nature synthesis

Supplementary information

https://doi.org/10.1038/s44160-024-00578-6

Pd-catalysed direct β-C(sp^3)–H fluorination of aliphatic carboxylic acids

In the format provided by the authors and unedited

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1. General Information

Solvents, Reagents and Techniques

All reactions were conducted in oven-dried glassware (100 °C). Reaction temperatures refer to the temperature of the aluminum-block or oil bath surrounding the reaction vessel. Commercially available chemicals were obtained from ABCR, Acros Organics, BLD-pharm, Alfa Aesar, Deutero, Eurisotop, Fluorochem, Sigma Aldrich, or TCI Europe and used as received. HFIP was purchased from Fluorochem and used as received. Solvents used for column chromatography were distilled prior to use.

Chromatography

Analytical thin layer chromatography (TLC) was performed on silica gel ALUGRAM Xtra SIL G/UV254 plates (Macherey-Nagel) or aluminum oxide 150 F254, neutral plates (Merck). Compounds were visualized by ultraviolet light (254 nm or 366 nm) or by staining with $KMnO_4$ (1 g $KMnO_4$, 6 g K_2CO_3 and 0.1 g KOH in 100 mL of H_2O) or bromocresol green (40 mg bromocresol green in 100 mL EtOH; addition of $0.1M_{(aq.)}$ NaOH until the blue color appears in the solution) and developed with a heat gun if necessary. Flash chromatography was performed on silica gel 60M (0.04-0.063 mm) or aluminum oxide (aluminum oxide 90, neutral, activity level 1) with a positive nitrogen overpressure.

Nuclear Magnetic Resonance (NMR) Spectroscopy

^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded at room temperature on a Bruker AvanceNeo 500 or a Bruker Avance 600 device. Chemical shifts (δ) are given relative to tetramethylsilane (TMS) and using the residual solvent peaks for calibration. ^{19}F-NMR spectra are externally referenced with CCl_3F. Chemical shifts are reported with two decimal numbers (^{1}H) or one decimal number (^{13}C, ^{19}F). Data is reported in the following order: Chemical shift (multiplicity [s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, hept = septet, m = multiplet, br = broad signal], coupling constant (*J*, Hz) and integration). All NMR-spectra were processed using MestReNova.

General Remarks for the scope entries: Some ^{19}F-NMR spectra display signals of trace impurities. Peaks appearing at δ = –228 - –231 ppm (^{19}F NMR) correspond to di-fluorinated product derived from α-quaternary starting materials. The di-fluorinated products are not reported if the mono/di ratio was found to be larger than 20:1. Peaks appearing in the range δ = –58 - –76 ppm (^{19}F NMR) correspond to Naphthalen-2-ylmethyl 4-(trifluoromethyl)benzoate (generated from oxidant, δ = –63.6 ppm, 1 × CF_3), Naphthalen-2-ylmethyl 3-(2,4-bis(trifluoromethyl)benzamido)butanoate (generated from ligand, δ = –59.5, –60.5, ppm, 2 × CF_3), (((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)benzene (δ = –76.2 , 2 × CF_3), or 2-(((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)methyl)naphthalene (δ = –76.2 , 2 × CF_3). These signals appear

strongly in the spectrum due to the number of equivalent fluorine atoms, but, unless otherwise specified, the amount of these impurities remains below 5%.

Infrared spectroscopy (IR)

IR-spectroscopy was performed on a Perkin Elmer ATR spectrometer. Samples were measured neat. The wave numbers (ν) of recorded IR-signals are reported in cm^{-1}.

Mass Spectrometry (MS)

High resolution mass spectra (HRMS) were recorded on a Jeol AccuTOF (EI) or a ThermoFisher Orbitrap (ESI) device.

2. Preparation of Oxidants

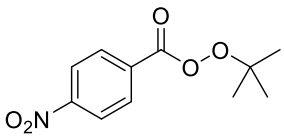
General Procedure A.[1]

The benzoyl chloride (5.4 mmol, 1.0 equiv.) derivative was dissolved in dry CH_2Cl_2 (20 mL) and the mixture was cooled to –30 °C. Pyridine (0.52 mL, 6.5 mmol, 1.2 equiv.), followed by *tert*-butyl hydroperoxide (1.18 mL, 6.48 mmol, 1.2 equiv.) were added slowly to the mixture under a nitrogen atmosphere. The reaction mixture was stirred at –30 °C for 4 h and was then allowed to slowly warm to room temperature overnight. The reaction mixture was diluted with CH_2Cl_2 (10 mL), and washed with 1 M aqueous HCl solution (3 × 50 mL), followed by saturated $NaHCO_3$ solution (3 × 50 mL). The organic phase was concentrated under reduced pressure and the crude product was purified by silica gel column chromatography using Et_2O: pentane (2: 98 to 5:95 v/v).

General Procedure B.[2]

An aqueous solution of 1 M NaOH (17.6 mL, 17.6 mmol, 2.0 equiv.) was added to a 100 mL Erlenmeyer flask immersed in an ice-bath maintained at 0-5 °C. H_2O_2 (30%, 8.8 mmol, 1.0 equiv.) was added dropwise and the resulting mixture was stirred for 10 minutes. This solution was then slowly added to a 50 mL round bottom flask containing benzoyl chloride derivative (17.6 mmol, 2.00 equiv.) placed in an ice-bath maintained at 0-5 °C (this addition should take 25-30 minutes). The cooling bath was removed and the mixture was stirred at room temperature for additional 30 minutes. The colorless precipitate was collected through vacuum filtration, dissolved in CH_2Cl_2 (colorless precipitates are better soluble in warm CH_2Cl_2) and passed through a short silica bed (a length of 5-7 cm) using CH_2Cl_2 (500-800 mL) as an eluent. The solvent was evaporated to afford the desired product.

***tert*-Butyl 4-nitrobenzoperoxoate (OX1)**



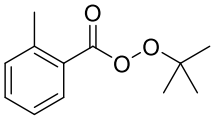
Following the general procedure **A** using 4-nitrobenzoyl chloride (1.0 g) the target compound **OX1** was obtained as a pale yellow solid (1.0 g, 4.2 mmol, 78%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.31 (d, *J* = 9.1 Hz, 2H), 8.13 (d, *J* = 9.0 Hz, 2H), 1.42 (s, 9H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 162.6, 150.8, 133.3, 130.4, 123.9, 84.8, 26.2.

IR (cm^{-1}): 2982, 1752, 1520, 1343, 1275, 1057, 849, 749

***tert*-Butyl 2-methylbenzoperoxoate (OX5)**



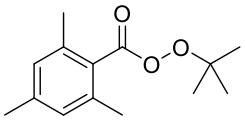
Following the general procedure **A** using 2-methyl benzoyl chloride (0.8 g) the target compound **OX5** was obtained as a colorless liquid (1.0 g, 4.8 mmol, 89%).

^{1}H-NMR (500 MHz, $(CD_3)_2CO$): δ = 7.74 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.50 (td, *J* = 7.7, 1.8 Hz, 1H), 7.38 – 7.30 (m, 2H), 2.53 (s, 3H), 1.37 (s, 9H) ppm.

^{13}C-NMR (126 MHz, $(CD_3)_2CO$): 166.0, 140.0, 133.3, 132.7, 130.4, 128.9, 127.0, 84.2, 26.6, 21.2 ppm.

IR (cm^{-1}): 2981, 1755, 1457, 1228, 1188, 1365, 838, 733

***tert*-Butyl 2,4,6-trimethylbenzoperoxoate (OX7)**



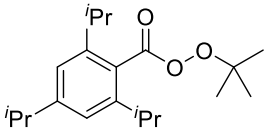
Following the general procedure **A** using 2,4,6-trimethylbenzoyl chloride (1.0 g) the target compound **OX7** was obtained as a colorless liquid (1.1 g, 4.6 mmol, 85%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 6.87 (s, 2H), 2.33 (s, 6H), 2.29 (s, 3H), 1.39 (s, 9H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 167.6, 140.4, 136.3, 128.6, 127.7, 83.5, 26.7, 21.3, 19.7 ppm.

IR (cm^{-1}): 2981, 1761, 1611, 1365, 1228, 1189, 1015, 847, 746

***tert*-Butyl 2,4,6-triisopropylbenzoperoxoate (OX8)**



2,4,6-triisopropyl benzoyl chloride was prepared following the literature procedure.[3]

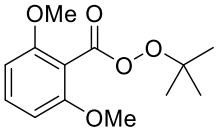
Following the general procedure **A** using 2,4,6-triisopropylbenzoyl chloride (1.4 g) the target compound **OX8** was obtained as a colorless solid (1.3 g, 4.1 mmol, 76%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.03 (s, 2H), 2.97-2.85 (m, 3H), 1.39 (s, 9H), 1.25 (dd, *J* = 6.9, 4.6 Hz, 18H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 168.0, 151.5, 146.6, 126.5, 121.3, 83.2, 34.7, 32.0, 26.5, 24.5, 24.0 ppm.

IR (cm^{-1}): 2959, 1753, 1462, 1364, 1223, 1058, 880, 844, 750

***tert*-Butyl 2,6-dimethoxybenzoperoxoate (OX9)**



2,6-dimethoxybenzoyl chloride was prepared following the literature procedure.[3]

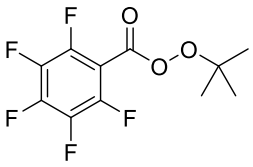
Following the general procedure **A** using 2,6-dimethoxybenzoyl chloride (1.1 g) the target compound **OX9** was obtained as a colorless solid (1.2 g, 4.7 mmol, 87%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.32 (t, *J* = 8.8 Hz, 1H), 6.54 (d, *J* = 8.4 Hz, 2H), 3.81 (s, 6H), 1.39 (s, 9H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 164.6, 158.5, 132.5, 109.7, 104.2, 84.3, 56.4, 26.7 ppm.

IR (cm^{-1}): 2982, 1771, 1592, 1475, 1256, 1109, 844, 750

***tert*-Butyl 2,3,4,5,6-pentafluorobenzoperoxoate (OX10)**



Following the general procedure **A** using 2,3,4,5,6-pentafluorobenzoyl chloride (1.2 g) the target compound **OX10** was obtained as a colorless solid (1.2 g, 4.2 mmol, 78%).

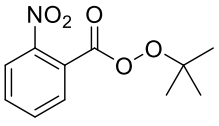
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.39 (s, 9H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 156.80, 146.4-144.8 (m), 144.4-142.7 (m), 139.0-136.8 (m), 105.7-105.4 (m), 85.4, 26.4 ppm.

^{19}F NMR (471 MHz, $CDCl_3$): δ = –137.3 - –137.4 (m), –147.5 - –147.6 (m), –159.8 - –159.9 (m) ppm.

IR (cm^{-1}): 2987, 1744, 1652, 1499, 1421, 1323, 1275, 844, 750

***tert*-Butyl 2-nitrobenzoperoxoate (OX11)**



2-nitrobenzoyl chloride was prepared following the literature procedure.**[3]**

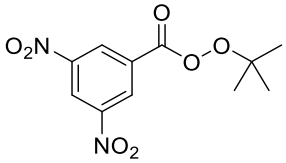
Following the general procedure **A** using 2-nitrobenzoyl chloride (1.0 g) the target compound **OX11** was obtained as a colorless solid (1.1 g, 4.6 mmol, 85%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.06 (d, *J* = 7.5 Hz, 1H), 7.76 – 7.64 (m, 3H), 1.38 (s, 9H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 163.8, 147.4, 133.7, 132.3, 130.1, 125.7, 124.5, 85.1, 26.3 ppm.

IR (cm^{-1}): 2982, 1768, 1532, 1349, 1232, 1051, 827, 744

***tert*-Butyl 3,5-dinitrobenzoperoxoate (OX12)**



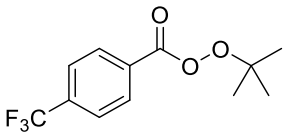
Following the general procedure **A** using 3,5-dinitrobenzoyl chloride (1.2 g) the target compound **OX12** was obtained as a pale yellow solid (1.1 g, 3.9 mmol, 72%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 9.25 (t, *J* = 2.1 Hz, 1H), 9.06 (d, *J* = 2.1 Hz, 2H), 1.45 (s, 9H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 160.6, 148.9, 131.5, 129.1, 122.9, 85.7, 26.2 ppm.

IR (cm^{-1}): 2982, 1762, 1540, 1342, 1260, 1033, 847, 750

***tert*-Butyl 4-(trifluoromethyl)benzoperoxoate (OX13)**



Following the general procedure **A** using 4-(trifluoromethyl)benzoyl chloride (1.1 g) the target compound **OX13** was obtained as a colorless liquid (1.2 g, 4.6 mmol, 85%).

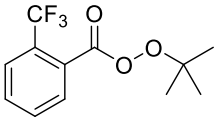
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 8.1 Hz, 2H), 7.73 (d, *J* = 8.1 Hz, 2H), 1.42 (s, 9H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 163.3, 135.0 (q, *J* = 32.8 Hz), 131.2, 129.7, 125.8 (d, *J* = 3.7 Hz), 123.5 (q, *J* = 272.9 Hz), 84.6, 26.4 ppm.

^{19}F NMR (471 MHz, $CDCl_3$): δ = –63.8 ppm.

IR (cm^{-1}): 2984, 1762, 1411, 1367, 1322, 1171, 857, 834, 765

***tert*-Butyl 2-(trifluoromethyl)benzoperoxoate (OX14)**



2-(trifluoromethyl)benzoyl chloride was prepared following the literature procedure.[4]

Following the general procedure **A** using 2-(trifluoromethyl)benzoyl chloride (1.1 g) the target compound **OX14** was obtained as a colorless liquid (1.1 g, 4.4 mmol, 81%).

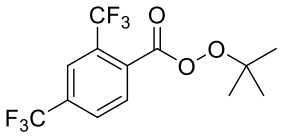
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.77 – 7.75 (m, 1H), 7.70 – 7.68 (m, 1H), 7.65 – 7.63 (m, 2H), 1.39 (s, 9H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 164.7, 132.1, 131.7, 130.2, 129.3-128.8 (m), 127.0-126.8(m), 124.3, 122.1, 84.6, 26.3 ppm.

^{19}F NMR (471 MHz, $CDCl_3$): δ = –60.1 (s) ppm.

IR (cm^{-1}): 2984, 1773, 1449, 1368, 1232, 1136, 833, 767

***tert*-Butyl 2,4-bis(trifluoromethyl)benzoperoxoate (OX15)**



2,4-(trifluoromethyl)benzoyl chloride was prepared following the literature procedure.[4] Following the general procedure **A** using 2,4-(trifluoromethyl)benzoyl chloride (1.5 g) the target compound **OX15** was obtained as a colorless liquid (1.3 g, 3.9 mmol, 72%).

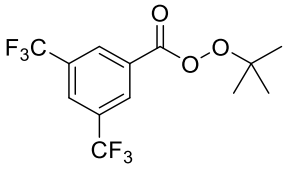
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.01 (s, 1H), 7.92 (d, *J* = 8.6 Hz, 1H), 7.85 (d, *J* = 8.8 Hz, 1H), 1.39 (s, 9H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 163.5, 134.0 (q, *J* = 34.0 Hz), 131.9, 131.1, 130.0 (q, *J* = 33.9 Hz), 129.1 (d, *J* = 3.7 Hz), 124.2, 122.8 (q, *J* = 273.0 Hz), 122.6 (q, *J* = 273.0 Hz), 85.0, 26.3 ppm.

^{19}F NMR (471 MHz, $CDCl_3$): δ = –60.4 (s), –63.8 (s) ppm.

IR (cm^{-1}): 2983, 1775, 1369, 1343, 1273, 1132, 844, 690

***tert*-Butyl 3,5-bis(trifluoromethyl)benzoperoxoate (OX16)**



Following the general procedure **A** using 3,5-(trifluoromethyl)benzoyl chloride (1.5 g) the target compound **OX16** was obtained as a colorless liquid (1.5 g, 4.5 mmol, 83%).

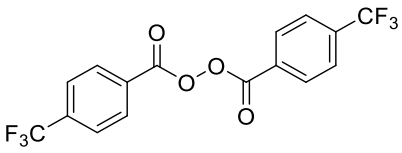
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.38 (s, 2H), 8.10 (s, 1H), 1.44 (s, 9H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 162.0, 132.7 (q, *J* = 34.3 Hz), 130.1, 129.4, 127.0-126.9 (m), 122.8 (q, *J* = 273.0 Hz), 85.1, 26.4 ppm.

^{19}F NMR (471 MHz, $CDCl_3$): δ = –63.5 ppm.

IR (cm^{-1}): 2986, 1767, 1624, 1369, 1276, 1131, 844, 751

4-(trifluoromethyl)benzoic peroxyanhydride (OX2)



Following the general procedure **B** using 4-(trifluoromethyl)benzoyl chloride (3.7 g) the target compound **OX2** was obtained as a colorless solid (2.8 g, 7.4 mmol, 84%).

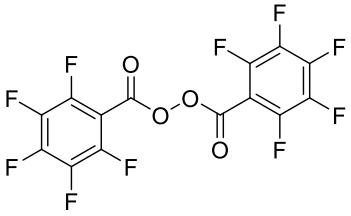
The analytical data are in good agreement with those reported in the literature.[5]

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.21 (d, *J* = 8.1 Hz, 4H), 7.81 (d, *J* = 8.1 Hz, 4H) ppm.

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 161.9 (C=O), 136.1 (q, *J* = 32.9 Hz, C), 130.4(CH), 126.2-126.1 (m, CH), 123.3 (q, *J* = 272.5 Hz,CF_3) ppm.

^{19}F NMR (471 MHz, $CDCl_3$): –63.9 (s) ppm.

2,3,4,5,6-pentafluorobenzoic peroxyanhydride (OX17)

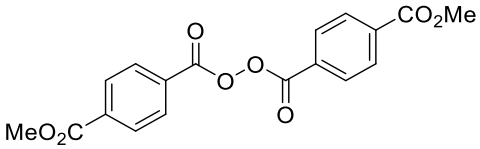


Following the general procedure **B** using 2,3,4,5,6-pentafluorobenzoyl chloride 4.1 g) the target compound **OX17** was obtained as a colorless solid (2.3 g, 6.9 mmol, 78%).

^{13}C-NMR (126 MHz, $(CD_3)_2CO$): δ = 156.2, 148.3-147.0 (m), 146.3-144.9 (m), 140.5-138.2 (m), 103.5-11(m) ppm.

^{19}F NMR (471 MHz, $(CD_3)_2CO$): δ = –135.8 - –135.9 (m), –145.6 - –145.7 (m), –160.4 - –160.5 (m) ppm.

4-(methoxycarbonyl)benzoic peroxyanhydride (OX18)



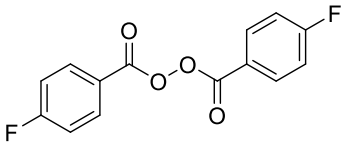
Following the general procedure **B** using methyl 4-(chlorocarbonyl)benzoate (3.5 g) the target compound **OX18** was obtained as a colorless solid (2.1 g, 6.2 mmol, 70%).

The analytical data are in good agreement with those reported in the literature.[6]

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.18 (d, *J* = 8.9 Hz, 4H), 8.14 (d, *J* = 8.9 Hz, 4H), 3.97 (s, 6H) ppm.

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 165.9, 162.3, 135.4, 130.1, 129.9, 129.3, 52.7 ppm.

4-fluorobenzoic peroxyanhydride (OX19)



Following the general procedure **B** using methyl 4-fluorobenzoyl chloride (2.8 g) the target compound **OX19** was obtained as a colorless solid (1.6 g, 5.7 mmol, 65%).

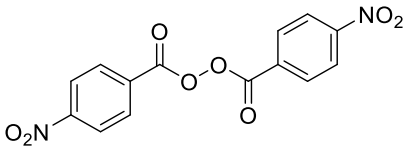
The analytical data are in good agreement with those reported in the literature.[5]

^{1}H-NMR (500 MHz, $(CD_3)_2CO$): δ = 8.17 (dd, *J* = 9.1, 5.4 Hz, 4H), 7.42 (t, *J* = 8.8 Hz, 4H) ppm.

^{13}C-NMR (125 MHz, $(CD_3)_2CO$): δ = 166.4, 162.8, 133.4, 122.7, 117.3ppm.

^{19}F NMR (471 MHz, $(CD_3)_2CO$): –103.2 ppm.

4-nitrobenzoic peroxyanhydride (OX20)



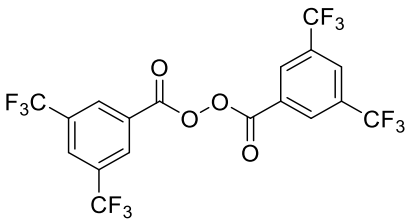
Following the general procedure **B** using methyl 4-nitrobenzoyl chloride (3.3 g) the target compound **OX20** was obtained as a colorless solid (1.7 g, 5.3 mmol, 60%).

The analytical data are in good agreement with those reported in the literature.[5]

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.39 (d, *J* = 8.1 Hz, 4H), 8.27 (d, *J* = 8.1 Hz, 4H) ppm.

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 161.2, 151.5, 131.2, 130.7, 124.2 ppm.

3,5-bis(trifluoromethyl)benzoic peroxyanhydride (OX21)



Following the general procedure **B** using 3,5-bis(trifluoromethyl)benzoyl chloride (4.9 g) the target compound **OX21** was obtained as a colorless solid (3.3 g, 6.4 mmol, 73%).

^{1}H-NMR (500 MHz, $(CD_3)_2CO$): δ = 8.65 (s, 4H), 8.55 (s, 2H) ppm.

^{13}C-NMR (125 MHz, $(CD_3)_2CO$): δ = 161.4, 133.4 (q, *J* = 34.3 Hz), 131.0, 129.3, 128.7, 123.7 (q, *J* = 273.0 Hz) ppm.

^{19}F NMR (471 MHz, $(CD_3)_2CO$): –62.6 (s) ppm.

3. Preparation of Ligands

General Procedure C:[7, 8]

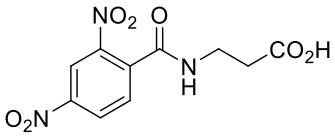
Ethyl 3-aminopropanoate hydrochloride (1.3 g, 8.4 mmol, 1.2 equiv.) and triethylamine (2.9 mL, 25 mmol 3.0 equiv.) were dissolved in CH_2Cl_2 (30 mL), the reaction mixture was cooled to 0 °C and the required benzoyl chloride derivative (1.0 equiv, 7.0 mmol) was added dropwise. The reaction mixture was stirred for 30 min at 0 °C and was then allowed to slowly warm to room temperature overnight. The reaction mixture was diluted with CH_2Cl_2 (10 mL), and washed with 1 M aqueous HCl solution (2 × 60 mL), followed by saturated $NaHCO_3$ solution (2 × 60 mL). The combined organic phases were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The product was used in the following step without further purification.

The product from the previous step was dissolved in a mixture (1:1 v/v) of THF (20 mL) and H_2O (20 mL). $LiOH{\cdot}H_2O$ (2.0 equiv.) was added and the reaction mixture was stirred at room temperature for 6 h. THF was removed under reduced pressure and the solution was washed with EtOAc (2 × 10 mL). The aqueous phase was acidified with conc. aq. HCl to reach a pH value of 2-3 and extracted with EtOAc (3 × 10 mL). The extracts were concentrated under reduced pressure and the crude product was purified via silica gel column chromatography using a mixture of pentane and EtOAc (30:70 - 20:80 v/v) acidified with HCOOH (0.2 mL for 100 mL of solvent mixture) as the eluent.

General Procedure for the preparation of methyl aminobutanoate hydrochloride derivative :[9]

$SOCl_2$ (1.2 equiv.) was added dropwise to a suspension of methyl aminobutanoate derivative in MeOH at 0 °C. The reaction mixture was stirred at 0 °C for 15 min and was then allowed to slowly warm to room temperature overnight. The solvent was removed under reduced pressure to obtain the desired product.

3-(2,4-dinitrobenzamido)propanoic acid (L1)



Following the general procedure **C** using 2,4-dinitrobenzoyl chloride (1.6 g) the target compound **L1** was obtained as a pale yellow solid (1.1 g, 3.9 mmol, 56%).

^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ = 8.80 (d, *J* = 2.3 Hz, 1H), 8.62 (dd, *J* = 8.4, 2.3 Hz, 1H), 8.14 (s, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 3.65 (q, *J* = 6.4 Hz, 2H), 2.69 (t, *J* = 6.6 Hz, 2H) ppm.

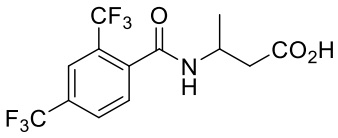
^{13}C NMR (126 MHz, $(CD_3)_2CO$): δ = 173.1, 165.2, 149.1, 148.1, 139.0, 131.6, 128.9, 120.5, 36.4, 33.7 ppm.

HRMS (ESIpos) m/z: Calcd for $C_{10}H_{10}N_3O_7$ 284.0513, Found 284.0513.

IR (cm^{-1}): 3311, 3072, 1705, 1646, 1600, 1534, 1355, 1273, 1213, 923, 868, 723

Melting Point: 150 °C (decomp)

3-(2,4-bis(trifluoromethyl)benzamido)butanoic acid (L2)



2,4-(trifluoromethyl)benzoyl chloride was prepared following the literature procedure.[4] Following the general procedure **C** using 2,4-(trifluoromethyl)benzoyl chloride (1.9 g) and **methyl 3-aminobutanoate hydrochloride** (1.3 g, 8.3 mmol) the target compound **L2** was obtained as a colorless solid (1.5 g, 4.4 mmol, 63%).

^{1}H-NMR (500 MHz, $(CD_3)_2CO$): δ 8.12 – 7.98 (m, 2H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.72 (s, 1H), 4.55 – 4.39 (m, 1H), 2.73 (dd, *J* = 15.7, 6.0 Hz, 1H), 2.56 (dd, *J* = 15.7, 7.2 Hz, 1H), 1.33 (d, *J* = 6.7 Hz, 3H) ppm.

^{13}C-NMR (126 MHz, $(CD_3)_2CO$): δ 172.6, 166.1, 141.6, 131.9 (q, *J* = 33.4 Hz), 130.8, 130.1 (d, *J* = 3.8 Hz), 128.7 (q, *J* = 32.8 Hz), 124.4 (q, *J* = 273.0 Hz), 124.2 (p, *J* = 4.6 Hz), 124.1 (q, *J* = 273.0 Hz), 43.9, 40.5, 20.1 ppm.

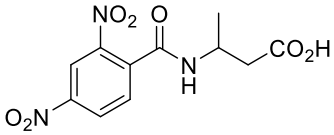
^{19}F NMR (471 MHz, $(CD_3)_2CO$): δ = –58.9 (s), –62.5 (s) ppm.

HRMS (ESIpos) m/z: Calcd for $C_{13}H_{11}F_6NO_3Na$ 363.0535, Found 363.0530

IR (cm^{-1}): 3281, 2970, 1738, 1642, 1545, 1428, 1365, 1274, 1217, 1056, 915, 764

Melting Point: 158.8 °C

3-(2,4-dinitrobenzamido)butanoic acid (L3)



Following the general procedure **C** using 2,4-dinitrobenzoyl chloride (1.6 g) methyl **3-aminobutanoate hydrochloride** (1.3 g, 8.4 mmol) the target compound **L3** was obtained as a pale yellow solid (1.3 g, 4.4 mmol, 63%).

^{1}H-NMR (500 MHz, $(CD_3)_2CO$): δ = 8.80 (d, *J* = 2.2 Hz, 1H), 8.62 (dd, *J* = 8.4, 2.2 Hz, 1H), 8.00 (s, 1H), 7.93 (d, *J* = 8.3 Hz, 1H), 4.52-4.41 (m, 1H), 2.76 (dd, *J* = 15.8, 5.8 Hz, 1H), 2.57 (dd, *J* = 15.8, 7.3 Hz, 1H), 1.35 (d, *J* = 6.7 Hz, 3H) ppm.

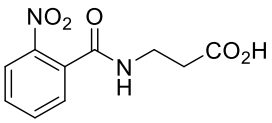
^{13}C-NMR (126 MHz, $(CD_3)_2CO$): δ = 172.5, 164.4, 149.16, 148.16, 139.2, 131.6, 128.9, 120.6, 44.00, 40.3, 19.9 ppm.

HRMS (ESIpos) m/z: Calcd for $C_{11}H_{12}N_3O_7$ 298.0669, Found 298.0668

IR (cm^{-1}): 3281, 3096, 1708, 1647, 1599, 1524, 1430, 1356, 1149, 923, 837, 738

Melting Point: 130 °C (decomp)

3-(2-nitrobenzamido)propanoic acid (L4)



Following the general procedure **C** 2-nitrobenzoyl chloride (1.3 g) the target compound **L4** was obtained as a colorless solid (1.1 g, 4.6 mmol, 66%).

^{1}H-NMR (500 MHz, $(CD_3)_2CO$): δ = 8.02 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.88 (s, 1H), 7.77 (td, *J* = 7.5, 1.2 Hz, 1H), 7.68 (td, *J* = 7.8, 1.5 Hz, 1H), 7.62 (dd, *J* = 7.5, 1.5 Hz, 1H), 3.62 (q, *J* = 6.6 Hz, 2H), 2.68 (t, *J* = 6.8 Hz, 2H) ppm.

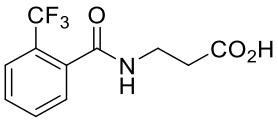
^{13}C-NMR (126 MHz, $(CD_3)_2CO$): δ = 173.2, 166.8, 148.3, 134.2, 134.0, 131.3, 129.8, 124.9, 36.4, 33.9 ppm.

HRMS (ESIpos) m/z: Calcd for $C_{10}H_{10}N_2O_5Na$ 261.0481, Found 261.0480

IR (cm^{-1}): 3257, 3090, 1698, 1640, 1557, 1517, 1348, 1280, 1221, 1078, 910, 852

Melting Point: 148.7 °C

3-(2-(trifluoromethyl)benzamido)propanoic acid (L5)



Following the general procedure **C** using 2-(trifluoromethyl)benzoyl chloride (1.5 g) the target compound **L5** was obtained as a colorless solid (1.1 g, 4.2 mmol, 60%).

^{1}H-NMR (500 MHz, $(CD_3)_2CO$): δ = 7.75 (d, *J* = 7.8 Hz, 1H), 7.70 – 7.59 (m, 3H), 7.55 (d, *J* = 7.5 Hz, 1H), 3.63 (q, *J* = 6.5 Hz, 2H), 2.66 (t, *J* = 6.8 Hz, 2H) ppm.

^{13}C-NMR (126 MHz, $(CD_3)_2CO$): δ = 173.2, 168.2, 137.7, 133.0, 130.4, 129.4, 127.1 (q, *J* = 5.0 Hz), 124.8 (q, *J* = 273.0 Hz), 121.6, 36.4, 34.0 ppm.

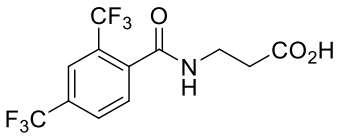
^{19}F NMR (471 MHz, $(CD_3)_2CO$): δ = –58.5 (s) ppm

HRMS (ESIpos) m/z: Calcd for $C_{11}H_{11}F_3NO_3$ 262.0685, Found 262.0685

IR (cm^{-1}): 3260, 3075, 1706, 1639, 1541, 1310, 1183, 1112, 1033, 766

Melting Point: 121.3 °C

3-(2,4-bis(trifluoromethyl)benzamido)propanoic acid (L6)



Following the general procedure **C** using 2,4-(trifluoromethyl)benzoyl chloride (1.9 g) the target compound **L6** was obtained as a colorless solid (1.3 g, 3.9 mmol, 56%).

^{1}H-NMR (500 MHz, $(CD_3)_2CO$): δ = 8.12 – 8.02 (m, 2H), 7.86 (s, 1H), 7.82 (d, *J* = 7.9 Hz, 1H), 3.65 (q, *J* = 6.4 Hz, 2H), 2.67 (t, *J* = 6.7 Hz, 2H) ppm.

^{13}C-NMR (126 MHz, $(CD_3)_2CO$): δ = 173.2, 167.0, 141.4, 131.9 (q, *J* = 33.3 Hz), 130.8, 130.1,128.8 (q, *J* = 32.9 Hz), 124.5 (q, *J* = 273.0 Hz), 124.3-124.1 (m), 123.9 (q, *J* = 273.0 Hz) ,36.5, 33.9 ppm.

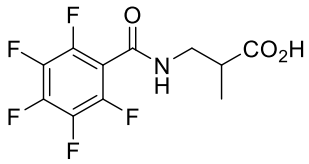
^{19}F NMR (471 MHz, $(CD_3)_2CO$): δ = –59.0 (s), –62.5 (s) ppm.

HRMS (ESIpos) m/z: Calcd for $C_{12}H_9F_6NO_3Na$ 352.0378, Found 352.0371

IR (cm^{-1}): 3302, 1692, 1648, 1541, 1332, 1267, 1134, 1082, 914, 856, 750

Melting Point: 149 °C

2-methyl-3-(perfluorobenzamido)propanoic acid (L7)



Following the general procedure **C** using 2,3,4,5,6-pentafluorobenzoyl chloride (1.6 g) and **methyl 3-aminoisobutanoate hydrochloride** (1.3 g, 8.3 mmol) the target compound **L7** was obtained as a colorless solid (1.3 g, 4.5 mmol, 64%).

^{1}H-NMR (500 MHz, $(CD_3)_2CO$): δ = 8.05 (s, 1H), 3.67 – 3.49 (m, 2H), 2.85-2.78 (m, 1H), 1.24 (d, *J* = 7.2 Hz, 3H) ppm.

^{13}C-NMR (126 MHz, $(CD_3)_2CO$): 176.0, 158.0, 145.7-143.6 (m), 141.7-141.3 (m), 139.5-137.4 (m), 113.9-113.6 (m), 43.1, 40.0, 15.1 ppm.

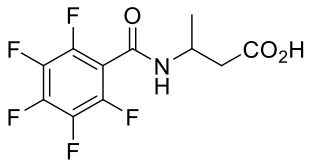
^{19}F NMR (471 MHz, $(CD_3)_2CO$): δ = –142.3 - –142.4 (m), –154.5 - –154.6 (m) , –162.5 - –162.7 (m) ppm.

HRMS (ESIpos) m/z: Calcd for $C_{11}H_8F_5NO_3Na$ 320.0316, Found 320.0314

IR (cm^{-1}): 3005, 2970, 1738, 1699, 1365, 1275, 1260, 1217, 987, 750

Melting Point: 162.2 °C

3-(perfluorobenzamido)butanoic acid (L8)



Following the general procedure **C** using 2,3,4,5,6-pentafluorobenzoyl chloride (1.6 g) and **methyl 3-aminobutanoate hydrochloride** (1.3 g, 8.3 mmol) the target compound **L8** was obtained as a colorless solid (1.4 g, 4.7 mmol, 67%).

^{1}H-NMR (500 MHz, $(CD_3)_2CO$): δ = 7.97 (s, 1H), 4.52-4.43 (m, 1H), 2.70 (dd, *J* = 15.9, 6.1 Hz, 1H), 2.57 (dd, *J* = 15.8, 7.0 Hz, 1H), 1.33 (d, *J* = 6.7 Hz, 3H).

^{13}C-NMR (126 MHz, $(CD_3)_2CO$): δ 172.3, 156.9, 145.8-143.5 (m), 141.8-141.5 (m), 139.5-137.3 (m), 114.1-113.7 (m), 44.3, 40.4, 20.2 ppm.

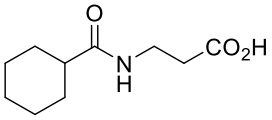
^{19}F NMR (471 MHz, $(CD_3)_2CO$): δ = –142.4 - –142.5 (m), –154.4 - –154.5 (m), –162.5 - –162.7 (m) ppm.

HRMS (ESIpos) m/z: Calcd for $C_{11}H_8F_5NO_3Na$ 320.0316, Found 320.0313

IR (cm^{-1}): 3005, 2970, 1738, 1699, 1365, 1275, 1260, 1217, 987, 750

Melting Point: 128.4 °C

3-(cyclohexanecarboxamido)propanoic acid (L9)



Following the general procedure **C** using cyclohexanecarbonyl chloride (1.0 g) the target compound **L9** was obtained as a colorless solid (0.90 g, 4.3 mmol, 61%).

^{1}H-NMR (500 MHz, $(CD_3)_2CO$): δ = 3.40 (q, *J* = 6.5 Hz, 2H), 2.49 (t, *J* = 6.7 Hz, 2H), 2.17-2.11 (m, 1H), 1.76-1.71 (m, 4H), 1.63 – 1.60 (m, 1H), 1.44-1.36 (m, 2H), 1.29-1.16 (m, 3H) ppm

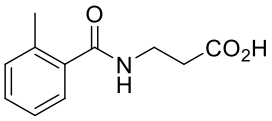
^{13}C NMR (126 MHz, $(CD_3)_2CO$): δ = 176.5, 173.4, 45.6, 35.8, 34.6, 30.4, 26.6, 26.4 ppm.

HRMS (ESIpos) m/z: Calcd for $C_{10}H_{18}NO_3$ 200.1281, Found 200.1279

IR (cm^{-1}): 3291, 2934, 1697, 1635, 1547, 1444, 1303, 1257, 924, 750

Melting Point: 129.3 °C

3-(2-methylbenzamido)propanoic acid (L10)



Following the general procedure **C** using 2-methylbenzoyl chloride (1.1 g) the target compound **L10** was obtained as a colorless solid (1.0 g, 4.8 mmol, 69%).

^{1}H-NMR (500 MHz, $(CD_3)_2CO$): δ = 7.46 (s, 1H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.28 (td, *J* = 7.5, 1.2 Hz, 1H), 7.23 – 7.15 (m, 2H), 3.62 (q, *J* = 6.6 Hz, 2H), 2.66 (t, *J* = 6.8 Hz, 2H), 2.39 (s, 3H) ppm.

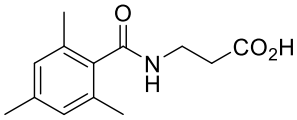
^{13}C-NMR (126 MHz, $(CD_3)_2CO$): δ = 173.4, 170.3, 138.1, 136.7, 131.4, 130.2, 127.8, 126.3, 36.3, 34.4, 19.9 ppm.

HRMS (ESIpos) m/z: Calcd for $C_{11}H_{13}NO_3Na$ 230.0787, Found 230.0785

IR (cm^{-1}): 3408, 2967, 1705, 1614, 1595, 1531, 1420, 1274, 1199, 1163, 750

Melting Point: 96.1 °C

3-(2,4,6-trimethylbenzamido)propanoic acid (L11)



Following the general procedure **C** using 2,4,6-trimethylbenzoyl chloride (1.3 g) the target compound **L11** was obtained as a colorless solid (1.1 g, 5.3 mmol, 76%).

^{1}H-NMR (500 MHz, $(CD_3)_2CO$): δ = 7.34 (s, 1H), 6.80 (s, 2H), 3.62 (q, *J* = 6.6 Hz, 2H), 2.66 (t, *J* = 6.7 Hz, 2H), 2.23 (s, 3H), 2.20 (s, 6H) ppm.

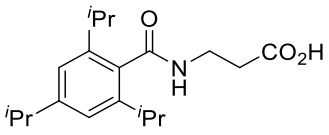
^{13}C-NMR (126 MHz, $(CD_3)_2CO$): δ = 173.3, 170.6, 138.4, 136.7, 134.7, 128.6, 36.1, 34.3, 21.1, 19.2 ppm.

HRMS (ESIpos) m/z: Calcd for $C_{13}H_{17}NO_3Na$ 258.1100, Found 258.1099.

IR (cm^{-1}): 3286, 2981, 1732, 1598, 1545, 1401, 1317, 1277, 1169, 853, 763.

Melting Point: 131.4 °C

3-(2,4,6-triisopropylbenzamido)propanoic acid (L12)



Following the general procedure **C** using 2,4,6-triisopropylbenzoyl chloride (1.9 g) the target compound **L12** was obtained as a colorless solid (1.3 g, 4.1 mmol, 59%).

^{1}H-NMR (500 MHz, $(CD_3)_2CO$): δ = 7.03 (s, 2H), 3.62 (q, *J* = 6.6 Hz, 2H), 3.00 (hept, *J* = 6.9 Hz, 2H), 2.88 (hept, *J* = 6.9 Hz, 1H), 2.66 (t, *J* = 6.7 Hz, 2H), 1.25 – 1.09 (m, 18H) ppm.

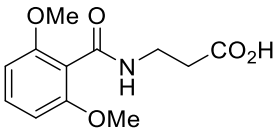
^{13}C-NMR (126 MHz, $(CD_3)_2CO$): δ = 173.2, 170.7, 149.9, 145.6, 135.5, 121.3, 36.0, 35.1, 34.2, 31.5, 24.9, 24.4 ppm

HRMS (ESIpos) m/z: Calcd for $C_{19}H_{30}NO_3$ 320.2220, Found 320.2213.

IR (cm^{-1}): 3298, 2959, 1705, 1619, 1527, 1431, 1311, 1275, 1183, 1112, 1054, 766.

Melting Point: 186 °C

3-(2,6-dimethoxybenzamido)propanoic acid (L13)



Following the general procedure **C** using 2,6-dimethoxybenzoyl chloride (1.4 g) the target compound **L13** was obtained as a colorless solid (1.3 g, 4.1 mmol, 58%).

^{1}H-NMR (500 MHz, $(CD_3)_2CO$): δ = 7.25 (t, *J* = 8.4 Hz, 1H), 6.62 (d, *J* = 8.4 Hz, 2H), 3.75 (s, 6H), 3.56 (t, *J* = 6.8 Hz, 2H), 2.63 (t, *J* = 6.8 Hz, 2H) ppm.

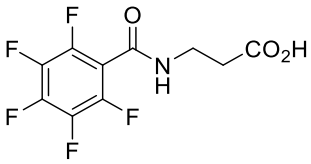
^{13}C-NMR (125 MHz, $(CD_3)_2CO$): δ = 173.3, 165.7, 131.0, 118.0, 104.9, 56.2, 35.9, 34.4 ppm.

HRMS (ESIpos) m/z: Calcd for $C_{12}H_{16}NO_5$ 254.1023, Found 254.1020

IR (cm^{-1}): 3271, 2972, 1708, 1599, 1574, 1477, 1434, 1255, 1108, 1029, 788

Melting Point: 149.7 °C

3-(perfluorobenzamido)propanoic acid (L14)



Following the general procedure **C** using 2,3,4,5,6-pentafluorobenzoyl chloride (1.6 g) the target compound **L14** was obtained as a colorless solid (1.5 g, 5.3 mmol, 76%).

^{1}H-NMR (500 MHz, $(CD_3)_2CO$): δ = 8.07 (s, 1H), 3.66 (q, *J* = 6.4 Hz, 2H), 2.66 (t, *J* = 6.6 Hz, 2H) ppm.

^{13}C-NMR (126 MHz, $(CD_3)_2CO$): δ = 173.0, 157.8, 145.8-143.6 (m), 141.7-141.6 (m), 139.5-137.2 (m), 113.9-113.6 (m), 36.6, 34.0 ppm.

^{19}F NMR (471 MHz, $(CD_3)_2CO$): δ = –142.4 - –142.5 (m), –154.4 - –154.5 (m), –162.5 - –162.6 (m) ppm.

HRMS (ESIpos) m/z: Calcd for $C_{10}H_6F_5NO_3Na$ 306.0160, Found 306.0157

IR (cm^{-1}): 3246, 2981, 1705, 1651, 1488, 1339, 1275, 1032, 989, 797

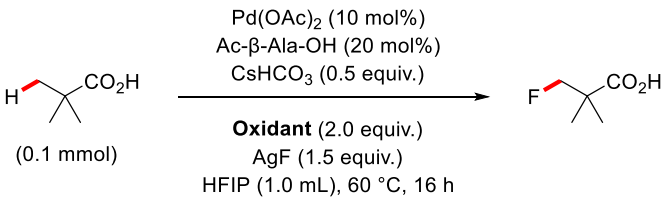
Melting Point: 155.9 °C

4. Optimization of the Reaction Conditions

General Procedure for the Optimization Reactions:

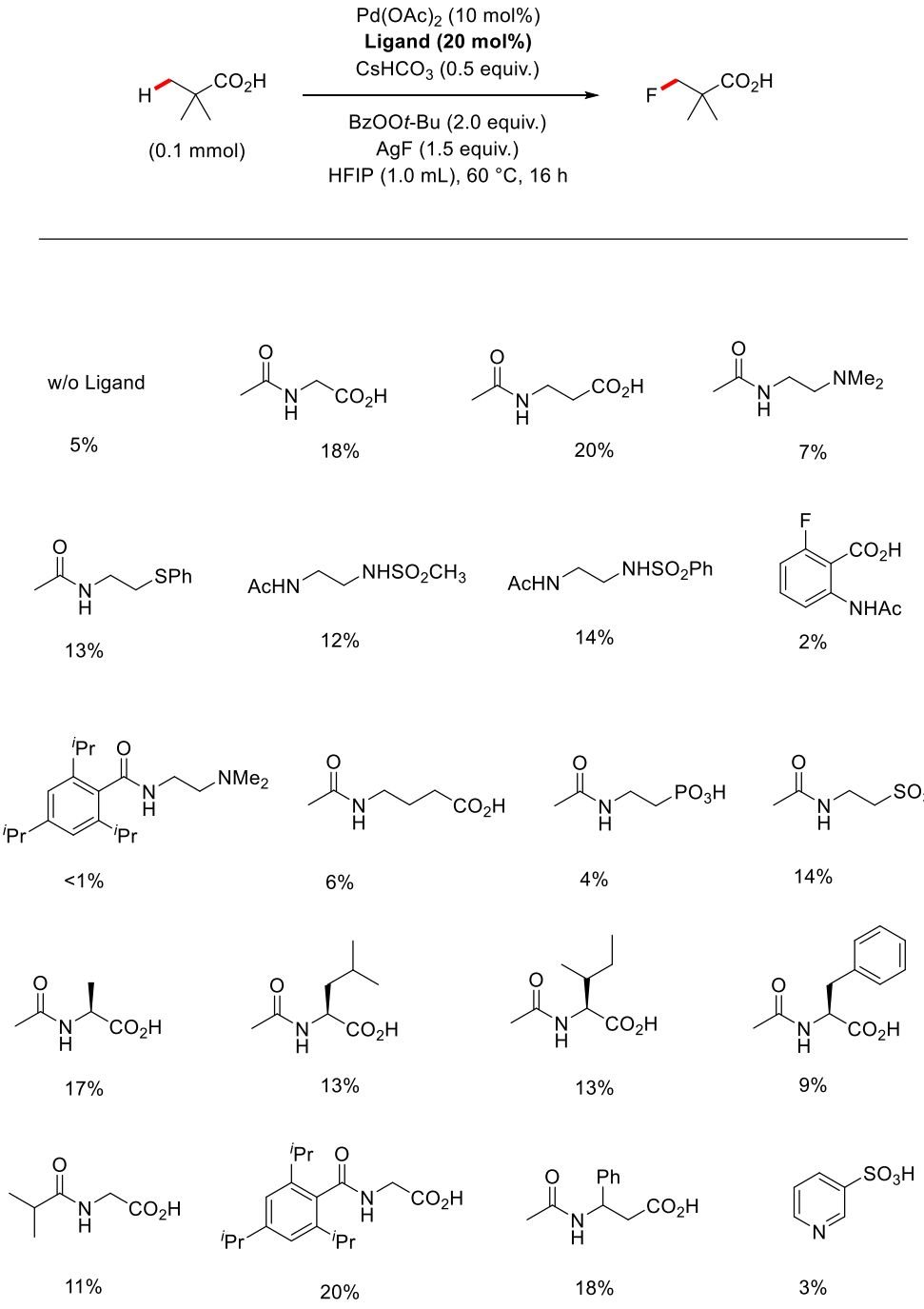
An oven dried 10 mL Schlenk tube was charged with $Pd(OAc)_2$, ligand, base, oxidant, silver fluoride, carboxylic acid (0.1 mmol) and HFIP (This order of addition was same throughout the optimization studies). The vessel was placed into a preheated aluminum block and the reaction mixture was stirred (stirring speed = 900 rpm) at the indicated temperature. After the indicated time, the reaction mixture was allowed to cool to room temperature. Formic acid (0.1 mL) was added to the reaction mixture and it was filtered over a pad of Celite®. The residue was washed with CH_2Cl_2 (30 mL) followed by addition of 1,3,5-trimethoxybenzene (16.8 mg, 0.100 mmol) as internal standard. All volatiles were removed under reduced pressure. $CDCl_3$ (0.8 mL) was used to prepare a sample for NMR analysis. All yields during the optimization studies were determined by ^{1}H-NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as internal standard.

Optimization for α-Quaternary Carboxylic Acids:

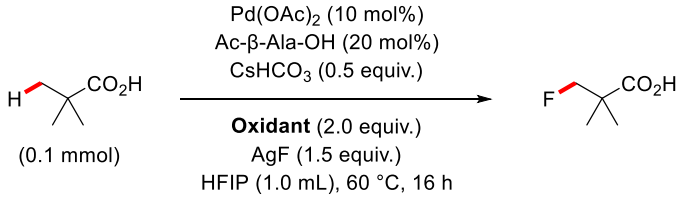


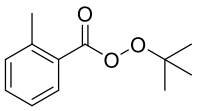
Entry	Oxidant	NMR-Yield (%)	Entry	Oxidant	NMR-Yield (%)
1.	w/o	0	7.	H_2O_2	3
2.	TBHP (ca 5.5 M in decane)	15	8.	*m*CPBA	0
3.	TBHP (70% in H_2O)	13	9.	$PhI(OAc)_2$	3
4.	$(t\text{-BuO})_2$	N.D	10.	AcO*t*-Bu	18
5.	BzO*t*-Bu	20	11.	NFSI	3
6.	BzOOBz	18	12.	Selectfluor	3

Scheme S1: Preliminary screening of oxidants.

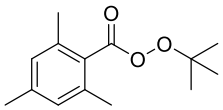


Scheme S2: Screening of ligands with BzOO*t*-Bu

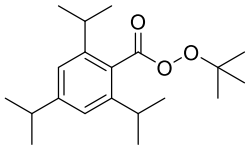




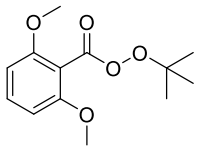
OX5, 14%



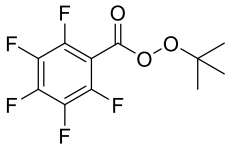
OX7, 5%



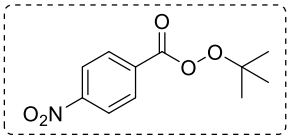
OX8, 7%



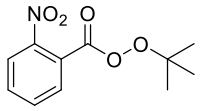
OX9, 1%



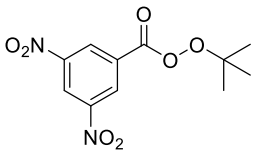
OX10, 14%



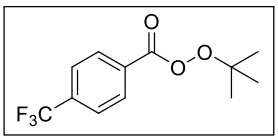
OX1, 34%



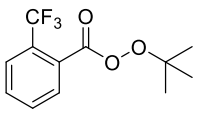
OX11, 24%



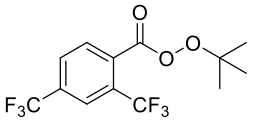
OX12, 22%



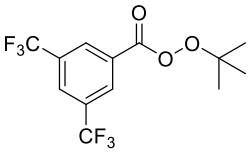
OX13, 31%



OX14, 21%

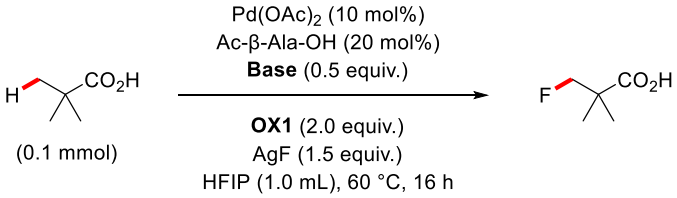


OX15, 20%



OX16, 27%

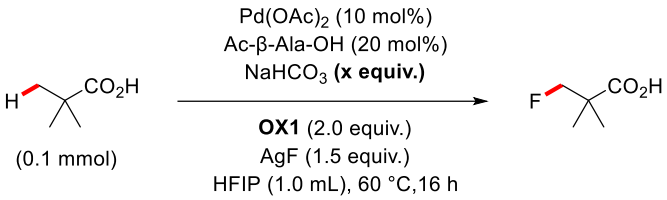
Scheme S3: Optimization of the oxidant structure



(0.1 mmol)

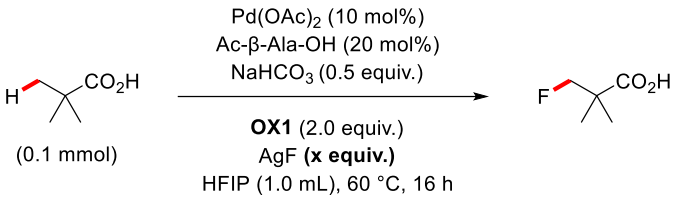
Entry	Base	NMR-Yield (%)
1.	$Na_2HPO_4 \cdot 7H_2O$	16
2.	Na_2HPO_4	24
3.	Na_2CO_3	34
4.	$NaHCO_3$	35
5.	$NaOAc \cdot 3H_2O$	15
6.	NaTFA	22
7.	K_2HPO_4	9
8.	KH_2PO_4	8
9.	K_2CO_3	33
10.	$KHCO_3$	26
11.	KOAc	35
12.	KHFIP	29
13.	K_3PO_4	<1%
14.	LiHFIP	33
15.	Cs_2CO_3	28
16.	CsOAc	24

Scheme S4: Screening of bases with new oxidant (OX1)



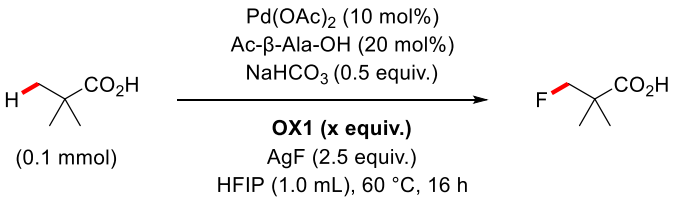
Entry	x (equiv.)	NMR-Yield (%)
1.	0.25	32
2.	0.5	35
3.	0.75	31
4.	1.0	23

Scheme S5: Screening of equivalents of $NaHCO_3$



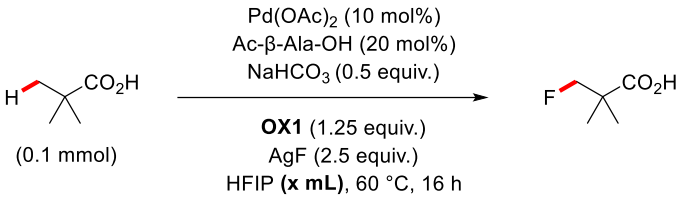
Entry	x (equiv.)	NMR-Yield (%)
1.	1.25	27
2.	1.5	35
3.	2.0	36
4.	2.5	40
5.	3.0	37

Scheme S6: Screening of equivalents of silver fluoride



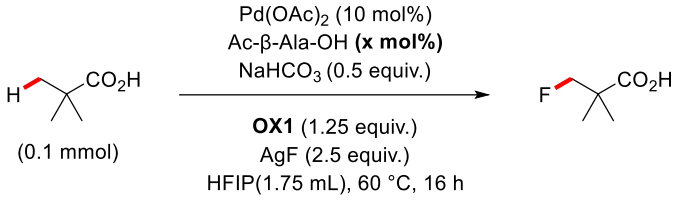
Entry	x (equiv.)	NMR-Yield (%)
1.	1.0	32
2.	1.25	40
3.	1.5	39
4.	2.0	40
5.	2.5	36

Scheme S7: Screening of equivalents of oxidant (OX1)



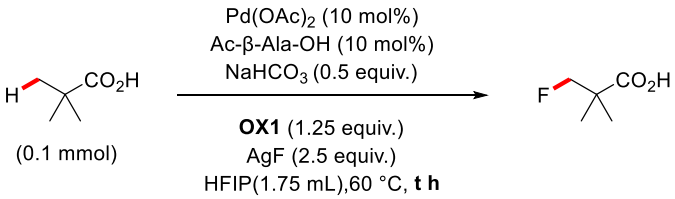
Entry	x (mL)	NMR-Yield (%)
1.	1.0	40
2.	1.25	39
3.	1.5	42
4.	1.75	45
5.	2.0	41

Scheme S8: Screening of solvent volume



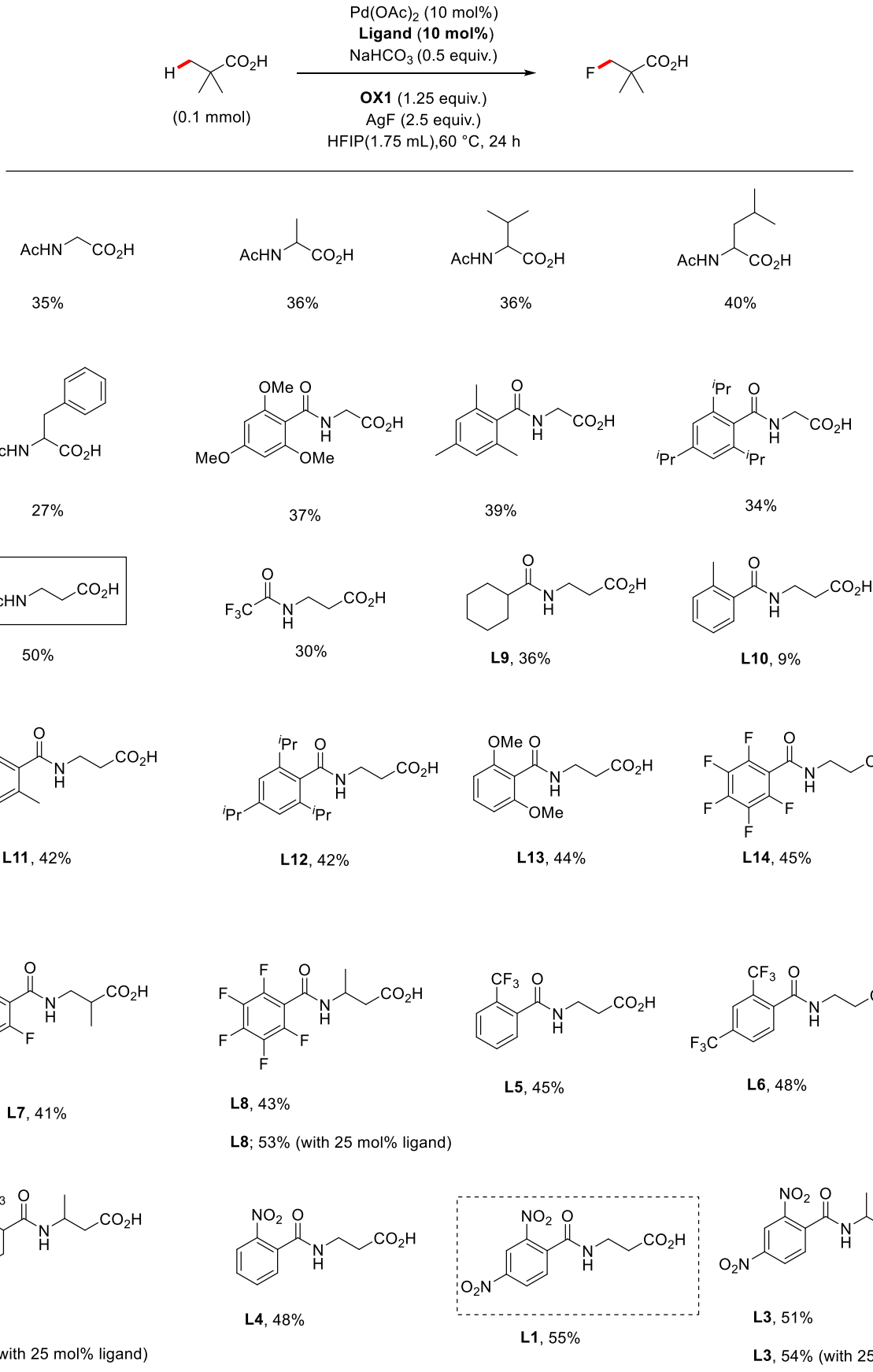
Entry	x (mol%)	NMR-Yield (%)
1.	10	45
2.	15	44
3.	20	45

Scheme S9: Screening of ligand loading

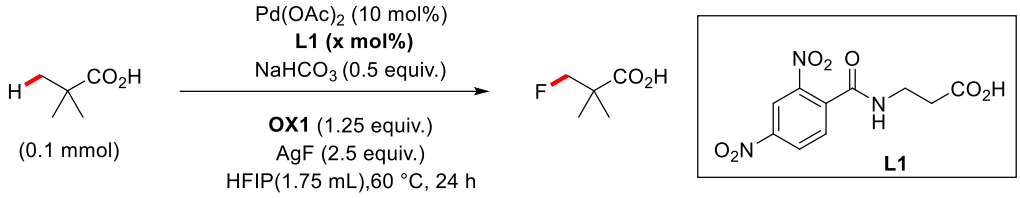


Entry	t (h)	NMR-Yield (%)
1.	16	45
2.	24	50
3.	48	48
4.	72	47

Scheme S10: Time screening

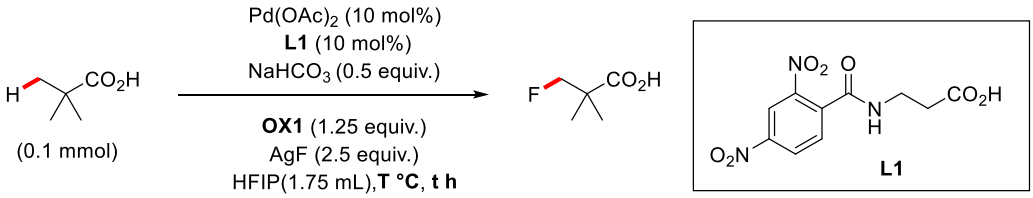


Scheme S11: Re-evaluation of ligand structure with the oxidant (OX1)



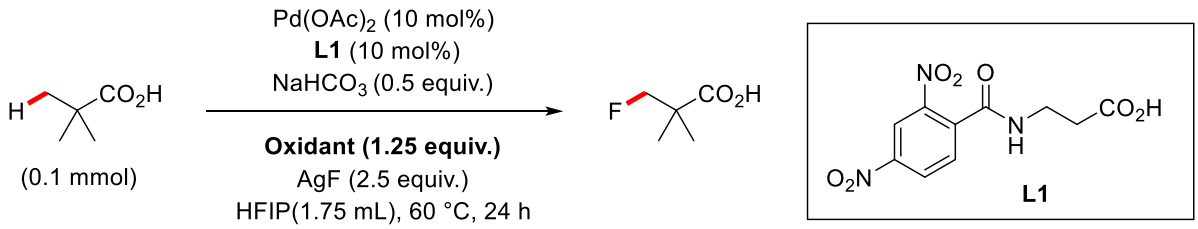
Entry	x (mol%)	NMR-Yield (%)
1.	10	55
2.	15	49
3.	20	50
4.	25	48

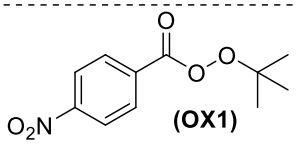
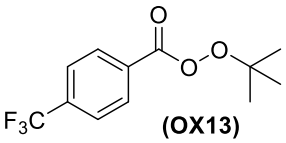
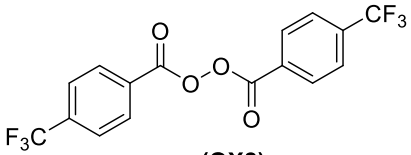
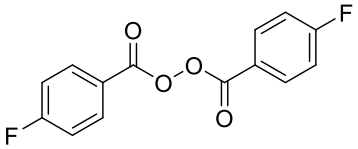
Scheme S12: Screening of ligand (L1) loading



T (°C)	t (h)	NMR-Yield (%)
50	24	51
	48	55
	72	48
55	24	50
	48	54
	72	53
65	24	48
	36	51
	48	47

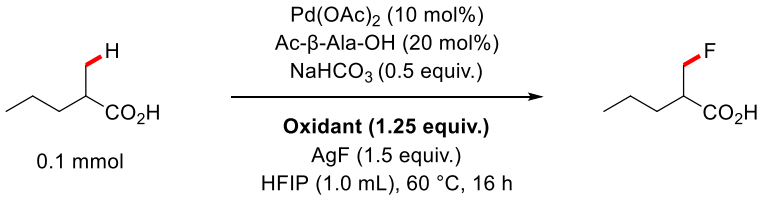
Scheme S13: Temperature and time screening with L1

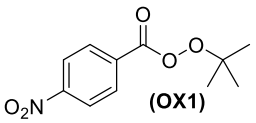
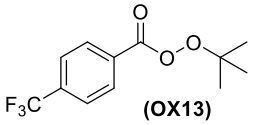
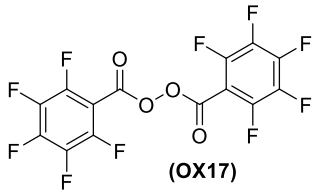
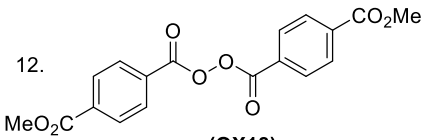
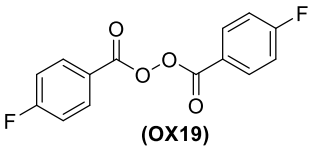
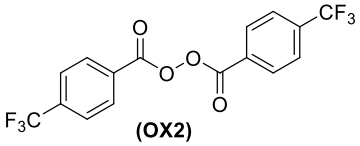
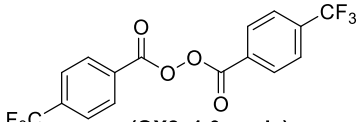
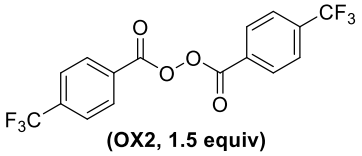
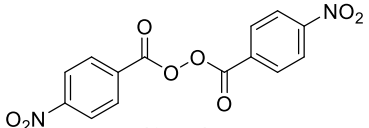
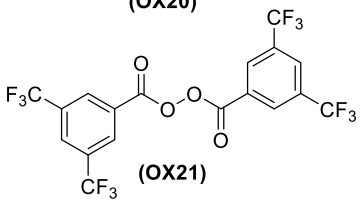


Entry	Oxidant	NMR-Yield (%)
1.	TBHP (ca 5.5 M in decane)	20
2.	BzOO*t*-Bu	21
3.	BzOOBz	24
4.	 (OX1)	55
5.	 (OX13)	44
6.	 (OX2)	42
7.	 (OX19)	30

Scheme S14: Re-screening of oxidants with L1

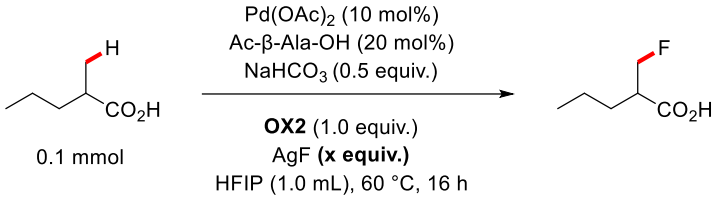
Optimization for α-Non-Quaternary Carboxylic Acids



Entry	Oxidant	NMR-Yield (%)
1.	TBHP (70% in H_2O)	4
2.	TBHP (ca 5.5 M in decane)	5
3.	BzOO*t*-Bu	2
4.	BzOOBz	5
5.	H_2O_2	4
6.	$K_2S_2O_8$	3
7.	$PhI(OAc)_2$	3
8.	Selectfluor	5
9.	 (OX1)	3
10.	 (OX13)	3
11.	 (OX17)	<1
12.	 (OX18)	3
13.	 (OX19)	16
14.	 (OX2)	17
15.	 (OX2, 1.0 equiv)	17
16.	 (OX2, 1.5 equiv)	15
17.	 (OX20)	12
18.	 (OX21)	15

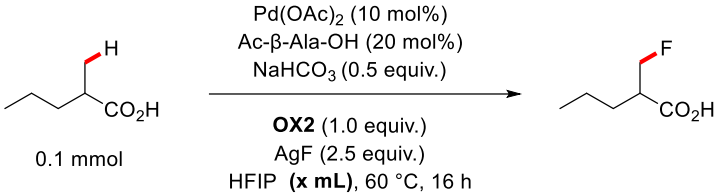
S

Scheme S15: Screening of various oxidants



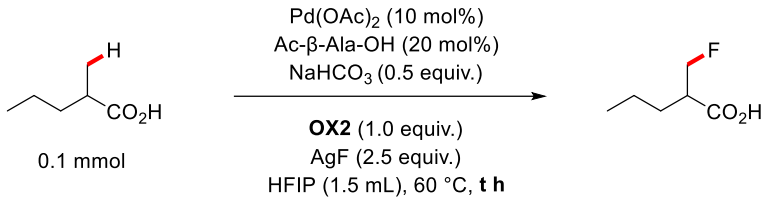
Entry	x (equiv.)	NMR-Yield (%)
1.	1.0	10
2.	1.5	17
3.	2.0	19
4.	2.5	21
5.	3.0	20

