Electronic Supplementary Information

Photo- and dioxygen-enabled radical C(sp^3)—N(sp^2) cross-coupling: synthesis of N^2-perfluoroalkacylguanidines

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1. General Information

All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. Some guanidines **2** were prepared according to literature reported procedure.[1] The products were purified by column chromatography over silica gel. ^{1}H, ^{19}F and ^{13}C NMR spectra were recorded at 25 ℃ on a Varian 600MHz or 500 MHz or 400 MHz or 300 MHz for ^{1}H, at 564 MHz or 470 MHz or 376 MHz for ^{19}F and at 150 MHz or 125 MHz or 100 MHz for ^{13}C, respectively, in $CDCl_3$ or $(CD_3)_2SO$. Chemical shifts are reported in ppm relative to the residual signals of the deuterated solvents as the internal standard ($CDCl_3$: δ H = 7.26, δ C = 77.16 ppm, $(CD_3)_2SO$: δ H = 2.50, δ C = 39.52 ppm). ^{1}H NMR spectra were recorded using TMS as the internal standard, ^{13}C NMR spectra were recorded using residual protonated solvent as an internal reference, and ^{19}F NMR spectra were recorded using CF_3COOH as external reference. Multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad). Coupling constants, *J*, are reported in Hertz. UV-vis absorption spectra were measured on a Shimadzu UV-2600 spectrophotometer. High-resolution mass-spectra were obtained on an Agilient 1100 LCMsD mass spectrometer. Melting points (m.p.) are uncorrected.

2. The generated nitrogen-centered radicals by single-electron oxidation of N–H substrates

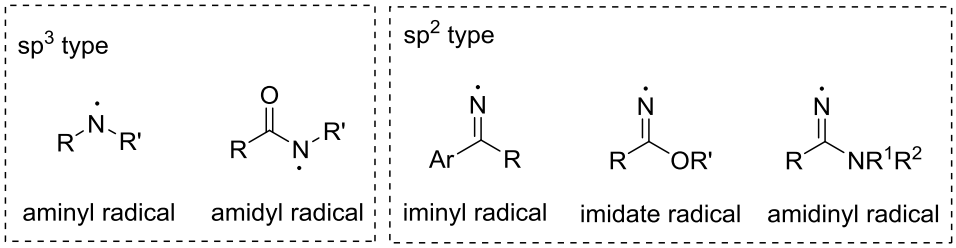


Figure S1 Representative Nitrogen-Centered Radical Intermediates.

3. Representative Experimental Procedure

Representative procedure for the preparation of **3** (with **3a** as an example): A 25-mL round-bottomed flask, equipped with a magnetic stirring bar, is charged with **1a** (1.0 mmol, 0.13

mL), **2a** (1.1 mmol, 0.19 mL) and Cs_2CO_3 (1.5 mmol, 489 mg) in MeCN (2 mL). The reaction mixture was irradiated with 36 W CFL. After the starting material **1a** was consumed as indicated by TLC. The reaction mixture was poured into water and then extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phase was washed with water (3 x 10 mL), dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography on 200-300 mesh silica gel that was dealt with Et_3N/PE (1:9) (petroleum ether : ethyl acetate = 1:1) to give N-(bis(dimethylamino)methylene)-2,2,3,3,4,4,4-heptafluorobutanamide **3a** (215 mg, 69%) as a white solid (R_f = 0.25, petroleum ether : ethyl acetate = 1 : 3).

4. Mechanistic Studies

1) The possibility of radical homolytic cleavage of perfluorobutyl iodide (**2a**) under 36 W CFL irradiation to generate perfluorobutyl radical and iodine radical can be excluded according to the photostability experiment, reported in the literature.[2]

2) We have conducted a heavy oxygen water experiment to elucidate the source of oxygen in products **3**.

A 5 mL round-bottomed flask equipped with a magnetic stirring bar, **1a** (0.1 mmol, 12.5 μL), **2a** (1.1 mmol, 18.9 μL**)** and Cs_2CO_3 (0.15 mmol, 48.9 mg) were dissolved in super dry CH_3CN (0.5 mL). H_2O^{18} (0.1 mmol, 1.8 μL) was added to the solution and the mixture was irradiated by 36 W CFL. After 12 h, the labeled product O^{18}-**3c** was detected by HRMS analysis.

HRMS (ESI) (*m/z*): Calcd for $C_9H_{12}F_7N_3O$ $(M+Na)^+$: 336.0766, found 336.2000.

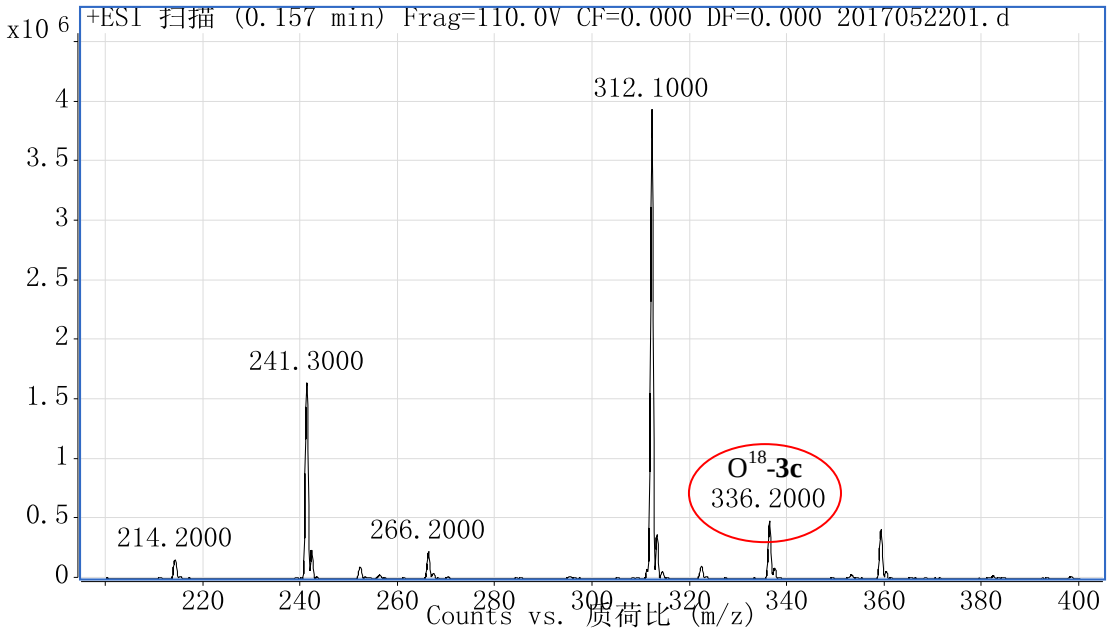


Figure S2. HRMS analysis of H_2O^{18} labeling experiment.

3) 2,3-Dimethyl-but-2-ene can be used as a trapping agent for singlet oxygen. Upon addition of 2, 3-dimethyl-but-2-ene to the reaction system, product **4** was detected by ^{1}H NMR spectroscopy, indicating the presence of $^1O_2$.

A solution of **1a, 2a** and Cs_2CO_3 in CH_3CN (0.5 mM) was put into a 25 mL round-bottomed flask with a magnetic stirring bar. A 30-fold excess of 2, 3 dimethyl-2-butene was added to the solution and the sample was irradiated by 36 W CFL. After 20 h, the yield of the product **3a** decreased obviously as indicated by TLC. ^{1}H NMR spectra was acquired with simultaneous saturation of the large signal at about 1.6 ppm due to unreacted 2,3-dimethyl-2-butene, 2.9 ppm due to achieved product **3a** and 2.0 ppm derived from solvent CH_3CN. The characteristic two olefin proton signals for trapped hydroperoxide appear in the open window of 4.97 and 5.01 ppm, which is consistent with that reported in the literature.[3]

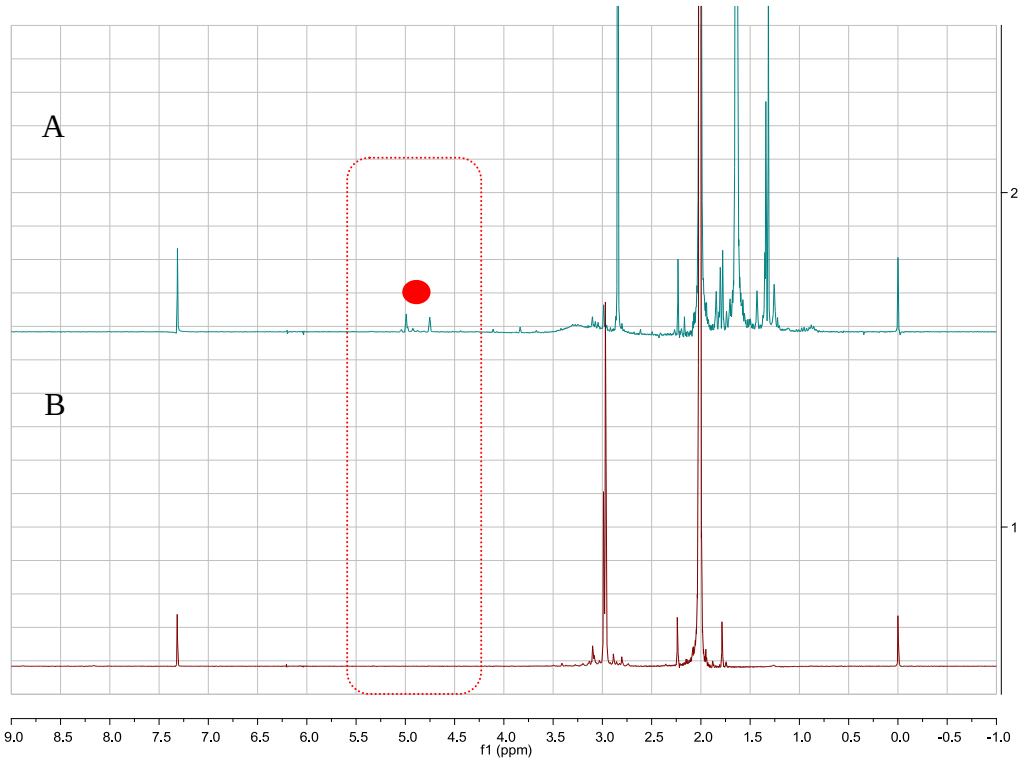


Figure S3. Parallel ^{1}H NMR spectra of TMG and C_4F_9I reaction mixture: (A) in the presence of 30-fold excess 2,3-dimethyl-2-butene. (B) no additive. red ball in A: signals at 4.97 and 5.01 ppm correspond to the two olefin protons for trapped product **4**.

5. DFT Calculation

Computational Details:

All geometries were optimized without symmetry constraints at the level of the (U)B3LYP-D3 functional.[4] The solvent effect was considered by employing the SMD model and acetonitrile (CH_3CN) solvent. The LanL2DZ and corresponding Hay−Wadt effective core potential (ECP) were applied for the core electrons of I, while the standard 6-31G(d) basis set was used for the other main-group elements. The vibrational frequency was calculated to check the nature of each stationary structure at the same theoretical level with optimization. No imaginary frequency was found for all reactants, intermediates, and products. All the DFT calculations were performed with the Gaussian 09 package.[5]

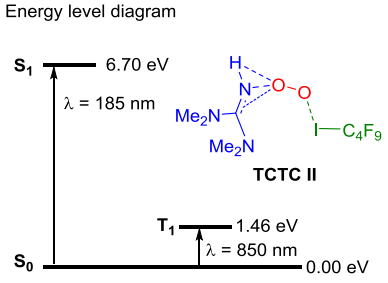
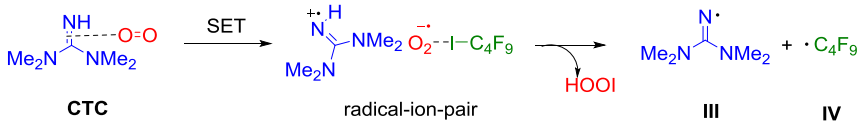


Figure S4. The energy level diagram of TCTC **II**.

alternative O_2-facilited SET process



Scheme S1. Proposed alternative mechanism for the O_2-facilited SET process.

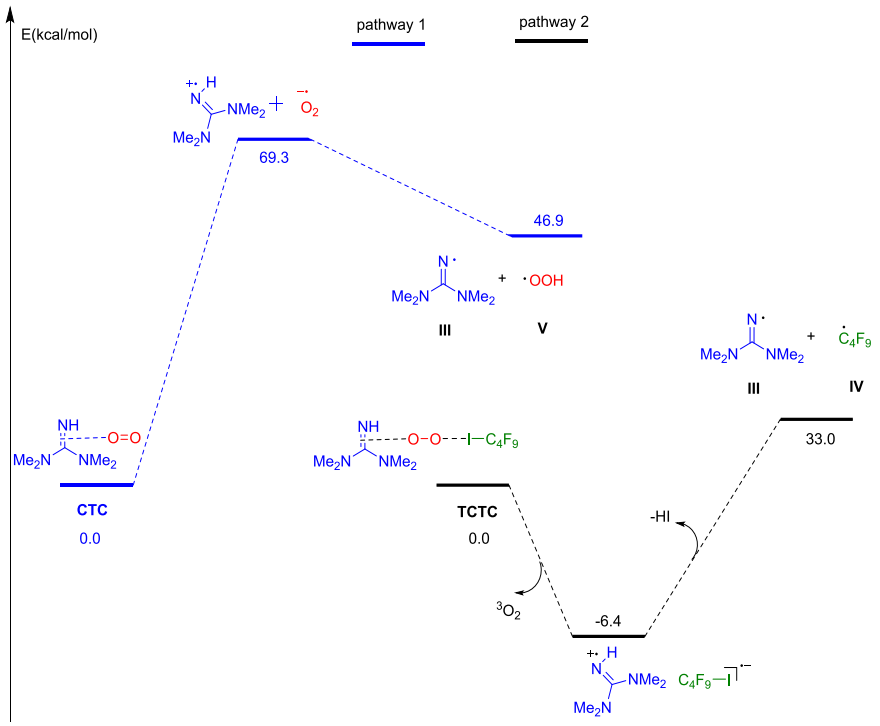
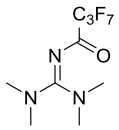


Figure S5. The energy profiles of O_2-facilited SET process.

6. Analytical Data for Compounds 3

***N*-(bis(dimethylamino)methylene)-2,2,3,3,4,4,4-heptafluorobutanamide (3a)**



3a

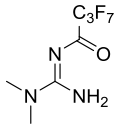
215 mg, 69% yield; White solid; m. p. 46-47 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 2.99 (s, 12H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 40.3, 106.4-107.5 (m), 108.2, 108.5, 108.8, (t, *J* = 37.5 Hz), 109.3-110.6 (m), 114.6-116.9 (m), 114.2, 114.5, 114.9 (t, *J* = 43.8 Hz), 116.5, 116.8, 117.1 (t, *J* = 37.5 Hz), 118.8, 119.1, 119.5 (t, *J* = 43.8 Hz), 121.0, 121.3, 121.7 (t, *J* = 43.8 Hz), 161.3, 161.5, 161.7 (t, *J* = 31.3 Hz), 168.4;

^{19}F NMR (470 MHz, $CDCl_3$): δ -128.3 (s, 2F), -120.0 (q, *J* = 4.5 Hz, 2F), -82.6 (t, *J* = 8.9 Hz, 3F);

HRMS (ESI) (*m/z*): Calcd for $C_9H_{12}F_7N_3O$ $(M+H)^+$: 312.0947, found 312.0951.

(*E*)-*N*-(amino(dimethylamino)methylene)-2,2,3,3,4,4,4-heptafluorobutanamide (3b)



3b

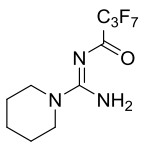
173 mg, 61% yield; White solid; m. p. 83-84 °C. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 2.97 (s, 3H), 3.05 (s, 3H), 7.85 (s, 1H), 8.58 (s, 1H);

^{13}C NMR (100 MHz, DMSO-d_6): δ 36.1, 37.1, 105.5, 105.8, 106.2, 106.6 (q, *J* = 36.7 Hz), 110.8-113.7 (m), 115.9 116.2, 116.5 (t, *J* = 30.0 Hz), 118.7, 119.1, 119.4 (t, *J* = 35.0 Hz), 121.5, 121.9, 122.2 (t, *J* = 35.0 Hz), 160.3, 163.1, 163.3, 163.5 (t, *J* = 20.0 Hz);

^{19}F NMR (376 MHz, DMSO-d_6): δ -126.0 (s, 2F), -117.4 (s, 2F), -80.2 (d, *J* = 7.9 Hz, 3F);

HRMS (ESI) (*m/z*): Calcd for $C_7H_8F_7N_3O$ $(M+H)^+$: 284.0634, found 284.0637.

(*E*)-*N*-(amino(piperidin-1-yl)methylene)-2,2,3,3,4,4,4-heptafluorobutanamide (3c)



3c

210 mg, 65% yield; White solid; m. p. 109-110 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 1.65 (m, 6H),

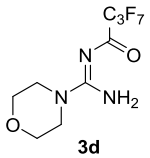
3.57 (s, 4H), 7.45 (s, 2H);

^{13}C NMR (150 MHz, $CDCl_3$): δ 23.9, 25.2, 45.2, 106.7-107.4 (m), 108.4, 108.7, 108.9 (t, *J* = 37.5 Hz), 110.2-110.9 (m), 114.7, 115.0, 115.3 (t, *J* = 45.0 Hz), 116.6, 116.9, 117.3 (t, *J* = 52.5 Hz), 118.5, 118.8, 119.2 (t, *J* = 52.5 Hz), 120.4, 120.7 121.1 (t, *J* = 52.5 Hz), 159.1, 166.3, 166.4, 166.6 (t, *J* = 22.5 Hz);

^{19}F NMR (376 MHz, $CDCl_3$): δ -126.4 (s, 2F), -118.7 (q, *J* = 4.1 Hz, 2F), -80.7 (t, *J* = 9.0 Hz, 3F);

HRMS (ESI) (*m/z*): Calcd for $C_{10}H_{12}F_7N_3O$ $(M+H)^+$: 324.0947, found 324.0950.

(*E*)-*N*-(amino(morpholino)methylene)-2,2,3,3,4,4,4-heptafluorobutanamide (3d)



3d

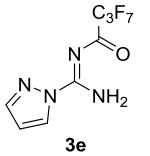
215 mg, 66% yield; White solid; m. p. 81-82 °C. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 3.62 (s, 8H), 8.13 (s, 1H), 8.72 (s, 1H);

^{13}C NMR (100 MHz, DMSO-d_6): δ 44.1, 65.4, 105.5, 105.8, 106.1, 106.5 (q, *J* = 33.3 Hz), 108.1-109.1 (m), 110.7-111.8 (m), 113.0, 113.3, 113.6 (t, *J* = 30.0 Hz), 115.8, 116.2, 116.5 (t, *J* = 35.0 Hz), 118.7, 119.0, 119.4 (t, *J* = 35.0 Hz), 121.5, 121.9, 122.2 (t, *J* = 35.0 Hz), 159.3, 163.7, 163.9, 164.2 (t, *J* = 25.0 Hz);

^{19}F NMR (376 MHz, DMSO-d_6): δ -126.0 (s, 2F), -117.5 (d, *J* = 7.9 Hz, 2F), -80.3 (s, 3F);

HRMS (ESI) (*m/z*): Calcd for $C_9H_{10}F_7N_3O_2$ $(M+H)^+$: 326.0739, found 326.0743.

