Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting information

Catalyst Free Synthesis of α-Fluorinated Aroylacyl Imides

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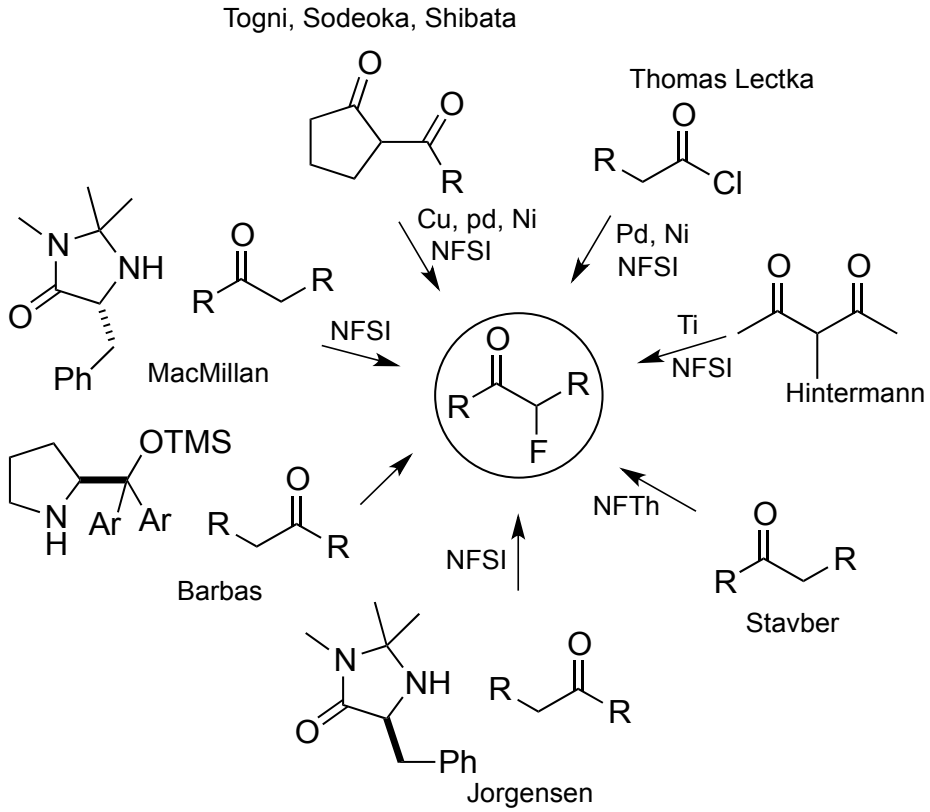


Figure 1. Traditional methods for α-fluorination using electrophilic fluorination.

Figure 1 describes the available methodology to synthesis of α-flourinated compounds. In almost all cases, researches employed electrophilic fluorinating agents such as *N*-fluorodibenenesulfonimide (NFSi), Selectfluor and NFTh in the presence of either metal or organocatalysed.[1,2] For the first

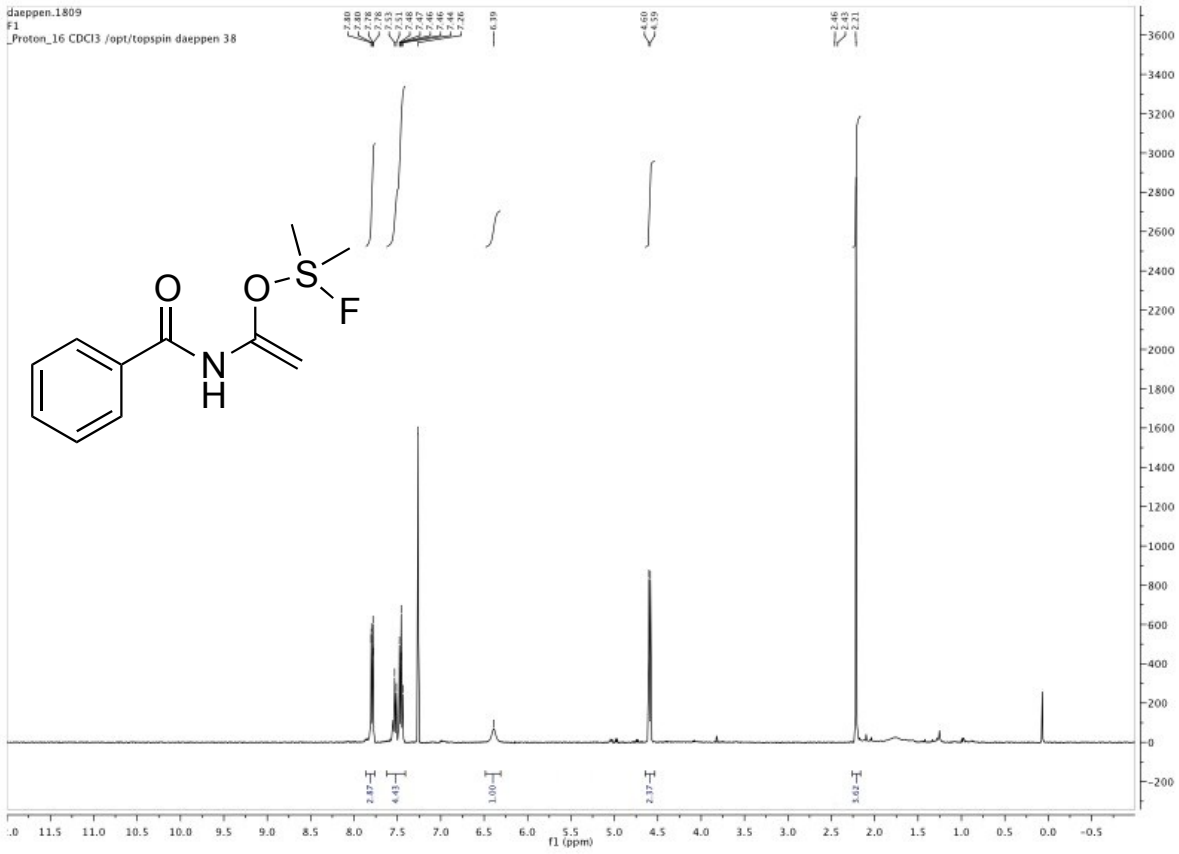
time we are reporting a novel one-pot synthetic strategy for synthesis of α-fluorinated amides in good yields employing cost effective chemicals such as NaF and DMSO.

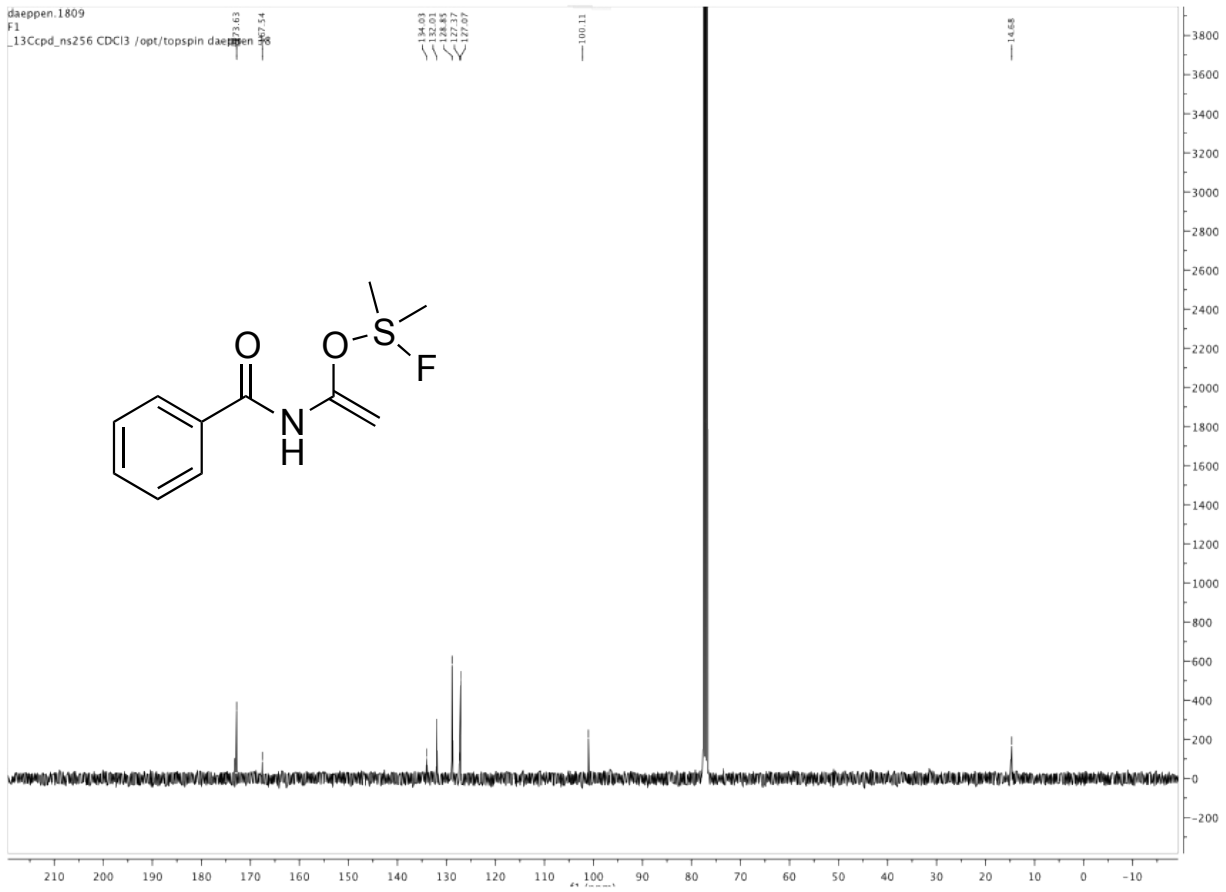
[1] a) Z. Jin, R. S. Hidinger, B. Xu, G. B. Hammond, *J. Org. Chem.* **2012**, *77*, 7725-7726; b) L. Hintermann, A. Togni, *Angew. Chem.* **2000**, *112*, 4530-4533; *Angew. Chem. Int. Ed.* **2000**, *39*, 4359-4362; c) M. Perseghini, M. Massaccesi, Y. Liu, A. Togni, *Tetrahedron* **2006**, *62*, 7180-7190; d) Y. Hamashima, K. Yagi, H.Takano, L. Tamás, M. Sodeoka. *J Am Chem Soc.* **2002**, *124*, 14530-14531; e) Y. Hamashima, T. Suzuki, H. Takano, Y. Shimura, M. Sodeoka, *J Am Chem Soc.* **2005**, *127,* 10164-

10165; f) T. Suzuki, Y. Hamashima, M. Sodeoka, *Angew. Chem.* **2007**, *118*, 5435-5439; *Angew. Chem. Int. Ed.* **2007**, *46*, 5435-5439; Y. g) Hamashima, H. Takano, D. Hotta, M. Sodeoka, *Org. Lett.* **2003**, *5*, 3225-3228; h) N. Shibata, J. Kohno, K. Takai, T. Ishimaru, S. Nakamura, T. Toru, S. Kanemasa, *Angew. Chem.* **2005**, *117*, 4276-4279; *Angew. Chem. Int. Ed.* **2005**, *44*, 4204-4207; i) D. S. Reddy, N. Shibata, J. Nagai, S. Nakamura, T. Toru, S. Kanemasa. *Angew. Chem.* **2008**, *120*, 170-174; *Angew. Chem. Int. Ed.* **2008**, *47*, 164-168.

[2] a) T. D. Beeson, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2005**, *127*, 8826-8828; b) P. Kwiatkowski, T. D. Beeson, J. C. Conrad, D. W. C. MacMillan. *J. Am. Chem. Soc.* **2011**, *133*, 1738-1741; c) M. Marigo, D. Feilenbach, A. Braunton, A. Kjaersgaard, K. A. Jorgensen, *Angew. Chem.* **2005**, *117*, 3769-3772; *Angew. Chem. Int. Ed.* **2005**, *44*, 3703-3706; d) J. Franzén, M. Marigo, D. Fielenbach, T. C. Wabnitz, A. Kjærsgaard, K. A. Jørgensen. *J. Am. Chem. Soc.* **2005**, *127*, 18296-18304; e) D. D. Steiner, N. Mase, B. C. F. III, *Angew. Chem.* **2005**, *117*, 3772-3776; *Angew. Chem. Int. Ed.* **2005**, *44*, 3706-3710; f) D. Enders, M. R. M. Hüttl, *Synlett.* **2005**, 991-993.

NMR Spectrum

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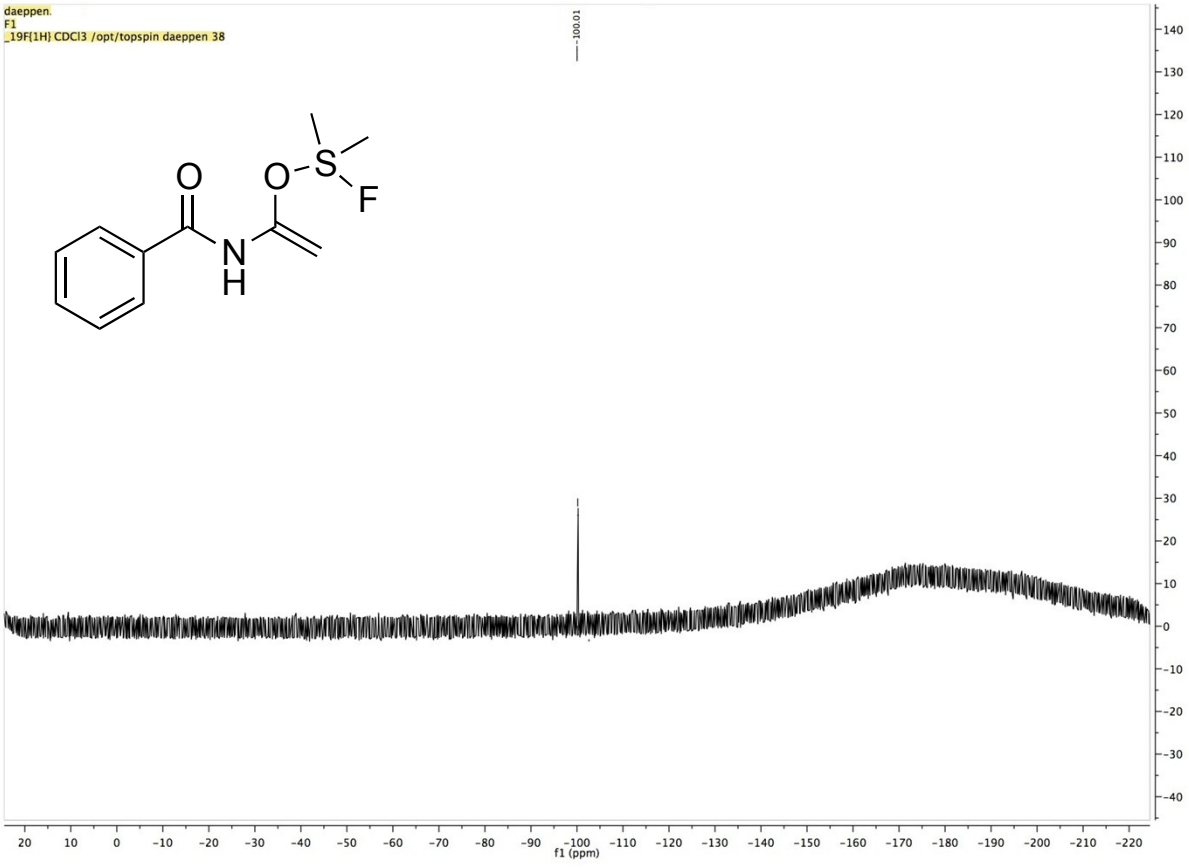
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S
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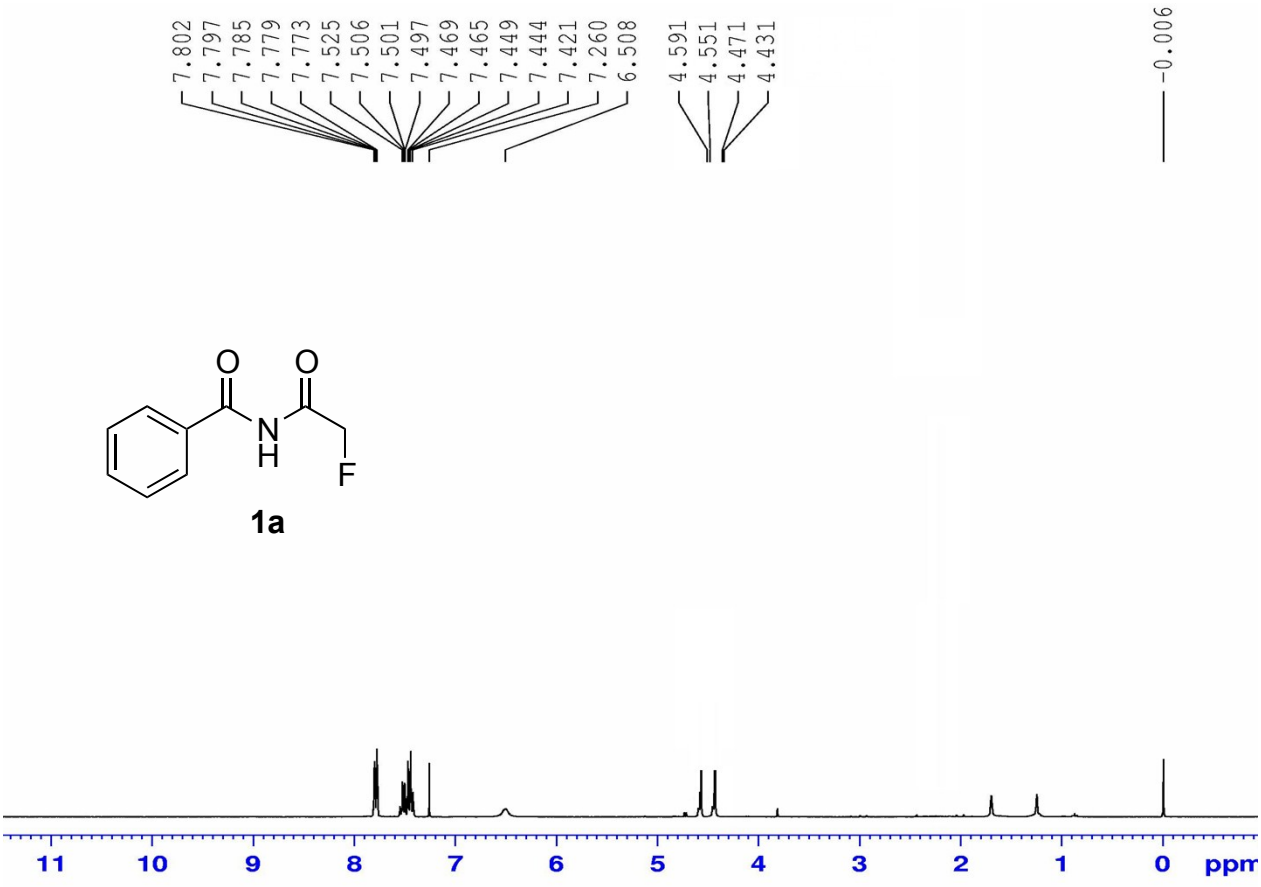
f1 (ppm)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7.421
7.260
6.508
4.591
4.551
4.471
4.431
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H
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10
9
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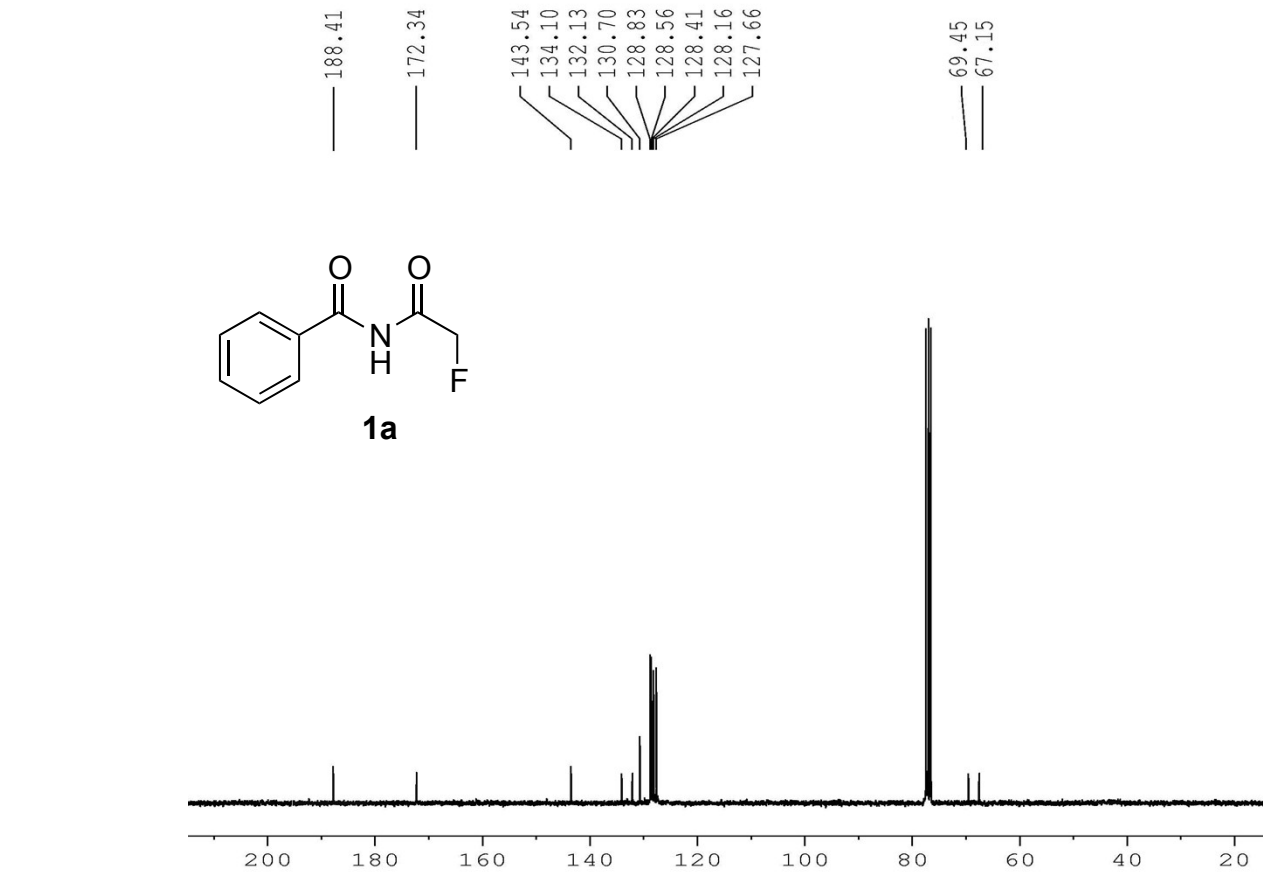
6
5
4
3
2
1
0
ppm