Scheme S16: Screening of equivalents of silver fluoride



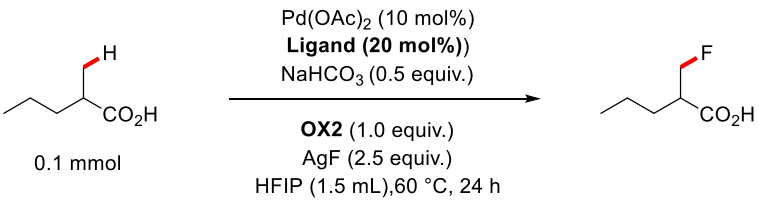
Entry	x (mL)	NMR-Yield (%)
1.	1.0	22
2.	1.25	21
3.	1.5	25
4.	1.75	23
5.	2.0	20

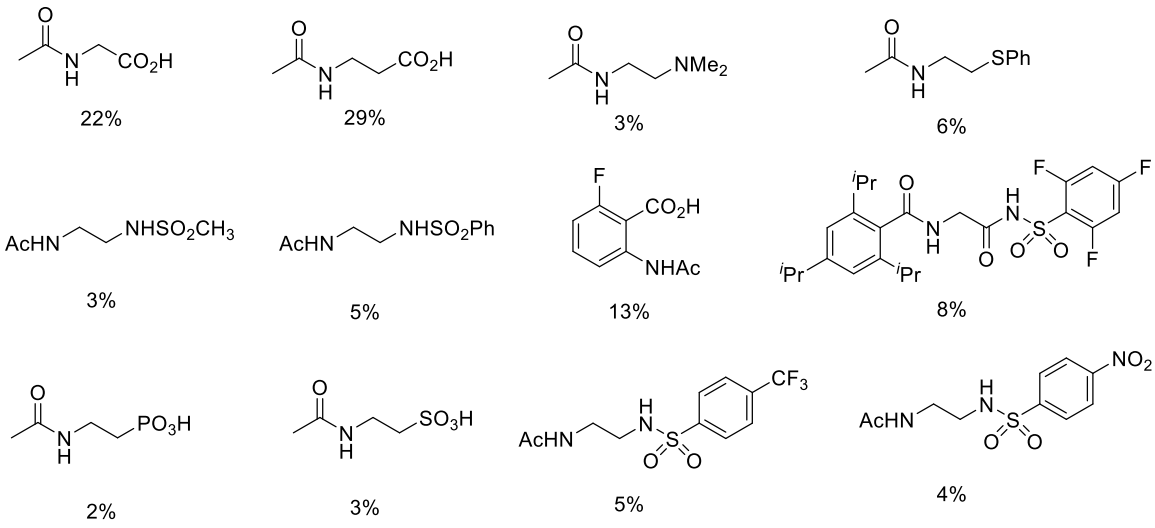
SchemeS17: Screening of solvent volume



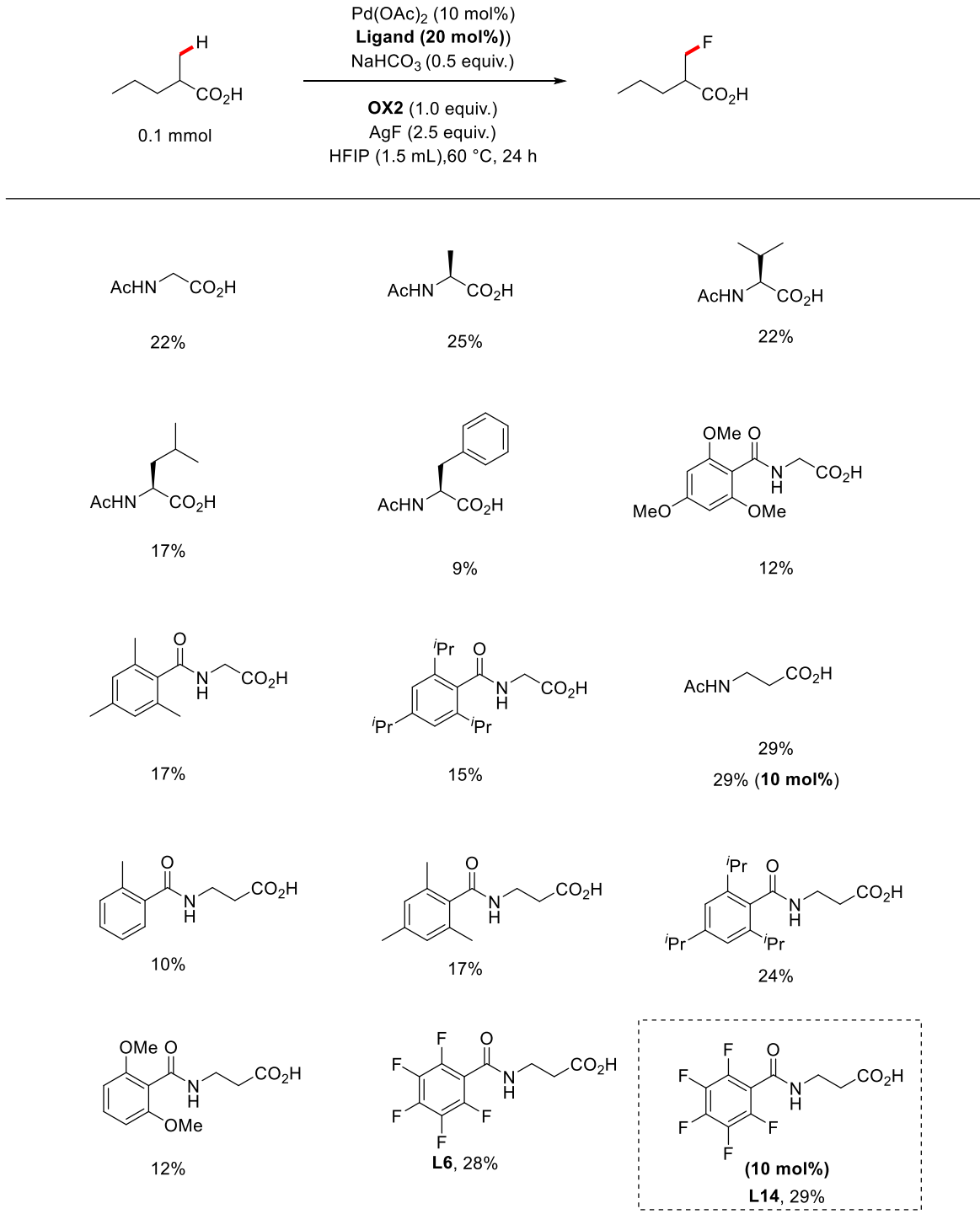
Entry	t (h)	NMR-Yield (%)
1.	16	25
2.	24	29
3.	36	25
4.	48	24

Scheme S18: Time screening

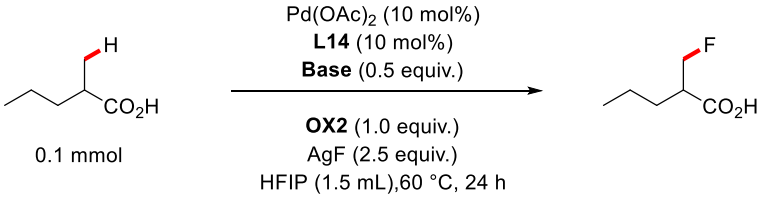




Scheme S19: Screening of different ligand classes

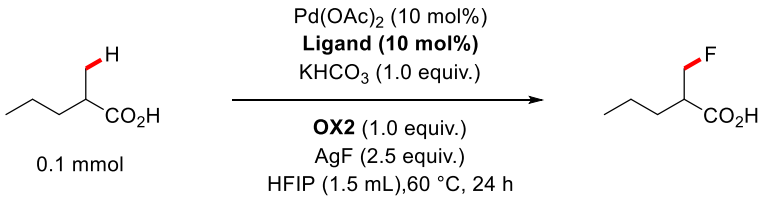


Scheme S20: Screening of amino acid derivatives

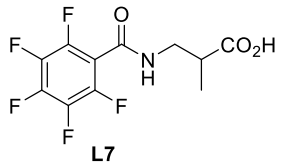
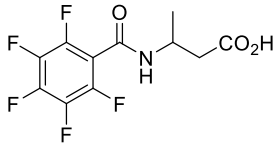
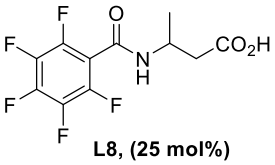
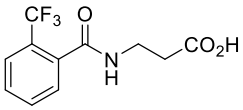
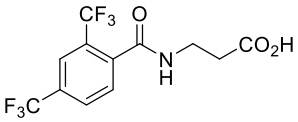
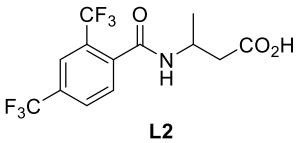
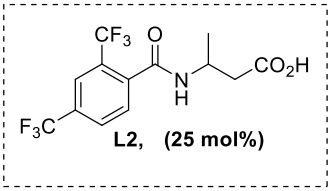
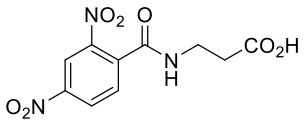


Entry	Base	NMR-Yield (%)
1.	$Na_2HPO_4 \cdot 7H_2O$	16
2.	Na_2HPO_4	25
3.	Na_2HPO_4 (0.75 equiv)	20
4.	Na_2CO_3	22
5.	$NaHCO_3$	29
6.	$NaHCO_3$ (0.75 equiv)	24
7.	$NaOAc \cdot 3H_2O$	25
8.	$NaOAc.3H_2O$ (0.75 equiv)	19
9.	NaTFA	22
10.	K_2HPO_4	14
11.	K_2CO_3	20
12.	$KHCO_3$	28
13.	$KHCO_3$ (0.75 equiv)	30
14.	$KHCO_3$ (**1.0 equiv**)	32
15.	$KHCO_3$ (**1.25 equiv**)	27
16.	KOAc	24
17.	Cs_2CO_3	17
18.	$CsHCO_3$	26

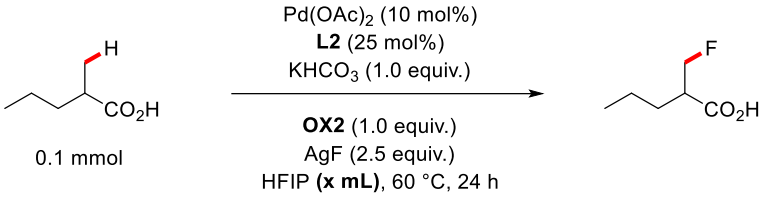
Scheme S21: Screening of bases



0.1 mmol

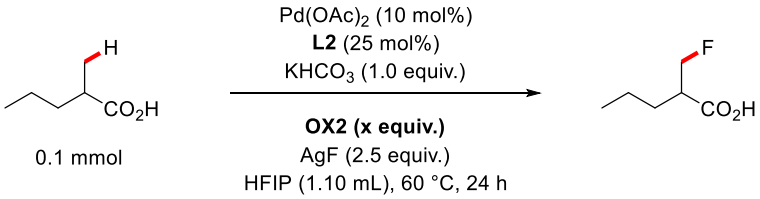
Entry	Ligand	NMR-Yield(%)
1.	 L7	25%
2.	 L8	32%
3.	 L8, (25 mol%)	41%
4.	 L5	27%
5.	 L6	36%
6.	 L2	33%
7.	 L2, (25 mol%)	44%
8.	 L1	32%

Screening S22: Final optimization of ligand structure



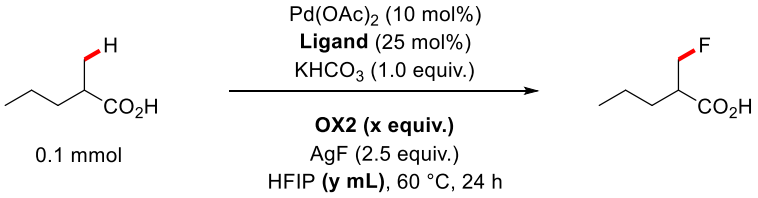
Entry	x (mL)	NMR-Yield (%)
1.	1.0 mL	40%
2.	1.10 mL	44%
3.	1.25 mL	43%
4.	1.5 mL	44%

Scheme S23: Re-screening of solvent volume

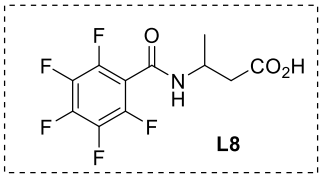
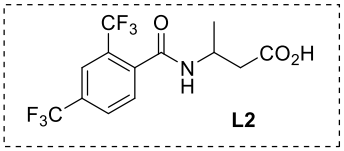


Entry	x (equiv.)	NMR-Yield (%)
1.	1.0	44
2.	1.25	44
3.	1.5	46
4.	1.75	51
5.	2.0	46

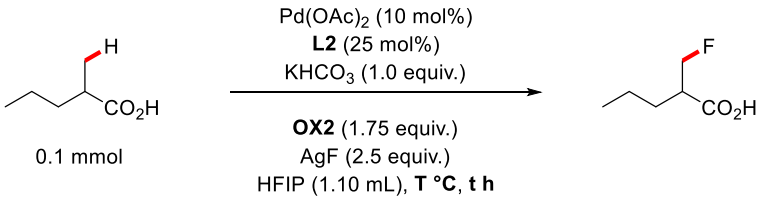
Scheme S24: Screening of equivalents of oxidant



0.1 mmol

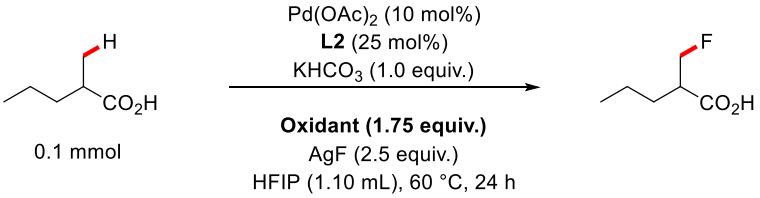
Ligand	x (equiv.)	y (mL)	NMR-Yield (%)
 **L8**	x = 1.0 eq.	y = 1.1 mL	40%
	x = 1.0 eq.	y = 1.5 mL	43%
	x = 1.75 eq.	y = 1.1 mL	40%
	x = 1.75 eq.	y = 1.5 mL	38%
 **L2**	x = 1.0 eq.	y = 1.1 mL	44%
	x = 1.0 eq.	y = 1.5 mL	43%
	x = 1.75 eq.	y = 1.1 mL	51%
	x = 1.75 eq.	y = 1.5 mL	46%

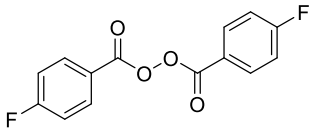
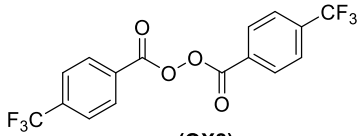
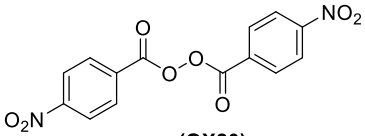
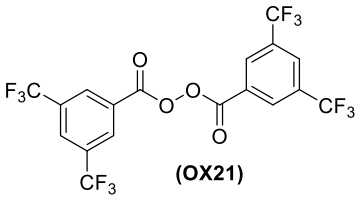
Scheme S25: Screening of oxidant and solvent amount with L2 and L8



Temperature (**T**)	Reaction time (**t**)	NMR Yield (%)
T = 50 °C	t = 24 h	45%
	t = 48 h	41%
	t = 72 h	40%
T = 55 °C	t = 24 h	45%
	t = 48 h	39%
	t = 72 h	40%
T = 65 °C	t = 24 h	40%
	t = 36 h	38%
	t = 48 h	38%

Scheme S26: Temperature and time screening with L2



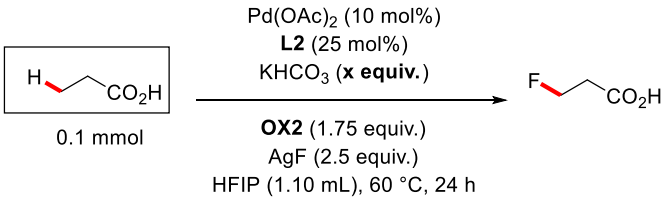
Entry	Oxidant	NMR-Yield (%)
1.	TBHP (ca 5.5 M in decane)	29
2.	BzOO*t*-Bu	20
3.	BzOOBz	23
4.	 **(OX15)**	38
5.	 **(OX2)**	51
6.	 **(OX20)**	28
7.	 **(OX21)**	30

Scheme S27: Re-screening of oxidant with newly optimized conditions

Investigation of Propionic Acid as Substrate for the β-C(sp^3)–H Fluorination

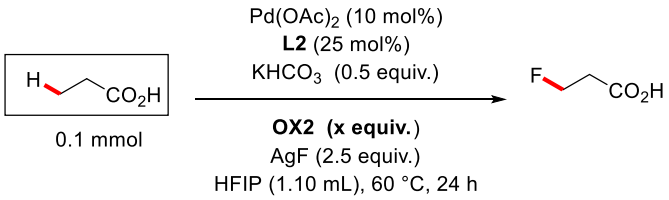
Entry	Conditions	NMR-Yield (%)
1.	**Conditions A**	< 3
2.	**Conditions B**	7

Scheme S28: Screening of the previously optimized conditions



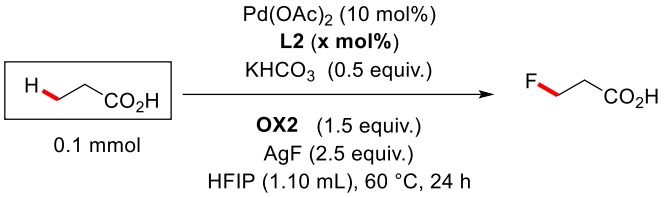
Entry	x (equiv.)	NMR-Yield (%)
1.	1.0	7
2.	0.75	10
3.	0.5	12
4.	0.25	9

Scheme S29: Re-screening of base amount



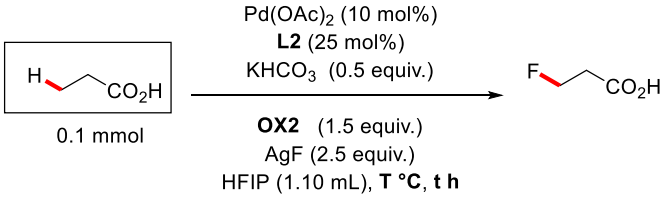
Entry	x (equiv.)	NMR-Yield (%)
1.	2.0	11
2.	1.75	12
3.	1.50	16
4.	1.25	14
5.	1.25	12

Scheme S30: Re-screening of oxidant amount



Entry	x (mol%)	NMR-Yield (%)
1.	30	14%
2.	25	16%
3.	20	13%
4.	15	10%
5.	10	8%

Scheme S31: Re-screening of ligand loading

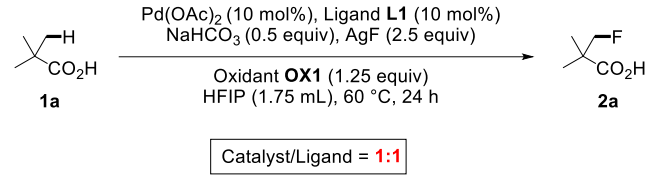


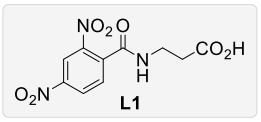
Temperature (T)	Reaction time (t)	NMR Yield (%)
T = 50 °C	t = 24 h	13
	t = 48 h	11
	t = 72 h	10
T = 60 °C	t = 24 h	16
	t = 48 h	13
	t = 72 h	11
T = 70 °C	t = 24 h	11
	t = 36 h	9
	t = 48 h	8

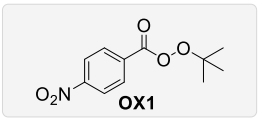
Scheme S32: Re-screening of temperature and time

Plausible rationalization for the different catalyst to ligand ratio in Conditions A and Conditions B

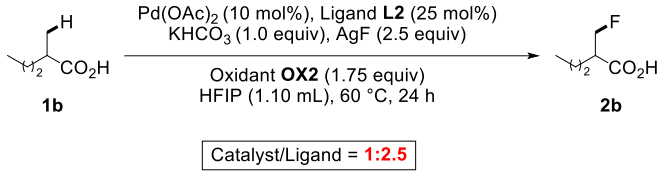
Conditions A: α- quaternary substrates

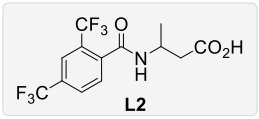


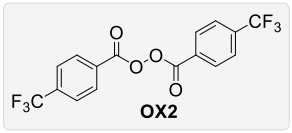




Conditions B: α-non-quaternary substrates

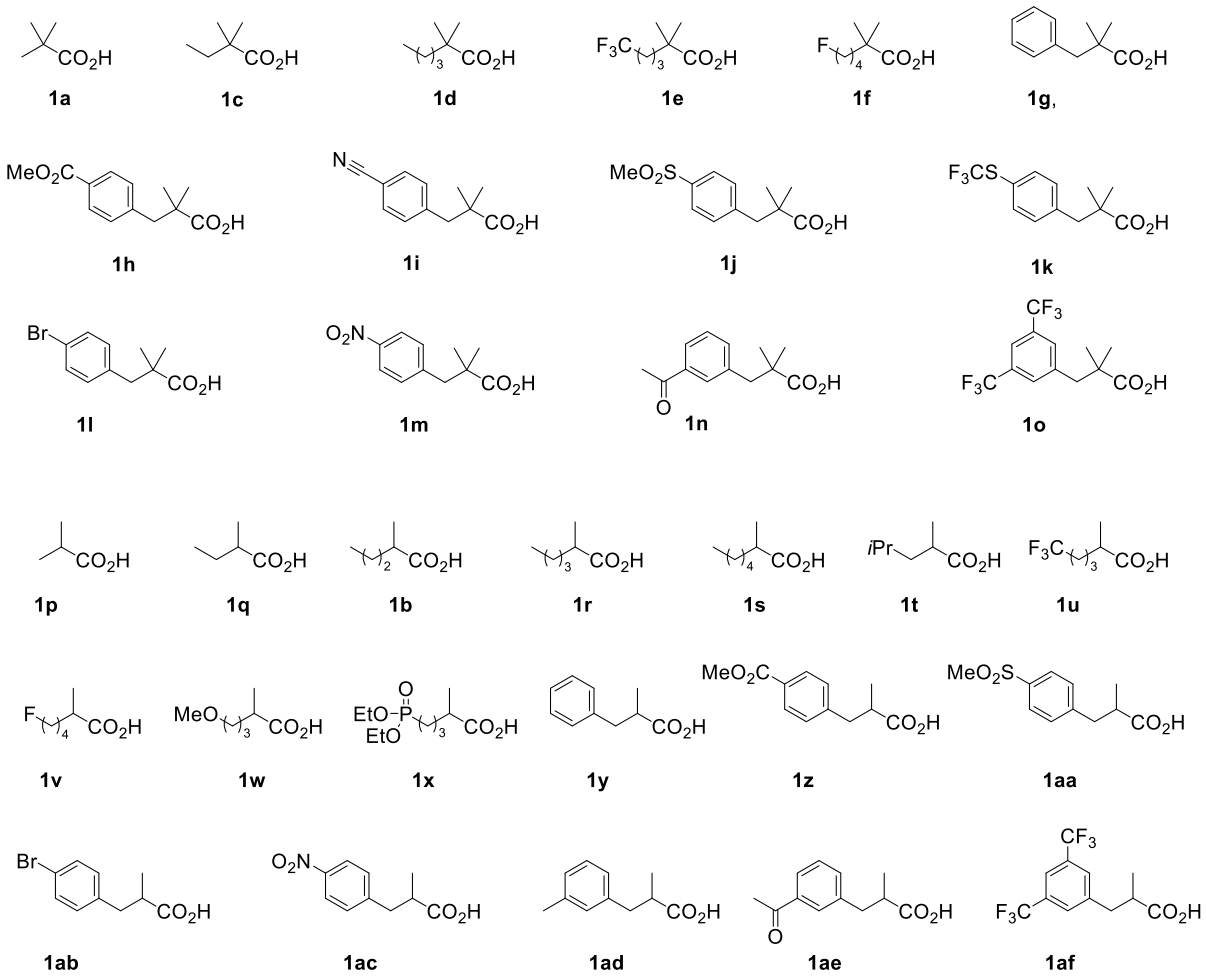






The peroxide-based oxidants with the general structure YOOZ, after oxidative addition with Pd(II), generate side products YO^- and ZO^-. While **OX1** produces (4-NO_2)$PhCOO^-$ and *t*-BuO^- as side products, **OX2**, produces **2** × (4-CF_3)$PhCOO^-$ as side product in the reaction mixture. Therefore, the concentration of carboxylate generated from the oxidant is twice as high in case of **Conditions B** compared to **Conditions A**. Considering the well-known coordinating ability of carboxylate with palladium, these carboxylates can compete with the bidentate ligand for coordination to palladium. Thus, **Conditions B** require a higher loading of the bidentate ligand to ensure that the active catalyst can form despite the higher carboxylate amounts forming over the course of the reaction.

5. Synthesis of Starting Materials



Aliphatic carboxylic acids were obtained commercially available or synthesized following the literature procedures.[10-12]

6. Scope Studies

General Procedure D: Fluorination of α-Quaternary Carboxylic Acids and Isolation as the Corresponding Benzyl Ester

An oven dried 10 mL Schlenk tube was charged with $Pd(OAc)_2$ (4.5 mg, 0.020 mmol, 10 mol%), **L1** (5.7 mg, 0.020 mmol, 10 mol%), $NaHCO_3$ (8.4 mg, 0.10 mmol, 0.5 equiv.), **OX1** (59.8 mg, 0.250 mmol, 1.25 equiv.), AgF (63.4 mg, 0.500 mmol, 2.5 equiv.), carboxylic acid (0.2 mmol, 1.0 equiv.) and HFIP (3.5 mL). The reaction mixture was stirred (stirring speed = 900 rpm) at 60 °C for 24 h in a preheated metal block. The reaction mixture was allowed to cool to rt and formic acid (0.2 mL) was added. The mixture was filtered through a pad of Celite® using CH_2Cl_2 (35 mL) to complete the elution and the volatiles were removed under reduced pressure. K_2CO_3 (138 mg**,** 1.00 mmol, 5 equiv.), NaI (4.5 mg, 0.060 mmol, 0.3 equiv.), benzyl bromide (118 µL, 1.00 mmol, 5.0 equiv.) and acetone (5 mL) were added and the resulting mixture was stirred at rt for 24 h. The mixture was filtered through a pad of Celite® using CH_2Cl_2 (25 mL) to complete the elution, all volatiles were removed under reduced pressure, and the residue was purified by silica gel column chromatography (In general, the length of the silica bed should be between 45 to 50 cm for a successful separation)

General Procedure E: Fluorination of α-Quaternary Carboxylic Acids and Isolation as the Corresponding Naphthyl Ester

An oven dried 10 mL Schlenk tube was charged with $Pd(OAc)_2$ (4.5 mg, 0.020 mmol, 10 mol%), **L1** (5.7 mg, 0.020 mmol, 10 mol%), $NaHCO_3$ (8.4 mg, 0.10 mmol, 0.5 equiv.), **OX1** (59.8 mg, 0.250 mmol, 1.25 equiv.), AgF (63.4 mg, 0.500 mmol, 2.5 equiv.), carboxylic acid (0.2 mmol, 1.0 equiv.) and HFIP (3.5 mL). The reaction mixture was stirred (stirring speed = 900 rpm) at 60 °C for 24 h in a preheated metal block. The reaction mixture was allowed to cool to rt and formic acid (0.2 mL) was added. The mixture was filtered through a pad of Celite® using CH_2Cl_2 (35 mL) to complete the elution and the volatiles were removed under reduced pressure. K_2CO_3 (138 mg, 1.00 mmol, 5.0 equiv.), NaI (4.5 mg, 0.060 mmol, 0.3 equiv.), 2-(Bromomethyl)naphthalene (220 mg, 1.00 mmol, 5.0 equiv.) and acetone (5 mL) were added and the resulting mixture was stirred at rt for 24 h. The mixture was filtered through a pad of Celite® using CH_2Cl_2 (25 mL) to complete the elution, all volatiles were removed under reduced pressure, and the residue was purified by silica gel column chromatography.

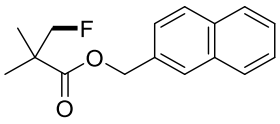
General Procedure F: Fluorination of α-Non-Quaternary Carboxylic Acids and Isolation as the Corresponding Benzyl Ester

An oven dried 10 mL Schlenk tube was charged with $Pd(OAc)_2$ (4.5 mg, 0.020 mmol, 10 mol%), **L2** (17.2 mg, 50.0 µmol, 25 mol%), $KHCO_3$ (20 mg, 0.20 mmol, 1.0 equiv.), **OX2** (132.4 mg, 350.0 µmol, 1.75 equiv.), AgF (63.4 mg, 0.500 mmol, 2.5 equiv.), carboxylic acid (0.2 mmol, 1.0 equiv.) and HFIP (2.2 mL). The reaction mixture was stirred (stirring speed = 900 rpm) at 60 °C for 24 h in a preheated metal block. The reaction mixture was allowed to cool to rt and formic acid (0.2 mL) was added. The mixture was filtered through a pad of Celite® using CH_2Cl_2 (35 mL) to complete the elution and the volatiles were removed under reduced pressure. Cs_2CO_3 (425 mg, 1.00 mmol, 6.5 equiv.) , NaI (75 mg, 0.050 mmol, 2.5 equiv.), benzyl bromide (118 µL, 1.00 mmol, 5.0 equiv.) and acetone (5 mL) were added and the resulting mixture was stirred at rt for 24 h. The mixture was filtered through a pad of Celite® using CH_2Cl_2 (25 mL) to complete the elution, all volatiles were removed under reduced pressure, and the residue was purified by silica gel column chromatography.

General Procedure G: Fluorination of α-Non-Quaternary Carboxylic Acids and Isolation as the Corresponding Naphthyl Ester

An oven dried 10 mL Schlenk tube was charged with $Pd(OAc)_2$ (4.5 mg, 0.020 mmol, 10 mol%), **L2** (17.2 mg, 50.0 µmol, 25 mol%), $KHCO_3$ (20 mg, 0.20 mmol, 1.0 equiv.), **OX2** (132.4 mg, 350.0 µmol, 1.75 equiv.), AgF (63.4 mg, 0.500 mmol, 2.5 equiv.), carboxylic acid (0.2 mmol, 1.0 equiv.) and HFIP (2.2 mL). The reaction mixture was stirred (stirring speed = 900 rpm) at 60 °C for 24 h in a preheated metal block. The reaction mixture was allowed to cool to rt and formic acid (0.2 mL) was added. The mixture was filtered through a pad of Celite® using CH_2Cl_2 (35 mL) to complete the elution and the volatiles were removed under reduced pressure. Cs_2CO_3 (425 mg, 1.00 mmol, 6.5 equiv.), NaI (75 mg, 0.050 mmol, 2.5 equiv.), 2-(Bromomethyl)naphthalene (220 mg, 1.00 mmol, 5.0 equiv.) and acetone (5 mL) were added and the resulting mixture was stirred at rt for 24 h. The mixture was filtered through a pad of Celite® using CH_2Cl_2 (25 mL) to complete the elution, all volatiles were removed under reduced pressure, and the residue was purified by silica gel column chromatography.

Naphthalen-2-ylmethyl 3-fluoro-2,2-dimethylpropanoate (2a-Naph):



2a-Naph

Following the general procedure **E**, using **1a** (20.4 mg) and pentane/EtOAc (99:1 v/v) as an eluent, the target compound **2a-Naph** was obtained as a pale yellow oil (33.2 mg, 0.110 mmol, 55%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.87 – 7.84 (m, 4H), 7.52 – 7.48 (m, 2H), 7.46 (dd, *J* = 8.5, 1.9 Hz, 1H), 5.33 (s, 2H), 4.45 (d, *J* = 47.1 Hz, 2H), 1.28 (d, *J* = 1.6 Hz, 6H) ppm.

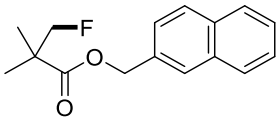
^{13}C-NMR (126 MHz, $CDCl_3$): δ = 175.2 (d, *J* = 3.7 Hz), 133.5, 133.3, 133.2, 128.5, 128.1, 127.8, 127.2, 126.5, 126.4, 125.7, 88.7 (d, *J* = 174.6 Hz), 66.8, 43.9 (d, *J* = 18.8 Hz), 21.4 (d, *J* = 5.5 Hz) ppm.

^{19}F NMR (471 MHz, $CDCl_3$): δ = –222.4 (s, 1F), –229.3 (s, 0.40 F, di-fluorinated product, 20%) ppm. [Mono/Di = y (mmol): 0.2y (mmol) = 5:1]

HRMS (EI) m/z: Calcd for $C_{16}H_{17}FO_2$ 260.1212, Found 260.1212

HRMS (EI) m/z (di-fluorinated product)**:** Calcd for $C_{16}H_{16}F_2O_2$ 278.11184, Found 278.11182

Naphthalen-2-ylmethyl 3-fluoro-2,2-dimethylpropanoate (2a-Naph):



2a-Naph

Following the general procedure **E** using **OX1** (47.8 mg, 0.200. mmol, **1.00 equiv.**) and **1a** (51.1 mg, 0.500 mmol, **2.5 equiv.**), the target compound **2a-Naph** was obtained as a pale yellow oil (31.8 mg, 0.122 mmol, 61%) using pentane/EtOAc (99:1 v/v) as an eluent.

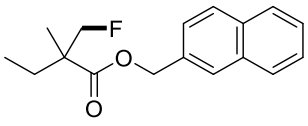
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.87 – 7.84 (m, 4H), 7.52 – 7.48 (m, 2H), 7.46 (dd, *J* = 8.5, 1.9 Hz, 1H), 5.33 (s, 2H), 4.45 (d, *J* = 47.1 Hz, 2H), 1.28 (d, *J* = 1.6 Hz, 6H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 175.2 (d, *J* = 3.7 Hz), 133.5, 133.3, 133.2, 128.5, 128.1, 127.8, 127.2, 126.5, 126.4, 125.7, 88.7 (d, *J* = 174.6 Hz), 66.8, 43.9 (d, *J* = 18.8 Hz), 21.4 (d, *J* = 5.5 Hz) ppm.

^{19}F NMR (471 MHz, $CDCl_3$): δ = –222.4 (s).

HRMS (EI) m/z: Calcd for $C_{16}H_{17}FO_2$ 260.1212, Found 260.1212

Naphthalen-2-ylmethyl 2-(fluoromethyl)-2-methylbutanoate (2c-Naph)



2c-Naph

Following the general procedure **E,** using **1c** (23.2 mg) and pentane/EtOAc (99:1 v/v) as an eluent, the target compound **2c-Naph** was obtained as a pale yellow oil (35.8 mg, 0.130 mmol, 65%).

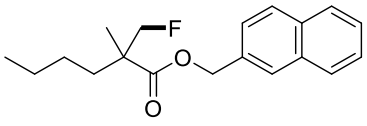
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.86 – 7.82 (m, 4H), 7.52-7.48 (m, 2H), 7.46 (dd, *J* = 8.5, 1.9 Hz, 1H), 5.33 (s, 2H), 4.58 (dd, *J* = 47.2, 8.9 Hz, 1H), 4.41 (dd, *J* = 47.2, 8.9 Hz, 1H), 1.77 – 1.54 (m, 2H), 1.29 (d, *J* = 1.5 Hz, 3H), 0.88 (t, *J* = 7.5 Hz, 3H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 174.7 (d, *J* = 4.6 Hz), 133.5, 133.3, 133.2, 128.5, 128.1, 127.8, 127.3, 126.4, 126.4, 125.8, 87.3 (d, *J* = 173.7 Hz), 66.7, 47.8 (d, *J* = 17.9 Hz), 27.7 (d, *J* = 5.5 Hz), 18.8 (d, *J* = 4.1 Hz), 8.6 ppm.

^{19}F NMR (471 MHz, $CDCl_3$): δ = –225.9 (s, 1F), –231.6 (s, di-fluorinated product, 0.16 F, 8%) ppm.

HRMS (ESIpos) m/z: Calcd for $C_{17}H_{20}FO_2$ 275.1441, Found 275.1438

Naphthalen-2-ylmethyl 2-(fluoromethyl)-2-methylhexanoate (2d-Naph)



2d-Naph

Following the general procedure **E**, using **1d** (28.8 mg) and pentane/EtOAc (99:1 v/v) as an eluent, the target compound **2d-Naph** was obtained as a pale yellow oil (32.1 mg, 0.106 mmol, 53%).

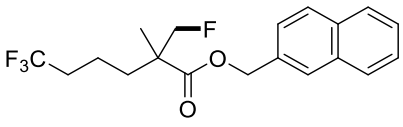
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.86 – 7.80 (m, 4H), 7.51 – 7.48 (m, 2H), 7.45 (dd, *J* = 8.5, 1.8 Hz, 1H), 5.32 (s, 2H), 4.58 (dd, *J* = 47.2, 8.8 Hz, 1H), 4.38 (dd, *J* = 47.2, 8.8 Hz, 1H), 1.66-1.60 (m, 1H), 1.53-1.46 (m, 1H), 1.29 (d, *J* = 1.5 Hz, 3H), 1.27-1.15 (m, 4H), 0.88 (t, *J* = 7.5 Hz, 3H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 174.6 (d, *J* = 4.6 Hz), 133.4, 133.2, 133.1, 128.4, 128.0, 127.7, 127.2, 126.3, 126.3, 125.7, 87.4 (d, *J* = 174.2 Hz), 66.6, 47.4 (d, *J* = 17.9 Hz), 34.6 (d, *J* = 5.1 Hz), 26.3, 23.0, 19.1 (d, *J* = 4.1 Hz), 13.8 ppm.

^{19}F NMR (471 MHz, $CDCl_3$): δ = –225.6 (s) ppm.

HRMS (EI) m/z: Calcd for $C_{19}H_{23}FO_2$ 302.1682, Found 302.1683

Naphthalen-2-ylmethyl 6,6,6-trifluoro-2-(fluoromethyl)-2-methylhexanoate (2e-Naph)



2e-Naph

Following the general procedure **E**, using **1e** (39.6 mg) and pentane/EtOAc (98:2 v/v) as an eluent, the target compound **2e-Naph** was obtained as a colorless oil (44.5 mg, 0.124 mmol, 62%).

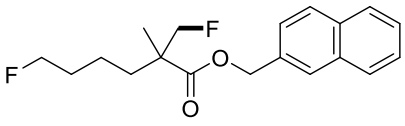
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.87 – 7.81 (m, 4H), 7.53 – 7.49 (m, 2H), 7.44 (dd, *J* = 8.4, 1.8 Hz, 1H), 5.34 (s, 2H), 4.51 (dd, *J* = 47.2, 8.8 Hz, 1H), 4.46 (dd, *J* = 47.2, 8.8 Hz, 1H), 2.07-1.96 (m, 2H), 1.76-1.70 (m, 1H), 1.64-1.50 (m, 3H), 1.30 (d, *J* = 1.5 Hz, 3H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 174.1 (d, *J* = 5.1 Hz), 133.3 (2C), 133.1, 128.6, 128.1, 127.8, 127.5, 126.5 (2C), 125.8, 87.0 (d, *J* = 175.1 Hz), 67.1, 47.2 (d, *J* = 18.4 Hz), 34.1 (q, *J* = 28.5 Hz), 33.8 (d, *J* = 4.6 Hz), 19.3 (d, *J* = 4.6 Hz), 17.2 ppm.

^{19}F NMR (471 MHz, $CDCl_3$): δ = –66.8 (s, 3F, -CF_3), –225.7 (s, 1F), –231.2 (s, di-fluorinated product, 0.12 F; 6%) ppm.

HRMS (EI) m/z: Calcd for $C_{19}H_{20}F_4O_2$ 356.1399, Found 356.1398

Naphthalen-2-ylmethyl 6-fluoro-2-(fluoromethyl)-2-methylhexanoate (2f-Naph)



2f-Naph

Following the general procedure **E**, using **1f** (32.4 mg) and pentane/EtOAc (99:1 v/v) as an eluent, the target compound **2f-Naph** was obtained as a colorless oil (40.0 mg, 0.124 mmol, 62%).

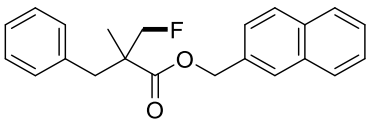
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.86 – 7.81 (m, 4H), 7.53 – 7.48 (m, 2H), 7.45 (dd, *J* = 8.5, 1.8 Hz, 1H), 5.33 (s, 2H), 4.56 (dd, *J* = 47.2, 8.9 Hz, 1H), 4.49 – 4.36 (m, 2H), 4.29 (t, *J* = 6.0 Hz, 1H), 1.72 – 1.53 (m, 4H), 1.41 – 1.31 (m, 2H), 1.30 (d, *J* = 1.5 Hz, 3H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 174.5 (d, *J* = 4.6 Hz), 133.4, 133.3, 133.2, 128.5, 128.1, 127.83, 127.4, 126.4(8), 126.4(6), 125.8, 87.3 (d, *J* = 174.6 Hz), 83.7 (d, *J* = 164.5 Hz), 66.8, 47.4 (d, *J* = 18.4 Hz), 34.5 (d, *J* = 5.1 Hz), 30.8 (d, *J* = 19.8 Hz), 20.2 (d, *J* = 5.5 Hz), 19.2 (d, *J* = 4.1 Hz) ppm.

^{19}F NMR (471 MHz, $CDCl_3$): δ = –218.9 (s, 1F), –225.7 (s, 1F), –231.2 (s, di-fluorinated product, 0.23 F 11.5%) ppm.

HRMS (EI) m/z: Calcd for $C_{19}H_{22}F_2O_2$ 320.1587, Found 320.1589

Naphthalen-2-ylmethyl 2-benzyl-3-fluoro-2-methylpropanoate (2g-Naph)



2g-Naph

Following the general procedure **E**, using **1g** (35.7 mg) and pentane/EtOAc (99:1 v/v) as an eluent, the target compound **2g-Naph** was obtained as a colorless oil (27.4 mg, 81.0 µmol, 41%).

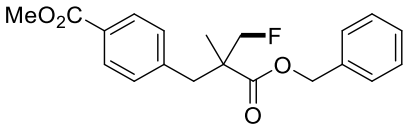
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.85 – 7.77 (m, 4H), 7.52 – 7.48 (m, 2H), 7.37 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.20 – 7.17 (m, 3H), 7.10-7.05 (m, 2H), 5.29 (s, 2H), 4.46 (dd, *J* = 47.2, 8.9 Hz, 1H), 4.44 (dd, *J* = 47.2, 8.9 Hz, 1H), 2.96 (s, 2H), 1.28 (d, *J* = 1.6 Hz, 3H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 174.1 (d, *J* = 4.6 Hz), 141.4, 136.2, 133.3, 133.1, 130.3, 128.5, 128.4, 128.2, 127.8, 127.6, 126.9, 126.5, 125.7, 124.8, 86.0 (d, *J* = 173.7 Hz), 66.9, 48.5 (d, *J* = 18.4 Hz), 40.4 (d, *J* = 4.1 Hz), 19.4 (d, *J* = 4.6 Hz) ppm.

^{19}F NMR (471 MHz, $CDCl_3$): δ = –225.9 (s) ppm.

HRMS (EI) m/z: Calcd for $C_{22}H_{21}FO_2$ 336.1525, Found 336.1525

Methyl 4-(3-(benzyloxy)-2-(fluoromethyl)-2-methyl-3-oxopropyl)benzoate (2h-Bn)



2h-Bn

Following the general procedure **D**, using **1h** (47.3 mg) and pentane/EtOAc (95:5 v/v) as an eluent, the target compound **2h-Bn** was obtained as a colorless solid (29.1 mg, 84.0 µmol, 42%).

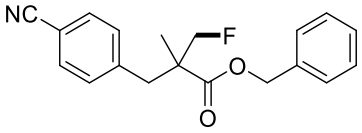
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 8.4 Hz, 2H), 7.36 – 7.33 (m, 3H), 7.29 – 7.27 (m, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 5.13 (s, 2H), 4.43 (dd, *J* = 47.2, 8.9 Hz, 1H), 4.40 (dd, *J* = 47.2, 8.9 Hz, 1H), 3.91 (s, 3H), 3.00 (s, 2H), 1.26 (d, *J* = 1.5 Hz, 3H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 173.8 (d, *J* = 5.5 Hz), 167.0, 141.7, 135.6, 130.4, 130.0, 128.9, 128.7, 128.5, 128.3, 85.7 (d, *J* = 174.2 Hz), 66.9, 52.2, 48.3 (d, *J* = 18.8 Hz), 40.2 (d, *J* = 4.1 Hz), 19.6 (d, *J* = 4.5 Hz) ppm.

^{19}F NMR (471 MHz, $CDCl_3$): δ = –226.0 (s) ppm.

HRMS (ESIpos) m/z: Calcd for $C_{20}H_{22}FO_4$ 345.1496, Found 345.1488

Benzyl 2-(4-cyanobenzyl)-3-fluoro-2-methylpropanoate (2i-Bn)



2i-Bn

Following the general procedure **D,** using **1i** (40.7 mg) and pentane/EtOAc (92:8 v/v) as an eluent, the target compound **2i-Bn** was obtained as a colorless oil (27.4 mg, 88.0 µmol, 44%).

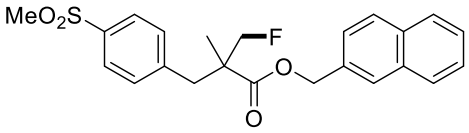
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.47 (d, *J* = 8.4 Hz, 2H), 7.38 – 7.35 (m, 3H), 7.30 – 7.27 (m, 2H), 7.14 (d, *J* = 8.3 Hz, 2H), 5.13 (s, 2H), 4.41 (dd, *J* = 47.2, 8.9 Hz, 1H), 4.38 (dd, *J* = 47.2, 8.9 Hz, 1H), 2.99 (s, 2H), 1.26 (d, *J* = 1.6 Hz, 3H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 173.4 (d, *J* = 6.0 Hz), 142.0, 135.4, 132.1, 131.1, 128.8, 128.7, 128.5, 118.9, 110.9, 85.5 (d, *J* = 174.2 Hz), 67.0, 48.3 (d, *J* = 18.8 Hz), 40.2 (d, *J* = 3.7 Hz), 19.8 (d, *J* = 4.1 Hz) ppm.

^{19}F NMR (471 MHz, $CDCl_3$): δ = –226.2 (s) ppm.

HRMS (ESIpos) m/z: Calcd for $C_{19}H_{19}FNO_2$ 312.1394, Found 312.1386

Naphthalen-2-ylmethyl 3-fluoro-2-methyl-2-(4-(methylsulfonyl)benzyl)propanoate (2j-Naph)



2j-Naph

Following the general procedure **E**, using **1j** (51.3 mg) and pentane/EtOAc (70:30 v/v) as an eluent, the target compound **2j-Naph** was obtained as a colorless oil (49.9 mg, 0.120 mmol, 60%).

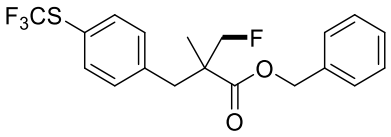
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.87-7.82 (m, 4H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.53-7.49 (m, 2H), 7.39 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.23 (d, *J* = 8.4 Hz, 2H), 5.30 (s, 2H), 4.43 (dd, *J* = 47.2, 8.9 Hz, 1H), 4.41 (dd, *J* = 47.2, 8.9 Hz, 1H), 3.04 (s, 3H), 2.94 (s, 2H), 1.28 (d, *J* = 1.5 Hz, 3H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 173.5 (d, *J* = 5.5 Hz), 142.9, 139.1, 133.3, 133.2, 132.7, 131.2, 128.6, 128.1, 127.9, 127.8, 127.3, 126.7, 126.6, 126.0, 85.5 (d, *J* = 174.6 Hz), 67.2, 48.4 (d, *J* = 18.8 Hz), 44.4, 39.9 (d, *J* = 4.1 Hz), 19.7 (d, *J* = 4.1 Hz) ppm.

^{19}F NMR (471 MHz, $CDCl_3$): δ = –225.9 (s) ppm.

HRMS (ESIpos) m/z: Calcd for $C_{23}H_{24}FO_4S$ 415.1373, Found 415.1364

Benzyl 3-fluoro-2-methyl-2-(4-((trifluoromethyl)thio)benzyl)propanoate (2k-Bn)



2k-Bn

Following the general procedure **D**, using **1k** (55.7 mg) and pentane/EtOAc (99:1v/v) as an eluent, the target compound **2k-Bn** was obtained as a colorless oil (40.4 mg, 0.104 mmol, 52%).

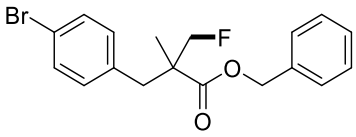
^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.50 (d, *J* = 8.1 Hz, 2H), 7.38-7.34 (m, 3H), 7.30-7.28 (m, 2H), 7.12 (d, *J* = 8.3 Hz, 2H), 5.14 (s, 2H), 4.43 (dd, *J* = 47.2, 8.9 Hz, 1H), 4.40 (dd, *J* = 47.2, 8.9 Hz, 1H), 2.98 (s, 2H) 1.27 (d, *J* = 1.5 Hz, 3H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 173.8 (d, *J* = 5.5 Hz), 145.0, 143.2, 139.7, 136.3, 131.5, 128.7, 128.6, 128.4, 85.7 (d, *J* = 174.2 Hz), 66.9, 48.3 (d, *J* = 18.8 Hz), 39.9 (d, *J* = 4.1 Hz), 19.7 (d, *J* = 4.1 Hz). ppm.

^{19}F NMR (471 MHz, $CDCl_3$): δ = –43.3 (s), –226.1 (s) ppm.

HRMS (ESIpos) m/z: Calcd for $C_{19}H_{18}F_4O_2S$ 387.1036, Found 387.1026

Benzyl 2-(4-bromobenzyl)-3-fluoro-2-methylpropanoate (2l-Bn)



2l-Bn

Following the general procedure **D**, using **1l** (51.4 mg) and pentane/EtOAc (99:1 v/v) as an eluent, the target compound **2l-Bn** was obtained as a colorless solid (41.8 mg, 0.114 mmol, 57%).

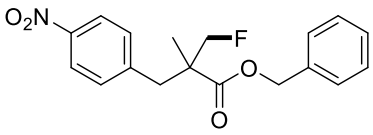
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.38 – 7.32 (m, 5H), 7.30 – 7.27 (m, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 5.13 (s, 2H), 4.42 (dd, *J* = 47.2, 8.9 Hz, 1H), 4.40 (dd, *J* = 47.2, 8.9 Hz, 1H), 2.90 (s, 2H), 1.25 (d, *J* = 1.5 Hz, 3H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 173.7 (d, *J* = 6.0 Hz), 143.7, 140.3, 135.5, 135.1, 131.9, 131.4, 128.6, 128.3, 85.6 (d, *J* = 173.7 Hz), 66.7, 48.2 (d, *J* = 18.4 Hz), 39.5 (d, *J* = 4.1 Hz), 19.44 (d, *J* = 4.1 Hz) ppm.

^{19}F NMR (471 MHz, $CDCl_3$): δ = –226.2 (s) ppm.

HRMS (ESIpos) m/z: Calcd for $C_{18}H_{19}BrFO_2$ 365.0547, Found 365.0540

Benzyl 3-fluoro-2-methyl-2-(4-nitrobenzyl)propanoate (2m-Bn)



2m-Bn

Following the general procedure **D**, using **1m** (44.7 mg) and pentane/EtOAc (92:8 v/v) as an eluent, the target compound **2m-Bn** was obtained as a colorless solid (35.4 mg, 0.106 mmol, 53%).

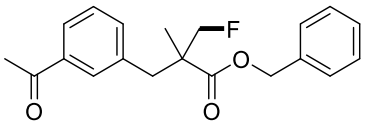
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 8.8 Hz, 2H), 7.37 – 7.35 (m, 3H), 7.30 – 7.27 (m, 2H), 7.19 (d, *J* = 8.7 Hz, 2H), 5.14 (s, 2H), 4.42 (dd, *J* = 47.2, 8.9 Hz, 1H), 4.40 (dd, *J* = 47.2, 8.9 Hz, 1H), 3.06 (d, *J* = 13.5 Hz, 1H), 3.03 (d, *J* = 13.5 Hz, 1H), 1.29 (d, *J* = 1.5 Hz, 3H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 173.3 (d, *J* = 6.0 Hz), 147.1, 144.1, 135.4, 131.1, 128.8, 128.7, 128.5, 123.5, 85.5 (d, *J* = 174.6 Hz), 67.0, 48.3 (d, *J* = 18.8 Hz), 39.9 (d, *J* = 4.1 Hz), 19.8 (d, *J* = 4.6 Hz) ppm.

^{19}F NMR (471 MHz, $CDCl_3$): δ = –226.2 (s, 1F), –230.4 (s, di-fluorinated product, 0.10 F, 5%) ppm.

HRMS (ESIpos) m/z: Calcd for $C_{18}H_{19}FNO_4$ 332.1292, Found 332.1284

Benzyl 2-(3-acetylbenzyl)-3-fluoro-2-methylpropanoate (2n-Bn)



2n-Bn

Following the general procedure **D**, using **1n** (44.1 mg) and pentane/EtOAc (90:10 v/v) as an eluent, the target compound **2n-Bn** was obtained as a colorless solid (37.5 mg, 0.114 mmol, 57%).

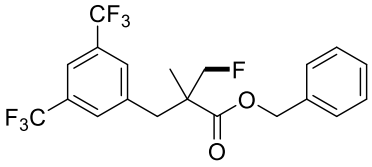
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 8.4 Hz, 2H), 7.36-7.33 (m, 3H), 7.30-7.26 (m, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 5.13 (s, 2H), 4.42 (dd, *J* = 47.2, 8.9 Hz, 1H), 4.40 (dd, *J* = 47.2, 8.9 Hz, 1H), 3.00 (s, 2H), 2.57 (s, 3H), 1.26 (d, *J* = 1.6 Hz, 3H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 197.8, 173.7 (d, *J* = 5.5 Hz), 147.4, 142.0, 135.9, 135.5, 130.5, 128.71, 128.5, 128.4, 128.4, 85.7 (d, *J* = 174.2 Hz), 66.9, 48.4 (d, *J* = 18.8 Hz), 40.2 (d, *J* = 4.1 Hz), 26.7, 19.6 (d, *J* = 4.6 Hz) ppm.

^{19}F NMR (471 MHz, $CDCl_3$): δ = –226.0 (s) ppm.

HRMS (ESIpos) m/z: Calcd for $C_{20}H_{22}FO_3$ 329.1547, Found 329.1537

Benzyl 2-(3,5-bis(trifluoromethyl)benzyl)-3-fluoro-2-methylpropanoate (2o-Bn)



2o-Bn

Following the general procedure **D**, using **1o** (62.8 mg) and pentane/EtOAc (99:1 v/v) as an eluent, the target compound **2o-Bn** was obtained as a colorless solid (37.5 mg, 0.114 mmol, 57%).

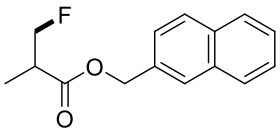
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.77 (s, 1H), 7.61 (s, 2H), 7.38 – 7.33 (m, 3H), 7.29 – 7.26 (m, 2H), 5.13 (d, *J* = 12.3 Hz, 1H), 5.11 (d, *J* = 12.3 Hz, 1H), 4.45 (dd, *J* = 47.2, 8.9 Hz, 1H), 4.38 (dd, *J* = 47.2, 8.9 Hz, 1H), 3.12 (d, *J* = 13.7 Hz, 1H), 3.09 (d, *J* = 13.7 Hz, 1H), 1.28 (d, *J* = 1.6 Hz, 3H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 173.3 (d, *J* = 6.0 Hz), 139.1, 135.3, 131.7 (q, *J* = 33.3 Hz), 130.5, 128.8, 128.7, 128.2, 123.2 (q, *J* = 273 Hz), 120.9, 85.3 (d, *J* = 174.6 Hz), 67.2, 48.4 (d, *J* = 18.8 Hz), 39.7 (d, *J* = 4.1 Hz), 19.7 (d, *J* = 4.6 Hz) ppm.

^{19}F NMR (471 MHz, $CDCl_3$): δ = –63.3 (s), –226.1 (s) ppm.

HRMS (EI) m/z: Calcd for $C_{20}H_{17}F_7O_2$ 422.1116, Found 422.1117

Naphthalen-2-ylmethyl 3-fluoro-2-methylpropanoate (2p-Naph)



2p-Naph

Following the general procedure **G**, using **1p** (17.6 mg) and pentane/EtOAc (99:1 v/v) as an eluent, the target compound **2p-Naph** was obtained as a colorless oil (27.2 mg, 0.112 mmol, 56%).

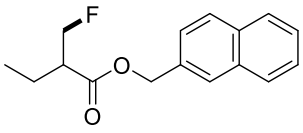
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.87 – 7.79 (m, 4H), 7.51 – 7.48 (m, 2H), 7.45 (dd, *J* = 8.4, 1.8 Hz, 1H), 5.33 (s, 2H), 4.71 – 4.43 (m, 2H), 2.99 – 2.86 (m, 1H), 1.26 (dd, *J* = 7.2, 1.1 Hz, 3H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ 173.3 (d, *J* = 6.0 Hz), 133.3, 133.2 (2C), 128.6, 128.1, 127.9, 127.4, 126.5, 126.4, 125.8, 84.5 (d, *J* = 171.4 Hz), 66.9, 40.8 (d, *J* = 20.7 Hz), 12.9 (d, *J* = 6.9 Hz) ppm.

^{19}F NMR (471 MHz, $CDCl_3$): δ = –222.0 (s) ppm.

HRMS (EI) m/z: Calcd for $C_{15}H_{15}FO_2$ 246.1056, Found 246.1055

Naphthalen-2-ylmethyl 2-(fluoromethyl)butanoate (2q-Naph)



2q-Naph

Following the general procedure **G**, using **1q** (20.4 mg) and pentane/EtOAc (99:1 v/v) as an eluent, the target compound **2q-Naph** was obtained as a colorless oil (29.7 mg, 0.114 mmol, 57%).

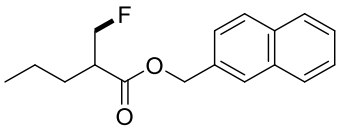
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.87 – 7.81 (m, 4H), 7.52 – 7.48 (m, 2H), 7.46 (dd, *J* = 8.5, 1.8 Hz, 1H), 5.36 (d, *J* = 12.2 Hz, 1H), 5.32 (d, *J* = 12.2 Hz, 1H), 4.75 – 4.45 (m, 2H), 2.85 – 2.74 (m, 1H), 1.78 – 1.59 (m, 2H), 0.96 (t, *J* = 7.5 Hz, 3H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 173.0 (d, *J* = 5.5 Hz), 133.3 (2C), 133.2, 128.6, 128.1, 127.8, 127.5, 126.5 (3), 126.4, 125.9, 83.2 (d, *J* = 170.5 Hz), 66.8, 47.9 (d, *J* = 19.3 Hz), 21.1 (d, *J* = 6.4 Hz), 11.5 ppm.

^{19}F NMR (471 MHz, $CDCl_3$): δ = –222.2 (s) ppm.

HRMS (EI) m/z: Calcd for $C_{16}H_{17}FO_2$ 260.1212, Found 260.1212

Naphthalen-2-ylmethyl 2-(fluoromethyl)pentanoate (2b-Naph)



2b-Naph

Following the general procedure **G**, using **1b** (23.2 mg) and pentane/EtOAc (99:1 v/v) as an eluent, the target compound **2b-Naph** was obtained as a colorless oil (28.0 mg, 0.102 mmol, 51%).

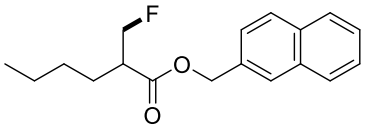
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.87 – 7.81 (m, 4H), 7.52 – 7.48 (m, 2H), 7.45 (dd, *J* = 8.5, 1.8 Hz, 1H), 5.34 (s, 2H), 4.74 – 4.44 (m, 2H), 2.93 – 2.81 (m, 1H), 1.72 – 1.63 (m, 1H), 1.57-1.48 (m, 1H), 1.40-1.31 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 173.2 (d, *J* = 5.1 Hz), 133.3 (2C), 133.2, 128.5, 128.1, 127.9, 127.4, 126.5, 126.4, 125.9, 83.6 (d, *J* = 171.0 Hz), 66.8, 46.3 (d, *J* = 19.8 Hz), 29.9 (d, *J* = 6.4 Hz), 20.3, 14.0 ppm.

^{19}F NMR (471 MHz, $CDCl_3$): δ = –221.2 (s) ppm.

HRMS (EI) m/z: Calcd for $C_{17}H_{19}FO_2$ 274.1369, Found 274.1367

Naphthalen-2-ylmethyl 2-(fluoromethyl)hexanoate (2r-Naph)



2r-Naph

Following the general procedure **G**, using **1r** (26.0 mg) and pentane/EtOAc (99:1 v/v) as an eluent, the target compound **2r-Naph** was obtained as a colorless oil (31.1 mg, 0.107 mmol, 54%).

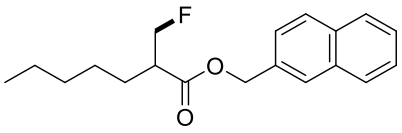
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.87 – 7.80 (m, 4H), 7.51 – 7.48 (m, 2H), 7.45 (dd, *J* = 8.4, 1.8 Hz, 1H), 5.36 (d, *J* = 12.2 Hz, 1H), 5.32 (d, *J* = 12.2 Hz, 1H), 4.72 – 4.45 (m, 2H), 2.91-2.80 (m, 1H), 1.71-1.64 (m, 1H), 1.60-1.51 (m, 1H), 1.34 – 1.27 (m, 4H), 0.85 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 173.2 (d, *J* = 5.1 Hz), 133.3(2C), 133.2, 128.5, 128.1, 127.8, 127.5, 126.5, 126.4, 125.9, 83.6 (d, *J* = 171.0 Hz), 66.8, 46.5 (d, *J* = 19.8 Hz), 29.2, 27.5 (d, *J* = 6.0 Hz), 22.6, 13.9 ppm.

^{19}F NMR (471 MHz, $CDCl_3$): δ = –221.2 (s) ppm.

HRMS (EI) m/z: Calcd for $C_{18}H_{21}FO_2$ 288.1525, Found 288.1526

Naphthalen-2-ylmethyl 2-(fluoromethyl)heptanoate (2s-Naph)



2s-Naph

Following the general procedure **G**, using **1s** (28.8 mg) and pentane/EtOAc (99:1 v/v) as an eluent, the target compound **2s-Naph** was obtained as a colorless oil (31.7 mg, 0.105 mmol, 52%).

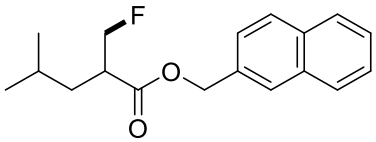
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.87 – 7.80 (m, 4H), 7.51 – 7.47 (m, 2H), 7.45 (dd, *J* = 8.4, 1.8 Hz, 1H), 5.35 (d, *J* = 12.2 Hz, 1H), 5.32 (d, *J* = 12.2 Hz, 1H), 4.72 – 4.44 (m, 2H), 2.91 – 2.81 (m, 1H), 1.72 – 1.62 (m, 1H), 1.58-1.51 (m, 1H), 1.35 – 1.21 (m, 6H), 0.83 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 173.2 (d, *J* = 5.1 Hz), 133.3 (2C), 133.2, 128.5, 128.1, 127.8, 127.5, 126.5, 126.4, 125.9, 83.6 (d, *J* = 171.0 Hz), 66.8, 46.5 (d, *J* = 19.8 Hz), 31.7, 27.8 (d, *J* = 6.4 Hz), 26.7, 22.5, 14.0 ppm.

^{19}F NMR (471 MHz, $CDCl_3$): δ = –221.2 (s) ppm.

HRMS (EI) m/z: Calcd for $C_{19}H_{23}FO_2$ 302.1682, Found 302.1683

Naphthalen-2-ylmethyl 2-(fluoromethyl)-4-methylpentanoate (2t-Naph)



2t-Naph

Following the general procedure **G**, using **1t** (26.0 mg) and pentane/Et_2O (95:5 v/v) as an eluent, the target compound **2t-Naph** was obtained as a colorless oil (27.8 mg, 94.0 µmol, 48%).

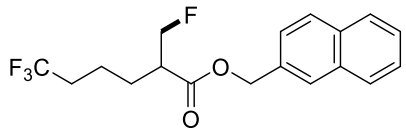
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.87 – 7.82 (m, 4H), 7.51 – 7.48 (m, 2H), 7.45 (dd, *J* = 8.4, 1.8 Hz, 1H), 5.34 (s, 2H), 4.69-4.42 (m, 2H), 3.00-2.89 (m, 1H), 1.64-1.58 (m, 2H), 1.36-1.29 (m, 1H), 0.93 (d, *J* = 6.5 Hz, 3H), 0.90 (d, *J* = 6.4 Hz, 3H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 173.5 (d, *J* = 5.1 Hz), 133.3 (2C), 133.2, 128.5, 128.1, 127.9, 127.4, 126.5, 126.4, 125.8, 84.1 (d, *J* = 171.9 Hz), 66.8, 44.8 (d, *J* = 19.3 Hz), 36.7 (d, *J* = 6.0 Hz), 26.0, 22.9, 22.2 ppm.

^{19}F NMR (471 MHz, $CDCl_3$): δ = –220.2 (s) ppm.

HRMS (EI) m/z: Calcd for $C_{18}H_{21}FO_2$ 288.1525, Found 288.1524

Naphthalen-2-ylmethyl 6,6,6-trifluoro-2-(fluoromethyl)hexanoate (2u-Naph)



2u-Naph

Following the general procedure **G**, using **1u** (36.8 mg) and pentane/EtOAc (95:5 v/v) as an eluent, the target compound **2u-Naph** was obtained as a colorless oil (30.8 mg, 90.0 µmol, 45%)

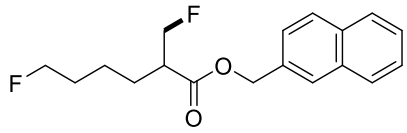
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.87-7.80 (m, 4H), 7.52-7.48 (m, 2H), 7.44 (dd, *J* = 8.4, 1.8 Hz, 1H), 5.34 (s, 2H), 4.72 – 4.48 (m, 2H), 2.89 – 2.79 (m, 1H), 2.14 – 2.00 (m, 2H), 1.84 – 1.73 (m, 1H), 1.71 – 1.58 (m, 3H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 172.3 (d, *J* = 6.4 Hz), 133.3(3), 133.3(1), 133.0, 128.7, 128.1, 127.9, 127.7, 126.6 (2C), 125.9, 83.2 (d, *J* = 171.9 Hz), 67.2, 46.1 (d, *J* = 20.2 Hz), 33.7 (q, *J* = 29.0 Hz), 26.9 (d, *J* = 6.0 Hz), 19.8 ppm.

^{19}F NMR (471 MHz, $CDCl_3$): δ = –66.8 (s), –222.6 (s) ppm.

HRMS (EI) m/z: Calcd for $C_{18}H_{18}F_4O_2$ 342.1242, Found 342.1241

Naphthalen-2-ylmethyl 6-fluoro-2-(fluoromethyl)hexanoate (2v-Naph)



2v-Naph

Following the general procedure **G**, using **1v** (29.6 mg) and pentane/EtOAc (99:1 v/v) as an eluent, the target compound **2v-Naph** was obtained as a colorless oil (28.9 mg, 95.0 µmol, 47%)

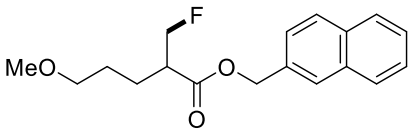
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.88 – 7.81 (m, 4H), 7.53 – 7.48 (m, 2H), 7.45 (dd, *J* = 8.4, 1.8 Hz, 1H), 5.36 (d, *J* = 12.3 Hz, 1H), 5.32 (d, *J* = 12.3 Hz, 1H), 4.75 – 4.47 (m, 2H), 4.38 (dt, *J* = 47.2, 6.0 Hz, 2H), 2.90-2.81 (m, 1H), 1.80 – 1.59 (m, 4H), 1.49 – 1.43 (m, 2H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 172.8 (d, *J* = 5.5 Hz), 133.3(2C), 133.2, 128.6, 128.1, 127.8, 127.6, 126.5 (2C), 125.9, 84.3 (d, *J* = 31.7 Hz), 82.9 (d, *J* = 38.1 Hz), 66.9, 46.4 (d, *J* = 19.8 Hz), 30.3 (d, *J* = 19.8 Hz), 27.4 (d, *J* = 6.0 Hz), 23.0 (d, *J* = 5.1 Hz) ppm.

^{19}F NMR (471 MHz, $CDCl_3$): δ = –219.1 (s), –221.8 (s) ppm.

