Supporting Information for

Perfluoroalkylative Pyridylation of Alkenes *via* 4-Cyanopyridine-Boryl Radicals

Jia Cao, Guoqiang Wang, Liuzhou Gao, Hui Chen, Xueting Liu, Xu Cheng, Shuhua Li*

[*] J. Cao, G. Wang, L. Gao, H. Chen, X. Liu, Prof. Dr. X. Cheng. Prof. Dr. S. Li*
Key Laboratory of Mesoscopic Chemistry of Ministry of Education, Institute of Theoretical and Computational Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210093, P. R. China
Prof. Dr. X. Cheng
Institute of Chemistry and Biomedical Sciences, Jiangsu Key Laboratory of Advanced Organic Material, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210093, P. R. China
J. Cao
Shaanxi Key Laboratory of Chemical Reaction Engineering, School of Chemistry and Chemical Engineering, Yan'an University, Yan'an 716000, P. R. China

E-mail: shuhua@nju.edu.cn

1. Computational Investigations

1.1 Computational Details

All calculations were performed with the Gaussian 16 package.[1] A "broken-symmetry" guess was used for calculations on open-shell systems. Geometry structures of all the stationary points were optimized by using the M06-2X[2] method. The LANL2DZ basis set is employed for the iodine atom, and the 6-31G(d,p) basis set is used for all the other atoms. At the same level of theory, vibrational frequencies of all the stationary points were further calculated to check the nature of the minima and the transition states. To confirm that each transition state connects the desired reactants and products along the reaction path, we performed intrinsic reaction coordinate (IRC)[3] calculations at the same level. In order to obtain reliable energies, single point energies (Esol) were computed using M06-2X method with a larger basis set. The cc-PVTZ basis set is used for all the other atoms (the LANL2DZ basis set for the iodine atom). The solvent effect was treated with the polarizable continuum model (PCM) with benzene as the solvent.[4] The 3D structures were generated with CLY view.[5]

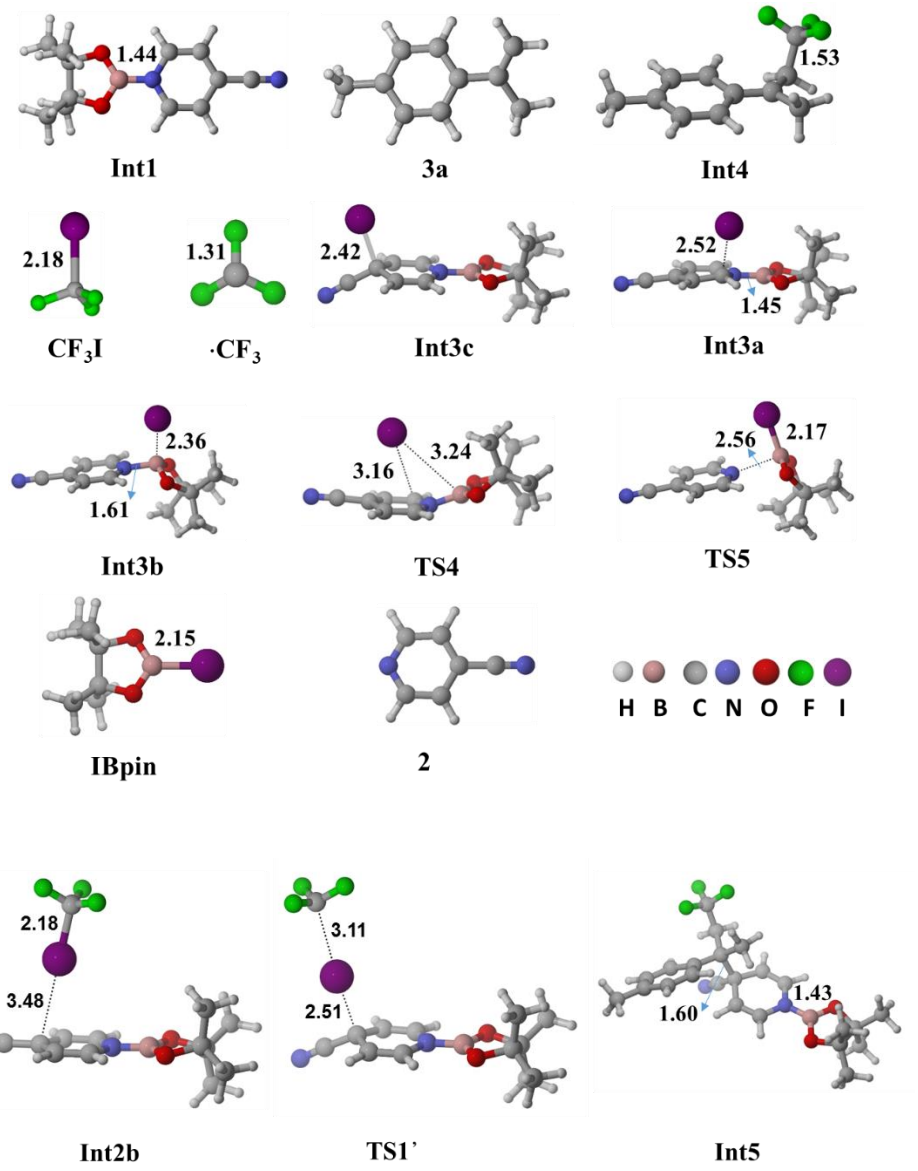


Figure S1. Optimized structures of all minimum species and some transition states in the alkene difunctionalization. Interatomic distances are in Å.

1.2 Theoretical studies on the C-I bond homolysis of CF_3I mediated by 4-cyanopyridine-boryl radical at the C4 position

The C-I bond homolysis by the 4-cyanopyridine-boryl radicals at the C4 position is also investigated (shown in Figure S2). This process is endergonic by 31.0 kcal/mol, with a barrier of 37.7 kcal/mol (relative to **Int1** and **1b**), suggesting that the pathway is less favorable.

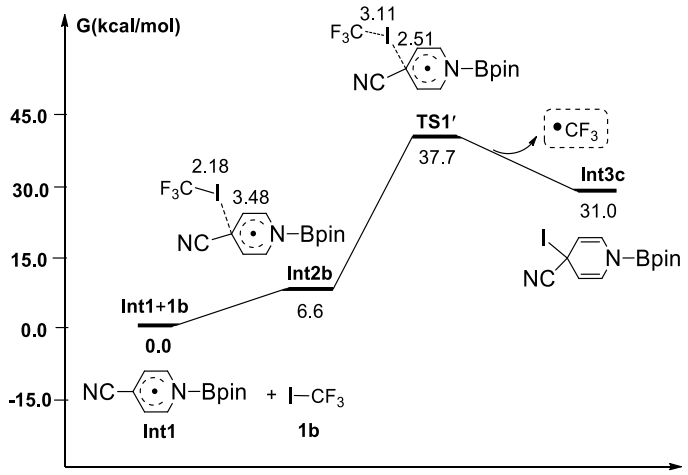


Figure S2. Calculated Gibbs free energy (in kcal/mol) profile for the C-I bond homolysis by the 4-cyanopyridine-boryl radicals at the C4 position. Interatomic distances are in Å.

1.3 Theoretical studies on the isomerization of the intermediate Int3a

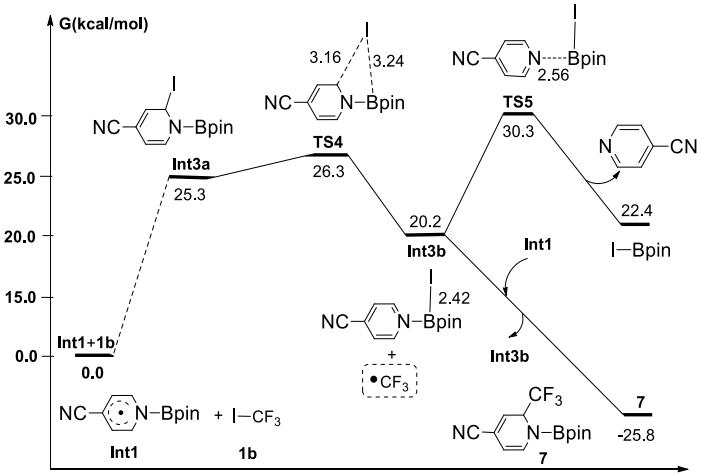
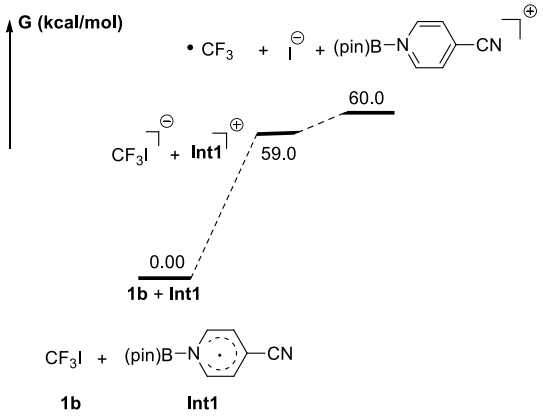


Figure S3. Computed Gibbs free energy (in kcal/mol) profile for the isomerization of **Int3**; Interatomic distances are in Å.

We calculate the isomerization reaction of **Int3a (**see Figure S3). Starting from **Int3a**, the intramolecular migration of the iodine atom from C2 atom to B atom *via* **TS4**, could yield another isomer **Int3b**, which further proceeds through the breaking of the B-N bond (*via* **TS5**) to regenerate 4-cyanopyridine. Overall, the rate-determining barrier height of this process is 10.1 kcal/mol and endergonic by 2.9 kcal/mol (relative to **Int3a**), indicating that the C-I bond homolysis is a catalytic process by 4-

cyanopyridine. In addition, the generated trifluoromethyl radical can react with **Int1** to produce the compound **7**, which is exothermic by 25.8 kcal/mol.

1.4 The calculated results for a single electron transfer (SET) process



	HOMO	LUMO (a.u)
Int1	-0.1877	0.0245
1b	-0.3353	-0.0337

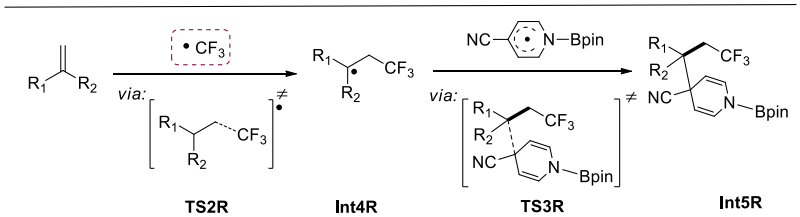
Figure S4. SET process between CF_3I (**1b**) and **Int1**

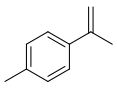
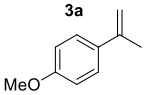
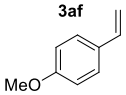
Moreover, our calculations suggest that the direct single electron transfer (SET) process from the 4-cyanopyridine-boryl radical to CF_3I is highly endergonic by 60.0 kcal/mol (see Figure S4). Thus, the SET mechanism is unlikely responsible for the generation of the perfluoroalkyl radicals in the reaction.

1.5 Theoretical Investigations on the reactivity of various alkenes

Our calculations suggest that the barrier heights of the addition of trifluoromethyl radical to internal alkene or terminal monosubstituted styrene is higher than that of terminal disubstituted styrene by 1.1~3.4 kcal/mol (see Table S1). Thus, internal alkenes or terminal monodisubstituted styrenes are not suitable for the present transformation.

Table S1 The calculated activation barrier ($\Delta G^{\neq}$) and reaction energies (ΔG) for the reaction of the trifluoromethyl radical with various alkenes



Alkenes	CF_3 radical addition		cross-coupling	
	$\Delta G^{\neq}$	ΔG	$\Delta G^{\neq}$	ΔG
 **3a**	9.0	-31.2	-24.7	-50.3
 **3af**	9.3	-32.7	-24.8	-50.5
 **3m**	10.4	-31.9	-23.4	-55.3
 **3r**	10.2	-29.6	-20.0	-48.2
3s	12.4	-22.5	-10.1	-46.6

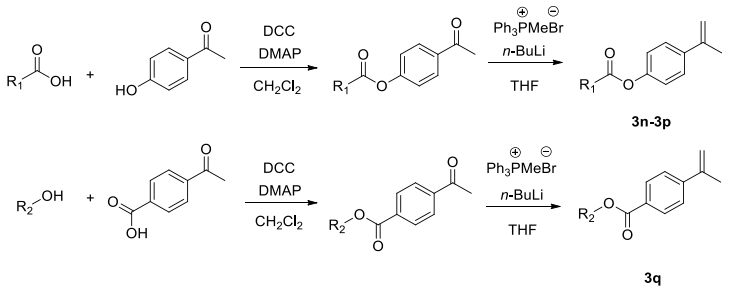
2. Experiment studies on the Substrate Scope

2.1 General information

All reactions were carried out under argon atmosphere. All commercially available reagents were used without further purification. Dry CH_3CN, CH_2Cl_2, methyl tert-butyl ether (MTBE) and THF were purchased from Acros and used as received. All NMR spectra were recorded on a Bruker AVANCE Ⅲ–400 spectrometer at room temperature with $CDCl_3$ as the solvent and TMS as the internal standard. Chemical shifts (δ) were reported in ppm with respect to the residue solvent peak. Coupling constant (*J*) were reported in Hert (Hz), abbreviations for signal couplings are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad. Infrared spectra were recorded on a ThermoFisher Nicolet iS5 FTIR using neat thin film technique. The electron paramagnetic resonance (EPR) spectra were obtained using a Bruker EMX-10/2 EPR spectrometer at 298.15 K. High-resolution mass spectra (HRMS) were recorded on

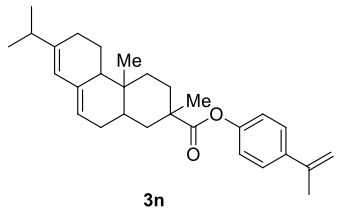
Thermo Quest Finnigan LCQDECA system equipped with electrospray ionization (ESI).

2.2 Synthesis of alkenes



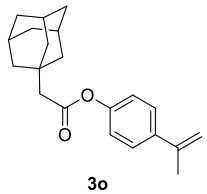
Scheme S1 Synthesis of substrates (**3n-3q)**

Alkenes **3n-3q** were synthesized according to the reported procedure (see Scheme S1).[6-8] At first, a sealed reaction bottle charged with a magnetic stir bar, carboxylic acid (10.0 mmol, 1.0 equiv), DCC (dicyclohexylcarbodiimide) (12.0 mmol, 1.2 equiv), DMAP (4-dimethylaminepyridine) (1.5 mmol, 0.15 equiv) and 4-hydroxyacetophenone (12.0 mmol, 1.2 equiv) in CH_2Cl_2 (20 mL). The reaction mixtures were stirred at room temperature for 24 h. Then it was filtered through a plug of silica gel (washed with EA, ethyl acetate). The filtrate was concentrated in *vacuo* and the residue was purified by chromatography on silica gel, eluting with PE/EA=10: 1 (v/v) to afford the corresponding product.[6-7] Second, under argon atmosphere, a stirred solution of methyltriphenylphosphonium bromide (5 mmol, 1.8 g) in THF (10 mmol), *n*-butyl lithium (5.0 mmol) in hexane was added dropwise at 0 ◦C for 30 min. After the addition, the reaction mixture was further stirred 30 min. Subsequently, a THF solution of ketone was added dropwise for 30 min. The reaction mixture was stirred for 12 h at room temperature. Then reaction mixture was quenched with saturated ammonium chloride solution and was extracted with EtOAc. The combined organic layer was dried over Na_2SO_4 and then concentrated in vacuo. The crude reaction mixture was purified by flash column chromatography on silica gel to give the corresponding product.[8]



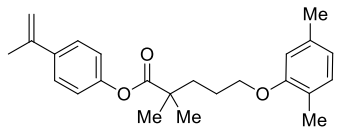
3n

3n, Colorless oil, 40% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.7 Hz, 2H), 6.99 (d, *J* = 8.7 Hz, 2H), 5.83 (s, 1H), 5.44 (s, 1H), 5.35 (s, 1H), 5.09 (t, *J* = 1.6 Hz, 1H), 2.30 – 2.24 (m, 2H), 2.15 (d, *J* = 1.3 Hz, 3H), 2.13 – 2.10 (m, 2H), 2.06 – 1.94 (m, 4H), 1.88 – 1.80 (m, 2H), 1.60 (s, 3H), 1.41 (s, 3H), 1.29 – 1.24 (m, 2H), 1.07 – 1.03 (m, 6H), 0.91 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 177.0, 150.5, 145.3, 142.4, 138.6, 135.6, 126.4, 122.4, 121.2, 120.4, 112.5, 46.9, 45.1, 38.3, 37.1, 34.9, 34.6, 27.5, 25.8, 22.5, 21.9, 21.4, 20.9, 18.2, 17.1, 14.1. IR (film): 2924, 2870, 1750, 1728, 1584, 1508, 1472, 1264, 1205, 1123, 1047, 803. HRMS (ESI-TOF) exact mass calculated for $C_{27}H_{39}O_2$ $[M+H]^+$ 419.2945, found 419.2943.



3o

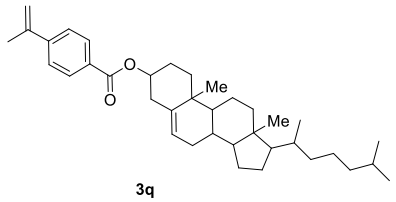
3o, Colorless oil, 30% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.44 (m, 2H), 7.07 – 7.01 (m, 2H), 5.33 – 5.32 (m, 1H), 5.07 – 5.05 (m, 1H), 2.30 (s, 2H), 2.13 (s, 3H), 2.04 – 1.99 (m, 2H), 1.77 – 1.70 (m, 13H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 150.0, 142.4, 138.8, 126.5, 121.3, 112.5, 63.8, 48.7, 42.4, 36.7, 28.6, 21.9; IR (film): 2902, 2848, 1755, 1629, 1601, 1507, 1452, 1372, 1329, 1008, 1123, 1097, 812. HRMS (ESI-TOF) exact mass calculated for $C_{21}H_{26}O_2Na$ $[M+Na]^+$ 333.1825, found 333.1820.



3p

3p, Colorless oil, 50% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.47 (m, 2H), 7.07 – 7.02 (m, 3H), 6.72 – 6.66 (m, 2H), 5.40 – 5.37 (m, 1H), 5.13 – 5.10 (m, 1H), 4.06 – 4.00 (m, 2H), 2.35 (s, 3H), 2.23 (s, 3H), 2.19 (s, 3H), 1.95 – 1.91 (m, 4H), 1.42 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.2, 155.9, 149.3, 141.4, 137.7, 135.4, 129.3, 125.4, 122.6, 120.1, 119.6, 111.1, 110.8, 66.7, 41.3, 36.1, 28.6, 24.2, 24.1, 20.8, 20.3,

14.7; IR (film): 2930, 2872, 1747, 1722, 1601, 1507, 1457, 1385, 1307, 1206, 1168, 1129, 1099, 888, 734. HRMS (ESI-TOF) exact mass calculated for $C_{24}H_{31}O_3Na$ $[M+Na]^+$ 367.2273, found 367.2268.



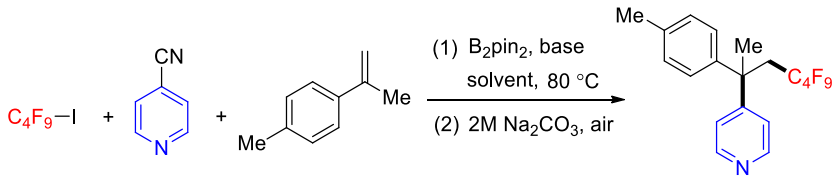
3q

3q, White solid, mp 162-163, 50% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.97 (m, 2H), 7.52 – 7.49 (m, 2H), 5.46 (s, 1H), 5.44 – 5.40 (m, 1H), 5.20 – 5.17 (m, 1H), 4.91 – 4.81 (m, 1H), 2.49 – 2.44 (m, 2H), 2.17 – 2.16 (m, 3H), 2.07 – 1.89 (m, 4H), 1.87 – 1.70 (m, 2H), 1.63 – 1.46 (m, 6H), 1.41 – 1.27 (m, 4H), 1.20 – 0.96 (m, 13H), 0.93 (d, *J* = 6.5 Hz, 3H), 0.87 (dd, *J* = 6.6, 1.8 Hz, 6H), 0.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 145.6, 142.6, 139.8, 129.7, 129.6, 125.4, 122.8, 114.5, 74.6, 56.8, 56.2, 50.1, 42.4, 29.8, 29.6, 28.3, 37.1, 36.7, 36.3, 35.9, 32.1, 32.0, 28.3, 28.1, 28.0, 24.4, 23.9, 22.9, 22.7, 21.8, 21.2, 19.5, 18.8, 12.0. IR (film): 2939, 2853, 1712, 1602, 1457, 1269, 1124, 1104, 1006, 851. HRMS (ESI-TOF) exact mass calculated for $C_{37}H_{54}O_2Na$ $[M+Na]^+$ 553.4018, found 553.4016.

2.3 Optimization studies of the reaction conditions

We optimized the reaction conditions using perfluorobutyl iodide **1a** and 4-methylisopropenylbenzene **3a** as model substrates. As shown in Table S2, a mixture of perfluorobutyl iodide, 4-methylisopropenylbenzene, 4-canopyridine, and B_2pin_2 in ethyl acetate (EA) was stirred at 80 ◦C, forming the desired product **4a** in 39% yield (entry 1). Notably, the addition of organic base, such as DABCO, NMM, DMEDA, and DIPEA, increased the yield (entry 2-5, 47%~70%). Decreasing the amount of base led to a lower yield (entry 6). When the reaction performed at 60◦ C, the yield of **4a** was decreased (entry 7). Solvent screening found that tert-butyl methyl ether (MTBE) and trifluoromethyl benzene ($PhCF_3$) were also suitable for the present reaction in good yield (entry 8-9). When the reaction occurred under irradiation with 10 W blue LED for 24 h, the corresponding product **4a** was obtained in only about 40% yield (entry 13-14).

Table S2. Optimization of the reaction conditions.[a]



1a **2** **3a** **4a**

Entry	solvent	base	yield[b]
1	EA	--	39%
2	EA	DABCO	47%
3	EA	NMM	56%
4	EA	DMEDA	68%
5	EA	DIPEA	70%
6	EA	DIPEA	38%[c]
7	EA	DIPEA	39%[d]
8	EA	DIPEA	68%[e]
9	$PhCF_3$	DIPEA	72%
10	**MTBE**	**DIPEA**	**74%**
11	CH_3CN	DIPEA	53%
13	EA	DIPEA	41%[f]
14	EA	--	43%[f]

[a] Reaction conditions: **1** (0.2 mmol), B_2pin_2 (0.3 mmol), 4-cyanopyridine (0.3 mmol), 4-methylisopropenylbenzene (0.4 mmol), solvent (1.0 mL), base (0.2 mmol), 80 °C. [b] Isolated yield. [c] with 0.3 equiv. of DIPEA. [d] at 60 °C. [e] with 2.0 equiv. of DIPEA. [f] 24 h irradiated by 10 W blue LED at room temperature. MTBE = tert-butyl methyl ether; EA = ethyl acetate; THF = Tetrahydrofuran; DMEDA = N,N,N',N'-Tetraethylethylenediamine; NMM = 4-Methylmorpholine; DIPEA = Ethyldiisopropylamine; DABCO = 1,4-Diaza[2.2.2]bicyclooctane.

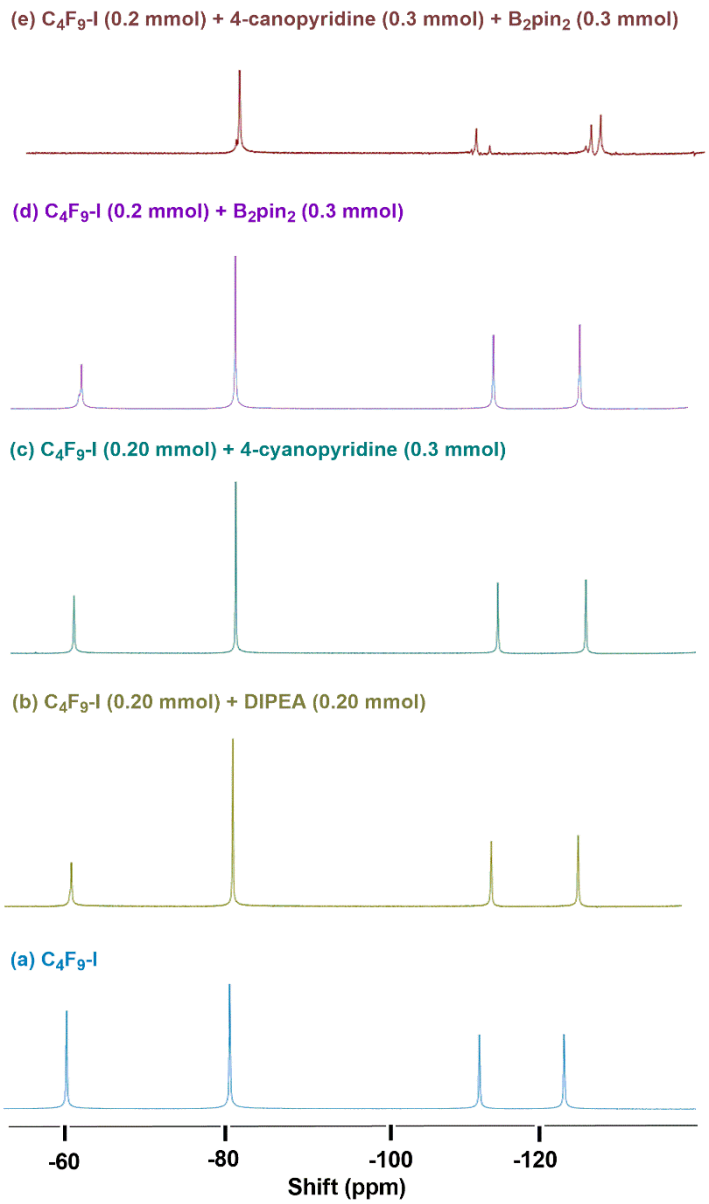
2.4 General procedure for the difunctionalization of alkenes

Under argon atmosphere, a sealed reaction tube was charged with a magnetic stir bar, perfluoroalkyl iodides or bromides (0.2 mmol), 4-cyanopyridine (0.3 mmol, 1.5 equiv), B_2pin_2 (0.3 mmol, 1.5 equiv), alkene (4 mmol, 2.0 equiv). N, N-diisopropylethylamine (DIPEA, 0.4 mmol, 0.2 equiv) and MTBE (1 mL). The reaction mixture was stirred at 80 °C. After 24 h, the reaction mixture was cooled and quenched with 2 M Na_2CO_3 aqueous solution (3 mL). Then, the reaction tube was stirred under air for another 15 minutes. The reaction mixture was extracted with EtOAc (3×10 mL).

The combined organic layer was dried over Na_2SO_4 and then concentrated in vacuo to afford the crude product. This crude material was purified by preparative TLC on silca gel to afford the desired product.

3. Experiment studies on the Reaction mechanism

3.1 ^{19}F NMR spectra analysis



As shown above, samples with varied combination of reagents was measured with ^{19}F NMR technique. The ^{19}F NMR chemical shift at ~60 ppm did not show any significantly changes for the mixture of C_4F_9I and B_2pin_2 or DIPEA (see Figure S5a-

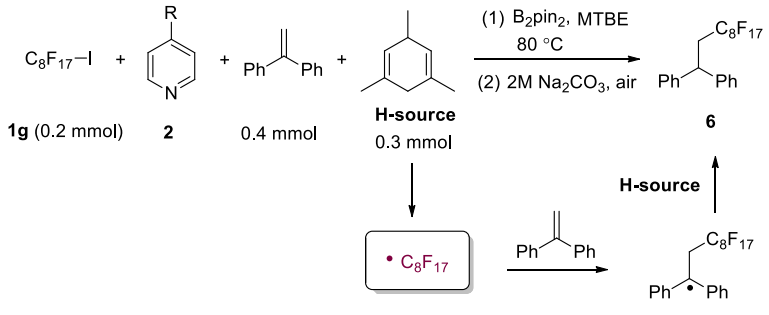
S5e), whereas it disapeared in a 1:1.5:1.5 mixtures of C_4F_9I, B_2pin_2 and 4-cyanopyridine, suggesting that the cleavage of C-I bond is induced by 4-cyanopyridine-boryl radicals (see Figure S5d).

Experimental procedure: according to the general procedure for the difunctionalization of alkenes. A sealed reaction tube charged with a magnetic stir bar, the corresponding components in each reaction mixture using MTBE as solvent were placed in a heated oil bath at 80 °C. After 24 hours, the reaction tube was cooled to the room temperature, and then subjected to the ^{19}F NMR analysis.

3.2 Trapping the perfluoroalkyl radical by 1.1-diphenylethylene

The involvement of the perfluoroalkyl radical was further confirmed by radical trapping experiment with 1,1-diphenylethylene (shown in Table S2). When 1,1-diphenylethylene and hydrogen source (1,3,5-trimethyl-1,4-cyclohexadiene) was added in the reaction mixture of $C_8F_{17}I$, B_2pin_2, 4-cyanopyridine (20%), C_8F_{17} radical reacted with 1,1-diphenylethylene, the product **6** could be obtained in 50 yield. This result indicates the 4-cyanopyridine-boryl radical could activate the $C_8F_{17}I$ to form the C_8F_{17} radical, then which could be trapped by 1,1-diphenylethylene.

Table S2. Radical trapping experiment.

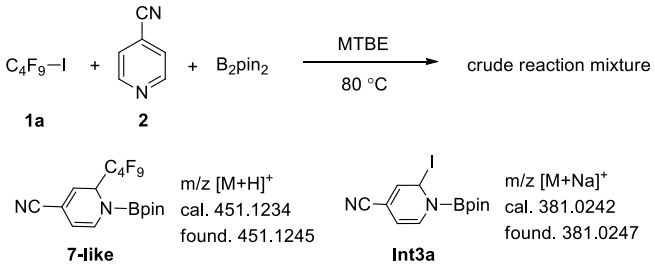


amount of 4-canopyridine	6, isolated yield
0.3 mmol (1.5 equiv.)	63%
0.04 mmol (20%)	50%

Experimental procedure: A sealed reaction tube charged with a magnetic stir bar, **1g** (0.20 mmol), B_2pin_2 (0.30 mmol, 1.5 equiv), 4-cyanopyridine, 1,3,5-trimethyl-1,4-cyclohexadiene (0.3 mmol, 1.5 equiv), MTBE (1 mL), 1,1-diphenylethylene (0.4 mmol,

2.0 equiv) were placed in a heated oil bath (80 °C). After 24 hours, the reaction was cooled and quenched with 2M Na_2CO_3 aqueous solution (3 mL). The reaction mixture was stirred under air for another 15 minutes. The reaction mixture was extracted with EtOAc (3×10 mL). The combined organic layer was dried over Na_2SO_4 and then concentrated in vacuo to afford the crude product. This crude material was purified by preparative TLC on silca gel (PE/EA=20:1) to afford the product **6**.

3.3 Trapping the intermediates by HRMS



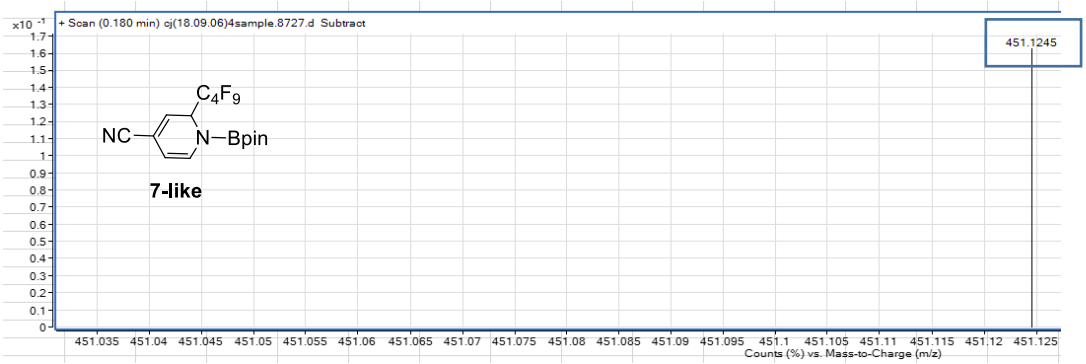


Figure S5

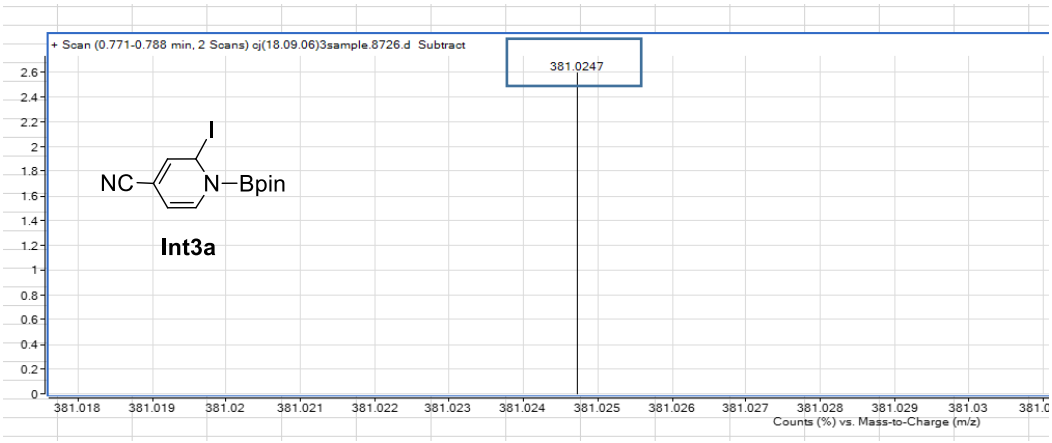
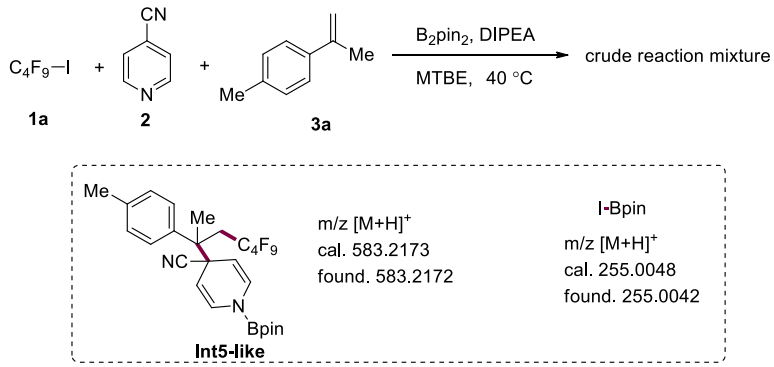


Figure S6

Experimental procedure: A sealed reaction tube charged with a magnetic stir bar, **1a** (0.20 mmol), B_2pin_2 (0.30 mmol, 1.5 equiv), 4-cyanopyridine (0.3 mmol, 1.5 eqviv),

and MTBE (1 mL) were placed in a heated oil bath (80 °C). After 24 hours, the reaction mixture was cooled to room temperature. The crude reaction mixture was subject to the HRMS analysis.



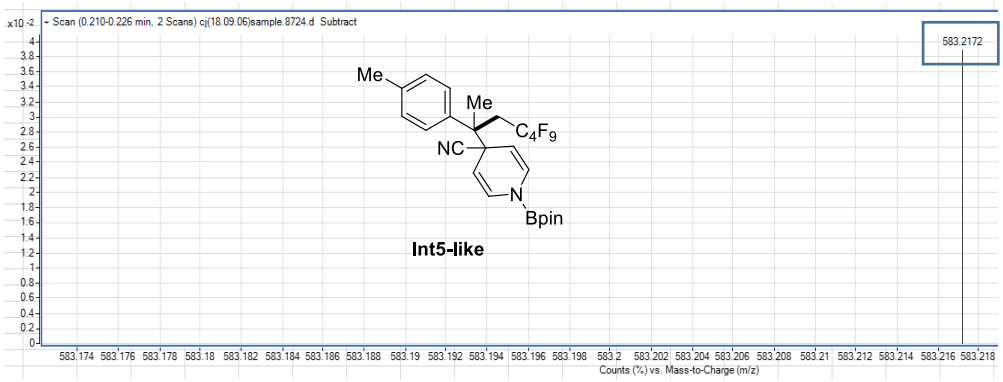


Figure S7

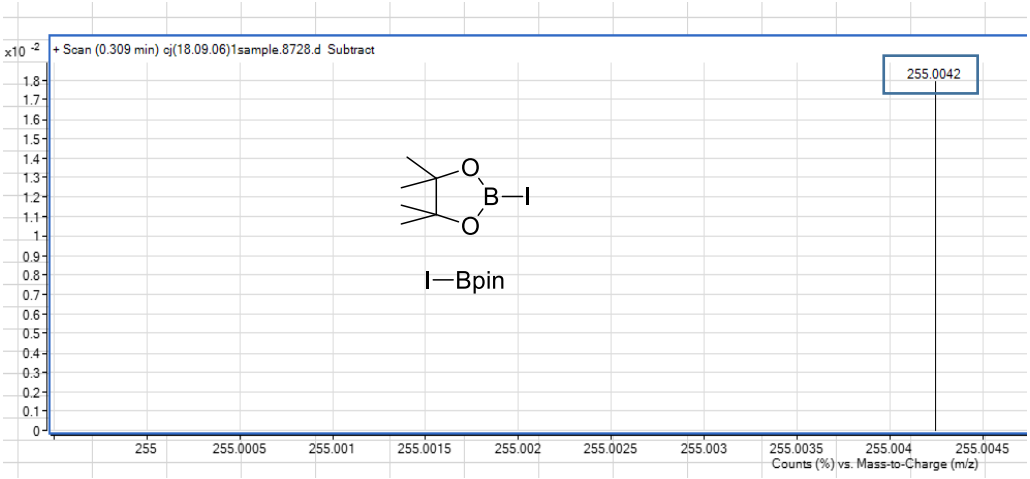


Figure S8

Experimental procedure: A sealed reaction tube charged with a magnetic stir bar, 1a (0.20 mmol), B_2pin_2 (0.30 mmol, 1.5 equiv), 4-cyanopyridine (0.3 mmol, 1.5 eqviv), MTBE (1 mL), 4-methylisopropenylbenzene **3a** (0.4 mmol, 2.0 equiv), DIPEA (0.2

mmol, 1.0 equiv) were placed in a heated oil bath (40 °C). After 24 hours, the reaction mixture was cooled to room temperature. The crude reaction mixture was subject to the HRMS analysis.

3.4 Radical clock experiment

We performed a radical-clock experiment using substrate **3r**. After the generation of C_4F_9 radical, which add to the alkene at the terminal position, and simultaneously the resulting alkyl radical coupled to the 4-cyanopyridne-boryl radicals at the C4 position to form the ring-opening product **5r**.

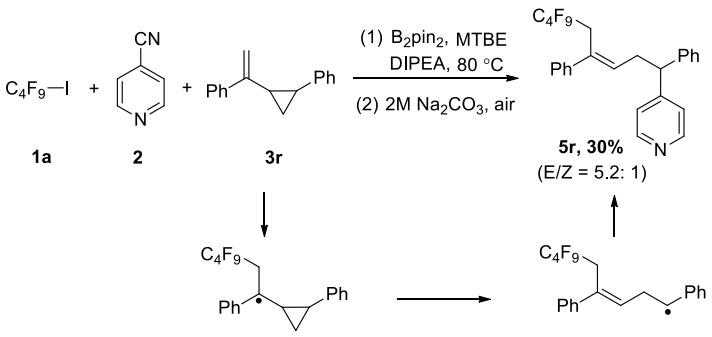


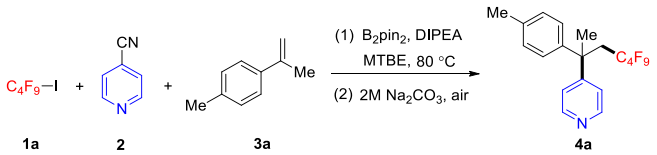
Figure S9

Experimental procedure: A sealed reaction tube charged with a magnetic stir bar, **1a** (0.20 mmol), B_2pin_2 (0.30 mmol, 1.5 equiv), 4-cyanopyridine (0.3 mmol, 1.5 eqviv), MTBE (1 mL), **3v** (0.4 mmol, 2.0 equiv), DIPEA (0.2 mmol, 1.0 equiv) were placed in a heated oil bath (80 °C). After 24 hours, the reaction was cooled and quenched with 2M Na_2CO_3 aqueous solution (3 mL). The reaction tube was stirred under air for another 15 minutes. The reaction mixture was extracted with EtOAc (3×10 mL). The combined organic layer was dried over Na_2SO_4 and then concentrated in vacuo to afford the crude product. This crude material was purified by preparative TLC on silca gel (PE/EA=20:1) to afford the product **5r** in 30% yield (E/Z = 5.2: 1).

5r: Pale-yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 – 8.50 (m, 1.60H), 8.49 – 8.43 (m, 0.32H), 7.36 – 7.18 (m, 11H), 7.11 – 7.05 (m, 0.50H), 7.04 – 7.01 (m, 0.50H), 5.91 (t, *J* = 7.1 Hz, 0.84H), 5.66 (t, *J* = 7.2 Hz, 0.16H), 4.11 – 4.04 (m, 0.85H), 4.01 – 3.94 (m, 0.14H), 3.25 – 3.13 (m, 1.73H), 3.08 – 3.01 (m, 0.36H), 3.00 – 2.94 (m, 1.79H), 2.80 – 2.75 (m, 0.38H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 149.7, 133.6, 133.2,

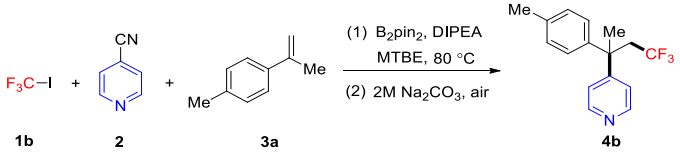
130.7, 129.0, 128.8, 128.5, 128.3, 128.0, 127.6, 127.3, 127.1, 126.4, 123.5, 50.8, 50.5, 31.3 (t, J = 22.2 Hz), ^{13}C-NMR for C_4F_9 could not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.7 – 81.2 (m, 3F), -111.16 – -111.5 (m, 1.83F), -112.3 – -112.6 (m, 0.31F), -123.9 – -124.5 (m, 2F), -125.7 – -125.9 (m, 2F). IR (film): 3061, 3028, 2930, 1596, 1494, 1494, 1453, 1430, 1348, 1235, 1132, 878, 755; HRMS (ESI-TOF) exact mass calculated for $C_{26}H_{20}F_9N$ $[M+H]^+$ 518.1525, found 518.1525.

4. Spectroscopic Characterization of the Products



4a: Prepared following *general procedure* using **1a** (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv), **3a** (58.4 μL, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **4a** (63.5 mg, 74% yield).

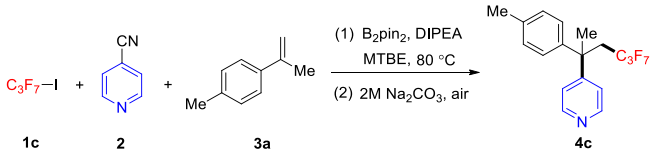
4a: Pale-yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 – 8.51 (m, 2H), 7.14 – 7.10 (m, 4H), 7.05 – 7.02 (m, 2H), 3.02 – 2.91 (m, 2H), 2.32 (s, 3H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 149.9, 143.3, 136.7, 129.3, 126.5, 121.4-107.6 (m, 4C, -C_4F_9), 122.0, 43.9, 39.8 (t, $J_{C\text{-}F}$ = 19.6 Hz), 27.1, 20.9, ^{13}C-NMR for C_4F_9 could not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.1 – -81.8 (m, 3F), -108.1 – -110.5 (m, 2F), -124.5 (m, 2F), -125.7 (m, 2F). IR (film): 3026, 2986, 2926, 1682, 1594, 1552, 1439, 1387, 1314, 1236, 1018, 995, 848 cm^{-1}. HRMS (ESI-TOF) exact mass calculated for $C_{19}H_{17}F_9N$ $[M+H]^+$ 430.1212, found 430.1212.



4b: Prepared following *general procedure* using prepared trifluoroiodomethane solution in MTBE (**1b,** 0.65 M), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv), **3a** (58.4 μL, 0.4 mmol, 2.0 equiv), DIPEA (33.1

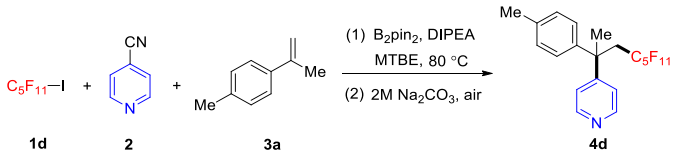
μL, 0.4 mmol, 0.2 equiv) and MTBE (0.5 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **4b** (30.2 mg, 54% yield).

4b: Pale-yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (m, 2H), 7.12 (m, 4H), 7.02 (d, J = 8.3 Hz, 2H), 3.01 (m, 2H), 2.32 (s, 3H), 1.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 149.5, 143.0, 136.7, 129.3, 126.6, 126.3 (q, $J_{C\text{-}F}$ = 278.9 Hz), 122.3, 44.1 (q, $J_{C\text{-}F}$ = 26.5 Hz). 43.5, 26.8, 21.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.3. IR (film): 3026, 2985, 2925, 1594, 1514, 1411, 1366, 1260, 1121, 1036, 817 cm^{-1}. HRMS (ESI-TOF) exact mass calculated for $C_{16}H_{17}F_3N$ $[M+H]^+$ 280.1308 found 280.1308.



4c: Prepared following *general procedure* using **1c** (28.9 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv), **3a** (58.4 μL, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **4c** (54.6 mg, 72% yield).

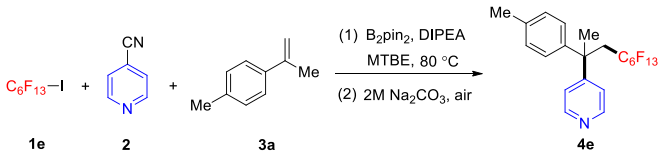
4c: Pale-yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, J = 4.9 Hz, 2H), 7.20 – 7.07 (m, 4H), 7.06 – 7.01 (m, 2H), 3.02 – 2.89 (m, 2H), 2.32 (s, 3H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 149.7, 143.2, 136.7, 129.3, 126.5, 122.1, 120.2-108.5 (m, 3C, -C_3F_7), 43.9, 39.6 (t, $J_{C\text{-}F}$ = 19.5 Hz), 27.1, 20.9, ^{13}C-NMR for C_3F_7 could not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.0 (t, J = 9.9 Hz, 3F), -109.9 – -110.3 (m, 2F), -127.8 (m, 2F). IR (film): 2985, 2985, 2926, 1682, 1595, 1514, 1457, 1351, 1147, 1112, 884 cm^{-1}. HRMS (ESI-TOF) exact mass calculated for $C_{18}H_{17}F_7N$ $[M+H]^+$ 380.1244, found 380.1247.



4d: Prepared following *general procedure* using **1d** (38.3 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv),

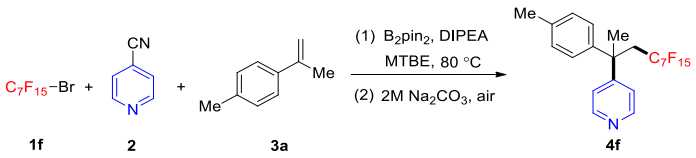
3a (58.4 μL, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **4d** (67.1 mg, 70% yield).

4d: Pale-yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 – 8.50 (m, 2H), 7.14 – 7.10 (m, 4H), 7.04 (d, *J* = 8.3 Hz, 2H), 3.02 – 2.90 (m, 2H), 2.32 (s, 3H), 1.89 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 149.9, 143.3, 136.7, 129.3, 126.5, 122.0, 119.2 –107.7 (m, 5C, -C_5F_{11}), 43.9, 39.9 (t, $J_{C\text{-}F}$ = 19.5 Hz), 27.1, 20.9, ^{13}C-NMR for C_5F_{11} could not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.5 – -80.2 (m, 3F), -107.7 – -110.7 (m, 2F), -121.0 – -122.7 (m, 2F), -123.2 – -124.8 (m, 2F), -125.6 – -127.6 (m, 2F). IR (film): 3026, 2986, 2927, 1594, 1514, 1411, 1306, 1239, 1140, 1040, 741 cm^{-1}. HRMS (ESI-TOF) exact mass calculated for $C_{20}H_{17}F_{11}N$ $[M+H]^+$ 480.1180 found 480.1183.



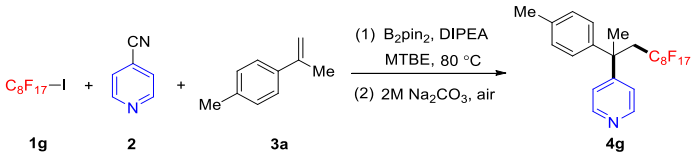
4e: Prepared following *general procedure* using **1e** (43.2 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv), **3a** (58.4 μL, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **4e** (80.4 mg, 76% yield).

4e: Pale-yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 – 8.49 (m, 2H), 7.14 – 7.10 (m, 4H), 7.04 (d, *J* = 8.3 Hz, 2H), 3.03 – 2.91 (m, 2H), 2.32 (s, 3H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 149.8, 143.2, 136.6, 129.2, 126.4, 121.9, 119.4 – 107.5 (m, 6C, -C_5F_{13}), 44.0, 39.9 (t, $J_{C\text{-}F}$ = 19.5 Hz), 27.1, 20.9. ^{13}C-NMR for C_6F_{13} could not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.4 – -81.3 (m, 3F), -108.1 – -110.1 (m, 2F), -121.1 – -121.8 (m, 2F), -122.1 – -123.2 (m, 2F), -123.4 – -124.0 (m, 2F), -125.8 – -126.6 (m, 2F). IR (film): 3025, 2986, 2927, 1595, 1514, 1410, 1387, 1239, 1144, 1119, 1050, 813 cm^{-1}. HRMS (ESI-TOF) exact mass calculated for $C_{21}H_{17}F_{13}N$ $[M+H]^+$ 530.1148 found 530.1149.



4f: Prepared following *general procedure* using **1f** (47.4 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv), **3a** (58.4 μL, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **4f** (60.2 mg, 52% yield).

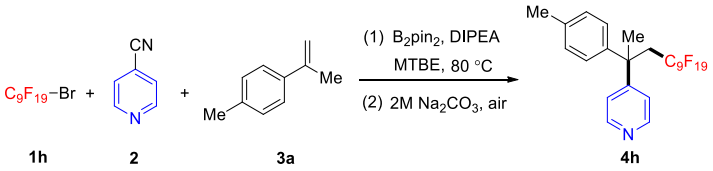
4f: Pale-yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 – 8.50 (m, 2H), 7.14 – 7.10 (m, 4H), 7.05 – 7.02 (m, 2H), 3.03 – 2.90 (m, 2H), 2.32 (s, 3H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 149.9, 143.3, 136.7, 129.3, 126.5, 122.1, 121.3 – 108.2 (m, 7C, -C_7F_{15}), 44.0, 39.9 (t, $J_{C\text{-}F}$ = 19.6 Hz), 27.1, 20.9, ^{13}C-NMR for C_7F_{15} could not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.6 – -81.0 (m, 3F), -108.5 – -109.4 (m, 2F), -121.2 – -121.6 (m, 2F), -121.7 – -122.4 (m, 2F), -122.6 – -123.2 (m, 2F), -123.5 – -123.8 (m, 2F), -126.0 – -126.4 (m, 2F). IR (film): 3026, 2896, 2927, 1595, 1514, 1363, 1211, 1148, 1043, 1005, 815 cm^{-1}. HRMS (ESI-TOF) exact mass calculated for $C_{22}H_{17}F_{15}N$ $[M+H]^+$ 580.1116 found 580.1116.



4g: Prepared following *general procedure* using **1g** (52.8 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv), **3a** (58.4 μL, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **4g** (89.3 mg, 71% yield).

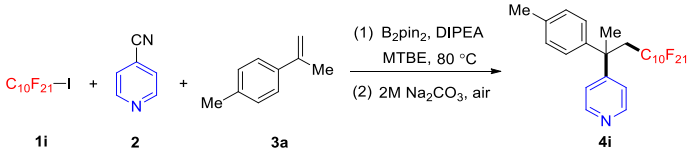
4g: gum; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 – 8.50 (m, 2H), 7.14 – 7.10 (m, 4H), 7.04 (d, J = 8.3 Hz, 2H), 3.02 – 2.90 (m, 2H), 2.32 (s, 3H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 149.9, 143.3, 136.7, 129.3, 126.5, 122.1, 121.4 – 107.0 (m, 8C, -C_8F_{17}), 44.0, 39.9 (t, $J_{C\text{-}F}$ = 19.6 Hz), 27.1, 20.9, ^{13}C-NMR for C_8F_{17} could not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.88 – -80.9 (m, 3F), -108.1 – -109.9 (m,

2F), -121.3 – -121.5 (m, 2F), -121.8 – -122.0 (m, 4F), -122.6 – -122.9 (m, 2F), -123.5 – -123.7 (m, 2F), -125.8 – -126.5 (m, 2F). IR (film): 3026, 2986, 2926, 1594, 1514, 1410, 1363, 1240, 1207, 1150, 1115, 1073, 1036, 816 cm^{-1}. HRMS (ESI-TOF) exact mass calculated for $C_{23}H_{17}F_{17}N$ $[M+H]^+$ 630.1084 found 630.1082.



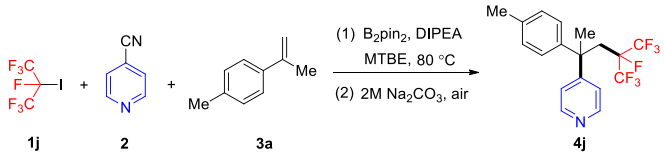
4h: Prepared following *general procedure* using **1h** (109.8 mg, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv), **3a** (58.4 μL, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **4h** (70.6 mg, 52% yield).

4h: gum; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 – 8.48 (m, 2H), 7.15 – 7.10 (m, 4H), 7.05 – 7.02 (m, 2H), 3.03 – 2.89 (m, 2H), 2.32 (s, 3H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 149.8, 143.2, 136.6, 129.2, 126.4, 121.9, 119.9 – 107.2 (m, 9C, -C_9F_{19}), 43.8, 39.8 (t, $J_{C\text{-}F}$ = 19.6 Hz), 27.0, 20.8, ^{13}C-NMR for C_9F_{19} could not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.8 – -80.7 (m, 3F), -108.4 – -109.3 (m, 2F), -121.1 – -121.5 (m, 2F), -121.7 – -122.2 (m, 6F), -122.6 – -123.2 (m, 2F), -123.4 – -123.8 (m, 2F), -126.0 – -126.4 (m, 2F). IR (film): 3027, 2986, 2927, 1595, 1515, 1456, 1387, 1211, 1149, 1122, 1044, 912, 816 cm^{-1}. HRMS (ESI-TOF) exact mass calculated for $C_{24}H_{17}F_{19}N$ $[M+H]^+$ 680.1052 found 680.1053.



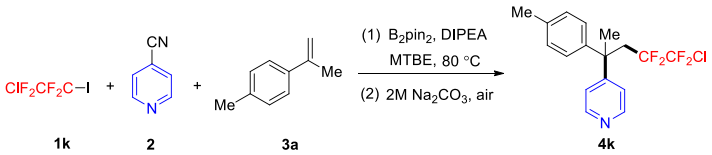
4i: Prepared following *general procedure* using **1i** (129.2 mg, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv), **3a** (58.4 μL, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **4i** (90.4 mg, 62% yield).

4i: gum; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 – 8.51 (m, 2H), 7.14 – 7.10 (m, 4H), 7.04 (d, *J* = 8.2 Hz, 2H), 3.03 – 2.89 (m, 2H), 2.32 (s, 3H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 149.9, 143.3, 136.7, 129.3, 126.5, 122.0, 119.3 – 107.2 (m, 10C, -$C_{10}F_{21}$), 44.0, 39.9 (t, $J_{C\text{-}F}$ = 19.6 Hz), 27.1, 20.8, ^{13}C-NMR for $C_{10}F_{21}$ could not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.4 – -81.6 (m, 3F), -108.4 – -109.5 (m, 2F), -121.1 – -121.5 (m, 2F), -121.54 – -122.6 (m, 8F), -122.7 – -123.4 (m, 2F), -123.6 – -124.0 (m, 2F), -125.9 – -126.7 (m, 2F). IR (film): 3025, 2983, 2926, 1593, 1514, 1410, 1305, 1159, 1118, 1074, 1083, 817 cm^{-1}. HRMS (ESI-TOF) exact mass calculated for $C_{25}H_{17}F_{21}N$ $[M+H]^+$ 730.1020 found 730.1021.



4j: Prepared following *general procedure* using **1j** (28.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv), **3a** (58.4 μL, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **4j** (34.2 mg, 45% yield).

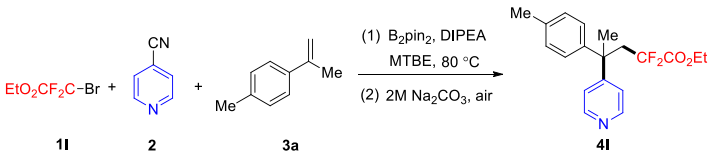
4j: Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 – 8.49 (m, 2H), 7.15 – 7.07 (m, 4H), 7.04 – 7.00 (m, 2H), 3.01 (d, *J* = 13.3 Hz, 2H), 2.32 (s, 3H), 1.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 149.7, 143.5, 136.6, 129.1, 126.8, 122.4, 119.6 (d, $J_{C\text{-}F}$ = 28.2 Hz), 93.6 – 89.8 (m, 2C, -$2CF_3$), 45.0, 36.9 (d, $J_{C\text{-}F}$ = 17.8 Hz). 27.4, 20.9, ^{13}C-NMR for -$2CF_3$ could not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) δ -77.1 – -77.7 (m, 6F), -188.7 – -188.1 (m, 1F). IR (film): 3025, 2983, 2926, 1593, 1514, 1410, 1359, 1305, 1269, 1159, 1118, 1038, 995, 817 cm^{-1}. HRMS (ESI-TOF) exact mass calculated for $C_{18}H_{17}F_7N$ $[M+H]^+$ 380.1244 found 380.1249.



4k: Prepared following *general procedure* using **1k** (37.8 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv),

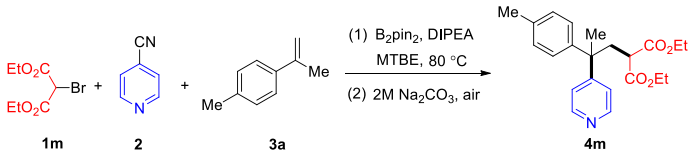
3a (58.4 μL, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **4k** (41.4 mg, 60% yield).

4k: Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 – 8.49 (m, 2H), 7.14 – 7.10 (m, 4H), 7.06 – 7.02 (m, 2H), 3.03 – 2.91 (m, 2H), 2.32 (s, 3H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 149.8, 143.2, 136.5, 129.1, 126.4, 122.0, 121.0 – 114.0 (m, 2C, CF_2CF_2), 43.9, 39.7 (t, $J_{C\text{-}F}$ = 19.7 Hz), 26.9, 20.8, ^{13}C-NMR for CF_2CF_2 could not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.6 – -72.4 (m, 2F), -108.2 – -110.1 (m, 2F). IR (film): 3025, 2984, 2925, 1595, 1514, 1410, 1259, 1211, 1151, 1087, 1038, 948, 817, 593 cm^{-1}. HRMS (ESI-TOF) exact mass calculated for $C_{17}H_{17}ClF_4N$ $[M+H]^+$ 346.0980 found 346.0981.



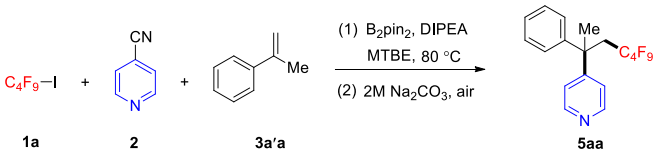
4l: Prepared following *general procedure* using **1l** (25.7 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv), **3a** (58.4 μL, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **4l** (30.0 mg, 45% yield).

4l: Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 – 8.46 (m, 2H), 7.12 – 7.07 (m, 4H), 7.04 – 7.01 (m, 2H), 3.86 – 3.79 (m, 2H), 3.08 – 2.98 (m, 2H), 2.31 (s, 3H), 1.80 (s, 3H), 1.18 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7 (t, $J_{C\text{-}F}$ = 32.3 Hz), 157.5, 149.6, 142.7, 136.6, 129.0, 127.2, 122.4, 115.9 (t, $J_{C\text{-}F}$ = 251.9 Hz), 62.9, 44.2 (t, $J_{C\text{-}F}$ = 22.4 Hz), 43.7, 27.3, 20.9, 13.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -95.2 – -100.6 (m). IR (film): 2983, 2927, 1770, 1712, 1594, 1551, 1514, 1455, 1259, 1211, 1087, 835, 593 cm^{-1}. HRMS (ESI-TOF) exact mass calculated for $C_{19}H_{22}F_2NO_2$ 334.1613 $[M+H]^+$ found 334.1614.



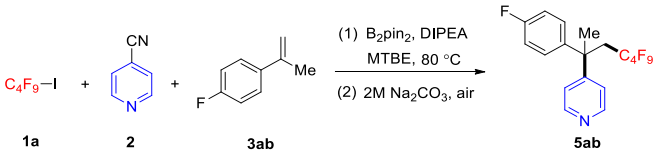
4m: Prepared following *general procedure* using **1m** (34.1 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv), **3a** (58.4 μL, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **4m** (36.2 mg, 49% yield).

4m: Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 – 8.40 (m, 2H), 7.14 – 7.04 (m, 6H), 4.09 – 3.96 (m, 4H), 3.17 – 3.13 (m, 1H), 2.90 – 2.80 (m, 2H), 2.30 (s, 3H), 1.58 (s, 3H), 1.21 – 1.14 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 169.6, 157.8, 149.6, 142.8, 136.3, 129.1, 127.4, 122.7, 61.7, 61.7, 48.8, 45.8, 39.0, 26.9, 20.9, 14.0, 13.9. IR (film): 2980, 2936, 1732, 1594, 1513, 1463, 1277, 1149, 1019, 819, 586 cm^{-1}. HRMS (ESI-TOF) exact mass calculated for $C_{22}H_{28}NO_4$ $[M+H]^+$ 370.2013 found 370.2013.



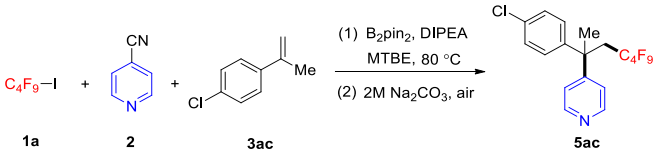
5aa: Prepared following *general procedure* using **1a** (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv), 2-Phenyl-1-propene (52.0 μL, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **5aa** (49.8 mg, 60% yield).

5aa: Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 – 8.52 (m, 2H), 7.33 – 7.28 (m, 2H), 7.26 – 7.22 (m, 1H), 7.17 – 7.12 (m, 4H), 3.04 – 2.93 (m, 2H), 1.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 150.0, 146.2, 128.6, 127.0, 126.6, 122.1, 121.4-109.6 (m, 4C, -C_4F_9), 44.3, 39.8 (t, J_{C-F} = 19.6 Hz), 27.1, ^{13}C-NMR for C_4F_9 could not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.0 – -81.1 (m, 3F), -109.1 – -109.4 (m, 2F), -124.5 – -124.5 (m, 2F), -125.6 – -125.7 (m, 2F). IR (film): 3061, 3028, 2928, 1594, 1496, 1446, 1352, 1221, 1133, 1049, 1016, 874, 734 cm^{-1}. HRMS (ESI-TOF) exact mass calculated for $C_{18}H_{15}F_9N$ $[M+H]^+$ 416.1055 found 416.1059.



5ab: Prepared following *general procedure* using **1a** (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv), **3ab** (58.0 μL, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **5ab** (65.0 mg, 75% yield).

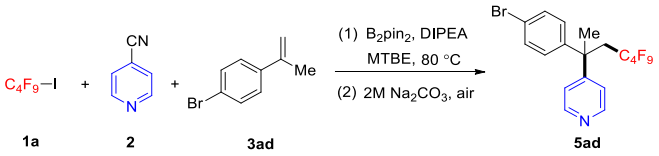
5ab: Pale-yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, J = 5.2 Hz, 2H), 7.15 – 7.10 (m, 4H), 7.05 – 6.94 (m, 2H), 3.00 – 2.89 (m, 2H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5 (d, $J_{C\text{-}F}$ = 247.0 Hz), 156.7, 149.8, 141.6 (d, $J_{C\text{-}F}$ = 3.6 Hz), 128.3 (d, $J_{C\text{-}F}$ = 7.9 Hz), 122.0, 120.2-110.6 (m, 4C, -C_4F_9), 115.3 (d, $J_{C\text{-}F}$ = 21.4 Hz), 43.9, 39.9 (t, $J_{C\text{-}F}$ = 19.6 Hz), 27.5, ^{13}C-NMR for C_4F_9 could not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.9 – -81.2 (m, 3F), -109.1 – -109.7 (m, 2F), -114.9 – -116.3 (m, 1F), -124.3 – -124.6 (m, 2F), -125.5 – -125.9 (m, 2F). IR (film): 2986, 2951, 1595, 1511, 1471, 1353, 1232, 1167, 1133, 1015, 875, 735 cm^{-1}. HRMS (ESI-TOF) exact mass calculated for $C_{18}H_{14}F_{10}N$ $[M+H]^+$ 434.0961 found 434.0962.



5ac: Prepared following *general procedure* using **1a** (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv), **3ac** (57.4 μL, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **5ac** (65.6 mg, 73% yield).

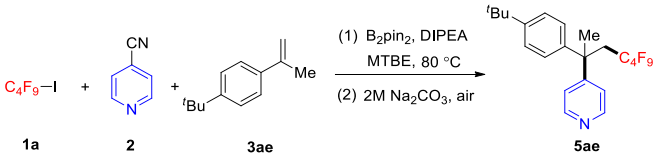
5ac: Pale-yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 – 8.52 (m, 2H), 7.34 – 7.22 (m, 2H), 7.12 – 7.07 (m, 4H), 3.00 – 2.88 (m, 2H), 1.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 149.8, 144.4, 133.1, 128.8, 128.2, 122.0, 121.2-112.3 (m, 4C, -

C_4F_9), 44.1, 39.7 (t, $J_{C\text{-}F}$ = 19.6 Hz), 27.3, ^{13}C-NMR for C_4F_9 could not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.0 – 81.1 (m, 3F), -109.2 – 109.4 (m, 2F), -124.4 – 124.5 (m, 2F), -125.6 – -125.7 (m, 2F). IR (film): 3029, 2985, 2930, 1595, 1494, 1411, 1352, 1232, 1133, 1013, 875, 723 cm^{-1}. HRMS (ESI-TOF) exact mass calculated for $C_{18}H_{14}ClF_9N$ $[M+H]^+$ 450.0666 found 450.0666.



5ad: Prepared following *general procedure* using **1a** (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv), **3ad** (58.4 μL, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **5ad** (69.0 mg, 70% yield).

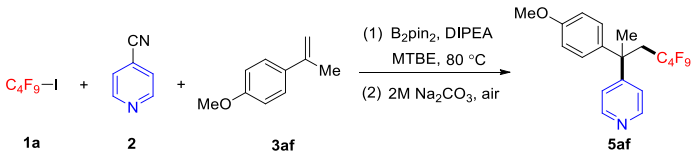
5ad: Pale-yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 – 8.50 (m, 2H), 7.47 – 7.39 (m, 2H), 7.11 – 7.08 (m, 2H), 7.05 – 7.02 (m, 2H), 3.00 – 2.87 (m, 2H), 1.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 150.0, 145.0, 131.8, 128.6, 121.9, 121.2, 121.3-108.3 (m, 4C, -C_4F_9), 44.1, 39.6 (t, $J_{C\text{-}F}$ = 19.5 Hz), 27.2, ^{13}C-NMR for C_4F_9 could not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) -80.2 – -82.2 (m, 3F), -108.3 – -110.2 (m, 2F), -123.7 – -124.8 (m, 2F), -125.2 – -126.7 (m, 2F). IR (film): 3027, 2985, 1596, 1491, 1411, 1352, 1221, 1133, 1074, 1008, 875, 738, 585 cm^{-1}. HRMS (ESI-TOF) exact mass calculated for $C_{18}H_{14}F_9NBr$ $[M+H]^+$ 494.0160 found 494.0162.



5ae: Prepared following *general procedure* using **1a** (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv), **3ae** (80.8 μL, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with

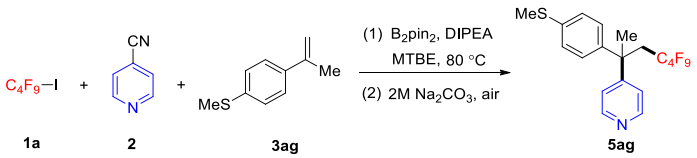
preparative TLC on silica (PE/EA = 20:1) to afford the product **5ae** (67.9 mg, 72% yield).

5ae: Pale-yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, J = 5.8 Hz, 2H), 7.33 – 7.29 (m, 2H), 7.17 – 7.14 (m, 2H), 7.06 – 7.03 (m, 2H), 3.06 – 2.88 (m, 2H), 1.90 (s, 3H), 1.29 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 149.9, 149.8, 143.4, 126.1, 125.5, 122.2, 121.8-108.2 (m, 4C, -C_4F_9), 43.9, 39.9 (t, J_{C-F} = 19.6 Hz), 34.4, 31.3, 27.0, ^{13}C-NMR for C_4F_9 could not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.9 – -81.2 (m, 3F), -108.1 – -110.3 (m, 2F), -124.5 – -124.6 (m, 2F), -125.6 – -125.8 (m, 2F). IR (film): 3030, 2965, 2907, 1594, 1513, 1463, 1352, 1236, 1163, 1048, 1016, 875, 736 cm^{-1}. HRMS (ESI-TOF) exact mass calculated for $C_{22}H_{23}F_9N$ $[M+H]^+$ 472.1681 found 472.1681.



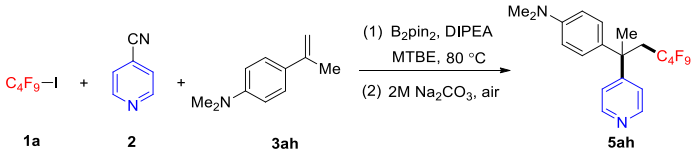
5af: Prepared following *general procedure* using **1a** (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv), **3af** (59.3 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **5af** (59.7 mg, 67% yield).

5af: Pale-yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 – 8.50 (m, 2H), 7.14 – 7.10 (m, 2H), 7.08 – 7.04 (m, 2H), 6.86 – 6.80 (m, 2H), 3.78 (s, 3H), 3.01 – 2.87 (m, 2H), 1.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 157.1, 149.7, 138.0, 127.6, 121.9, 113.8, 121.7-109.6 (m, 4C, -C_4F_9), 55.3, 43.7, 39.9 (t, J_{C-F} = 19.5 Hz), 27.3, ^{13}C-NMR for C_4F_9 could not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.1 – -81.9 (m, 3F), -108.2 – -110.6 (m, 2F), -124.2 – -124.9 (m, 2F), -125.4 – -126.8 (m, 2F). IR (film): 2998, 2955, 2839, 1595, 1514, 1466, 1411, 1352, 1294, 1232, 1132, 1035, 848 cm^{-1}. HRMS (ESI-TOF) exact mass calculated for $C_{19}H_{17}F_9NO$ $[M+H]^+$ 446.1161 found 446.1164.



5ag: Prepared following *general procedure* using **1a** (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv), **3ag** (65.7 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **5ag** (66.4 mg, 72% yield).

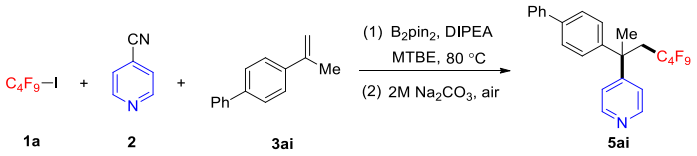
5ag: Pale-yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 – 8.50 (m, 2H), 7.20 – 7.15 (m, 2H), 7.12 – 7.09 (m, 2H), 7.08 – 7.04 (m, 2H), 3.00 – 2.87 (m, 2H), 2.45 (s, 3H), 1.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 149.9, 142.8, 137.4, 127.2, 126.4, 122.0, 121.8-109.8 (m, 4C, -C_4F_9), 43.9, 39.7 (t, $J_{C\text{-}F}$ = 19.5 Hz), 27.1, 15.6, ^{13}C-NMR for C_4F_9 could not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.6 – -81.5 (m, 3F), -108.4 – -109.9 (m, 2F), -124.2 – -124.7 (m, 2F), -125.5 – -126.0 (m, 2F). IR (film): 3080, 3025, 2986, 2924, 1594, 1495, 1439, 1352, 1232, 1132, 1073, 1015, 875, 737 cm^{-1}. HRMS (ESI-TOF) exact mass calculated for $C_{19}H_{17}F_9NS$ $[M+H]^+$ 462.0933 found 462.0932.



5ah: Prepared following *general procedure* using **1a** (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv), **3ah** (64.5 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **5ah** (57.7 mg, 63% yield).

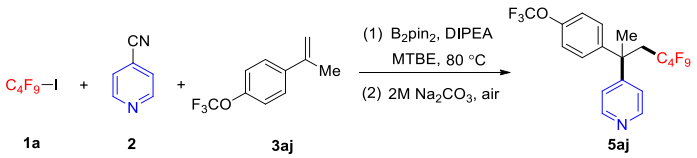
5ah: Pale-yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 – 8.48 (m, 2H), 7.18 – 7.14 (m, 2H), 7.01 – 6.97 (m, 2H), 6.67 – 6.63 (m, 2H), 3.03 – 2.83 (m, 8H), 1.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 149.6, 149.1, 133.8, 127.3, 122.2, 121.3-

112.7 (m, 4C, -C_4F_9), 112.2, 43.4, 40.4, 39.8 (t, J_{C-F} = 19.7 Hz), 27.1, ^{13}C-NMR for C_4F_9 could not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.9 – -81.2 (m, 3F), -108.8 – -109.9 (m, 2F), -124.4 – -124.6 (m, 2F), -125.5 – -125.9 (m, 2F). IR (film): 2984, 2947, 2889, 1614, 1520, 1445, 1352, 1232, 1167, 1132, 874 cm^{-1}. HRMS (ESI-TOF) exact mass calculated for $C_{20}H_{20}F_9N_2$ $[M+H]^+$ 459.1477 found 459.1477.