(*E*)-*N*-(amino(1H-pyrazol-1-yl)methylene)-2,2,3,3,4,4,4-heptafluorobutanamide (3e)



3e

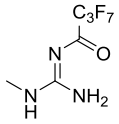
184 mg, 60% yield; White solid; m. p. 127-128 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 6.37 (s, 1H), 6.54 (s, 1H), 6.85 (s, 1H), 7.87 (s, 1H), 8.60 (d, *J* = 1.5 Hz, 1H);

^{13}C NMR (100 MHz, DMSO-d_6): δ 104.1-106.3(m), 107.1-108.9 (m), 110.8, 111.2-113.4 (m), 114.7, 115.7, 116.0, 116.4 (t, *J* = 35.0 Hz), 118.5, 118.8, 119.2 (t, *J* = 35.0 Hz), 121.3, 121.6, 122.0 (t, *J* = 35.0 Hz), 130.0, 144.9, 164.7, 164.9 165.2 (t, *J* = 25.0 Hz), 167.4;

^{19}F NMR (376 MHz, $CDCl_3$): δ -126.1 (s, 2F), -118.4 (q, *J* =4.5 Hz, 2F), -80.3 (t, *J* = 9.0 Hz, 3F);

HRMS (ESI) (*m/z*): Calcd for $C_8H_5F_7N_4O$ $(M+H)^+$: 307.0430, found 307.0433.

(*E*)-*N*-(amino(methylamino)methylene)-2,2,3,3,4,4,4-heptafluorobutanamide (3f)



3f

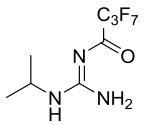
159 mg, 59% yield; White solid; m. p. 89-90 ^{o}C. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 2.73 (d, J = 11.2 Hz, 3H), 7.58 (s, 1H), 8.26 (s, 1H), 8.53 (s, 1H);

^{13}C NMR (100 MHz, DMSO-d_6): δ 27.4, 105.6, 105.9, 106.2, 106.5 (q, J = 30.0 Hz), 108.1-109.5 (m), 110.8-112.2 (m), 113.0, 113.3, 113.7 (t, J = 35.0 Hz) 115.8, 116.2, 116.5 (t, J = 35.0 Hz), 118.7, 119.0, 119.4 (t, J = 35.0 Hz), 121.5, 121.9, 122.2 (t, J = 35.0 Hz), 161.9, 164.1, 164.4, 164.6 (t, J = 25.0 Hz);

^{19}F NMR (376 MHz, DMSO-d_6): δ -126.7 (s, 2F), -119.2 (d, J = 3.9 Hz, 2F), -80.7 (t, J = 8.3 Hz, 3F);

HRMS (ESI) (*m/z*): Calcd for $C_6H_6F_7N_3O$ $(M+H)^+$: 270.0477, found 270.0475.

(*E*)-*N*-(amino(isopropylamino)methylene)-2,2,3,3,4,4,4-heptafluorobutanamide (3g)



3g

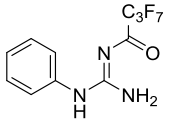
187 mg, 63% yield; White solid; m. p. 126-127 ^{o}C. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 1.09-1.15 (m, 6H), 3.72-4.00 (m, 6H), 7.23 (s, 1H), 7.67 (s, 1H), 8.36-8.51 (m, 1H);

^{13}C NMR (100 MHz, DMSO-d_6): δ 21.9, 22.2, 42.5, 105.5, 105.8, 106.1, 106.4 (q, J = 30.0 Hz) 107.8-109.3 (m), 110.3-114.7 (m), 115.8, 116.2, 116.5 (t, J = 35.0 Hz), 118.7, 119.0, 119.4 (t, J = 35.0 Hz), 121.6, 121.9, 122.2 (t, J = 30.0 Hz), 160.1, 164.1-164.9 (m);

^{19}F NMR (376 MHz, DMSO-d_6): δ -126.0 (s, 2F), -117.3- -117.6 (m, 2F), -80.3 (s, 3F);

HRMS (ESI) (*m/z*): Calcd for $C_8H_{10}F_7N_3O$ $(M+H)^+$: 298.0790, found 298.0786.

(*E*)-*N*-(amino(phenylamino)methylene)-2,2,3,3,4,4,4-heptafluorobutanamide (3h)



3h

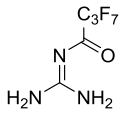
189 mg, 57% yield; White solid; m. p. 71-72 °C. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 7.19 (s, 1H), 7.35-7.39 (m, 4H), 7.61 (s, 2H), 8.71 (s, 1H), 9.82 (s, 1H);

^{13}C NMR (100 MHz, DMSO-d_6): δ 105.5, 105.8, 106.1, 106.5 (t, *J* = 33.3 Hz), 108.0-109.1 (m), 110.7-113.3 (m), 115.8, 116.1, 116.5 (t, *J* = 35.0 Hz), 118.6, 119.0, 119.3 (t, *J* = 35.0 Hz), 123.0, 125.2, 129.0, 136.6, 159.7, 165.2, 165.4, 165.7 (t, *J* = 25.0 Hz);

^{19}F NMR (376 MHz, $CDCl_3$): δ -126.5 (s, 2F), -119.2 (q, *J* = 8.3 Hz, 2F), -80.7 (t, *J* = 8.6 Hz, 3F);

HRMS (ESI) (*m/z*): Calcd for $C_{11}H_8F_7N_3O$ $(M+H)^+$: 332.0634, found 332.0630.

***N*-(diaminomethylene)-2,2,3,3,4,4,4-heptafluorobutanamide (3i)**



3i

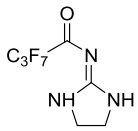
133 mg, 52% yield; White solid; m. p. 85-86 °C. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 7.27 (s, 2H), 7.44 (s, 2H);

^{13}C NMR (100 MHz, DMSO-d_6): δ 105.3, 105.6, 105.8, 106.0 (q, *J* = 23.3 Hz), 107.3-109.0 (m), 109.7-113.1 (m), 115.7, 116.0, 116.3 (t, *J* = 30.0 Hz), 118.5, 118,9 119.2 (t, *J* = 35.0 Hz), 121.4, 121.7, 122.1 (t, *J* = 35.0 Hz), 163.4, 163.6, 163.9 (t, *J* = 25.0 Hz), 166.7;

^{19}F NMR (376 MHz, DMSO-d_6): δ -126.1 (s, 2F), -117.9 (d, *J* = 7.9 Hz, 2F), -80.1 (s, 3F);

HRMS (ESI) (*m/z*): Calcd for $C_5H_4F_7N_3O$ $(M+H)^+$: 256.0321, found 256.0325.

2,2,3,3,4,4,4-Heptafluoro-*N*-(imidazolidin-2-ylidene)butanamide (3j)



3j

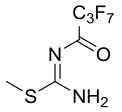
169 mg, 60% yield; White solid; m. p. 157-158 °C. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 3.58 (s, 4H), 8.44 (s, 2H);

^{13}C NMR (100 MHz, DMSO-d_6): δ 41.6, 105.8, 106.1, 106.4 (t, *J* = 30.0 Hz), 108.1-109.2 (m), 110.6-111.8 (m), 113.0, 113.3, 133.7 (t, *J* = 35.0 Hz), 115.8, 116.2, 116.5 (t, *J* = 35.0 Hz), 118.7, 119.0, 119.4 (t, *J* = 35.0 Hz), 121.6, 121.9, 122.2 (t, *J* = 30.0 Hz), 164.5, 164.7, 164.9, 165.1 (t, *J* = 20.0 Hz);

^{19}F NMR (376 MHz, DMSO-d_6): δ -126.1 (s, 2F), -117.5 (q, *J* = 8.2 Hz, 2F), -80.3 (t, *J* = 8.5 Hz, 3F);

HRMS (ESI) (*m/z*): Calcd for $C_7H_6F_7N_3O$ $(M+H)^+$: 282.0477, found 282.0479.

Methyl (*E*)-*N'*-(2,2,3,3,4,4,4-heptafluorobutanoyl)carbamimidothioate (3k)



3k

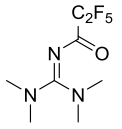
177 mg, 62% yield; White solid; m. p. 66-67 ^{o}C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 2.54 (s, 3H), 6.58 (s, 1H), 9.71 (s, 1H);

^{13}C NMR (150 MHz, $CDCl_3$): δ 9.2, 101.9-104.0 (m), 105.4, 110.1-111.8, 112.0, 112.3, 112.7 (t, *J* = 37.5 Hz), 113.7, 113.9, 114.2 (t, *J* = 37.5 Hz), 115.8, 162.1, 162.3, 162.5 (t, *J* = 30.0 Hz), 173.6;

^{19}F NMR (376 MHz, DMSO-d_6): δ -126.1 (s, 2F), -117.9 (q, *J* = 4.3 Hz, 2F), -80.0 (t, *J* = 8.3 Hz, 3F);

HRMS (ESI) (*m/z*): Calcd for $C_6H_5F_7N_2OS$ $(M+H)^+$: 287.0089, found 287.0091.

***N*-(bis(dimethylamino)methylene)-2,2,3,3,3-pentafluoropropanamide (3l)**



3l

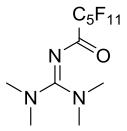
188 mg, 72% yield; White solid; m. p. 50-51 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.99 (s, 12H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 40.2, 104.5, 104.9, 105.2, 105.6 (q, *J* = 33.3 Hz), 107.1, 107.4, 107.8, 108.2 (q, *J* = 36.7 Hz), 109.7, 110.0, 110.4 (t, *J* = 35.0 Hz), 114.2, 114.5, 114.9 (t, *J* = 35.0 Hz), 117.2, 117.4, 117.7 (t, *J* = 25.0 Hz), 119.9, 120.2, 120.6 (t, *J* = 35.0 Hz), 122.7, 123.1, 123.4 (t, *J* = 35.0 Hz), 161.2, 161.4, 161.7 (t, *J* = 25.0 Hz), 168.4;

^{19}F NMR ($CDCl_3$, 376 MHz): δ -120.6 (s, 2F), -82.3 (s, 3F);

HRMS (ESI) (*m/z*): Calcd for $C_8H_{12}F_5N_3O$ $(M+H)^+$: 262.0979, found 262.0981.

***N*-(bis(dimethylamino)methylene)-2,2,3,3,4,4,5,5,6,6,6-undecafluorohexanamide (3m)**



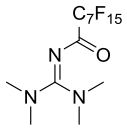
3m

280 mg, 68% yield; White solid; m. p. 51-52 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 2.99 (s, 12H); **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ 40.3, 105.1-107.9 (m), 106.4-107.5 (m), 108.3-110.5 (m), 111.0-114.1 (m), 114.9, 115.8, 116.3 (t, *J* = 45.0 Hz), 118.8, 119.2, 119.6 (t, *J* = 30.0 Hz), 120.9, 121.3, 121.7 (t, *J* = 30.0 Hz), 161.2, 161.5, 161.8 (t, *J* = 22.5 Hz), 168.3;

^{19}F NMR (376 MHz, $CDCl_3$): δ -126.2 (q, *J* = 5.5 Hz, 2F), -122.4 (s, 2F), -122.0 (s, 2F), -117.1 (t, *J* = 12.8 Hz, 2F), -80.8 (m, 3F);

HRMS (ESI) (*m/z*): Calcd for $C_{11}H_{12}F_{11}N_3O$ $(M+H)^+$: 412.0883, found 412.0880.

***N*-(bis(dimethylamino)methylene)-2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctanamide (3n)**



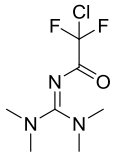
3n

378 mg, 74% yield; White solid; m. p. 38-39 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 2.99 (s, 12H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ 39.8, 104.7, 106.0, 106.4, 106.7 (q, *J* = 33.3 Hz), 106.6-108.8 (m), 109.5-111.1 (m), 111.6-114.2 (m), 114.8, 115.2, 155.5 (t, *J* = 35.0 Hz), 117.7, 118.0, 118.4 (t, *J* = 35.0 Hz), 120.6, 120.9, 121.2 (t, *J* = 30.0 Hz), 158.8, 159.1, 159.3 (t, *J* = 25.0 Hz), 166.9;

^{19}F NMR (376 MHz, $CDCl_3$): δ -126.1 (s, 2F), -122.7 (s, 2F), -122.0 (s, 2F), -121.8 (d, *J* = 5.6 Hz, 2F), -121.5 (s, 2F), -117.1 (t, *J* = 12.8 Hz, 2F), -80.8 (m, 3F);

HRMS (ESI) (*m/z*): Calcd for $C_{13}H_{12}F_{15}N_3O$ $(M+H)^+$: 512.0819, found 512.0817.

***N*-(bis(dimethylamino)methylene)-2-chloro-2,2-difluoroacetamide (3o)**



3o

137 mg, 60% yield; White solid; m. p. 178-179 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 2.99 (s, 12H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ 39.9, 117.8, 120.8, 123.8, 161.0, 161.2, 161.5 (t, *J* = 25.0 Hz), 167.1;

^{19}F NMR (376 MHz, DMSO-d_6): δ -60.3 (s, 2F);

HRMS (ESI) (m/z): Calcd for $C_7H_{12}ClF_2N_3O$ $(M+H)^+$: 228.0715, found 228.0717

7. References

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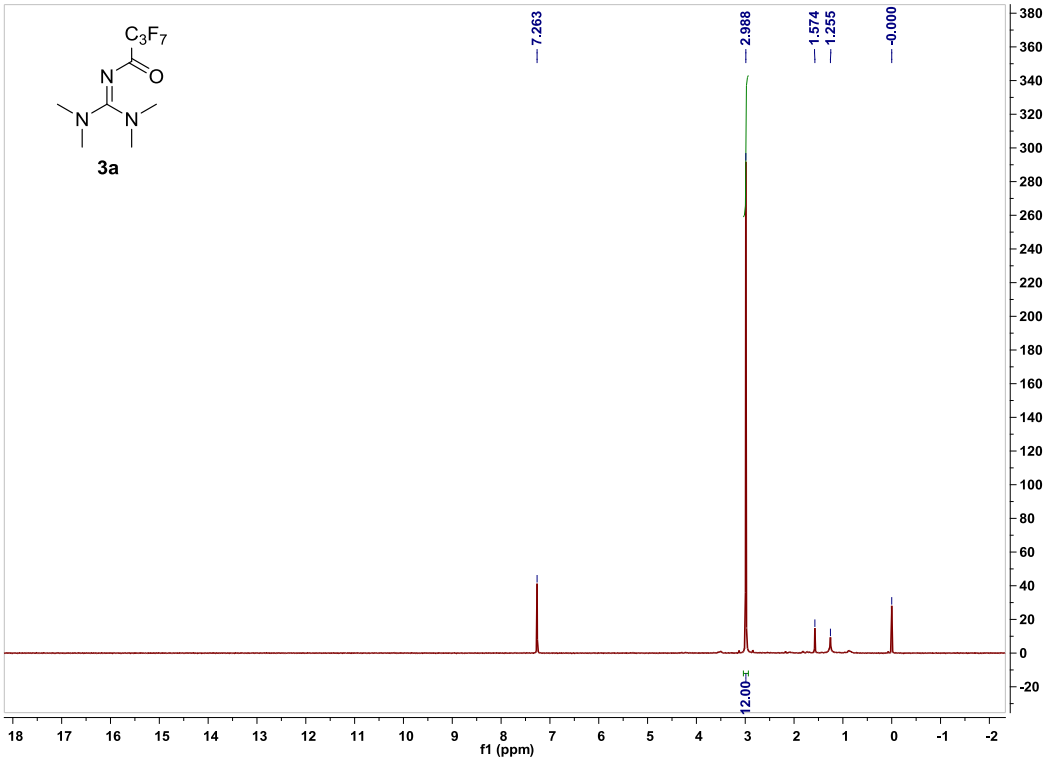
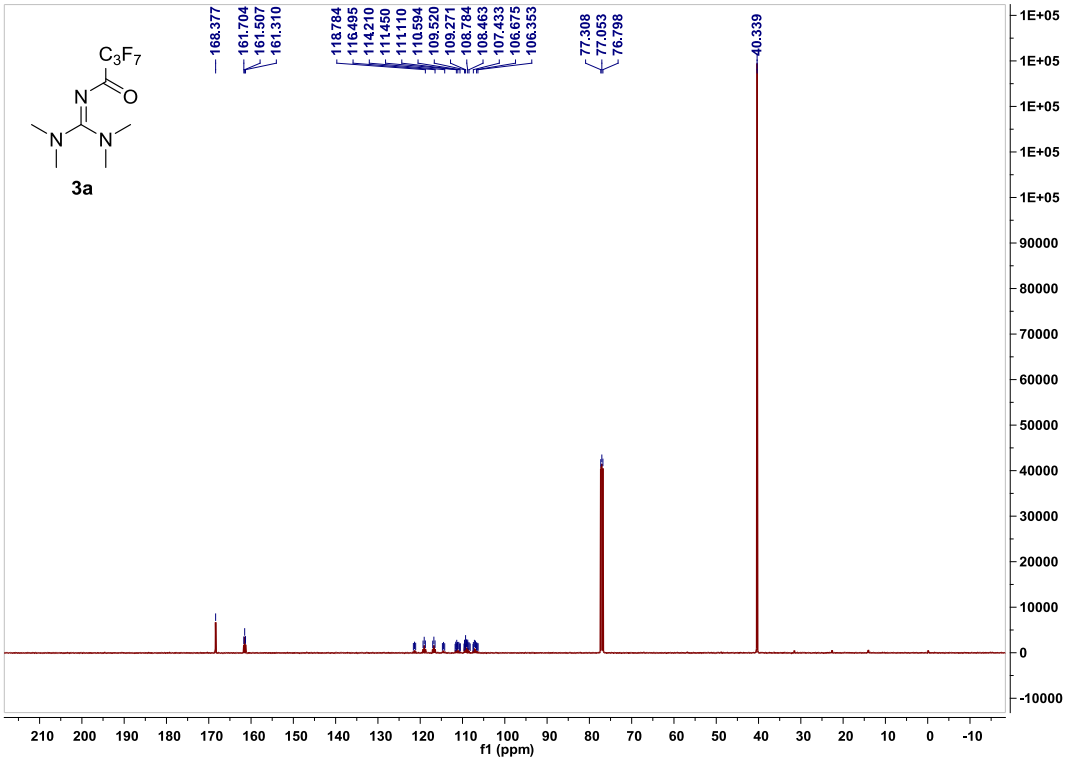
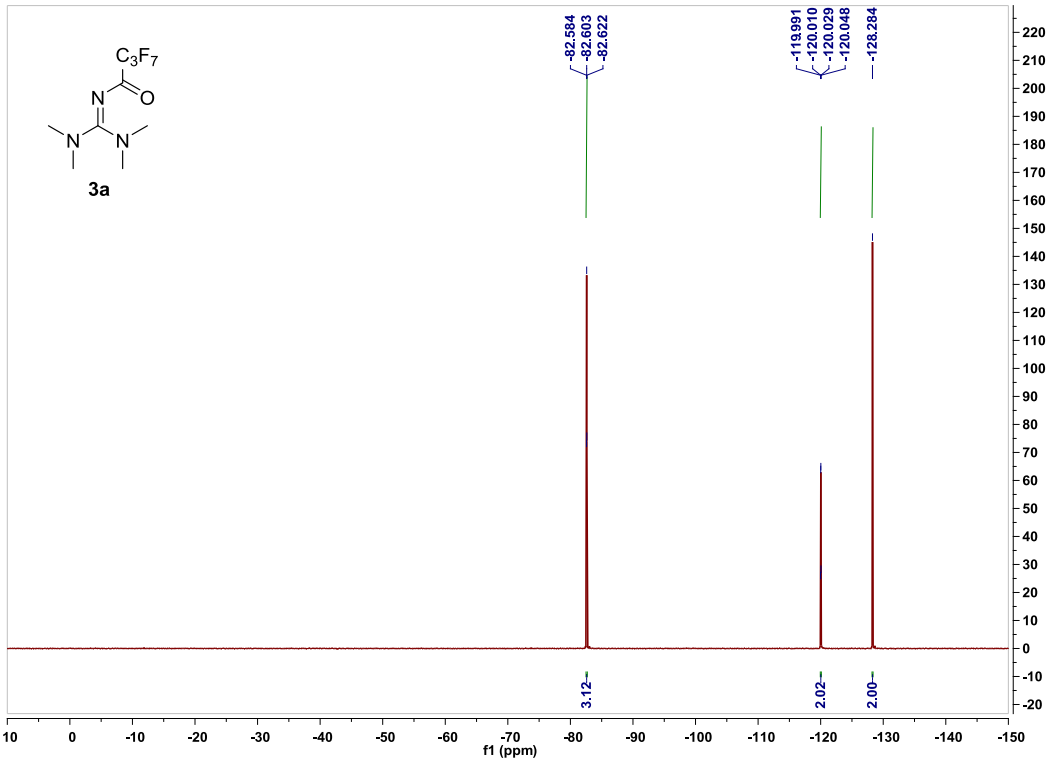
8. Copies of ^{1}H and ^{13}C NMR Spectra for Compounds 3.



