Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

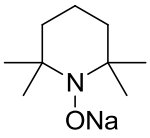
Determintation of Rate Constants for Trifluoromethyl Radical Addition to Various Alkenes via a Practical Method

Marcel Hartmann, Yi Li and Armido Studer*

Institute of Organic Chemistry, Westfälische Wilhelms-University Münster, Corrensstrasse 40, 48149 Münster, Germany
studer@uni-muenster.de

General: All reactions involving air- or moisture-sensitive reagents or intermediates were carried out in pre-heated glassware under an argon atmosphere using standard *Schlenk* techniques. THF was freshly distilled from K under argon. All other solvents and reagents were purified according to standard procedures or were used as received from Aldrich, TCI, Acros or ABCR. IR spectra were recorded on a *Digilab FTS 4000* with a *Specac MKII Golden Gate Single Reflection ART System.* ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a *DPX* 300 *or DD2 600* at 300 K. Spectra were calibrated relative to solvent's residual proton and carbon chemical shift: $CHCl_3$ (δ = 7.26 for ^{1}H NMR and δ = 77.0 for ^{13}C NMR). TLC was performed using Merck silica gel 60 F-254 plates, detection of compounds with UV light or dipping into a solution of $KMnO_4$ (1.5 g in 400 mL H_2O, 5 g $NaHCO_3$), followed by heating. Flash column chromatography (FC) was performed using Merck or Fluka silica gel 60 (40-63 μm) applying an argon pressure of about 0.2 bar. Mass spectra were recorded on a *Finnigan MAT 4200S*, a *Bruker Daltonics Micro Tof*, a *Waters-Micromass Quatro LCZ* (ESI); peaks are given in *m/z* (% of basis peak).

General procedure for the preparation of sodium 2,2,6,6-tetramethylpiperidine-1-olate (2) (TEMPONa)[1] solution (GP1):



Freshly cleaned sodium (0.22 g, 9.5 mmol, 1.4 eq.) was placed in a flame-dried Schlenk-tube under argon. The sodium was melted with a heat-gun (200 °C) until a sodium mirror was formed at the bottom of the tube. The tube was allowed to cool to room temperature, and THF (8 mL), TEMPO (1.06 g, 6.8 mmol, 1.0 eq.) and naphthalene (0.85 g, 10 mol%) were added under argon. The reaction mixture was stirred at room temperature until a dark blue-black color persisted (1-2 h).

General procedure to determine the rate constants (GP 2):

The TEMPONa solution (0.18 ml, 0.15 mmol, 1.2 equiv. 0.85 M) was added to *Togni*-reagent **1**[2] (40 mg, 125 μmol, 1.0 equiv) or **5**[3] (46 mg, 125 μmol, 1.0 equiv.), alkene (2.5 mmol, 20 equiv.) and TEMPO (0.5 or 2.9 or 3.34 equiv.) in THF (0.5 ml) under Argon via syringe pump over 2 h at room temperature. After completion, the crude reaction mixture was filtered through a short cotton plug and afterwards the ratios of the respective compounds were determined by crude ^{19}F-NMR. The TEMPO anion is readily oxidized and therefore it is necessary to use a freshly prepared TEMPONa solution for the kinetic experiments.

Following, the crude ^{19}F-NMR spectra of the kinetic competition experiments are given. For each compound, one spectrum with the relative ratios is given exemplary. For the determination of the rate constants of the C_2F_5-radical addition, the ratio was determined by integrating the peak areas of the CF_3 moieties.

We additionally ran some experiments at different TEMPO concentrations with styrene as radical acceptor under otherwise identical conditions (**GP2**) and calculated the rate constants:

2.26 equiv TEMPO: 5.0 x 10^7 $M^{-1}s^{-1}$

2.90 equiv TEMPO: 5.5 x 10^7 $M^{-1}s^{-1}$

3.11 equiv TEMPO: 6.3 x 10^7 $M^{-1}s^{-1}$

3.34 equiv TEMPO: 5.0 x 10^7 $M^{-1}s^{-1}$

3.56 equiv TEMPO: 5.7 x 10^7 $M^{-1}s^{-1}$

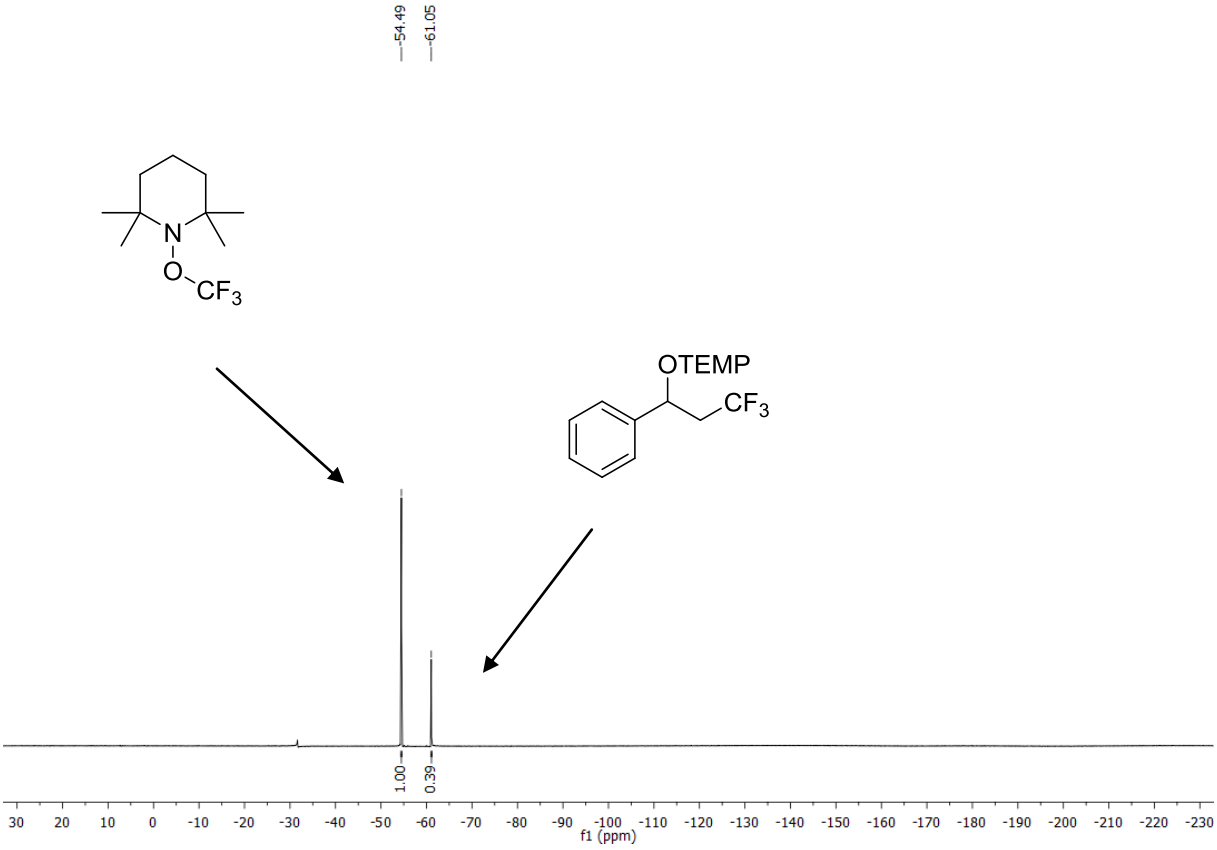
3.78 equiv TEMPO: 5.5 x 10^7 $M^{-1}s^{-1}$