5ai: Prepared following *general procedure* using **1a** (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv), **3ai** (77.1 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **5ai** (72.7 mg, 74% yield).

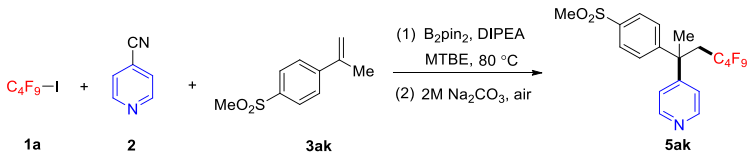
5ai: Pale-yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 – 8.53 (m, 2H), 7.60 – 7.53 (m, 4H), 7.46 – 7.41 (m, 2H), 7.36 (d, J = 7.3 Hz, 1H), 7.24 – 7.17 (m, 4H), 3.09 – 2.96 (m, 2H), 1.96 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 149.9, 145.2, 140.2, 139.8, 128.9, 127.6, 127.3, 127.1, 127.1, 122.1, 121.3-108.3 (m, 4C, -C_4F_9), 44.1, 39.8 (t, J_{C-F} = 19.6 Hz), 27.1, ^{13}C-NMR for C_4F_9 could not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.6 – -81.5 (m, 3F), -107.4 – -111.2 (m, 2F), -124.0 – -124.7 (m, 2F), -125.2 – -126.2 (m, 2F). IR (film): 3030, 2987, 1594, 1488, 1411, 1352, 1232, 1133, 1072, 1016, 875 cm^{-1}. HRMS (ESI-TOF) exact mass calculated for $C_{24}H_{19}F_9N$ $[M+H]^+$ 492.1368 found 492.1367.



5aj: Prepared following *general procedure* using **1a** (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv), **3aj** (80.9 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with

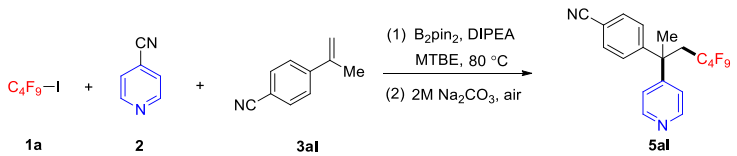
preparative TLC on silica (PE/EA = 20:1) to afford the product **5aj** (44.9 mg, 45% yield).

5aj: Pale-yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 5.2 Hz, 2H), 7.21 – 7.15 (m, 4H), 7.12 – 7.09 (m, 2H), 3.02 – 2.89 (m, 2H), 1.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 150.1, 148.1, 144.6, 128.3, 121.9, 120.9, 119.2-108.5 (m, 5C, -C_4F_9 and –OCF_3), 44.1, 39.8 (t, J_{C-F} = 19.6 Hz), 27.4, ^{13}C-NMR for C_4F_9 and OCF_3 could not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.9 (s, 3F), -80.7 – -81.5 (m, 3F), -107.7 – -110.6 (m, 2F), -124.3 – -124.6 (m, 2F), -125.2 – -126.7 (m, 2F). IR (film): 3029, 2987, 2930, 1595, 1510, 1471, 1353, 1217, 1133, 1072, 1018, 876 cm^{-1}. HRMS (ESI-TOF) exact mass calculated for $C_{19}H_{14}F_{12}NO$ $[M+H]^+$ 500.0878 found 500.0881.



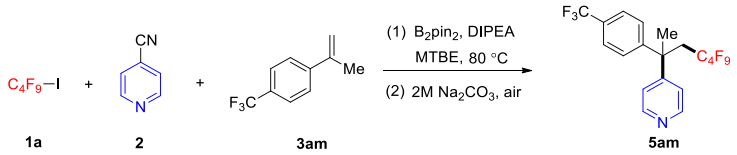
5ak: Prepared following *general procedure* using **1a** (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv), **3ak** (78.4 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **5ak** (59.2 mg, 60% yield).

5ak: Pale-yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 5.1 Hz, 2H), 7.91 – 7.87 (m, 2H), 7.40 – 7.37 (m, 2H), 7.09 – 7.06 (m, 2H), 3.06 – 2.95 (m, 5H), 1.94 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 152.0, 150.1, 139.3, 127.8, 127.6, 121.7, 121.2-108.8 (m, 4C, -C_4F_9), 44.5, 44.4, 39.5 (t, J_{C-F} = 19.7 Hz), 27.1, ^{13}C-NMR for C_4F_9 could not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.8 – -81.2 (m, 3F), -108.9 – -109.2 (m, 2F), -124.3 – -124.5 (m, 2F), -125.5 – -125.9 (m, 2F). IR (film): 2992, 2954, 1727, 1611, 1594, 1437, 1411, 1352, 1283, 1232, 1132, 1018, 736 cm^{-1}. HRMS (ESI-TOF) exact mass calculated for $C_{19}H_{17}F_9NO_2S$ $[M+H]^+$ 494.0831 found 494.0831.



5al: Prepared following *general procedure* using **1a** (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv), **3al** (57.3 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **5al** (37.8 mg, 43% yield).

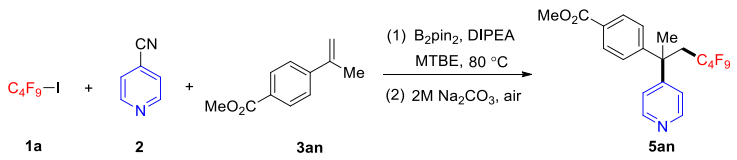
5al: Pale-yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 5.2 Hz, 2H), 7.64 – 7.60 (m, 2H), 7.31 – 7.29 (m, 2H), 7.08 – 7.06 (m, 2H), 3.03 – 2.93 (m, 2H), 1.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 150.9, 150.1, 132.3, 127.6, 121.7, 118.2, 111.2, 121.1-108.8 (m, 4C, -C_4F_9), 44.7, 39.5 (t, J_{C-F} = 19.7 Hz), 27.1, ^{13}C-NMR for C_4F_9 could not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.3 – -81.8 (m, 3F), -108.9 – -109.3 (m, 2F), -124.1 – -124.7 (m, 2F), -125.4 – -126.0 (m, 2F). IR (film): 2987, 2229, 1594, 1506, 1411, 1353, 1232, 1133, 1071, 1018, 876 cm^{-1}. HRMS (ESI-TOF) exact mass calculated for $C_{19}H_{14}F_9N_2$ $[M+H]^+$ 441.1008 found 441.1010.



5am: Prepared following *general procedure* using **1a** (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv), **3am** (57.3 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **5am** (71.5 mg, 74% yield).

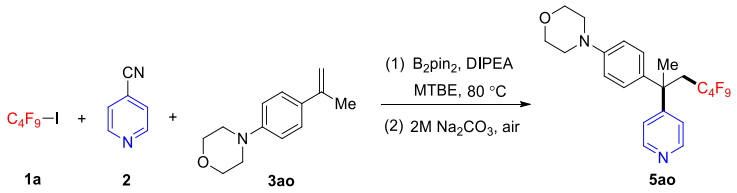
5am: Pale-yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 – 8.54 (m, 2H), 7.61 – 7.53 (m, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 7.11 – 7.07 (m, 2H), 3.04 – 2.93 (m, 2H), 1.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 150.2, 149.9, 129.5 (q, J_{C-F} = 33.1, 32.7 Hz, -CF_3), 127.3, 125.6, 125.6, 121.9, 121.4-108.9 (m, 4C, -C_4F_9), 44.4, 39.73 (t, J_{C-F} = 19.6 Hz), 27.2, ^{13}C-NMR for C_4F_9 could not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7 (3F), -81.0 – -81.2 (m, 3F), -109.1 – -109.3 (m, 2F), -124.5 – -124.5 (m, 2F), -125.6 – -125.8 (m, 2F). IR (film): 3026, 2987, 2951, 1620, 1595, 1555, 1412, 1352,

1328, 1224, 1132, 1073, 1016, 853 cm^{-1}. HRMS (ESI-TOF) exact mass calculated for $C_{19}H_{14}F_{12}N$ 484.0929 $[M+H]^+$ found 484.0932.



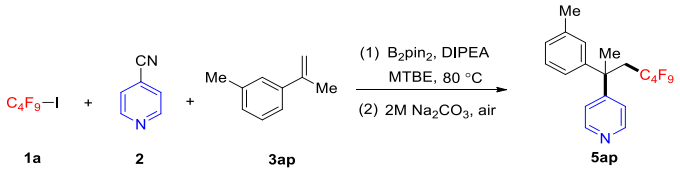
5an: Prepared following *general procedure* using **1a** (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv), **3an** (70.4 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **5an** (60.5 mg, 64% yield).

5an: Pale-yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 – 8.51 (m, 2H), 8.01 – 7.94 (m, 2H), 7.26 – 7.23 (m, 2H), 7.10 – 7.07 (m, 2H), 3.88 (s, 3H), 3.04 – 2.93 (m, 2H), 1.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 156.2, 150.9, 150.0, 129.9, 129.0, 126.9, 121.9, 121.0-108.6 (m, 4C, -C_4F_9), 52.2, 44.5, 39.6 (t, $J_{C\text{-}F}$ = 19.6 Hz), 27.1, ^{13}C-NMR for C_4F_9 could not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.29 – -81.93 (m, 3F), -108.7 – -109.7 (m, 2F), -124.0 – -124.8 (m, 2F), -125.3 – -126.1 (m, 2F); IR (film): 2992, 2954, 1940, 1747, 1611, 1437, 1411, 1352, 1283, 1232, 1048, 1017, 877 cm^{-1}. HRMS (ESI-TOF) exact mass calculated for $C_{20}H_{17}F_9NO_2$ $[M+H]^+$ 474.1110 found 474.1111.



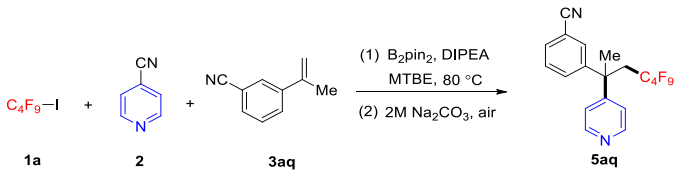
5ao: Prepared following *general procedure* using **1a** (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv), **3ao** (81.3 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **5ao** (55.0 mg, 55% yield).

5ao: Pale-yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 5.2 Hz, 2H), 7.15 – 7.12 (m, 2H), 7.05 – 7.02 (m, 2H), 6.84 – 6.81 (m, 2H), 3.85 – 3.82 (m, 4H), 3.16 – 3.13 (m, 4H), 3.00 – 2.87 (m, 2H), 1.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 149.8, 149.7, 137.2, 127.4, 122.1, 115.2, 121.4-108.3 (m, 4C, -C_4F_9), 66.9, 48.9, 43.6, 39.8 (t, $J_{C\text{-}F}$ = 19.5 Hz), 27.1, ^{13}C-NMR for C_4F_9 could not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.0 – -81.1 (m, 3F), -109.2 – -110.2 (m, 2F), -124.4 – -124.6 (m, 2F), -125.6 – -125.7 (m, 2F). IR (film): 2963, 2856, 1612, 1594, 1517, 1451, 1351, 1410, 1351, 1303, 1232, 1132, 1070, 1017, 932, 732 cm^{-1}. HRMS (ESI-TOF) exact mass calculated for $C_{22}H_{22}F_9NO_2$ $[M+H]^+$ 501.1583 found 501.1583.



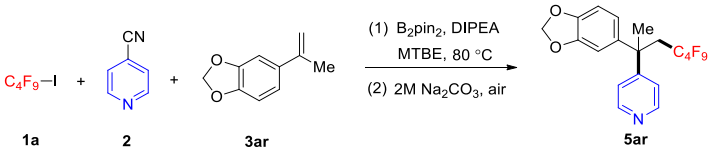
5ap: Prepared following *general procedure* using **1a** (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv), **3ap** (52.9 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **5ap** (44.6 mg, 52% yield).

5ap: Pale-yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 – 8.51 (m, 2H), 7.23 – 7.17 (m, 1H), 7.16 – 7.11 (m, 2H), 7.05 (d, *J* = 7.5 Hz, 1H), 6.96 – 6.92 (m, 2H), 3.05 – 2.90 (m, 2H), 2.31 (s, 3H), 1.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 149.9, 146.3, 138.3, 128.5, 127.8, 127.3, 123.7, 122.1, 121.6-109.9 (m, 4C, -C_4F_9), 44.1, 39.8 (t, $J_{C\text{-}F}$ = 19.5 Hz), 27.0, 21.7, ^{13}C-NMR for C_4F_9 could not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.7 – -81.6 (m, 3F), -108.3 – -110.1 (m, 2F), -124.2 – -124.8 (m, 2F), -125.5 – -126.3 (m, 2F). IR (film): 3026, 2885, 2927, 1594, 1553, 1492, 1352, 1236, 1133, 1017, 880 cm^{-1}. HRMS (ESI-TOF) exact mass calculated for $C_{19}H_{17}F_9N$ $[M+H]^+$ 430.1212 found 430.1216.



5aq: Prepared following *general procedure* using **1a** (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv), **3aq** (57.2 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **5aq** (54.6 mg, 62% yield).

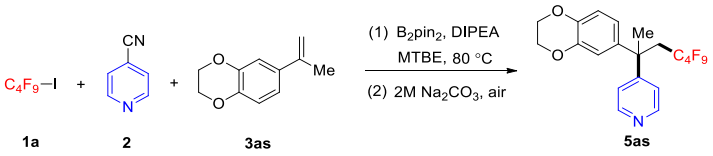
5aq: Pale-yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 – 8.55 (m, 2H), 7.57 (d, *J* = 7.3 Hz, 1H), 7.50 (s, 1H), 7.46 – 7.39 (m, 2H), 7.13 – 7.08 (m, 2H), 3.03 – 2.91 (m, 2H), 1.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 149.9, 147.3, 131.5, 131.0, 130.4, 129.6, 122.0, 118.5, 113.0, 120.9-108.7 (m, 4C, -C_4F_9), 44.4, 39.6 (t, $J_{C\text{-}F}$ = 19.6 Hz), 27.2, ^{13}C-NMR for C_4F_9 could not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.9 – -81.1 (m, 3F), -109.1 – -109.2 (m, 2F), -124.3 – -124.5 (m, 2F), -125.6 – -125.8 (m, 2F). IR (film): 2986, 2929, 2856, 2231, 1595, 1485, 1421, 1393, 1224, 1133, 1018, 877 cm^{-1}. HRMS (ESI-TOF) exact mass calculated for $C_{19}H_{14}F_9N_2$ $[M+H]^+$ 441.1008 found 441.1007.



5ar: Prepared following *general procedure* using **1a** (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv), **3ar** (64.8 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **5ar** (66.1 mg, 72% yield).

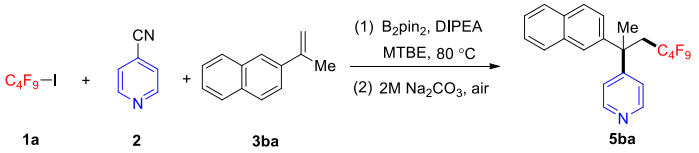
5ar: Pale-yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 – 8.50 (m, 2H), 7.13 – 7.10 (m, 2H), 6.73 (d, *J* = 8.2 Hz, 1H), 6.64 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.57 (d, *J* = 2.0 Hz, 1H), 5.92 (s, 2H), 2.99 – 2.83 (m, 2H), 1.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$)

δ 156.9, 149.9, 148.0, 146.5, 140.1, 121.9, 119.7, 108.0, 107.7, 121.4-108.2 (m, 4C, -C_4F_9), 101.3, 44.1, 39.8 (t, J_{C-F} = 19.5 Hz), 27.3, ^{13}C-NMR for C_4F_9 could not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.9 – -81.2 (m, 3F), -109.1 – -109.8 (m, 2F), -124.3 – -124.6 (m, 2F), -125.5 – -125.9 (m, 2F). IR (film): 3021, 2986, 2895, 2779, 1730, 1594, 1551, 1505, 1488, 1435, 1352, 1240, 1166, 1132, 1041, 736 cm^{-1}. HRMS (ESI-TOF) exact mass calculated for $C_{19}H_{15}F_9NO_2$ $[M+H]^+$ 460.0954 found 460.0954.



5as: Prepared following *general procedure* using **1a** (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv), **3as** (70.4 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **5as** (66.2 mg, 70% yield).

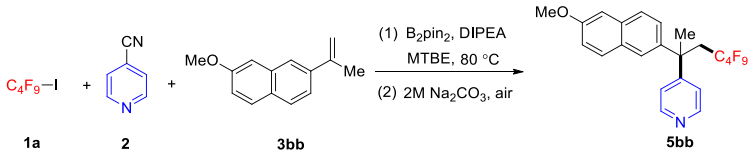
5as: Pale-yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, J = 5.2 Hz, 2H), 7.14 – 7.11 (m, 2H), 6.77 (d, J = 8.5 Hz, 1H), 6.64 (d, J = 2.4 Hz, 1H), 6.58 (dd, J = 8.5, 2.5 Hz, 1H), 4.22 – 4.21 (m, 4H), 2.99 – 2.82 (m, 2H), 1.85 (d, J = 1.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 149.8, 143.3, 142.4, 139.6, 122.0, 119.6, 117.2, 115.8, 121.6-108.3 (m, 4C, -C_4F_9), 64.4, 64.4, 43.7, 39.8 (t, J_{C-F} = 19.5 Hz), 27.0, ^{13}C-NMR for C_4F_9 could not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.0 – -81.1 (m, 3F), -109.0 – -109.8 (m, 2F), -124.5 – -124.6 (m, 2F), -125.6 – -125.8 (m, 2F). IR (film): 2983, 2936, 2882, 1593, 1507, 1459, 1411, 1352, 1288, 1232, 1132, 1068, 1049, 734 cm^{-1}. HRMS (ESI-TOF) exact mass calculated for $C_{20}H_{17}F_9NO_2$ $[M+H]^+$ 474.1110 found 474.1110.



5ba: Prepared following *general procedure* using **1a** (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol,

1.5 equiv), **3ba** (67.2 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **5ba** (67.9 mg, 73% yield).

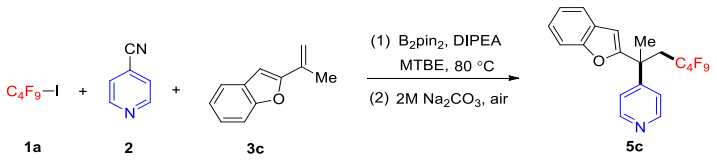
5ba: Pale-yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 5.0 Hz, 2H), 7.84 – 7.73 (m, 4H), 7.54 – 7.47 (m, 2H), 7.18 – 7.15 (m, 2H), 7.11 (dd, *J* = 8.7, 2.1 Hz, 1H), 3.16 – 3.05 (m, 2H), 2.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 149.9, 143.3, 133.1, 132.2, 128.5, 128.2, 127.6, 126.6, 126.5, 125.5, 124.7, 122.2, 120.7-108.4 (m, 4C, -C_4F_9), 44.4, 39.63 (t, $J_{C\text{-}F}$ = 19.6 Hz), 27.1, ^{13}C-NMR for C_4F_9 could not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.1 – -82.1 (m, 3F), -105.9 – -112.3 (m, 2F), -123.6 – -124.9 (m, 2F), -125.1 – -126.8 (m, 2F). IR (film): 3058, 3024, 2985, 1594, 1551, 1494, 1457, 1410, 1351, 1220, 1133, 1017, 733 cm^{-1}. HRMS (ESI-TOF) exact mass calculated for $C_{22}H_{17}F_9N$ 466.1212 $[M+H]^+$ found 466.1211.



5bb: Prepared following *general procedure* using **1a** (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv), **3bb** (79.3 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **5bb** (69.3 mg, 70% yield).

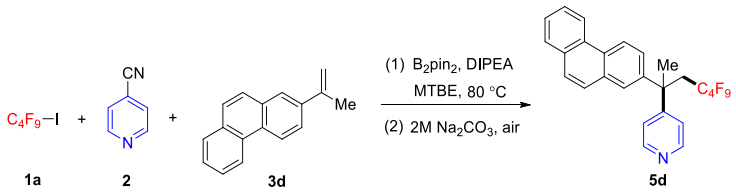
5bb: Pale-yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 4.9 Hz, 2H), 7.71 (d, *J* = 9.0 Hz, 1H), 7.66 – 7.64 (m, 2H), 7.19 – 7.15 (m, 3H), 7.11 – 7.06 (m, 2H), 3.91 (s, 3H), 3.13 – 3.02 (m, 2H), 1.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 156.9, 149.9, 141.1, 133.3, 129.7, 128.5, 127.4, 126.0, 124.5, 122.2, 119.4, 121.4-107.5 (m, 4C, -C_4F_9), 105.6, 55.4, 44.2, 39.6 (t, $J_{C\text{-}F}$ = 19.5 Hz), 27.1, ^{13}C NMR for C_4F_9 could not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.2 – -81.9 (m, 3F), -107.7 – -111.0 (m, 2F), -124.0 – -124.7 (m, 2F), -125.2 – -126.7 (m, 2F). IR (film): 3060, 3000, 2940,

2844, 1633, 1606, 1552, 1504, 1440, 1351, 1221, 1165, 1032, 819 cm^{-1}. HRMS (ESI-TOF) exact mass calculated for $C_{23}H_{19}F_9NO$ $[M+H]^+$ 496.1317 found 496.1316.



5c: Prepared following *general procedure* using **1a** (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv), **3c** (63.3 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **5c** (34.6 mg, 38% yield).

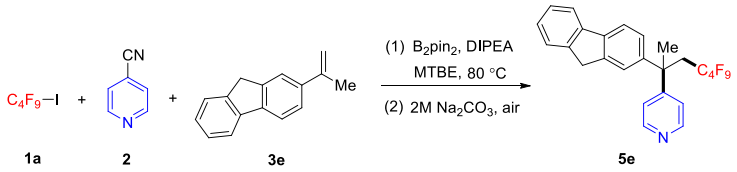
5c: Pale-yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 5.1 Hz, 2H), 7.54 – 7.51 (m, 1H), 7.42 – 7.38 (m, 1H), 7.27 – 7.19 (m, 4H), 6.55 (s, 1H), 3.21 – 3.07 (m, 1H), 2.98 – 2.86 (m, 1H), 1.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 154.8, 153.6, 150.8, 150.1, 128.0, 125.3, 124.5, 123.2, 121.3, 121.1, 111.3, 120.9-108.6 (m, 4C, -C_4F_9), 103.6, 41.8, 38.2 (t, J_{C-F} = 19.8 Hz), 24.3, ^{13}C-NMR for C_4F_9 could not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.0 – -81.1 (m, 3F), -109.1 – -112.6 (m, 2F), -124.5 – -124.5 (m, 2F), -125.6 – -125.8 (m, 2F). IR (film): 3033, 298, 1595, 1454, 1411, 1371, 1223, 1185, 1133, 1050, 1018, 751 cm^{-1}. HRMS (ESI-TOF) exact mass calculated for $C_{20}H_{15}F_9NO$ $[M+H]^+$ 456.1004 found 456.1005.



5d: Prepared following *general procedure* using **1a** (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv), **3d** (87.2 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **5d** (72.1 mg, 70% yield).

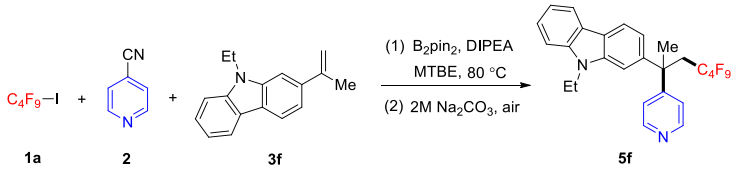
5d: Pale-yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 – 8.51 (m, 4H), 7.90 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.80 – 7.59 (m, 5H), 7.33 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.27 – 7.22 (m, 2H), 3.20 – 3.08 (m, 2H), 2.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1,

149.8, 144.2, 132.2, 131.9, 129.9, 129.1, 128.7, 127.8, 126.9, 126.9, 126.9, 125.8, 125.8, 123.4, 122.7, 122.3, 120.2 – 110.1 (m, 4C, -C_4F_9), 44.4, 39.8 (t, $J_{C\text{-}F}$ = 19.6 Hz), 27.3, ^{13}C-NMR for C_4F_9 could not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.6 – -81.4 (m, 3F), -108.1 – -110.4 (m, 2F), -124.0 – -124.5 (m, 2F), -125.3 – -125.9 (m, 2F). IR (film): 3028, 2928, 2855, 1594, 1411, 1352, 1232, 1132, 1017, 746 cm^{-1}. HRMS (ESI-TOF) exact mass calculated for $C_{26}H_{19}F_9N$ $[M+H]^+$ 516.1368 found 516.1368.



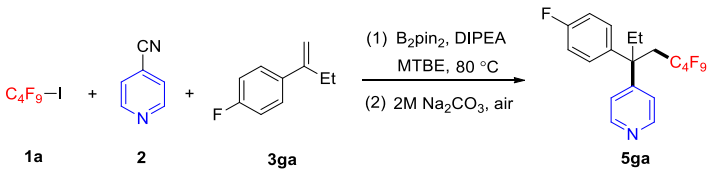
5e: Prepared following *general procedure* using **1a** (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv), **3e** (82.5 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **5e** (52.3 mg, 52% yield).

5e: Pale-yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, J = 5.6 Hz, 2H), 7.64 (dd, J = 18.9, 7.8 Hz, 2H), 7.44 (d, J = 7.4 Hz, 1H), 7.29 – 7.17 (m, 3H), 7.10 – 7.06 (m, 3H), 3.77 (s, 2H), 3.02 – 2.90 (m, 2H), 1.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 149.9, 144.8, 143.7, 143.5, 141.0, 140.7, 127.0, 126.9, 125.4, 125.1, 123.3, 122.1, 120.1, 119.9, 121.6-108.2 (m, 4C, -C_4F_9), 44.4, 37.1, 39.9 (t, $J_{C\text{-}F}$ = 19.5 Hz), 27.4, ^{13}C-NMR for C_4F_9 could not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.9 – -81.1 (m, 3F), -109.0 – -109.3 (m, 2F), -124.3 – -124.5 (m, 2F), -125.6 – -125.7 (m, 2F); IR (film): 3021, 2987, 2926, 2855, 1687, 1594, 1552, 1466, 1410, 1352, 1224, 1132, 1017, 880, 735 cm^{-1}. HRMS (ESI-TOF) exact mass calculated for $C_{25}H_{19}F_9N$ $[M+H]^+$ 504.1368 found 504.1368.



5f: Prepared following *general procedure* using **1a** (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv), **3f** (94.1 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **5f** (53.2 mg, 50% yield).

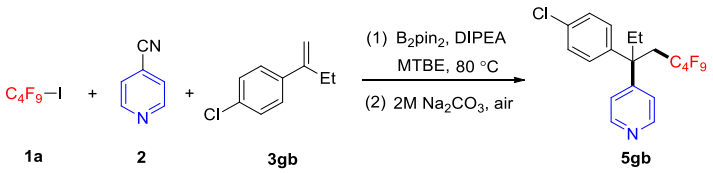
5f: Pale-yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 – 8.50 (m, 2H), 8.07 (d, *J* = 7.8 Hz, 1H), 7.96 (d, *J* = 1.9 Hz, 1H), 7.50 – 7.40 (m, 2H), 7.32 (d, *J* = 8.7 Hz, 1H), 7.25 – 7.15 (m, 4H), 4.34 (t, *J* = 7.2 Hz, 2H), 3.18 – 3.07 (m, 2H), 2.05 (s, 3H), 1.43 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 149.7, 140.5, 138.7, 136.7, 126.0, 124.9, 122.8, 122.7, 122.3, 120.4, 119.1, 117.9, 108.7, 121.1-108.6 (m, 4C, -C_4F_9), 108.6, 44.3, 40.2 (t, $J_{C\text{-}F}$ = 19.5 Hz), 37.7, 27.7, 14.0, ^{13}C-NMR for C_4F_9 could not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.8 – -81.2 (m, 3F), -108.2 – -110.4 (m, 2F), -124.2 – -124.5 (m, 2F), -125.5 – -125.8 (m, 2F). IR (film): 2979, 2933, 2893, 1595, 1493, 1427, 1440, 1350, 1234, 1132, 1016, 878, 747 cm^{-1}. HRMS (ESI-TOF) exact mass calculated for $C_{26}H_{22}F_9N_2$ $[M+H]^+$ 533.1634 found 533.1634.



5ga: Prepared following *general procedure* using **1a** (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv), **3ga** (60.1 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **5ga** (49.2 mg, 55% yield).

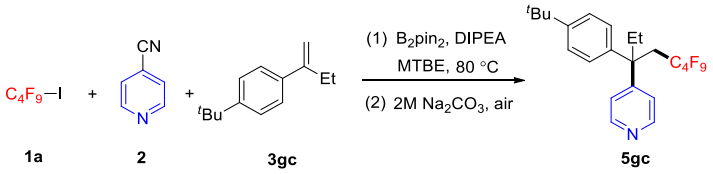
5ga: Pale-yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 5.0 Hz, 2H), 7.11 – 7.06 (m, 4H), 7.01 – 6.96 (m, 2H), 2.99 – 2.89 (m, 2H), 2.41 – 2.36 (m, 2H), 0.71 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5 (d, $J_{C\text{-}F}$ = 246.9 Hz), 156.3, 149.7, 141.0 (d, $J_{C\text{-}F}$ = 3.4 Hz), 129.1 (d, $J_{C\text{-}F}$ = 8.0 Hz), 122.7, 115.4 (d, $J_{C\text{-}F}$ = 21.3 Hz), 121.2-108.7 (m, 4C, -C_4F_9), 47.5, 35.3 (t, $J_{C\text{-}F}$ = 19.1 Hz), 30.9, 8.51, ^{13}C-NMR for C_4F_9 could

not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.0 – -81.1 (m, 3F), -110.9 – -111.0 (m, 2F), -115.5 – -115.6 (m, 1F), -124.4 – -124.6 (m, 2F), -125.6 – -125.7 (m, 2F); IR (film): 2980, 2945, 2889, 1595, 1456, 1353, 1234, 1167, 1133, 1025, 879, 735 cm^{-1}. HRMS (ESI-TOF) exact mass calculated for $C_{19}H_{16}F_{10}N$ $[M+H]^+$ 448.1118 found 448.1120.



5gb: Prepared following *general procedure* using **1a** (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv), **3gb** (66.4 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **5gb** (44.5 mg, 48% yield).

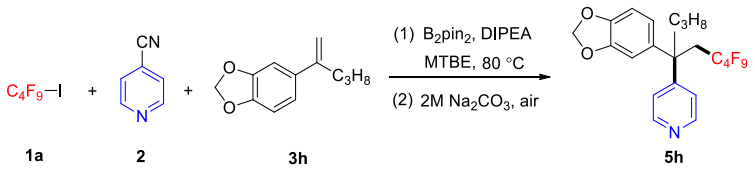
5gb: Pale-yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 – 8.50 (m, 2H), 7.32 – 7.23 (m, 2H), 7.11 – 7.03 (m, 4H), 3.00 – 2.88 (m, 2H), 2.43 – 2.34 (m, 2H), 0.72 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 149.7, 143.8, 133.0, 128.8, 128.7, 122.7, 121.3-108.3 (m, 4C, -C_4F_9), 47.6, 35.2 (t, $J_{C\text{-}F}$ = 19.1 Hz), 30.7, 8.49, ^{13}C-NMR for C_4F_9 could not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.8 – -81.4 (m, 3F), -110.6 – -111.2 (m, 2F), -124.3 – -124.7 (m, 2F), -125.4 – -126.0 (m, 2F). IR (film): 2979, 2944, 2888, 1594, 1494, 1353, 1233, 1133, 1100, 1013, 871, 721 cm^{-1}. HRMS (ESI-TOF) exact mass calculated for $C_{19}H_{16}F_9NCl$ $[M+H]^+$ 464.0822 found 464.0822.



5gc: Prepared following *general procedure* using **1a** (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv), **3gc** (94.1 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with

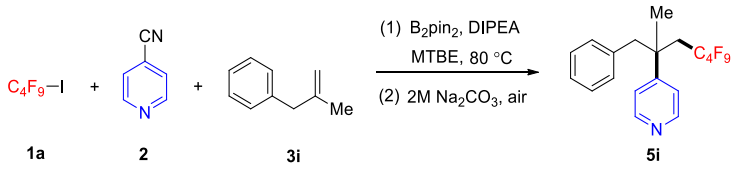
preparative TLC on silica (PE/EA = 20:1) to afford the product **5gc** (58.2 mg, 60% yield).

5gc: Pale-yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 4.9 Hz, 2H), 7.27 (d, *J* = 6.6 Hz, 2H), 7.13 – 7.10 (m, 2H), 7.01 – 6.97 (m, 2H), 3.01 – 2.88 (m, 2H), 2.46 – 2.29 (m, 2H), 1.28 (s, 9H), 0.70 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 149.7, 149.6, 142.0, 126.9, 125.3, 122.9, 122.1-110.3 (m, 4C, -C_4F_9), 47.5, 35.3 (t, J_{C-F} = 19.1 Hz), 34.4, 31.3, 30.6, 8.5, ^{13}C-NMR for C_4F_9 could not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.0 – -81.1 (m, 3F), -110.9 – -111.0 (m, 2F), -124.5 – -124.7 (m, 2F), -125.6 – -125.8 (m, 2F). IR (film): 3030, 2967, 2907, 1594, 1514, 1410, 1385, 1352, 1235, 1133, 1024, 879, 737 cm^{-1}. HRMS (ESI-TOF) exact mass calculated for $C_{23}H_{25}F_9N$ $[M+H]^+$ 486.1838 found 486.1838.



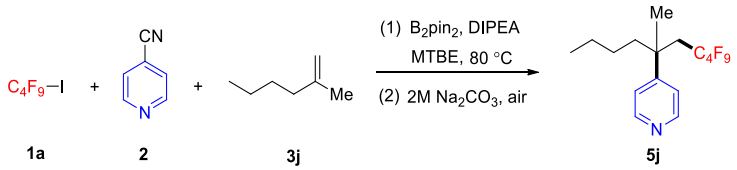
5h: Prepared following *general procedure* using **1a** (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv), **3h** (76.1 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **5h** (43.9 mg, 45% yield).

5h: Pale-yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 5.1 Hz, 2H), 7.11 – 7.09 (m, 2H), 6.73 (d, *J* = 8.2 Hz, 1H), 6.63 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.50 (d, *J* = 1.9 Hz, 1H), 5.93 (s, 2H), 2.96 – 2.86 (m, 2H), 2.27 – 2.22 (m, 2H), 1.06 – 0.99 (m, 2H), 0.89 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 149.6, 148.0, 146.4, 139.5, 122.5, 120.1, 108.1, 107.8, 121.3-108.3 (m, 4C, -C_4F_9), 101.3, 47.3, 40.3, 35.9 (t, J_{C-F} = 19.0 Hz), 17.4, 14.4, ^{13}C-NMR for C_4F_9 could not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.0 – -81.9 (m, 3F), -110.6 – -111.6 (m, 2F), -123.7 – -125.0 (m, 2F), -125.4 – -126.0 (m, 2F). IR (film): 2965, 2936, 2879, 1595, 1505, 1489, 1435, 1352, 1236, 1133, 1041, 1017, 883, 737 cm^{-1}; HRMS (ESI-TOF) exact mass calculated for $C_{21}H_{19}F_9NO_2$ 488.1267 $[M+H]^+$ found 488.1267.



5i: Prepared following *general procedure* using **1a** (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv), **3i** (52.8 mg, 0.4 mmol, 2.0 equiv), DIPEA, (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **5i** (46.4 mg, 54% yield).

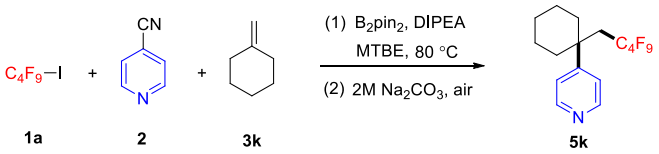
5i: Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 5.2 Hz, 2H), 7.21 – 7.13 (m, 5H), 6.75 – 6.71 (m, 2H), 2.97 (d, *J* = 13.3 Hz, 1H), 2.92 – 2.84 (m, 1H), 2.85 – 2.73 (m, 1H), 2.45 – 2.31 (m, 1H), 1.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 149.4, 135.3, 130.5, 127.9, 126.9, 121.5, 121.3-108.3 (m, 4C, -C_4F_9), 51.0, 40.4, 39.6 (t, $J_{C\text{-}F}$ = 19.9 Hz), 22.6, ^{13}C-NMR for C_4F_9 could not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.2 – -82.0 (m, 3F), -105.6 – -112.0 (m, 2F), -124.3 – -124.9 (m, 2F), -124.9 – -128.1 (m, 2F). IR (film): 3030, 2984, 2930, 1704, 1596, 1516, 1412, 1353, 1232, 1133, 1075, 1021, 879 cm^{-1}. HRMS (ESI-TOF) exact mass calculated for $C_{19}H_{17}F_9N$ $[M+H]^+$ 430.1212 found 430.1215.



5j: Prepared following *general procedure* using **1a** (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv), **3j** (39.3 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **5j** (35.6 mg, 44% yield).

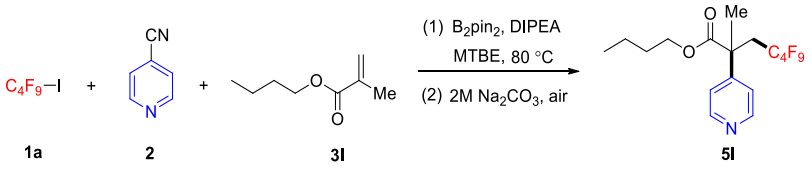
5j: Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 – 8.52 (m, 2H), 7.23 – 7.19 (m, 2H), 2.68 – 2.52 (m, 1H), 2.38 – 2.24 (m, 1H), 1.77 – 1.64 (m, 2H), 1.53 (d, *J* = 1.9 Hz, 3H), 1.30 – 1.04 (m, 4H), 0.82 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 149.9, 121.3, 121.3-108.3 (m, 4C, -C_4F_9), 43.6, 41.0 (t, $J_{C\text{-}F}$ = 20.5 Hz), 39.5,

25.8, 23.1, 23.0, 13.9, ^{13}C NMR for C_4F_9 could not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.6 – -81.6 (m, 3F), -107.9 – -111.7 (m, 2F), -124.3 – -125.0 (m, 2F), -125.4 – -126.2 (m, 2F). IR (film): 2961, 2936, 2865, 1596, 1551, 1412, 1352, 1236, 1132, 1019, 878, 736 cm^{-1}; HRMS (ESI-TOF) exact mass calculated for $C_{16}H_{19}F_9N$ $[M+H]^+$ 396.1368 found 396.1372.



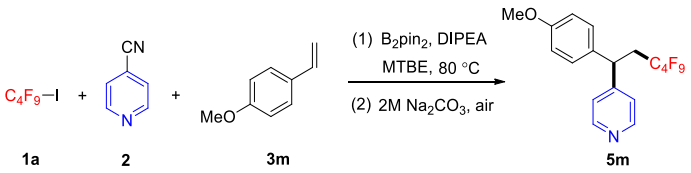
5k: Prepared following *general procedure* using **1a** (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv), **3k** (38.4 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **5k** (26.7 mg, 34% yield).

5k: Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 5.5 Hz, 2H), 7.31 – 7.27 (m, 2H), 2.43 – 2.32 (m, 2H), 2.23 – 2.16 (m, 2H), 1.86-1.78 (m, 2H), 1.61 – 1.54 (m, 2H), 1.49-1.36 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 149.9, 122.2, 121.5-110.3 (m, 4C, -C_4F_9), 41.8 – 41.6 (m), 39.8, 36.4, 25.8, 22.0, ^{13}C-NMR for C_4F_9 could not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.5 – -81.9 (m, 3F), -109.6 – -110.6 (m, 2F), -124.2 – 124.9 (m, 2F), -125.5 – 126.1 (m, 2F). IR (film): 3027, 2939, 2864, 1596, 1551, 1456, 1411, 1351, 1236, 1132, 1012, 735 cm^{-1}. HRMS (ESI-TOF) exact mass calculated for $C_{16}H_{17}F_9N$ $[M+H]^+$ 394.1212 found 394.1216.



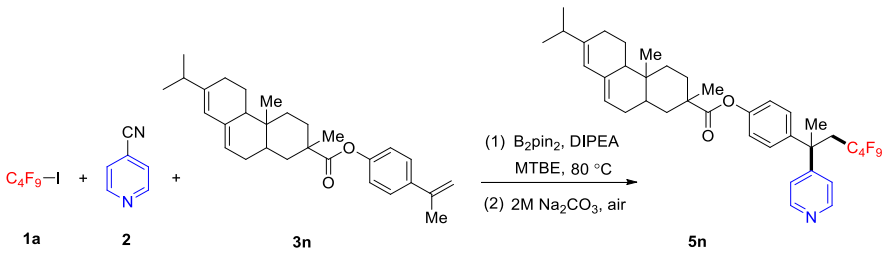
5l: Prepared following *general procedure* using **1a** (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv), **3l** (56.8 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **5l** (22.0 mg, 25% yield).

5l: Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 5.2 Hz, 2H), 7.22 – 7.19 (m, 2H), 4.05 (t, *J* = 6.6 Hz, 2H), 3.14 – 3.00 (m, 1H), 2.60 – 2.46 (m, 1H), 1.72 (s, 3H), 1.52 – 1.45 (m, 2H), 1.22 – 1.16 (m, 2H), 0.80 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 151.0, 150.3, 120.8, 118.7-110.1 (m, 4C, -C_4F_9), 66.1, 47.3, 38.2 (t, J_{C-F} = 19.7 Hz), 30.3, 21.7, 19.0, 13.6, ^{13}C-NMR for C_4F_9 could not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.0 – -81.1 (m, 3F), -106.6 – -113.3 (m, 2F), -124.6 – -124.8 (2F), -125.7 – -125.8 (m, 2F). IR (film): 2985, 2928, 1747, 1710, 1512, 1226, 1130, 913, 743 cm^{-1}; HRMS (ESI-TOF) exact mass calculated for $C_{17}H_{19}F_9NO_2$ $[M+H]^+$ 440.1267 found 440.1271.



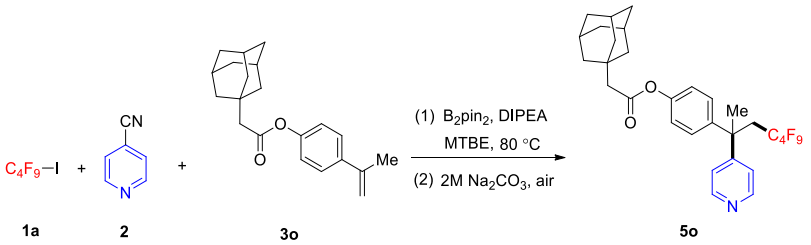
5m: Prepared following *general procedure* using **1a** (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv), **3m** (53.6 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **5m** (30.2 mg, 35% yield).

5m: Pale-yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 – 8.49 (m, 2H), 7.21 – 7.18 (m, 2H), 7.16 – 7.12 (m, 2H), 6.88 – 6.85 (m, 2H), 4.38 (t, *J* = 7.1 Hz, 1H), 3.78 (s, 3H), 2.91 – 2.80 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 152.3, 150.0, 133.4, 128.5, 122.9, 114.2, 120.4-109.1 (m, 4C, -C_4F_9), 55.4, 42.9, 35.7 (t, J_{C-F} = 21.0 Hz), ^{13}C-NMR for C_4F_9 could not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.6 – -81.4 (m, 3F), -111.8 – -113.7 (m, 2F), -124.0 – -124.7 (m,2F), -125.6 – -126.3 (m, 2F). IR (film): 2935, 2840, 1611, 1596, 1513, 1464, 1416, 1354, 1235, 1181, 1133, 1036, 880, 740 cm^{-1}; HRMS (ESI-TOF) exact mass calculated for $C_{18}H_{15}F_9NO$ $[M+H]^+$ 432.1004 found 432.1004.



5n: Prepared following *general procedure* using **1a** (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv), **3n** (167.3 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **5n** (57.2 mg, 40% yield).

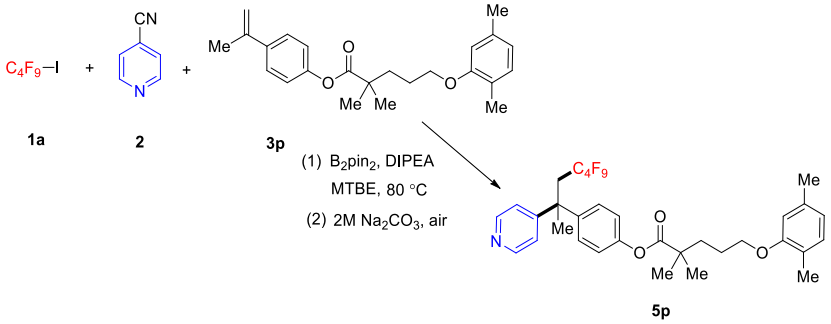
5n: Pale-yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 5.1 Hz, 2H), 7.16 – 7.11 (m, 4H), 6.99 – 6.95 (m, 2H), 5.78 (s, 1H), 5.41 – 5.37 (m, 1H), 3.04 – 2.83 (m, 2H), 2.27 – 2.01 (m, 6H), 1.89 (s, 4H), 1.84 – 1.77 (m, 2H), 1.67 – 1.61 (m, 2H), 1.39 – 1.35 (m, 3H), 1.31 – 1.15 (m, 4H), 1.01 (dd, *J* = 6.8, 3.6 Hz, 6H), 0.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.1, 156.8, 150.0, 149.8, 145.7, 143.2, 135.7, 127.7, 122.4, 122.1, 121.7, 120.4, 121.1-110.2 (m, 4C, -C_4F_9), 51.0, 47.0, 45.2, 44.1, 39.9 (t, $J_{C\text{-}F}$ = 19.7 Hz), 38.4, 37.1, 35.0, 34.7, 27.5, 27.3, 25.9, 22.6, 21.5, 20.9, 18.2, 17.2, 14.1, ^{13}C-NMR for C_4F_9 could not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.9 – 81.0 (m, 3F), -109.1 – -109.4 (m, 2F), -124.4- – 125.5 (m, 2F), -125.6- – 125.7 (m, 2F). IR (film): 2931, 2871, 1745, 1594, 1462, 1411, 1352, 1232, 1173, 1132, 1101, 1016, 908, 734 cm^{-1}; HRMS (ESI-TOF) exact mass calculated for $C_{38}H_{43}F_9NO_2$ $[M+H]^+$ 716.3145 found 716.3145.



5o: Prepared following *general procedure* using **1a** (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv), **3o** (124.1 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE

(1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **5o** (72.9 mg, 60% yield).

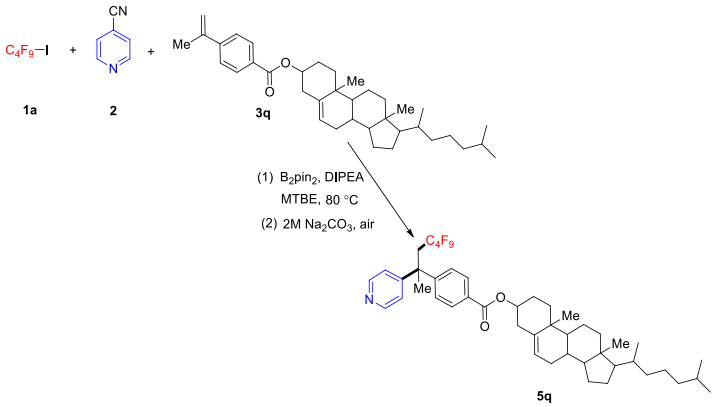
5o: Pale-yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 5.6 Hz, 2H), 7.16 – 7.11 (m, 4H), 7.06 – 7.02 (m, 2H), 3.03 – 2.86 (m, 2H), 2.28 (s, 2H), 1.99 (s, 3H), 1.89 (s, 3H), 1.74 – 1.62 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 156.4, 149.9, 149.5, 143.5, 127.7, 122.0, 121.8, 121.2-108.5 (m, 4C, -C_4F_9), 48.8, 44.0, 42.5, 39.8 (t, J_{C-F} = 19.6 Hz), 36.7, 33.3, 28.7, 27.2, ^{13}C-NMR for C_4F_9 could not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.0 – -81.1 (m, 3F), -108.3 – -110.3 (m, 2F), -124.4 – -124.6 (m, 2F), -125.6 – -125.8 (m, 2F). IR (film): 2982, 2905, 2849, 1754, 1594, 1507, 1471, 1411, 1351, 1224, 1132, 1016, 851, 735 cm^{-1}; HRMS (ESI-TOF) exact mass calculated for $C_{30}H_{31}F_9NO_2$ $[M+H]^+$ 608.2206 found 608.2206.



5p: Prepared following *general procedure* using **1a** (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv), **3p** (146.5 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **5p** (79.6 mg, 60% yield).

5p: Pale-yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 – 8.53 (s, 2H), 7.17 – 7.13 (m, 4H), 7.03 – 6.98 (m, 3H), 6.66 (d, *J* = 7.4 Hz, 1H), 6.62 (s, 1H), 3.98 (s, 2H), 3.06 – 2.89 (m, 2H), 2.30 (s, 3H), 2.17 (s, 3H), 1.89 (d, *J* = 13.8 Hz, 7H), 1.37 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.3, 156.9, 156.7, 149.9, 149.8, 143.3, 136.5, 130.4, 127.9, 123.7, 122.1, 121.6, 120.8, 112.0, 120.1-107.3 (m, 4C, -C_4F_9), 67.8, 44.0, 42.5, 39.8 (t, J_{C-F} = 19.5 Hz), 37.2, 27.3, 25.3, 25.2, 21.4, 15.8, ^{13}C NMR for C_4F_9 could not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.4 – -81.6 (m, 3F), -107.9 – -110.7 (m, 2F), -124.1 – -124.7 (m, 2F), -125.2 – -126.3 (m, 2F). IR (film): 3025, 2976, 2927, 1754,

1594, 1506, 1473, 1412, 1285, 1173, 1110, 875, 735 cm^{-1}; HRMS (ESI-TOF) exact mass calculated for $C_{33}H_{35}F_9NO_3$ $[M+H]^+$ 664.2468 found 664.2467.

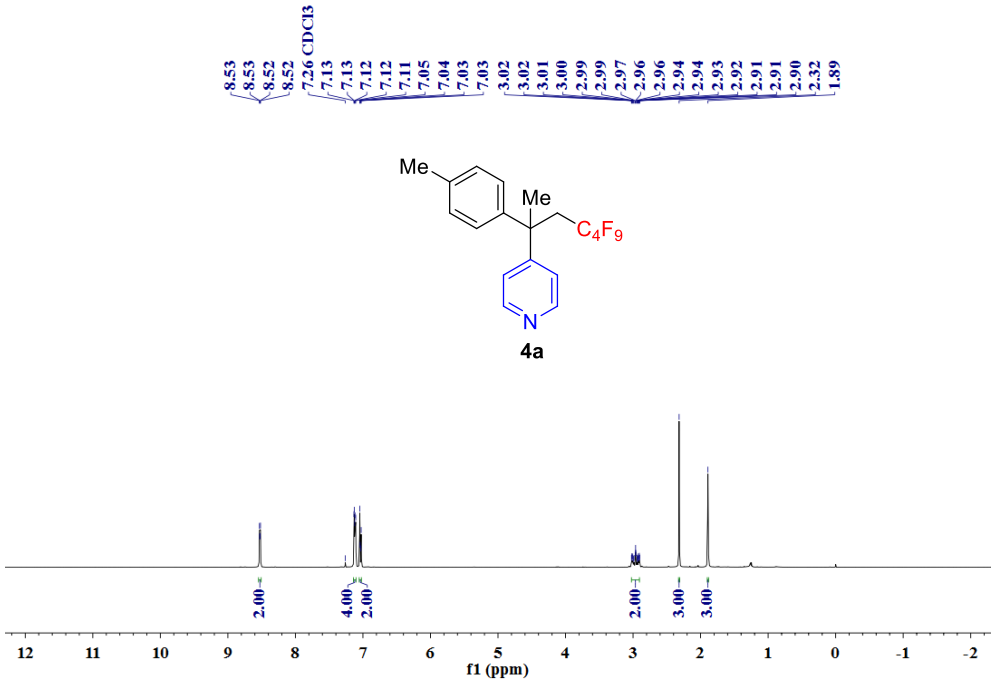


5q: Prepared following *general procedure* using **1a** (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv), **3q** (116.7 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **5q** (91.0 mg, 55% yield).

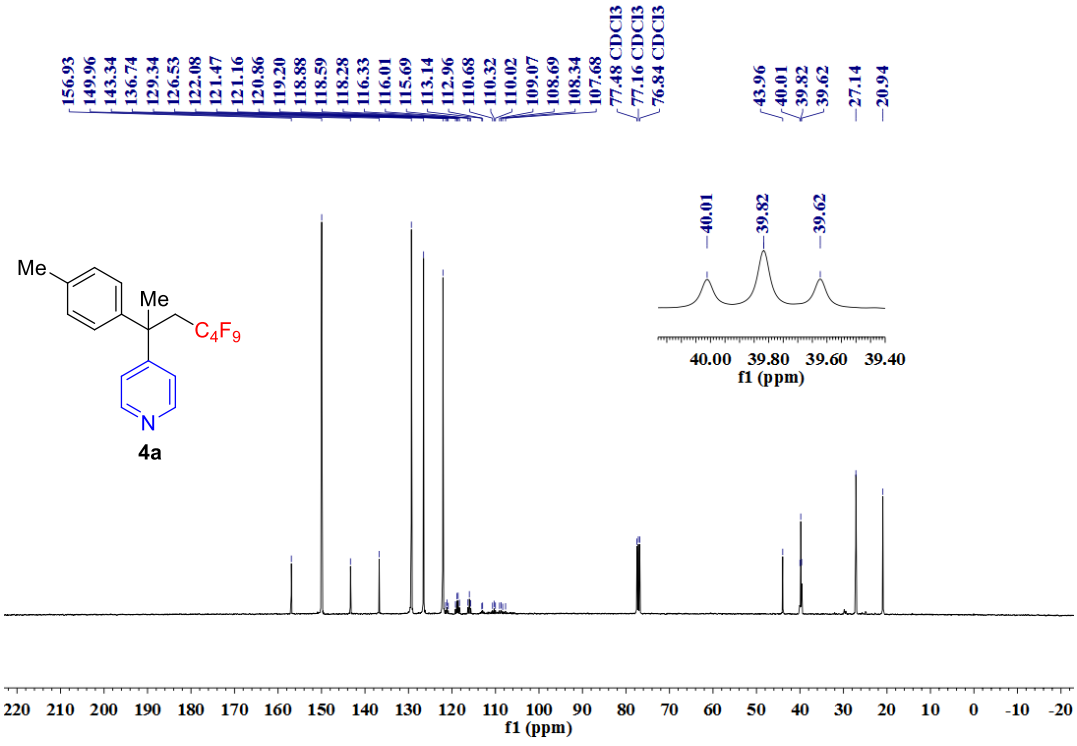
5q: Pale-yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 5.3 Hz, 2H), 7.92 (d, *J* = 8.6 Hz, 2H), 7.17 (d, *J* = 8.6 Hz, 2H), 7.03 – 7.00 (m, 2H), 5.34 (dd, *J* = 4.9, 1.8 Hz, 1H), 4.82 – 4.73 (m, 1H), 2.98 – 2.87 (m, 2H), 2.37 (d, *J* = 8.1 Hz, 2H), 1.96 – 1.77 (m, 8H), 1.74 – 1.53 (m, 2H), 1.50 – 1.32 (m, 6H), 1.31 – 1.18 (m, 4H), 1.17 – 1.10 (m, 2H), 1.04 – 0.87 (m, 10H), 0.85 (d, *J* = 6.5 Hz, 3H), 0.79 (dd, *J* = 6.6, 1.8 Hz, 6H), 0.61 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 156.3, 150.7, 150.0, 139.6, 129.9, 129.7, 126.8, 122.9, 121.9, 121.3-108.3 (m, 4C, -C_4F_9), 74.8, 56.8, 56.2, 50.1, 44.5, 42.4, 39.8, 39.7 (d, J_{C-F} = 21.9 Hz), 39.4, 38.3, 37.1, 36.7, 36.3, 35.9, 32.1, 32.0, 28.3, 28.1, 27.9, 27.1, 24.4, 23.9, 22.9, 22.6, 21.1, 19.4, 18.8, 11.9, ^{13}C-NMR for C_4F_9 could not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.3 – -81.4 (m, 3F), -108.7 – -109.8 (m, 2F), -123.7 – -124.9 (m, 2F), -125.1 – -126.5 (m, 2F). IR (film): 2947, 2868, 2225, 1721, 1611, 1594, 1469, 1410, 1369, 1318, 1275, 1133, 1017, 909, 736 cm^{-1}. HRMS (ESI-TOF) exact mass calculated for $C_{46}H_{59}F_9NO_2$ $[M+H]^+$ 828.4397 found 828.4381.

5. NMR Spectra

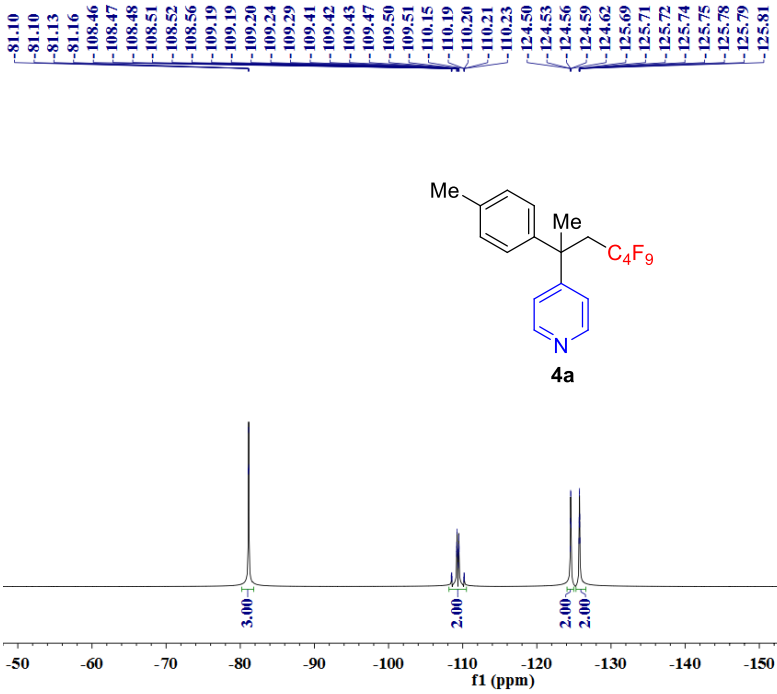
^{1}H NMR (400 MHz, $CDCl_3$):



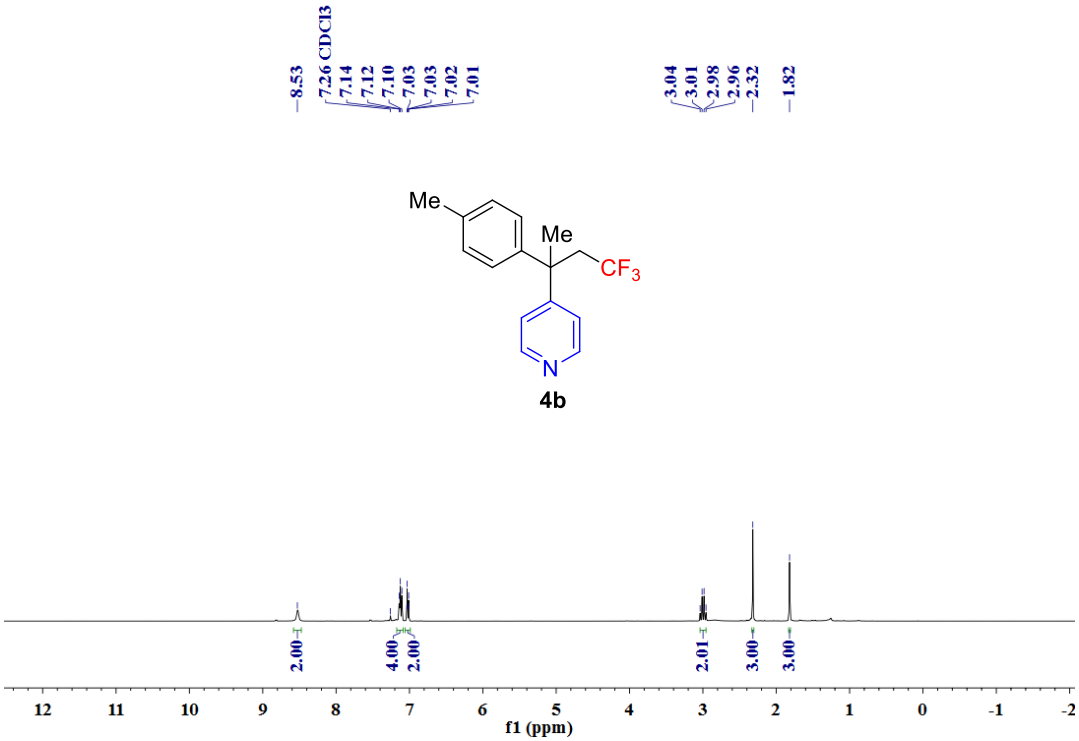
^{13}C NMR (100 MHz, $CDCl_3$):



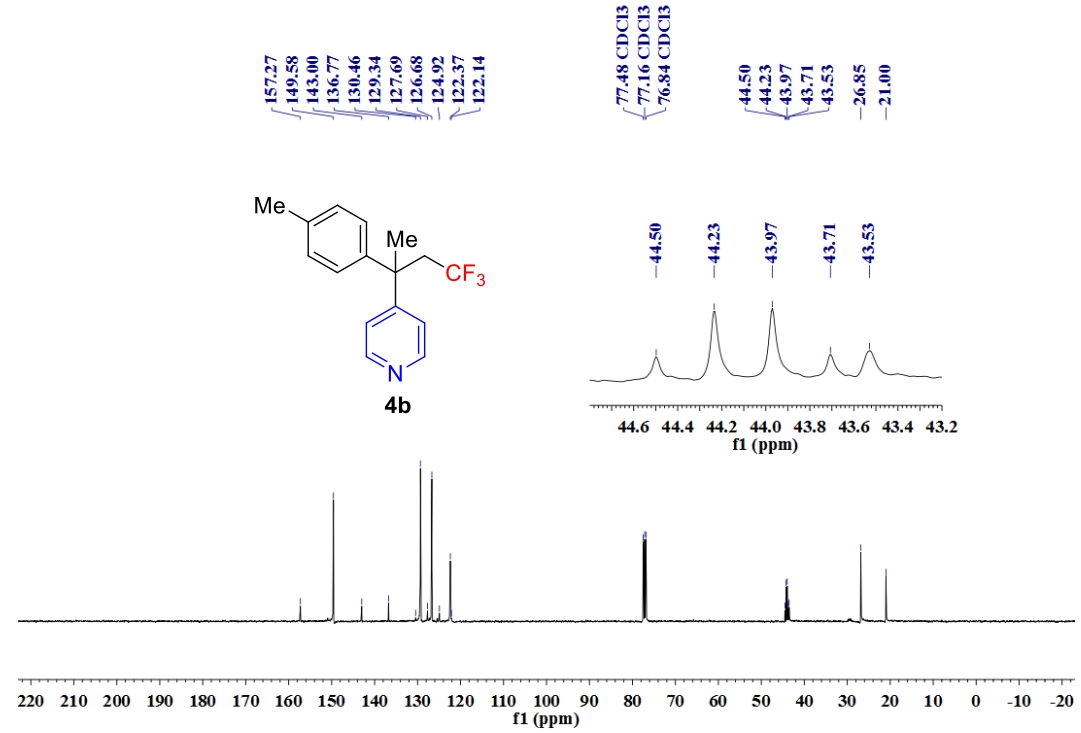
^{19}F NMR (376 MHz, $CDCl_3$):



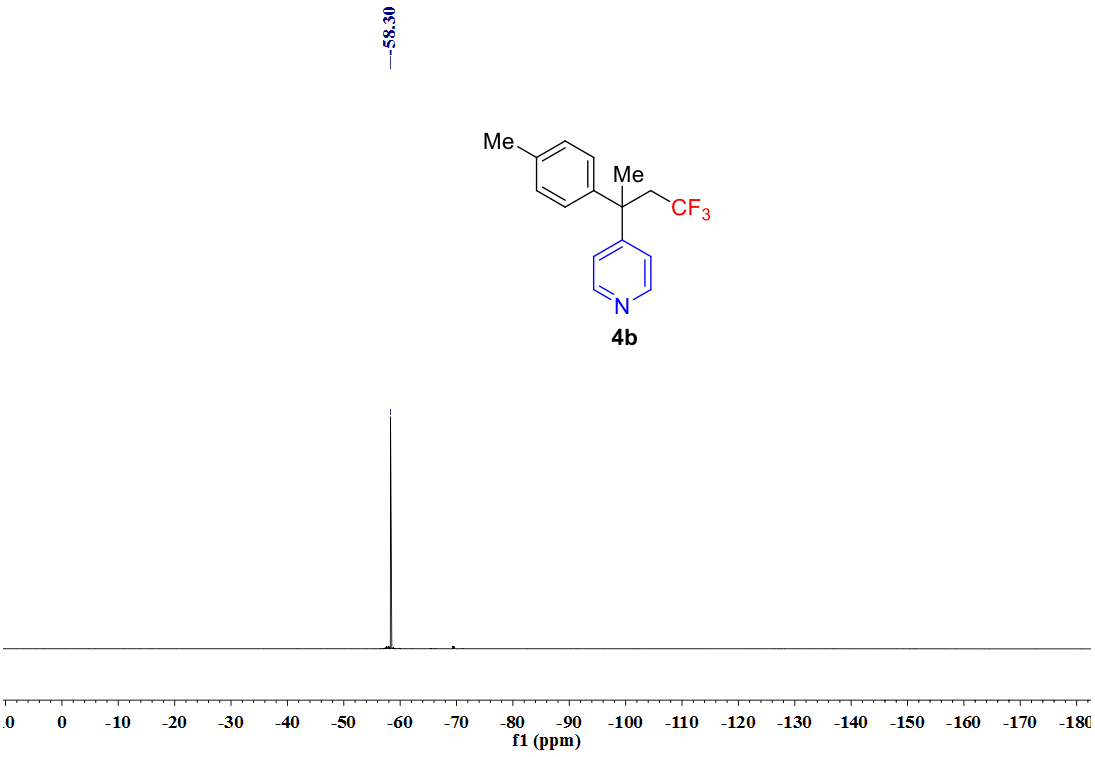
^{1}H NMR (400 MHz, $CDCl_3$):



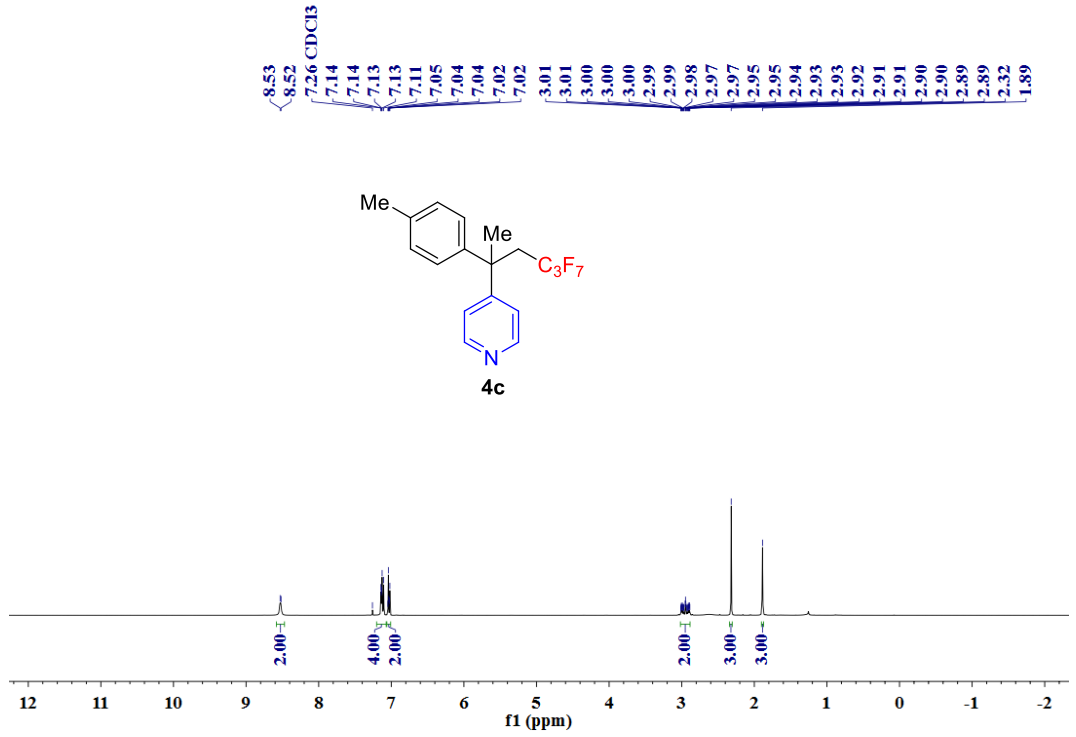
^{13}C NMR (100 MHz, $CDCl_3$):



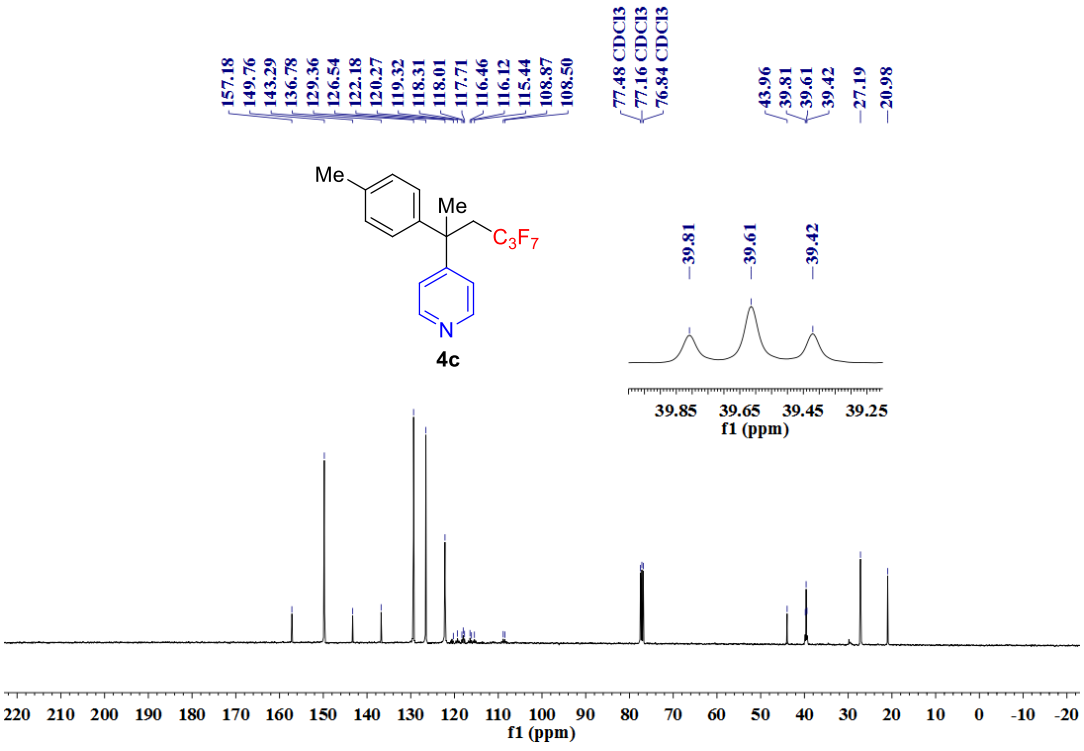
^{19}F NMR (376 MHz, $CDCl_3$):



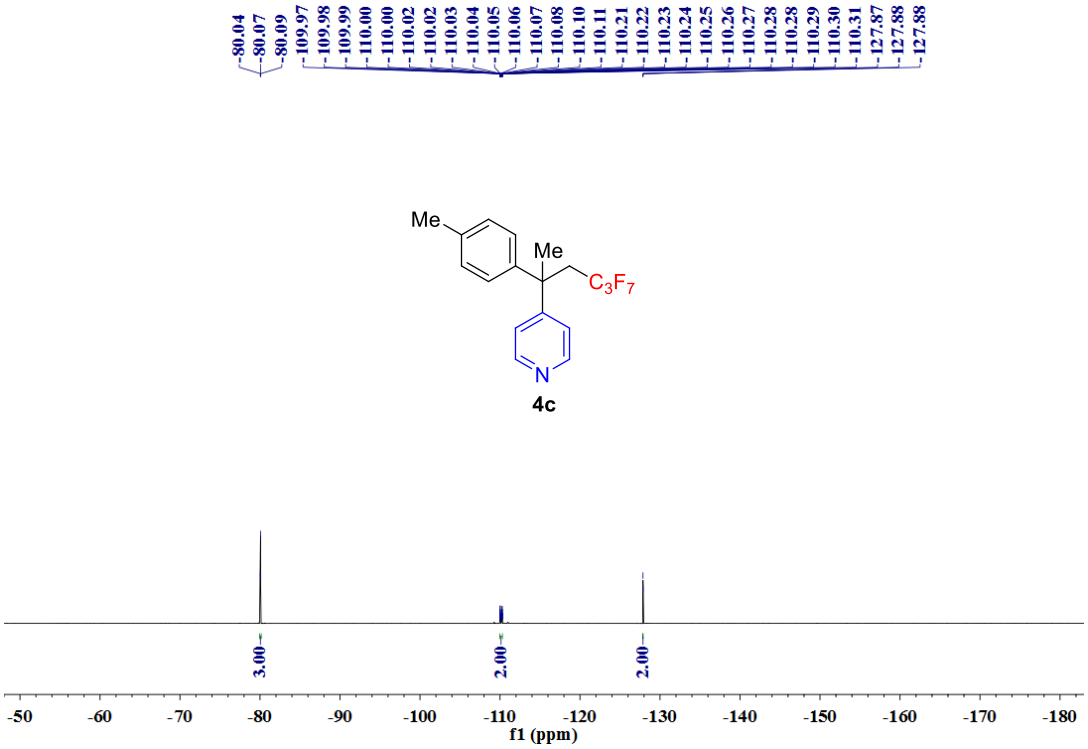
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):



^{19}F NMR (376 MHz, $CDCl_3$):



