Palladium-Catalyzed Direct C-H trifluoroethylation of aromatic amides**

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Content

I. General Methods

Unless otherwise stated, all commercial reagents and solvents were used without additional purification. Analytical thin layer chromatography (TLC) was performed on pre-coated silica gel 60 F254 plates. Visualization on TLC was achieved by the use of UV light (254 nm). Column chromatography was undertaken on silica gel (400-630 mesh) using a proper eluent system. 1H NMR was recorded on Bruker Avance 400 MHz. Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. The following abbreviations were used to describe peak splitting patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, td = triplet of doublet, ddd = doublet of doublet of doublet, m = multiplet. Coupling constants, *J*, were reported in hertz unit (Hz). 13C NMR was recorded on Bruker Avance 400 MHz (100 MHz)and was fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the center of a triplet at 77.0 ppm of chloroform-*d*. High resolution mass spectra were obtained on Waters Q– Tof Permier Spectrometer. Palladium acetate (98%) was purchased from Strem Chemicals Co., Ltd. Other reagents or catalysts were directly used from purchased without further purification unless otherwise specified.

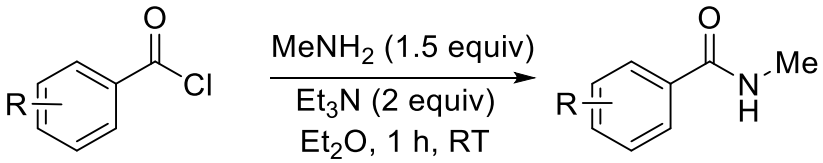
II. General Procedure for the Preparation of Starting Materials

II-1. Mesityl(2,2,2-trifluoroethyl)iodonium trifluoromethanesulfonate (2)

2 was prepared following the procedure of previous literature.[1]

II-2. Preparation of arene substrates

II-2-1. Procedure for the synthesis of N-methyl benzamides[2]



$MeNH_2$ methanol solution (33.3%) (1.5 equiv.), acid chloride (1.0 equiv.), Et_3N (2.0 equiv.) and Et_2O (0.5 M) were added into a round bottom flask capped with a septum. The mixture was stirred at room temperature. After 1 h, the crude reaction mixture was extracted with Et_2O, purified by flash chromatography to get the corresponding N-methyl benzamides.

II-2-2. Preparation of additional arene substrates

[1] Toth, L. B.; Kovacs, S.; Salyi, G.; Novak Z. *Angew. Chem. Int. Ed.* 2016, 55, 1988–1992; *Angew. Chem.* **2016**, 128, 2028–2032

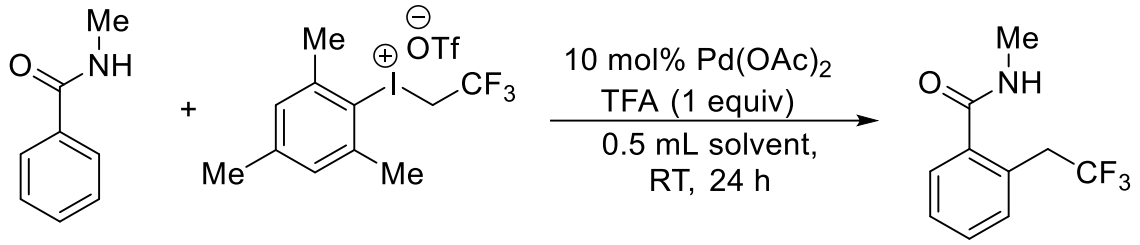
[2] Tang, Q.; Xia, D.; Jin, X.; Zhang, Q.; Sun, Q. X.; Wang, C. *J. Am. Chem. Soc.*, **2013**, *135*, 4628–4631

Methyl benzoyl-*L*-phenylalaninate,[3] methyl benzoyl-*L*-leucinate,[4] and other benzamides were prepared according to the previously reported synthetic methods.

III. Optimization of reaction conditions

III-1. Solvent Effect

A 4 mL screw-cap vial equipped with a stirring bar was charged with *palladium(II) acetate* (0.007 mmol, 10 mol%, 1.6 mg), *N-methylbenzamide* (0.07 mmol, 10.0 mg) and *mesityl(2,2,2-trifluoroethyl)iodonium trifluoromethanesulfonate* (0.08 mmol, 42.4 mg). 0.5 mL *solvent* was added and the dark brown mixture was stirred at room temperature. T*rifluoroacetic acid* (0.05 mmol, 3.8 μl) was added instantly and the vessel was capped for 24 hours. After that reaction conversion was initially checked by TLC. The solvent was then removed under vacuum and the crude was dissolved in $CDCl_3$ solvent and NMR was run for the sample to calculate the percentage of conversion.

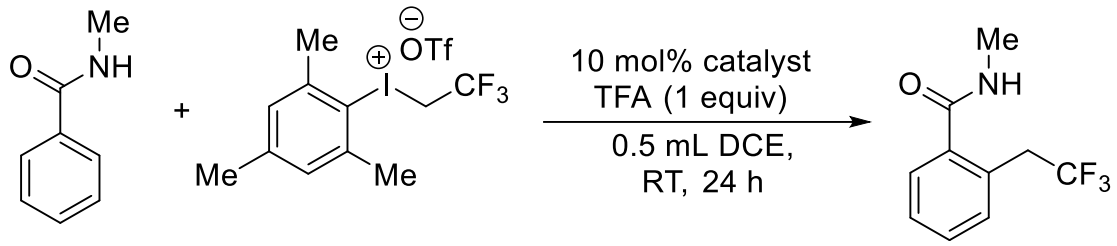


Entry	Solvent	Yield
1	MeOH	0
2	CH_3CN	0
3	Acetone	0
4	THF	20
5	DMF	0
6	DMSO	0
7	EtOAc	50
8	Et_2O	90
9	Toluene	45
10	DCM	93
11	DCE	96

[3] Thalhammer, A.; Mecinović, J.; Schofield, J. C. *Tetrahedron Lett.* **2009**, *31*, 1045-1047.
[4] Das, S.; Li, Y.; Lu, Q. L.; Junge, K.; Beller, M. *Chem. Eur. J.* **2016**, *22*, 7050-7053.

III-2. Screening of catalysts

A 4 mL screw-cap vial equipped with a stirring bar was charged with *metal catalyst* (0.007 mmol, 10 mol%), *N-methylbenamide* (0.07 mmol, 10.0 mg) and *mesityl(2,2,2-trifluoroethyl)iodonium trifluoromethanesulfonate* (0.08 mmol, 42.4 mg). 0.5 mL *1, 2-dichloroethane* was added and the dark brown mixture was stirred at room temperature. T*rifluoroacetic acid* (0.05 mmol, 3.8 µl) was added instantly and the vessel was capped for 24 hours. After that reaction conversion was initially checked by TLC. Then the solvent was removed under vaccum and the crude was dissolved in $CDCl_3$ solvent and NMR was run for the sample to calculate the percentage of conversion.

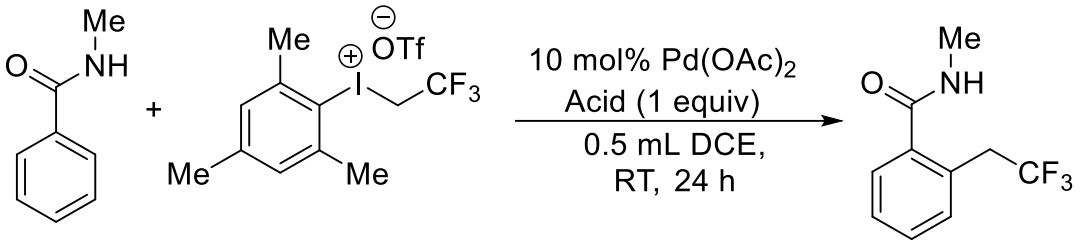


Entry	Catalyst	Yield
1	$Mn(OAc)_2$	0
2	$Cu(OAc)_2$	0
3	$Zn(OAc)_2$	0
4	$Cu(OTf)_2$	0
5	$Fe(OAc)_2$	0
6	$PdCl_2$	0
7	$Pd(TFA)_2$	80
8	$Pd(dba)_3$	45
9	$Pd(OAc)_2$	96

III-3. Effect of Acid additives

A 4 mL screw-cap vial equipped with a stirring bar was charged with *palladium(II) acetate* (0.007 mmol, 10 mol%, 1.6 mg), *N-methylbenamide* (0.07 mmol, 10.0 mg) and *mesityl(2,2,2-trifluoroethyl)iodonium trifluoromethanesulfonate* (0.08 mmol, 42.4 mg). 0.5 mL *1, 2-dichloroethane* was added and the dark brown mixture was stirred at room temperature. A*cid additive* (0.05 mmol, 3.8 µl) was added instantly and the vessel was capped for 24 hours. After

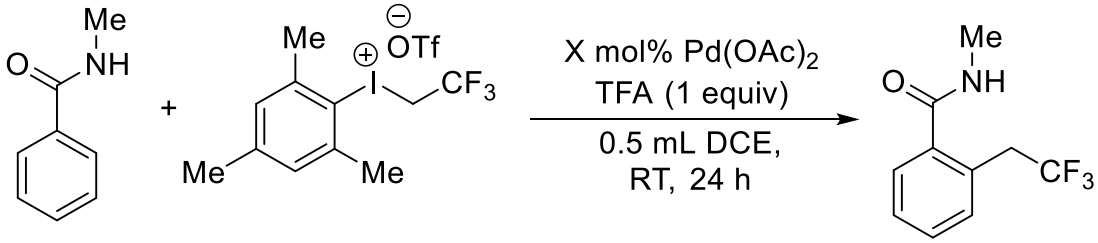
that reaction conversion was initially checked by TLC. Then the solvent was removed under vaccum and the crude was dissolved in $CDCl_3$ solvent and NMR was run for the sample to calculate the percentage of conversion.



Entry	Acid	Yield
1	No acid	25
2	H_2SO_4	56
3	HBF_4	92
4	AcOH	15
5	TfOH	28
6	TsOH. H_2O	88
7	BF_3.OEt	91

III-4. Catalyst Loading

A 4 mL screw-cap vial equipped with a stirring bar was charged with *palladium(II) acetate* (x mol%), *N-methylbenamide* (0.07 mmol, 10.0 mg) and *mesityl(2,2,2-trifluoroethyl)iodonium trifluoromethanesulfonate* (0.08 mmol, 42.4 mg). 0.5 mL *1, 2-dichloroethane* was added and the dark brown mixture was stirred at room temperature. T*rifluoroacetic acid* (0.05 mmol, 3.8 µl) was added instantly and the vessel was capped for 24 hours. After that reaction conversion was initially checked by TLC. Then the solvent was removed under vaccum and the crude was dissolved in $CDCl_3$ solvent and NMR was run for the sample to calculate the percentage of conversion.

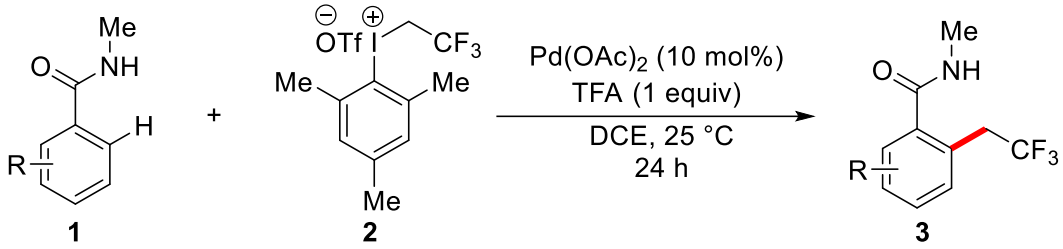


Entry	X mol%	Yield (%)
1	2.5	10
2	5.0	32

3	7.5	67
4	10.0	96

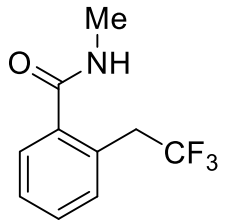
IV Experimental Procedure for Pd-Catalyzed C-H Trifluoroethylation of Arenes and Spectroscopic Data of Compounds Obtained in this Study

IV-1 Palladium catalyzed direct C-C bond formation of N-methyl aromatic amides with 1 (Table 1)



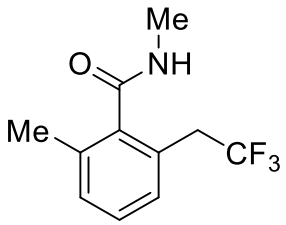
A 4 mL screw-cap vial equipped with a stirring bar was charged with *palladium(II) acetate* (0.1 mmol, 10 mol%), *N-methylbenzamide* (**1**, 1 mmol) and *mesityl(2,2,2-trifluoroethyl)iodonium trifluoromethanesulfonate* (**2**,1.2 mmol). 0.5 mL *DCE* was added and the dark brown mixture was stirred at room temperature. T*rifluoroacetic acid* (1 mmol) was added instantly and the vessel was capped for 24 hours. After the completion, the reaction mixture was washed with $NaHCO_3$ solution and extracted with EtOAc (3 x 20mL). The combined organics were dried over $MgSO_4$, filtered and dried under vacuum to get the crude product, which was further purified by flash column chromatography using EtOAc and Hexane solvent system to furnish the desired product **3**.

N-methyl-2-(2,2,2-trifluoroethyl)benzamide (3a)



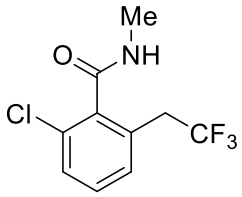
Following the general procedure, **3a** was obtained as a white solid (42 mg, 0.193 mmol, 96%). **MP** =168-169 ^oC **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.47 – 7.33 (m, 4H), 6.00 (s, 1H), 3.80 (q, *J*=11.0 Hz, 2H), 2.98 (d, *J*=4.9 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -65.33. **^{13}C NMR** (101 MHz, ^{19}F coupled, $CDCl_3$) δ = 170.16, 137.56, 132.26, 130.16, 128.76, 128.73, 128.20, 127.28, 127.11, 124.53, 36.66, 36.37, 36.07, 35.78, 26.68.**HRMS** (ESI): m/z calculated for $C_{10}H_{10}F_3NO$ $[M+H]^+$: 218.0793, found: 218.0804.

N,2-dimethyl-6-(2,2,2-trifluoroethyl)benzamide (3b)



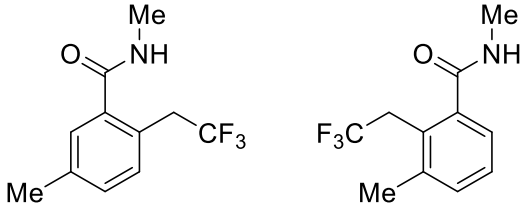
Following the general procedure, **3b** was obtained as a white solid (34 mg, 0.147 mmol, 70%). **MP** =126-127 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.26 (t, *J*=7.6 Hz, 1H), 7.18 (t, *J*=6.8 Hz, 2H), 5.80 (s, 1H), 3.44 (q, *J*=10.9 Hz, 2H), 3.01 (d, *J*=4.9 Hz, 3H), 2.34 (s, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -64.99. **^{13}C NMR** (101 MHz, ^{19}F coupled, $CDCl_3$) δ = 169.97, 138.90, 134.93, 130.11, 128.99, 128.42, 127.15, 126.82, 126.79, 126.47, 124.40, 37.51, 37.21, 36.91, 36.62, 26.39, 19.44. **HRMS** (ESI): m/z calculated for $C_{11}H_{12}F_3NO$ $[M+H]^+$: 232.0949, found: 232.0960.

2-chloro-*N*-methyl-6-(2,2,2-trifluoroethyl)benzamide (3c)



Following the general procedure **3c** was obtained as a white yellow solid (25 mg, 0.099 mmol, 52%). **MP** =108-109 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.41 – 7.24 (m, 3H), 5.85 (s, 1H), 3.51 (q, *J*=10.6 Hz, 2H), 3.03 (d, *J*=4.9 Hz, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -64.99. **^{13}C NMR** (101 MHz, ^{19}F coupled, $CDCl_3$) δ = 166.91, 137.94, 131.31, 130.17, 129.69, 129.67, 129.62, 129.53, 129.29, 126.81, 124.06, 37.51, 37.21, 36.91, 36.61, 26.57. **HRMS** (ESI): m/z calculated for $C_{10}H_9ClF_3NO$ $[M+H]^+$: 252.0403, found: 252.0411.

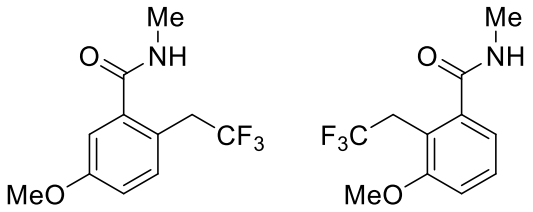
N,5-dimethyl-2-(2,2,2-trifluoroethyl)benzamide (3d) and *N*,3-dimethyl-2-(2,2,2-trifluoroethyl)benzamide (3d')



Following the general procedure, **3d and 3d′** were obtained as inseparable mixture as white solid (40 mg, 0.173 mmol, 82%, **3d**: **3d′** = 5:1). **MP** =196-197 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.30 – 7.18 (m, 4H), 5.87 (s, 1H), 3.73 (q, *J*=11.0 Hz, 2H), 2.98 (d, *J*=4.9 Hz, 3H), 2.35 (s, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -64.37. **^{13}C NMR** (101 MHz, ^{19}F coupled, $CDCl_3$) δ = 170.29,

138.17, 137.46, 137.43, 132.15, 130.83, 127.79, 120.00, 36.29, 36.01, 35.70, 35.44, 26.69, 20.98. **HRMS** (ESI): m/z calculated for $C_{11}H_{12}F_3NO$ $[M+H]^+$: 232.0949, found: 232.0941.

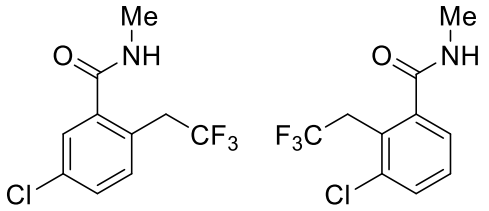
5-methoxy-*N*-methyl-2-(2,2,2-trifluoroethyl)benzamide (3e) and **3-methoxy-*N*-methyl-2-(2,2,2-trifluoroethyl)benzamide (3e')**



3e 3e'

Following the general procedure, **3e and 3e′** were obtained as inseparable mixture as white solid (34.3 mg, 0.138 mmol, 77%, **3e**: **3e′** = 5:1). **MP** = 165-166 °C.**^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.27 (dd, *J*=7.9, 4.2 Hz, 1H), 6.96 – 6.90 (m, 2H), 5.96 (s, 1H), 3.81 (s, 3H), 3.67 (q, *J*=11.0 Hz, 2H), 2.96 (d, *J*=4.9 Hz, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -64.92. **^{13}C NMR** (101 MHz, ^{19}F coupled, $CDCl_3$) δ = 169.93, 159.21, 138.67, 133.42, 129.29, 127.38, 124.65, 120.40, 120.37, 119.04, 115.25, 113.09, 112.52, 55.44, 35.97, 35.67, 35.38, 35.08, 26.67. **HRMS** (ESI): m/z calculated for $C_{11}H_{12}F_3NO_2$ $[M+H]^+$: 248.0898, found: 248.0894.

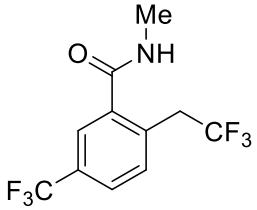
5-chloro-*N*-methyl-2-(2,2,2-trifluoroethyl)benzamide (3f) and **3-chloro-*N*-methyl-2-(2,2,2-trifluoroethyl)benzamide (3f')**



3f 3f'

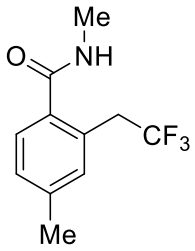
Following the general procedure, **3f** and **3f′** were obtained as white solid (25 mg, 0.099 mmol, 56%). ***Major* 3f MP** = 175-176 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.54 (dd, *J*=6.9, 2.5 Hz, 1H), 7.37 – 7.30 (m, 2H), 5.91 (s, 1H), 4.15 (q, *J*=10.7 Hz, 2H), 3.02 (d, *J*=4.9 Hz, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -64.45.**^{13}C NMR** (101 MHz, ^{19}F coupled, $CDCl_3$) δ = 169.53, 139.78, 137.42, 131.51, 129.32, 127.22, 127.17, 125.55, 124.41, 33.08, 32.77, 32.47, 32.17, 26.79. **HRMS** (ESI): m/z calculated for $C_{10}H_9ClF_3NO$ $[M+H]^+$: 252.0403, found: 252.0414. ***Minor* 3f′ (**7.4 mg, 0.029 mmol, 16.5% **MP** = 170-171 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.45 – 7.39 (m, 2H), 7.33 (d, *J*=8.1 Hz, 1H), 5.94 (s, 1H), 3.77 (q, *J*=10.9 Hz, 2H), 3.01 (d, *J*=4.9, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -65.42. **^{13}C NMR** (101 MHz, ^{19}F coupled, $CDCl_3$) δ = 168.66, 138.96, 134.30, 133.59, 130.24, 127.34, 127.31, 127.27, 124.24, 36.20, 35.90, 35.61, 35.31, 26.78. **HRMS** (ESI): m/z calculated for $C_{10}H_9ClF_3NO$ $[M+H]^+$: 252.0403, found: 252.0414.

N-methyl-2-(2,2,2-trifluoroethyl)-5-(trifluoromethyl)benzamide (3g)



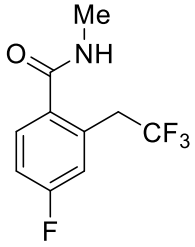
Following the general procedure, **3g** was obtained as a white solid (28.6 mg, 0.100 mmol, 67%). **MP** = 177-178 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.69 (d, *J*=5.9 Hz, 2H), 7.52 (d, *J*=8.4 Hz, 1H), 5.99 (s, 1H), 3.85 (q, *J*=10.8 Hz, 2H), 3.01 (d, *J*=4.9 Hz, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -62.89, -65.08. **^{13}C NMR** (101 MHz, ^{19}F coupled, $CDCl_3$) δ = 168.62, 138.24, 132.84, 130.87, 130.54, 126.86, 126.83, 124.77, 124.11, 124.07, 122.06, 36.66, 36.36, 36.06, 35.76, 26.82. **HRMS** (ESI): m/z calculated for $C_{11}H_9F_6NO$ $[M+H]^+$: 286.0667, found: 285.0667.

N,4-dimethyl-2-(2,2,2-trifluoroethyl)benzamide (3h)



Following the general procedure, **3h** was obtained as a white solid (51.7 mg, 0.223 mmol, 78%). **MP** =199-200 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.31 (d, *J*=7.7 Hz, 1H), 7.15 (d, *J*=10.6 Hz, 2H), 5.86 (s, 1H), 3.78 (q, *J*=11.0 Hz, 2H), 2.97 (d, *J*=4.9 Hz, 3H), 2.37 (s, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -65.28. **^{13}C NMR** (101 MHz, ^{19}F coupled, $CDCl_3$) δ = 170.24, 140.40, 134.65, 133.02, 128.81, 127.36, 127.11, 124.60, 36.59, 36.30, 36.01, 35.71, 26.70, 21.21. **HRMS** (ESI): m/z calculated for $C_{11}H_{12}F_3NO$ $[M+H]^+$: 232.0949, found: 232.0955.

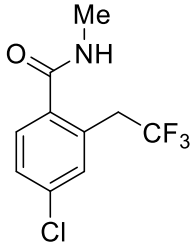
4-fluoro-*N*-methyl-2-(2,2,2-trifluoroethyl)benzamide (3i)



Following the general procedure, **3i** was obtained as a white solid (55 mg, 0.0.234 mmol, 68%). **MP** = 160-161 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.42 (dd, *J*=8.5, 5.7 Hz, 1H), 7.12 – 7.00 (m, 2H), 5.94 (s, 1H), 3.80 (q, *J*=10.8 Hz, 2H), 2.97 (d, *J*=4.9 Hz, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -65.22, -109.54 - -109.60. **^{13}C NMR** (101 MHz, ^{19}F coupled, $CDCl_3$) δ = 169.23, 164.34, 161.85, 133.73, 133.70, 131.76, 131.68, 129.19, 129.10, 126.97, 124.21, 119.40, 119.18, 115.24,

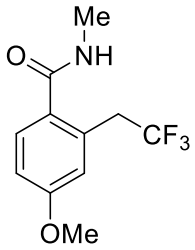
115.03, 36.62, 36.33, 36.03, 35.73, 26.77. **HRMS** (ESI): m/z calculated for $C_{10}H_9F_4NO$ $[M+H]^+$: 236.0699, found: 236.0706.

4-chloro-*N*-methyl-2-(2,2,2-trifluoroethyl)benzamide (3j)



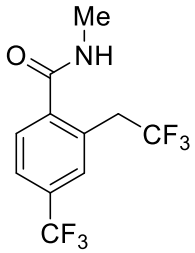
Following the general procedure, **3j** was obtained as a white solid (55 mg, 0.219 mmol, 75%). **MP** =168-169 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.40 – 7.30 (m, 4H), 5.93 (s, 1H), 3.77 (q, *J*=10.8 Hz, 2H), 2.97 (d, *J*=4.9 Hz, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -65.20. **^{13}C NMR** (101 MHz, ^{19}F coupled, $CDCl_3$) δ = 169.13, 136.14, 135.86, 132.28, 130.87, 130.82, 128.43, 128.40, 126.95, 124.19, 36.48, 36.18, 35.88, 35.58, 26.77. **HRMS** (ESI): m/z calculated for $C_{10}H_9ClF_3NO$ $[M+H]^+$: 252.0403, found: 252.0403.

4-methoxy-*N*-methyl-2-(2,2,2-trifluoroethyl)benzamide (3k)



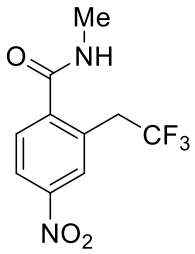
Following the general procedure, **3k** was obtained as a white solid (37.3 mg, 0.151 mmol, 84%). **MP.** =196-197 ºC **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.40 (d, *J*=8.4 Hz, 1H), 6.94 – 6.84 (m, 2H), 5.88 (s, 1H), 3.90 – 3.80 (m, 5H), 2.99 (d, *J*=4.9 Hz, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -65.17. **^{13}C NMR** (101 MHz, ^{19}F coupled, $CDCl_3$) δ = 169.95, 160.65, 130.98, 130.95, 129.81, 128.73, 118.06, 113.00, 55.40, 36.75, 36.45, 36.16, 35.86, 26.74. **HRMS** (ESI): m/z calculated for $C_{11}H_{12}F_3NO_2$ $[M+H]^+$: 248.0898, found: 248.0892.

N-methyl-2-(2,2,2-trifluoroethyl)-4-(trifluoromethyl)benzamide (3l)



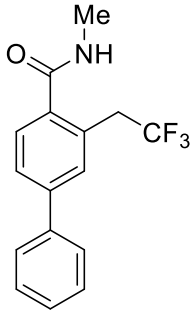
Following the general procedure, **3l** was obtained as a white solid (37.6 mg, 0.131 mmol, 74%). **MP** = 171-172 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.64 (d, *J*=6.3 Hz, 2H), 7.55 (d, *J*=8.4 Hz, 1H), 5.95 (s, 1H), 3.83 (q, *J*=10.8 Hz, 2H), 3.01 (d, *J*=4.9 Hz, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -63.06, -65.28. **^{13}C NMR** (101 MHz, ^{19}F coupled, $CDCl_3$) δ = 168.76, 140.83, 132.80, 132.48, 132.15, 131.82, 129.91, 129.88, 129.58, 129.05, 129.01, 127.62, 126.83, 125.34, 125.31, 125.27, 125.23, 124.66, 124.07, 121.95, 36.68, 36.38, 36.08, 35.78, 26.81. **HRMS** (ESI): m/z calculated for $C_{11}H_9F_6NO$ $[M+H]^+$: 286.0667, found: 286.0667.

N-methyl-4-nitro-2-(2,2,2-trifluoroethyl)benzamide (3m)



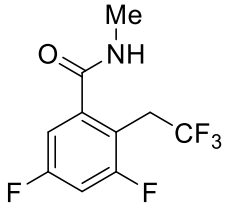
Following the general procedure, **3m** was obtained as a white solid (28.0 mg, 0.106 mmol, 65%). **MP** =225-226 ºC. **^{1}H NMR** (400 MHz, DMSO) δ = 8.70 (d, *J*=4.2 Hz, 1H), 8.37 (d, *J*=1.9 Hz, 1H), 8.30 (dd, *J*=8.4 Hz, 2.4, 1H), 7.74 (d, *J*=8.4 Hz, 1H), 4.12 (q, *J*=11.4 Hz, 2H), 2.79 (d, *J*=4.5 Hz, 3H). **^{19}F NMR** (376 MHz, DMSO) δ = -63.84. **^{13}C NMR** (101 MHz, ^{19}F coupled, DMSO) δ = 167.71, 148.18, 143.86, 143.80, 130.91, 130.88, 129.97, 127.72, 127.13, 124.96, 123.73, 35.52, 35.23, 34.94, 34.65, 26.54. **HRMS** (ESI): m/z calculated for $C_{10}H_9F_3N_2O_3$ $[M+H]^+$: 263.0644, found: 263.0641.

N-methyl-3-(2,2,2-trifluoroethyl)-[1, 1'-biphenyl]-4-carboxamide (3n)



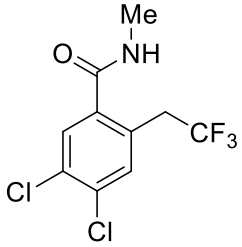
Following the general procedure, **3n** was obtained as a white solid (48 mg, 0.163 mmol, 82%). **MP** =230-231 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.57 (dt, *J*=4.8, 1.6 Hz, 4H), 7.47 (t, *J*=11.5 Hz, 3H), 7.42 – 7.36 (m, 1H), 5.95 (s, 1H), 3.88 (q, *J*=11.0 Hz, 2H), 3.01 (d, *J*=4.9 Hz, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -65.19. **^{13}C NMR** (101 MHz, ^{19}F coupled, $CDCl_3$) δ = 169.95, 143.21, 139.60, 136.14, 131.09, 129.47, 129.43, 129.42, 129.37, 128.97, 128.11, 127.64, 127.32, 127.19, 126.83, 124.57, 53.41, 36.83, 36.53, 36.24, 35.94, 26.77. **HRMS** (ESI): m/z calculated for $C_{16}H_{14}F_3NO$ $[M+H]^+$: 294.1106, found: 294.1115.

3, 5-difluoro-*N*-methyl-2-(2,2,2-trifluoroethyl)benzamide (3o)



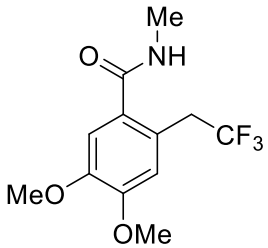
Following the general procedure, **3o** was obtained as a white solid (46.3 mg, 0.183 mmol, 65%). **MP** =159-160 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.01 – 6.90 (m, 2H), 6.17 (s, 1H), 3.84 (q, *J*=10.6 Hz, 2H), 2.97 (d, *J*=4.8 Hz, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -65.70, -65.73, -65.75, -65.78, -108.09 - -108.65. **^{13}C NMR** (101 MHz, ^{19}F coupled, $CDCl_3$) δ = 167.77, 163.56, 163.44, 161.06, 160.94, 140.43, 140.35, 126.79, 124.04, 112.93, 112.76, 110.71, 110.67, 110.48, 110.45, 105.89, 105.64, 105.62, 105.37, 29.11, 29.08, 28.80, 28.76, 28.48, 28.45, 28.17, 28.14, 26.74. **HRMS** (ESI): m/z calculated for $C_{10}H_8F_5NO$ $[M+H]^+$: 254.0604, found: 254.0608.

4, 5-dichloro-*N*-methyl-2-(2,2,2-trifluoroethyl)benzamide (3p)



Following the general procedure, **3p** was obtained as a white solid (31 mg, 0.108 mmol, 67%). **MP** =216-217 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.53 (s, 1H), 7.47 (s, 1H), 5.89 (s, 1H), 3.75 (q, *J*=10.7 Hz, 2H), 2.99 (d, *J*=4.9 Hz, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -65.28. **^{13}C NMR** (101 MHz, ^{19}F coupled, $CDCl_3$) δ = 167.79, 136.98, 134.49, 134.03, 132.68, 129.07, 128.98, 128.88, 36.05, 35.75, 35.45, 35.15, 26.84. **HRMS** (ESI): m/z calculated for $C_{10}H_8Cl_2F_3NO$ $[M+H]^+$: 286.0013, found: 286.0011.

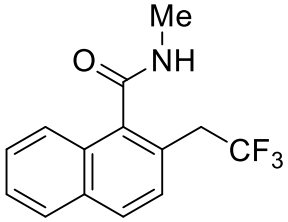
4, 5-dimethoxy-*N*-methyl-2-(2,2,2-trifluoroethyl)benzamide (3q)



Following the general procedure, **3q** was obtained as a white solid (38.1 mg, 0.137 mmol, 79%). **MP** =208-209 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 6.91 (s, 1H), 6.81 (s, 1H), 5.92 (s, 1H), 3.89 (d, *J*=10.0 Hz, 6H), 3.72 (q, *J*=10.9 Hz, 2H), 2.97 (d, *J*=4.7 Hz, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -65.40. **^{13}C NMR** (101 MHz, ^{19}F coupled, $CDCl_3$) δ = 169.89, 150.08, 148.47, 130.03, 127.38,

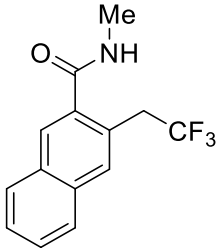
124.58, 121.54, 114.65, 110.47, 56.09, 56.05, 36.35, 36.06, 35.76, 35.47, 26.74. **HRMS** (ESI): m/z calculated for $C_{12}H_{14}F_3NO_3$ $[M+H]^+$: 278.1004, found: 278.1003.

N-methyl-2-(2,2,2-trifluoroethyl)-1-naphthamide (3r)



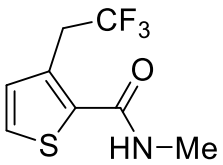
Following the general procedure, **3r** was obtained as a white solid (31.8 mg, 0.119 mmol, 67%). **MP** =160-161 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.89 (ddd, *J*=15.8, 7.9, 1.5 Hz, 2H), 7.54 – 7.45 (m, 3H), 7.42 (d, *J*=8.0 Hz, 1H), 6.21 (s, 1H), 4.01 (dd, *J*=21.2, 10.5 Hz, 2H), 3.05 (d, *J*=4.9 Hz, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -64.58. **^{13}C NMR** (101 MHz, ^{19}F coupled, $CDCl_3$) δ = 173.11, 135.12, 134.31, 132.16, 131.54, 130.01, 128.75, 127.65, 127.32, 126.24, 126.21, 125.81, 124.89, 124.49, 38.35, 38.06, 37.77, 37.48, 27.00. **HRMS** (ESI): m/z calculated for $C_{14}H_{12}F_3NO$ $[M+H]^+$: 268.0949, found: 268.0949

N-methyl-3-(2,2,2-trifluoroethyl)-2-naphthamide (3s)



Following the general procedure, **3s** was obtained as a white solid (34.8 mg, 0.130 mmol, 75%). **MP** =217-218 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.96 (s, 1H), 7.87 (d, *J*=7.6 Hz, 3H), 7.63 – 7.54 (m, 2H), 6.08 (s, 1H), 4.00 (q, *J*=11.0 Hz, 2H), 3.08 (d, *J*=4.9 Hz, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -65.36. **^{13}C NMR** (101 MHz, ^{19}F coupled, $CDCl_3$) δ = 170.26, 134.96, 133.57, 132.06, 132.01, 127.89, 127.74, 127.71, 127.26, 127.12, 125.81, 125.77, 125.71, 125.68, 36.86, 36.57, 36.27, 35.95, 26.84.**HRMS** (ESI): m/z calculated for $C_{14}H_{12}F_3NO$ $[M+H]^+$: 268.0949, found: 268.0952

N-methyl-3-(2,2,2-trifluoroethyl)thiophene-2-carboxamide (3t)

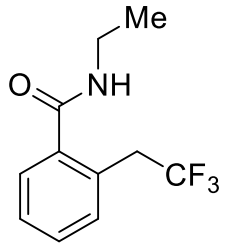


Following the general procedure, **3t** was obtained as a white solid (18 mg, 0.080 mmol, 20%). **MP** =147-148 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.32 (d, *J*=5.1 Hz, 1H), 7.09 (d, *J*=5.0 Hz, 1H),

5.91 (s, 1H), 3.97 (q, *J*=10.9 Hz, 2H), 2.97 (d, *J*=4.9 Hz, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -65.00. **^{13}C NMR** (101 MHz, ^{19}F coupled, $CDCl_3$) δ = 162.95, 134.00, 133.96, 133.59, 130.98, 126.96, 126.08, 124.21, 33.35, 33.05, 32.74, 32.44, 26.75. **HRMS** (ESI): m/z calculated for $C_8H_8F_3NOS$ $[M+H]^+$: 224.0357, found: 224.0366.

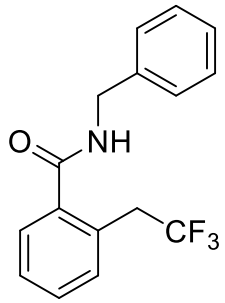
IV-2 Palladium catalyzed direct C-C bond formation of aromatic amides with 1 (Table 2)

N-ethyl-2-(2,2,2-trifluoroethyl)benzamide (5a)



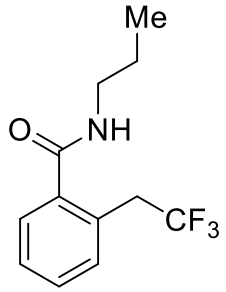
Following the general procedure, **5a** was obtained as a white solid (42.8 mg, 0.185 mmol, 76%). **MP** =142-143 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.45 – 7.30 (m, 4H), 5.98 (s, 1H), 3.78 (q, *J*=11.0 Hz, 2H), 3.44 (qd, *J*=7.3, 5.9 Hz, 2H), 1.21 (t, *J*=7.3 Hz, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ = --65.25. **^{13}C NMR** (101 MHz, ^{19}F coupled, $CDCl_3$) δ = 169.40, 137.79, 132.24, 130.07, 128.66, 128.63, 128.19, 127.32, 127.09, 124.57, 36.64, 36.34, 36.04, 35.75, 34.82, 14.67. **HRMS** (ESI): m/z calculated for $C_{11}H_{12}F_3NO$ $[M+H]^+$: 232.0949, found: 232.0952.

N-benzyl-2-(2,2,2-trifluoroethyl)benzamide (5b)



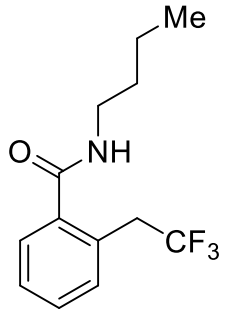
Following the general procedure, **5b** was obtained as a white solid (21.5 mg, 0.073 mmol, 52%). **MP** =146-147 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.47 – 7.27 (m, 9H), 6.20 (s, 1H), 4.60 (d, *J*=5.7 Hz, 2H), 3.82 (q, *J*=11.0 Hz, 2H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -65.17. **^{13}C NMR** (101 MHz, ^{19}F coupled, $CDCl_3$) δ = 169.21, 137.79, 137.28, 132.38, 130.33, 128.97, 128.94, 128.84, 128.25, 127.91, 127.74, 127.29, 127.15, 44.12, 36.64, 36.34, 36.05, 35.75. **HRMS** (ESI): m/z calculated for $C_{16}H_{14}F_3NO$ $[M+H]^+$: 294.1106, found: 294.1112

N-propyl-2-(2,2,2-trifluoroethyl)benzamide (5c)



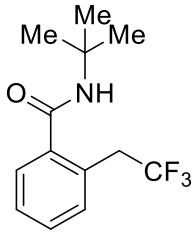
Following the general procedure, **5c** was obtained as a white solid (41.5 mg, 0.169 mmol, 80%). **MP** =130-131 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.45 – 7.30 (m, 4H), 5.99 (s, 1H), 3.78 (q, *J*=11.0 Hz, 2H), 3.41 – 3.34 (m, 2H), 1.68 – 1.55 (m, 2H), 0.97 (t, *J*=7.4 Hz, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -65.24. **^{13}C NMR** (101 MHz, ^{19}F coupled, $CDCl_3$) δ = 169.49, 137.87, 132.24, 130.08, 128.69, 128.66, 128.19, 127.31, 127.09, 124.55, 41.69, 36.64, 36.34, 36.05, 35.75, 22.75, 11.31**. HRMS** (ESI): m/z calculated for $C_{12}H_{14}F_3NO$ $[M+H]^+$: 246.1106, found: 246.1112

N-butyl-2-(2,2,2-trifluoroethyl)benzamide (5d)



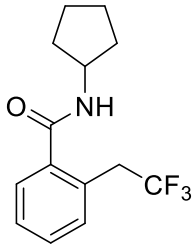
Following the general procedure, **5d** was obtained as a white solid (32.6 mg, 0.125 mmol, 72%). **MP** =127-129 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.45 – 7.31 (m, 4H), 5.95 (s, 1H), 3.78 (q, *J*=11.0 Hz, 2H), 3.41 (dd, *J*=13.1, 7.0 Hz, 2H), 1.62 – 1.53 (m, 2H), 1.40 (dq, *J*=14.4, 7.3 Hz, 2H), 0.95 (t, *J*=7.3 Hz, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -65.24. **^{13}C NMR** (101 MHz, ^{19}F coupled, $CDCl_3$) δ = 169.44, 137.87, 132.23, 130.07, 128.69, 128.66, 128.19, 127.31, 127.09, 124.55, 39.70, 36.64, 36.35, 36.05, 35.76, 31.53, 20.05, 13.69. **HRMS** (ESI): m/z calculated for $C_{13}H_{16}F_3NO$ $[M+H]^+$: 260.1262, found: 260.1273

N-(tert-butyl)-2-(2,2,2-trifluoroethyl)benzamide (5f)



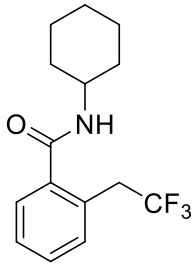
Following the general procedure, **5f** was obtained as a white solid (41.5 mg, 0.160 mmol, 85%). **MP** =117-118 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.43 – 7.29 (m, 4H), 5.71 (s, 1H), 3.76 (q, *J*=11.0 Hz, 2H), 1.45 (s, 9H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -65.12. **^{13}C NMR** (101 MHz, ^{19}F coupled, $CDCl_3$) δ = 169.02, 138.89, 132.19, 129.78, 128.28, 128.25, 128.15, 127.36, 127.03, 124.61, 52.00, 36.57, 36.27, 35.97, 35.68, 28.65. **HRMS** (ESI): m/z calculated for $C_{13}H_{16}F_3NO$ $[M+H]^+$: 260.1262, found: 260.1253

N-cyclopentyl-2-(2,2,2-trifluoroethyl)benzamide (5g)



Following the general procedure, **5g** was obtained as a white solid (33.1 mg, 0.122mmol, 73%). **MP** =154-155 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.44 – 7.32 (m, 4H), 5.86 (s, 1H), 4.44 – 4.30 (m, 1H), 3.77 (q, *J*=11.0 Hz, 2H), 2.12 – 2.01 (m, 2H), 1.75 – 1.60 (m, 4H), 1.48 (tt, *J*=13.1, 4.0 Hz, 2H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -65.20. **^{13}C NMR** (101 MHz, ^{19}F coupled, $CDCl_3$) δ = 169.10, 137.97, 132.24, 130.02, 128.57, 128.54, 127.33, 127.10, 124.58, 51.67, 36.66, 36.36, 36.07, 35.77, 33.03, 23.70. **HRMS** (ESI): m/z calculated for $C_{14}H_{16}F_3NO$ $[M+H]^+$: 272.1262, found: 272.1275

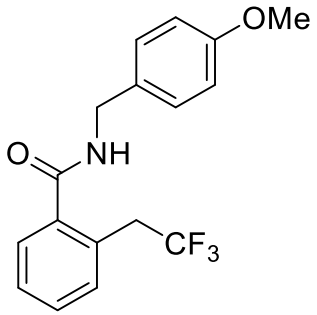
N-cyclohexyl-2-(2,2,2-trifluoroethyl)benzamide (5h)



Following the general procedure, **5h** was obtained as a white solid (35.4 mg, 0.124 mmol, 78%). **MP** =189-190 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.47 – 7.34 (m, 4H), 5.79 (d, *J*=6.6 Hz, 1H), 4.03 – 3.92 (m, 1H), 3.80 (q, *J*=11.0 Hz, 2H), 2.10 – 2.00 (m, 2H), 1.82 – 1.73 (m, 2H), 1.66 (dd, *J*=9.2, 5.3 Hz, 1H), 1.53 – 1.39 (m, 2H), 1.23 (tdd, *J*=16.8, 7.6, 4.1 Hz, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -65.14. **^{13}C NMR** (101 MHz, ^{19}F coupled, $CDCl_3$) δ = 168.62, 138.09, 132.24, 130.00,

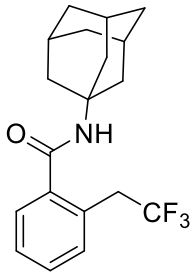
128.55, 128.52, 128.21, 127.33, 127.08, 126.81, 124.58, 48.68, 36.67, 36.38, 36.08, 35.79, 32.99, 25.51, 24.83. **HRMS** (ESI): m/z calculated for $C_{15}H_{18}F_3NO$ $[M+H]^+$: 286.1419, found: 286.1416.

N-(4-methoxybenzyl)-2-(2,2,2-trifluoroethyl)benzamide (5i)



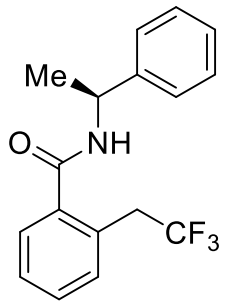
Following the general procedure, **5i** was obtained as a white solid (33.0 mg, 0.102 mmol, 64%). **MP** =141-142 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.44 – 7.31 (m, 4H), 7.29 – 7.24 (m, 2H), 6.88 (d, *J*=8.6 Hz, 2H), 6.13 (s, 1H), 4.54 (d, *J*=5.6 Hz, 2H), 3.90 – 3.72 (m, 5H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -65.17. **^{13}C NMR** (101 MHz, ^{19}F coupled, $CDCl_3$) δ = 169.12, 159.22, 137.37, 132.35, 130.27, 129.86, 129.28, 128.92, 128.89, 128.23, 127.30, 127.14, 124.57, 114.22, 55.32, 43.60, 36.64, 36.35, 36.05, 35.76. **HRMS** (ESI): m/z calculated for $C_{17}H_{16}F_3NO$ $[M+H]^+$: 324.1211, found: 324.1213

N-((3s, 5s, 7s)-adamantan-1-yl)-2-(2,2,2-trifluoroethyl)benzamide (5j)



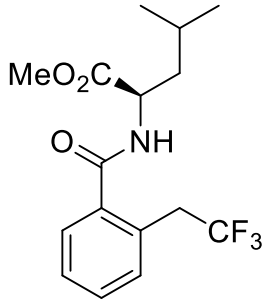
Following the general procedure, **5j** was obtained as a white solid (36.0 mg, 0.106mmol, 88%). **MP** =184-185 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.42 – 7.31 (m, 4H), 6.89 – 6.85 (m, 1H), 5.54 (s, 1H), 3.76 (q, *J*=11.0 Hz, 2H), 2.43 (s, 2H), 2.12 (d, *J*=7.5 Hz, 9H), 1.72 (s, 6H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -64.96. **^{13}C NMR** (101 MHz, ^{19}F coupled, $CDCl_3$) δ = 168.76, 141.75, 138.99, 137.32, 132.16, 129.74, 129.21, 128.30, 128.27, 128.24, 128.14, 127.94, 127.40, 127.03, 124.64, 52.76, 41.51, 36.60, 36.35, 36.30, 35.97, 35.71, 29.48. **HRMS** (ESI): m/z calculated for $C_{19}H_{22}F_3NO$ $[M+H]^+$: 338.1732, found: 338.1716.

(S)-*N*-(phenylethyl)-2-(2,2,2-trifluoroethyl)benzamide (5k)



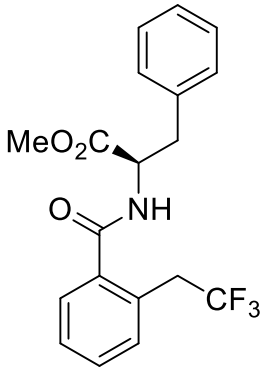
Following the general procedure, **5k** was obtained as a white solid (26.0 mg, 0.084 mmol, 46%). **MP** =160-161 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.45 – 7.26 (m, 9H), 6.14 (d, *J*=6.9 Hz, 1H), 5.35 – 5.24 (m, 1H), 3.87 (dq, *J*=14.8, 11.0 Hz, 1H), 3.67 (dq, *J*=14.8, 11.0 Hz, 1H), 1.58 (d, *J*=6.9 Hz, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -65.13. **^{13}C NMR** (101 MHz, ^{19}F coupled, $CDCl_3$) δ = 168.48, 142.73, 137.56, 132.32, 130.22, 128.79, 128.23, 127.57, 127.30, 127.14, 126.22, 124.55, 49.28, 36.60, 36.31, 36.01, 35.71, 21.46. **HRMS** (ESI): m/z calculated for $C_{17}H_{16}F_3NO$ $[M+H]^+$: 308.1262, found: 308.1273. ee = 96%. HPLC with an AS-H column at 254 nm (2-propanol: hexane = 10:90), 1.0 mL/min; major enantiomer t_{major}= 11.49 min, minoe enantiomer t_{minor}= 14.38 min.

Methyl (2-(2,2,2-trifluoroethyl)benzoyl)-*D*-leucinate (5l)



Following the general procedure, **5l** was obtained as a white solid (36.0 mg, 0.108 mmol, 74%). **MP** =125-126 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.44 (ddd, *J*=18.0, 14.4, 4.8 Hz, 4H), 6.26 (d, *J*=7.7 Hz, 1H), 4.81 (dd, *J*=10.2, 7.2 Hz, 1H), 3.96 – 3.65 (m, 5H), 1.81 – 1.57 (m, 3H), 0.98 (dd, *J*=8.9, 5.6 Hz, 6H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -65.19. **^{13}C NMR** (101 MHz, ^{19}F coupled, $CDCl_3$) δ = 173.23, 169.00, 136.93, 132.27, 130.48, 128.92, 128.90, 128.87, 128.29, 127.41, 127.25, 124.49, 52.37, 51.09, 41.48, 36.55, 36.26, 35.96, 35.67, 24.93, 22.80, 21.83. **HRMS** (ESI): m/z calculated for $C_{17}H_{16}F_3NO$ $[M+H]^+$: 332.1474, found: 332.1466. ee = 95%. HPLC with an AS-H column at 254 nm (2-propanol: hexane = 10:90), 1.0 mL/min; major enantiomer t_{major}= 6.32 min, minoe enantiomer t_{minor}= 9.18 min.

