Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information for

Silver-catalyzed radical carbofluorination of unactivated alkenes with acetic acid in aqueous solution

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1. Synthesis of Substrates

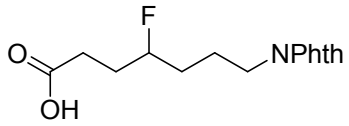
The following alkenes were commercially available and directly used without further purification.

1-octene (**A-1d**), 5-bromo-1-penten (**A-1e**), allyl benzoate (**A-1g**).

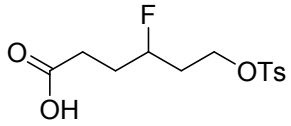
The following alkenes were prepared according to literature methods. The references are given below.

entry	reference	alkene
1	Whittaker, A. M; Lalic, G. *Org. Lett.* **2013**, *15*, 1112.	**A-1a**
2	Wang, L.; Prabhudas, B.; Clive, D. L. J. *J. Am. Chem. Soc.* **2009**, *131*, 6003.	**A-1b**
3	Shigehisa, H.; Aoki, T.; Yamaguchi, S.; Shimizu, N.; Hiroya, K. *J. Am. Chem. Soc.* **2013**, *135*, 10306.	**A-1c**
4	Sylvester, K. T.; Chirik, P. J. *J. Am. Chem. Soc.* **2009**, *131*, 8772.	**A-1f**
5	Hong, S.; Tian, S.; Metz, M. V.; Marks, T. J. *J. Am. Chem. Soc.* **2003**, *125*, 14768.	**A-1h**
6	Zhang, C.; Li, Z.; Zhu, L.; Yu L.; Wang, Z.; Li, C. *J. Am. Chem. Soc.* **2013**, *135*, 14082.	**A-1i, A-1k, A-1l, A-1o, A-3**
7	Zhu, L.; Chen, H.; Wang, Z.; Li, C. *Org. Chem. Front*., **2014**, *1*, 1299.	**A-1j ,A-1p**
8	Li, Z.; Zhang, C.; Zhu, L.; Liu, C.; *Org. Chem. Front*., **2014**, *1*, 100.	**A-1m ,A-1n**

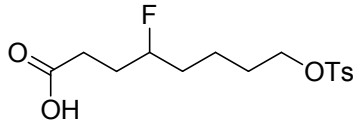
2. Characterizations of Products



7-(1,3-Dioxoisoindolin-2-yl)-4-fluoroheptanoic acid (2a). White solid. Mp: 86-88 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83-7.85 (m, 2H), 7.70-7.72 (m, 2H), 4.48-4.64 (m, 1H), 3.69-376 (m, 2H), 2.46-2.57 (m, 2H), 1.55-1.96 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.6, 168.4, 133.9, 132.0, 123.2, 92.4 (d, *J* = 169.0 Hz), 37.5, 32.2 (d, *J* = 20.6 Hz), 29.9 (d, *J* = 21.0 Hz), 29.5 (d, *J* = 4.3 Hz), 24.3 (d, *J* = 3.9 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ -183.8 (m, 1F); IR (KBr): ν (cm^{-1}) 2942, 1772, 1719, 1713, 1707, 1440, 1400, 1367, 1051, 721; ESI-MS: (*m/z*) 316.1 (M+Na); HRMS calcd for $C_{15}H_{16}FNNaO_4$ (M+Na): 316.0956, found 316.0966.

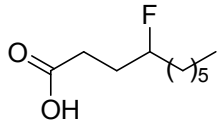


4-Fluoro-6-(tosyloxy)hexanoic acid (2b). White solid. Mp: 68-70 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 7.79 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 4.51-4.73 (m, 1H), 4.16 (t, *J* = 6.4 Hz, 2H), 2.41-2.58 (m, 5H), 1.80-2.06 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.9, 145.0, 132.6, 129.9, 127.9, 89.0 (d, *J* = 169.3 Hz), 66.2 (d, *J* = 4.6 Hz), 34.5 (d, *J* = 20.5 Hz), 29.8 (d, *J* = 21.3 Hz), 29.4 (d, *J* = 3.8 Hz), 21.6; ^{19}F NMR (282 MHz, $CDCl_3$): δ -183.7 (m, 1F); IR (KBr): ν (cm^{-1}) 2938, 1709, 1596, 1358, 1189, 1175, 1097, 963, 911, 816, 665, 554; ESI-MS: (*m/z*) 326.9 (M^{+}+Na); HRMS calcd for $C_{13}H_{18}FO_5S$ (M+H): 305.0853, found 305.0851.

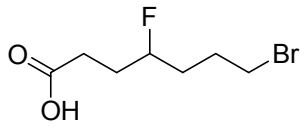


4-Fluoro-8-(tosyloxy)octanoic acid (2c). White solid. Mp: 72-74 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 7.79 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 4.36-4.59 (m, 1H), 4.03 (t, *J* = 6.8 Hz, 2H), 2.42-2.61 (m, 5H), 1.80-1.99 (m, 2H), 1.35-1.76 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.1, 144.8, 132.9, 129.9, 127.8, 92.7 (d, *J* = 167.8 Hz), 70.2, 34.2 (d, *J* = 20.5 Hz), 29.9 (d, *J* = 20.5 Hz), 29.6 (d, *J* = 4.6 Hz), 28.5, 21.6, 21.0

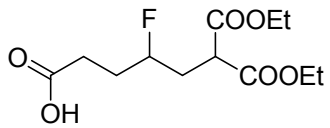
(d, J = 5.4 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ -184.1 (m, 1F); IR (KBr): ν (cm^{-1}) 3056, 2953, 1712, 1598, 1358, 1189, 1174, 1097, 934, 816, 664, 576, 555; ESI-MS: (*m/z*) 355.1 (M^++Na); HRMS calcd for $C_{15}H_{21}FNaO_5S$ (M+Na): 355.0986, found 355.0984.



4-Fluorodecanoic acid (2d). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): 4.41-4.65 (m, 1H), 2.44-2.64 (m, 2H), 1.82-2.03 (m, 2H), 1.20-1.74 (m, 10H), 0.82-0.97 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.6, 93.2 (d, J = 167.8 Hz), 35.0 (d, J = 19.8 Hz), 31.7, 30.0 (d, J = 21.2 Hz), 29.7 (d, J = 4.6 Hz), 29.0, 24.9 (d, J = 4.5 Hz), 22.5, 14.0; ^{19}F NMR (282 MHz, $CDCl_3$): δ -183.4 (m, 1F); IR (neat): ν (cm^{-1}) 2933, 2860, 1713, 1417, 1284, 1216, 1035, 923; EIMS: *m/z* (rel intensity) 170 (M^+-HF, 1), 152 (12), 123 (23), 111 (63), 100 (36), 84 (39), 81 (48), 69 (100), 60 (70), 55 (87), 41 (67); HRMS calcd for $C_{10}H_{18}O_2$ (M-HF): 170.1307, found 170.1304.

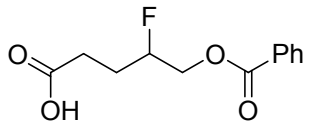


7-Bromo-4-fluoroheptanoic acid (2e). Light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): 4.45-4.72 (m, 1H), 3.38-3.59 (m, 2H), 2.45-2.70 (m, 2H), 1.68-2.16 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.2, 92.3 (d, J = 168.6 Hz), 33.6 (d, J = 20.5 Hz), 33.3, 30.0 (d, J = 21.3 Hz), 29.6 (d, J = 3.8 Hz), 28.3 (d, J = 3.8 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ -184.3 (m, 1F); IR (neat): ν (cm^{-1}) 2935, 1712, 1441, 1255, 1070, 916, 874, 649, 561; EIMS: *m/z* (rel intensity) 226 (M^+, 1), 169 (52), 127 (55), 109 (32), 100 (18), 85 (48), 81 (66), 73 (29), 67 (28), 60 (100), 41 (35); HRMS calcd for $C_7H_{12}BrFO_2$ (M): 226.0005, found 226.0008.

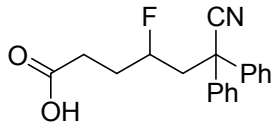


7-Ethoxy-6-(ethoxycarbonyl)-4-fluoro-7-oxoheptanoic acid (2f). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): 4.48-4.75 (m, 1H), 4.14-4.34 (m, 4H), 3.60 (t, J = 6.8 Hz,

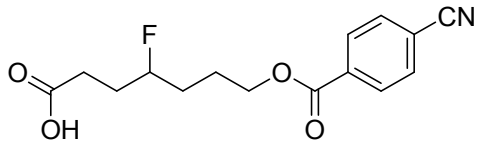
1H), 2.45-2.63 (m, 2H), 2.13-2.32 (m, 2H), 1.85-2.05 (m, 2H), 1.22-1.33 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.5, 169.1, 168.9, 90.9 (d, J = 169.3 Hz), 61.7, 48.2 (d, J = 3.0 Hz), 34.1 (d, J = 20.5 Hz), 30.0 (d, J = 20.5 Hz), 29.4 (d, J = 3.8 Hz), 14.0; ^{19}F NMR (282 MHz, $CDCl_3$): δ -186.2 (m, 1F); IR (neat): ν (cm^{-1}) 2984, 2940, 1732, 1446, 1371, 1243, 1096, 1052, 916, 863; ESI-MS: (*m/z*) 301.1 (M^++Na); HRMS calcd for $C_{12}H_{19}FNaO_6$ (M+Na): 301.1058, found 301.1047.



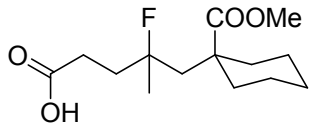
5-(Benzoyloxy)-4-fluoropentanoic acid (2g). White solid. Mp: 56-57 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 8.07 (d, J = 7.2 Hz, 2H), 7.58 (t, J = 7.6 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 4.79-5.03 (m, 1H), 4.35-4.60 (m, 2H), 2.53-2.71 (m, 2H), 1.93-2.20 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.6, 166.3, 133.3, 129.7, 129.5, 128.4, 90.1 (d, J = 172.4 Hz), 65.8 (d, J = 22.1 Hz), 29.2 (d, J = 3.8 Hz), 26.4 (d, J = 21.2 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ -190.4 (m, 1F); IR (KBr): ν (cm^{-1}) 3065, 2956, 1719, 1602, 1584, 1452, 1274, 1178, 1113, 1071, 1027, 900, 712; ESI-MS: (*m/z*) 263.1 (M^++Na); HRMS calcd for $C_{12}H_{13}FNaO_4$ (M+Na): 263.0690, found 263.0688.



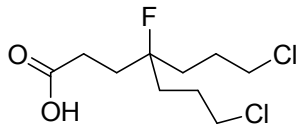
6-Cyano-4-fluoro-6,6-diphenylhexanoic acid (2h). White solid. Mp: 135-138 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 7.28-7.47 (m, 10H), 4.47-4.76 (m, 1H), 2.92 (td, J = 15.2, 8.0 Hz, 1H), 2.38-2.66 (m, 3H), 1.82-2.12 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.4, 139.8, 139.2, 129.1, 128.9, 128.24, 128.17, 126.9, 121.8, 89.7 (d, J = 171.6 Hz), 49.0, 44.6 (d, J = 20.5 Hz), 30.6 (d, J = 20.5 Hz), 29.3 (d, J = 4.6 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ -181.5 (m, 1F); IR (KBr): ν (cm^{-1}) 3061, 2928, 2240, 1711, 1593, 1494, 1449, 1279, 1071, 1031, 930, 755, 699; ESI-MS: (*m/z*) 334.1 (M^++Na); HRMS calcd for $C_{19}H_{18}FNNaO_2$ (M+Na): 334.1214, found 334.1215.



7-((4-Cyanobenzoyl)oxy)-4-fluoroheptanoic acid (2i). White solid. Mp: 100-102 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 8.14 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 4.51-4.75 (m, 1H), 4.33-4.48 (m, 2H), 2.47-2.67 (m, 2H), 1.65-2.07 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.2, 164.9, 134.0, 132.2, 130.1, 117.9, 116.4, 92.5 (d, *J* = 168.5 Hz), 65.3, 31.7 (d, *J* = 21.3 Hz), 30.0 (d, *J* = 20.5 Hz), 29.6 (d, *J* = 3.8 Hz), 24.4 (d, *J* = 3.8 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ -180.7 (m, 1F); IR (KBr): ν (cm^{-1}) 2945, 2230, 1702, 1277, 1103, 962, 864, 766, 691, 549; ESI-MS: (*m/z*) 316.0 (M^{+}+Na); HRMS calcd for $C_{15}H_{16}FNNaO_4$ (M+Na): 316.0956, found 316.0950.

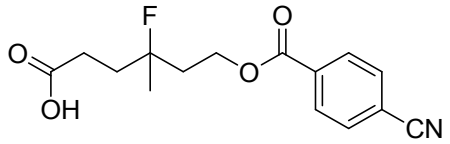


4-Fluoro-5-(1-(methoxycarbonyl)cyclohexyl)-4-methylpentanoic acid (2j). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): 3.68 (s, 3H), 2.46 (t, *J* = 7.6 Hz, 2H), 1.75-2.18 (m, 6H), 1.23-1.62 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.4, 177.5, 96.1 (d, *J* = 170.8 Hz), 51.7, 48.6 (d, *J* = 19.7 Hz), 45.1, 35.9 (d, *J* = 3.1 Hz), 35.8 (d, *J* = 23.5 Hz), 34.9, 28.4 (d, *J* = 5.3 Hz), 25.7, 24.1 (d, *J* = 24.3 Hz), 22.7, 22.6; ^{19}F NMR (282 MHz, $CDCl_3$): δ -146.0 (m, 1F); IR (neat): ν (cm^{-1}) 2940, 2856, 1727, 1716, 1453, 1214, 1160, 1134, 1110, 1004, 919, 894, 851, 828; ESI-MS: (*m/z*) 297.2 (M^{+}+Na); HRMS calcd for $C_{14}H_{23}FNaO_4$ (M+Na): 294.1473, found 297.1469.

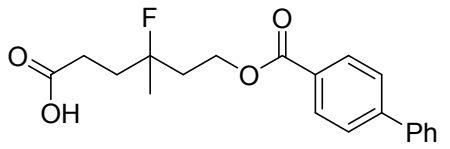


7-Chloro-4-(3-chloropropyl)-4-fluoroheptanoic acid (2k). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): 3.57 (t, *J* = 6.0 Hz, 4H), 2.48 (t, *J* = 7.6 Hz, 2H), 1.99 (dt, *J* = 19.6, 8.0 Hz, 2H), 1.68-1.93 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.2, 97.1 (d, *J* = 172.4 Hz), 44.9, 34.0 (d, *J* = 22.7 Hz), 31.6 (d, *J* = 23.5 Hz), 28.1 (d, *J* = 5.3 Hz), 26.5 (d, *J* = 6.0 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ -153.8 (m, 1F); IR (neat): ν (cm^{-1})

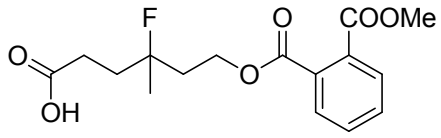
2961, 1713, 1446, 1418, 1314, 1232, 1086, 925, 867, 720, 653; ESI-MS: (*m/z*) 281.1 (M^++Na); HRMS calcd for $C_{10}H_{17}Cl_2FNaO_2$ (M+Na): 281.0482, found 281.0473.



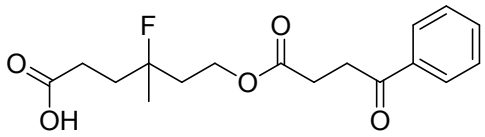
6-((4-Cyanobenzoyl)oxy)-4-fluoro-4-methylhexanoic acid (2l). White solid. Mp: 102-103 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 8.14 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 4.53 (t, *J* = 6.8 Hz, 2H), 2.54 (t, *J* = 7.6 Hz, 2H), 1.94-2.28 (m, 4H), 1.44 (d, *J* = 21.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.2, 164.8, 133.8, 132.3, 130.1, 117.9, 116.4, 94.9 (d, *J* = 170.0 Hz), 61.3 (d, *J* = 6.1 Hz), 38.1 (d, *J* = 23.5 Hz), 34.5 (d, *J* = 22.8 Hz), 28.4 (d, *J* = 5.3 Hz), 24.0 (d, *J* = 24.3 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ -148.8 (m, 1F); IR (KBr): ν (cm^{-1}) 3101, 2982, 2232, 1731, 1610, 1407, 1387, 1279, 1178, 1108, 1019, 863, 768, 692, 547; ESI-MS: (*m/z*) 316.1 (M^++Na); HRMS calcd for $C_{15}H_{16}FNNaO_4$ (M+Na): 316.0956, found 316.0952.



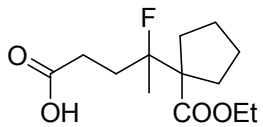
6-(([1,1'-Biphenyl]-4-carbonyl)oxy)-4-fluoro-4-methylhexanoic acid (2m). White solid. Mp: 101-102 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 8.09 (d, *J* = 8.4 Hz, 2H), 7.61-7.66 (m, 4H), 7.46 (t, *J* = 7.2 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 1H), 4.49 (t, *J* = 6.8 Hz, 2H), 2.53 (t, *J* = 8.0 Hz, 2H), 1.94-2.25 (m, 4H), 1.43 (d, *J* = 21.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.1, 166.4, 145.8, 139.9, 130.1, 128.9, 128.7, 128.2, 127.3, 127.1, 95.0 (d, *J* = 169.3 Hz), 60.5 (d, *J* = 6.9 Hz), 38.2 (d, *J* = 22.8 Hz), 34.5 (d, *J* = 22.7 Hz), 28.4 (d, *J* = 4.6 Hz), 24.1 (d, *J* = 24.3 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ -147.6 (m, 1F); IR (KBr): ν (cm^{-1}) 3060, 3032, 2981, 2934, 1713, 1609, 1406, 1278, 1113, 859, 748, 699; ESI-MS: (*m/z*) 367.1 (M^++Na); HRMS calcd for $C_{20}H_{21}FNaO_4$ (M+Na): 367.1316, found 367.1308.



4-Fluoro-6-((2-(methoxycarbonyl)benzoyl)oxy)-4-methylhexanoic acid (2n). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): 7.69-7.74 (m, 2H), 7.50-7.56 (m, 2H), 4.47 (t, *J* = 6.8 Hz, 2H), 3.91 (s, 3H), 2.51 (t, *J* = 8.0 Hz, 2H), 1.90-2.23 (m, 4H), 1.40 (d, *J* = 22.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.0, 167.9, 167.6, 132.0, 131.7, 131.2, 131.1, 129.0, 128.7, 94.9 (d, *J* = 170.1 Hz), 61.2 (d, *J* = 6.8 Hz), 52.7, 37.9 (d, *J* = 22.8 Hz), 34.5 (d, *J* = 22.7 Hz), 28.3 (d, *J* = 5.3 Hz), 24.0 (d, *J* = 24.3 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ -148.2 (m, 1F); IR (neat): ν (cm^{-1}) 3078, 2955, 1732, 1600, 1580, 1489, 1435, 1386, 1293, 1130, 1077, 959, 886, 745, 705; ESI-MS: (*m/z*) 349.1 (M^++Na); HRMS calcd for $C_{16}H_{19}FNaO_6$ (M+Na): 349.1058, found 349.1063.