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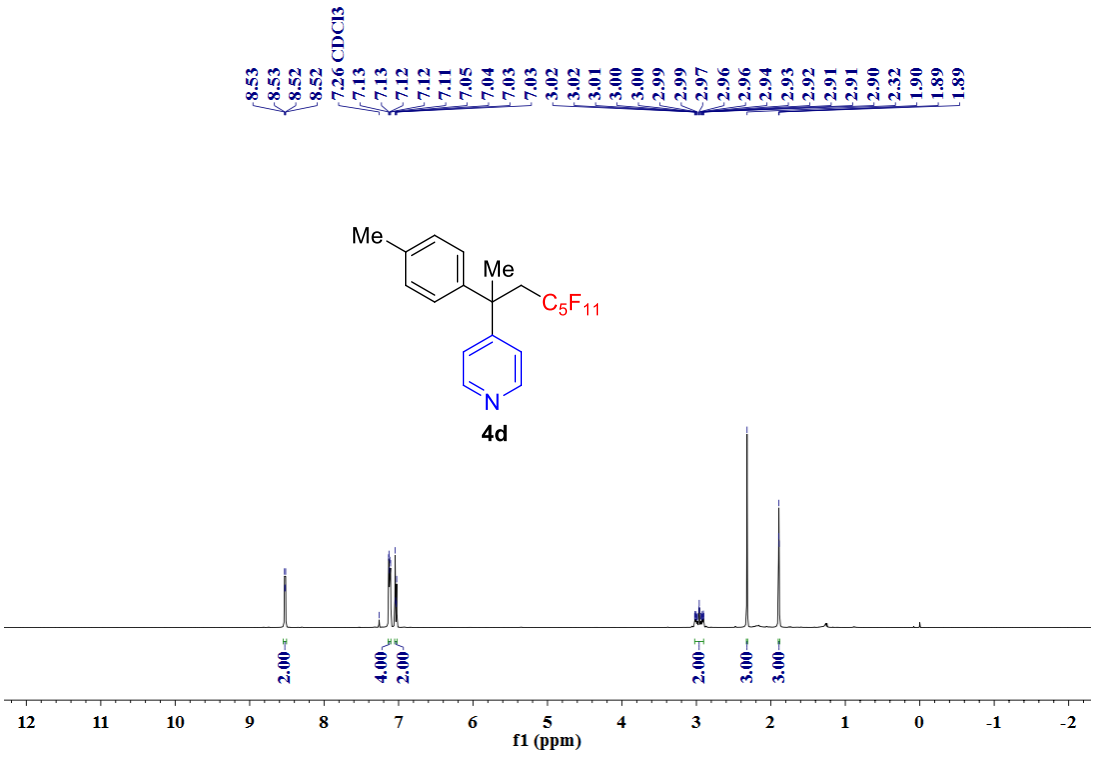
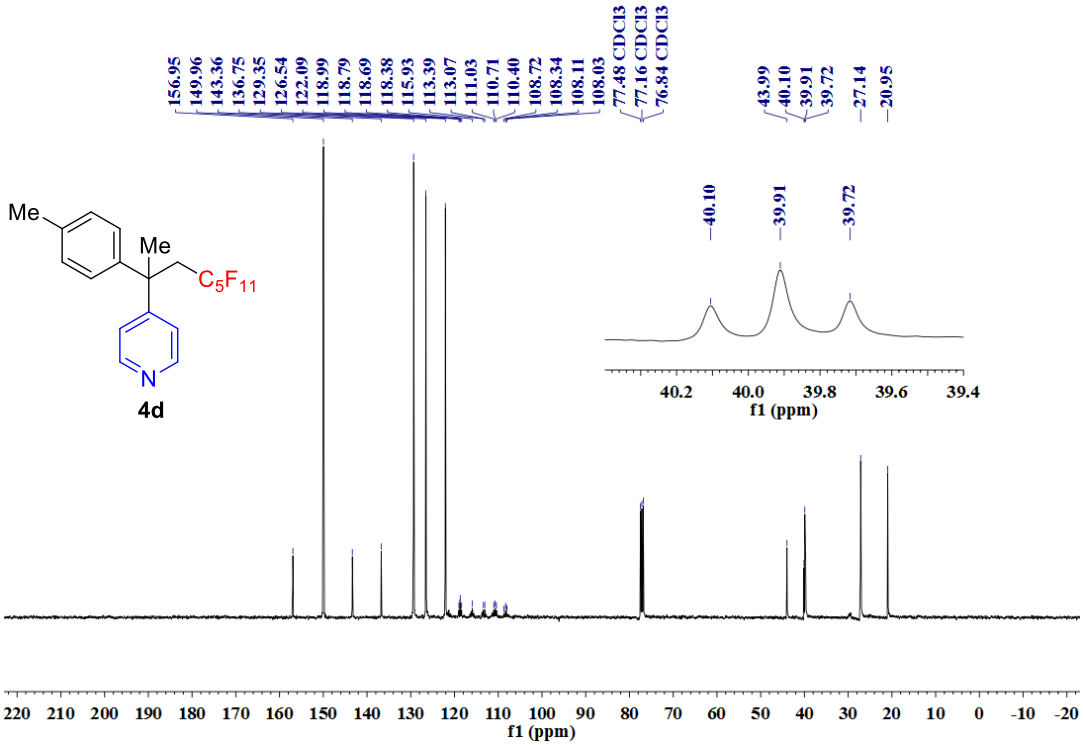


^{13}C NMR (100 MHz, $CDCl_3$):



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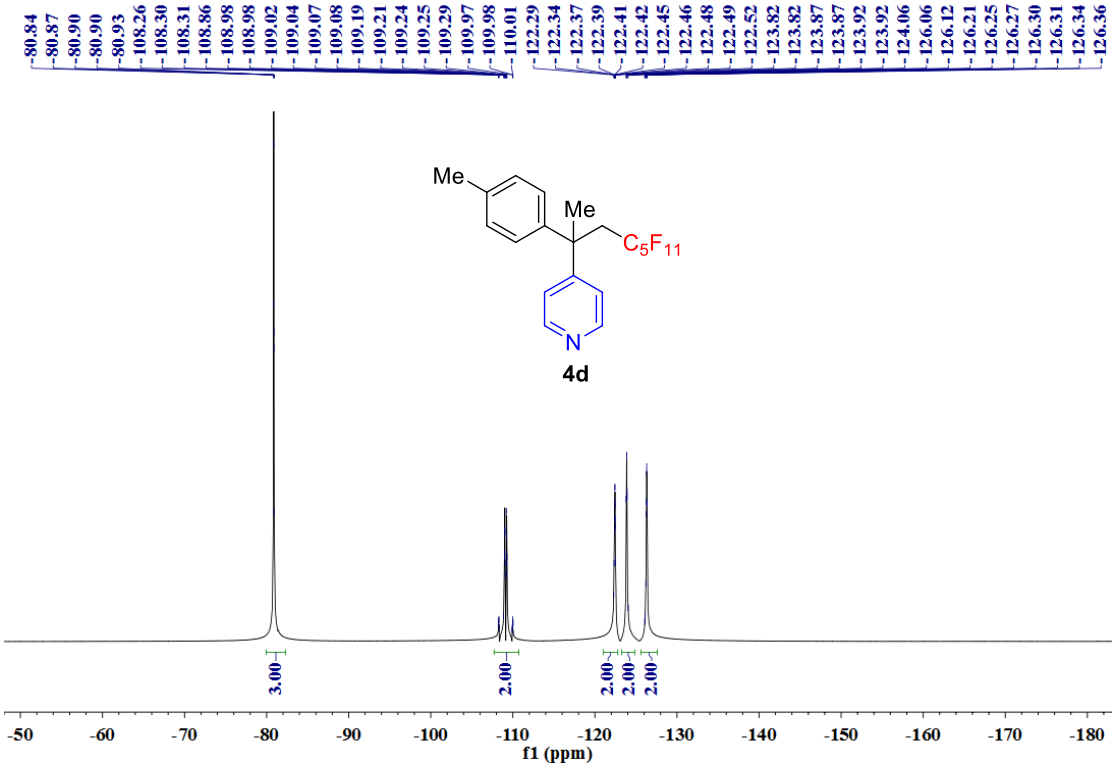

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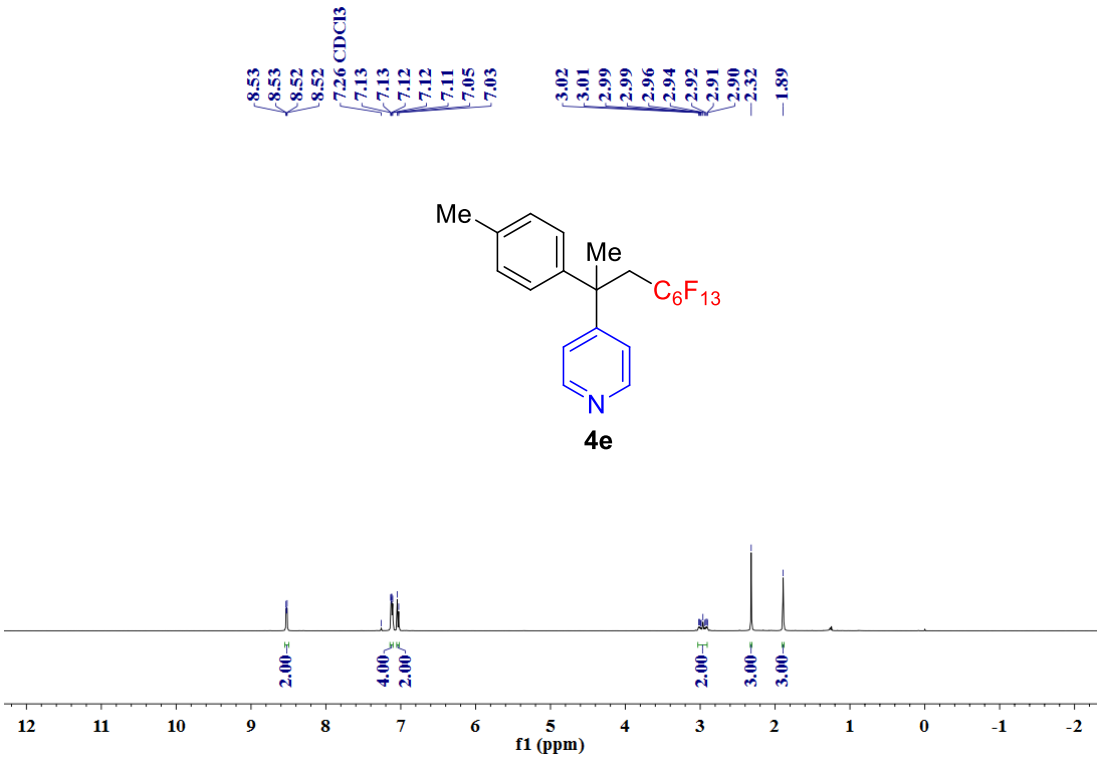

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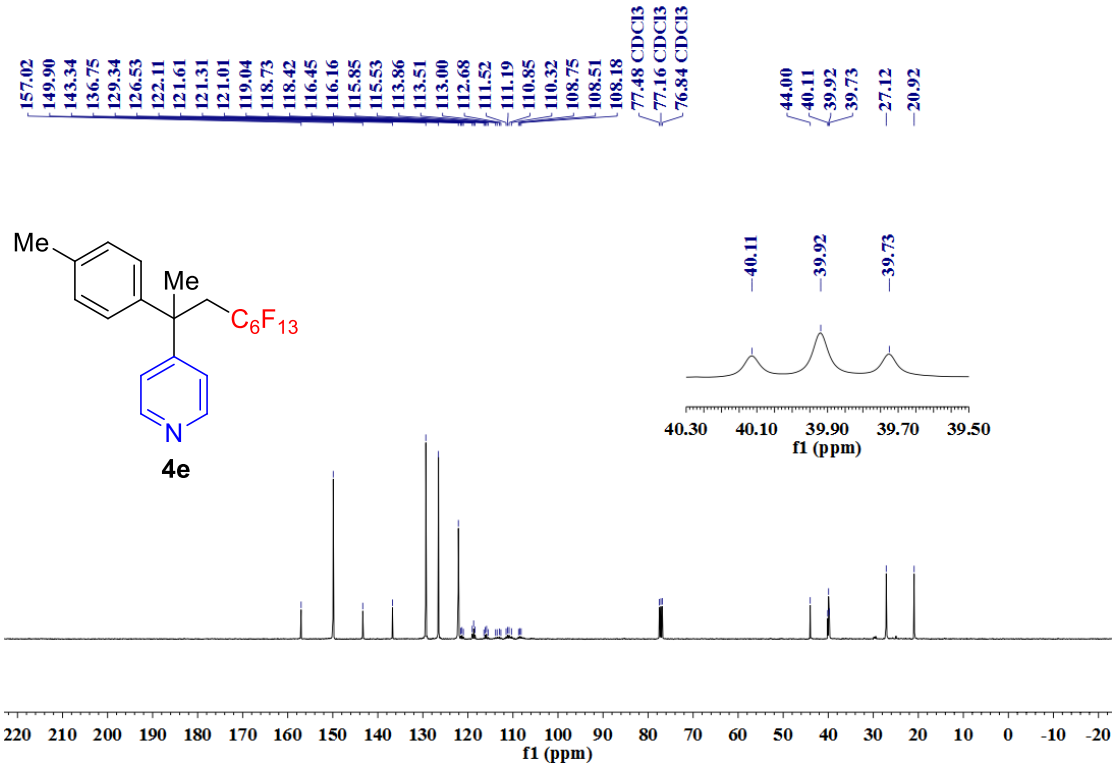

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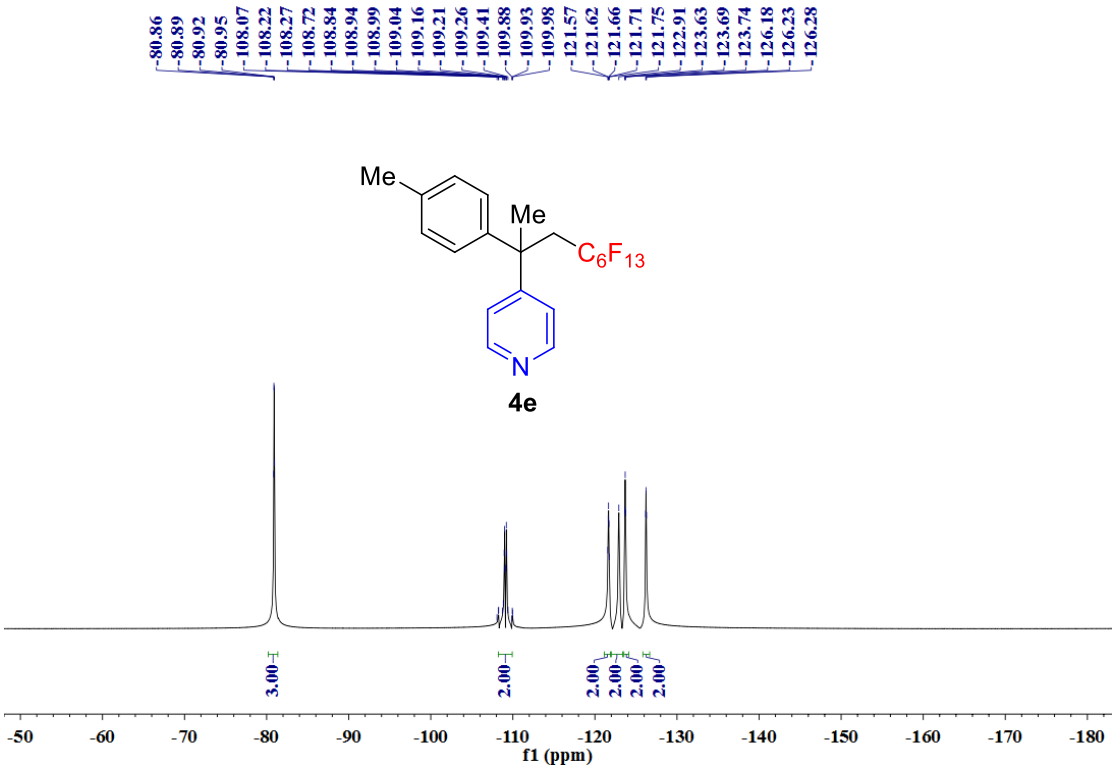

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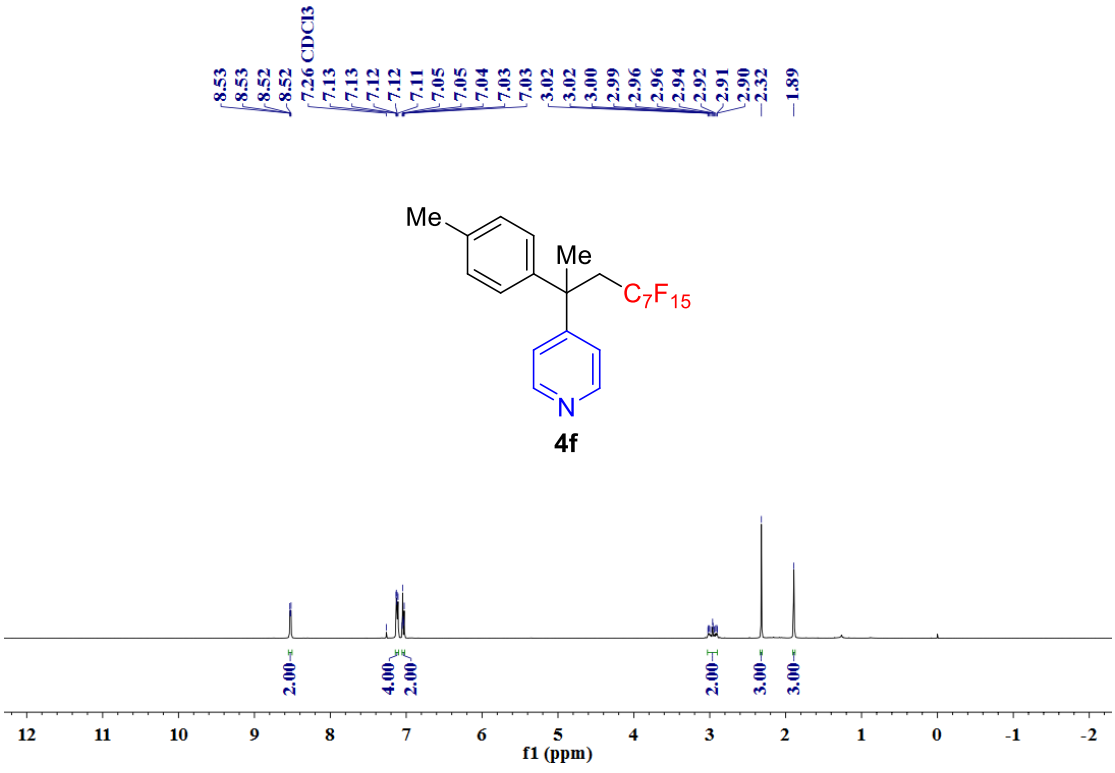

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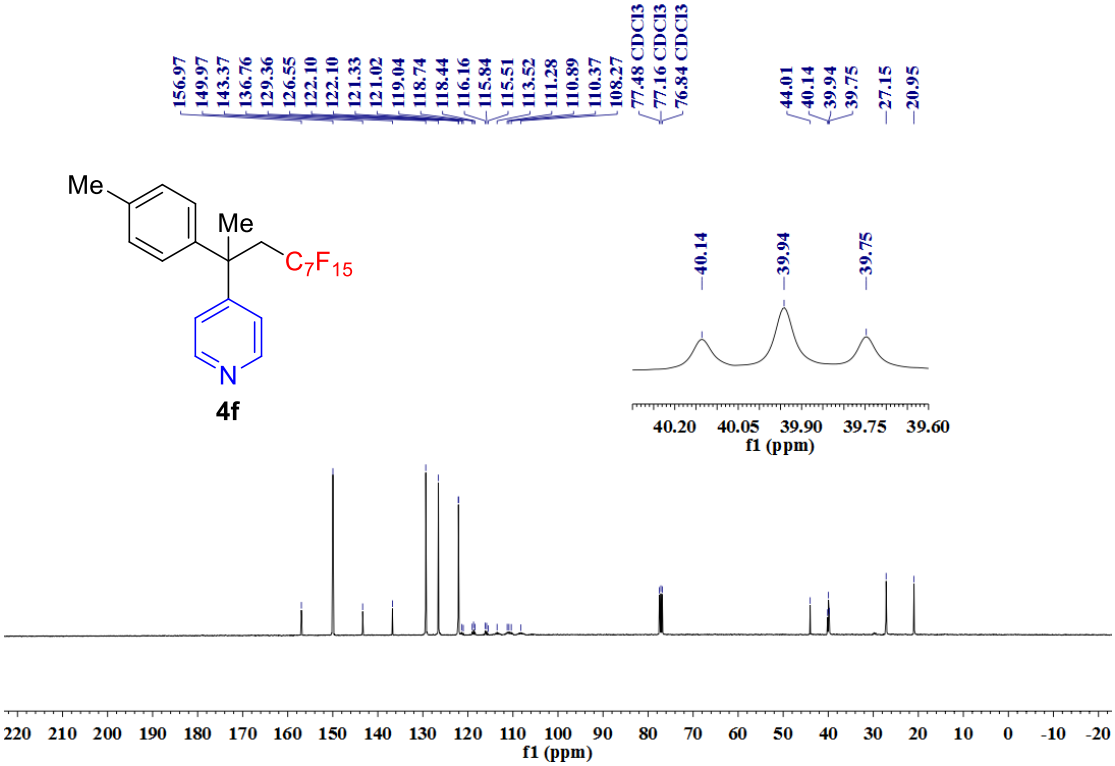

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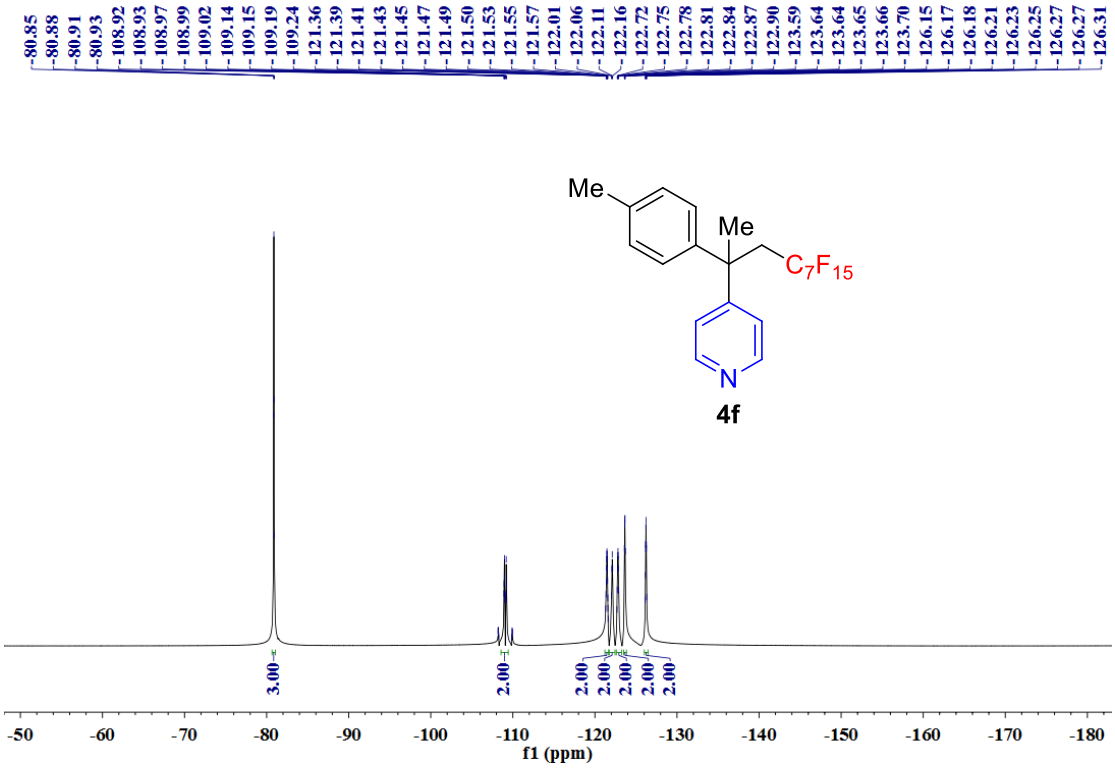

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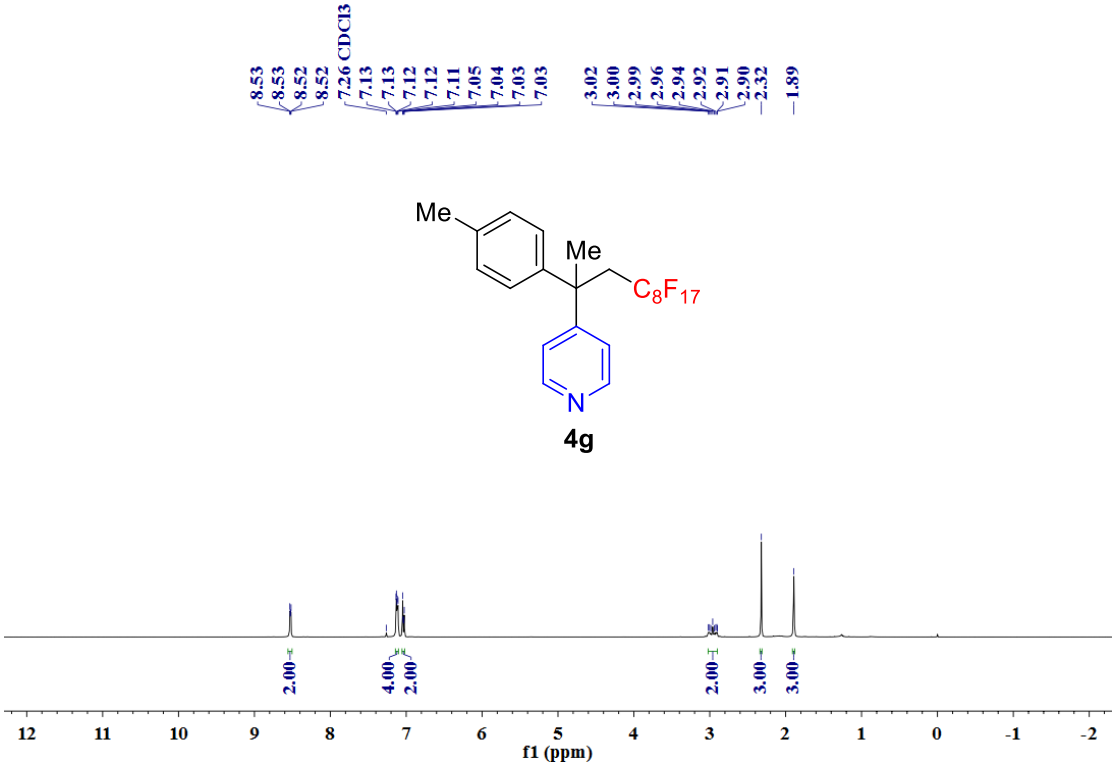

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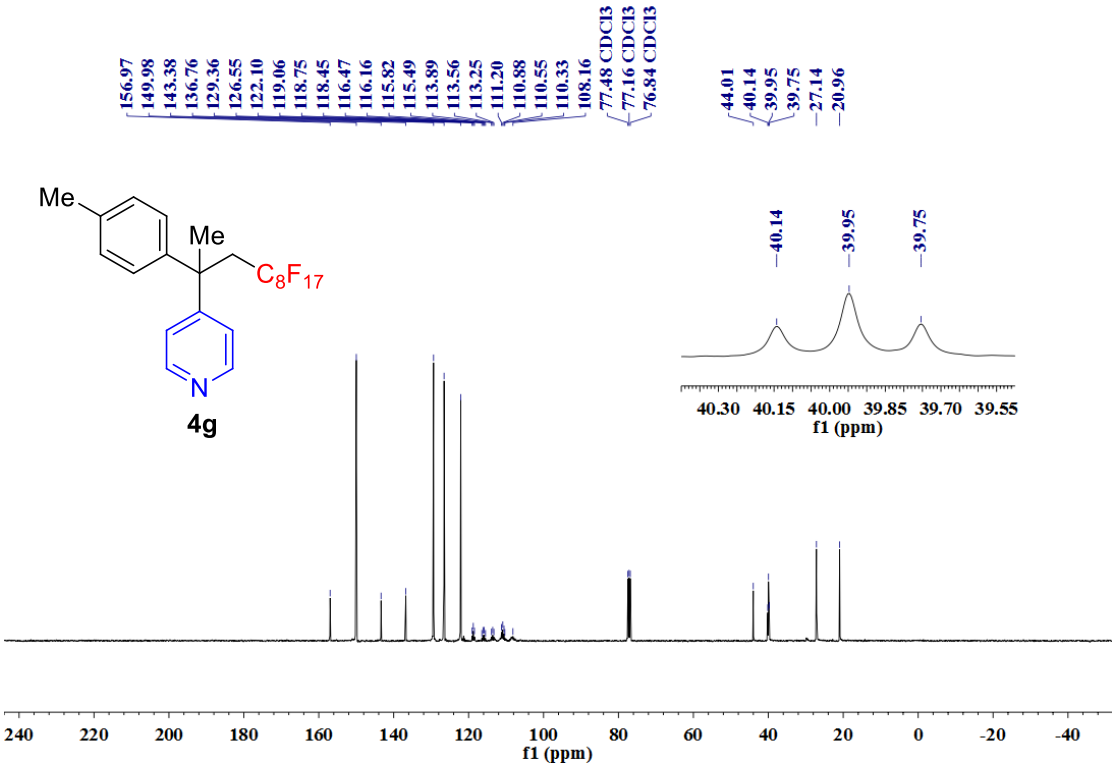

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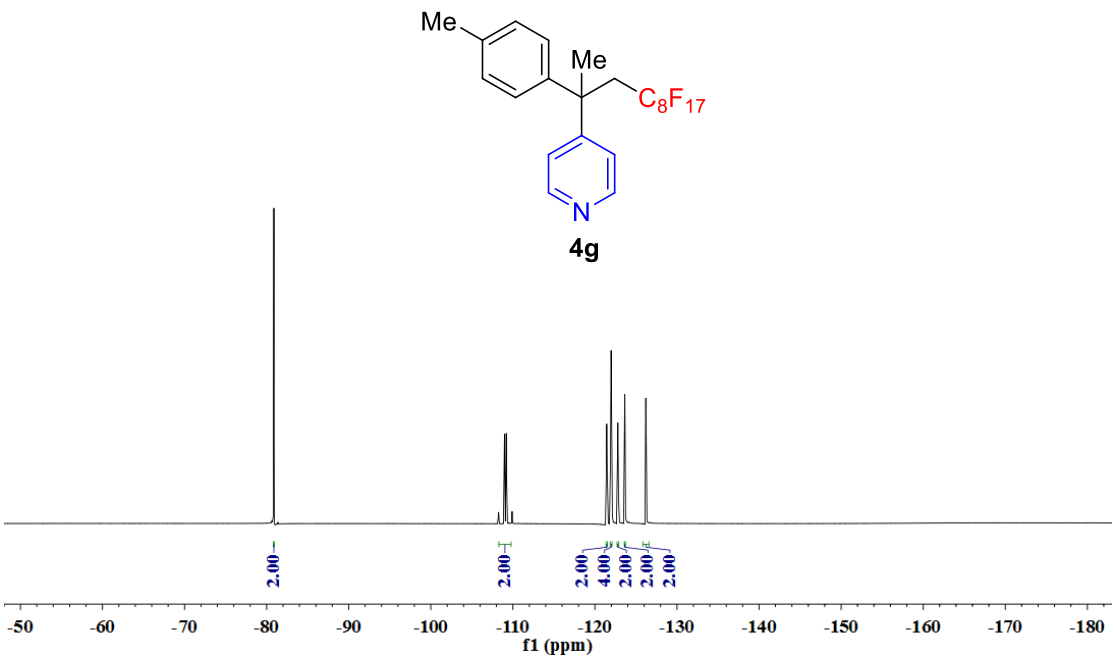

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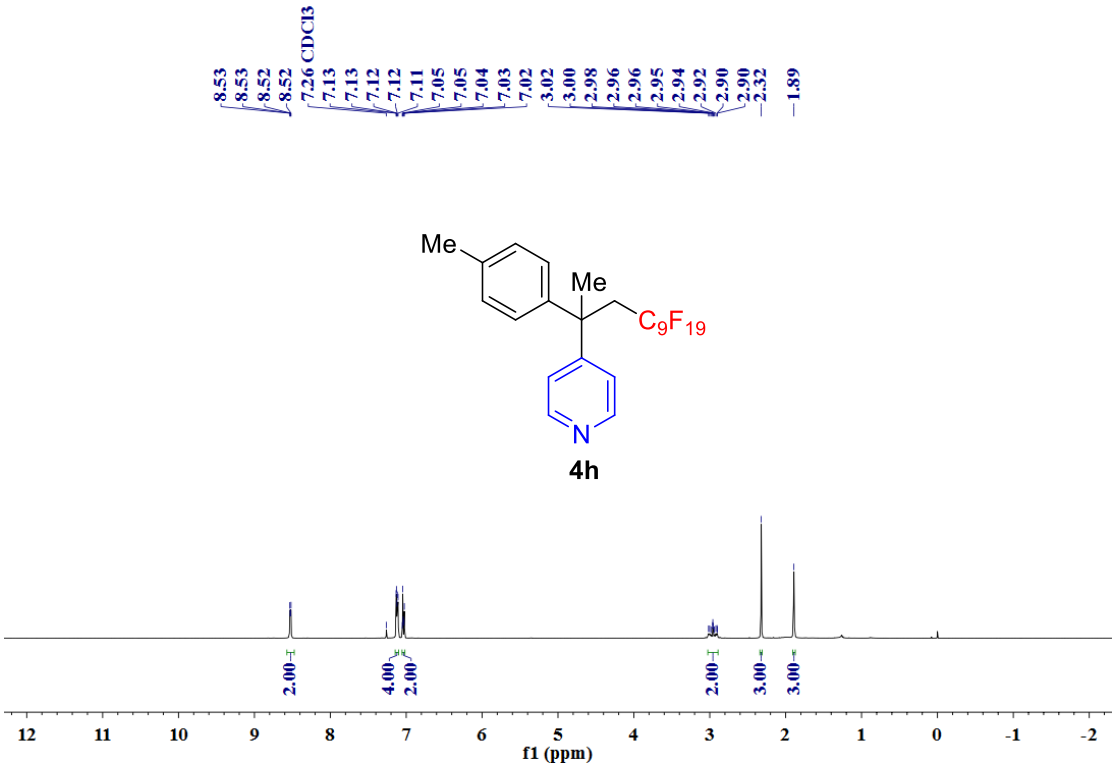

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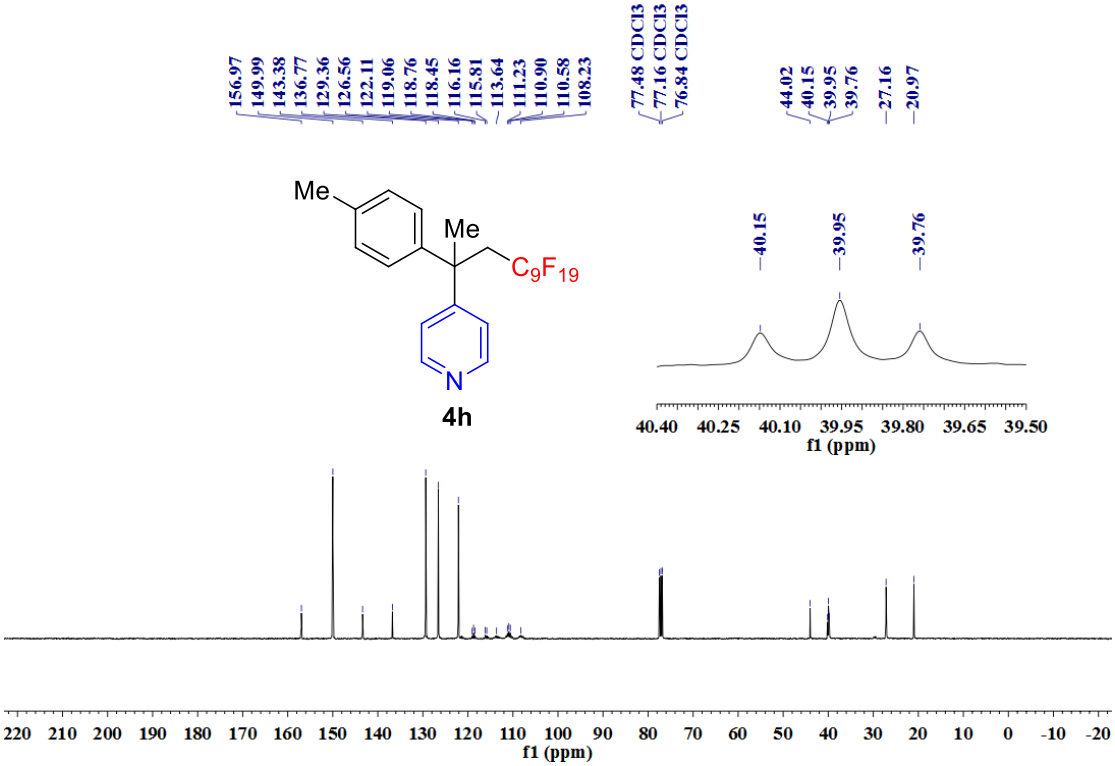

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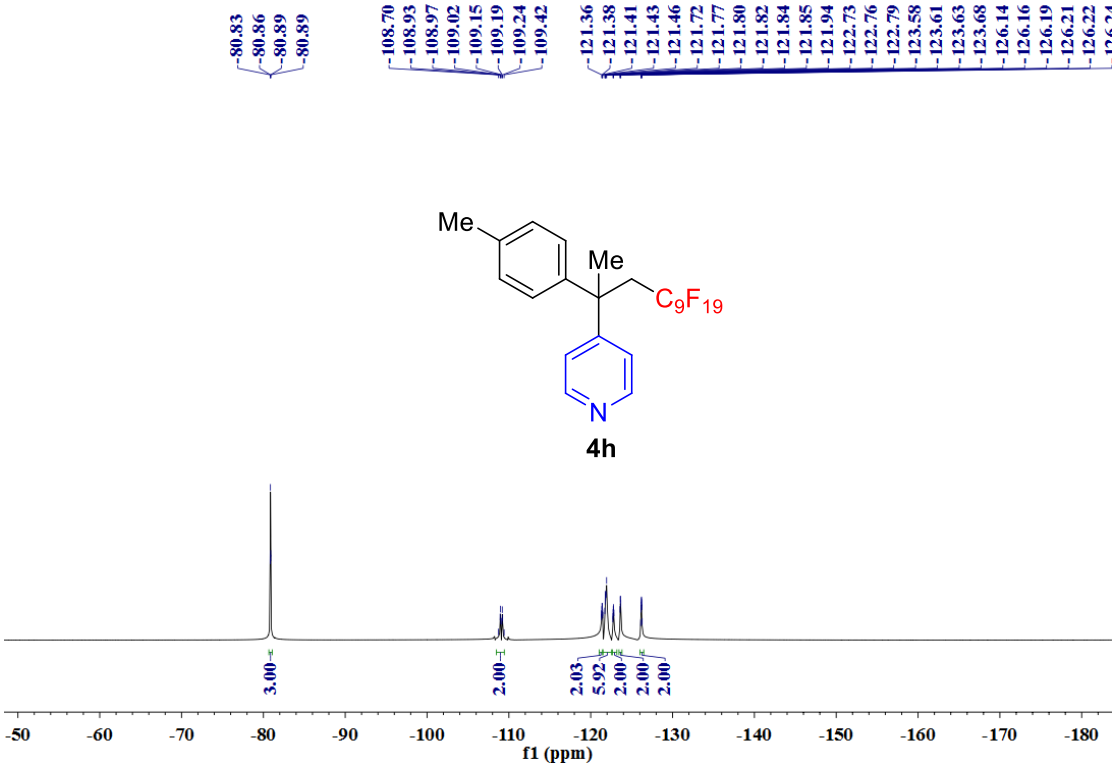

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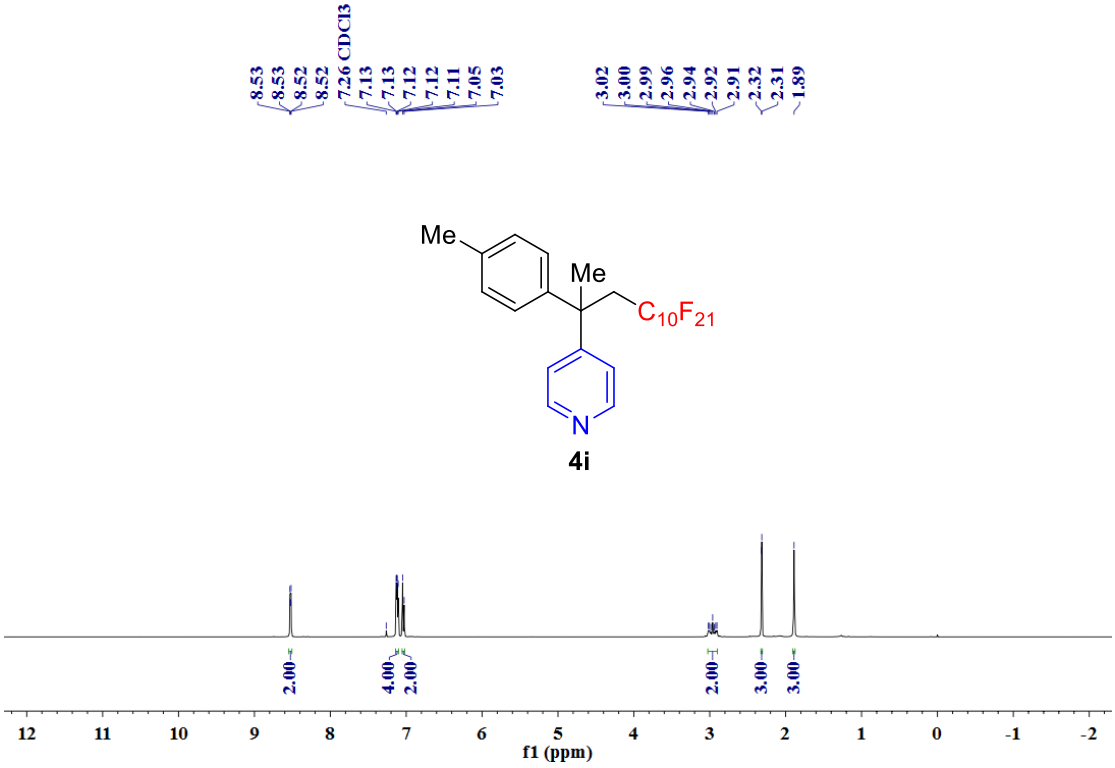

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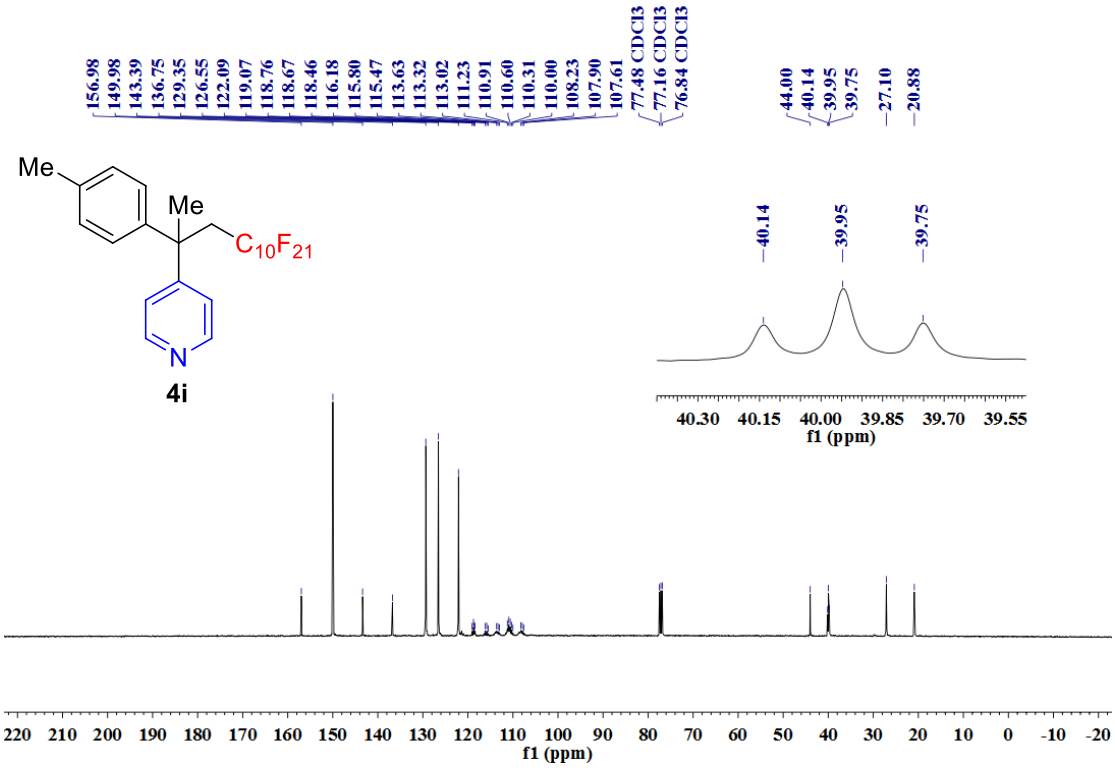

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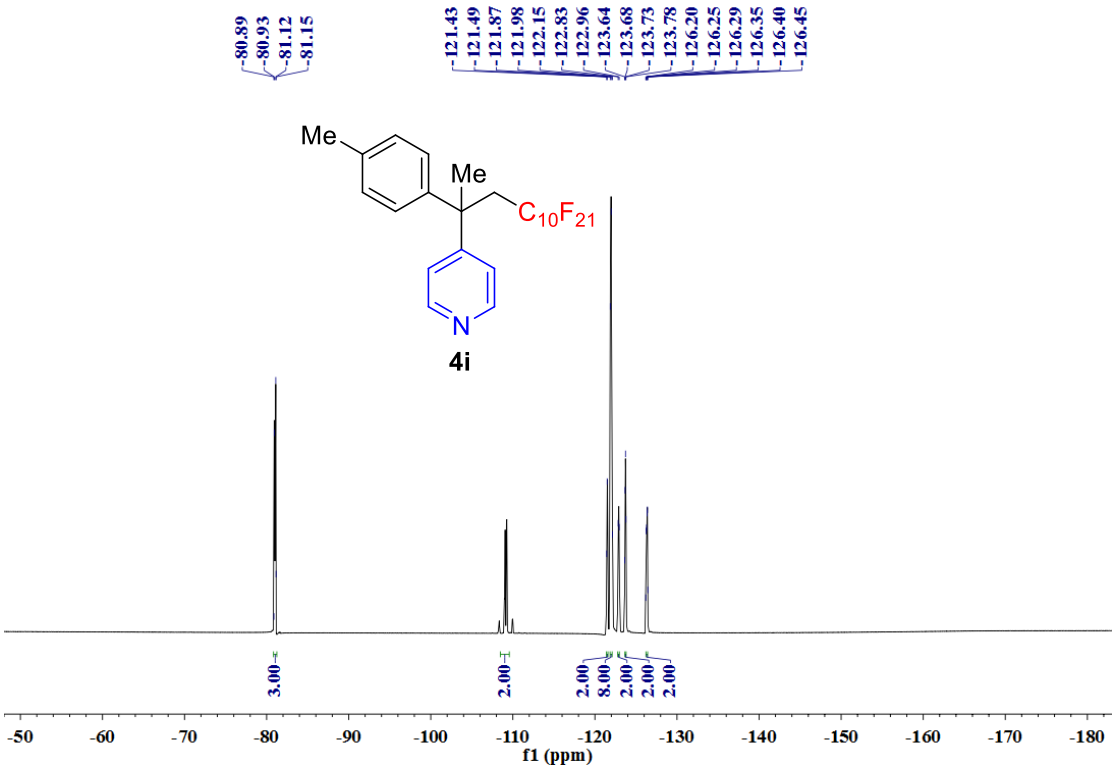

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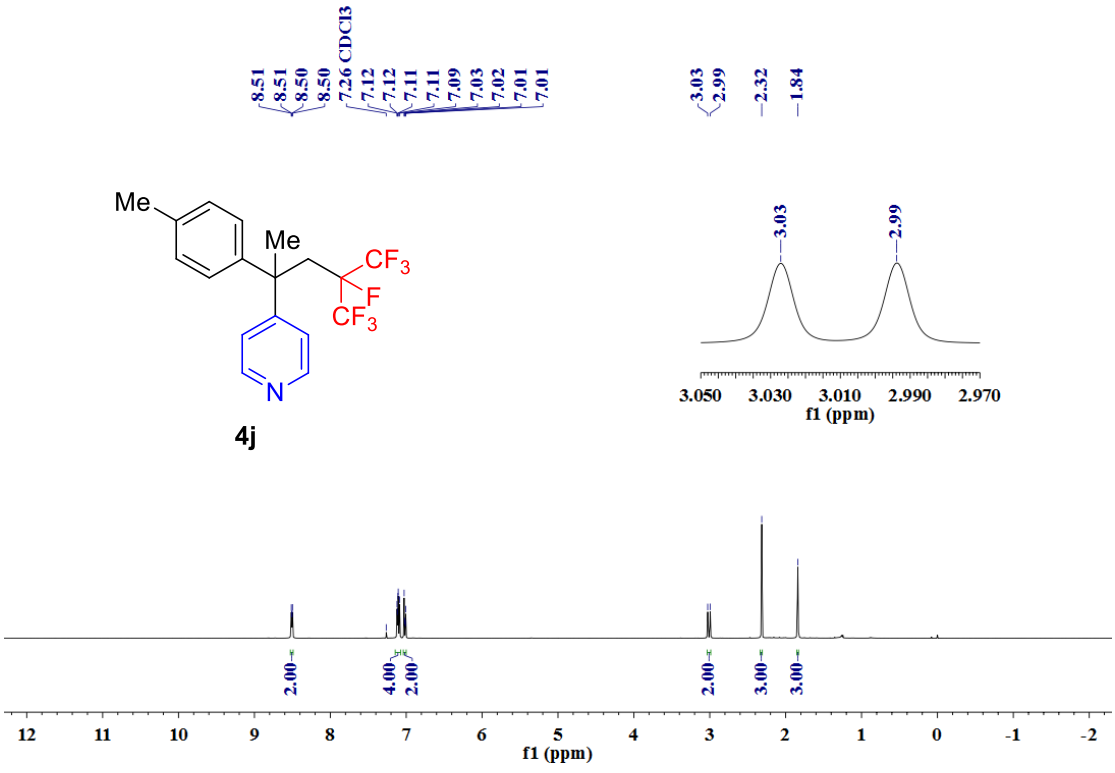

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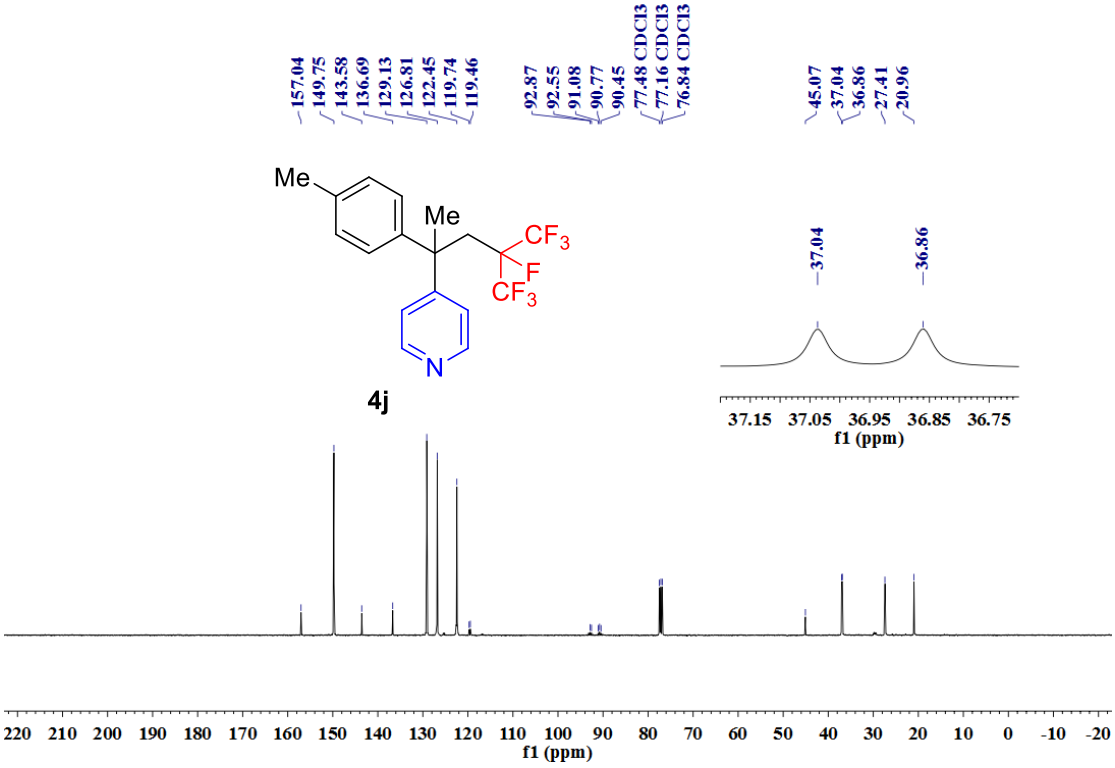

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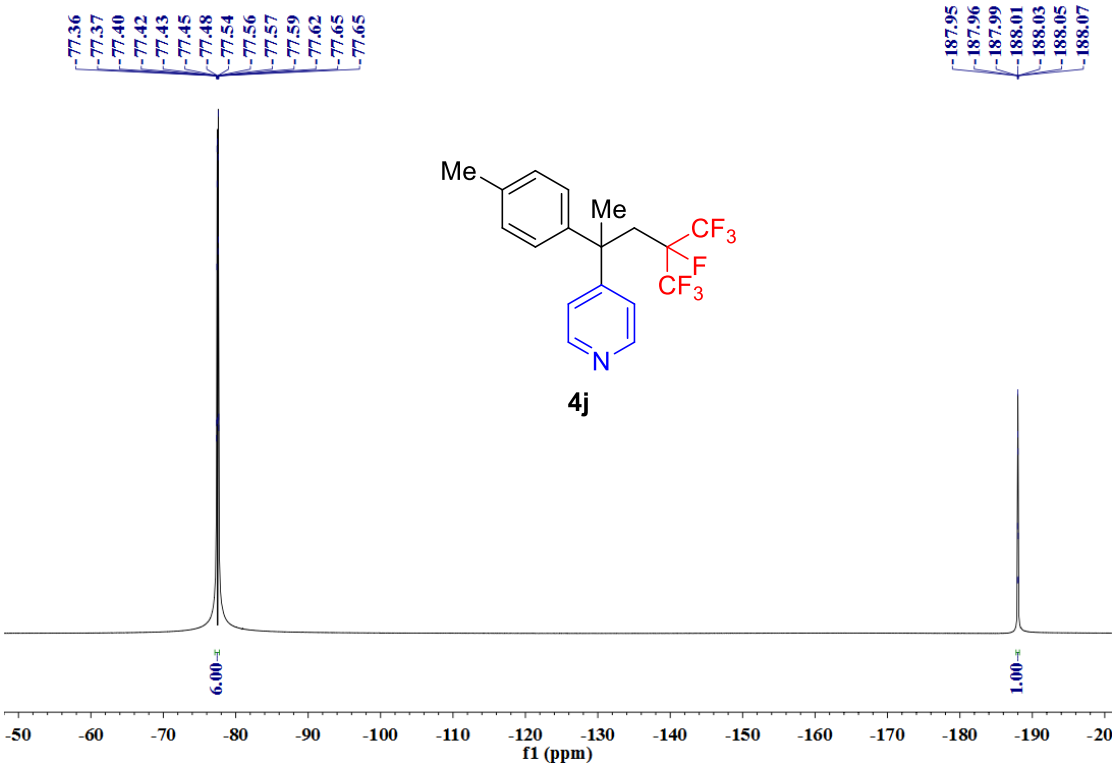

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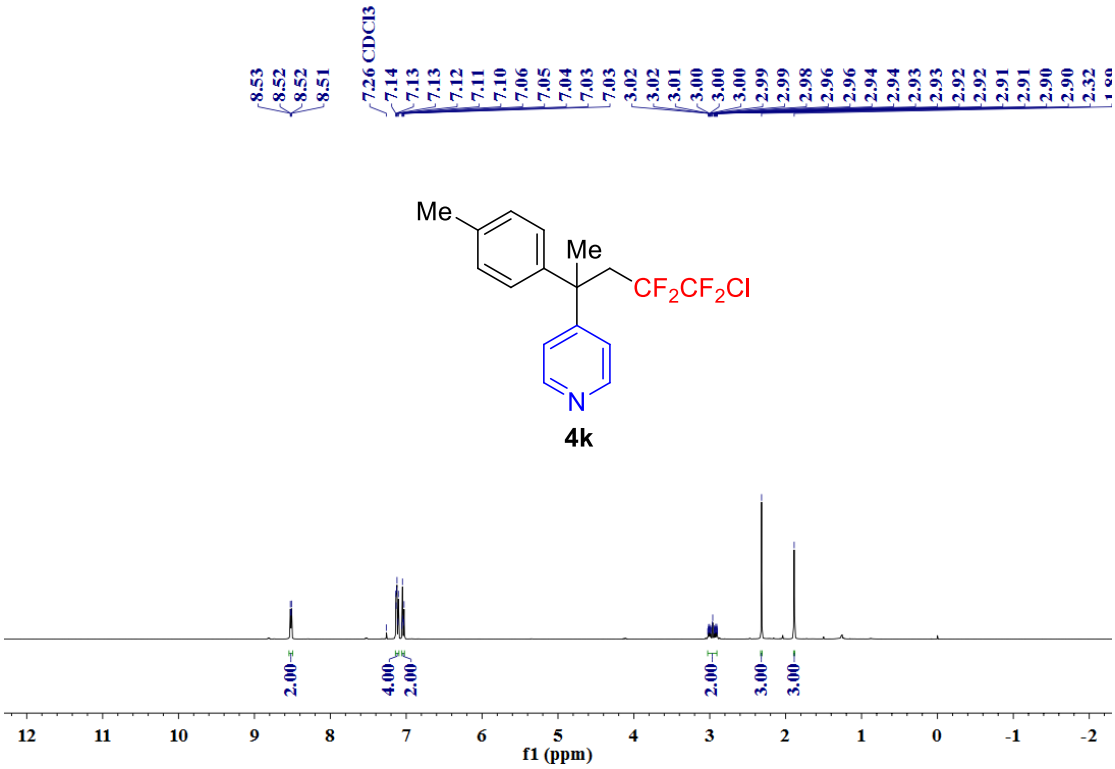

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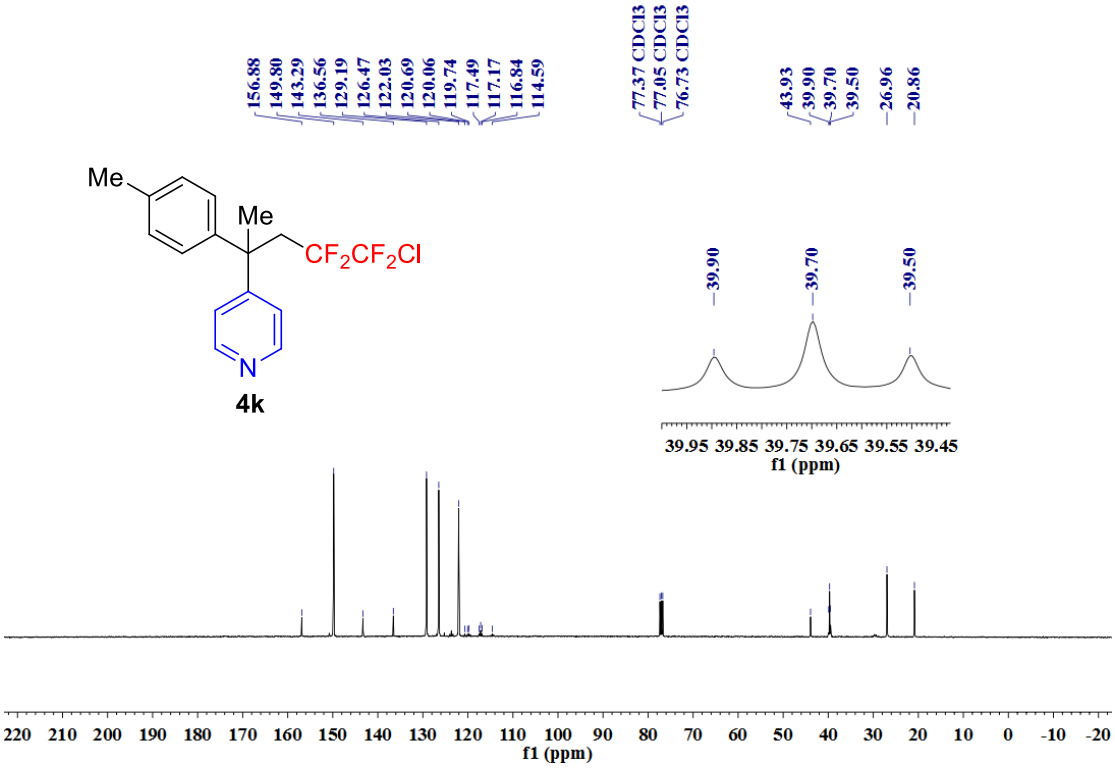

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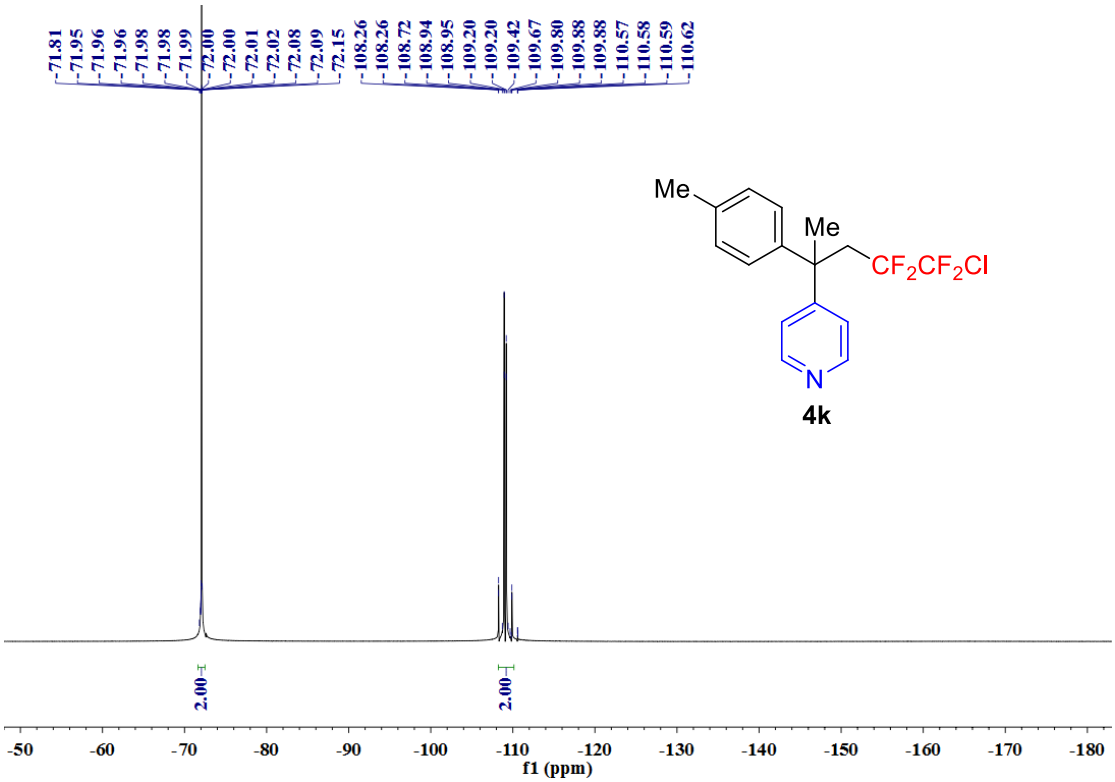

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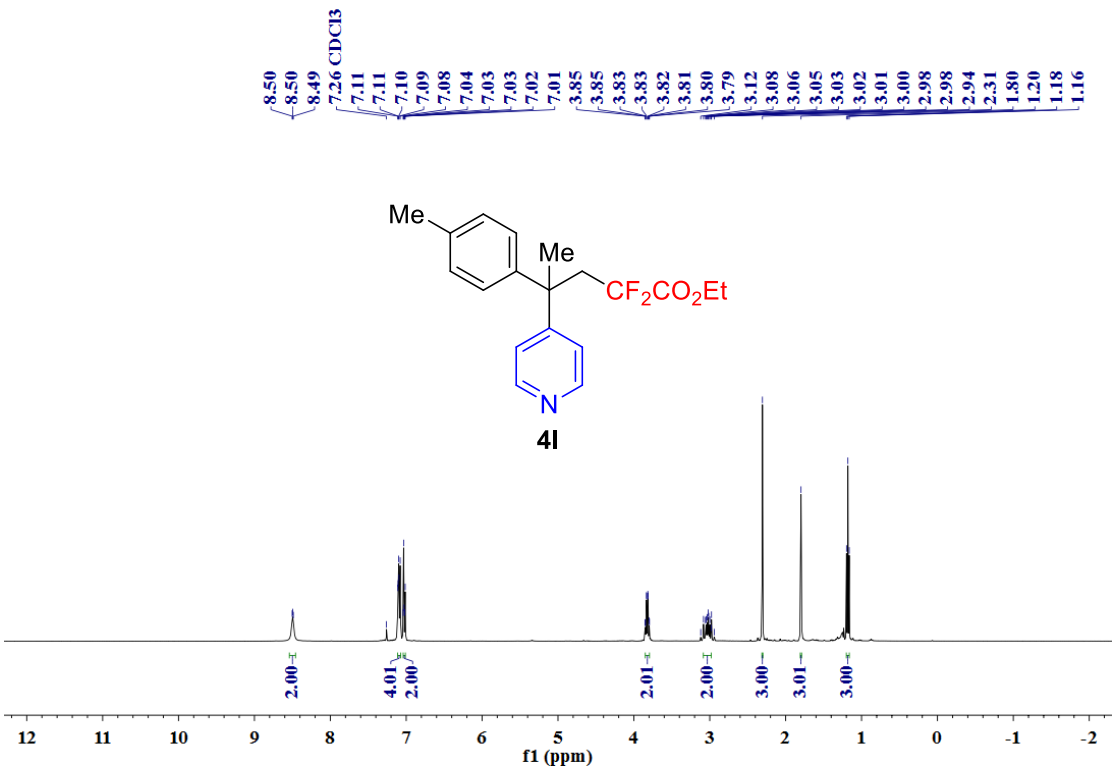

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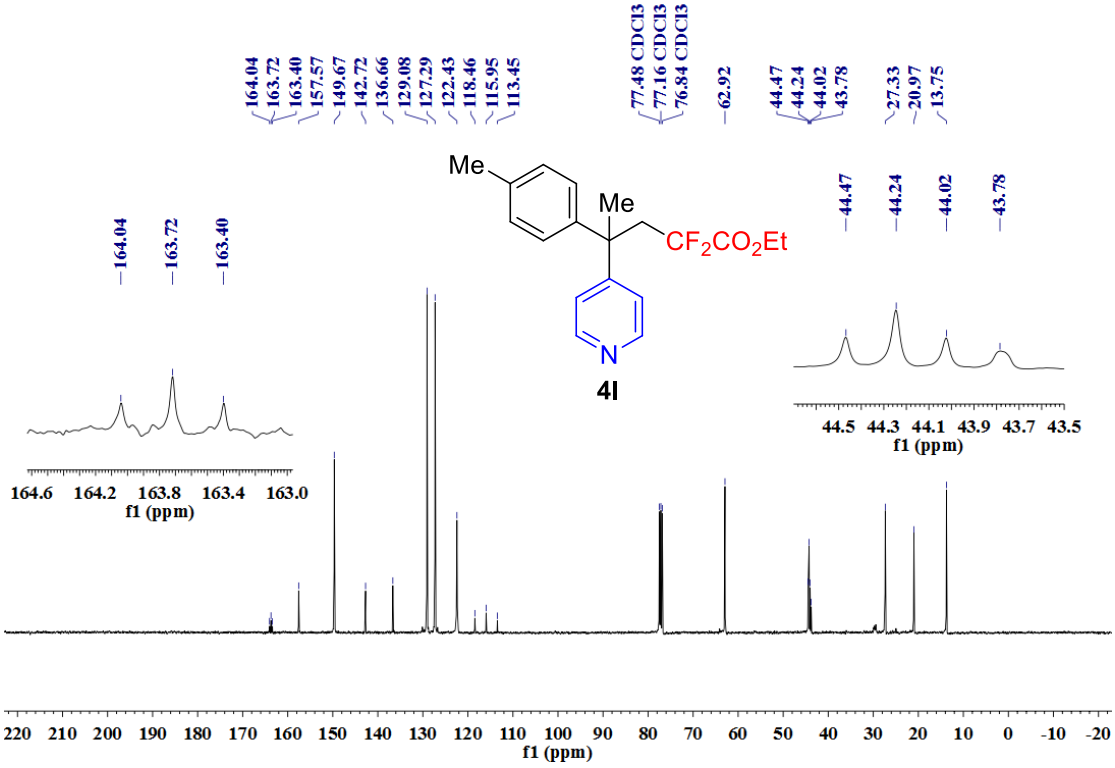

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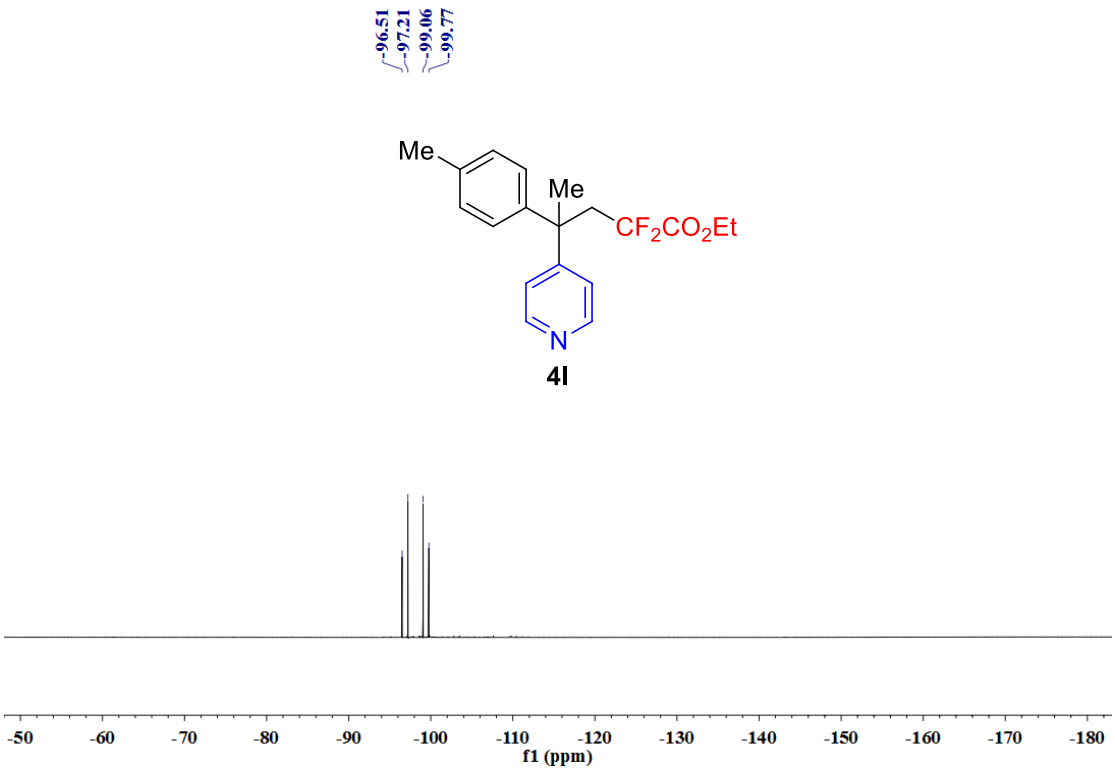

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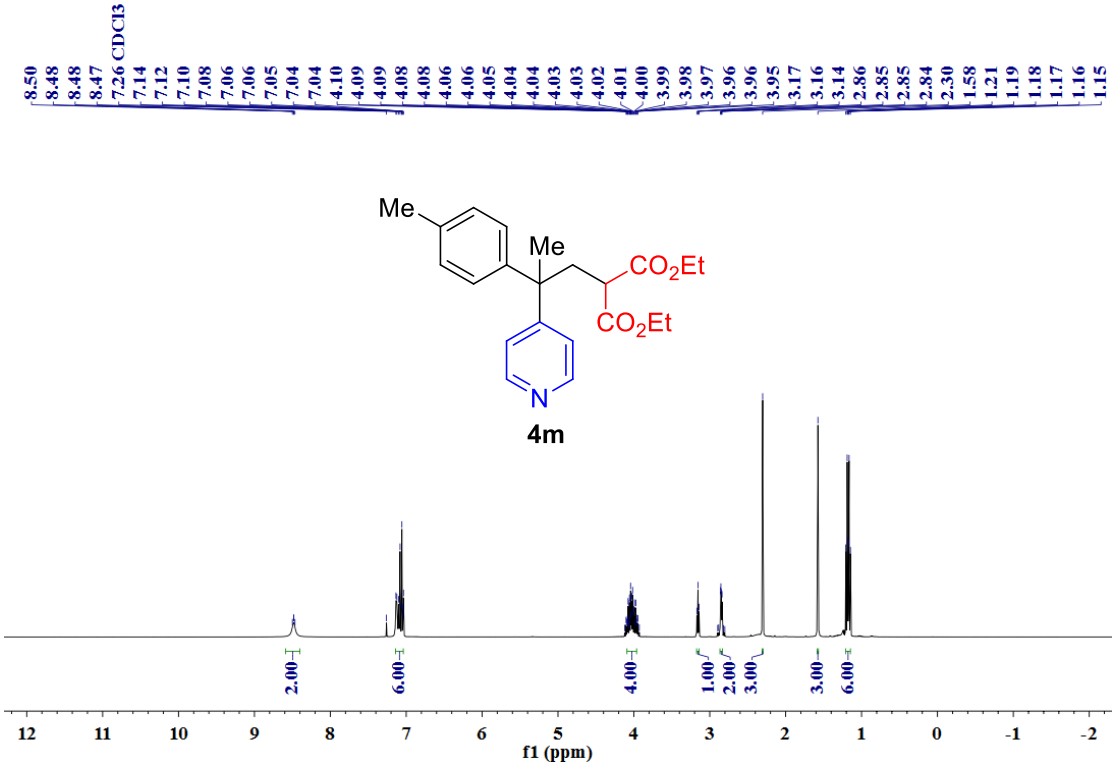