1a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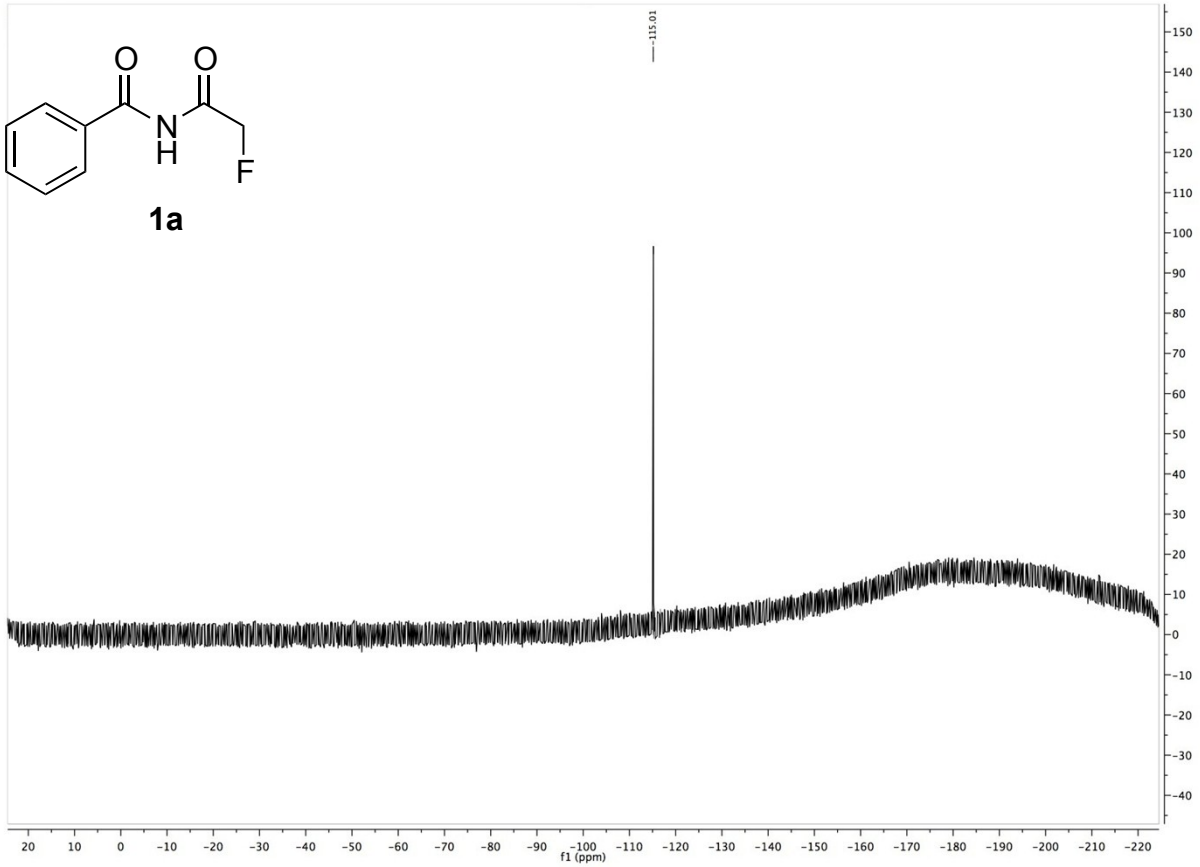
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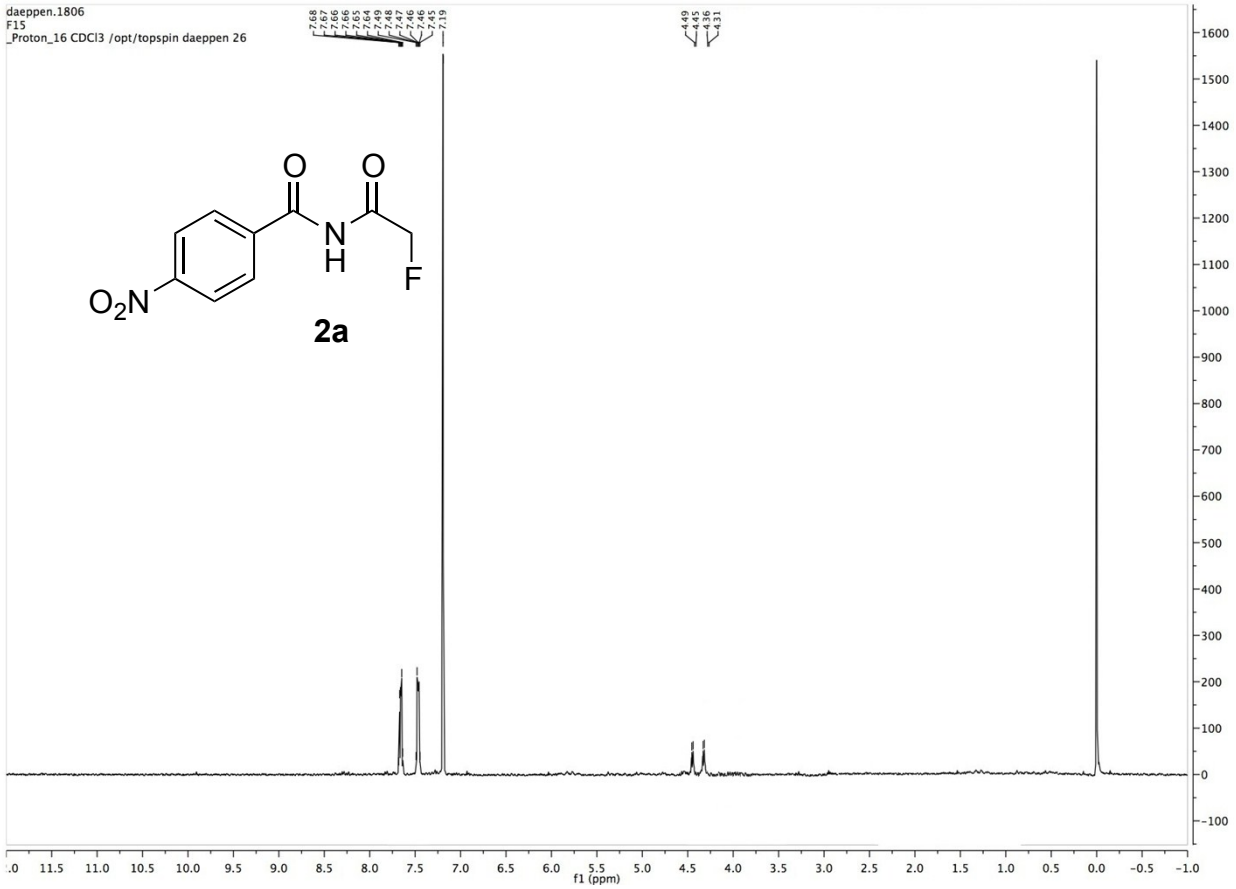
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H
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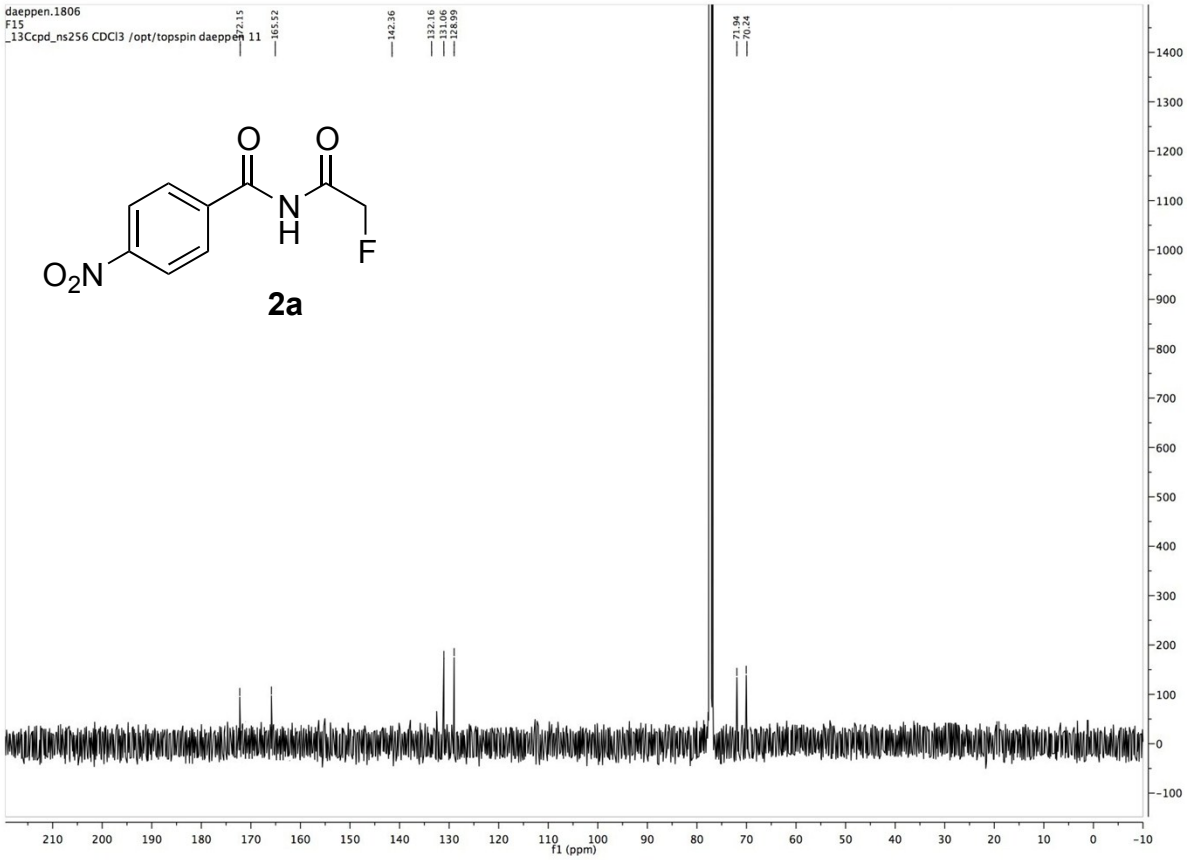
f1 (ppm)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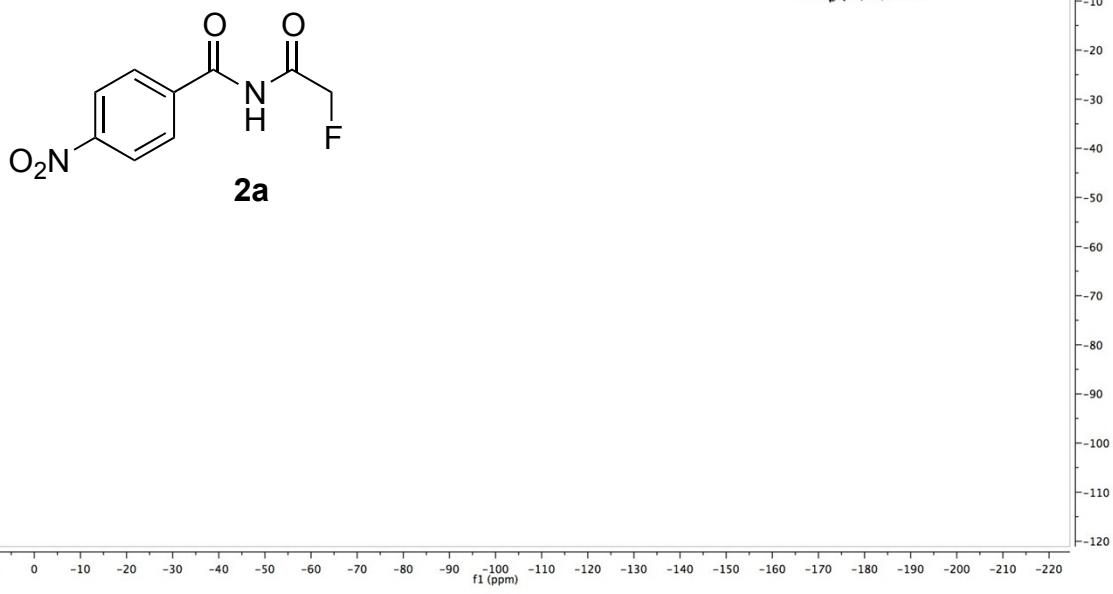
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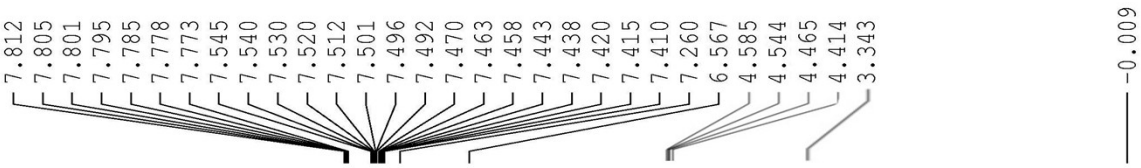
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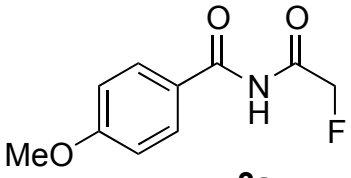
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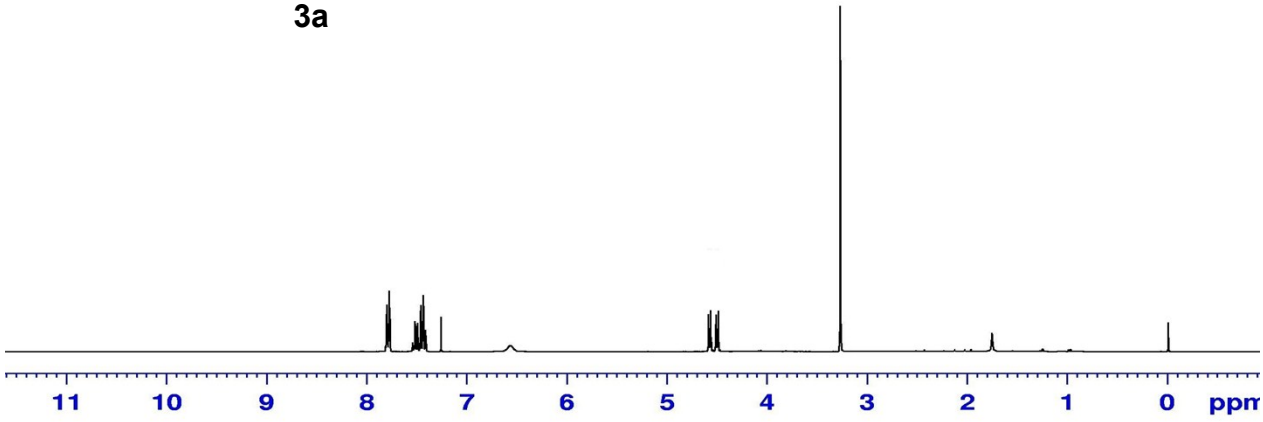
3a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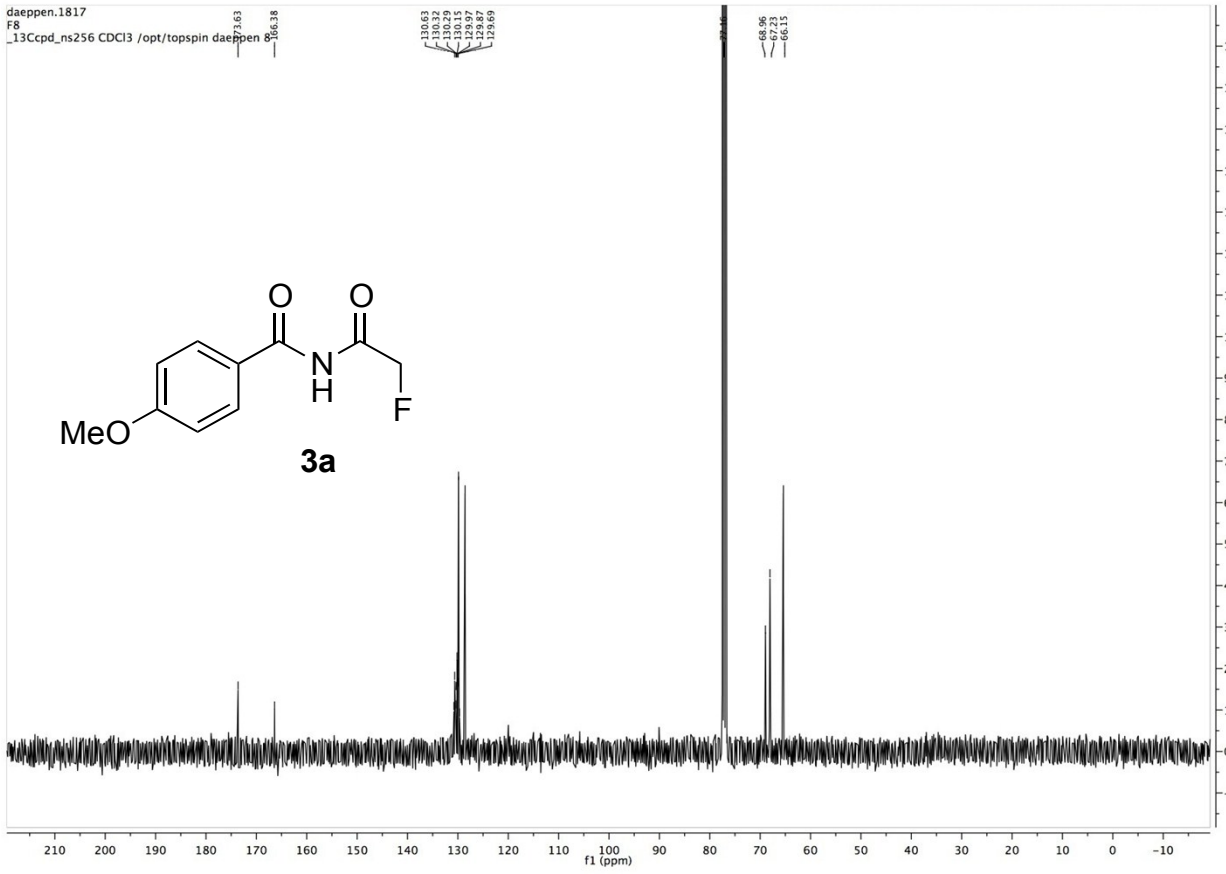
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F
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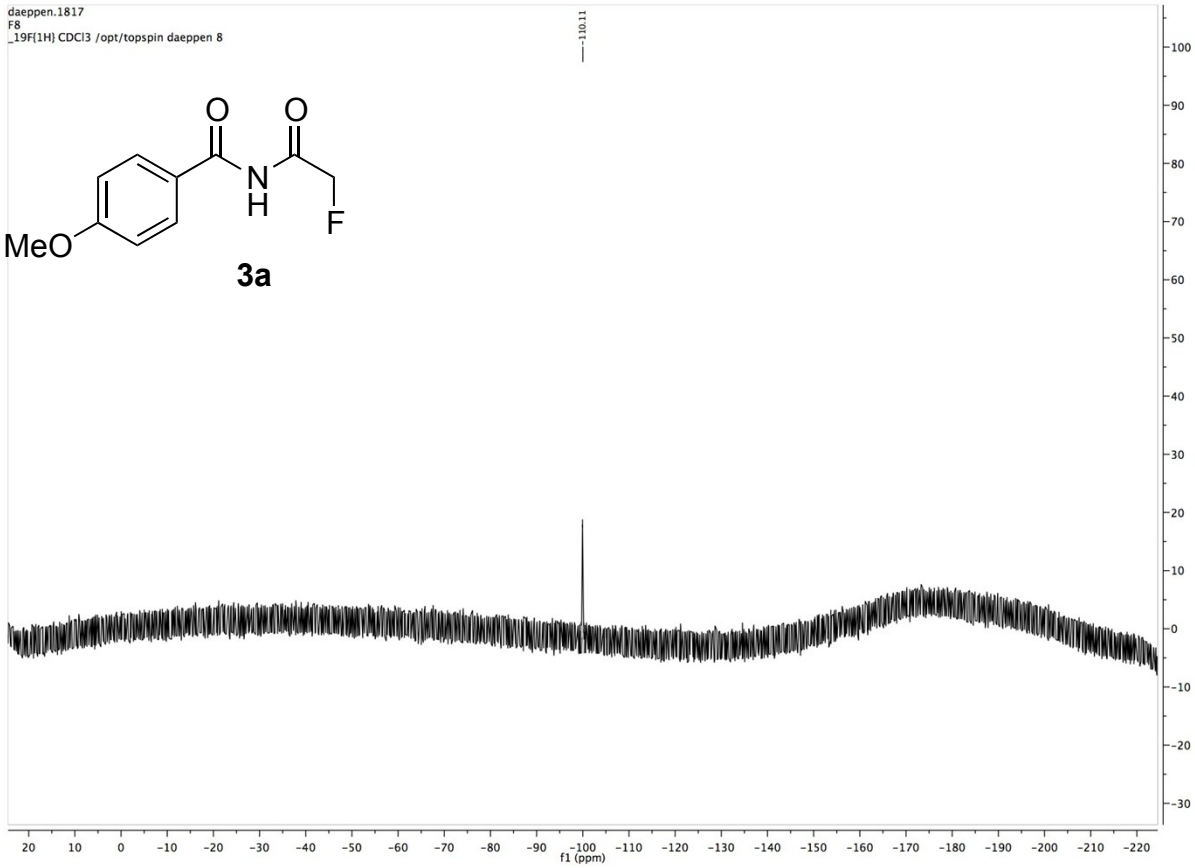