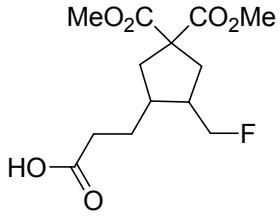


4-Fluoro-4-methyl-6-((4-oxo-4-phenylbutanoyl)oxy)hexanoic acid (2o). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): 7.98 (d, *J* = 7.2 Hz, 2H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.2 Hz, 2H), 4.26 (t, *J* = 6.8 Hz, 2H), 3.32 (t, *J* = 6.8 Hz, 2H), 2.76 (t, *J* = 6.8 Hz, 2H), 2.49 (t, *J* = 7.6 Hz, 2H), 1.88-2.14 (m, 4H), 1.36 (d, *J* = 21.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.1, 179.0, 172.9, 136.4, 133.3, 128.6, 128.0, 95.0 (d, *J* = 168.5 Hz), 60.2 (d, *J* = 6.8 Hz), 38.0 (d, *J* = 23.6 Hz), 34.4 (d, *J* = 22.8 Hz), 33.3, 28.4 (d, *J* = 5.3 Hz), 28.2, 24.0 (d, *J* = 24.3 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ -147.9 (m, 1F); IR (neat): ν (cm^{-1}) 3061, 2981, 2928, 1733, 1709, 1689, 1597, 1449, 1417, 1359, 1218, 1165, 750, 691; ESI-MS: (*m/z*) 347.2 (M^++Na); HRMS calcd for $C_{17}H_{21}FNaO_5$ (M+Na): 347.1265, found 347.1274.

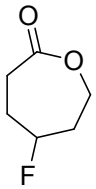


4-(1-(Ethoxycarbonyl)cyclopentyl)-4-fluoropentanoic acid (2p). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): 4.15 (q, *J* = 7.2 Hz, 2H), 2.42-2.57 (m, 2H), 2.17-2.34 (m,

3H), 1.77-2.04 (m, 3H), 1.50-1.73 (m, 4H), 1.38 (d, J = 22.4 Hz, 3H), 1.26 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.7, 174.9 (d, J = 10.6 Hz), 97.0 (d, J = 179.9 Hz), 63.4 (d, J = 22.8 Hz), 61.0, 31.8 (d, J = 22.8 Hz), 31.4 (d, J = 3.0 Hz), 30.7 (d, J = 3.8 Hz), 28.6 (d, J = 5.4 Hz), 24.8, 24.6, 21.1 (d, J = 25.1 Hz), 14.0; ^{19}F NMR (282 MHz, $CDCl_3$): δ -153.8 (m, 1F); IR (neat): ν (cm^{-1}) 2960, 2876, 1716, 1448, 1418, 1386, 1242, 1180, 1026, 934, 867; ESI-MS: (*m/z*) 283.1 (M^++Na); HRMS calcd for $C_{13}H_{21}FNaO_4$ (M+Na): 283.1316, found 283.1315.

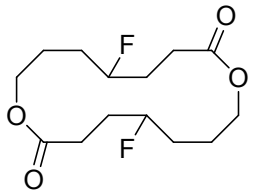


3-(2-(Fluoromethyl)-4,4-bis(methoxycarbonyl)cyclopentyl)propanoic acid (4). This compound was isolated as the mixture of two stereoisomers in 83:17 ratio determined by ^{19}F NMR. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.29-4.54 (m, 2H), 3.68-3.78 (m, 6H), 2.30-2.62 (m, 5H), 2.07-2.22 (m, 2H), 1.94-2.03 (m, 1H), 1.80-1.91 (m, 1H), 1.51-1.69 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.7/178.6, 172.8/172.6, 172.6/172.5, 84.7 (d, J = 168.5 Hz)/83.6 (d, J = 167.8 Hz), 58.7/58.6, 52.9, 45.4 (d, J = 18.4 Hz)/41.4 (d, J = 17.7 Hz), 40.4 (d, J = 3.1 Hz), 40.0/39.1, 36.4 (d, J = 6.2 Hz)/35.6 (d, J = 7.7 Hz), 32.8/32.5, 28.9/24.7; ^{19}F NMR (282 MHz, $CDCl_3$): δ -220.6/-222.2 (2m, 1F); IR (neat): ν (cm^{-1}) 2957, 1733, 1436, 1263, 1201, 1170, 999, 857; ESI-MS: (*m/z*) 291.1 (M^++H); HRMS calcd for $C_{13}H_{20}FO_6$ (M+H): 291.1238, found 291.1237.



5-Fluorooxepan-2-one (5). To the solution of **2b** (30.4 mg, 0.1 mmol) in anhydrous DMF (4 mL) was added Cs_2CO_3 (39.1 mg, 0.12 mmol) at room temperature. The reaction mixture was stirring at 50 °C for 4 h. Water (5 mL) was added and the

solution was extracted with Et_2O (3 × 10 mL). The combined organic phases were washed with water (2 × 20 mL) and then dried over anhydrous Na_2SO_4. After the removal of solvent under reduced pressure, the crude product was purified by column chromatography on silica gel with hexane/ethyl acetate (4:1, v:v) as the eluent to give the pure product **5** as a colorless oil. Yield: 9.4 mg (71%). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): 4.89-5.07 (m, 1H), 4.53 (dd, *J* = 13.2, 10.8 Hz, 1H), 4.13 (ddd, *J* = 13.2, 5.6, 2.0 Hz, 1H), 2.97-3.09 (m, 1H), 4.13 (ddd, *J* = 14.4, 7.6, 1.6 Hz, 1H), 1.83-2.31 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.0, 88.1 (d, *J* = 169.2 Hz), 62.2 (d, *J* = 3.7 Hz), 34.5 (d, *J* = 21.2 Hz), 28.2 (d, *J* = 22.6 Hz), 27.2 (d, *J* = 4.4 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ -182.6 (m, 1F); IR (neat): ν (cm^{-1}) 2951, 1741, 1441, 1294, 1151, 1065, 1024, 905; EIMS: *m/z* (rel intensity) 132 (M^+, 20), 102 (14), 74 (40), 60 (100), 55 (51), 42 (30); HRMS calcd for $C_6H_9FO_2$ (M): 132.0587, found 132.0589.

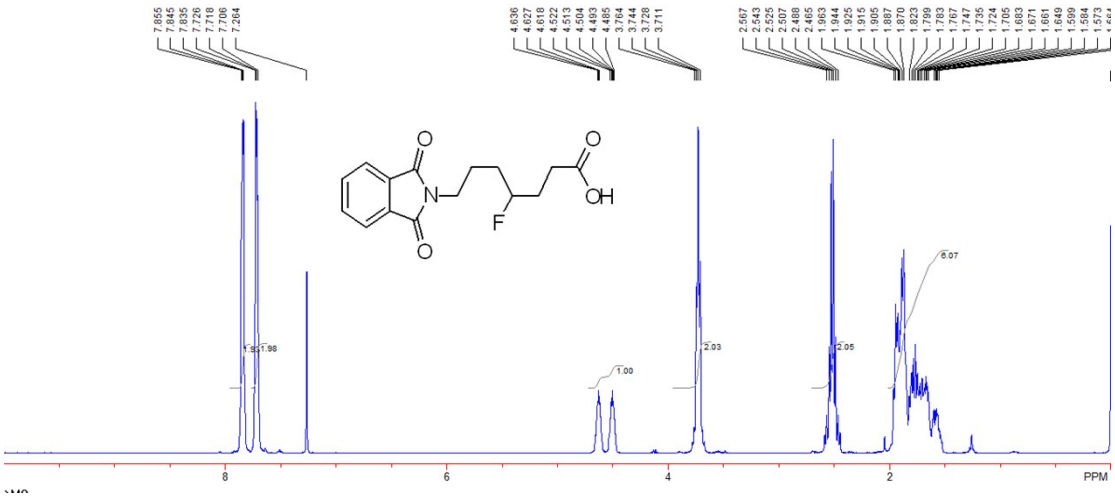


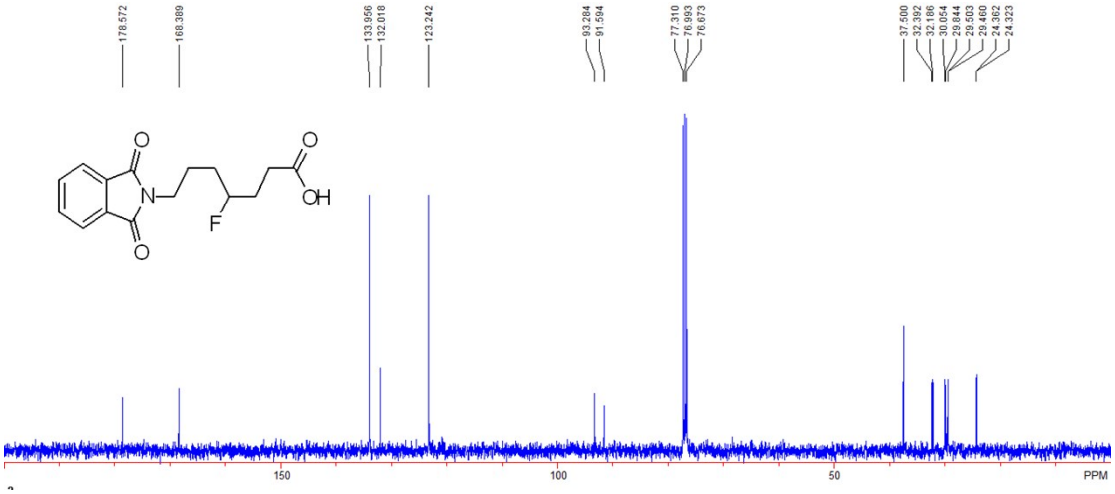
5,13-Difluoro-1,9-dioxacyclohexadecane-2,10-dione (6). This compound was obtained as the 1:1 mixture of two stereoisomers. The two isomers were separated by column chromatography on silica gel. **One isomer**: Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.46-4.69 (m, 2H), 4.23-4.32 (m, 2H), 4.03-4.12 (m, 2H), 4.27 (t, *J* = 6.4 Hz, 4H), 1.51-2.13 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.8, 91.8 (d, *J* = 167.7 Hz), 63.6, 30.7 (d, *J* = 21.2 Hz), 30.3 (d, *J* = 21.1 Hz), 29.5 (d, *J* = 5.9 Hz), 24.2 (d, *J* = 3.7 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ -184.3 (m, 2F); IR (neat): ν (cm^{-1}) 2959, 2860, 1735, 1437, 1389, 1368, 1260, 1166, 1085, 1021, 983, 928, 811; EIMS: *m/z* (rel intensity) 292 (M^+, 0.1), 147 (17), 127 (61), 108 (100), 81 (64), 67 (23), 55 (45), 41 (22); HRMS calcd for $C_{14}H_{22}F_2O_4$ (M): 292.1486, found 292.1490. **The other isomer**: Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.43-4.66 (m, 2H), 4.21-4.30 (m, 2H), 4.05-4.14 (m, 2H), 2.39-2.54 (m, 4H), 1.92-2.08 (m, 4H), 1.52-1.90 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.8, 92.3 (d, *J* = 168.5 Hz), 63.7, 31.0 (d, *J* =

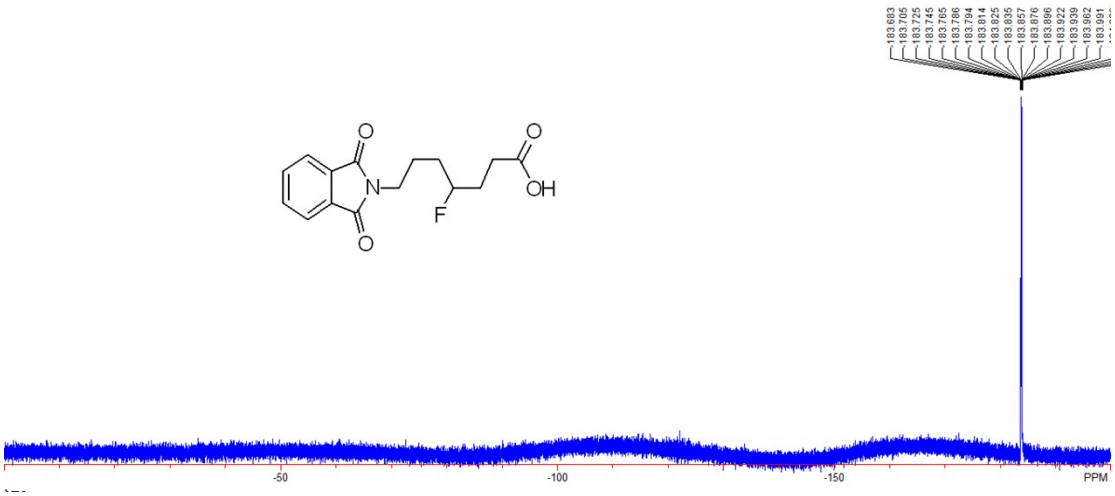
21.1 Hz), 30.5 (d, J = 21.9 Hz), 29.8 (d, J = 5.8 Hz), 24.2 (d, J = 3.0 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ -183.7 (m, 2F); IR (neat): ν (cm^{-1}) 2963, 2941, 2925, 1726, 1453, 1329, 1294, 1259, 1172, 1160, 1053, 987, 922; EIMS: *m/z* (rel intensity) 147 (17), 127 (66), 108 (100), 87 (21), 81 (63), 73 (18), 67 (23), 55 (43), 41 (21); HRMS calcd for $C_{14}H_{22}F_2O_4$ (M): 292.1486, found 292.1479.

3. ^{1}H, ^{13}C and ^{19}F NMR Spectra of Products

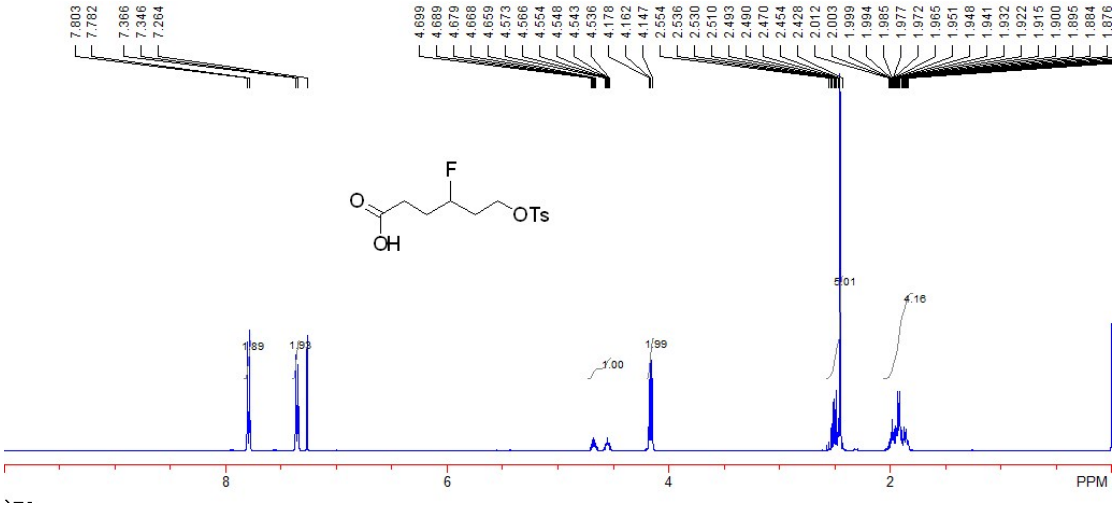
Compound **2a**







Compound **2b**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1.884
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6
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2
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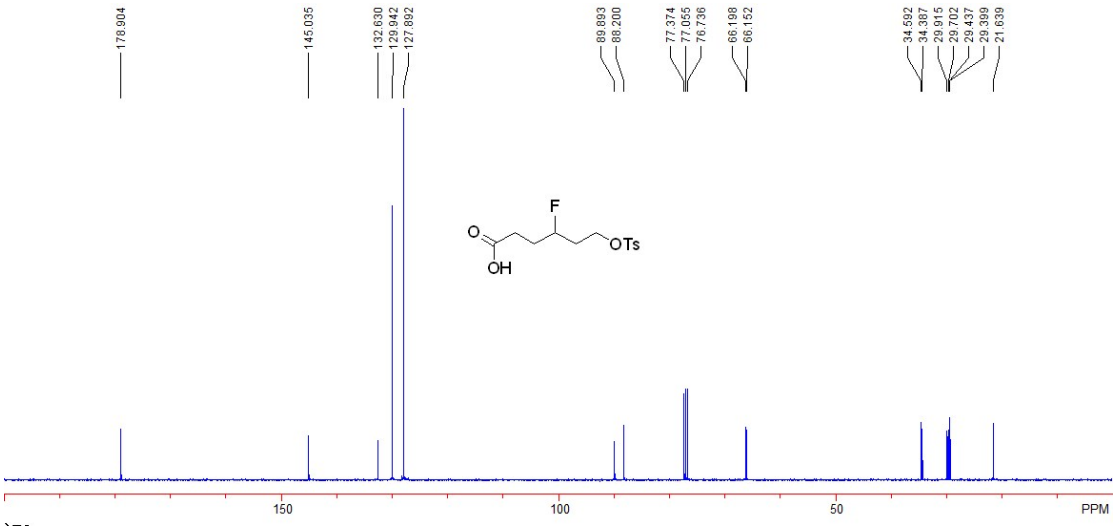
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66.152
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29.399
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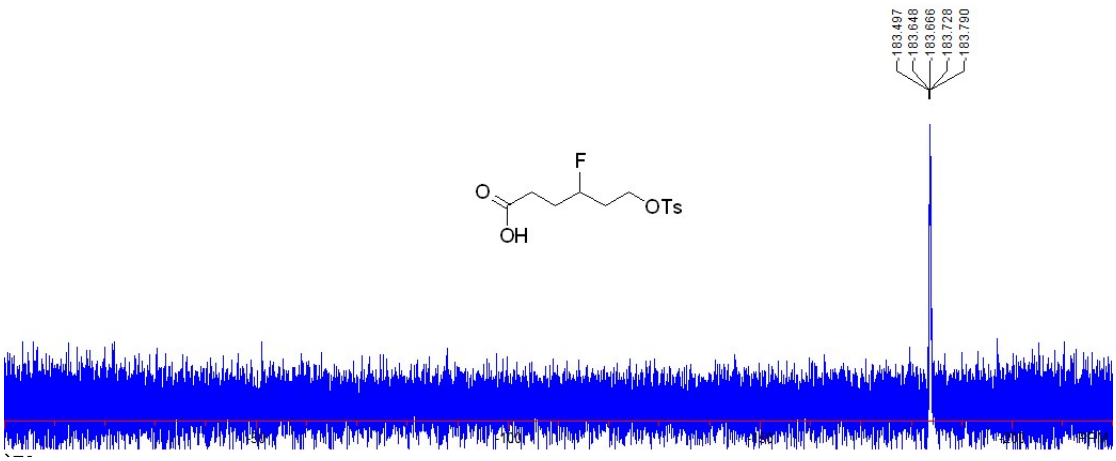
F
O
OTs
OH
150
100
50
PPM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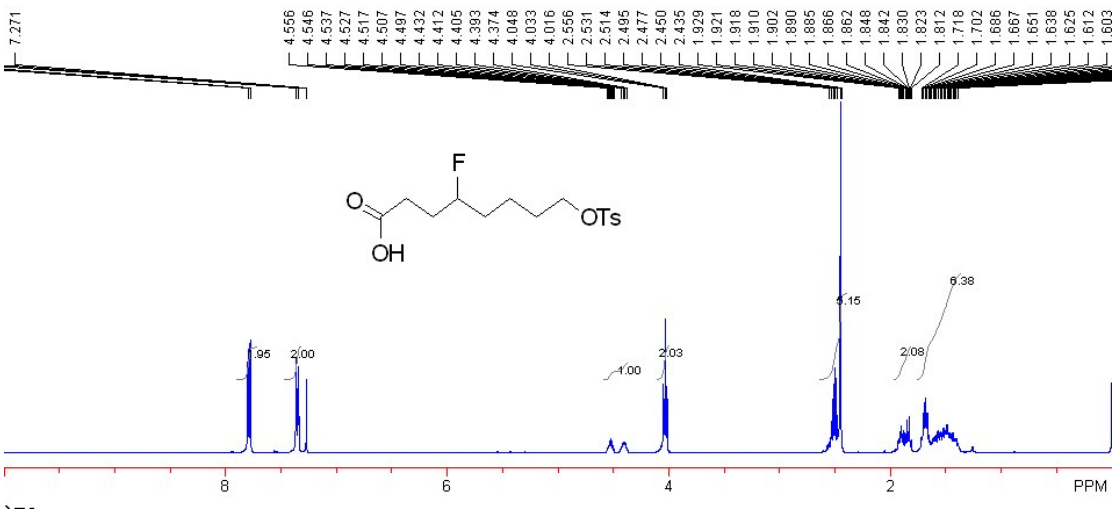
O
OTs
OH

