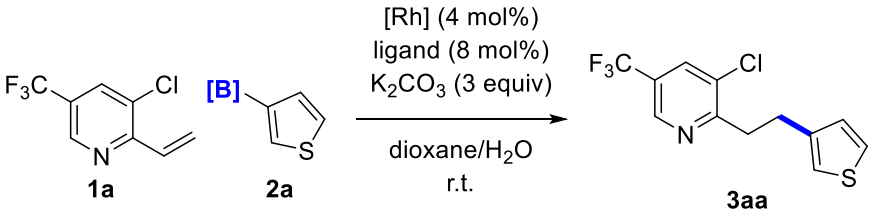
Melting points are on materials obtained directly from column chromatography (and solvents used therein) unless otherwise stated.

$[Rh(COD)OH]_2$, $[Rh(COD)Cl]_2$ $[Rh(C_2H_4)_2Cl]_2$ $Pd(OAc)_2$, Pd_2dba_3, tBuX-Phos, dppbenz and $Pd(PPh_3)_4$ were purchased from Strem Chemicals and were used as received. All pyridines, boronic acids, and other reagents were purchased from Alfa Aesar, TCI, Combi-Blocks, or Sigma-Aldrich and were used as received. Commercial anhydrous potassium carbonate and potassium phosphate (tribasic) were finely ground into powders and were stored in a dessicator. Tetrahydrofuran (THF) and dioxane were distilled from Na/benzophenone before use. Dimethoxyethane (DME), acetonitrile, and dichloromethane (DCM) were distilled from calcium hydride before use. Methanesulfonylchloride (Mesyl chloride, MsCl) was distilled from phosphorus pentoxide before use.

Experimental section

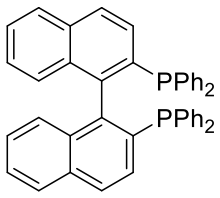
1) Optimization of the reaction conditions

Table S1 Optimization of the reaction parameters for the Rh-catalyzed hydroarylation.

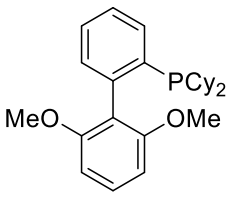


Entry	B ([equiv])	Rh	ligand	t [h]	Yield [%][a]
1	$B(OH)_2$ (1.5)	$[\{Rh(cod)Cl\}_2]$	none	1	44
2	BPin (1.5)	$[\{Rh(cod)Cl\}_2]$	none	1	71
3	BF_3K (1.5)	$[\{Rh(cod)Cl\}_2]$	none	1	< 2
4	BMIDA (1.5)	$[\{Rh(cod)Cl\}_2]$	none	1	7
5	BPin (1.1)	$[\{Rh(cod)OH\}_2]$	none	16	99
6	BPin (1.1)	$[\{Rh(C_2H_4)_2Cl\}_2]$	*rac*-BINAP	4	27
7[b]	$B(OH)_2$ (1.5)	$[\{Rh(C_2H_4)_2Cl\}_2]$	SPhos	1	0
8[b]	$B(OH)_2$ (1.5)	$[\{Rh(C_2H_4)_2Cl\}_2]$	*t*-BuXPhos	1	0
9[b]	$B(OH)_2$ (1.5)	$[\{Rh(C_2H_4)_2Cl\}_2]$	L1	1	3
10[b]	$B(OH)_2$ (1.5)	$[\{Rh(C_2H_4)_2Cl\}_2]$	*rac*-BINAP	1	95
11	$B(OH)_2$ (1.5)	$[\{Rh(C_2H_4)_2Cl\}_2]$	dppbenz	1	70
12[c]	$B(OH)_2$ (1.5)	$[\{Rh(C_2H_4)_2Cl\}_2]$	dppbenz	1	57
13[b]	$B(OH)_2$ (1.5)	$[\{Rh(C_2H_4)_2Cl\}_2]$	dppbenz	1	99
14[b]	$B(OH)_2$ (1.5)	$[\{Rh(C_2H_4)_2Cl\}_2]$	dppbenz	0.5	99
15[b]	$B(OH)_2$ (1.5)	$[\{Rh(cod)Cl\}_2]$	dppbenz	2	38
16[b,d]	$B(OH)_2$ (1.5)	$RhCl(PPh_3)_3$	none	3	0
17[b]	$B(OH)_2$ (1.5)	$[\{Rh(C_2H_4)_2Cl\}_2]$	none	1	< 2
18[e]	$B(OH)_2$ (1.5)	$[\{Rh(C_2H_4)_2Cl\}_2]$	dppbenz	1	62
19[e]	$B(OH)_2$ (1.5)	$[\{Rh(C_2H_4)_2Cl\}_2]$	dppbenz	24	63

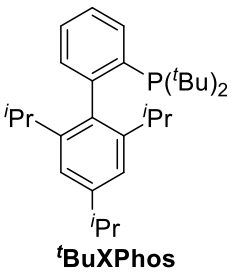
Reaction conditions: **1a** (1 equiv), [Rh] (4 mol%), ligand (8 mol%), K_2CO_3 (3 equiv) and **2a** in dioxane/water (10:1) under nitrogen, stirred at room temperature. [a]Yields determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. [b]The rhodium precursor, ligand and boronic acid were pre-stirred for 10 min at r.t. prior to the addition of the starting material and the base. [c]The rhodium precursor and ligand were pre-stirred for 10 min at r.t. prior to the addition of the starting material, the base and the boronic acid. [d]8 mol% of the rhodium precursor were used. [e]2 mol% of the rhodium precursor and 4 mol% of the ligand were used.



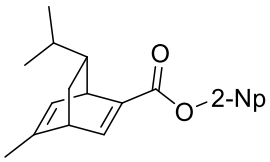
***rac*-BINAP**



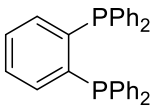
SPhos



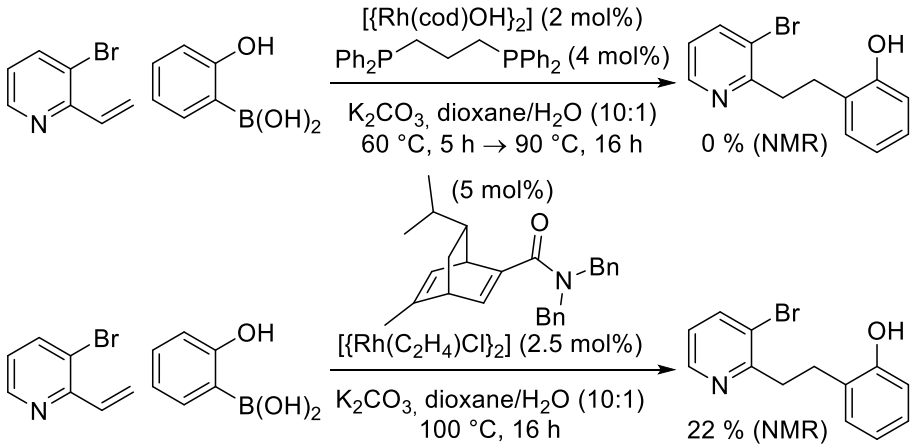
^{t}BuXPhos



L1

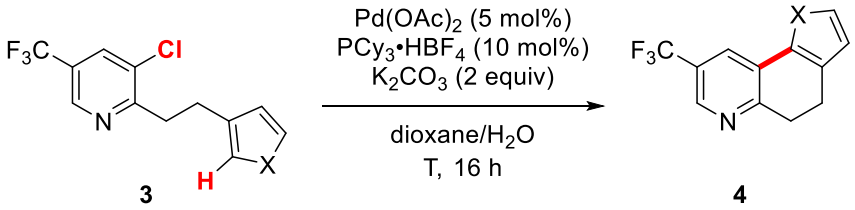


dppbenz



Scheme S1 Experiments showing the incompatibility of 3-bromo-2-vinylpyridine for the Rh(I)-catalyzed hydroarylation reaction.

Table S2 Temperature dependence of the Pd-catalyzed C–H arylation.



3 **4**

T =	150 °C	130 °C	100 °C	
Yield [%][a]	100 (98)	100	0	X = S
	100	0	0	X = CH=CH

Reaction conditions: **3** (1 equiv), [Pd] (4 mol%), $PCy_3 \cdot HBF_4$ (10 mol%) and K_2CO_3 (2 equiv) in dioxane/water (10:1) under nitrogen, stirred at the given temperature. [a]Yields determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. Yields in parentheses are of isolated material.

2) Decomposition study

A decomposition study was conducted by ^{1}H NMR to investigate the stability of thiophen-3-ylboronic acid under the reaction conditions of the hydroarylation reaction. Thiophen-3-ylboronic acid (38.4 mg, 0.3 mmol), $[Rh(cod)Cl]_2$ (3.9 mg, 8 µmol), K_2CO_3 (82.9 mg, 0.6 mmol) and 1,3,5-trimethoxybenzene (2.6 mg, 15 µmol) as internal standard were added to pressurizable flask. The flask was purged with nitrogen. 1,4-dioxane (2 mL) and dem. H_2O (0.2 mL) were added and the mixture was stirred at room temperature. At the indicated times an aliquot (~30 µL) were taken from the mixture via pipette, flushed through a short pad of celite with EtOAc, concentrated under vacuum and submitted to the NMR in $CDCl_3$.

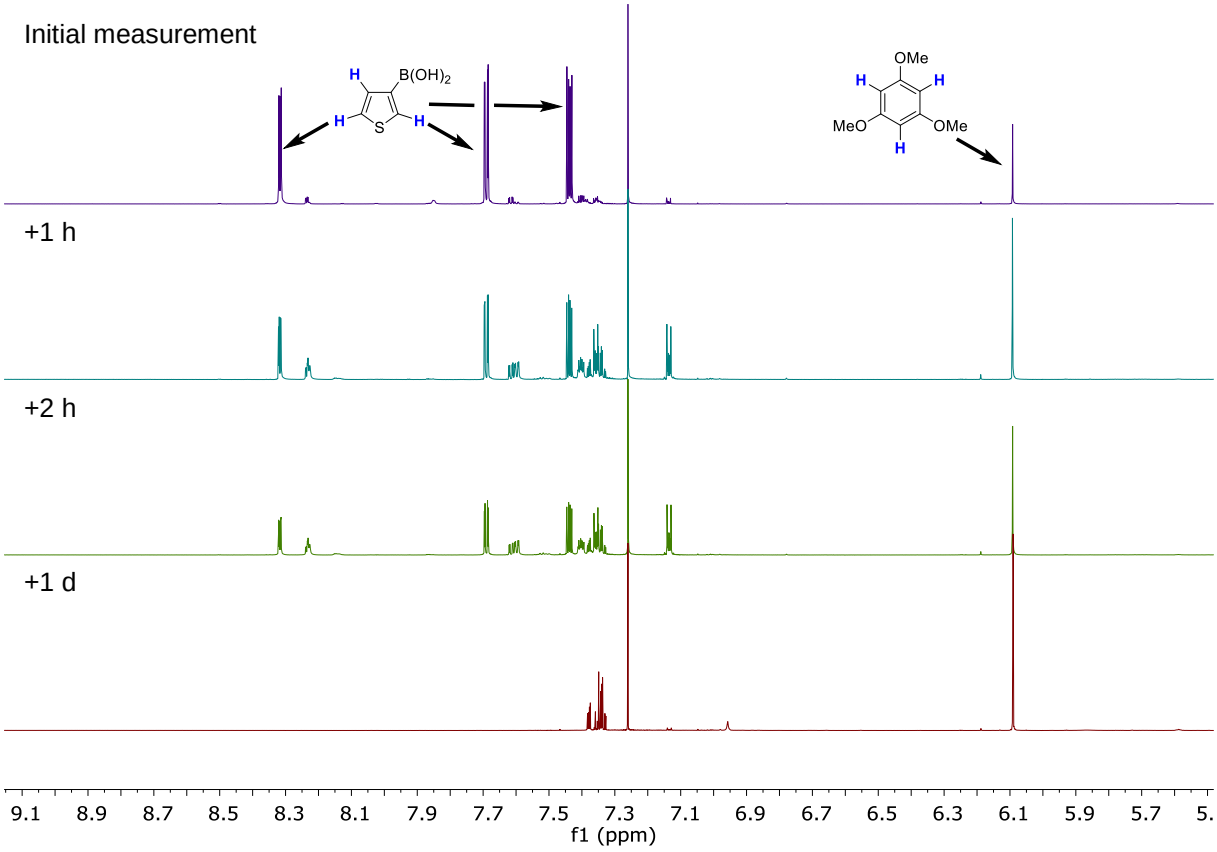


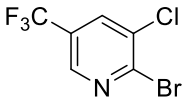
Figure S1 ^{1}H NMR decomposition study of thiophen-3-ylboronic acid under the hydroarylation conditions.

Table S3 ^{1}H NMR yields of the remaining boronic acid in the decomposition study.

Measurement	initial	+1 h	+2 h	+1 d
Boronic acid remaining	82%	23%	15%	0%

3) Substrate preparation

2-bromo-3-chloro-5-(trifluoromethyl)pyridine (I)

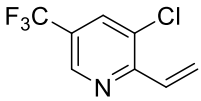


2,3-dichloro-5-(trifluoromethyl)pyridine (10.80 g, 50.0 mmol) was added to a flame dried 150 mL Schlenk tube. 70 mL of dry acetonitrile were added, followed by slow addition of trimethylsilylbromide (15.31 g, 100.0 mmol, 2.0 eq). The solution was heated to 100 °C for 16 h. The reaction mixture was cooled to room temperature and poured into 2M NaOH (60 mL) to which ice had been added. The aqueous layer was extracted with Et_2O (3 x 50 mL), the combined organic layers were washed with H_2O (2 x 50 mL) and brine (50 mL), dried ($MgSO_4$) and the solvent was removed under reduced pressure. Purification by column chromatography on silica (pentane/Et_2O = 20/1) afforded 2-bromo-3-chloro-5-(trifluoromethyl)pyridine **I** as a colorless oil (12.46 g, 47.9 mmol, 96%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ/ppm = 8.55 (s, 1H), 7.96 (s, 1H);

^{19}F-NMR (377 MHz, $CDCl_3$): δ/ppm = -62.3.

3-chloro-5-(trifluoromethyl)-2-vinylpyridine (1a)



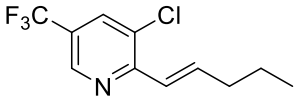
Potassium trifluorovinylborate (2.95 g, 22.0 mmol, 1.1 equiv.), $Pd(PPh_3)_4$ (1.16 g, 1.0 mmol, 5 mol %) and K_2CO_3 (11.06 g, 80.0 mmol, 4.0 equiv.) were added to a 250 mL Schlenk flask. The flask was evacuated and backfilled with argon thrice before 120 mL of 1,2-dimethoxyethane and 60 mL of dem. H_2O followed by 2-bromo-3-chloro-5-(trifluoromethyl)pyridine **I** (5.21 g, 20.0 mmol) were added. The flask was sealed and the reaction mixture was stirred at 80 °C for 16 h. After cooling to amboient temperature H_2O (90 mL) was added and the aqueous phase was extracted with Et_2O (3 x 90 mL). The combined organic phases were washed with H_2O (90 mL) and brine (90 mL) consecutively and dried over $MgSO_4$. The resulting solution was carefully concentrated under reduced pressure (CAUTION: PRODUCT VOLATILE !). Purification by column chromatography on silica (pentane/Et_2O = 250/1) afforded 3-chloro-5-(trifluoromethyl)-2-vinylpyridine **1a** as a light yellow oil which turns brown over time and needs to be stored at -20 °C (2.35 g, 11.3 mmol, 57%).

^{1}H-NMR (400 MHz, CDCl3): δ/ppm = 8.72 (d, J = 0.8 Hz, 1H), 7.89 (d, J = 1.5 Hz, 1H), 7.27 (dd, J = 16.6, 11.0 Hz, 1H), 6.62 (dd, J = 17.0, 1.8 Hz, 1H), 5.74 (dd, J = 10.7, 1.8 Hz, 1H);

^{13}C-NMR (101 MHz, CD_2Cl_2): δ/ppm = 155.3 (q, J = 2 Hz), 144.3 (q, J= 4 Hz), 134.7 (q, J = 4 Hz), 130.6 130.0, 126.0 (q, J = 34 Hz), 124.0, 123.0 (q, J = 273 Hz);

^{19}F-NMR (377 MHz, CD_2Cl_2): δ/ppm = -63.7.

(*E*)-3-chloro-2-(pent-1-en-1-yl)-5-(trifluoromethyl)pyridine (1h)



(*E*)-pent-1-en-1-ylboronic acid (1.71 g, 15.0 mmol, 1.5 equiv.), $PdCl_2$(dppf) (366 mg, 0.5 mmol, 5 mol%) and Na_2CO_3 (3.50 g, 33.0 mmol, 3.3 equiv.) were added to a 250 mL Schlenk flask. The flask was evacuated and backfilled with argon thrice before 100 mL of 1,4-dioxane and 16.7 mL of dem. H_2O followed by 2,3-dichloro-5-(trifluoromethyl)pyridine (2.16 g, 10.0 mmol) were added. The flask was sealed and the reaction mixture was stirred at 80 °C for 16 h. After cooling to amboient temperature the layers were separated and the aqueous phase was extracted with EtOAc (3 x 20 mL). The combined organic phases were washed with H_2O (90 mL) and dried over $MgSO_4$. The resulting solution was concentrated under reduced pressure. Purification by column chromatography on silica (pentane/DCM = 96/4) afforded (*E*)-3-chloro-2-(pent-1-en-1-yl)-5-(trifluoromethyl)pyridine **1h** as a colorless oil (2.25 g, 9.0 mmol, 90%).

^{1}H-NMR (400 MHz, CDCl3): δ/ppm = 8.65 (d, *J* = 2.6 Hz, 1H), 7.85 (d, *J* = 2.1 Hz, 1H), 7.17 (dt, *J* = 15.3, 7.1 Hz, 1H), 6.93 (dt, *J* = 15.1, 1.6 Hz, 1H), 2.32 (qd, *J* = 7.2, 1.5 Hz, 2H), 1.57 (h, *J* = 7.4 Hz, 2H), 0.99 (t, *J* = 7.4 Hz, 3H);

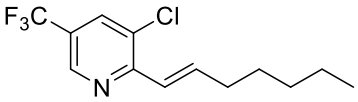
^{13}C-NMR (101 MHz, CD_2Cl_2): δ/ppm = 155.9 (d, *J* = 2 Hz), 144.1 (q, *J* = 4. Hz), 142.9, 134.5 (q, *J* = 4 Hz), 129.1, 125.2 (q, *J* = 34 Hz), 124.0, 123.0 (q, *J* = 272 Hz), 35.3, 22.1, 14.0;

^{19}F-NMR (377 MHz, CD_2Cl_2): δ/ppm = -62.2.

ESI-MS: calculated $[C_{11}H_{11}ClF_3NH]^+$: 250.0605, found: 250.0615;

ATR-FTIR (cm^{-1}): 2963, 1651, 1597, 1458, 1397, 1319, 1281, 1157, 1134, 1088, 1049, 972, 910, 872, 718, 571, 556.

(*E*)-3-chloro-2-(hept-1-en-1-yl)-5-(trifluoromethyl)pyridine (1g)



A non flame-dried round bottom flask was charged with 2-bromo-3-chloro-5-(trifluoromethyl)pyridine **I** (500 mg, 1.92 mmol), (1*E*)-8hept-1-en-1-yl)boronic acid (409 mg, 2.88 mmol, 1.5 equiv.), $Pd(PPh_3)_4$ (111 mg, 0.10 mmol, 5 mol%), and K_2CO_3 (795 mg, 5.76 mmol, 3 equiv.). The reagents were dissolved in a mixture of dimethoxyethane/dem. H_2O (10 mL/5 mL), the flask was equipped with reflux condenser (purged with argon) and heated to 100 °C for 18 h. After cooling to r.t. the reaction was quenched with dem. H_2O and the product extracted with diethyl ether (3 x 30 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and the solvent was removed *in vacuo.* Purification by column chromatography on silica (petroleum ether/Et_2O = 100/1) afforded (*E*)-3-chloro-2-(hept-1-en-1-yl)-5-(trifluoromethyl)pyridine **1g** as a colorless oil (490 mg, 1.77 mmol, 92%). The product was stored at – 20 °C.

R_f (petroleum ether/EtOAc = 50:1): 0.52;

^{1}H-NMR (500 MHz, $CDCl_3$): δ/ppm = 8.65 (s, 1H), 7.85 (s, 1H), 7.21 – 7.25 (m, 1H), 6.94 – 6.91 (m, 1H), 2.36 – 2.32 (m, 2H), 1.58 – 1.52 (m, 2H), 1.37 – 1.34 (m, 4H), 0.92 – 0.90 (m, 3H);

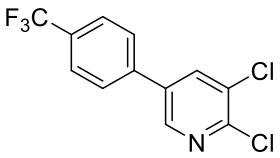
^{13}C-NMR (126 MHz, $CDCl_3$): δ/ppm = 160.0 (d, *J* = 1.1 Hz), 144.1 (q, *J* = 4.1 Hz), 143.2, 134.5 (q, *J* = 3.7 Hz), 129.1, 125.2 (q, *J* = 33.5 Hz), 123.9, 123.1 (q, *J* = 272.4 Hz), 33.3, 31.6, 28.6, 22.7, 15.2;

^{19}F-NMR (377 MHz, $CDCl_3$): δ/ppm = -62.2;

ESI-MS: calculated $[C_{13}H_{15}ClF_3NH]^+$: 278.0918, found: 278.0920;

ATR-FTIR (cm^{-1}): 2959, 2929, 2859, 1600, 1393, 1316, 1280, 1159, 1132, 1089, 1052, 921, 645.

2,3-dichloro-5-(4-(trifluoromethyl)phenyl)pyridine (II)



A non flame-dried round bottom flask was charged with 5-bromo-2,3-dichloropyridine (1.00 g, 4.41 mmol), 4-(trifluoromethyl)phenylboronic acid (1.00 g, 5.29 mmol, 1.2 equiv.), $Pd(PPh_3)_4$ (254.8 mg, 0.22 mmol, 5 mol%), and K_2CO_3 (1.22 g, 8.82 mmol, 2.0 equiv.). The flask was purged with argon to which a mixture of DME/H_2O (25 mL/12.5 mL) was added. A reflux condenser equipped the flask and the reaction mixture was heated to 100 °C for 15 h. After cooling to room temperature, the reaction was quenched with additional water, partitioned with EtOAc, the organic layer seperated and the aqueous layer extracted with EtOAc (2 x 25 mL). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. Purification by column chromatography on silica (hexane/EtOAc = 40/1) afforded 2,3-dichloro-5-(4-(trifluoromethyl)phenyl)pyridine **II** as a white solid (1.19 g, 4.10 mmol, 93%).

R_f (hexane/EtOAc = 20:1): 0.29;

Melting point: 92 – 93 °C

^{1}H-NMR (500 MHz, $CDCl_3$): δ/ppm = 8.52 (d, *J* = 2.3 Hz, 1H), 7.98 (d, *J* = 2.2 Hz, 1H), 7.78 – 7.73 (m, 2H), 7.68 – 7.65 (m, 2H);

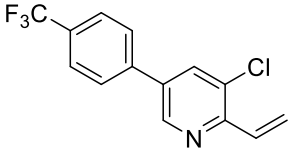
^{13}C-NMR (128 MHz, $CDCl_3$): δ/ppm = 149.0, 145.6, 139.0 (d, *J* = 1.3 Hz), 137.2, 135.8, 131.2 (q, *J* = 32.9 Hz), 131.0, 127.7, 126.5 (q, *J* = 3.8 Hz), 124.0 (q, *J* = 272.3 Hz);

^{19}F-NMR (377 MHz, $CDCl_3$): δ/ppm = -62.7;

ESI-MS: calculated $[C_{12}H_6F_3NCl_2H]^+$: 291.9908, found: 291.9915;

ATR-FTIR (cm^{-1}): 2460, 2197, 2079, 1617, 1582, 1434, 1415, 1370, 1317, 1280, 1229, 1164, 1109, 1070, 1044, 1034, 1012, 905, 843, 834, 720, 666.

3-chloro-5-(4-(trifluoromethyl)phenyl)-2-vinylpyridine (1f)



A flame-dried round bottom flask was charged with 2,3-dichloro-5-(4-(trifluoromethyl)phenyl)pyridine **II** (1.08 g, 3.71 mmol), anhydrous LiCl (188.7 mg, 4.45 mmol, 1.2 equiv.), and $Pd(PPh_3)_4$ (214.4 mg, 0.19 mmol, 5 mol%). The flask was purged with argon and dioxane (25 mL) was added, followed by tributylvinyltin (1.30 mL, 4.45 mmol, 1.2 equiv.) dropwise. The flask was equipped with a reflux condenser (purged with argon)

and the reaction mixture was heated to 85 °C for 15 h. After cooling to room temperature, the mixture was filtered through celite, washed with dichloromethane (3 x 25 mL) and the solvent was removed *in vacuo*. Purification by column chromatography on silica (hexane/EtOAc = 40/1) afforded 3-chloro-5-(4-(trifluoromethyl)phenyl)-2-vinylpyridine **1f** as a white solid (798 mg, 2.82 mmol, 76%).

R_f (hexane/EtOAc = 20:1): 0.29;

Melting point: 55 – 56 °C

^{1}H-NMR (500 MHz, $CDCl_3$): δ/ppm = 8.72 (dd, *J* = 2.1, 0.5 Hz, 1H), 7.88 (d, *J* = 2.1 Hz, 1H), 7.78 – 7.72 (m, 2H), 7.71 – 7.67 (m, 2H), 7.33 – 7.24 (m, 1H), 6.55 (dd, *J* = 17.0, 1.9 Hz, 1H), 5.65 (dd, *J* = 10.7, 1.9 Hz, 1H);

^{13}C-NMR (126 MHz, $CDCl_3$): δ/ppm = 151.6, 146.0, 139.9 (d, *J* = 1.4 Hz), 135.7, 135.3, 131.2, 130.8 (d, *J* = 32.7 Hz), 130.6, 127.5, 126.5 (q, *J* = 273.2 Hz), 126.3 (q, *J* = 3.8 Hz), 122.0 (d, *J* = 2.4 Hz);

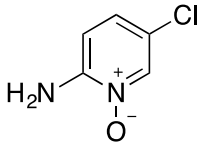
^{19}F-NMR (377 MHz, $CDCl_3$): δ/ppm = -62.7;

ESI-MS: calculated $[C_{14}H_9F_3NClH]^+$: 284.0454, found: 284.0455;

ATR-FTIR (cm^{-1}): 2936, 1888, 1618, 1583, 1457, 1417, 1324, 1305, 1167, 1103, 1073, 1057, 1041, 1022, 1015, 988, 938, 909, 864, 842, 836, 787, 776, 716.

2-amino-5-chloropyridine-1-oxide (II)

A round bottom flask was charged with 5-chloropyridin-2-amine (1 g, 7.78 mmol) and



dissolved in dichloromethane (20 mL). The mixture was cooled to 0 ºC to which *m*-CPBA (2.87 g, 11.67 mmol, 70%, 1.5 equiv.) was added portionwise over a period of 10 min. The reaction mixture was allowed to warm to r.t. overnight. The reaction was quenched with saturated $NaHCO_3$ and the product extracted with dichloromethane (3 x 30 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and the solvent was removed *in vacuo.* Purification by column chromatography on silica (dichloromethane/methanol = 10/1) afforded 2-amino-5-chloropyridne-1-oxide **II** as a light brown solid (840 mg, 5.84 mmol, 75%).

R_f (dichloromethane/methanol = 1:1): 0.40;

Melting point: 170 – 175 °C

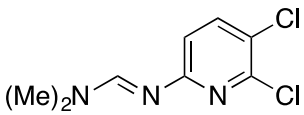
^{1}H-NMR (500 MHz, $CDCl_3$): δ/ppm = 8.17 (d, *J* = 2.1 Hz, 1H), 7.13 (dd, *J* = 8.9, 2.2 Hz, 1H), 6.71 (d, *J* = 8.9 Hz, 1H), 5.65 (s, 2H);

^{13}C-NMR (126 MHz, $CDCl_3$): δ/ppm = 149.1, 136.9, 128.6, 120.0, 109.4;

ESI-MS: calculated $[C_5H_5ClN_2H]^+$: 145.0163, found: 145.0160;

ATR-FTIR (cm^{-1}): 3362, 3249, 3188, 3136, 3071, 1638, 1565, 1505, 1345, 1212, 1090, 911, 841, 812, 671.

(*E*)-*N*'-(5,6-dichloropyridin-2-yl)-*N,N*-dimethylformimidamide (III)



A round bottom flask was charged with 2-amino-5-chloropyridne-1-oxide **II** (680 mg, 4.70 mmol) and $POCl_3$ (5 mL). The mixture was cooled to 0 ºC to which DMF (1.5 mL) was added dropwise over a period of 10 min. The reaction mixture was heated to 80 ºC for 2 h. The reaction was again cooled to 0 ºC and carefully quenched with 5% aq. solution NaOH. The product was extracted with ethyl acetate (3 x 20 mL) and the combined organic layers were dried over anhydrous $MgSO_4$ after which the solvent was removed *in vacuo.* Purification by column chromatography on silica (petroleum ether/ethyl acetate = 5/3 (with 1% Et_3N)) afforded (*E*)-*N*'-(5,6-dichloropyridin-2-yl)-*N,N*-dimethylformimidamide **III** as a yellow oil (673 mg, 3.10 mmol, 66%).

R_f (petroleum ether/EtOAc = 1:1): 0.38;

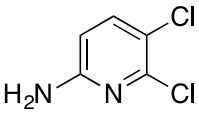
^{1}H-NMR (500 MHz, $CDCl_3$): δ/ppm = 8.42 (s, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 3.11 (s, 3H), 3.07 (s, 3H);

^{13}C-NMR (126 MHz, $CDCl_3$): δ/ppm = 160.5, 156.3, 146.5, 140.0, 122.1, 117.7, 41.1, 35.0;

ESI-MS: calculated $[C_8H_9Cl_2N_3H]^+$: 218.0246, found: 218.0249;

ATR-FTIR (cm^{-1}): 2909, 2811, 1625, 1565, 1432, 1398, 1337, 1228, 1107, 1018, 824, 634.

5,6-dichloropyridin-2-amine (IV)



A round bottom flask was charged with (*E*)-*N*'-(5,6-dichloropyridin-2-yl)-*N,N*-dimethylformimidamide **III** (1.20 g, 5.53 mmol) and dissolved in a mixture of methanol (10 mL) and 5M KOH (10 mL). The mixture was stirred overnight. The reaction was quenched with dem. H_2O and the product extracted with ethyl acetate (3 x 30 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and the solvent was removed *in vacuo.* Purification by column chromatography on silica (petroleum ether/ethyl acetate = 3/1) afforded 5,6-dichloropyridin-2-amine **IV** as a white solid (726 mg, 4.48 mmol, 81%).

R_f (petroleum ether/EtOAc = 5:3): 0.42

Melting point: 141 – 142 °C

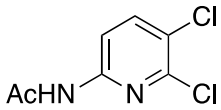
^{1}H-NMR (500 MHz, $CDCl_3$): δ/ppm = 7.45 (d, *J* = 8.5 Hz, 1H), 6.37 (d, *J* = 8.5 Hz, 1H), 4.59 (s, 2H);

^{13}C-NMR (126 MHz, $CDCl_3$): δ/ppm = 156.5, 146.7, 140.2, 118.1, 108.1;

ESI-MS: calculated $[C_5H_4Cl_2N_2H]^+$: 162.9824, found: 162.9823;

ATR-FTIR (cm^{-1}): 3346, 3190, 1636, 1589, 1548, 1452, 1406, 1316, 1277, 1024, 820, 686;

***N*-(5,6-dichloropyridin-2-yl)acetamide (V)**



A round bottom flask was charged with (5,6-dichloropyridin-2-amine **IV** (500 mg, 3.09 mmol) and pyridine (2 mL). The mixture was cooled to 0 ºC to which acetic anhydride (320 μL, 3.40 mmol, 1.1 equiv.) was added dropwise in a period of 10 min. The mixture was stirred overnight and then with dem. H_2O and the product extracted with ethyl acetate (3 x 30 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and the solvent was removed *in vacuo.* Purification by column chromatography on silica (petroleum ether/ethyl acetate = 3/1) afforded *N*-(5,6-dichloropyridin-2-yl)acetamide **V** as a white solid (580 mg, 2.84 mmol, 92%).

R_f (petroleum ether/EtOAc = 5:3): 0.45;

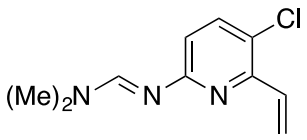
^{1}H-NMR (500 MHz, $CDCl_3$): δ/ppm = 8.12 (d, *J* = 8.6 Hz, 1H), 7.94 (s, 1H), 7.74 (d, *J* = 8.6 Hz, 1H), 2.20 (s, 3H);

^{13}C-NMR (126 MHz, $CDCl_3$): δ/ppm = 168.7, 149.1, 146.5, 141.0, 124.7, 113.3, 24.8;

ESI-MS: calculated $[C_7H_6Cl_2N_2OH]^+$: 204.9930, found: 204.9933;

ATR-FTIR (cm^{-1}): 3226, 3144, 3080, 3033, 1661, 1574, 1536, 1423, 1379, 1350, 1259, 1030, 885, 830, 795.

(*E*)-*N*'-(5-chloro-6-vinylpyridin-2-yl)-*N,N*-dimethylformimidamide (1i)



A non flame-dried round bottom flask was charged with (*E*)-*N*'-(5,6-dichloropyridin-2-yl)-*N,N*-dimethylformimidamide **III** (243 mg, 1.16 mmol), anhydrous LiCl (59 mg, 1.39 mmol, 1.2 equiv.), and $Pd(PPh_3)_4$ (67 mg, 0.06 mmol, 5 mol%). The flask was purged with argon and dioxane (6 mL) was added, followed by tributylvinyltin (373 μL, 1.28 mmol, 1.1 equiv.) dropwise. The flask was equipped with a reflux condenser (purged with argon) and the reaction mixture was heated to 100 °C for 16 h. After cooling to room temperature, the mixture was filtered through celite, washed with ethyl acetate (3 x 5 mL) and the solvent was removed *in vacuo*. Purification by column chromatography on silica (petroleum ether/ethyl acetate = 5/3 (with 1% Et_3N)) afforded (*E*)-*N*'-(5-chloro-6-vinylpyridin-2-yl)-*N,N*-dimethylformimidamide **1i** as yellow oil (167 mg, 0.80 mmol, 69%). The product was stored at – 20 °C.

R_f (petroleum ether/EtOAc = 3:1): 0.32;

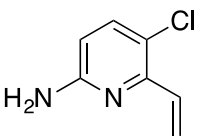
^{1}H-NMR (500 MHz, $CDCl_3$): δ/ppm = 8.49 (s, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.18 (dd, *J* = 17.0, 10.6 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 6.44 (dd, *J* = 17.0, 2.3 Hz, 1H), 5.49 (dd, *J* = 10.6, 2.3 Hz, 1H), 3.10 (s, 3H), 3.08 (s, 3H);

^{13}C-NMR (126 MHz, $CDCl_3$): δ/ppm = 159.9, 155.9, 149.3, 139.0, 132.2, 123.8, 119.9, 118.7, 41.0, 34.9;

ESI-MS: calculated $[C_{10}H_{12}ClN_3H]^+$: 210.0793, found: 210.0795;

ATR-FTIR (cm^{-1}): 2921, 2808, 1693, 1617, 1556, 1437, 1412, 1373, 1234, 1101, 982, 930, 828.

5-chloro-6-vinylpyridin-2-amine (1j)



A non flame-dried round bottom flask was charged with (*E*)- 5,6-dichloropyridin-2-amine **IV** (250 mg, 1.54 mmol), anhydrous LiCl (78 mg, 1.85 mmol, 1.2 equiv.), and $Pd(PPh_3)_4$ (89 mg, 0.08 mmol, 5 mol%). The flask was purged with argon and dioxane (6 mL) was added, followed by tributylvinyltin (496 µL, 1.70 mmol, 1.1 equiv.) dropwise. The flask was equipped with a reflux condenser (purged with argon) and the reaction mixture was heated to 100 °C for 16 h. After cooling to room temperature, the mixture was filtered through celite, washed with ethyl acetate (3 x 5 mL) and the solvent was removed *in vacuo*. Purification by column chromatography on silica (petroleum ether/ethyl acetate = 3/1) afforded (**5-**chloro-6-vinylpyridin-2-amine **1j** as yellow oil (154 mg, 1.00 mmol, 65%). The product was stored at – 20 °C.

R_f (petroleum ether/EtOAc = 5:3): 0.41;

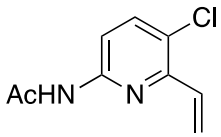
^{1}H-NMR (500 MHz, $CDCl_3$): δ/ppm = 7.36 (d, *J* =8.5 Hz, 1H), 7.12 (dd, *J* = 17.0, 10.7 Hz, 1H), 6.40 – 6.29 (m, 2H), 5.49 (dd, *J* = 10.6, 2.2 Hz, 1H), 4.44 (s, 2H);

^{13}C-NMR (126 MHz, $CDCl_3$): δ/ppm = 156.3, 149.6, 139.1, 131.8, 120.2, 119.8, 109.6;

ESI-MS: calculated $[C_7H_7ClN_2H]^+$: 155.0371, found: 155.0371;

ATR-FTIR (cm^{-1}): 3481, 333, 3196, 2957, 2925, 1609, 1579, 1561, 1452, 1388, 815.

N-(5-chloro-6-vinylpyridin-2-yl)acetamide (1k)



A non flame-dried round bottom flask was charged with *N*-(5,6-dichloropyridin-2-yl)acetamide **V** (130 mg, 0.64 mmol), anhydrous LiCl (33 mg, 0.77 mmol, 1.2 equiv.), and $Pd(PPh_3)_4$ (37 mg, 0.03 mmol, 5 mol%). The flask was purged with argon and dioxane (3 mL) was added, followed by tributylvinyltin (205 µL, 0.70 mmol, 1.1 equiv.) dropwise. The flask was equipped with a reflux condenser (purged with argon) and the reaction mixture was heated to 100 °C for 16 h. After cooling to room temperature, the mixture was filtered through celite, washed with ethyl acetate (3 x 5 mL) and the solvent was removed *in vacuo*. Purification by column chromatography on silica (petroleum ether/ethyl acetate = 3/1) afforded *N*-(5-chloro-6-vinylpyridin-2-yl)acetamide **1k** as white solid (74 mg, 0.38 mmol, 59%). The product was stored at – 20 °C.

R_f (petroleum ether/EtOAc = 5:3): 0.40;

Melting point: 136 – 140 °C

^{1}H-NMR (500 MHz, $CDCl_3$): δ/ppm = 8.13 (s, 1H), 8.06 (d, *J* = 8.8 Hz, 1H), 7.63 (d, *J* = 8.8 Hz, 1H), 7.16 (dd, *J* = 17.0, 10.7 Hz, 1H), 6.33 (dd, *J* = 17.0, 2.0 Hz, 1H), 5.54 (dd, *J* = 10.7, 2.0 Hz, 1H) 2.18 (s, 3H);

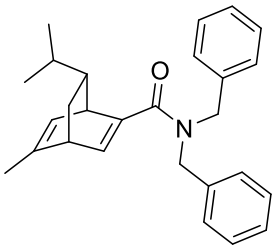
^{13}C-NMR (126 MHz, $CDCl_3$): δ/ppm = 168.8, 150.0, 149.3, 139.7, 131.2, 125.0, 121.1, 114.1, 21.8;

ESI-MS: calculated $[C_9H_9ClN_2H]^+$: 197.0476, found: 197.0478;

ATR-FTIR (cm^{-1}): 3243, 3138, 1658, 1578, 1530, 1433, 1371, 1296, 1011, 923, 825.

4) Ligand preparation

(1*R*,4*R*,7*R*)-*N*,*N*-dibenzyl-7-isopropyl-5-methylbicyclo[2.2.2]octa-2,5-diene-2-carboxamide (L*)



L* was prepared following the literature procedure[1]. (1*R*,4*R*,7*R*)-7-isopropyl-5-methylbicyclo[2.2.2]octa-2,5-diene-2-carboxylic acid (103.1 mg, 0.5 mmol) and dry *N*,*N*-dimethylformamide (9 µL, 0.12 mmol, 0.23 equiv.) were dissolved in 1 mL dry dichloromethane. The resulting solution was cooled to 0 °C and oxalyl dichloride (47 µL, 0.55 mmol, 1.1 equiv.) was added dropwise over a period of two minutes. The reaction mixture was stirred for 1.5 h at 0 °C and transferred dropwise to a second flask containing a mixture of dibenzylamine (88 µL, 0.46 mmol, 0.91 equiv.) in 1 mL dichloromethane and 1 mL sat. aq. Na_2CO_3 at 0 °C. The resulting biphasic reaction mixture was stirred for 21 h at room temperature. 10 mL of sat. aq. $NaHCO_3$ and 10 mL dichloromethane were added and the layers were separated. The aqueous phase was extracted thrice with dichloromethane (3x10 mL).The organic phases were combined, washed with aq. HCl (10 wt% in H_2O) and dried ($MgSO_4$). Purification by column chromatography on silica (pentane/EtOAc = 97/3) afforded (1*R*,4*R*,7*R*)-*N*,*N*-dibenzyl-7-isopropyl-5-methylbicyclo[2.2.2]octa-2,5-diene-2-carboxamide **L*** as a colorless oil (145 mg, 0.38 mmol, 83%).

^{1}H-NMR (300 MHz, $CDCl_3$): δ/ppm = 7.38 – 7.27 (m, 6H), 7.23 – 7.11 (m, 4H), 6.49 (dd, *J* = 6.1, 1.8 Hz, 1H), 5.76 (dt, *J* = 5.9, 1.8 Hz, 1H), 4.79 – 4.24 (m, 4H), 3.81 (dt, *J* = 5.9, 2.0 Hz, 1H), 3.26 (dt, *J* = 7.0, 2.4 Hz, 1H), 1.78 (d, *J* = 1.7 Hz, 3H), 1.62 (ddd, *J* = 11.5, 8.9, 2.9 Hz, 1H), 1.46 – 1.35 (m, 1H), 1.13 – 0.99 (m, 1H), 0.95 (d, *J* = 6.2 Hz, 3H), 0.91 – 0.87 (m, 1H), 0.80 (d, *J* = 6.3 Hz, 2H);

^{13}C-NMR (75 MHz, $CDCl_3$): δ/ppm = 171.4, 144.6, 144.0, 137.3, 135.2, 128.8, 127.5, 123.7, 48.3, 43.5, 43.0, 34.1, 32.2, 21.9, 21.5, 19.3;

ESI-MS: calculated $[C_{27}H_{31}NOH]^+$: 386.2478, found: 386.2482;

[1] Saxena, A.; Lam, H. W. *Chem. Sci.* **2011**, *2*, 2326-2331

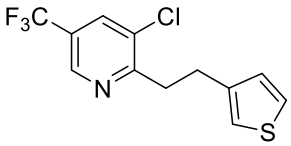
5) Catalysis

General procedure for the Rh(I) catalyzed 1,4-addition of (hetero)arylboronic acids to 2-vinylpyridines

A 50 mL Schlenk flask was equipped with a magnetic stir bar. $[RhCl(C_2H_4)_2]_2$ (15.6 mg, 0.04 mmol, 4 mol %), dppbenz (35.7 mg, 0.08 mmol, 8 mol %) and the corresponding boronic acid (1.5 mmol, 1.5 equiv.) were added and the flask was evacuated and backfilled with argon thrice. 5.0 mL of 1,4-dioxane and 0.5 mL of dem. H_20 were added and the resulting suspension was stirred for 15 min at room temperature. A solution of the corresponding 2-vinylpyridine (1.0 mmol) in 5.0 mL of 1,4-dioxane and a solution of K_2CO_3 (414.6 mg, 3.0 mmol, 3.0 equiv.) in 0.5 mL of dem. H_2O were prepared in two separate vials and transferred to the prestirred mixture in the Schlenk flask via syringe. The resulting reaction mixture was stirred for 1 h at room temperature. Brine (30 mL) was added and the resulting biphasic system was extracted with EtOAc (3 x 50 mL). The combined organic layers were dried ($MgSO_4$) and the solvent was removed under reduced pressure. The crude material was purified by column chromatography on silica.

6) Product purification and characterization

3-chloro-2-(2-(thiophen-3-yl)ethyl)-5-(trifluoromethyl)pyridine (3aa)



Following the general procedure, a solution of 3-chloro-5-(trifluoromethyl)-2-vinylpyridine **1a** (207.6 mg, 1.0 mmol, 1.0 equiv.) in 5.0 mL 1,4-dioxane and a solution of K_2CO_3 (414.6 mg, 3.0 mmol, 3.0 equiv) in 0.5 mL dem. H_2O were added to a prestirred (15 min, r.t.) mixture of $[RhCl(C_2H_4)_2]_2$ (15.6 mg, 0.04 mmol, 4 mol %), dppbenz (35.7 mg, 0.08 mmol, 8 mol %) and thiophen-3-ylboronic acid (191.9 mg, 1.5 mmol, 1.5 equiv.) in 5.0 mL 1,4-dioxane and 0.5 mL dem. H_2O. The resulting mixture was stirred for 1 h at r.t. Purification by column chromatography on silica (hexane/Et_2O = 100/1) afforded 3-chloro-2-(2-(thiophen-3-yl)ethyl)-5-(trifluoromethyl)pyridine **3aa** as a pale yellow solid (285 mg, 0.98 mmol, 98%).

R_f (hexane/EtOAc = 30:1): 0.35;

^{1}H-NMR (500 MHz, $CDCl_3$): δ/ppm = 8.71 (dd, *J* = 2.0, 0.9 Hz, 1H), 7.88 (dd, *J* = 2.1, 0.7 Hz, 1H), 7.29 – 7.25 (m, 1H), 7.01 – 6.99 (m, 2H), 3.43 (dd, *J* = 9.4, 6.6 Hz, 2H), 3.16 – 3.09 (m, 2H);

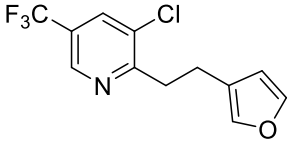
^{13}C-NMR (126 MHz, $CDCl_3$): δ/ppm = 162.5 (d, *J* = 1.9 Hz), 144.0 (q, *J* = 4.0 Hz), 141.3, 133.9 (q, *J* = 3.6 Hz), 131.5, 128.3, 125.8 (q, *J* = 33.4 Hz), 125.7, 123.0 (q, *J* = 272.7 Hz), 120.8, 36.5, 28.3;

^{19}F-NMR (377 MHz, $CDCl_3$): δ/ppm = -62.2;

ESI-MS: calculated $[C_{12}H_9F_3NSClH]^+$: 292.0175, found: 292.0170;

ATR-FTIR (cm^{-1}): 3074, 2930, 2863, 1603, 1395, 1318, 1166, 1129, 1088, 1057, 912, 837, 774, 742.

3-chloro-2-(2-(furan-3-yl)ethyl)-5-(trifluoromethyl)pyridine (3ab)



Following the general procedure, a solution of 3-chloro-5-(trifluoromethyl)-2-vinylpyridine **1a** (207.6 mg, 1.0 mmol, 1.0 equiv.) in 5.0 mL 1,4-dioxane and a solution of K_2CO_3 (414.6 mg, 3.0 mmol, 3.0 equiv) in 0.5 mL dem. H_2O were added to a prestirred (15 min, r.t.) mixture of $[RhCl(C_2H_4)_2]_2$ (15.6 mg, 0.04 mmol, 4 mol %), dppbenz (35.7 mg, 0.08 mmol, 8 mol %) and furan-3-ylboronic acid (168.0 mg, 1.5 mmol, 1.5 equiv.) in 5.0 mL 1,4-dioxane and 0.5 mL dem. H_2O. The resulting mixture was stirred for 1 h at 40 °C. Purification by column chromatography on silica (hexane/Et_2O = 100/1) afforded 3-chloro-2-(2-(furan-3-yl)ethyl)-5-(trifluoromethyl)pyridine **3ab** as a colorless oil (270 mg, 0.98 mmol, 98%).

R_f (hexane/EtOAc = 20:1): 0.51;

^{1}H-NMR (500 MHz, $CDCl_3$): δ/ppm = 8.71 (dd, *J* = 2.0, 0.9 Hz, 1H), 7.92 – 7.84 (m, 1H), 7.36 – 7.35 (m, 1H), 7.26 – 7.25 (m, 1H), 6.30 (ddt, *J* = 1.8, 0.9, 0.4 Hz, 1H), 3.28 – 3.24 (m, 2H), 2.94 – 2.91 (m, 2H);

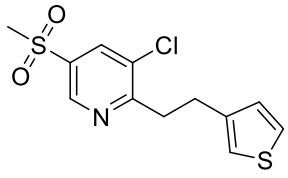
^{13}C-NMR (126 MHz, $CDCl_3$): δ/ppm = 162.5 (d, *J* = 1.4 Hz), 144.0 (q, *J* = 4.0 Hz), 143.0, 139.3, 133.9 (q, *J* = 3.6 Hz), 131.5, 125.8 (q, *J* = 33.5), 123.9, 123.0 (q, *J* = 272.6 Hz), 36.0, 23.0;

^{19}F-NMR (377 MHz, $CDCl_3$): δ/ppm = -62.2;

ESI-MS: calculated $[C_{12}H_9F_3NOClH]^+$: 276.0403, found: 276.0403;

ATR-FTIR (cm^{-1}): 2930, 2865, 1603, 1502, 1396, 1321, 1161, 1134, 1090, 1059, 1025, 915, 874, 782.

3-chloro-2-(2-(thiophen-3-yl)ethyl)-5-(methylsulfonyl)pyridine (3ba)



Following the general procedure, a solution of 3-chloro-5-(methylsulfonyl)-2-vinylpyridine **1c** (217.0 mg, 1.0 mmol, 1.0 equiv.) in 5.0 mL 1,4-dioxane and a solution of K_2CO_3 (414.6 mg, 3.0 mmol, 3.0 equiv) in 0.5 mL dem. H_2O were added to a prestirred (15 min, r.t.) mixture of $[RhCl(C_2H_4)_2]_2$ (15.6 mg, 0.04 mmol, 4 mol %), dppbenz (35.7 mg, 0.08 mmol, 8 mol %) and thiophen-3-ylboronic acid (191.9 mg, 1.5 mmol, 1.5 equiv.) in 5.0 mL 1,4-dioxane and 0.5 mL dem. H_2O. The resulting mixture was stirred for 1 h at r.t. Purification by column chromatography on silica (hexane/EtOAc = 5/1) afforded 3-chloro-2-(2-(thiophen-3-yl)ethyl)-5-(methylsulfonyl)pyridine **3ba** as a white solid (259 mg, 0.86 mmol, 86%).

R_f (hexane/EtOAc = 5:3): 0.50;

Melting point: 99 – 100 °C

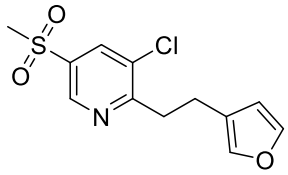
^{1}H-NMR (500 MHz, $CDCl_3$): δ/ppm = 8.95 (d, *J* = 2.1 Hz, 1H), 8.16 (d, *J* = 2.1 Hz, 1H), 7.27 – 7.26 (m, 1H), 7.01 – 6.97 (m, 2H), 3.38 – 3.33 (m, 2H), 3.16 – 3.11 (m, 5H);

^{13}C-NMR (126 MHz, $CDCl_3$): δ/ppm = 164.4, 145.8, 141.0, 135.7 (2C), 131.9, 128.2, 125.8, 120.9, 45.1, 36.7, 28.1;

ESI-MS: calculated $[C_{12}H_{12}NO_2S_2ClH]^+$: 302.0076, found: 302.0081;

ATR-FTIR (cm^{-1}): 3064, 3002, 3013, 2919, 1571, 1541, 1446, 1378, 1309, 1266, 1181, 1151, 1106, 1058, 1041, 970, 793, 770, 747.

3-chloro-2-(2-(furan-3-yl)ethyl)-5-(methylsulfonyl)pyridine (3bb)



Following the general procedure, a solution of 3-chloro-5-(methylsulfonyl)-2-vinylpyridine **1c** (217.0 mg, 1.0 mmol, 1.0 equiv.) in 5.0 mL 1,4-dioxane and a solution of K_2CO_3 (414.6 mg, 3.0 mmol, 3.0 equiv) in 0.5 mL dem. H_2O were added to a prestirred (15 min, r.t.) mixture of $[RhCl(C_2H_4)_2]_2$ (15.6 mg, 0.04 mmol, 4 mol %), dppbenz (35.7 mg, 0.08 mmol, 8 mol %) and furan-3-ylboronic acid (168.0 mg, 1.5 mmol, 1.5 equiv.) in 5.0 mL 1,4-dioxane and 0.5 mL dem. H_2O. The resulting mixture was stirred for 1 h at 40 °C Purification by column chromatography on silica (hexane/EtOAc = 3/1) afforded 3-chloro-2-(2-(furan-3-yl)ethyl)-5-(methylsulfonyl)pyridine **3bb** as a white solid (245 mg, 0.86 mmol, 86%).

R_f (hexane/EtOAc = 1:1): 0.42;

Melting point: 88 – 89 °C

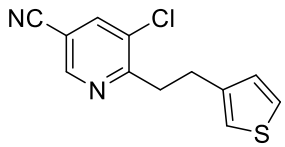
^{1}H-NMR (500 MHz, $CDCl_3$): δ/ppm = 8.95 (d, *J* = 2.1 Hz, 1H), 8.16 (d, *J* = 2.1 Hz, 1H), 7.36 – 7.35 (m, 1H), 7.27 – 7.24 (m, 1H), 6.30 (ddt, *J* = 1.8, 0.8, 0.4 Hz, 1Hz), 3.32 – 3.26 (m, 2H), 3.12 (s, 3H), 2.96 – 2.91 (m, 2H);

^{13}C-NMR (126 MHz, $CDCl_3$): δ/ppm = 164.3, 145.8, 143.1, 139.3, 135.7 (2C), 131.9, 123.7, 111.0, 45.1, 36.1, 22.9;

ESI-MS: calculated $[C_{12}H_{12}NO_3SClH]^+$: 286.0305, found: 286.0296;

ATR-FTIR (cm^{-1}): 3138, 3061, 3002, 2921, 1572, 1311, 1297, 1178, 1152, 1107, 1063, 1042, 1024, 968, 960, 874, 800, 756, 734.

3-chloro-2-(2-(thiophen-3-yl)ethyl)-5-cyanopyridine (3ca)



Following the general procedure, a solution of 3-chloro-5-cyano-2-vinylpyridine **1b** (164.0 mg, 1.0 mmol, 1.0 equiv.) in 5.0 mL 1,4-dioxane and a solution of K_2CO_3 (414.6 mg, 3.0 mmol, 3.0 equiv) in 0.5 mL dem. H_2O were added to a prestirred (15 min, r.t.) mixture of $[RhCl(C_2H_4)_2]_2$ (15.6 mg, 0.04 mmol, 4 mol %), dppbenz (35.7 mg, 0.08 mmol, 8 mol %) and thiophen-3-ylboronic acid (191.9 mg, 1.5 mmol, 1.5 equiv.) in 5.0 mL 1,4-dioxane and 0.5 mL dem. H_2O. The resulting mixture was stirred for 1 h at 40 °C. Purification by column chromatography on silica (hexane/Et_2O = 20/1) afforded 3-

chloro-2-(2-(thiophen-3-yl)ethyl)-5-cyanopyridine **3ca** as a white solid (240 mg, 0.97 mmol, 97%).

R_f (hexane/EtOAc = 20:1): 0.24;

Melting point: 77 – 78 °C

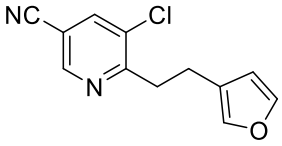
^{1}H-NMR (500 MHz, $CDCl_3$): δ/ppm = 8.71 (d, *J* = 1.9 Hz, 1H), 7.90 (d, *J* = 1.9 Hz, 1H), 7.33 – 7.20 (m, 1H), 6.99 – 6.96 (m, 2H), 3.36 – 3.29 (m, 2H), 3.15 – 3.09 (m, 2H);

^{13}C-NMR (126 MHz, $CDCl_3$): δ/ppm = 163.4, 149.7, 141.0, 139.3, 131.7, 128.2, 125.8, 120.9, 115.6, 108.7, 36.7, 28.1;

ESI-MS: calculated $[C_{12}H_9NSClH]^+$: 249.0253, found: 249.0253;

ATR-FTIR (cm^{-1}): 3093, 3078, 2960, 2920, 2231, 1588, 1578, 1451, 1441, 1408, 1386, 1195, 1059, 908, 899, 803, 780, 764.

3-chloro-2-(2-(furan-3-yl)ethyl)-5-cyanopyridine (3cb)



Following the general procedure, a solution of 3-chloro-5-cyano-2-vinylpyridine **1b** (164.0 mg, 1.0 mmol, 1.0 equiv.) in 5.0 mL 1,4-dioxane and a solution of K_2CO_3 (414.6 mg, 3.0 mmol, 3.0 equiv) in 0.5 mL dem. H_2O were added to a prestirred (15 min, r.t.) mixture of $[RhCl(C_2H_4)_2]_2$ (15.6 mg, 0.04 mmol, 4 mol %), dppbenz (35.7 mg, 0.08 mmol, 8 mol %) and furan-3-ylboronic acid (168.0 mg, 1.5 mmol, 1.5 equiv.) in 5.0 mL 1,4-dioxane and 0.5 mL dem. H_2O. The resulting mixture was stirred for 1 h at 60 °C. Purification by column chromatography on silica (hexane/EtOAc = 30/1) afforded 3-chloro-2-(2-(furan-3-yl)ethyl)-5-cyanopyridine **3cb** as a white solid (186 mg, 0.80 mmol, 80%).
R_f (hexane/EtOAc = 10:1): 0.37;

Melting point: 64 – 65 °C

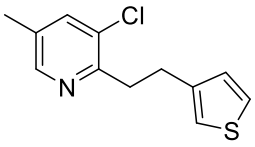
^{1}H-NMR (500 MHz, $CDCl_3$): δ/ppm = 8.71 (d, *J* = 1.9 Hz, 1H), 7.90 (d, *J* = 1.9 Hz, 1H), 7.38 – 7.31 (m, 1H), 7.24 – 7.23 (m, 1H), 6.30 – 6.27 (m, 1H), 3.30 – 3.09 (m, 2H), 2.96 – 2.87 (m, 2H);

^{13}C-NMR (126 MHz, $CDCl_3$): δ/ppm = 163.3, 149.7, 143.1, 139.3 (2C), 131.7, 123.7, 115.6, 111.0, 108.7, 36.2, 22.8;

ESI-MS: calculated $[C_{12}H_9N_2OClH]^+$: 233.0482, found: 233.0480;

ATR-FTIR (cm^{-1}): 3114, 3074, 3062, 2954, 2915, 2237, 1585, 1506, 1458, 1439, 1420, 1377, 1198, 1151, 1062, 1041, 1018, 919, 899, 876, 787, 759.

3-chloro-5-methyl-2-(2-(thiophen-3-yl)ethyl)pyridine (3da)



Following the general procedure, a solution of 3-chloro-5-methyl-2-vinylpyridine **1f** (153.0 mg, 1.0 mmol, 1.0 equiv.) in 5.0 mL 1,4-dioxane and a solution of K_2CO_3 (414.6 mg, 3.0 mmol, 3.0 equiv) in 0.5 mL dem. H_2O were added to a prestirred (15 min, r.t.) mixture of $[RhCl(C_2H_4)_2]_2$ (15.6 mg, 0.04 mmol, 4 mol %), dppbenz (35.7 mg, 0.08 mmol, 8 mol %) and thiophen-3-ylboronic acid (575.7 mg, 3.0 mmol, 3.0 equiv.) in 5.0 mL 1,4-dioxane and 0.5 mL dem. H_2O. The resulting mixture was stirred for 1 h at 60 °C Purification by column chromatography on silica (hexane/EtOAc = 10/1) afforded 3-chloro-5-methyl-2-(2-(thiophen-3-yl)ethyl)pyridine **3da** as a pale yellow oil (178 mg, 0.75 mmol, 75%).
R_f (hexane/EtOAc = 5:1): 0.38;

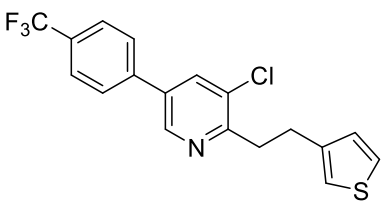
^{1}H-NMR (500 MHz, $CDCl_3$): δ/ppm = 8.27 (dd, *J* = 1.9, 0.8 Hz, 1H), 7.47 (dd, *J* = 1.9 Hz, 1H), 7.26 – 7.23 (m, 1H), 7.01 – 6.98 (m, 2H), 3.24 – 3.19 (m, 2H), 3.09 – 3.04 (m, 2H), 2.30 (s, 3H);

^{13}C-NMR (126 MHz, $CDCl_3$): δ/ppm = 155.2, 147.8, 142.0, 137.4, 132.5, 130.8, 128.4, 125.4, 120.6, 36.0, 28.9, 17.8;

ESI-MS: calculated $[C_{12}H_{12}NSClH]^+$: 238.0457, found: 238.0453;

ATR-FTIR (cm^{-1}): 2923, 2858, 1594, 1547, 1459, 1384, 1058, 907, 881, 837, 772, 683.

3-chloro-2-(2-(thiophen-3-yl)ethyl)-5-(4-(trifluoromethyl)phenyl)pyridine (3ea)



Following the general procedure, a solution of 3-chloro-5-(4-(trifluoromethyl)phenyl)-2-vinylpyridine **1d** (283.0 mg, 1.0 mmol, 1.0 equiv.) in 5.0 mL 1,4-dioxane and a solution of K_2CO_3 (414.6 mg, 3.0 mmol, 3.0 equiv) in 0.5 mL dem. H_2O were added to a prestirred (15 min, r.t.) mixture of $[RhCl(C_2H_4)_2]_2$ (15.6 mg, 0.04 mmol, 4 mol %), dppbenz (35.7 mg, 0.08 mmol, 8 mol %) and thiophen-3-

ylboronic acid (575.7 mg, 3.0 mmol, 3.0 equiv.) in 5.0 mL 1,4-dioxane and 0.5 mL dem. H_2O. The resulting mixture was stirred for 1 h at 60 °C Purification by column chromatography on silica (hexane/EtOAc = 15/1) afforded 3-chloro-2-(2-(thiophen-3-yl)ethyl)-5-(4-(trifluoromethyl)phenyl)pyridine **3ea** as a white solid (331 mg, 0.91 mmol, 91%).

R_f (hexane/EtOAc = 1:1): 0.50;

Melting point: 78 – 79 °C

^{1}H-NMR (500 MHz, $CDCl_3$): δ/ppm = 8.69 (d, *J* = 2.1 Hz, 1H), 7.86 (d, *J* = 2.1 Hz, 1H), 7.77 – 7.73 (m, 2H), 7.71 – 7.65 (m, 2H), 7.27 (ddt, *J* = 4.8, 3.0, 0.4 Hz, 1H), 7.05 – 7.01 (m, 2H), 3.35 – 3.29 (m, 2H), 3.17 – 3.12 (m, 2H);

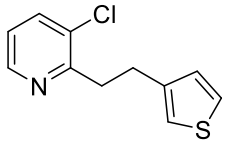
^{13}C-NMR (126 MHz, $CDCl_3$): δ/ppm = 158.0, 145.6, 141.7, 140.0 (d, *J* = 1.4 Hz), 135.3, 134.6, 131.6, 130.7 (q, *J* = 32.7 Hz), 128.4, 127.5, 127.4, 126.3 (q, *J* = 3.8 Hz), 125.6, 125.2, 123.1, 120.7, 36.3, 28.7.

^{19}F-NMR (377 MHz, $CDCl_3$): δ/ppm = -62.6;

ESI-MS: calculated $[C_{18}H_{13}F_3NSClH]^+$: 368.0488, found: 368.0481;

ATR-FTIR (cm^{-1}): 3095, 2934, 2850, 1617, 1457, 1446, 1326, 1285, 1150, 1107, 1071, 1058, 1041, 1015, 836, 774, 750.

3-chloro-2-(2-(thiophen-3-yl)ethyl)pyridine (3fa)



Following the general procedure, a solution of 3-chloro-2-vinylpyridine **1e** (139.0 mg, 1.0 mmol, 1.0 equiv.) in 5.0 mL 1,4-dioxane and a solution of K_2CO_3 (414.6 mg, 3.0 mmol, 3.0 equiv) in 0.5 mL dem. H_2O were added to a prestirred (15 min, r.t.) mixture of $[RhCl(C_2H_4)_2]_2$ (15.6 mg, 0.04 mmol, 4 mol %), dppbenz (35.7 mg, 0.08 mmol, 8 mol %) and thiophen-3-ylboronic acid (575.7 mg, 3.0 mmol, 3.0 equiv.) in 5.0 mL 1,4-dioxane and 0.5 mL dem. H_2O. The resulting mixture was stirred for 1 h at 60 °C Purification by column chromatography on silica (hexane/EtOAc = 10/1) afforded 3-chloro-2-(2-(thiophen-3-yl)ethyl)pyridine **3fa** as a colorless oil (210 mg, 0.94 mmol, 94%).

R_f (hexane/EtOAc = 5:1): 0.42;

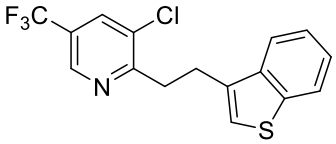
^{1}H-NMR (500 MHz, $CDCl_3$): δ/ppm = 8.46 (dd, *J* = 4.7, 1.5 Hz, 1H), 7.65 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.30 – 7.23 (m, 1H), 7.12 (ddt, *J* = 8.0, 4.7, 0.4 Hz, 1H), 7.04 – 6.99 (m, 2H), 3.30 – 3.26 (m, 2H), 3.13 – 3.08 (m, 2H);

^{13}C-NMR (126 MHz, $CDCl_3$): δ/ppm = 158.4, 147.3, 141.8, 136.9, 131.3, 128.4, 125.4, 122.5, 120.6, 36.5, 28.7;

ESI-MS: calculated $[C_{11}H_{10}NSClH]^+$: 224.0301, found: 224.0300;

ATR-FTIR (cm^{-1}): 3096, 3052, 2927, 2859, 1573, 1447, 1425, 1125, 1067, 1040, 855, 831, 791, 779.

2-(2-(benzo[b]thiophen-3-yl)ethyl)-3-chloro-5-(trifluoromethyl)pyridine (3ac)



Following the general procedure, a solution of 3-chloro-5-(trifluoromethyl)-2-vinylpyridine **1a** (207.6 mg, 1.0 mmol) in 5.0 mL 1,4-dioxane and a solution of K_2CO_3 (414.6 mg, 3.0 mmol, 3.0 equiv) in 0.5 mL dem. H_2O were added to a prestirred (15 min, r.t.) mixture of $[RhCl(C_2H_4)_2]_2$ (15.6 mg, 0.04 mmol, 4 mol %), dppbenz (35.7 mg, 0.08 mmol, 8 mol %) and benzo[b]thiophen-3-ylboronic acid (267.0 mg, 1.5 mmol, 1.5 equiv.) in 5.0 mL 1,4-dioxane and 0.5 mL dem. H_2O. The resulting mixture was stirred for 1 h at r.t. Purification by column chromatography on silica (pentane/EtOAc = 50/1) afforded 2-(2-(benzo[b]thiophen-3-yl)ethyl)-3-chloro-5-(trifluoromethyl)pyridine **3ac** as a colorless solid (318 mg, 0.93 mmol, 93%).

R_f (n-pentane/EtOAc = 100:3): 0.40;

Melting point: 75 – 77 °C

^{1}H-NMR (300 MHz, $CDCl_3$): δ/ppm = 8.74 (dd, *J* = 2.1, 1.0 Hz, 1H), 7.94 – 7.77 (m, 3H), 7.38 (pd, *J* = 7.1, 1.5 Hz, 2H), 7.18 (d, *J* = 1.1 Hz, 1H), 3.50 – 3.40 (m, 2H), 3.38 – 3.28 (m, 2H);

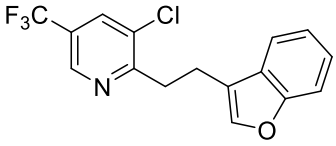
^{13}C-NMR (101 MHz, $CDCl_3$): δ/ppm = 162.5 (d, *J* = 2 Hz), 144.1 (q, *J* = 4 Hz), 140.6, 138.9, 135.5, 134.0 (q, *J* = 4 Hz), 131.5, 125.9 (q, *J* = 34 Hz), 124.4, 124.1, 123.1, 122.9 (q, *J* = 273 Hz), 122.0, 121.7, 35.3, 26.8;

^{19}F-NMR (282 MHz, $CDCl_3$): δ/ppm = -62.2;

ESI-MS: calculated $[C_{16}H_{11}ClF_3NSNa]^+$: 364.0151, found: 364.0152;

ATR-FTIR (cm^{-1}): 1605, 1559, 1397, 1319, 1261, 1161, 1146, 1119, 1092, 1057, 1018, 988, 887, 849, 806, 768, 737, 702.

2-(2-(benzofuran-3-yl)ethyl)-3-chloro-5-(trifluoromethyl)pyridine (3ad)



Following the general procedure, a solution of 3-chloro-5-(trifluoromethyl)-2-vinylpyridine **1a** (207.6 mg, 1.0 mmol) in 5.0 mL 1,4-dioxane and a solution of K_2CO_3 (414.6 mg, 3.0 mmol, 3.0 equiv) in 0.5 mL dem. H_2O were added to a prestirred (15 min, r.t.) mixture of $[RhCl(C_2H_4)_2]_2$ (15.6 mg, 0.04 mmol, 4 mol %), dppbenz (35.7 mg, 0.08 mmol, 8 mol %) and benzofuran-3-ylboronic acid (242.9 mg, 1.5 mmol, 1.5 equiv.) in 5.0 mL 1,4-dioxane and 0.5 mL dem. H_2O. The resulting mixture was stirred for 1 h at r.t. Purification by automated SiO2 gel column chromatography (100 g SiO_2, gradient pentane/EtOAc 2-15%) afforded 2-(2-(benzofuran-3-yl)ethyl)-3-chloro-5-(trifluoromethyl)pyridine **3ad** as a colorless solid (238 mg, 0.73 mmol, 73%).

R_f (n-pentane/EtOAc = 19:1): 0.45;

Melting point: 68 – 70 °C

^{1}H-NMR (300 MHz, $CDCl_3$): δ/ppm = 8.73 (dd, *J* = 2.1, 1.0 Hz, 1H), 7.89 (d, *J* = 2.0 Hz, 1H), 7.71 – 7.54 (m, 1H), 7.52 – 7.44 (m, 2H), 7.28 (dtd, *J* = 16.2, 7.2, 1.4 Hz, 2H), 3.41 (dd, *J* = 9.5, 6.3 Hz, 2H), 3.18 (dd, *J* = 9.7, 5.8 Hz, 2H);

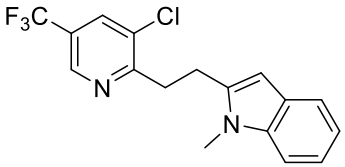
^{13}C-NMR (101 MHz, $CDCl_3$): δ/ppm = 162.4, 155.5, 144.1 (q, *J* = 4 Hz), 141.6, 134.0 (q, *J* = 4 Hz), 131.5, 128.1, 125.9 (q, *J* = 34 Hz), 124.4, 122.9 (q, *J* = 273 Hz), 122.5, 119.6, 111.7, 35.2, 21.9;

^{19}F-NMR (282 MHz, $CDCl_3$): δ/ppm = -62.2;

ESI-MS: calculated $[C_{16}H_{11}NOClF_3H]^+$: 326.0560, found: 326.0554;

ATR-FTIR (cm^{-1}): 1601, 1559, 1451, 1397, 1323, 1277, 1165, 1130, 1088, 1057, 991, 914, 887, 856, 822, 795, 745, 721, 698.

2-(2-(3-chloro-5-(trifluoromethyl)pyridin-2-yl)ethyl)-1-methyl-1*H*-indole (3ae)



Following the general procedure, a solution of 3-chloro-5-(trifluoromethyl)-2-vinylpyridine **1a** (207.6 mg, 1.0 mmol) in 5.0 mL 1,4-dioxane and a solution of K_2CO_3 (414.6 mg, 3.0 mmol, 3.0 equiv) in 0.5 mL dem. H_2O were added to a prestirred (15 min, r.t.) mixture of $[RhCl(C_2H_4)_2]_2$ (15.6 mg, 0.04 mmol, 4 mol %), dppbenz (35.7 mg, 0.08 mmol, 8 mol %) and (1-methyl-1*H*-indol-2-yl)boronic acid (262.5 mg, 1.5 mmol, 1.5 equiv.) in 5.0 mL 1,4-dioxane and 0.5 mL dem. H_2O. The resulting mixture was stirred for 1 h at r.t. Purification by column chromatography on silica (pentane/EtOAc = 19/1) afforded 2-(2-(3-chloro-5-(trifluoromethyl)pyridin-2-yl)ethyl)-1-methyl-1*H*-indole **3ae** as a white solid (230 mg, 0.68 mmol, 68%).
R_f (n-pentane/EtOAc = 19:1): 0.36;

Melting point: 121 – 123 °C

^{1}H-NMR (300 MHz, $CDCl_3$): δ/ppm **=** 8.74 (dd, *J* = 2.0, 1.0 Hz, 1H), 7.92 (d, *J* = 2.0 Hz, 1H), 7.55 (dt, *J* = 7.7, 1.0 Hz, 1H), 7.30 (dq, *J* = 8.2, 0.9 Hz, 1H), 7.19 (ddd, *J* = 8.2, 7.0, 1.3 Hz, 1H), 7.09 (ddd, *J* = 8.0, 7.0, 1.2 Hz, 1H), 6.33 (d, *J* = 0.9 Hz, 1H), 3.76 (s, 3H), 3.45 (dd, *J* = 9.8, 6.0 Hz, 2H), 3.27 (ddd, *J* = 8.4, 6.0, 1.0 Hz, 2H);

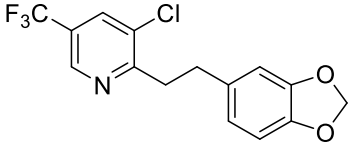
^{13}C-NMR (75 MHz, $CDCl_3$): δ/ppm **=** 161.9 (d, *J* = 2 Hz), 144.1 (q, *J* = 4 Hz), 139.7, 137.5, 134.0 (q, *J* = 4 Hz), 131.5, 127.9, 125.9 (q, *J* = 34 Hz), 122.9 (q, *J* = 273 Hz), 121.0, 120.0, 119.5, 109.0, 99.1, 34.4, 29.7, 24.8;

^{19}F-NMR (282 MHz, $CDCl_3$): δ/ppm **=** -62.2;

ESI-MS: calculated $[C_{17}H_{14}ClF_3N_2H]^+$: 339.0870, found: 339.0880;

ATR-FTIR (cm^{-1}): 1605, 1543, 1466, 1435, 1404, 1319, 1281, 1234, 1188, 1150, 1119, 1088, 1065, 1042, 1011, 903, 880, 787, 764, 741, 710, 633, 602, 571, 556.

