"On Water" Metal-Free Direct C-H Amination and Imination of Olefins via Tandem SNAr, Click Chemistry, and Molecular Nitrogen Release

Sudripet Sharma,[a] Seyedesahar Miraghaee,[a] and Sachin Handa[a,b]

[a]Department of Chemistry, 2320 S. Brook Street, University of Louisville, Louisville, Kentucky 40292, United States
[b]Department of Chemistry, 601 S College Ave, University of Missouri, Columbia, MO 65211, United States

*sachin.handa@missouri.edu

Supplementary Material

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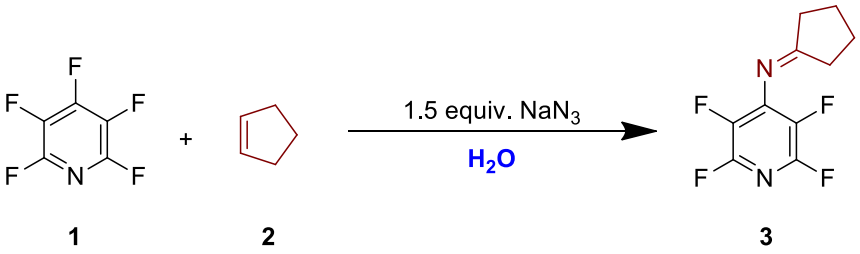
1. GENERAL EXPERIMENTAL DETAILS

All manipulations were carried out under argon atmosphere unless otherwise noted. TLC plates (UV 254 indicator, glass backed, thickness 200 mm) and silica gel (standard grade, 230 – 400 mesh) were purchased from Merck. NaN_3 was purchased from Sigma Aldrich and was used as such without further purification. Polyfluoroarenes and (hetero)aryl alkenes were purchased from Sigma-Aldrich, Combi-Block, Alfa Aesar, and Ambeed chemicals. Pure NMR solvents were purchased from Cambridge Isotopes Laboratories or Sigma-Aldrich. All the catalytic reactions were performed in 4 mL close-cap microwave vials under argon atmosphere. Reaction vials were also recycled and reused. Melting points were determined using a MEL-TEMP II melting point apparatus with samples in Kimble Kimex 51 capillaries (1.5-1.8 x 90 mm). Unless otherwise mentioned, all NMR spectra were recorded at 25 °C on Varian Unity INOVA (400, 500 and 700) spectrometers. Reported chemical shifts are referenced to residual solvent peaks. HRMS spectra were obtained on a Thermo Electron MAT 95XP mass spectrometer using either electron ionization (EI) or chemical ionization (CI).

2. REACTION OPTIMIZATION

2.1. Effect of temperature

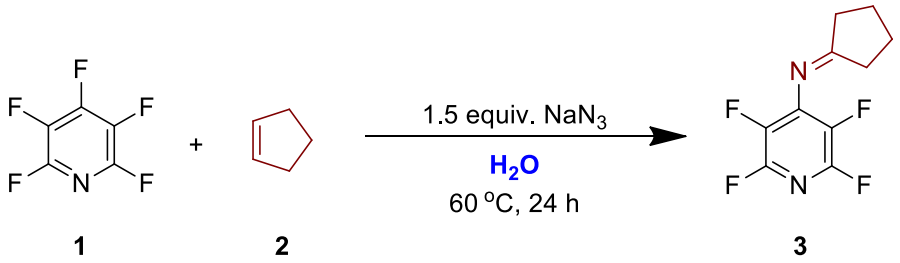


1 **2** **3**

entry	T (°C)	**3** (%)[a]
1	rt	11
2	35 °C	45
3	45 °C	60
4	**60 °C**	**92**

Conditions. **1** (0.25 mmol), **2** (0.50 mmol), NaN_3 (0.375 mmol, 1.5 equiv.), 1 mL H_2O, 24 h. [a]All yields are based on GCMS conversion using (0.25 mmol) mesitylene as internal standard.

2.2. Effect of solvent

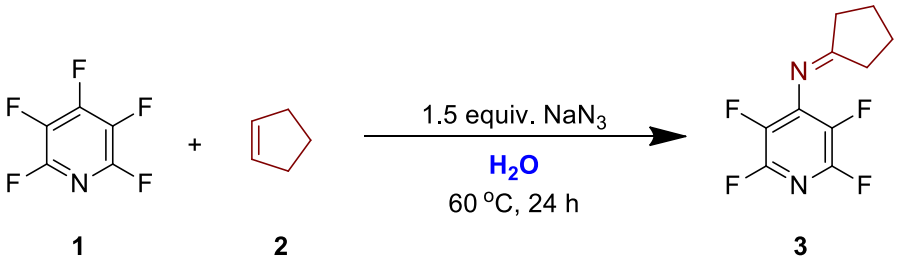


1 **2** **3**

entry	solvent	**3** (%)[a]
1	3 wt % SDS	17
2	DMSO	13.5
3	3 wt % Tween-20	67
4	3 wt % PS-750-M	72
5	**H_2O**	**92**
6	THF	75
7	DMF	12
8	Toluene	traces*
9	CH_3CN	12

Conditions. 1 (0.25 mmol), **2** (0.50 mmol), NaN_3 (0.375 mmol, 1.5 equiv.), 1 mL **solvent**, 24 h. [a]All yields are based on GC-MS conversion using (0.25 mmol) mesitylene as internal standard. * No perfluoroazide formation was observed.

2.3. Effect of Global Concentration

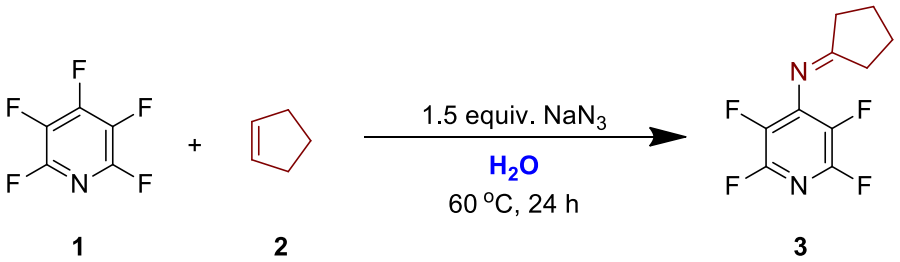


1 **2** **3**

entry	H_2O (M)	**3** (%)[a]
1	**0.25**	**92**
2	1	86
3	1.5	86.5

Conditions. 1 (0.25 mmol), **2** (0.50 mmol), NaN_3 (0.375 mmol, 1.5 equiv.), x M **H_2O**, 24 h. [a]All yields are based on GC-MS conversion using (0.25 mmol) mesitylene as internal standard.

2.4. Effect of NaN_3 equivalents



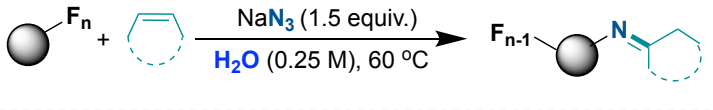
1 **2** **3**

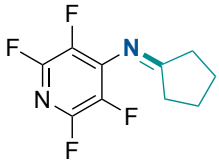
entry	NaN_3	**3** (%)[a]
1	**No deviation**	**92**
2	2.0 equiv. instead of 1.5 equiv.	91

3. GENERAL REACTION PROCEDURE

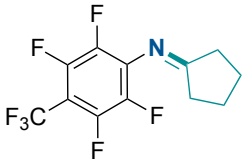
Perfluoroarene (0.5 mmol, 1 equiv.), alkene (1.0 mmol, 2 equiv.), and NaN_3 (0.75 mmol, 1.5 equiv.) were taken in a 4 mL reaction vial equipped with a PTFE-coated magnetic stir bar. The reaction vial was closed with a rubber septum, and 1 mL water was added to the reaction mixture. The septum was wrapped with a parafilm. The reaction mixture was then stirred at 60 °C until complete consumption of the starting materials. **Initially, the mixture was biphasic, but it became monophasic upon completion of the reaction.** After reaction completion, as monitored by TLC or GC-MS for the consumption of perfluorazide intermediate, the reaction mixture was cooled to rt. 1 mL EtOAc was added to the reaction mixture and the mixture was stirred for a minute. Stirring was stopped and the organic layer was withdrawn with the aid of a syringe needle. The same protocol was repeated twice (2 x 1 mL EtOAc). The combined organic layers were dried over anhydrous sodium sulfate. Finally, volatiles were removed under reduced pressure to obtain a crude product, which was further purified by flash chromatography (if needed) using EtOAc/hexanes as eluent.

4. SUBSTRATE SCOPE USING INTERNAL CYCLOALKENES

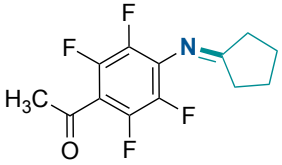




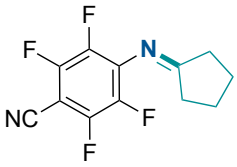
3 67% (13 h)



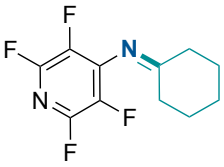
4 96% (14 h)*



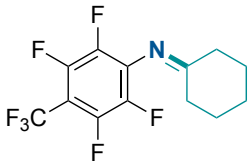
5 90% (14 h)*



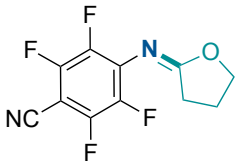
6 93% (10 h)*



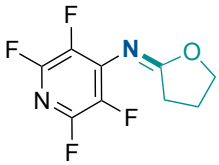
7 69% (12 h)



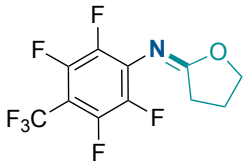
8 92% (16 h)*



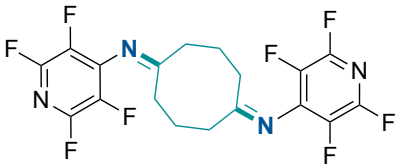
9 93% (12 h)*



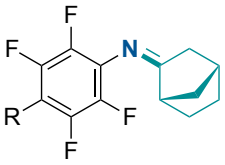
10 85% (16 h)



11 74% (12 h)*



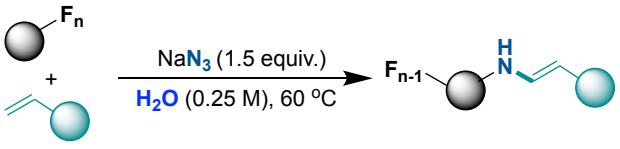
12 27%, 23 h

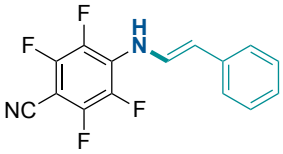


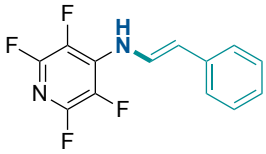
13 R = CN, 85% (12 h)*
14 R = CO_2Me, 71% (16 h)**

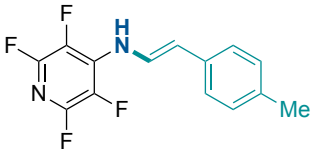
Conditions: Perfluoroarene (0.25 mmol), alkene (0.50 mmol), NaN_3 (0.375 mmol, 1.5 equiv.), 0.25 M H_2O, 60 °C. *Tetrabutylammonium chloride (20 mol %) was used as additive. All yields are isolated.

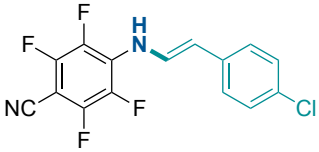
5. SUBSTRATE SCOPE USING STYRENES

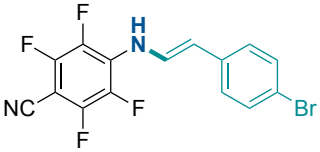


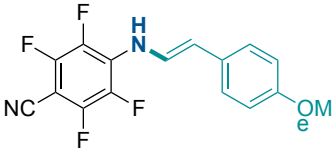

15 64% (12 h)*

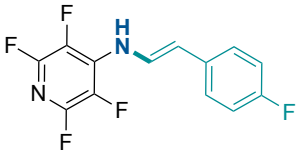

16 62% (12 h)

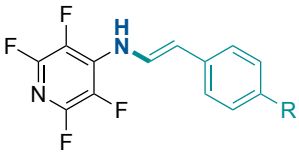

17 54% (10 h)

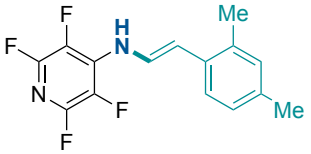

18 52% (12 h)*

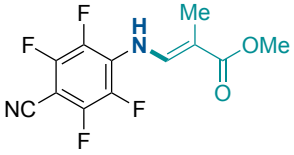

19 57% (12 h)*

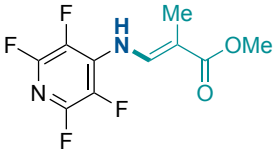

20 55% (14 h)*

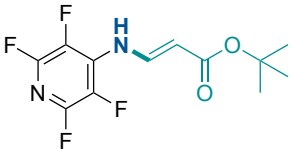

21 66% (12 h)


22 R = Br, 61% (12 h)
23 R = OMe, 50% (12 h)


24 69%, 12 h

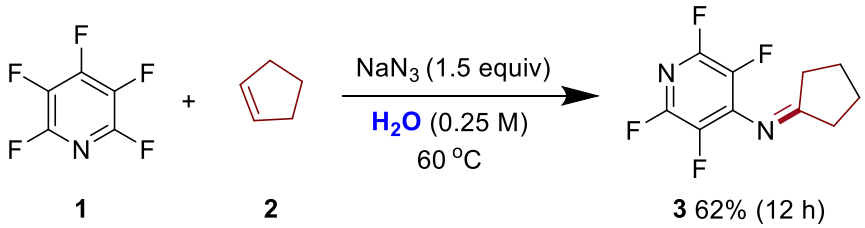

25 51% (15 h)*


26 51% (12 h)


27 74% (12 h)

Conditions: Perfluoroarene (0.25 mmol), alkene (0.50 mmol), NaN_3 (0.375 mmol, 1.5 equiv.), 0.25 M H_2O, 60 °C. *Tetrabutylammonium chloride (20 mol %) was used as additive. All yields are isolated.

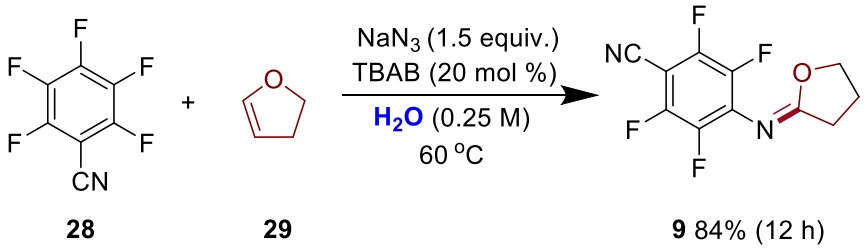
6. GRAM-SCALE REACTIONS FOR THE SYNTHESIS OF 3



Scheme S1. Gram-scale reaction for the synthesis of **3**

Perfluoropyridine (1g, 5.91 mmol, 1.0 equiv.), cyclopentene (971 mg, 11.82 mmol, 2.0 equiv.) and NaN_3 (576 mg, 8.86 mmol, 1.5 equiv.) were taken in a 50 mL round-bottom flask equipped with a PTFE-coated magnetic stir bar. Reaction vial was closed with a rubber septum and 12 mL H_2O was added to the reaction mixture. Septum was wrapped with PTFE tape and a parafilm. and reaction mixture was stirred at 60 °C on pre-heated oil bath for 12 hours. After 12 hours, reaction mixture was cooled to rt. 10 mL EtOAc was added to the reaction mixture, and it was stirred for 2 minutes. Reaction completion was monitored by TLC (ethyl acetate/hexane, 0.5:9.5, R_f = 0.5). The organic layer was separated from the aqueous layer using a separatory funnel. The same protocol was repeated two times (5 mL of EtOAc/time). Combined organic layers were dried over anhydrous sodium sulfate. Finally, volatiles were removed under reduced pressure to obtain crude product, which was further purified by flash chromatography using 5% EtOAc/hexanes as eluent. The purified product was dried under reduced pressure to obtain *N*-(perfluoropyridin-4-yl)cyclopentanimine (**3**) as final product (850 mg, 62%). The pure compound was then characterized by ^1H and ^{13}C NMR analysis.

7. GRAM-SCALE REACTIONS FOR SYNTHESIS OF 9

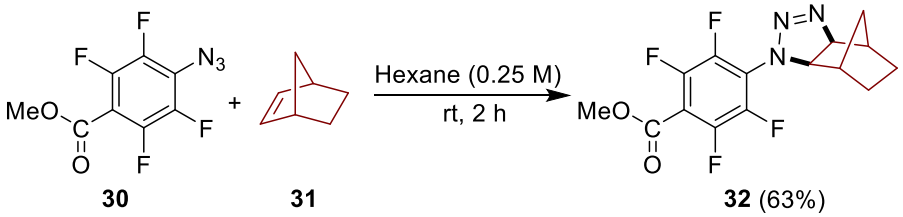


28 **29** **9** 84% (12 h)

Scheme S2. Gram-scale reaction for synthesis of **9**

2,3,4,5,6-pentafluorobenzonitrile (1g, 5.2 mmol, 1.0 equiv.), 2,3-dihydrofuran (729 mg, 10.4 mmol, 2.0 equiv.) and NaN_3 (507 mg, 7.8 mmol, 1.5 equiv.) were taken in a 50 mL round-bottom flask equipped with a PTFE-coated magnetic stir bar. Reaction vial was closed with a rubber septum and 10 mL H_2O was added to the reaction mixture. Septum was wrapped with PTFE tape and a parafilm. and reaction mixture was stirred at 60 °C on pre-heated oil bath for 12 hours. After 12 hours, reaction mixture was cooled to rt. 10 mL EtOAc was added to the reaction mixture, and it was stirred for 2 minutes. Reaction completion was monitored by TLC (ethyl acetate/hexane, 1:9). The Organic layer was separated from the aqueous layer using a separatory funnel. The same protocol was repeated two times (5 mL of EtOAc/time). Combined organic layers were dried over anhydrous sodium sulfate. Finally, volatiles were removed under reduced pressure to obtain crude product, which was further purified by flash chromatography using 5% EtOAc/hexanes as eluent. The purified product was dried under reduced pressure to obtain 4-((dihydrofuran-2(3*H*)-ylidene)amino)-2,3,5,6-tetrafluorobenzonitrile (**9**) as final product (1.02 g, 84%). The pure compound was then characterized by ^{1}H and ^{13}C NMR analysis.

8. MECHANISTIC INVESTIGATION



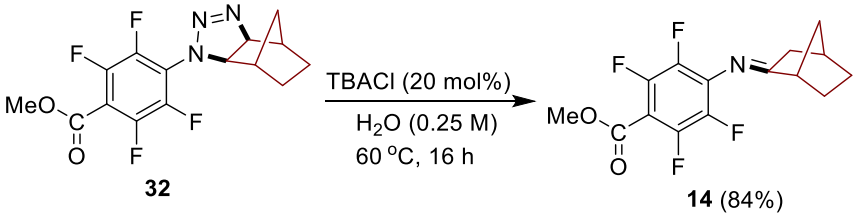
Conditions: 30 (0.5 mmol), **31** (0.6 mmol), hexane (0.25 M), rt, 2 h.

Scheme S3. Synthesis and isolation of triazoline intermediate (**31**)

8a) Synthesis of triazoline intermediate 31

Procedure: The synthesis of **32** was performed following the reported literature procedure. methyl 4-azido-2,3,5,6-tetrafluorobenzoate (**30**) (56.5 mg, 0.6 mmol, 1.2 equiv.) and norbornene (**31**) (124.5 mg mg, 0.5 mmol, 1.0 equiv.) and *n*-hexane (2 mL) were taken in a 4 mL reaction vial. Reaction vial was closed with a rubber septum and the reaction mixture was kept as is without any stirring. After 3 hours, the white solid was obtained. The white solid was separated from the hexane solution and washed three times with 3x1 mL of hexane. The solid collected was dried under reduced pressure to obtain methyl 2,3,5,6-tetrafluoro-4-3a,4,5,6,7,7a-hexahydro-1*H*-4,7-methanobenzo[d][1,2,3]triazol-1-yl)benzoate (**32**) as the final product (130 mg, 63%). The pure compound was then characterized by ^{1}H NMR analysis based on the literature report (Xie, S.; Lopez, S. A.; Ramström, O.; Yan, M.; Houk, K. N. 1,3-Dipolar Cycloaddition Reactivities of Per-fluorinated Aryl Azides with Enamines and Strained Dipolarophiles. *J Am Chem Soc* **2015**, 137, 2958–2966. https://doi.org/10.1021/ja511457g).

8b) Conversion of 31 to final product 16 in water

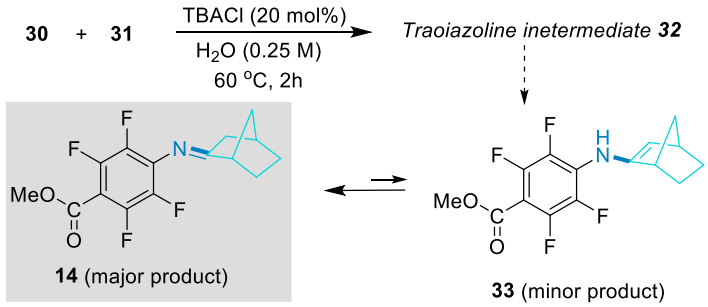


Conditions: 31 (0.25 mmol), TBACl (20 mol%), H_2O (0.25 M), 60 °C, 16 h.

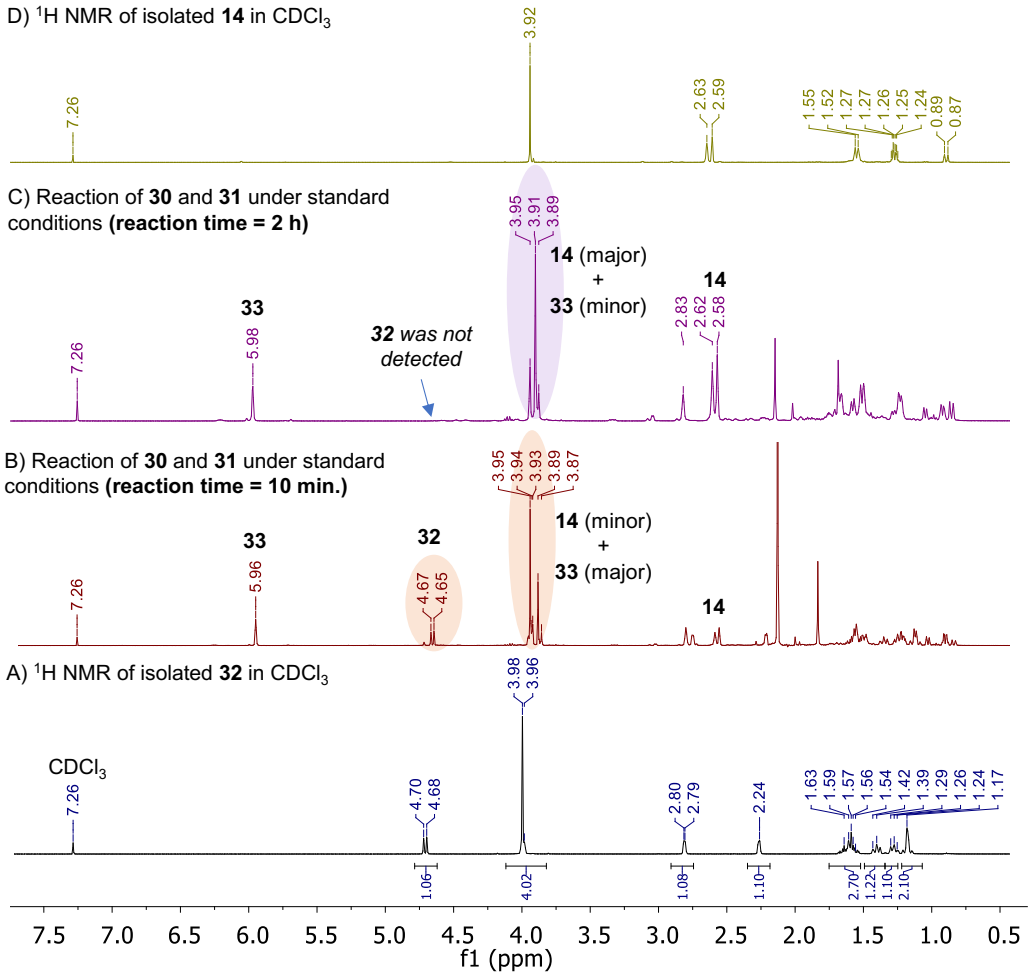
Scheme S4. Synthesis of **14** from **32** under standard conditions

Procedure: Methyl-2,3,5,6-tetrafluoro-4-3a,4,5,6,7,7a-hexahydro-1*H*-4,7-methanobenzo[d][1,2,3]triazol-1-yl)benzoate (**32**) (0.25 mmol, 1 equiv.) and Tetrabutylammonium chloride (20 mol%, 0.05 mmol) were taken in a 4 mL reaction vial equipped with a PTFE-coated magnetic stir bar. Reaction vial was closed with a rubber septum and 1 mL water was added to the reaction mixture. Septum was wrapped with PTFE tape and a parafilm. The reaction mixture was then stirred at 60 °C for 16 hours. The reaction mixture was allowed to cool to rt. 2 mL EtOAc was added to the reaction mixture, and it was stirred for a minute. Reaction completion was monitored by TLC. Organic layer was withdrawn with the aid of syringe needle. The same protocol was repeated two times (2 x 2 mL EtOAc). The combined organic layer was dried over anhydrous sodium sulfate. Finally, volatiles was removed under reduced pressure to obtain crude product, which was further purified by flash chromatography using 5% EtOAc/hexanes as eluent. The viscous gel collected was dried under reduced pressure to obtain Methyl-4-(bicyclo[2.2.1]heptan-2-ylidene)amino-2,3,5,6-tetrafluorobenzoate (**14**) as the final product (66 mg, 84%). The pure compound was then characterized by ^{1}H and ^{13}C NMR analysis.

9. CONTROL ^{1}H NMR ANALYSIS



Conditions: **30** (0.25 mmol), **31** (0.25 mmol), TBACl (20 mol%), H_2O (1 mL, 0.25 M), 60 °C. Reaction mixture was extracted with 0.6 mL $CDCl_3$ for ^{1}H NMR analysis

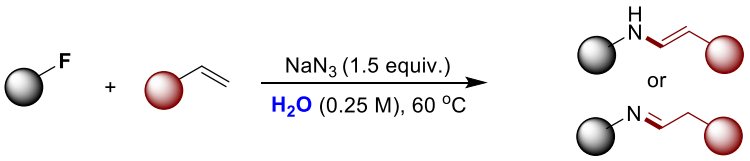


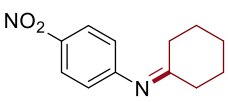
Scheme S5. Control ^{1}H NMR analysis of the reaction to understand the various intermediates involved in the reaction

Procedure: A set of 3 reactions were set up according to the general procedure. To each reaction, methyl-4-azido-2,3,5,6-tetrafluorobenzoate (**29**) (62.25mg, 0.25 mmol, 1.2 equiv.) and norbornene (**30**) (23.5 mg,

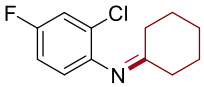
0.25 mmol, 1.0 equiv.) and tetrabutylammonium chloride (13.64 mg, 20 mol %, 0.05 mmol) were taken in a 4 mL reaction vial equipped with a PTFE-coated magnetic stir bar. Reaction vials were closed with a rubber septum and 1 mL water was added to the reaction mixture. Septum was wrapped with PTFE tape and a parafilm. The reaction mixtures were then stirred at 60 °C. After 10 minutes, one of reaction vial was removed from the heating and quickly quenched with 0.5 mL of $CDCl_3$. The organic layer was allowed to separate from the water. From the organic layer, 0.2 mL of $CDCl_3$ was transferred into the NMR tube using a needle syringe. An additional 0.4 mL of $CDCl_3$ was added to the NMR pure, which was quickly subjected to the NMR analysis to record ^1H NMR. A similar procedure was performed to the rest of the reaction after 1h and 2 h, and ^1H NMR was reordered.

10. UNSUCCESSFUL REACTIONS

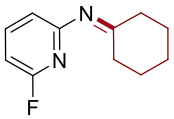




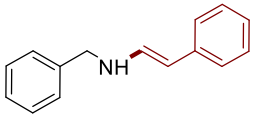
n.d.



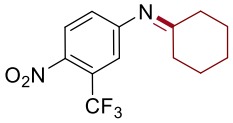
n.d.*



n.d.



n.d.*

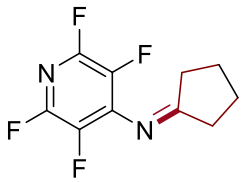


n.d.

Conditions: Fluoroarene (0.25 mmol), alkene (0.50 mmol), NaN_3 (0.375 mmol, 1.5 equiv.), 0.25 M H_2O, 60 °C.
*Isolated azide was used as a starting material (No NaN_3 was used). n.d. = not detected.

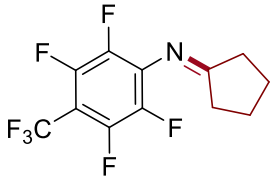
11. ANALYTICAL DATA

N-(perfluoropyridin-4-yl)cyclopentanimine (3)



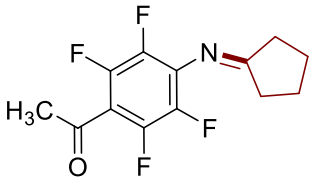
Colorless liquid, yield 75 mg (67%), R_f 0.5 (9.5:0.5, hexanes/ethyl acetate). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.66 (s, 2H), 2.17 (s, 2H), 1.95 (s, 4H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -91.29 – - 91.28 (m, 2F), -153.18 – -155.36 (m, 2F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.9, 143.6 (dd, *J* = 258.9, 13.8 Hz), 134.2 – 133.9 (m), 132.8 (dd, *J* = 255.3, 34.6 Hz), 36.8, 33.5, 24.7, 24.5. **IR** ν (cm^{-1}) = 3210 (m), 2950 (m), 1643(s). **HRMS** [(EI), ($C_{10}H_8F_4N_2$-H)$^-$] calcd 231.0551, found m/z 231.0546.

N-cyclopentylidene-2,3,5,6-tetrafluoro-4-(trifluoromethyl)aniline (4)



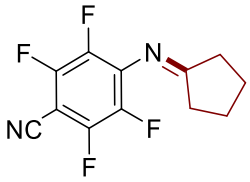
Pale yellow solid, mp = 60-62 °C, yield 145 mg (96%), R_f 0.5 (9:1 hexanes/ethyl acetate), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.64 (t, *J* = 7.2 Hz, 2H), 2.15 (t, *J* = 7.1 Hz, 2H), 2.03 – 1.83 (m, 4H). **^{19}F NMR** (376 MHz, $CDCl_3$). δ -56.21 (t, *J* = 21.5 Hz, 3F), -139.12 – -146.54 (m, 2F), -149.77 – -155.68 (m, 2F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 192.2, 144.6 (dd, *J* = 258.9, 14.4 Hz), 137.9 (dd, *J* = 247.2, 13.8 Hz), 134.7 (t, *J* = 14.9 Hz), 121.3 (q, *J* = 272.5 Hz), 106.4 – 100.7 (m), 36.8, 33.5, 24.8, 24.6. **IR** ν (cm^{-1}) = 2972 (w), 1682 (w), 1652 (m), 1488 (s). **HRMS** [(ESI), ($C_{12}H_8F_7N$+H)$^+$] calcd 300.0618, found m/z 300.0620.

1-(4-(Cyclopentylideneamino)-2,3,5,6-tetrafluorophenyl)ethenone (5)



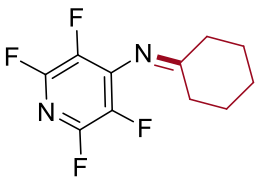
Pale yellow, mp = 54-56 °C, yield 128 mg (90 %), R_f 0.5 (9:1 hexanes/ethyl acetate), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.64 (t, *J* = 7.2 Hz, 2H), 2.15 (t, *J* = 7.1 Hz, 2H), 2.03 – 1.83 (m, 4H). **^{19}F NMR** (400 MHz, $CDCl_3$) δ -142.33 (dd, *J* = 21.8, 10.3 Hz), -152.16 (dd, *J* = 21.3, 9.7 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 192.2, 191.8, 144.8 (dd, *J* = 260.3, 7.2 Hz), 137.6 (dd, *J* = 247.2, 15.2 Hz), 133.7 (t, *J* = 14.8 Hz), 113.5 (t, *J* = 15.9 Hz), 36.7, 33.3, 32.6, 24.8, 24.6. **IR** ν (cm^{-1}) = 3387 (w), 2977 (w), 1698 (s), 1674 (m) 1641 (m), 1476 (s). **HRMS** [(ESI), $(C_{13}H_{11}F_4NO+H)^+$] calcd 274.0850, found m/z 274.0852.

4-(Cyclopentylideneamino)-2,3,5,6-tetrafluorobenzonitrile (6)



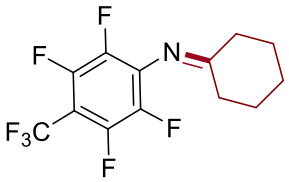
White solid, mp = 48-50 °C, yield 120 mg (93%), R_f 0.5(9:1 hexanes/ethyl acetate), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.66 (s, 1H), 2.15 (s, 1H), 1.95 (s, 2H). **^{19}F NMR** (400 MHz, $CDCl_3$) δ -62.61 (s), -132.55 – -134.11 (m), -149.26 – -150.54 (m). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 192.6, 147.8 (dd, *J* = 260.4, 11.3 Hz), 135.5 (dd, *J* = 243.6, 14.6 Hz), 133.5 – 129.7 (m), 109.2 – 108.6 (m), 108.1, 36.9, 33.7, 24.9, 24.6. **IR** ν (cm^{-1}) = 3356 (w), 2975 (w), 2239 (m), 1680 (m), 1645 (s), 1476 (s) **HRMS** [(ESI), $(C_{12}H_8F_4N_2+H)^+$] calcd 257.0696, found m/z 257.0697.

***N*-cyclohexylidene-2,3,5,6-tetrafluoropyridin-4-amine (7)**



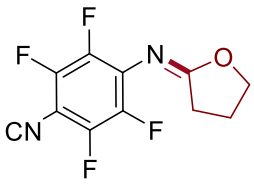
Colorless oil, yield 85 mg (69%), R_f 0.5 (9.5:0.5 n-hexanes/ethyl acetate). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.58 (s, 2H), 2.24 – 2.07 (m, 2H), 2.02 – 1.81 (m, 2H), 1.79 – 1.67 (m, 4H). **^{19}F NMR** (400 MHz, $CDCl_3$) δ -55.58 (s), -55.64 (s), -55.70 (s), -141.97 – -142.23 (m), -151.31 – -151.52 (m). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.2, 143.7 (dd, *J* = 242.6, 16.2 Hz), 141.3 (d, *J* = 17.0 Hz), 133.1 (ddd, *J* = 253.5, 27.8, 6.1 Hz), 39.2, 34.1, 27.9, 27.3, 25.4. **IR** ν (cm^{-1}) = 3348 (w), 2925 (w), 2854 (w), 1643 (m), 1486 (s).

_N_-cyclohexylidene-2,3,5,6-tetrafluoro-4-(trifluoromethyl)aniline (8)



Pale yellow gel, yield 143 mg (92%), R_f 0.5 (9.5:0.5 hexanes/ethyl acetate), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.59 (t, *J*=8.0 Hz, 2H), 2.16 (t, *J* = 6.0 Hz, 2H), 2.03 – 1.88 (m, 2H), 1.77 – 1.64 (m, 4H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -55.64 (t, *J* = 21.5 Hz, 3F), -139.39 – -144.28 (m, 1F), -146.52 – -153.78 (m, 1F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.36, 144.49 (dd, *J* = 258.8, 15.5 Hz), 138.01 (dd, *J* = 246.6, 13.8 Hz), 133.6 (t, *J* = 15.4 Hz), 121.36 (q, *J* = 273.3 Hz), 104.2 – 102.7 (m), 39.3, 33.9, 27.9, 27.2, 25.4. **IR** ν (cm^{-1}) =3333 (w), 2945 (w), 2866 (w), 2125 (w), 1651 (m), 1486 (s). **HRMS** [(CI), $(C_{13}H_{10}F_7N+H)^+$] calcd 314.0774, found m/z 314.0778.

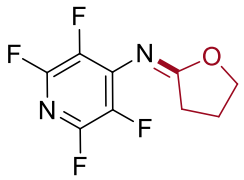
(*E*)-4-((dihydrofuran-2(3H)-ylidene)amino)-2,3,5,6-tetrafluorobenzonitrile (9)



Yellow solid, mp = 60-61 °C, yield 120 mg (93%), R_f 0.5 (8:2 hexanes/ethyl acetate), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.42 (t, *J* = 6.8 Hz, 2H), 2.89 (t, *J* = 7.4 Hz, 2H), 2.38 – 2.22 (m, 2H). **^{19}F NMR** (400 MHz, $CDCl_3$) δ -135.05 (d, *J* = 11.9 Hz), -148.09 (d, *J* = 11.9 Hz).**^{13}C NMR** (100 MHz, $CDCl_3$). δ 170.2, 147.4 (dd, *J* = 259.9, 14.5 Hz), 139.54 (dd, *J* = 248.8, 11.6 Hz), 134.31 (t, *J* = 14.0 Hz), 108.28, 87.34

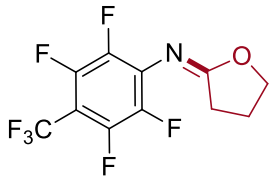
(t, *J* = 17.6 Hz), 73.03, 29.83, 23.28. **IR** ν (cm^{-1}) = 3345 (w), 2931 (w), 2238 (m), 1700 (m), 1493 (s). **HRMS** [(EI), $(C_{11}H_6F_4N_2O+H)^+$] calcd 259.0489, found m/z 259.0490.

(*E*)-*N*-(dihydrofuran-2(3H)-ylidene)-2,3,5,6-tetrafluoropyridin-4-amine (10)



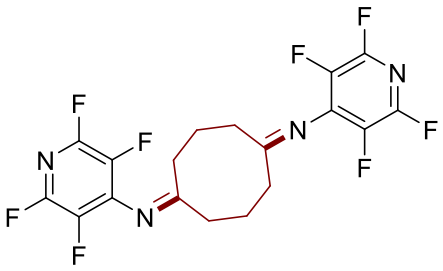
Colorless liquid, yield 99.5 mg (85%), R_f 0.5 (8.5:1.5 hexanes/ethyl acetate). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.51 – 4.14 (m, *J* = 3.2, 2.7, 1.1 Hz, 1H), 3.06 – 2.78 (m, 1H), 2.49 – 2.24 (m, *J* = 13.0, 6.8 Hz, 1H).**^{19}F NMR** (400 MHz, $CDCl_3$) δ -92.52 (s, 2F), -152.17 (s, 2F). **IR** ν (cm^{-1}) = 3331 (s), 1694 (w), 1635 (m). **^{13}C NMR** (176 MHz, $CDCl_3$) δ 169.7, 143.6 (d, *J* = 265.6 Hz), 135 (d, *J* = 281.9 Hz), 72.9, 30, 23.4, 14.40. **HRMS** [(EI), $(C_9H_6F_4N_2O+)^+$] calcd 234.0411, found m/z 234.0412

(E)-N-(dihydrofuran-2(3H)-ylidene)-2,3,5,6-tetrafluoro-4-(trifluoromethyl)aniline (11)



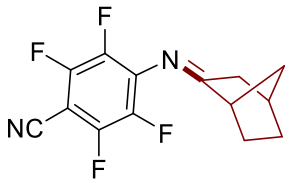
White solid, mp = 110-112 °C, yield 112 mg 74%, R_f 0.3 (9.6:0.4, hexanes/ethyl acetate). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.41 (t, *J* = 7.0 Hz, 1H), 2.89 (t, *J* = 8.0 Hz, 1H), 2.35 – 2.25 (m, 1H). **^{19}F NMR** (400 MHz, $CDCl_3$) δ -56.31 (d, *J* = 46.4 Hz), -143.33 (d, *J* = 372.5 Hz), -150.71 (d, *J* = 433.9 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.8, 144.4 (dd, *J* = 253.6, 19.0 Hz), 139.9 (dd, *J* = 245.0, 8.8 Hz), 131.8 (t, *J* = 19.7 Hz), 118.3 (q, *J* = 281.2 Hz), 105.3 – 101.6 (m), 72.8, 29.8, 23.3. **IR** ν (cm^{-1}) = 3342 (w), 2919 (w), 1692 (m), 1649 (m), 1485 (s). **HRMS** [(ESI), $(C_{11}H_6F_7NO+H)^+$] calcd 302.0410, found m/z 302.0412.

***N*1, *N*5-bis(perfluoropyridin-4-yl)cyclooctane-1,5-diimine (12)**



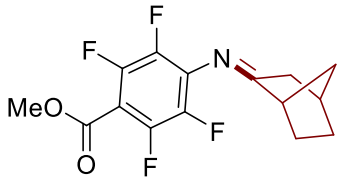
Off white solid, mp = 98- 100 °C, yield 59 mg (27%), R_f 0.5 (9:1 hexanes/ethyl acetate) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.19 – 2.61 (m, 5H), 2.39 (s, 3H), 2.14 – 1.62 (m, 4H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -81.97 – -94.75 (m, 2F), -138.56 – -167.97 (m, 2F). **^{13}C NMR** (176 MHz, $CDCl_3$) δ 176.8, 143.7 (dd, *J* = 241.2, 17.0 Hz), 141.4 – 140 (m), 132.3 (dd, *J* = 257.1, 28.5 Hz), 39.2, 37.1, 36.5, 35.3, 34.2, 29.9, 27, 23.9, 22.7. **IR** ν (cm^{-1}) = 3348 (w), 3219 (w), 2949 (w), 1663 (s), 1485 (s). HRMS [(CI), ($C_{18}H_{11}F_8N_4O$-H)-] calcd 435.0861, found m/z 435.0855.

4-Bicyclo[2.2.1]heptan-2-ylidene)amino)-2,3,5,6-tetrafluorobenzonitrile (13)



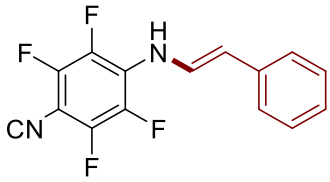
White solid, mp = 160- 162 °C, yield 120 mg (85%), R_f 0.5 (9.5:0.5 hexanes/ethyl acetate). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.65 (s, 3H), 1.70 – 1.44 (m, 4H), 1.38 – 1.21 (m, 2H), 0.91 (d, *J* = 10.2 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -134.43 – -136.73 (m, 2F), -146.94 – -154.90 (m, 2F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.6 (dd, *J* = 260.2, 12.6 Hz), 140.4 (dd, *J* = 249.3, 12.7 Hz), 138.1 (t, *J* = 8.3 Hz), 108.5, 84.4 (t, J = 17.5 Hz), 43.5, 36.4, 28.3, 25.9. **IR ν (cm^{-1})** = 2928 (w), 2235 (m), 2130 (w), 1647 (s), 1485 (s). **HRMS** [(ESI), ($C_{14}H_9F_4N_2$-H)$^-$] calcd 281.0707, found m/z 281.0700.

Methyl 4-bicyclo[2.2.1]heptan-2-ylidene)amino)-2,3,5,6-tetrafluorobenzoate (14)



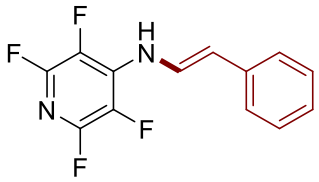
Viscous gel, yield 56 mg (71%), R_f 0.5 (9.5:0.5 hexanes/ethyl acetate). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.92 (s, 3 H), 2.60 (d, *J* = 12 Hz, 3H), 1.53 (d, *J* = 8.6 Hz, 4H), 1.26– 1.24 (m, 2H), 0.88 (d, *J* = 10 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -139.84 – -142.87 (m, 2 F), -151.75 – -155.24 (m, 2F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161, 145.83 (dd, *J* = 255.1, 9.9 Hz), 137.52 (dd, *J* = 404, 13.1 Hz), 103.3, 52.9, 43.1, 36.3, 28.3, 26. **IR ν (cm^{-1})** = 2925 (w), 2245 (m), 2144 (w), 1677 (s), 1437 (s). **HRMS** [(APCI), ($C_{15}H_{14}F_4N_2$+H)$^+$] calcd 316.0955, found m/z 316.0958.

(*E*)-2,3,5,6-Tetrafluoro-4-(styrylamino)benzonitrile (15)



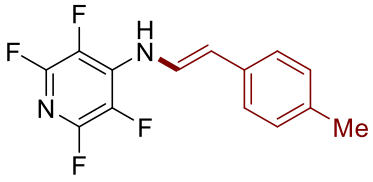
Colourless liquid, yield 94 mg (64%), R_f 0.5 (9:1 hexanes/ethyl acetate). **^{1}H NMR** (400 MHz, $CDCl_3$**)** δ 7.51 – 7.40 (m, 1H), 7.36 – 7.27 (m, 4H), 7.23 -7.20 (m, 1H), 6.43 (d, *J* = 12 Hz, 1H), 6.15 (d, *J* = 16 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$**)** δ -129.37 – -141.35 (m, 2F), -157.81 - -157.90 (m, 2F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.7 (d, *J* = 32.2 Hz), 135.2 (d, *J* = 35.8 Hz), 129.0, 128.76, 128.0, 127.1, 125.5, 125.2, 125.1, 114.1, 108.5. **IR** ν (cm^{-1}) = 3300 (m), 2924 (w), 2232 (m), 1646 (s), 1512 (s). **HRMS** [(EI), ($C_{15}H_8F_4N_2$-H)$^-$] calcd 291.0551, found m/z 291.0541.

(***E*)-2,3,5,6-Tetrafluoro-*N*-styrylpyridin-4-amine (16)**



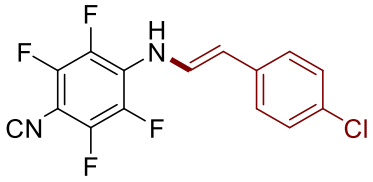
Viscous yellow liquid, yield 83 mg (62%), R_f 0.5 (9:1 hexanes/ethyl acetate). **^{1}H NMR** (400 MHz, $CDCl_3$**)** δ 7.56 – 7.45 (m, 1H), 7.35 – 7.28 (m, 4H), 7.22 (m, 1H), 6.52 (d, *J* = 12 Hz, 1H), 6.15 (d, *J* = 12 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$**)** δ -88.60 – -94.64 (m, 2F), -159.55 – -164.25 (m, 2F). **^{13}C NMR** (176 MHz, $CDCl_3$**)** δ 145.0 – 143.5 (m), 135.3, 132.6, 132.4 – 130.4 (m), 129.8, 126.9, 125.4, 124.7, 113.8. **IR** ν (cm^{-1}) = 3400 (m), 2945 (m), 2239 (m), 1517 (s) **HRMS** [(EI), ($C_{13}H_8F_4N_2$+)$^+$] calcd 268.0619, found m/z 268.0620.

(*E*)-2,3,5,6-tetrafluoro-N-(4-methylstyryl)pyridin-4-amine (17)



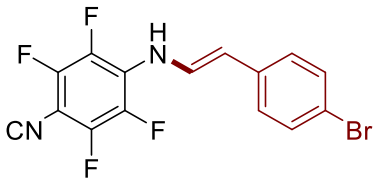
White solid, mp = 125 – 127 °C, yield 76 mg (54%), R_f 0.5 (9:1 hexanes/ethyl acetate). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 – 7.37 (m, 1H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.48 (d, *J* = 10.6 Hz, 1H), 6.13 (d, *J* = 13.8 Hz, 1H), 2.34 (s, 3H).**^{19}F NMR** (376 MHz, $CDCl_3$) δ -91.17 – -95.37 (m, 2F), -161.93 – -162.04 (m, 2F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.7 (d, *J* = 16.1 Hz), 143.20 (d, *J* = 15.0 Hz), 136.9, 132.9, 132.5, 129.7, 125.5, 124.1, 114.0, 21.3. **IR** ν (cm^{-1}) = 3340 (w), 2927 (w), 1636 (s), 1477 (s) **HRMS** [(EI), ($C_{14}H_{10}F_4N_2$+)] calcd 282.0775, found m/z 282.0773.