4.01 equiv TEMPO: 5.3 x 10^7 $M^{-1}s^{-1}$

4.22 equiv TEMPO: 4.7 x 10^7 $M^{-1}s^{-1}$

4.45 equiv TEMPO: 5.1 x 10^7 $M^{-1}s^{-1}$

Average: 5.3 x 10^7 (± 0.5) $M^{-1}s^{-1}$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CF3
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0.39
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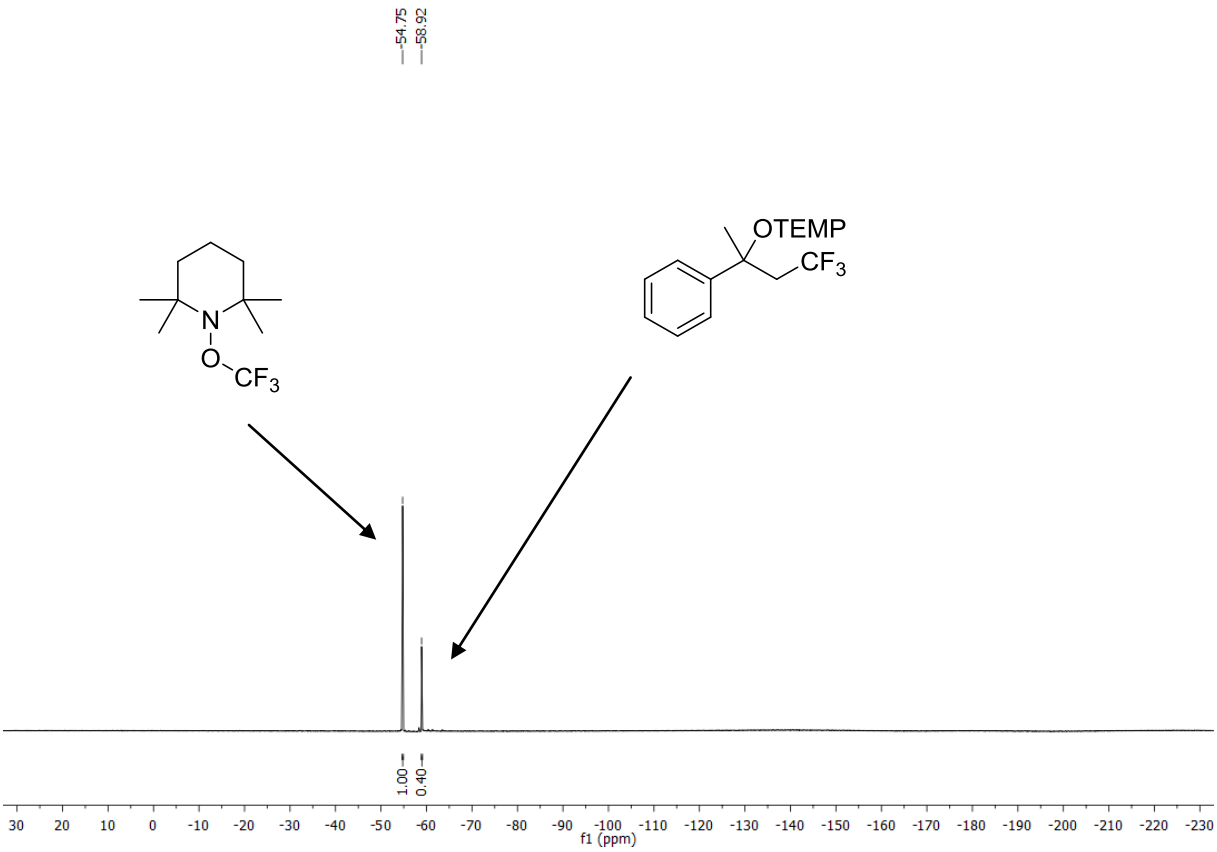
f1 (ppm)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0.40
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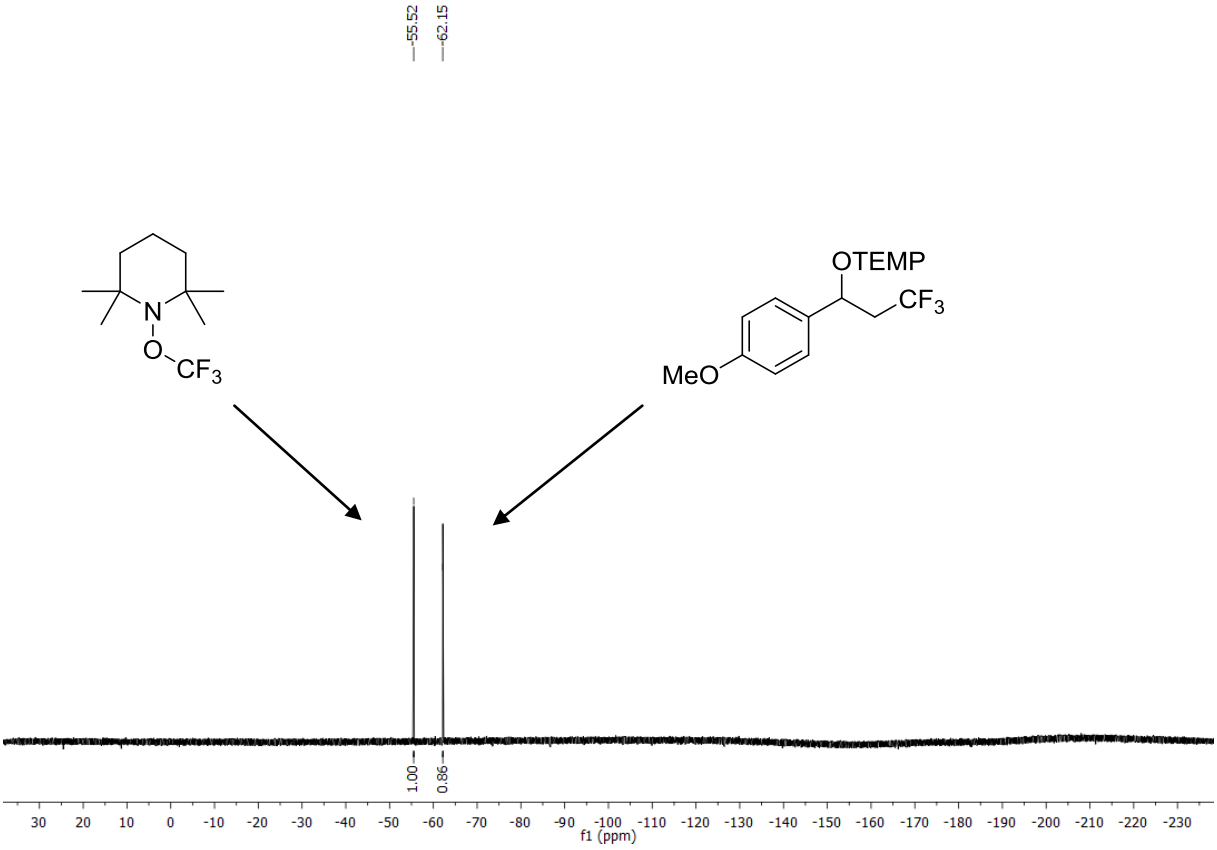
f1 (ppm)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CF3
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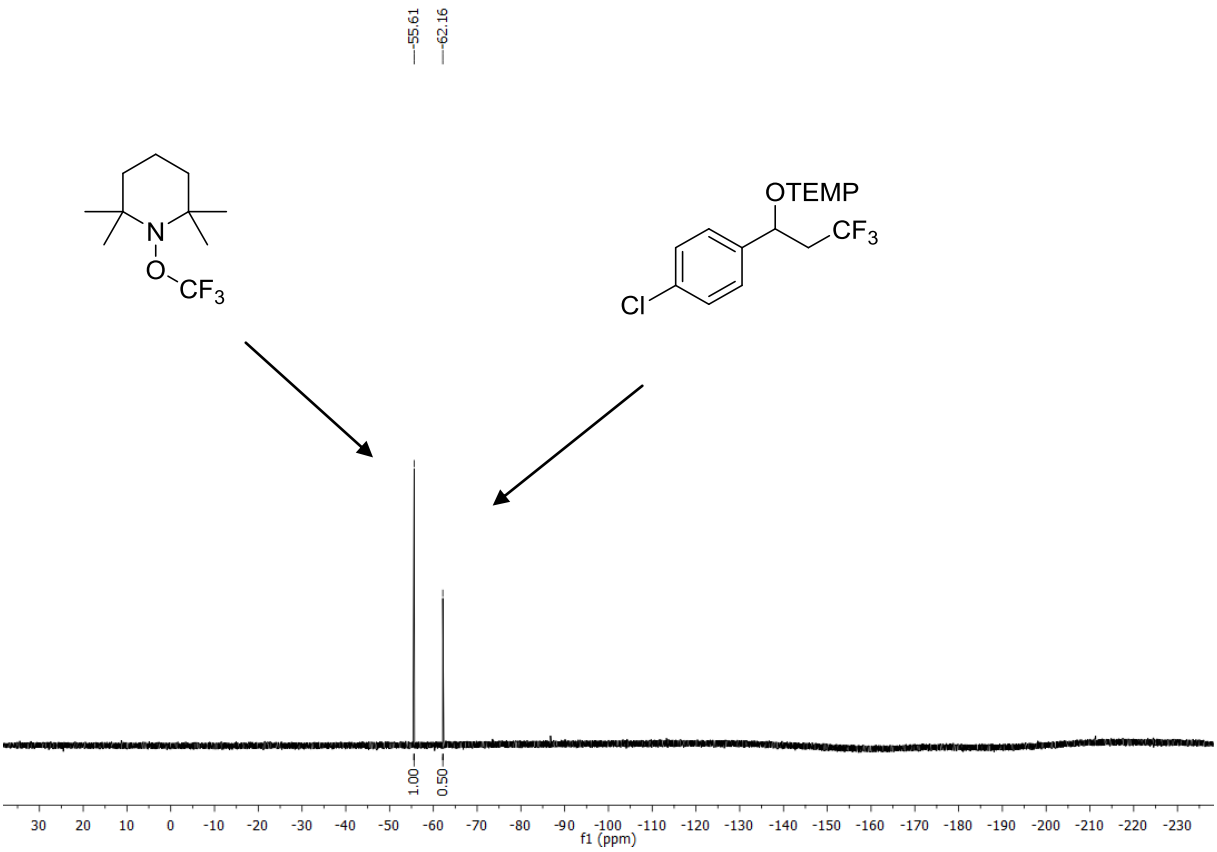
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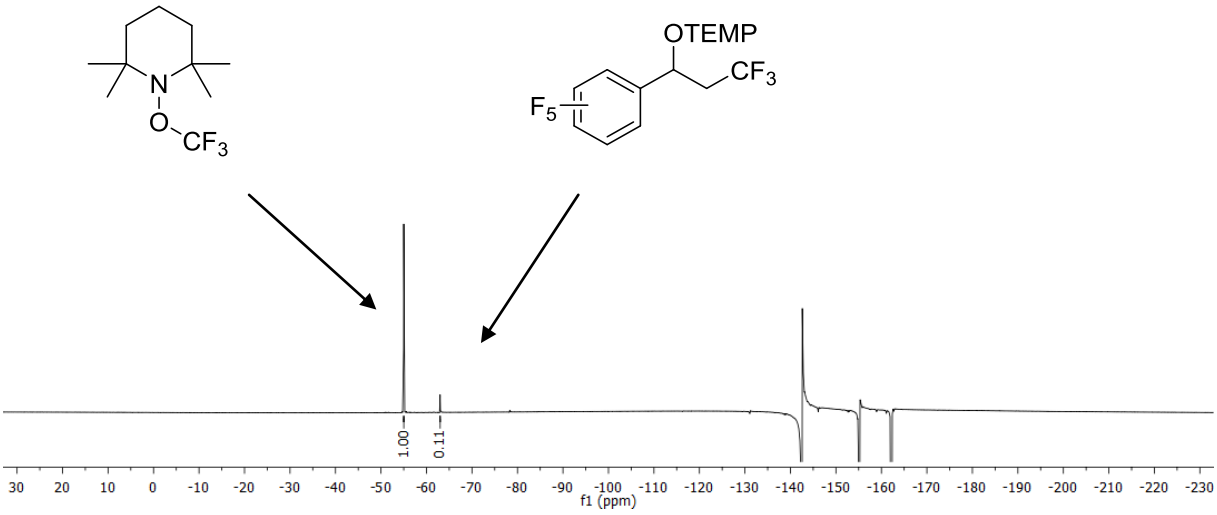
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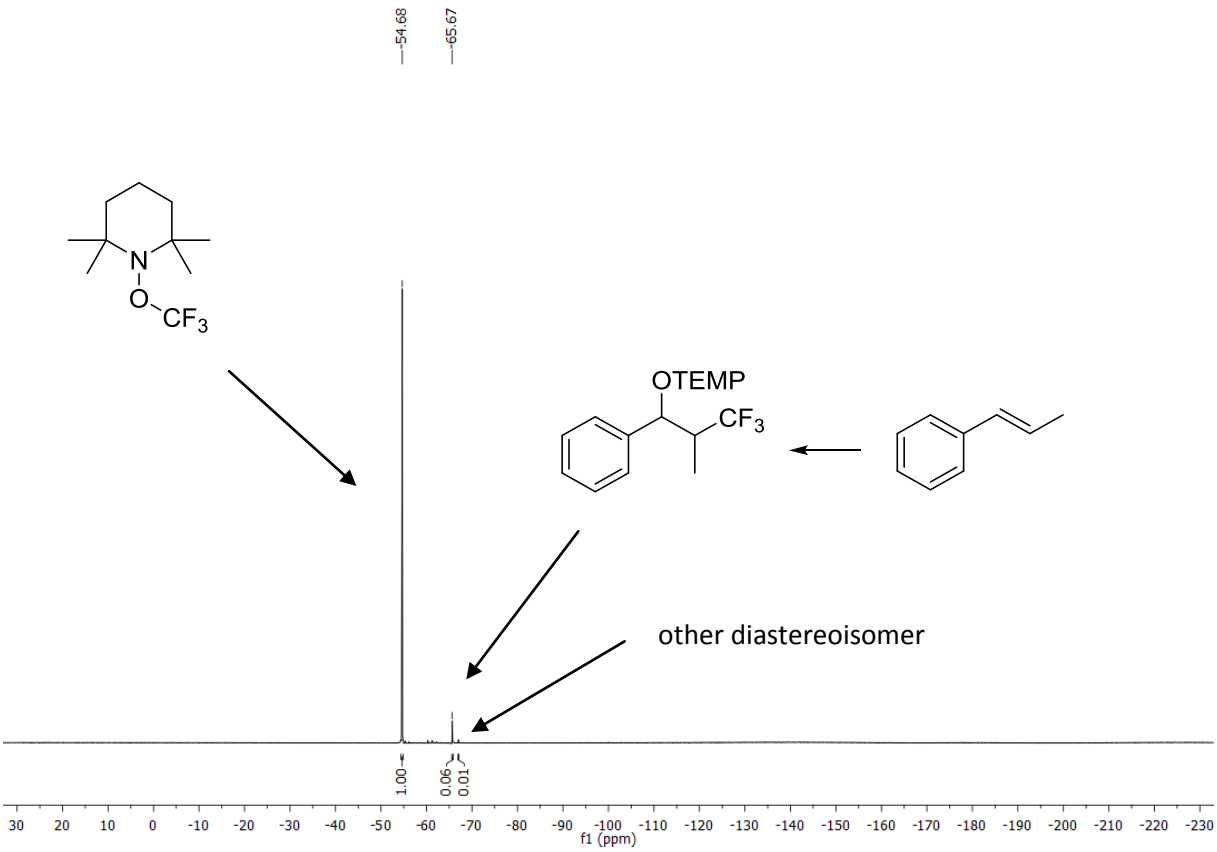
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OTEMP
CF3
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1.00
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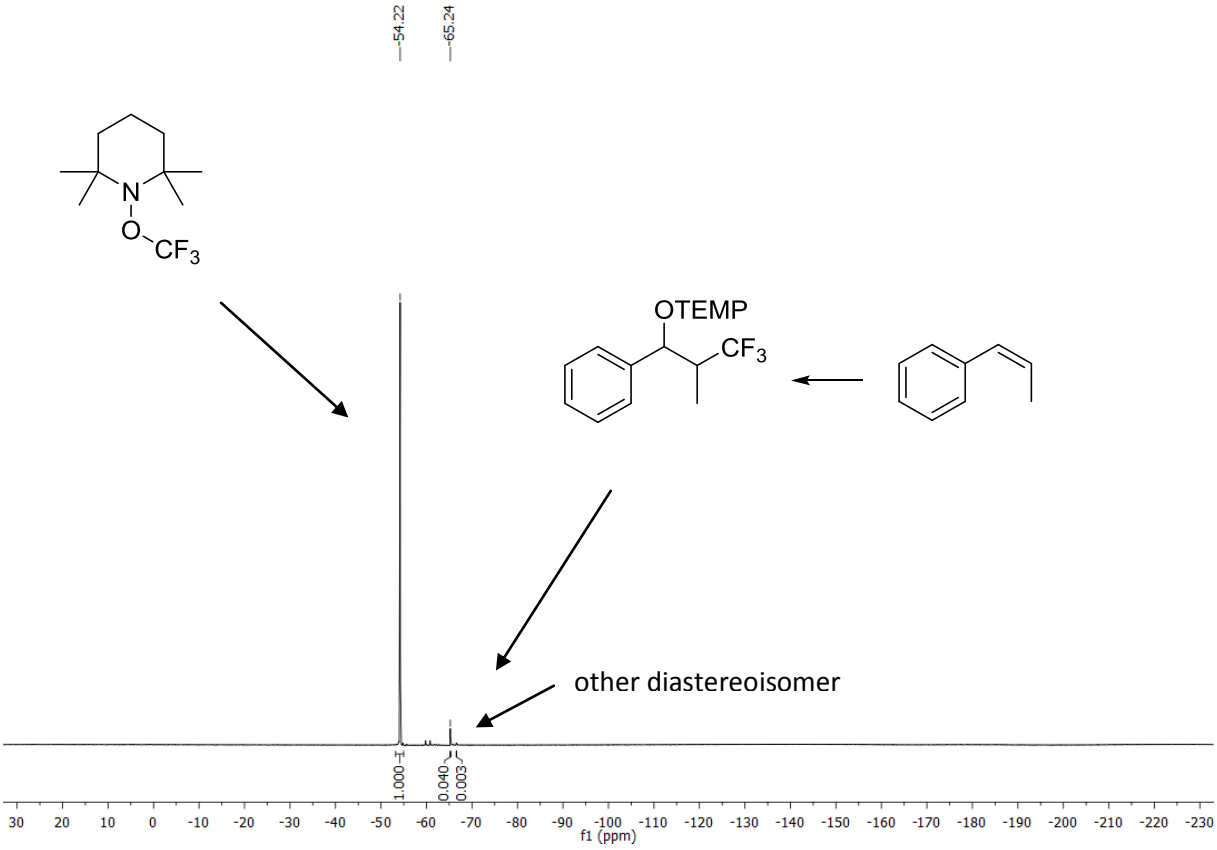
f1 (ppm)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0.040
0.003