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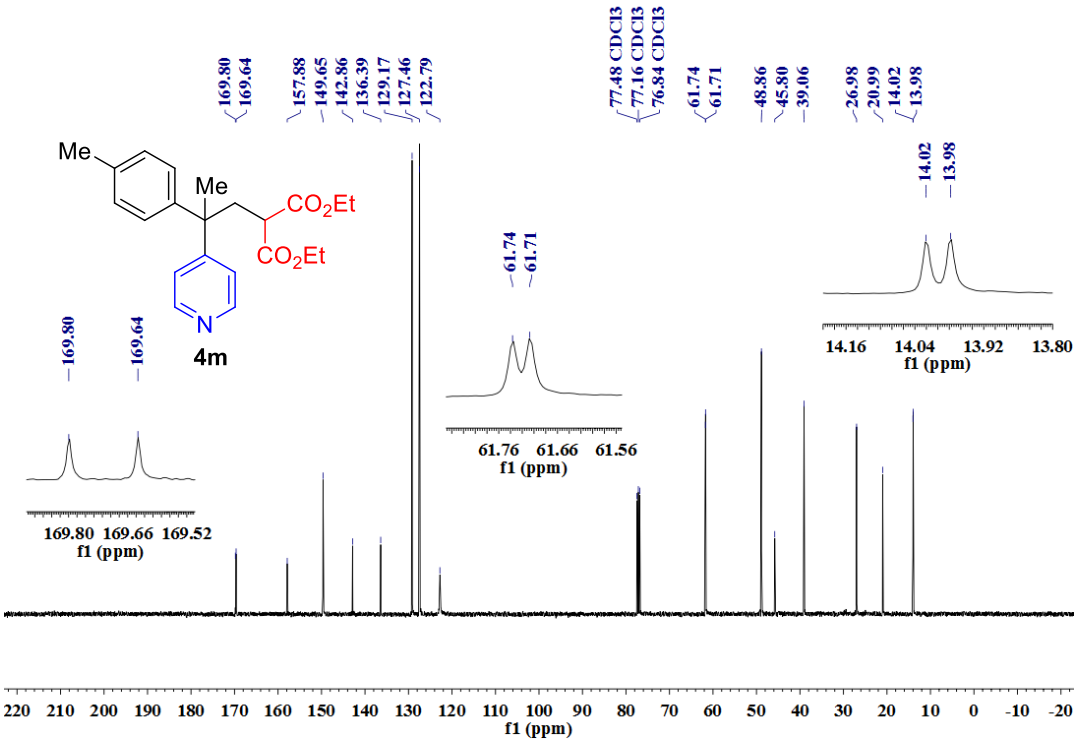

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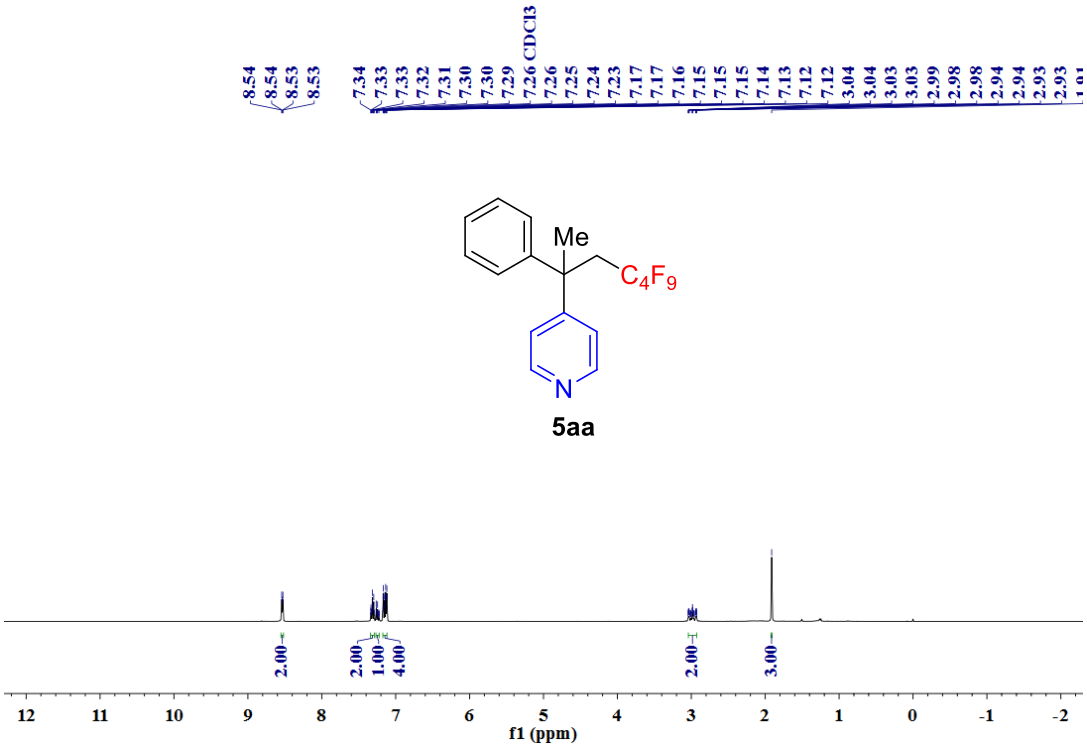

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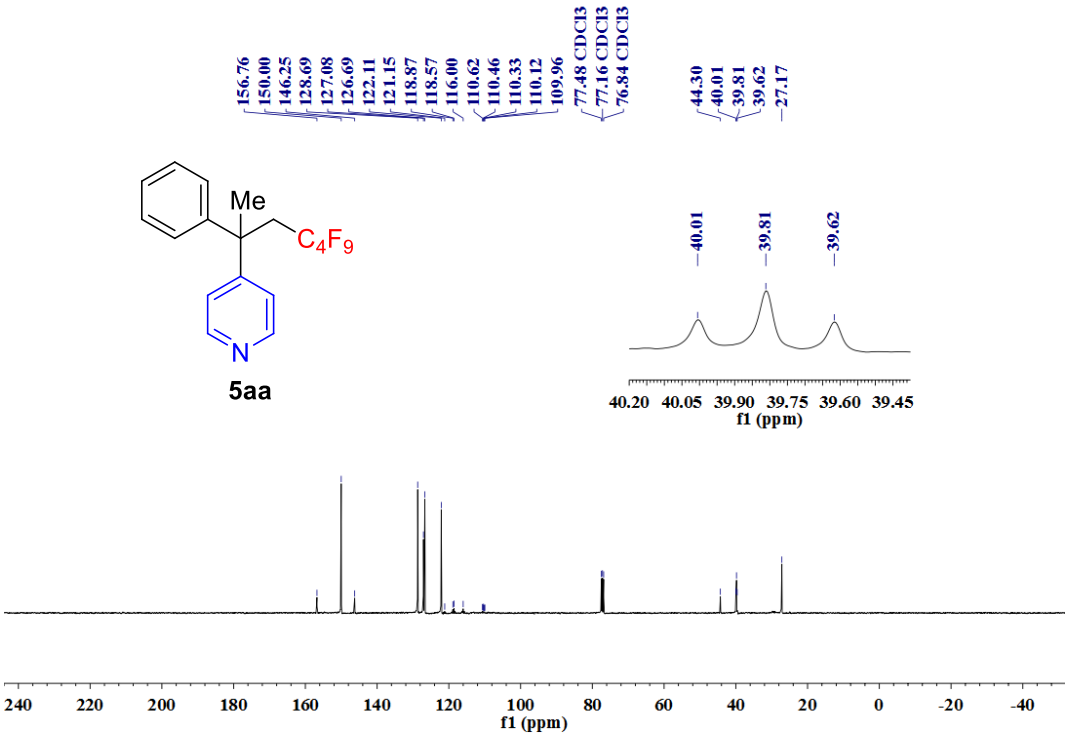

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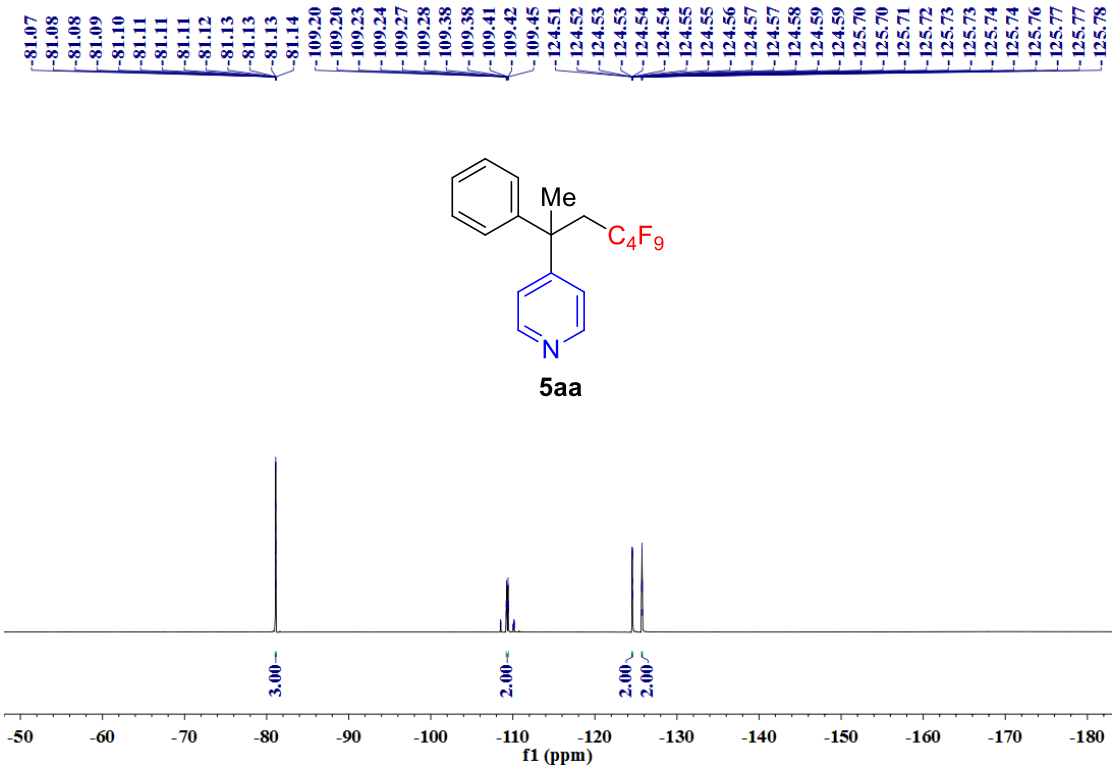

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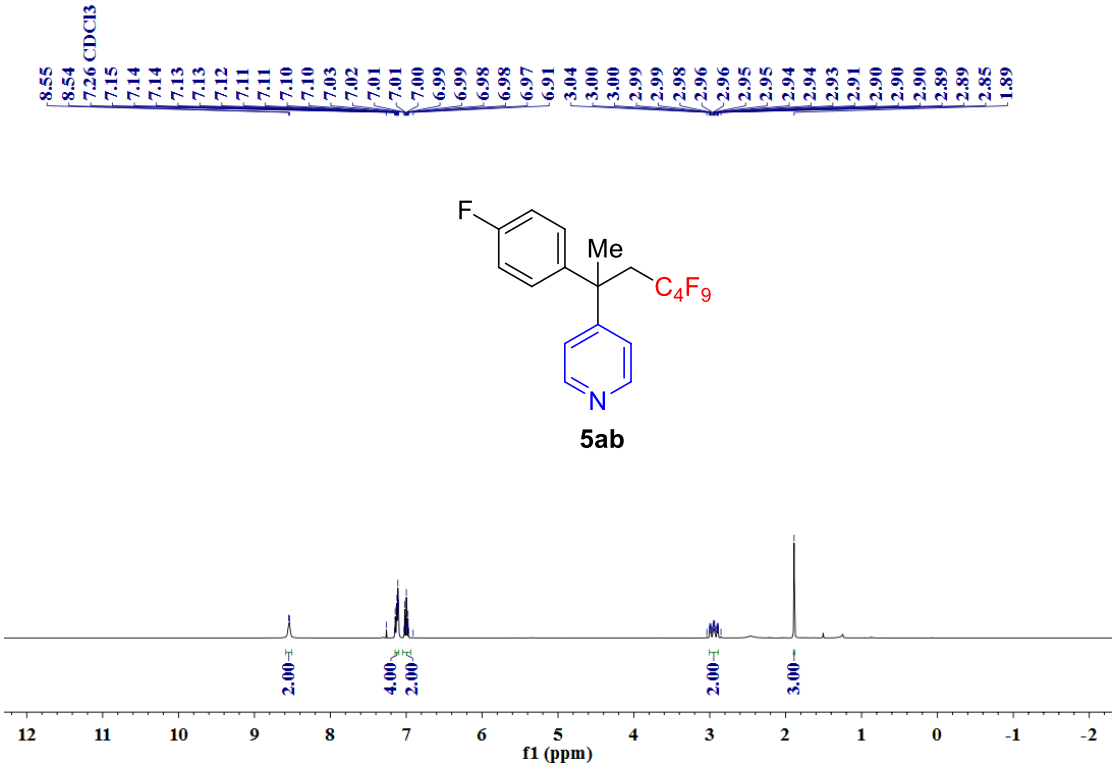

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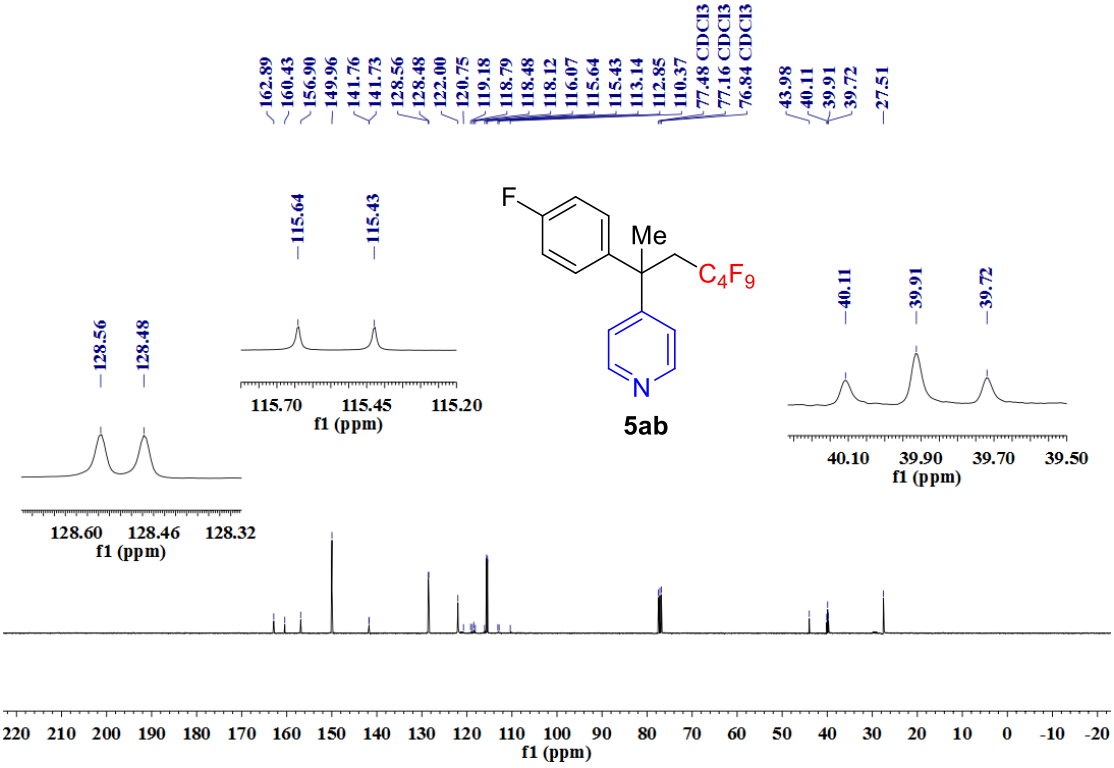

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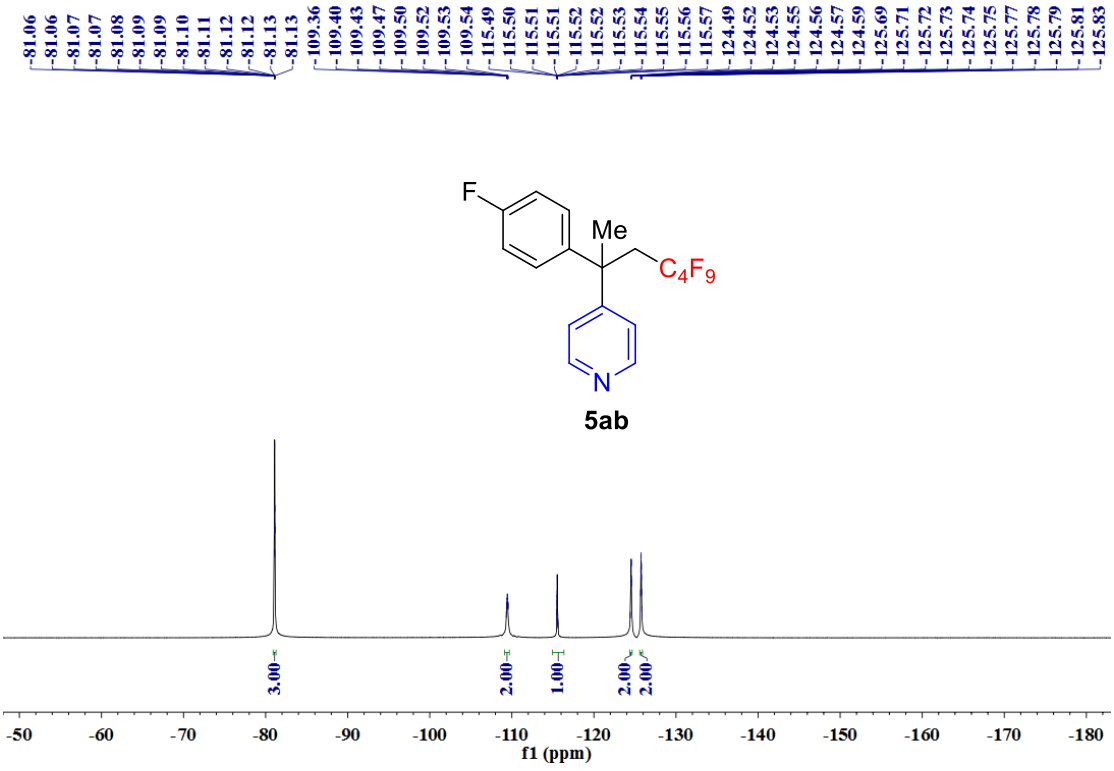

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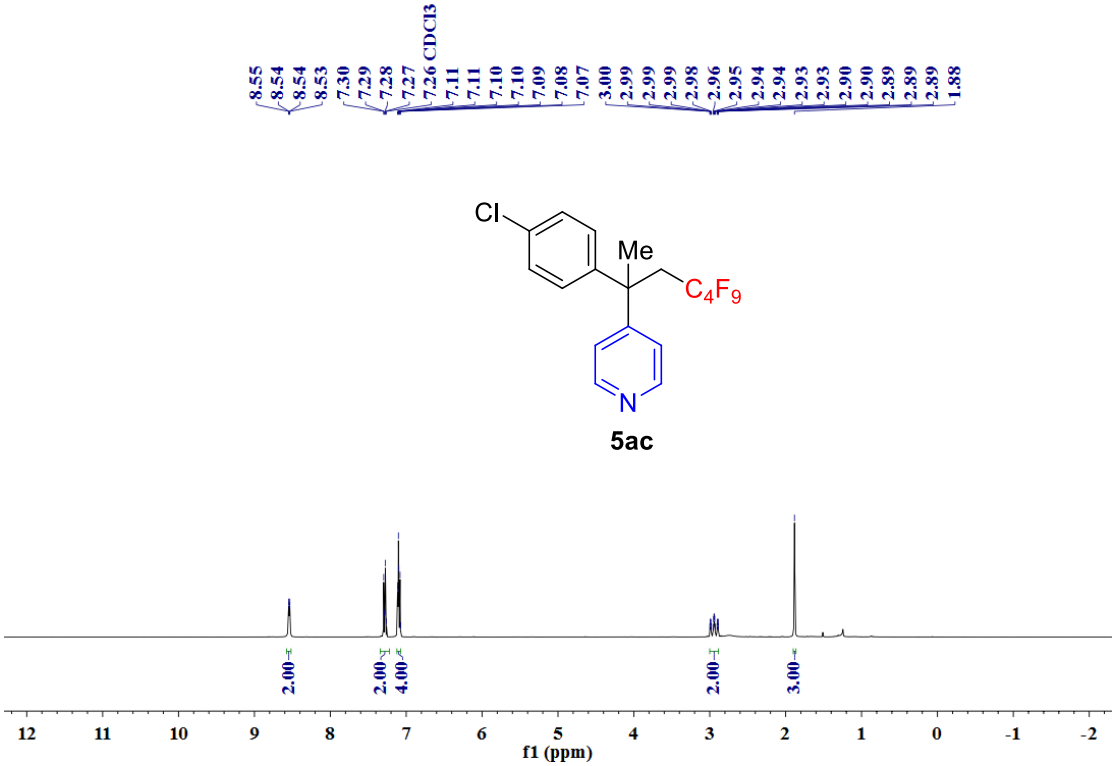

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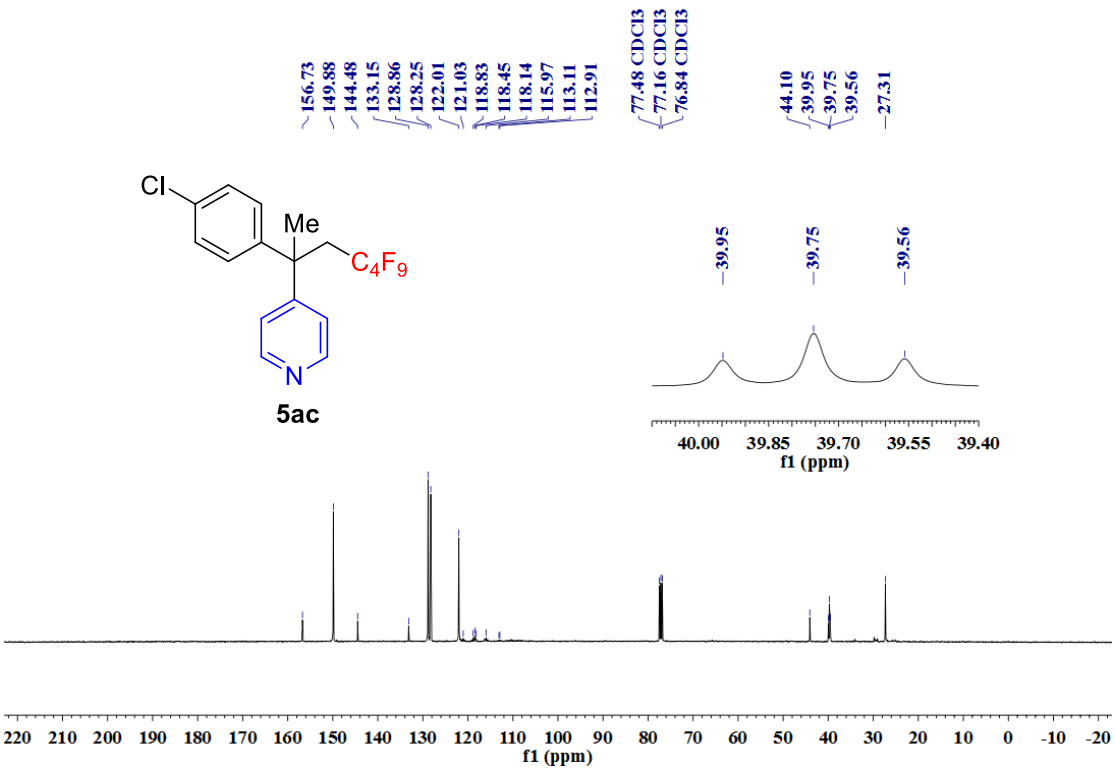

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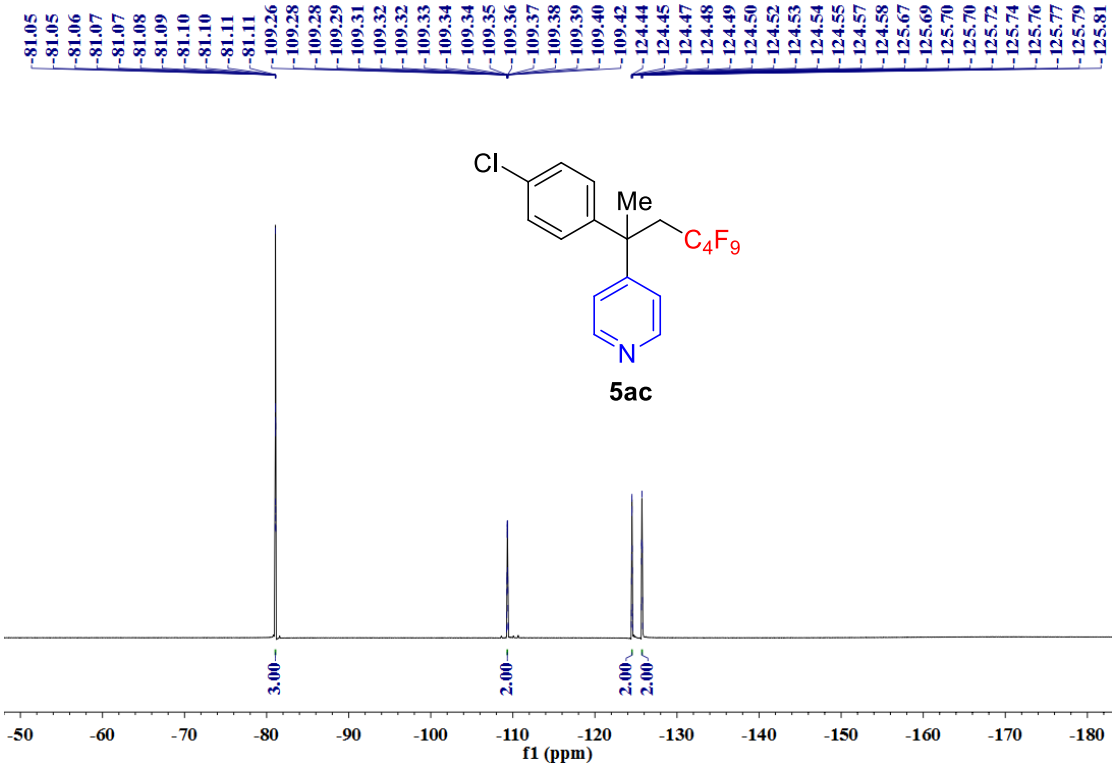

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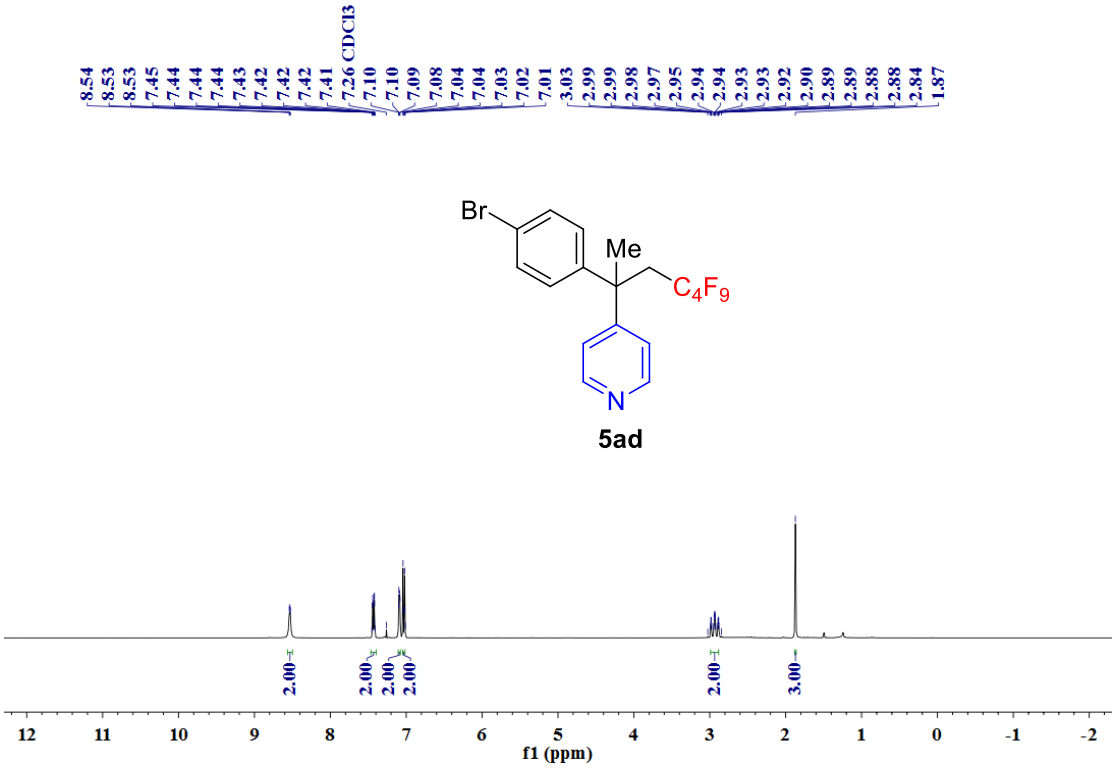

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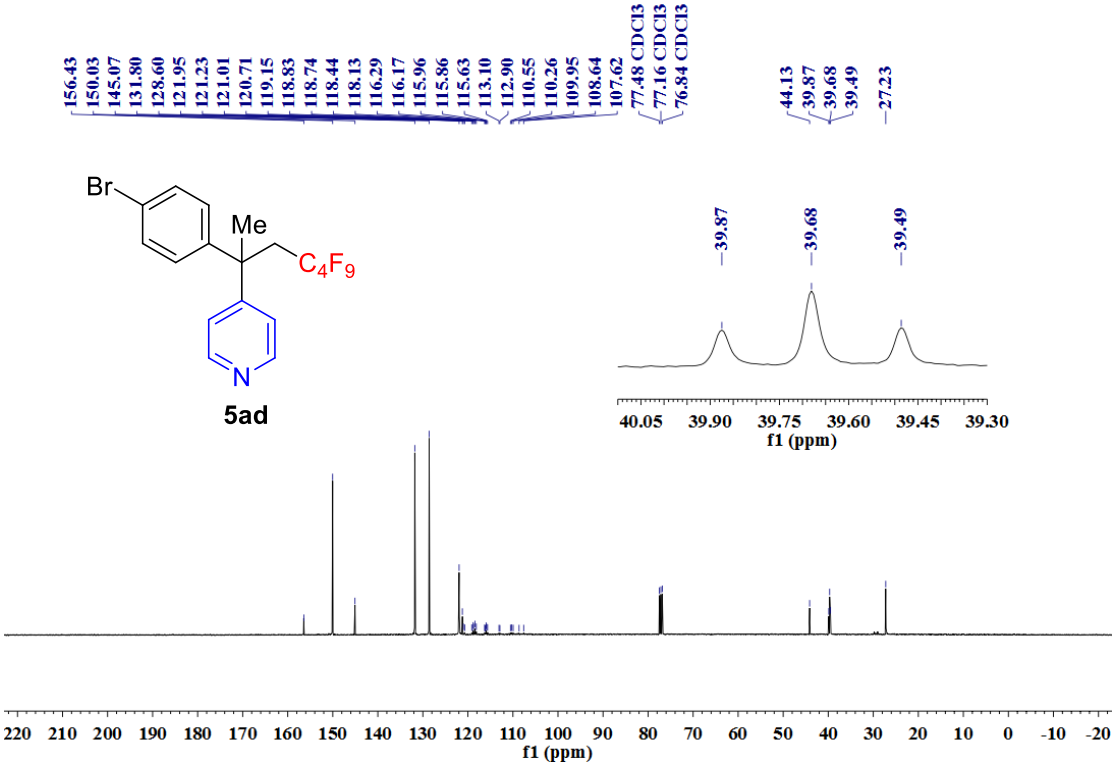

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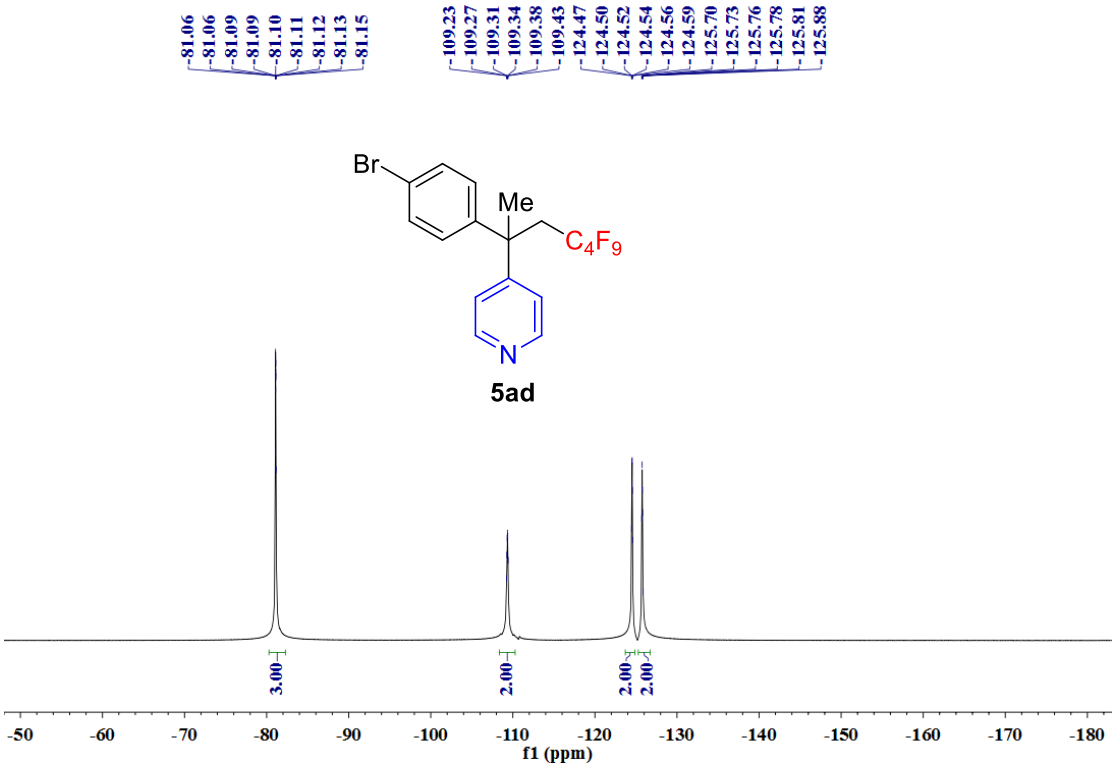

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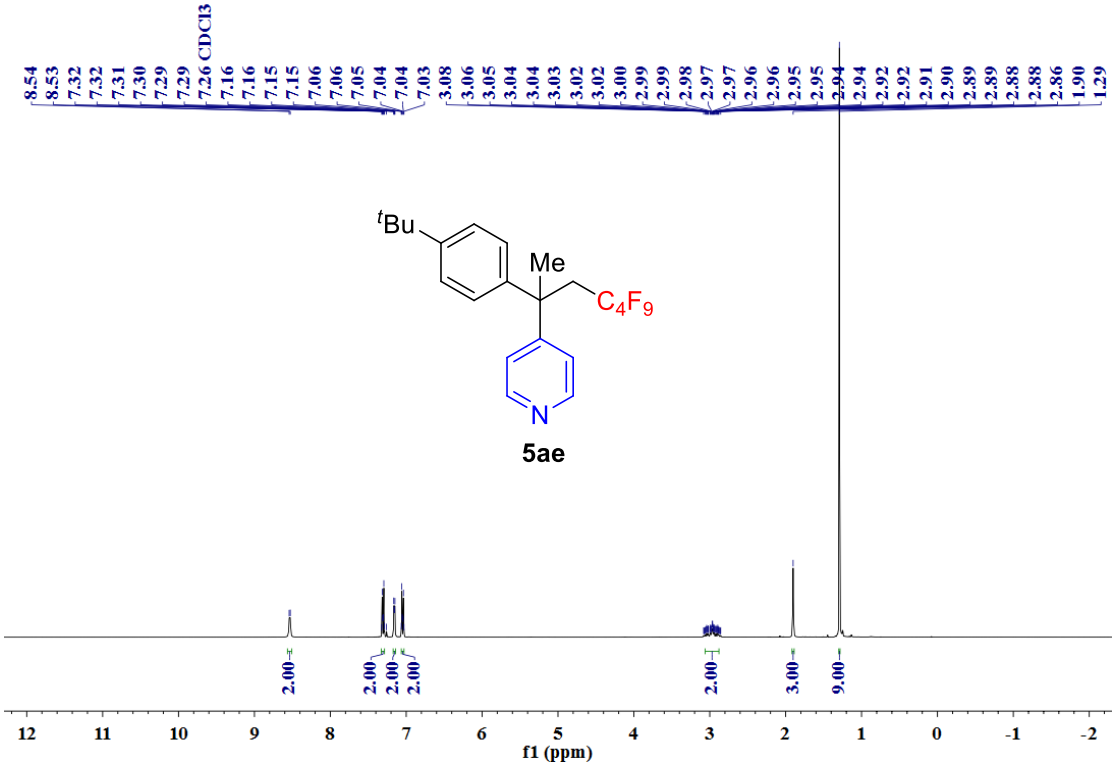

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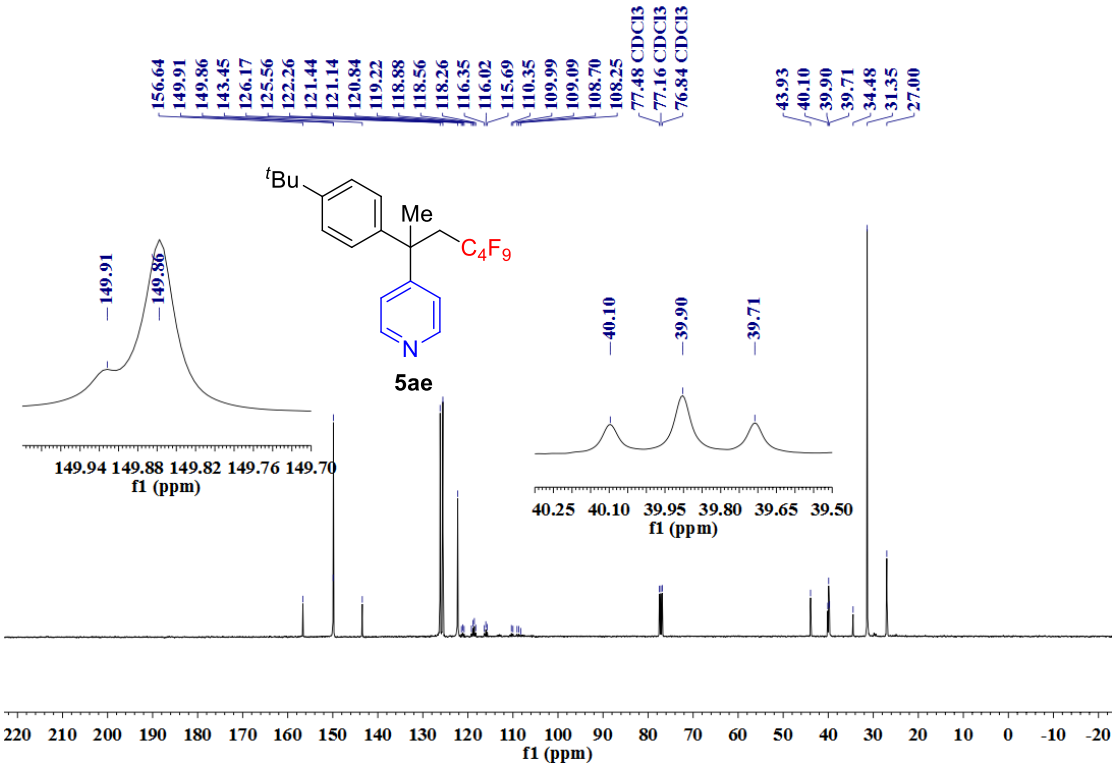

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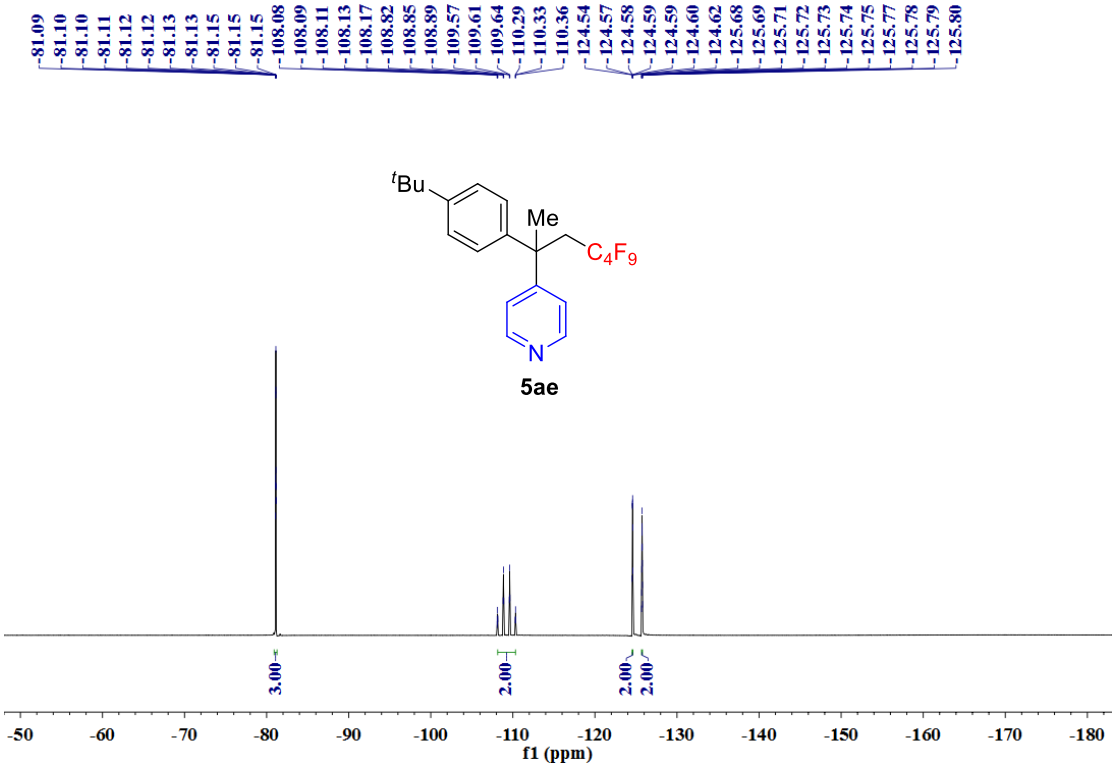

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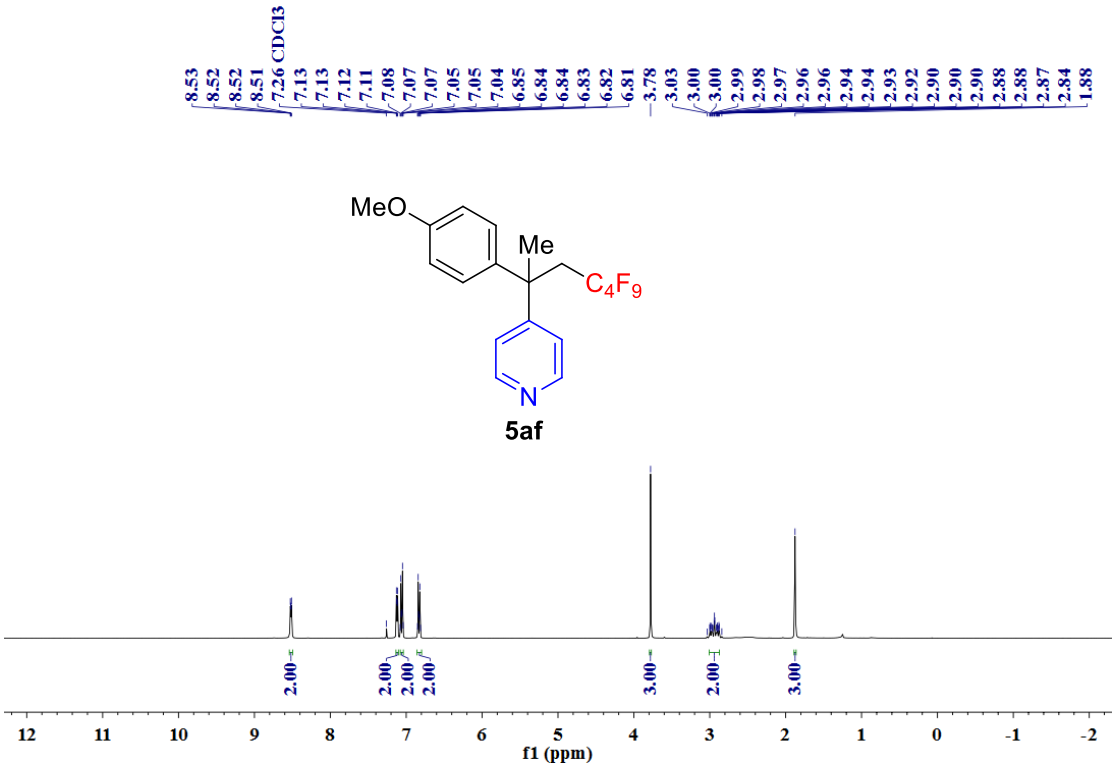

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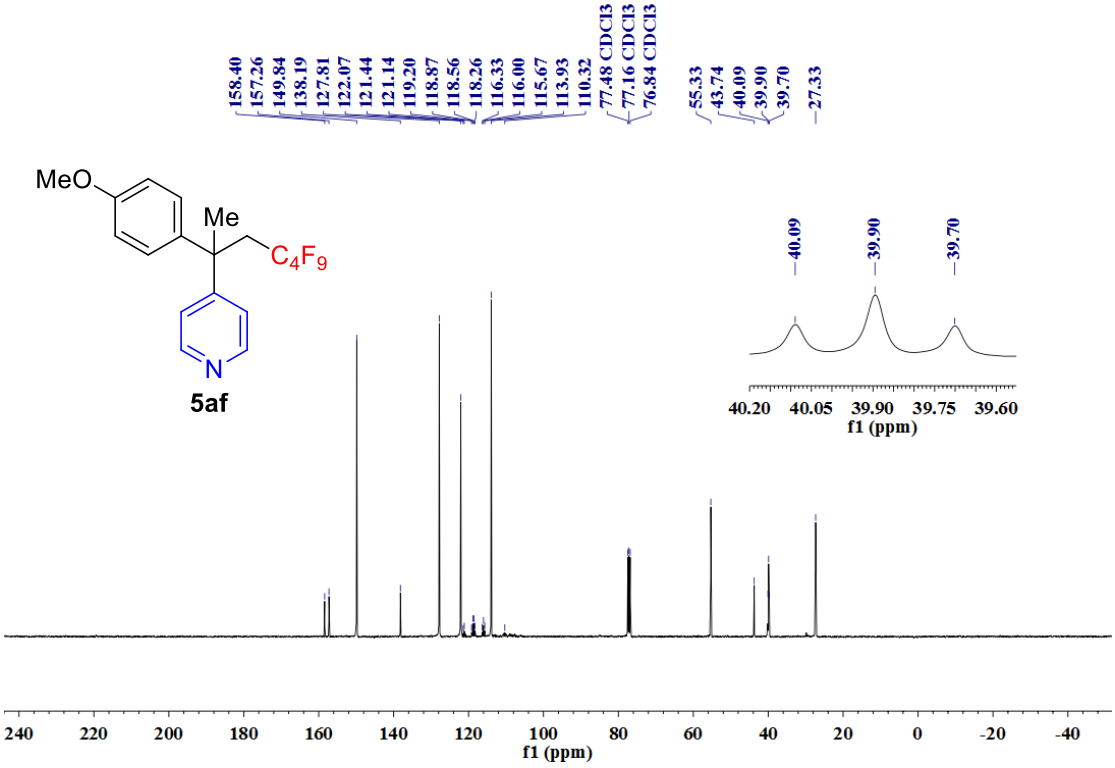

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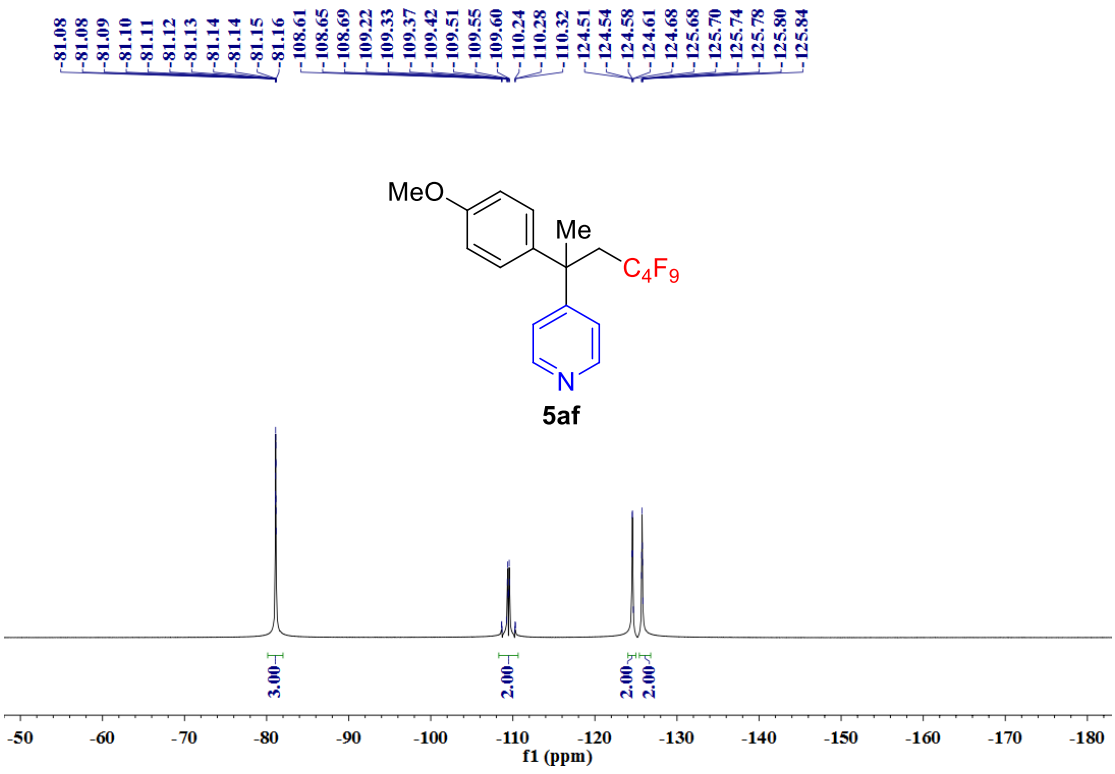
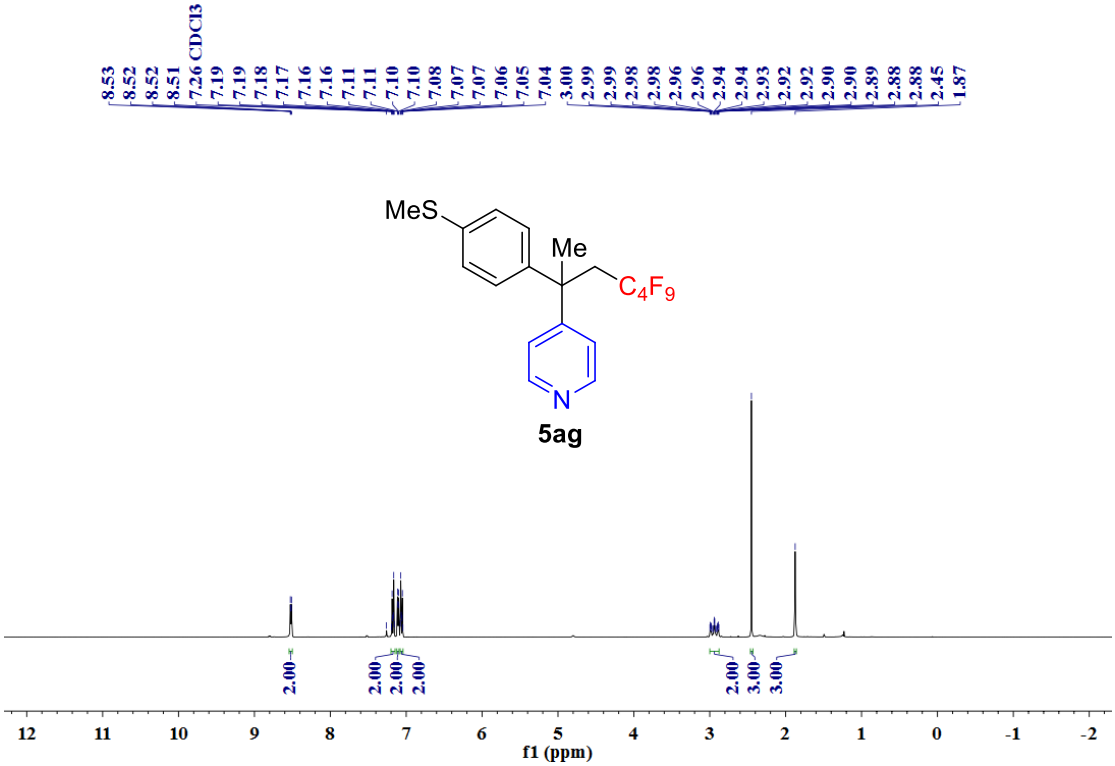
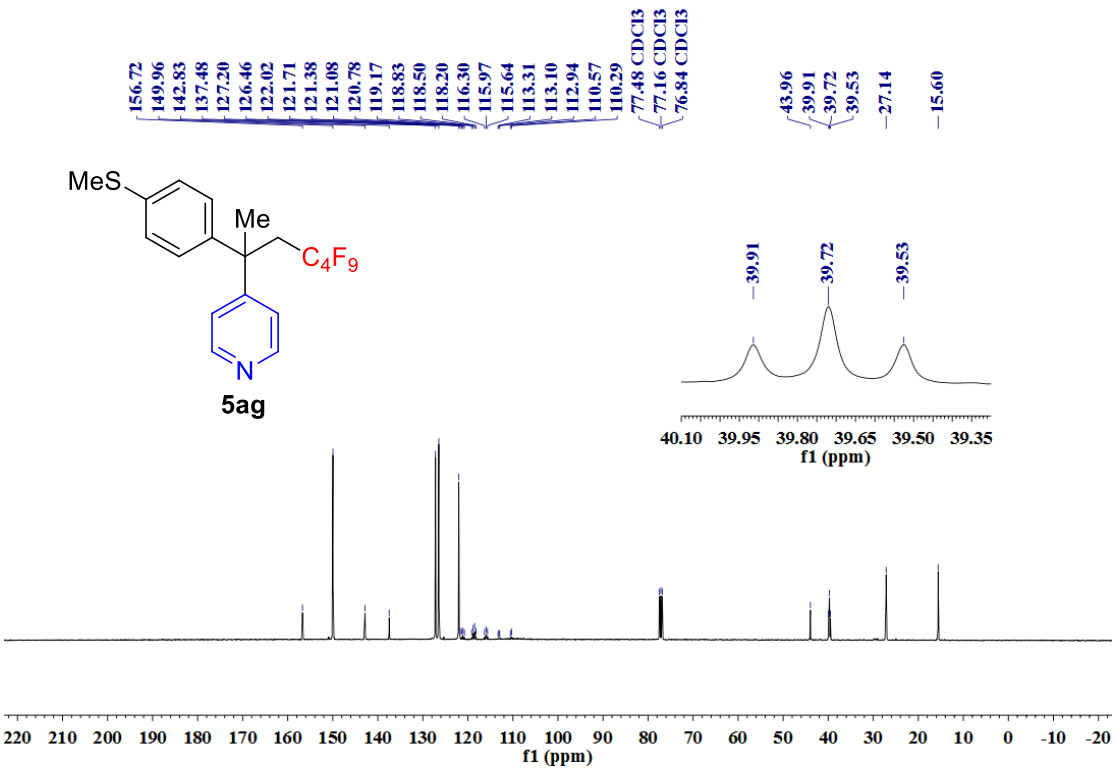


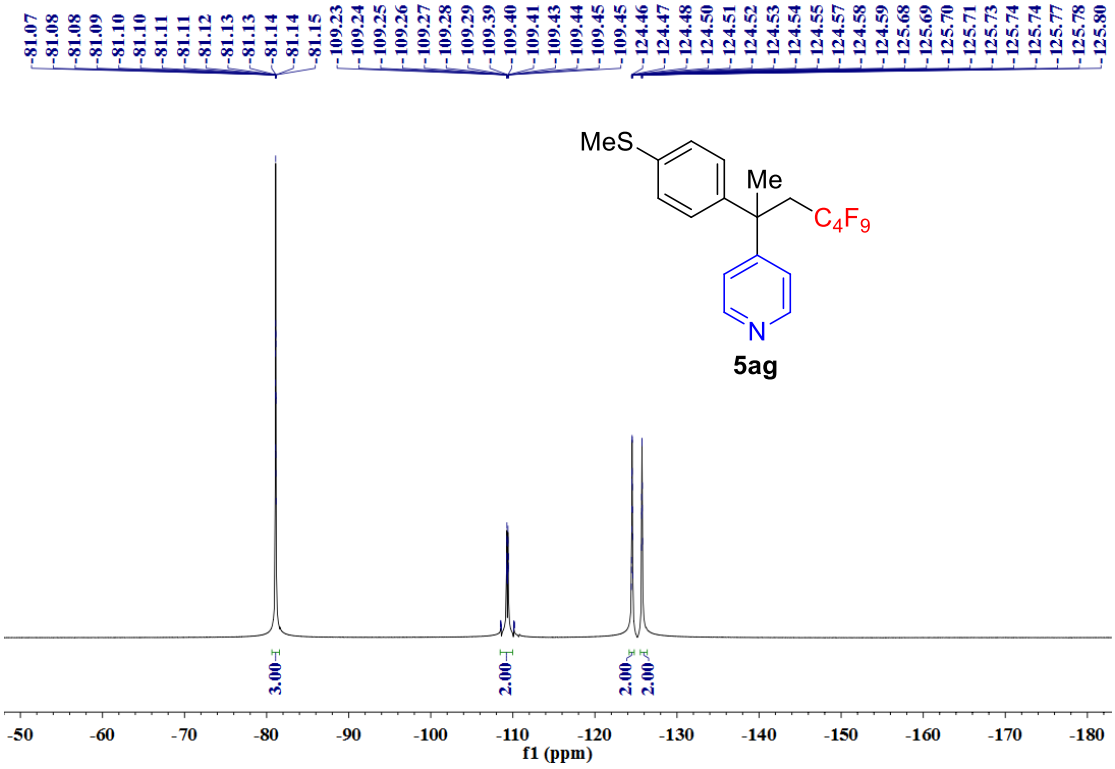
^{1}H NMR (400 MHz, $CDCl_3$):



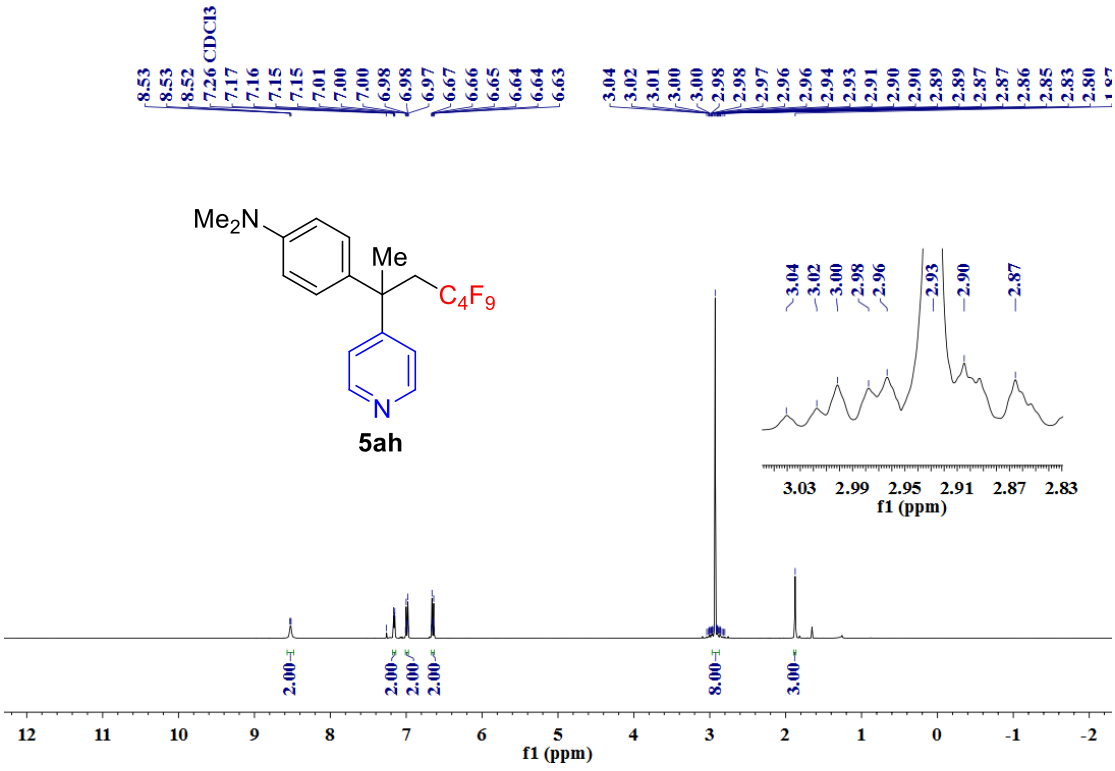
^{13}C NMR (100 MHz, $CDCl_3$):



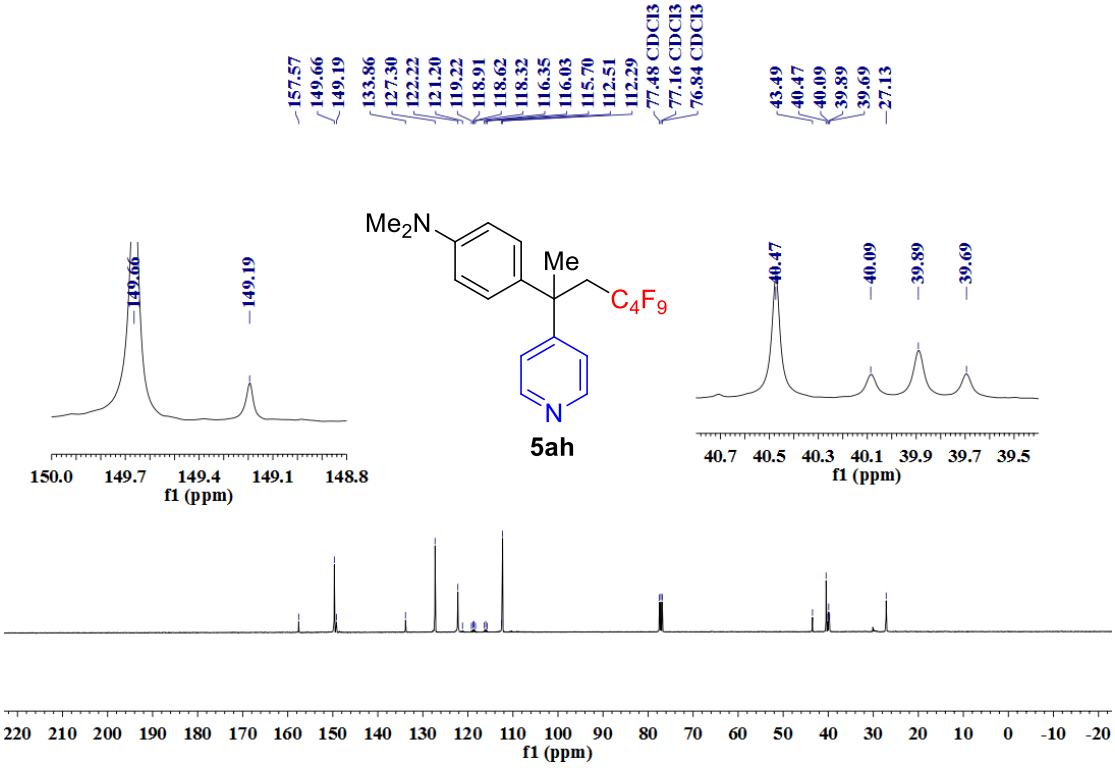
^{19}F NMR (376 MHz, $CDCl_3$):



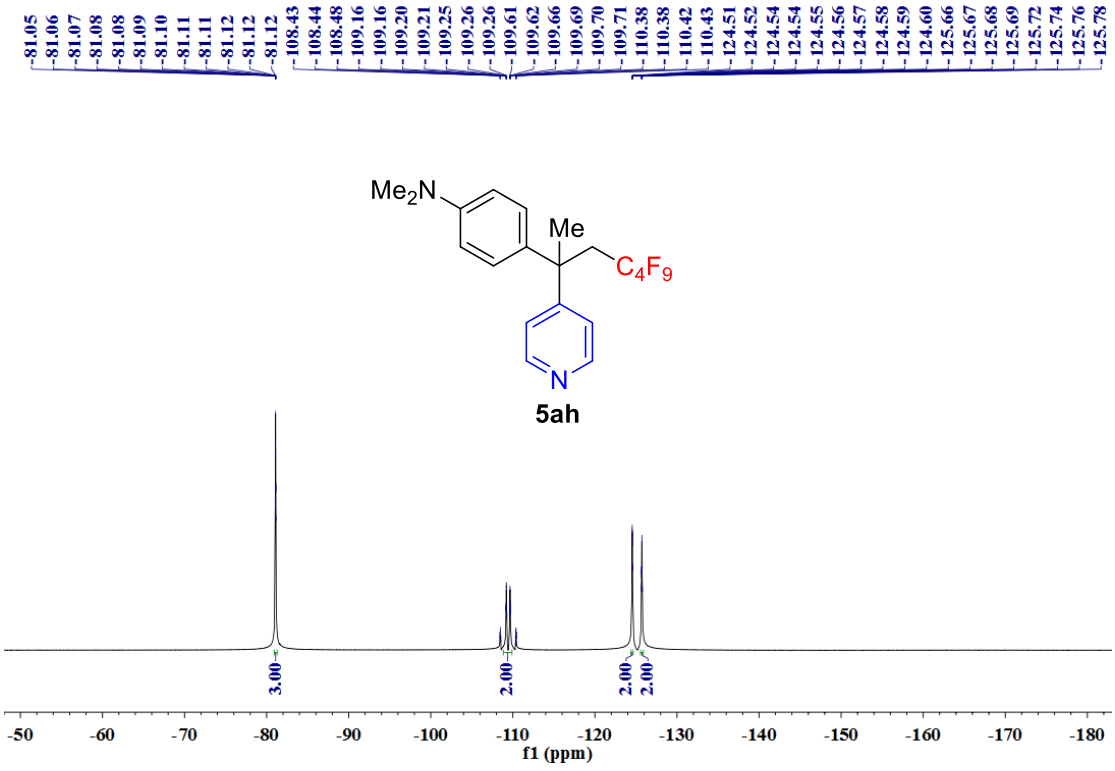
^{1}H NMR (400 MHz, $CDCl_3$):



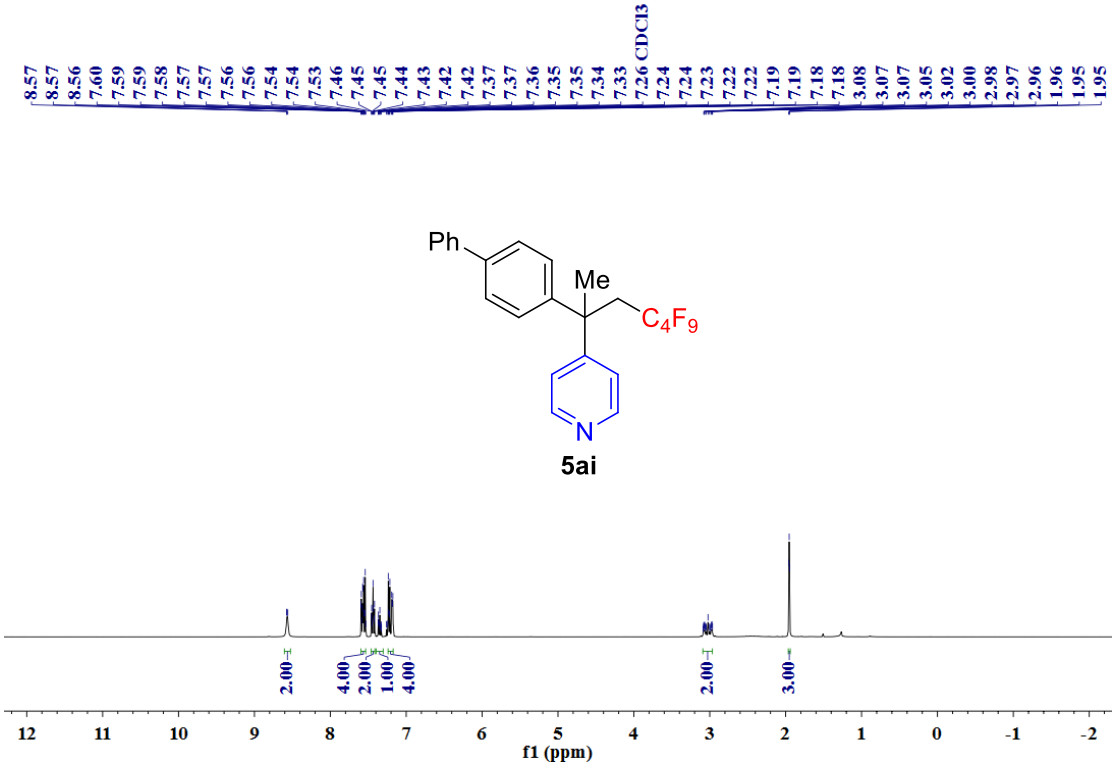
^{13}C NMR (100 MHz, $CDCl_3$):



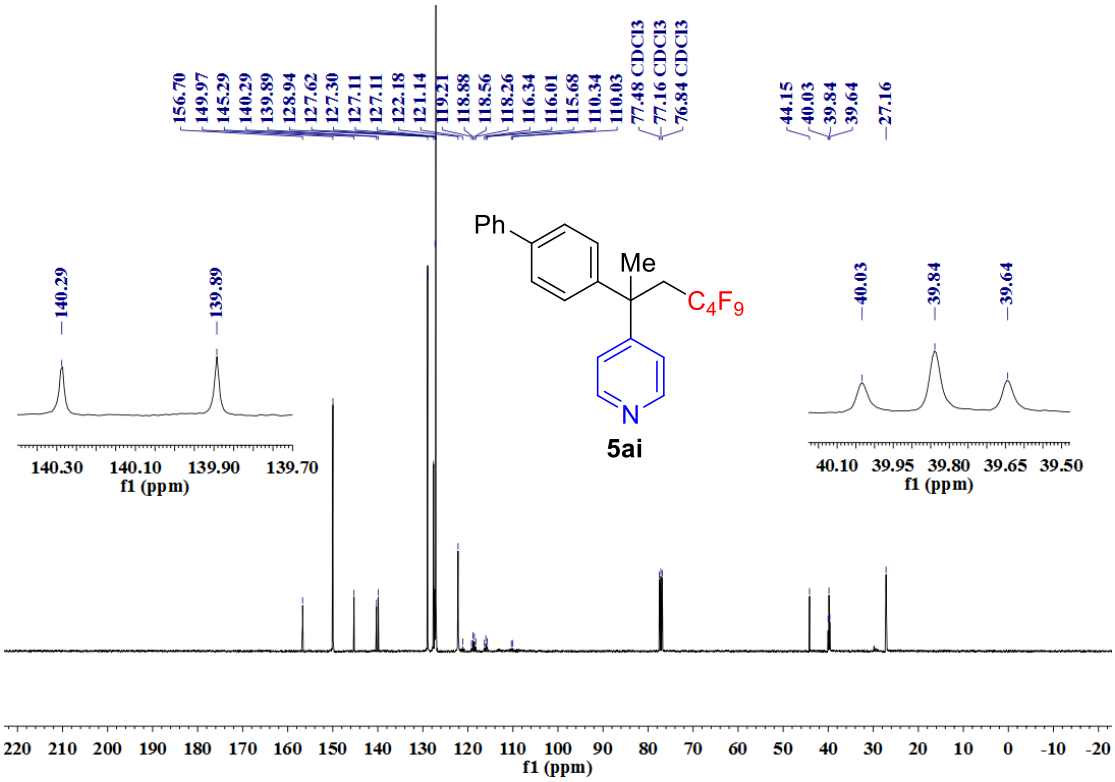
^{19}F NMR (376 MHz, $CDCl_3$):



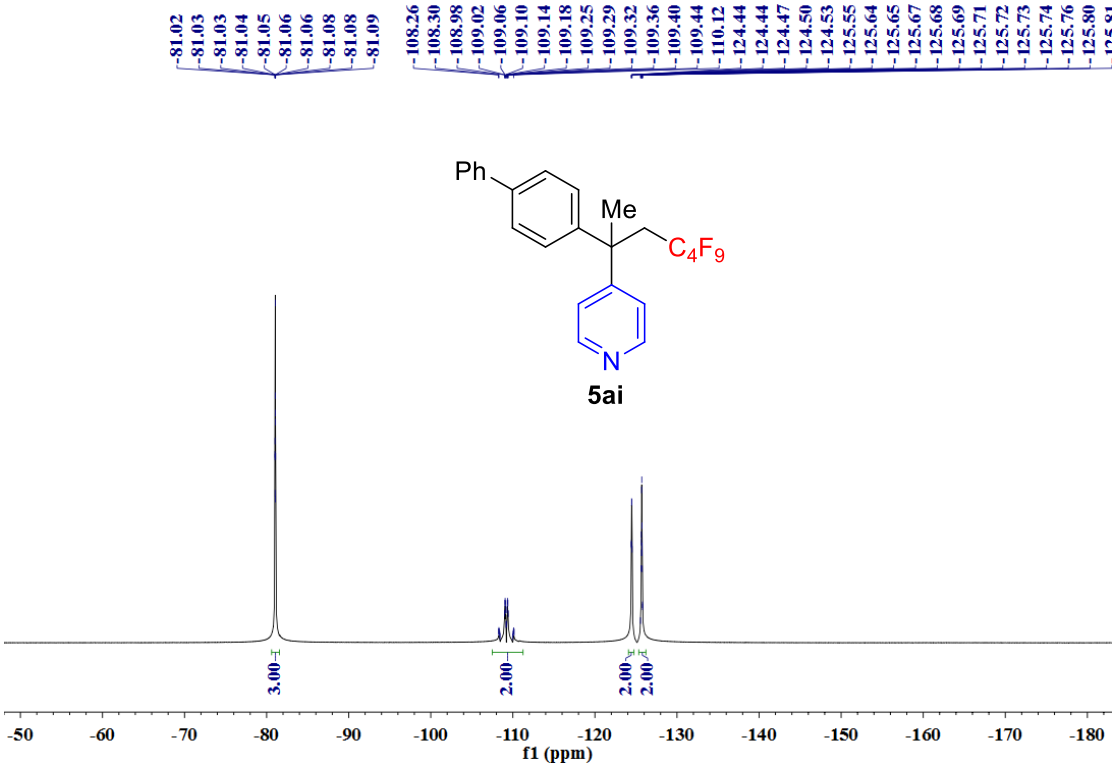
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):