(*E*)-4-((4-Chlorostyryl)amino)-2,3,5,6-tetrafluorobenzonitrile (18)



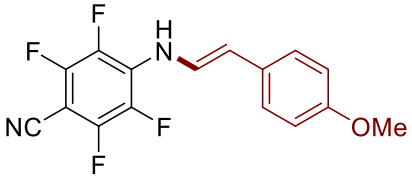
Waxy liquid, yield 85 mg (52%), R_f 0.3 (9:1, hexanes/ethyl acetate). **^{1}H NMR** (500 MHz, $CDCl_3$**)** δ 7.45 – 7.37 (m, 1H), 7.28 (d, *J* = 8 Hz, 2H), 7.21 (d, *J* = 8 Hz, 2H), 6.43 (d, *J* = 12 Hz, 1H), 6.10 (d, *J* = 13 Hz, 1H) **^{19}F NMR** (376 MHz, $CDCl_3$**)** δ -130.95 – -134.50 (m, 2F), -147.59 – -151.00 (m, 2F). **^{13}C NMR** (176 MHz, $CDCl_3$**)** δ 148.8 – 146.8 (m), 136.8 – 134.6 (m), 133.9, 132.3, 131.5, 130.9, 129.7 – 129.1 (m), 128.9 (d, *J* = 12.0 Hz), 126.5, 125.5, 112.6, 108.5 (d, *J* = 63 Hz). **IR** ν (cm^{-1}) = 3455 (m), 3353 (m), 3226 (w), 2239 (m), 1665 (m), 1517 (s). **HRMS** [(EI), ($C_{15}H_7ClF_4N_2$+)$^+$] calcd 326.0234, found m/z 326.0233.

(*E*)-4-((4-Bromostyryl)amino)-2,3,5,6-tetrafluorobenzonitrile (19)



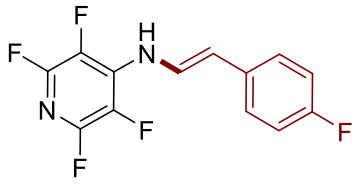
Viscous yellow liquid, yield 106 mg (57%), R_f 0.5 (9:1 hexanes/ethyl acetate). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49 – 7.39 (m, 3H), 7.15 (d, *J* = 8.4 Hz, 2H), 6.45 (d, *J* = 10.7 Hz, 1H), 6.08 (d, *J* = 13.9 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$**)** δ -132.43 – -134.82 (m, 2F), -157.16 (d, J = 14.7 Hz, 2F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.5 (d, *J* = 10.1 Hz), 146.9 (d, *J* = 14.0 Hz), 134.4, 132.7, 132.1, 129.7, 127, 125.7 (t, *J* = 6.8 Hz), 120.6, 112.8, 108.4. **IR** ν (cm^{-1}) = 3300 (m), 2924 (w), 2232 (m), 1646 (s), 1512 (s). **HRMS** [(APCI), ($C_{15}H_7BrF_4N_2$- H)$^-$] calcd 370.9637, found m/z 370.9634.

(*E*)-2,3,5,6-Tetrafluoro-4-((4-methoxystyryl)amino)benzonitrile (20)



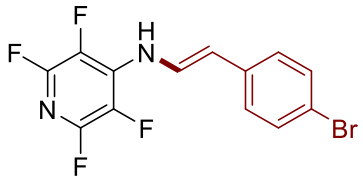
Dark brown liquid, yield 90 mg (55%), R_f 0.5 (9:1 hexanes/ethyl acetate). **^{1}H NMR** (400 MHz, $CDCl_3$**)** δ 7.39 – 7.11 (m, 1H), 6.85 (d, *J* = 8.3 Hz, 1H), 6.39 (d, *J* = 10.4 Hz, 1H), 6.10 (d, *J* = 13.6 Hz, 1H), 3.80 (s, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$**)** δ -129.46 – -136.43 (m, 2F), -157.60 (d, J = 15 Hz, 2F). **^{13}C NMR** (176 MHz, $CDCl_3$**)** δ 158.7 (d, *J* = 16.7 Hz), 147.9 (dd, *J* = 274.0, 16.5 Hz), 135.8 (dd, *J* = 229.7, 15.4 Hz), 128.1 (s), 127.8 (d, *J* = 17.2 Hz), 126.4 (d, *J* = 17.1 Hz), 123.2 (s), 114.2 (d, *J* = 17.2 Hz), 113.7 (d, *J* = 16.5 Hz), 108.5 (d, *J* = 16.3 Hz), 80.7 (d, *J* = 17.1 Hz), 55.2 (d, *J* = 17.4 Hz). **IR** ν (cm^{-1}) = 3461(w), 3348 (m), 3222 (m), 2234 (s), 1663 (s), 1513 (s). **HRMS** [(EI), ($C_{16}H_{10}F_4N_2O$+)$^+$] calcd 268.0624, found m/z 268.0627.

(*E*)-2,3,5,6-tetrafluoro-*N*-(4-fluorostyryl)pyridin-4-amine (21)



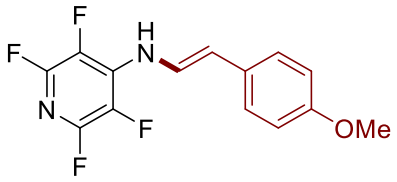
White solid, mp = 158 – 160 °C, yield 94 mg (66%), R_f 0.5 (9:1 hexanes/ethyl acetate). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 (m, 1H), 7.29 – 7.18 (m, 2H), 7.11 – 6.93 (m, 2H), 6.49 (d, *J* = 10.8 Hz, 1H), 6.11 (d, *J* = 13.9 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.76 – -93.21 (m, 2F), -111.14 – -119.89 (m, 1F), -149.39 – -167.81 (m, 2F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.5 (d, *J* = 5.0 Hz), 137.4 (d, *J* = 19.4 Hz), 135.5 (d, *J* = 15.6 Hz), 129.0, 128.8, 128.0, 127.1, 125.5, 125.2 (d, *J* = 6.3 Hz), 114.1. **IR** ν (cm^{-1}) = 3303 (w), 3121 (w), 1637 (s), 1482 (s). **HRMS** [(ESI), ($C_{13}H_7F_5N_2$-H)$^-$] calcd 285.0457, found m/z 285.0452.

***(E)*-*N*-(4-bromostyryl)-2,3,5,6-tetrafluoropyridin-4-amine (22)**



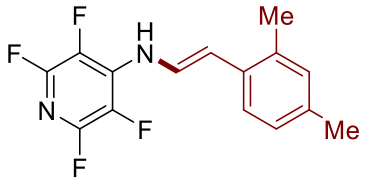
Off-white solid, mp = 120 – 122 °C, yield 105 mg (61%), R_f 0.5 (9:1 hexanes/ethyl acetate). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 (m, 1H), 7.46 – 7.45 (m, 1H), 7.44 – 7.42 (m, 2H), 7.19 – 7.14 (m, 2H), 6.53 (d, *J* = 11.4 Hz, 1H), 6.08 (d, *J* = 13.9 Hz, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -89.72 – -96.56 (m, 2F), -158.08 – -168.64 (m, 2F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.73 (d, *J* = 16.3 Hz), 143.33 (d, *J* = 20.0 Hz), 134.47, 132.59, 132.06, 127.00, 125.46 (t, *J* = 6.4 Hz), 120.56, 112.69. **IR** ν (cm^{-1}) = 3323 (w), 3100 (w), 1646 (s), 1524 (s) **HRMS** [(ESI), ($C_{13}H_7BrF_4N_2$+H)$^+$] calcd 346.9625, found m/z 346.9629.

(*E*)-2,3,5,6-tetrafluoro-N-(4-methoxystyryl)pyridin-4-amine (23)



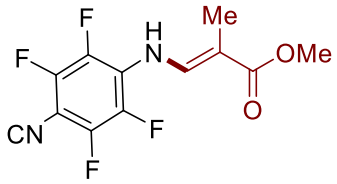
Yellow viscous liquid, yield 75 mg (50%), R_f 0.5 (9:1 hexanes/ethyl acetate). **^{1}H NMR** (400 MHz, $CDCl_3$**)** δ 7.62 – 7.37 (m, 1H), 7.39 – 7.26 (m, 2H), 6.95 (d, *J* = 8.6 Hz, 2H), 6.53 (d, *J* = 10.5 Hz, 1H), 6.19 (d, *J* = 13.8 Hz, 1H), 3.90 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$**)** δ -86.21 – -97.71 (m, 2F), -156.33 – -168.40 (m, 2F). **^{13}C NMR** (100 MHz, $CDCl_3$**)** δ 158.9 (s), 144.4 (dd, *J* = 239.5, 17.4 Hz), 132.9 (s), 131.2 (dd, *J* = 219.9, 29.3 Hz), 128.0, 126.7, 123.2, 114.5, 113.8, 55.5. **IR** ν (cm^{-1}) = 3355 (w), 2842 (w), 1684 (s), 1598 (s) **HRMS** [(ESI), ($C_{14}H_{10}F_4N_2O$+ H)$^+$] calcd 298.0728, found m/z 299.0728.

(*E*)-*N*-(2,4-dimethylstyryl)-2,3,5,6-tetrafluoropyridin-4-amine (24)



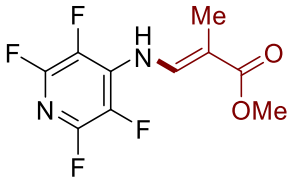
Off-white solid, mp = 140 – 142 °C, yield 102 mg (69%), R_f 0.5 (9:1 hexanes/ethyl acetate). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 (m, 1H), 7.19 (d, *J* = 8.3 Hz, 1H), 6.99 – 6.91 (m, 2H), 6.49 (d, *J* = 11.0 Hz, 1H), 6.24 (d, *J* = 13.7 Hz, 1H), 2.26 (s, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.50 – -93.94 (m, 2F), -159.92 – -164.99 (m, 2F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.7 (d, *J* = 16.6 Hz), 143.4 (d, *J* = 18.0 Hz), 137.0, 134.9, 132.9, 131.4, 131.4, 131.1, 127.2, 124.9, 112.0, 21.2, 20.1. **IR** ν (cm^{-1}) = 3320 (w), 28430 (w), 1624 (s), 1551 (s) **HRMS** [(ESI), ($C_{15}H_{12}F_4N_2$-H)$^-$] calcd 295.0859, found m/z 295.0864.

(E)-methyl 3-((4-cyano-2,3,5,6-tetrafluorophenyl)imino)-2-methylpropanoate (25)



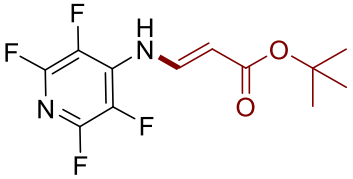
Pale yellow liquid (viscos gel), yield 74 mg (51%), R_f 0.5(8:2 hexanes/ethyl acetate), **^{1}H NMR** ^{1}H NMR (400 MHz, $CDCl_3$ δ 8.04 – 7.93 (m, 1H), 6.35 (d, *J* = 12.3 Hz, 1H), 3.76 (s, 3H), 1.90 (d, *J* = 1.4 Hz, 3H). **^{19}F NMR (376 MHz, $CDCl_3$).** δ -131.98 – -133.19 (m, 2F), -152.96 – -156.90 (m, 2F). **^{13}C NMR (100 MHz, CDCl3)** δ 167.95, 148.10 (dd, *J* = 259.7, 13.9 Hz), 137.03 (dd, *J* = 246.8, 14.3 Hz), 134.87 (t, *J* = 6.8 Hz), 127.18 (d, *J* = 9.6 Hz), 108.16, 107.91, 51.96, 31.00, 9.64. **IR** ν (cm^{-1}) = 3342 (w), 2238 (w),1702 (m), 1645 (s), 1509 (s). **HRMS** [(EI), ($C_{12}H_8F_4N_2O_2$+)$^+$] calcd 288.0516, found m/z 288.0509.

(*E*)-methyl 2-methyl-3-((perfluoropyridin-4-yl)amino)acrylate (26)



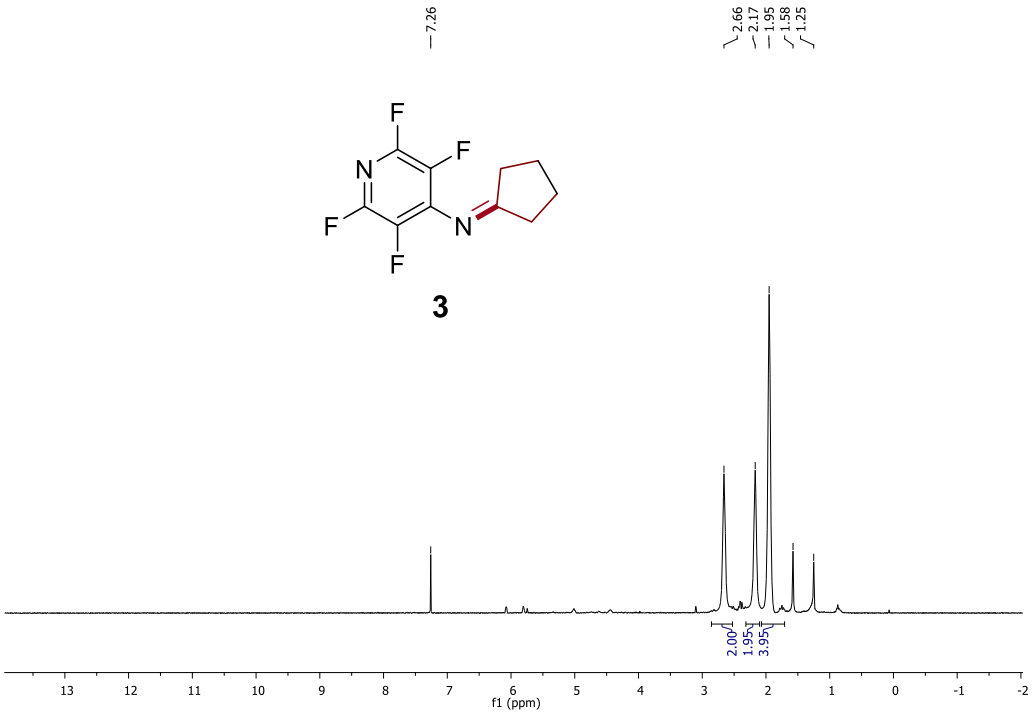
White solid, mp = 124-126 °C, yield 67 mg (51%), R_f: 0.5(9.5:0.5 hexanes/ethyl acetate), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 12.6 Hz, 1H), 6.38 (d, *J* = 12.2 Hz, 1H), 3.77 (s, 3H), 1.90 (d, *J* = 1.2 Hz,. **^{19}F NMR** (400 MHz, $CDCl_3$) δ -132.90 (d, *J* = 12.3 Hz), -155.43 (m). **^{13}C NMR** (176 MHz, $CDCl_3$) δ 185.2, 167.9, 144.3 (dd, *J* = 244.1, 17.8 Hz), 134.5 – 133.9 (m), 132 (dd, *J* = 249.1, 11.4 Hz), 108.3, 52, 9.7. **IR** ν (cm^{-1}) =, 3418 (w), 3319 (w), 2957 (w), 1698 (m) 1645 (s), 1636 (s), 1535 (m). **HRMS** [(CI), ($C_{10}H_8F_4N_2O_2$-H)$^-$] calcd 263.0449, found m/z 263.0445.

(*E*)-tert-butyl 3-((perfluoropyridin-4-yl)amino)acrylate (27)

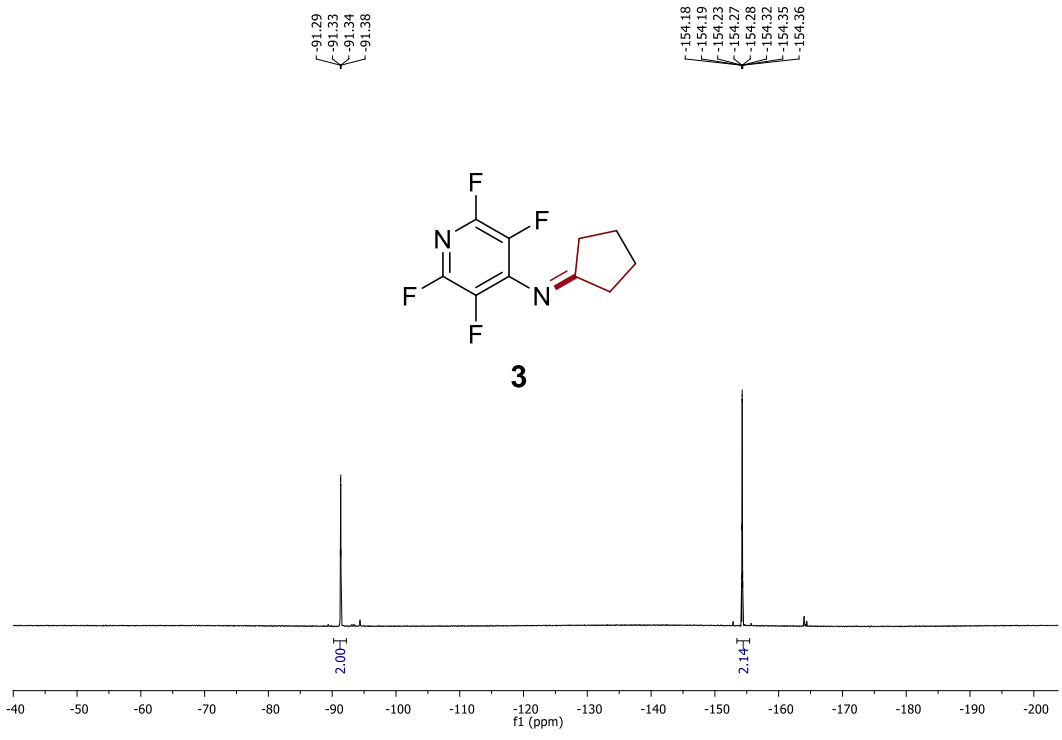


White solid, mp = 130-132 °C, yield 108 mg (74%), R_f: 0.5(9:1 hexanes/ethyl acetate), **^{1}H NMR (**500 MHz, $CDCl_3$) δ 8.00 (t, *J* = 13.0 Hz, 1H), 6.75 (d, *J* = 12.3 Hz, 1H), 5.42 (d, *J* = 13.3 Hz, 1H), 1.50 (s, 9H) **^{19}F NMR (400 MHz, $CDCl_3$)** δ -90.65 (m, *J* = 14.6 Hz), -159.31 (t, *J* = 16.0 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.0, 144.3 (dd, *J* = 246.9, 17.5 Hz), 143.6 – 142.8 (m), 139.3, 132.2 (dd, *J* = 253.8, 29.3 Hz), 104.2, 80.8, 28.4. **IR** ν (cm^{-1}) = 3221 (w), 3065 (w), 2987 (w), 1643 (s), 1626 (s) **HRMS** [(EI), $(C_{12}H_{12}F_4N_2O_2\text{-}H)^-$] calcd 291.0762, found m/z 291.0758.

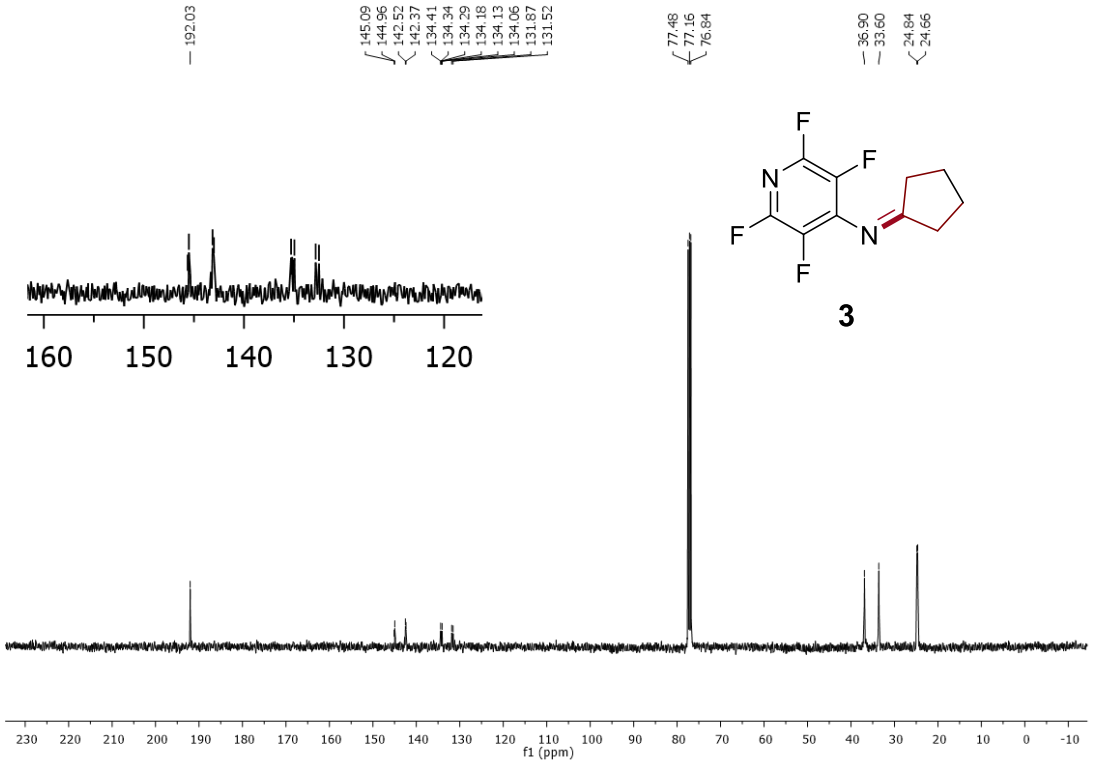
12. NMR DATA



3



3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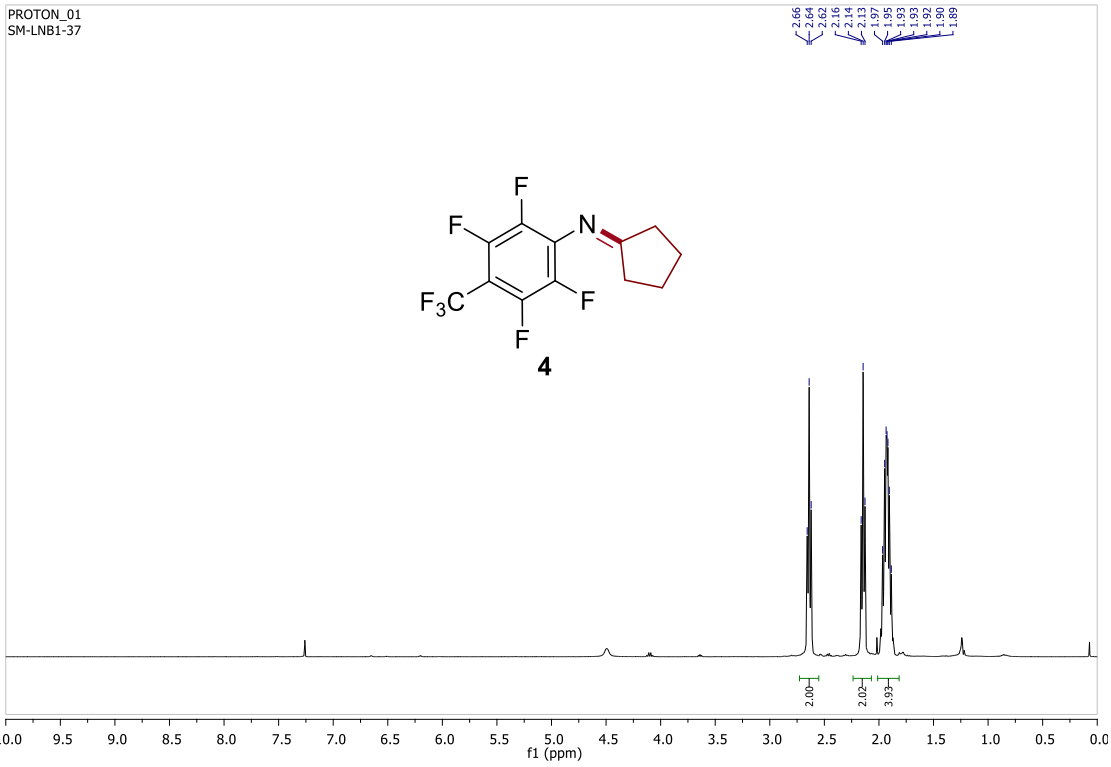
144.96
142.52
142.37
134.41
134.34
134.29
134.18
134.13
134.06
131.87
131.52
77.48
77.16
76.84
36.90
33.60
24.84
24.66
160
150
140
130
120
F
F
N
F
N
F
3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


PROTON_01
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2.62
2.16
2.14
2.13
1.97
1.95
1.93
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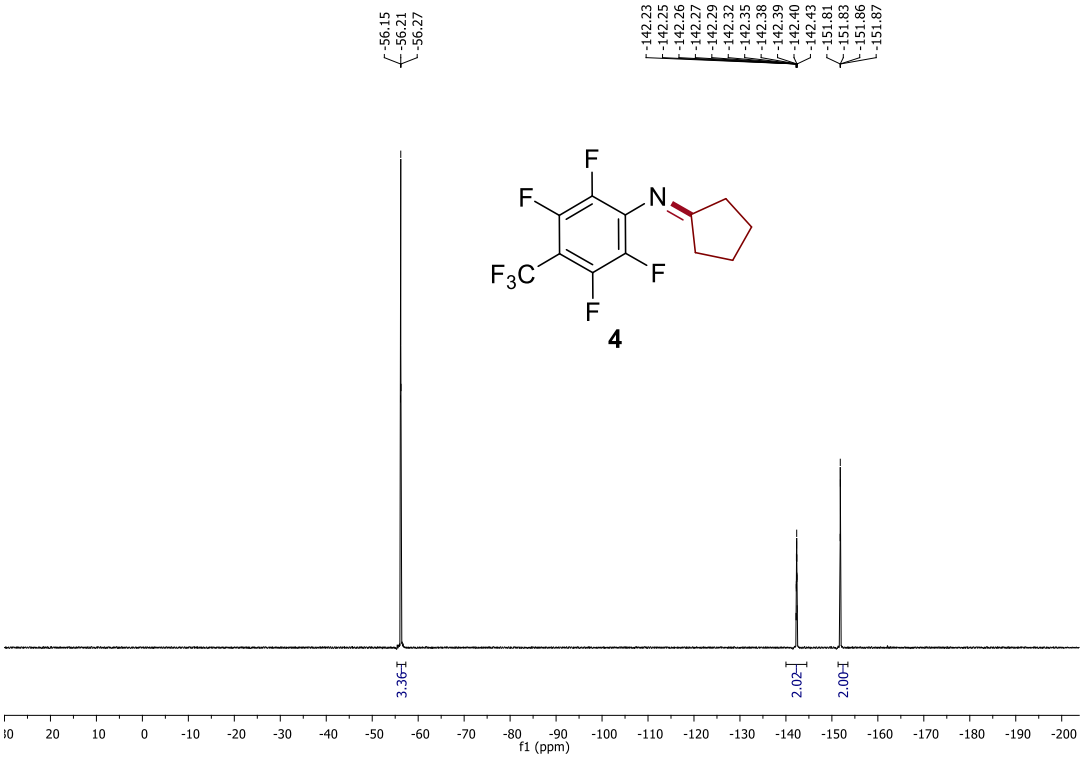
1.92
1.90
1.89
F
F
N
F3C
F
F
4
2.00
2.02
3.93
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


-56.15
-56.21
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-142.29
-142.32
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-142.39
-142.40
-142.43
-151.81
-151.83
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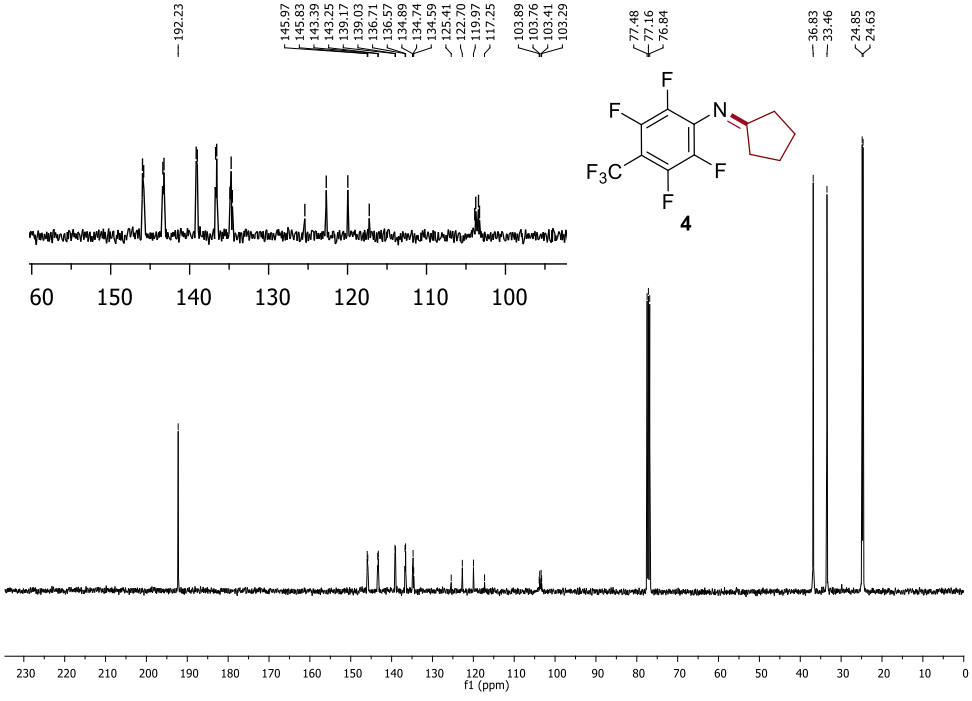
F
F
N
F3C
F
F
4
3.36
2.02
2.00
f1 (ppm)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143.25
139.17
139.03
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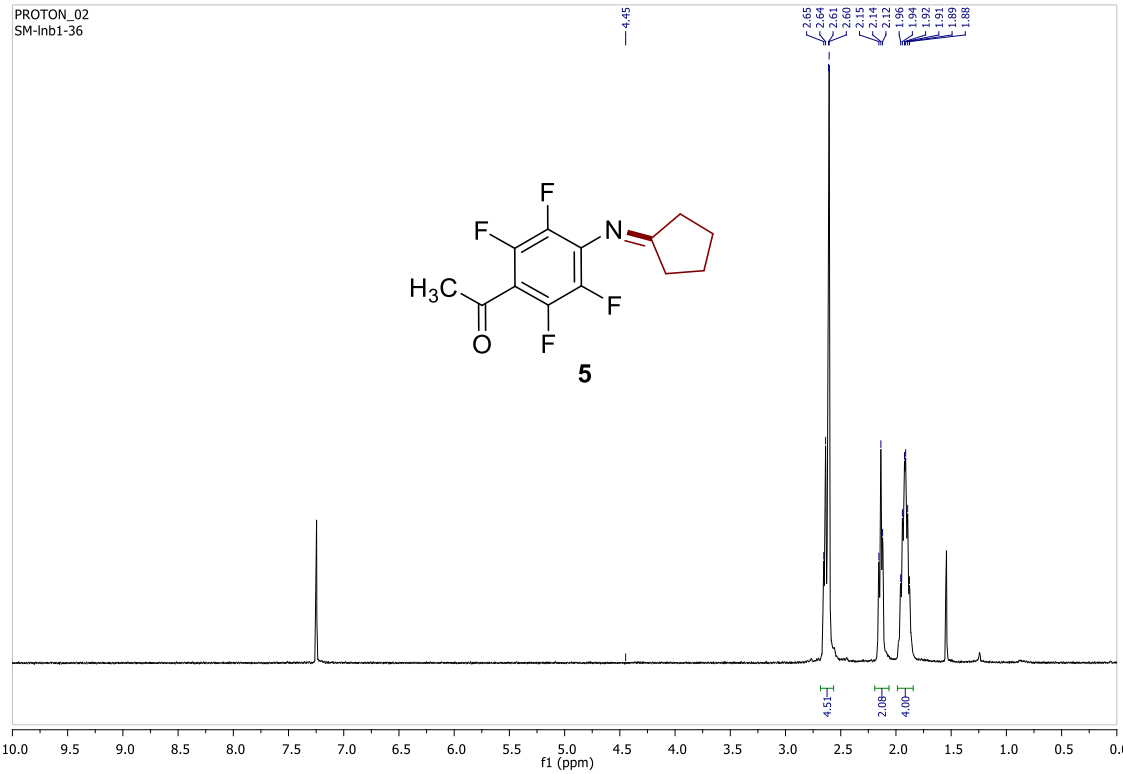
136.57
134.89
134.74
134.59
125.41
122.70
119.97
117.25
103.89
103.76
103.41
103.29
77.48
77.16
76.84
36.83
33.46
24.85
24.63
F
F
N
F3C
F
F
4
60
150
140
130
120
110
100
f1 (ppm)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2.12
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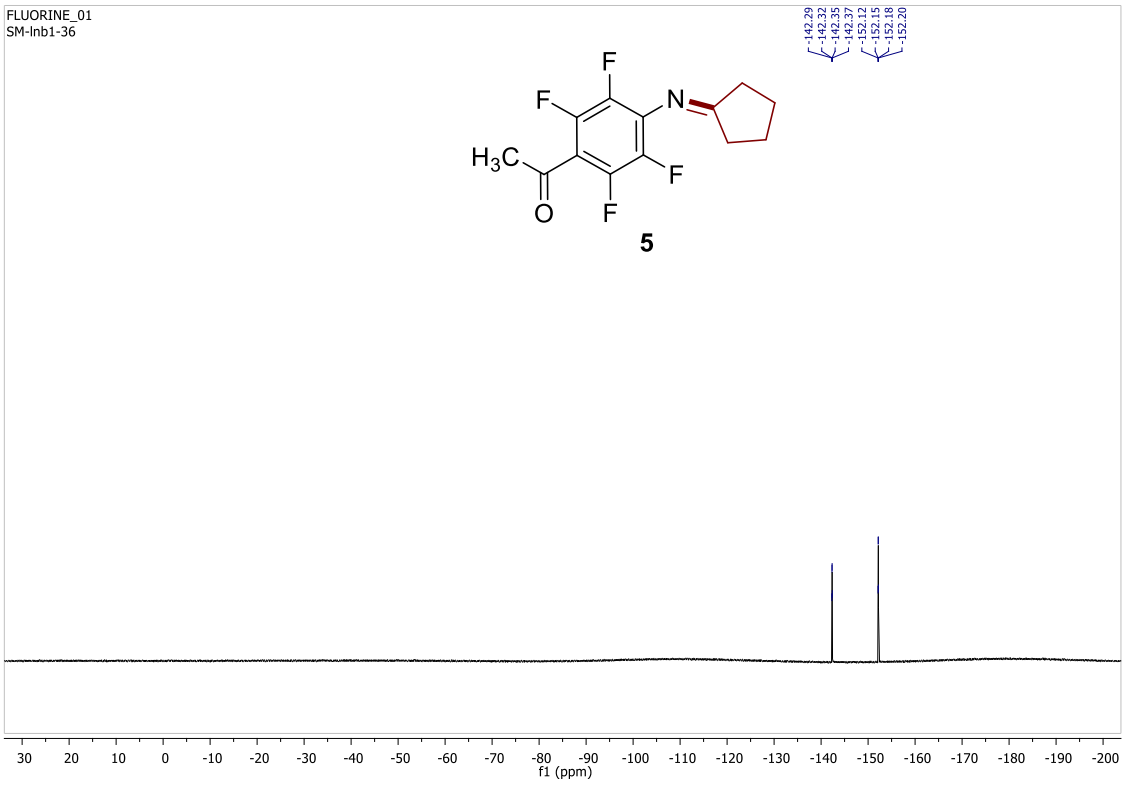
1.91
1.89
1.88
F
F
N
H3C
O
F
F
5
4.51
2.08
4.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


FLUORINE_01
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-142.35
-142.37
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F
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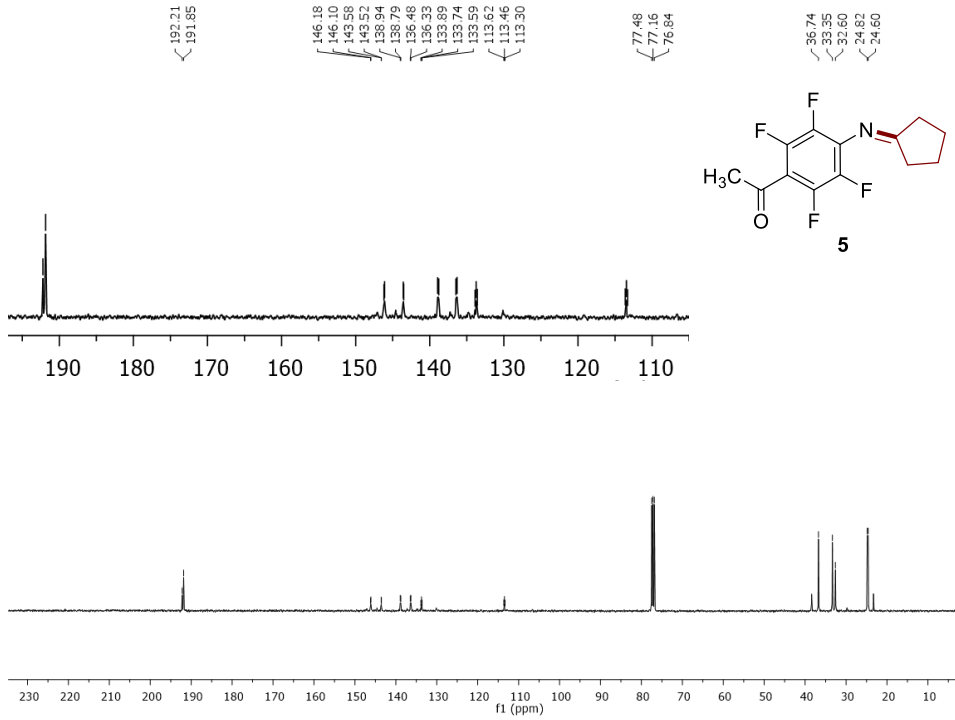
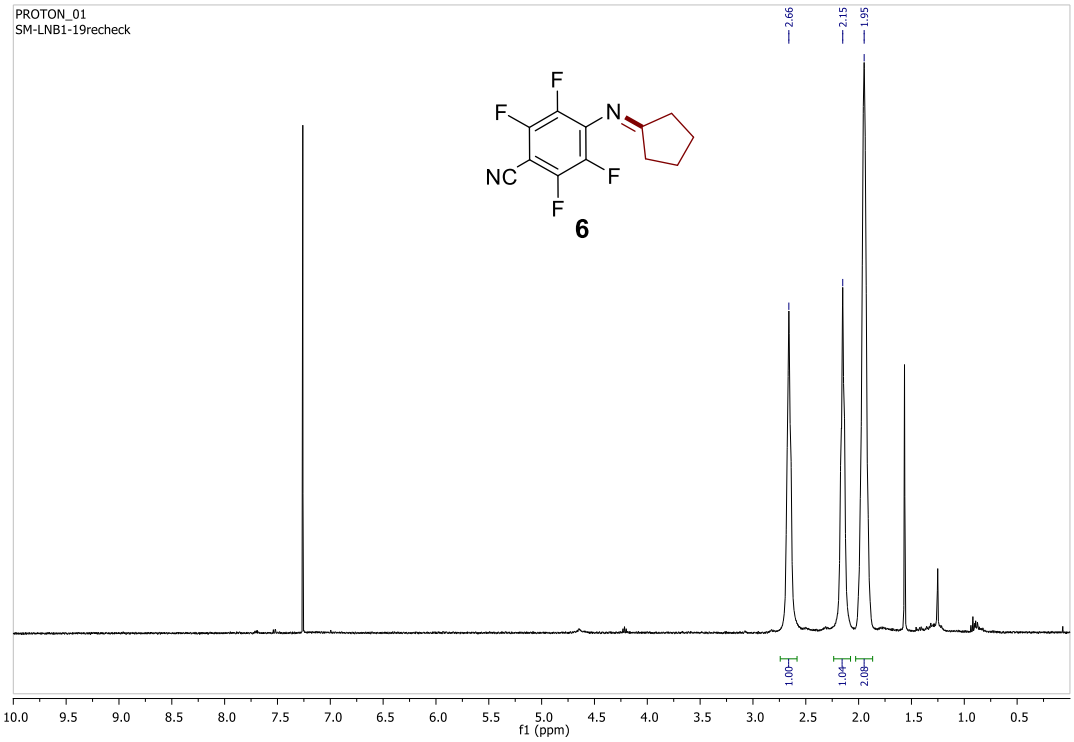
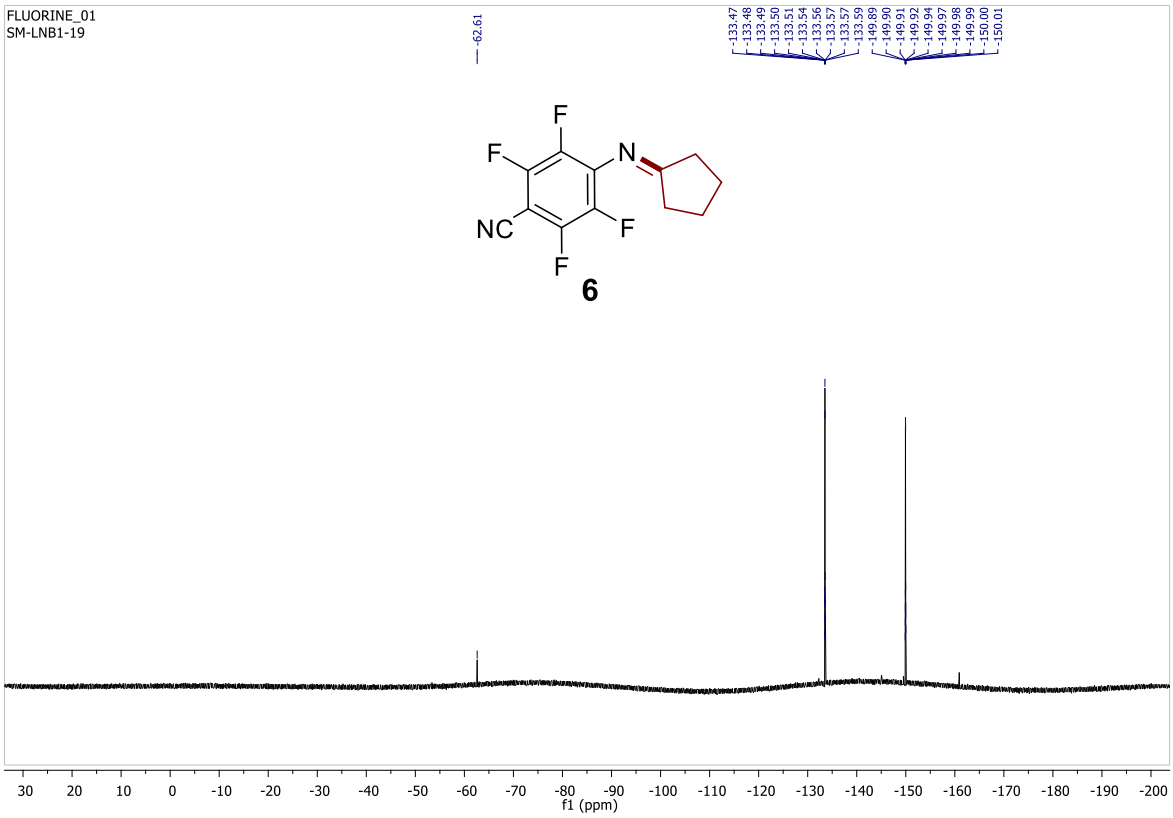
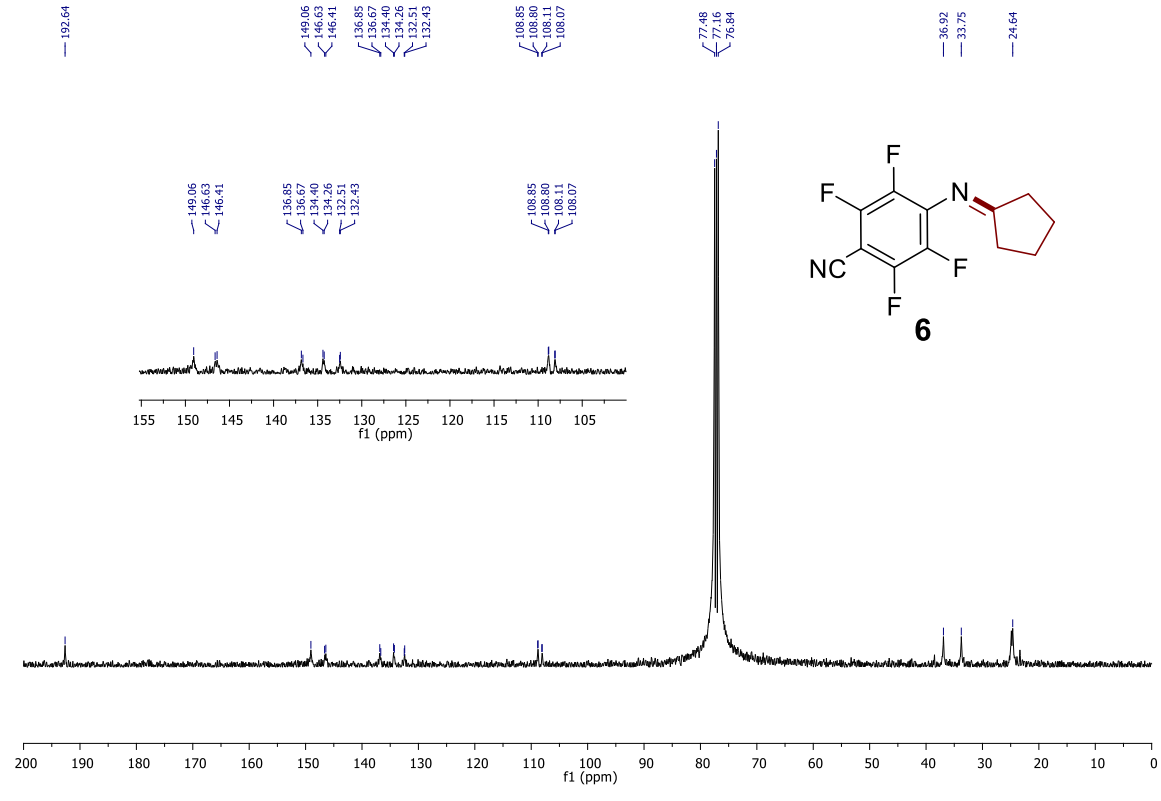
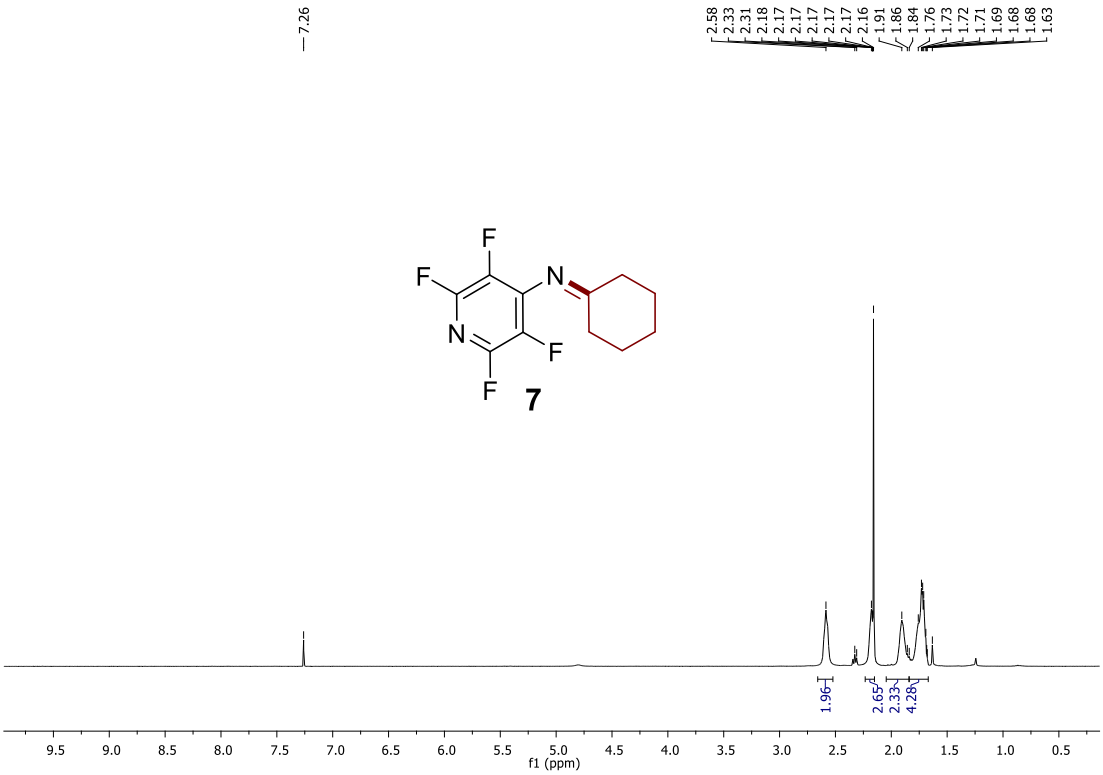
H3C
O
F
F
5
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