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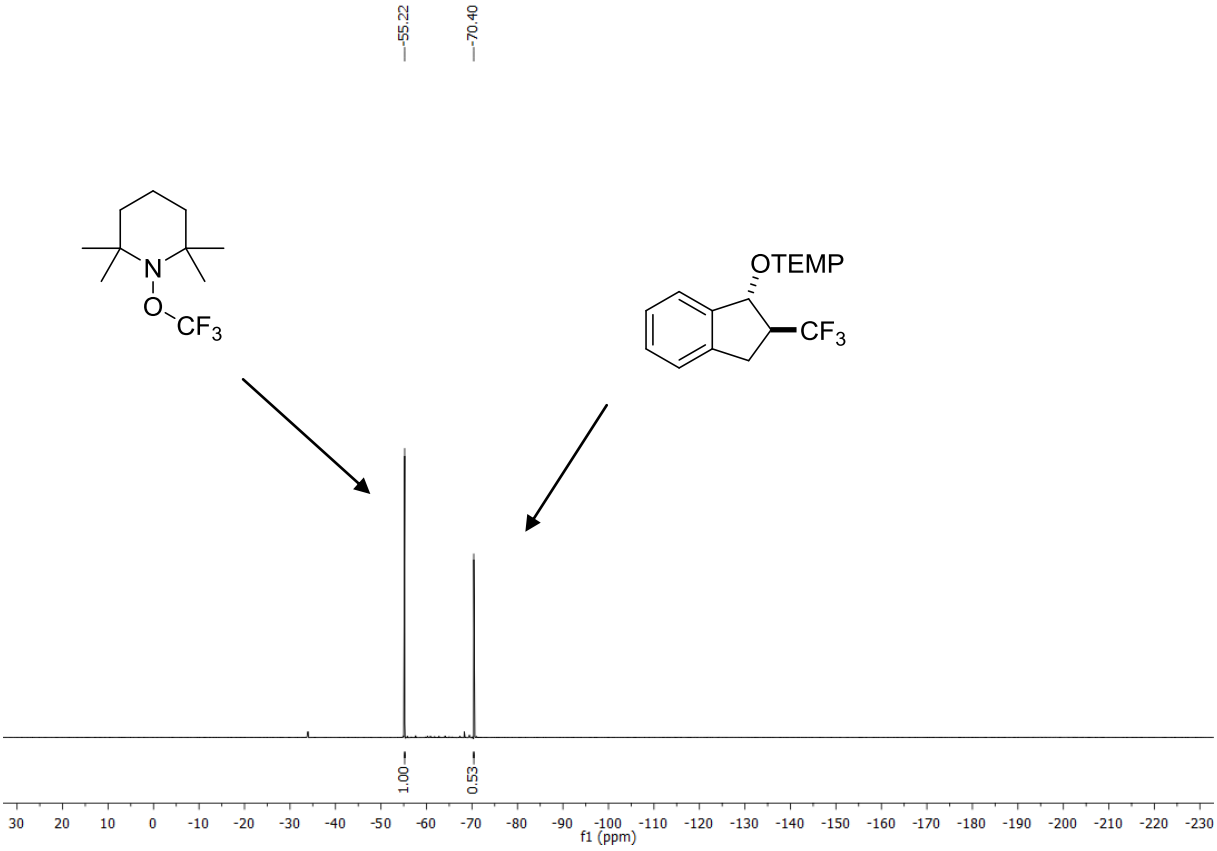
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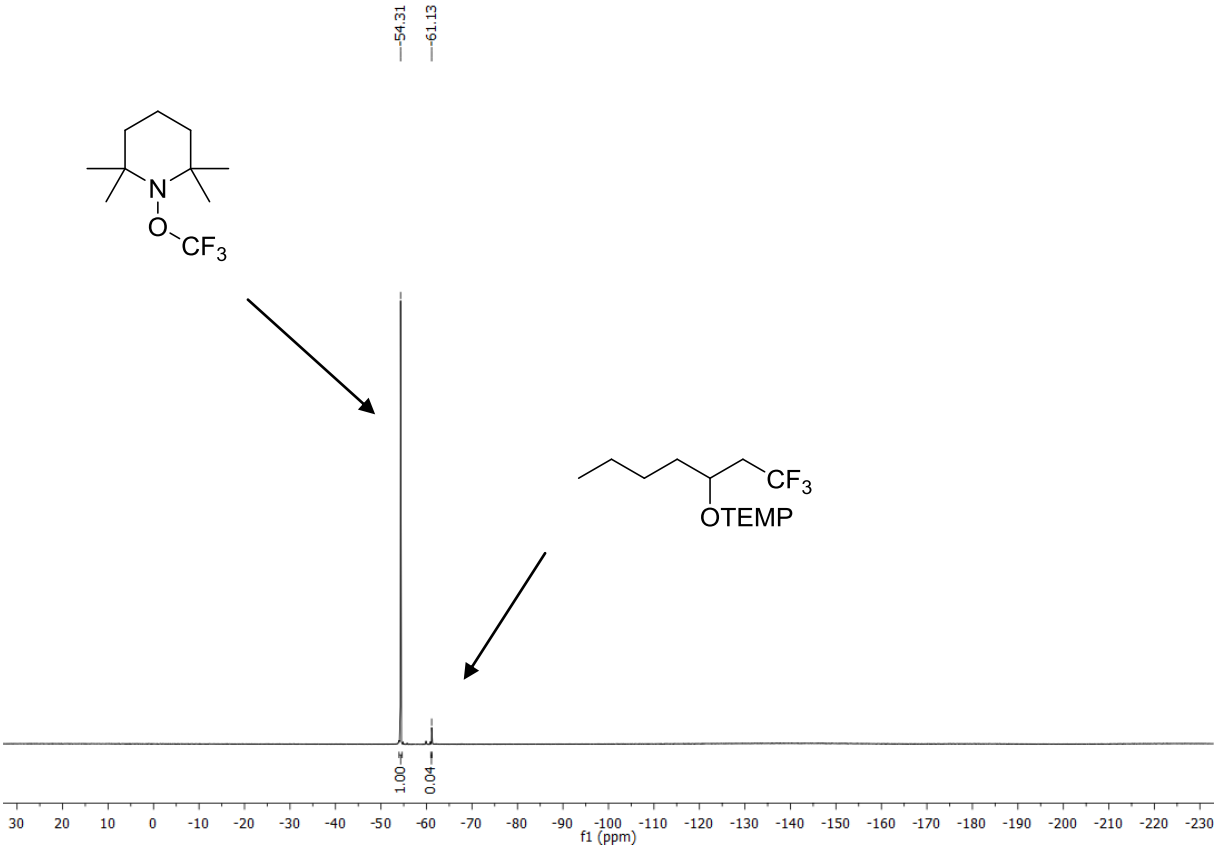
f1 (ppm)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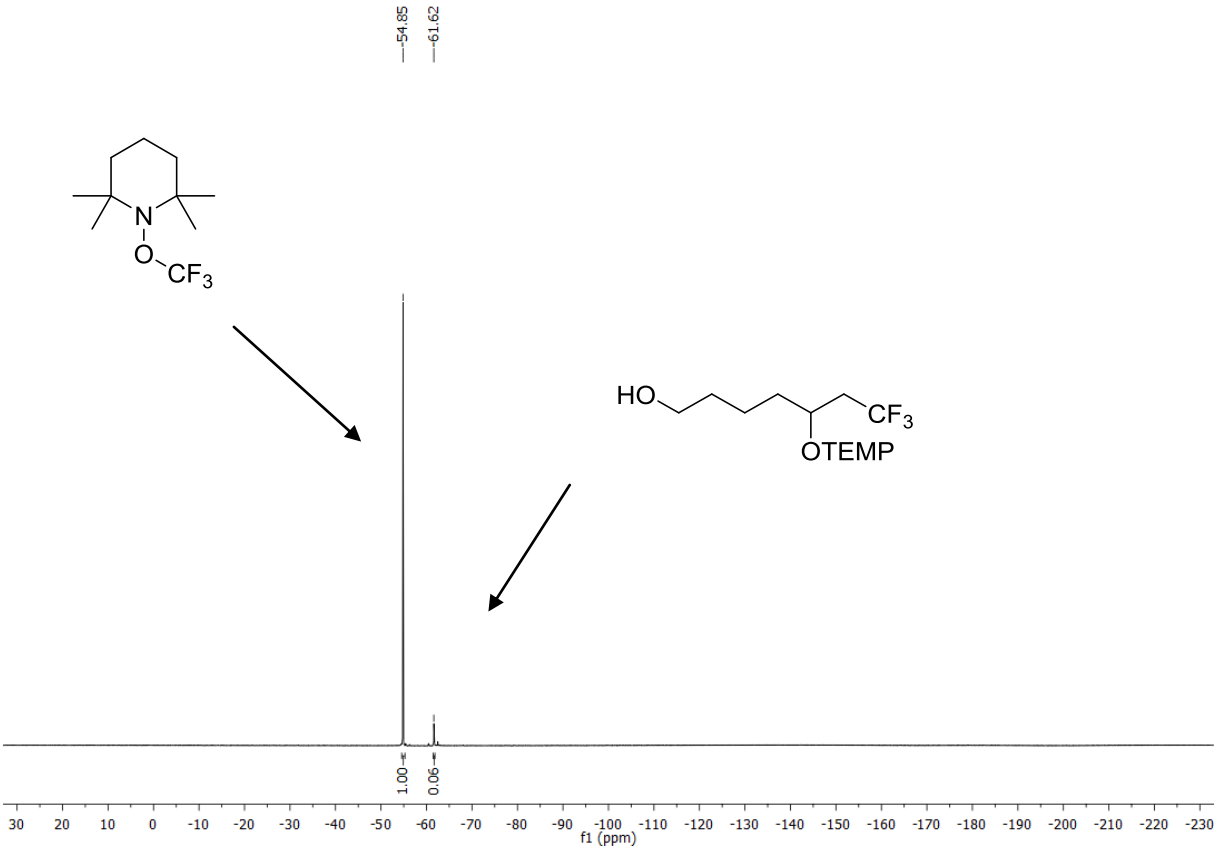
f1 (ppm)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-61.62
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HO
CF3
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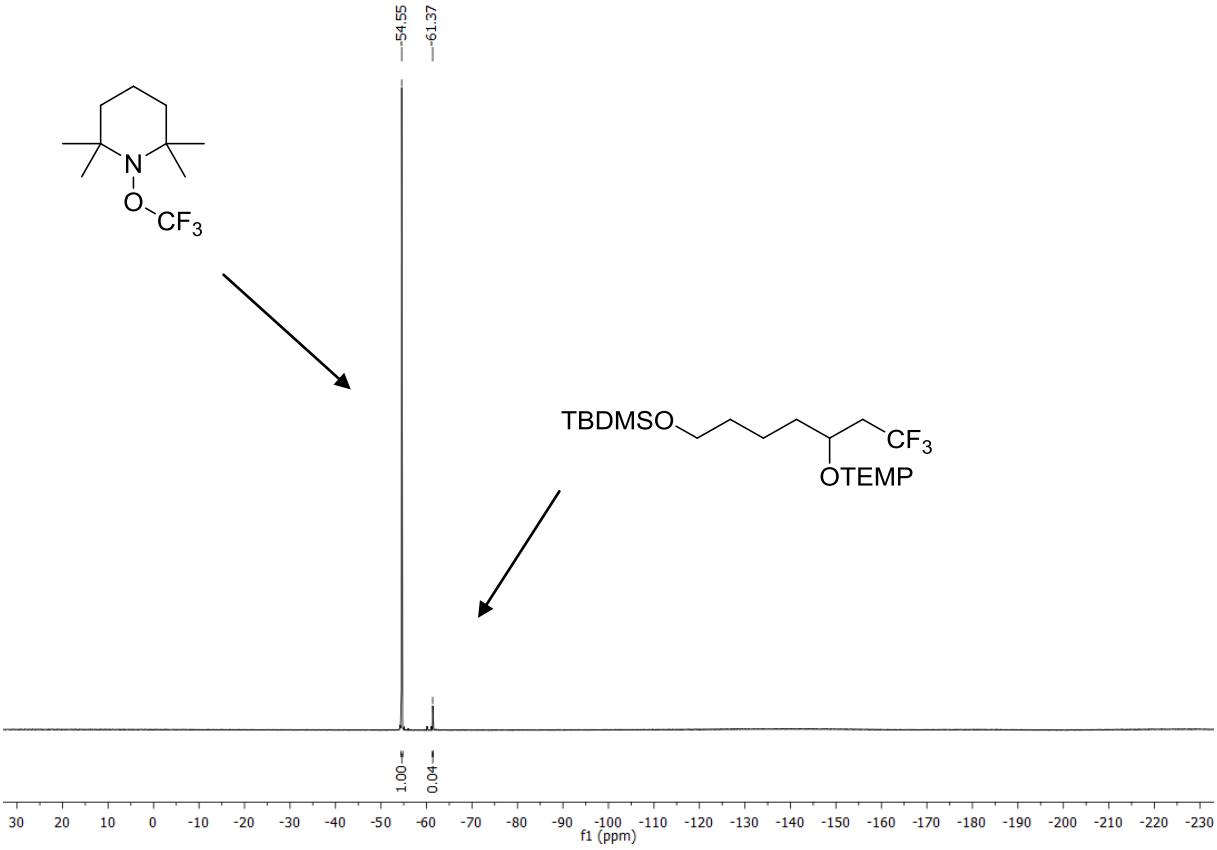
f1 (ppm)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CF3
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CF3
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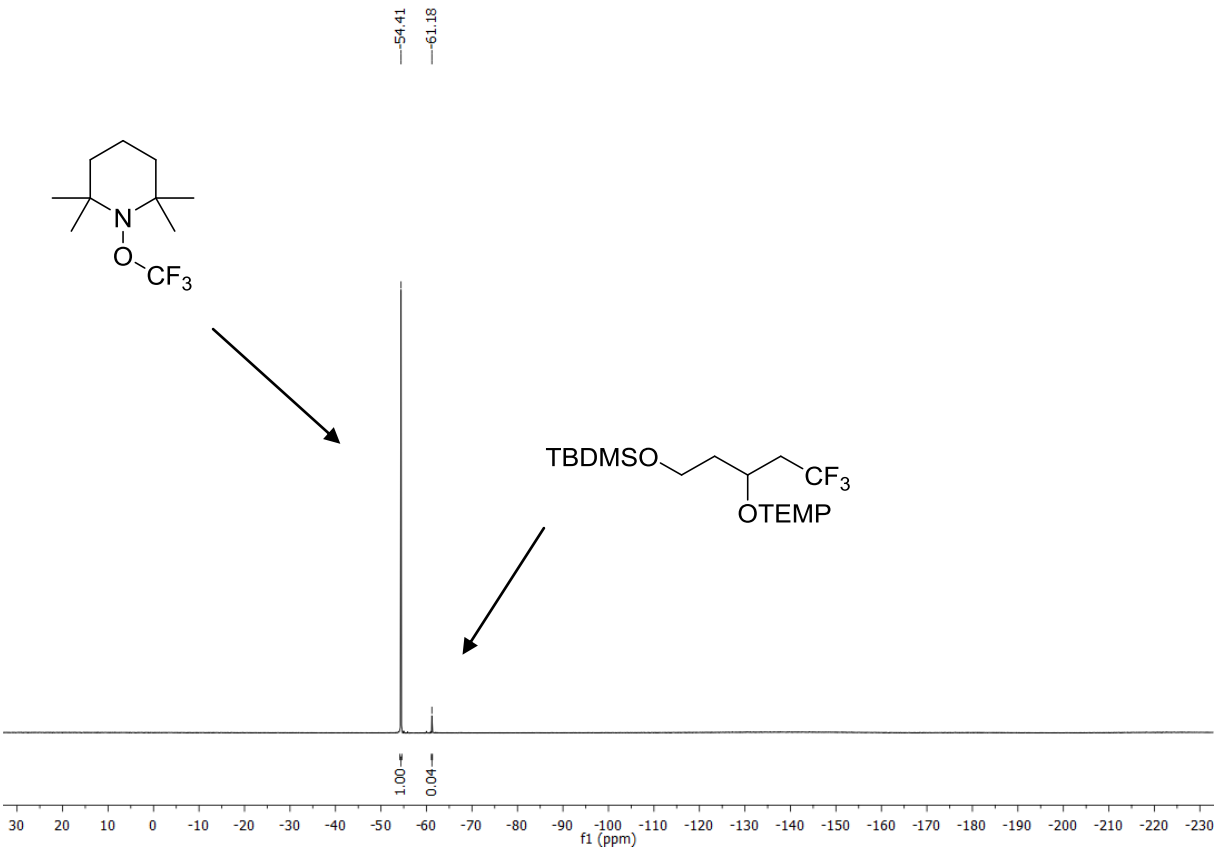
f1 (ppm)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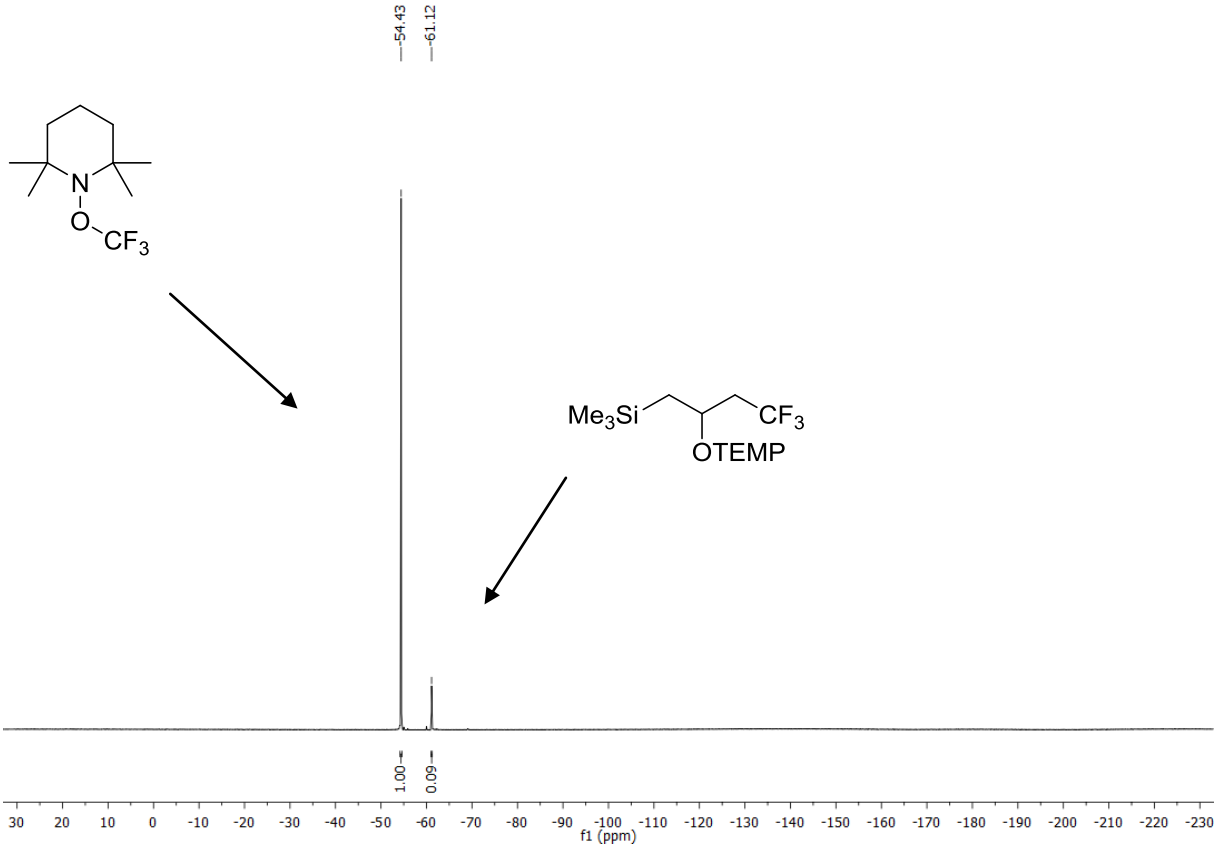
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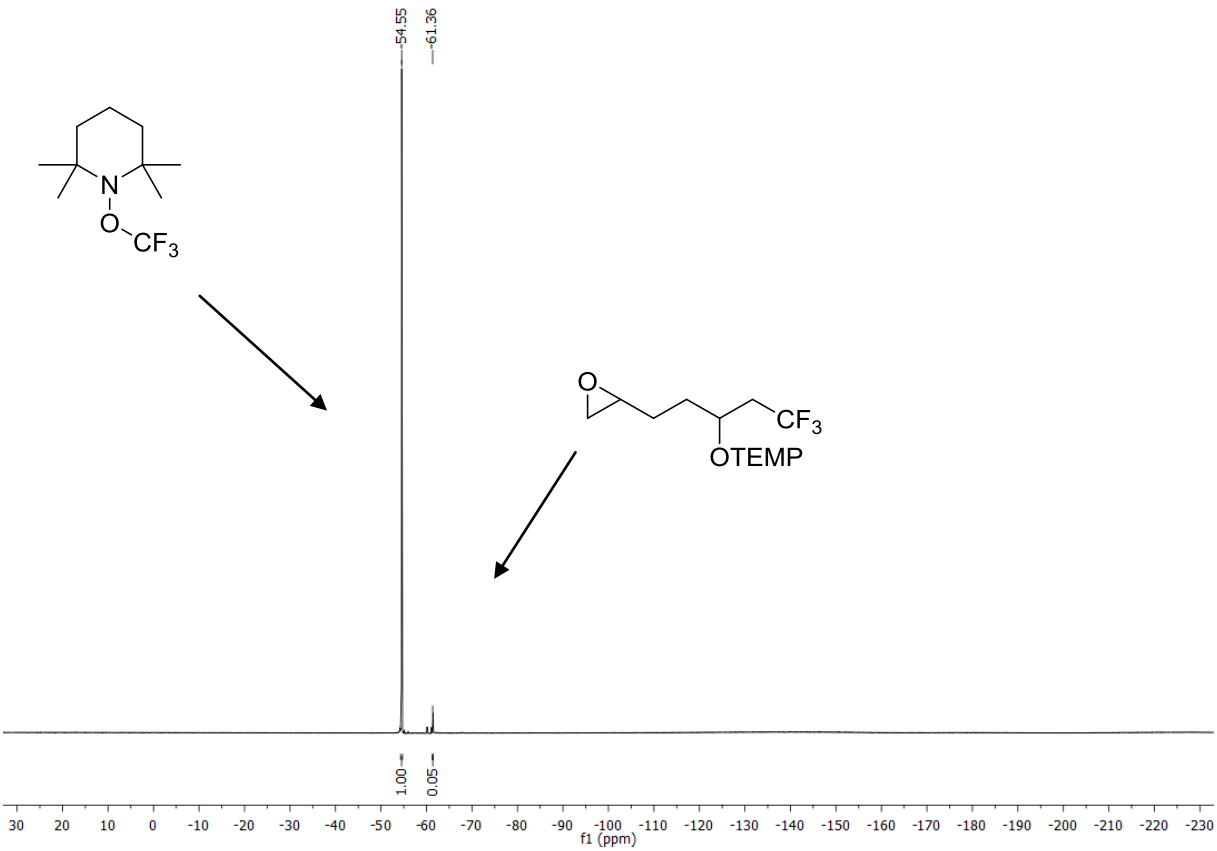
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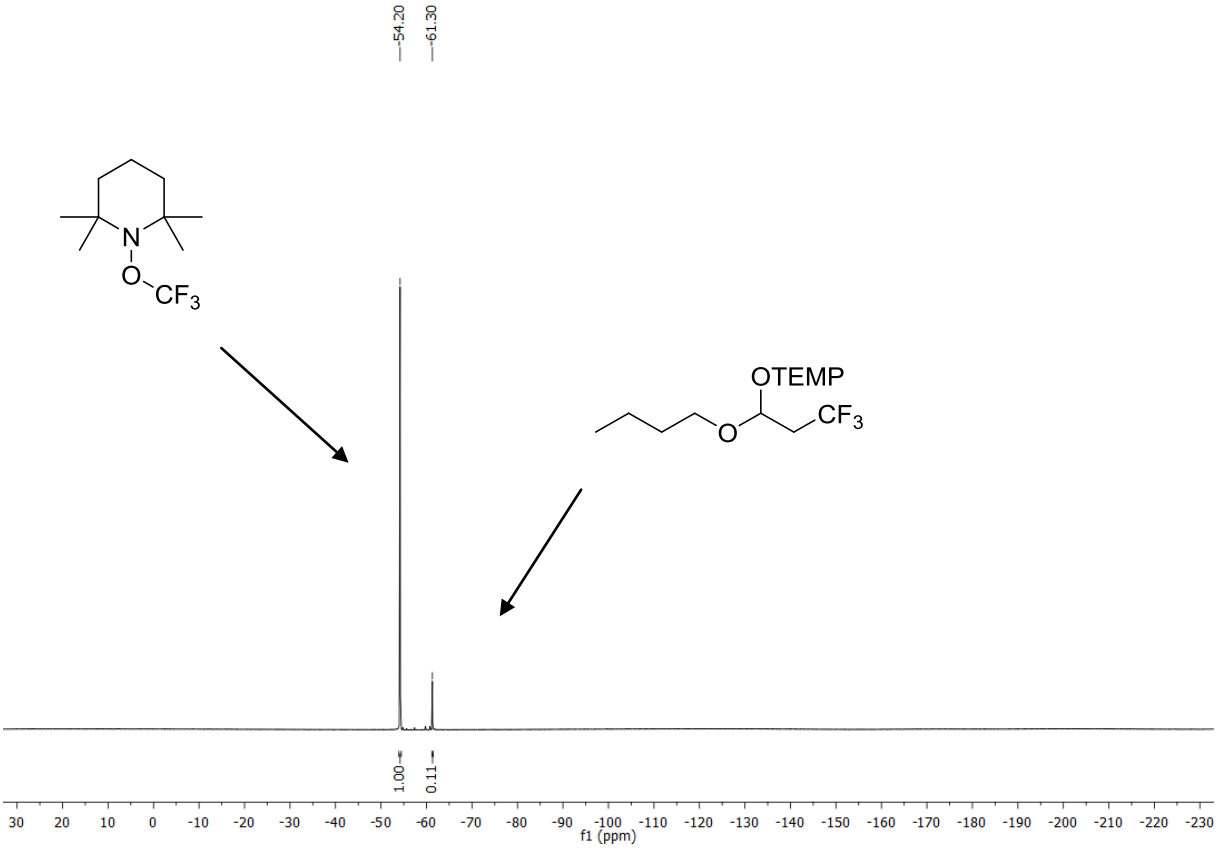
f1 (ppm)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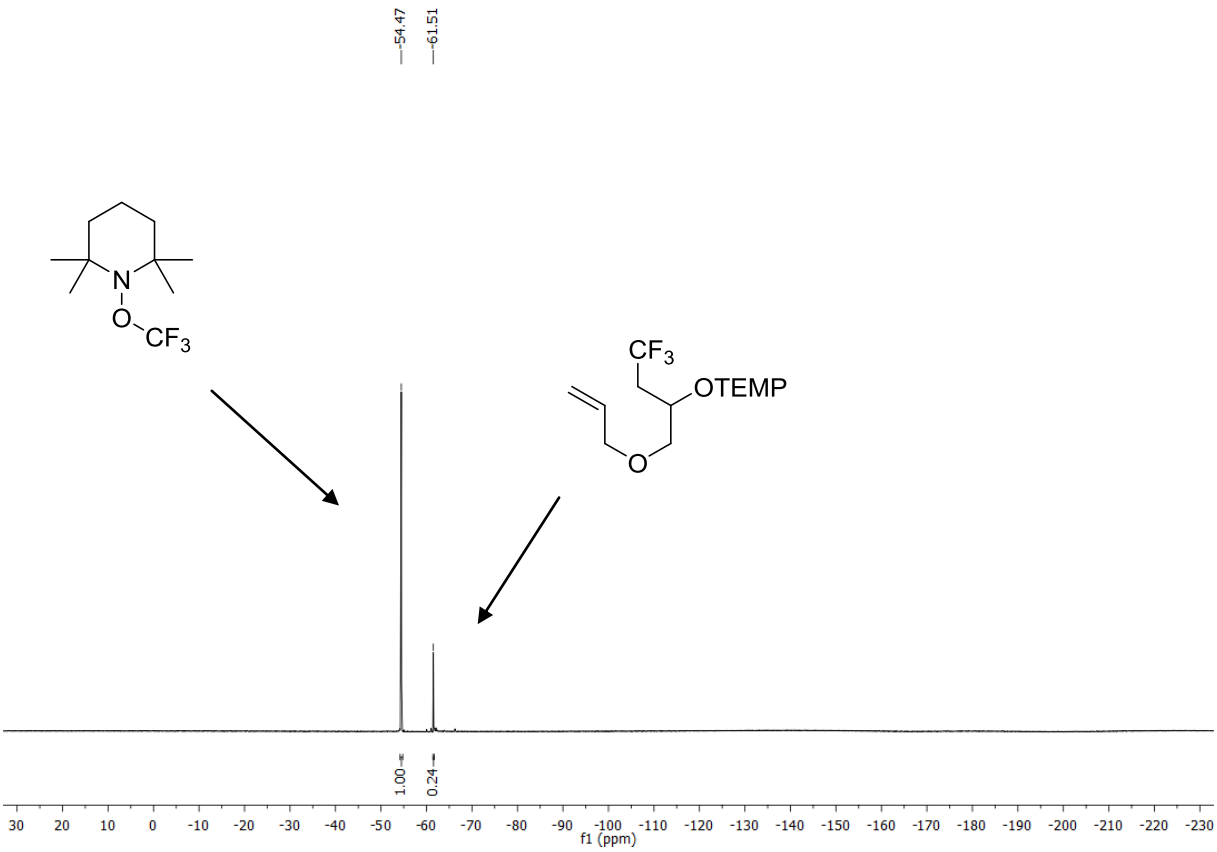
f1 (ppm)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CF3