3a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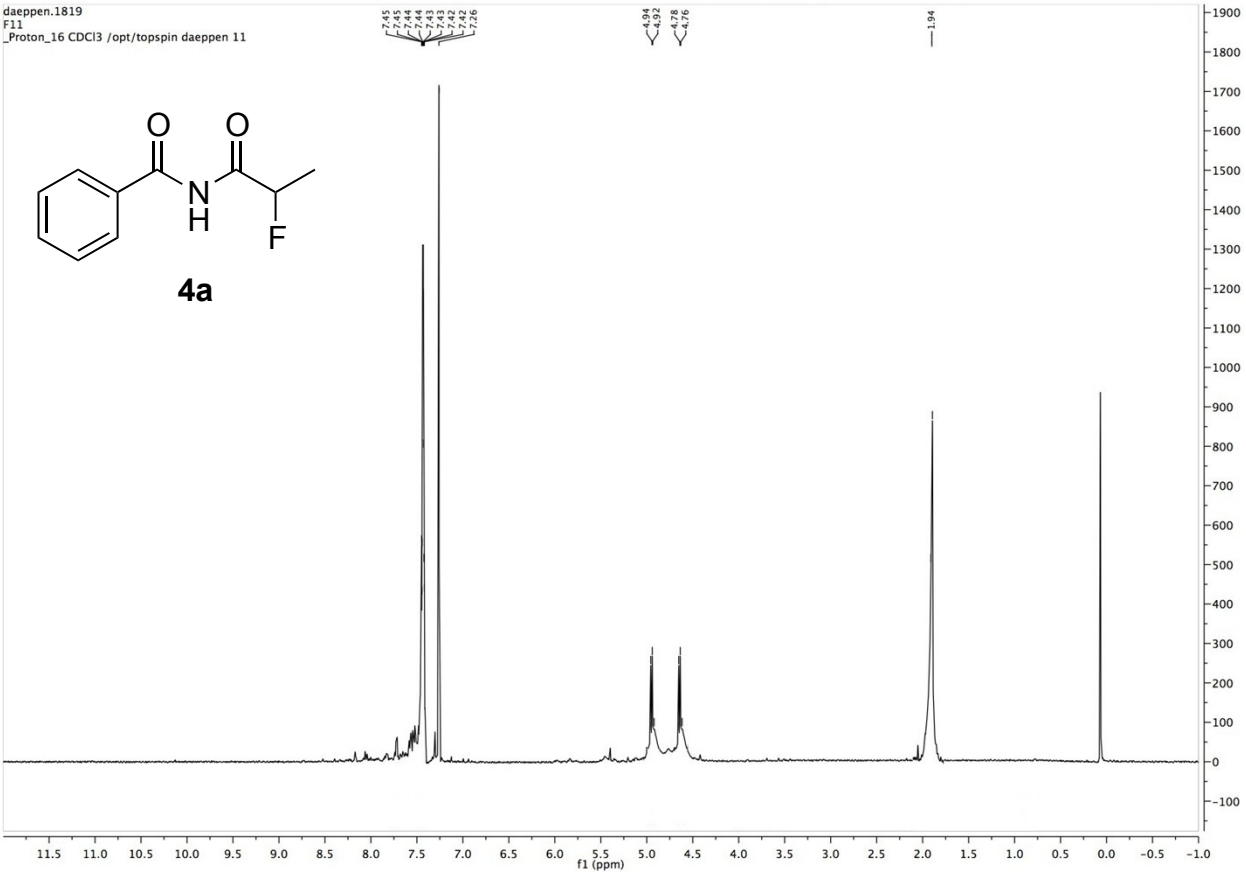
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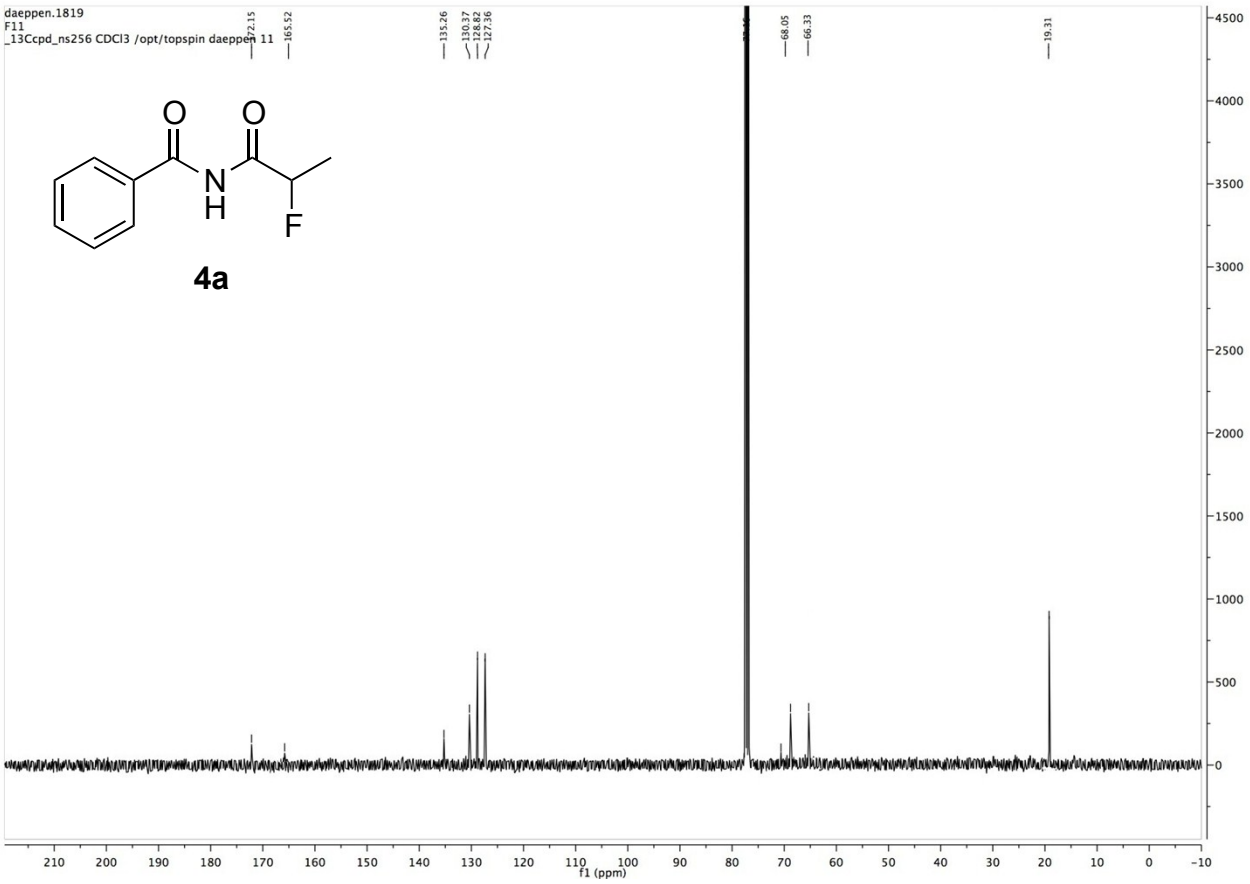
4a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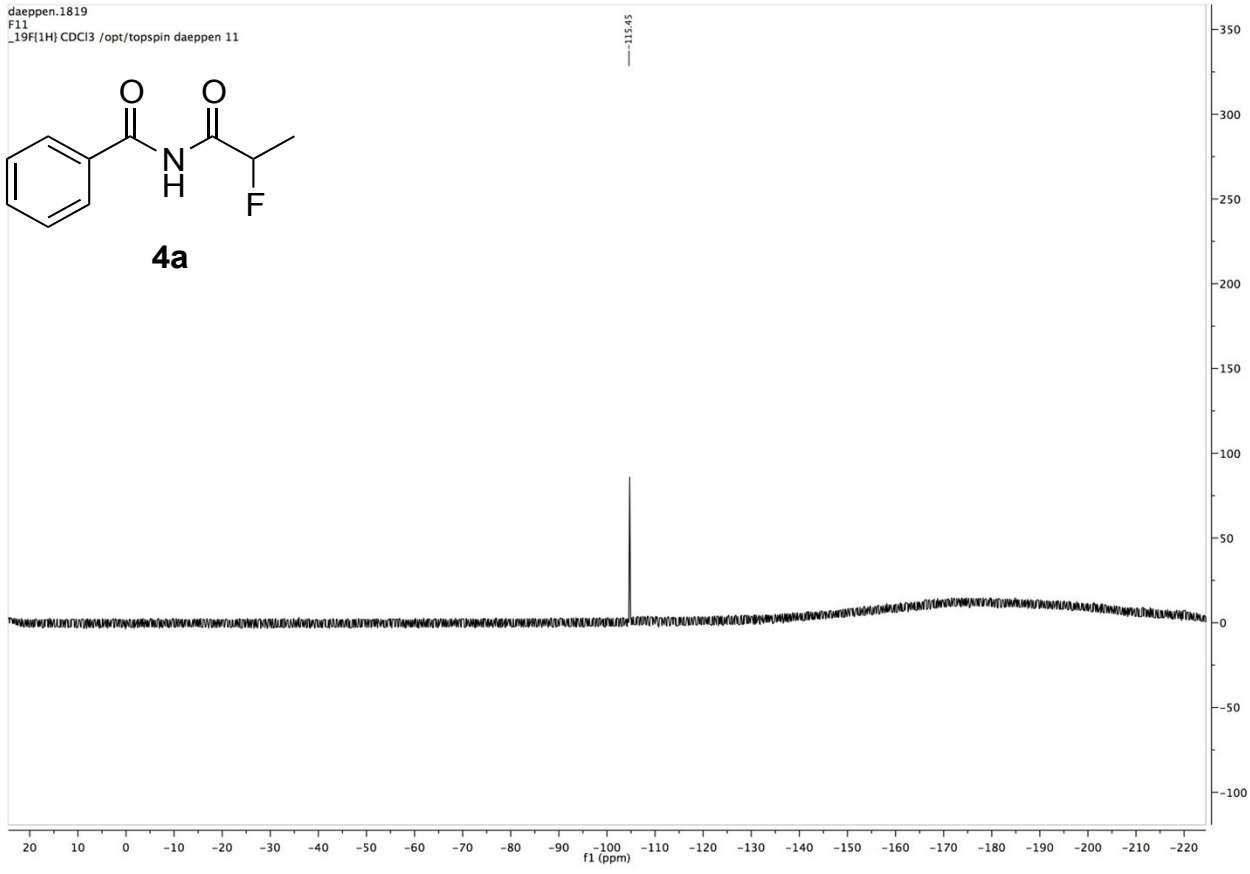
f1 (ppm)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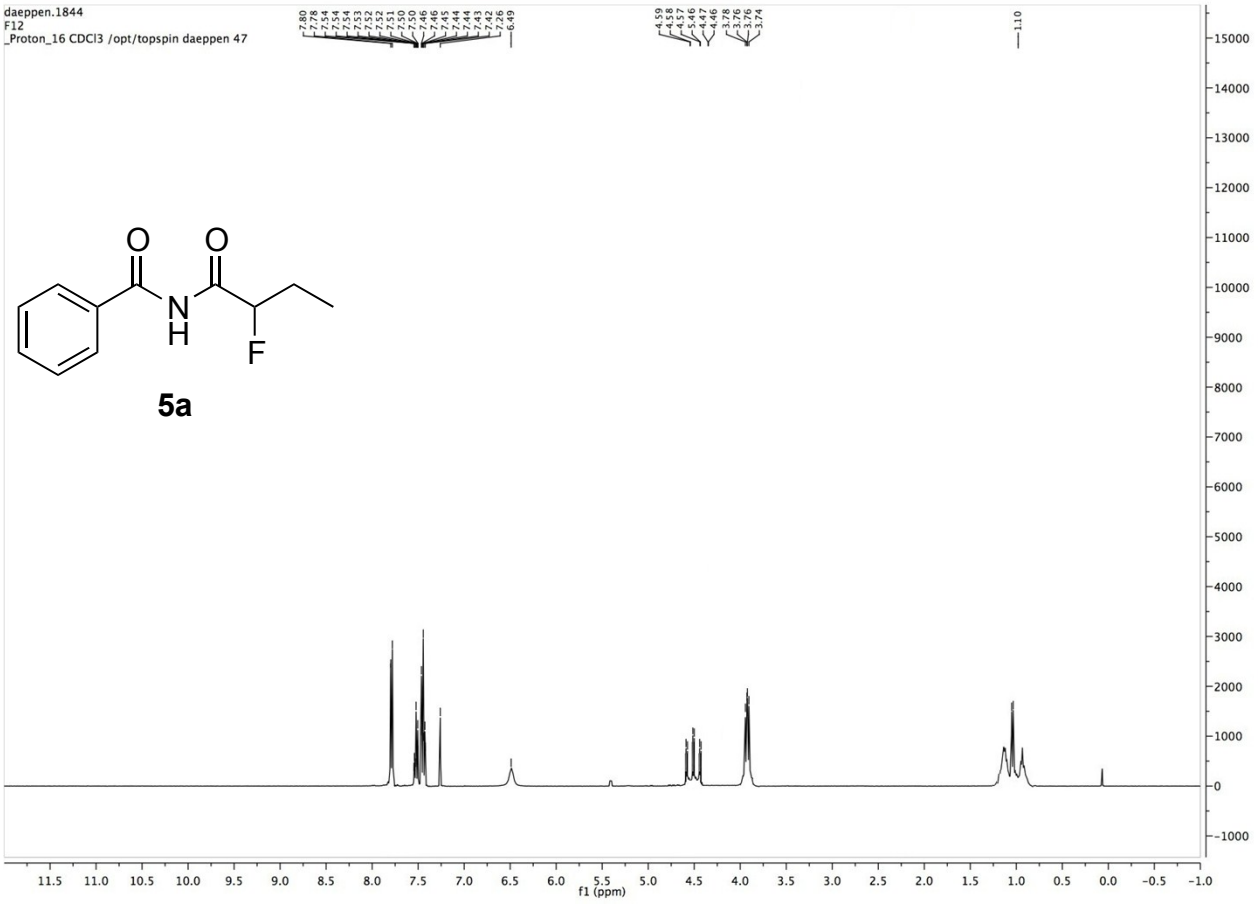
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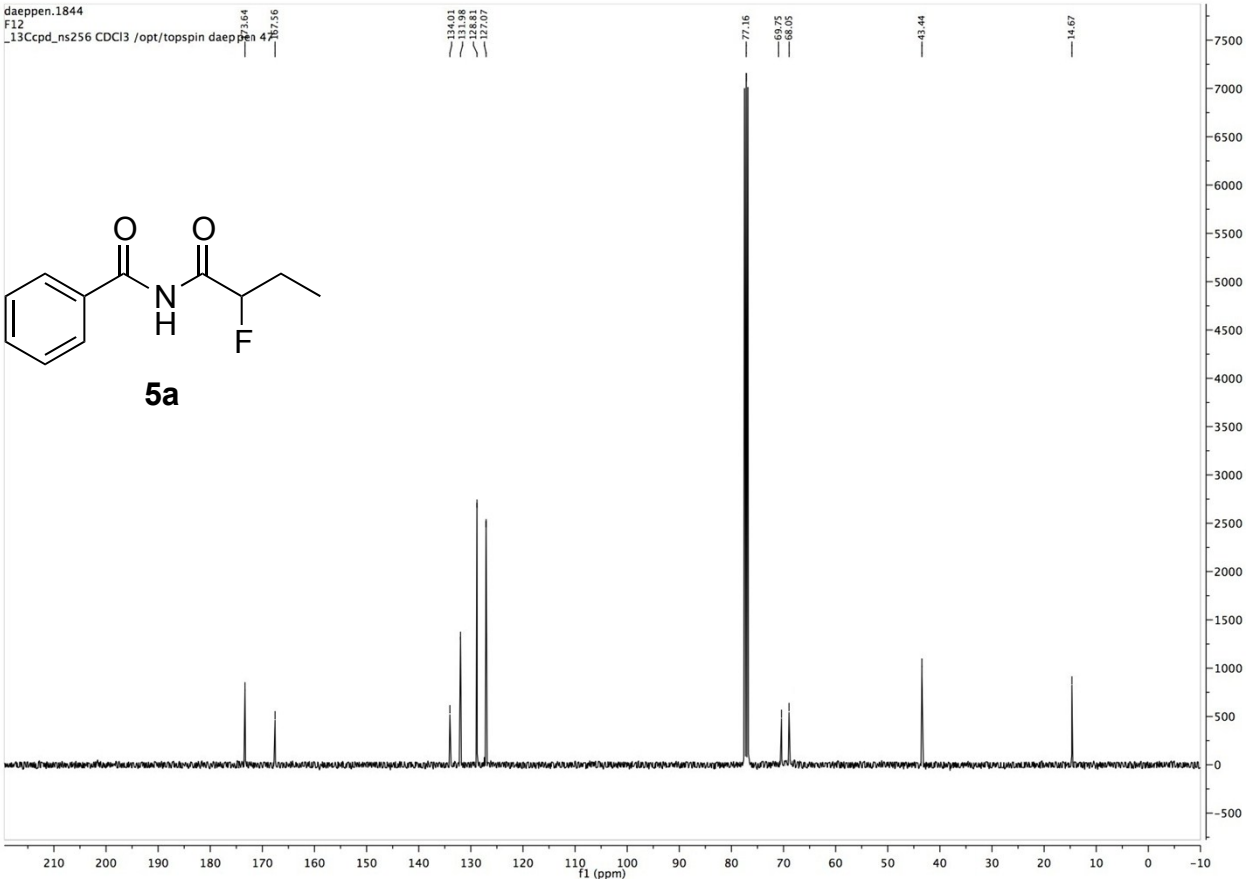
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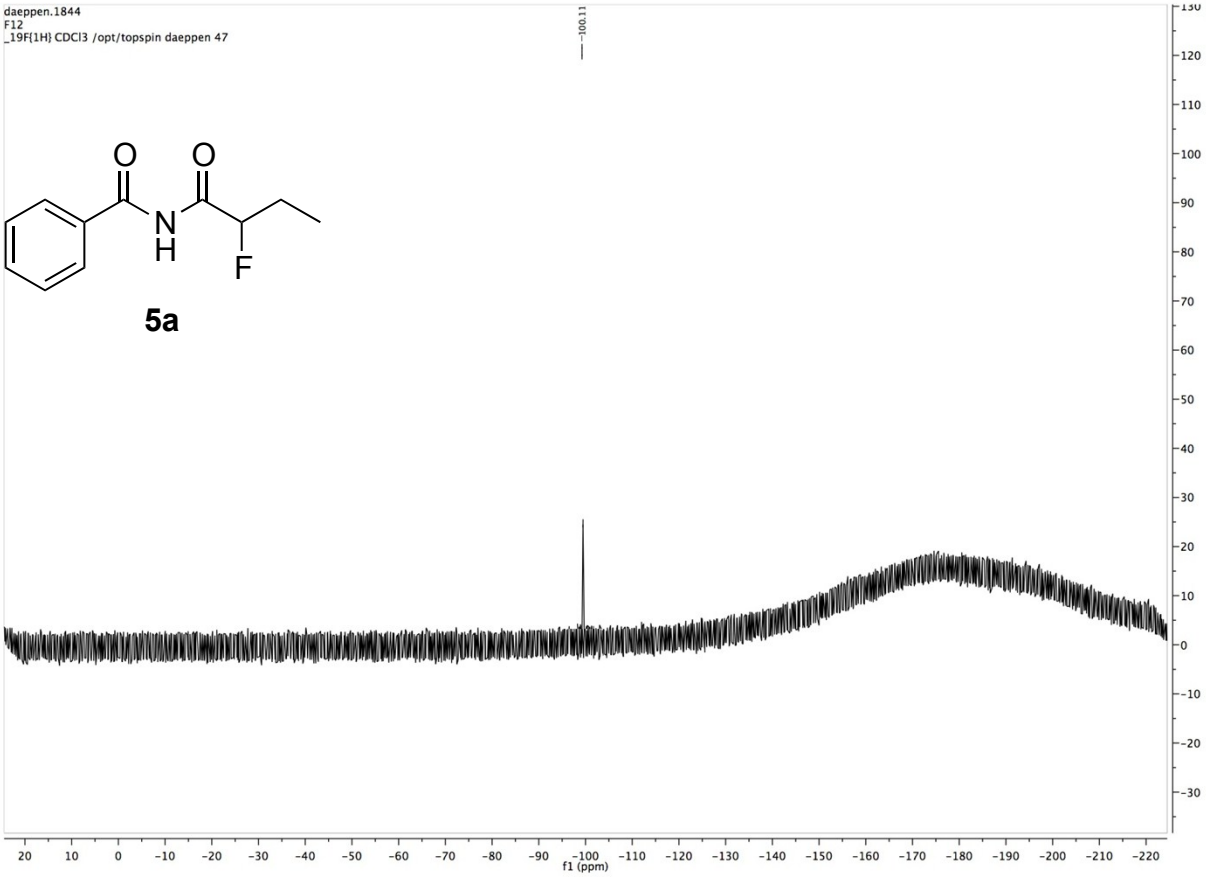
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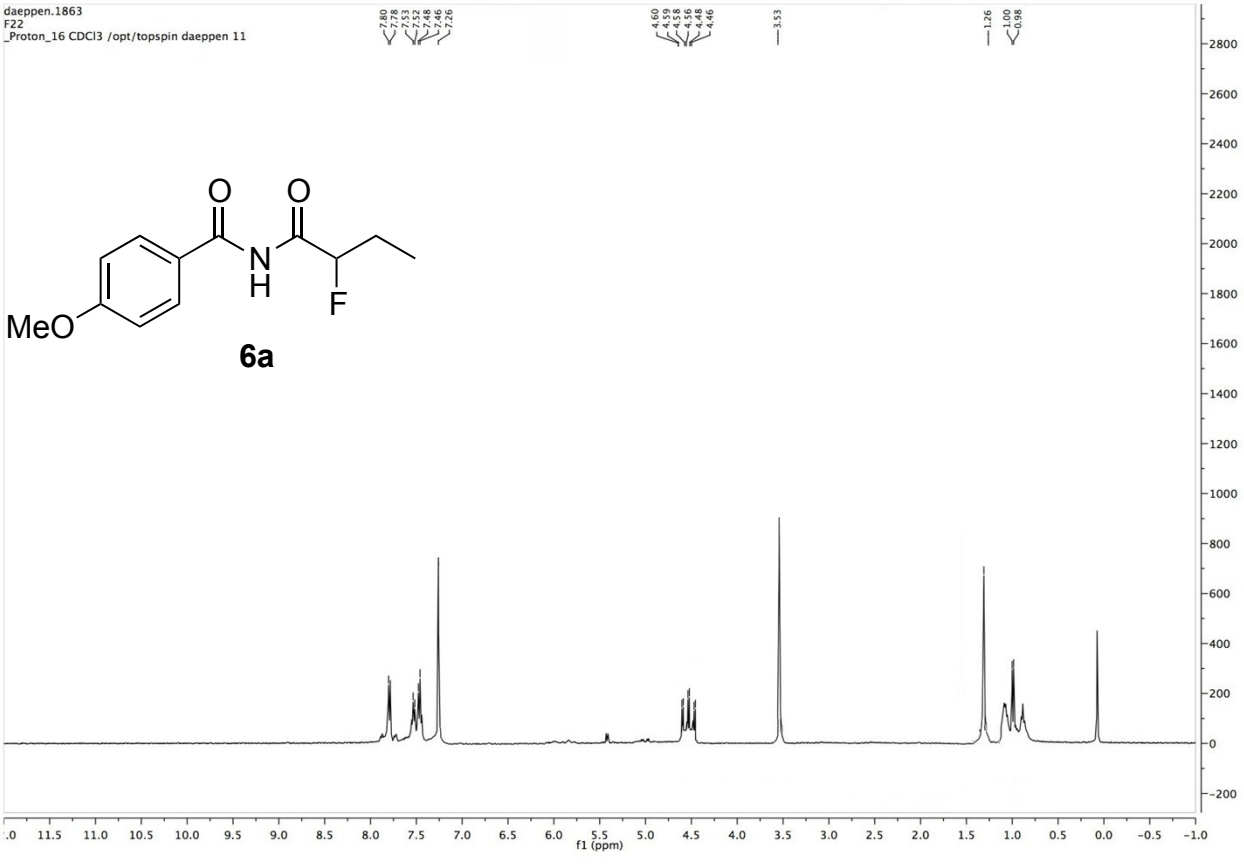
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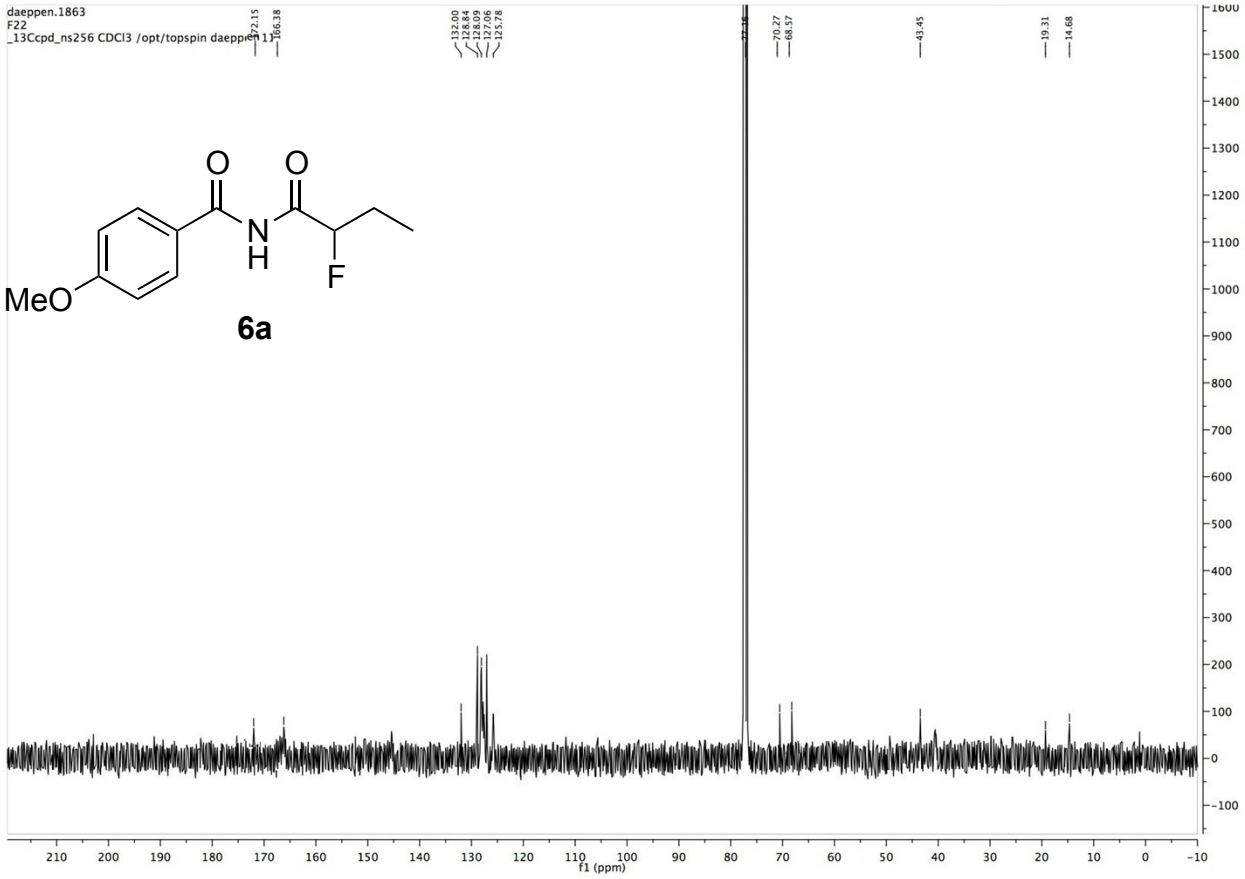
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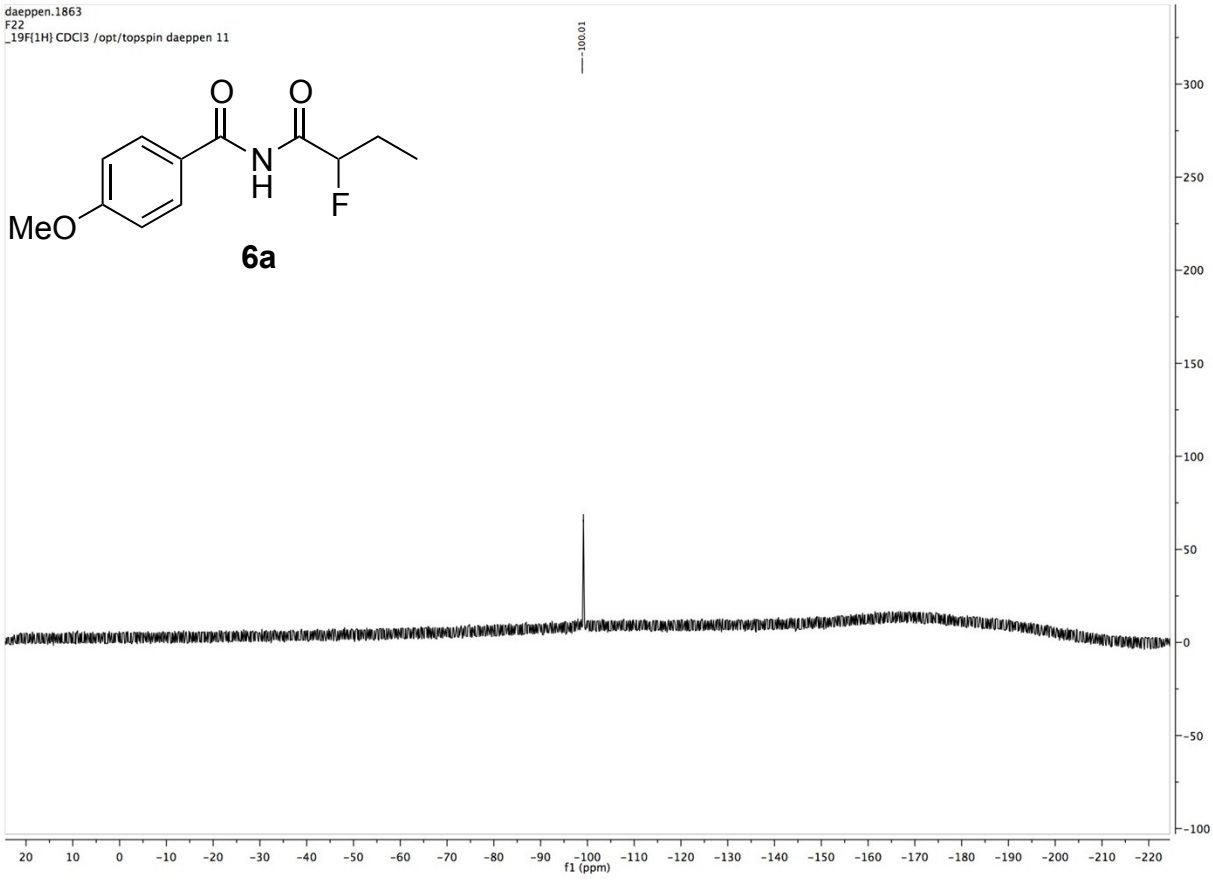
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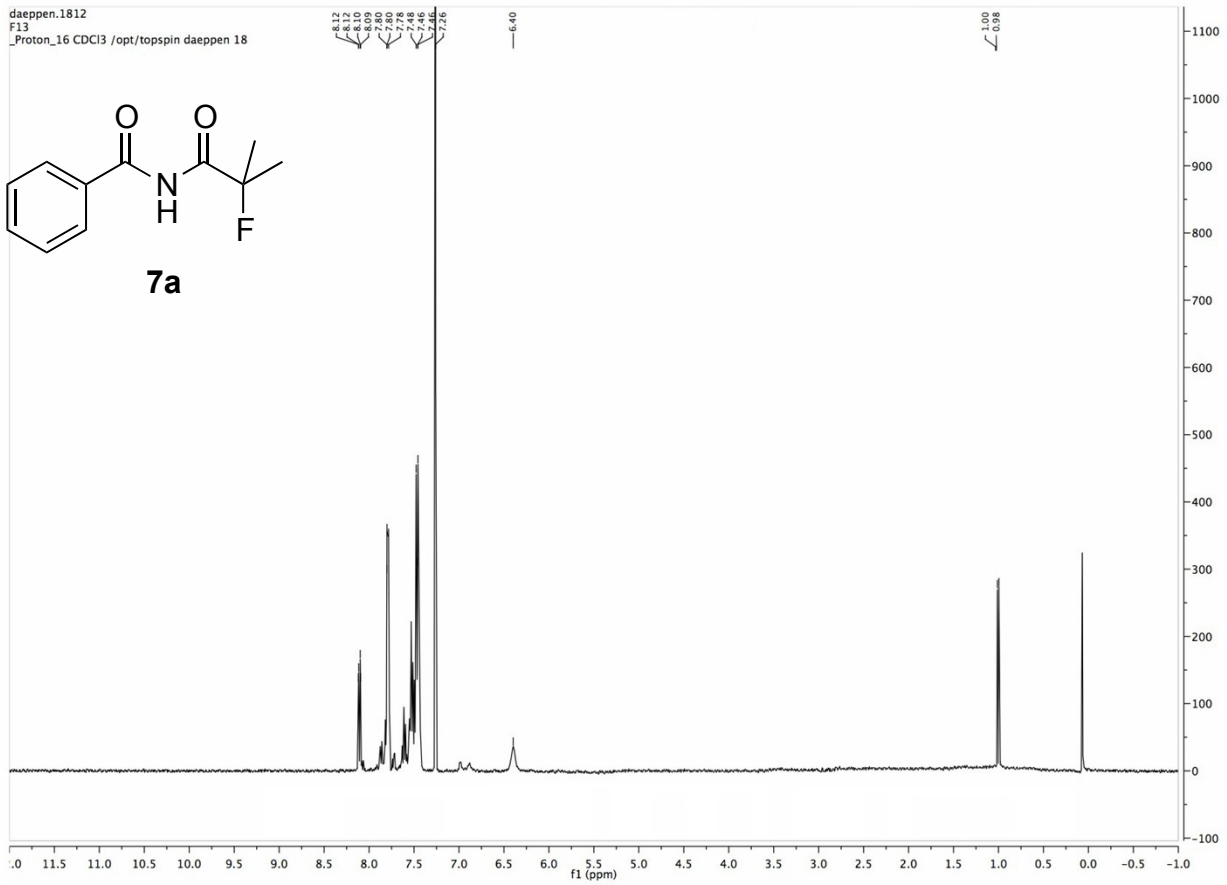
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O
N
H
F
f1 (ppm)