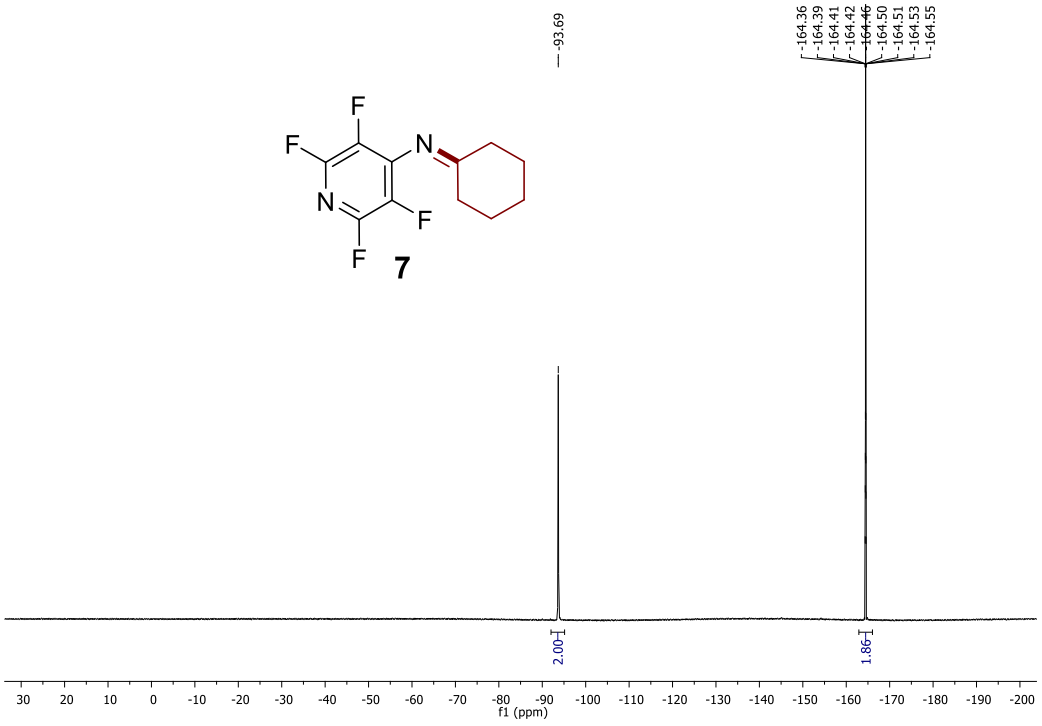

192.21
191.85
146.18
146.10
143.58
143.52
138.94
138.79
136.48
136.33
133.89
133.74
133.59
113.62
113.46
113.30
77.48
77.16
76.84
36.74
33.35
32.60
24.82
24.60
F
F
N
H3C
F
O
F
5
190 180 170 160 150 140 130 120 110
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

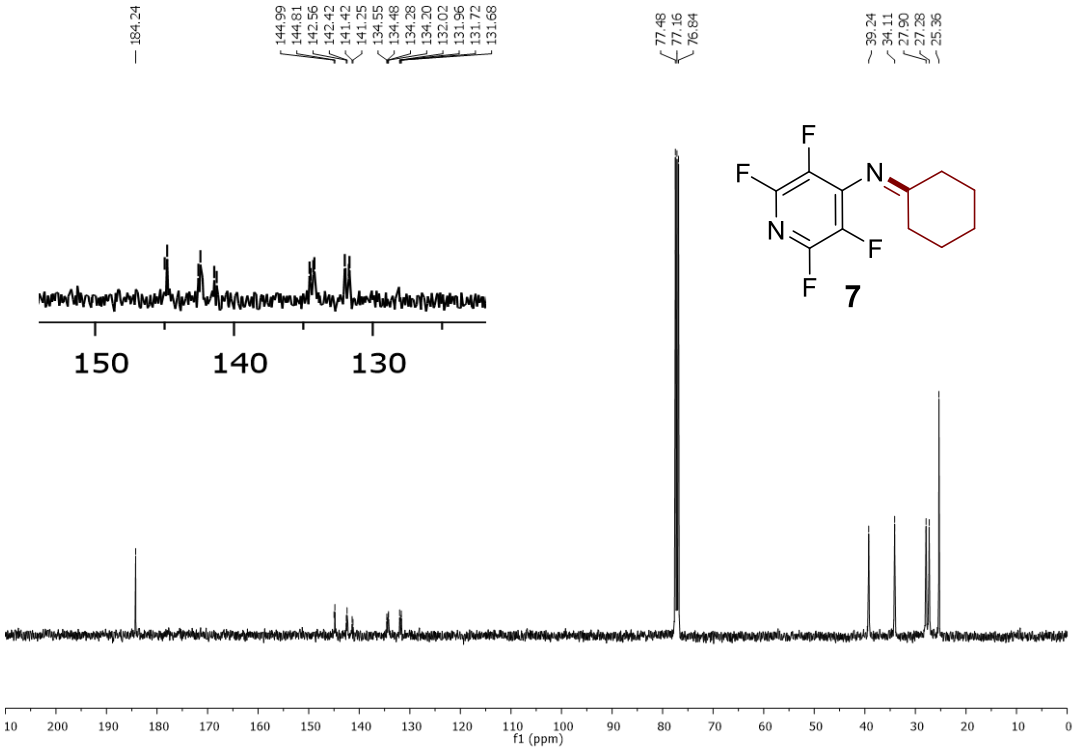

PROTON_01
SM-LNB1-19recheck
2.66
2.15
1.95
F
F
N
NC
F
F
6
1.00
1.04
2.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

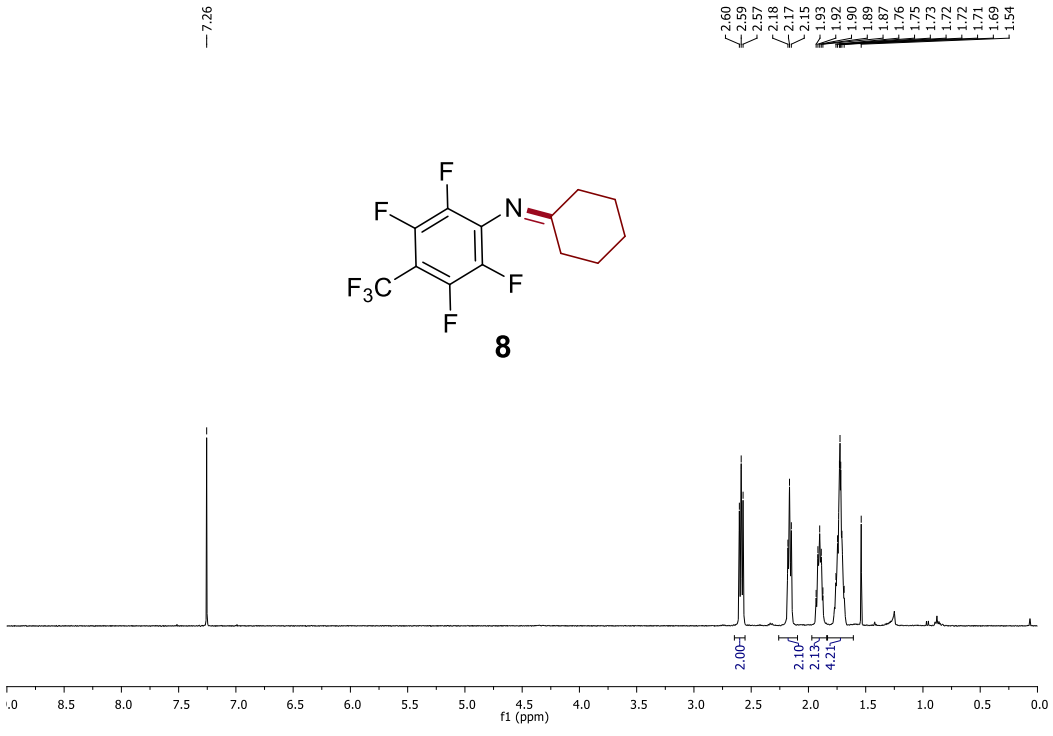

FLUORINE_01
SM-LNB1-19
-62.61
-133.47
-133.48
-133.49
-133.50
-133.51
-133.54
-133.56
-133.57
-133.57
-133.59
-149.89
-149.90
-149.91
-149.92
-149.94
-149.97
-149.98
-149.99
-150.00
-150.01
F
F
N
NC
F
F
6
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

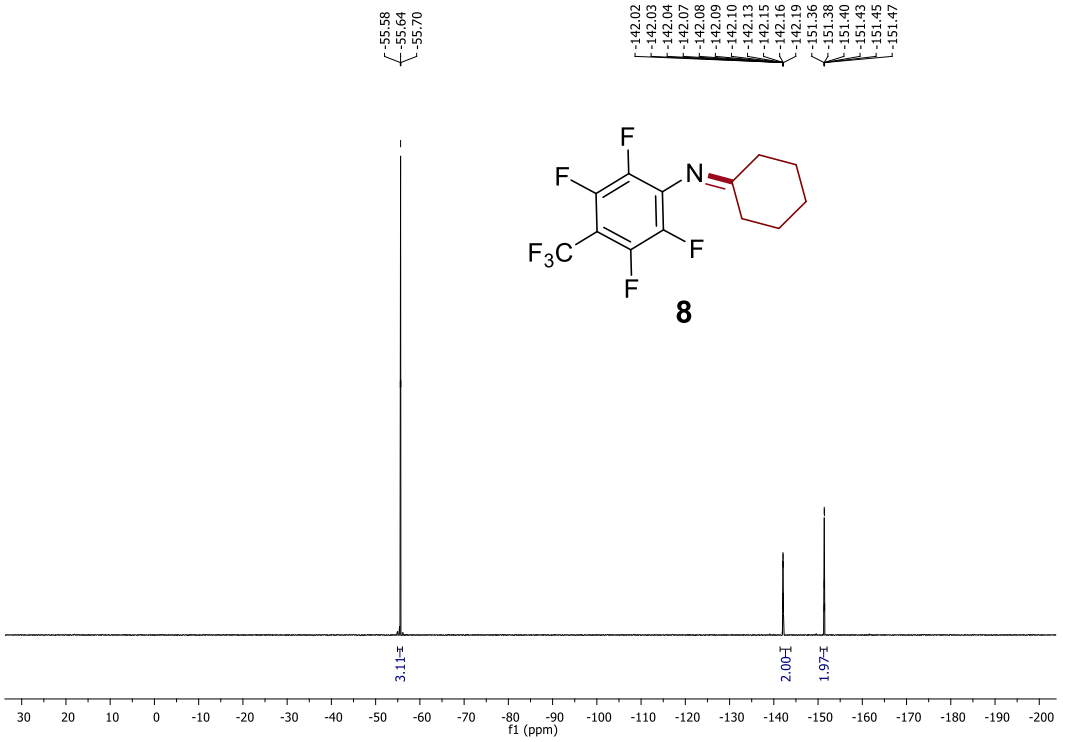

192.64
149.06
146.63
146.41
136.85
136.67
134.40
134.26
132.51
132.43
108.85
108.80
108.11
108.07
77.48
77.16
76.84
36.92
33.75
24.64
F
F
N
NC
F
F
6
155 150 145 140 135 130 125 120 115 110 105
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

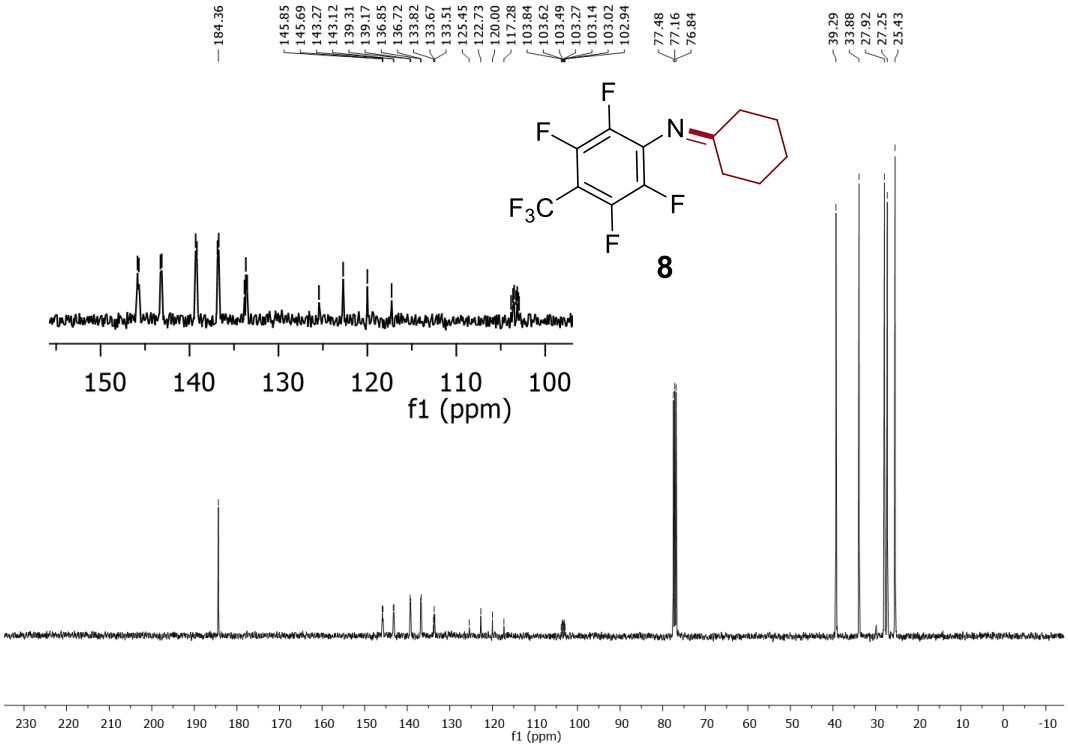

7.26
2.58
2.33
2.31
2.18
2.17
2.17
2.17
2.17
2.17
2.16
1.91
1.86
1.84
1.76
1.73
1.72
1.71
1.69
1.68
1.68
1.63
F
F
N
N
F
F
7
1.96
2.65
2.33
4.28
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

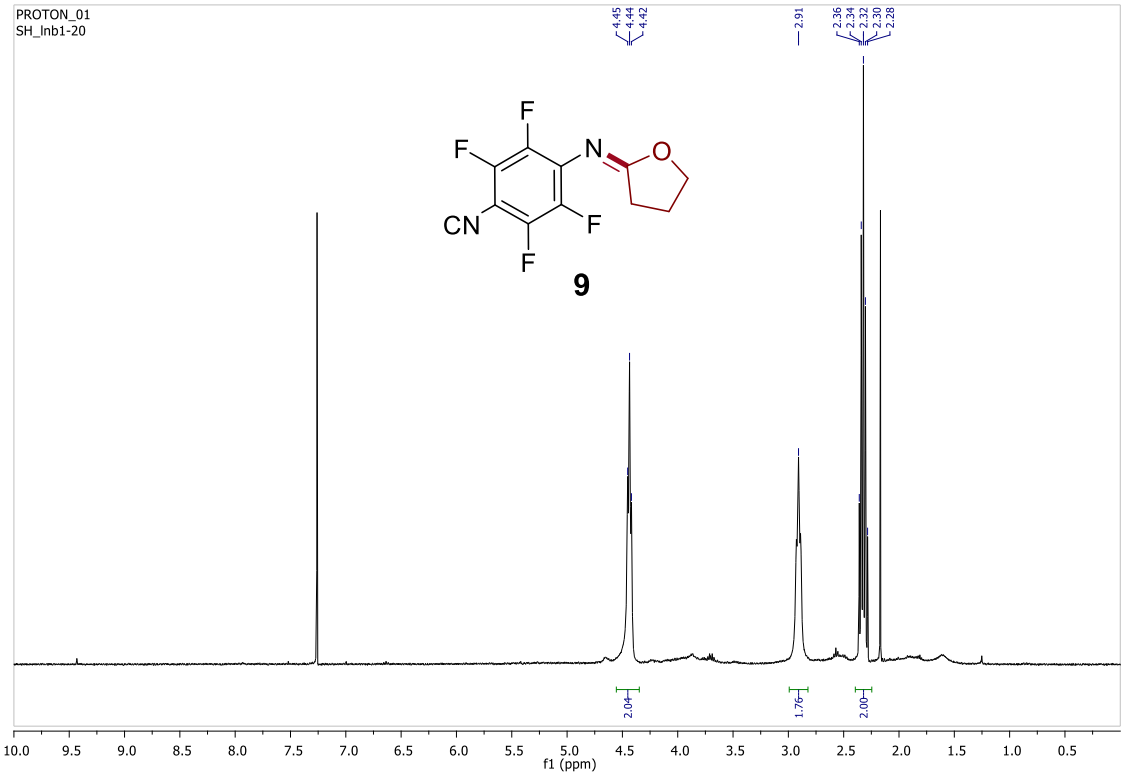

-93.69
-164.36
-164.39
-164.41
-164.42
-164.46
-164.50
-164.51
-164.53
-164.55
F
F
N
N
F
F
7
2.00
1.86
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

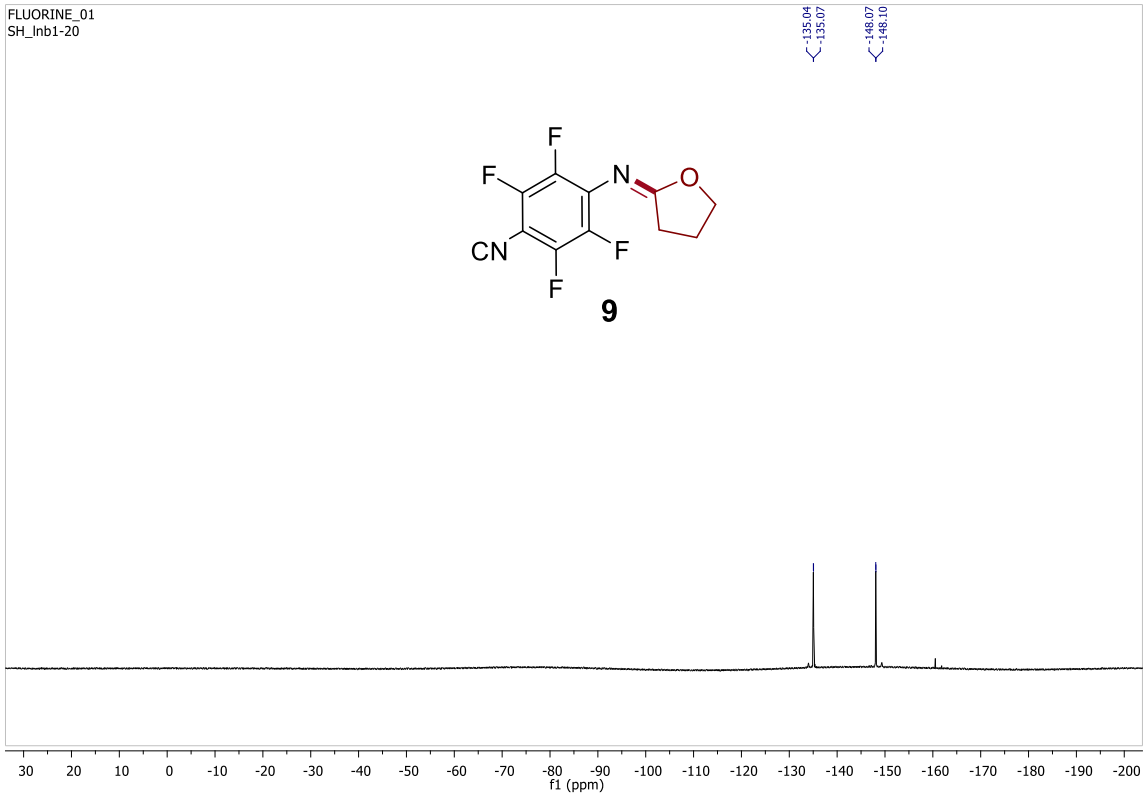

184.24
144.99
144.81
142.56
142.42
141.42
141.25
134.55
134.48
134.28
134.20
132.02
131.96
131.72
131.68
77.48
77.16
76.84
39.24
34.11
27.90
27.28
25.36
F
F
N
N
F
F
7
150
140
130
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.26
2.60
2.59
2.57
2.18
2.17
2.15
1.93
1.92
1.90
1.89
1.87
1.76
1.75
1.73
1.72
1.72
1.71
1.69
1.54
F
F
N
F3C
F
F
8
2.00
2.10
2.13
4.21
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

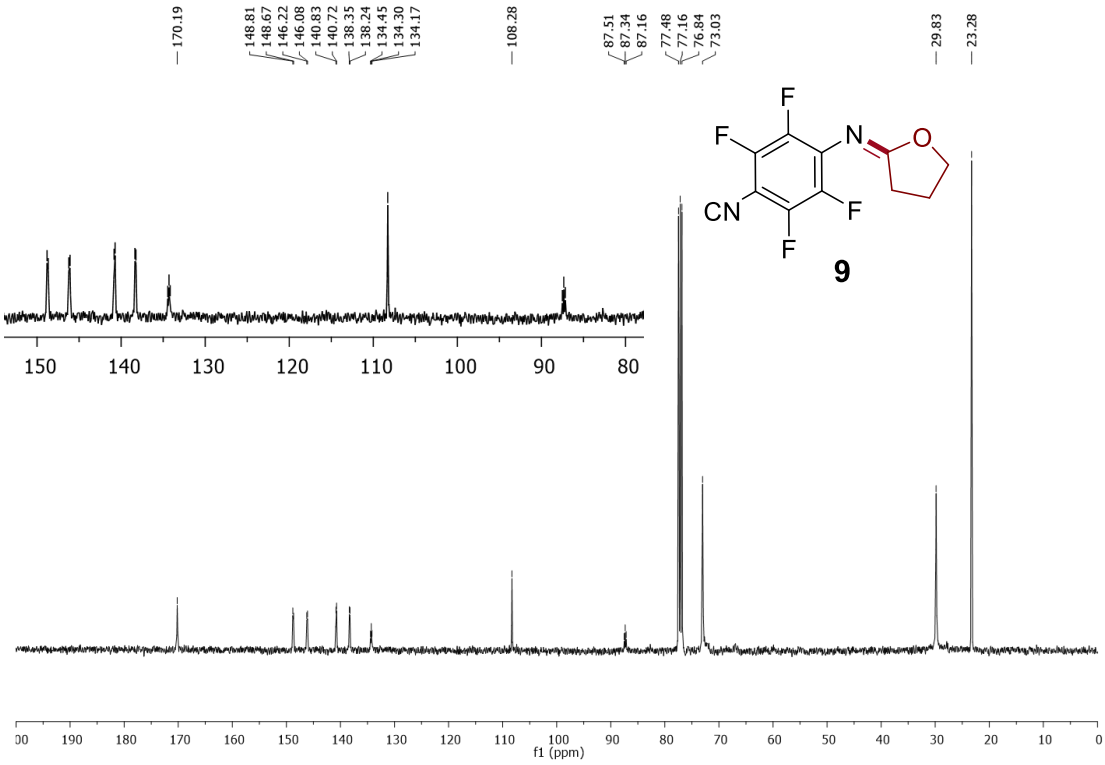

-55.58
-55.64
-55.70
-142.02
-142.03
-142.04
-142.07
-142.08
-142.09
-142.10
-142.13
-142.15
-142.16
-142.19
-151.36
-151.38
-151.40
-151.43
-151.45
-151.47
F
F
N
F3C
F
F
8
3.11
2.00
1.97
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

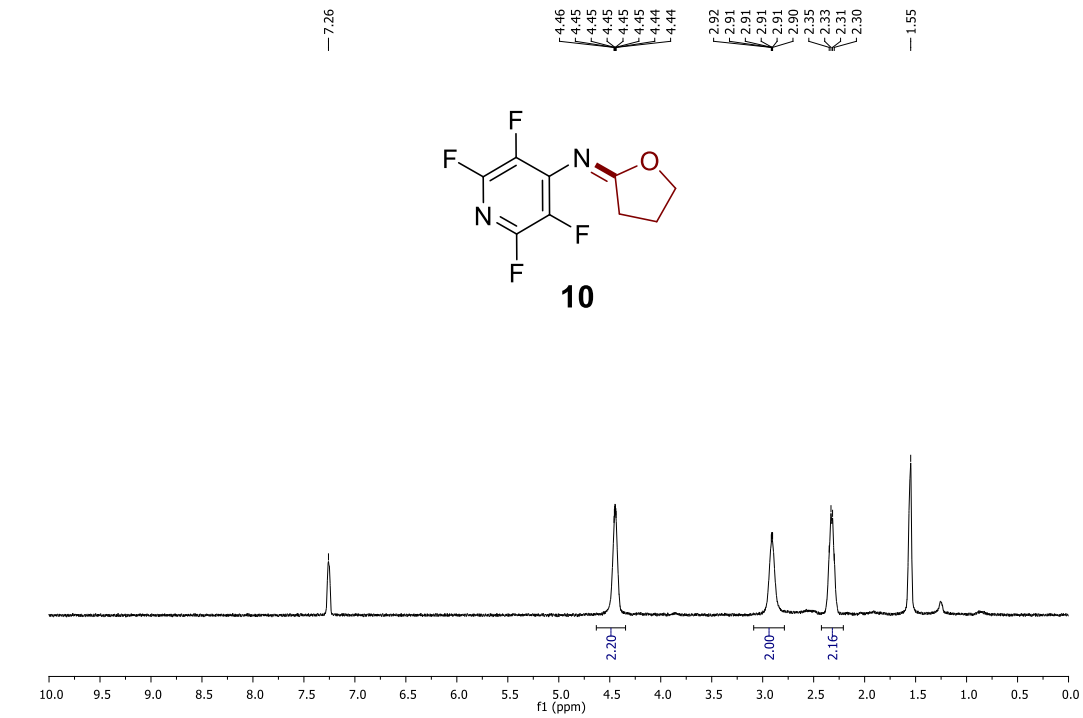

184.36
145.85
145.69
143.27
143.12
139.31
139.17
136.85
136.72
133.82
133.67
133.51
125.45
122.73
120.00
117.28
103.84
103.62
103.49
103.27
103.14
103.02
102.94
77.48
77.16
76.84
39.29
33.88
27.92
27.25
25.43
F
F
N
F3C
F
F
8
150 140 130 120 110 100
f1 (ppm)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

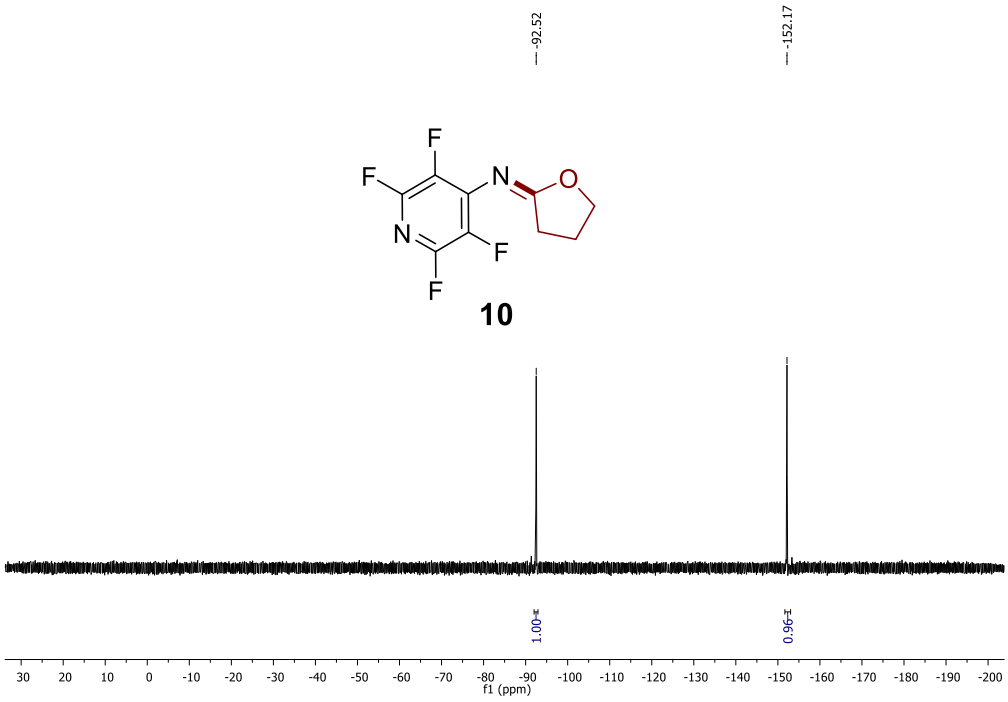

PROTON_01
SH_lnb1-20
4.45
4.44
4.42
2.91
2.36
2.34
2.32
2.30
2.28
F
F
N
O
CN
F
F
9
2.04
1.76
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

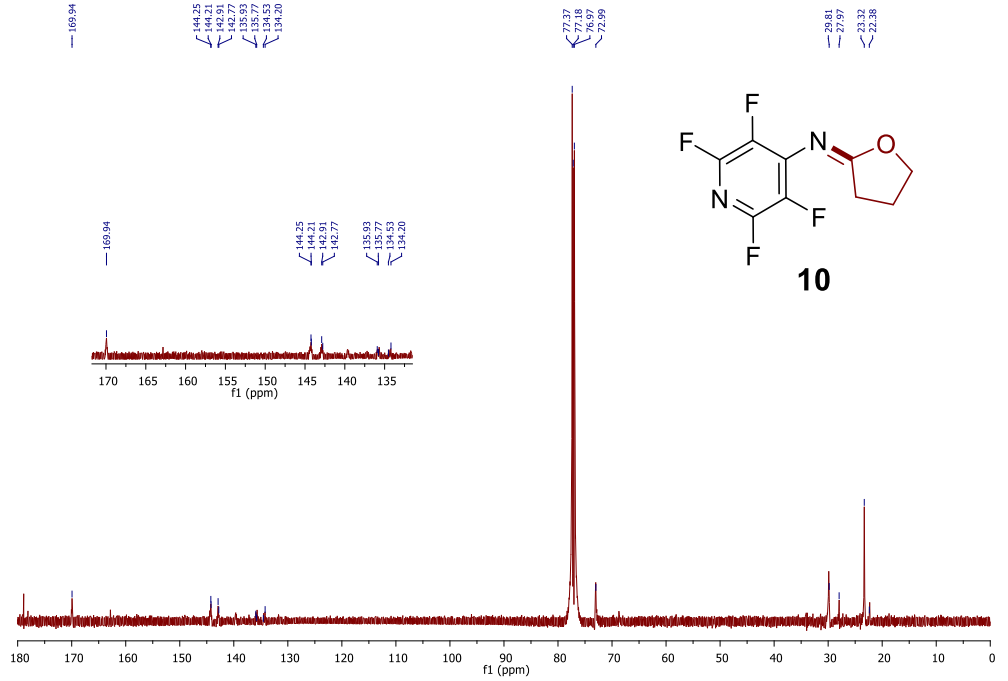

FLUORINE_01
SH_lnb1-20
-135.04
-135.07
-148.07
-148.10
F
F
N
O
CN
F
F
9
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

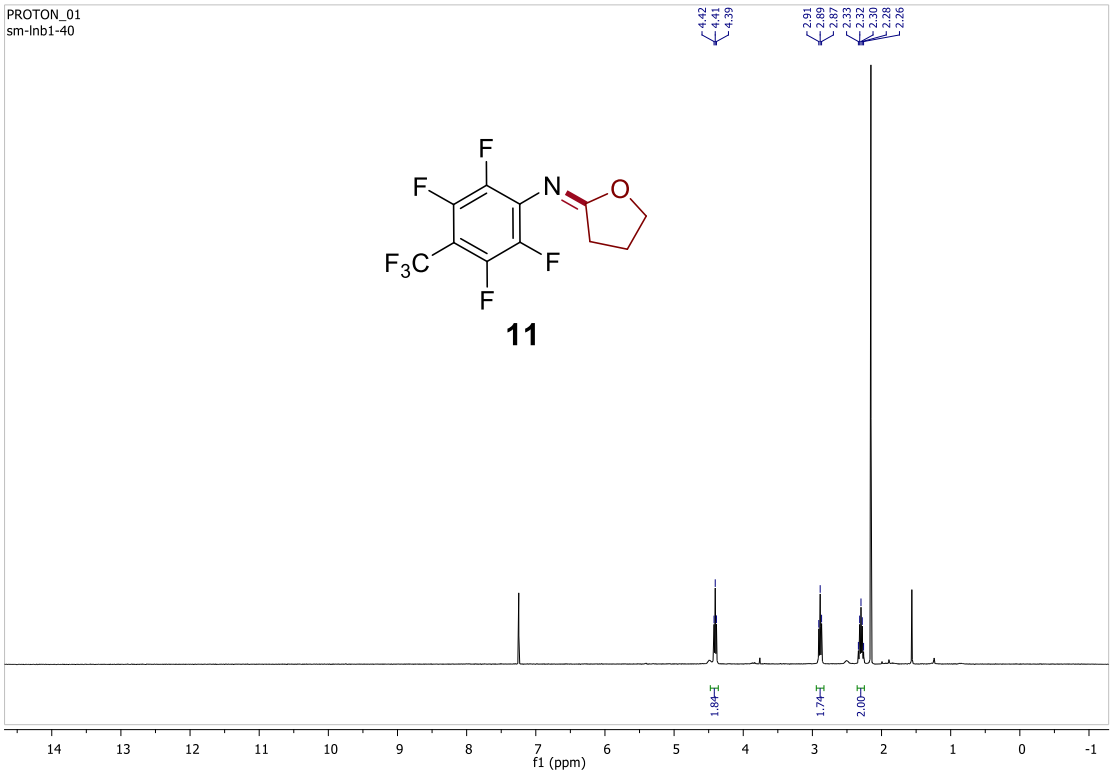
=

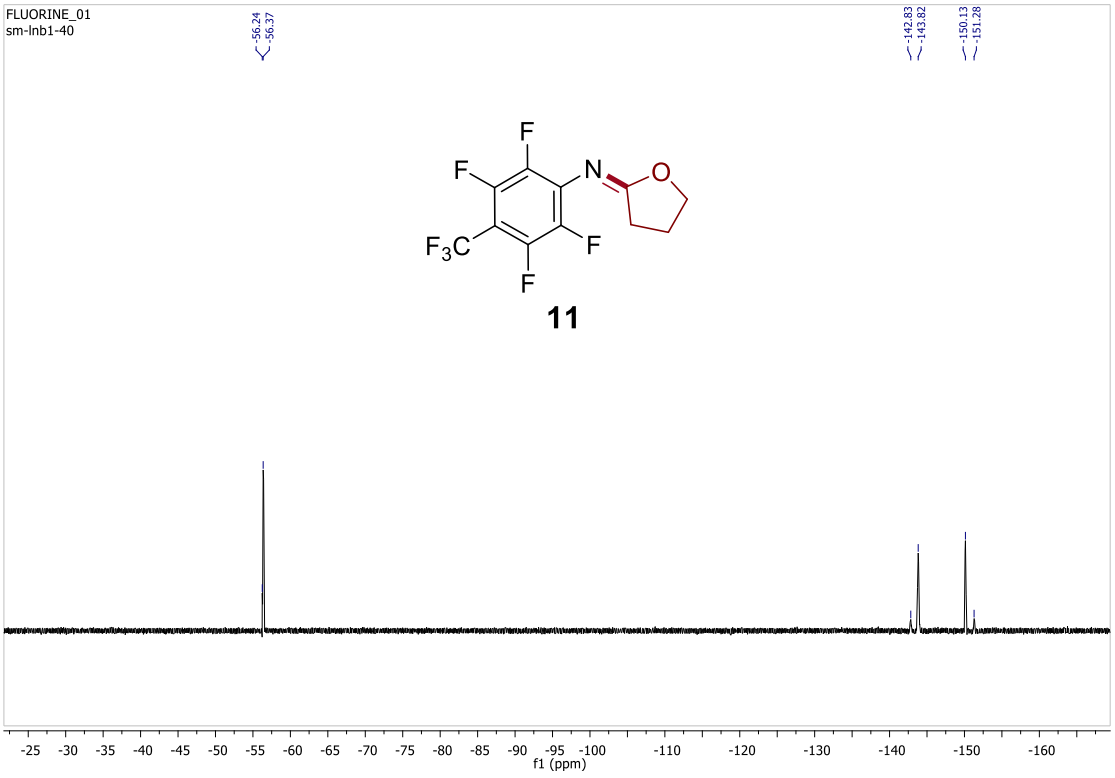

170.19
148.81
148.67
146.22
146.08
140.83
140.72
138.35
138.24
134.45
134.30
134.17
108.28
87.51
87.34
87.16
77.48
77.16
76.84
73.03
29.83
23.28
F
F
N
O
CN
F
F
9
150
140
130
120
110
100
90
80
f1 (ppm)

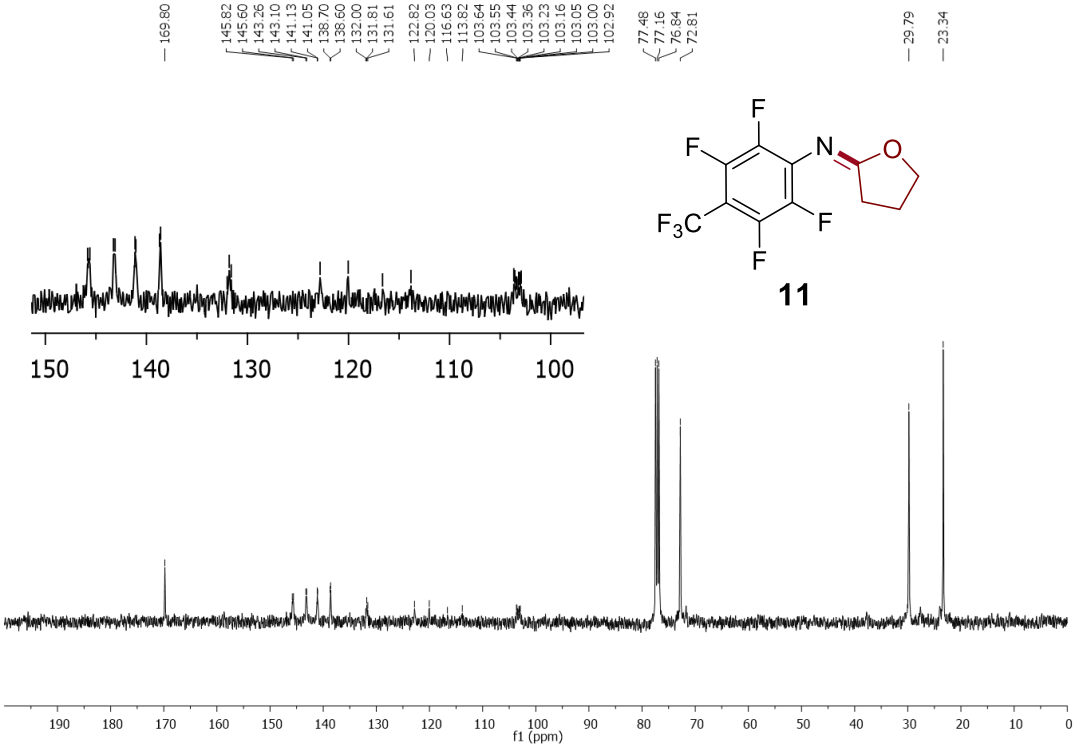

7.26
4.46
4.45
4.45
4.45
4.45
4.44
4.44
2.92
2.91
2.91
2.91
2.91
2.90
2.35
2.33
2.31
2.30
1.55
F
F
N
O
N
F
F
10
2.20
2.00
2.16
f1 (ppm)


-92.52
-152.17
F
F
N
O
N
F
F
10
1.00
0.96
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


169.94
144.25
144.21
142.91
142.77
135.93
135.77
134.53
134.20
77.37
77.18
76.97
72.99
29.81
27.97
23.32
22.38
F
F
N
O
N
F
F
10
169.94
144.25
144.21
142.91
142.77
135.93
135.77
134.53
134.20
170 165 160 155 150 145 140 135
f1 (ppm)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


PROTON_01
sm-lnb1-40
4.42
4.41
4.39
2.91
2.89
2.87
2.33
2.32
2.30
2.28
2.26
F
F
N
O
F3C
F
F
11
1.84
1.74
2.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)


FLUORINE_01
sm-lnb1-40
-56.24
-56.37
-142.83
-143.82
-150.13
-151.28
F
F
N
O
F3C
F
F
11
-25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)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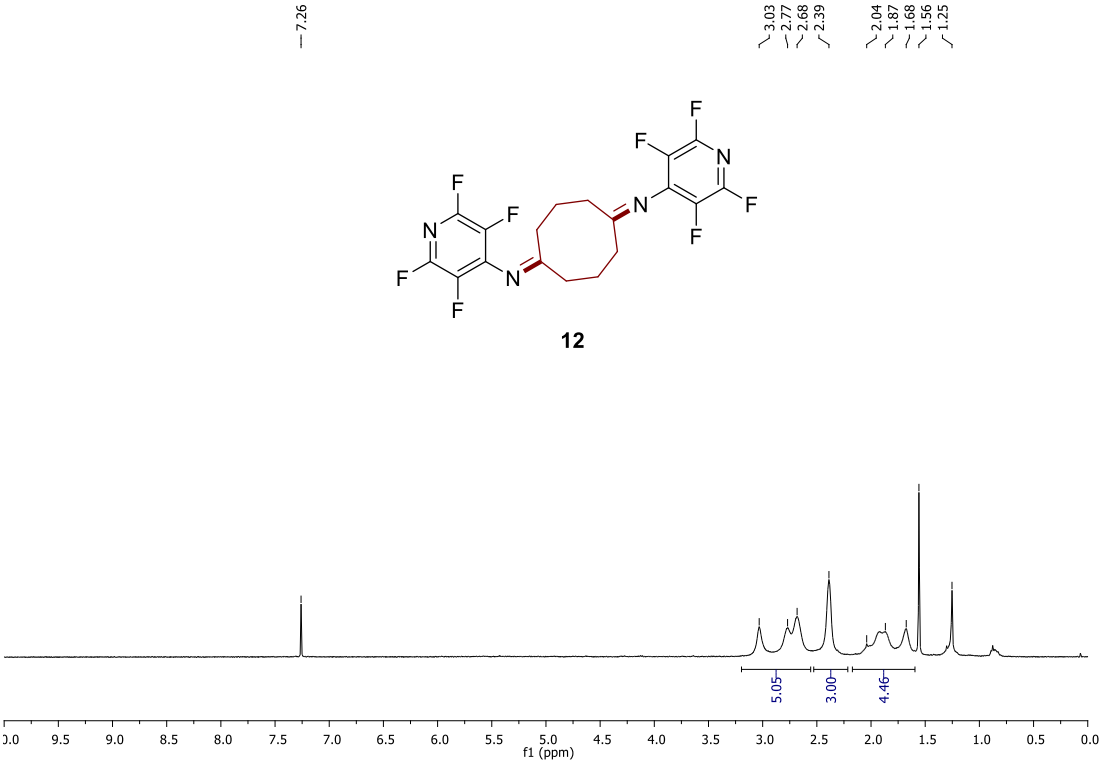
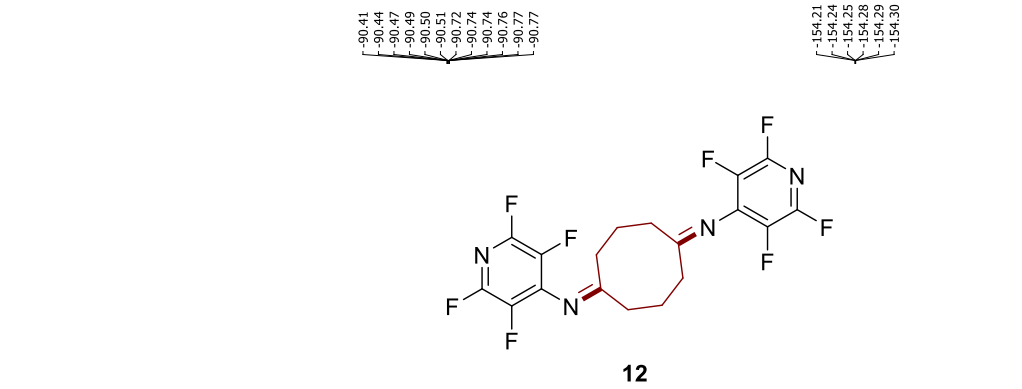
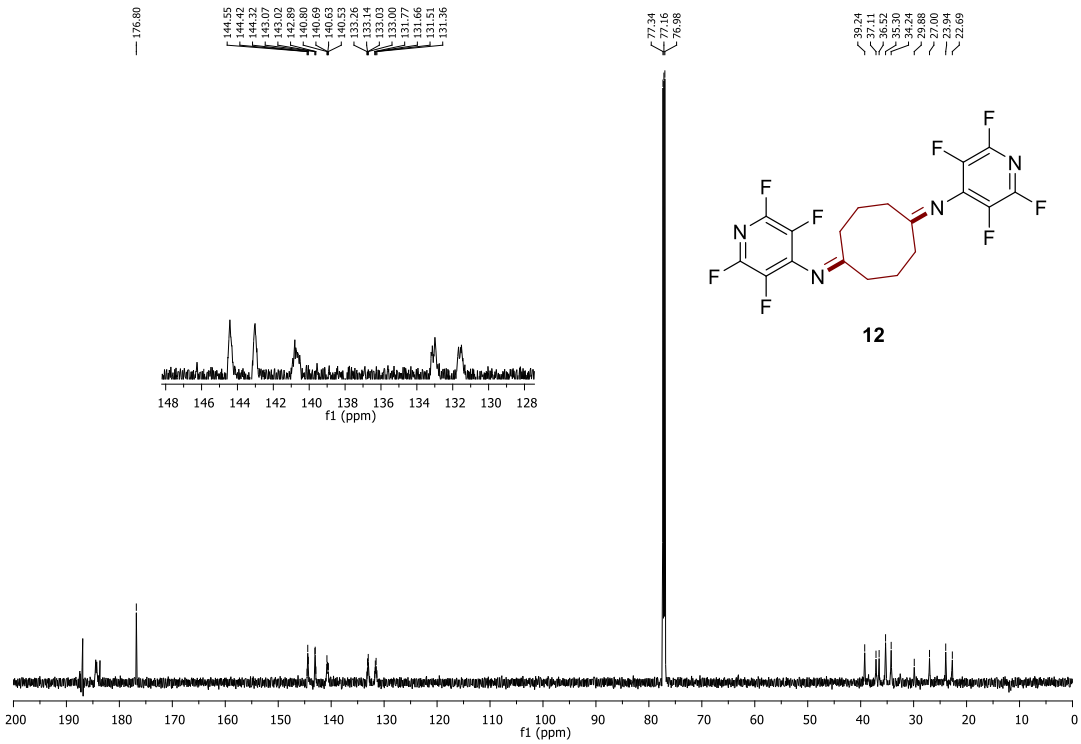
145.82
145.60
143.26
143.10
141.13
141.05
138.70
138.60
132.00
131.81
131.61
122.82
120.03
116.63
113.82
103.64
103.55
103.44
103.36
103.23
103.16
103.05
103.00
102.92
77.48
77.16
76.84
72.81
29.79
23.34
F
F
N
O
F3C
F
F
11
150
140
130
120
110
100
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.26
3.03
2.77
2.68
2.39
2.04
1.87
1.68
1.56
1.25
F
F
N
F
F
N
F
F
N
F
F
12
5.05
3.00
4.46
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


-90.41
-90.44
-90.47
-90.49
-90.50
-90.51
-90.72
-90.74
-90.74
-90.76
-90.77
-90.77
-154.21
-154.24
-154.25
-154.28
-154.29
-154.30
F
F
F
N
F
N
F
F
N
F
F
N
F
F
12
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)