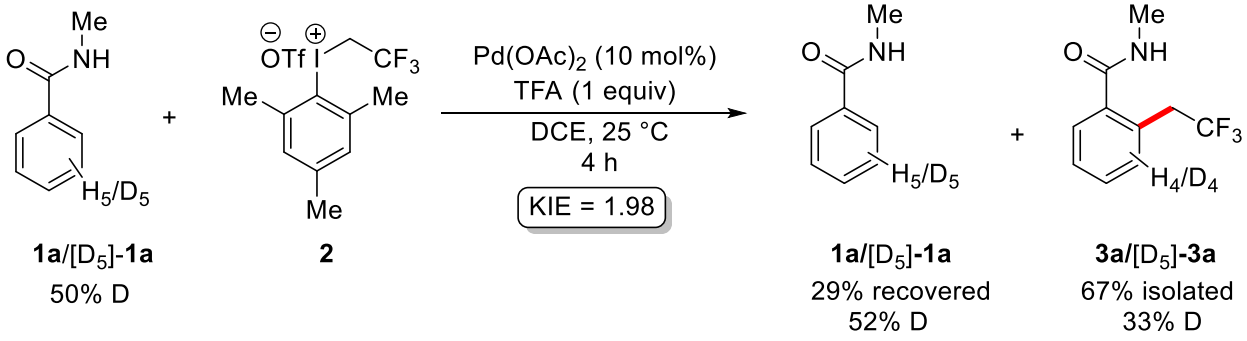
Methyl (2-(2,2,2-trifluoroethyl)benzoyl)-*D*-phenylalaninate (5m)



Following the general procedure, **5m** was obtained as a white solid (28.4 mg, 0.077 mmol, 65%). **MP** =155-156 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.49 – 7.25 (m, 7H), 7.19 (d, *J*=5.2 Hz, 2H), 6.35 (s, 1H), 5.16 – 5.05 (m, 1H), 3.82 (t, *J*=9.0 Hz, 5H), 3.27 (ddd, *J*=19.2, 13.8, 8.3 Hz, 2H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -65.28. **^{13}C NMR** (101 MHz, ^{19}F coupled, $CDCl_3$) δ = 171.79, 168.68, 136.56, 135.74, 132.27, 130.56, 129.23, 129.05, 128.70, 128.29, 127.42, 127.27, 127.01, 124.47, 53.41, 52.47, 37.93, 36.50, 36.21, 35.91, 35.62. **HRMS** (ESI): m/z calculated for $C_{17}H_{16}F_3NO$ $[M+H]^+$: 366.1317, found: 366.1312. ee = 99%. HPLC with an AS-H column at 254 nm (2-propanol: hexane = 10:90), 1.0 mL/min; major enantiomer t_{major}= 11.81 min.

V. Mechanistic Studies

V-1. Deuterium labeling test



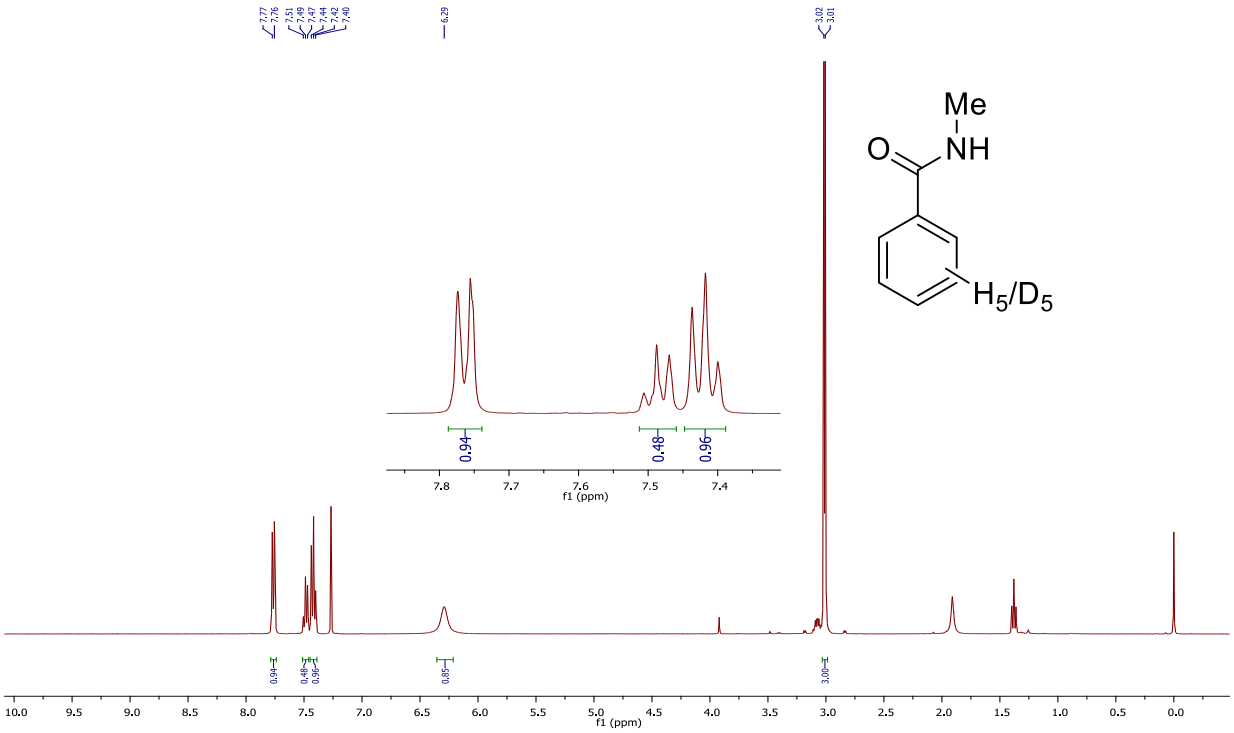
1a/[D_5]-**1a**
50% D

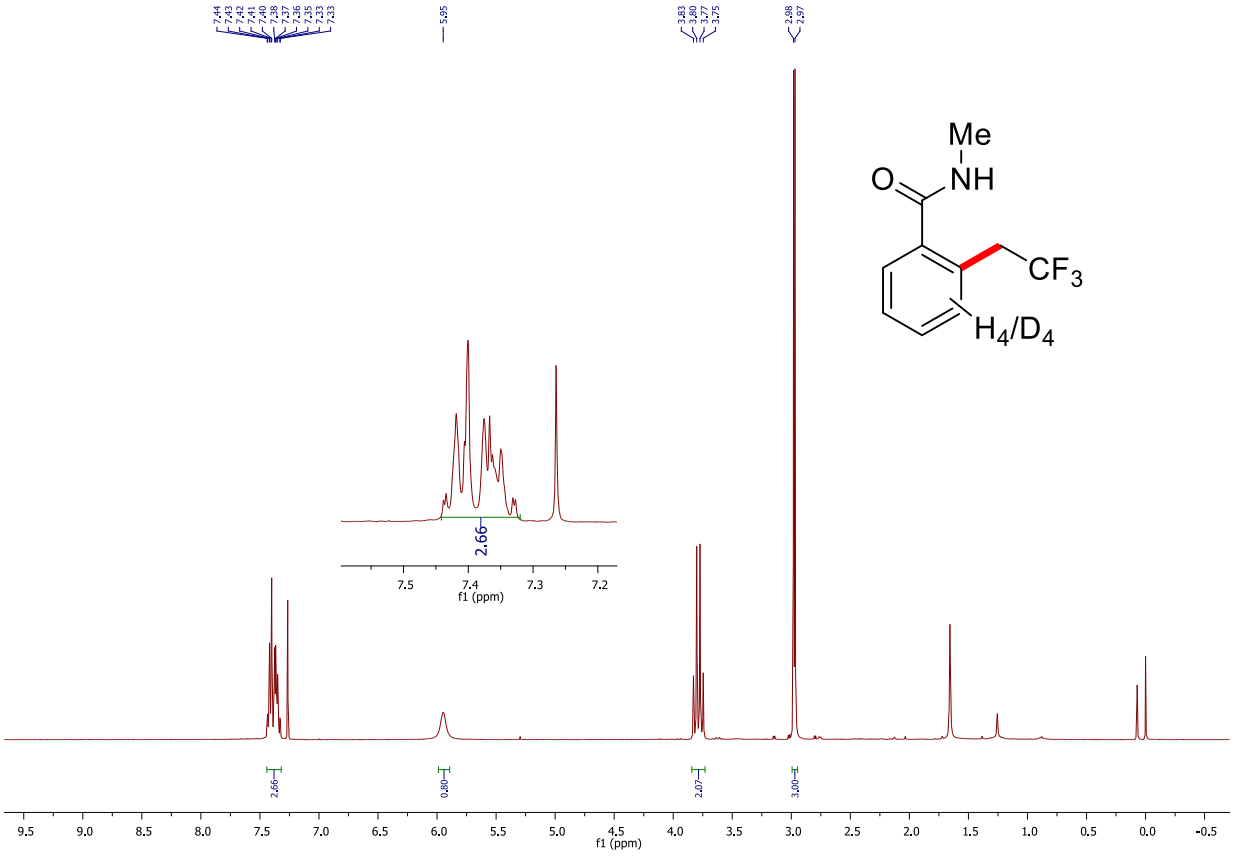
2

1a/[D_5]-**1a**
29% recovered
52% D

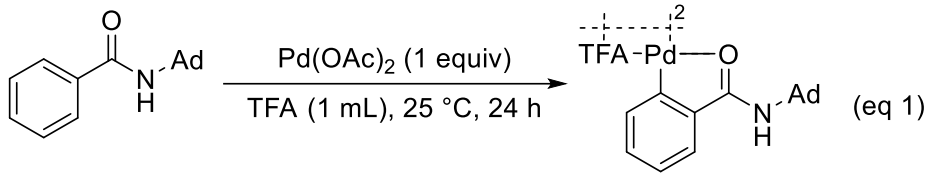
3a/[D_5]-**3a**
67% isolated
33% D

To a screw cap vial equipped with a stirbar were added *N-methylbenzamide* (**1a**, 15 mg, 0.1 mmol), *N-methylbenzamide* (1**a-D$_5$**, 15 mg, 0.1 mmol), *mesityl(2,2,2-trifluoroethyl)iodonium trifluoromethanesulfonate* (**2**, 127 mg, 0.24mmol), $Pd(OAc)_2$ (5.0 mg, 0.01 mmol, 10 mol %) and 1,2-dichloroethane (1.0 mL) under atmospheric conditions. T*rifluoroacetic acid* (0.1 mmol) was added instantly and the vessel was capped for 4 hours. After reaction mixture was washed with $NaHCO_3$ solution and extracted with EtOAc (3 x 20mL). Organic solvents were removed under reduced pressure and the residue was purified by chromatography on silica gel (*n*-hexane/EtOAc) to obtain the desired products with recovery of starting materials.


Me
NH
O
H_5/D_5
f1 (ppm)

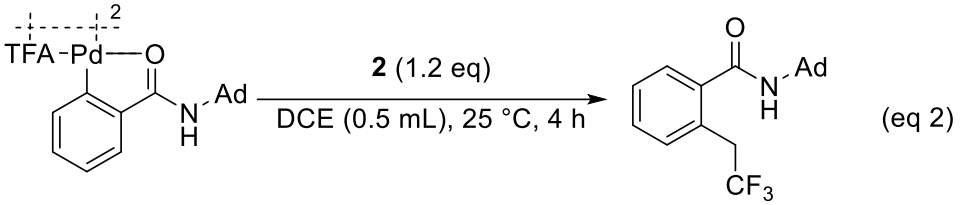

Me
NH
O
CF_3
H_4/D_4
f1 (ppm)

V-2 Procedure for the synthesis of Palladacycle compound



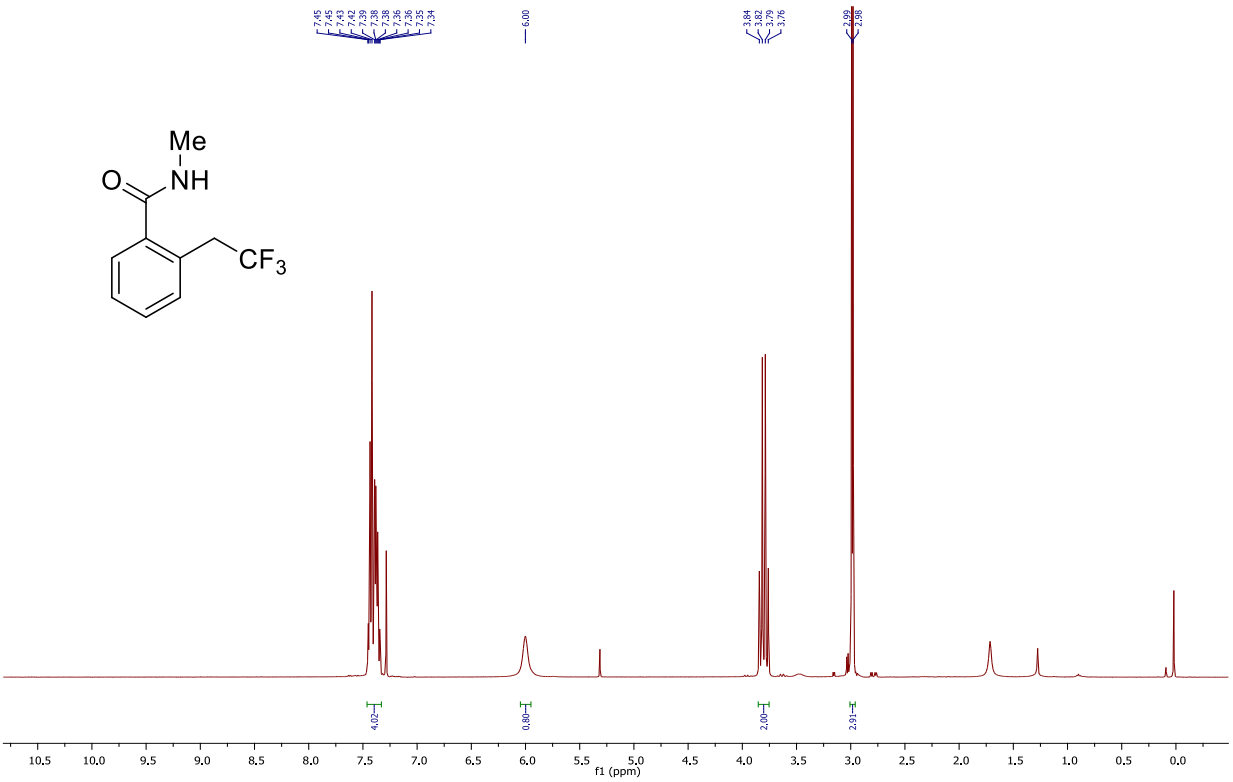
4j **6**, 78%

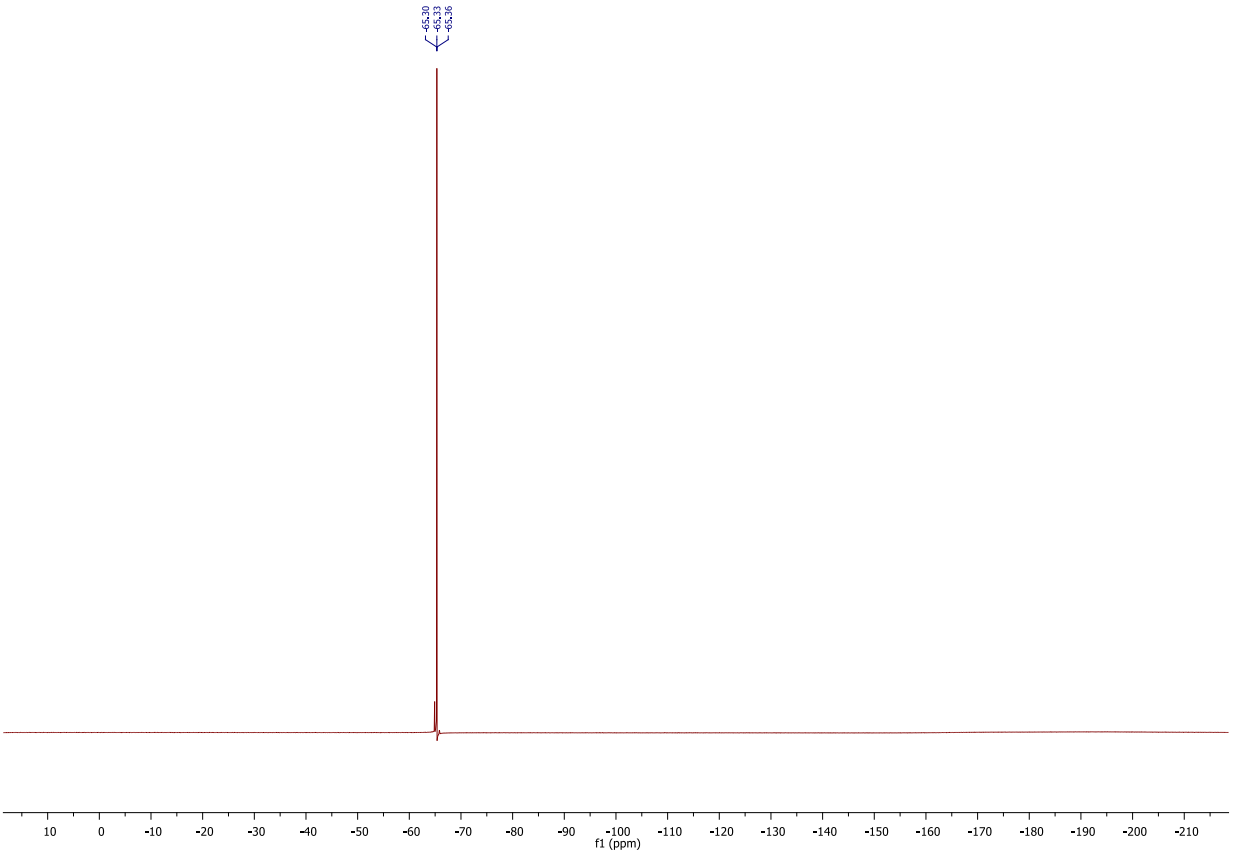
To a 15ml sealed-tube were added N-((3s,5s,7s)adamantan-1-yl)benzamide (50 mg, 0.20 mmol), $Pd(OAc)_2$ (44mg, 0.20 mmol) and 1ml TFA. The tube was sealed and stirred at rt for 24h. Then the reaction mixture was filtered and washed with hexane to give the desired TFA bridged palladacycle product **6** as a yellowish green solid (78 mg, 82%). The yellowish green solid was then recrystallized from hexane/DCE to give crystal that can be characterized by X-ray crystallography. **MP** = °C. **^{1}H NMR** (400 MHz, CD_2Cl_2) δ = 7.15 (s, 2H), 6.97 (s, 1H), 6.71 (d, *J*=34.4 Hz, 1H), 6.34 (s, 1H), 5.09 (s, 2H), 2.13 (s, 9H), 1.70 (s, 6H). **^{19}F NMR** (377 MHz, CD_2Cl_2) δ = -73.88, -74.26, -74.35, -74.83, -76.08. **^{13}C NMR** (101 MHz, ^{19}F coupled, CD_2Cl_2) δ = 179.11, 143.96, 140.64, 131.93, 131.05, 130.97, 130.86, 130.81, 125.03, 124.33, 54.82, 41.08, 35.97, 29.54.



6 **5j**, 80%

A 4 mL screw-cap vial equipped with a stirring bar was charged with *palladacycle* compound (**6**, 20.0 mg, 0.2 mmol) and *mesityl(2,2,2-trifluoroethyl)iodonium trifluoromethanesulfonate* (**2**, 0.22 mmol). Then 0.5 mL *DCE* was added and started to stir the dark brown mixture at room temperature. After the completion of the reaction, Reaction mixture was washed with $NaHCO_3$ solution and extracted with EtOAc (3 x 20mL). The combined organics were dried over $MgSO_4$, filtered and dried under vacuum to get the crude product, which was further purified by flash column chromatography using EtOAc and Hexane solvent system to furnish desired product **5j** in 80% yield.


Me
NH
O
CF3
7.45
7.45
7.43
7.42
7.39
7.38
7.38
7.36
7.36
7.35
7.34
6.00
3.84
3.82
3.79
3.76
2.99
2.98
4.02
0.80
2.00
2.91
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
0.0
f1 (ppm)


-65.30
-65.33
-65.36
10
0
-10
-20
-30
-40
-50
-60
-70
-80
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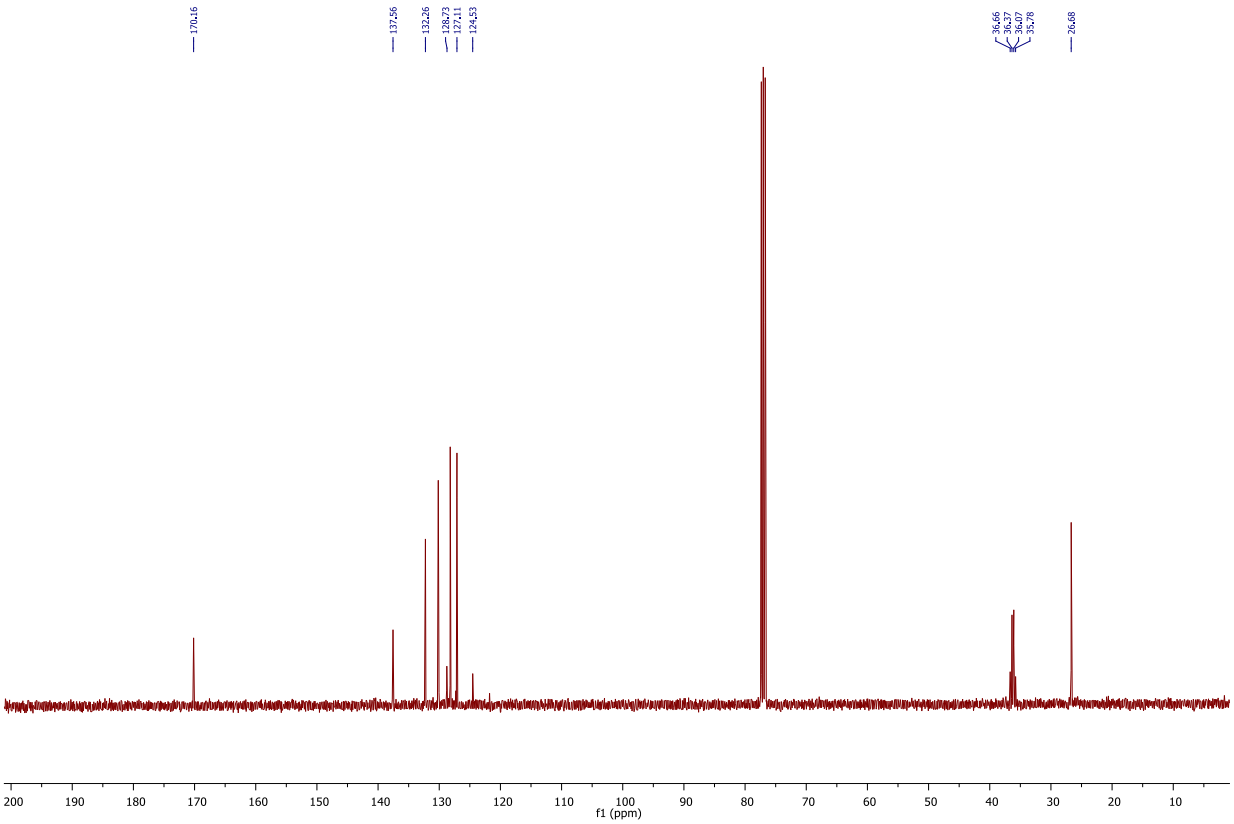
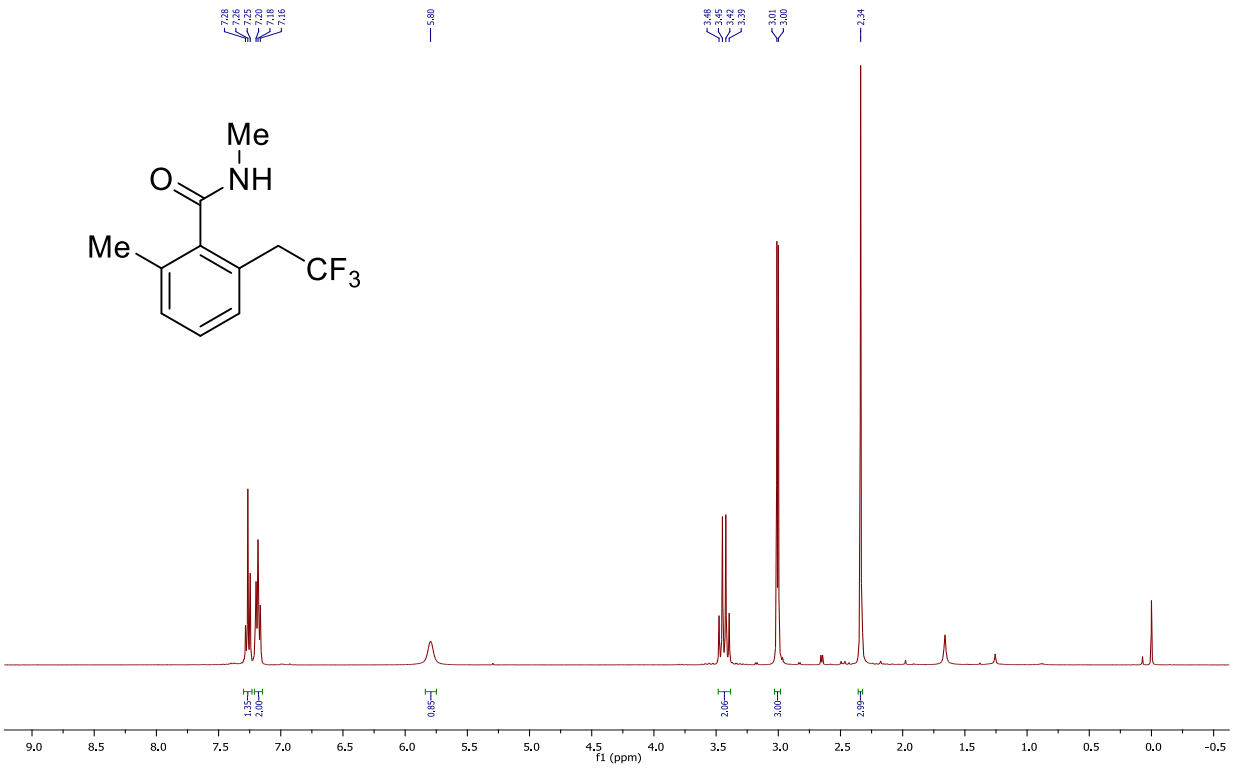
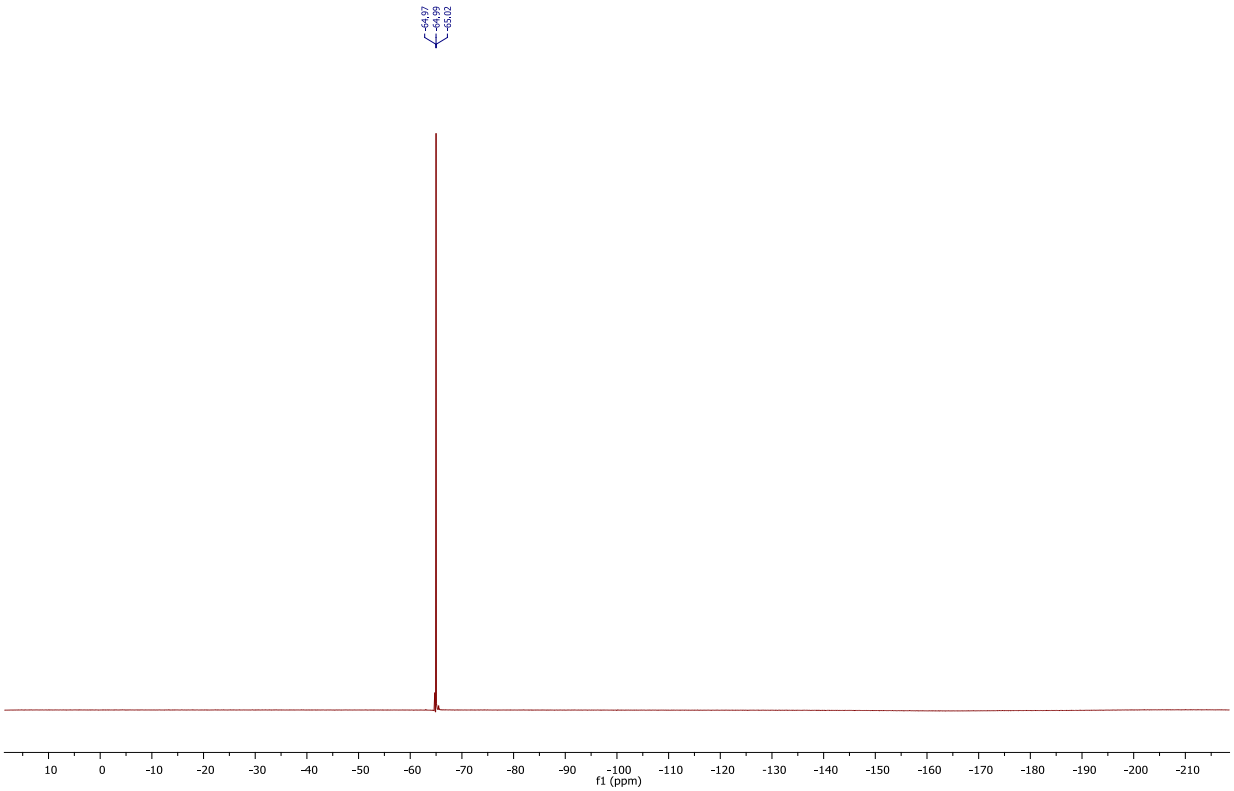
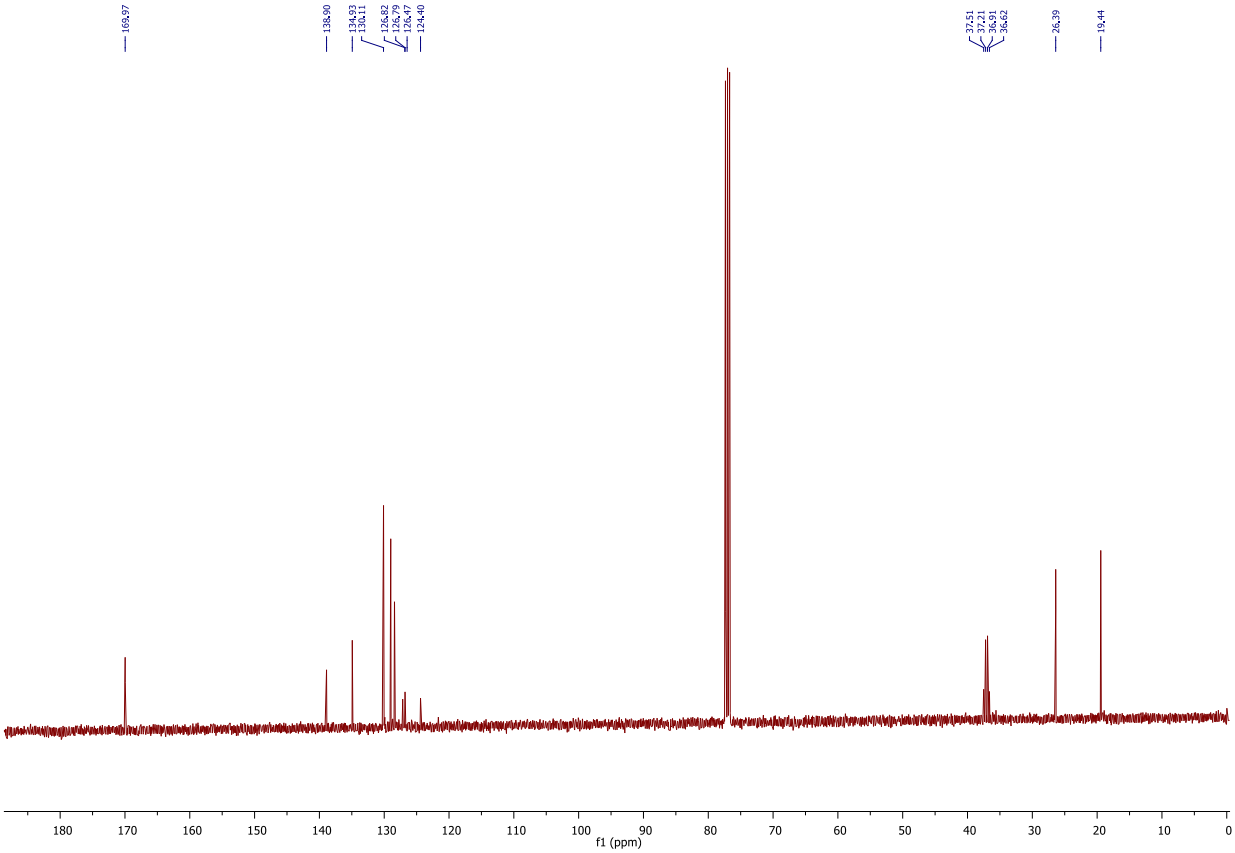
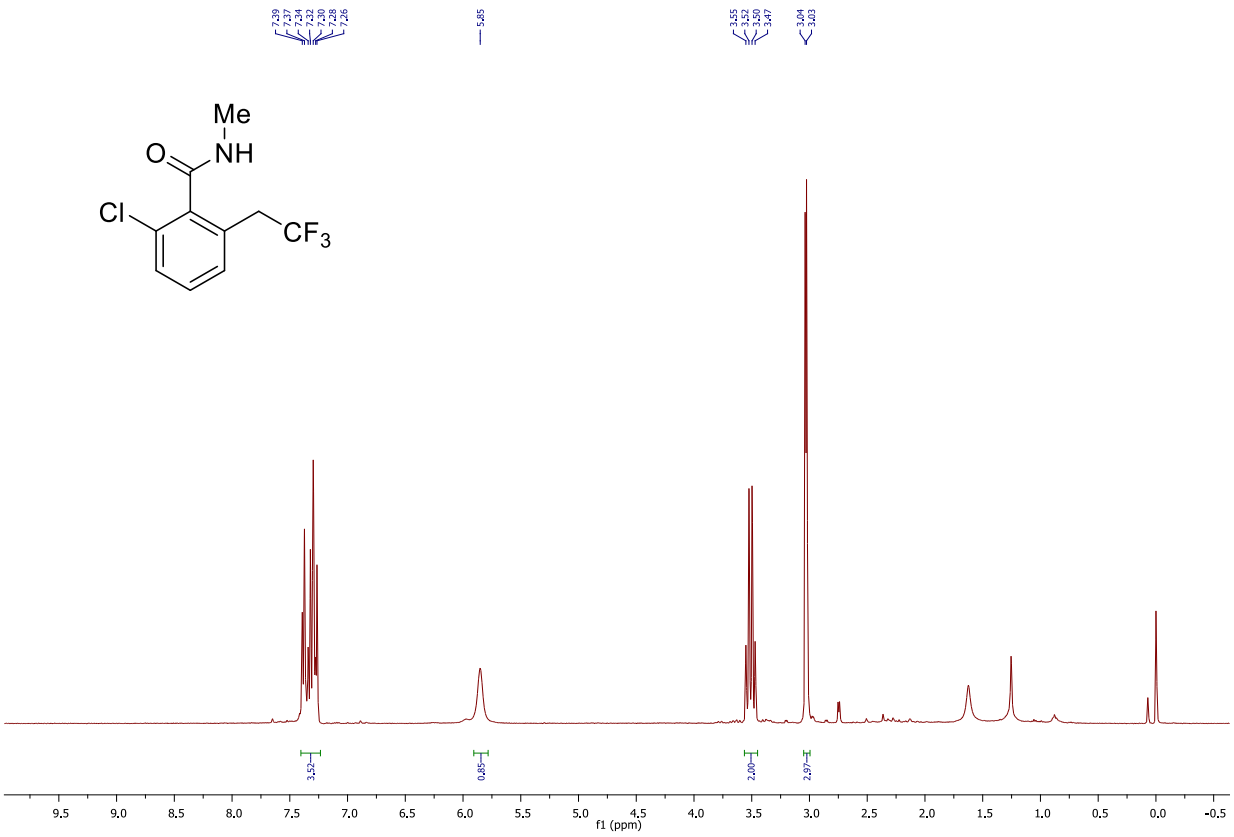
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

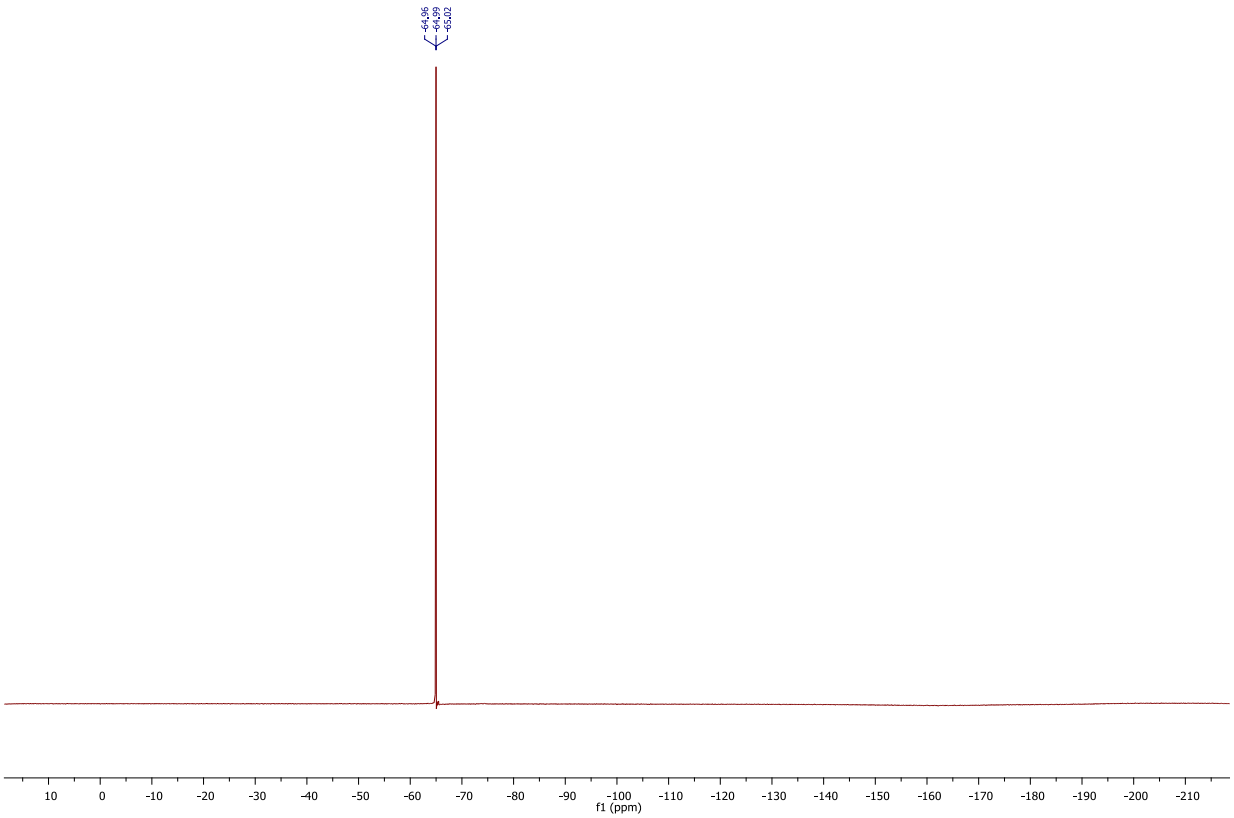

170.16
137.56
132.26
128.73
127.11
124.53
36.66
36.37
36.07
35.78
26.68
f1 (ppm)

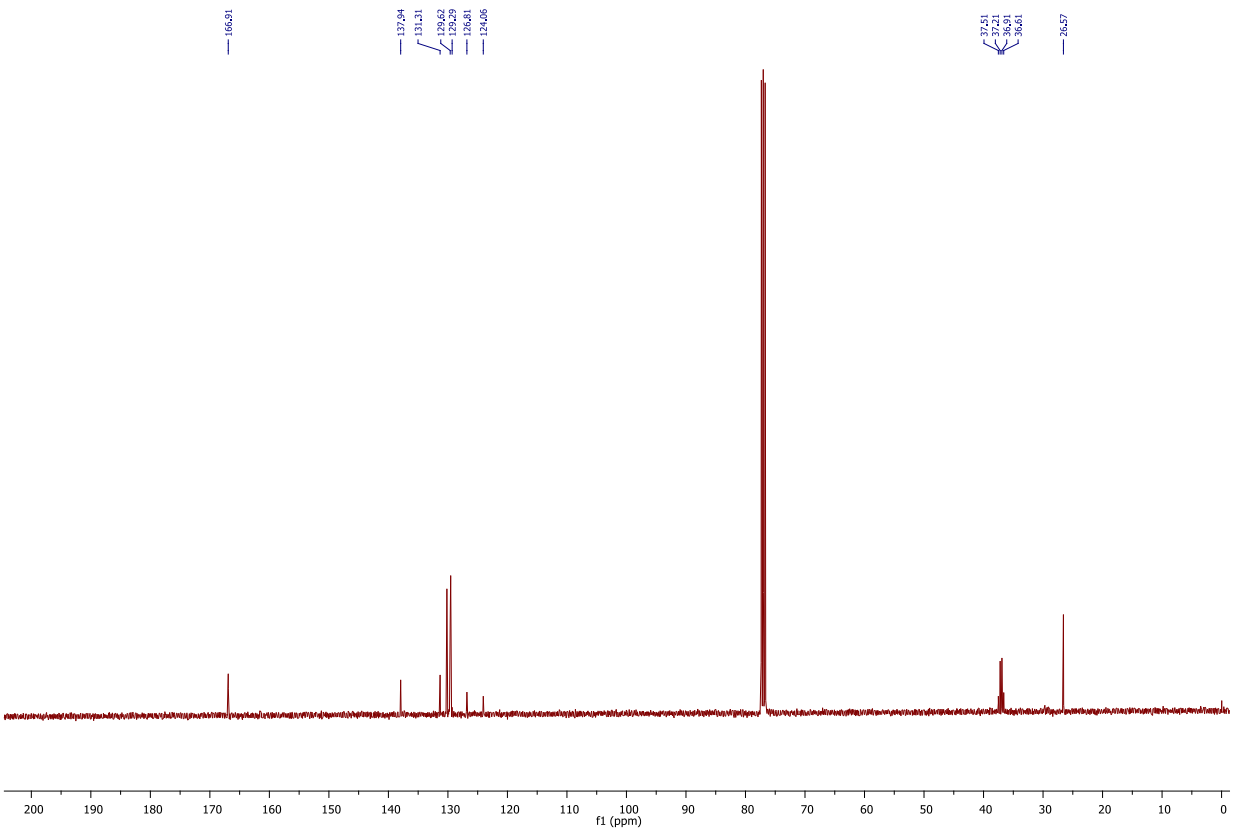

7.28
7.26
7.25
7.20
7.18
7.16
5.80
3.48
3.45
3.42
3.39
3.01
3.00
2.24
Me
O
NH
Me
CF3
1.35
2.00
0.85
2.06
3.00
2.99
f1 (ppm)

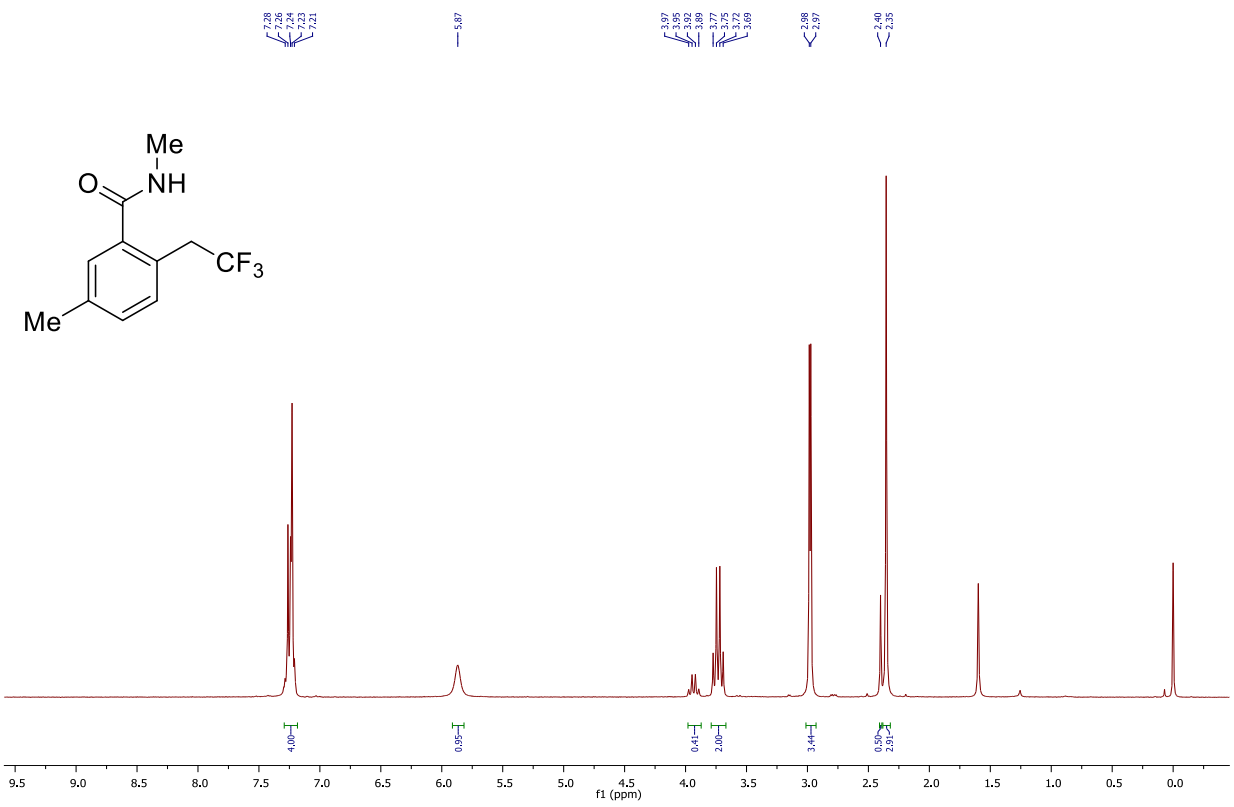

-64.97
-64.99
-65.02
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

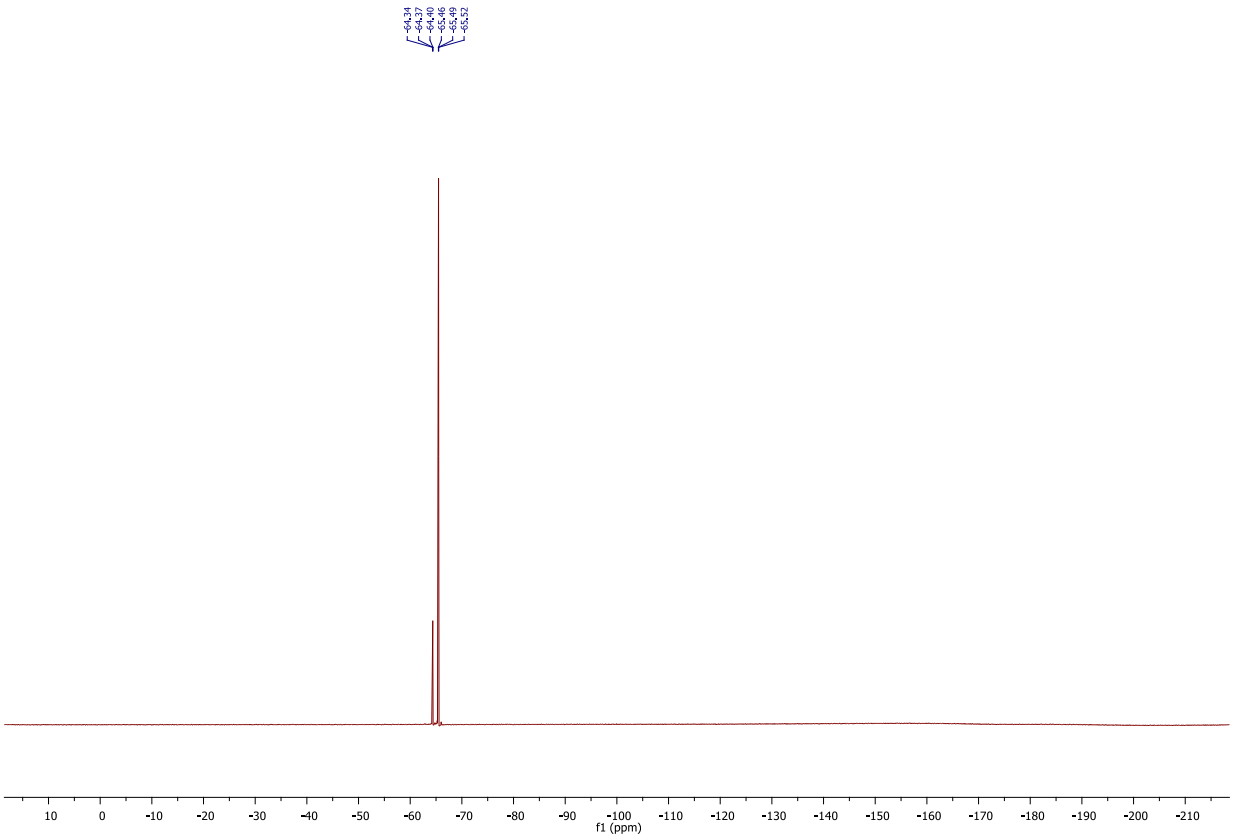

169.97
138.90
134.93
130.11
126.82
126.79
126.47
124.40
37.51
37.21
36.91
36.62
26.39
19.44
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

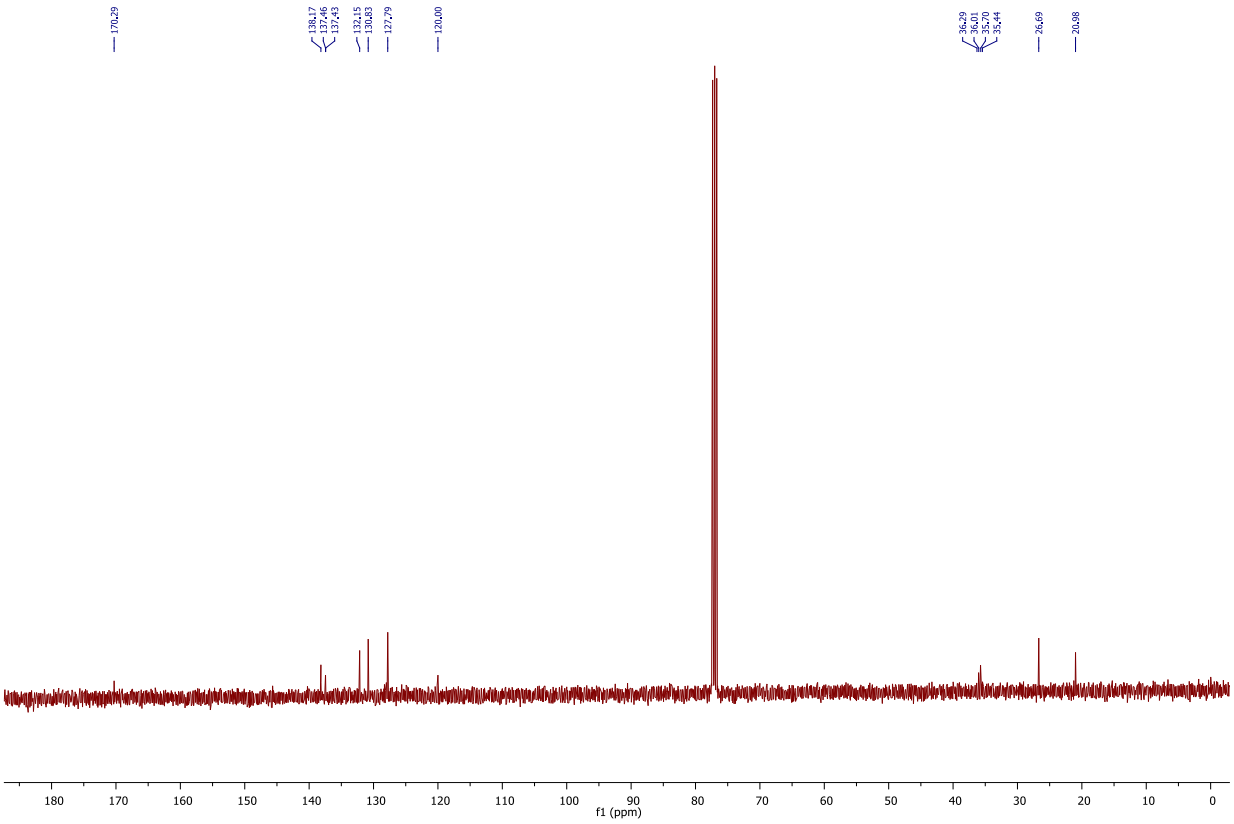

7.39
7.37
7.34
7.32
7.30
7.28
7.26
5.85
3.55
3.52
3.50
3.47
3.04
3.03
Me
O
NH
Cl
CF3
3.52
0.85
2.00
2.97
f1 (ppm)