2-(2-(benzo[d][1,3]dioxol-5-yl)ethyl)-3-chloro-5-(trifluoromethyl)pyridine (3af)



Following the general procedure, a solution of 3-chloro-5-(trifluoromethyl)-2-vinylpyridine **1a** (207.6 mg, 1.0 mmol) in 5.0 mL 1,4-dioxane and a solution of K_2CO_3 (414.6 mg, 3.0 mmol, 3.0 equiv) in 0.5 mL dem. H_2O were added to a prestirred (15 min, r.t.) mixture of $[RhCl(C_2H_4)_2]_2$ (15.6 mg, 0.04 mmol, 4 mol %), dppbenz (35.7 mg, 0.08 mmol, 8 mol %) and benzo[d][1,3]dioxol-5-ylboronic acid (248.9 mg, 1.5 mmol, 1.5 equiv.) in 5.0 mL

1,4-dioxane and 0.5 mL dem. H_2O. The resulting mixture was stirred for 1 h at r.t. Purification by automated SiO2 gel column chromatography (100 g SiO_2, gradient pentane/EtOAc 5-15%) afforded 2-(2-(benzo[d][1,3]dioxol-5-yl)ethyl)-3-chloro-5-(trifluoromethyl)pyridine **3af** as a colorless solid (295 mg, 0.89 mmol, 89%).

R_f (n-pentane/EtOAc = 19:1): 0.37;

Melting point: 83 – 85 °C

^{1}H-NMR (300 MHz, $CDCl_3$): δ/ppm = 8.71 (dd, *J* = 2.0, 1.0 Hz, 1H), 7.88 (d, *J* = 2.1 Hz, 1H), 6.80 – 6.65 (m, 3H), 5.93 (s, 2H), 3.26 (dd, *J* = 9.8, 6.3 Hz, 2H), 3.05 – 2.93 (m, 2H);

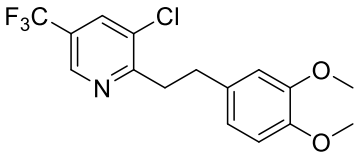
^{13}C-NMR (101 MHz, $CDCl_3$): δ/ppm = 162.6, 147.8, 146.1, 144.0 (q, *J* = 4 Hz), 134.8, 134.0 (q, *J* = 4 Hz), 131.4, 125.8 (q, *J* = 34 Hz), 122.9 (q, *J* = 273 Hz), 121.4, 109.1, 108.4,101.0, 37.8, 33.7;

^{19}F-NMR (282 MHz, $CDCl_3$): δ/ppm = -62.2;

ESI-MS: calculated $[C_{16}H_{11}NOClF_3H]^+$: 326.0560, found: 326.0554;

ATR-FTIR (cm^{-1}): 1605, 1501, 1485, 1443, 1400, 1385, 1323, 1300, 1242, 1192, 1161, 1134, 1088, 1038, 995, 926, 887, 856, 802, 748, 702.

3-chloro-2-(3,4-dimethoxyphenethyl)-5-(trifluoromethyl)pyridine (3ag)



Following the general procedure, a solution of 3-chloro-5-(trifluoromethyl)-2-vinylpyridine **1a** (207.6 mg, 1.0 mmol) in 5.0 mL 1,4-dioxane and a solution of K_2CO_3 (414.6 mg, 3.0 mmol, 3.0 equiv) in 0.5 mL dem. H_2O were added to a prestirred (15 min, r.t.) mixture of $[RhCl(C_2H_4)_2]_2$ (15.6 mg, 0.04 mmol, 4 mol %), dppbenz (35.7 mg, 0.08 mmol, 8 mol %) and (3,4-dimethoxyphenyl)boronic acid (273.0 mg, 1.5 mmol, 1.5 equiv.) in 5.0 mL 1,4-dioxane and 0.5 mL dem. H_2O. The resulting mixture was stirred for 1 h at r.t. Purification by column chromatography on silica (pentane/EtOAc = 9/1) afforded 3-chloro-2-(3,4-dimethoxyphenethyl)-5-(trifluoromethyl)pyridine **3ag** as a white solid (314 mg, 0.91 mmol, 91%).

R_f (n-pentane/EtOAc = 20:1): 0.12;

Melting point: 61 – 63 °C

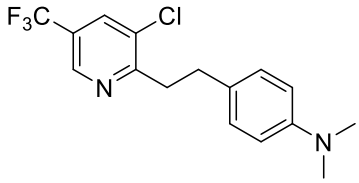
^{1}H-NMR (300 MHz, $CDCl_3$): δ/ppm = 8.71 (dd, *J* = 2.1, 1.0 Hz, 1H), 7.87 (d, *J* = 2.0 Hz, 1H), 6.86 – 6.68 (m, 3H), 3.86 (s, 3H), 3.86 (s, 3H), 3.35 – 3.24 (m, 2H), 3.08 – 2.96 (m, 2H);

^{13}C-NMR (101 MHz, $CDCl_3$): δ/ppm = 162.7 (d, *J* = 2 Hz), 149.0, 147.6, 144.0 (q, *J* = 4 Hz), 133.9 (q, *J* = 4 Hz), 133.6, 131.4, 125.7 (q, *J* = 34 Hz), 123.0 (q, *J* = 273 Hz), 120.4, 111.9, 111.4, 56.1, 56.0, 37.8, 33.7;

^{19}F-NMR (282 MHz, $CDCl_3$): δ/ppm = -62.2;

ESI-MS: calculated $[C_{16}H_{15}ClF_3NO_2Na]^+$: 368,0641, found: 368.0633;

4-(2-(3-chloro-5-(trifluoromethyl)pyridin-2-yl)ethyl)-*N,N*-dimethylaniline (3ah)



Following the general procedure, a solution of 3-chloro-5-(trifluoromethyl)-2-vinylpyridine **1a** (207.6 mg, 1.0 mmol) in 5.0 mL 1,4-dioxane and a solution of K_2CO_3 (414.6 mg, 3.0 mmol, 3.0 equiv) in 0.5 mL dem. H_2O were added to a prestirred (15 min, r.t.) mixture of $[RhCl(C_2H_4)_2]_2$ (15.6 mg, 0.04 mmol, 4 mol %), dppbenz (35.7 mg, 0.08 mmol, 8 mol %) and (4-(dimethylamino)phenyl)boronic acid (247.5 mg, 1.5 mmol, 1.5 equiv.) in 5.0 mL 1,4-dioxane and 0.5 mL dem. H_2O. The resulting mixture was stirred for 1 h at r.t. Purification by column chromatography on silica (pentane/EtOAc = 19/1) afforded 4-(2-(3-chloro-5-(trifluoromethyl)pyridin-2-yl)ethyl)-N,N-dimethylaniline **3ah** as a bright yellow solid (302 mg, 0.92 mmol, 92%).

R_f (n-pentane/EtOAc = 20:1): 0.27;

Melting point: 68 – 70 °C

^{1}H-NMR (300 MHz, $CDCl_3$): δ/ppm = 8.71 (dd, *J* = 2.1, 1.0 Hz, 1H), 7.88 (dd, *J* = 2.1, 0.8 Hz, 1H), 7.18 – 7.10 (m, 2H), 6.75 – 6.67 (m, 2H), 3.33 – 3.23 (m, 2H), 3.02 – 2.94 (m, 2H), 2.93 (s, 6H);

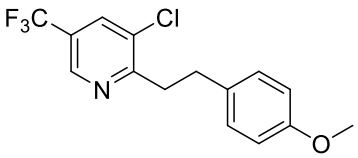
^{13}C-NMR (101 MHz, $CDCl_3$): δ/ppm = 163.1 (d, *J* = 1 Hz), 149.4, 144.0 (q, *J* = 4 Hz), 133.9 (q, *J* = 4 Hz), 131.4, 129.2, 125.6 (q, *J* = 34 Hz), 123.0 (q, *J* = 273 Hz), 113.1, 41.0, 38.1, 33.1;

^{19}F-NMR (282 MHz, $CDCl_3$): δ/ppm = -62.2;

ESI-MS: calculated $[C_{16}H_{16}ClF_3N_2H]^+$: 329,1032, found: 329.1027;

ATR-FTIR (cm^{-1}): 1605, 1524, 1447, 1393, 1319, 1223, 1165, 1126, 1088, 1057, 988, 945, 907, 887, 845, 810, 783, 748, 694.

3-chloro-2-(4-methoxyphenethyl)-5-(trifluoromethyl)pyridine (3ai)



Following the general procedure, a solution of 3-chloro-5-(trifluoromethyl)-2-vinylpyridine **1a** (207.6 mg, 1.0 mmol) in 5.0 mL 1,4-dioxane and a solution of K_2CO_3 (414.6 mg, 3.0 mmol, 3.0 equiv) in 0.5 mL dem. H_2O were added to a prestirred (15 min, r.t.) mixture of $[RhCl(C_2H_4)_2]_2$ (15.6 mg, 0.04 mmol, 4 mol %), dppbenz (35.7 mg, 0.08 mmol, 8 mol %) and (4-methoxyphenyl)boronic acid (227.9 mg, 1.5 mmol, 1.5 equiv.) in 5.0 mL 1,4-dioxane and 0.5 mL dem. H_2O. The resulting mixture was stirred for 1 h at r.t. Purification by column chromatography on silica (pentane/EtOAc = 25/1) afforded 3-chloro-2-(4-methoxyphenethyl)-5-(trifluoromethyl)pyridine **3ai** as a white solid (296 mg, 0.94 mmol, 94%).

R_f (n-pentane/EtOAc = 100:3): 0.26;

Melting point: 61 – 63 °C

^{1}H-NMR (300 MHz, $CDCl_3$): δ/ppm = 8.71 (dd, *J* = 2.0, 1.0 Hz, 1H), 7.88 (dd, *J* = 2.0, 0.8 Hz, 1H), 7.22 – 7.11 (m, 2H), 6.88 – 6.80 (m, 2H), 3.80 (s, 3H), 3.36 – 3.20 (m, 2H), 3.08 – 2.94 (m, 2H);

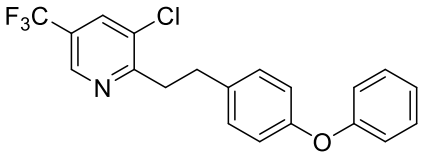
^{13}C-NMR (101 MHz, $CDCl_3$): δ/ppm = 162.8 (d, *J* = 2 Hz), 158.2, 144.0 (q, *J* = 4 Hz), 133.9 (q, *J* = 4 Hz), 133.1, 131.4, 129.5, 125.7 (q, *J* = 34 Hz), 123.0 (q, *J* = 273 Hz), 114.0, 55.4, 37.8, 33.2;

^{19}F-NMR (282 MHz, $CDCl_3$): δ/ppm = -62.2;

ESI-MS: calculated $[C_{15}H_{13}ClF_3NONa]^+$: 338.0535, found: 338.0538;

ATR-FTIR (cm^{-1}): 2940, 2916, 2862, 2839, 1601, 1582, 1512, 1470, 1443, 1393, 1319, 1246, 1165, 1119, 1088, 1057, 1034, 991, 941, 907, 891, 841, 795, 737, 718, 698.

3-chloro-2-(4-phenoxyphenethyl)-5-(trifluoromethyl)pyridine (3aj)



Following the general procedure, a solution of 3-chloro-5-(trifluoromethyl)-2-vinylpyridine **1a** (207.6 mg, 1.0 mmol) in 5.0 mL 1,4-dioxane and a solution of K_2CO_3 (414.6 mg, 3.0 mmol, 3.0 equiv) in 0.5 mL dem. H_2O were added to a prestirred (15 min, r.t.) mixture of $[RhCl(C_2H_4)_2]_2$ (15.6 mg, 0.04 mmol, 4 mol %), dppbenz (35.7 mg, 0.08 mmol, 8 mol %) and (4-phenoxyphenyl)boronic acid (321.0 mg, 1.5 mmol, 1.5 equiv.) in 5.0 mL 1,4-dioxane and 0.5 mL dem. H_2O. The resulting mixture was stirred for 1 h at r.t. Purification by column chromatography on silica (pentane/EtOAc = 25/1) afforded 3-chloro-2-(4-phenoxyphenethyl)-5-(trifluoromethyl)pyridine **3aj** as a white solid (274 mg, 0.92 mmol, 92%).

R_f (n-pentane/EtOAc = 100:3): 0.32;

Melting point: 52 – 54 °C

^{1}H-NMR (300 MHz, $CDCl_3$): δ/ppm = 8.71 (dd, *J* = 2.0, 1.0 Hz, 1H), 7.88 (d, *J* = 2.0 Hz, 1H), 7.20 – 7.08 (m, 4H), 3.37 – 3.21 (m, 2H), 3.12 – 2.94 (m, 2H), 2.34 (s, 3H);

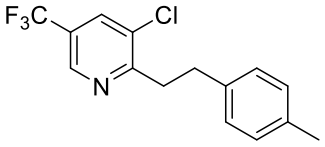
^{13}C-NMR (101 MHz, $CDCl_3$): δ/ppm = 162.6 (d, *J* = 1 Hz), 157.6, 155.7, 144.1 (q, *J* = 4 Hz), 136.0, 133.9 (q, *J* = 4 Hz), 131.4, 129.8, 129.8, 125.8 (q, *J* = 34 Hz), 122.9 (q, *J* = 273 Hz), 119.2, 118.7, 37.6, 33.3;

^{19}F-NMR (282 MHz, $CDCl_3$): δ/ppm = -62.2;

ESI-MS: calculated $[C_{15}H_{13}ClF_3NH]^+$: 300.0767, found: 300.0750;

ATR-FTIR (cm^{-1}): 1601, 1589, 1559, 1508, 1489, 1474, 1458, 1397, 1323, 1288, 1242, 1200, 1165, 1150, 1126, 1099, 1084, 1057, 937, 910, 891, 872, 837, 748, 729, 691.

3-chloro-2-(4-methylphenethyl)-5-(trifluoromethyl)pyridine (3ak)



Following the general procedure, a solution of 3-chloro-5-(trifluoromethyl)-2-vinylpyridine **1a** (207.6 mg, 1.0 mmol) in 5.0 mL 1,4-dioxane and a solution of K_2CO_3 (414.6 mg, 3.0 mmol, 3.0 equiv) in 0.5 mL dem. H_2O were added to a prestirred (15 min, r.t.) mixture of $[RhCl(C_2H_4)_2]_2$ (15.6 mg, 0.04 mmol, 4 mol %), dppbenz (35.7 mg, 0.08 mmol, 8 mol %) and *p*-tolylboronic acid (203.9 mg, 1.5 mmol, 1.5 equiv.) in 5.0 mL 1,4-dioxane and 0.5 mL dem. H_2O. The resulting mixture was stirred for 1 h at r.t. Purification by column

chromatography on silica (pentane/EtOAc = 50/1) afforded 3-chloro-2-(4-methylphenethyl)-5-(trifluoromethyl)pyridine **3ak** as a white solid (370 mg, 0.98 mmol, 98%).

R_f (n-pentane/EtOAc = 100:3): 0.47;

Melting point: 51 – 53 °C

^{1}H-NMR (300 MHz, $CDCl_3$): δ/ppm **=** 8.72 (dd, *J* = 2.0, 1.0 Hz, 1H), 7.89 (d, *J* = 2.0 Hz, 1H), 7.37 – 7.29 (m, 2H), 7.25 – 7.18 (m, 2H), 7.09 (ddt, *J* = 8.5, 70.0, 1.2 Hz, 1H), 7.04 – 6.92 (m, 4H), 3.38 – 3.25 (m, 2H), 3.13 – 2.98 (m, 2H);

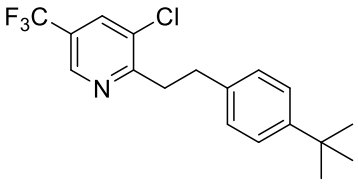
^{13}C-NMR (101 MHz, $CDCl_3$): δ/ppm **=** 162.8 (d, *J* = 1 Hz), 144.0 (q, *J* = 4 Hz), 138.0, 135.9, 133.9 (q, *J* = 4 Hz), 131.4, 129.3, 128.4, 125.7 (q, *J* = 34 Hz), 123.0 (q, *J* = 273 Hz), 37.7, 33.6, 21.2;

^{19}F-NMR (282 MHz, $CDCl_3$): δ/ppm **=** -62.2;

ESI-MS: calculated $[C_{20}H_{15}ClF_3NOH]^+$: 378.0873, found: 378.0863;

ATR-FTIR (cm^{-1}): 2924, 1601, 1555, 1516, 1454, 1389, 1323, 1300, 1219, 1161, 1134, 1088, 1057, 1022, 999, 957, 934, 918, 891, 849, 799, 741, 698.

2-(4-(*tert*-butyl)phenethyl)-3-chloro-5-(trifluoromethyl)pyridine (3al)



Following the general procedure, a solution of 3-chloro-5-(trifluoromethyl)-2-vinylpyridine **1a** (207.6 mg, 1.0 mmol) in 5.0 mL 1,4-dioxane and a solution of K_2CO_3 (414.6 mg, 3.0 mmol, 3.0 equiv) in 0.5 mL dem. H_2O were added to a prestirred (15 min, r.t.) mixture of $[RhCl(C_2H_4)_2]_2$ (15.6 mg, 0.04 mmol, 4 mol %), dppbenz (35.7 mg, 0.08 mmol, 8 mol %) and (4-(*tert*-butyl)phenyl)boronic acid (267.1 mg, 1.5 mmol, 1.5 equiv.) in 5.0 mL 1,4-dioxane and 0.5 mL dem. H_2O. The resulting mixture was stirred for 1 h at r.t. Purification by column chromatography on silica (pentane/EtOAc = 50/1) afforded 3-chloro-2-(4-methylphenethyl)-5-(trifluoromethyl)pyridine **3al** as a white solid (291 mg, 0.85 mmol, 85%).

R_f (n-pentane/EtOAc = 100:3): 0.14;

Melting point: 40 – 42 °C

^{1}H-NMR (400 MHz, $CDCl_3$): δ/ppm = 8.73 (dd, *J* = 2.1, 1.0 Hz, 1H), 7.90 (d, *J* = 2.1 Hz, 1H), 7.38 – 7.32 (m, 2H), 7.25 – 7.19 (m, 2H), 3.35 – 3.27 (m, 2H), 3.10 – 3.00 (m, 2H), 1.33 (s, 9H);

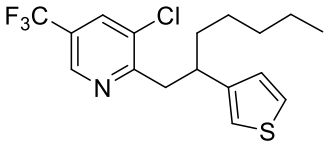
^{13}C-NMR (101 MHz, $CDCl_3$): δ/ppm = 162.9 (d, *J* = 1 Hz), 149.2, 144.1 (q, *J* = 4 Hz), 138.0, 133.9 (q, *J* = 4 Hz), 131.4, 128.2, 125.8 (q, *J* = 33 Hz), 125.6, 123.0 (q, *J* = 273 Hz), 37.6, 34.6, 33.5, 31.5;

^{19}F-NMR (282 MHz, $CDCl_3$): δ/ppm = -62.2;

ESI-MS: calculated $[C_{20}H_{15}ClF_3NOH]^+$: 378.0873, found: 378.0863;

ATR-FTIR (cm^{-1}): 2967, 1601, 1466, 1393, 1323, 1292, 1250, 1204, 1157, 1130, 1088, 1057,1018, 988, 910, 891, 853, 837, 818, 752, 737, 702.

3-chloro-2-(2-(thiophen-3-yl)heptyl)-5-(trifluoromethyl)pyridine (3ga)



Following the general procedure, a solution of (*E*)-3-chloro-2-(hept-1-en-1-yl)-5-(trifluoromethyl)pyridine **1g** (361.1 mg, 1.0 mmol, 1.0 equiv.) in 5.0 mL 1,4-dioxane and a solution of K_2CO_3 (414.6 mg, 3.0 mmol, 3.0 equiv) in 0.5 mL dem. H_2O were added to a prestirred (15 min, r.t.) mixture of $[RhCl(C_2H_4)_2]_2$ (38.9 mg, 0.10 mmol, 10 mol %), dppbenz (89.3 mg, 0.20 mmol, 20 mol %) and thiophen-3-ylboronic acid (384.0 mg, 3.0 mmol, 3.0 equiv.) in 5.0 mL 1,4-dioxane and 0.5 mL dem. H_2O. The resulting mixture was stirred for 1 h at 100 °C Purification by column chromatography on silica (petroleum ether/Et_2O = 100/2) afforded 3-chloro-2-(2-(thiophen-3-yl)heptyl)-5-(trifluoromethyl)pyridine **3ga** as a pale yellow oil (253 mg, 0.70 mmol, 70%).

R_f (petroleum ether/EtOAc = 50:1): 0.49;

^{1}H-NMR (500 MHz, $CDCl_3$): δ/ppm = 8.65 (d, *J* = 1.4 Hz, 1H), 7.81 (d, *J* = 2.0 Hz, 1H), 7.21 (dd, *J* = 5.0, 2.9 Hz, 1H), 6.94 (dd, *J* = 5.0, 1.3 Hz, 1H), 6.86 (dd, *J* = 3.0, 1.3 Hz, 1H), 3.48 – 3.36 (m, 2H), 3.26 – 3.25 (m, 2H), 1.70 – 1.64 (m, 2H), 1.24 – 1.20 (m, 6H), 0.84 – 0.82 (m, 3H);

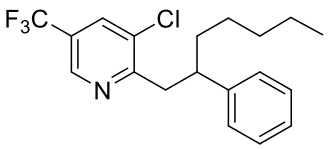
^{13}C-NMR (126 MHz, $CDCl_3$): δ/ppm = 162.3, 145.2, 143.8 (q, *J* = 4.1 Hz), 133.9 (q, *J* = 3.4 Hz), 131.8, 126.8, 125.4, 120.4, 42.4, 40.2, 36.0, 31.9, 27.2, 22.7, 14.2;

^{19}F-NMR (377 MHz, $CDCl_3$): δ/ppm = -62.2;

ESI-MS: calculated $[C_{17}H_{19}ClF_3NSH]^+$: 362.0952, found: 362.0952;

ATR-FTIR (cm^{-1}): 2957, 2928, 2857, 1320, 1135, 1089, 1056, 913, 777, 655.

3-chloro-2-(2-phenylheptyl)-5-(trifluoromethyl)pyridine (3gm)



Following the general procedure, a solution of (*E*)-3-chloro-2-(hept-1-en-1-yl)-5-(trifluoromethyl)pyridine **1g** (361.1 mg, 1.0 mmol, 1.0 equiv.) in 5.0 mL 1,4-dioxane and a solution of K_2CO_3 (414.6 mg, 3.0 mmol, 3.0 equiv) in 0.5 mL dem. H_2O were added to a prestirred (15 min, r.t.) mixture of $[RhCl(C_2H_4)_2]_2$ (19.4 mg, 0.05 mmol, 5 mol %), dppbenz (44.6 mg, 0.10 mmol, 10 mol %) and phenylboronic acid (365.8 mg, 3.0 mmol, 3.0 equiv.) in 5.0 mL 1,4-dioxane and 0.5 mL dem. H_2O. The resulting mixture was stirred for 1 h at r.t. Purification by column chromatography on silica (petroleum ether/Et_2O = 100/2) afforded 3-chloro-2-(2-phenylheptyl)-5-(trifluoromethyl)pyridine **3gm** as a colorless oil (295 mg, 0.83 mmol, 83%).

R_f (petroleum ether/EtOAc = 50:1): 0.48;

^{1}H-NMR (500 MHz, $CDCl_3$): δ/ppm = 8.64 (d, *J* = 1.1 Hz, 1H), 7.79 (d, *J* = 2.0 Hz, 1H), 7.25 – 7.21 (m, 2H), 7.19 – 7.13 (m, 3H), 3.29 – 3.24 (m, 3H), 1.80 – 1.59 (m, 2H), 1.26 – 1.07 (m, 6H), 0.84 – 0.74 (m, 3H);

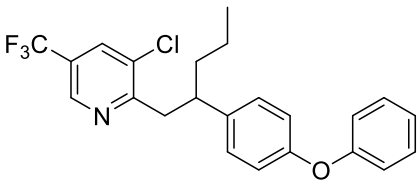
^{13}C-NMR (126 MHz, $CDCl_3$): δ/ppm = 162.4, 144.4, 143.8 (q, *J* = 3.9 Hz), 133.9 (q, *J* = 3.6 Hz), 131.7, 128.4, 127.8, 126.4, 125.4 (d, *J* = 33.5 Hz), 124.7 (q, *J* = 271.7 Hz), 45.0, 42.7, 35.8, 32.0, 27.3, 22.7, 14.2;

^{19}F-NMR (377 MHz, $CDCl_3$): δ/ppm = -62.2;

ESI-MS: calculated $[C_{19}H_{21}ClF_3NH]^+$: 356.1387, found: 356.1386;

ATR-FTIR (cm^{-1}): 2957, 2925, 2855, 1603, 1320, 1135, 1088, 1055, 912, 698.

3-chloro-2-(2-(4-phenoxyphenyl)pentyl)-5-(trifluoromethyl)pyridine (3hj)



Following the general procedure, a solution of (*E*)-3-chloro-2-(pent-1-en-1-yl)-5-(trifluoromethyl)pyridine **1h** (99.9 mg, 0.4 mmol) in 2.0 mL 1,4-dioxane and a solution of K_2CO_3 (165.9 mg, 1.2 mmol, 3.0 equiv) in 0.2 mL dem. H_2O were added to a prestirred (15 min, r.t.) mixture of $[RhCl(C_2H_4)_2]_2$ (6.2 mg, 0.016 mmol, 4 mol %), dppbenz (14.3 mg, 0.032 mmol, 8 mol %) and (4-phenoxyphenyl)boronic acid (128.4 mg, 0.6 mmol, 1.5 equiv.) in 2.0 mL 1,4-dioxane and 0.2 mL dem. H_2O. The resulting mixture was stirred for 1 h at r.t. Purification by column chromatography on silica (pentane/EtOAc = 100/3) afforded 3-chloro-2-(2-(4-phenoxyphenyl)pentyl)-5-(trifluoromethyl)pyridine **3hj** as a yellow oil (137 mg, 0.33 mmol, 82%).

R_f (n-pentane/EtOAc = 100:3): 0.23;

^{1}H-NMR (300 MHz, $CDCl_3$): δ/ppm **=** 8.66 (dd, *J* = 2.0, 1.0 Hz, 1H), 7.81 (dd, *J* = 2.0, 0.8 Hz, 1H), 7.39 – 7.24 (m, 2H), 7.15 – 7.04 (m, 3H), 7.01 – 6.93 (m, 2H), 6.95 – 6.81 (m, 2H), 3.28 (d, *J* = 1.9 Hz, 3H), 1.77 – 1.61 (m, 2H), 1.29 – 1.15 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H);

^{13}C-NMR (75 MHz, $CDCl_3$): δ/ppm **=** 162.3 (d, *J* = 1 Hz), 157.6, 155.5, 143.8 (q, *J* = 4 Hz), 139.2, 133.9 (q, *J* = 4 Hz), 131.7, 129.8, 128.9, 125.6 (q, *J* = 34 Hz), 123.1, 122.9 (q, *J* = 273 Hz), 119.0, 118.6, 44.1, 42.8, 38.1, 20.8, 14.2;

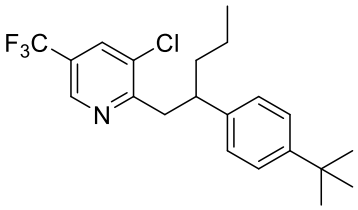
^{19}F-NMR (282 MHz, $CDCl_3$): δ/ppm = -62.1;

ESI-MS: calculated $[C_{23}H_{21}ClF_3NOH]^+$: 420.1337, found: 420.1333;

ATR-FTIR (cm^{-1}): 3040, 2932, 2870, 1589, 1505, 1466, 1397, 1319, 1234, 1173, 1134, 1088, 1057, 1018, 910, 872, 833, 748, 694, 571, 556.

2-(2-(4-(*tert*-butyl)phenyl)pentyl)-3-chloro-5-(trifluoromethyl)pyridine (3hl)

Following the general procedure, a solution of (*E*)-3-chloro-2-(pent-1-en-1-yl)-5-(trifluoromethyl)pyridine **1h** (99.9 mg, 0.4 mmol) in 2.0 mL 1,4-dioxane and a solution of K_2CO_3 (165.9 mg, 1.2 mmol, 3.0 equiv) in 0.2 mL dem. H_2O were added to a prestirred (15 min, r.t.) mixture of $[RhCl(C_2H_4)_2]_2$ (6.2 mg, 0.016 mmol, 4 mol %), dppbenz (14.3 mg, 0.032 mmol, 8 mol %) and (4-(*tert*-butyl)phenyl)boronic acid (106.8 mg, 0.6 mmol, 1.5 equiv.) in 2.0 mL 1,4-dioxane and 0.2 mL dem. H_2O. The resulting



mixture was stirred for 1 h at r.t. Purification by column chromatography on silica (pentane/EtOAc = 100/3) afforded 2-(2j-(4-(*tert*-butyl)phenyl)pentyl)-3-chloro-5-(trifluoromethyl)pyridine **3hl** as a colorless oil (131 mg, 0.34 mmol, 85%).

R_f (n-pentane/EtOAc = 100:3): 0.25;

^{1}H-NMR (300 MHz, $CDCl_3$): δ/ppm = 8.66 (dd, *J* = 2.0, 1.0 Hz, 1H), 7.82 (d, *J* = 2.6 Hz, 1H), 7.27 (dd, *J* = 7.7, 3.0 Hz, 2H), 7.17 – 7.02 (m, 2H), 3.27 (d, *J* = 2.0 Hz, 3H), 1.79 – 1.49 (m, 2H), 1.30 (s, 9H), 1.25 – 1.08 (m, 2H), 0.83 (t, *J* = 7.3 Hz, 3H);

^{13}C-NMR (75 MHz, $CDCl_3$): δ/ppm = 162.6 (d, *J* = 2 Hz), 149.1, 143.8 (q, *J* = 4 Hz), 141.4, 133.8 (q, *J* = 4 Hz), 131.8, 127.3, 125.3 (q, *J* = 34 Hz), 125.3, 123.0 (q, *J* = 273 Hz), 44.0, 42.9, 37.8, 34.5, 31.5, 20.8, 14.2;

^{19}F-NMR (282 MHz, $CDCl_3$): δ/ppm = -62.2;

ESI-MS: calculated $[C_{21}H_{25}ClF_3NH]^+$: 384.1700, found: 384.1699;

ATR-FTIR (cm^{-1}): 2932, 2870, 1605, 1512, 1458, 1397, 1319, 1273, 1173, 1134, 1096, 1057, 980, 910, 880, 833, 702, 633, 571.

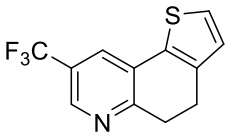
General procedure for the Pd catalyzed intramolecular cyclization

The corresponding starting material (0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 5 mol%), $PCy_3 \cdot HBF_4$ (14.7 mg, 0.04 mmol, 10 mol%) and K_2CO_3 (110.6 mg, 0.8 mmol, 2.0 equiv.) were added to a pressurizable flask. The flask was purged with argon and 4.0 mL of 1,4-dioxane and 0.4 mL of dem. H_2O were added. The resulting mixture was heated to 150 °C for 18 h. Brine (15 mL) was added and the aqueous phase was extracted with EtOAc (3 x 25 mL). The combined organic layers were dried ($MgSO_4$) and the solvent was removed under reduced pressure. The crude material was purified by column chromatography on silica.

General procedure for the Rh and Pd catalyzed one-pot reaction

A 10 mL Schlenk flask was equipped with a magnetic stir bar. $[RhCl(C_2H_4)_2]_2$ (6.2 mg, 0.016 mmol, 4 mol%), dppbenz (14.3 mg, 0.032 mmol, 8 mol%) and the corresponding boronic acid (0.6 mmol, 1.5 equiv.) were added and the flask was evacuated and backfilled with argon thrice. 2.0 mL of 1,4-dioxane and 0.2 mL of dem. H_2O were added and the resulting suspension was stirred for 15 min at room temperature. A second 10 mL Schlenk flask was equipped with a magnetic stir bar. $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 5 mol%) and $PCy_3 \cdot HBF_4$ (14.7 mg, 0.04 mmol, 10 mol%) were added and the flask was evacuated and backfilled with argon thrice. 1.0 mL of 1,4-dioxane and 0.05 mL of dem. H_2O were added and the resulting suspension was stirred at room temperature. A solution of the corresponding 2-vinylpyridine (0.4 mmol) in 1.0 mL of 1,4-dioxane and a solution of K_2CO_3 (165.9 mg, 1.2 mmol, 3.0 equiv.) in 0.15 mL of dem. H_2O were prepared in two separate vials and transferred to the pre-stirred mixture in the first Schlenk flask via syringe. The resulting reaction mixture was stirred for 1 h at room temperature. Now, the pre-stirred mixture from the second Schlenk flask was transferred to the first flask and the resulting reaction mixture was heated to 150 °C for 18 h. Brine (15 mL) was added and the aqueous phase was extracted with EtOAc (3 x 25 mL). The combined organic layers were dried ($MgSO_4$) and the solvent was removed under reduced pressure. The crude material was purified by column chromatography on silica.

8-(trifluoromethyl)-4,5-dihydrothieno[2,3-*f*]quinoline (4aa)



Following the general procedure, 3-chloro-2-(2-(thiophen-3-yl)ethyl)-5-(trifluoromethyl)pyridine **3aa** (116.4 mg, 0.40 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 5 mol%), $PCy_3 \cdot HBF_4$ (14.7 mg, 0.04 mmol, 10 mol%) and K_2CO_3 (110.6 mg, 0.8 mmol, 2.0 equiv.) were added to a pressurizable flask. The flask was purged with argon and 4.0 mL of 1,4-dioxane and 0.4 mL of dem. H_2O were added. The resulting mixture was heated to 150 °C for 18 h. Purification by column chromatography on silica (hexane/EtOAc = 30/1) afforded 8-(trifluoromethyl)-4,5-dihydrothieno[2,3-f]quinoline **4aa** as a white solid (97 mg, 0.38 mmol, 95%).

Yield of the one-pot reaction: 70 mg, 0.28 mmol, 69%;

R_f (hexane/EtOAc = 5:1): 0.35;

Melting point: 44 – 45 °C;

^{1}H-NMR (500 MHz, $CDCl_3$): δ/ppm = 8.57 (d, *J* = 2.0 Hz, 1H), 7.75 (d, *J* = 2.0 Hz, 1H), 7.33 (d, *J* = 5.0 Hz, 1H), 6.97 (dt, *J* = 5.0, 0.5 Hz, 1H), 3.26 (t, *J* = 7.9 Hz, 2H), 3.04 – 3.01 (m, 2H);

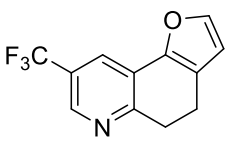
^{13}C-NMR (126 MHz, $CDCl_3$): δ/ppm = 159.3 (d, *J* = 1.5 Hz), 143.3 (q, *J* = 4.3 Hz), 139.3, 132.8, 128.1, 127.6, 126.3, 125.9 (q, *J* = 3.4 Hz), 125.5 (q, *J* = 32.9 Hz), 123.8 (q, *J* = 272.5 Hz), 31.9, 23.6;

^{19}F-NMR (377 MHz, $CDCl_3$): δ/ppm = -62.4;

ESI-MS: calculated $[C_{12}H_8F_3NSH]^+$: 256.0408, found: 256.0404;

ATR-FTIR (cm^{-1}): 3112, 2945, 2851, 1607, 1441, 1346, 1333, 1263, 1115, 1081, 996, 904, 726.

8-(trifluoromethyl)-4,5-dihydrofuro[2,3-*f*]quinoline (4ab)



Following the general procedure, 3-chloro-2-(2-(furan-3-yl)ethyl)-5-(trifluoromethyl)pyridine **3ab** (110.0 mg, 0.40 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 5 mol%), PCy_3*HBF_4 (14.7 mg, 0.04 mmol, 10 mol%) and K_2CO_3 (110.6 mg, 0.8 mmol, 2.0 equiv.) were added to a pressurizable flask. The flask was purged with argon and 4.0 mL of 1,4-dioxane and 0.4 mL of dem. H_2O were added. The resulting mixture was heated to 150 °C for 18 h. Purification by

column chromatography on silica (hexane/EtOAc = 20/1) afforded 8-(trifluoromethyl)-4,5-dihydrofuro[2,3-f]quinoline **4ab** as a white solid (67 mg, 0.28 mmol, 70%).

Yield of the one-pot reaction: 39 mg, 0.16 mmol, 41%;

R_f (hexane/EtOAc = 10:1): 0.29;

Melting point: 45 – 46 °C;

^{1}H-NMR (500 MHz, $CDCl_3$): δ/ppm = 8.53 (d, *J* = 1.7 Hz, 1H), 7.85 (d, *J* = 1.7 Hz, 1H), 7.47 (d, *J* = 1.8 Hz, 1H), 6.40 (dt, *J* = 1.8, 0.4 Hz, 1H), 3.26 – 3.22 (m, 2H), 2.90 (t, *J* = 8.0 Hz, 2H);

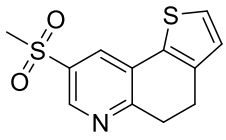
^{13}C-NMR (126 MHz, $CDCl_3$): δ/ppm = 159.5 (d, *J* = 1.7 Hz), 147.2, 144.5, 142.8 (q, *J* = 4.3 Hz), 125.3 (d, *J* = 32.9 Hz), 124.1, 123.9 (q, *J* = 272.0 Hz), 122.3 (q, *J* = 3.5 Hz), 121.8, 111.5, 31.9, 20.0;

^{19}F-NMR (377 MHz, $CDCl_3$): δ/ppm = -62.6;

ESI-MS: calculated $[C_{12}H_8F_3NOH]^+$: 240.0636, found: 240.0637;

ATR-FTIR (cm^{-1}): 3086, 2953, 2917, 2887, 1633, 1461, 1343, 1336, 1318, 1290, 1270, 1151, 1113, 1084, 1074, 1053, 1024, 897, 883, 829, 751, 729, 703.

8-(methylsulfonyl)-4,5-dihydrothieno[2,3-*f*]quinoline (4ba)



Following the general procedure, 3-chloro-2-(2-(thiophen-3-yl)ethyl)-5-(methylsulfonyl)pyridine **3ba** (120.4 mg, 0.40 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 5 mol%), $PCy_3{\cdot}HBF_4$ (14.7 mg, 0.04 mmol, 10 mol%) and K_2CO_3 (110.6 mg, 0.8 mmol, 2.0 equiv.) were added to a pressurizable flask. The flask was purged with argon and 4.0 mL of 1,4-dioxane and 0.4 mL of dem. H_2O were added. The resulting mixture was heated to 150 °C for 18 h. Purification by column chromatography on silica (hexane/EtOAc = 5/3) afforded 8-(methylsulfonyl)-4,5-dihydrothieno[2,3-f]quinoline **4ba** as a white solid (102 mg, 0.38 mmol, 96%).

Yield of the one-pot reaction: 48 mg, 0.18 mmol, 45%;

R_f (hexane/EtOAc = 1:1): 0.25;

Melting point: 150 – 151 °C;

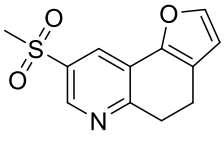
^{1}H-NMR (500 MHz, $CDCl_3$): δ/ppm = 8.81 (d, *J* = 2.2 Hz, 1H), 8.01 (d, *J* = 2.2 Hz, 1H), 7.35 (d, *J* = 5.0 Hz, 1H), 6.96 (dt, *J* = 5.0, 0.5 Hz, 1H), 3.29 – 3.24 (m, 2H), 3.31 (s, 3H), 3.05 – 3.02 (m, 2H);

^{13}C-NMR (126 MHz, $CDCl_3$): δ/ppm = 161.1, 145.1, 139.7, 135.7, 132.4, 128.2, 128.1, 127.4, 127.0, 45.1, 32.2, 23.4;

ESI-MS: calculated $[C_{12}H_{11}NO_2S_2H]^+$: 266.0309, found: 266.0314;

ATR-FTIR (cm^{-1}): 3116, 2995, 2904, 1842, 1579, 1557, 1534, 1440, 1409, 1389, 1302, 1276, 1235, 1133, 1099, 1001, 974, 891, 842, 803, 768, 756, 733, 701.

8-(methylsulfonyl)-4,5-dihydrofuro[2,3-*f*]quinoline (4bb)



Following the general procedure, 3-chloro-2-(2-(furan-3-yl)ethyl)-5-(methylsulfonyl)pyridine **3bb** (114.0 mg, 0.40 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 5 mol%), $PCy_3{\cdot}HBF_4$ (14.7 mg, 0.04 mmol, 10 mol%) and K_2CO_3 (110.6 mg, 0.8 mmol, 2.0 equiv.) were added to a pressurizable flask. The flask was purged with argon and 4.0 mL of 1,4-dioxane and 0.4 mL of dem. H_2O were added. The resulting mixture was heated to 150 °C for 18 h. Purification by column chromatography on silica (hexane/EtOAc = 5/3) afforded 8-(methylsulfonyl)-4,5-dihydrofuro[2,3-f]quinoline **4bb** as a white solid (92 mg, 0.37 mmol, 93%).

Yield of the one-pot reaction: 7 mg, 0.03 mmol, 7%;

R_f (hexane/EtOAc = 1:1): 0.29;

Melting point: 118 – 120 °C;

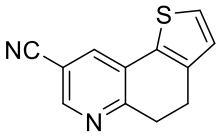
^{1}H-NMR (500 MHz, $CDCl_3$): δ/ppm = 8.79 (d, *J* = 2.2 Hz, 1H), 8.12 (d, *J* = 2.2 Hz, 1H), 7.50 (d, *J* = 1.8 Hz, 1H), 6.42 (dt, *J* = 1.8, 0.4 Hz, 1H), 3.31 – 3.26 (m, 2H), 3.12 (s, 3H), 2.93 (t, *J* = 8.0 Hz, 2H);

^{13}C-NMR (126 MHz, $CDCl_3$): δ/ppm = 161.3, 146.7, 144.9, 144.7, 135.5, 124.5, 123.7, 122.4, 111.5, 45.0, 32.1, 19.8;

ESI-MS: calculated $[C_{12}H_{11}NO_3SH]^+$: 250.0538, found: 250.0531;

ATR-FTIR (cm^{-1}): 3146, 3008, 2984, 2911, 1630, 1549, 1458, 1418, 1386, 1325, 1305, 1276, 1144, 1101, 1079, 978, 895, 765, 756, 748.

8-cyano-4,5-dihydrothieno[2,3-*f*]quinoline (4ca)



Following the general procedure, 3-chloro-2-(2-(thiophen-3-yl)ethyl)-5-cyanopyridine **3ca** (99.2 mg, 0.40 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 5 mol%), $PCy_3 \cdot HBF_4$ (14.7 mg, 0.04 mmol, 10 mol%) and K_2CO_3 (110.6 mg, 0.8 mmol, 2.0 equiv.) were added to a pressurizable flask. The flask was purged with argon and 4.0 mL of 1,4-dioxane and 0.4 mL of dem. H_2O were added. The resulting mixture was heated to 150 °C for 18 h. Purification by column chromatography on silica (hexane/EtOAc = 15/1) afforded 8-cyano-4,5-dihydrothieno[2,3-f]quinoline **4ca** as a white solid (84 mg, 0.39 mmol, 99%).

Yield of the one-pot reaction: 14 mg, 0.07 mmol, 17%;

R_f (hexane/EtOAc = 5:3): 0.51;

Melting point: 98 – 99 °C;

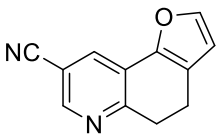
^{1}H-NMR (500 MHz, $CDCl_3$): δ/ppm = 8.57 (d, *J* = 2.0 Hz, 1H), 7.76 (d, *J* = 2.0 Hz, 1H), 7.34 (d, *J* = 5.0 Hz, 1H), 6.96 (dt, *J* = 5.0, 0.5 Hz, 1H), 3.26 – 3.21 (m, 2H), 3.04 – 3.00 (m, 2H);

^{13}C-NMR (126 MHz, $CDCl_3$): δ/ppm = 159.9, 149.2, 139.6, 132.1, 131.2, 128.2, 127.9, 126.9, 117.0, 108.4, 32.2, 23.4;

ESI-MS: calculated $[C_{12}H_8N_2SH]^+$: 213.0487, found: 213.0483;

ATR-FTIR (cm^{-1}): 3058, 2939, 2906, 2848, 2229, 1591, 1534, 1436, 1421, 1390, 1301, 1210, 1149, 1073, 996, 898, 876, 858, 812, 761, 718, 699, 673.

8-cyano-4,5-dihydrofuro[2,3-*f*]quinoline (4cb)



Following the general procedure, 3-chloro-2-(2-(furan-3-yl)ethyl)-5-cyanopyridine **3cb** (92.8 mg, 0.40 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 5 mol%), $PCy_3 \cdot HBF_4$ (14.7 mg, 0.04 mmol, 10 mol%) and K_2CO_3 (110.6 mg, 0.8 mmol, 2.0 equiv.) were added to a pressurizable flask. The flask was purged with argon and 4.0 mL of 1,4-dioxane and 0.4 mL of dem. H_2O were added. The resulting mixture was heated to 150 °C for 18 h. Purification by column

chromatography on silica (hexane/EtOAc = 10/1) afforded 8-cyano-4,5-dihydrofuro[2,3-f]quinoline **4cb** as a white solid (59 mg, 0.30 mmol, 75%).

R_f (hexane/EtOAc = 3:1): 0.44;

Melting point: 85 – 86 °C;

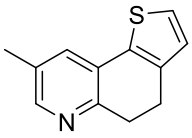
^{1}H-NMR (500 MHz, $CDCl_3$): δ/ppm = 8.52 (d, *J* = 2.0 Hz, 1H), 7.83 (dd, *J* = 2.0, 0.3 Hz, 1H), 7.48 (d, *J* = 1.8 Hz, 1H), 6.41 (dt, *J* = 1.8, 0.4 Hz, 1H), 3.27 – 3.20 (m, 2H), 2.94 – 2.88 (m, 2H);

^{13}C-NMR (126 MHz, $CDCl_3$): δ/ppm = 160.1, 148.9, 146.5, 144.9, 127.5, 124.4, 122.3, 117.2, 111.5, 108.2, 32.1, 9.8;

ESI-MS: calculated $[C_{12}H_8N_2OH]^+$: 197.0715, found: 197.0709;

ATR-FTIR (cm^{-1}): 3118, 3061, 2919, 2851, 2231, 1703, 1630, 1545, 1457, 1385, 1197, 1082, 1028, 906, 883, 743, 703.

8-methyl-4,5-dihydrothieno[2,3-*f*]quinoline (4da)



Following the general procedure, 3-chloro-5-methyl-2-(2-(thiophen-3-yl)ethyl)pyridine **3da** (94.8 mg, 0.40 mmol), $Pd(OAc)_2$ (9.0 mg, 0.04 mmol, 10 mol%), $PCy_3{\cdot}HBF_4$ (29.5 mg, 0.08 mmol, 20 mol%) and K_2CO_3 (110.6 mg, 0.8 mmol, 2.0 equiv.) were added to a pressurizable flask. The flask was purged with argon and 4.0 mL of 1,4-dioxane and 0.4 mL of dem. H_2O were added. The resulting mixture was heated to 150 °C for 18 h. Purification by column chromatography on silica (hexane/EtOAc = 5/1) afforded 4,5-dihydrothieno[2,3-f]quinoline **4da** as a pale yellow oil (79 mg, 0.39 mmol, 98%).

Yield of the one-pot reaction: 55 mg, 0.27 mmol, 68%;

R_f (hexane/EtOAc = 1:1): 0.37;

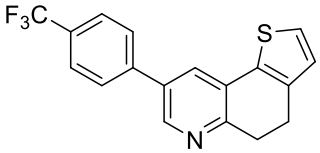
^{1}H-NMR (500 MHz, $CDCl_3$): δ/ppm = 8.14 (dd, *J* = 2.0, 0.9 Hz, 1H), 7.38 (dd, *J* = 1.8, 0.8 Hz, 1H), 7.20 (d, *J* = 5.0 Hz, 1H), 6.91 (dt, *J* = 5.0, 0.5 Hz, 1H), 3.14 – 3.08 (m, 2H), 2.97 – 2.92 (m, 2H), 2.32 – 2.29 (m, 3H);

^{13}C-NMR (126 MHz, $CDCl_3$): δ/ppm = 152.6, 147.2, 138.0, 134.3, 131.6, 130.2, 128.0, 126.8, 124.6, 31.4, 24.0, 18.3;

ESI-MS: calculated $[C_{12}H_{11}NSH]^+$: 202.0690, found: 202.0690;

ATR-FTIR (cm^{-1}): 2933, 2891, 2842, 1600, 1558, 1448, 1391, 1233, 1208, 1089, 965, 875, 808, 762, 724, 701.

8-(4-(trifluoromethyl)phenyl)-4,5-dihydrothieno[2,3-*f*]quinoline (4ea)



Following the general procedure, 3-chloro-2-(2-(thiophen-3-yl)ethyl)-5-(4-(trifluoromethyl)phenyl)pyridine **3ea** (146.8 mg, 0.40 mmol), $Pd(OAc)_2$ (9.0 mg, 0.04 mmol, 10 mol%), $PCy_3{\cdot}HBF_4$ (29.5 mg, 0.08 mmol, 20 mol%) and K_2CO_3 (110.6 mg, 0.8 mmol, 2.0 equiv.) were added to a pressurizable flask. The flask was purged with argon and 4.0 mL of 1,4-dioxane and 0.4 mL of dem. H_2O were added. The resulting mixture was heated to 150 °C for 18 h. Purification by column chromatography on silica (hexane/EtOAc = 5/3) afforded 8-(4-(trifluoromethyl)phenyl)-4,5-dihydrothieno[2,3-f]quinoline **4ea** as a white solid (128 mg, 0.39 mmol, 97%).

Yield of the one-pot reaction: 49 mg, 0.15 mmol, 37%;

R_f (hexane/EtOAc = 5:3): 0.46;

Melting point: 75 – 76 °C;

^{1}H-NMR (500 MHz, $CDCl_3$): δ/ppm = 8.55 (d, *J* = 2.2 Hz, 1H), 7.76 – 7.70 (m, 5H), 7.29 (d, *J* = 5.0 Hz, 1H), 6.97 (d, *J* = 5.0 Hz, 1H), 3.25 – 3.22 (m, 2H), 3.06 – 3.00 (m, 2H);

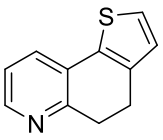
^{13}C-NMR (126 MHz, $CDCl_3$): δ/ppm = 155.3, 145.1, 141.5, 138.7, 134.0 (d, *J* = 49.1 Hz), 130.3 (d, *J* = 32.7 Hz), 128.2, 127.9, 127.6, 127.5, 126.2 (q, *J* = 3.8 Hz), 125.4, 124.3 (q, *J* = 272.1 Hz), 31.6, 23.9;

^{19}F-NMR (377 MHz, $CDCl_3$): δ/ppm = -62.5;

ESI-MS: calculated $[C_{18}H_{12}F_3NSH]^+$: 332.0721, found: 332.0716;

ATR-FTIR (cm^{-1}): 3057, 2941, 1920, 1616, 1582, 1442, 1414, 1389, 1377, 1322, 1162, 1101, 1072, 1053, 1014, 986, 704.

4,5-dihydrothieno[2,3-*f*]quinoline (4fa)



Following the general procedure, 3-chloro-2-(2-(thiophen-3-yl)ethyl)pyridine **3fa** (89.2 mg, 0.40 mmol), $Pd(OAc)_2$ (9.0 mg, 0.04 mmol, 10 mol%), $PCy_3 \cdot HBF_4$ (29.5 mg, 0.08 mmol, 20 mol%) and K_2CO_3 (110.6 mg, 0.8 mmol, 2.0 equiv.) were added to a pressurizable flask. The flask was purged with argon and 4.0 mL of 1,4-dioxane and 0.4 mL of dem. H_2O were added. The resulting mixture was heated to 150 °C for 18 h. Purification by column chromatography on silica (hexane/EtOAc = 5/1) afforded 4,5-dihydrothieno[2,3-f]quinoline **4fa** as a pale yellow oil (72 mg, 0.38 mmol, 96%).

Yield of the one-pot reaction: 50 mg, 0.27 mmol, 67%;

R_f (hexane/EtOAc = 5:3): 0.35;

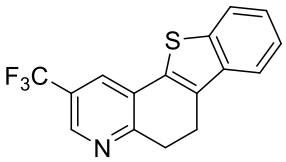
^{1}H-NMR (500 MHz, $CDCl_3$): δ/ppm = 8.31 (dd, *J* = 4.9, 1.6 Hz, 1H), 7.56 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.22 (d, *J* = 5.0 Hz, 1H), 7.12 (ddt, *J* = 7.7, 5.0, 0.6 Hz, 1H), 6.92 (dt, *J* = 5.0, 0.6 Hz, 1H), 3.19 – 3.13 (m, 2H), 3.00 – 2.94 (m, 2H);

^{13}C-NMR (126 MHz, $CDCl_3$): δ/ppm = 155.4, 146.9, 138.0, 134.2, 129.5, 128.0, 127.4, 124.8, 122.2, 31.8, 23.8;

ESI-MS: calculated $[C_{11}H_9NSH]^+$: 188.0534, found: 188.0533;

ATR-FTIR (cm^{-1}): 3051, 2935, 2891, 2838, 1585, 1567, 1459, 1440, 1415, 1385, 1309, 1230, 1203, 1119, 978, 857, 797, 788, 715, 692.

2-(trifluoromethyl)-5,6-dihydrobenzo[4,5]thieno[2,3-*f*]quinoline (4ac)



Following the general procedure, 2-(2-(benzo[b]thiophen-3-yl)ethyl)-3-chloro-5-(trifluoromethyl)pyridine **3ac** (136.7 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 5 mol%), $PCy_3 \cdot HBF_4$ (14.7 mg, 0.04 mmol, 10 mol%) and K_2CO_3 (110.6 mg, 0.8 mmol, 2.0 equiv.) were added to a pressurizable flask. The flask was purged with argon and 4.0 mL of 1,4-dioxane and 0.4 mL of dem. H_2O were added. The resulting mixture was heated to 150 °C for 18 h. Purification by column chromatography on silica (pentane/EtOAc = 9/1) afforded 2-(trifluoromethyl)-5,6-dihydrobenzo[4,5]thieno[2,3-*f*]quinoline **4ac** as a white solid (112 mg, 0.37 mmol, 92%).

Yield of the one-pot reaction: 77 mg, 0.25 mmol, 63%;

R_f (n-pentane/EtOAc = 9:1): 0.25;

Melting point: 133 - 135 °C;

^{1}H-NMR (300 MHz, $CDCl_3$): δ/ppm = 8.63 (dd, *J* = 2.1, 1.0 Hz, 1H), 7.90 – 7.84 (m, 1H), 7.80 – 7.70 (m, 2H), 7.49 – 7.33 (m, 2H), 3.43 – 3.29 (m, 2H), 3.20 (ddd, *J* = 8.7, 7.3, 1.2 Hz, 2H);

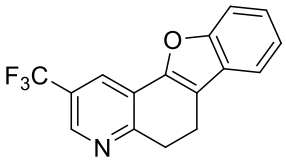
^{13}C-NMR (101 MHz, $CDCl_3$): δ/ppm = 160.2 (d, *J* = 1 Hz), 144.1 (q, *J* = 4 Hz), 140.0, 138.6, 133.6, 132.8, 127.6, 126.9 (q, *J* = 4 Hz), 125.8, 125.5 (q, *J* = 33 Hz), 125.0, 123.7 (q, *J* = 273 Hz), 123.1, 122.2, 31.4, 21.7;

^{19}F-NMR (282 MHz, $CDCl_3$): δ/ppm = -62.4;

ESI-MS: calculated $[C_{16}H_{10}F_3NSH]^+$: 306.0564, found: 306.0559;

ATR-FTIR (cm^{-1}): 1574, 1539, 1439, 1427, 1408, 1339, 1312, 1269, 1250, 1169, 1123, 1084, 1049, 1022, 991, 918, 903, 845, 756, 733, 710, 687, 664.

2-(trifluoromethyl)-5,6-dihydrobenzofuro[2,3-*f*]quinoline (4ad)



Following the general procedure, 2-(2-(benzofuran-3-yl)ethyl)-3-chloro-5-(trifluoromethyl)pyridine **3ad** (130.3 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 5 mol%), $PCy_3{\cdot}HBF_4$ (14.7 mg, 0.04 mmol, 10 mol%) and K_2CO_3 (110.6 mg, 0.8 mmol, 2.0 equiv.) were added to a pressurizable flask. The flask was purged with argon and 4.0 mL of 1,4-dioxane and 0.4 mL of dem. H_2O were added. The resulting mixture was heated to 150 °C for 18 h. Purification by column chromatography on silica (pentane/EtOAc = 9/1) afforded 2-(trifluoromethyl)-5,6-dihydrobenzofuro[2,3-*f*]quinoline **4ad** as a white solid (112 mg, 0.39 mmol, 97%).

Yield of the one-pot reaction: 35 mg, 0.12 mmol, 30%;

R_f (n-pentane/EtOAc = 9:1): 0.27;

Melting point: 130 – 132 °C;

^{1}H-NMR (300 MHz, $CDCl_3$): δ/ppm = 8.61 (dd, *J* = 2.3, 1.1 Hz, 1H), 8.04 (d, *J* = 2.2 Hz, 1H), 7.58 – 7.50 (m, 2H), 7.39 – 7.24 (m, 2H), 3.42 – 3.33 (m, 2H), 3.17 – 3.08 (m, 2H);

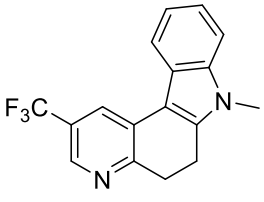
^{13}C-NMR (101 MHz, $CDCl_3$): δ/ppm = 160.6 (d, *J* = 2 Hz), 156.2, 148.7, 144.0 (q, *J* = 4 Hz), 127.6, 125.6, 125.4 (q, *J* = 33 Hz), 124.0, 123.8 (q, *J* = 273 Hz), 123.7 (q, *J* = 4 Hz), 123.5, 120.0, 116.7, 111.8, 31.5, 18.4;

^{19}F-NMR (282 MHz, $CDCl_3$): δ/ppm = -62.5;

ESI-MS: calculated $[C_{16}H_{10}F_3NOH]^+$: 290,0793, found: 290.0787;

ATR-FTIR (cm^{-1}): 1435, 1420, 1350, 1327, 1304, 1292, 1238, 1180, 1146, 1111, 1099, 1080, 1049, 1007, 930, 910, 891, 845, 787, 745, 729, 714, 679.

7-methyl-2-(trifluoromethyl)-6,7-dihydro-5*H*-pyrido[2,3-*c*]carbazole (4ae)



Following the general procedure, 2-(2-(3-chloro-5-(trifluoromethyl)pyridin-2-yl)ethyl)-1-methyl-1*H*-indole **3ae** (150.7 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 5 mol%), $PCy_3{\cdot}HBF_4$ (14.7 mg, 0.04 mmol, 10 mol%) and K_2CO_3 (110.6 mg, 0.8 mmol, 2.0 equiv.) were added to a pressurizable flask. The flask was purged with argon and 4.0 mL of 1,4-dioxane and 0.4 mL of dem. H_2O were added. The resulting mixture was heated to 150 °C for 18 h. Purification by column chromatography on silica (pentane/EtOAc = 1/1) afforded 7-methyl-2-(trifluoromethyl)-6,7-dihydro-5*H*-pyrido[2,3-*c*]carbazole **4ae** as a white solid (102 mg, 0.34 mmol, 84%).

R_f (n-pentane/EtOAc = 1:1): 0.25;

Melting point: 192 – 194 °C;

^{1}H-NMR (300 MHz, $CDCl_3$): δ/ppm = 8.47 (dd, *J* = 2.2, 1.1 Hz, 1H), 8.14 (d, *J* = 2.1 Hz, 1H), 7.92 (ddt, *J* = 6.3, 4.0, 2.0 Hz, 1H), 7.42 – 7.34 (m, 1H), 7.33 – 7.23 (m, 2H), 3.75 (s, 3H), 3.34 (t, *J* = 7.9 Hz, 2H), 3.20 – 3.08 (m, 2H);

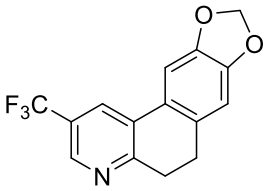
^{13}C-NMR (75 MHz, $CDCl_3$): δ/ppm = 158.0 (d, *J* = 2 Hz), 140.5 (q, *J* = 4 Hz), 139.7, 138.3, 129.9, 125.3 (q, *J* = 32 Hz), 124.4, 124.2 (q, *J* = 272 Hz), 124.1 (q, *J* = 4 Hz), 122.1, 121.3, 119.1, 110.0, 107.4, 32.0, 29.8, 20.4;

^{19}F-NMR (282 MHz, $CDCl_3$): δ/ppm = -62.3;

ESI-MS: calculated $[C_{17}H_{13}F_3N_2H]^+$: 303.1104, found: 303.1109;

ATR-FTIR (cm^{-1}): 3063, 2940, 1605, 1543, 1481, 1466, 1412, 1366, 1343, 1312, 1265, 1234, 1188, 1142, 1111, 1080, 1018, 964, 887, 849, 772, 733, 679, 664, 610, 563.

2-(trifluoromethyl)-5,6-dihydro-[1,3]dioxolo[4',5':4,5]benzo[1,2-*f*]quinolone (4af)



Following the general procedure, 2-(2-(benzo[*d*][1,3]dioxol-5-yl)ethyl)-3-chloro-5-(trifluoromethyl)pyridine **3af** (131.9 mg, 0.4 mmol), $Pd(OAc)_2$ (9.0 mg, 0.04 mmol, 10 mol%), $PCy_3 \cdot HBF_4$ (29.5 mg, 0.08 mmol, 20 mol%) and K_2CO_3 (110.6 mg, 0.8 mmol, 2.0 equiv.) were added to a pressurizable flask. The flask was purged with argon and 4.0 mL of 1,4-dioxane and 0.4 mL of dem. H_2O were added. The resulting mixture was heated to 150 °C for 18 h. Purification by column chromatography on silica (pentane/EtOAc = 9/1) afforded 2-(trifluoromethyl)-5,6-dihydro-[1,3]dioxolo[4',5':4,5]benzo[1,2-*f*]quinolone **4af** as a white solid (101 mg, 0.34 mmol, 86%).

Yield of the one-pot reaction: 73 mg, 0.25 mmol, 62%;

R*f* (n-pentane/EtOAc = 9:1): 0.33;

Melting point: 157 – 159 °C;

^{1}H-NMR (400 MHz, $CDCl_3$): δ/ppm = 8.65 (dd, *J* = 2.2, 1.0 Hz, 1H), 8.56 (d, *J* = 1.8 Hz, 1H), 6.81 – 6.71 (m, 2H), 6.09 (s, 2H), 3.14 (dd, *J* = 8.7, 5.7 Hz, 2H), 3.02 – 2.81 (m, 2H);

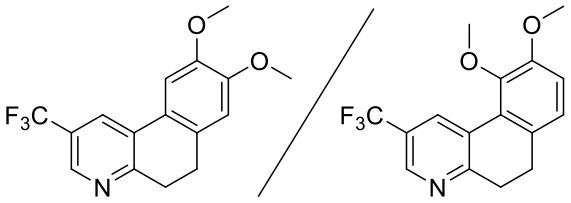
^{13}C-NMR (101 MHz, $CDCl_3$): δ/ppm = 161.3 (d, *J* = 2 Hz), 147.0, 145.3, 144.2 (q, *J* = 4 Hz), 130.8 (q, *J* = 4 Hz), 130.6, 127.2, 125.2 (q, *J* = 33 Hz), 123.9 (q, *J* = 272 Hz), 120.8, 114.8, 108.7, 101.6, 32.4, 28.0;

^{19}F-NMR (282 MHz, $CDCl_3$): δ/ppm = -62.2;

ESI-MS: calculated $[C_{15}H_{10}F_3NO_2H]^+$: 294.0742, found: 294.0746;

ATR-FTIR (cm^{-1}): 2963, 2916, 1717, 1605, 1489, 1466, 1435, 1400, 1331, 1304, 1273, 1246, 1161, 1119, 1088, 1045, 1030, 995, 961, 914, 822, 799, 737, 714, 667.

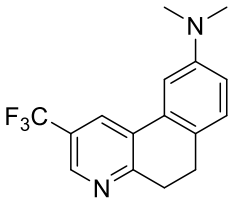
8,9-dimethoxy-2-(trifluoromethyl)-5,6-dihydrobenzo[*f*]quinoline (4ag)



Following the general procedure, 2-(2-(benzo[*d*][1,3]dioxol-5-yl)ethyl)-3-chloro-5-(trifluoromethyl)pyridine **3ag** (138.3 mg, 0.4 mmol), $Pd(OAc)_2$ (9.0 mg, 0.04 mmol, 10 mol%), $PCy_3 \cdot HBF_4$ (29.5 mg, 0.08 mmol, 20 mol%) and K_2CO_3 (110.6 mg, 0.8 mmol, 2.0 equiv.) were added to a pressurizable flask. The flask was purged with argon and 4.0 mL of 1,4-dioxane and 0.4 mL of dem. H_2O were added. The resulting mixture was heated to 150 °C for 18 h. Analysis by GC-MS showed a mixture of **4ag**, its regioisomer **4ag'** and traces of their corresponding oxidized analogues **5ag** and **5ag'**. The mixture proofed to be inseparable by column column chromatography on silica. Yields and ratios of regioisomers given were determined by GC-MS analysis. Yields: **4ag** = 52%, **4ag'** = 19%.

Yields of the one-pot reaction: 4ag = 46%, **4ag'** = 23%.;

***N*,*N*-dimethyl-2-(trifluoromethyl)-5,6-dihydrobenzo[*f*]quinolin-9-amine (4ah)**



Following the general procedure, 4-(2-(3-chloro-5-(trifluoromethyl)pyridin-2-yl)ethyl)-*N*,*N*-dimethylaniline **3ah** (131.5 mg, 0.4 mmol), $Pd(OAc)_2$ (9.0 mg, 0.04 mmol, 10 mol%), $PCy_3 \cdot HBF_4$ (29.5 mg, 0.08 mmol, 20 mol%) and K_2CO_3 (110.6 mg, 0.8 mmol, 2.0 equiv.) were added to a pressurizable flask. The flask was purged with argon and 4.0 mL of 1,4-dioxane and 0.4 mL of dem. H_2O were added. The resulting mixture was heated to 150 °C for 18 h. Purification by column chromatography on silica (pentane/EtOAc = 9/1) afforded *N*,*N*-dimethyl-2-(trifluoromethyl)-5,6-dihydrobenzo[*f*]quinolin-9-amine **4ah** as an inseparable 1.2:1 mixture with *N*,*N*-dimethyl-2-(trifluoromethyl)benzo[*f*]quinolin-9-amine **5ah** as a bright yellow solid (95 mg, 0.33 mmol, 81% combined yield).

Yield of the one-pot reaction: 50 mg, 0.17 mmol, 43% yield (**4ah**:**5ah** = 1.2:1);

R_f (n-pentane/EtOAc = 9:1): 0.27;

Melting point: 119 – 121 °C;

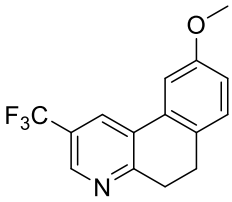
^{1}H-NMR (400 MHz, $CDCl_3$): δ/ppm = 8.66 (dd, *J* = 2.2, 1.0 Hz, 1H), 8.13 (d, *J* = 2.1 Hz, 1H), 7.16 (d, *J* = 8.4 Hz, 1H), 7.02 (d, *J* = 2.6 Hz, 1H), 6.75 (dd, *J* = 8.4, 2.6 Hz, 1H), 3.13 (dd, *J* = 8.6, 6.0 Hz, 2H), 3.02 (s, 6H), 2.92 (dd, *J* = 8.6, 5.9 Hz, 2H);

^{13}C-NMR (101 MHz, $CDCl_3$): δ/ppm = 162.3 (d, *J* = 2 Hz), 150.4, 144.1 (q, *J* = 4 Hz), 131.9, 130.7, 129.2, 127.2 (q, *J* = 4 Hz), 125.4 (q, *J* = 33 Hz), 124.0 (q, *J* = 272 Hz), 123.0, 114.2, 107.9, 41.1, 32.5, 27.2;

^{19}F-NMR (282 MHz, $CDCl_3$): δ/ppm = -62.1;

ESI-MS: calculated $[C_{16}H_{15}F_3N_2H]^+$: 293.1266, found: 293.1261;

9-methoxy-2-(trifluoromethyl)-5,6-dihydrobenzo[*f*]quinoline (4ai)



Following the general procedure, 3-chloro-2-(4-methoxyphenethyl)-5-(trifluoromethyl)pyridine **3ai** (126.3 mg, 0.4 mmol), $Pd(OAc)_2$ (9.0 mg, 0.04 mmol, 10 mol%), $PCy_3{\cdot}HBF_4$ (29.5 mg, 0.08 mmol, 20 mol%) and K_2CO_3 (110.6 mg, 0.8 mmol, 2.0 equiv.) were added to a pressurizable flask. The flask was purged with argon and 4.0 mL of 1,4-dioxane and 0.4 mL of dem. H_2O were added. The resulting mixture was heated to 150 °C for 18 h. Purification by column chromatography on silica (pentane/EtOAc = 9/1) afforded 9-methoxy-2-(trifluoromethyl)-5,6-dihydrobenzo[*f*]quinoline **4ai** as a white solid (58 mg, 0.21 mmol, 52%).

Yield of the one-pot reaction: 47 mg, 0.17 mmol, 42%;

R_f (n-pentane/EtOAc = 9:1): 0.29;

Melting point: 67 – 69 °C;

^{1}H-NMR (400 MHz, $CDCl_3$): δ/ppm = 8.68 (d, *J* = 2.1 Hz, 1H), 8.13 (d, *J* = 2.2 Hz, 1H), 7.25 – 7.19 (m, 2H), 6.89 (dd, *J* = 8.4, 2.6 Hz, 1H), 3,88 (s, 1H), 3.15 (dd, *J* = 8.7, 5.9 Hz, 2H), 2.96 (dd, *J* = 8.7, 5.9 Hz, 2H);

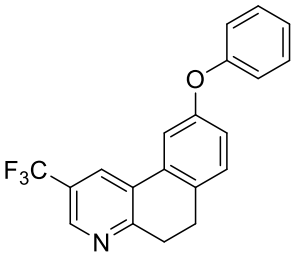
^{13}C-NMR (101 MHz, $CDCl_3$): δ/ppm = 162.0, 159.2, 144.5 (d, *J* = 3 Hz), 136.1, 132.6, 129.6, 129.3, 127.6 (q, *J* = 4 Hz), 125.6 (q, *J* = 34 Hz), 123.9 (q, *J* = 273 Hz), 114.8, 109.9, 55.7, 32.2, 27.4;

^{19}F-NMR (282 MHz, $CDCl_3$): δ/ppm = -62.2;

ESI-MS: calculated $[C_{15}H_{12}F_3NOH]^+$: 280.0949, found: 280.0945;

ATR-FTIR (cm^{-1}): 1717, 1613, 1582, 1505, 1431, 1393, 1335, 1288, 1265, 1223, 1126, 1092, 1034, 984, 914, 868, 814, 737, 702.

9-phenoxy-2-(trifluoromethyl)-5,6-dihydrobenzo[*f*]quinoline (4aj)



Following the general procedure, 3-chloro-2-(4-phenoxyphenethyl)-5-(trifluoromethyl)pyridine **3aj** (151.1 mg, 0.4 mmol), $Pd(OAc)_2$ (9.0 mg, 0.04 mmol, 10 mol%), $PCy_3{\cdot}HBF_4$ (29.5 mg, 0.08 mmol, 20 mol%) and K_2CO_3 (110.6 mg, 0.8 mmol, 2.0 equiv.) were added to a pressurizable flask. The flask was purged with argon and 4.0 mL of 1,4-dioxane and 0.4 mL of dem. H_2O were added. The resulting mixture was heated to 150 °C for 18 h. Purification by column chromatography on silica (pentane/EtOAc = 9/1) afforded 9-phenoxy-2-(trifluoromethyl)-5,6-dihydrobenzo[*f*]quinoline **4aj** as a white solid (62 mg, 0.18 mmol, 45%).

Yield of the one-pot reaction: 50 mg, 0.15 mmol, 37%;

R_f (n-pentane/EtOAc = 9:1): 0.29;

Melting point: 55 – 57 °C;

^{1}H-NMR (400 MHz, $CDCl_3$): δ/ppm = 8.70 (d, *J* = 2.1 Hz, 1H), 8.07 (d, *J* = 2.1 Hz, 1H), 7.43 (d, *J* = 2.4 Hz, 1H), 7.42 – 7.31 (m, 2H), 7.27 (d, *J* = 6.7 Hz, 1H), 7.15 – 7.10 (m, 1H), 7.08 – 7.00 (m, 2H), 6.98 (dd, *J* = 8.2, 2.4 Hz, 1H), 3.19 (dd, *J* = 8.7, 6.0 Hz, 2H), 3.02 (dd, *J* = 8.7, 5.9 Hz, 2H);

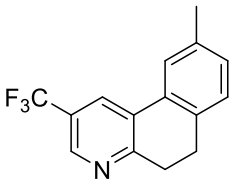
^{13}C-NMR (101 MHz, $CDCl_3$): δ/ppm = 161.7 (d, *J* = 2 Hz), 157.5, 156.6, 144.7 (q, *J* = 4 Hz), 133.2, 132.1, 130.0, 129.9, 129.6, 127.7 (q, *J* = 4 Hz), 125.6 (q, *J* = 33 Hz), 123.8 (q, *J* = 272 Hz), 123.4, 120.0, 118.6, 115.2, 32.0, 27.6;

^{19}F-NMR (282 MHz, $CDCl_3$): δ/ppm = -62.2;

ESI-MS: calculated $[C_{20}H_{14}F_3NOH]^+$: 342.1106, found: 342.1107;

ATR-FTIR (cm^{-1}): 1613, 1589, 1489, 1435, 1335, 1296, 1277, 1223, 1123, 1092, 1076, 1038, 1026, 941, 918, 872, 829, 756, 737, 691, 664.