176.80
144.55
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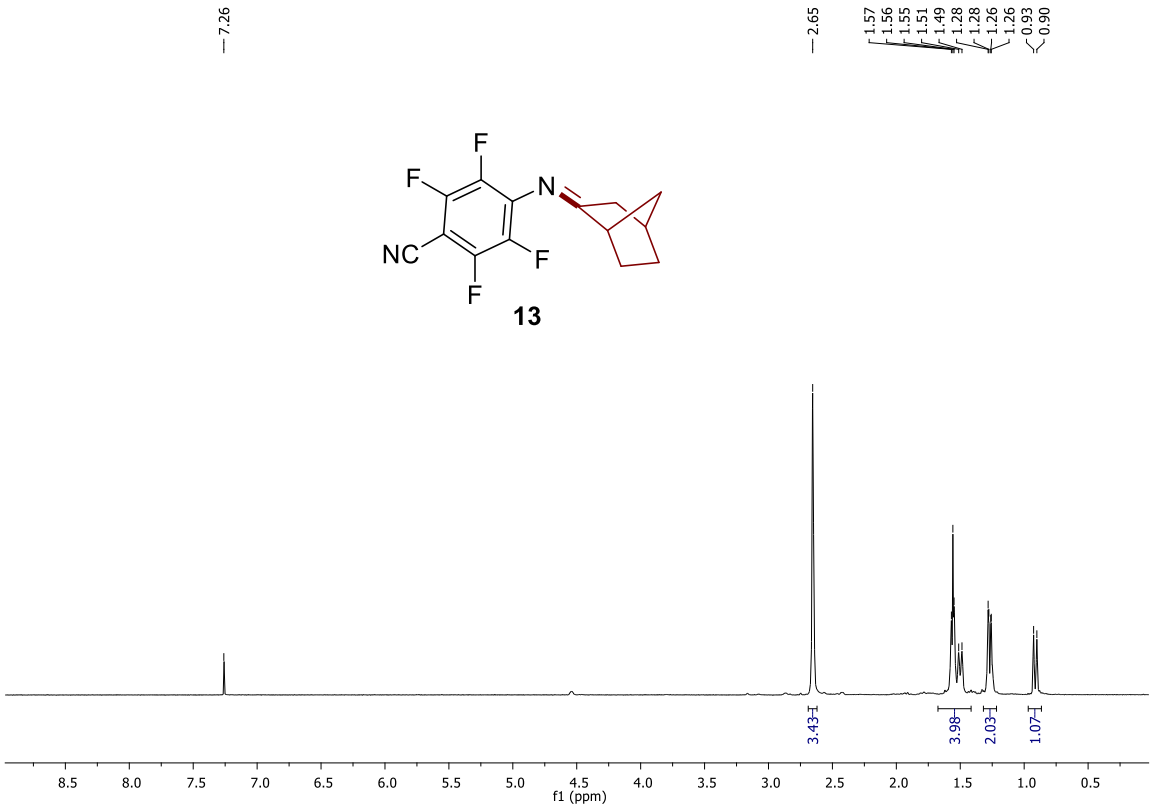
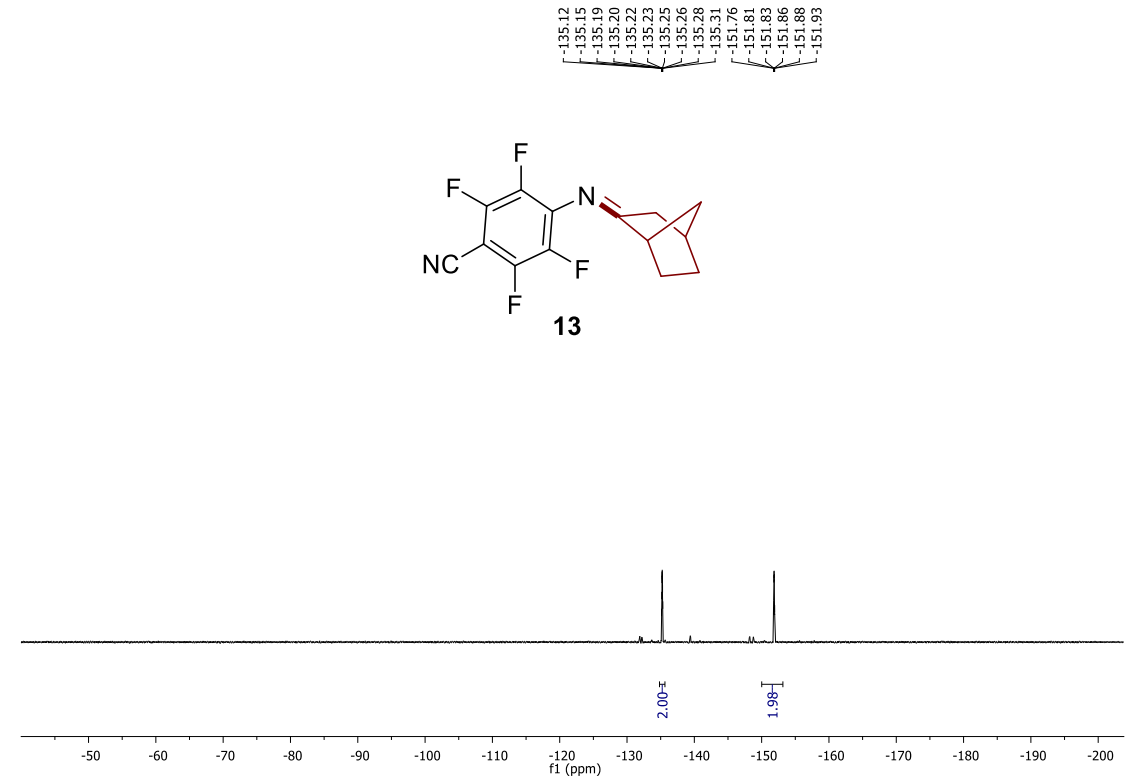
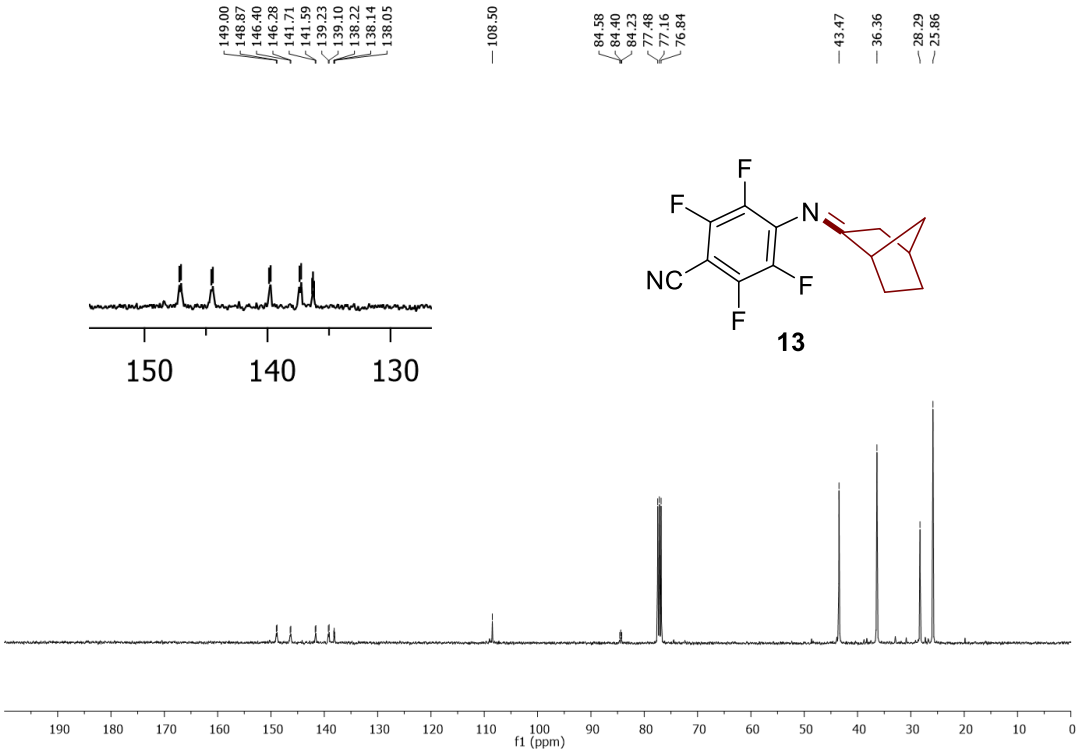
144.32
143.07
143.02
142.89
140.80
140.69
140.63
140.53
133.26
133.14
133.03
133.00
131.77
131.66
131.51
131.36
77.34
77.16
76.98
39.24
37.11
36.52
35.30
34.24
29.88
27.00
23.94
22.69
F
F
F
N
F
N
F
F
N
F
F
N
F
F
12
148
146
144
142
140
138
136
134
132
130
128
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

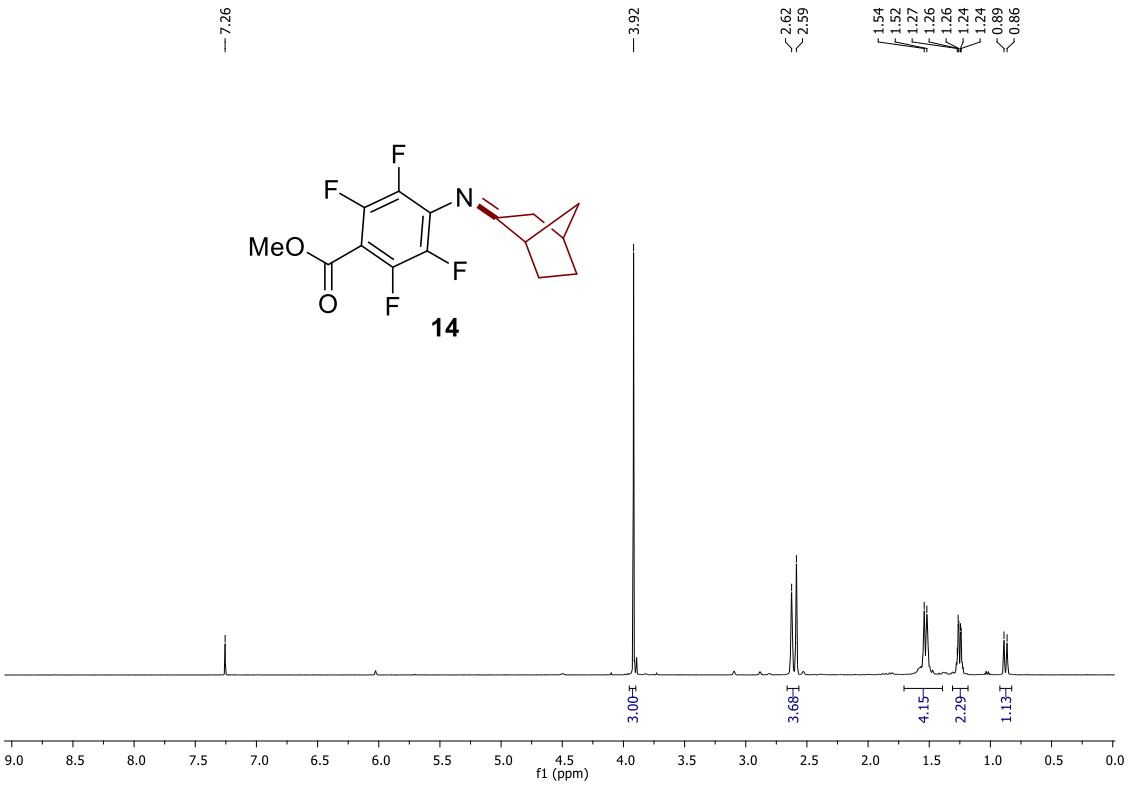

7.26
2.65
1.57
1.56
1.55
1.51
1.49
1.28
1.28
1.26
1.26
0.93
0.90
F
F
N
NC
F
F
3.43
3.98
2.03
1.07
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

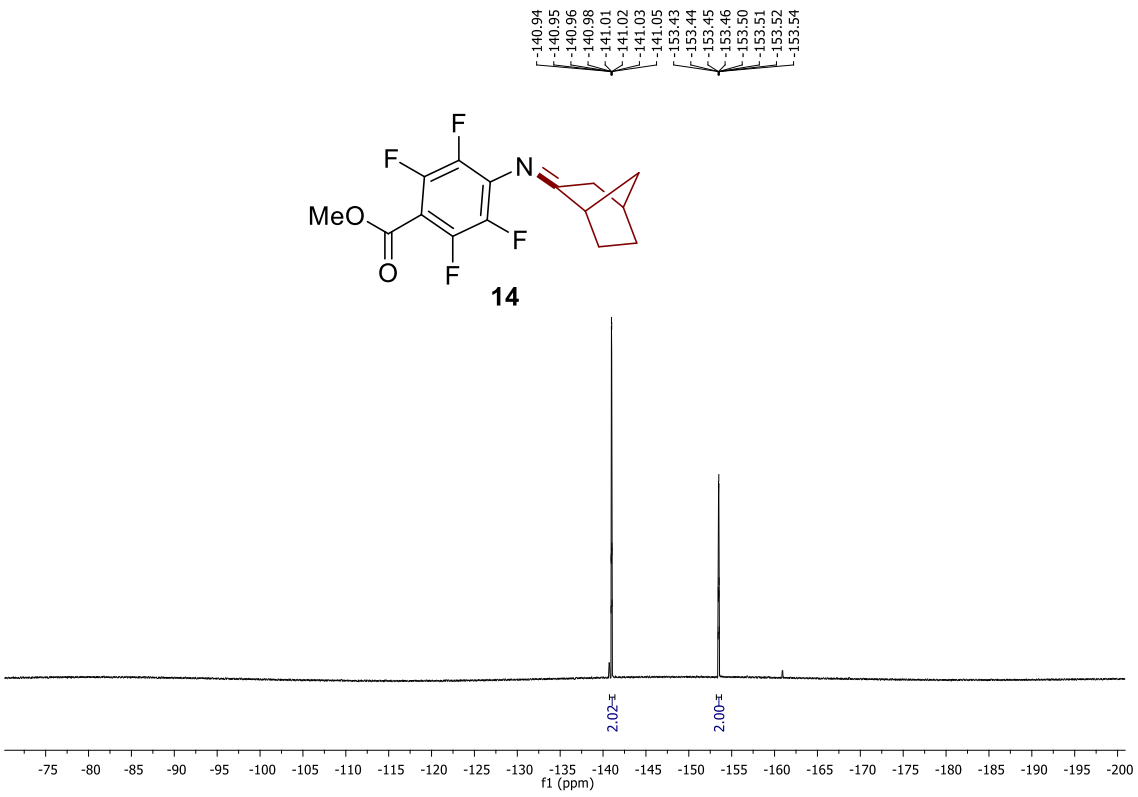
13


-135.12
-135.15
-135.19
-135.20
-135.22
-135.23
-135.25
-135.26
-135.28
-135.31
-151.76
-151.81
-151.83
-151.86
-151.88
-151.93
F
F
N
NC
F
F
2.00
1.98
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

13


149.00
148.87
146.40
146.28
141.71
141.59
139.23
139.10
138.22
138.14
138.05
108.50
84.58
84.40
84.23
77.48
77.16
76.84
43.47
36.36
28.29
25.86
F
F
N
NC
F
F
13
150
140
130
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.26
3.92
2.62
2.59
1.54
1.52
1.27
1.26
1.26
1.24
1.24
0.89
0.86
F
F
N
MeO
F
O
F
14
3.00
3.68
4.15
2.29
1.13
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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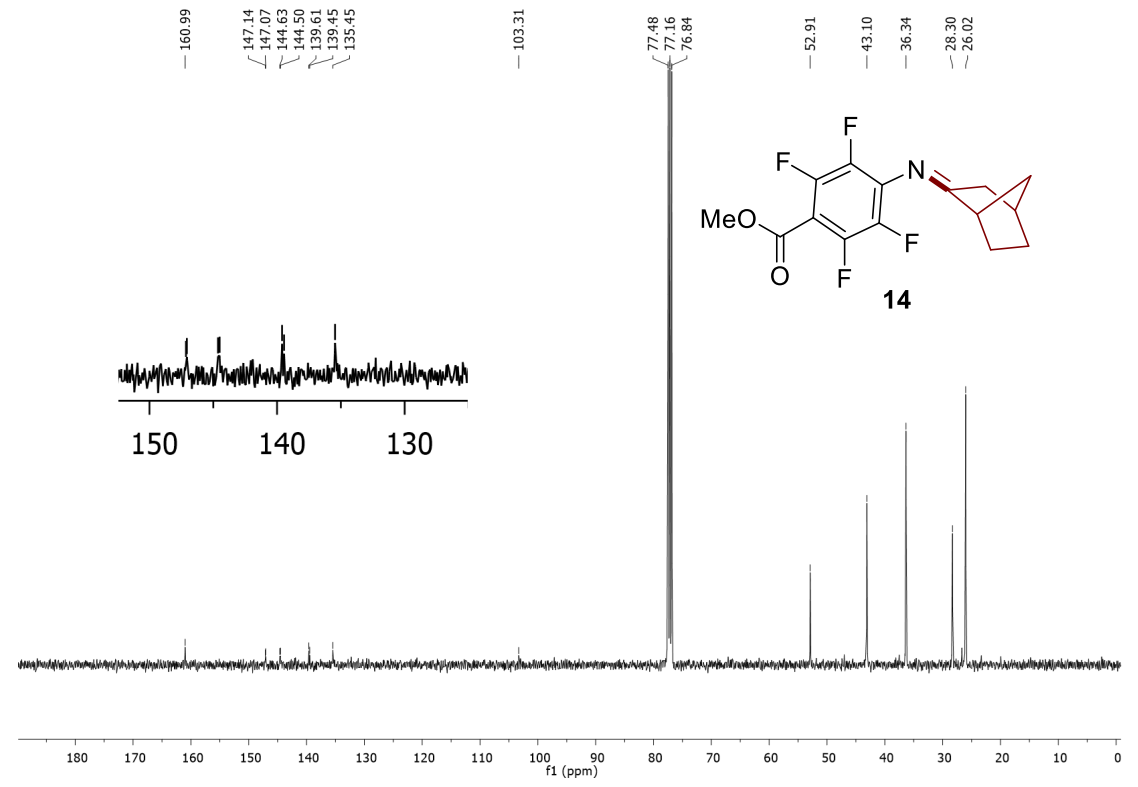
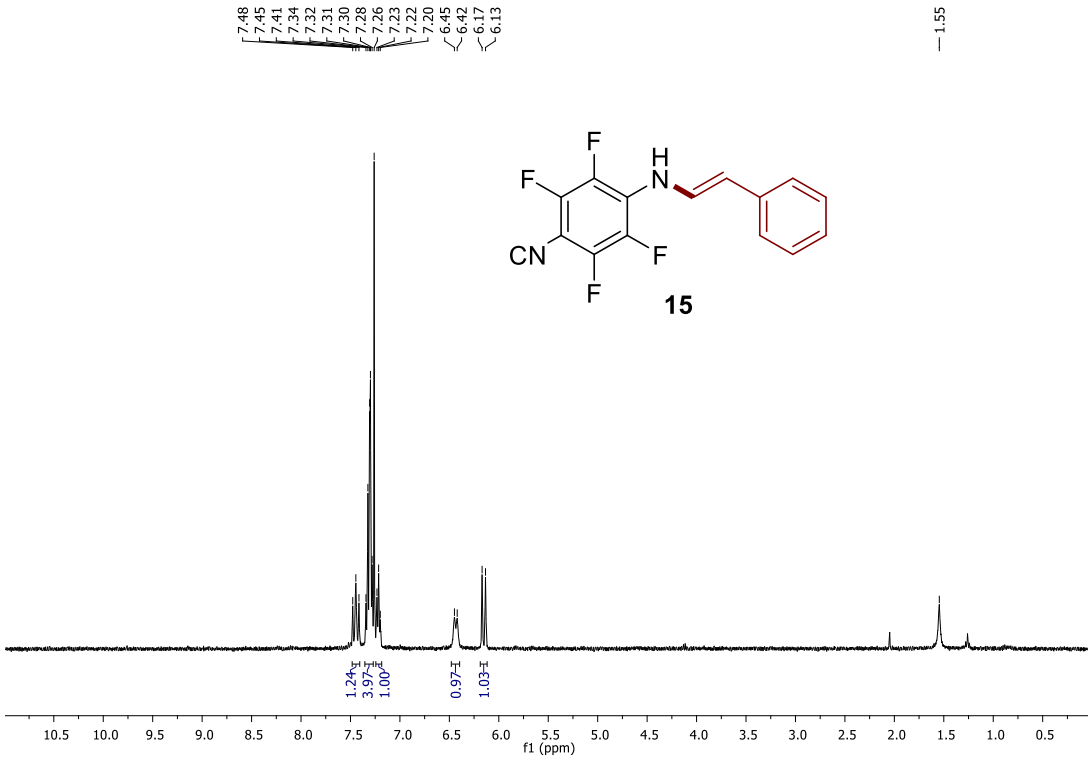
-140.95
-140.96
-140.98
-141.01
-141.02
-141.03
-141.05
-153.43
-153.44
-153.45
-153.46
-153.50
-153.51
-153.52
-153.54
F
F
N
MeO
O
F
F
14
2.02
2.00
-75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185 -190 -195 -200
f1 (ppm)


160.99
147.14
147.07
144.63
144.50
139.61
139.45
135.45
103.31
77.48
77.16
76.84
52.91
43.10
36.34
28.30
26.02
F
F
N
MeO
O
F
F
14
150
140
130
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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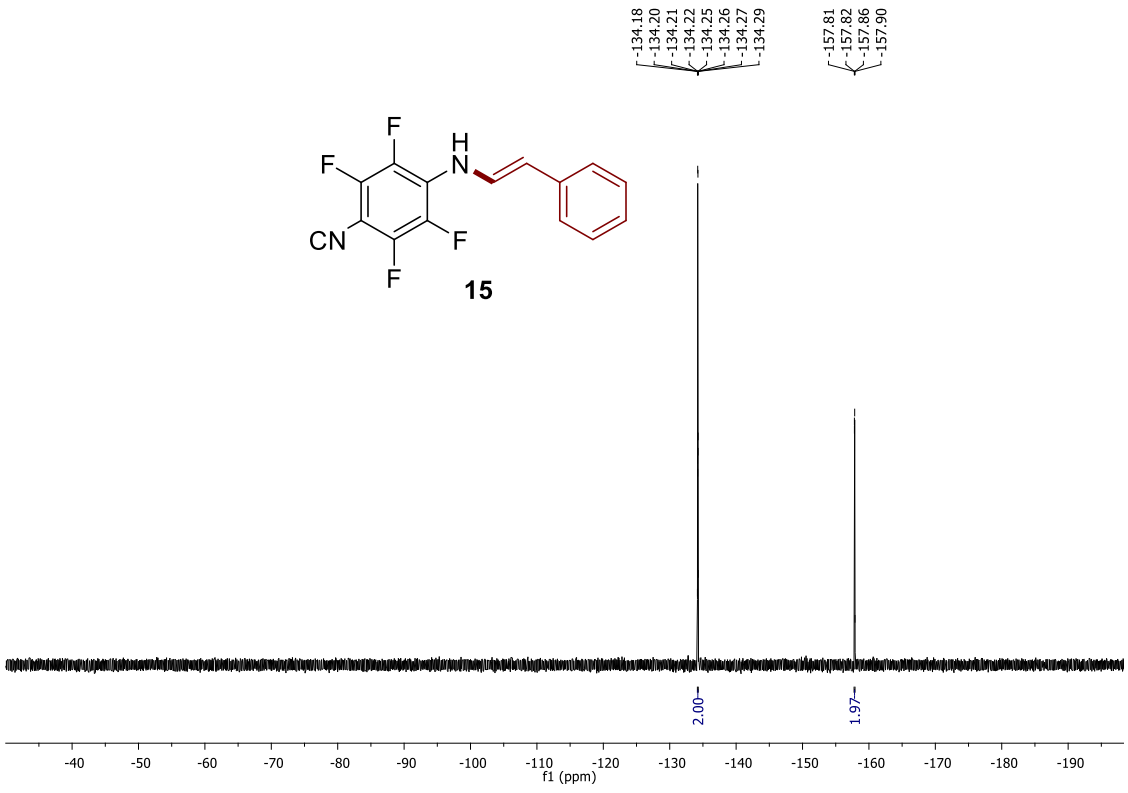
7.45
7.41
7.34
7.32
7.31
7.30
7.28
7.26
7.23
7.22
7.20
6.45
6.42
6.17
6.13
1.55
F
H
N
F
CN
F
F
15
1.24
3.97
1.00
0.97
1.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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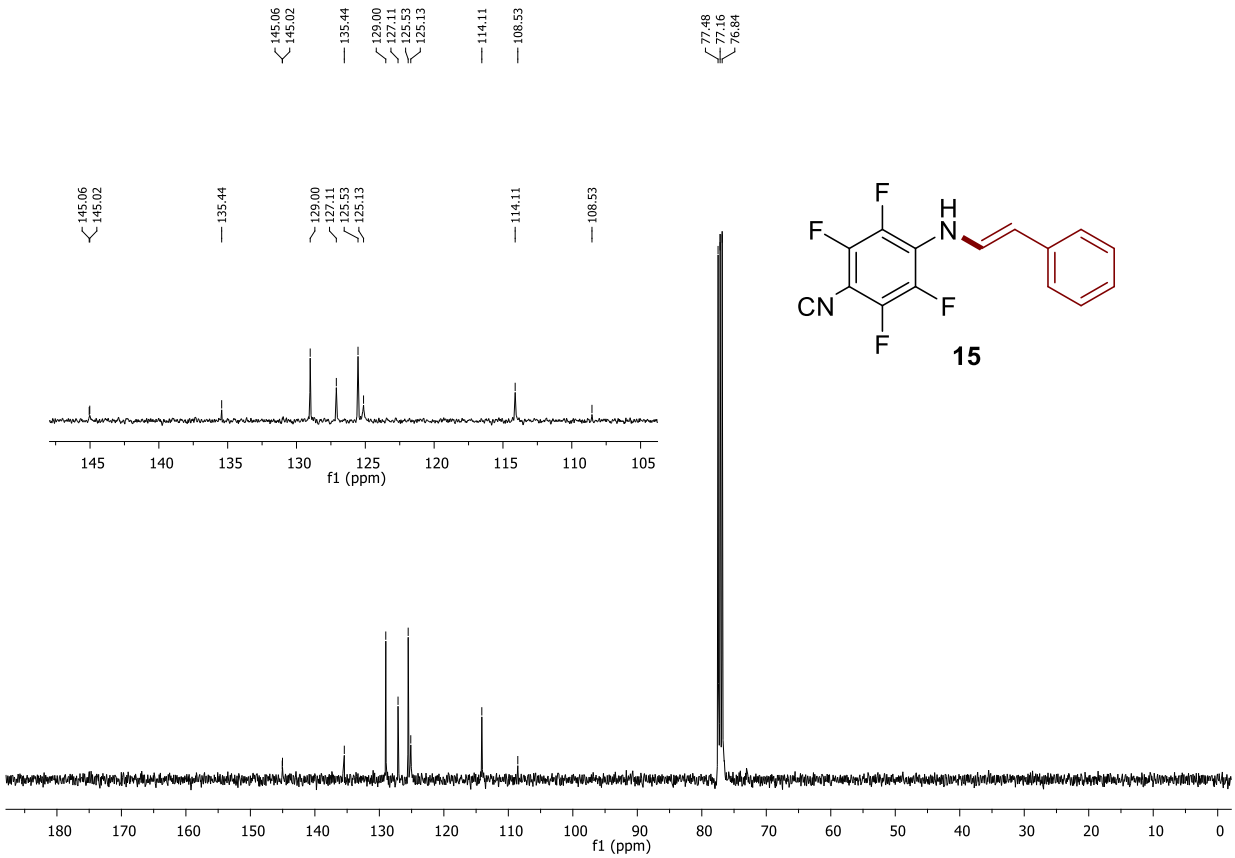
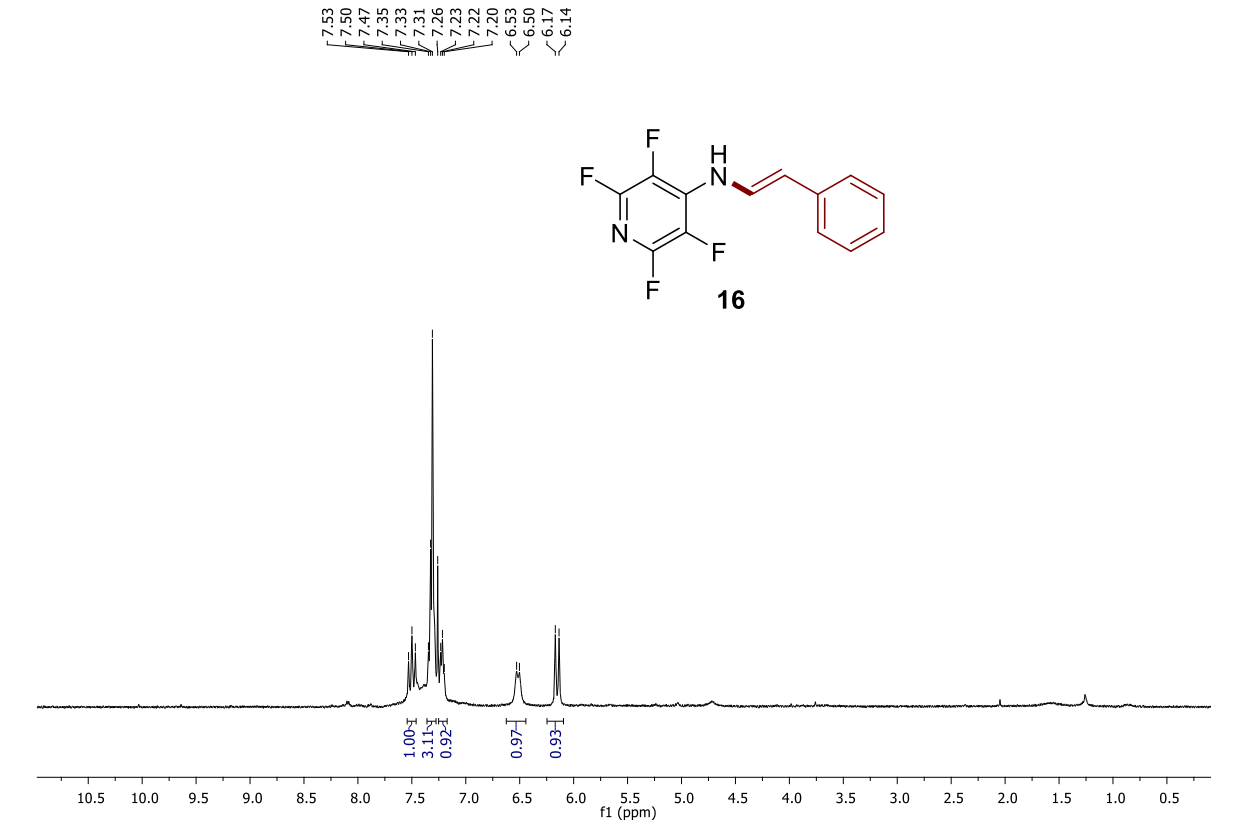
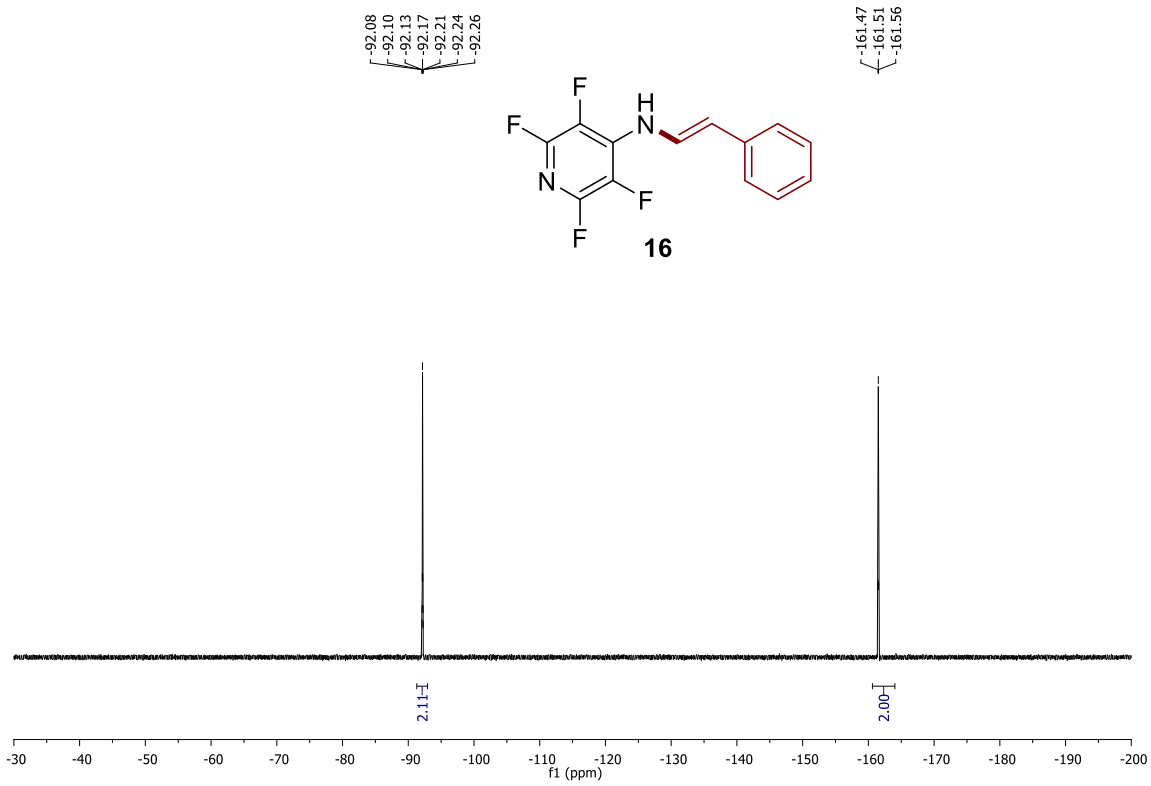
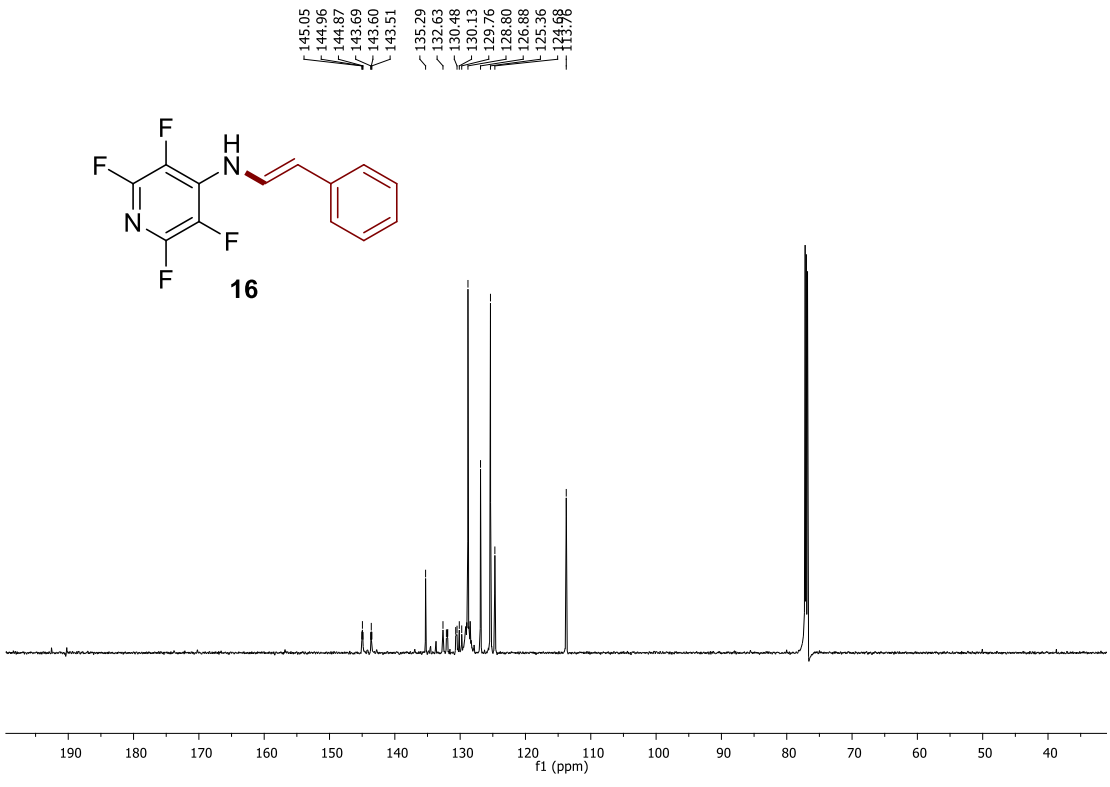
-134.26
-134.27
-134.29
-157.81
-157.82
-157.86
-157.90
F
H
N
F
CN
F
F
15
2.00
1.97
-40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)


145.06
145.02
135.44
129.00
127.11
125.53
125.13
114.11
108.53
77.48
77.16
76.84
f1 (ppm)
F
H
N
F
CN
F
F
15


7.53
7.50
7.47
7.35
7.33
7.31
7.26
7.23
7.22
7.20
6.53
6.50
6.17
6.14
1.00
3.11
0.92
0.97
0.93
f1 (ppm)
F
H
N
F
N
F
F
16


-92.08
-92.10
-92.13
-92.17
-92.21
-92.24
-92.26
-161.47
-161.51
-161.56
F
H
N
F
N
F
F
16
2.11
2.00
-30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)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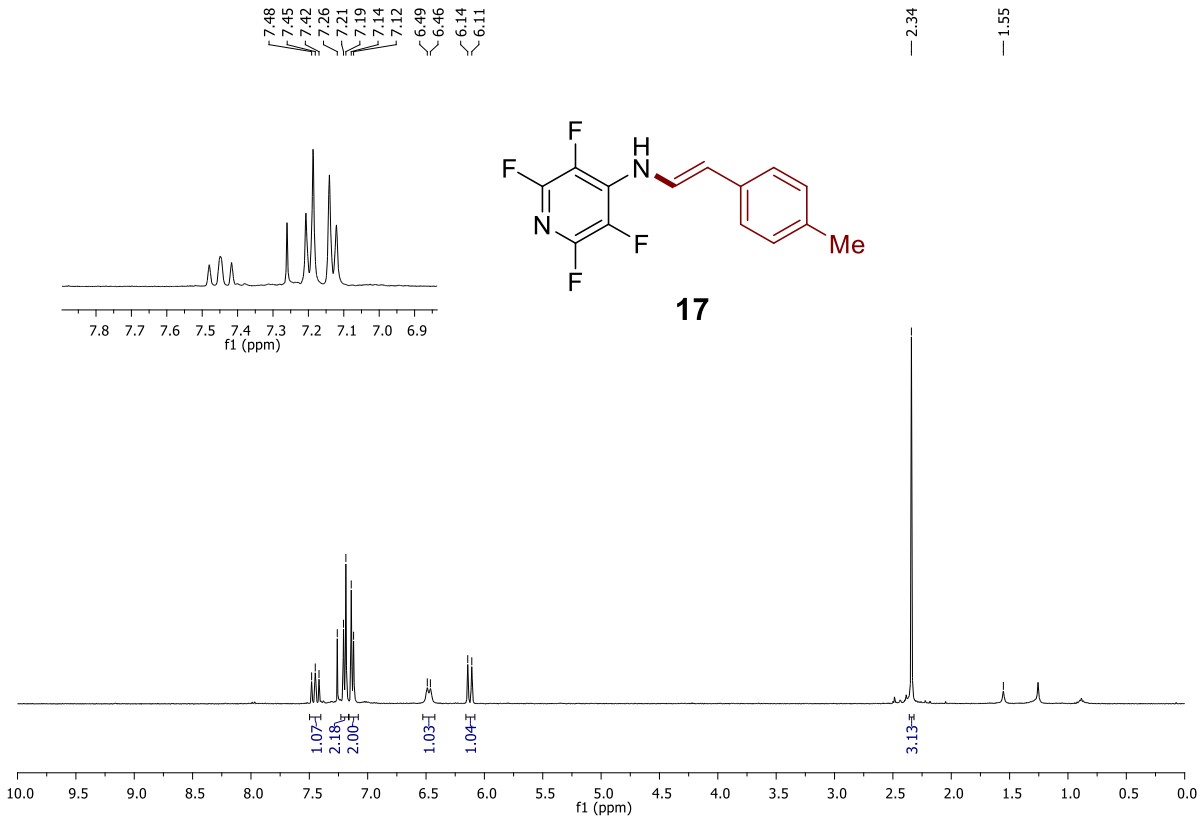
144.87
143.69
143.60
143.51
135.29
132.63
130.48
130.13
129.76
128.80
126.88
125.36
124.68
113.98
F
H
N
F
N
F
F
16
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40
f1 (ppm)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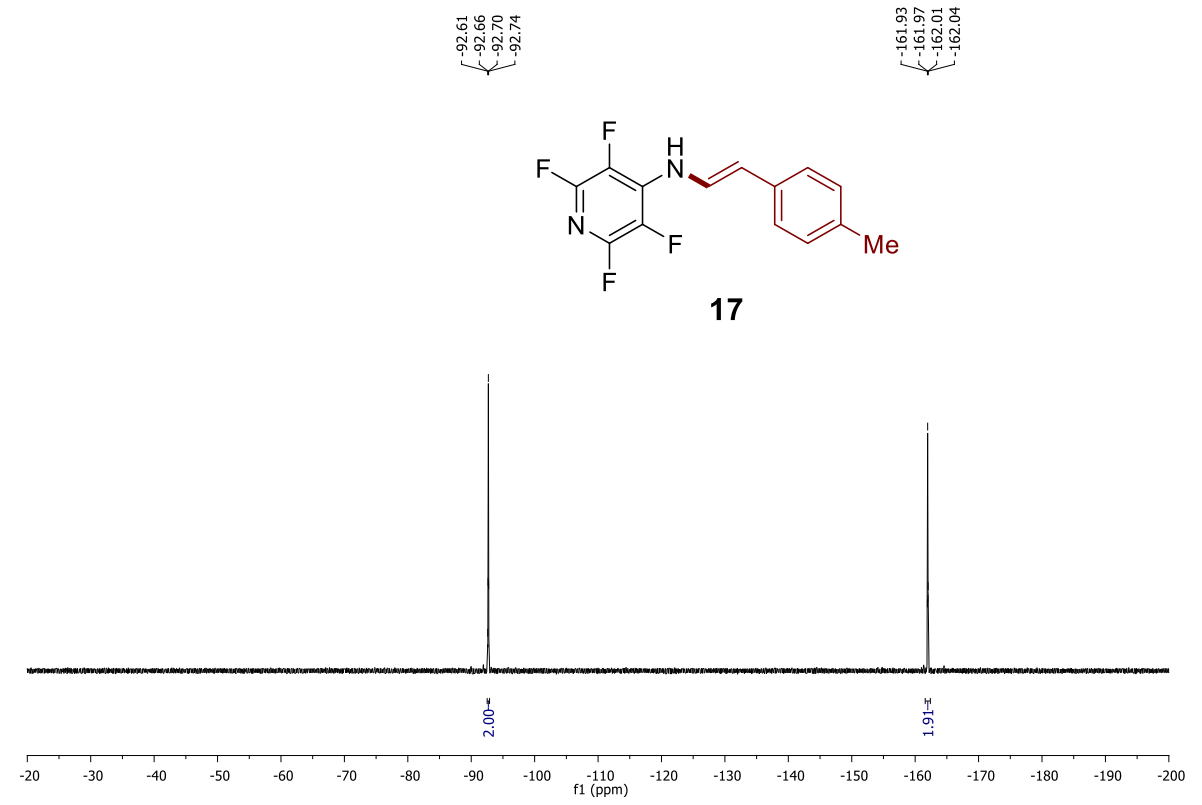
7.45
7.42
7.26
7.21
7.19
7.14
7.12
6.49
6.46
6.14
6.11
2.34
1.55
F
H
N
F
N
F
F
Me
17
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9
f1 (ppm)
1.07
2.18
2.00
1.03
1.04
3.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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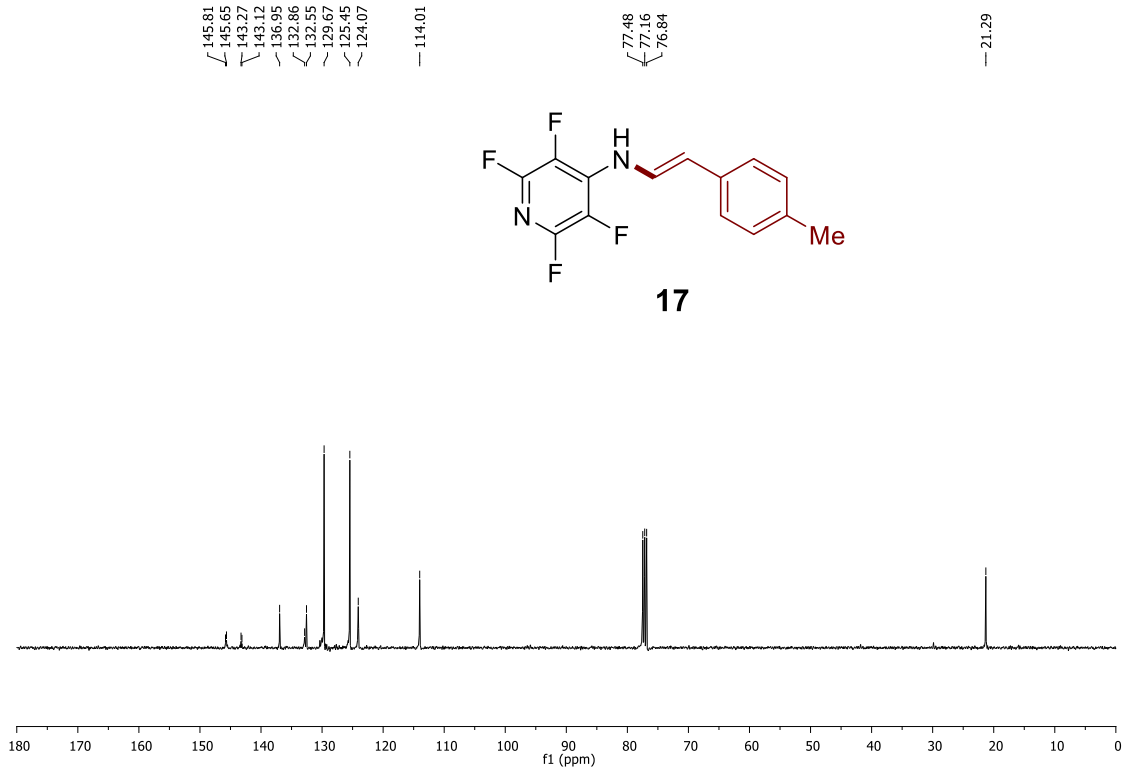
-92.66
-92.70
-92.74
-161.93
-161.97
-162.01
-162.04
F
H
N
F
N
F
F
Me
17
2.00
1.91
-20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)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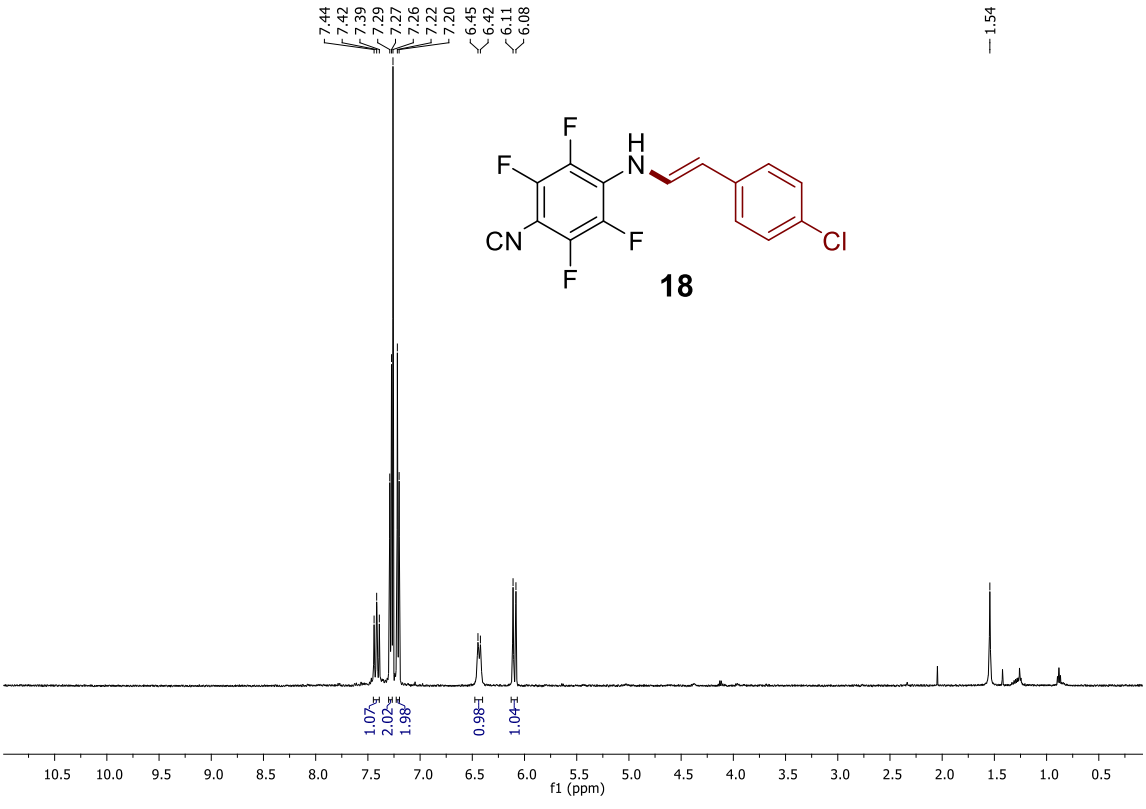
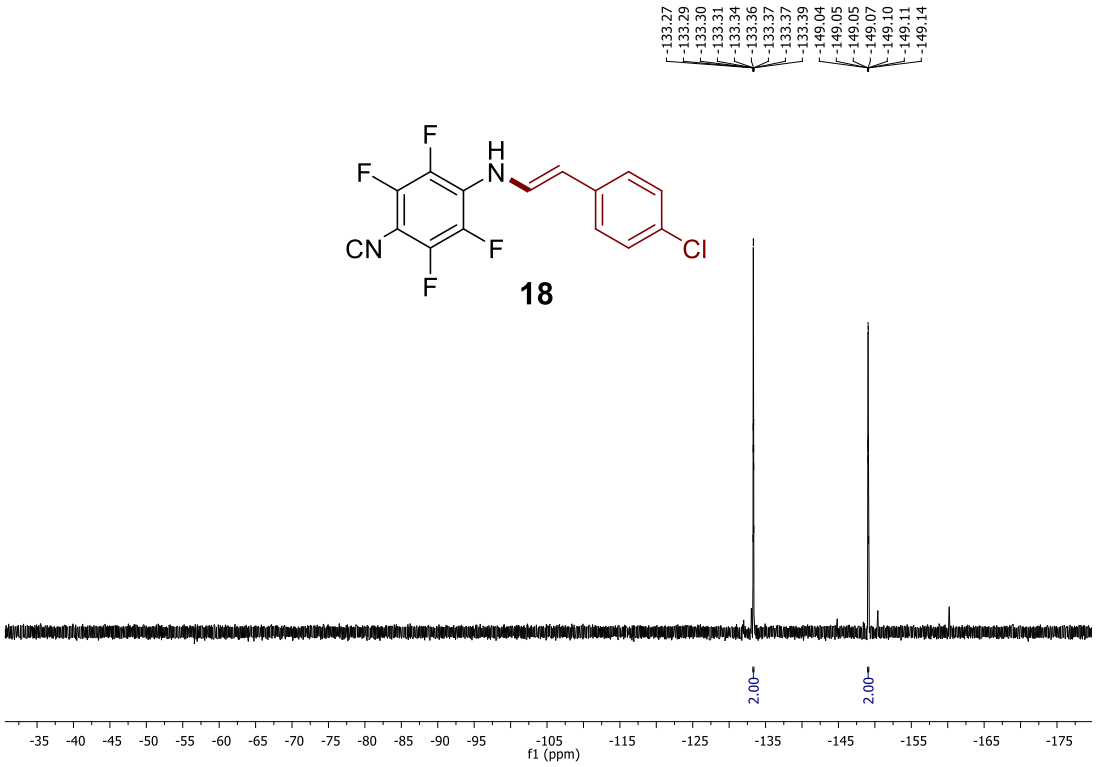
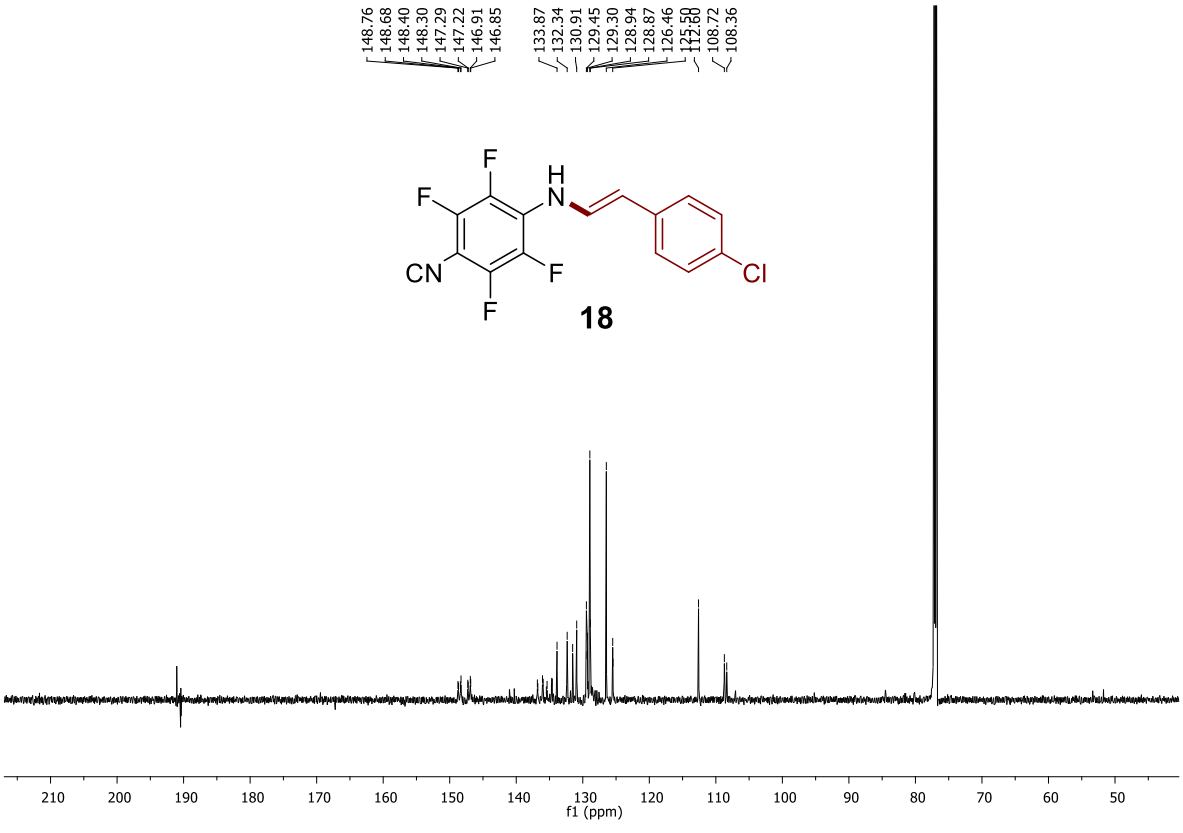
145.65
143.27
143.12
136.95
132.86
132.55
129.67
125.45
124.07
114.01
77.48
77.16
76.84
21.29
F
F
H
N
N
F
F
Me
17
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.44
7.42
7.39
7.29
7.27
7.26
7.22
7.20
6.45
6.42
6.11
6.08
1.54
F
F
H
N
CN
F
F
Cl
18
1.07
2.02
1.98
0.98
1.04
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