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-82.603
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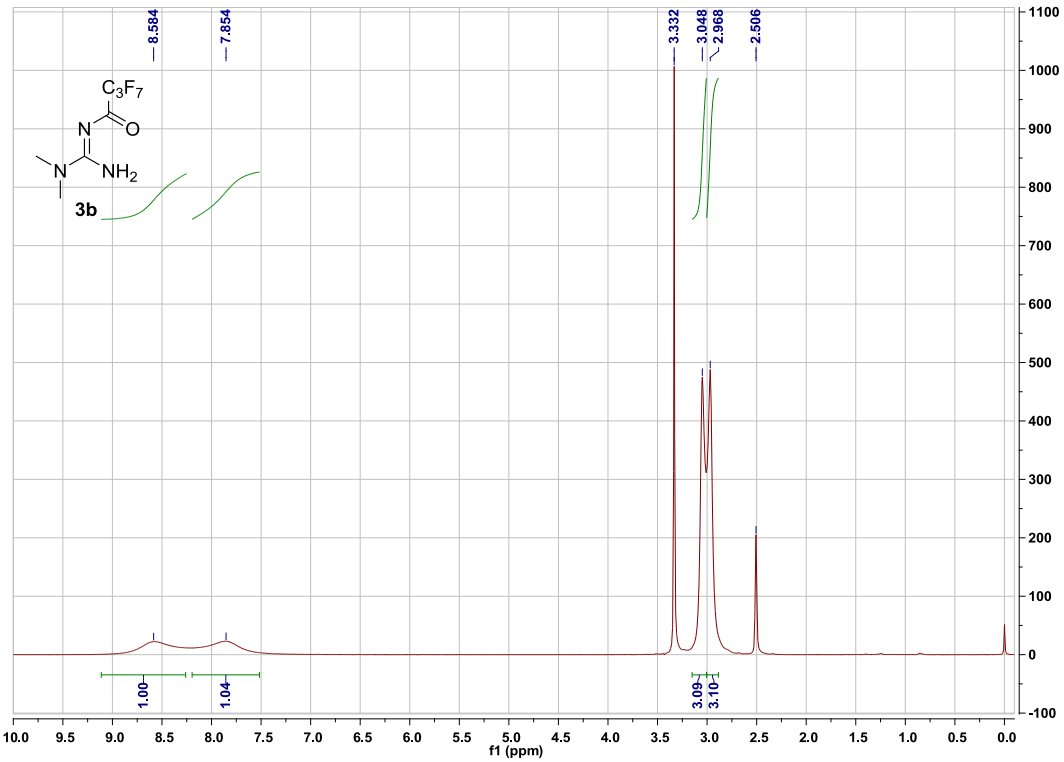
-120.010
-120.029
-120.048
-128.284
3.12
2.02
2.00
f1 (ppm)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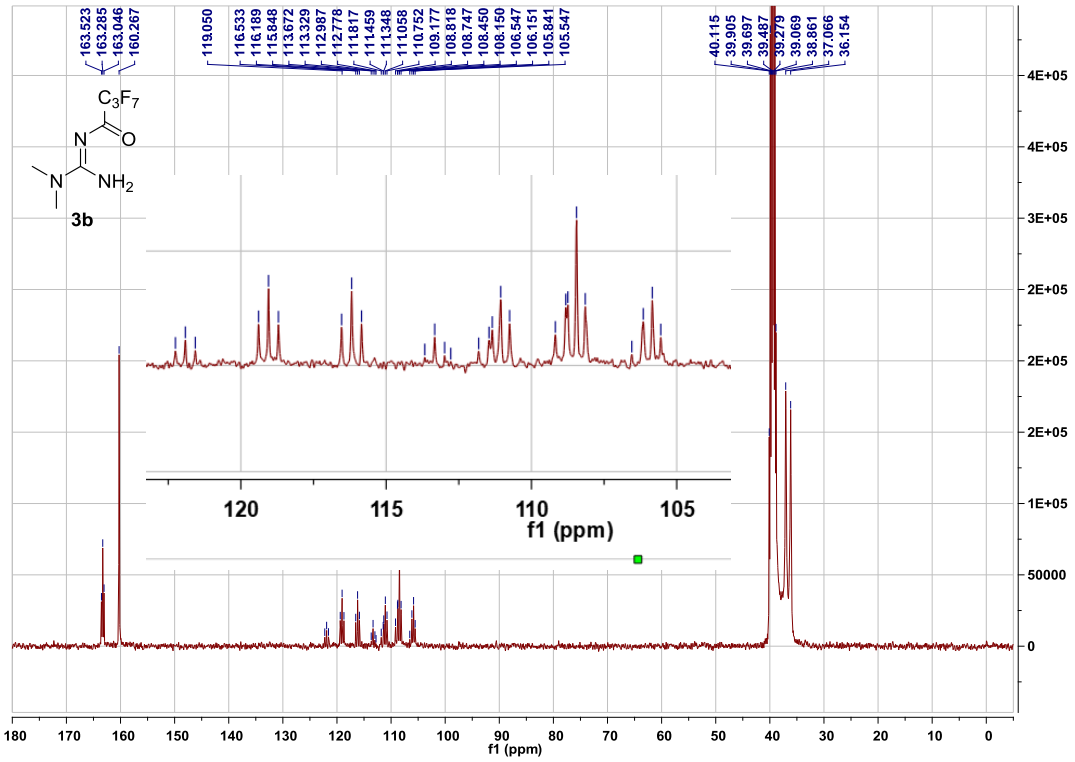
3.332
3.048
2.968
2.506
1.00
1.04
3.09
3.10
f1 (ppm)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163.285
163.046
160.267
119.050
116.533
116.189
115.848
113.672
113.329
112.987
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111.817
111.459
111.348
111.058
110.752
109.177
108.818
108.747
108.450
108.150
106.547
106.151
105.841
105.547
40.115
39.905
39.697
39.487
39.279
39.069
38.861
37.066
36.154
C3F7
N
O
N
NH2
3b
120
115
110
105
f1 (ppm)
4E+05
4E+05
3E+05
2E+05
2E+05
2E+05
1E+05
50000
0
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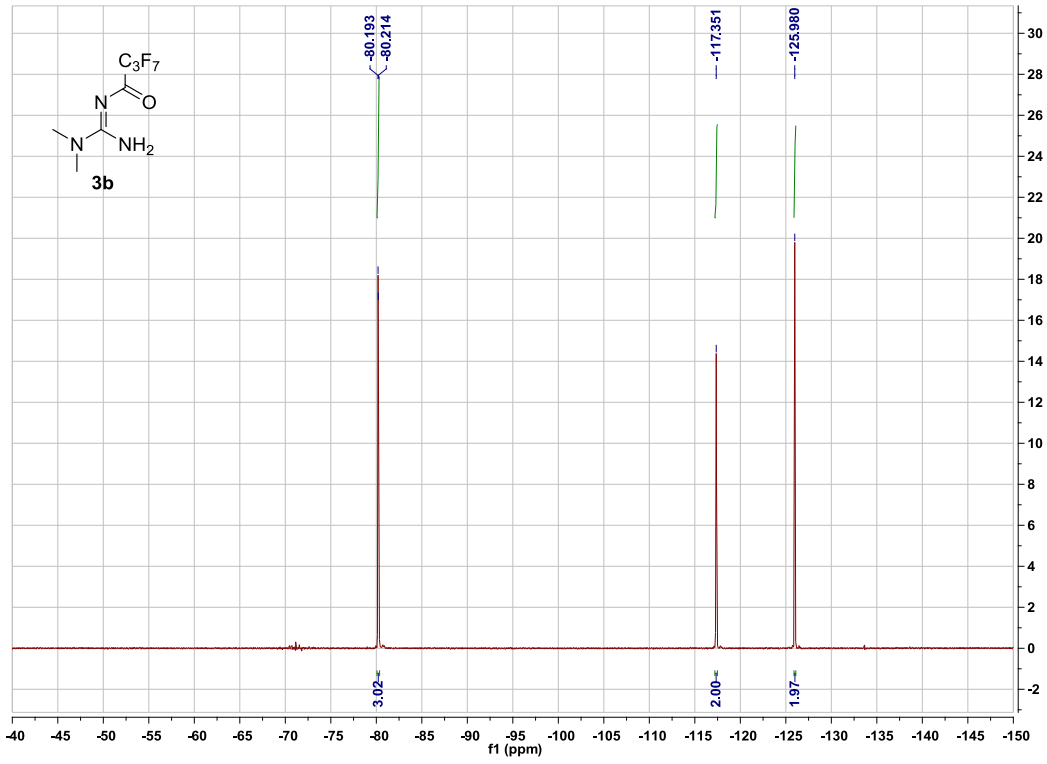
f1 (ppm)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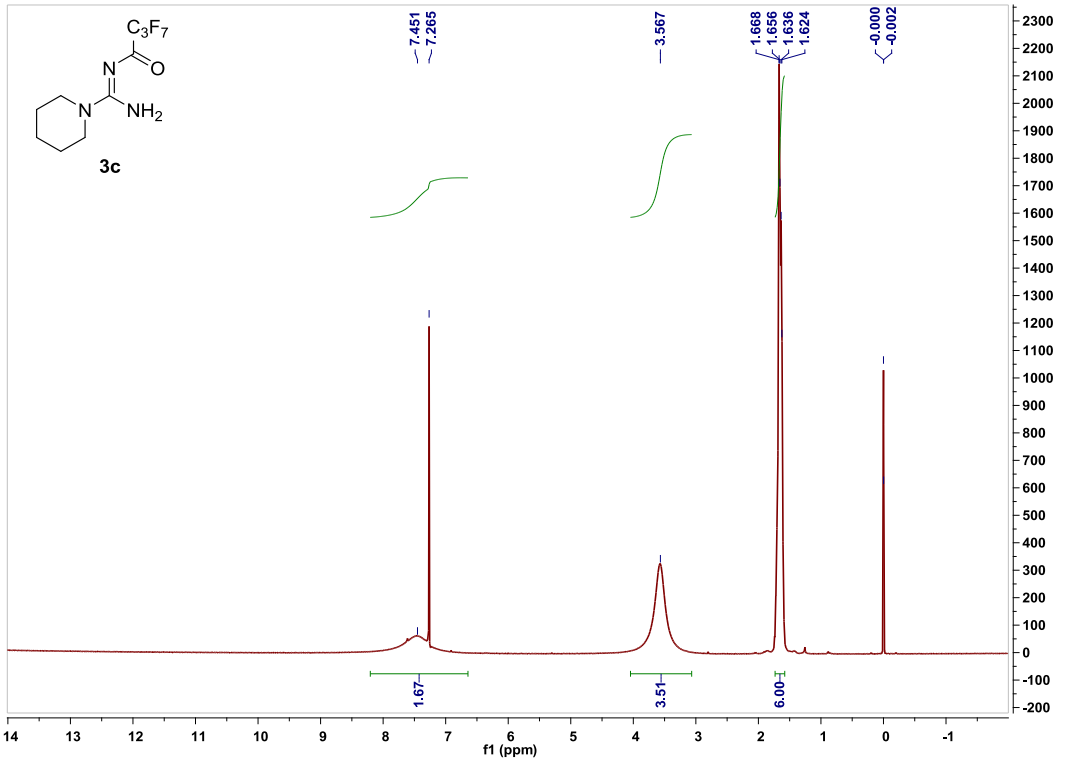
-117.351
-125.980
C3F7
N
O
N
NH2
3b
3.02
2.00
1.97
30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0 -2
-40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150
f1 (ppm)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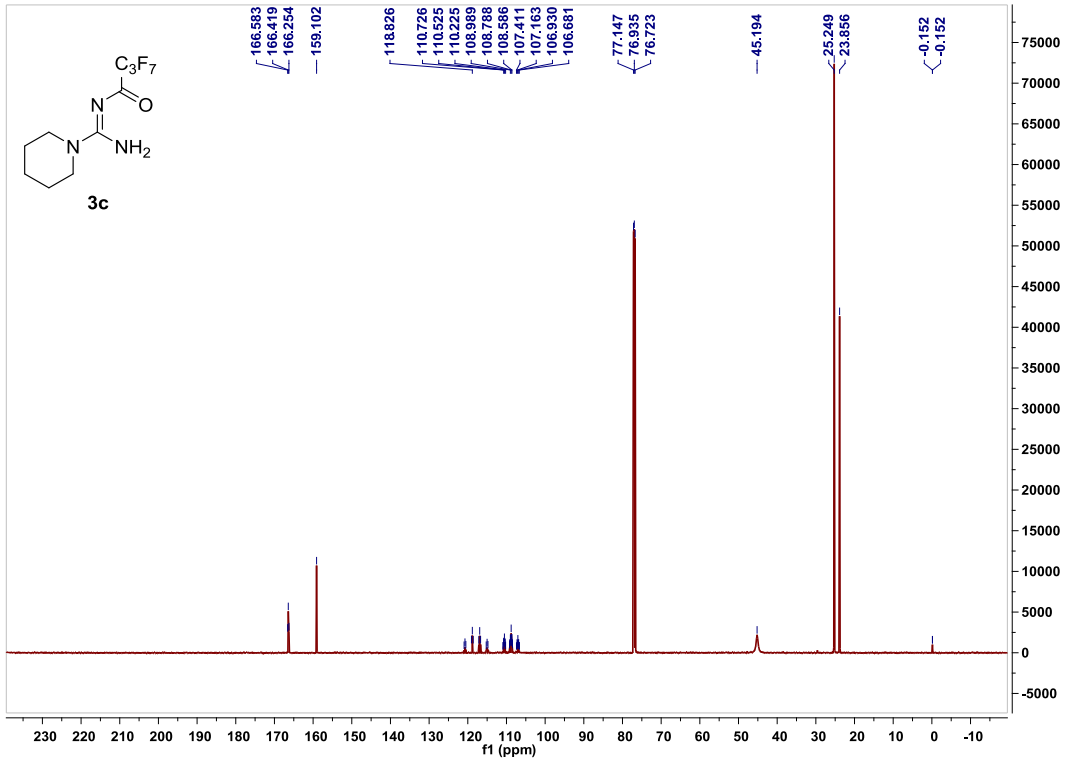
1.67
3.51
6.00
f1 (ppm)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166.419
166.254
159.102
118.826
110.726
110.525
110.225
108.989
108.788
108.586
107.411
107.163
106.930
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76.935
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23.856
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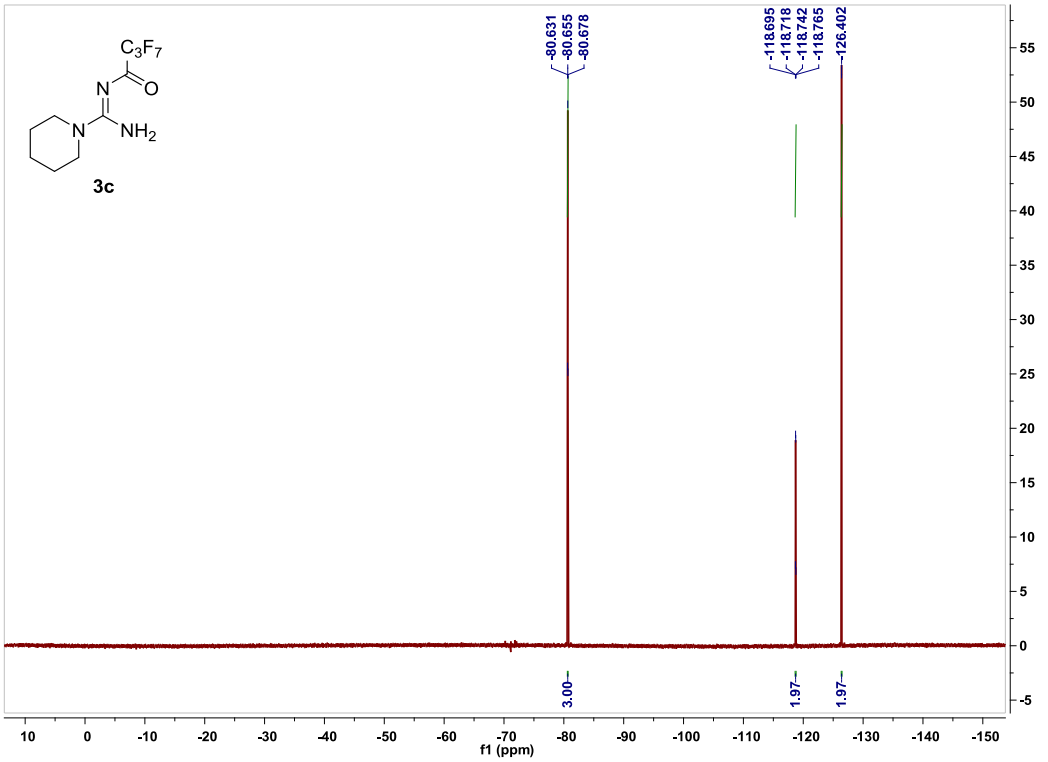
-0.152
f1 (ppm)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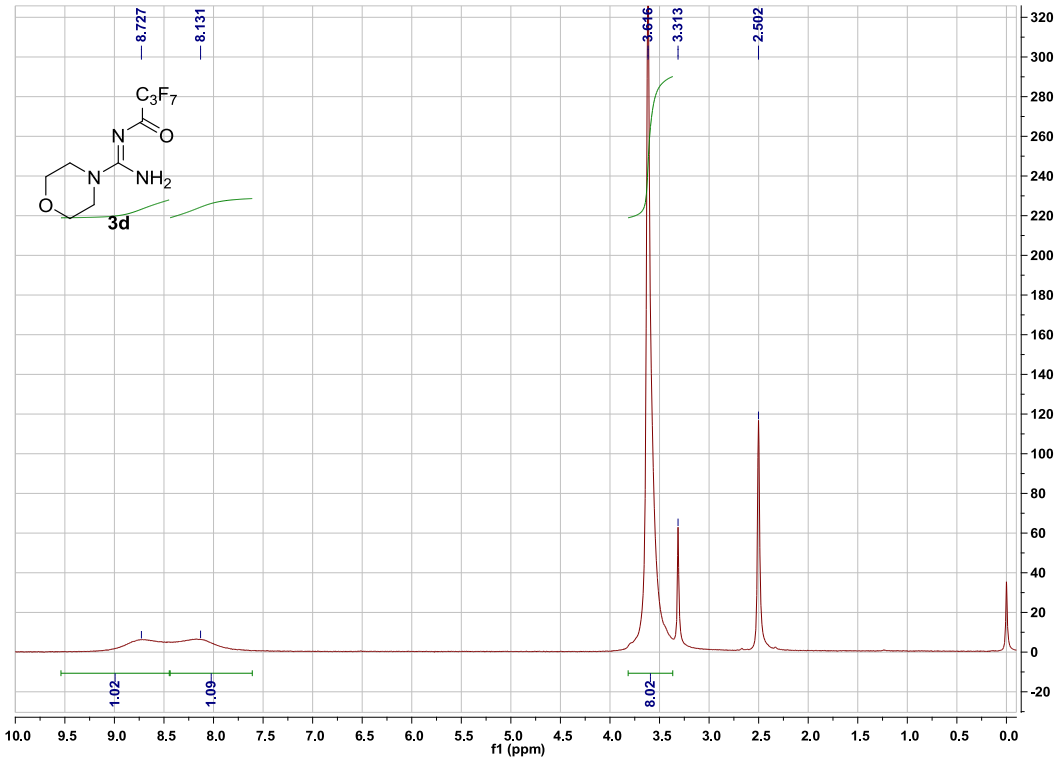
3.00
1.97
1.97
f1 (ppm)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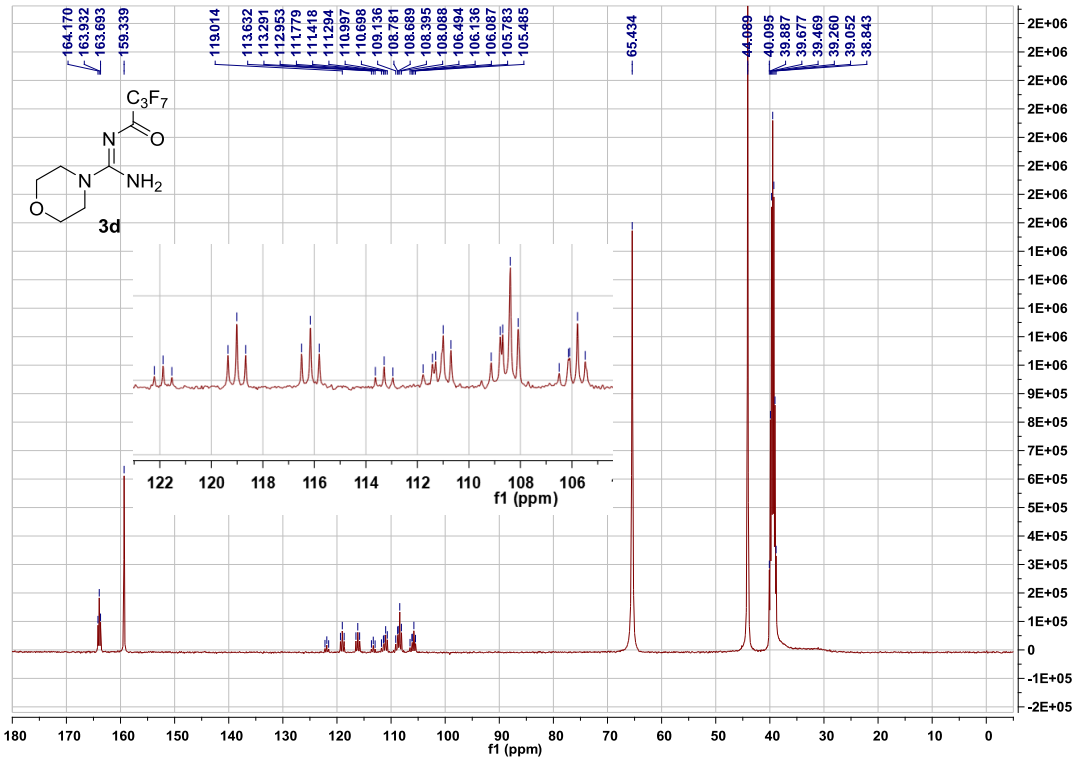
3.616
3.313
2.502
1.02
1.09
8.02
f1 (ppm)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113.632
113.291
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108.781
108.689
108.395
108.088
106.494
106.136
106.087
105.783
105.485
65.434
44.088
40.095
39.887
39.677
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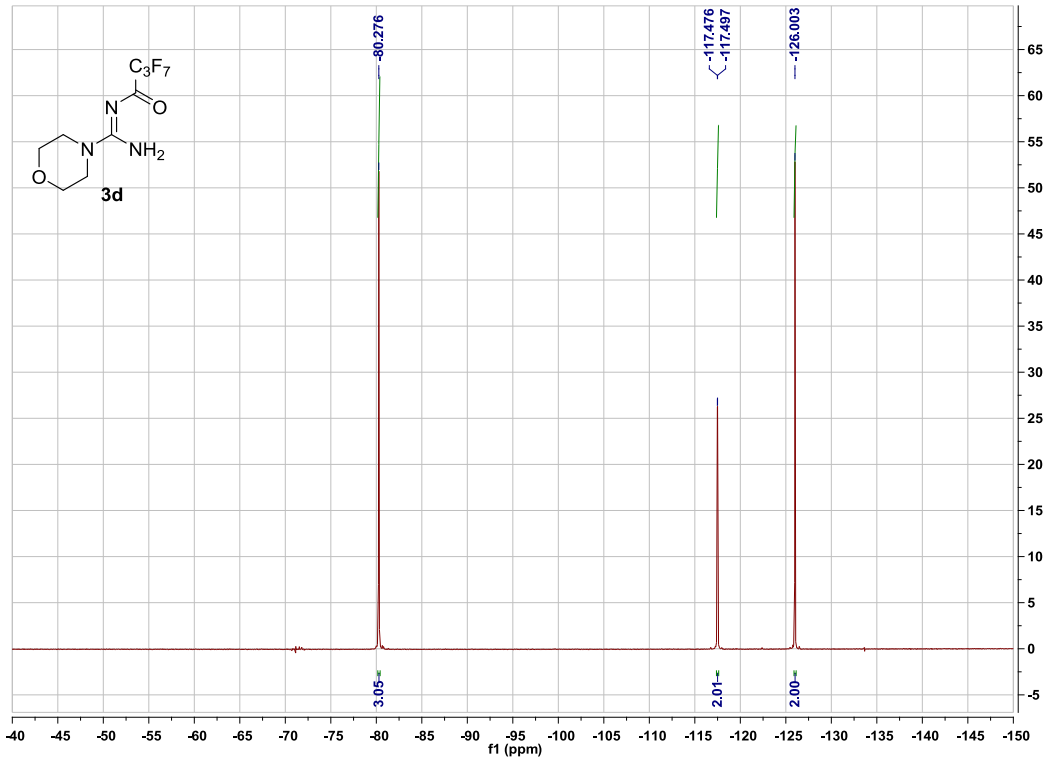
39.052
38.843
C3F7
N
O
N
NH2
O
3d
f1 (ppm)
f1 (ppm)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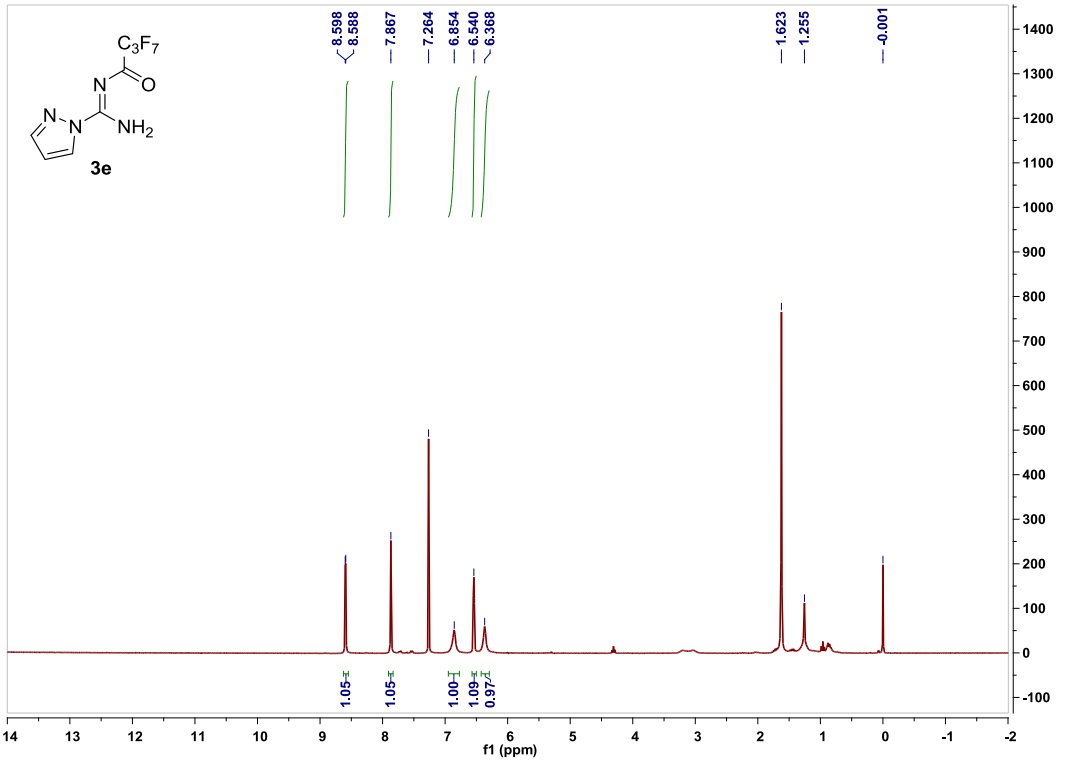
N
NH2
O
3d
3.05
2.01
2.00
f1 (ppm)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7.264
6.854
6.540
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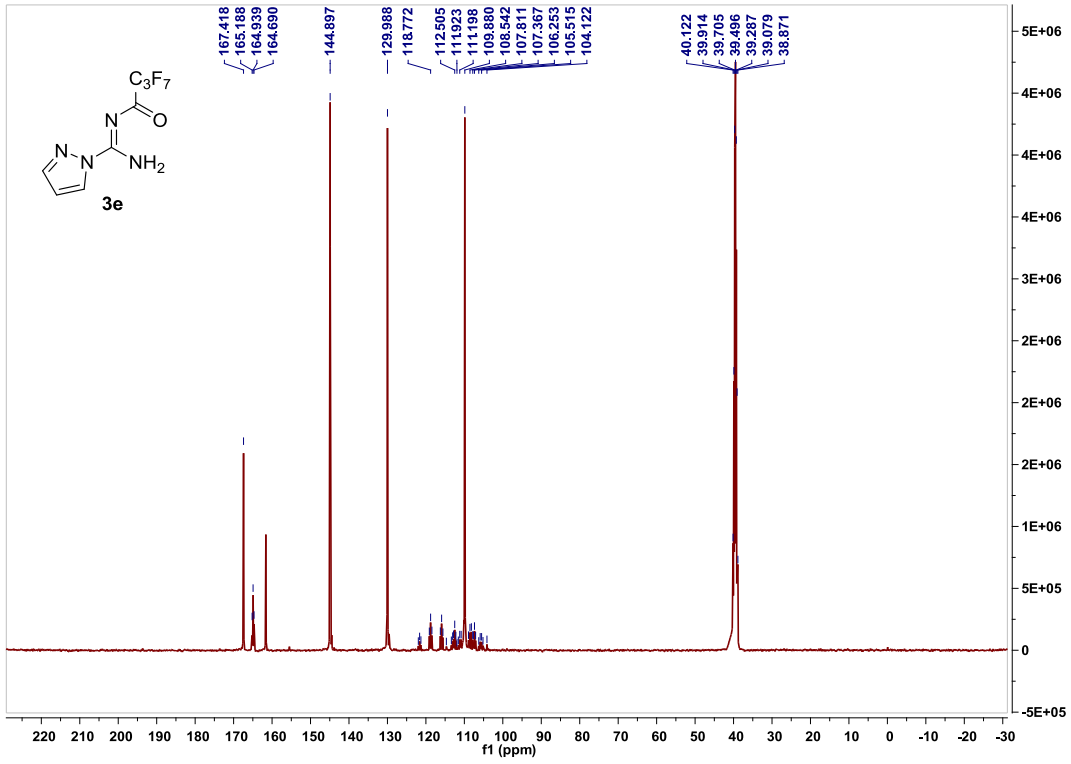
1.05
1.05
1.00
1.09
0.97
f1 (ppm)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144.897
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111.923
111.198
109.880
108.542
107.811
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39.287
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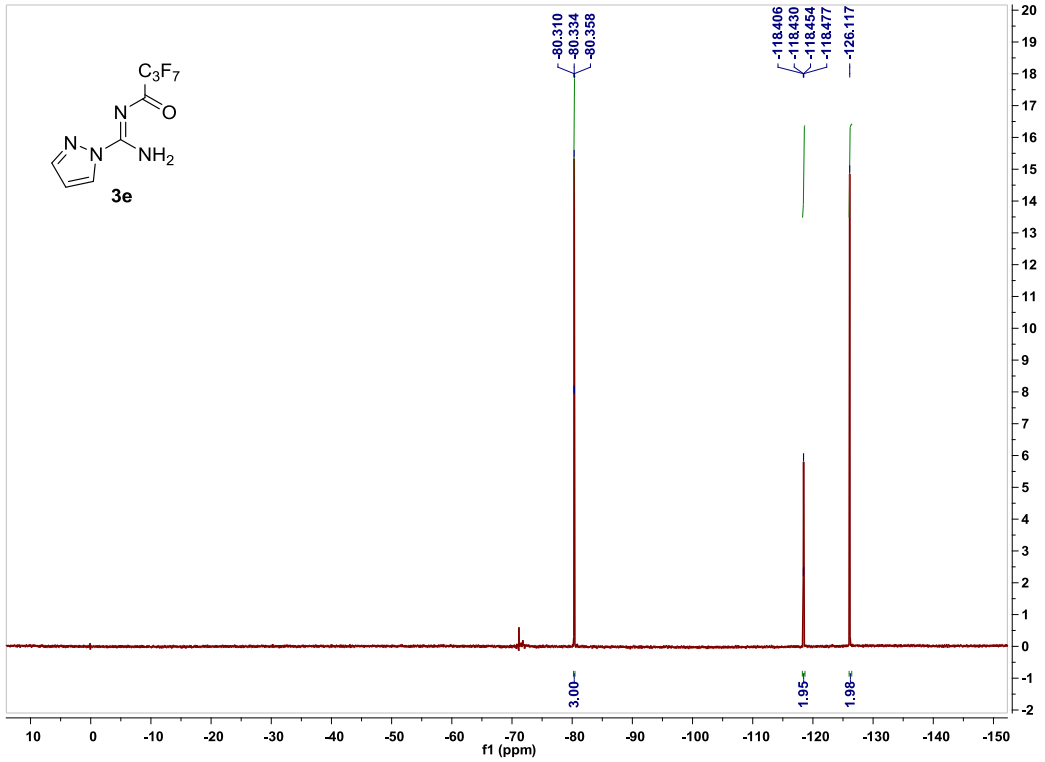
38.871
f1 (ppm)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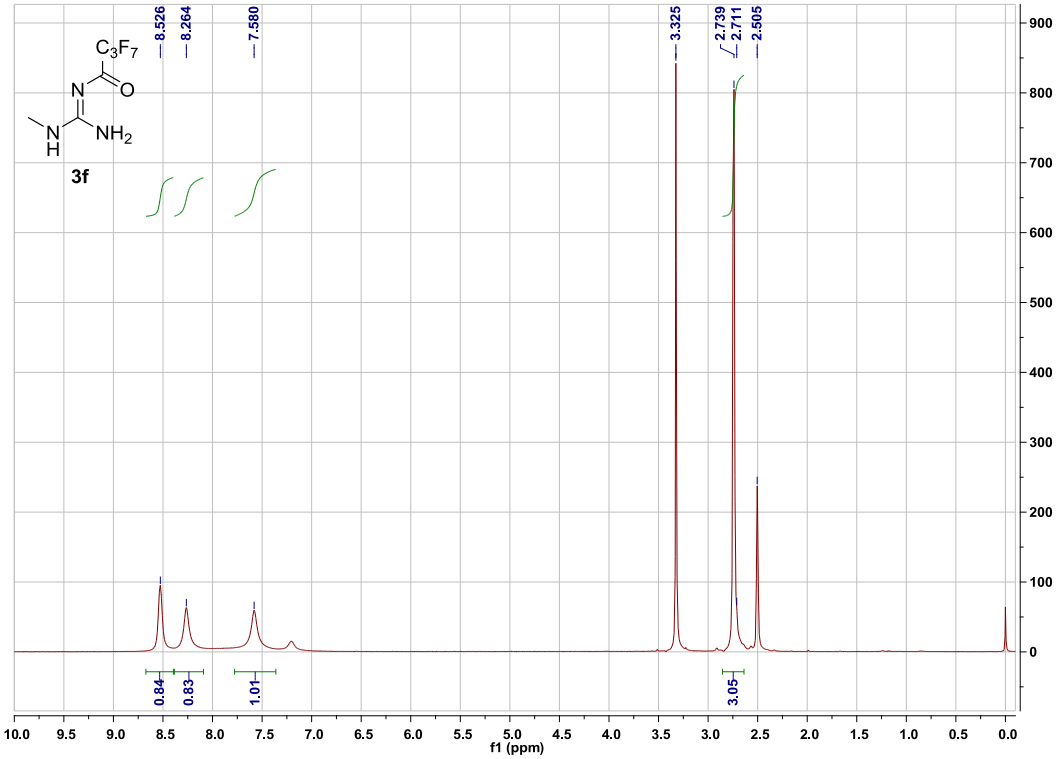
3.00
1.95
1.98
f1 (ppm)