Compound **2c**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4.033
4.016
2.556
2.531
2.514
2.495
2.477
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2.435
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1.918
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1.902
1.890
1.885
1.866
1.862
1.848
1.842
1.830
1.823
1.812
1.718
1.702
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1.651
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1.625
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1.603
F
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2
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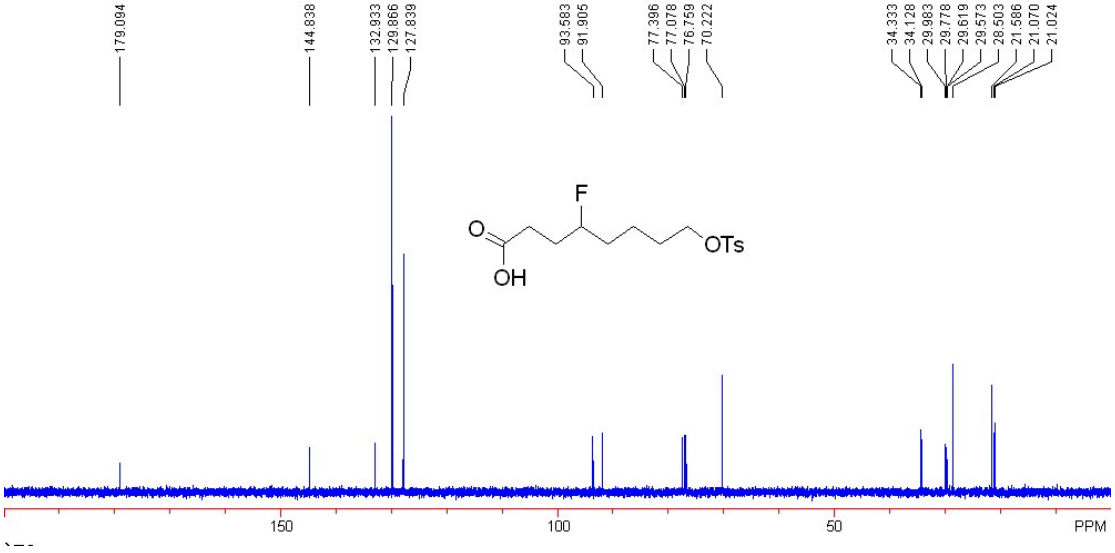
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OH
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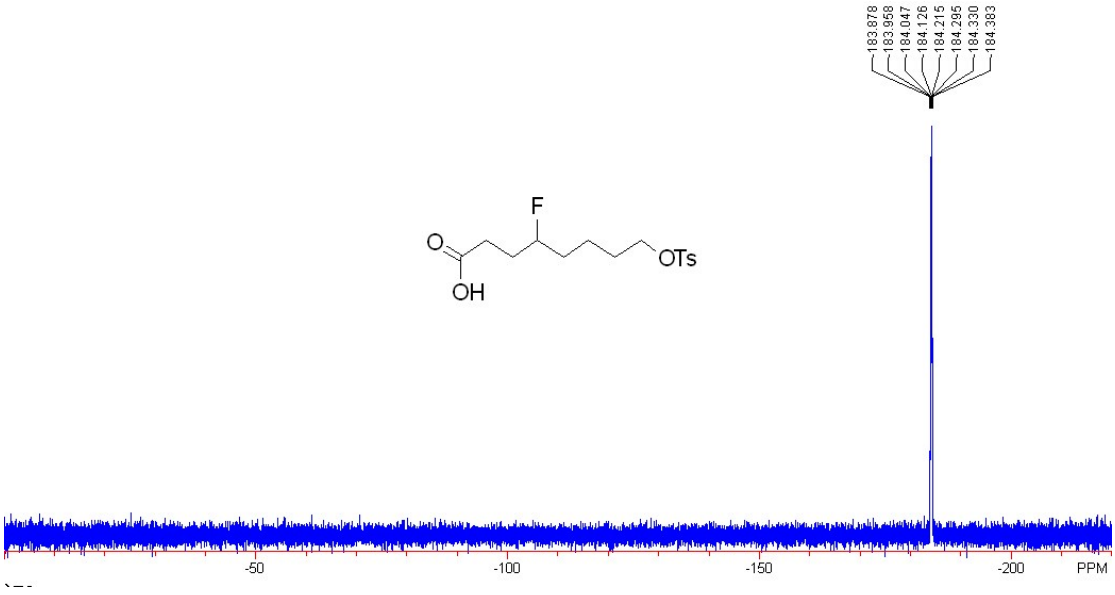
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OTs
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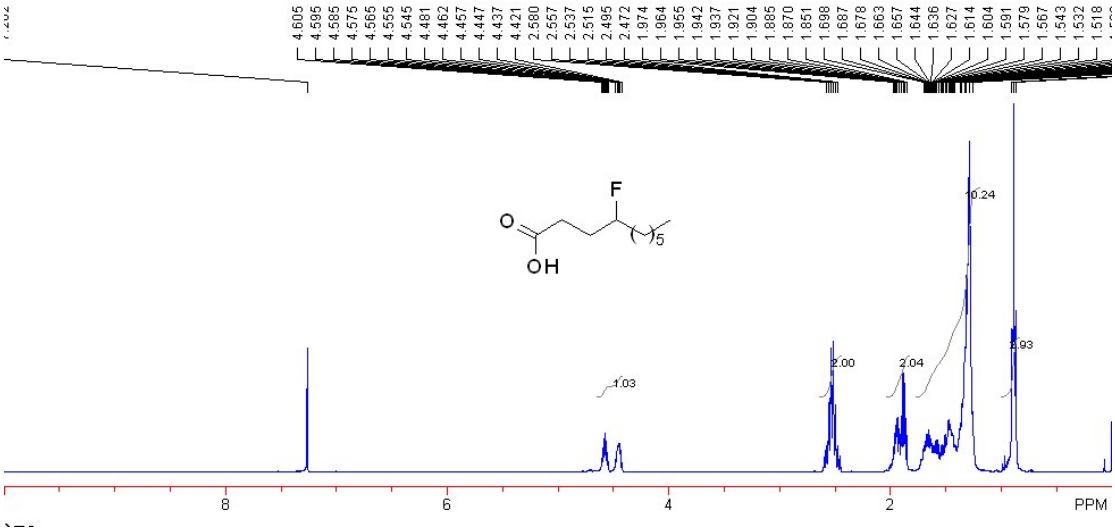
-150
-200
PPM

Compound **2d**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2.580
2.557
2.537
2.515
2.495
2.472
1.974
1.964
1.955
1.942
1.937
1.921
1.904
1.885
1.870
1.851
1.698
1.687
1.678
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1.657
1.644
1.636
1.627
1.614
1.604
1.591
1.579
1.567
1.543
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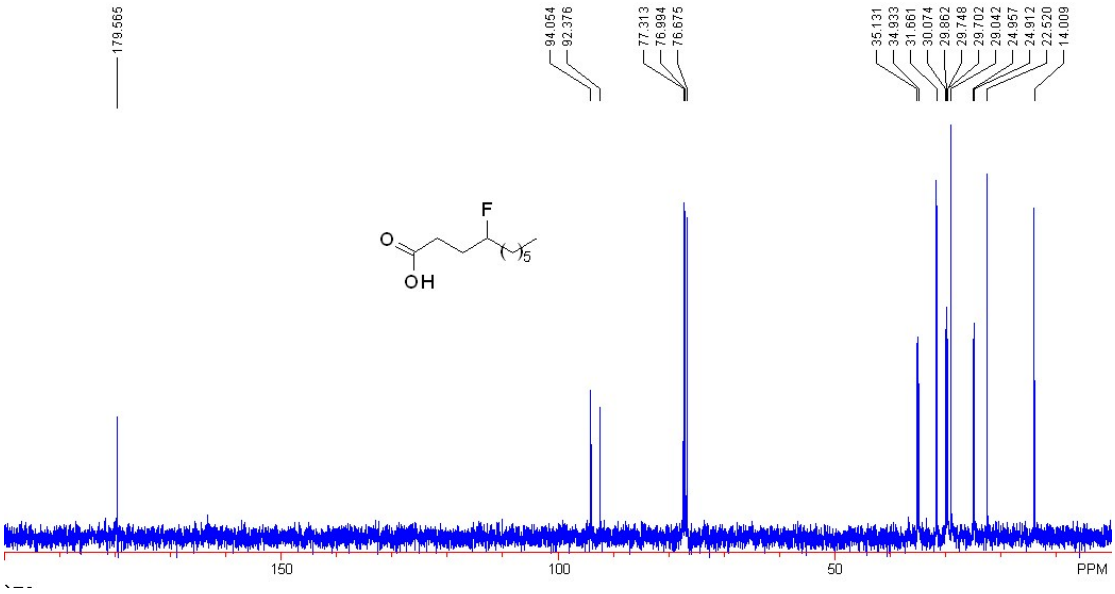
4
2
PPM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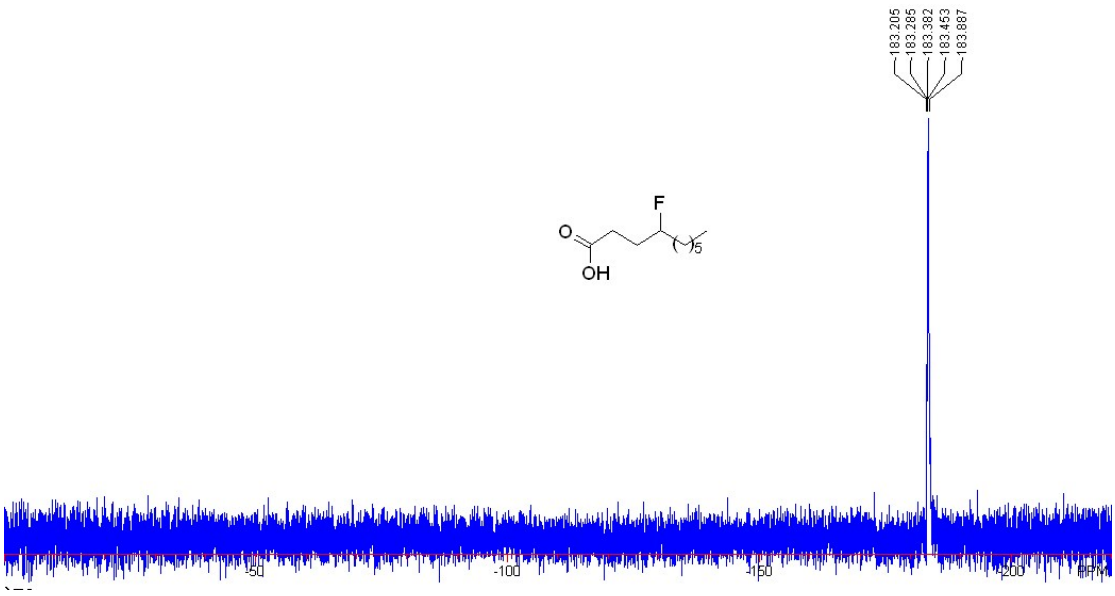
29.042
24.957
24.912
22.520
14.009
F
O
OH
5
150
100
50
PPM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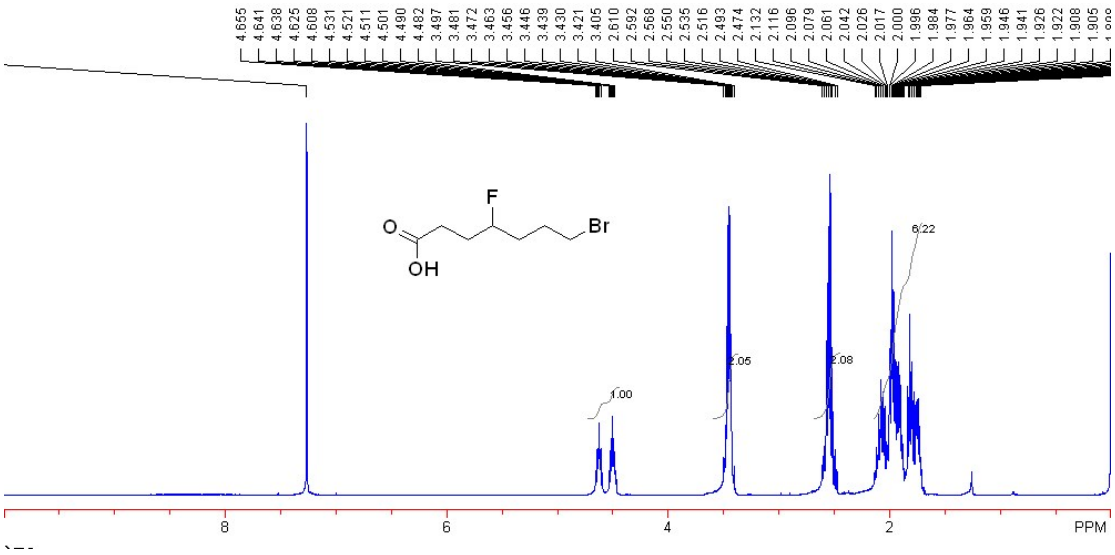
PPM

Compound **2e**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4.511
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4.490
4.482
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3.472
3.463
3.456
3.446
3.439
3.430
3.421
3.405
2.610
2.592
2.568
2.550
2.535
2.516
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1.984
1.977
1.964
1.959
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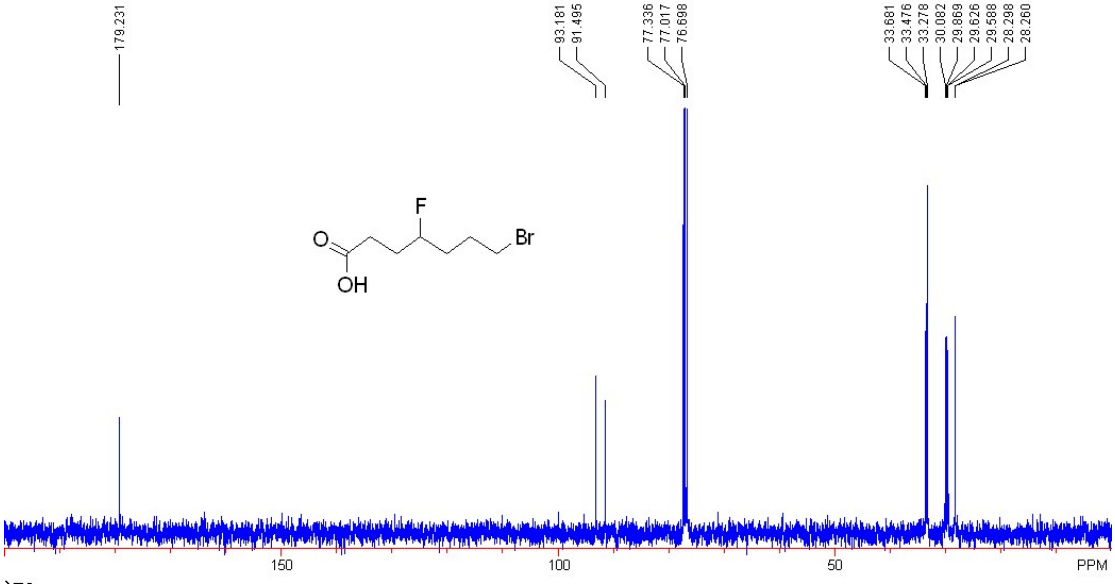
2
PPM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150
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50
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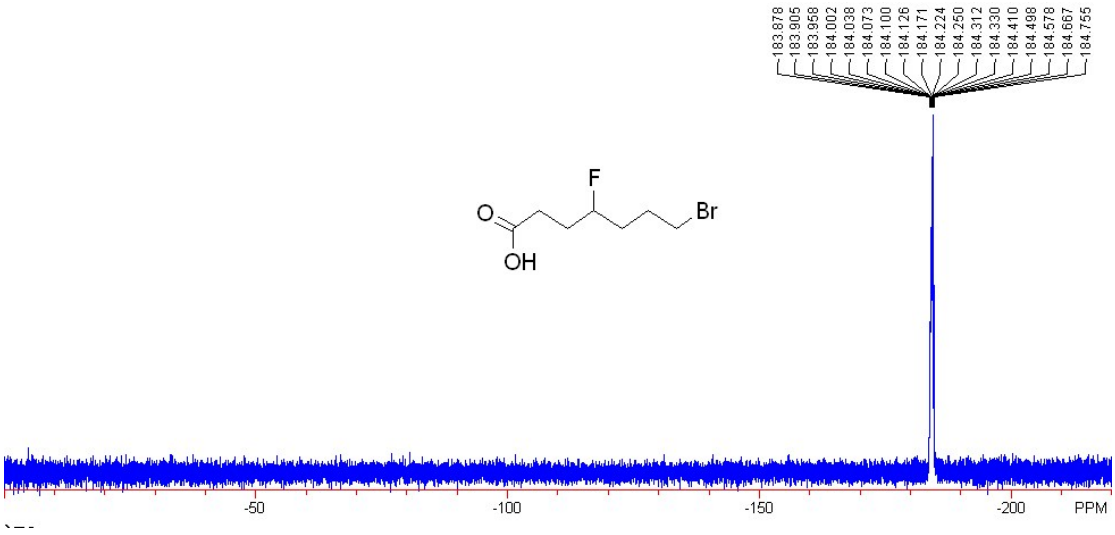
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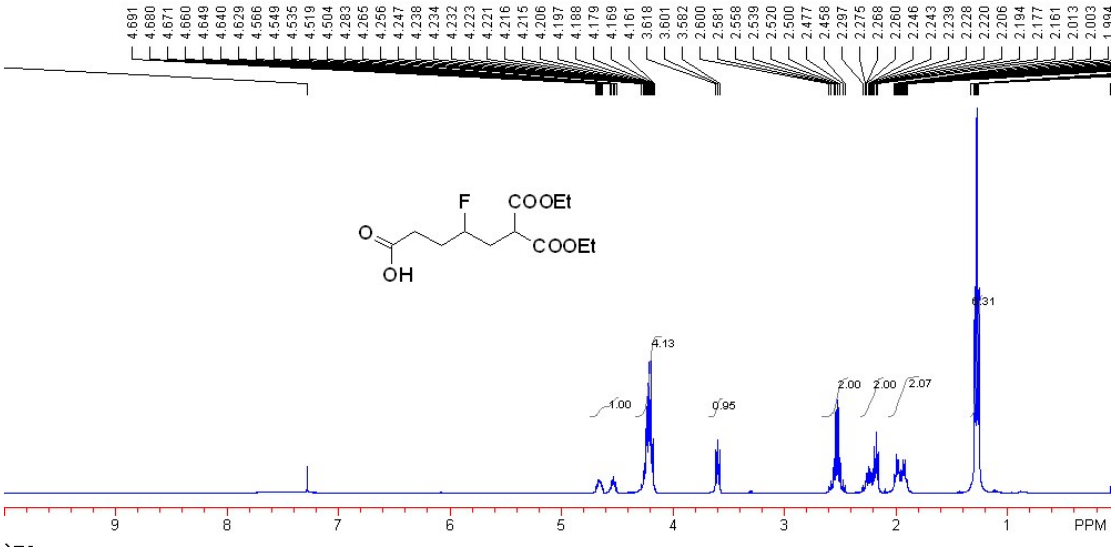
F
O
Br
OH
-50
-100
-150
-200
PPM