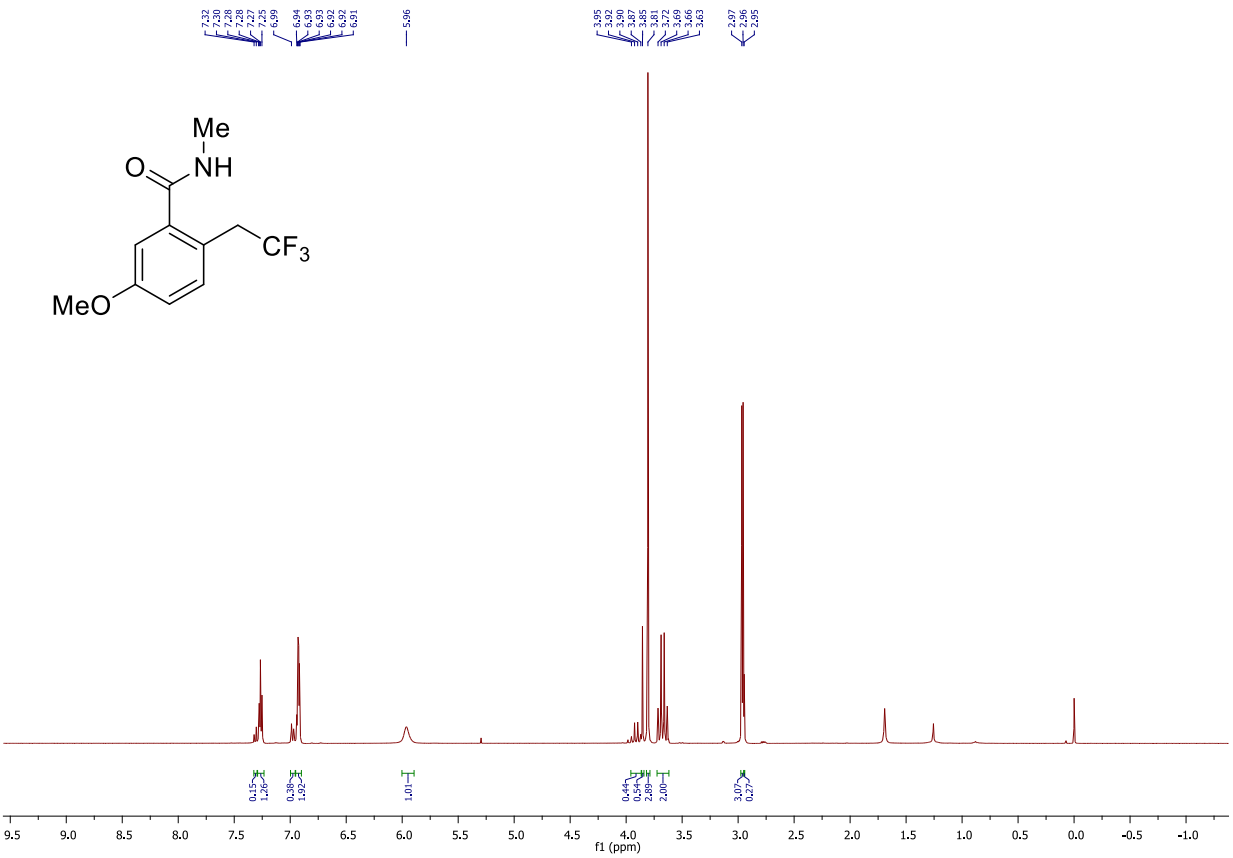

-64.96
-64.99
-65.02
f1 (ppm)

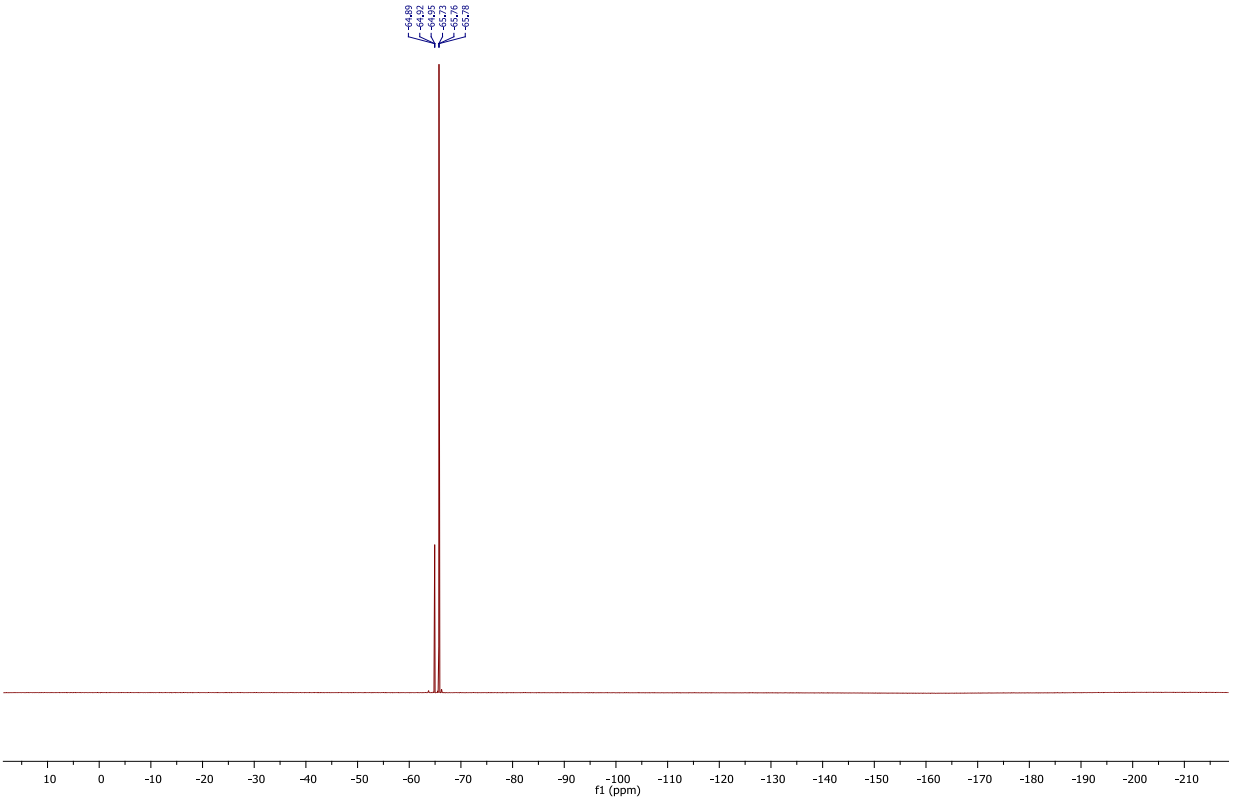

166.91
137.94
131.21
129.62
129.29
126.81
124.06
37.51
37.21
36.91
36.61
26.57
f1 (ppm)

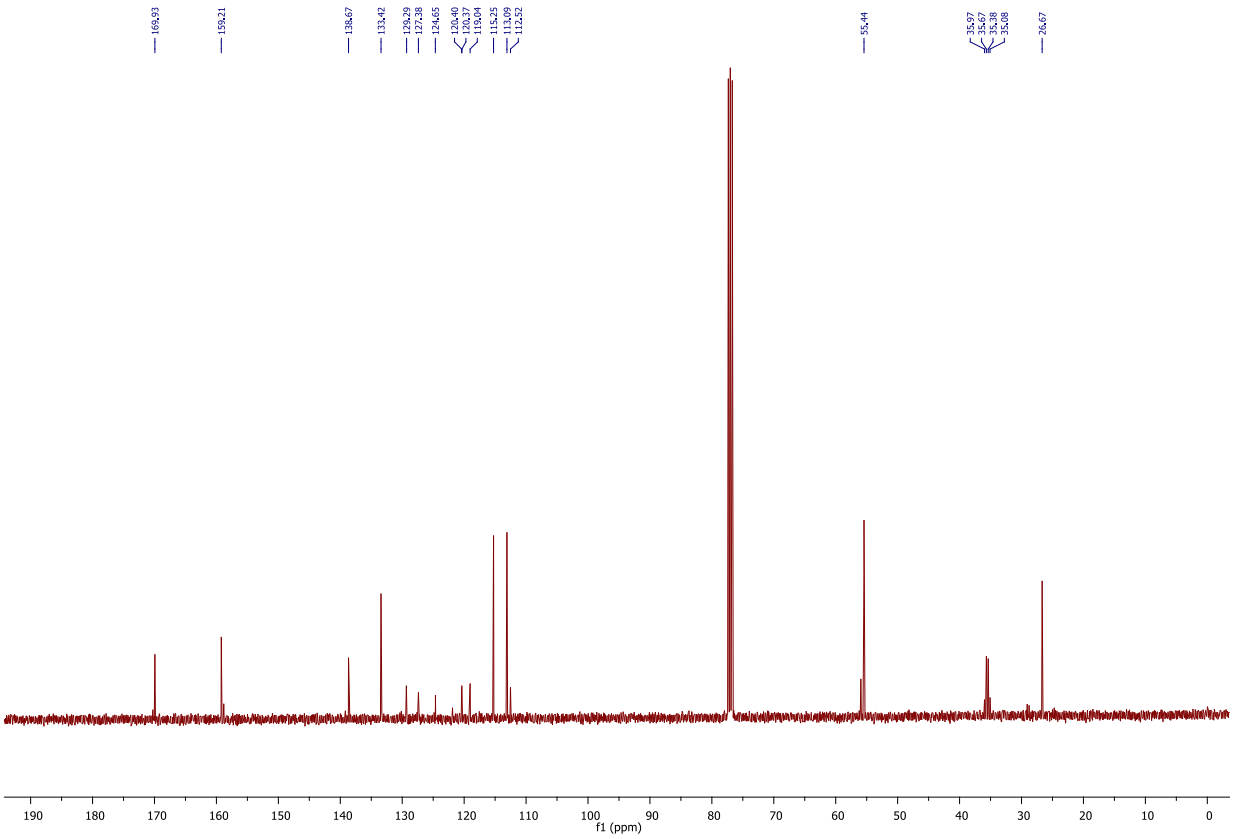

7.28
7.26
7.24
7.23
7.21
5.87
3.97
3.95
3.92
3.89
3.77
3.75
3.72
3.69
2.98
2.97
2.40
2.35
Me
O
NH
CF3
Me
4.00
0.95
0.41
2.00
3.44
0.50
2.91
f1 (ppm)

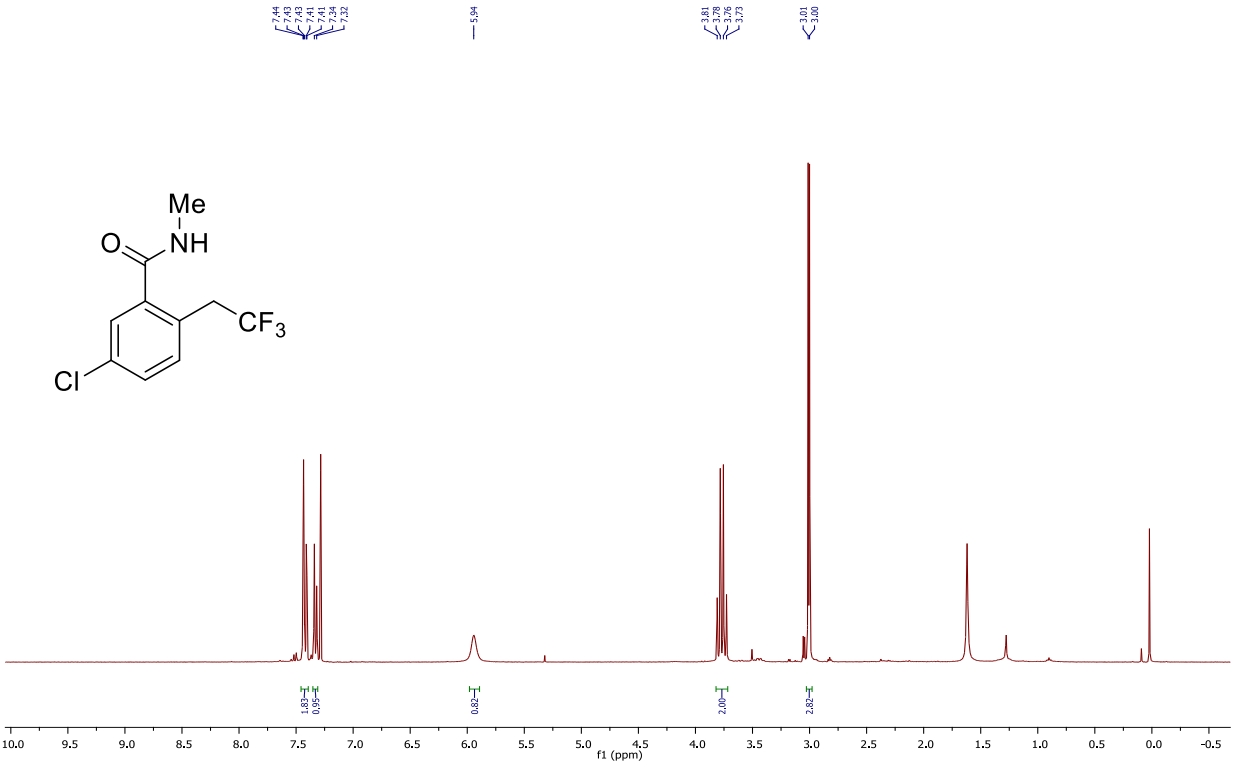

-64.34
-64.37
-64.40
-65.46
-65.49
-65.52
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


170.29
138.17
137.46
137.43
132.15
130.83
127.79
120.00
26.29
26.01
25.70
25.44
26.69
20.98
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Me
NH
O
CF3
MeO
f1 (ppm)


f1 (ppm)


169.93
159.21
138.67
133.42
129.29
127.38
124.65
120.40
120.37
116.04
115.25
113.09
112.52
55.44
35.97
35.67
35.38
35.08
26.67
f1 (ppm)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7.43
7.43
7.41
7.41
7.24
7.22
5.94
3.81
3.78
3.76
3.73
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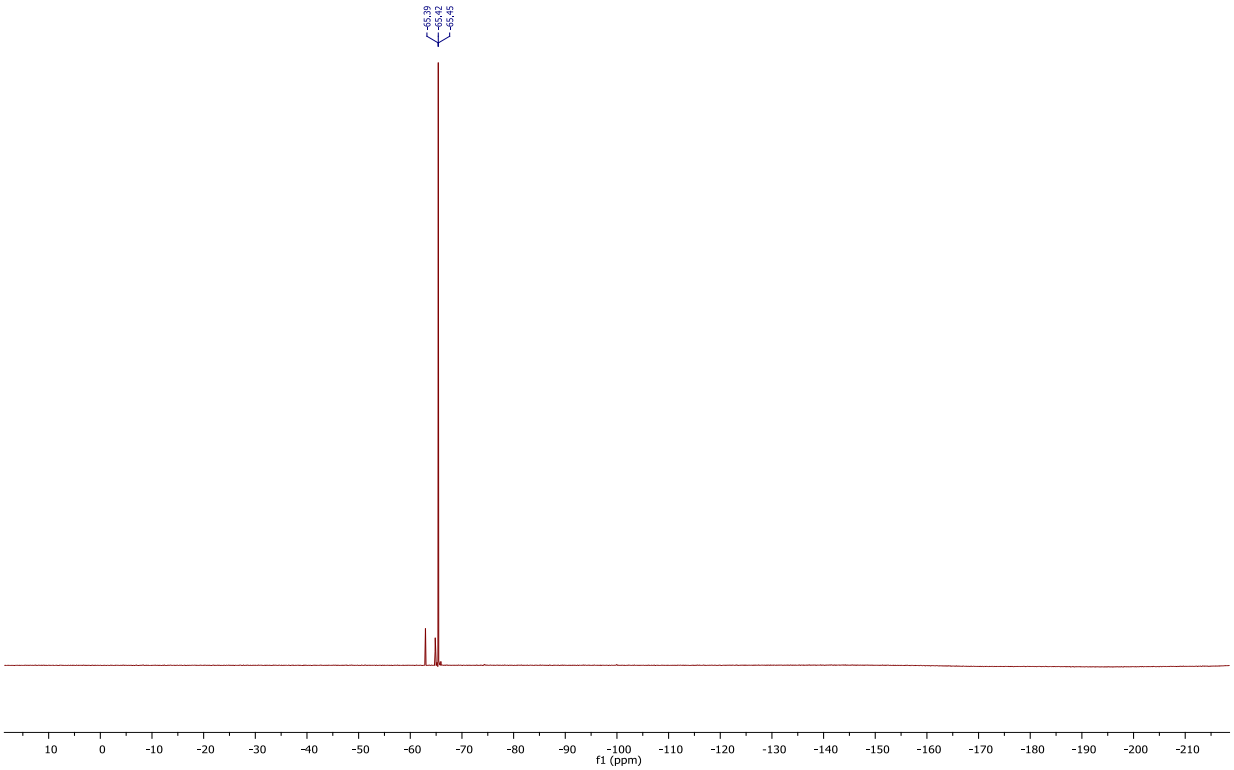
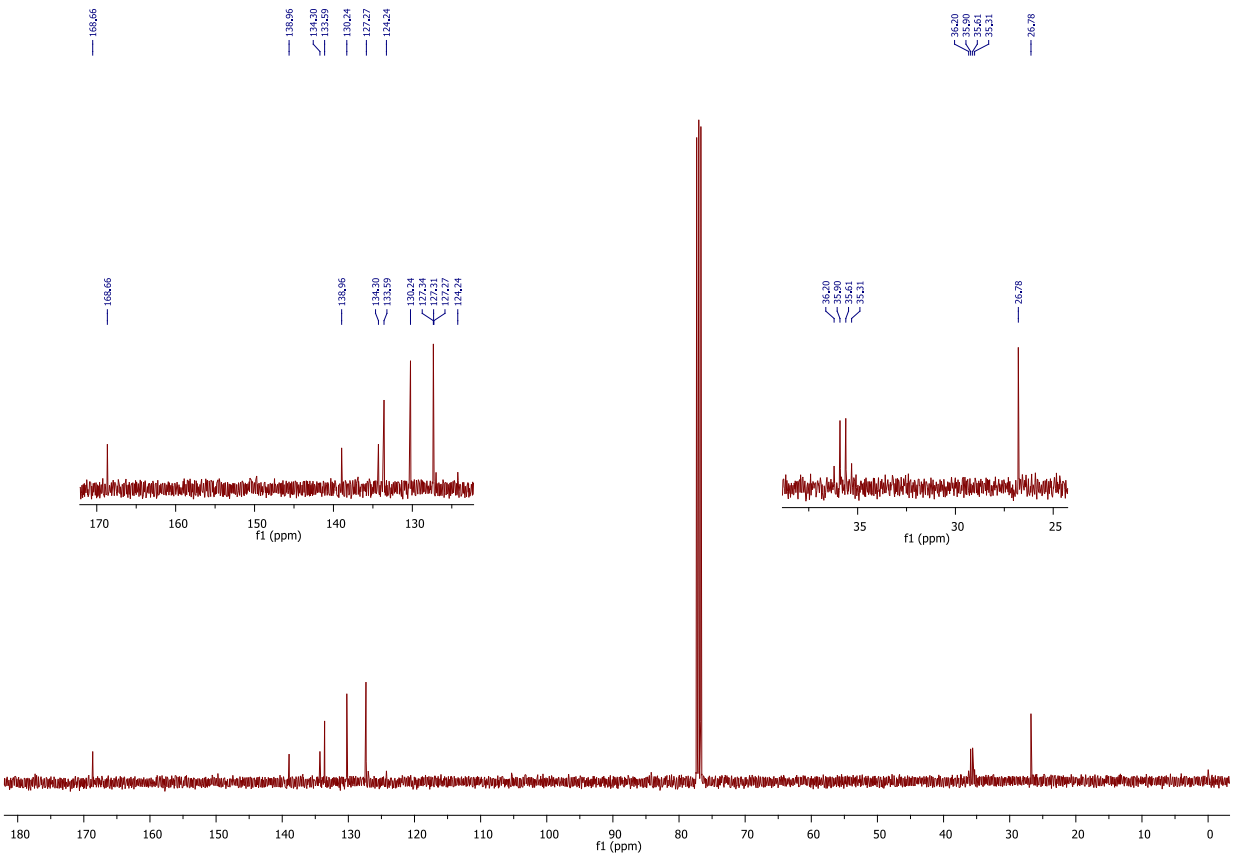
3.00
Me
NH
O
CF3
Cl
1.83
0.95
0.82
2.00
2.82
f1 (ppm)


-65,39
-65,42
-65,45
f1 (ppm)


168,66
138,96
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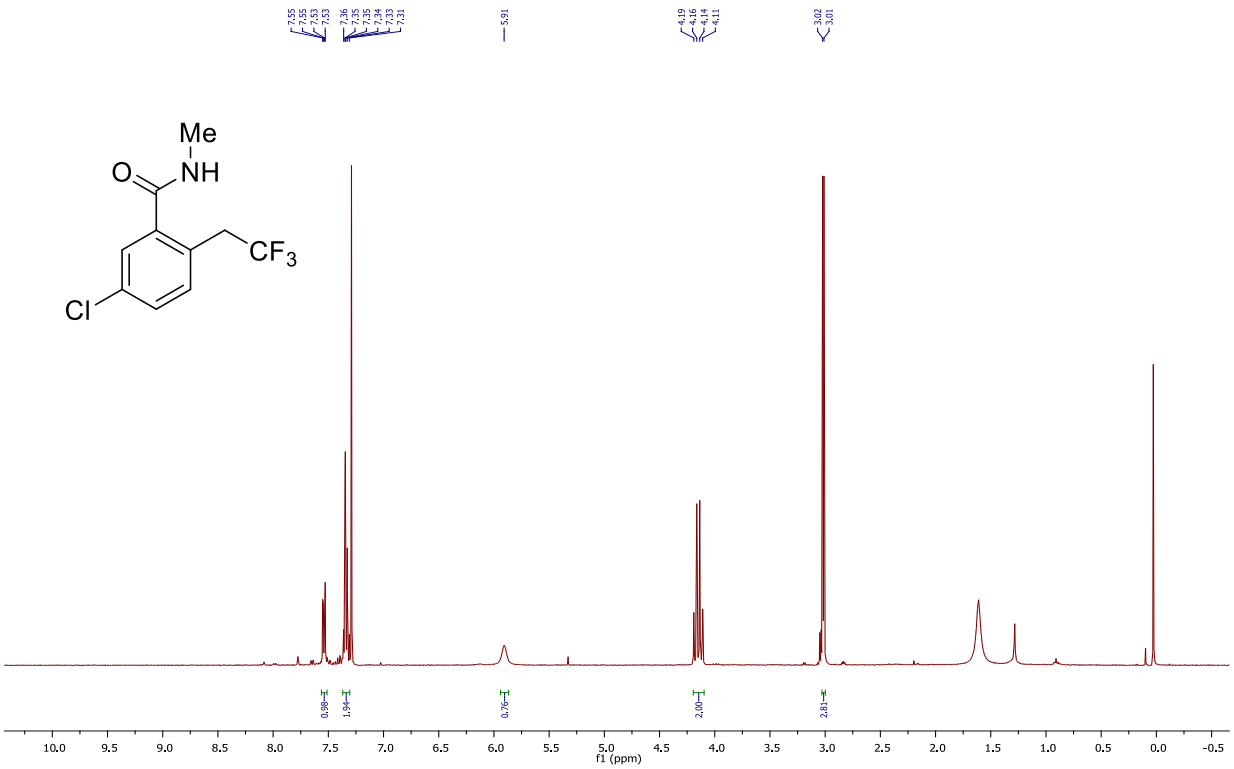
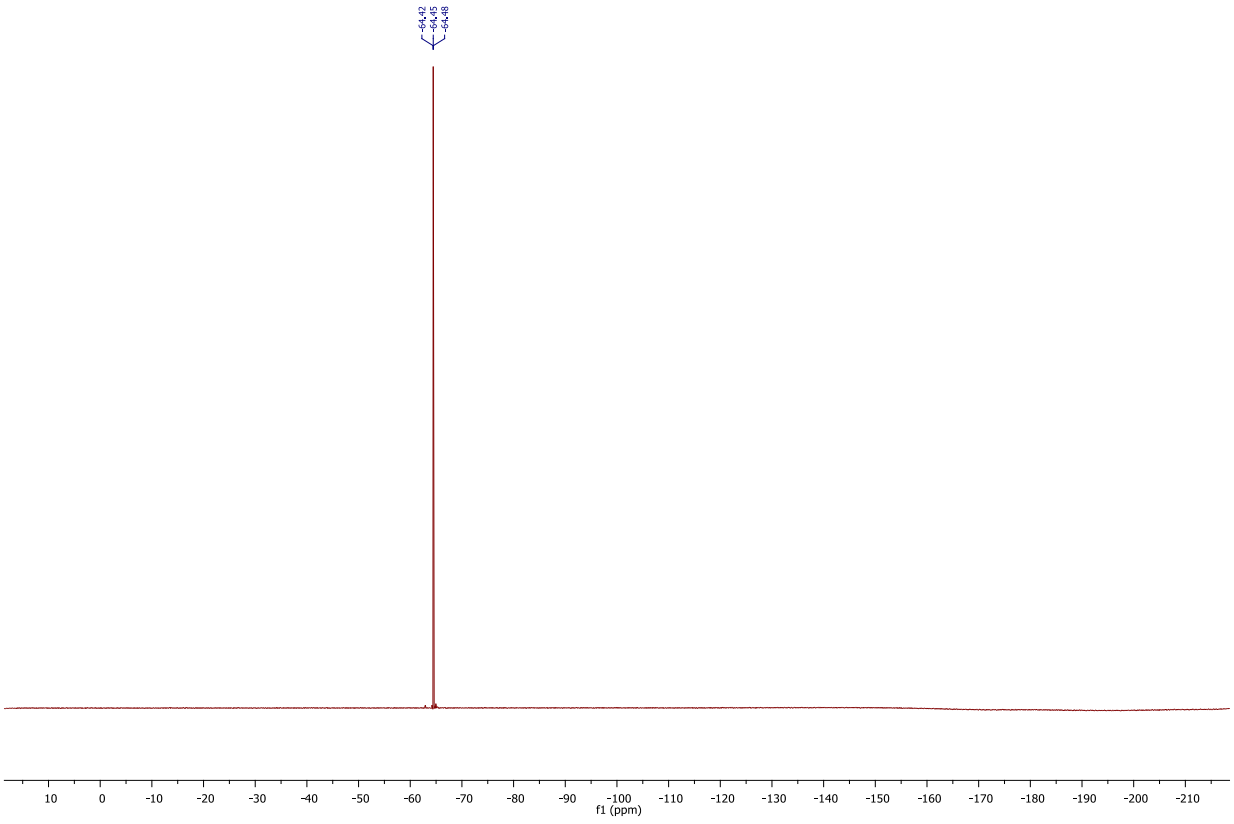
127,27
124,24
36,20
35,90
35,61
35,31
26,78
f1 (ppm)


7.55
7.55
7.53
7.53
7.36
7.35
7.35
7.34
7.33
7.31
5.91
4.19
4.16
4.14
4.11
3.02
3.01
Me
NH
O
CF3
Cl
0.88
1.94
0.76
2.00
2.81
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


-64.42
-64.45
-64.48
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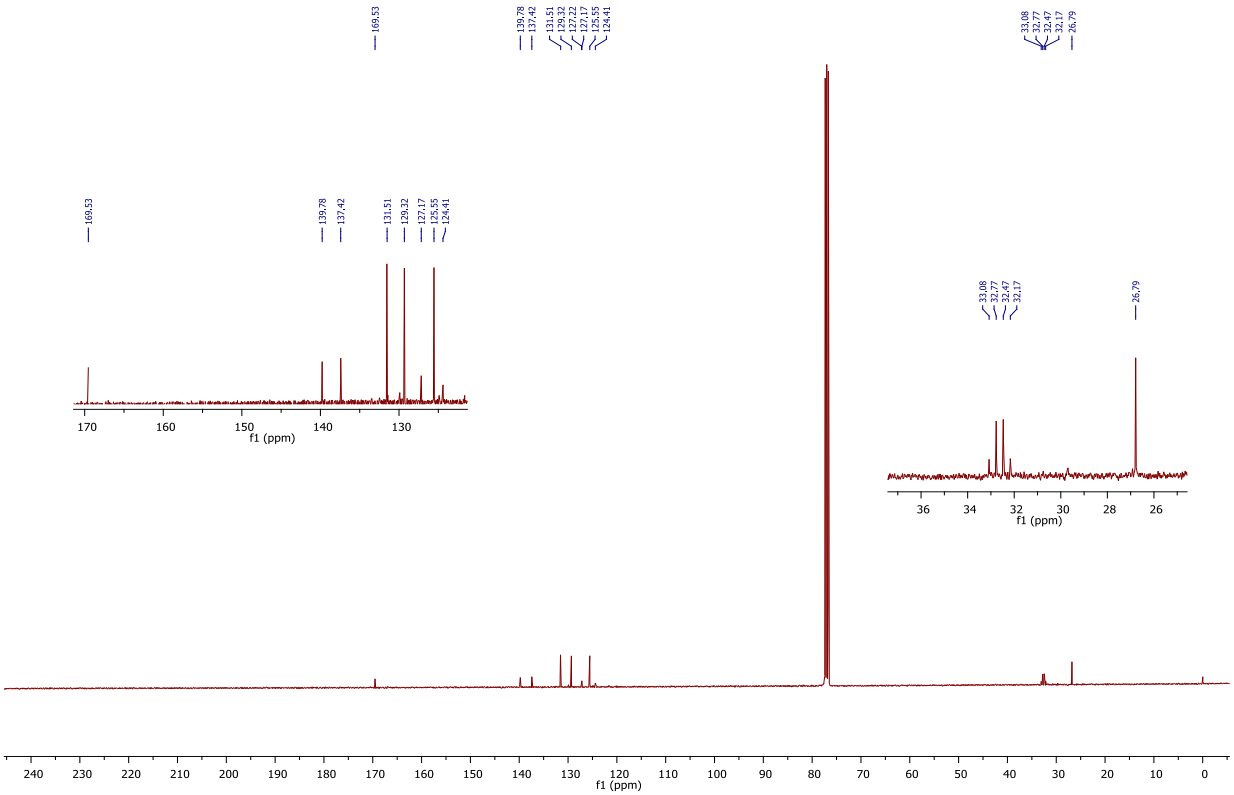
f1 (ppm)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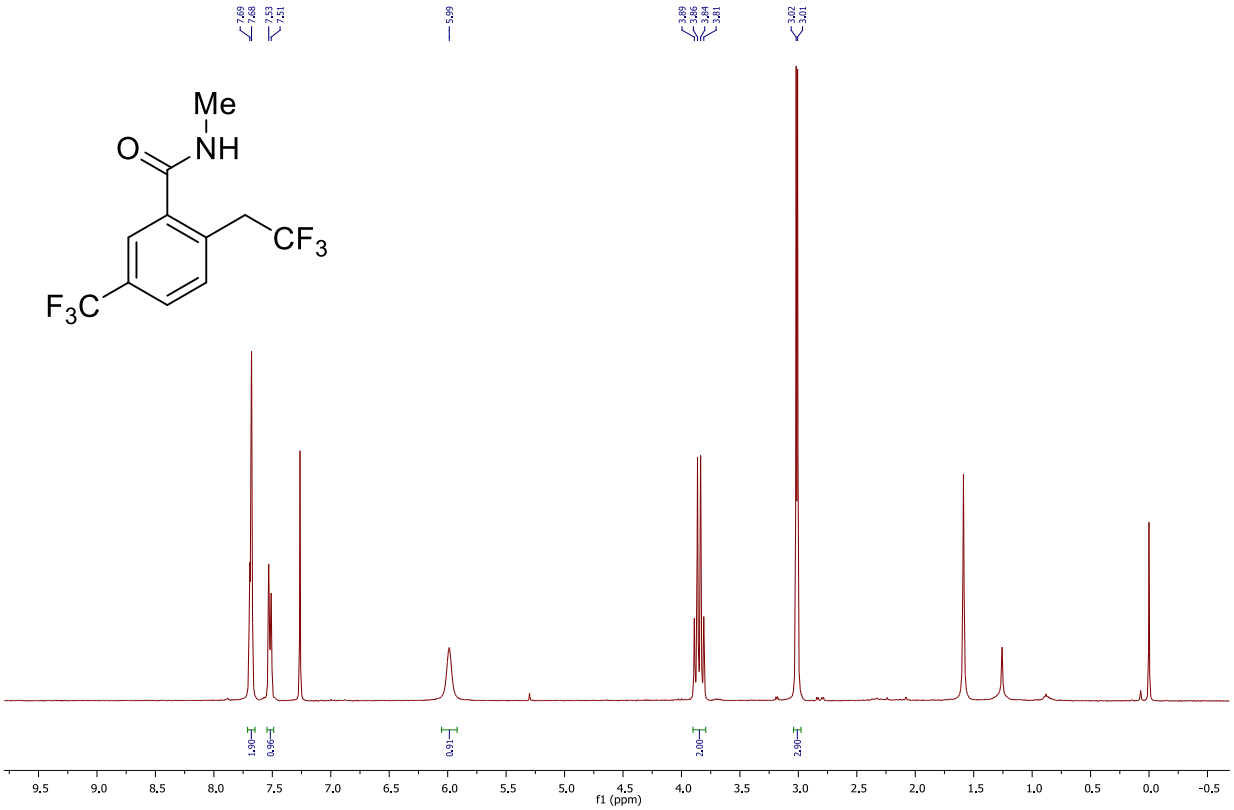
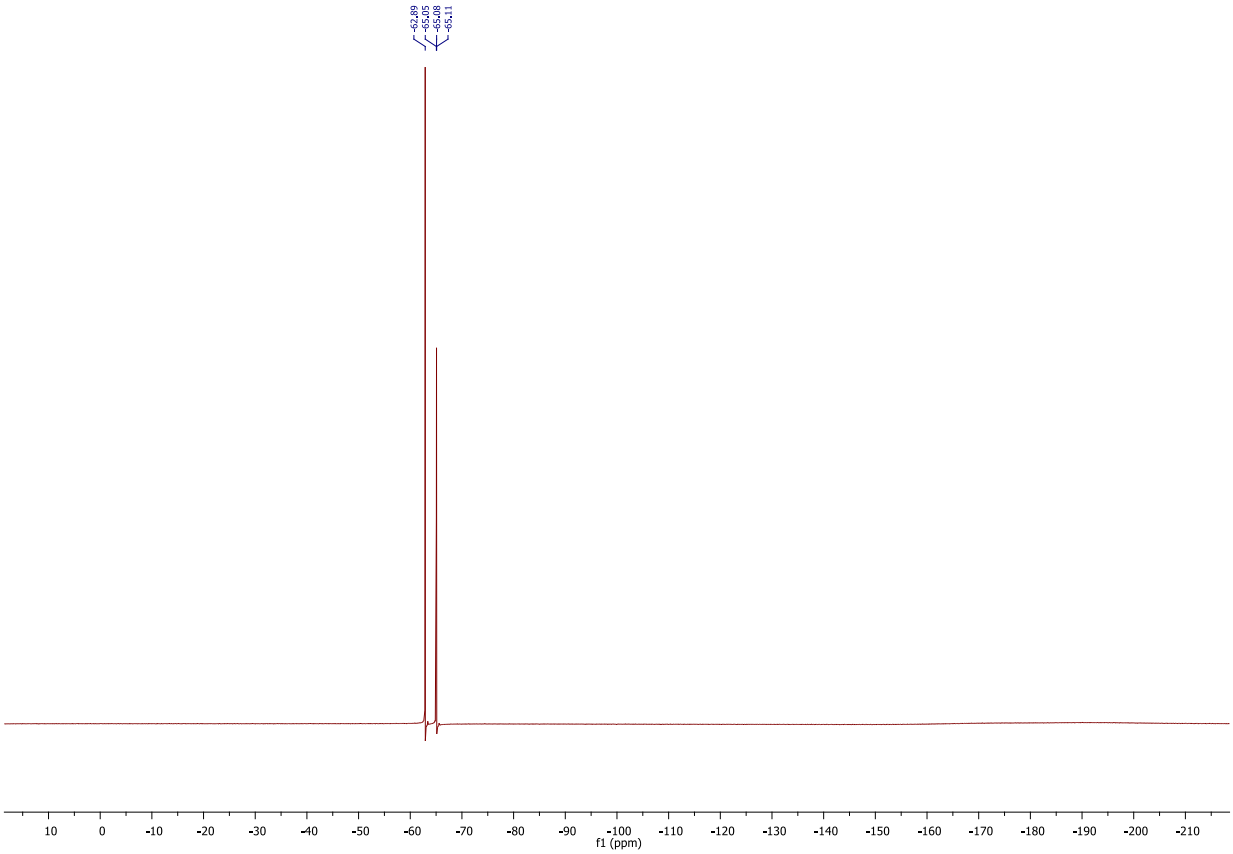
139.78
137.42
131.51
129.32
127.22
127.17
125.55
124.41
33.08
32.77
32.47
32.17
26.79
f1 (ppm)


7.69
7.68
7.53
7.51
5.99
3.89
3.86
3.84
3.81
3.02
3.01
Me
NH
O
CF3
F3C
1.90
0.96
0.91
2.00
2.90
f1 (ppm)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-65.05
-65.08
-65.11
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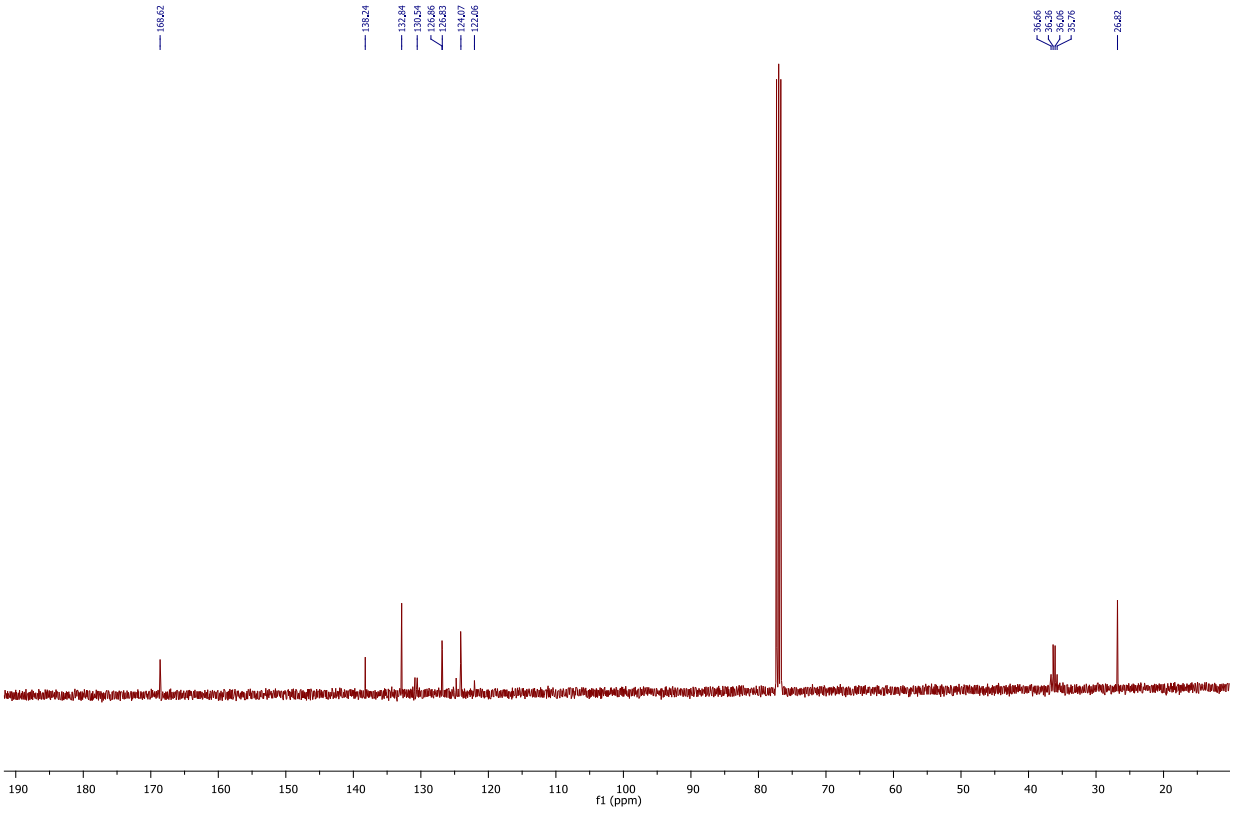
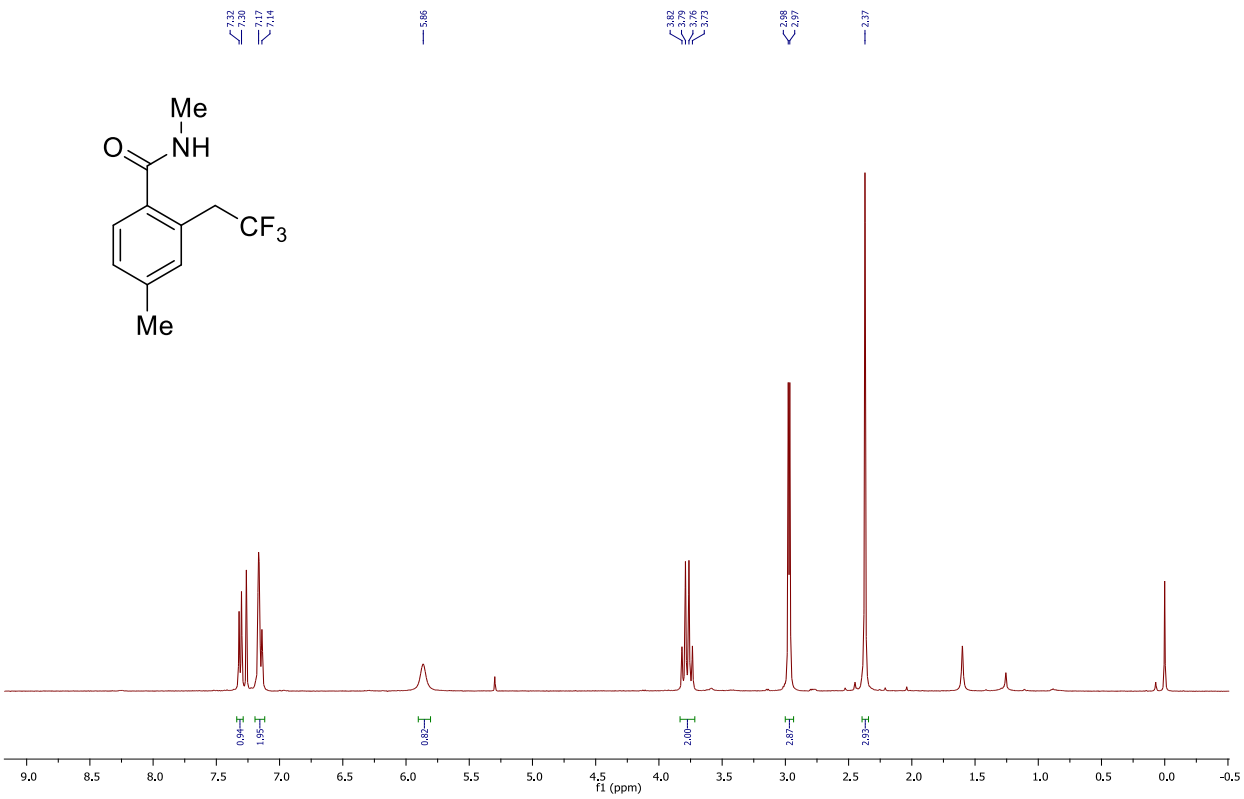
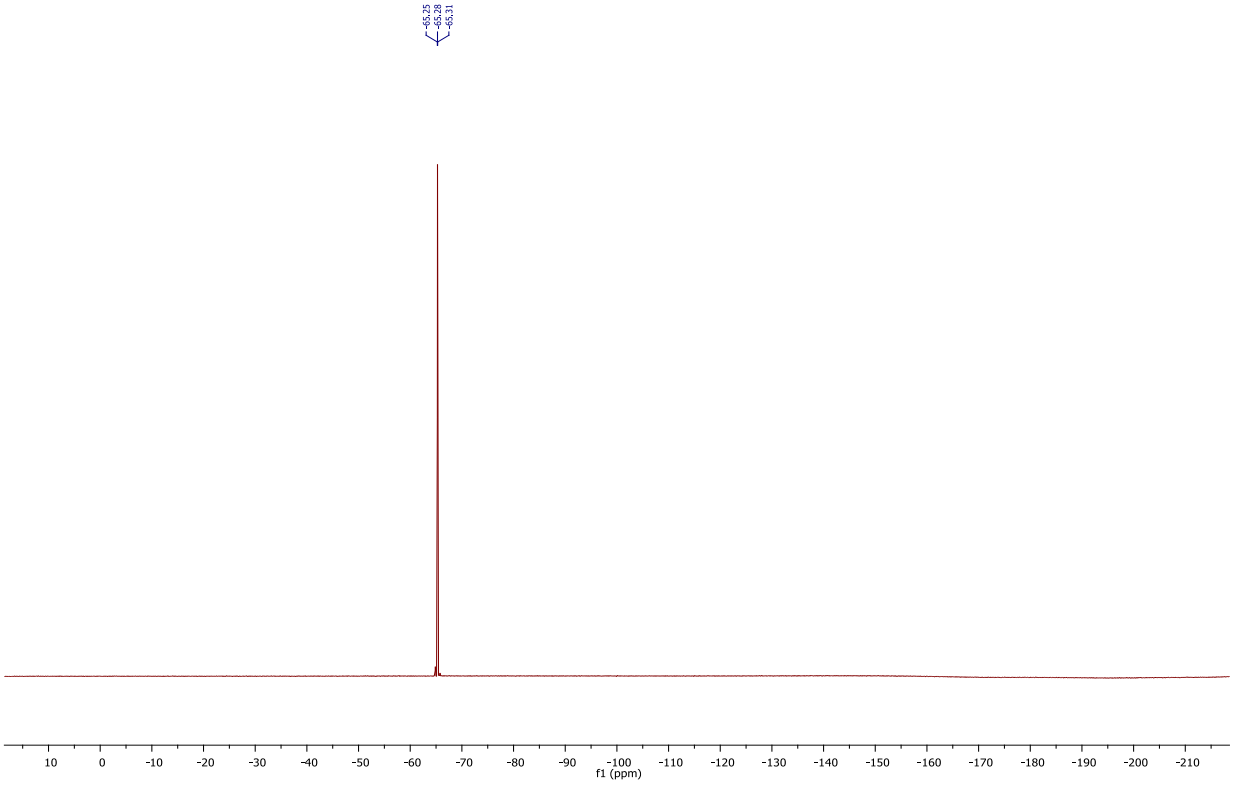
f1 (ppm)


166.62
138.24
132.84
130.54
126.85
126.83
124.07
122.06
36.66
36.26
36.06
35.76
26.82
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)


7.32
7.30
7.17
7.14
5.86
3.82
3.79
3.76
3.73
2.98
2.97
2.37
Me
O
NH
CF3
Me
0.94
1.95
0.82
2.00
2.87
2.93
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