HRMS (EI) m/z: Calcd for $C_{18}H_{20}F_2O_2$ 306.1431, Found 306.1429

Naphthalen-2-ylmethyl 2-(fluoromethyl)-5-methoxypentanoate (2w-Naph)



2w-Naph

Following the general procedure **G** using **1w** (29.2 mg), **OX2** (170.2 mg, 468 µmol, 2.25 equiv.) and pentane/EtOAc (99:1 v/v) as an eluent, the target compound **2w-Naph** was obtained as a colorless oil (23.2 mg, 77.0 µmol, 38%)

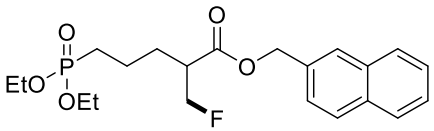
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.86 – 7.81 (m, 4H), 7.51 – 7.48 (m, 2H), 7.45 (dd, *J* = 8.5, 1.7 Hz, 1H), 5.33 (s, 2H), 4.50 – 4.32 (m, 2H), 3.63 (dd, *J* = 9.2, 7.6 Hz, 1H), 3.51 (dd, *J* = 9.2, 5.5 Hz, 1H), 3.33 (s, 3H), 2.81-2.75 (m, 1H), 1.80 – 1.65 (m, 4H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 174.0, 133.6, 133.3, 133.2, 128.5, 128.1, 127.8, 127.4, 126.5, 126.4, 125.9, 83.7 (d, *J* = 165.0 Hz), 73.4, 66.6, 59.1, 45.8, 28.2 (d, *J* = 19.8 Hz), 24.8 (d, *J* = 5.1 Hz) ppm.

^{19}F NMR (471 MHz, $CDCl_3$): δ = –219.6 (s) ppm.

HRMS (EI) m/z: Calcd for $C_{18}H_{21}FO_3$ 304.1474, Found 304.1773

Naphthalen-2-ylmethyl 6-(diethoxyphosphoryl)-2-(fluoromethyl)hexanoate (2x-Naph)



2x-Naph

Following the general procedure **G** using **1x** (50.4 mg), **OX2** (170.2 mg, 468 µmol, 2.25 equiv.) and pentane/Acetone (1:1 v/v) as an eluent, the target compound **2x-Naph** was obtained as a colorless oil (27.9 mg, 68.0 µmol, 34%).

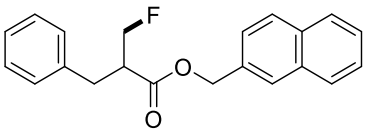
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.87 – 7.82 (m, 4H), 7.51 – 7.47 (m, 2H), 7.45 (dd, *J* = 8.5, 1.7 Hz, 1H)**,** 5.33 (s, 2H), 4.71-4.50 (m, 2H), 4.06-4.02 (m, 4H), 2.90-2.80 (m, 1H), 1.84-1.64 (m, 6H), 1.27 (t, *J* = 7 Hz, 6H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 172.5 (d, *J* = 5.5 Hz), 133.3(2C), 133.1, 128.6, 128.1, 127.8, 127.6, 126.5 (2C), 125.9, 83.3 (d, *J* = 171.9 Hz), 67.0, 61.7 (d, *J* = 6.9 Hz), 46.1 (d, *J* = 19.8 Hz), 26.2, 25.1, 20.4 (d, *J* = 5.1 Hz), 16.6 (d, *J* = 6.0 Hz) ppm.

^{19}F NMR (471 MHz, $CDCl_3$): δ = –222.2 (s) ppm.

HRMS (EI) m/z: Calcd for $C_{21}H_{28}FO_5P$ 410.1658, Found 410.1656

Naphthalen-2-ylmethyl 2-benzyl-3-fluoropropanoate (2y-Naph)



2y-Naph

Following the general procedure **G** using **1y** (32.8 mg), **OX2** (170.2 mg, 468 µmol, 2.25 equiv.), 2-benzyl-3-fluoropropanoic acid was obtained with 43% crude NMR-yield (using CH_2Br_2 as an internal standard). The subsequent naphthylation step afforded a mixture of **2y-Naph** and a side product Naphthalen-2-ylmethyl 4-(trifluoromethyl)benzoate (colorless oil, 17.5 mg). A complete removal of the side product could not be achieved despite several purification attempts. Taking the amount of side product into consideration, the isolated mixture was calculated to contain 0.043 mmol (21 % yield) of **2y-Naph.**

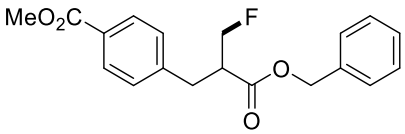
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.86-7.81 (m, 4H), 7.50-7.48 (m, 2H), 7.46 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.25-7.18 (m, 3H), 7.17-7.11 (m, 2H), 5.30 (s, 2H), 4.67-4.50 (m, 2H), 3.15-3.01 (m, 2H), 2.97-2.89 (m, 1H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 172.3 (d, *J* = 5.5 Hz), 137.8, 133.3, 133.1, 129.1, 128.7, 128.5, 128.2, 127.8, 127.6, 127.5, 126.9, 126.5, 126.06, 126.0, 82.7 (d, *J* = 171.4 Hz), 67.0, 48.2 (d, *J* = 20.2 Hz), 33.7 (d, *J* = 6.0 Hz) ppm.

^{19}F NMR (471 MHz, $CDCl_3$): –224.0 (s) ppm.

HRMS (EI) m/z: Calcd for $C_{21}H_{19}FO_2$ 322.1369, Found 322.1367

Methyl 4-(3-(benzyloxy)-2-(fluoromethyl)-3-oxopropyl)benzoate (2z-Bn)



2z-Bn

Following the general procedure **F**, using **1z** (44.4 mg) and pentane/EtOAc (94:6 v/v) as an eluent, the target compound **2z-Bn** was obtained as a colorless oil (28.2 mg, 85.0 µmol, 43%)

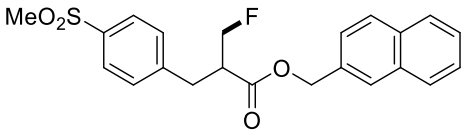
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.92 (d, *J* = 8.5 Hz, 2H), 7.34 – 7.31 (m, 3H), 7.24 – 7.20 (m, 4H), 5.12 (d, *J* = 12.2 Hz, 1H), 5.09 (d, *J* = 12.2 Hz, 1H), 4.63 – 4.60 (m, 1H), 4.54 – 4.51 (m, 1H), 3.91 (s, 3H), 3.13 – 3.05 (m, 2H), 3.01 – 2.94 (m, 1H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 171.6 (d, *J* = 5.5 Hz), 167.0, 143.3, 135.5, 130.1, 129.2, 128.9, 128.7, 128.5, 128.4, 82.5 (d, *J* = 172.4 Hz), 67.0, 52.2, 47.8 (d, *J* = 20.2 Hz), 33.6 (d, *J* = 5.5 Hz) ppm.

^{19}F NMR (471 MHz, $CDCl_3$): δ = –224.3 (s) ppm.

HRMS (ESI pos) m/z: Calcd for $C_{19}H_{20}FO_4$ 331.1340, Found 331.1336

Naphthalen-2-ylmethyl 3-fluoro-2-(4-(methylsulfonyl)benzyl)propanoate (2aa-Naph)



2aa-Naph

Following the general procedure **G**, using **1aa** (48.5 mg) and pentane/EtOAc (70:30 v/v) as an eluent, the target compound **2aa-Naph** was obtained as a colorless oil (34.6 mg, 86.0 µmol, 43%)

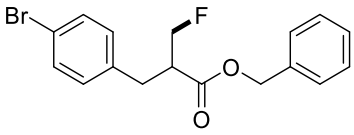
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.86-7.81 (m, 3H) 7.78 – 7.75 (m, 3H), 7.53-7.48 (m, 2H),7.36 – 7.31 (m, 3H), 5.30 (d, *J* = 12.2 Hz, 1H), 5.27 (d, *J* = 12.2 Hz, 1H), 4.68 – 4.62 (m, 1H), 4.59 – 4.53 (m, 1H), 3.17 – 3.08 (m, 2H), 3.08 – 3.00 (m, 1H), 2.95 (s, 3H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 171.4 (d, *J* = 5.5 Hz), 144.5, 139.2, 133.3, 133.2(2C), 132.7, 130.1, 128.7, 128.1, 127.9, 127.8, 126.7, 126.6, 126.0, 82.4 (d, *J* = 172.8 Hz), 67.3, 47.7 (d, *J* = 20.7 Hz), 44.5, 33.5 (d, *J* = 5.5 Hz) ppm.

^{19}F NMR (471 MHz, $CDCl_3$): δ = –224.4 (s) ppm.

HRMS (EI) m/z: Calcd for $C_{22}H_{21}FO_4S$ 400.1144, Found 400.1146

Benzyl 2-(4-bromobenzyl)-3-fluoropropanoate (2ab-Bn)



2ab-Bn

Following the general procedure **F**, using **1ab** (48.6 mg) and pentane/EtOAc (99:1 v/v) as an eluent, the target compound **2ab-Bn** was obtained as a colorless oil (30.3 mg, 86.0 µmol, 43%)

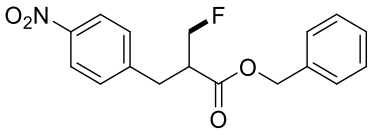
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.39 – 7.32 (m, 5H), 7.24 – 7.19 (m, 2H), 7.03 – 6.98 (m, 2H), 5.14 (d, *J* = 12.2 Hz, 1H), 5.08 (d, *J* = 12.2 Hz, 1H), 4.65 – 4.48 (m, 2H), 3.09 – 2.94 (m, 2H), 2.92-2.83 (m, 1H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ 171.9 (d, *J* = 5.5 Hz), 136.8, 135.5, 131.8, 130.9, 128.7, 128.5, 128.4, 120.8, 82.4 (d, *J* = 172.8 Hz), 66.9, 47.9 (d, *J* = 20.2 Hz), 32.9 (d, *J* = 6.0 Hz) ppm.

^{19}F NMR (471 MHz, $CDCl_3$): δ = –224.2 (s) ppm.

HRMS (ESI pos) m/z: Calcd for $C_{17}H_{17}BrFO_2$ 351.0390, Found 351.0386

Benzyl 3-fluoro-2-(4-nitrobenzyl)propanoate (2ac-Bn)



2ac-Bn

Following the general procedure **F**, using **1ac** (41.8 mg) and pentane/EtOAc (92:8 v/v) as an eluent, the target compound **2ac-Bn** was obtained as a colorless oil (28.6 mg, 90.0 µmol, 45%)

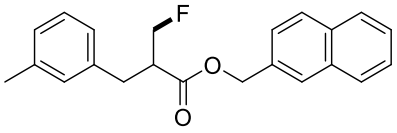
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 8.8 Hz, 2H), 7.34 – 7.31 (m, 3H), 7.28 (d, *J* = 8.8 Hz, 2H), 7.24 – 7.21 (m, 2H), 5.14 (d, *J* = 12.2 Hz, 1H), 5.07 (d, *J* = 12.2 Hz, 1H), 4.60 (dd, *J* = 46.5, 5.2 Hz, 2H), 3.15 – 3.01 (m, 3H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 171.3 (d, *J* = 6.0 Hz), 147.0, 145.6, 135.3, 130.0, 128.7(3), 128.7(0), 128.6, 123.9, 82.4 (d, *J* = 172.8 Hz), 67.1, 47.6 (d, *J* = 20.2 Hz), 33.5 (d, *J* = 5.5 Hz) ppm.

^{19}F NMR (471 MHz, $CDCl_3$): δ = –224.3 (s) ppm.

HRMS (EI) m/z: Calcd for $C_{17}H_{16}FNO_4$ 317.1063, Found 317.1062

Naphthalen-2-ylmethyl 3-fluoro-2-(3-methylbenzyl)propanoate (2ad-Naph)



2ad-Naph

Following the general procedure **G** using **1ad** (35.6 mg) and **OX2** (170.2 mg, 468 µmol, 2.25 equiv.), 3-fluoro-2-(3-methylbenzyl)propanoic acid was obtained in 44% crude NMR-yield (using CH_2Br_2 as an internal standard). The subsequent naphthylation step afforded a mixture of **2ad-Naph** and a side product Naphthalen-2-ylmethyl 4-(trifluoromethyl)benzoate (colorless oil, 19.2 mg). A complete removal of the side product could not be achieved despite several purification attempts. Taking the amount of side product into consideration, the isolated mixture was calculated to contain 0.044 mmol (22% yield) of **2ad-Naph.**

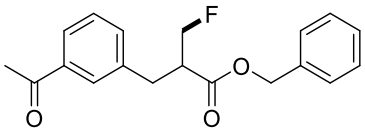
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.86-7.77 (m, 4H), 7.50-7.44 (m, 3H), 7.15-7.10 (m, 1H), 7.03-6.92 (m, 3H), 5.28 (d, *J* = 2.9 Hz, 2H), 4.68-4.48 (m, 2H), 3.15-2.98 (m, 2H), 2.90-2.83 (m, 1H), 2.27 (s, 3H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 172.3 (d, *J* = 5.5 Hz), 138.2, 137.6, 133.1, 132.9, 129.7, 129.6, 128.5, 128.4, 128.0, 127.7, 127.4, 126.3, 126.0, 125.8, 82.6 (d, *J* = 171.4 Hz), 66.8, 48.0 (d, *J* = 20.2 Hz), 33.4 (d, *J* = 6.0 Hz), 21.3 ppm.

^{19}F NMR (471 MHz, $CDCl_3$): –223.6 (s) ppm.

HRMS (EI) m/z: Calcd for $C_{22}H_{21}FO_2$ 336.1525, Found 336.1525

Benzyl 2-(3-acetylbenzyl)-3-fluoropropanoate (2ae-Bn)



2ae-Bn

Following the general procedure **F**, using **1ae** (41.2 mg) and pentane/EtOAc (90:10 v/v) as an eluent, the target compound **2ae-Bn** was obtained as a colorless oil (25.9 mg, 83.0 µmol, 41%)

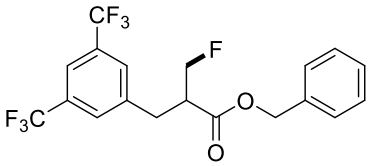
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.83 – 7.76 (m, 2H), 7.37 – 7.35 (m, 2H), 7.33-7.30 (m, 3H), 7.25 – 7.22 (m, 2H), 5.13 (d, *J* = 12.3 Hz, 1H), 5.10 (d, *J* = 12.3 Hz, 1H), 4.65 – 4.62 (m, 1H), 4.55 – 4.51 (m, 1H), 3.15 – 3.06 (m, 2H), 3.01-2.97 (m, 1H), 2.56 (s, 3H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 198.1, 171.8 (d, *J* = 5.1 Hz), 138.5, 137.6, 135.5, 133.9, 129.0, 128.8, 128.7, 128.5, 128.3, 127.0, 82.5 (d, *J* = 172.4 Hz), 67.0, 47.9 (d, *J* = 20.2 Hz), 33.4 (d, *J* = 6.0 Hz), 26.8 ppm.

^{19}F NMR (471 MHz, $CDCl_3$): δ = –224.3 (s) ppm.

HRMS (ESI pos) m/z: Calcd for $C_{19}H_{20}FO_3$ 315.1391, Found 315.1388

Benzyl 2-(3,5-bis(trifluoromethyl)benzyl)-3-fluoropropanoate (2af-Bn)



2af-Bn

Following the general procedure **F**, using **1af** (60.0 mg) and pentane/EtOAc (99:1 v/v) as an eluent, the target compound **2af-Bn** was obtained as a colorless oil (41.4 mg, 0.102 mmol, 51%)

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.74 (s, 1H), 7.64 (s, 2H), 7.35-7.31 (m, 3H), 7.24-7.21 (m, 2H), 5.11 (s, 2H), 4.69 – 4.61 (m, 1H), 4.60 – 4.52 (m, 1H), 3.21-3.06 (m, 3H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 171.1 (d, *J* = 6.0 Hz), 140.6, 135.2, 132.0 (q, *J* = 33.3 Hz), 129.3, 128.8, 128.7, 128.3, 123.3 (q, *J* = 273 Hz), 120.9, 82.3 (d, *J* = 174.6 Hz), 67.3, 47.6 (d, *J* = 18.8 Hz), 33.3 (d, *J* = 4.1 Hz) ppm

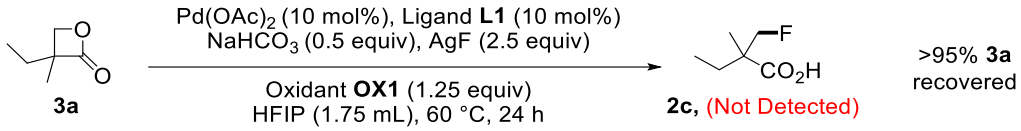
^{19}F NMR (471 MHz, $CDCl_3$): δ = –63.3, –224.7 ppm.

HRMS (EI) m/z: Calcd for $C_{19}H_{15}F_7O_2$ 408.0960 , Found 408.0961

7. Preliminary Mechanistic Investigations

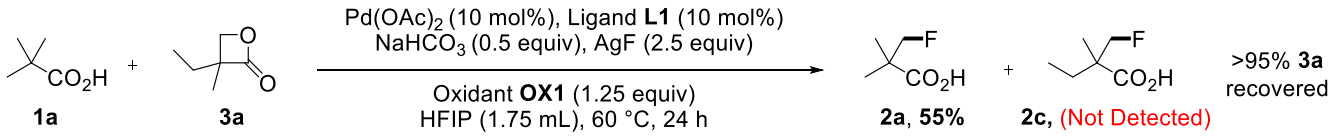
Control Experiment A:

An oven dried 10 mL Schlenk tube was charged with $Pd(OAc)_2$ (2.3 mg, 10 µmol, 10 mol%), **L1** (2.8 mg, 10 µmol, 10 mol%), $NaHCO_3$ (4.2 mg, 50 µmol, 0.5 equiv.), **OX1** (29.9 mg, 0.120 mmol, 1.25 equiv.), AgF (31.7 mg, 0.250 mmol, 2.50 equiv.), **3a** (0.1 mmol, 1.0 equiv.) and HFIP (1.75 mL). The reaction mixture was stirred at 60 °C for 24 h in a preheated metal block. The reaction mixture was allowed to cool to rt and was then filtered through a pad of Celite® using CH_2Cl_2 (30 mL) to complete the elution. All the volatiles were removed under reduced pressure and the crude reaction mixture was analyzed via ^1H and ^{19}F NMR using CH_2Br_2 as internal standard.



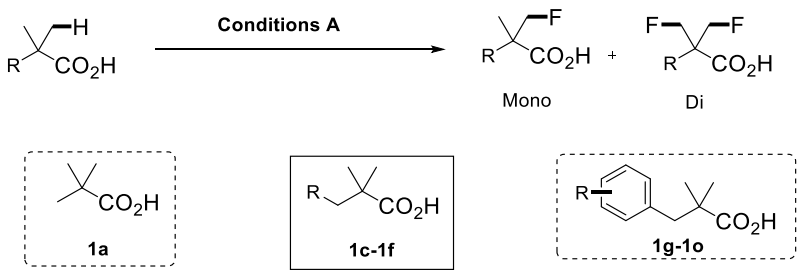
Control Experiment B:

An oven dried 10 mL Schlenk tube was charged with $Pd(OAc)_2$ (2.3 mg, 10 µmol, 10 mol%), L1 (2.8 mg, 10 µmol, 10 mol%), $NaHCO_3$ (4.2 mg, 50 µmol, 0.5 equiv.), OX1 (29.9 mg, 0.120 mmol, 1.25 equiv.), AgF (31.7 mg, 0.250 mmol, 2.50 equiv.), **1a** (0.1 mmol, 1.0 equiv.), **3a** (0.1 mmol, 1.0 equiv.) and HFIP (1.75 mL). The reaction mixture was stirred at 60 °C for 24 h in a preheated metal block. The reaction mixture was allowed to cool to rt and was then filtered through a pad of Celite® using CH_2Cl_2 (30 mL) to complete the elution. All the volatiles were removed under reduced pressure and the crude reaction mixture was analyzed via ^1H and ^{19}F NMR using CH_2Br_2 as internal standard.



3a was prepared following the literature procedure of Yu *et al.*[13]

Discussion on the Factors Controlling the Formation of Di-Fluorinated Products



The α-quaternary carboxylic acids used in this study can be classified into different categories based on the number of accessible β-methyl-groups and functional groups. The substrate **1a** contains three methyl groups, **1c-1f** contain two methyl groups along with either longer hydrocarbon chain or heteroatom on the remaining chain, **1g-1o** contain two methyl groups along with substituted phenyl ring on the side chain.

The first fluorination is in any case expected to take place in one of the available methyl groups. After this, the product **2a** formed from **1a** still has two reactive methyl groups, leading to substantial di-fluorination. All other substrates only feature one remaining position that can react (Note: the di-fluorination occurs on a methyl group and not the methylene/benzylic positions, as evidenced by the symmetric spectrum of the di-fluorinated compounds). Now, comparing the reactions of **1c-1f** vs **1g-1o**, the respective mono-fluorinated compounds featuring benzylic positions face a competition between di-fluorination and decomposition via unspecific reactions of the benzylic position (Note: Due to the inherently lower bond dissociation energy of benzylic C(sp^3)–H bonds, **1g-1o** are more prone to such side reactions). As a result, these compounds form very low amounts of di-fluorinated products. In contrast, for **1c-1f**, which lack this competition, more di-fluorinated product is generally detected. The exclusive detection of mono product for **2d** could be attributed to either an inherently lower reactivity or the possibility of di-fluorinated product getting seperated during the purification for this compound.

Evaluation of a Possible Reaction between the Oxidant and AgF to Form a New Reactive Species

During the evaluation of this manuscript one reviewer suggested that the oxidant and AgF might react to form a new reactive species before inducing the fluorination. For this reason, the following control experiments were performed:

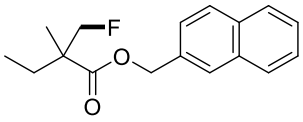
Experiment 1: A 10 mL Schlenk tube was charged with **OX1** (0.1 mmol, 1.0 equiv.) and AgF (1.5 equiv.). HFIP (1.0 mL) was added and the reaction mixture was stirred for 6 h at 60 °C. It was then cooled to r.t and was diluted with CH_2Cl_2 (5 mL). A TLC analysis showed the presence of unreacted **OX1** while no other side product was detected. Furthermore, a crude NMR using CH_2Br_2 as internal standard was performed which showed more than 99% of **OX1** was recovered.

Experiment 2: A 10 mL Schlenk tube was charged with **OX1** (0.1 mmol, 1.0 equiv.), pivalic acid (1.0 equiv.), $NaHCO_3$ (0.5 equiv.), **L1** (10 mol%), AgF (1.5 equiv.). HFIP (1.0 mL) was added to the Schlenk tube and the reaction mixture was stirred for 6 h at 60 °C. It was then cooled to r.t and was diluted with CH_2Cl_2 (5 mL). No product other than the unreacted **OX1** was detected in TLC. Furthermore, a crude NMR using CH_2Br_2 as internal standard was recorded which showed more than 99% of **OX1** was recovered.

The experiments shows that a direct reaction between fluoride and peroxide does not occur under our reaction conditions.

8. Preparative Scale Applications

Naphthalen-2-ylmethyl 3-fluoro-2,2-dimethylpropanoate (2c-Naph):



2c-Naph

An oven dried 150 mL Schlenk tube was charged with $Pd(OAc)_2$ (22.4 mg, 0.100 mmol, 10 mol%), **L1** (28.3 mg, 0.100 mmol, 10 mol%), $NaHCO_3$ (42 mg, 0.50 mmol, 0.5 equiv.), **OX1** (299 mg, 1.25 mmol, 1.25 equiv.), AgF (317 mg, 2.50 mmol, 2.50 equiv.), **2,2-dimethyl butanoic acid** (**1.0 mmol,** 1.0 equiv.) and HFIP (**17.5** mL). The reaction mixture was stirred at 60 °C for 24 h in a preheated metal block. The reaction mixture was allowed to cool to rt and formic acid (1.0 mL) was added. The mixture was filtered through a pad of Celite® using CH_2Cl_2 (60 mL) to complete the elution and all volatiles were removed under reduced pressure. K_2CO_3 (0.7 g, 5.0 mmol, 5 equiv.), NaI (22 mg, 0.30 mmol, 0.3 equiv.), 2-(Bromomethyl)naphthalene (1.1 g, 5.0 mol, 5 equiv.) and acetone (25 mL) were added and the resulting mixture was stirred at rt for 24 h. The mixture was filtered through a pad of Celite® using CH_2Cl_2 (30 mL) to complete the elution, all volatiles were removed under reduced pressure, and the residue was purified by silica gel column chromatography (pentane:EtOAc = 99:1) to afford the target compound **2c-Naph** as a pale yellow oil (151.3 mg, 551.0 µmol, 55%).

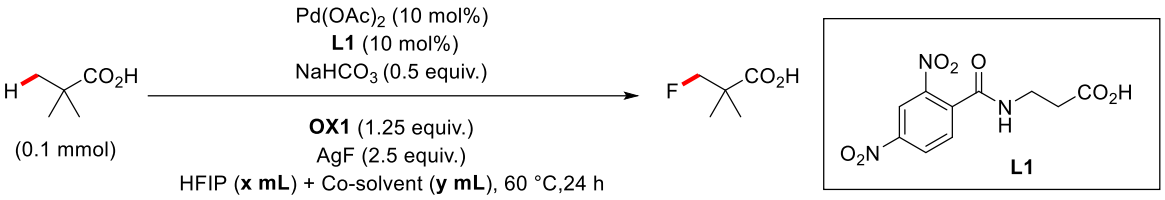
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.86 – 7.83 (m, 4H), 7.52-7.49 (m, 2H), 7.46 (dd, *J* = 8.5, 1.9 Hz, 1H), 5.33 (s, 2H), 4.59 (dd, *J* = 47.2, 8.9 Hz, 1H), 4.42 (dd, *J* = 47.2, 8.9 Hz, 1H), 1.77 – 1.53 (m, 2H), 1.29 (d, *J* = 1.5 Hz, 3H), 0.89 (t, *J* = 7.5 Hz, 3H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 174.7 (d, *J* = 4.6 Hz), 133.5, 133.3, 133.2, 128.5, 128.1, 127.84, 127.3, 126.4, 126.4, 125.8, 87.3 (d, *J* = 173.7 Hz), 66.7, 47.8 (d, *J* = 17.9 Hz), 27.7 (d, *J* = 5.5 Hz), 18.8 (d, *J* = 4.1 Hz), 8.6 ppm.

^{19}F NMR (471 MHz, $CDCl_3$): δ = –225.9 (s) ppm.

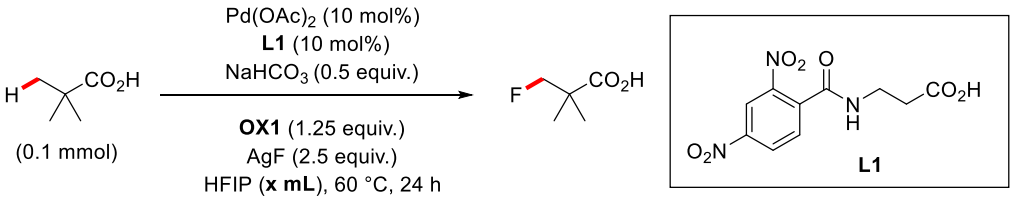
HRMS (ESIpos) m/z: Calcd for $C_{17}H_{20}FO_2$ 275.1441, Found 275.1438

Investigation of Solvent Amount for Large Scale Reactions



Entry	HFIP (x mL)	Co-solvent (y mL)	NMR-Yield (%)
1.	1.75	None	55
2.	1.0	TFE (0.75)	30
3.	1.0	CH_3CN (0.75)	< 5
4.	1.0	THF (0.75)	< 2
5.	1.0	Acetone (0.75)	< 5
6.	1.0	DCE (0.75)	46
7.	1.0	CH_2Cl_2 (0.75)	48

Scheme S33: Screening of co-solvents

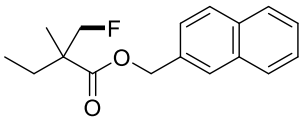


Entry	(x mL)	NMR-Yield (%)
1.	1.75	55
2.	1.5	53
3.	1.25	50
4.	1.0	48
5.	0.85	44
6.	0.7	42
7.	0.5	38

Scheme S34: Screening of HFIP amount

Large Scale Reaction with Reduced Amount of HFIP

Naphthalen-2-ylmethyl 3-fluoro-2,2-dimethylpropanoate (2c-Naph):



2c-Naph

An oven dried 150 mL Schlenk tube was charged with $Pd(OAc)_2$ (22.4 mg, 0.100 mmol, 10 mol%), **L1** (28.3 mg, 0.100 mmol, 10 mol%), $NaHCO_3$ (42 mg, 0.50 mmol, 0.5 equiv.), **OX1** (299 mg, 1.25 mmol, 1.25 equiv.), AgF (317 mg, 2.50 mmol, 2.50 equiv.), **2,2-dimethyl butanoic acid** (**1.0 mmol**, 1.0 equiv.) and HFIP (**10 mL**). The reaction mixture was stirred at 65 °C for 24 h in a preheated metal block. The reaction mixture was allowed to cool to rt and formic acid (1.0 mL) was added. The mixture was filtered through a pad of Celite® using CH_2Cl_2 (60 mL) to complete the elution and all volatiles were removed under reduced pressure. K_2CO_3 (1.0 g, 5.0 mmol, 7.5 equiv.), NaI (22 mg, 0.30 mmol, 0.3 equiv.), 2-(Bromomethyl)naphthalene (1.1 g, 5.0 mol, 5 equiv.) and acetone (25 mL) were added and the resulting mixture was stirred at rt for 24 h. The mixture was filtered through a pad of Celite® using CH_2Cl_2 (30 mL) to complete the elution, all volatiles were removed under reduced pressure, and the residue was purified by silica gel column chromatography (pentane:EtOAc = 99:1) to afford the target compound **2c-Naph** as a pale yellow oil (132.8 mg, 484.0 µmol, 48%).

9. References

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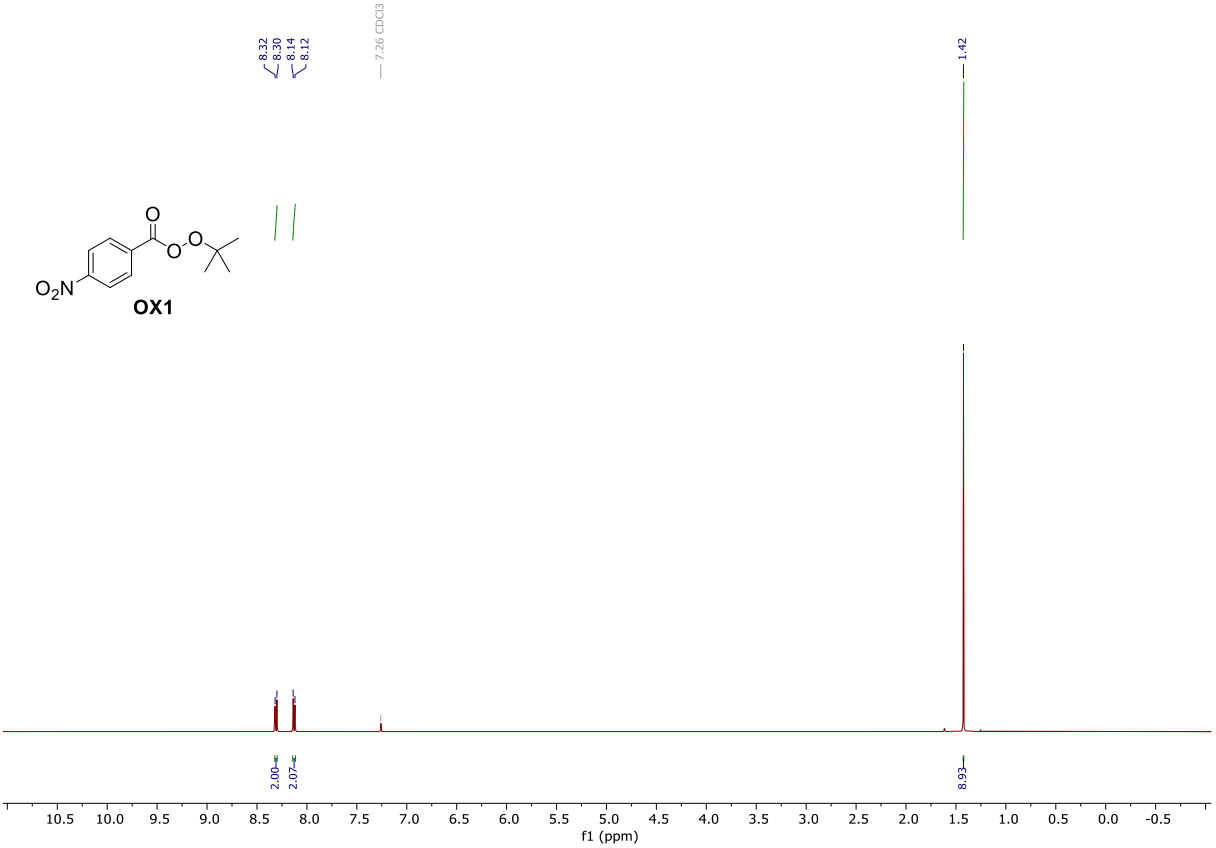
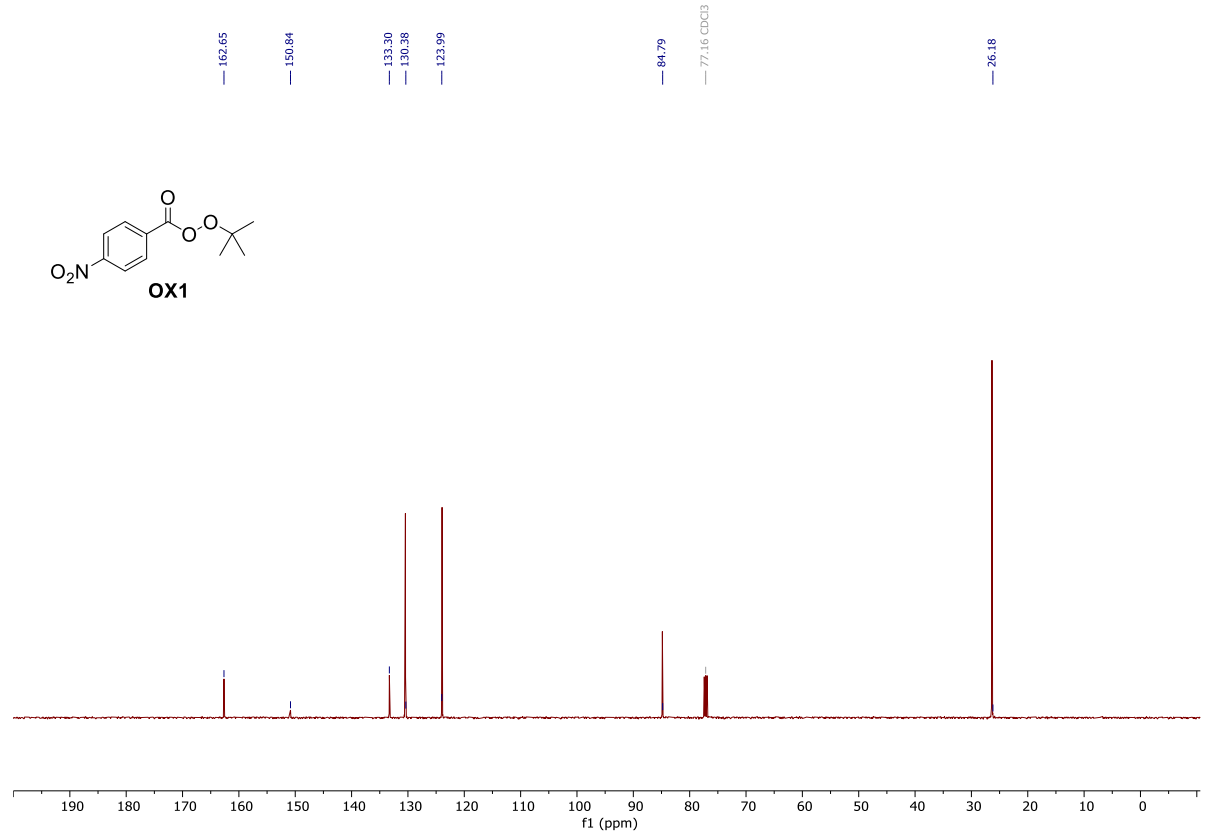
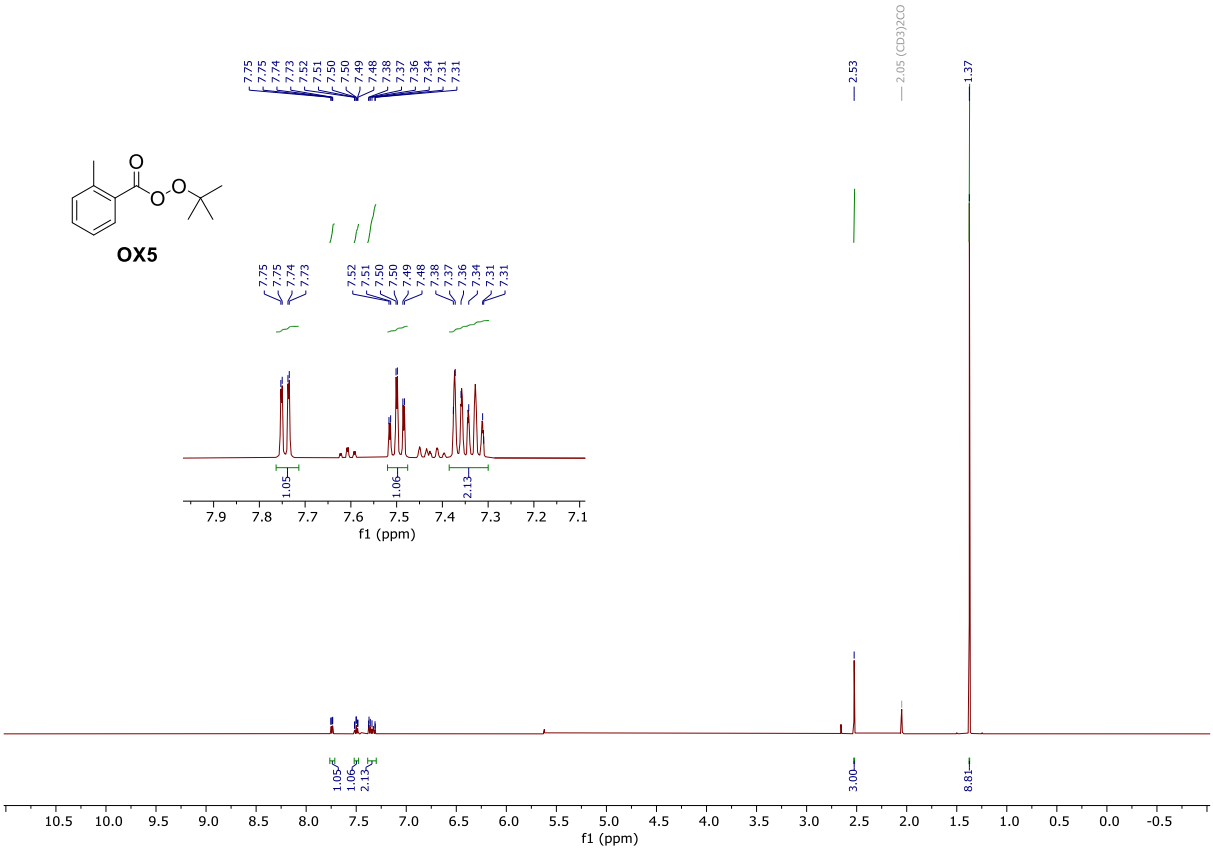
10. NMR Spectra



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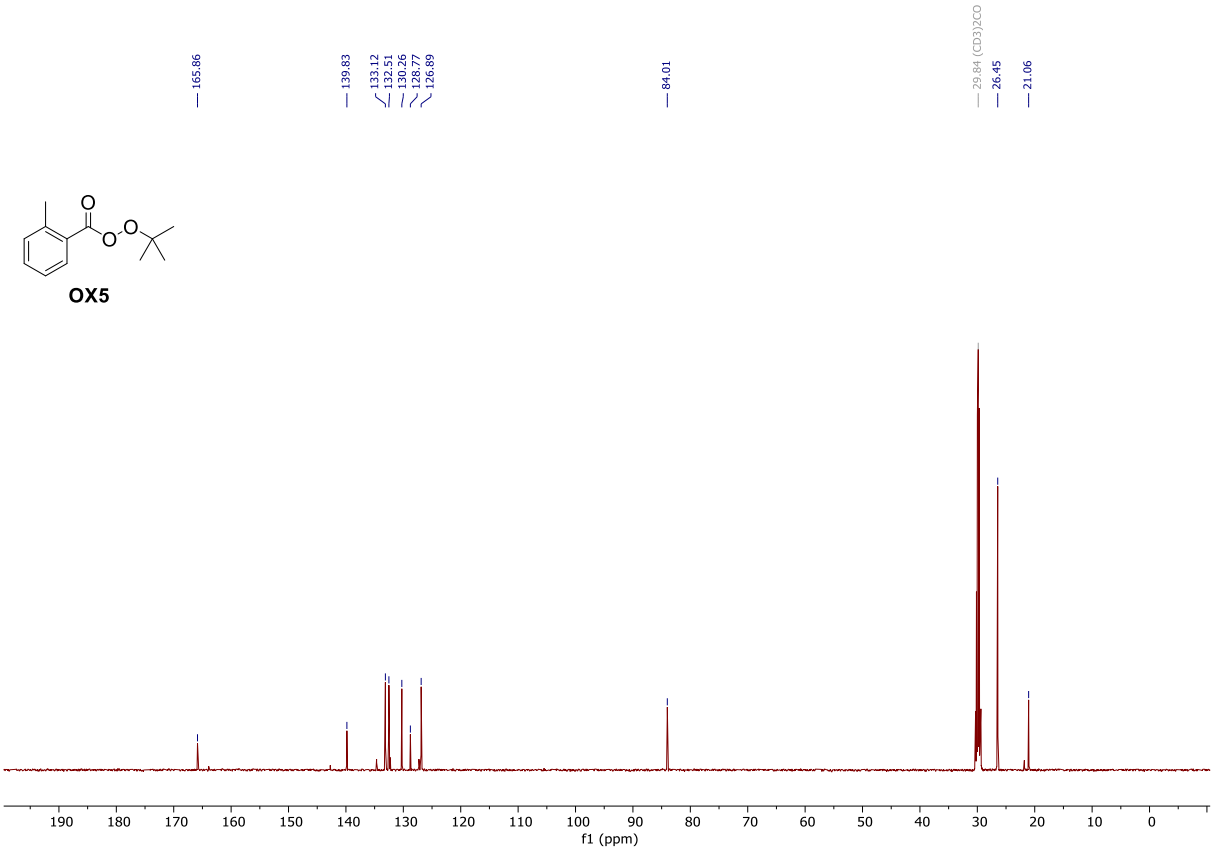
7.75
7.74
7.73
7.52
7.51
7.50
7.50
7.49
7.48
7.38
7.37
7.36
7.34
7.31
7.31
2.53
2.05 (CD3)2CO
1.37
1.05
1.06
2.13
3.00
8.81
f1 (ppm)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139.83
133.12
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130.26
128.77
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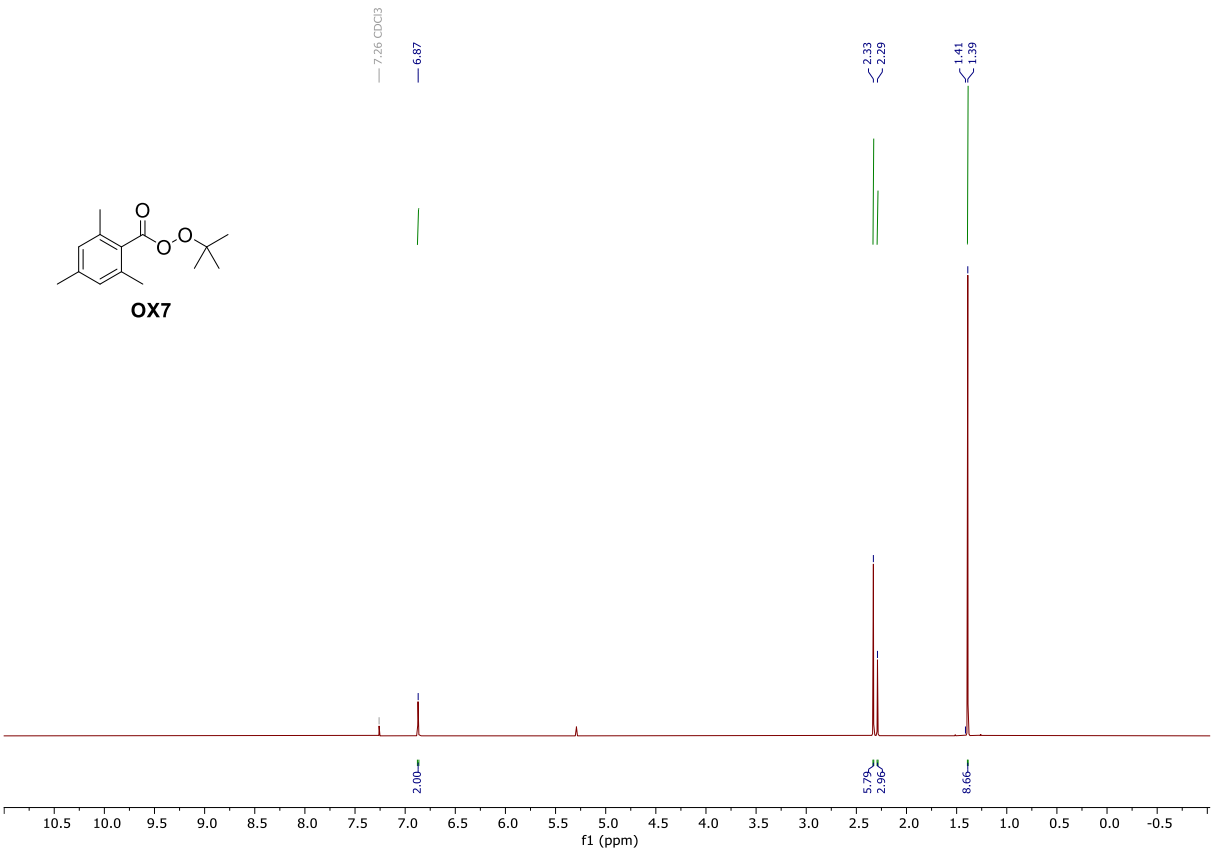
84.01
29.84 (CD3)2CO
26.45
21.06
f1 (ppm)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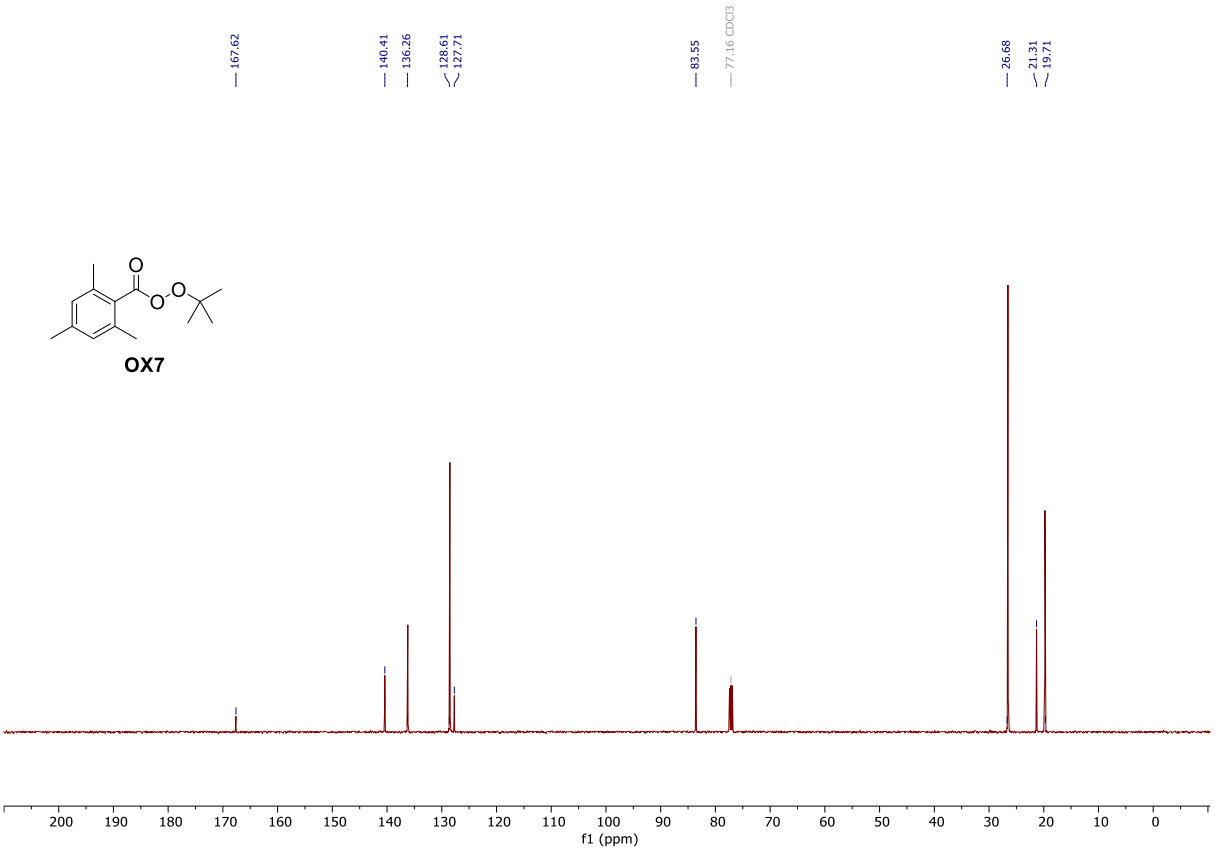
f1 (ppm)

OX7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127.71
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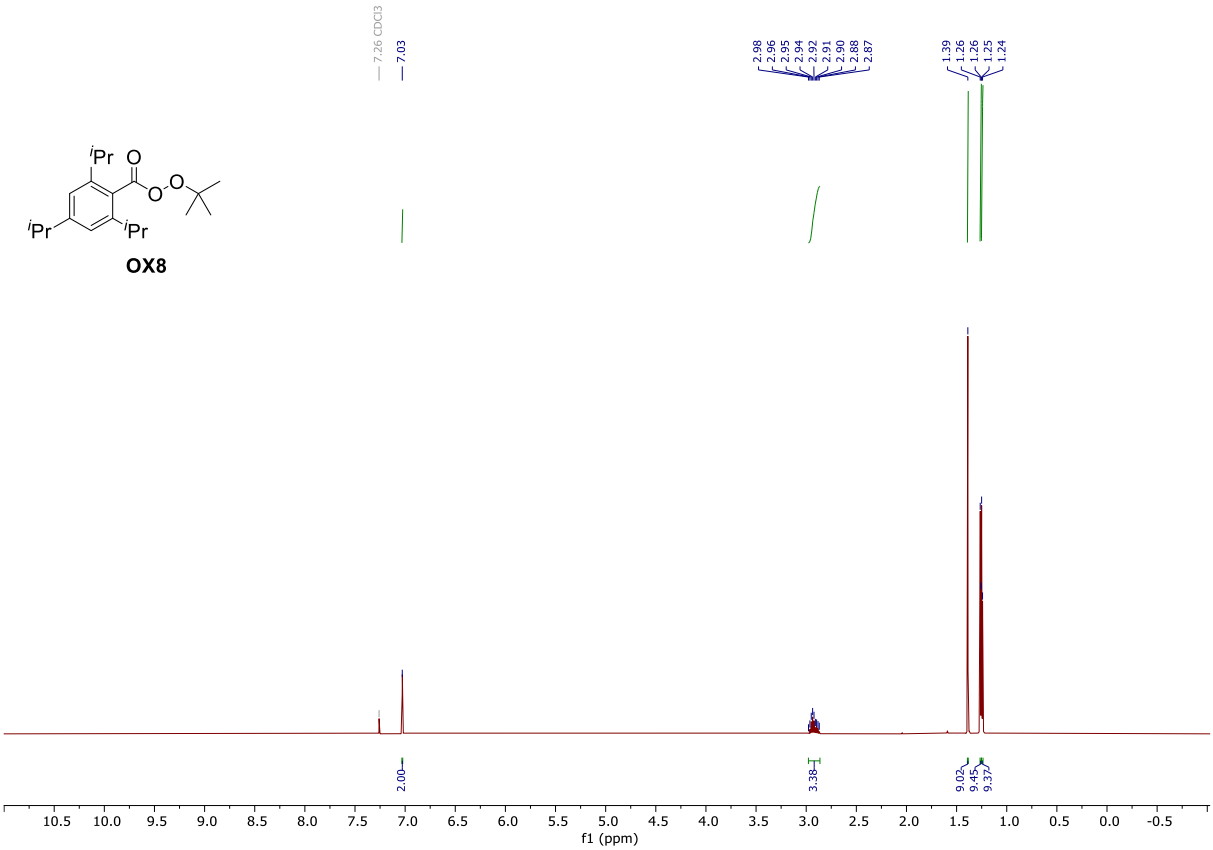
77.16 CDCl3
26.68
21.31
19.71
f1 (ppm)

OX7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7.03
2.98
2.96
2.95
2.94
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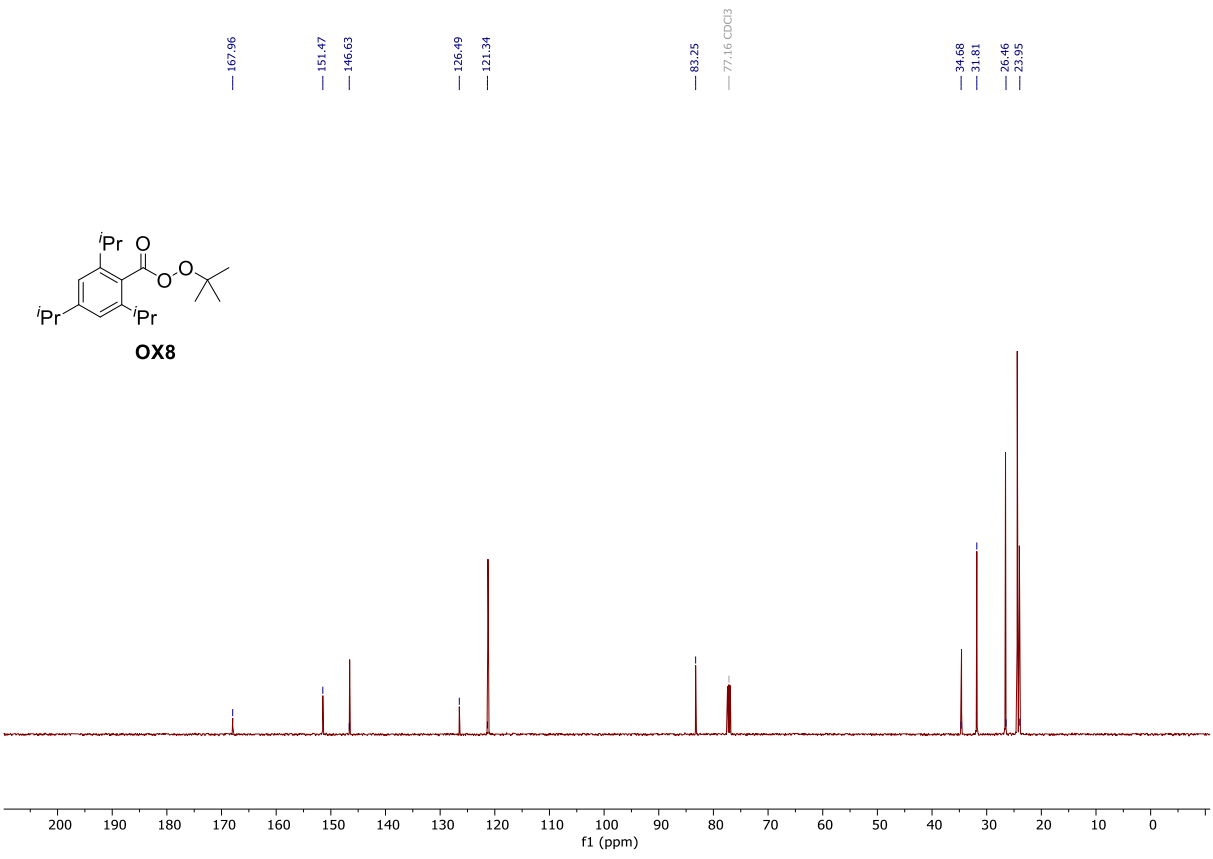
2.90
2.88
2.87
1.39
1.26
1.26
1.25
1.24
2.00
3.38
9.02
9.45
9.37
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

OX8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146.63
126.49
121.34
83.25
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34.68
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26.46
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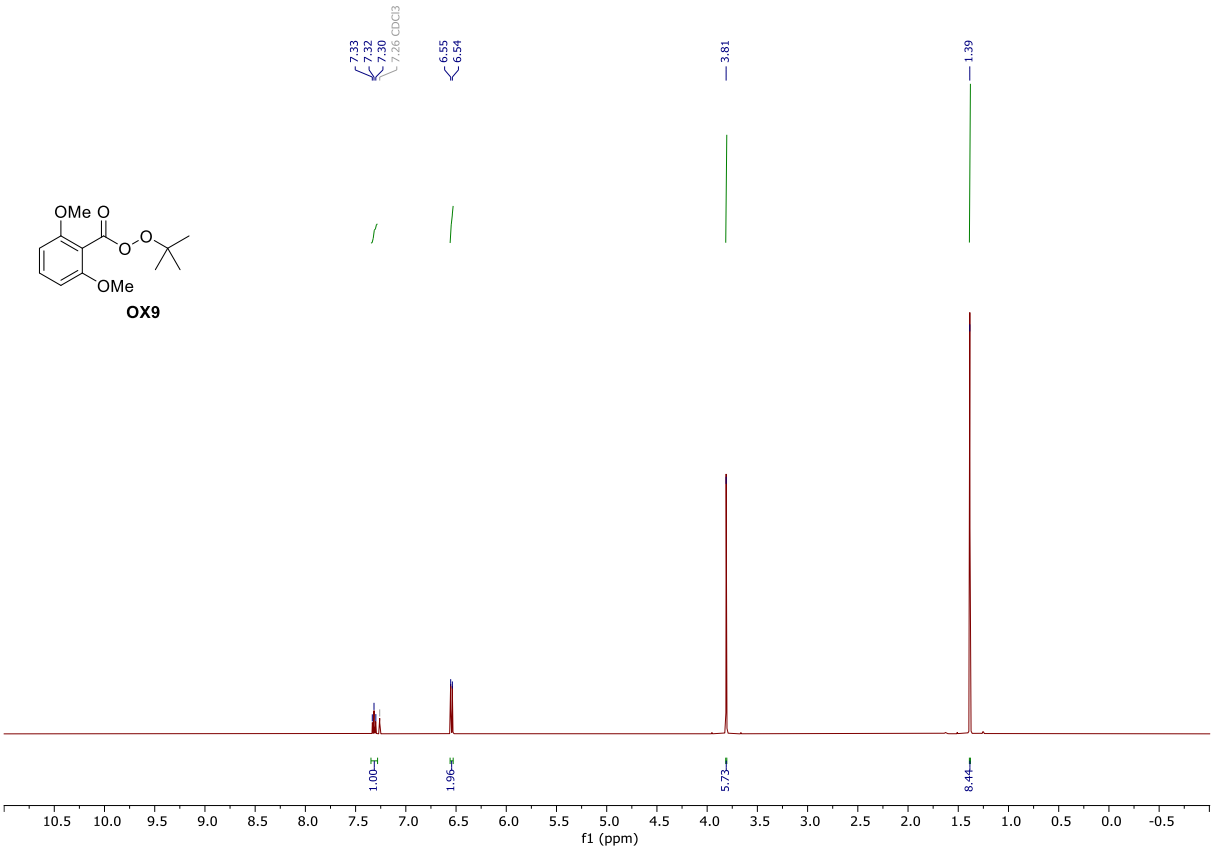
f1 (ppm)

OX8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7.32
7.30
7.26 CDCl3
6.55
6.54
3.81
1.39
OMe O
O
O
OMe
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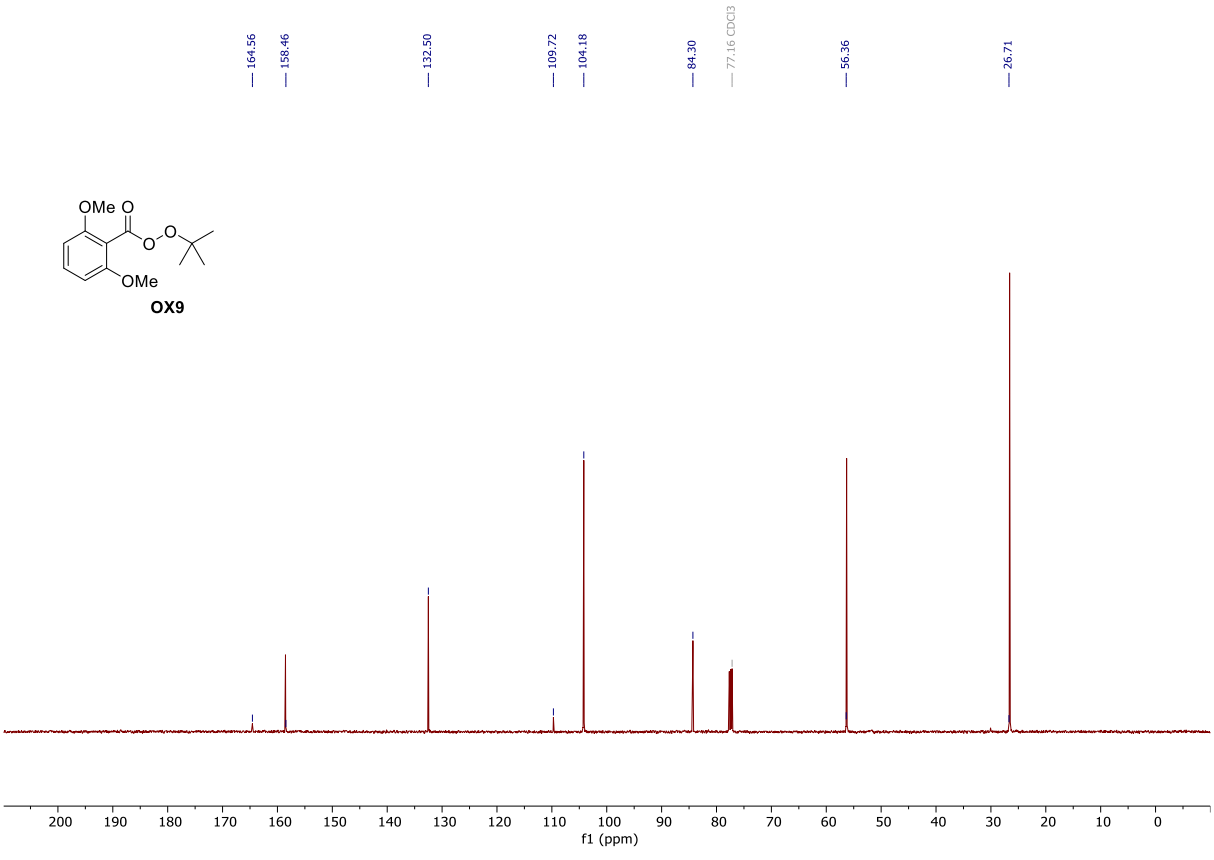
1.96
5.73
8.44
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

OX9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84.30
77.16 CDCl3
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OMe O
O
O
OMe
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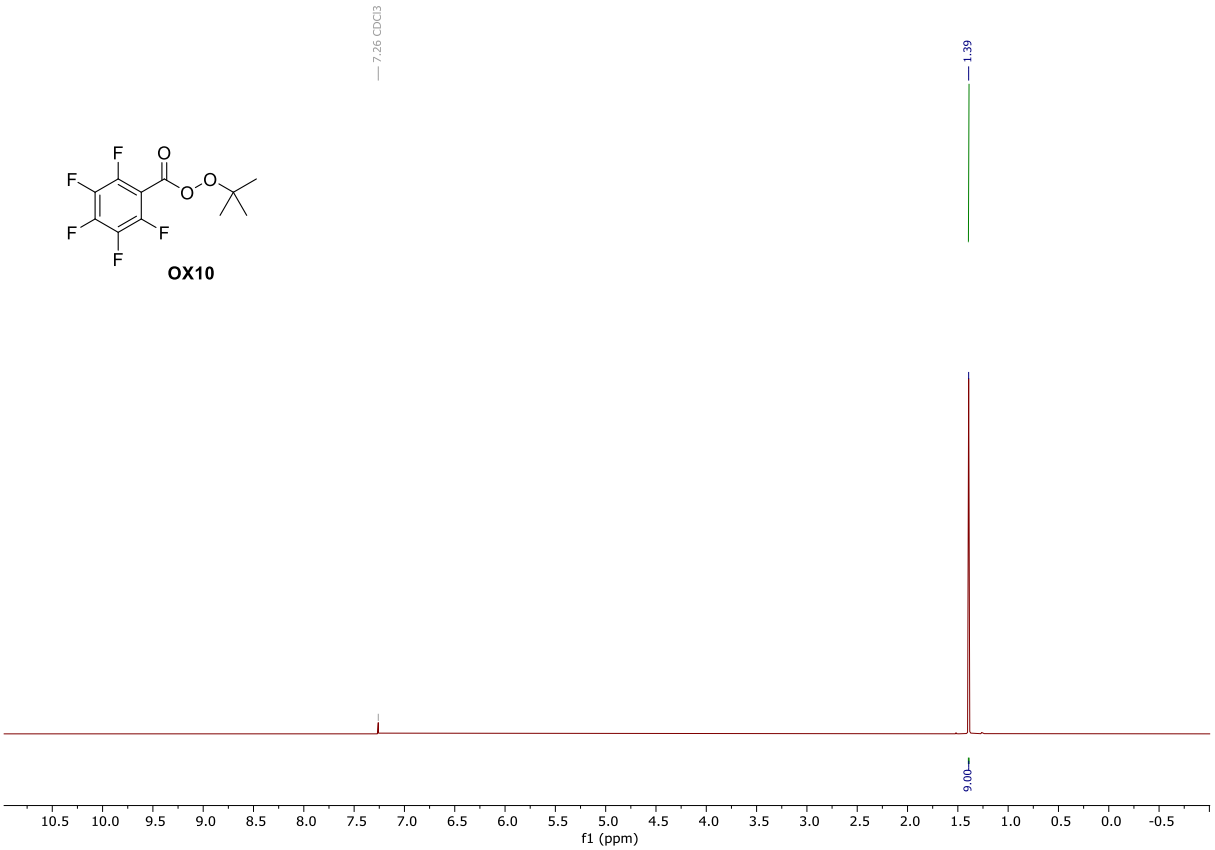
f1 (ppm)

OX9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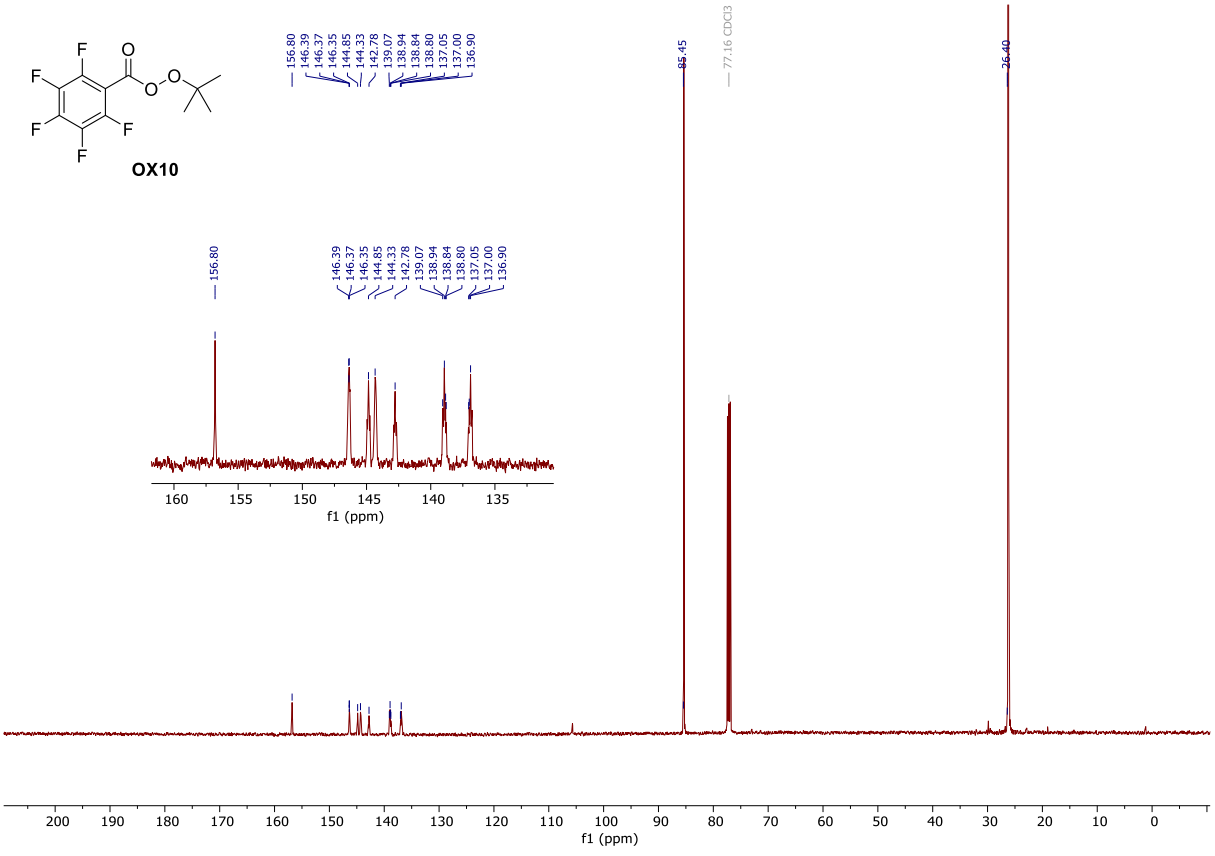
1.39
9.00
f1 (ppm)