7a


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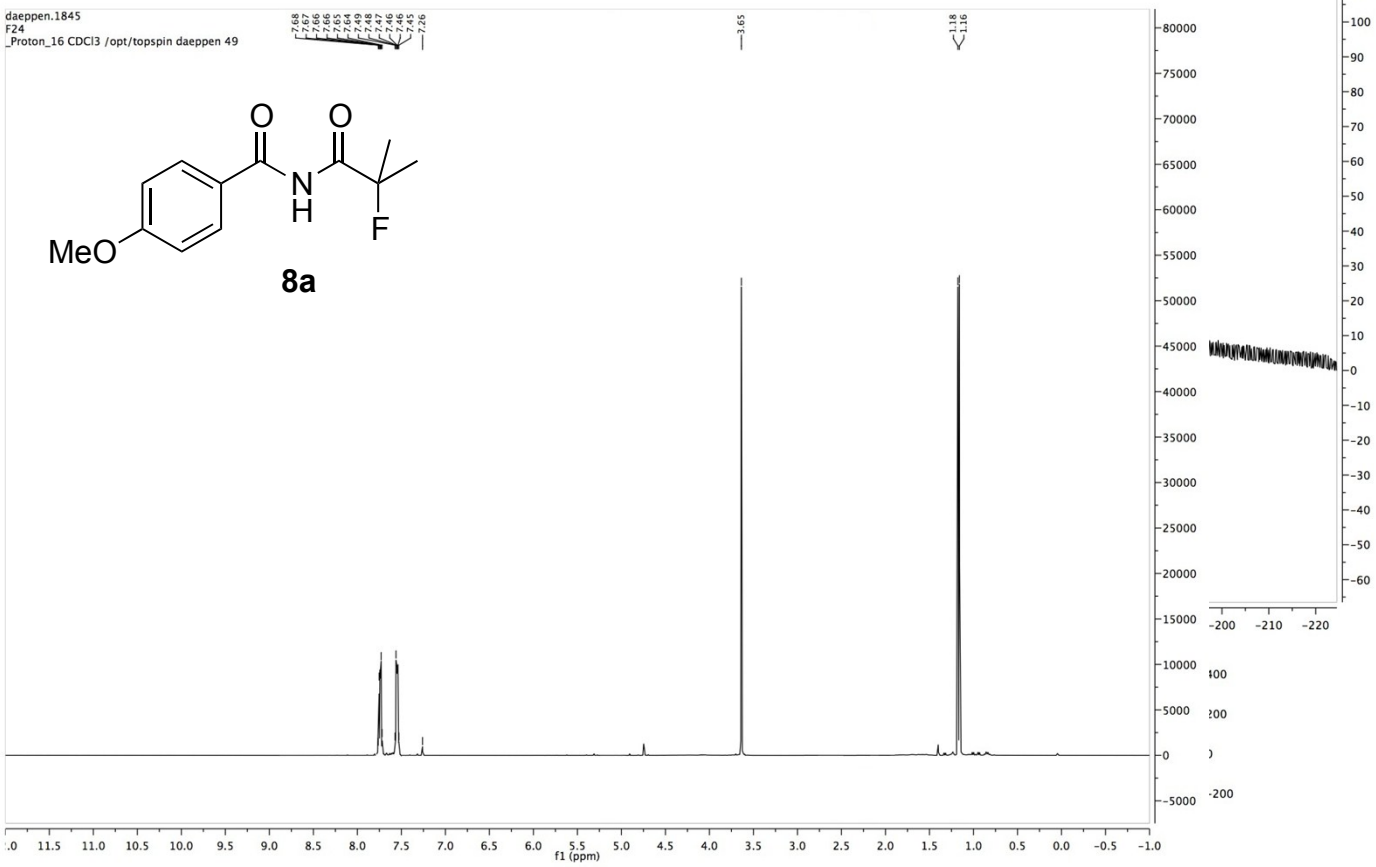
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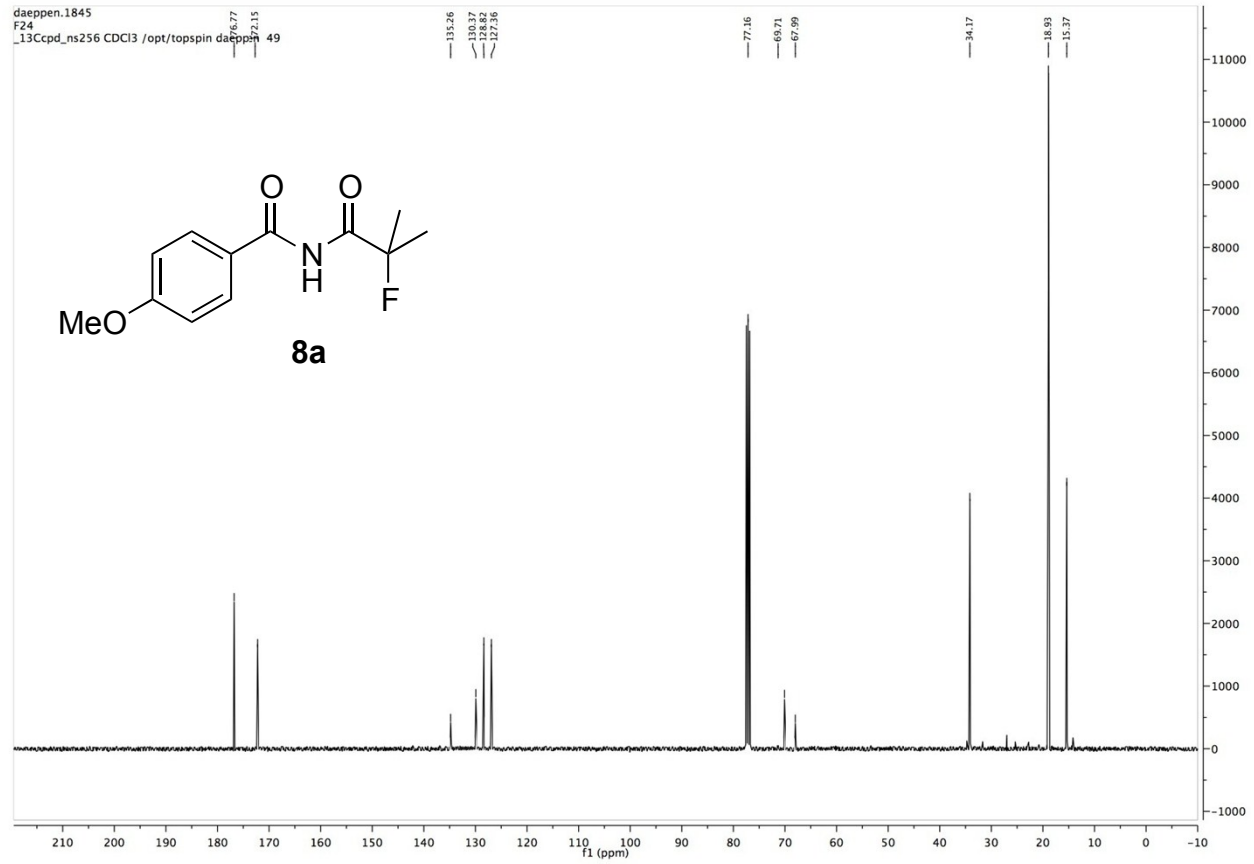
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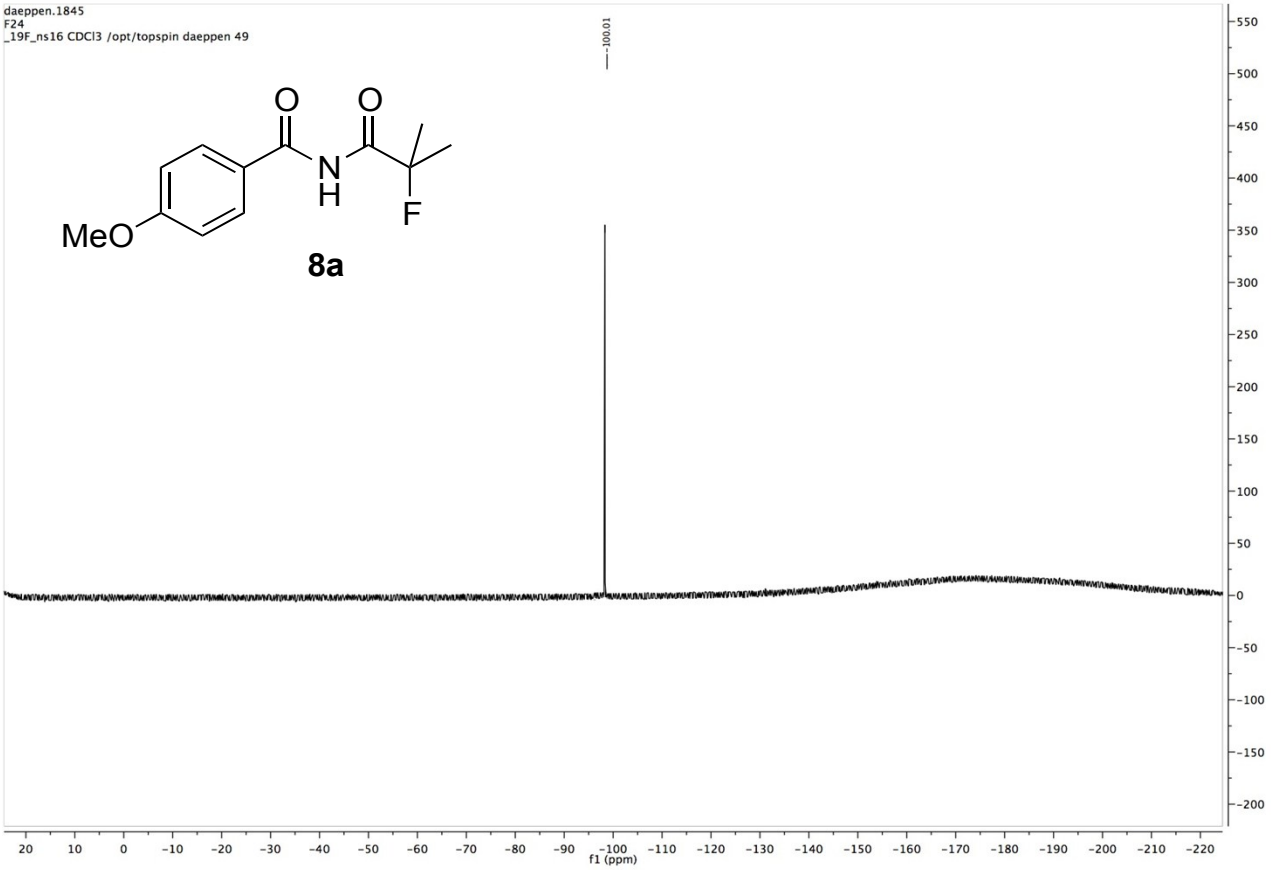
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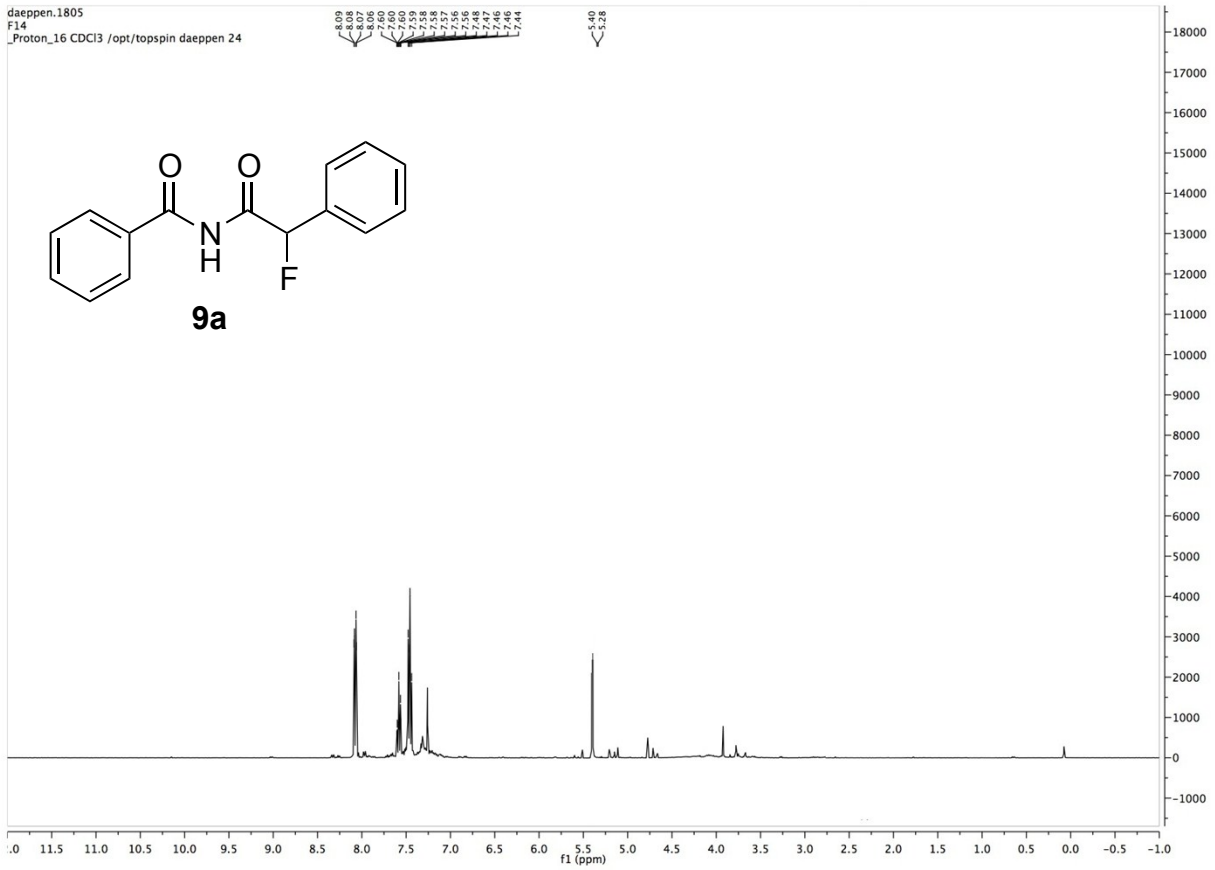
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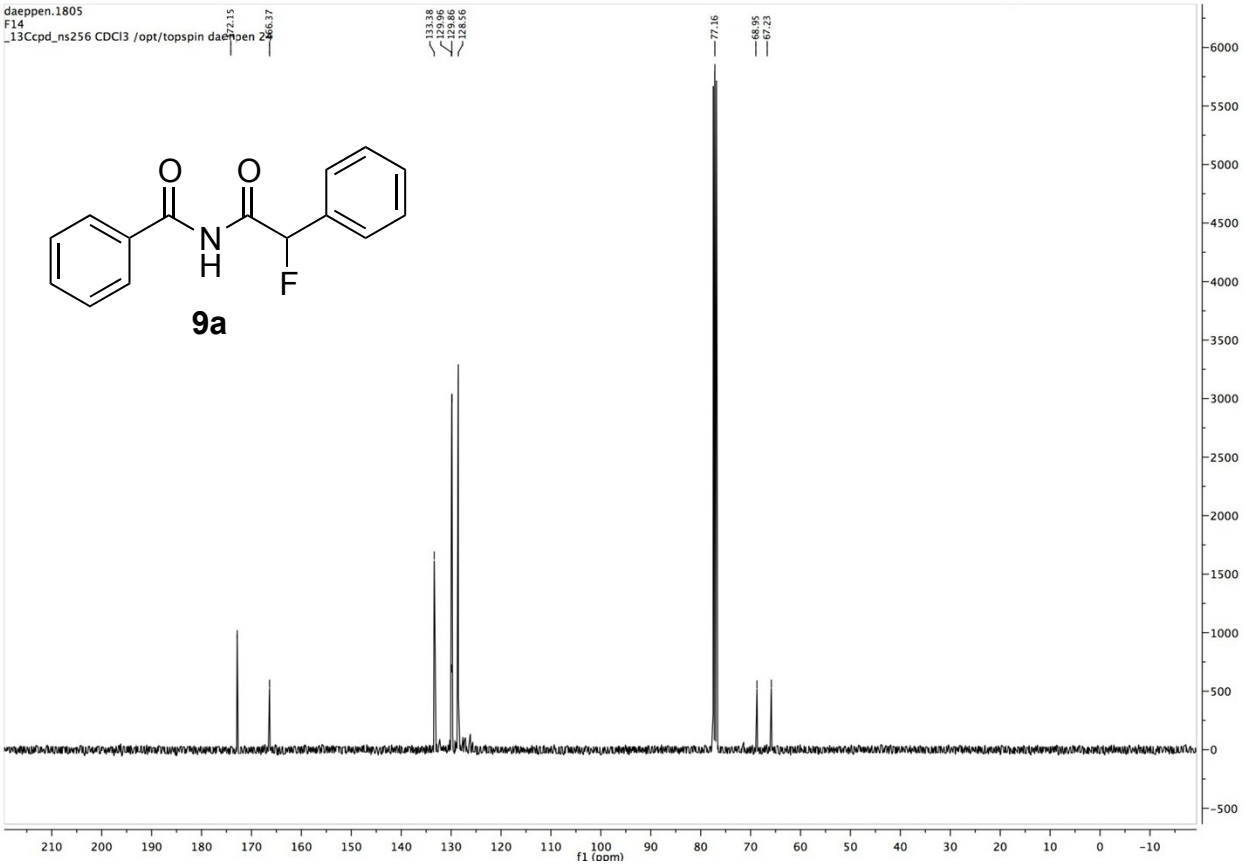
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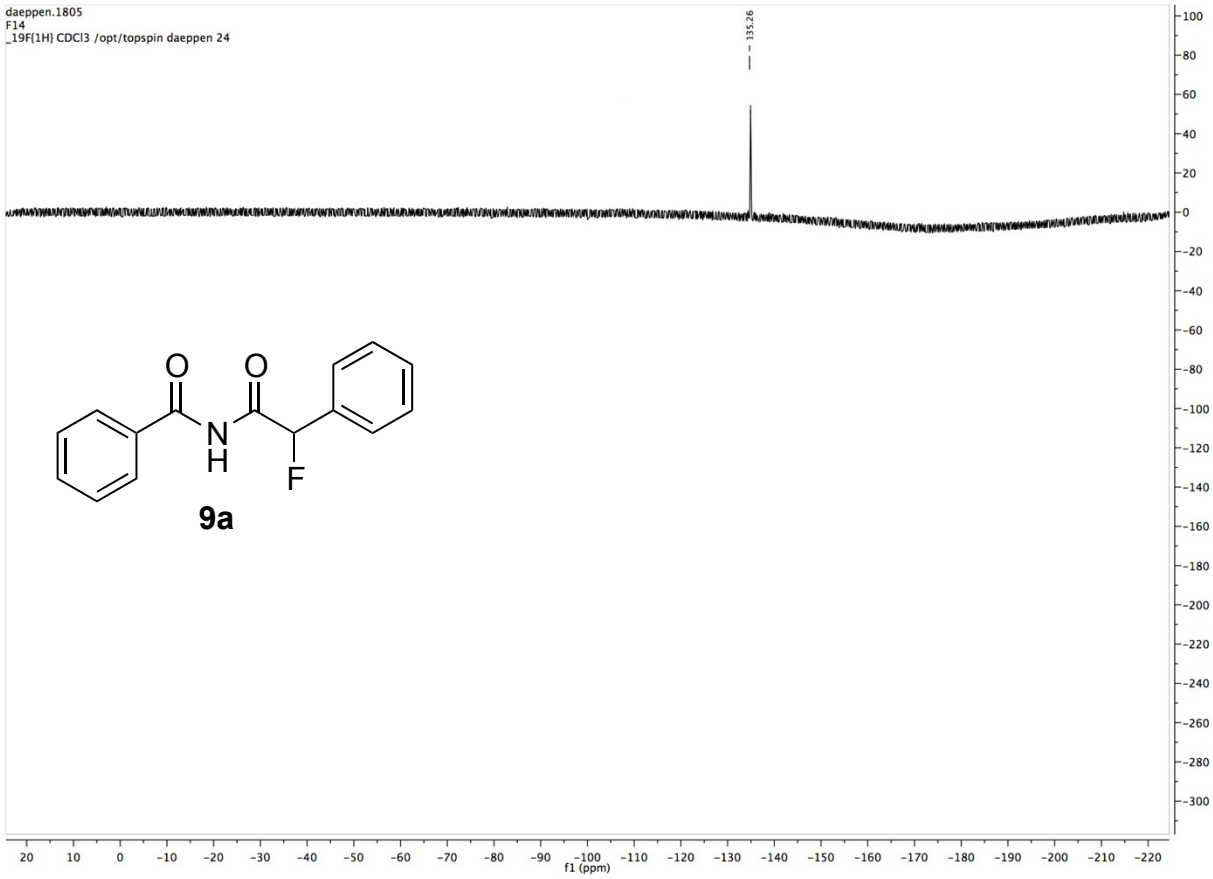
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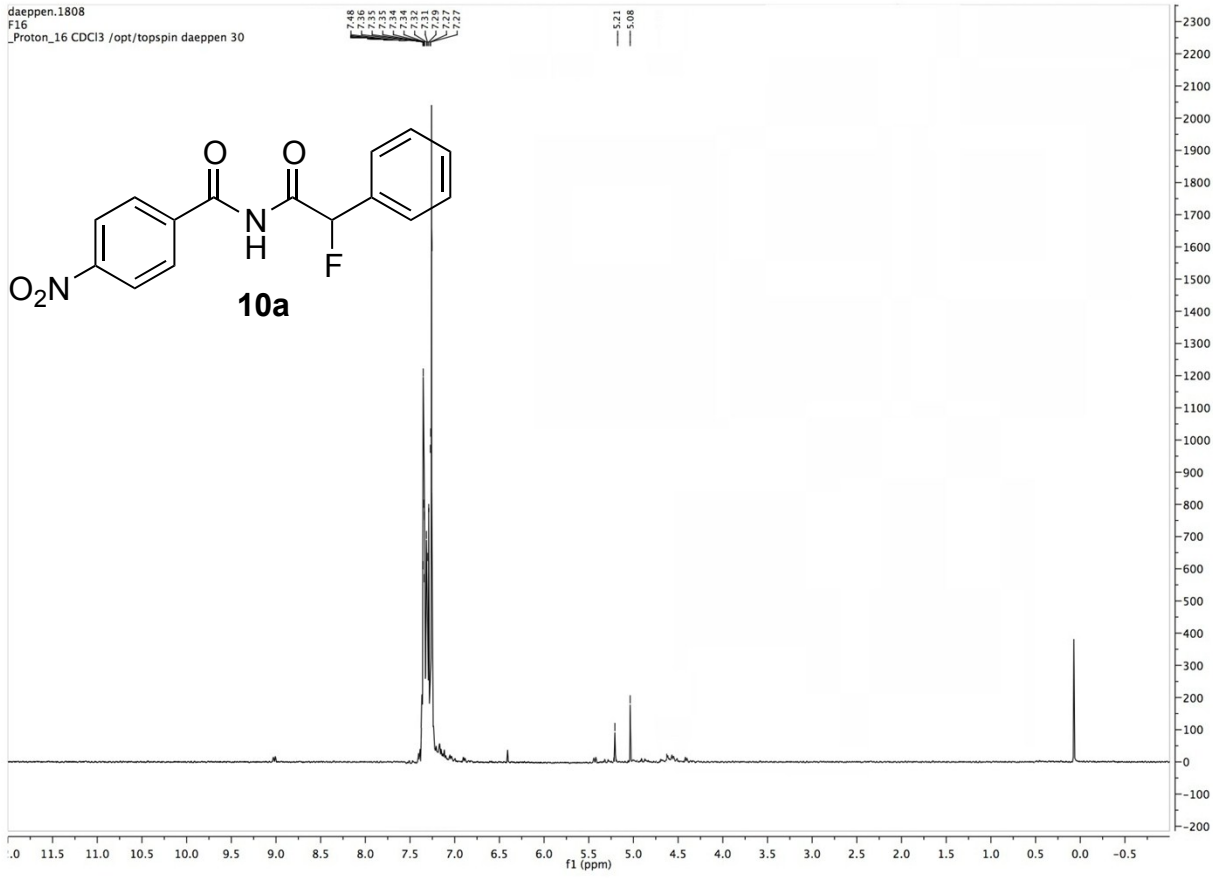
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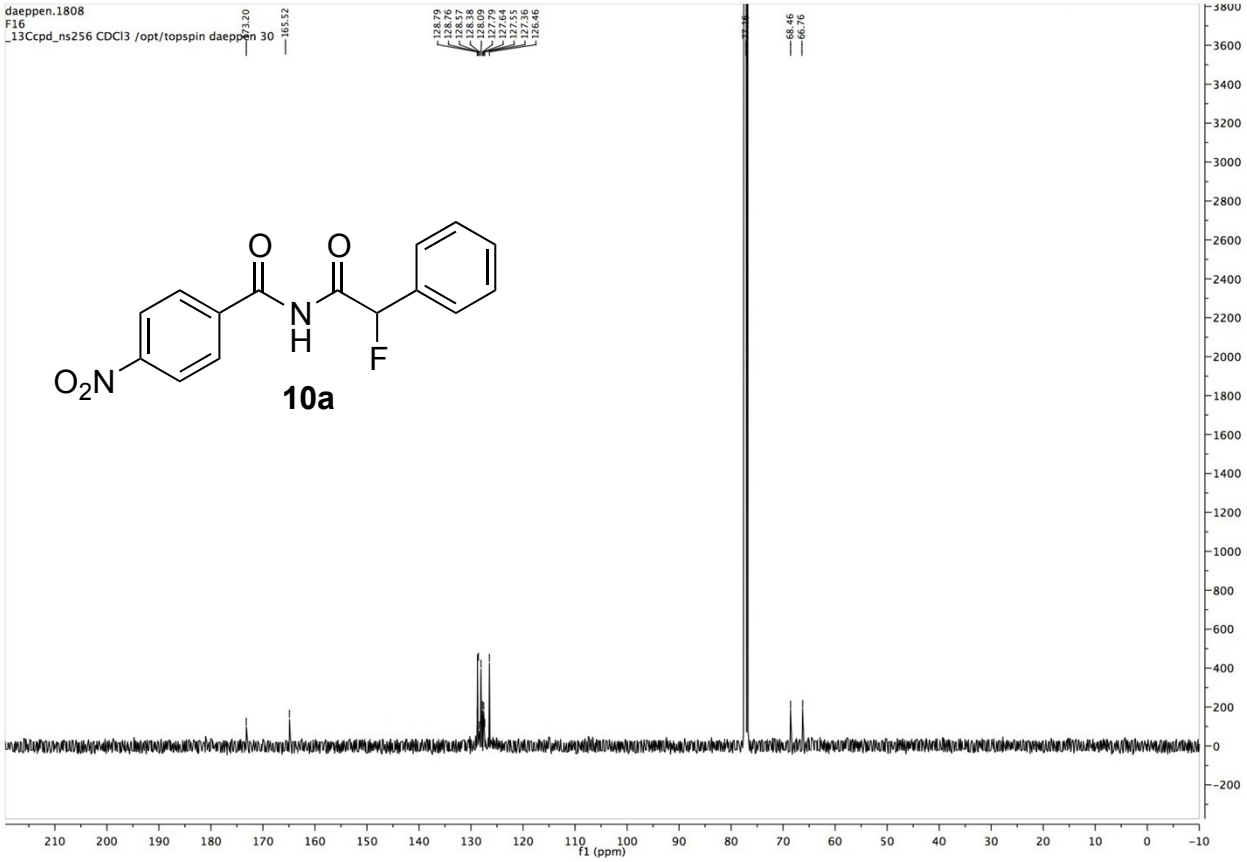
10a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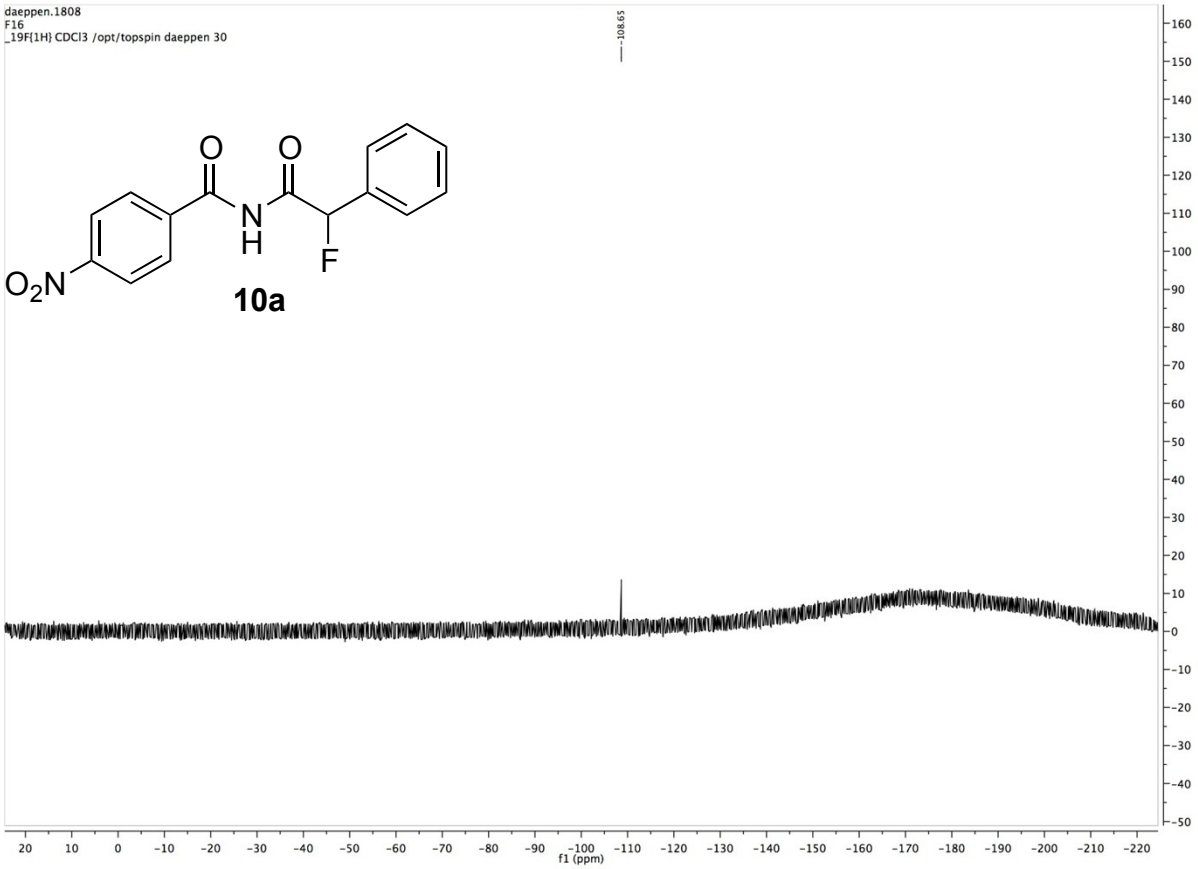
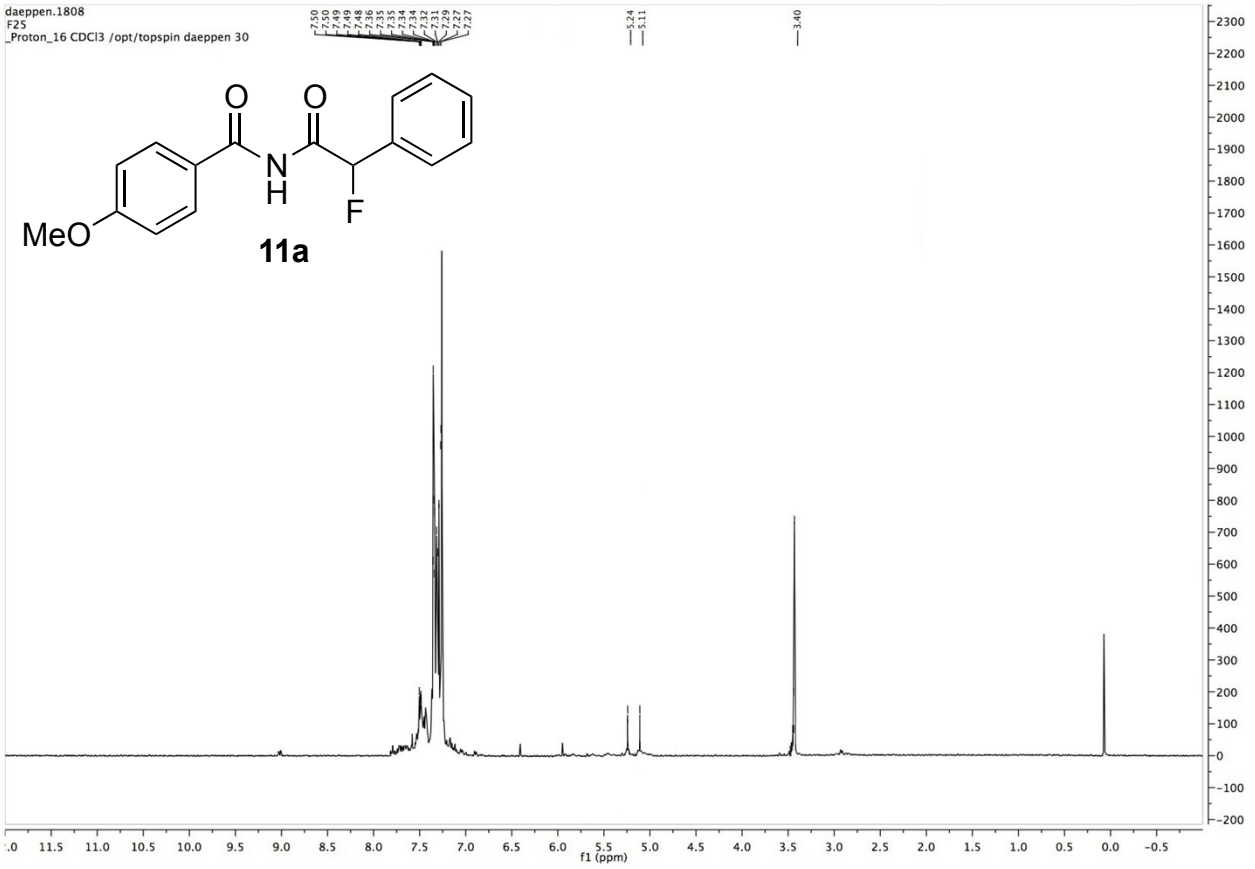
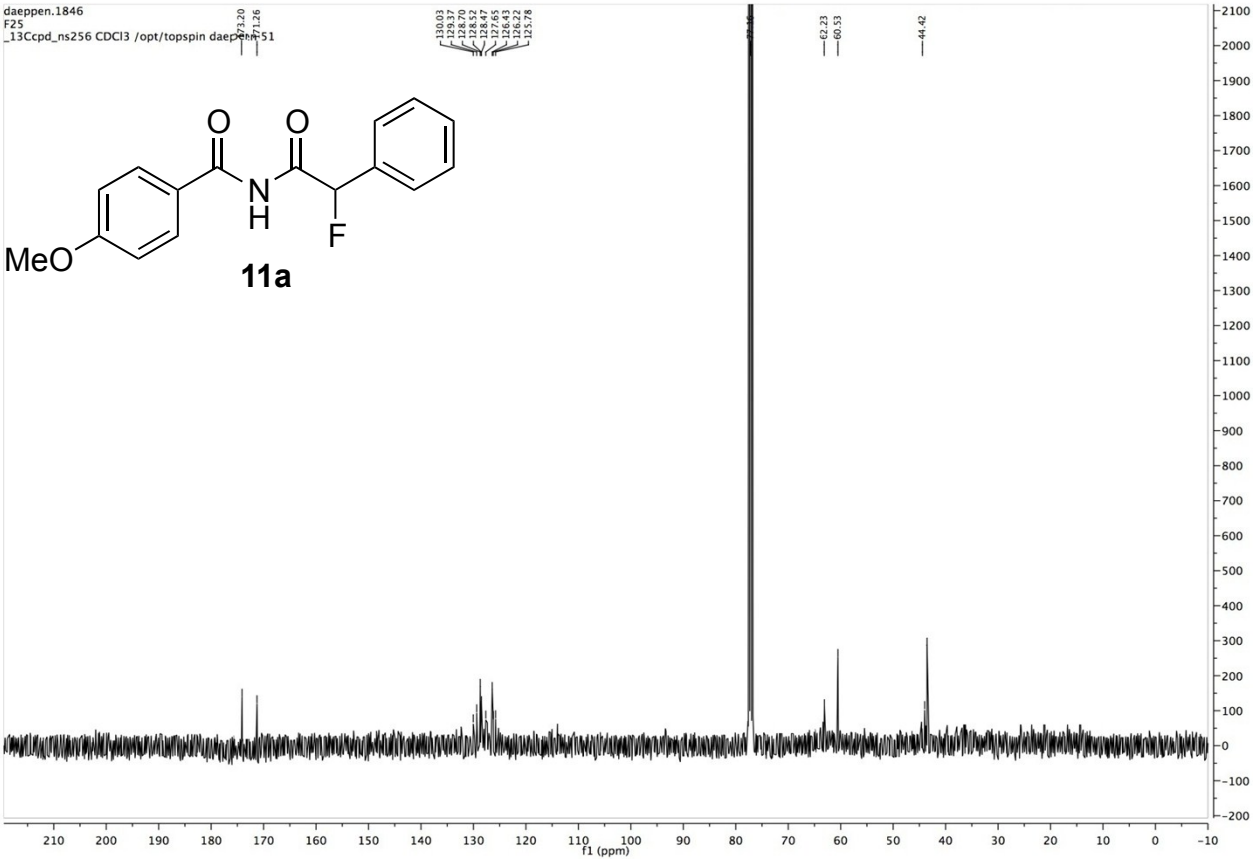
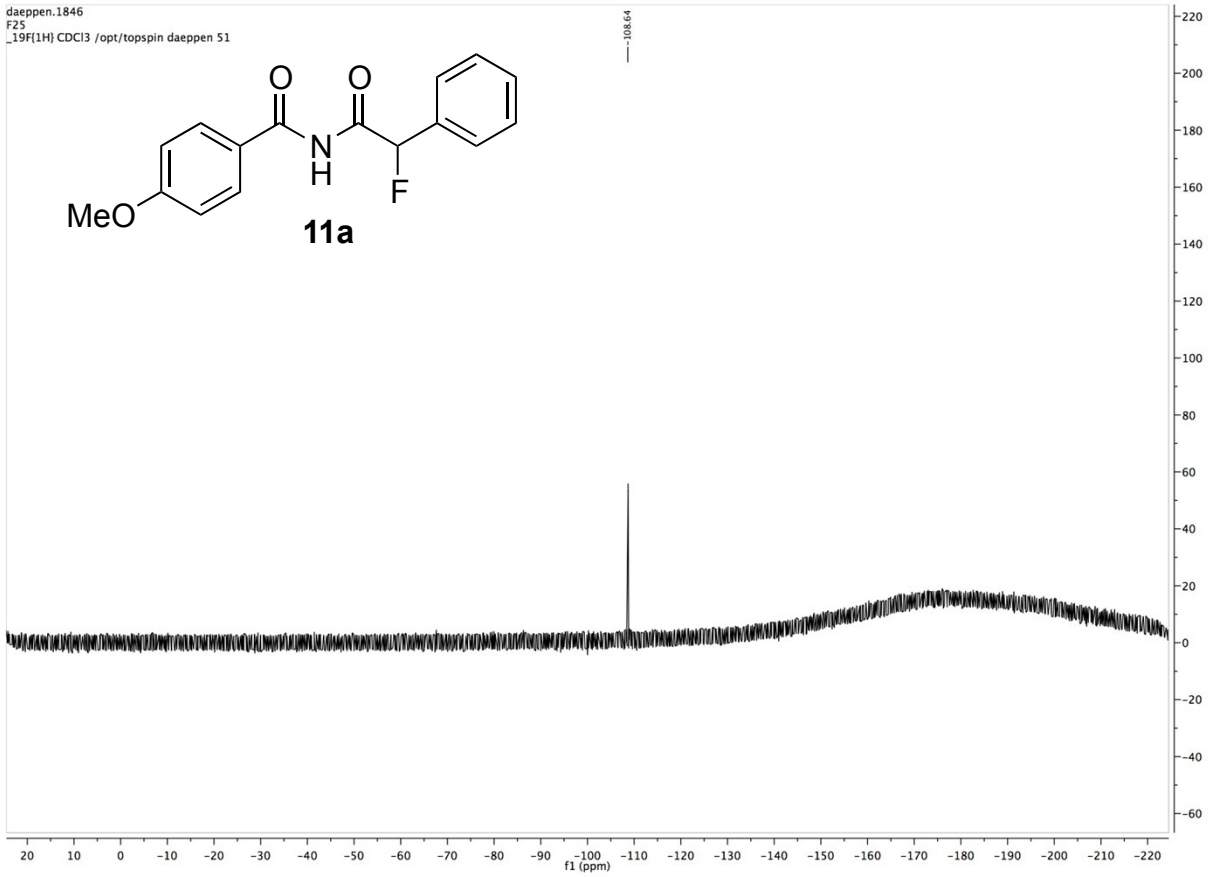
O
N
H
F
O2N
10a
f1 (ppm)

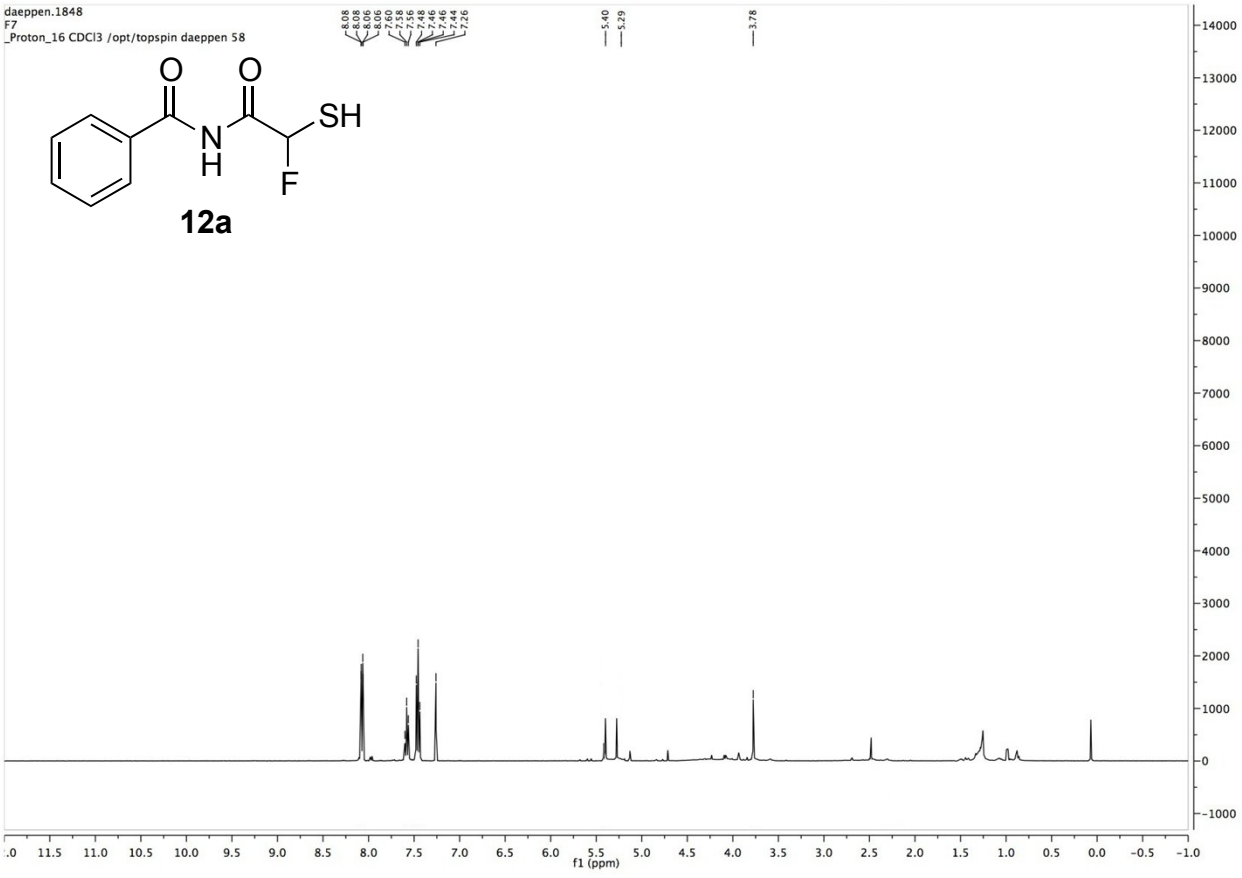

daeppen.1808
F16
_19F{1H} CDCl3 /opt/topspin daeppen 30
-108.65
O
O
N
H
F
O2N
10a
f1 (ppm)


daeppen.1808
F25
_Proton_16 CDCl3 /opt/topspin daeppen 30
7.50
7.50
7.49
7.49
7.48
7.36
7.35
7.35
7.34
7.34
7.32
7.31
7.29
7.27
7.27
5.24
5.11
3.40
O
O
N
H
F
MeO
11a
f1 (ppm)

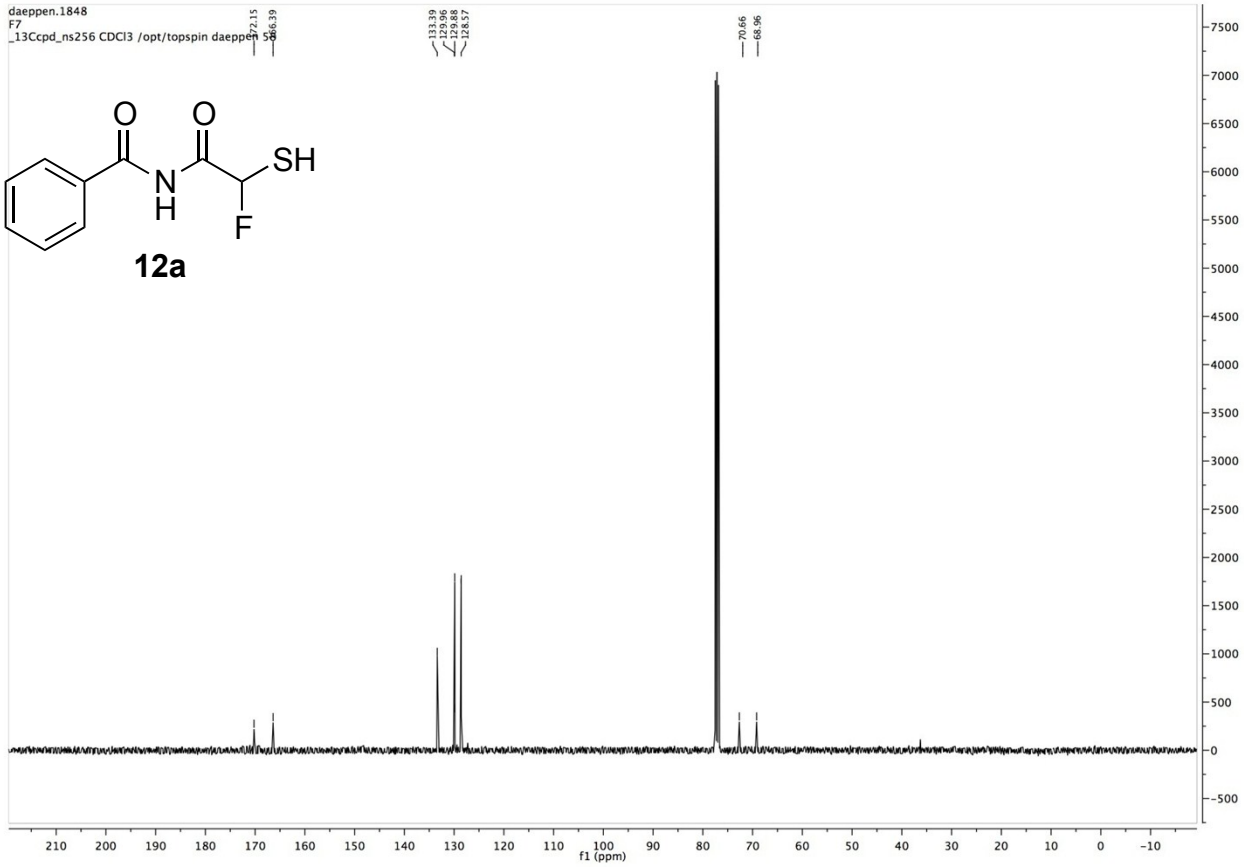

daeppen.1846
F25
_13Ccpd_ns256 CDCl3 /opt/topspin daeppen 51
173.20
171.26
130.03
129.37
128.70
128.52
128.47
127.65
125.43
126.22
125.78
62.23
60.53
44.42
O
O
N
H
F
MeO
11a
f1 (ppm)


daeppen.1846
F25
_19F[1H] CDCl3 /opt/topspin daeppen 51
-108.64
O
O
N
H
F
MeO
f1 (ppm)

