# Supporting Information

# A Photocatalyzed Aliphatic Fluorination

**Steven Bloom, James Levi Knippel, and Thomas Lectka***

***Department of Chemistry***

***Johns Hopkins University***

***3400 North Charles Street, Baltimore, MD 21218***
***lectka@jhu.edu***

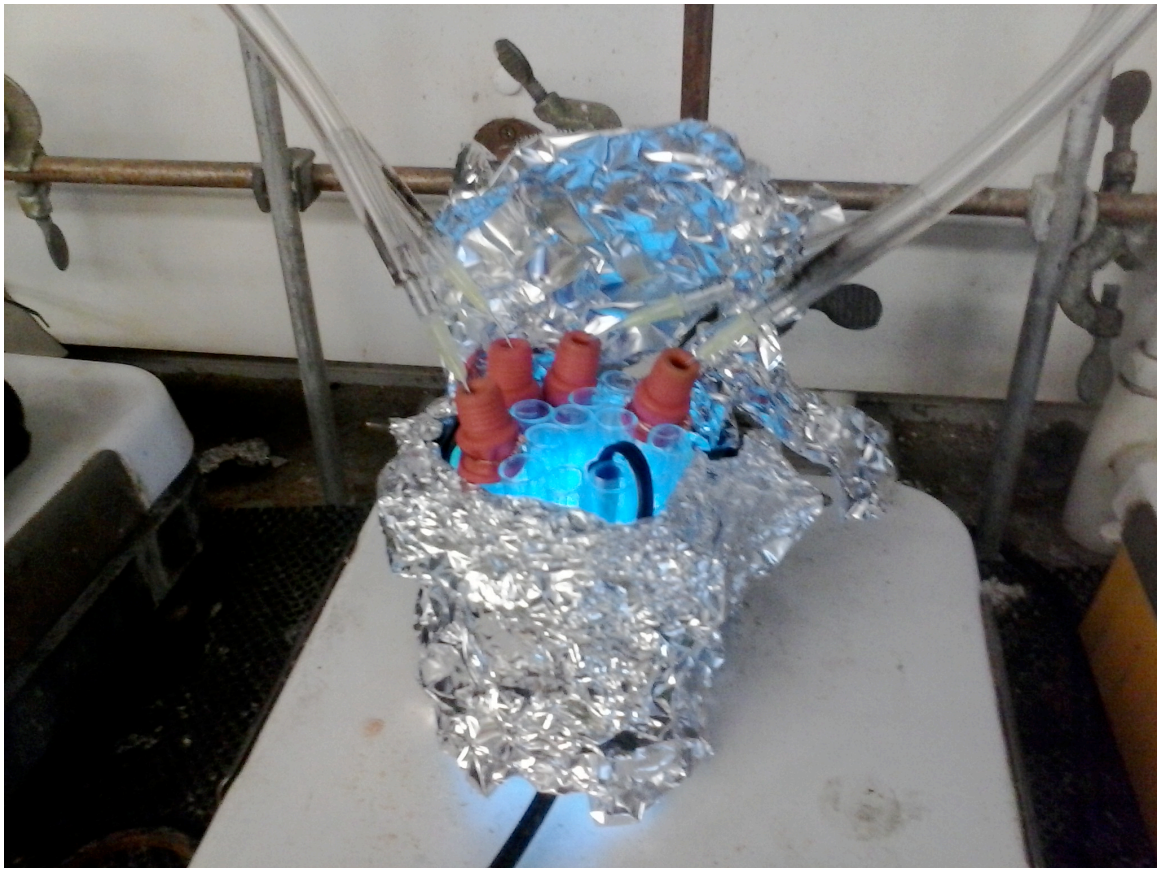
**General:**

Unless otherwise stated, all reactions were carried out under strictly anhydrous, air-free conditions under nitrogen. All solvents and compounds were dried and/or distilled by standard methods. $^{1}H$ spectra were acquired on a 400 MHz NMR in $CDCl_3$; $^{13}C$ and $^{19}F$ spectra were taken on a 300 MHz NMR in $CDCl_3$. The $^{1}H$, $^{13}C$, and $^{19}F$ chemical shifts are given in parts per million (δ) with respect to an internal tetramethylsilane (TMS, δ 0.00 ppm) standard and/or 3-chlorobenzotrifluoride (δ -64.2 ppm relative to $CFCl_3$). NMR data are reported in the following format: chemical shift (multiplicity (s = singlet, d= doublet, t = triplet, q = quartet, m = multiplet), integration, coupling constants [Hz]). IR data were obtained using an FT-IR and standard NaCl cell. High resolution mass spectra (HRMS) were recorded using ESI-TOF (electrospray ionization-time of flight) mass spectrometry. All measurements were recorded at 25 °C unless otherwise stated. Characterization of 1-fluoroadamantane (**1**),[1] 1-fluorocyclododecane (**2**),[2] fluorobicyclo[2.2.1]heptane (**3**),[3] 1-fluorocycloheptane (**4**),[2,4] 1-fluorocyclooctane (**5**),[5] 1-fluorocyclohexane (**7**),[6] fluorododecane (**8**),[7] 1-fluoroundecanoic δ-lactone (**10**),[8] and fluorosclareolide (**11**)[9] were consistent with the literature precedents. Spectral data was processed with ACD/NMR Processor Academic Edition.[10]

[1] (a) Aoyama, M.; Fukuhara, T.; Hara, S. *J. Org. Chem*. **2008,** *73*, 4186-4189.
[2] (a) Amaoka, Y.; Nagatomo, M. Inoue, M. *Org. Lett*. **2013,** 15, 2160-2163. (c) Olah, G. A.; Li, X.-Y.; Wang, Q.; Surya Prakash, G. K. *Synthesis* **1993**, *7*, 693-699. (d) Schneider, H.-J.; Gschwendtner, W.; Heiske, D.; Hoppen, V.; Thomas, F. *Tetrahedron* **1977,** *33*, 1769-1773.
[3] (a) Namavari, M.; Satyamurthy, N.; Barrio, J. R. *J. Fluorine Chem*. **1995,** *72*, 89-93. (b) Adcock, W.; Abeywickrema, A. N.; Kok, G. B. *J. Org. Chem*. **1984,** *49*, 1387-1397. (c) Bradshaw, T. K.; Hine, P. T.; Della, E. W. *Org. Mag. Res*. **1981,** *16*, 26-27. (d) Shackelford, S. A. *J. Org. Chem*. **1979**, *44*, 3485-3491. (e) Roberts, J. D.; Grutzner, J. B.; Jautelat, M.; Dence, J. B.; Smith, R. A. *J. Am. Chem. Soc*. **1970,** *92*, 7107-7110.
[4] Bucsi, I.; Török, B.; Marco, A. I.; Rasul, G.; Surya Prakash, G. K.; Olah, G. A. *J. Am. Chem. Soc.* **2002,** *124*, 7728-7736.
[5] (a) Srivastava, V. P.; Yadav, A. K.; Yadav, L.; Dhar, S. *Chem. Commun*. **2013,** *49*, 2154-2156. (b) Lheureux, A.; Bequlieu, F.; Laflamme, F.; Couturier, M.; Bennett, C.; Clayton, S.; Tovell, D.; Bill, D. R.; Mirmehrabi, M.; Tadayon, S. *J. Org. Chem*. **2010,** *75*, 3401-3411.
[6] Chambers, R. D.; Kenwright, A. M.; Parsons, M.; Sandford, G.; Moilliet, J. S. *J. Chem. Soc., Perkin Trans. 1* **2002,** *19*, 2190-2197.
[7] Kobayashi, S.; Yoneda, A.; Fukuhara, T.; Hara, S. *Tetrahedron* **2004,** *60*, 6923-6930.
[8] Bloom, S.; Pitts, C. R.; Miller, D. C.; Haselton, N.; Holl, M. G.; Urheim, E.; Lectka, T. *Angew. Chem. Int. Ed. Engl.* **2012,** *51*, 10580-10583.
[9] Liu, W.; Huang, X.; Cheng, M.-J.; Nielsen, R. J.; Goddard, W. A. III; Groves, J. T. *Science* **2012,** *337*, 1322-1325.
[10] ACD/NMR Processor Academic Edition, version 12.0, Advanced Chemistry Development, Inc., Toronto, ON, Canada, www.acdlabs.com, **2012**.