9-methyl-2-(trifluoromethyl)-5,6-dihydrobenzo[*f*]quinoline (4ak)



Following the general procedure, 3-chloro-2-(4-methylphenethyl)-5-(trifluoromethyl)pyridine **3ak** (119.9 mg, 0.4 mmol), $Pd(OAc)_2$ (9.0 mg, 0.04 mmol, 10 mol%), $PCy_3 \cdot HBF_4$ (29.5 mg, 0.08 mmol, 20 mol%) and K_2CO_3 (110.6 mg, 0.8 mmol, 2.0 equiv.) were added to a pressurizable flask. The flask was purged with argon and 4.0 mL of 1,4-dioxane and 0.4 mL of dem. H_2O were added. The resulting mixture was heated to 150 °C for 18 h. Purification by column chromatography on silica (pentane/EtOAc = 9/1) afforded 9-methyl-2-(trifluoromethyl)-5,6-dihydrobenzo[*f*]quinoline **4ak** as a white solid (37 mg, 0.14 mmol, 35%).

Yield of the one-pot reaction: 26 mg, 0.10 mmol, 24%;

R_f (n-pentane/EtOAc = 9:1): 0.41;

Melting point: 63 – 65 °C;

^{1}H-NMR (400 MHz, $CDCl_3$): δ/ppm **=** 8.67 (s, 1H), 8.17 (d, *J* = 2.1 Hz, 1H), 7.54 (d, *J* = 1.6 Hz, 1H), 7.22 – 7.12 (m, 2H), 3.15 (dd, *J* = 8.7, 5.8 Hz, 2H), 2.98 (dd, *J* = 8.7, 5.8 Hz, 2H), 2.42 (s, 1H);

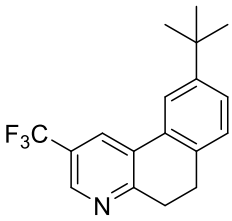
^{13}C-NMR (75 MHz, $CDCl_3$): δ/ppm **=** 161.8 (d, *J* = 2 Hz), 144.2 (q, *J* = 4 Hz), 137.2, 134.1, 131.4, 130.2, 128.5, 127.4 (q, *J* = 4 Hz), 125.5 (q, *J* = 34 Hz), 124.8, 124.0 (q, *J* = 272 Hz), 32.0, 27.8, 21,4;

^{19}F-NMR (282 MHz, $CDCl_3$): δ/ppm **=** -62.2;

ESI-MS: calculated $[C_{15}H_{12}F_3NH]^+$: 264.1000, found: 264.0999;

ATR-FTIR (cm^{-1}): 2951, 2909, 2851, 1605, 1505, 1435, 1381, 1335, 1296, 1281, 1261, 1242, 1115, 1088, 1045, 1026, 1003, 910, 880, 806, 768, 702.

9-(*tert*-butyl)-2-(trifluoromethyl)-5,6-dihydrobenzo[*f*]quinoline (4al)



Following the general procedure, 2-(4-(*tert*-butyl)phenethyl)-3-chloro-5-(trifluoromethyl)pyridine **3al** (136.7 mg, 0.4 mmol), $Pd(OAc)_2$ (9.0 mg, 0.04 mmol, 10 mol%), $PCy_3 \cdot HBF_4$ (29.5 mg, 0.08 mmol, 20 mol%) and K_2CO_3 (110.6 mg, 0.8 mmol, 2.0 equiv.) were added to a pressurizable flask. The flask was purged with argon and 4.0 mL of 1,4-dioxane and 0.4 mL of dem. H_2O were added. The resulting mixture was heated to 150 °C for 18 h. Purification by column chromatography on silica (pentane/EtOAc = 9/1) afforded 9-(*tert*-butyl)-2-(trifluoromethyl)-5,6-dihydrobenzo[*f*]quinoline **4al** as a white solid (35 mg, 0.12 mmol, 29%).

Yield of the one-pot reaction: 37 mg, 0.12 mmol, 30%;

R_f (n-pentane/EtOAc = 9:1): 0.43;

Melting point: 116 – 118 °C;

^{1}H-NMR (400 MHz, $CDCl_3$): δ/ppm = 8.68 (s, 1H), 8.18 (d, *J* = 2.1 Hz, 1H), 7.73 (d, *J* = 1.9 Hz, 1H), 7.39 (dd, *J* = 7.9, 2.0 Hz, 1H), 7.24 (d, *J* = 7.9 Hz, 1H), 3.16 (dd, *J* = 8.7, 5.9 Hz, 2H), 3.00 (dd, *J* = 8.7, 5.8 Hz, 2H), 1.40 (s, 9H);

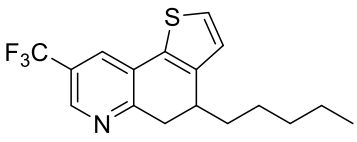
^{13}C-NMR (75 MHz, $CDCl_3$): δ/ppm = 162.0, 150.7, 144.2 (q, *J* = 4 Hz), 137.5, 134.2, 131.1, 128.4, 127.3 (q, *J* = 3 Hz), 126.6, 124.0 (q, *J* = 272 Hz), 121.0, 34.9, 32.0, 31.5, 27.8;

^{19}F-NMR (282 MHz, $CDCl_3$): δ/ppm = -62.1;

ESI-MS: calculated $[C_{18}H_{18}F_3NH]^+$: 306.1464, found: 306.1458;

ATR-FTIR (cm^{-1}): 2955, 2936, 2905, 1613, 1431, 1389, 1366, 1331, 1304, 1242, 1150, 1119, 1092, 1042, 1026, 910, 883, 829, 768, 733, 725, 671.

4-pentyl-8-(trifluoromethyl)-4,5-dihydrothieno[2,3-*f*]quinoline (4ga)



Following the general procedure, 3-chloro-2-(2-(thiophen-3-yl)heptyl)-5-(trifluoromethyl)pyridine **3ga** (144.4 mg, 0.40 mmol), $Pd(OAc)_2$ (8.9 mg, 0.04 mmol, 10 mol%), PCy_3*HBF_4 (29.5 mg, 0.08 mmol, 20 mol%) and K_2CO_3 (110.6 mg, 0.8 mmol, 2.0 equiv.) were added to a pressurizable flask. The flask was purged with argon and 4.0 mL of 1,4-dioxane and 0.4 mL of dem. H_2O were added. The resulting mixture was

heated to 150 °C for 18 h. Purification by column chromatography on silica (petroleum ether/Et_2O = 100/5) afforded 4-pentyl-8-(trifluoromethyl)-4,5-dihydrothieno[2,3-*f*]quinoline **4ga** as a colorless oil (105 mg, 0.32 mmol, 81%).

Yield of the one-pot reaction: 13 mg, 0.04 mmol, 10%;

R_f (petroleum ether/EtOAc = 50:1): 0.50;

^{1}H-NMR (500 MHz, $CDCl_3$): δ/ppm = 8.57 (d, *J* = 1.2 Hz, 1H), 7.47 (d, *J* = 2.1 Hz, 1H), 7.32 (d, *J* = 5.0 Hz, 1H), 7.00 (d, *J* = 5.0 Hz, 1H), 3.37 – 3.27 (m, 1H), 3.14 – 3.04 (m, 2H), 1.64 – 1.40 (m, 3H), 1.83 – 1.23 (m, 5H), 0.87 (t, *J* = 6.8 Hz, 3H);

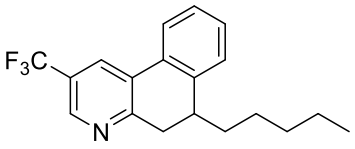
^{13}C-NMR (126 MHz, $CDCl_3$): δ/ppm = 161.7, 159.1 (d, *J* = 1.7 Hz), 143.9, 143.5 (q, *J* = 4.2 Hz), 132.2, 127.8, 127.2, 126.1, 125.7 (q, *J* = 3.4 Hz), 125.5 (q, *J* = 271.1 Hz), 37.7, 34.8, 34.7, 31.9, 26.8, 22.7, 14.2;

^{19}F-NMR (377 MHz, $CDCl_3$): δ/ppm = -62.4;

ESI-MS: calculated $[C_{17}H_{18}F_3NSH]^+$: 326.1185, found: 326.1187;

ATR-FTIR (cm^{-1}): 2956, 2927, 2857, 1339, 1262, 1206, 1151, 1128, 1086, 1000, 907.

6-pentyl-2-(trifluoromethyl)-5,6-dihydrobenzo[*f*]quinoline (4gm)



Following the general procedure, 3-chloro-2-(2-phenylheptyl)-5-(trifluoromethyl)pyridine **3gm** (142.1 mg, 0.40 mmol), $Pd(OAc)_2$ (8.9 mg, 0.04 mmol, 10 mol%), PCy_3*HBF_4 (29.5 mg, 0.08 mmol, 20 mol%) and K_2CO_3 (110.6 mg, 0.8 mmol, 2.0 equiv.) were added to a pressurizable flask. The flask was purged with argon and 4.0 mL of 1,4-dioxane and 0.4 mL of dem. H_2O were added. The resulting mixture was heated to 150 °C for 18 h. Purification by column chromatography on silica (petroleum ether/Et_2O = 100/3) afforded 6-pentyl-2-(trifluoromethyl)-5,6-dihydrobenzo[*f*]quinoline **4gm** as a colorless oil (92 mg, 0.29 mmol, 72%).

Yield of the one-pot reaction: 24 mg, 0.08 mmol, 19%;

R_f (petroleum ether/EtOAc = 50:1): 0.48;

^{1}H-NMR (500 MHz, $CDCl_3$): δ/ppm = 8.69 (s, 1H), 8.17 (d, *J* = 2.1 Hz, 1H), 7.78 – 7.71 (m, 1H), 7.39 – 7.33 (m, 2H), 7.31 – 7.26 (m, 1H), 3.30 (ddd, *J* = 16.1, 5.8, 1.5 Hz, 1H),

3.15, (dd, *J* = 16.1, 3.2 Hz, 1H), 3.08 – 2.95 (m, 1H), 1.43 – 1.33 (m, 3H), 1.28 – 1.18 (m, 5H), 0.86 – 0.82 (m, 3H);

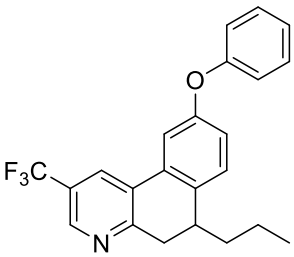
^{13}C-NMR (126 MHz, $CDCl_3$): δ/ppm = 160.6, 144.6 (q, *J* = 4.2 Hz), 141.3, 130.6, 130.0, 129.3, 128.8, 127.5, 127.1 (q, *J* = 3.5 Hz), 125.5 (q, *J* = 32.7 Hz), 124.5, 124.1 (q, *J* = 272.4 Hz), 38.6, 36.9, 34.3, 31.9, 27.2, 22.7, 14.2;

^{19}F-NMR (377 MHz, $CDCl_3$): δ/ppm = -62.2;

ESI-MS: calculated $[C_{19}H_{20}F_3NH]^+$: 320.1621, found: 320.1621;

ATR-FTIR (cm^{-1}): 2957, 2928, 2856, 1409, 1339, 1152, 1130, 1090, 1049, 917, 768.

9-phenoxy-6-propyl-2-(trifluoromethyl)-5,6-dihydrobenzo[*f*]quinoline (4hj)



Following the general procedure, 3-chloro-2-(2-(4-phenoxyphenyl)pentyl)-5-(trifluoromethyl)pyridine **3hj** (84.0 mg, 0.2 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), $PCy_3{\cdot}HBF_4$ (14.7 mg, 0.04 mmol, 20 mol%) and K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.) were added to a pressurizable flask. The flask was purged with argon and 2.0 mL of 1,4-dioxane and 0.2 mL of dem. H_2O were added. The resulting mixture was heated to 150 °C for 18 h. Purification by column chromatography on silica (pentane/EtOAc = 19/1) afforded 9-phenoxy-6-propyl-2-(trifluoromethyl)-5,6-dihydrobenzo[*f*]quinoline **4hj** as a colorless oil (46 mg, 0.12 mmol, 60%).

R_f (n-pentane/EtOAc = 19:1): 0.27;

^{1}H-NMR (300 MHz, $CDCl_3$): δ/ppm = 8.69 (dd, *J* = 2.1, 1.0 Hz, 1H), 8.05 (d, *J* = 2.1 Hz, 1H), 7.42 (d, *J* = 2.5 Hz, 1H), 7.40 – 7.32 (m, 2H), 7.24 (d, *J* = 8.3 Hz, 1H), 7.19 – 7.07 (m, 1H), 7.08 – 7.01 (m, 2H), 6.98 (dd, *J* = 8.3, 2.5 Hz, 1H), 3.32 (ddd, *J* = 16.1, 5.9, 1.4 Hz, 1H), 3.15 (dd, *J* = 16.1, 3.2 Hz, 1H), 3.02 (qd, *J* = 6.8, 3.2 Hz, 1H), 1.43 – 1.20 (m, 4H), 0.92 – 0.81 (m, 3H);

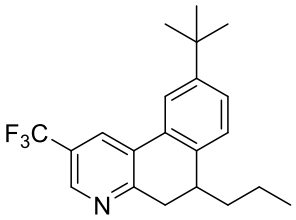
^{13}C-NMR (75 MHz, $CDCl_3$): δ/ppm = 160.7 (d, *J* = 2 Hz), 157.4, 156.5, 144.9 (q, *J* = 4 Hz), 136.2, 132.2, 130.1, 130.0, 129.2, 127.3 (q, *J* = 4 Hz), 125.6 (q, *J* = 33 Hz), 123.9 (q, *J* = 272 Hz), 123.5, 119.8, 118.7, 115.3, 37.7, 37.1, 36.7, 20.6, 14.1;

^{19}F-NMR (282 MHz, $CDCl_3$): δ/ppm = -62.2;

ESI-MS: calculated $[C_{23}H_{20}F_3NOH]^+$: 384.1570, found: 384.1569;

ATR-FTIR (cm^{-1}): 2932, 1589, 1489, 1435, 1397, 1335, 1273, 1219, 1150, 1126, 1088, 1042, 941, 918, 849, 756, 694, 617, 556.

9-(*tert*-butyl)-6-propyl-2-(trifluoromethyl)-5,6-dihydrobenzo[*f*]quinoline (4hl)



Following the general procedure, 2-(2-(4-(*tert*-butyl)phenyl)pentyl)-3-chloro-5-(trifluoromethyl)pyridine **3hl** (76.8 mg, 0.2 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), $PCy_3 \cdot HBF_4$ (14.7 mg, 0.04 mmol, 20 mol%) and K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.) were added to a pressurizable flask. The flask was purged with argon and 2.0 mL of 1,4-dioxane and 0.2 mL of dem. H_2O were added. The resulting mixture was heated to 150 °C for 18 h. Purification by column chromatography on silica (pentane/EtOAc = 19/1) afforded 9-(*tert*-butyl)-6-propyl-2-(trifluoromethyl)-5,6-dihydrobenzo[*f*]quinoline **4hl** as a white solid (32 mg, 0.09 mmol, 46%).

R_f (n-pentane/EtOAc = 19:1): 0.33;

Melting point: 67 – 69 °C;

^{1}H-NMR (300 MHz, $CDCl_3$): δ/ppm = 8.68 (dd, *J* = 2.1, 1.1 Hz, 1H), 8.16 (d, *J* = 2.1 Hz, 1H), 7.71 (d, *J* = 2.0 Hz, 1H), 7.39 (dd, *J* = 7.9, 2.0 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 3.29 (dd, *J* = 16.0, 5.8 Hz, 1H), 3.12 (dd, *J* = 16.0, 3.4 Hz, 1H), 3.00 (ddt, *J* = 12.8, 6.3, 2.9 Hz, 2H), 1.39 (s, 9H), 1.34 – 1.23 (m, 3H), 0.85 (t, *J* = 6.8 Hz, 2H);

^{13}C-NMR (75 MHz, $CDCl_3$): δ/ppm = 160.9 (d, *J* = 1 Hz), 150.4, 144.4 (q, *J* = 4 Hz), 138.3, 130.1, 130.1, 128.4, 127.0 (q, *J* = 4 Hz), 126.5, 125.4 (q, *J* = 33 Hz), 124.0 (q, *J* = 272 Hz), 121.2, 37.8, 37.1, 36.6, 34.9, 31.6, 20.6, 14.2;

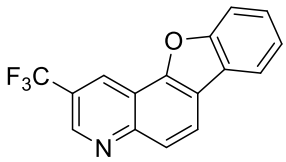
^{19}F-NMR (282 MHz, $CDCl_3$): δ/ppm = -62.1;

ESI-MS: calculated $[C_{21}H_{24}F_3NH]^+$: 348.1934, found: 348.1942;

ATR-FTIR (cm^{-1}): 2963, 2924, 1613, 1505, 1466, 1435, 1366, 1335, 1288, 1273, 1250, 1126, 1088, 1042, 910, 833, 741, 702, 633, 594.

Fully aromatic side products

2-(trifluoromethyl)benzofuro[2,3-*f*]quinoline (5ad)



5ab was obtained as the major byproduct in the one-pot reaction of 3-chloro-5-(trifluoromethyl)-2-vinylpyridine **1a** (83.0 mg, 0.4 mmol) and benzofuran-3-ylboronic acid (97.2 mg, 0.6 mmol, 1.5 equiv.) with [{Rh(C_2H_4)$_2$Cl}$_2$] (6.2 mg, 0.016 mmol, 4 mol%), dppbenz (14.3 mg, 0.032 mmol, 8 mol%), Pd(OAc)$_2$ (4.5 mg, 0.02 mmol, 5 mol%) and PCy$_3$·HBF$_4$ (14.7 mg, 0.04 mmol, 10 mol%) and K_2CO_3 (165.9 mg, 1.2 mmol, 3.0 equiv.) in 4.0 mL of 1,4-dioxane and 0.4 mL of dem. H_2O. Purification by column chromatography on silica (pentane/EtOAc = 9/1) afforded 2-(trifluoromethyl)benzofuro[2,3-*f*]quinoline **5ad** as a white solid (37 mg, 0.13 mmol, 32%).

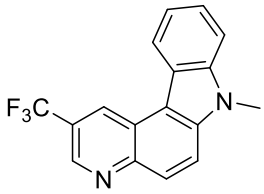
R*f* (n-pentane/EtOAc = 9:1): 0.36;

^{1}H-NMR (300 MHz, CDCl$_3$): δ/ppm = 9.15 (d, *J* = 2.3 Hz, 1H), 9.02 (dt, *J* = 2.1, 1.0 Hz, 1H), 8.35 (d, *J* = 8.8 Hz, 1H), 8.12 (d, *J* = 8.8 Hz, 1H), 8.04 (dt, *J* = 7.6, 0.9 Hz, 1H), 7.73 (dt, *J* = 8.3, 0.8 Hz, 1H), 7.56 (ddd, *J* = 8.4, 7.3, 1.4 Hz, 1H), 7.46 (td, *J* = 7.5, 1.1 Hz, 1H);

^{19}F-NMR (282 MHz, CDCl$_3$): δ/ppm = -61.7;

ESI-MS: calculated [$C_{16}H_8F_3NOH$]$^+$: 288.0631, found: 288.0643;

7-methyl-2-(trifluoromethyl)-7*H*-pyrido[2,3-*c*]carbazole (5ae)



5ae was obtained as the only product in the one-pot reaction of 3-chloro-5-(trifluoromethyl)-2-vinylpyridine **1a** (83.0 mg, 0.4 mmol) and (1-methyl-1*H*-indol-2-yl)boronic acid (105.0 mg, 0.6 mmol, 1.5 equiv.) with [{Rh(C_2H_4)$_2$Cl}$_2$] (6.2 mg, 0.016 mmol, 4 mol%), dppbenz (14.3 mg, 0.032 mmol, 8 mol%), Pd(OAc)$_2$ (4.5 mg, 0.02 mmol, 5 mol%) and PCy$_3$·HBF$_4$ (14.7 mg, 0.04 mmol, 10 mol%) and K_2CO_3 (165.9 mg, 1.2 mmol, 3.0 equiv.) in 4.0 mL of 1,4-dioxane and 0.4 mL of dem. H_2O. Purification by column chromatography on silica (pentane/EtOAc = 1/1) afforded 7-methyl-2-(trifluoromethyl)-7*H*-pyrido[2,3-*c*]carbazole **5ae** as a white solid (90 mg, 0.30 mmol, 75%).

Yield of the two-step reaction: 9 mg, 0.03 mmol, 8%;

R*f* (n-pentane/EtOAc = 1:1): 0.46;

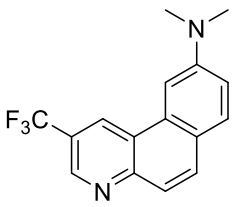
^{1}H-NMR (300 MHz, $CDCl_3$): δ/ppm = 9.26 (dt, *J* = 2.0, 0.9 Hz, 1H), 9.08 (d, *J* = 2.2 Hz, 1H), 8.47 (dt, *J* = 8.0, 1.0 Hz, 1H), 8.21 (dd, *J* = 9.2, 0.8 Hz, 1H), 7.99 (d, *J* = 9.2 Hz, 1H), 7.63 – 7.54 (m, 2H), 7.45 (ddd, *J* = 8.1, 5.7, 2.5 Hz, 1H), 4.03 (s, 3H);

^{13}C-NMR (75 MHz, $CDCl_3$): δ/ppm = 146.1 (dd, *J* = 1 Hz), 142.4 (q, *J* = 3 Hz), 140.5, 138.5, 128.7 (q, *J* = 4 Hz), 127.9, 125.5, 124.3 (d, *J* = 273 Hz), 123.1 (d, *J* = 27 Hz), 121.7, 120.8, 116.3, 110.0, 29.9;

^{19}F-NMR (282 MHz, $CDCl_3$): δ/ppm = -61.2;

ESI-MS: calculated $[C_{17}H_{11}F_3N_2H]^+$: 301.0947, found: 301.0948;

***N*,*N*-dimethyl-2-(trifluoromethyl)benzo[*f*]quinolin-9-amine (5ah)**



5ah was obtained as the major byproduct in the one-pot reaction of 3-chloro-5-(trifluoromethyl)-2-vinylpyridine **1a** (83.0 mg, 0.4 mmol) and (4-(dimethylamino)phenyl)boronic acid (99.0 mg, 0.6 mmol, 1.5 equiv.) with $[\{Rh(C_2H_4)_2Cl\}_2]$ (6.2 mg, 0.016 mmol, 4 mol%), dppbenz (14.3 mg, 0.032 mmol, 8 mol%), $Pd(OAc)_2$ (9.0 mg, 0.04 mmol, 10 mol%) and $PCy_3{\cdot}HBF_4$ (29.5 mg, 0.08 mmol, 20 mol%) and K_2CO_3 (165.9 mg, 1.2 mmol, 3.0 equiv.) in 4.0 mL of 1,4-dioxane and 0.4 mL of dem. H_2O. Purification by column chromatography on silica (pentane/EtOAc = 9/1) afforded *N*,*N*-dimethyl-2-(trifluoromethyl)-5,6-dihydrobenzo[*f*]quinolin-9-amine **4ah** and *N*,*N*-dimethyl-2-(trifluoromethyl)benzo[*f*]quinolin-9-amine **5ah** in a 1.2:1 mixture as a bright yellow solid (50 mg, 0.17 mmol, 43% combined yield).

R_f (n-pentane/EtOAc = 9:1): 0.27;

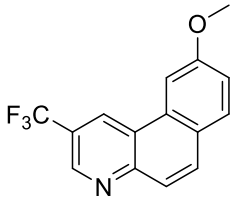
^{1}H-NMR (400 MHz, $CDCl_3$): δ/ppm = 9.11 (d, *J* = 2.1 Hz, 1H), 9.05 (d, *J* = 2.1 Hz, 1H), 7.95 (d, *J* = 8.9 Hz, 1H), 7.79 (d, *J* = 8.9 Hz, 1H), 7.74 (d, *J* = 9.0 Hz, 1H), 7.62 (d, *J* = 2.4 Hz, 1H), 7.22 (dd, *J* = 8.8, 2.5 Hz, 1H), 3.18 (s, 6H);

^{13}C-NMR (101 MHz, $CDCl_3$): δ/ppm = 151.0 (dd, *J* = 3, 1 Hz), 150.1, 145.4 (q, *J* = 4 Hz), 133.4, 131.1, 130.0, 128.3 (q, *J* = 4 Hz), 125.3, 124.3 (d, *J* = 273 Hz), 123.6, 123.5, 122.7 (q, *J* = 33 Hz), 115.9, 102.5, 40.8;

^{19}F-NMR (282 MHz, $CDCl_3$): δ/ppm = -61.0;

ESI-MS: calculated $[C_{16}H_{13}F_3N_2H]^+$: 291.1104, found: 291.1108;

9-methoxy-2-(trifluoromethyl)benzo[*f*]quinoline (5ai)



5ag was obtained as the major byproduct in the one-pot reaction of 3-chloro-5-(trifluoromethyl)-2-vinylpyridine **1a** (83.0 mg, 0.4 mmol) and (4-methoxyphenyl)boronic acid (91.2 mg, 0.6 mmol, 1.5 equiv.) with [{Rh(C_2H_4)$_2$Cl}$_2$] (6.2 mg, 0.016 mmol, 4 mol%), dppbenz (14.3 mg, 0.032 mmol, 8 mol%), Pd(OAc)$_2$ (9.0 mg, 0.04 mmol, 10 mol%) and PCy_3·HBF_4 (29.5 mg, 0.08 mmol, 20 mol%) and K_2CO_3 (165.9 mg, 1.2 mmol, 3.0 equiv.) in 4.0 mL of 1,4-dioxane and 0.4 mL of dem. H_2O. Purification by column chromatography on silica (pentane/EtOAc = 9/1) afforded 9-methoxy-2-(trifluoromethyl)benzo[*f*]quinoline **5ai** as a white solid (7 mg, 0.02 mmol, 6%).

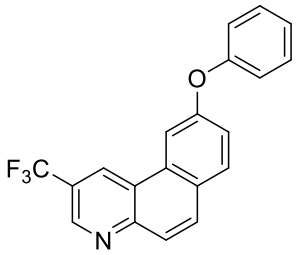
R*f* (n-pentane/EtOAc = 9:1): 0.25;

^{1}H-NMR (300 MHz, $CDCl_3$): δ/ppm = 9.16 (d, *J* = 1.4 Hz, 1H), 9.10 (bs, 1H), 8.05 (d, *J* = 9.0 Hz, 1H), 7.97 (d, *J* = 2.5 Hz, 1H), 7.92 (d, *J* = 2.2 Hz, 1H), 7.89 (d, *J* = 1.7 Hz, 1H), 7.36 (dd, *J* = 8.8, 2.5 Hz, 1H), 4.06 (s, 3H);

^{19}F-NMR (282 MHz, $CDCl_3$): δ/ppm **=** -61.2;

ESI-MS: calculated [$C_{15}H_{10}F_3NOH]^+$: 278.0787, found: 278.0797;

9-phenoxy-2-(trifluoromethyl)benzo[*f*]quinoline (5aj)



5ah was obtained as the major byproduct in the one-pot reaction of 3-chloro-5-(trifluoromethyl)-2-vinylpyridine **1a** (83.0 mg, 0.4 mmol) and (4-phenoxyphenyl)boronic acid (128.4 mg, 0.6 mmol, 1.5 equiv.) with [{Rh(C_2H_4)$_2$Cl}$_2$] (6.2 mg, 0.016 mmol, 4 mol%), dppbenz (14.3 mg, 0.032 mmol, 8 mol%), Pd(OAc)$_2$ (9.0 mg, 0.04 mmol, 10 mol%) and PCy_3·HBF_4 (29.5 mg, 0.08 mmol, 20 mol%) and K_2CO_3 (165.9 mg, 1.2 mmol, 3.0 equiv.) in 4.0 mL of 1,4-dioxane and 0.4 mL of dem. H_2O. Purification by column chromatography on silica (pentane/EtOAc = 9/1) afforded 9-phenoxy-2-(trifluoromethyl)benzo[*f*]quinoline **5aj** as a white solid (11 mg, 0.03 mmol, 8%).

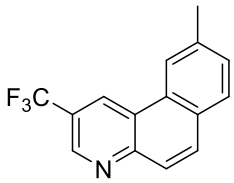
R*f* (n-pentane/EtOAc = 9:1): 0.28;

^{1}H-NMR (300 MHz, $CDCl_3$): δ/ppm = 9.17 (d, *J* = 2.1 Hz, 1H), 8.99 (bs, 1H), 8.21 (d, *J* = 2.3 Hz, 1H), 8.09 (d, *J* = 9.1 Hz, 1H), 7.98 (d, *J* = 9.1 Hz, 1H), 7.97 (d, *J* = 8.7 Hz, 1H), 7.46 – 7.38 (m, 3H), 7.24 – 7.17 (m, 1H), 7.15 – 7.08 (m, 2H);

^{19}F-NMR (282 MHz, $CDCl_3$): δ/ppm = -61.3;

ESI-MS: calculated $[C_{20}H_{12}F_3NOH]^+$: 340.0944, found: 340.0950;

9-methyl-2-(trifluoromethyl)benzo[*f*]quinoline (5ak)



5ai was obtained as the major byproduct in the one-pot reaction of 3-chloro-5-(trifluoromethyl)-2-vinylpyridine **1a** (83.0 mg, 0.4 mmol) and p-tolylboronic acid (81.6 mg, 0.6 mmol, 1.5 equiv.) with $[\{Rh(C_2H_4)_2Cl\}_2]$ (6.2 mg, 0.016 mmol, 4 mol%), dppbenz (14.3 mg, 0.032 mmol, 8 mol%), $Pd(OAc)_2$ (9.0 mg, 0.04 mmol, 10 mol%) and $PCy_3{\cdot}HBF_4$ (29.5 mg, 0.08 mmol, 20 mol%) and K_2CO_3 (165.9 mg, 1.2 mmol, 3.0 equiv.) in 4.0 mL of 1,4-dioxane and 0.4 mL of dem. H_2O. Purification by column chromatography on silica (pentane/EtOAc = 9/1) afforded 9-methyl-2-(trifluoromethyl)benzo[*f*]quinoline **5ak** as a white solid (6 mg, 0.02 mmol, 6%).

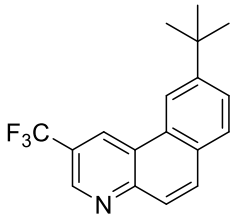
R_f (n-pentane/EtOAc = 9:1): 0.38;

^{1}H-NMR (300 MHz, $CDCl_3$): δ/ppm = 9.22 – 9.07 (m, 2H), 8.44 (s, 1H), 8.08 (d, *J* = 9.1 Hz, 1H), 7.98 (d, *J* = 9.1 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.56 (dd, *J* = 8.2, 1.6 Hz, 1H), 2.67 (s, 3H);

^{19}F-NMR (282 MHz, $CDCl_3$): δ/ppm = -61.3;

ESI-MS: calculated $[C_{15}H_{10}F_3NH]^+$: 262.0838, found: 262.0840;

9-(*tert*-butyl)-2-(trifluoromethyl)benzo[*f*]quinoline (5al)



5ai was obtained as the major byproduct in the one-pot reaction of 3-chloro-5-(trifluoromethyl)-2-vinylpyridine **1a** (83.0 mg, 0.4 mmol) and (4-(*tert*-butyl)phenyl)boronic acid (106.8 mg, 0.6 mmol, 1.5 equiv.) with $[\{Rh(C_2H_4)_2Cl\}_2]$ (6.2 mg, 0.016 mmol, 4 mol%), dppbenz (14.3 mg, 0.032 mmol, 8 mol%), $Pd(OAc)_2$ (9.0 mg, 0.04 mmol, 10 mol%) and $PCy_3{\cdot}HBF_4$ (29.5 mg, 0.08 mmol, 20 mol%) and K_2CO_3 (165.9 mg, 1.2 mmol, 3.0

equiv.) in 4.0 mL of 1,4-dioxane and 0.4 mL of dem. H_2O. Purification by column chromatography on silica (pentane/EtOAc = 9/1) afforded 9-(*tert*-butyl)-2-(trifluoromethyl)benzo[*f*]quinoline **5al** as a white solid (7 mg, 0.02 mmol, 6%).

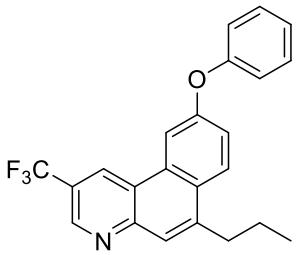
R_f (n-pentane/EtOAc = 9:1): 0.45;

^{1}H-NMR (300 MHz, $CDCl_3$): δ/ppm = 9.20 (s, 1H), 9.17 (bs, 1H), 8.60 (d, *J* = 1.8 Hz, 1H), 8.09 (d, *J* = 9.0 Hz, 1H), 8.00 (d, *J* = 9.1 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.82 (dd, *J* = 8.4, 1.8 Hz, 1H), 1.52 (s, 9H);

^{19}F-NMR (282 MHz, $CDCl_3$): δ/ppm = -61.2;

ESI-MS: calculated $[C_{18}H_{16}F_3NH]^+$: 304.1308, found: 304.1314;

9-phenoxy-6-propyl-2-(trifluoromethyl)benzo[*f*]quinoline (5hj)



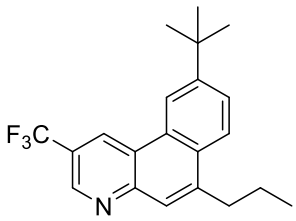
5hj was obtained as the major byproduct in the one-pot reaction of (*E*)-3-chloro-2-(pent-1-en-1-yl)-5-(trifluoromethyl)pyridine **1h** (49.9 mg, 0.2 mmol) and (4-phenoxyphenyl)boronic acid (64.2 mg, 0.3 mmol, 1.5 equiv.) with $[\{Rh(C_2H_4)_2Cl\}_2]$ (3.1 mg, 0.008 mmol, 4 mol%), dppbenz (7.1 mg, 0.016 mmol, 8 mol%), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%) and $PCy_3{\cdot}HBF_4$ (14.7 mg, 0.04 mmol, 20 mol%) and K_2CO_3 (82.9 mg, 0.6 mmol, 3.0 equiv.) in 2.0 mL of 1,4-dioxane and 0.2 mL of dem. H_2O. Purification by column chromatography on silica (pentane/EtOAc = 19/1) afforded 9-phenoxy-6-propyl-2-(trifluoromethyl)benzo[*f*]quinoline **5hj** as a white solid (15 mg, 0.04 mmol, 20%).

R_f (n-pentane/EtOAc = 19:1): 0.37;

^{19}F-NMR (282 MHz, $CDCl_3$): δ/ppm = -61.2;

ESI-MS: calculated $[C_{23}H_{18}F_3NOH]^+$: 382.1413, found: 382.1406;

9-(*tert*-butyl)-6-propyl-2-(trifluoromethyl)benzo[*f*]quinoline (5hl)



5hl was obtained as the major byproduct in the one-pot reaction of (*E*)-3-chloro-2-(pent-1-en-1-yl)-5-(trifluoromethyl)pyridine **1h** (49.9 mg, 0.2 mmol) and (4-(*tert*-butyl)phenyl)boronic acid (53.4 mg, 0.3 mmol, 1.5 equiv.) with [{Rh(C_2H_4)$_2$Cl}$_2$] (3.1 mg, 0.008 mmol, 4 mol%), dppbenz (7.1 mg, 0.016 mmol, 8 mol%), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%) and $PCy_3 \cdot HBF_4$ (14.7 mg, 0.04 mmol, 20 mol%) and K_2CO_3 (82.9 mg, 0.6 mmol, 3.0 equiv.) in 2.0 mL of 1,4-dioxane and 0.2 mL of dem. H_2O. Purification by column chromatography on silica (pentane/EtOAc = 19/1) afforded 9-(*tert*-butyl)-6-propyl-2-(trifluoromethyl)benzo[*f*]quinoline **5hl** as a white solid (18 mg, 0.05 mmol, 26%).

R_f (n-pentane/EtOAc = 19:1): 0.44;

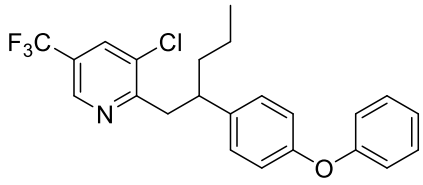
^{1}H-NMR (300 MHz, $CDCl_3$): δ/ppm = 9.18 – 9.06 (m, 2H), 8.63 (d, *J* = 2.0 Hz, 1H), 8.14 (d, *J* = 8.7 Hz, 1H), 7.86 – 7.81 (m, 2H), 3.19 – 3.12 (m, 2H), 1.90 (h, *J* = 7.4 Hz, 2H), 1.52 (s, 9H), 1.10 (t, *J* = 7.3 Hz, 3H);

^{19}F-NMR (282 MHz, $CDCl_3$): δ/ppm **=** -61.1;

ESI-MS: calculated $[C_{21}H_{22}F_3NH]^+$: 346.1777, found: 346.1777;

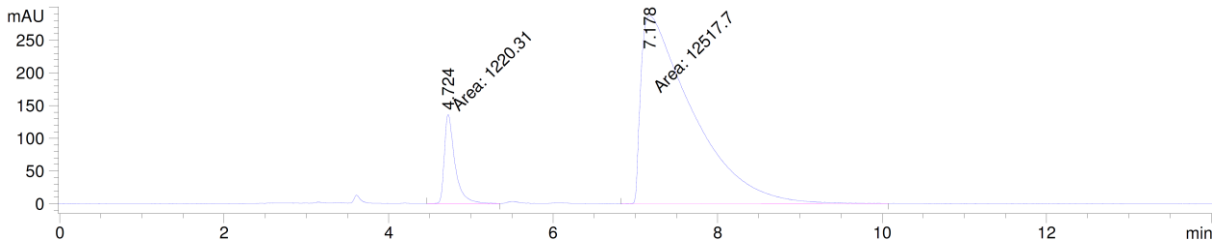
Enantioselective catalysis

3-chloro-2-(2-(4-phenoxyphenyl)pentyl)-5-(trifluoromethyl)pyridine (3hj)

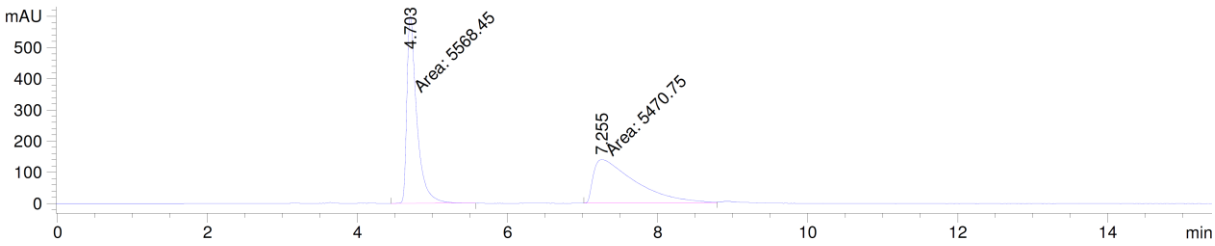


A solution of (*E*)-3-chloro-2-(pent-1-en-1-yl)-5-(trifluoromethyl)pyridine **1h** (124.8 mg, 0.5 mmol) in 2.5 mL 1,4-dioxane and a solution of K_2CO_3 (138.2 mg, 1.0 mmol, 2.0 equiv) in 0.25 mL dem. H_2O were added to a prestirred (15 min, r.t.) mixture of $[RhCl(C_2H_4)_2]_2$ (9.7 mg, 0.025 mmol, 5 mol %), **L*** (19.3 mg, 0.05 mmol, 10 mol %) and (4-phenoxyphenyl)boronic acid (428.1 mg, 2.0 mmol, 4.0 equiv.) in 2.5 mL 1,4-dioxane and 0.25 mL dem. H_2O. The resulting mixture was stirred for 1 h at r.t. Purification by column chromatography on silica (pentane/EtOAc = 100/3) afforded 3-chloro-2-(2-(4-phenoxyphenyl)pentyl)-5-(trifluoromethyl)pyridine **3hj** as a yellow oil (141 mg, 0.34 mmol, 67%).

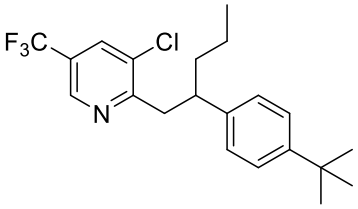
HPLC: 82% *ee* (Chiralcel AD-H, n-hexane/i-PrOH = 200/1, 1 mL/min, 230 nm, tR = 4.72 min (minor), tR = 7.18 min (major));



HPLC: *rac* (Chiralcel AD-H, n-hexane/i-PrOH = 200/1, 1 mL/min, 230 nm, tR = 4.70 min (minor), tR = 7.26 min (major)).



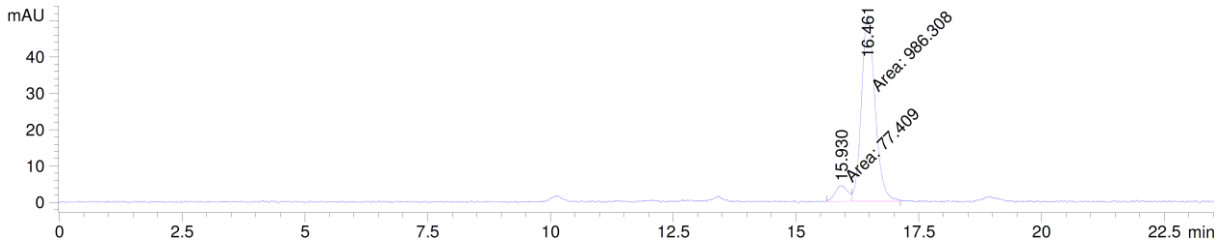
2-(2-(4-(*tert*-butyl)phenyl)pentyl)-3-chloro-5-(trifluoromethyl)pyridine (3hl)



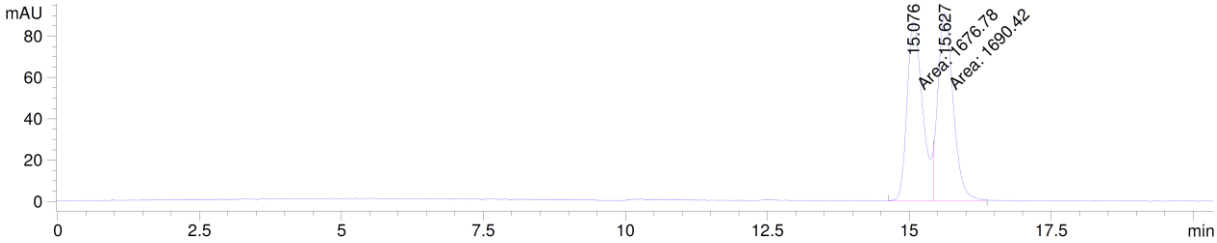
A solution of (*E*)-3-chloro-2-(pent-1-en-1-yl)-5-(trifluoromethyl)pyridine **1h** (124.8 mg, 0.5 mmol) in 2.5 mL 1,4-dioxane and a solution of K_2CO_3 (138.2 mg, 1.0 mmol, 2.0 equiv) in 0.25 mL dem. H_2O were added to a prestirred

(15 min, r.t.) mixture of $[RhCl(C_2H_4)_2]_2$ (9.7 mg, 0.025 mmol, 5 mol %), **L*** (19.3 mg, 0.05 mmol, 10 mol %) and (4-(*tert*-butyl)phenyl)boronic acid (356.1 mg, 2.0 mmol, 4.0 equiv.) in 2.5 mL 1,4-dioxane and 0.25 mL dem. H_2O. The resulting mixture was stirred for 1 h at r.t. Purification by column chromatography on silica (pentane/EtOAc = 100/3) afforded 2-(2j-(4-(*tert*-butyl)phenyl)pentyl)-3-chloro-5-(trifluoromethyl)pyridine **3hl** as a colorless oil (155 mg, 0.40 mmol, 81%).

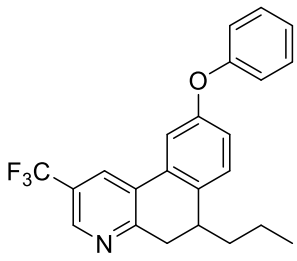
HPLC: 86% *ee* (Chiralcel OD-H, n-hexane, 0.3 mL/min, 230 nm, tR = 15.93 min (minor), tR = 15.46 min (major));



HPLC: *rac* (Chiralcel OD-H, n-hexane, 0.3 mL/min, 230 nm, tR = 15.08 min (minor), tR = 15.63 min (major)).

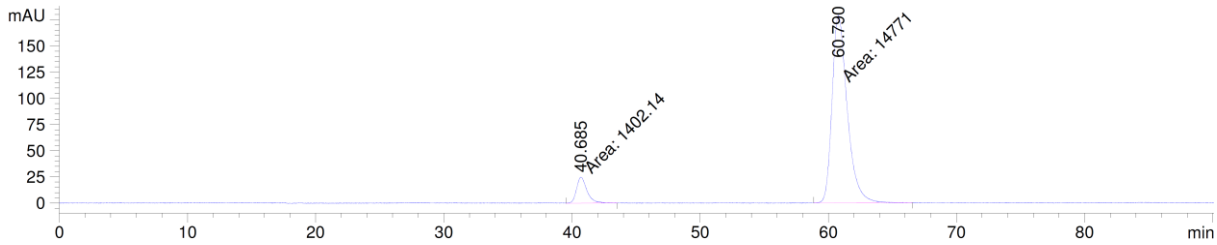


9-phenoxy-6-propyl-2-(trifluoromethyl)-5,6-dihydrobenzo[*f*]quinoline (4hj)

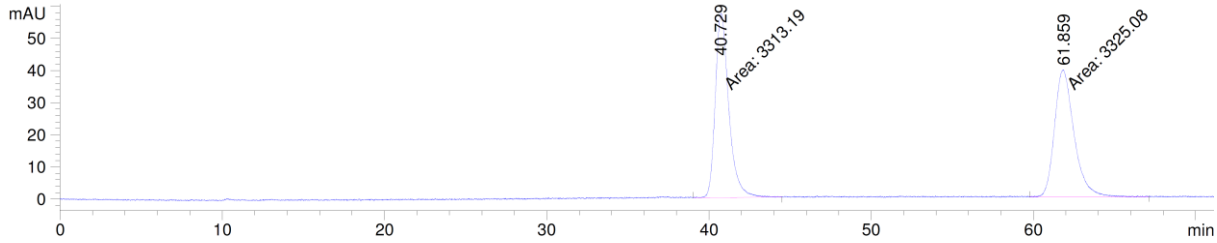


Enantioenriched 3-chloro-2-(2-(4-phenoxyphenyl)pentyl)-5-(trifluoromethyl)pyridine **3hj** (42.0 mg, 0.1 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol, 10 mol%), $PCy_3{\cdot}HBF_4$ (7.4 mg, 0.02 mmol, 20 mol%) and K_2CO_3 (27.6 mg, 0.2 mmol, 2.0 equiv.) were added to a pressurizable flask. The flask was purged with argon and 1.0 mL of 1,4-dioxane and 0.1 mL of dem. H_2O were added. The resulting mixture was heated to 150 °C for 18 h. Purification by column chromatography on silica (pentane/EtOAc = 19/1) afforded 9-phenoxy-6-propyl-2-(trifluoromethyl)-5,6-dihydrobenzo[*f*]quinoline **4hj** as a colorless oil (20 mg, 0.05 mmol, 52%).

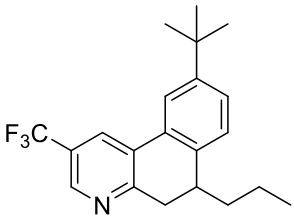
HPLC: 82% *ee* (Chiralcel AD-H, n-hexane/i-PrOH = 200/1, 0.3 mL/min, 230 nm, tR = 40.69 min (minor), tR = 60.79 min (major));



HPLC: *rac* (Chiralcel AD-H, n-hexane/i-PrOH = 200/1, 0.3 mL/min, 230 nm, tR = 40.73 min (major), tR = 61.86 min (minor)).

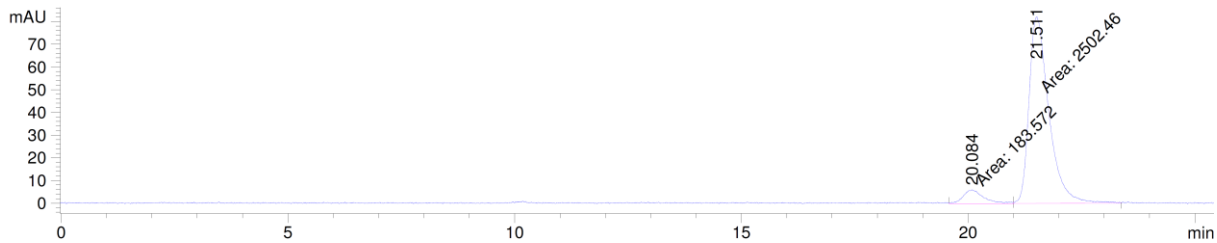


9-(*tert*-butyl)-6-propyl-2-(trifluoromethyl)-5,6-dihydrobenzo[*f*]quinoline (4hl)

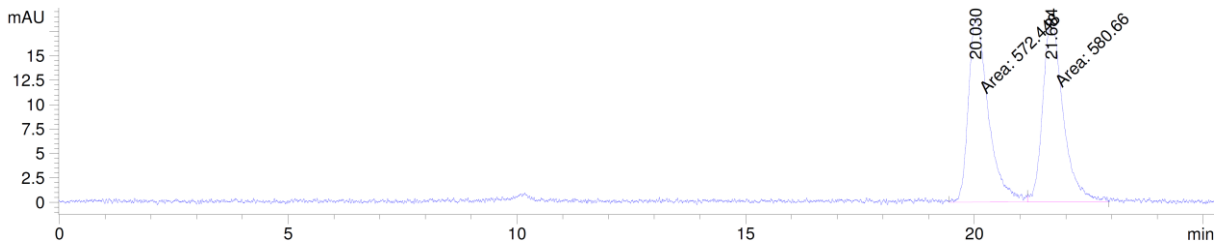


Enantioenriched 2-(2-(4-(*tert*-butyl)phenyl)pentyl)-3-chloro-5-(trifluoromethyl)pyridine **3hl** (76.8 mg, 0.2 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), $PCy_3{\cdot}HBF_4$ (14.7 mg, 0.04 mmol, 20 mol%) and K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.) were added to a pressurizable flask. The flask was purged with argon and 2.0 mL of 1,4-dioxane and 0.2 mL of dem. H_2O were added. The resulting mixture was heated to 150 °C for 18 h. Purification by column chromatography on silica (pentane/EtOAc = 19/1) afforded 9-(*tert*-butyl)-6-propyl-2-(trifluoromethyl)-5,6-dihydrobenzo[*f*]quinoline **4hl** as a white solid (30 mg, 0.09 mmol, 43%).

HPLC: 86% *ee* (Chiralcel OD-H, n-hexane, 0.3 mL/min, 230 nm, tR = 20.08 min (minor), tR = 21.51 min (major));

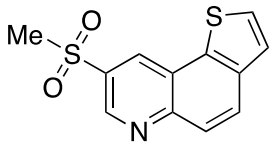


HPLC: *rac* (Chiralcel OD-H, n-hexane, 0.3 mL/min, 230 nm, tR = 20.03 min (minor), tR = 21.68 min (major)).



Three-step-one-pot synthesis

8-(methylsulfonyl)thieno[2,3-*f*]quinoline (5ca)



A solution of 3-chloro-5-(methylsulfonyl)-2-vinylpyridine **1c** (86.8 mg, 0.4 mmol, 1.0 equiv.) in 1.0 mL 1,4-dioxane and a solution of K_2CO_3 (165.6 mg, 1.2 mmol, 3.0 equiv) in 0.1 mL dem. H_2O were added to a prestirred (15 min, r.t.) mixture of $[RhCl(C_2H_4)_2]_2$ (6.2 mg, 0.016 mmol, 4 mol %), dppbenz (14.3 mg, 0.032 mmol, 8 mol %) and thiophen-3-ylboronic acid (76.8 mg, 0.6 mmol, 1.5 equiv.) in 2.0 mL 1,4-dioxane and 0.2 mL dem. H_2O. The resulting mixture was stirred for 1 h at r.t. to which $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 5 mol%) and $PCy_3 \cdot HBF_4$ (14.7 mg, 0.04 mmol, 10 mol%) were added (prestirred for 15 min at r.t. in 1.0 mL of dioxane and 0.1 mL of dem. H_2O). The resulting mixture was heated to 150 °C for 18 h then cooled to r.t. to which 2,3-dichloro-5,6-dicyano1,4-benzoquinone (DDQ, 181.6 mg, 0.8 mmol, 2.0 equiv) was added. The reaction mixture was heated for the second time to 100 °C for 1 h. Purification by column chromatography on silica (hexane/EtOAc = 1/1) afforded 8-(methylsulfonyl)thieno[2,3-*f*]quinoline **5ca** as a yellow solid (100 mg, 0.38 mmol, 95%)

R_f (DCM/MeOH = 10:1): 0.46;

Melting point: 220 – 222 °C

^{1}H-NMR (500 MHz, DMSO-d_6): δ/ppm = 9.33 (d, *J* = 2.2 Hz, 1H), 9.08 (dd, *J* = 2.2, 0.9 Hz, 1H), 8.41 (d, *J* = 8.9 Hz, 1H), 8.12 (d, *J* = 5.2 Hz, 1H), 8.07 (dd, *J* = 8.9, 0.8 Hz, 1H), 7.76 (d, *J* = 5.2 Hz, 1H), 3.48 (s, 3H);

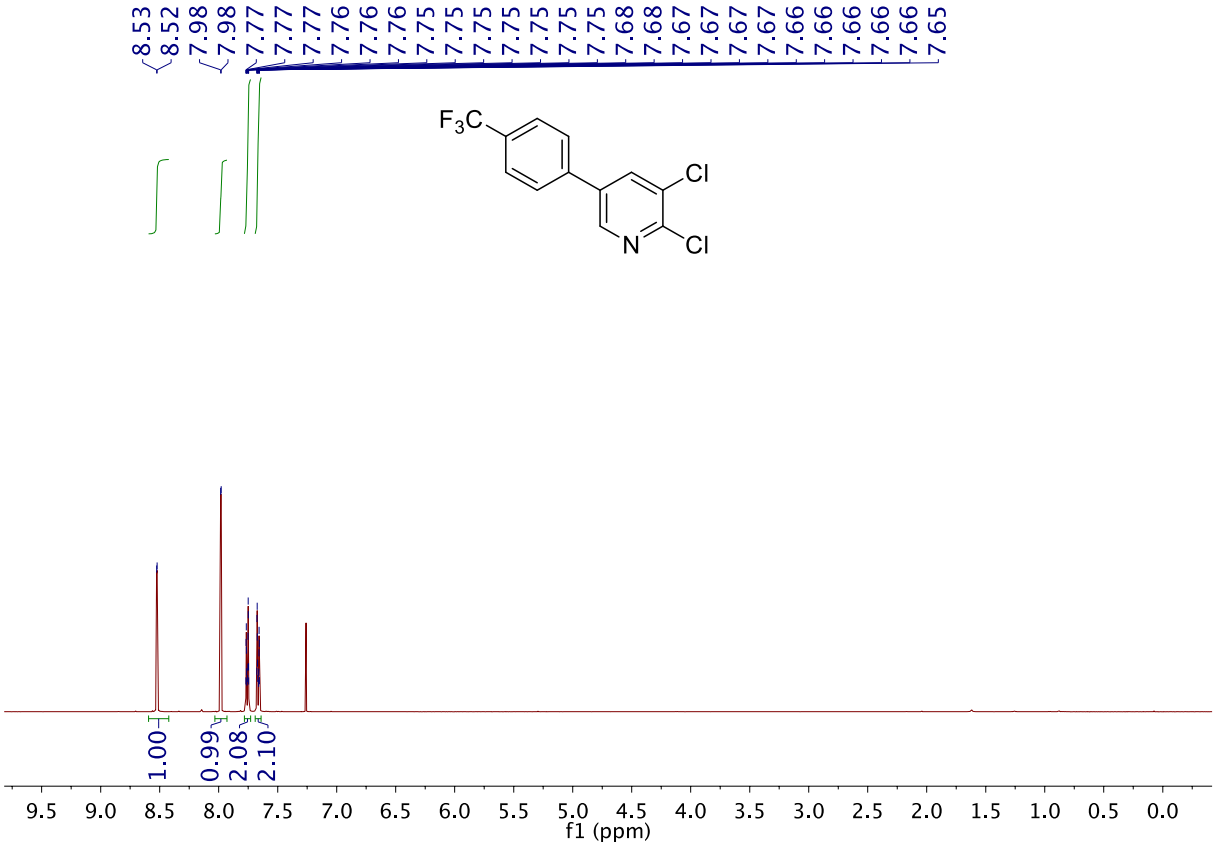
^{13}C-NMR (126 MHz, DMSO-d_6): δ/ppm = 147.7, 145.9, 138.7, 137.0, 133.9, 131.9, 129.6, 129.0, 125.9, 125.3, 122.0, 43.9;

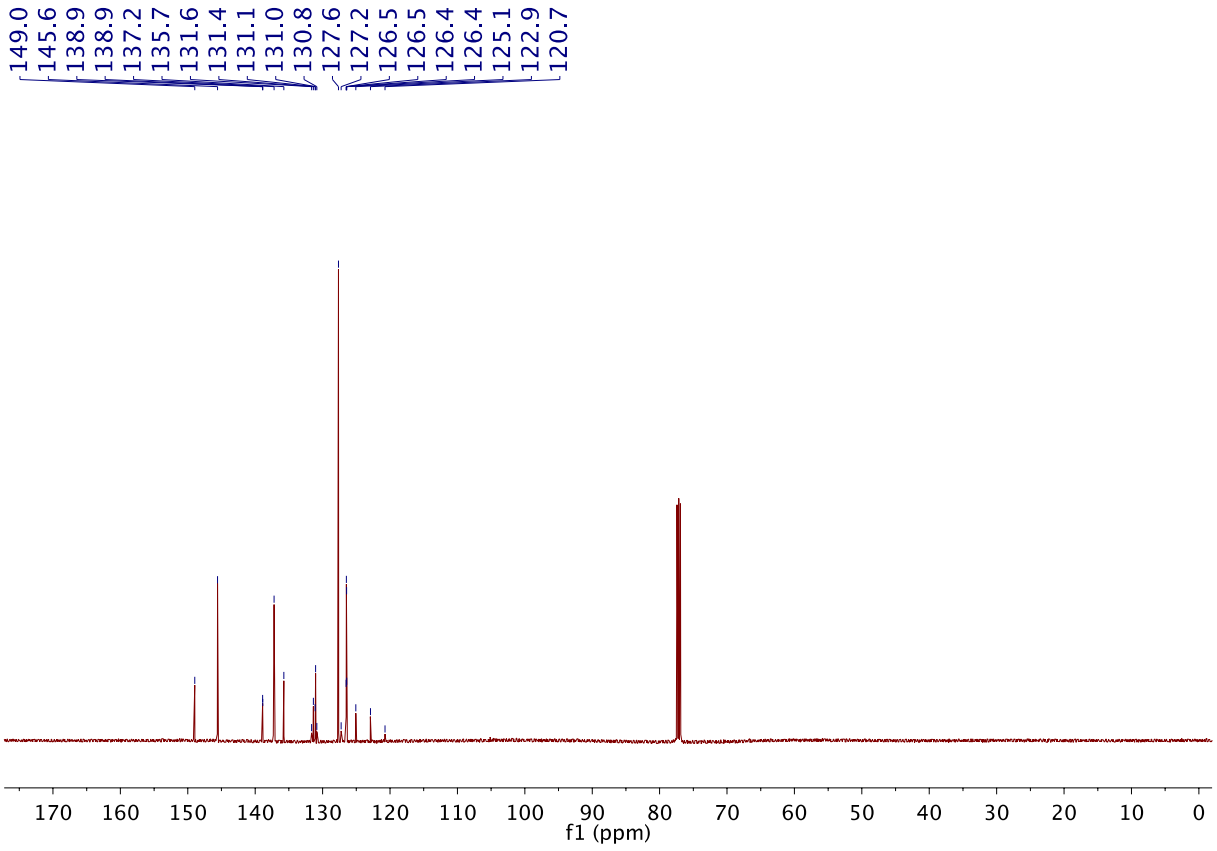
^{19}F-NMR (282 MHz, $CDCl_3$): δ/ppm **=** -61.7;

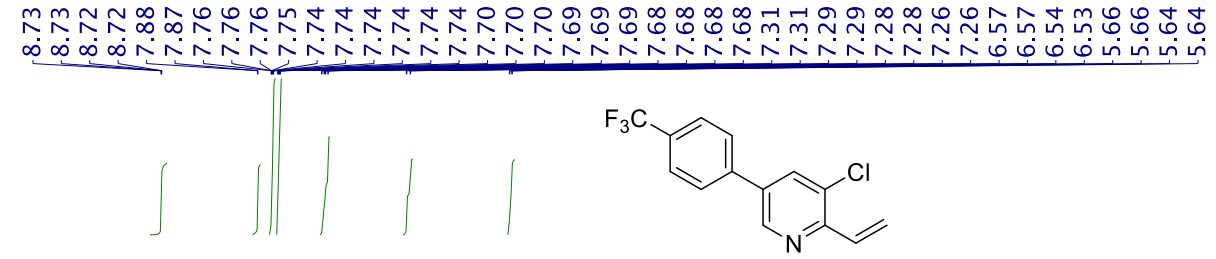
ESI-MS: calculated $[C_{12}H_9NO_2S_2H]^+$: 264.0153, found: 264.0150;

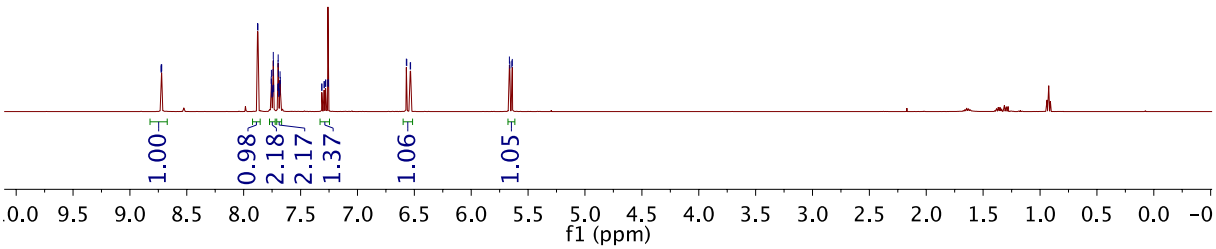
ATR-FTIR (cm^{-1}): 2928, 2228, 1587, 1508, 1552, 1411, 1399, 1298, 1134, 1092, 1015, 970, 962, 849, 788.

NMR Spectra of Products

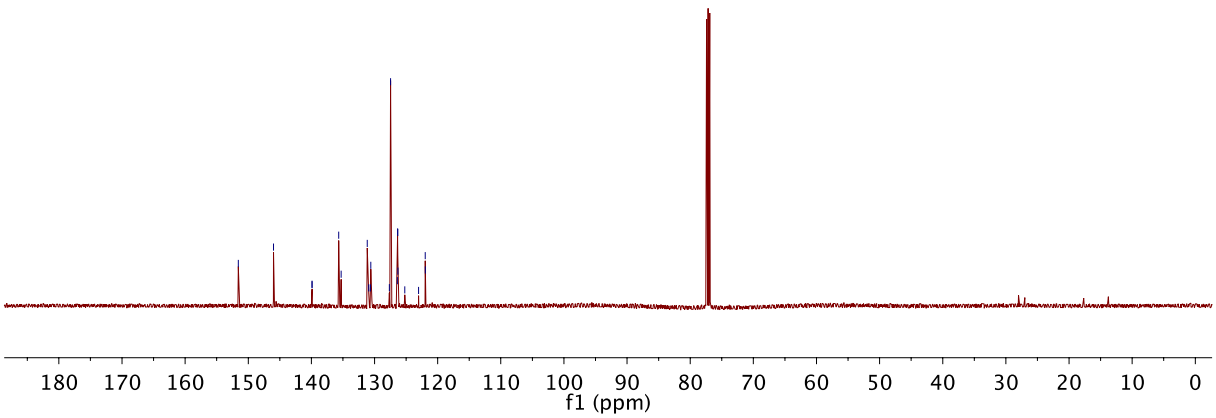


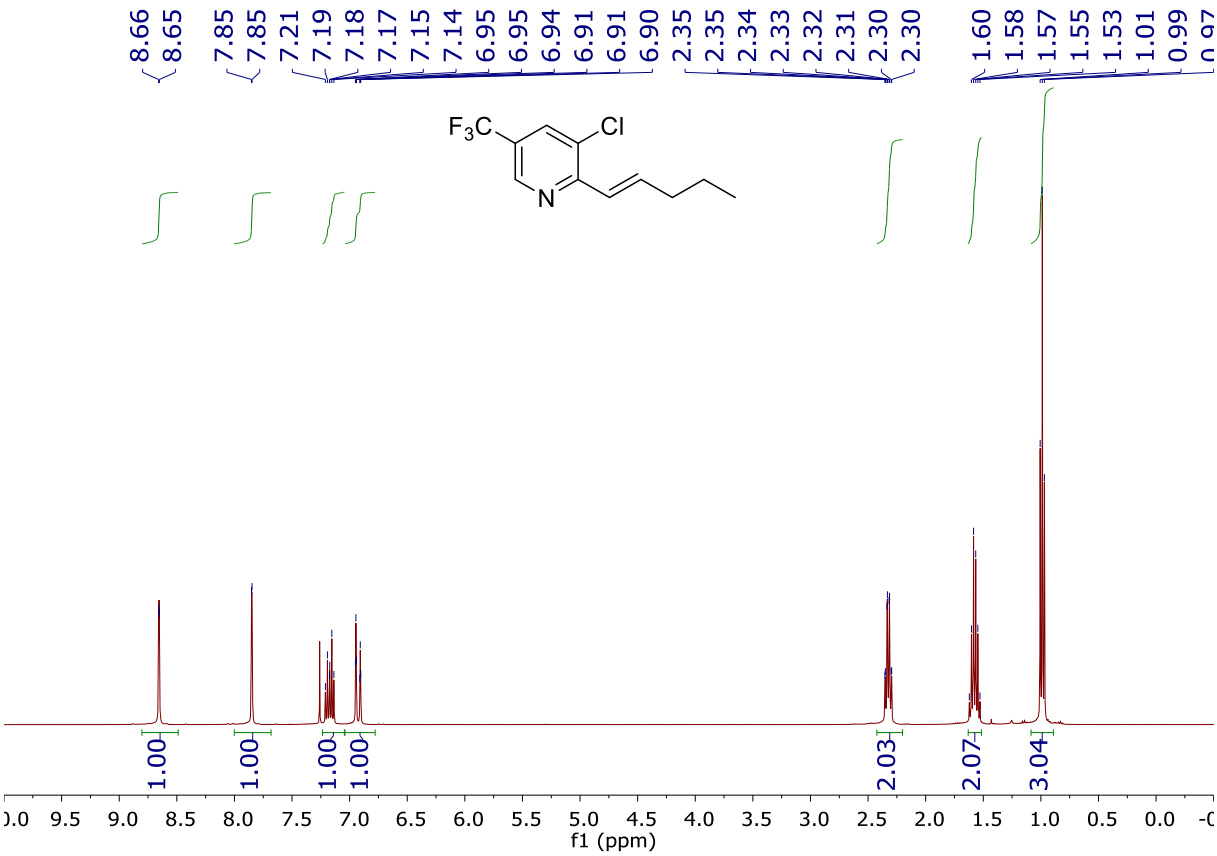


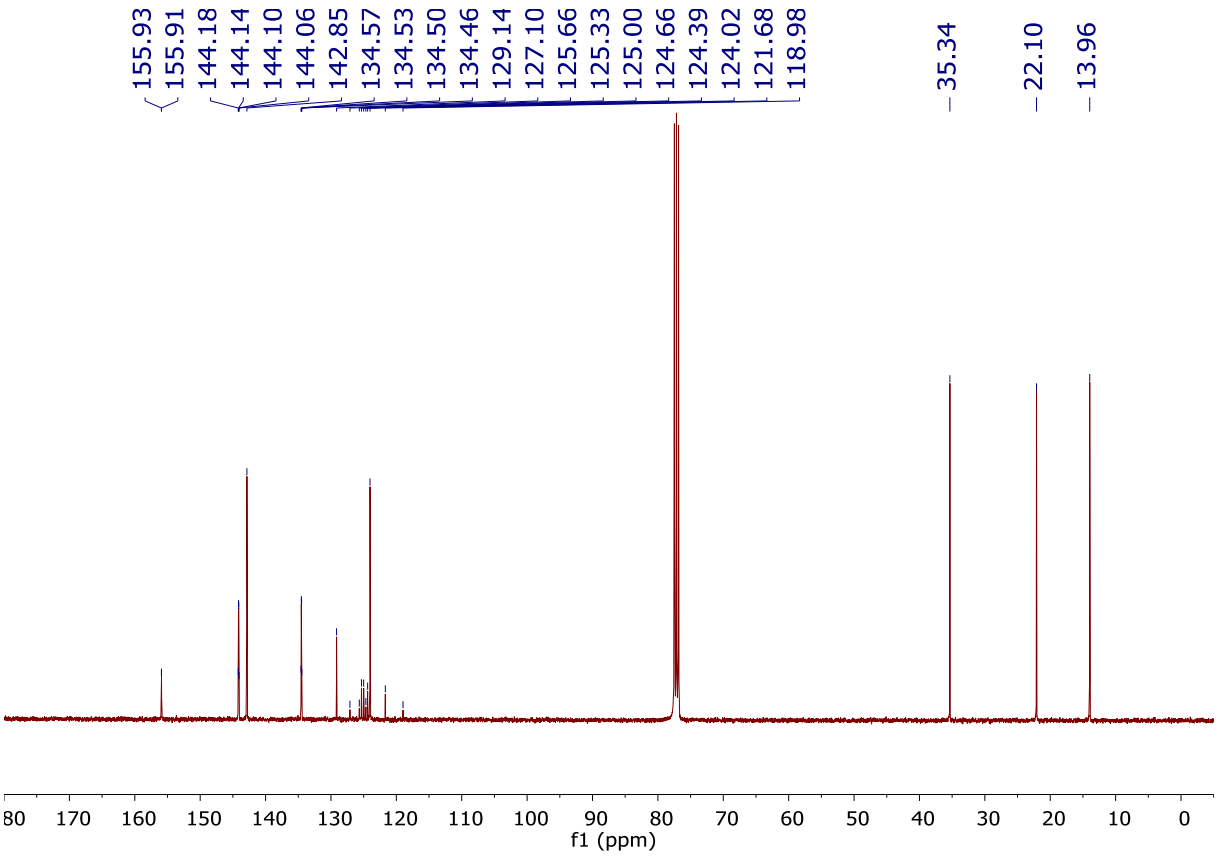

8.73
8.73
8.72
8.72
7.88
7.87
7.76
7.76
7.76
7.75
7.74
7.74
7.74
7.74
7.74
7.74
7.70
7.70
7.70
7.69
7.69
7.69
7.68
7.68
7.68
7.68
7.31
7.31
7.29
7.29
7.28
7.28
7.26
7.26
6.57
6.57
6.54
6.53
5.66
5.66
5.64
5.64
F3C
Cl
N

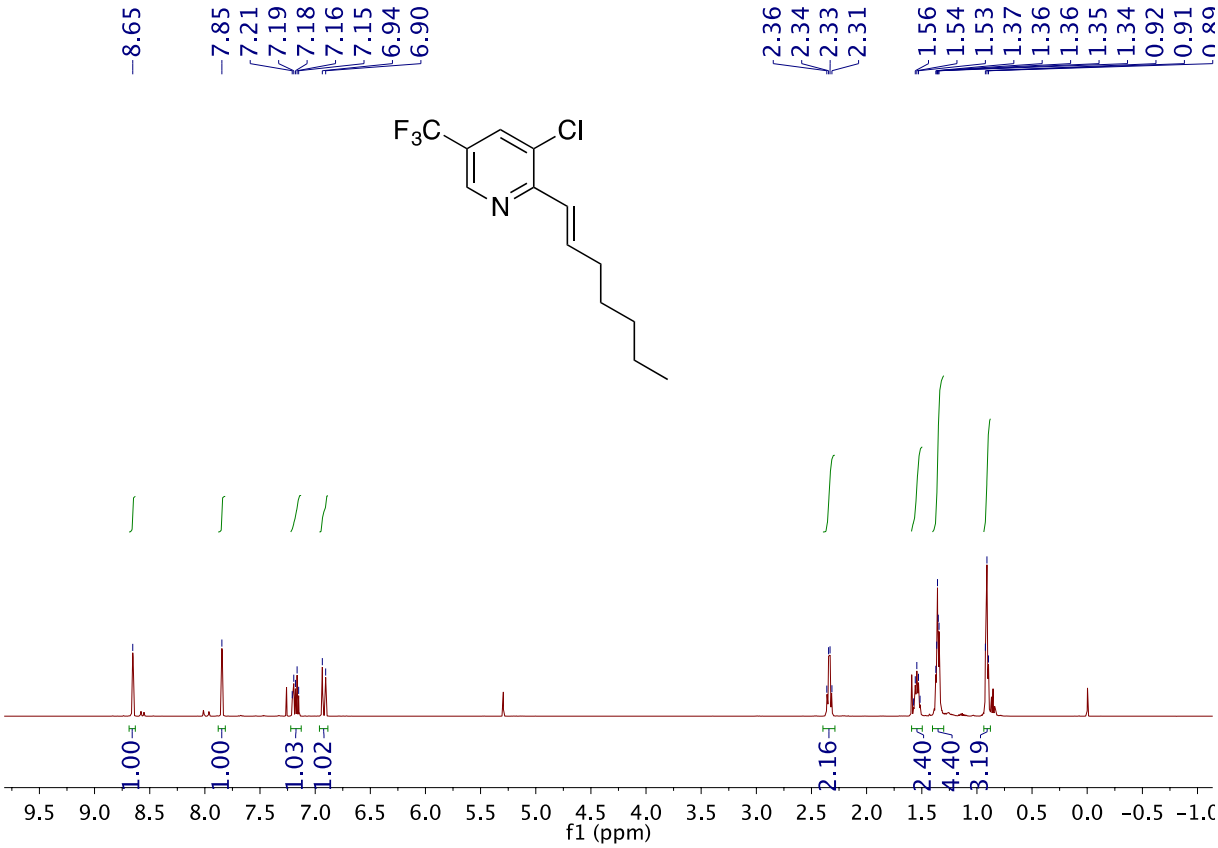

1.00
0.98
2.18
2.17
1.37
1.06
1.05
f1 (ppm)