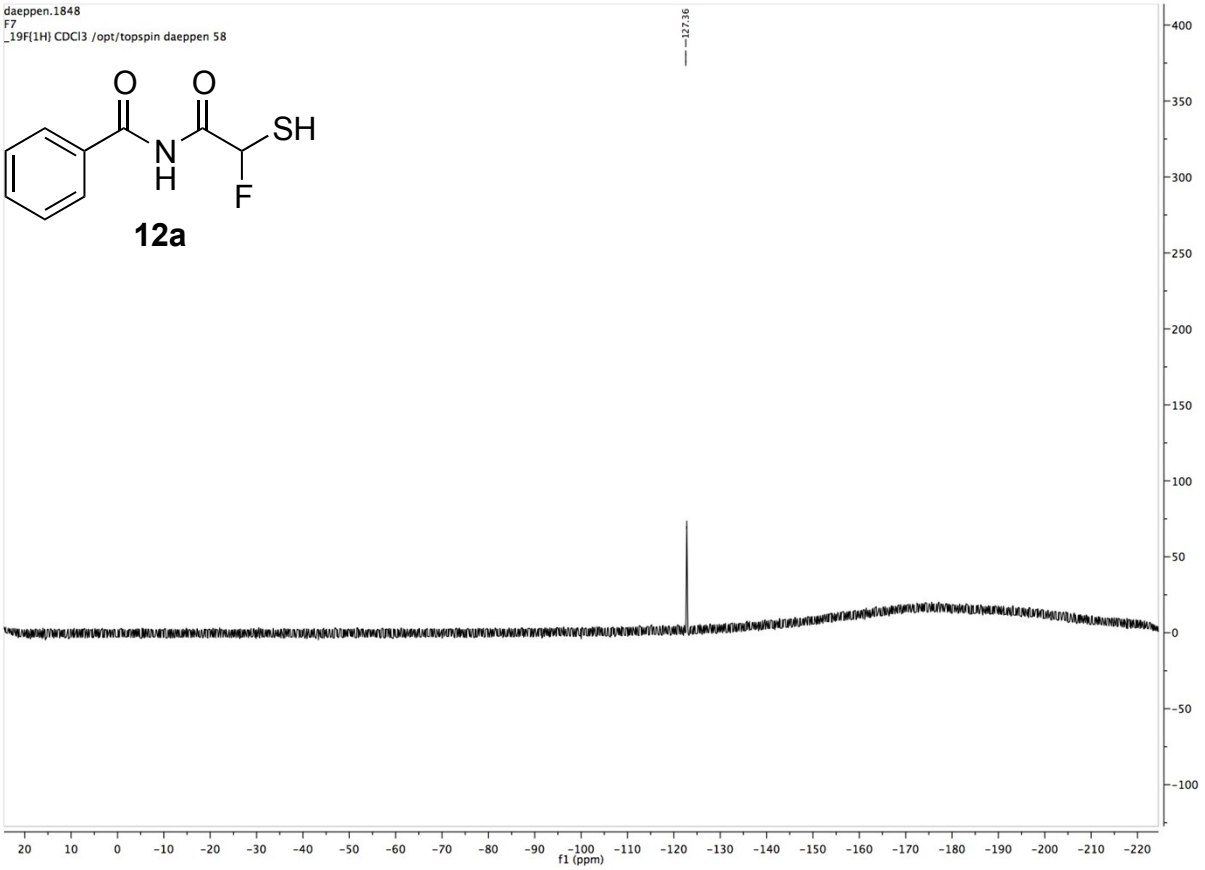
11a


daeppen.1848
F7
_Proton_16 CDCl3 /opt/topspin daeppen 58
8.08
8.08
8.06
8.06
7.58
7.56
7.48
7.46
7.46
7.44
7.26
5.40
5.29
3.78
O
O
N
H
SH
F
f1 (ppm)

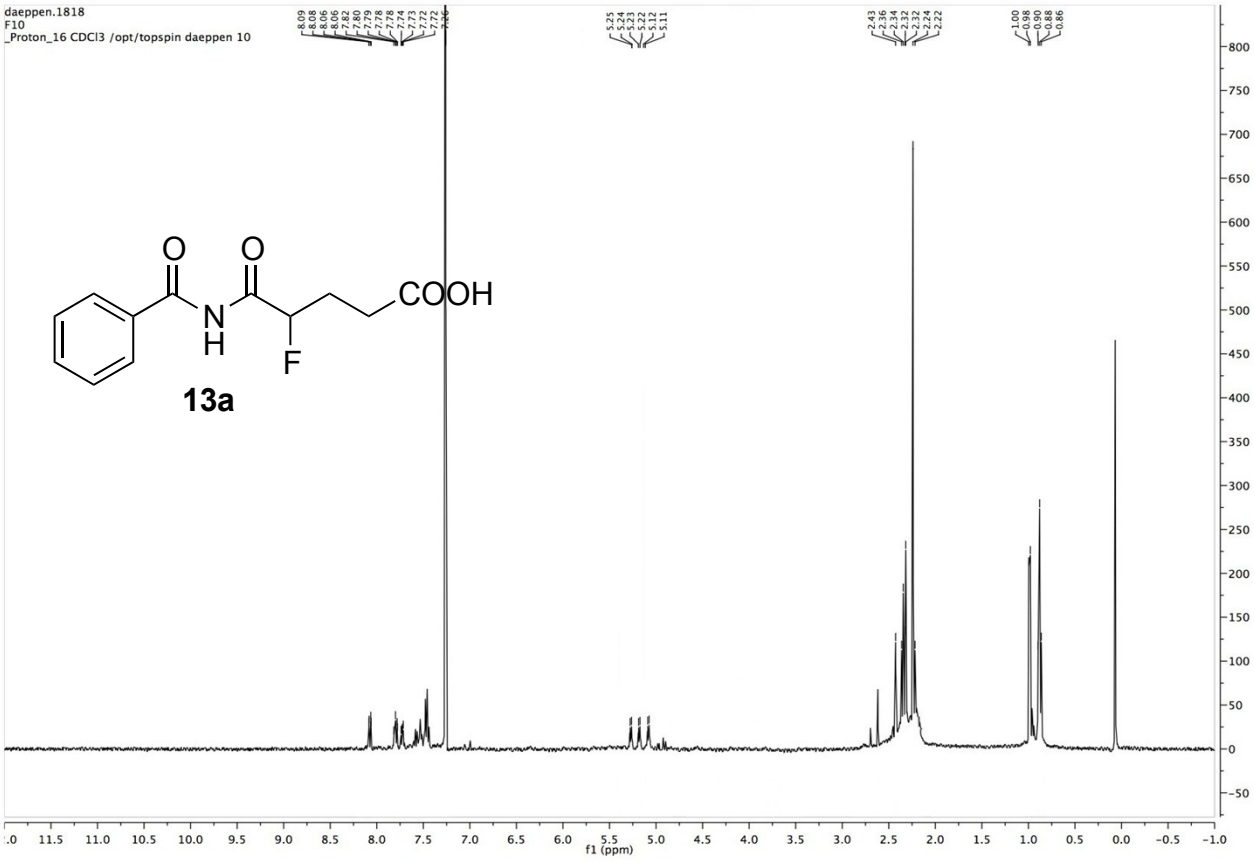
12a

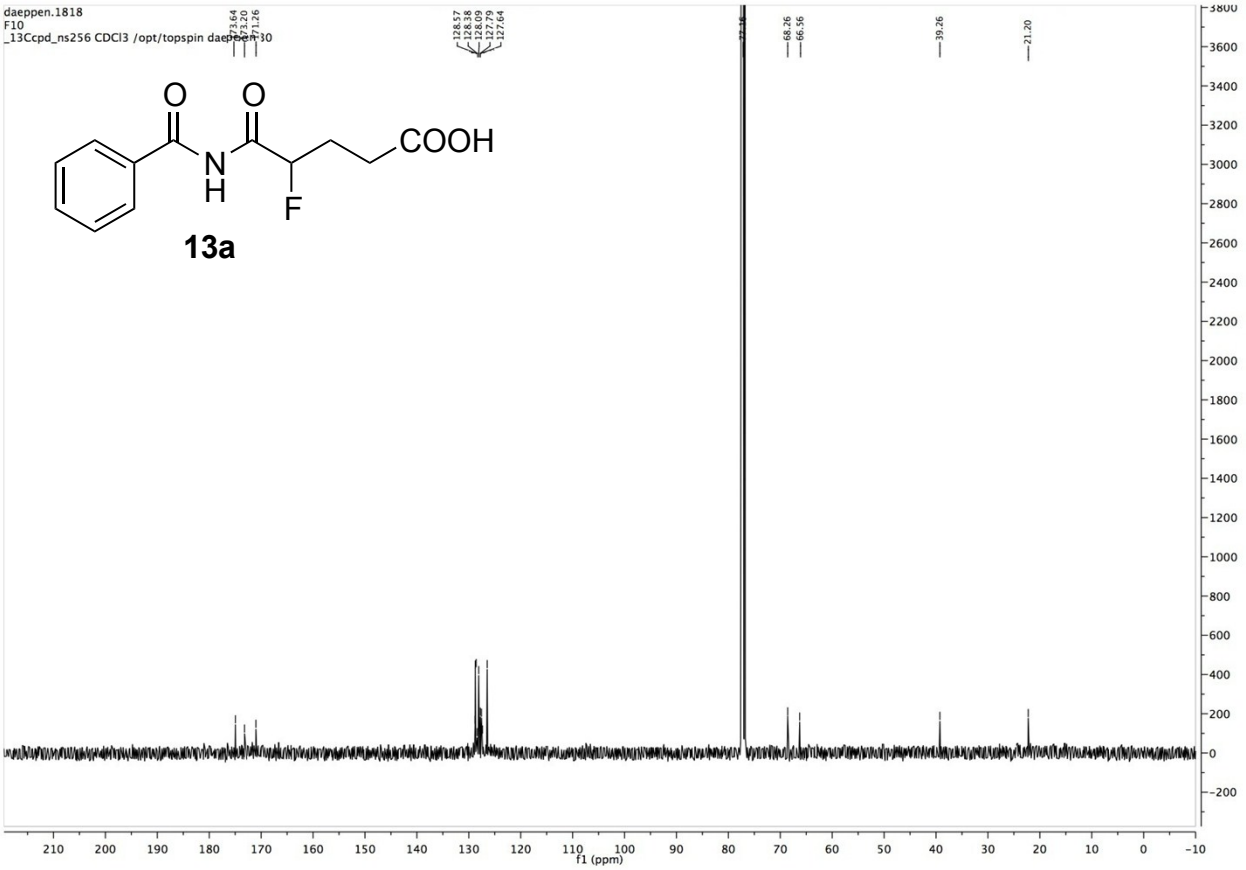

daeppen.1848
F7
_13Ccpd_ns256 CDCl3 /opt/topspin daeppen 5
169.15
166.39
133.39
129.96
129.88
128.57
70.66
68.96
O
O
N
H
SH
F
f1 (ppm)

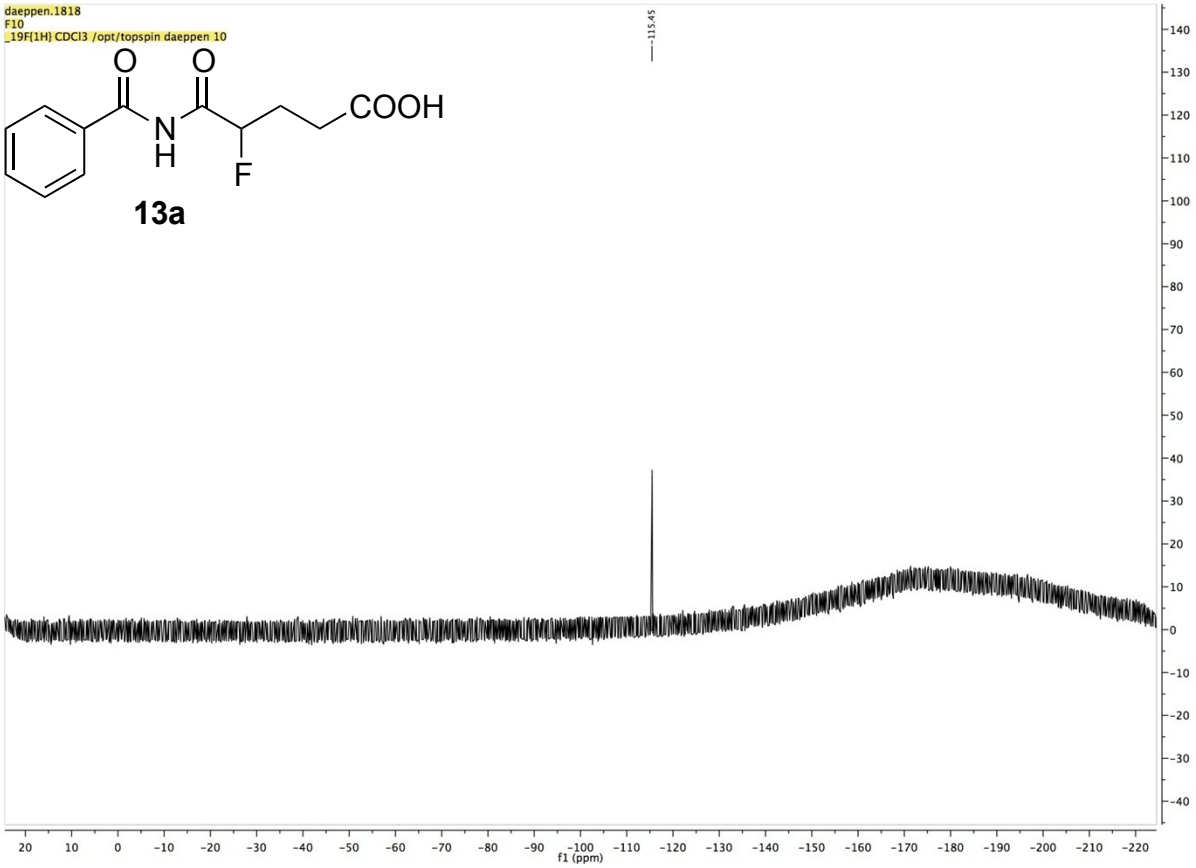
12a

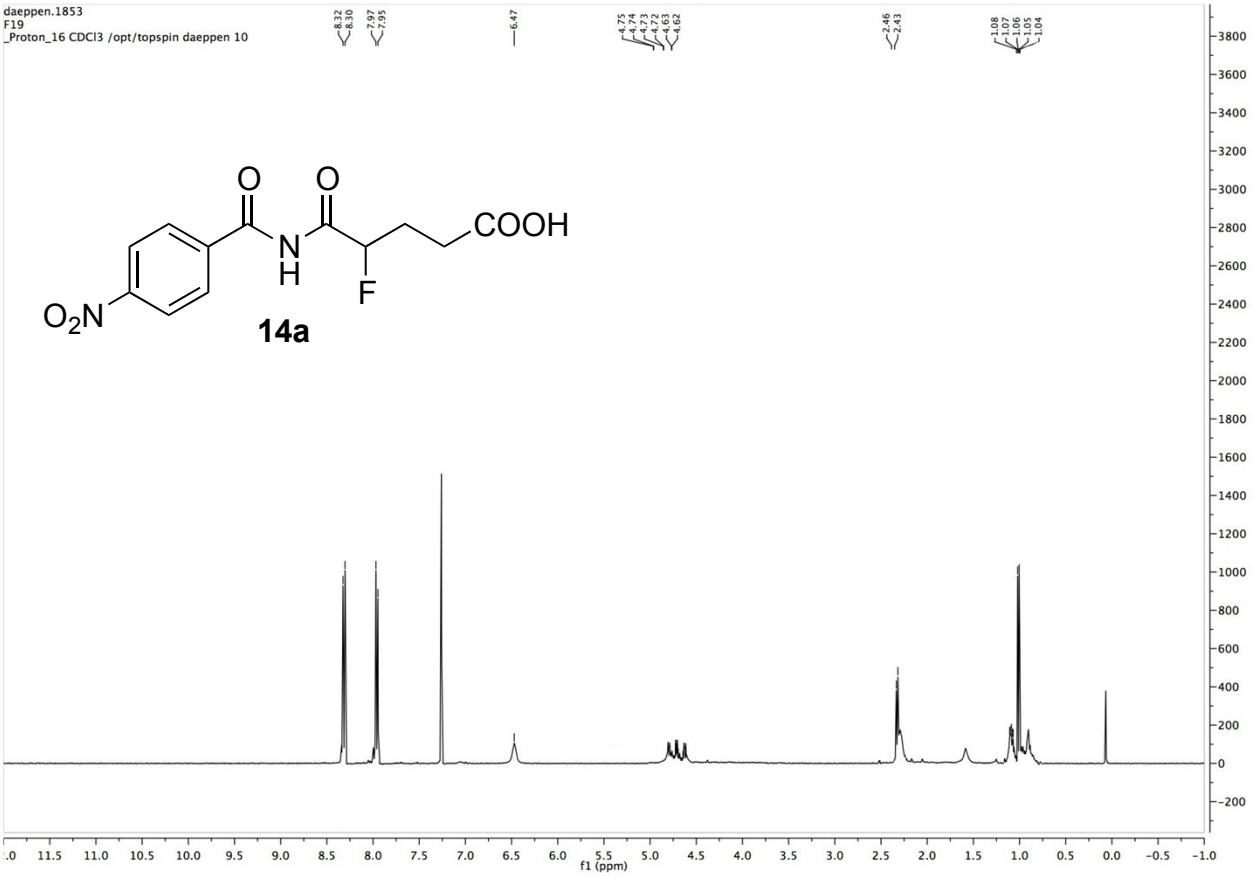

daeppen.1848
F7
_19F{1H} CDCl3 /opt/topspin daeppen 58
-127.36
O
O
N
H
SH
F
f1 (ppm)

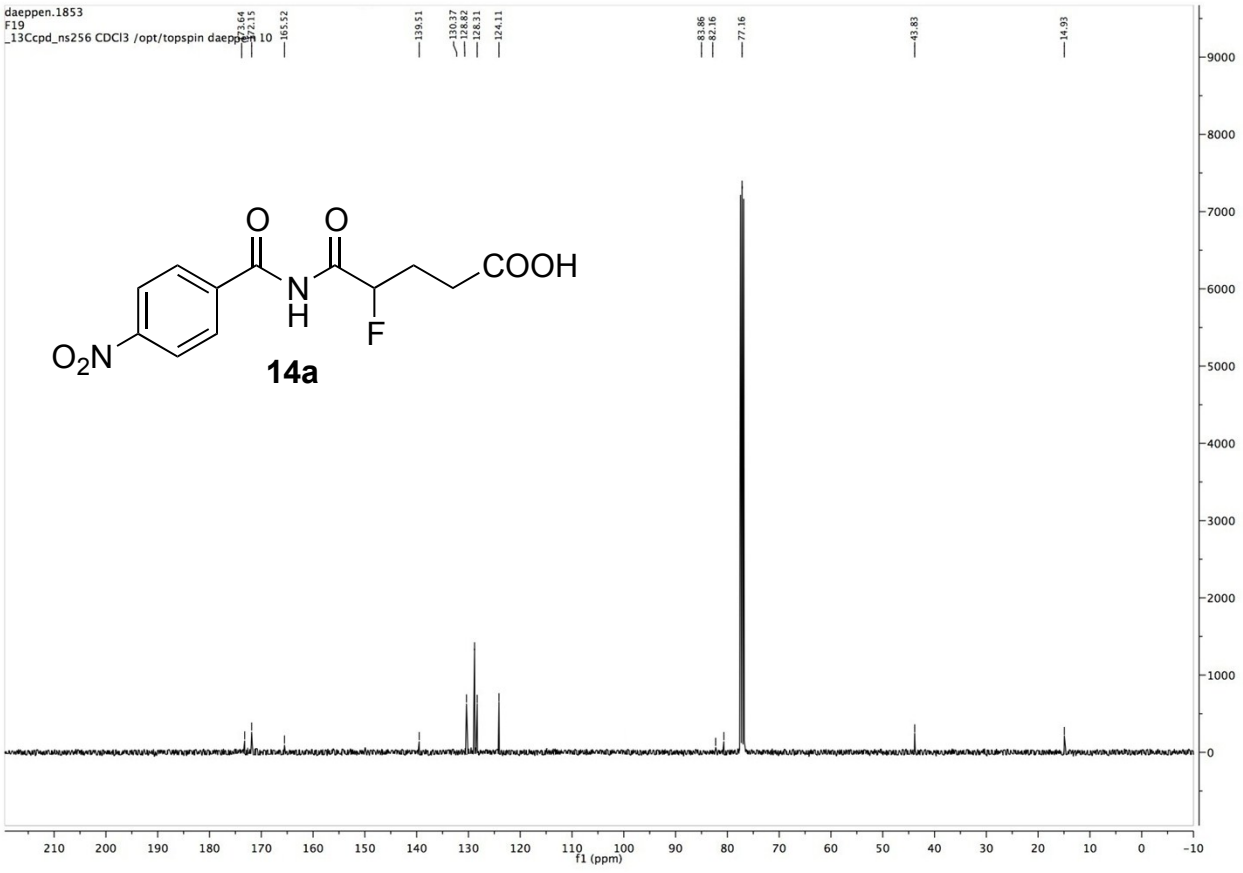
12a

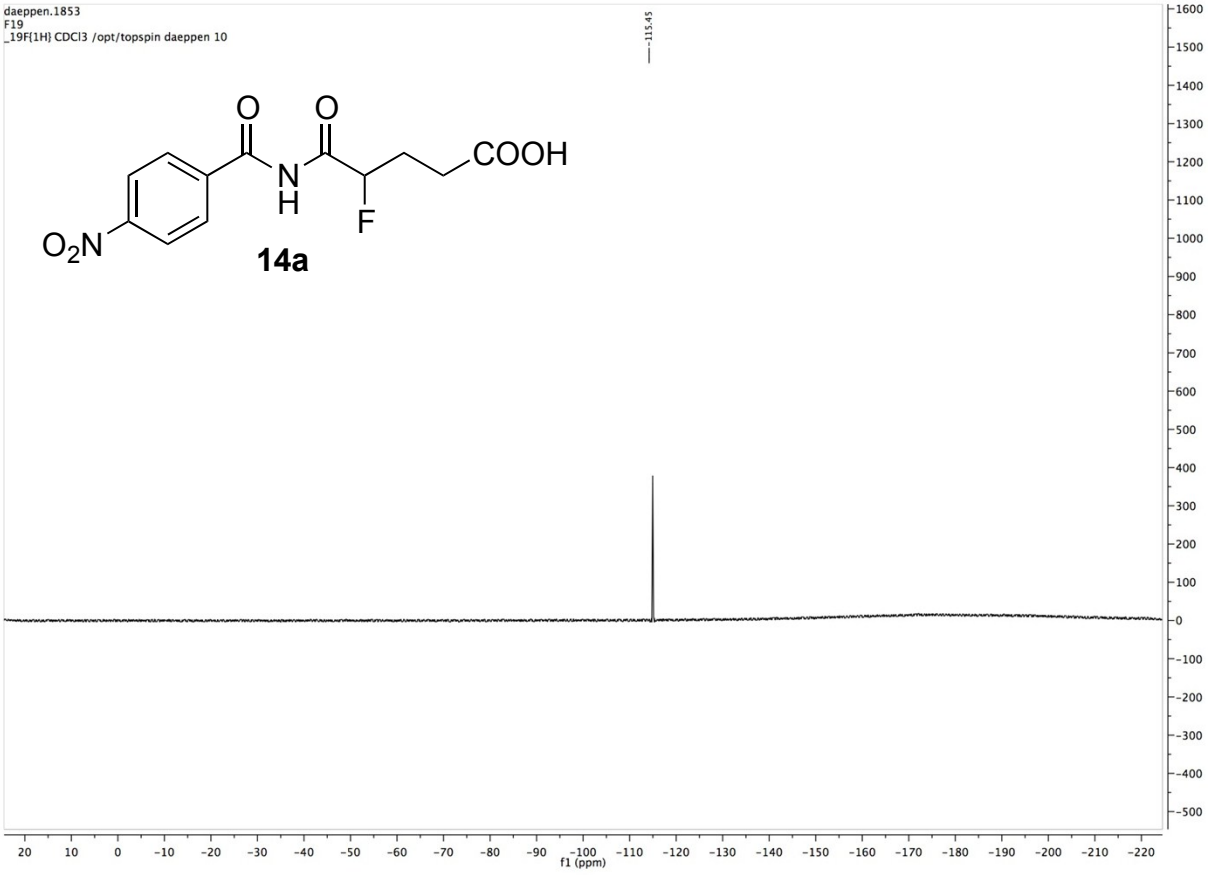

daeppen.1818
F10
_Proton_16 CDCl3 /opt/topspin daeppen 10
O
O
N
H
F
COOH
13a
f1 (ppm)

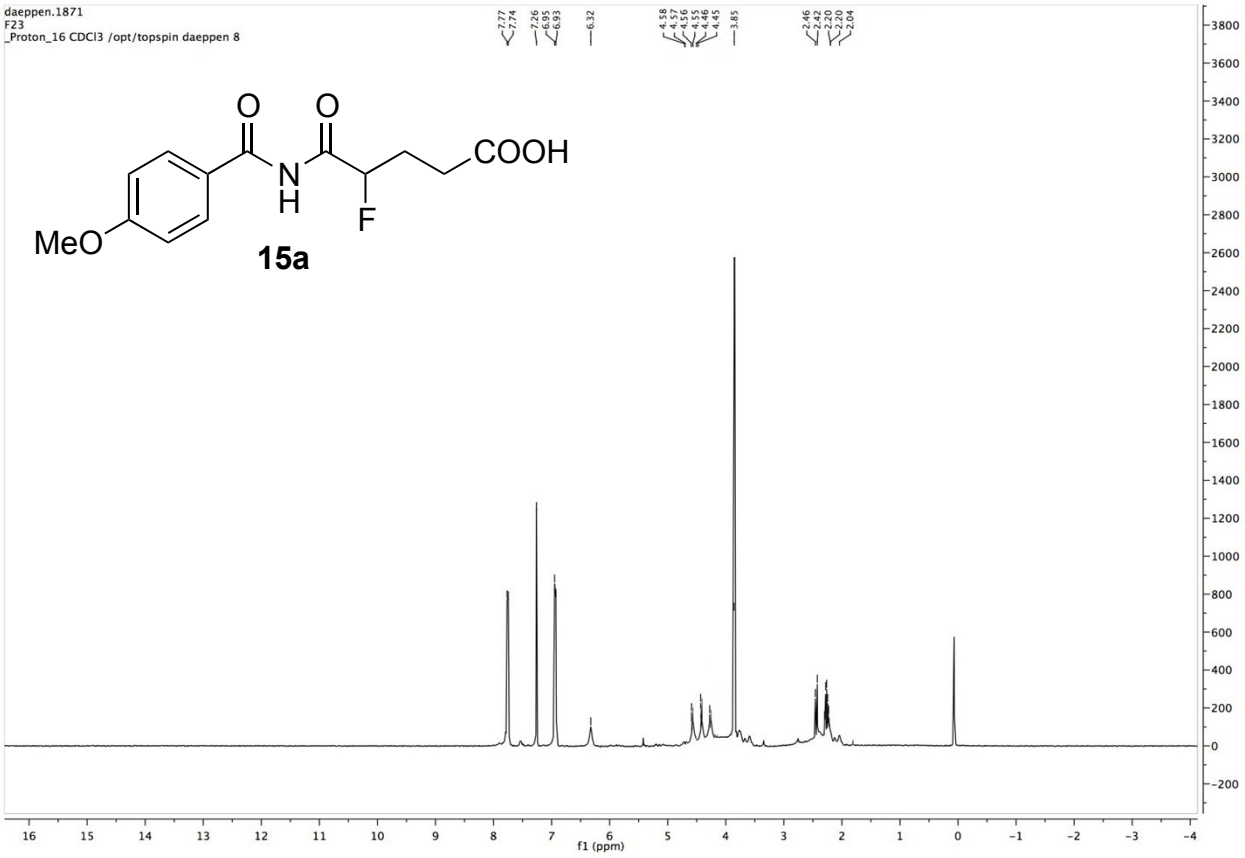

daeppen.1818
F10
_13Ccpd_ns256 CDCl3 /opt/topspin daeppen 30
O
O
N
H
F
COOH
13a
f1 (ppm)

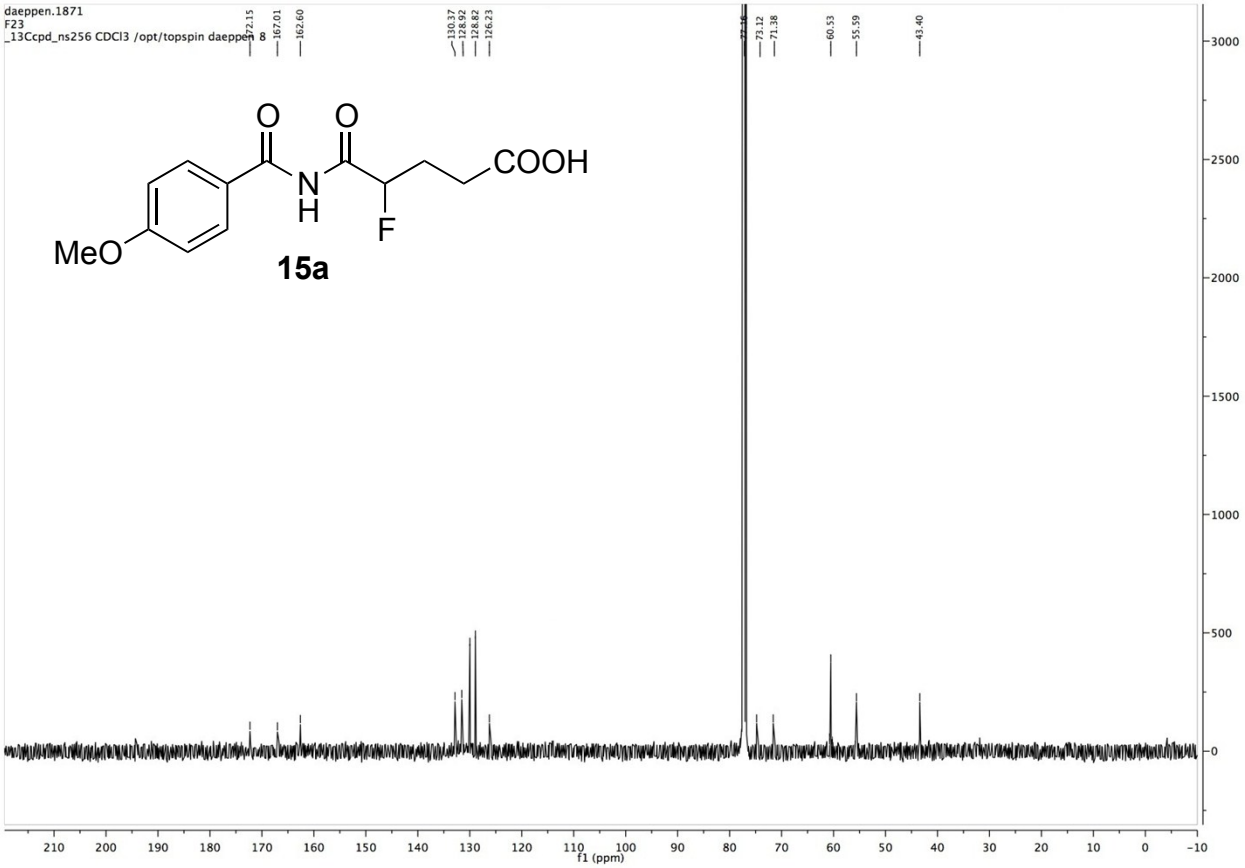

daeppen.1818
F10
_19F{1H} CDCl3 /opt/topspin daeppen 10
O
O
N
H
COOH
F
13a
-115.45
f1 (ppm)