Compound **2f**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4.247
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4.234
4.232
4.223
4.221
4.216
4.215
4.206
4.197
4.188
4.179
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4.161
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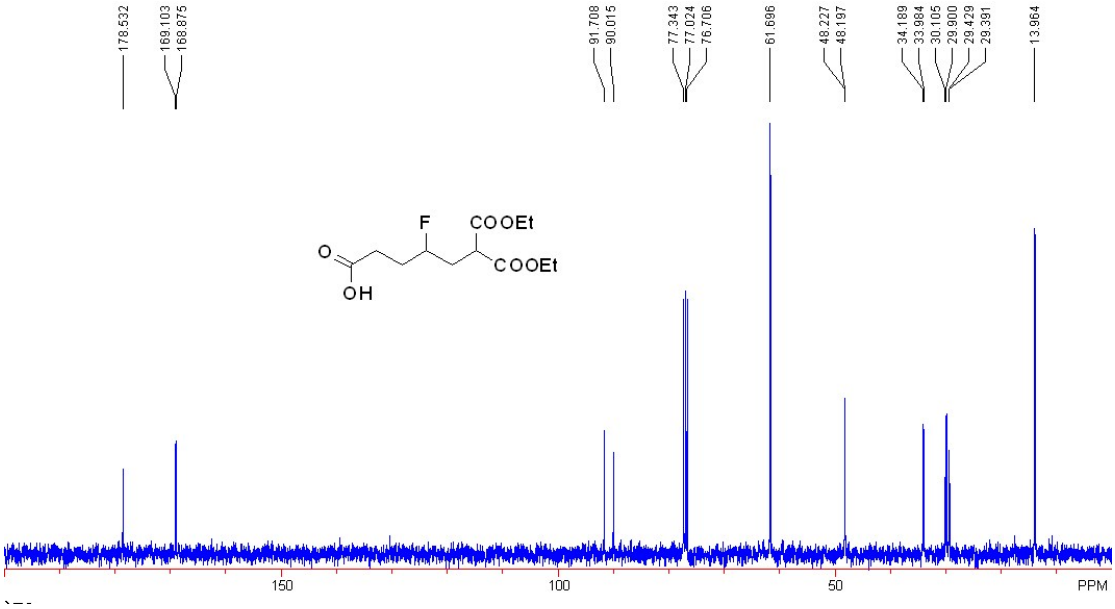
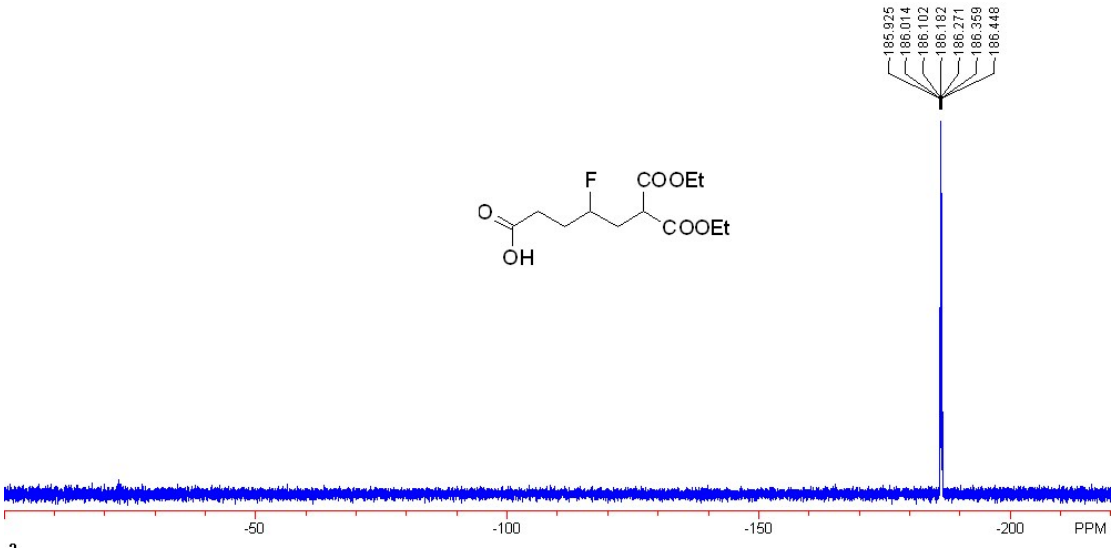
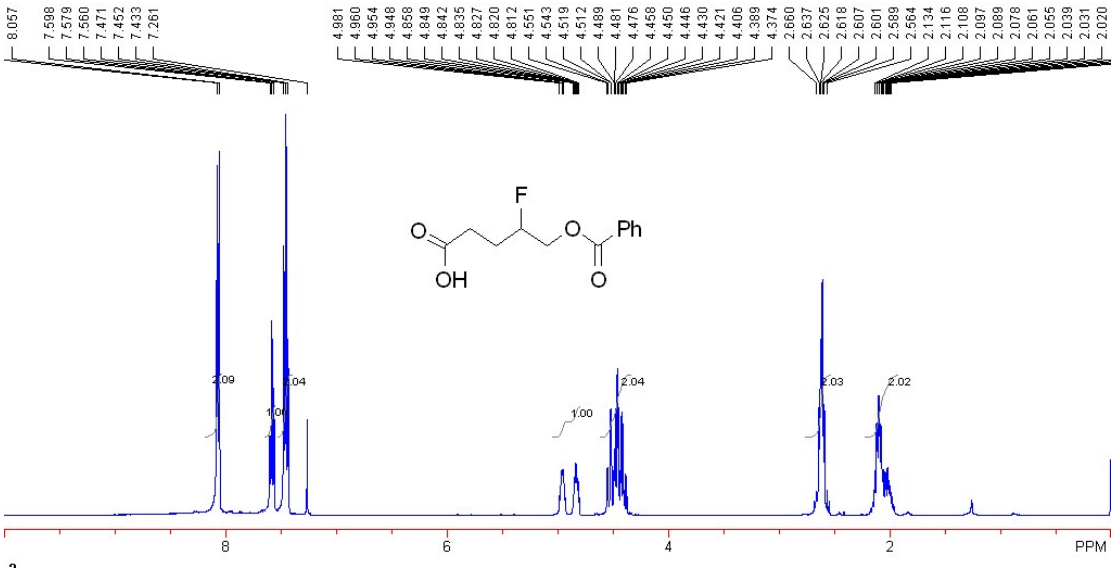
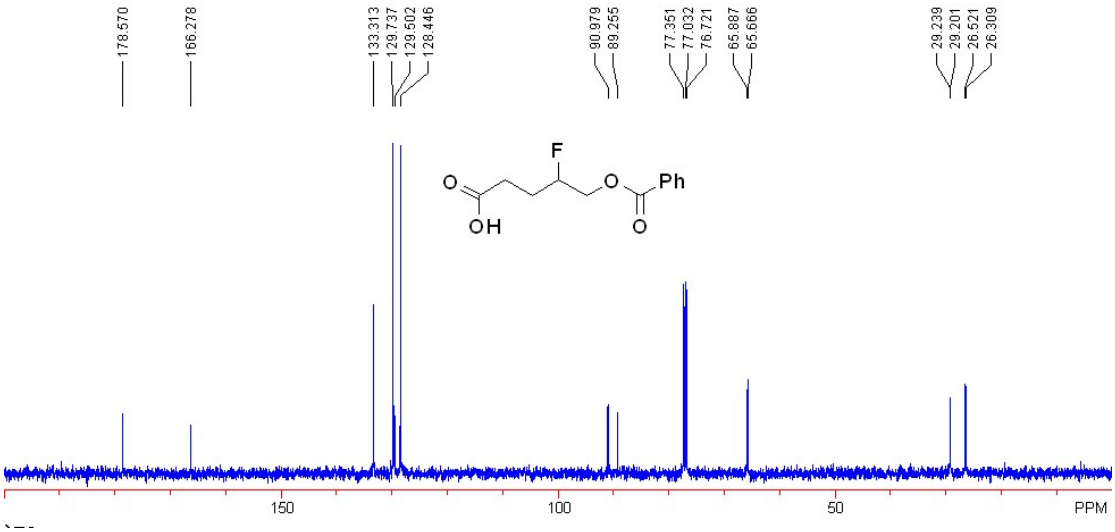
2.00
2.07
9 8 7 6 5 4 3 2 1 PPM

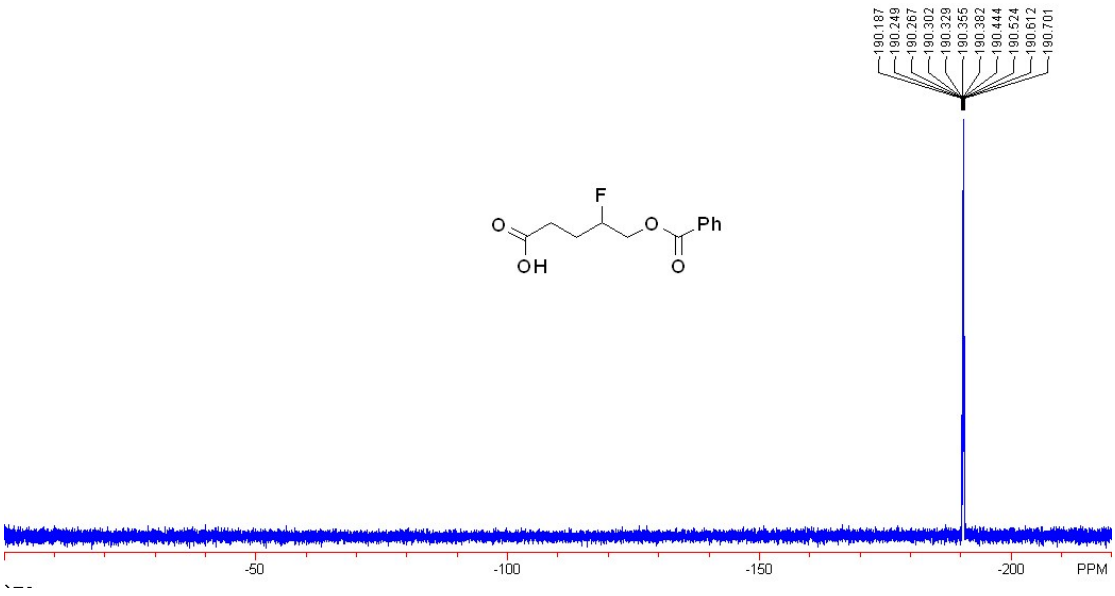

178.532
169.103
168.875
91.708
90.015
77.343
77.024
76.706
61.696
48.227
48.197
34.189
33.984
30.105
29.900
29.429
29.391
13.964
F
COOEt
O
COOEt
OH
150 100 50 PPM


185.925
186.014
186.102
186.182
186.271
186.359
186.448
F
COOEt
O
COOEt
OH
-50 -100 -150 -200 PPM

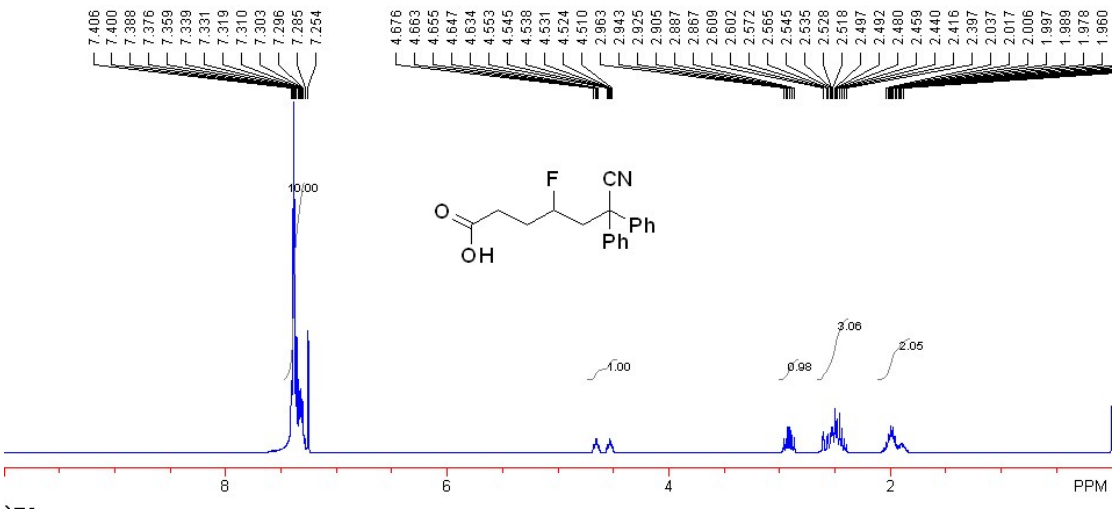
Compound **2g**

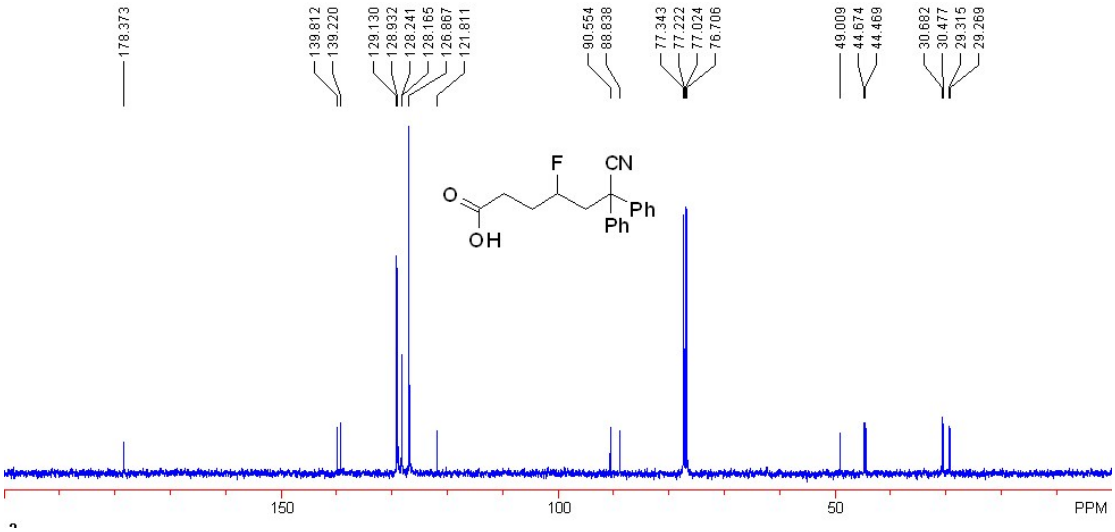

8.057
7.598
7.579
7.560
7.471
7.452
7.433
7.261
4.981
4.960
4.954
4.948
4.858
4.849
4.842
4.835
4.827
4.820
4.812
4.551
4.543
4.519
4.512
4.489
4.481
4.476
4.458
4.450
4.446
4.430
4.421
4.406
4.389
4.374
2.660
2.637
2.625
2.618
2.607
2.601
2.589
2.564
2.134
2.116
2.108
2.097
2.089
2.078
2.061
2.055
2.039
2.031
2.020
F
O
O
Ph
OH
O
2.09
1.00
2.04
1.00
2.04
2.03
2.02
8
6
4
2
PPM

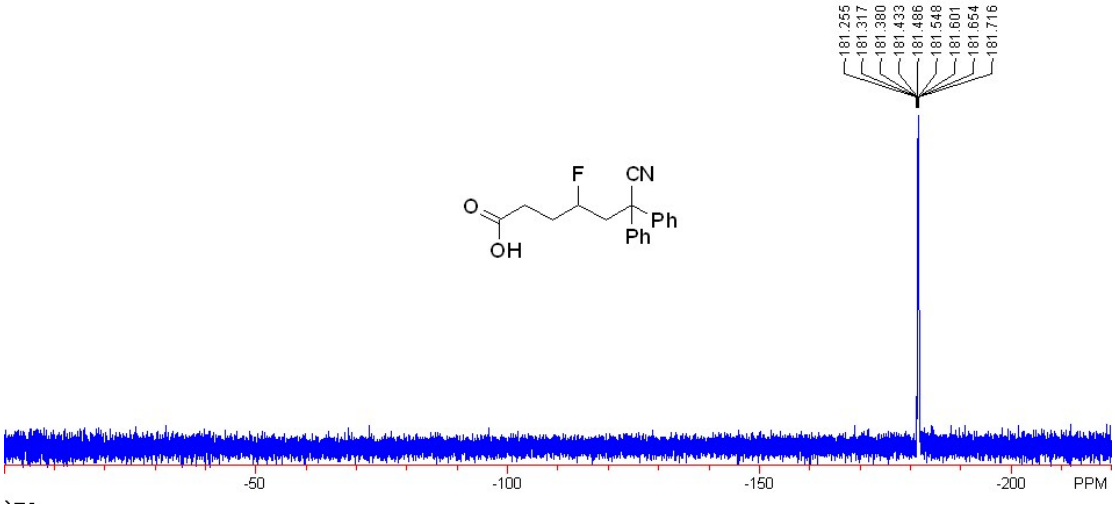

178.570
166.278
133.313
129.737
129.502
128.446
90.979
89.255
77.351
77.032
76.721
65.887
65.666
29.239
29.201
26.521
26.309
F
O
O
Ph
OH
O
150
100
50
PPM


190.187
190.249
190.267
190.302
190.329
190.355
190.382
190.444
190.524
190.612
190.701
F
O
O
Ph
OH
O
-50
-100
-150
-200
PPM