3e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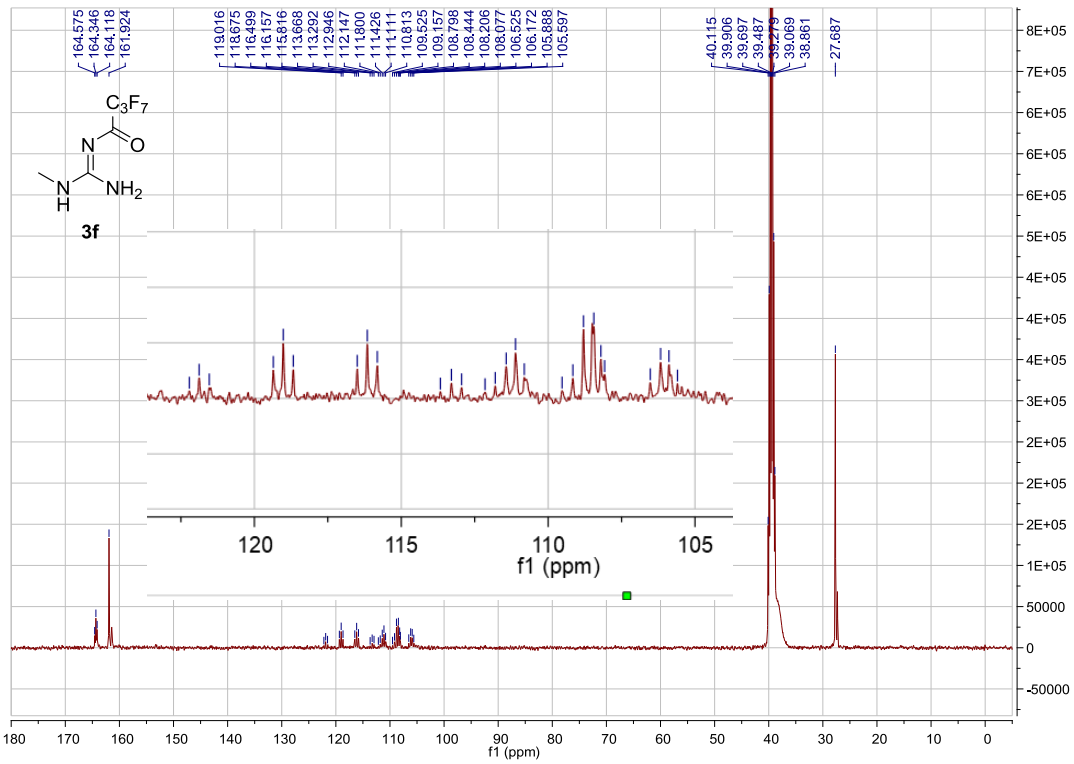
0.83
1.01
3.05
f1 (ppm)