^{19}F NMR (376 MHz, $CDCl_3$):



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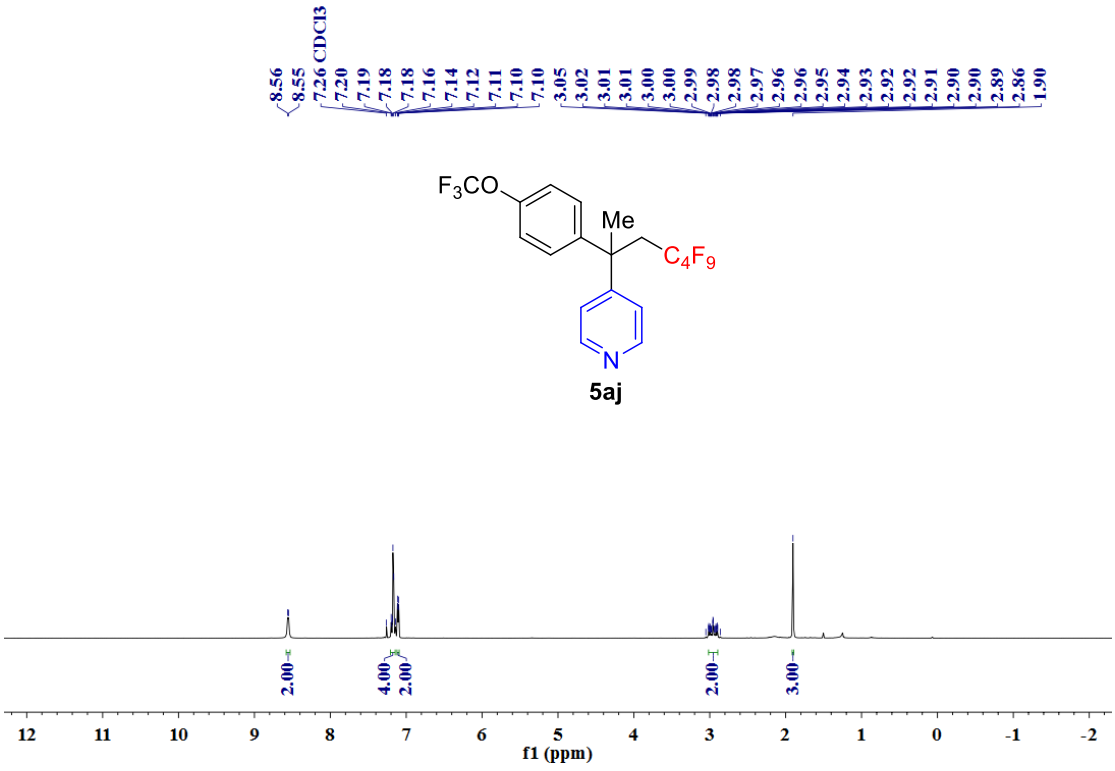

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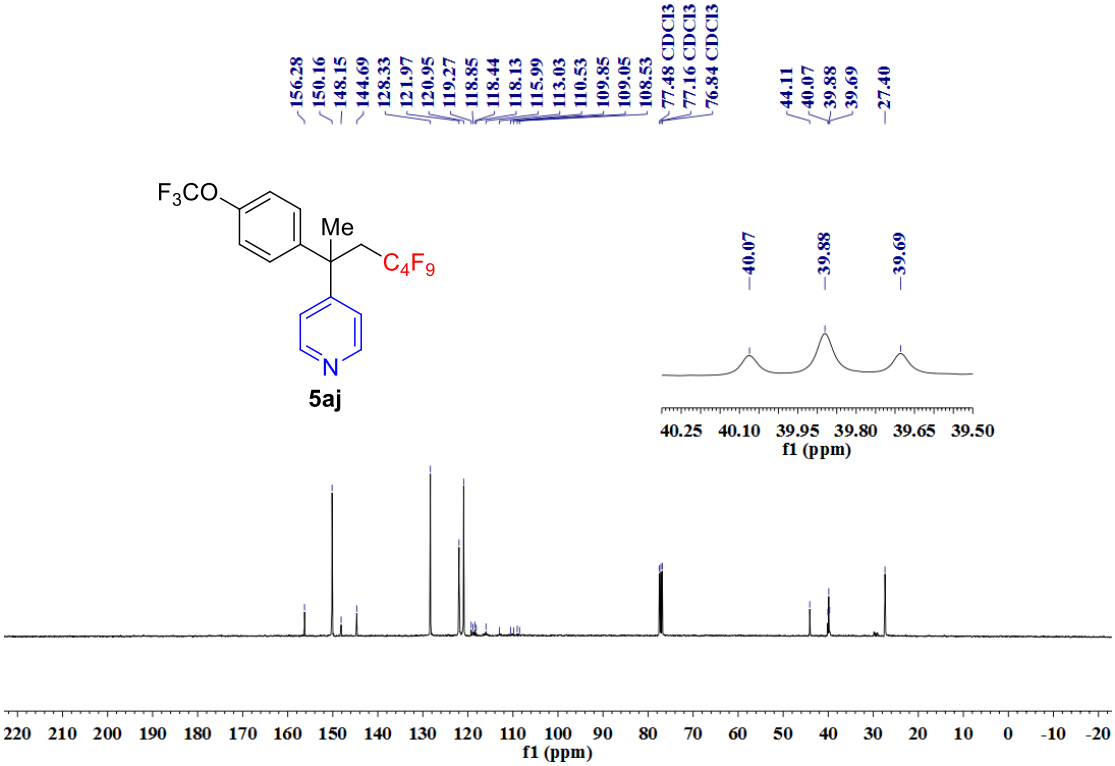

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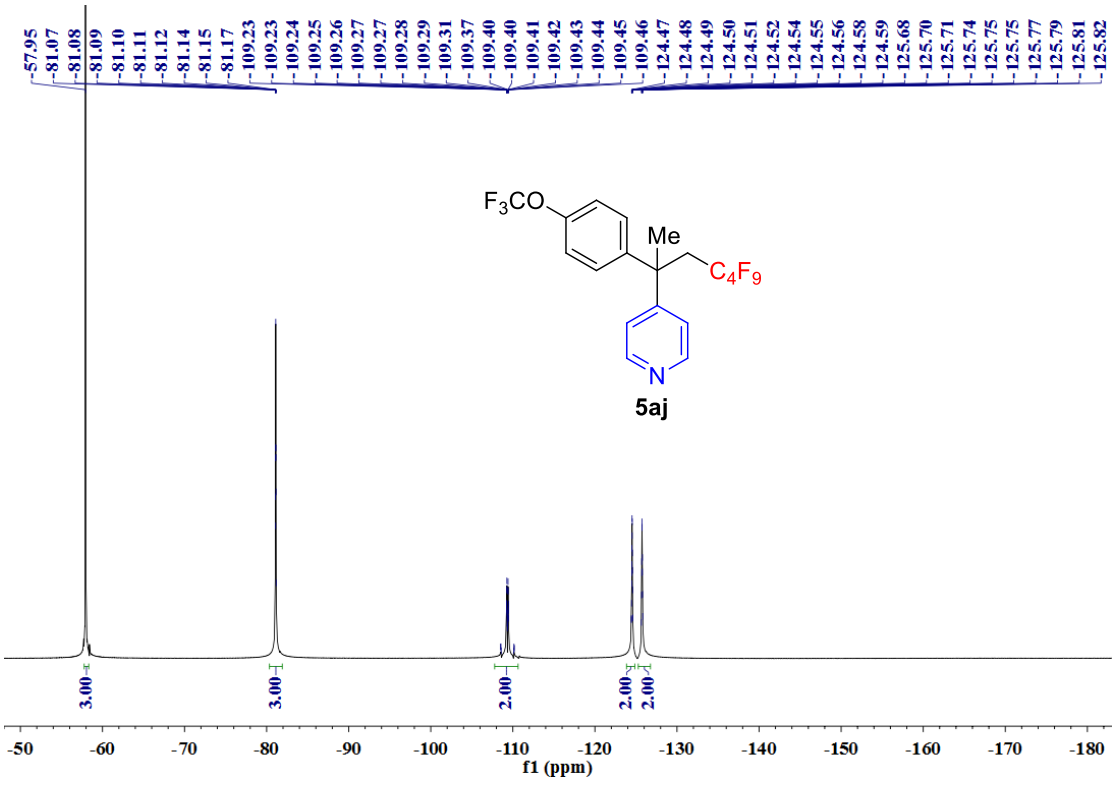

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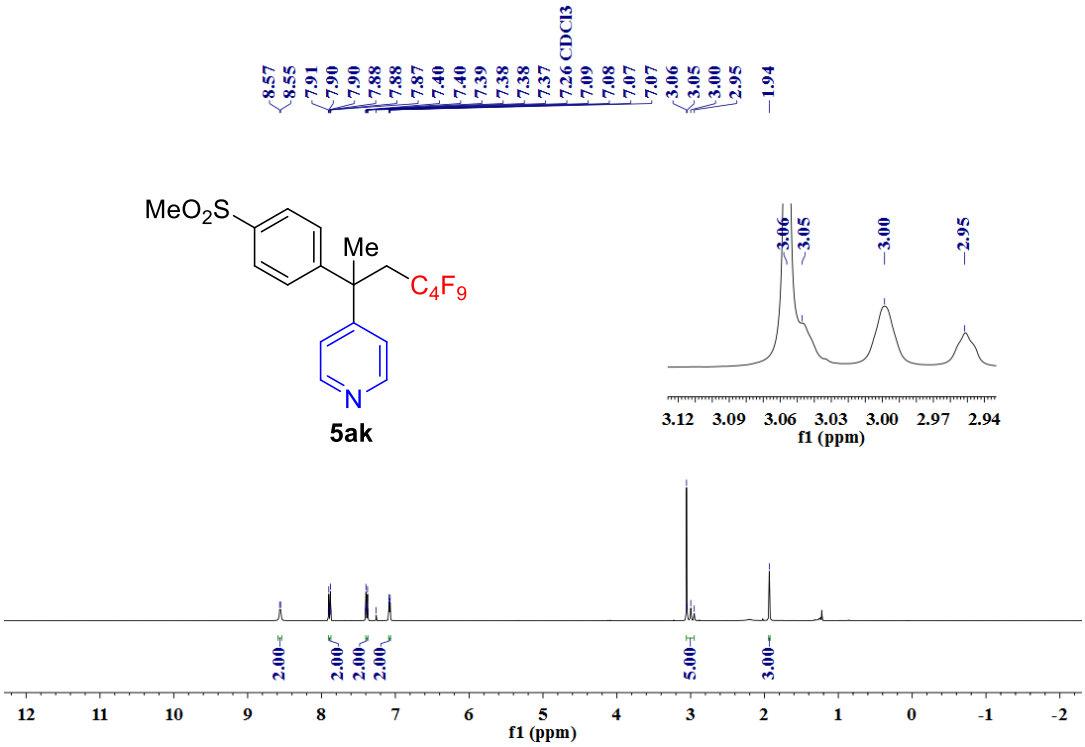

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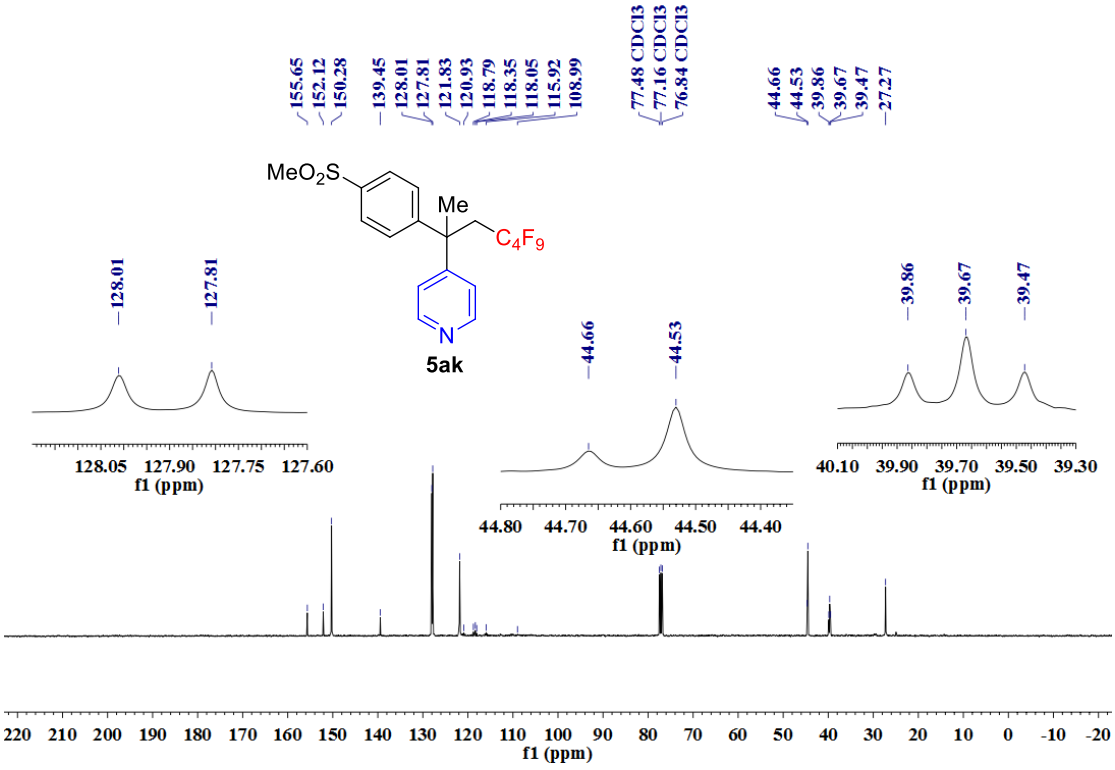

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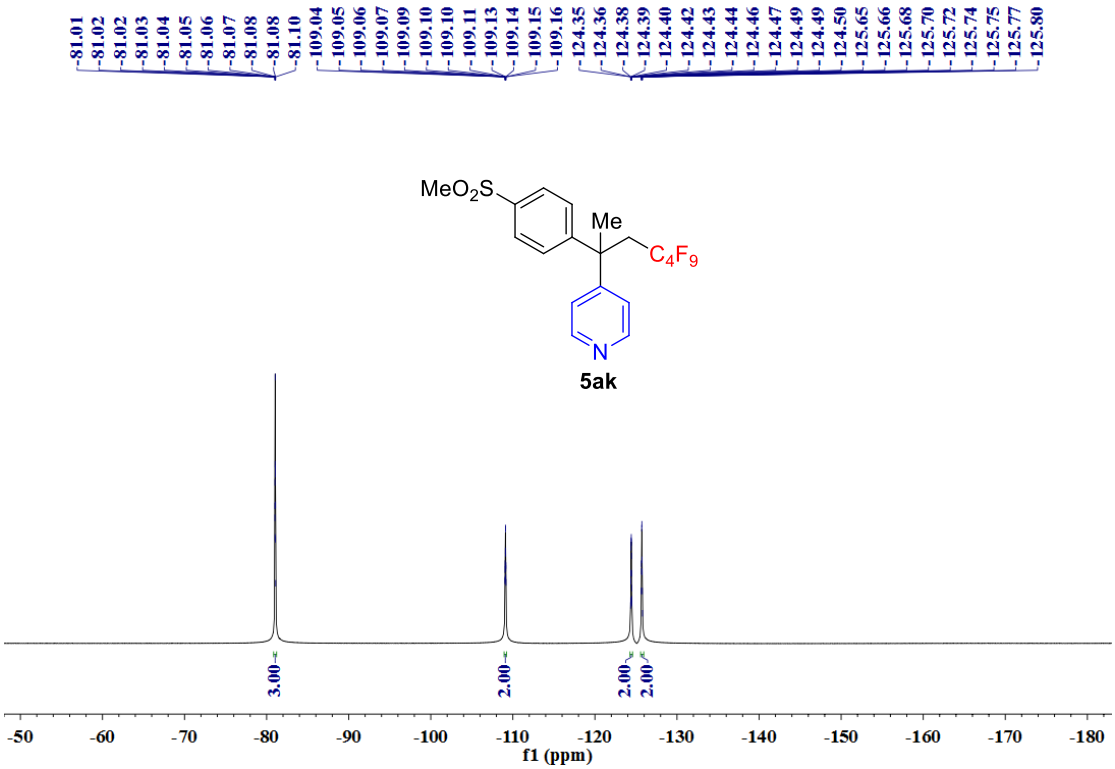

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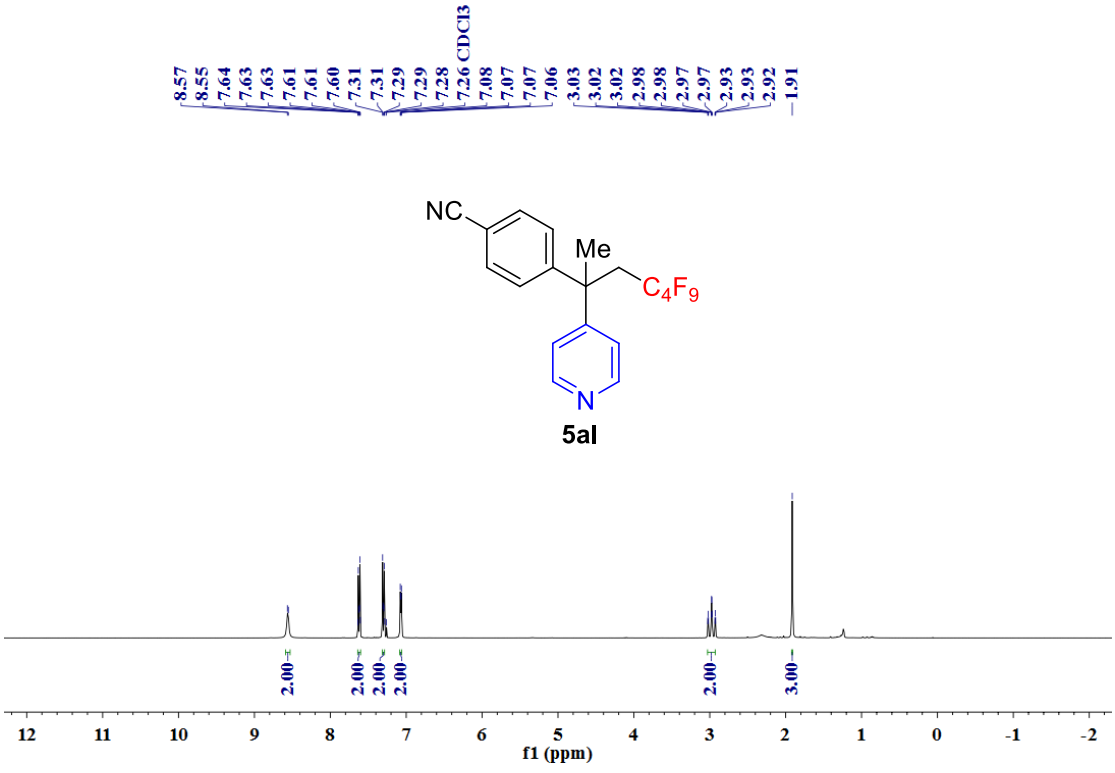

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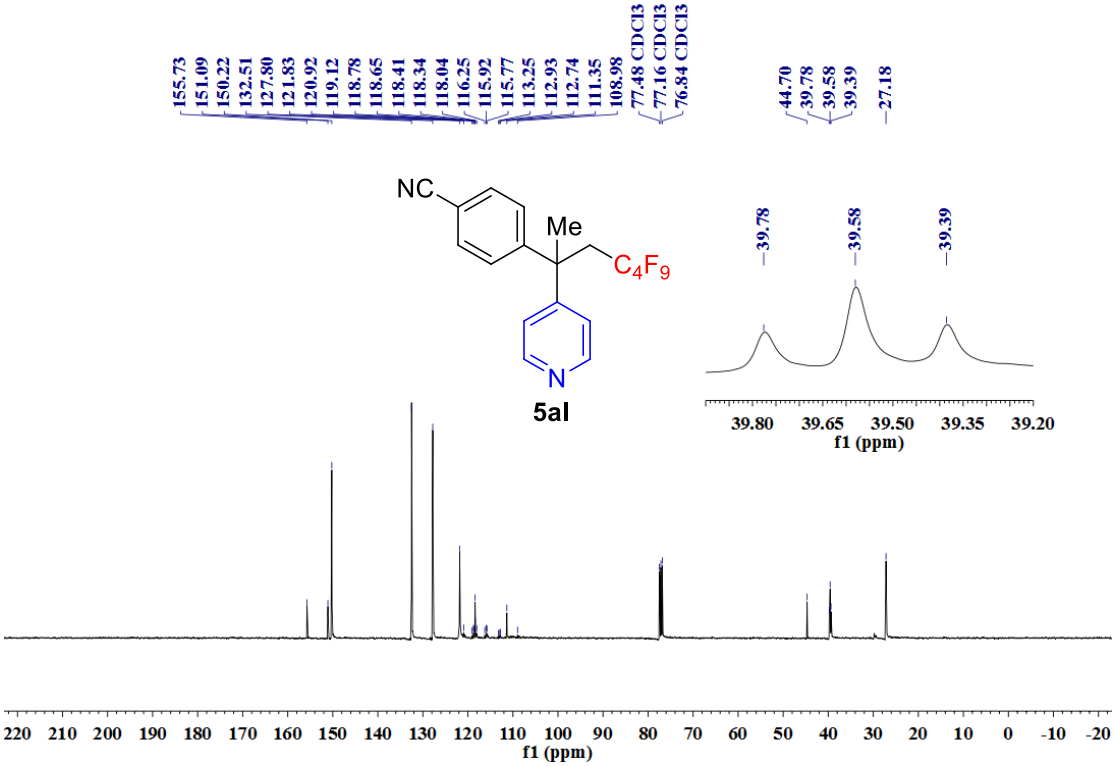
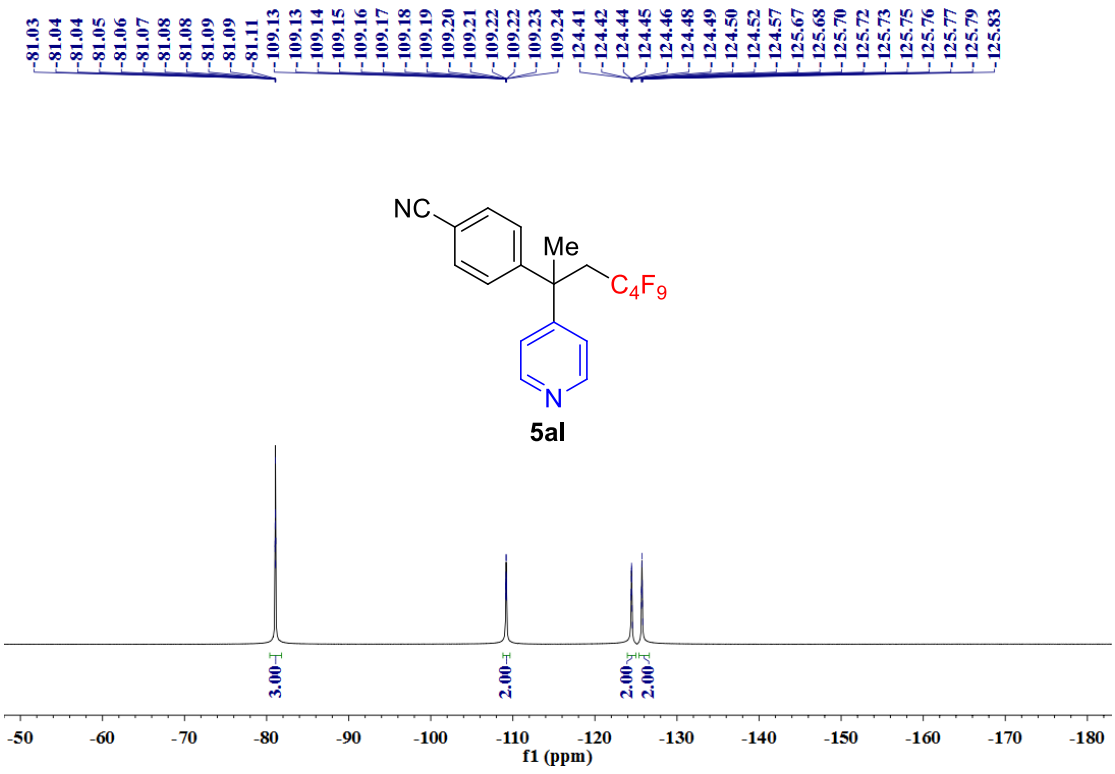


^{19}F NMR (376 MHz, $CDCl_3$)



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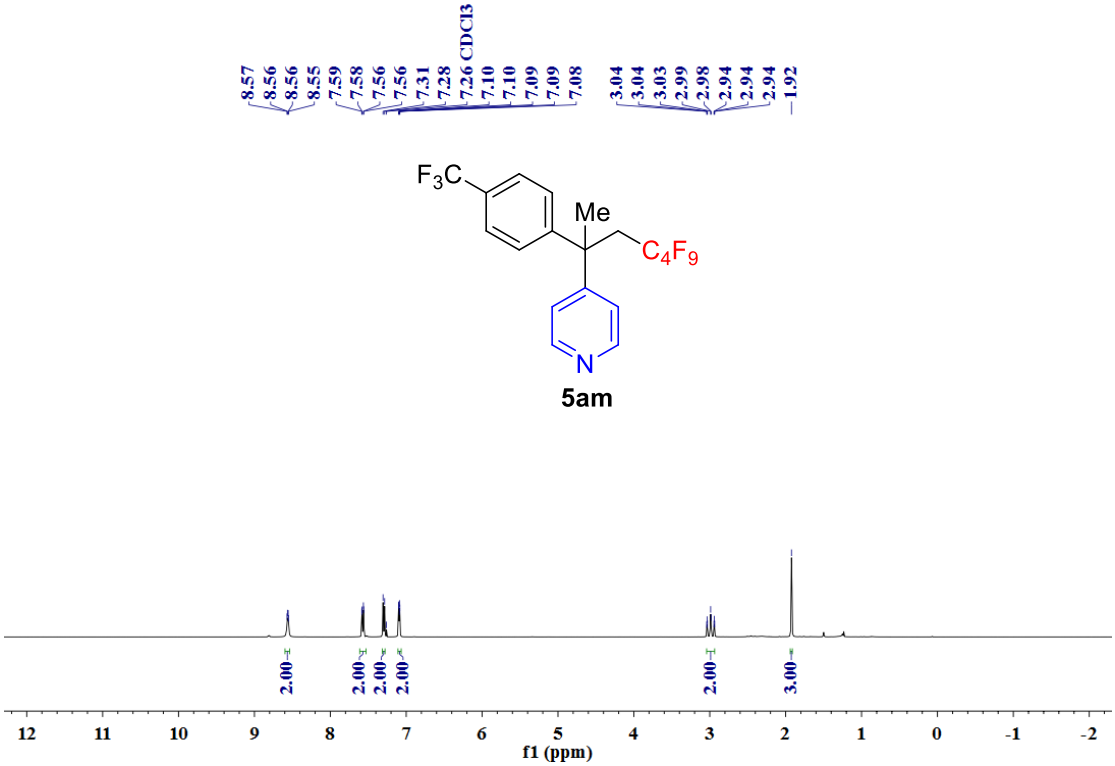

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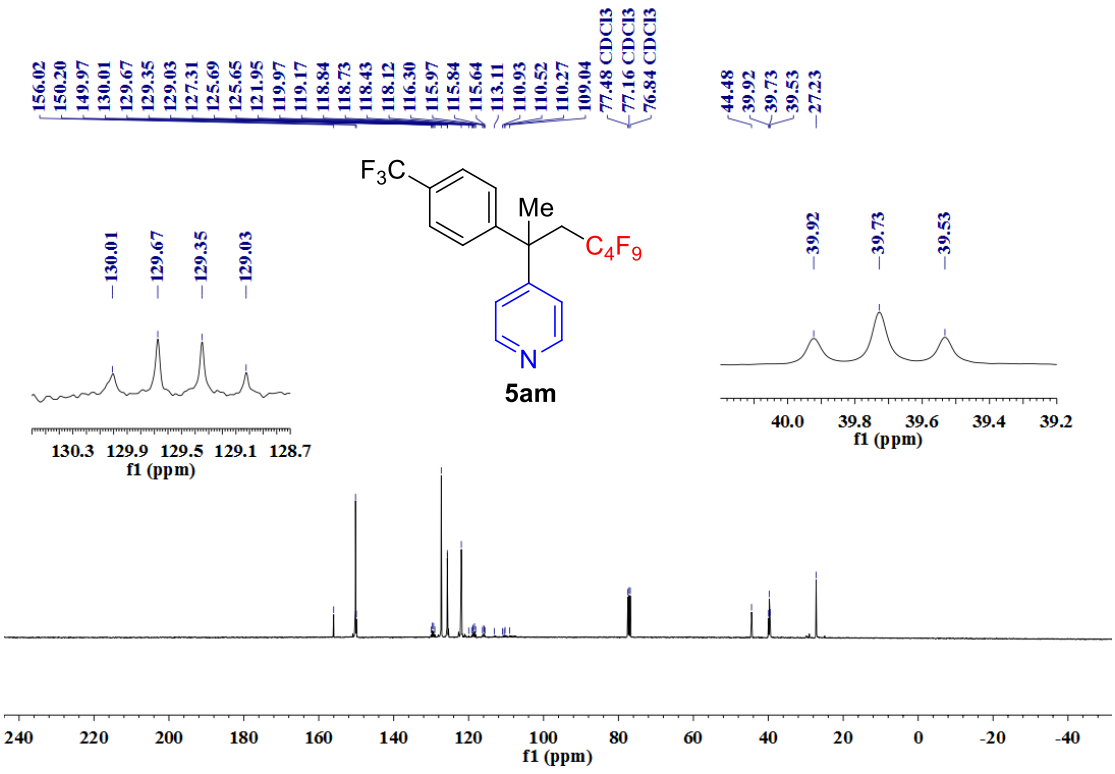

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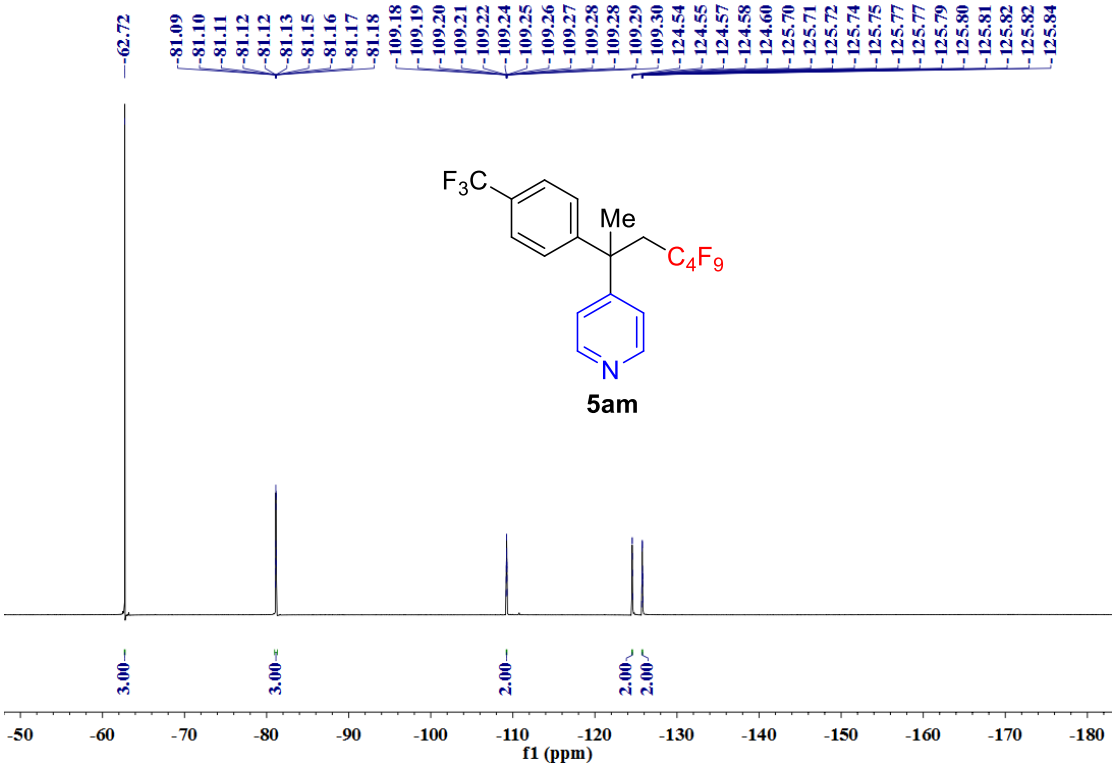

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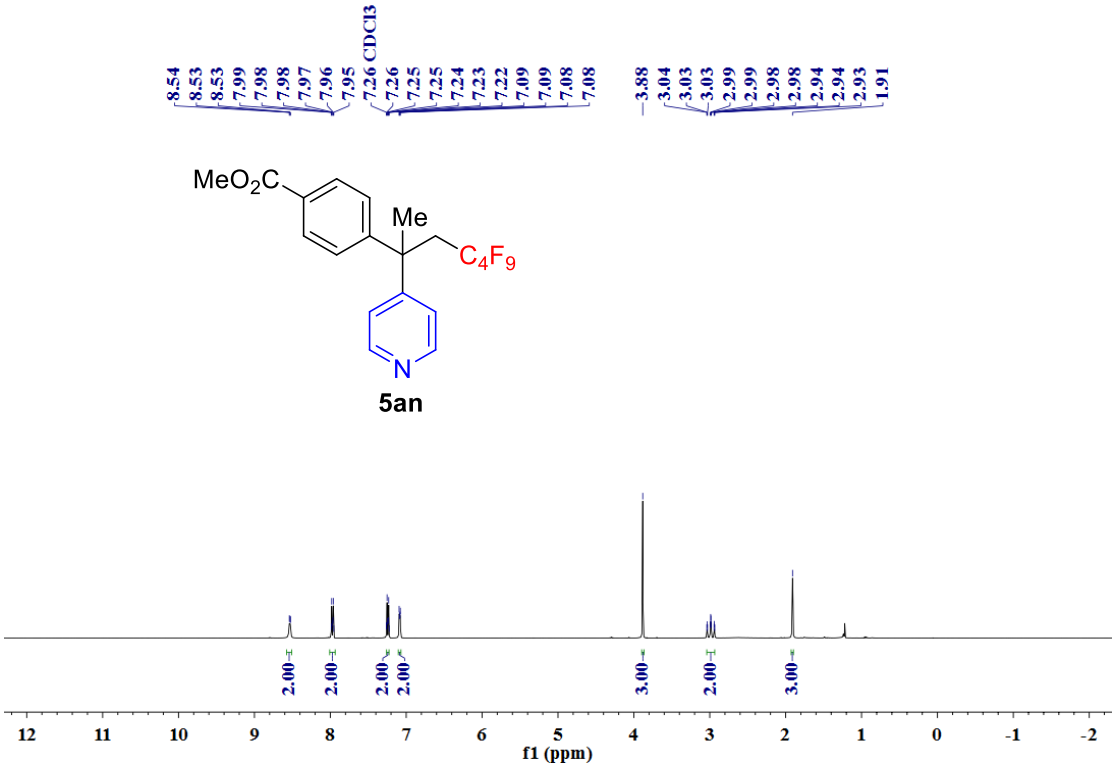

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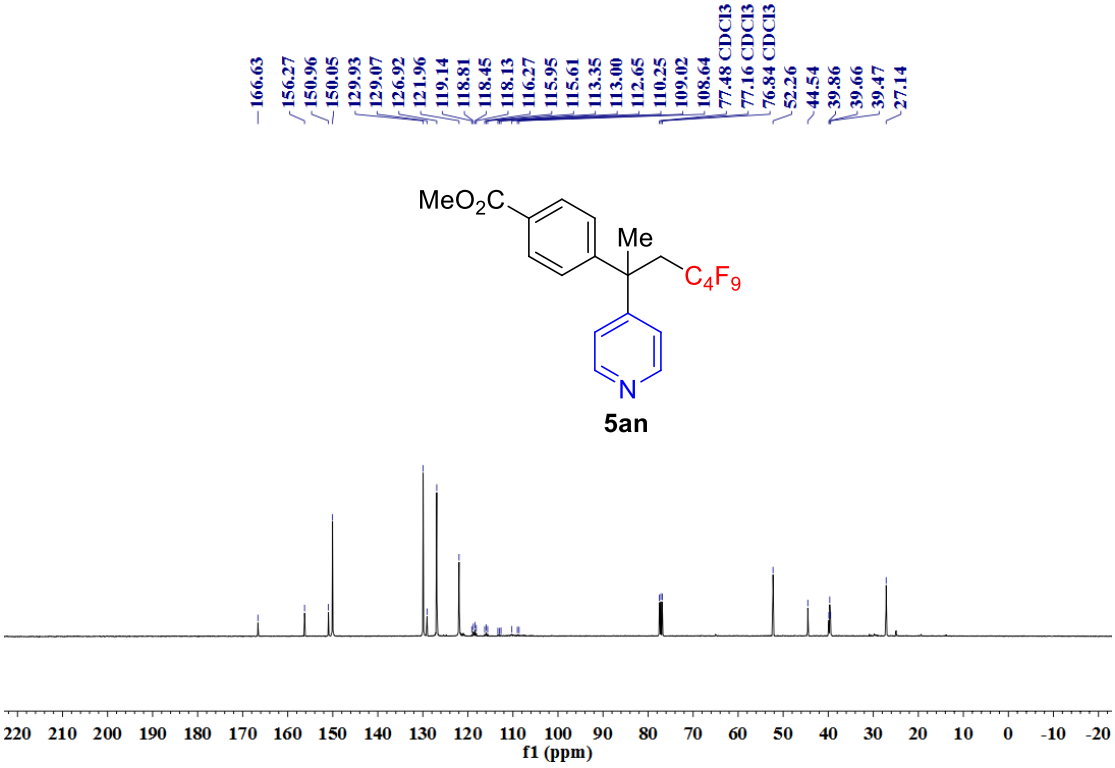

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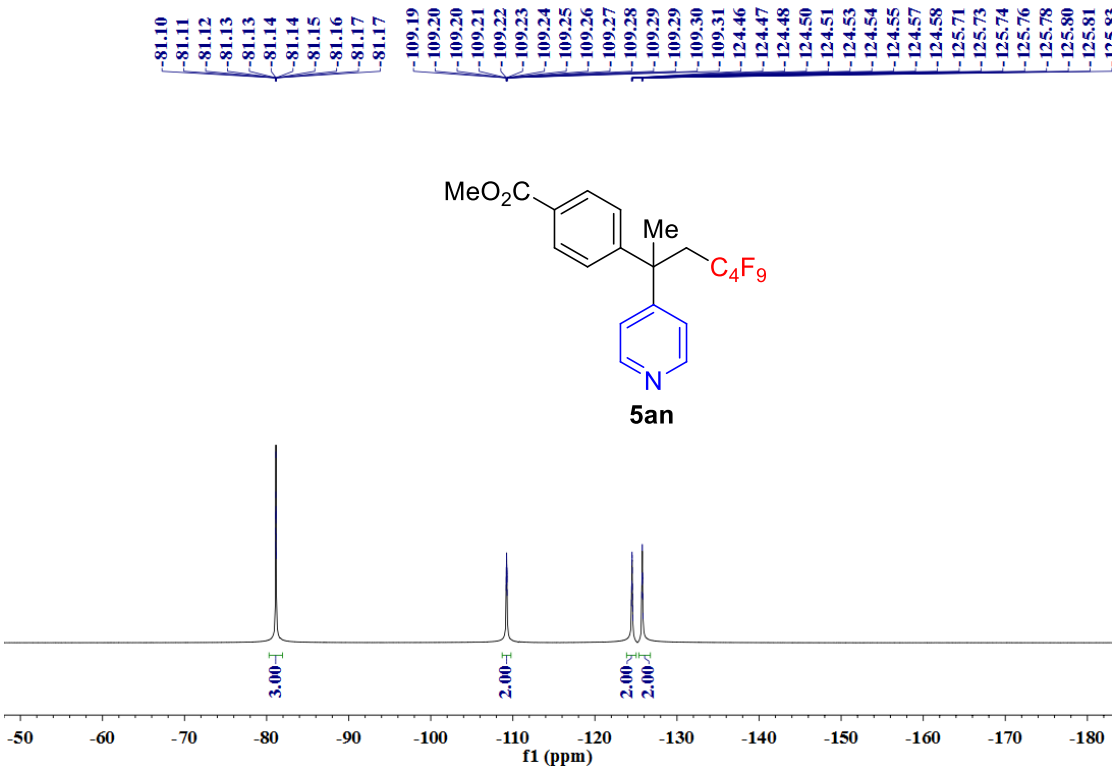

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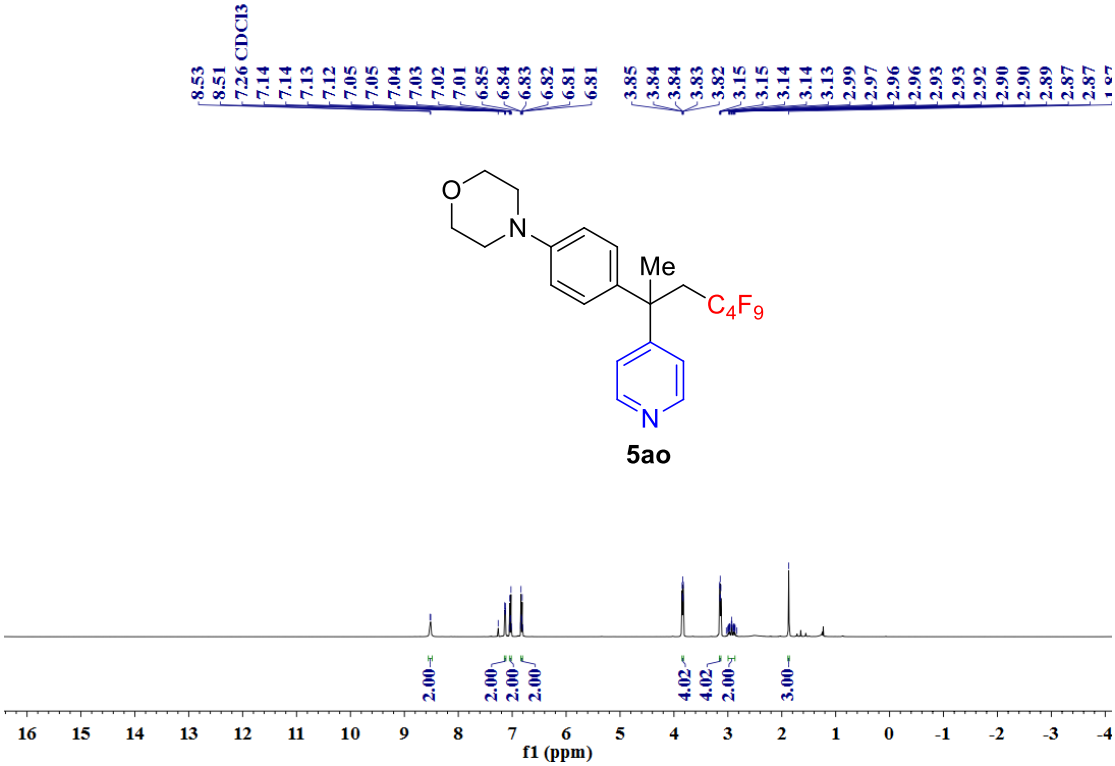

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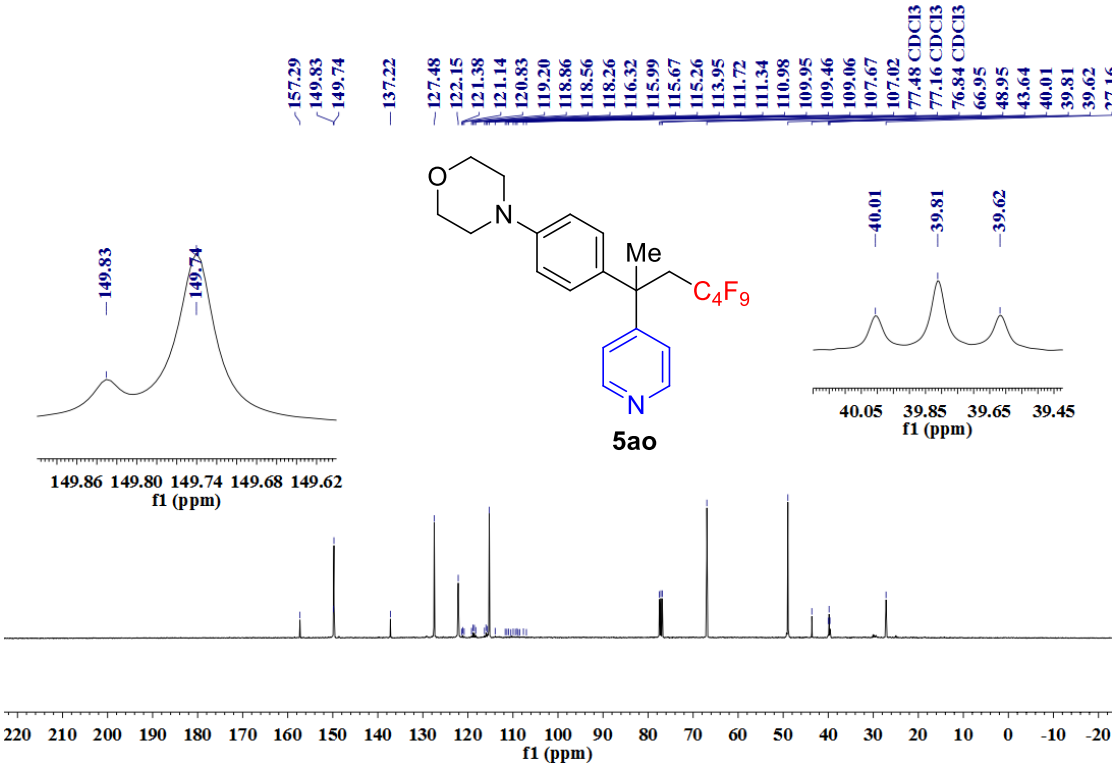

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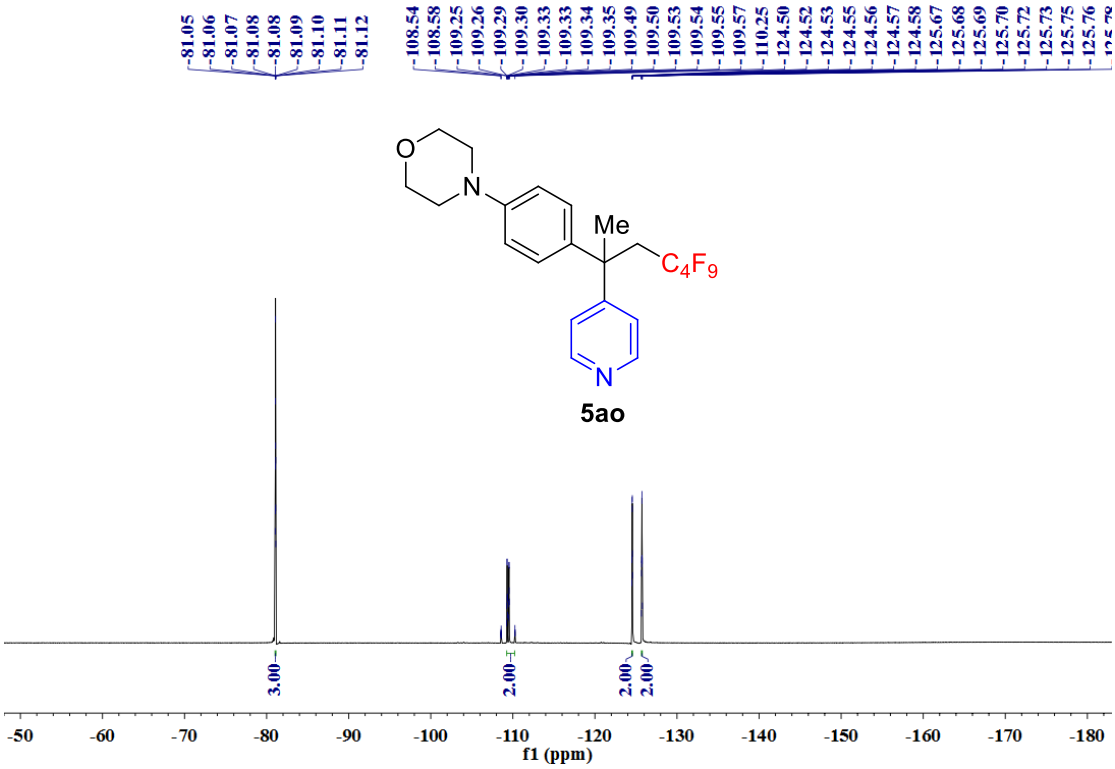

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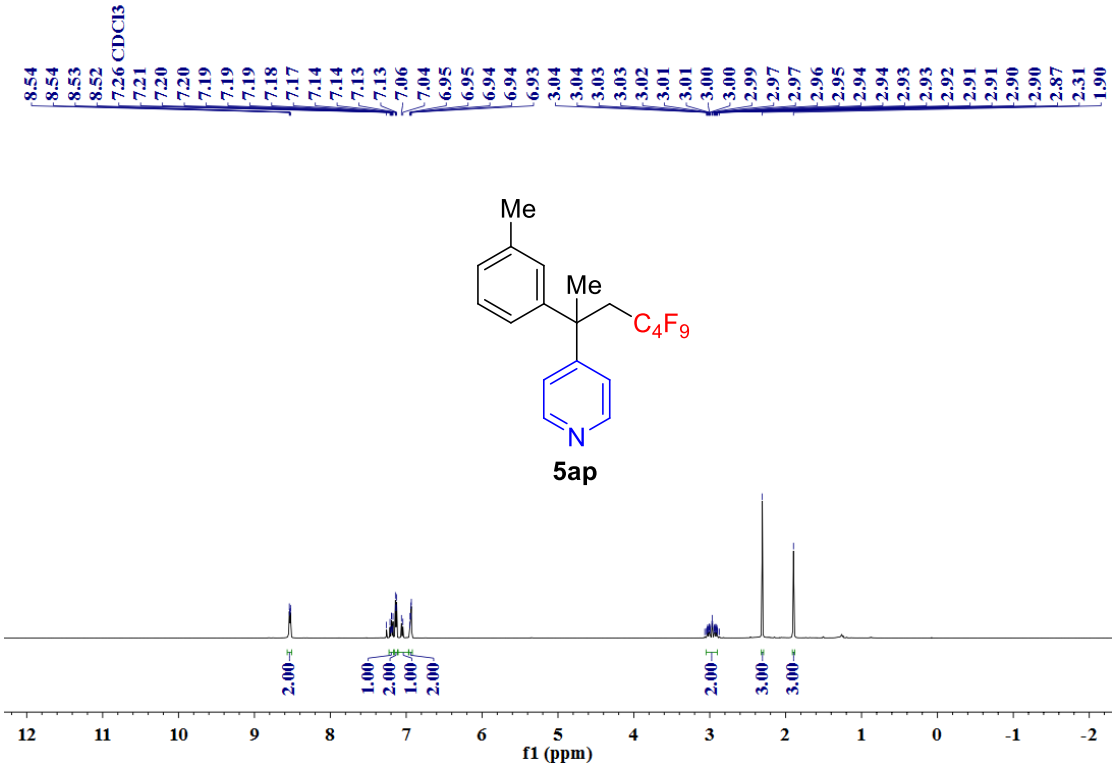

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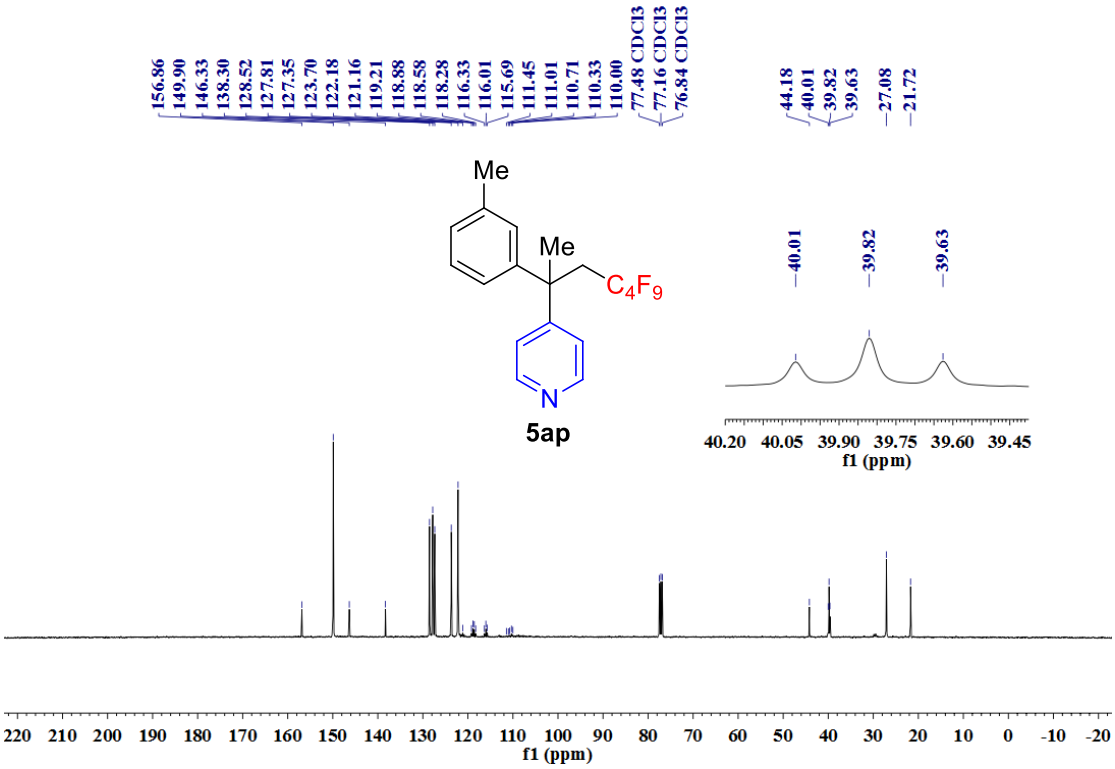

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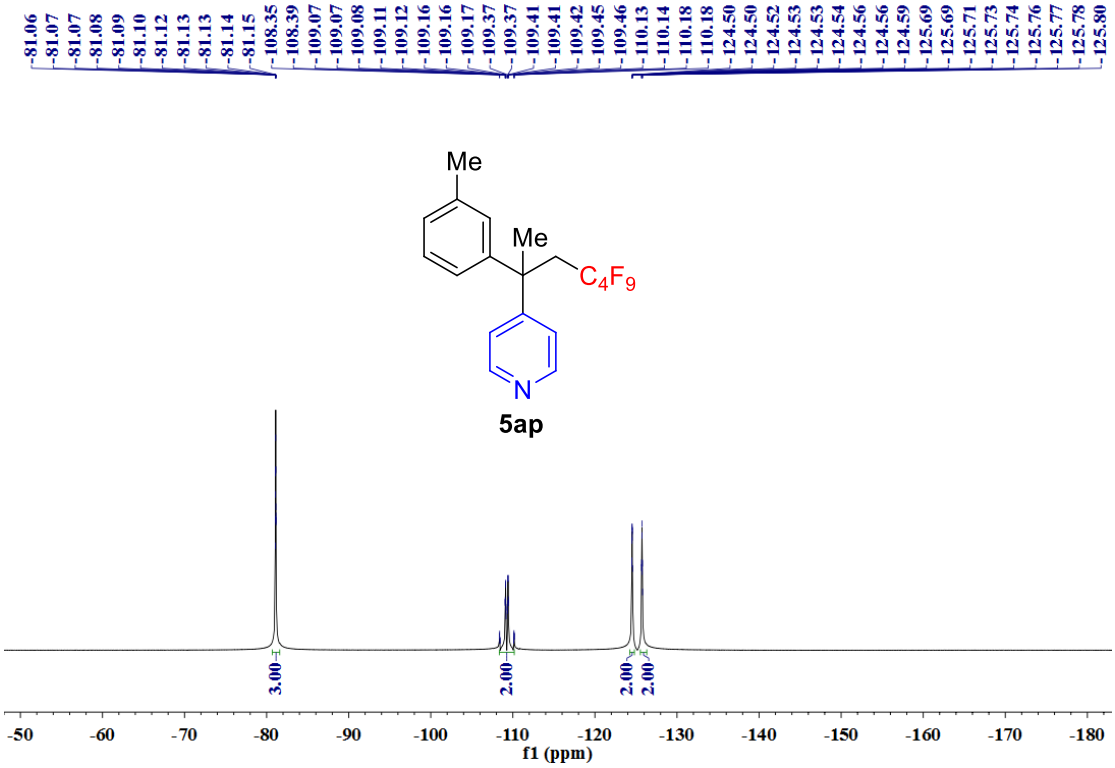

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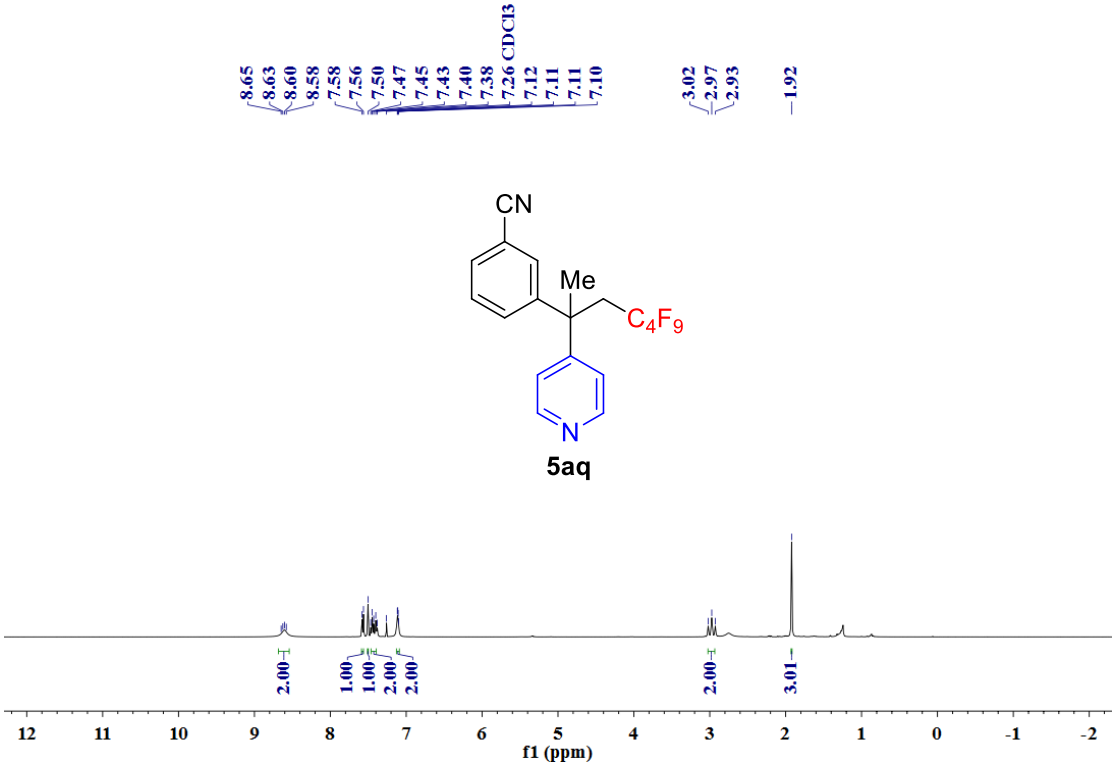

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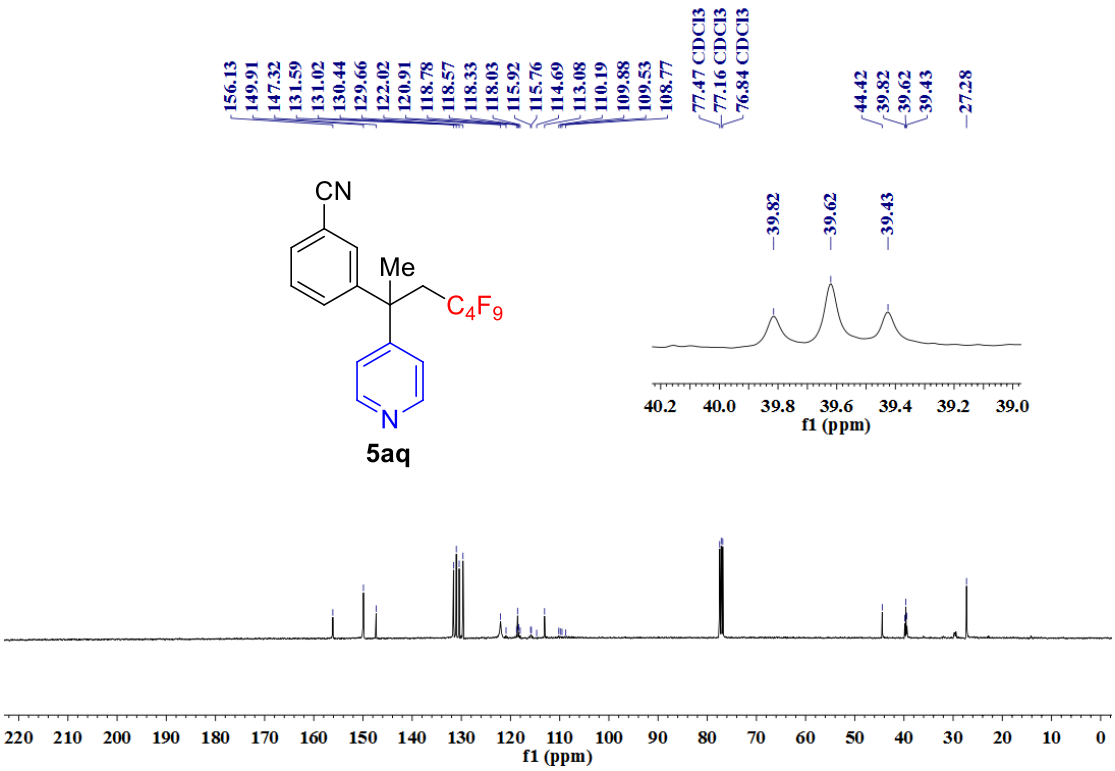

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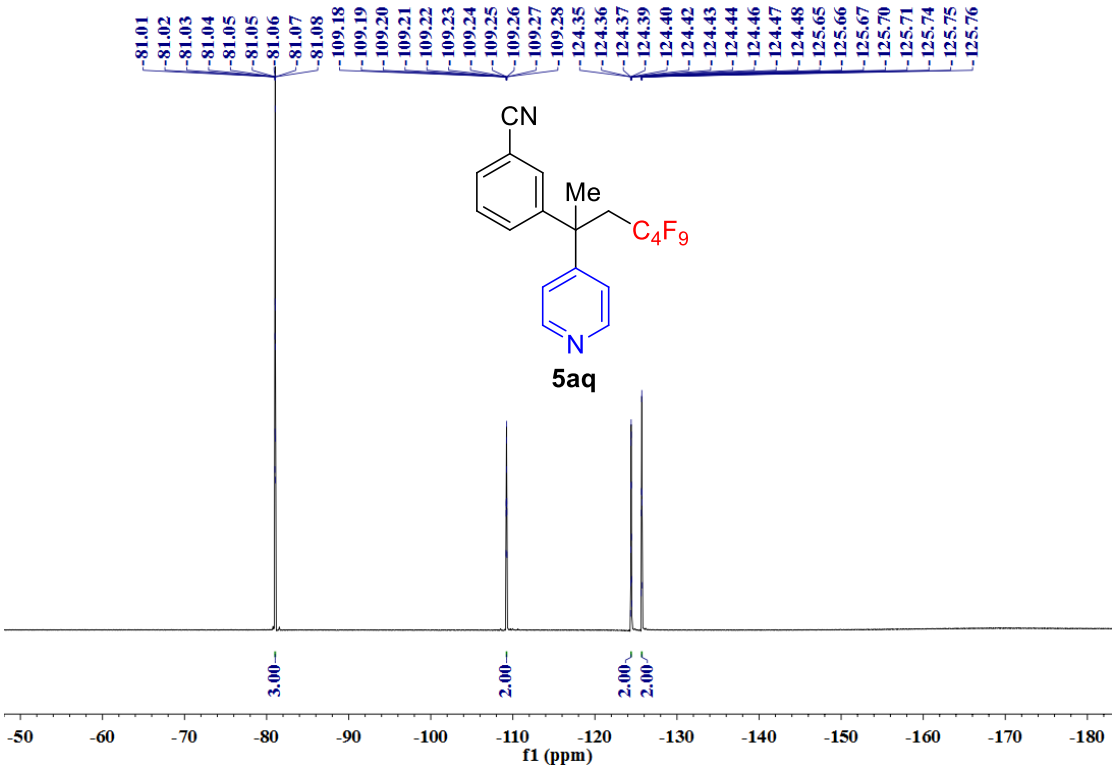

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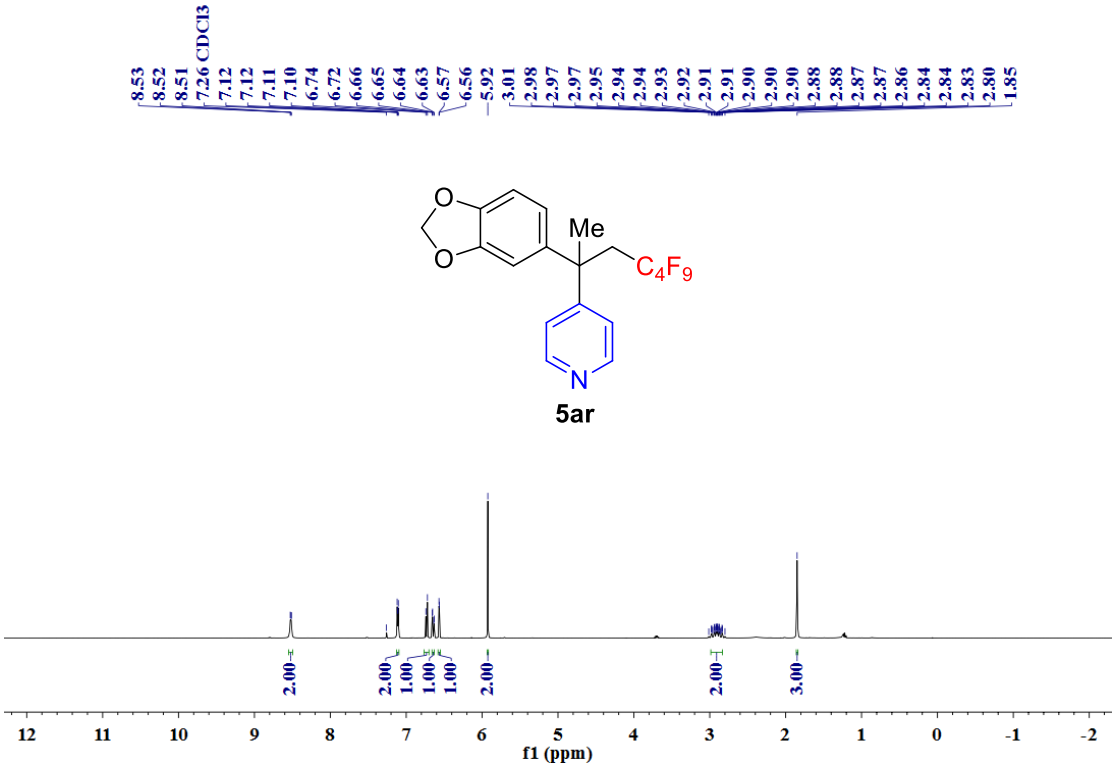

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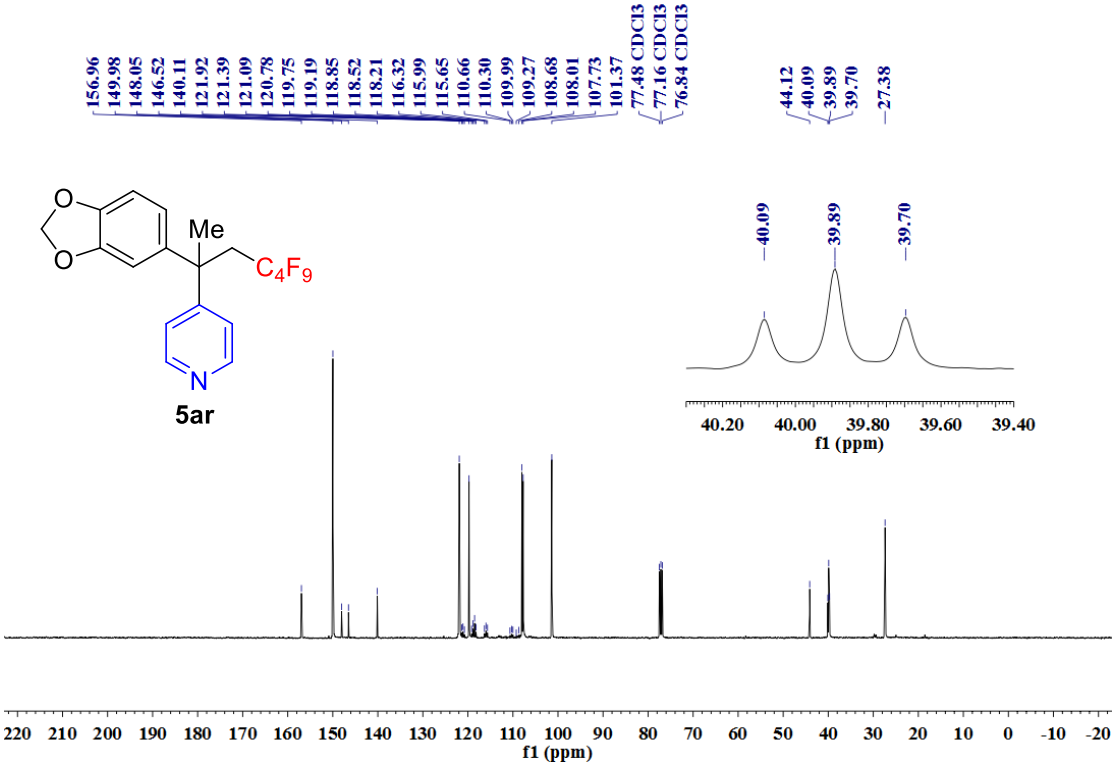

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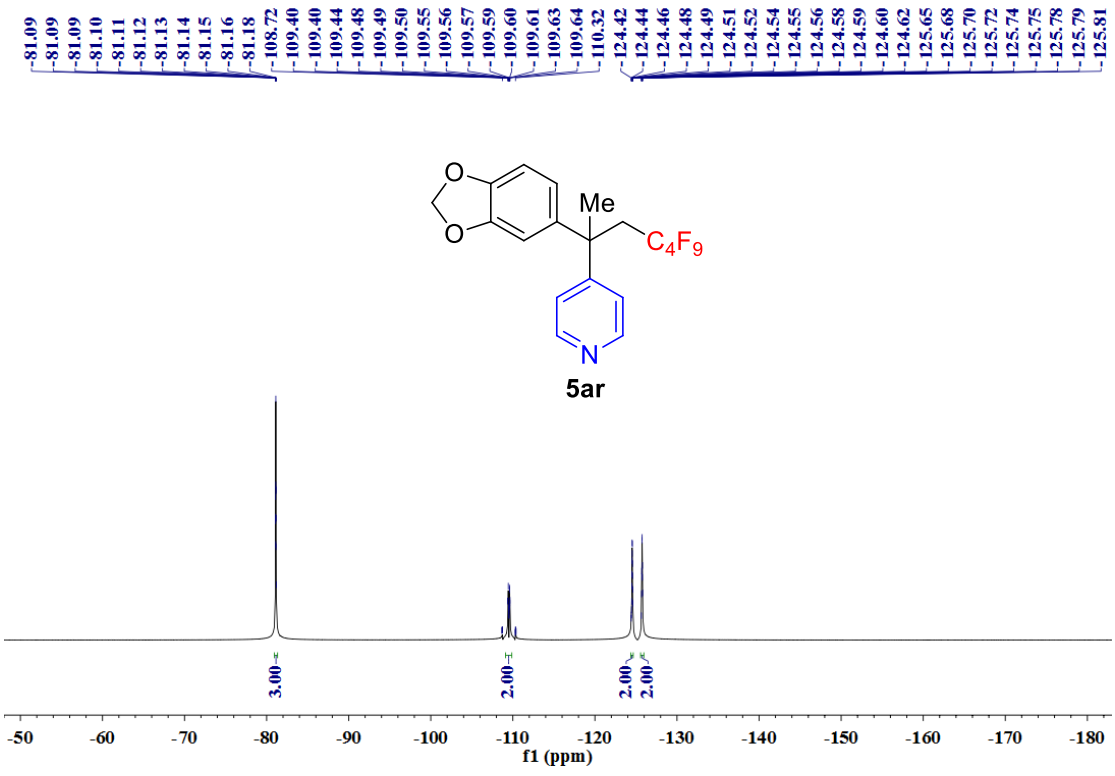