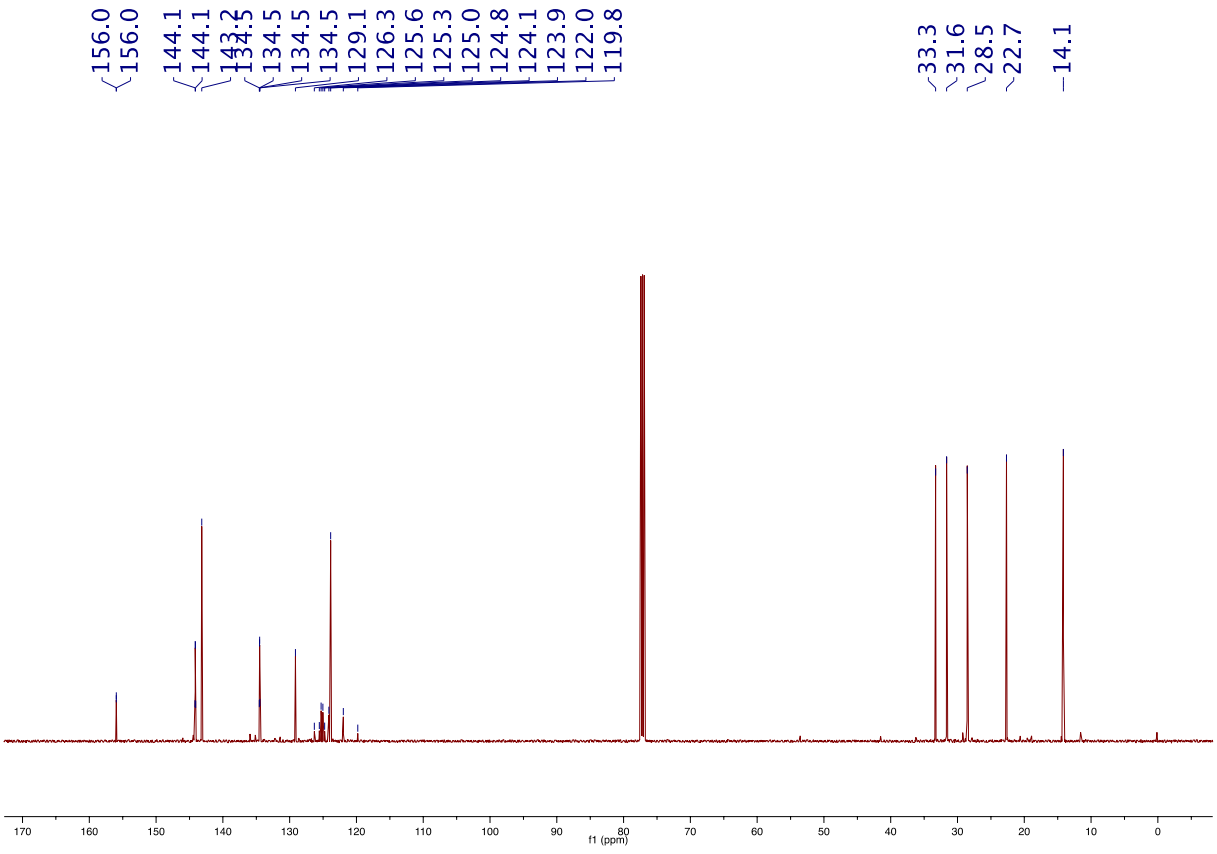

151.6
146.0
139.9
139.9
135.7
135.3
131.2
130.9
130.7
130.6
127.7
127.5
126.4
126.4
126.3
126.3
125.2
123.0
122.0
121.9

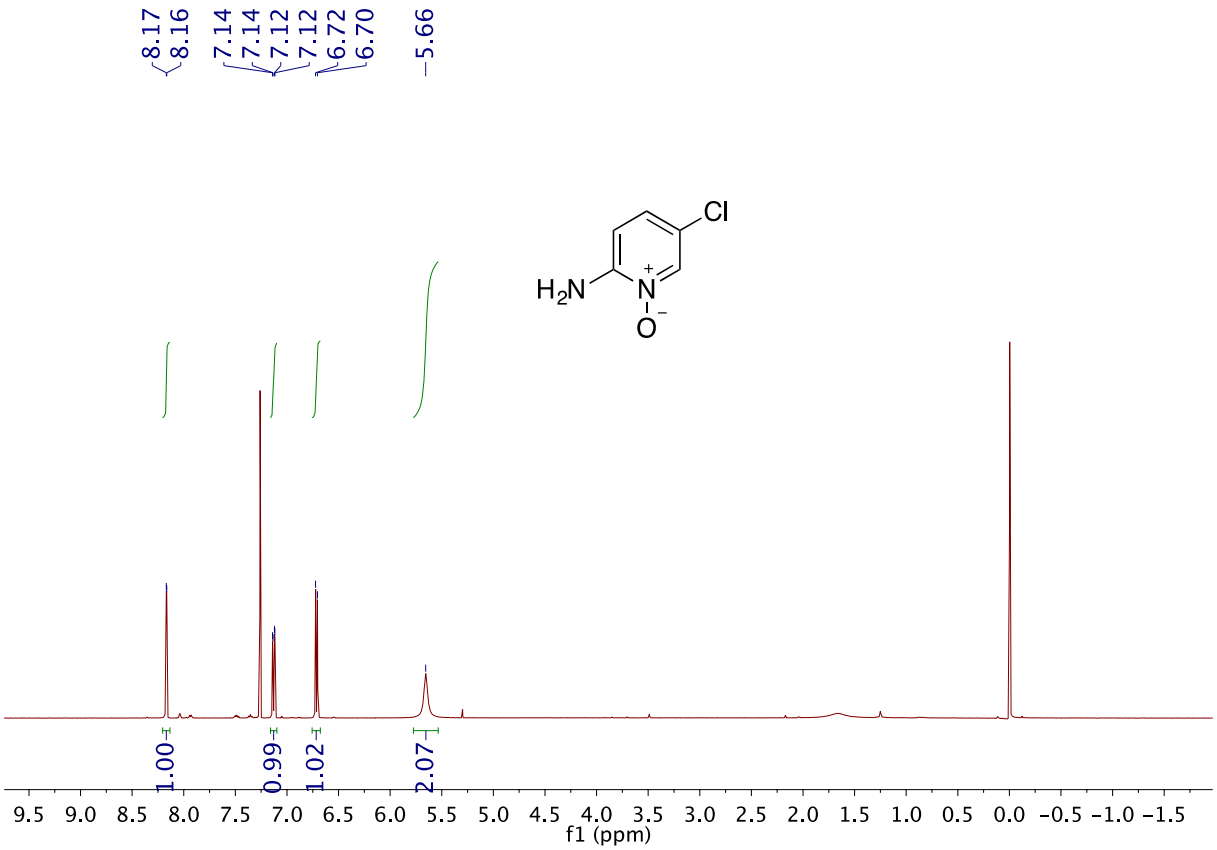

f1 (ppm)

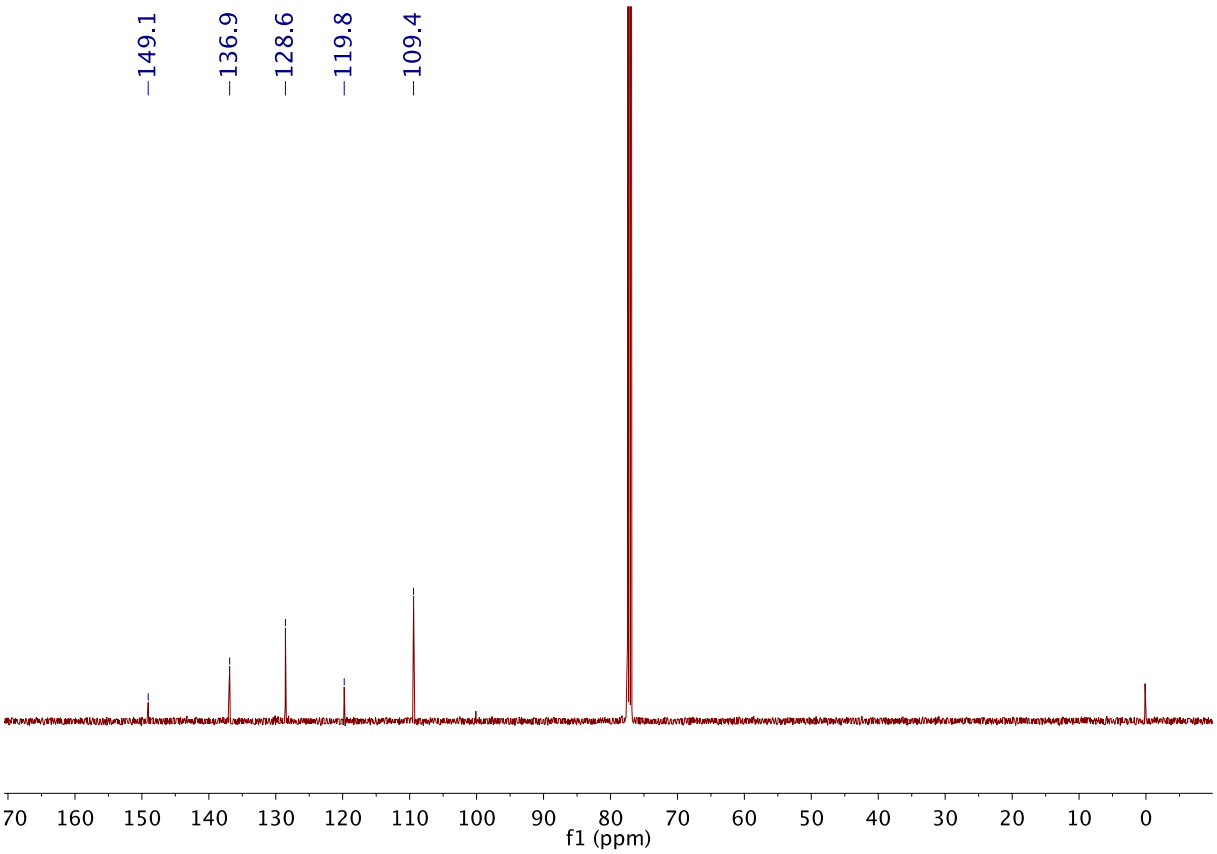

8.66
8.65
7.85
7.85
7.21
7.19
7.18
7.17
7.15
7.14
6.95
6.95
6.94
6.91
6.91
6.90
2.35
2.35
2.34
2.33
2.32
2.31
2.30
2.30
1.60
1.58
1.57
1.55
1.53
1.01
0.99
F3C
Cl
N
1.00
1.00
1.00
1.00
2.03
2.07
3.04
f1 (ppm)

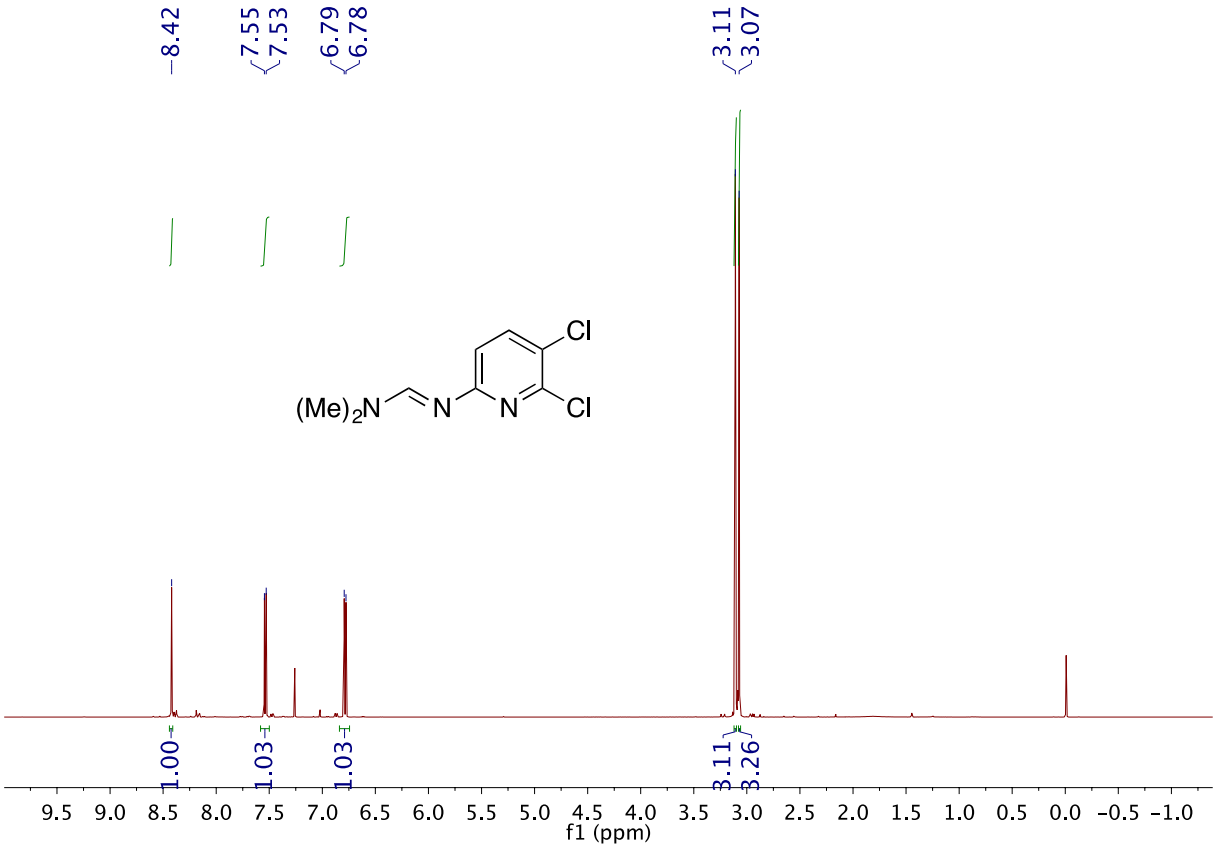

155.93
155.91
144.18
144.14
144.10
144.06
142.85
134.57
134.53
134.50
134.46
129.14
127.10
125.66
125.33
125.00
124.66
124.39
124.02
121.68
118.98
35.34
22.10
13.96
f1 (ppm)

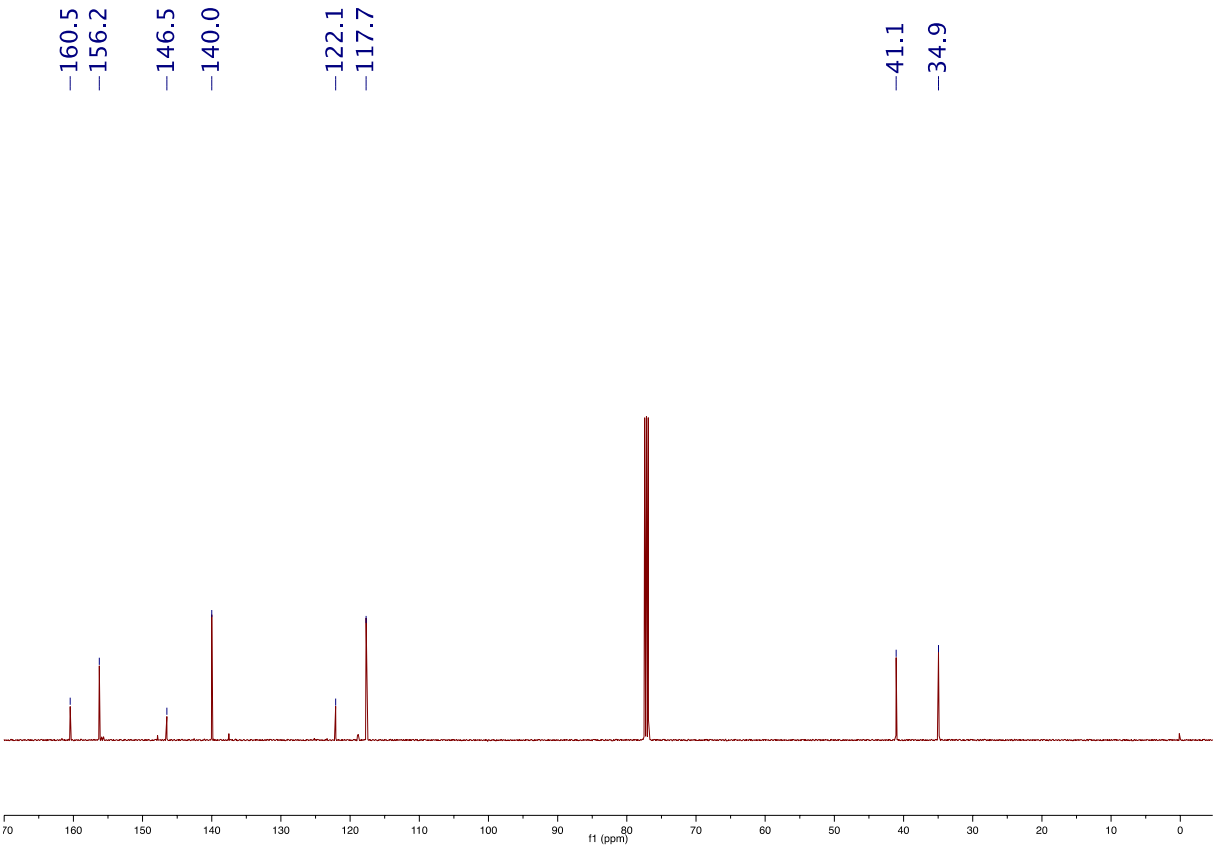

8.65
7.85
7.21
7.19
7.18
7.16
7.15
6.94
6.90
2.36
2.34
2.33
2.31
1.56
1.54
1.53
1.37
1.36
1.36
1.35
1.34
0.92
0.91
F3C
Cl
N
1.00
1.00
1.03
1.02
2.16
2.40
4.40
3.19
f1 (ppm)

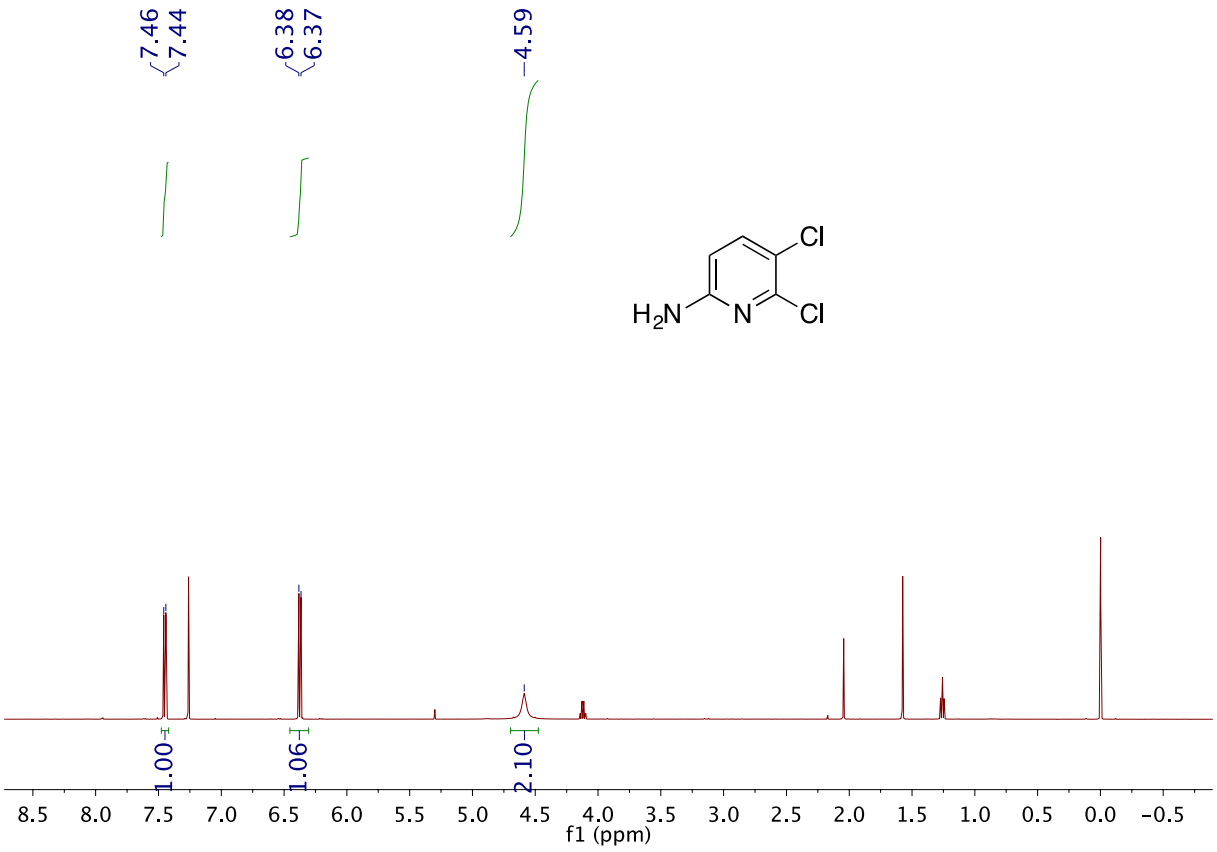

156.0
156.0
144.1
144.1
134.5
134.5
134.5
129.1
126.3
125.6
125.3
125.0
124.8
124.1
123.9
122.0
119.8
33.3
31.6
28.5
22.7
14.1
f1 (ppm)

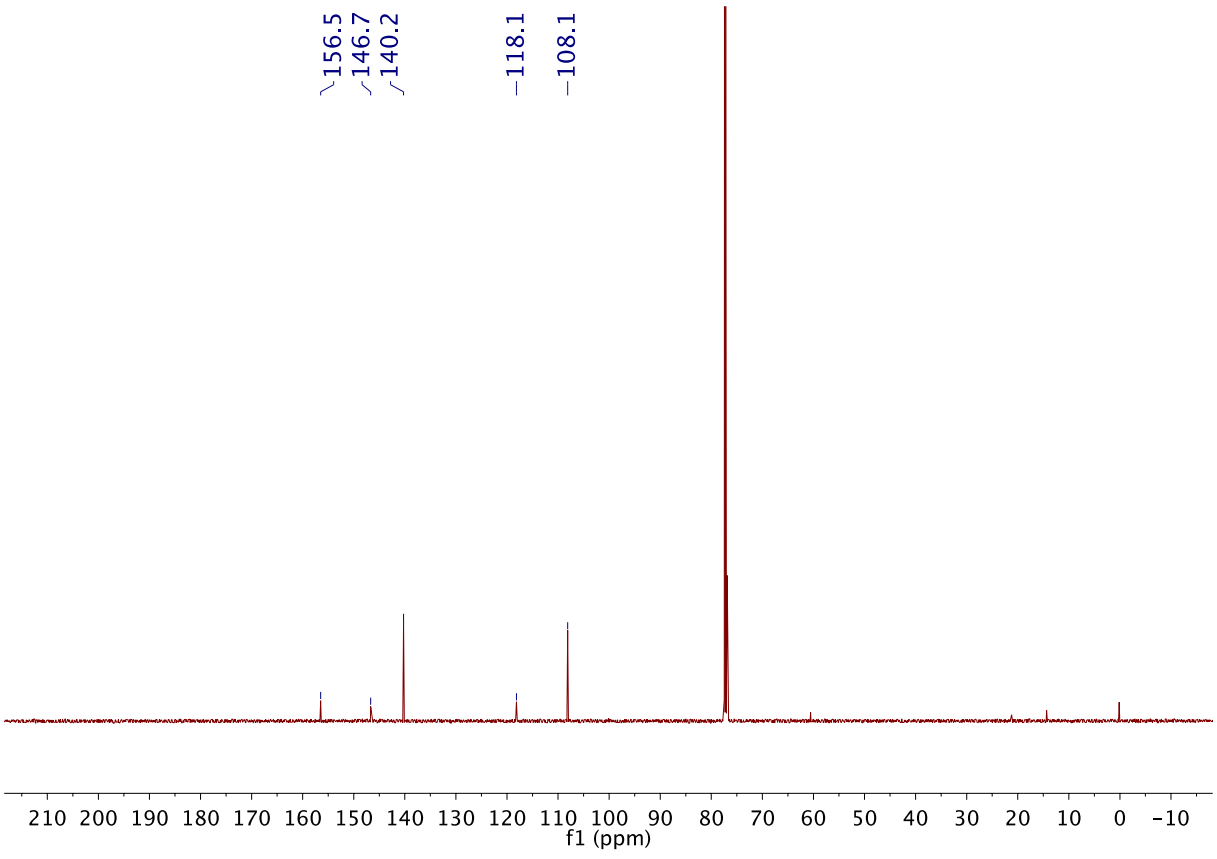

8.17
8.16
7.14
7.14
7.12
7.12
6.72
6.70
5.66
Cl
H2N
N
O
1.00
0.99
1.02
2.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

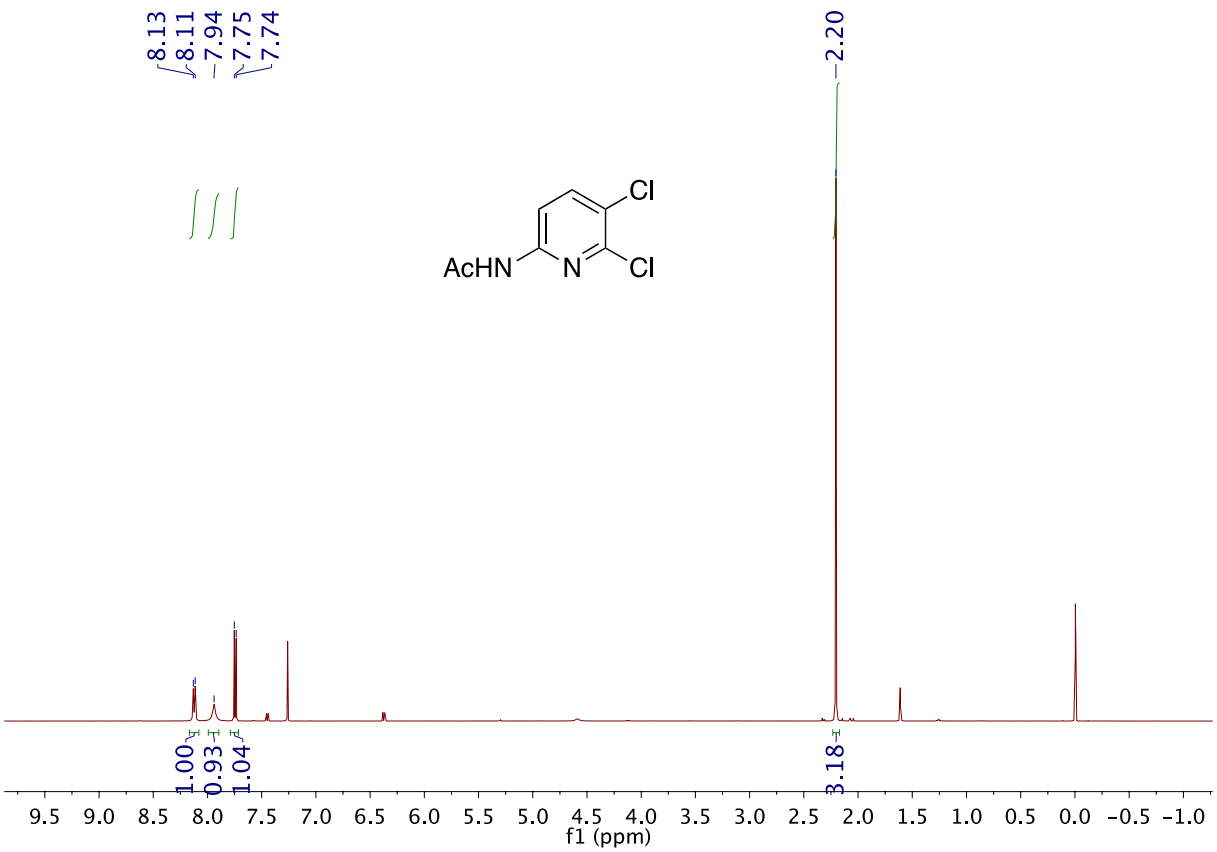

149.1
136.9
128.6
119.8
109.4
70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

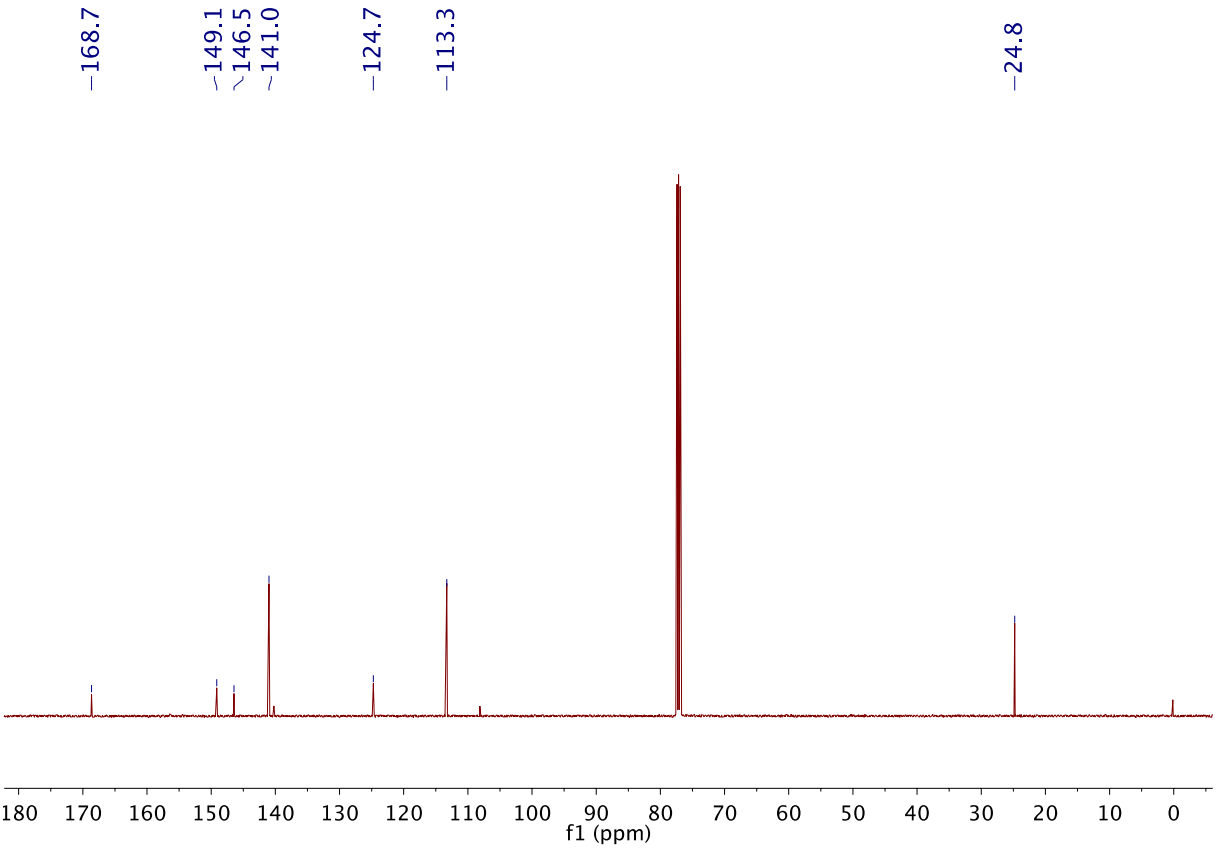

8.42
7.55
7.53
6.79
6.78
3.11
3.07
Cl
(Me)2N
N
N
Cl
1.00
1.03
1.03
3.11
3.26
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

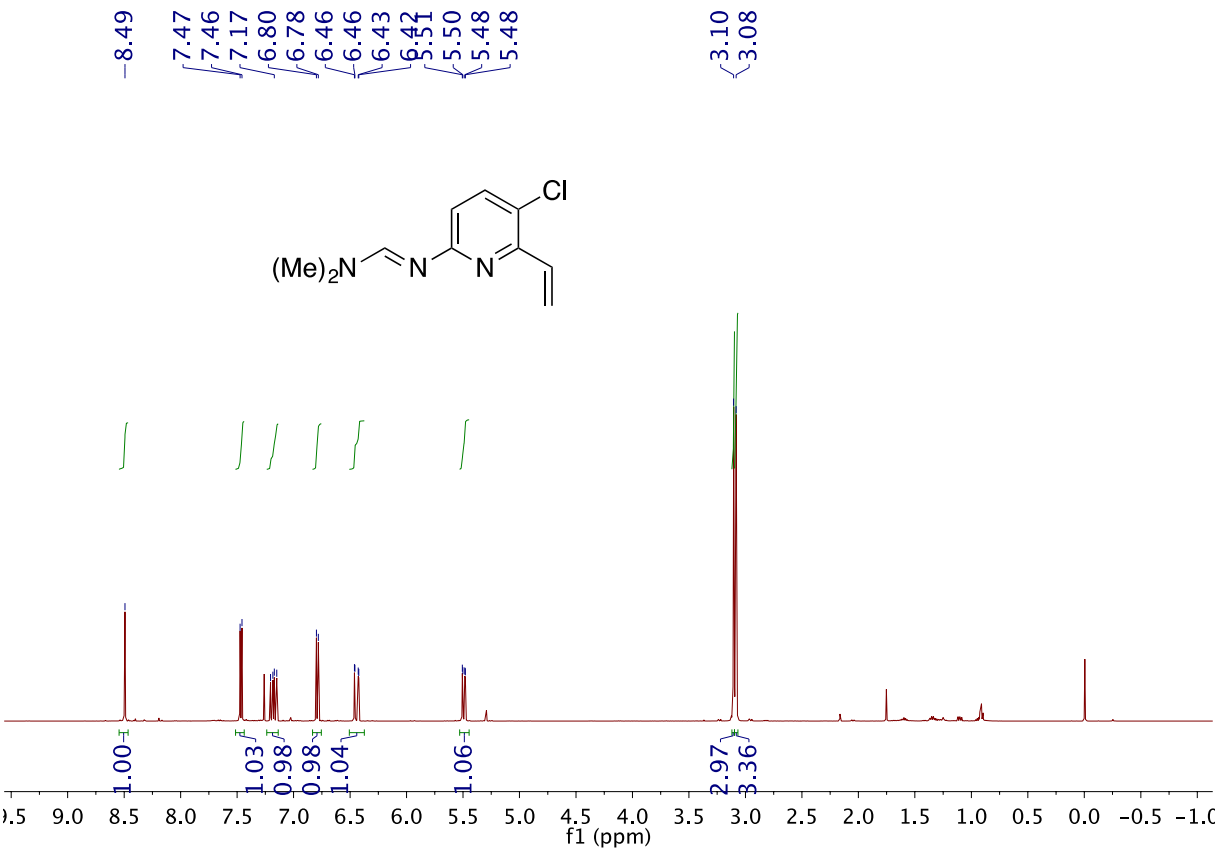

160.5
156.2
146.5
140.0
122.1
117.7
41.1
34.9
70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

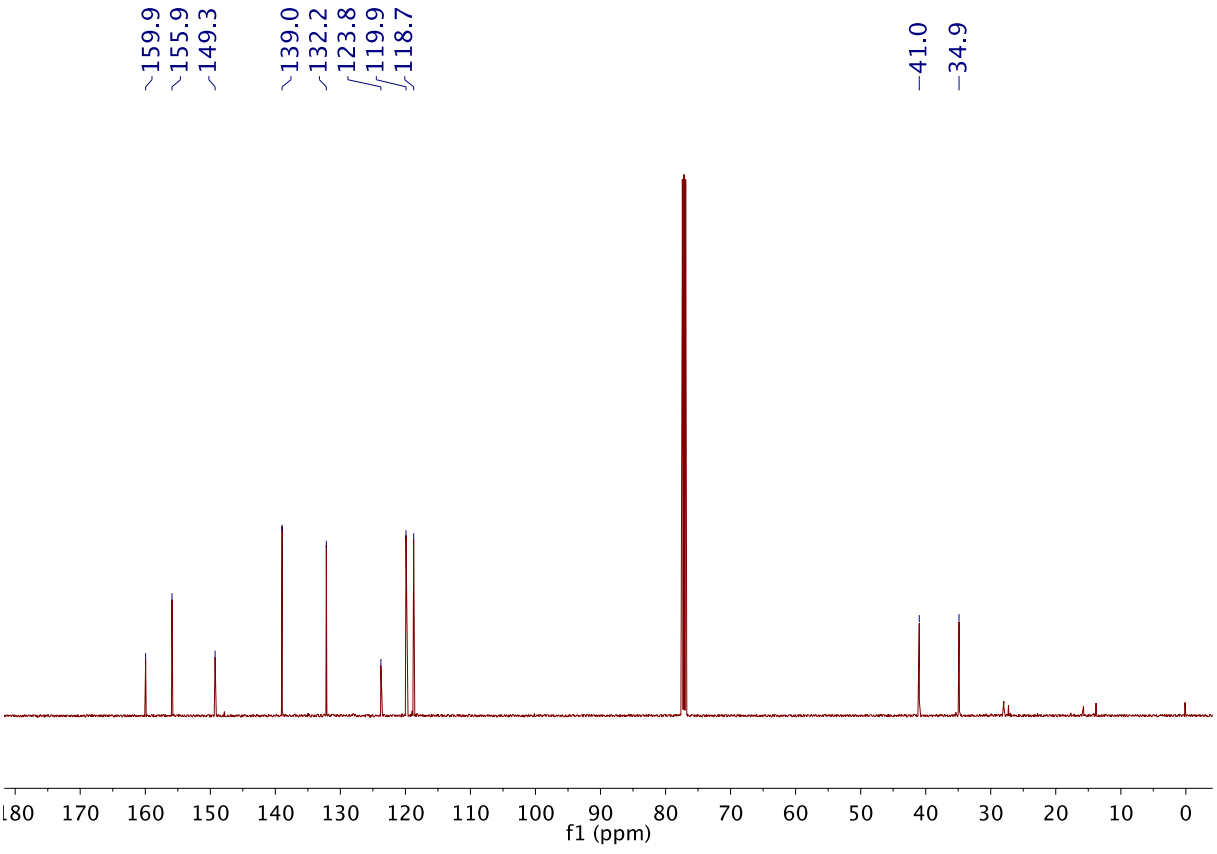

7.46
7.44
6.38
6.37
4.59
Cl
H2N
N
Cl
1.00
1.06
2.10
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

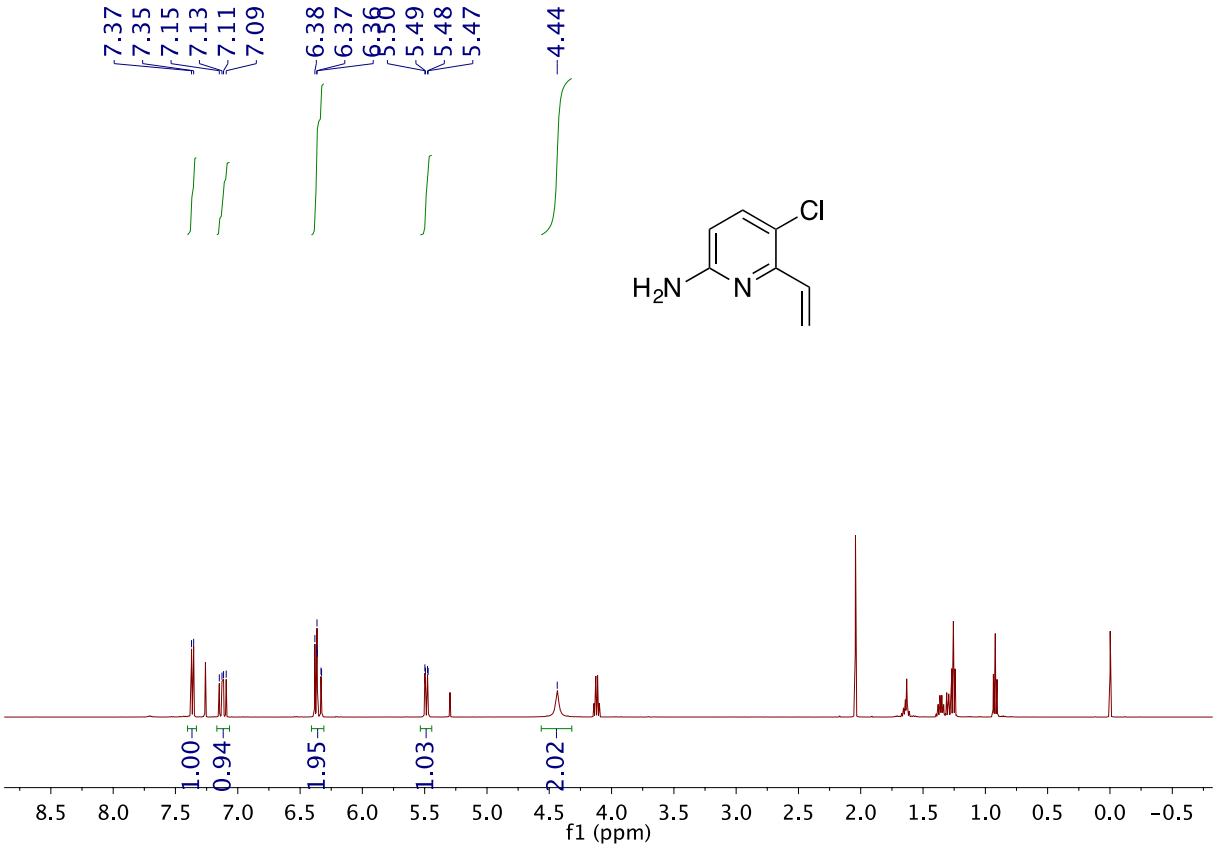

156.5
146.7
140.2
118.1
108.1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

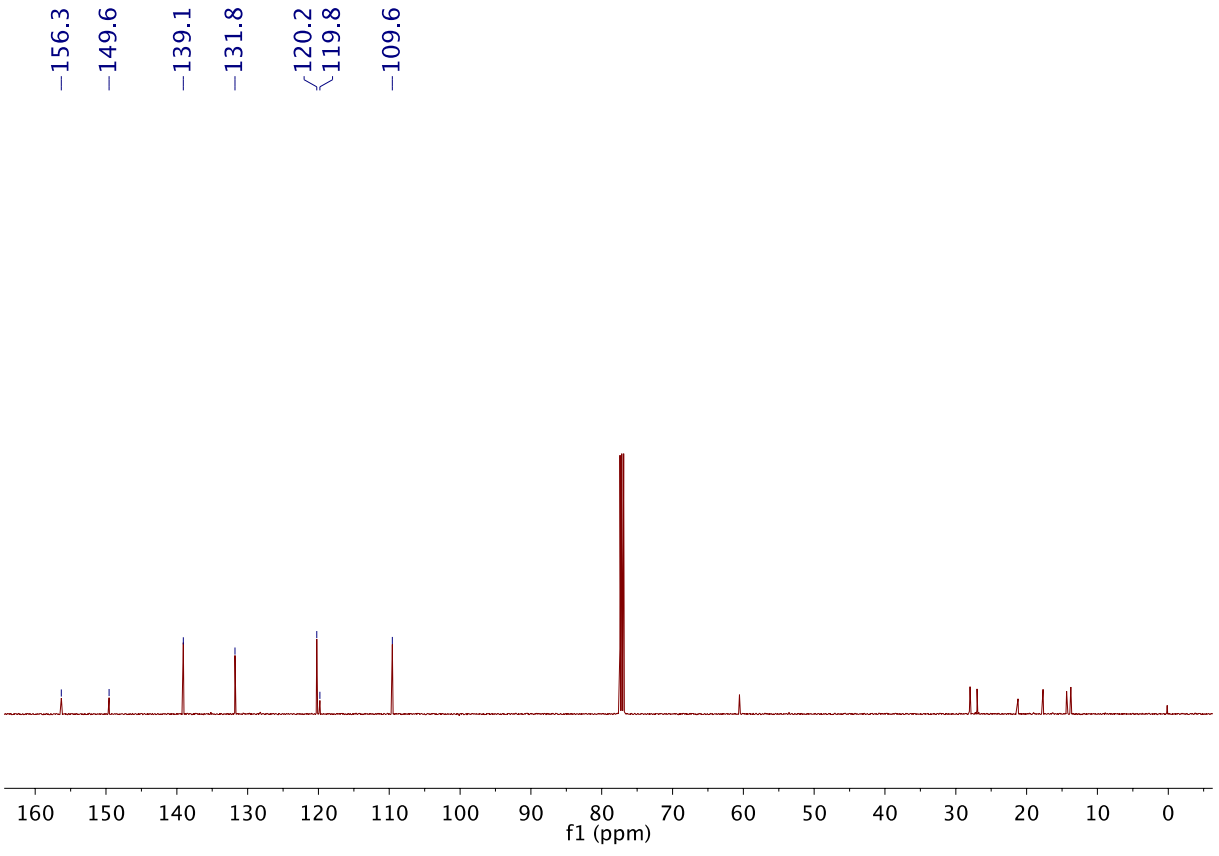

8.13
8.11
7.94
7.75
7.74
2.20
Cl
AcHN
N
Cl
1.00
0.93
1.04
3.18
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

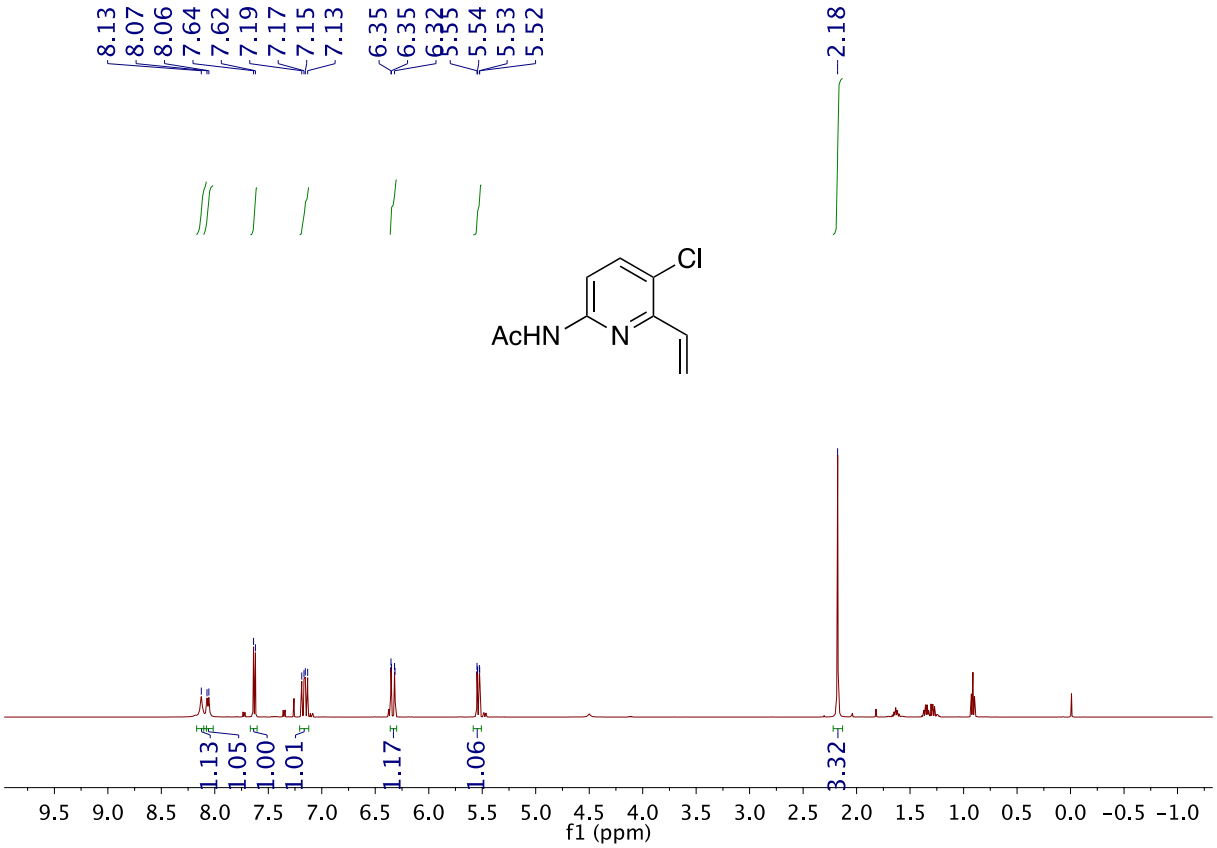

168.7
149.1
146.5
141.0
124.7
113.3
24.8
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

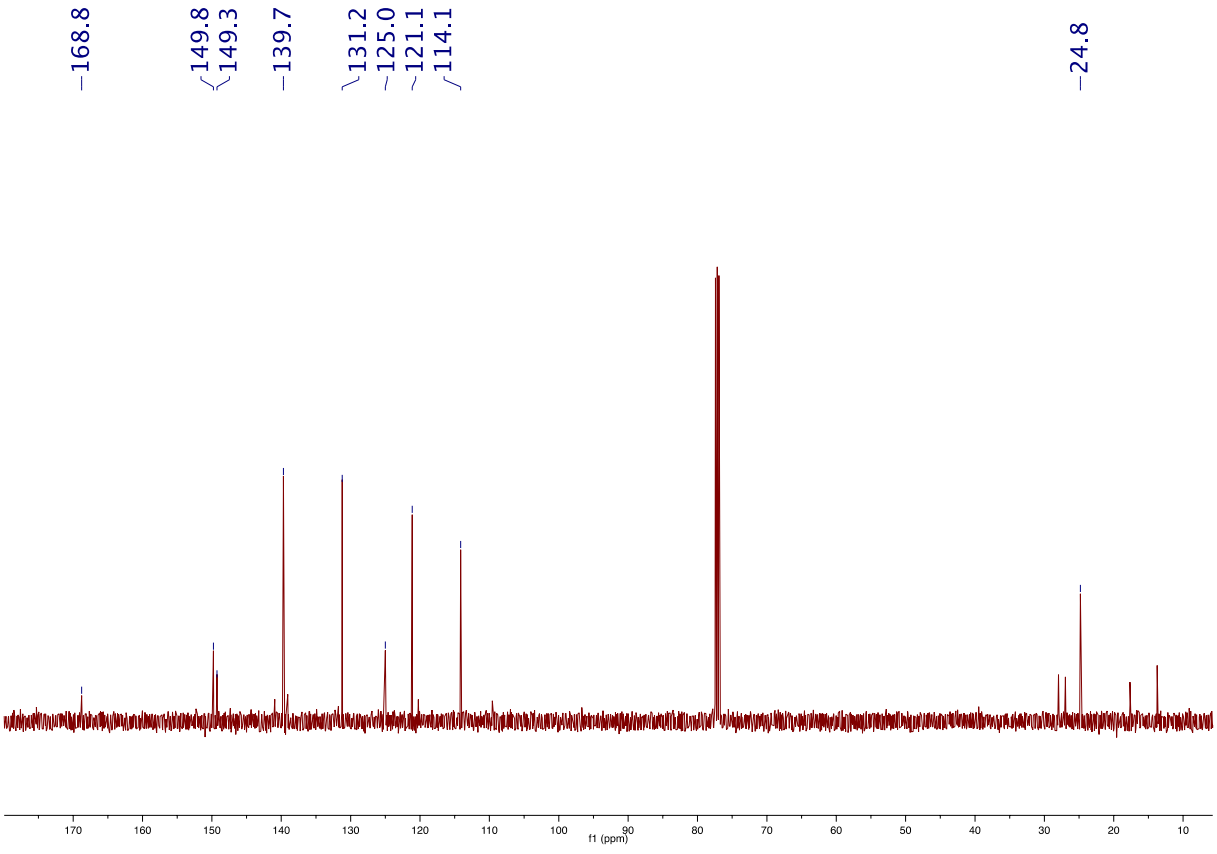

8.49
7.47
7.46
7.17
6.80
6.78
6.46
6.46
6.43
6.42
5.51
5.50
5.48
5.48
3.10
3.08
Cl
(Me)2N
N
N
1.00
1.03
0.98
0.98
1.04
1.06
2.97
3.36
f1 (ppm)

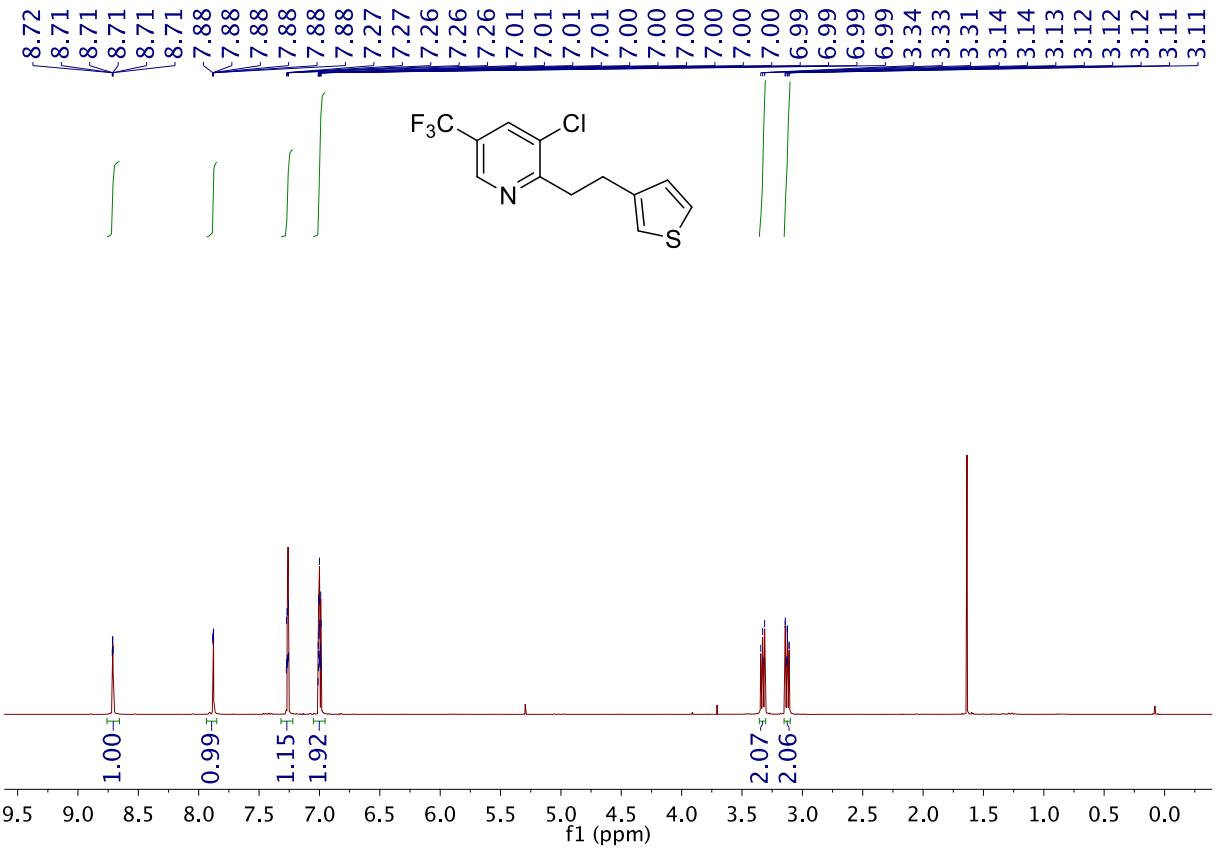

159.9
155.9
149.3
139.0
132.2
123.8
119.9
118.7
41.0
34.9
f1 (ppm)

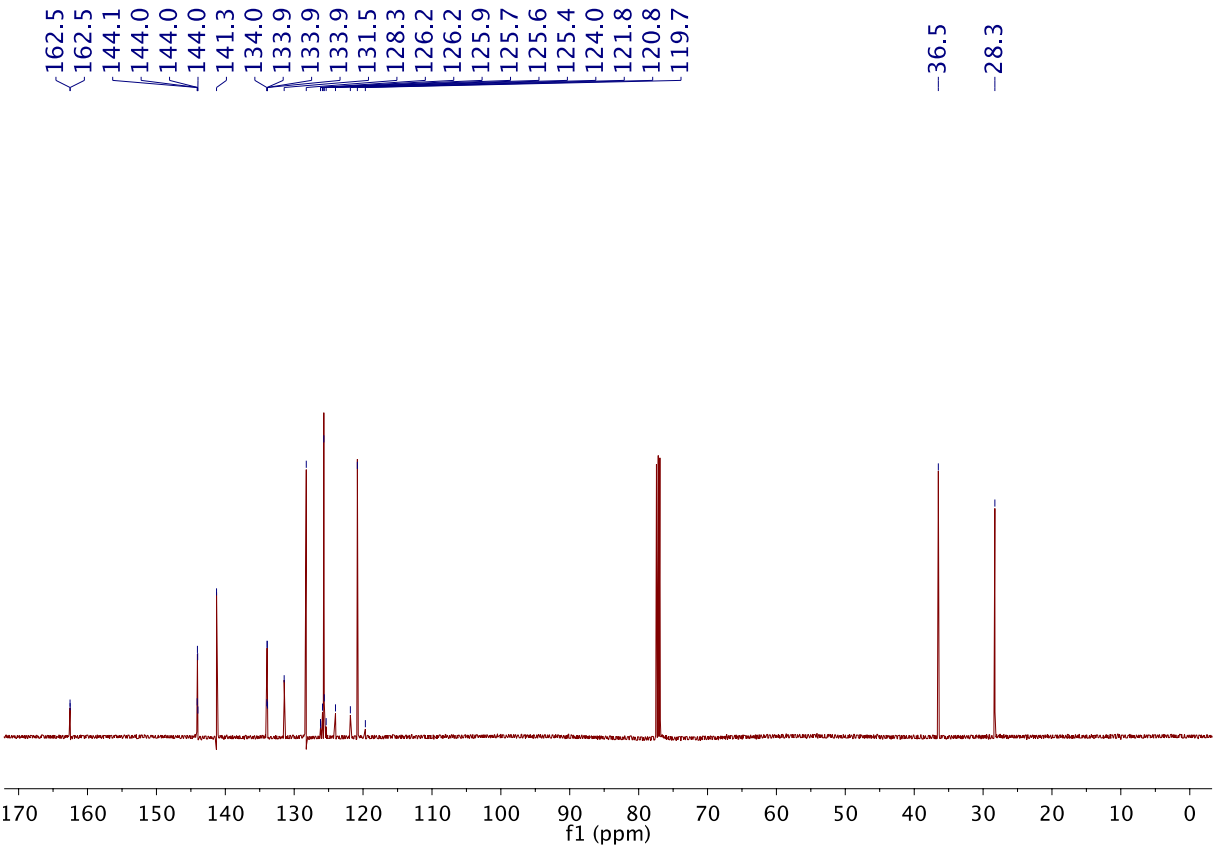

7.37
7.35
7.15
7.13
7.11
7.09
6.38
6.37
6.36
5.50
5.49
5.48
5.47
4.44
Cl
H2N
N
1.00
0.94
1.95
1.03
2.02
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

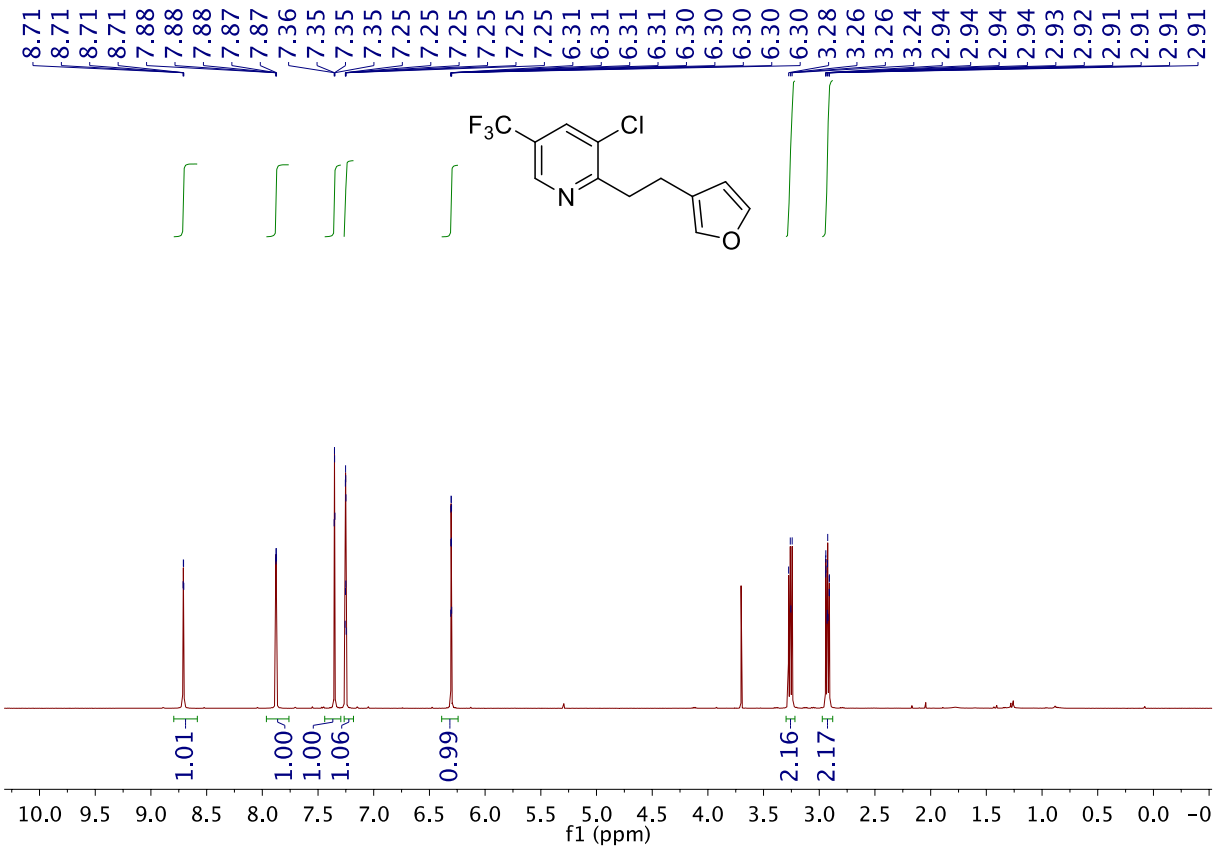

156.3
149.6
139.1
131.8
120.2
119.8
109.6
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

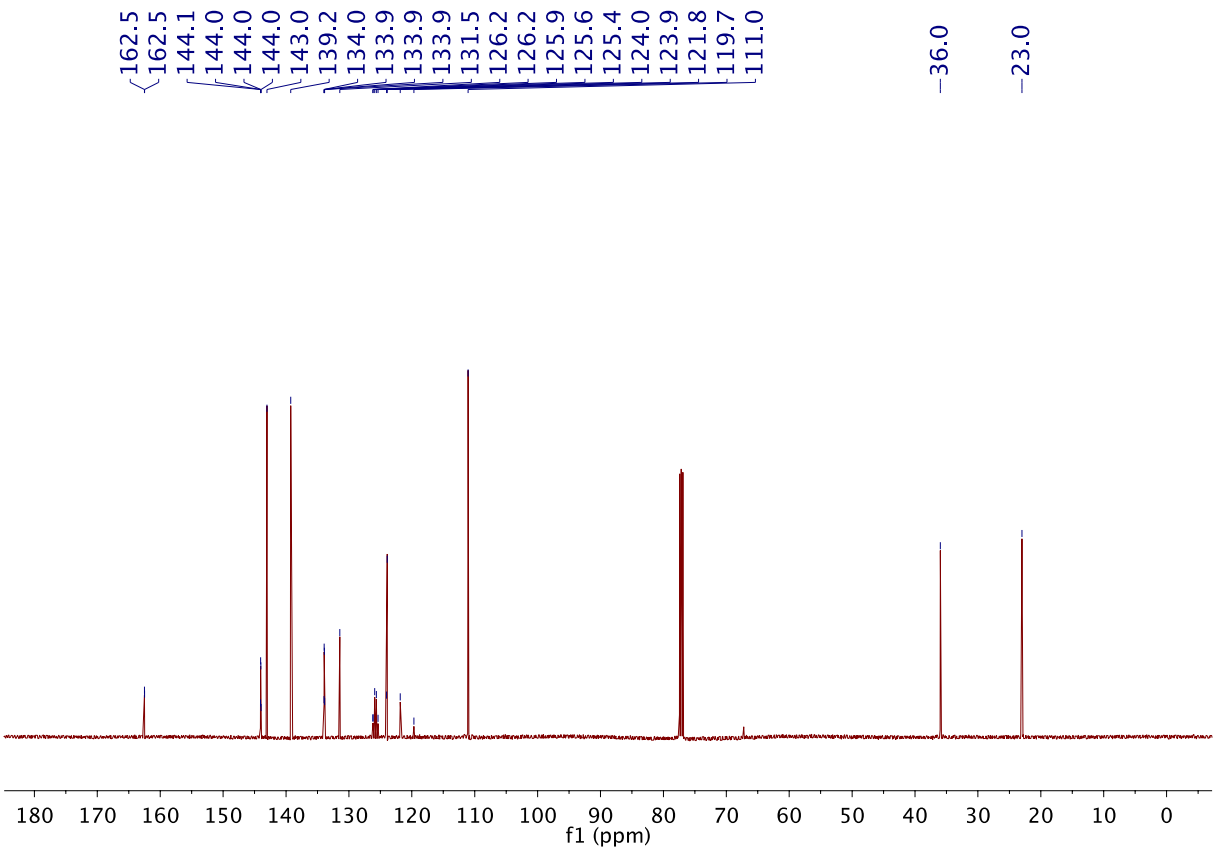

8.13
8.07
8.06
7.64
7.62
7.19
7.17
7.15
7.13
6.35
6.35
6.32
5.55
5.54
5.53
5.52
2.18
Cl
AcHN
N
1.13
1.05
1.00
1.01
1.17
1.06
3.32
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

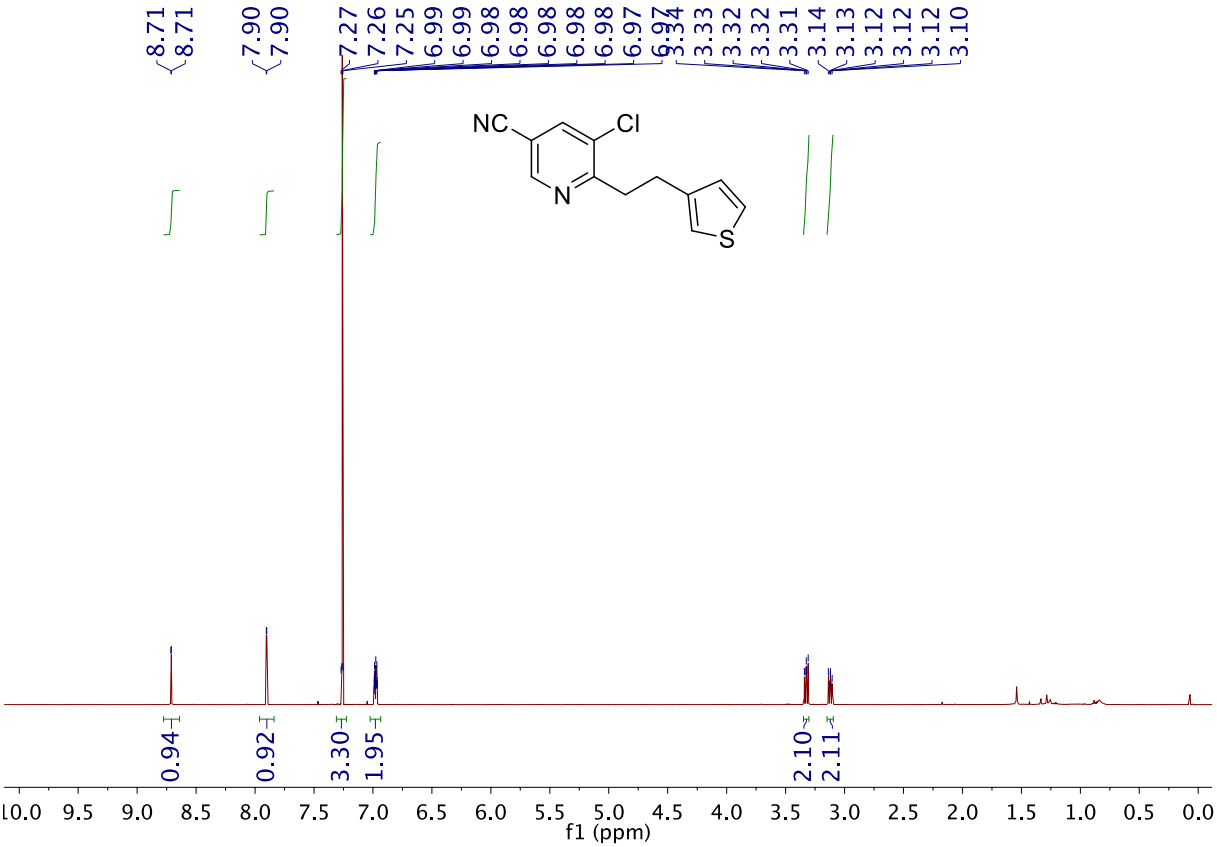

168.8
149.8
149.3
139.7
131.2
125.0
121.1
114.1
24.8
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

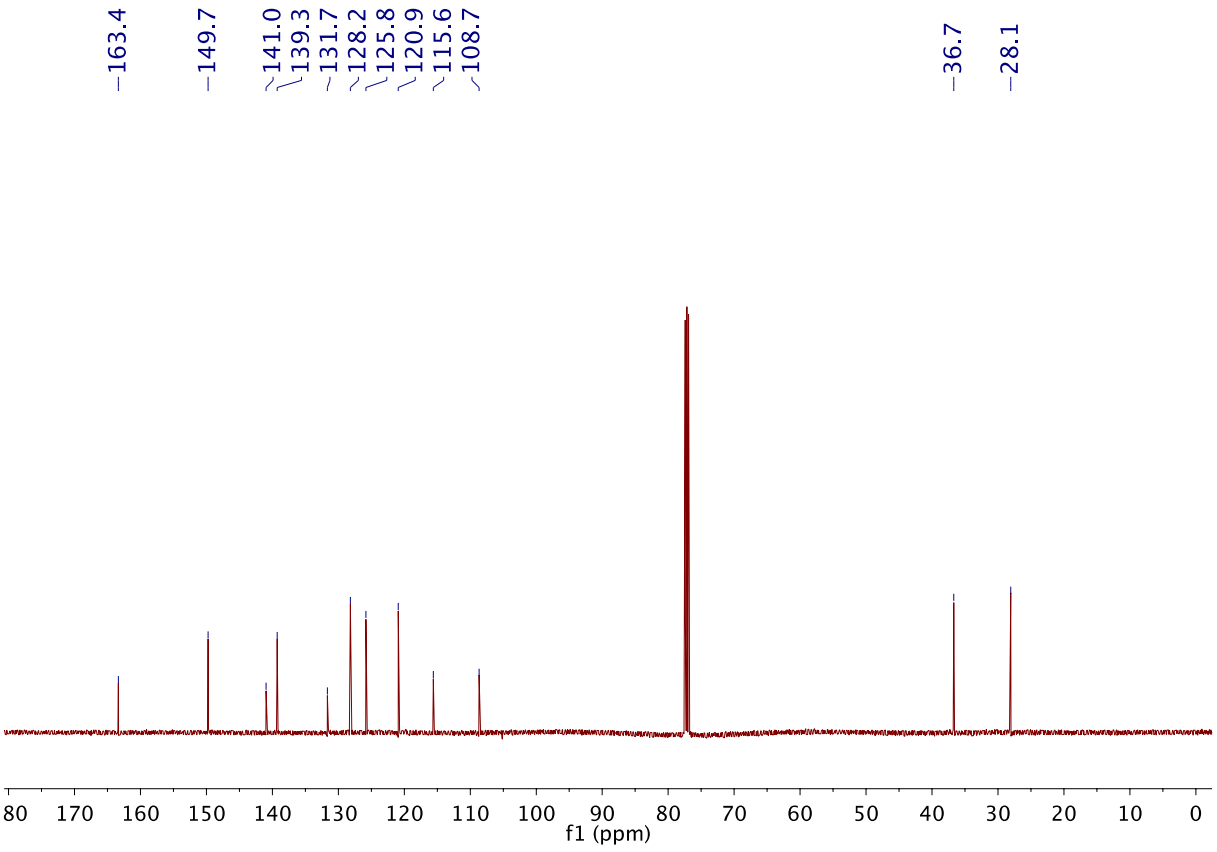

8.72
8.71
8.71
8.71
8.71
8.71
7.88
7.88
7.88
7.88
7.88
7.88
7.27
7.27
7.26
7.26
7.26
7.01
7.01
7.01
7.01
7.00
7.00
7.00
7.00
7.00
7.00
6.99
6.99
6.99
6.99
3.34
3.33
3.31
3.14
3.14
3.13
3.12
3.12
3.12
3.11
3.11
F3C
Cl
N
S
1.00
0.99
1.15
1.92
2.07
2.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

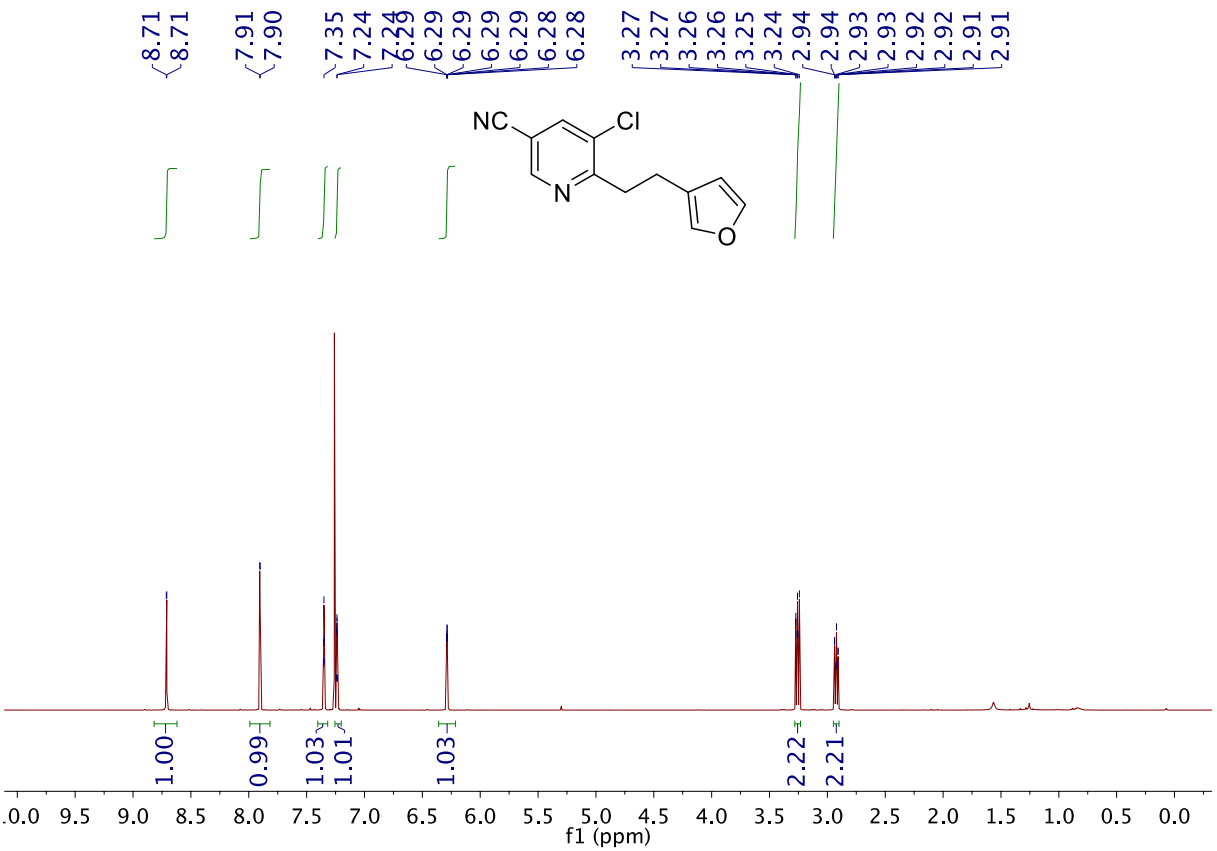

162.5
162.5
144.1
144.0
144.0
144.0
141.3
134.0
133.9
133.9
133.9
131.5
128.3
126.2
126.2
125.9
125.7
125.6
125.4
124.0
121.8
120.8
119.7
36.5
28.3
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