-133.27
-133.29
-133.30
-133.31
-133.34
-133.36
-133.37
-133.37
-133.39
-149.04
-149.05
-149.05
-149.07
-149.10
-149.11
-149.14
F
F
H
N
CN
F
F
Cl
18
2.00
2.00
-35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -105 -115 -125 -135 -145 -155 -165 -175
f1 (ppm)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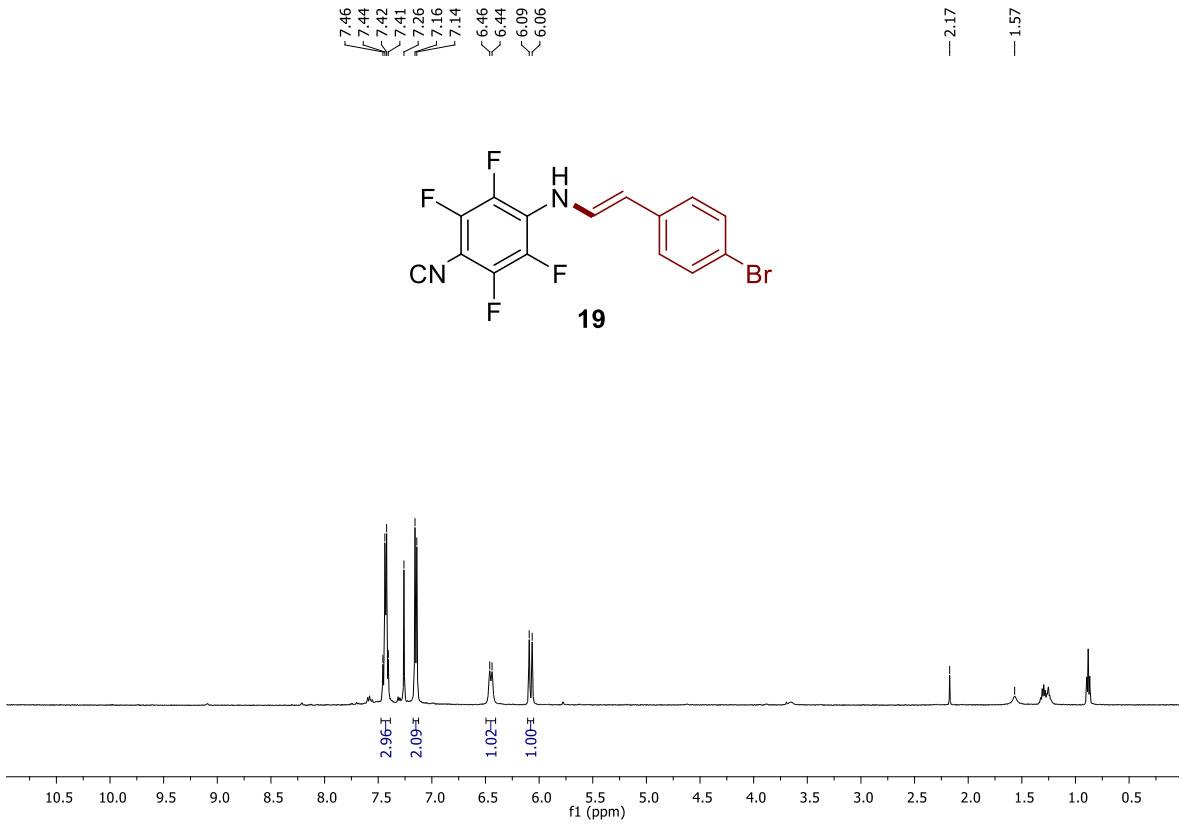
148.68
148.40
148.30
147.29
147.22
146.91
146.85
133.87
132.34
130.91
129.45
129.30
128.94
128.87
126.46
125.50
112.80
108.72
108.36
F
F
H
N
CN
F
F
Cl
18
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50
f1 (ppm)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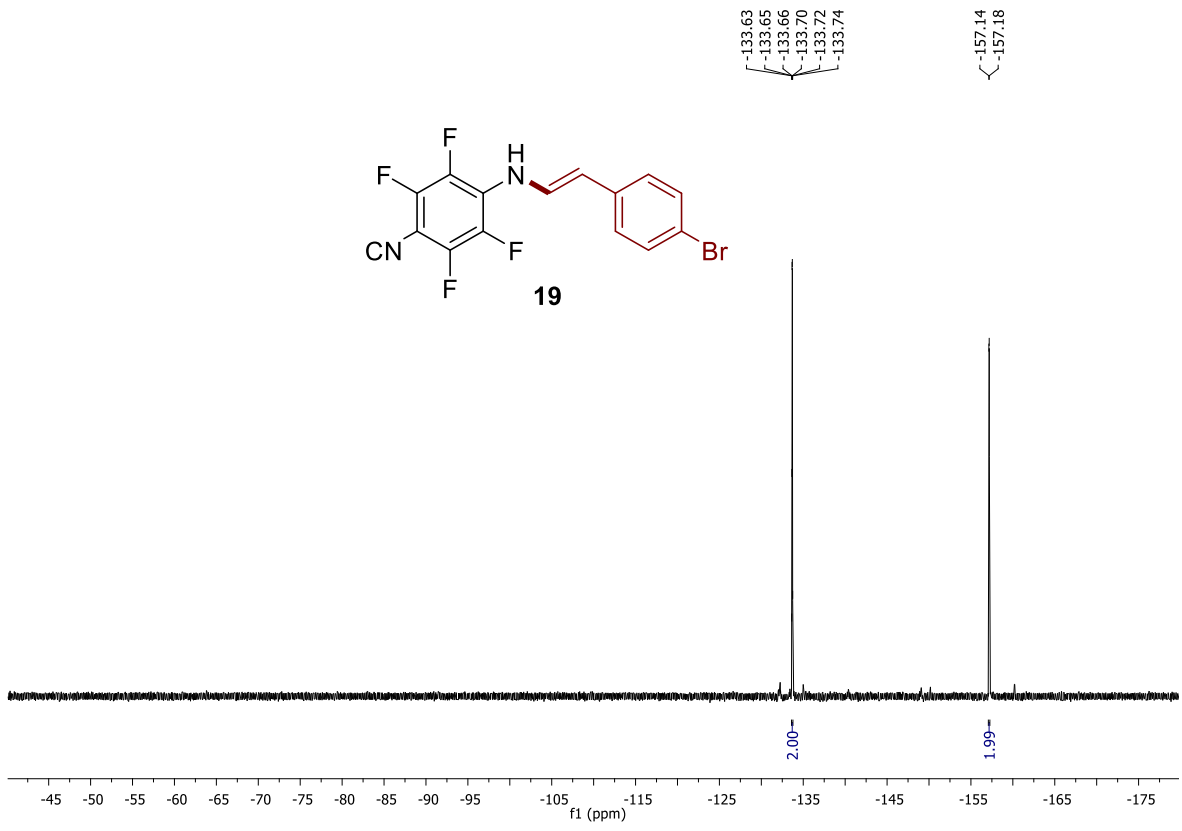
7.44
7.42
7.41
7.26
7.16
7.14
6.46
6.44
6.09
6.06
2.17
1.57
F
H
N
F
CN
F
F
Br
19
2.96
2.09
1.02
1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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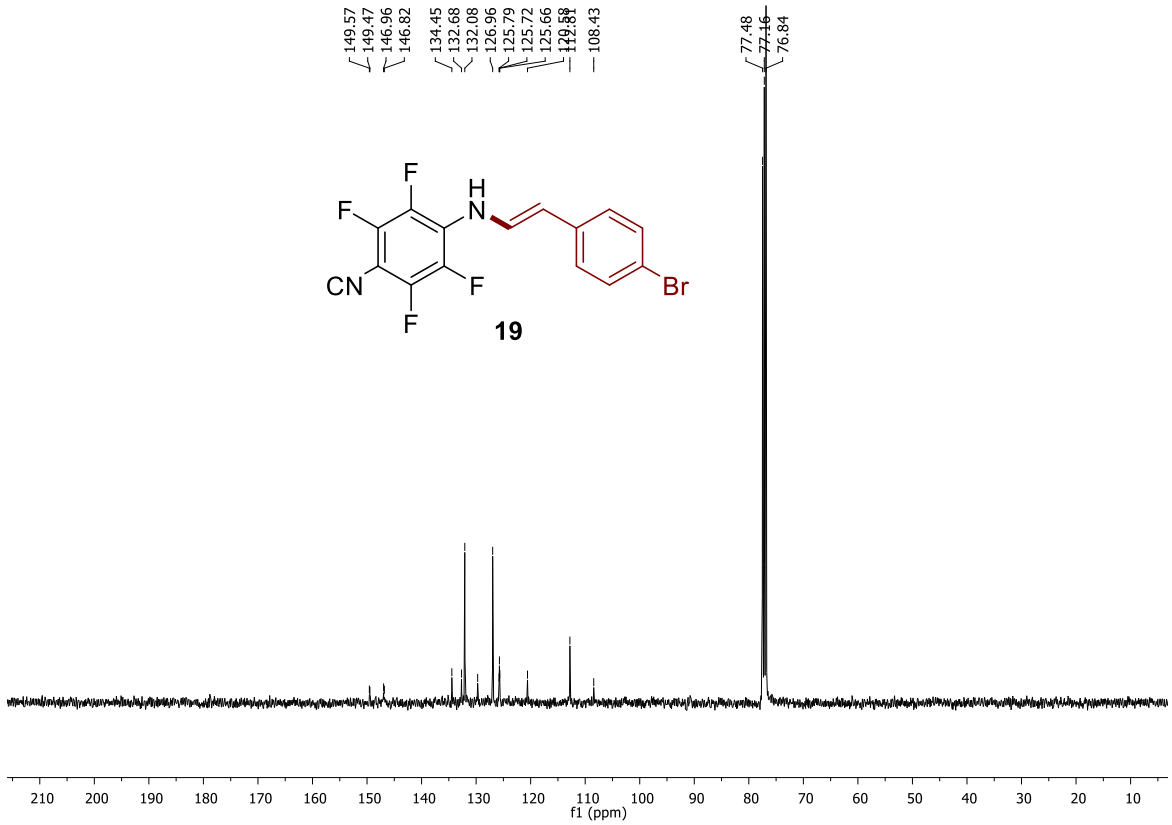
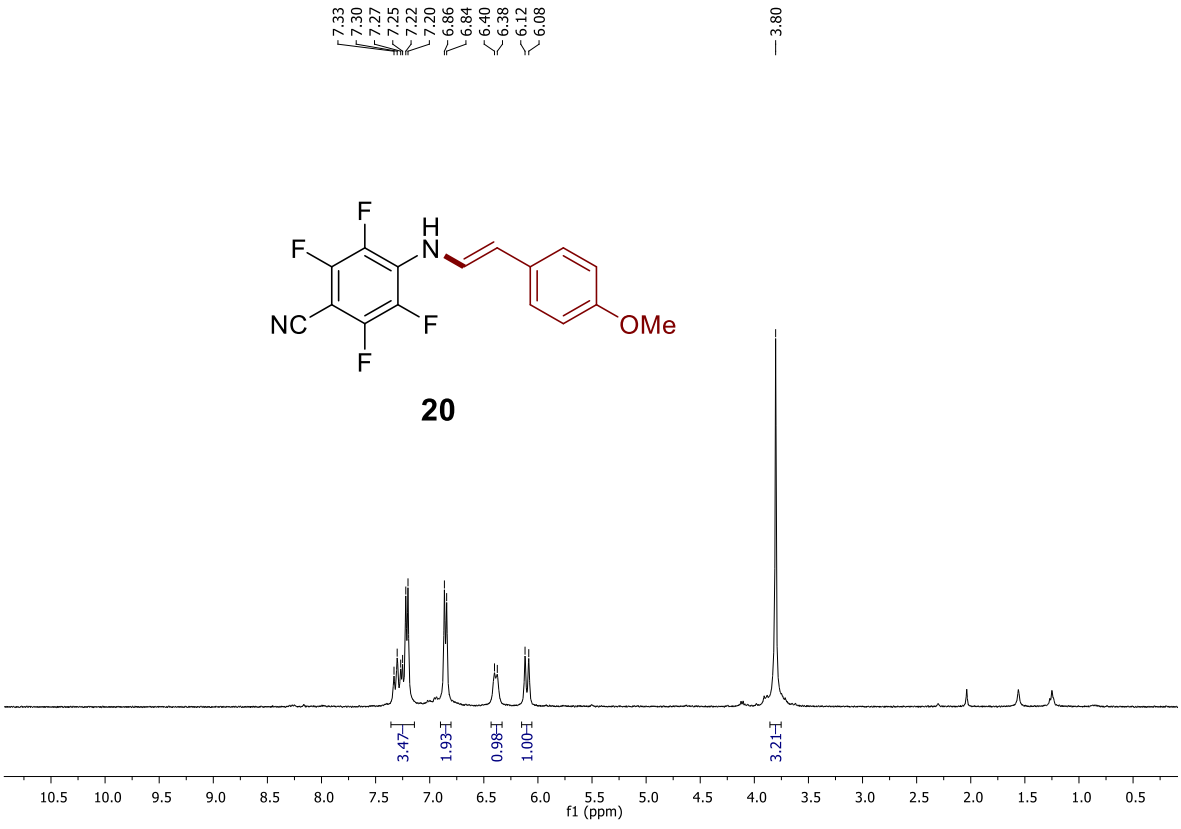
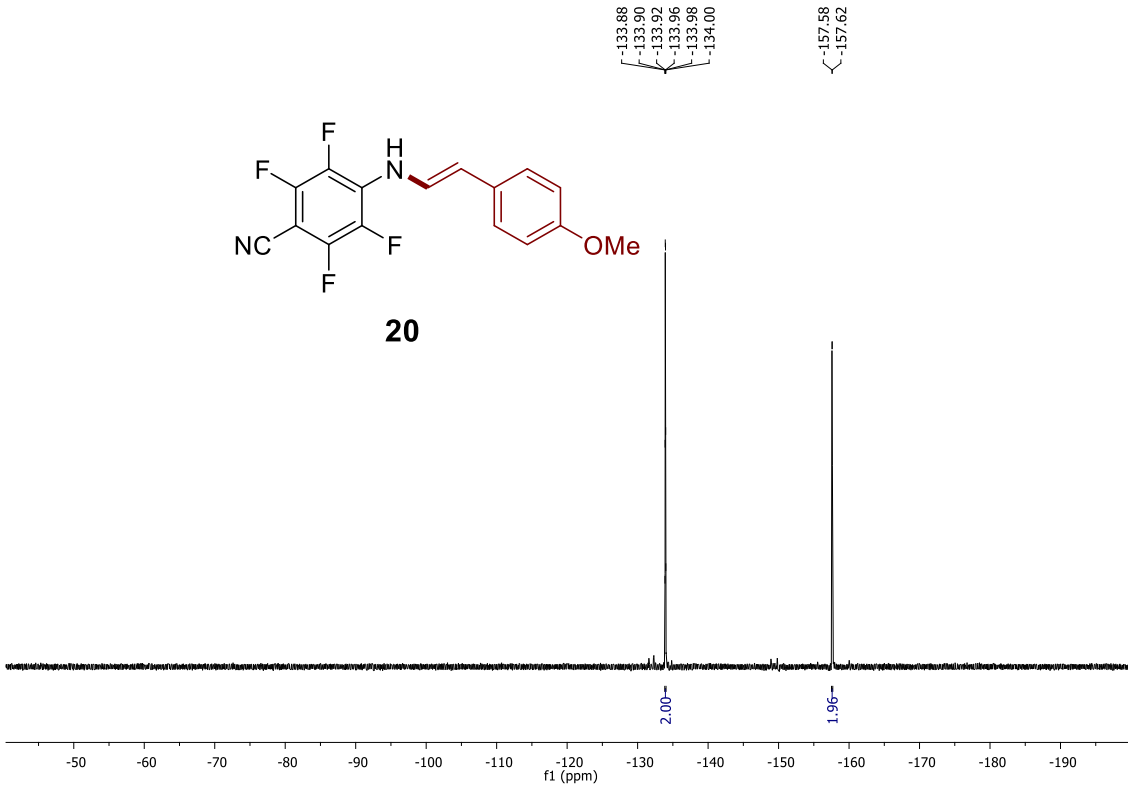
-133.65
-133.66
-133.70
-133.72
-133.74
-157.14
-157.18
F
H
N
F
CN
F
F
Br
19
2.00
1.99
-45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -105 -115 -125 -135 -145 -155 -165 -175
f1 (ppm)


149.57
149.47
146.96
146.82
134.45
132.68
132.08
126.96
125.79
125.72
125.66
108.43
77.48
77.16
76.84
F
F
H
N
CN
F
F
Br
19
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


7.33
7.30
7.27
7.25
7.22
7.20
6.86
6.84
6.40
6.38
6.12
6.08
3.80
F
F
H
N
NC
F
F
OMe
20
3.47
1.93
0.98
1.00
3.21
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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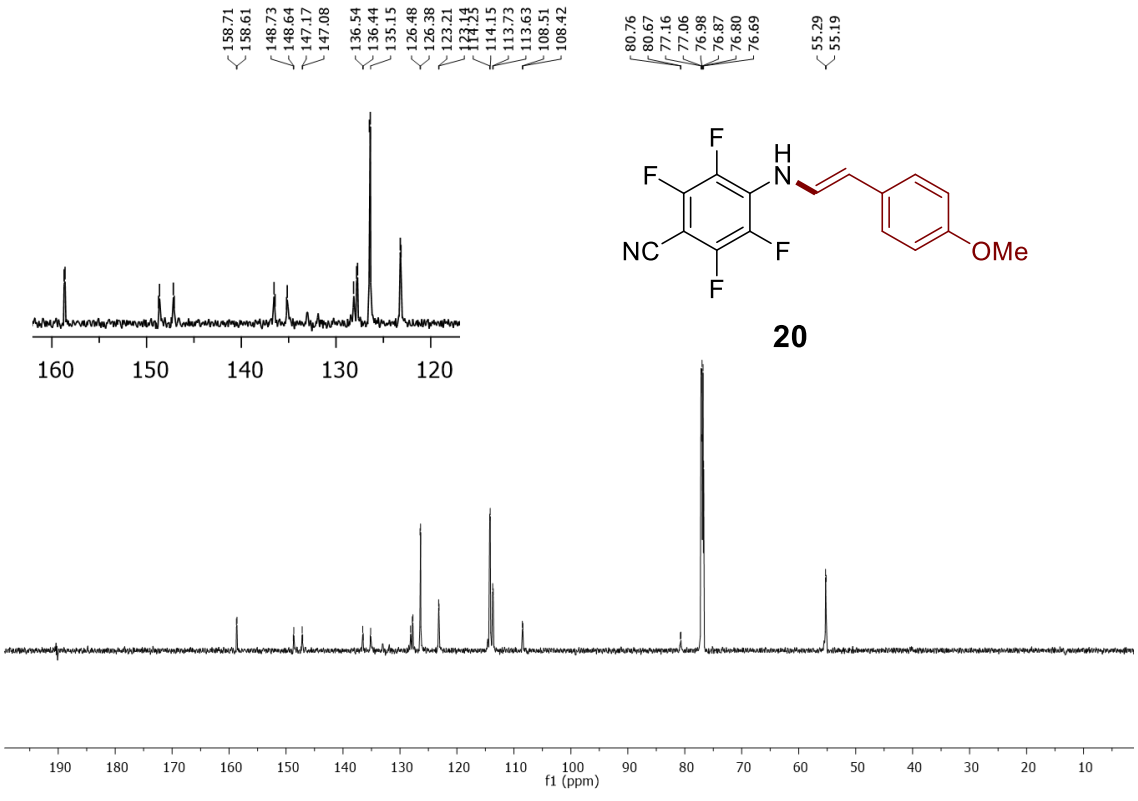
-133.90
-133.92
-133.96
-133.98
-134.00
-157.58
-157.62
F
F
H
N
NC
F
F
OMe
2.00
1.96
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

20


158.71
158.61
148.73
148.64
147.17
147.08
136.54
136.44
135.15
126.48
126.38
123.21
114.15
113.73
113.63
108.51
108.42
80.76
80.67
77.16
77.06
76.98
76.87
76.80
76.69
55.29
55.19
F
F
H
N
NC
F
F
OMe
160
150
140
130
120
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

20


7.42
7.40
7.39
7.36
7.26
7.25
7.25
7.24
7.24
7.23
7.22
7.02
7.01
7.00
7.00
6.98
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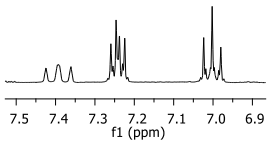
6.47
6.13
6.09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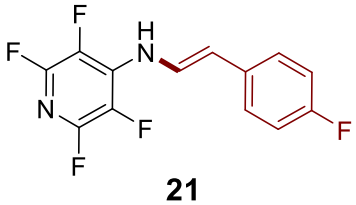
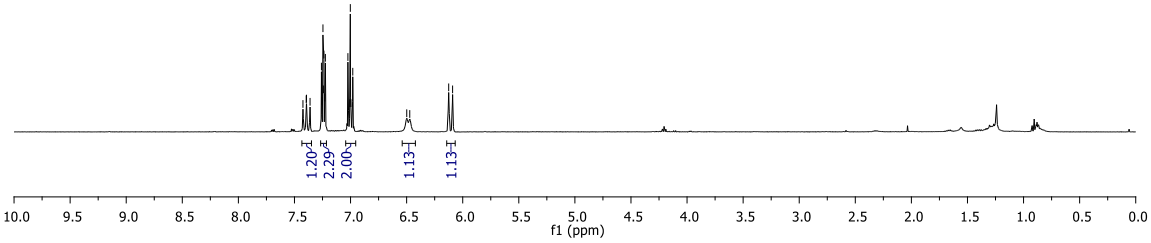
7.4
7.3
7.2
7.1
7.0
6.9
f1 (ppm)


F
H
N
F
N
F
F
F

21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1.13
1.13
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


-92.48
-92.51
-92.54
-92.58
-92.62
-92.64
-92.67
-115.48
-115.49
-115.50
-115.51
-115.52
-115.53
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-115.55
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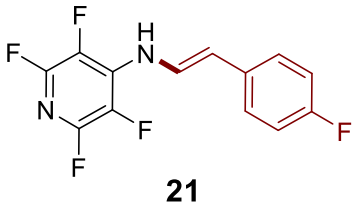
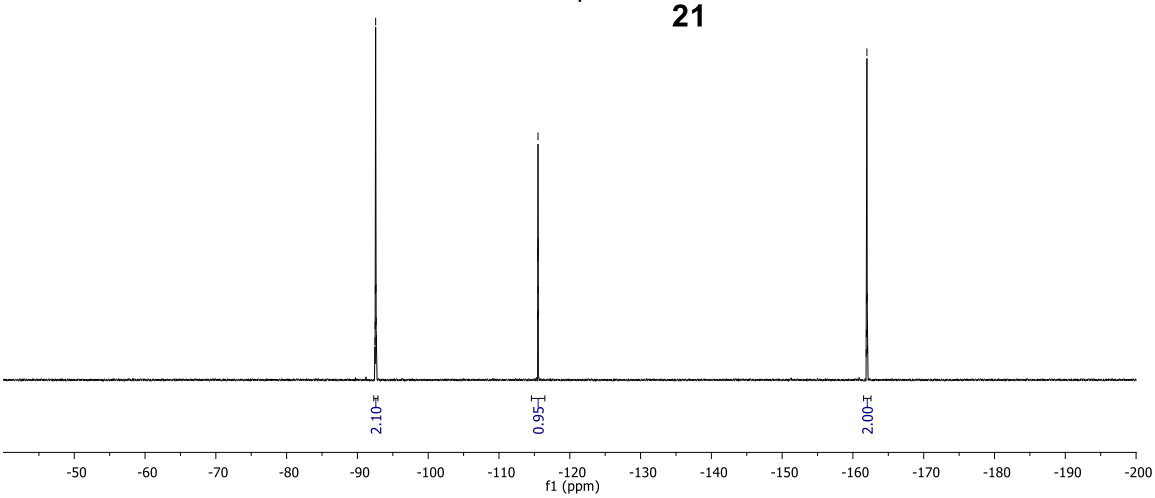
-161.90
-161.93
-161.97
-162.02
-162.04
-162.06


F
H
N
F
N
F
F
F

21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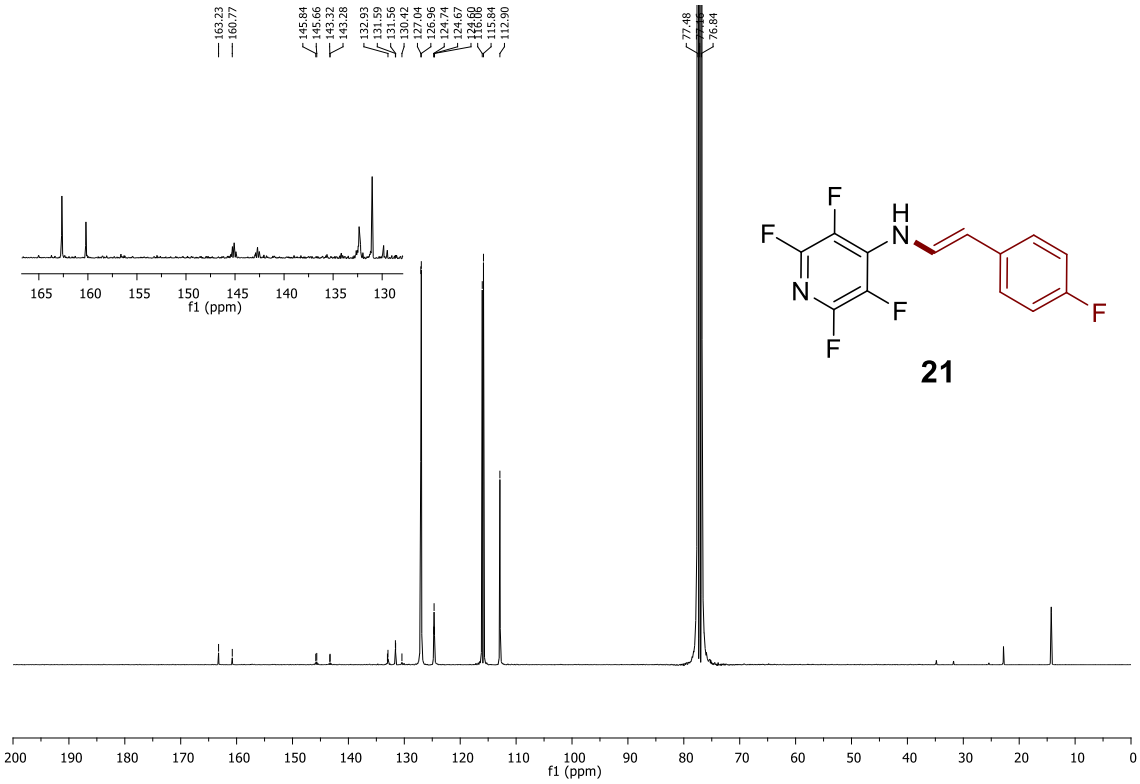
0.95
2.00
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)


163.23
160.77
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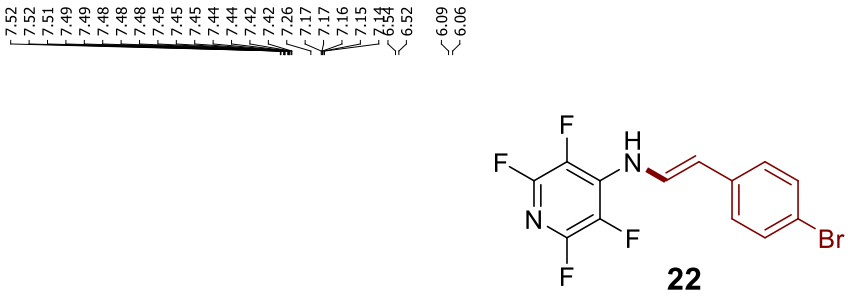
145.66
145.32
145.28
132.93
131.59
131.56
130.42
127.04
126.96
124.74
124.67
115.84
112.90
77.48
77.16
76.84
f1 (ppm)
F
H
N
F
N
F
F
F
21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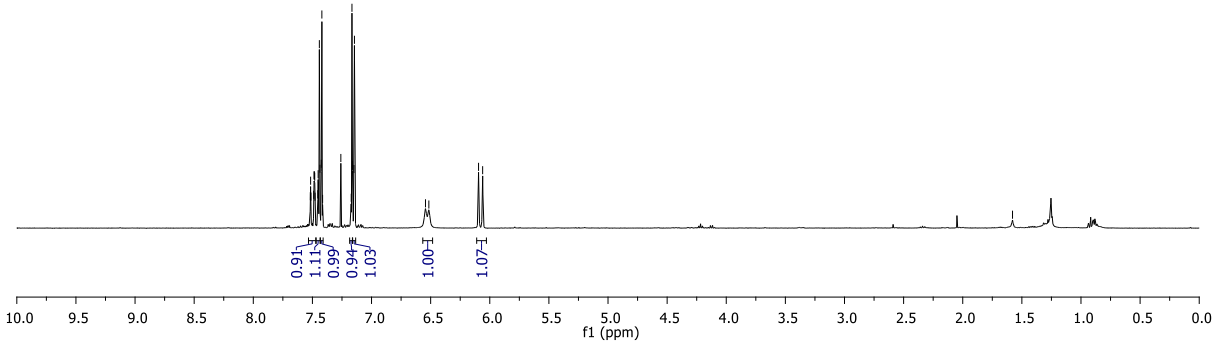
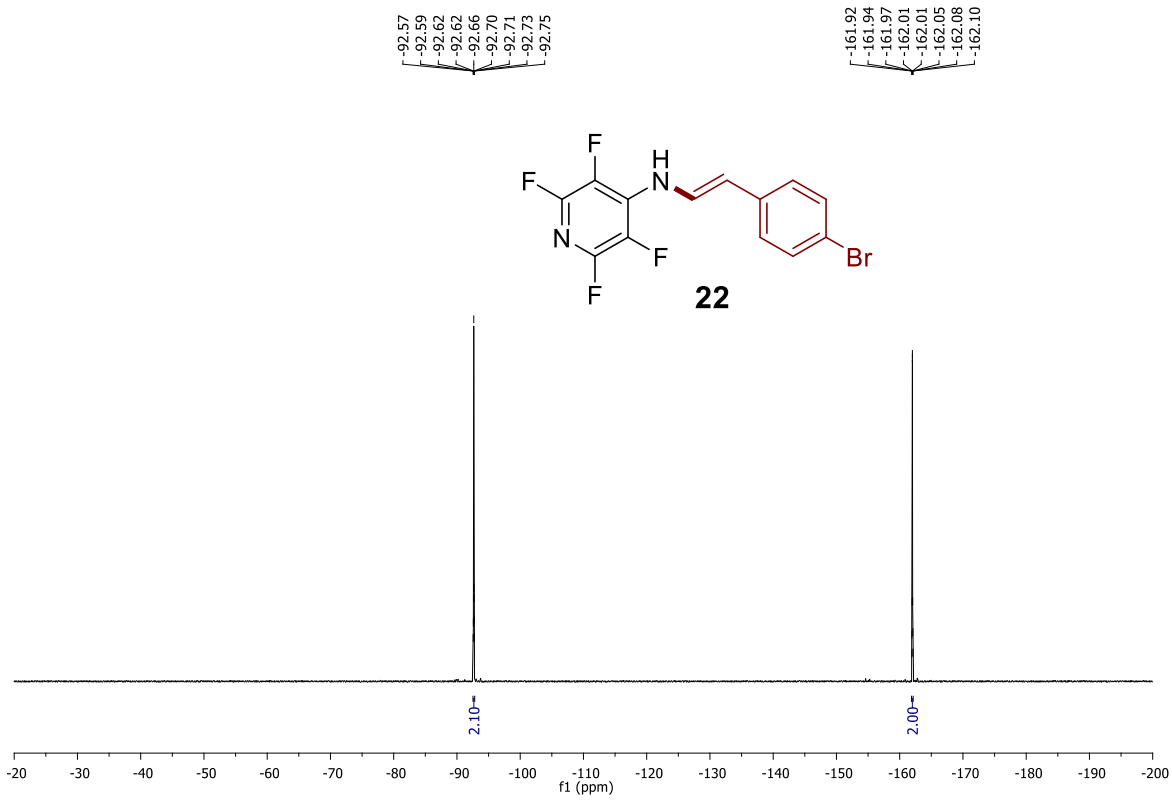
7.52
7.51
7.49
7.49
7.48
7.48
7.48
7.45
7.45
7.45
7.44
7.44
7.42
7.42
7.26
7.17
7.16
7.15
7.14
6.54
6.52
6.09
6.06
1.58
F
H
N
F
N
F
F
Br
22


0.91
1.11
0.99
0.94
1.03
1.00
1.07
f1 (ppm)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-92.59
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-92.62
-92.66
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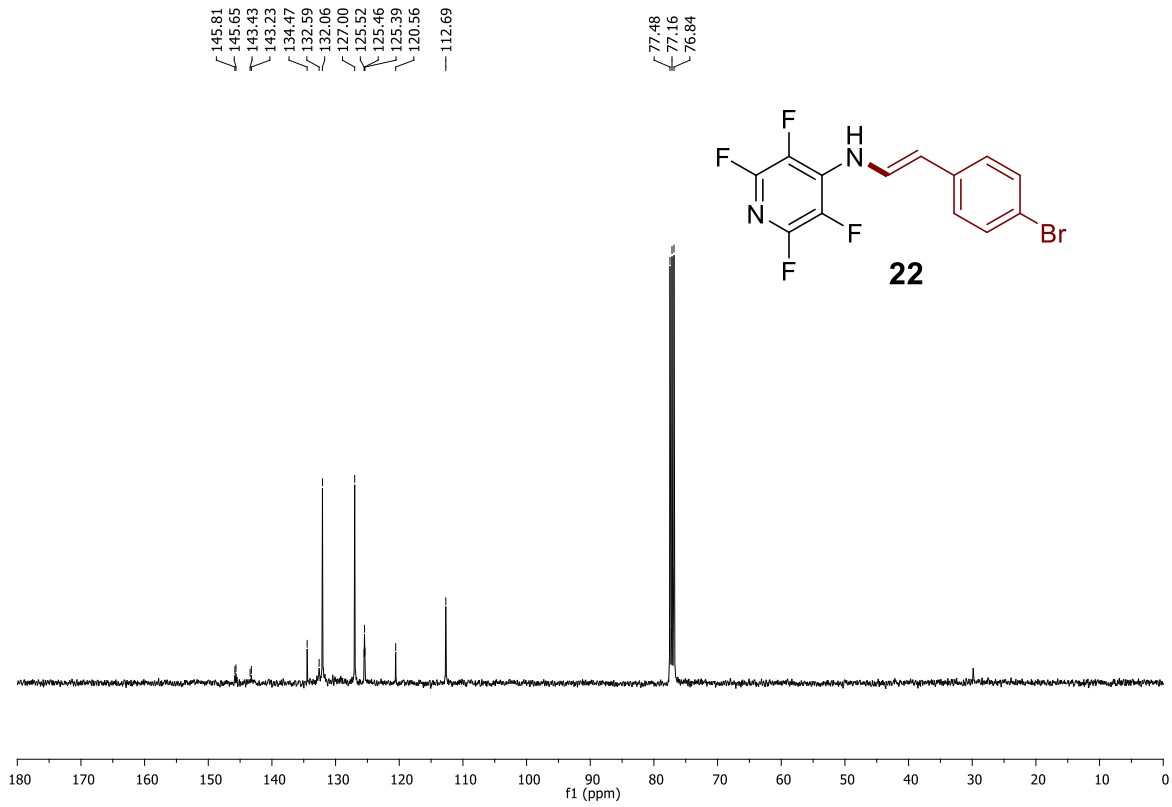
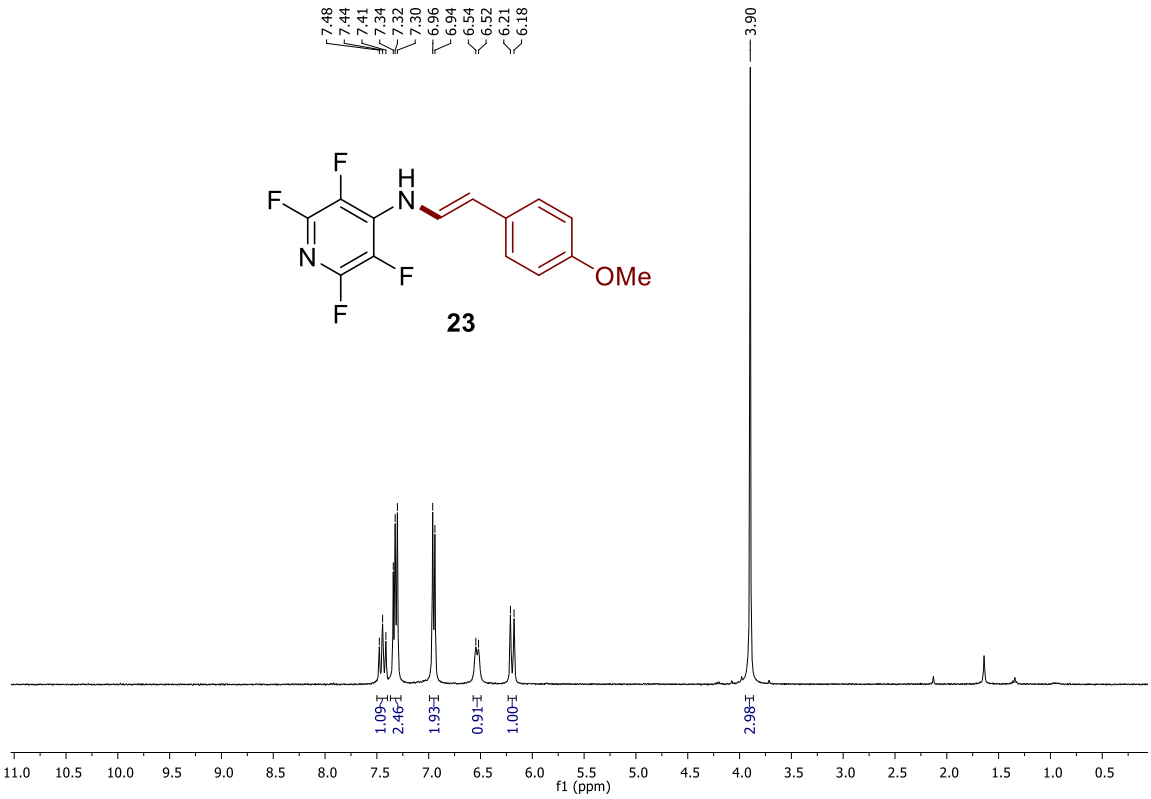
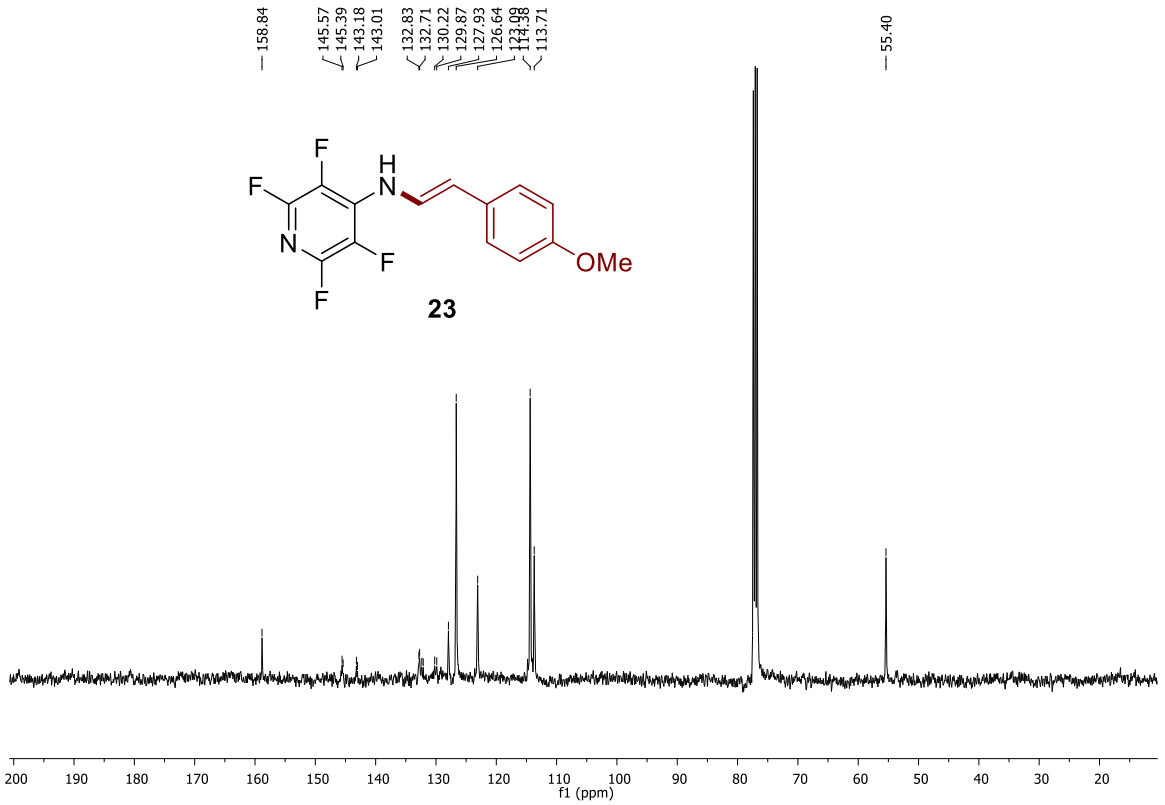
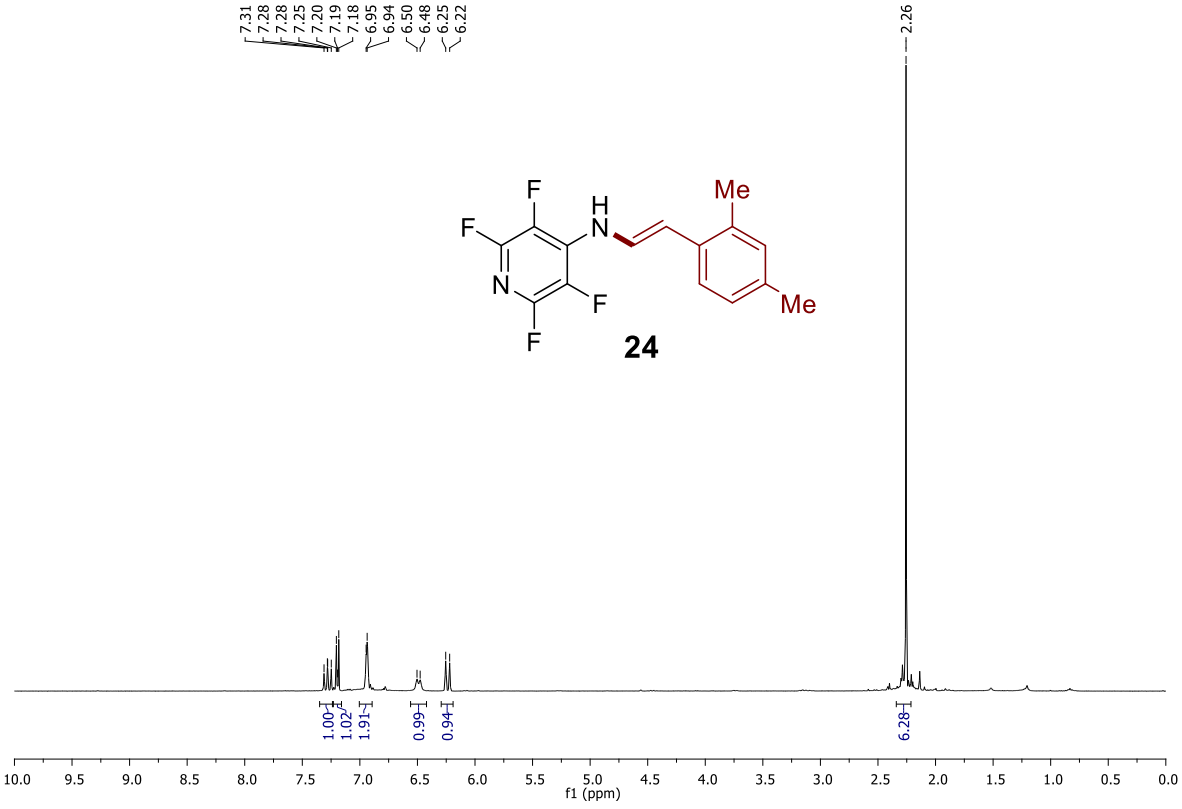
-92.71
-92.73
-92.75
-161.92
-161.94
-161.97
-162.01
-162.01
-162.05
-162.08
-162.10
F
H
N
F
N
F
F
Br
22
2.10
2.00
-20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