**Experimental Setup:**

Starting materials and acetonitrile were placed in a *Fisherbrand* 13 x 100 mm culture tube, sealed with a septum/copper wire, and placed under an atmosphere of $N_2$. The culture tubes were then arranged in a beaker making sure to fill empty spaces with additional culture tubes. Once arranged, a UV Pen lamp (302 nm) was placed in a separate culture tube and the beaker filled halfway with water. At this point, the setup was covered by aluminum foil and the samples irradiated for 16 h.



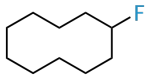
**Fluorination of α-santonin:**

To an 13 x 100 mm glass culture tube equipped with a stir bar and septum was placed α-santonin (61.6 mg, 0.25 mmol, 1.0 equiv) under an atmosphere of $N_2$ followed by MeCN (3.0 ml). Control experiments were performed in the presence and in the absence of the following: Selectfluor (195 mg, 0.55 mmol, 2.2 equiv), 1,2,4,5-tetracyanobenzene ( 4.45 mg, 0.025 mmol, 0.1 equiv), UV irradiation (302 nm) and previously isolated fluorosantonin (**12**). Products were determined either by NMR spectroscopy or column chromatography on silica.

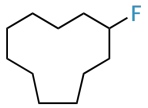
**Fluorination of α,β-unsaturated aryl ester:**

To an 13 x 100 mm glass culture tube equipped with a stir bar and septum was placed α,β-unsaturated aryl ester (58.1 mg, 0.25 mmol, 1.0 equiv) under an atmosphere of $N_2$, Selectfluor (195 mg, 0.55 mmol, 2.2 equiv) and 1,2,4,5-tetracyanobenzene ( 4.45 mg, 0.025 mmol, 0.1 equiv), were then added, followed by MeCN (3.0 mL). The reaction mixture was then placed in a water bath and irradiated using a UV Pen Lamp at 302 nm for 16 h. Product identity and yields were determined by $^{19}$F NMR spectroscopy in comparison to known literature values and 3-chlorobenzotrifluoride as an internal standard.

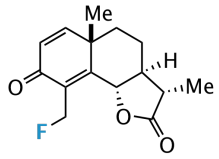
**Compound Characterization:**



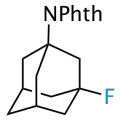

1-fluorocyclodecane (**6**). Clear oil. $^1$H NMR ($CDCl_3$): δ 4.81 (brd, $J$ = 46 Hz, 1H), 2.15-1.42 (m, 6H), 1.39-1.19 (m, 2H), 1.02-0.79 (m, 1H); $^{13}$C NMR (CDCl3): δ 93.2 (d, $J$ = 155 Hz), 31.1, 30.9, 30.7, 29.7, 29.4, 24.1, 23.7, 21.0, 20.9; $^{19}$F NMR (CDCl3): δ – 166.4 (m, 1F). Isolation and subsequent characterization of **6** proved difficult due to product volatility. For additional characterization data see: Matsui, T.; Deguchi, M.; Yoshizawa, H. *U.S. Pat. Appl. Publ.* **2005,** US 20050158623 A1 20050721.



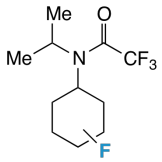

1-fluorocycloundecane (**9**). Clear oil. $^1$H NMR ($CDCl_3$): δ 4.72 (brd, $J$ = 47 Hz, 1H), 2.13-1.19 (m, 1H), 1.87-1.70 (m, 2H), 1.64-1.16 (m, 6H), 0.95-0.78 (m, 1H); $^{13}$C NMR (CDCl3): δ 94.7 (d, $J$ = 165 Hz), 32.8, 32.7, 29.7, 26.5, 26.2, 26.0, 25.7, 25.3, 22.4, 22.3; $^{19}$F NMR (CDCl3): δ – 166.4 (m, 1F); HRMS-(ESI+) calcd for $C_{11}H_{21}FNa^+$ : 195.1454, found 195.1463.



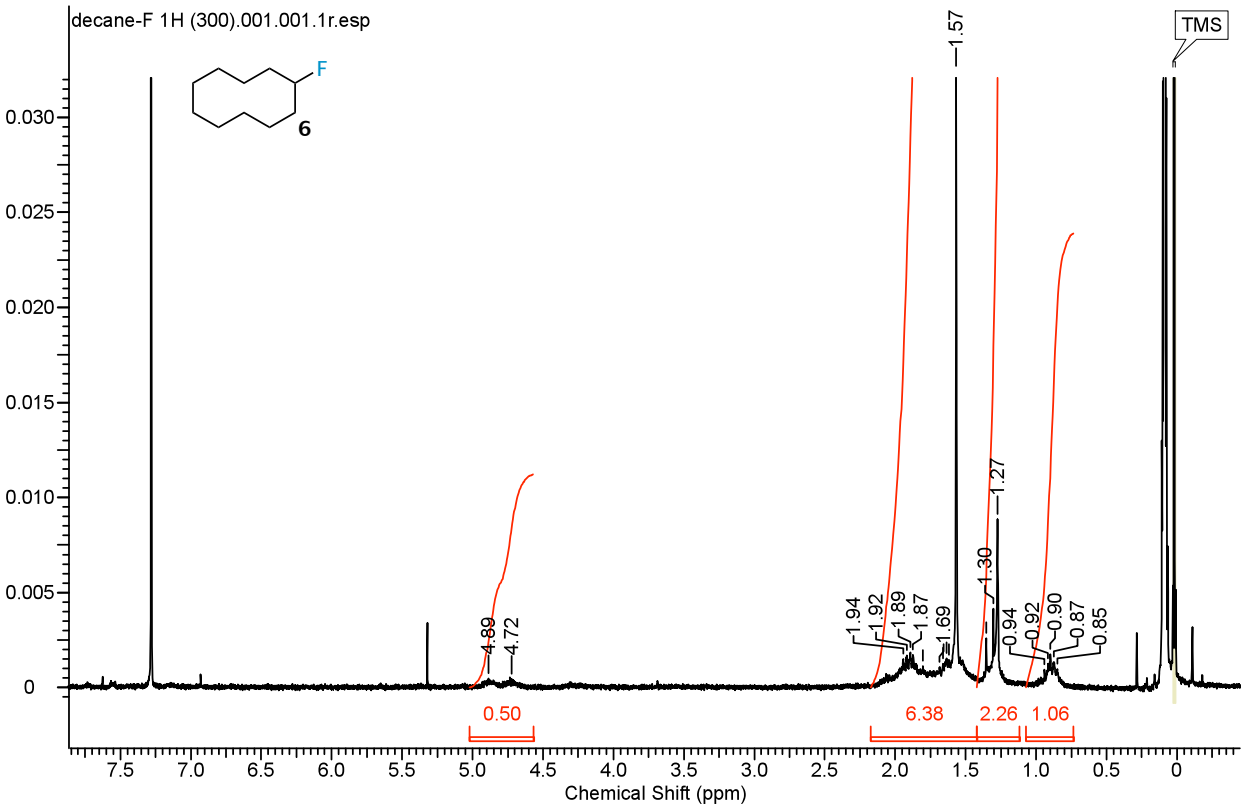

Fluorosantonin (**12**). Amorphous solid. $^{1}$H NMR ($CDCl_3$): δ 6.74 (d, *J* = 10 Hz, 1H), 6.33 (d, *J* = 10 Hz, 1H), 5.58 (dd, 48, 16 Hz, 1H), 5.56 (dd, 48, 16 Hz, 1H), 4.86 (dd, *J* = 11.3, 6.7 Hz, 1H), 2.46 (dq, *J* = 12.2, 6.9 Hz, 1H), 2.13-1.55 (m, 5H), 1.42 (s, 3H), 1.3 (d, *J* = 6.8 Hz, 3H); $^{13}$C NMR (CDCl3): δ 184.2, 176.7, 158.6, 154.8, 127.3 (d, *J* = 14.6 Hz), 126.2, 80.8, 74.5, 72.9, 53.8 (d, *J* = 2.2 Hz), 40.9, 38.2, 36.6, 25.3 (d, *J* = 1.5 Hz), 24.7, 23.1, 12.5; $^{19}$F NMR (CDCl3): δ – 207.5 (dt, J = 93.3, 47.4 Hz, 1F); IR ($CH_2Cl_2$): 1782, 1661, 1627, 1618 cm$^{-1}$; HRMS-(ESI+) calcd for $C_{15}H_{17}FO_3Na^+$ : 287.1054, found 287.1095.