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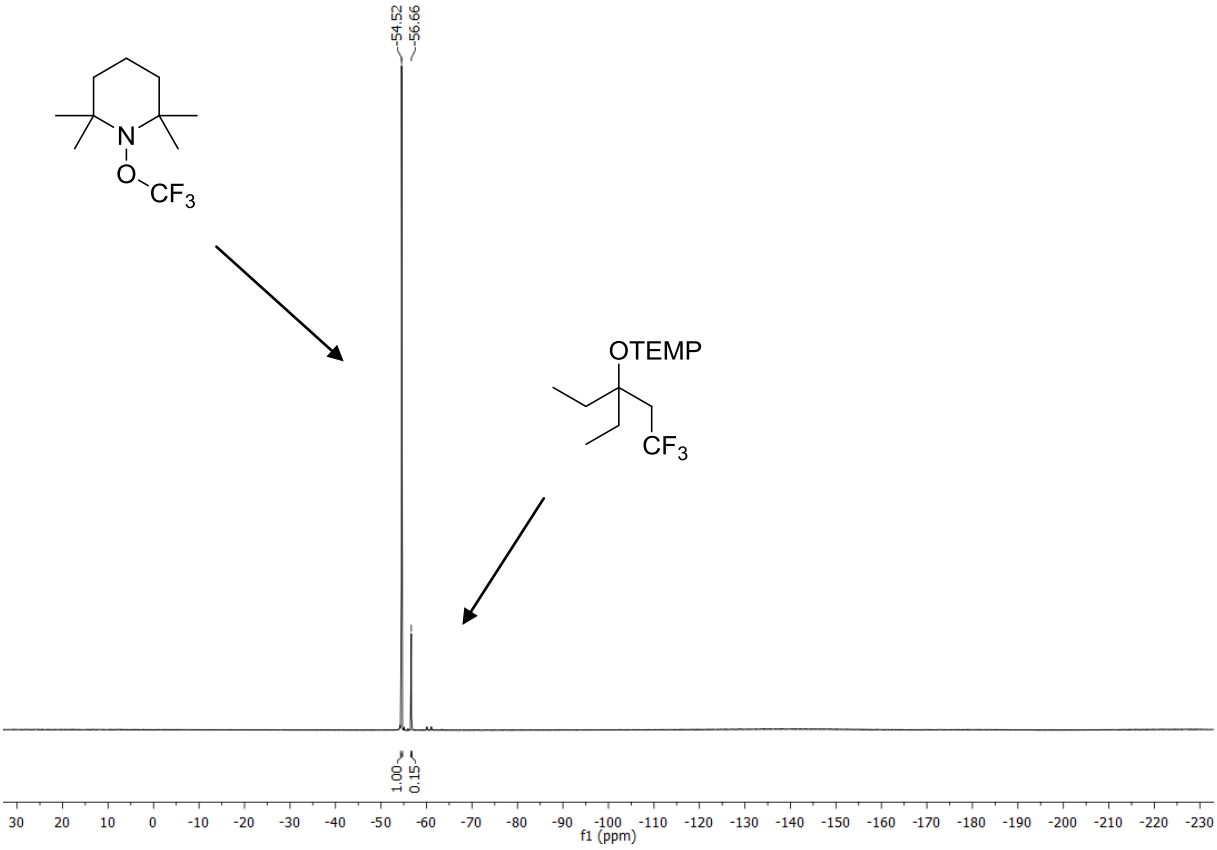
f1 (ppm)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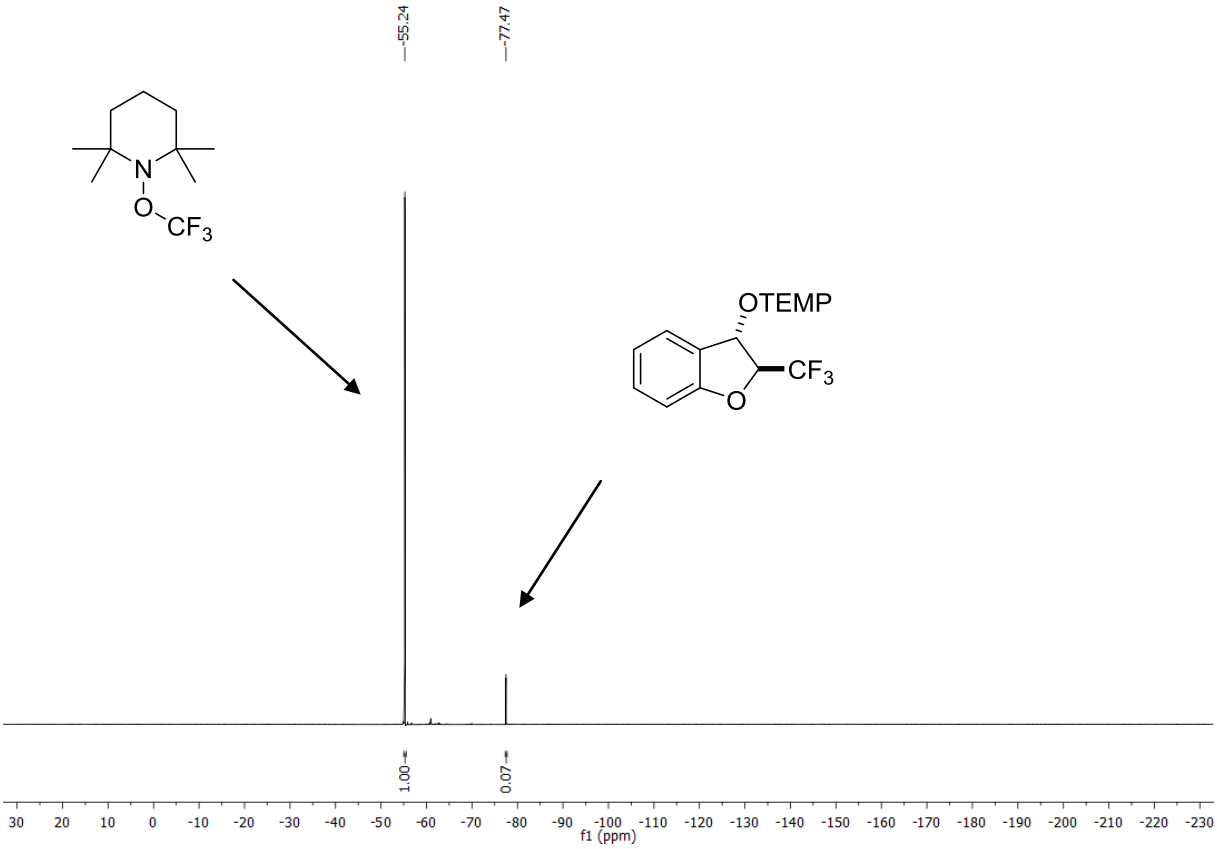
f1 (ppm)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CF3
OTEMP
CF3
O
1.00
0.07
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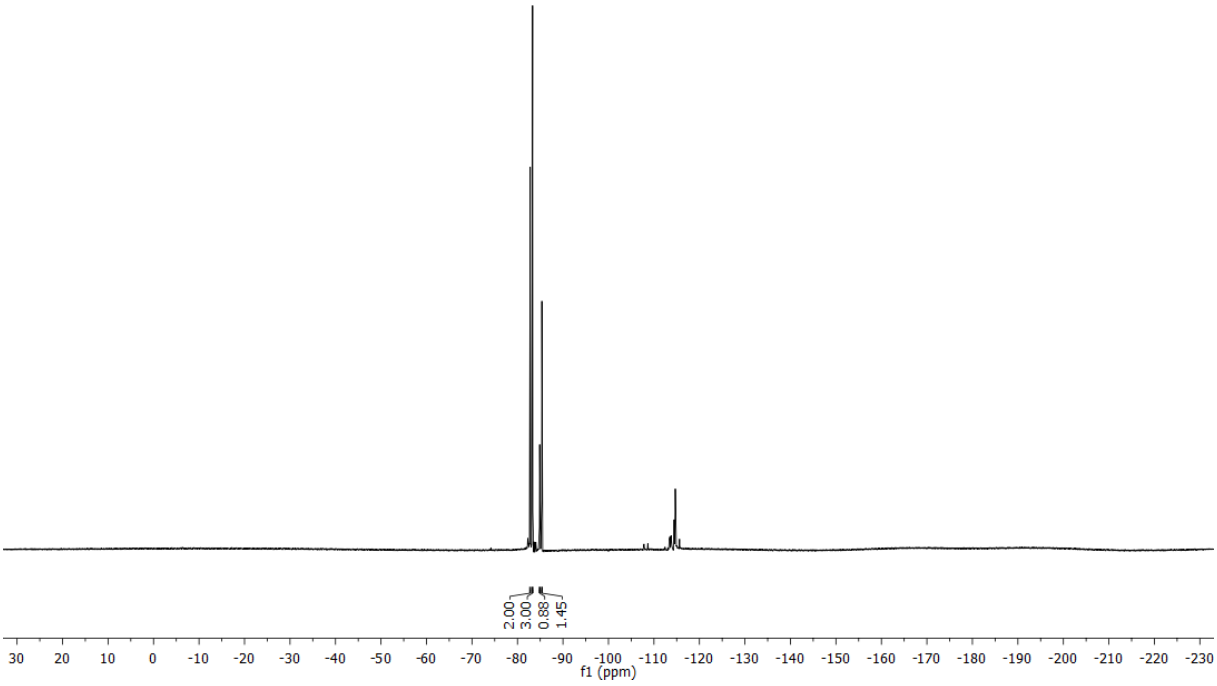
f1 (ppm)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3.00
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1.45
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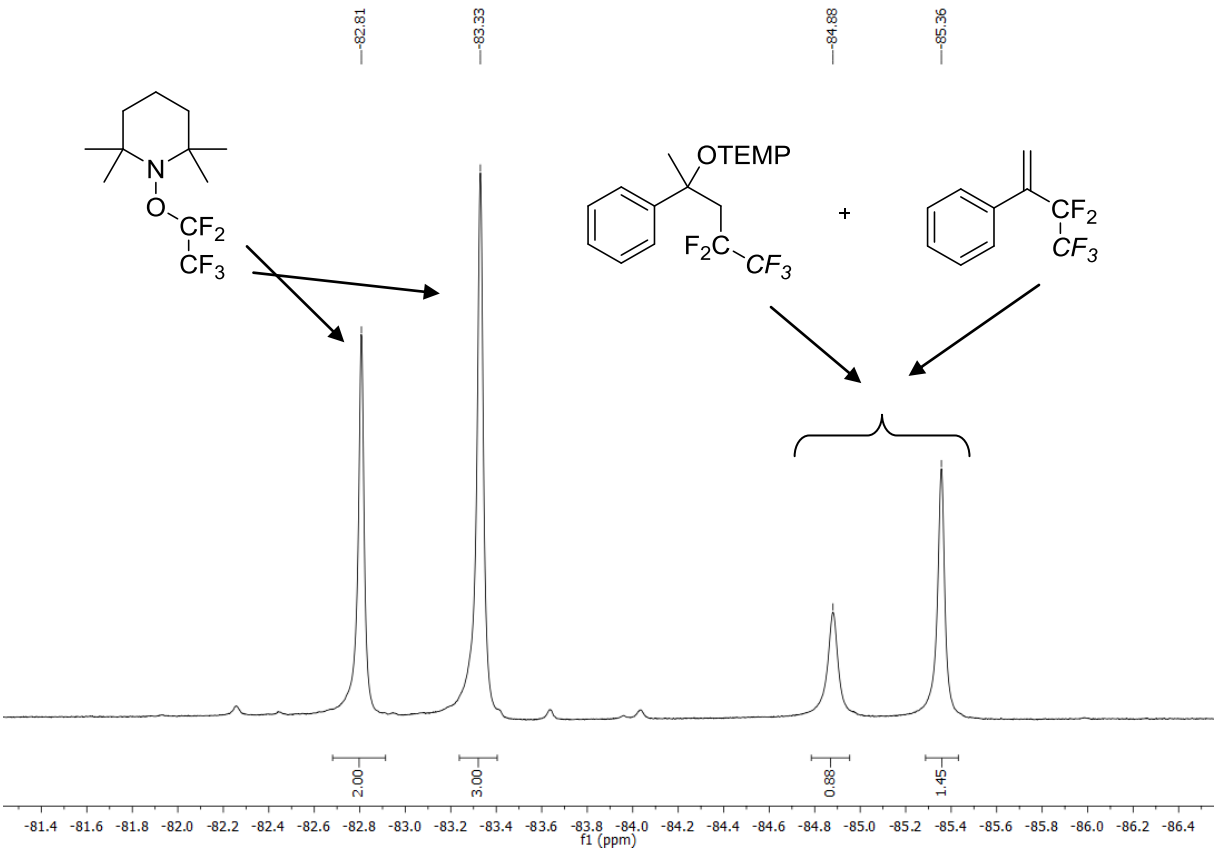
f1 (ppm)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O
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CF3
OTEMP
F2C
CF3
+
CF2
CF3
2.00
3.00
0.88
1.45
-81.4 -81.6 -81.8 -82.0 -82.2 -82.4 -82.6 -82.8 -83.0 -83.2 -83.4 -83.6 -83.8 -84.0 -84.2 -84.4 -84.6 -84.8 -85.0 -85.2 -85.4 -85.6 -85.8 -86.0 -86.2 -86.4
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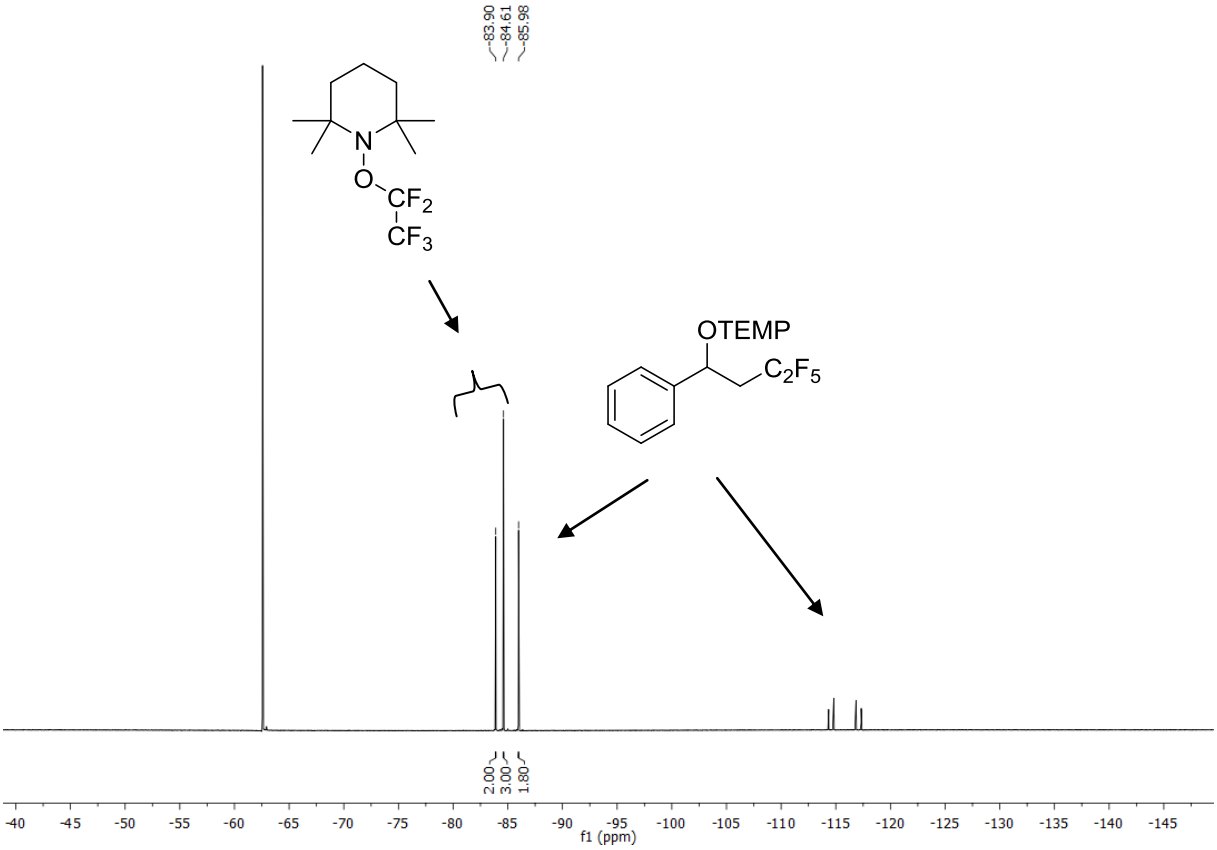
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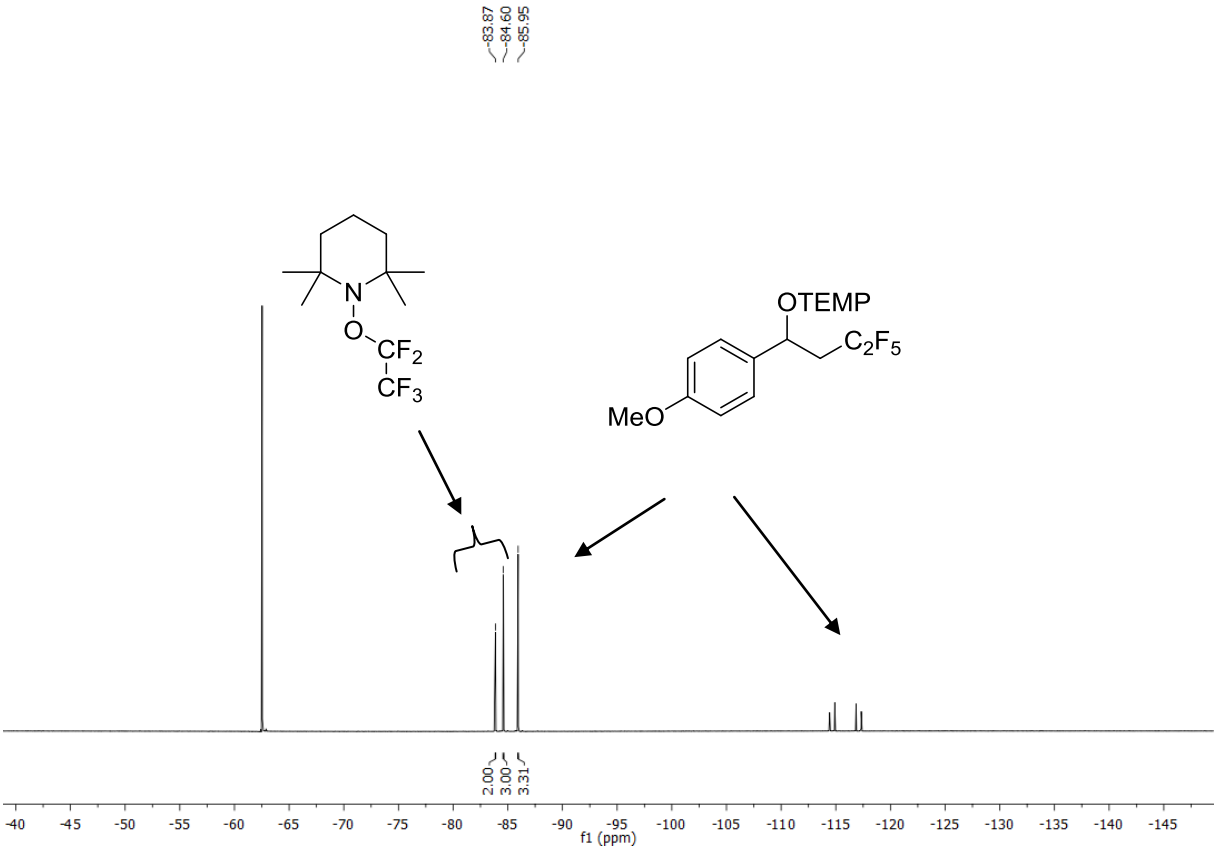
f1 (ppm)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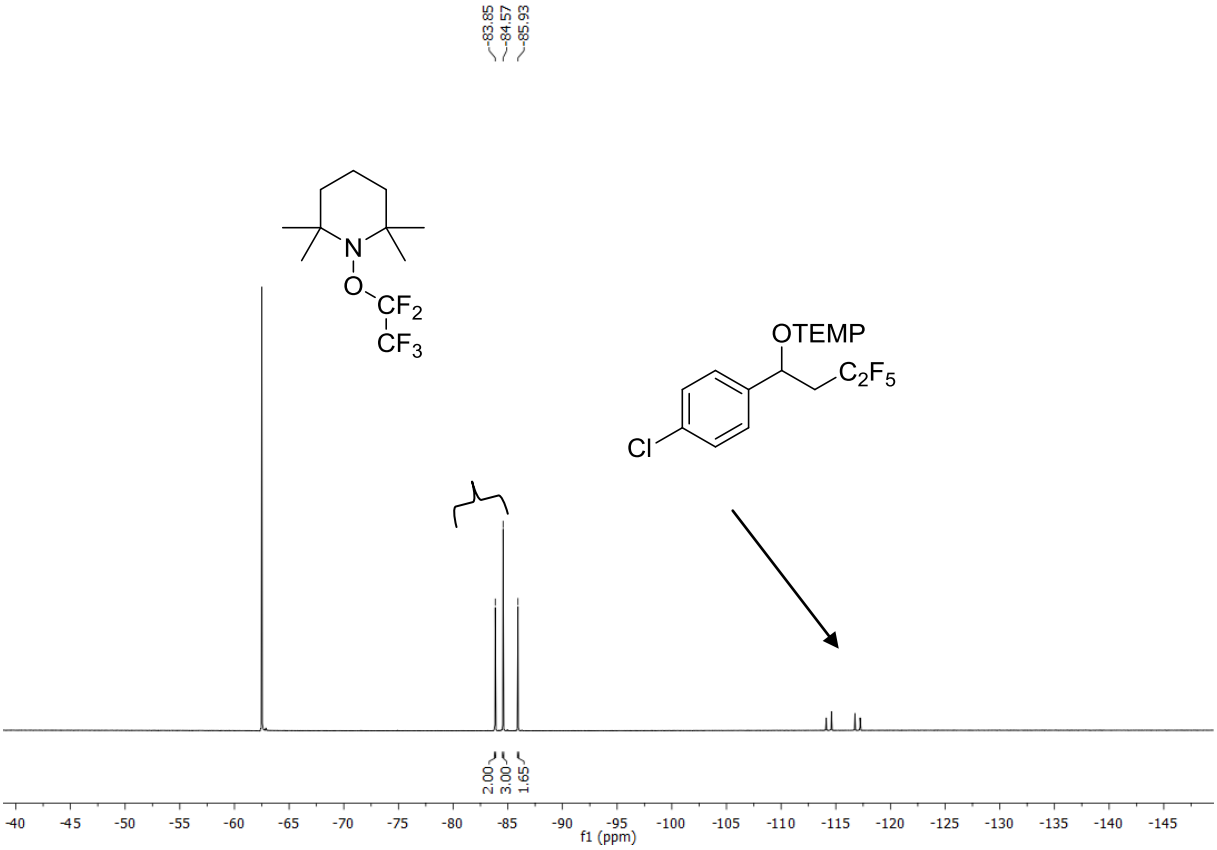
f1 (ppm)