OX10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144.33
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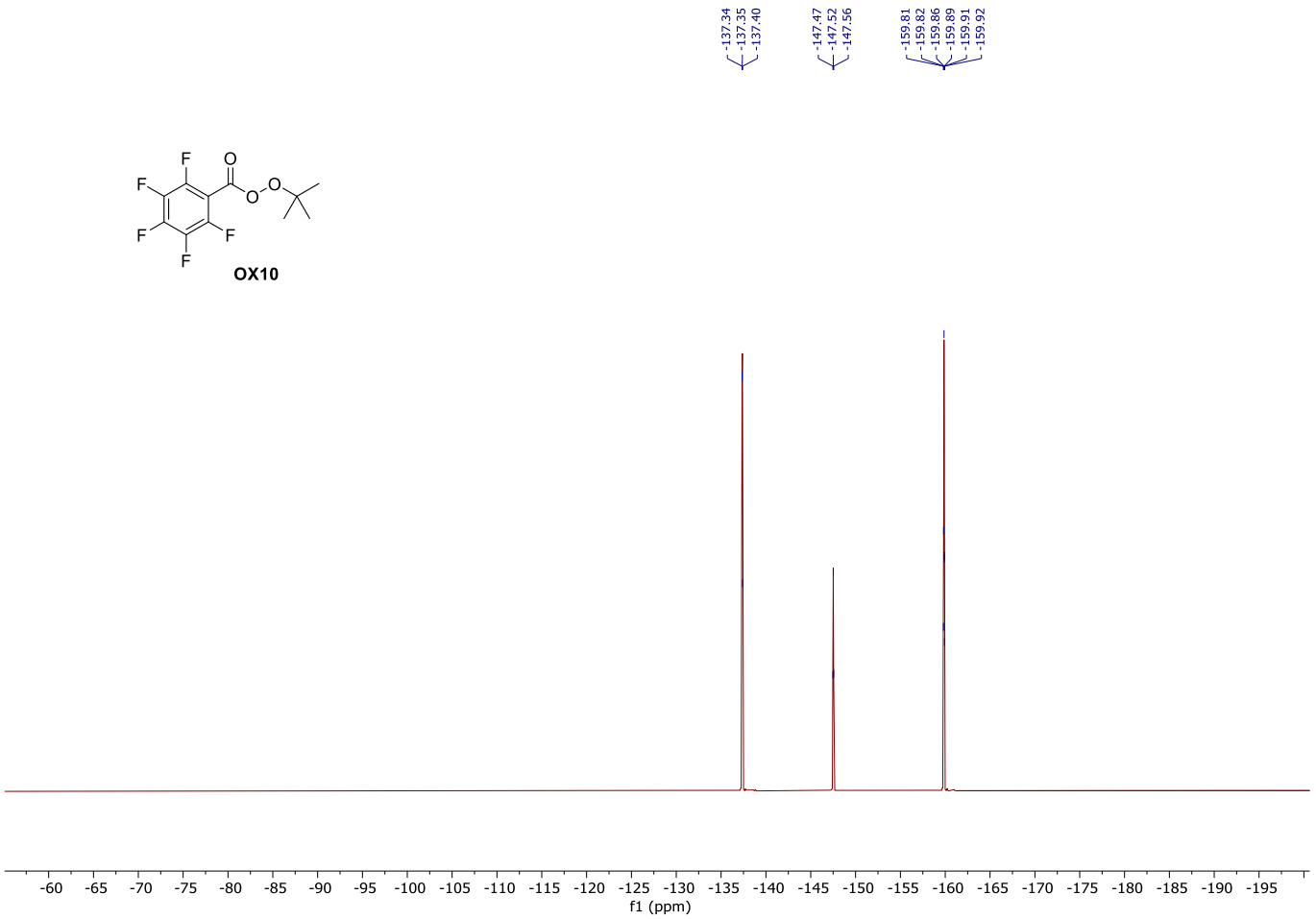
f1 (ppm)

OX10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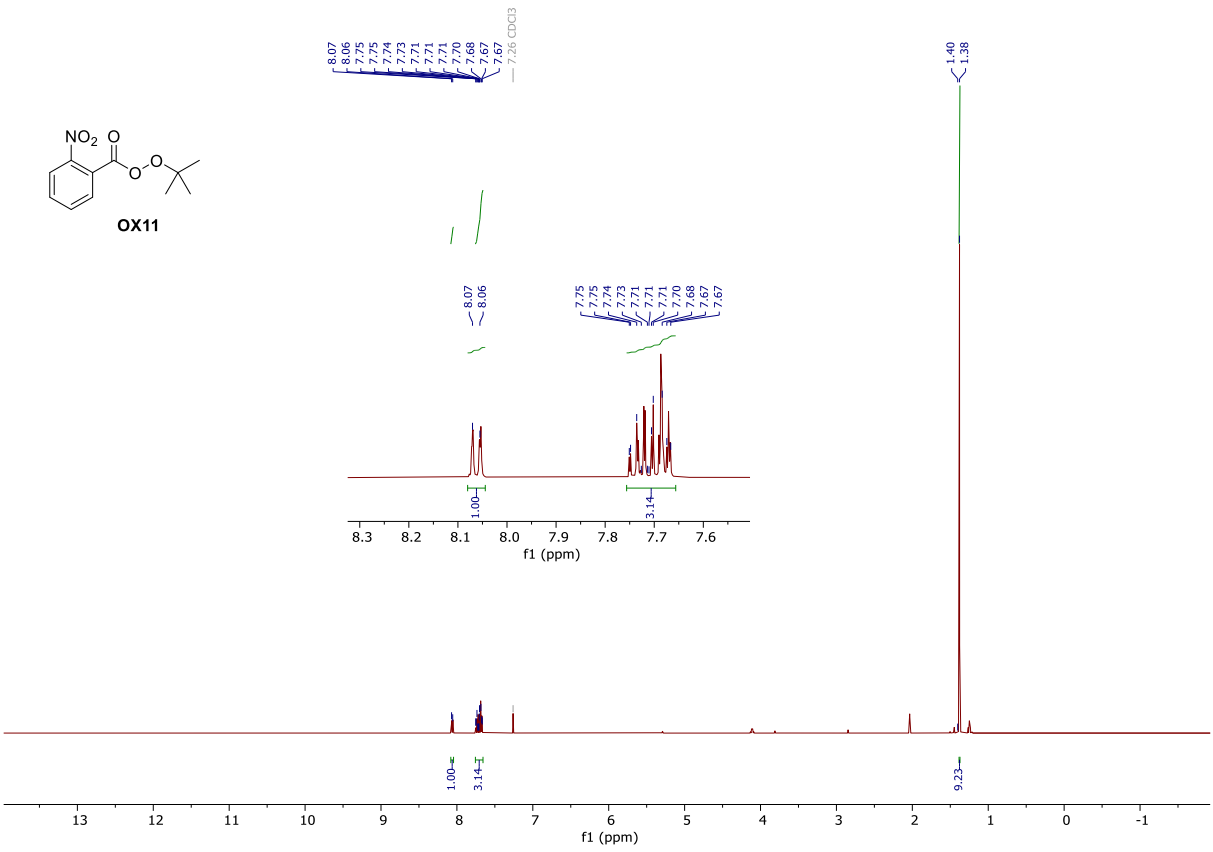
-159.91
-159.92
F
O
F
O
O
F
F
F
OX10
-60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185 -190 -195
f1 (ppm)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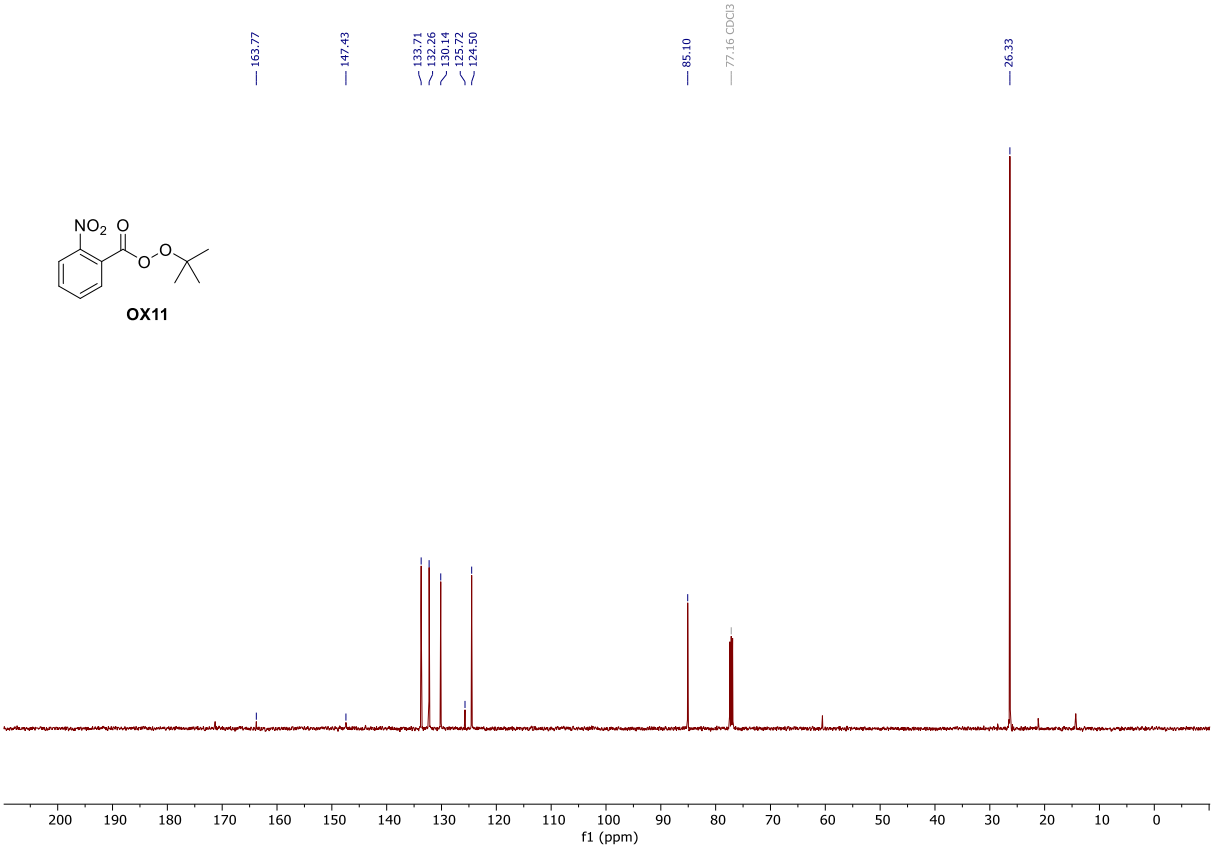
9.23
f1 (ppm)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85.10
77.16 CDCl3
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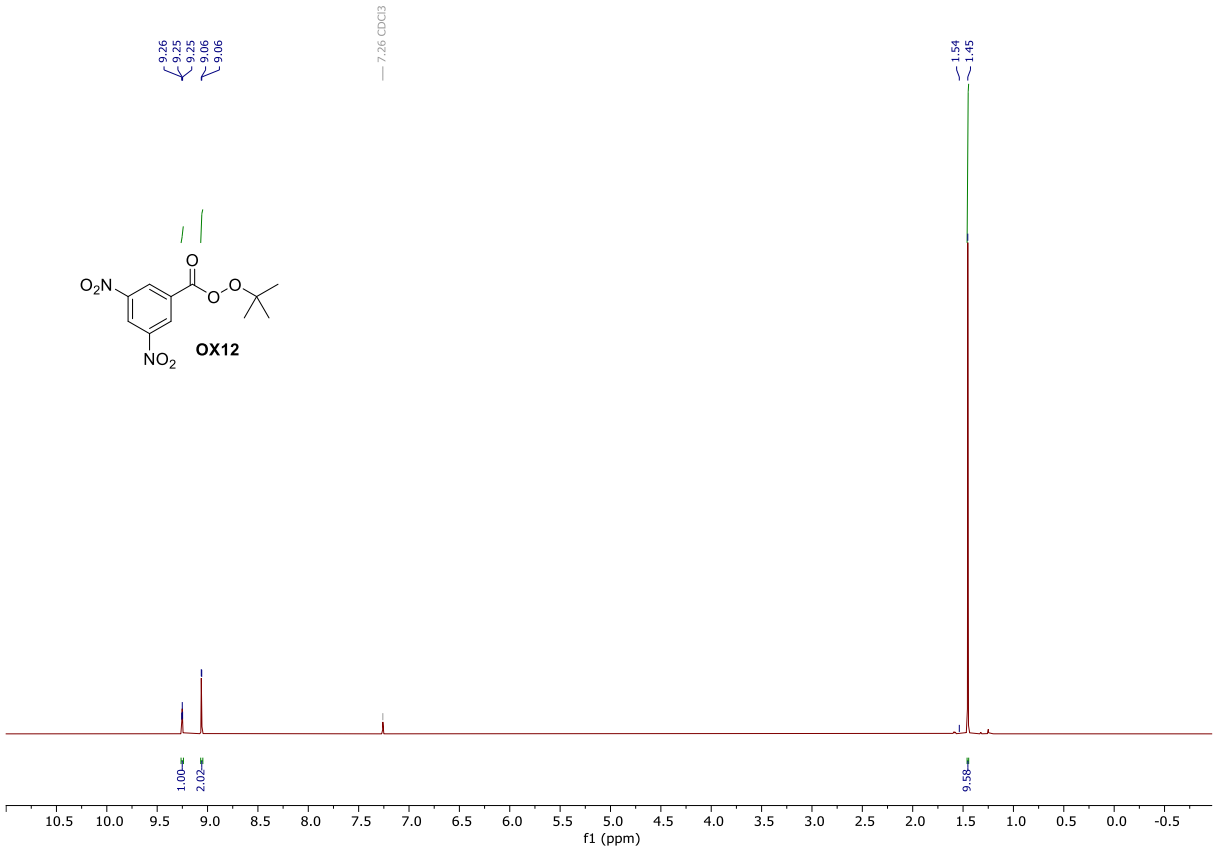
f1 (ppm)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9.25
9.25
9.06
9.06
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1.45
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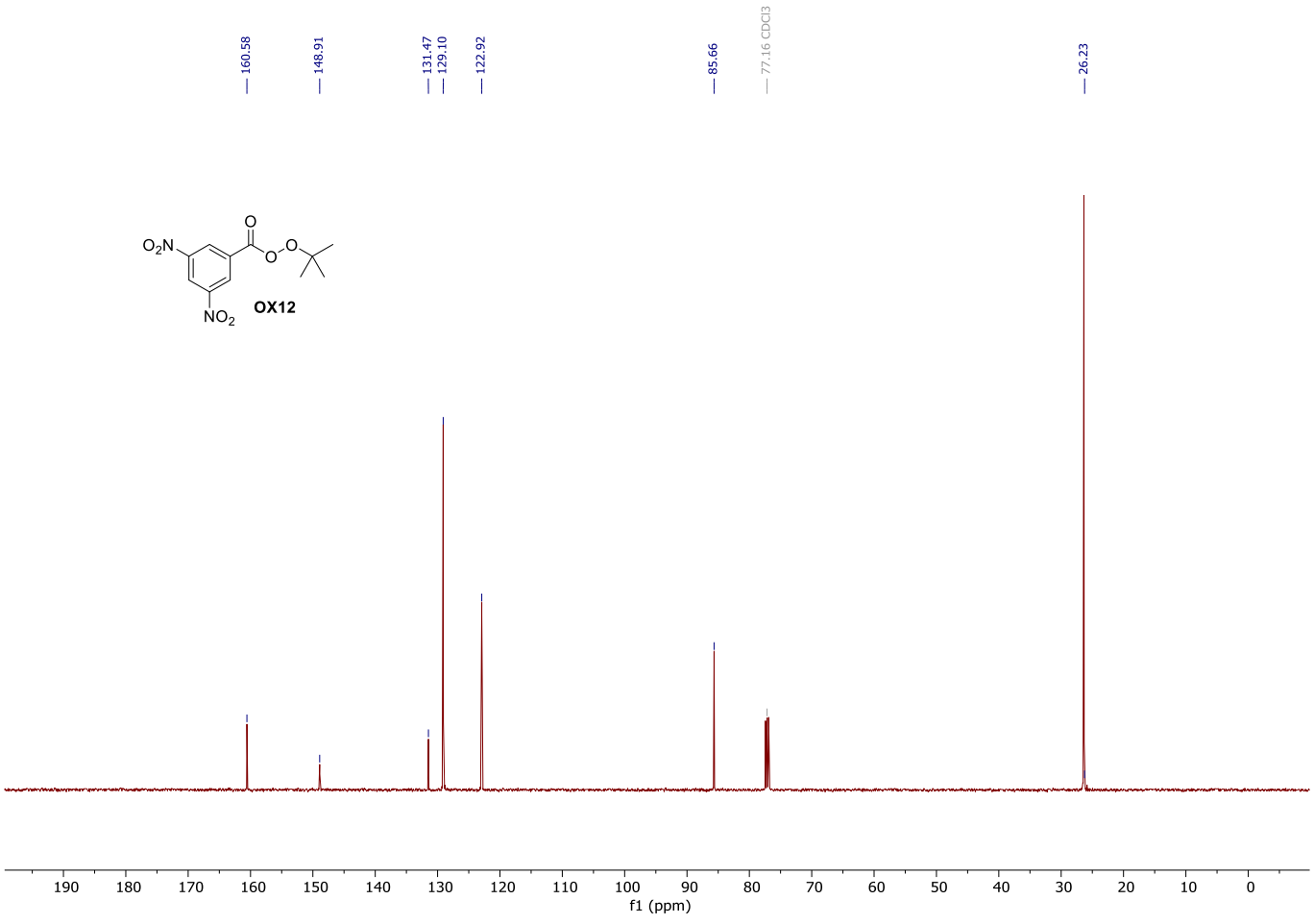
NO2
O
O
O
OX12
1.00
2.02
9.58
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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NO2
O
O
O
OX12
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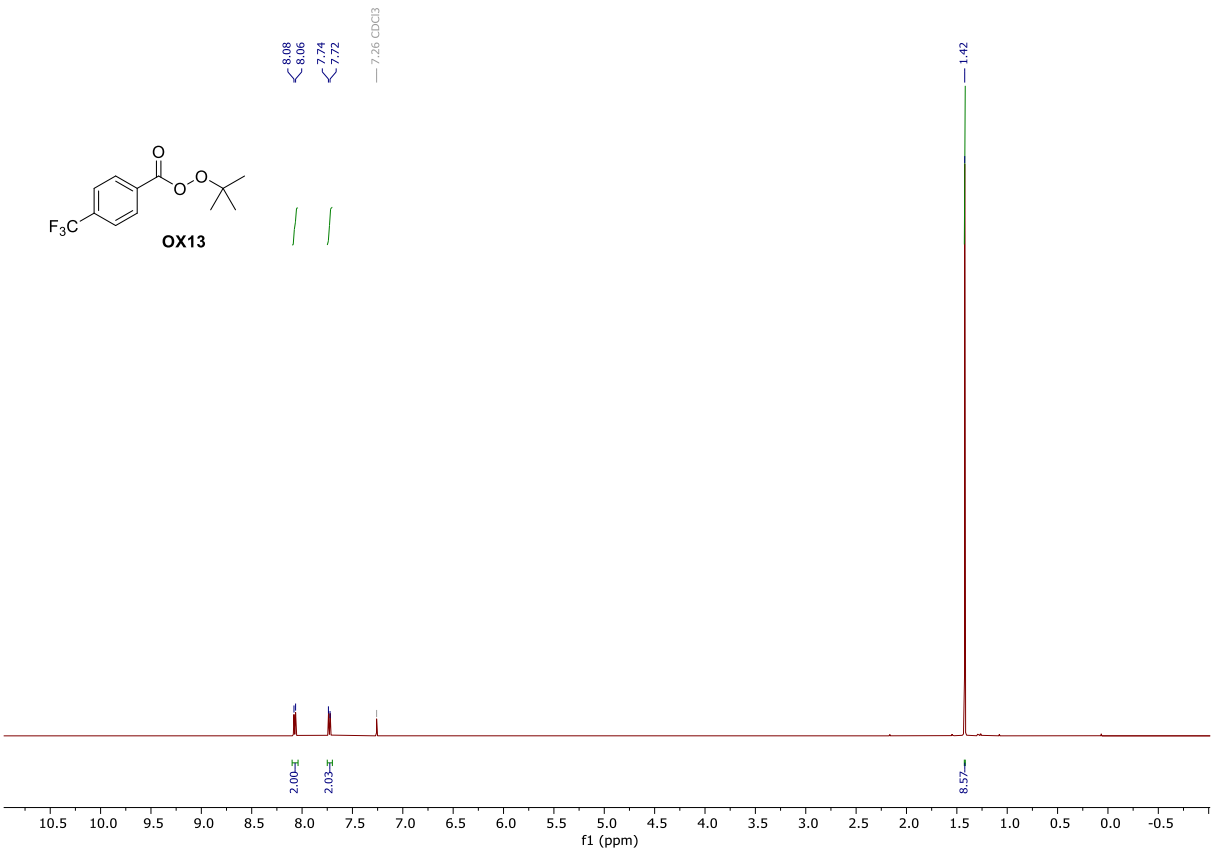
f1 (ppm)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O
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OX13
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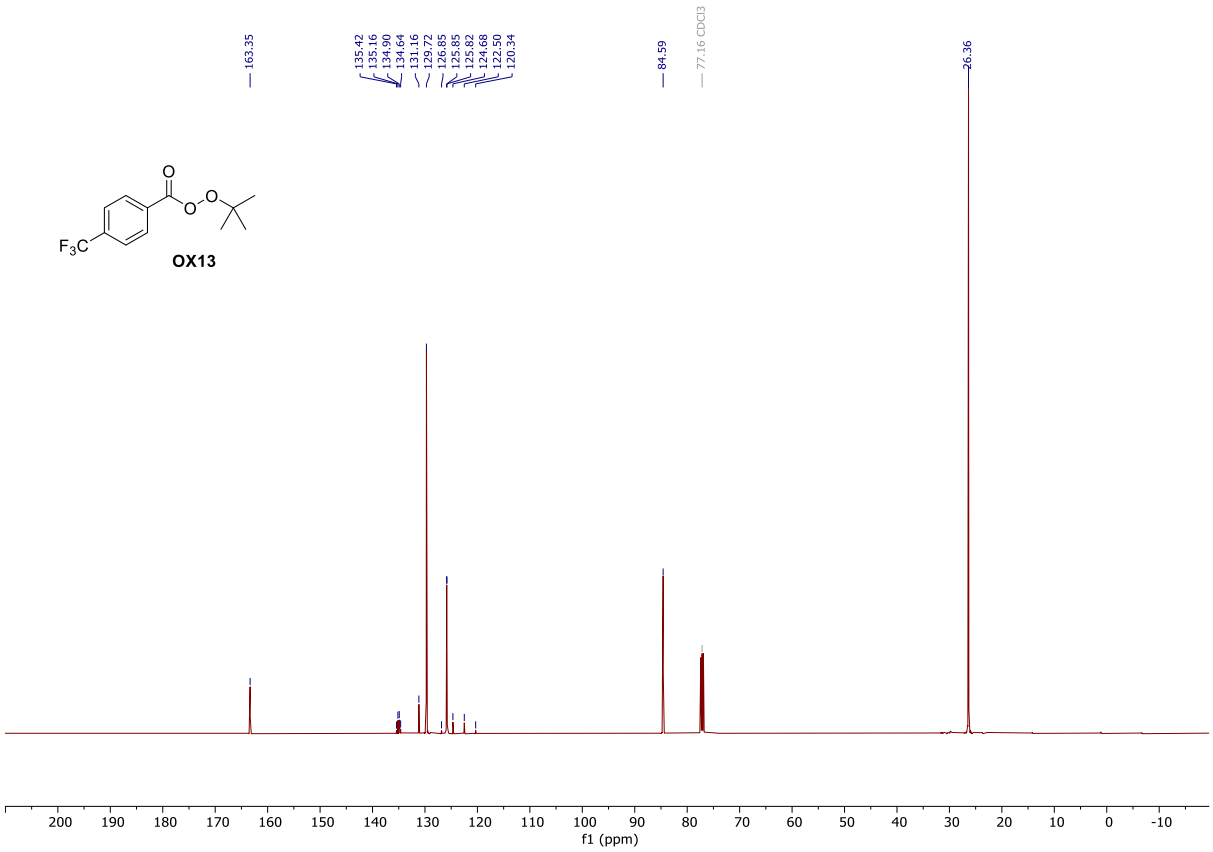
8.57
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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120.34
84.59
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O
O
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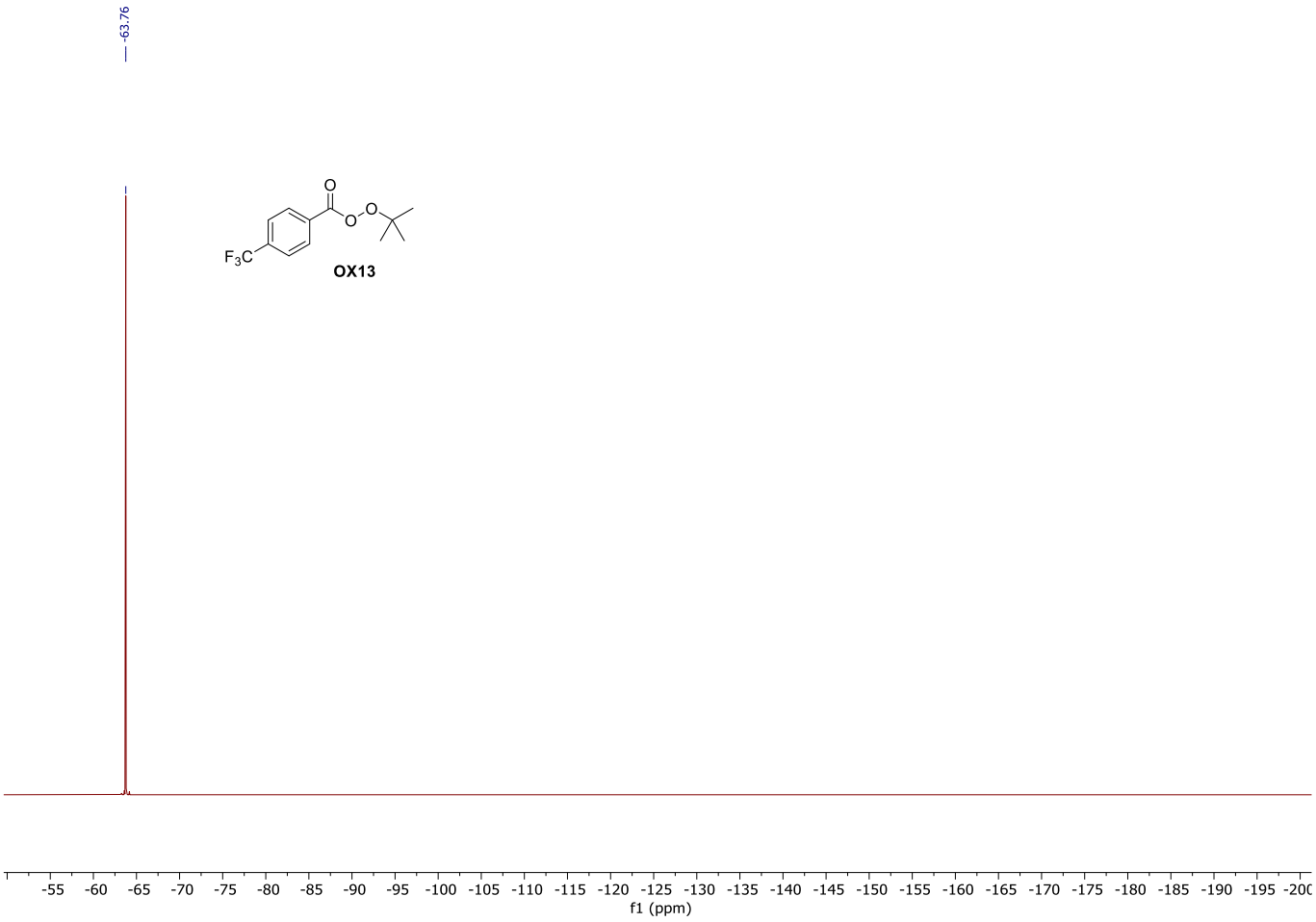
f1 (ppm)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O
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OX13
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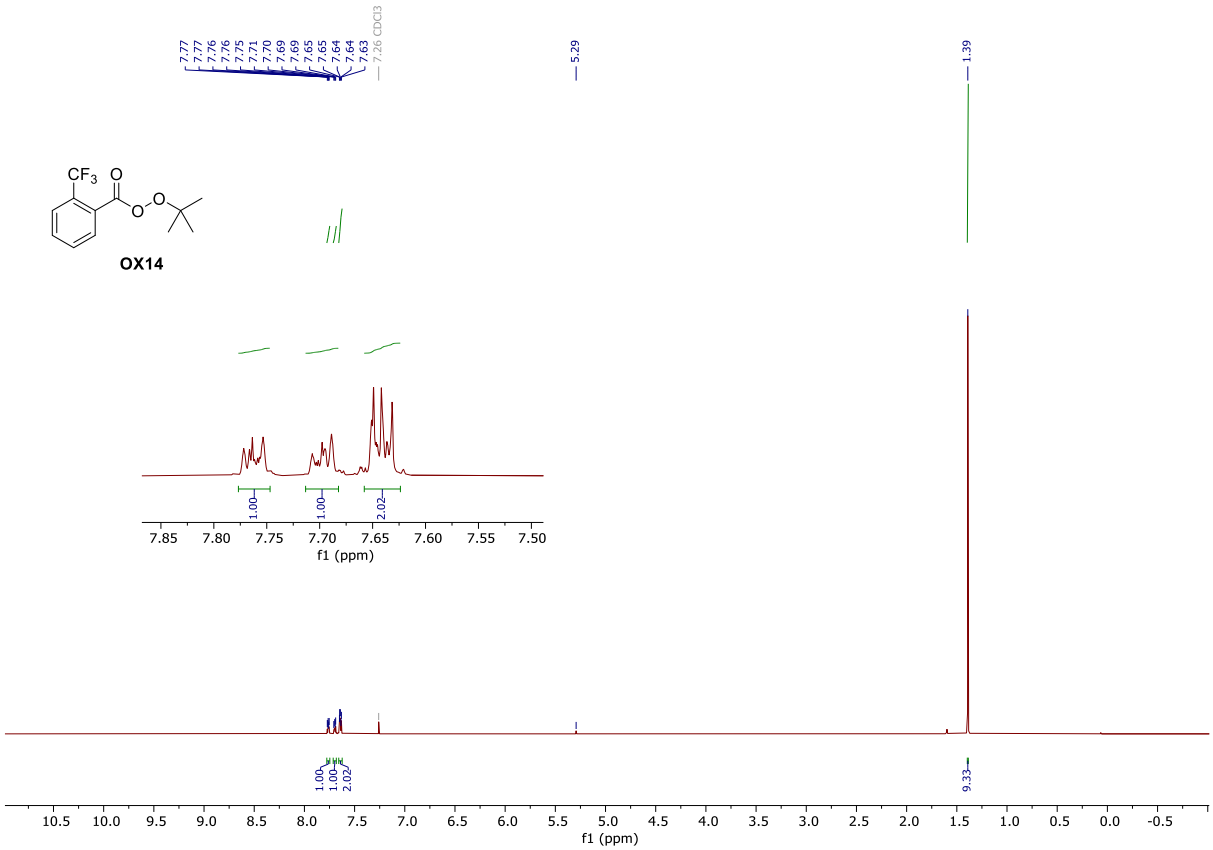
f1 (ppm)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7.71
7.70
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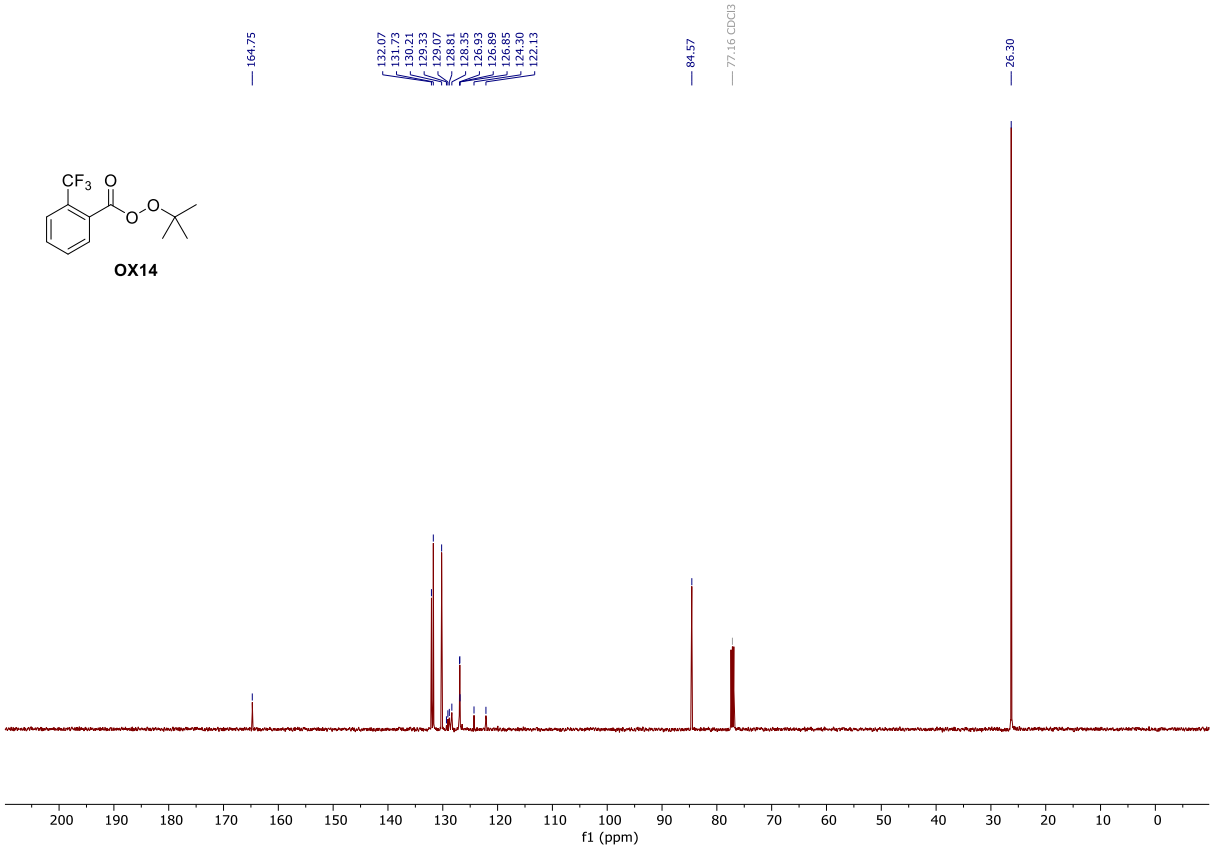
7.69
7.65
7.64
7.64
7.63
7.26 CDCl3
5.29
1.39
CF3
O
O
O
OX14
1.00
1.00
2.02
7.85 7.80 7.75 7.70 7.65 7.60 7.55 7.50
f1 (ppm)
1.00
1.00
2.02
9.33
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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122.13
84.57
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O
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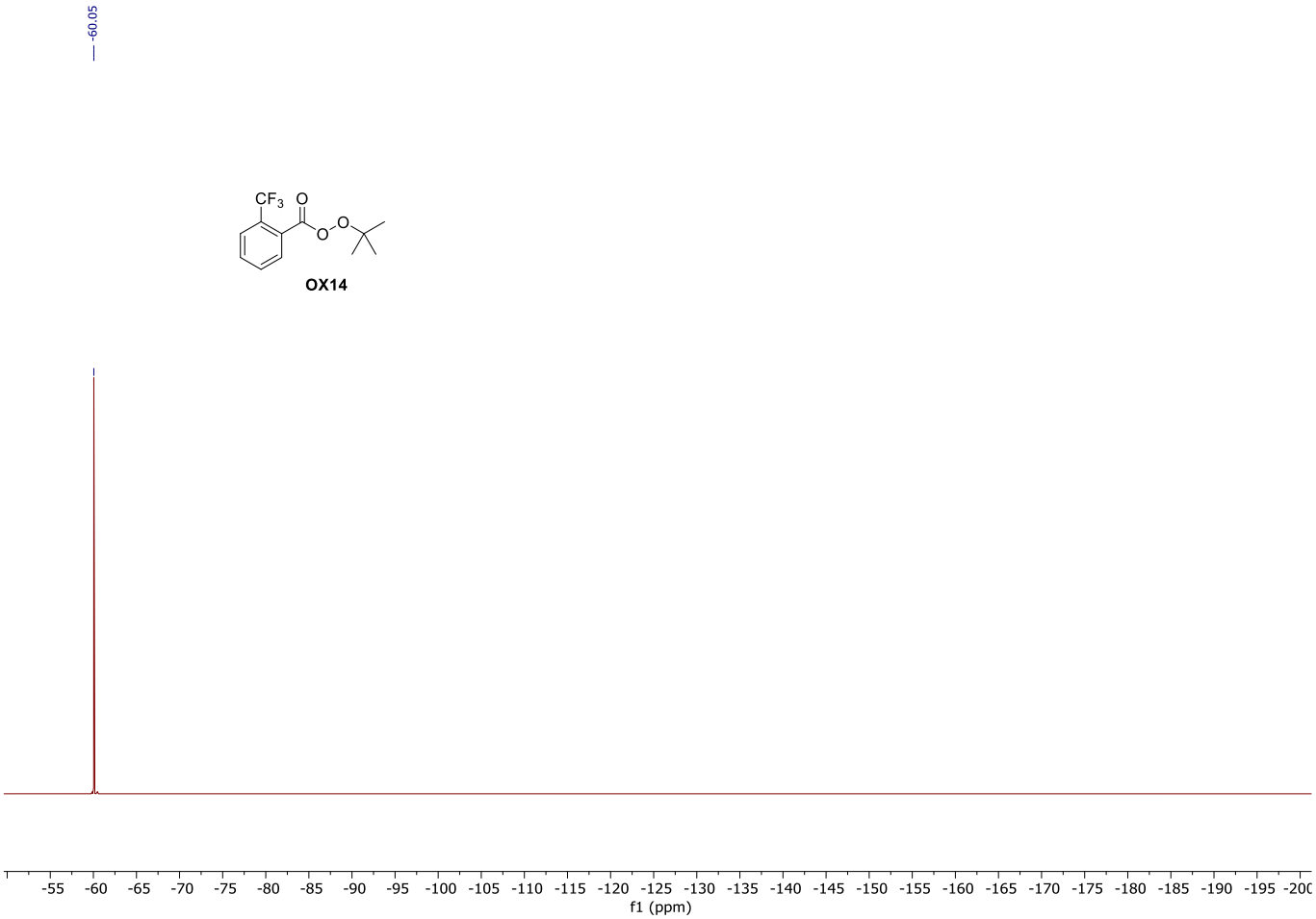
f1 (ppm)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O
O
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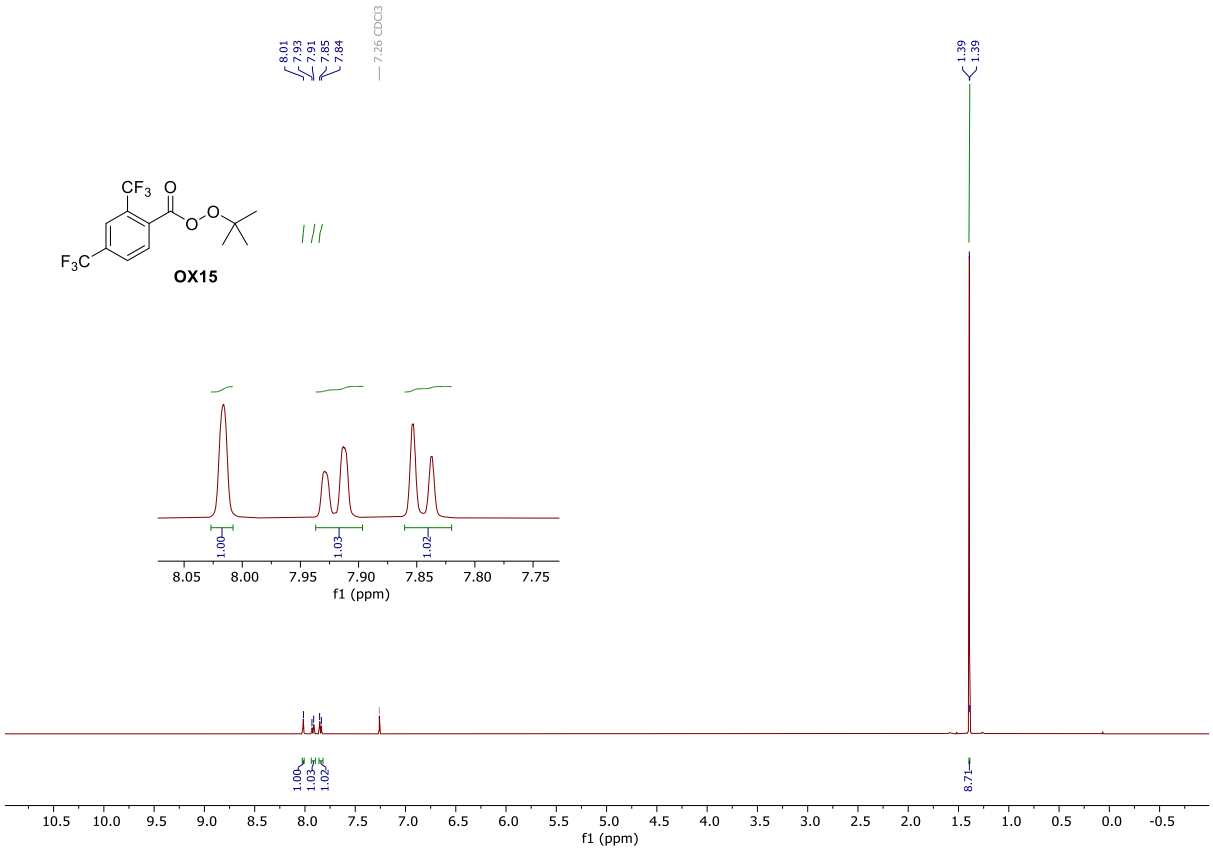
f1 (ppm)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1.39
OX15
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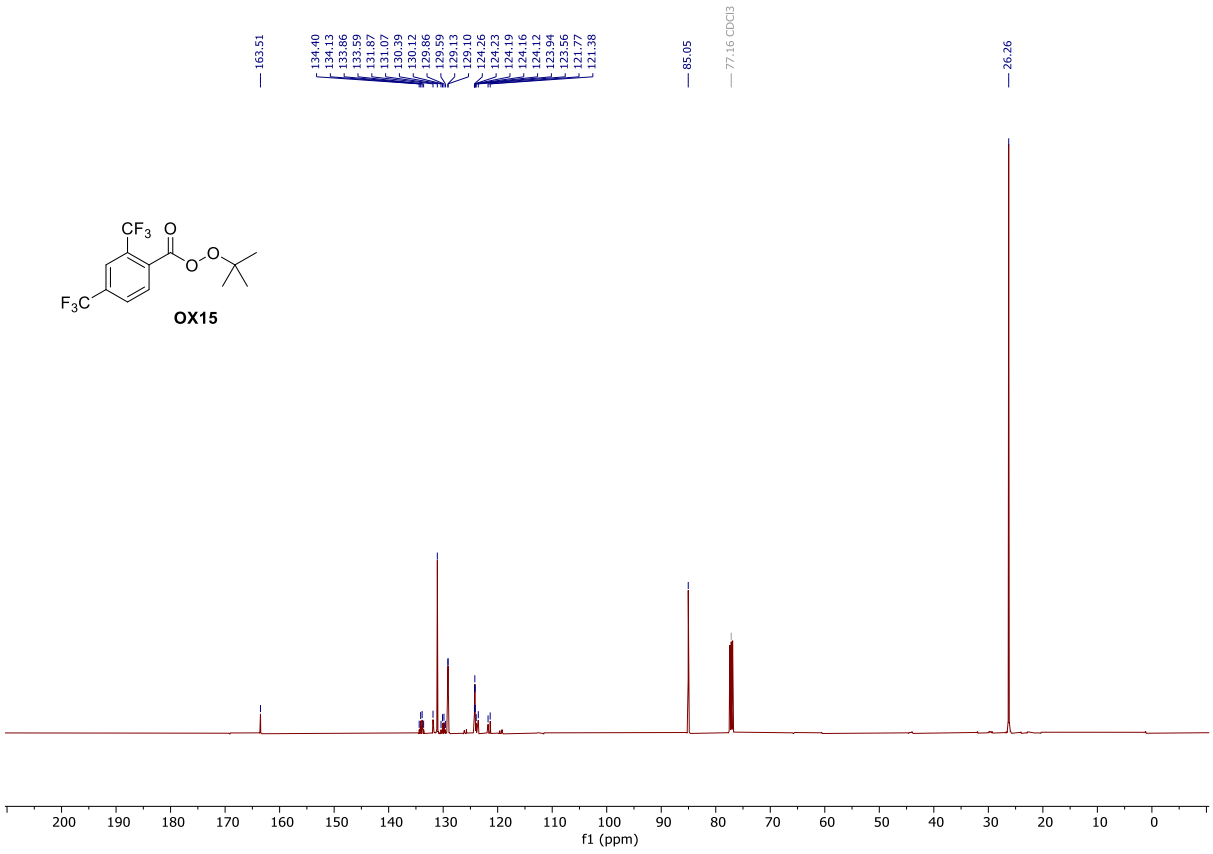
1.03
1.02
8.05 8.00 7.95 7.90 7.85 7.80 7.75
f1 (ppm)
1.00
1.03
1.02
8.71
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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124.23
124.19
124.16
124.12
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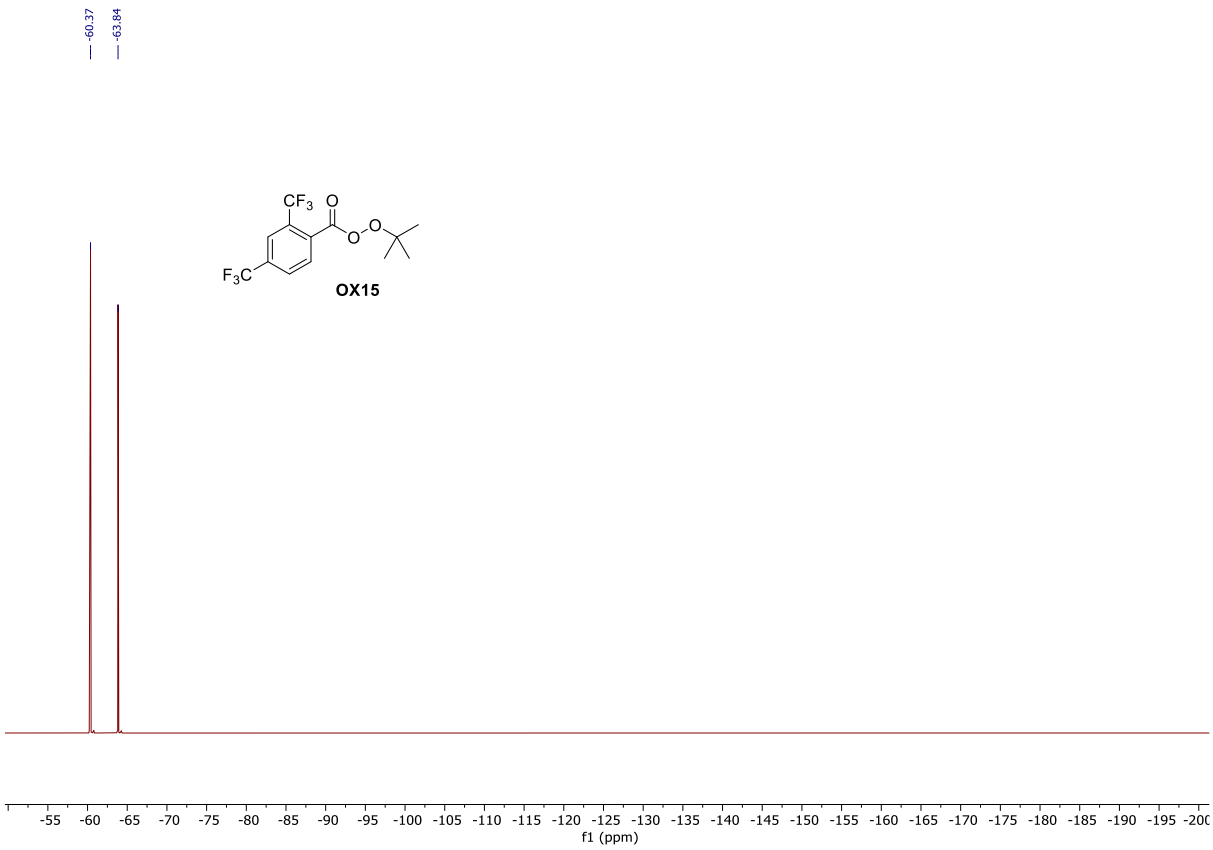
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F3C
OX15
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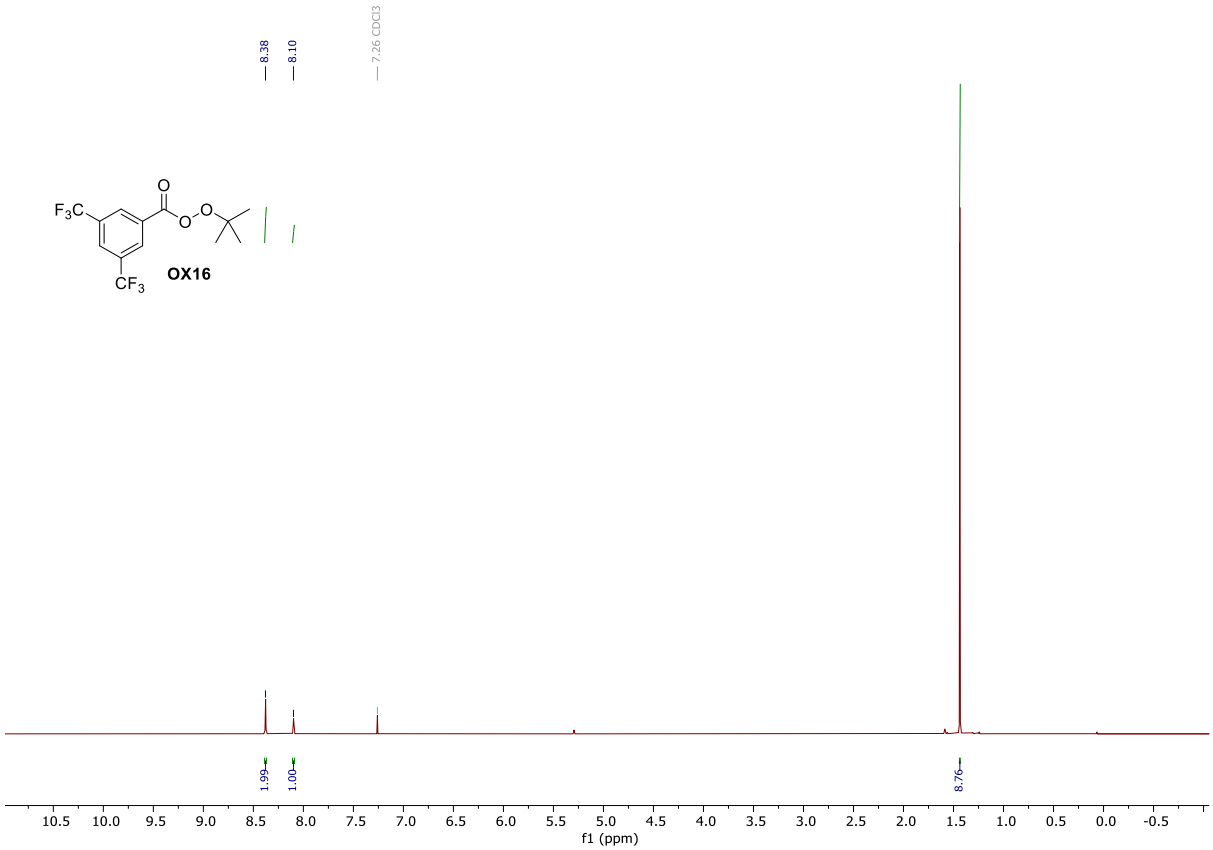
f1 (ppm)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O
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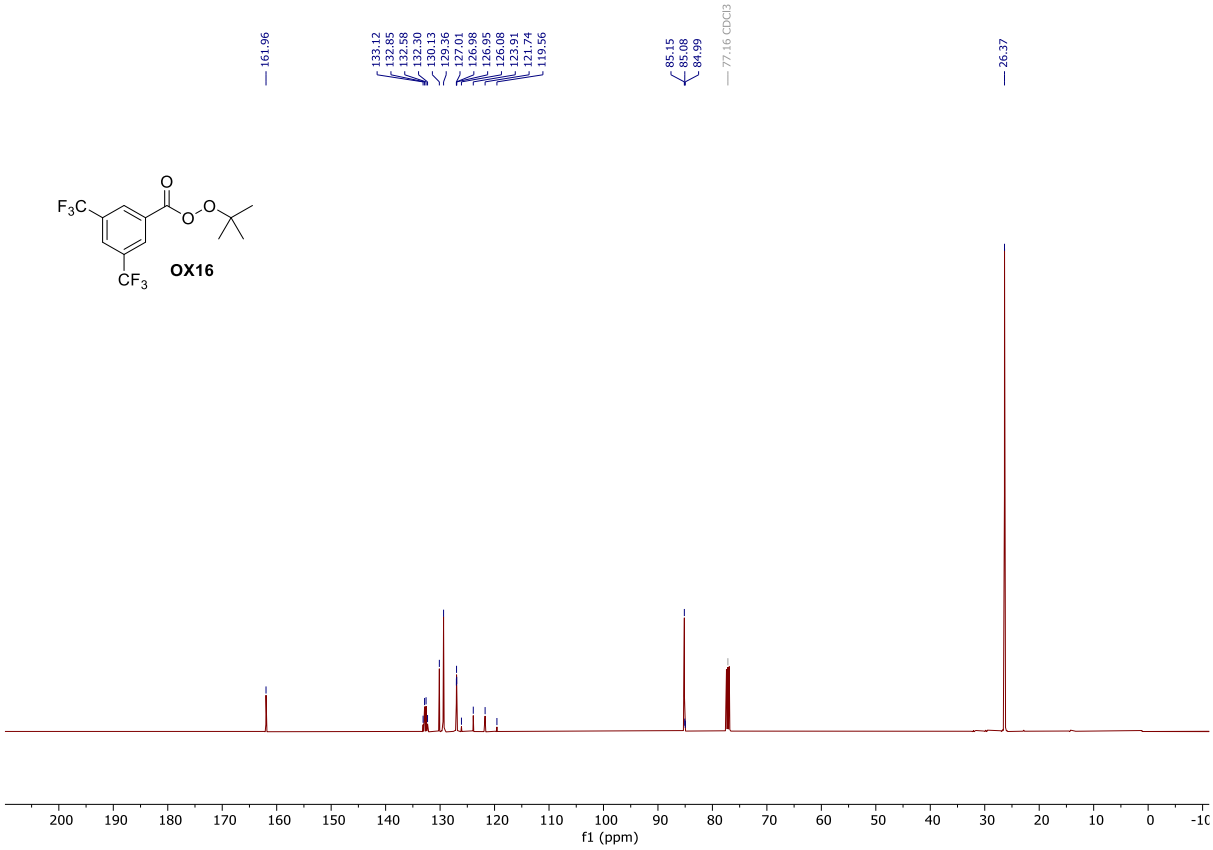
f1 (ppm)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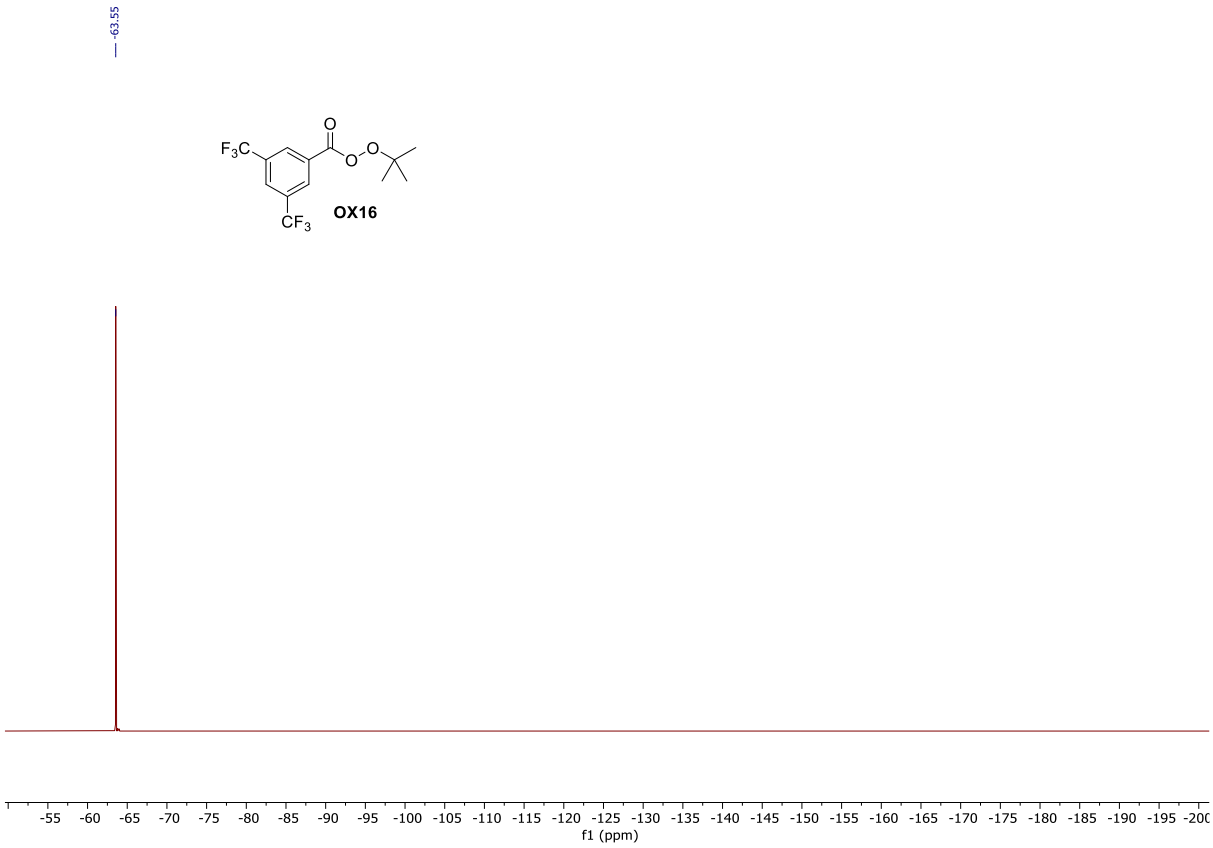
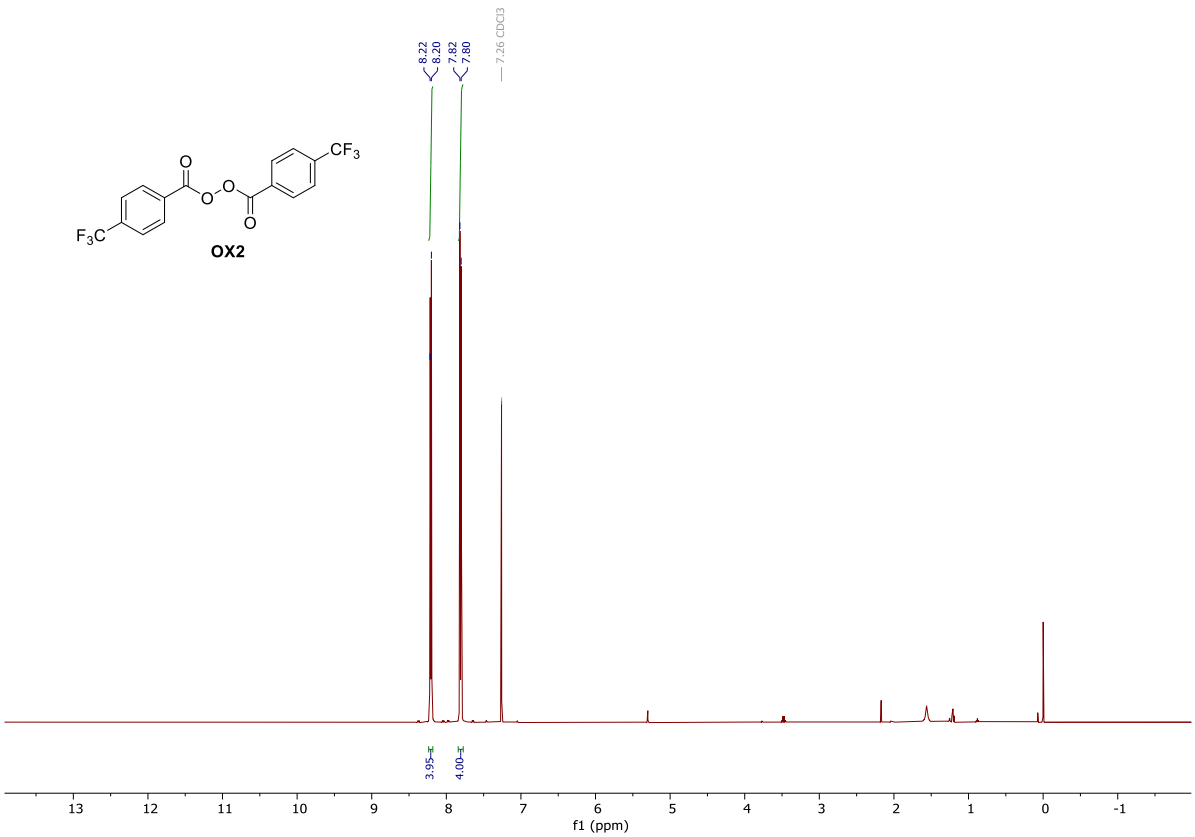
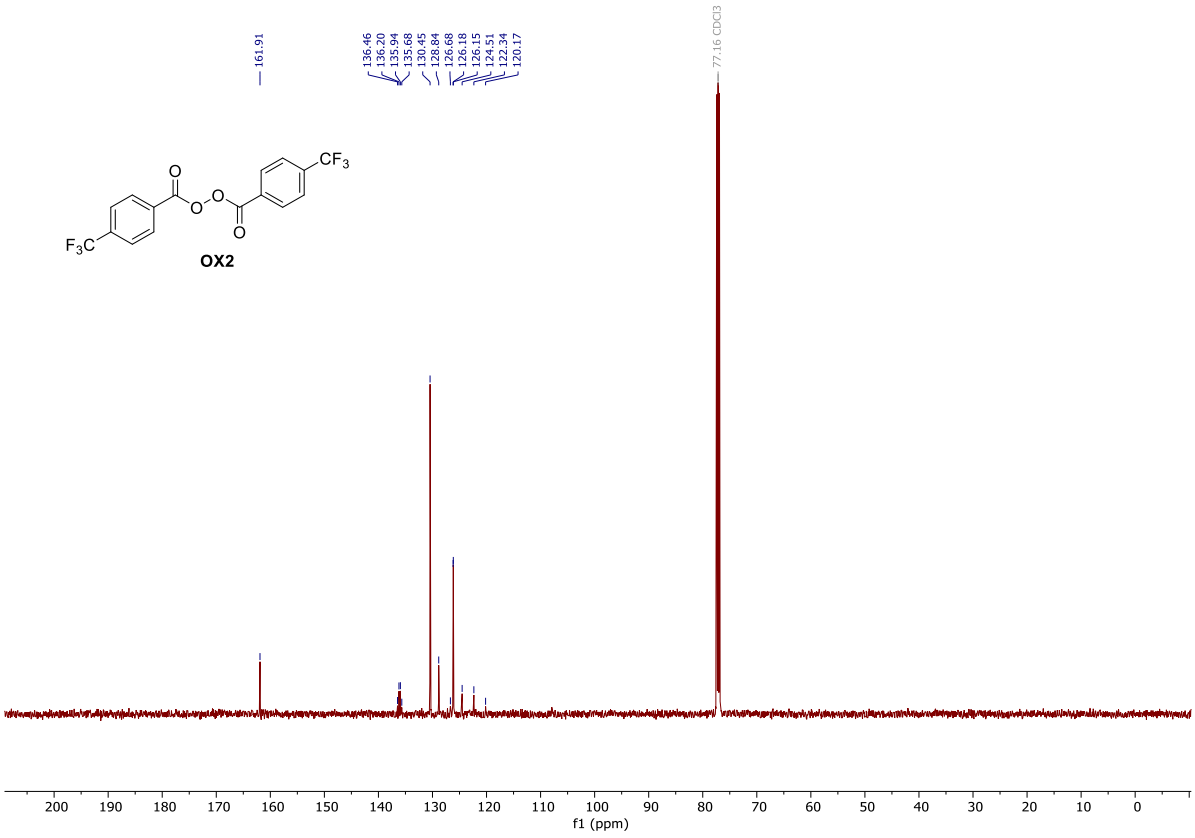
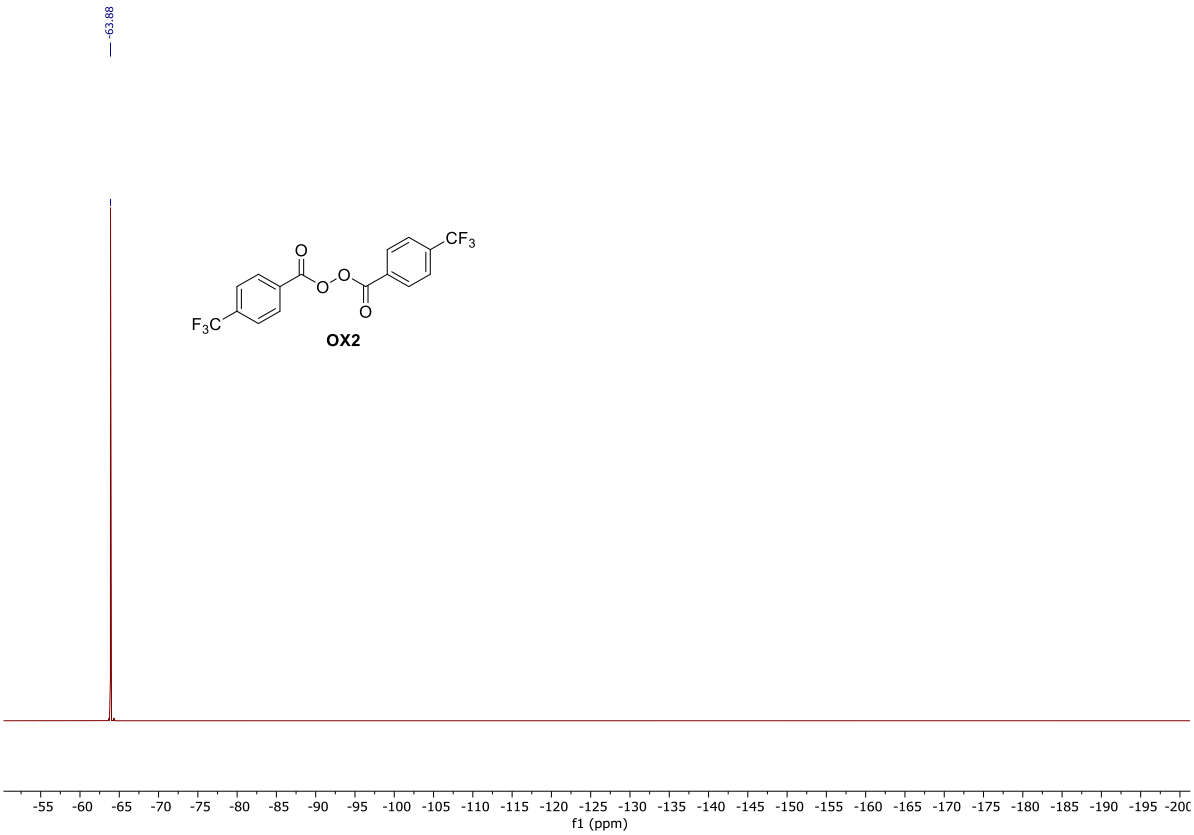
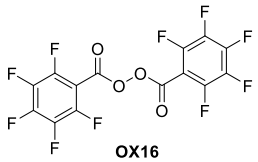
123.91
121.74
119.56
85.15
85.08
84.99
77.16 CDCl3
26.37
F3C
CF3
O
O
O
OX16
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-63.55
F3C
O
O
O
CF3
OX16
-55 -60 -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 -190 -195 -200
f1 (ppm)

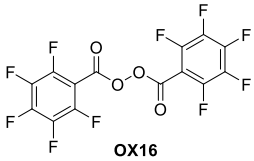

8.22
8.20
7.82
7.80
7.26 CDCl3
O
O
O
O
CF3
F3C
OX2
3.95
4.00
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)


161.91
136.46
136.20
135.94
135.68
130.45
128.84
128.68
126.18
126.15
124.51
122.34
120.17
77.16 CDCl3
O
O
O
O
CF3
F3C
OX2
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