-65.25
-65.28
-65.31
10
0
-10
-20
-30
-40
-50
-60
-70
-80
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-130
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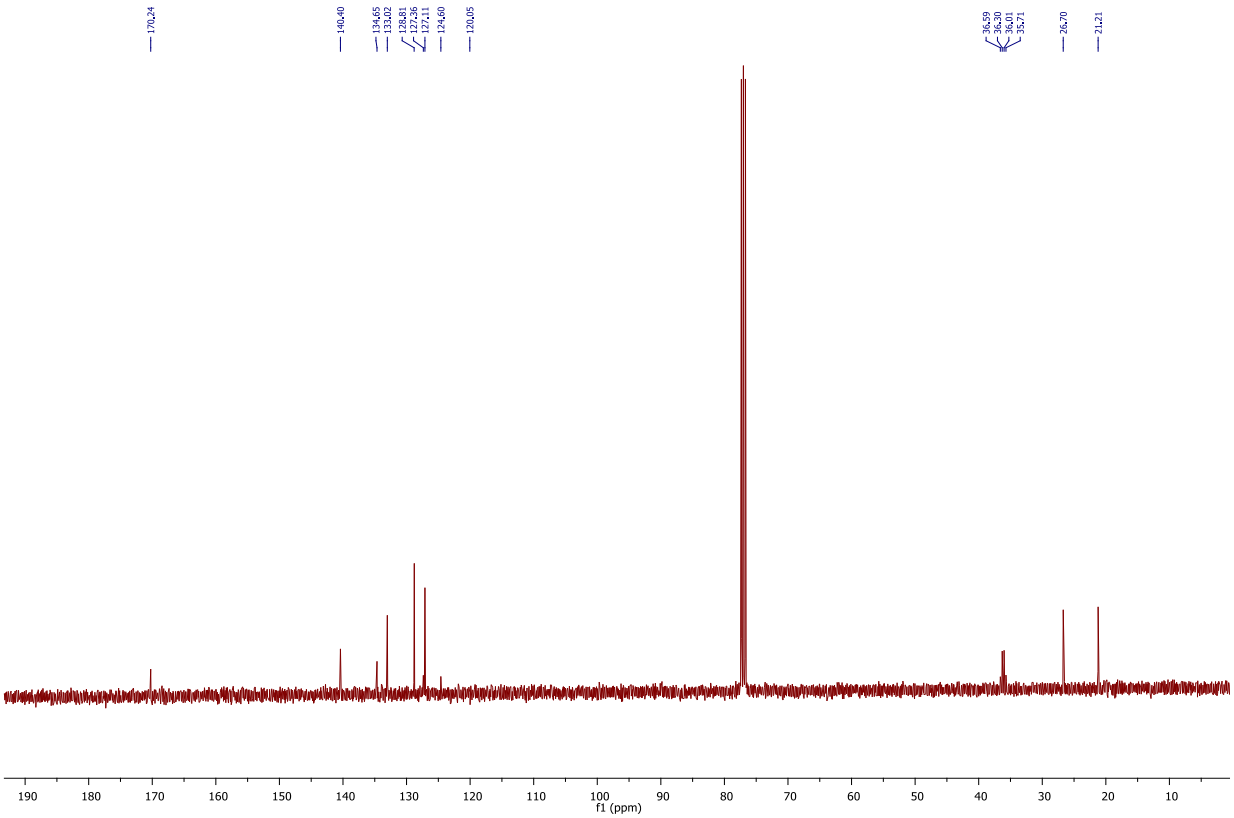
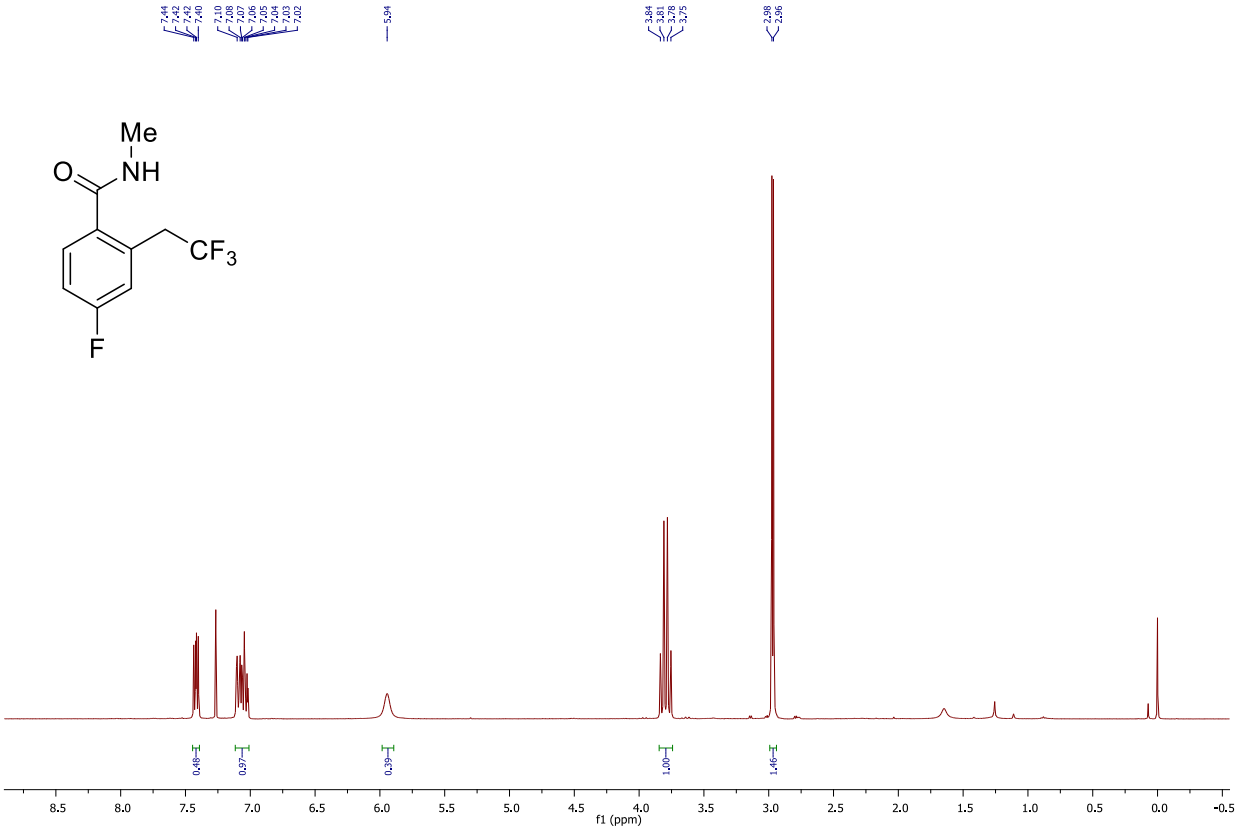
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


170.24
140.40
134.65
131.02
128.81
127.36
127.11
124.60
120.05
36.59
36.30
36.01
35.71
26.70
21.21
f1 (ppm)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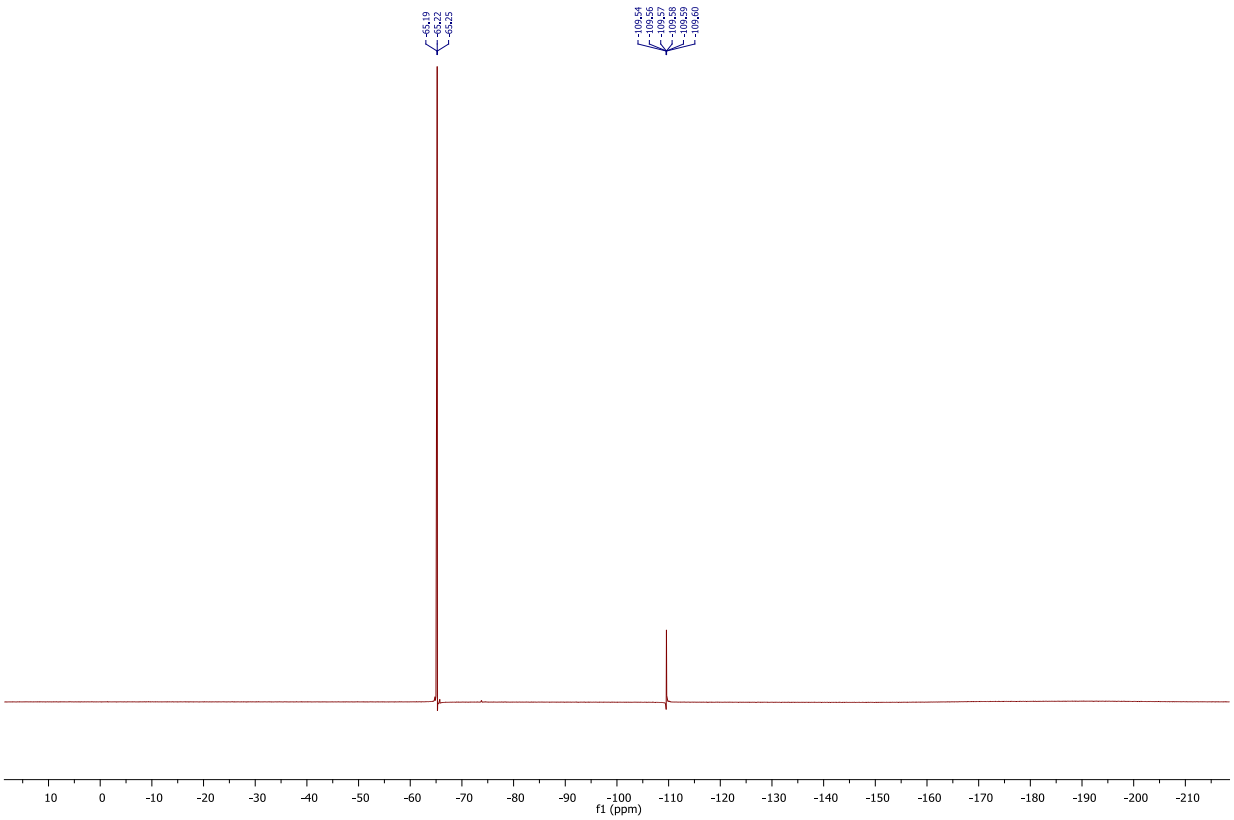
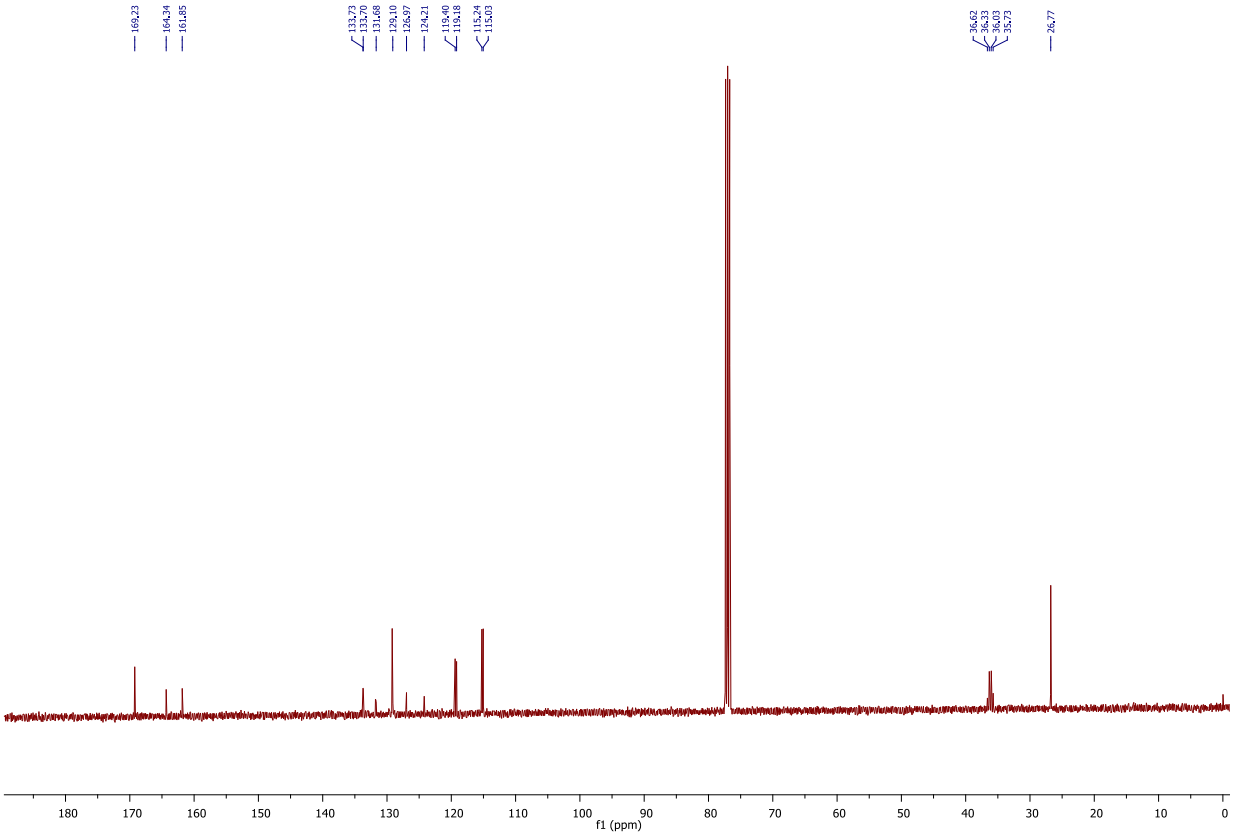
7.42
7.42
7.40
7.10
7.08
7.07
7.06
7.05
7.04
7.03
7.02
5.94
3.84
3.81
3.78
3.75
2.98
2.96
Me
NH
O
CF3
F
0.48
0.97
0.39
1.00
1.46
f1 (ppm)


-65.19
-65.22
-65.25
-109.54
-109.56
-109.57
-109.58
-109.59
-109.60
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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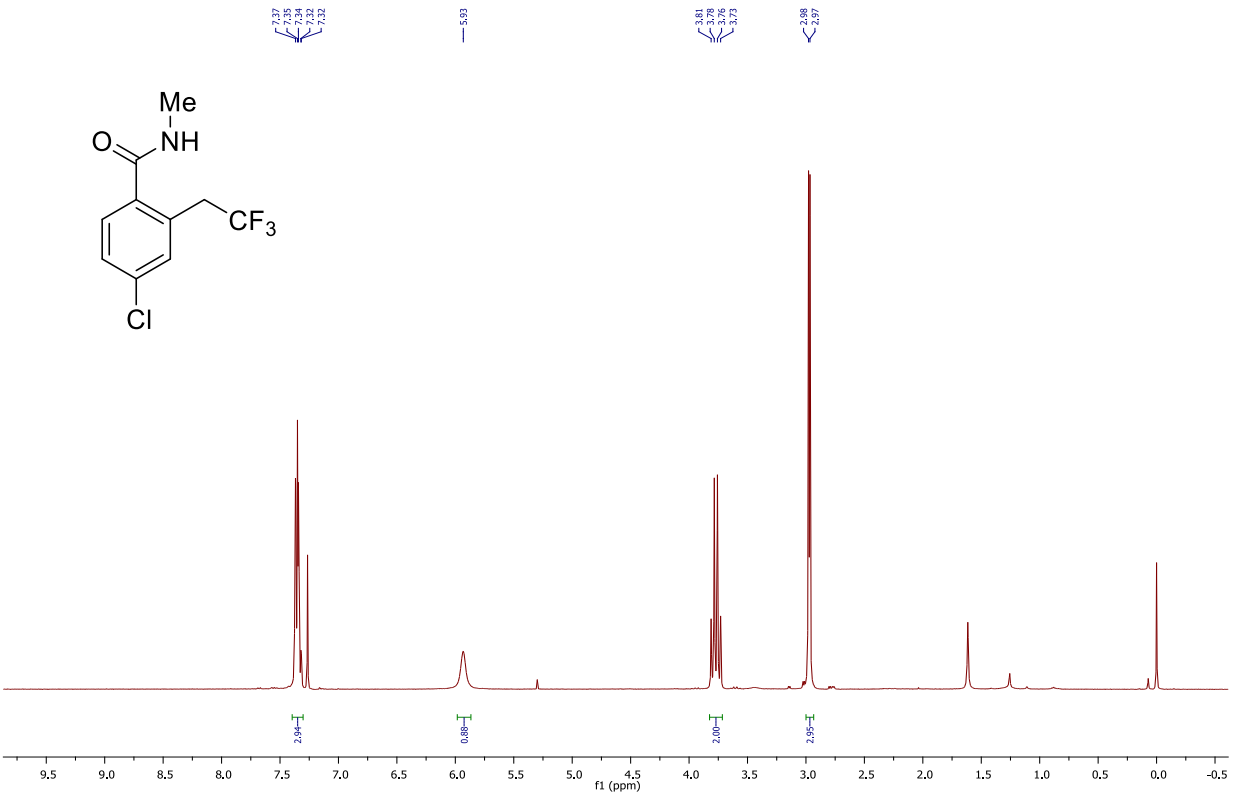
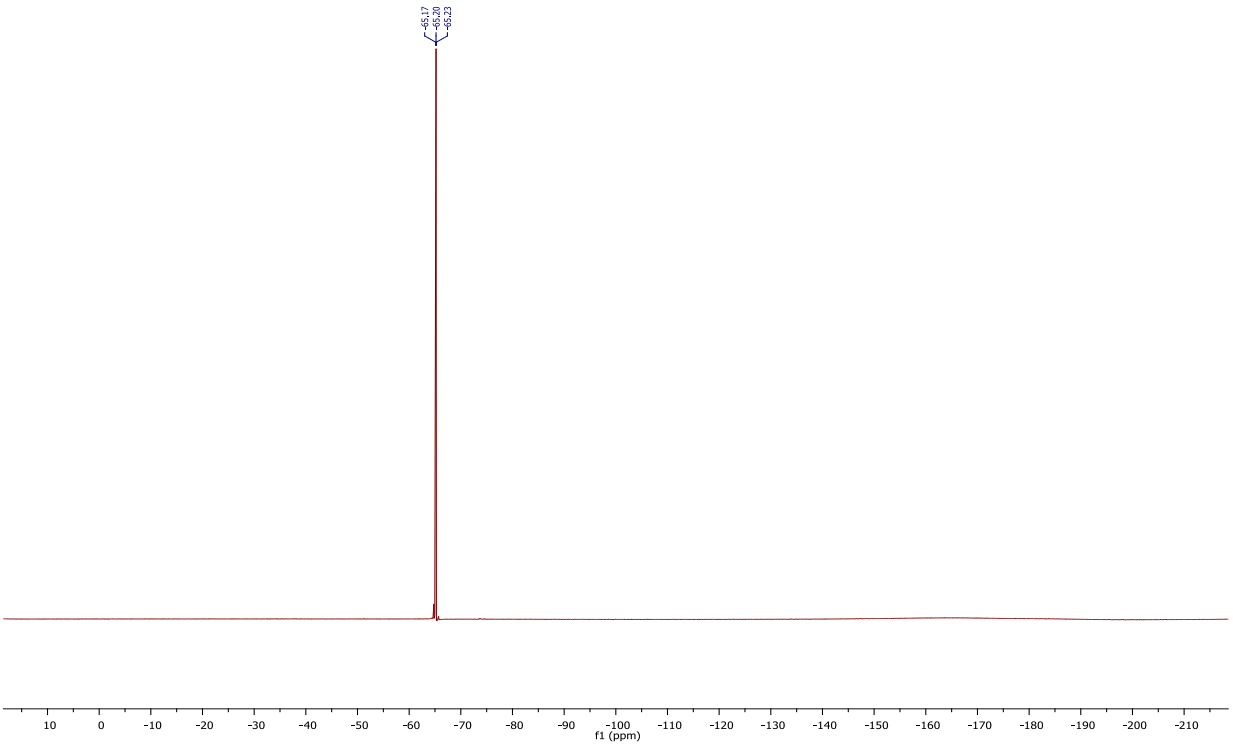
164.34
161.85
133.73
133.70
131.68
129.10
126.97
124.21
119.40
119.18
115.24
115.03
36.62
36.33
36.03
35.73
26.77
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Me
NH
O
CF3
Cl
7.37
7.35
7.34
7.32
7.32
5.93
3.81
3.78
3.76
3.73
2.98
2.97
2.94
0.88
2.00
2.95
f1 (ppm)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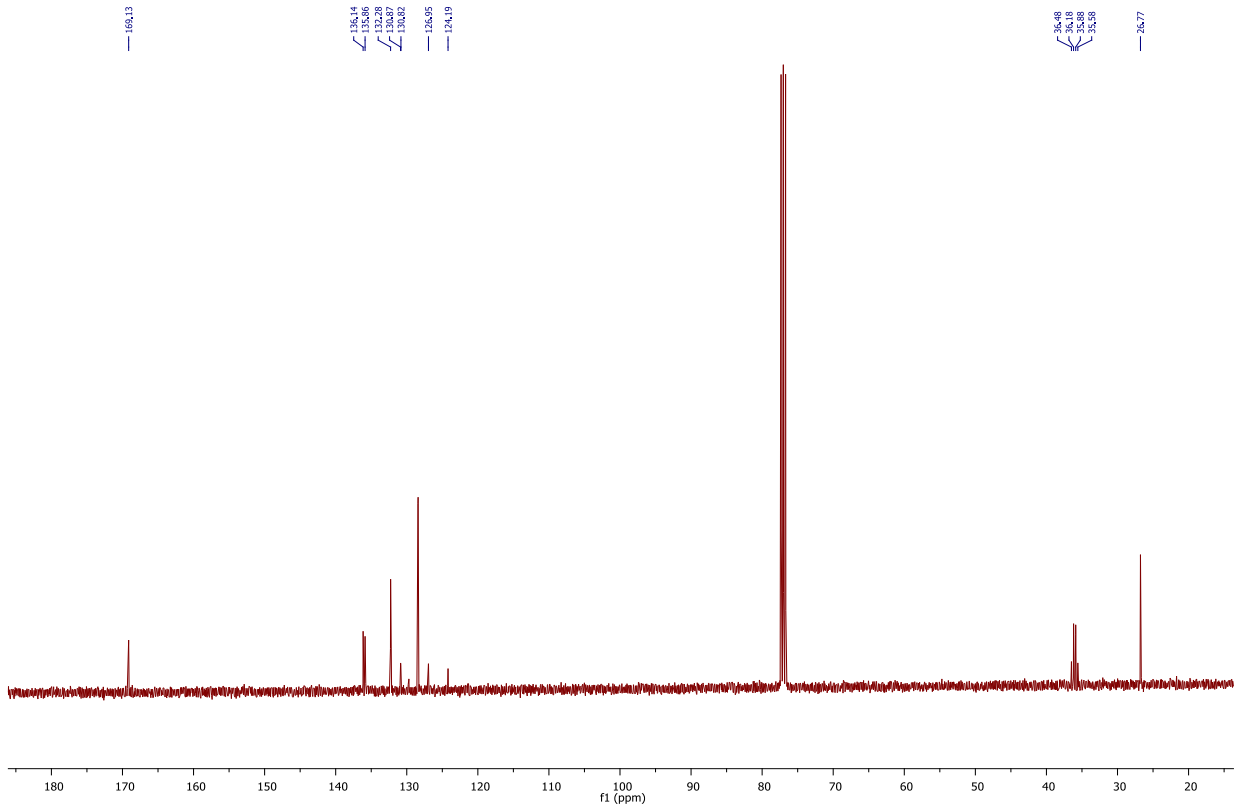
-65.20
-65.23
f1 (ppm)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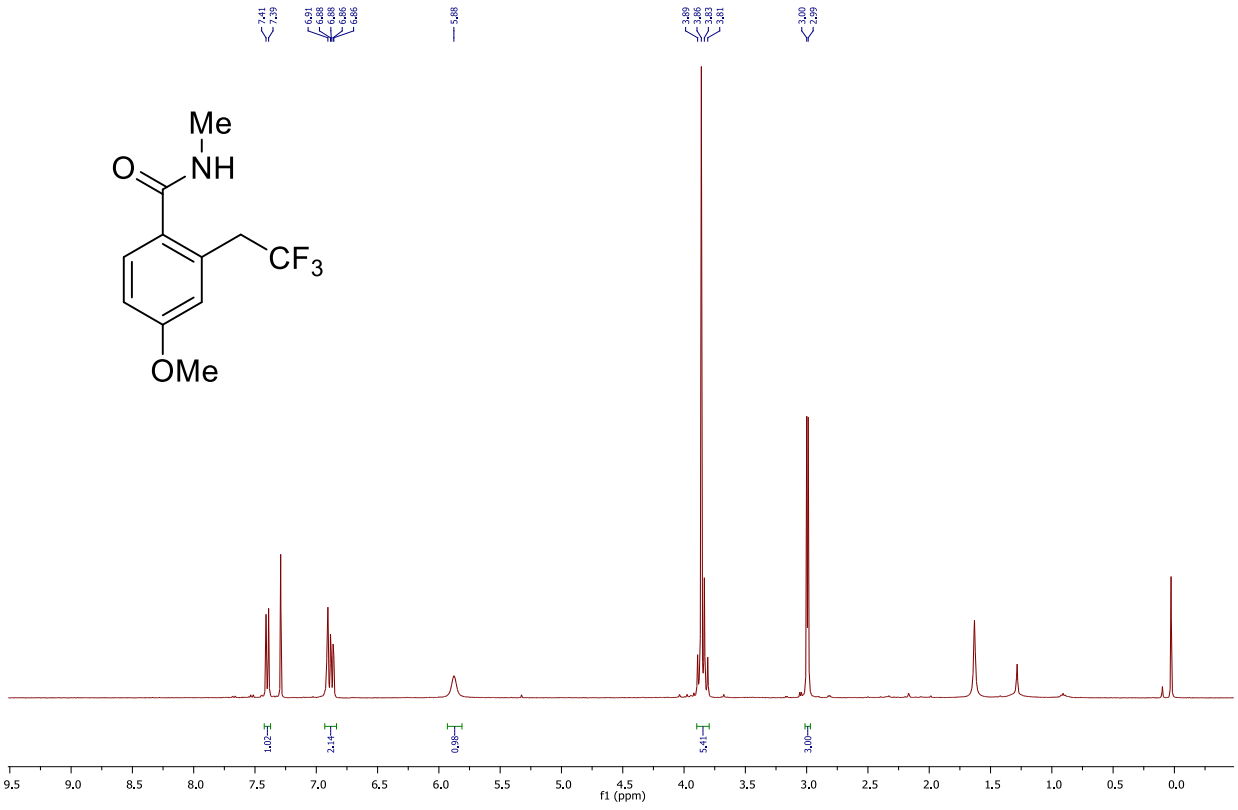
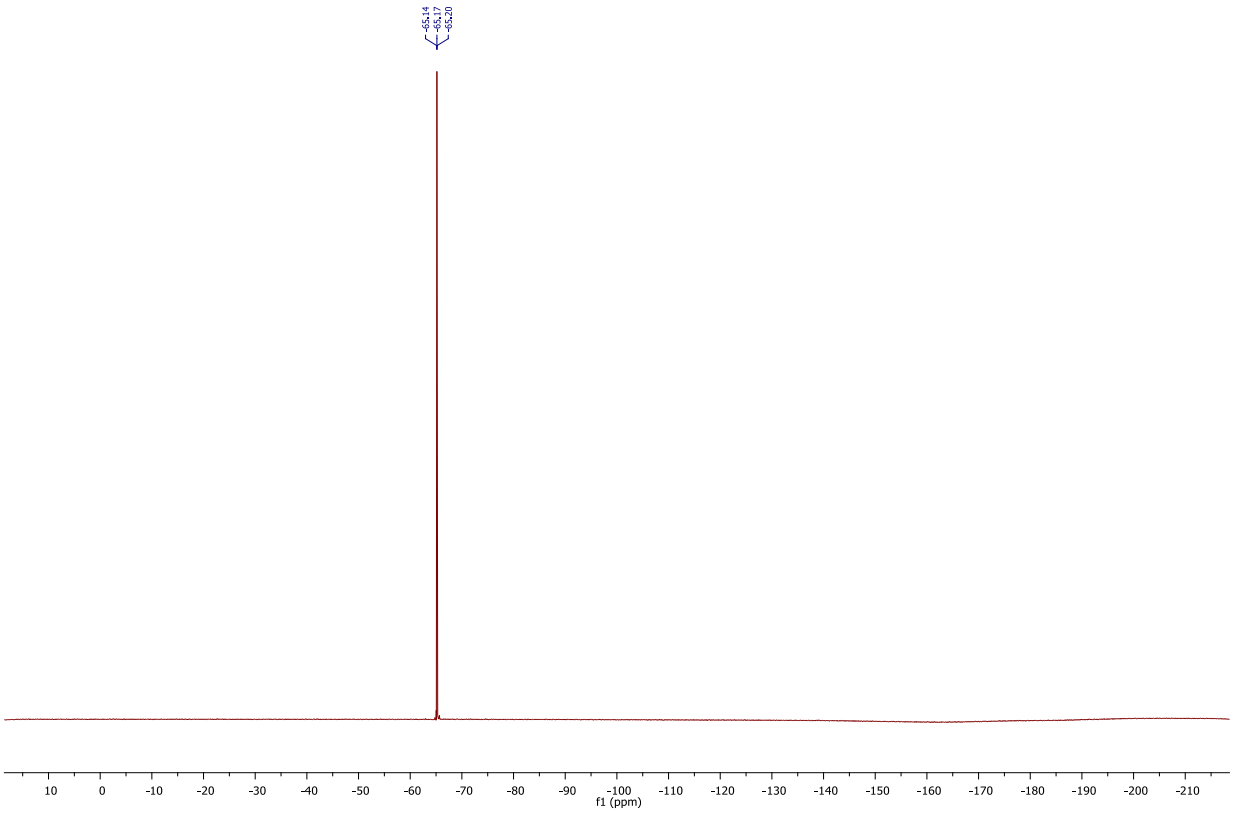
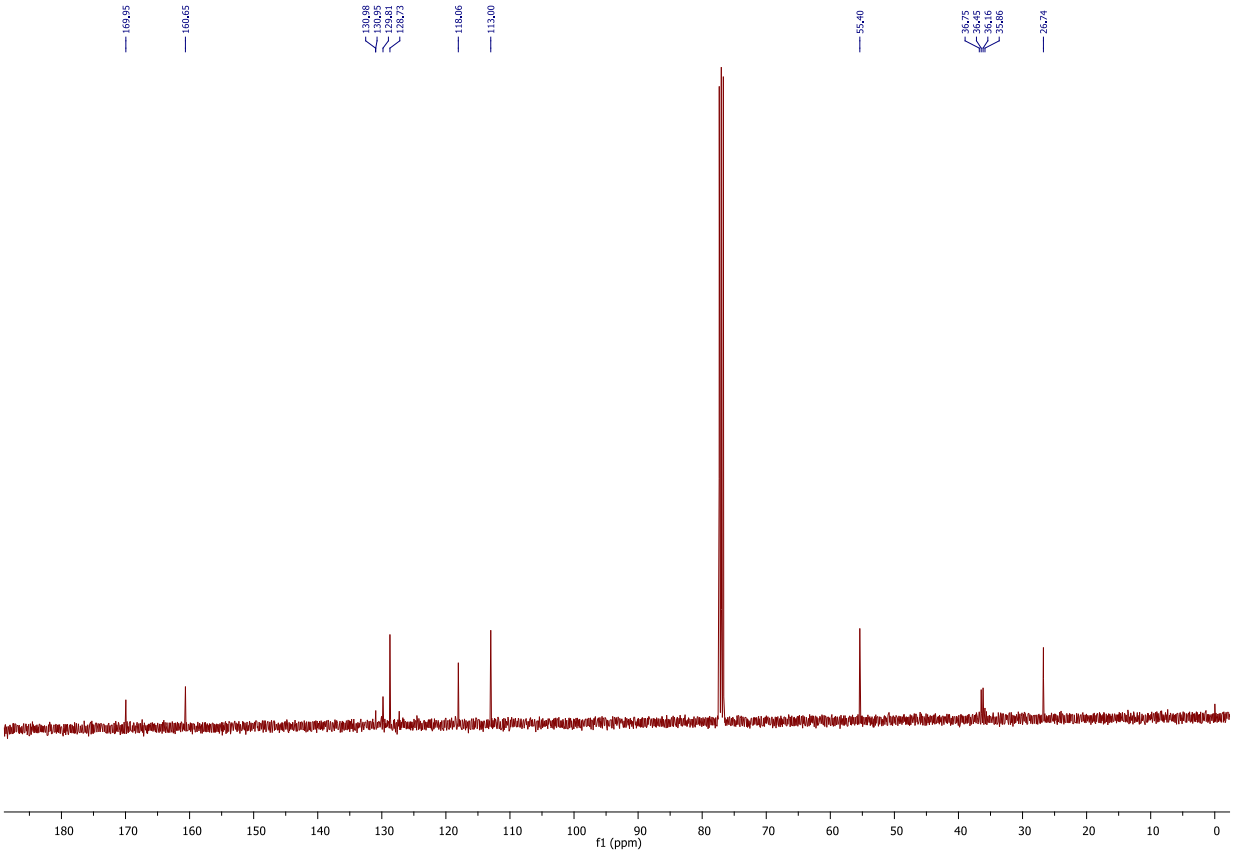
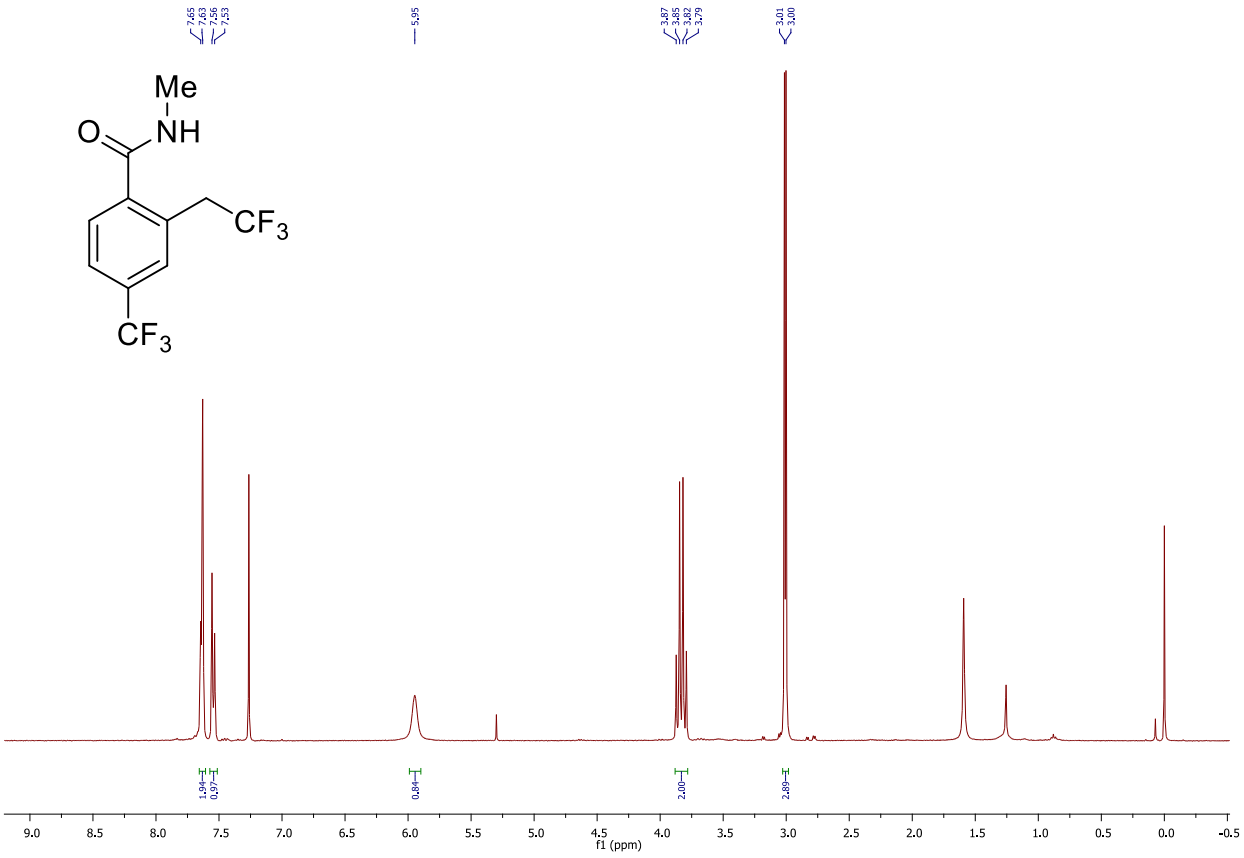
136.14
135.66
132.28
130.87
130.82
126.95
124.19
36.48
36.18
35.88
35.58
26.77
f1 (ppm)


7.41
7.39
6.91
6.88
6.88
6.86
6.86
5.88
3.89
3.86
3.83
3.81
3.00
2.99
Me
NH
O
CF3
OMe
1.02
2.14
0.98
5.41
3.00
f1 (ppm)


-65.14
-65.17
-65.20
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


169,95
160,65
130,98
130,35
129,31
128,73
118,06
113,00
55,40
36,75
36,45
36,16
35,86
26,74
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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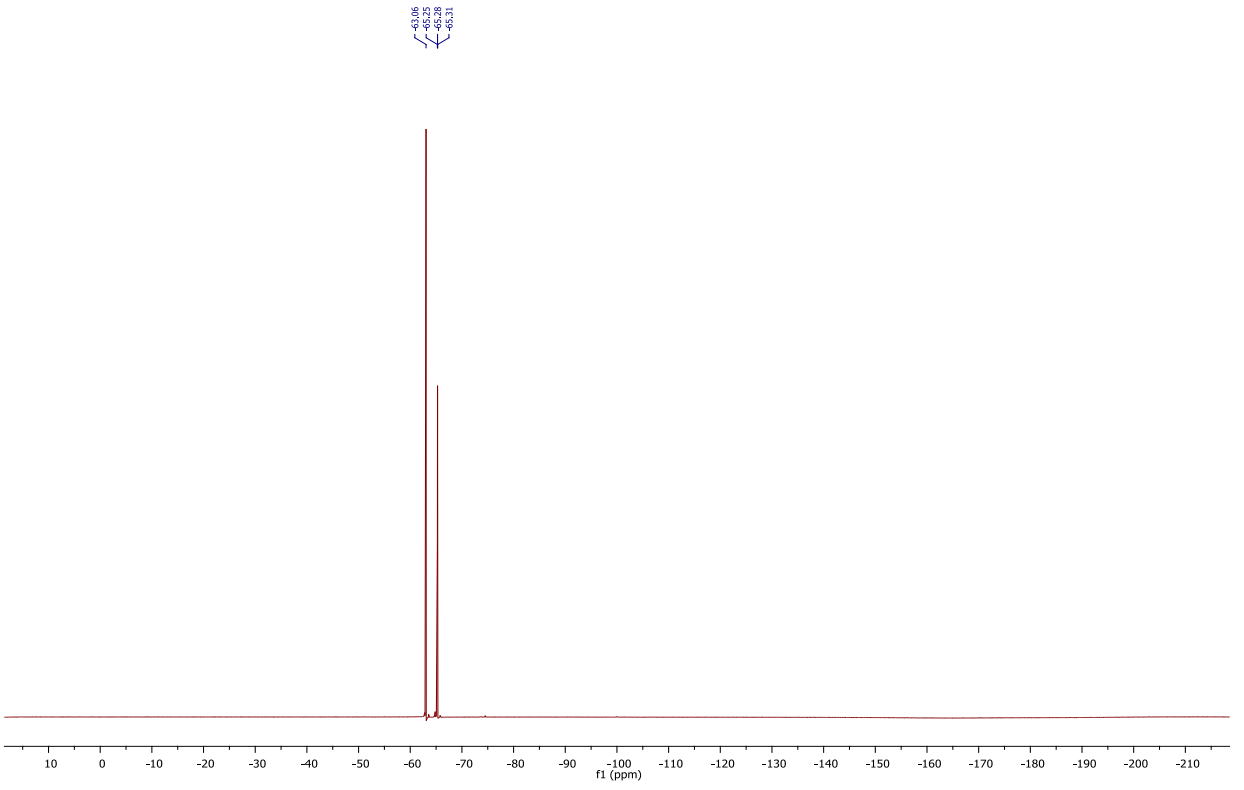
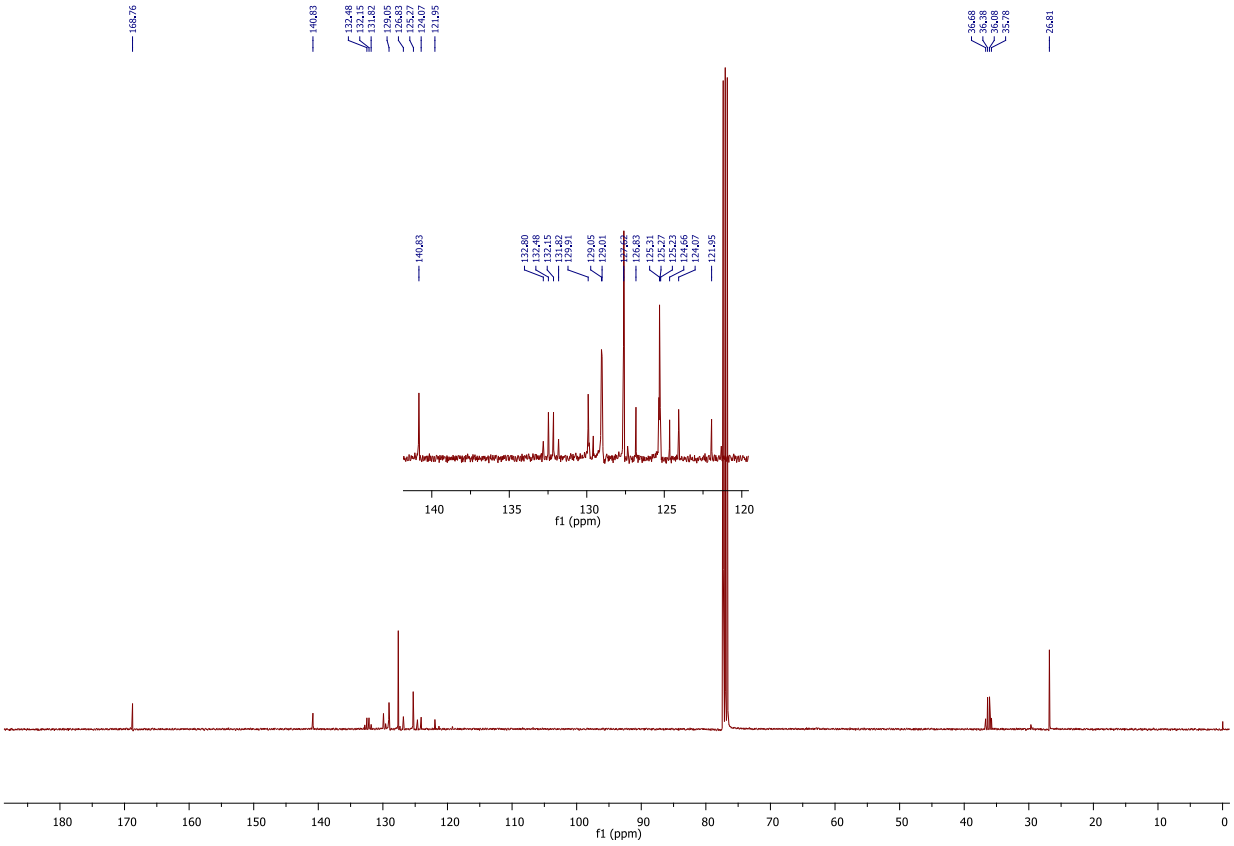
7.63
7.56
7.53
5.95
3.87
3.85
3.82
3.79
3.01
3.00
Me
NH
O
CF3
CF3
1.94
0.97
0.84
2.00
2.89
f1 (ppm)


-63.06
-65.25
-65.28
-65.31
f1 (ppm)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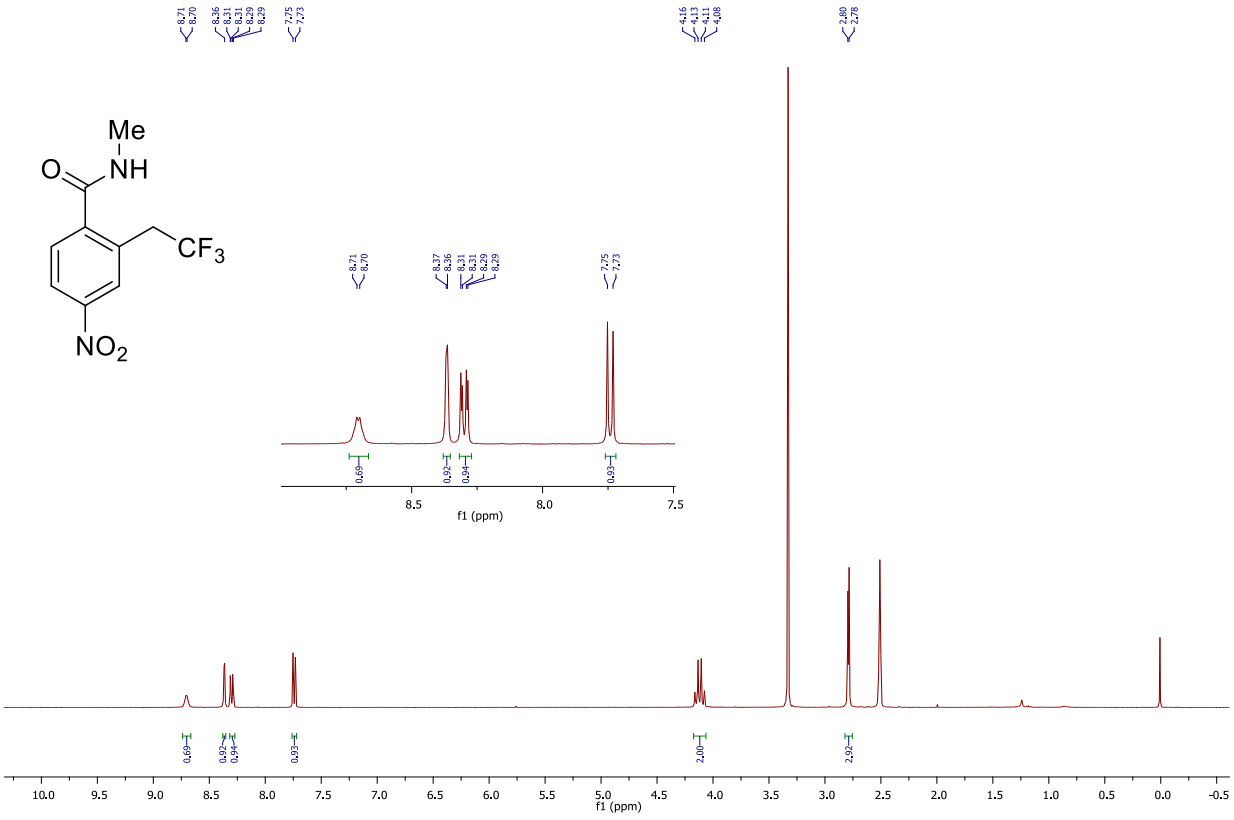
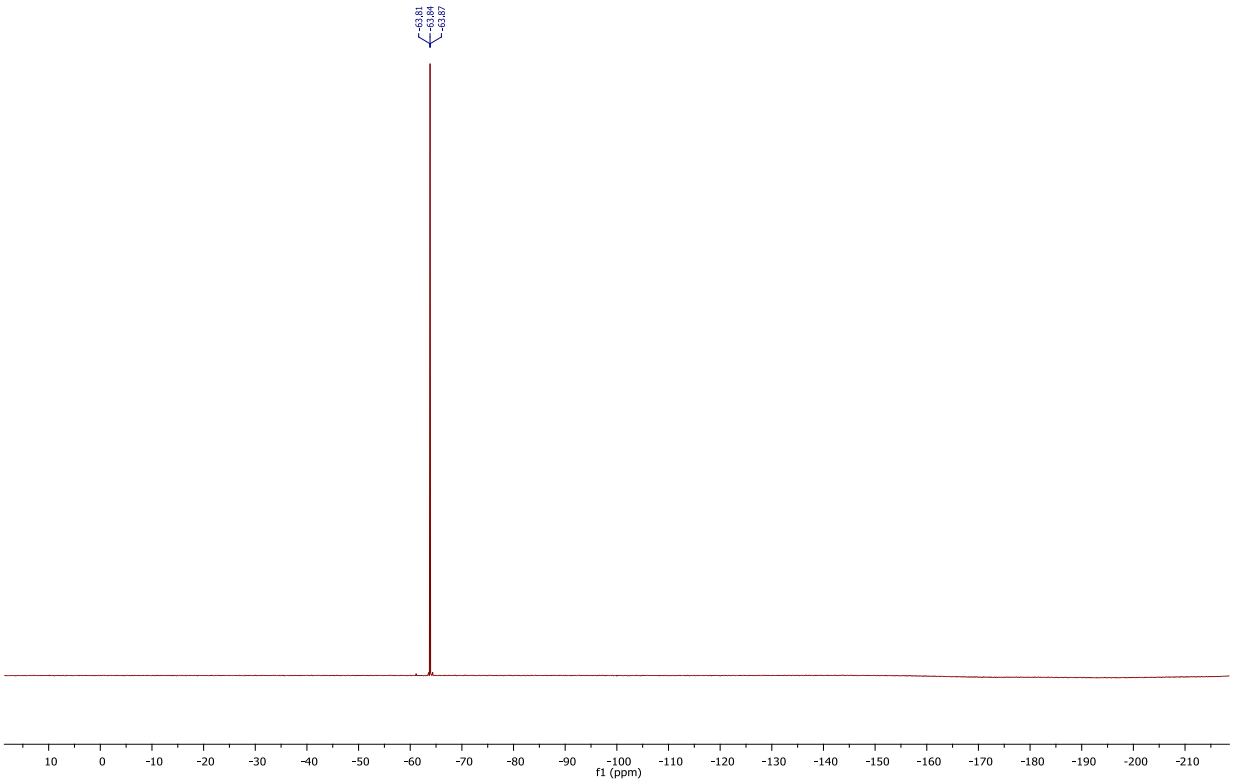
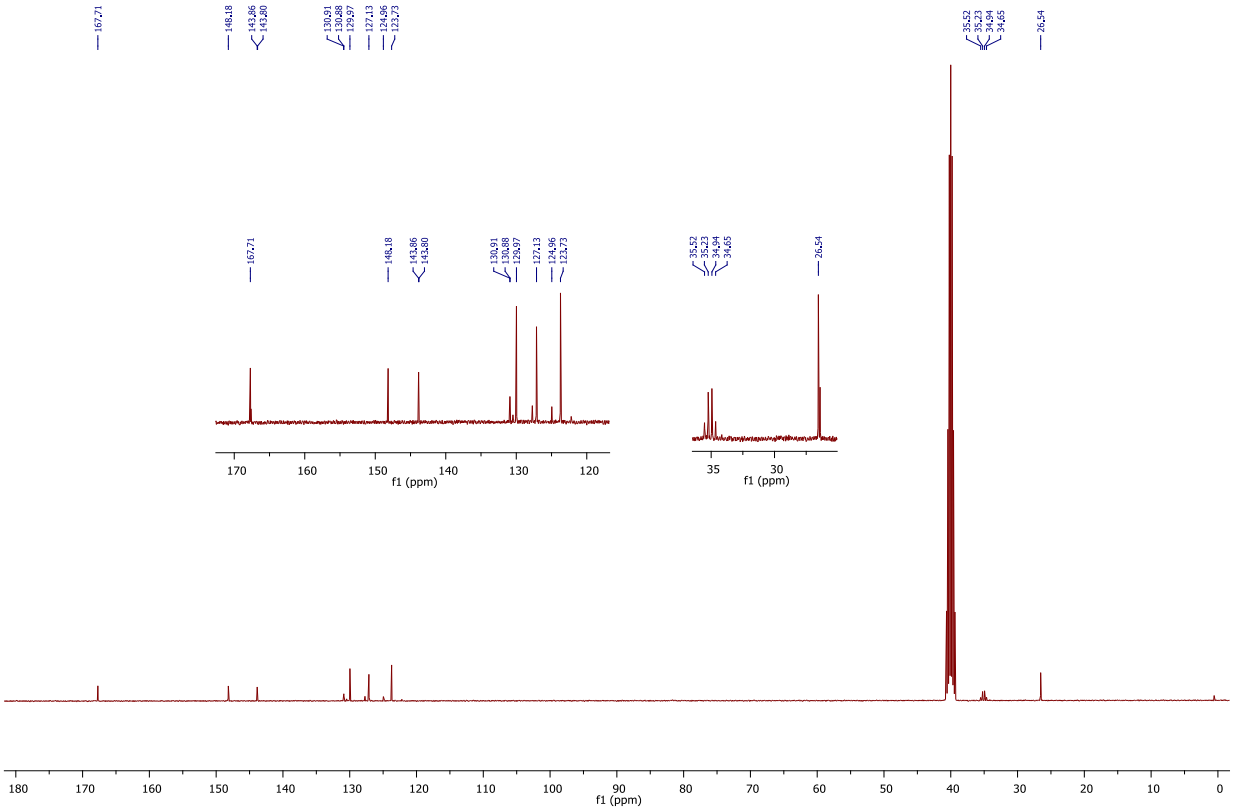
140.83
132.48
132.15
131.82
129.05
126.83
125.27
124.07
121.95
36.68
36.38
36.08
35.78
26.81
f1 (ppm)


Me
NH
O
CF3
NO2
8.71
8.70
8.36
8.31
8.31
8.29
8.29
7.75
7.73
4.16
4.13
4.11
4.08
2.80
2.78
0.69
0.92
0.94
0.93
2.00
2.93
f1 (ppm)