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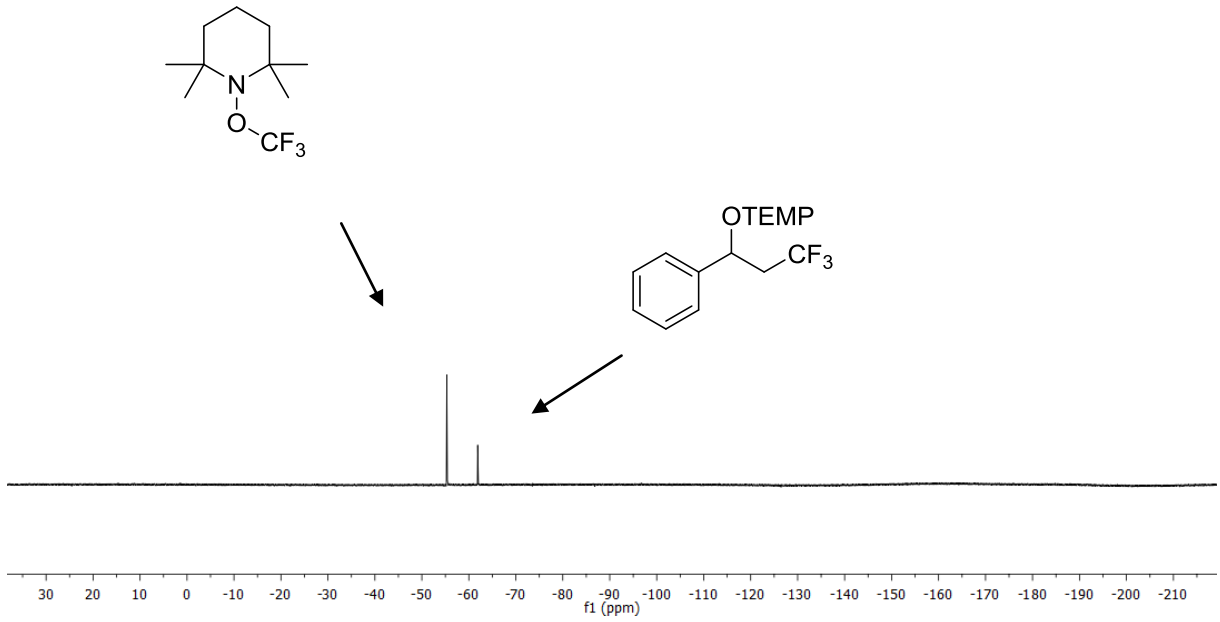
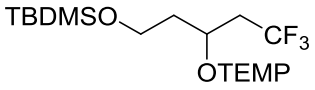
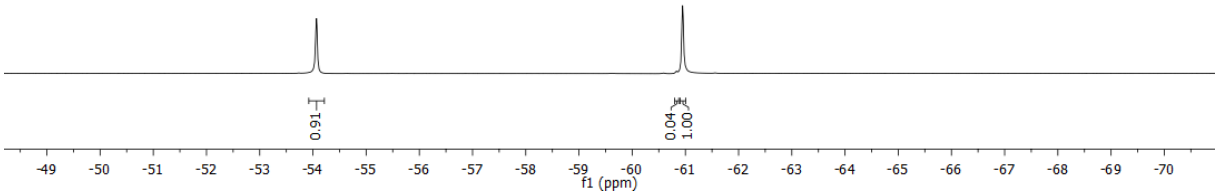
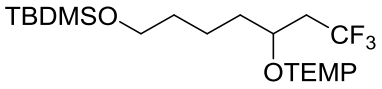