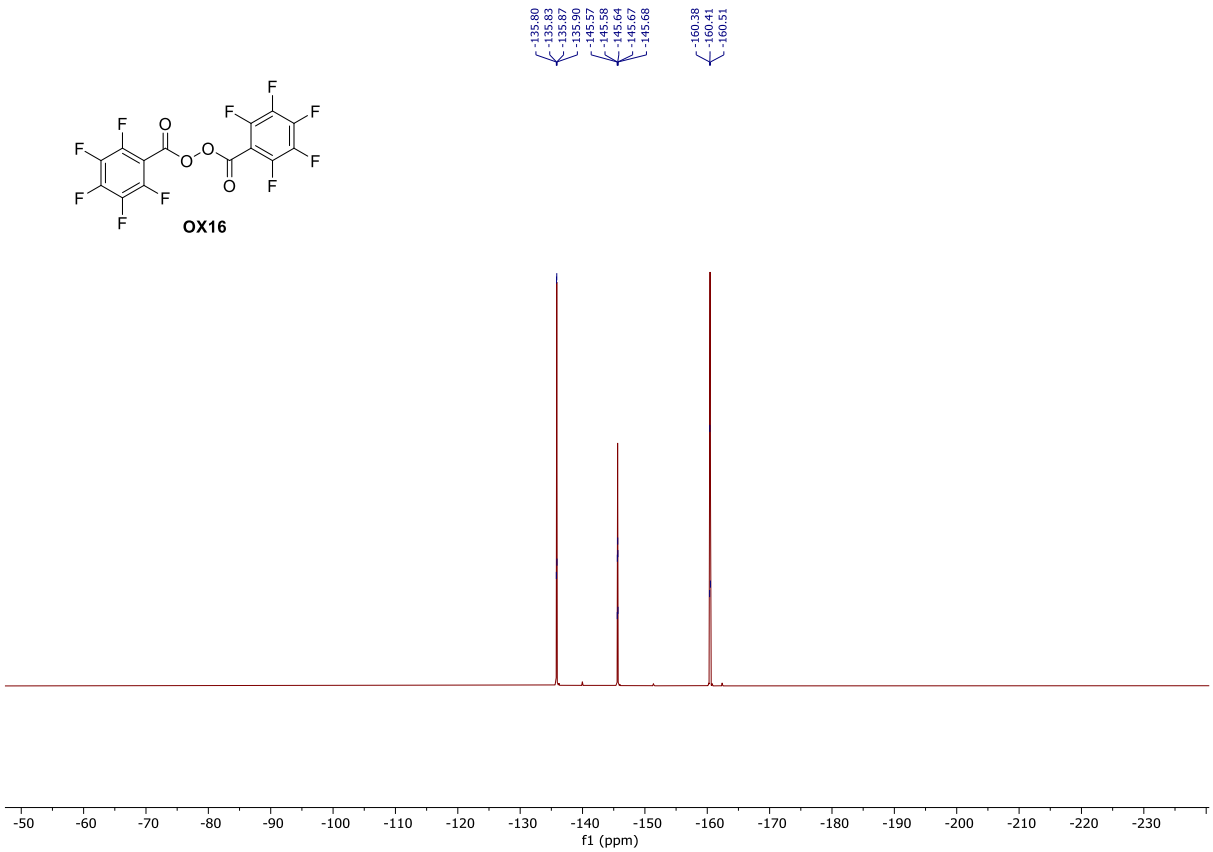

-63.88
CF3
O
O
O
O
F3C
OX2
-55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185 -190 -195 -200
f1 (ppm)

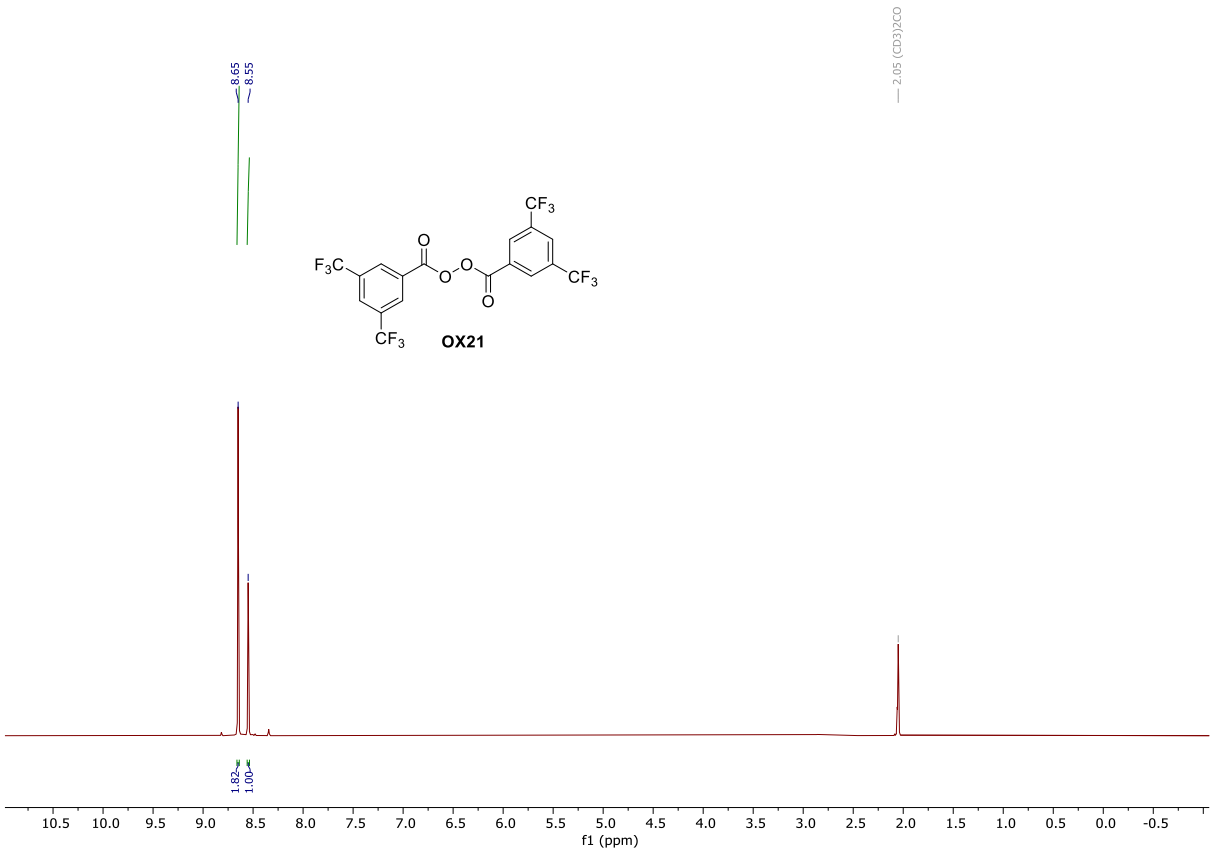

OX16

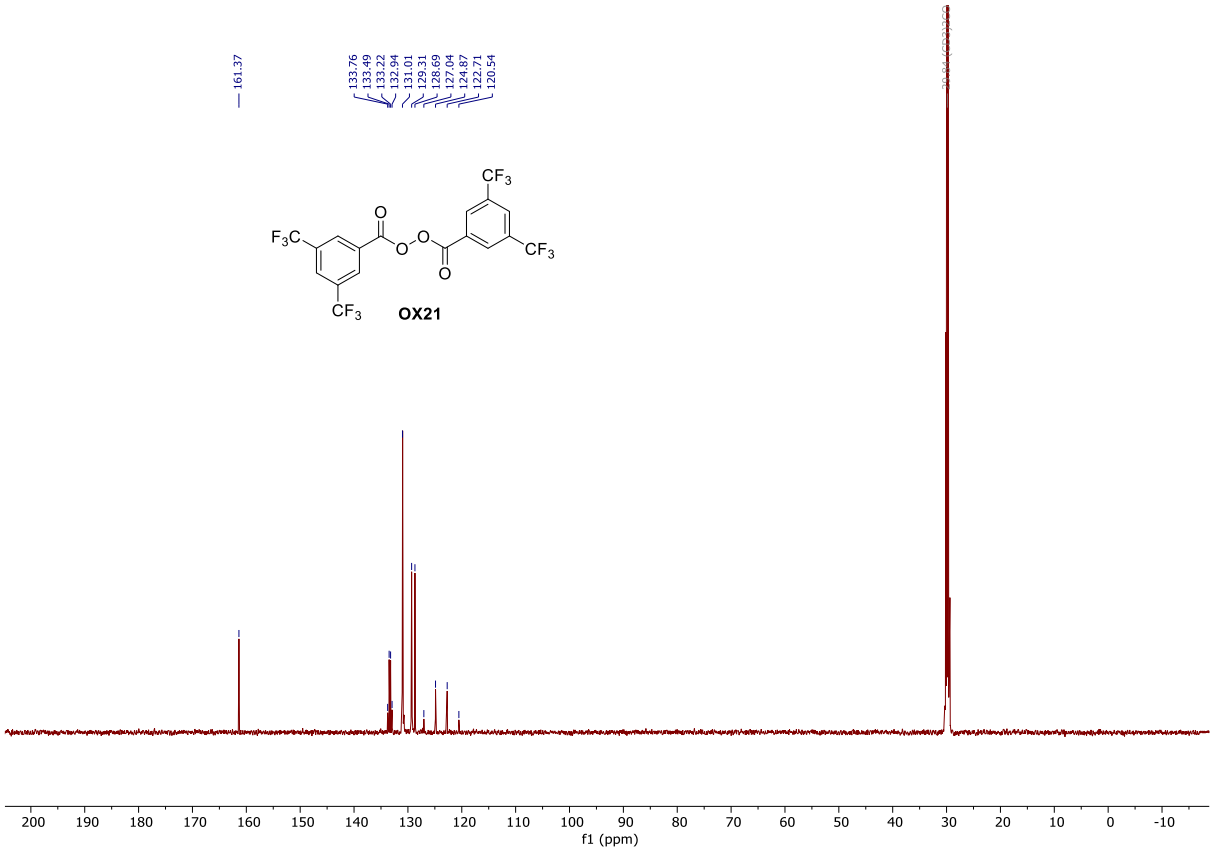
2.05 (CD3)2CO
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

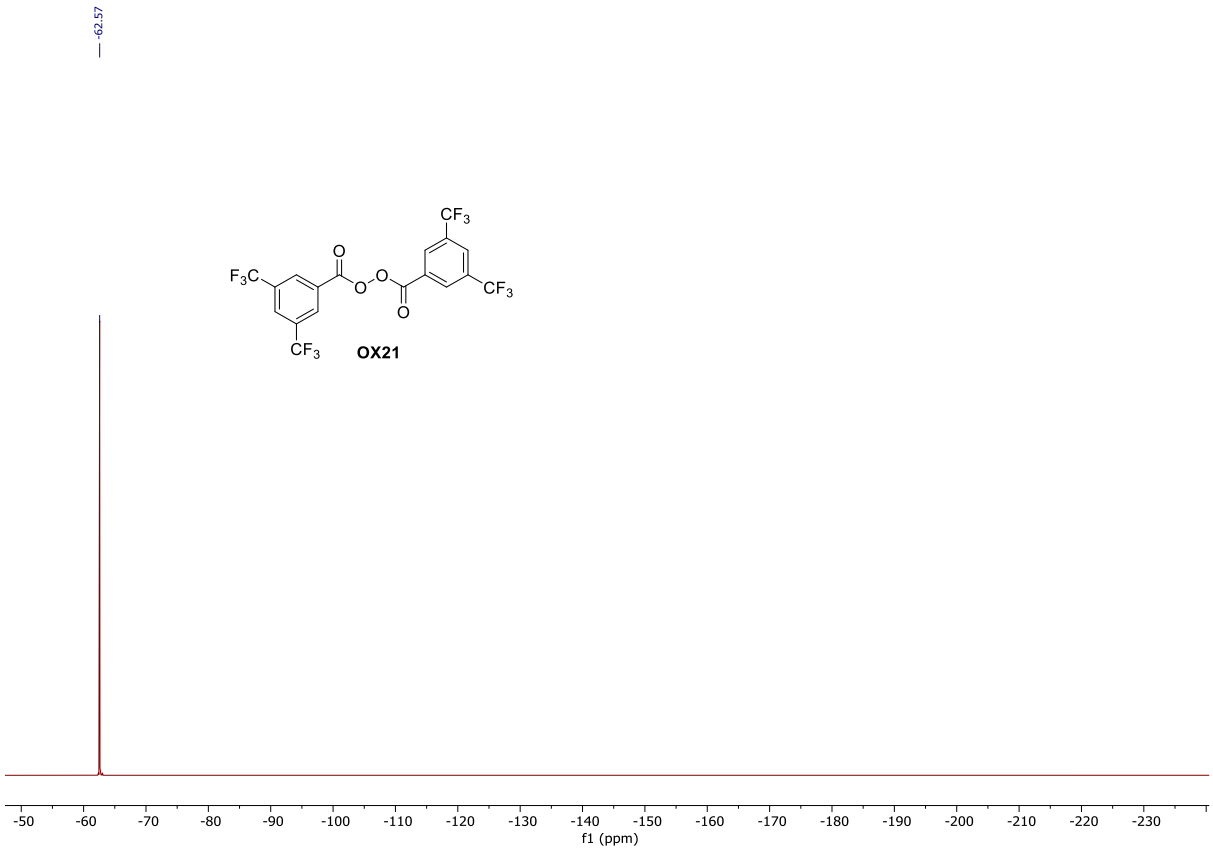

OX16

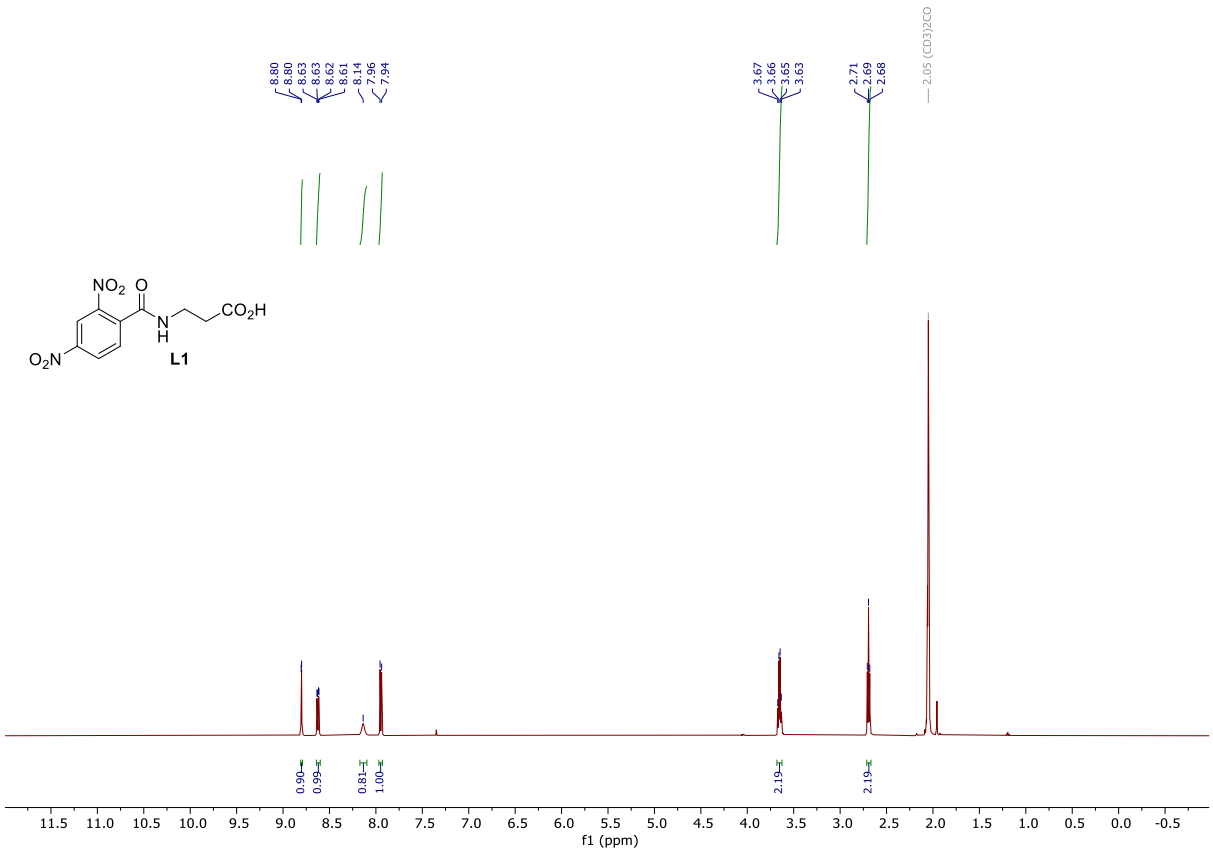
156.07
148.16
147.04
146.08
144.97
140.26
138.23
103.23
150 140 130 120 110
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

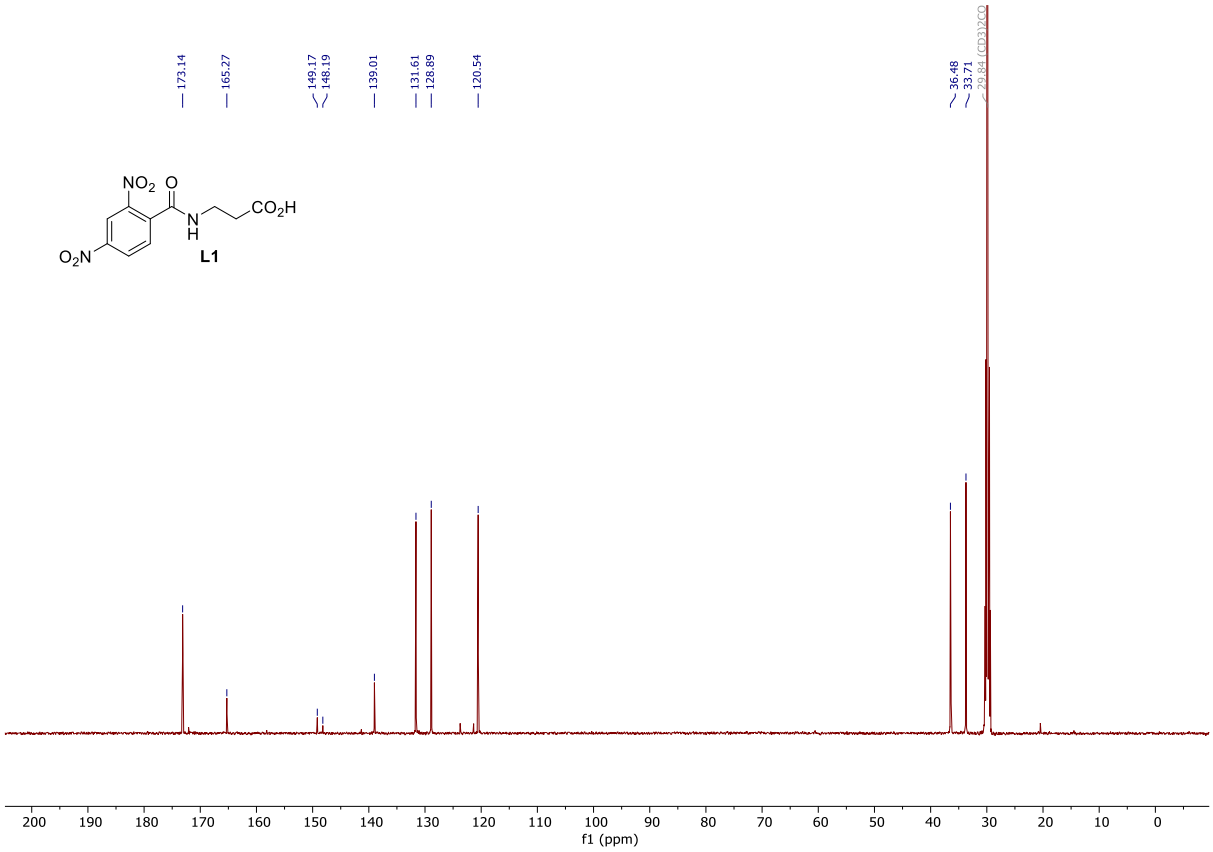

-135.80
-135.83
-135.87
-135.90
-145.57
-145.58
-145.64
-145.67
-145.68
-160.38
-160.41
-160.51
F
O
O
O
O
F
F
F
F
F
F
F
F
OX16
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
f1 (ppm)

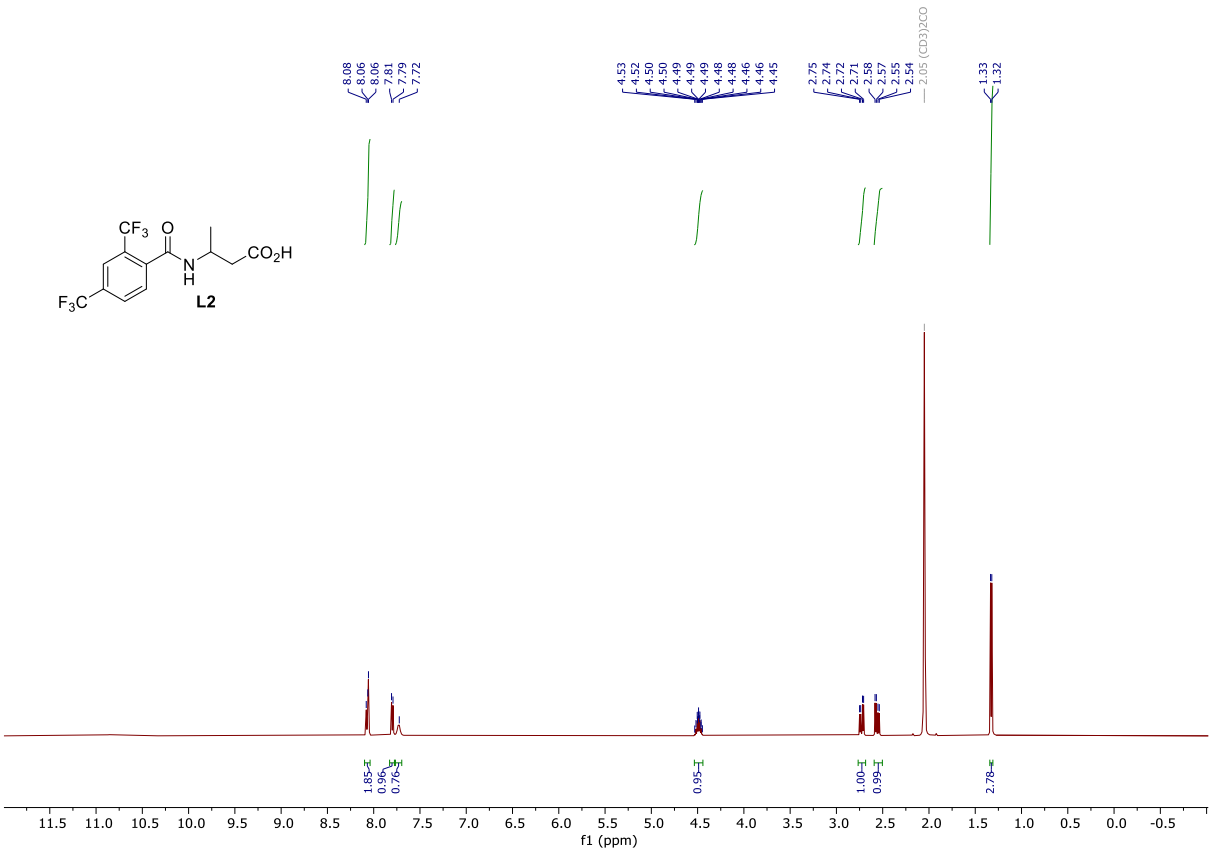

8.65
8.55
2.05 (CD3)2CO
CF3
F3C
O
O
O
O
CF3
CF3
OX21
1.82
1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

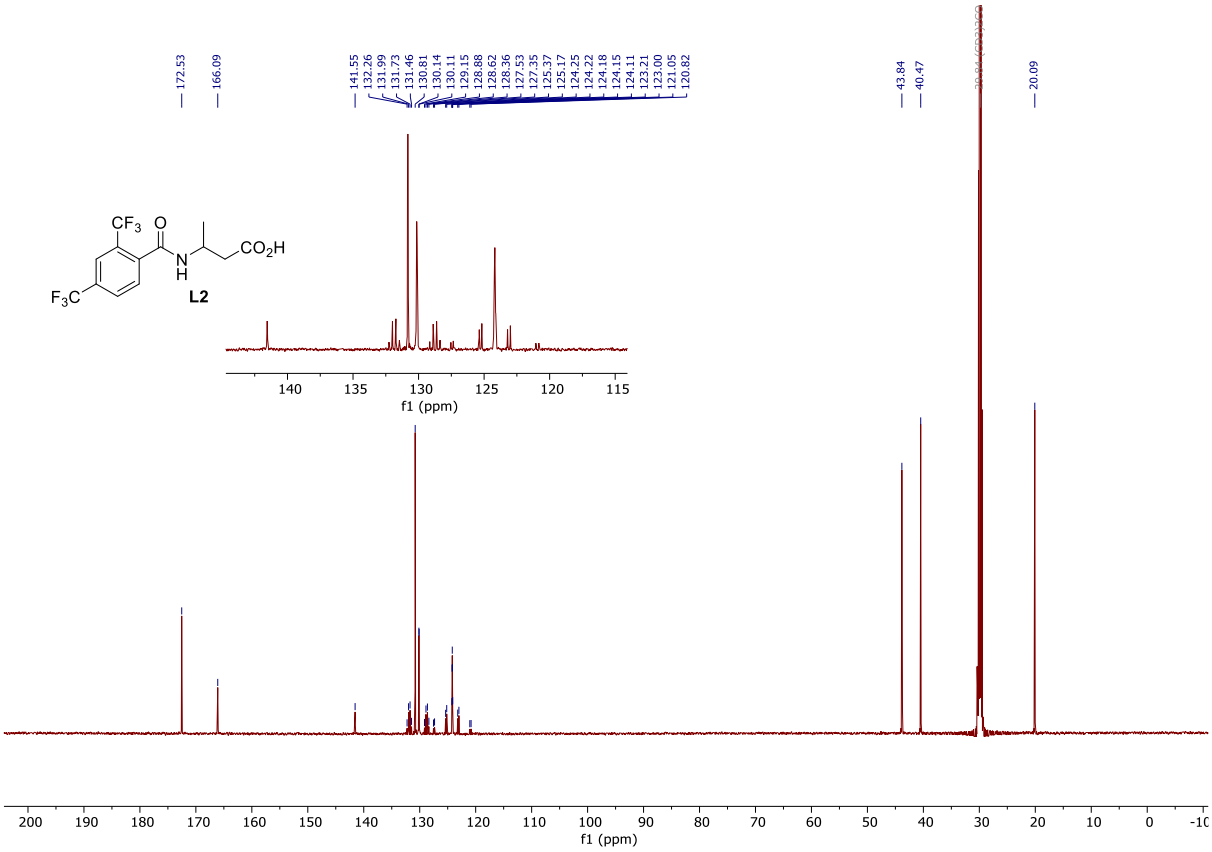

161.37
133.76
133.49
133.22
132.94
131.01
129.31
128.69
127.04
124.87
122.71
120.54
CF3
F3C
O
O
O
O
CF3
CF3
OX21
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

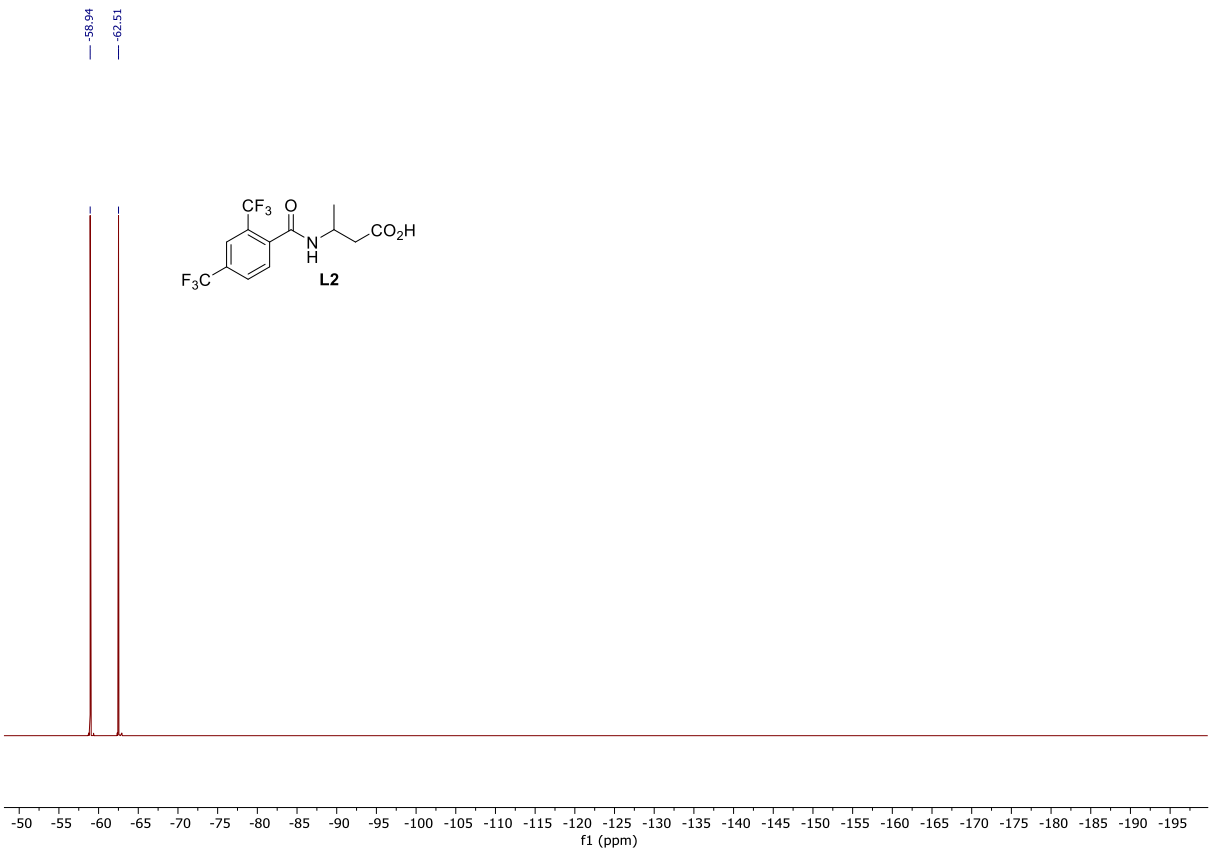

-62.57
CF3
F3C
O
O
O
O
CF3
CF3
OX21
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
f1 (ppm)

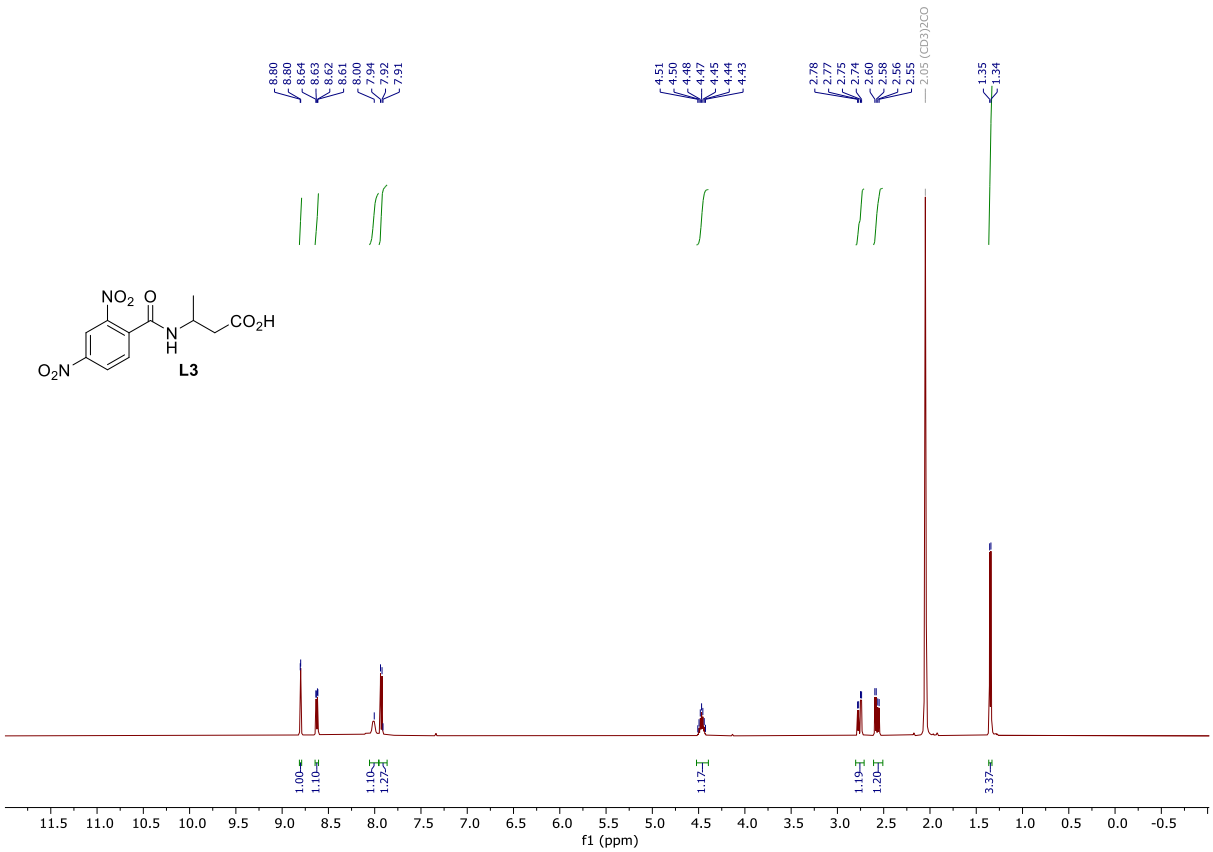

8.80
8.80
8.63
8.63
8.62
8.61
8.14
7.96
7.94
3.67
3.66
3.65
3.63
2.71
2.69
2.68
2.05 (CD3)2CO
NO2
O
N
H
CO2H
O2N
L1
0.90
0.99
0.81
1.00
2.19
2.19
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

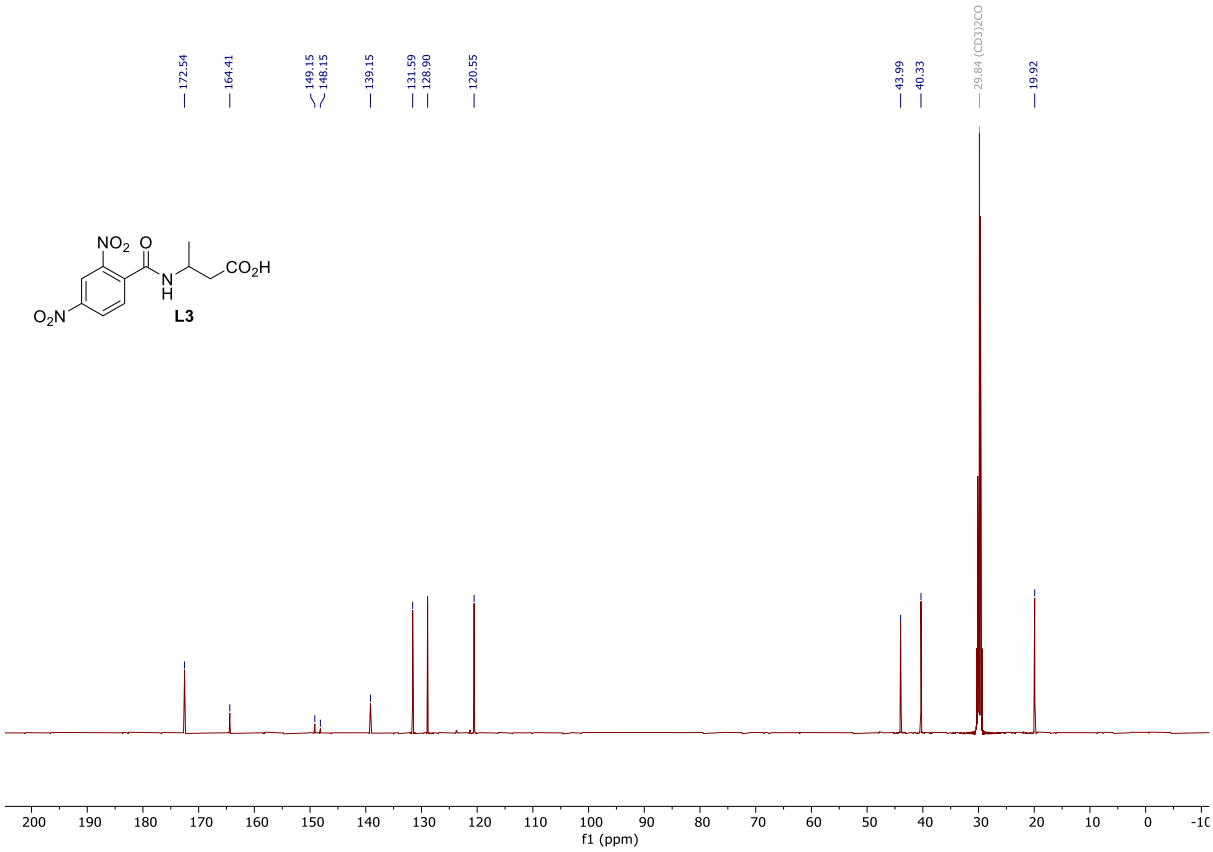

173.14
165.27
149.17
148.19
139.01
131.61
128.89
120.54
36.48
33.71
29.84 (CD3)2CO
NO2
O
N
H
CO2H
O2N
L1
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

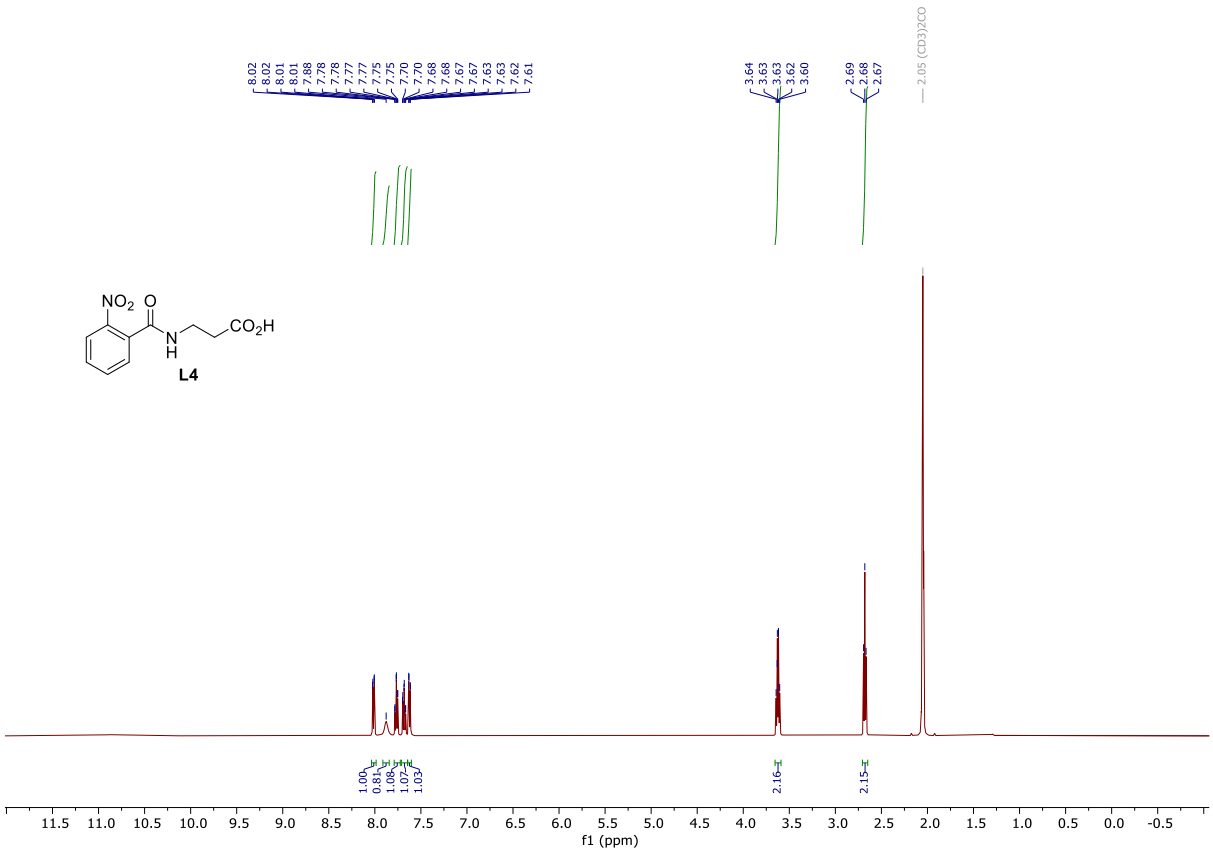

8.08
8.06
8.06
7.81
7.79
7.72
4.53
4.52
4.50
4.50
4.49
4.49
4.49
4.48
4.48
4.46
4.46
4.45
2.75
2.74
2.72
2.71
2.58
2.57
2.55
2.54
2.05 (CD3)2CO
1.33
1.32
CF3
O
N
H
CO2H
F3C
L2
1.85
0.96
0.76
0.95
1.00
0.99
2.78
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

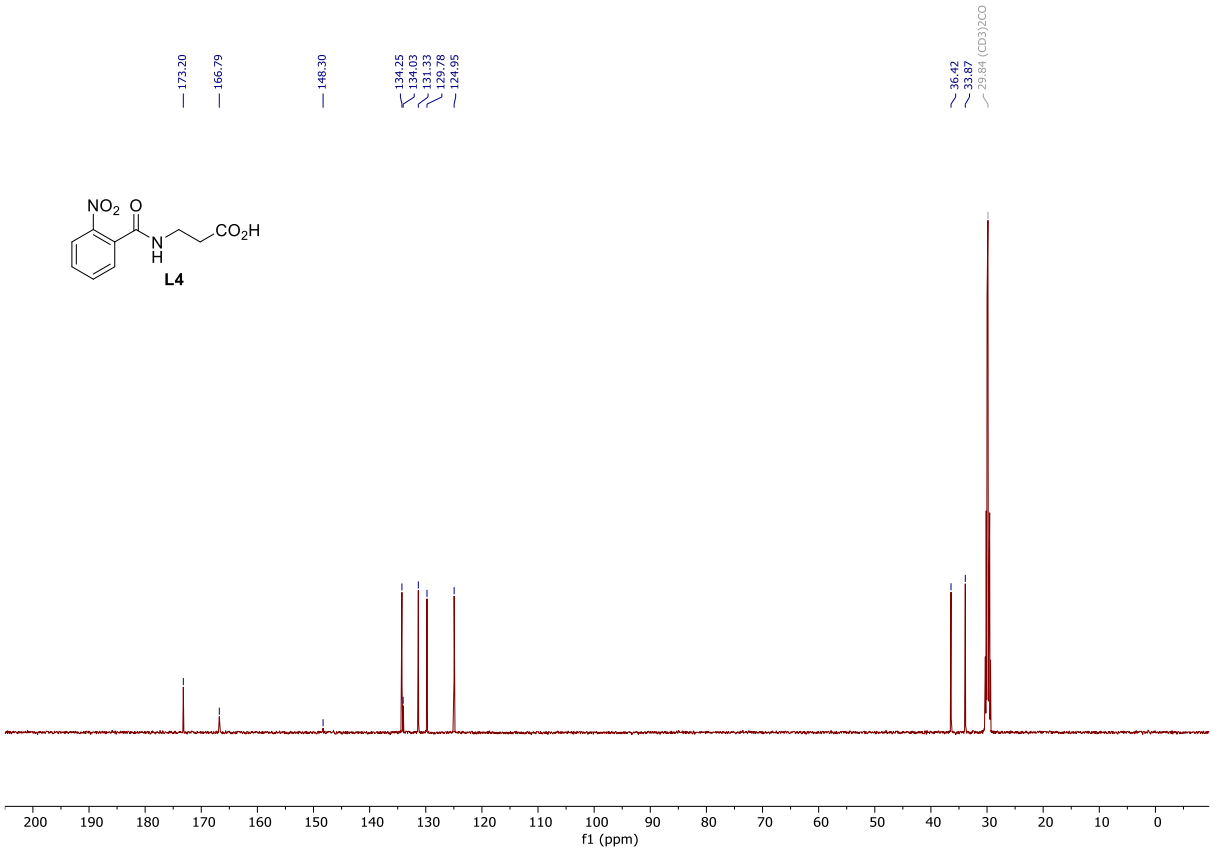

172.53
166.09
141.55
132.26
131.99
131.73
131.46
130.81
130.14
130.11
129.15
128.88
128.62
128.36
127.53
127.35
125.37
125.17
124.25
124.22
124.18
124.15
124.11
123.21
123.00
121.05
120.82
43.84
40.47
20.09
CF3
O
N
H
CO2H
F3C
L2
140 135 130 125 120 115
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

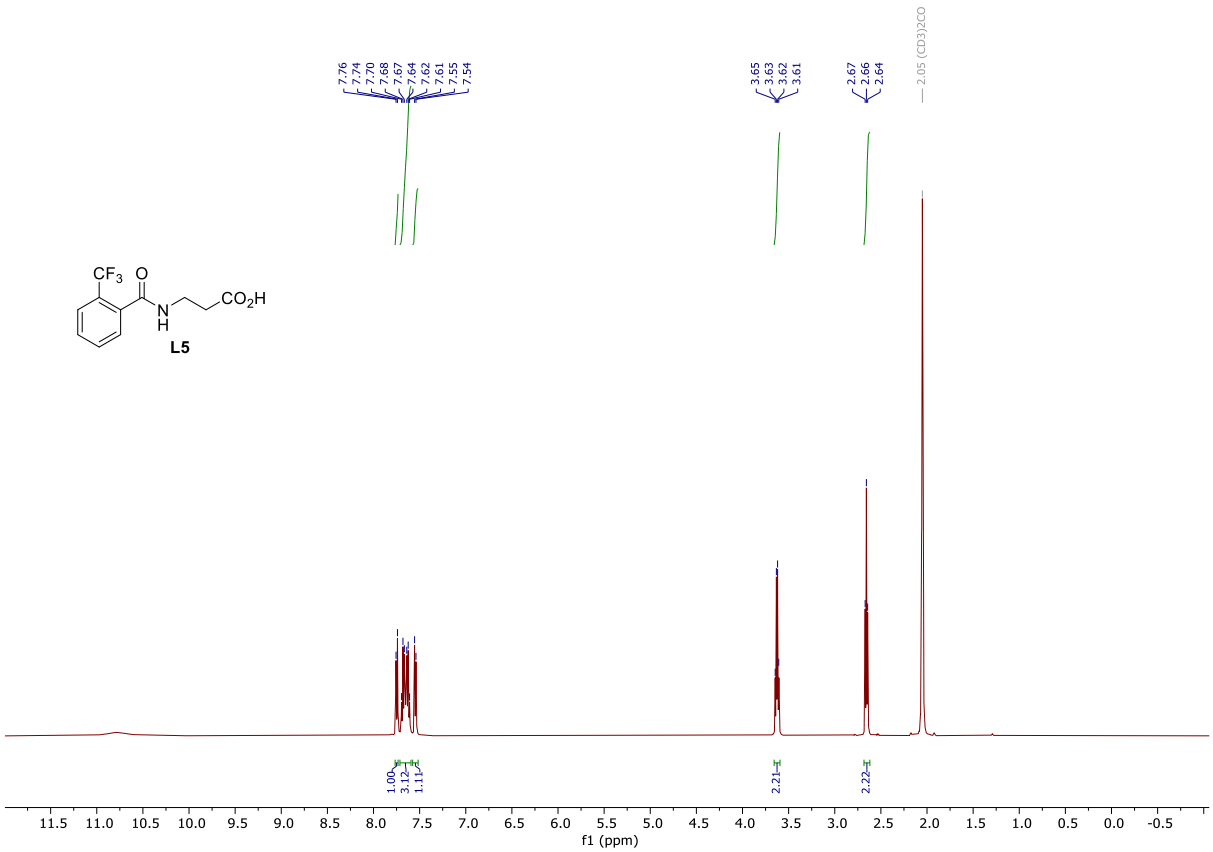

-58.94
-62.51
CF3
O
N
H
CO2H
F3C
L2
-50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185 -190 -195
f1 (ppm)

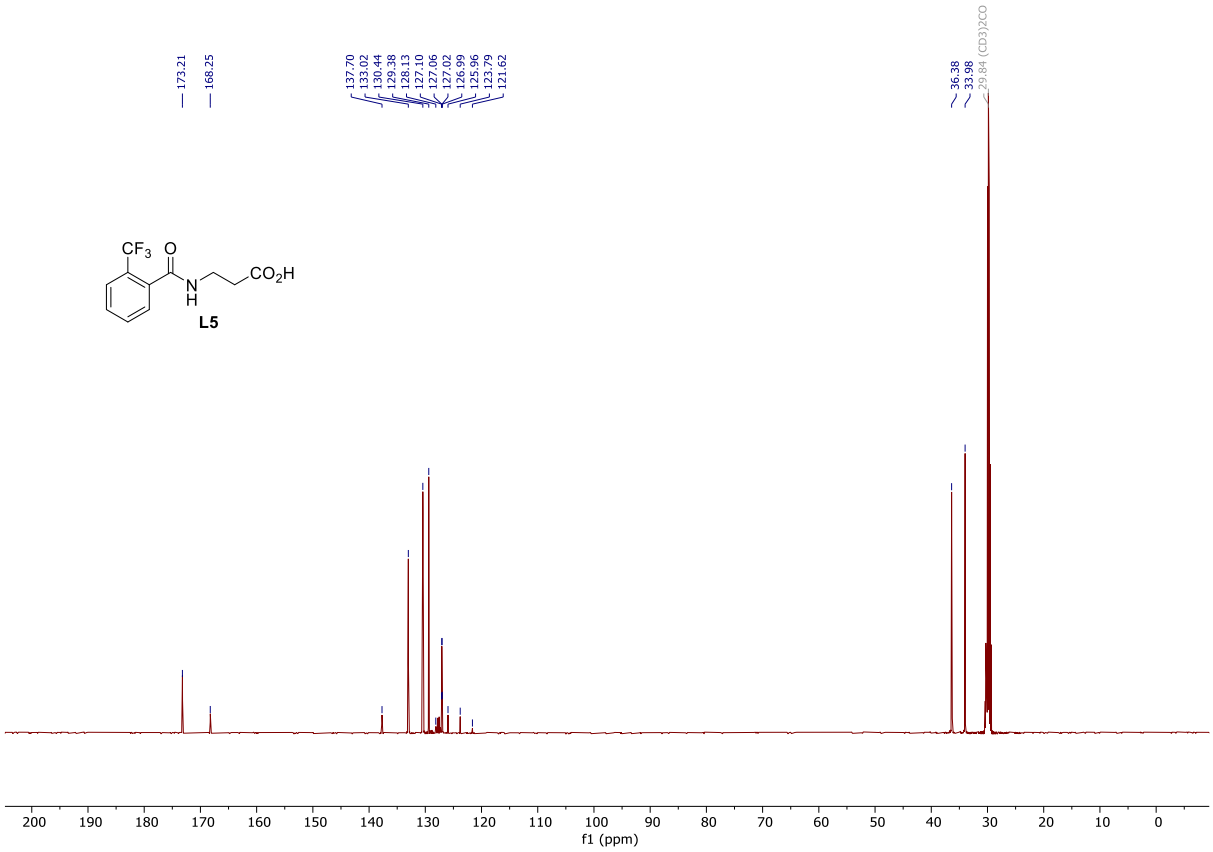

8.80
8.80
8.64
8.63
8.62
8.61
8.00
7.94
7.92
7.91
4.51
4.50
4.48
4.47
4.45
4.44
4.43
2.78
2.77
2.75
2.74
2.60
2.58
2.56
2.55
2.05 (CD3)2CO
1.35
1.34
NO2
O
N
H
CO2H
O2N
L3
1.00
1.10
1.10
1.27
1.17
1.19
1.20
3.37
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

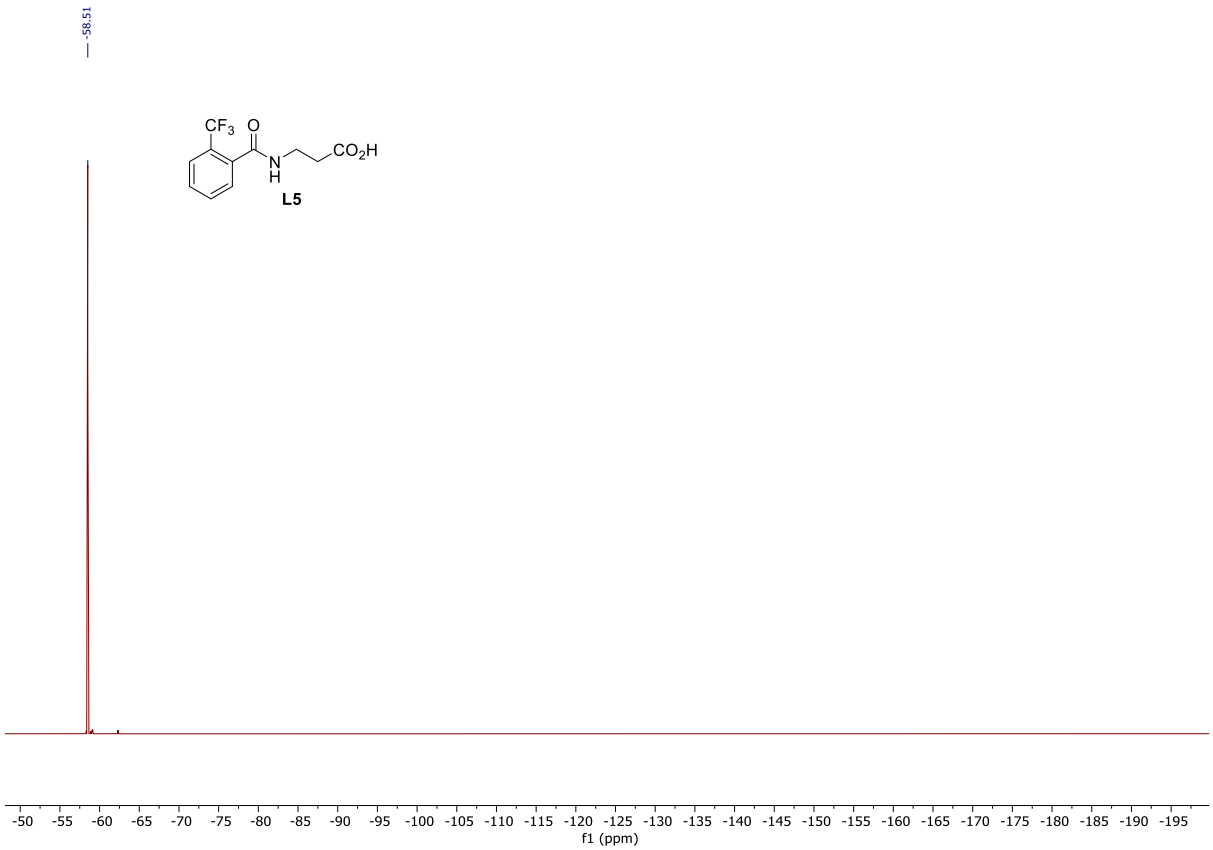

172.54
164.41
149.15
148.15
139.15
131.59
128.90
120.55
43.99
40.33
29.84 (CD3)2CO
19.92
NO2
O
N
H
CO2H
O2N
L3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

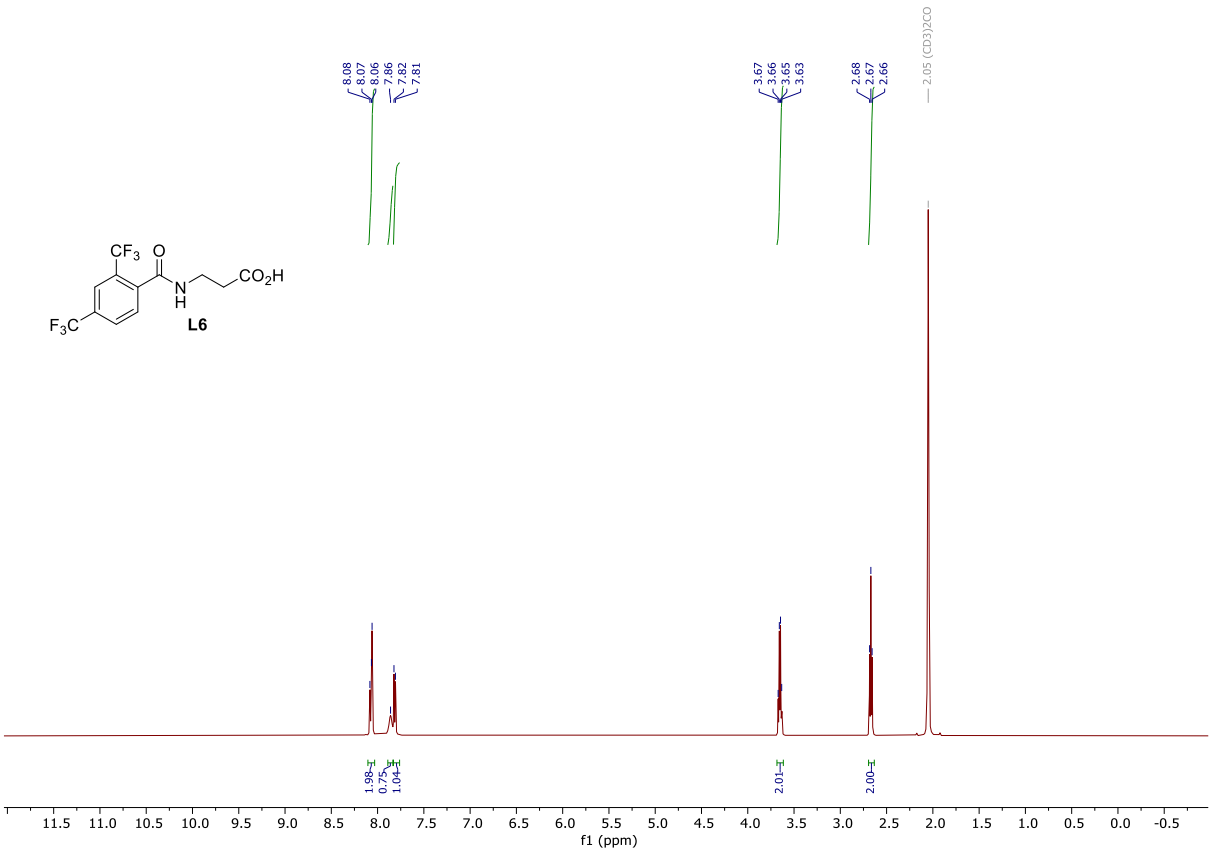

8.02
8.02
8.01
8.01
7.88
7.78
7.78
7.77
7.77
7.75
7.75
7.70
7.70
7.68
7.68
7.67
7.67
7.63
7.63
7.62
7.61
3.64
3.63
3.63
3.62
3.60
2.69
2.68
2.67
2.05 (CD3)2CO
NO2
O
N
H
CO2H
L4
1.00
0.81
1.08
1.07
1.03
2.16
2.15
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

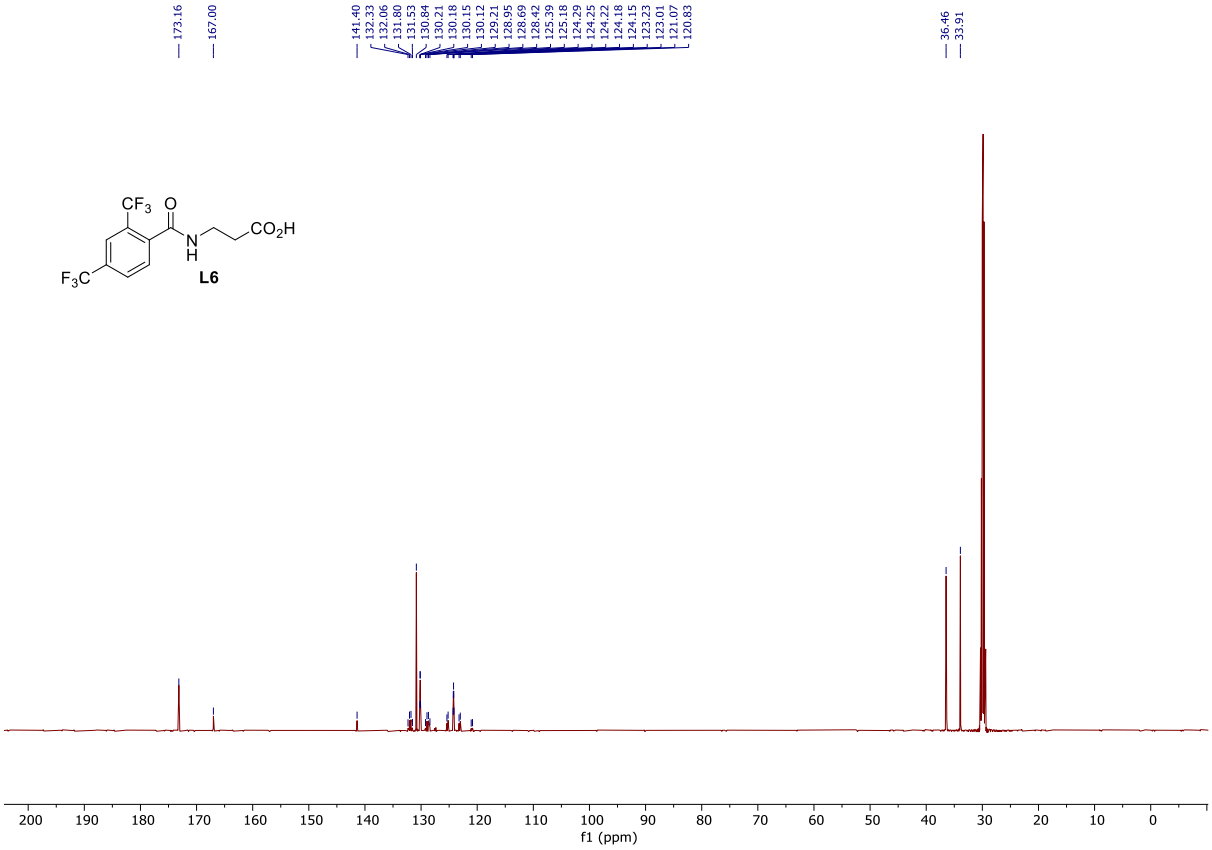

173.20
166.79
148.30
134.25
134.03
131.33
129.78
124.95
36.42
33.87
29.84 (CD3)2CO
NO2
O
N
H
CO2H
L4
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

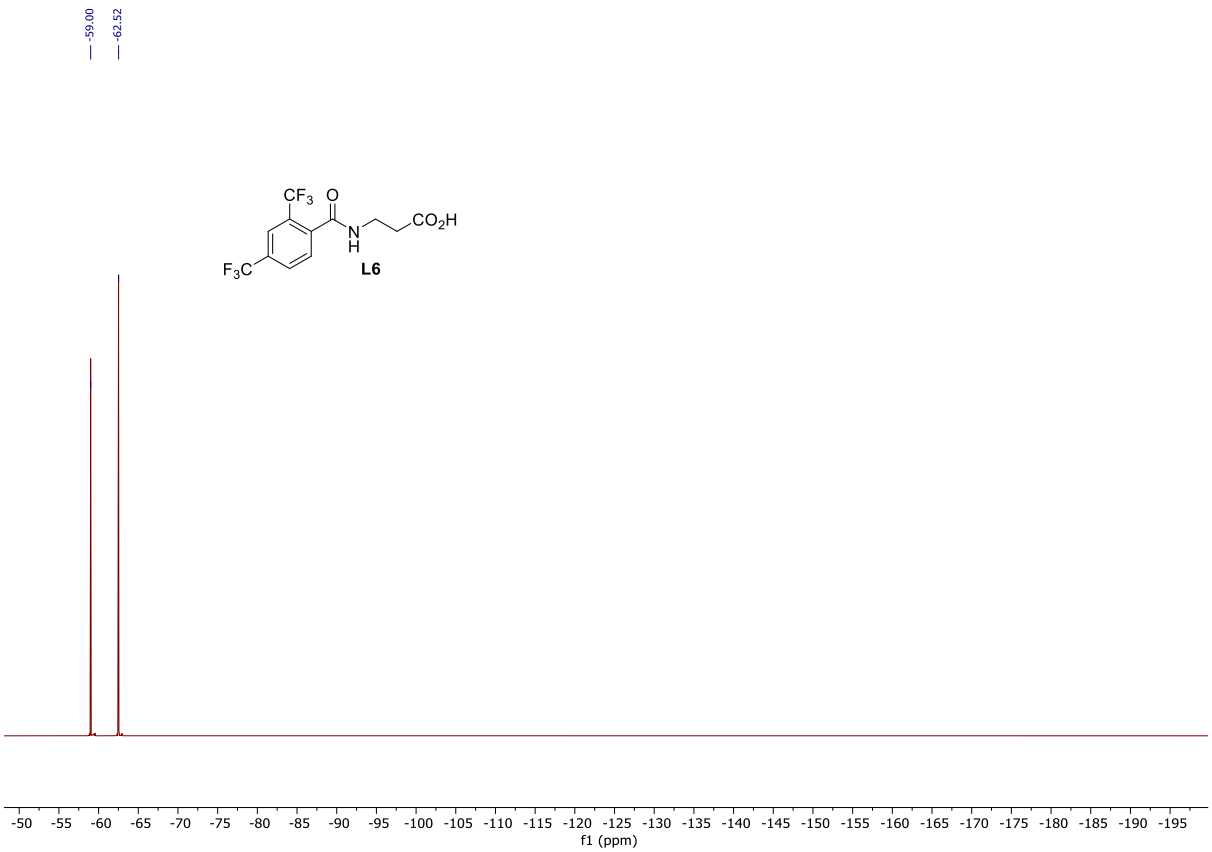

7.76
7.74
7.70
7.68
7.67
7.64
7.62
7.61
7.55
7.54
3.65
3.63
3.62
3.61
2.67
2.66
2.64
2.05 (CD3)2CO
CF3
O
N
H
CO2H
L5
1.00
3.12
1.11
2.21
2.22
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

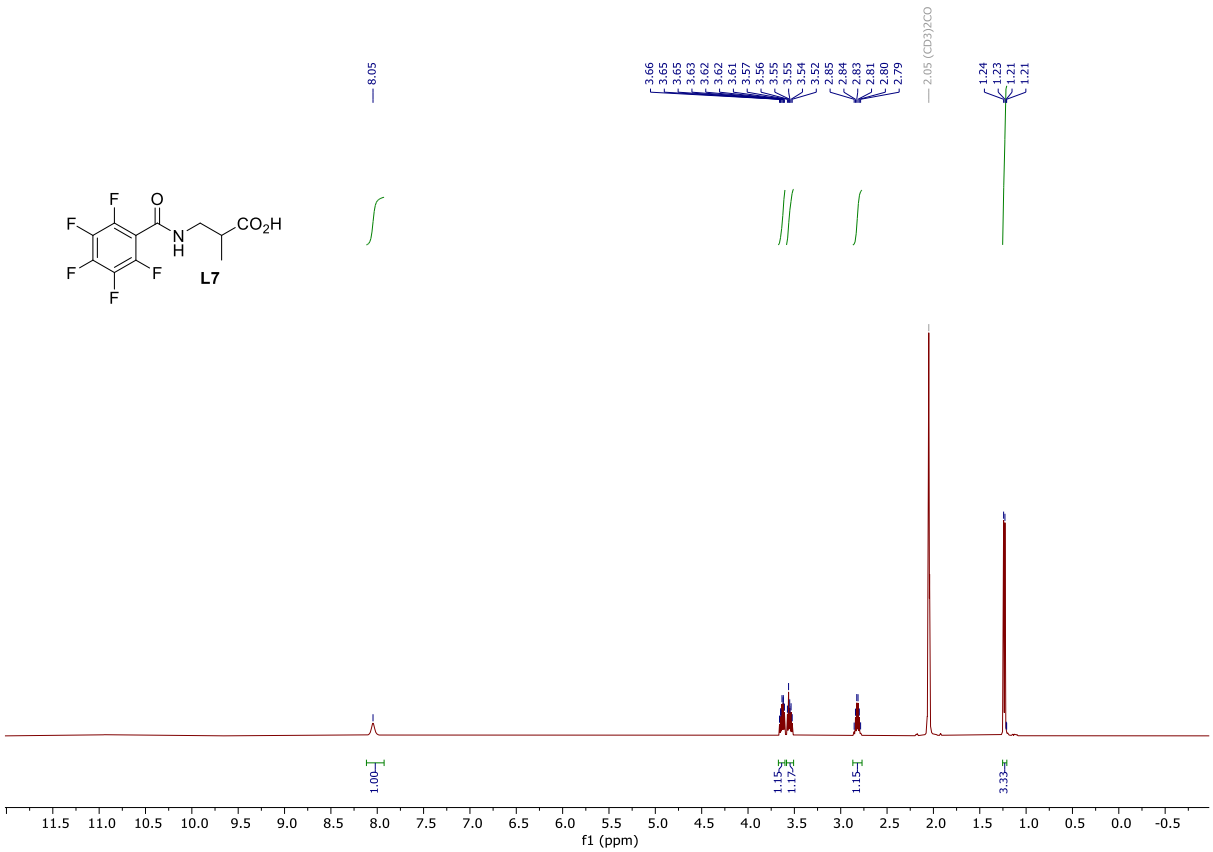

173.21
168.25
137.70
133.02
130.44
129.38
128.13
127.10
127.06
127.02
126.99
125.96
123.79
121.62
36.38
33.98
29.84 (CD3)2CO
CF3
O
N
H
CO2H
L5
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