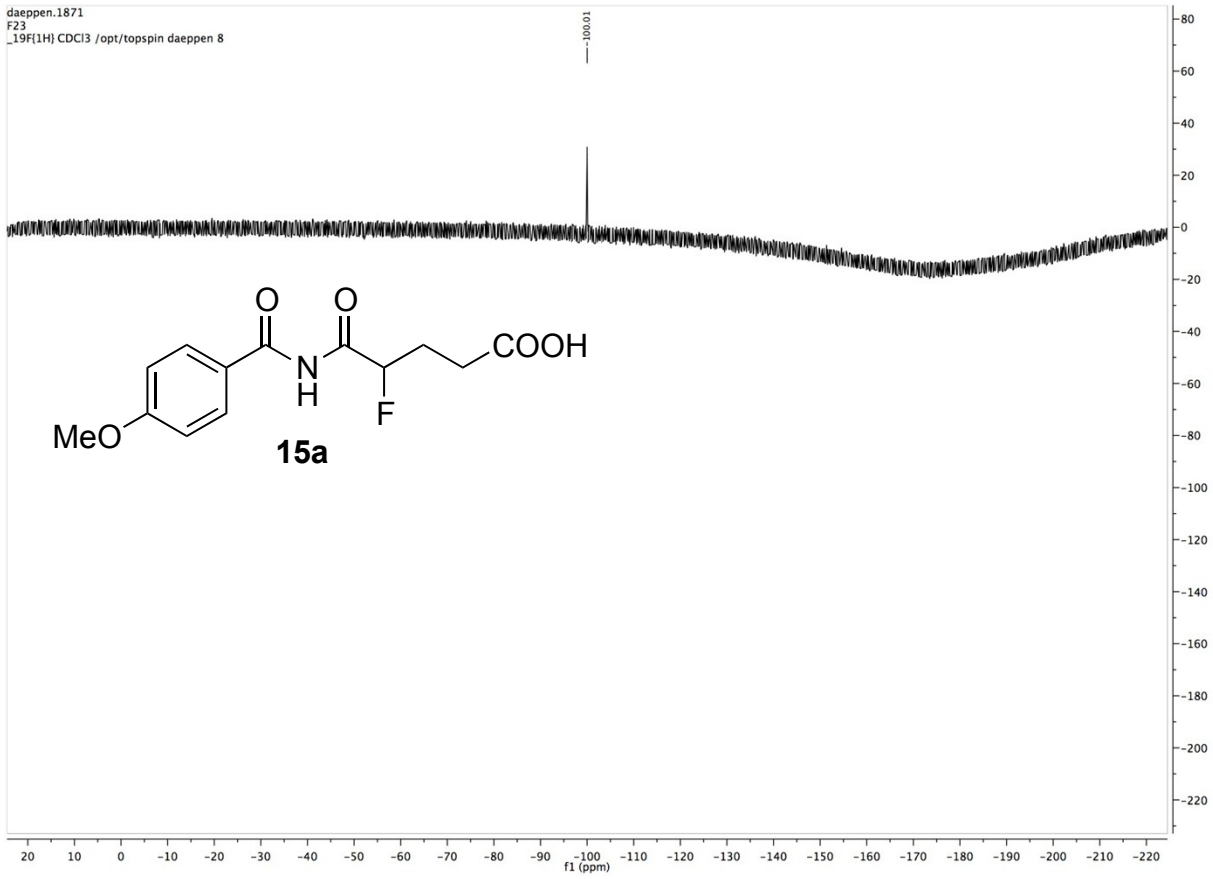

daeppen.1853
F19
_Proton_16 CDCl3 /opt/topspin daeppen 10
8.32
8.30
7.97
7.95
6.47
4.75
4.74
4.73
4.72
4.65
4.62
2.46
2.43
1.08
1.07
1.06
1.05
1.04
O
O
N
H
COOH
F
O2N
14a
f1 (ppm)


daeppen.1853
F19
_13Ccpd_ns256 CDCl3 /opt/topspin daeppen 10
173.64
172.15
165.52
139.51
130.37
128.82
128.31
124.11
83.86
82.16
77.16
43.83
14.93
O
O
N
H
F
COOH
O2N
14a
f1 (ppm)

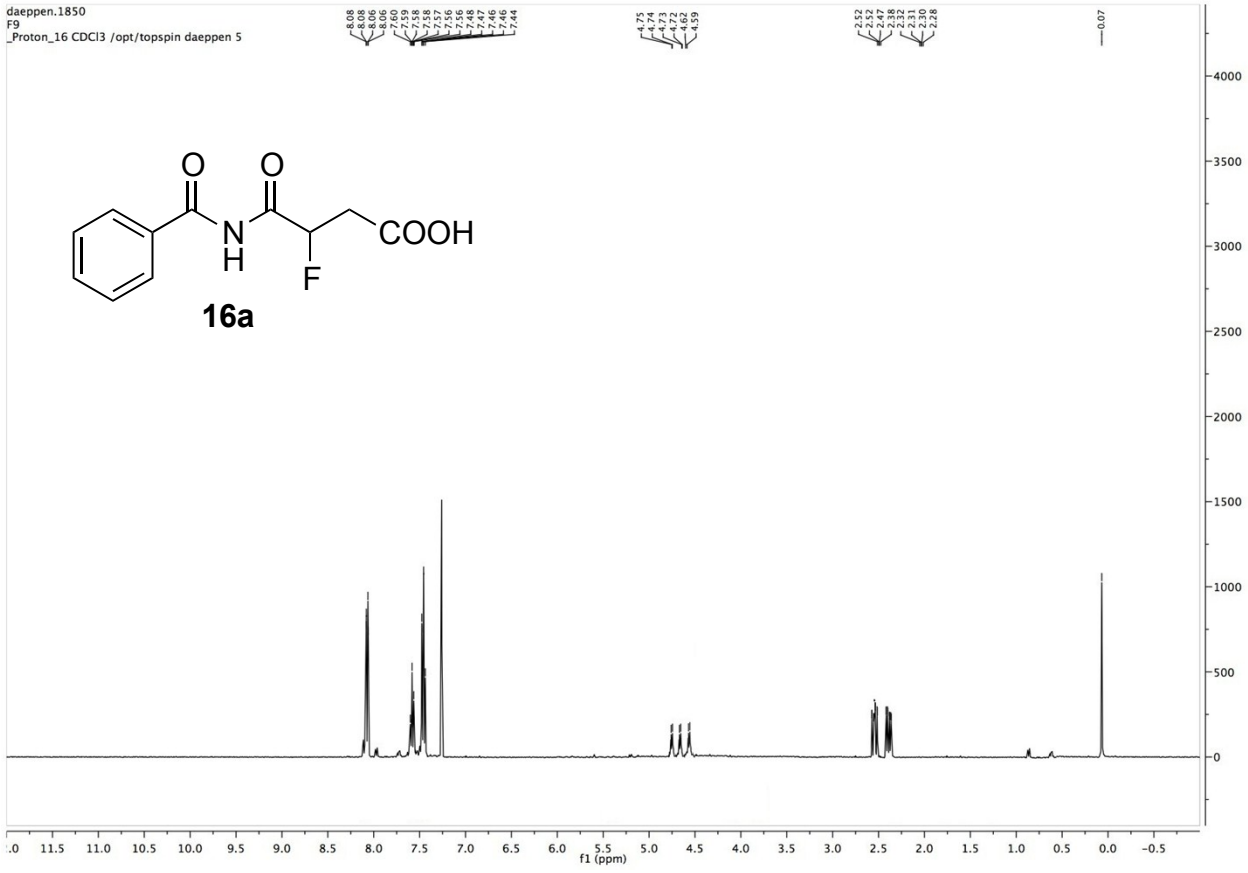

daeppen.1853
F19
_19F[1H] CDCl3 /opt/topspin daeppen 10
115.45
O
O
N
H
F
COOH
O2N
14a
f1 (ppm)


daeppen.1871
F23
_Proton_16 CDCl3 /opt/topspin daeppen 8
7.77
7.74
7.26
6.95
6.93
6.32
4.58
4.57
4.56
4.55
4.46
4.45
3.85
2.46
2.42
2.20
2.20
2.04
O
O
N
H
F
COOH
MeO
15a
f1 (ppm)

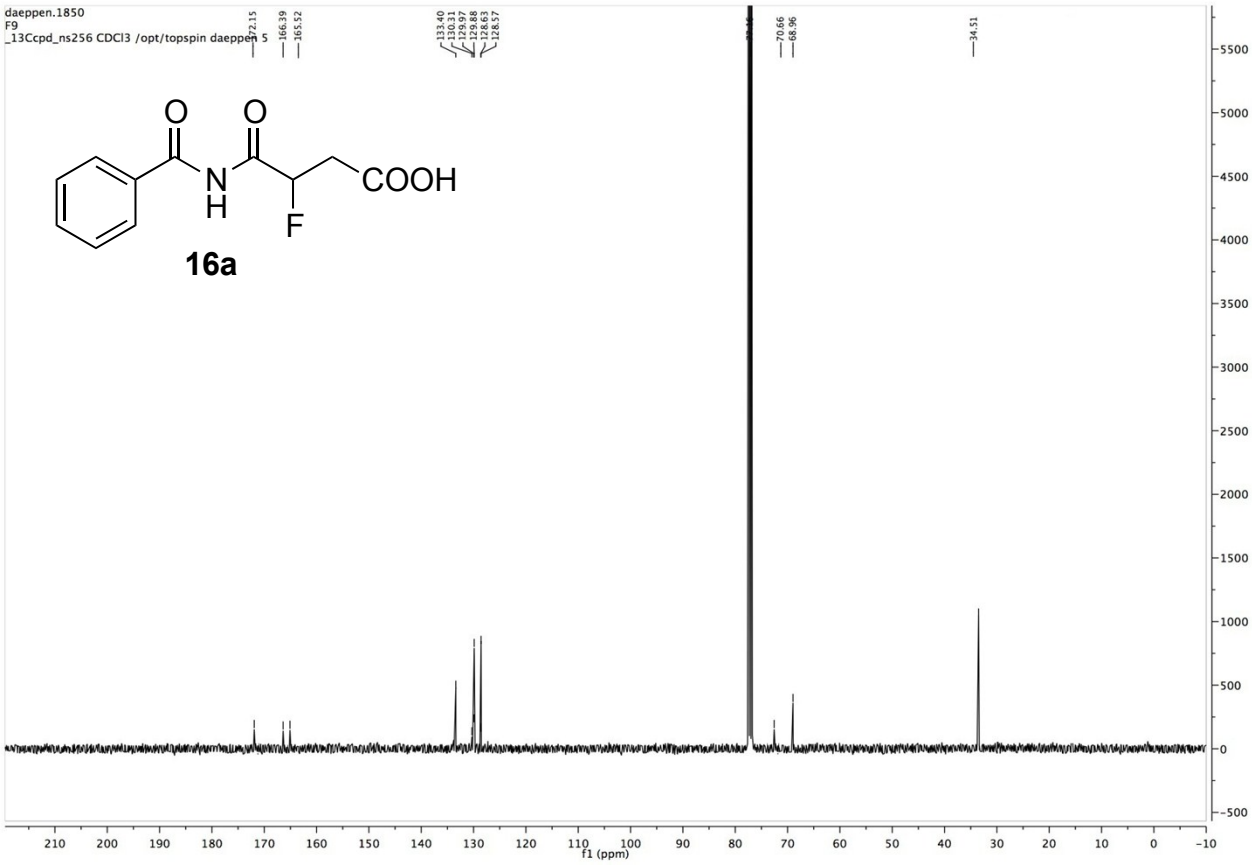

daeppen.1871
F23
_13Ccpd_ns256 CDCl3 /opt/topspin daeppen 8
172.15
167.01
162.60
130.37
129.97
128.82
126.23
73.12
71.38
60.53
55.59
43.40
O
O
N
H
F
COOH
MeO
15a
f1 (ppm)

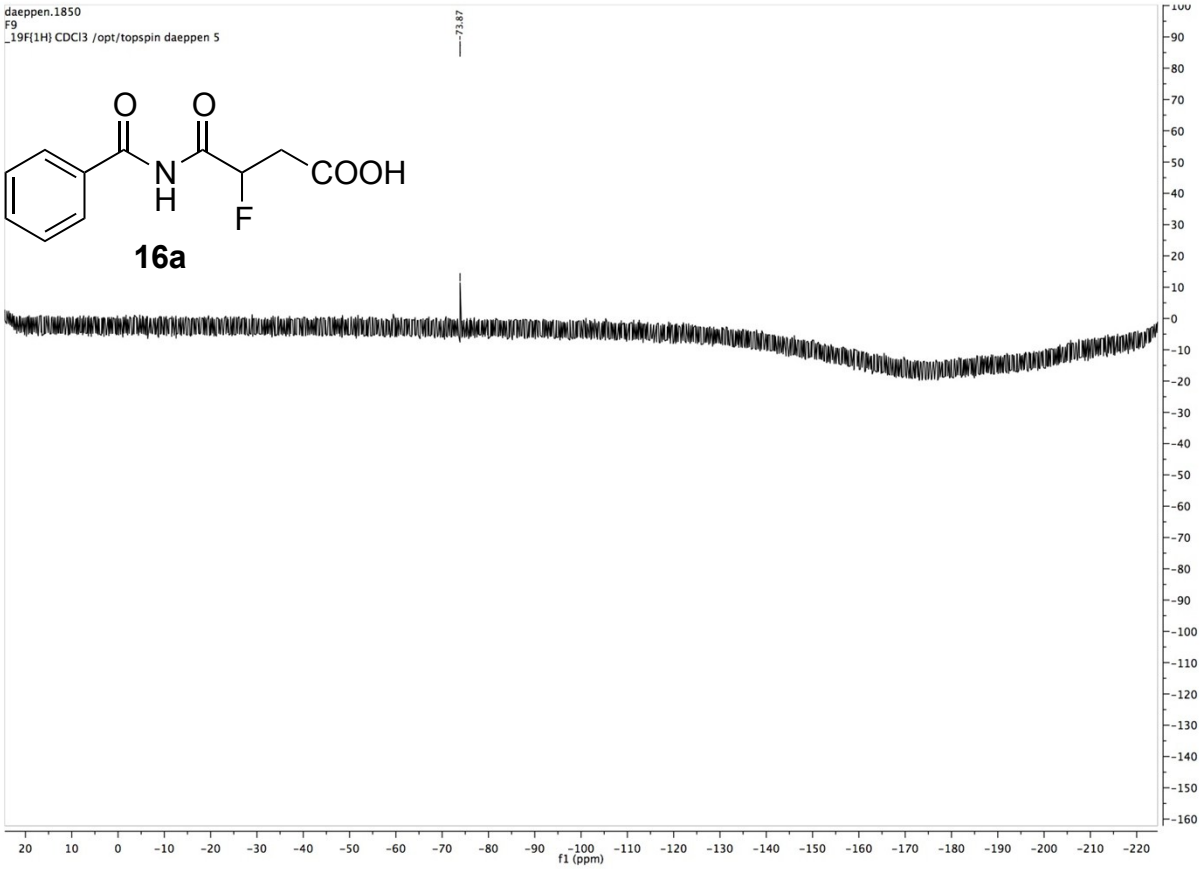

daeppen.1871
F23
_19F{1H} CDCl3 /opt/topspin daeppen 8
-100.01
O
O
N
H
F
COOH
MeO
f1 (ppm)

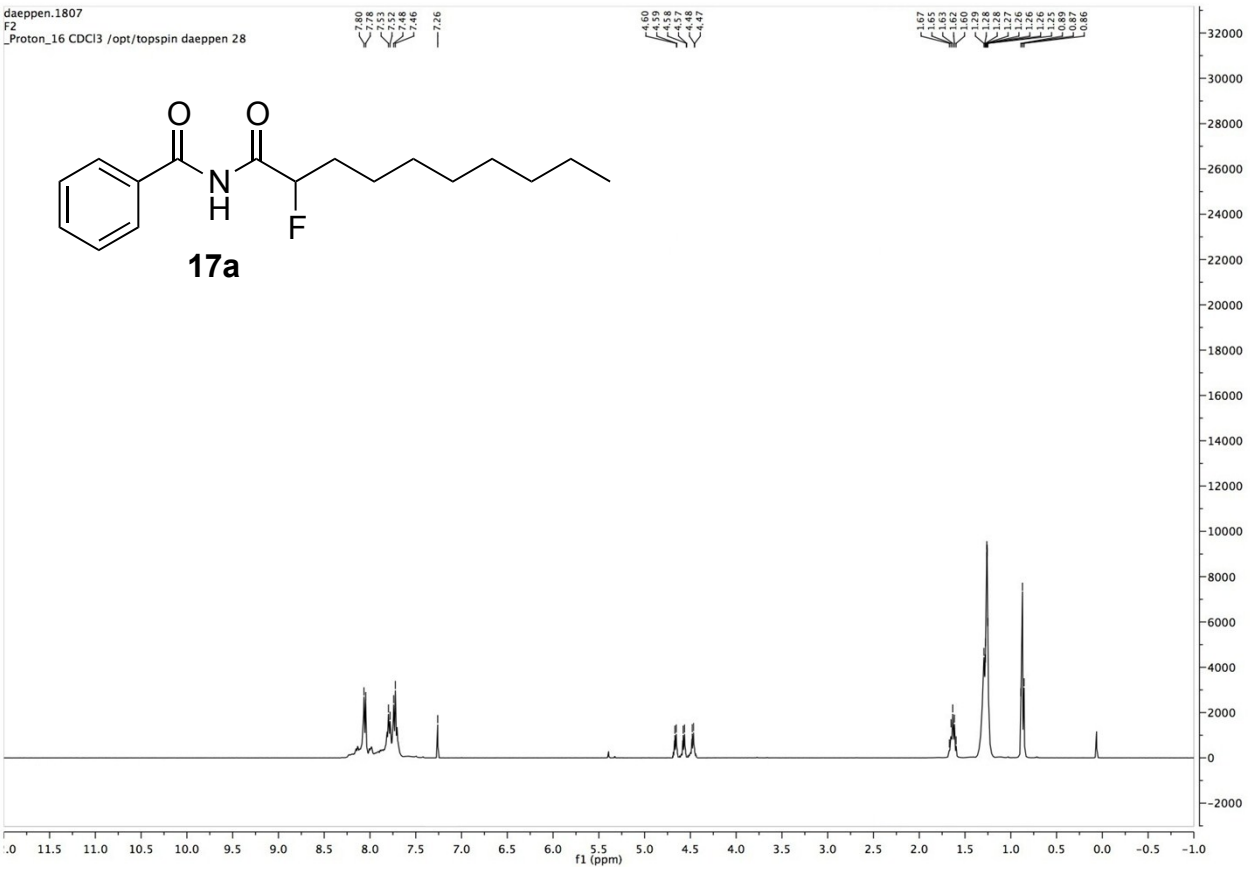
15a

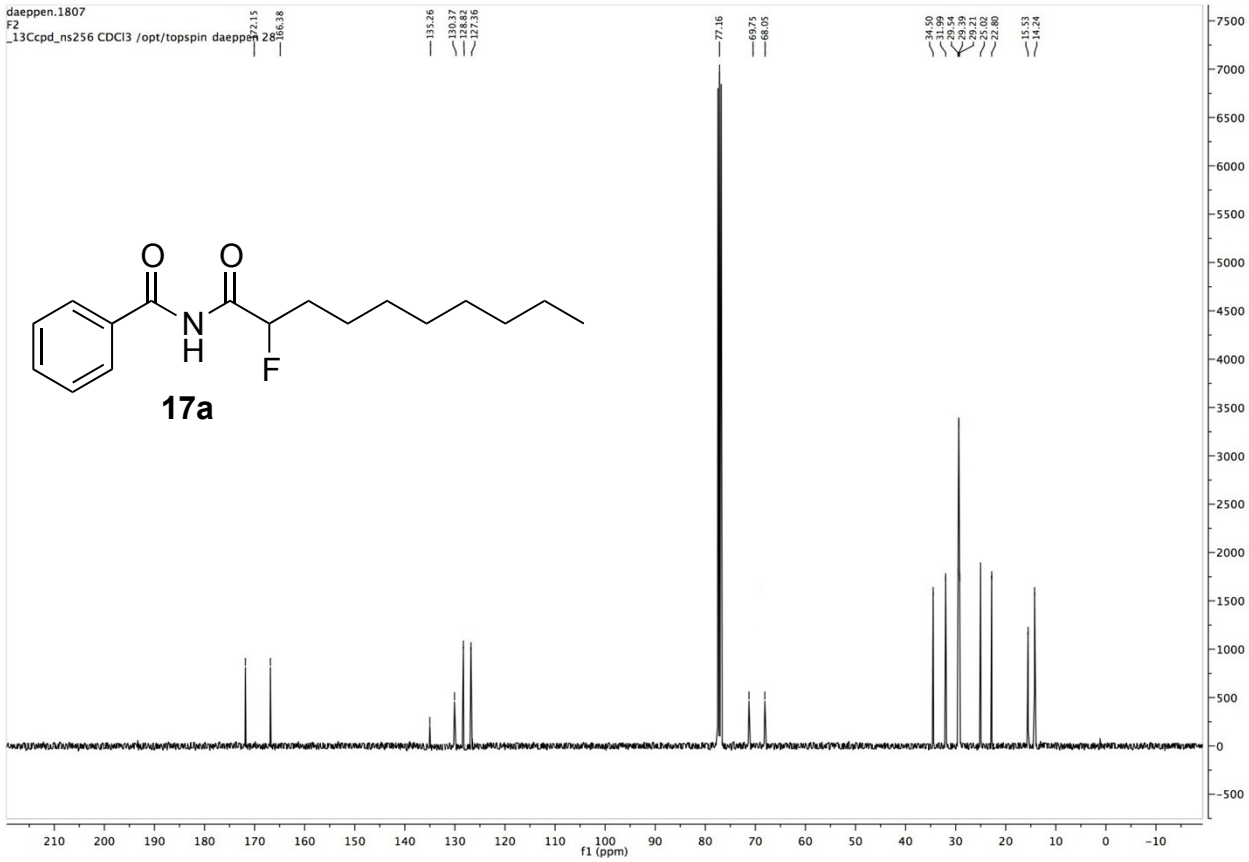

daeppen.1850
F9
_Proton_16 CDCl3 /opt/topspin daeppen 5
8.08
8.08
8.06
8.06
7.60
7.59
7.58
7.58
7.57
7.56
7.56
7.48
7.47
7.46
7.46
7.44
4.75
4.74
4.73
4.72
4.68
4.68
4.59
2.52
2.52
2.47
2.38
2.32
2.31
2.30
2.28
0.07
O
O
N
H
F
COOH
f1 (ppm)

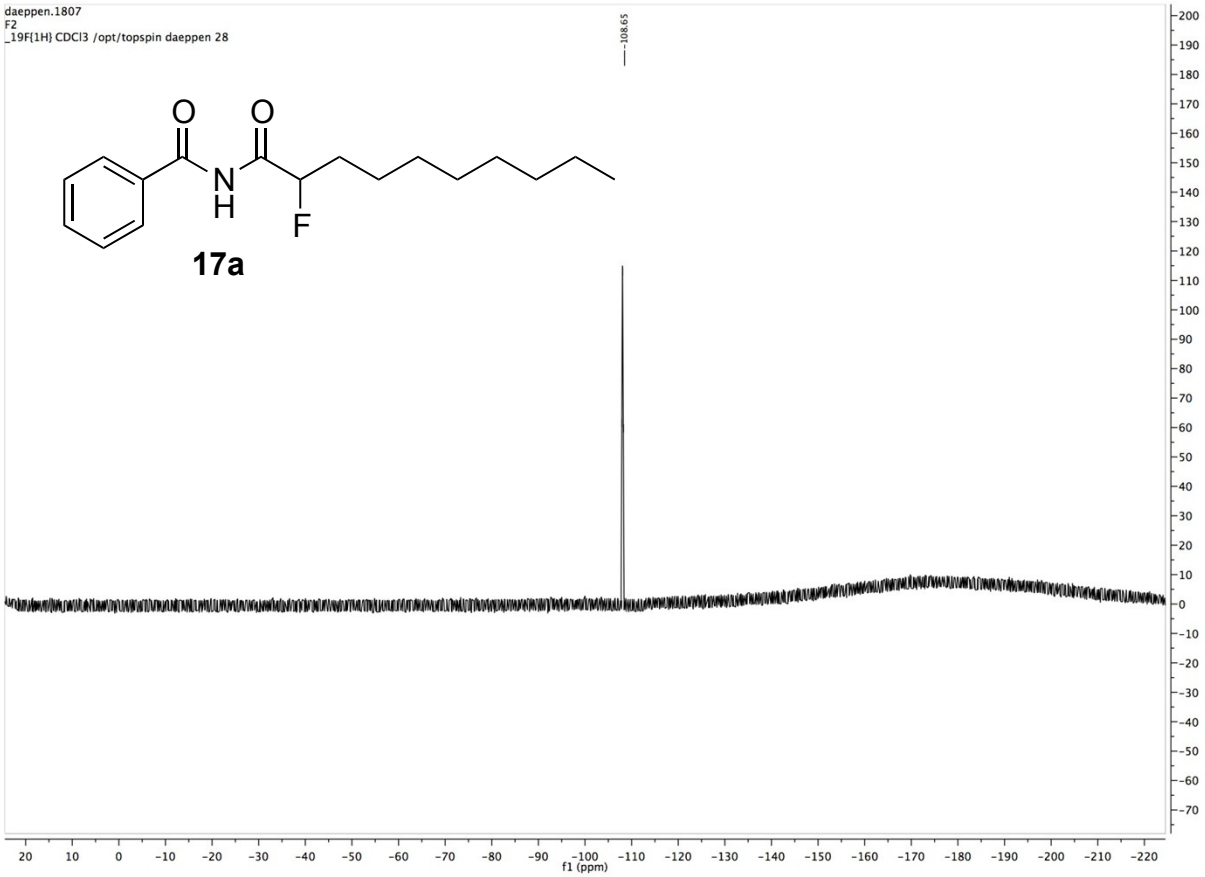
16a

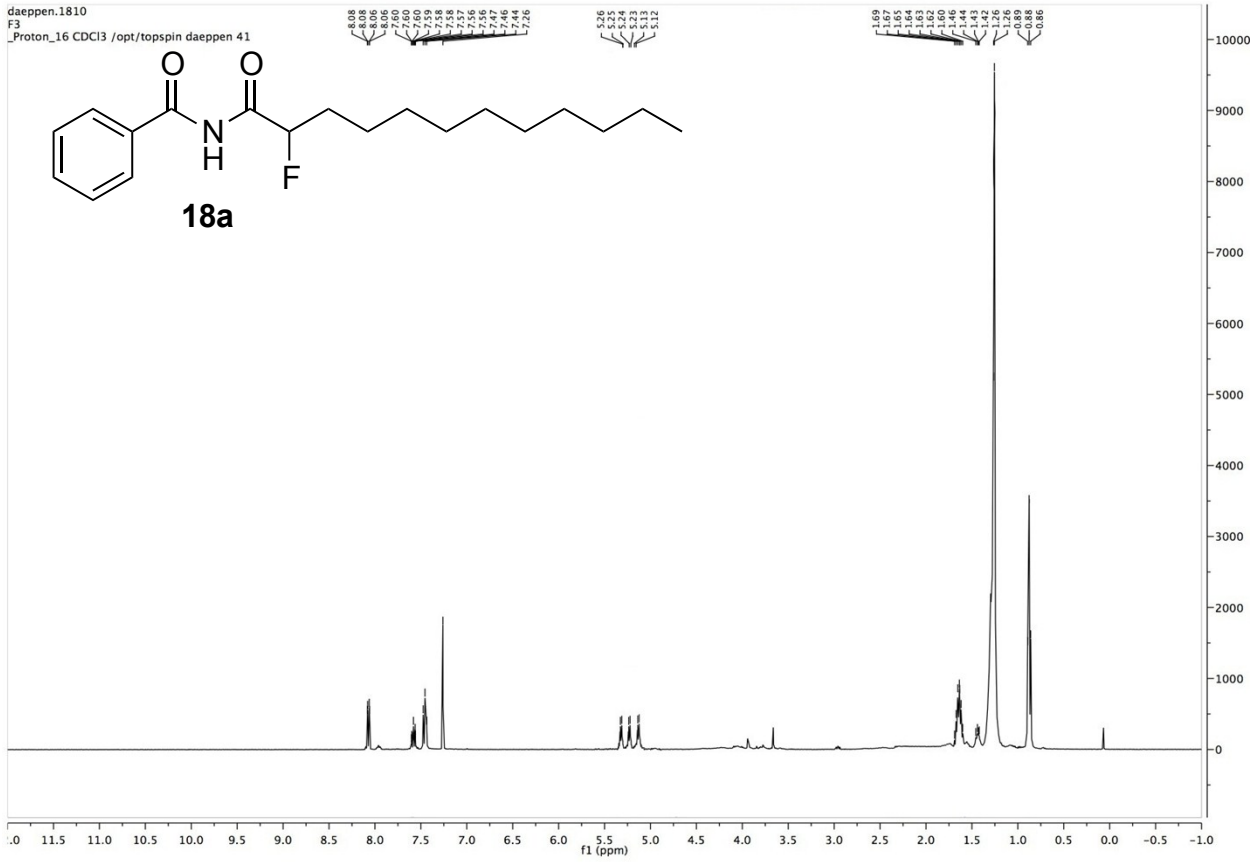

daeppen.1850
F9
_13Ccpd_ns256 CDCl3 /opt/topspin daeppen 5
172.15
166.39
165.52
133.40
133.11
129.97
129.88
128.63
128.57
70.66
68.96
34.51
O
O
N
H
F
COOH
16a
f1 (ppm)

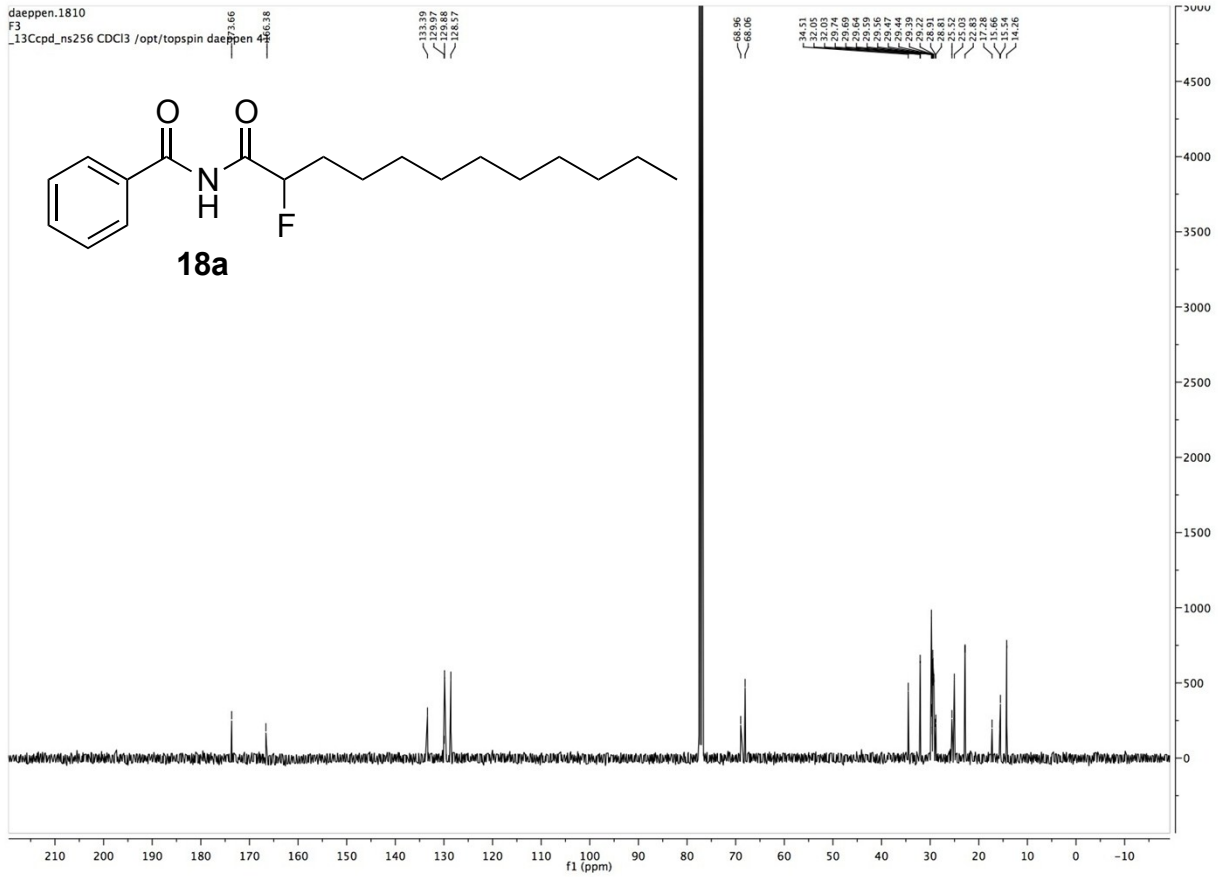

daeppen.1850
F9
_19F{1H} CDCl3 /opt/topspin daeppen 5
-73.87
O
O
N
H
F
COOH
16a
f1 (ppm)