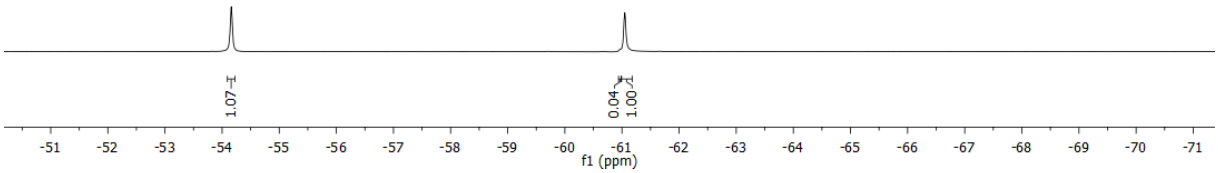
with internal standard ($PhCF_3$)

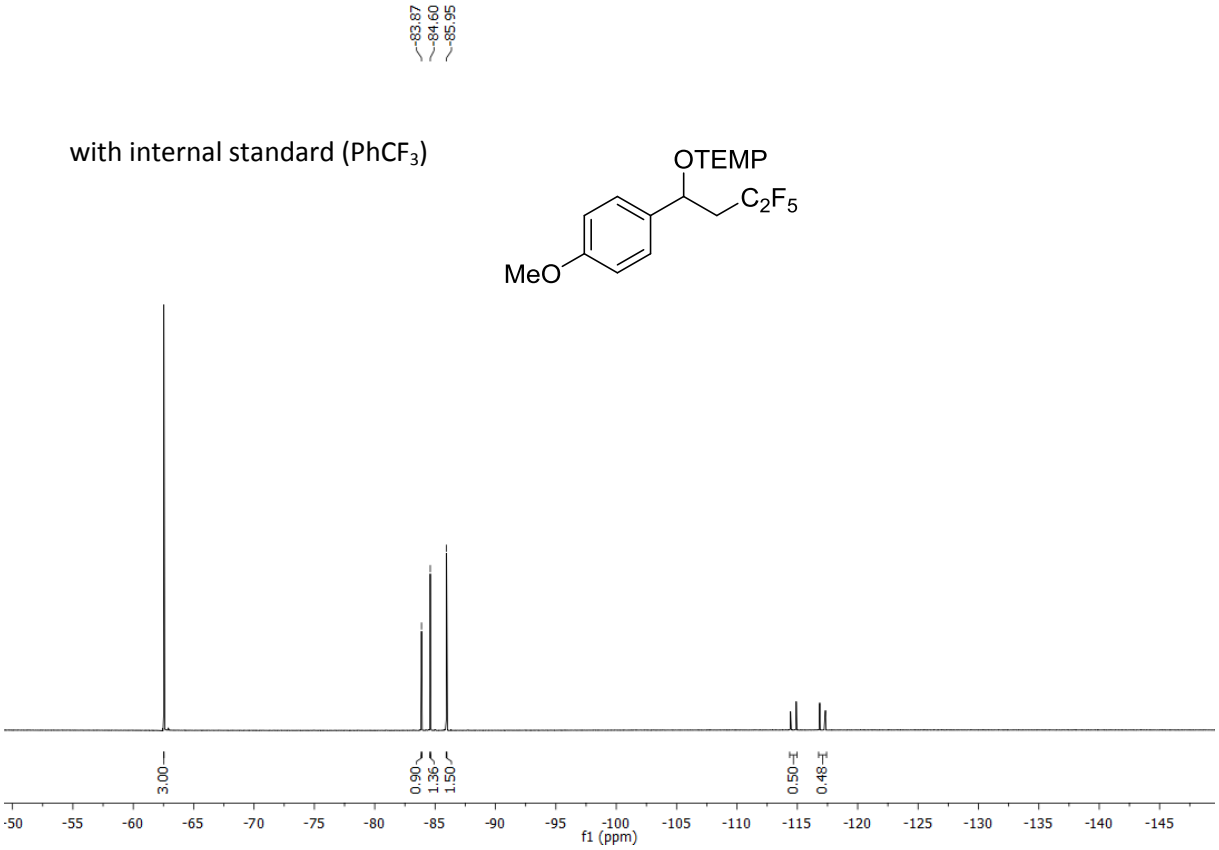


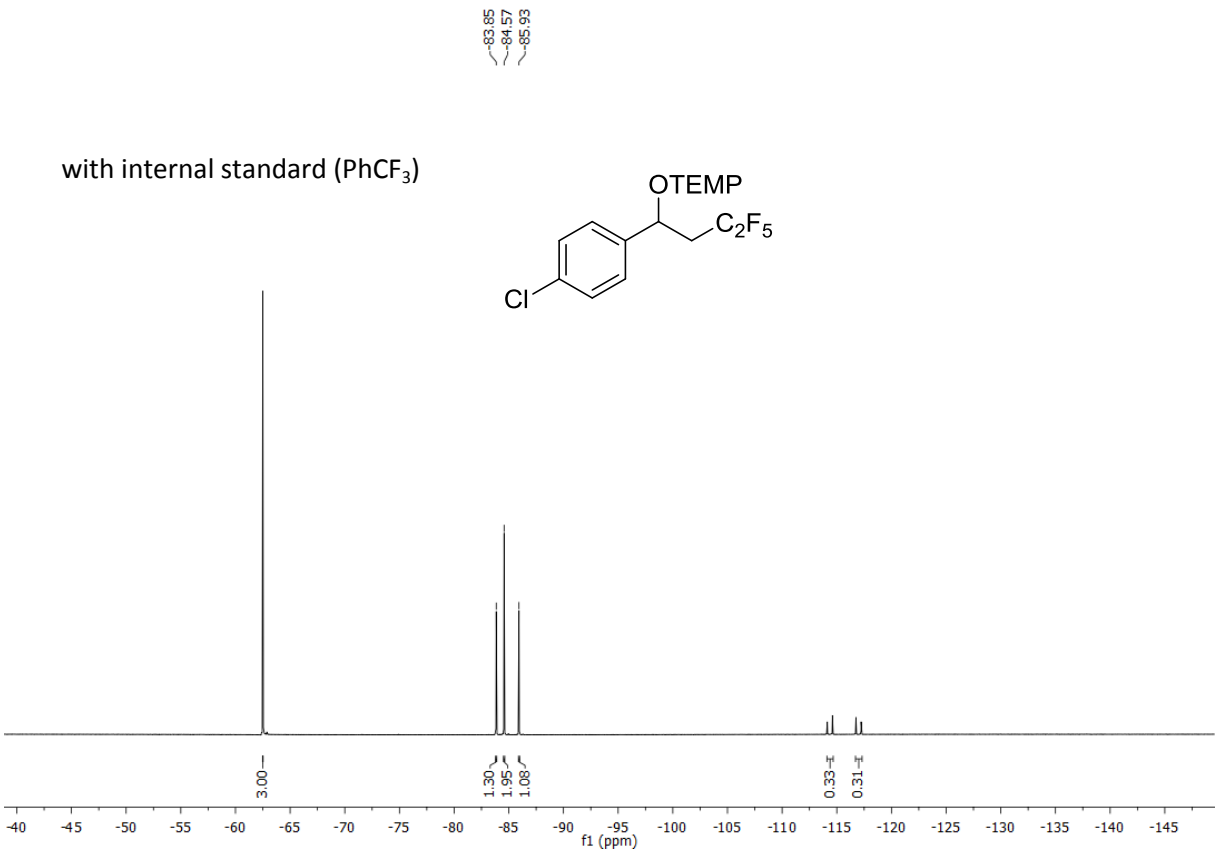


with internal standard ($PhCF_3$)





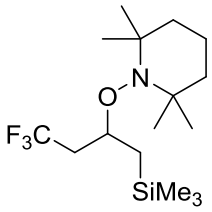

-83.87
-84.60
-85.95
with internal standard ($PhCF_3$)
OTEMP
C_2F_5
MeO
3.00
0.90
1.36
1.50
0.50
0.48
-50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145
f1 (ppm)


-83.85
-84.57
-85.93
with internal standard ($PhCF_3$)
OTEMP
C_2F_5
Cl
3.00
1.30
1.95
1.08
0.33
0.31
-40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145
f1 (ppm)

Analytical data for unknown compounds.

Analytical data for compounds not listed below can be found under reference 3.

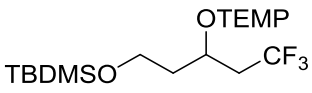
2,2,6,6-Tetramethyl-1-((4,4,4-trifluoro-1-(trimethylsilyl)butan-2-yl)oxy)piperidine



According to a literature procedure[3] with Togni reagent (**1**, 80 mg, 0.25 mmol, 1.0 eq.), allyltrimethylsilane (286 mg, 2.5 mmol, 10.0 eq.) and TEMPONa (0.35 ml, 0.30 mmol, 1.2 eq., 0.85 M in THF). Crude product was purified by flash column chromatography on silica gel by using pentane as an eluent to provide analytically pure product as colorless oil.