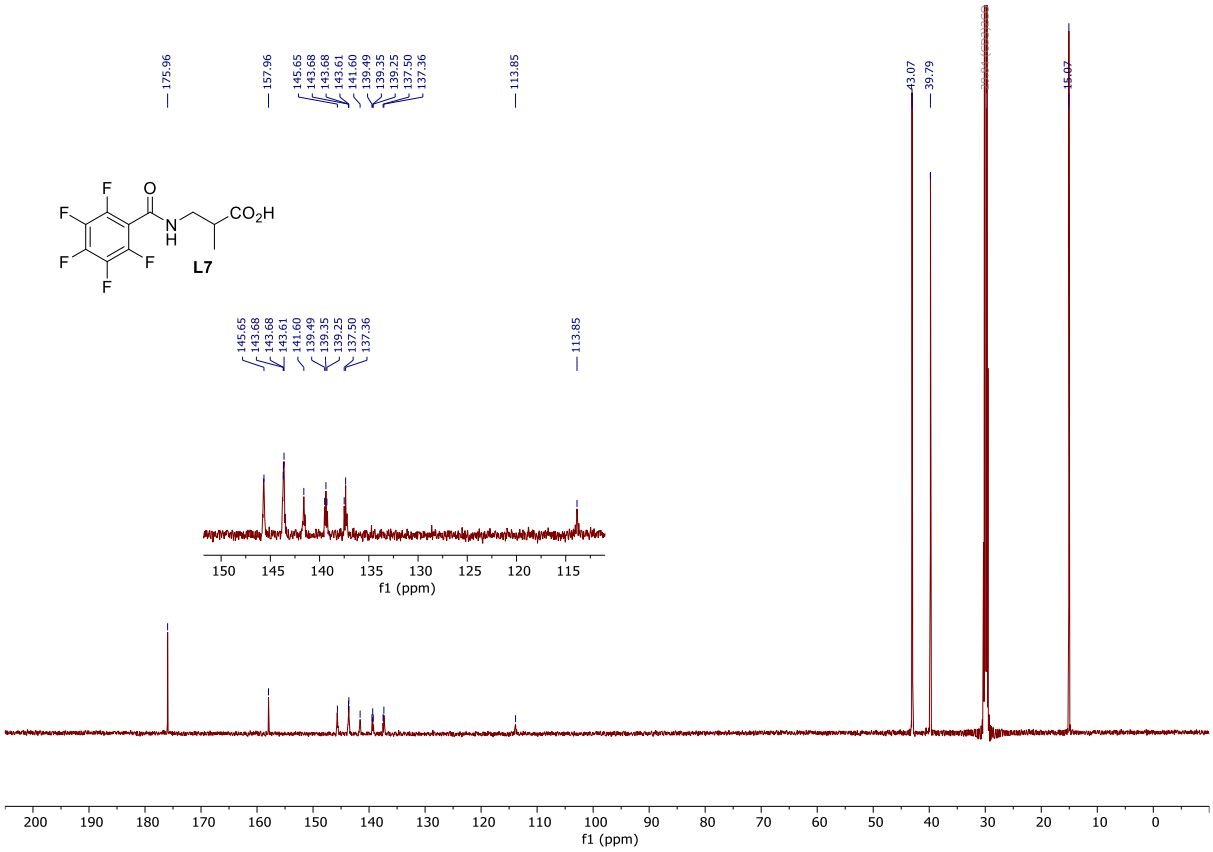

-58.51
CF3
O
N
H
CO2H
L5
-50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185 -190 -195
f1 (ppm)

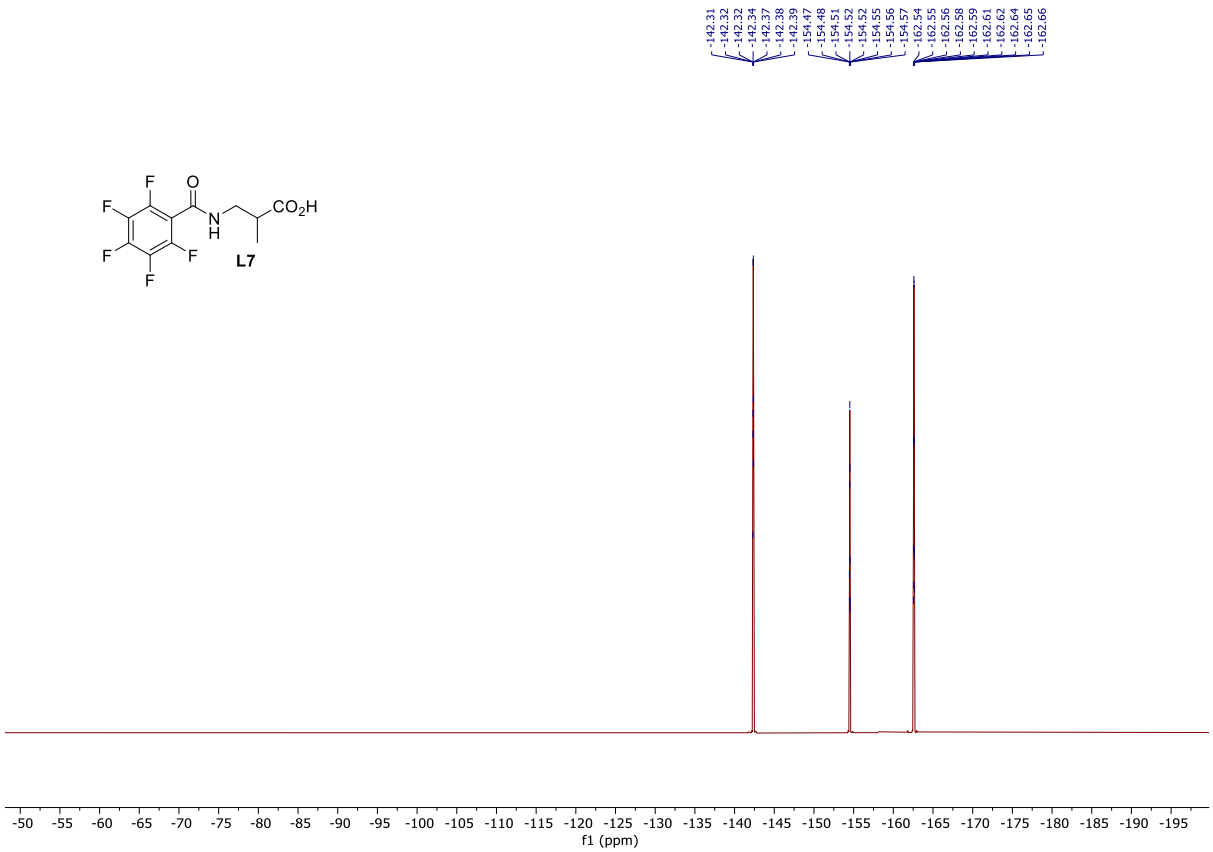

8.08
8.07
8.06
7.86
7.82
7.81
3.67
3.66
3.65
3.63
2.68
2.67
2.66
2.05 (CD3)2CO
CF3
O
N
H
CO2H
F3C
L6
1.98
0.75
1.04
2.01
2.00
f1 (ppm)

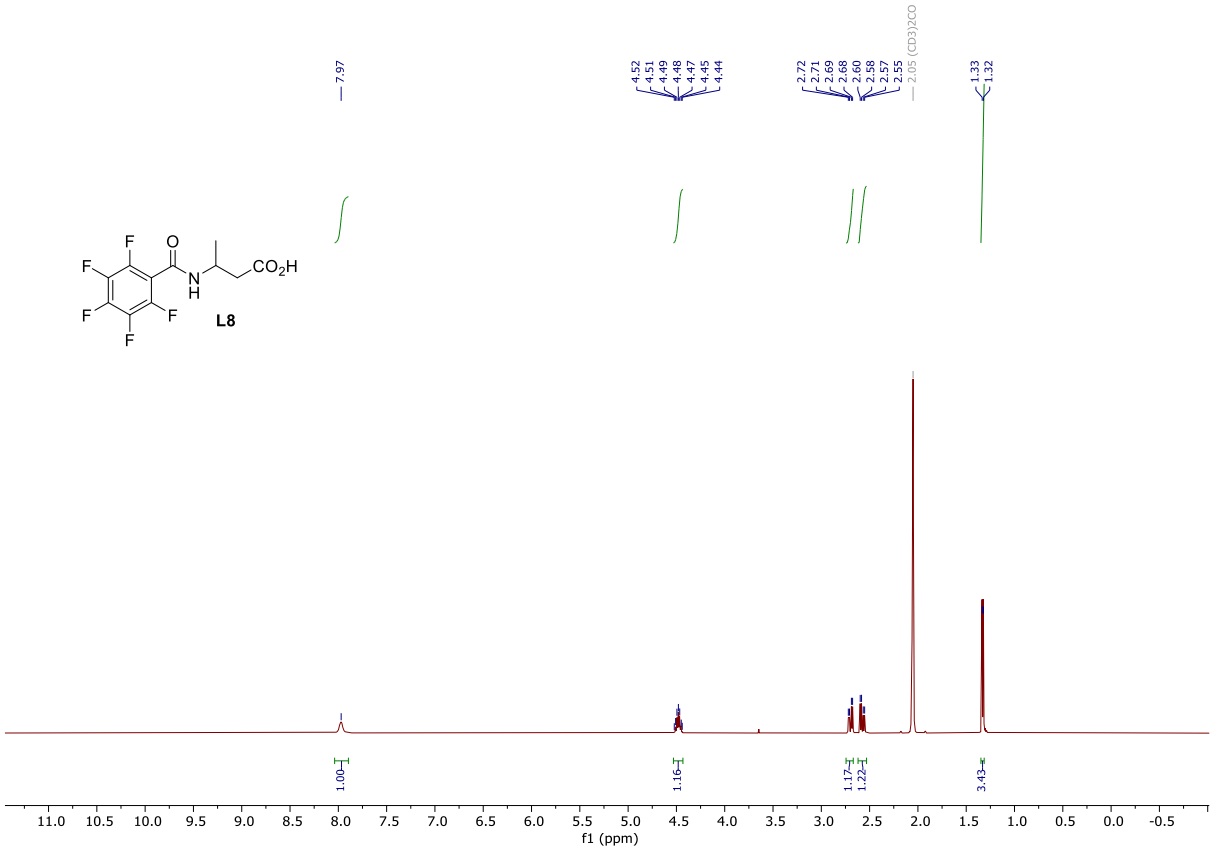

173.16
167.00
141.40
132.33
132.06
131.80
131.53
130.84
130.21
130.18
130.15
130.12
129.21
128.95
128.69
128.42
125.39
125.18
124.29
124.25
124.22
124.18
124.15
123.23
123.01
121.07
120.83
36.46
33.91
CF3
O
N
H
CO2H
F3C
L6
f1 (ppm)

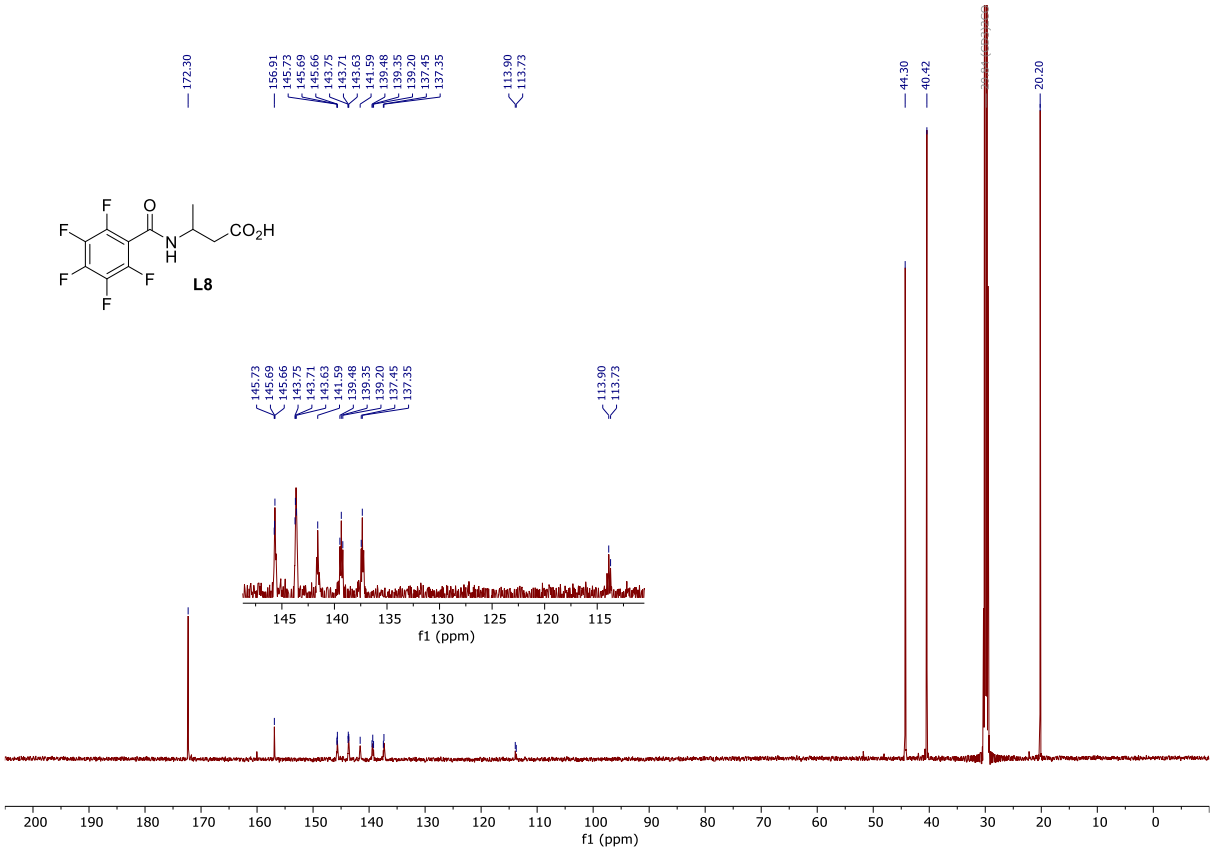

-59.00
-62.52
CF3
O
N
H
CO2H
F3C
L6
-50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185 -190 -195
f1 (ppm)

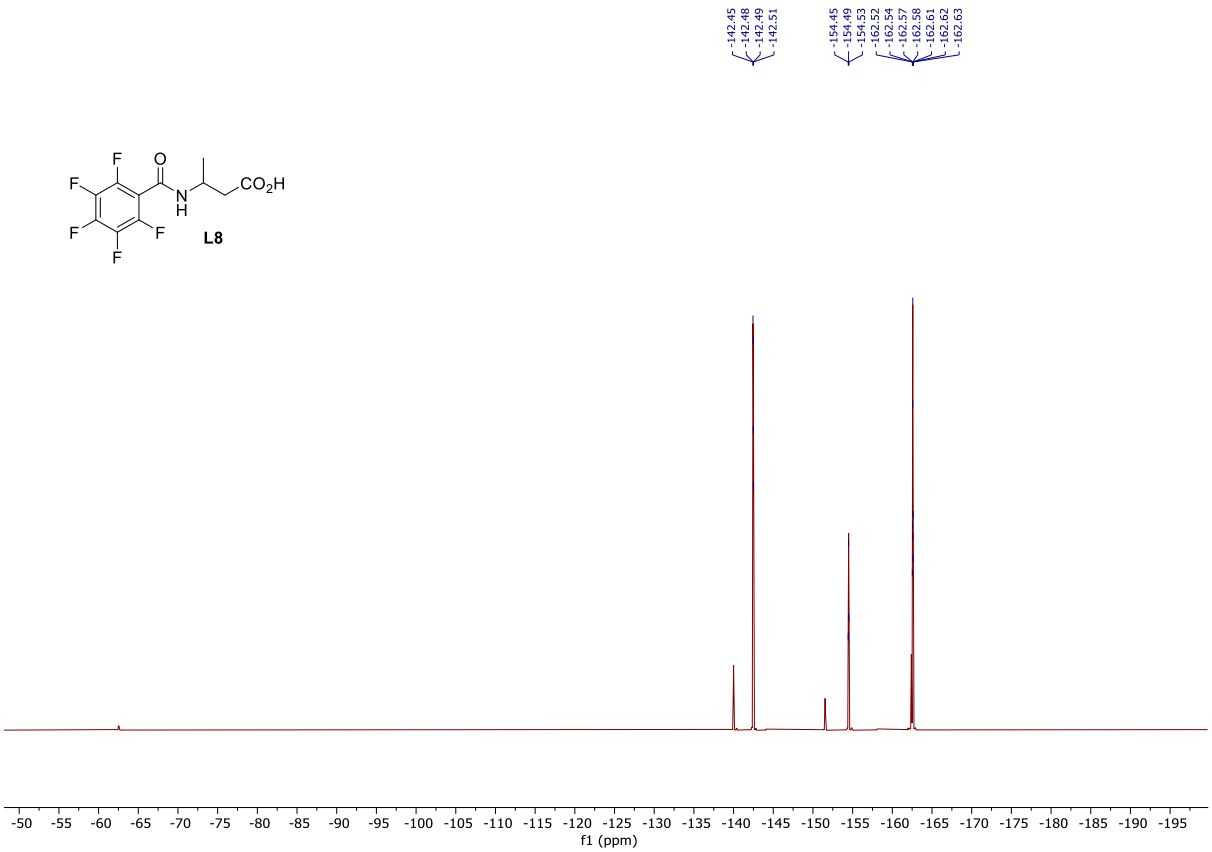

L7
f1 (ppm)

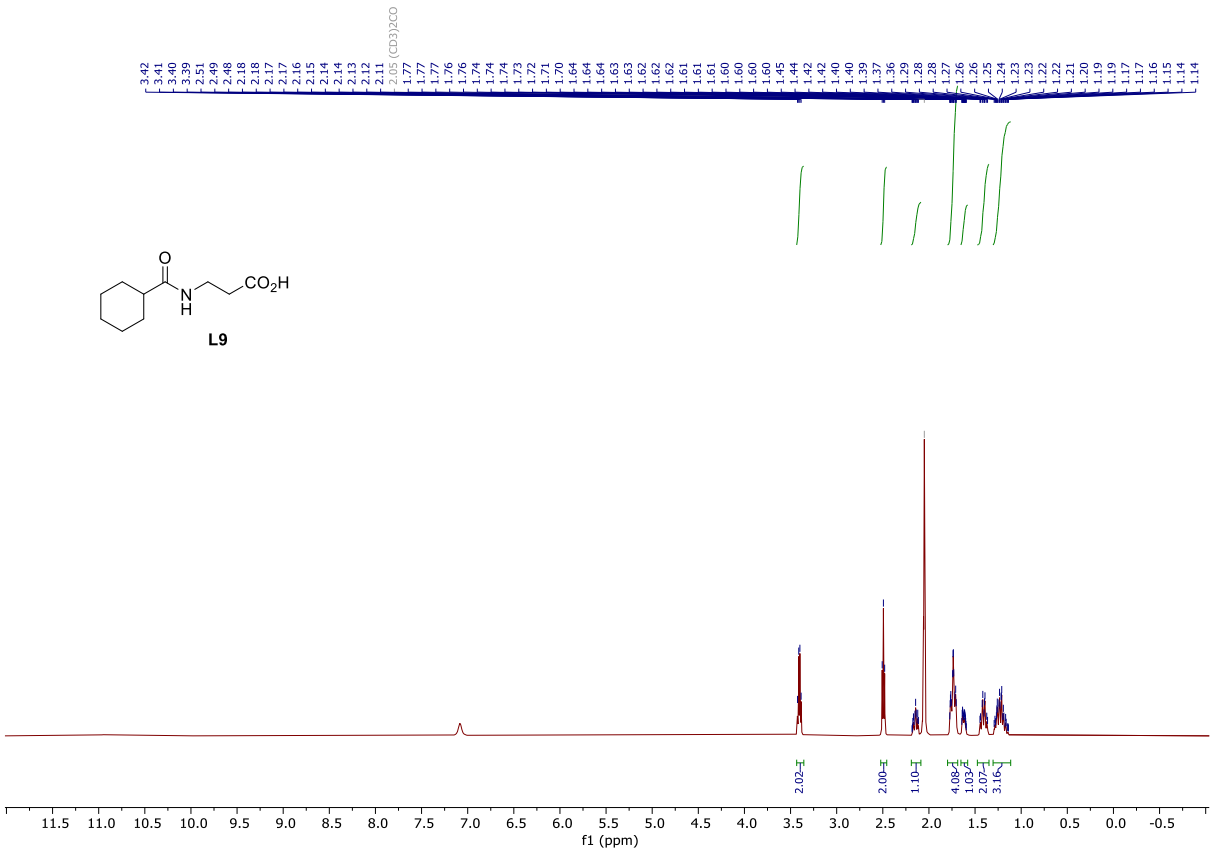

L7
f1 (ppm)
f1 (ppm)

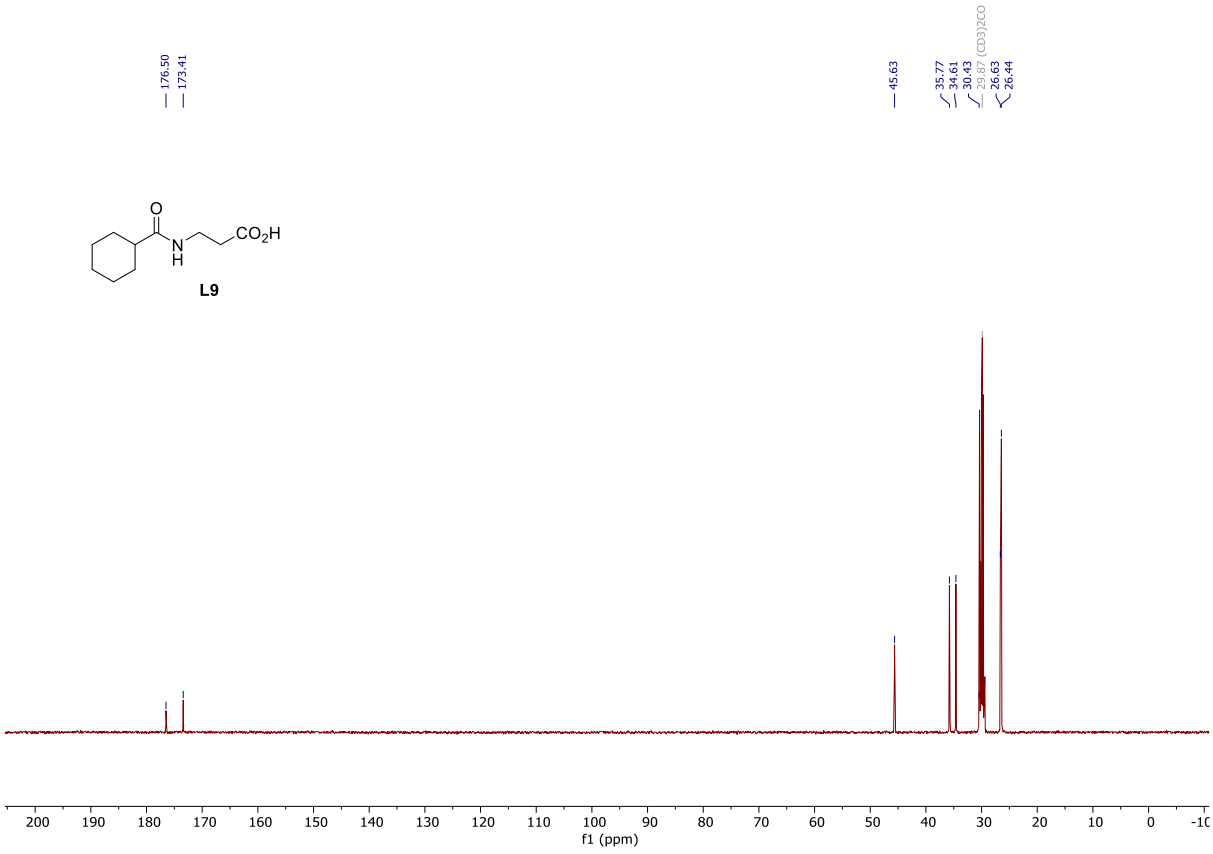

-142.31
-142.32
-142.32
-142.34
-142.37
-142.38
-142.39
-154.47
-154.48
-154.51
-154.52
-154.52
-154.55
-154.56
-154.57
-162.54
-162.55
-162.56
-162.58
-162.59
-162.61
-162.62
-162.64
-162.65
-162.66
F
O
F
N
H
CO2H
F
F
F
L7
-50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185 -190 -195
f1 (ppm)

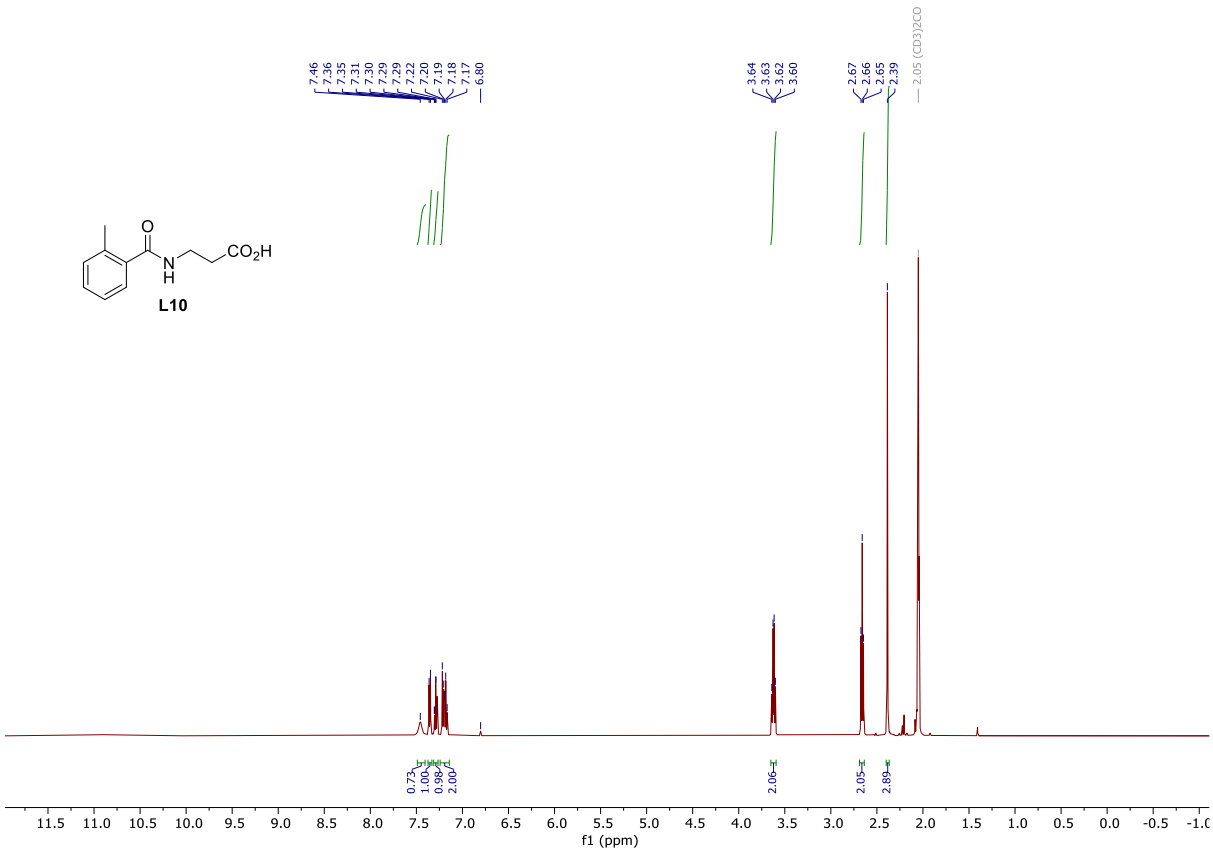

7.97
4.52
4.51
4.49
4.48
4.47
4.45
4.44
2.72
2.71
2.69
2.68
2.60
2.58
2.57
2.55
2.05 ((CD3)2CO
1.33
1.32
L8
1.00
1.16
1.17
1.22
3.43
f1 (ppm)

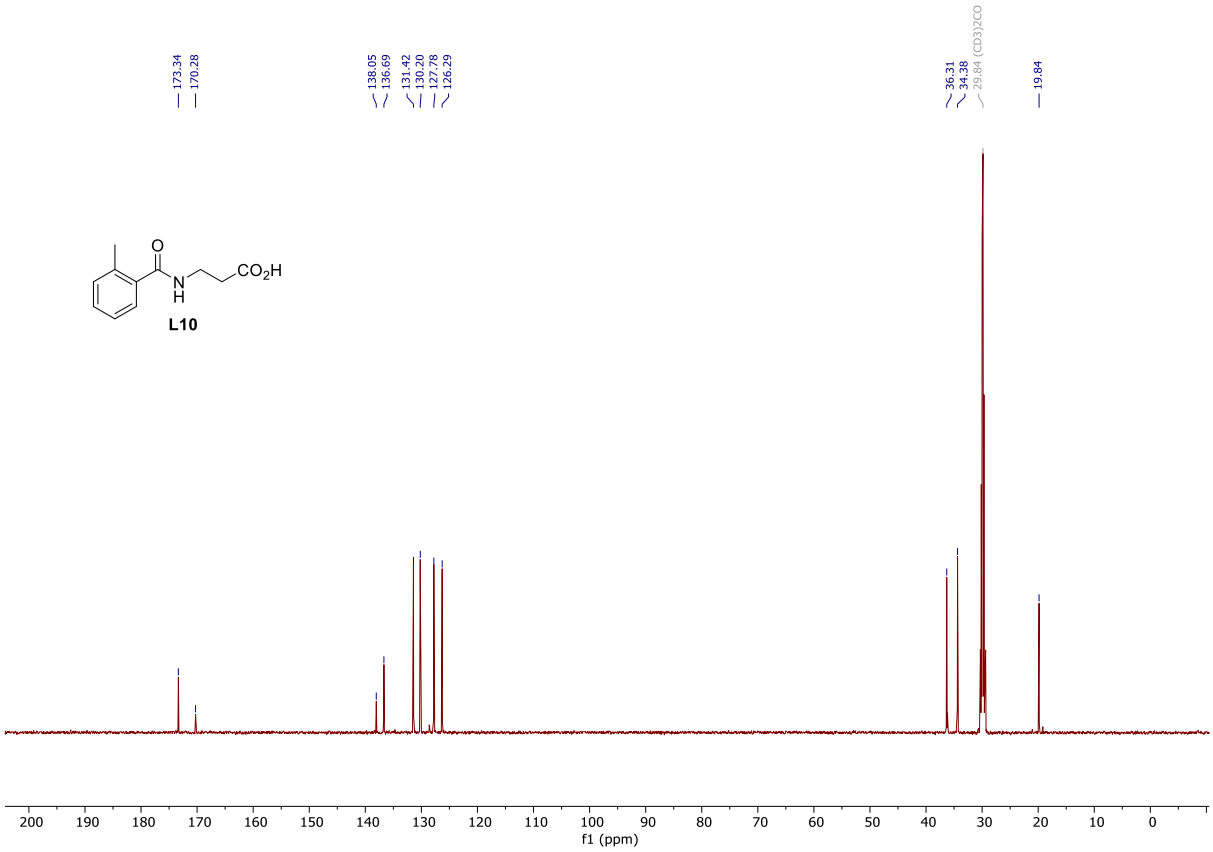

172.30
156.91
145.73
145.69
145.66
143.75
143.71
143.63
141.59
139.48
139.35
139.20
137.45
137.35
113.90
113.73
44.30
40.42
20.20
L8
f1 (ppm)

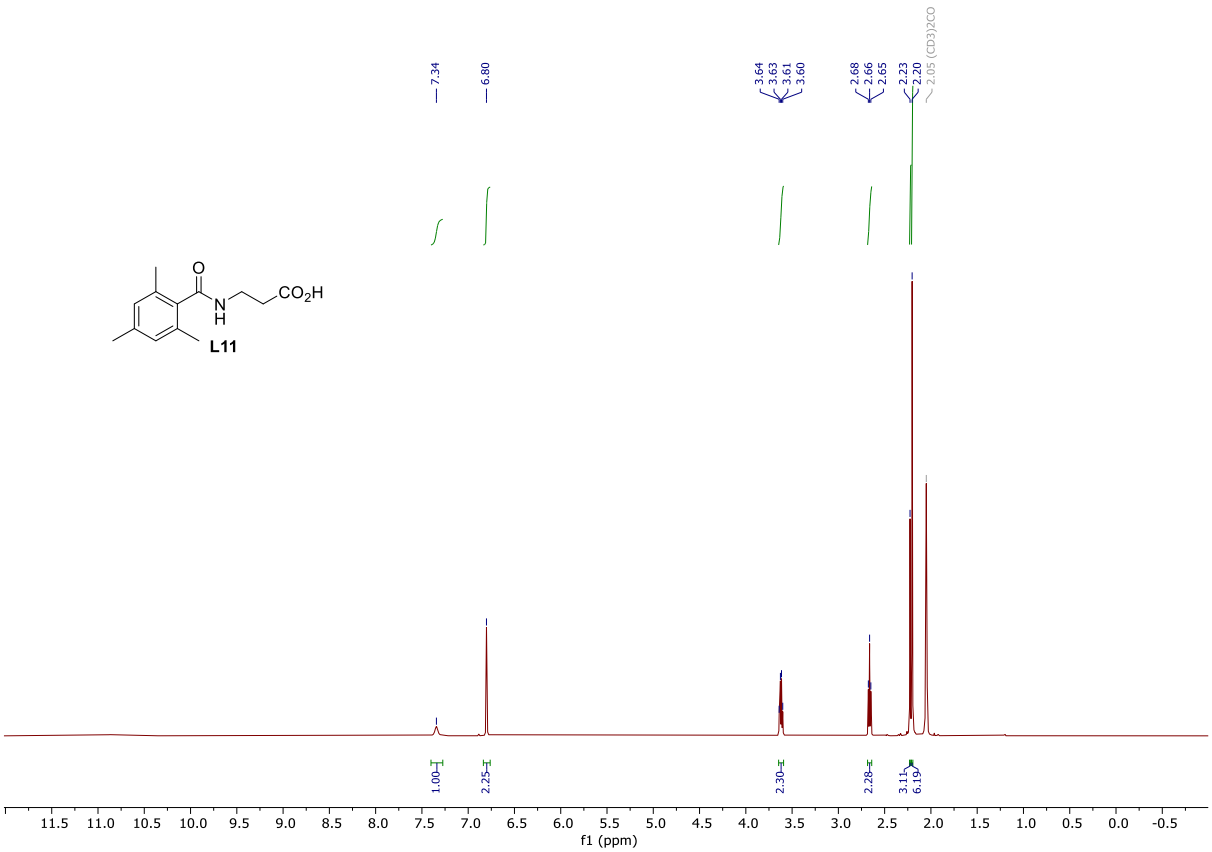

-142.45
-142.48
-142.49
-142.51
-154.45
-154.49
-154.53
-162.52
-162.54
-162.57
-162.58
-162.61
-162.62
-162.63
F
O
F
N
H
CO2H
F
F
F
L8
-50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185 -190 -195
f1 (ppm)

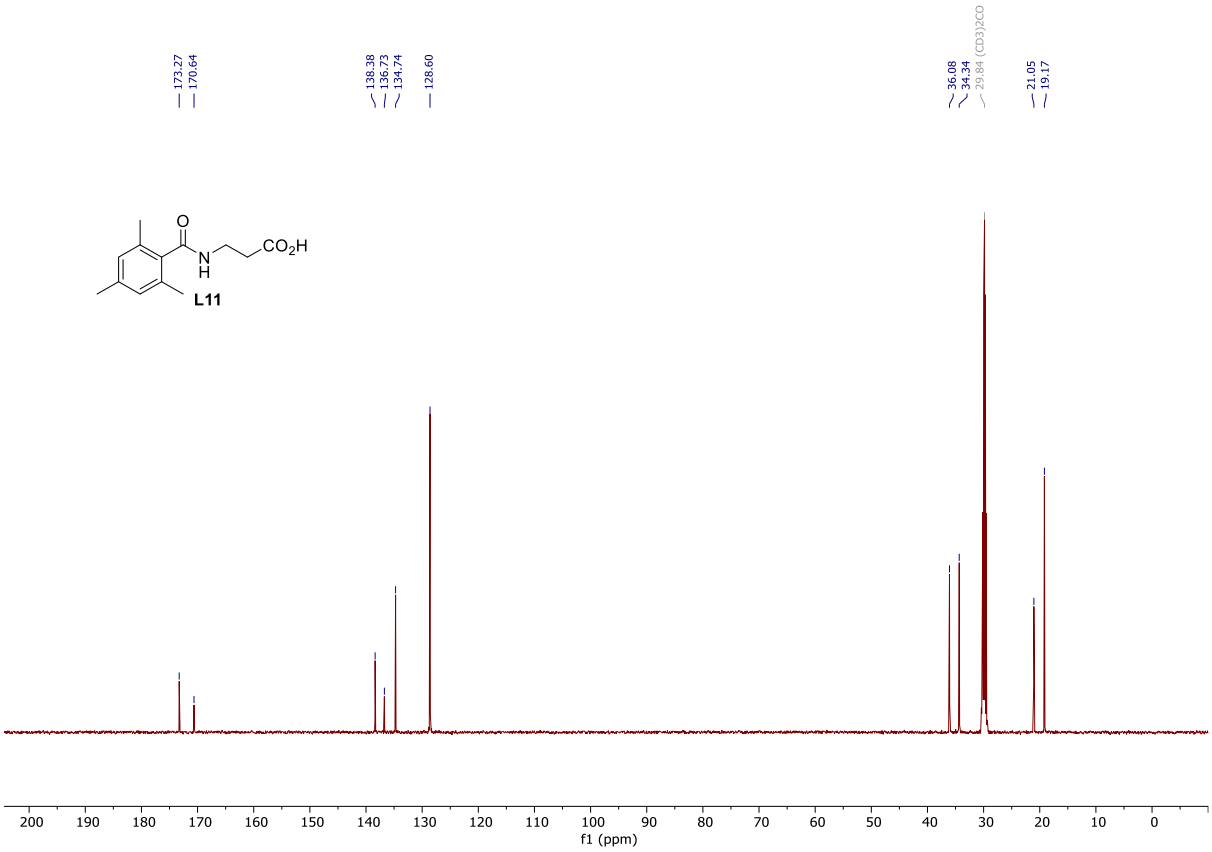

L9
f1 (ppm)

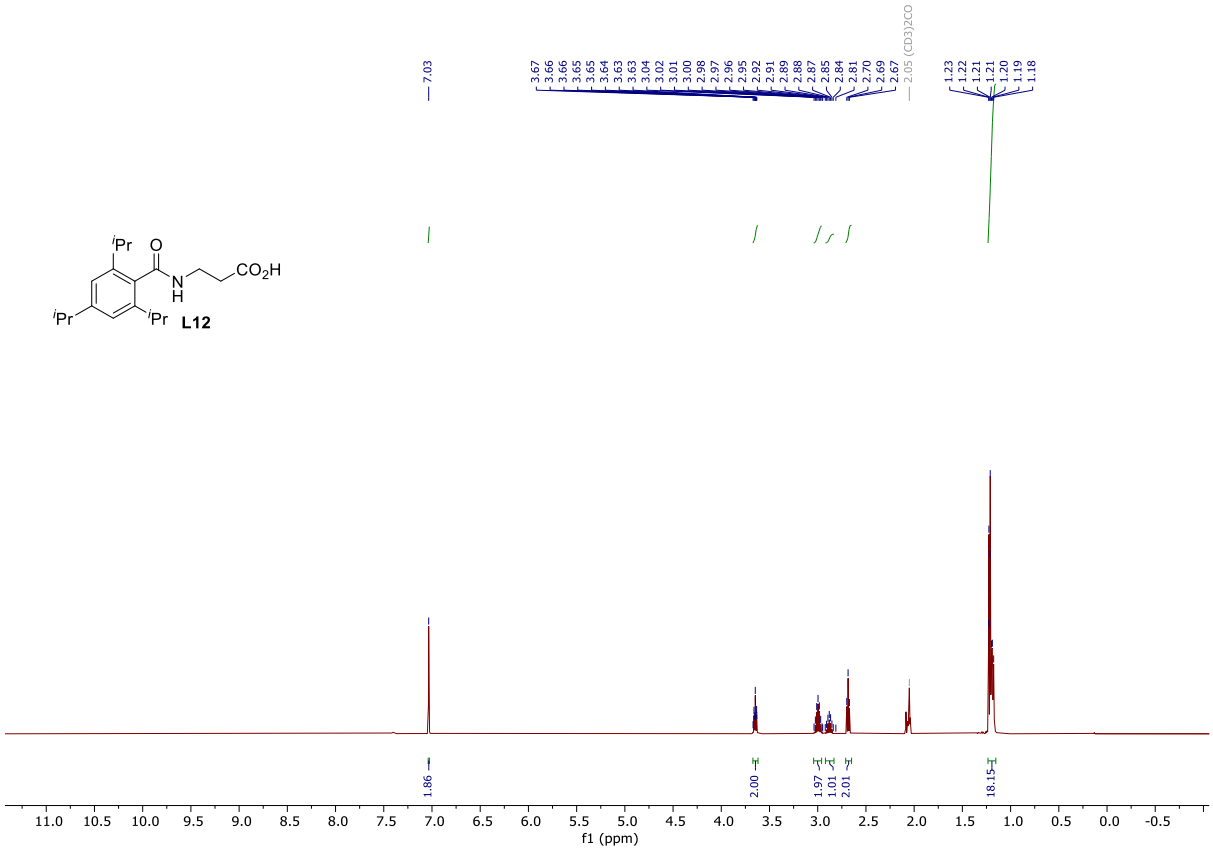

L9
f1 (ppm)

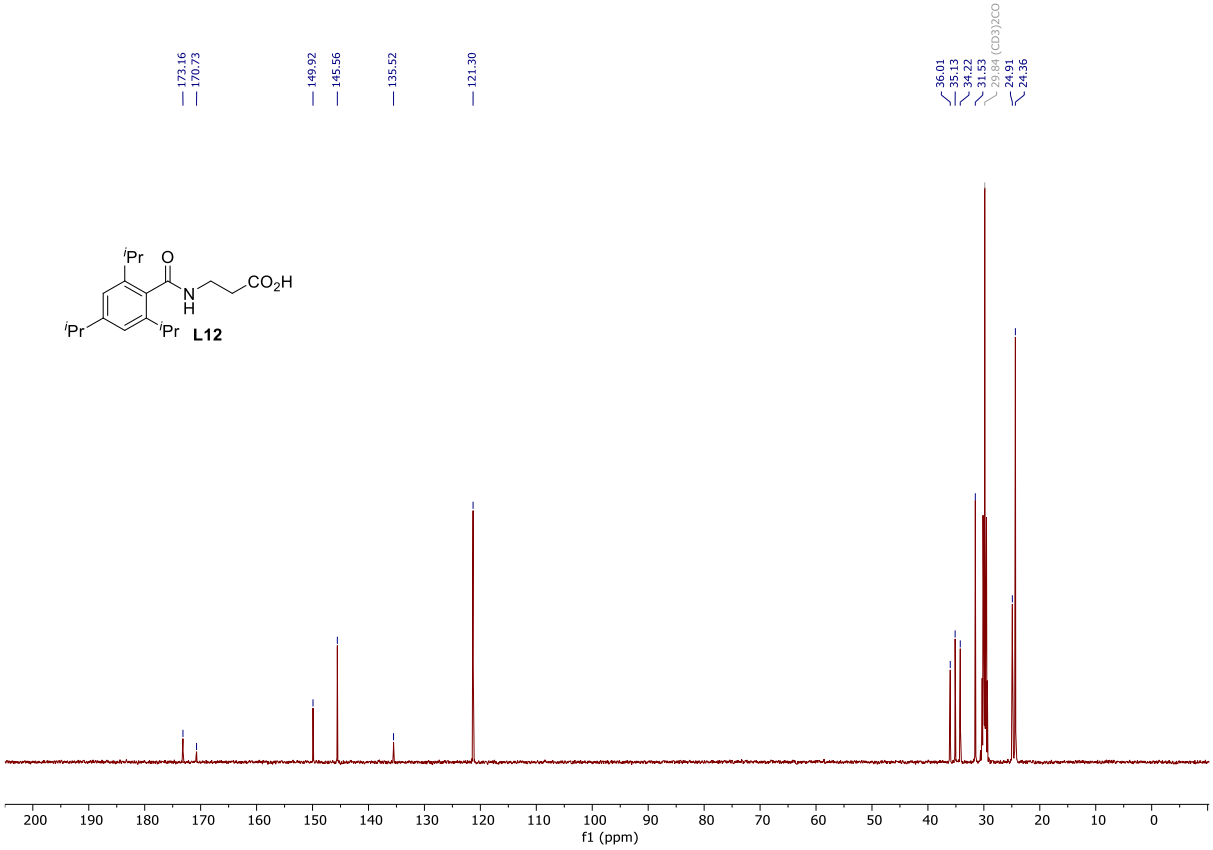

7.46
7.36
7.35
7.31
7.30
7.29
7.29
7.22
7.20
7.19
7.18
7.17
6.80
3.64
3.63
3.62
3.60
2.67
2.66
2.65
2.39
2.05 (CD3)2CO
O
N
H
CO2H
L10
0.73
1.00
0.98
2.00
2.06
2.05
2.89
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

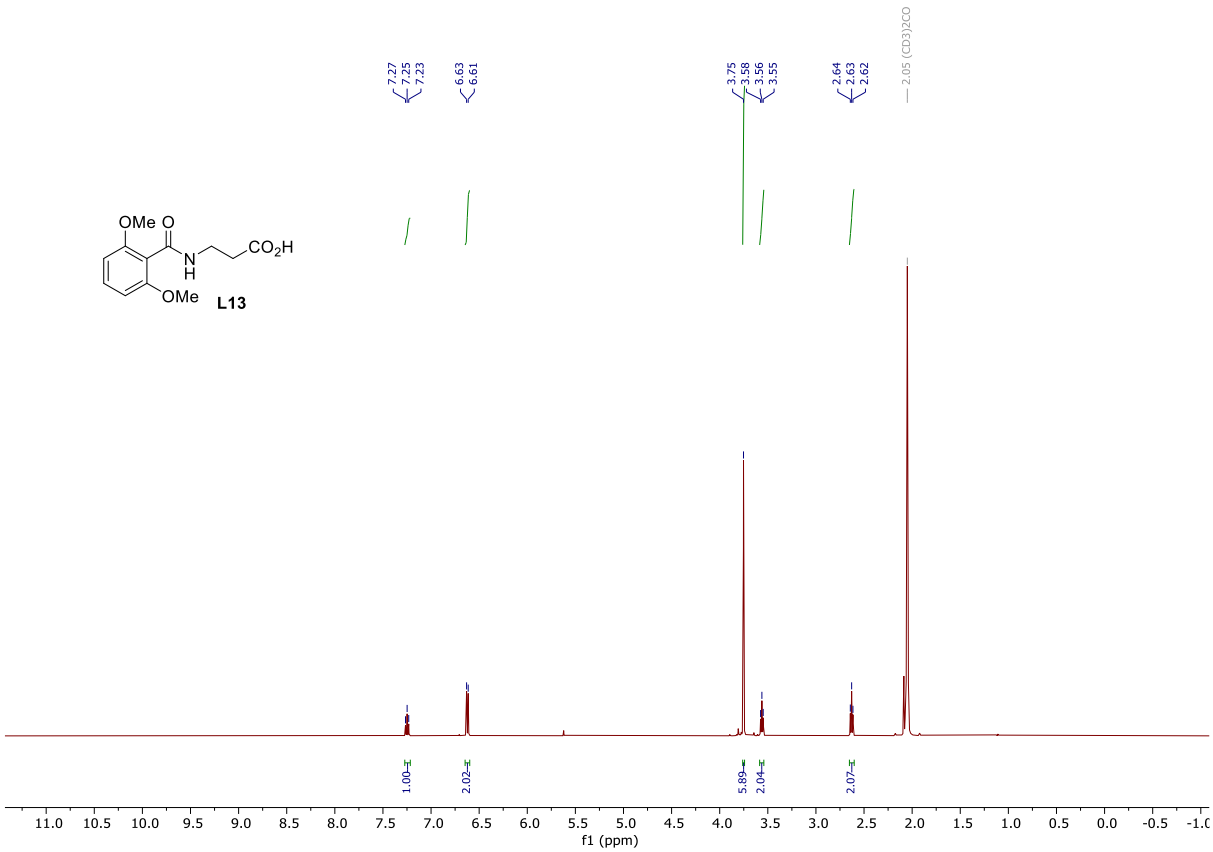

173.34
170.28
138.05
136.69
131.42
130.20
127.78
126.29
36.31
34.38
29.84 (CD3)2CO
19.84
O
N
H
CO2H
L10
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

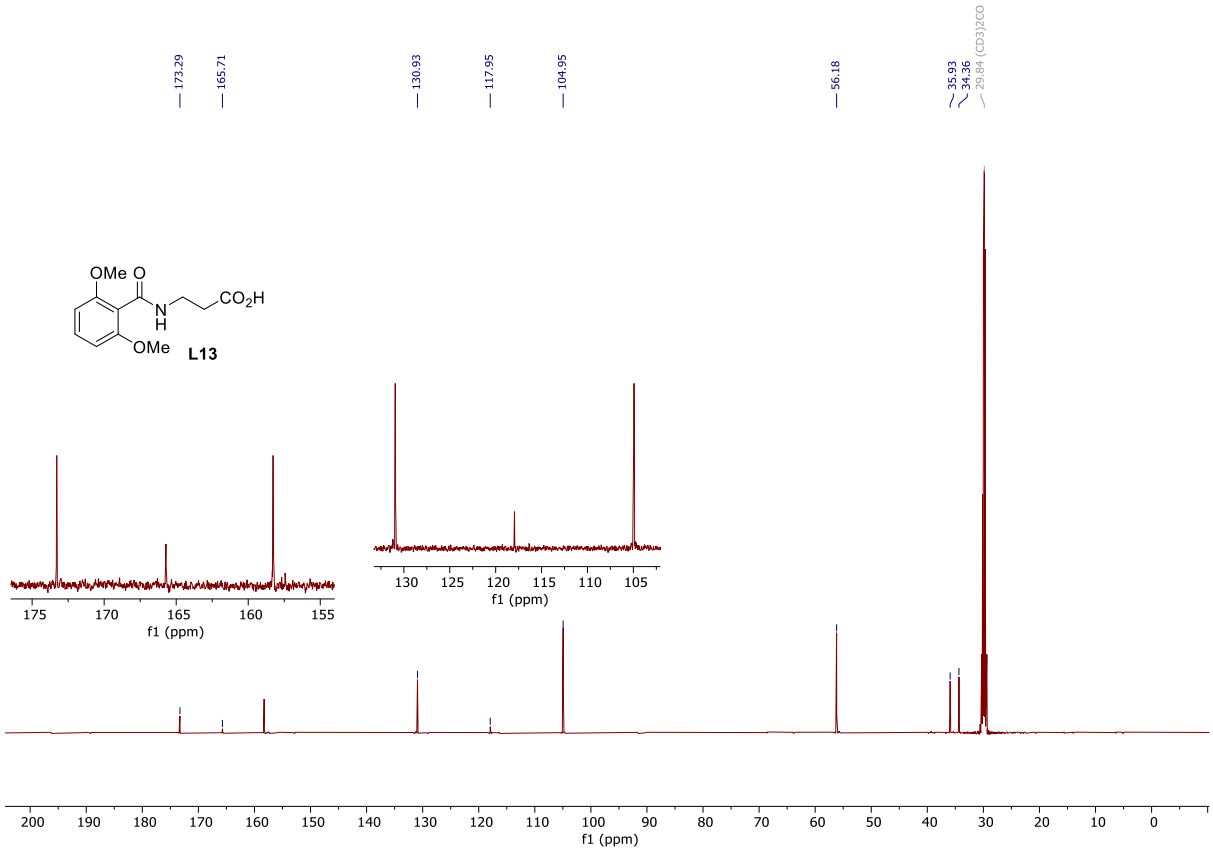

7.34
6.80
3.64
3.63
3.61
3.60
2.68
2.66
2.65
2.23
2.20
2.05 (CD3)2CO
O
N
H
CO2H
L11
1.00
2.25
2.30
2.28
3.11
6.19
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

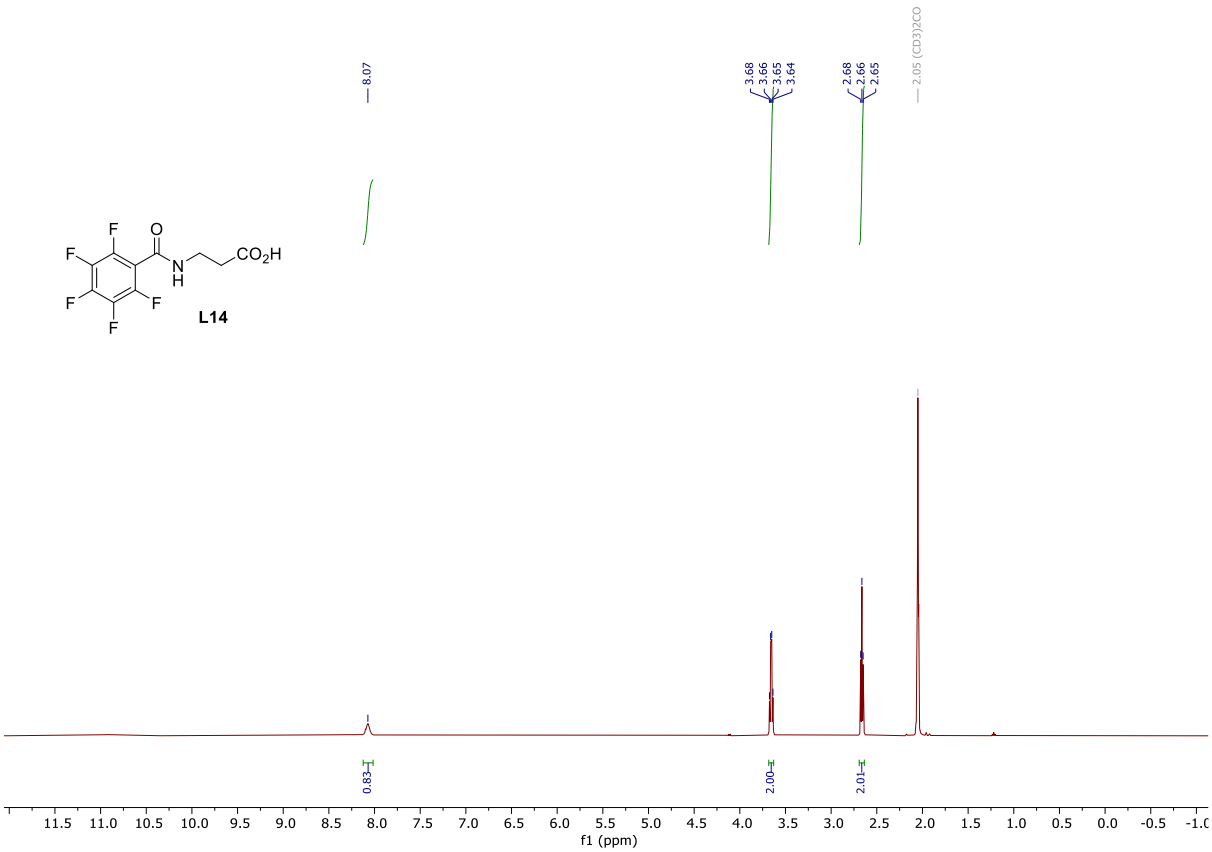

173.27
170.64
138.38
136.73
134.74
128.60
36.08
34.34
29.84 (CD3)2CO
21.05
19.17
O
N
H
CO2H
L11
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

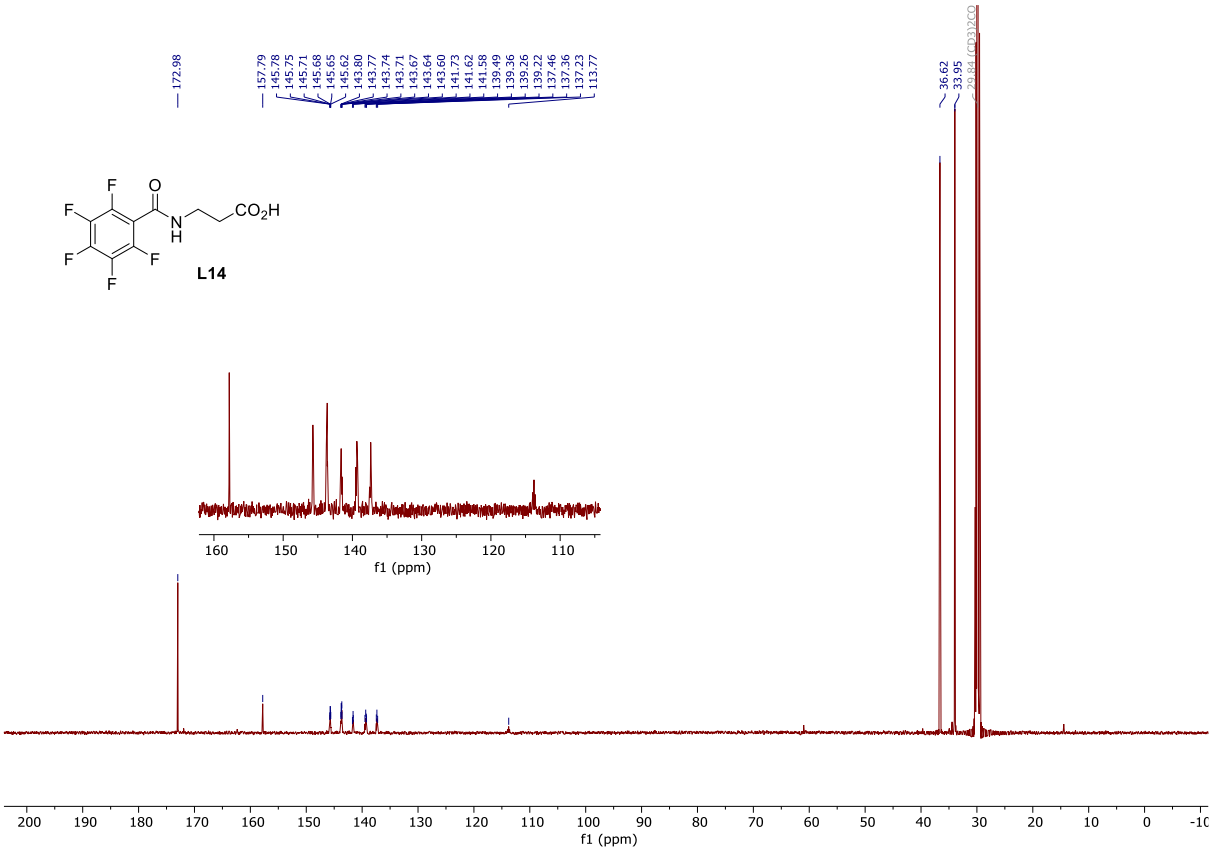

7.03
3.67
3.66
3.66
3.65
3.65
3.64
3.63
3.63
3.04
3.02
3.01
3.00
2.98
2.97
2.96
2.95
2.92
2.91
2.89
2.88
2.87
2.85
2.84
2.81
2.70
2.69
2.67
2.05 (CD3)2CO
1.23
1.22
1.21
1.21
1.20
1.19
1.18
iPr
O
N
H
CO2H
iPr
iPr
L12
1.86
2.00
1.97
1.01
2.01
18.15
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


173.16
170.73
149.92
145.56
135.52
121.30
36.01
35.13
34.22
31.53
29.84 (CD3)2CO
24.91
24.36
iPr
O
N
H
CO2H
iPr
iPr
L12
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.27
7.25
7.23
6.63
6.61
3.75
3.58
3.56
3.55
2.64
2.63
2.62
2.05 (CD3)2CO
OMe O
N
H
CO2H
OMe
L13
1.00
2.02
5.89
2.04
2.07
f1 (ppm)


173.29
165.71
130.93
117.95
104.95
56.18
35.93
34.36
29.84 (CD3)2CO
OMe O
N
H
CO2H
OMe
L13
f1 (ppm)
f1 (ppm)
f1 (ppm)


8.07
3.68
3.66
3.65
3.64
2.68
2.66
2.65
2.05 (CD3)2CO
L14
0.83
2.00
2.01
f1 (ppm)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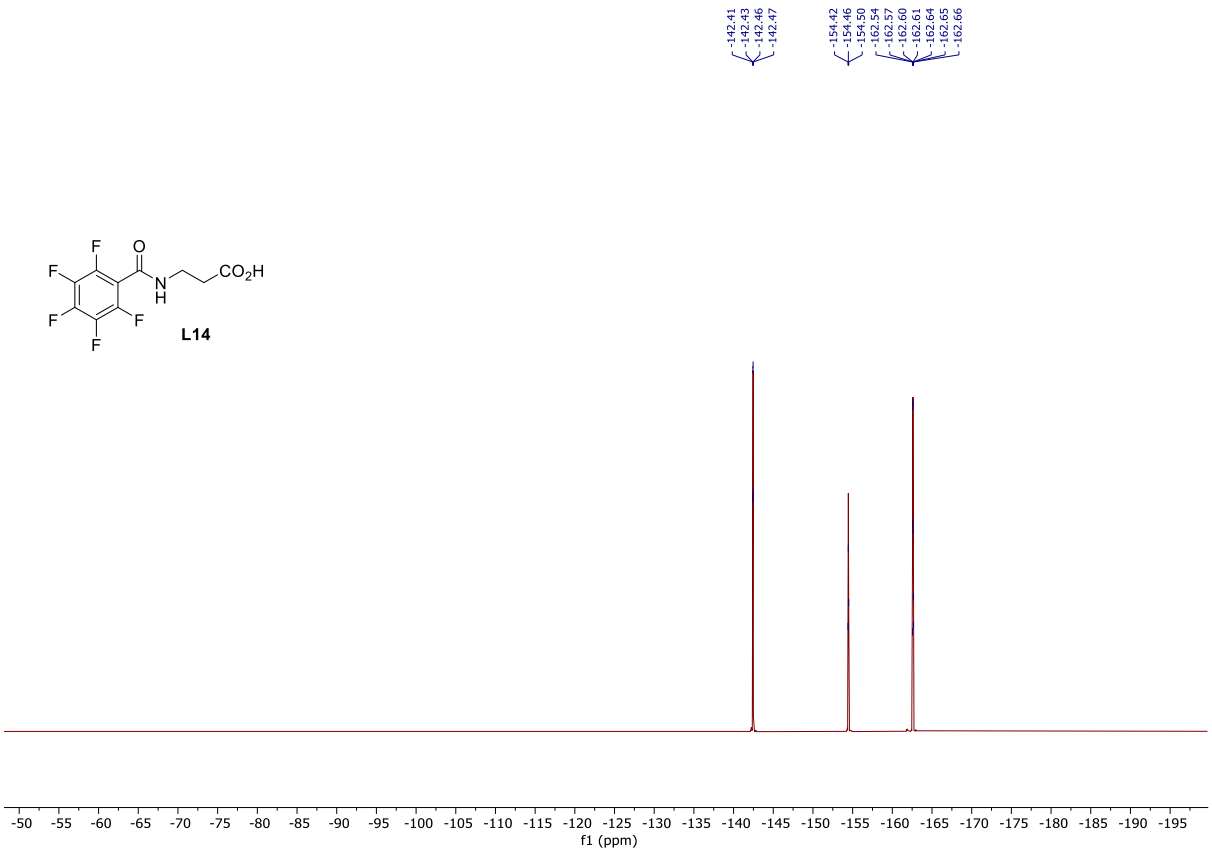
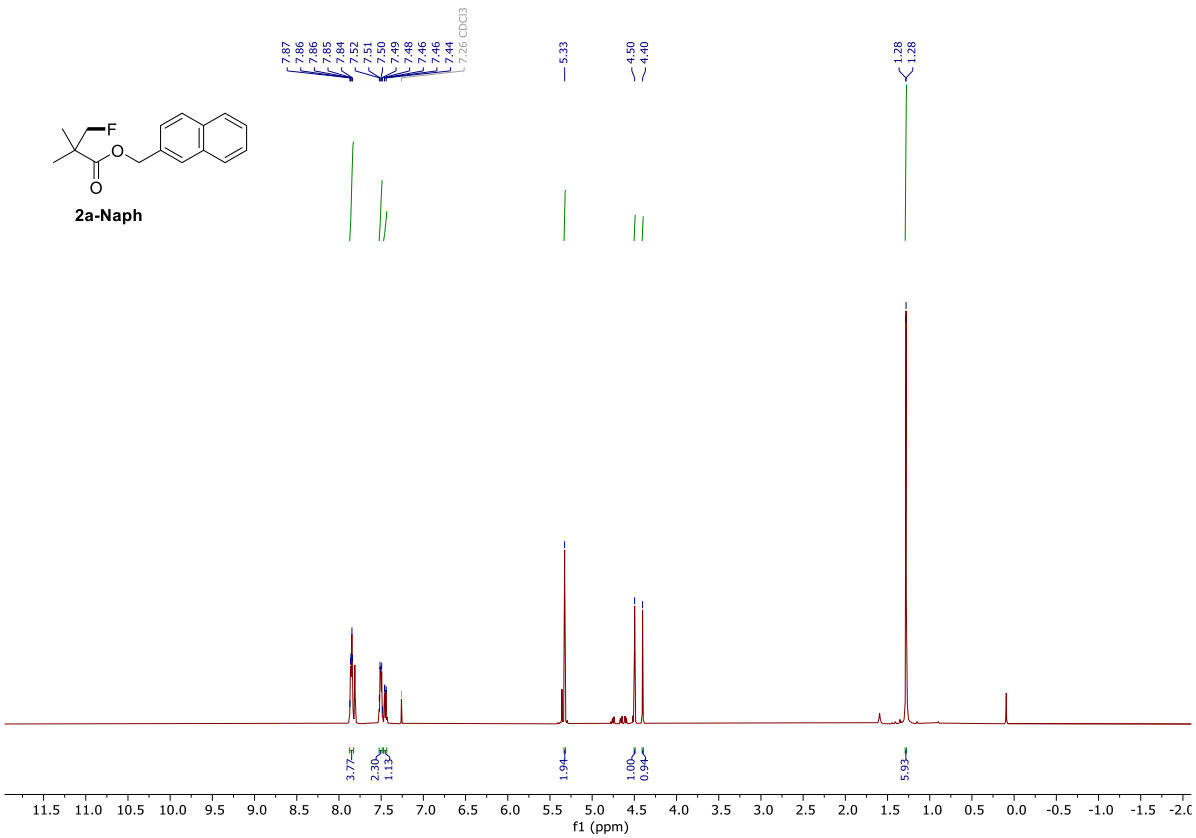
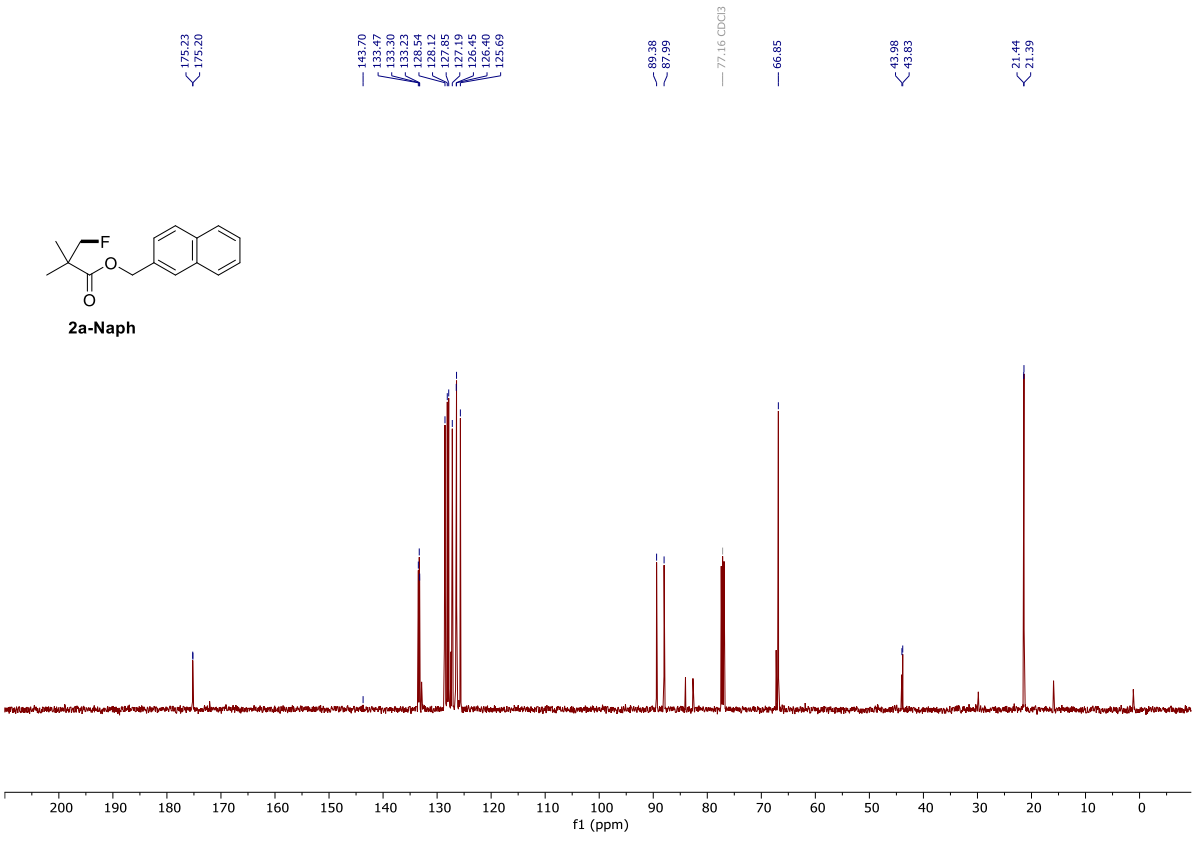
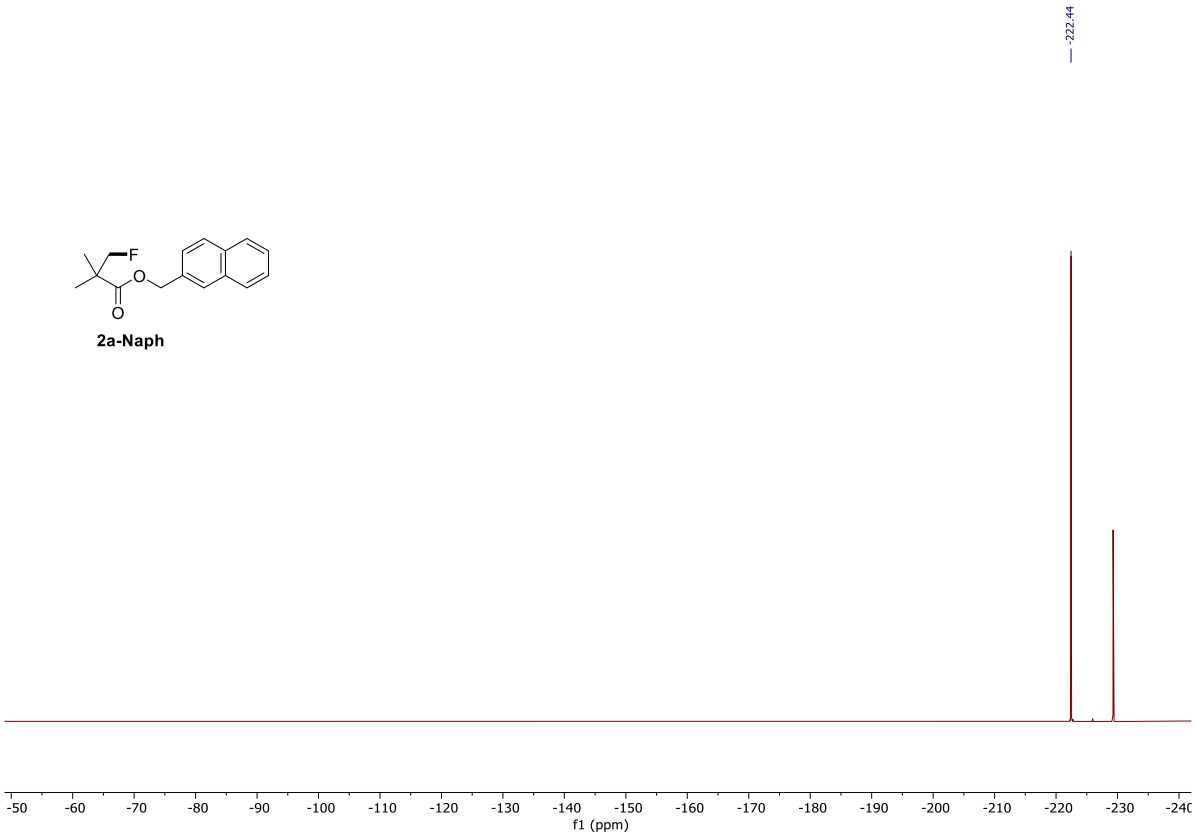
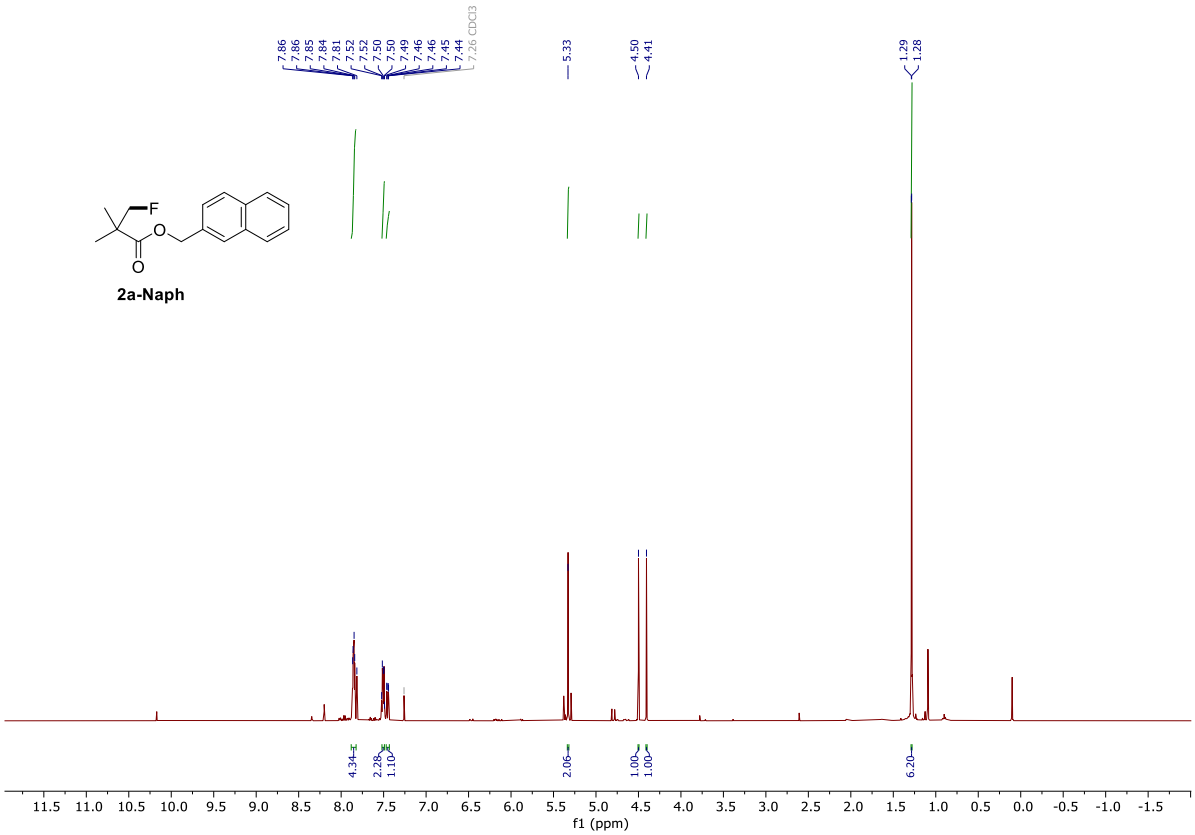
157.79
145.78
145.75
145.71
145.68
145.65
145.62
143.80
143.77
143.74
143.71
143.67
143.64
143.60
141.73
141.62
141.58
139.49
139.36
139.26
139.22
137.46
137.36
137.23
113.77
36.62
33.95
29.84 (CD3)2CO
L14
f1 (ppm)
f1 (ppm)