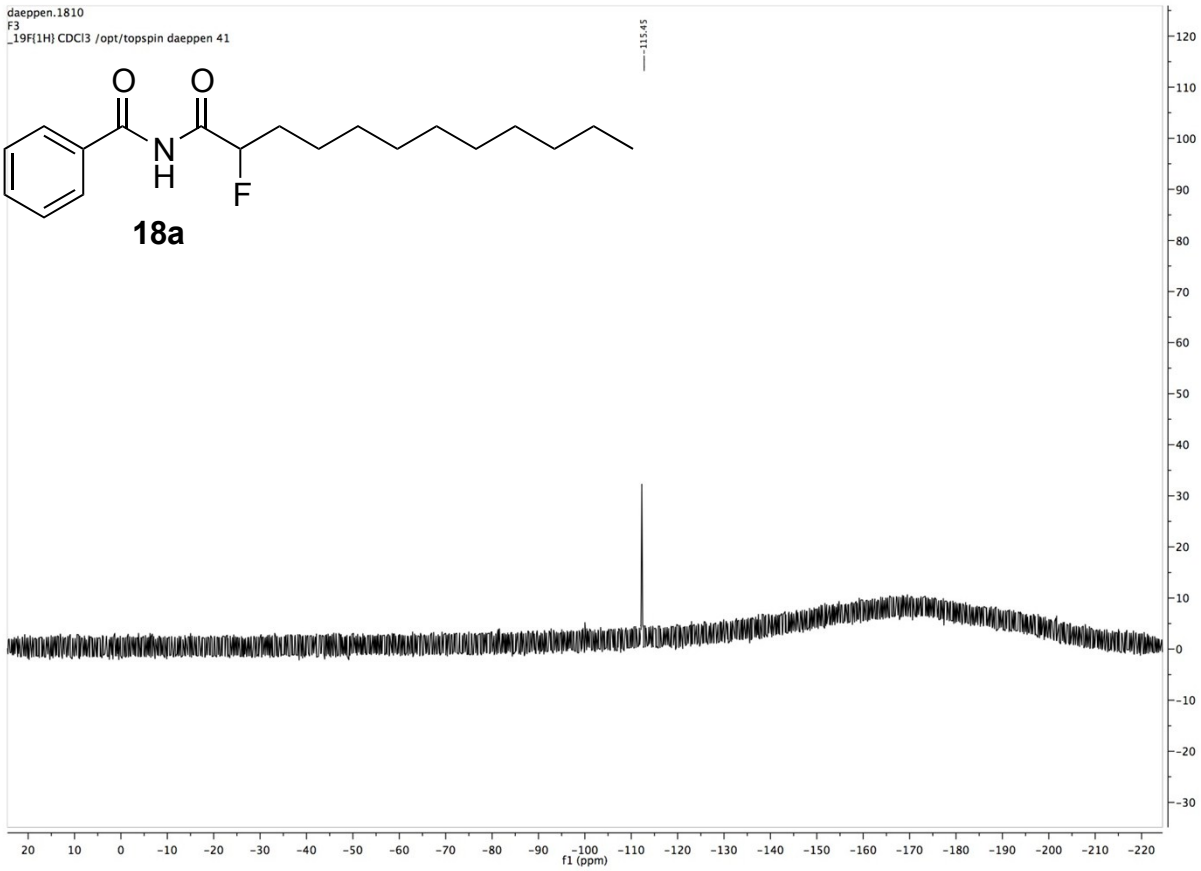

daeppen.1807
F2
_Proton_16 CDCl3 /opt/topspin daeppen 28
7.80
7.78
7.53
7.52
7.48
7.46
7.26
4.60
4.59
4.58
4.57
4.48
4.47
1.67
1.65
1.63
1.62
1.60
1.29
1.28
1.28
1.27
1.26
1.26
1.26
1.25
0.89
0.87
0.86
O
O
N
H
F
17a
f1 (ppm)


daeppen.1807
F2
_13Ccpd_ns256 CDCl3 /opt/topspin daeppen 28
172.15
166.38
135.26
130.37
128.72
127.36
77.16
69.75
68.05
34.50
31.99
29.54
29.39
29.21
25.02
22.80
15.53
14.24
O
O
N
H
F
17a
f1 (ppm)

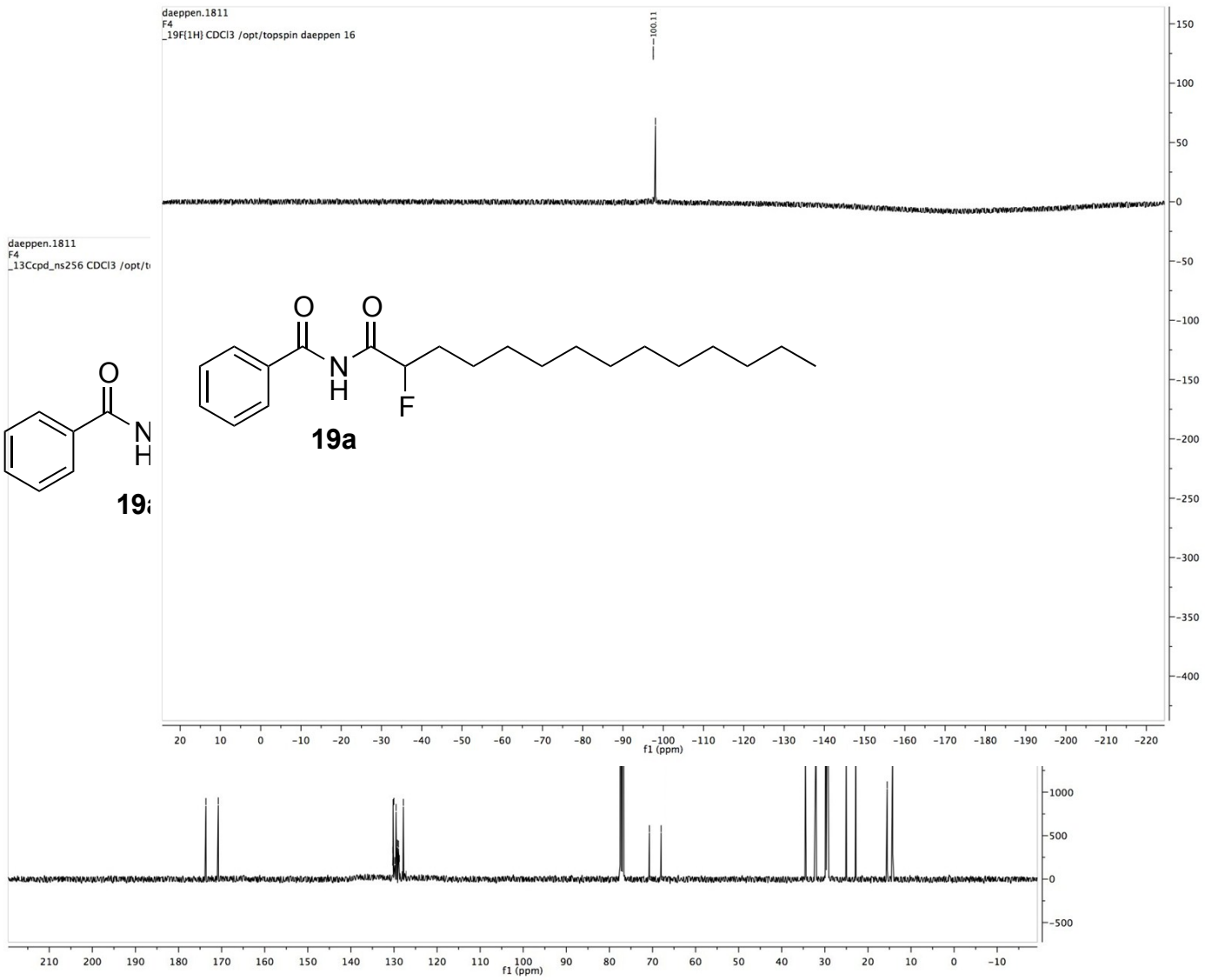

daeppen.1807
F2
_19F{1H} CDCl3 /opt/topspin daeppen 28
-108.65
O
O
N
H
F
17a
f1 (ppm)

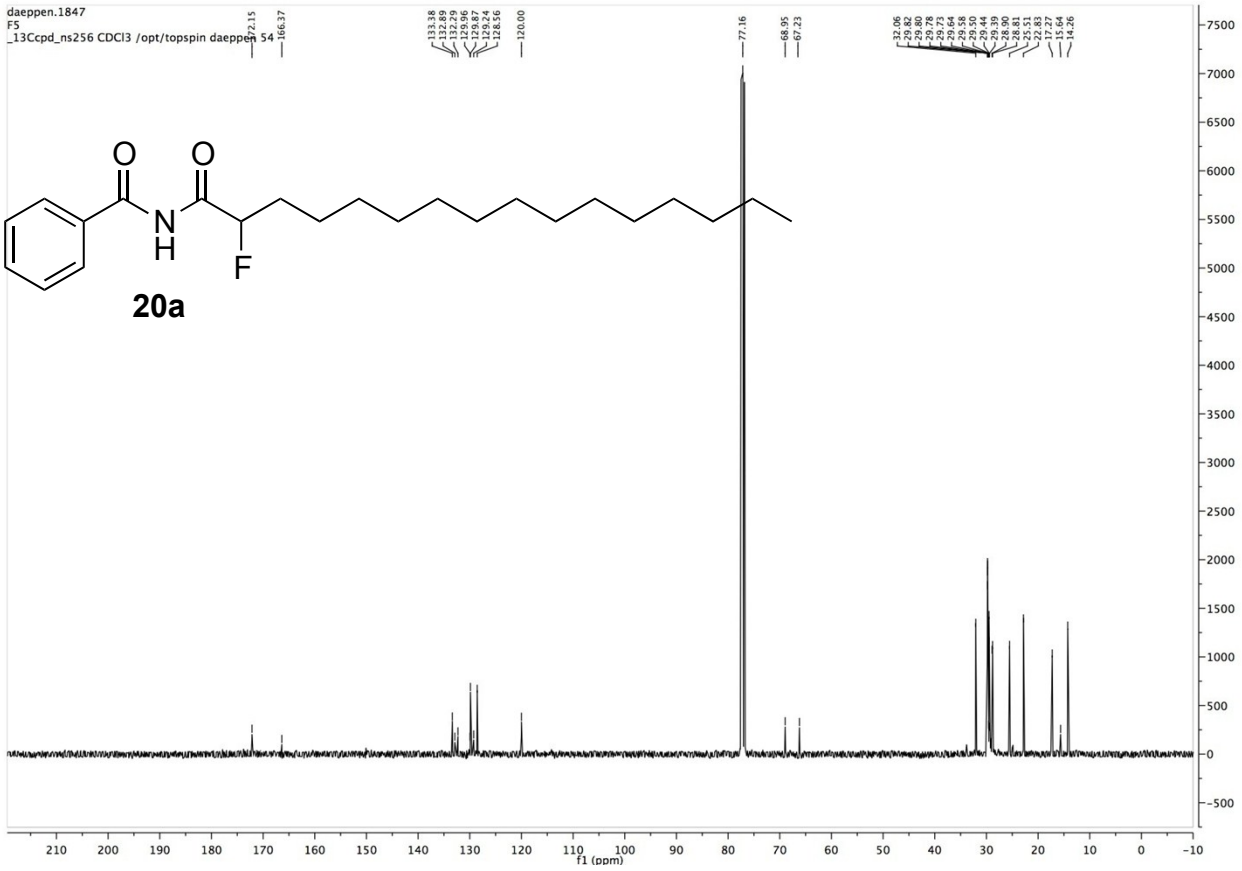

daeppen.1810
F3
_Proton_16 CDCl3 /opt/topspin daeppen 41
8.08
8.08
8.06
8.06
7.60
7.60
7.60
7.59
7.58
7.58
7.57
7.56
7.56
7.47
7.46
7.44
7.26
5.26
5.25
5.24
5.23
5.13
5.13
5.12
1.69
1.67
1.65
1.64
1.63
1.62
1.60
1.46
1.44
1.43
1.42
1.26
1.26
1.26
0.89
0.88
0.86
O
O
N
H
F
18a
f1 (ppm)

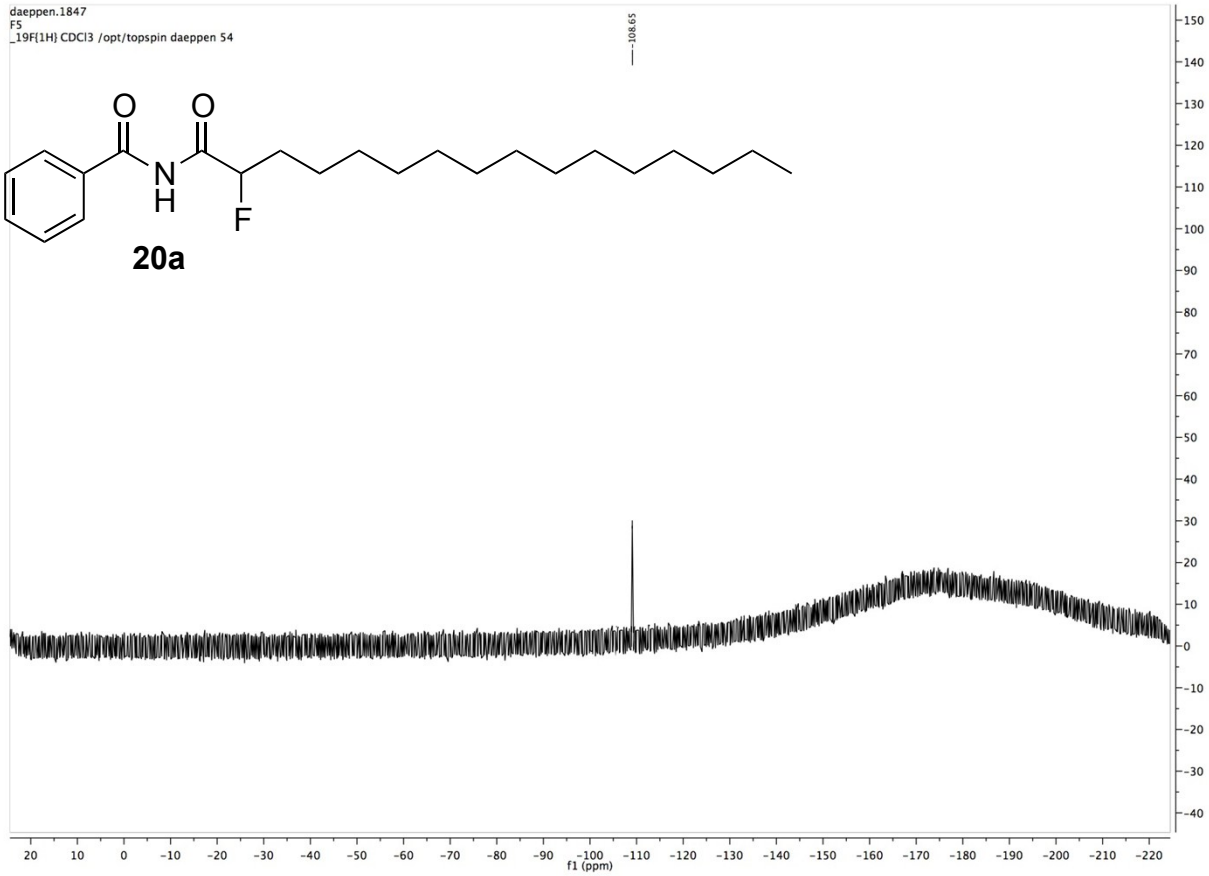

daeppen.1810
F3
_13Ccpd_ns256 CDCl3 /opt/topspin daeppen 41
O
O
N
H
F
18a
f1 (ppm)


daeppen.1810
F3
_19F{1H} CDCl3 /opt/topspin daeppen 41
O
O
N
H
F
18a
f1 (ppm)

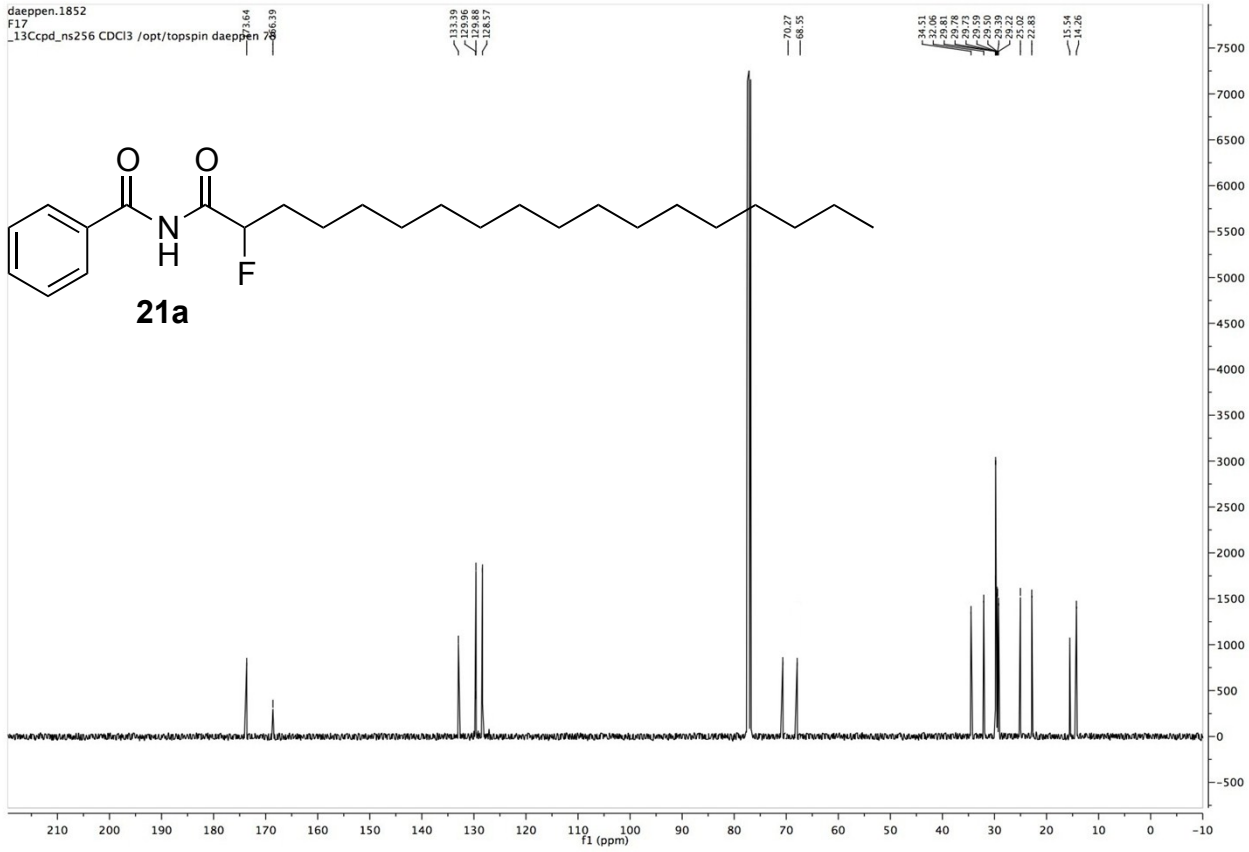

daeppen.1811
F4
_Proton_16 CDCl3 /opt/topspin daeppen 16
19a
f1 (ppm)

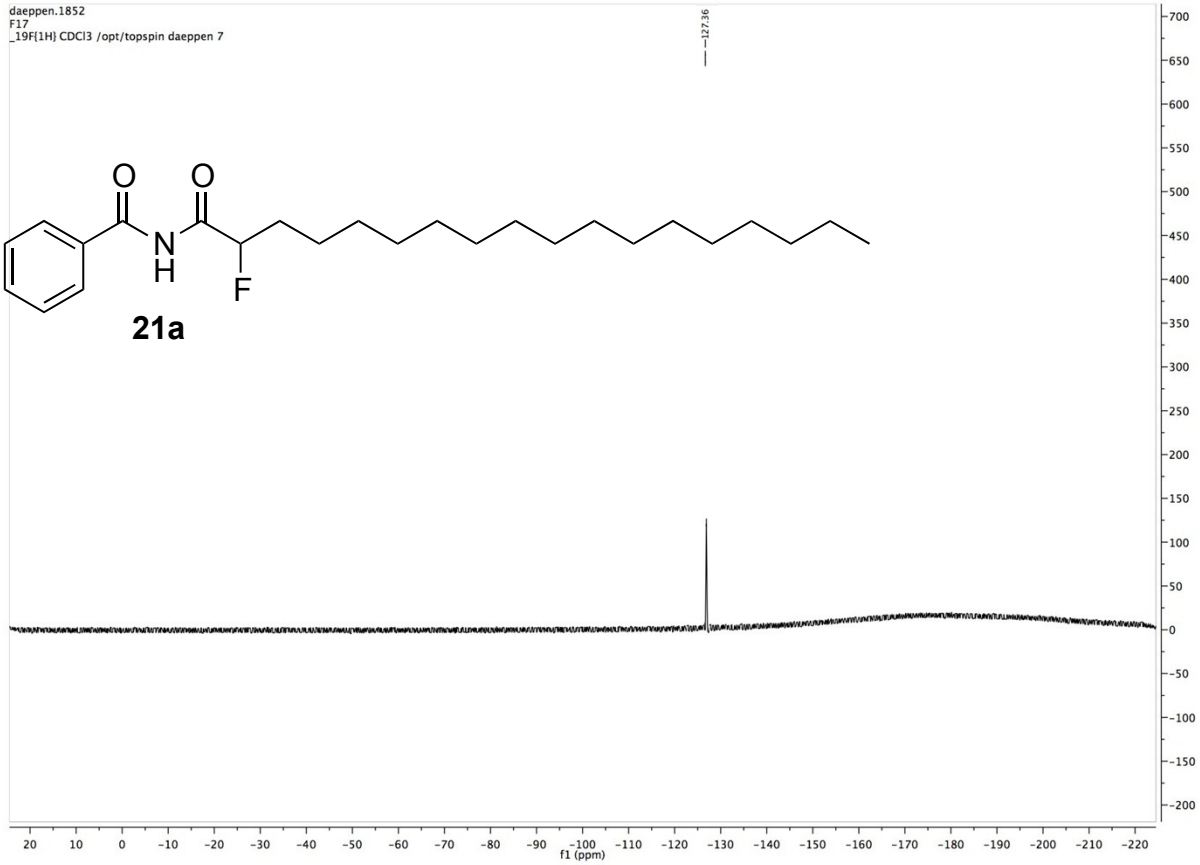

daeppen.1811
F4
_19F{1H} CDCl3 /opt/topspin daeppen 16
daeppen.1811
F4
_13Ccpd_ns256 CDCl3 /opt/t
19a
19
f1 (ppm)
f1 (ppm)

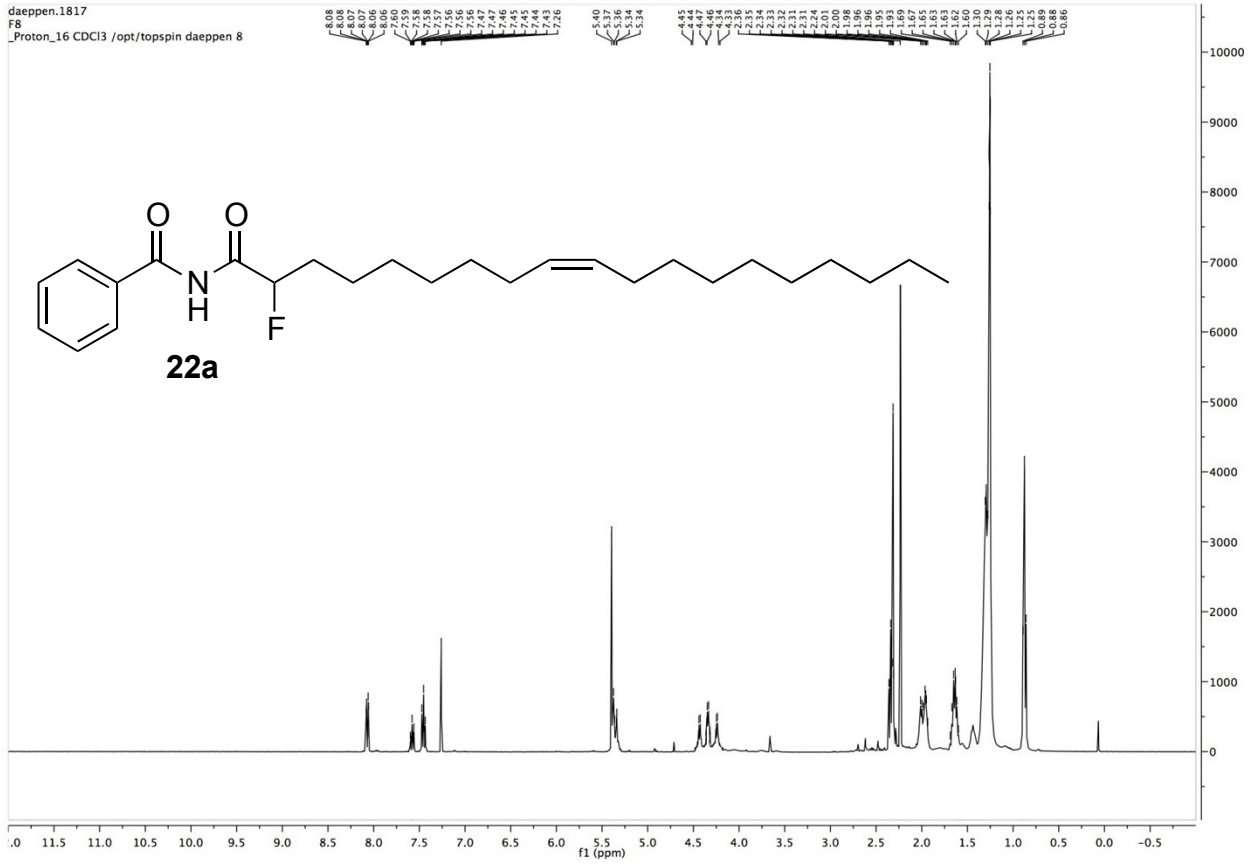

daeppen.1847
F5
_13Ccpd_ns256 CDCl3 /opt/topspin daeppen 54
172.15
166.37
133.38
132.89
132.29
129.96
129.87
128.74
128.56
120.00
77.16
68.95
67.23
32.06
29.82
29.80
29.78
29.73
29.64
29.58
29.50
29.44
29.39
28.90
28.81
25.51
22.83
17.27
15.64
14.06
O
O
N
H
F
20a
f1 (ppm)

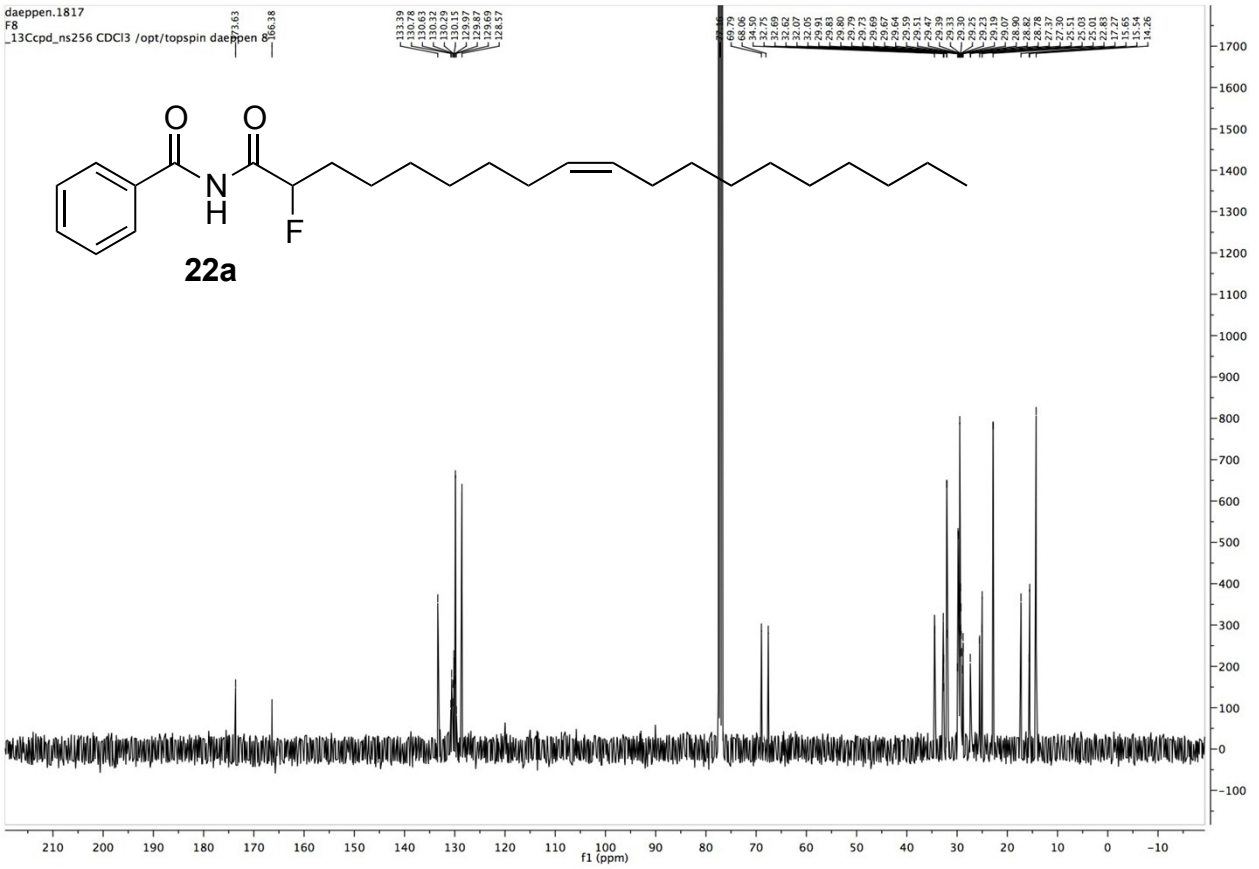

daeppen.1847
F5
_19F{1H} CDCl3 /opt/topspin daeppen 54
-108.65
O
O
N
H
F
20a
f1 (ppm)


daeppen.1852
F17
_Proton_16 CDCl3 /opt/topspin daeppen 7
8.08
8.06
7.60
7.58
7.55
7.48
7.46
7.46
7.44
7.26
5.25
5.24
5.23
5.21
5.12
5.11
1.67
1.65
1.63
1.62
1.60
1.25
0.89
0.88
0.86
O
O
N
H
F
21a
f1 (ppm)