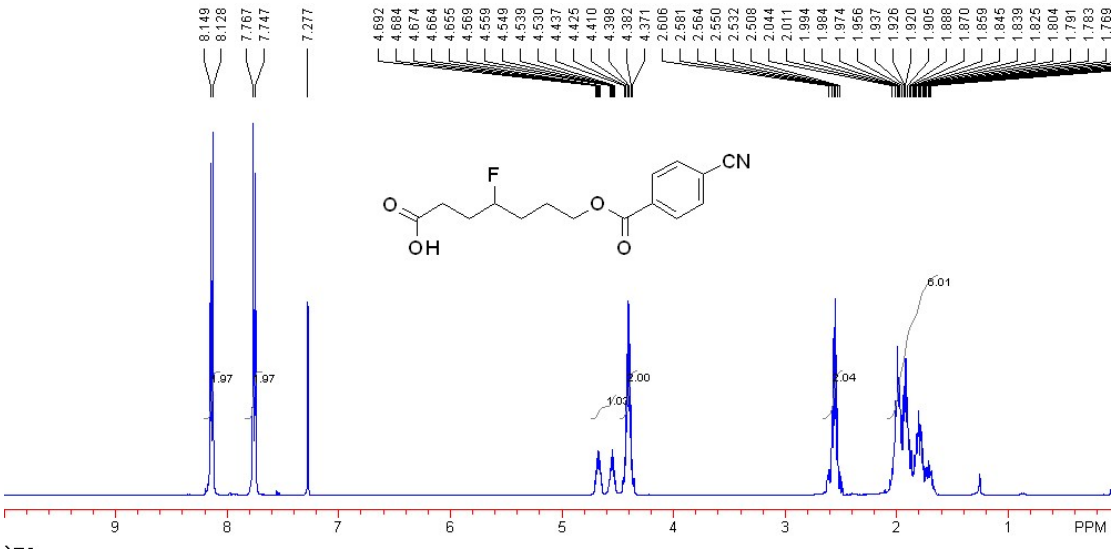
Compound **2h**

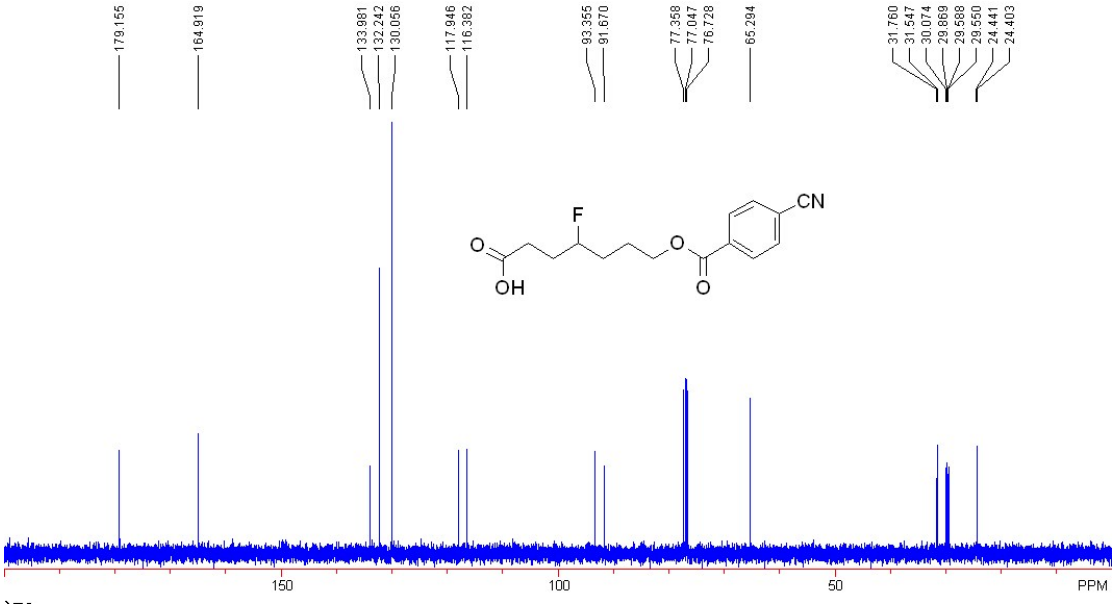

7.406
7.400
7.388
7.376
7.359
7.339
7.331
7.319
7.310
7.303
7.296
7.285
7.254
4.676
4.663
4.655
4.647
4.634
4.553
4.545
4.538
4.531
4.524
4.510
2.963
2.943
2.925
2.905
2.887
2.867
2.609
2.602
2.572
2.565
2.545
2.535
2.528
2.518
2.497
2.492
2.480
2.459
2.440
2.416
2.397
2.037
2.017
2.006
1.997
1.989
1.978
1.960
10.00
1.00
0.98
3.06
2.05
F
CN
O
OH
Ph
Ph
8
6
4
2
PPM

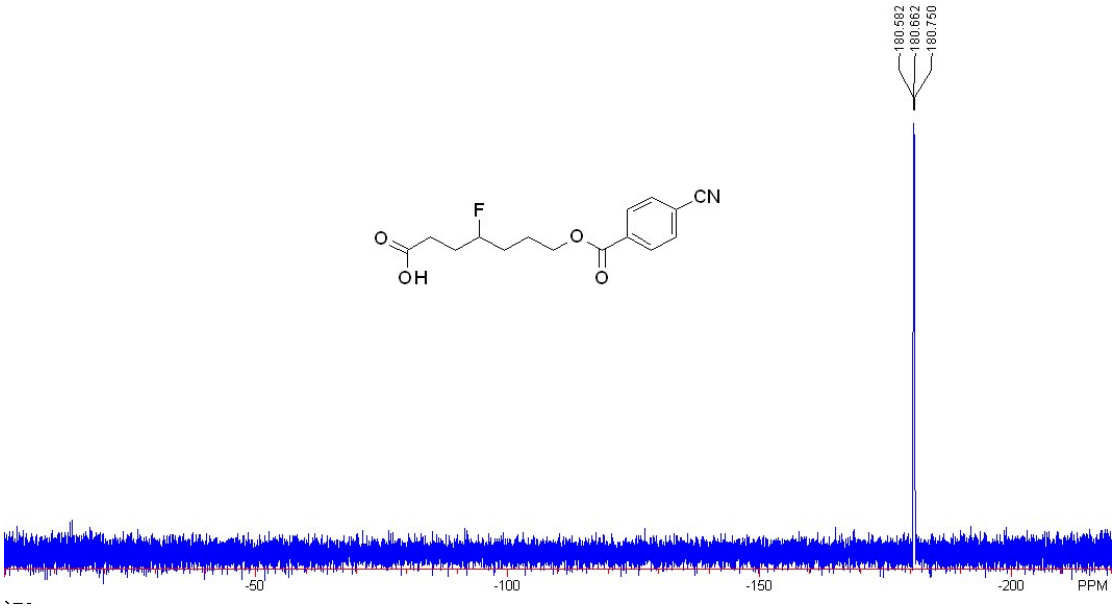

178.373
139.812
139.220
129.130
128.932
128.241
128.165
126.867
121.811
90.554
88.838
77.343
77.222
77.024
76.706
49.009
44.674
44.469
30.682
30.477
29.315
29.269
F
CN
O
OH
Ph
Ph
150
100
50
PPM


181.255
181.317
181.380
181.433
181.486
181.548
181.601
181.654
181.716
F
CN
O
OH
Ph
Ph
-50
-100
-150
-200
PPM

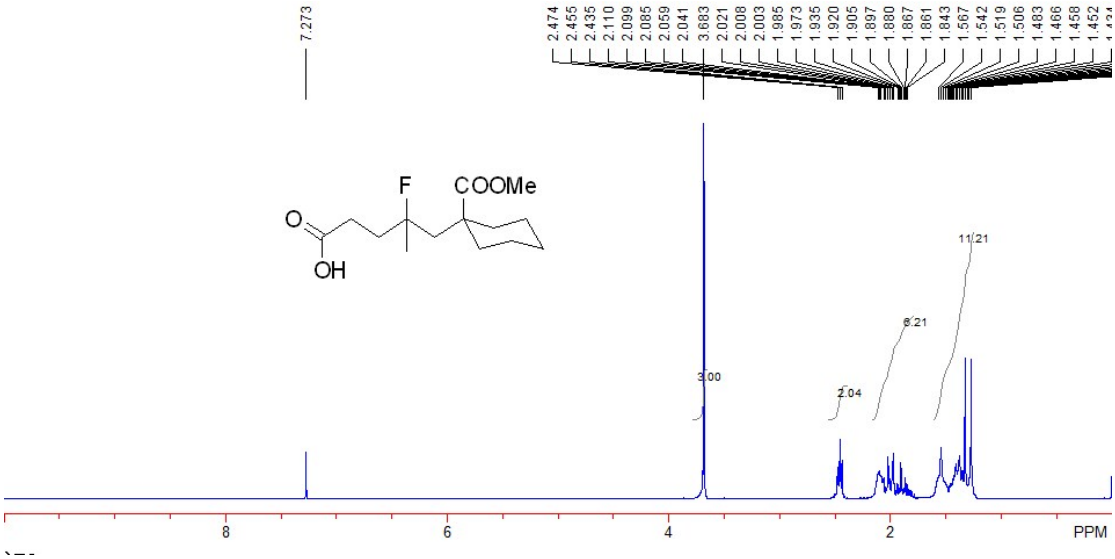
Compound **2i**

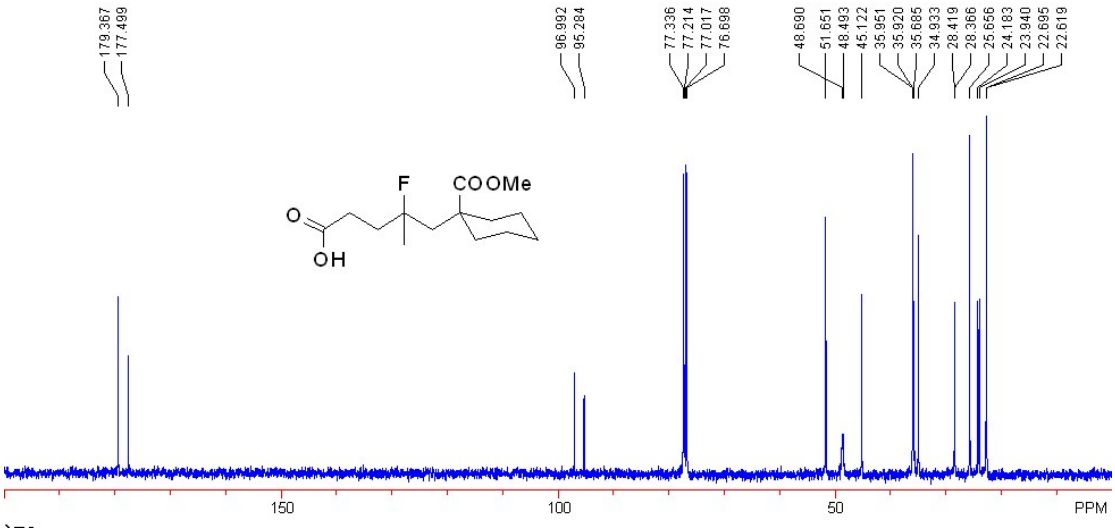

8.149
8.128
7.767
7.747
7.277
4.692
4.684
4.674
4.664
4.655
4.569
4.559
4.549
4.539
4.530
4.437
4.425
4.410
4.398
4.382
4.371
2.606
2.581
2.564
2.550
2.532
2.508
2.044
2.011
1.994
1.984
1.974
1.956
1.937
1.926
1.920
1.905
1.888
1.870
1.859
1.845
1.839
1.825
1.804
1.791
1.783
1.769
F
O
O
OH
O
CN
1.97
1.97
1.03
2.00
2.04
6.01
9
8
7
6
5
4
3
2
1
PPM

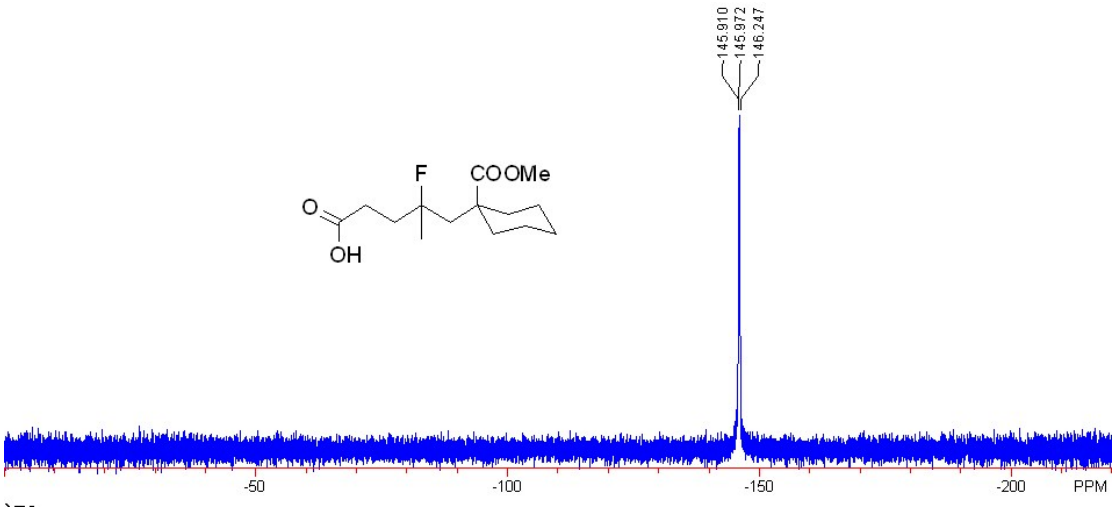

179.155
164.919
133.981
132.242
130.056
117.946
116.382
93.355
91.670
77.358
77.047
76.728
65.294
31.760
31.547
30.074
29.869
29.588
29.550
24.441
24.403
F
O
O
OH
O
CN
150
100
50
PPM


180.582
180.662
180.750
F
CN
O
OH
O
O
-50
-100
-150
-200
PPM

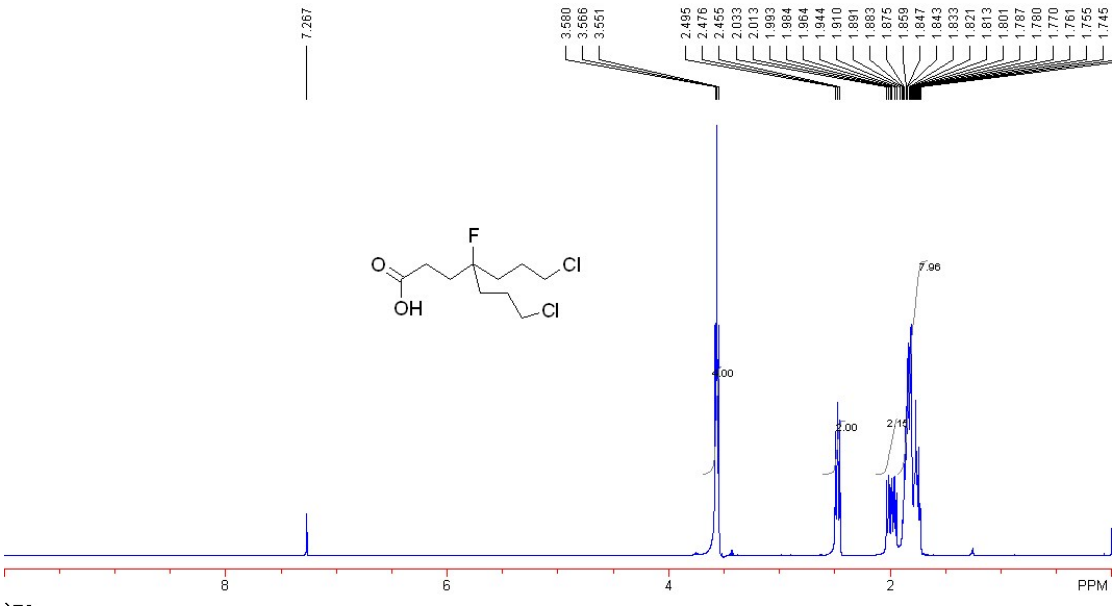
Compound **2j**

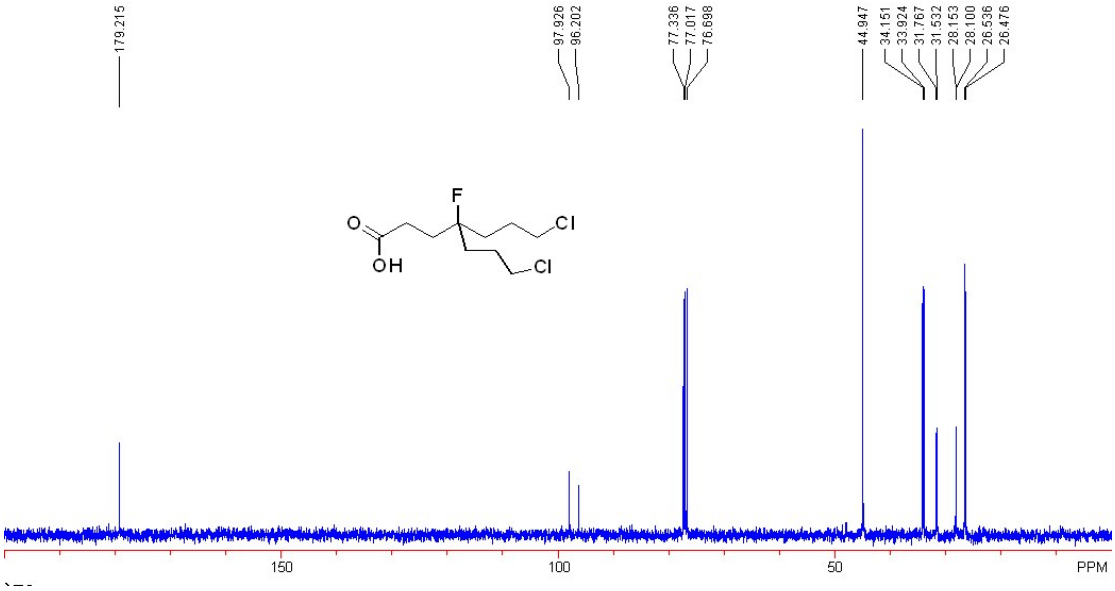

7.273
2.474
2.455
2.435
2.110
2.099
2.085
2.059
2.041
3.683
2.021
2.008
2.003
1.985
1.973
1.935
1.920
1.905
1.897
1.880
1.867
1.861
1.843
1.567
1.542
1.519
1.506
1.483
1.466
1.458
1.452
F
COOMe
O
OH
11.21
6.21
3.00
2.04
8
6
4
2
PPM

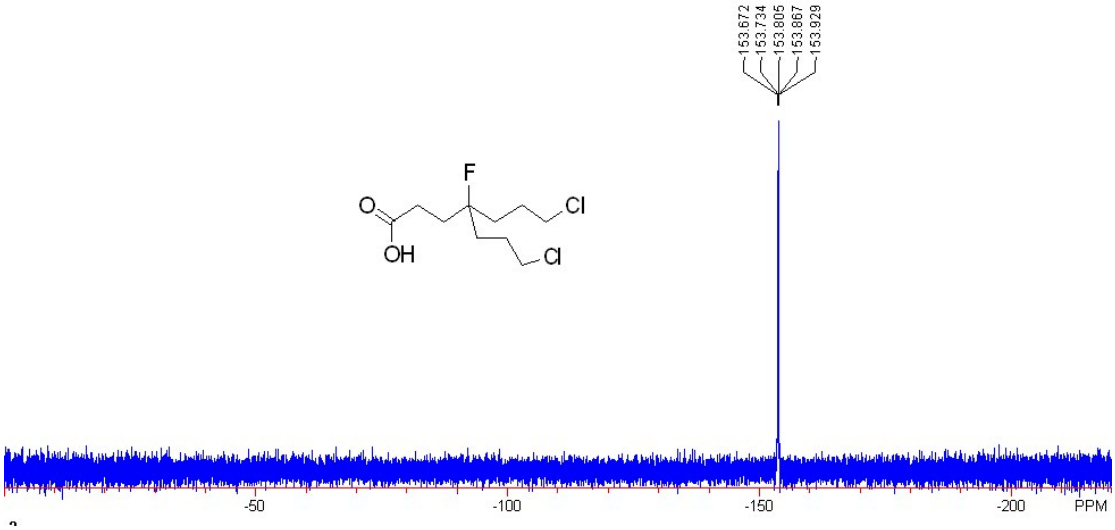

179.367
177.499
96.992
95.284
77.336
77.214
77.017
76.698
48.690
51.651
48.493
45.122
35.951
35.920
35.685
34.933
28.419
28.366
25.656
24.183
23.940
22.695
22.619
F
COOMe
O
OH
150
100
50
PPM