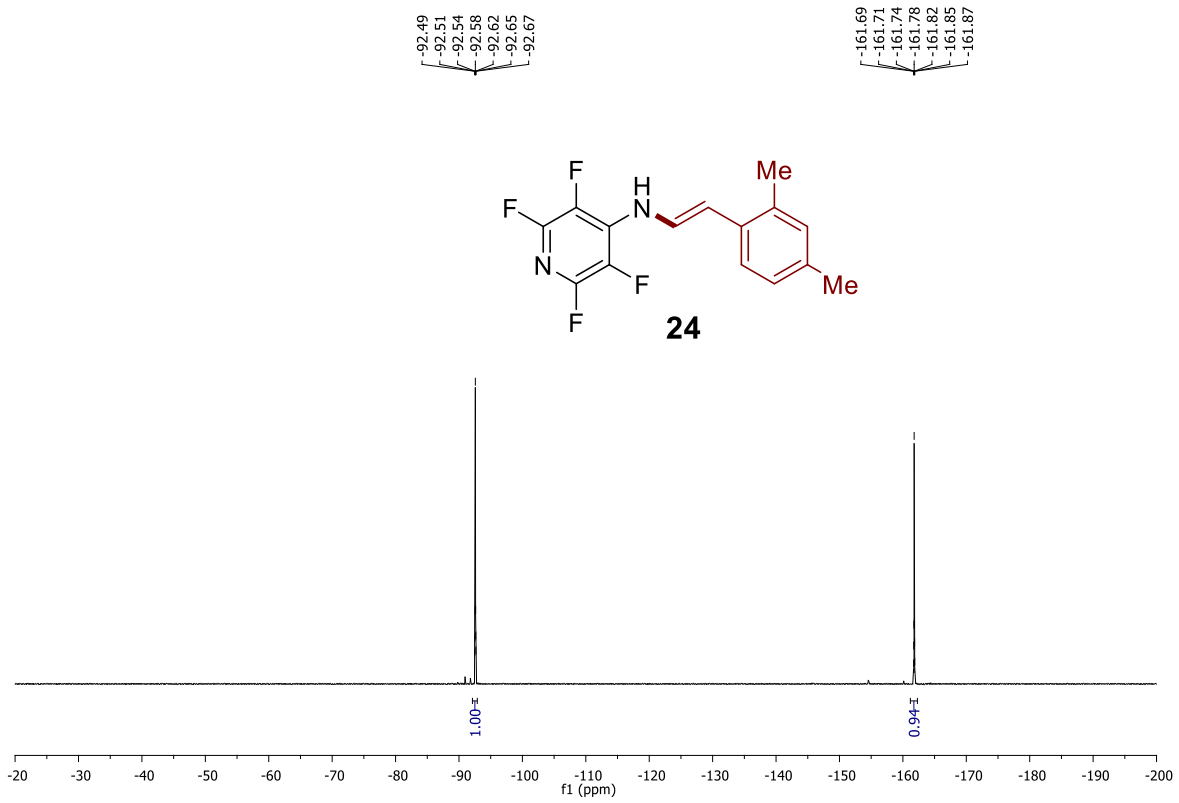

145.81
145.65
143.43
143.23
134.47
132.59
132.06
127.00
125.52
125.46
125.39
120.56
112.69
77.48
77.16
76.84
F
H
N
F
N
F
F
Br
22
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

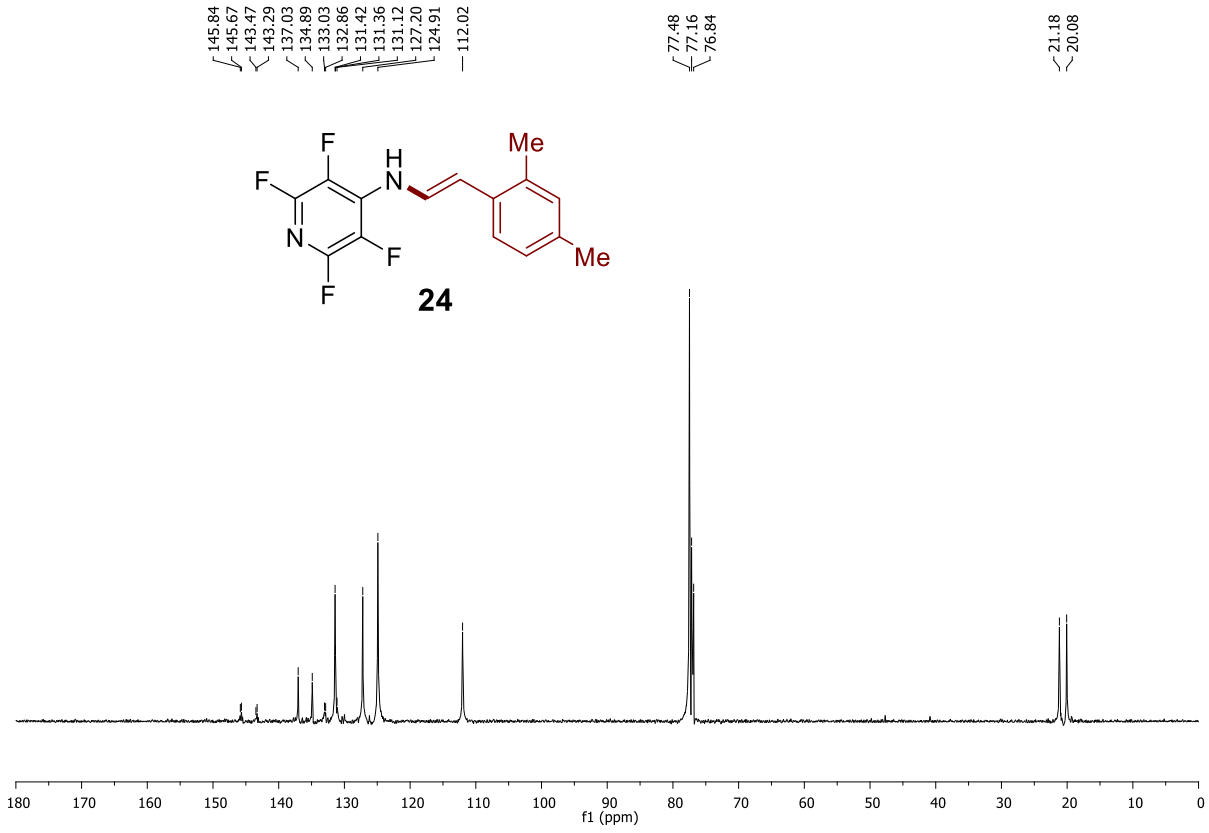

7.48
7.44
7.41
7.34
7.32
7.30
6.96
6.94
6.54
6.52
6.21
6.18
3.90
F
H
N
F
N
F
F
OMe
23
1.09
2.46
1.93
0.91
1.00
2.98
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

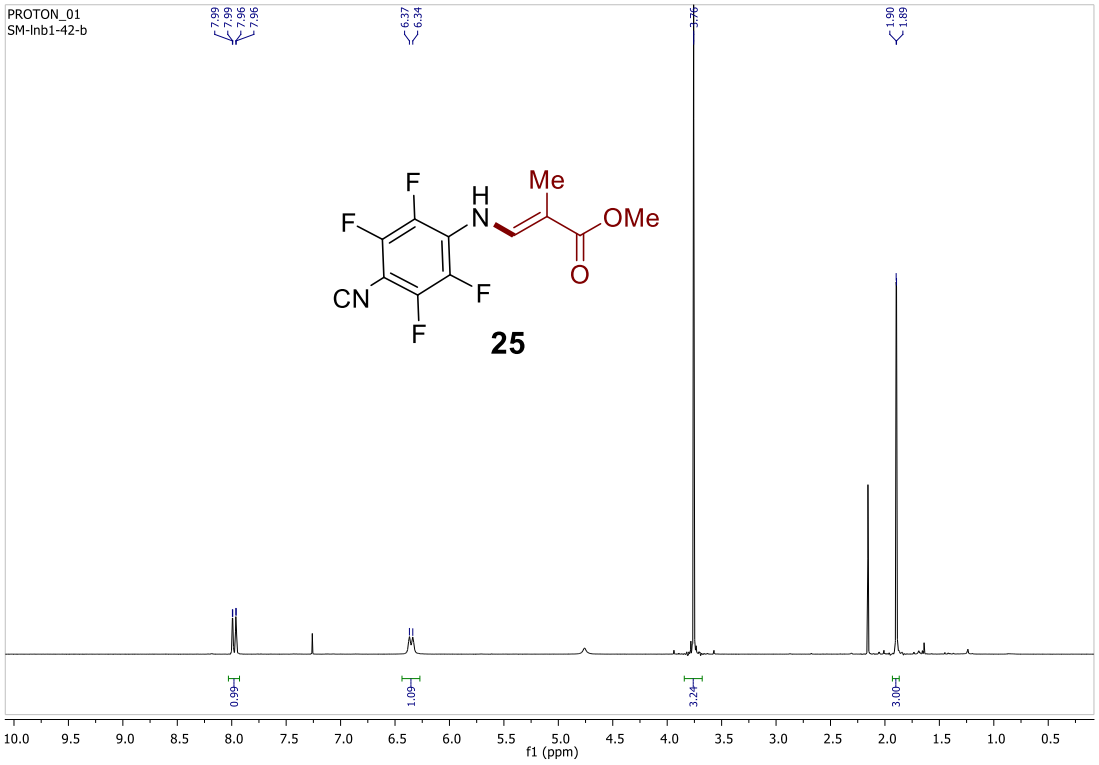

-91.92
-91.94
-91.97
-92.01
-92.05
-92.08
-92.10
-161.28
-161.31
-161.33
-161.37
-161.41
-161.44
-161.46
F
H
N
F
F
N
F
OMe
23
2.00
1.90
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


158.84
145.57
145.39
143.18
143.01
132.83
132.71
130.22
129.87
127.93
126.64
123.09
114.38
113.71
55.40
F
H
N
F
N
F
F
OMe
23
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)

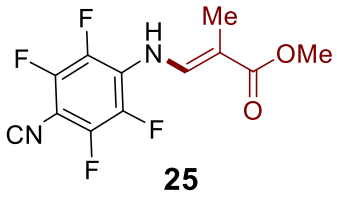

7.31
7.28
7.28
7.25
7.20
7.19
7.18
6.95
6.94
6.50
6.48
6.25
6.22
2.26
F
H
N
F
N
F
F
Me
Me
24
1.00
1.02
1.91
0.99
0.94
6.28
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

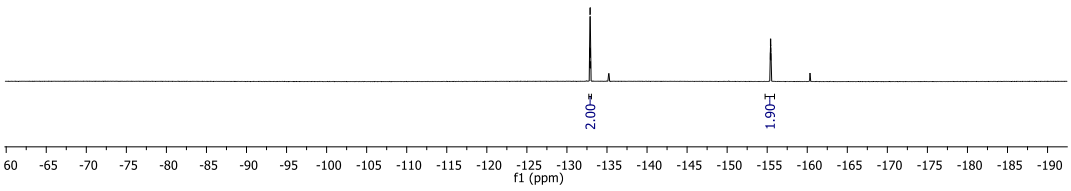

-92.49
-92.51
-92.54
-92.58
-92.62
-92.65
-92.67
-161.69
-161.71
-161.74
-161.78
-161.82
-161.85
-161.87
F
H
N
F
N
F
F
Me
Me
24
1.00
0.94
-20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

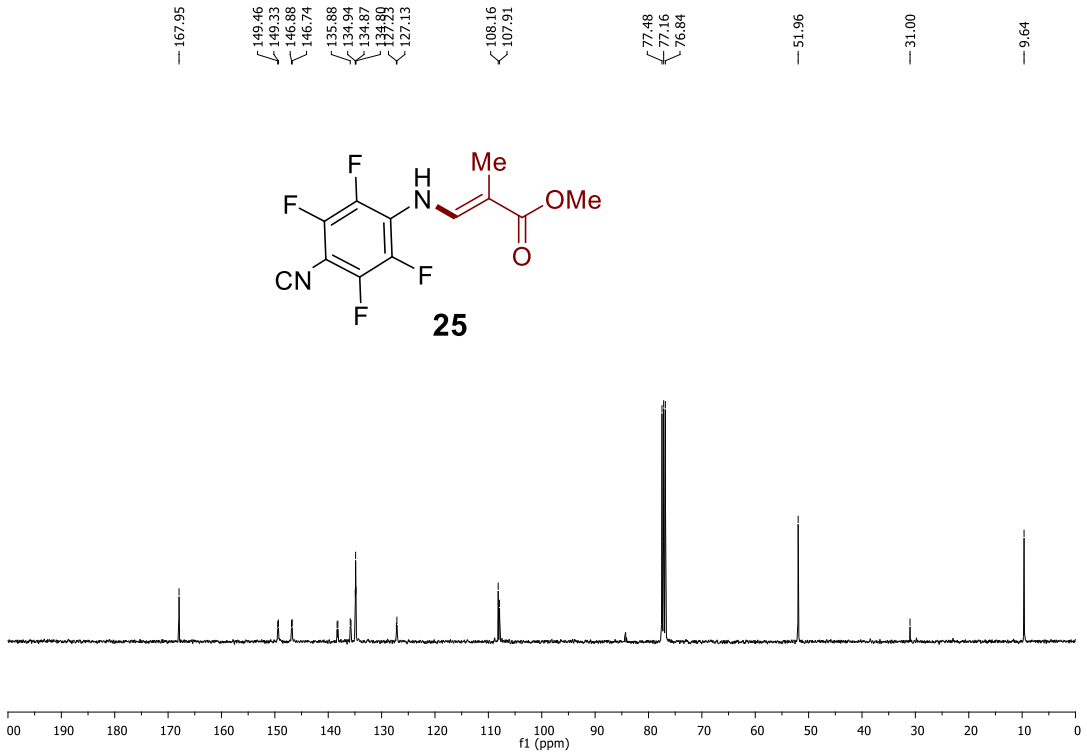

145.84
145.67
143.47
143.29
137.03
134.89
133.03
132.86
131.42
131.36
131.12
127.20
124.91
112.02
77.48
77.16
76.84
21.18
20.08
F
H
N
F
N
F
F
Me
Me
24
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


PROTON_01
SM-Inb1-42-b
7.99
7.99
7.96
7.96
6.37
6.34
3.76
1.90
1.89
F
H
N
Me
OMe
O
F
CN
F
F
25
0.99
1.09
3.24
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

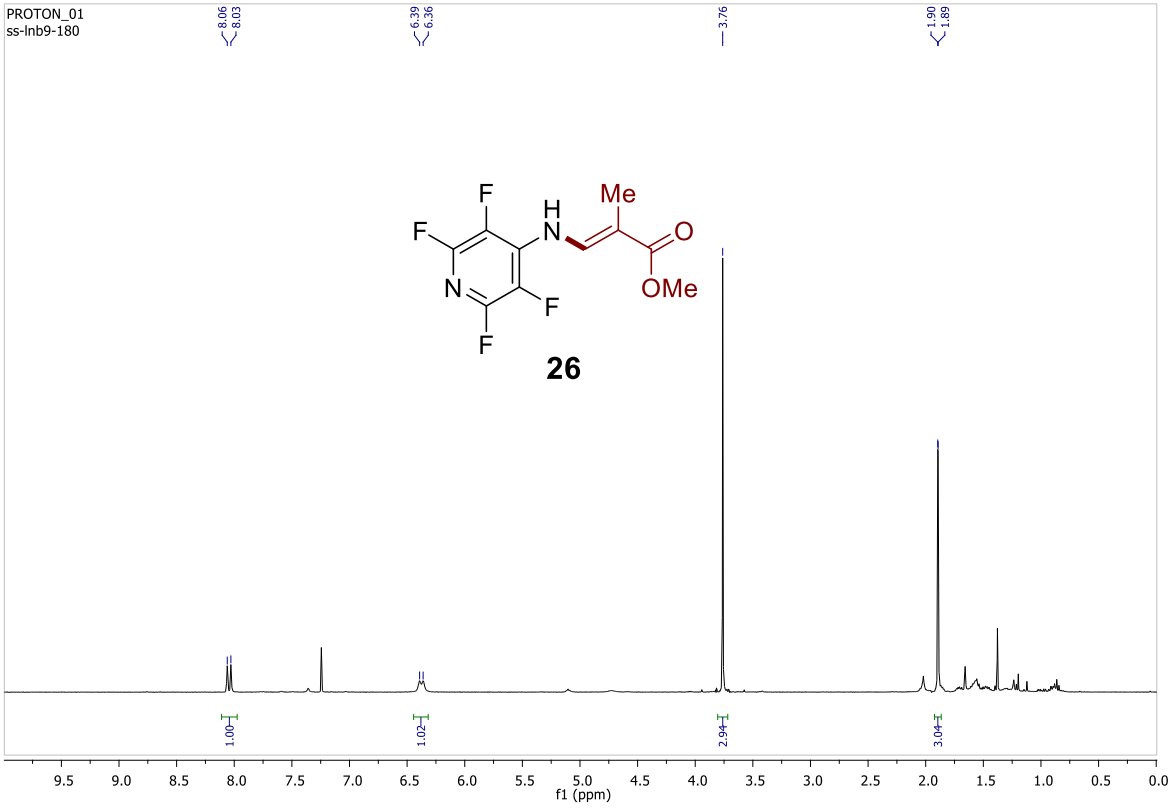

-132.84
-132.86
-132.87
-132.88
-132.91
-132.92
-132.93
-132.95
-155.40
-155.41
-155.41
-155.44
-155.45
-155.46


F
H
N
Me
OMe
O
F
CN
F
F
25

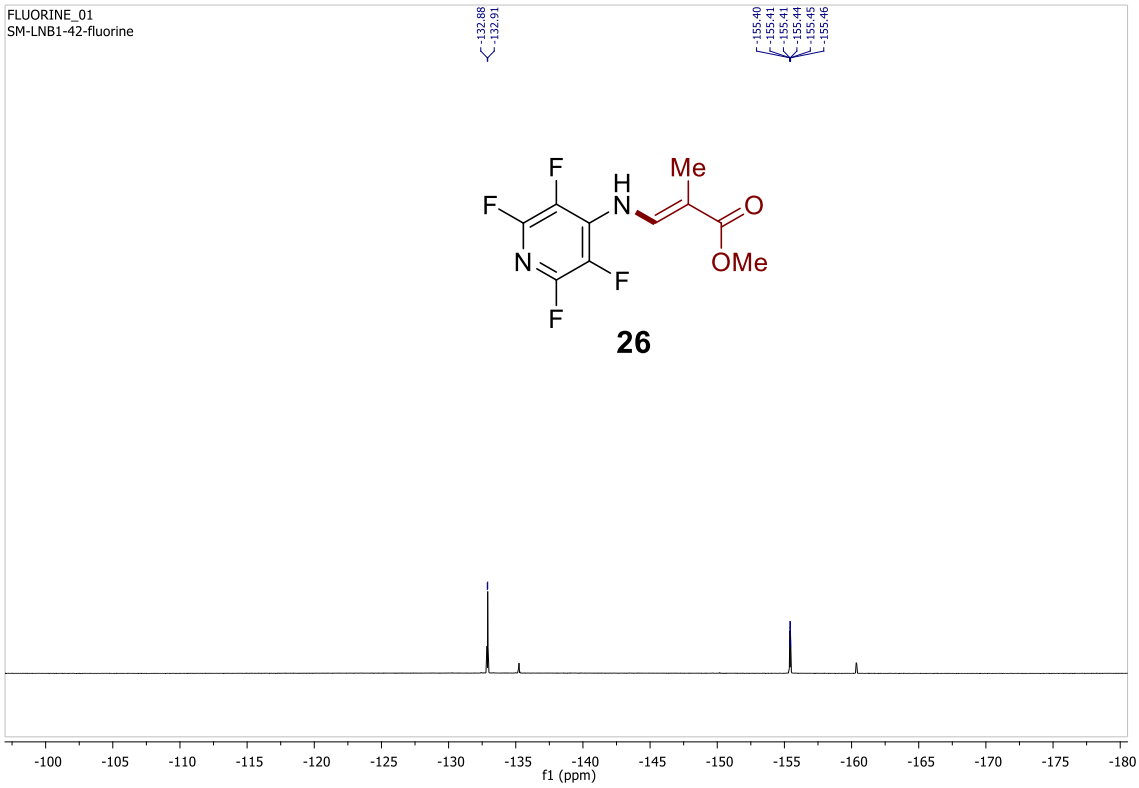

2.00
1.90
60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
-170
-175
-180
-185
-190
f1 (ppm)

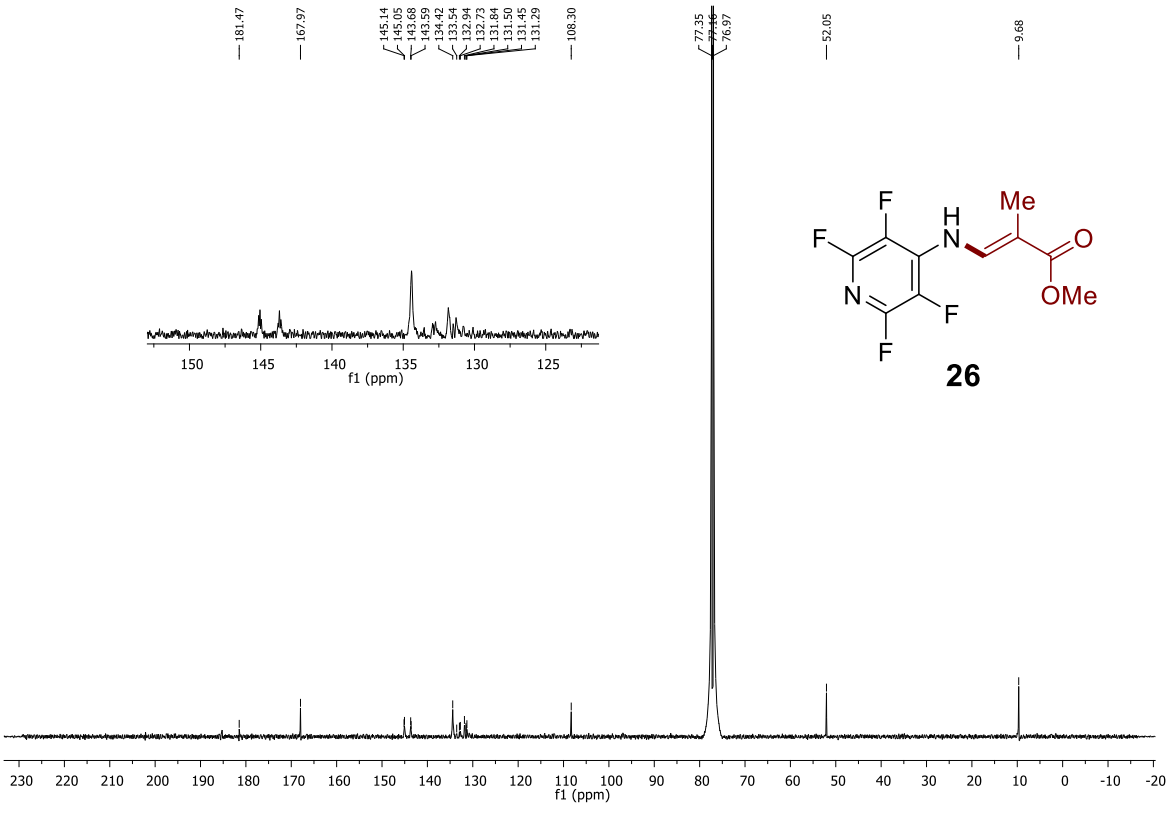

167.95
149.46
149.33
146.88
146.74
135.88
134.94
134.87
127.13
108.16
107.91
77.48
77.16
76.84
51.96
31.00
9.64
F
H
N
Me
OMe
O
F
CN
F
F
f1 (ppm)

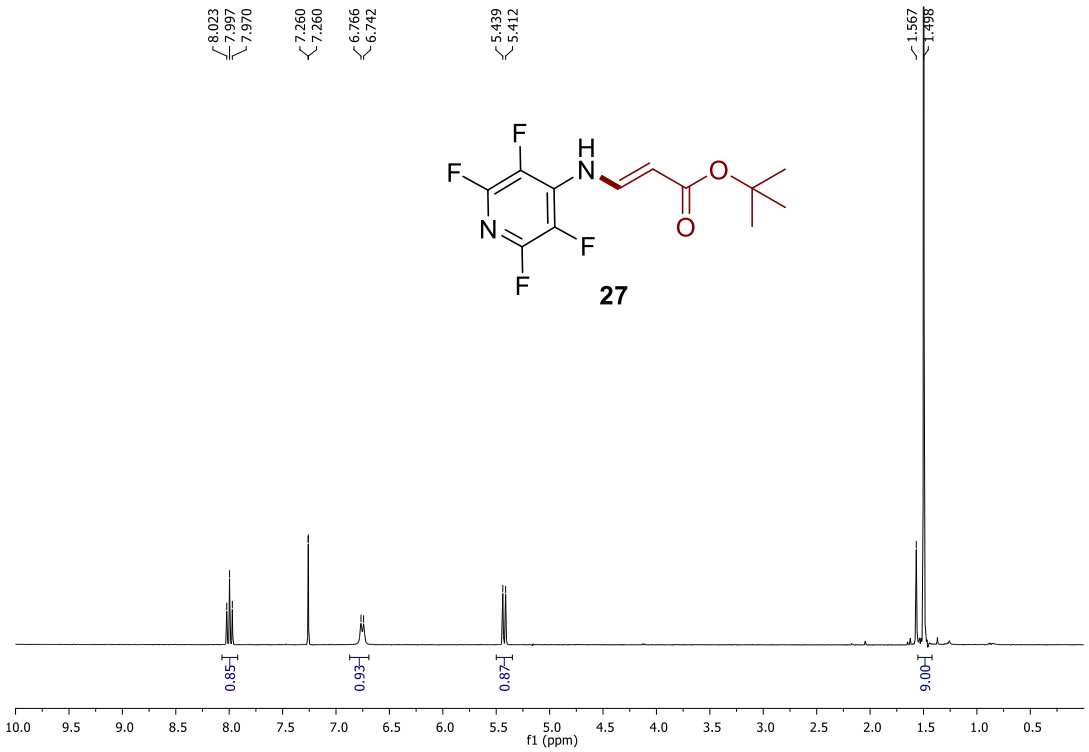
25

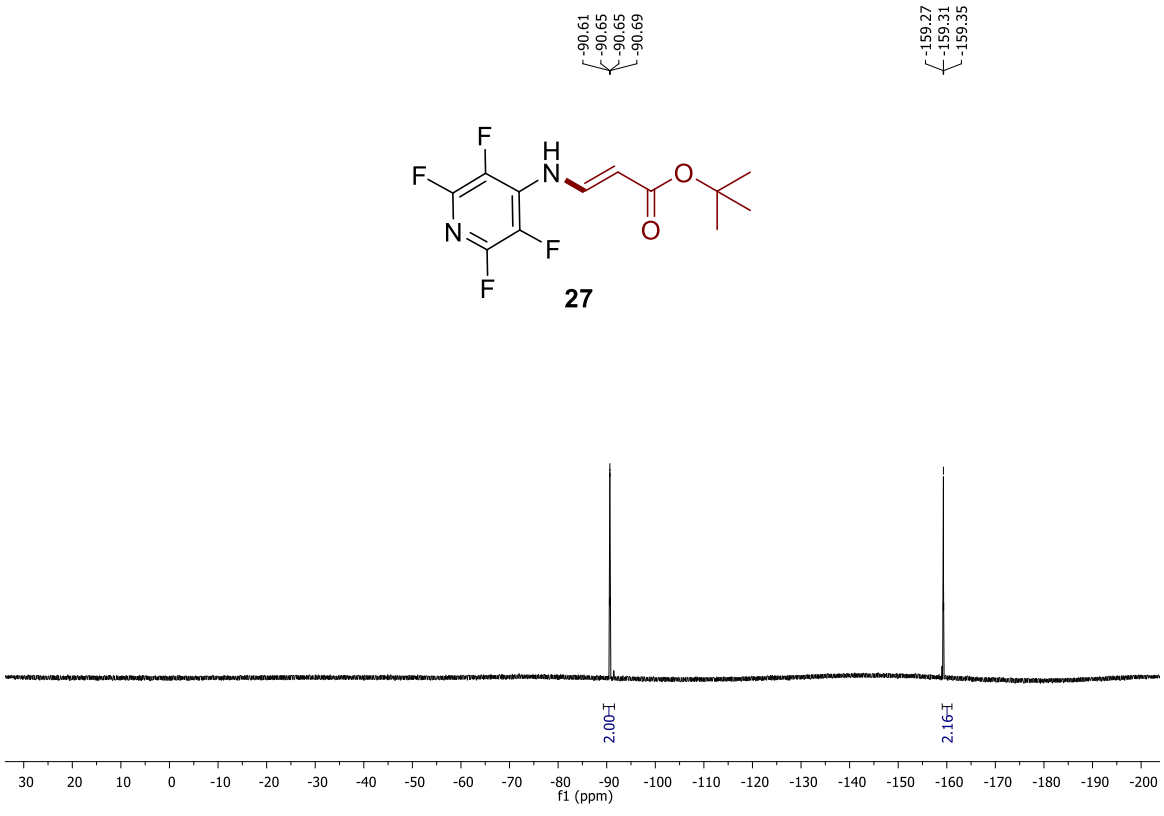

PROTON_01
ss-lnb9-180
8.06
8.03
6.39
6.36
3.76
1.90
1.89
F
H
N
Me
O
F
N
F
OMe
F
1.00
1.02
2.94
3.04
f1 (ppm)

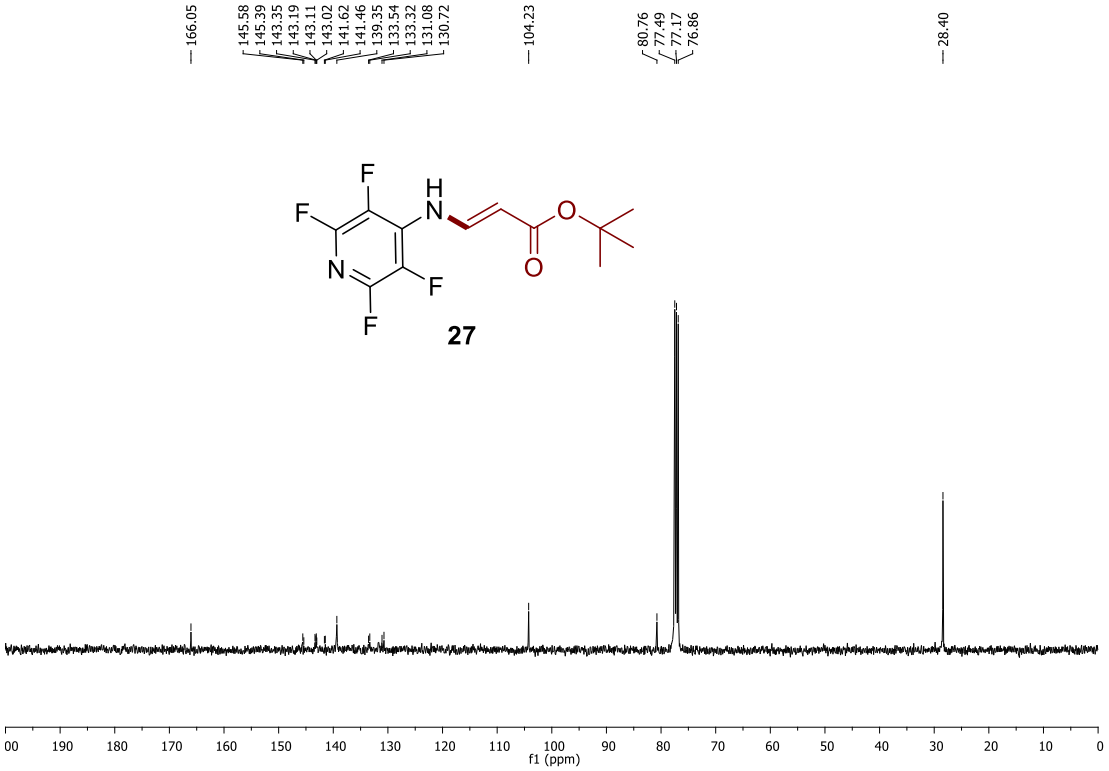
26

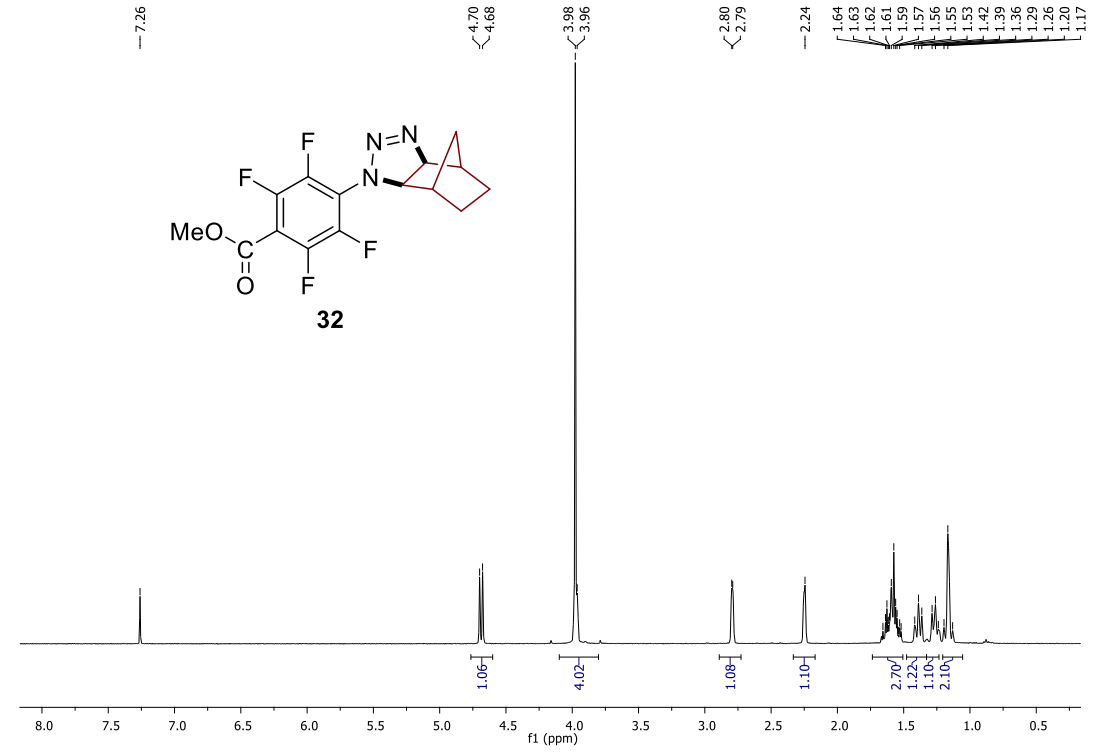

FLUORINE_01
SM-LNB1-42-fluorine
-132.88
-132.91
-155.40
-155.41
-155.41
-155.44
-155.45
-155.46
F
F
H
N
Me
O
OMe
N
F
F
26
-100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180
f1 (ppm)

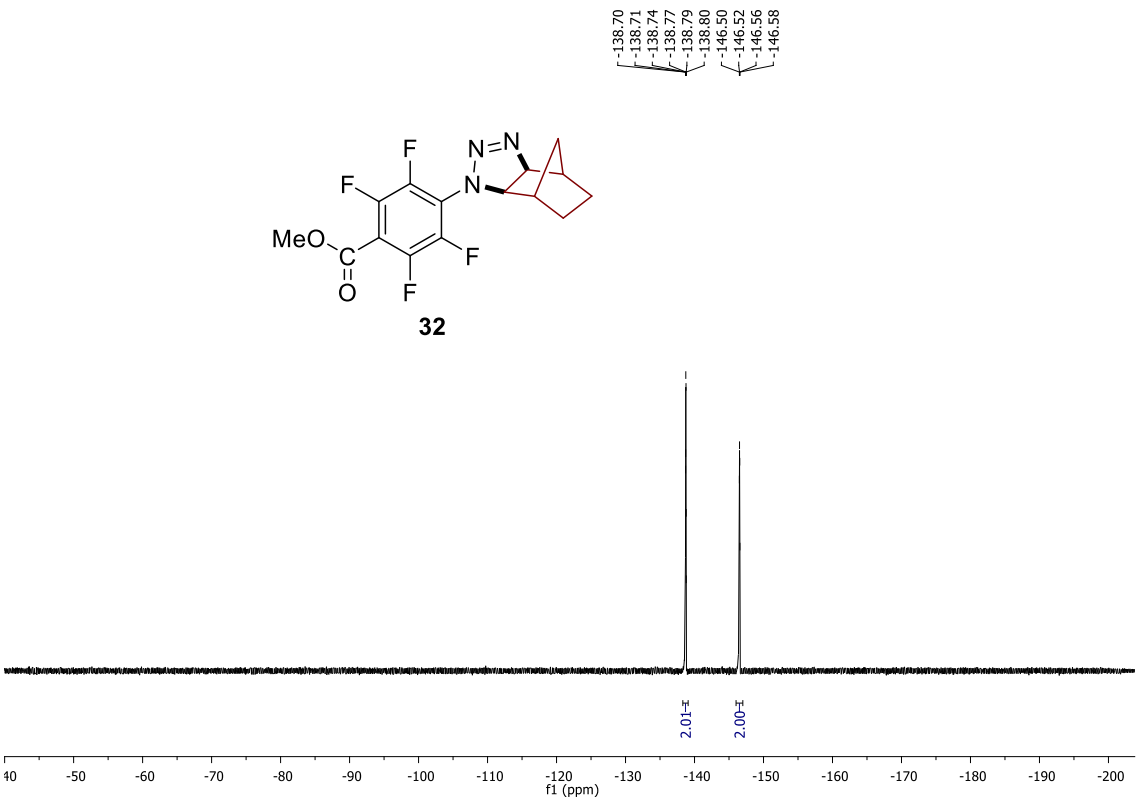

181.47
167.97
145.14
145.05
143.68
143.59
134.42
133.54
132.94
132.73
131.84
131.50
131.45
131.29
108.30
77.35
77.16
76.97
52.05
9.68
F
F
H
N
Me
O
OMe
N
F
F
26
150 145 140 135 130 125
f1 (ppm)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


8.023
7.997
7.970
7.260
7.260
6.766
6.742
5.439
5.412
1.567
1.498
F
F
H
N
O
N
F
F
O
27
0.85
0.93
0.87
9.00
f1 (ppm)


-90.61
-90.65
-90.65
-90.69
-159.27
-159.31
-159.35
F
F
H
N
O
N
F
F
O
27
2.00
2.16
f1 (ppm)

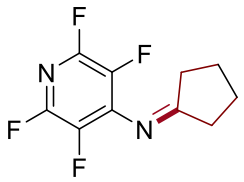

166.05
145.58
145.39
143.35
143.19
143.11
143.02
141.62
141.46
139.35
133.54
133.32
131.08
130.72
104.23
80.76
77.49
77.17
76.86
28.40
F
H
N
F
O
N
O
F
F
27
f1 (ppm)


7.26
4.70
4.68
3.98
3.96
2.80
2.79
2.24
1.64
1.63
1.62
1.61
1.59
1.57
1.56
1.55
1.53
1.42
1.39
1.36
1.29
1.26
1.20
1.17
F
N=N
F
N
MeO
C
O
F
F
32
1.06
4.02
1.08
1.10
2.70
1.22
1.10
2.10
f1 (ppm)

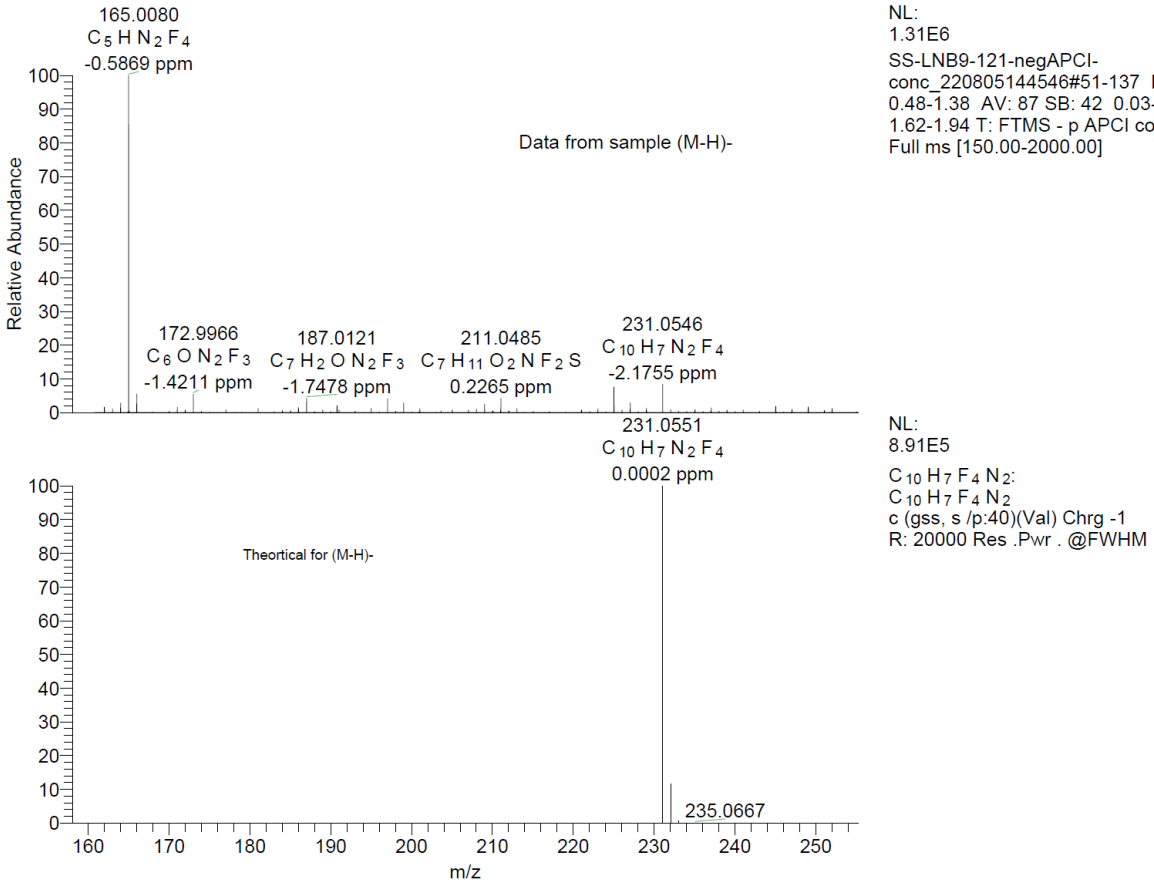

-138.70
-138.71
-138.74
-138.77
-138.79
-138.80
-146.50
-146.52
-146.56
-146.58
F
N=N
F
N
MeO
C
O
F
F
2.01
2.00
40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