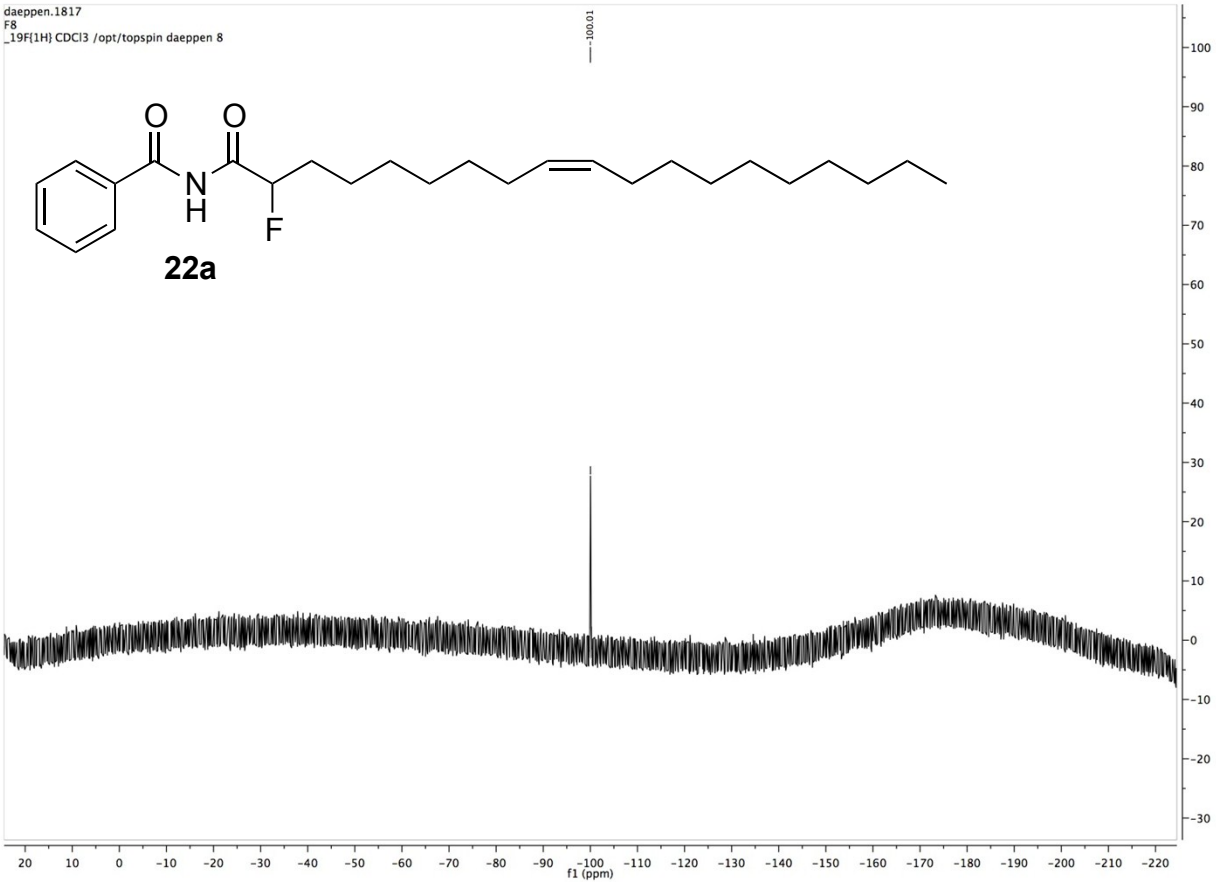

daeppen.1852
F17
_13Ccpd_ns256 CDCl3 /opt/topspin daeppen 78
173.64
166.39
133.39
131.96
129.88
128.57
70.27
68.55
34.51
32.06
29.81
29.78
29.73
29.59
29.50
29.39
29.22
25.02
22.83
15.54
14.26
O
O
N
H
F
21a
f1 (ppm)


daeppen.1852
F17
_19F{1H} CDCl3 /opt/topspin daeppen 7
-127.36
O
O
N
H
F
21a
f1 (ppm)

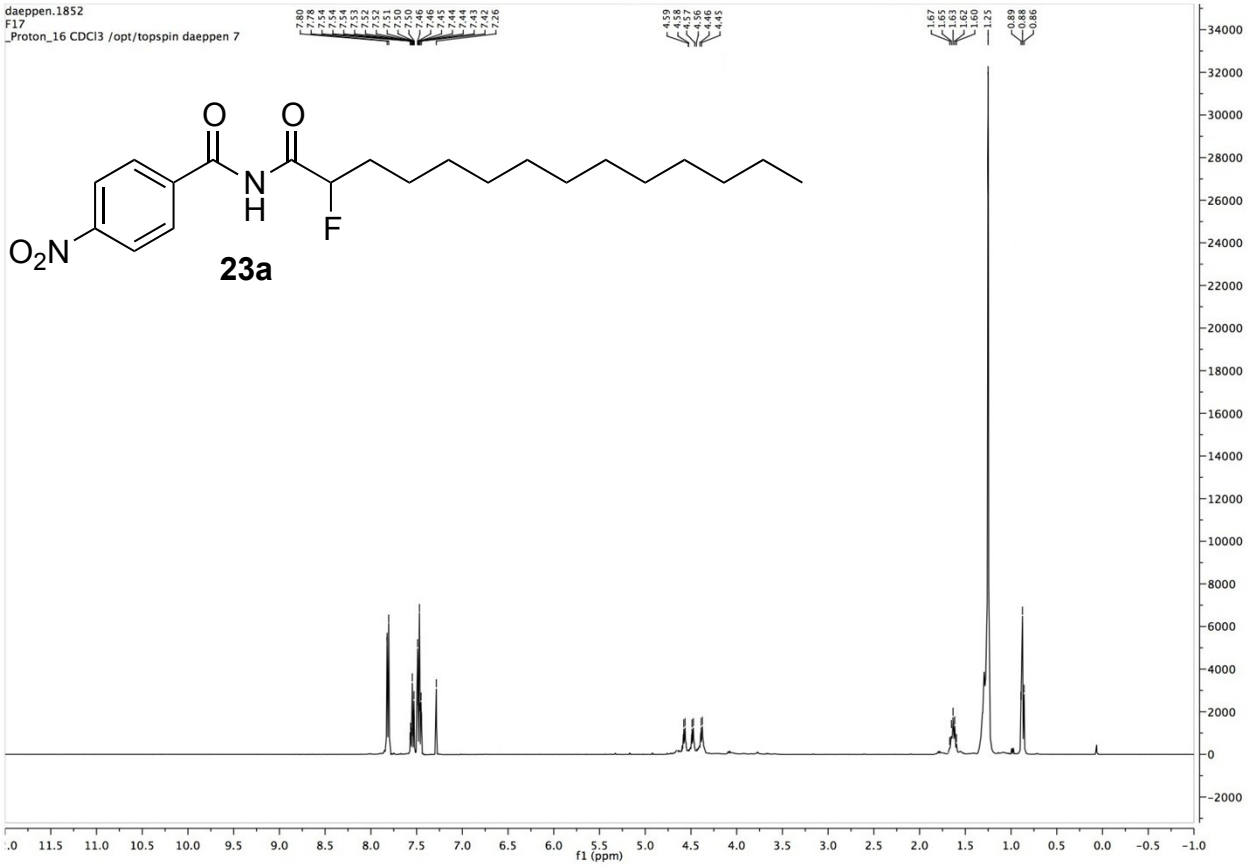

daeppen.1817
F8
_Proton_16 CDCl3 /opt/topspin daeppen 8
O
O
N
H
F
22a
f1 (ppm)

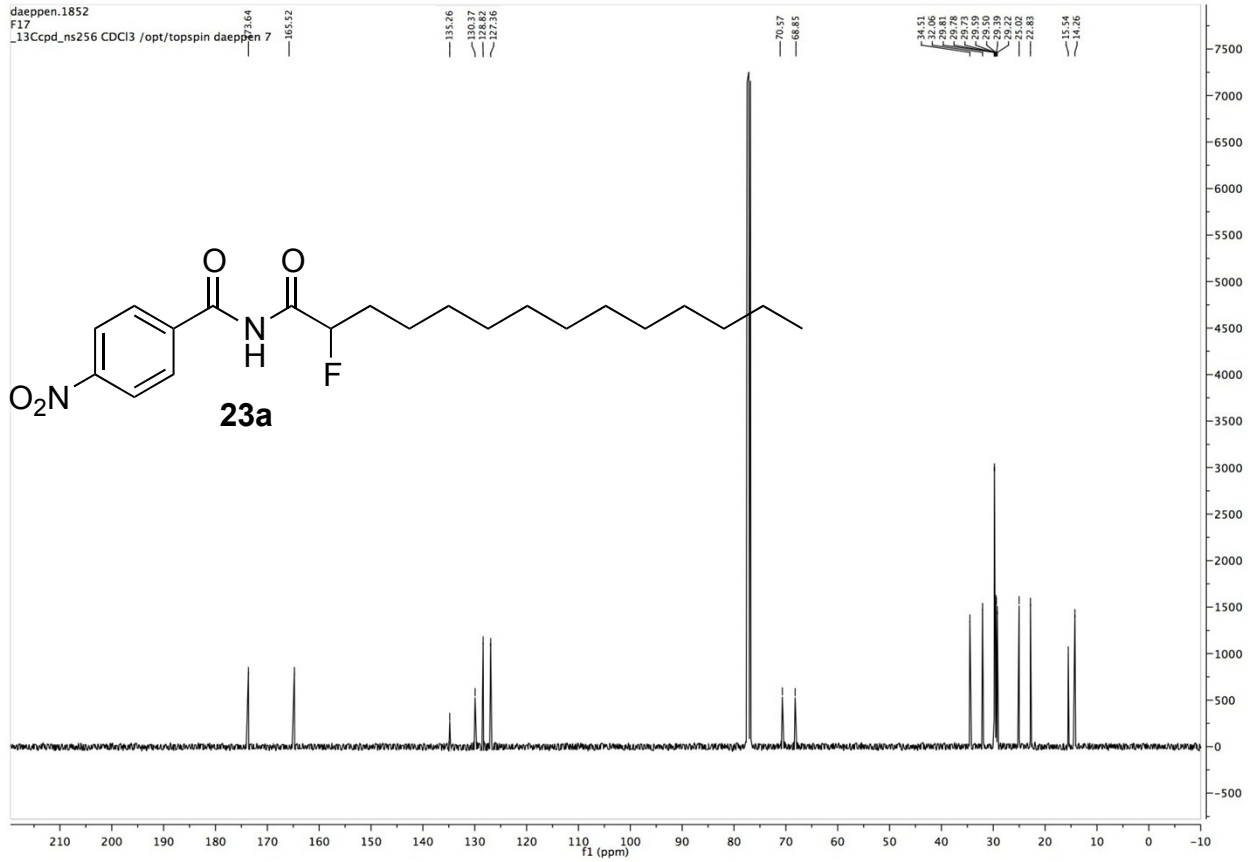

daeppen.1817
F8
_13Ccpd_ns256 CDCl3 /opt/topspin daeppen 8
f1 (ppm)

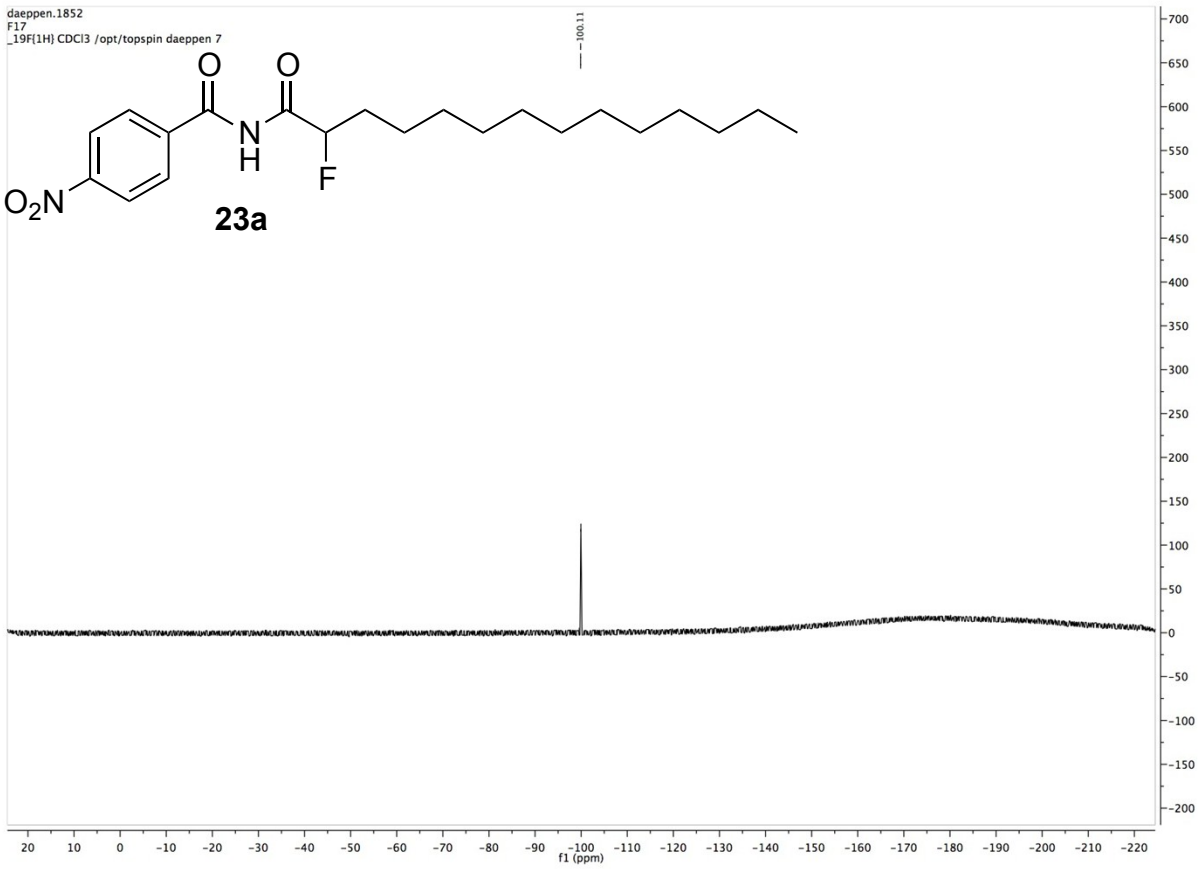
22a

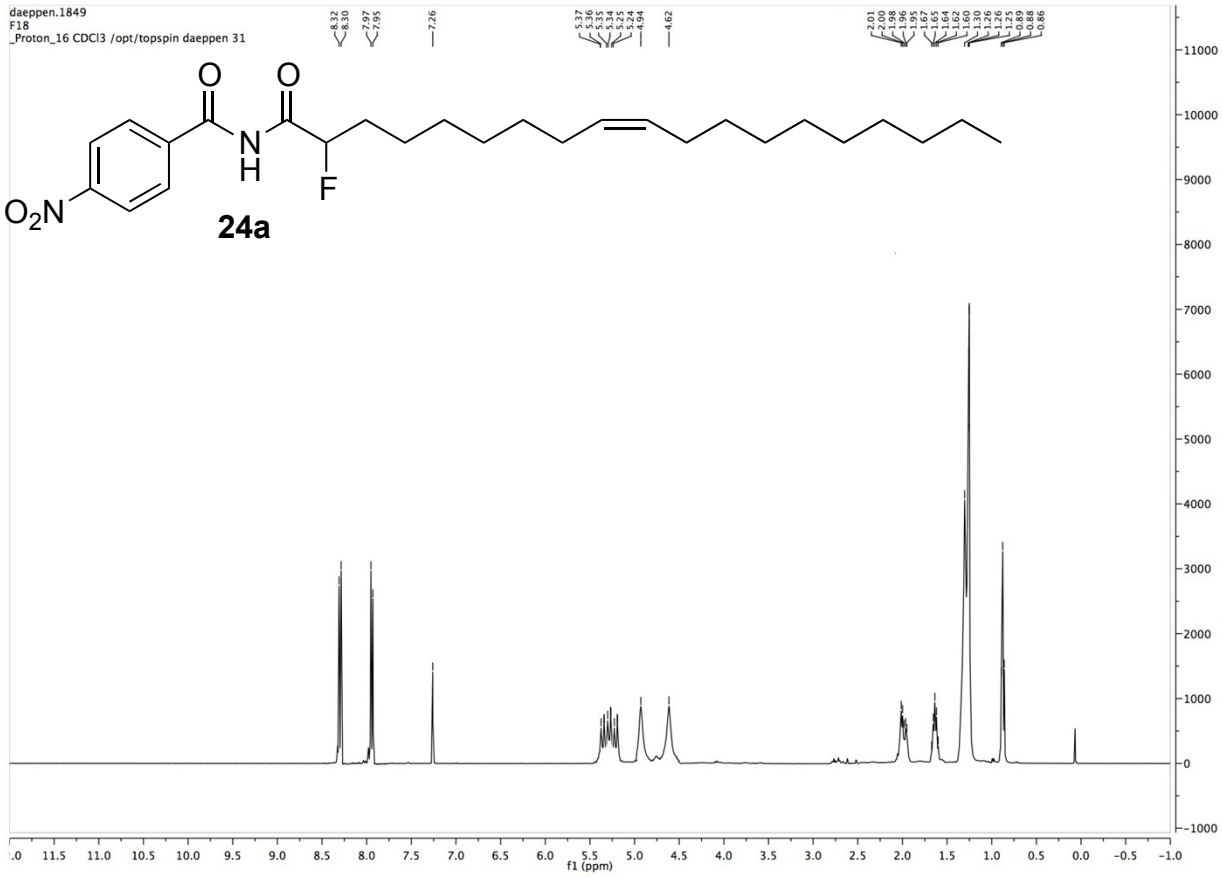

daeppen.1817
F8
_19F{1H} CDCl3 /opt/topspin daeppen 8
f1 (ppm)

22a

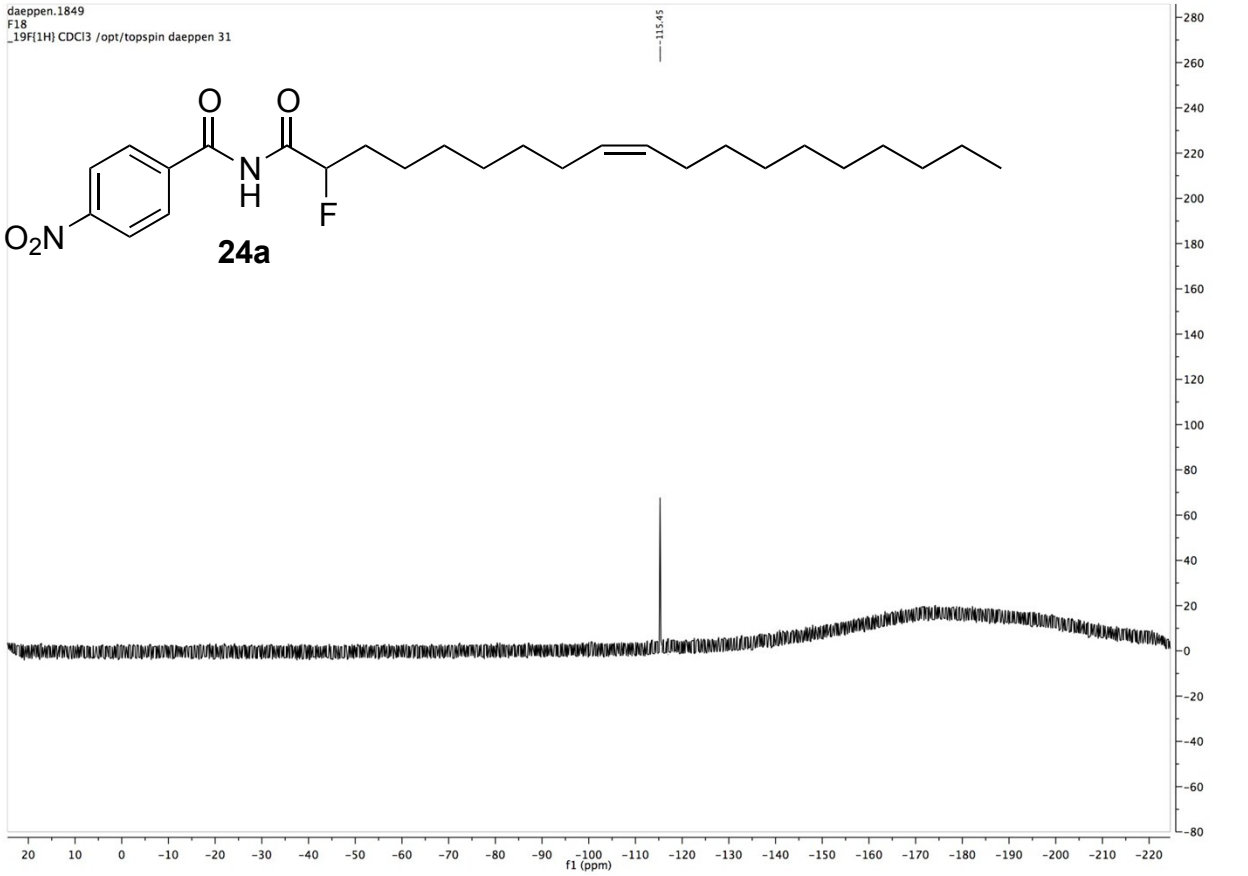

daeppen.1852
F17
_Proton_16 CDCl3 /opt/topspin daeppen 7
7.80
7.78
7.54
7.54
7.54
7.53
7.52
7.52
7.51
7.50
7.50
7.46
7.46
7.45
7.44
7.44
7.43
7.42
7.26
4.59
4.58
4.57
4.56
4.46
4.45
1.67
1.65
1.63
1.62
1.60
1.25
0.89
0.88
0.86
O
O
N
H
F
O_2N
23a
f1 (ppm)

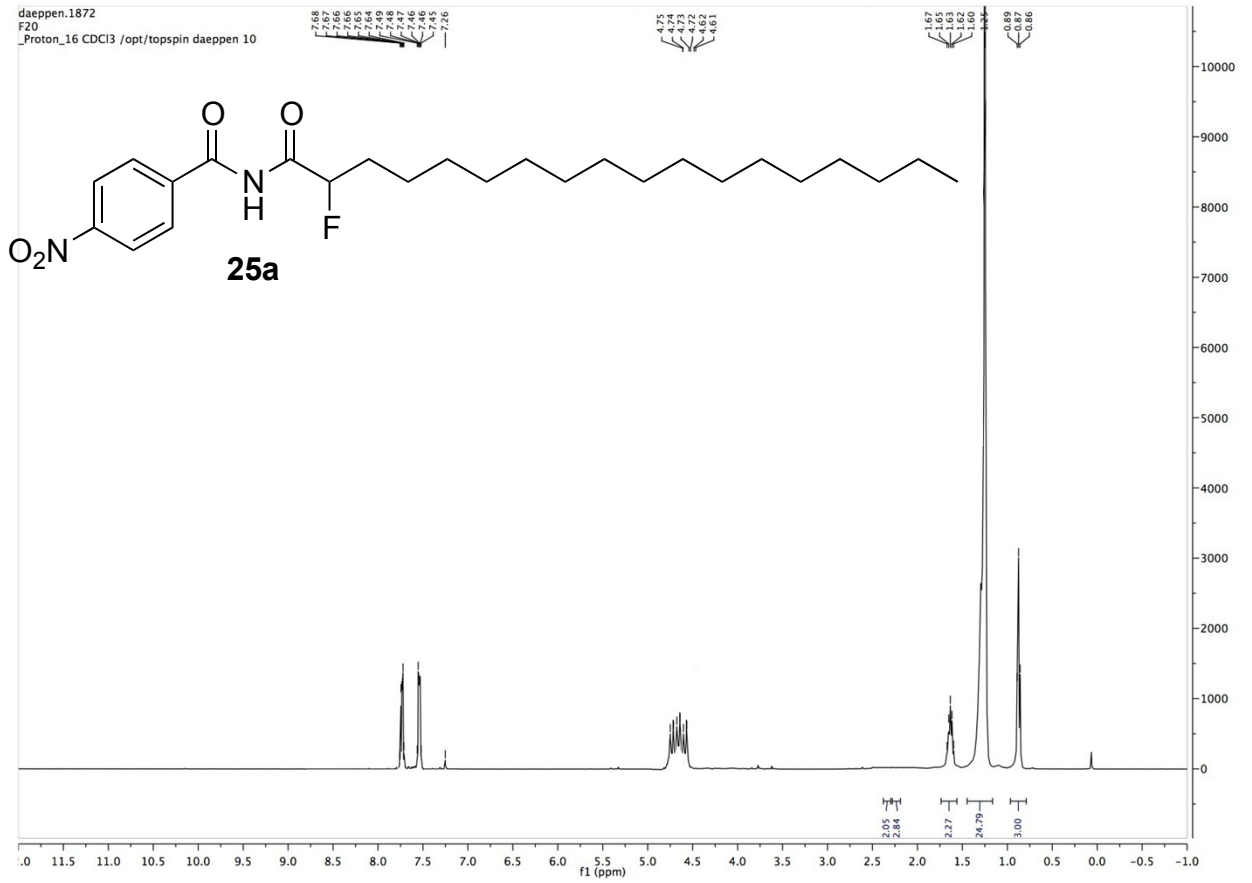

daeppen.1852
F17
_13Ccpd_ns256 CDCl3 /opt/topspin daeppen 7
173.64
165.52
135.26
130.37
128.82
127.36
70.57
68.85
34.51
32.06
29.81
29.78
29.73
29.59
29.50
29.39
29.22
29.02
22.83
15.54
14.26
O
O
N
H
F
O_2N
23a
f1 (ppm)

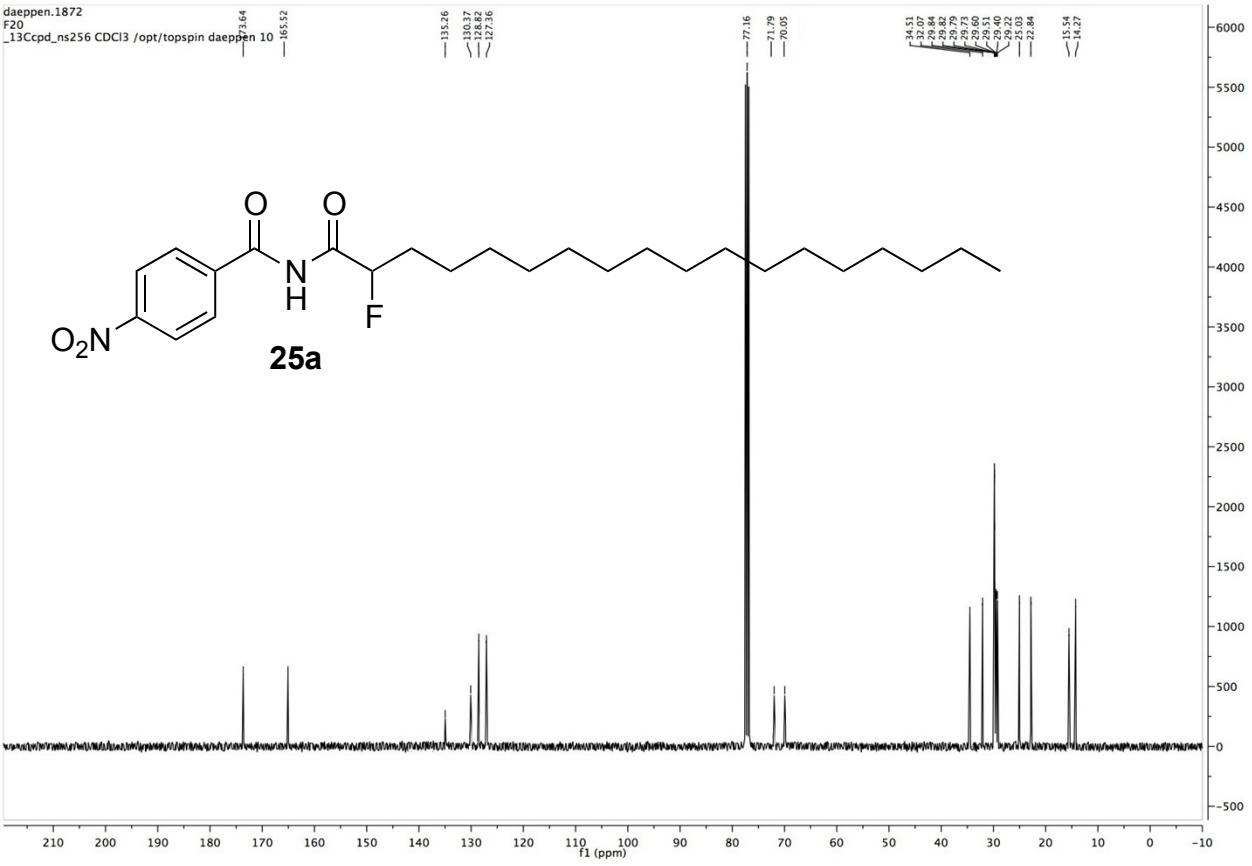

daeppen.1852
F17
_19F{1H} CDCl3 /opt/topspin daeppen 7
-100.11
O
O
N
H
F
O2N
23a
f1 (ppm)

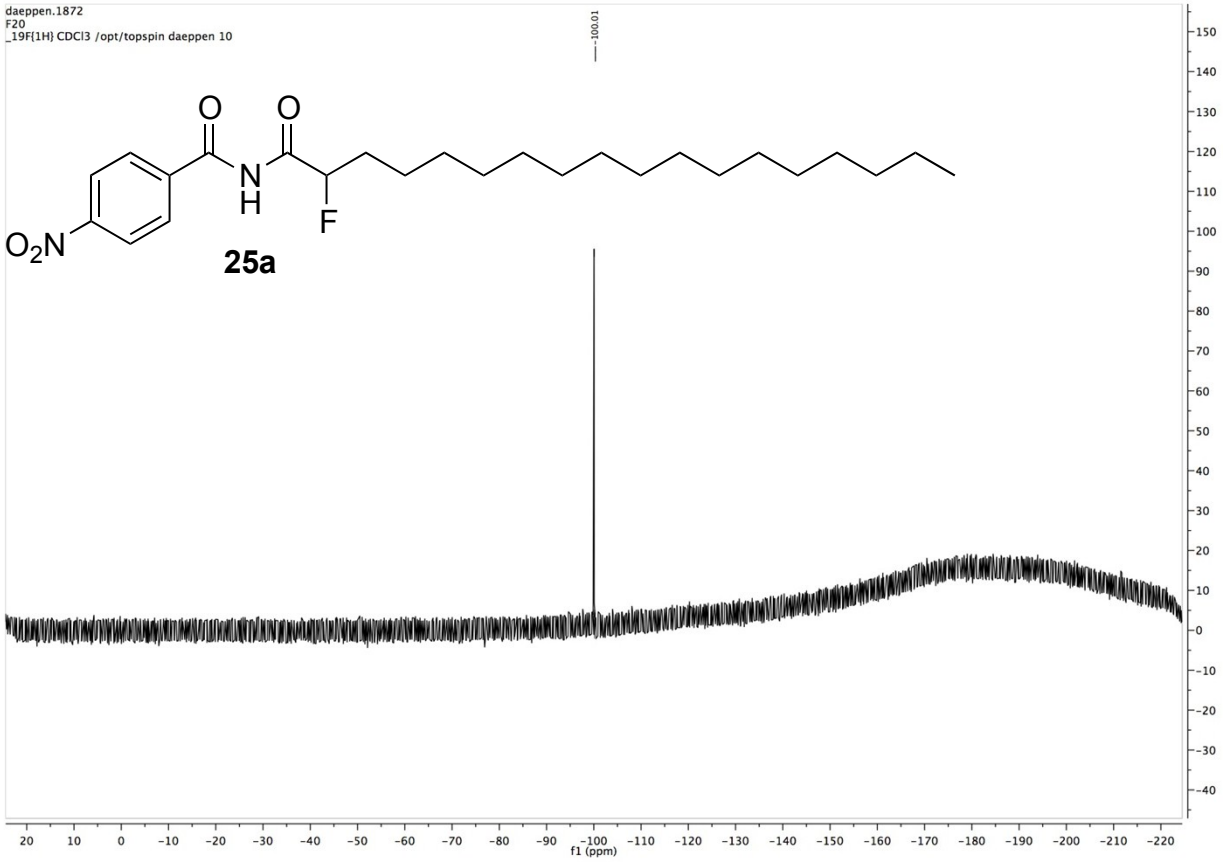

daeppen.1849
F18
_Proton_16 CDCl3 /opt/topspin daeppen 31
8.32
8.30
7.97
7.95
7.26
5.37
5.36
5.35
5.34
5.25
5.24
4.94
4.62
2.01
2.00
1.98
1.96
1.95
1.67
1.65
1.64
1.62
1.60
1.30
1.26
1.25
0.89
0.88
0.86
O
O
N
H
F
O2N
24a
f1 (ppm)


daeppen.1849
F18
_13Ccpd_ns256 CDCl3 /opt/topspin daeppen 31
O
O
N
H
F
O2N
24a
f1 (ppm)


daeppen.1849
F18
_19F{1H} CDCl3 /opt/topspin daeppen 31
-115.45
O
O
N
H
F
O2N
24a
f1 (ppm)


daeppen.1872
F20
_Proton_16 CDCl3 /opt/topspin daeppen 10
25a
f1 (ppm)


daeppen.1872
F20
_13Ccpd_ns256 CDCl3 /opt/topspin daeppen 10
25a
f1 (ppm)


daeppen.1872
F20
_19F{1H} CDCl3 /opt/topspin daeppen 10
-100.01
O
O
N
H
F
O2N
25a
f1 (ppm)