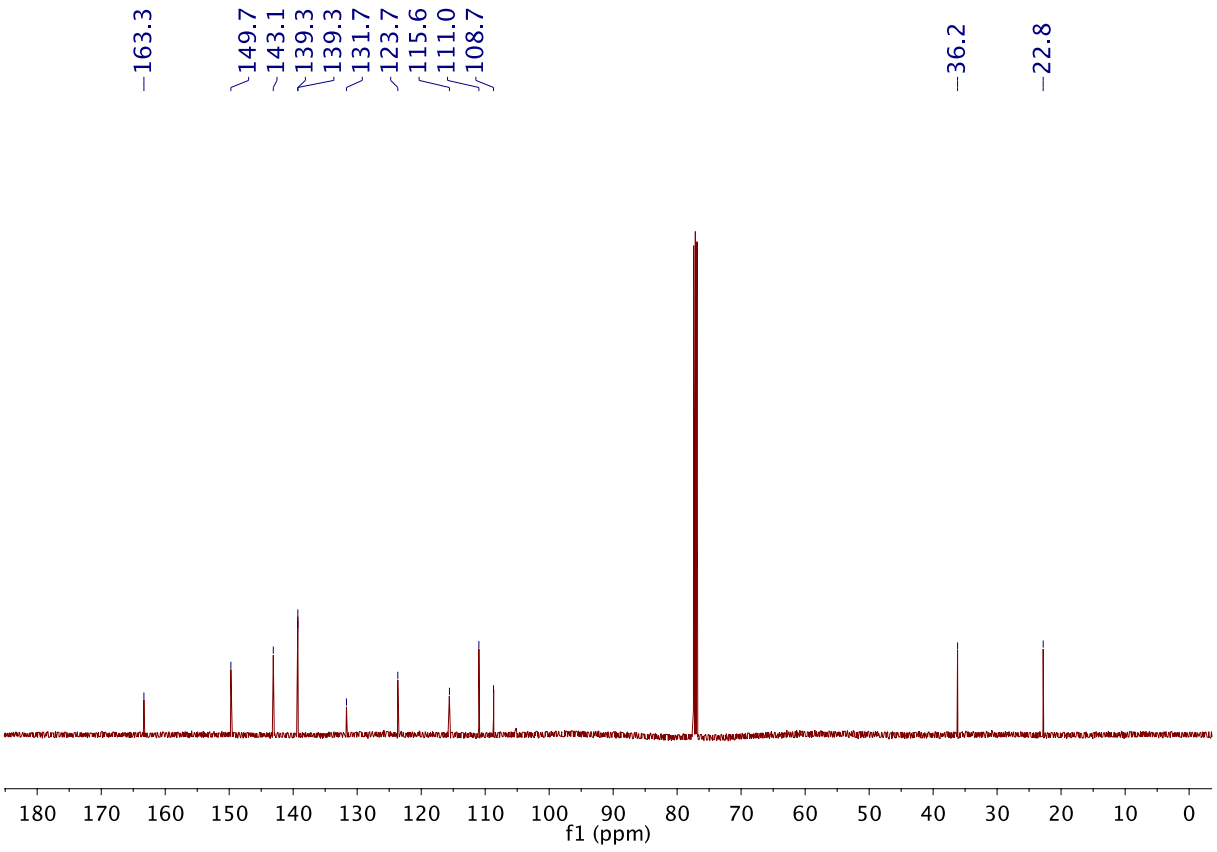

8.71 8.71 8.71 8.71 7.88 7.88 7.88 7.87 7.87 7.36 7.35 7.35 7.35 7.25 7.25 7.25 7.25 7.25 7.25 6.31 6.31 6.31 6.30 6.30 6.30 6.30 6.30 3.28 3.26 3.26 3.24 2.94 2.94 2.94 2.94 2.93 2.92 2.91 2.91 2.91 2.91
F3C
Cl
N
O
1.01
1.00
1.00
1.06
0.99
2.16
2.17
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

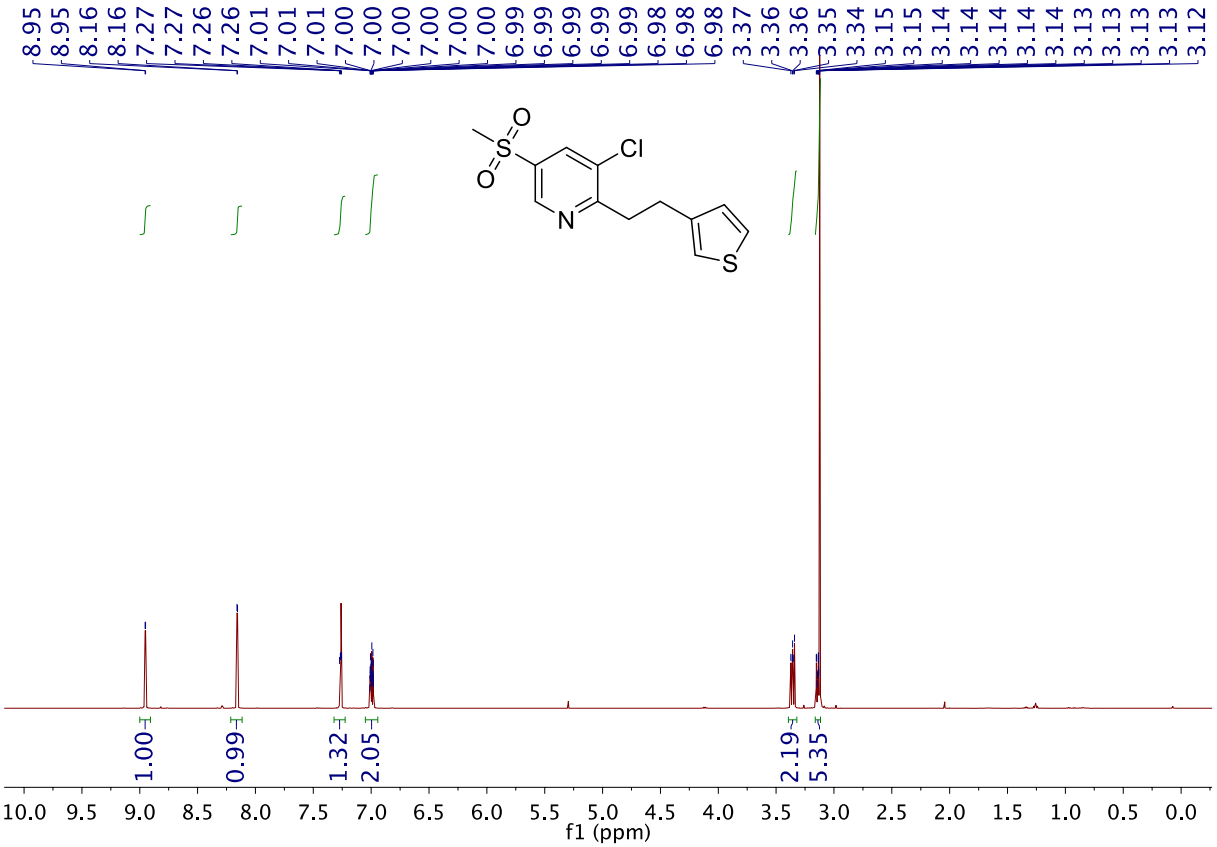

162.5 162.5 144.1 144.0 144.0 144.0 143.0 139.2 134.0 133.9 133.9 133.9 131.5 126.2 126.2 125.9 125.6 125.4 124.0 123.9 121.8 119.7 111.0
36.0
23.0
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

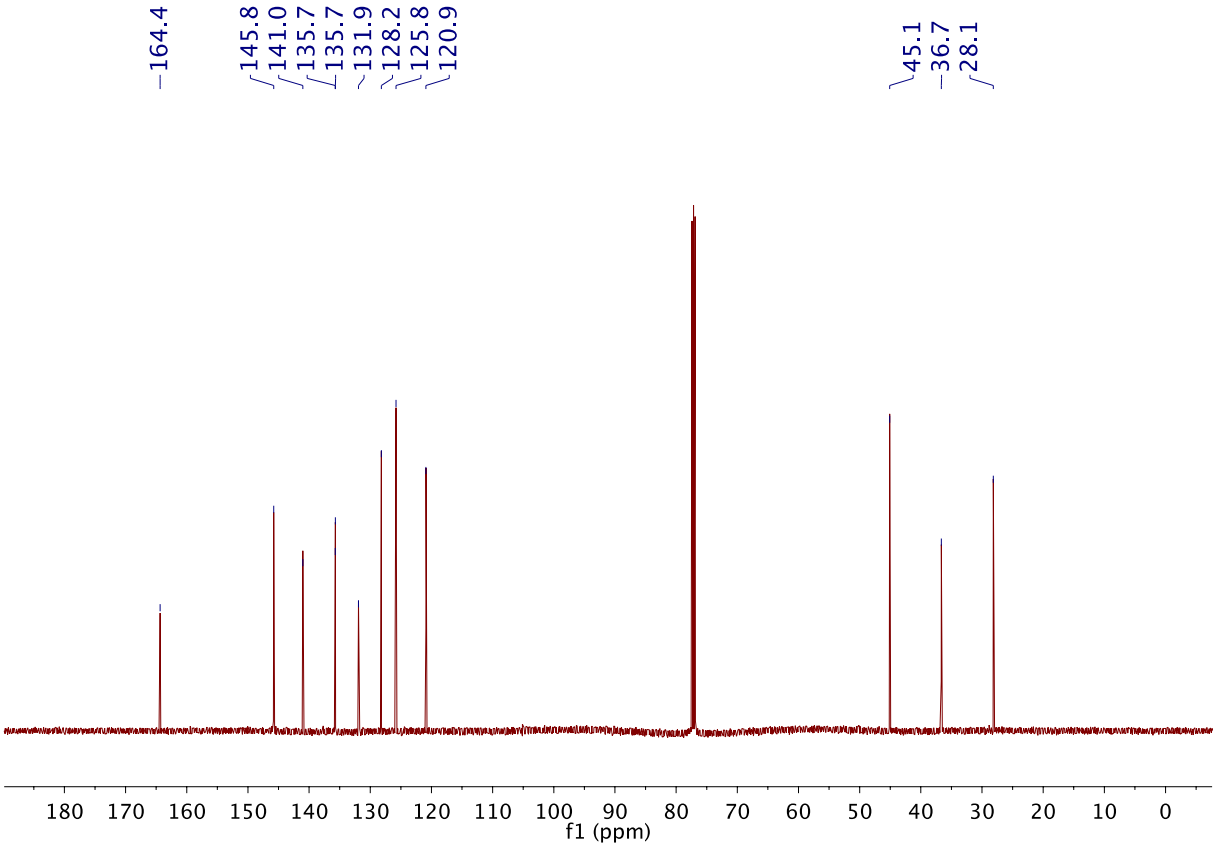

8.71
8.71
7.90
7.90
7.27
7.26
7.25
6.99
6.99
6.98
6.98
6.98
6.98
6.98
6.97
6.97
3.34
3.33
3.32
3.32
3.31
3.14
3.13
3.12
3.12
3.12
3.10
NC
Cl
N
S
0.94
0.92
3.30
1.95
2.10
2.11
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

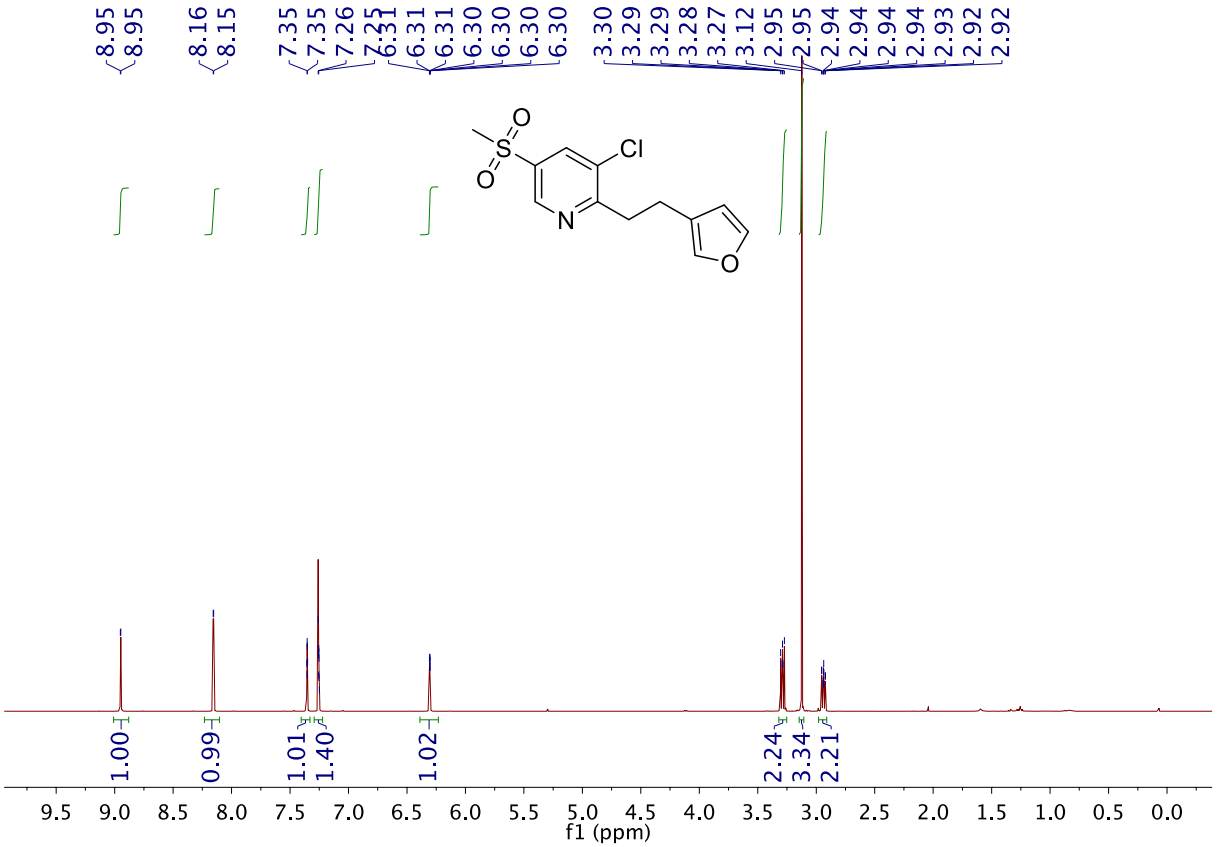

163.4
149.7
141.0
139.3
131.7
128.2
125.8
120.9
115.6
108.7
36.7
28.1
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

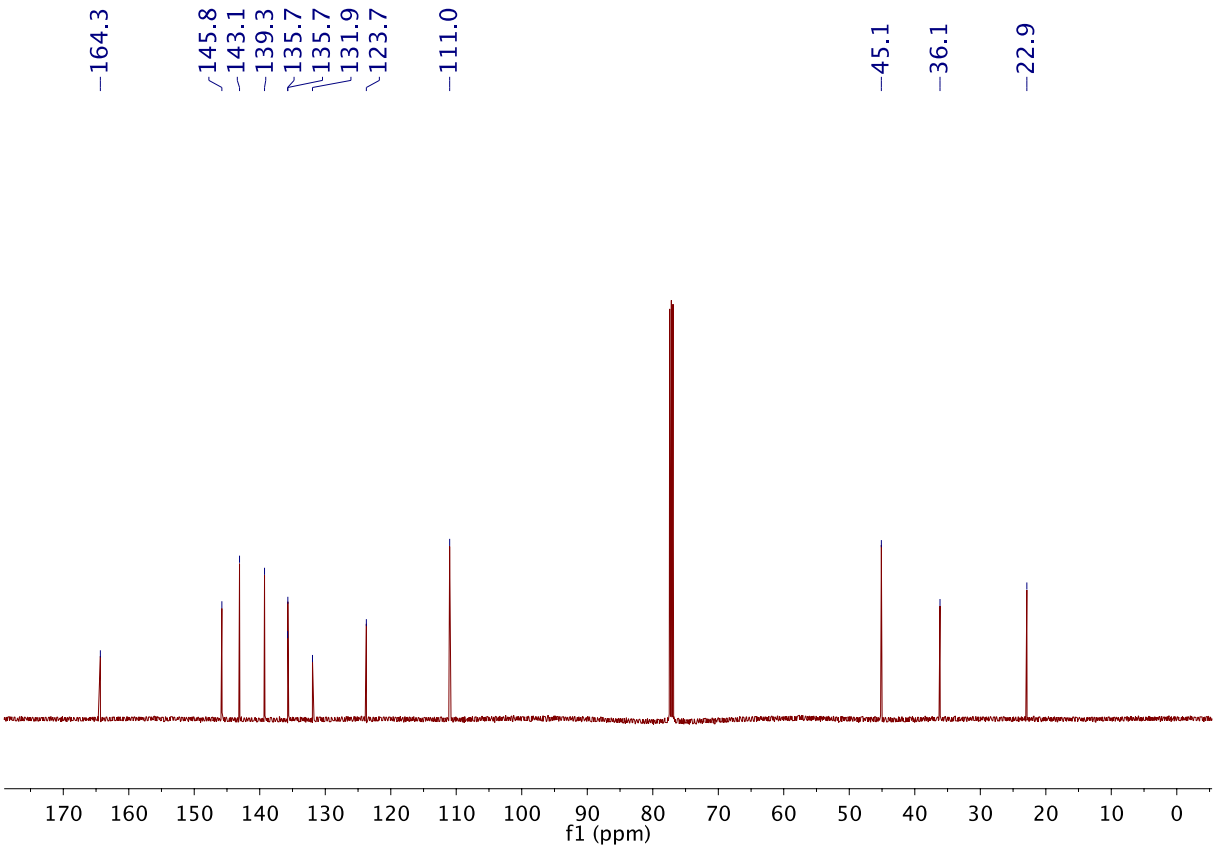

8.71
8.71
7.91
7.90
7.35
7.24
6.29
6.29
6.29
6.29
6.28
6.28
3.27
3.27
3.26
3.26
3.25
3.24
2.94
2.94
2.93
2.93
2.92
2.92
2.91
2.91
NC
Cl
N
O
1.00
0.99
1.03
1.01
1.03
2.22
2.21
f1 (ppm)

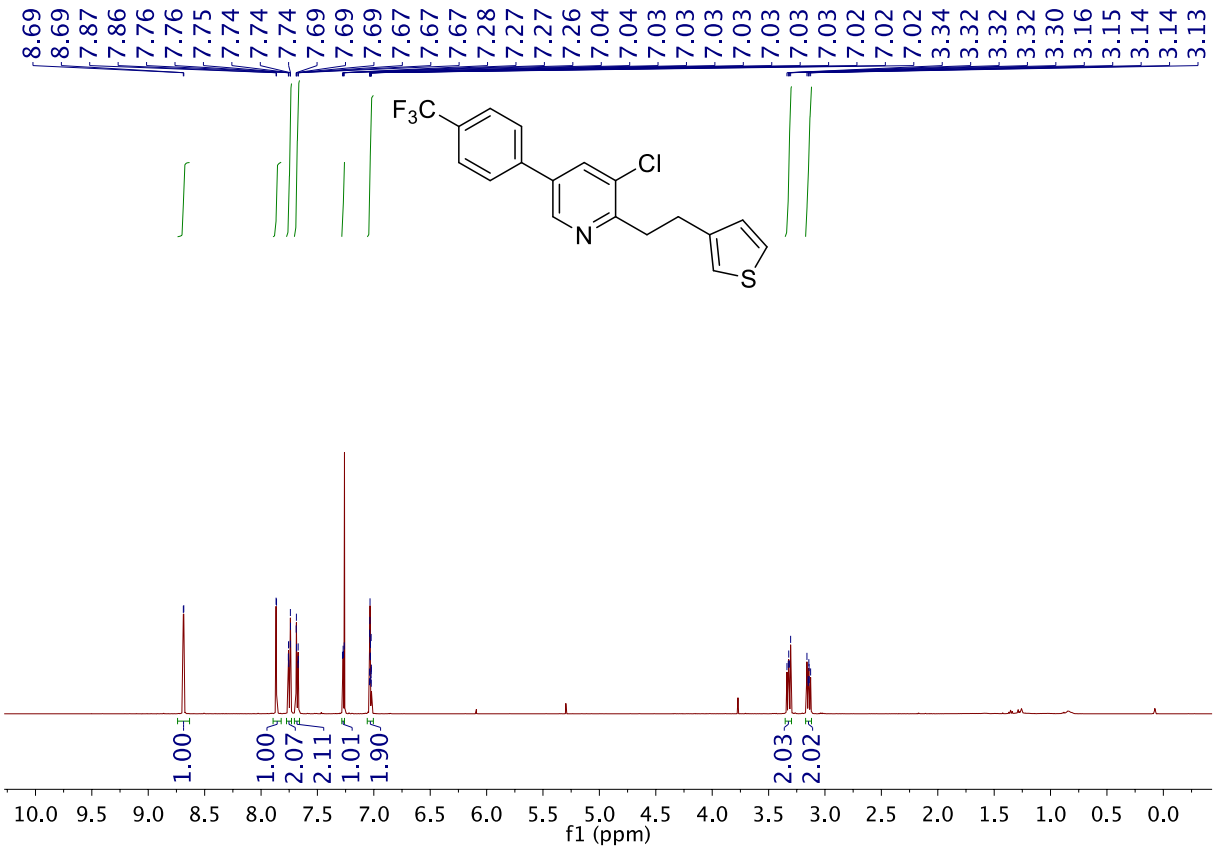

163.3
149.7
143.1
139.3
139.3
131.7
123.7
115.6
111.0
108.7
36.2
22.8
f1 (ppm)

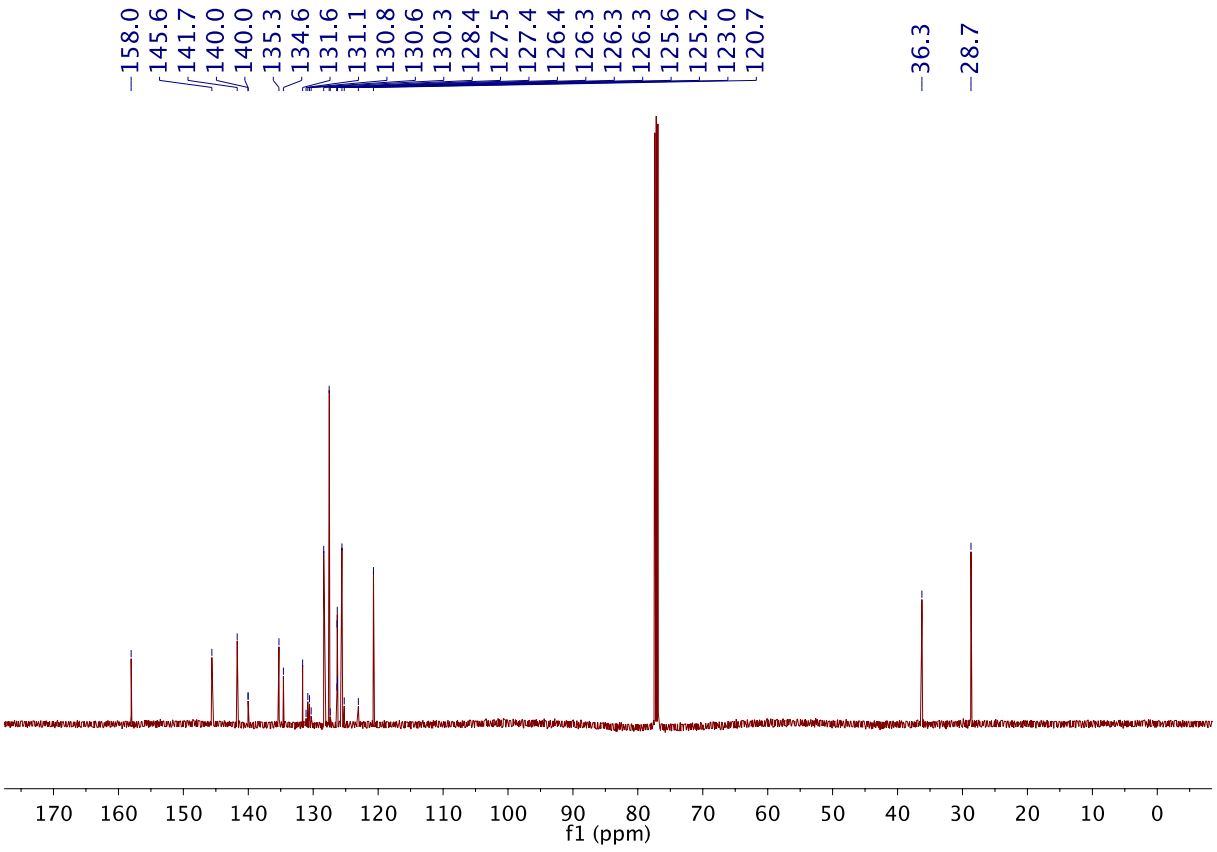

8.95
8.95
8.16
8.16
7.27
7.27
7.26
7.26
7.01
7.01
7.01
7.00
7.00
7.00
7.00
7.00
7.00
6.99
6.99
6.99
6.99
6.99
6.98
6.98
6.98
3.37
3.36
3.36
3.35
3.34
3.15
3.15
3.14
3.14
3.14
3.14
3.14
3.13
3.13
3.13
3.13
3.12
O
S
O
Cl
N
S
1.00
0.99
1.32
2.05
2.19
5.35
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

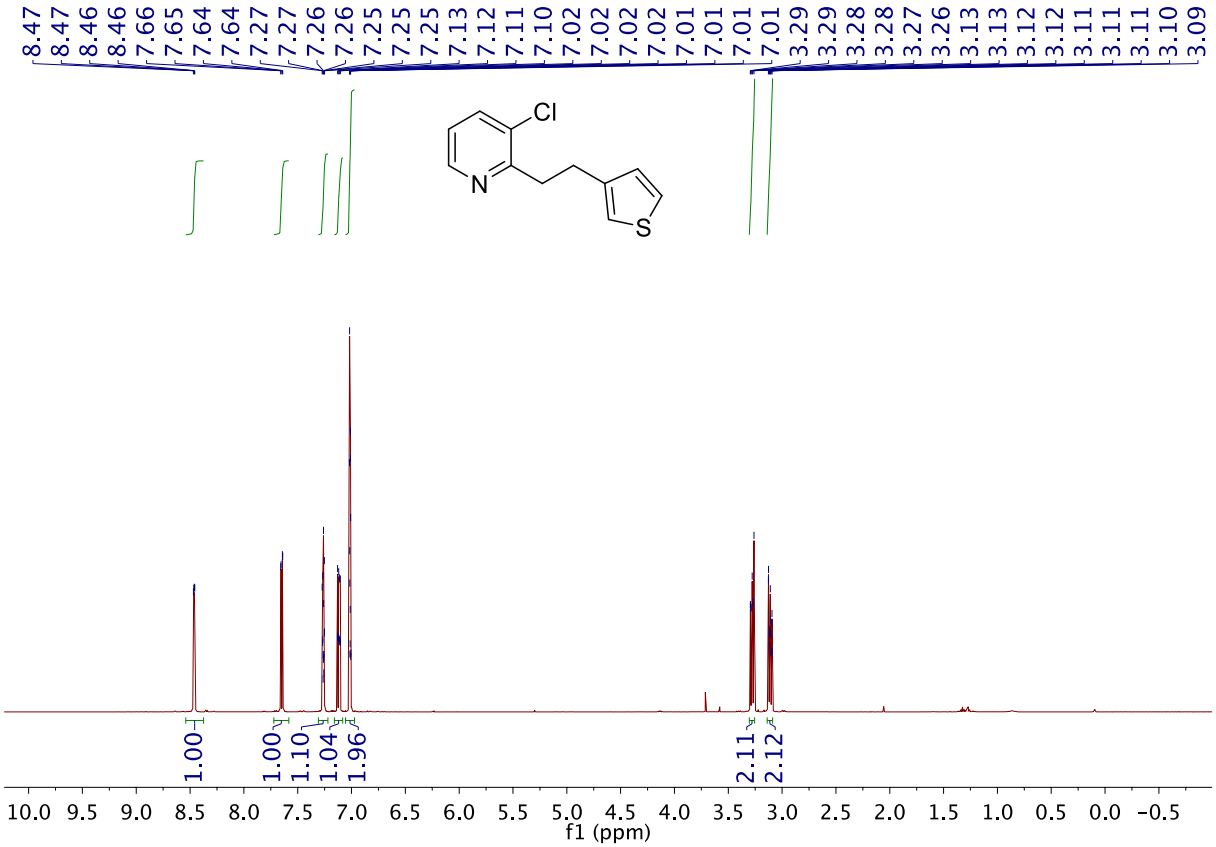

164.4
145.8
141.0
135.7
135.7
131.9
128.2
125.8
120.9
45.1
36.7
28.1
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

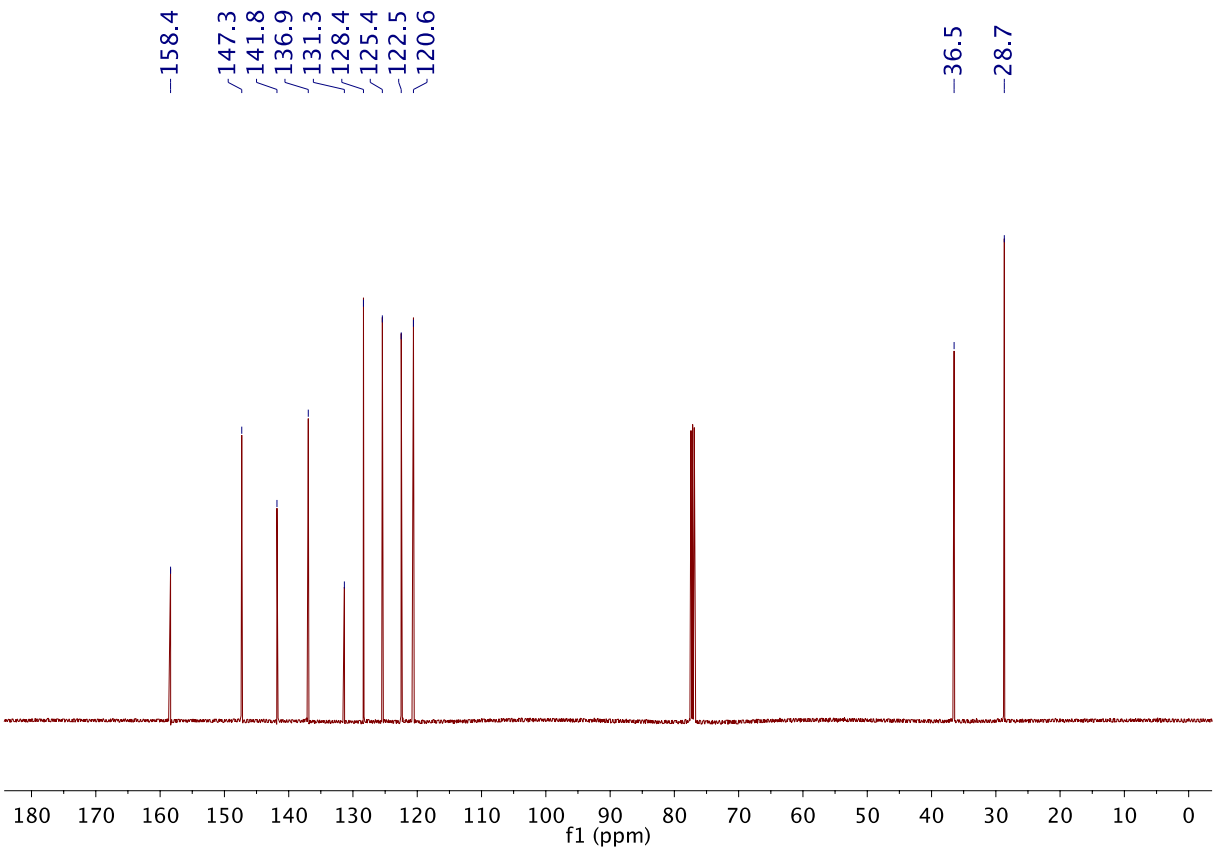

8.95
8.95
8.16
8.15
7.35
7.35
7.26
7.25
6.31
6.31
6.31
6.30
6.30
6.30
6.30
3.30
3.29
3.29
3.28
3.27
3.12
2.95
2.95
2.94
2.94
2.94
2.94
2.93
2.92
2.92
O
S
O
Cl
N
O
1.00
0.99
1.01
1.40
1.02
2.24
3.34
2.21
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

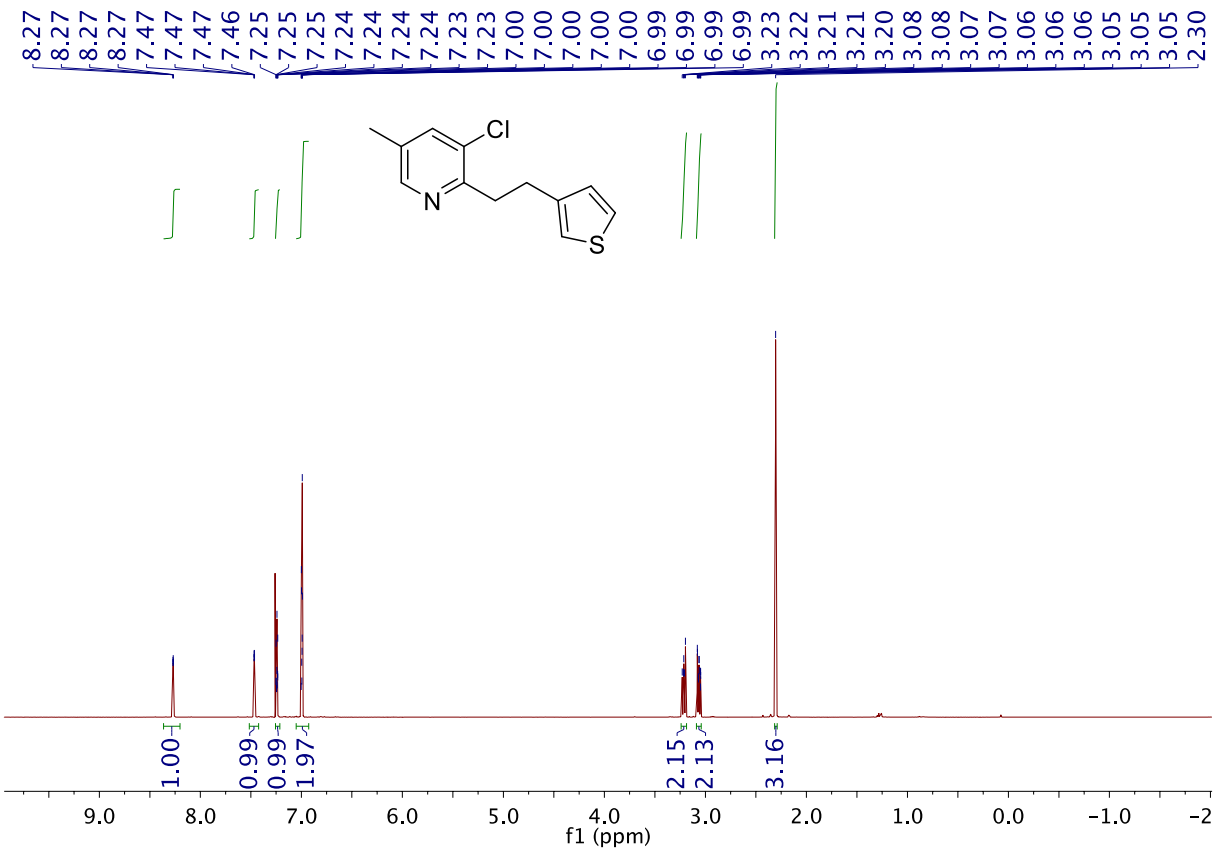

164.3
145.8
143.1
139.3
135.7
135.7
131.9
123.7
111.0
45.1
36.1
22.9
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

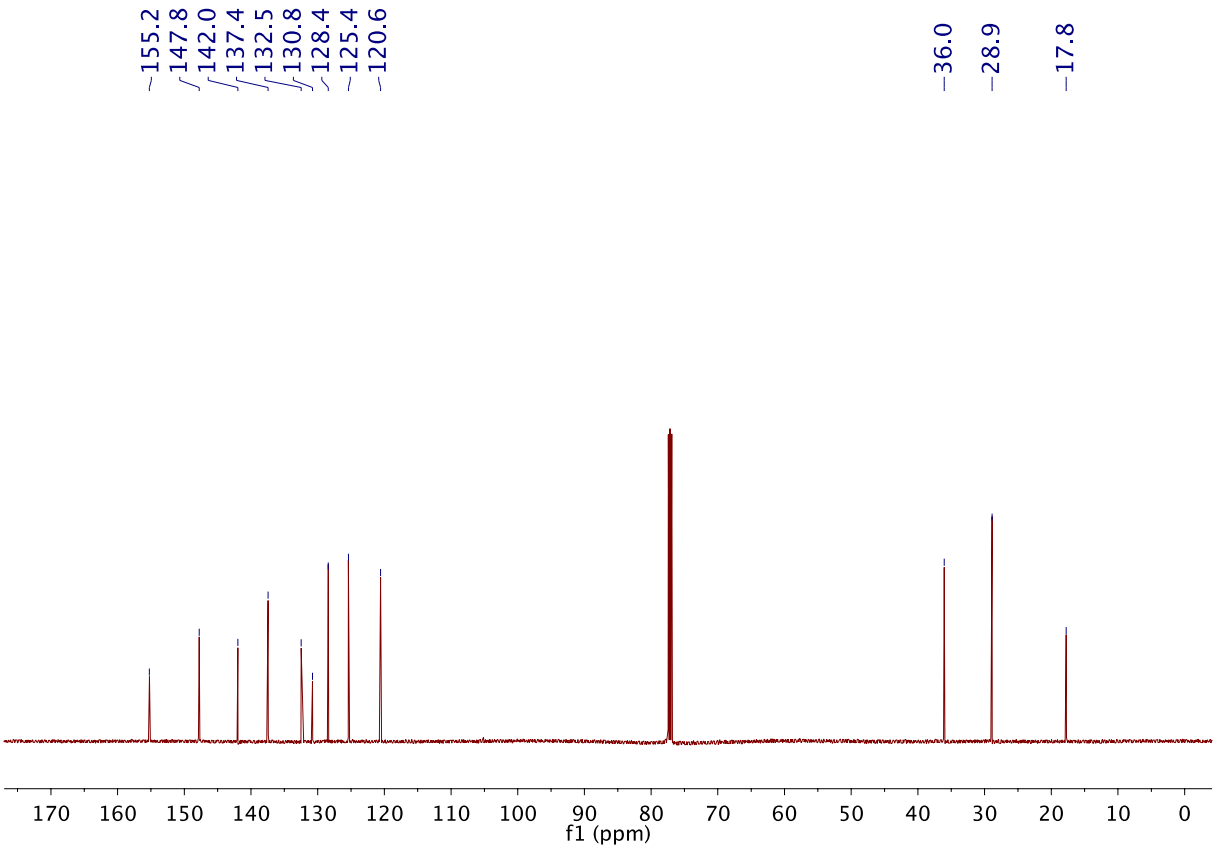

8.69
8.69
7.87
7.86
7.76
7.76
7.75
7.74
7.74
7.74
7.69
7.69
7.69
7.67
7.67
7.67
7.28
7.27
7.27
7.26
7.04
7.04
7.03
7.03
7.03
7.03
7.03
7.03
7.02
7.02
7.02
3.34
3.32
3.32
3.32
3.30
3.16
3.15
3.14
3.14
3.13
F3C
Cl
N
S
1.00
1.00
2.07
2.11
1.01
1.90
2.03
2.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

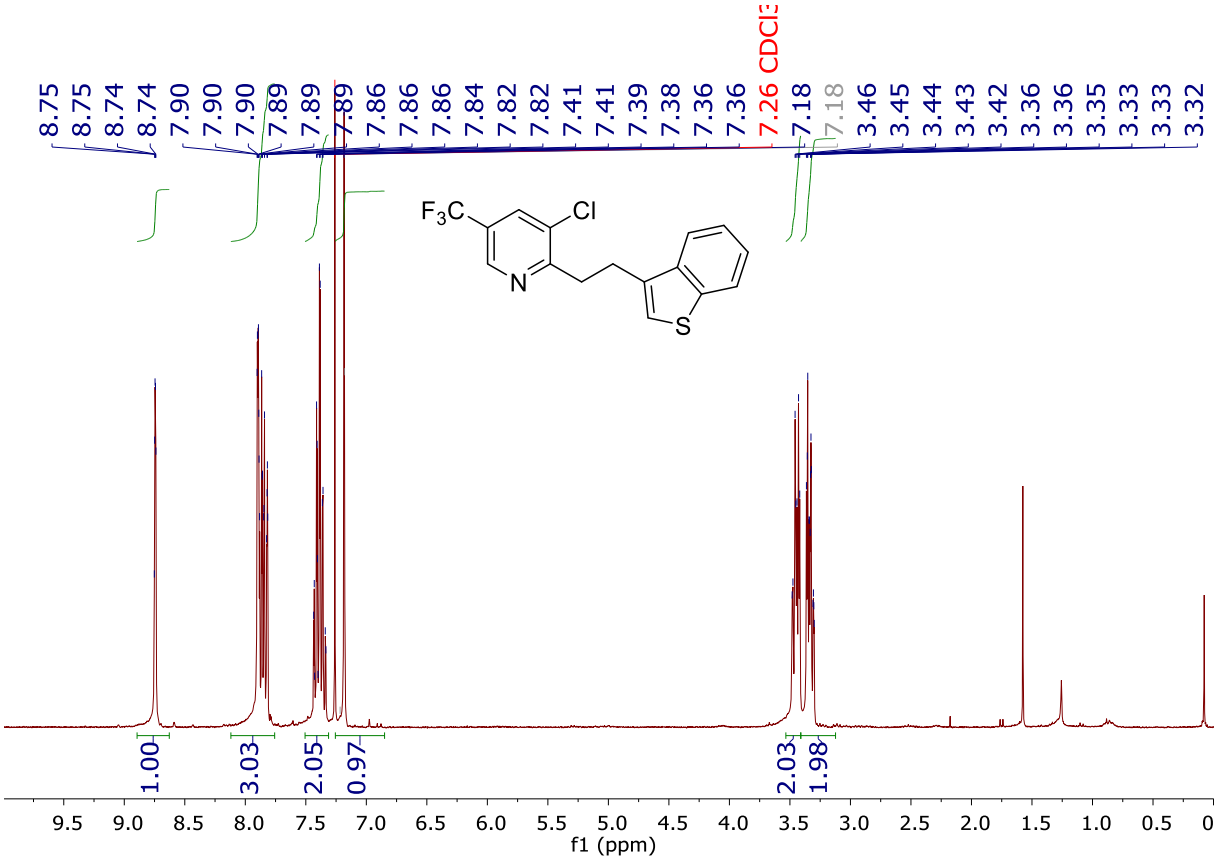

158.0
145.6
141.7
140.0
140.0
135.3
134.6
131.6
131.1
130.8
130.6
130.3
128.4
127.5
127.4
126.4
126.3
126.3
126.3
125.6
125.2
123.0
120.7
36.3
28.7
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

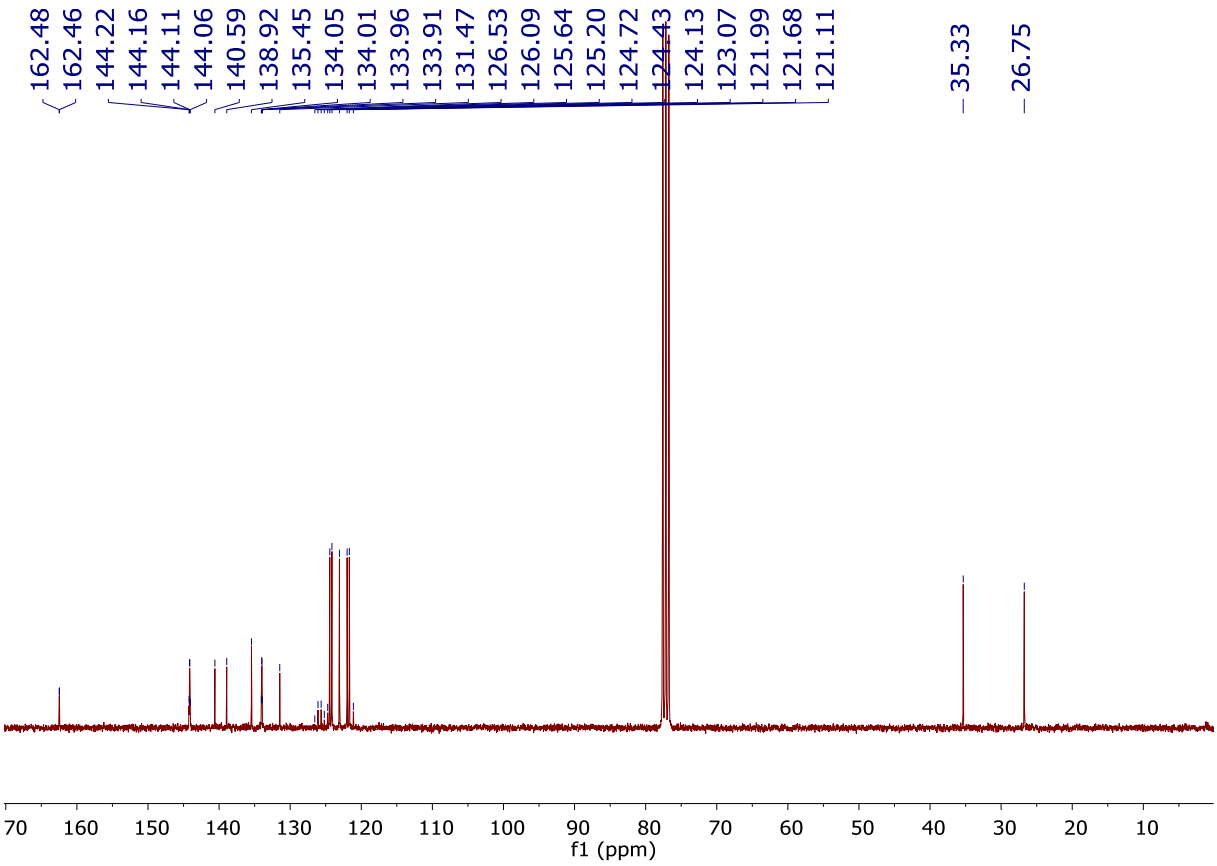

8.47
8.47
8.46
8.46
7.66
7.65
7.64
7.64
7.27
7.27
7.26
7.26
7.25
7.25
7.25
7.13
7.12
7.11
7.10
7.02
7.02
7.02
7.02
7.01
7.01
7.01
7.01
3.29
3.29
3.28
3.28
3.27
3.26
3.13
3.13
3.12
3.12
3.11
3.11
3.11
3.10
3.09
Cl
N
S
1.00
1.00
1.10
1.04
1.96
2.11
2.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

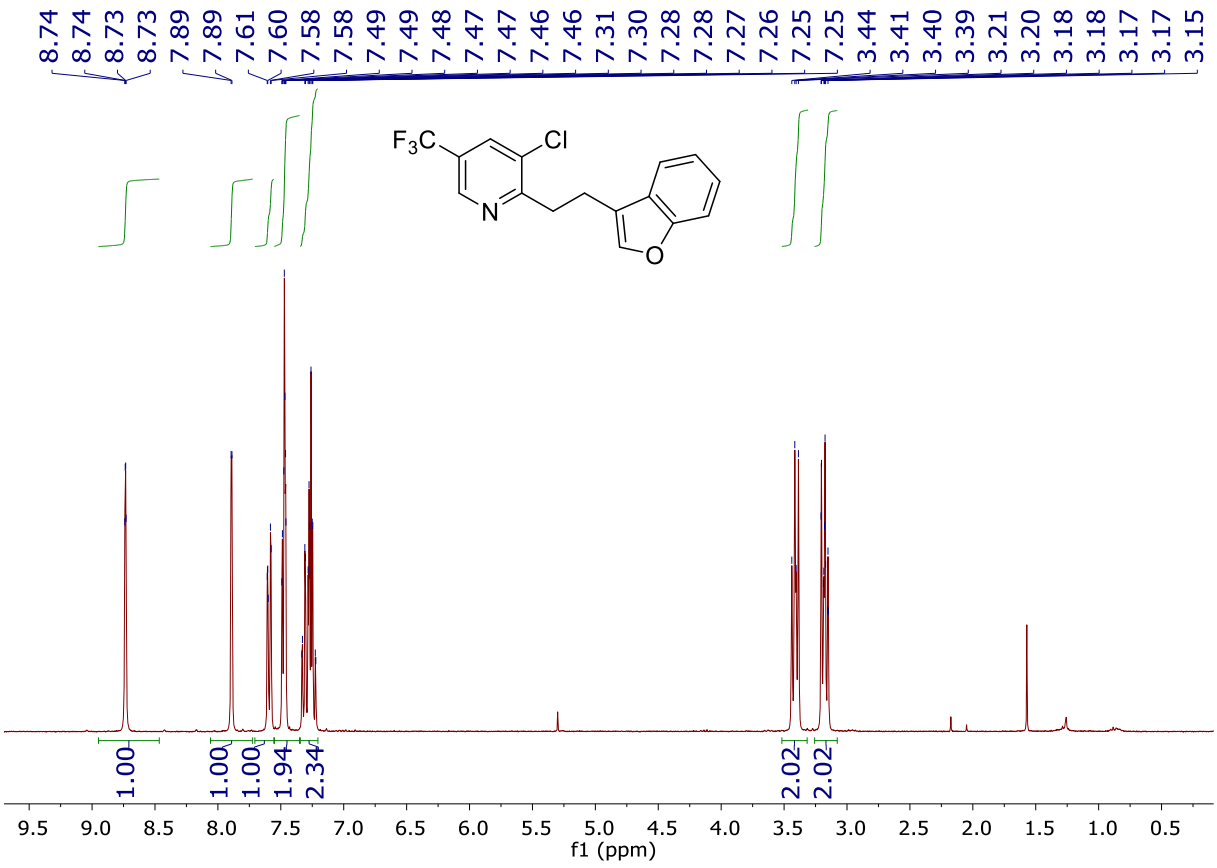

158.4
147.3
141.8
136.9
131.3
128.4
125.4
122.5
120.6
36.5
28.7
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

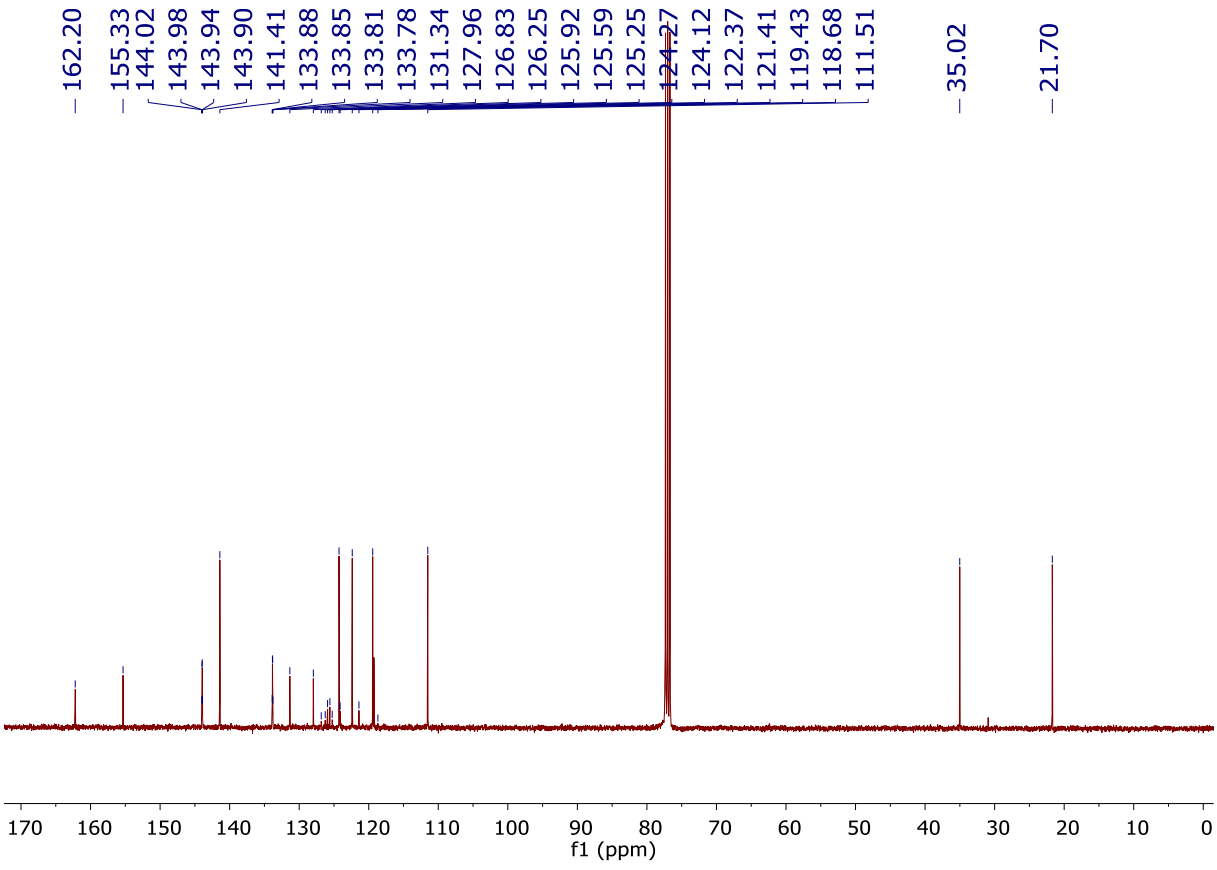

8.27
8.27
8.27
8.27
7.47
7.47
7.47
7.46
7.25
7.25
7.25
7.24
7.24
7.24
7.24
7.24
7.23
7.23
7.00
7.00
7.00
7.00
7.00
6.99
6.99
6.99
6.99
3.23
3.22
3.21
3.21
3.20
3.08
3.08
3.07
3.07
3.06
3.06
3.06
3.05
3.05
3.05
2.30
Cl
N
S
1.00
0.99
0.99
1.97
2.15
2.13
3.16
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2
f1 (ppm)

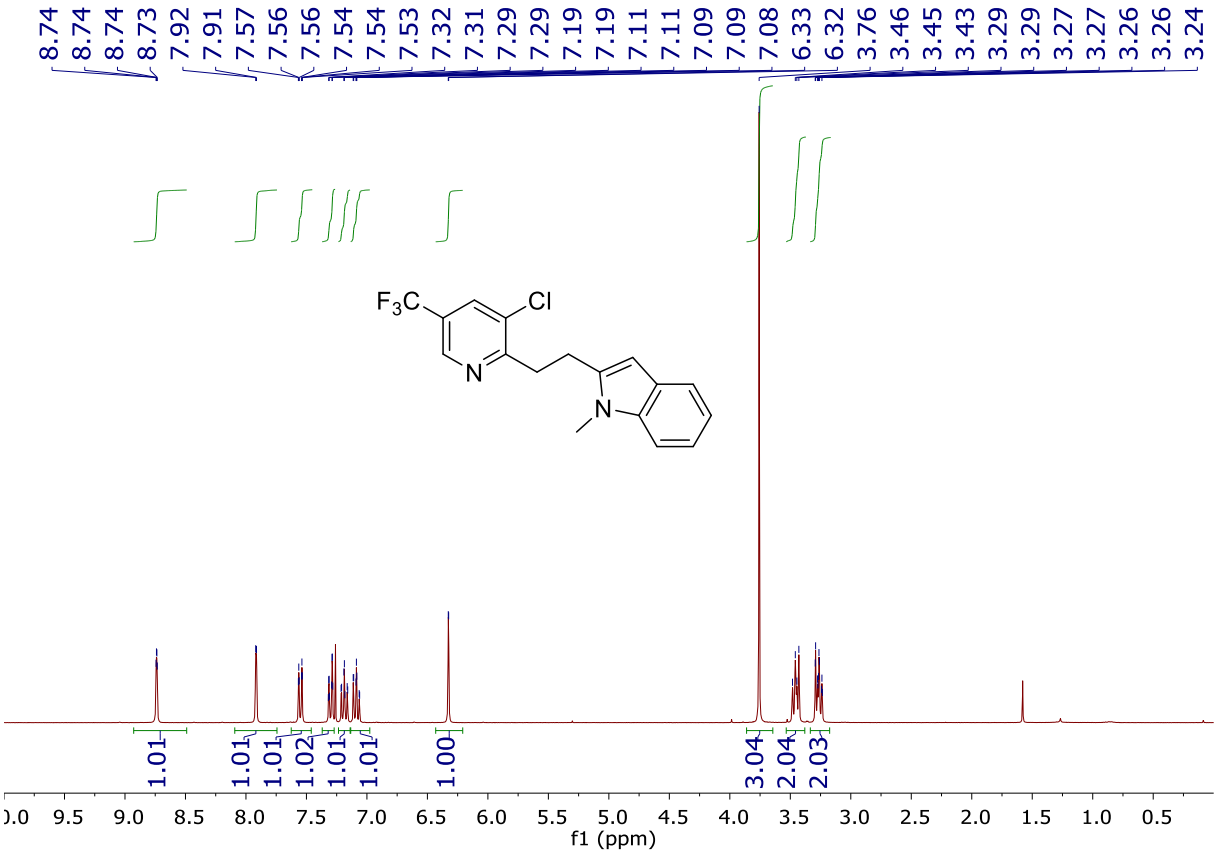

155.2
147.8
142.0
137.4
132.5
130.8
128.4
125.4
120.6
36.0
28.9
17.8
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

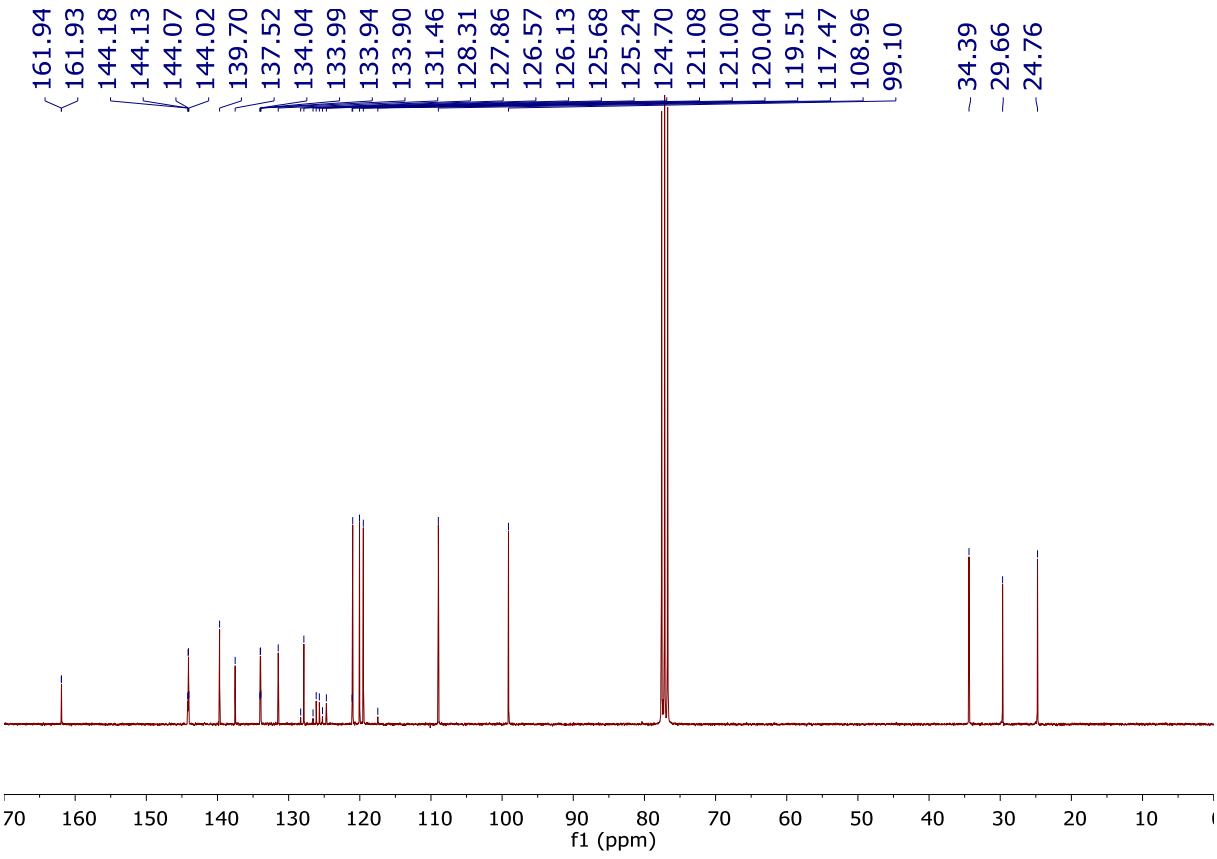

8.75 8.75 8.74 8.74 7.90 7.90 7.90 7.89 7.89 7.89 7.86 7.86 7.86 7.84 7.82 7.82 7.41 7.41 7.39 7.38 7.36 7.36 7.26 CDCl3 7.18 7.18 3.46 3.45 3.44 3.43 3.42 3.36 3.36 3.35 3.33 3.33 3.32
F3C
Cl
N
S
1.00 3.03 2.05 0.97 2.03 1.98
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)

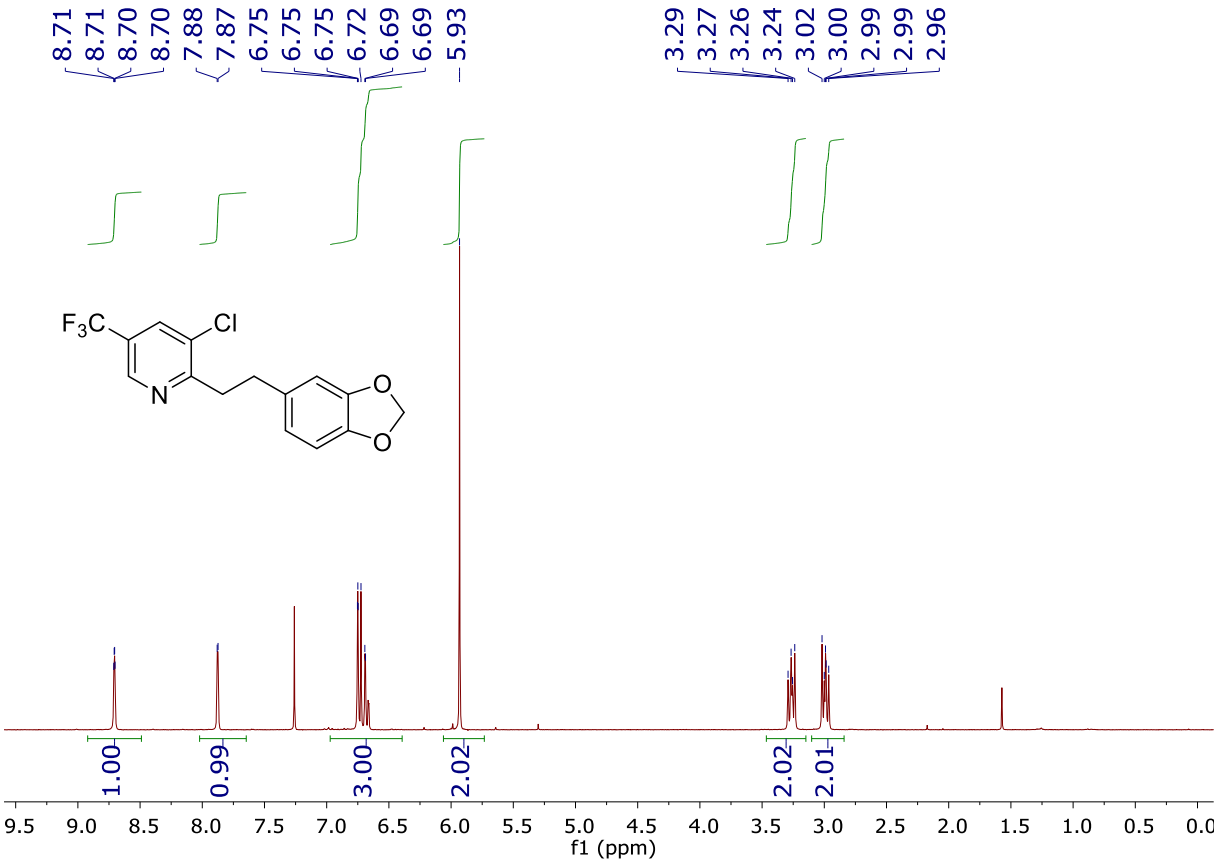

162.48 162.46 144.22 144.16 144.11 144.06 140.59 138.92 135.45 134.05 134.01 133.96 133.91 131.47 126.53 126.09 125.64 125.20 124.72 124.43 124.13 123.07 121.99 121.68 121.11
35.33
26.75
70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

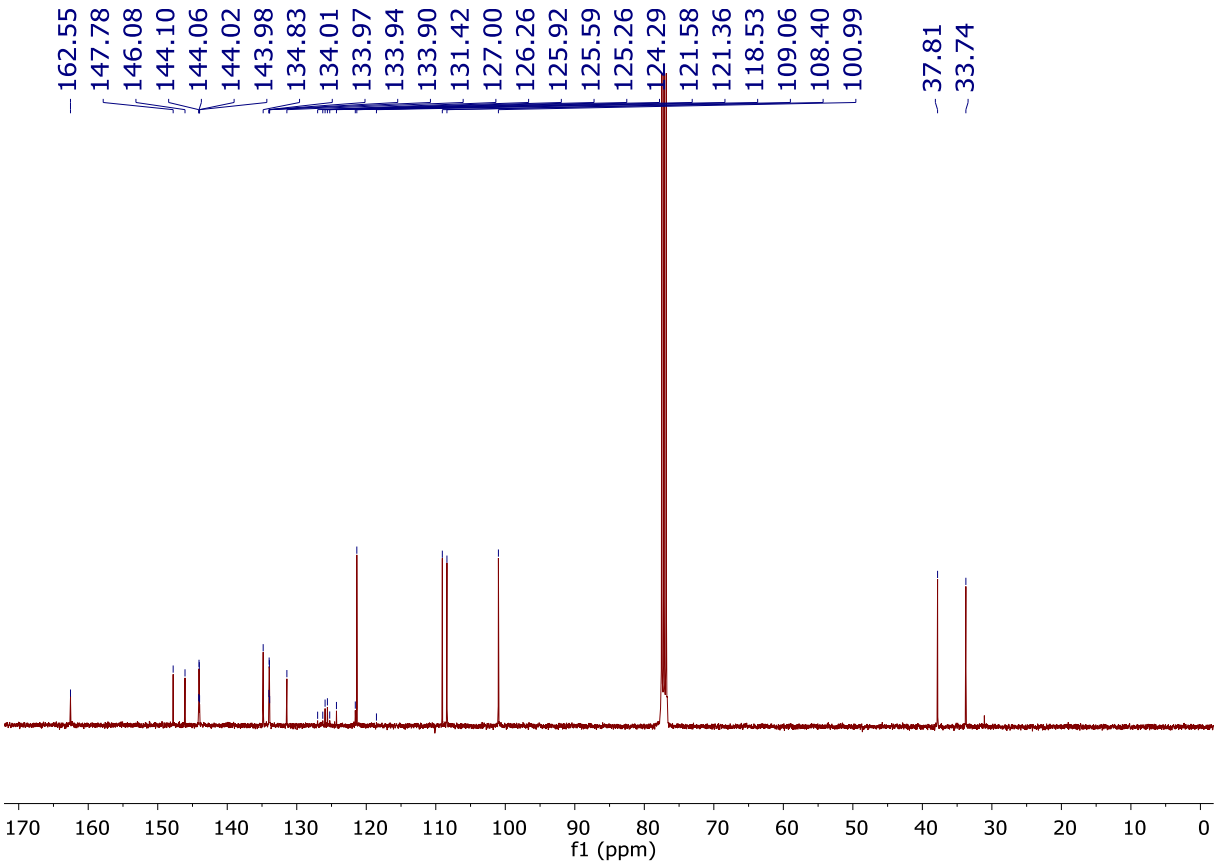

8.74
8.74
8.73
8.73
7.89
7.89
7.61
7.60
7.58
7.58
7.49
7.49
7.48
7.47
7.47
7.46
7.46
7.31
7.30
7.28
7.28
7.27
7.26
7.25
7.25
3.44
3.41
3.40
3.39
3.21
3.20
3.18
3.18
3.17
3.17
3.15
F3C
Cl
N
O
1.00
1.00
1.00
1.94
2.34
2.02
2.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

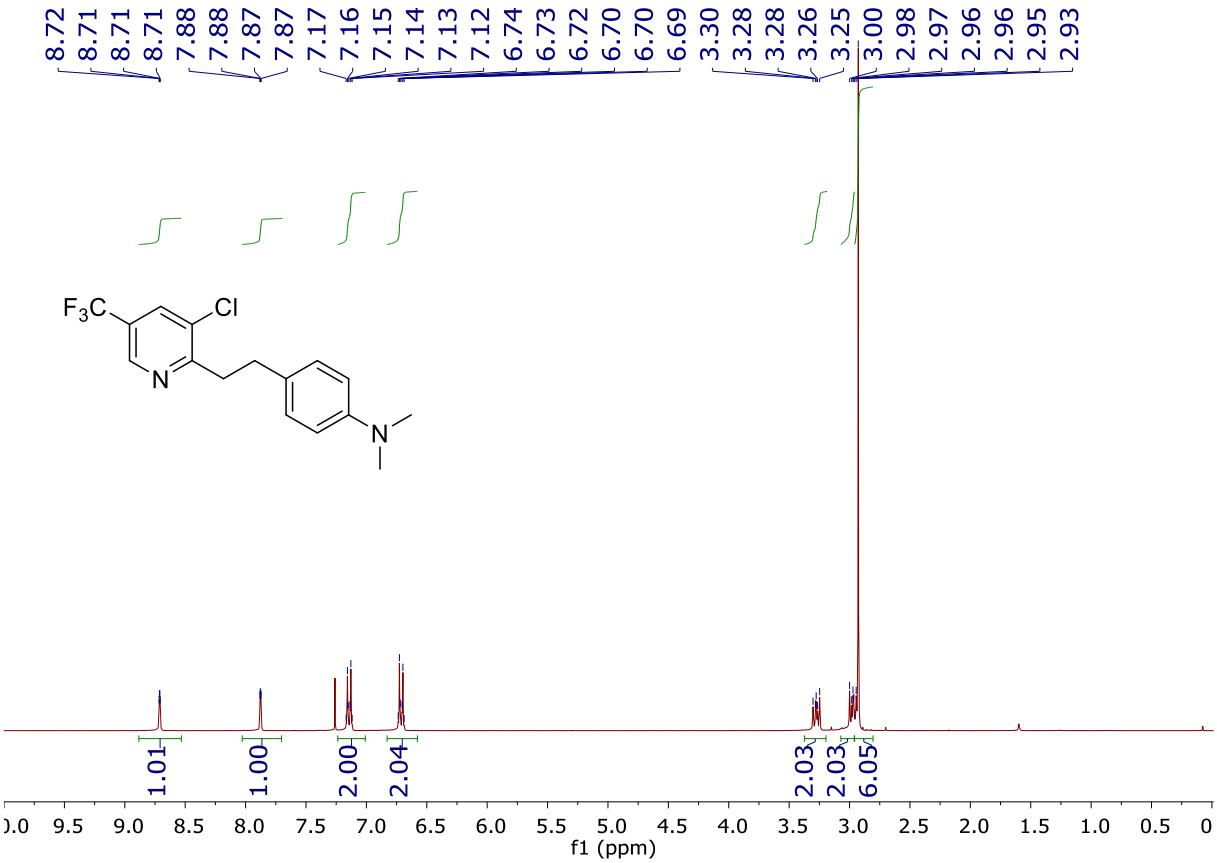

162.20
155.33
144.02
143.98
143.94
143.90
141.41
133.88
133.85
133.81
133.78
131.34
127.96
126.83
126.25
125.92
125.59
125.25
124.27
124.12
122.37
121.41
119.43
118.68
111.51
35.02
21.70
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

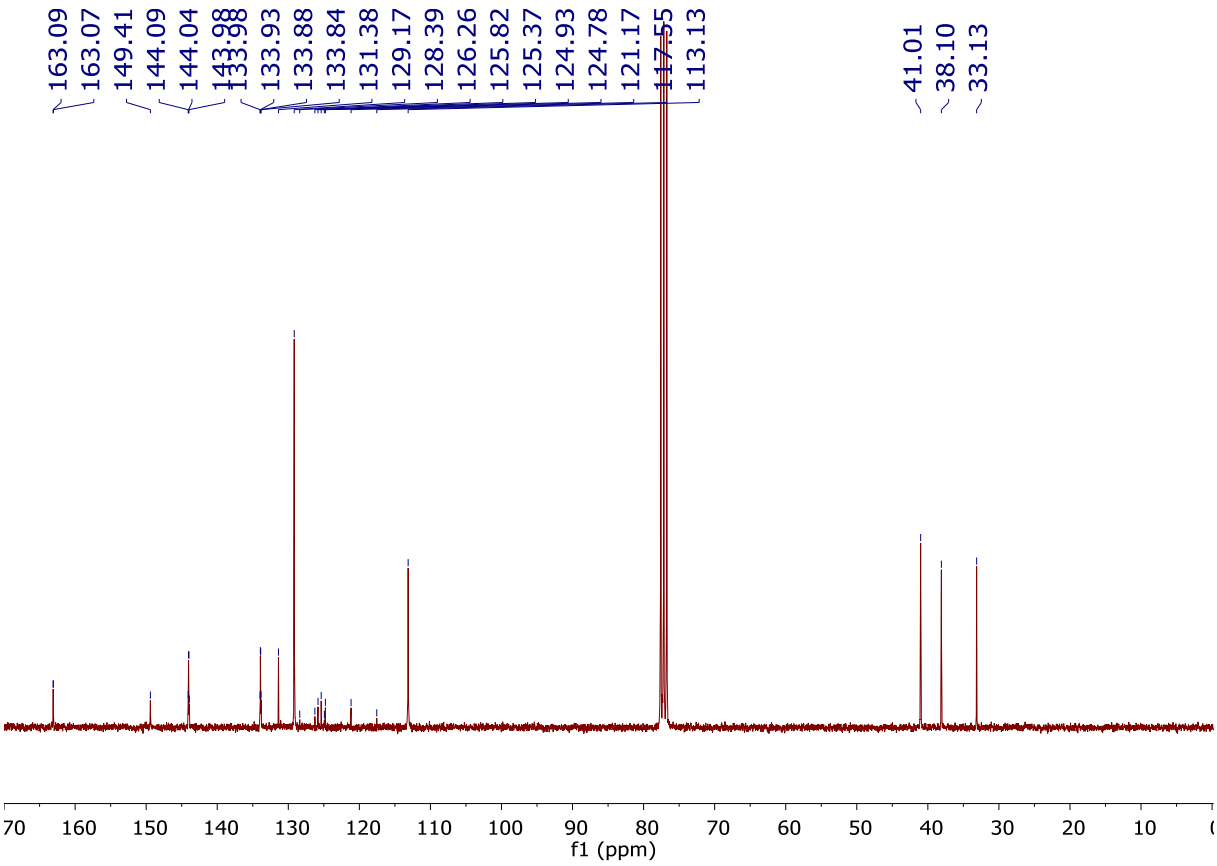

8.74
8.74
8.74
8.73
7.92
7.91
7.57
7.56
7.56
7.54
7.54
7.53
7.32
7.31
7.29
7.29
7.19
7.19
7.11
7.11
7.09
7.09
7.08
6.33
6.32
3.76
3.46
3.45
3.43
3.29
3.29
3.27
3.27
3.26
3.26
3.24
F3C
Cl
N
N
1.01
1.01
1.01
1.02
1.01
1.01
1.00
3.04
2.04
2.03
f1 (ppm)