3f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116.157
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113.668
113.292
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112.147
111.800
111.426
111.111
110.813
109.525
109.157
108.798
108.444
108.206
108.077
106.525
106.172
105.888
105.597
40.115
39.906
39.697
39.487
39.279
39.069
38.861
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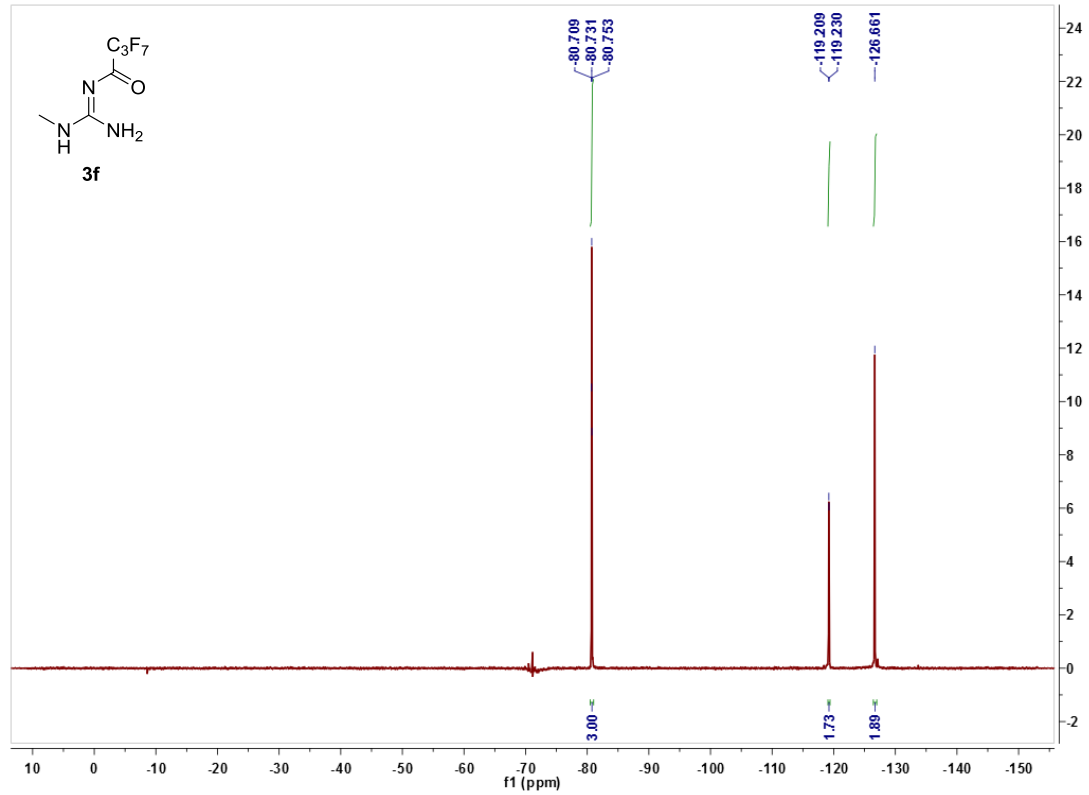
C_3F_7
N
O
N
H
NH_2
3f
120
115
110
105
f1 (ppm)
f1 (ppm)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H
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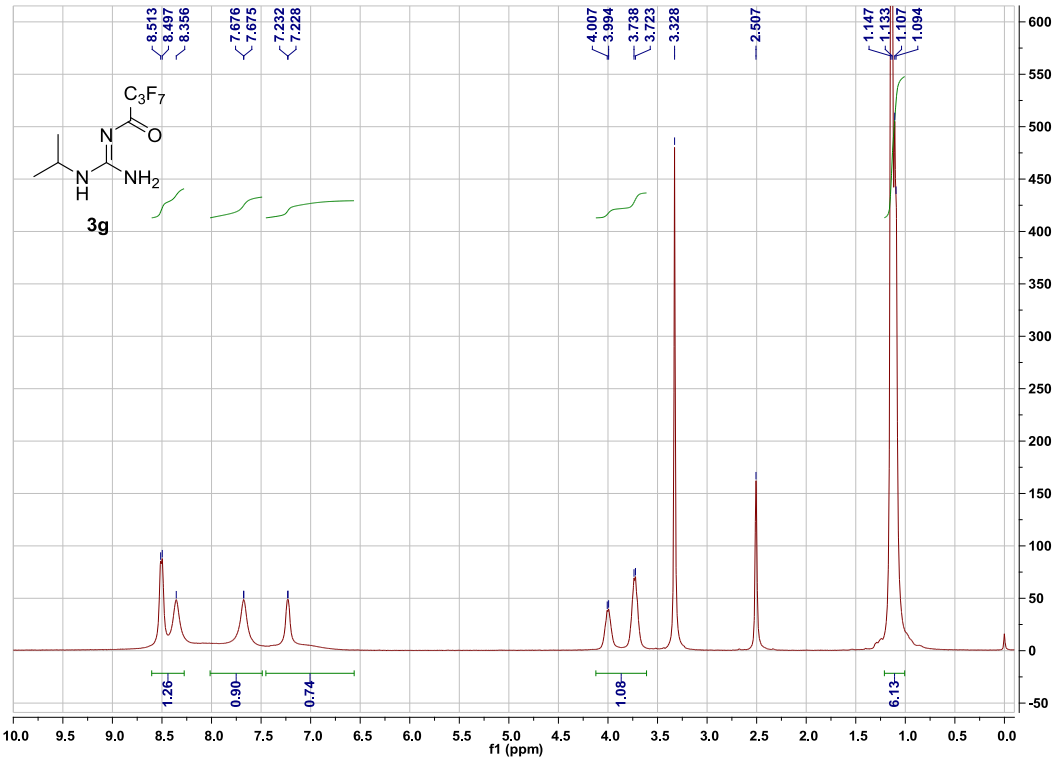
1.89
f1 (ppm)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4.007
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3g
1.26
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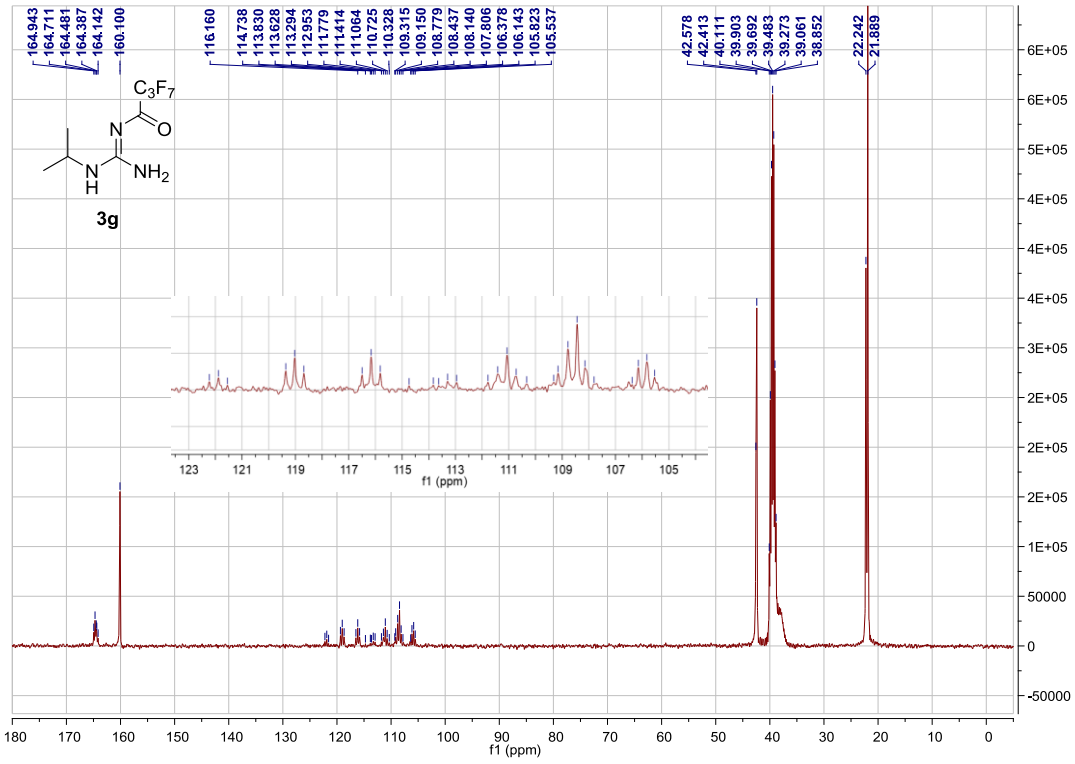
1.08
6.13
f1 (ppm)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111.414
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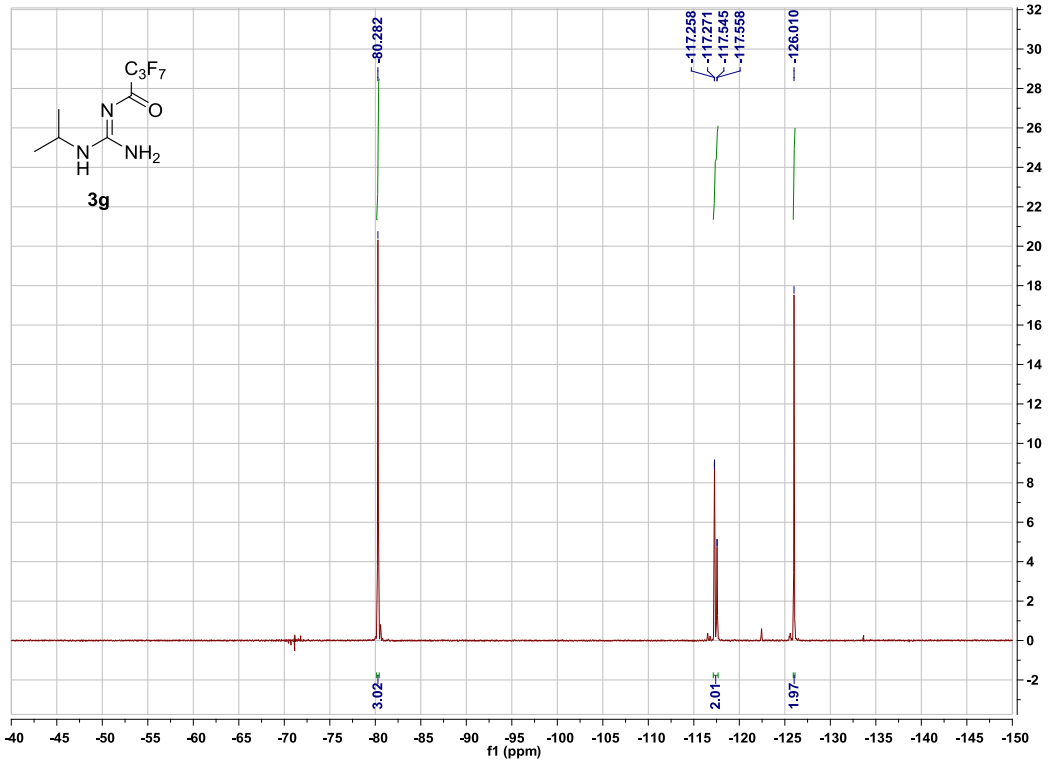
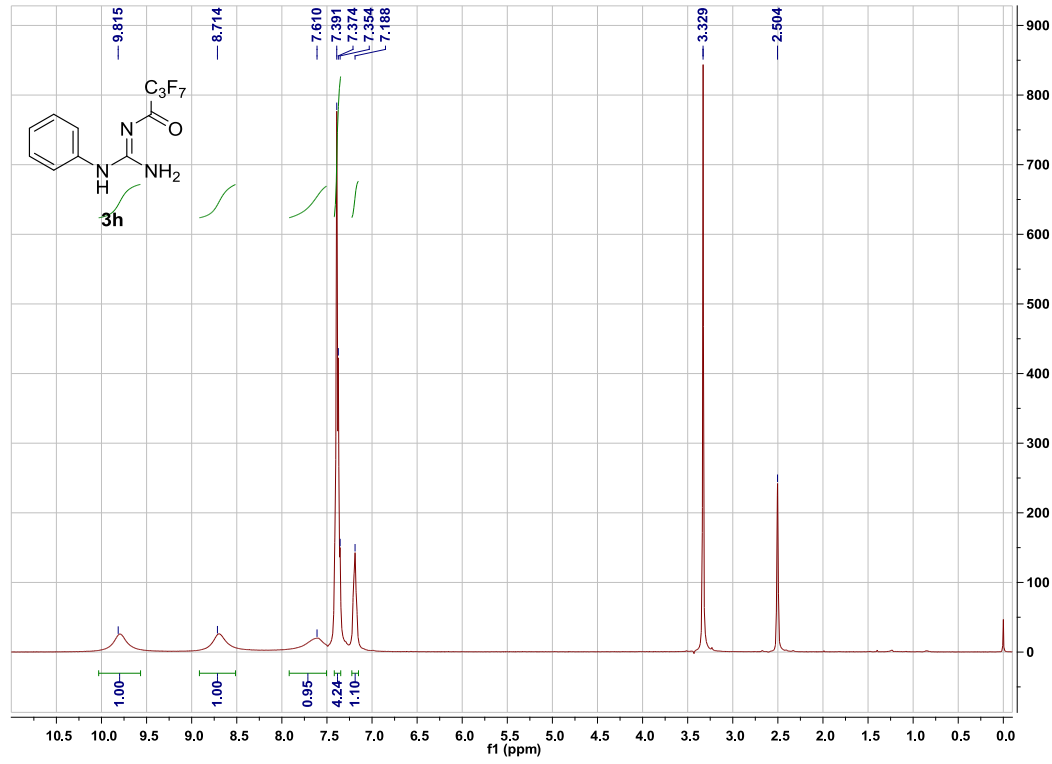
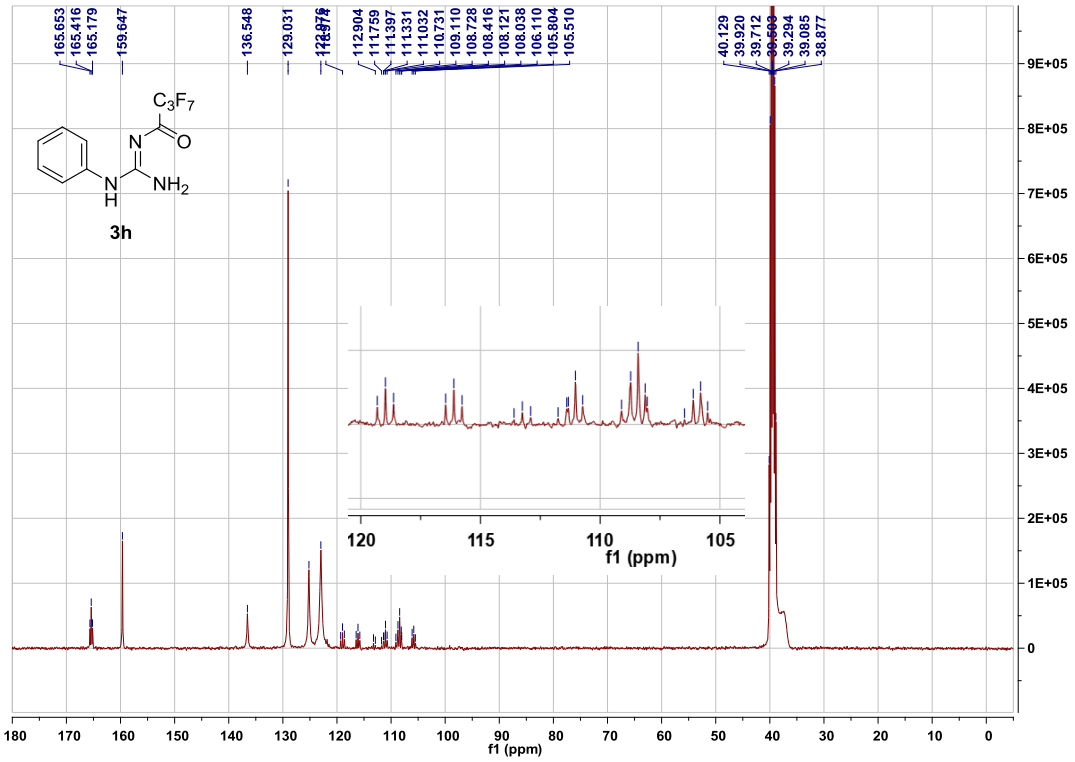
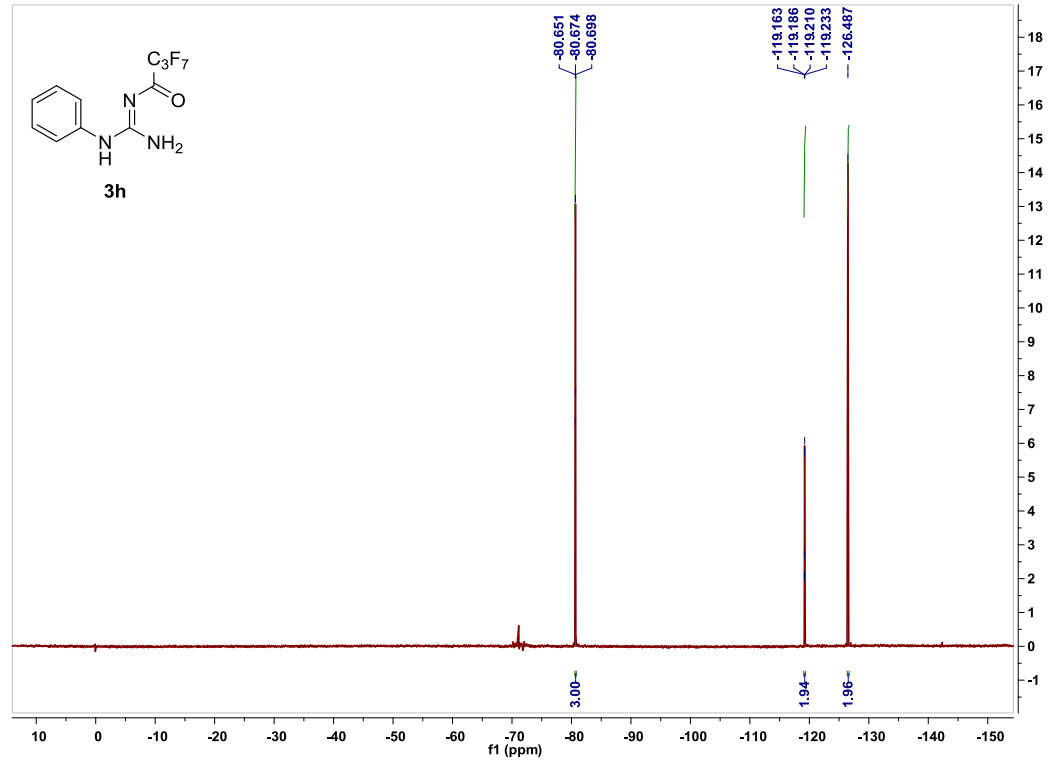
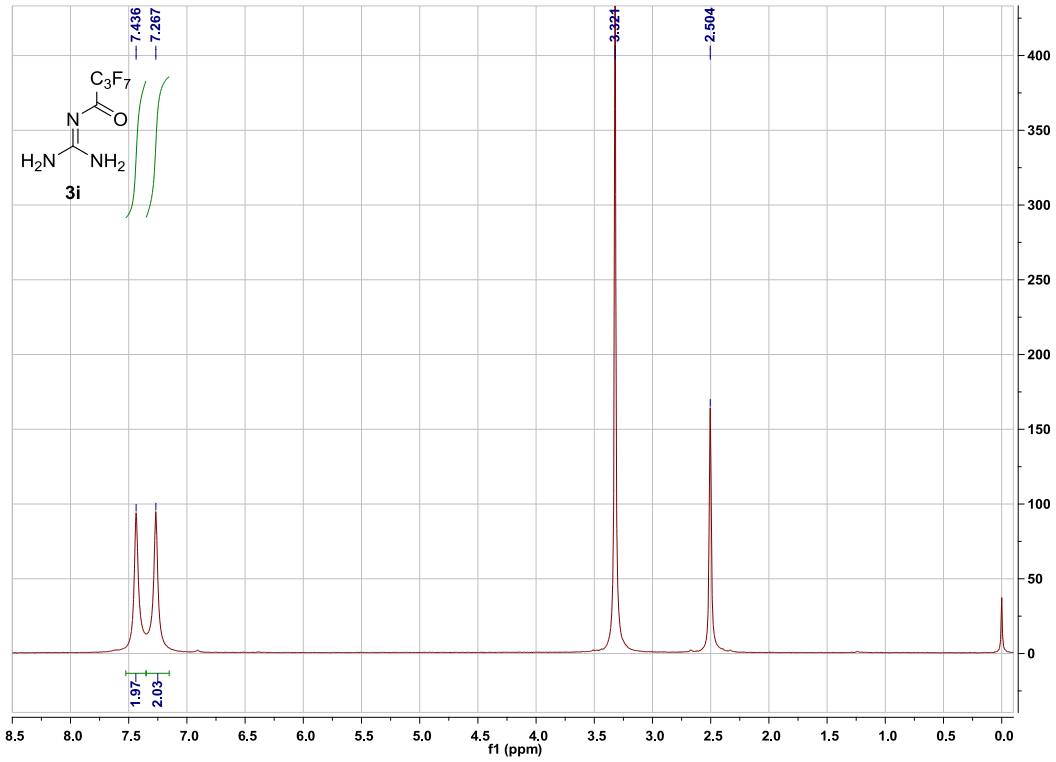
109.150
108.779
108.437
108.140
107.806
106.378
106.143
105.823
105.537
42.578
42.413
40.111
39.903
39.692
39.483
39.273
39.061
38.852
22.242
21.889
3g
f1 (ppm)
f1 (ppm)