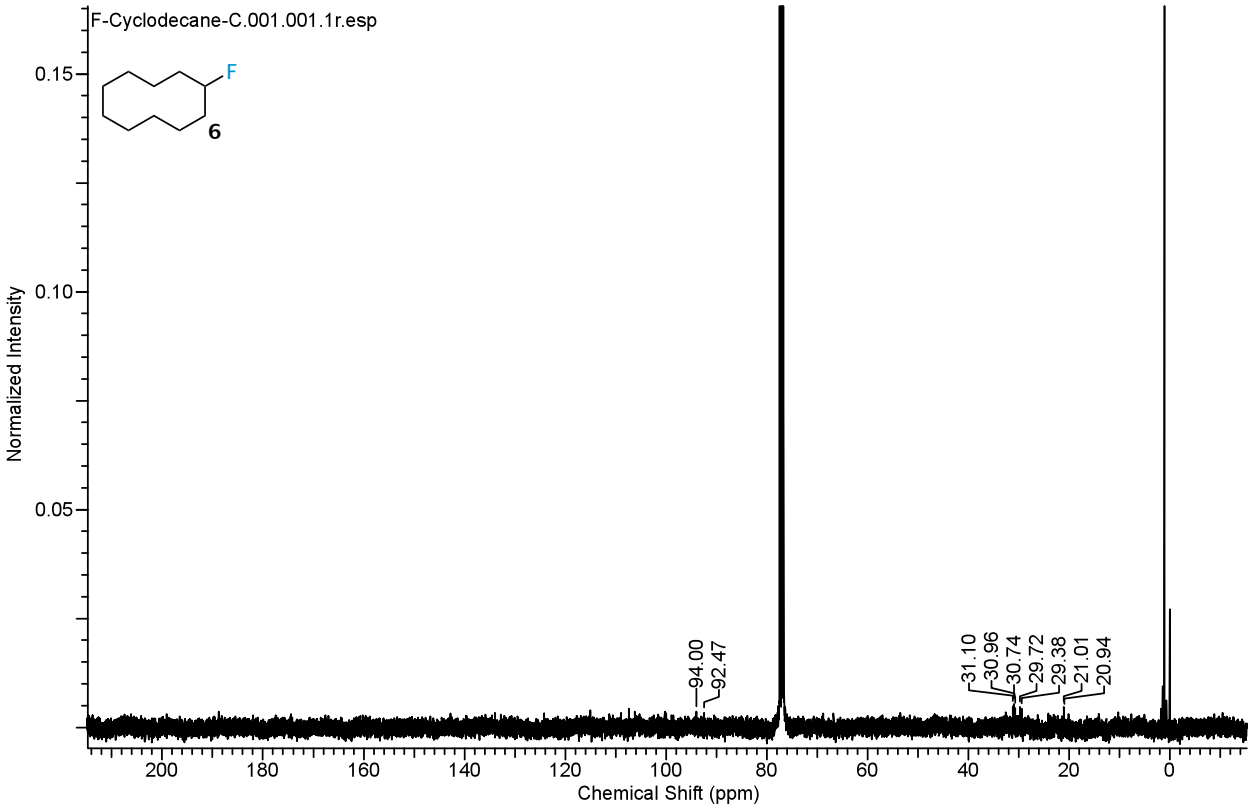


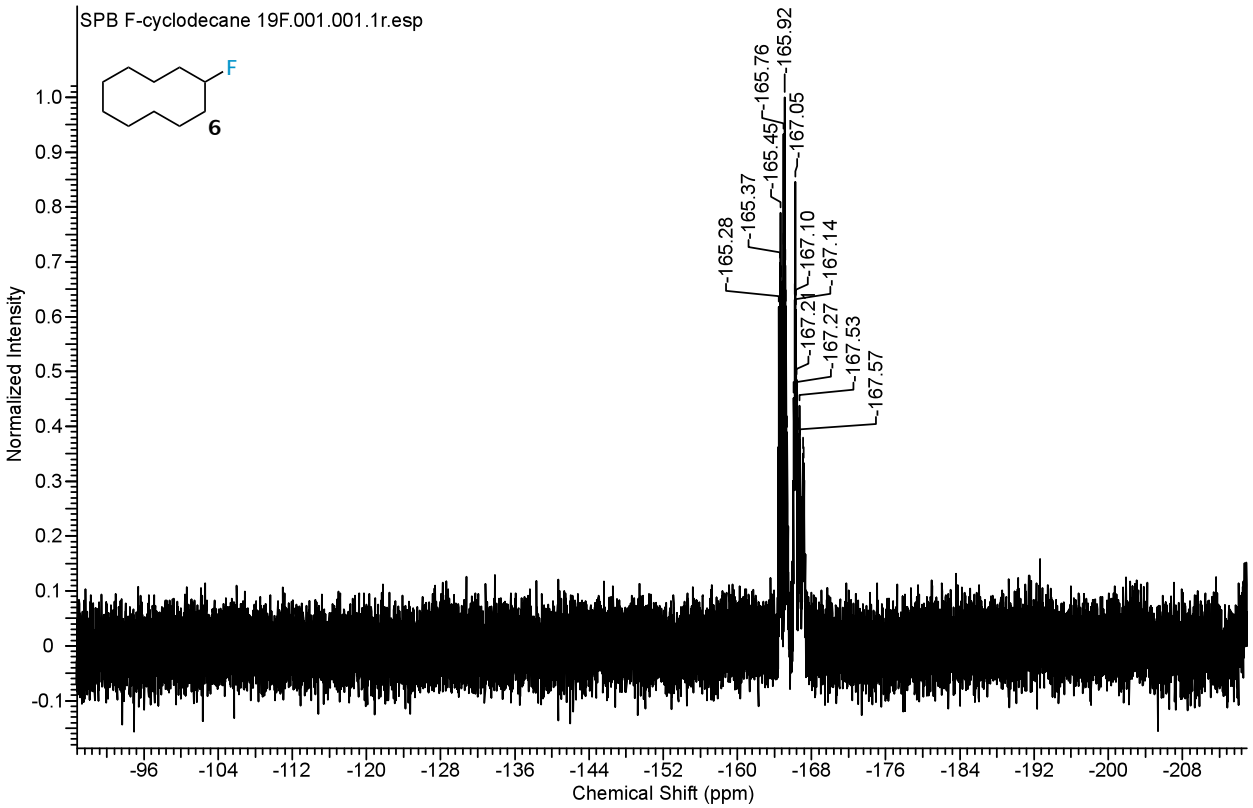

3-fluoroadamantan-1-ylisoindoline-1,3-dione (**13**). Amorphous solid. $^{1}$H NMR ($CDCl_3$): δ 7.85-7.69 (dm, 4H), 2.69 (m, 4H), 2.60-2.53 (m, 1H), 2.35 (s, 2H), 2.30-2.08 (m, 2H), 2.0-1.84 (m, 4H), 1.3 (brs, 1H); $^{13}$C NMR (CDCl3): δ 169.1, 134.1, 131.5, 123.0, 93.2 (d, *J* = 14.6 Hz), 91.3 (d, *J* = 14.6 Hz), 61.2, 47.2 (t, *J* = 19.2 Hz), 44.2 (dt, *J* = 19.4, 5.5 Hz), 40.1, 37.5, 29.2 (t, *J* = 11.2 Hz); $^{19}$F NMR (CDCl3): δ – 136.5 (s, 1F); IR ($CH_2Cl_2$): 1640 cm$^{-1}$; HRMS-(ESI+) calcd for $C_{18}H_{18}FNO_2Na^+$ : 322.1154 , found 322.1151.