145.910
145.972
146.247
F
COOMe
O
OH
-50
-100
-150
-200
PPM

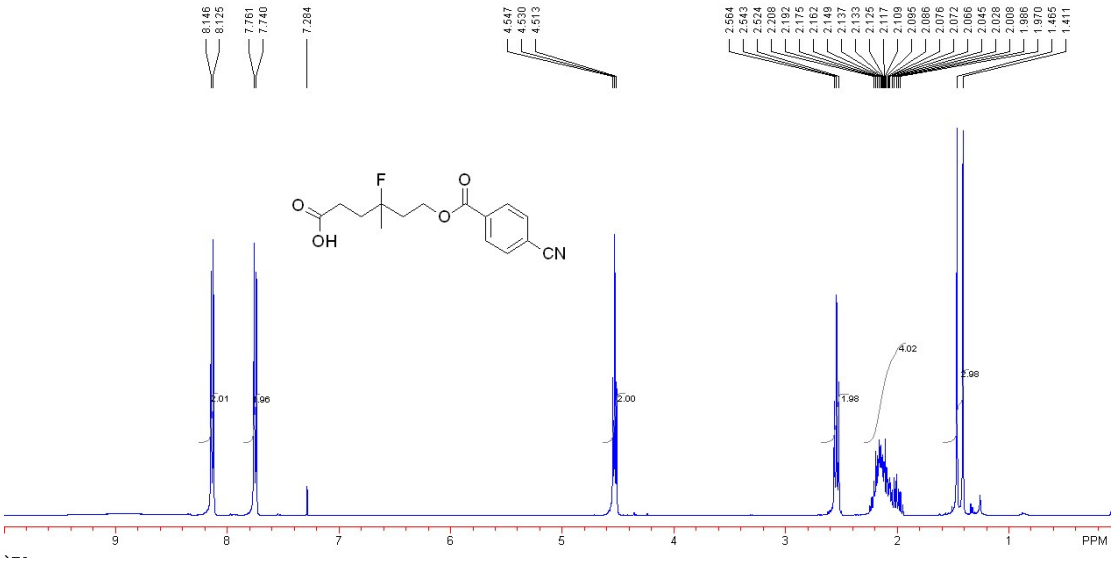
Compound **2k**

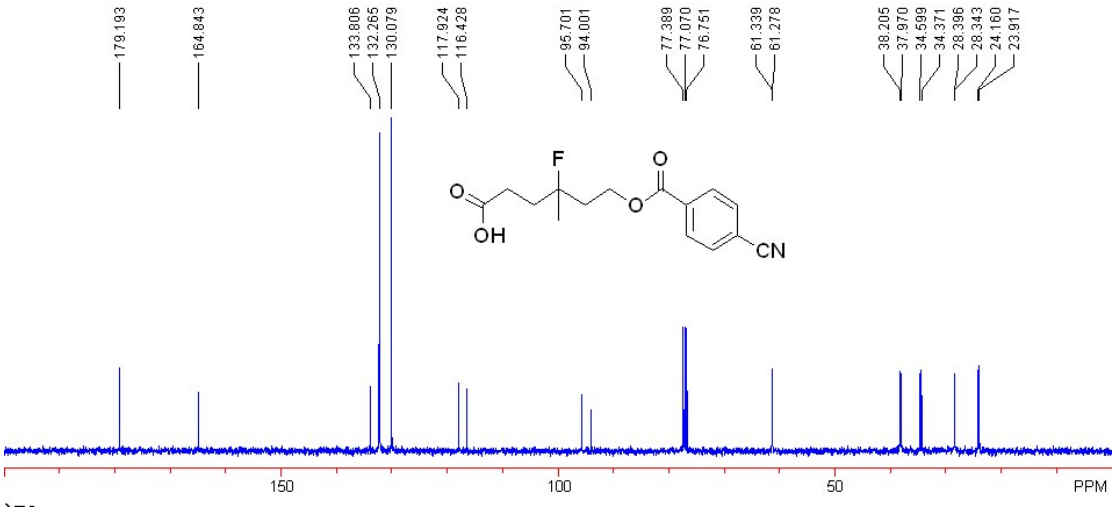

7.267
3.580
3.566
3.551
2.495
2.476
2.455
2.033
2.013
1.993
1.984
1.964
1.944
1.910
1.891
1.883
1.875
1.859
1.847
1.843
1.833
1.821
1.813
1.801
1.787
1.780
1.770
1.761
1.755
1.745
F
O
OH
Cl
Cl
4.00
2.00
2.10
7.96
8
6
4
2
PPM

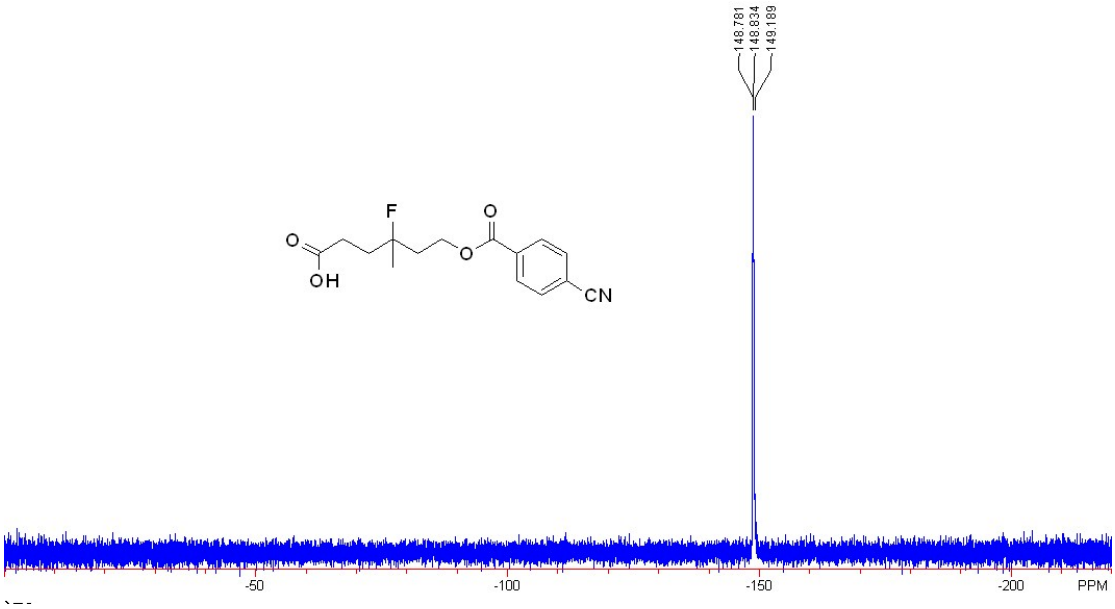

179.215
97.926
96.202
77.336
77.017
76.698
44.947
34.151
33.924
31.767
31.532
28.153
28.100
26.536
26.476
F
O
OH
Cl
Cl
150
100
50
PPM


153.672
153.734
153.805
153.867
153.929
F
O
OH
Cl
Cl
-50
-100
-150
-200
PPM

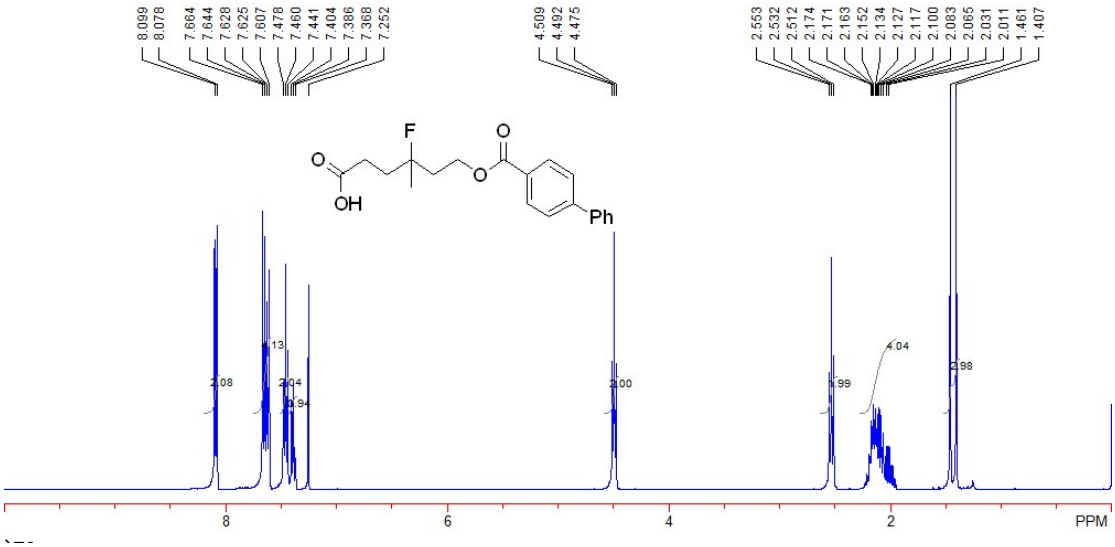
Compound **2l**

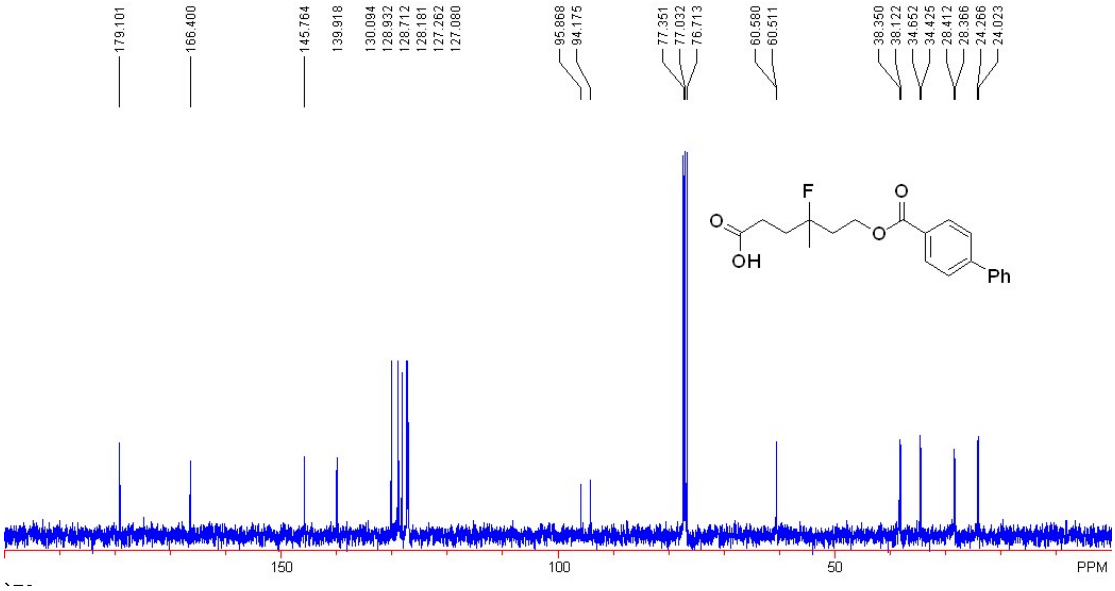

8.146
8.125
7.761
7.740
7.284
4.547
4.530
4.513
F
O
O
OH
CN
2.01
0.96
2.00
1.98
4.02
2.98
9
8
7
6
5
4
3
2
1
PPM

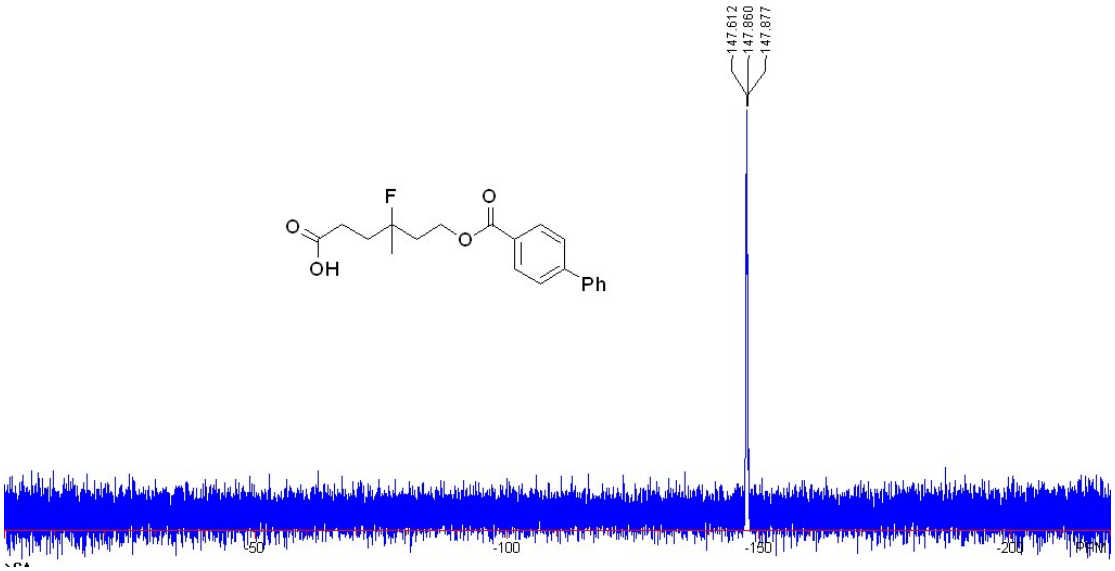

179.193
164.843
133.806
132.265
130.079
117.924
116.428
95.701
94.001
77.389
77.070
76.751
61.339
61.278
38.205
37.970
34.599
34.371
28.396
28.343
24.160
23.917
F
O
O
OH
O
CN
150
100
50
PPM


148.781
148.834
149.189
F
O
O
OH
O
CN
-50
-100
-150
-200
PPM

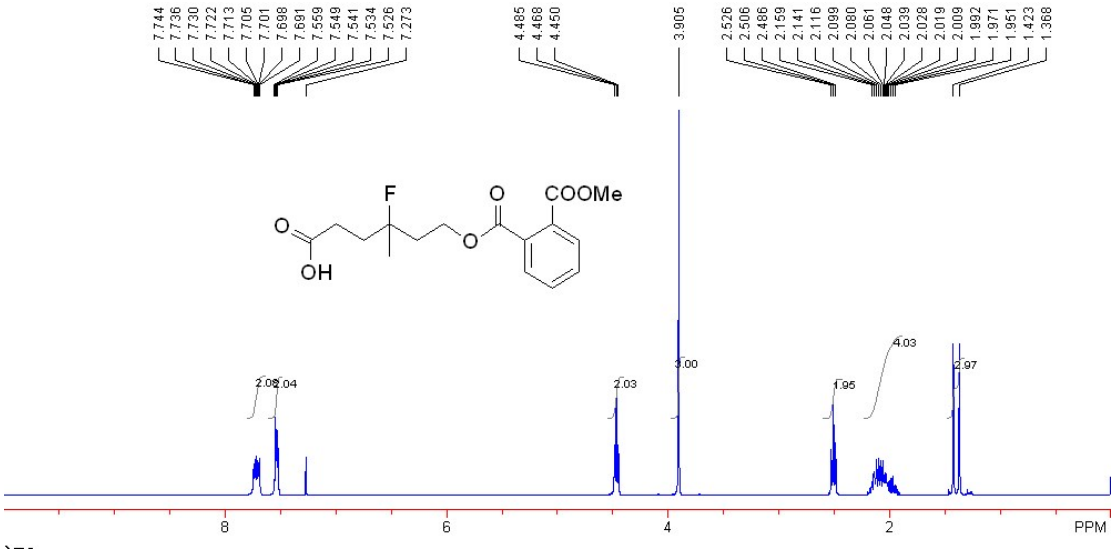
Compound **2m**

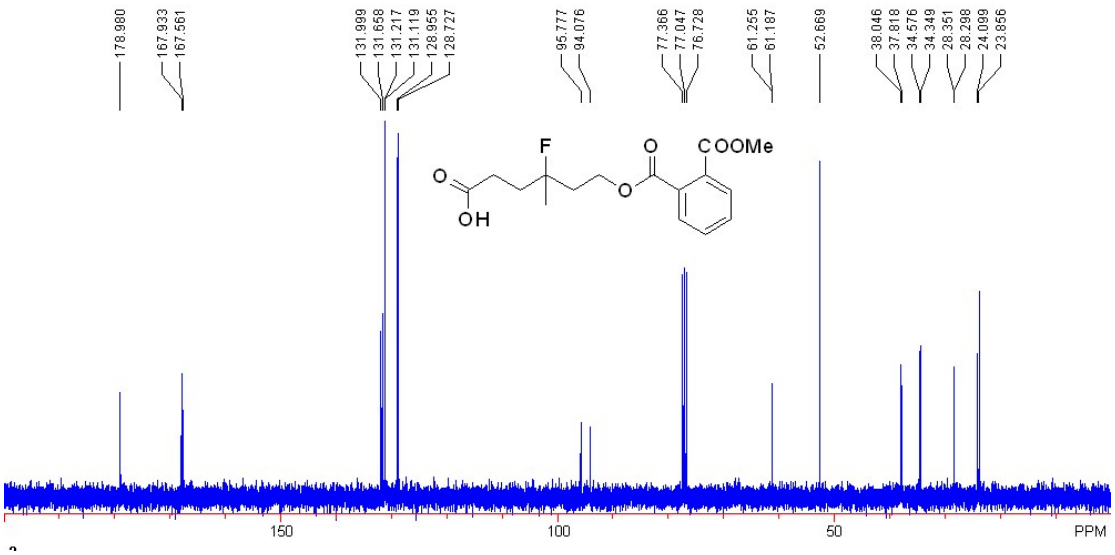

8.099
8.078
7.664
7.644
7.628
7.625
7.607
7.478
7.460
7.441
7.404
7.386
7.368
7.252
4.509
4.492
4.475
2.553
2.532
2.512
2.174
2.171
2.163
2.152
2.134
2.127
2.117
2.100
2.083
2.065
2.031
2.011
1.461
1.407
F
O
O
OH
O
Ph
2.08
3.13
2.04
0.94
2.00
1.99
4.04
2.98
8
6
4
2
PPM

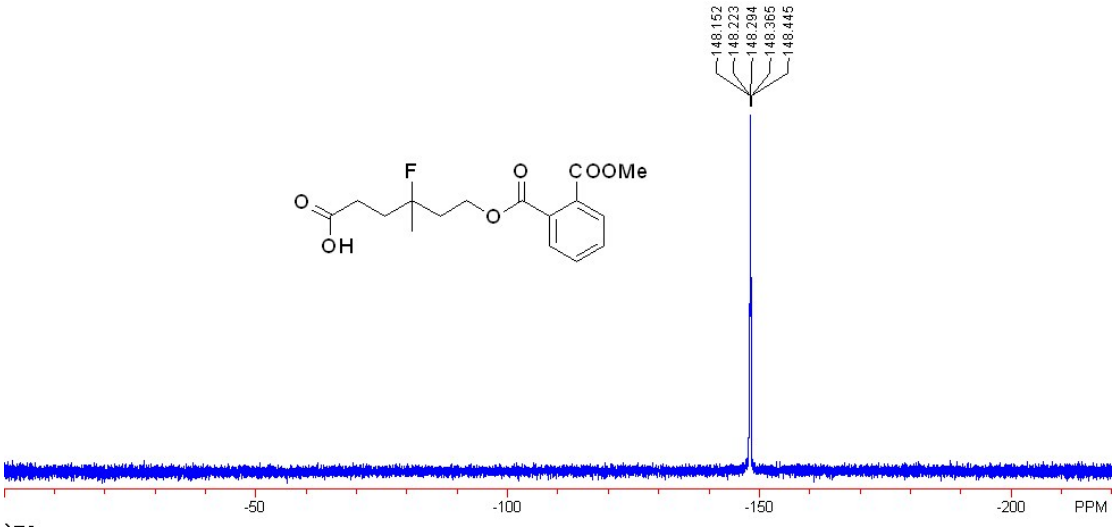

179.101
166.400
145.764
139.918
130.094
128.932
128.712
128.181
127.262
127.080
95.868
94.175
77.351
77.032
76.713
60.580
60.511
38.350
38.122
34.652
34.425
28.412
28.366
24.266
24.023
F
O
O
O
OH
Ph
150
100
50
PPM