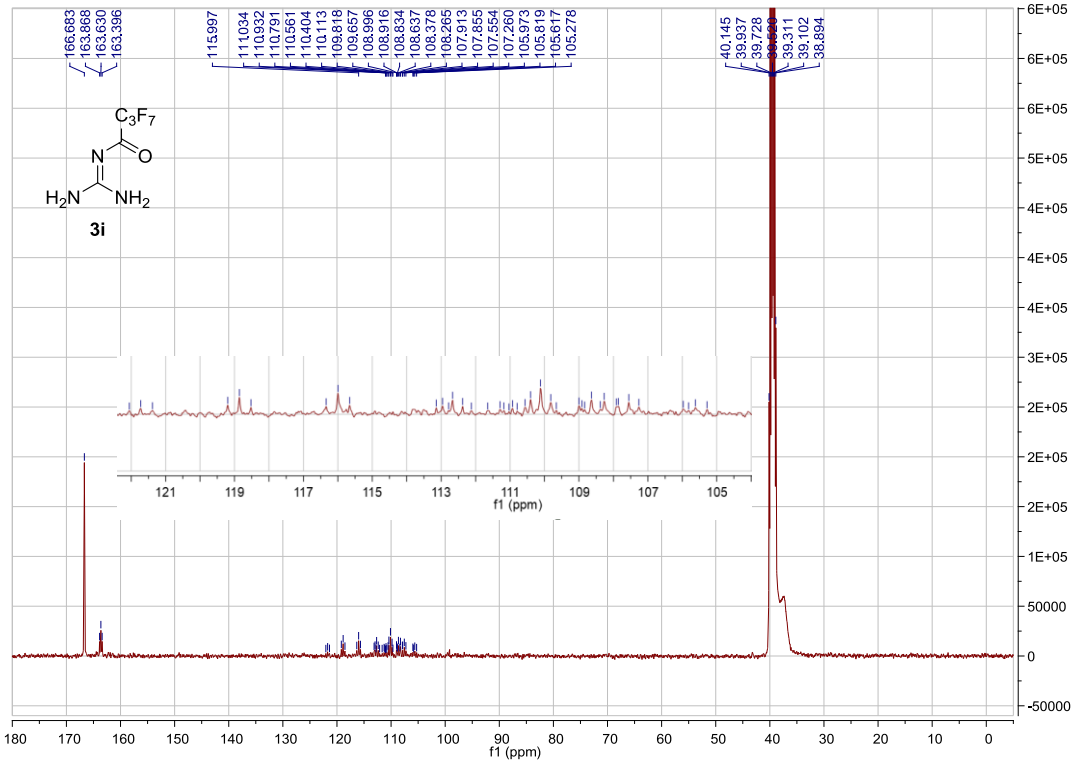

-80.282
-117.258
-117.271
-117.545
-117.558
-126.010
3.02
2.01
1.97
f1 (ppm)
3g

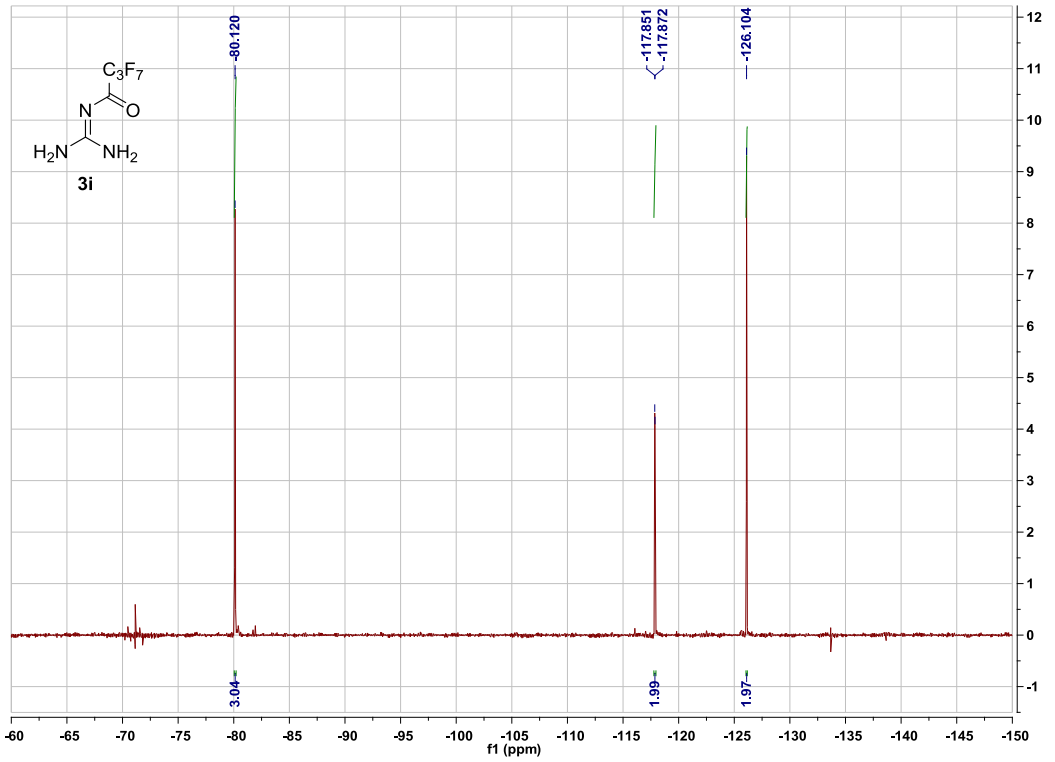

9.815
8.714
7.610
7.391
7.374
7.354
7.188
3.329
2.504
1.00
1.00
0.95
4.24
1.10
f1 (ppm)
3h

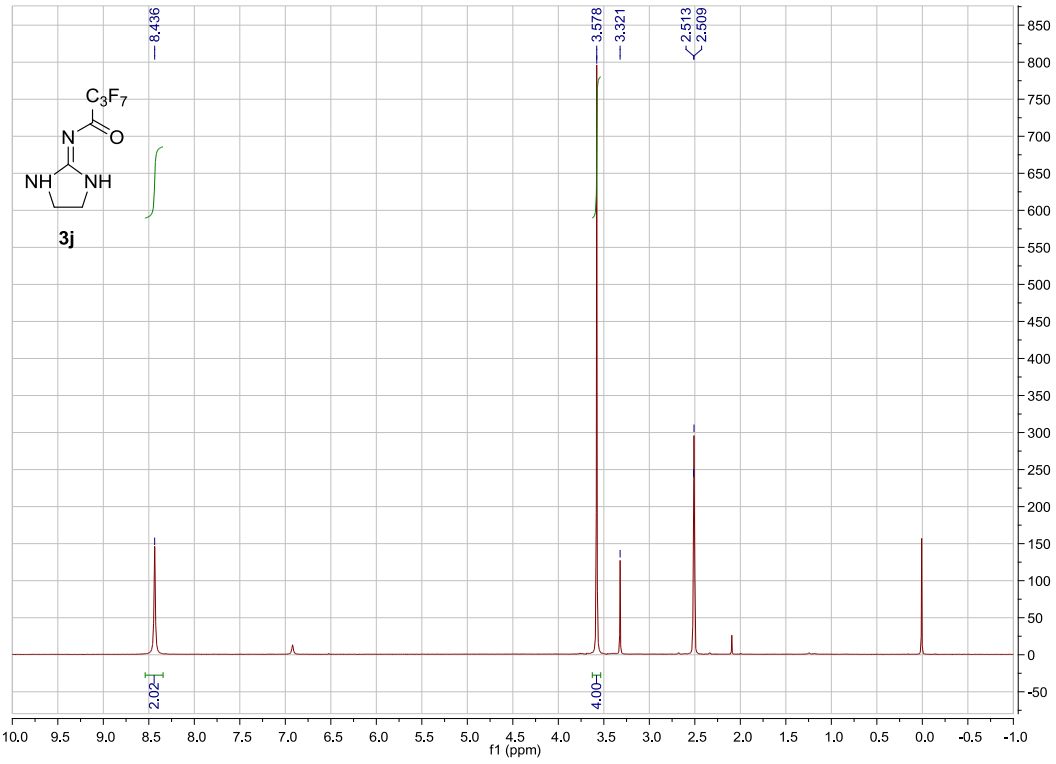

165.653
165.416
165.179
159.647
136.548
129.031
112.904
111.759
111.397
111.331
111.032
110.731
109.110
108.728
108.416
108.121
108.038
106.110
105.804
105.510
40.129
39.920
39.712
39.503
39.294
39.085
38.877
C3F7
N
O
N
H
NH2
3h
120
115
110
105
f1 (ppm)
9E+05
8E+05
7E+05
6E+05
5E+05
4E+05
3E+05
2E+05
1E+05
0
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

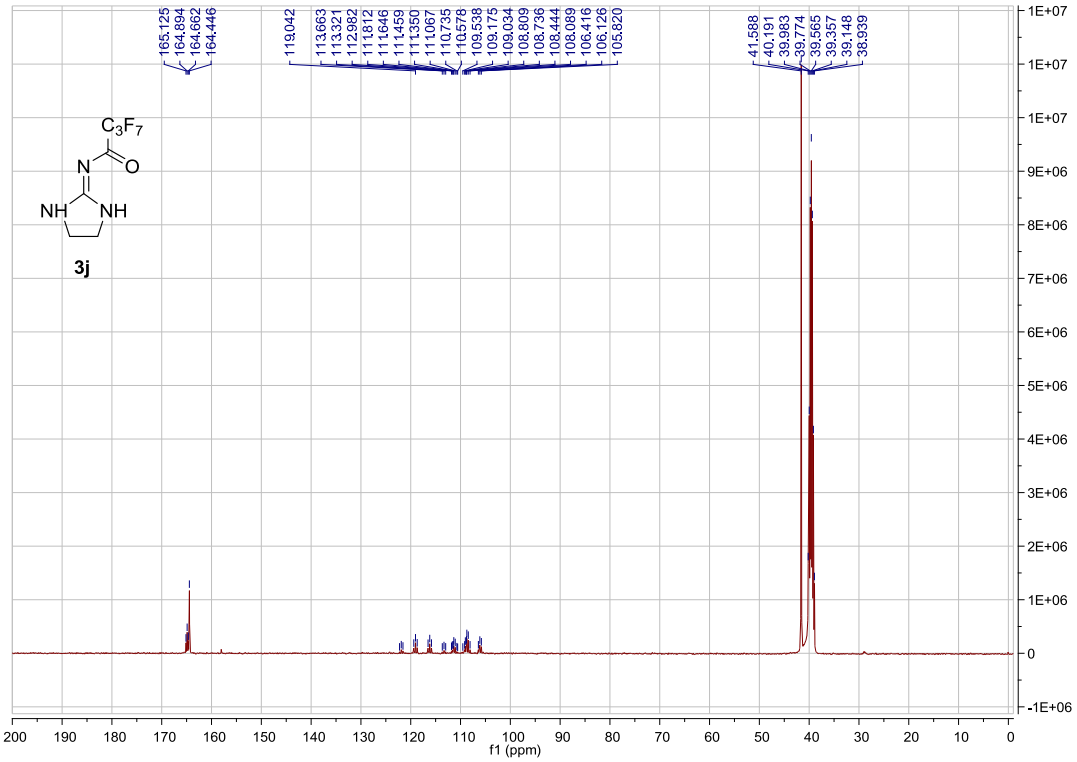

-80.651
-80.674
-80.698
-119.163
-119.186
-119.210
-119.233
-126.487
C3F7
N
O
N
H
NH2
3h
3.00
1.94
1.96
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
f1 (ppm)

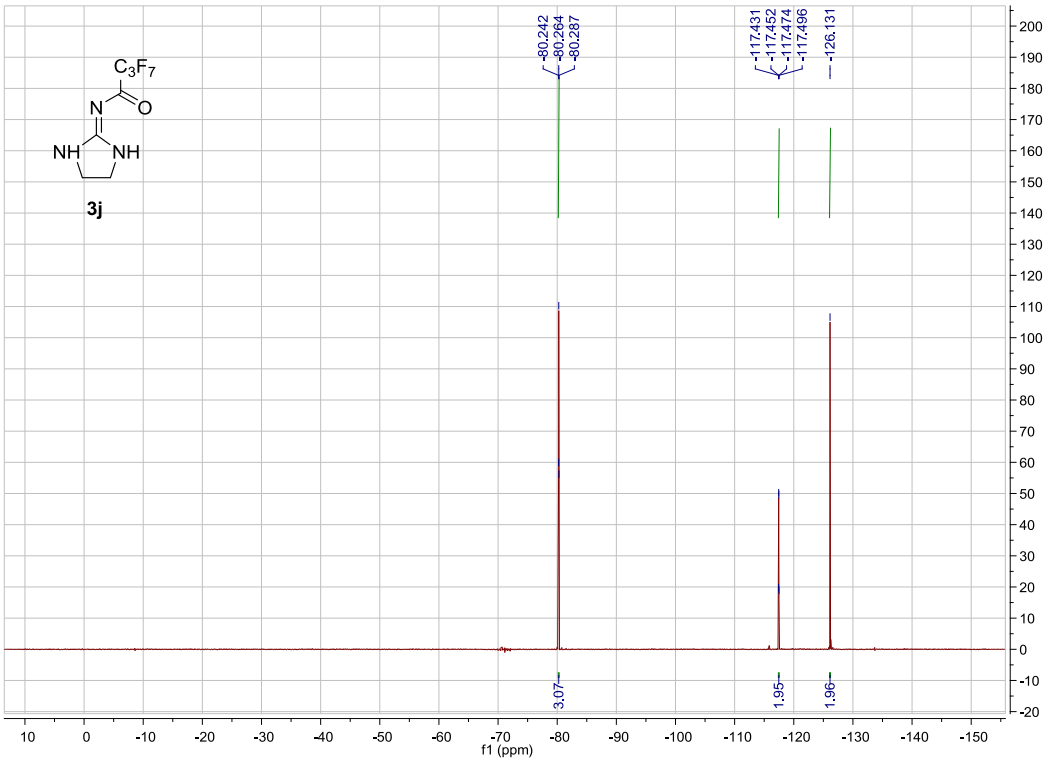

7.436
7.267
3.324
2.504
1.97
2.03
3i
f1 (ppm)

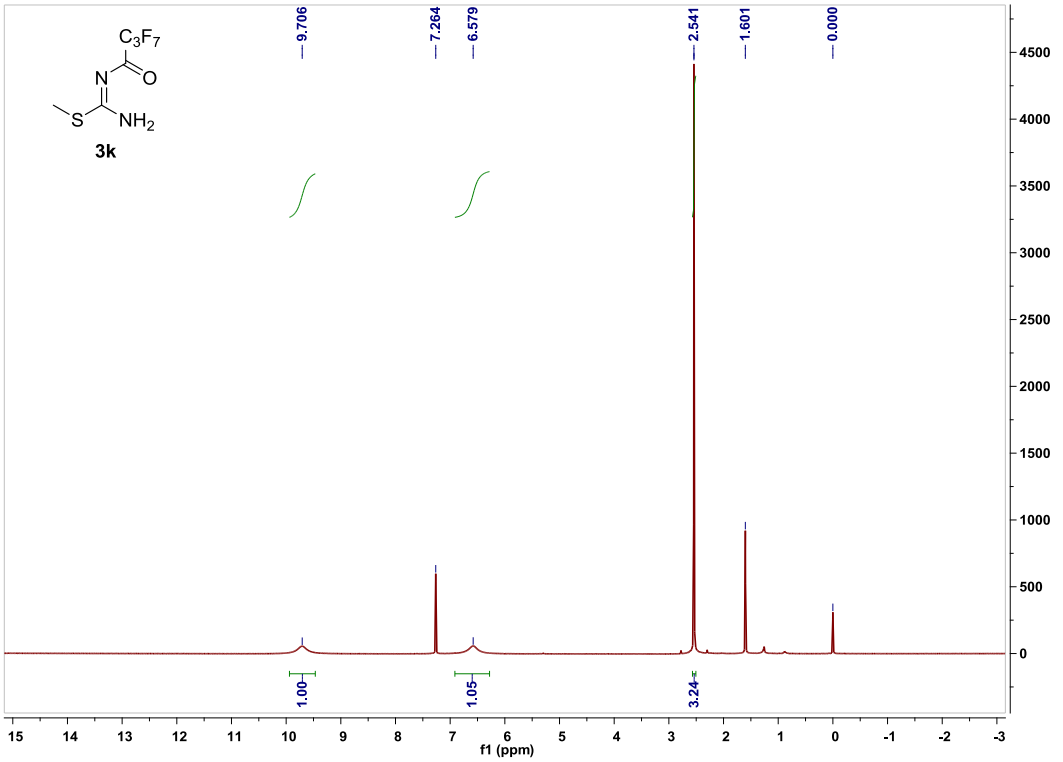

166.683
163.868
163.630
163.396
115.997
111.034
110.932
110.791
110.561
110.404
110.113
109.818
109.657
108.996
108.916
108.834
108.637
108.378
108.265
107.913
107.855
107.554
107.260
105.973
105.819
105.617
105.278
40.145
39.937
39.728
39.311
39.102
38.894
3i
f1 (ppm)