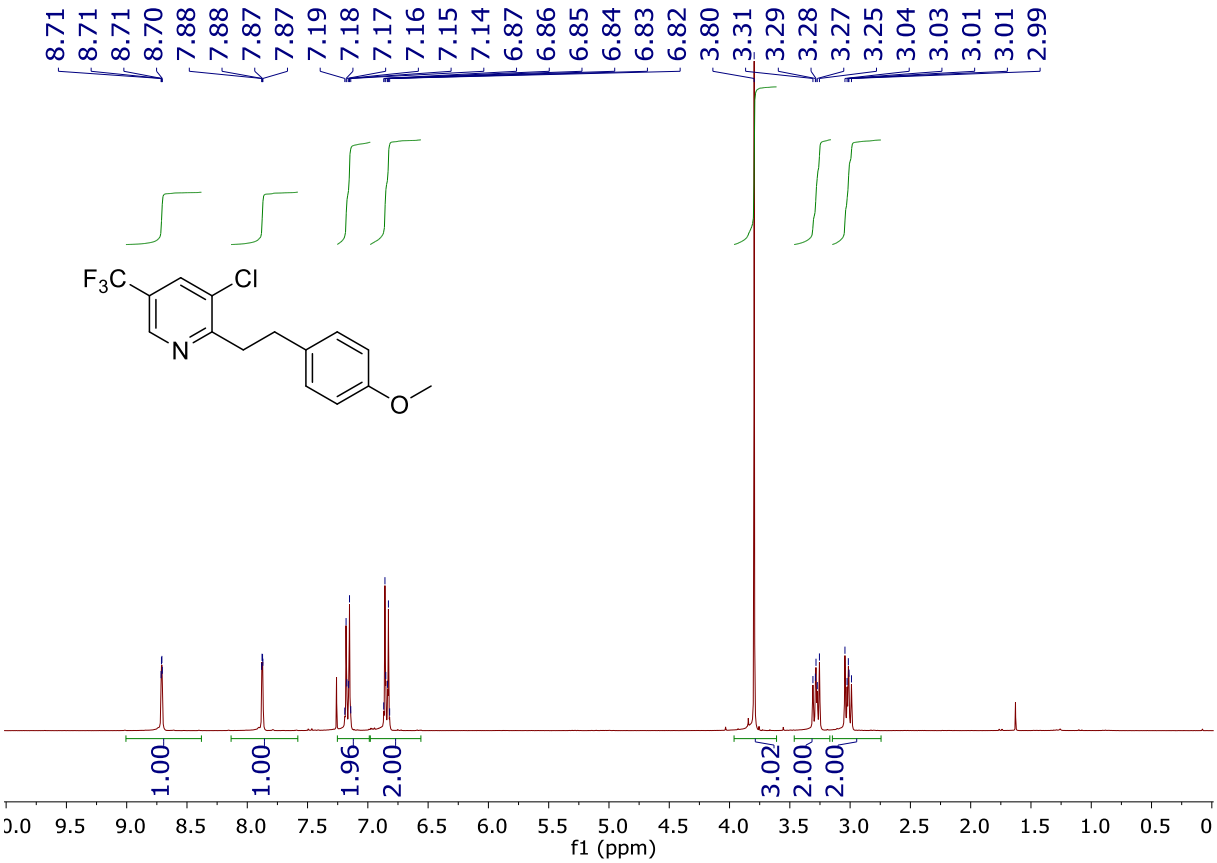

161.94
161.93
144.18
144.13
144.07
144.02
139.70
137.52
134.04
133.99
133.94
133.90
131.46
128.31
127.86
126.57
126.13
125.68
125.24
124.70
121.08
121.00
120.04
119.51
117.47
108.96
99.10
34.39
29.66
24.76
f1 (ppm)

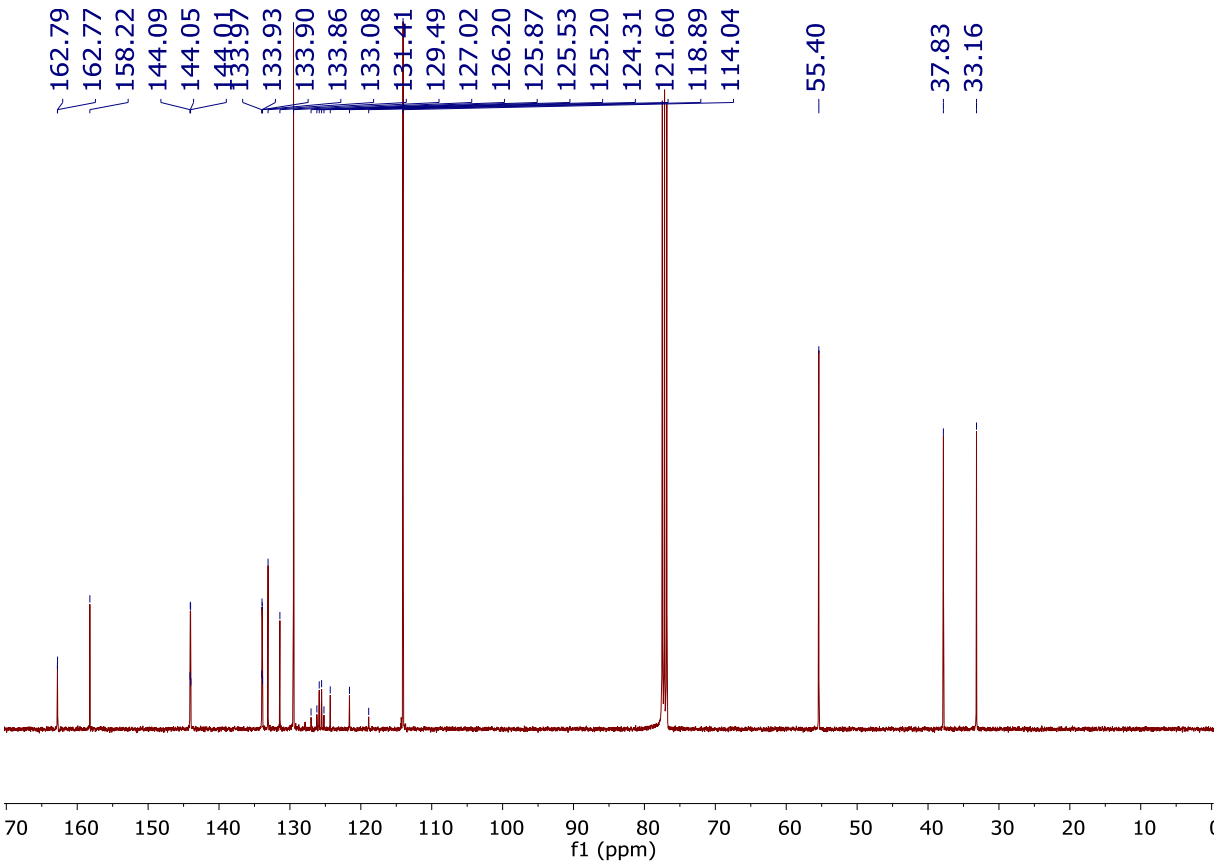

8.71
8.71
8.70
8.70
7.88
7.87
6.75
6.75
6.75
6.72
6.69
6.69
5.93
3.29
3.27
3.26
3.24
3.02
3.00
2.99
2.99
2.96
F3C
Cl
N
O
O
1.00
0.99
3.00
2.02
2.02
2.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

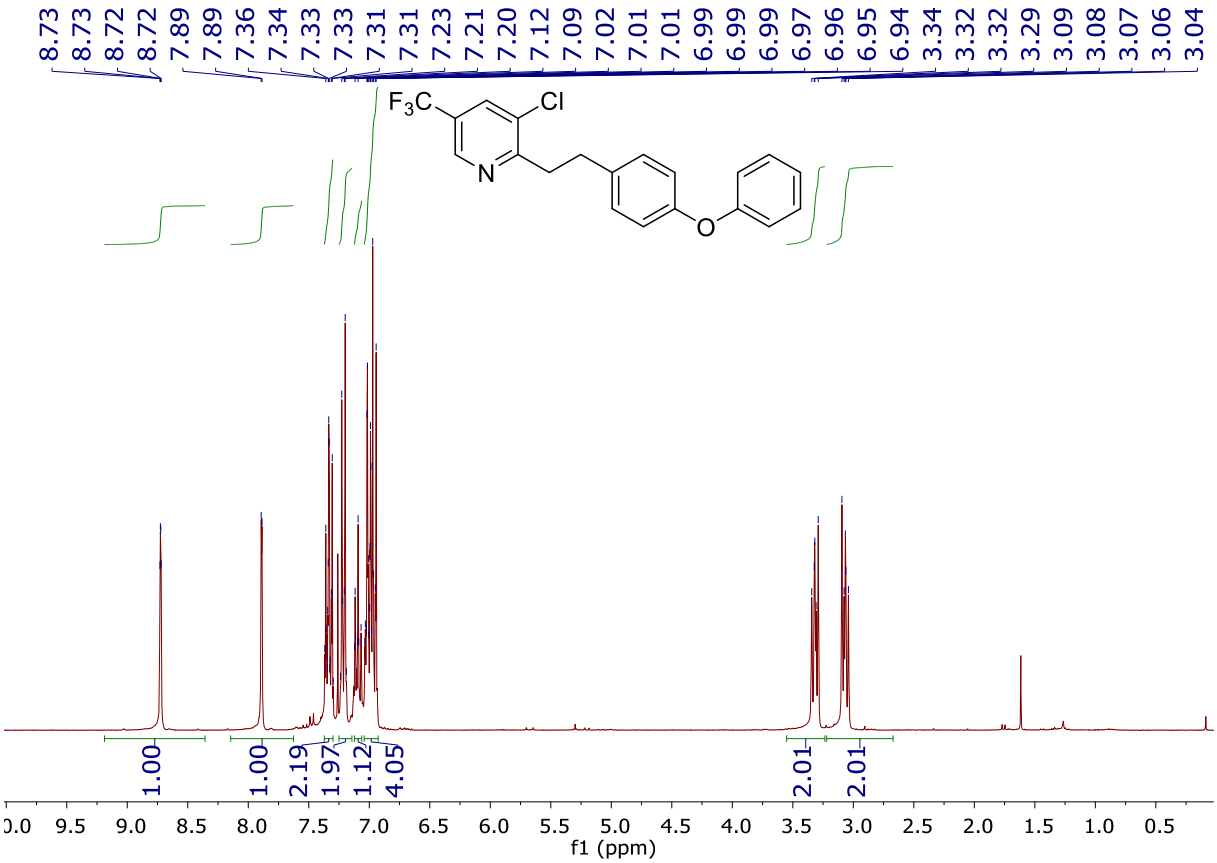

162.55
147.78
146.08
144.10
144.06
144.02
143.98
134.83
134.01
133.97
133.94
133.90
131.42
127.00
126.26
125.92
125.59
125.26
124.29
121.58
121.36
118.53
109.06
108.40
100.99
37.81
33.74
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

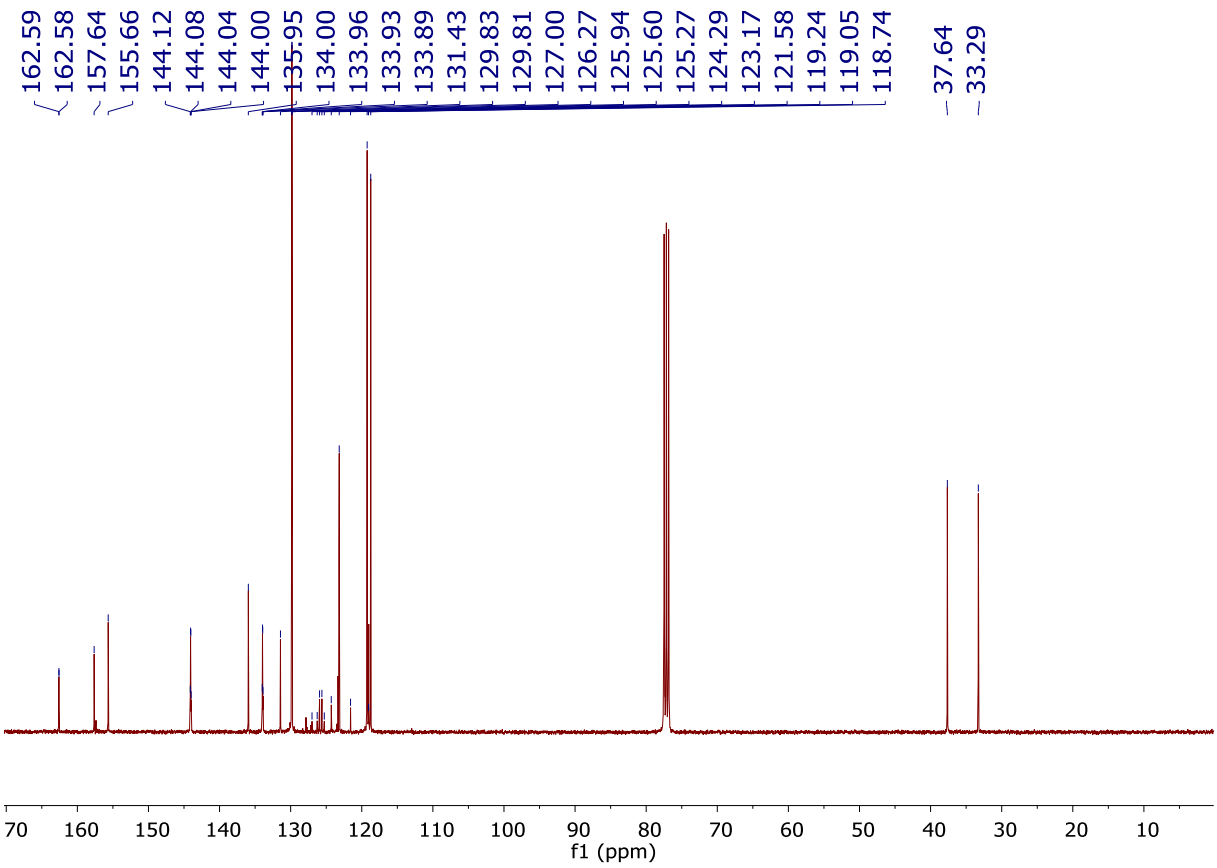

8.72
8.71
8.71
8.71
7.88
7.88
7.87
7.87
7.17
7.16
7.15
7.14
7.13
7.12
6.74
6.73
6.72
6.70
6.70
6.69
3.30
3.28
3.28
3.26
3.25
3.00
2.98
2.97
2.96
2.96
2.95
2.93
F3C
Cl
N
N
1.01
1.00
2.00
2.04
2.03
2.03
6.05
f1 (ppm)

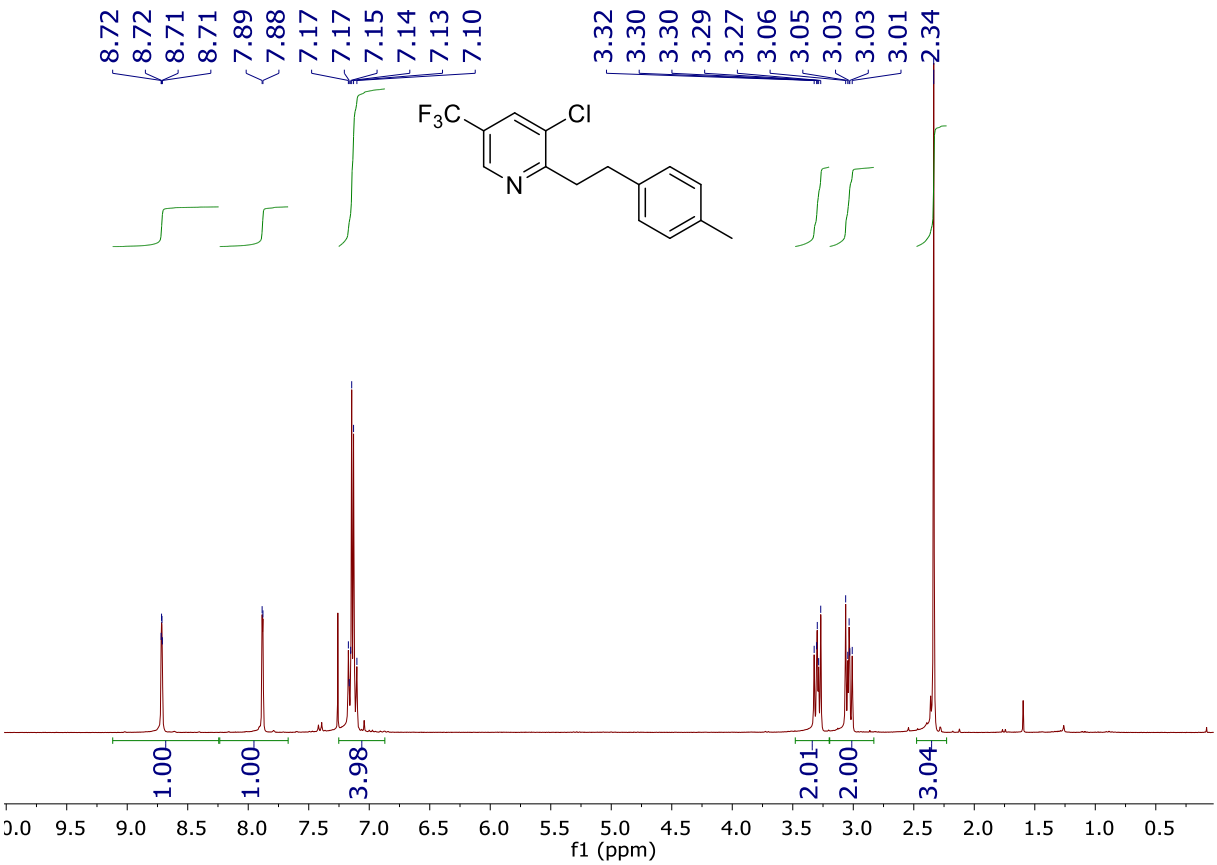

163.09
163.07
149.41
144.09
144.04
133.93
133.88
133.84
131.38
129.17
128.39
126.26
125.82
125.37
124.93
124.78
121.17
117.55
113.13
41.01
38.10
33.13
f1 (ppm)

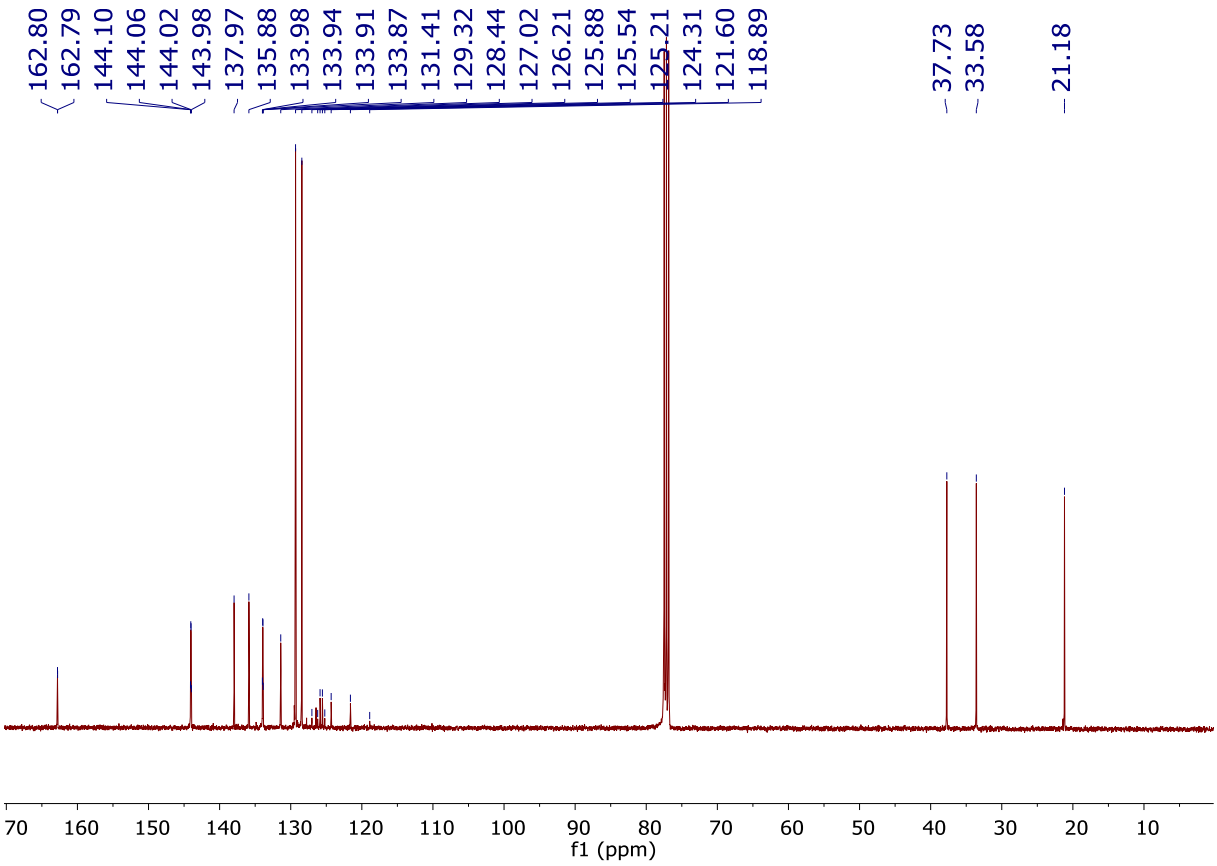

8.71
8.71
8.71
8.70
7.88
7.88
7.87
7.87
7.19
7.18
7.17
7.16
7.15
7.14
6.87
6.86
6.85
6.84
6.83
6.82
3.80
3.31
3.29
3.28
3.27
3.25
3.04
3.03
3.01
3.01
2.99
F3C
Cl
N
O
1.00
1.00
1.96
2.00
3.02
2.00
2.00
f1 (ppm)

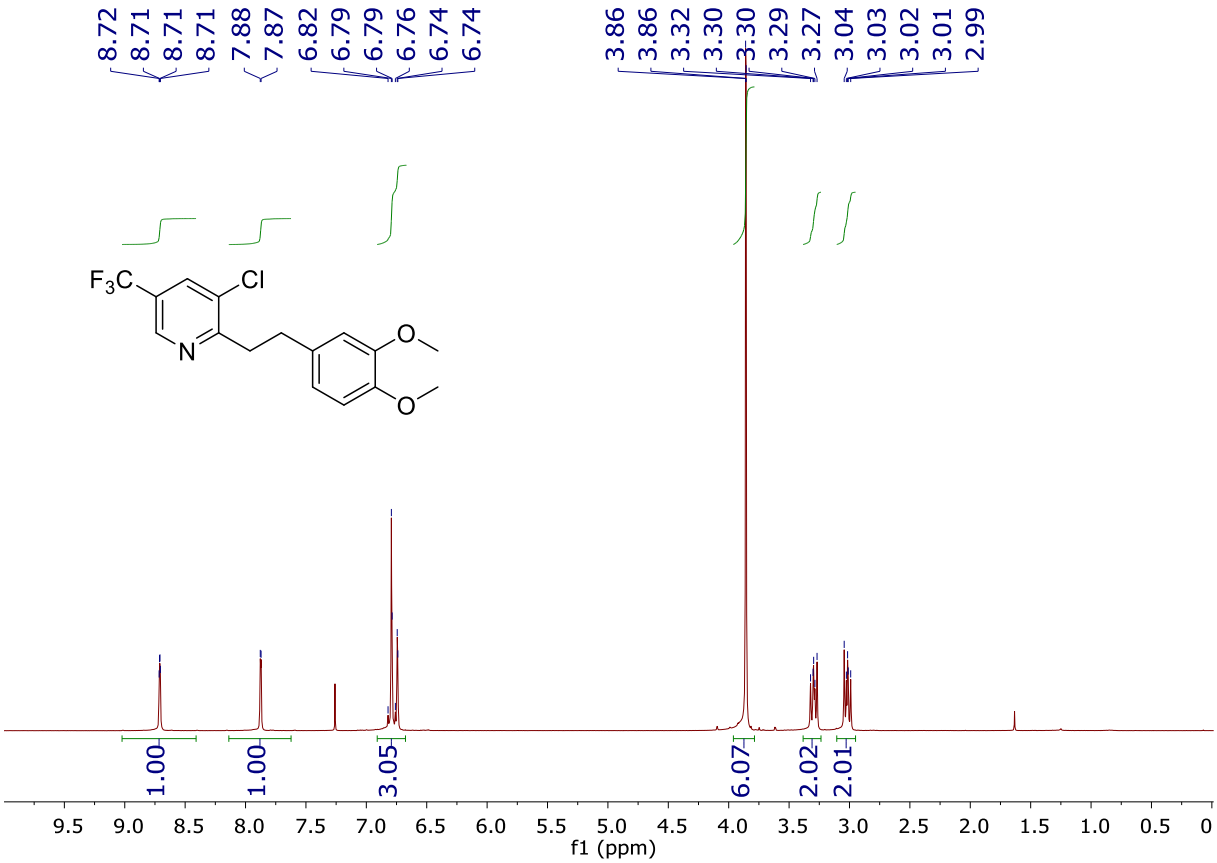

162.79
162.77
158.22
144.09
144.05
144.01
133.97
133.93
133.90
133.86
133.08
131.41
129.49
127.02
126.20
125.87
125.53
125.20
124.31
121.60
118.89
114.04
55.40
37.83
33.16
f1 (ppm)

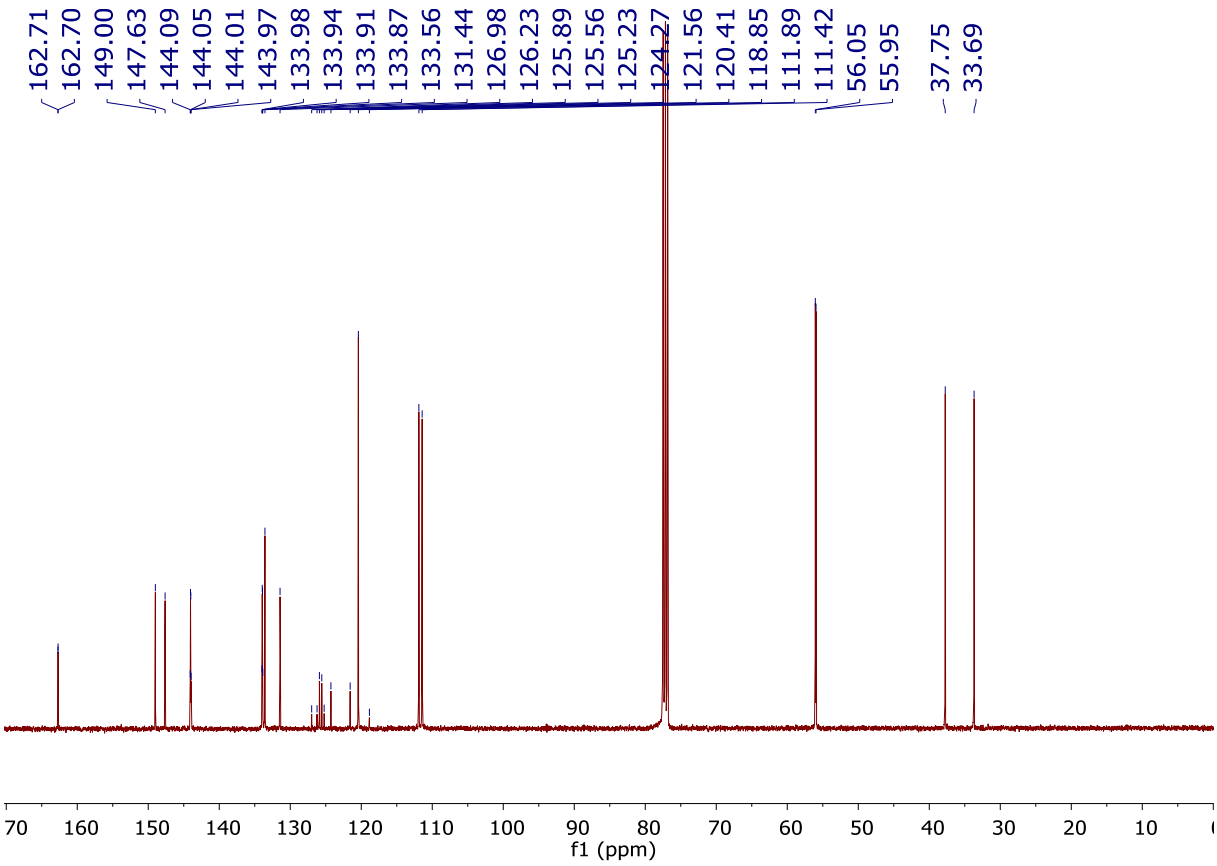

8.73
8.73
8.72
8.72
7.89
7.89
7.36
7.34
7.33
7.33
7.31
7.31
7.23
7.21
7.20
7.12
7.09
7.02
7.01
7.01
6.99
6.99
6.99
6.97
6.96
6.95
6.94
3.34
3.32
3.32
3.29
3.09
3.08
3.07
3.06
3.04
F3C
Cl
N
O
1.00
1.00
2.19
1.97
1.12
4.05
2.01
2.01
f1 (ppm)

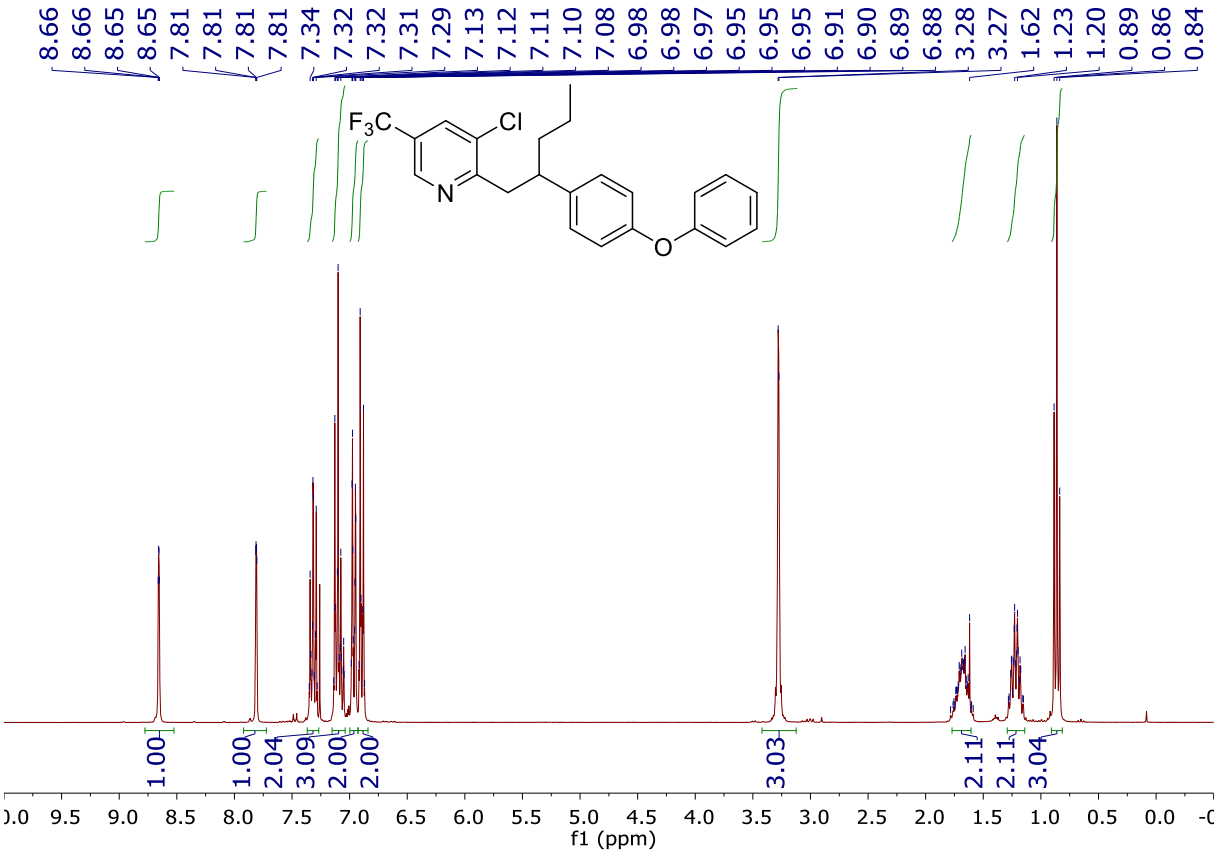

162.59
162.58
157.64
155.66
144.12
144.08
144.04
144.00
135.95
134.00
133.96
133.93
133.89
131.43
129.83
129.81
127.00
126.27
125.94
125.60
125.27
124.29
123.17
121.58
119.24
119.05
118.74
37.64
33.29
f1 (ppm)

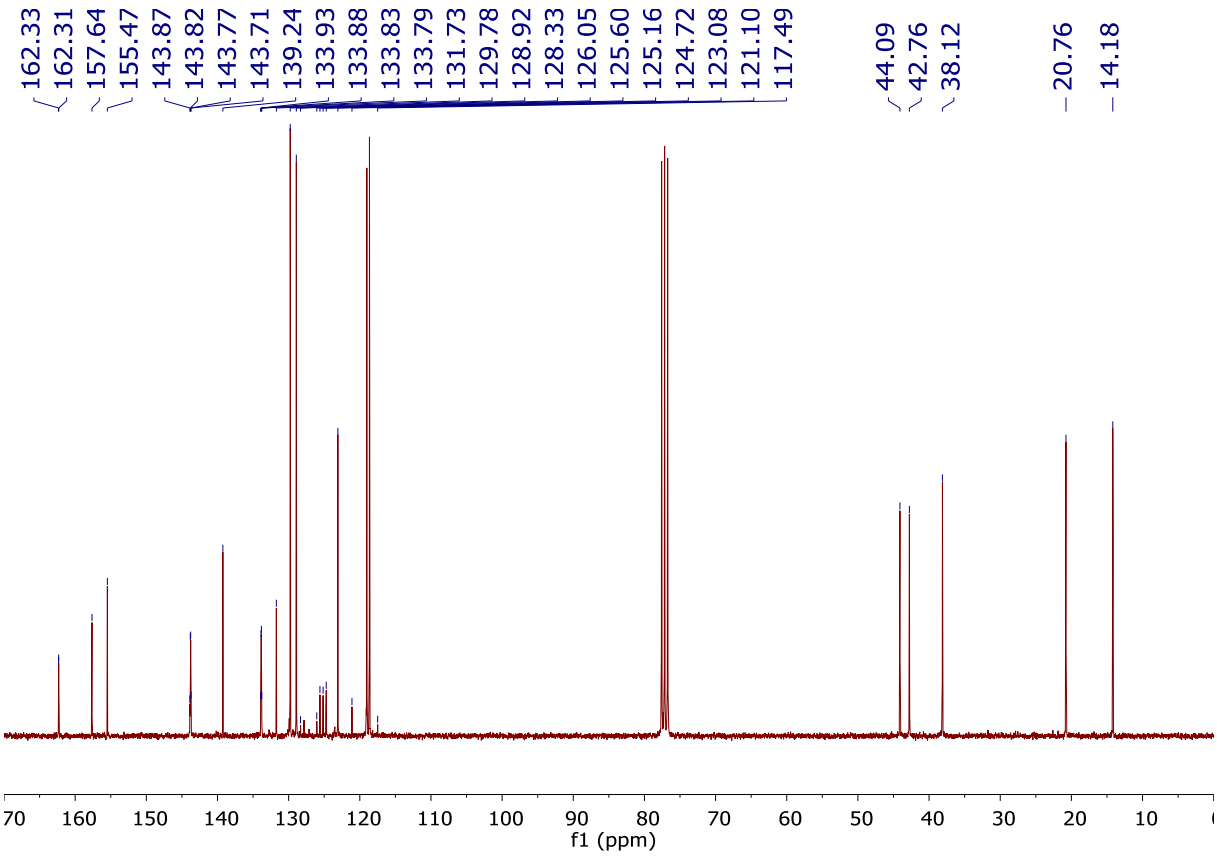

8.72
8.72
8.71
8.71
7.89
7.88
7.17
7.17
7.15
7.14
7.13
7.10
3.32
3.30
3.30
3.29
3.27
3.06
3.05
3.03
3.03
3.01
2.34
F3C
Cl
N
1.00
1.00
3.98
2.01
2.00
3.04
f1 (ppm)

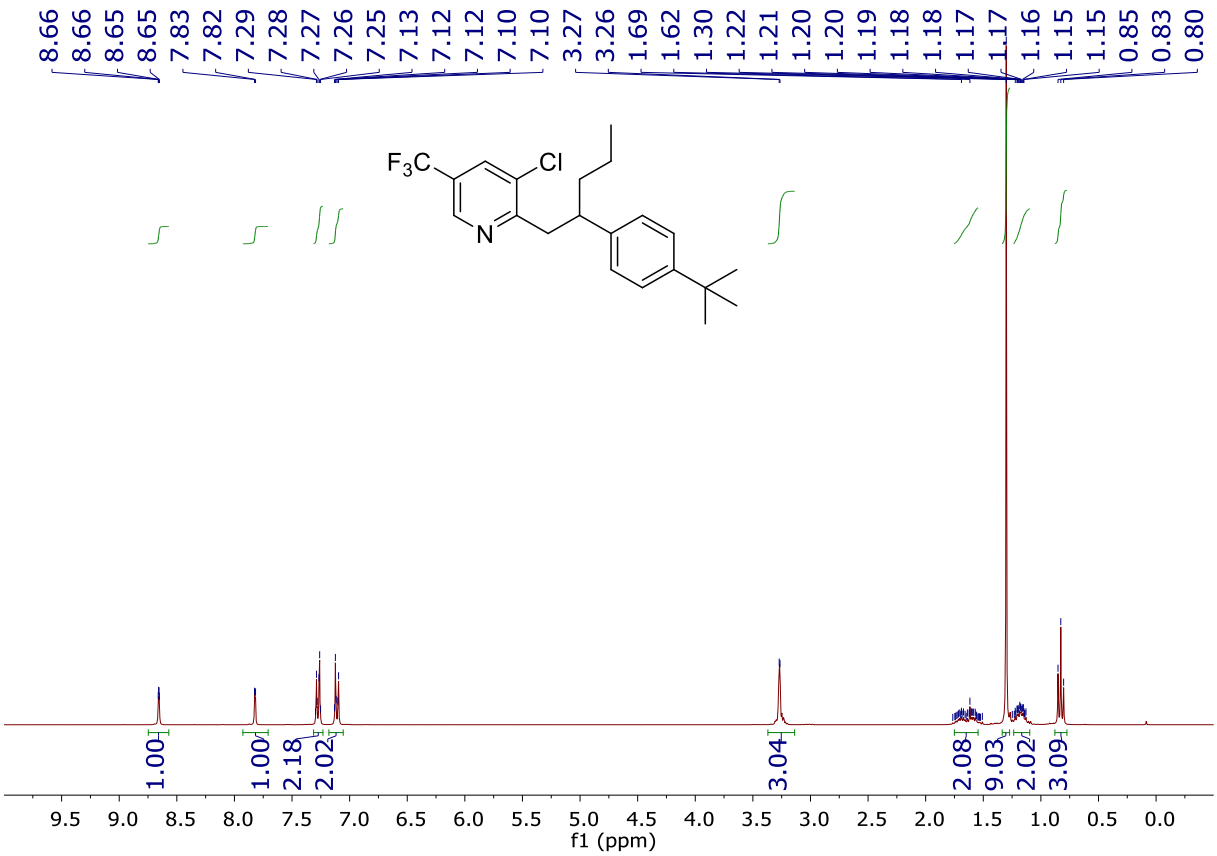

162.80
162.79
144.10
144.06
144.02
143.98
137.97
135.88
133.98
133.94
133.91
133.87
131.41
129.32
128.44
127.02
126.21
125.88
125.54
125.21
124.31
121.60
118.89
37.73
33.58
21.18
f1 (ppm)

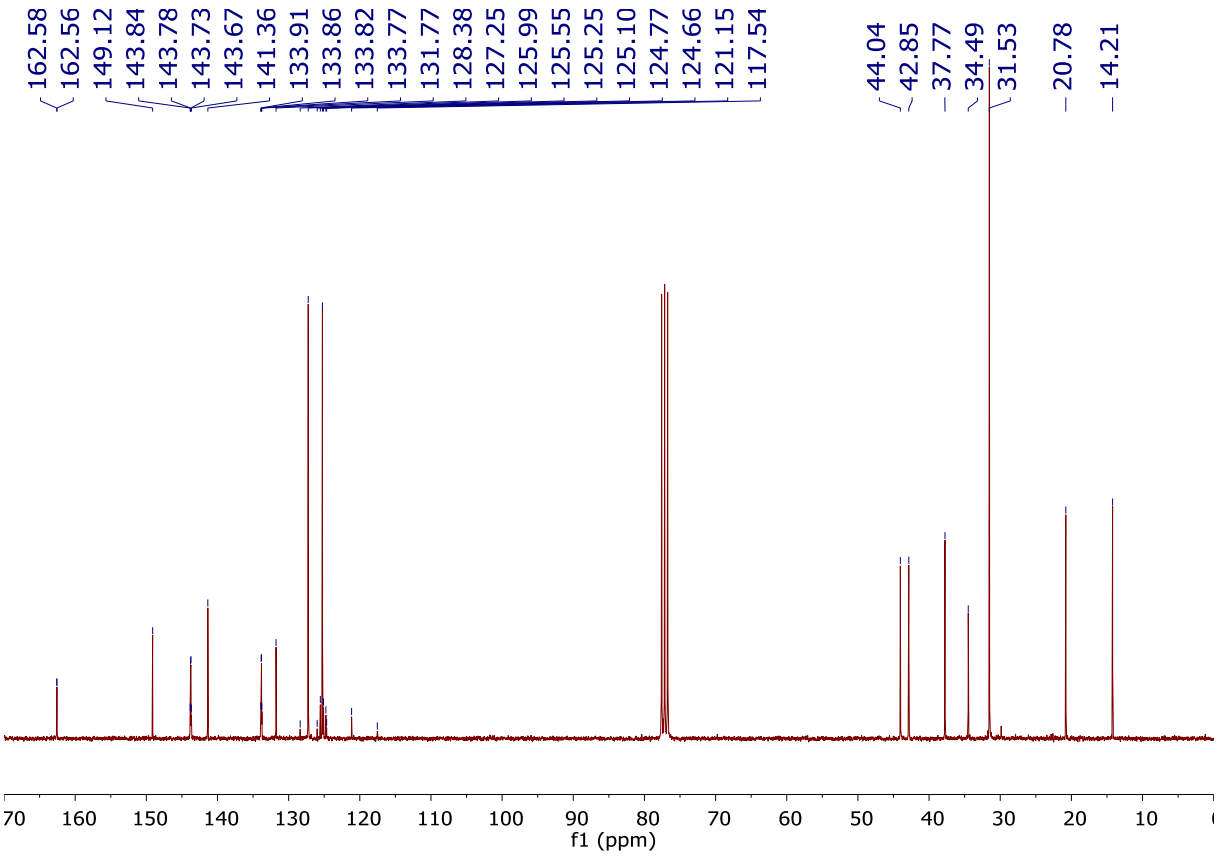

8.72
8.71
8.71
8.71
7.88
7.87
6.82
6.79
6.79
6.76
6.74
6.74
3.86
3.86
3.32
3.30
3.30
3.29
3.27
3.04
3.03
3.02
3.01
2.99
F3C
Cl
N
O
O
1.00
1.00
3.05
6.07
2.02
2.01
f1 (ppm)

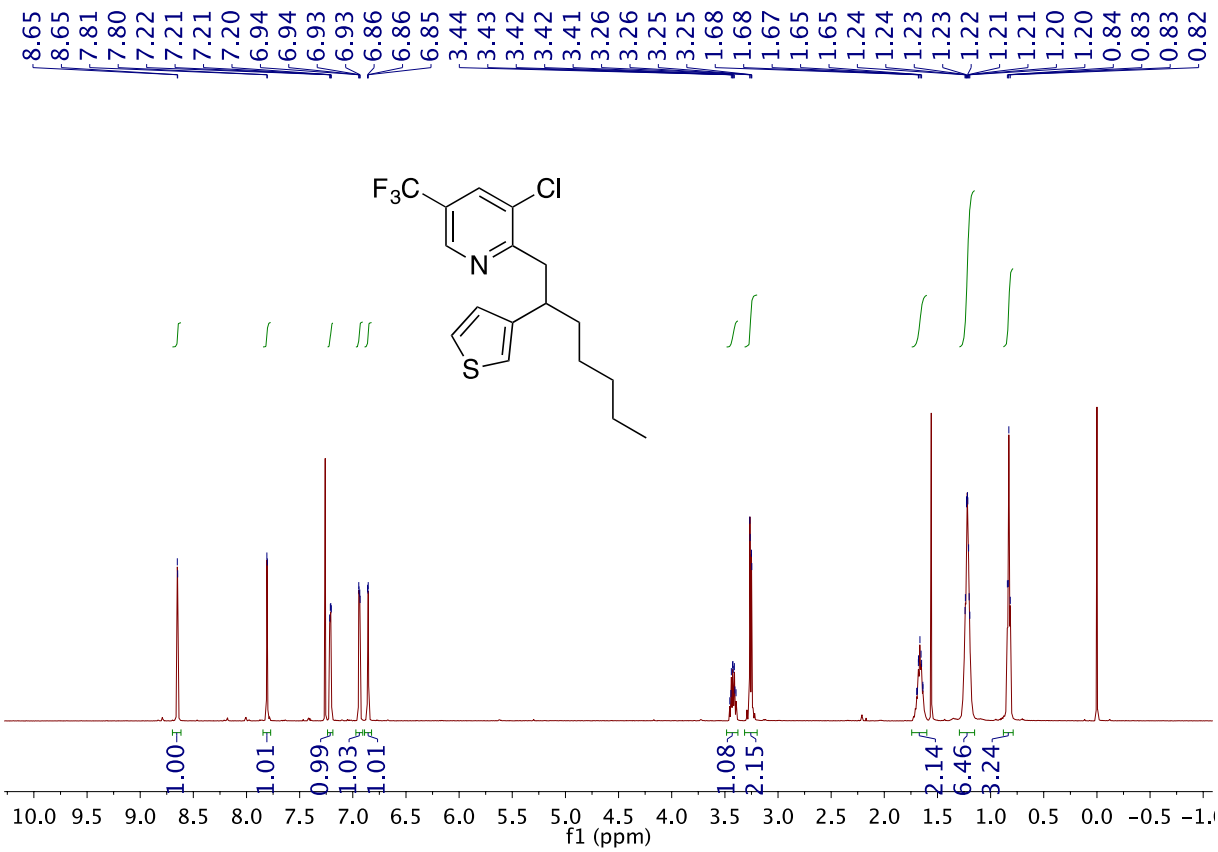

162.71
162.70
149.00
147.63
144.09
144.05
144.01
143.97
133.98
133.94
133.91
133.87
133.56
131.44
126.98
126.23
125.89
125.56
125.23
124.27
121.56
120.41
118.85
111.89
111.42
56.05
55.95
37.75
33.69
f1 (ppm)

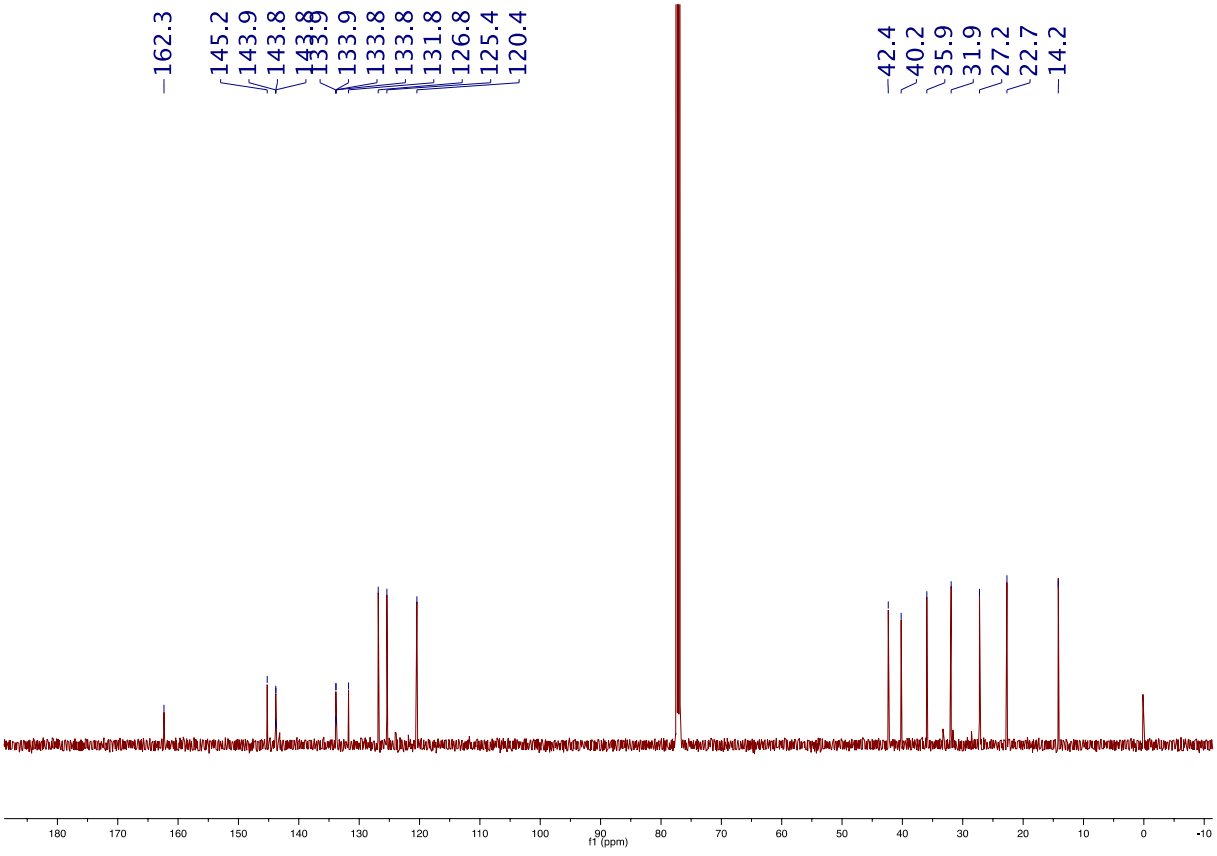

8.66 8.66 8.65 8.65 7.81 7.81 7.81 7.81 7.34 7.32 7.32 7.31 7.29 7.13 7.12 7.11 7.10 7.08 6.98 6.98 6.97 6.95 6.95 6.95 6.91 6.90 6.89 6.88 3.28 3.27 1.62 1.23 1.20 0.89 0.86 0.84
F3C
Cl
N
O
1.00 1.00 2.04 3.09 2.00 2.00 3.03 2.11 2.11 3.04
f1 (ppm)

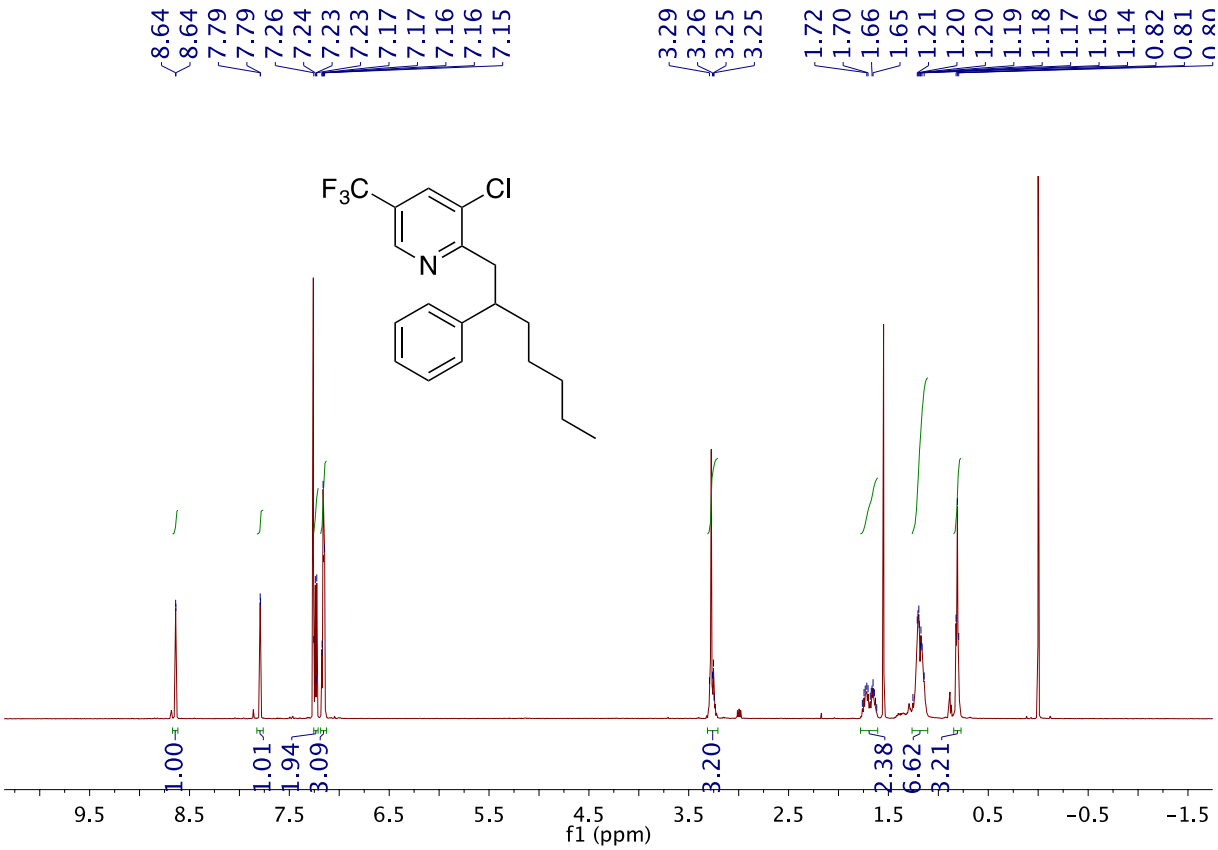

162.33 162.31 157.64 155.47 143.87 143.82 143.77 143.71 139.24 133.93 133.88 133.83 133.79 131.73 129.78 128.92 128.33 126.05 125.60 125.16 124.72 123.08 121.10 117.49 44.09 42.76 38.12 20.76 14.18
f1 (ppm)

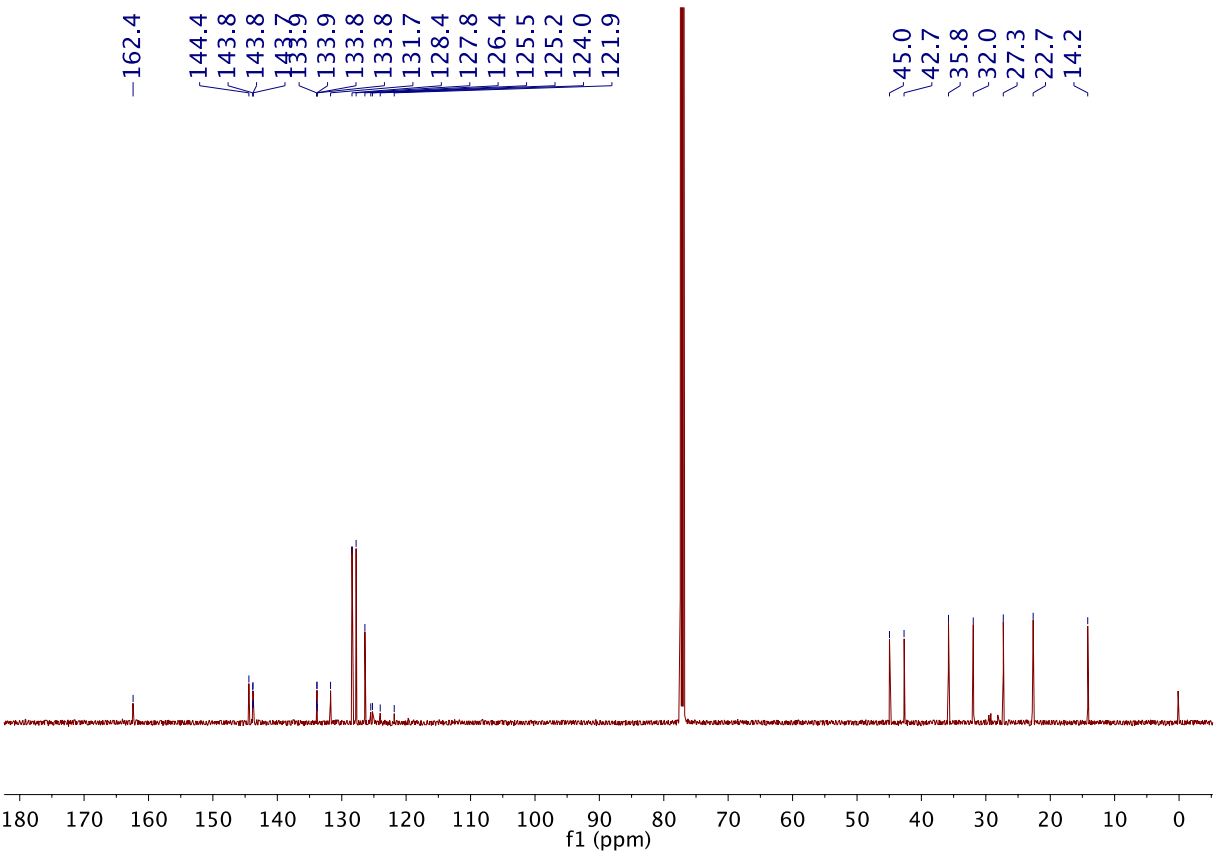

8.66 8.66 8.65 8.65 7.83 7.82 7.29 7.28 7.27 7.26 7.25 7.13 7.12 7.12 7.10 7.10 3.27 3.26 1.69 1.62 1.30 1.22 1.21 1.20 1.20 1.19 1.18 1.18 1.17 1.17 1.16 1.15 1.15 0.85 0.83 0.80
F3C
Cl
N
1.00 1.00 2.18 2.02 3.04 2.08 9.03 2.02 3.09
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

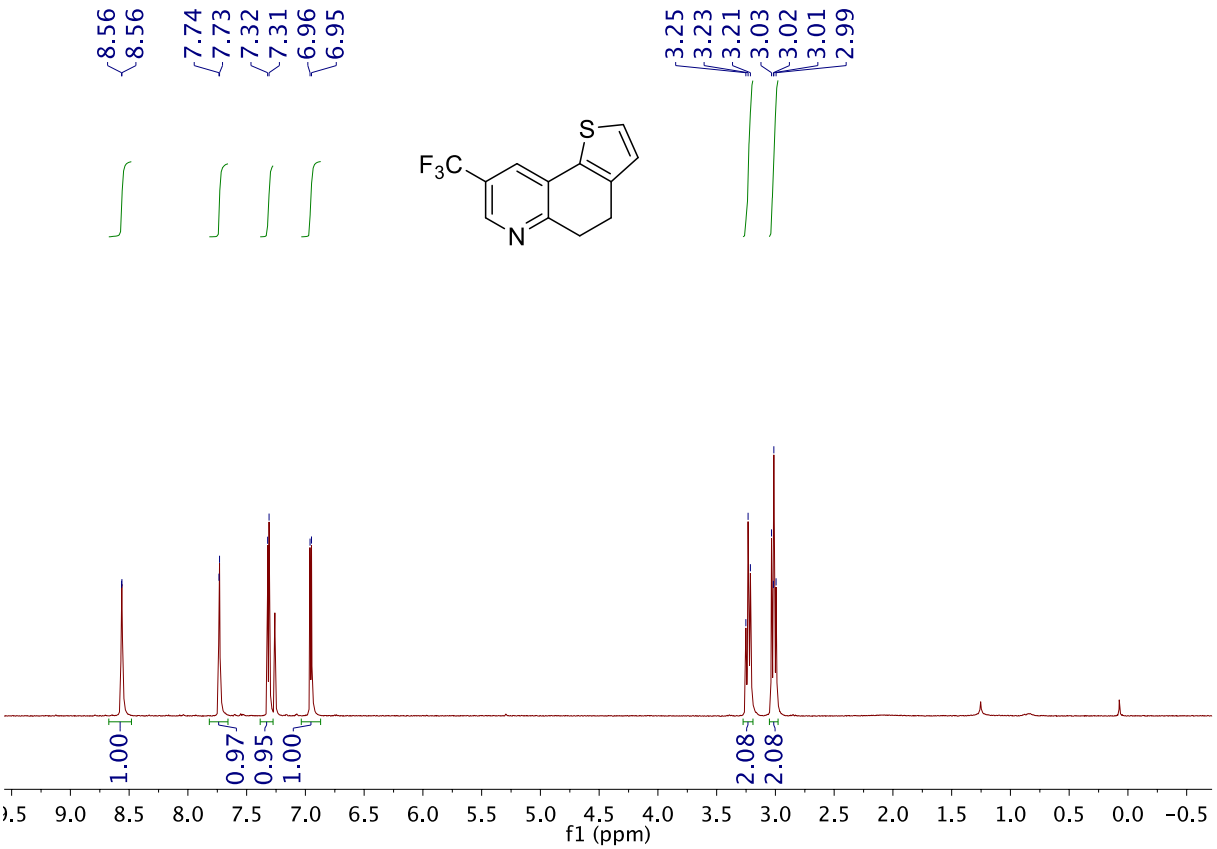

162.58 162.56 149.12 143.84 143.78 143.73 143.67 141.36 133.91 133.86 133.82 133.77 131.77 128.38 127.25 125.99 125.55 125.25 125.10 124.77 124.66 121.15 117.54
44.04 42.85 37.77 34.49 31.53 20.78 14.21
70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

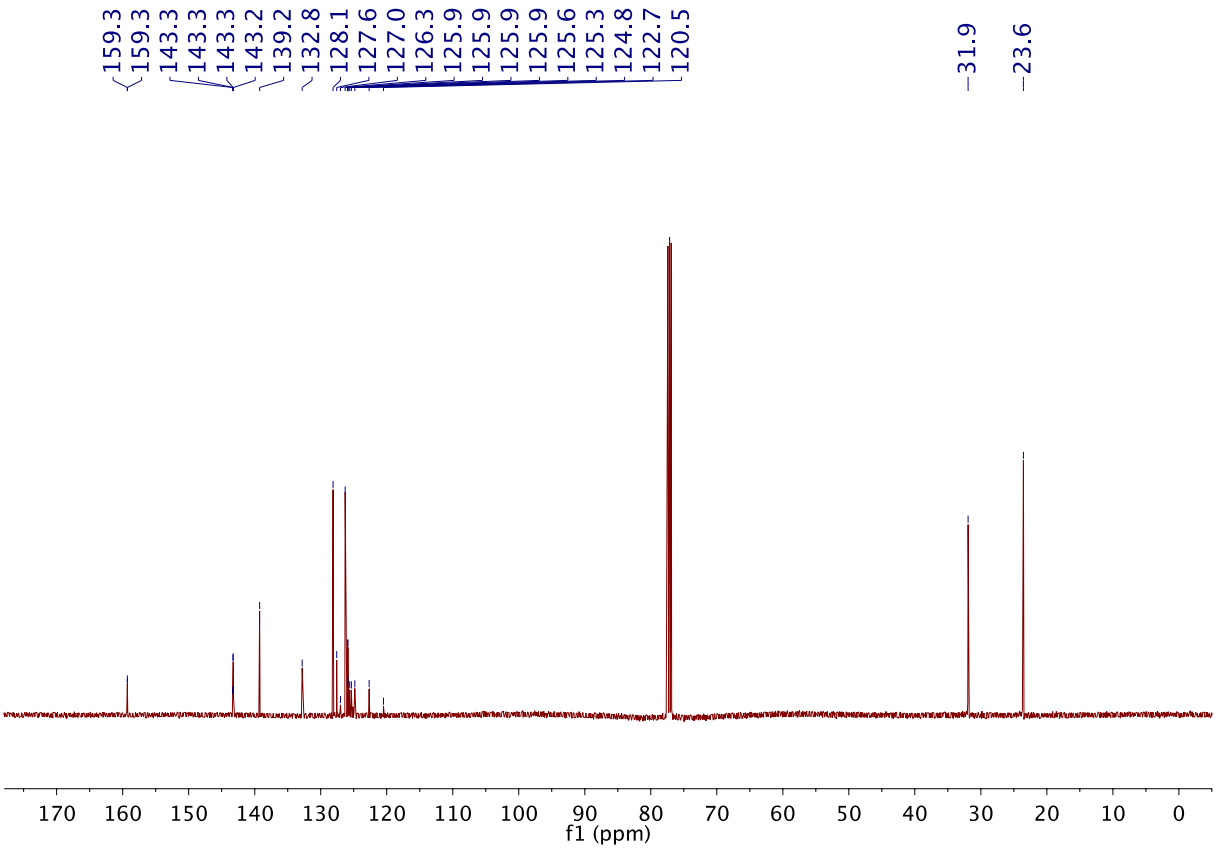

8.65 8.65 7.81 7.80 7.22 7.21 7.21 7.20 6.94 6.94 6.93 6.93 6.86 6.86 6.85 3.44 3.43 3.42 3.42 3.41 3.26 3.26 3.25 3.25 1.68 1.68 1.67 1.65 1.65 1.24 1.24 1.23 1.23 1.22 1.21 1.21 1.20 1.20 0.84 0.83 0.83 0.82
F3C
Cl
N
S
1.00 1.01 0.99 1.03 1.01 1.08 2.15 2.14 6.46 3.24
f1 (ppm)

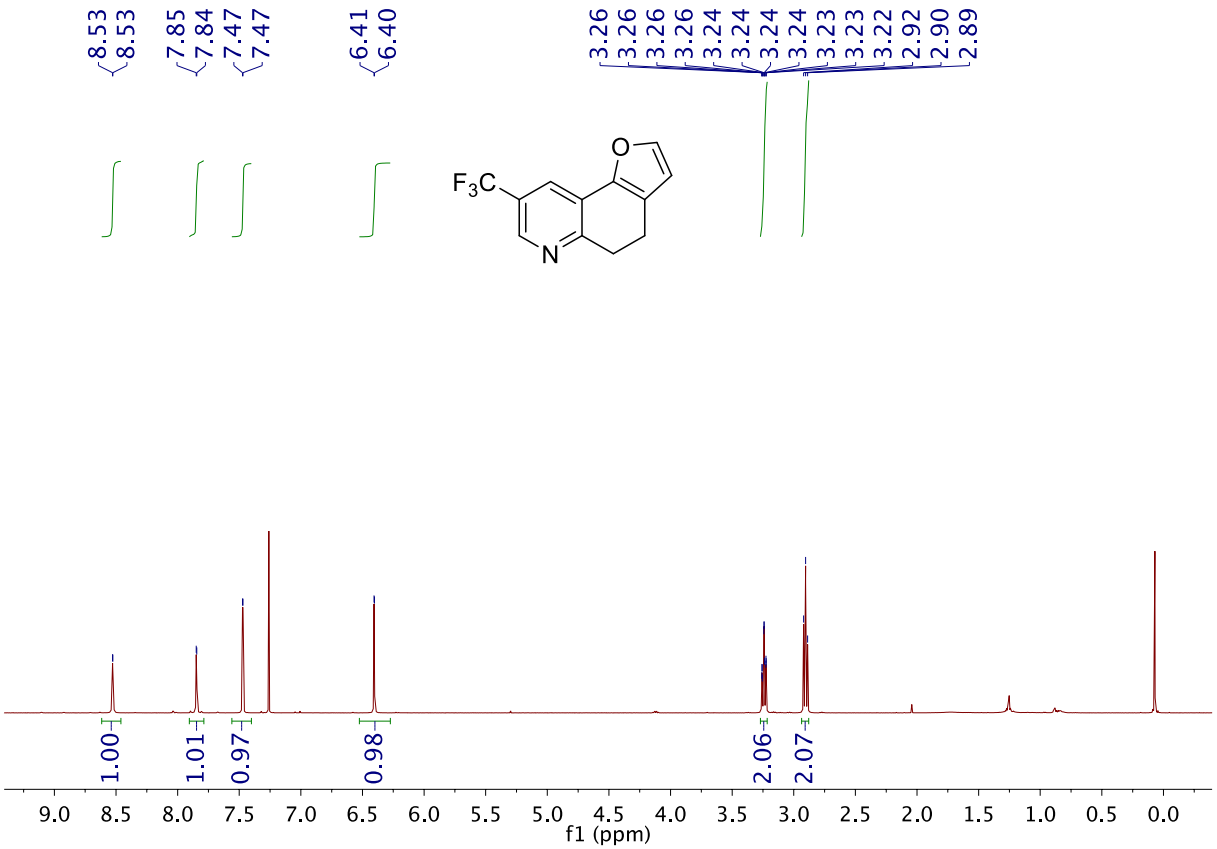

162.3 145.2 143.9 143.8 133.9 133.8 133.8 131.8 126.8 125.4 120.4
42.4 40.2 35.9 31.9 27.2 22.7 14.2
f1 (ppm)

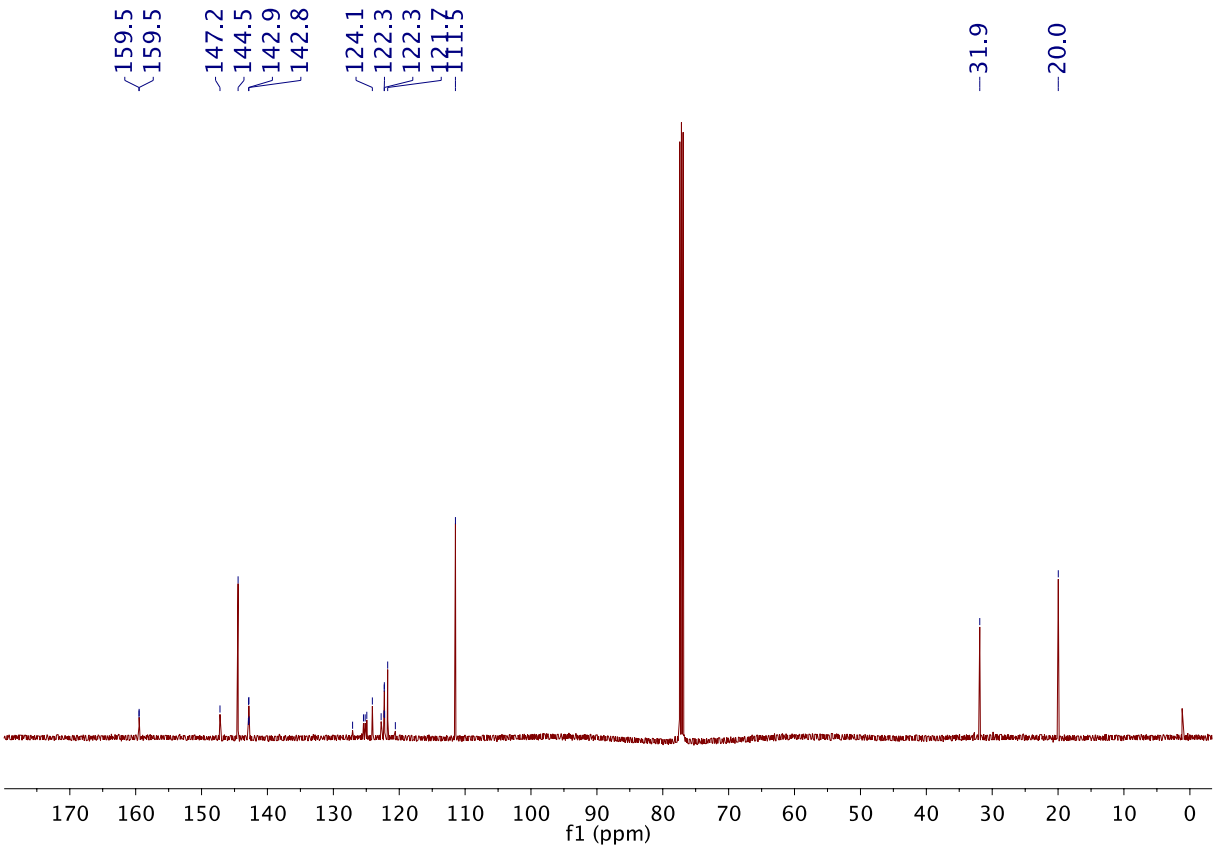

8.64
8.64
7.79
7.79
7.26
7.24
7.23
7.23
7.17
7.17
7.16
7.16
7.15
3.29
3.26
3.25
3.25
1.72
1.70
1.66
1.65
1.21
1.20
1.20
1.19
1.18
1.17
1.16
1.14
0.82
0.81
F3C
Cl
N
1.00
1.01
1.94
3.09
3.20
2.38
6.62
3.21
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5
f1 (ppm)