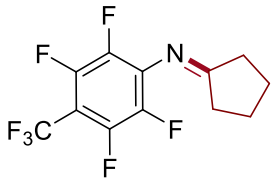
32

13. HRMS ANALYSIS

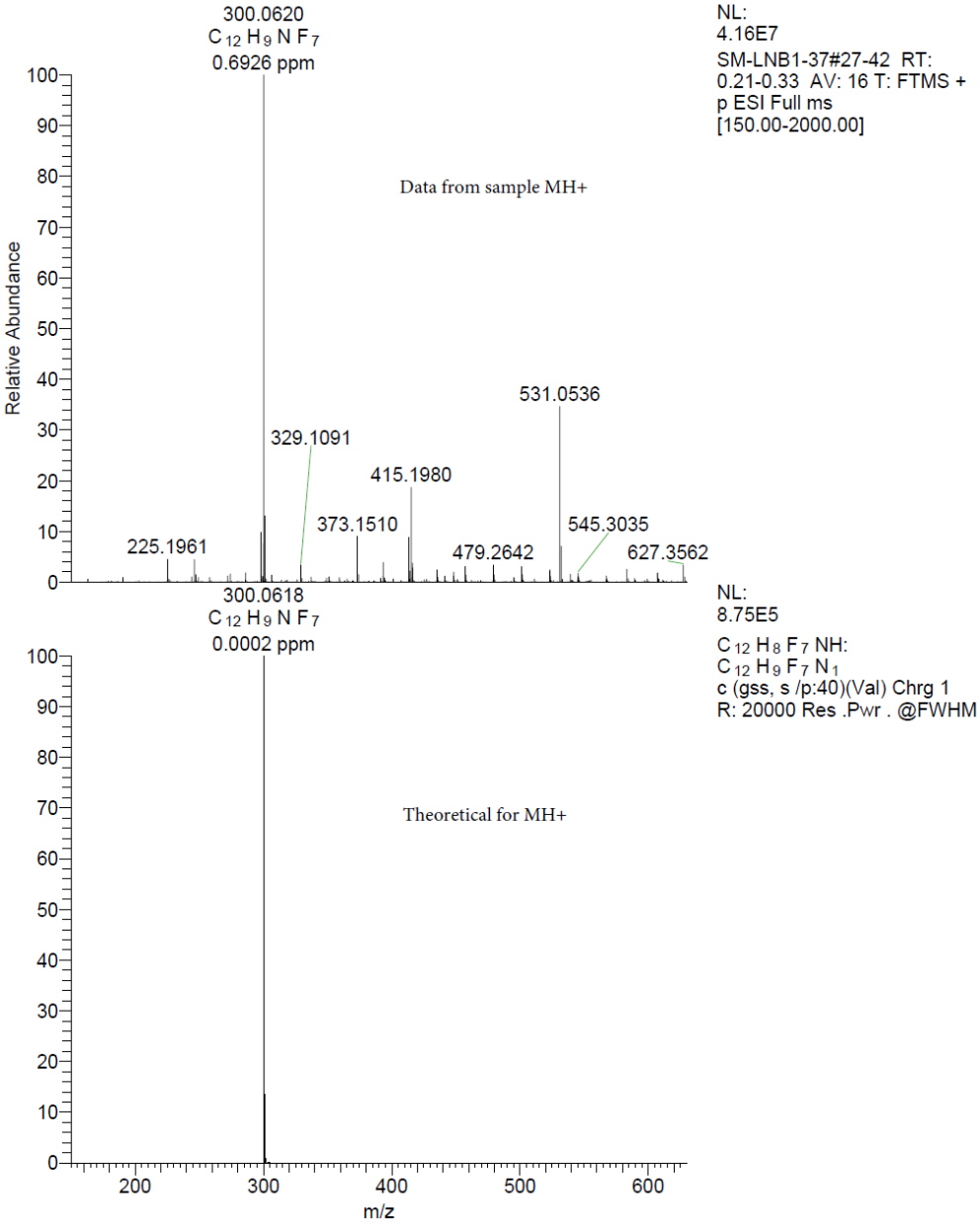


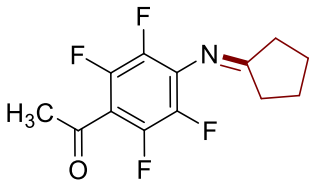
3



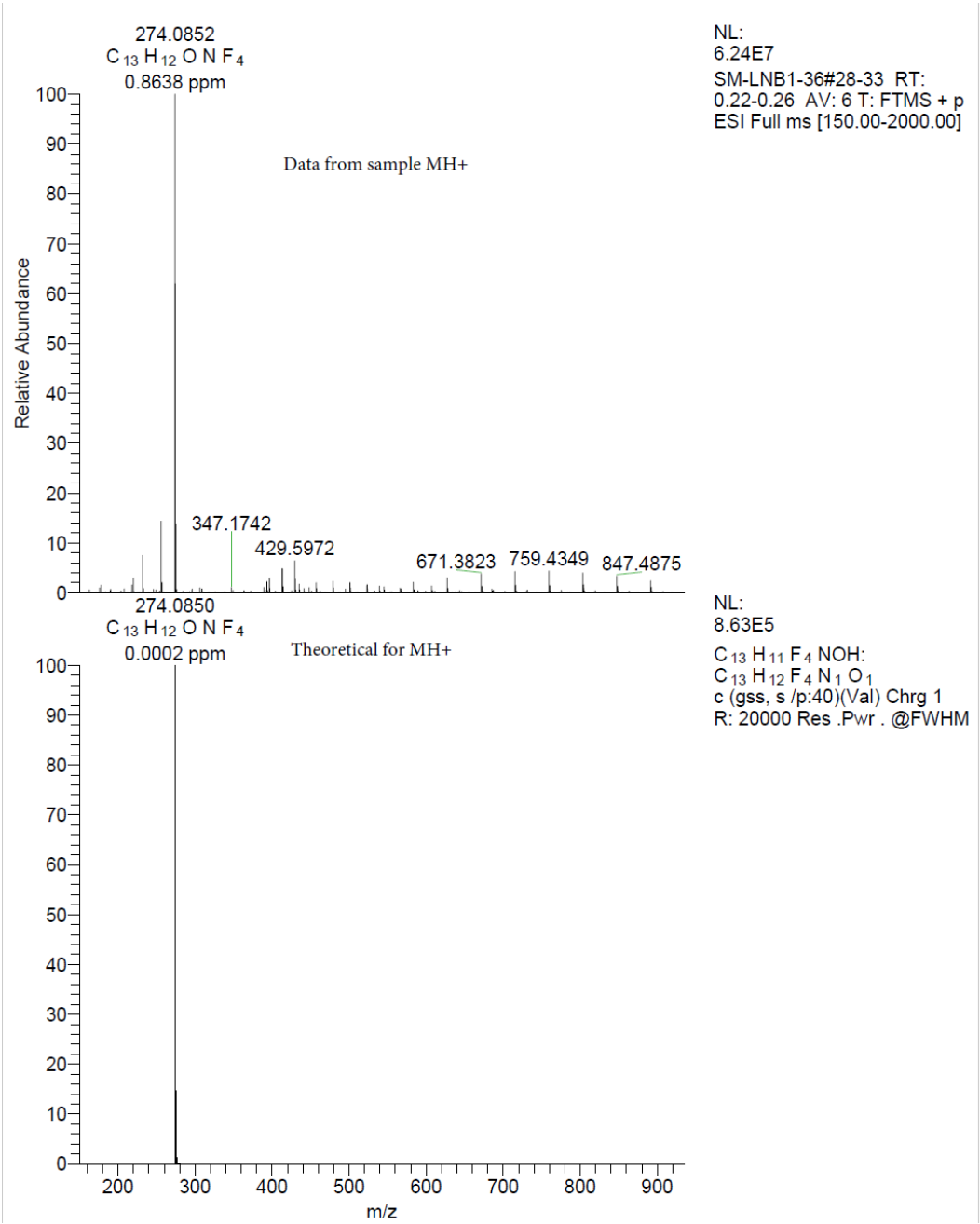

F
F
N
F3C
F
F

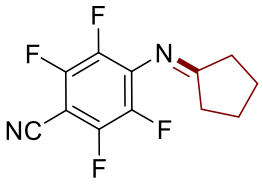
4


300.0620
C12 H9 N F7
0.6926 ppm
NL:
4.16E7
SM-LNB1-37#27-42 RT:
0.21-0.33 AV: 16 T: FTMS +
p ESI Full ms
[150.00-2000.00]
Data from sample MH+
Relative Abundance
531.0536
329.1091
415.1980
373.1510
545.3035
225.1961
479.2642
627.3562
300.0618
C12 H9 N F7
0.0002 ppm
NL:
8.75E5
C12 H8 F7 NH:
C12 H9 F7 N1
c (gss, s /p:40)(Val) Chrg 1
R: 20000 Res .Pwr . @FWHM
Theoretical for MH+
m/z

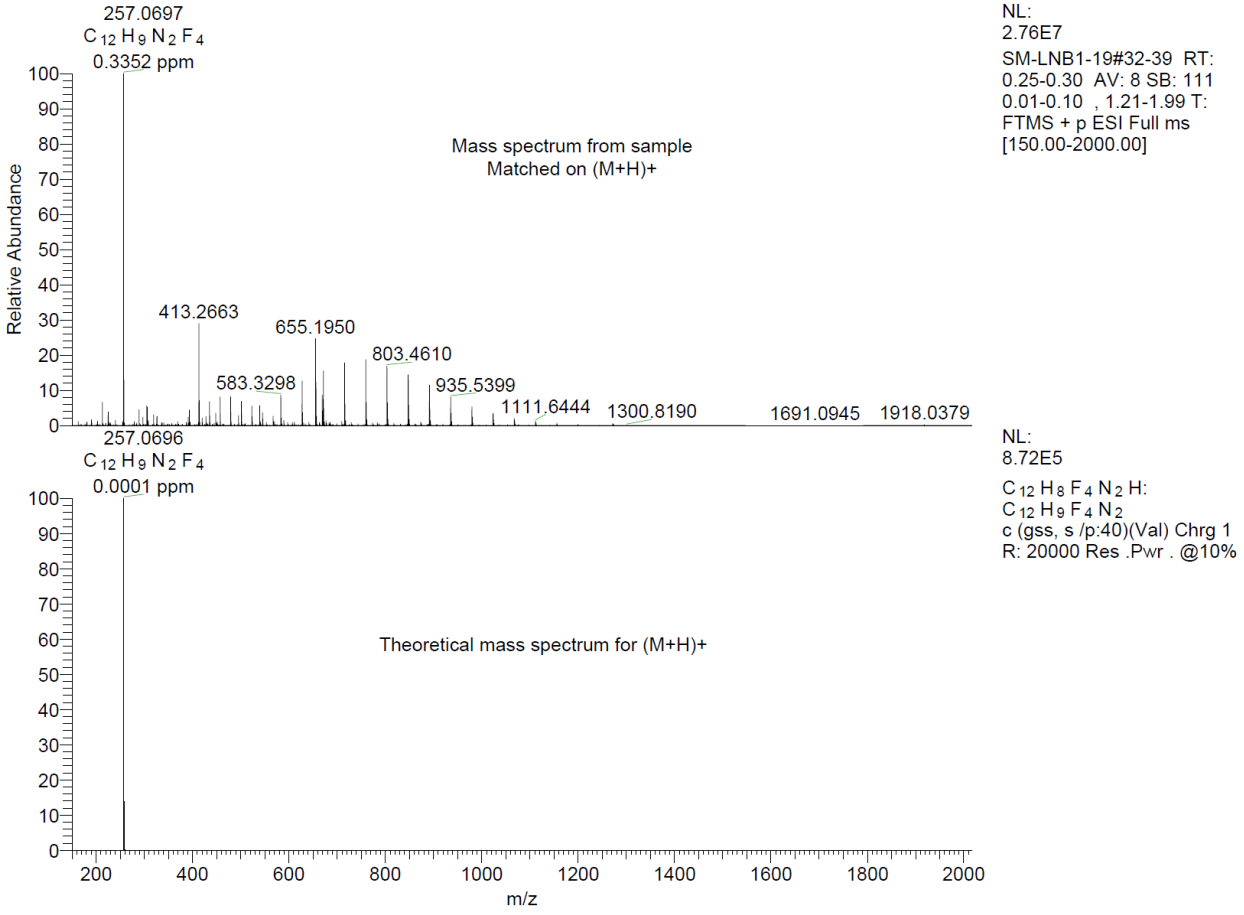

F
F
N
H3C
F
O
F

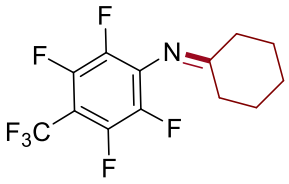
5


274.0852
C 13 H 12 O N F 4
0.8638 ppm
Data from sample MH+
NL:
6.24E7
SM-LNB1-36#28-33 RT:
0.22-0.26 AV: 6 T: FTMS + p
ESI Full ms [150.00-2000.00]
Relative Abundance
347.1742
429.5972
671.3823
759.4349
847.4875
274.0850
C 13 H 12 O N F 4
0.0002 ppm
Theoretical for MH+
NL:
8.63E5
C 13 H 11 F 4 NOH:
C 13 H 12 F 4 N 1 O 1
c (gss, s /p:40)(Val) Chrg 1
R: 20000 Res .Pwr . @FWHM
m/z

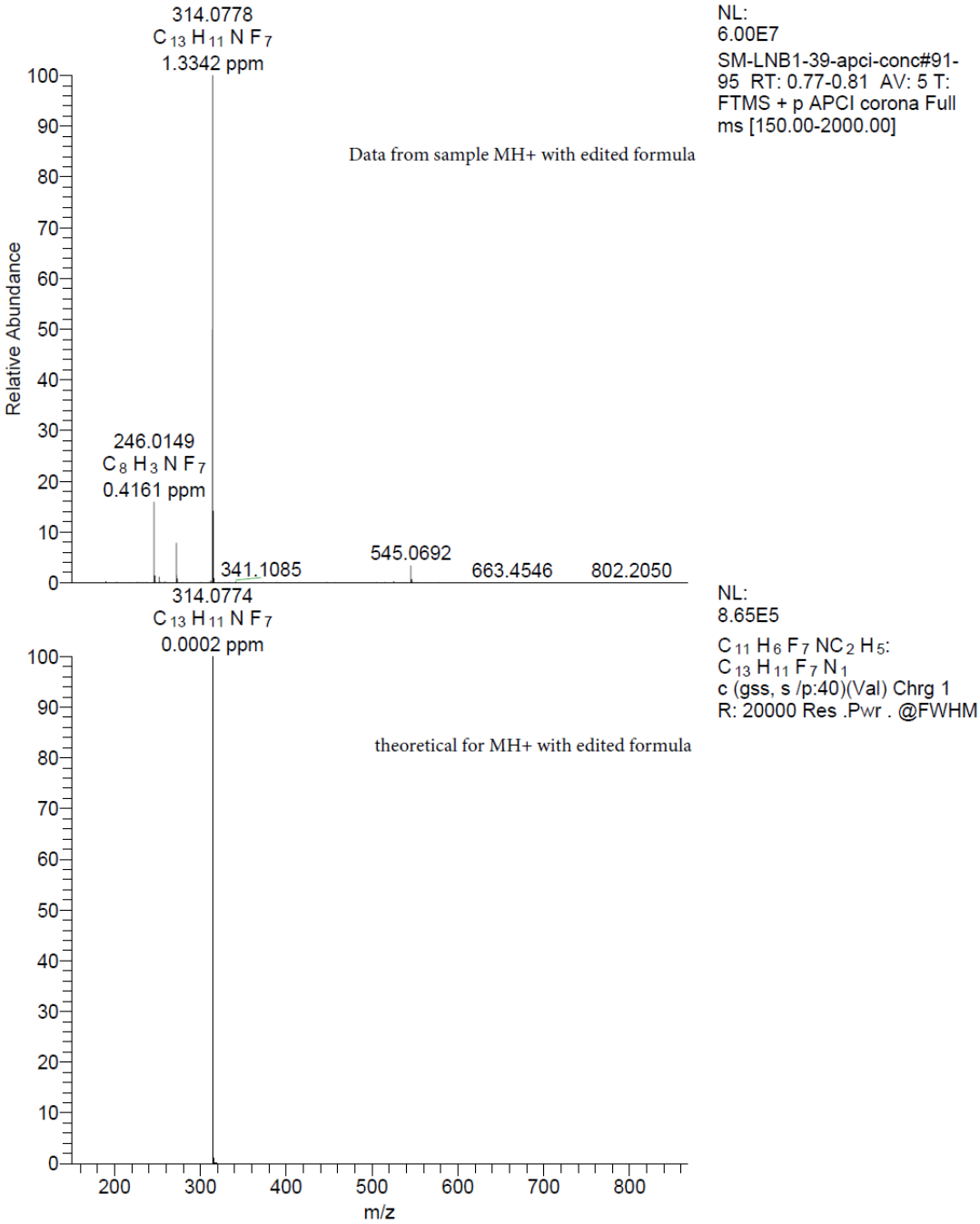

F
F
N
NC
F
F

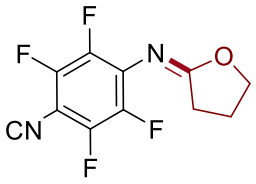
6


257.0697
C 12 H 9 N 2 F 4
0.3352 ppm
NL:
2.76E7
SM-LNB1-19#32-39 RT:
0.25-0.30 AV: 8 SB: 111
0.01-0.10 , 1.21-1.99 T:
FTMS + p ESI Full ms
[150.00-2000.00]
Mass spectrum from sample
Matched on (M+H)+
Relative Abundance
413.2663
655.1950
803.4610
583.3298
935.5399
1111.6444
1300.8190
1691.0945
1918.0379
257.0696
C 12 H 9 N 2 F 4
0.0001 ppm
NL:
8.72E5
C 12 H 8 F 4 N 2 H:
C 12 H 9 F 4 N 2
c (gss, s /p:40)(Val) Chrg 1
R: 20000 Res .Pwr . @10%
Theoretical mass spectrum for (M+H)+
m/z

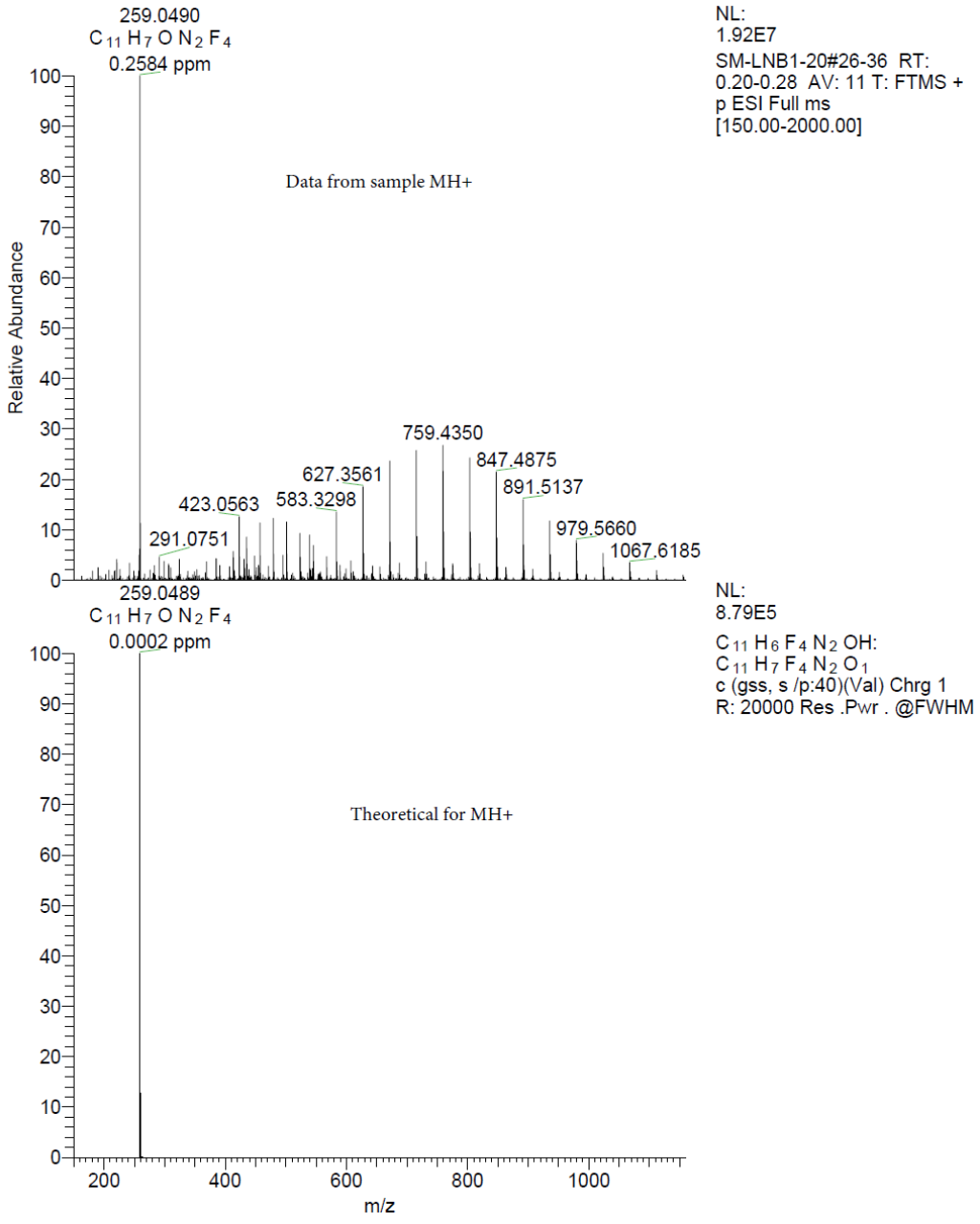

F
F
N
F3C
F
F

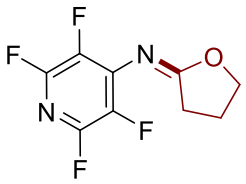
8


314.0778
C13 H11 N F7
1.3342 ppm
NL:
6.00E7
SM-LNB1-39-apci-conc#91-95 RT: 0.77-0.81 AV: 5 T: FTMS + p APCI corona Full ms [150.00-2000.00]
Data from sample MH+ with edited formula
Relative Abundance
246.0149
C8 H3 N F7
0.4161 ppm
341.1085
545.0692
663.4546
802.2050
314.0774
C13 H11 N F7
0.0002 ppm
NL:
8.65E5
C11 H6 F7 NC2 H5:
C13 H11 F7 N1
c (gss, s /p:40)(Val) Chrg 1
R: 20000 Res .Pwr . @FWHM
theoretical for MH+ with edited formula
m/z

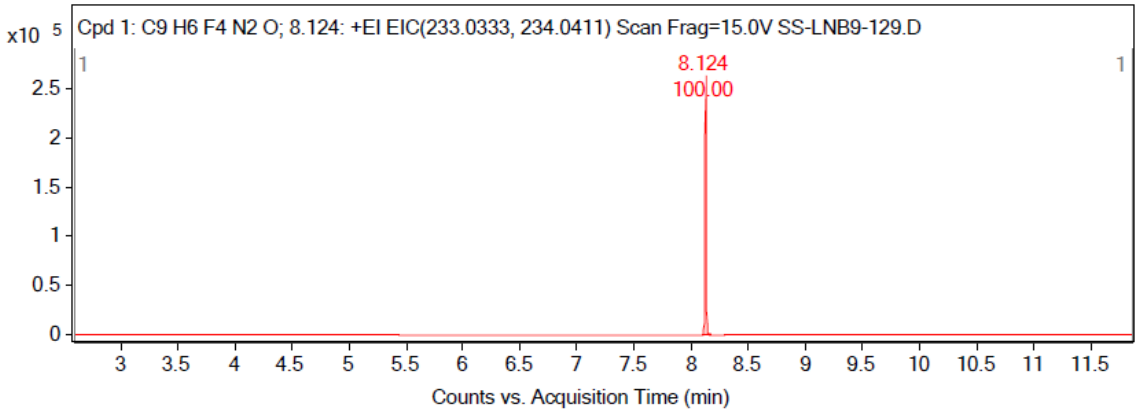

F
F
N
O
CN
F
F

9

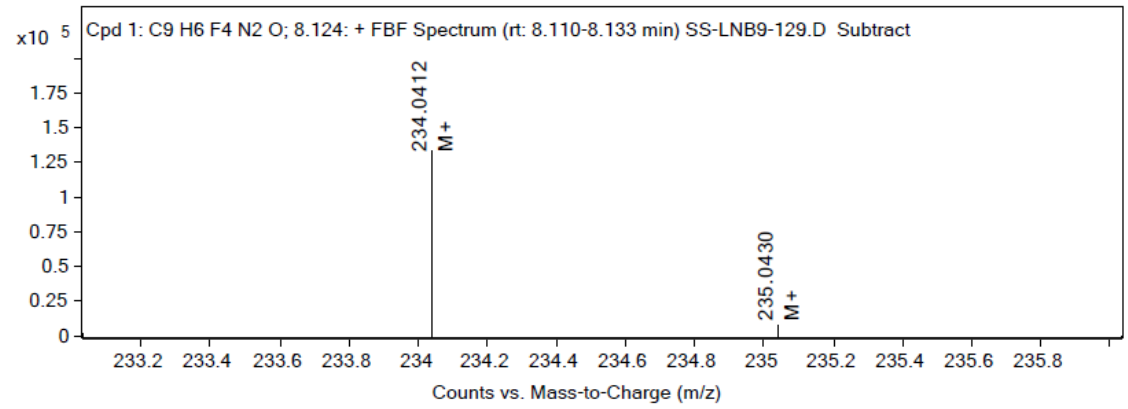

259.0490
C 11 H 7 O N 2 F 4
0.2584 ppm
NL:
1.92E7
SM-LNB1-20#26-36 RT:
0.20-0.28 AV: 11 T: FTMS +
p ESI Full ms
[150.00-2000.00]
Data from sample MH+
Relative Abundance
759.4350
847.4875
627.3561
891.5137
583.3298
423.0563
979.5660
291.0751
1067.6185
259.0489
C 11 H 7 O N 2 F 4
0.0002 ppm
NL:
8.79E5
C 11 H 6 F 4 N 2 OH:
C 11 H 7 F 4 N 2 O 1
c (gss, s /p:40)(Val) Chrg 1
R: 20000 Res .Pwr . @FWHM
Theoretical for MH+
m/z



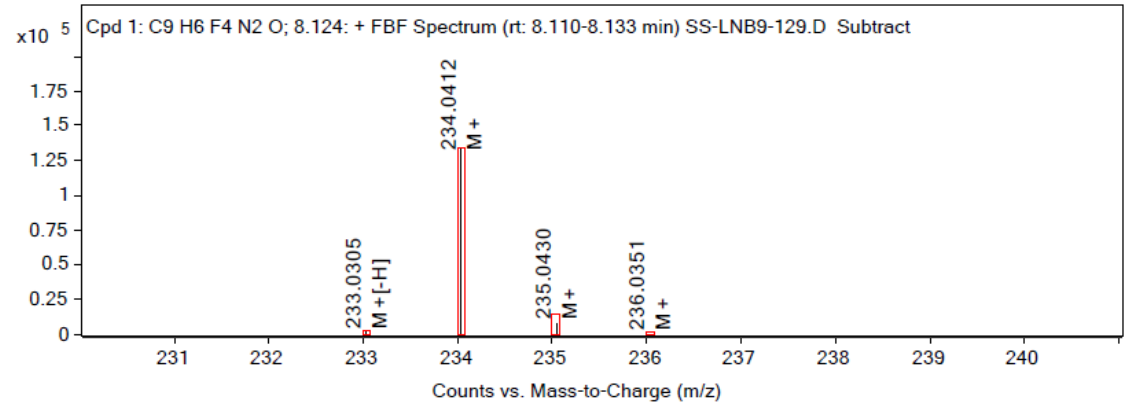
10

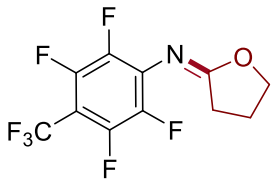


MS Spectrum

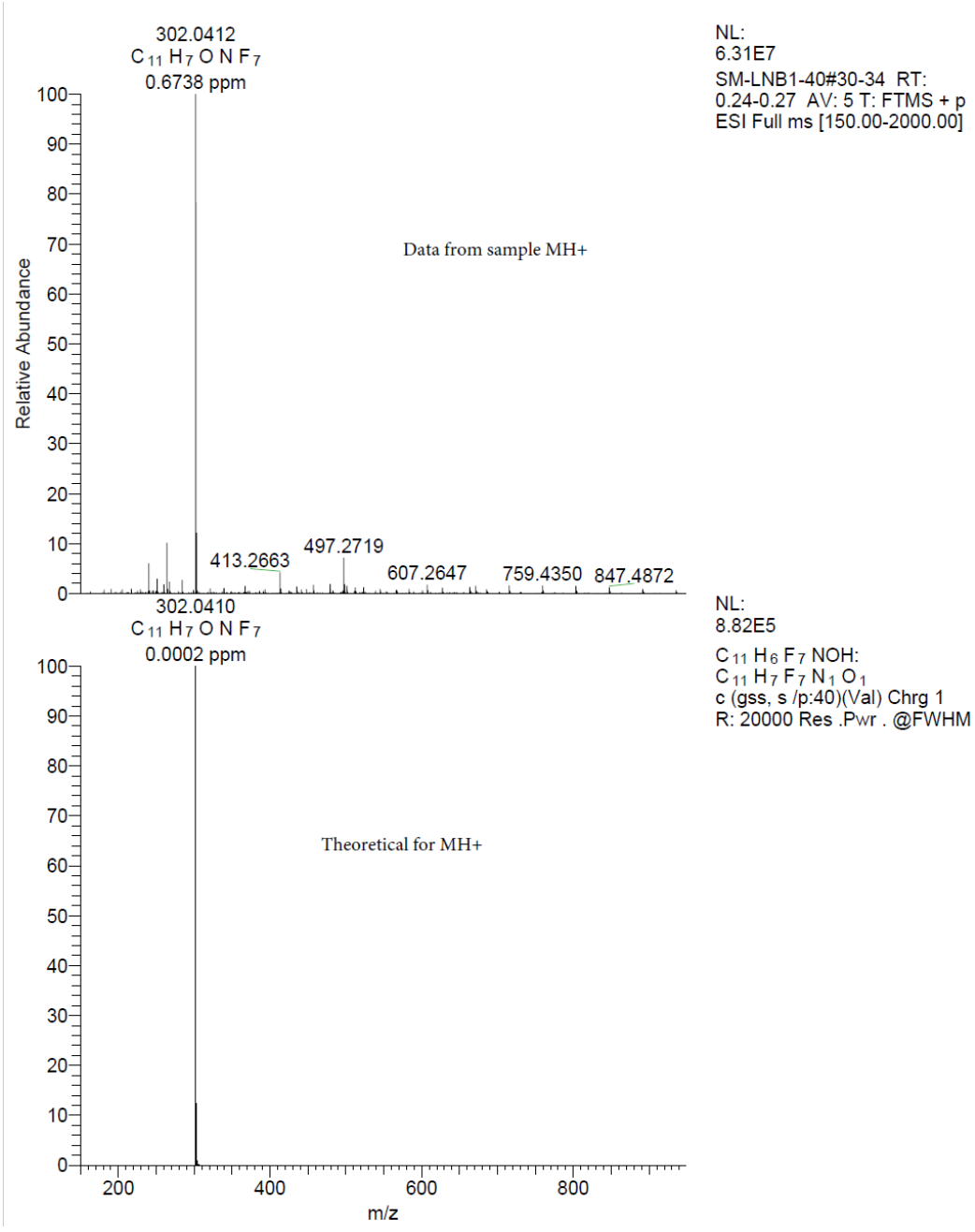


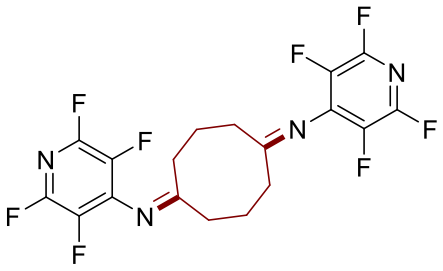
MS Zoomed Spectrum



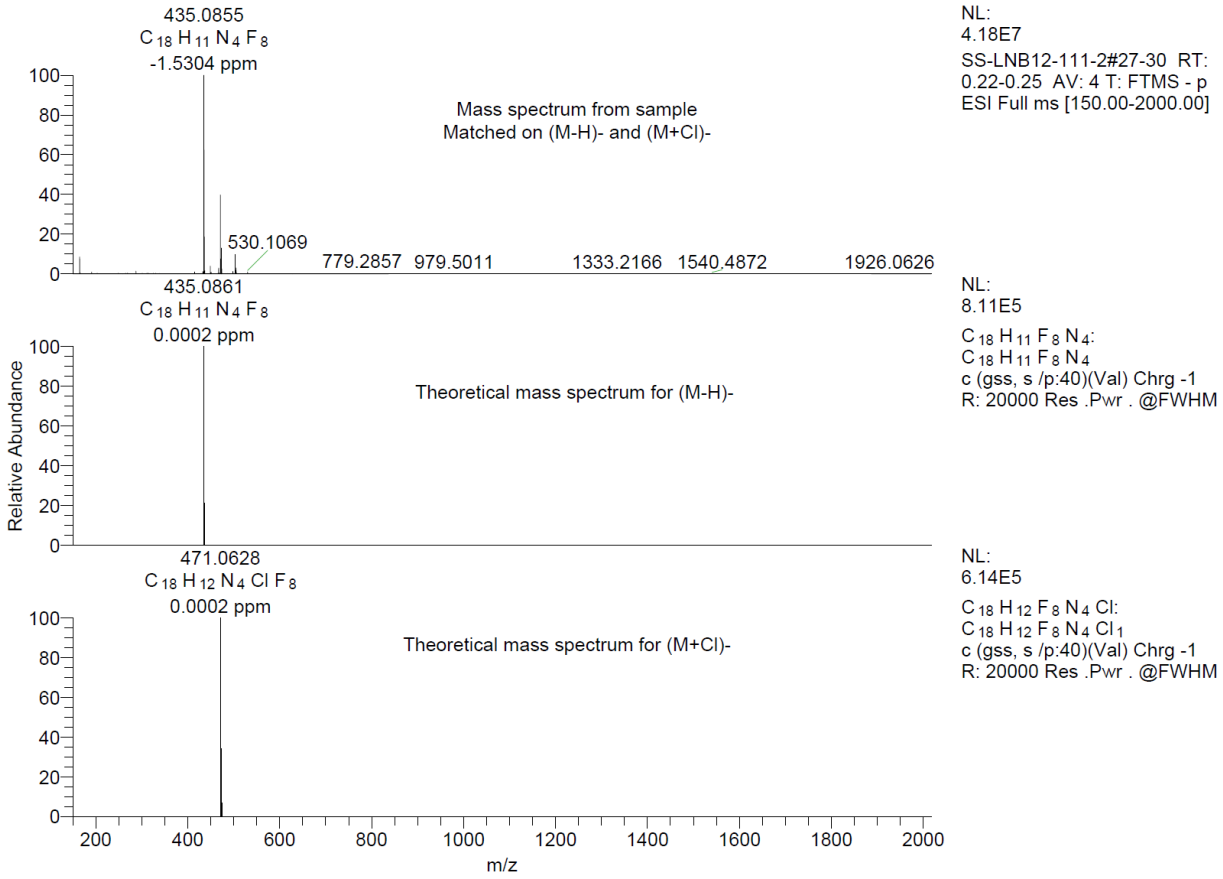

F
F
N
O
F3C
F
F

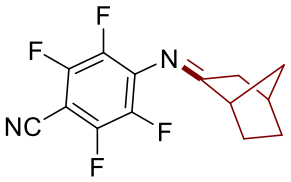
11


302.0412
C11 H7 O N F7
0.6738 ppm
NL:
6.31E7
SM-LNB1-40#30-34 RT:
0.24-0.27 AV: 5 T: FTMS + p
ESI Full ms [150.00-2000.00]
Data from sample MH+
Relative Abundance
413.2663
497.2719
607.2647
759.4350
847.4872
302.0410
C11 H7 O N F7
0.0002 ppm
NL:
8.82E5
C11 H6 F7 NOH:
C11 H7 F7 N1 O1
c (gss, s /p:40)(Val) Chrg 1
R: 20000 Res .Pwr . @FWHM
Theoretical for MH+
m/z

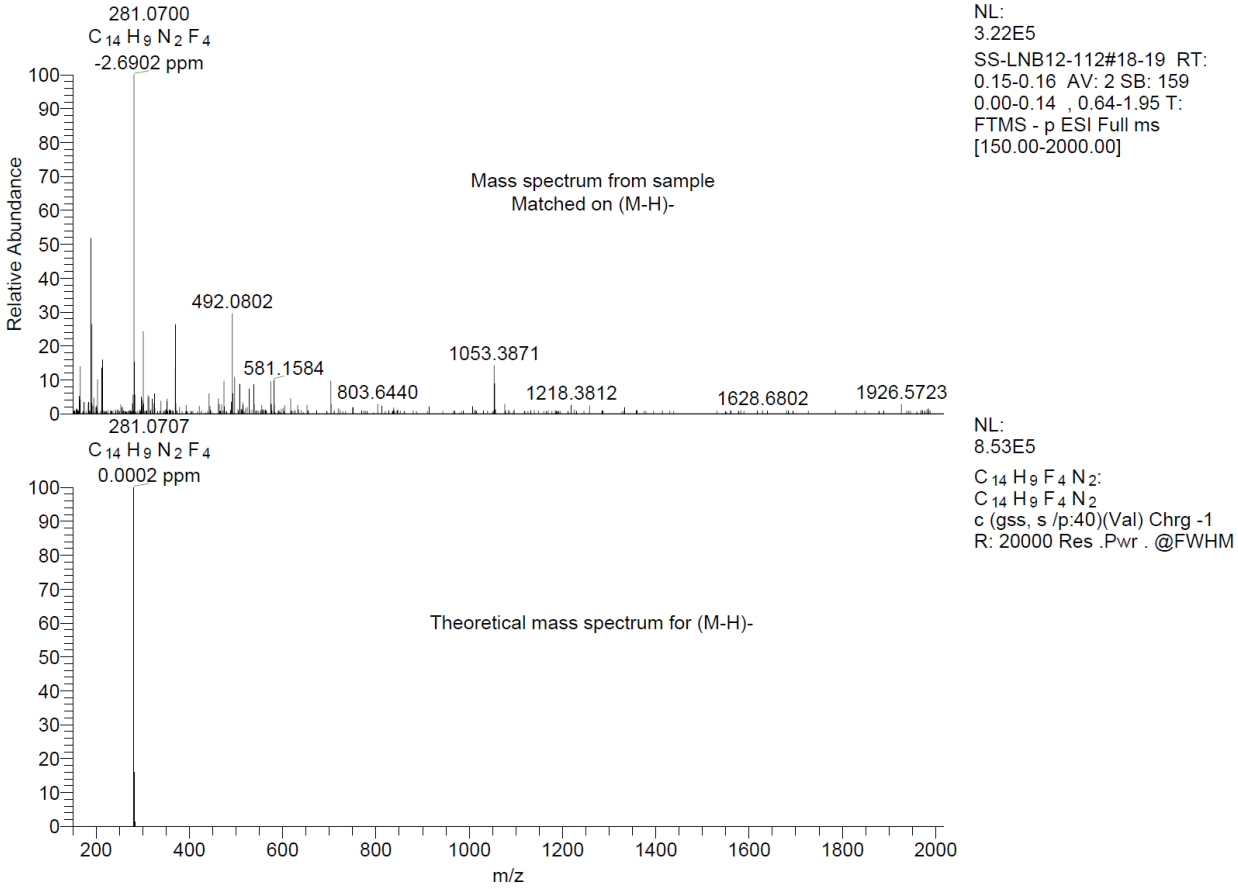


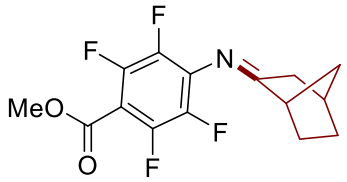
12


435.0855
C 18 H 11 N 4 F 8
-1.5304 ppm
Mass spectrum from sample
Matched on (M-H)- and (M+Cl)-
530.1069
779.2857
979.5011
1333.2166
1540.4872
1926.0626
NL:
4.18E7
SS-LNB12-111-2#27-30 RT:
0.22-0.25 AV: 4 T: FTMS - p
ESI Full ms [150.00-2000.00]
435.0861
C 18 H 11 N 4 F 8
0.0002 ppm
Theoretical mass spectrum for (M-H)-
NL:
8.11E5
C 18 H 11 F 8 N 4:
C 18 H 11 F 8 N 4
c (gss, s /p:40)(Val) Chrg -1
R: 20000 Res .Pwr . @FWHM
471.0628
C 18 H 12 N 4 Cl F 8
0.0002 ppm
Theoretical mass spectrum for (M+Cl)-
NL:
6.14E5
C 18 H 12 F 8 N 4 Cl:
C 18 H 12 F 8 N 4 Cl 1
c (gss, s /p:40)(Val) Chrg -1
R: 20000 Res .Pwr . @FWHM
Relative Abundance
m/z

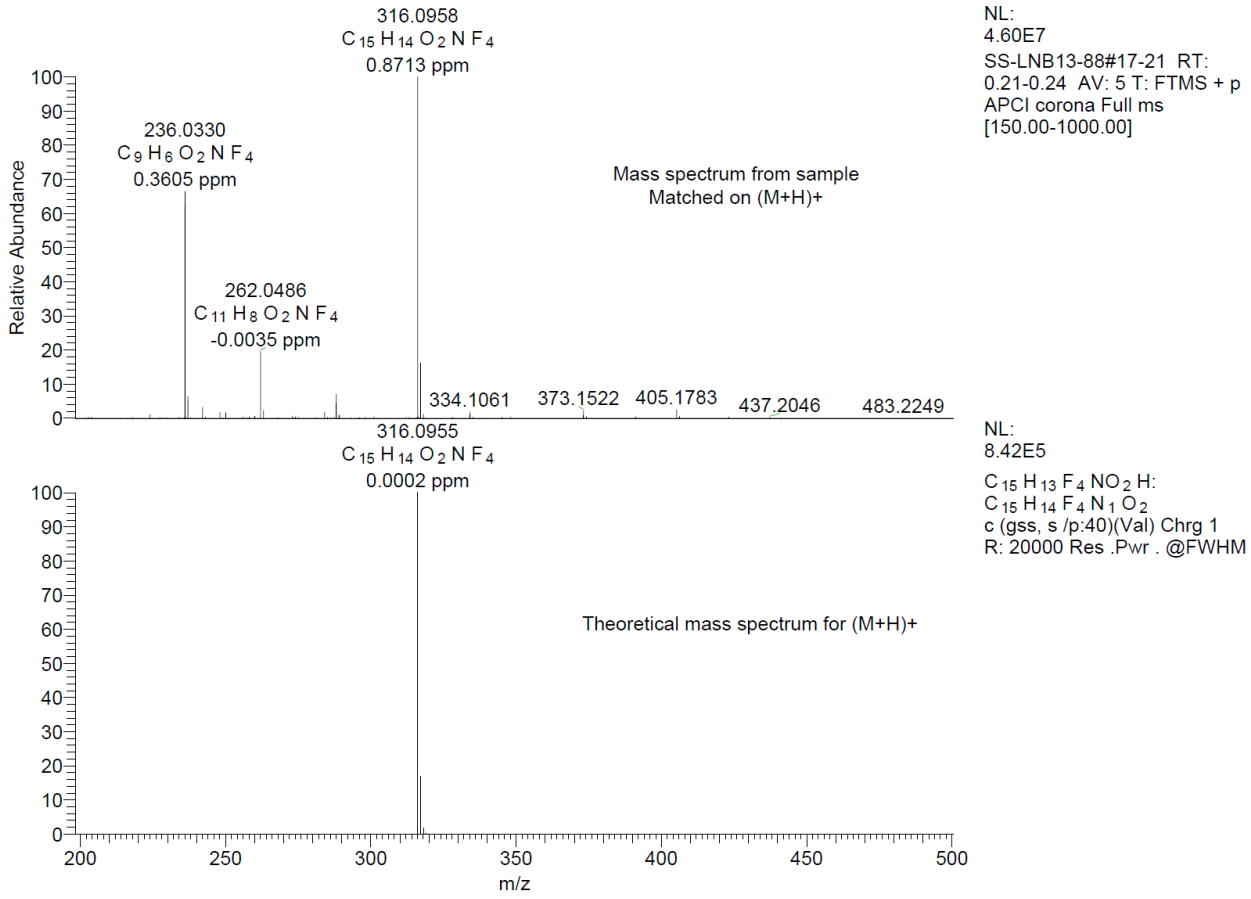

F
F
N
NC
F
F

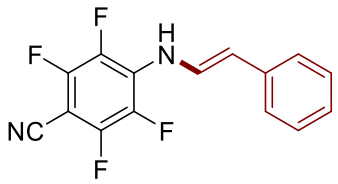
13


281.0700
C 14 H 9 N 2 F 4
-2.6902 ppm
Mass spectrum from sample
Matched on (M-H)-
NL:
3.22E5
SS-LNB12-112#18-19 RT:
0.15-0.16 AV: 2 SB: 159
0.00-0.14 , 0.64-1.95 T:
FTMS - p ESI Full ms
[150.00-2000.00]
Relative Abundance
492.0802
581.1584
803.6440
1053.3871
1218.3812
1628.6802
1926.5723
281.0707
C 14 H 9 N 2 F 4
0.0002 ppm
Theoretical mass spectrum for (M-H)-
NL:
8.53E5
C 14 H 9 F 4 N 2:
C 14 H 9 F 4 N 2
c (gss, s /p:40)(Val) Chrg -1
R: 20000 Res .Pwr . @FWHM
m/z

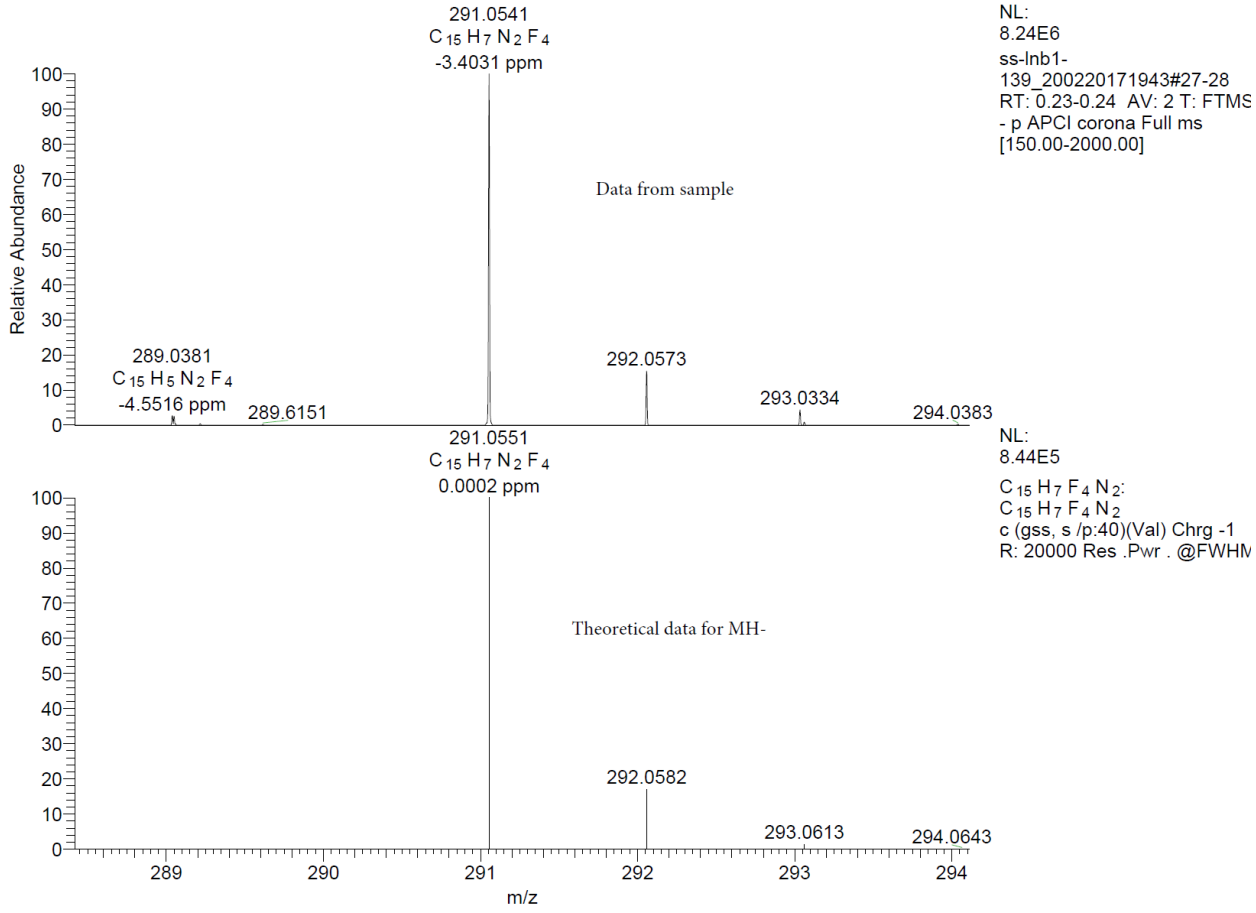

F
F
N
MeO
O
F
F

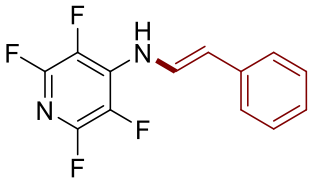
14


316.0958
C 15 H 14 O 2 N F 4
0.8713 ppm
236.0330
C 9 H 6 O 2 N F 4
0.3605 ppm
262.0486
C 11 H 8 O 2 N F 4
-0.0035 ppm
Mass spectrum from sample
Matched on (M+H)+
NL:
4.60E7
SS-LNB13-88#17-21 RT:
0.21-0.24 AV: 5 T: FTMS + p
APCI corona Full ms
[150.00-1000.00]
Relative Abundance
334.1061
373.1522
405.1783
437.2046
483.2249
316.0955
C 15 H 14 O 2 N F 4
0.0002 ppm
Theoretical mass spectrum for (M+H)+
NL:
8.42E5
C 15 H 13 F 4 NO 2 H:
C 15 H 14 F 4 N 1 O 2
c (gss, s /p:40)(Val) Chrg 1
R: 20000 Res .Pwr . @FWHM
m/z


F
H
N
F
NC
F
F

15


291.0541
C 15 H 7 N 2 F 4
-3.4031 ppm
NL:
8.24E6
ss-lnb1-
139_200220171943#27-28
RT: 0.23-0.24 AV: 2 T: FTMS
- p APCI corona Full ms
[150.00-2000.00]
Data from sample
Relative Abundance
289.0381
C 15 H 5 N 2 F 4
-4.5516 ppm
289.6151
292.0573
293.0334
294.0383
291.0551
C 15 H 7 N 2 F 4
0.0002 ppm
NL:
8.44E5
C 15 H 7 F 4 N 2:
C 15 H 7 F 4 N 2
c (gss, s /p:40)(Val) Chrg -1
R: 20000 Res .Pwr . @FWHM
Theoretical data for MH-
292.0582
293.0613
294.0643
m/z



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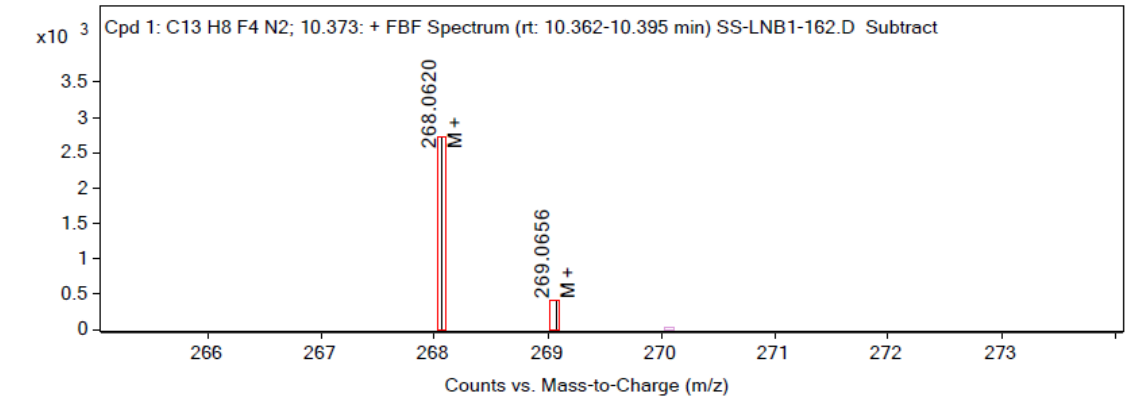
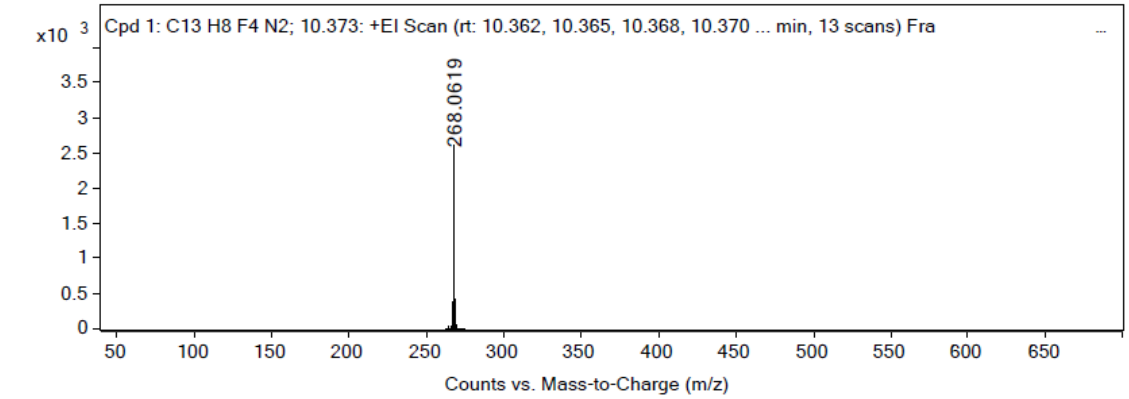
MS Zoomed Spectrum