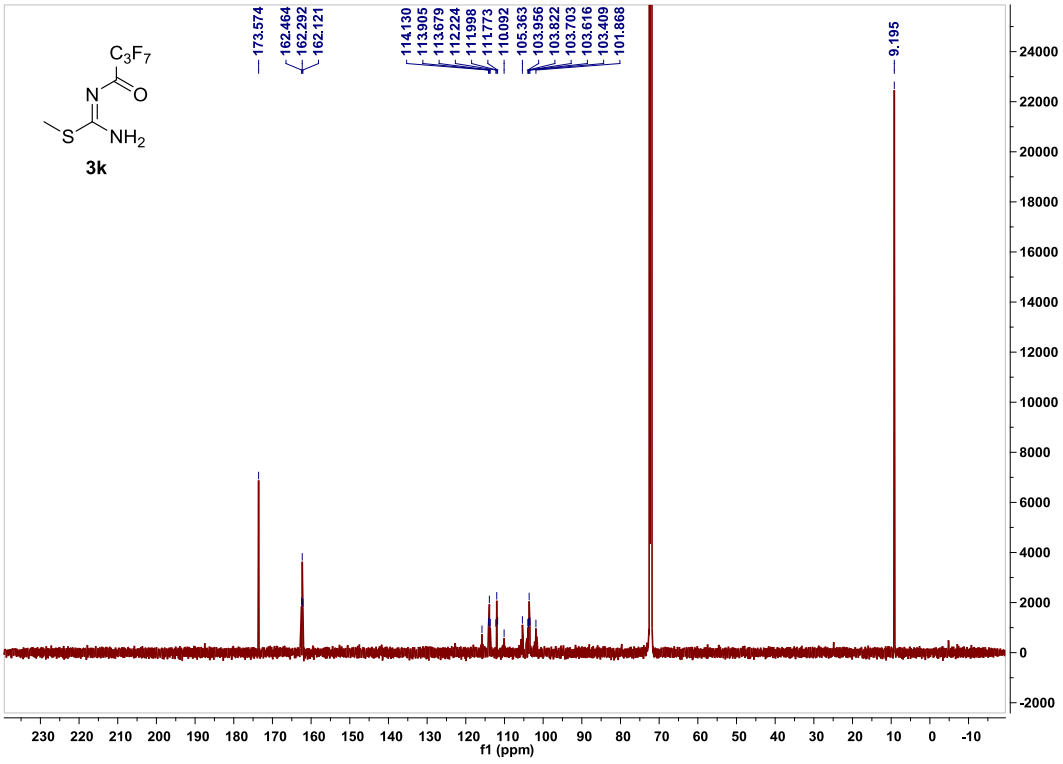

-80.120
-117.851
-117.872
-126.104
3.04
1.99
1.97
f1 (ppm)
3i

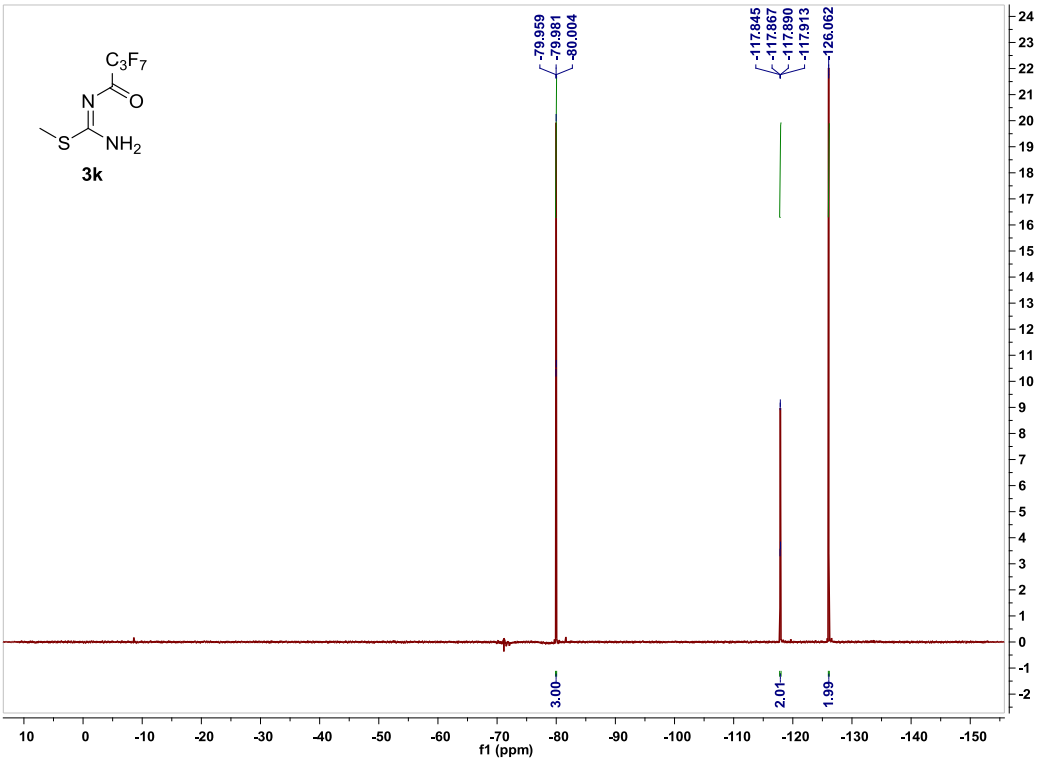

8.436
3.578
3.321
2.513
2.509
2.02
4.00
f1 (ppm)
3j

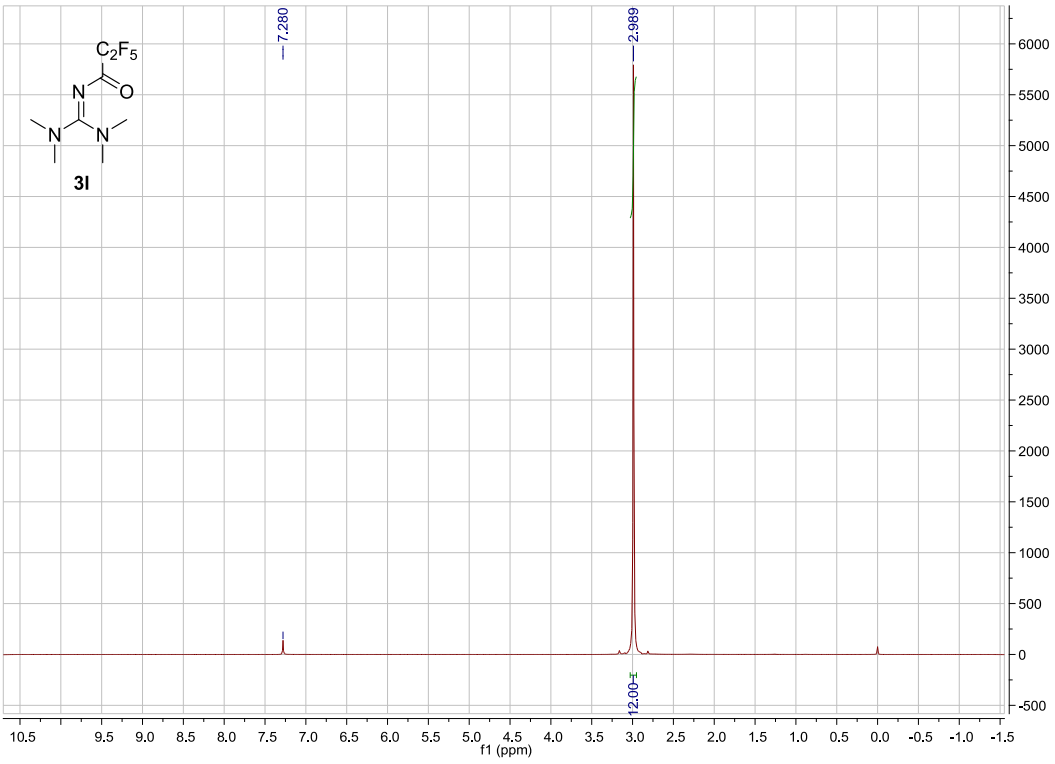

3j
f1 (ppm)

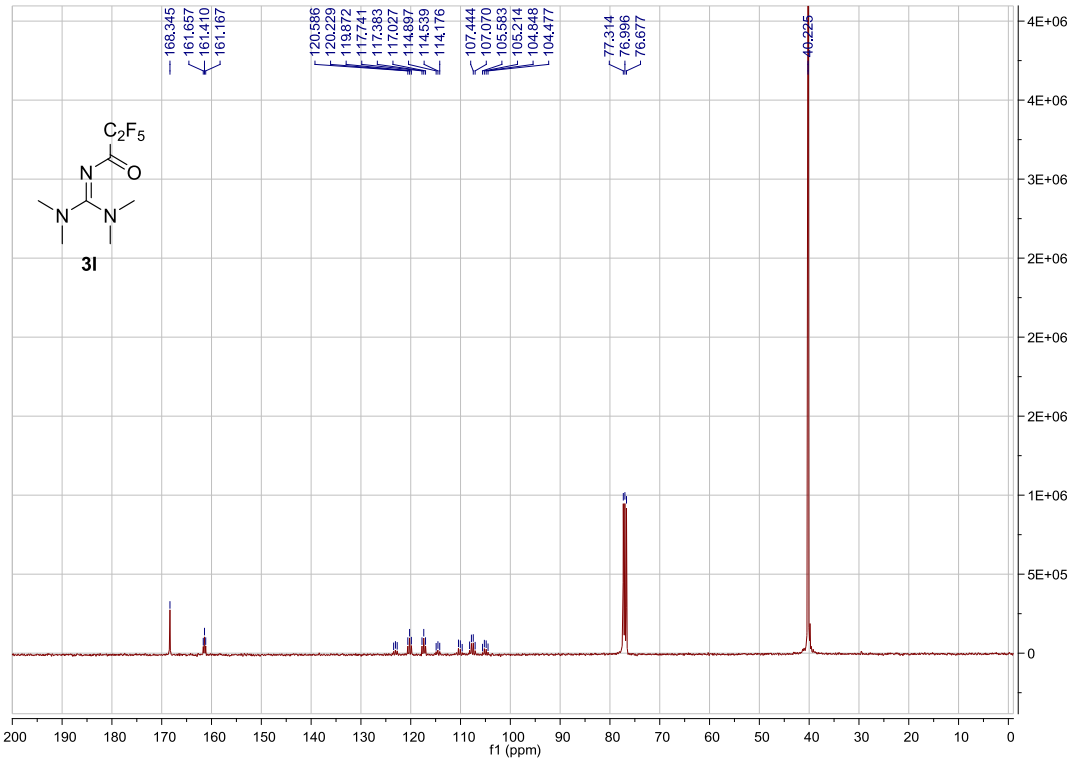

3j
f1 (ppm)

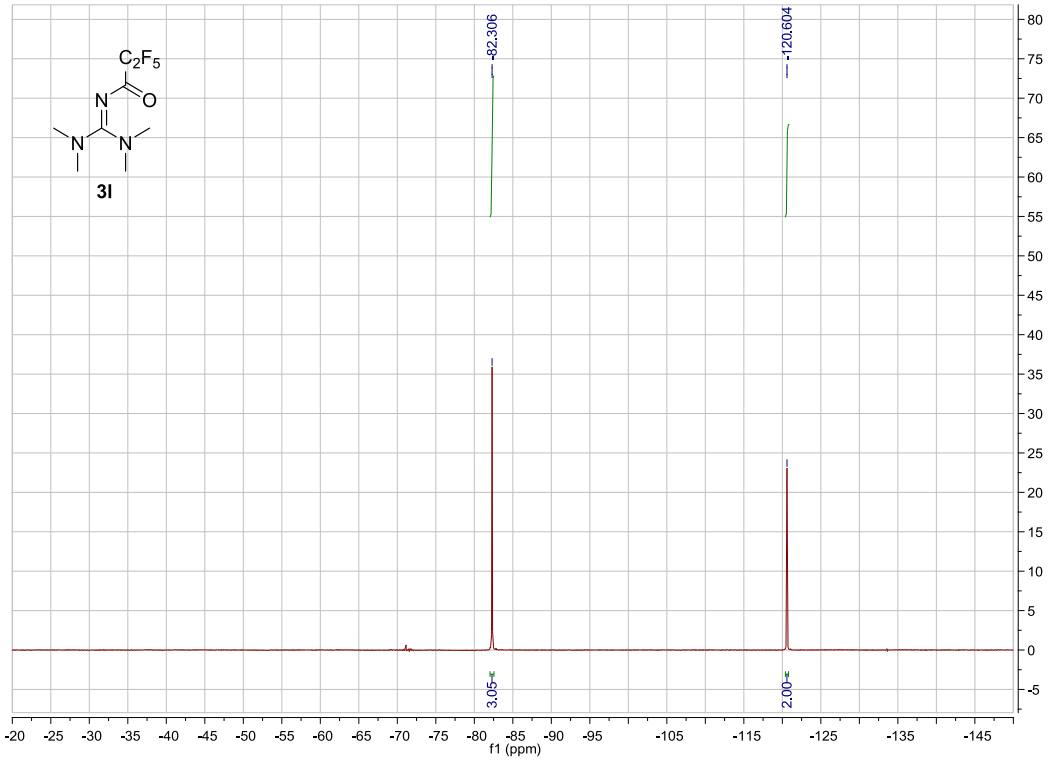

3k
9.706
7.264
6.579
2.541
1.601
0.000
1.00
1.05
3.24
f1 (ppm)

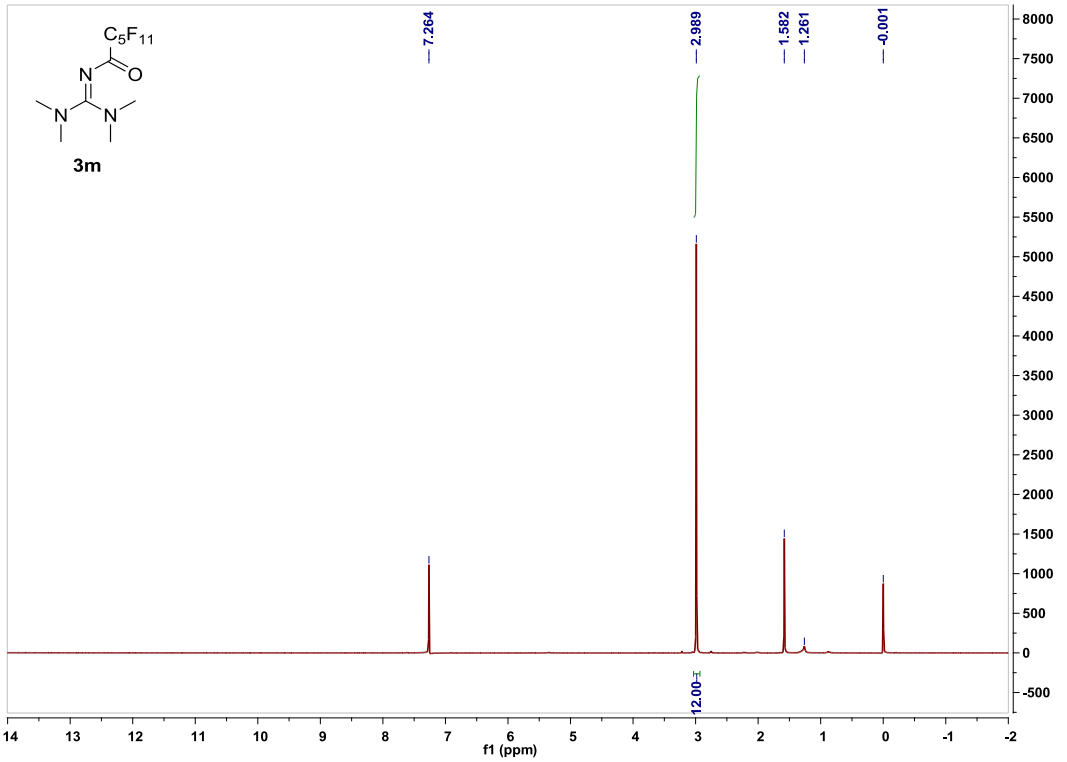

3k
173.574
162.464
162.292
162.121
114.130
113.905
113.679
112.224
111.998
111.773
110.092
105.363
103.956
103.822
103.703
103.616
103.409
101.868
9.195
f1 (ppm)

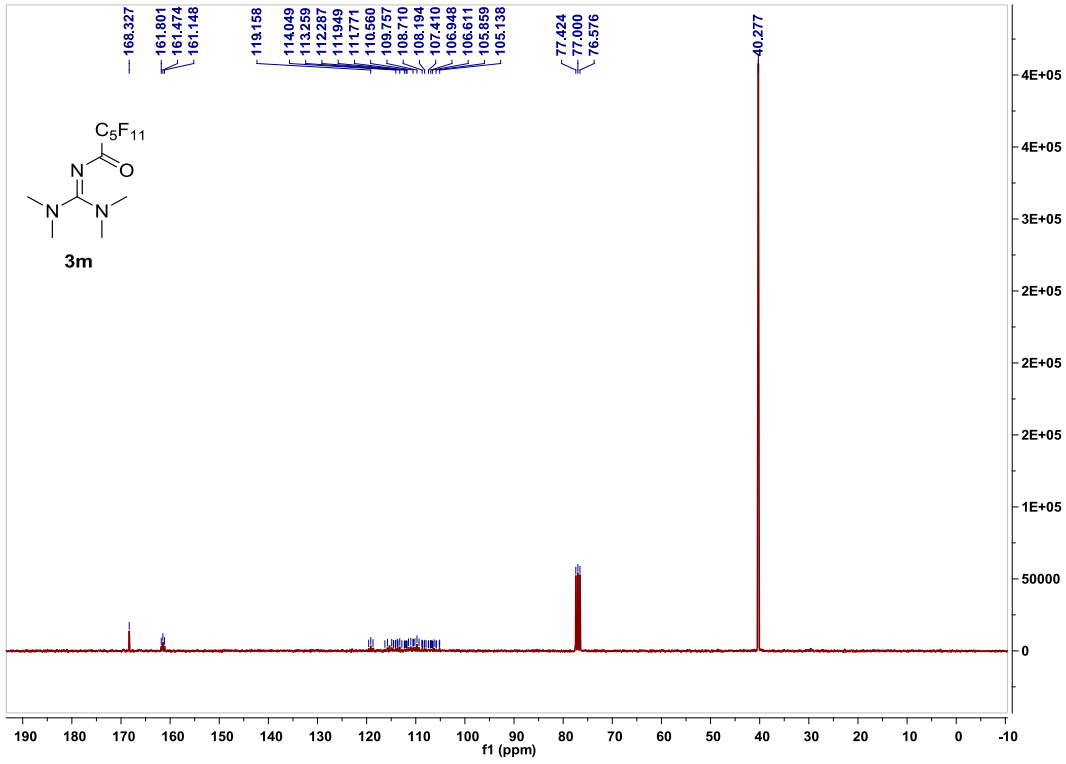

3k
-79.959
-79.981
-80.004
-117.845
-117.867
-117.890
-117.913
-126.062
3.00
2.01
1.99
f1 (ppm)