147.612
147.880
147.877
F
O
O
O
OH
Ph
-50
-100
-150
-200
PPM

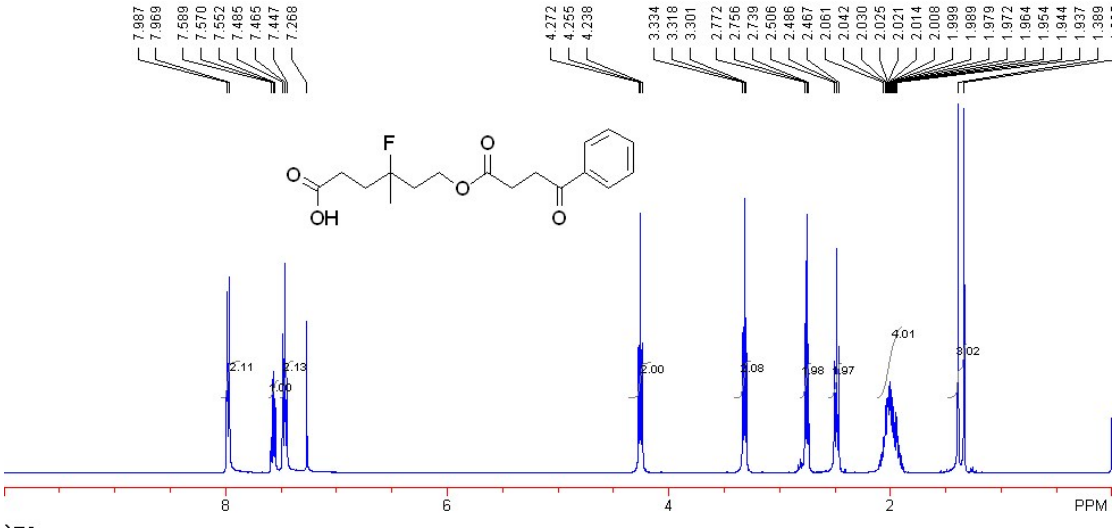
Compound **2n**

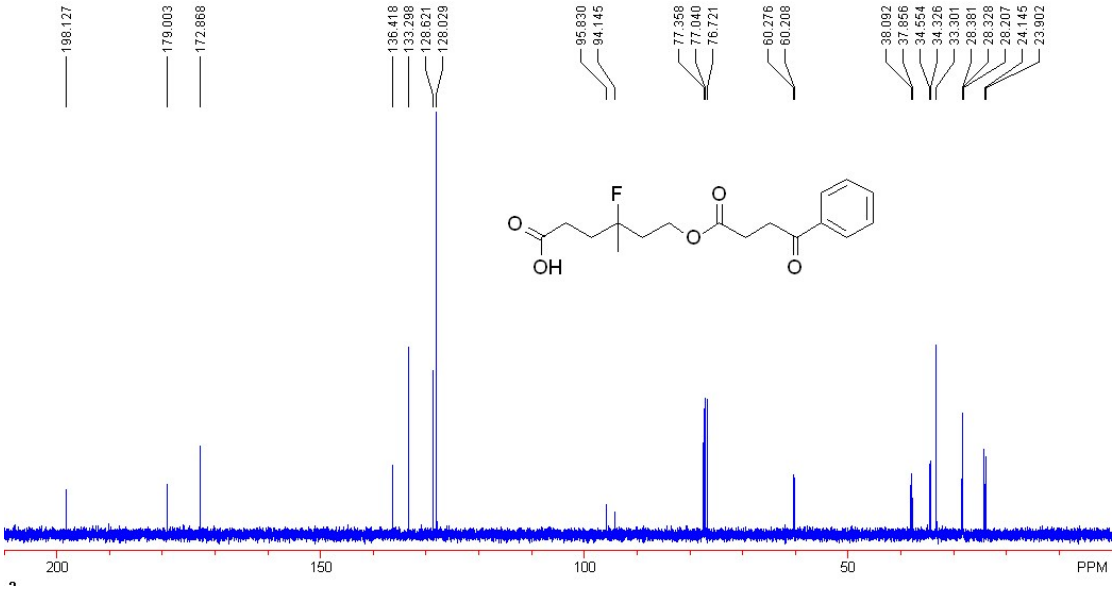

7.744
7.736
7.730
7.722
7.713
7.705
7.701
7.698
7.691
7.559
7.549
7.541
7.534
7.526
7.273
4.485
4.468
4.450
3.905
2.526
2.506
2.486
2.159
2.141
2.116
2.099
2.080
2.061
2.048
2.039
2.028
2.019
2.009
1.992
1.971
1.951
1.423
1.368
F
O
O
COOMe
O
O
OH
2.08
2.04
2.03
3.00
1.95
4.03
2.97
8
6
4
2
PPM

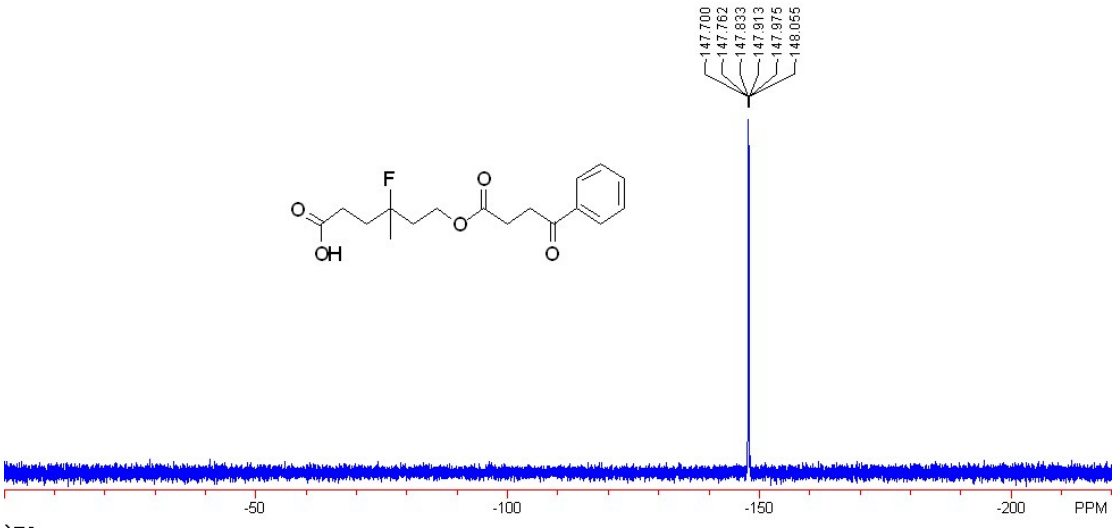

178.980
167.933
167.561
131.999
131.658
131.217
131.119
128.955
128.727
95.777
94.076
77.366
77.047
76.728
61.255
61.187
52.669
38.046
37.818
34.576
34.349
28.351
28.298
24.099
23.856
F
O
COOMe
O
O
OH
150
100
50
PPM


148.152
148.223
148.294
148.365
148.445
F
O
COOMe
O
O
OH
-50
-100
-150
-200
PPM

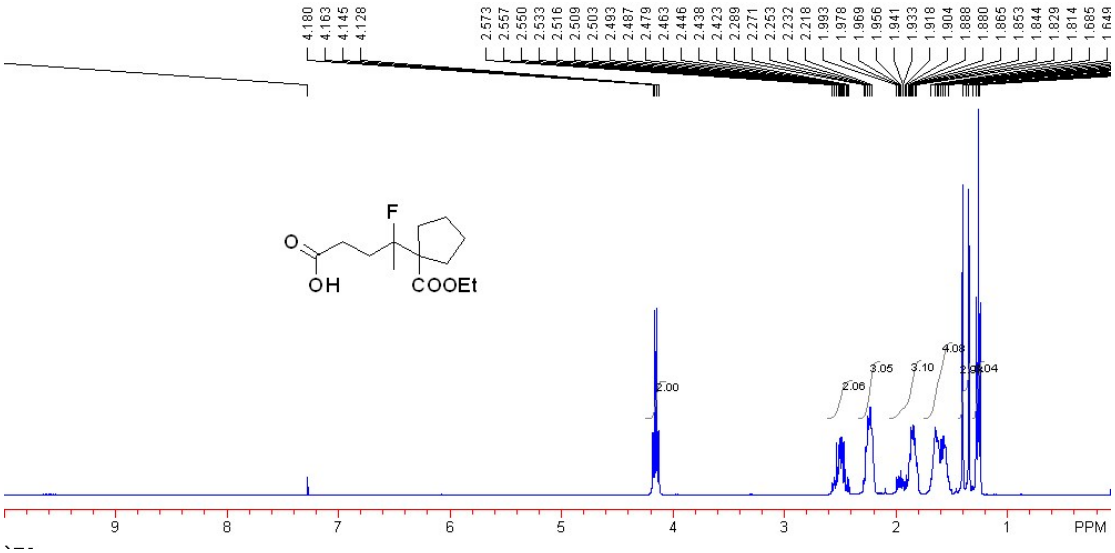
Compound **2o**

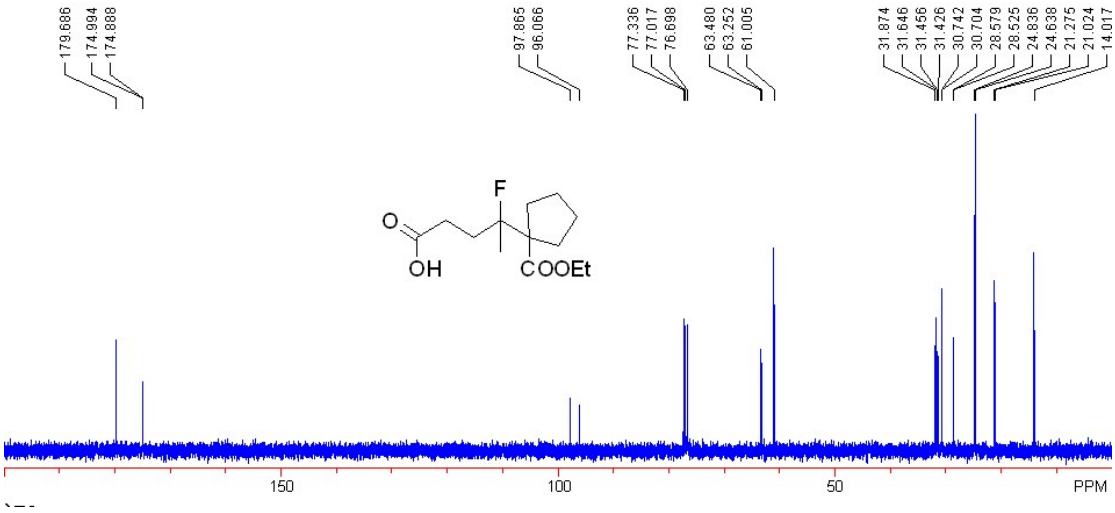

7.987
7.969
7.589
7.570
7.552
7.485
7.465
7.447
7.268
4.272
4.255
4.238
3.334
3.318
3.301
2.772
2.756
2.739
2.506
2.486
2.467
2.061
2.042
2.030
2.025
2.021
2.014
2.008
1.999
1.989
1.979
1.972
1.964
1.954
1.944
1.937
F
O
O
O
O
OH
O
2.11
2.13
2.00
2.08
1.98
1.97
4.01
3.02
8
6
4
2
PPM

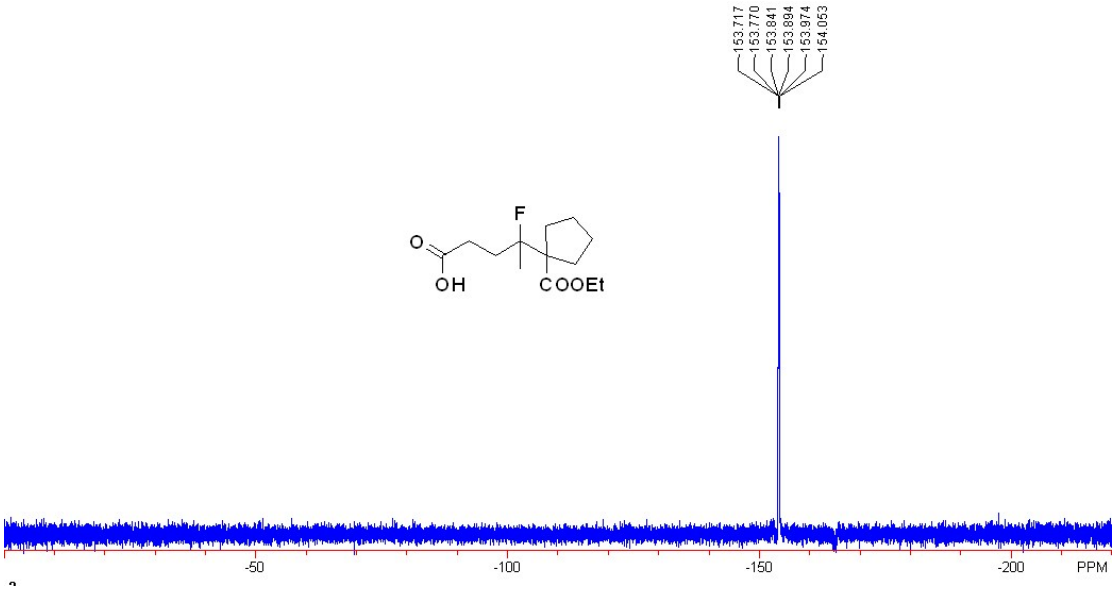

198.127
179.003
172.868
136.418
133.298
128.621
128.029
95.830
94.145
77.358
77.040
76.721
60.276
60.208
38.092
37.856
34.554
34.326
33.301
28.381
28.328
28.207
24.145
23.902
F
O
O
O
OH
O
200
150
100
50
PPM


147.700
147.762
147.833
147.913
147.975
148.055
F
O
O
O
OH
O
-50
-100
-150
-200
PPM

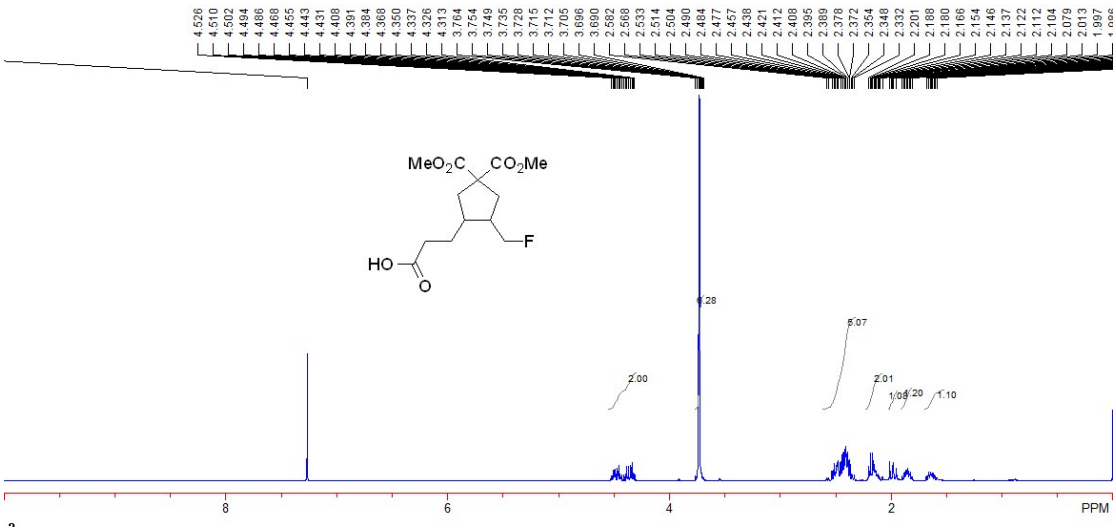
Compound **2p**

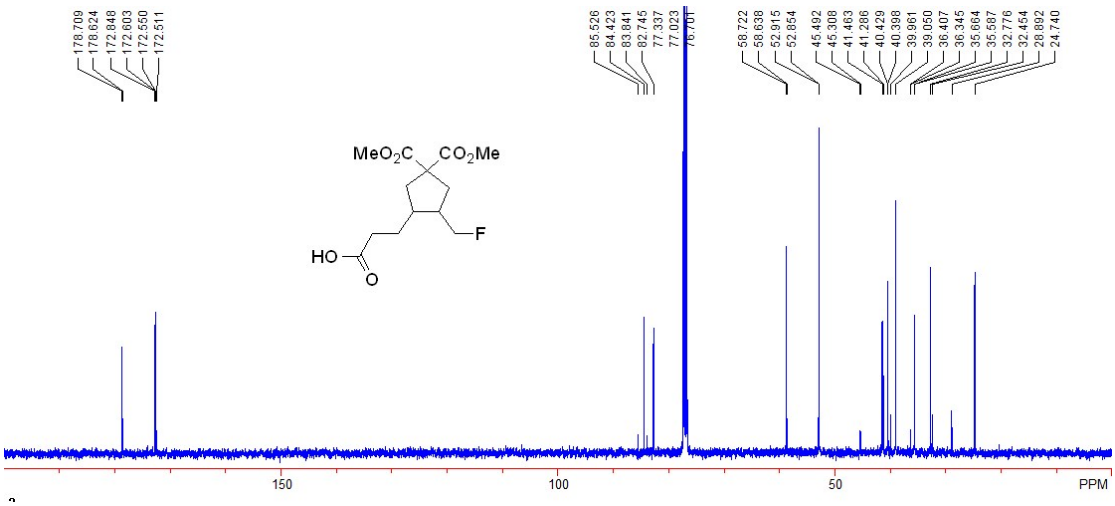

4.180
4.163
4.145
4.128
2.573
2.557
2.550
2.533
2.516
2.509
2.503
2.493
2.487
2.479
2.463
2.446
2.438
2.423
2.289
2.271
2.253
2.232
2.218
1.993
1.978
1.969
1.956
1.941
1.933
1.918
1.904
1.888
1.880
1.865
1.853
1.844
1.829
1.814
1.685
1.649
F
O
OH
COOEt
2.00
2.06
3.05
3.10
4.08
2.04
9
8
7
6
5
4
3
2
1
PPM