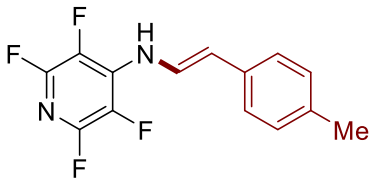


MS Spectrum Peak List

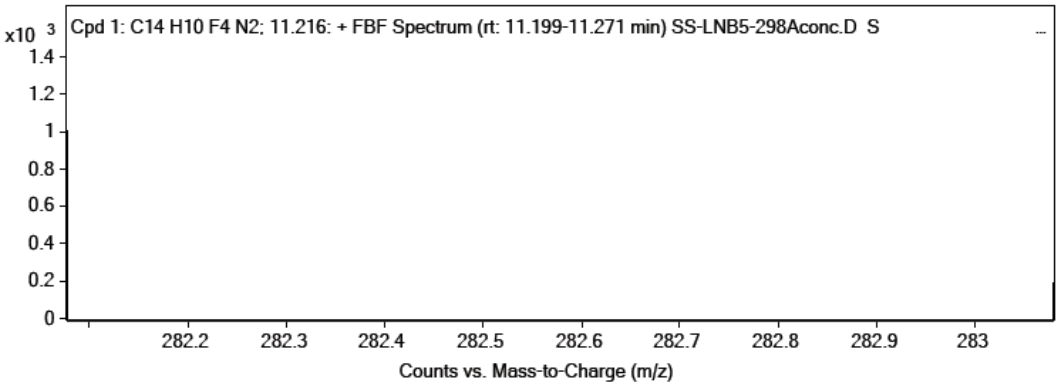
m/z	z	Abund	Ion
268.062	1	2712.26	M+
269.0656	1	398.66	M+

MS Spectrum

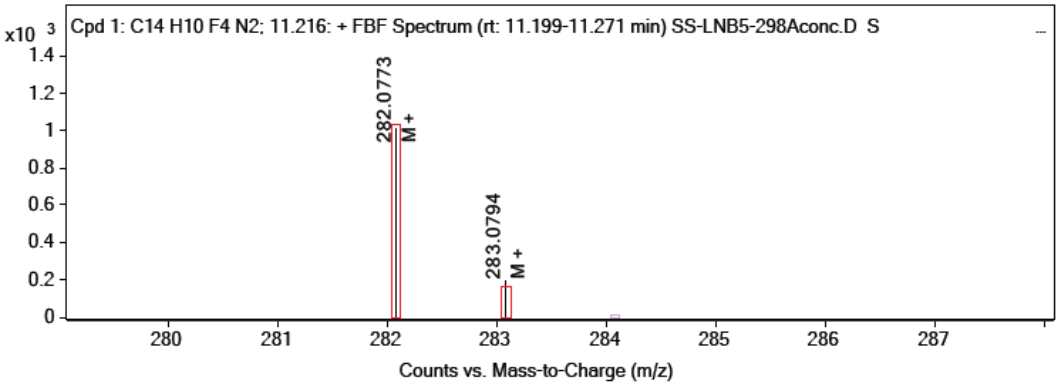




17



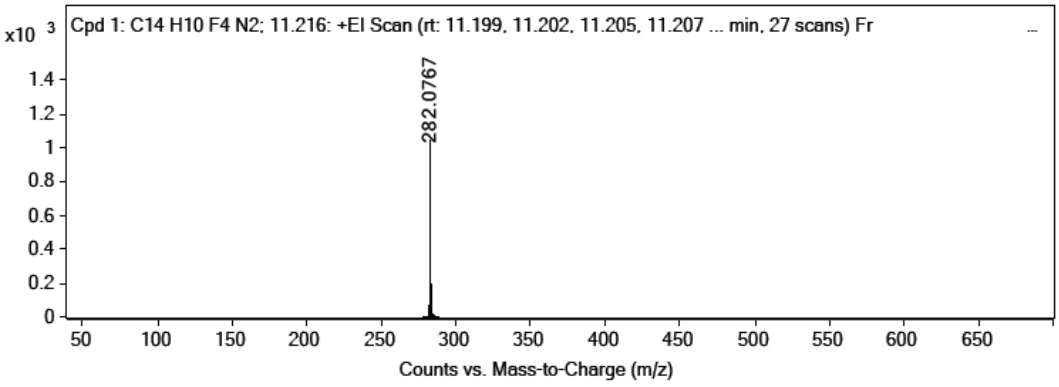
MS Zoomed Spectrum



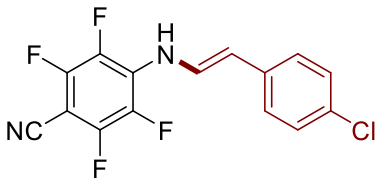
MS Spectrum Peak List

m/z	z	Abund	Ion
282.0773	1	1002.33	M+
283.0794	1	192.45	M+

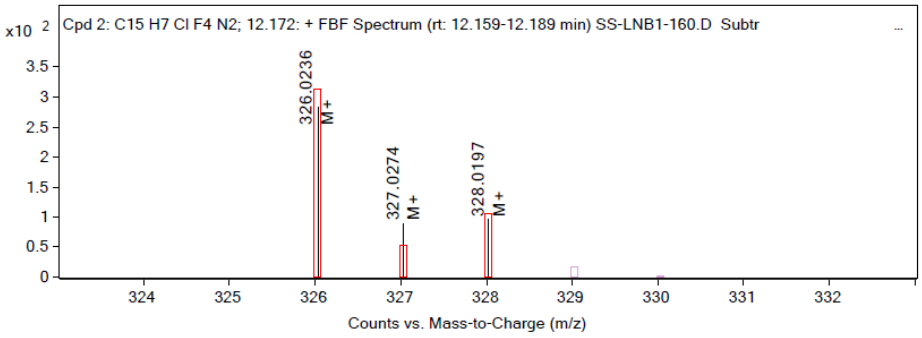
MS Spectrum



MS Zoomed Spectrum



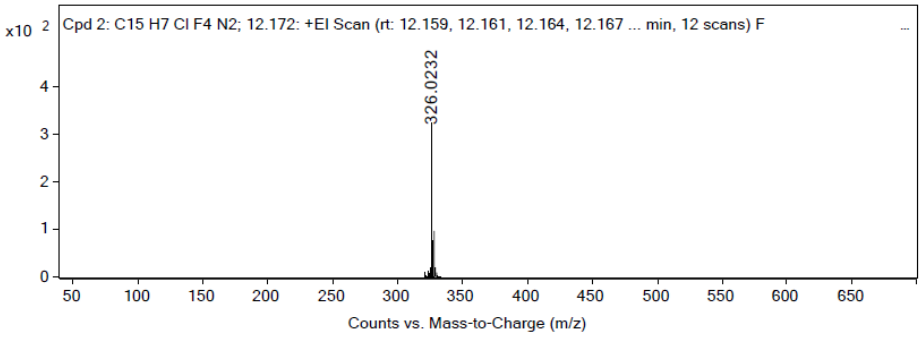
18



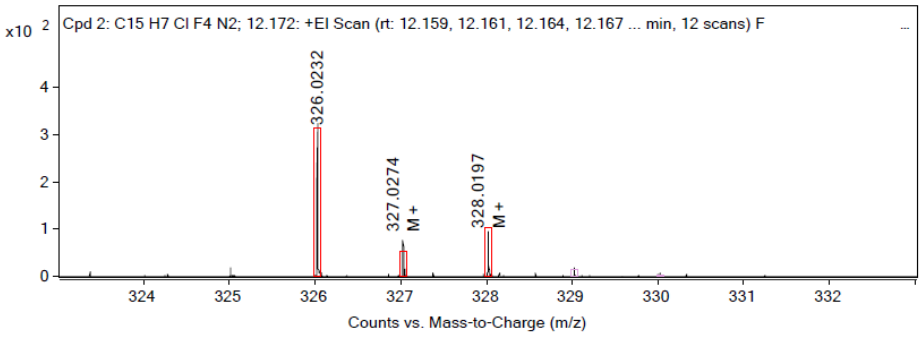
MS Spectrum Peak List

m/z	z	Abund	Ion
326.0236	1	283.73	M+
327.0274	1	89.13	M+
328.0197	1	96.43	M+

MS Spectrum

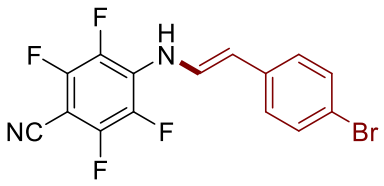


MS Zoomed Spectrum

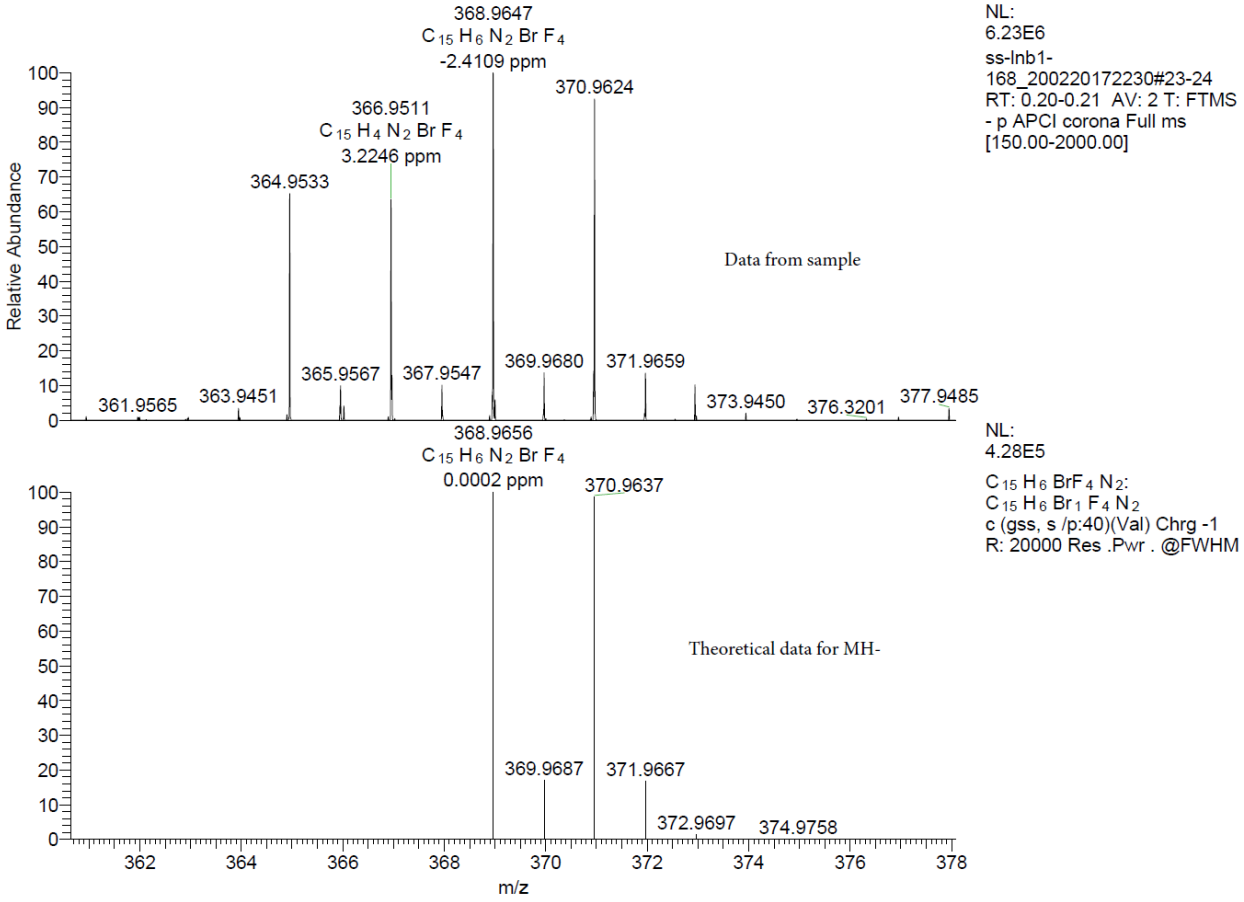


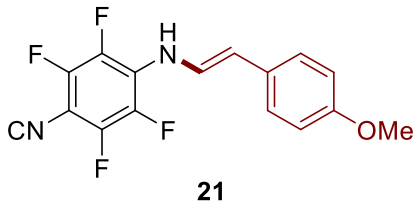
MS Spectrum Peak List

m/z	Calc m/z	Diff(ppm)	z	Abund	Ion
326.0232				322.97	
326.0236	326.0228	-2.25	1	283.73	M+
327.0274	327.0259	-4.33	1	89.13	M+
328.0197	328.0203	1.66	1	96.43	M+

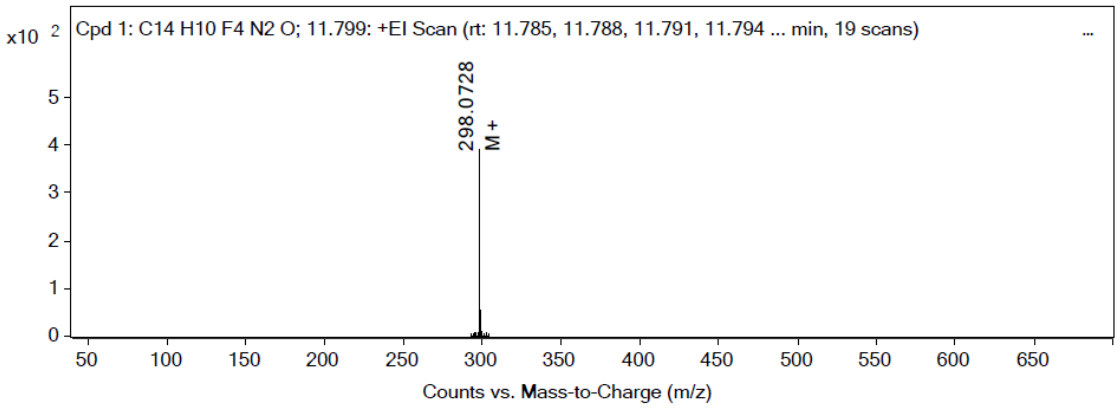

F
H
N
F
NC
F
F
Br

19


368.9647
C 15 H 6 N 2 Br F 4
-2.4109 ppm
370.9624
366.9511
C 15 H 4 N 2 Br F 4
3.2246 ppm
364.9533
Data from sample
365.9567
367.9547
369.9680
371.9659
361.9565
363.9451
373.9450
376.3201
377.9485
Relative Abundance
NL:
6.23E6
ss-lnb1-
168_200220172230#23-24
RT: 0.20-0.21 AV: 2 T: FTMS
- p APCI corona Full ms
[150.00-2000.00]
368.9656
C 15 H 6 N 2 Br F 4
0.0002 ppm
370.9637
Theoretical data for MH-
369.9687
371.9667
372.9697
374.9758
NL:
4.28E5
C 15 H 6 BrF 4 N 2:
C 15 H 6 Br 1 F 4 N 2
c (gss, s /p:40)(Val) Chrg -1
R: 20000 Res .Pwr . @FWHM
m/z

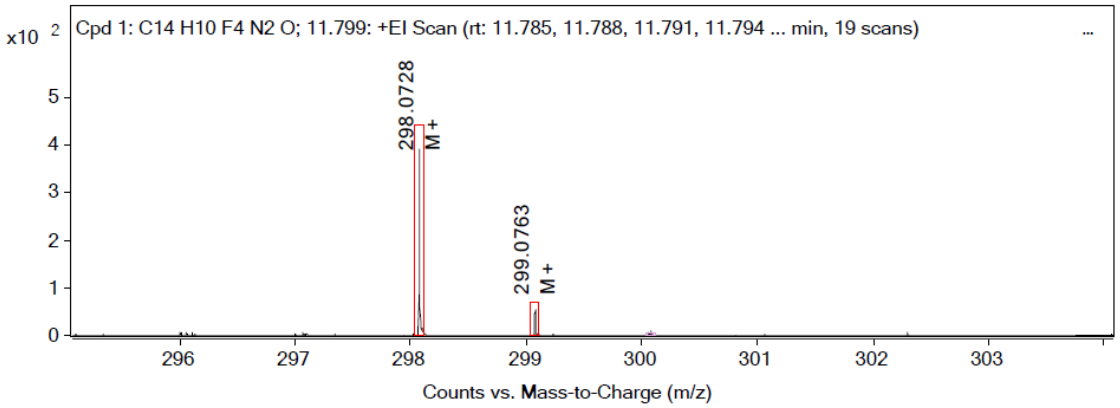


21



MS Zoomed Spectrum

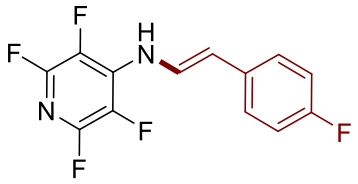
Qualitative Compound Report



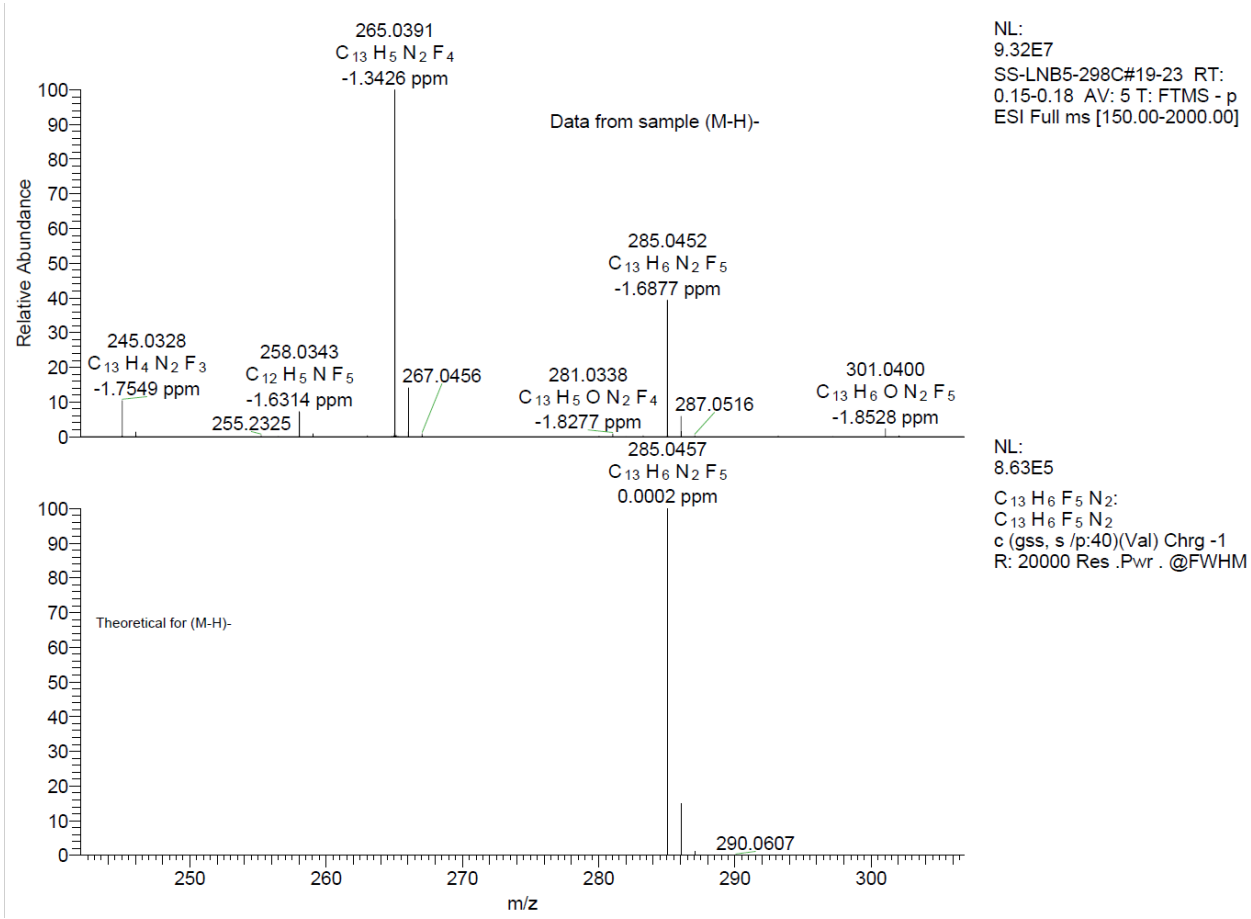
MS Spectrum Peak List

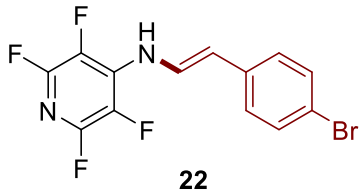
m/z	Calc m/z	Diff(ppm)	z	Abund	Ion
298.0727	298.0724	-1.19		391.04	
298.0728	298.0724	-1.47	1	436.39	M+
299.0763	299.0755	-2.78	1	78.22	M+

--- End Of Report ---

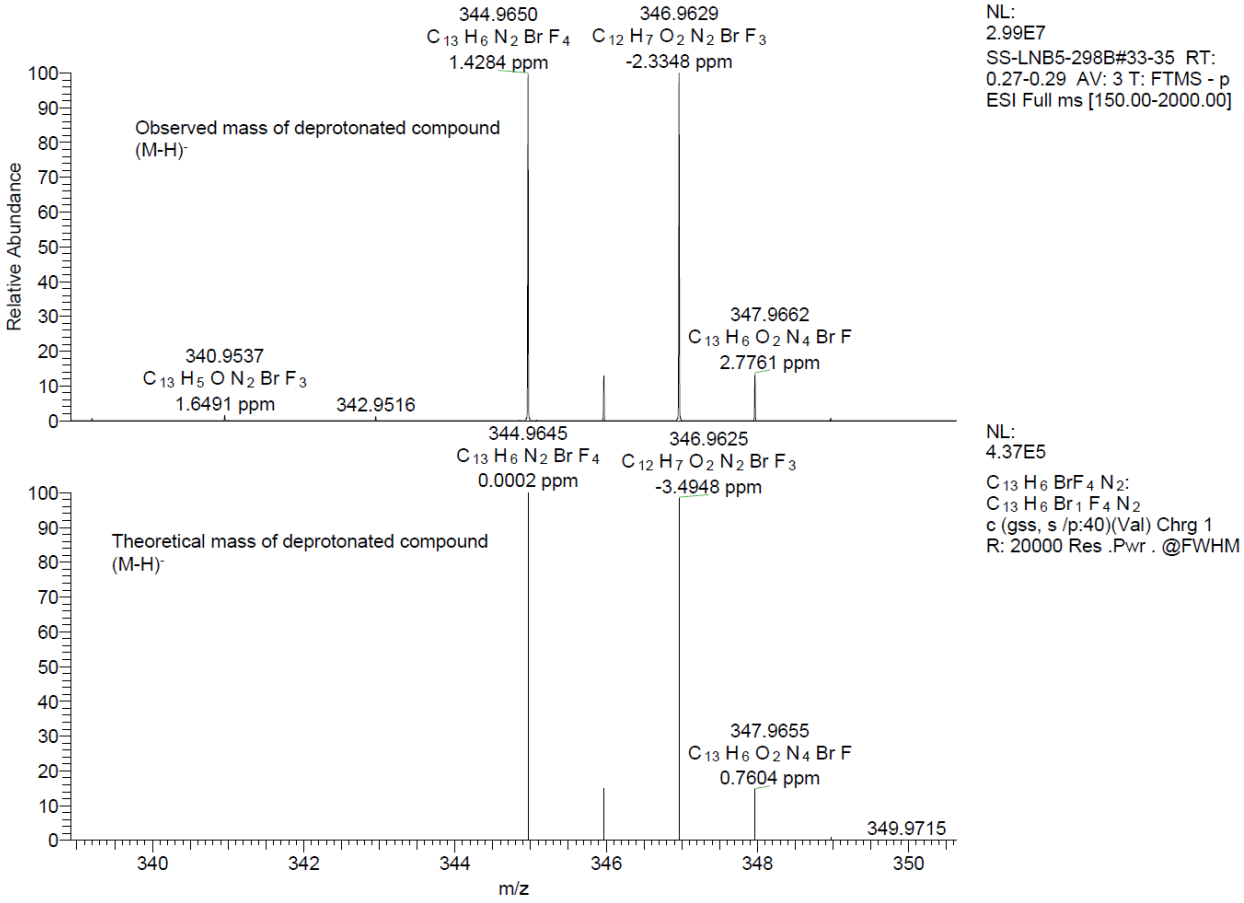


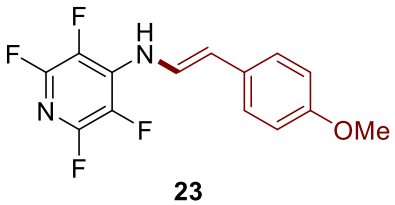
21


265.0391
C13 H5 N2 F4
-1.3426 ppm
Data from sample (M-H)-
285.0452
C13 H6 N2 F5
-1.6877 ppm
245.0328
C13 H4 N2 F3
-1.7549 ppm
258.0343
C12 H5 N F5
-1.6314 ppm
255.2325
267.0456
281.0338
C13 H5 O N2 F4
-1.8277 ppm
287.0516
301.0400
C13 H6 O N2 F5
-1.8528 ppm
Relative Abundance
NL:
9.32E7
SS-LNB5-298C#19-23 RT:
0.15-0.18 AV: 5 T: FTMS - p
ESI Full ms [150.00-2000.00]
285.0457
C13 H6 N2 F5
0.0002 ppm
Theoretical for (M-H)-
290.0607
NL:
8.63E5
C13 H6 F5 N2:
C13 H6 F5 N2
c (gss, s /p:40)(Val) Chrg -1
R: 20000 Res .Pwr . @FWHM
m/z


F
H
N
F
N
F
F
Br

22


344.9650
C 13 H 6 N 2 Br F 4
1.4284 ppm
346.9629
C 12 H 7 O 2 N 2 Br F 3
-2.3348 ppm
NL:
2.99E7
SS-LNB5-298B#33-35 RT:
0.27-0.29 AV: 3 T: FTMS - p
ESI Full ms [150.00-2000.00]
Observed mass of deprotonated compound
(M-H)-
Relative Abundance
347.9662
C 13 H 6 O 2 N 4 Br F
2.7761 ppm
340.9537
C 13 H 5 O N 2 Br F 3
1.6491 ppm
342.9516
344.9645
C 13 H 6 N 2 Br F 4
0.0002 ppm
346.9625
C 12 H 7 O 2 N 2 Br F 3
-3.4948 ppm
NL:
4.37E5
C 13 H 6 BrF 4 N 2:
C 13 H 6 Br 1 F 4 N 2
c (gss, s /p:40)(Val) Chrg 1
R: 20000 Res .Pwr . @FWHM
Theoretical mass of deprotonated compound
(M-H)-
347.9655
C 13 H 6 O 2 N 4 Br F
0.7604 ppm
349.9715
m/z



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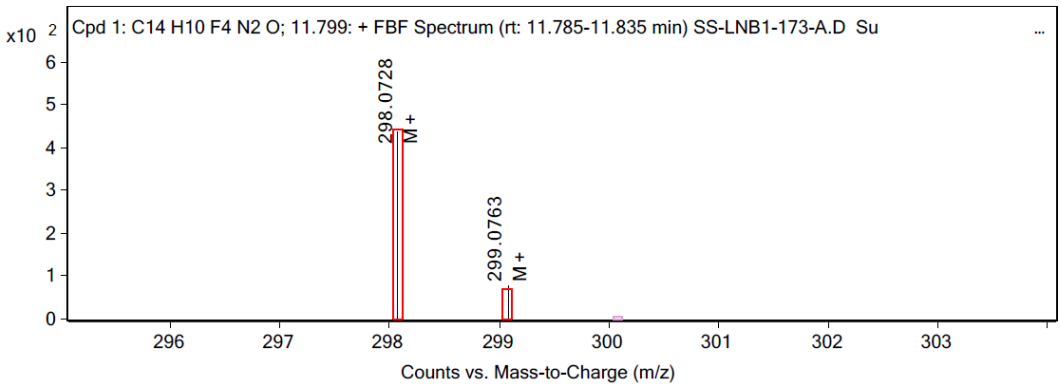
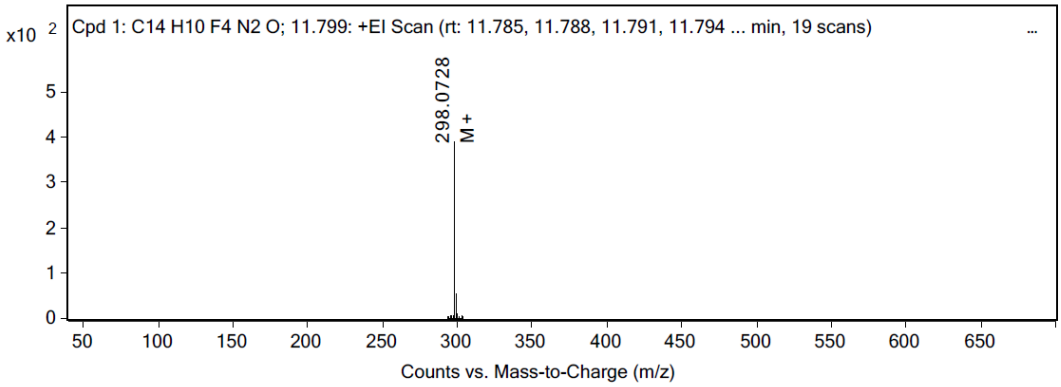
MS Zoomed Spectrum



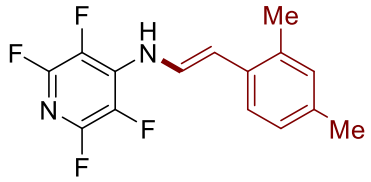
MS Spectrum Peak List

m/z	z	Abund	Ion
298.0728	1	436.39	M+
299.0763	1	78.22	M+

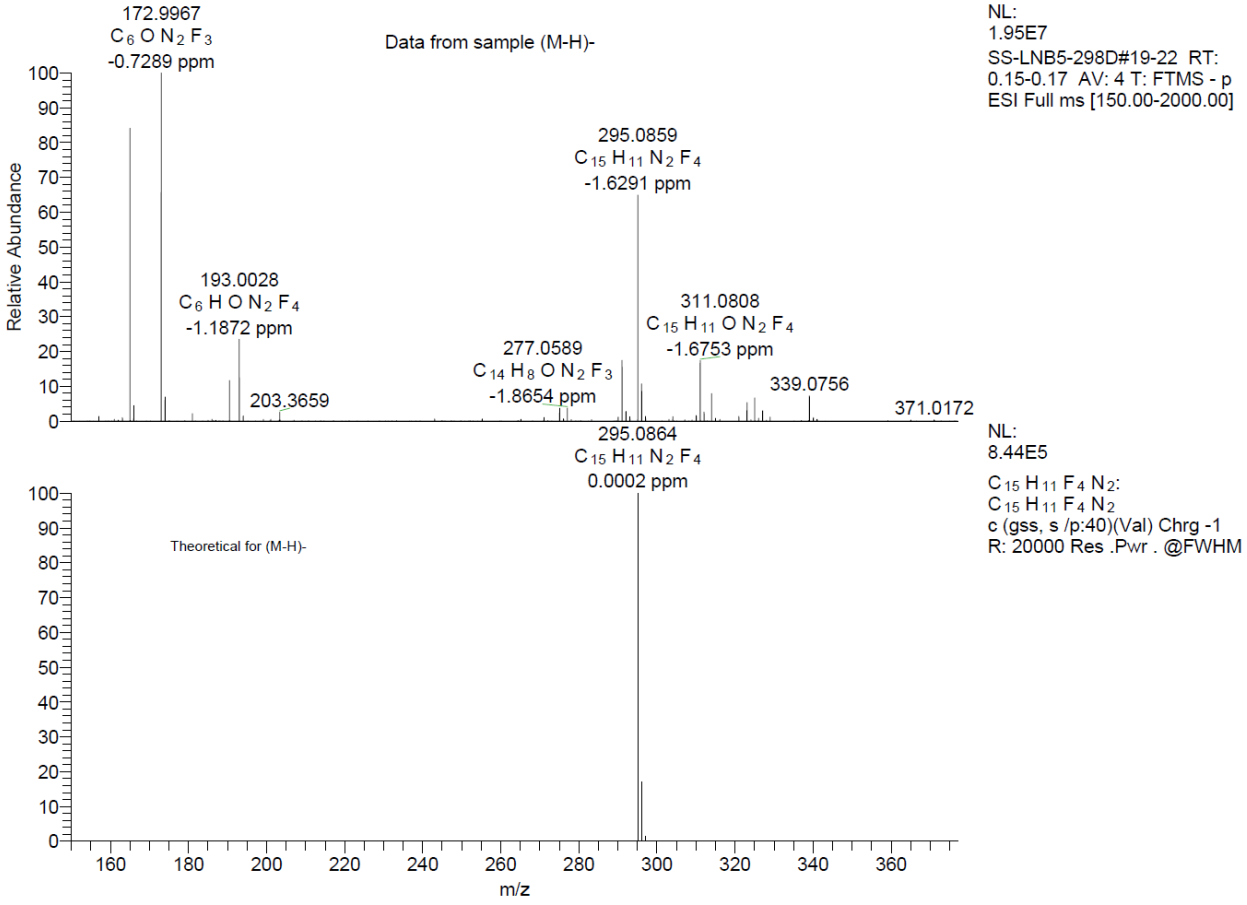
MS Spectrum

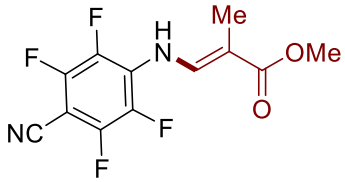


MS Zoomed Spectrum


F
H
N
Me
F
N
F
F
Me

24


172.9967
C6 O N2 F3
-0.7289 ppm
Data from sample (M-H)-
NL:
1.95E7
SS-LNB5-298D#19-22 RT:
0.15-0.17 AV: 4 T: FTMS - p
ESI Full ms [150.00-2000.00]
295.0859
C15 H11 N2 F4
-1.6291 ppm
193.0028
C6 H O N2 F4
-1.1872 ppm
311.0808
C15 H11 O N2 F4
-1.6753 ppm
277.0589
C14 H8 O N2 F3
-1.8654 ppm
339.0756
203.3659
371.0172
Relative Abundance
295.0864
C15 H11 N2 F4
0.0002 ppm
NL:
8.44E5
C15 H11 F4 N2:
C15 H11 F4 N2
c (gss, s /p:40)(Val) Chrg -1
R: 20000 Res .Pwr . @FWHM
Theoretical for (M-H)-
m/z



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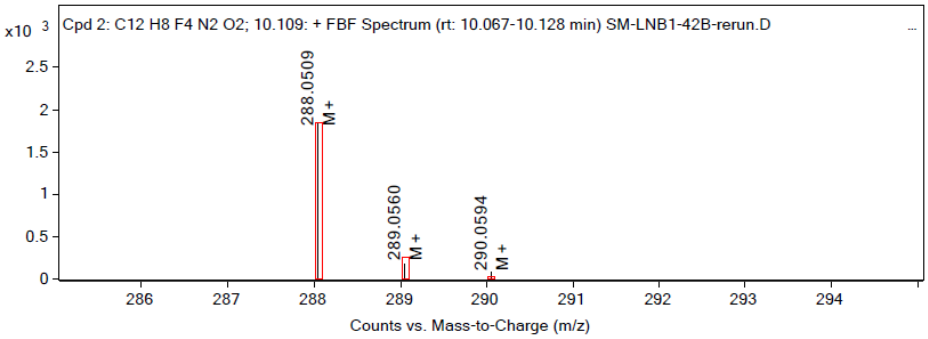
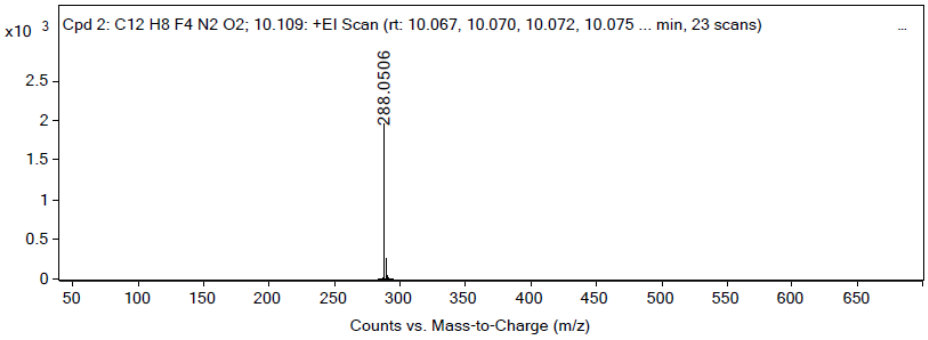


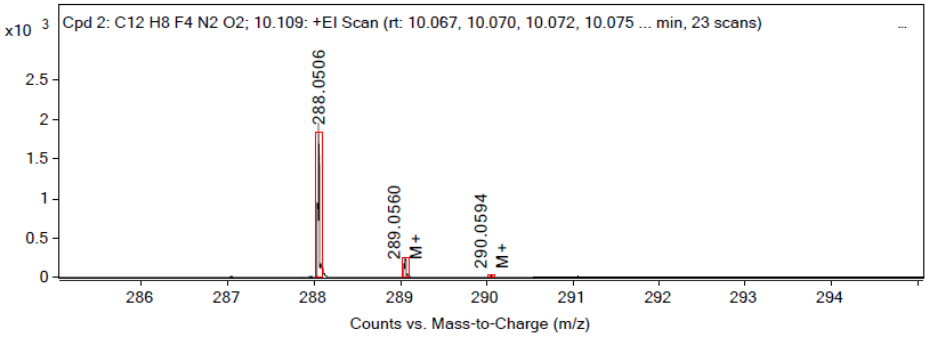
MS Spectrum Peak List

m/z	z	Abund	Ion
288.0509	1	1847.43	M+
289.056	1	185.92	M+
290.0594	1	70.91	M+

MS Spectrum

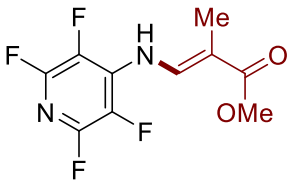


MS Zoomed Spectrum

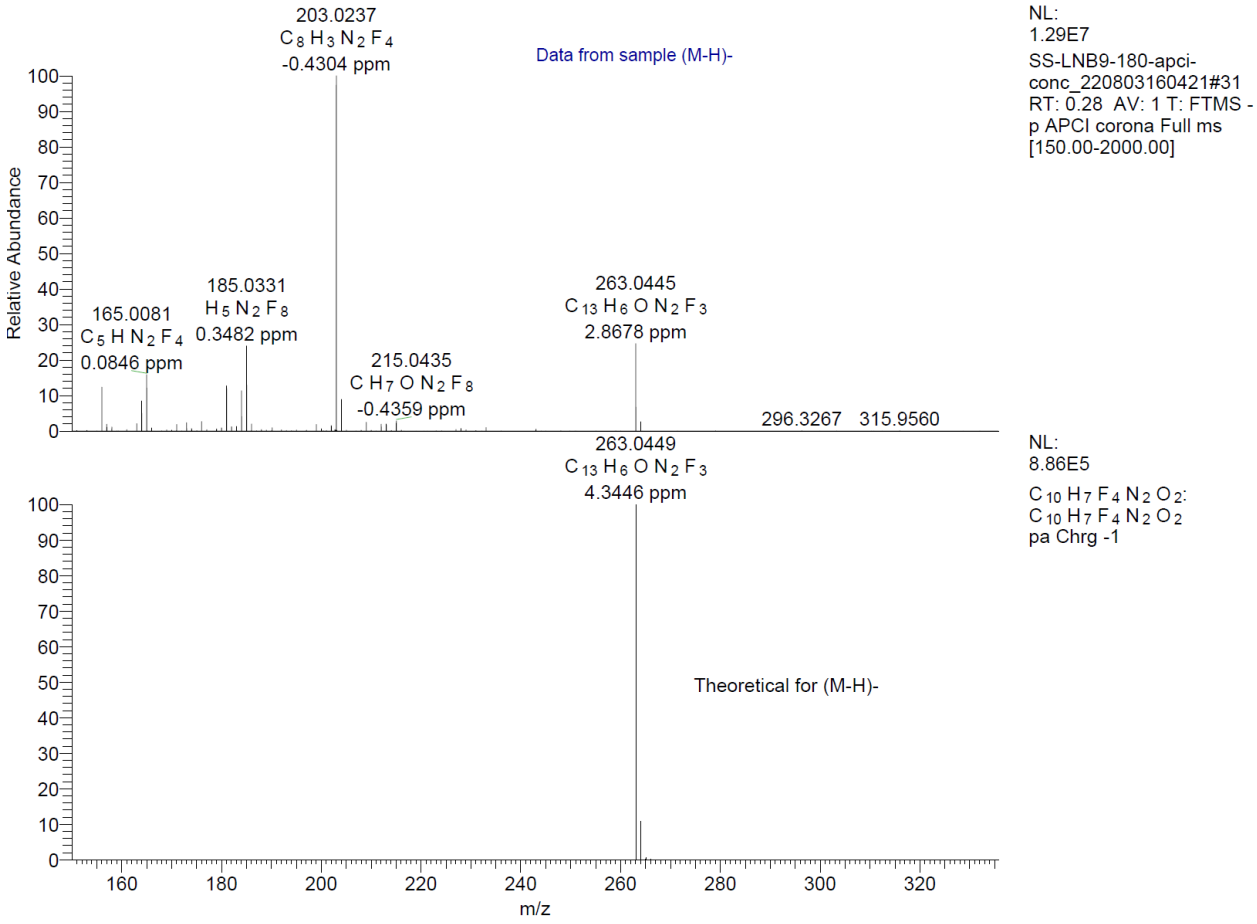


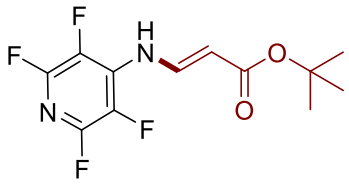
MS Spectrum Peak List

m/z	Calc m/z	Diff(ppm)	z	Abund	Ion
288.0506				1959.73	
288.0509	288.0516	2.72	1	1847.43	M+
289.056	289.0547	-4.52	1	185.92	M+
290.0594	290.0571	-7.82	1	70.91	M+


F
H
N
Me
F
O
N
OMe
F
F

26


203.0237
C 8 H 3 N 2 F 4
-0.4304 ppm
Data from sample (M-H)-
NL:
1.29E7
SS-LNB9-180-apci-conc_220803160421#31 RT: 0.28 AV: 1 T: FTMS - p APCI corona Full ms [150.00-2000.00]
Relative Abundance
165.0081
C 5 H N 2 F 4
0.0846 ppm
185.0331
H 5 N 2 F 8
0.3482 ppm
215.0435
C H 7 O N 2 F 8
-0.4359 ppm
263.0445
C 13 H 6 O N 2 F 3
2.8678 ppm
296.3267
315.9560
263.0449
C 13 H 6 O N 2 F 3
4.3446 ppm
NL:
8.86E5
C 10 H 7 F 4 N 2 O 2:
C 10 H 7 F 4 N 2 O 2
pa Chrg -1
Theoretical for (M-H)-
m/z



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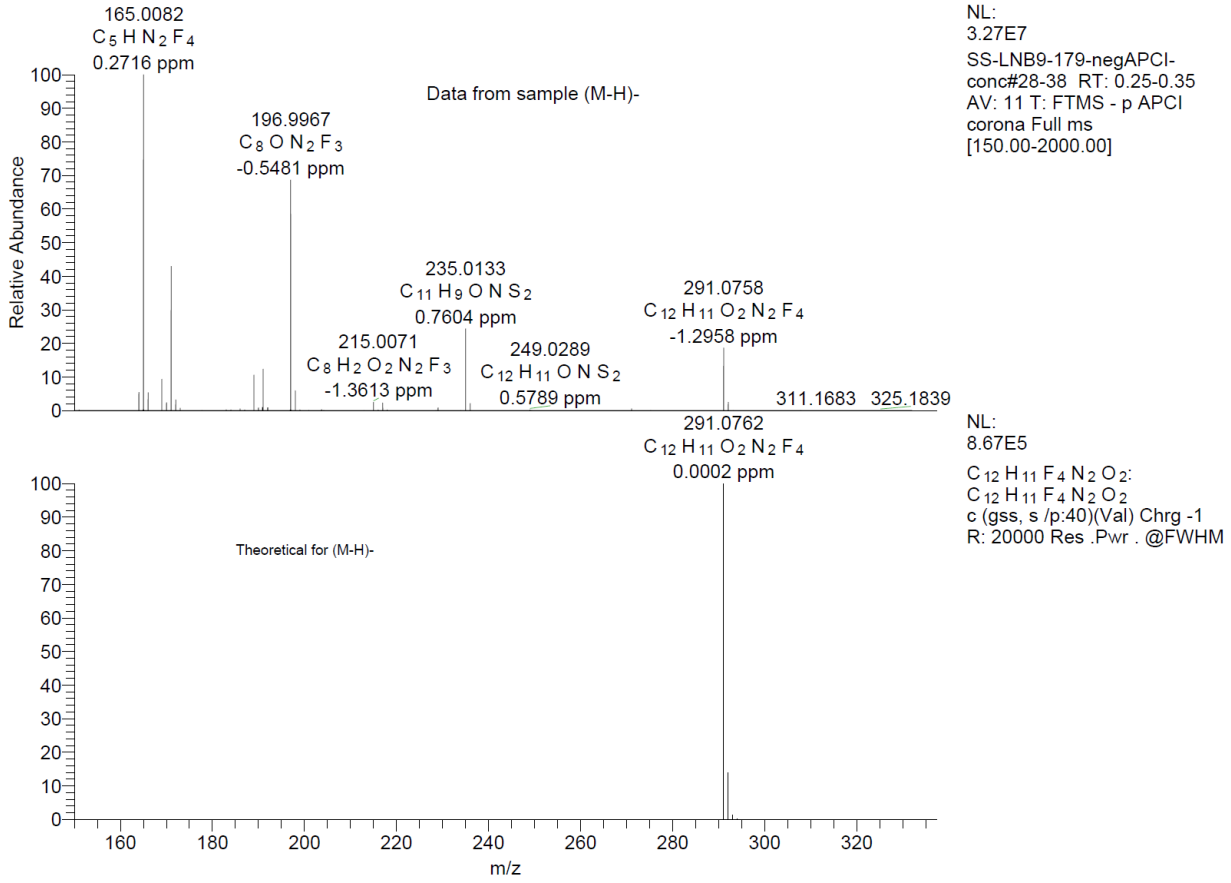
165.0082
C5 H N2 F4
0.2716 ppm
Data from sample (M-H)-
196.9967
C8 O N2 F3
-0.5481 ppm
235.0133
C11 H9 O N S2
0.7604 ppm
215.0071
C8 H2 O2 N2 F3
-1.3613 ppm
249.0289
C12 H11 O N S2
0.5789 ppm
291.0758
C12 H11 O2 N2 F4
-1.2958 ppm
311.1683
325.1839
Relative Abundance
NL:
3.27E7
SS-LNB9-179-negAPCI-conc#28-38 RT: 0.25-0.35 AV: 11 T: FTMS - p APCI corona Full ms [150.00-2000.00]
291.0762
C12 H11 O2 N2 F4
0.0002 ppm
Theoretical for (M-H)-
NL:
8.67E5
C12 H11 F4 N2 O2:
C12 H11 F4 N2 O2
c (gss, s /p:40)(Val) Chrg -1
R: 20000 Res .Pwr . @FWHM
m/z