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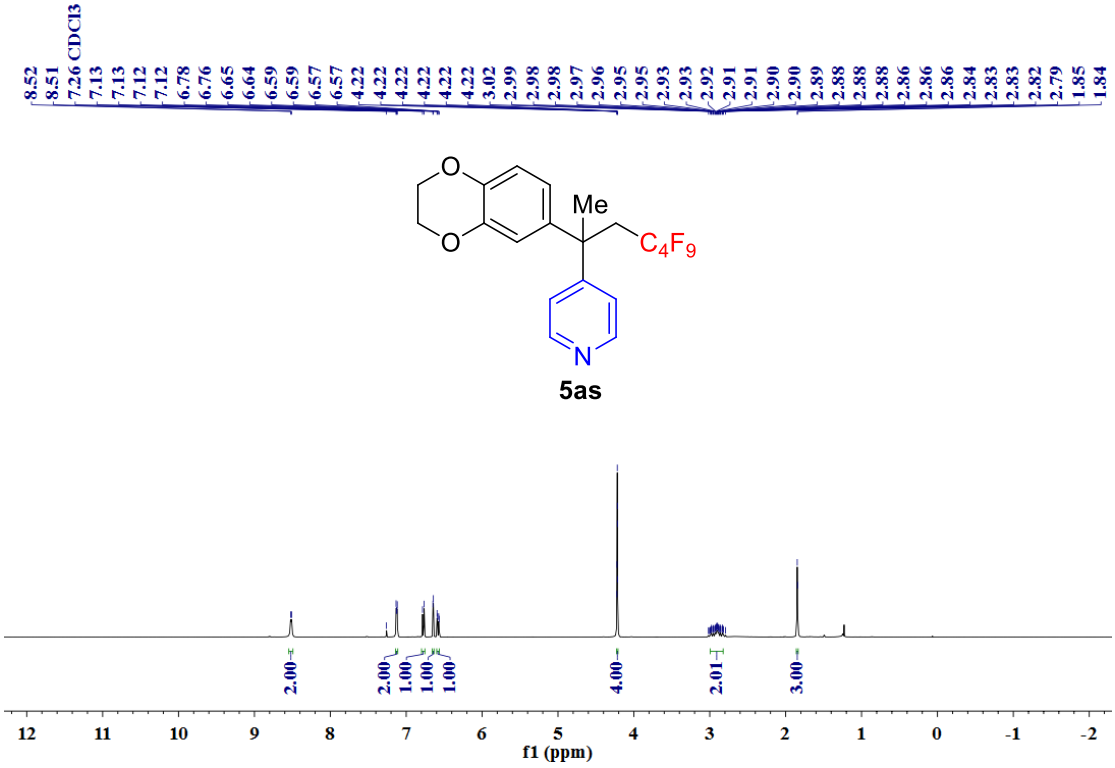

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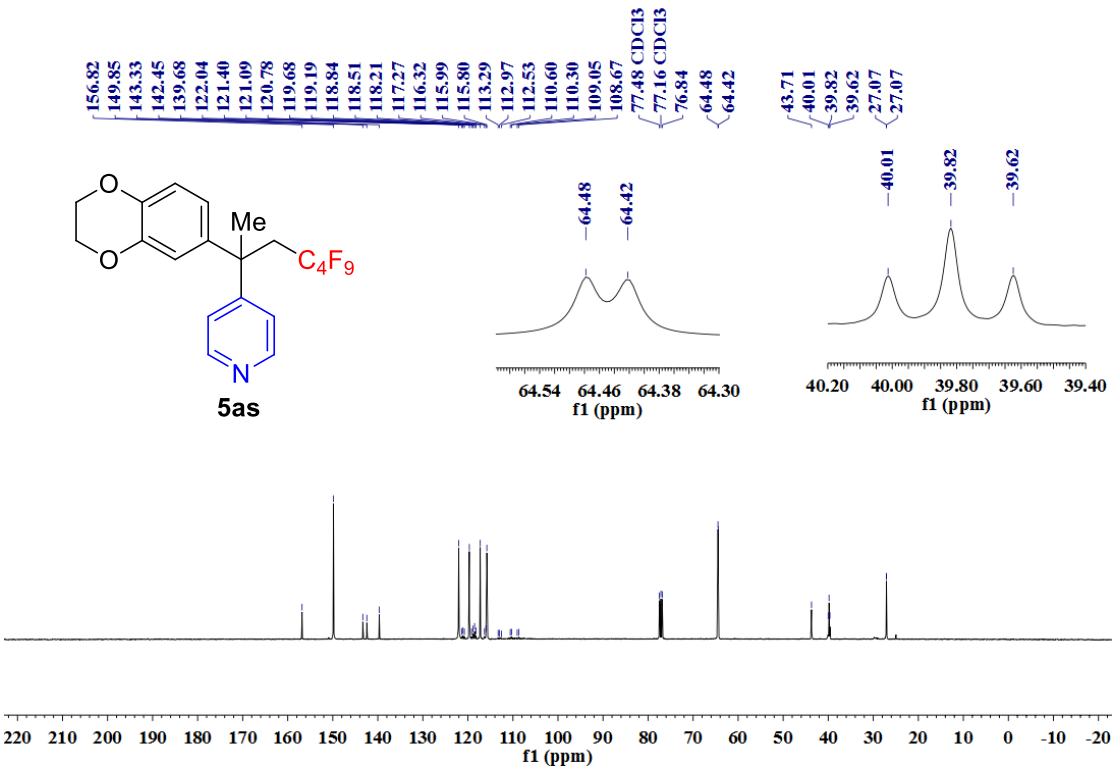

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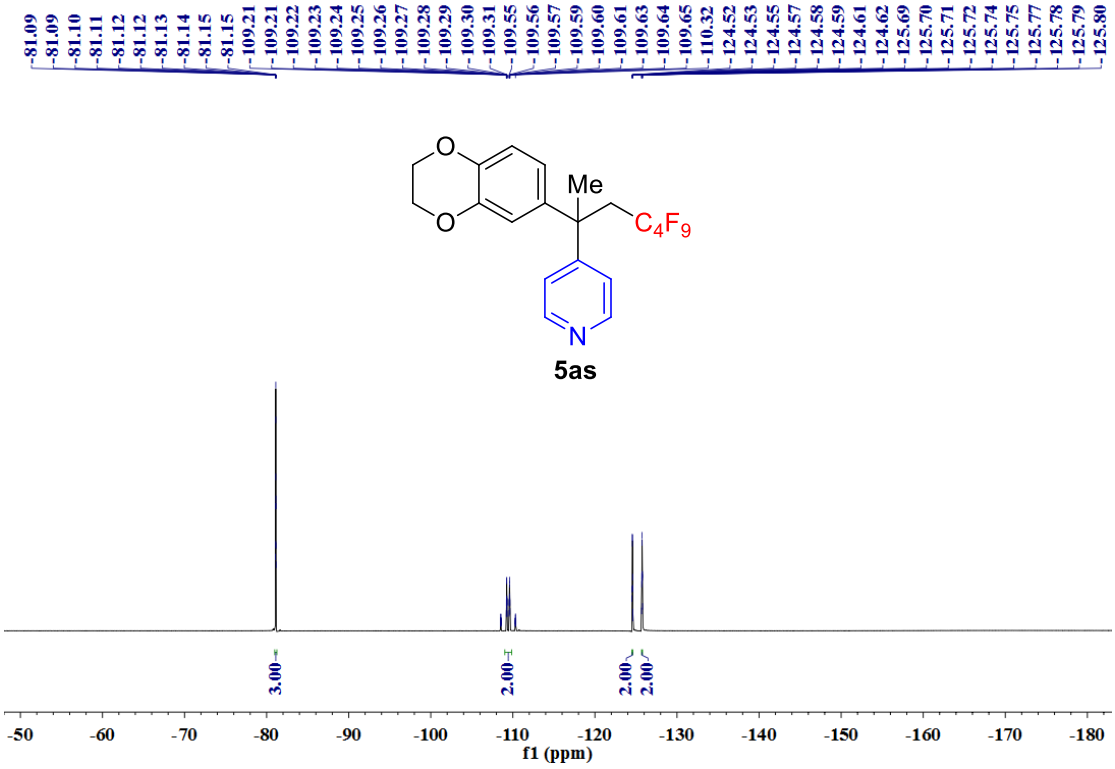

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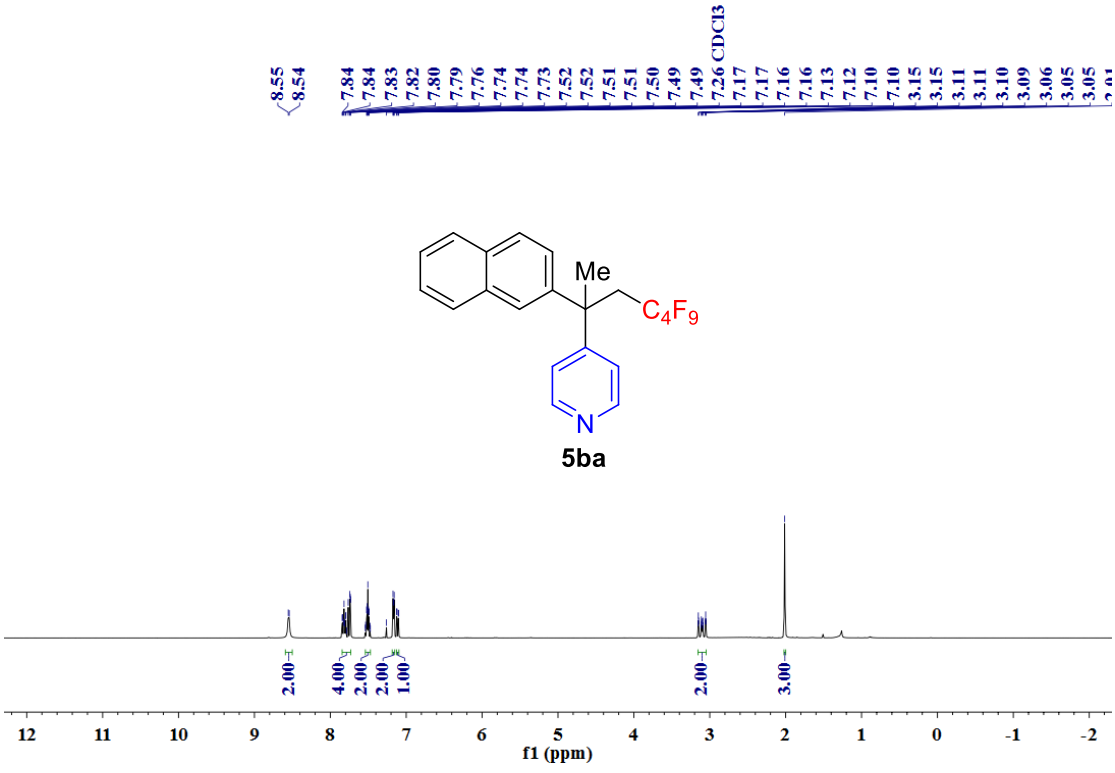

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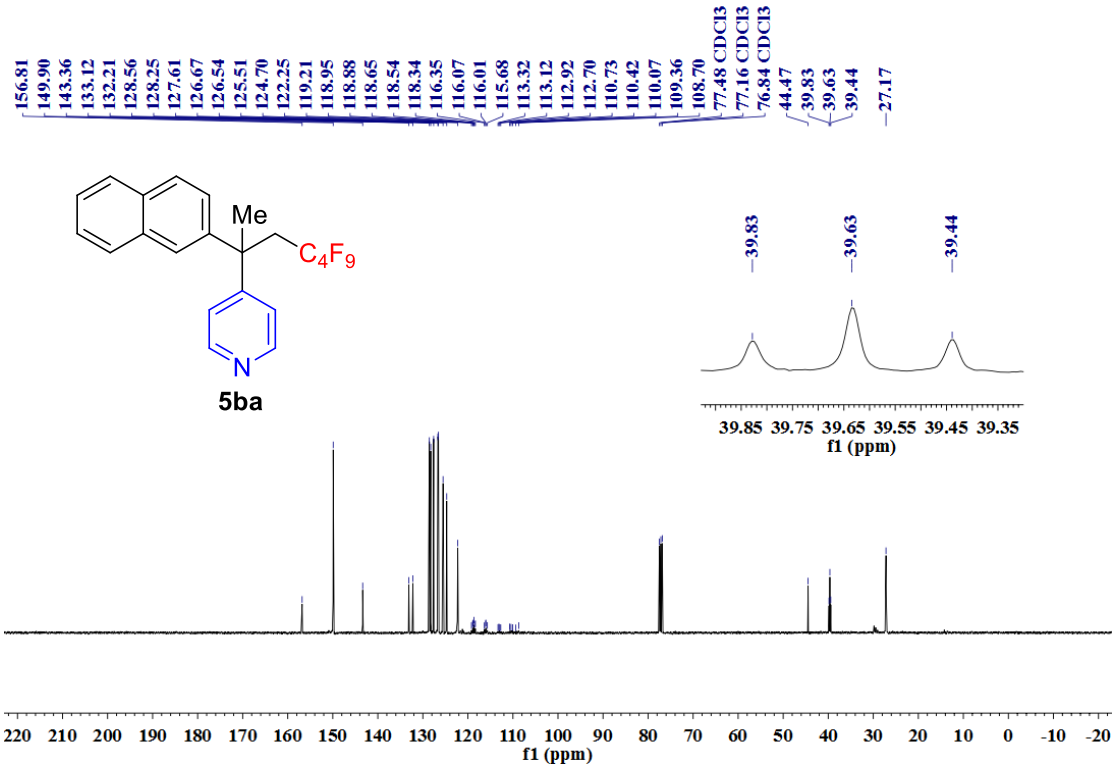

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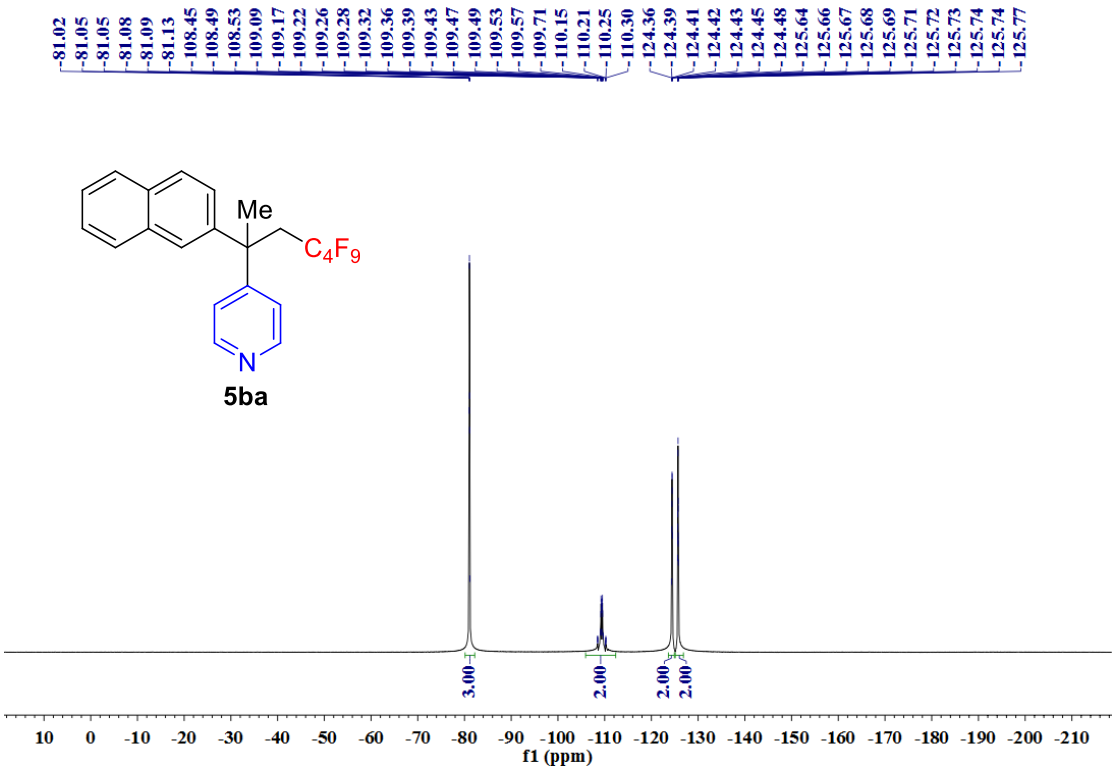

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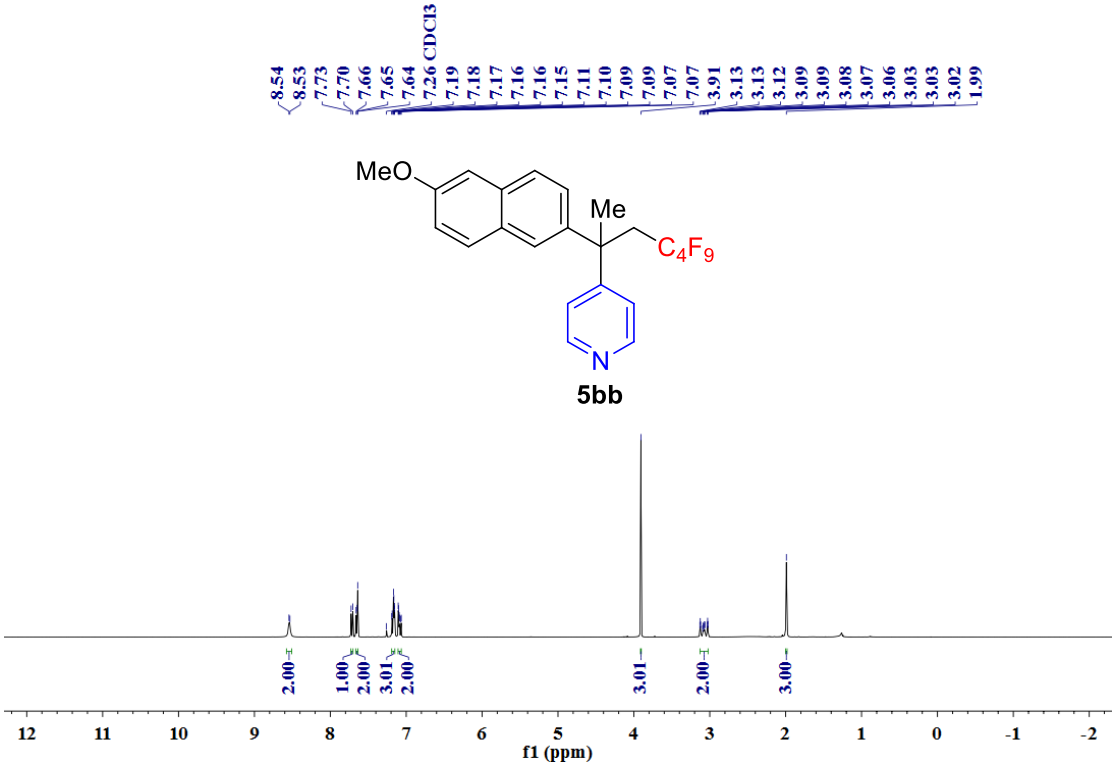

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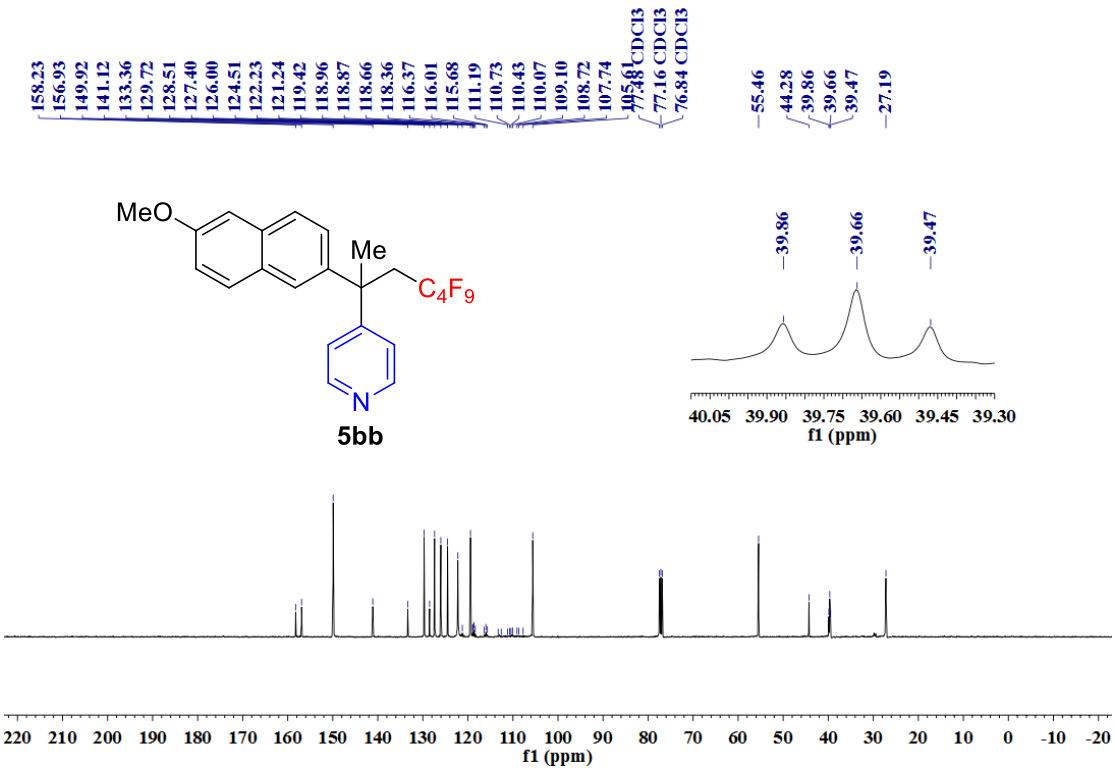

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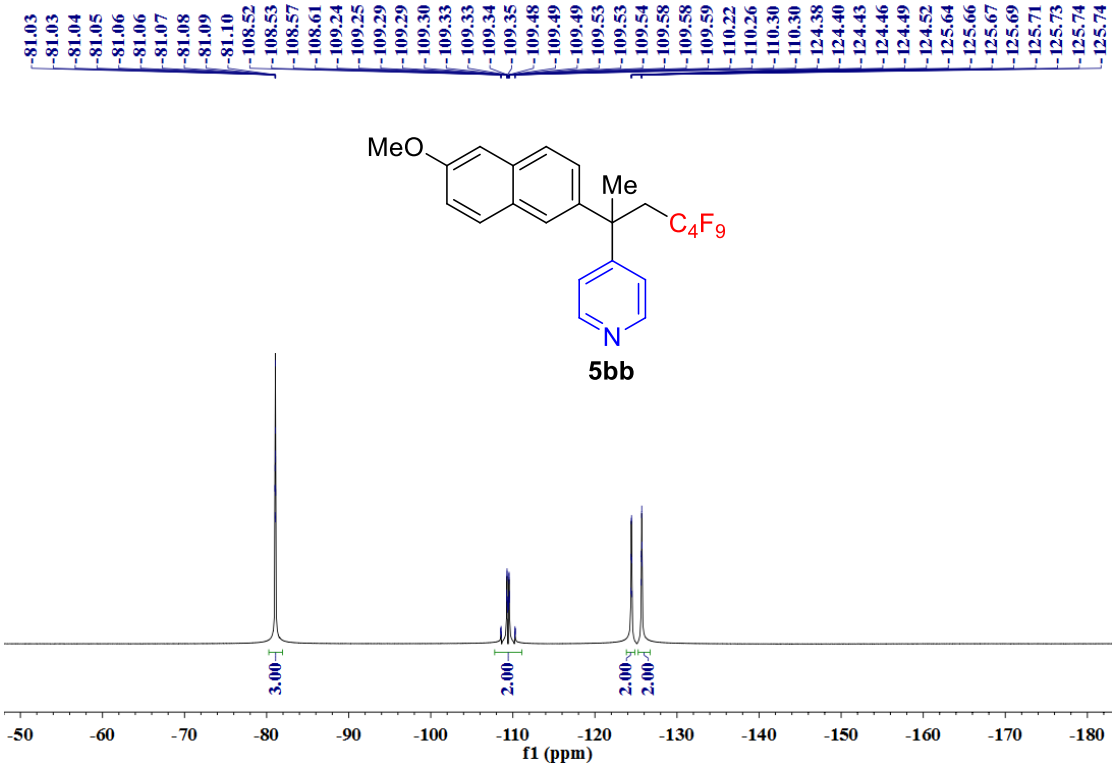

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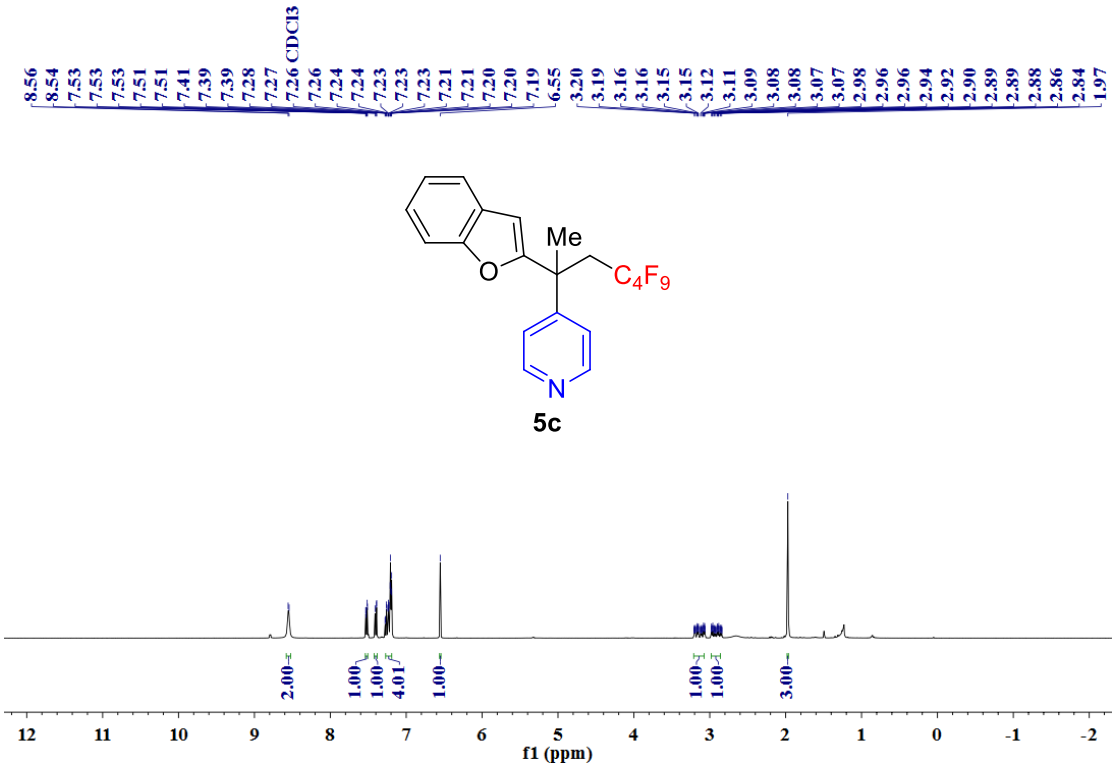

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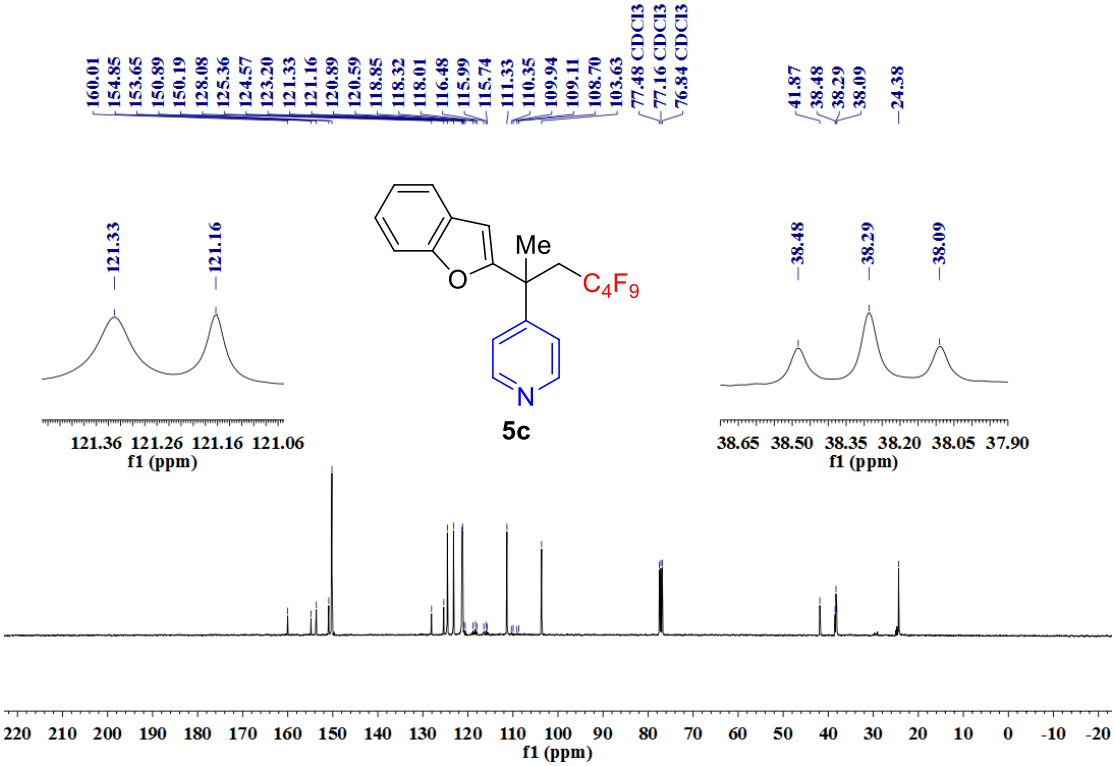

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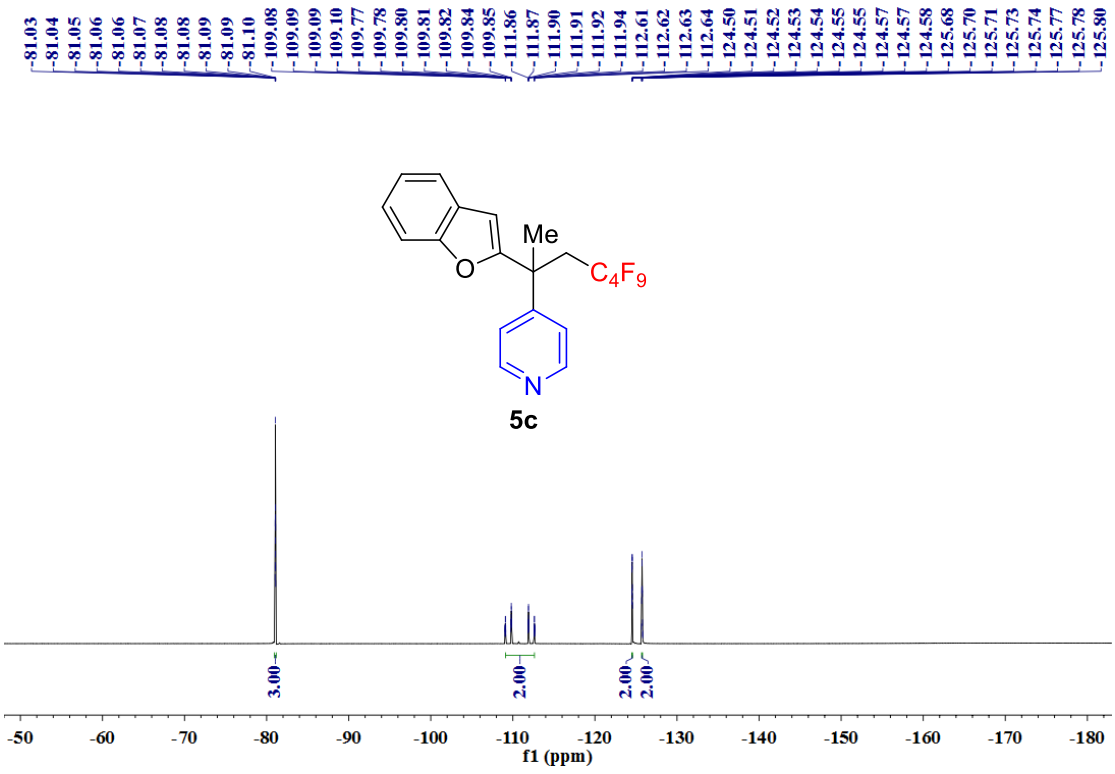

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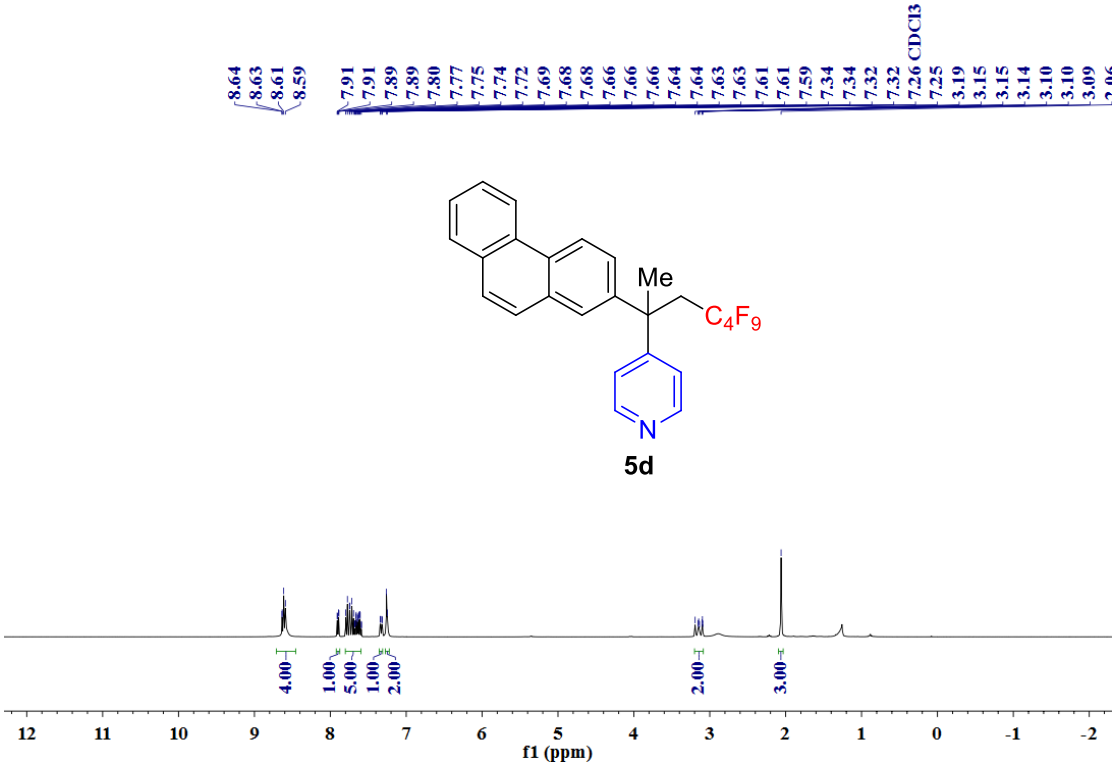

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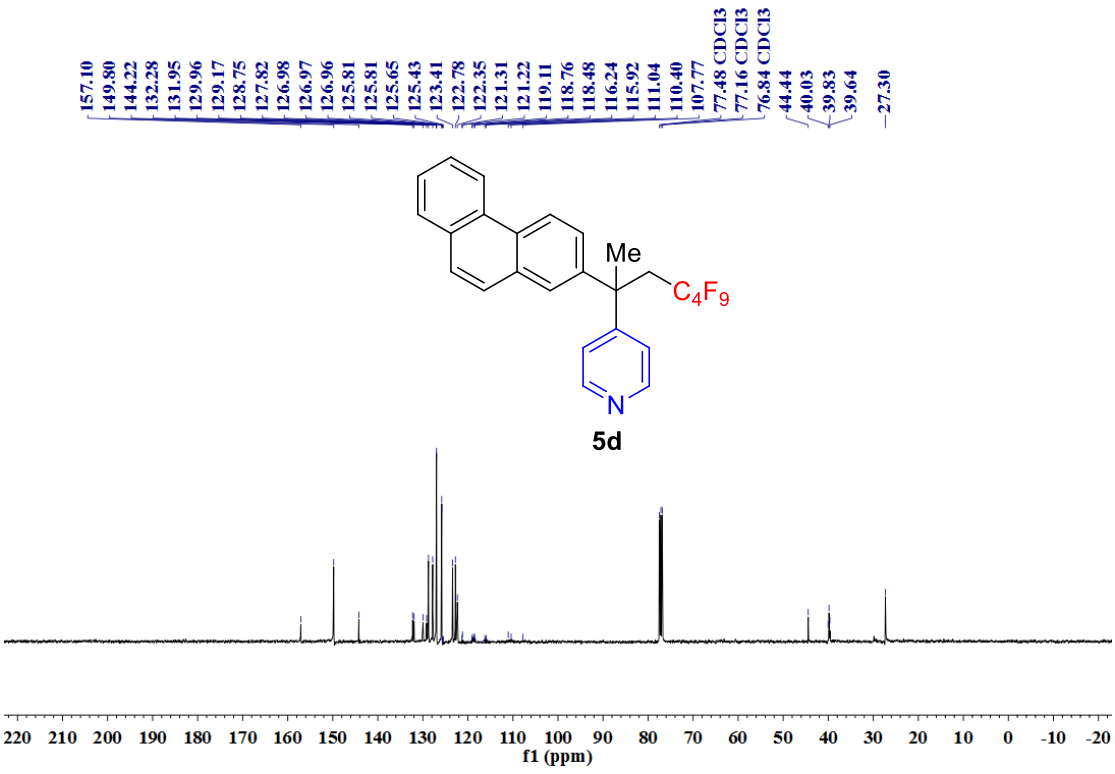

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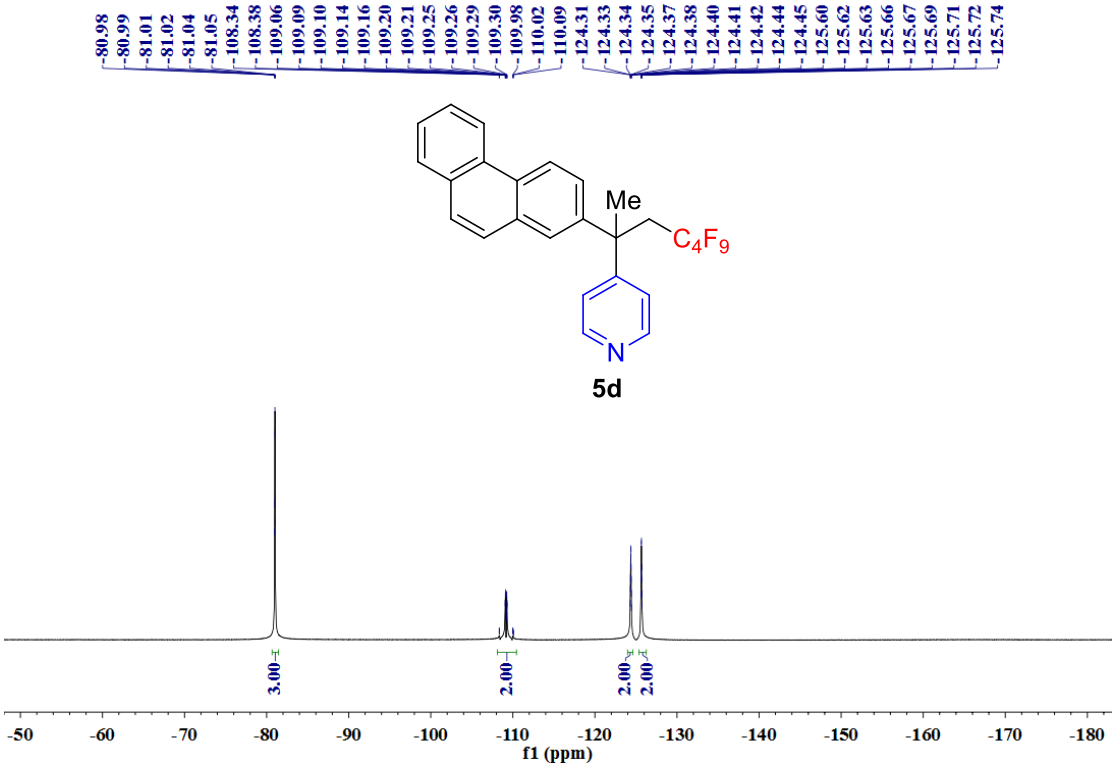

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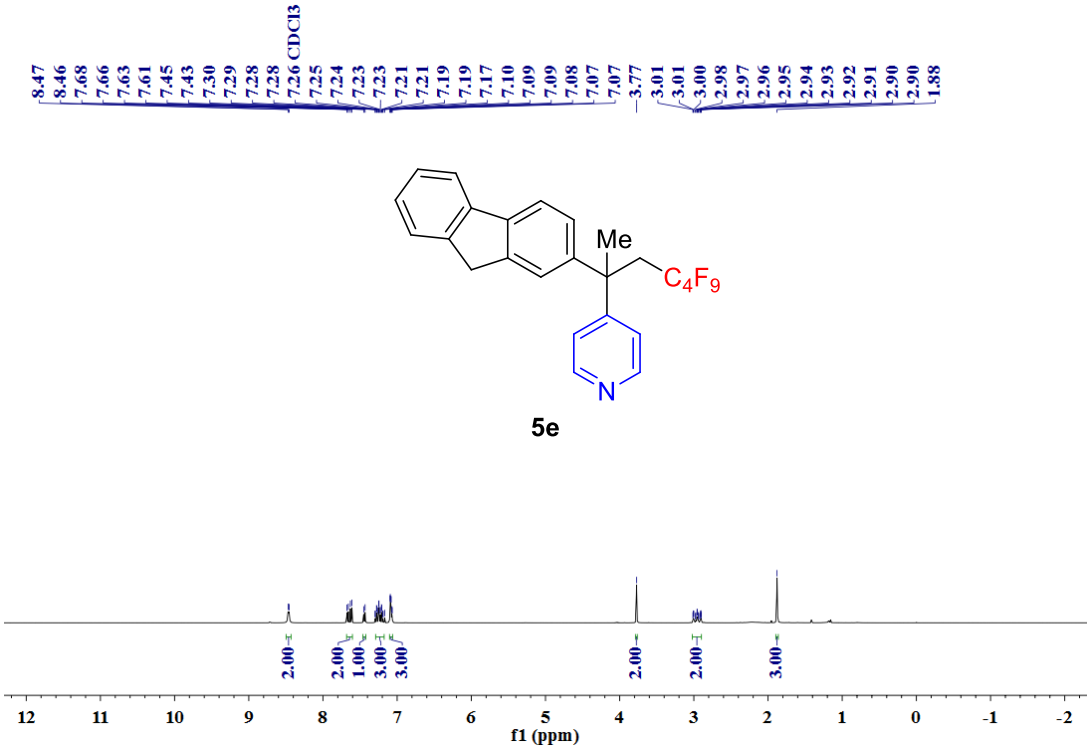

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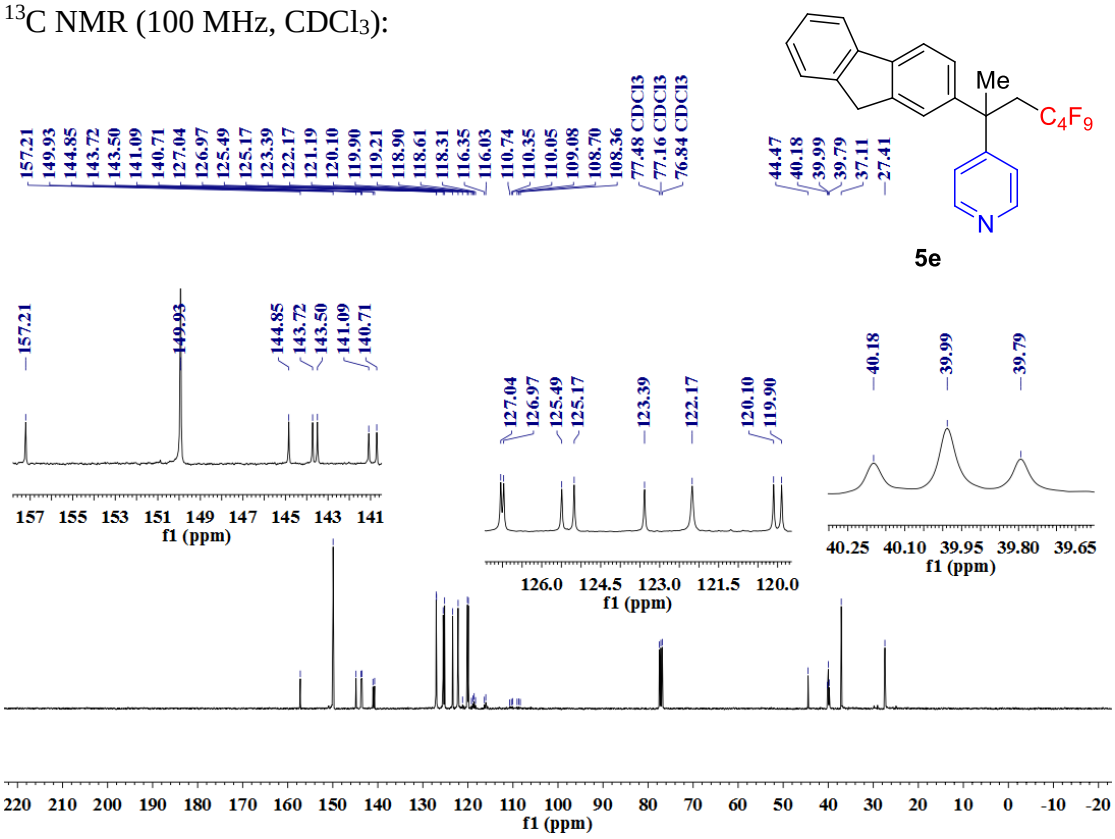
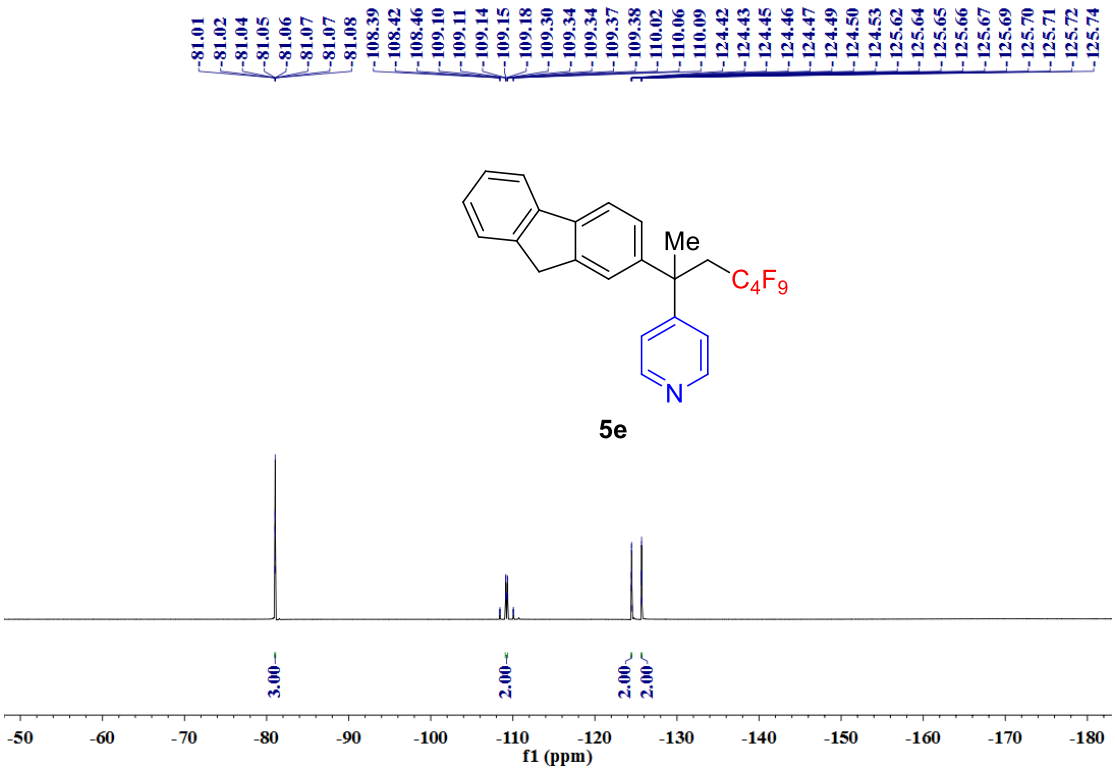
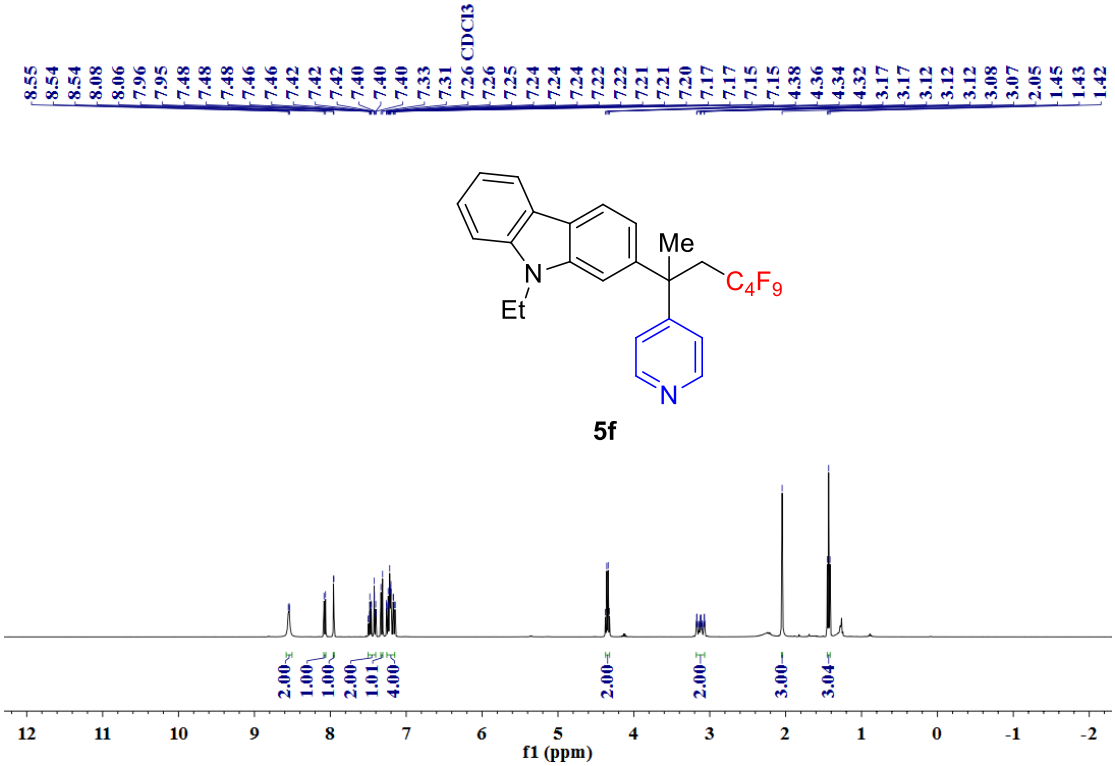


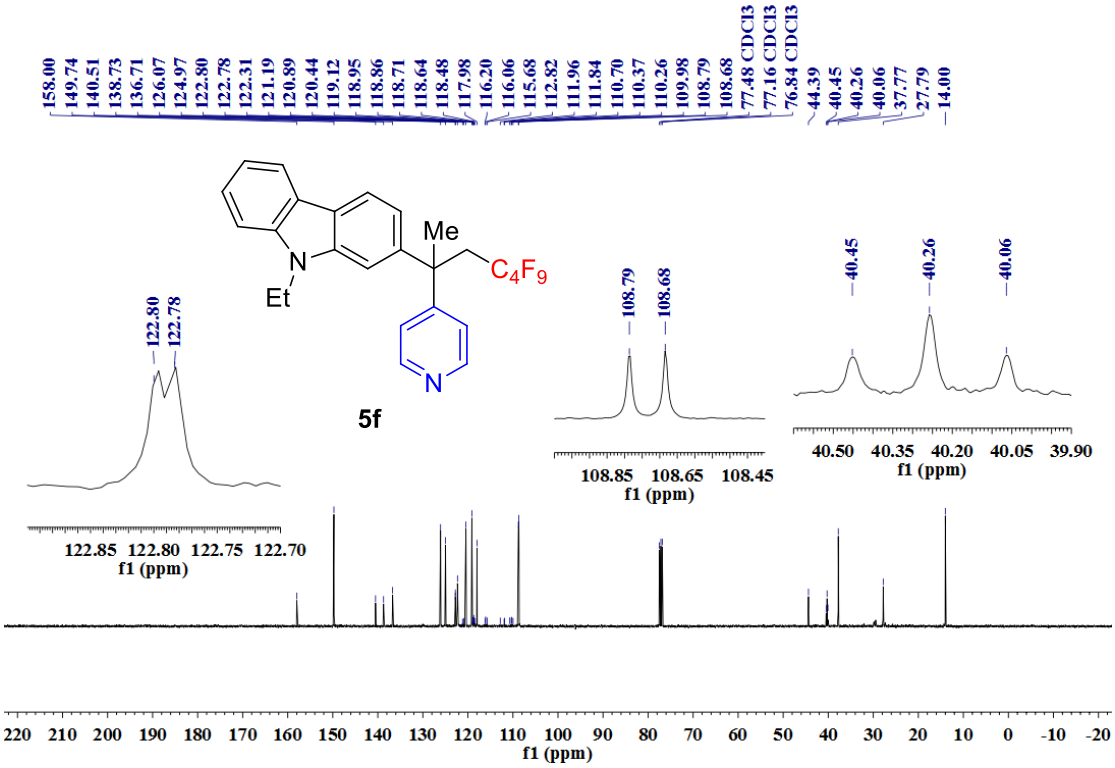
^{19}F NMR (376 MHz, $CDCl_3$):



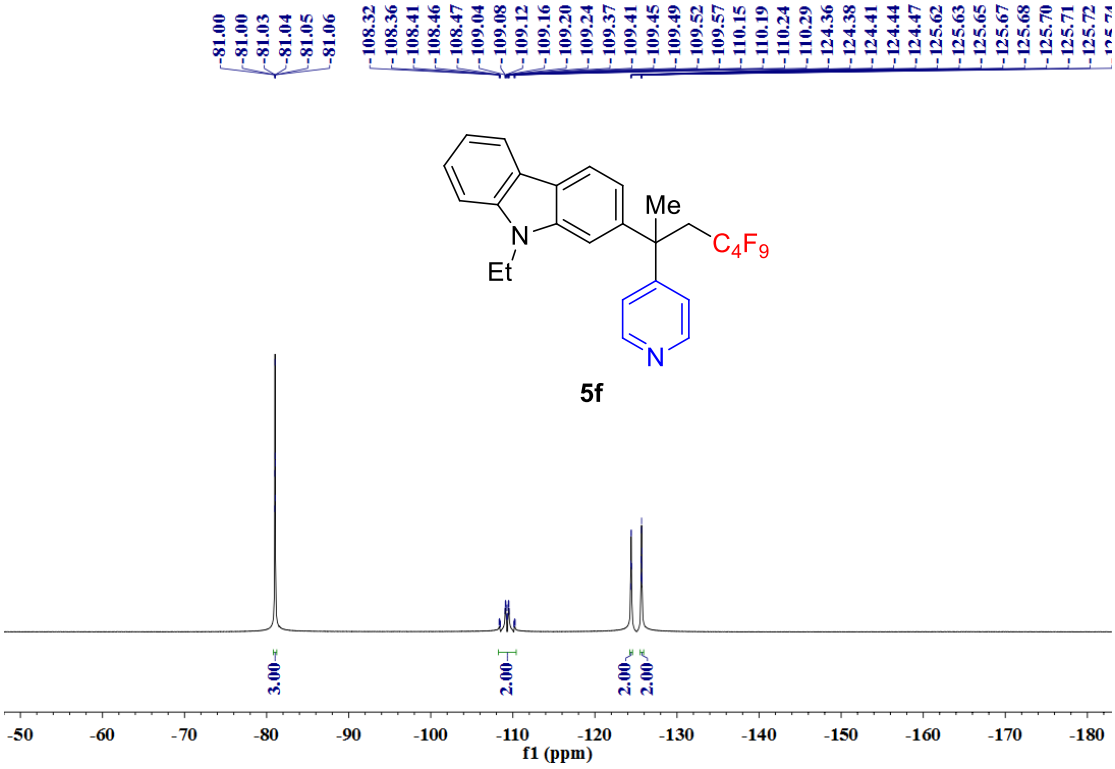
^{1}H NMR (400 MHz, $CDCl_3$):



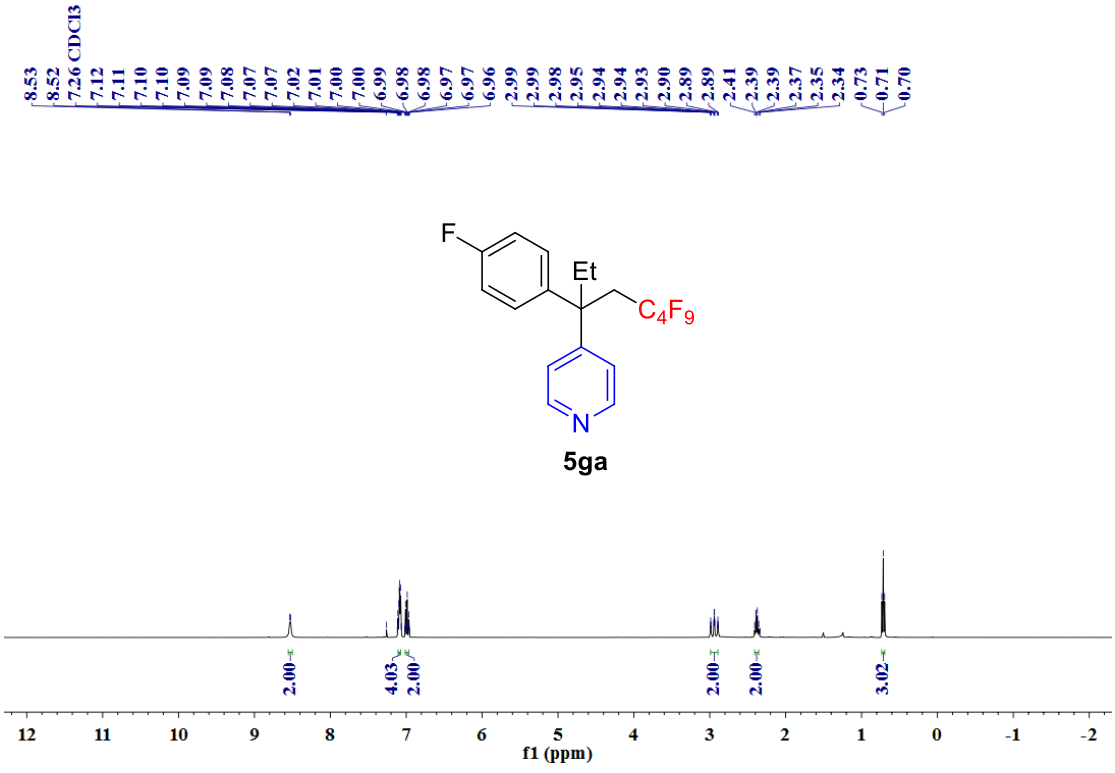
^{13}C NMR (100 MHz, $CDCl_3$):



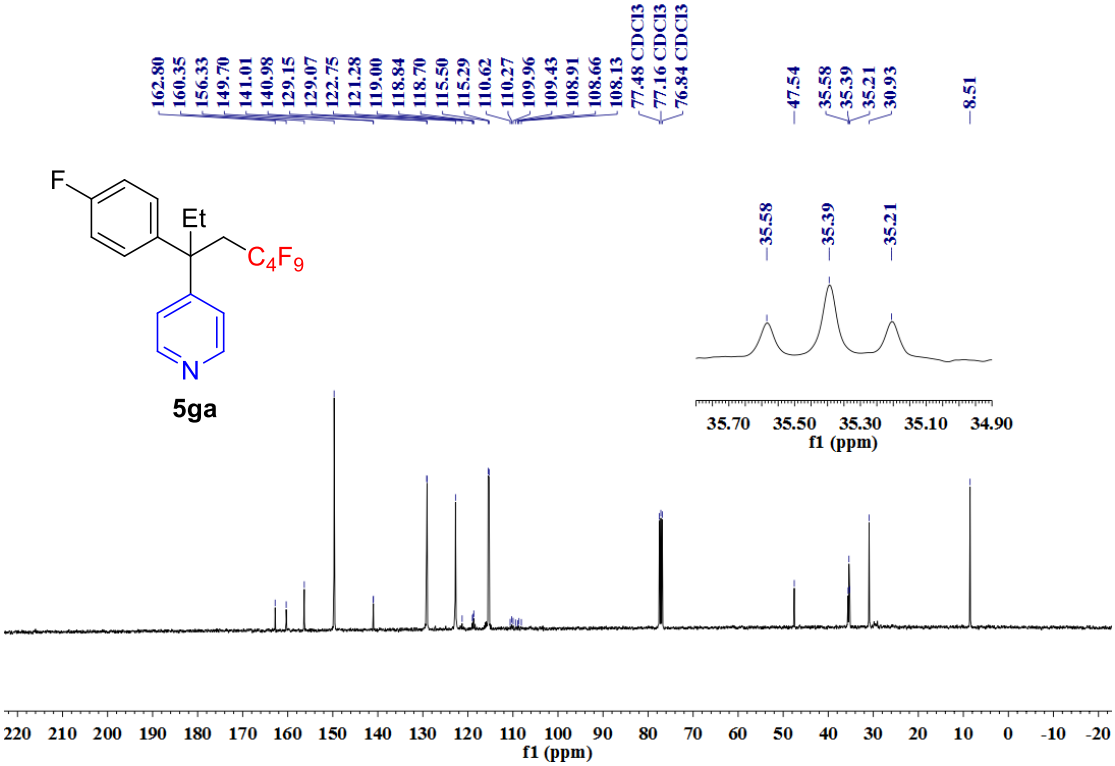
^{19}F NMR (376 MHz, $CDCl_3$):



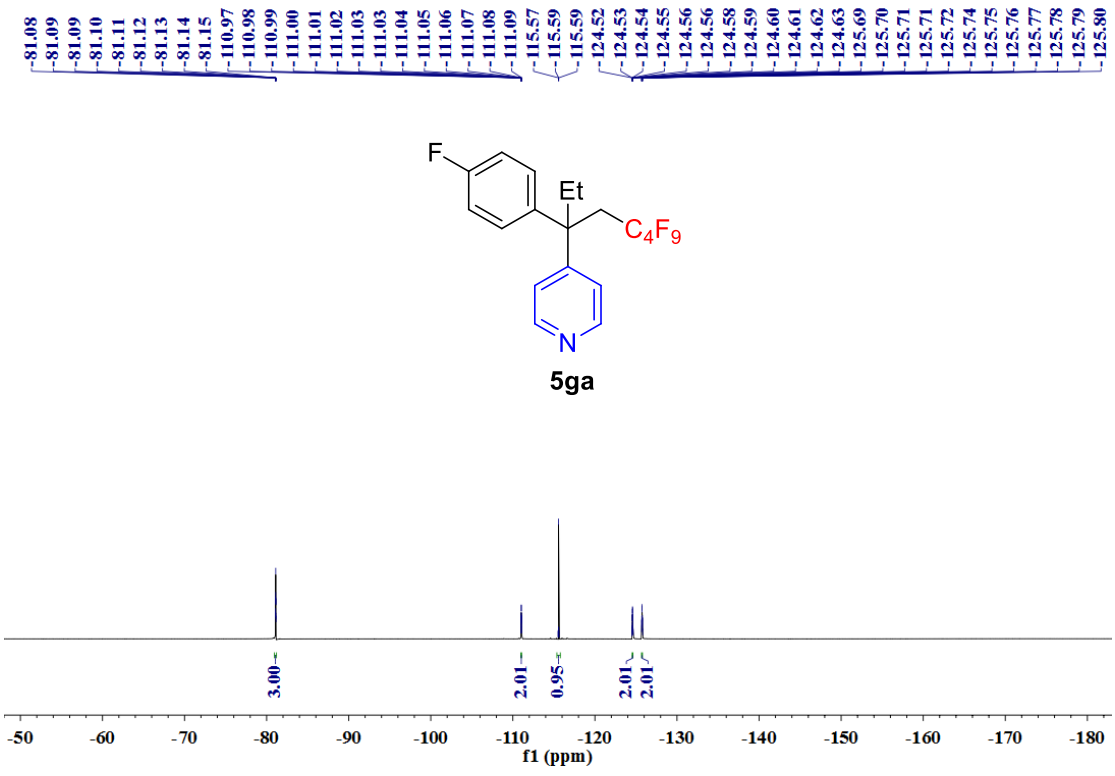
^{1}H NMR (400 MHz, $CDCl_3$):



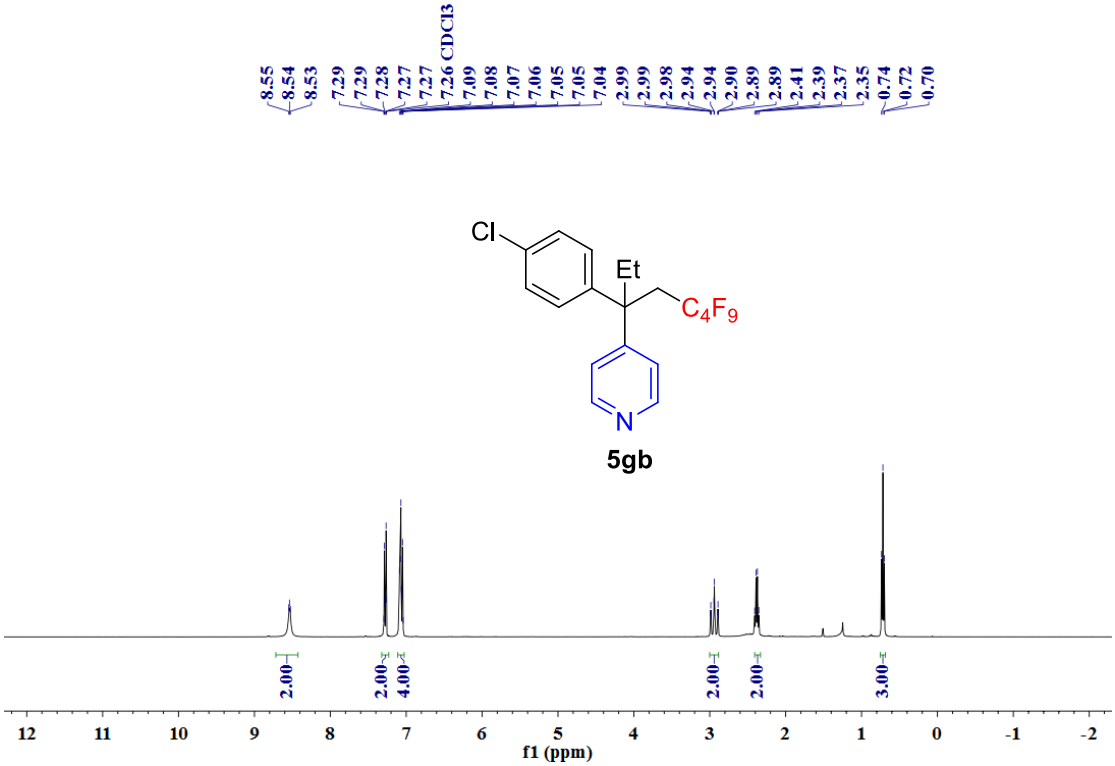
^{13}C NMR (100 MHz, $CDCl_3$):



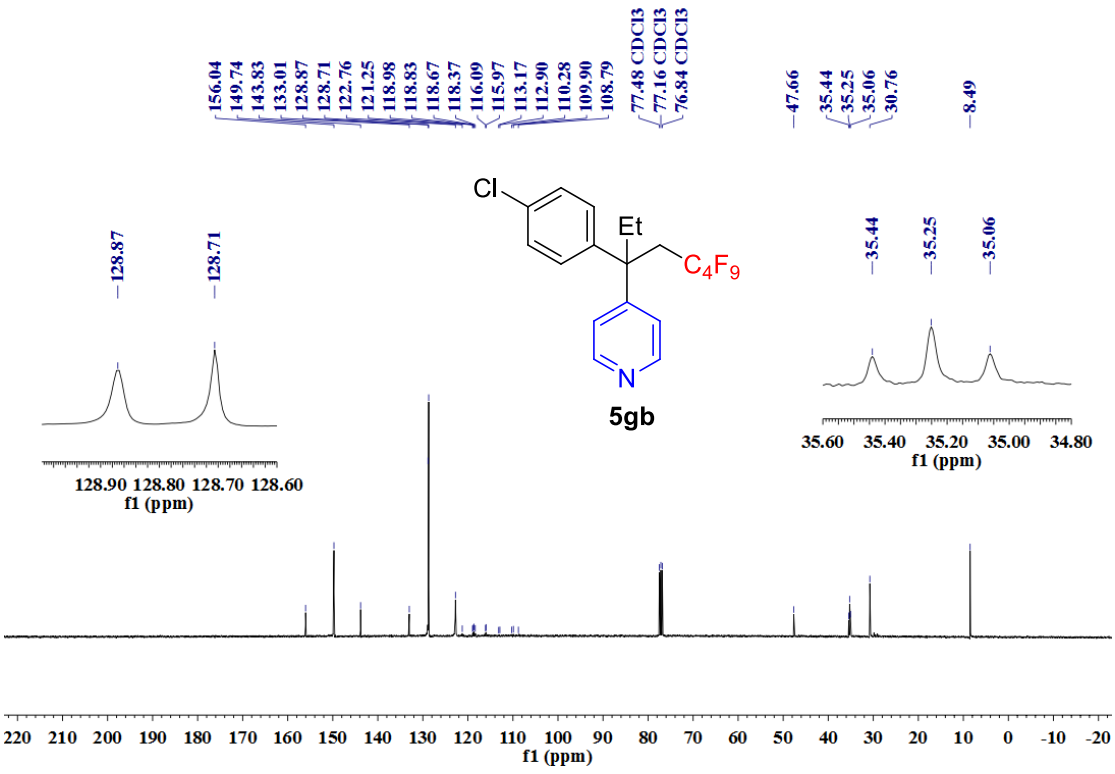
^{19}F NMR (376 MHz, $CDCl_3$):



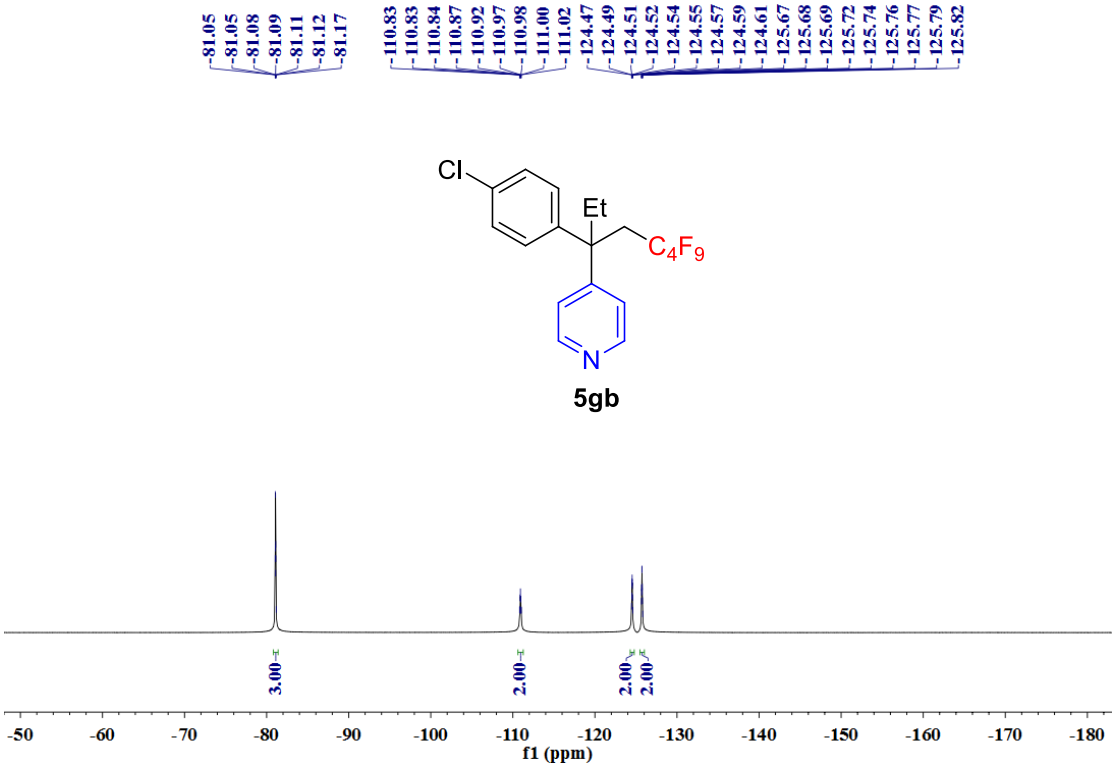
^{1}H NMR (400 MHz, $CDCl_3$):



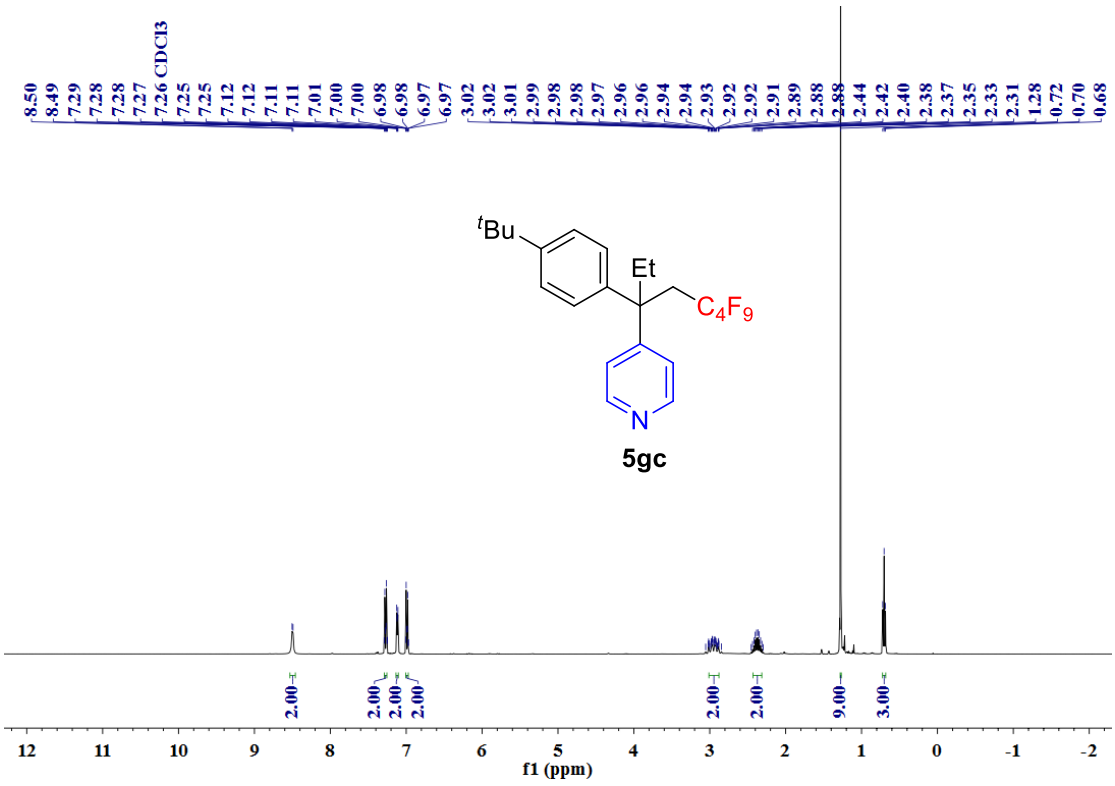
^{13}C NMR (100 MHz, $CDCl_3$):