-63.81
-63.84
-63.87
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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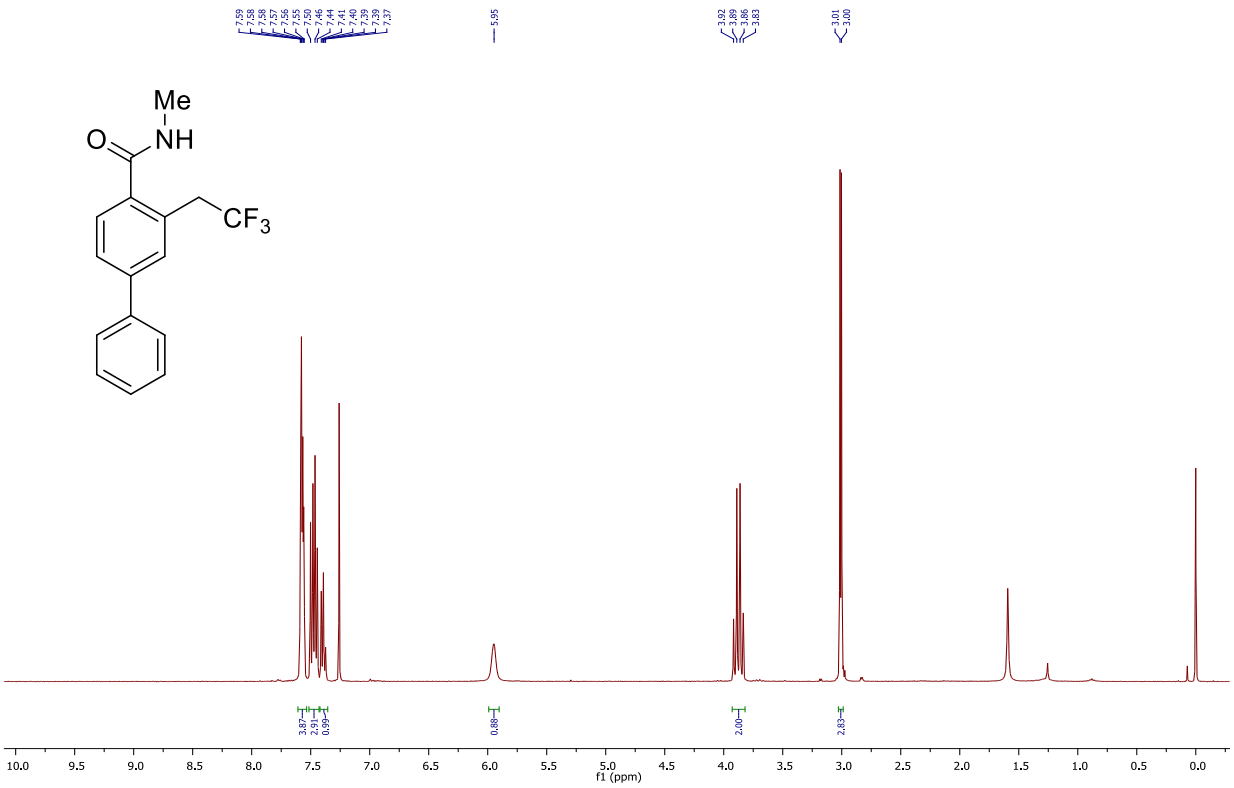
148.18
143.86
143.80
130.91
130.88
129.97
127.13
124.96
123.73
35.52
35.23
34.94
34.65
26.54
170 160 150 140 130 120
f1 (ppm)
35 30
f1 (ppm)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Me
NH
O
CF3
7.59
7.58
7.58
7.57
7.56
7.55
7.50
7.46
7.44
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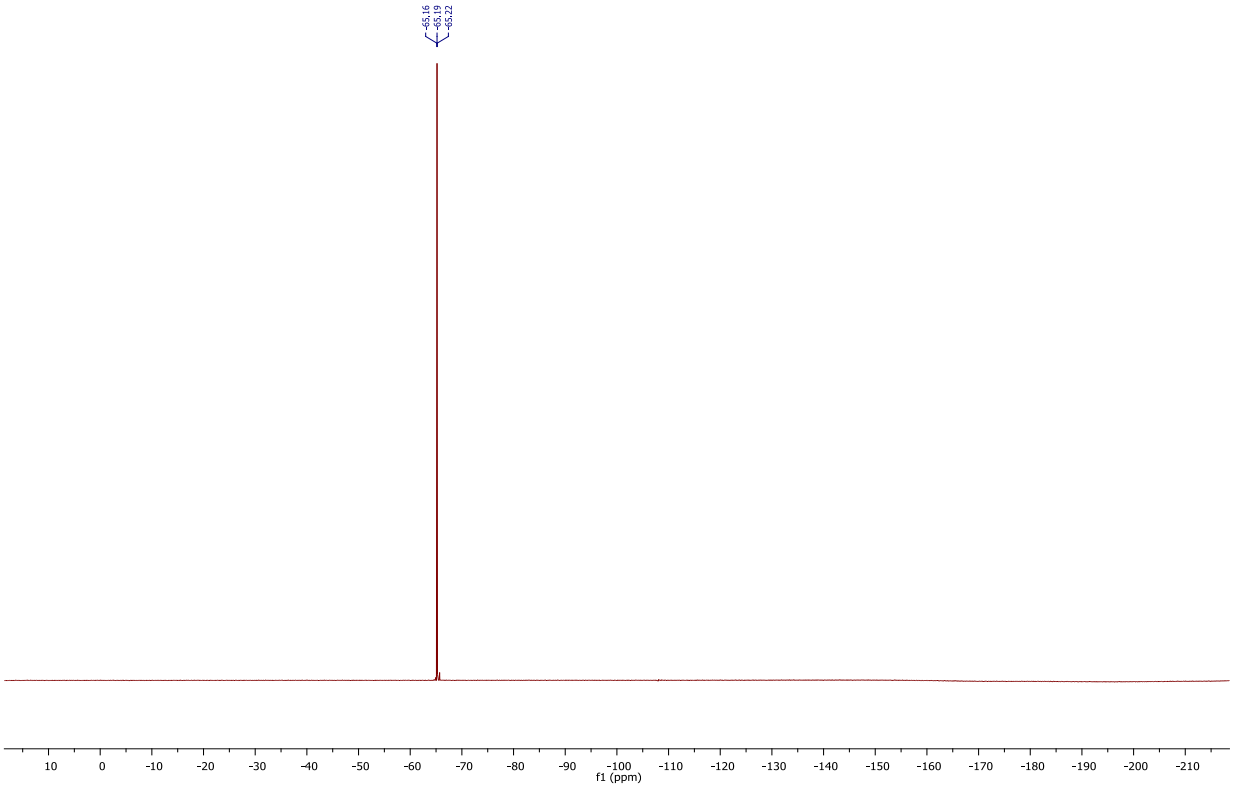
7.40
7.39
7.39
7.37
5.95
3.92
3.89
3.86
3.83
3.01
3.00
3.87
2.91
0.99
0.88
2.00
2.83
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


-65.16
-65.19
-65.22
10
0
-10
-20
-30
-40
-50
-60
-70
-80
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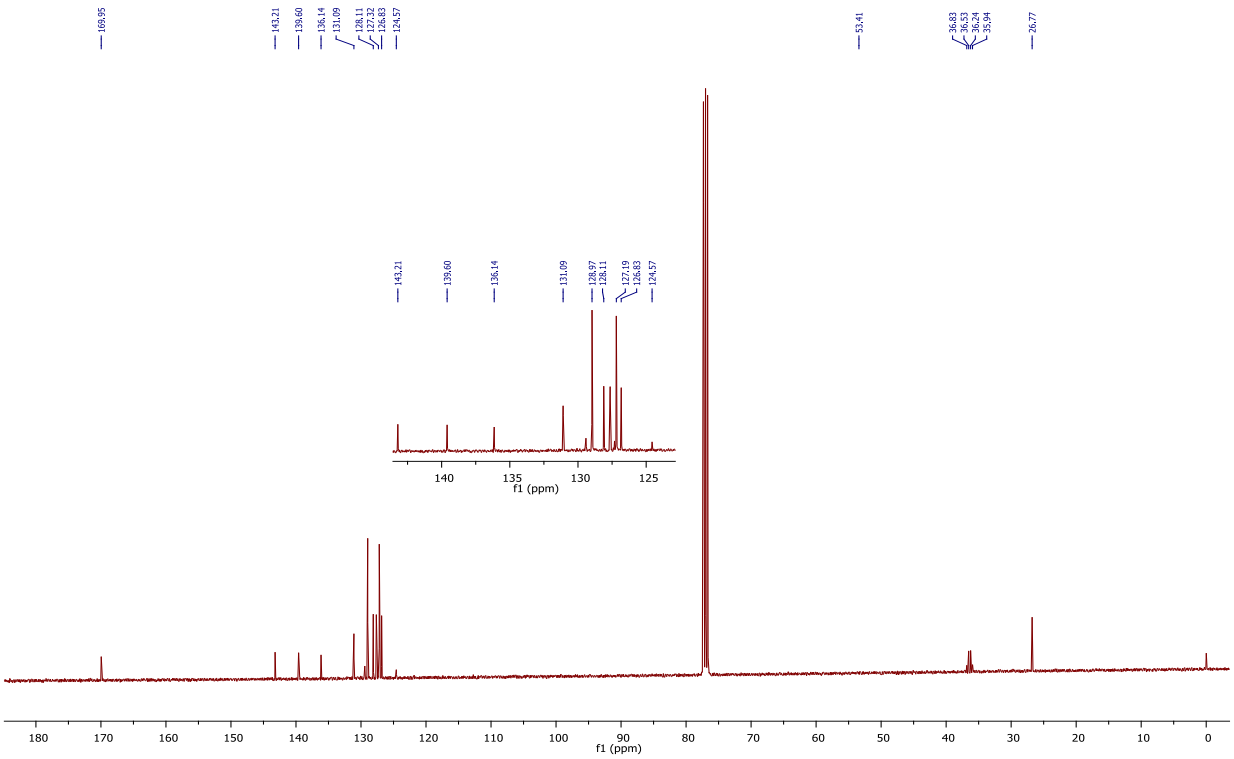
-160
-170
-180
-190
-200
-210
f1 (ppm)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143.21
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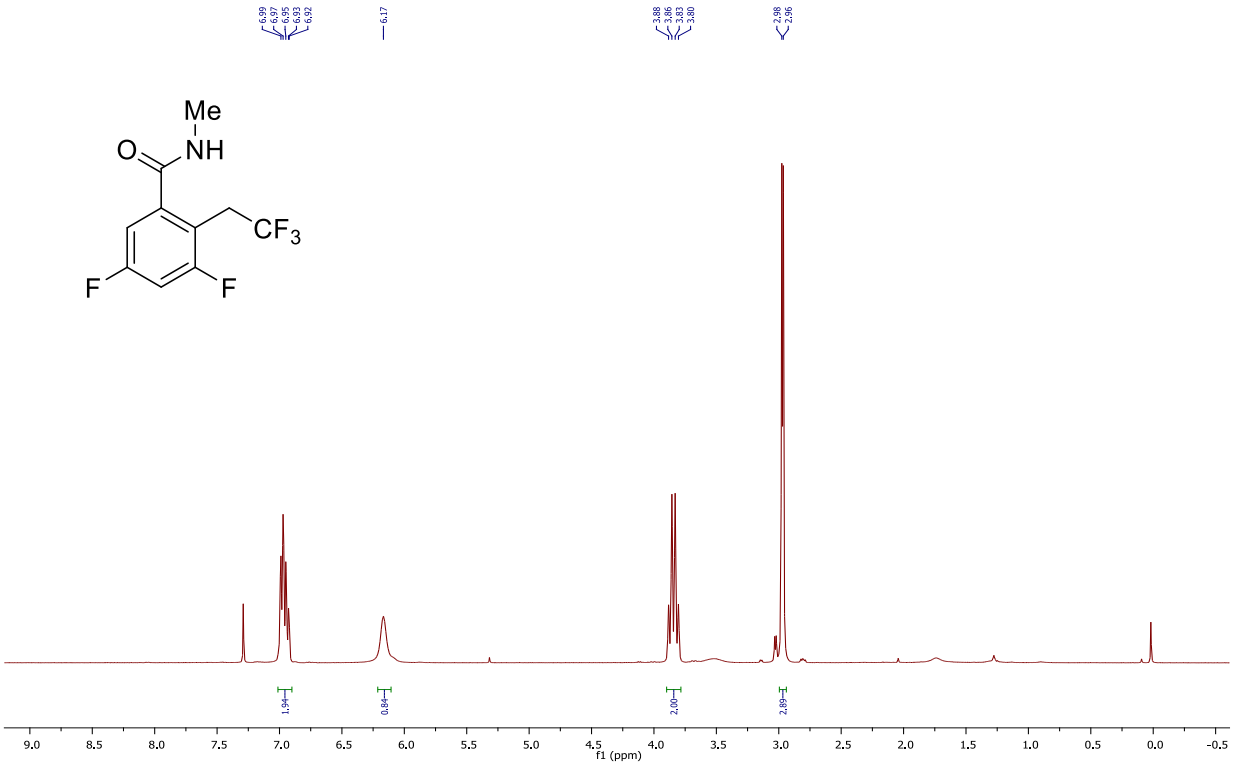
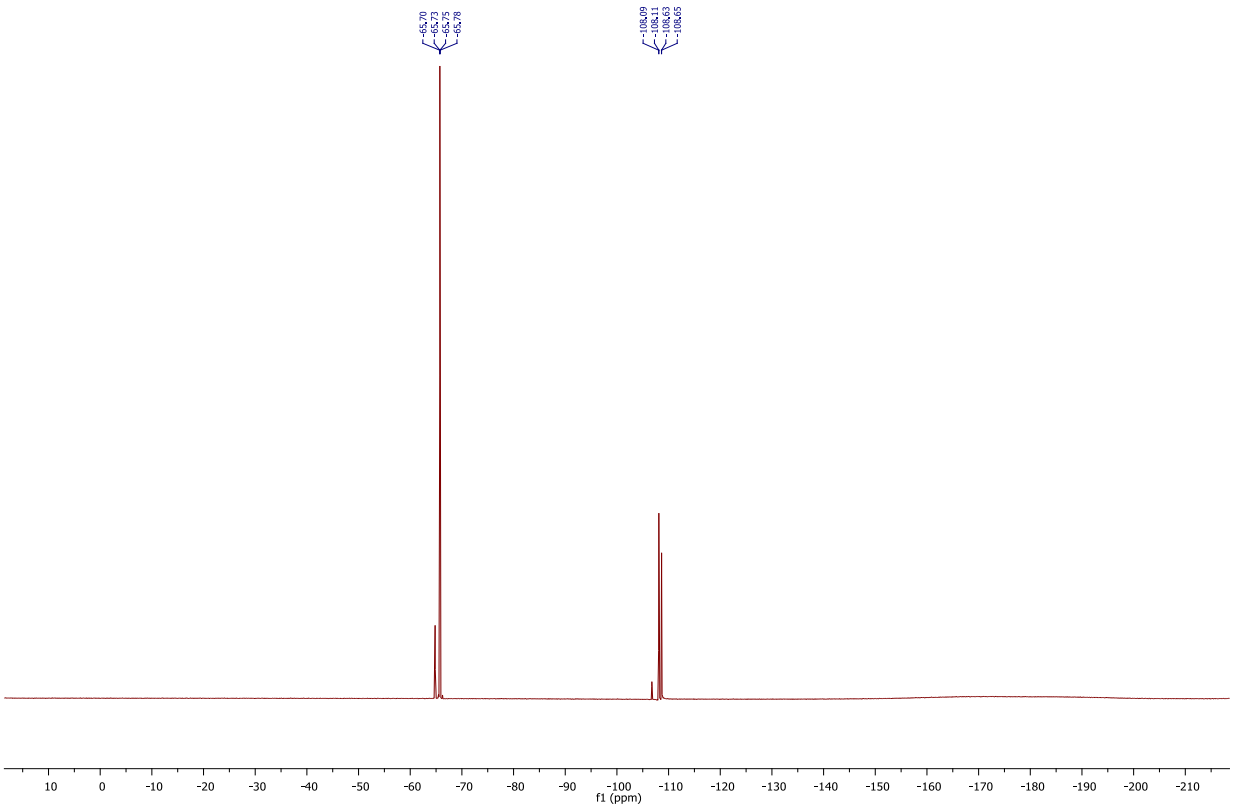
136.14
131.09
128.11
127.32
126.83
124.57
53.41
36.83
36.53
36.24
35.94
26.77
f1 (ppm)


6.99
6.97
6.95
6.93
6.92
6.17
3.88
3.86
3.83
3.80
2.98
2.96
Me
O
NH
CF3
F
F
1.94
0.89
2.00
2.89
f1 (ppm)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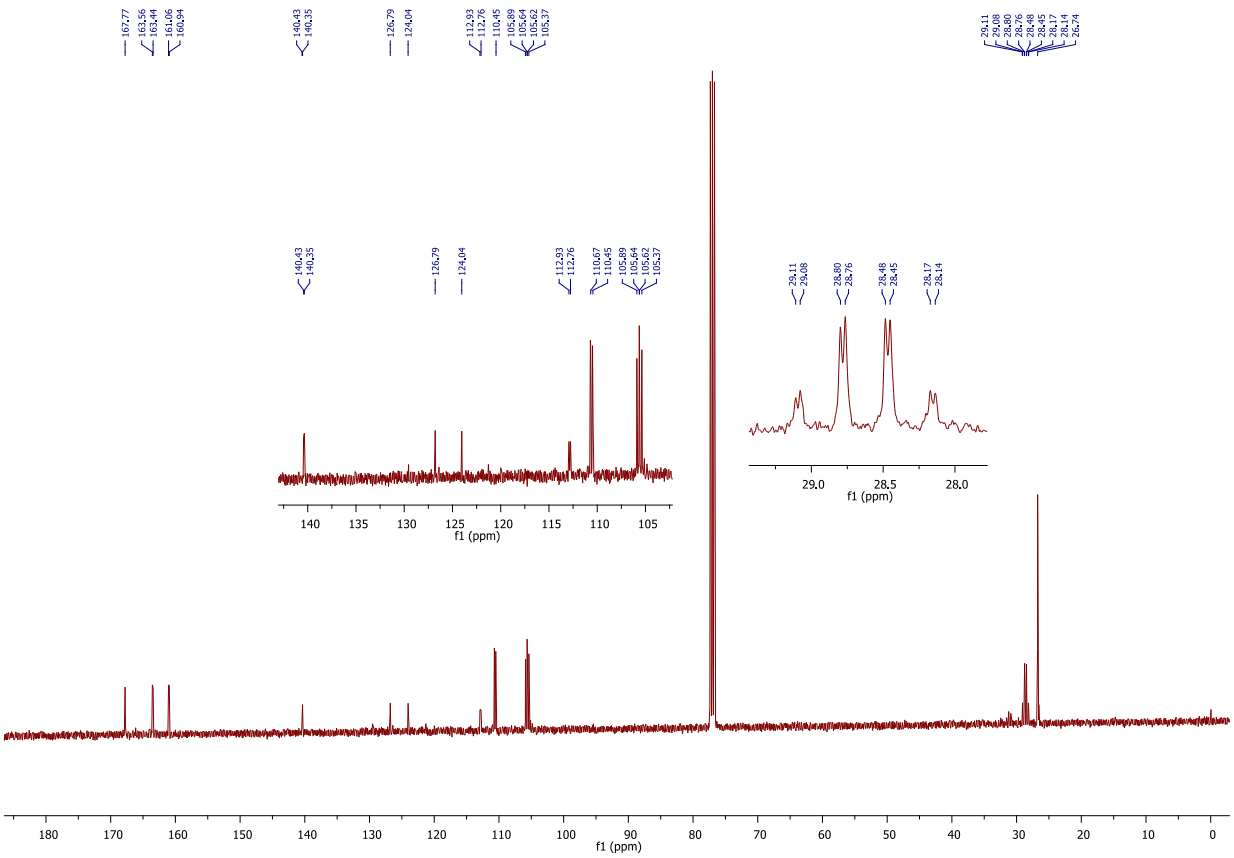
-65.75
-65.78
-108.09
-108.11
-108.63
-108.65
f1 (ppm)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163.56
163.44
161.06
160.94
140.43
140.35
126.79
124.04
112.93
112.76
110.45
105.89
105.64
105.62
105.37
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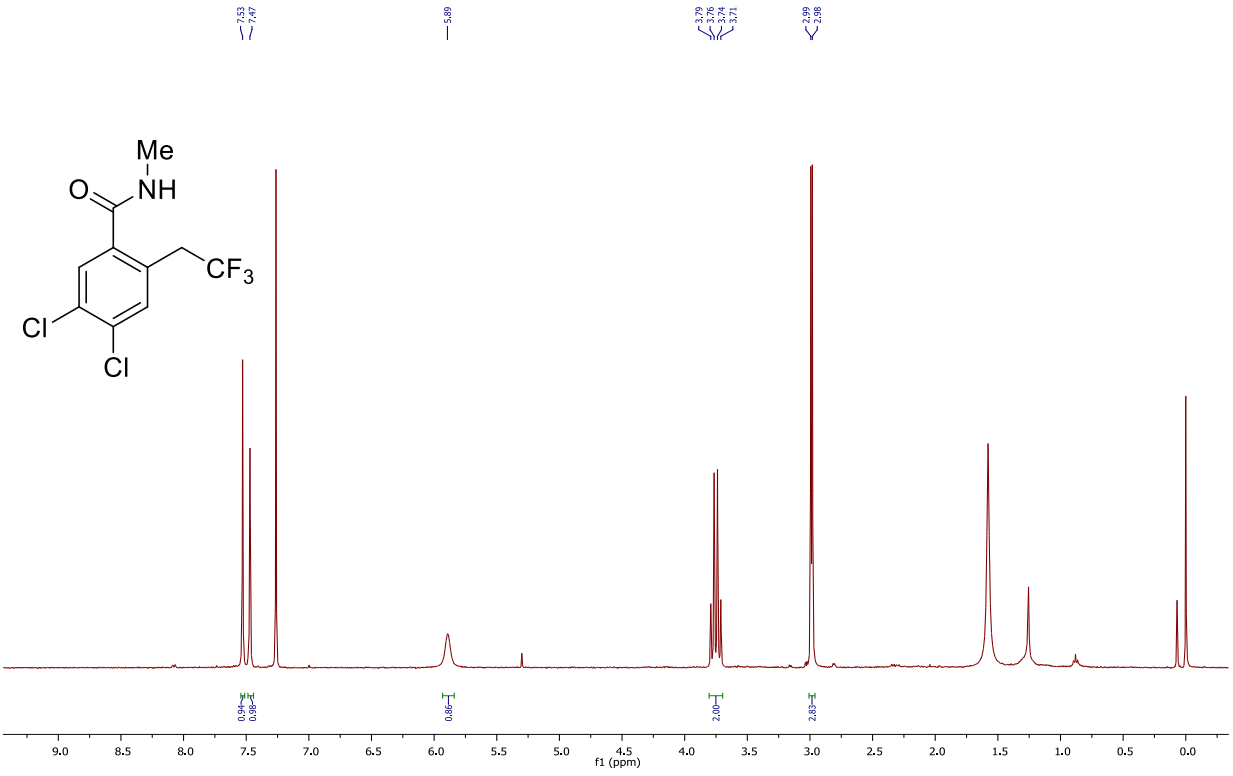
29.08
28.80
28.76
28.48
28.45
28.17
28.14
26.74
f1 (ppm)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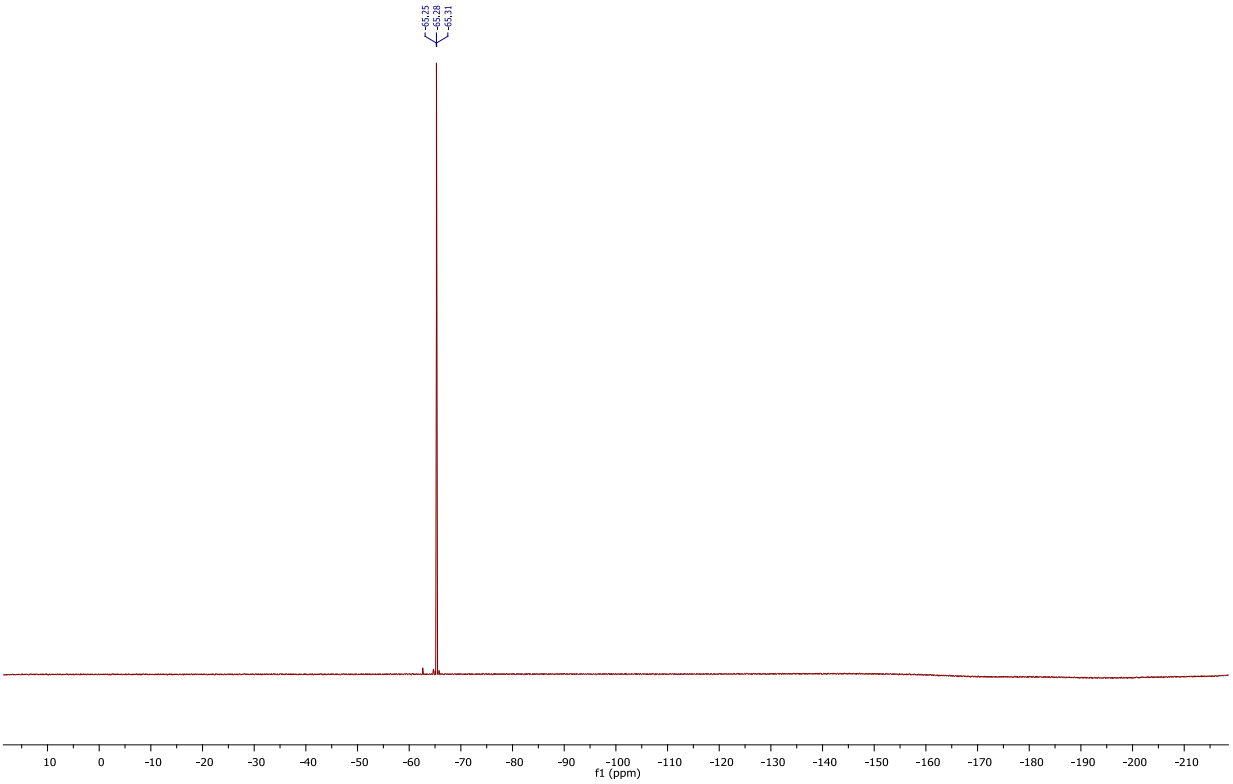
7.47
5.89
3.79
3.76
3.74
3.71
2.99
2.98
Me
NH
O
CF3
Cl
Cl
0.94
0.98
0.86
2.00
2.83
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


-65.25
-65.28
-65.31
10
0
-10
-20
-30
-40
-50
-60
-70
-80
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-120
-130
-140
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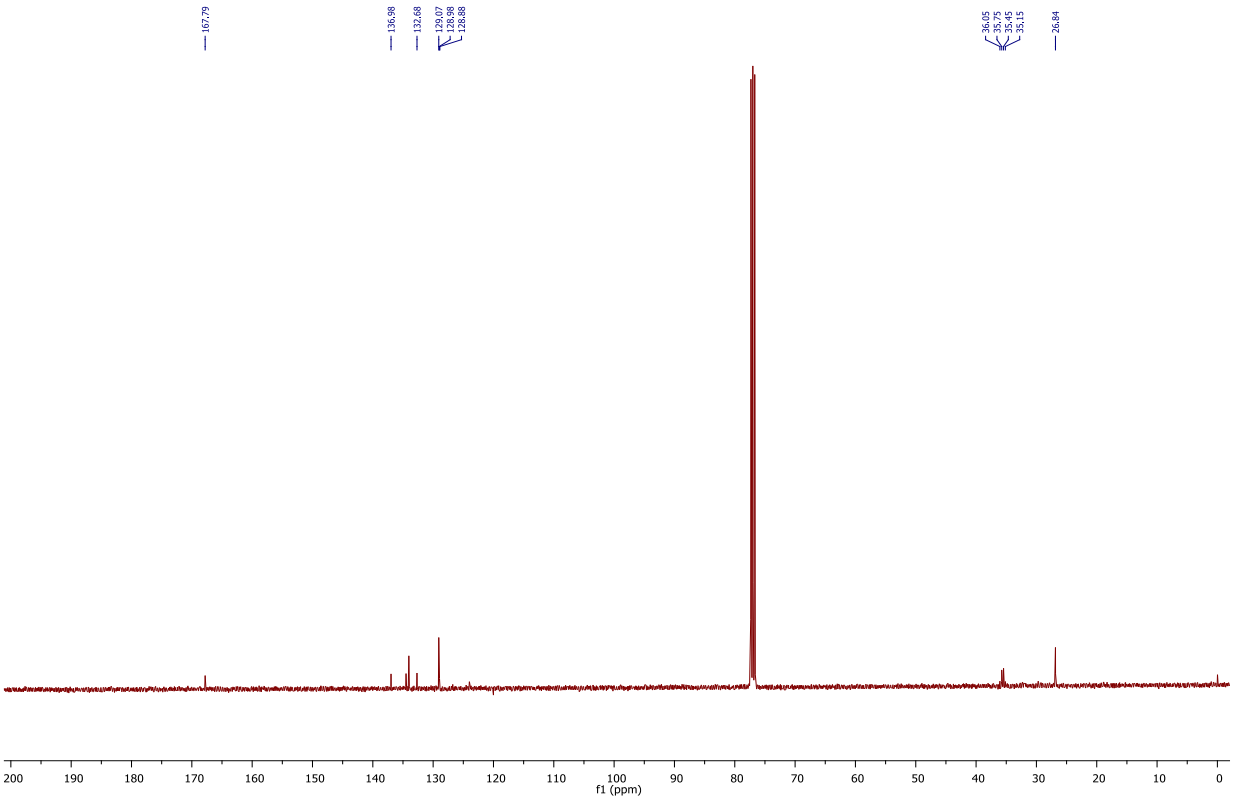
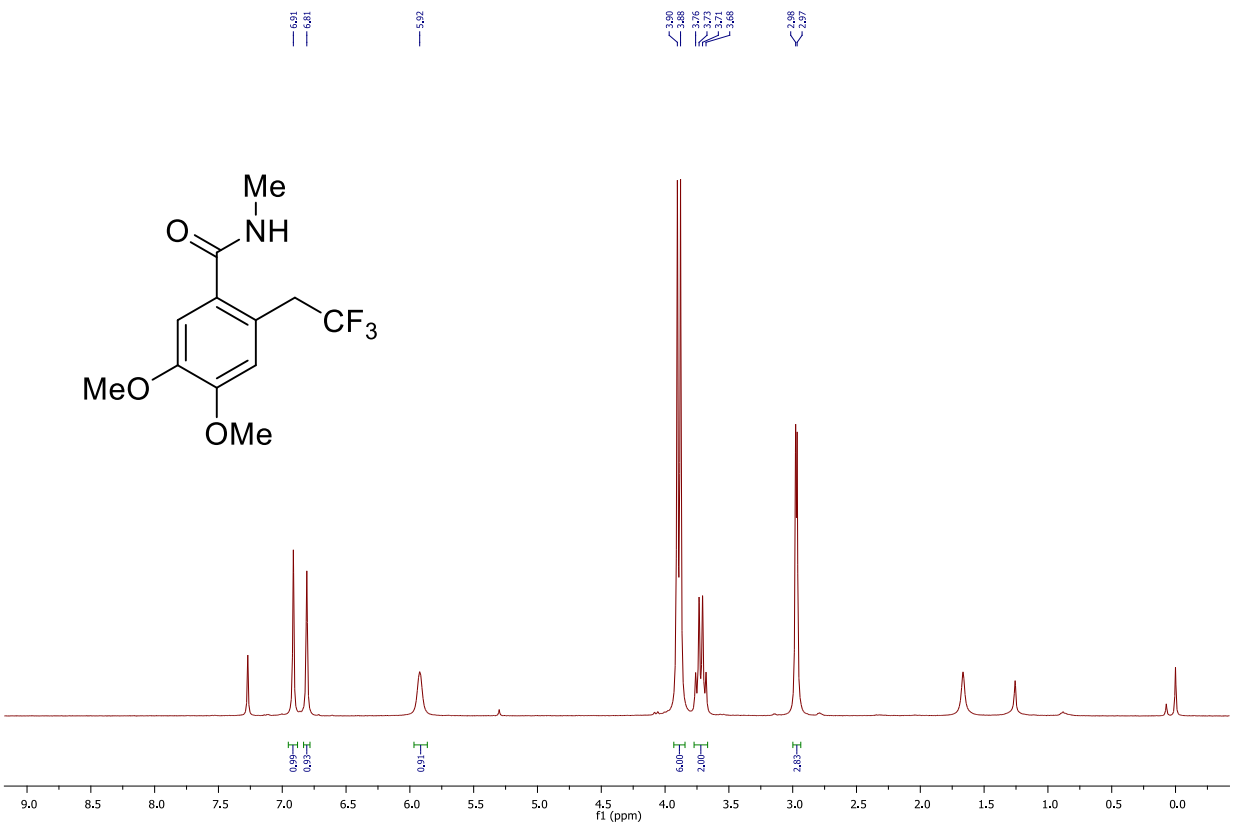
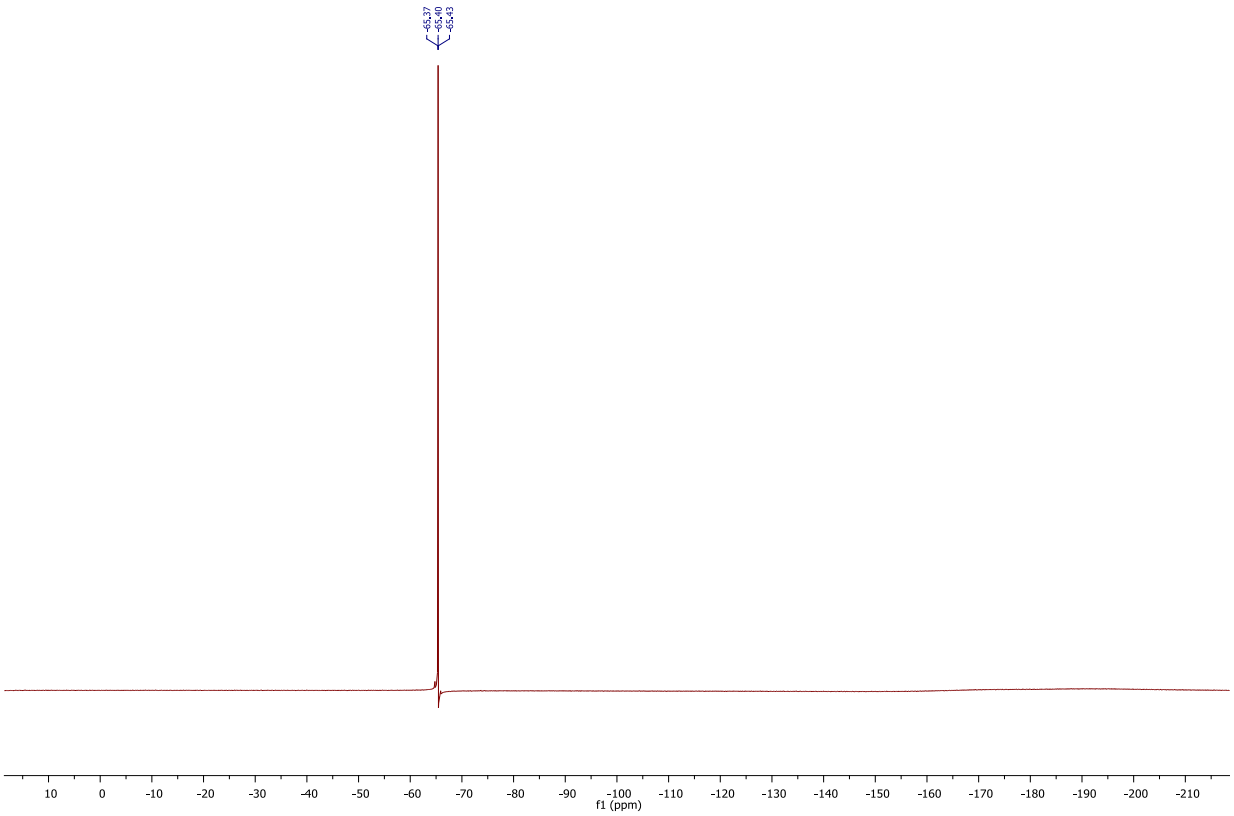
-160
-170
-180
-190
-200
-210
f1 (ppm)


167.79
136.98
132.68
129.07
126.98
126.88
36.05
35.75
35.45
35.15
26.84
f1 (ppm)


6.91
6.81
5.92
3.90
3.88
3.76
3.73
3.71
3.68
2.98
2.97
Me
O
NH
CF3
MeO
OMe
0.99
0.93
0.91
6.00
2.00
2.83
f1 (ppm)


-65,37
-65,40
-65,43
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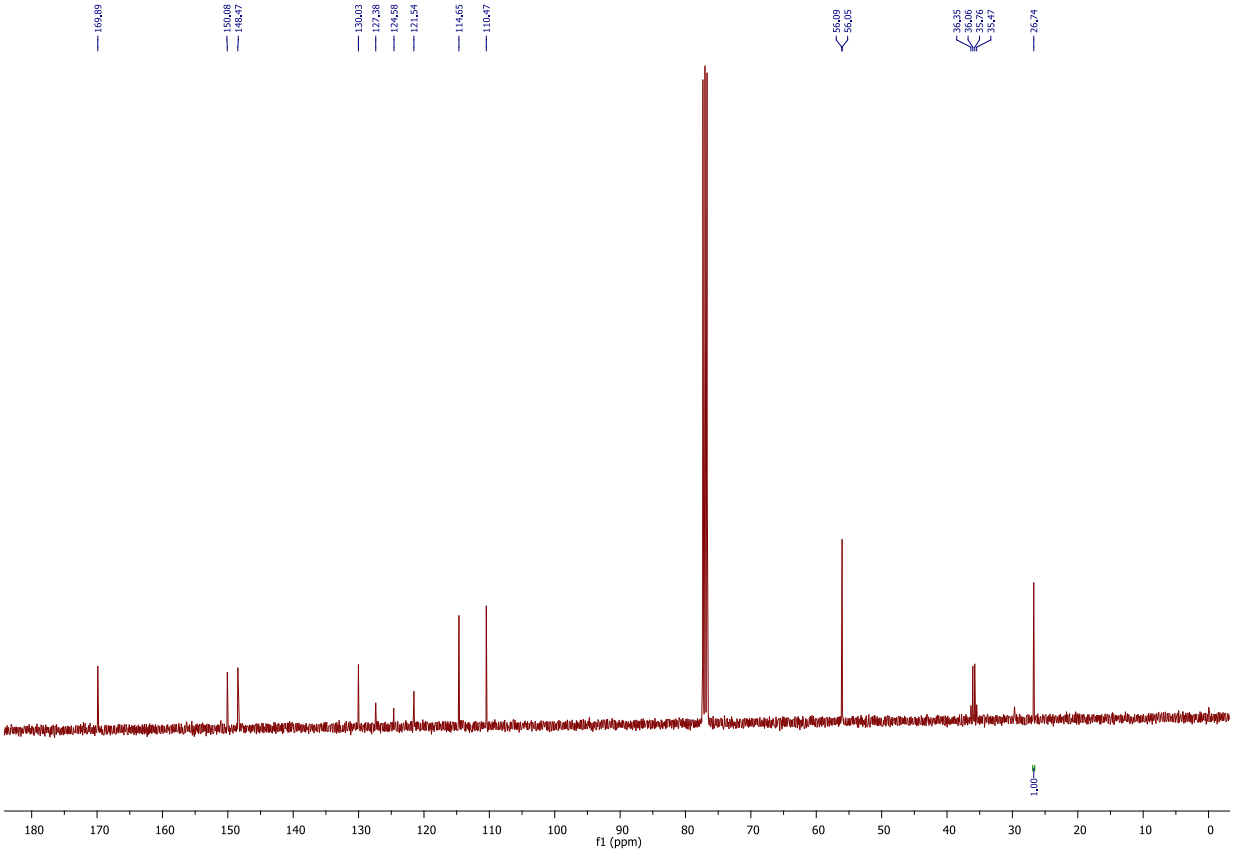
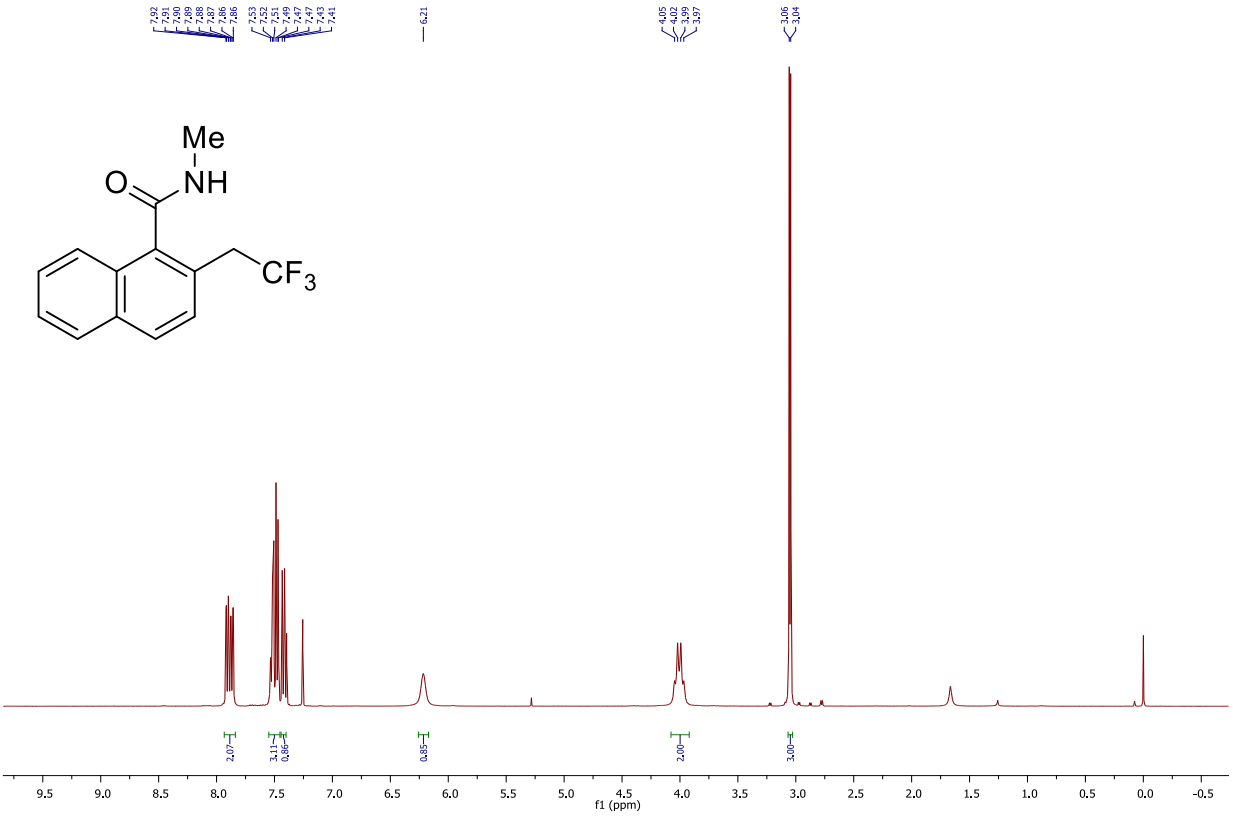
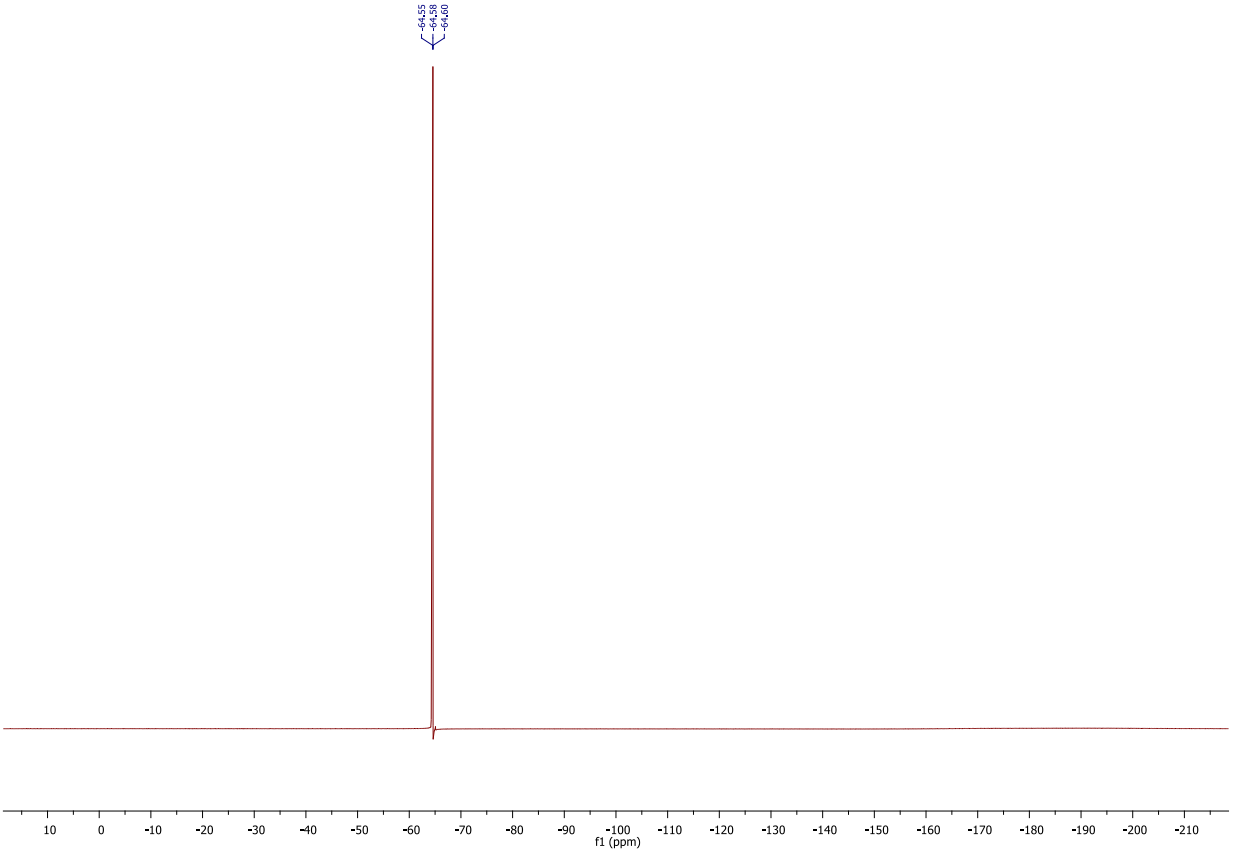
f1 (ppm)