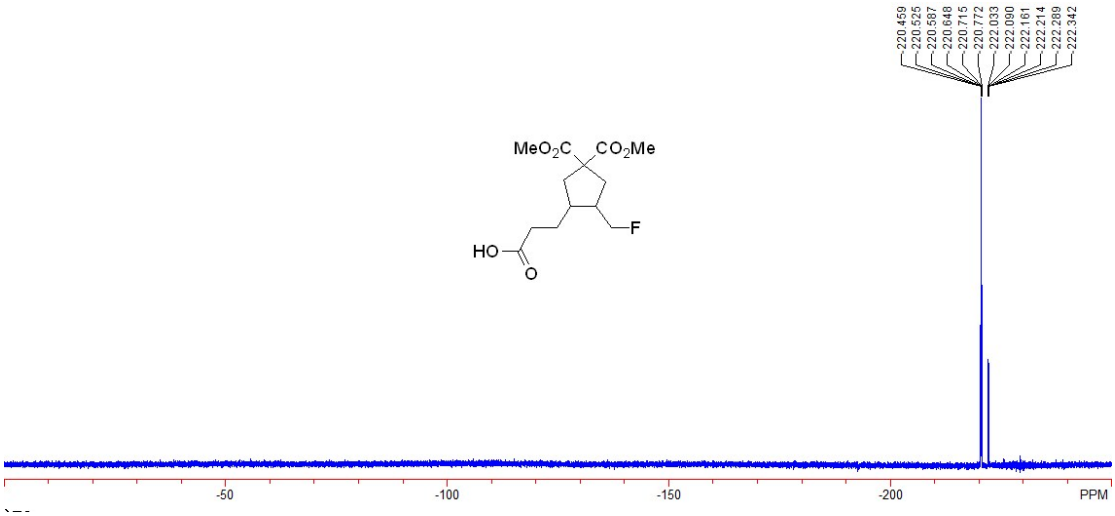

179.686
174.994
174.888
97.865
96.066
77.336
77.017
76.698
63.480
63.252
61.005
31.874
31.646
31.456
31.426
30.742
30.704
28.579
28.525
24.836
24.638
21.275
21.024
14.017
F
O
OH
COOEt
150
100
50
PPM


153.717
153.770
153.841
153.894
153.974
154.053
F
O
OH
COOEt
-50
-100
-150
-200
PPM

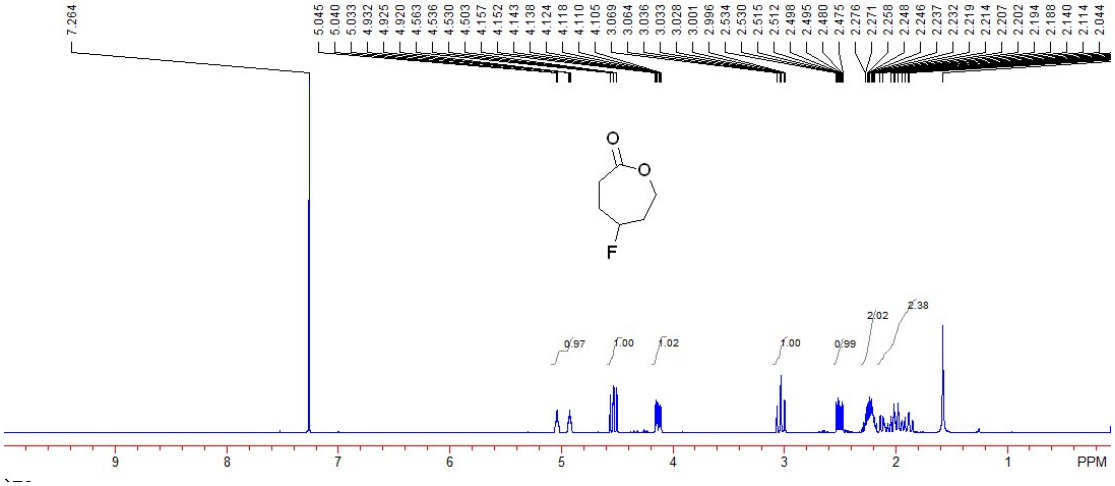
Compound **4**

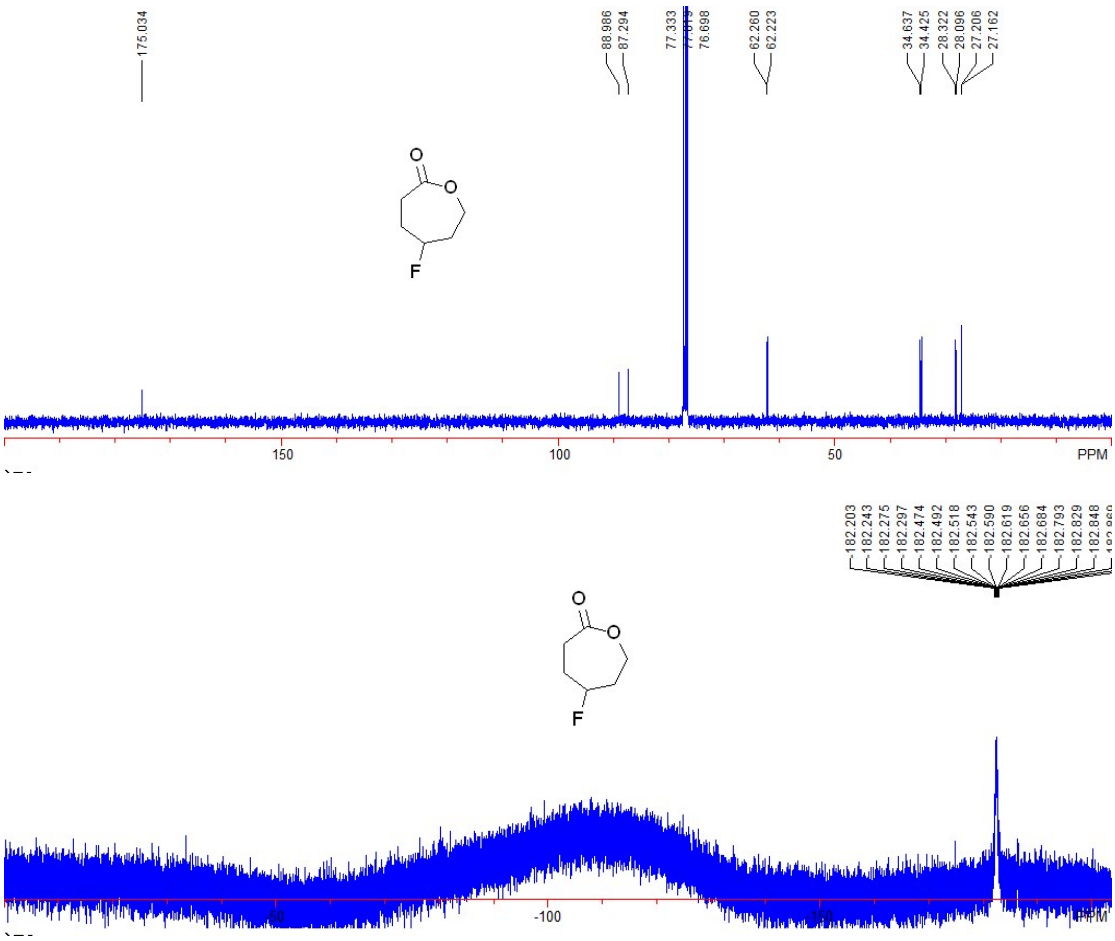

MeO2C
CO2Me
F
HO
O
2.00
6.28
5.07
2.01
1.20
1.10
8
6
4
2
PPM


178.709
178.624
172.848
172.603
172.550
172.511
85.526
84.423
83.841
82.745
77.337
77.023
76.701
58.722
58.638
52.915
52.854
45.492
45.308
41.463
41.286
40.429
40.398
39.961
39.050
36.407
36.345
35.664
35.587
32.776
32.454
28.892
24.740
MeO2C
CO2Me
HO
O
F
150
100
50
PPM


220.459
220.525
220.587
220.648
220.715
220.772
222.033
222.090
222.161
222.214
222.289
222.342
MeO2C
CO2Me
HO
O
F
-50
-100
-150
-200
PPM

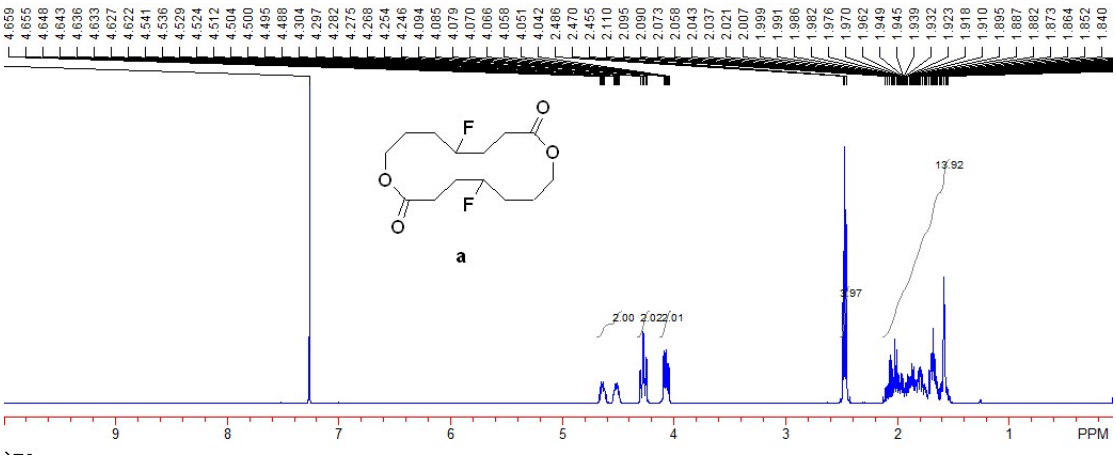
Compound **5**

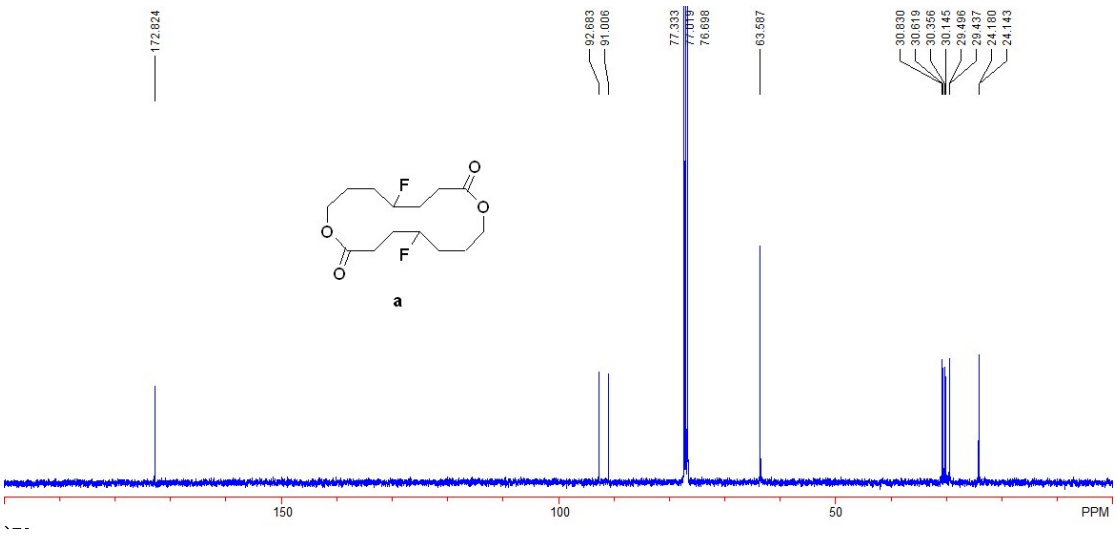

7.264
5.045
5.040
5.033
4.932
4.925
4.920
4.563
4.536
4.530
4.503
4.157
4.152
4.143
4.138
4.124
4.118
4.110
4.105
3.069
3.064
3.036
3.033
3.028
3.001
2.996
2.534
2.530
2.515
2.512
2.498
2.495
2.480
2.475
2.276
2.271
2.258
2.248
2.246
2.237
2.232
2.219
2.214
2.207
2.202
2.194
2.188
2.140
2.114
2.044
O
O
F
0.97
1.00
1.02
1.00
0.99
2.02
2.38
9
8
7
6
5
4
3
2
1
PPM

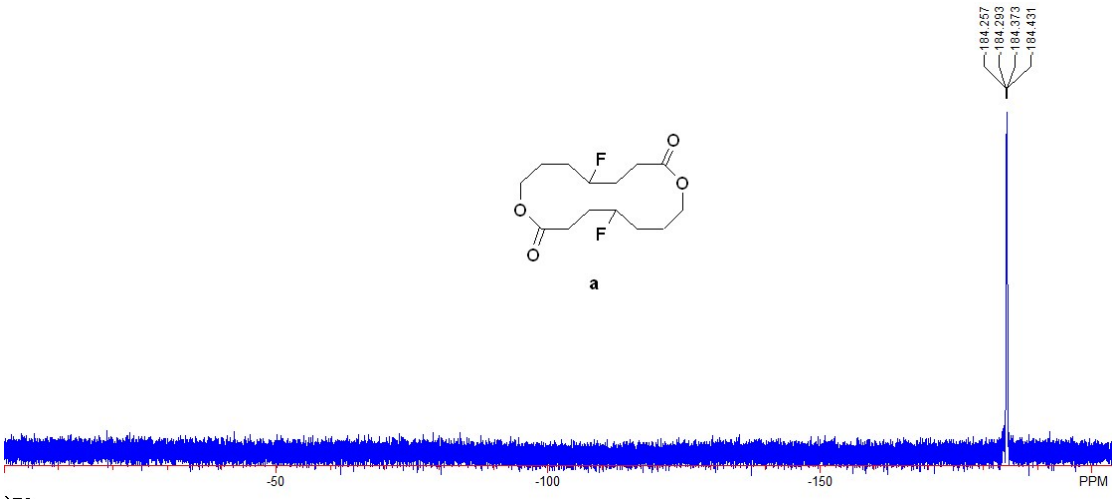


Compound **6**

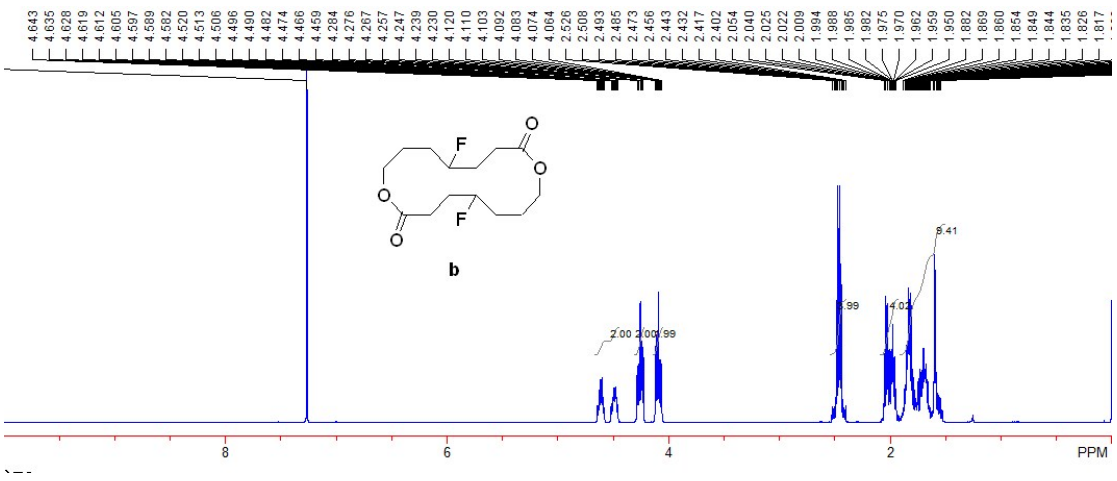
One isomer:

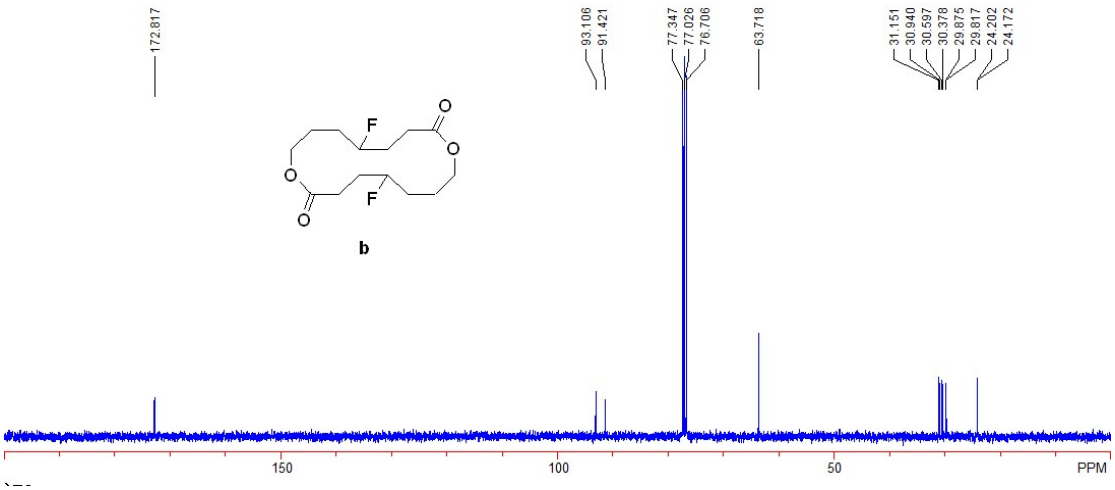


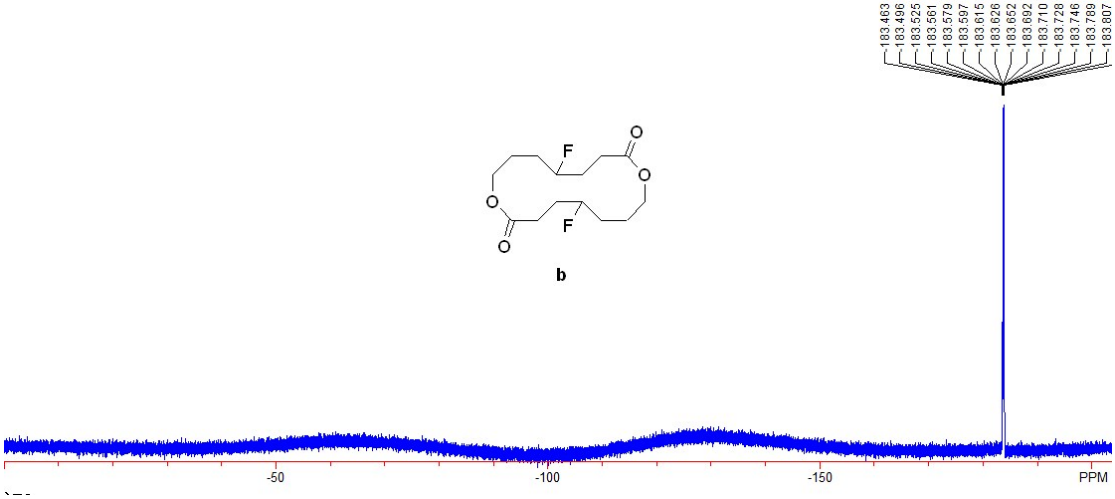




The other isomer:




172.817
93.106
91.421
77.347
77.026
76.706
63.718
31.151
30.940
30.597
30.378
29.875
29.817
24.202
24.172
F
O
O
O
F
O
b
150
100
50
PPM


183.463
183.496
183.525
183.561
183.579
183.597
183.615
183.626
183.652
183.692
183.710
183.728
183.746
183.789
183.807
F
O
O
O
F
O
b
-50
-100
-150
PPM