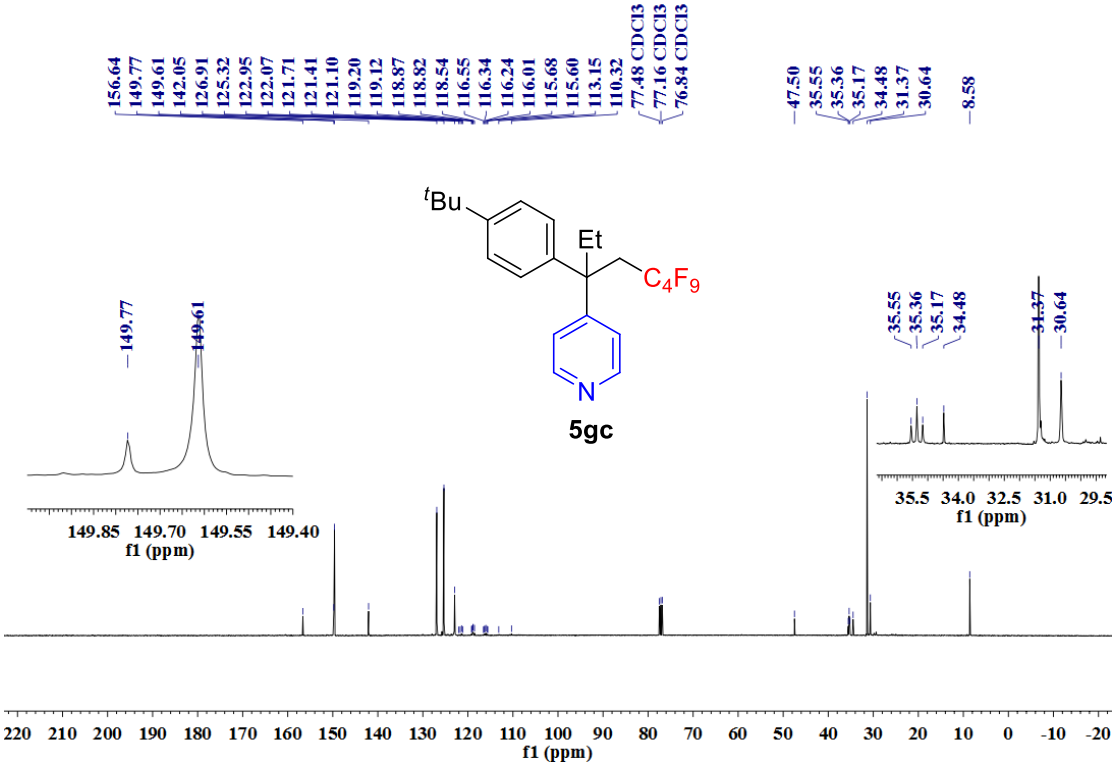
^{19}F NMR (376 MHz, $CDCl_3$):



^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):



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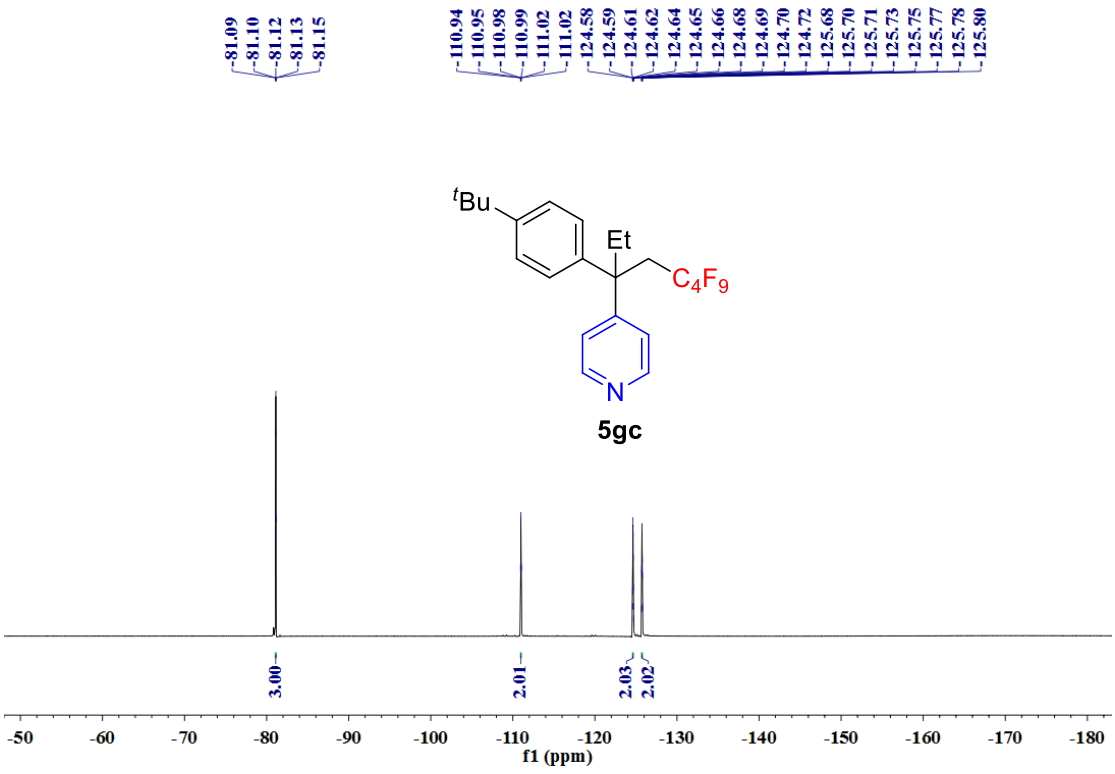
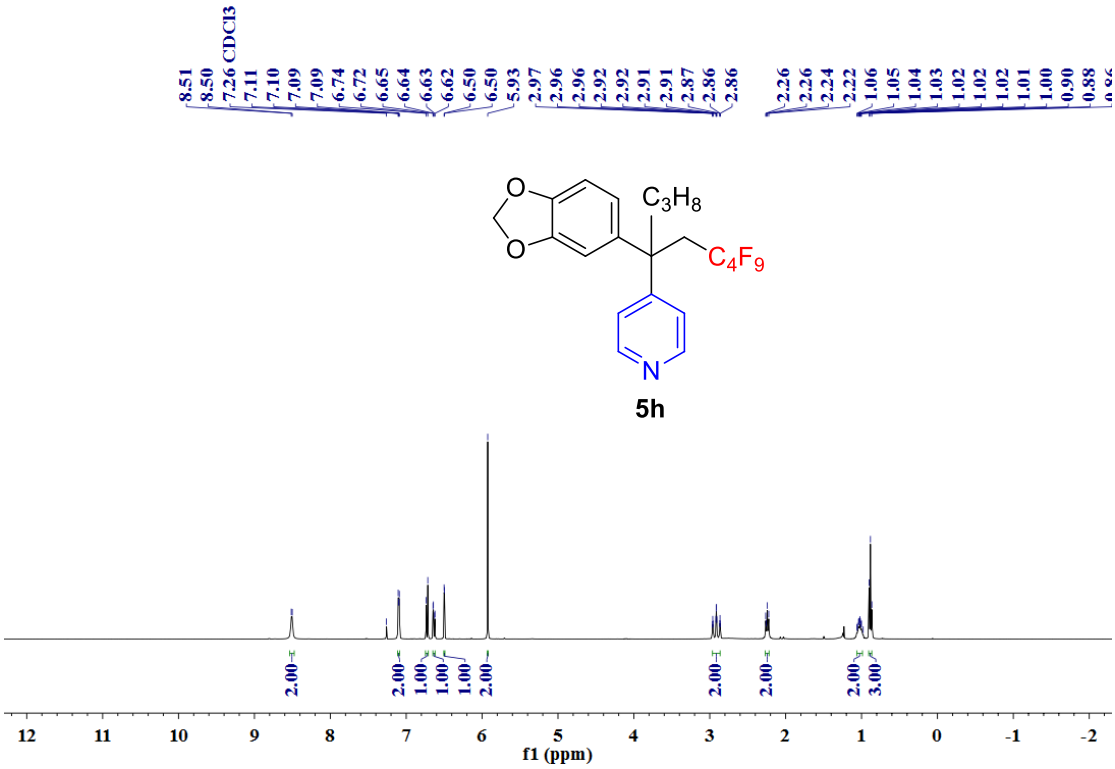
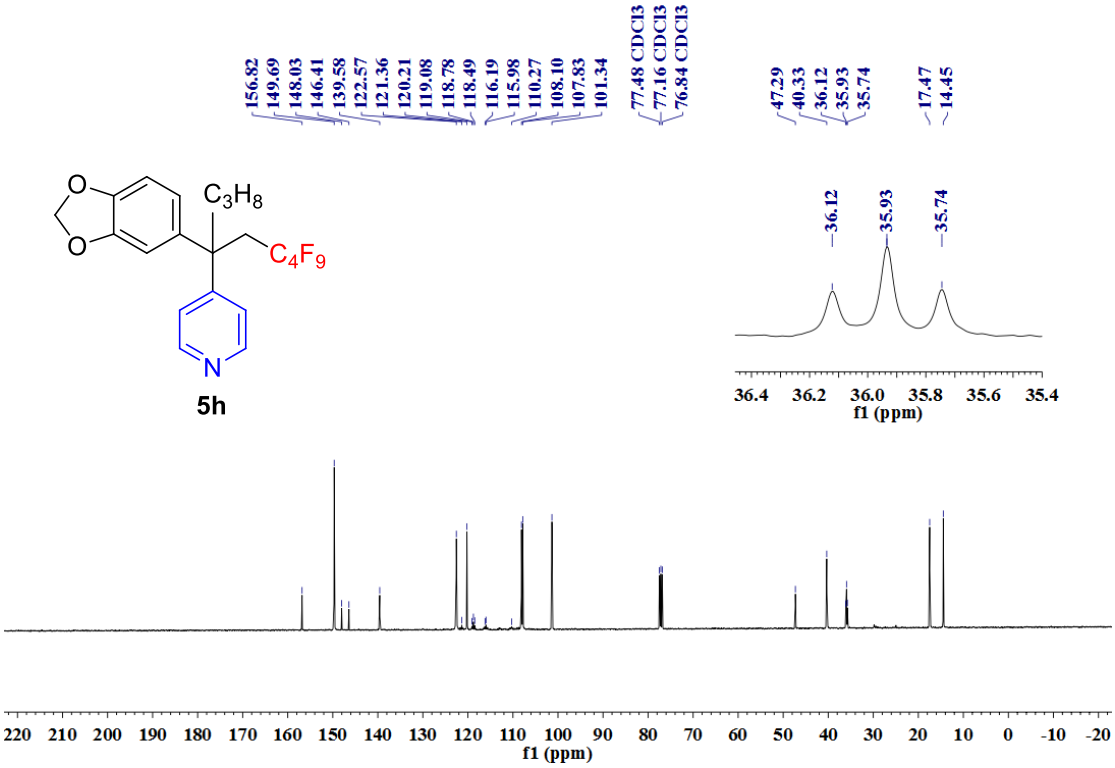


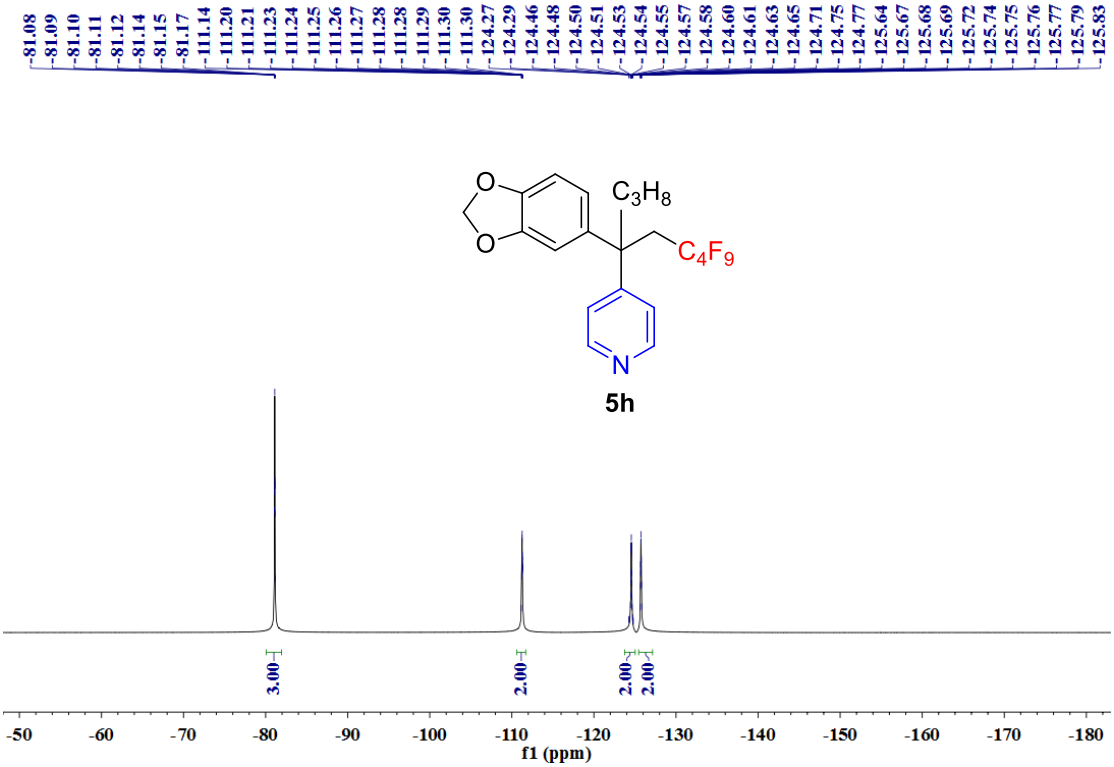
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):



^{19}F NMR (376 MHz, $CDCl_3$):



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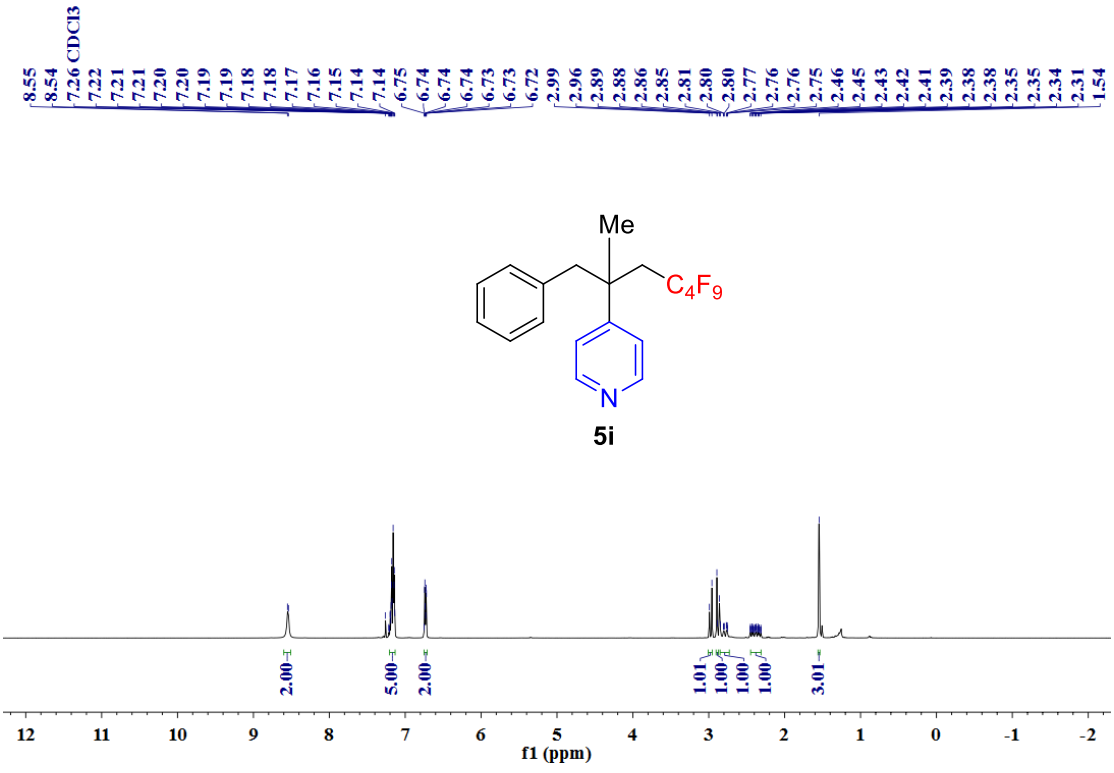
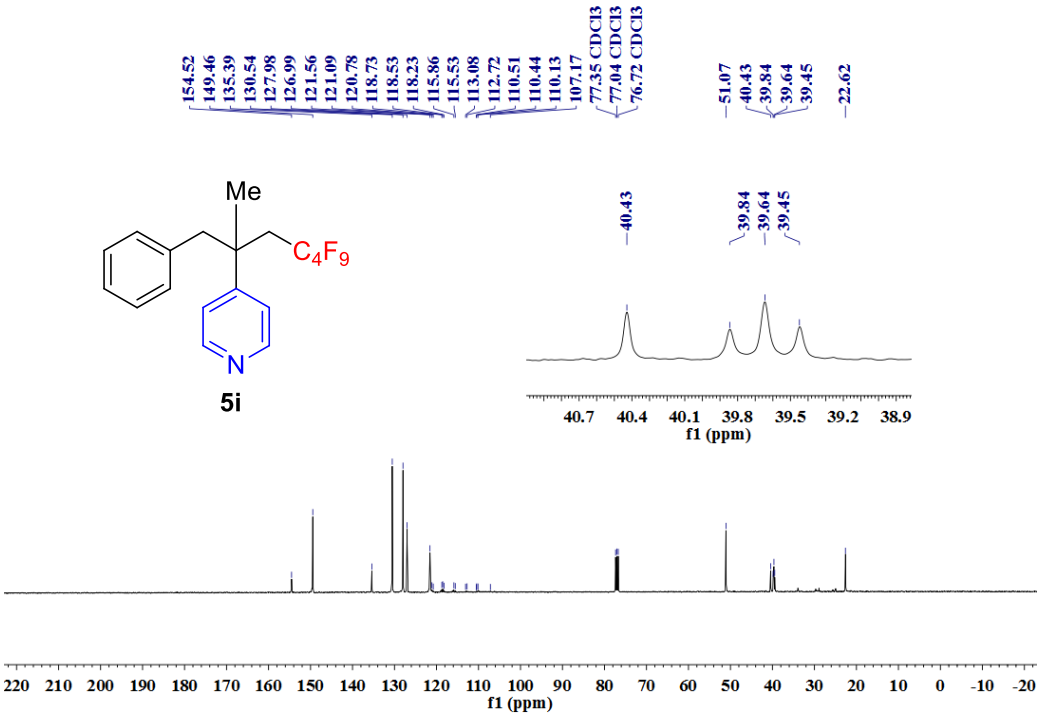
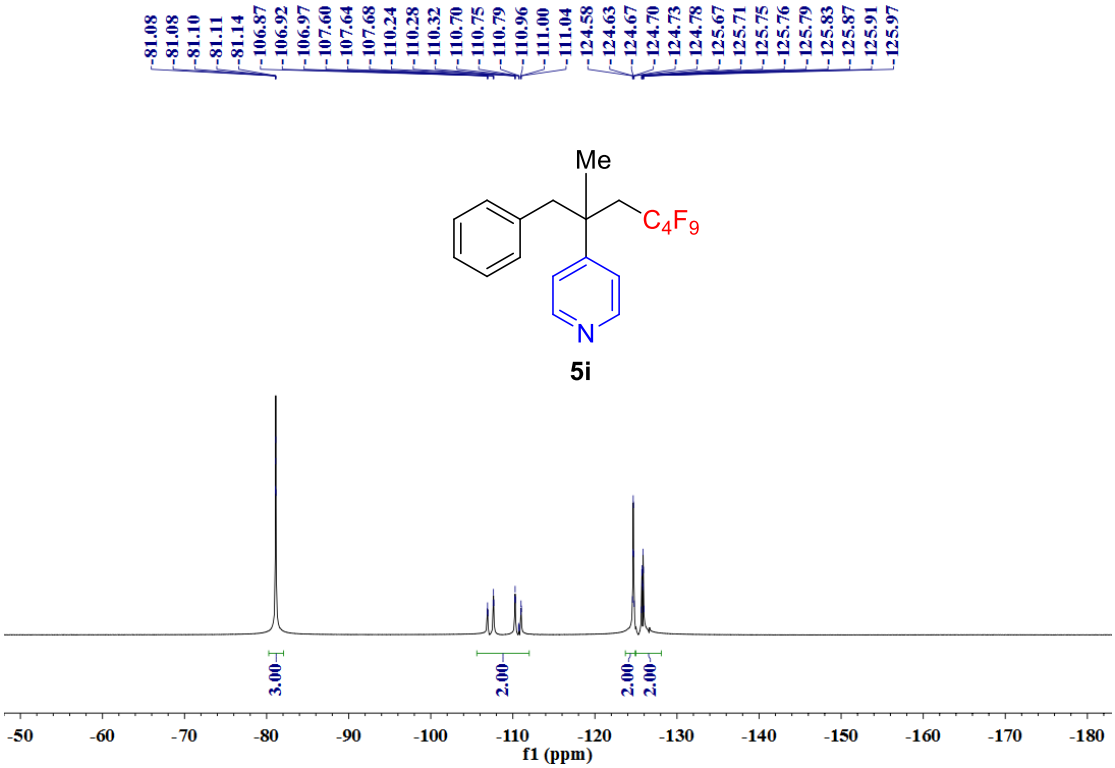


^{13}C NMR (100 MHz, $CDCl_3$):



^{19}F NMR (376 MHz, $CDCl_3$):



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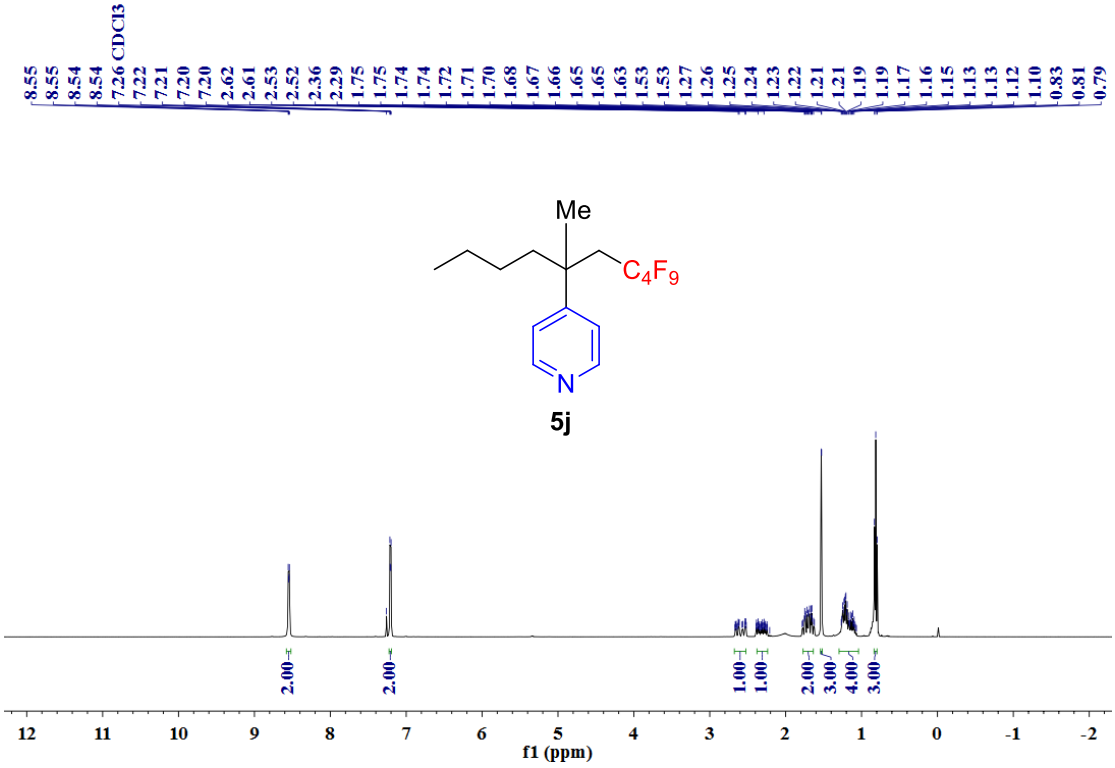

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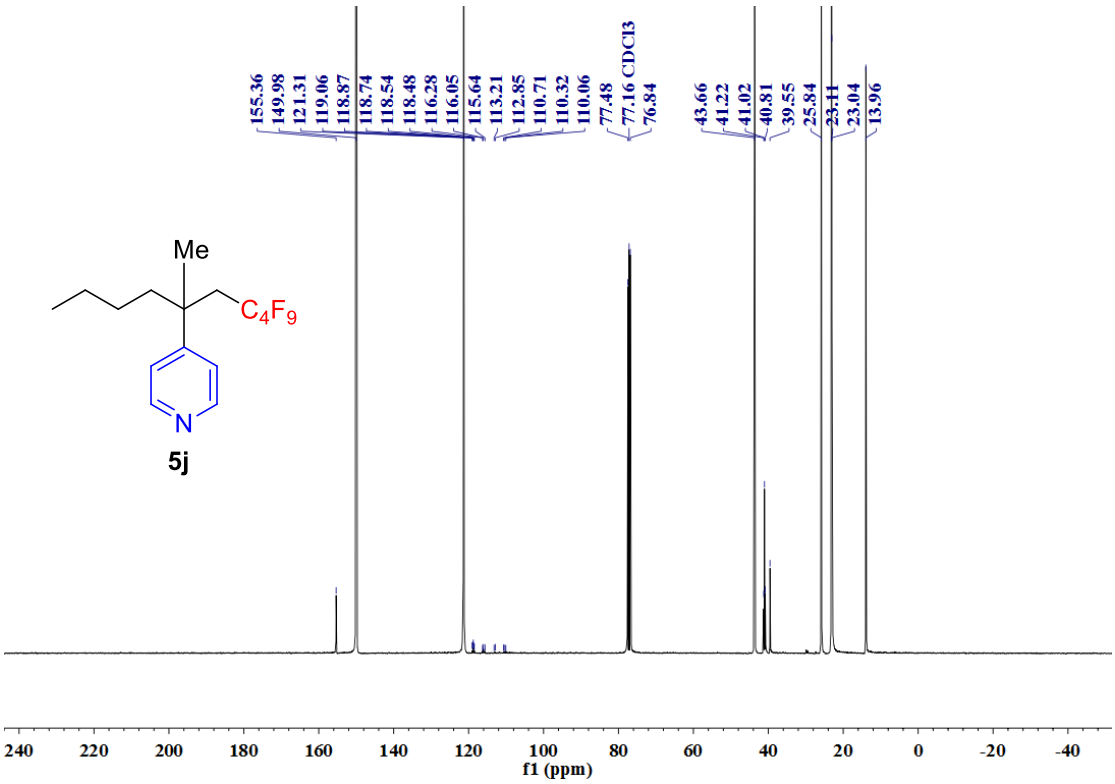

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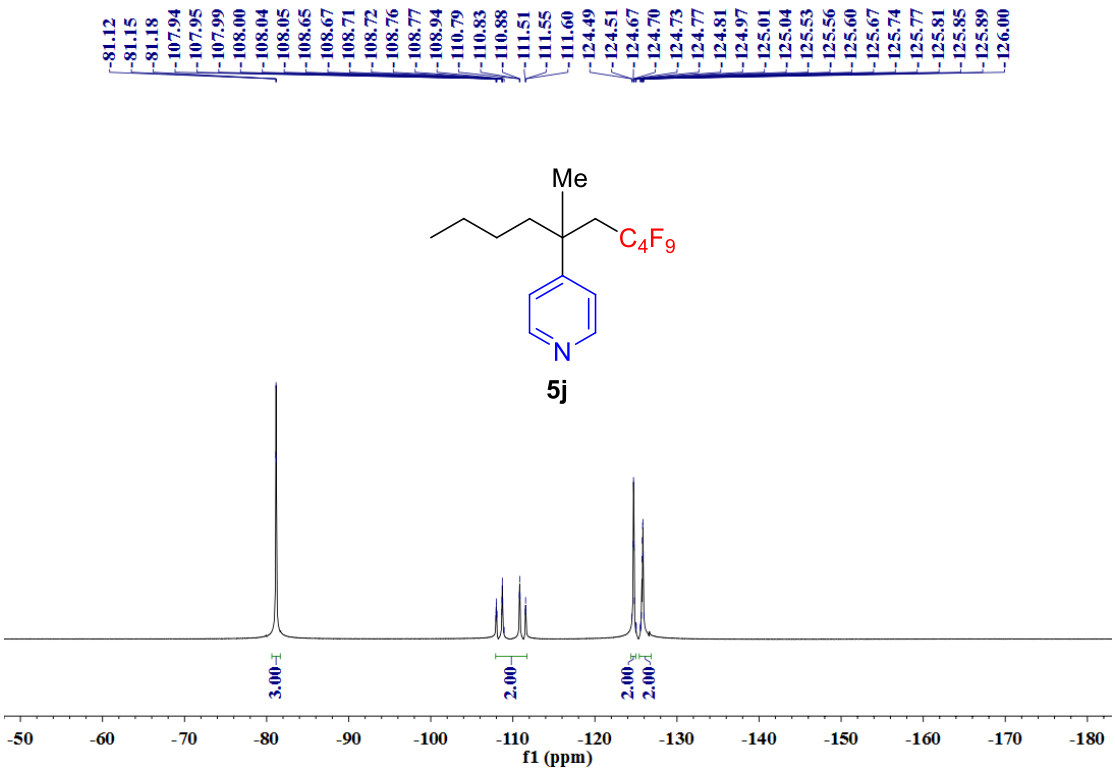
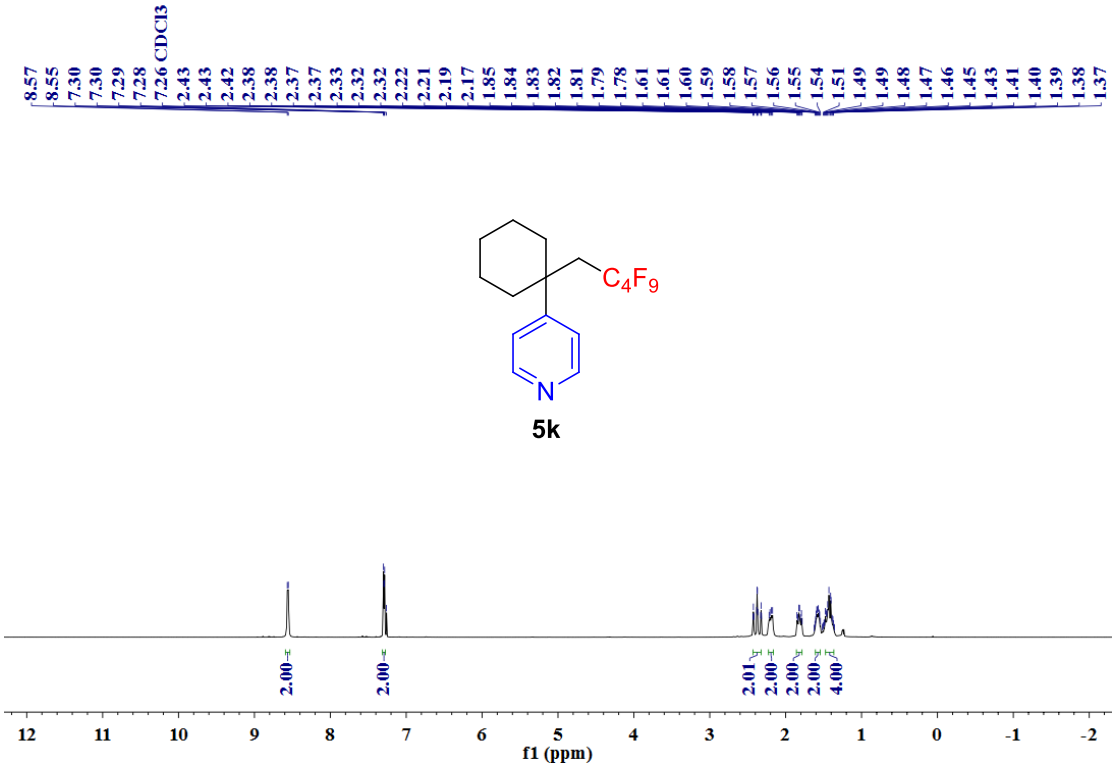


^{1}H NMR (400 MHz, $CDCl_3$):



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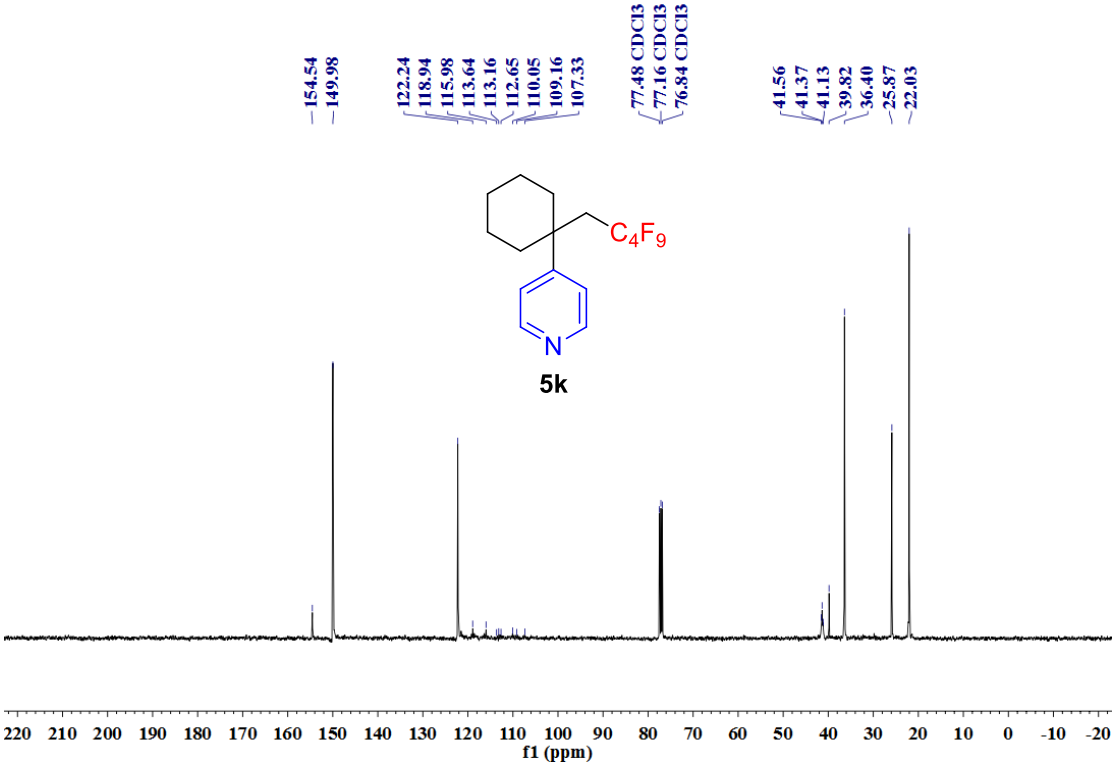
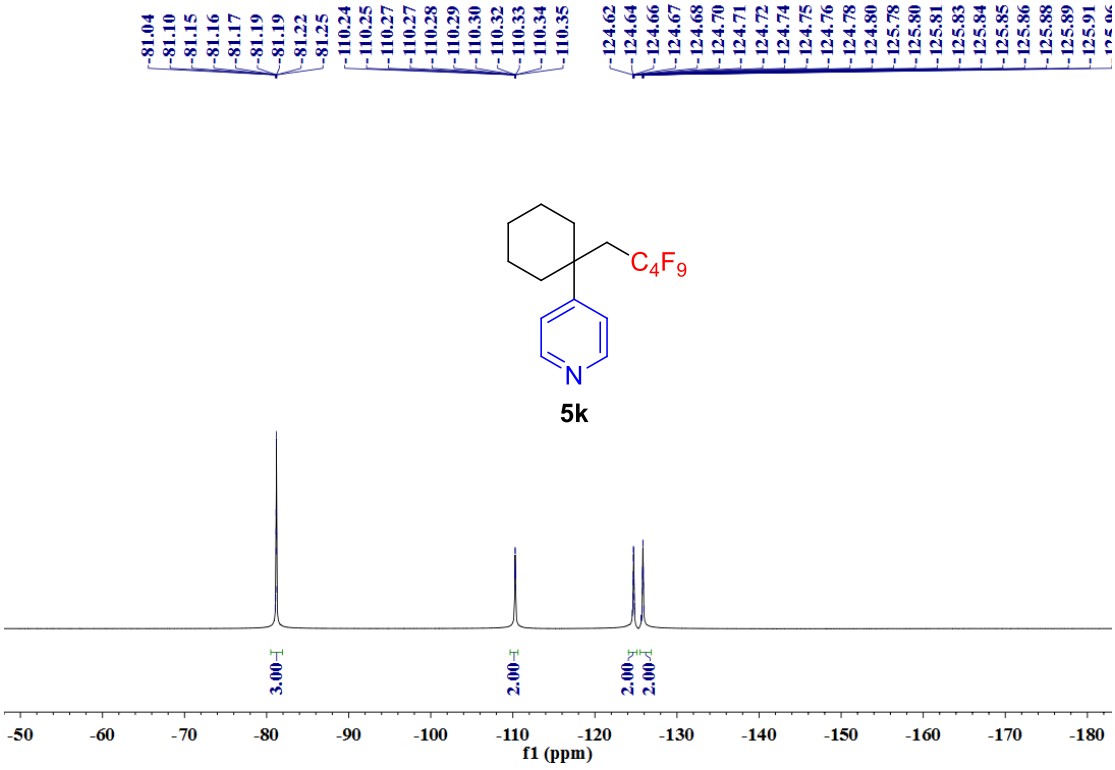
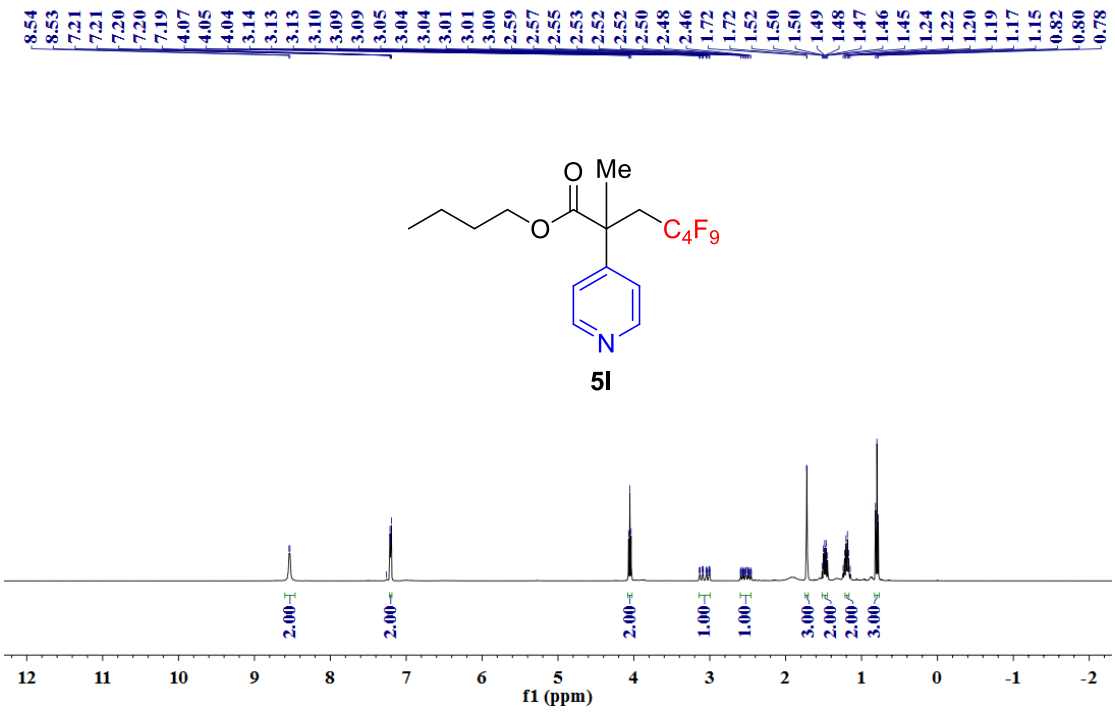


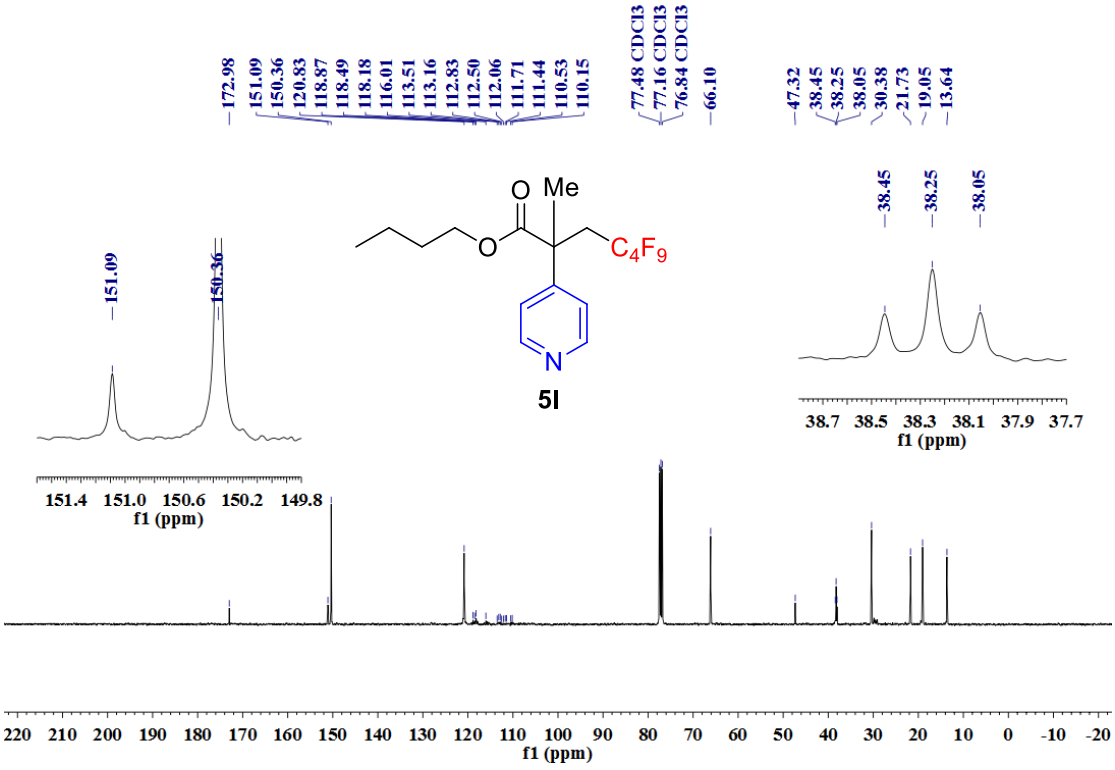
^{19}F NMR (376 MHz, $CDCl_3$):



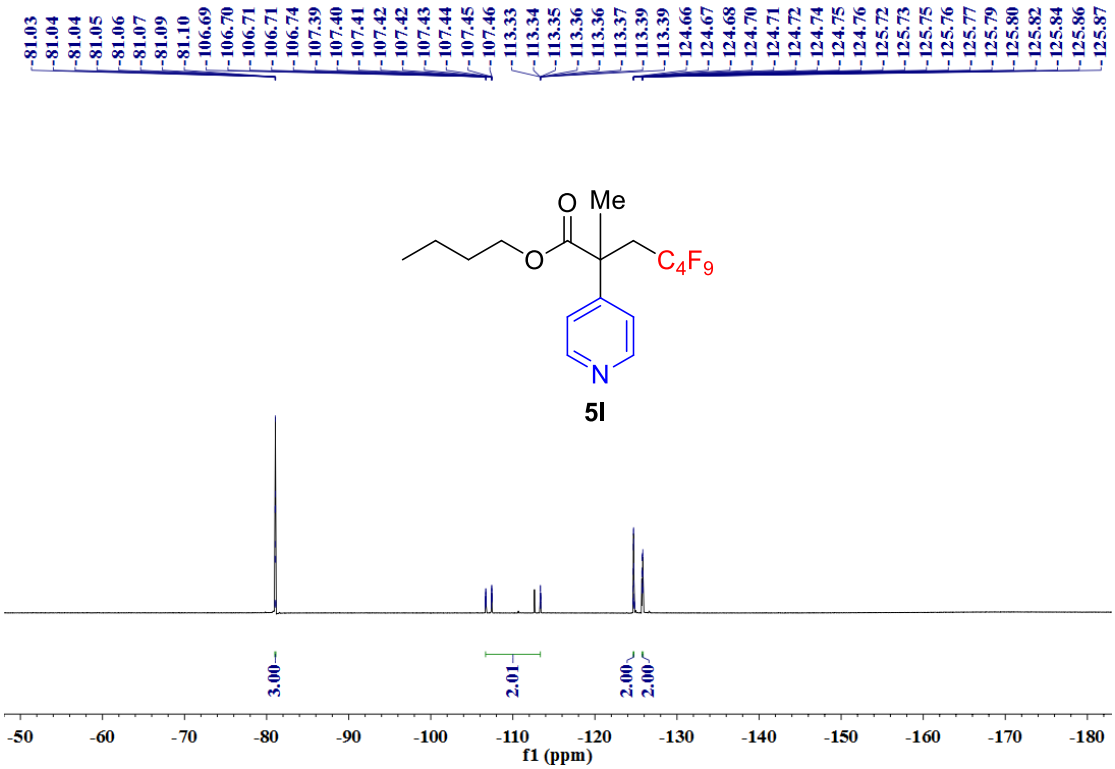
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):



^{19}F NMR (376 MHz, $CDCl_3$):



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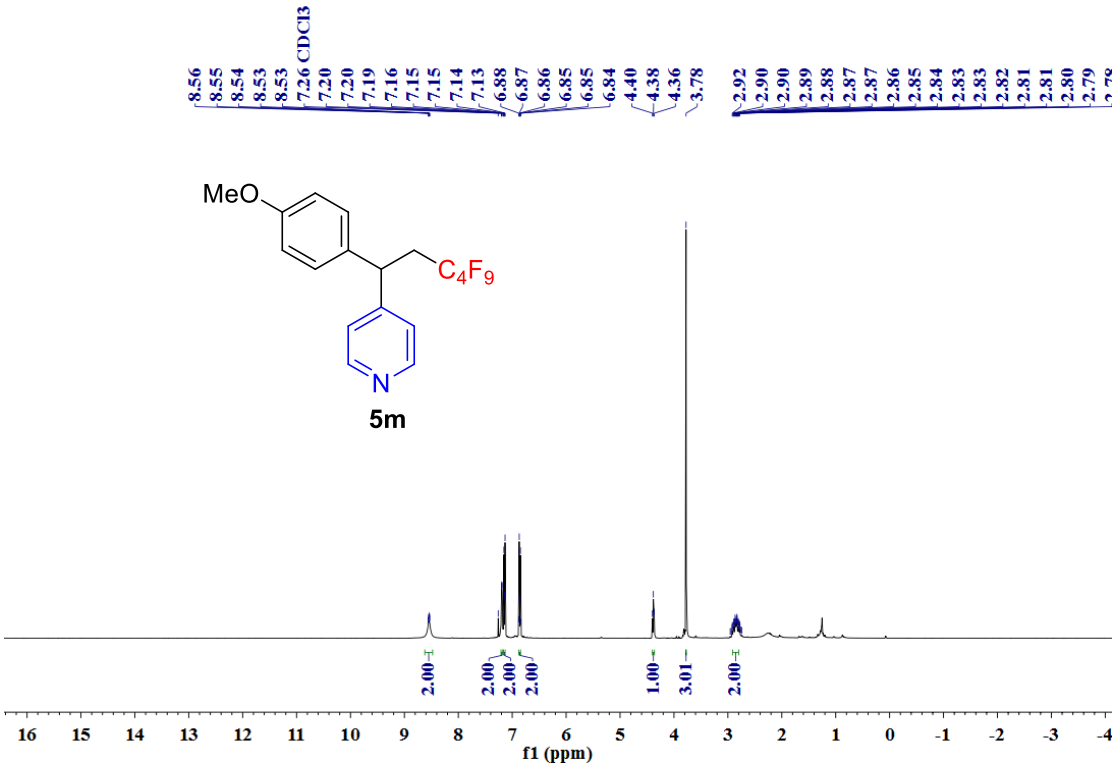
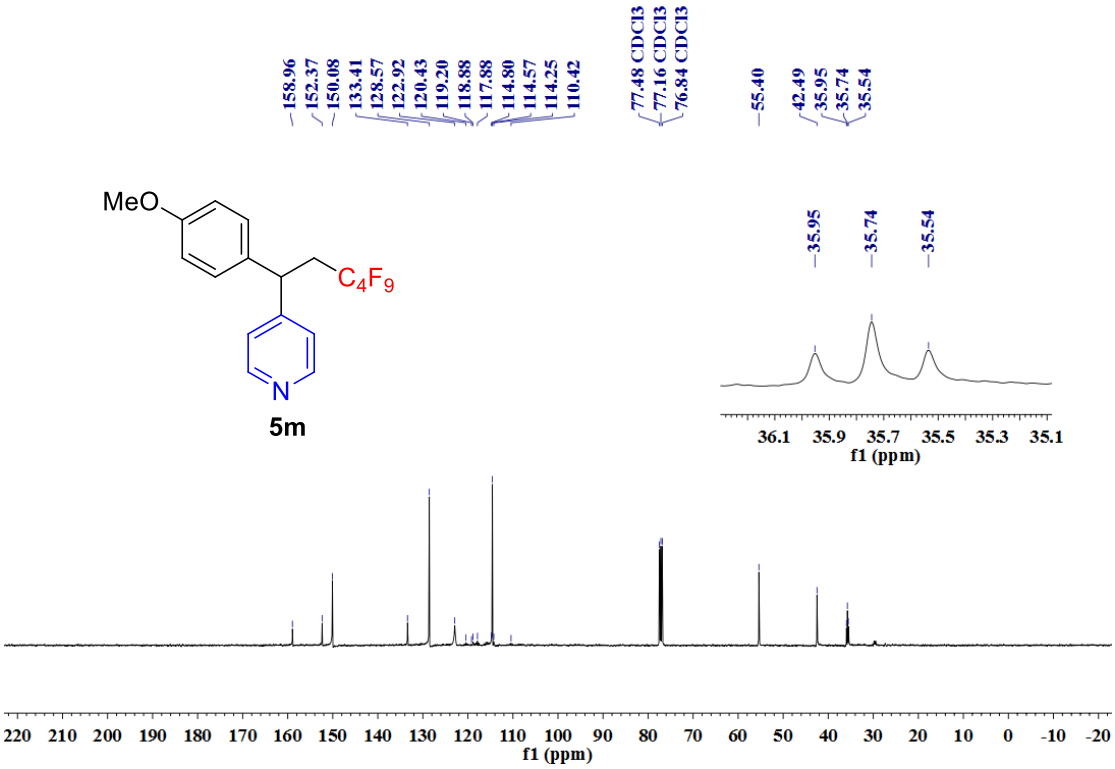


^{13}C NMR (100 MHz, $CDCl_3$):



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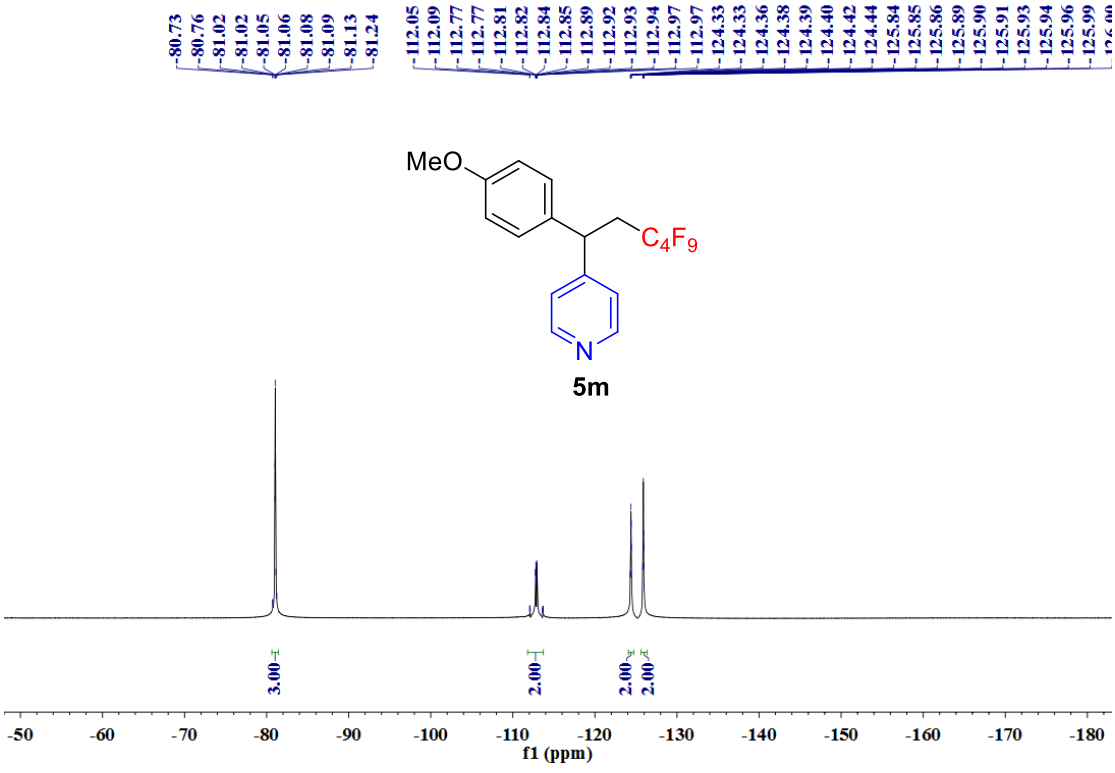

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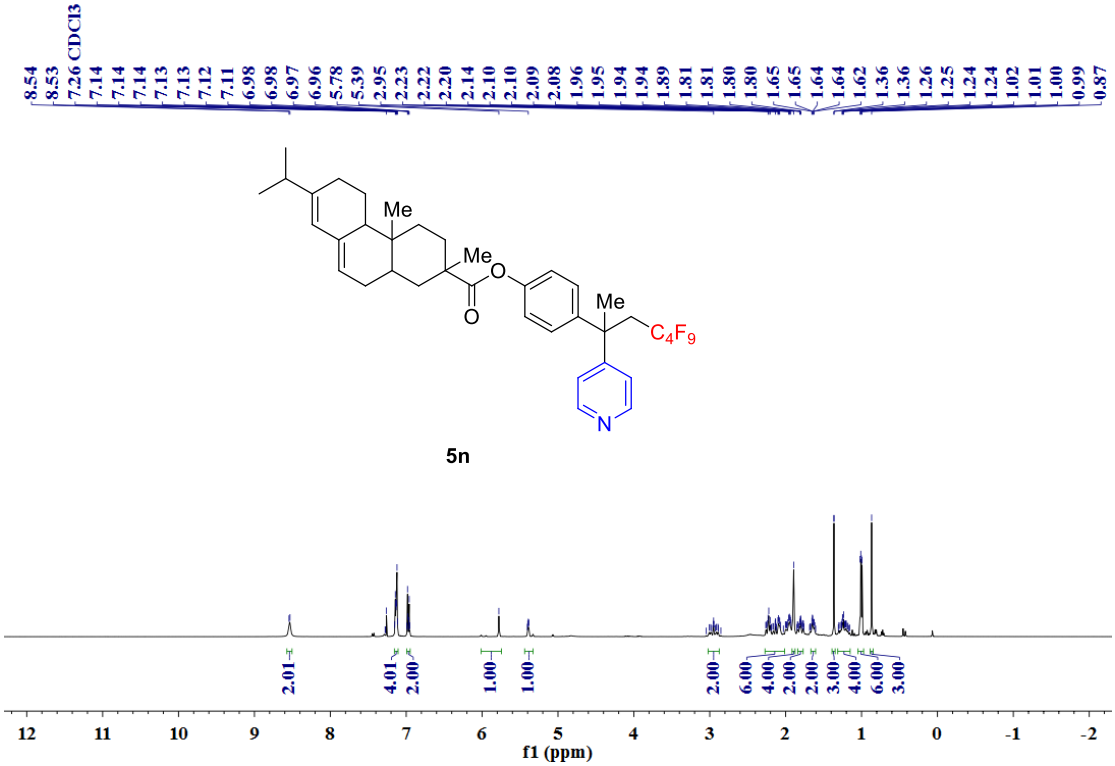
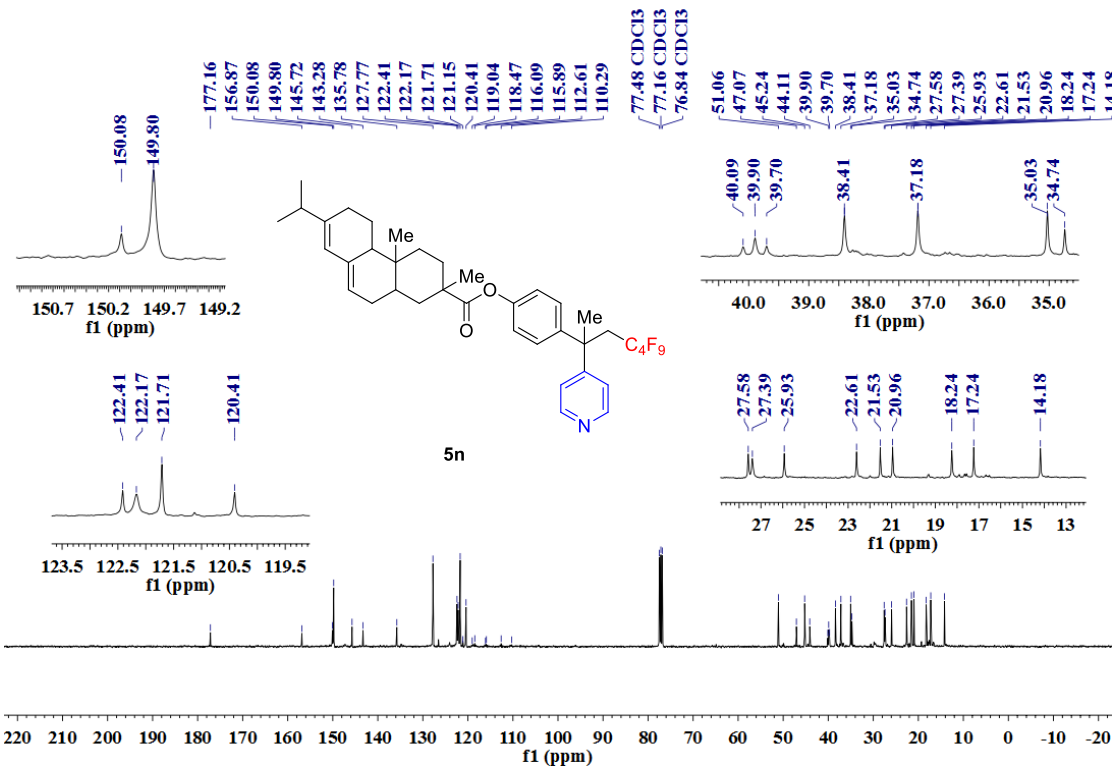
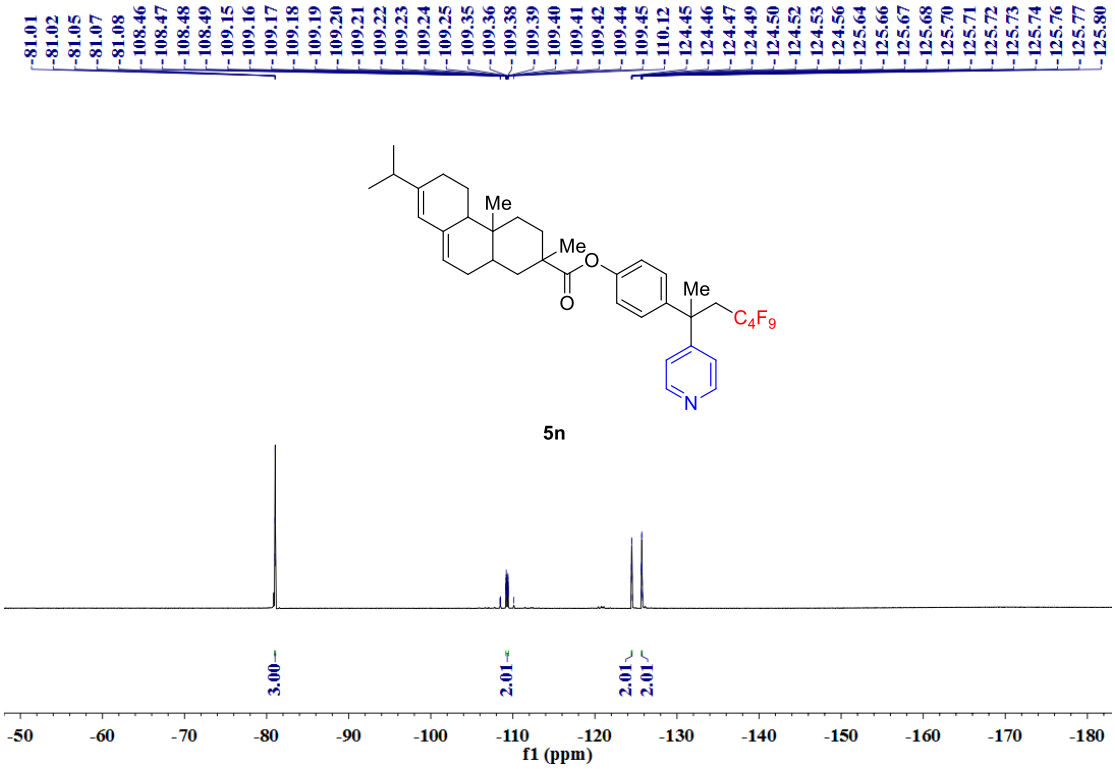


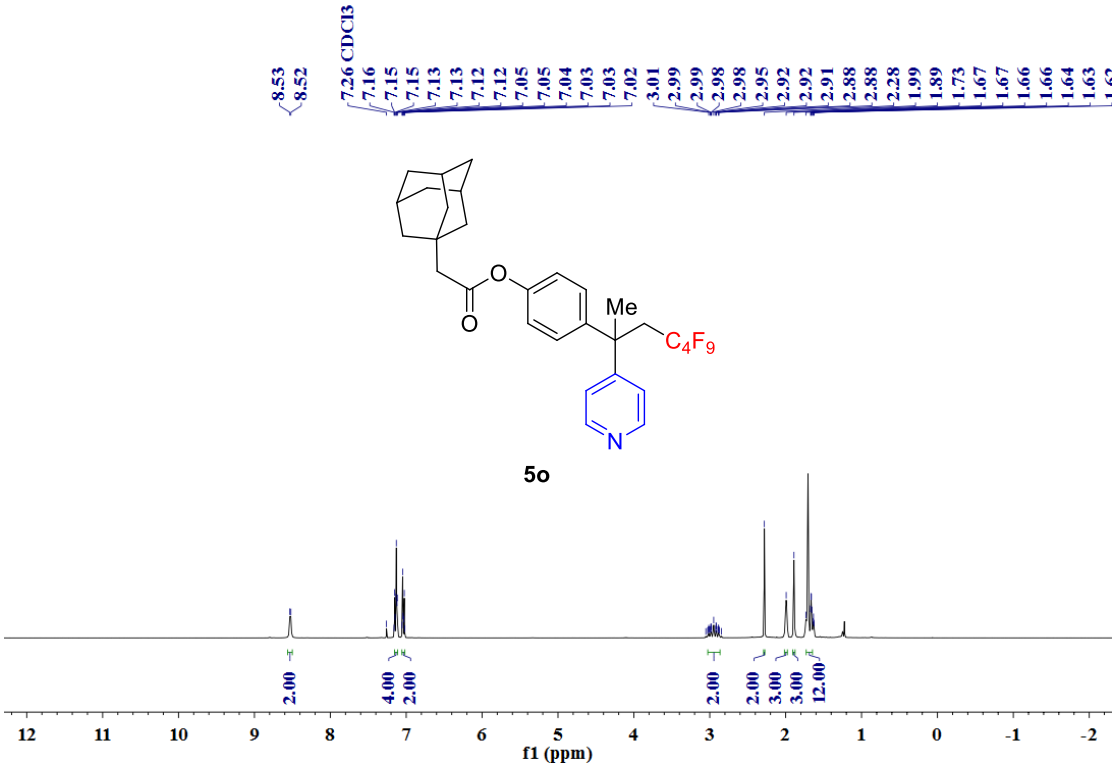
^{13}C NMR (100 MHz, $CDCl_3$):



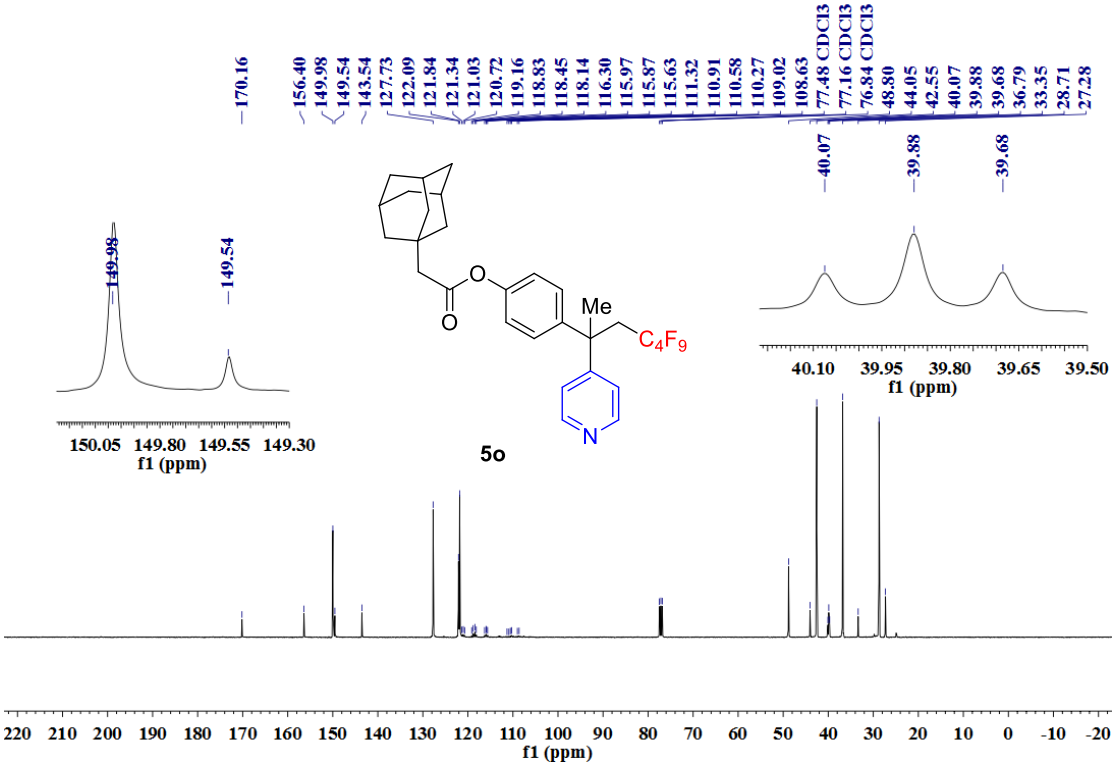
^{19}F NMR (376 MHz, $CDCl_3$):



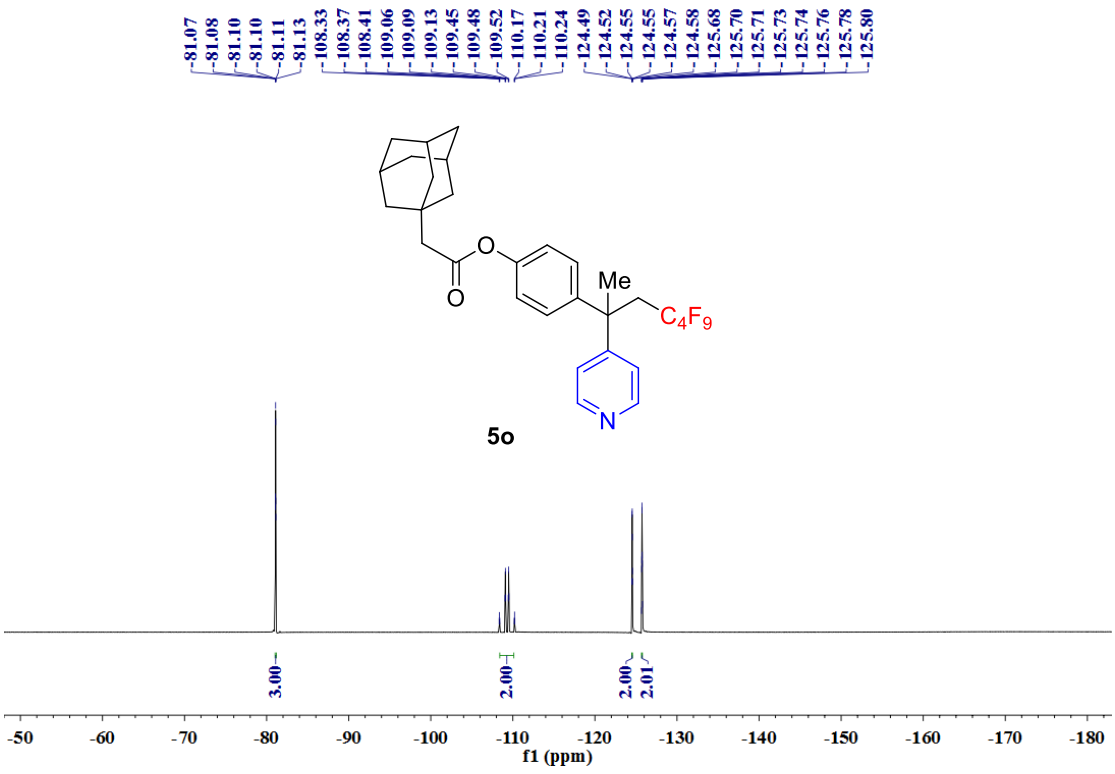
^{1}H NMR (400 MHz, $CDCl_3$):



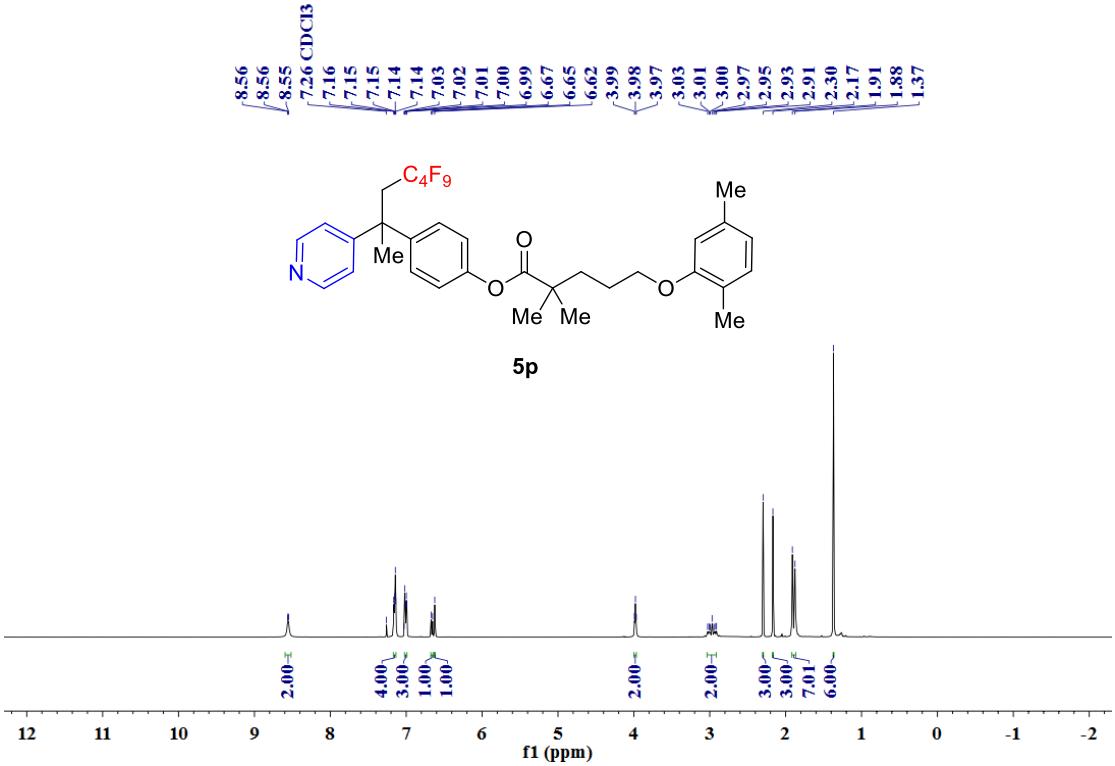
^{13}C NMR (100 MHz, $CDCl_3$):



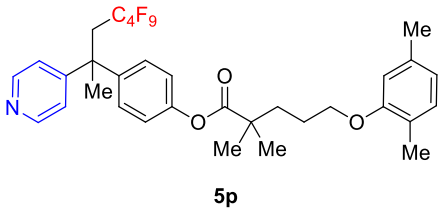
^{19}F NMR (376 MHz, $CDCl_3$):