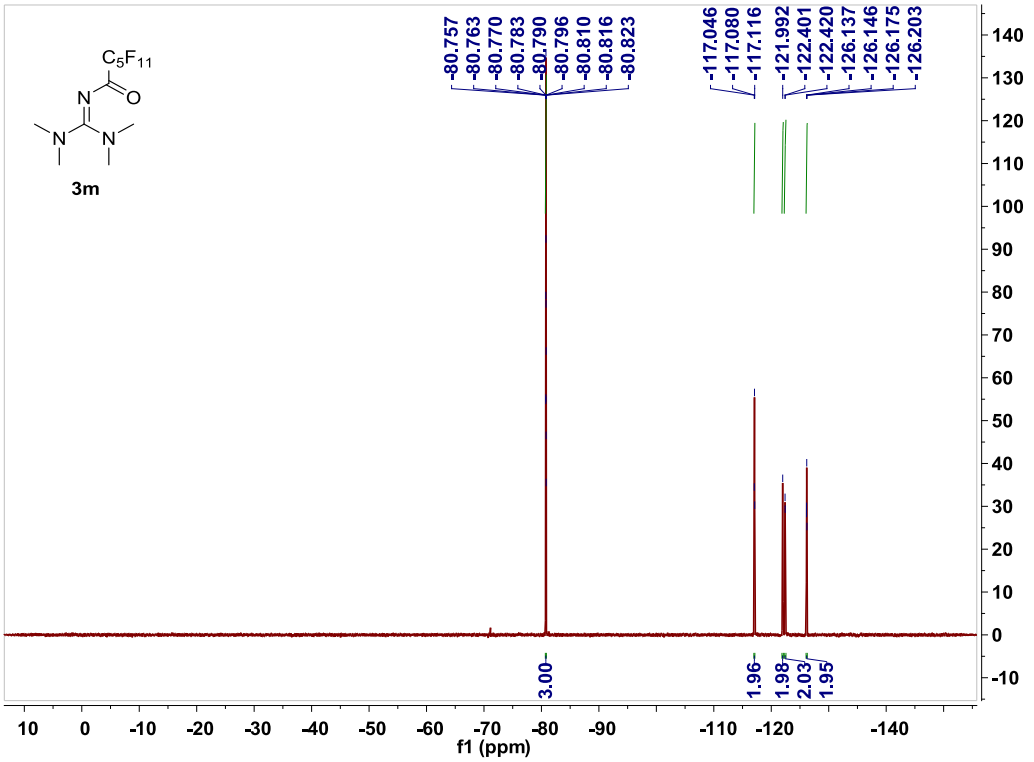

3l
7.280
2.989
12.00
f1 (ppm)

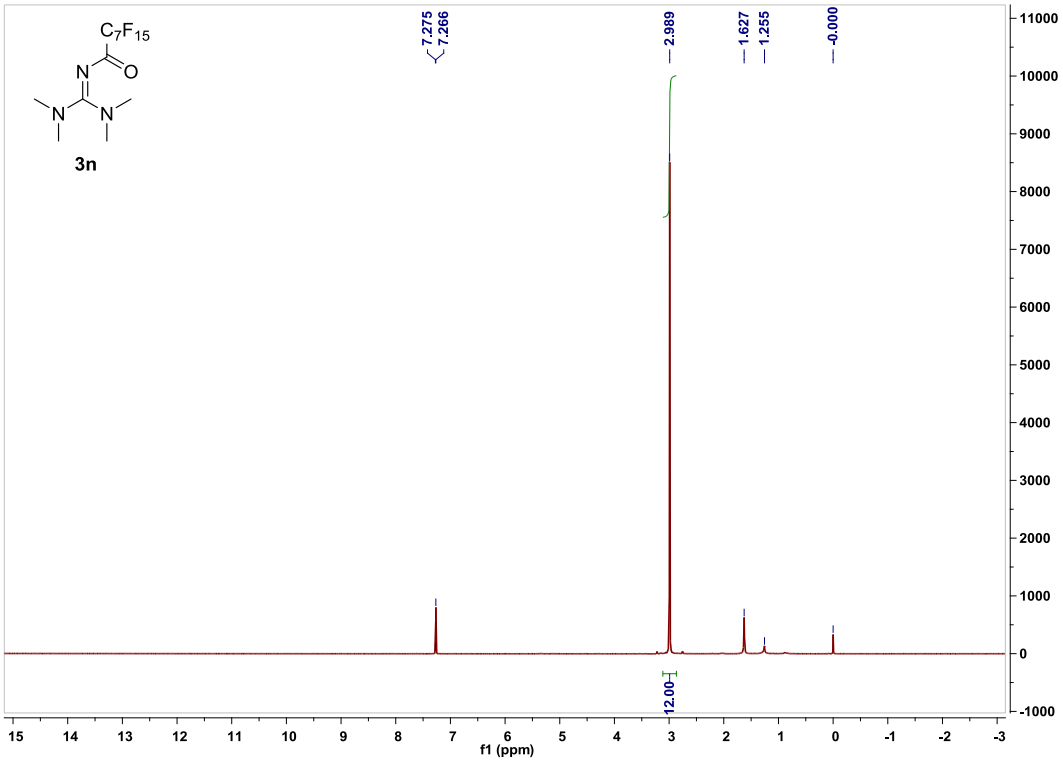

168.345
161.657
161.410
161.167
120.586
120.229
119.872
117.741
117.383
117.027
114.897
114.539
114.176
107.444
107.070
105.583
105.214
104.848
104.477
77.314
76.996
76.677
40.295
C_2F_5
N
O
N
N
3l
4E+06
4E+06
3E+06
2E+06
2E+06
2E+06
1E+06
5E+05
0
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

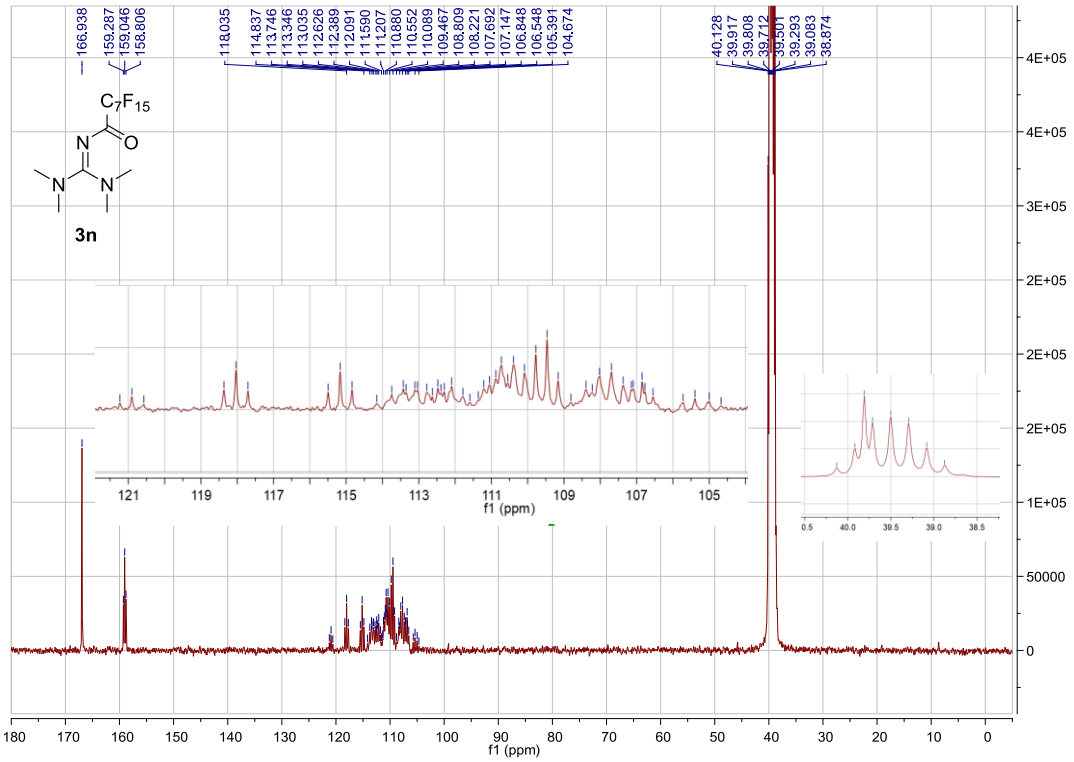

-82.306
-120.604
C_2F_5
N
O
N
N
3l
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
3.05
2.00
-20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -105 -115 -125 -135 -145
f1 (ppm)

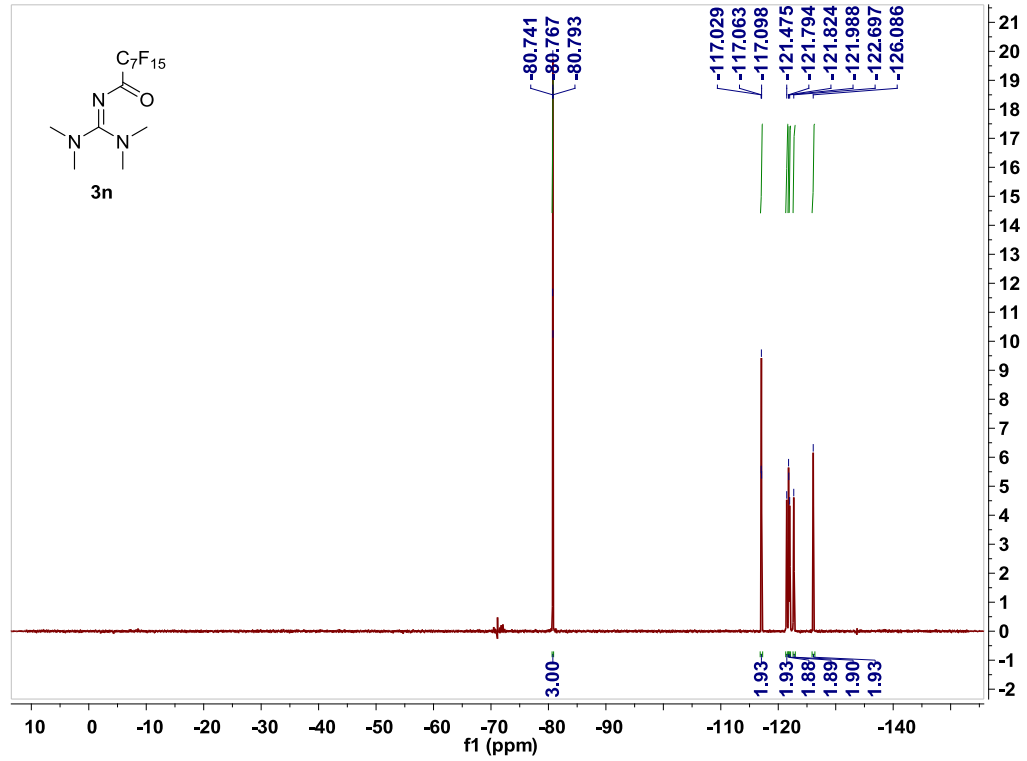

C5F11
N
O
N
N
3m
7.264
2.989
1.582
1.261
-0.001
12.00
f1 (ppm)

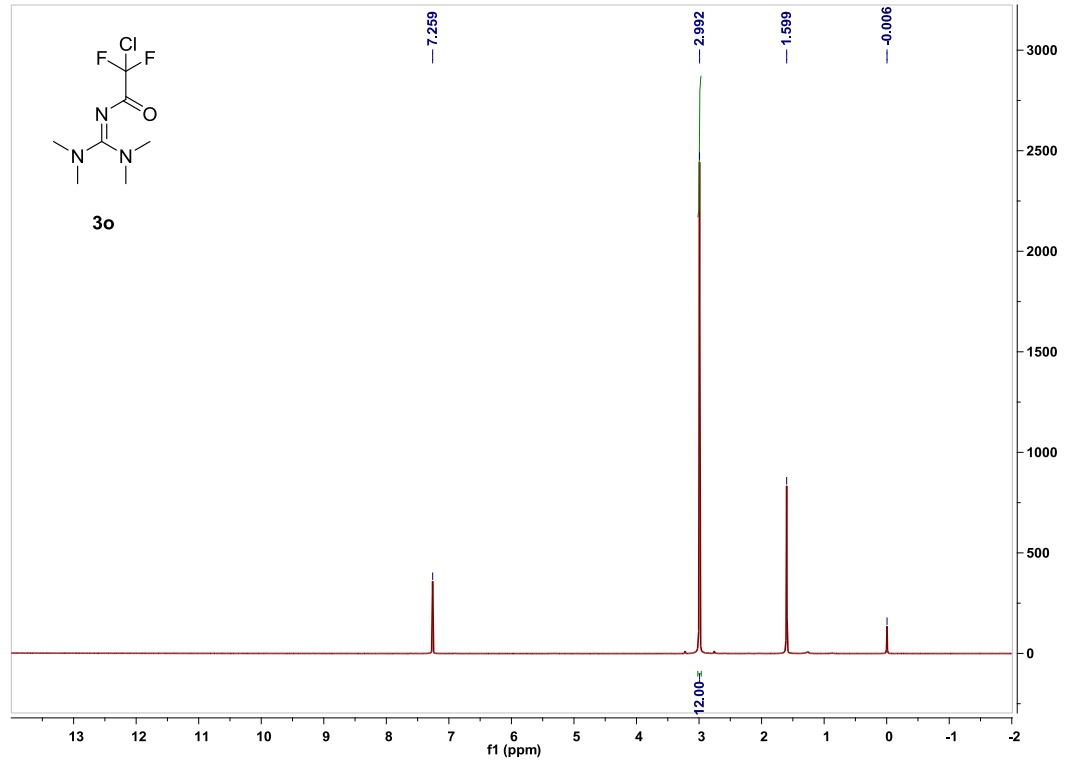

168.327
161.801
161.474
161.148
119.158
114.049
113.259
112.287
111.949
111.771
110.560
109.757
108.710
108.194
107.410
106.948
106.611
105.859
105.138
77.424
77.000
76.576
40.277
C5F11
N
O
N
N
3m
f1 (ppm)

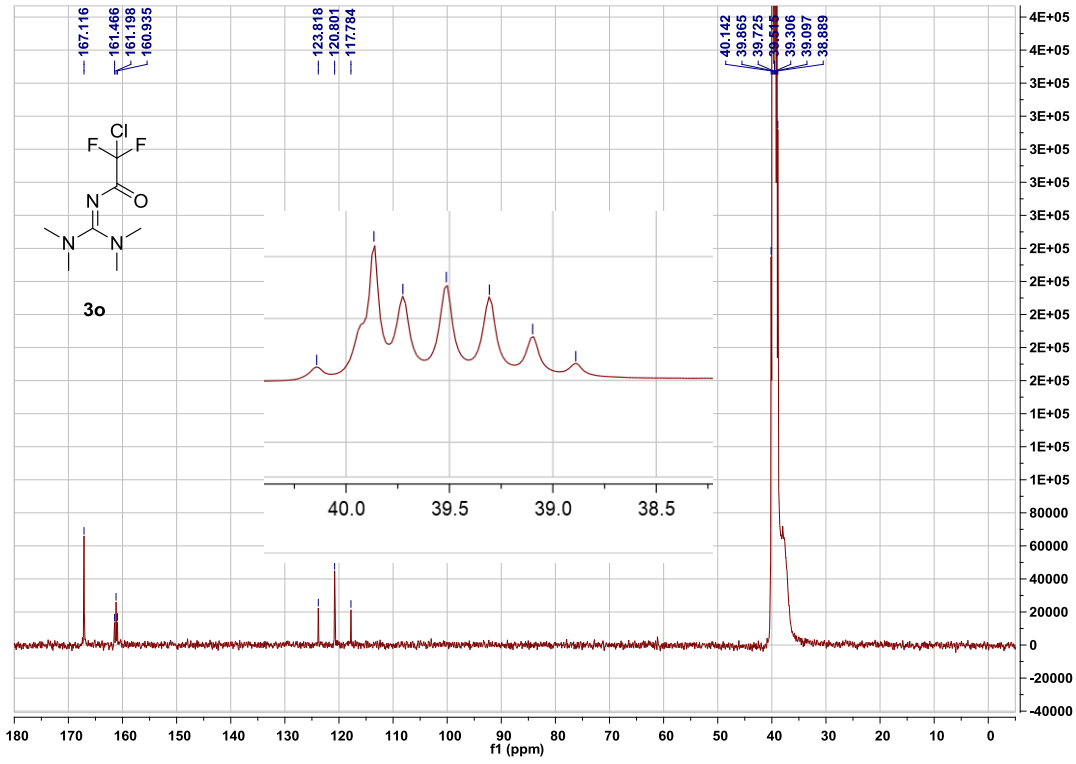

3m
-80.757
-80.763
-80.770
-80.783
-80.790
-80.796
-80.810
-80.816
-80.823
-117.046
-117.080
-117.116
-121.992
-122.401
-122.420
-126.137
-126.146
-126.175
-126.203
3.00
1.96
1.98
2.03
1.95
f1 (ppm)

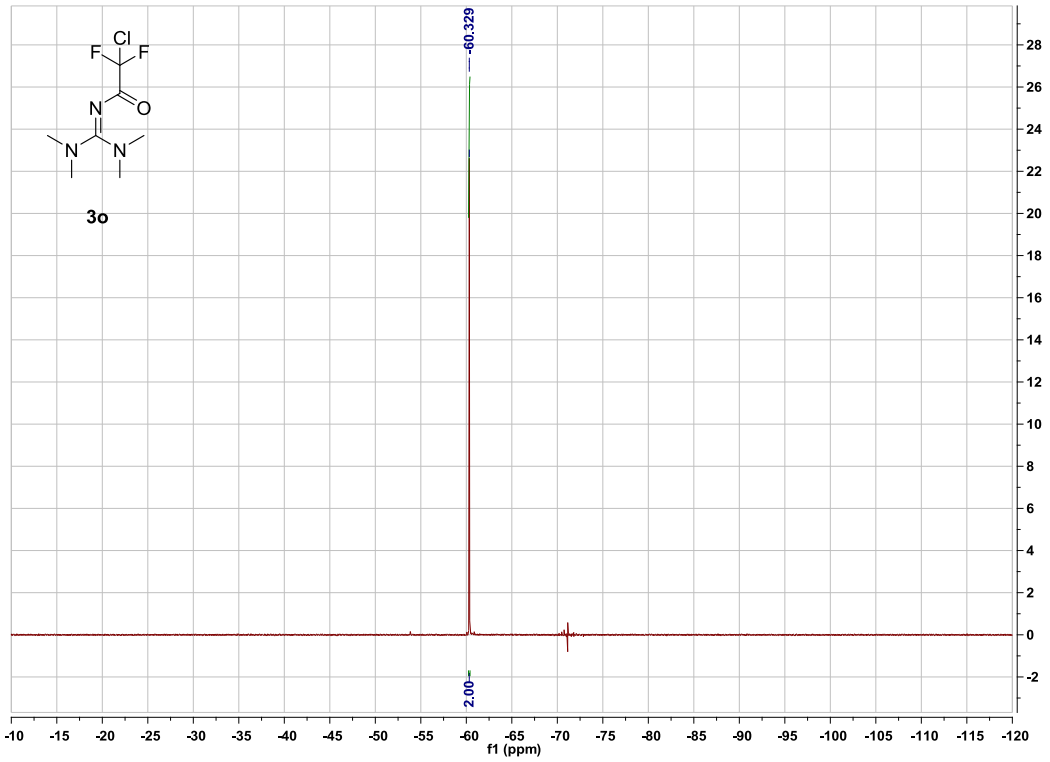

3n
7.275
7.266
2.989
1.627
1.255
0.000
12.00
f1 (ppm)


166.938
159.287
159.046
158.806
118.035
114.837
113.746
113.346
113.035
112.626
112.389
112.091
111.590
111.207
110.880
110.552
110.089
109.467
108.809
108.221
107.692
107.147
106.848
106.548
105.391
104.674
40.128
39.917
39.808
39.712
39.501
39.293
39.083
38.874
C7F15
3n
f1 (ppm)
f1 (ppm)


-80.741
-80.767
-80.793
-117.029
-117.063
-117.098
-121.475
-121.794
-121.824
-121.988
-122.697
-126.086
C7F15
3n
3.00
1.93
1.93
1.88
1.89
1.90
1.93
f1 (ppm)


7.259
2.992
1.599
-0.006
12.00
f1 (ppm)
3o


167.116
161.466
161.198
160.935
123.818
120.801
117.784
40.142
39.865
39.725
39.306
39.097
38.889
40.0
39.5
39.0
38.5
3o
f1 (ppm)


Cl
F
F
N
O
N
N
3o
-60.329
2.00
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
-2
-10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120
f1 (ppm)