2,2,2-trifluoro-*N*-(fluorocyclohexyl)-*N*-isopropylacetamide (**14**). Clear oil. $^{1}$H NMR ($CDCl_3$): δ 5.02 (bd, *J* = 48 Hz, 2H), 4.87 (bd, *J* = 48 Hz, 1H), 4.56 (dm, *J* = 49 Hz, 1H), 4.27-3.96 (m, 2H), 3.80-3.47 (m, 2H), 3.31-3.13 (m, 1H), 2.78-2.18 (m, 3H), 2.06-1.46 (m, 18H), 1.42-1.30 (m, 1H); $^{13}$C NMR (CDCl3): δ 96.8, 96.6, 95.8, 94.9, 94.2, 93.1, 91.8, 91.4, 61.6, 59.4, 57.8, 55.3, 55.0, 54.9, 54.8, 53.6, 53.4, 40.4, 40.1, 39.9, 36.8, 35.3, 35.1, 34.8, 34.7, 34.6, 34.5, 34.3, 34.1, 33.1, 32.4, 29.6, 28.0, 25.0, 24.9, 24.8, 24.6, 24.2, 24.1; $^{19}$F NMR (CDCl3): δ -64.0 (s, 3F), -64.1 (s, 3F), -64.2 (s, 3F), -64.3 (s, 3F), 64.4 (s, 3F), -163.3 (bd, *J* = 50 Hz, 0.5H), -163.6 (bd, *J* = 50 Hz, 0.5H), -179.0 to -180 (m, 3H), -181.3 (m, 1H); IR ($CH_2Cl_2$): 1685 cm$^{-1}$; HRMS-(ESI+) calcd for $C_{11}H_{17}F_4NONa^+$ : 278.1092, found 278.1088.



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6
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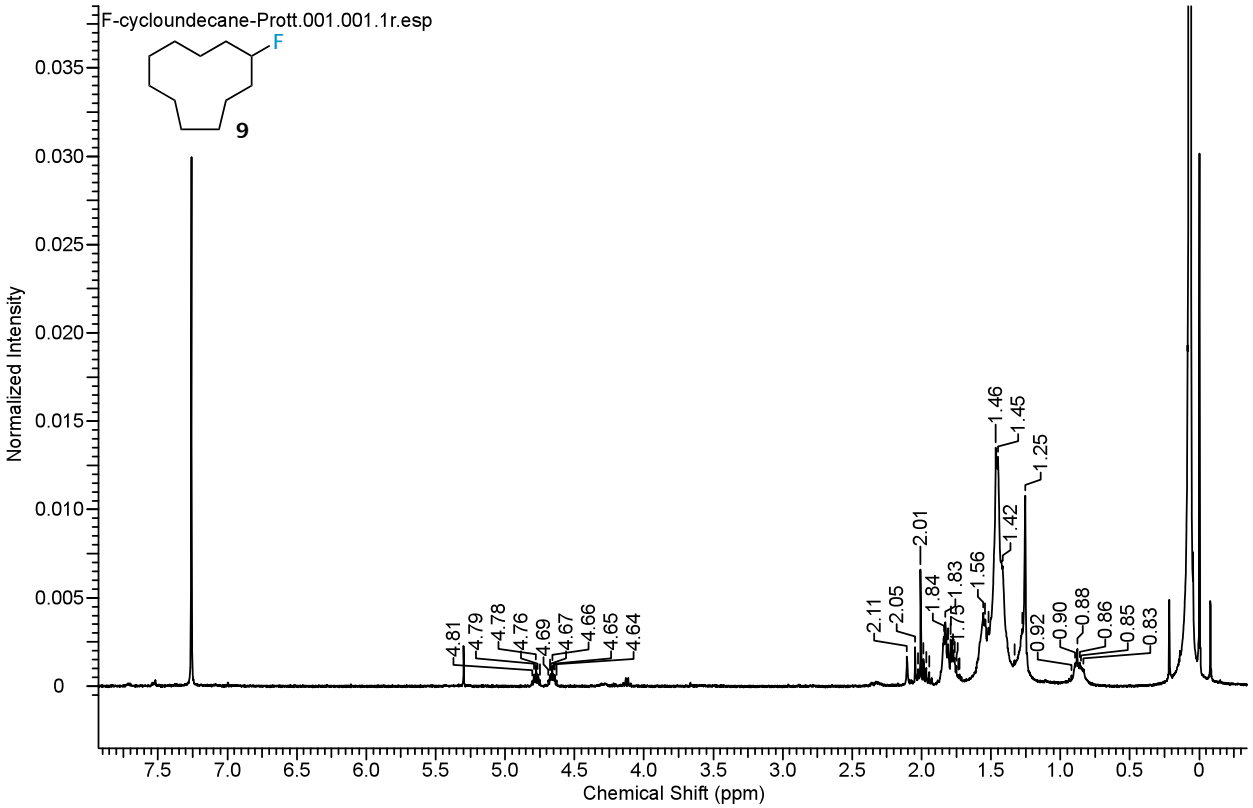
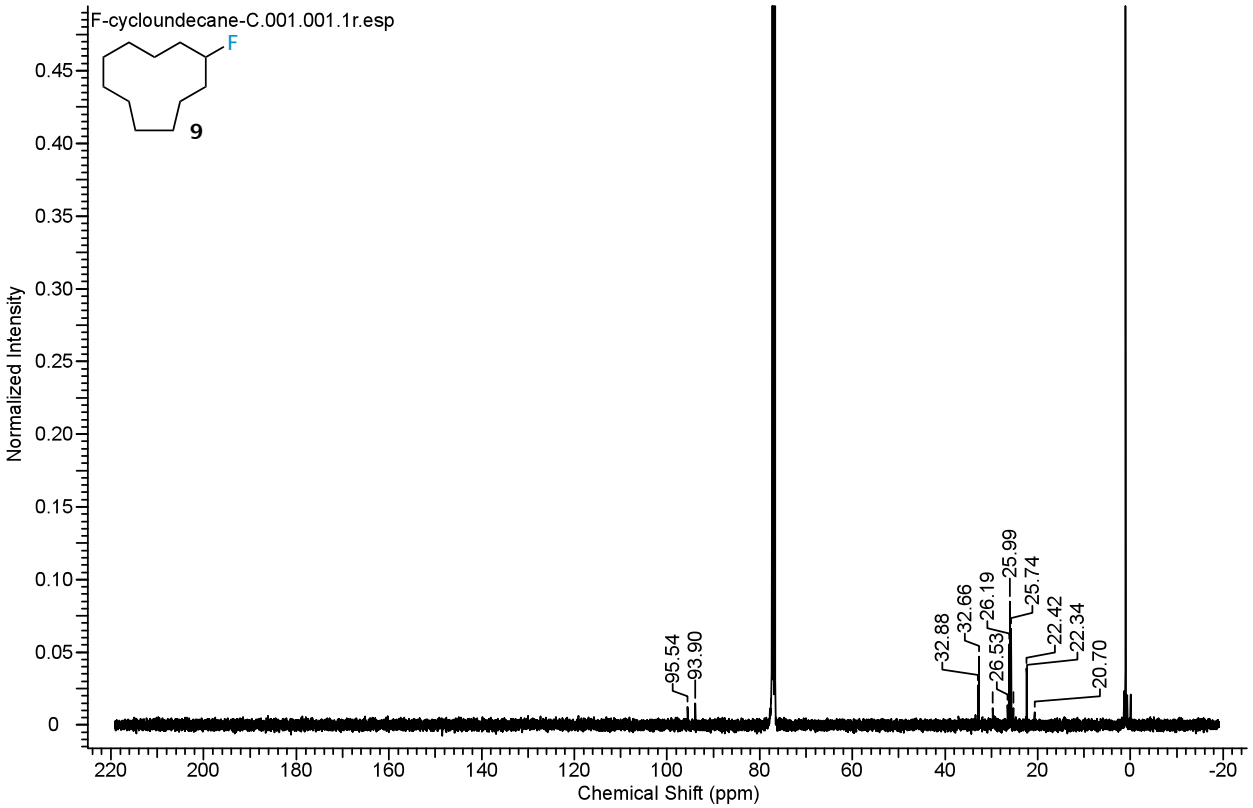
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
165.28
165.37
165.45
165.76
165.92
167.05
167.10
167.14
167.21
167.27
167.53
167.57
-96
-104
-112
-120
-128
-136
-144
-152
-160
-168
-176
-184
-192
-200
-208
Chemical Shift (ppm)