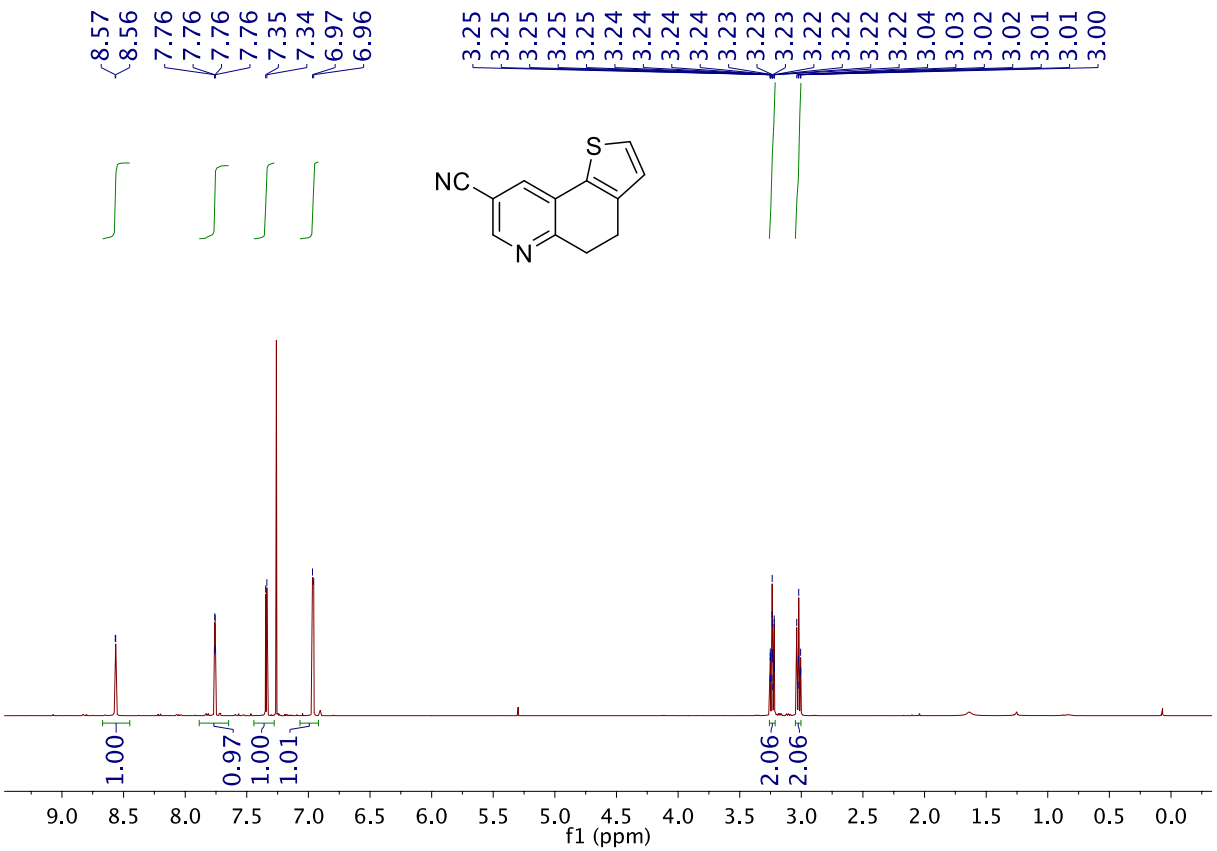

162.4
144.4
143.8
143.8
133.9
133.9
133.8
133.8
131.7
128.4
127.8
126.4
125.5
125.2
124.0
121.9
45.0
42.7
35.8
32.0
27.3
22.7
14.2
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

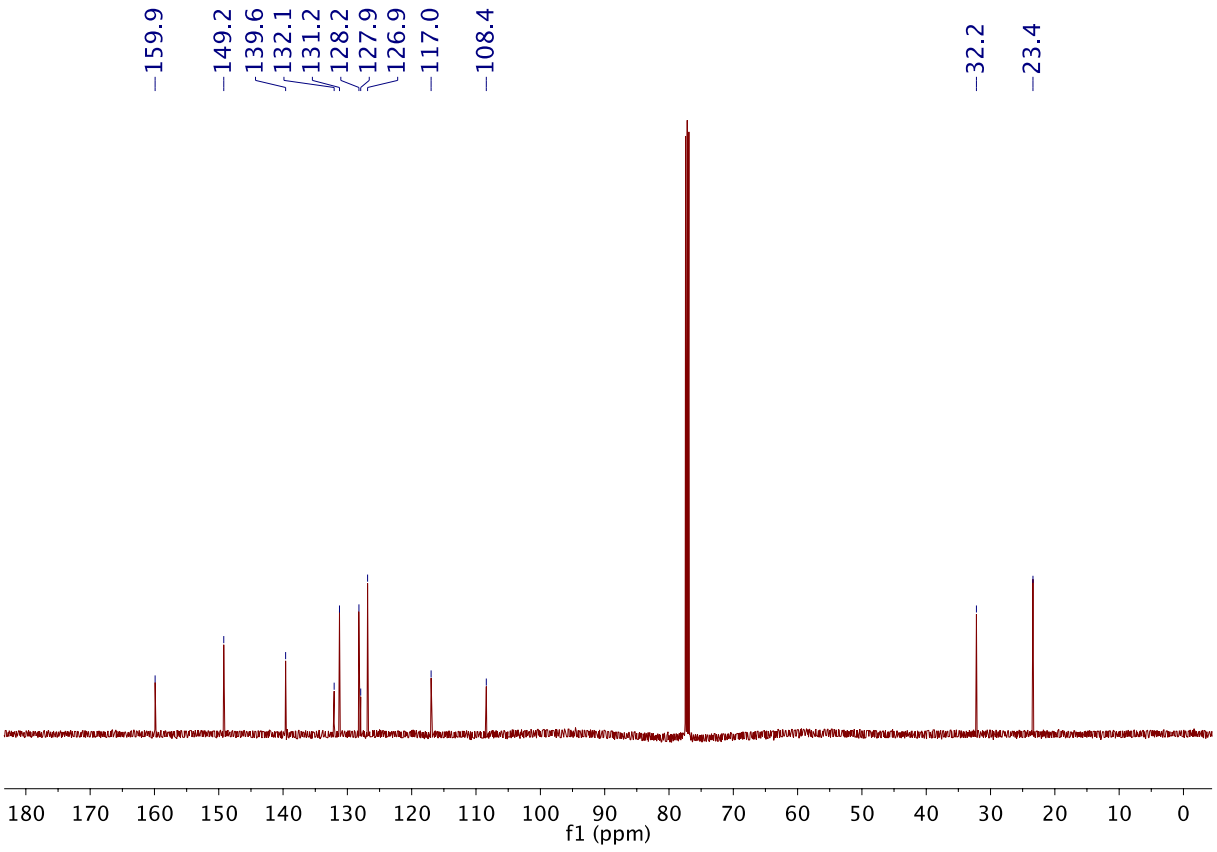

8.56
8.56
7.74
7.73
7.32
7.31
6.96
6.95
3.25
3.23
3.21
3.03
3.02
3.01
2.99
S
F3C
N
1.00
0.97
0.95
1.00
2.08
2.08
f1 (ppm)

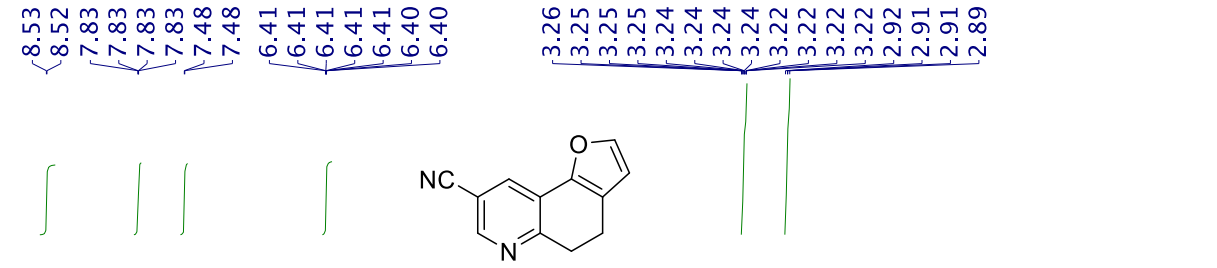

159.3
159.3
143.3
143.3
143.3
143.2
139.2
132.8
128.1
127.6
127.0
126.3
125.9
125.9
125.9
125.9
125.6
125.3
124.8
122.7
120.5
31.9
23.6
f1 (ppm)

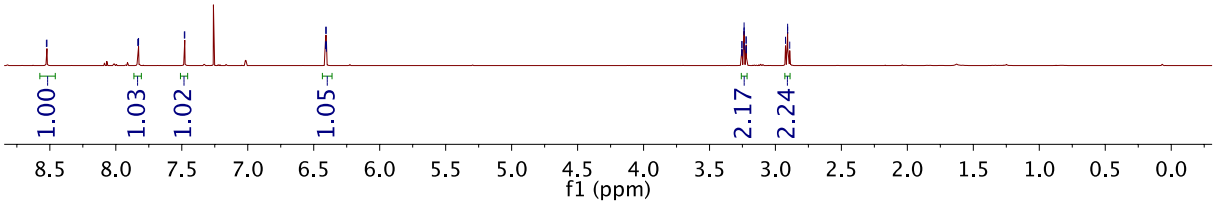

8.53
8.53
7.85
7.84
7.47
7.47
6.41
6.40
3.26
3.26
3.26
3.26
3.24
3.24
3.24
3.24
3.23
3.23
3.22
2.92
2.90
2.89
F3C
O
N
1.00
1.01
0.97
0.98
2.06
2.07
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

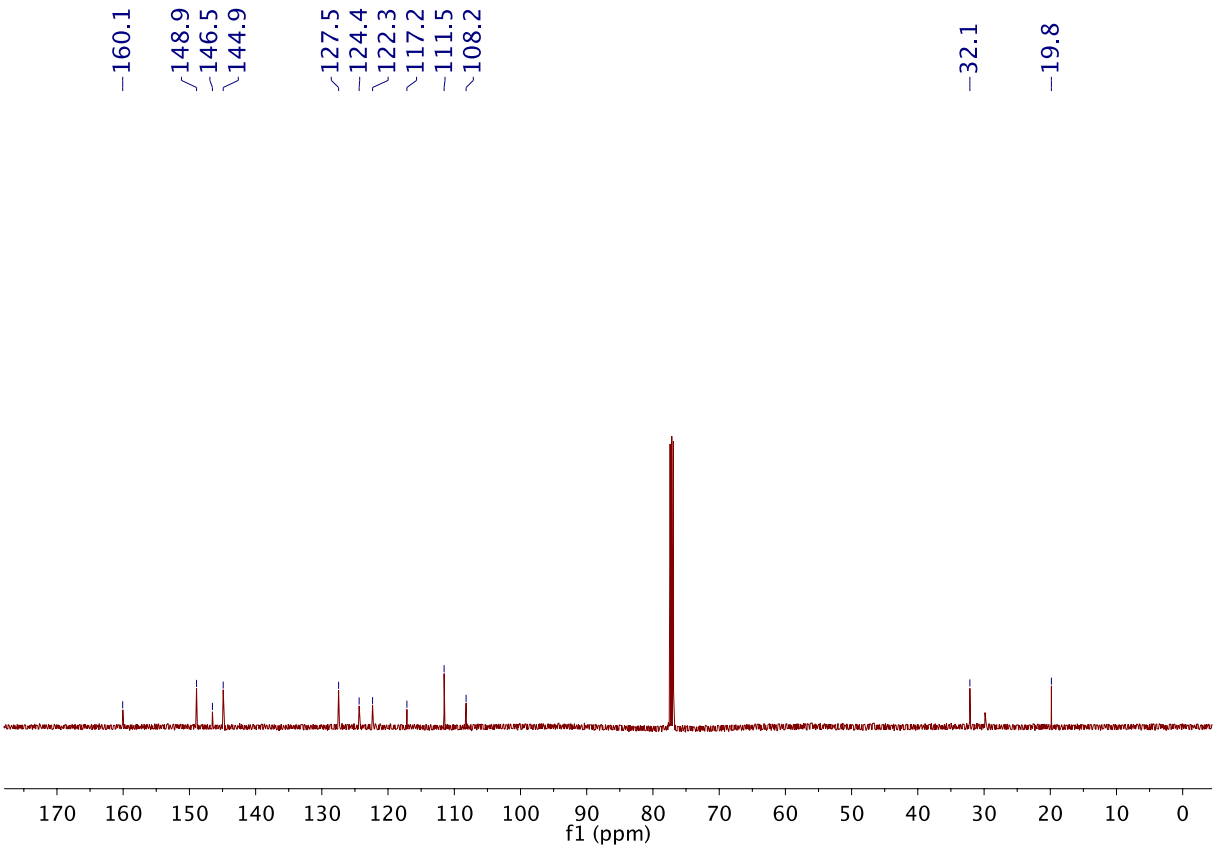

159.5
159.5
147.2
144.5
142.9
142.8
124.1
122.3
122.3
111.5
31.9
20.0
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

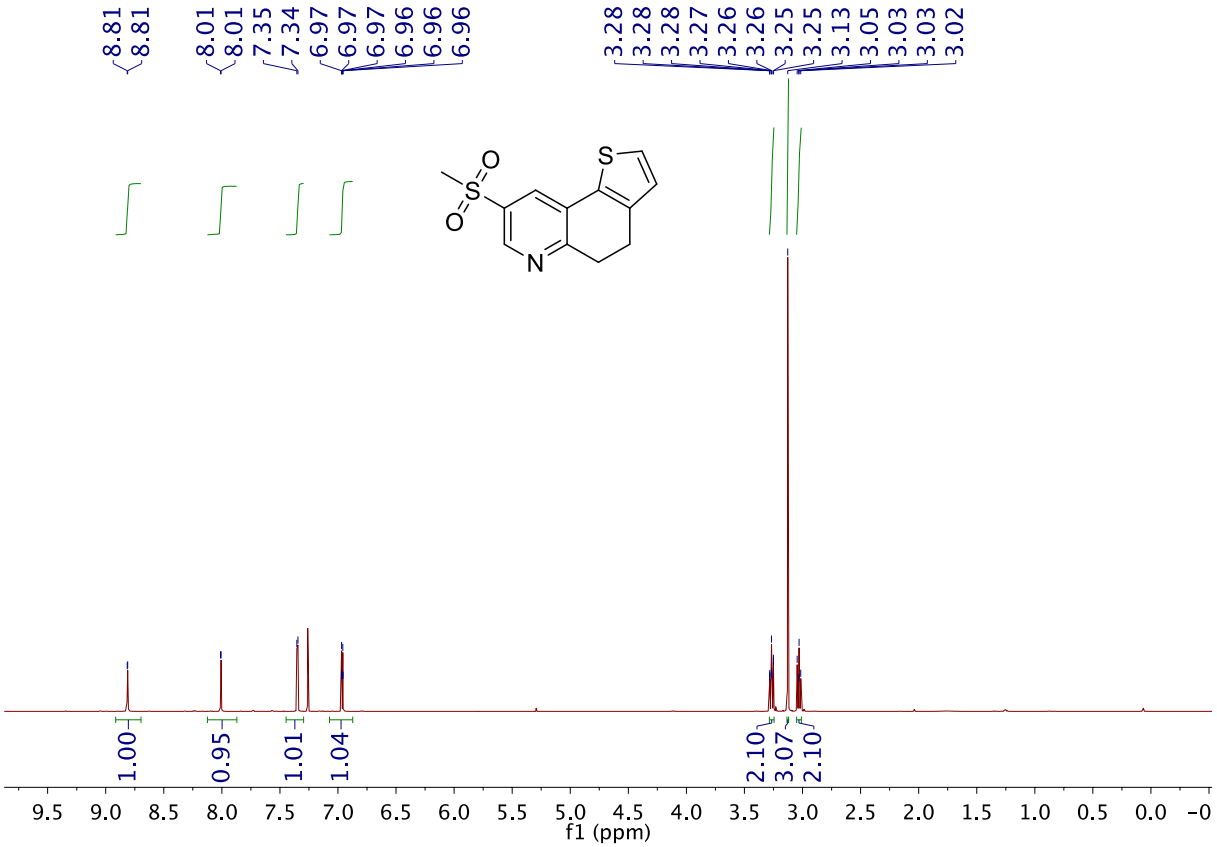

8.57
8.56
7.76
7.76
7.76
7.76
7.35
7.34
6.97
6.96
3.25
3.25
3.25
3.25
3.25
3.24
3.24
3.24
3.24
3.23
3.23
3.23
3.22
3.22
3.22
3.22
3.04
3.03
3.02
3.02
3.01
3.01
3.00
NC
S
N
1.00
0.97
1.00
1.01
2.06
2.06
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

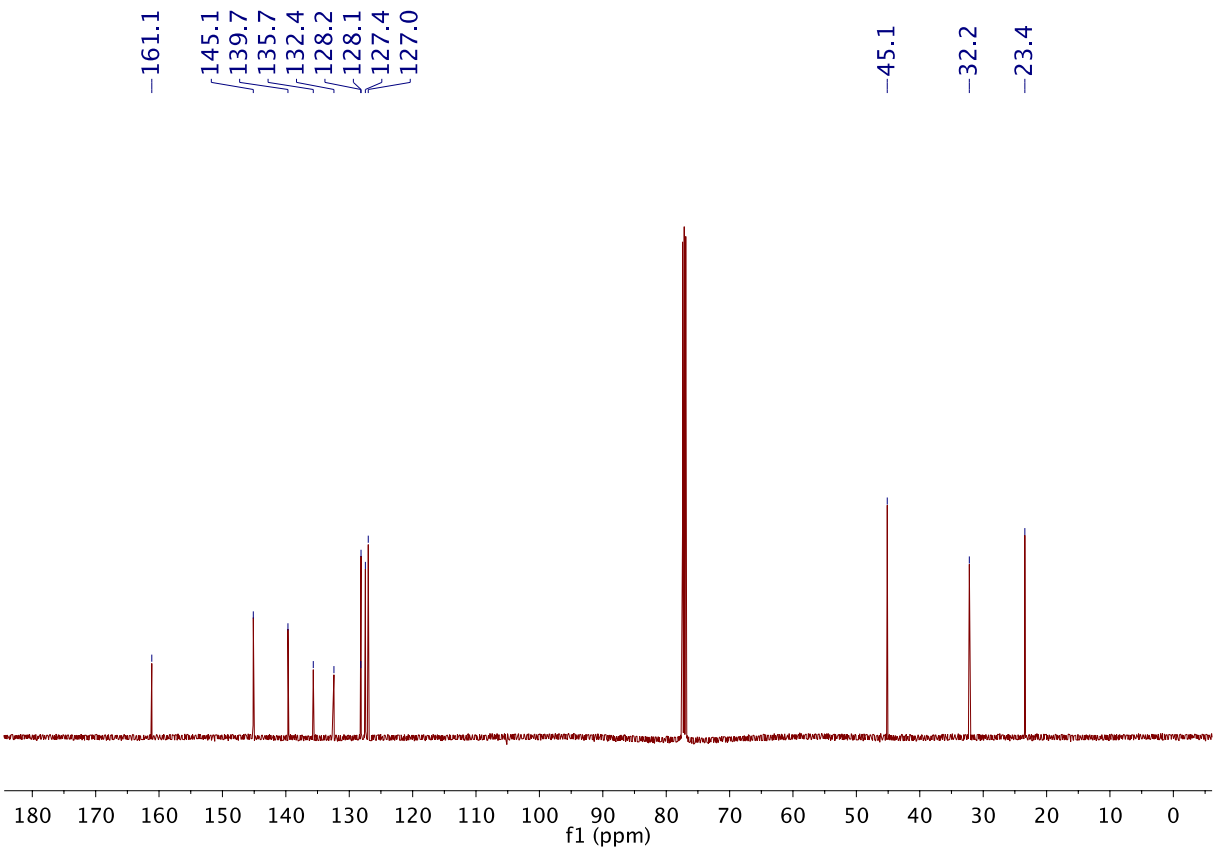

159.9
149.2
139.6
132.1
131.2
128.2
127.9
126.9
117.0
108.4
32.2
23.4
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

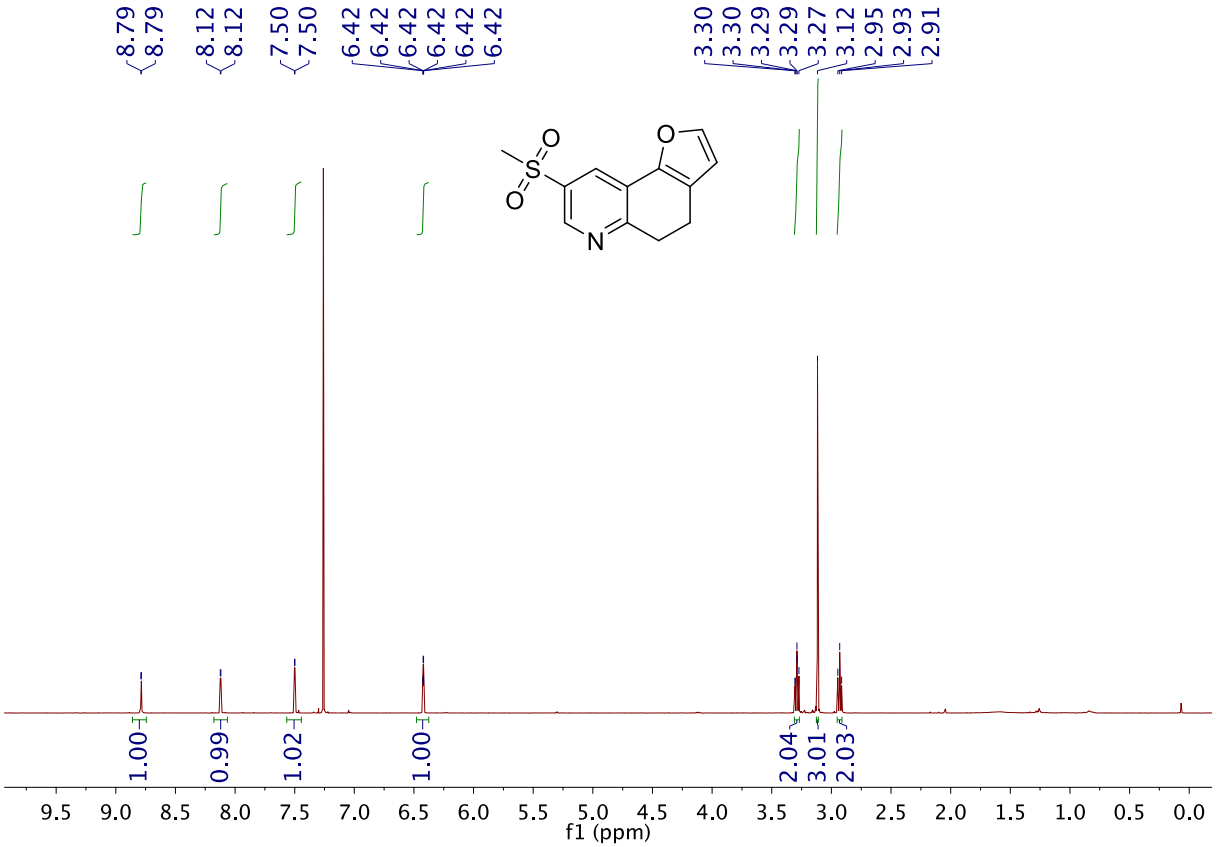

8.53
8.52
7.83
7.83
7.83
7.83
7.48
7.48
6.41
6.41
6.41
6.41
6.41
6.40
6.40
3.26
3.25
3.25
3.25
3.24
3.24
3.24
3.24
3.22
3.22
3.22
3.22
2.92
2.91
2.91
2.89
NC
O
N

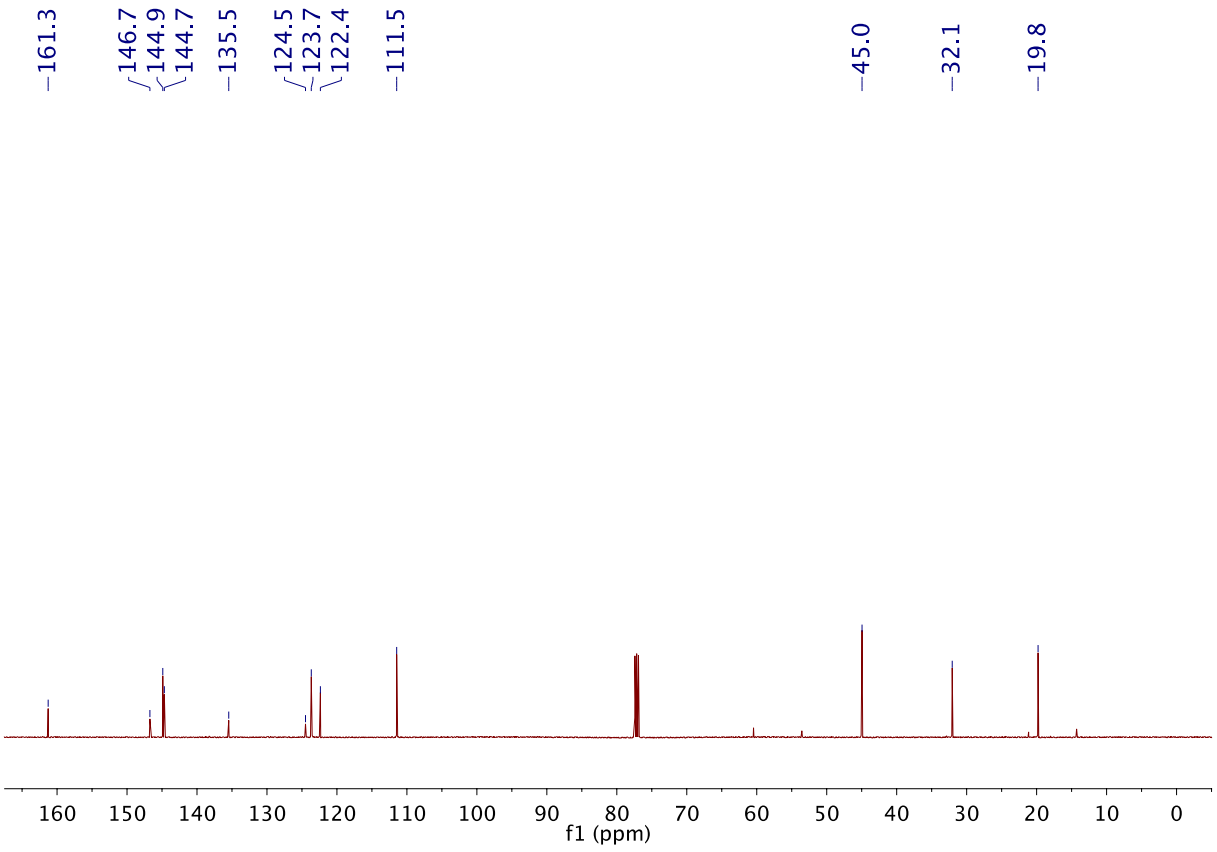

1.00
1.03
1.02
1.05
2.17
2.24
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

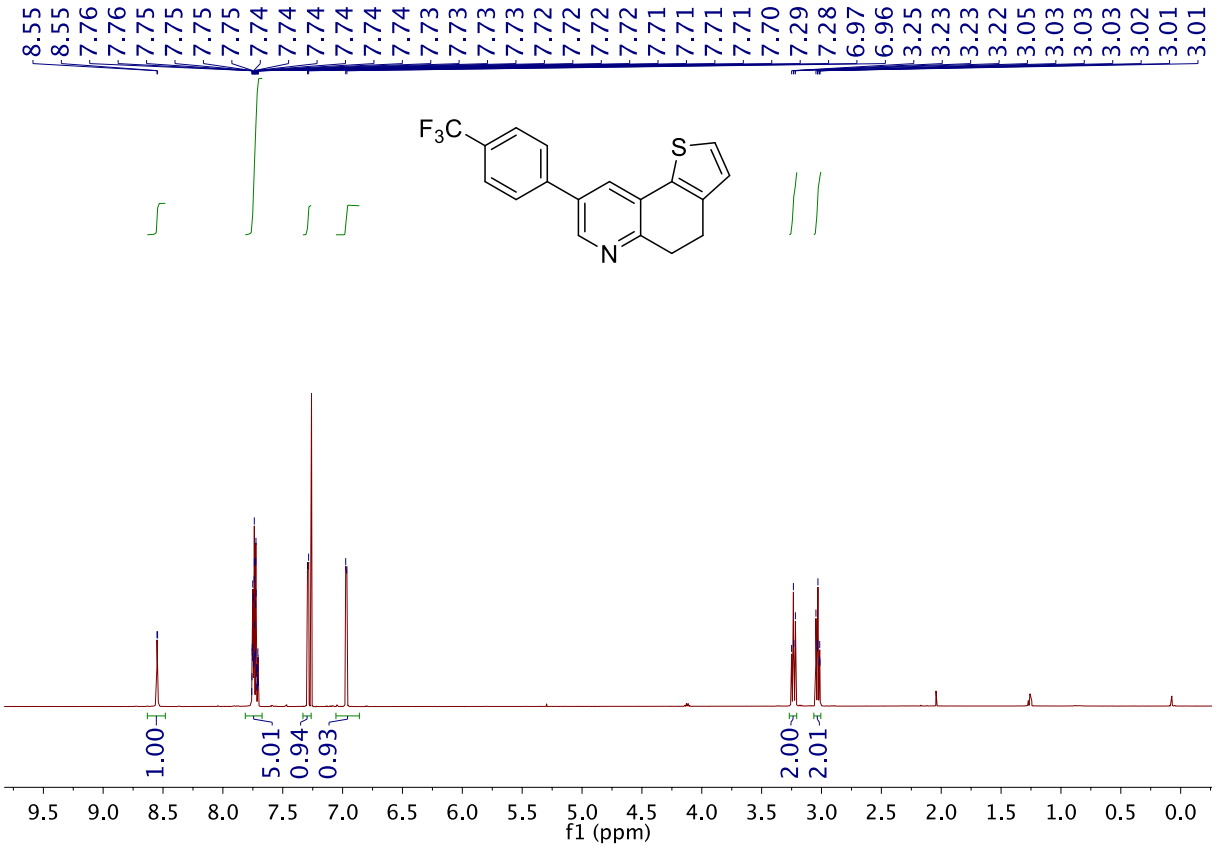

160.1
148.9
146.5
144.9
127.5
124.4
122.3
117.2
111.5
108.2
32.1
19.8
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

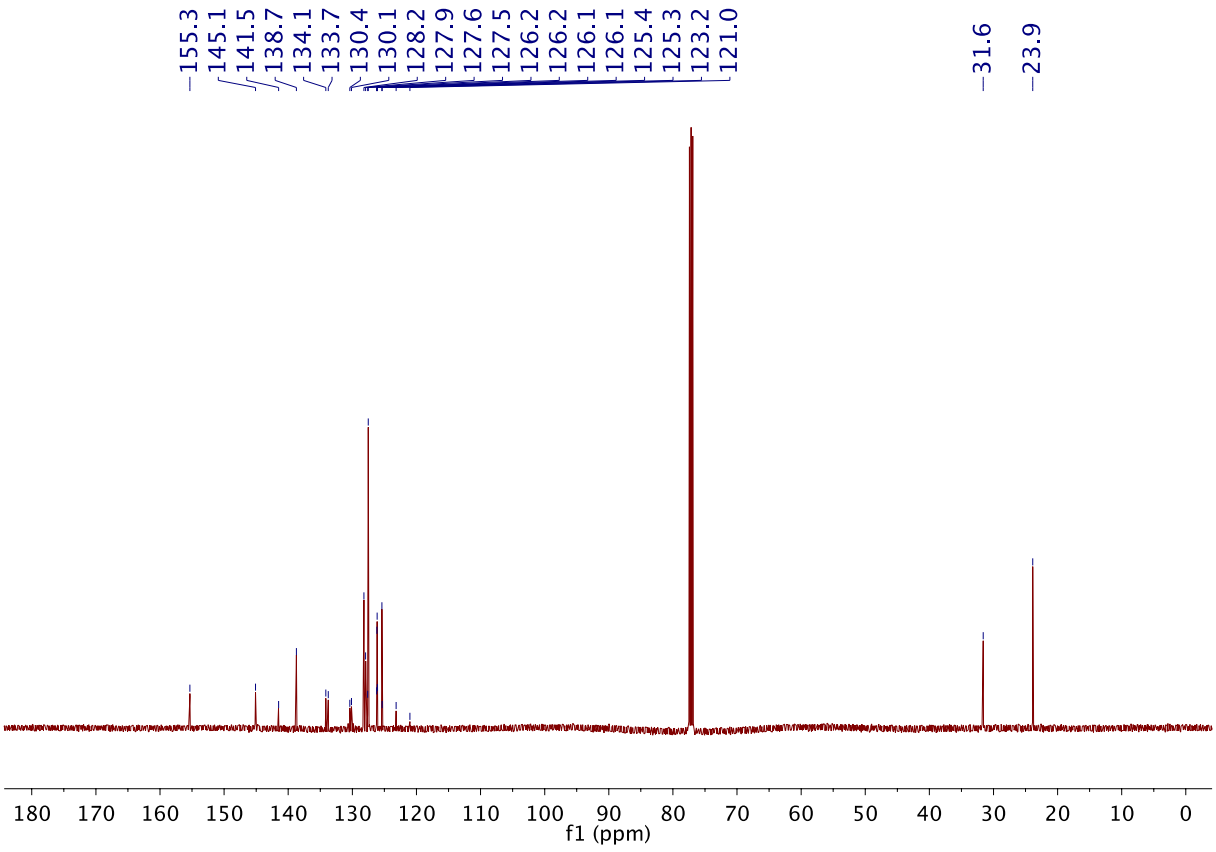

8.81
8.81
8.01
8.01
7.35
7.34
6.97
6.97
6.97
6.96
6.96
6.96
3.28
3.28
3.28
3.27
3.26
3.26
3.25
3.25
3.13
3.05
3.03
3.03
3.02
O
S
O
S
N
1.00
0.95
1.01
1.04
2.10
3.07
2.10
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

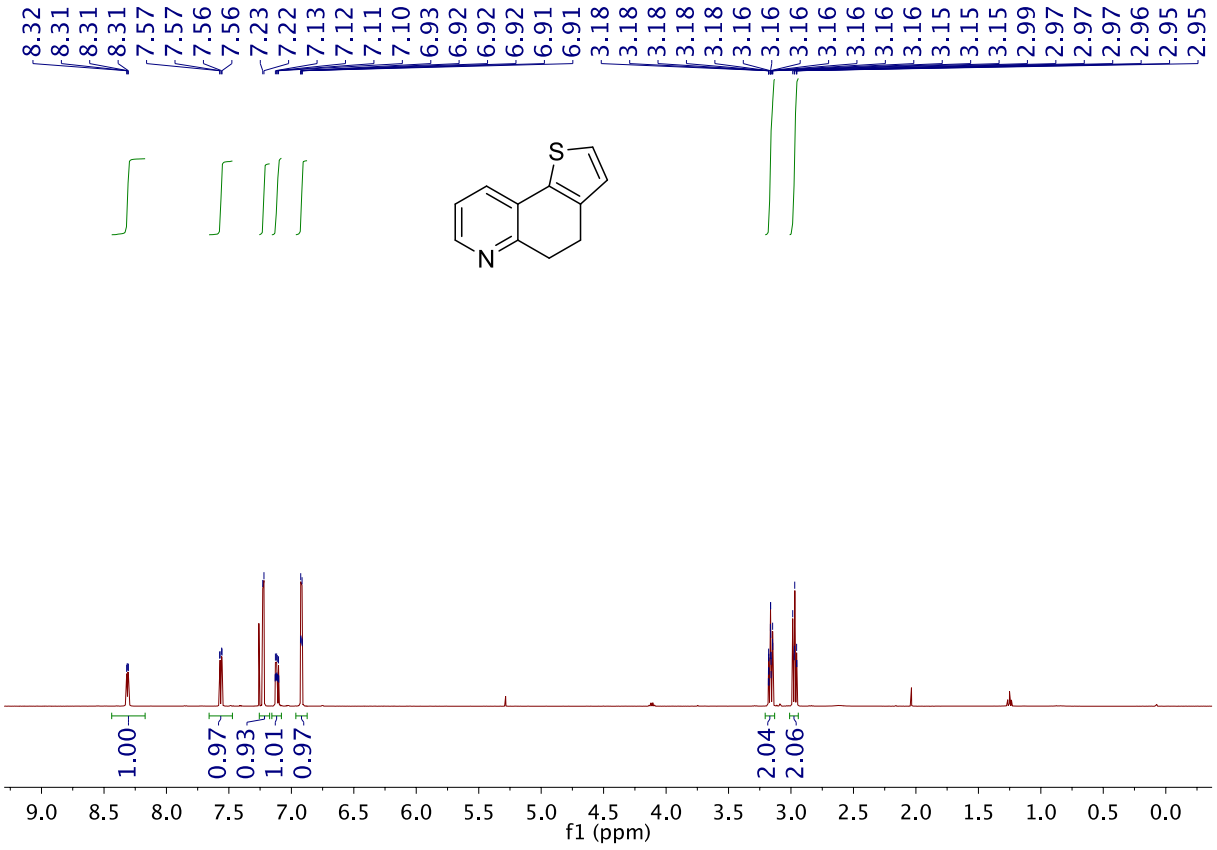

161.1
145.1
139.7
135.7
132.4
128.2
128.1
127.4
127.0
45.1
32.2
23.4
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

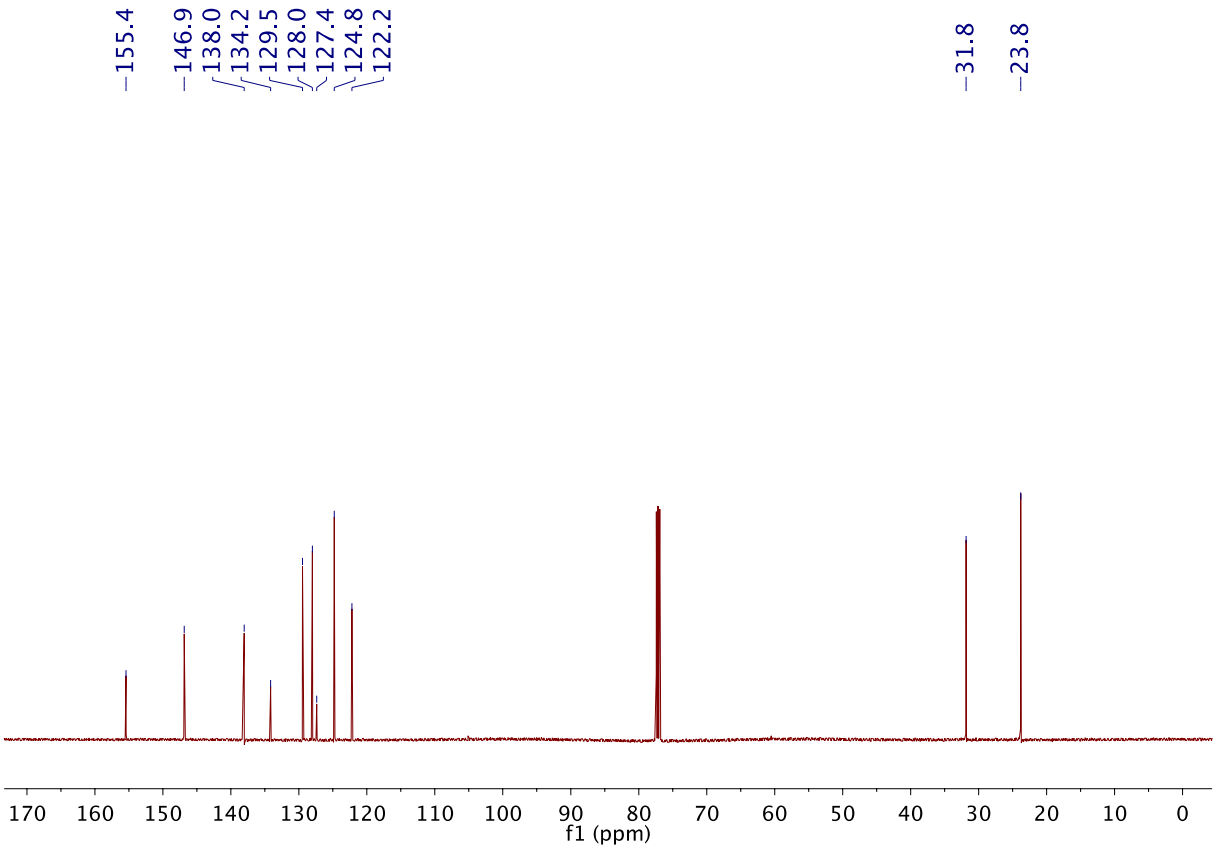

8.79
8.79
8.12
8.12
7.50
7.50
6.42
6.42
6.42
6.42
6.42
6.42
3.30
3.30
3.29
3.29
3.27
3.12
2.95
2.93
2.91
O
O
S
O
O
N
1.00
0.99
1.02
1.00
2.04
3.01
2.03
f1 (ppm)

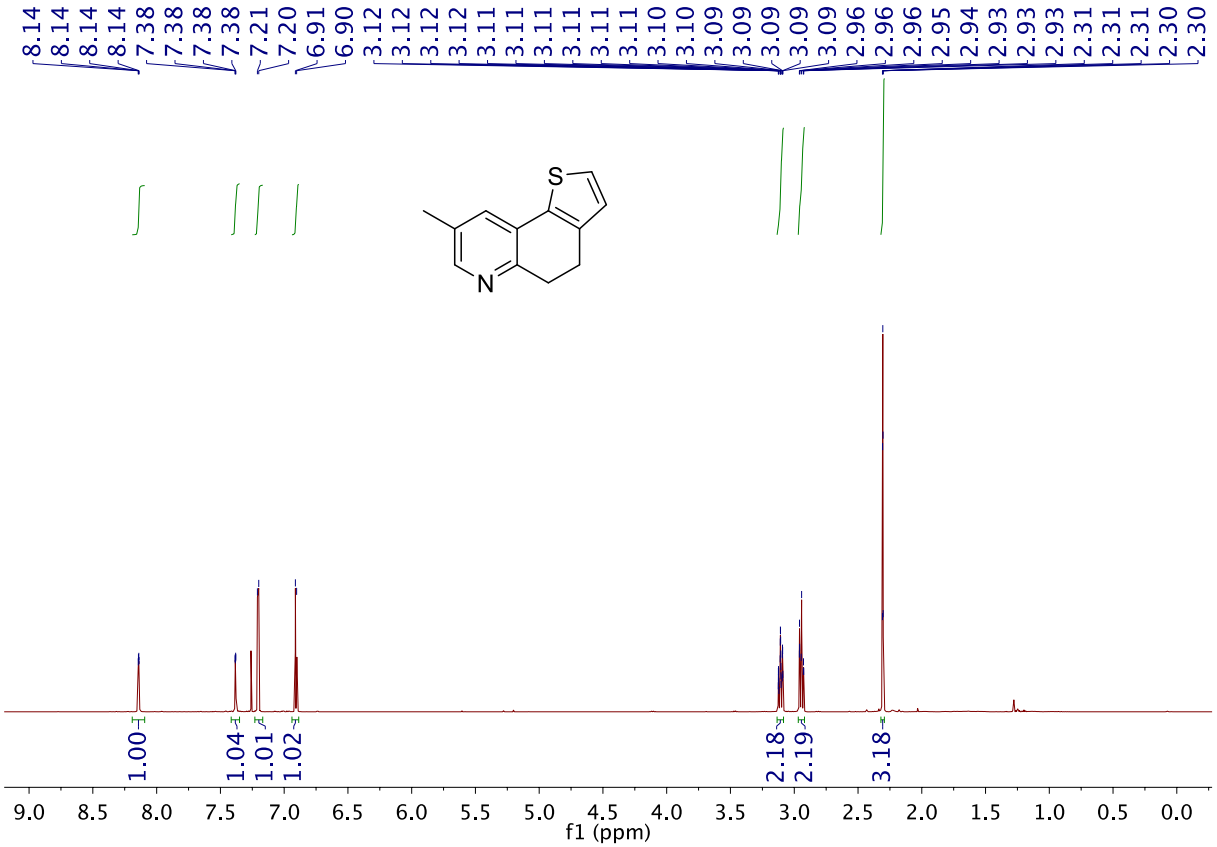

161.3
146.7
144.9
144.7
135.5
124.5
123.7
122.4
111.5
45.0
32.1
19.8
f1 (ppm)

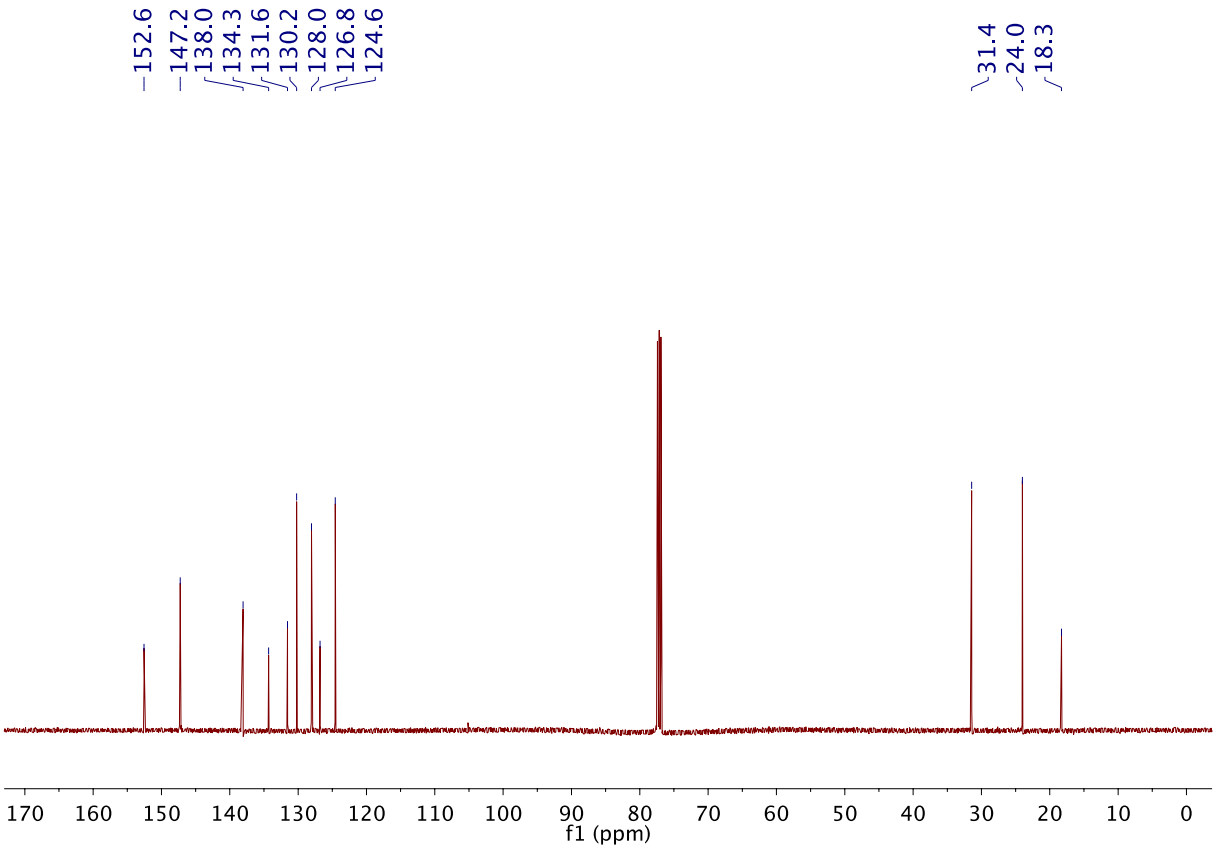

8.55
8.55
7.76
7.76
7.75
7.75
7.75
7.75
7.74
7.74
7.74
7.74
7.74
7.73
7.73
7.73
7.73
7.72
7.72
7.72
7.72
7.71
7.71
7.71
7.71
7.70
7.29
7.28
6.97
6.96
3.25
3.23
3.23
3.22
3.05
3.03
3.03
3.03
3.02
3.01
3.01
F3C
S
N
1.00
5.01
0.94
0.93
2.00
2.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

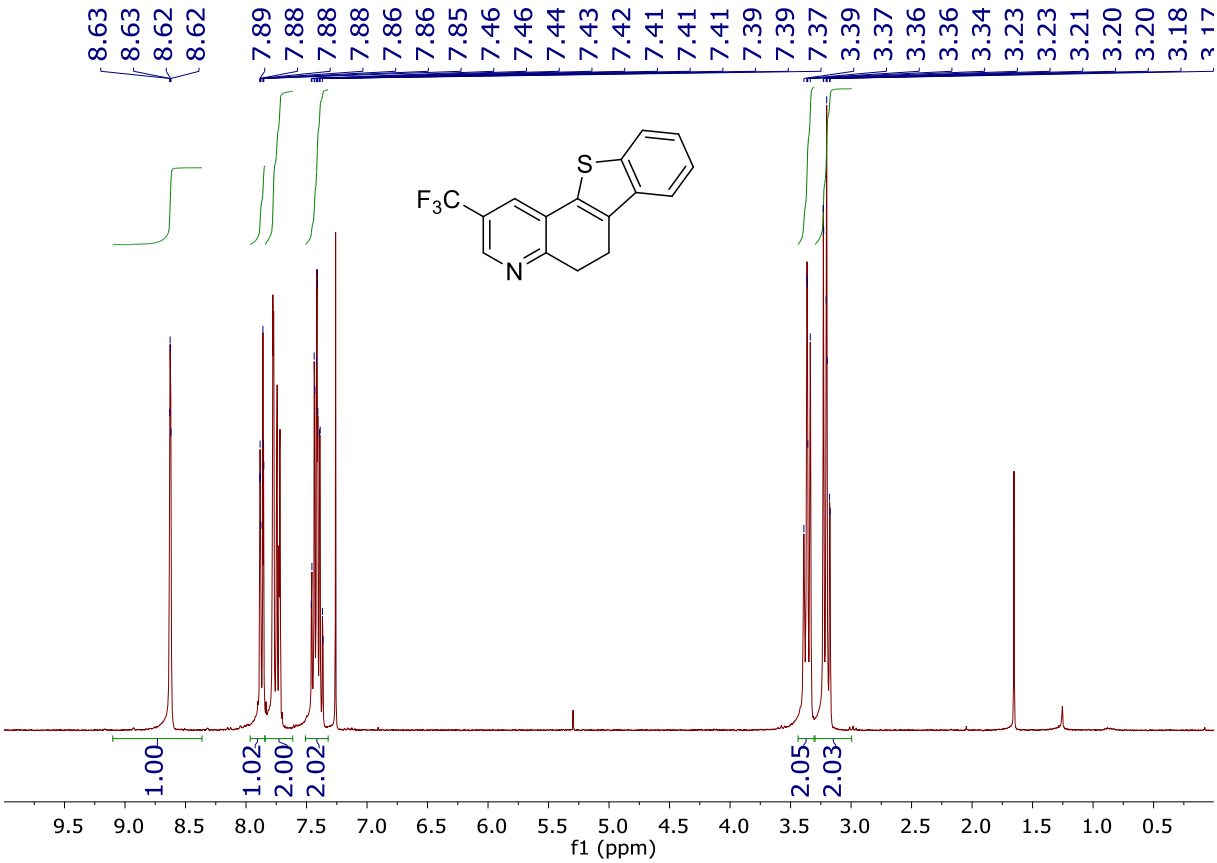

155.3
145.1
141.5
138.7
134.1
133.7
130.4
130.1
128.2
127.9
127.6
127.5
126.2
126.2
126.1
126.1
125.4
125.3
123.2
121.0
31.6
23.9
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

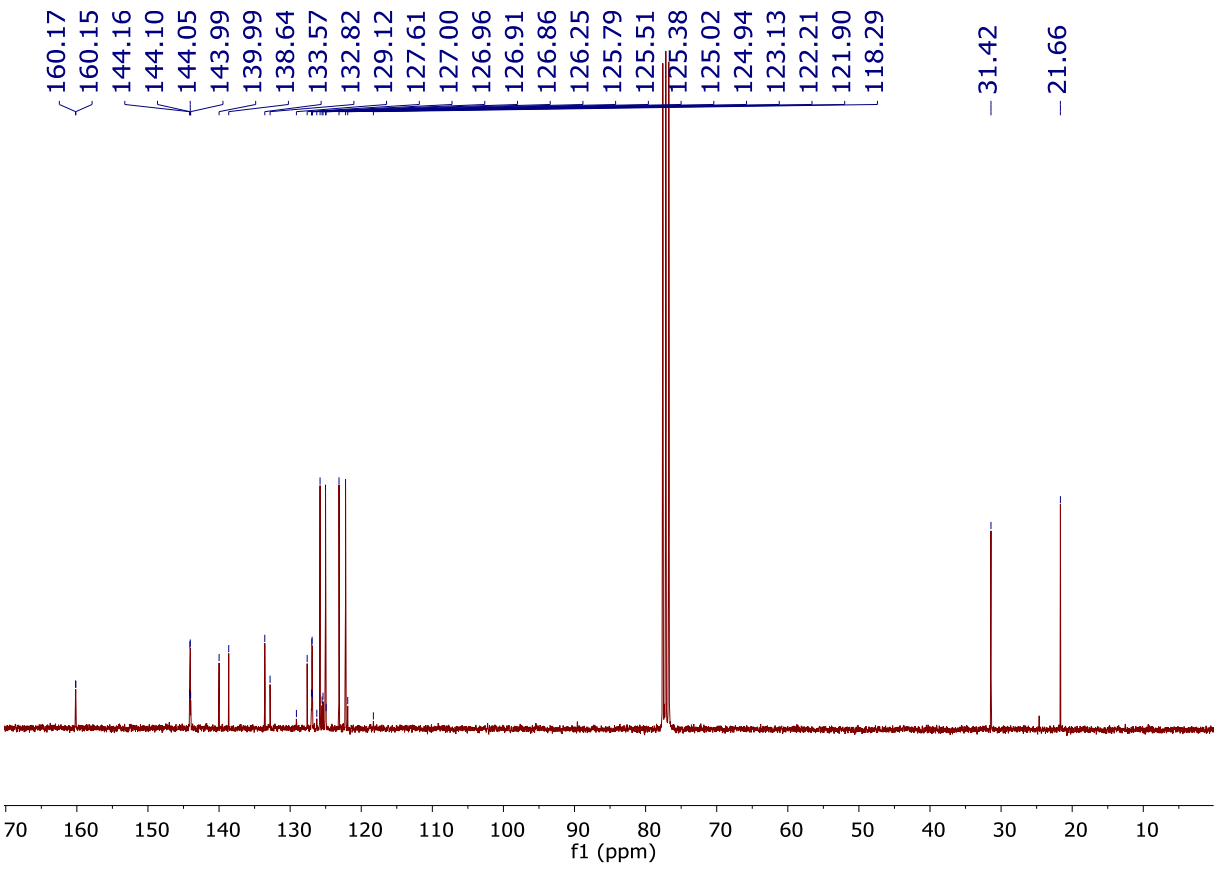

8.32
8.31
8.31
8.31
7.57
7.57
7.56
7.56
7.23
7.22
7.13
7.12
7.11
7.10
6.93
6.92
6.92
6.92
6.91
6.91
3.18
3.18
3.18
3.18
3.16
3.16
3.16
3.16
3.16
3.16
3.15
3.15
3.15
2.99
2.97
2.97
2.97
2.96
2.95
2.95
S
N
1.00
0.97
0.93
1.01
0.97
2.04
2.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

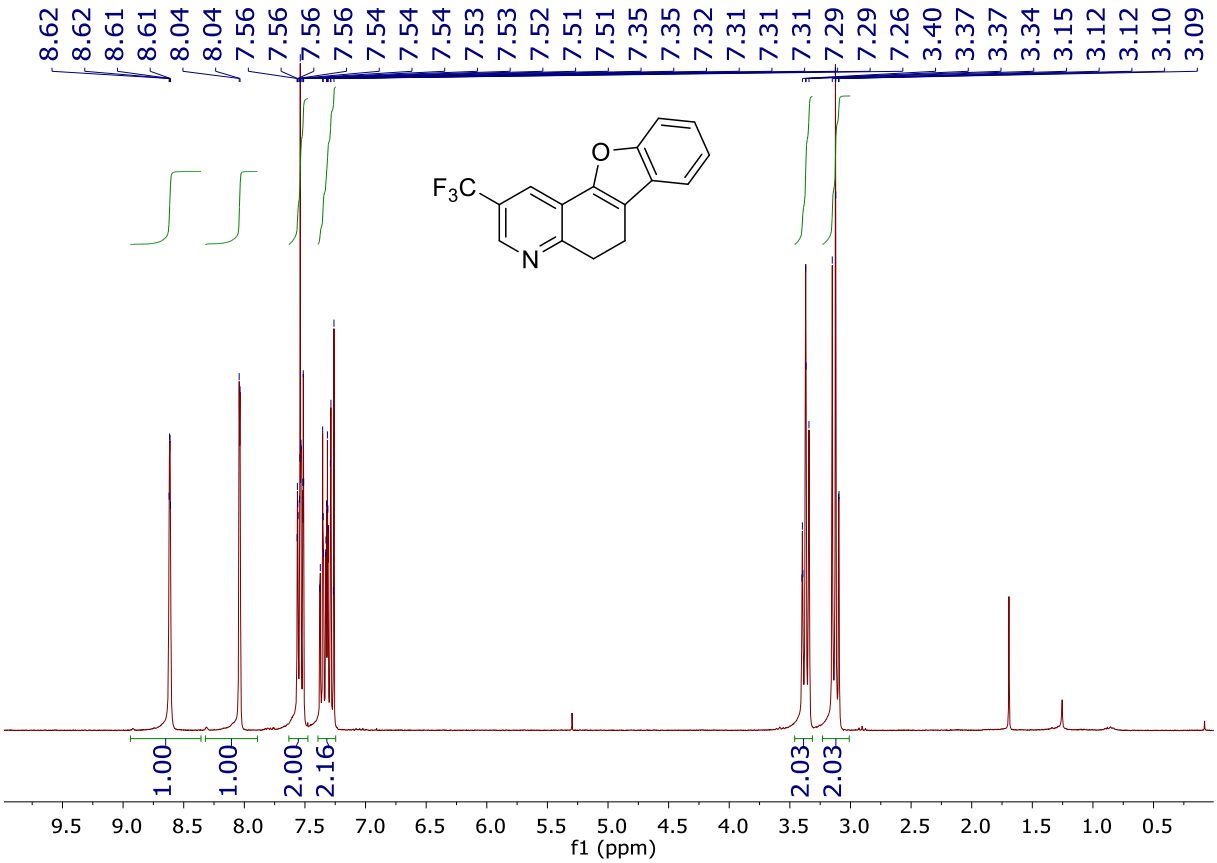

155.4
146.9
138.0
134.2
129.5
128.0
127.4
124.8
122.2
31.8
23.8
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

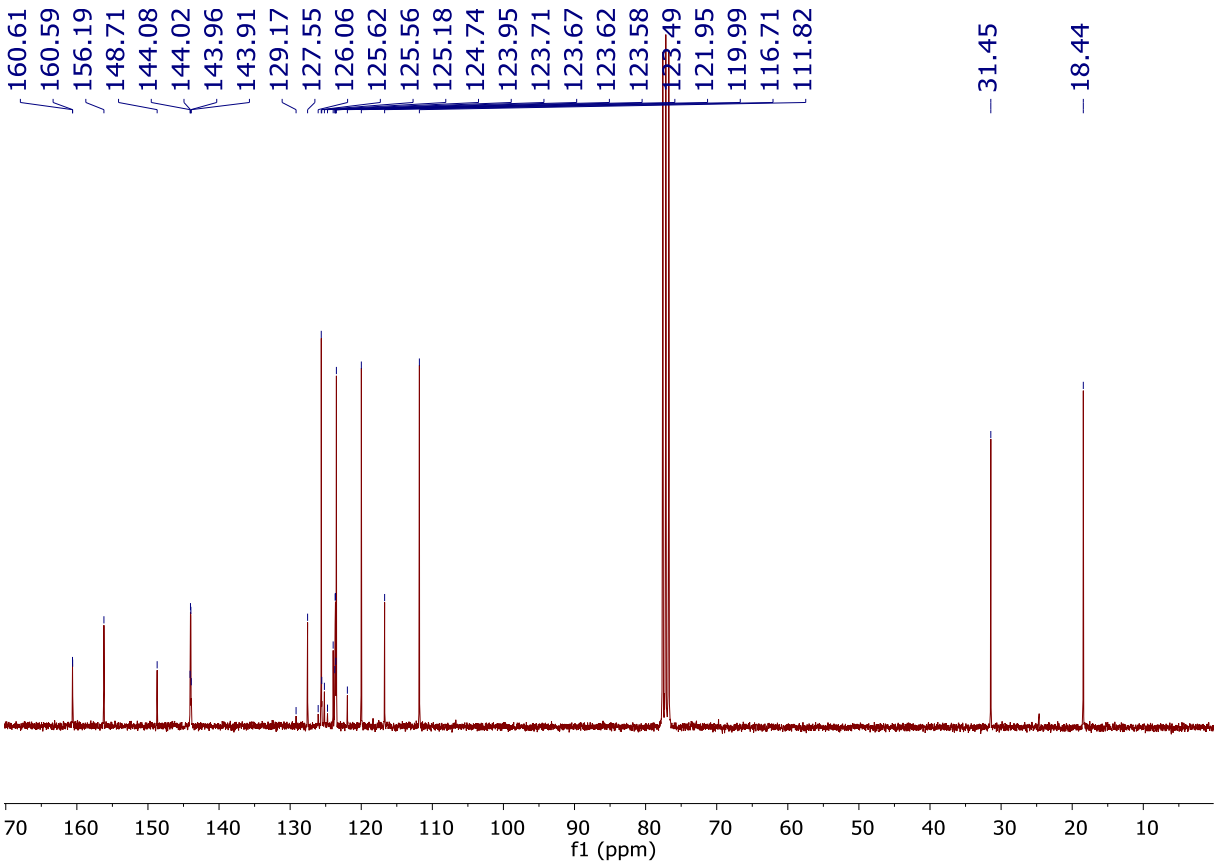

8.14
8.14
8.14
8.14
7.38
7.38
7.38
7.38
7.21
7.20
6.91
6.90
3.12
3.12
3.12
3.12
3.11
3.11
3.11
3.11
3.11
3.11
3.10
3.10
3.09
3.09
3.09
3.09
3.09
2.96
2.96
2.96
2.95
2.94
2.93
2.93
2.93
2.31
2.31
2.31
2.30
2.30
S
N
1.00
1.04
1.01
1.02
2.18
2.19
3.18
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

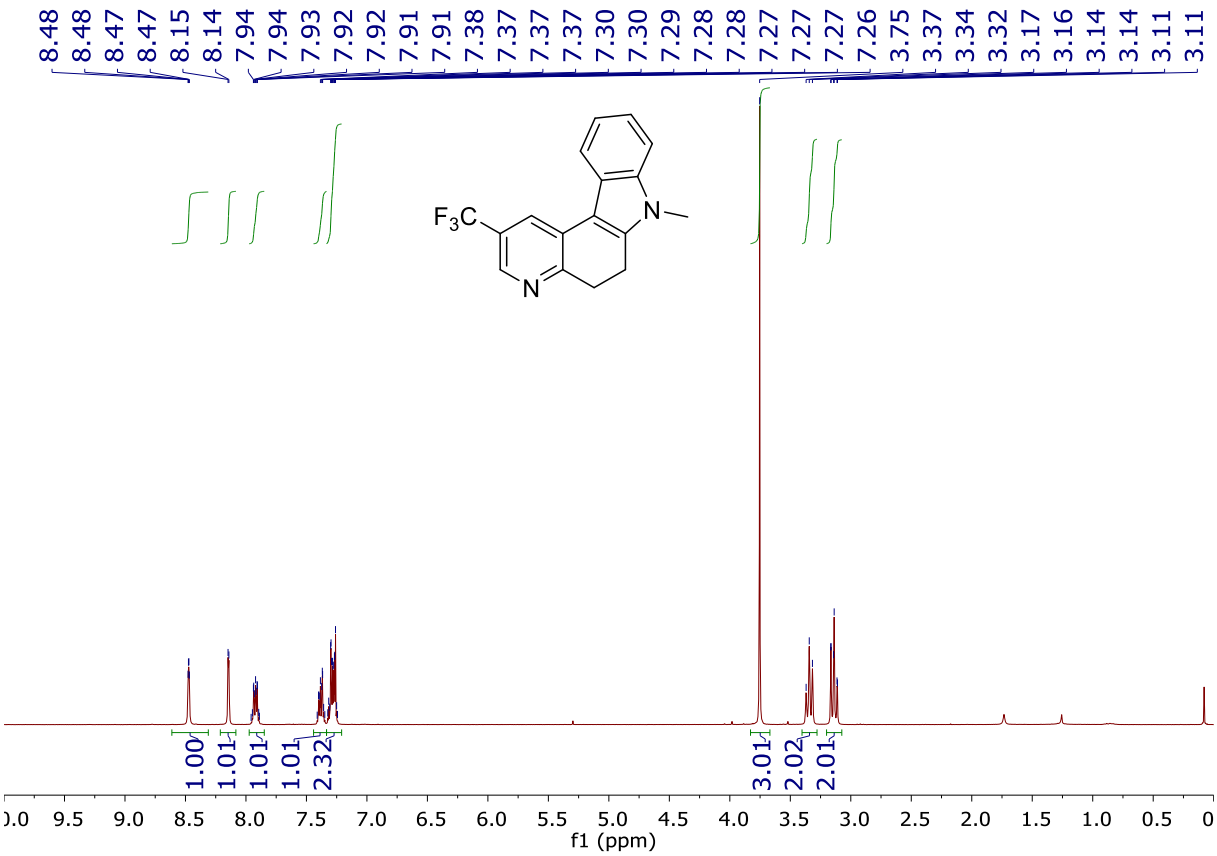

152.6
147.2
138.0
134.3
131.6
130.2
128.0
126.8
124.6
31.4
24.0
18.3
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

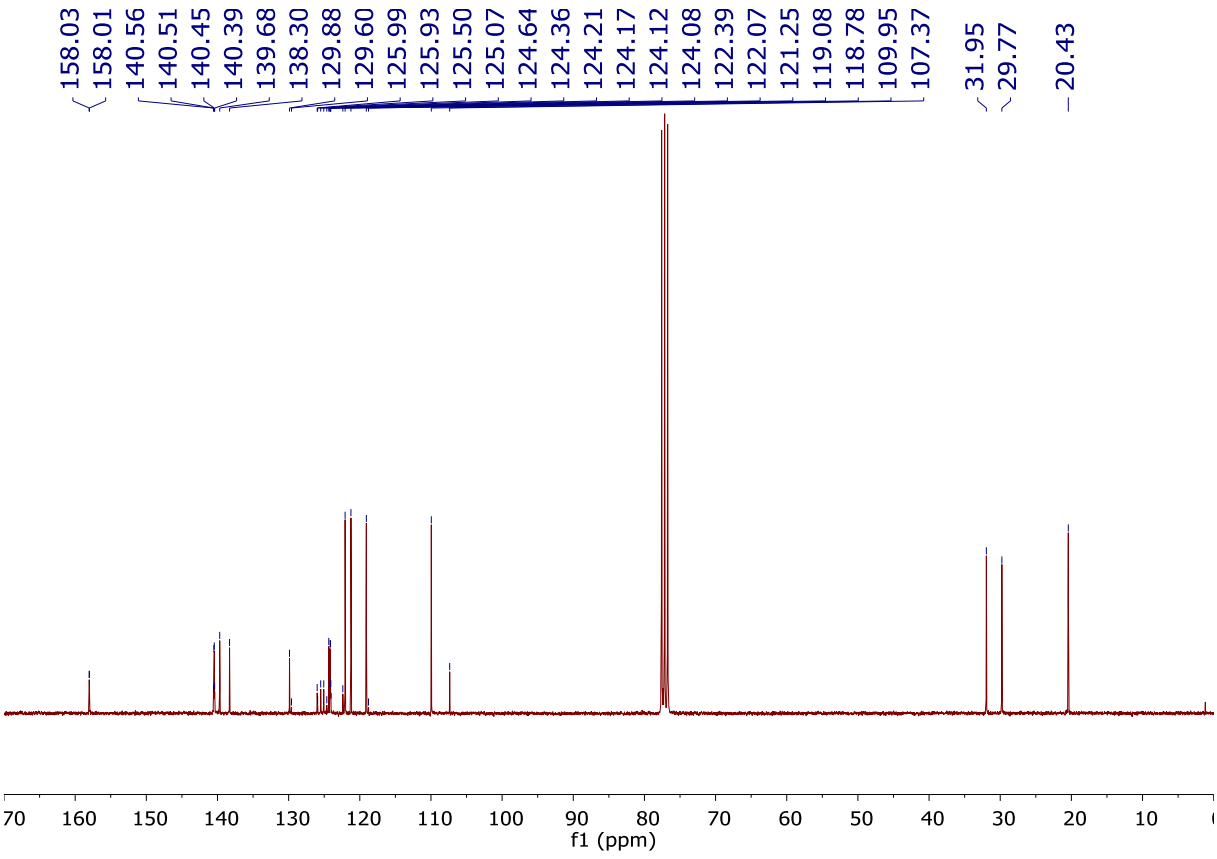

8.63
8.63
8.62
8.62
7.89
7.88
7.88
7.88
7.86
7.86
7.85
7.46
7.46
7.44
7.43
7.42
7.41
7.41
7.41
7.39
7.39
7.37
3.39
3.37
3.36
3.36
3.34
3.23
3.23
3.21
3.20
3.20
3.18
S
F3C
N
1.00
1.02
2.00
2.02
2.05
2.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

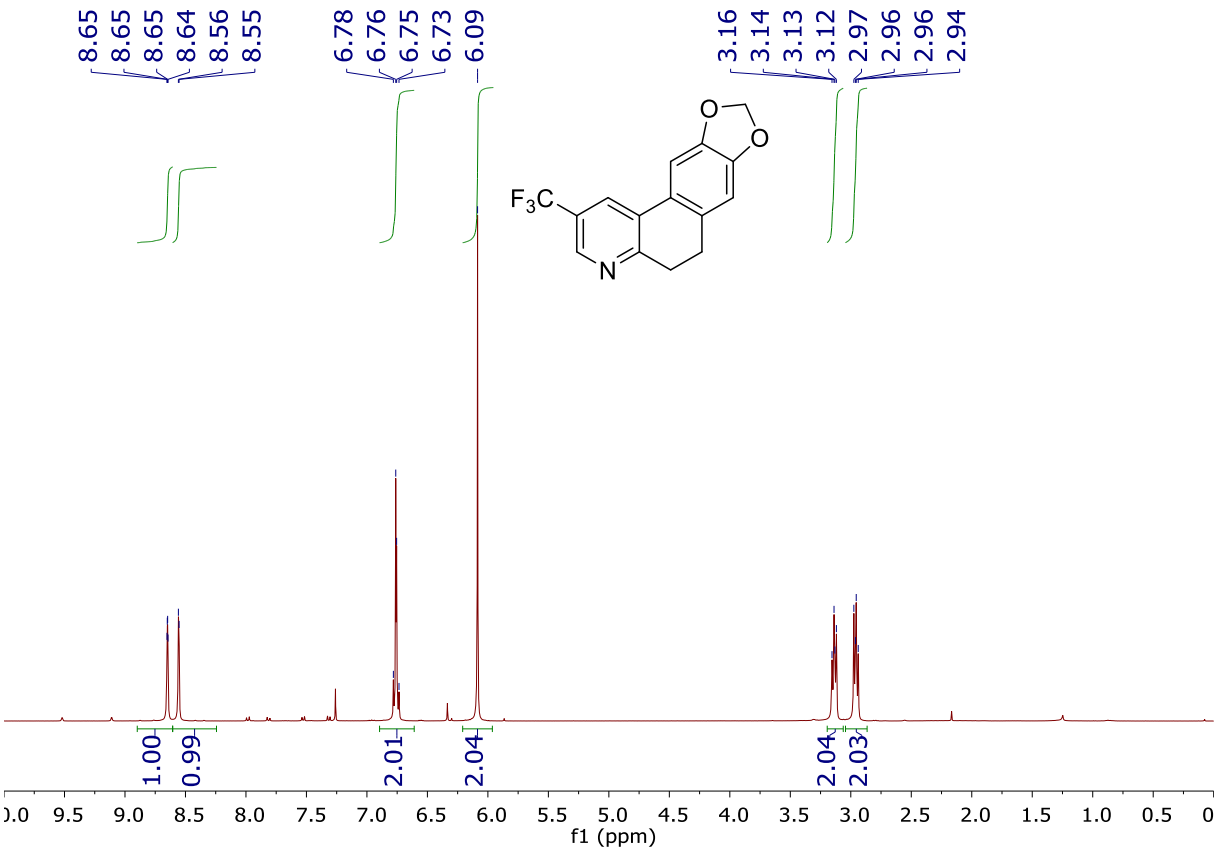

160.17
160.15
144.16
144.10
144.05
143.99
139.99
138.64
133.57
132.82
129.12
127.61
127.00
126.96
126.91
126.86
126.25
125.79
125.51
125.38
125.02
124.94
123.13
122.21
121.90
118.29
31.42
21.66
70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

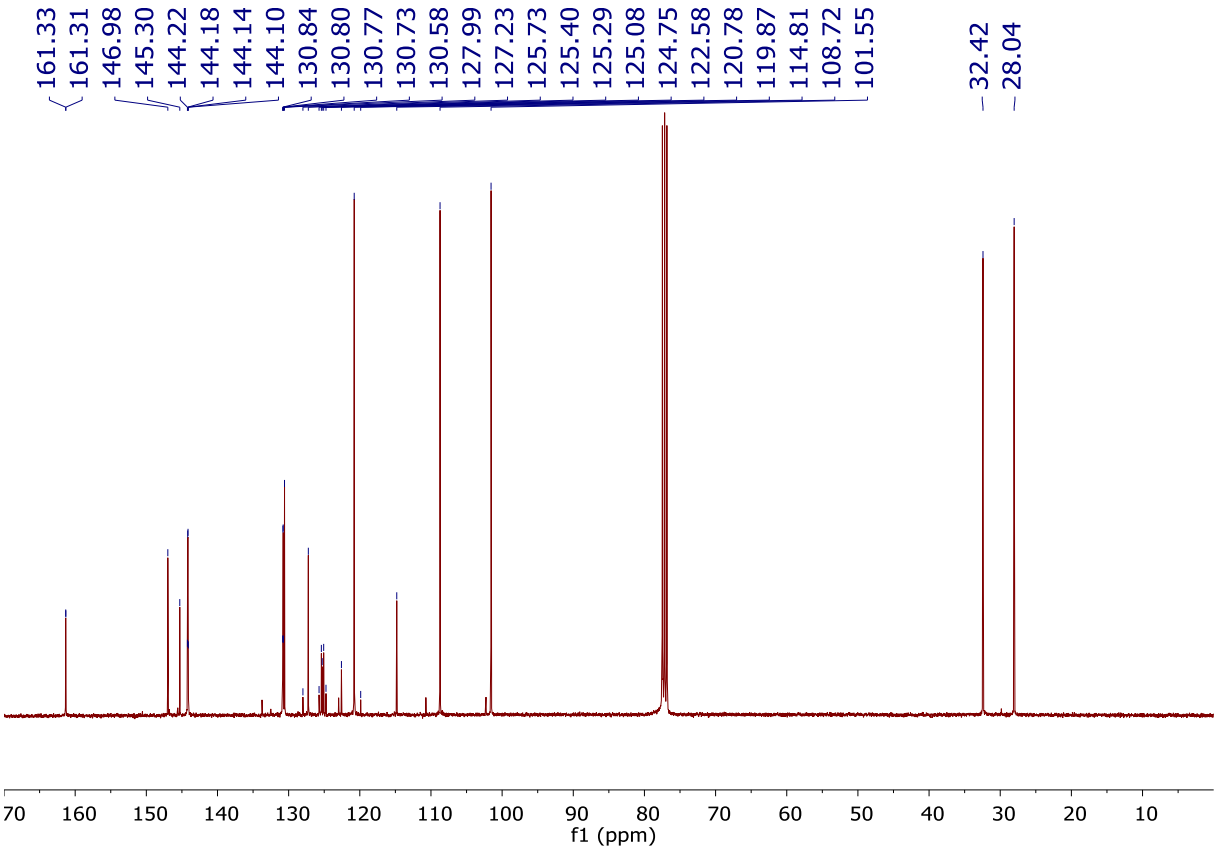

8.62 8.62 8.61 8.61 8.04 8.04 7.56 7.56 7.56 7.56 7.54 7.54 7.54 7.53 7.53 7.52 7.51 7.51 7.35 7.35 7.32 7.31 7.31 7.31 7.29 7.29 7.26 3.40 3.37 3.37 3.34 3.15 3.12 3.12 3.10 3.09
F3C
O
N
1.00 1.00 2.00 2.16 2.03 2.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