169,89
150,08
148,47
130,03
127,38
124,58
121,54
114,65
110,47
56,09
56,05
36,35
36,06
35,76
35,47
26,74
1,00
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.92
7.91
7.90
7.89
7.88
7.87
7.86
7.86
7.53
7.52
7.51
7.49
7.47
7.47
7.43
7.41
6.21
4.05
4.02
3.99
3.97
3.06
3.04
Me
O
NH
CF3
2.07
3.11
0.86
0.85
2.00
3.00
f1 (ppm)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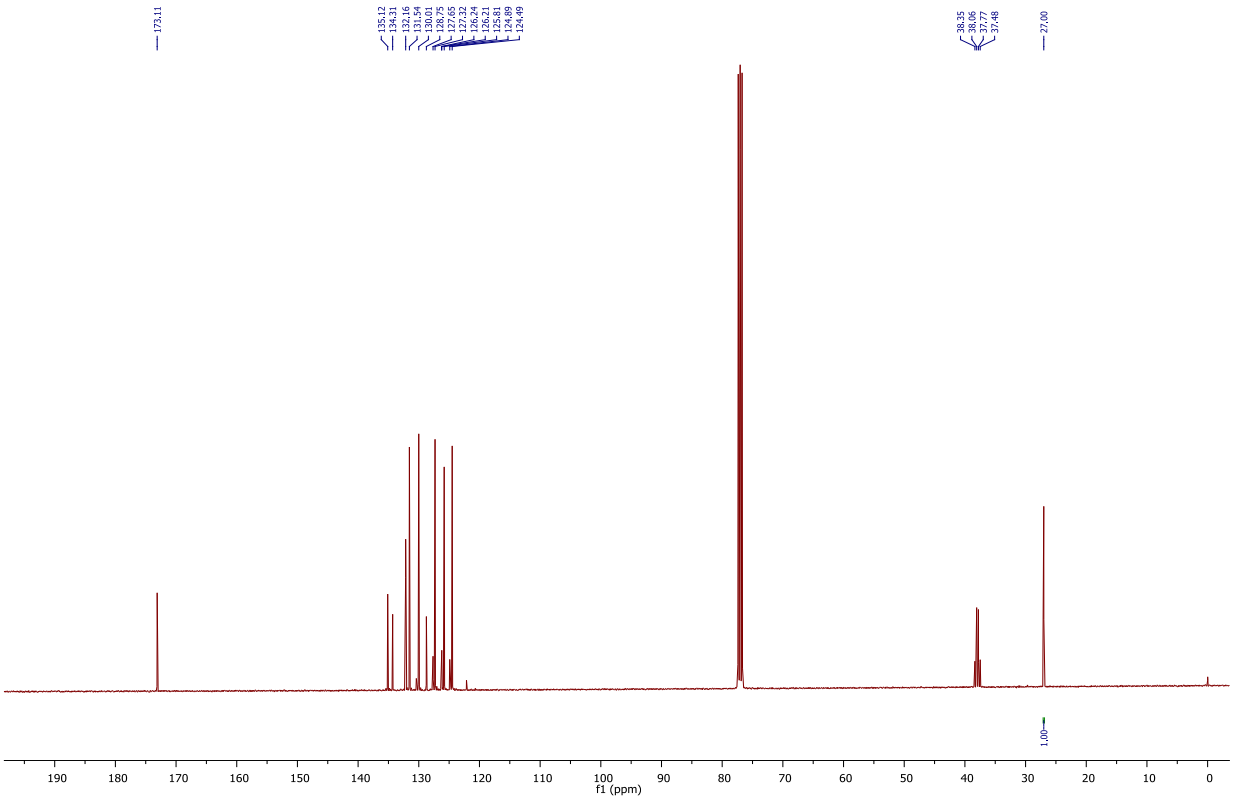
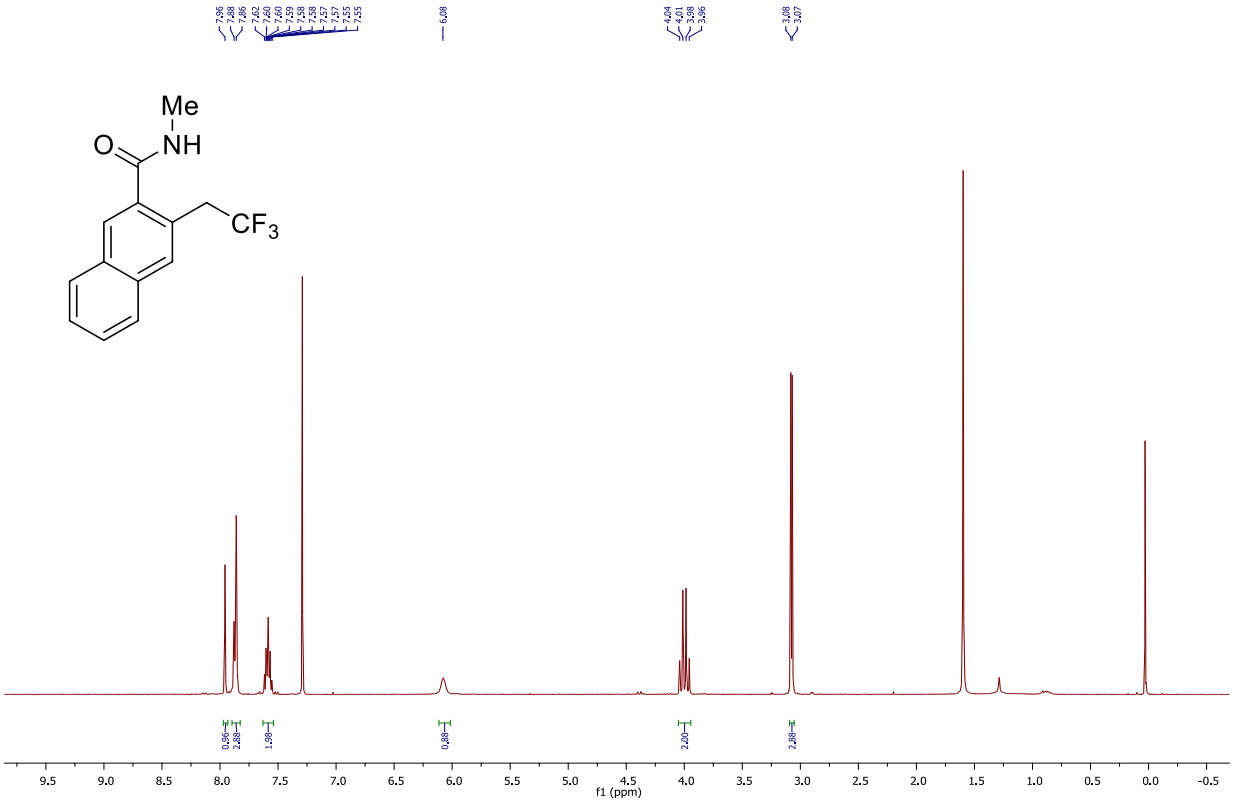
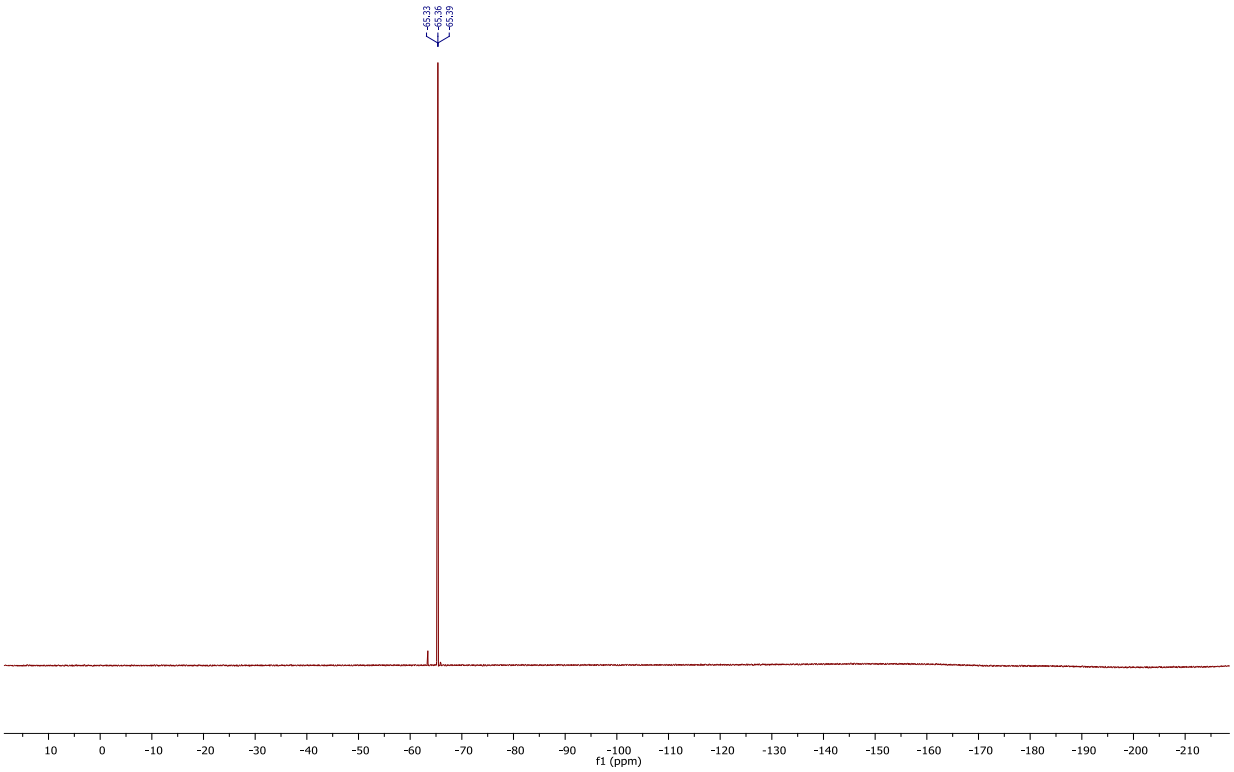
-64.58
-64.60
f1 (ppm)


173.11
135.12
134.31
132.16
131.54
130.01
128.75
127.65
127.32
126.24
125.71
125.81
124.89
124.49
38.35
38.06
37.77
37.48
27.00
1.00
f1 (ppm)


7.96
7.88
7.86
7.62
7.60
7.60
7.59
7.58
7.58
7.57
7.57
7.55
7.55
6.08
4.04
4.01
3.98
3.96
3.08
3.07
Me
NH
O
CF3
0.56
2.88
1.98
0.88
2.00
2.88
f1 (ppm)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-65.36
-65.39
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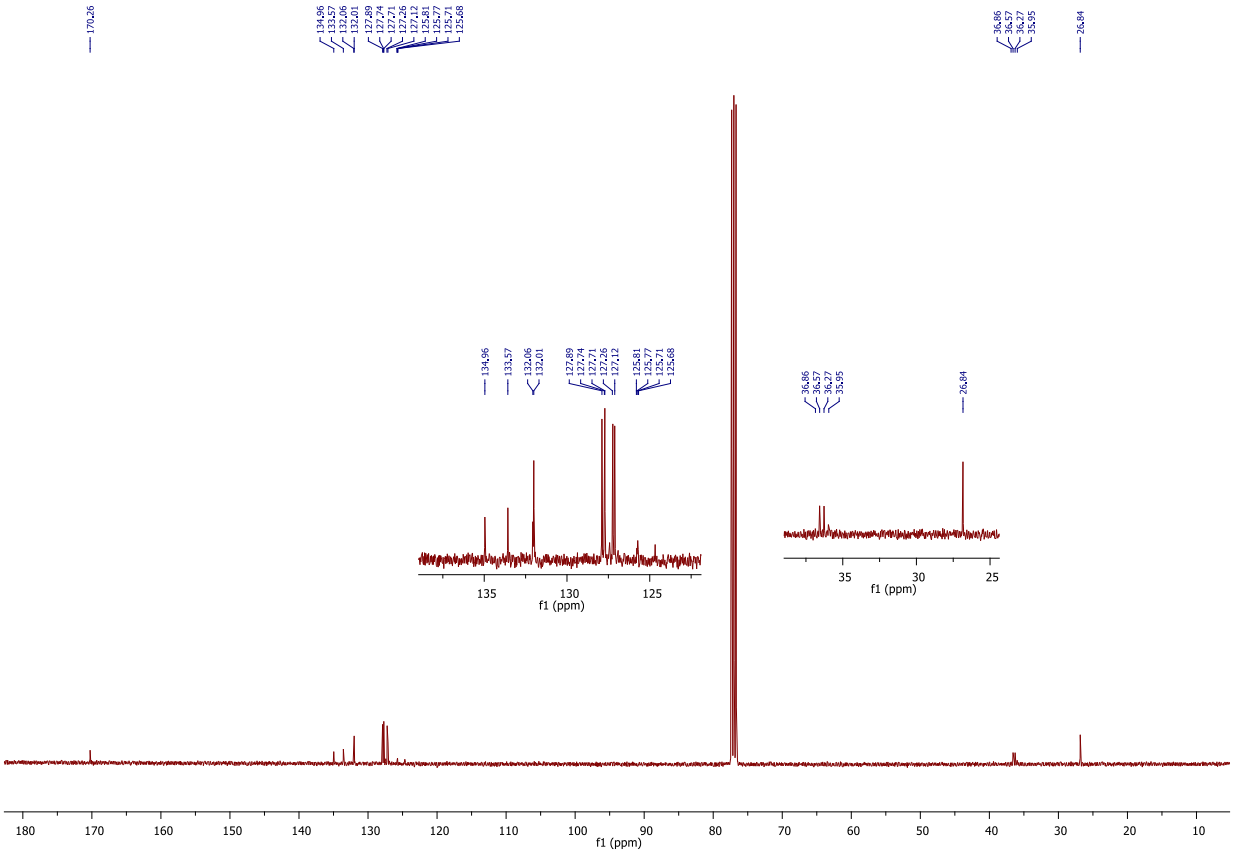
f1 (ppm)


170.26
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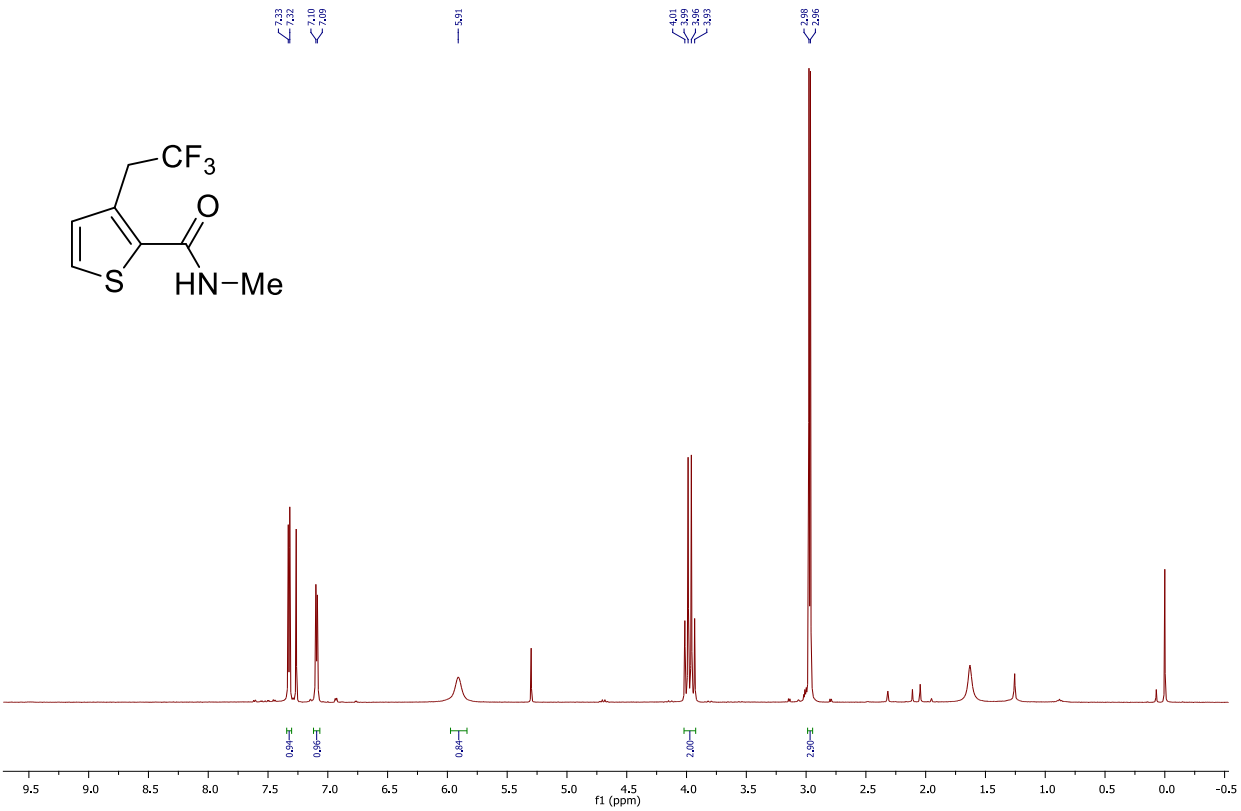
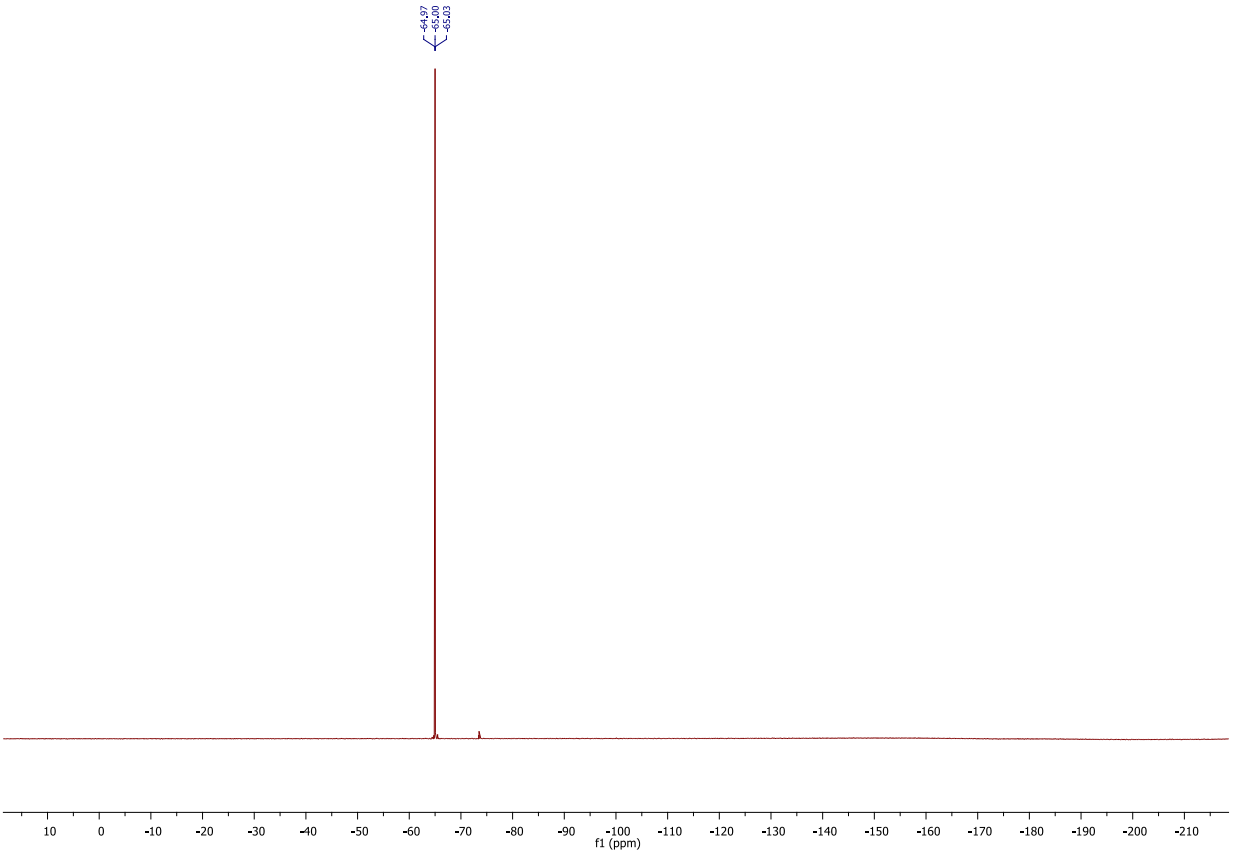
133.57
132.06
132.01
127.89
127.74
127.71
127.26
127.12
125.81
125.77
125.71
125.68
36.86
36.57
36.27
35.95
26.84
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)
135 130 125
f1 (ppm)
35 30 25
f1 (ppm)


7.33
7.32
7.10
7.09
5.91
4.01
3.99
3.95
3.93
2.98
2.96
CF3
O
S
HN−Me
0.94
0.96
0.84
2.00
2.90
f1 (ppm)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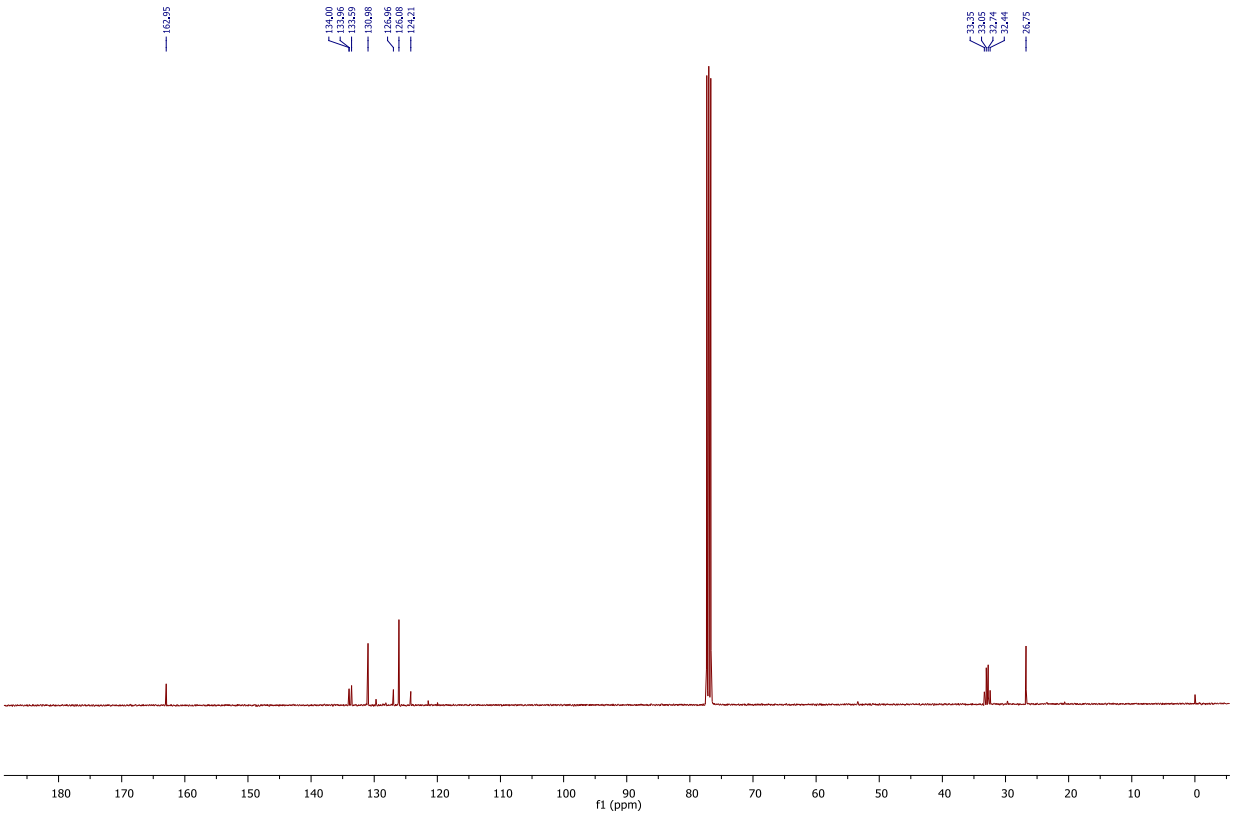
-65.03
f1 (ppm)


162.95
134.00
133.96
133.59
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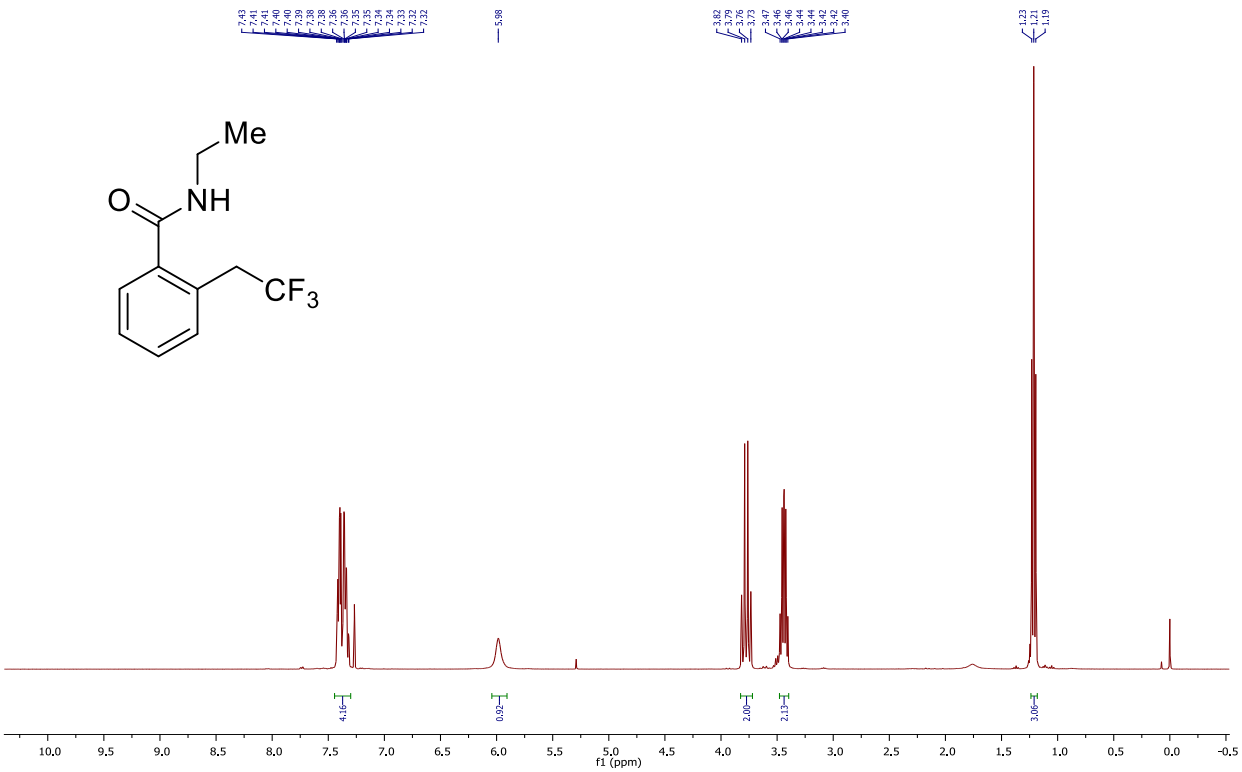
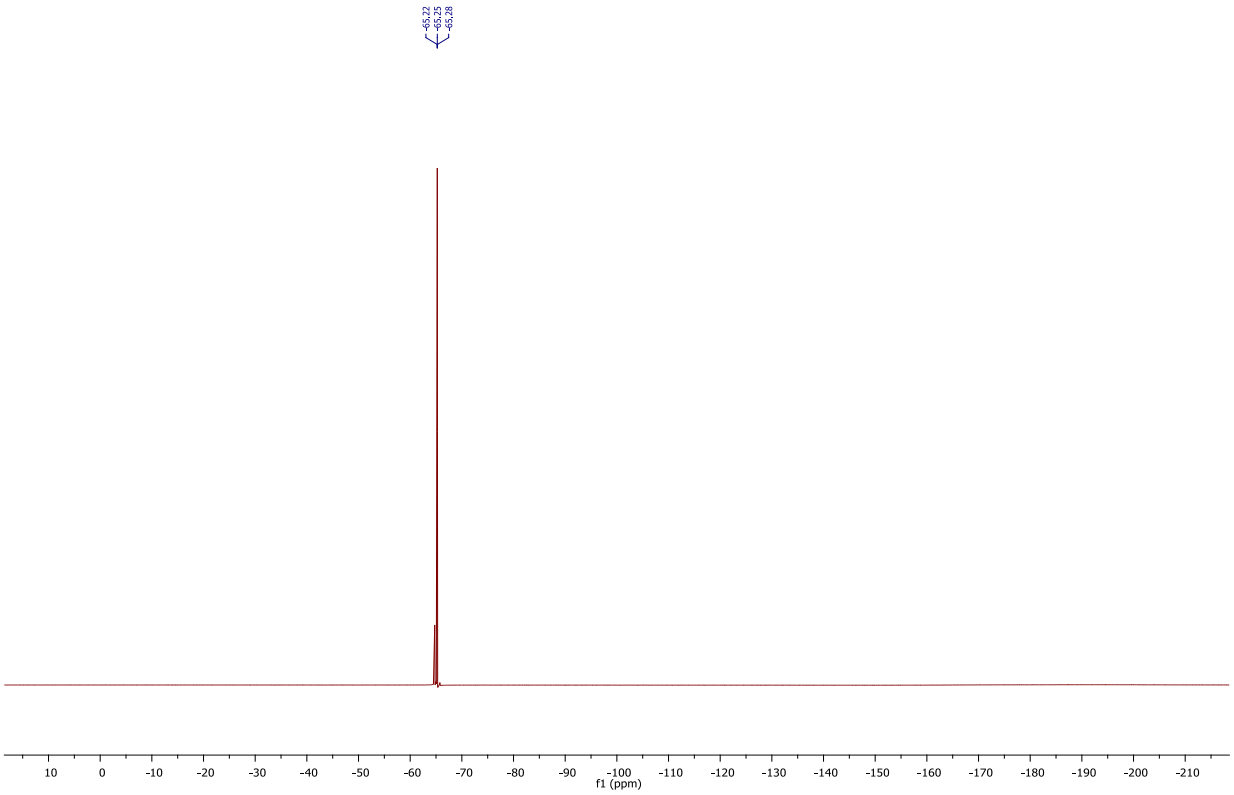
126.06
126.08
124.21
33.35
33.05
32.74
32.44
26.75
f1 (ppm)


Me
O
NH
CF3
f1 (ppm)


-65,22
-65,25
-65,28
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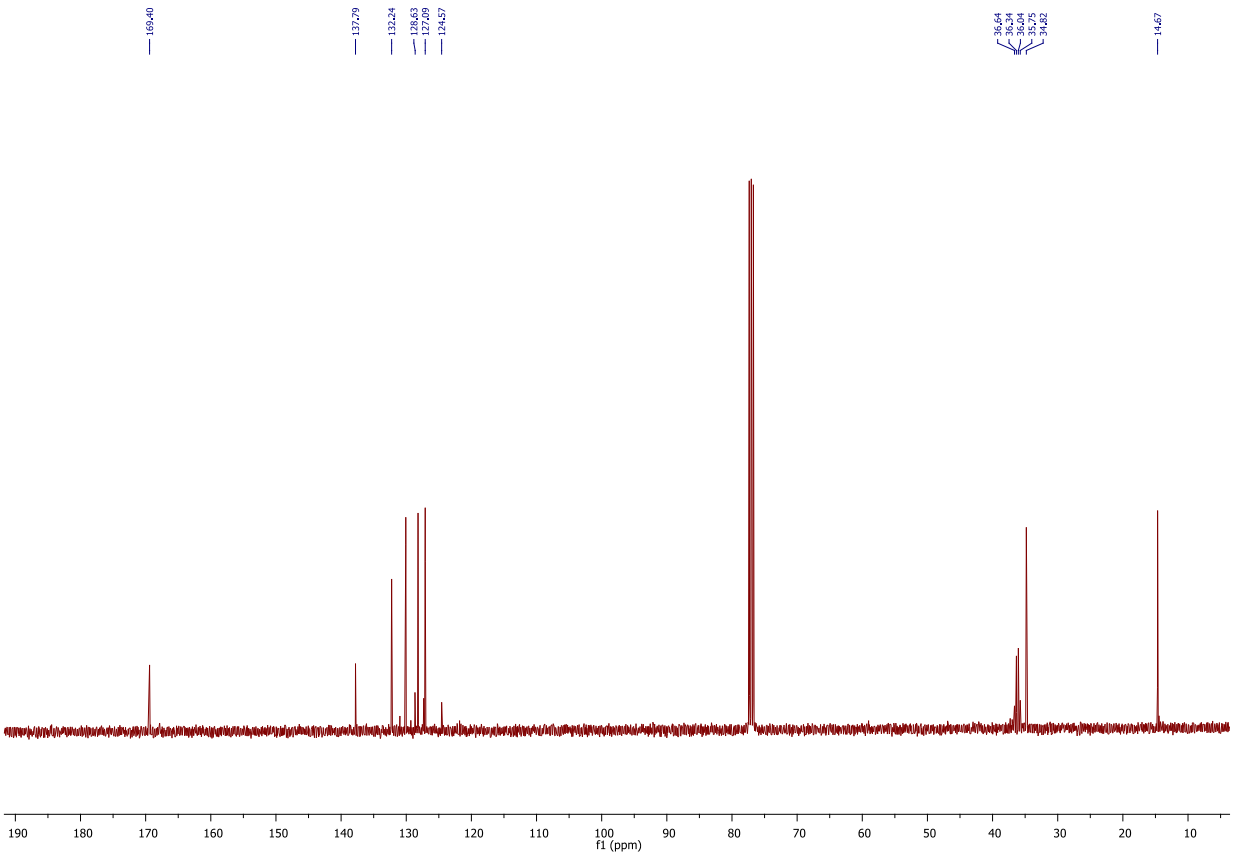
f1 (ppm)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137,79
132,24
128,63
127,09
124,57
36,64
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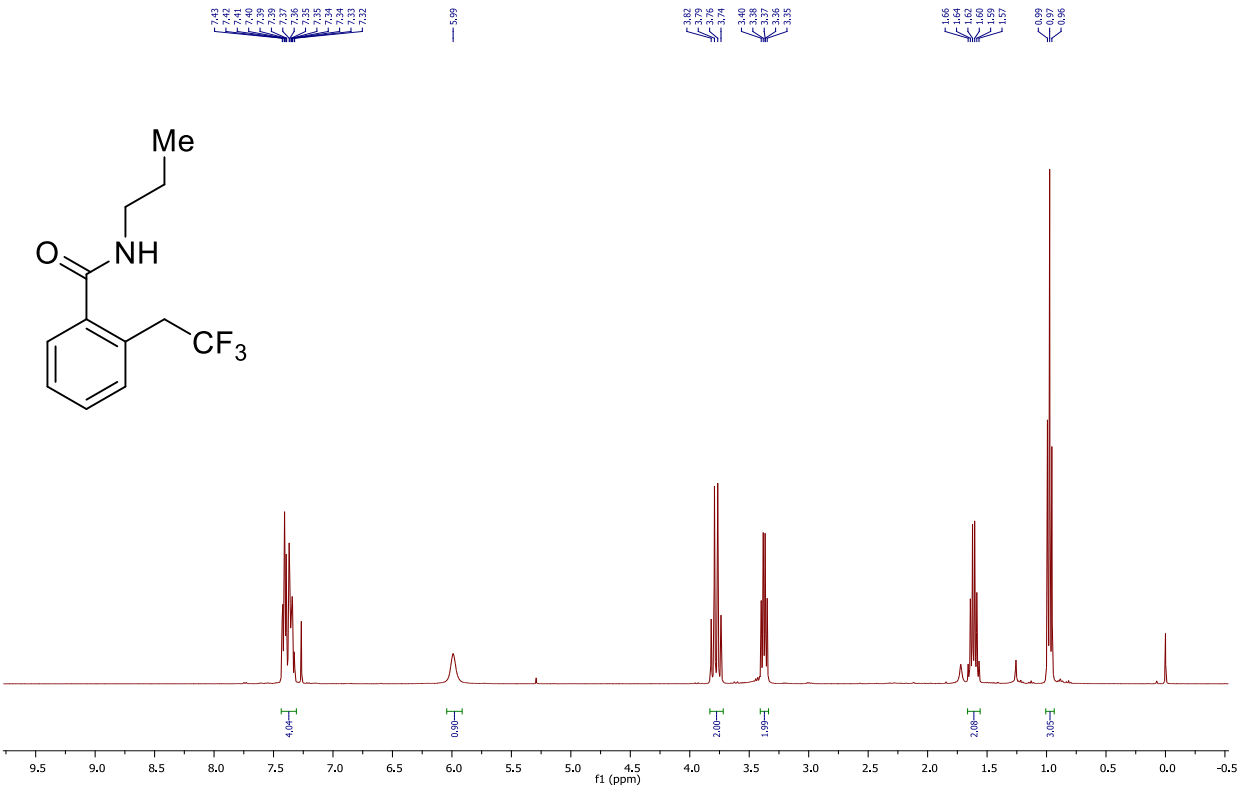
36,04
35,75
34,82
14,67
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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7.41
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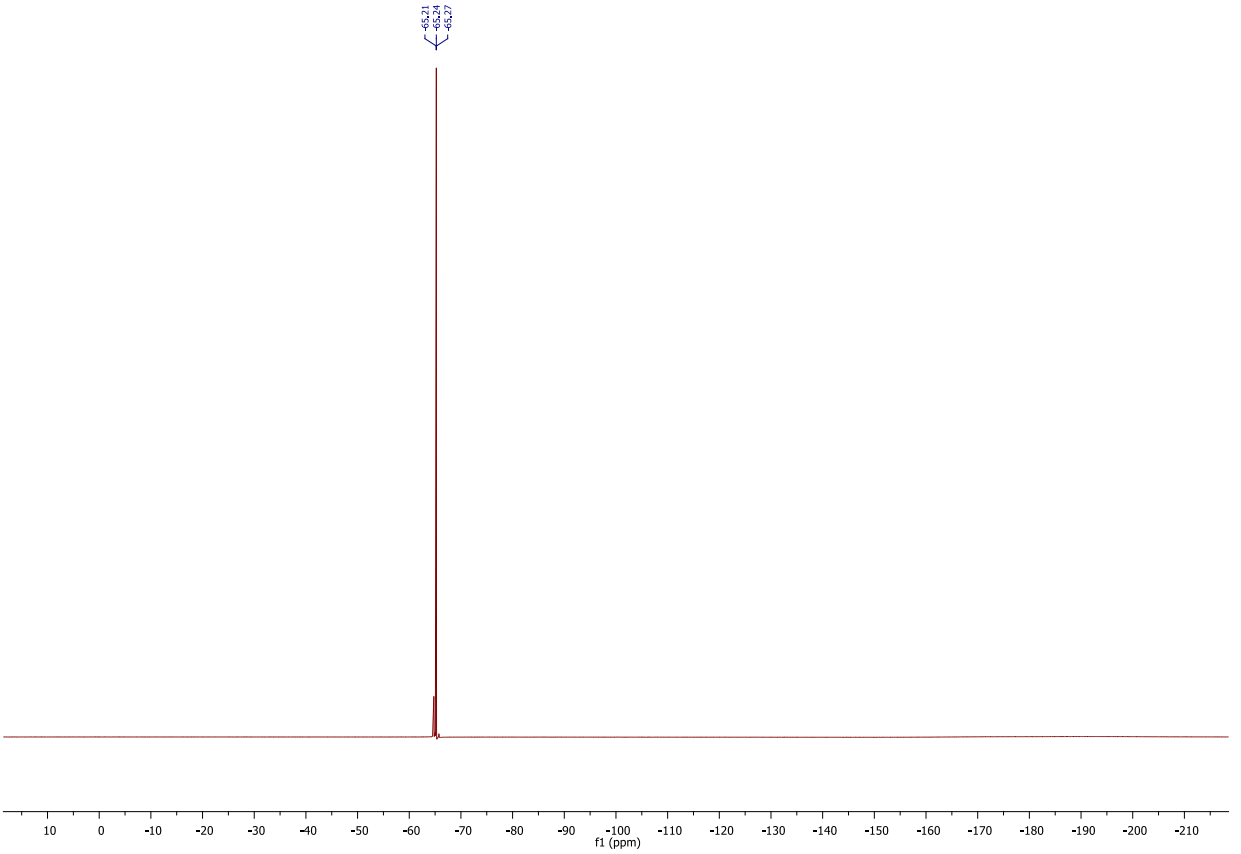
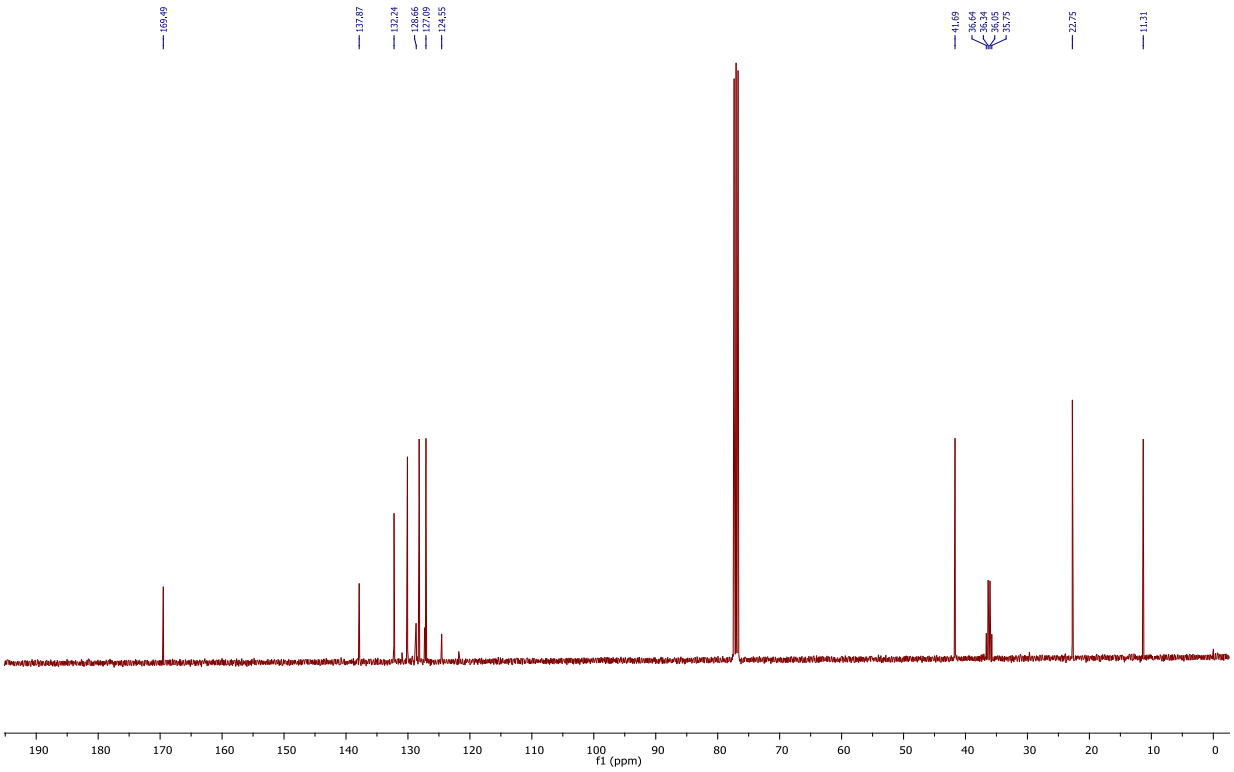
7.39
7.37
7.36
7.35
7.35
7.34
7.34
7.33
7.32
5.99
3.82
3.79
3.76
3.74
3.40
3.38
3.37
3.36
3.35
1.66
1.64
1.62
1.60
1.59
1.57
0.99
0.97
0.96
Me
O
NH
CF3
4.04
0.90
2.00
1.99
2.08
3.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


-65.21
-65.24
-65.27
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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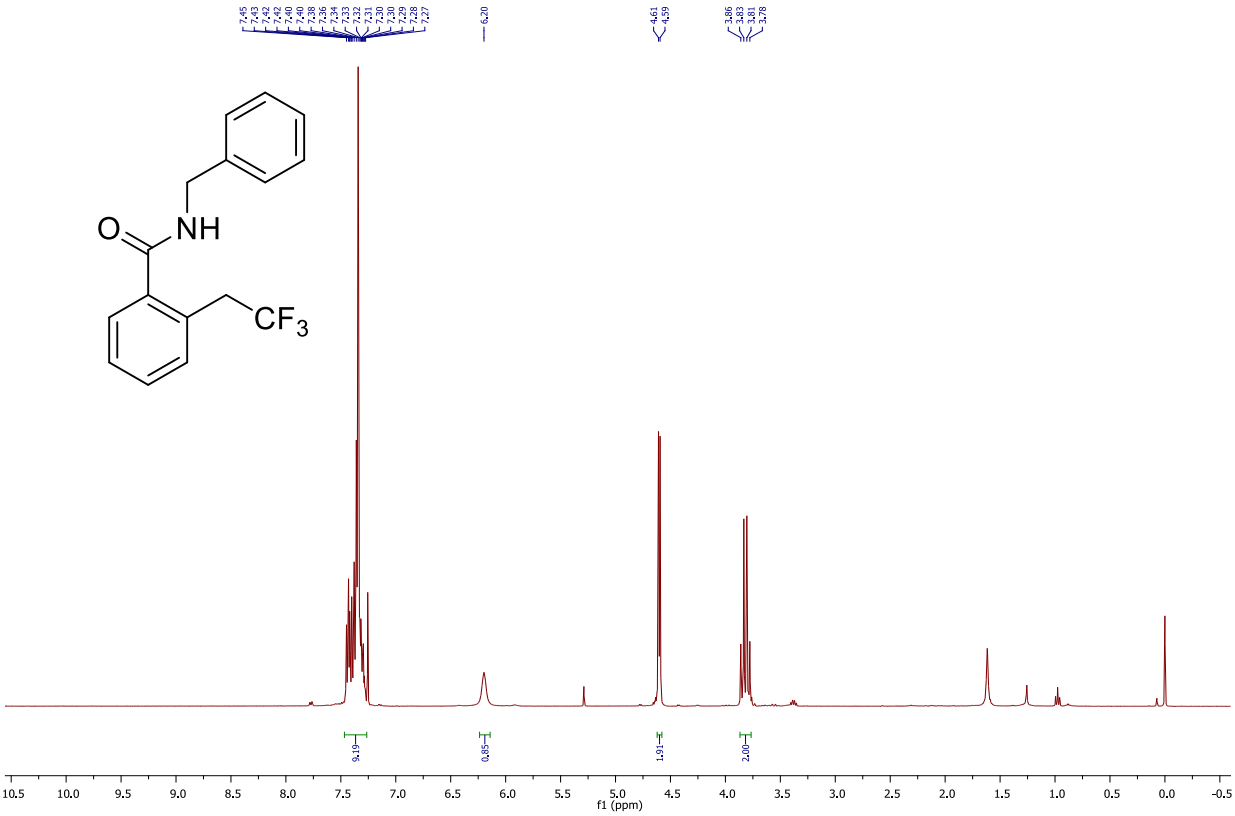
36.34
36.05
35.75
22.75
11.31
f1 (ppm)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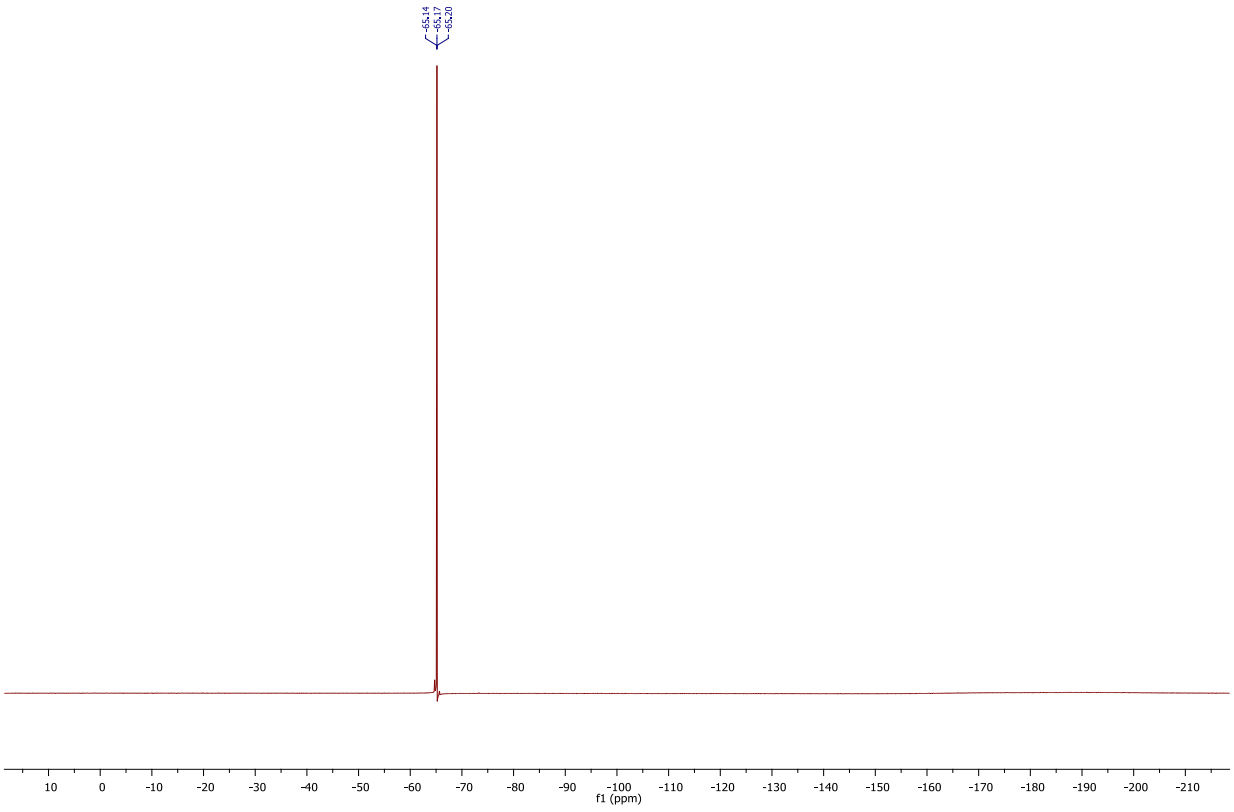
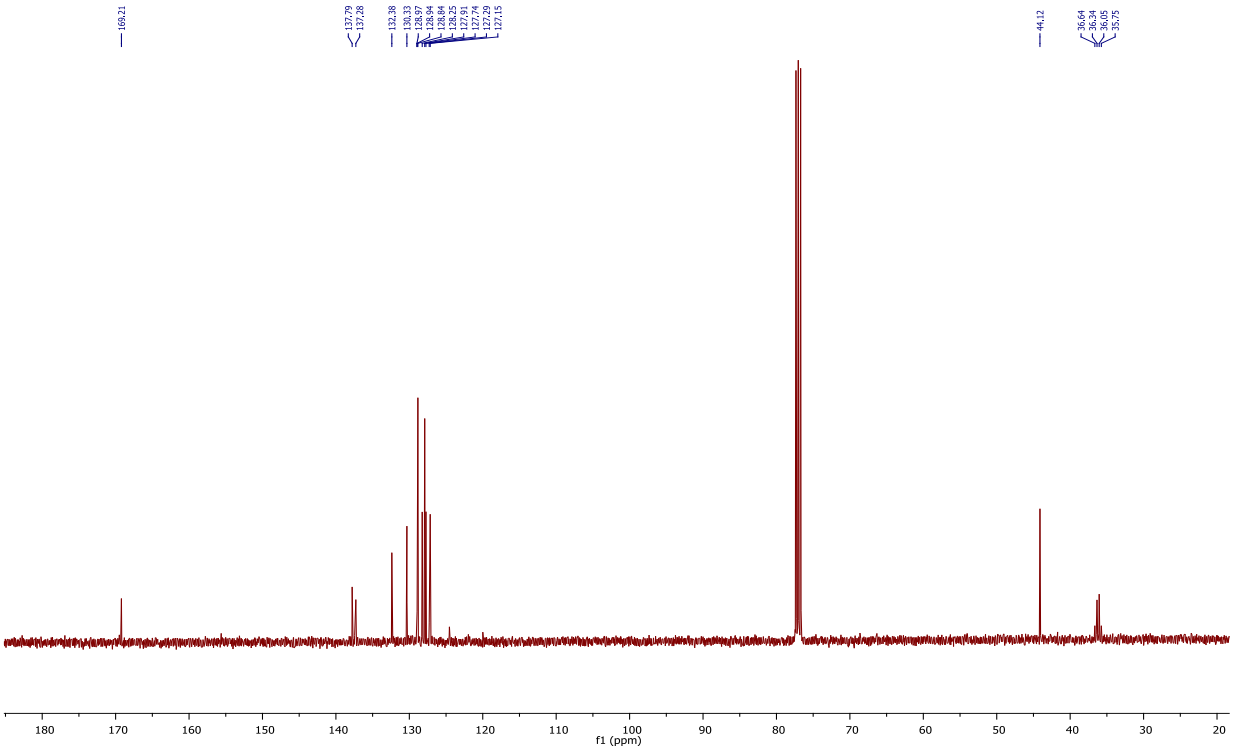
7.40
7.38
7.36
7.34
7.33
7.32
7.31
7.30
7.30
7.29
7.28
7.27
6.20
4.61
4.59
3.86
3.83
3.81
3.78
O
NH
CF3
9.19
0.85
1.91
2.00
f1 (ppm)