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0.30
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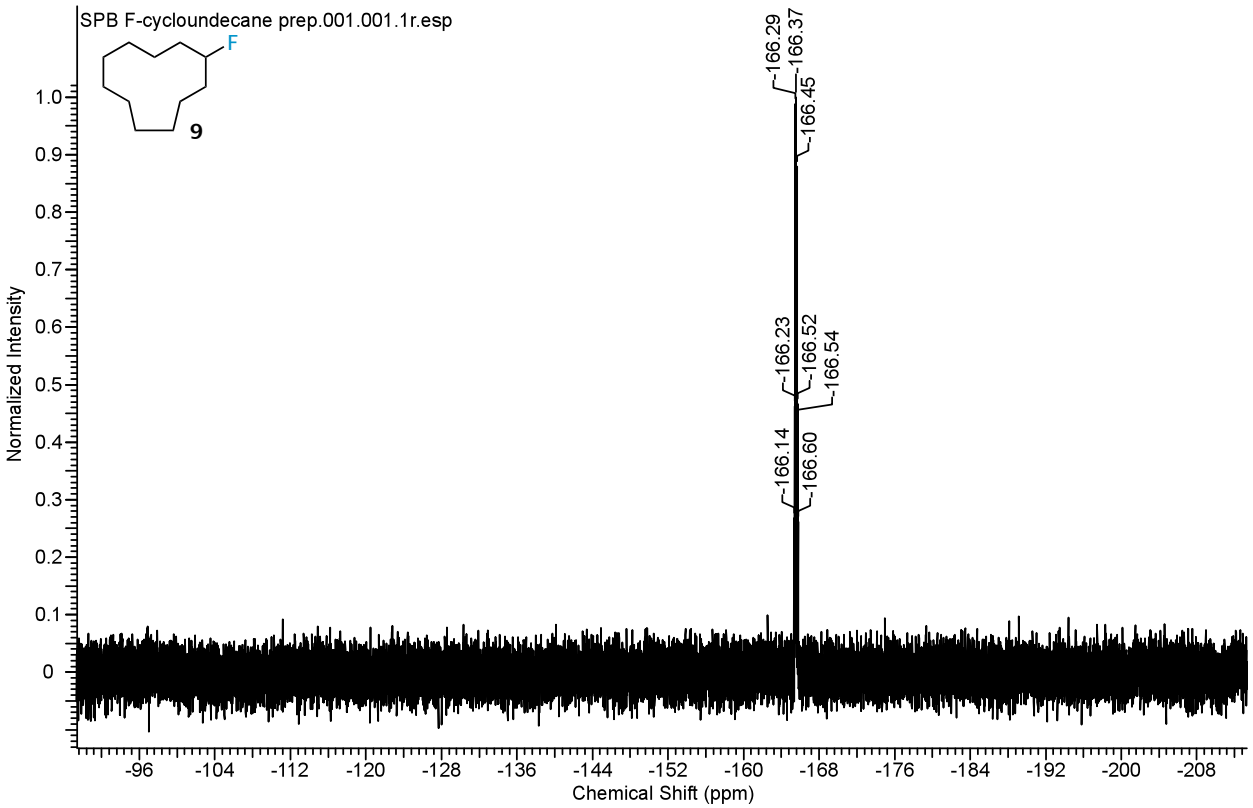
0.15
0.10
0.05
0
95.54
93.90
32.88
32.66
26.19
26.53
25.99
25.74
22.42
22.34
20.70
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)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9
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166.37
166.45
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166.52
166.54
166.14
166.60
Normalized Intensity
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0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-96
-104
-112
-120
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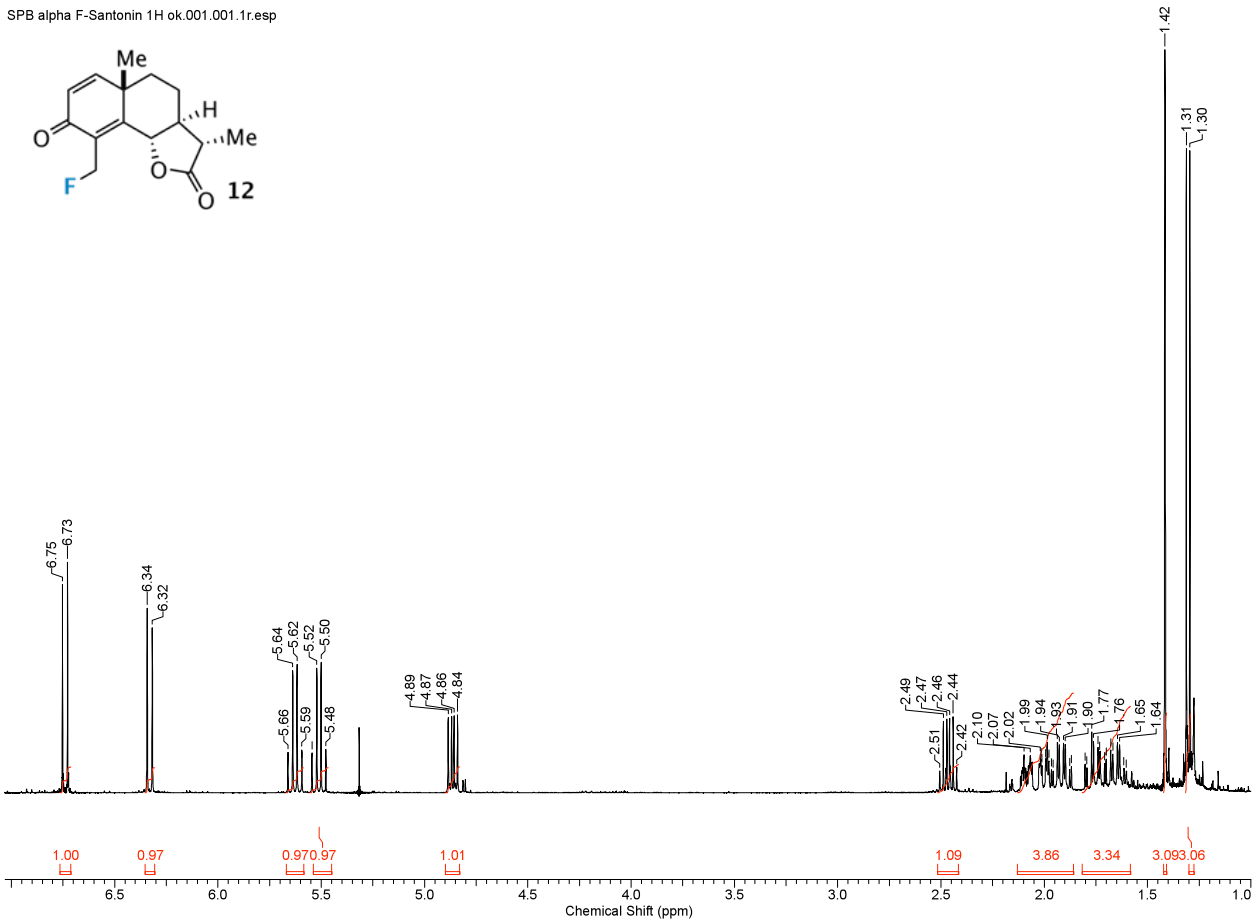
-160
-168
-176
-184
-192
-200
-208
Chemical Shift (ppm)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Me
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F
O
O
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6.32
5.64
5.62
5.52
5.50
5.66
5.59
5.48
4.89
4.87
4.86
4.84
2.49
2.47
2.46
2.44
2.51
2.42
2.10
2.07
2.02
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1.93
1.91
1.90
1.77
1.76
1.65
1.64
1.42
1.31
1.30
1.00