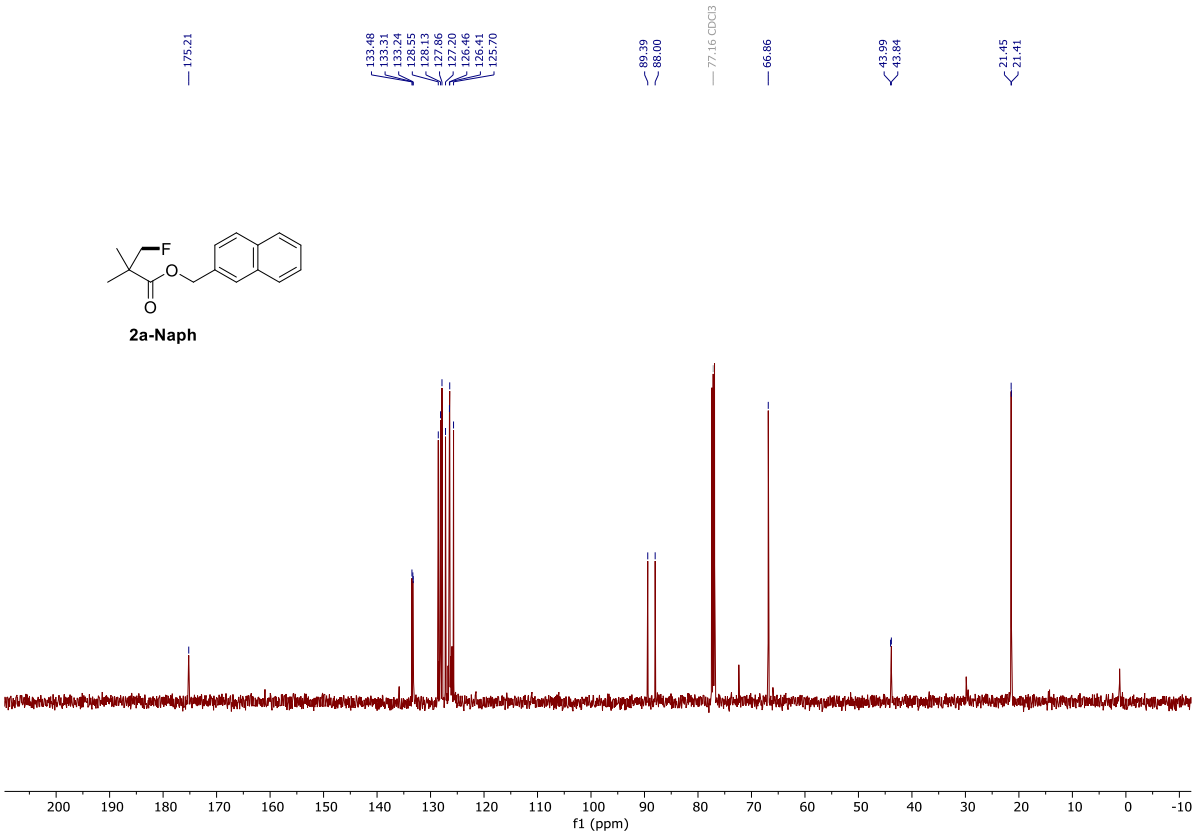

-142.41
-142.43
-142.46
-142.47
-154.42
-154.46
-154.50
-162.54
-162.57
-162.60
-162.61
-162.64
-162.65
-162.66
F
O
F
N
H
CO2H
F
F
F
L14
-50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185 -190 -195
f1 (ppm)

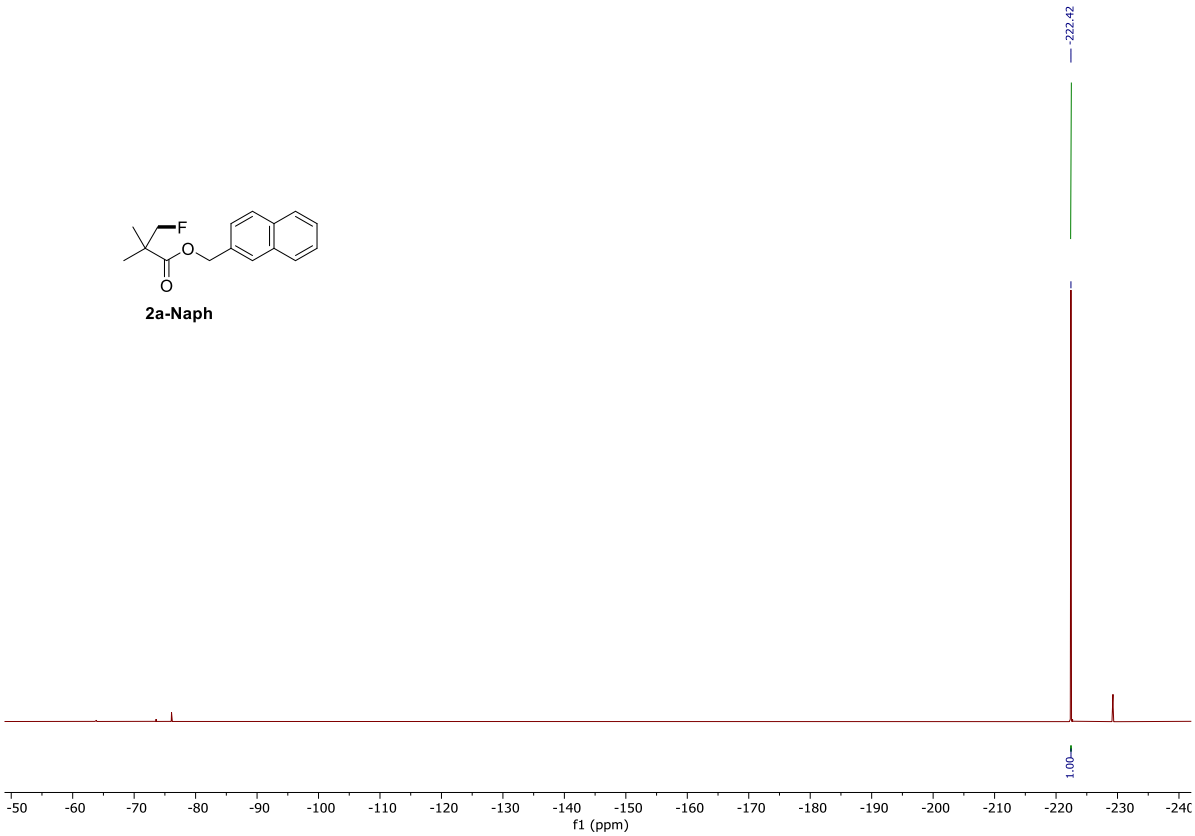

7.87
7.86
7.86
7.85
7.84
7.52
7.51
7.50
7.49
7.48
7.46
7.46
7.44
7.26 CDCl3
5.33
4.50
4.40
1.28
1.28
F
O
O
2a-Naph
3.77
2.30
1.13
1.94
1.00
0.94
5.93
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)

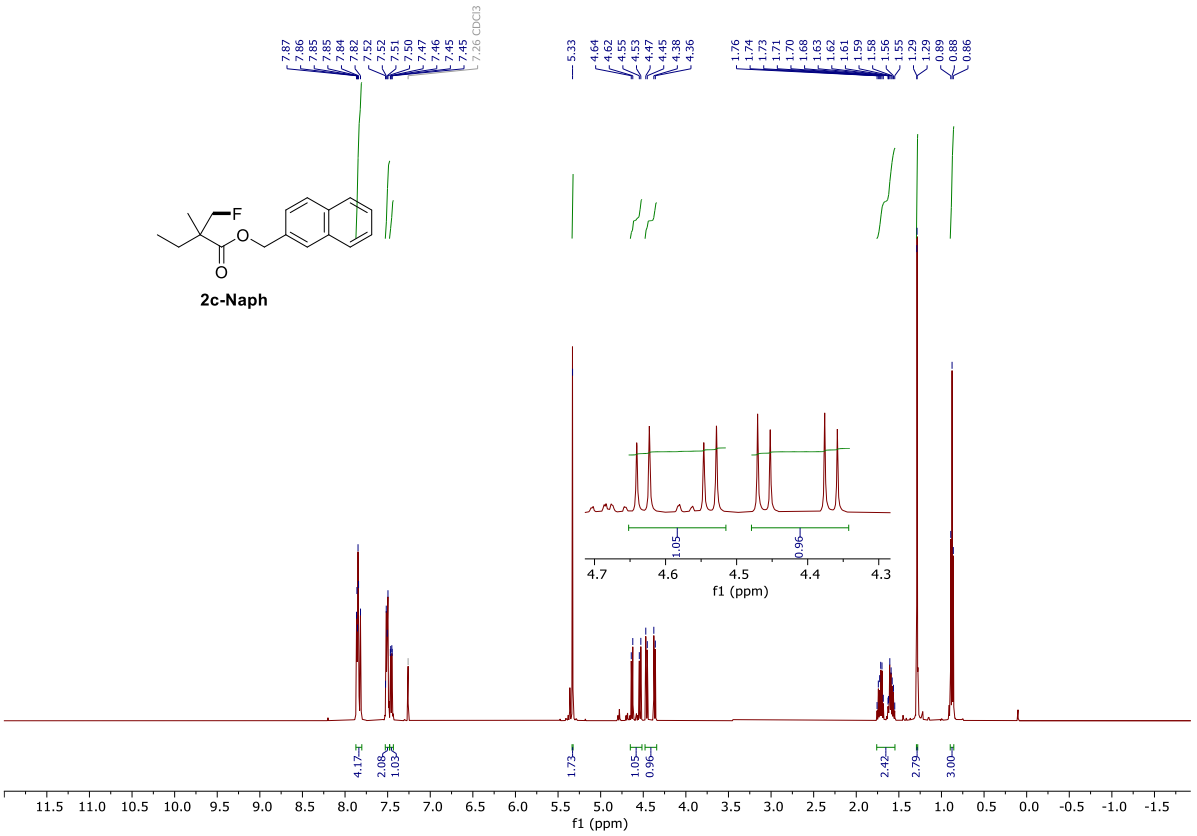

175.23
175.20
143.70
133.47
133.30
133.23
128.54
128.12
127.85
127.19
126.45
126.40
125.69
89.38
87.99
77.16 CDCl3
66.85
43.98
43.83
21.44
21.39
F
O
O
2a-Naph
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

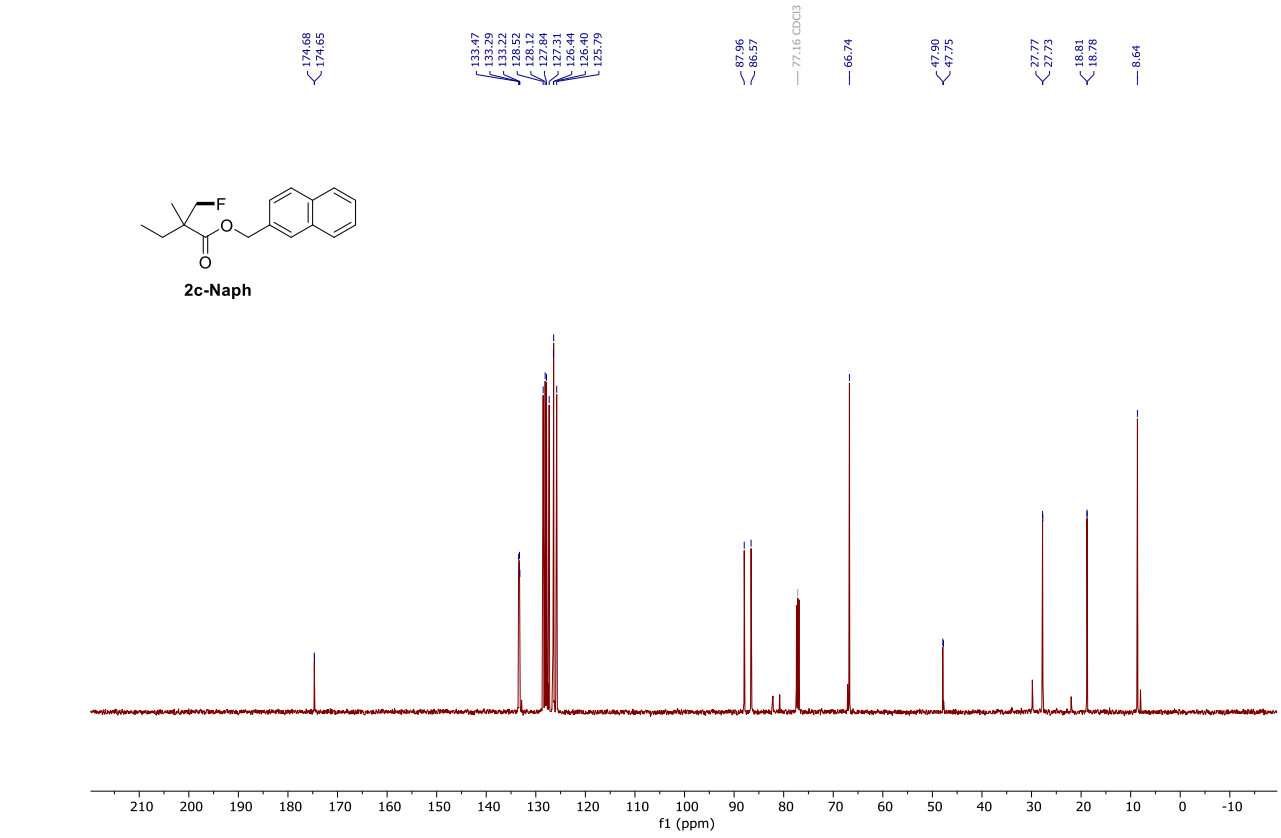

-222.44
F
O
O
2a-Naph
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
f1 (ppm)


7.86
7.86
7.85
7.84
7.81
7.52
7.50
7.50
7.49
7.46
7.46
7.45
7.44
7.26 CDCl3
5.33
4.50
4.41
1.29
1.28
F
O
O
2a-Naph
4.34
2.28
1.10
2.06
1.00
1.00
6.20
f1 (ppm)


175.21
133.48
133.31
133.24
128.55
128.13
127.86
127.20
126.46
126.41
125.70
89.39
88.00
77.16 CDCl3
66.86
43.99
43.84
21.45
21.41
F
O
O
2a-Naph
f1 (ppm)


F
O
O
2a-Naph
-222.42
1.00
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
f1 (ppm)


7.87
7.86
7.85
7.85
7.84
7.82
7.52
7.52
7.51
7.50
7.47
7.46
7.45
7.45
7.26 CDCl3
5.33
4.64
4.62
4.55
4.53
4.47
4.45
4.38
4.36
1.76
1.74
1.73
1.71
1.70
1.68
1.63
1.62
1.61
1.59
1.58
1.56
1.55
1.29
0.89
0.88
0.86
F
O
O
2c-Naph
1.05
0.96
4.7
4.6
4.5
4.4
4.3
f1 (ppm)
4.17
2.08
1.03
1.73
1.05
0.96
2.42
2.79
3.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)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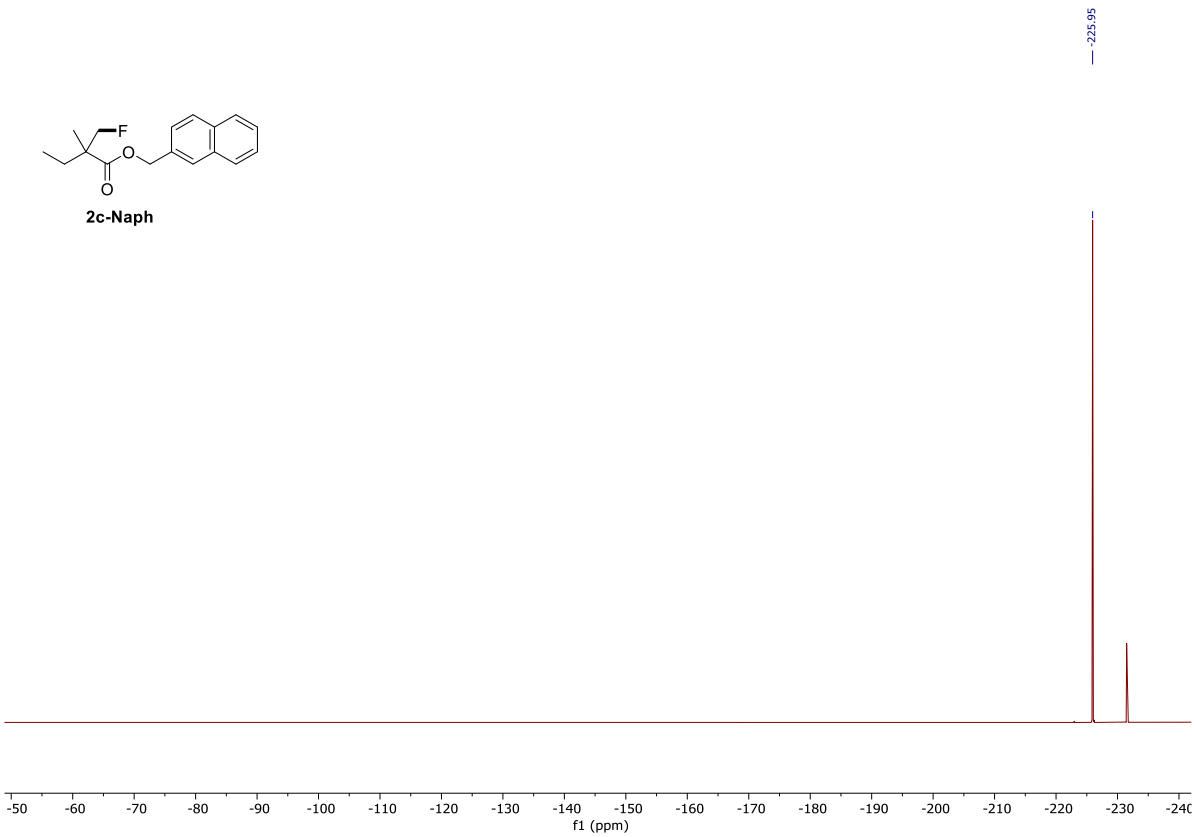
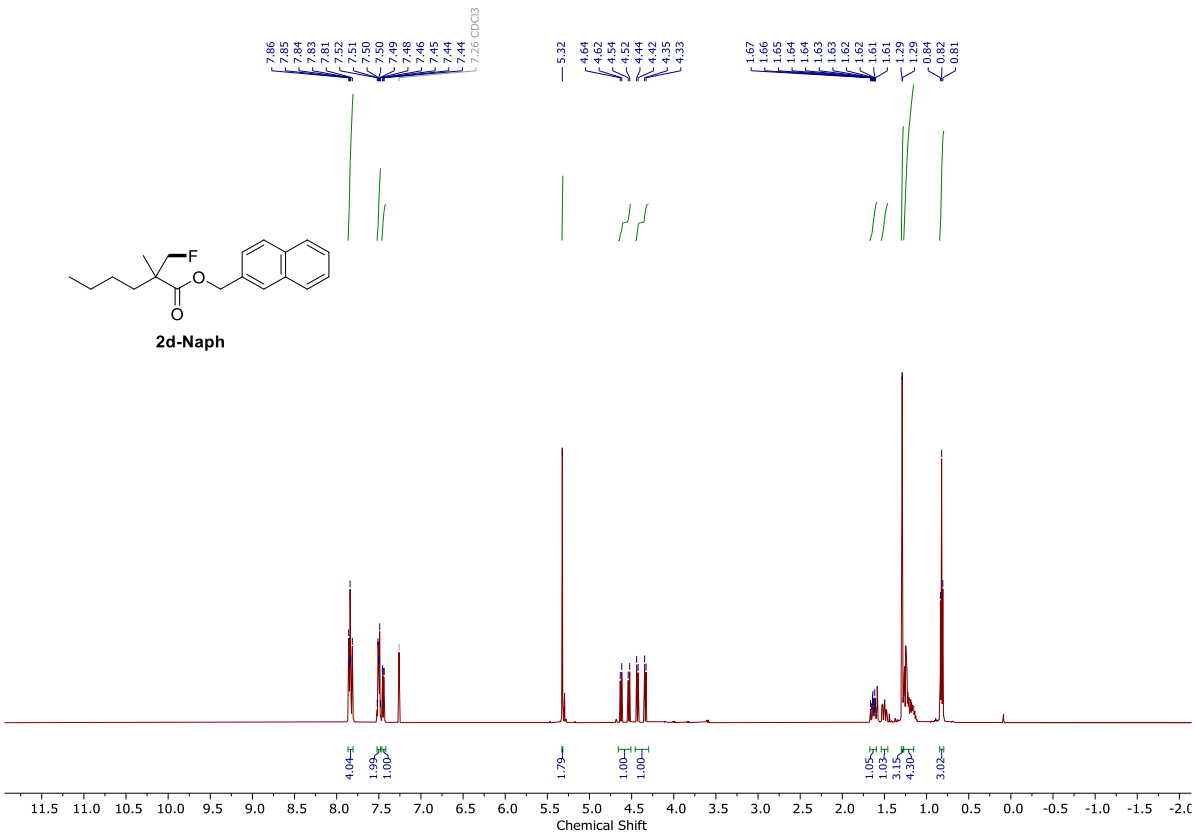
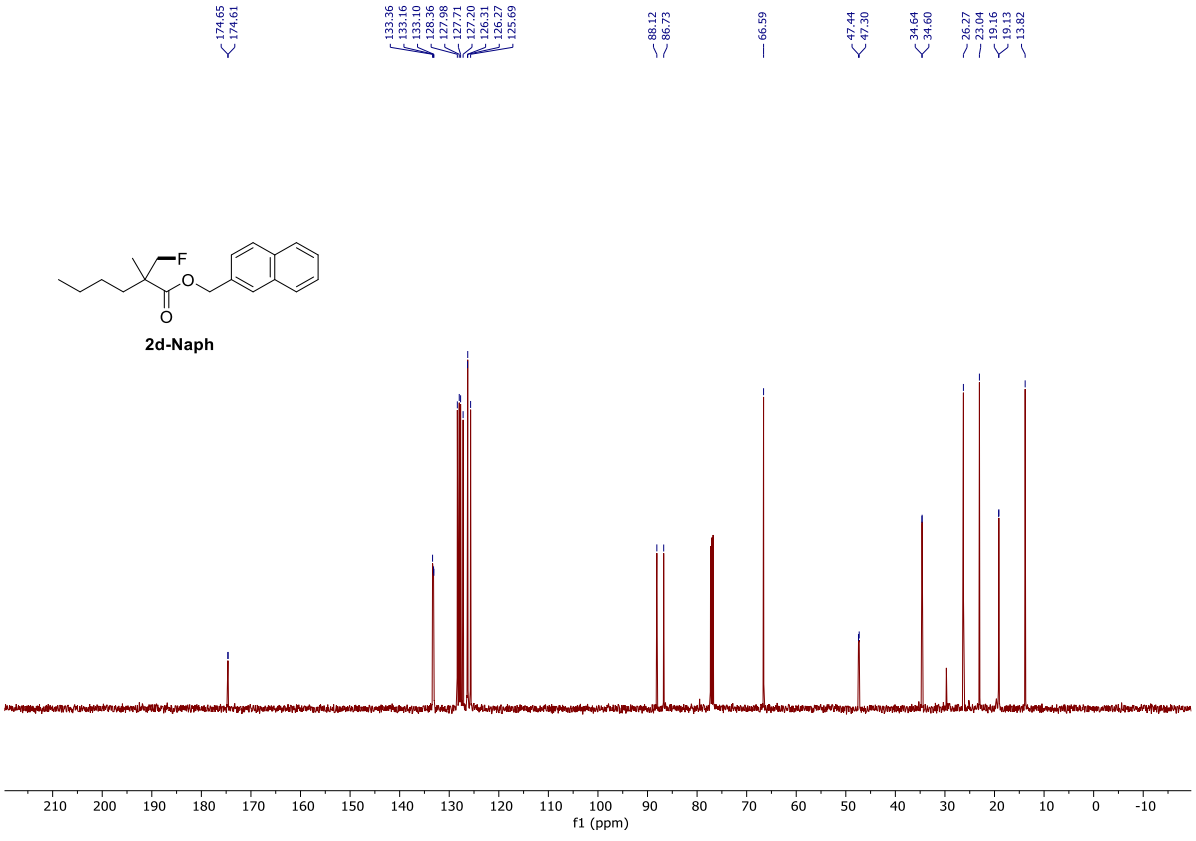
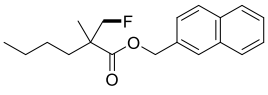
174.65
133.47
133.29
133.22
128.52
128.12
127.84
127.31
126.44
126.40
125.79
87.96
86.57
77.16 CDCl3
66.74
47.90
47.75
27.77
27.73
18.81
18.78
8.64
F
O
O
2c-Naph
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-225.95
F
O
O
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
f1 (ppm)

2c-Naph

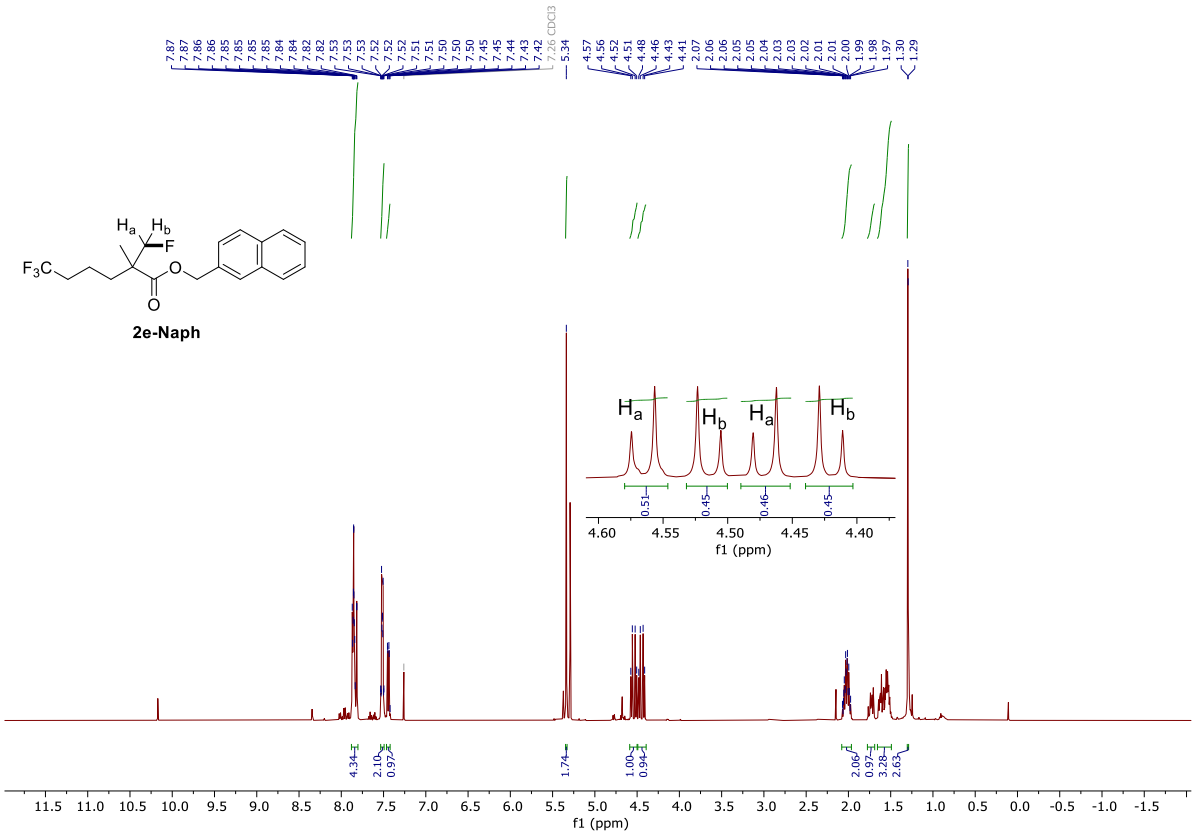

7.86
7.85
7.84
7.83
7.81
7.52
7.51
7.50
7.50
7.49
7.48
7.46
7.45
7.44
7.44
7.26 CDCl3
5.32
4.64
4.62
4.54
4.52
4.44
4.42
4.35
4.33
1.67
1.66
1.65
1.64
1.64
1.63
1.63
1.62
1.62
1.61
1.61
1.29
1.29
0.84
0.82
0.81
F
O
O
2d-Naph
4.04
1.99
1.00
1.79
1.00
1.00
1.05
1.03
3.15
4.30
3.02
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
Chemical Shift

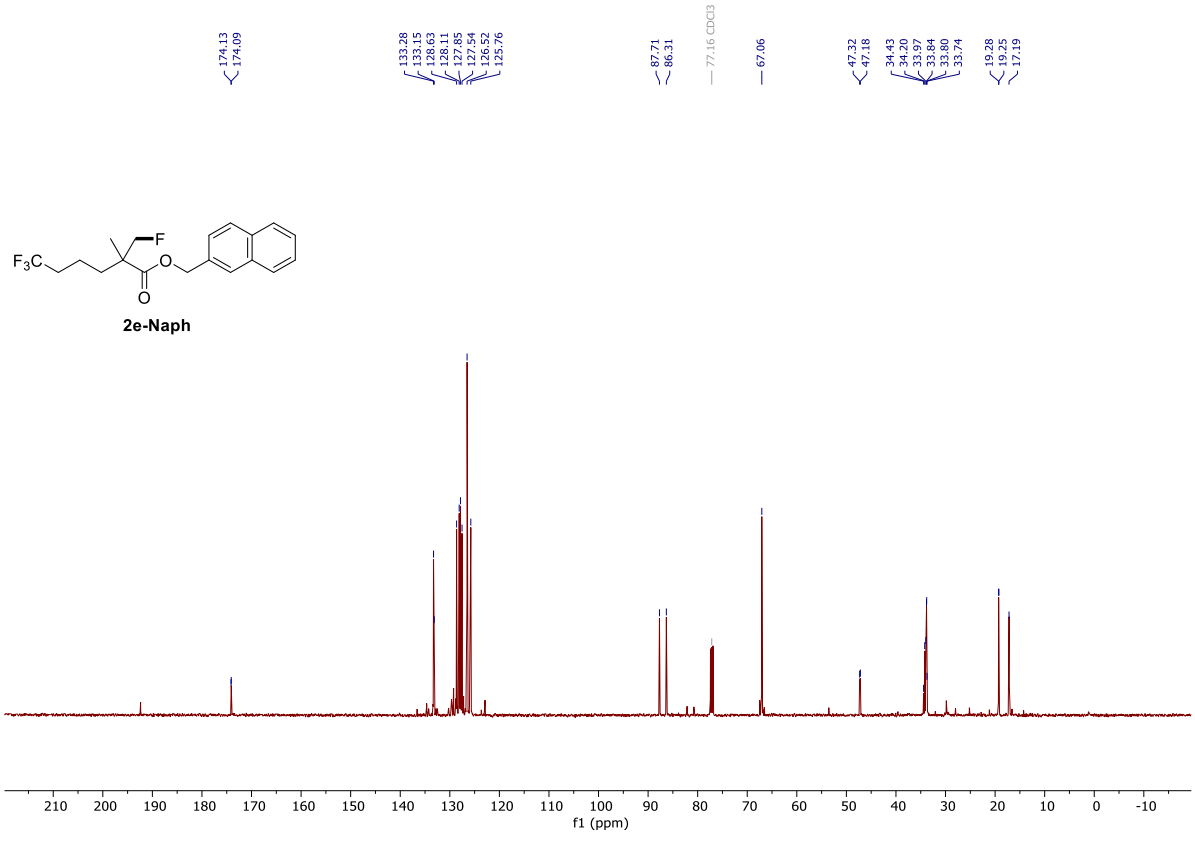

174.65
174.61
133.36
133.16
133.10
128.36
127.98
127.71
127.20
126.31
126.27
125.69
88.12
86.73
66.59
47.44
47.30
34.64
34.60
26.27
23.04
19.16
19.13
13.82
F
O
O
2d-Naph
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

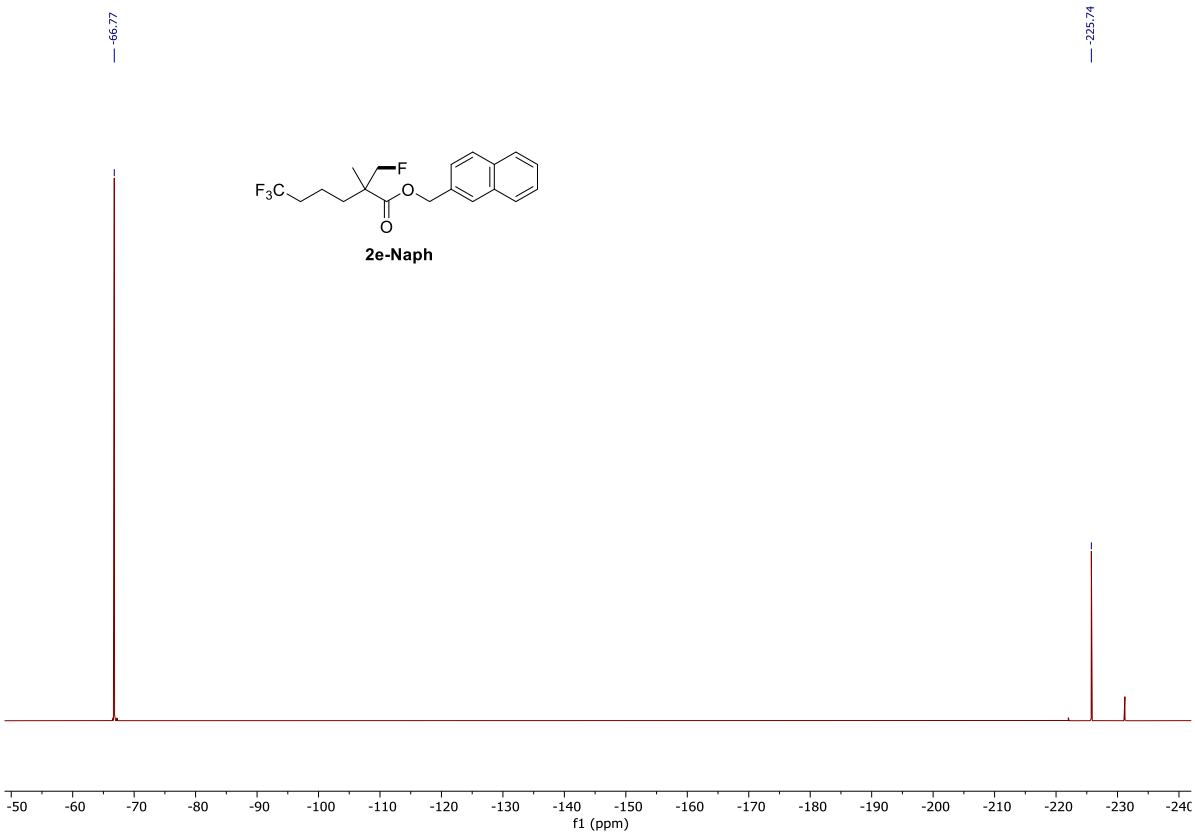

F
O
O

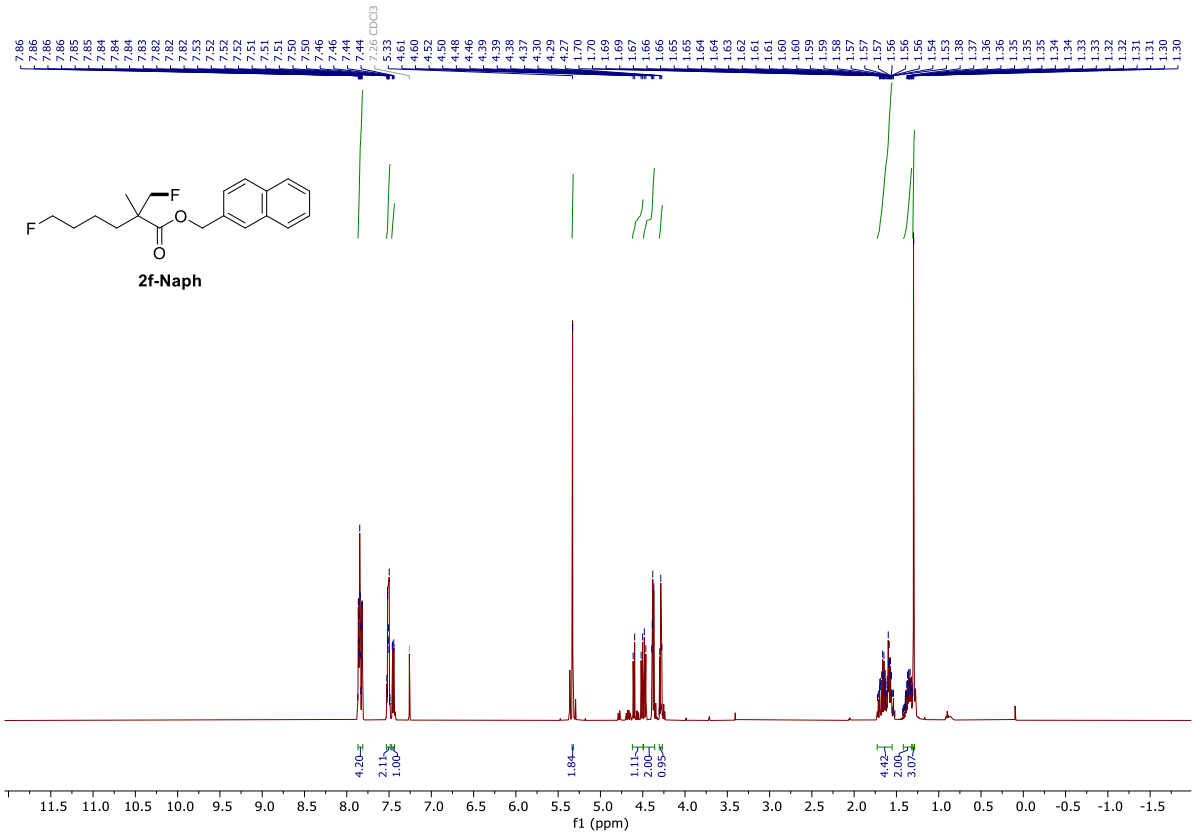
2d-Naph

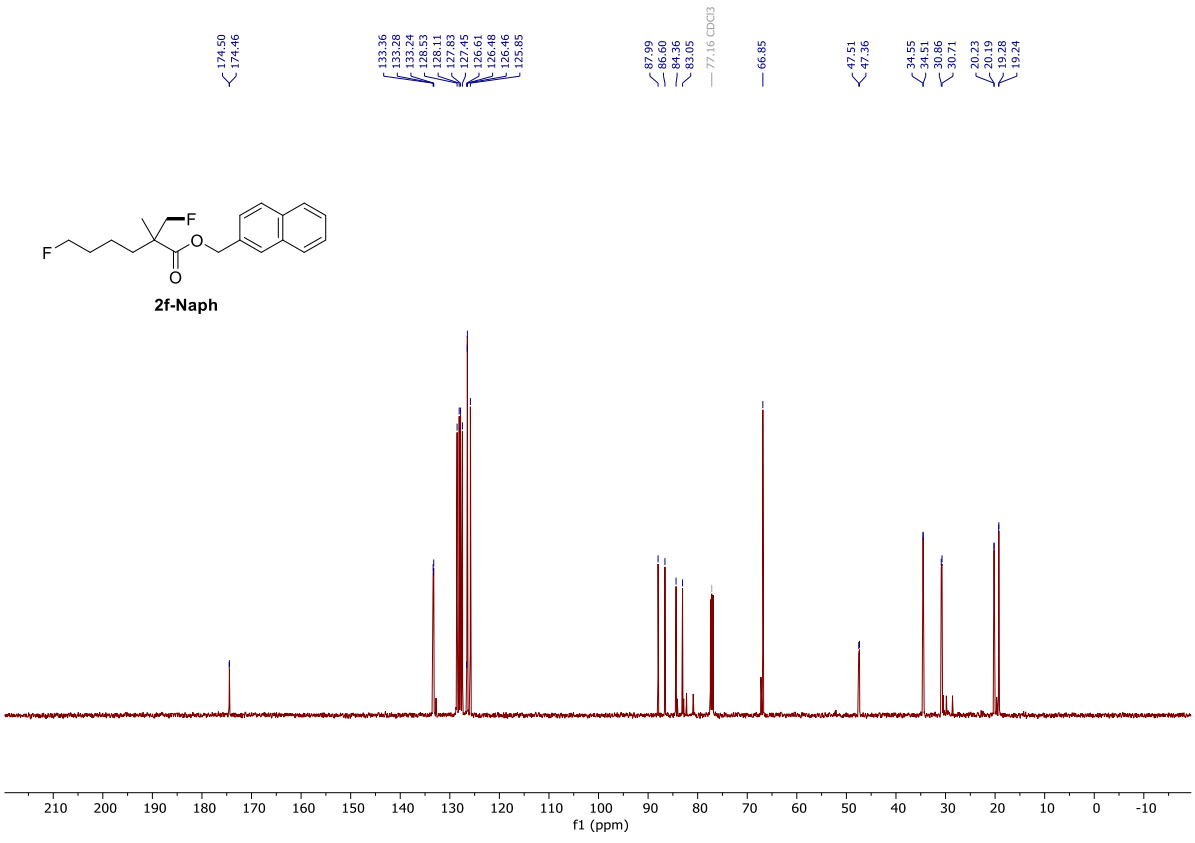
-225.59
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
f1 (ppm)

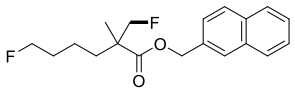

2e-Naph
Ha
Hb
Ha
Hb
f1 (ppm)
f1 (ppm)


2e-Naph
f1 (ppm)


-66.77
-225.74
F
F3C
O
O
2e-Naph
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
f1 (ppm)

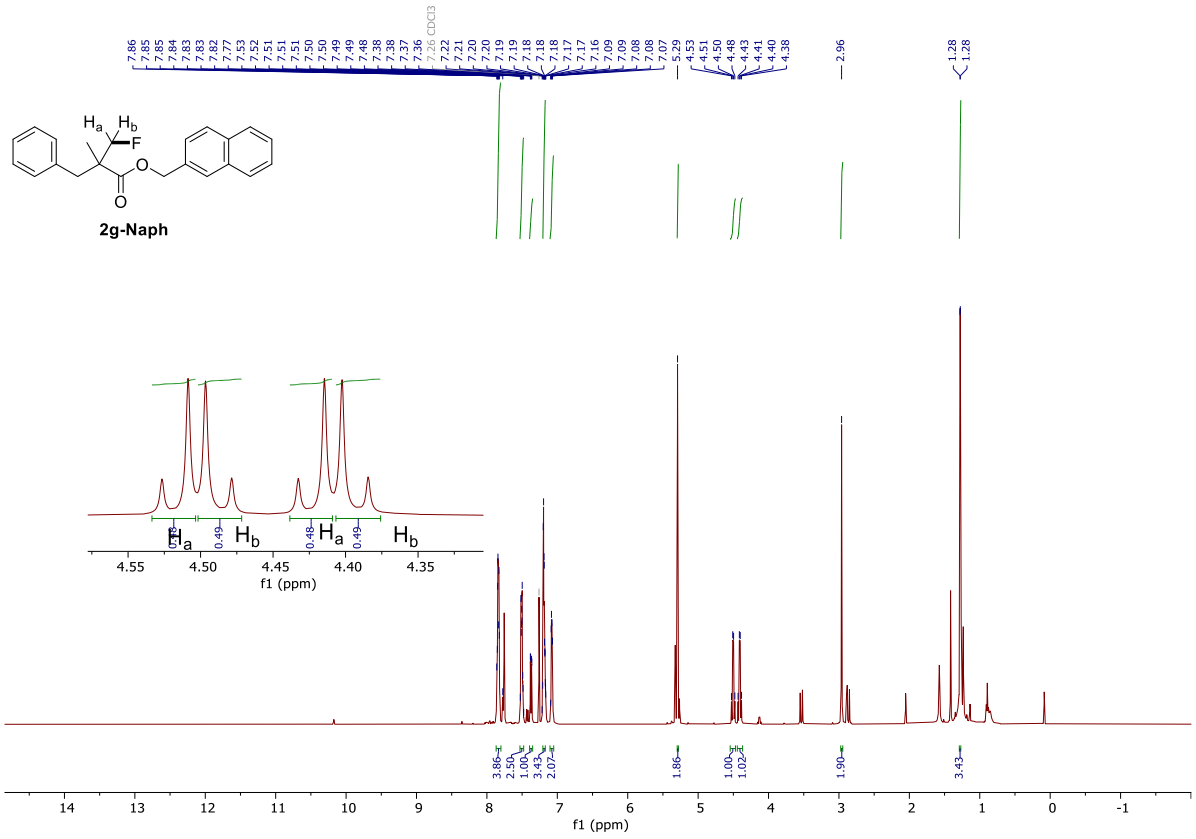

F
F
O
O
2f-Naph
f1 (ppm)

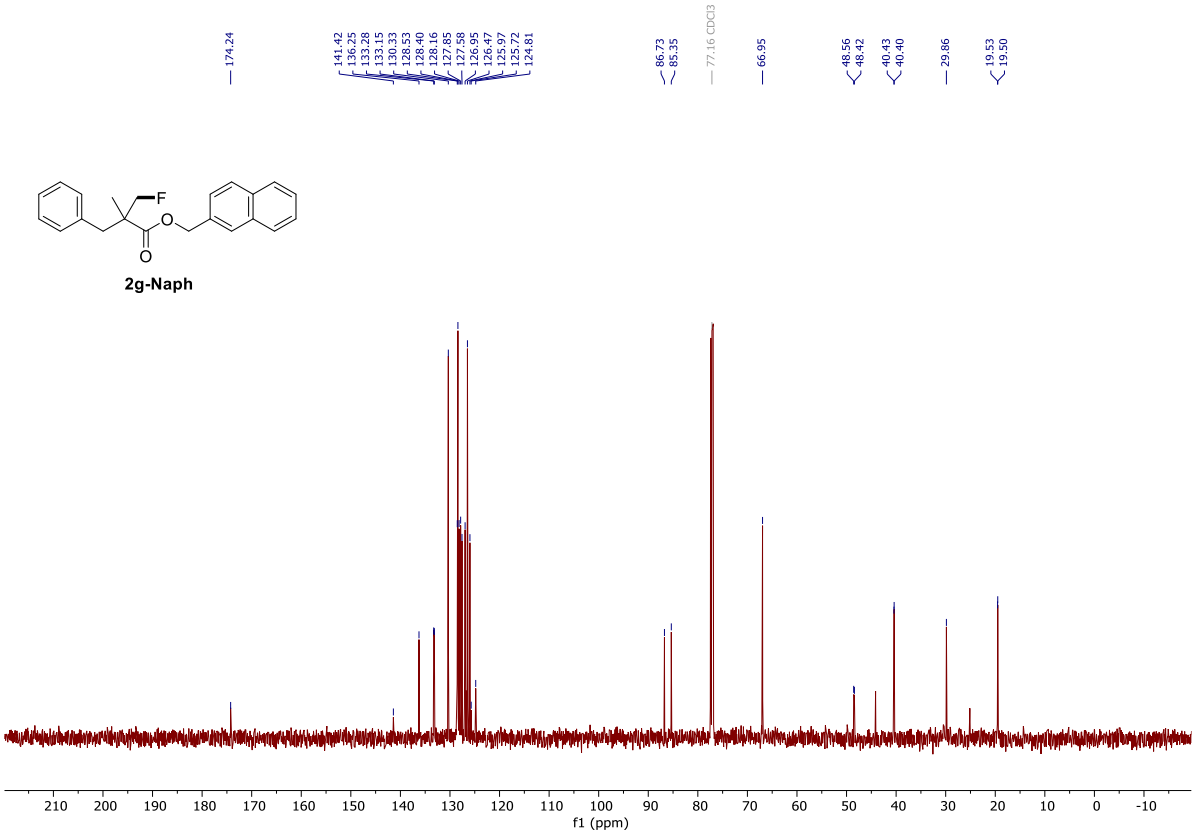

F
F
O
O
2f-Naph
f1 (ppm)

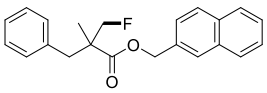

F
F
O
O

2f-Naph

-218.89
-225.69
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
f1 (ppm)

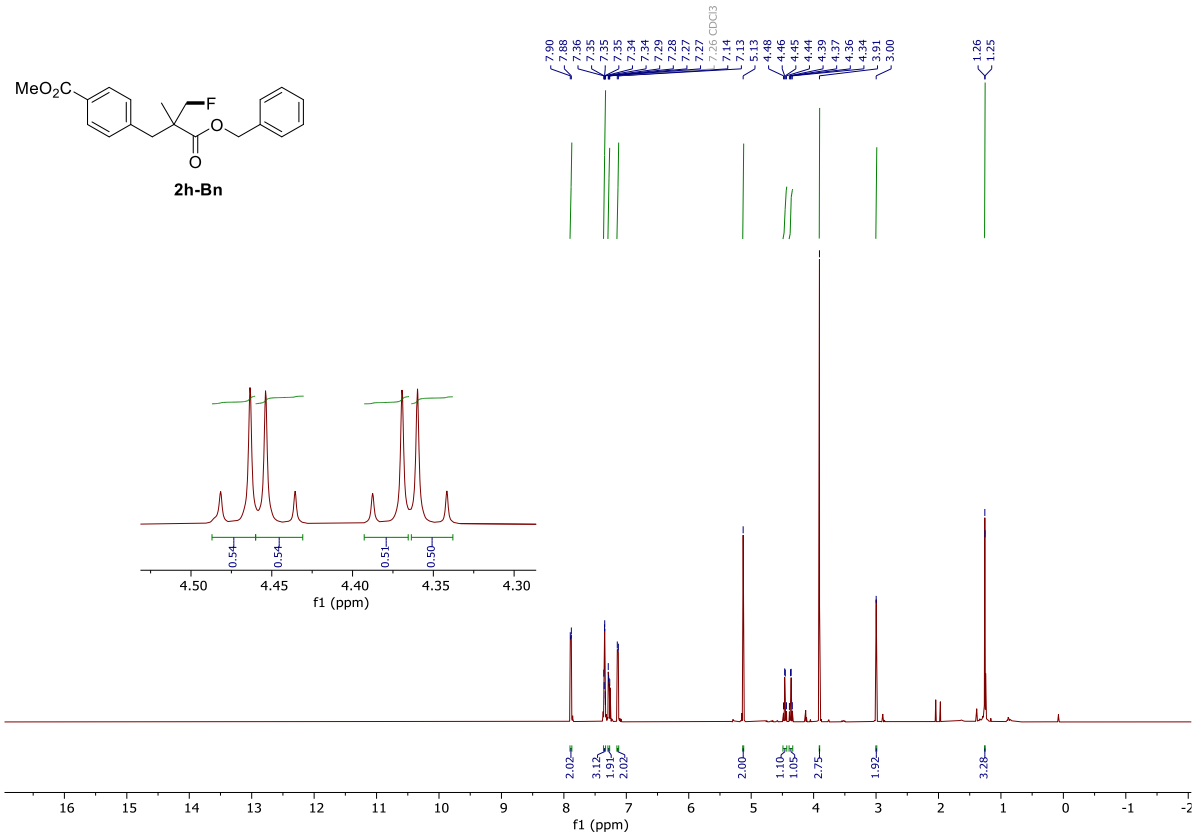

2g-Naph
Ha Hb
F
O
O
7.86 7.85 7.85 7.84 7.83 7.83 7.82 7.77 7.53 7.52 7.51 7.51 7.51 7.50 7.50 7.49 7.49 7.48 7.38 7.38 7.37 7.36 7.26 CDCl3 7.22 7.21 7.20 7.20 7.19 7.19 7.18 7.18 7.18 7.17 7.17 7.16 7.09 7.09 7.08 7.08 7.07 5.29 4.53 4.51 4.50 4.48 4.43 4.41 4.40 4.38 2.96 1.28 1.28
Ha Hb Ha Hb
0.49 0.48 0.49
4.55 4.50 4.45 4.40 4.35
f1 (ppm)
3.86 2.50 1.00 3.43 2.07 1.86 1.00 1.02 1.90 3.43
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

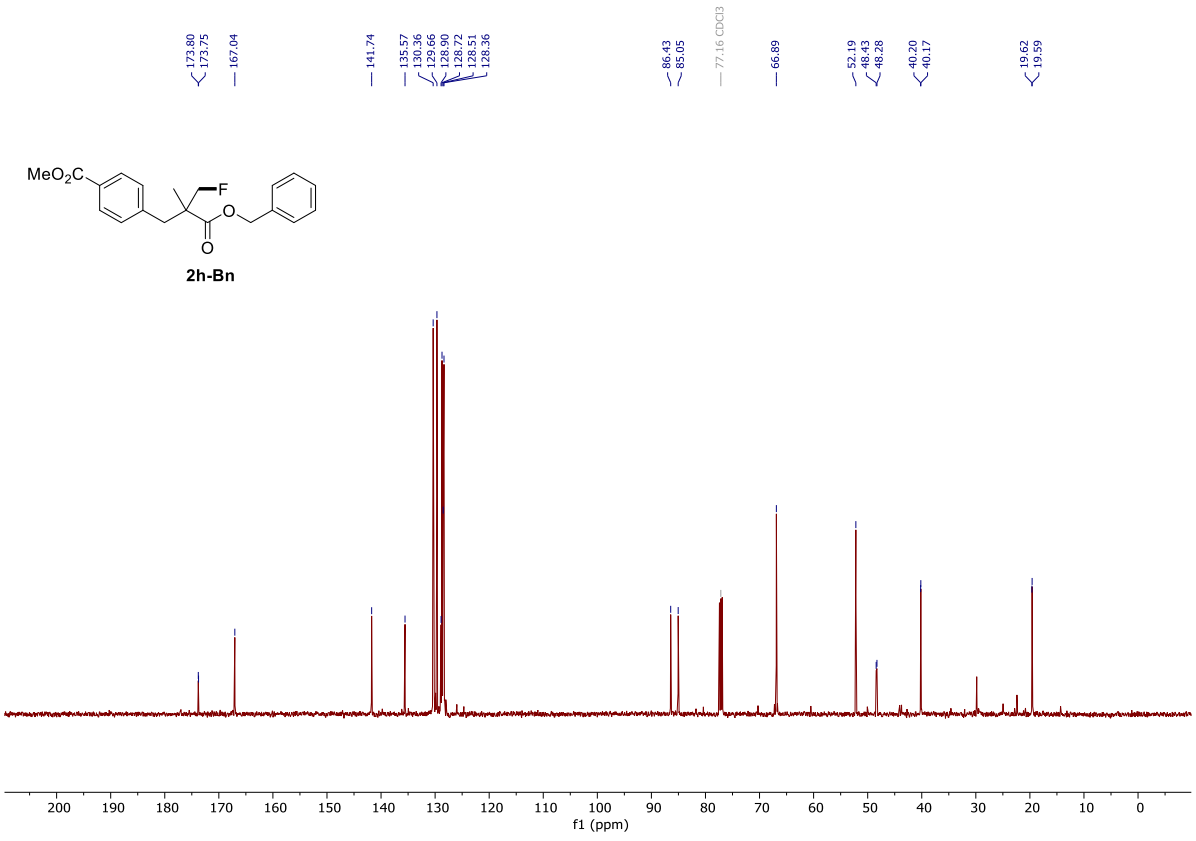

2g-Naph
F
O
O
174.24
141.42 136.25 133.28 133.15 130.33 128.53 128.40 128.16 127.85 127.58 126.95 126.47 125.97 125.72 124.81
86.73 85.35
77.16 CDCl3
66.95
48.56 48.42 40.43 40.40 29.86 19.53 19.50
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

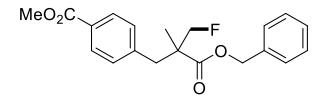

F
O
O

2g-Naph

-225.91
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
f1 (ppm)

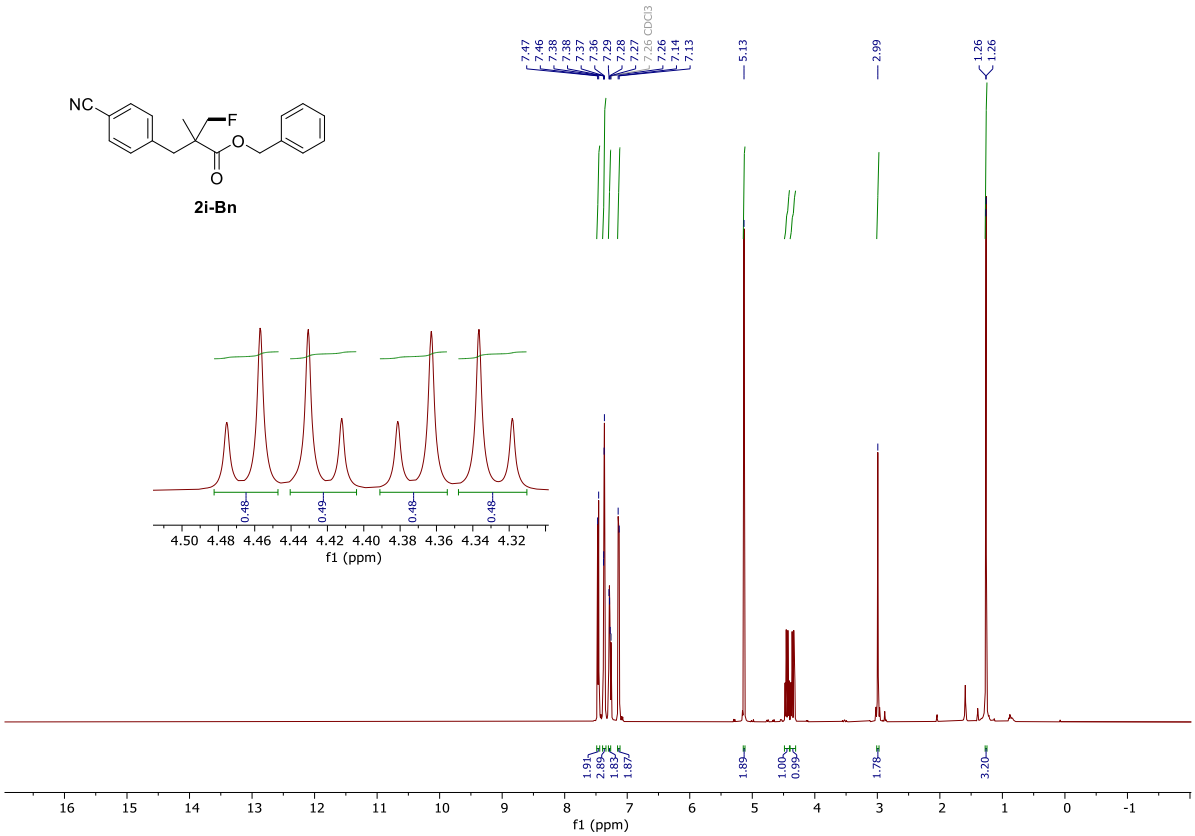

MeO2C
F
O
O
2h-Bn
7.90
7.88
7.36
7.35
7.35
7.35
7.34
7.34
7.29
7.28
7.27
7.27
7.26 CDCl3
7.14
7.13
5.13
4.48
4.46
4.45
4.44
4.39
4.37
4.36
4.34
3.91
3.00
1.26
1.25
0.54
0.54
0.51
0.50
4.50
4.45
4.40
4.35
4.30
f1 (ppm)
2.02
3.12
1.91
2.02
2.00
1.10
1.05
2.75
1.92
3.28
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

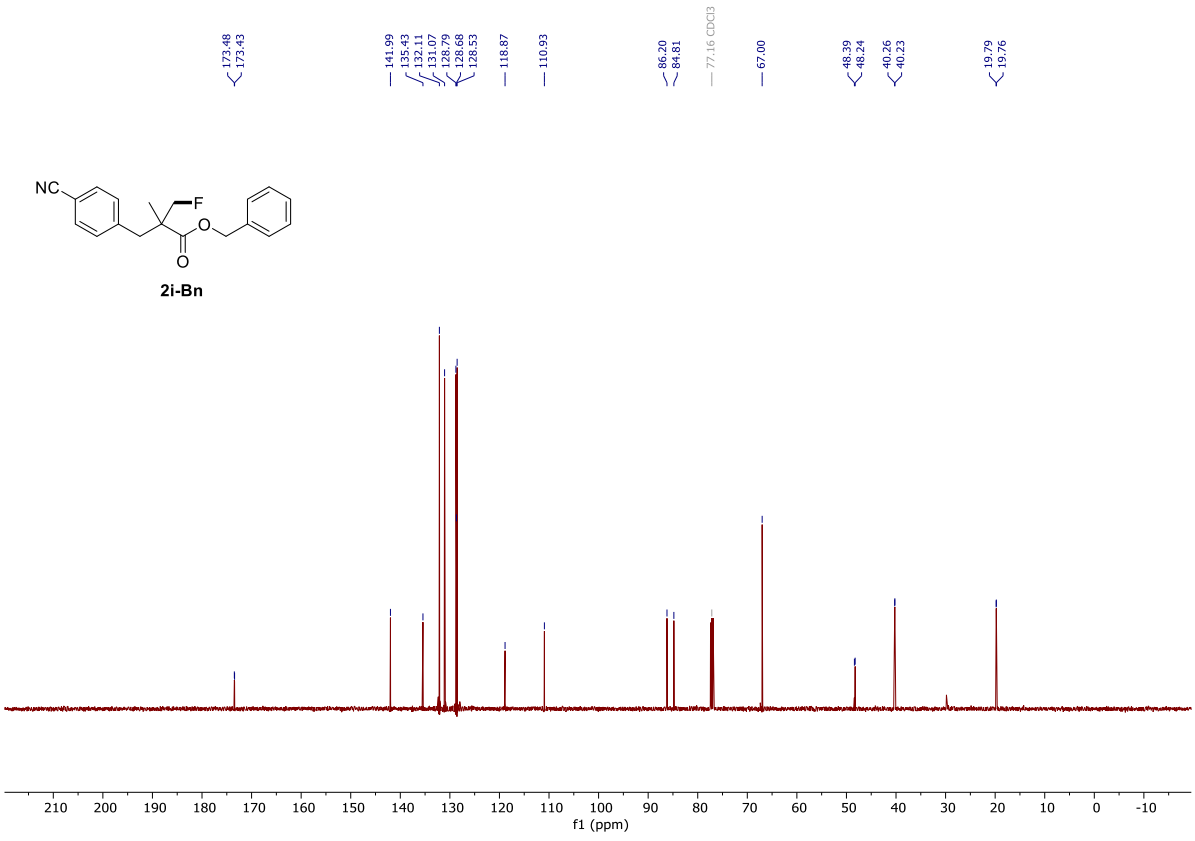

173.80
173.75
167.04
141.74
135.57
130.36
129.66
128.90
128.72
128.51
128.36
86.43
85.05
77.16 CDCl3
66.89
52.19
48.43
48.28
40.20
40.17
19.62
19.59
MeO2C
F
O
O
2h-Bn
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