-65.14
-65.17
-65.20
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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128.97
128.84
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128.25
127.91
127.74
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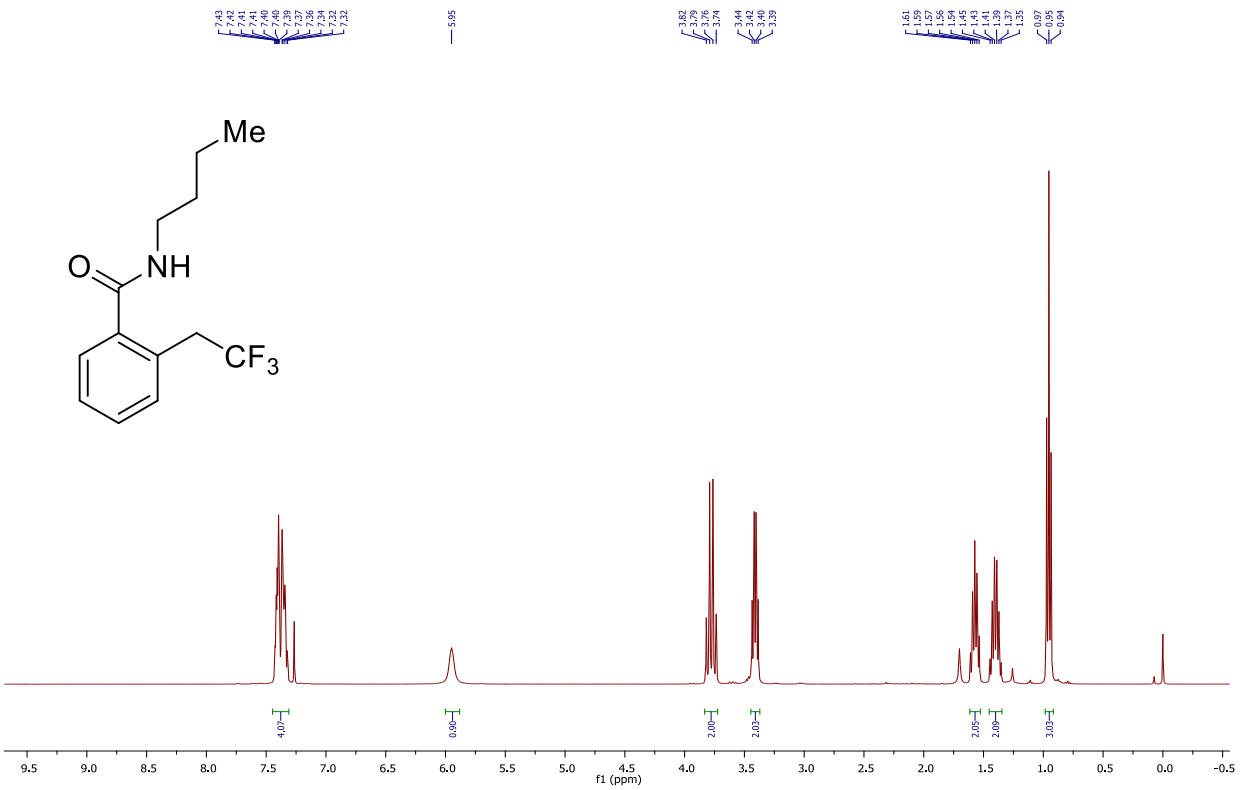
36.64
36.34
36.05
35.75
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)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7.32
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3.76
3.74
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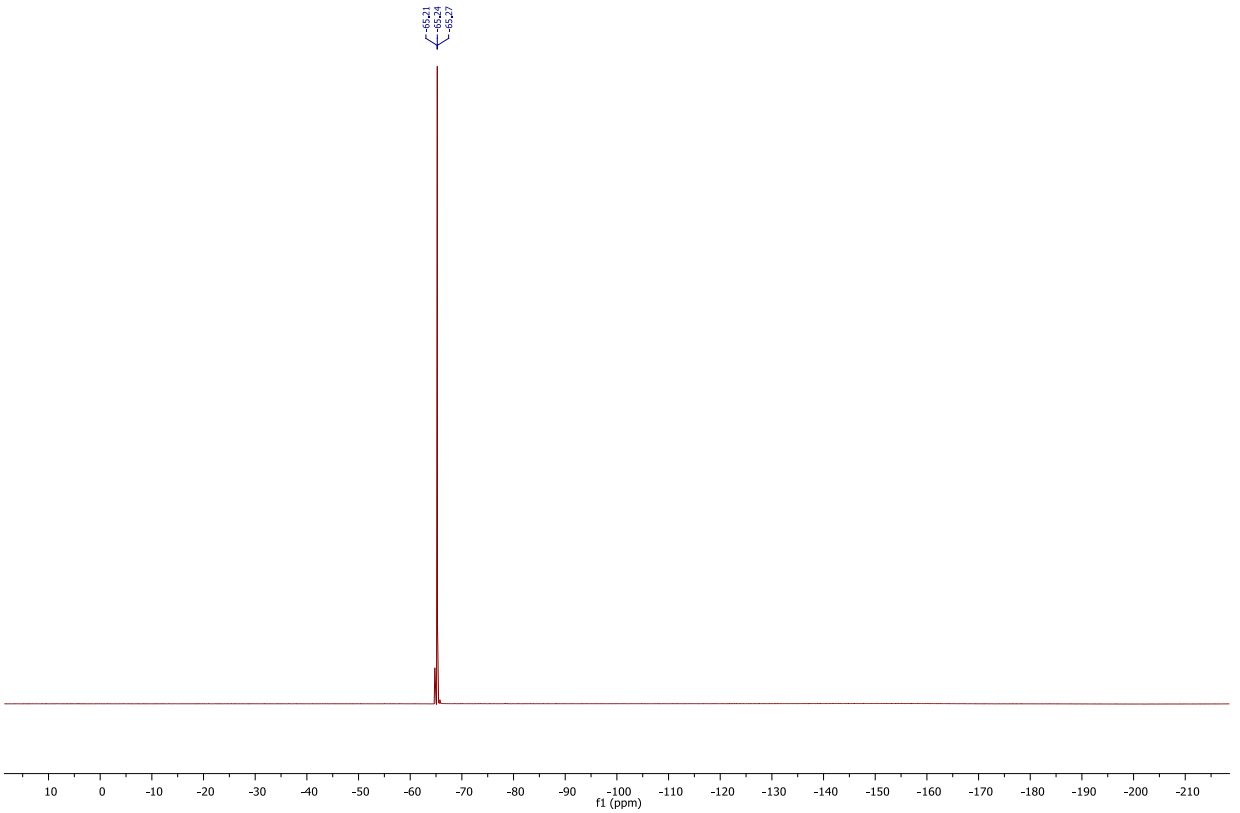
3.40
3.39
1.61
1.59
1.57
1.56
1.54
1.45
1.43
1.41
1.39
1.37
1.35
0.97
0.95
0.94
Me
O
NH
CF3
4.07
0.90
2.00
2.03
2.05
2.09
3.03
f1 (ppm)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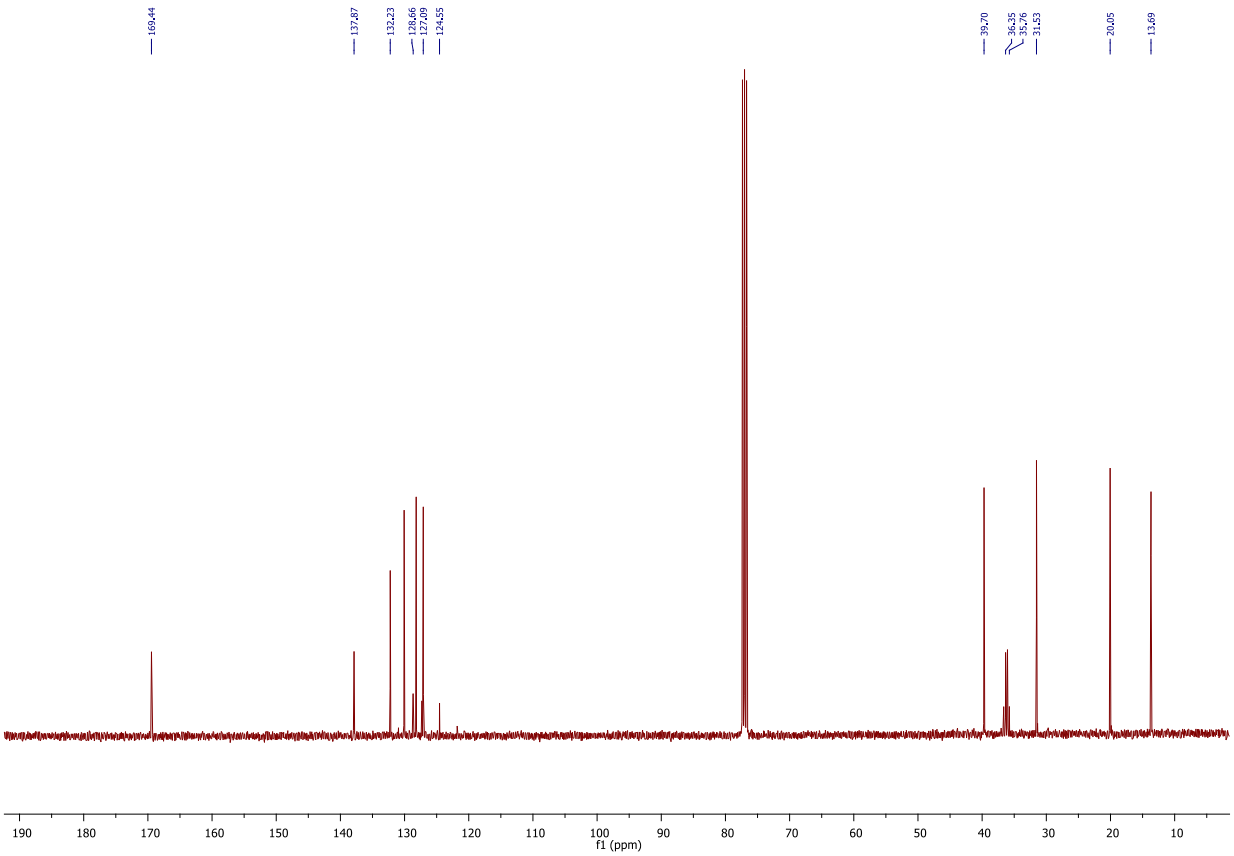
-65.27
f1 (ppm)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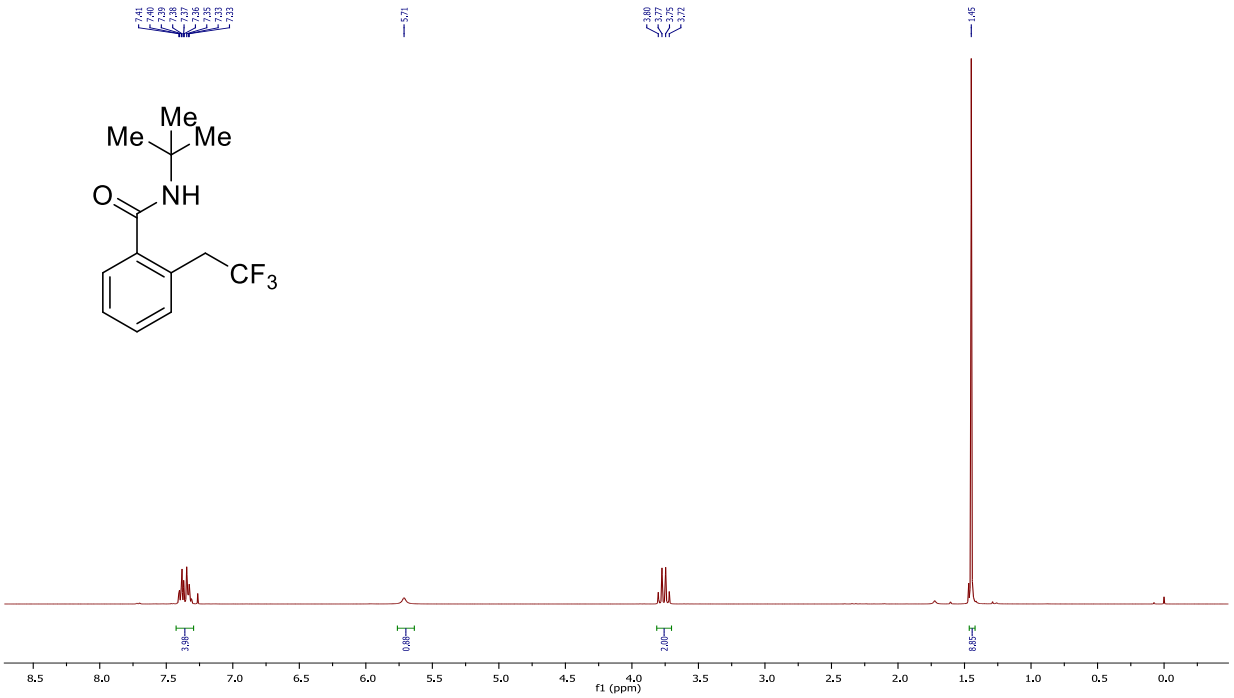
36.35
35.76
31.53
20.05
13.69
f1 (ppm)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7.36
7.35
7.33
7.33
5.71
3.80
3.77
3.75
3.72
1.45
Me
Me
Me
O
NH
CF3
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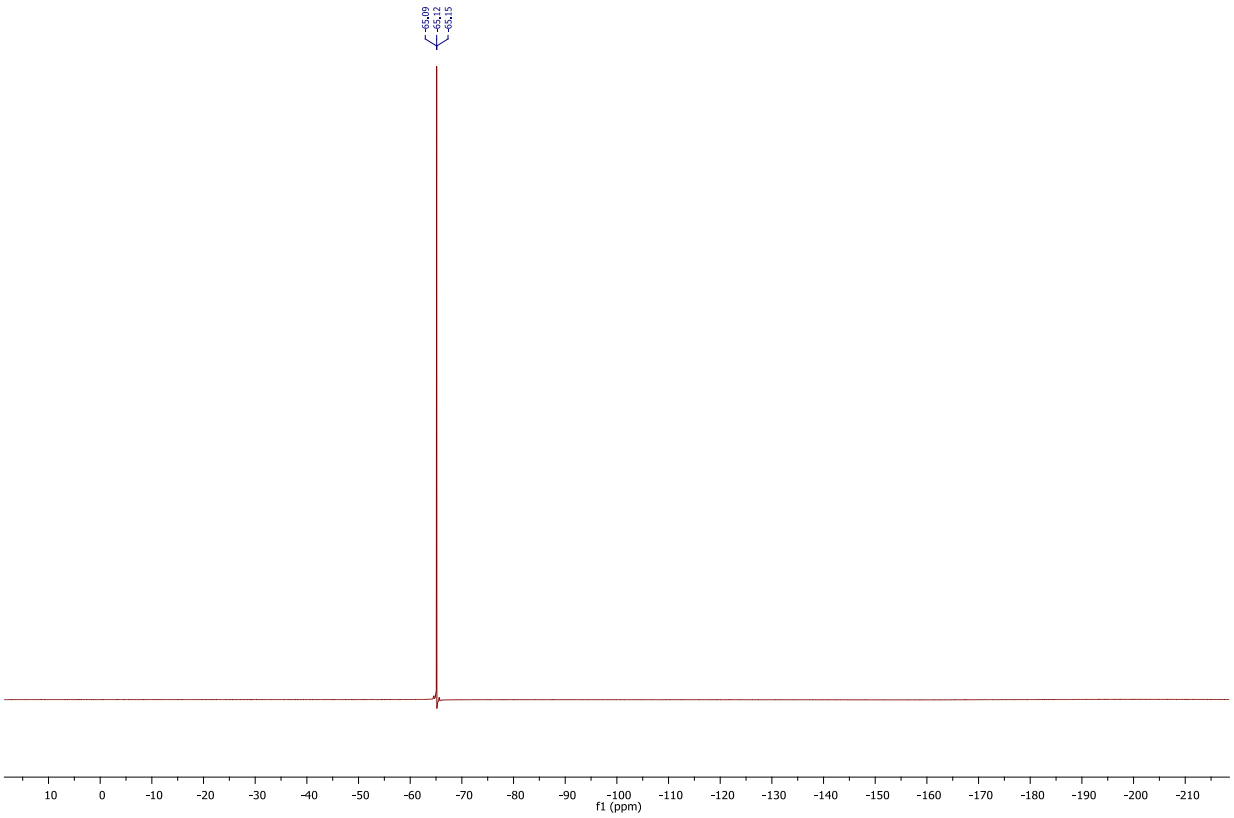
2.00
8.85
f1 (ppm)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-65.12
-65.15
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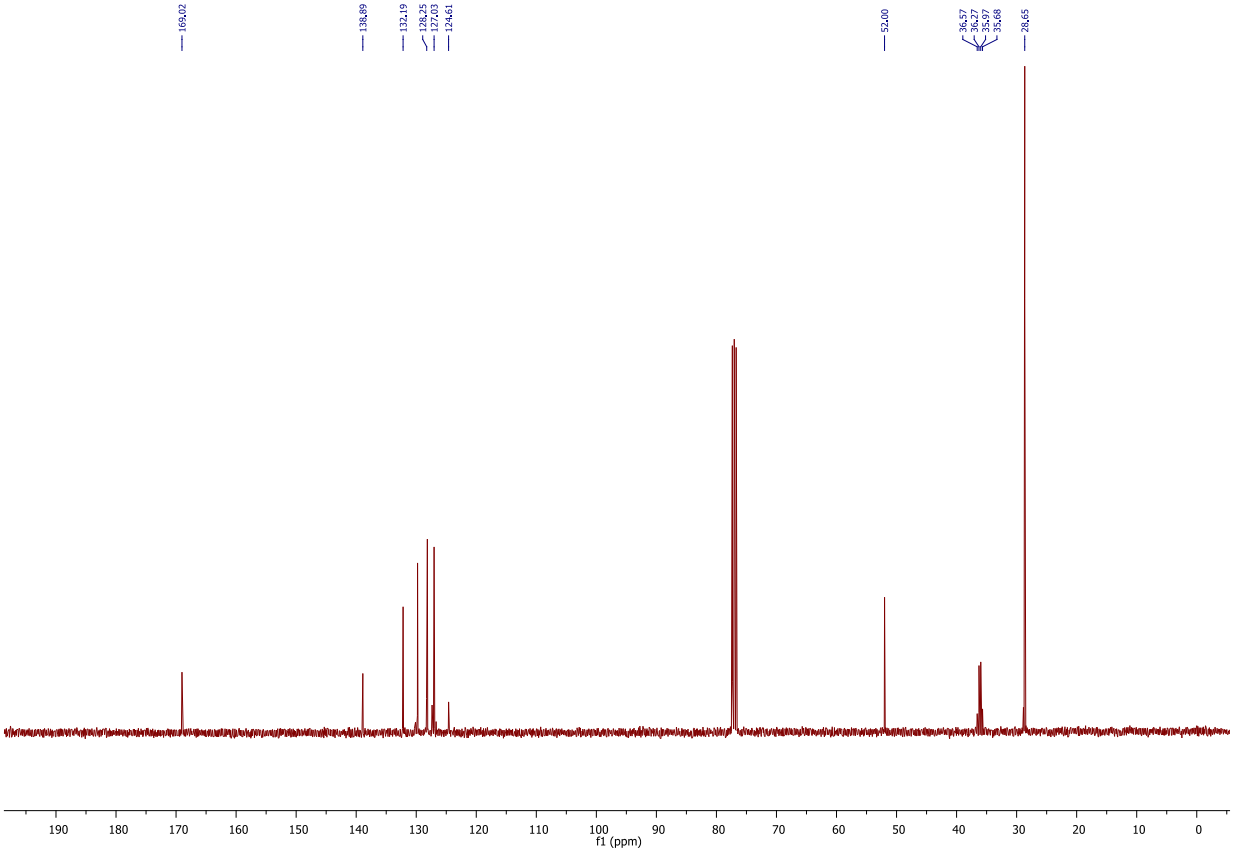
f1 (ppm)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35.97
35.68
28.65
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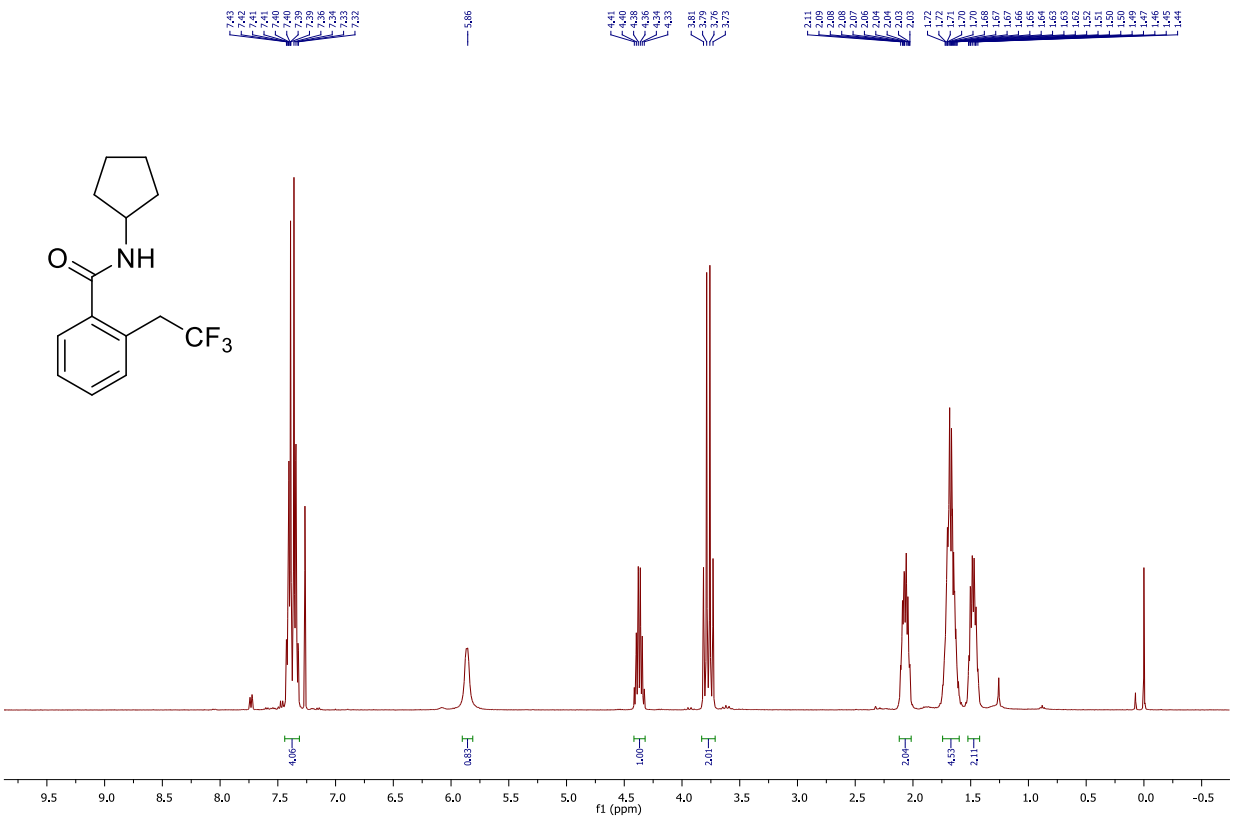
f1 (ppm)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4.38
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4.33
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3.79
3.76
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2.08
2.07
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2.03
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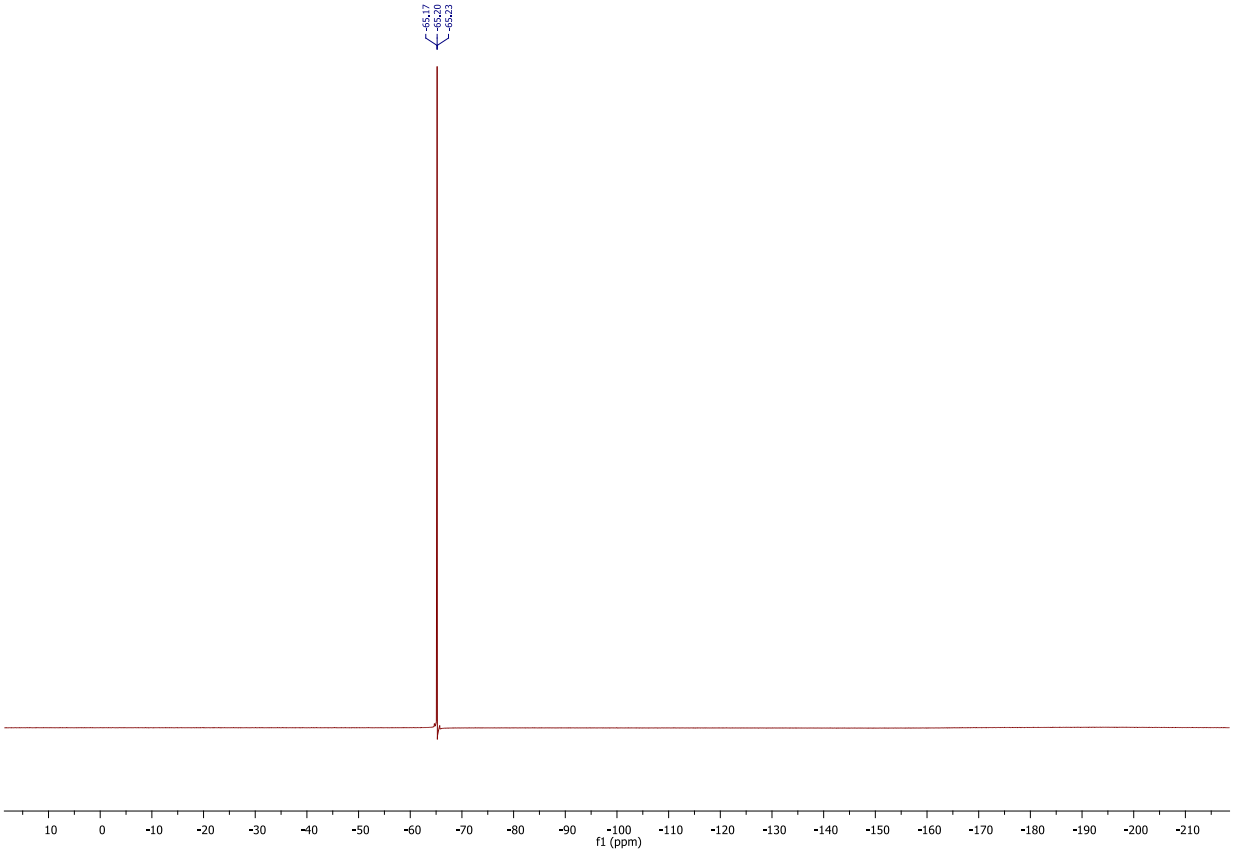
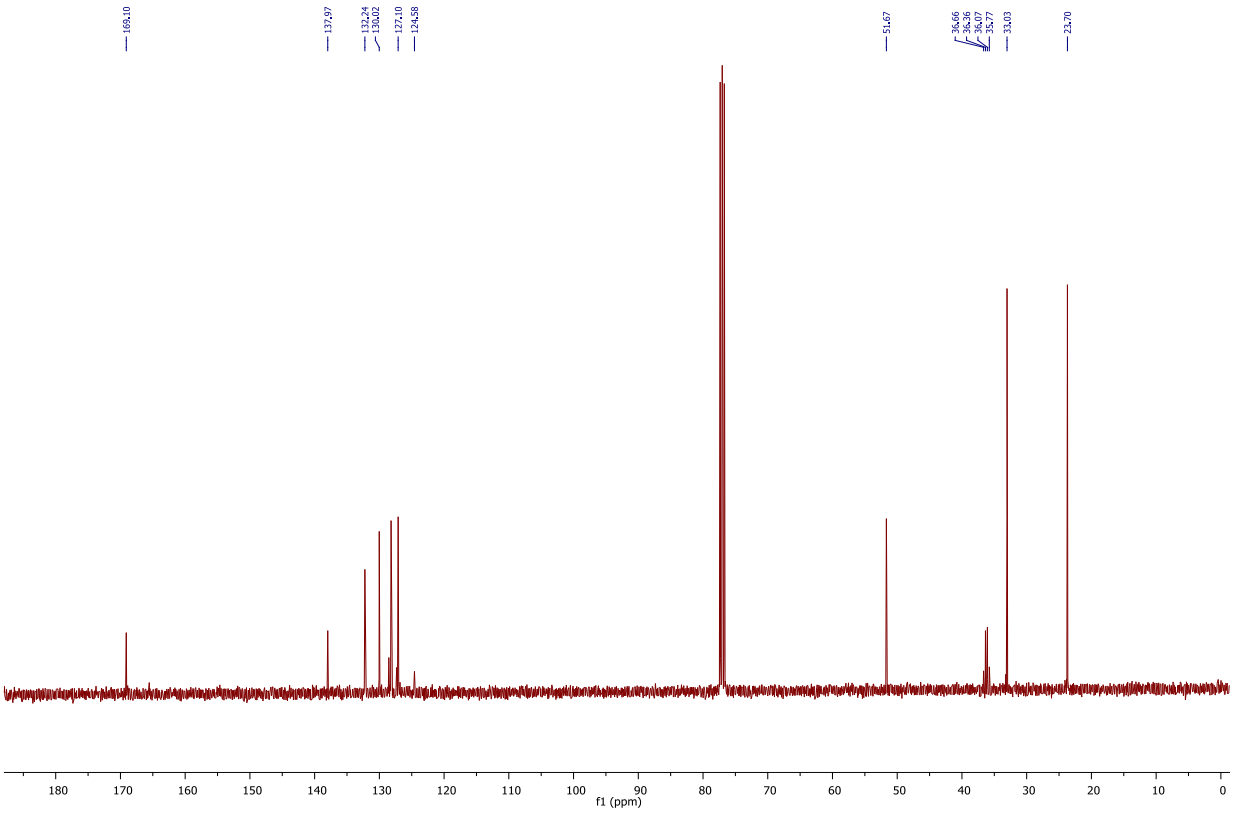
1.49
1.47
1.46
1.45
1.44
O
NH
CF3
4.06
0.83
1.00
2.01
2.04
4.53
2.11
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


-65.17
-65.20
-65.23
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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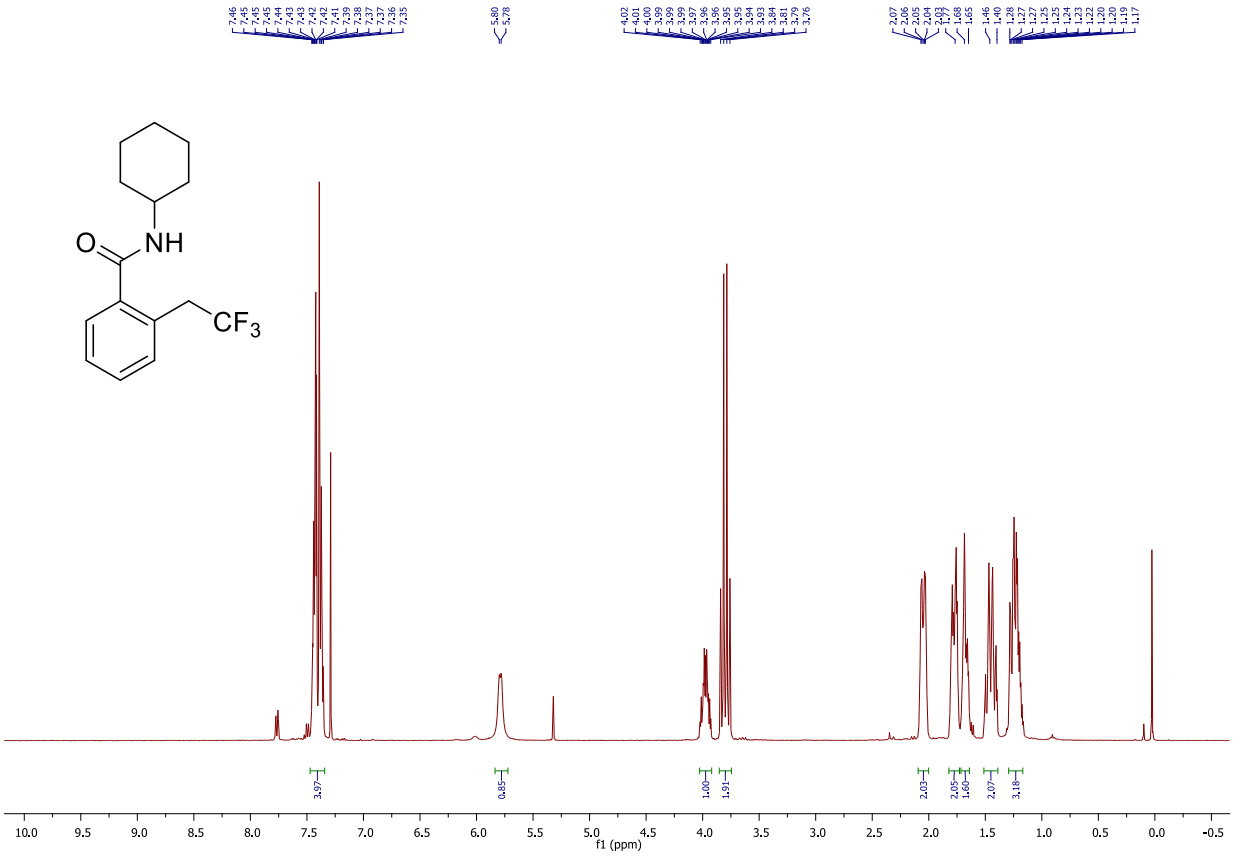
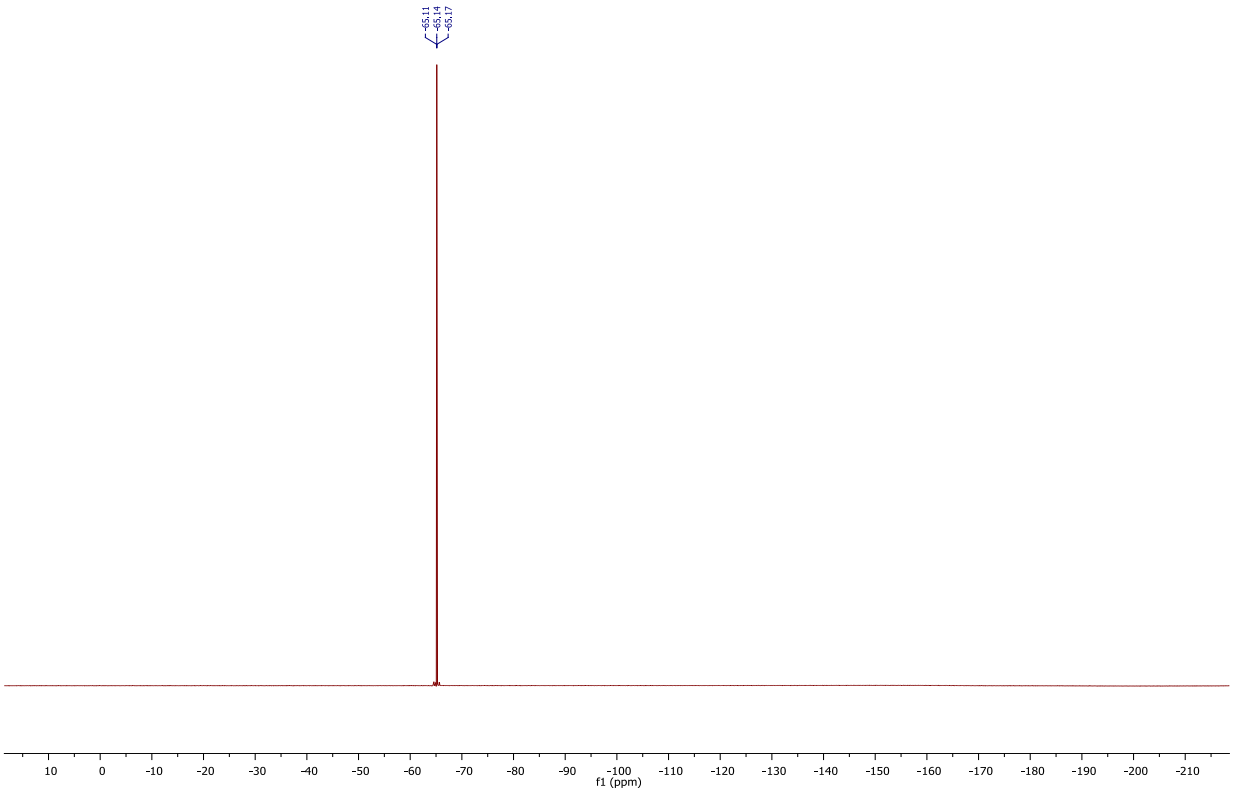
35.77
33.03
23.70
f1 (ppm)


O
NH
CF3
f1 (ppm)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-65.14
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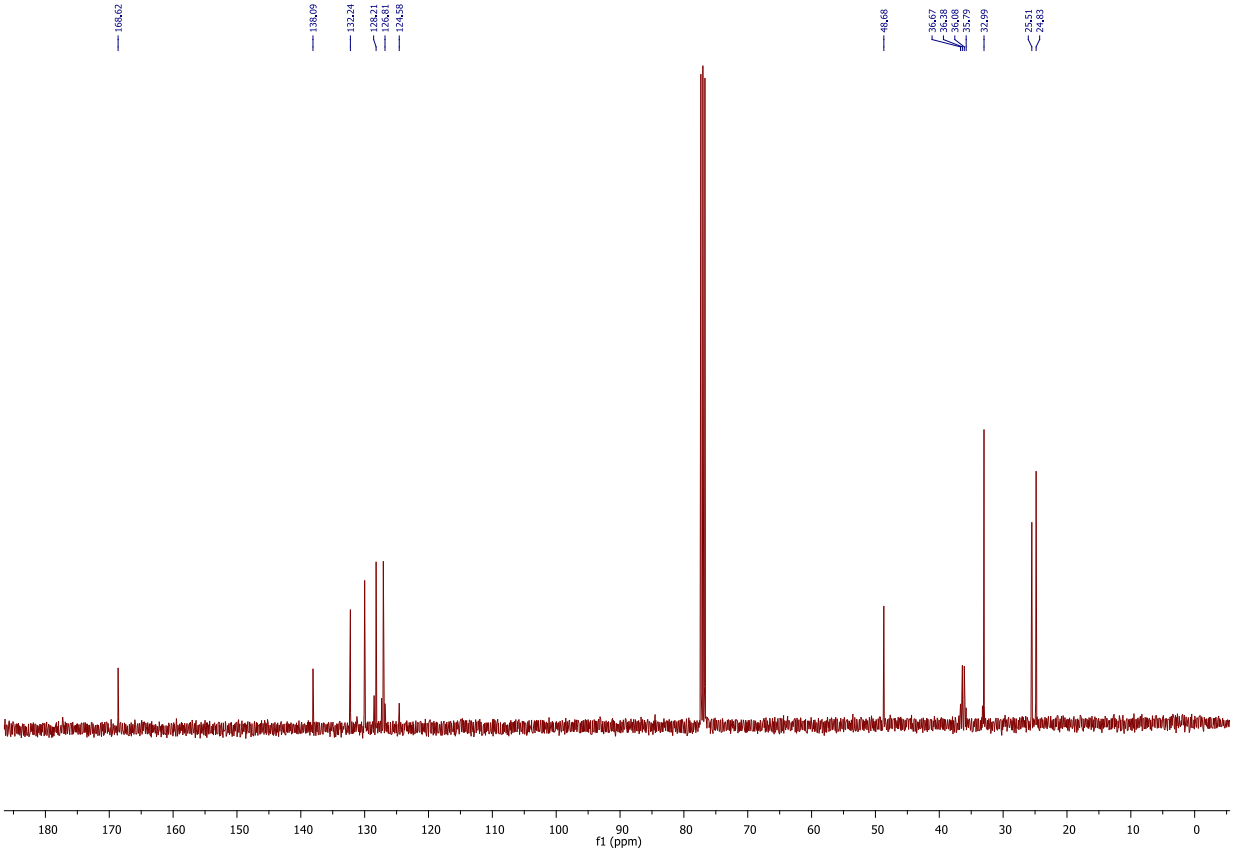
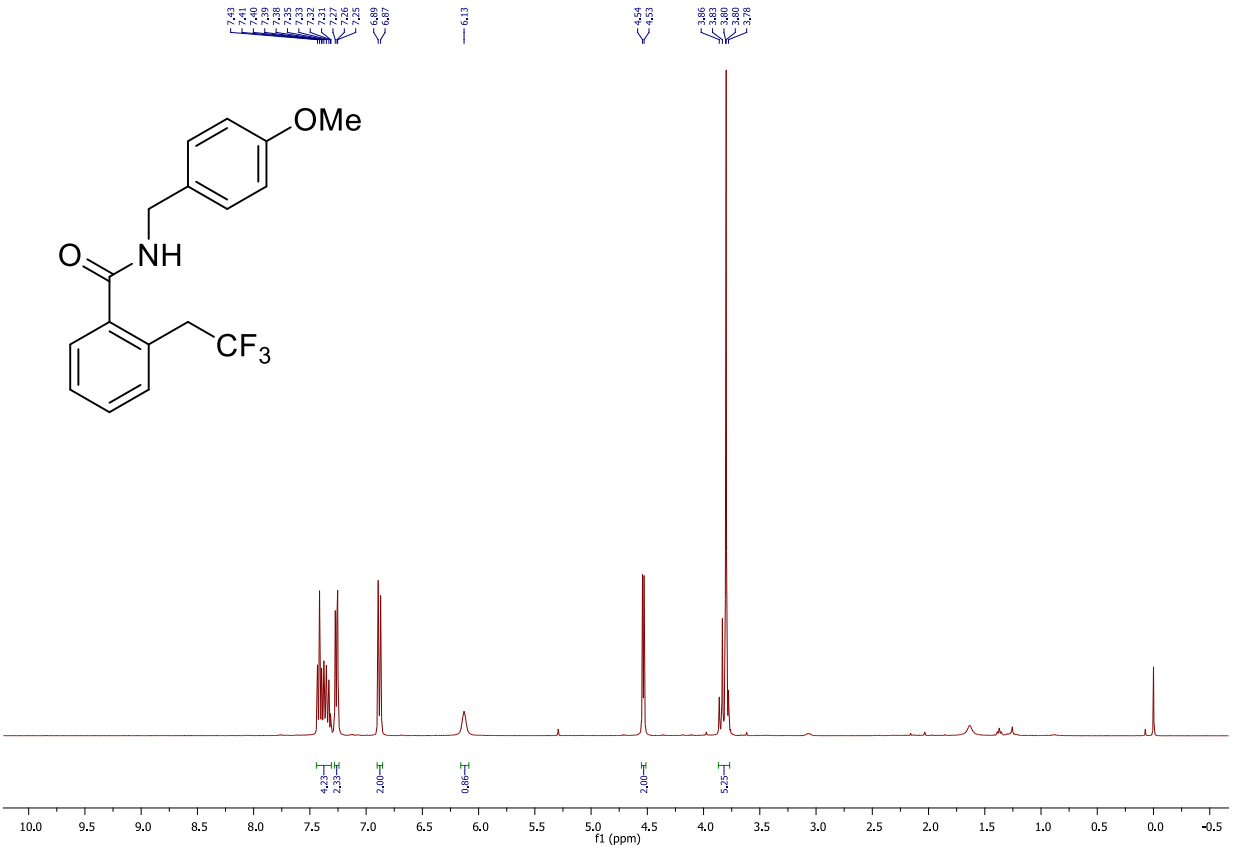
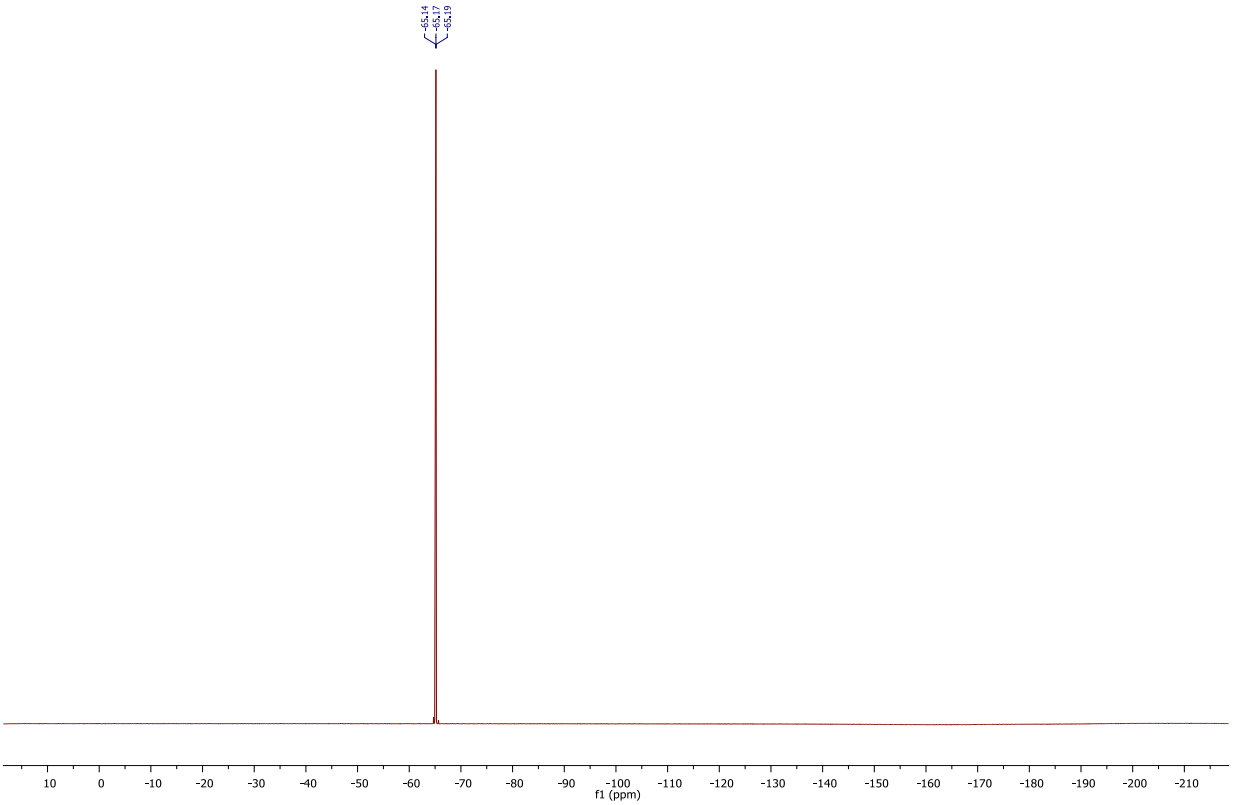
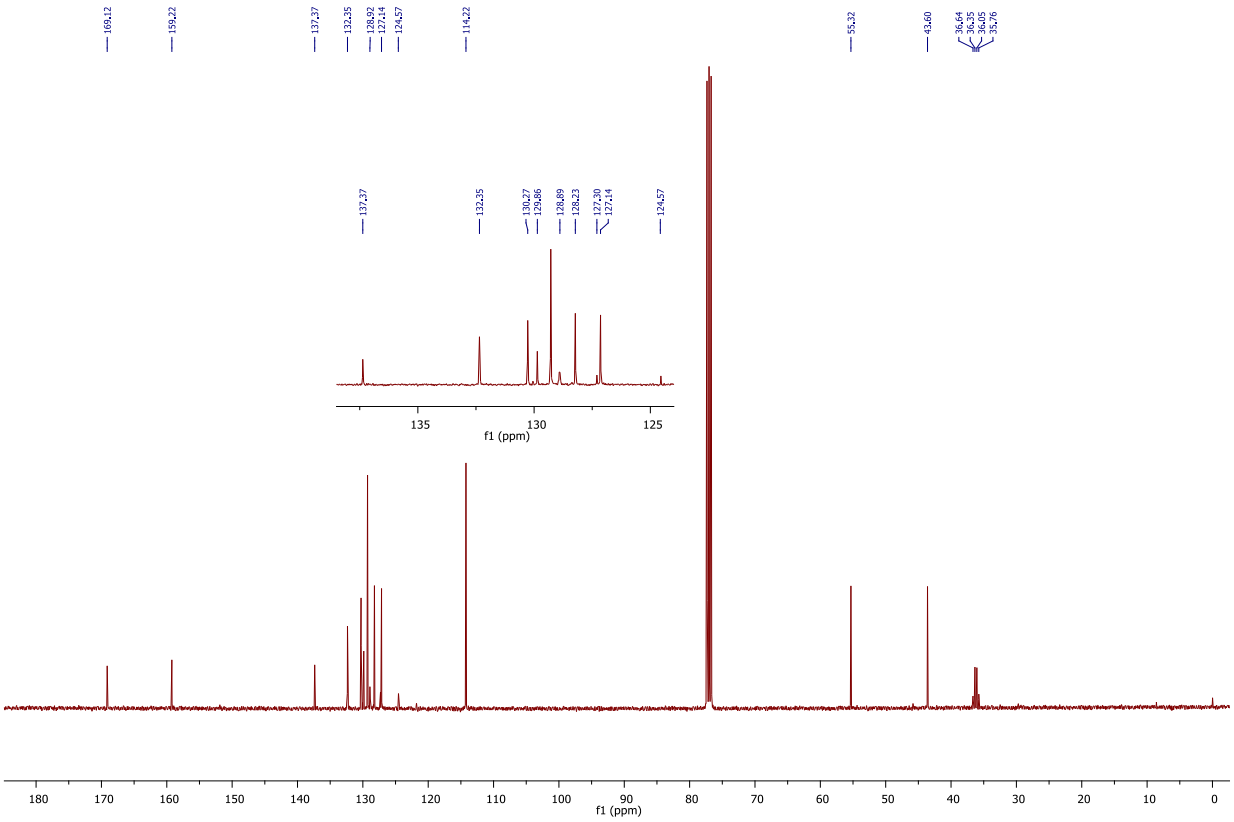
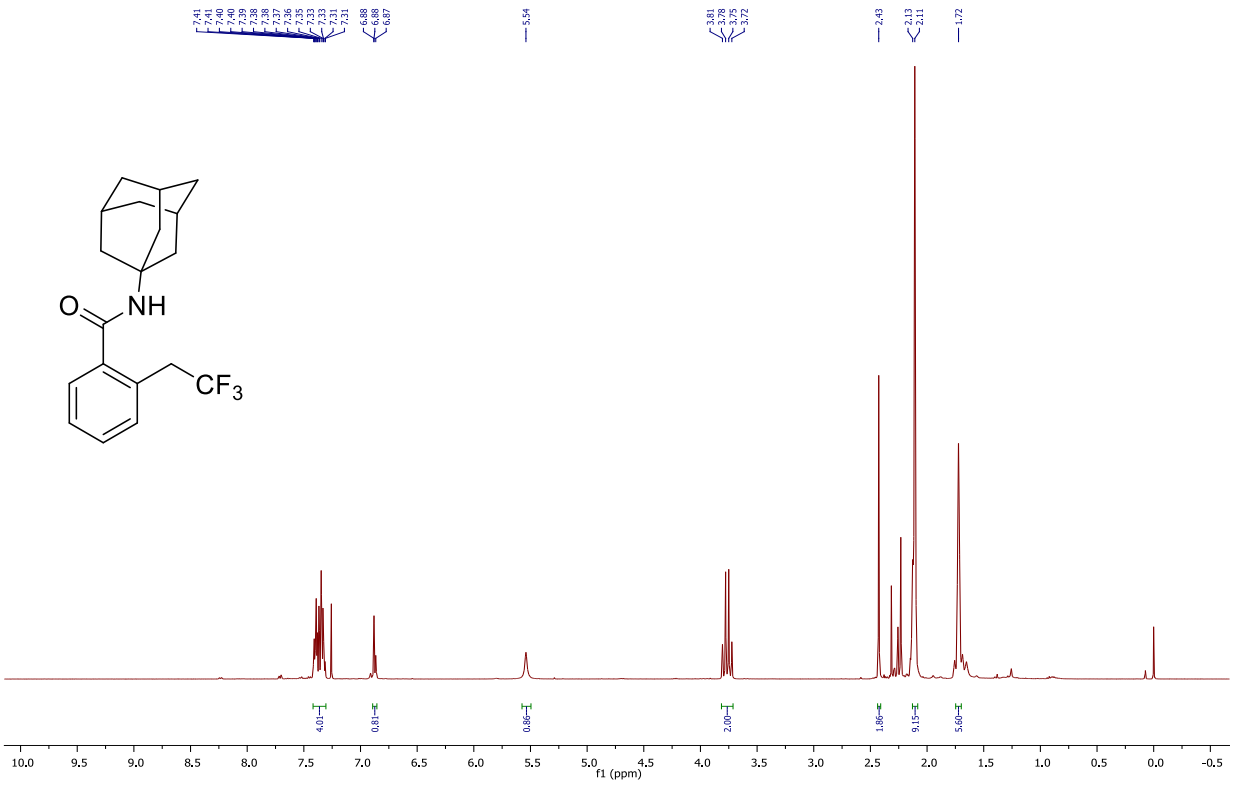
f1 (ppm)