0.97
0.97
0.97
1.01
1.09
3.86
3.34
3.09
3.06
6.5
6.0
5.5
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4.5
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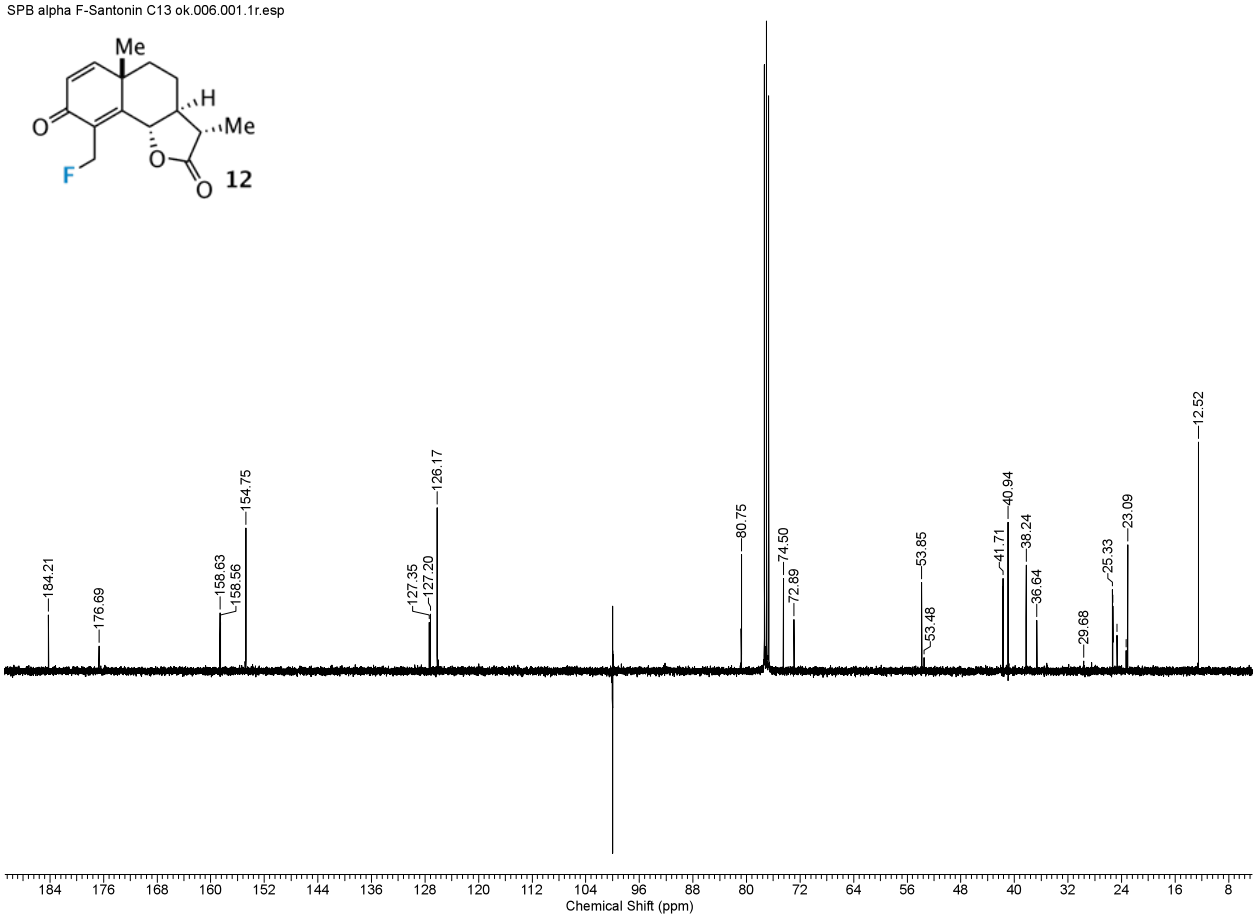
Chemical Shift (ppm)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H
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O
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O
O
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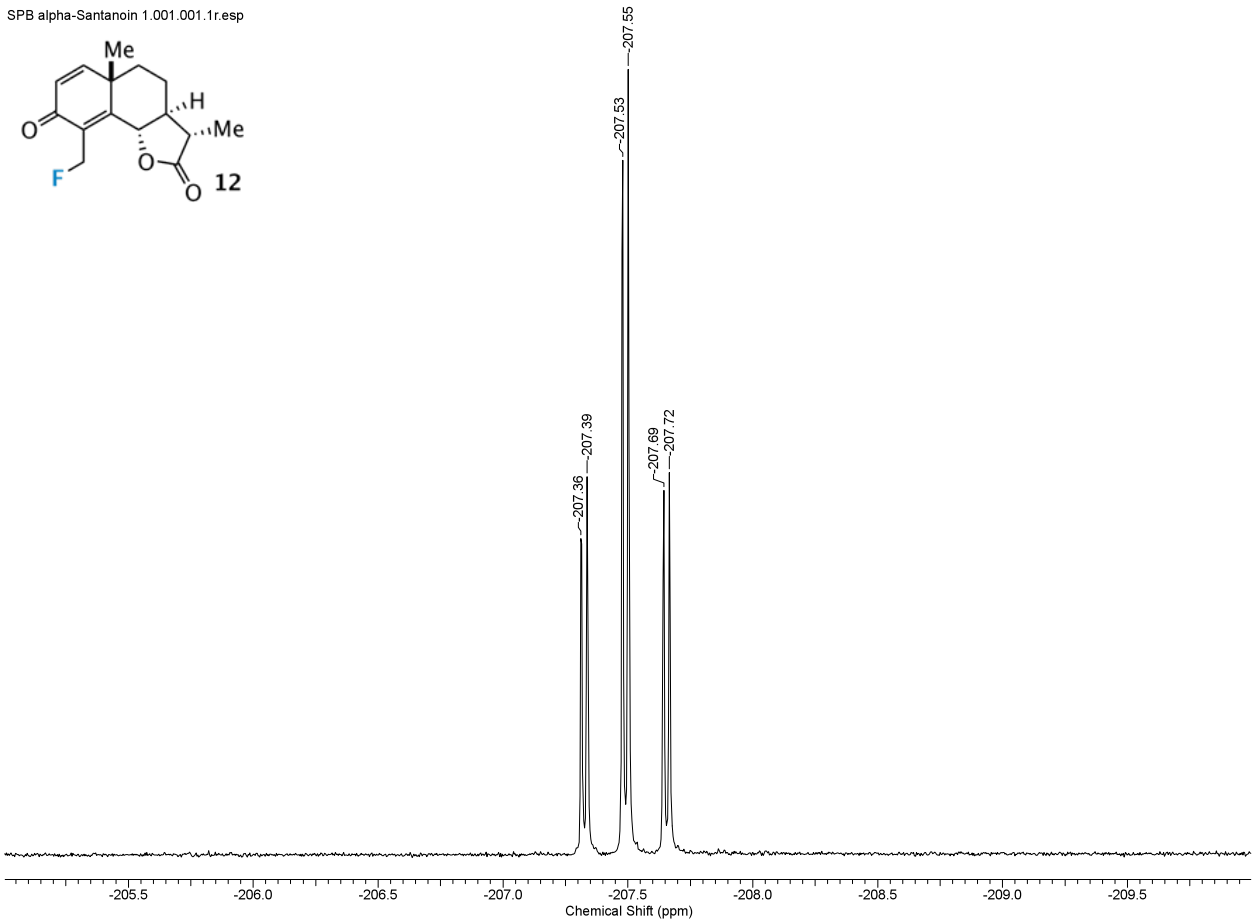
176.69
158.63
158.56
154.75
127.35
127.20
126.17
80.75
74.50
72.89
53.85
53.48
41.71
40.94
38.24
36.64
29.68
25.33
23.09
12.52
184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8
Chemical Shift (ppm)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O
O
F
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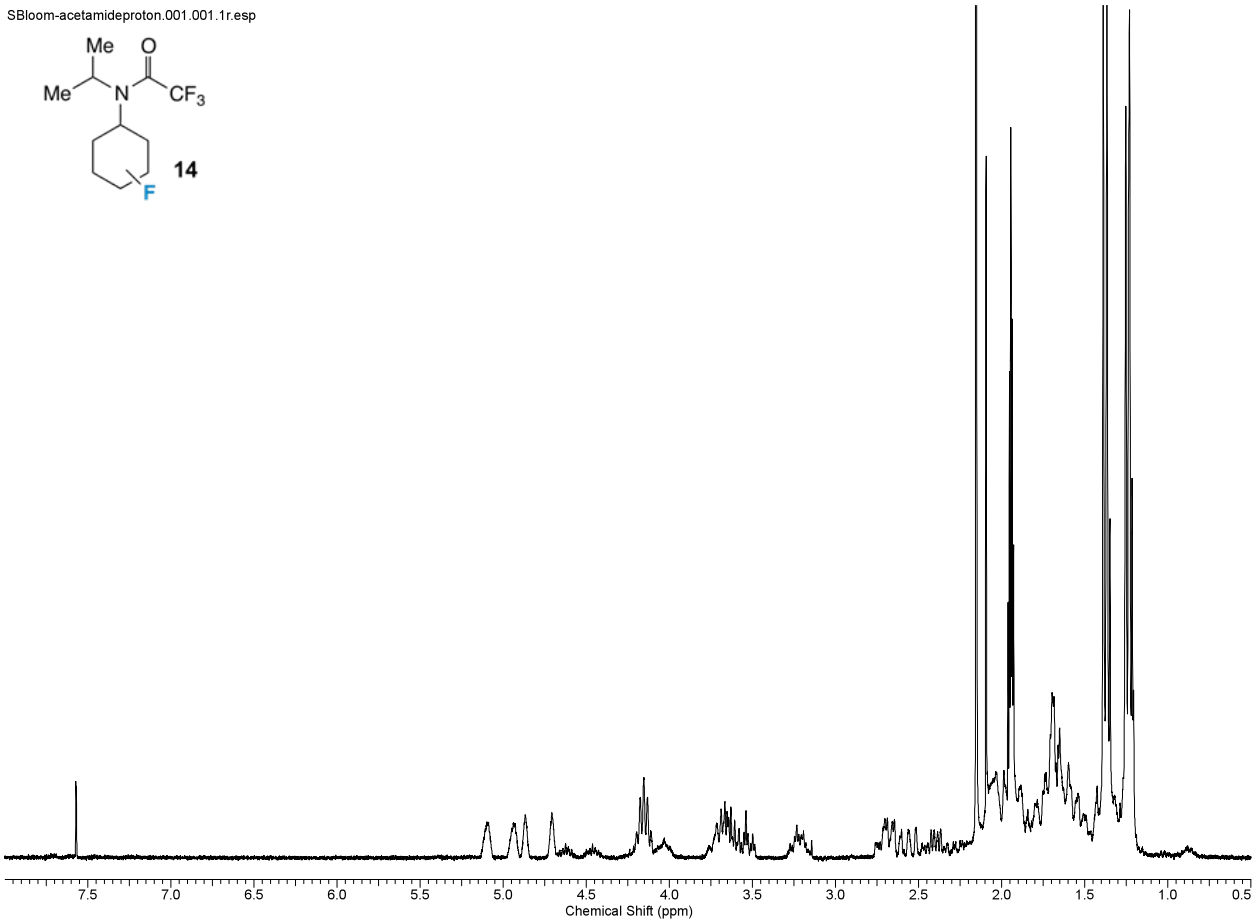
-208.5
-209.0
-209.5
Chemical Shift (ppm)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Me
N
CF3
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F
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7.0
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6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)