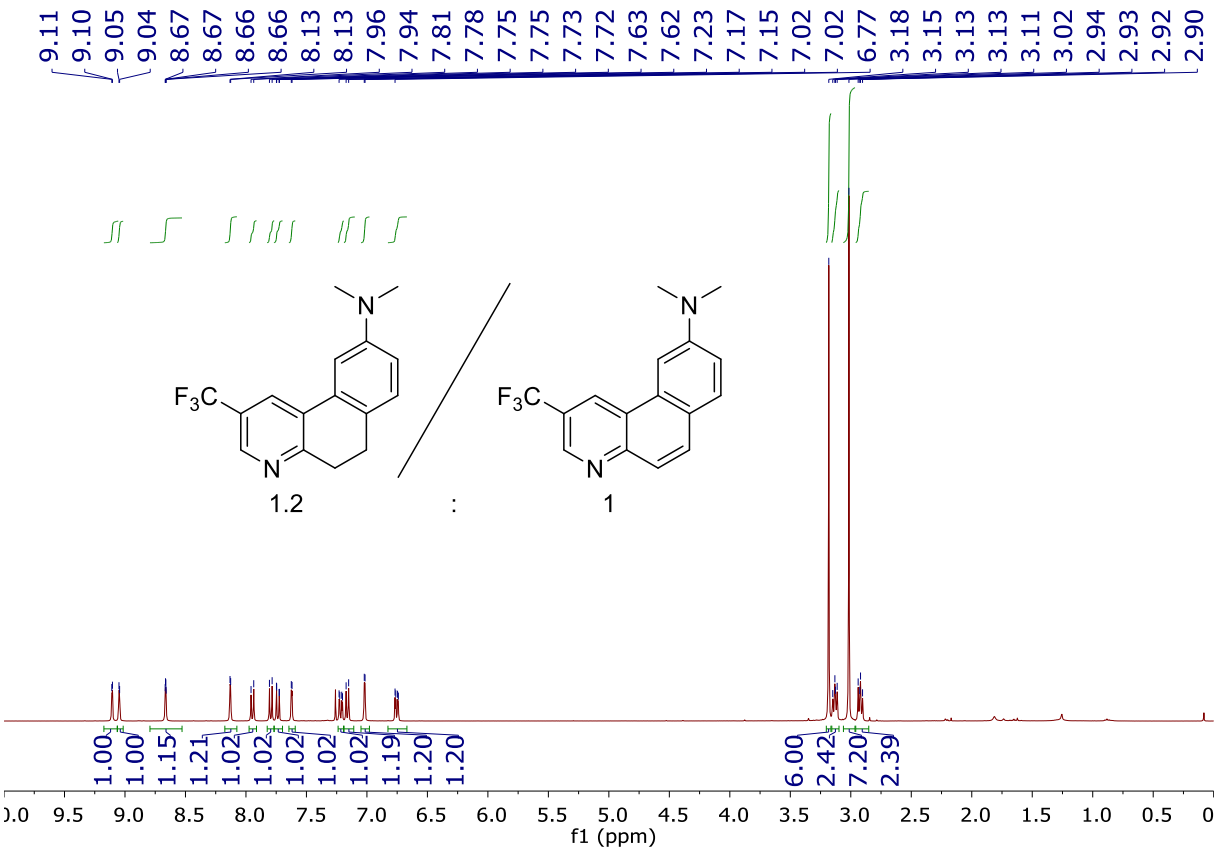

160.61 160.59 156.19 148.71 144.08 144.02 143.96 143.91 129.17 127.55 126.06 125.62 125.56 125.18 124.74 123.95 123.71 123.67 123.62 123.58 123.49 121.95 119.99 116.71 111.82
31.45
18.44
70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

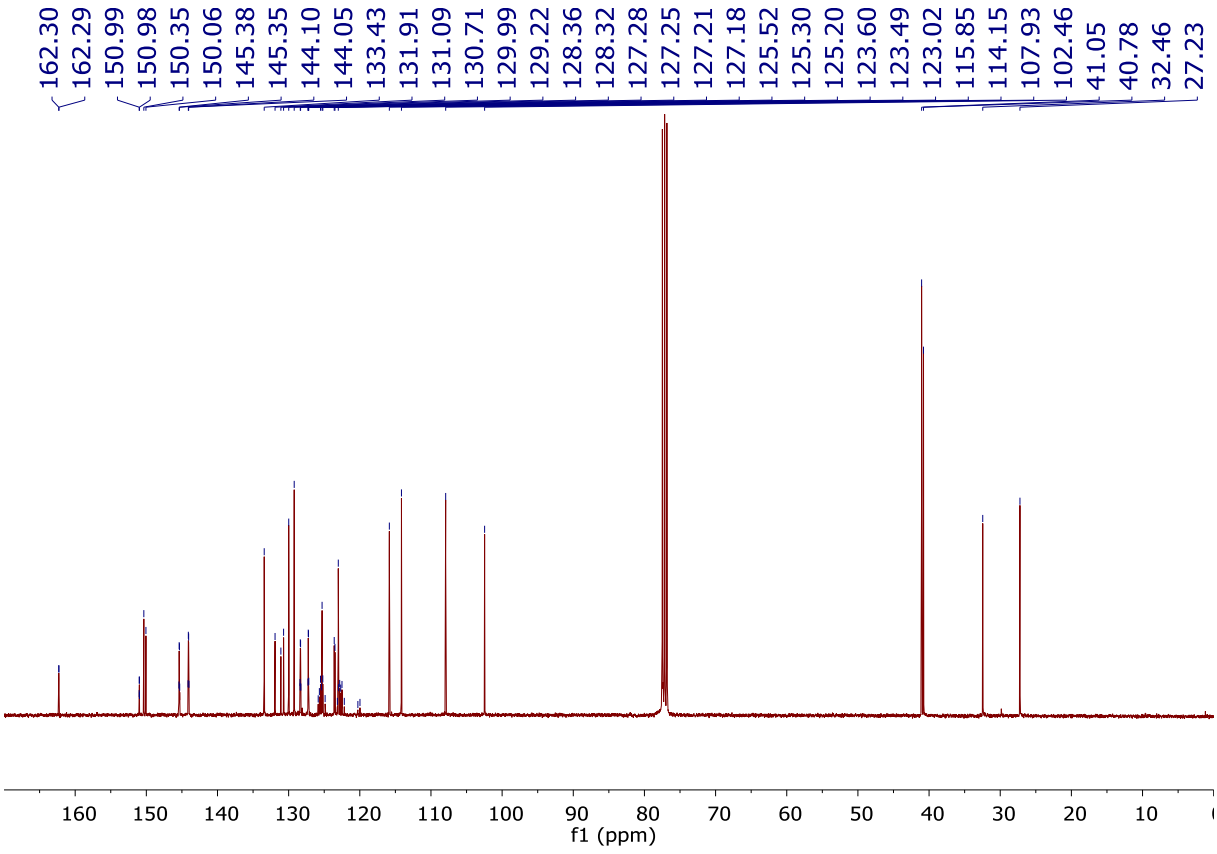

8.48 8.48 8.47 8.47 8.15 8.14 7.94 7.94 7.93 7.92 7.92 7.91 7.91 7.38 7.37 7.37 7.37 7.30 7.30 7.29 7.28 7.28 7.27 7.27 7.27 7.26 3.75 3.37 3.34 3.32 3.17 3.16 3.14 3.14 3.11 3.11
F3C
N
N
1.00 1.01 1.01 1.01 2.32 3.01 2.02 2.01
f1 (ppm)

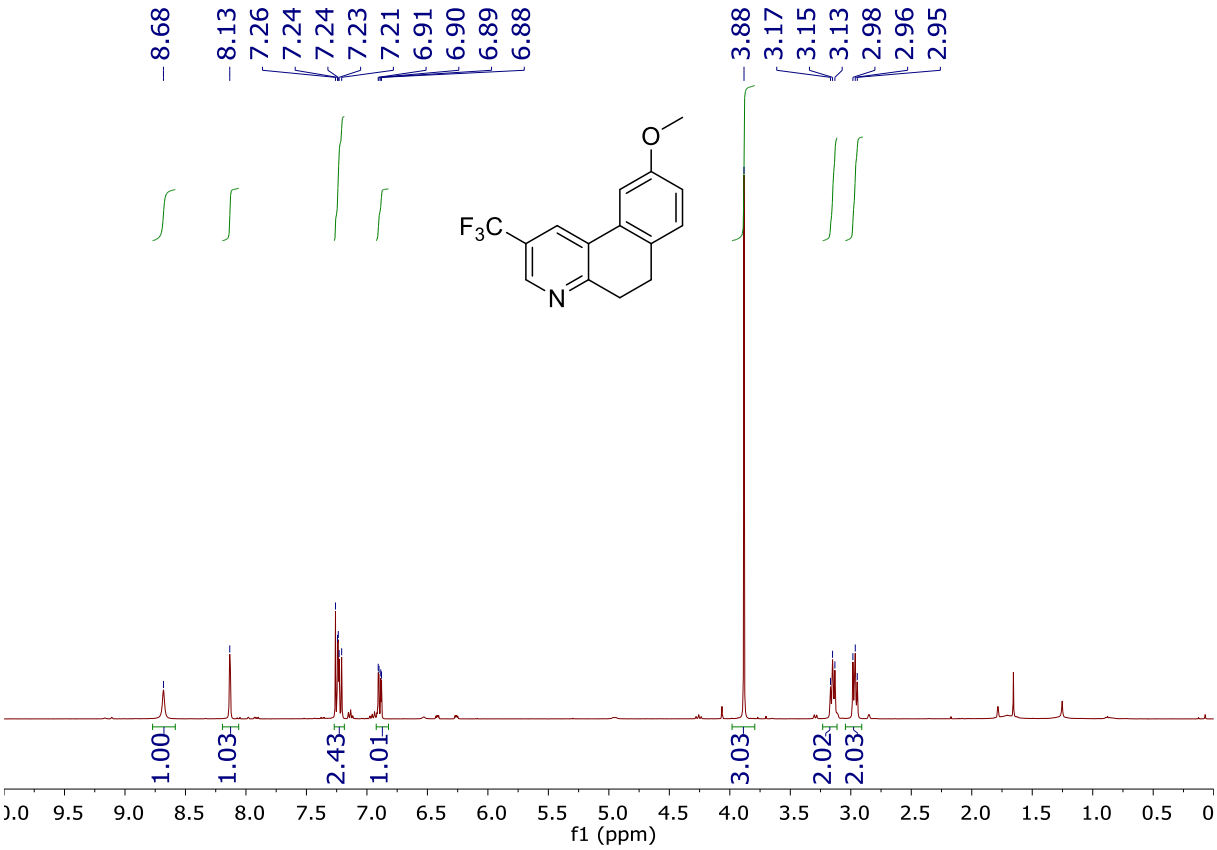

158.03 158.01 140.56 140.51 140.45 140.39 139.68 138.30 129.88 129.60 125.99 125.93 125.50 125.07 124.64 124.36 124.21 124.17 124.12 124.08 122.39 122.07 121.25 119.08 118.78 109.95 107.37 31.95 29.77 20.43
f1 (ppm)

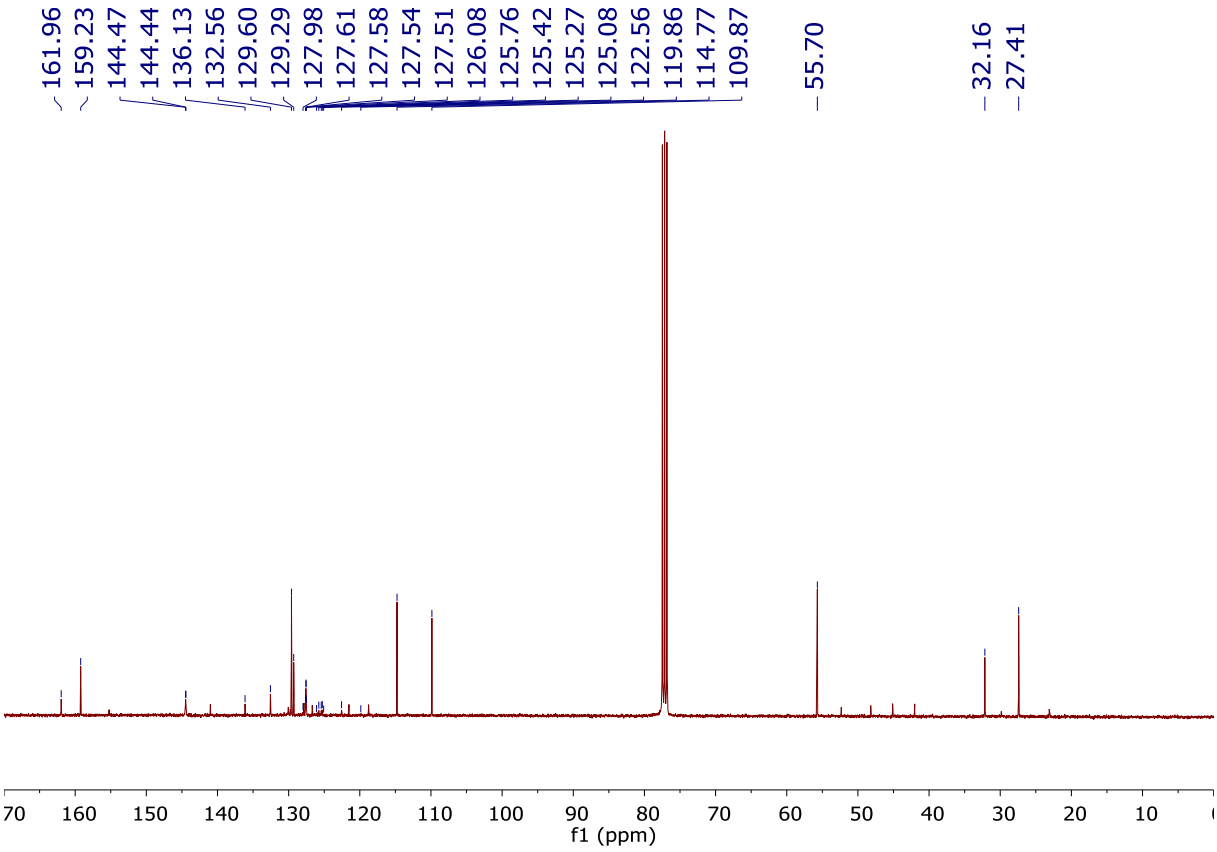

8.65
8.65
8.65
8.64
8.56
8.55
6.78
6.76
6.75
6.73
6.09
3.16
3.14
3.13
3.12
2.97
2.96
2.96
2.94
O
O
F3C
N
1.00
0.99
2.01
2.04
2.04
2.03
f1 (ppm)

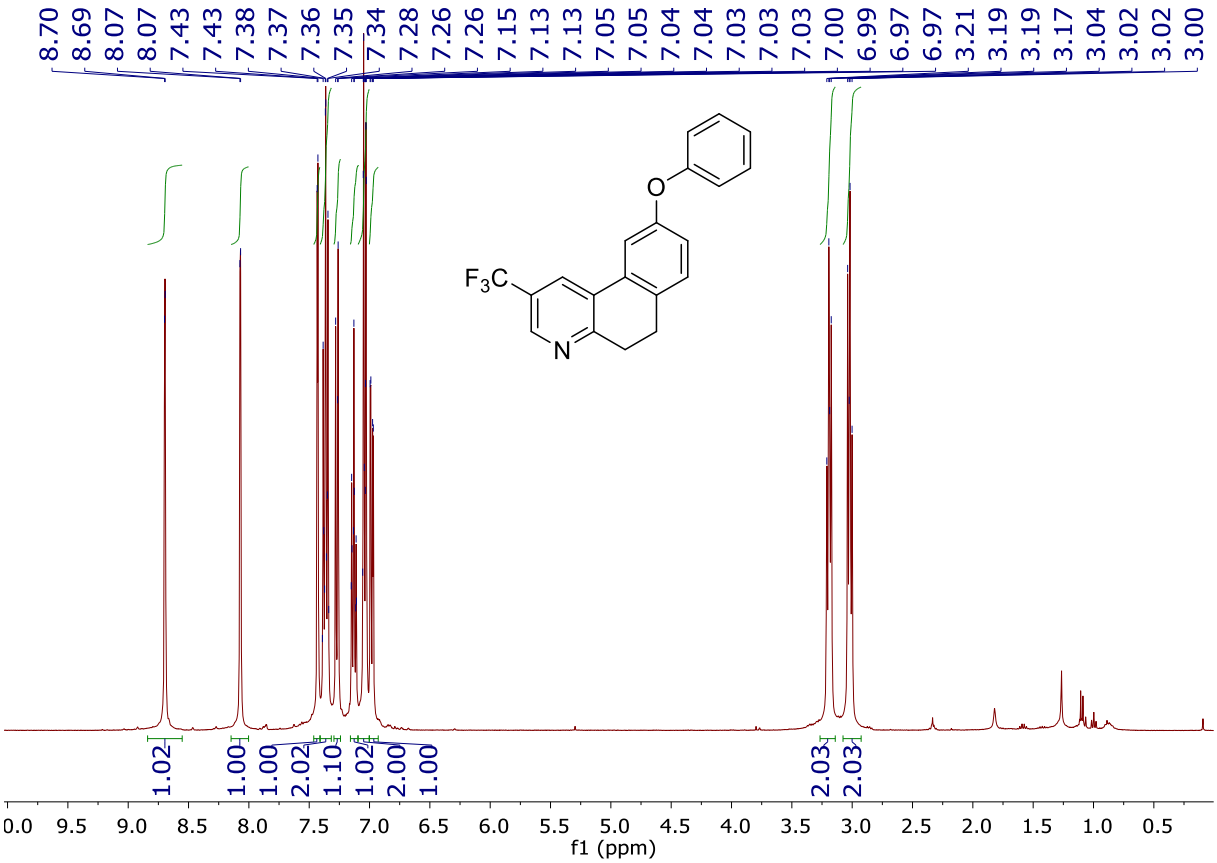

161.33
161.31
146.98
145.30
144.22
144.18
144.14
144.10
130.84
130.80
130.77
130.73
130.58
127.99
127.23
125.73
125.40
125.29
125.08
124.75
122.58
120.78
119.87
114.81
108.72
101.55
32.42
28.04
f1 (ppm)

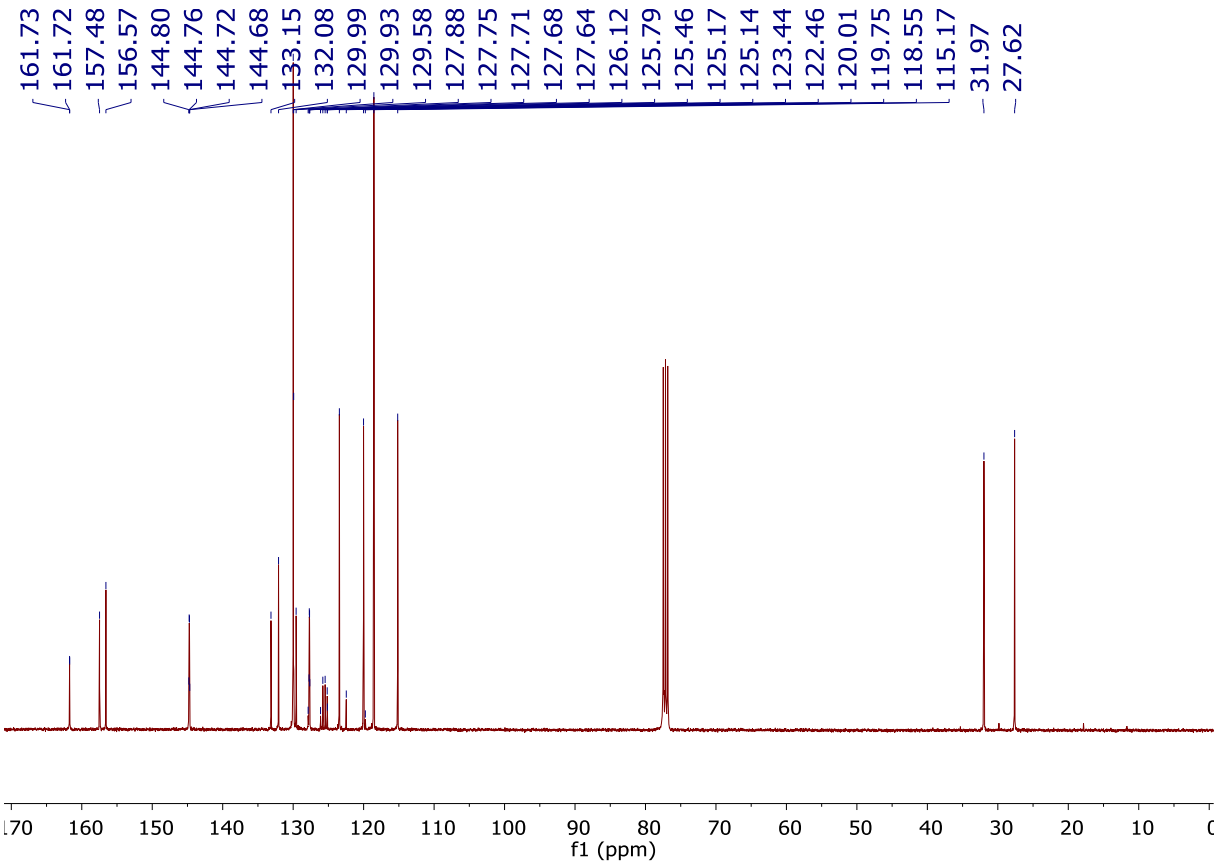

9.11 9.10 9.05 9.04 8.67 8.67 8.66 8.66 8.13 8.13 7.96 7.94 7.81 7.78 7.75 7.75 7.73 7.72 7.63 7.62 7.23 7.17 7.15 7.02 7.02 6.77 3.18 3.15 3.13 3.13 3.11 3.02 2.94 2.93 2.92 2.90
F3C
N
1.2
:
1
1.00 1.00 1.15 1.21 1.02 1.02 1.02 1.02 1.02 1.19 1.20 1.20
6.00 2.42 7.20 2.39
f1 (ppm)

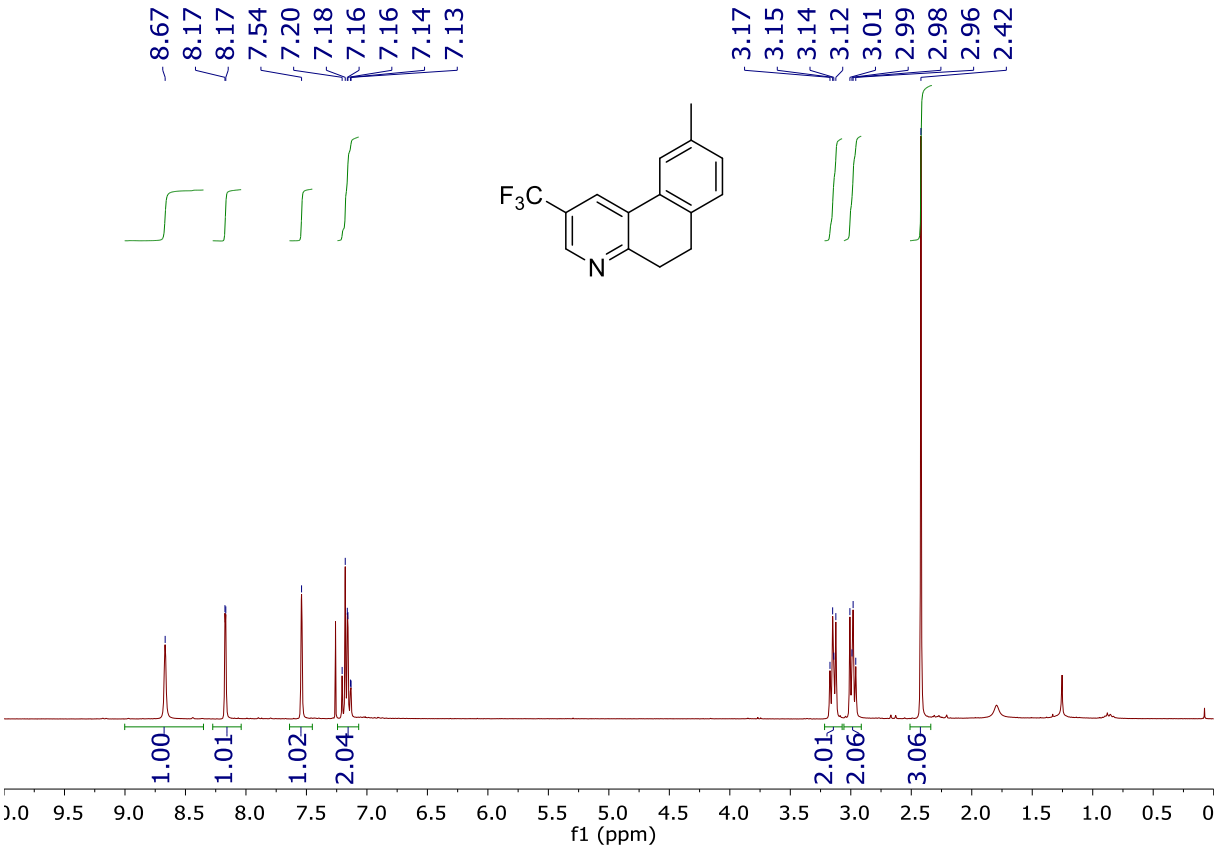

162.30 162.29 150.99 150.98 150.35 150.06 145.38 145.35 144.10 144.05 133.43 131.91 131.09 130.71 129.99 129.22 128.36 128.32 127.28 127.25 127.21 127.18 125.52 125.30 125.20 123.60 123.49 123.02 115.85 114.15 107.93 102.46 41.05 40.78 32.46 27.23
f1 (ppm)

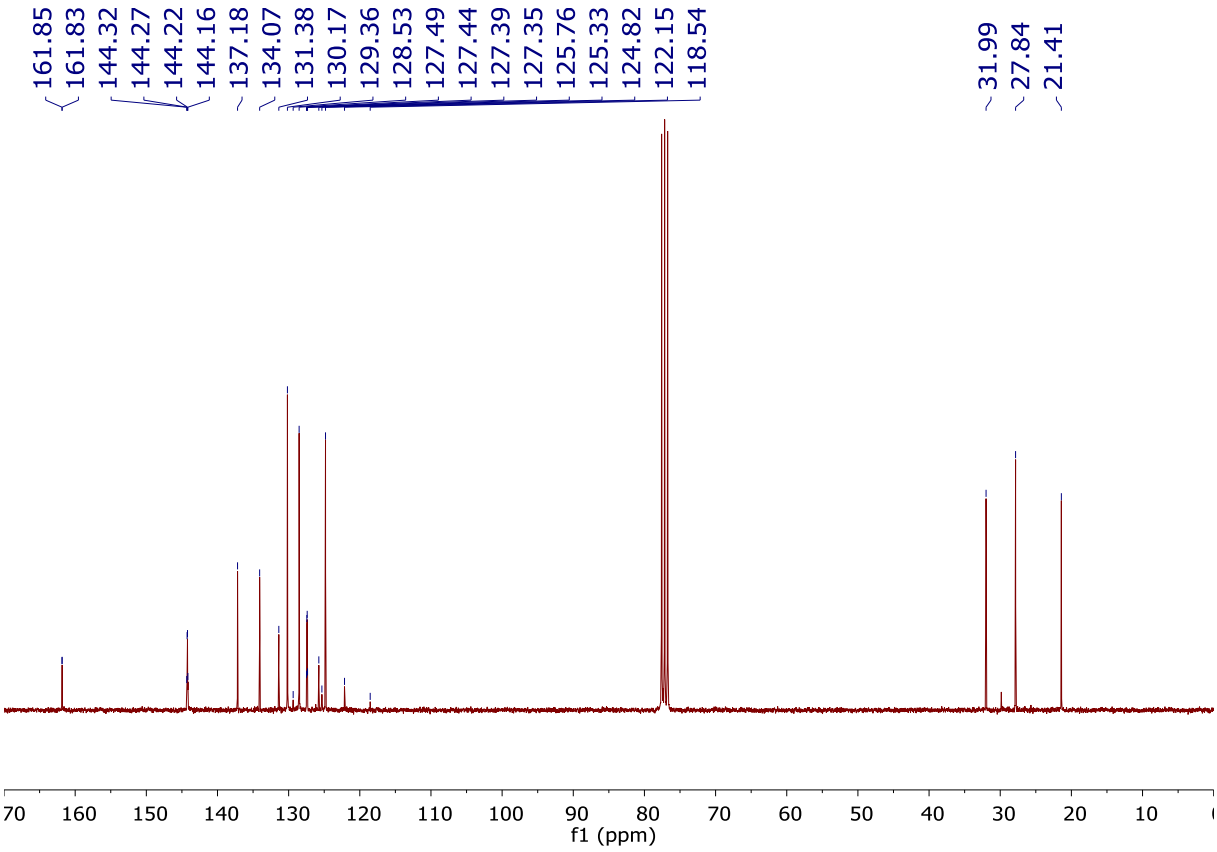

8.68
8.13
7.26
7.24
7.24
7.23
7.21
6.91
6.90
6.89
6.88
3.88
3.17
3.15
3.13
2.98
2.96
2.95
O
F3C
N
1.00
1.03
2.43
1.01
3.03
2.02
2.03
f1 (ppm)

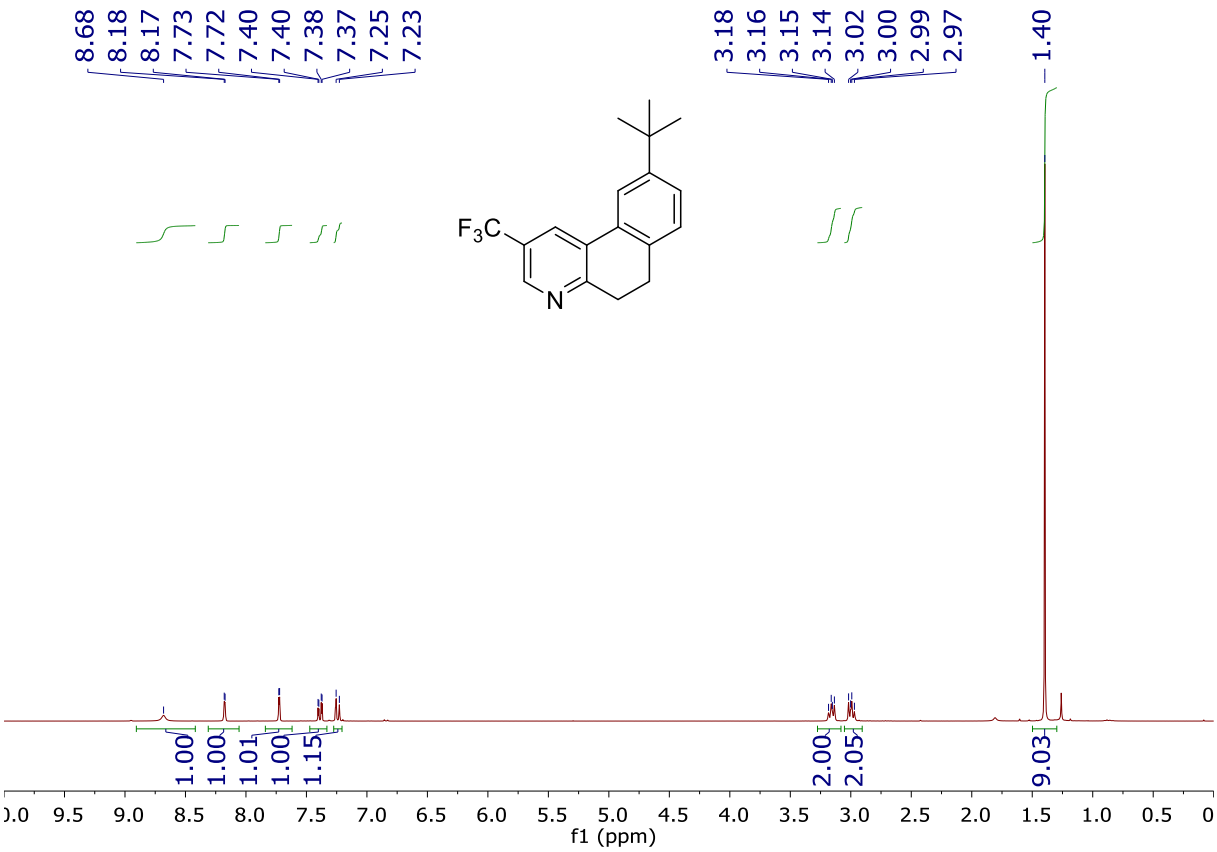

161.96
159.23
144.47
144.44
136.13
132.56
129.60
129.29
127.98
127.61
127.58
127.54
127.51
126.08
125.76
125.42
125.27
125.08
122.56
119.86
114.77
109.87
55.70
32.16
27.41
f1 (ppm)

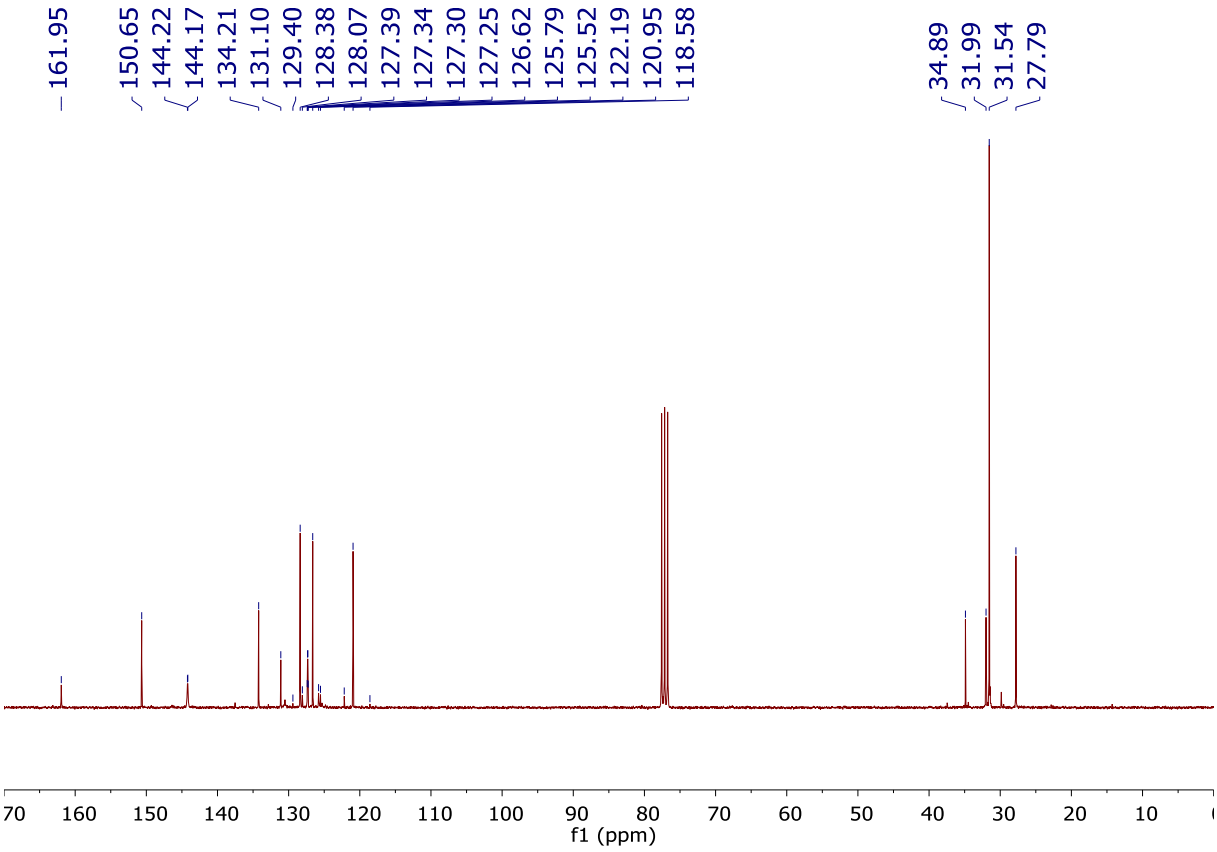

8.70 8.69 8.07 8.07 7.43 7.43 7.38 7.37 7.36 7.35 7.34 7.28 7.26 7.26 7.15 7.13 7.13 7.05 7.05 7.04 7.04 7.03 7.03 7.03 7.00 6.99 6.97 6.97 3.21 3.19 3.19 3.17 3.04 3.02 3.02 3.00
O
F3C
N
1.02 1.00 1.00 2.02 1.10 1.02 2.00 1.00 2.03 2.03
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

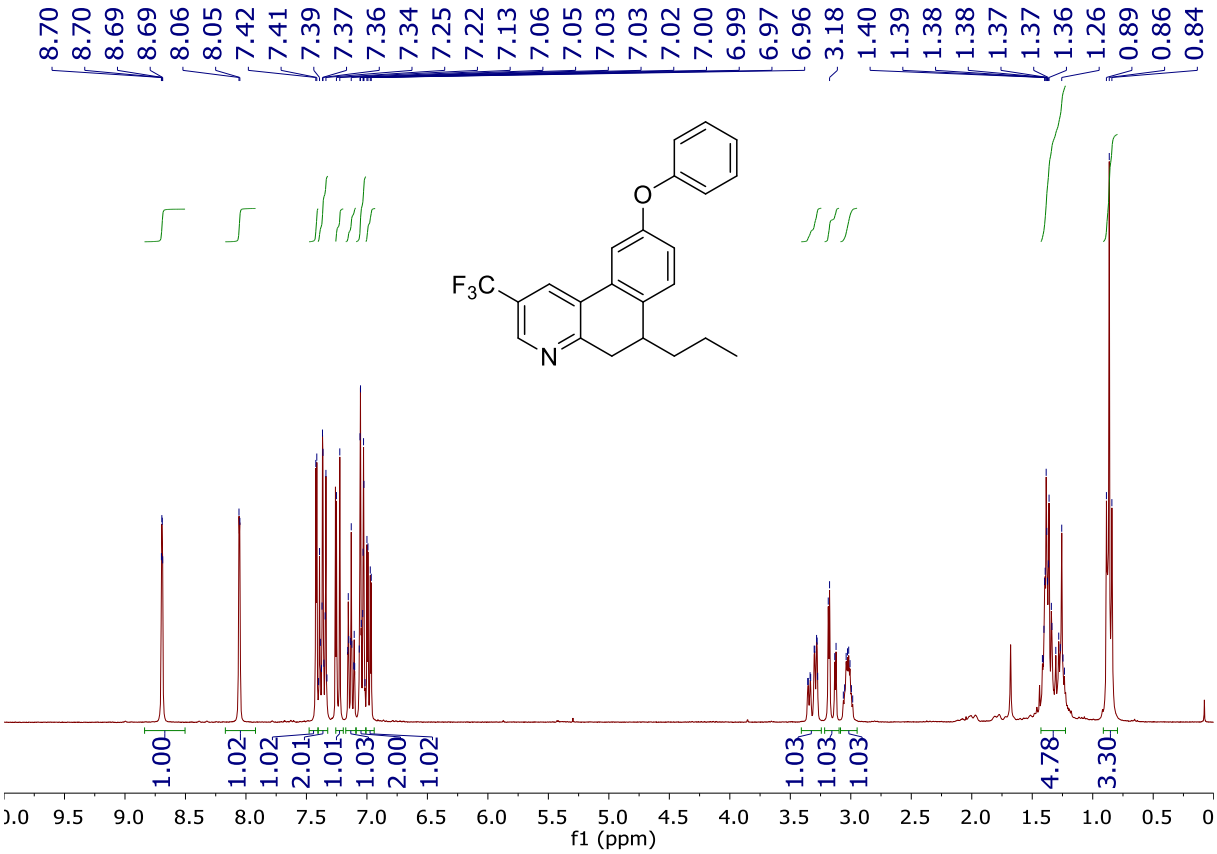

161.73 161.72 157.48 156.57 144.80 144.76 144.72 144.68 133.15 132.08 129.99 129.93 129.58 127.88 127.75 127.71 127.68 127.64 126.12 125.79 125.46 125.17 125.14 123.44 122.46 120.01 119.75 118.55 115.17 31.97 27.62
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

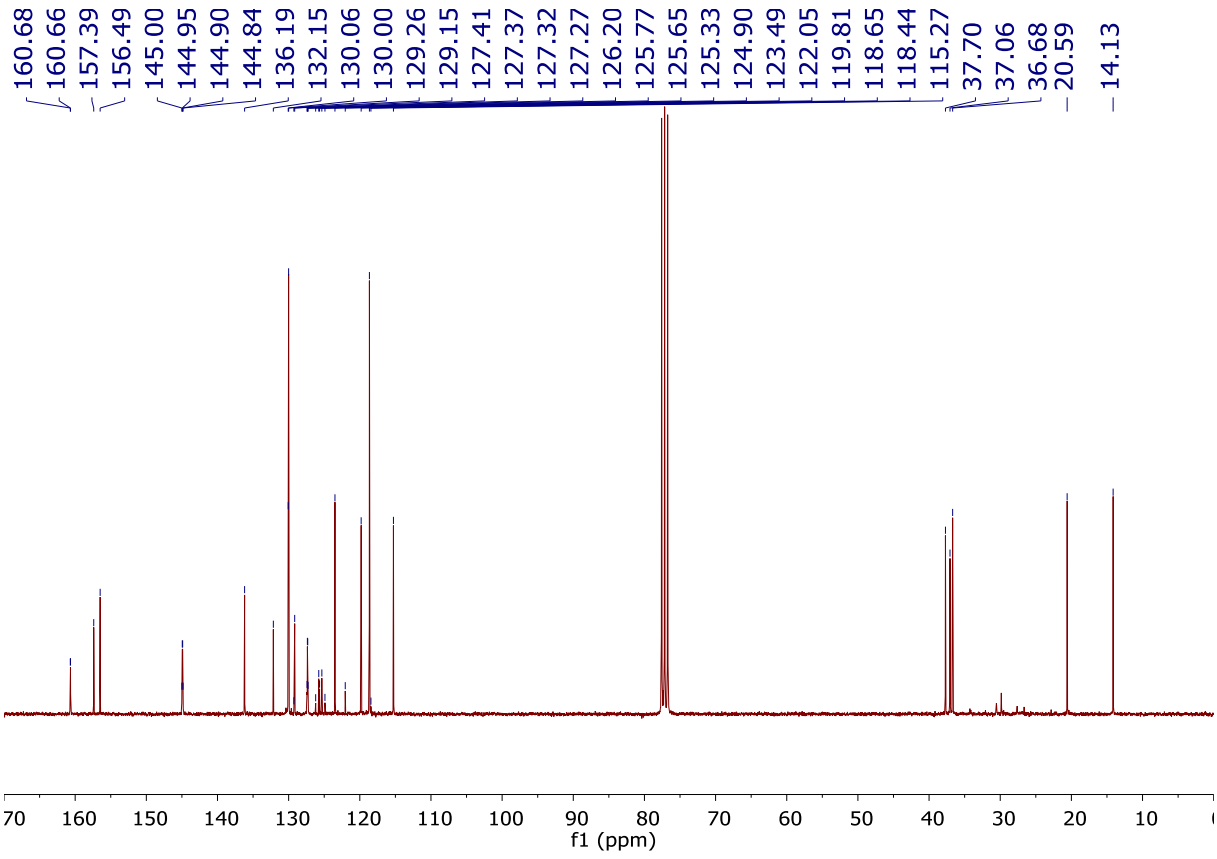

8.67
8.17
8.17
7.54
7.20
7.18
7.16
7.16
7.14
7.13
3.17
3.15
3.14
3.12
3.01
2.99
2.98
2.96
2.42
F3C
N
1.00
1.01
1.02
2.04
2.01
2.06
3.06
f1 (ppm)

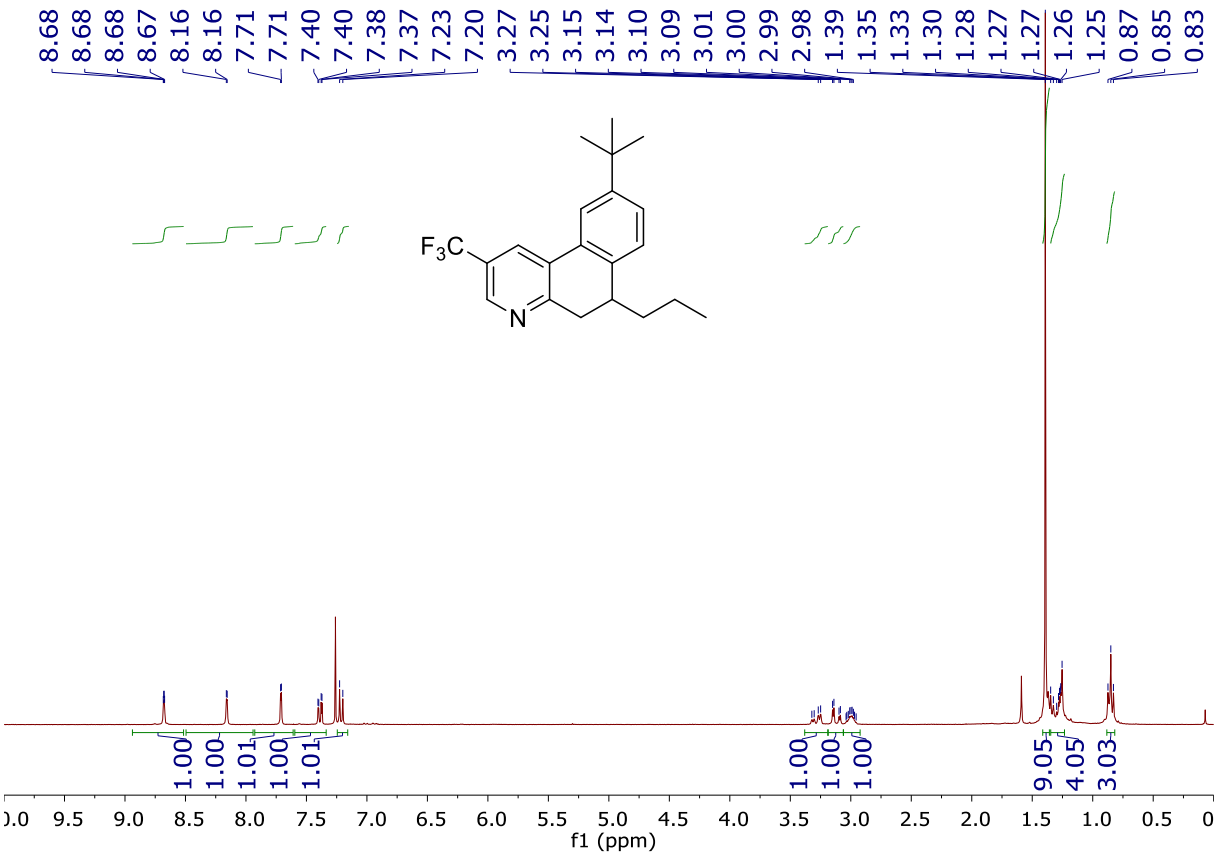

161.85
161.83
144.32
144.27
144.22
144.16
137.18
134.07
131.38
130.17
129.36
128.53
127.49
127.44
127.39
127.35
125.76
125.33
124.82
122.15
118.54
31.99
27.84
21.41
f1 (ppm)

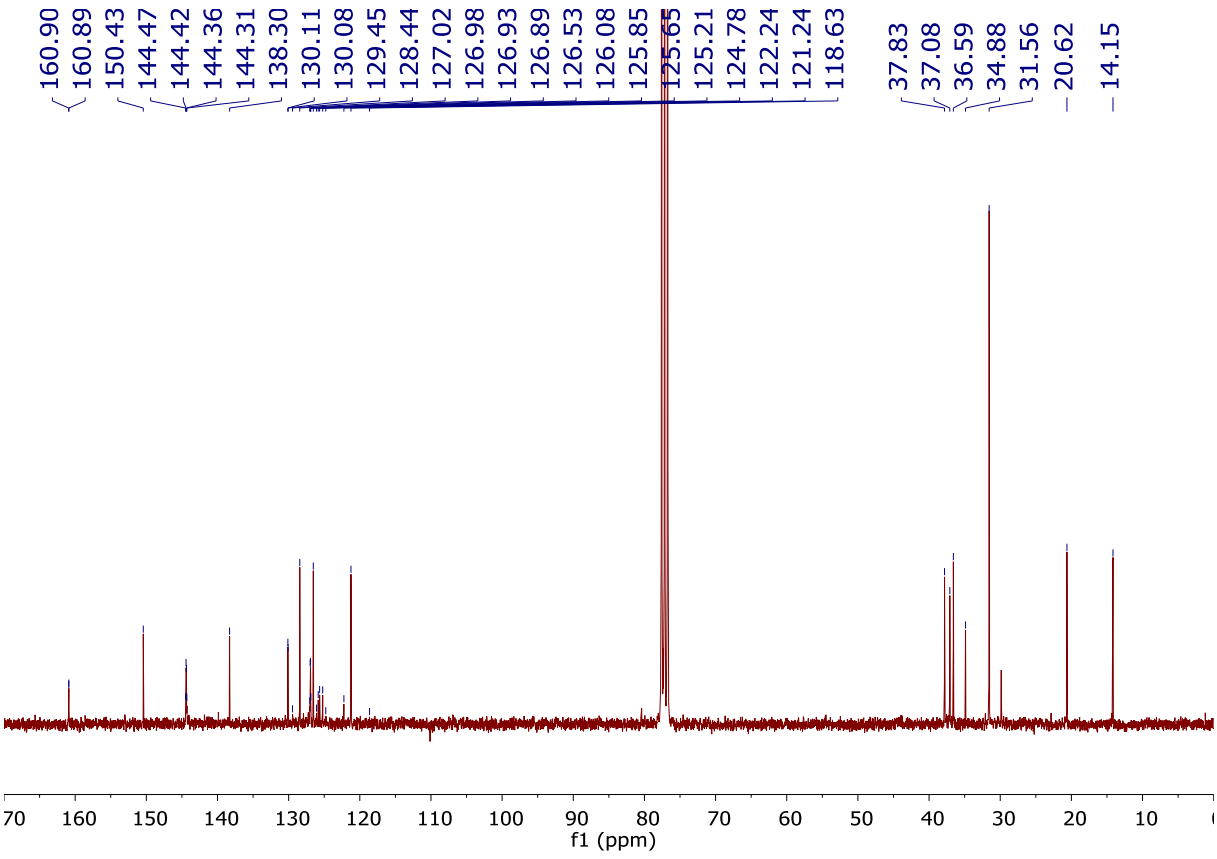

8.68
8.18
8.17
7.73
7.72
7.40
7.40
7.38
7.37
7.25
7.23
3.18
3.16
3.15
3.14
3.02
3.00
2.99
2.97
1.40
F3C
N
1.00
1.00
1.01
1.00
1.15
2.00
2.05
9.03
f1 (ppm)

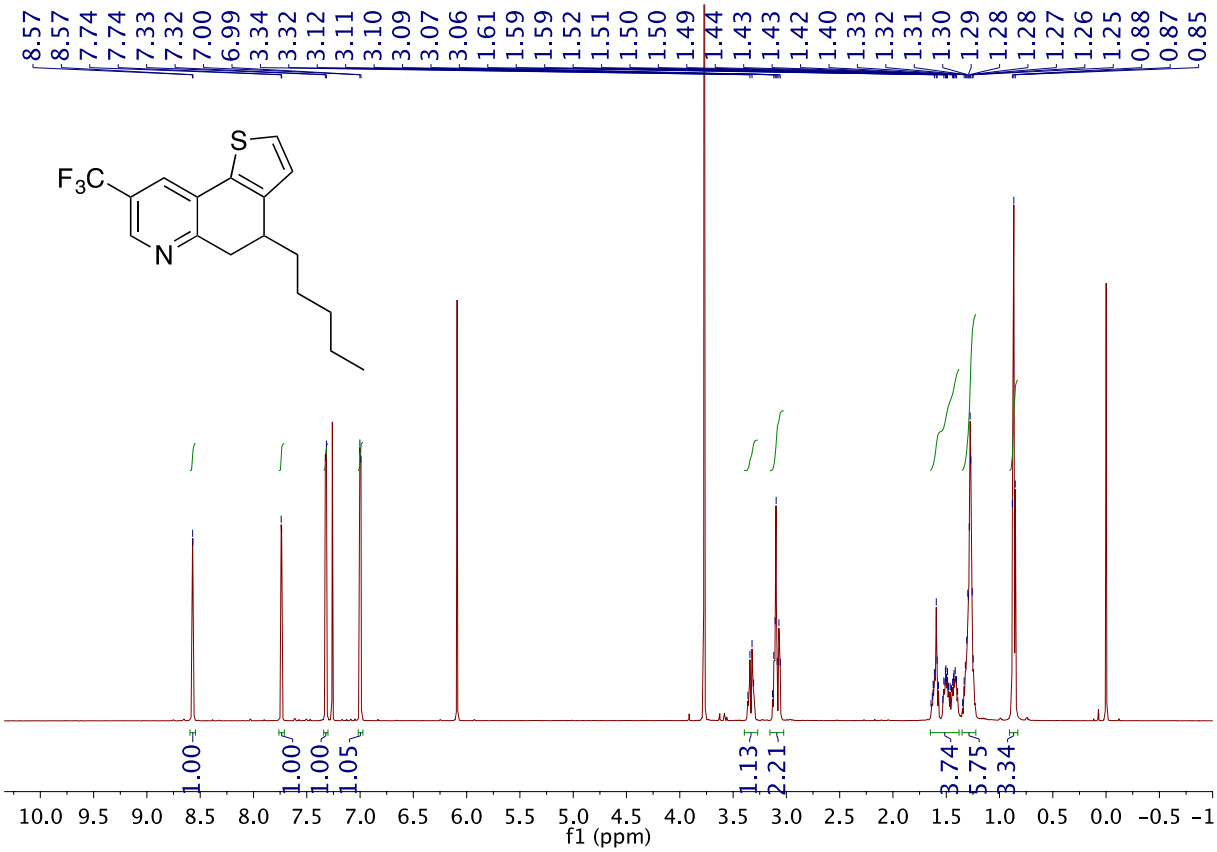

161.95
150.65
144.22
144.17
134.21
131.10
129.40
128.38
128.07
127.39
127.34
127.30
127.25
126.62
125.79
125.52
122.19
120.95
118.58
34.89
31.99
31.54
27.79
f1 (ppm)

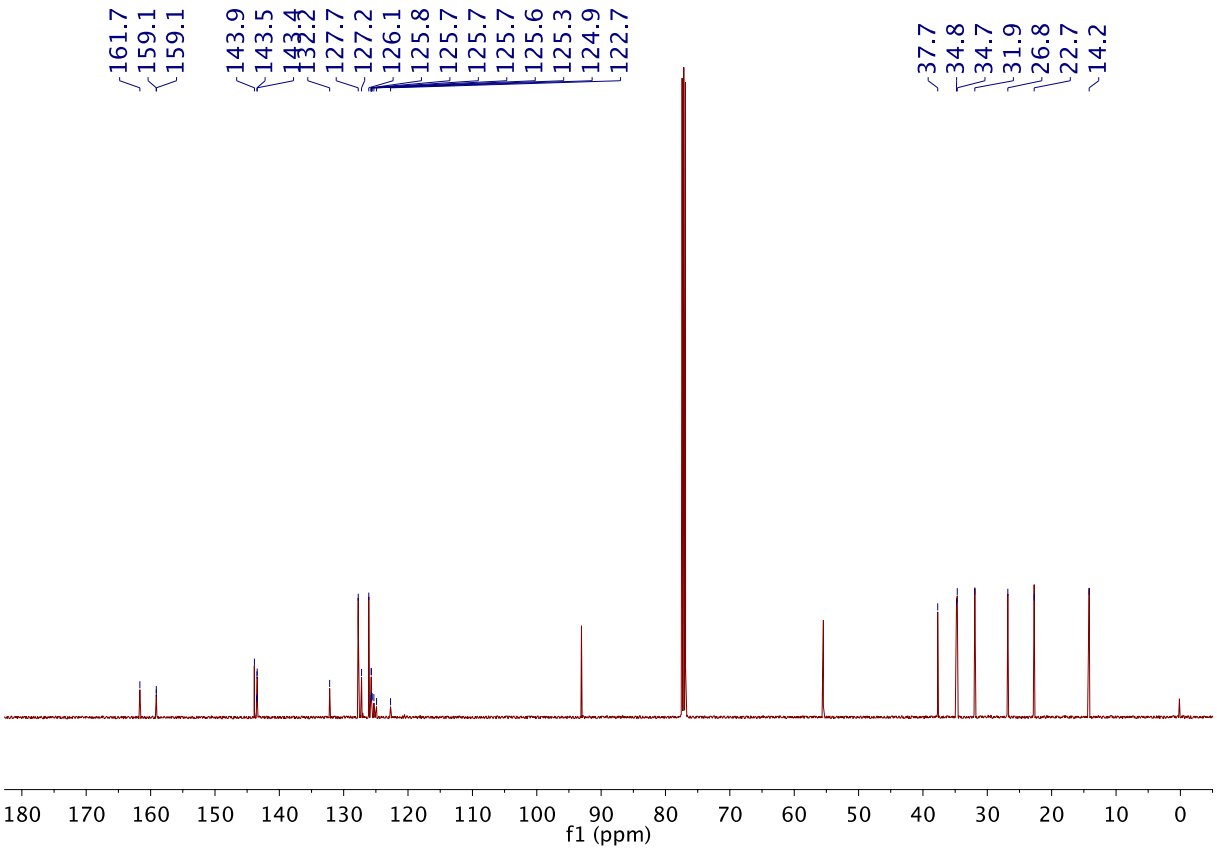

8.70 8.70 8.69 8.69 8.06 8.05 7.42 7.41 7.39 7.37 7.36 7.34 7.25 7.22 7.13 7.06 7.05 7.03 7.03 7.02 7.00 6.99 6.97 6.96 3.18 1.40 1.39 1.38 1.38 1.37 1.37 1.36 1.26 0.89 0.86 0.84
O
F3C
N
1.00 1.02 1.02 2.01 1.01 1.03 2.00 1.02 1.03 1.03 1.03 4.78 3.30
f1 (ppm)

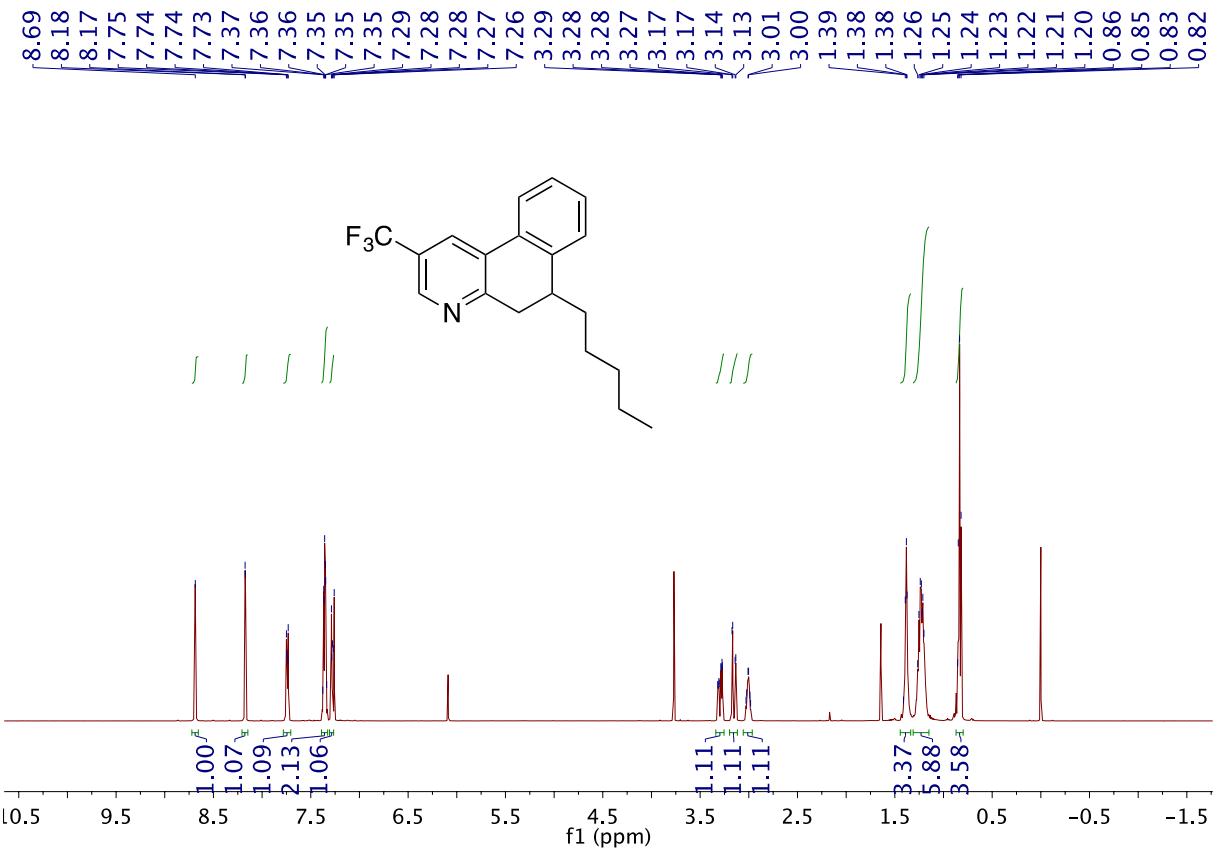

160.68 160.66 157.39 156.49 145.00 144.95 144.90 144.84 136.19 132.15 130.06 130.00 129.26 129.15 127.41 127.37 127.32 127.27 126.20 125.77 125.65 125.33 124.90 123.49 122.05 119.81 118.65 118.44 115.27 37.70 37.06 36.68 20.59 14.13
f1 (ppm)

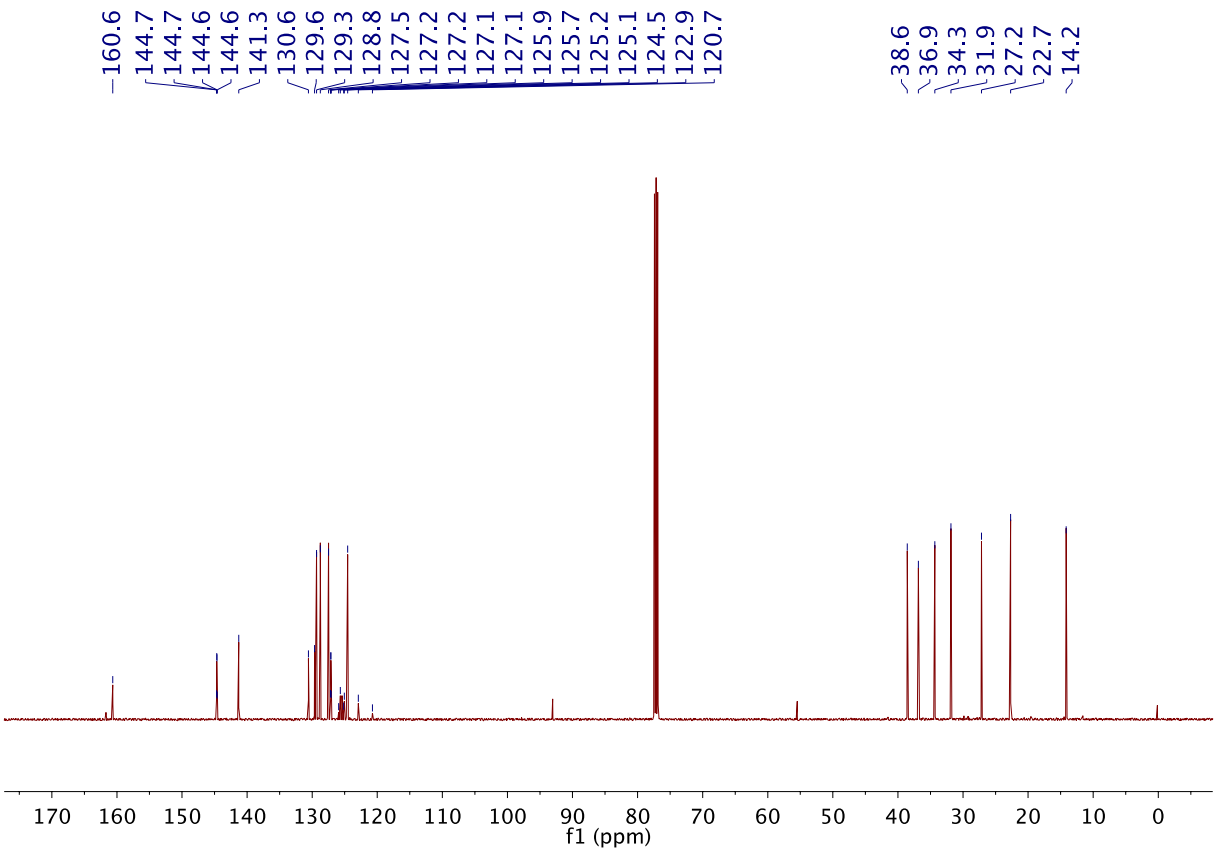

8.68
8.68
8.68
8.67
8.16
8.16
7.71
7.71
7.40
7.40
7.38
7.37
7.23
7.20
3.27
3.25
3.15
3.14
3.10
3.09
3.01
3.00
2.99
2.98
1.39
1.35
1.33
1.30
1.28
1.27
1.27
1.26
1.25
0.87
0.85
0.83
F3C
N
1.00
1.00
1.01
1.00
1.01
1.00
1.00
1.00
9.05
4.05
3.03
f1 (ppm)

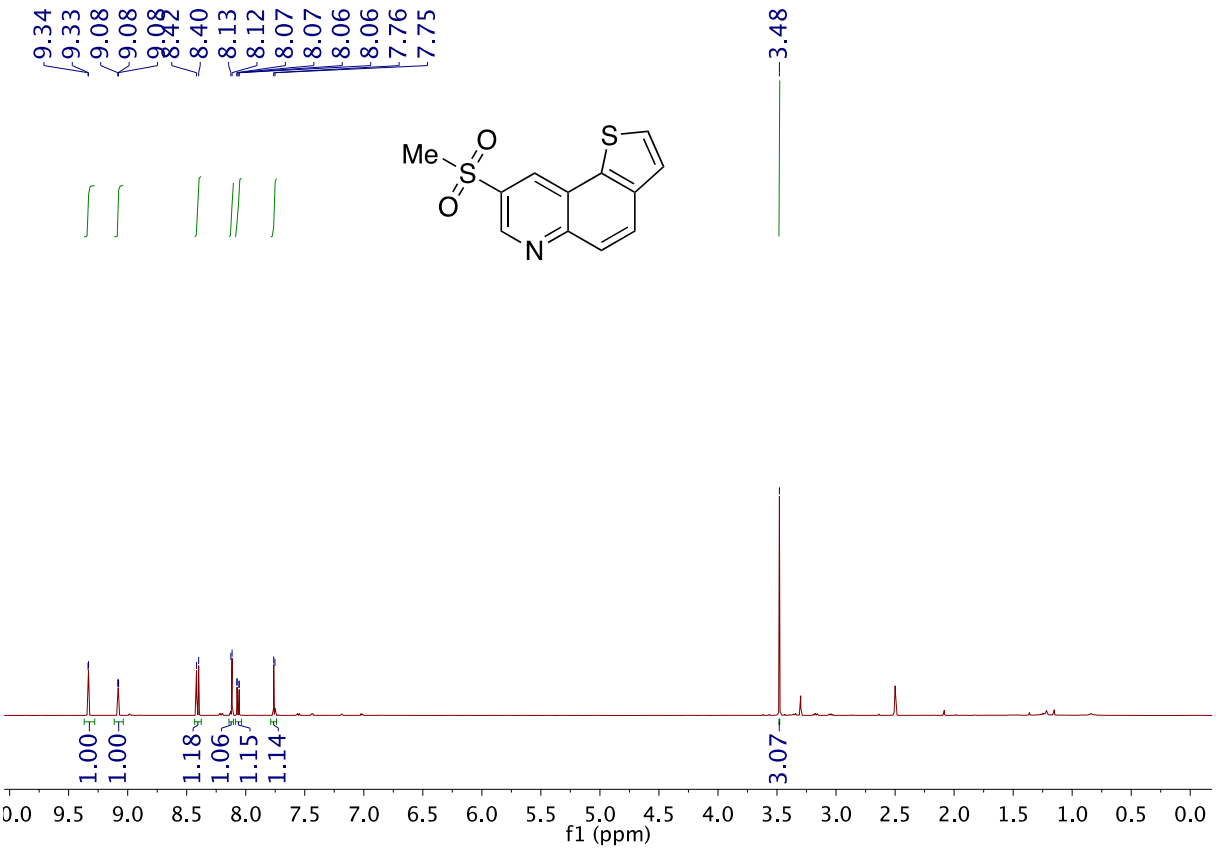

160.90
160.89
150.43
144.47
144.42
144.36
144.31
138.30
130.11
130.08
129.45
128.44
127.02
126.98
126.93
126.89
126.53
126.08
125.85
125.65
125.21
124.78
122.24
121.24
118.63
37.83
37.08
36.59
34.88
31.56
20.62
14.15
f1 (ppm)

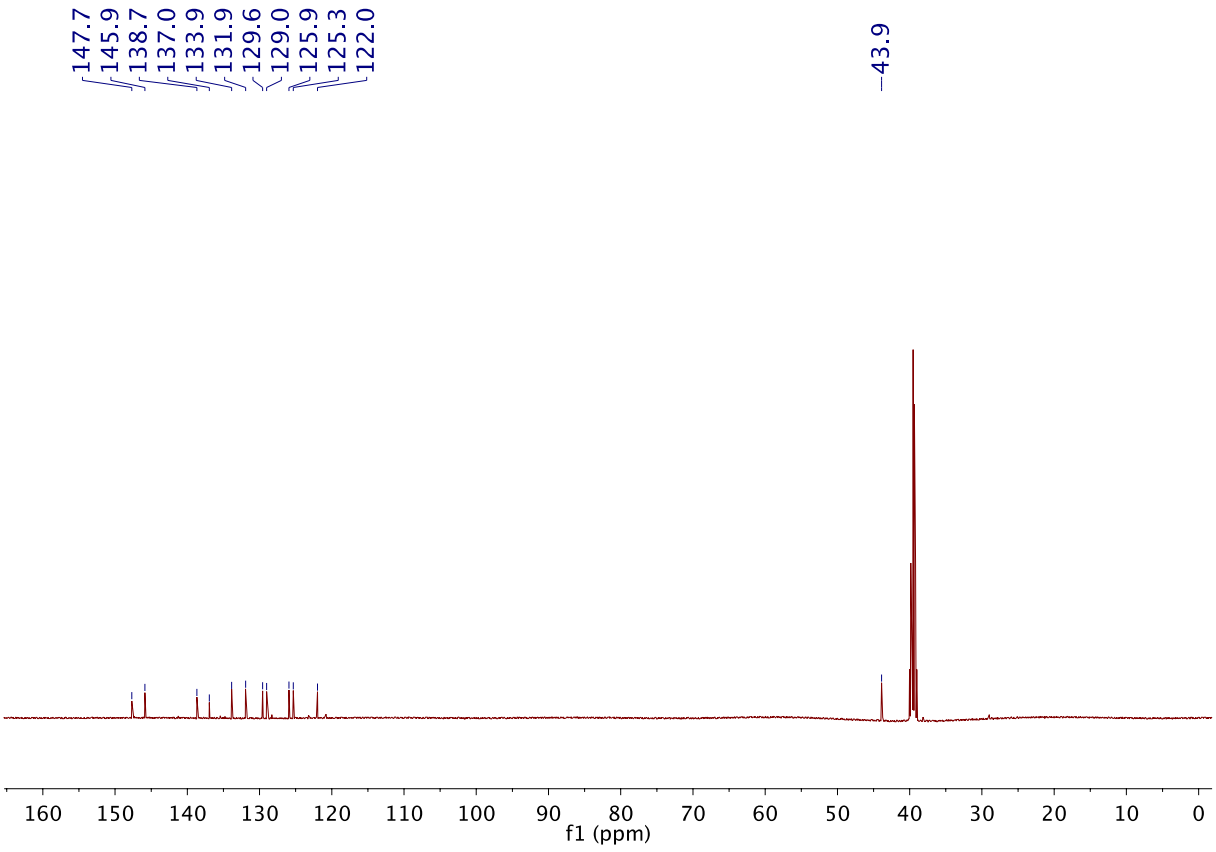

8.57 8.57 7.74 7.74 7.33 7.32 7.00 6.99 3.34 3.32 3.12 3.11 3.10 3.09 3.07 3.06 1.61 1.59 1.59 1.52 1.51 1.50 1.50 1.49 1.44 1.43 1.43 1.42 1.40 1.33 1.32 1.31 1.30 1.29 1.28 1.28 1.27 1.26 1.25 0.88 0.87 0.85
S
F3C
N
1.00 1.00 1.00 1.05 1.13 2.21 3.74 5.75 3.34
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


161.7 159.1 159.1 143.9 143.5 143.4 132.2 127.7 127.2 126.1 125.8 125.7 125.7 125.7 125.6 125.3 124.9 122.7
37.7 34.8 34.7 31.9 26.8 22.7 14.2
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.69 8.18 8.17 7.75 7.74 7.74 7.73 7.37 7.36 7.36 7.35 7.35 7.35 7.29 7.28 7.28 7.27 7.26 3.29 3.28 3.28 3.27 3.17 3.17 3.14 3.13 3.01 3.00 1.39 1.38 1.38 1.26 1.25 1.24 1.23 1.22 1.21 1.20 0.86 0.85 0.83 0.82
F3C
N
1.00 1.07 1.09 2.13 1.06 1.11 1.11 1.11 3.37 5.88 3.58
10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5 -1.5
f1 (ppm)


160.6 144.7 144.7 144.6 144.6 141.3 130.6 129.6 129.3 128.8 127.5 127.2 127.2 127.1 127.1 125.9 125.7 125.2 125.1 124.5 122.9 120.7
38.6 36.9 34.3 31.9 27.2 22.7 14.2
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


9.34
9.33
9.08
9.08
8.42
8.40
8.13
8.12
8.07
8.07
8.06
8.06
7.76
7.75
3.48
Me
O
S
O
S
N
1.00
1.00
1.18
1.06
1.15
1.14
3.07
f1 (ppm)


147.7
145.9
138.7
137.0
133.9
131.9
129.6
129.0
125.9
125.3
122.0
43.9
f1 (ppm)