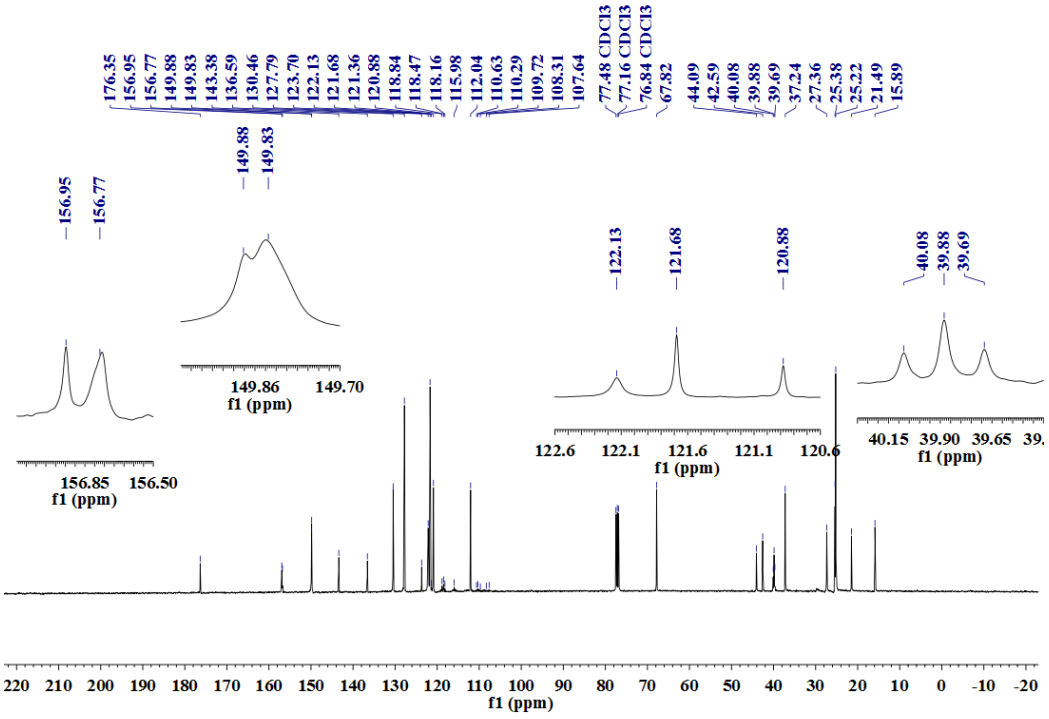


^{1}H NMR (400 MHz, $CDCl_3$):

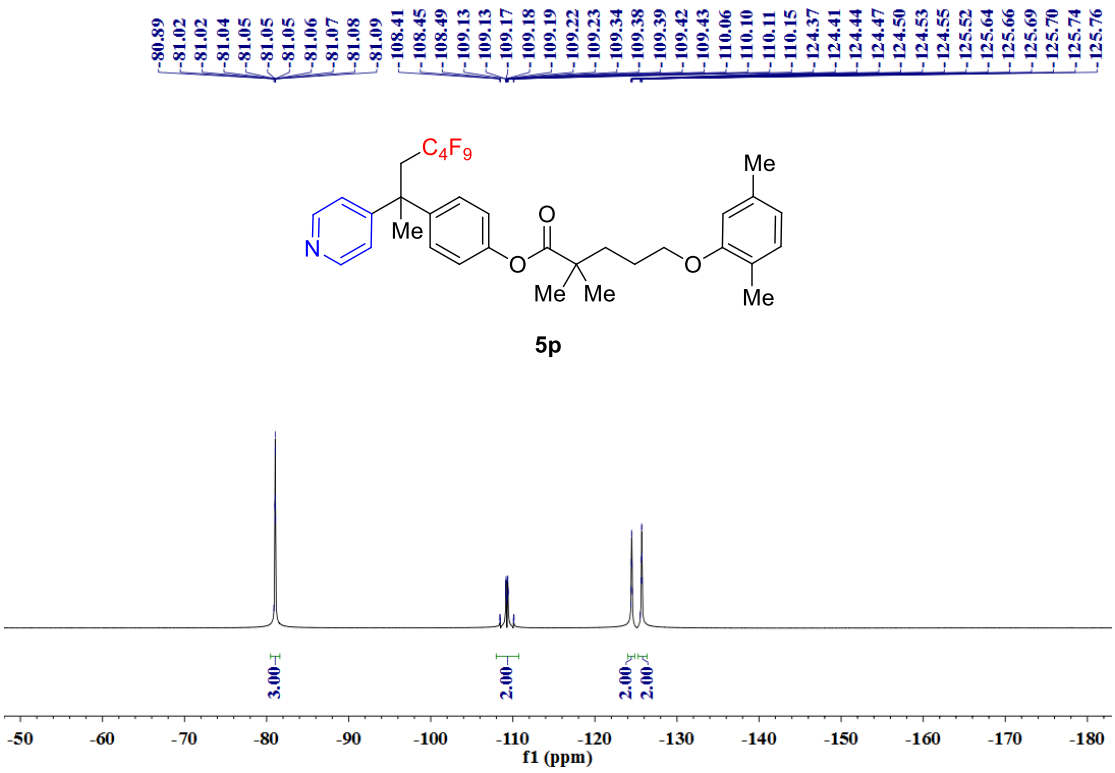


^{13}C NMR (100 MHz, $CDCl_3$):



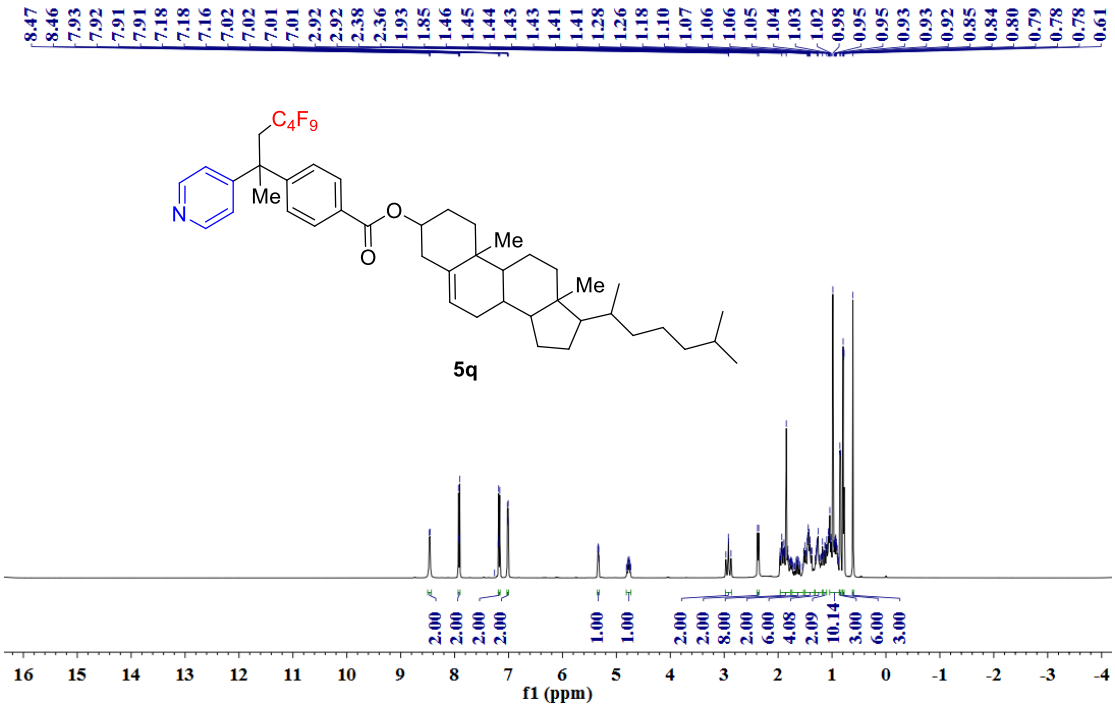


^{19}F NMR (376 MHz, $CDCl_3$):



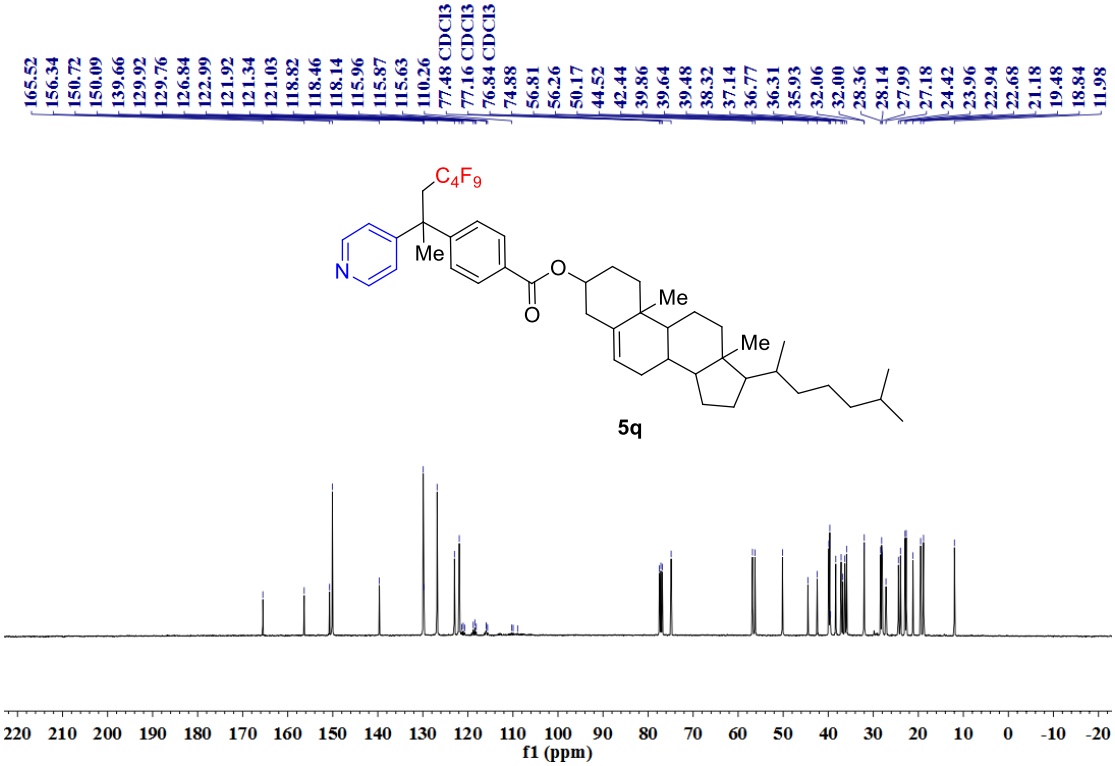
5p

^{1}H NMR (400 MHz, $CDCl_3$):

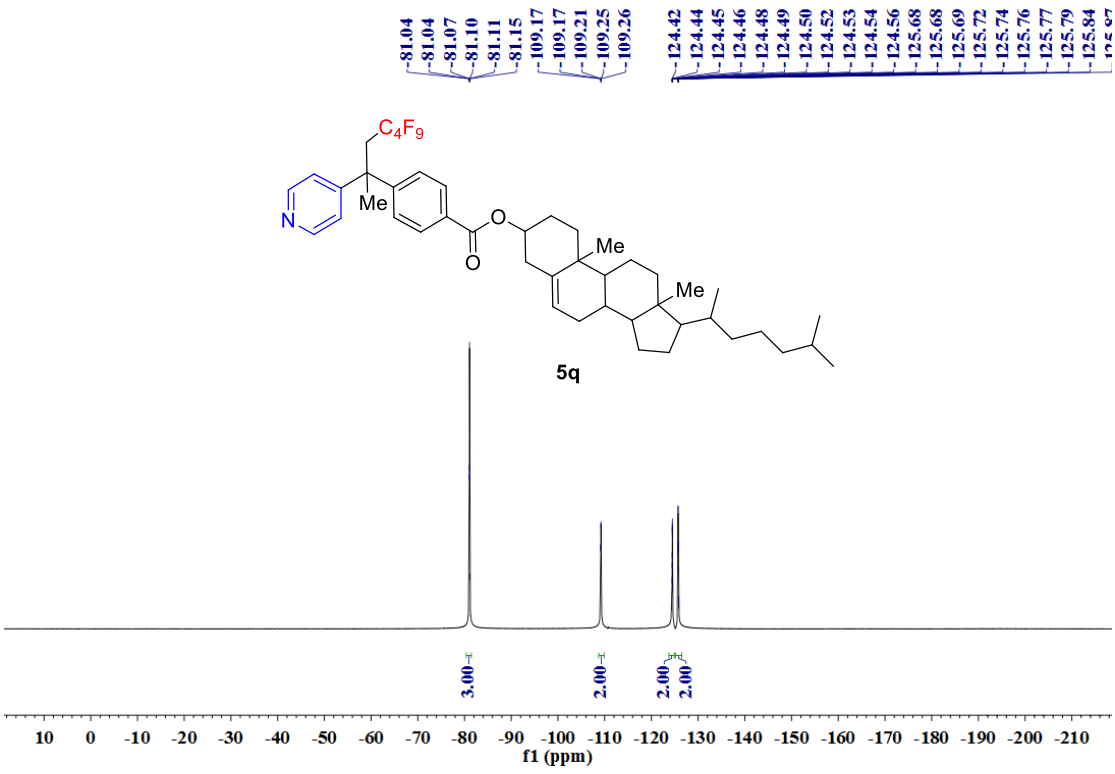


5q

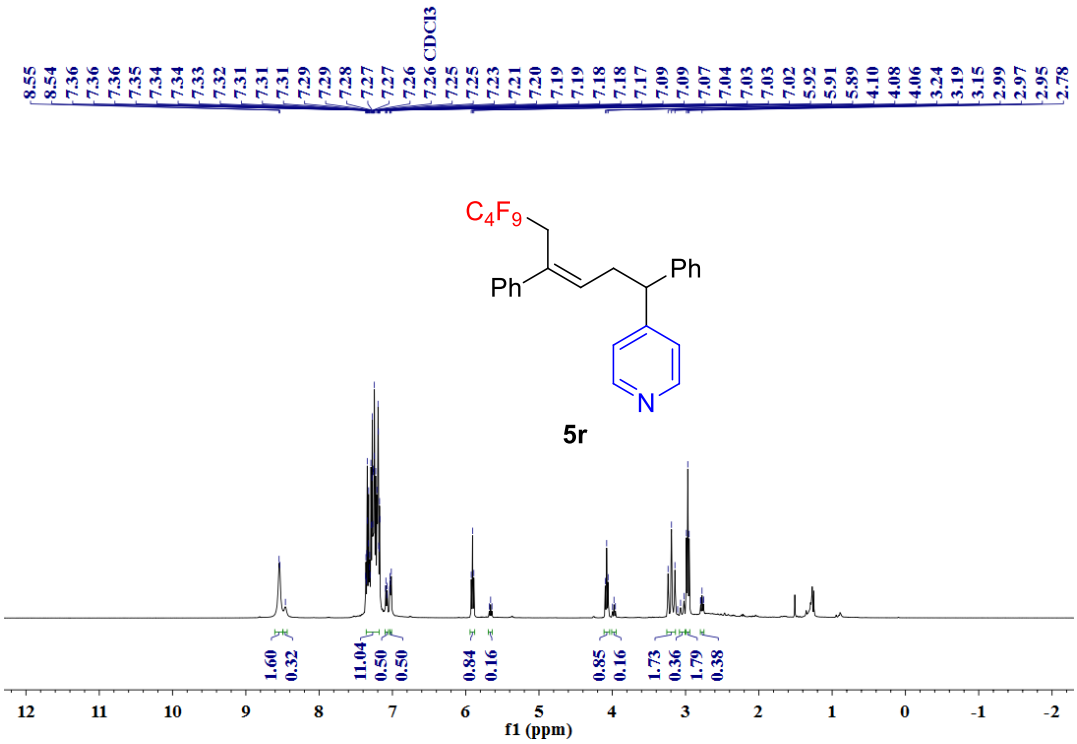
^{13}C NMR (100 MHz, $CDCl_3$):



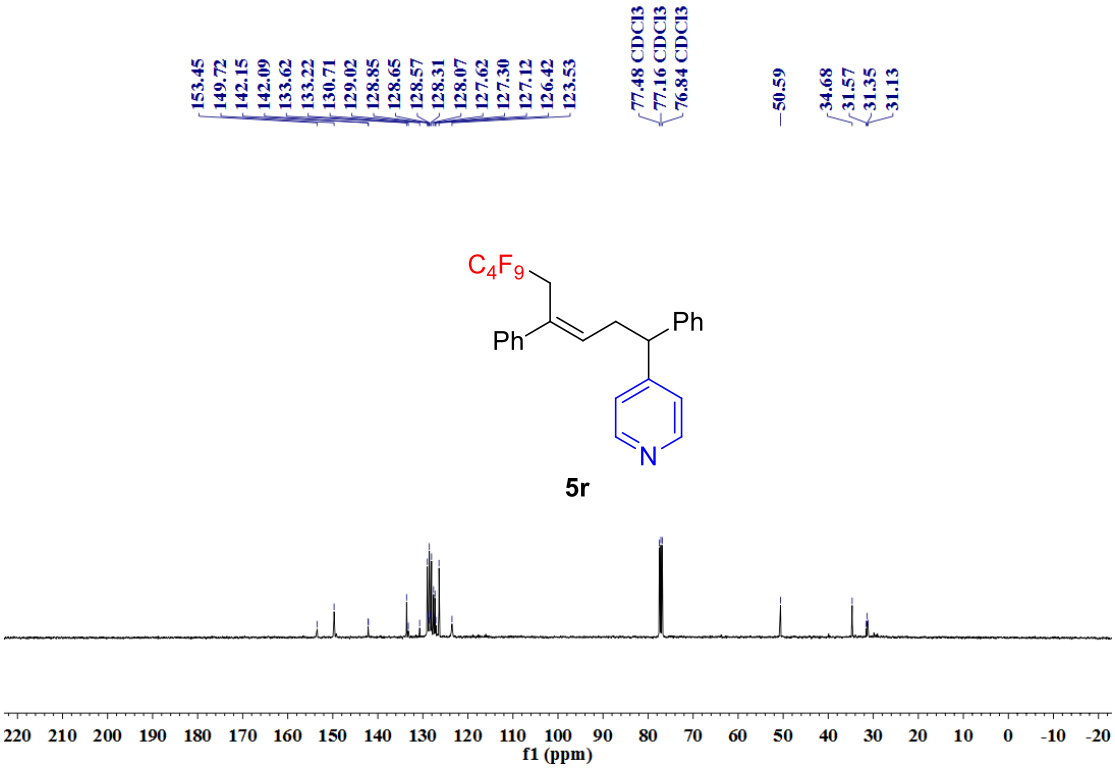
^{19}F NMR (376 MHz, $CDCl_3$):



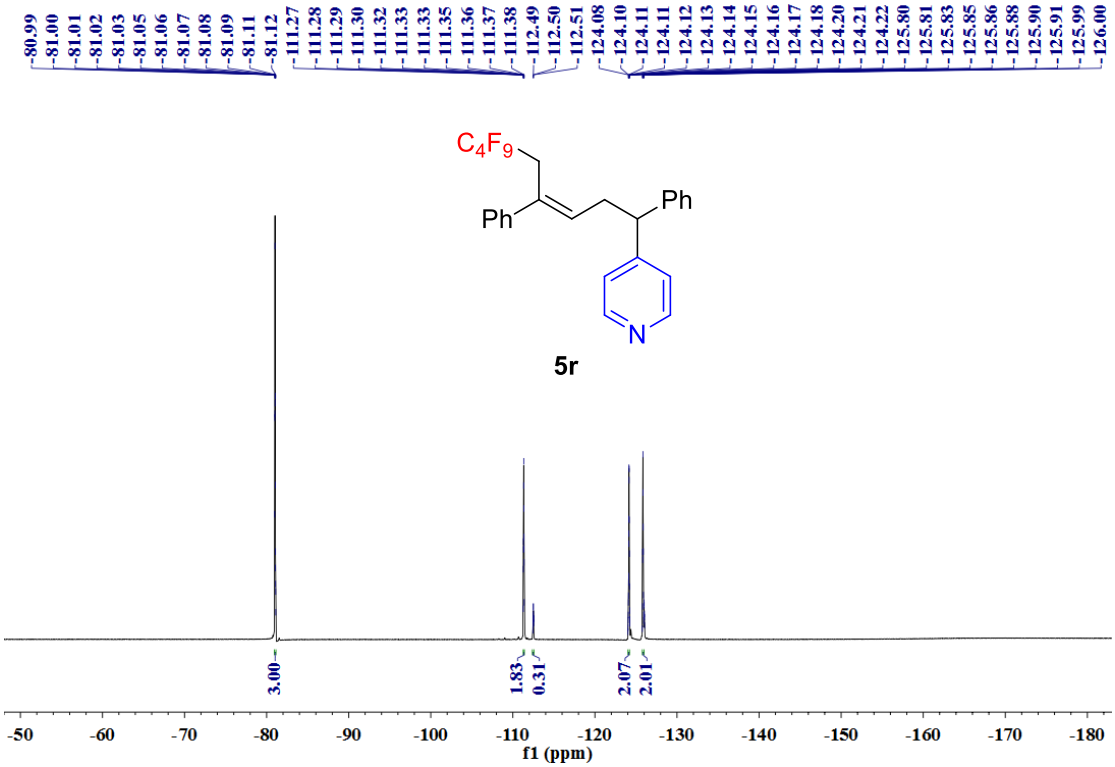
^{1}H NMR (400 MHz, $CDCl_3$):



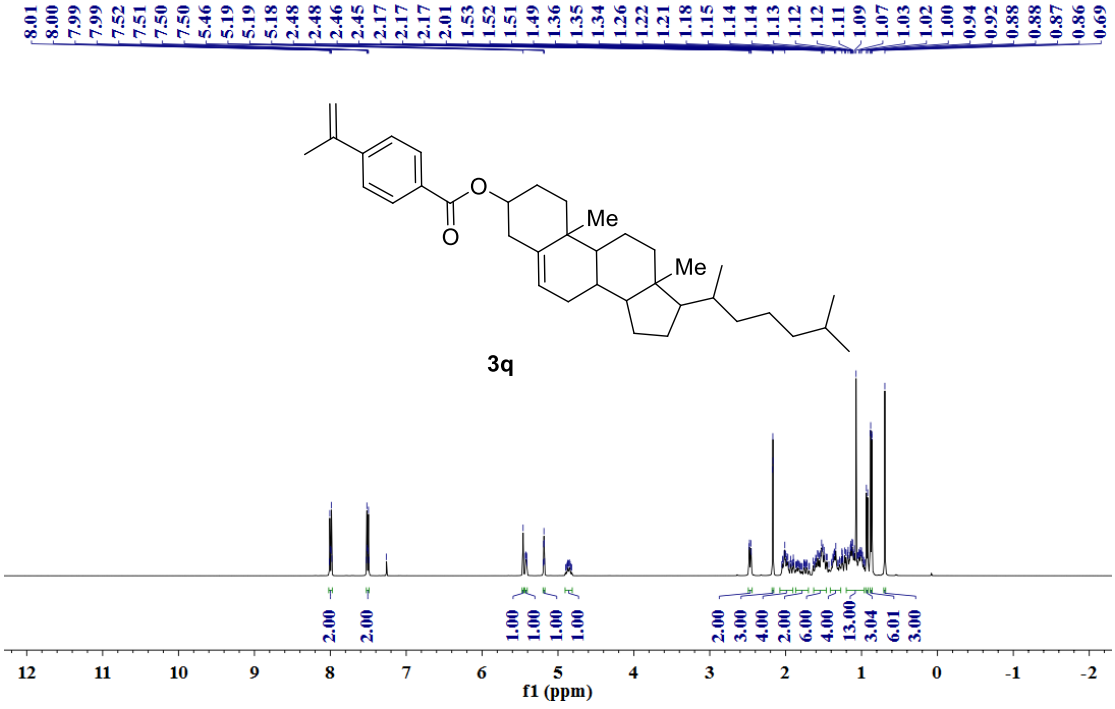
^{13}C NMR (100 MHz, $CDCl_3$):



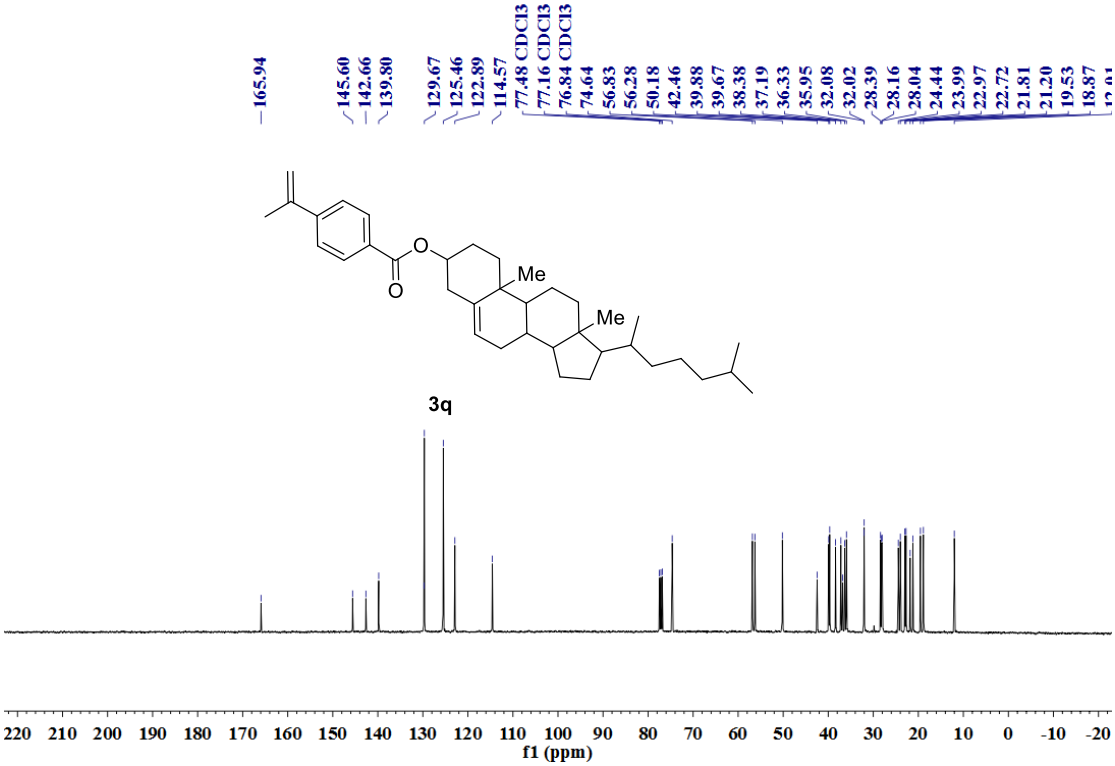
^{19}F NMR (376 MHz, $CDCl_3$):



^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):



6. Cartesian Coordinates of the Optimized Structures

CF_3I

Zero-point correction= 0.014644(Hartree/Particle)
Thermal correction to Energy= 0.019359
Thermal correction to Enthalpy= 0.020303
Thermal correction to Gibbs Free Energy= -0.015577
Sum of electronic and zero-point Energies= -348.816993
Sum of electronic and thermal Energies= -348.812278
Sum of electronic and thermal Enthalpies= -348.811333
Sum of electronic and thermal Free Energies= -348.847214

Esol = -348.9903869

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	9	0	-1.650388	1.239559	0.081260
2	9	0	-1.650236	-0.690139	1.032892
3	9	0	-1.650420	-0.549094	-1.113869
4	6	0	-1.196314	0.000127	0.000118
5	53	0	0.988652	-0.000274	-0.000230

CF_3I anion

Zero-point correction= 0.012252(Hartree/Particle)
Thermal correction to Energy= 0.018032
Thermal correction to Enthalpy= 0.018976
Thermal correction to Gibbs Free Energy= -0.021531
Sum of electronic and zero-point Energies= -348.858162
Sum of electronic and thermal Energies= -348.852382
Sum of electronic and thermal Enthalpies= -348.851438
Sum of electronic and thermal Free Energies= -348.891945

Esol = -349.0769734

Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	9	0	1.977625	0.882311	-0.883684
2	9	0	1.977573	-1.206691	-0.321930
3	9	0	1.978477	0.324281	1.206024
4	6	0	1.481827	-0.000023	0.000233
5	53	0	-1.513899	0.000008	-0.000548

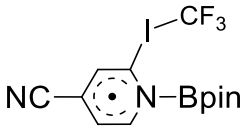
4-cyanopyridine-boryl (Int1)

Zero-point correction= 0.272426(Hartree/Particle)
Thermal correction to Energy= 0.288834
Thermal correction to Enthalpy= 0.289778
Thermal correction to Gibbs Free Energy= 0.227912
Sum of electronic and zero-point Energies= -751.250341
Sum of electronic and thermal Energies= -751.233933
Sum of electronic and thermal Enthalpies= -751.232989
Sum of electronic and thermal Free Energies= -751.294855

Esol = -751.7913445

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.659096	1.185973	-0.180389
2	6	0	3.014411	1.204109	-0.183755
3	6	0	3.757894	-0.000017	-0.000053
4	6	0	3.014407	-1.204136	0.183668
5	6	0	1.659092	-1.185990	0.180337
6	7	0	0.942727	-0.000006	-0.000016
7	1	0	1.051679	2.071756	-0.314909
8	1	0	3.531257	2.145335	-0.327519
9	1	0	3.531249	-2.145366	0.327418
10	1	0	1.051672	-2.071769	0.314874
11	6	0	5.172422	-0.000022	-0.000072
12	7	0	6.335976	-0.000025	-0.000087
13	5	0	-0.497292	0.000000	0.000005
14	8	0	-1.235849	-1.129146	0.227042
15	8	0	-1.235845	1.129154	-0.227011
16	6	0	-2.601367	-0.776254	-0.104468
17	6	0	-2.601356	0.776276	0.104543

18	6	0	-3.542222	-1.540887	0.809991
19	1	0	-4.576183	-1.223153	0.642282
20	1	0	-3.473353	-2.609868	0.594657
21	1	0	-3.290618	-1.385312	1.859912
22	6	0	-2.822209	-1.174404	-1.561111
23	1	0	-2.597029	-2.237333	-1.673512
24	1	0	-3.857039	-1.002112	-1.868613
25	1	0	-2.161107	-0.609992	-2.225328
26	6	0	-3.542231	1.540919	-0.809886
27	1	0	-4.576192	1.223209	-0.642133
28	1	0	-3.473330	2.609901	-0.594564
29	1	0	-3.290672	1.385330	-1.859815
30	6	0	-2.822149	1.174428	1.561193
31	1	0	-2.596958	2.237355	1.673587
32	1	0	-3.856970	1.002143	1.868728
33	1	0	-2.161030	0.610012	2.225389



Int2a

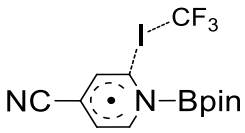
Zero-point correction=	0.288623(Hartree/Particle)
Thermal correction to Energy=	0.311740
Thermal correction to Enthalpy=	0.312684
Thermal correction to Gibbs Free Energy=	0.231236
Sum of electronic and zero-point Energies=	-1100.065643
Sum of electronic and thermal Energies=	-1100.042526
Sum of electronic and thermal Enthalpies=	-1100.041581
Sum of electronic and thermal Free Energies=	-1100.123029

Esol = -1100.7890144

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.502341	0.954554	-1.249748
2	6	0	2.857875	0.977417	-1.238711
3	6	0	3.602109	-0.202176	-0.932074
4	6	0	2.860150	-1.385438	-0.646604
5	6	0	1.501777	-1.373238	-0.674785

6	7	0	0.787144	-0.210649	-0.971231
7	1	0	0.894308	1.823993	-1.463528
8	1	0	3.375170	1.902709	-1.461254
9	1	0	3.377290	-2.309132	-0.415098
10	1	0	0.894153	-2.248330	-0.480876
11	6	0	5.017037	-0.198206	-0.910962
12	7	0	6.179958	-0.195110	-0.893610
13	5	0	-0.650204	-0.187669	-0.846728
14	8	0	-1.360834	-1.277739	-0.435797
15	8	0	-1.398474	0.926204	-1.102411
16	6	0	-2.757678	-0.920335	-0.571361
17	6	0	-2.708918	0.647344	-0.547946
18	6	0	-3.526457	-1.545526	0.580706
19	1	0	-4.568770	-1.211961	0.571343
20	1	0	-3.514262	-2.633349	0.479477
21	1	0	-3.077878	-1.285487	1.541027
22	6	0	-3.230755	-1.479426	-1.909797
23	1	0	-3.046622	-2.555930	-1.926327
24	1	0	-4.299575	-1.305504	-2.059000
25	1	0	-2.682313	-1.023930	-2.739345
26	6	0	-3.759800	1.328859	-1.407012
27	1	0	-4.763658	1.062914	-1.061814
28	1	0	-3.647520	2.412801	-1.329505
29	1	0	-3.660645	1.047676	-2.456246
30	6	0	-2.715841	1.217847	0.867509
31	1	0	-2.474982	2.282188	0.818568
32	1	0	-3.694071	1.100965	1.341262
33	1	0	-1.966735	0.723511	1.492404
34	53	0	0.771726	-0.783198	2.576765
35	6	0	-0.587154	-0.371659	4.230575
36	9	0	-0.298213	0.789562	4.794702
37	9	0	-0.508430	-1.322911	5.146339
38	9	0	-1.840756	-0.320359	3.784992

TS1



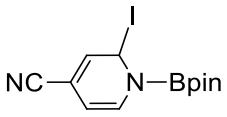
Zero-point correction= 0.288206(Hartree/Particle)
Thermal correction to Energy= 0.311163
Thermal correction to Enthalpy= 0.312107
Thermal correction to Gibbs Free Energy= 0.231338
Sum of electronic and zero-point Energies= -1100.029343

Sum of electronic and thermal Energies= -1100.006387
Sum of electronic and thermal Enthalpies= -1100.005443
Sum of electronic and thermal Free Energies= -1100.086212

Esol = -1100.7486466

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.507788	0.931813	-1.367221
2	6	0	2.864310	0.978608	-1.352614
3	6	0	3.586362	-0.199540	-0.983917
4	6	0	2.906172	-1.313349	-0.553069
5	6	0	1.497359	-1.280012	-0.486072
6	7	0	0.830691	-0.218072	-1.041383
7	1	0	0.883214	1.770534	-1.649234
8	1	0	3.388670	1.882569	-1.631294
9	1	0	3.427295	-2.202750	-0.221500
10	1	0	0.909782	-2.175080	-0.339630
11	6	0	5.020007	-0.206287	-1.053428
12	7	0	6.174800	-0.203035	-1.126133
13	5	0	-0.639325	-0.199333	-0.930356
14	8	0	-1.322866	-1.299118	-0.553334
15	8	0	-1.364395	0.921883	-1.156141
16	6	0	-2.729297	-0.924237	-0.588884
17	6	0	-2.664054	0.645065	-0.546034
18	6	0	-3.418150	-1.556335	0.607938
19	1	0	-4.457743	-1.219208	0.667170
20	1	0	-3.416576	-2.642983	0.495544
21	1	0	-2.906110	-1.304904	1.538059
22	6	0	-3.289015	-1.466205	-1.899322
23	1	0	-3.123389	-2.545184	-1.934058
24	1	0	-4.362301	-1.275894	-1.978470
25	1	0	-2.788473	-1.012315	-2.759601
26	6	0	-3.739139	1.347644	-1.354409
27	1	0	-4.729050	1.090863	-0.965396
28	1	0	-3.609744	2.428979	-1.270091
29	1	0	-3.692838	1.075002	-2.409652
30	6	0	-2.592965	1.196826	0.873460
31	1	0	-2.361763	2.263395	0.824454
32	1	0	-3.544683	1.069383	1.395578
33	1	0	-1.810638	0.698987	1.454159

34	53	0	1.061903	-0.871489	2.228092
35	6	0	-0.903767	-0.391563	4.376450
36	9	0	-0.642633	0.711768	5.053859
37	9	0	-0.965778	-1.427280	5.191814
38	9	0	-2.063184	-0.256636	3.733645



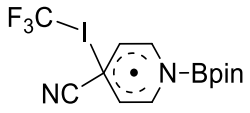
Int3a

Zero-point correction=	0.275542(Hartree/Particle)
Thermal correction to Energy=	0.293682
Thermal correction to Enthalpy=	0.294626
Thermal correction to Gibbs Free Energy=	0.228064
Sum of electronic and zero-point Energies=	-762.600992
Sum of electronic and thermal Energies=	-762.582852
Sum of electronic and thermal Enthalpies=	-762.581908
Sum of electronic and thermal Free Energies=	-762.648470

Esol = -763.1532994

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.344328	0.900812	-0.624581
2	6	0	2.768452	0.887494	-0.840266
3	6	0	3.438852	-0.295425	-0.799722
4	6	0	2.725862	-1.528797	-0.582004
5	6	0	1.374954	-1.496322	-0.595586
6	7	0	0.686618	-0.313535	-0.772425
7	1	0	0.771265	1.749837	-0.973221
8	1	0	3.283927	1.831435	-0.967566
9	1	0	3.260141	-2.461085	-0.462885
10	1	0	0.755301	-2.380568	-0.508010
11	6	0	4.864833	-0.326806	-0.980324
12	7	0	6.010614	-0.369670	-1.133639
13	5	0	-0.771919	-0.308714	-0.805906
14	8	0	-1.510686	-1.436680	-0.638157
15	8	0	-1.475343	0.835623	-0.997125
16	6	0	-2.884924	-1.042071	-0.910443
17	6	0	-2.846001	0.501848	-0.642879

18	6	0	-3.805971	-1.821435	0.010789
19	1	0	-4.837437	-1.474815	-0.104766
20	1	0	-3.770467	-2.882566	-0.246760
21	1	0	-3.510340	-1.709378	1.054481
22	6	0	-3.158183	-1.385199	-2.371449
23	1	0	-2.963352	-2.448570	-2.527386
24	1	0	-4.197586	-1.178127	-2.638436
25	1	0	-2.505935	-0.812892	-3.037443
26	6	0	-3.787421	1.320346	-1.507838
27	1	0	-4.824103	1.019832	-1.327682
28	1	0	-3.688798	2.377702	-1.252304
29	1	0	-3.563453	1.199826	-2.568647
30	6	0	-3.012102	0.855396	0.831681
31	1	0	-2.750373	1.906190	0.973092
32	1	0	-4.042448	0.698257	1.161570
33	1	0	-2.341722	0.260842	1.459218
34	53	0	1.101959	1.595933	1.788026



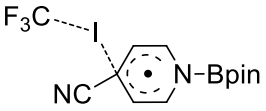
Int2b

Zero-point correction=	0.288474(Hartree/Particle)
Thermal correction to Energy=	0.311779
Thermal correction to Enthalpy=	0.312723
Thermal correction to Gibbs Free Energy=	0.228448
Sum of electronic and zero-point Energies=	-1100.063363
Sum of electronic and thermal Energies=	-1100.040059
Sum of electronic and thermal Enthalpies=	-1100.039114
Sum of electronic and thermal Free Energies=	-1100.123389

Esol = -1100.7873177

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.659096	1.185973	-0.180389
2	6	0	3.014411	1.204109	-0.183755
3	6	0	3.757894	-0.000017	-0.000053
4	6	0	3.014407	-1.204136	0.183668
5	6	0	1.659092	-1.185990	0.180337

6	7	0	0.942727	-0.000006	-0.000016
7	1	0	1.051679	2.071756	-0.314909
8	1	0	3.531257	2.145335	-0.327519
9	1	0	3.531249	-2.145366	0.327418
10	1	0	1.051672	-2.071769	0.314874
11	6	0	5.172422	-0.000022	-0.000072
12	7	0	6.335976	-0.000025	-0.000087
13	5	0	-0.497292	0.000000	0.000005
14	8	0	-1.235849	-1.129146	0.227042
15	8	0	-1.235845	1.129154	-0.227011
16	6	0	-2.601367	-0.776254	-0.104468
17	6	0	-2.601356	0.776276	0.104543
18	6	0	-3.542222	-1.540887	0.809991
19	1	0	-4.576183	-1.223153	0.642282
20	1	0	-3.473353	-2.609868	0.594657
21	1	0	-3.290618	-1.385312	1.859912
22	6	0	-2.822209	-1.174404	-1.561111
23	1	0	-2.597029	-2.237333	-1.673512
24	1	0	-3.857039	-1.002112	-1.868613
25	1	0	-2.161107	-0.609992	-2.225328
26	6	0	-3.542231	1.540919	-0.809886
27	1	0	-4.576192	1.223209	-0.642133
28	1	0	-3.473330	2.609901	-0.594564
29	1	0	-3.290672	1.385330	-1.859815
30	6	0	-2.822149	1.174428	1.561193
31	1	0	-2.596958	2.237355	1.673587
32	1	0	-3.856970	1.002143	1.868728
33	1	0	-2.161030	0.610012	2.225389

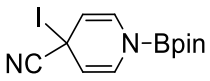


TS1'

Zero-point correction=	0.288218(Hartree/Particle)
Thermal correction to Energy=	0.311310
Thermal correction to Enthalpy=	0.312254
Thermal correction to Gibbs Free Energy=	0.229019
Sum of electronic and zero-point Energies=	-1100.018179
Sum of electronic and thermal Energies=	-1099.995088
Sum of electronic and thermal Enthalpies=	-1099.994144
Sum of electronic and thermal Free Energies=	-1100.077379

Esol = -1100.7382104

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.298074	1.054842	-1.314851
2	6	0	2.637879	1.153919	-1.420122
3	6	0	3.489706	0.021438	-1.087111
4	6	0	2.786836	-1.246121	-0.953204
5	6	0	1.442524	-1.275382	-0.863620
6	7	0	0.671238	-0.133406	-0.984613
7	1	0	0.632200	1.889459	-1.497484
8	1	0	3.095624	2.094849	-1.696568
9	1	0	3.359540	-2.160636	-0.869842
10	1	0	0.884867	-2.190966	-0.708578
11	6	0	4.757433	-0.036959	-1.790862
12	7	0	5.730717	-0.097790	-2.412908
13	5	0	-0.771986	-0.195010	-0.839385
14	8	0	-1.420745	-1.342636	-0.499941
15	8	0	-1.570844	0.889427	-1.036907
16	6	0	-2.833232	-1.063891	-0.695733
17	6	0	-2.884652	0.495771	-0.556528
18	6	0	-3.630357	-1.822310	0.350558
19	1	0	-4.689663	-1.555360	0.286930
20	1	0	-3.537158	-2.896301	0.173922
21	1	0	-3.271236	-1.607710	1.357741
22	6	0	-3.186547	-1.544774	-2.100112
23	1	0	-2.928577	-2.602540	-2.186216
24	1	0	-4.254378	-1.428434	-2.301842
25	1	0	-2.625778	-0.990208	-2.858181
26	6	0	-3.940947	1.175947	-1.409063
27	1	0	-4.938238	0.822156	-1.130391
28	1	0	-3.903233	2.255347	-1.245457
29	1	0	-3.781413	0.983645	-2.470755
30	6	0	-2.979215	0.957752	0.894584
31	1	0	-2.798022	2.033971	0.934614
32	1	0	-3.968962	0.754406	1.311170
33	1	0	-2.229399	0.459657	1.516044
34	53	0	4.398413	0.526253	1.204558
35	6	0	5.347502	1.149689	4.101568
36	9	0	5.881949	2.353157	4.118095
37	9	0	6.224246	0.240165	4.472868
38	9	0	4.273000	1.103588	4.863981

Int3c 

Zero-point correction=	0.275222(Hartree/Particle)
Thermal correction to Energy=	0.293334
Thermal correction to Enthalpy=	0.294279
Thermal correction to Gibbs Free Energy=	0.227704
Sum of electronic and zero-point Energies=	-762.591352
Sum of electronic and thermal Energies=	-762.573240
Sum of electronic and thermal Enthalpies=	-762.572295
Sum of electronic and thermal Free Energies=	-762.638870

Esol = -763.143816

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.393481	0.880304	-0.834736
2	6	0	2.736459	0.910364	-0.779910
3	6	0	3.501953	-0.297174	-0.455921
4	6	0	2.710971	-1.529588	-0.522654
5	6	0	1.368830	-1.483842	-0.586758
6	7	0	0.669545	-0.291787	-0.686305
7	1	0	0.797294	1.766030	-1.018311
8	1	0	3.267545	1.842848	-0.920602
9	1	0	3.222410	-2.481710	-0.465462
10	1	0	0.753967	-2.375797	-0.584381
11	6	0	4.795409	-0.380716	-1.119394
12	7	0	5.788266	-0.453261	-1.707753
13	5	0	-0.777761	-0.279710	-0.715787
14	8	0	-1.521439	-1.410561	-0.554886
15	8	0	-1.495644	0.862439	-0.910646
16	6	0	-2.882239	-1.034213	-0.892848
17	6	0	-2.874568	0.509084	-0.624821
18	6	0	-3.839663	-1.826426	-0.020225
19	1	0	-4.868651	-1.493000	-0.186080
20	1	0	-3.777804	-2.886201	-0.278066
21	1	0	-3.598071	-1.716031	1.037595
22	6	0	-3.082162	-1.377715	-2.366229
23	1	0	-2.865565	-2.438049	-2.513426
24	1	0	-4.110129	-1.184227	-2.683090
25	1	0	-2.406103	-0.796566	-3.000165

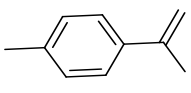
26	6	0	-3.784992	1.316928	-1.532674
27	1	0	-4.824993	1.001286	-1.405186
28	1	0	-3.714730	2.375562	-1.272373
29	1	0	-3.506526	1.201950	-2.580971
30	6	0	-3.124120	0.856179	0.840065
31	1	0	-2.895472	1.912712	0.995699
32	1	0	-4.166390	0.679688	1.117767
33	1	0	-2.481713	0.264692	1.498842
34	53	0	4.241553	-0.062655	1.840826

CF_3 radical

Zero-point correction= 0.012690(Hartree/Particle)
Thermal correction to Energy= 0.016102
Thermal correction to Enthalpy= 0.017046
Thermal correction to Gibbs Free Energy= -0.013995
Sum of electronic and zero-point Energies= -337.425185
Sum of electronic and thermal Energies= -337.421773
Sum of electronic and thermal Enthalpies= -337.420829
Sum of electronic and thermal Free Energies= -337.451870

Esol = -337.5898162

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.477950	-0.276754	0.025720
2	9	0	0.935391	0.369695	1.078557
3	9	0	0.935457	-1.511919	-0.007741
4	9	0	-0.838805	-0.257324	-0.007879

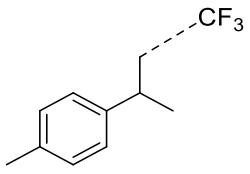
3a 

Zero-point correction= 0.190866(Hartree/Particle)
Thermal correction to Energy= 0.200724
Thermal correction to Enthalpy= 0.201668
Thermal correction to Gibbs Free Energy= 0.155120
Sum of electronic and zero-point Energies= -387.916954

Sum of electronic and thermal Energies= -387.907096
Sum of electronic and thermal Enthalpies= -387.906152
Sum of electronic and thermal Free Energies= -387.952700

Esol = -388.2364733

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.192137	-0.607695	-0.538838
2	6	0	-0.806015	-0.640159	-0.515333
3	6	0	-0.065449	0.411851	0.042856
4	6	0	-0.776189	1.478533	0.601383
5	6	0	-2.167770	1.508663	0.574137
6	6	0	-2.900382	0.471272	0.000733
7	1	0	-2.740352	-1.441348	-0.970796
8	1	0	-0.284891	-1.507066	-0.909297
9	1	0	-0.241495	2.305760	1.057185
10	1	0	-2.692781	2.354784	1.009594
11	6	0	1.421064	0.387475	0.056289
12	6	0	2.122236	-0.274903	-0.868562
13	1	0	3.206530	-0.301171	-0.834808
14	1	0	1.643621	-0.789566	-1.694787
15	6	0	2.116915	1.159923	1.148632
16	1	0	1.707570	0.909042	2.132008
17	1	0	3.187907	0.949965	1.148888
18	1	0	1.990185	2.239172	1.011029
19	6	0	-4.406113	0.501271	-0.042925
20	1	0	-4.804648	1.306663	0.577847
21	1	0	-4.765286	0.657340	-1.065229
22	1	0	-4.830191	-0.442712	0.310830



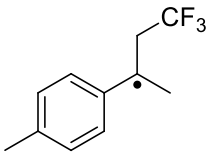
TS2

Zero-point correction= 0.203710(Hartree/Particle)
Thermal correction to Energy= 0.218171
Thermal correction to Enthalpy= 0.219115

Thermal correction to Gibbs Free Energy= 0.158546
Sum of electronic and zero-point Energies= -725.347459
Sum of electronic and thermal Energies= -725.332998
Sum of electronic and thermal Enthalpies= -725.332054
Sum of electronic and thermal Free Energies= -725.392623

Esol = -725.8294859

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.361868	-1.562230	1.374790
2	6	0	0.726134	-0.978167	0.743905
3	6	0	0.673829	0.351250	0.296105
4	6	0	-0.523332	1.052684	0.480602
5	6	0	-1.609689	0.463022	1.118282
6	6	0	-1.548242	-0.850851	1.581357
7	1	0	-0.298039	-2.597007	1.701644
8	1	0	1.617047	-1.571703	0.563467
9	1	0	-0.609391	2.077175	0.132904
10	1	0	-2.523926	1.034290	1.255514
11	6	0	1.832940	0.980147	-0.373589
12	6	0	3.093414	0.547871	-0.156445
13	1	0	3.935971	1.031141	-0.641333
14	1	0	3.324567	-0.172634	0.621461
15	6	0	1.562119	2.083923	-1.360027
16	1	0	1.172016	2.977683	-0.861111
17	1	0	2.475791	2.369526	-1.884477
18	1	0	0.815744	1.770942	-2.097186
19	6	0	-2.715693	-1.490125	2.286717
20	1	0	-2.530156	-1.561309	3.363415
21	1	0	-3.630785	-0.911338	2.143738
22	1	0	-2.892105	-2.504350	1.918318
23	6	0	3.190396	-1.297887	-1.781204
24	9	0	3.311369	-2.438763	-1.112357
25	9	0	2.021251	-1.255511	-2.395484
26	9	0	4.174206	-1.181283	-2.658966



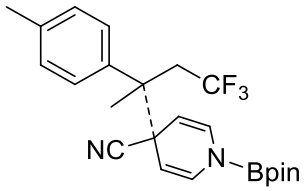
Int4

Zero-point correction=	0.206938(Hartree/Particle)
Thermal correction to Energy=	0.219764
Thermal correction to Enthalpy=	0.220708
Thermal correction to Gibbs Free Energy=	0.165924
Sum of electronic and zero-point Energies=	-725.419174
Sum of electronic and thermal Energies=	-725.406348
Sum of electronic and thermal Enthalpies=	-725.405403
Sum of electronic and thermal Free Energies=	-725.460187

Esol = -725.9015591

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.342146	-1.793973	1.254712
2	6	0	0.730181	-1.265287	0.561420
3	6	0	0.664067	0.024360	-0.025144
4	6	0	-0.555401	0.728087	0.124861
5	6	0	-1.620716	0.185291	0.824717
6	6	0	-1.540661	-1.083198	1.405813
7	1	0	-0.257956	-2.788261	1.686379
8	1	0	1.621893	-1.869459	0.438294
9	1	0	-0.656513	1.721125	-0.299932
10	1	0	-2.538216	0.758912	0.927239
11	6	0	1.761437	0.604145	-0.734246
12	6	0	3.121622	-0.029297	-0.732426
13	1	0	3.900992	0.738503	-0.779554
14	1	0	3.306370	-0.628497	0.162790
15	6	0	1.601214	1.887151	-1.492695
16	1	0	1.491966	2.748439	-0.818695
17	1	0	2.465740	2.072203	-2.132519
18	1	0	0.712829	1.867652	-2.132645
19	6	0	-2.702302	-1.684014	2.150758
20	1	0	-3.487190	-0.944620	2.324156
21	1	0	-3.142662	-2.513982	1.588211
22	1	0	-2.387627	-2.080251	3.120621
23	6	0	3.347812	-0.932792	-1.925498
24	9	0	2.500744	-1.972422	-1.930478

25	9	0	3.176531	-0.273117	-3.082120
26	9	0	4.593500	-1.431919	-1.930839



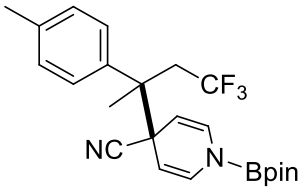
TS3

Zero-point correction= 0.482086(Hartree/Particle)
Thermal correction to Energy= 0.512671
Thermal correction to Enthalpy= 0.513615
Thermal correction to Gibbs Free Energy= 0.417978
Sum of electronic and zero-point Energies= -1476.684014
Sum of electronic and thermal Energies= -1476.653429
Sum of electronic and thermal Enthalpies= -1476.652485
Sum of electronic and thermal Free Energies= -1476.748122

Esol = -1477.7062327

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.106907	2.439404	0.432584
2	6	0	-3.772324	1.098874	0.393780
3	6	0	-2.643834	0.644528	-0.333729
4	6	0	-1.899083	1.625633	-1.028875
5	6	0	-2.254288	2.967468	-0.988743
6	6	0	-3.358529	3.404706	-0.256296
7	1	0	-4.973558	2.752598	1.009220
8	1	0	-4.383489	0.394116	0.944880
9	1	0	-1.036274	1.329958	-1.615326
10	1	0	-1.661741	3.692420	-1.541285
11	6	0	-2.214612	-0.726955	-0.312771
12	6	0	-3.113400	-1.816208	0.196070
13	1	0	-2.523432	-2.698810	0.466610
14	1	0	-3.683521	-1.524385	1.082090
15	6	0	-1.044178	-1.155479	-1.141333
16	1	0	-0.165200	-0.528286	-0.947315
17	1	0	-0.770972	-2.191612	-0.928865
18	1	0	-1.267629	-1.086108	-2.214278

19	6	0	-3.757625	4.855762	-0.219358
20	1	0	-4.697591	5.018372	-0.756989
21	1	0	-3.909460	5.197873	0.808681
22	1	0	-2.995694	5.488847	-0.679697
23	6	0	-4.106941	-2.274494	-0.848198
24	9	0	-4.950448	-1.295775	-1.202726
25	9	0	-3.490750	-2.692925	-1.968862
26	9	0	-4.848530	-3.299725	-0.399750
27	6	0	1.421164	-1.433161	1.284384
28	6	0	0.176744	-1.550948	1.801739
29	6	0	-0.687419	-0.408901	1.893470
30	6	0	-0.135478	0.853565	1.493579
31	6	0	1.110951	0.921903	0.971569
32	7	0	1.927172	-0.205097	0.856615
33	1	0	2.102644	-2.268141	1.182706
34	1	0	-0.168341	-2.520913	2.140794
35	1	0	-0.731854	1.754455	1.575274
36	1	0	1.559206	1.847381	0.632558
37	6	0	-1.892143	-0.464384	2.637811
38	7	0	-2.898837	-0.517925	3.219626
39	5	0	3.257154	-0.103022	0.313068
40	8	0	3.809746	1.088648	-0.066943
41	8	0	4.064858	-1.191454	0.131735
42	6	0	5.021234	0.746486	-0.785706
43	6	0	5.373882	-0.658118	-0.189775
44	6	0	6.061277	1.824203	-0.533729
45	1	0	7.017225	1.543911	-0.986805
46	1	0	5.731332	2.763033	-0.984623
47	1	0	6.210825	1.990391	0.533850
48	6	0	4.655664	0.684066	-2.266418
49	1	0	4.219536	1.640849	-2.561927
50	1	0	5.535895	0.495019	-2.886290
51	1	0	3.919749	-0.103071	-2.455063
52	6	0	6.064296	-1.604293	-1.156575
53	1	0	7.015057	-1.178573	-1.491950
54	1	0	6.272088	-2.552217	-0.654753
55	1	0	5.440467	-1.807162	-2.028016
56	6	0	6.149425	-0.564993	1.121629
57	1	0	6.173375	-1.552829	1.587024
58	1	0	7.177215	-0.232985	0.953628
59	1	0	5.666032	0.130367	1.814051



Int5

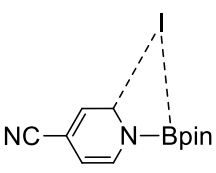
Zero-point correction=	0.486587(Hartree/Particle)
Thermal correction to Energy=	0.516472
Thermal correction to Enthalpy=	0.517416
Thermal correction to Gibbs Free Energy=	0.424399
Sum of electronic and zero-point Energies=	-1476.730969
Sum of electronic and thermal Energies=	-1476.701084
Sum of electronic and thermal Enthalpies=	-1476.700140
Sum of electronic and thermal Free Energies=	-1476.793157

Esol= -1477.7533334

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	7.704005	0.964369	-3.971408
2	6	0	6.621777	1.368646	-3.199504
3	6	0	6.004633	0.491535	-2.297857
4	6	0	6.527230	-0.801478	-2.204424
5	6	0	7.610679	-1.203421	-2.980523
6	6	0	8.217557	-0.330552	-3.881290
7	1	0	8.158586	1.672856	-4.658917
8	1	0	6.275577	2.390821	-3.303295
9	1	0	6.093928	-1.516343	-1.514457
10	1	0	7.989334	-2.217390	-2.880933
11	6	0	4.852849	0.947454	-1.393719
12	6	0	3.854619	1.844111	-2.154951
13	1	0	3.131682	2.277054	-1.456783
14	1	0	4.359446	2.677421	-2.647203
15	6	0	4.106774	-0.243131	-0.776920
16	1	0	4.724481	-0.741033	-0.024920
17	1	0	3.190101	0.092694	-0.289007
18	1	0	3.837993	-0.967137	-1.548687
19	6	0	9.369716	-0.770198	-4.746613
20	1	0	9.873500	-1.641878	-4.322597
21	1	0	9.022956	-1.041797	-5.748976
22	1	0	10.106167	0.029430	-4.860182
23	6	0	3.026346	1.149669	-3.211527

24	9	0	3.754168	0.385654	-4.034793
25	9	0	2.077840	0.358841	-2.676505
26	9	0	2.386556	2.057786	-3.967010
27	6	0	4.438027	1.621366	2.099524
28	6	0	4.423318	2.140181	0.869318
29	6	0	5.466237	1.805243	-0.180947
30	6	0	6.611221	1.061210	0.479372
31	6	0	6.544456	0.581415	1.722872
32	7	0	5.446237	0.777201	2.565063
33	1	0	3.666810	1.845722	2.827708
34	1	0	3.632988	2.834492	0.608719
35	1	0	7.508898	0.902135	-0.105154
36	1	0	7.358363	0.020543	2.167982
37	6	0	5.984787	3.084776	-0.721340
38	7	0	6.361270	4.097803	-1.133671
39	5	0	5.404065	0.219698	3.883890
40	8	0	6.427484	-0.523851	4.409717
41	8	0	4.337348	0.388723	4.727090
42	6	0	5.910416	-1.096188	5.634708
43	6	0	4.780727	-0.083550	6.021638
44	6	0	7.042039	-1.202543	6.642438
45	1	0	6.659918	-1.541615	7.610357
46	1	0	7.777437	-1.930135	6.290973
47	1	0	7.545375	-0.244226	6.776693
48	6	0	5.367238	-2.479703	5.286031
49	1	0	6.165709	-3.064715	4.824198
50	1	0	5.017951	-3.007320	6.177441
51	1	0	4.538696	-2.406361	4.575562
52	6	0	3.598091	-0.696983	6.751355
53	1	0	3.923884	-1.148937	7.693384
54	1	0	2.866405	0.081393	6.980404
55	1	0	3.108617	-1.459195	6.143724
56	6	0	5.312472	1.129440	6.781128
57	1	0	4.526360	1.886219	6.830039
58	1	0	5.606387	0.864267	7.800101
59	1	0	6.176577	1.563262	6.269489

TS4



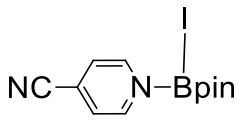
Zero-point correction= 0.275165(Hartree/Particle)

Thermal correction to Energy= 0.292695
Thermal correction to Enthalpy= 0.293639
Thermal correction to Gibbs Free Energy= 0.228582
Sum of electronic and zero-point Energies= -762.593986
Sum of electronic and thermal Energies= -762.576456
Sum of electronic and thermal Enthalpies= -762.575512
Sum of electronic and thermal Free Energies= -762.640570

Esol = -763.1522273

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.392252	0.846388	-0.583086
2	6	0	2.777818	0.844172	-0.649114
3	6	0	3.432775	-0.365252	-0.857800
4	6	0	2.696237	-1.552984	-1.004338
5	6	0	1.323157	-1.477589	-0.969710
6	7	0	0.699924	-0.293971	-0.797635
7	1	0	0.802295	1.736944	-0.413070
8	1	0	3.328588	1.764248	-0.504454
9	1	0	3.191961	-2.504633	-1.141927
10	1	0	0.672768	-2.339163	-1.059329
11	6	0	4.869430	-0.404340	-0.923474
12	7	0	6.022982	-0.439557	-0.991819
13	5	0	-0.797659	-0.260719	-0.603700
14	8	0	-1.499071	-1.411802	-0.523868
15	8	0	-1.490819	0.867923	-0.858930
16	6	0	-2.875098	-1.047222	-0.843741
17	6	0	-2.887638	0.511793	-0.621410
18	6	0	-3.801642	-1.820544	0.076625
19	1	0	-4.838452	-1.508493	-0.081458
20	1	0	-3.727147	-2.888261	-0.142624
21	1	0	-3.536723	-1.662202	1.122354
22	6	0	-3.090571	-1.448560	-2.299517
23	1	0	-2.887470	-2.516716	-2.405599
24	1	0	-4.119314	-1.257757	-2.615035
25	1	0	-2.415362	-0.900214	-2.963022
26	6	0	-3.744799	1.279900	-1.613012
27	1	0	-4.790479	0.969758	-1.525218
28	1	0	-3.686434	2.347109	-1.388334
29	1	0	-3.414852	1.124810	-2.641277

30	6	0	-3.224671	0.917081	0.807837
31	1	0	-3.024731	1.984622	0.924669
32	1	0	-4.281298	0.732084	1.020051
33	1	0	-2.603860	0.389176	1.535499
34	53	0	0.323088	0.400311	2.366189



Int3b

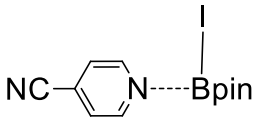
Zero-point correction=	0.274903(Hartree/Particle)
Thermal correction to Energy=	0.292892
Thermal correction to Enthalpy=	0.293836
Thermal correction to Gibbs Free Energy=	0.227883
Sum of electronic and zero-point Energies=	-762.608633
Sum of electronic and thermal Energies=	-762.590644
Sum of electronic and thermal Enthalpies=	-762.589700
Sum of electronic and thermal Free Energies=	-762.655653

Esol = -763.1611282

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.255771	0.856533	-0.685721
2	6	0	2.518009	0.790752	-1.248180
3	6	0	3.121903	-0.462545	-1.380663
4	6	0	2.446331	-1.608537	-0.954041
5	6	0	1.186016	-1.461913	-0.401576
6	7	0	0.627104	-0.251953	-0.272468
7	1	0	0.706952	1.780796	-0.543243
8	1	0	3.021893	1.690748	-1.576976
9	1	0	2.893777	-2.589398	-1.052328
10	1	0	0.581970	-2.288496	-0.043733
11	6	0	4.434679	-0.573000	-1.961858
12	7	0	5.486759	-0.662156	-2.432337
13	5	0	-0.835155	-0.128050	0.409534
14	8	0	-1.573074	-1.309789	0.235426
15	8	0	-1.494234	0.974467	-0.155148
16	6	0	-2.654917	-0.982813	-0.656598

17	6	0	-2.846416	0.545750	-0.395772
18	6	0	-3.855818	-1.844292	-0.303208
19	1	0	-4.730604	-1.544526	-0.889331
20	1	0	-3.636866	-2.891798	-0.526146
21	1	0	-4.092978	-1.763052	0.758178
22	6	0	-2.187382	-1.273154	-2.083747
23	1	0	-1.848317	-2.311218	-2.139159
24	1	0	-2.992272	-1.133114	-2.810674
25	1	0	-1.354583	-0.618540	-2.360725
26	6	0	-3.399225	1.326448	-1.577603
27	1	0	-4.385335	0.945425	-1.861746
28	1	0	-3.506867	2.378425	-1.301840
29	1	0	-2.734628	1.264908	-2.441254
30	6	0	-3.669558	0.824049	0.860898
31	1	0	-3.561945	1.879802	1.120742
32	1	0	-4.729175	0.607940	0.696235
33	1	0	-3.308963	0.230612	1.705090
34	53	0	-0.206104	0.163192	2.674290

TS5



Zero-point correction= 0.275165(Hartree/Particle)
Thermal correction to Energy= 0.292695
Thermal correction to Enthalpy= 0.293639
Thermal correction to Gibbs Free Energy= 0.228582
Sum of electronic and zero-point Energies= -762.593986
Sum of electronic and thermal Energies= -762.576456
Sum of electronic and thermal Enthalpies= -762.575512
Sum of electronic and thermal Free Energies= -762.640570

Esol = -763.1522273

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.392252	0.846388	-0.583086
2	6	0	2.777818	0.844172	-0.649114
3	6	0	3.432775	-0.365252	-0.857800

4	6	0	2.696237	-1.552984	-1.004338
5	6	0	1.323157	-1.477589	-0.969710
6	7	0	0.699924	-0.293971	-0.797635
7	1	0	0.802295	1.736944	-0.413070
8	1	0	3.328588	1.764248	-0.504454
9	1	0	3.191961	-2.504633	-1.141927
10	1	0	0.672768	-2.339163	-1.059329
11	6	0	4.869430	-0.404340	-0.923474
12	7	0	6.022982	-0.439557	-0.991819
13	5	0	-0.797659	-0.260719	-0.603700
14	8	0	-1.499071	-1.411802	-0.523868
15	8	0	-1.490819	0.867923	-0.858930
16	6	0	-2.875098	-1.047222	-0.843741
17	6	0	-2.887638	0.511793	-0.621410
18	6	0	-3.801642	-1.820544	0.076625
19	1	0	-4.838452	-1.508493	-0.081458
20	1	0	-3.727147	-2.888261	-0.142624
21	1	0	-3.536723	-1.662202	1.122354
22	6	0	-3.090571	-1.448560	-2.299517
23	1	0	-2.887470	-2.516716	-2.405599
24	1	0	-4.119314	-1.257757	-2.615035
25	1	0	-2.415362	-0.900214	-2.963022
26	6	0	-3.744799	1.279900	-1.613012
27	1	0	-4.790479	0.969758	-1.525218
28	1	0	-3.686434	2.347109	-1.388334
29	1	0	-3.414852	1.124810	-2.641277
30	6	0	-3.224671	0.917081	0.807837
31	1	0	-3.024731	1.984622	0.924669
32	1	0	-4.281298	0.732084	1.020051
33	1	0	-2.603860	0.389176	1.535499
34	53	0	0.323088	0.400311	2.366189

IBpin

Zero-point correction=	0.183964(Hartree/Particle)
Thermal correction to Energy=	0.194929
Thermal correction to Enthalpy=	0.195873
Thermal correction to Gibbs Free Energy=	0.146765
Sum of electronic and zero-point Energies=	-422.284105
Sum of electronic and thermal Energies=	-422.273140
Sum of electronic and thermal Enthalpies=	-422.272196
Sum of electronic and thermal Free Energies=	-422.321304

Esol = -422.6251154

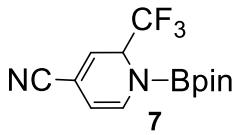
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	5	0	-0.790690	-0.321589	-0.863066
2	8	0	-1.534671	-1.437301	-0.663009
3	8	0	-1.493739	0.828967	-1.005479
4	6	0	-2.911756	-1.041421	-0.914209
5	6	0	-2.864705	0.498682	-0.648135
6	6	0	-3.820716	-1.823874	0.016874
7	1	0	-4.855171	-1.481980	-0.087847
8	1	0	-3.781933	-2.884489	-0.241621
9	1	0	-3.515018	-1.713320	1.057942
10	6	0	-3.203336	-1.384654	-2.372069
11	1	0	-3.008744	-2.447773	-2.528630
12	1	0	-4.245801	-1.176941	-2.627331
13	1	0	-2.556336	-0.814545	-3.044868
14	6	0	-3.804268	1.324875	-1.508402
15	1	0	-4.842663	1.031644	-1.324777
16	1	0	-3.696327	2.381990	-1.255266
17	1	0	-3.584244	1.202224	-2.569550
18	6	0	-3.027219	0.852871	0.827065
19	1	0	-2.771110	1.905306	0.966238
20	1	0	-4.055844	0.694524	1.161577
21	1	0	-2.358639	0.251535	1.449697
22	53	0	1.358284	-0.374235	-0.951483

4-cyanopyridine

Zero-point correction= 0.088413(Hartree/Particle)
Thermal correction to Energy= 0.094380
Thermal correction to Enthalpy= 0.095324
Thermal correction to Gibbs Free Energy= 0.058181
Sum of electronic and zero-point Energies= -340.300304
Sum of electronic and thermal Energies= -340.294337
Sum of electronic and thermal Enthalpies= -340.293393
Sum of electronic and thermal Free Energies= -340.330537

Esol = -340.5096342

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.501787	1.140544	-0.000004
2	6	0	0.111946	1.203226	0.000009
3	6	0	-0.594341	0.000000	0.000000
4	6	0	0.111946	-1.203225	-0.000009
5	6	0	1.501788	-1.140543	0.000005
6	7	0	2.193304	0.000000	0.000000
7	1	0	2.087034	2.056307	0.000016
8	1	0	-0.408026	2.153948	0.000025
9	1	0	-0.408026	-2.153948	-0.000024
10	1	0	2.087034	-2.056307	-0.000016
11	6	0	-2.035592	0.000000	0.000000
12	7	0	-3.192093	0.000000	0.000000



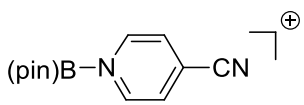
7

Zero-point correction=	0.291215(Hartree/Particle)
Thermal correction to Energy=	0.311002
Thermal correction to Enthalpy=	0.311946
Thermal correction to Gibbs Free Energy=	0.243296
Sum of electronic and zero-point Energies=	-1088.780983
Sum of electronic and thermal Energies=	-1088.761196
Sum of electronic and thermal Enthalpies=	-1088.760252
Sum of electronic and thermal Free Energies=	-1088.828902

Esol = -1089.484127

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.663492	1.220623	0.300410
2	6	0	3.083370	1.122599	-0.191455
3	6	0	3.713341	-0.064227	-0.141742
4	6	0	3.014414	-1.283824	0.252027

5	6	0	1.676328	-1.232801	0.354783
6	7	0	0.961812	-0.053527	0.193742
7	1	0	1.103687	1.975326	-0.260317
8	1	0	3.579824	2.019053	-0.541719
9	1	0	3.554134	-2.212893	0.364484
10	1	0	1.063820	-2.112237	0.520984
11	6	0	5.088311	-0.162802	-0.562759
12	7	0	6.192345	-0.258946	-0.894738
13	5	0	-0.467660	-0.052148	0.085770
14	8	0	-1.234116	-1.173619	0.254984
15	8	0	-1.177406	1.084413	-0.195107
16	6	0	-2.576497	-0.795524	-0.138445
17	6	0	-2.559838	0.754803	0.080203
18	6	0	-3.570712	-1.548436	0.728491
19	1	0	-4.590213	-1.208549	0.521338
20	1	0	-3.514479	-2.616854	0.506899
21	1	0	-3.359077	-1.406105	1.789005
22	6	0	-2.737212	-1.181675	-1.606274
23	1	0	-2.524841	-2.247569	-1.715275
24	1	0	-3.753743	-0.989907	-1.959688
25	1	0	-2.036859	-0.624406	-2.235123
26	6	0	-3.451547	1.540525	-0.865139
27	1	0	-4.495958	1.236534	-0.744401
28	1	0	-3.376990	2.606262	-0.636433
29	1	0	-3.157597	1.391065	-1.904961
30	6	0	-2.826059	1.149348	1.531055
31	1	0	-2.574850	2.204675	1.658429
32	1	0	-3.875560	1.001395	1.798825
33	1	0	-2.201345	0.567754	2.214992
34	6	0	1.636616	1.695192	1.756015
35	9	0	2.174150	2.917661	1.854818
36	9	0	2.316378	0.876395	2.562497
37	9	0	0.376459	1.757869	2.213953



Zero-point correction=	0.275528(Hartree/Particle)
Thermal correction to Energy=	0.291487
Thermal correction to Enthalpy=	0.292431
Thermal correction to Gibbs Free Energy=	0.232592
Sum of electronic and zero-point Energies=	-751.038204
Sum of electronic and thermal Energies=	-751.022246

Sum of electronic and thermal Enthalpies= -751.021302
Sum of electronic and thermal Free Energies= -751.081140

Esol = -751.609417

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.645404	1.169582	-0.157746
2	6	0	3.024294	1.202433	-0.163653
3	6	0	3.723220	-0.000017	-0.000054
4	6	0	3.024288	-1.202461	0.163564
5	6	0	1.645399	-1.169598	0.157697
6	7	0	0.985695	-0.000005	-0.000015
7	1	0	1.023470	2.050137	-0.275684
8	1	0	3.548928	2.141337	-0.291191
9	1	0	3.548917	-2.141370	0.291088
10	1	0	1.023460	-2.050148	0.275654
11	6	0	5.160311	-0.000023	-0.000075
12	7	0	6.316228	-0.000028	-0.000092
13	5	0	-0.529990	0.000002	0.000007
14	8	0	-1.206442	-1.136048	0.198568
15	8	0	-1.206438	1.136058	-0.198533
16	6	0	-2.609807	-0.778523	-0.108497
17	6	0	-2.609797	0.778546	0.108574
18	6	0	-3.516829	-1.548994	0.830185
19	1	0	-4.554494	-1.236154	0.682931
20	1	0	-3.450308	-2.616440	0.610668
21	1	0	-3.246810	-1.391249	1.874729
22	6	0	-2.838444	-1.185104	-1.557882
23	1	0	-2.629097	-2.251072	-1.666959
24	1	0	-3.875405	-1.006323	-1.850595
25	1	0	-2.186850	-0.630159	-2.239416
26	6	0	-3.516839	1.549026	-0.830081
27	1	0	-4.554503	1.236196	-0.682796
28	1	0	-3.450301	2.616471	-0.610567
29	1	0	-3.246853	1.391278	-1.874634
30	6	0	-2.838386	1.185129	1.557965
31	1	0	-2.629026	2.251095	1.667036
32	1	0	-3.875340	1.006358	1.850710
33	1	0	-2.186777	0.630178	2.239480

I anion

Zero-point correction=	0.000000(Hartree/Particle)
Thermal correction to Energy=	0.001416
Thermal correction to Enthalpy=	0.002360
Thermal correction to Gibbs Free Energy=	-0.016848
Sum of electronic and zero-point Energies=	-11.419267
Sum of electronic and thermal Energies=	-11.417851
Sum of electronic and thermal Enthalpies=	-11.416907
Sum of electronic and thermal Free Energies=	-11.436116

Esol = -11.476239

7. References

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