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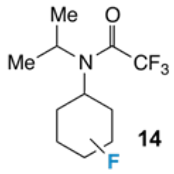
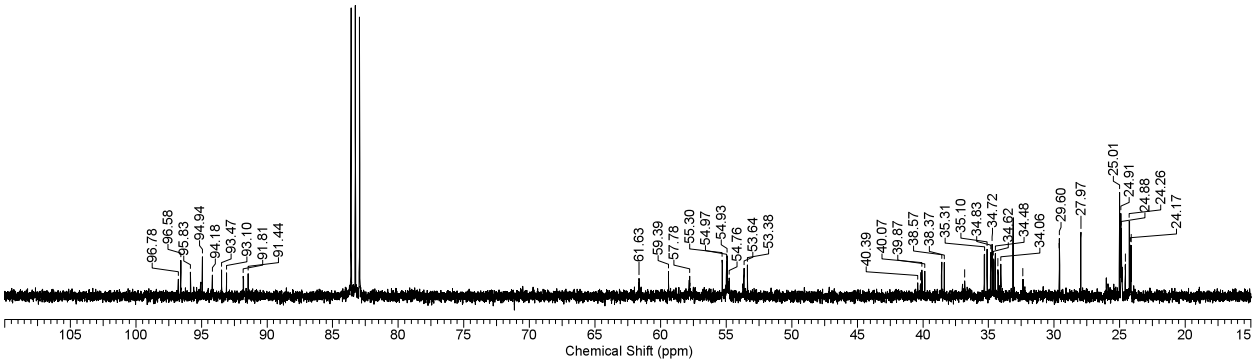
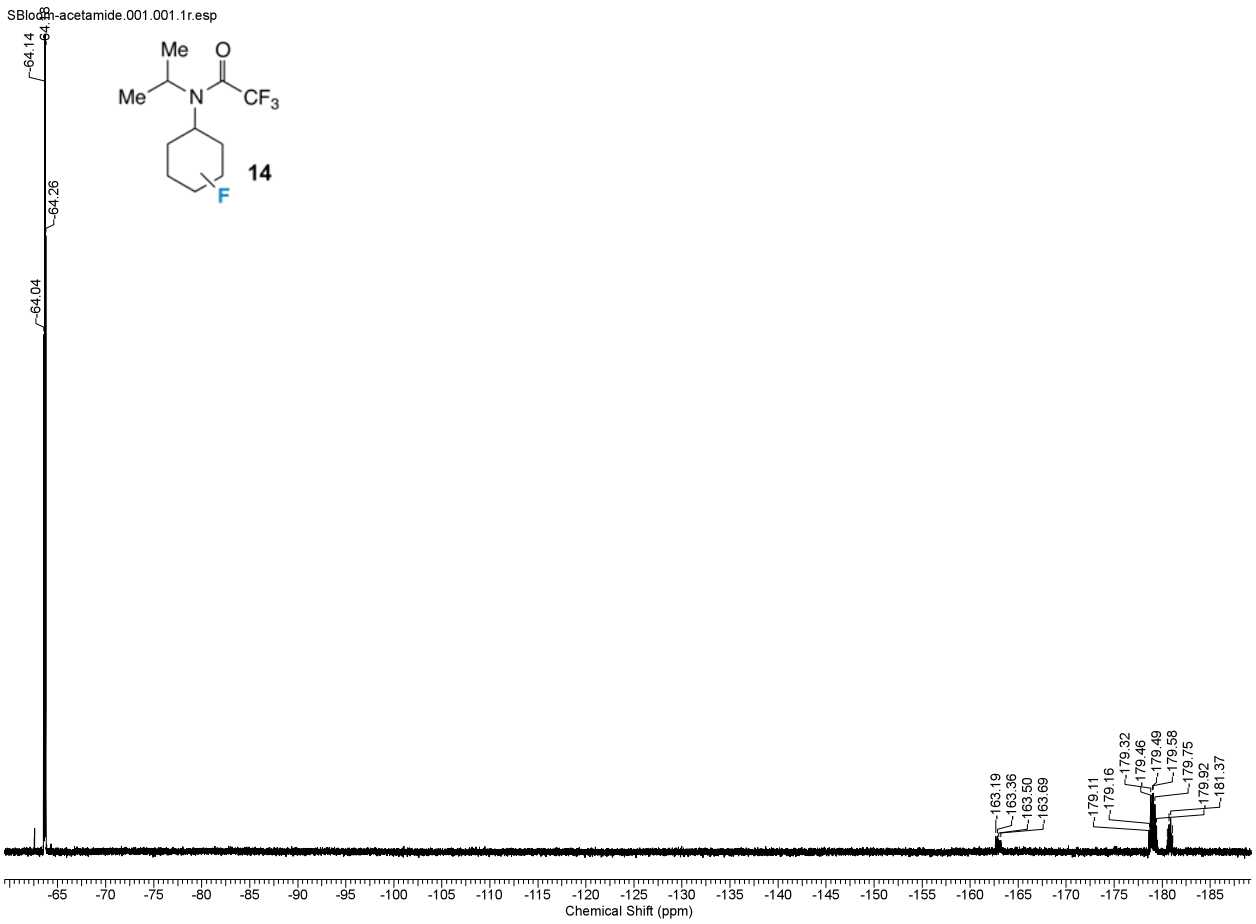