^{1}H-NMR (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 4.27 (*tdd*, *J* = 8.5, 5.3, 3.7 Hz, 1H, OCH), 3.34 – 3.21 (*m*, 1H, OCHCH_αH$_\beta$), 2.03 – 1.92 (*m*, 1H, OCHCH$_\alpha H_\beta$), 1.65 – 1.40 (*m*, 6H, 3 × TEMPO-CH_2), 1.33 (*dp*, *J* = 13.1, 3.4 Hz, 1H, SiCH_αH$_\beta$), 1.17 – 1.01 (*m*, 12H, 4 × TEMPO-CH_3), 0.91 (*dd*, *J* = 14.6, 5.3 Hz, 1H, SiCH$_\alpha H_\beta$), 0.10 (*s*, 9H, $SiMe_3$). **^{13}C-NMR** (151 MHz, $CDCl_3$, 300 K): δ (ppm) = 127.0 (*q*, *J* = 276.8 Hz, CF_3), 74.5 (*q*, *J* = 2.6 Hz, OCH), 60.1 (TEMPO-C), 59.4 (TEMPO-C), 40.5 (TEMPO-CH_2), 40.4 (TEMPO-CH_2), 39.6 (*q*, *J* = 25.8 Hz, CF_3CH_2), 34.1 (TEMPO-CH_3), 33.8 (TEMPO-CH_3), 23.6 ($SiCH_2$), 21.1 (TEMPO-CH_3), 21.0 (TEMPO-CH_3), 17.4 (TEMPO-CH_2), -0.4 (3 × CH_3). **^{19}F-NMR** (564 MHz, $CDCl_3$, 300 K): δ (ppm) = -62.4 (CF_3). **HRMS** (ESI) exact mass calculated for $C_{16}H_{32}F_3NOSiH$ ($[M+H]^+$): 340.2278, found: 340.2283. **IR** (neat): 2935*m*, 1382*w*, 1234*w*, 1251*m*, 1192*w*, 1136*s*, 1090*m*, 960*w*, 910*w*, 836*s*, 735*m*, 761*w*, 735*m*, 692*w*, 659*w*.

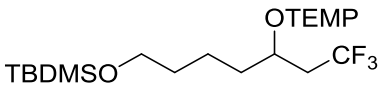
1-((5-((tert-Butyldimethylsilyl)oxy)-1,1,1-trifluoropentan-3-yl)oxy)-2,2,6,6-tetramethylpiperidine



According to a literature procedure[3] with Togni reagent (**1**, 40 mg, 0.125 mmol, 1.0 eq.), (but-3-en-1-yloxy)(tert-butyl)dimethylsilane (233 mg, 1.25 mmol, 10.0 eq.) and TEMPONa (0.18 ml, 0.15 mmol, 1.2 eq., 0.85 M in THF). Crude product was purified by flash column chromatography on silica gel by using pentane as an eluent to provide analytically pure product as colorless oil. **^{1}H-NMR** (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 4.29 (tt, *J* = 8.4, 4.7 Hz, 1H), 3.77 (dd, *J* = 7.1, 5.5 Hz, 2H), 3.06 – 2.96 (m, 1H), 2.21 – 2.10 (m, 1H), 1.98 (dq, *J* = 12.4, 5.8 Hz, 1H), 1.77 (dq, *J* = 13.2, 6.7 Hz, 1H), 1.49 – 1.28 (m, 5H), 1.17 – 1.04 (m, 12H), 0.89 (s, 9H), 0.05 (d, *J* = 1.8 Hz, 6H). **^{13}C-NMR** (151 MHz, $CDCl_3$, 300 K): δ (ppm) = 126.7 (*d*, *J* = 276.8 Hz, CF_3), 73.0 (OCH), 60.1

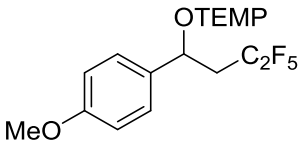
(TEMPO-C), 59.7 (OCH_2), 59.5 (TEMPO-C), 40.3 (TEMPO-CH_2), 40.2 (TEMPO-CH_2), 37.1 (d, J = 26.6 Hz, CF_3CH_2), 36.9 (OCH_2CH_2) , 34.1 (TEMPO-CH_3), 33.9 (TEMPO-CH_3), 25.8 (3 × CH_3), 20.7 (TEMPO-CH_3), 20.4 (TEMPO-CH_3), 18.2 (C), 17.2 (TEMPO-CH_2), -5.46 (CH_3), -5.48 (CH_3). **^{19}F-NMR** (564 MHz, $CDCl_3$, 300 K): δ (ppm) = -62.5 (CF_3). **HRMS** (ESI) exact mass calculated for $C_{20}H_{40}F_3NO_2SiH$ ($[M+H]^+$): 412.2853, found: 412.2836. **IR** (neat): 2932*m*, 1467*w*, 1364*w*, 1255*s*, 1140*s*.

1-((7-((tert-Butyldimethylsilyl)oxy)-1,1,1-trifluoroheptan-3-yl)oxy)-2,2,6,6-tetramethylpiperidine



According to a literature procedure[3] with Togni reagent (**1**, 40 mg, 0.125 mmol, 1.0 eq.), tert-butyl(hex-5-en-1-yloxy)dimethylsilane (286 mg, 2.5 mmol, 10.0 eq.) and TEMPONa (0.18 ml, 0.15 mmol, 1.2 eq., 0.85 M in THF). Due to problems upon separation the title compound from excess alkene used, the silyl group was removed[4] to afford 7,7,7-trifluoro-5-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)heptan-1-ol. The analytical data are in accordance with those reported in the literature.[3]

2,2,6,6-Tetramethyl-1-(3,3,4,4,4-pentafluoro-1-(4-methoxyphenyl)butoxy)piperidine

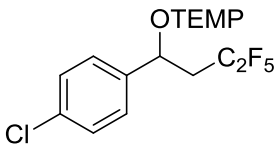


According to a literature procedure[3] with **5** (46 mg, 0.125 mmol, 1.0 eq.), 1-methoxy-4-vinylbenzene (168 mg, 1.25 mmol, 10.0 eq.) and TEMPONa (0.18 ml, 0.15 mmol, 1.2 eq., 0.85 M in THF). Crude product was purified by flash column chromatography on silica gel by using a 20:1 mixture of pentane/Et_2O as an eluent to provide analytically pure product as colorless oil.

^{1}H-NMR (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.31 – 7.21 (*m*, 2H, CH_{arom}), 6.87 (*d*, *J* = 8.3 Hz, 2H, CH_{arom}), 5.03 (*dd*, *J* = 10.1, 3.5 Hz, 1H, OCH), 3.81 (*s*, 3H, OCH_3), 3.19 – 3.05 (*m*, 1H, OCHC*H*αH_β), 2.52 – 2.40 (*m*, 1H, OCHCHα*H*$_\beta$), 1.51 – 1.21 (*m*, 9H, 3 × TEMPO-CH_2, TEMPO-CH_3), 1.14 (*s*, 3H, TEMPO-CH_3), 1.00 (*s*, 3H, TEMPO-CH_3), 0.66 (*s*, 3H, TEMPO-CH_3). **^{13}C-NMR** (151 MHz, $CDCl_3$, 300 K): δ (ppm) = 159.3 (C), 133.5 (C), 129.1 (2 × CH), 113.3 (2 × CH), 78.8 (OCH), 60.0 (TEMPO-C), 59.6 (TEMPO-C), 55.1 (CH_3), 40.3 (2 × TEMPO-CH_2), 35.8 (*t*, *J* = 19.8 Hz, $C_2F_5CH_2$), 34.1 (2 × TEMPO-CH_3), 20.3 (TEMPO-CH_3), 20.2 (TEMPO-CH_3), 17.0 (TEMPO-CH_2). **^{19}F-NMR** (564 MHz, $CDCl_3$,

300 K): δ (ppm) = -86.2 (*s*, CF_2CF_3), -115.0 (*ddd*, *J* = 265.0, 30.8, 7.0 Hz, CH_2CFFCF_3), -117.5 (*ddd*, *J* = 265.1, 29.1, 8.2 Hz, CH_2CFFCF_3). **HRMS** (ESI) exact mass calculated for $C_{20}H_{28}F_5NO_2SiH$ ($[M+H]^+$): 410.2113, found: 410.2111. **IR** (neat): 2934*w*, 1613*w*, 1514*w*, 1462*w*, 1359*w*, 1196*s*, 1095*w*, 1066*w*.

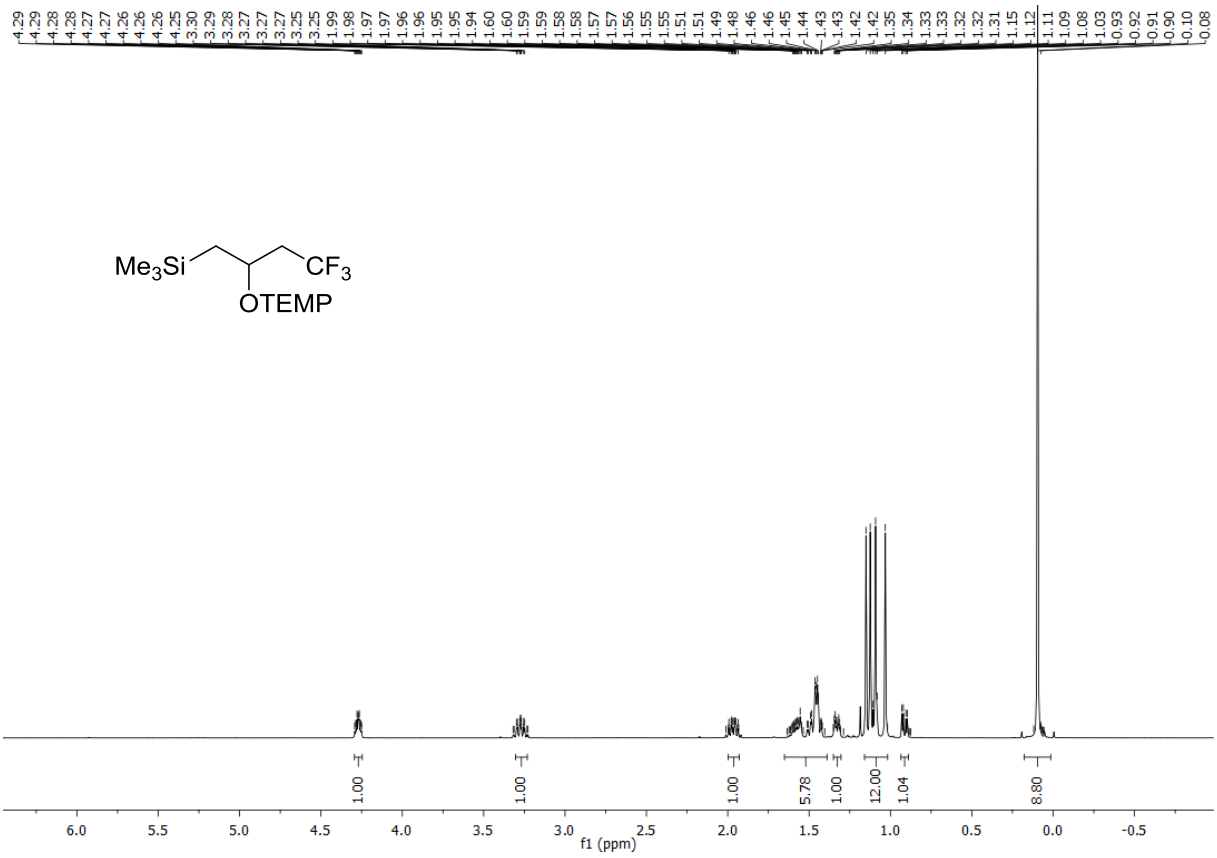
1-(1-(4-chlorophenyl)-3,3,4,4,4-pentafluorobutoxy)-2,2,6,6-tetramethylpiperidine

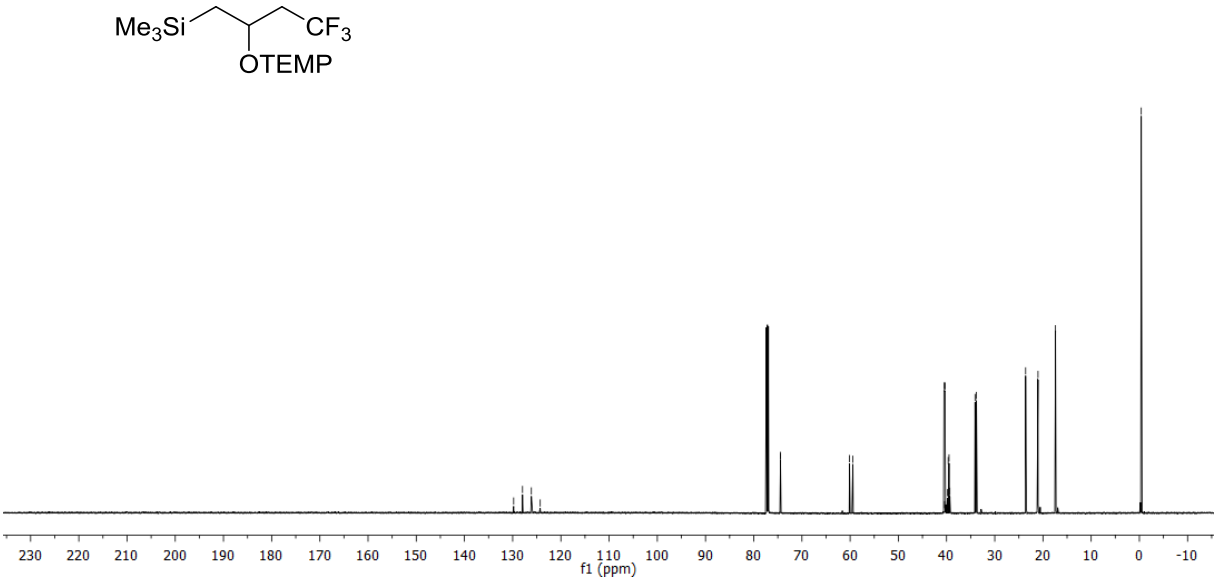


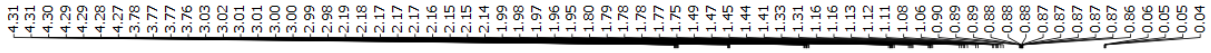
ccording to a literature procedure[3] with **5** (46 mg, 0.125 mmol, 1.0 eq.), 1-chloro-4-vinylbenzene (173 mg, 1.25 mmol, 10.0 eq.) and TEMPONa (0.35 ml, 0.30 mmol, 1.2 eq., 0.85 M in THF). Crude product was purified by flash column chromatography on silica gel by using pentane as an eluent to provide analytically pure product as colorless oil.