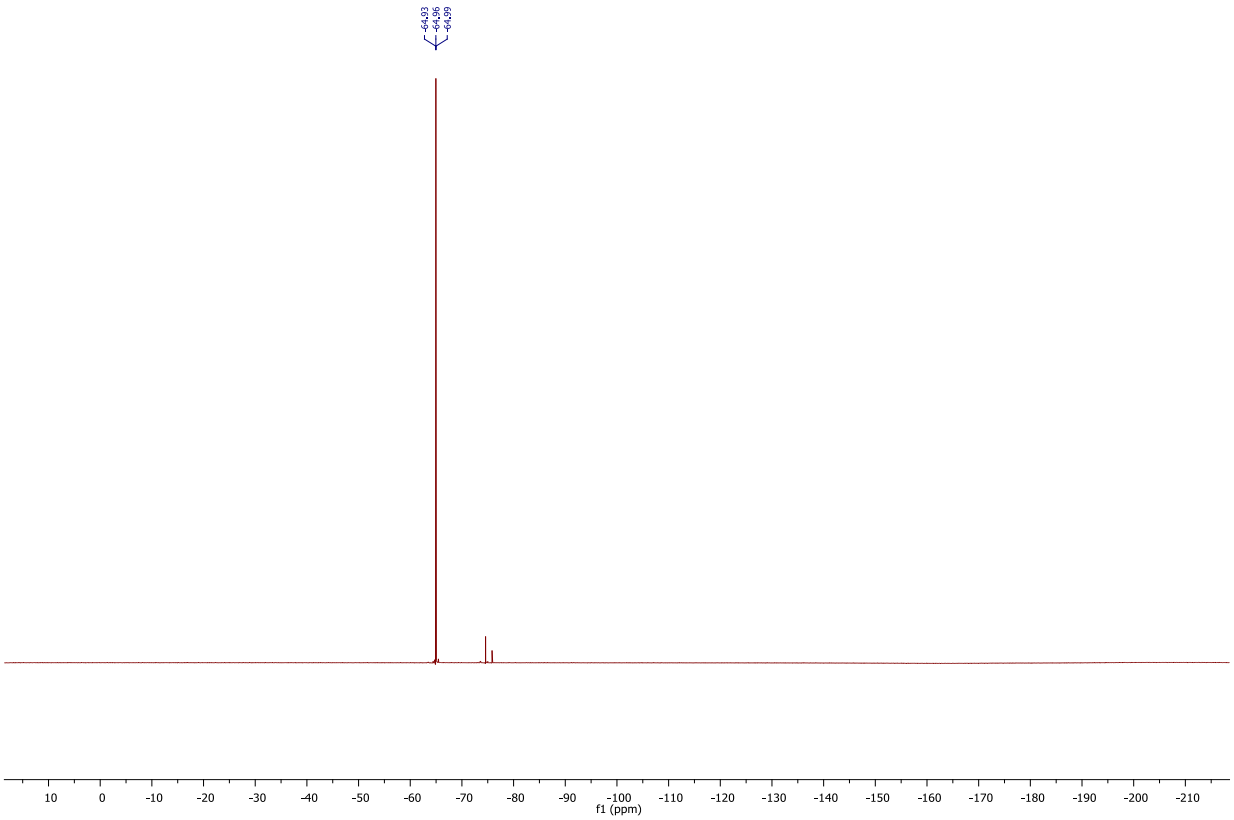

168.62
138.09
132.24
128.21
126.81
124.58
48.68
36.67
36.38
36.08
35.79
32.99
25.51
24.83
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

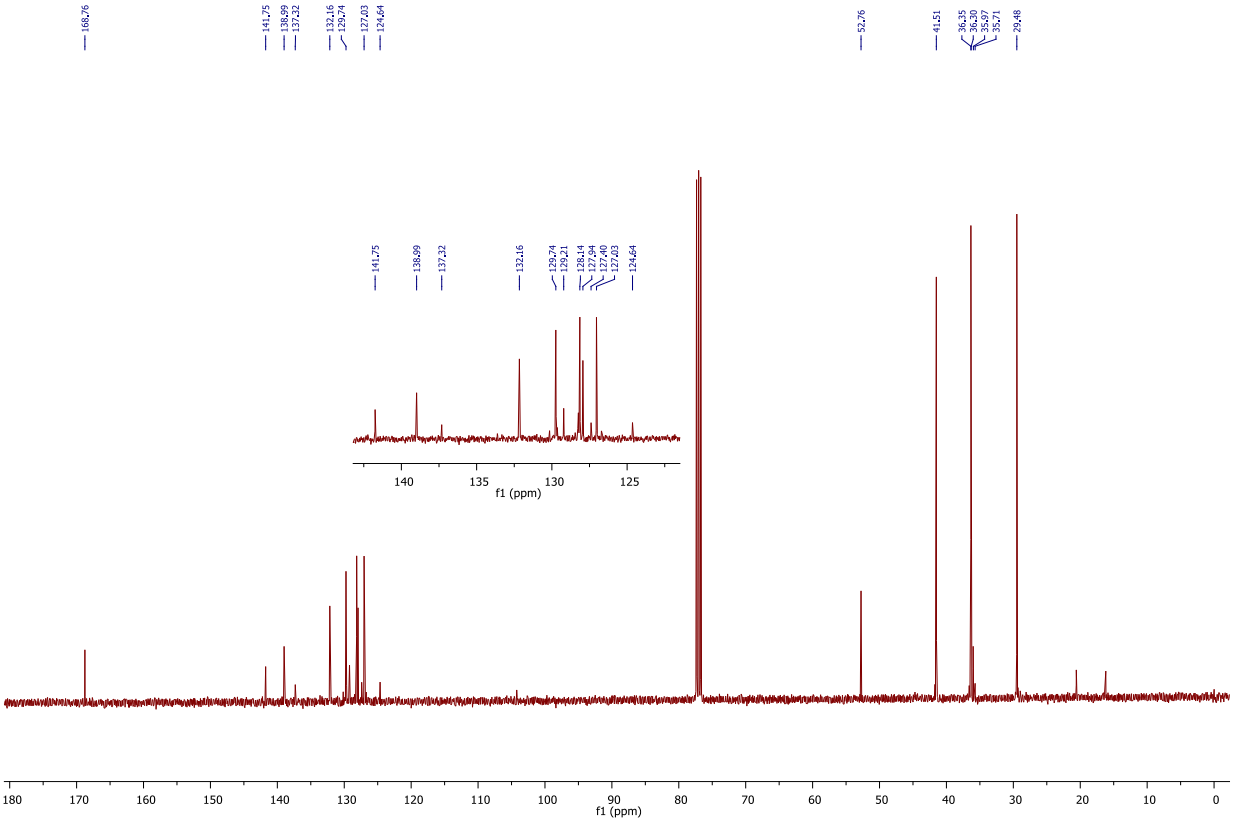

OMe
O
NH
CF3
f1 (ppm)

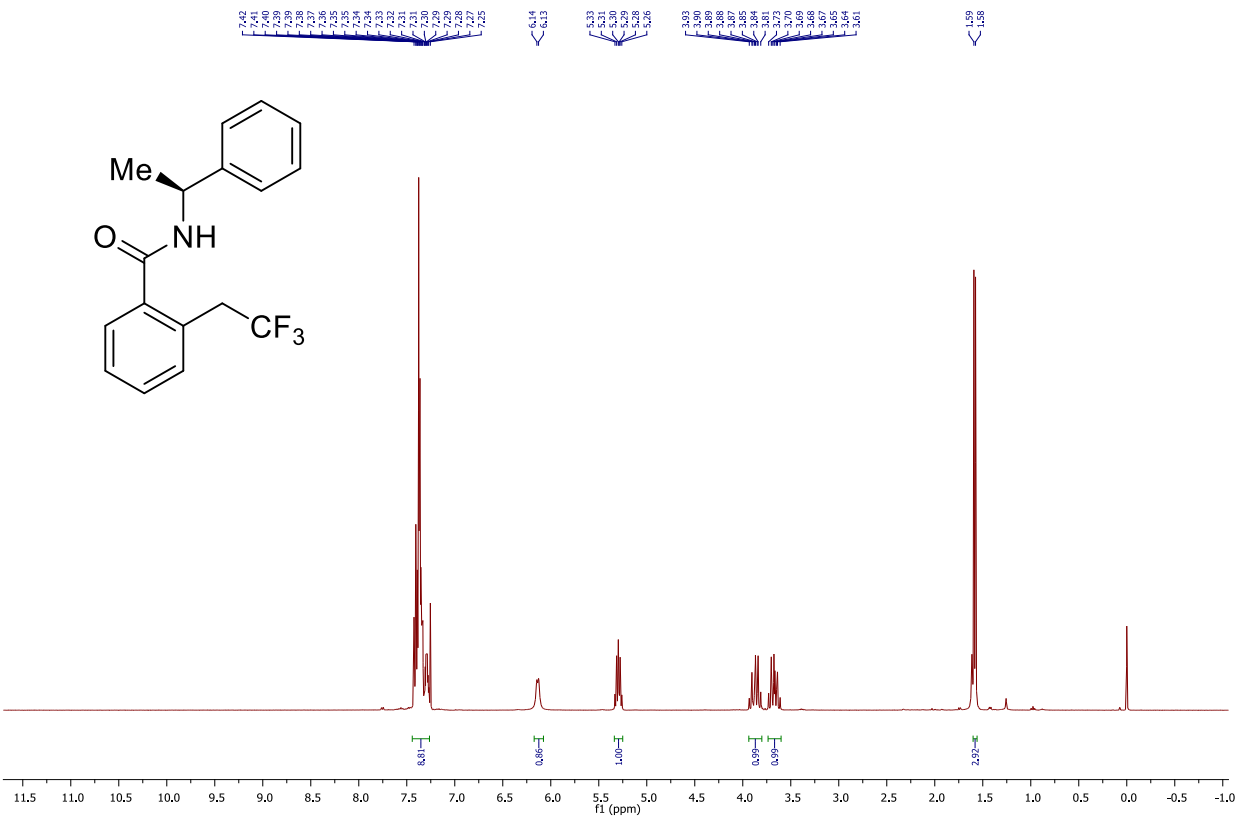

f1 (ppm)

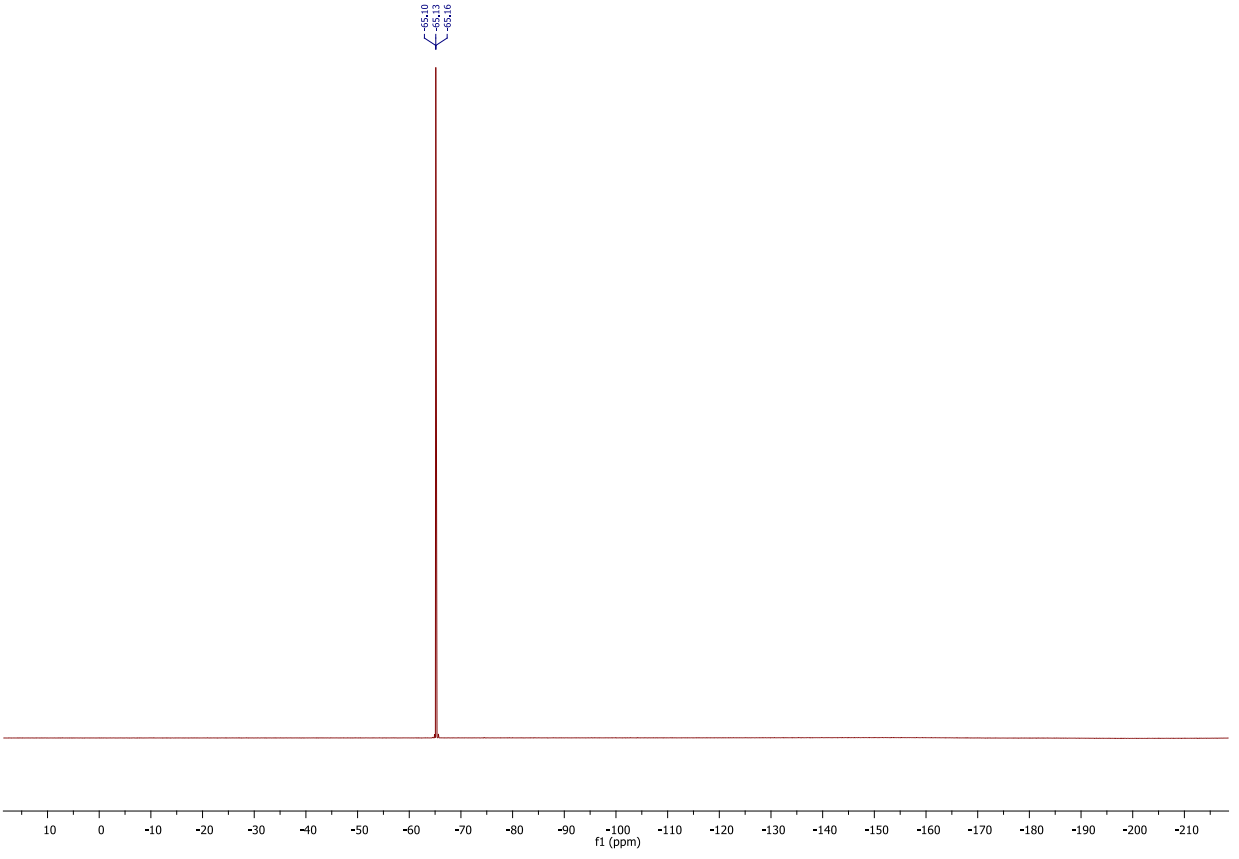

169.12
159.22
137.37
132.35
128.92
127.14
124.57
114.22
55.32
43.60
36.64
36.35
36.05
35.76
137.37
132.35
130.27
129.86
128.89
128.23
127.30
127.14
124.57
135
130
125
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

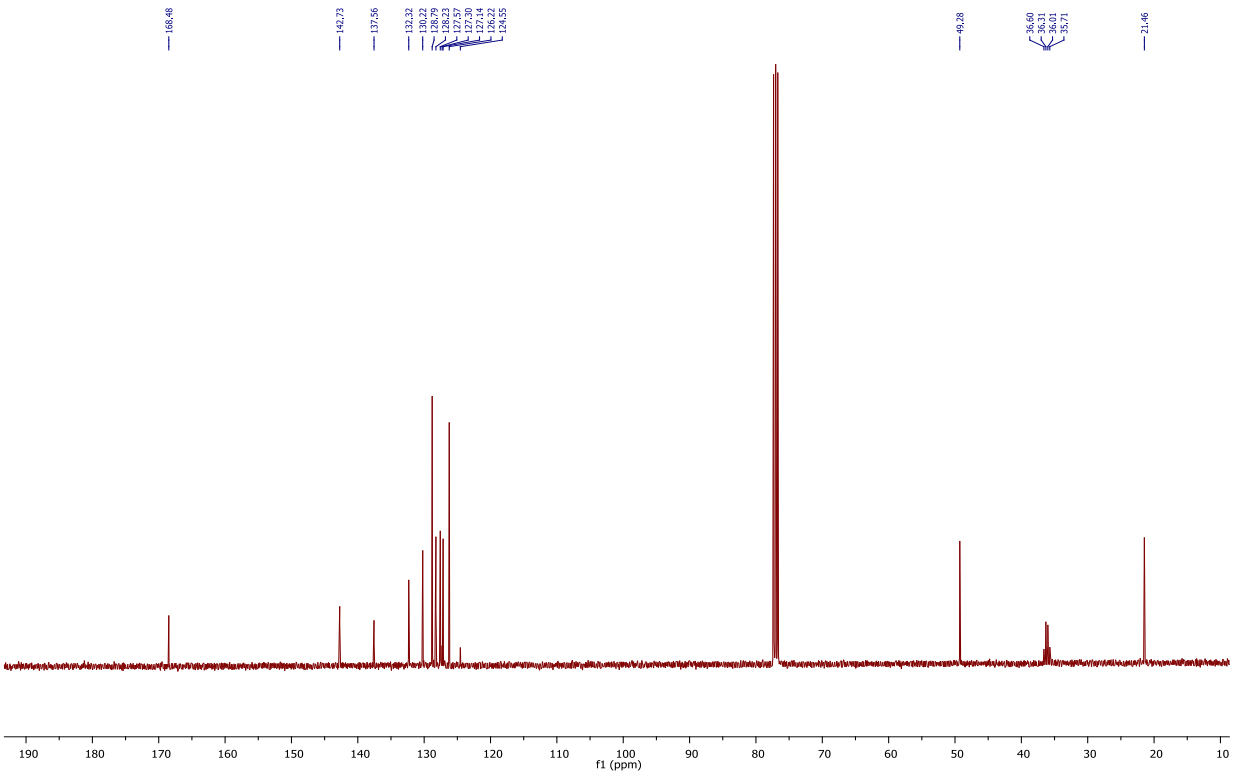

7.41
7.41
7.40
7.40
7.39
7.38
7.38
7.37
7.36
7.35
7.33
7.33
7.31
7.31
6.88
6.88
6.87
5.54
3.81
3.78
3.75
3.72
2.43
2.13
2.11
1.72
O
NH
CF3
4.01
0.81
0.86
2.00
1.86
9.15
5.60
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


-64.03
-64.96
-64.99
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

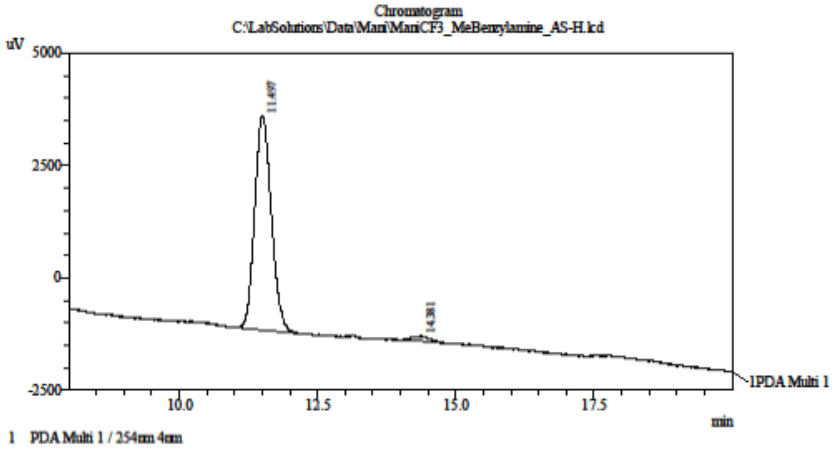

168.76
141.75
138.99
137.32
132.16
129.74
127.03
124.64
52.76
41.51
36.35
36.30
35.97
35.71
29.48
141.75
138.99
137.32
132.16
129.74
129.21
128.14
127.94
127.40
127.03
124.64
140 135 130 125
f1 (ppm)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Me
O
NH
CF3
f1 (ppm)


f1 (ppm)


168,48
142,73
137,56
132,32
130,22
128,79
128,23
127,57
127,30
127,14
126,22
124,55
49,28
36,60
36,31
36,01
35,71
21,46
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

ManiCF3_MeBenzylamine90% Hex AS-H 1ml_min 60min 23Mar201

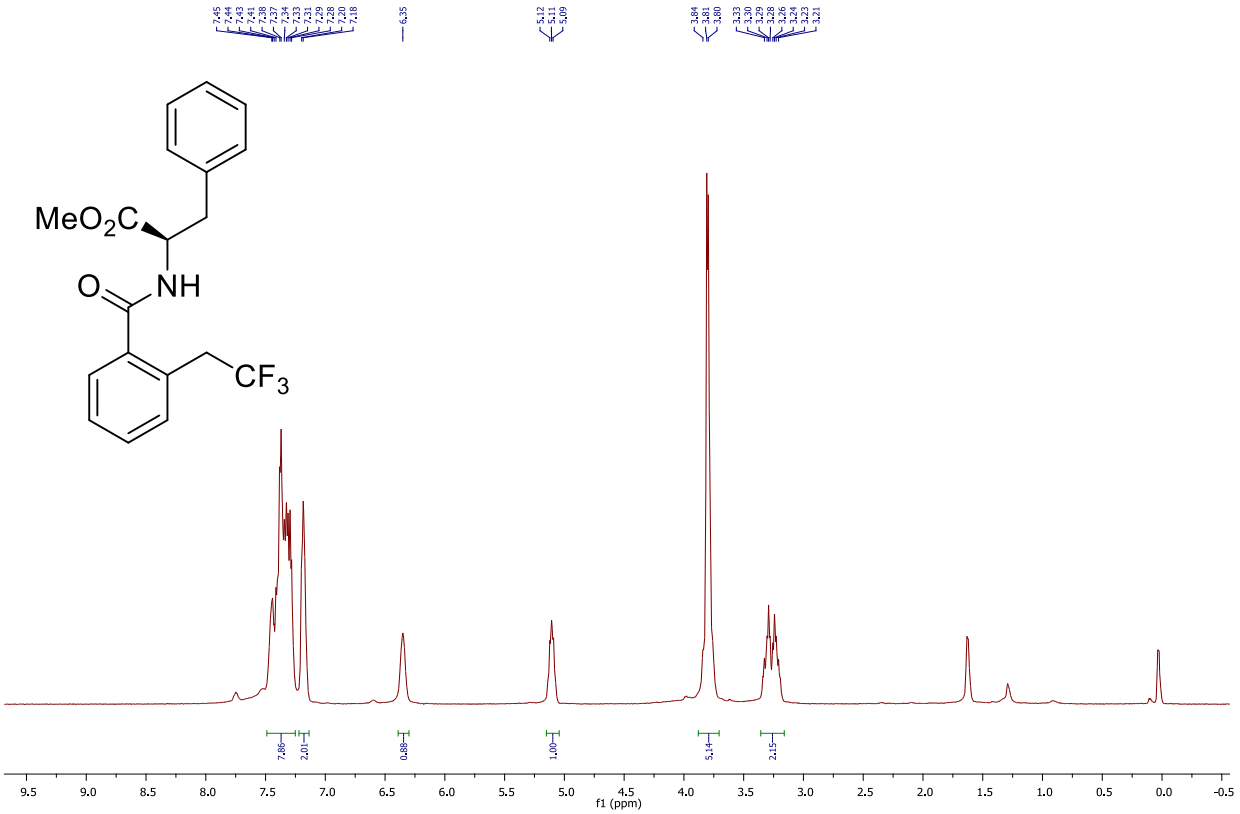


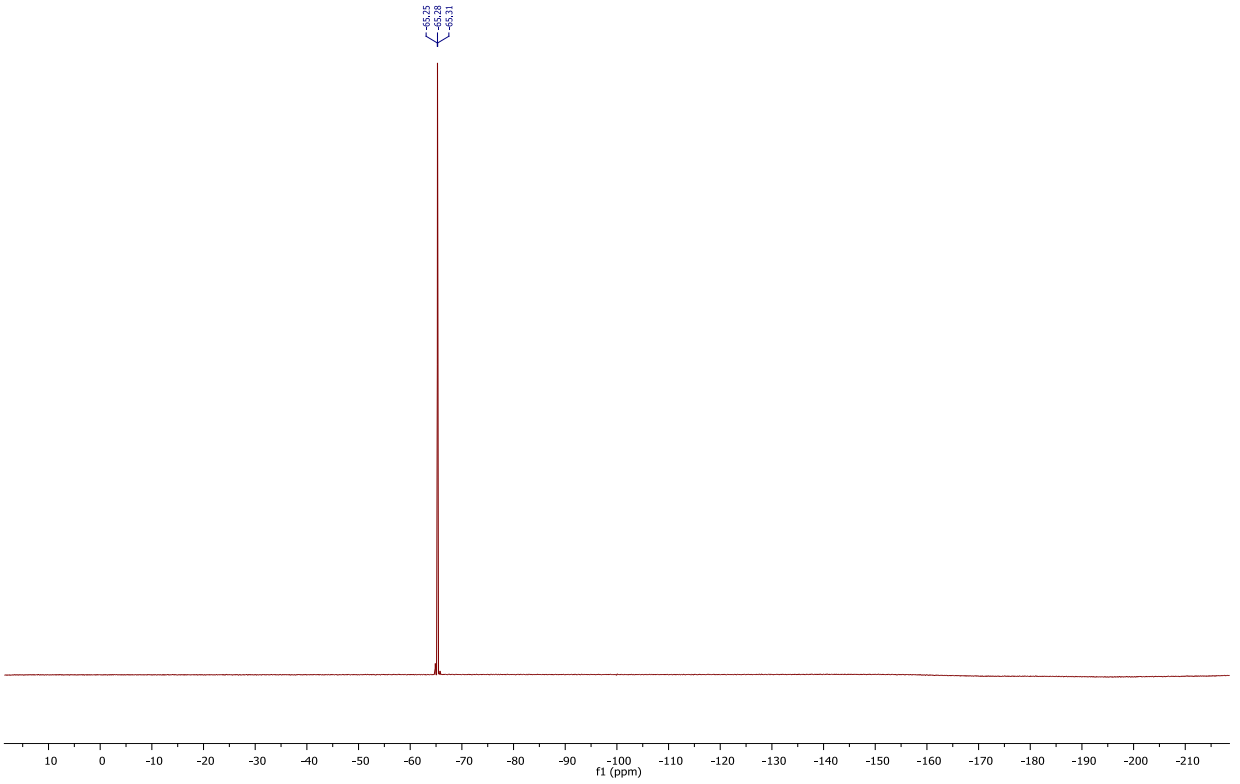
1 PDA Multi 1 / 254nm 4nm

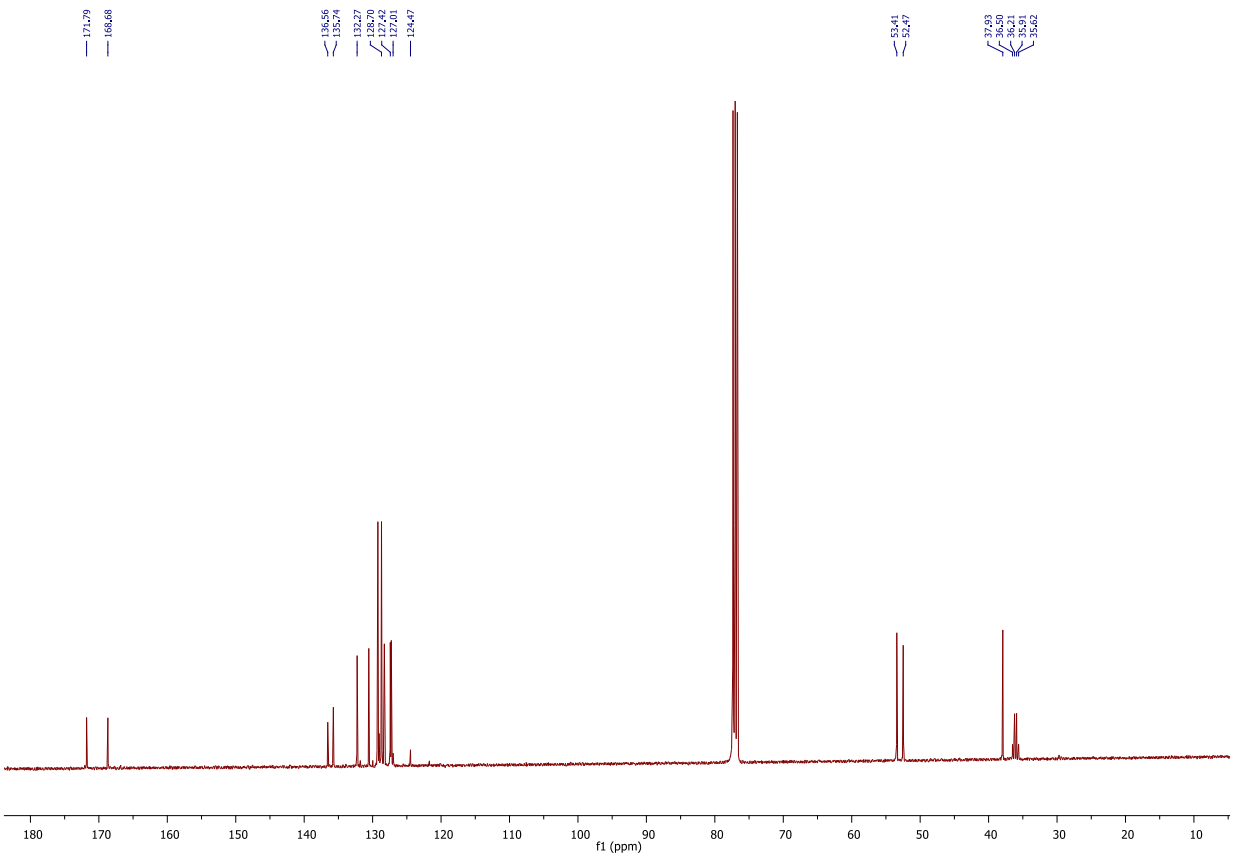
PeakTable

PDA Ch1 254nm 4nm

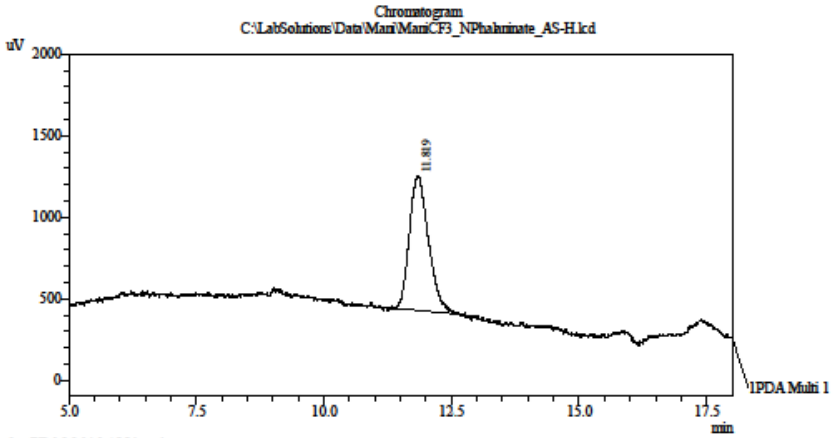
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.497	99271	4759	97.771	97.689
2	14.381	2263	113	2.229	2.311
Total		101535	4872	100.000	100.000


MeO2C
O
NH
CF3
f1 (ppm)


f1 (ppm)


171,79
168,68
136,56
135,74
132,27
128,70
127,42
127,01
124,47
53,41
52,47
37,93
36,50
36,21
35,91
35,62
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

ManiCF3_NPhalaninate90% Hex AS-H 1ml_min 30min 23Mar2017

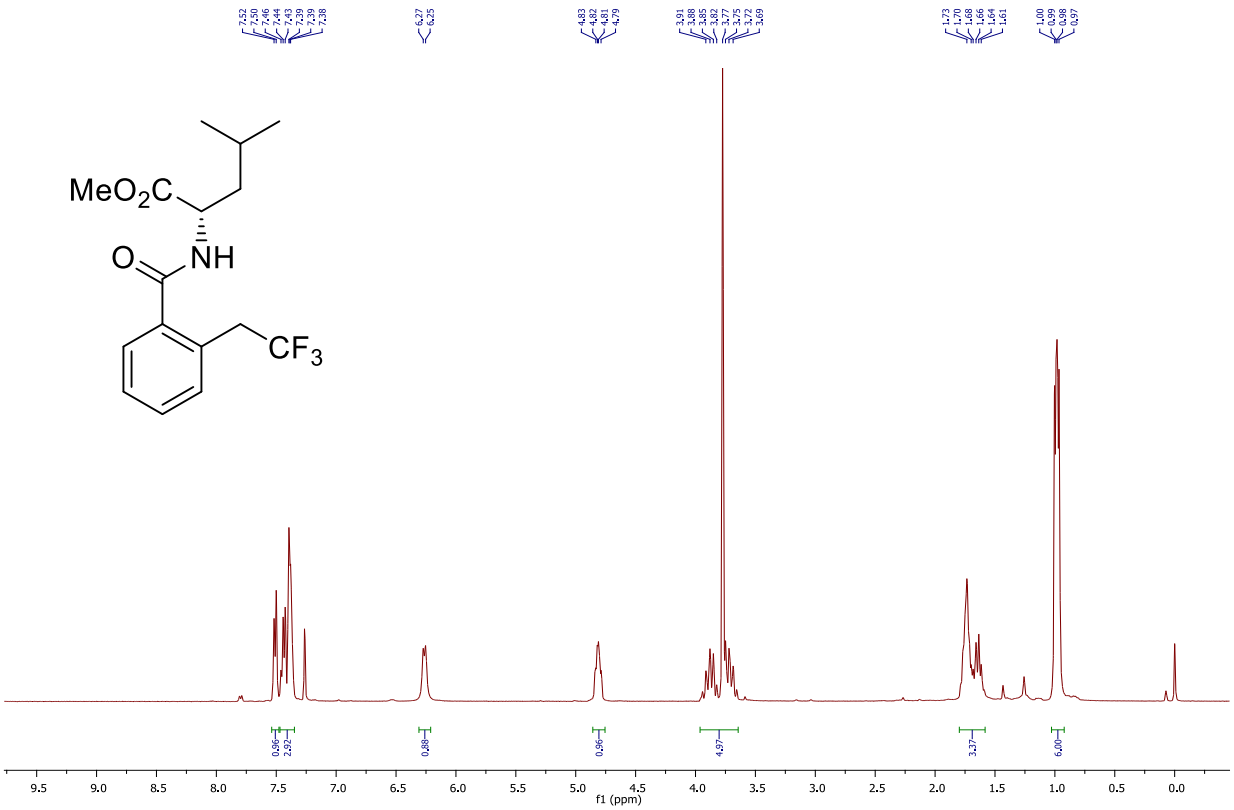


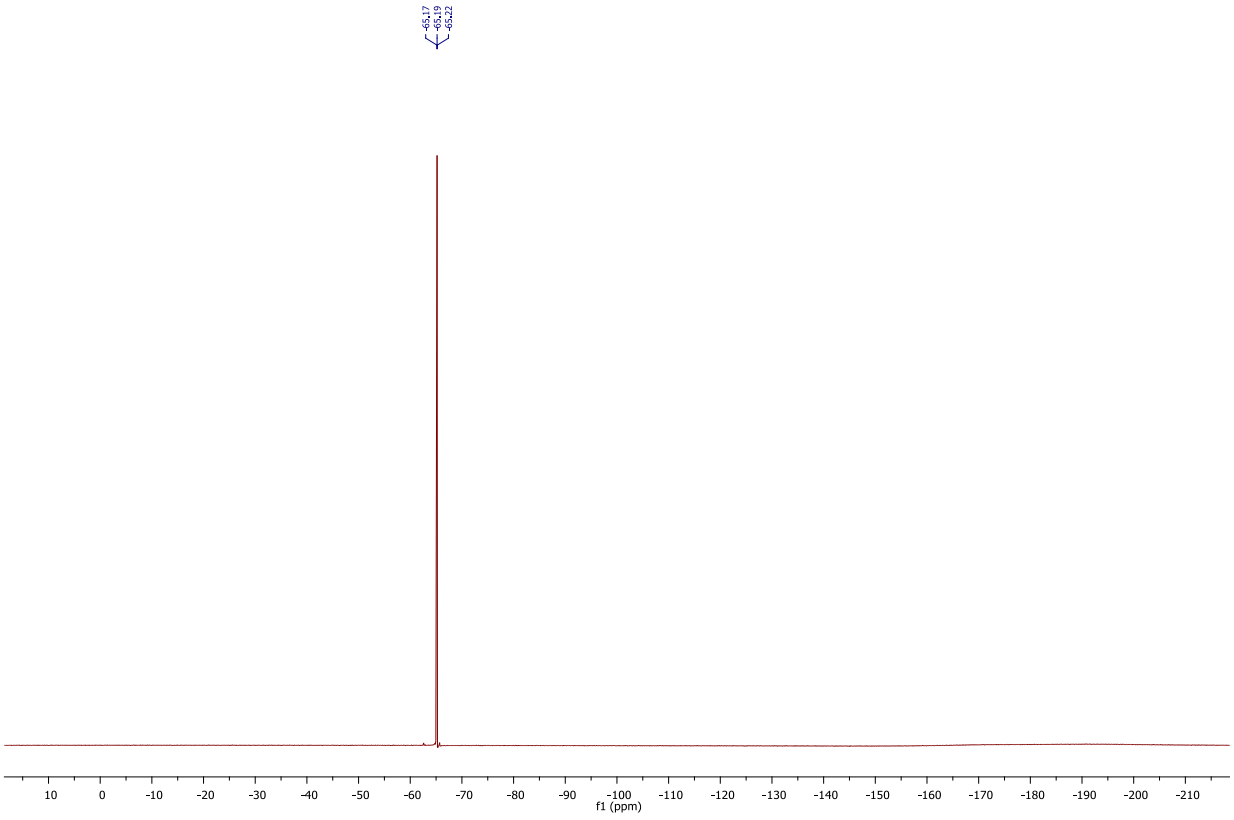
1 PDA Multi 1 / 254nm 4nm

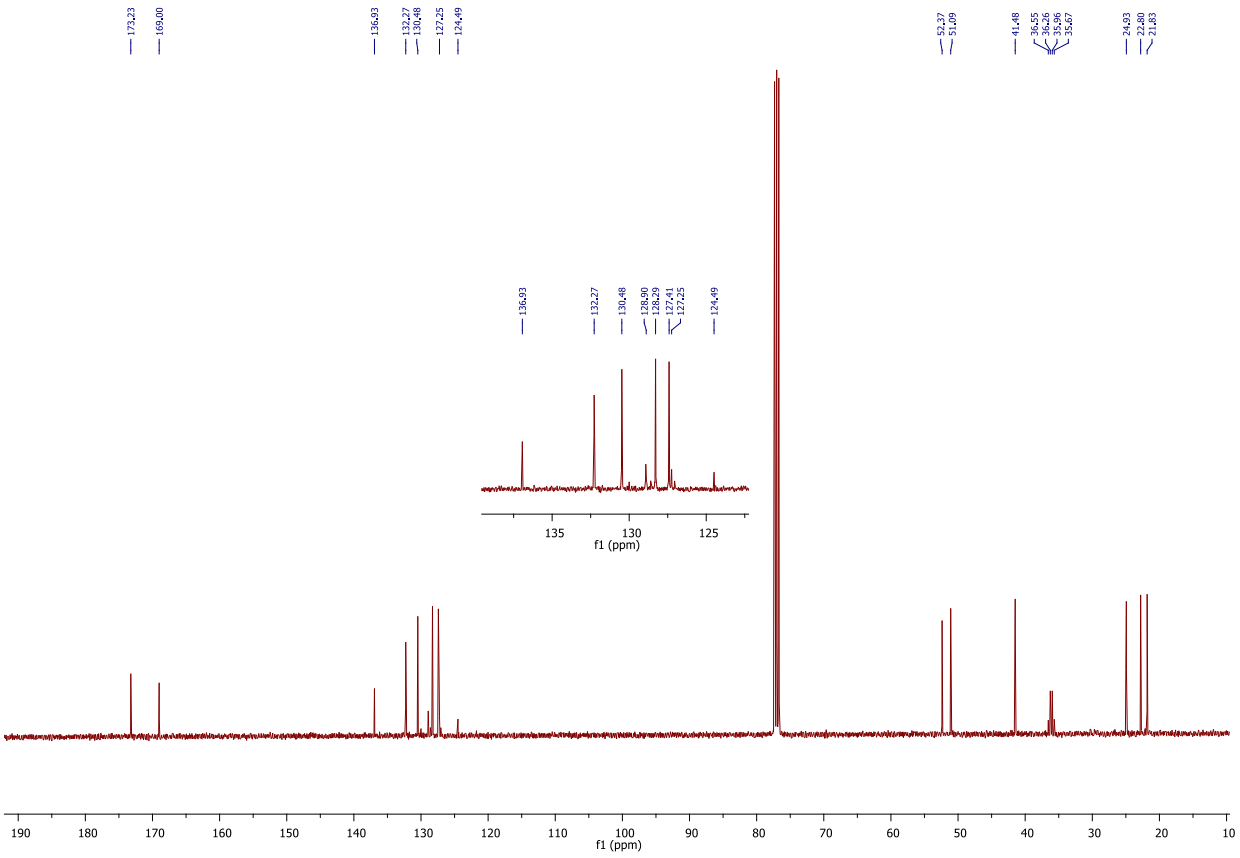
PeakTable

PDA Ch1 254nm 4nm

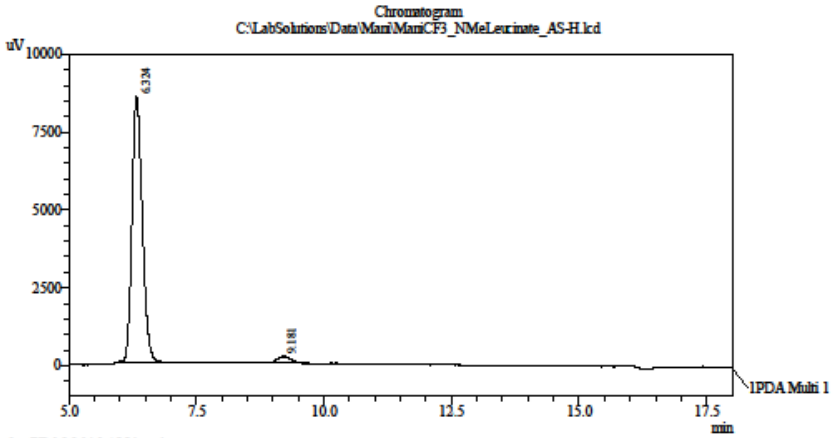
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.819	21560	829	100.000	100.000
Total		21560	829	100.000	100.000


7.52
7.50
7.46
7.44
7.43
7.39
7.39
7.38
6.27
6.25
4.83
4.82
4.81
4.79
3.91
3.88
3.85
3.82
3.77
3.75
3.72
3.69
1.73
1.70
1.68
1.66
1.64
1.61
1.00
0.99
0.98
0.97
MeO2C
O
NH
CF3
0.96
2.92
0.88
0.96
4.97
3.37
6.00
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)


-65.17
-65.19
-65.22
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


173,23
169,00
136,93
132,27
130,48
127,25
124,49
52,37
51,09
41,48
36,55
36,26
35,96
35,67
24,93
22,80
21,83
136,93
132,27
130,48
128,50
128,29
127,41
127,25
124,49
135
130
125
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

ManiCF3_NMeLeucinate90% Hex AS-H 1ml_min 60min 23Mar2017

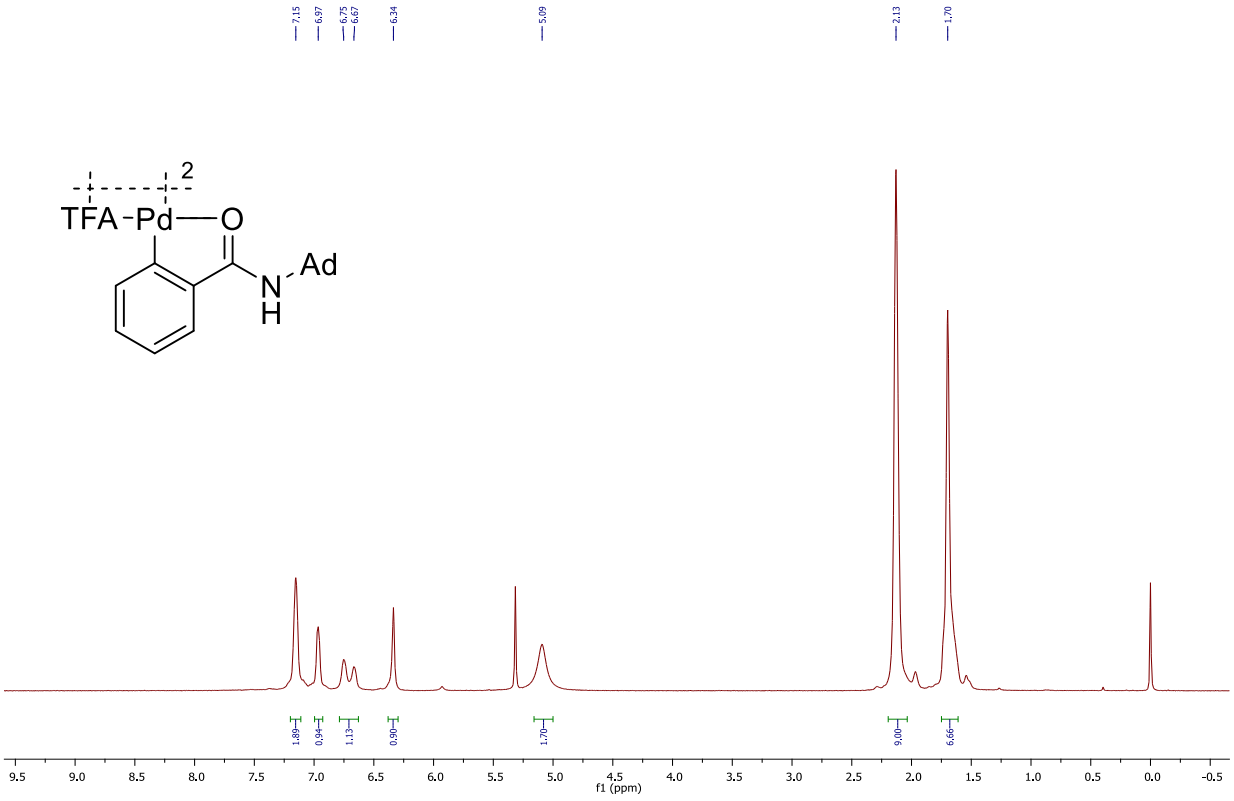


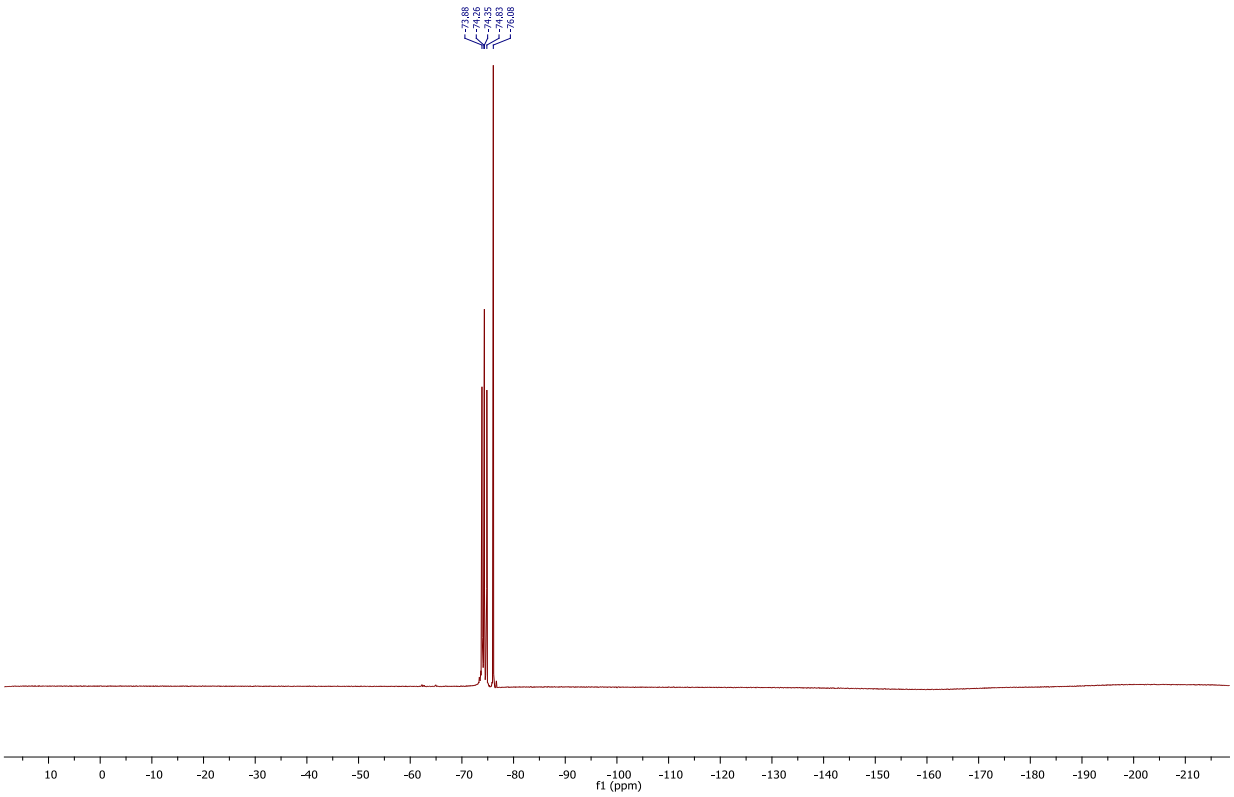
1 PDA Multi 1 / 254nm 4nm

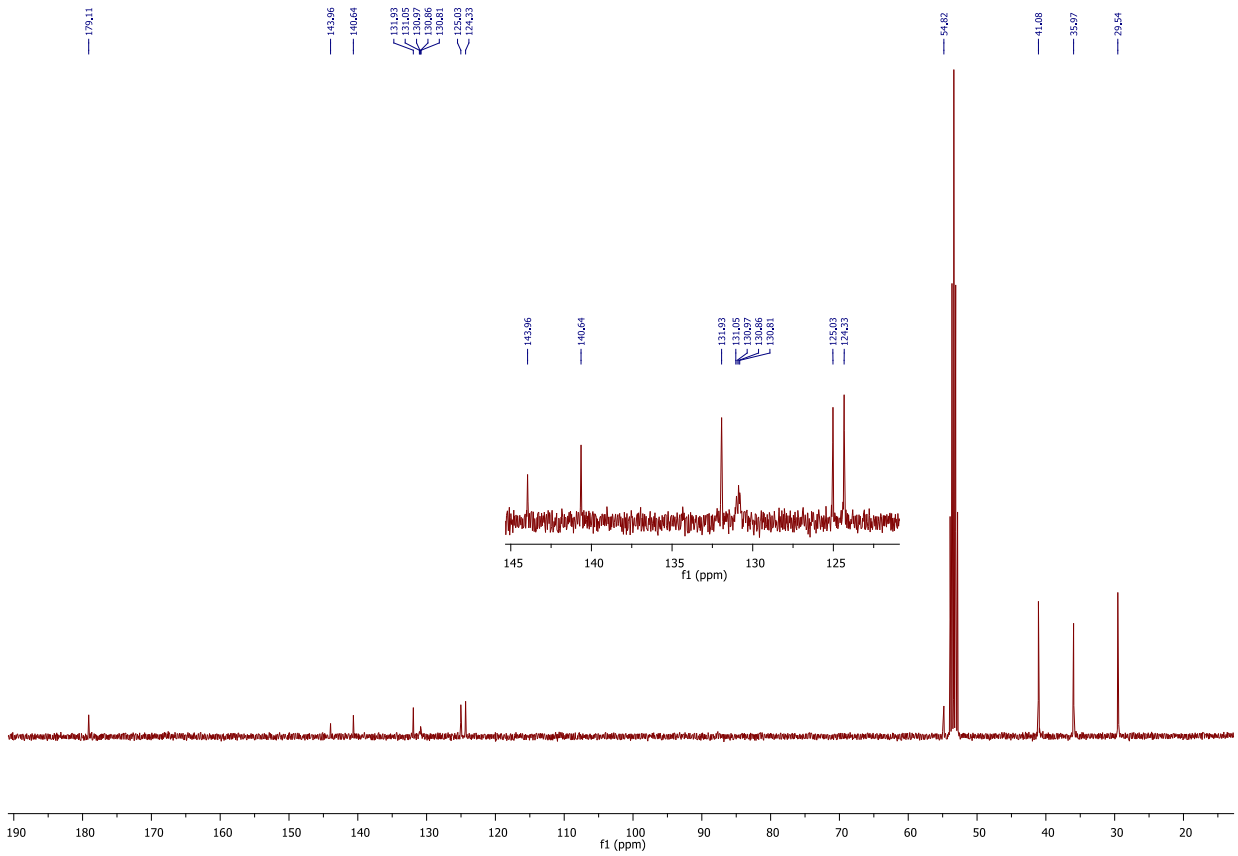
PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.324	120938	8543	97.201	97.736
2	9.181	3483	198	2.799	2.264
Total		124421	8741	100.000	100.000


7.15
6.97
6.75
6.67
6.34
5.09
2.13
1.70
2
TFA-Pd—O
N
H
Ad
1.89
0.94
1.13
0.90
1.70
9.00
6.66
f1 (ppm)


-73.88
-74.26
-74.35
-74.43
-76.08
f1 (ppm)


179.11
143.96
140.64
131.93
131.05
130.97
130.86
130.81
125.03
124.33
54.82
41.08
35.97
29.54
f1 (ppm)