**14**

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-64.26
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Me
O
Me
N
CF3
F
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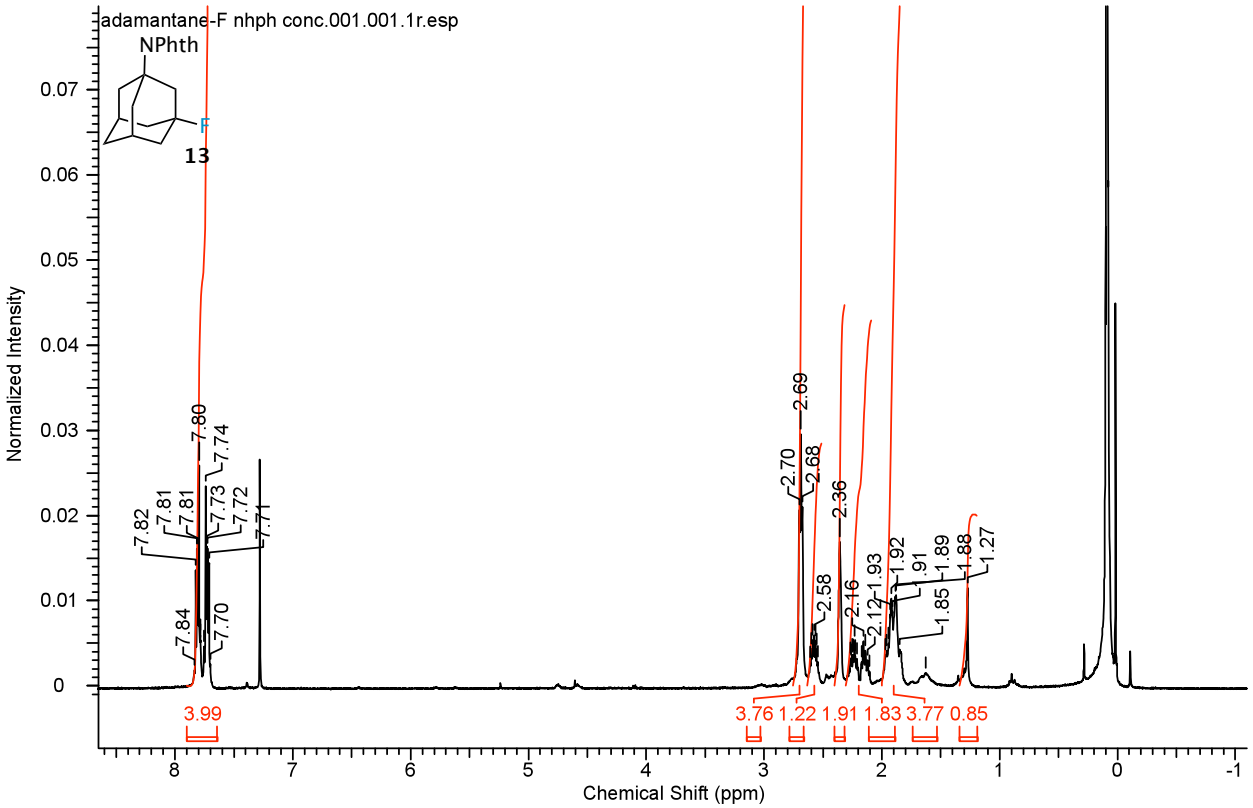
-163.36
-163.50
-163.69
-179.11
-179.16
-179.32
-179.46
-179.49
-179.58
-179.75
-179.92
-181.37
-65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185
Chemical Shift (ppm)


adamantane-F nhph conc.001.001.1r.esp
NPhth
F
13
Normalized Intensity
Chemical Shift (ppm)
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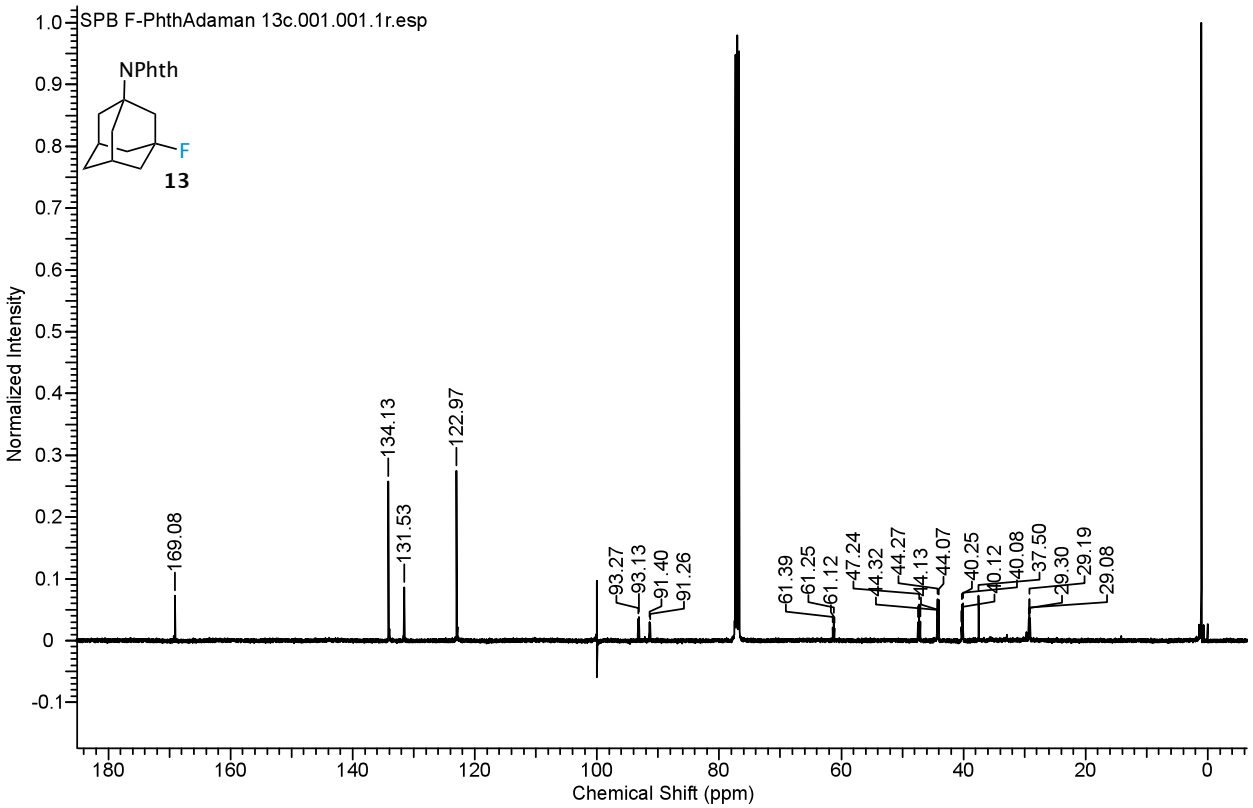
7.82
7.81
7.81
7.80
7.74
7.73
7.72
7.71
7.70
2.70
2.69
2.68
2.58
2.36
2.16
2.12
1.93
1.92
1.91
1.89
1.88
1.85
1.27
3.99
3.76
1.22
1.91
1.83
3.77
0.85


SPB F-PhthAdaman 13c.001.001.1r.esp
NPhth
F
13
Normalized Intensity
Chemical Shift (ppm)
169.08
134.13
131.53
122.97
93.27
93.13
91.40
91.26
61.39
61.25
61.12
47.24
44.32
44.27
44.13
44.07
40.25
40.12
40.08
37.50
29.30
29.19
29.08