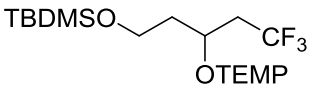
^{1}H-NMR (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.33 (*d*, *J* = 8.1 Hz, 2H, CH_{arom}), 7.28 (*d*, *J* = 8.4 Hz, 2H, CH_{arom}), 5.05 (*dd*, *J* = 10.2, 3.4 Hz, 1H, OCH), 3.20 – 3.08 (*m*, 1H, $OCHC\mathit{H}\alpha H_\beta$), 2.55 – 2.39 (*m*, 1H, $OCHCH\alpha\mathit{H}_\beta$), 1.52 – 1.25 (*m*,, 9H, 3 × TEMPO-CH_2, TEMPO-CH_3), 1.15 (*s*, 1H, TEMPO-CH_3), 1.01 (*s*, 1H, TEMPO-CH_3), 0.65 (*s*, 1H, TEMPO-CH_3). **^{13}C-NMR** (151 MHz, $CDCl_3$, 300 K): δ (ppm) = 139.9 (C), 133.8 (C), 129.2 (2 × CH), 128.3 (2 × CH), 78.9 (OCH), 60.1 (TEMPO-C), 59.8 (TEMPO-C), 40.2 (2 × TEMPO-CH_2), 36.0 (*t*, *J* = 21.0 Hz, $C_2F_5\mathit{C}H_2$), 34.1 (2 × TEMPO-CH_3), 20.3 (TEMPO-CH_3), 20.2 (TEMPO-CH_3), 17.0 (TEMPO-CH_2). **^{19}F-NMR** (564 MHz, $CDCl_3$, 300 K): δ (ppm) = -86.2 (*s*, $CF_2C\mathit{F}_3$), -114.7 (*ddd*, *J* = 265.4, 31.0, 7.0 Hz, $CH_2C\mathit{F}FCF_3$), -117.4 (*ddd*, *J* = 265.4, 29.0, 7.9 Hz, $CH_2C\mathit{F}FCF_3$). **HRMS** (ESI) exact mass calculated for $C_{19}H_{25}F_5NO_2SiH$ ($[M+H]^+$): 414.1618, found: 414.1618. **IR** (neat): 1934*w*, 1701*w*, 2596*w*, 1490*w*, 1359*w*, 1197*s*, 1093*m*.

NMR spectra of all new compounds:





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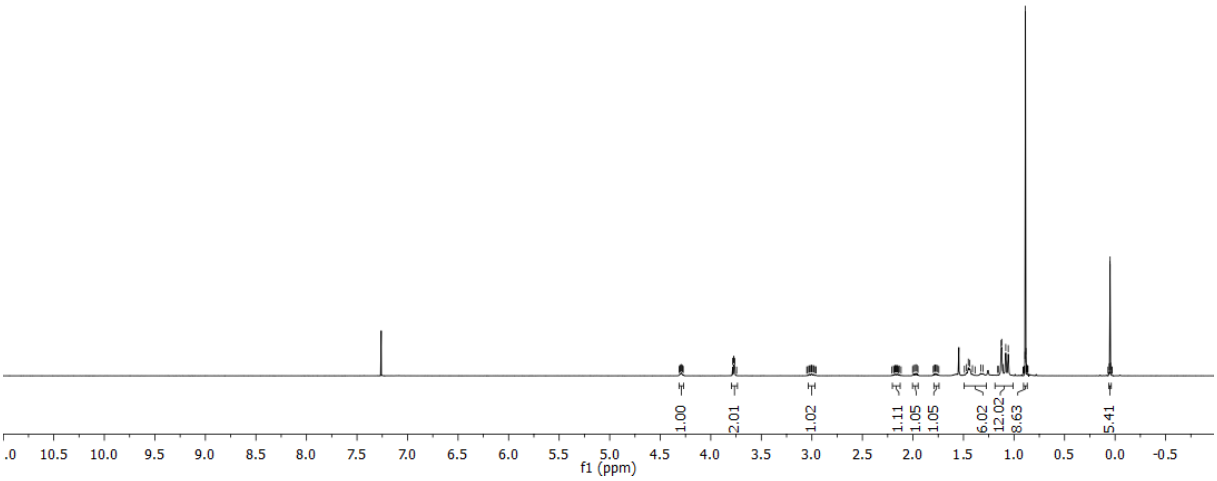
CF3
OTEMP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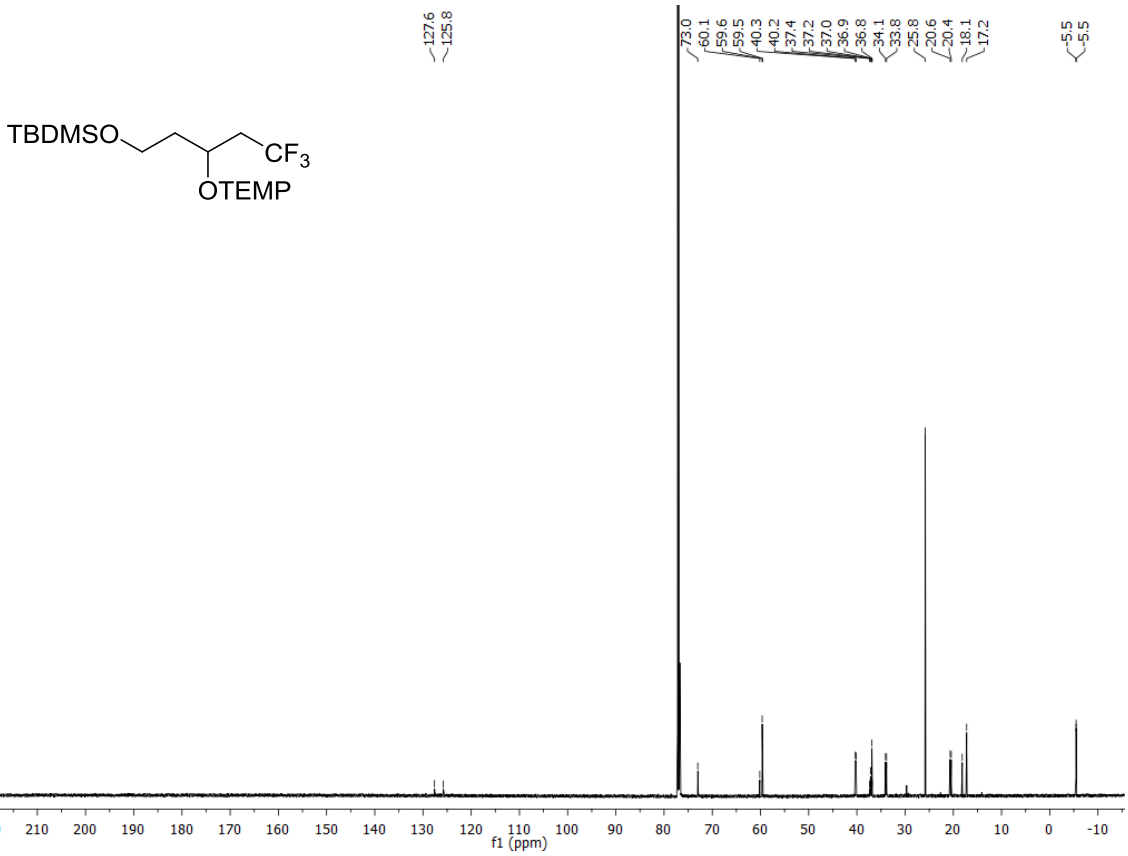
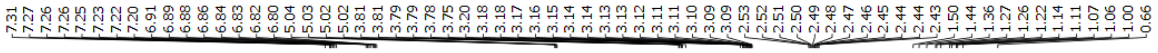
1.02
1.11
1.05
1.05
6.02
12.02
8.63
5.41
f1 (ppm)


127.6
125.8
73.0
60.1
59.6
59.5
40.3
40.2
37.4
37.2
37.0
36.9
36.8
34.1
33.8
25.8
20.6
20.4
18.1
17.2
-5.5
-5.5
f1 (ppm)

TBDMSO
CF3
OTEMP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7.26
7.25
7.23
7.22
7.20
6.91
6.89
6.88
6.86
6.84
6.83
6.82
6.80
5.04
5.03
5.02
5.02
3.81
3.79
3.79
3.78
3.75
3.20
3.18
3.18
3.17
3.16
3.15
3.14
3.14
3.13
3.13
3.12
3.11
3.11
3.10
3.09
3.09
2.53
2.52
2.51
2.50
2.49
2.48
2.47
2.46
2.45
2.44
2.44
2.43
1.50
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1.36
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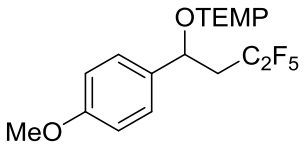
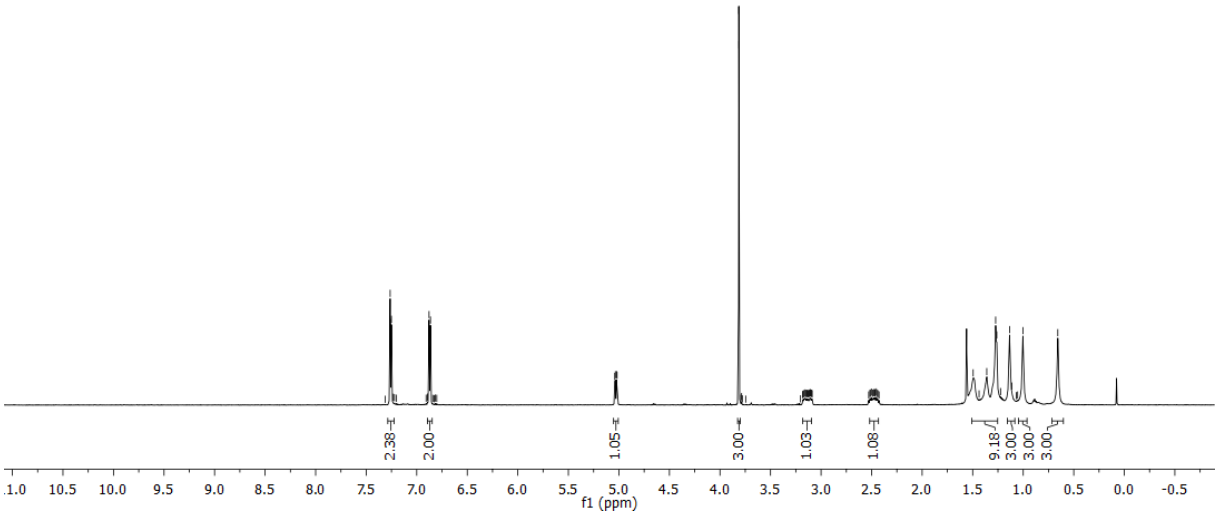
1.26
1.22
1.14
1.11
1.07
1.06
1.00
0.66


OTEMP
C_2F_5
MeO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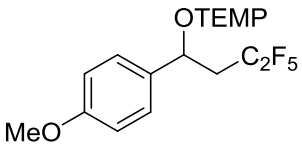
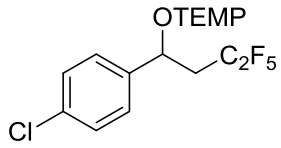
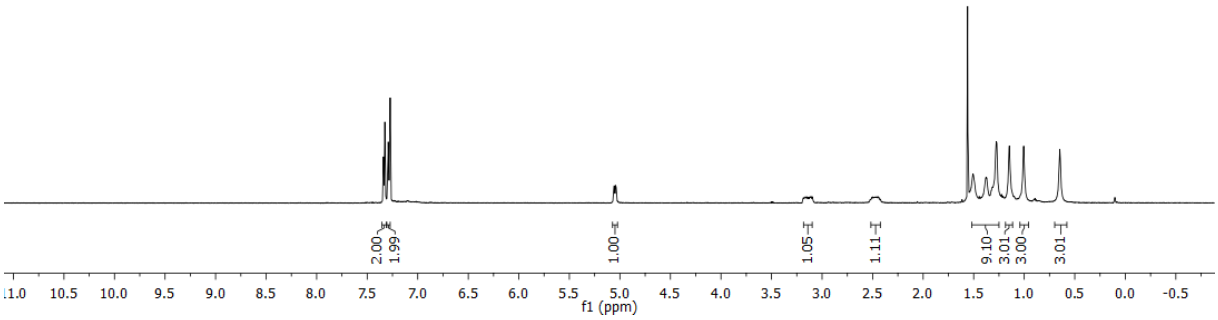
3.00
1.03
1.08
9.18
3.00
3.00
3.00
f1 (ppm)


159.5
133.8
129.4
113.6
79.0
60.3
59.9
55.3
40.5
36.1
34.3
20.6
20.5
17.3

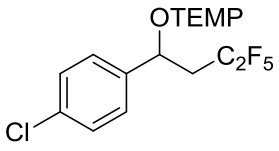

OTEMP
C_2F_5
MeO

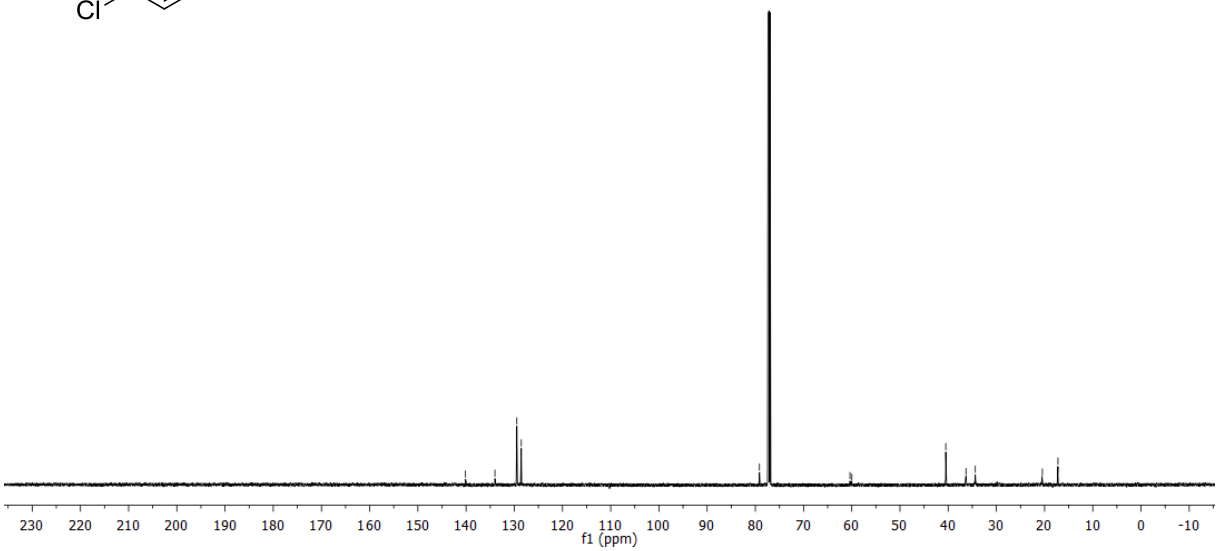
f1 (ppm)


OTEMP
C_2F_5
Cl


2.00
1.99
1.00
1.05
1.11
9.10
3.01
3.00
3.01
f1 (ppm)


140.1
134.0
129.5
128.5
79.1
60.4
60.0
40.5
36.3
34.4
20.5
17.2


OTEMP
C_2F_5
Cl


f1 (ppm)

Lieature

[1] T. Inokuchi, H. Kawafuchi, *Tetrahedron* **2004**, *60*, 11969.

[2] P. Eisenberger, S. Gischig, A. Toni, *Chem. Eur. J.* **2006**, *12*, 2579.

[3] Y. Li, A. Studer, *Angew. Chem. Int. Ed*. **2012**, *51*, 8221.

[4] K. Lehr, S. Schulthoff, Y. Ueda, R. MarizL. Leseurre, B. Gabor, A. Fürstner, *Chem. Eur. J*. **2015**, *21*, 219.