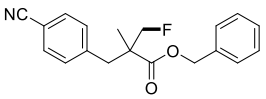

MeO2C
F
O
O

2h-Bn

-225.97
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
f1 (ppm)

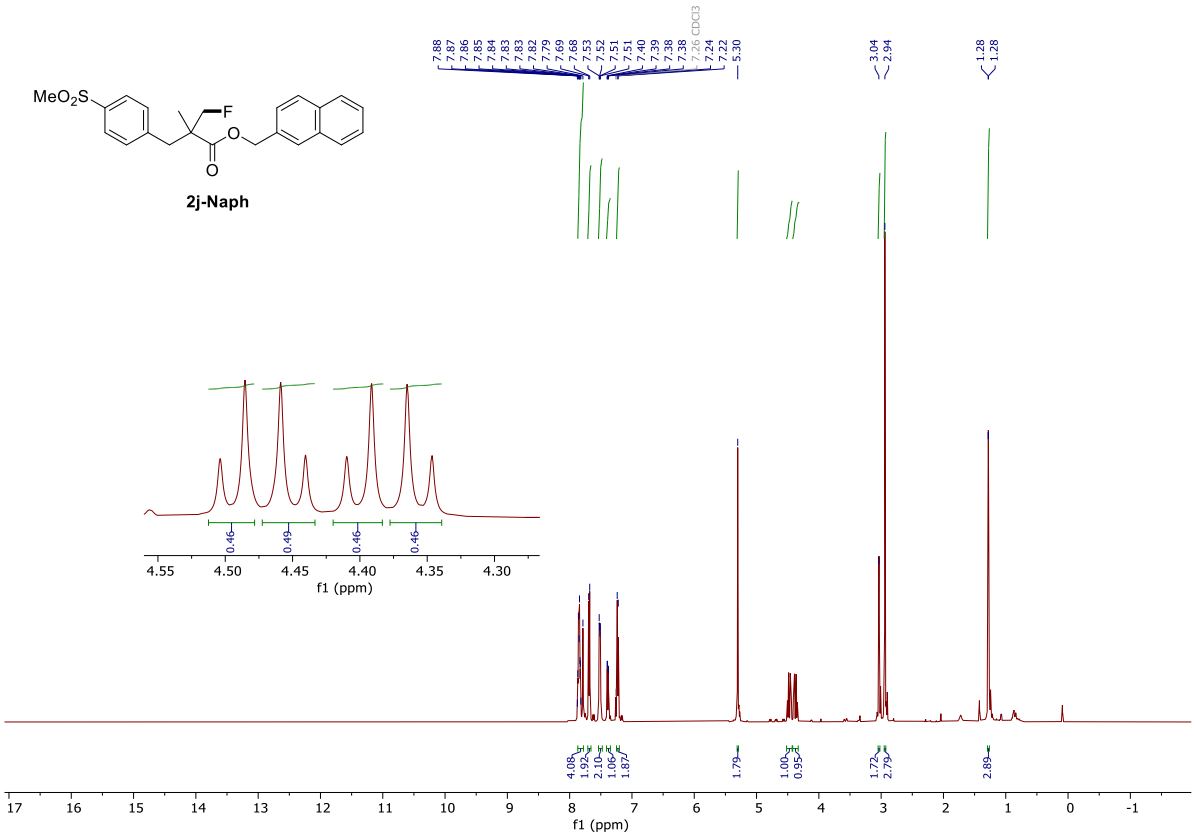

NC
F
O
O
2i-Bn
7.47
7.46
7.38
7.38
7.37
7.36
7.29
7.28
7.27
7.26 CDCl3
7.26
7.14
7.13
5.13
2.99
1.26
1.26
0.48
0.49
0.48
0.48
4.50 4.48 4.46 4.44 4.42 4.40 4.38 4.36 4.34 4.32
f1 (ppm)
1.91
2.89
1.83
1.87
1.89
1.00
0.99
1.78
3.20
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

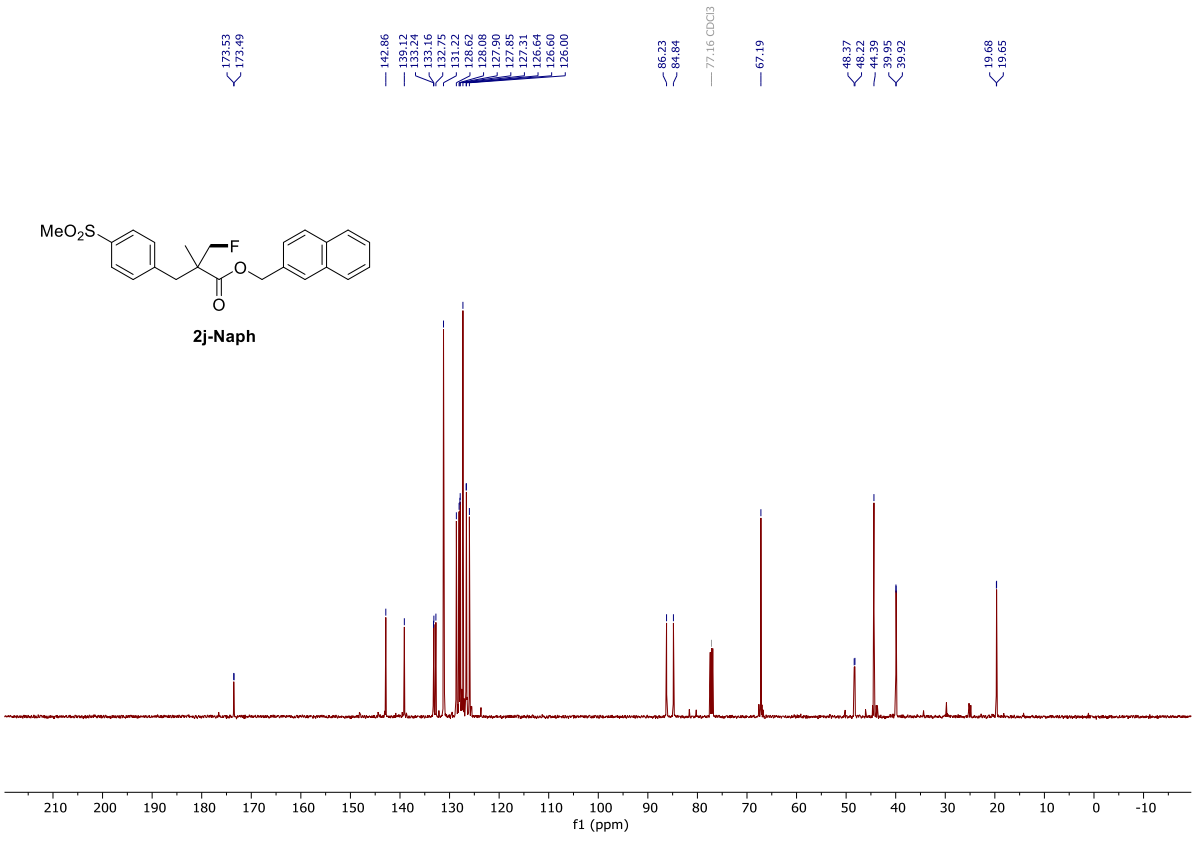

173.48
173.43
141.99
135.43
132.11
131.07
128.79
128.68
128.53
118.87
110.93
86.20
84.81
77.16 CDCl3
67.00
48.39
48.24
40.26
40.23
19.79
19.76
NC
F
O
O
2i-Bn
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

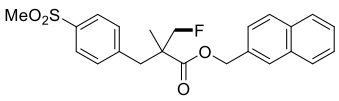

NC
F
O
O

2i-Bn

-226.22
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
f1 (ppm)

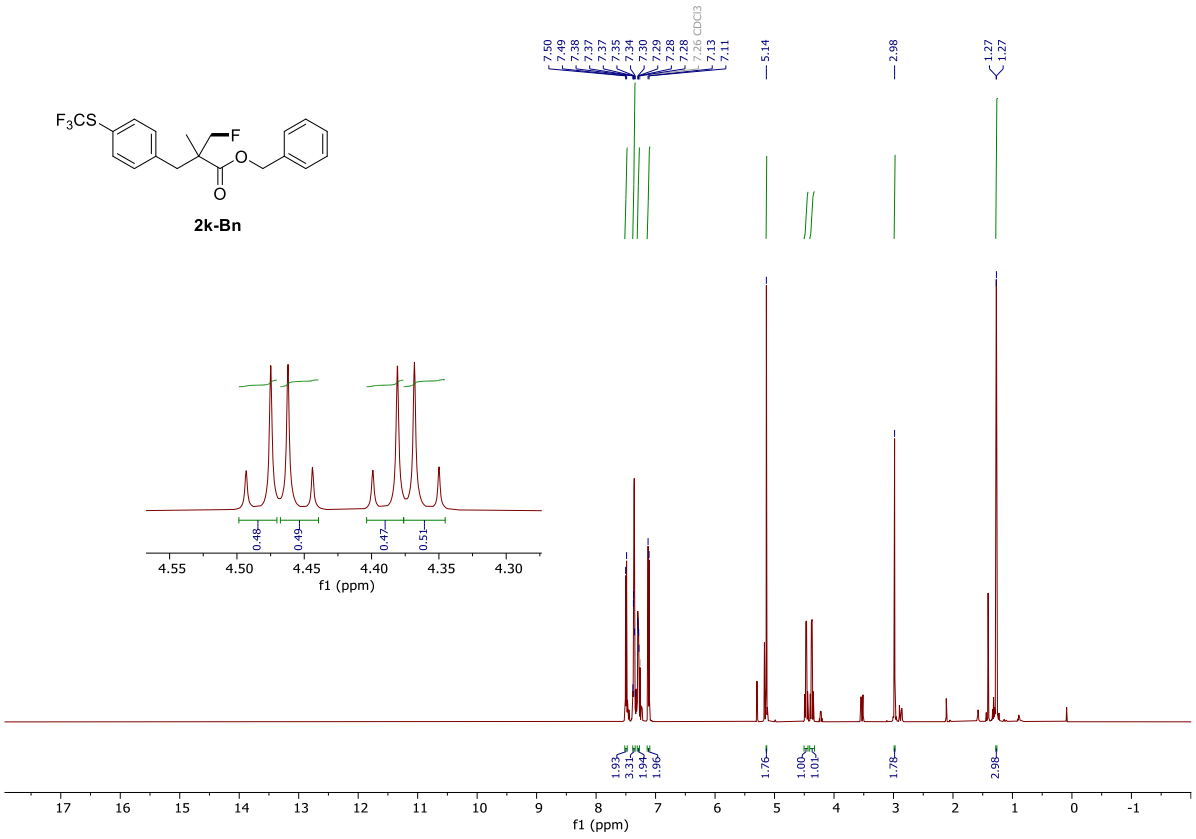

MeO2S
F
O
O
2j-Naph
7.88
7.87
7.86
7.85
7.84
7.83
7.82
7.79
7.69
7.68
7.53
7.52
7.51
7.51
7.40
7.39
7.38
7.38
7.26 CDCl3
7.24
7.22
5.30
3.04
2.94
1.28
1.28
0.46
0.49
0.46
0.46
4.55
4.50
4.45
4.40
4.35
4.30
f1 (ppm)
4.08
1.92
2.10
1.06
1.87
1.79
1.00
0.95
1.72
2.79
2.89
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

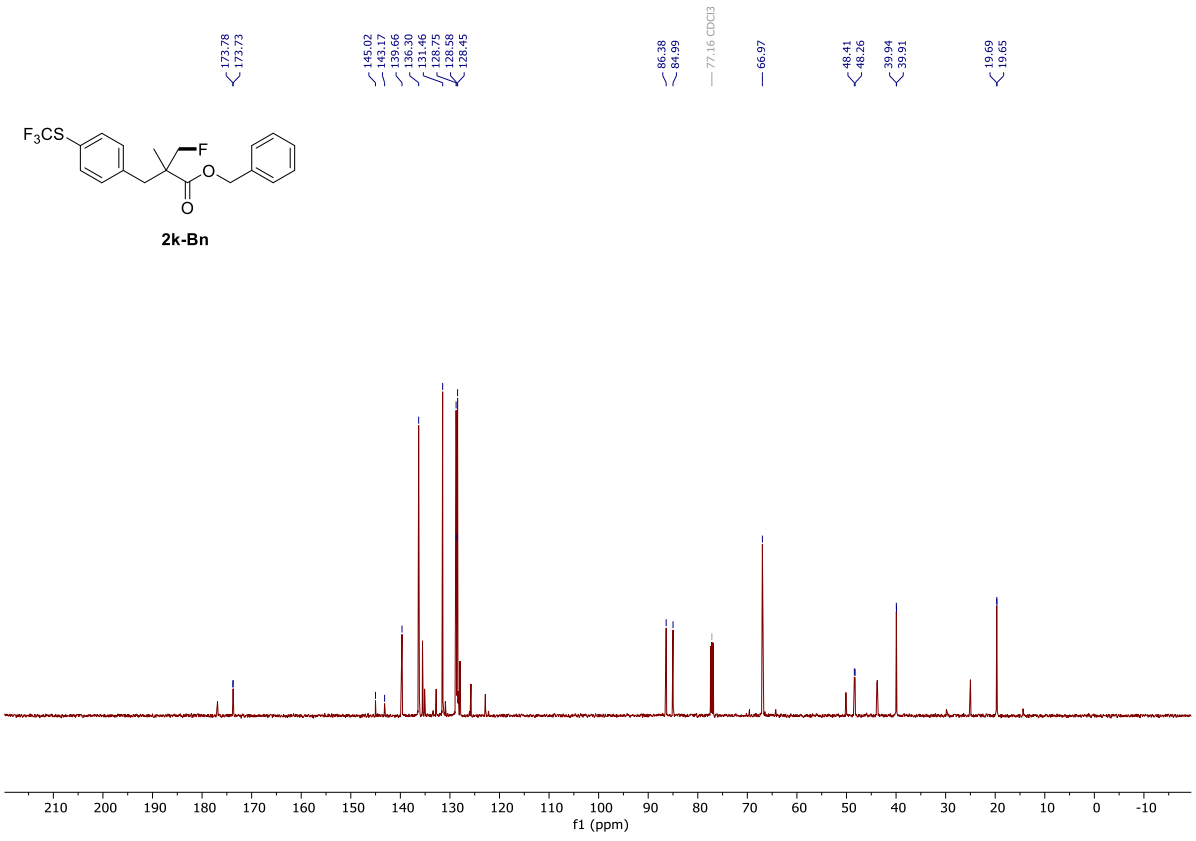

173.53
173.49
142.86
139.12
133.24
133.16
132.75
131.22
128.62
128.08
127.90
127.85
127.31
126.64
126.60
126.00
86.23
84.84
77.16 CDCl3
67.19
48.37
48.22
44.39
39.95
39.92
19.68
19.65
MeO2S
F
O
O
2j-Naph
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

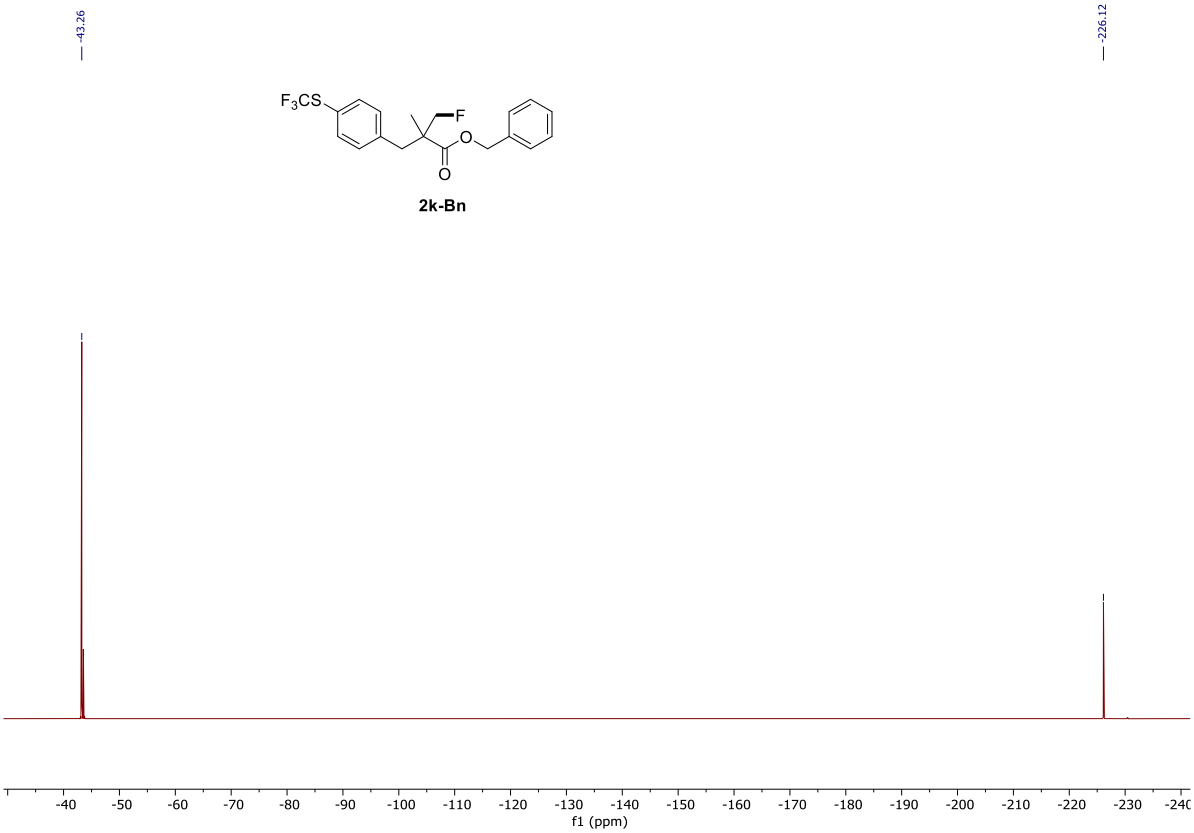

MeO2S
F
O
O

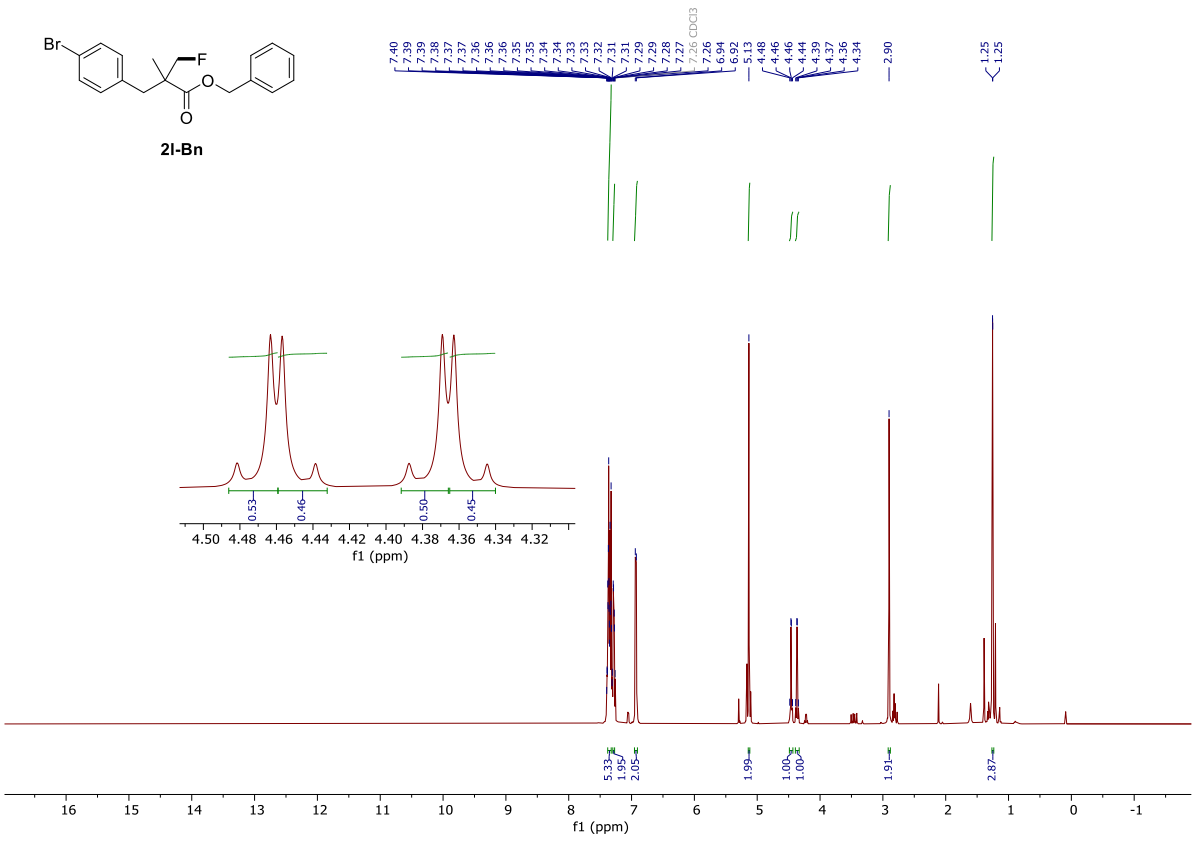
2j-Naph

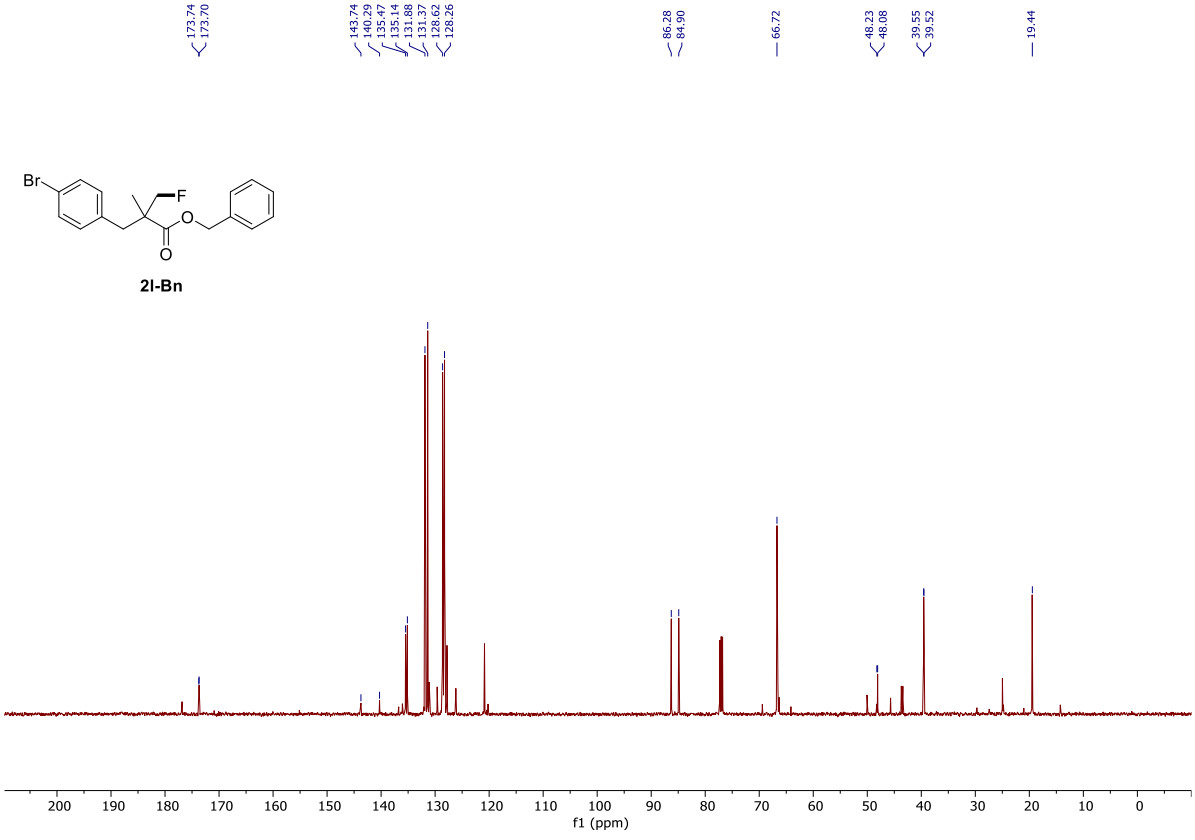
-225.86
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
f1 (ppm)

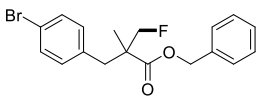

F3CS
F
O
O
2k-Bn
7.50
7.49
7.38
7.37
7.37
7.35
7.34
7.30
7.29
7.28
7.28
7.26 CDCl3
7.13
7.11
5.14
2.98
1.27
1.27
0.48
0.49
0.47
0.51
4.55
4.50
4.45
4.40
4.35
4.30
f1 (ppm)
1.93
3.31
1.94
1.96
1.76
1.00
1.01
1.78
2.98
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)


173.78
173.73
145.02
143.17
139.66
136.30
131.46
128.75
128.58
128.45
86.38
84.99
77.16 CDCl3
66.97
48.41
48.26
39.94
39.91
19.69
19.65
F3CS
F
O
O
2k-Bn
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


-43.26
-226.12
F3CS
F
O
O
2k-Bn
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
f1 (ppm)

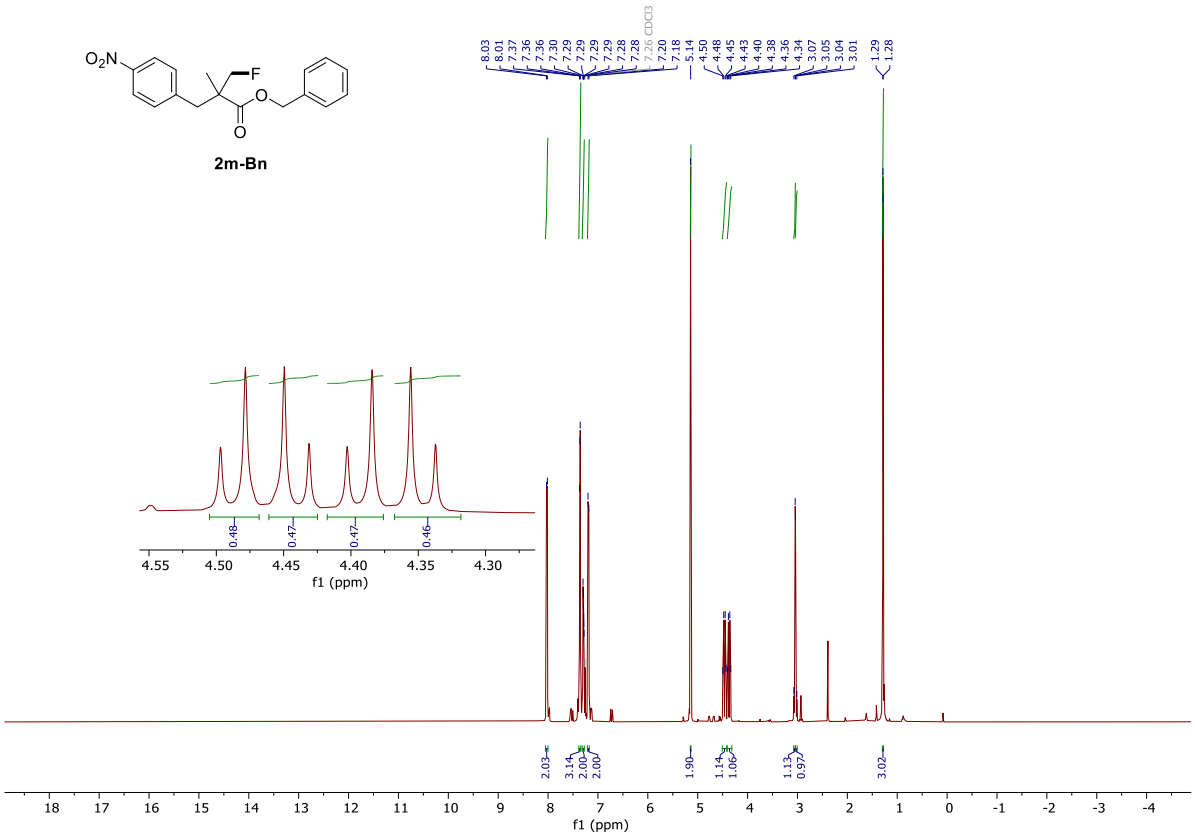

Br
F
O
O
2l-Bn
7.40 7.39 7.39 7.38 7.37 7.37 7.36 7.36 7.35 7.35 7.34 7.34 7.33 7.33 7.32 7.31 7.31 7.29 7.29 7.28 7.27 7.26 CDCl3 7.26 6.94 6.92 5.13 4.48 4.46 4.46 4.44 4.39 4.37 4.36 4.34 2.90 1.25 1.25
0.53 0.46 0.50 0.45
4.50 4.48 4.46 4.44 4.42 4.40 4.38 4.36 4.34 4.32
f1 (ppm)
5.33 1.95 2.05 1.99 1.00 1.00 1.91 2.87
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

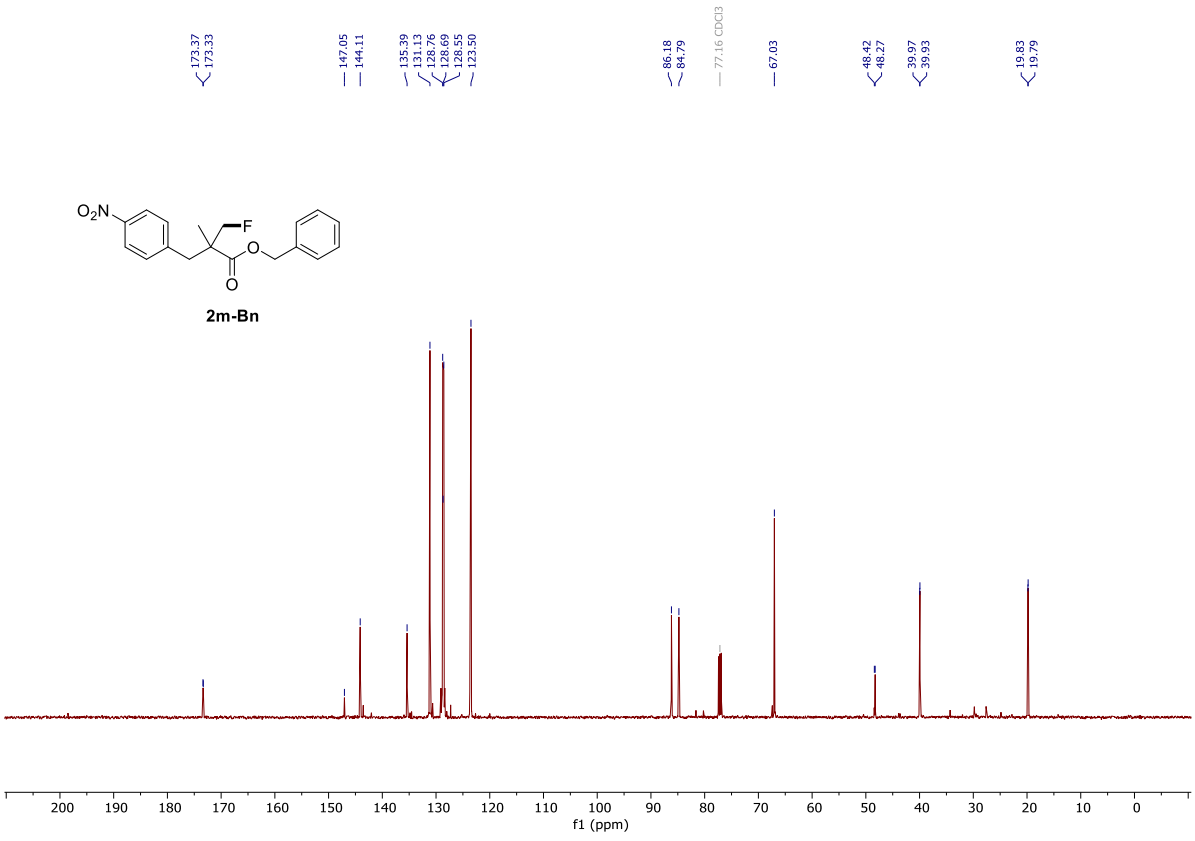

173.74 173.70 143.74 140.29 135.47 135.14 131.88 131.37 128.62 128.26 86.28 84.90 66.72 48.23 48.08 39.55 39.52 19.44
Br
F
O
O
2l-Bn
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

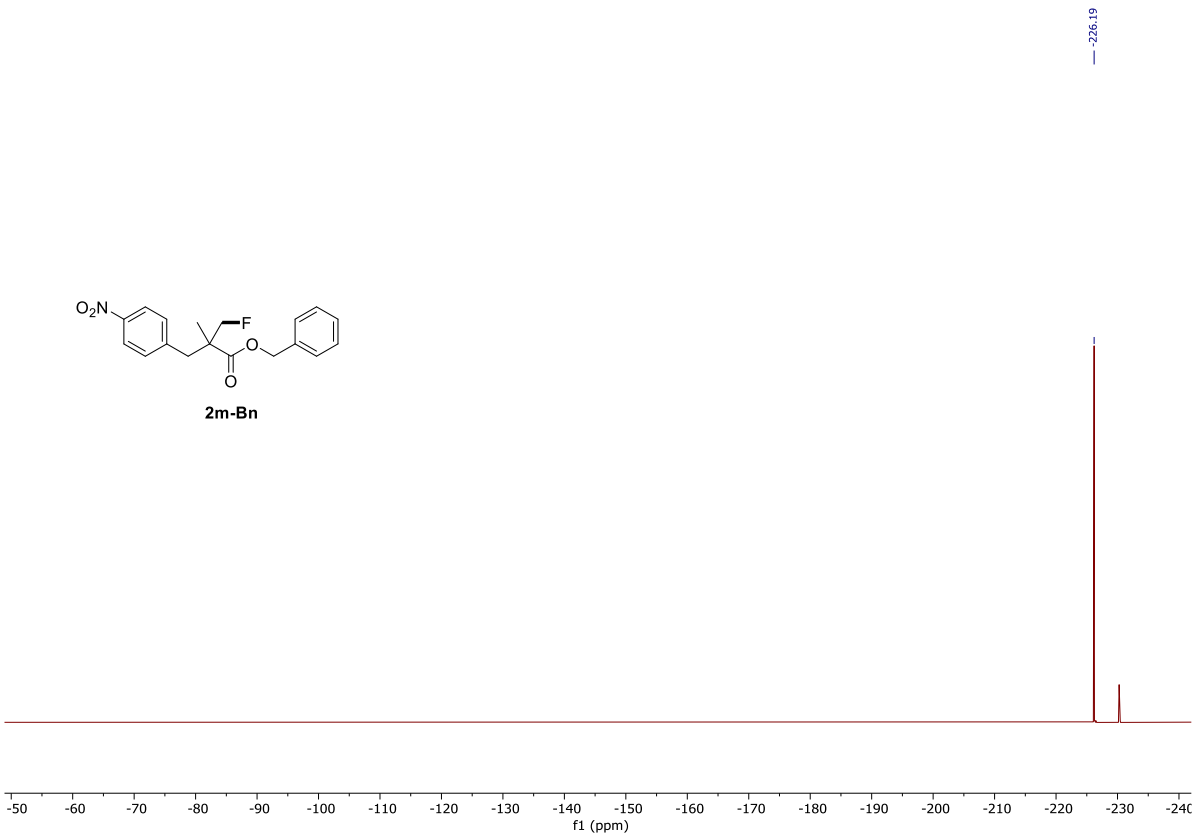

Br
F
O
O

2l-Bn

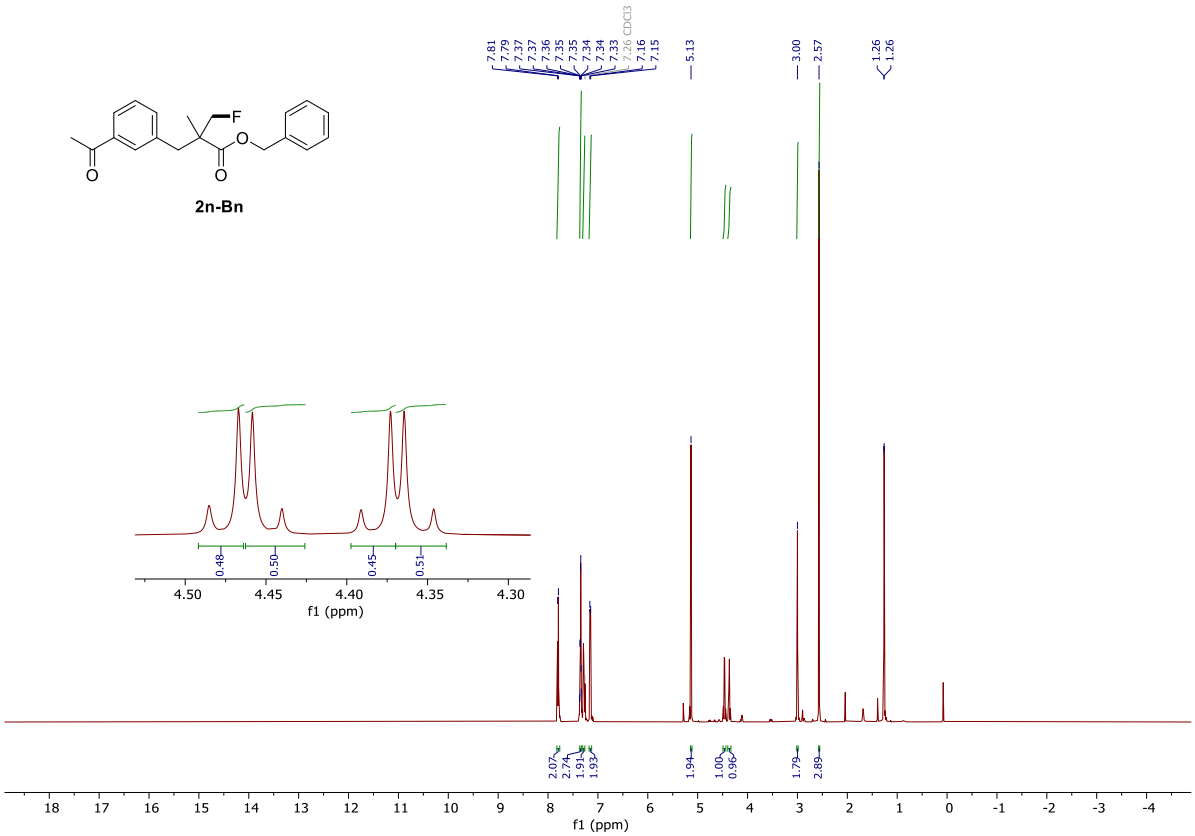
-226.19
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
f1 (ppm)

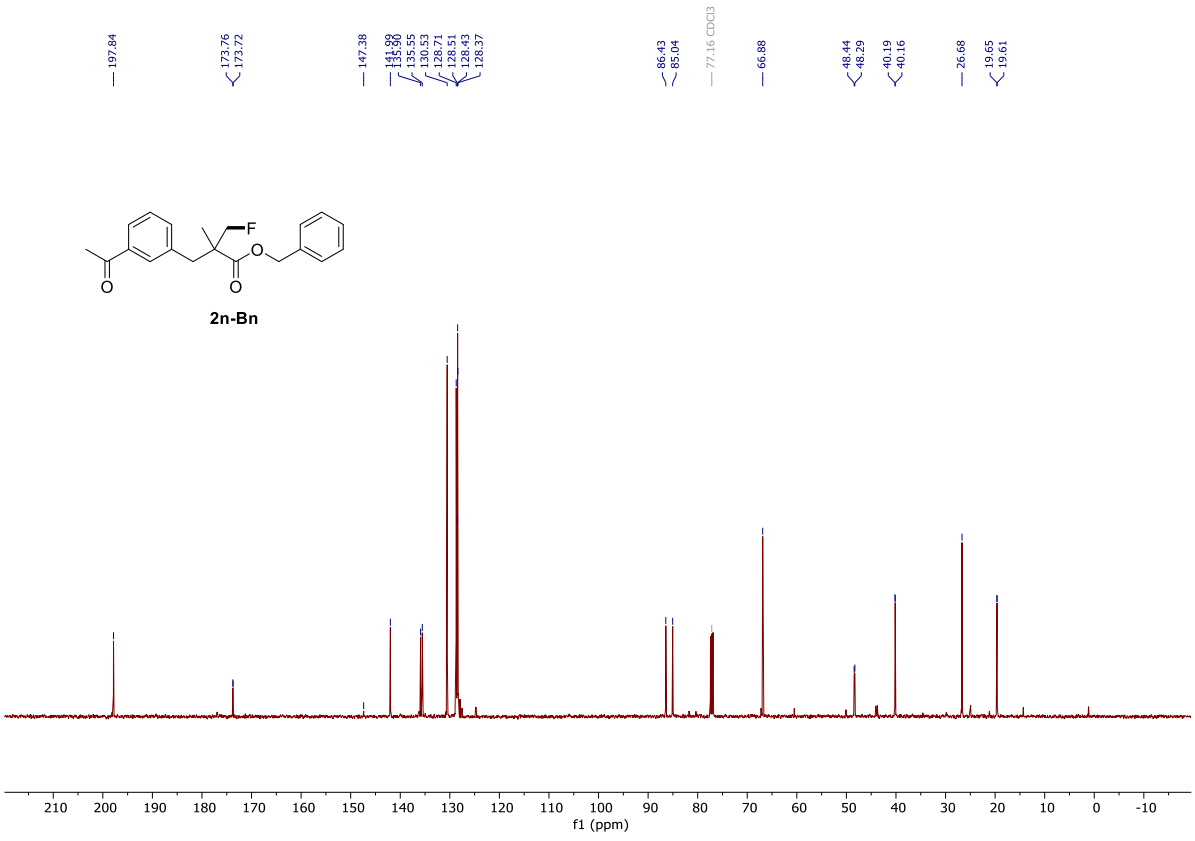

2m-Bn
f1 (ppm)

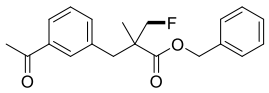

2m-Bn
f1 (ppm)


-226.19
O2N
F
O
O
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
f1 (ppm)

2m-Bn

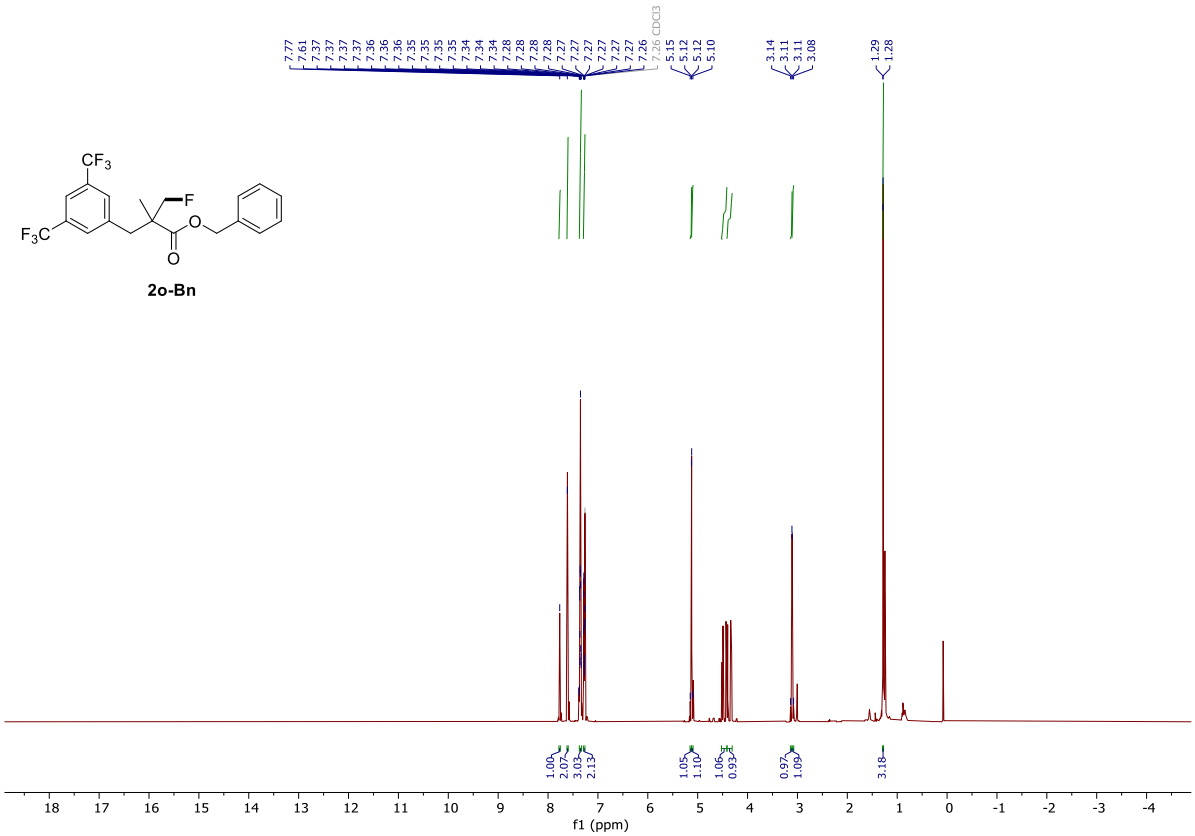

2n-Bn
7.81
7.79
7.37
7.36
7.35
7.35
7.34
7.34
7.33
7.26 CDCl3
7.16
7.15
5.13
3.00
2.57
1.26
1.26
0.48
0.50
0.45
0.51
4.50
4.45
4.40
4.35
4.30
f1 (ppm)
2.07
2.74
1.91
1.93
1.94
1.00
0.96
1.79
2.89
f1 (ppm)


197.84
173.76
173.72
147.38
141.99
135.90
135.55
130.53
128.71
128.51
128.43
128.37
86.43
85.04
77.16 CDCl3
66.88
48.44
48.29
40.19
40.16
26.68
19.65
19.61
2n-Bn
f1 (ppm)


F
O
O

2n-Bn

-226.00
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
f1 (ppm)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7.37
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7.36
7.36
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7.35
7.35
7.35
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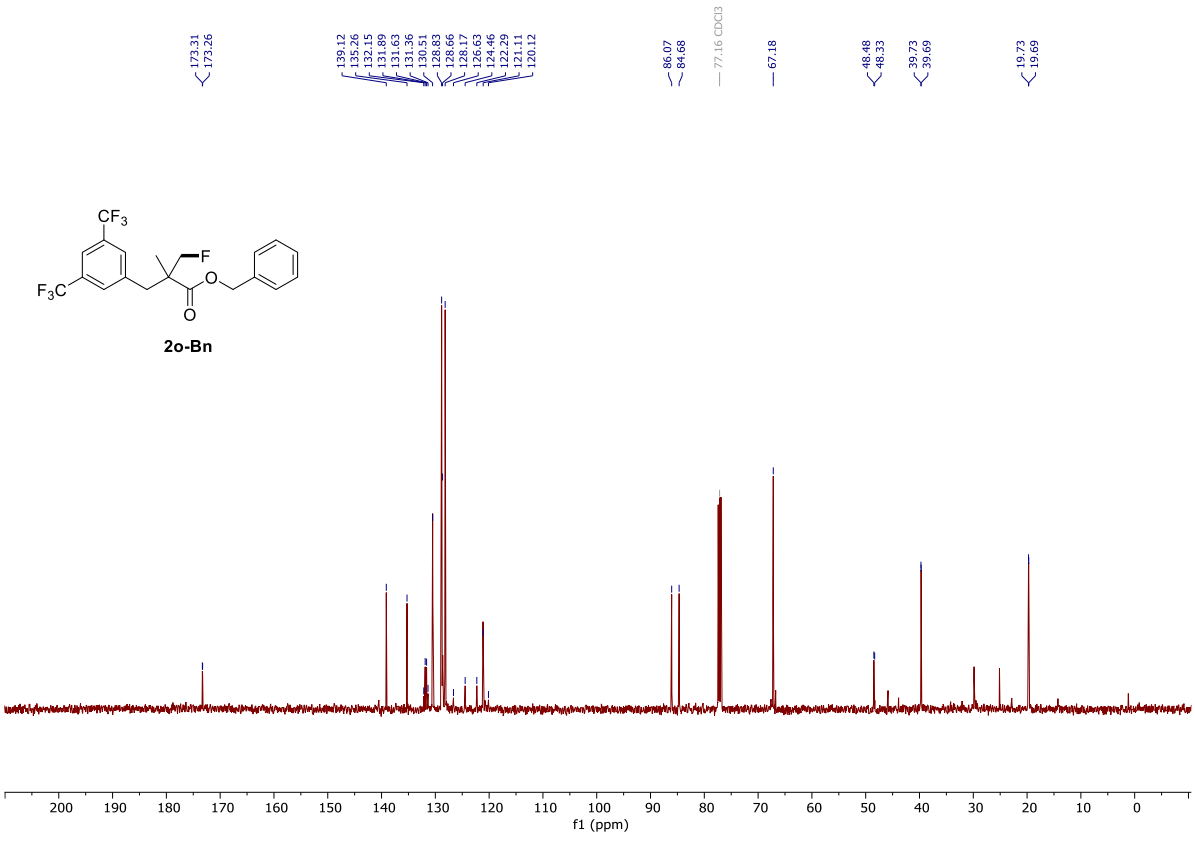
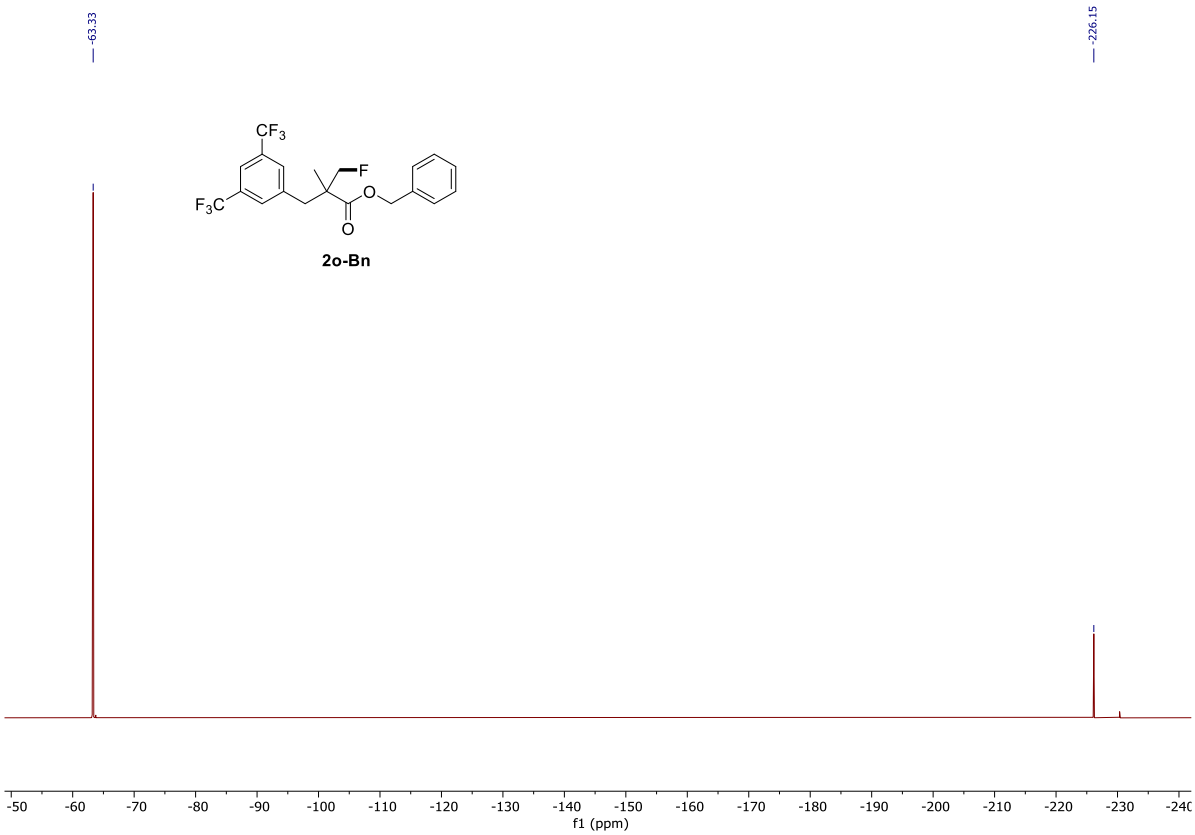
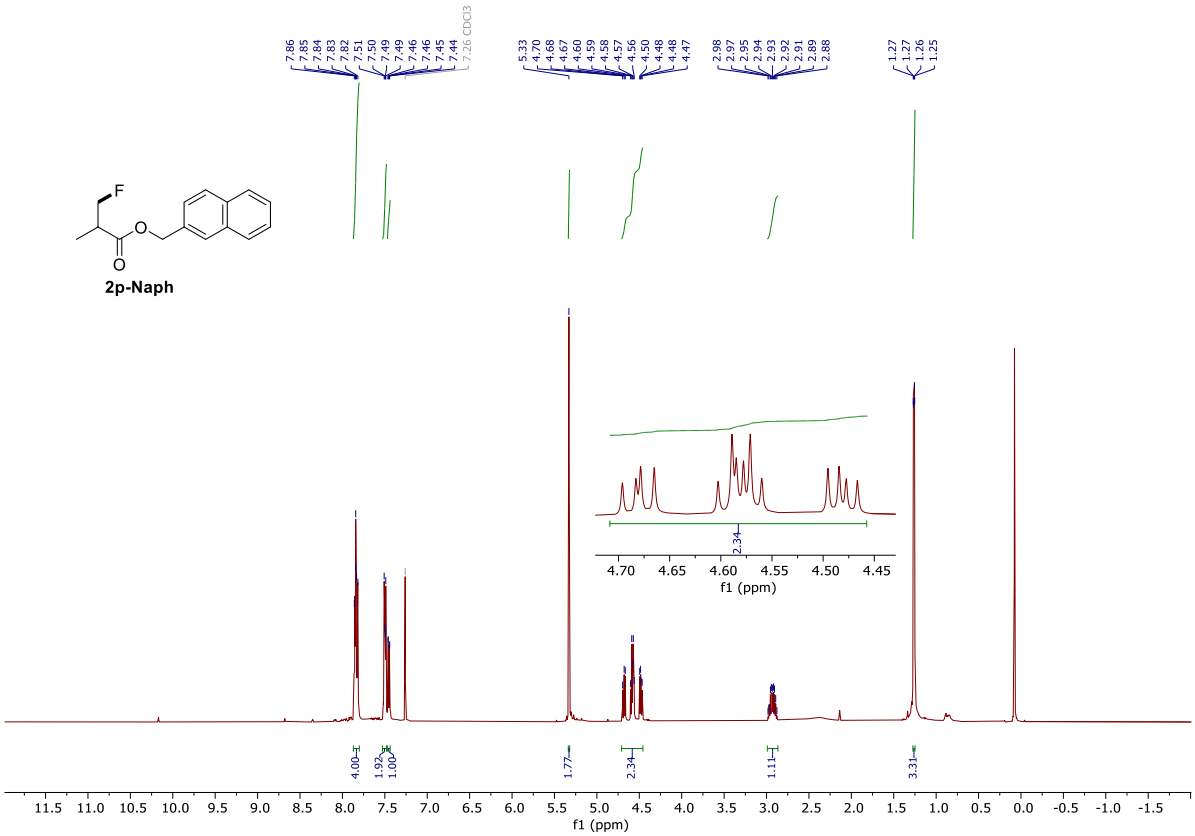
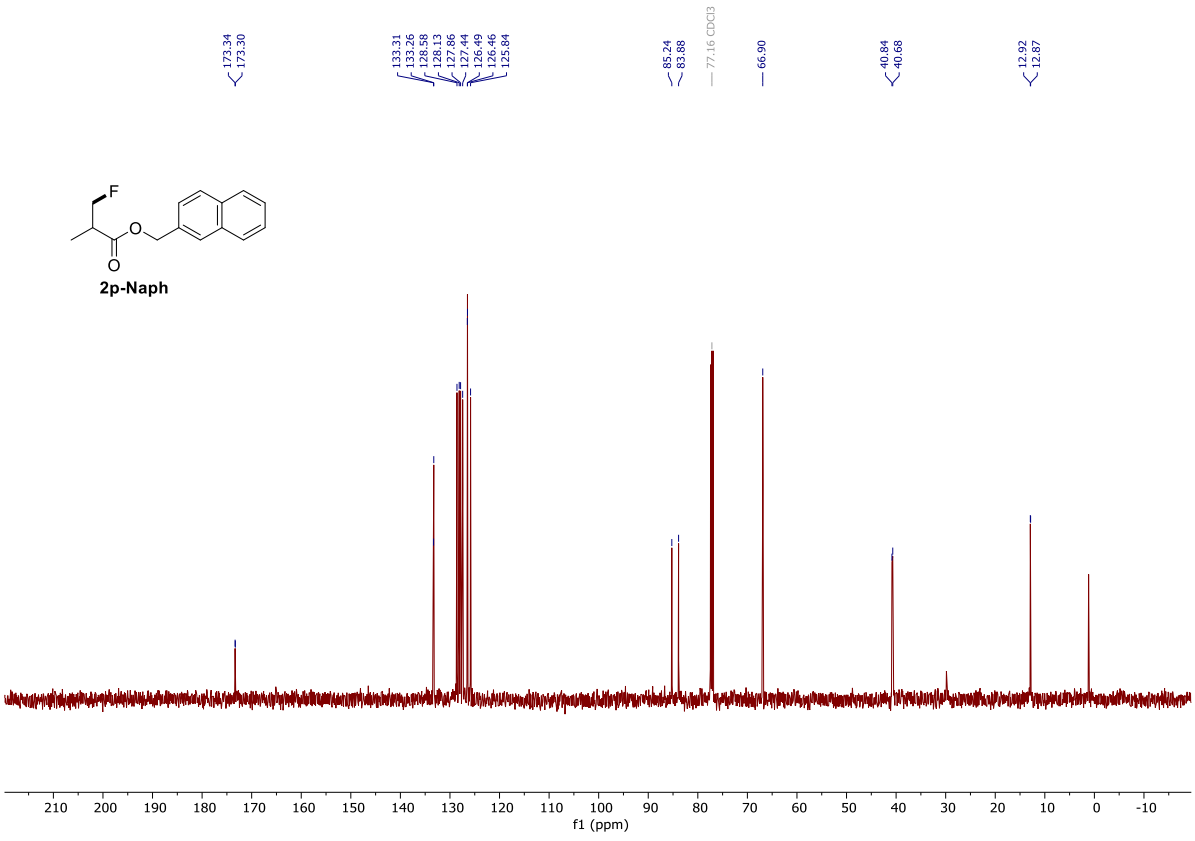
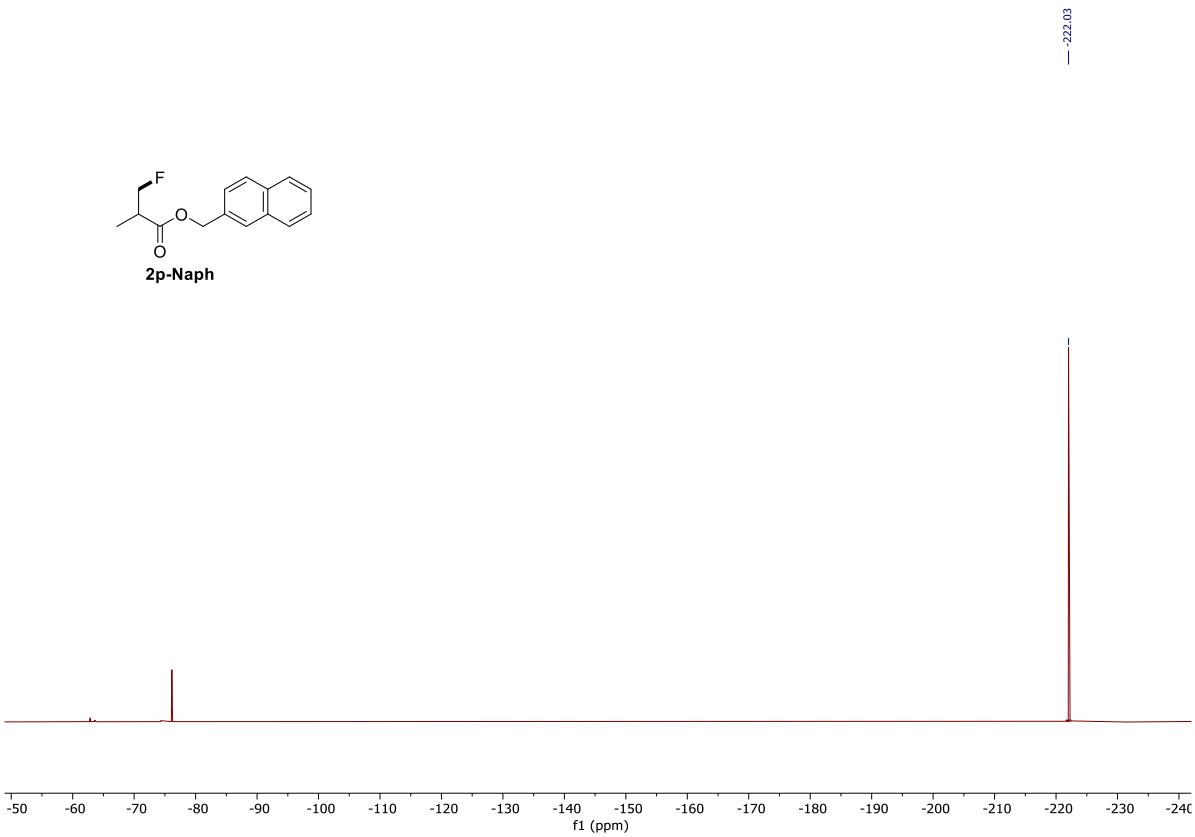
7.34
7.34
7.34
7.28
7.28
7.28
7.28
7.27
7.27
7.27
7.27
7.27
7.27
7.26
7.26 CDCl3
5.15
5.12
5.12
5.10
3.14
3.11
3.11
3.08
1.29
1.28
CF3
F
F3C
O
O
2o-Bn
1.00
2.07
3.03
2.13
1.05
1.10
1.06
0.93
0.97
1.09
3.18
18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

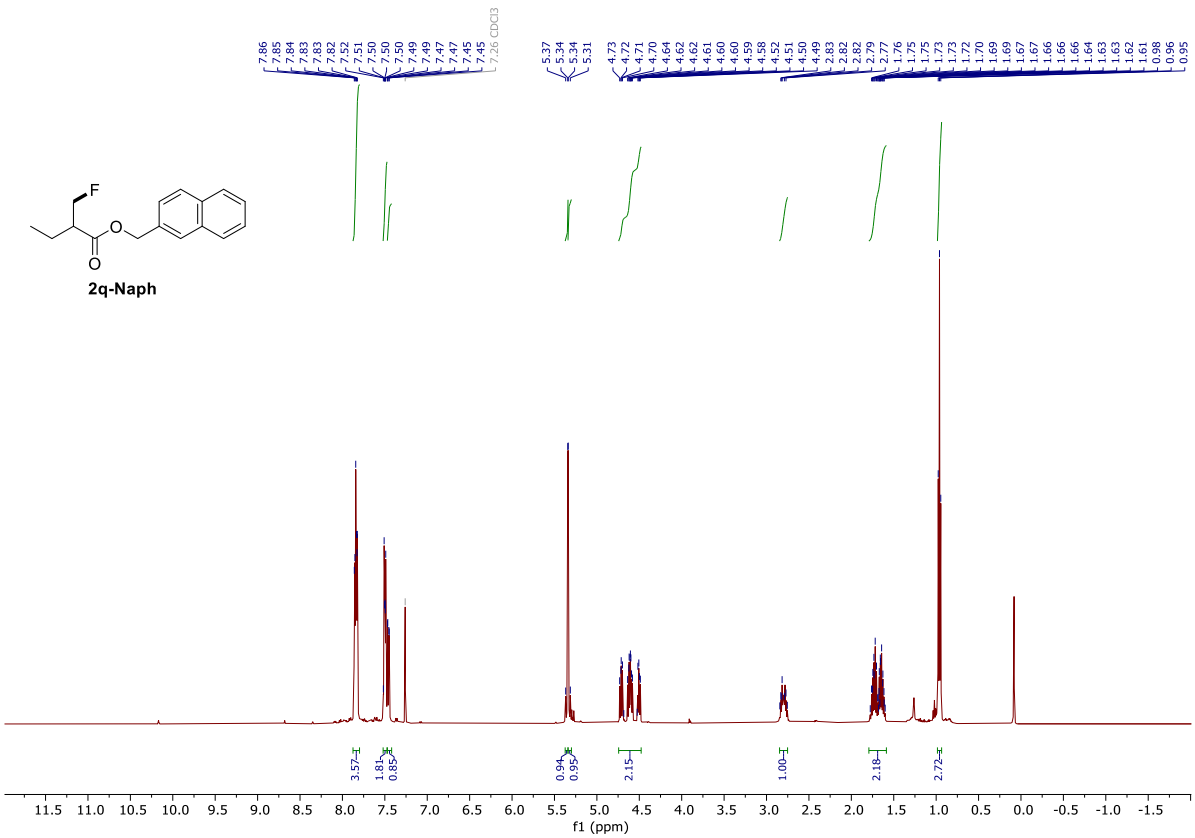

173.31
173.26
139.12
135.26
132.15
131.89
131.63
131.36
130.51
128.83
128.66
128.17
126.63
124.46
122.29
121.11
120.12
86.07
84.68
77.16 CDCl3
67.18
48.48
48.33
39.73
39.69
19.73
19.69
CF3
F
F3C
O
O
2o-Bn
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

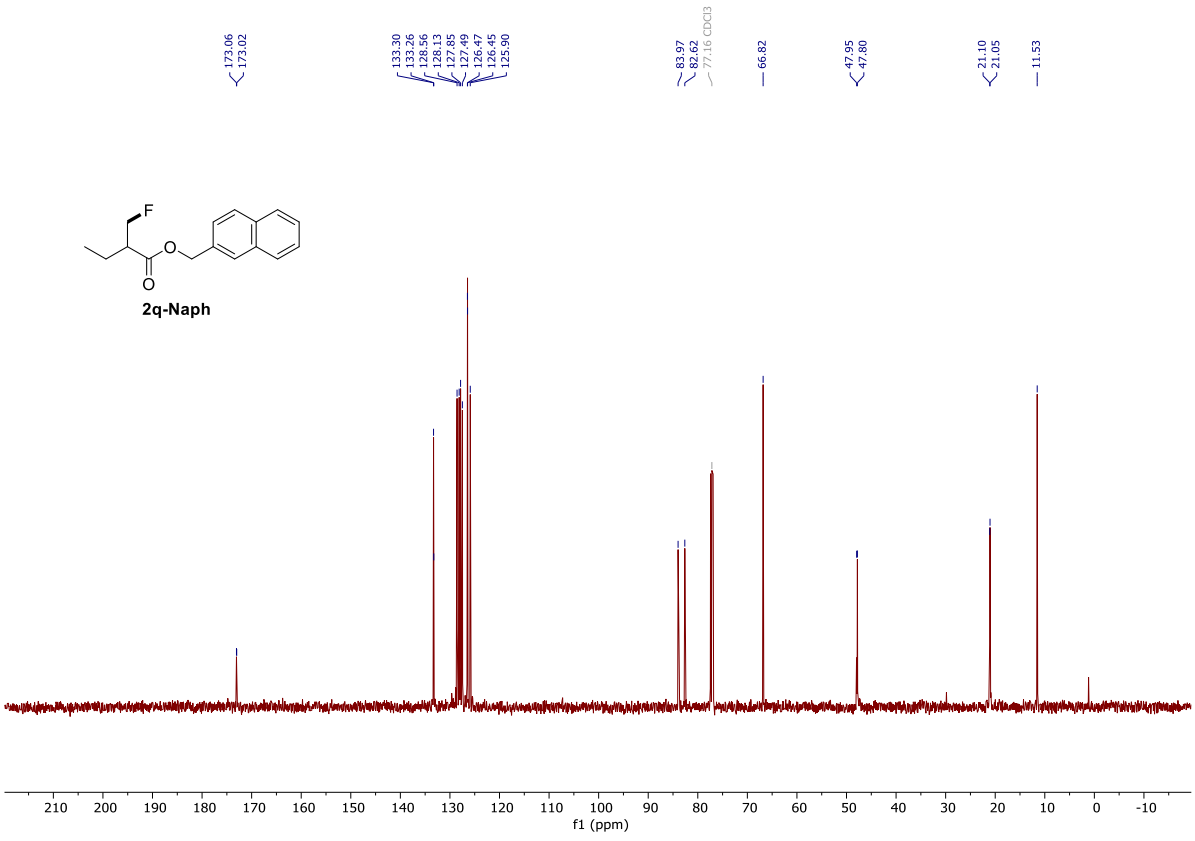

-63.33
-226.15
CF3
F
F3C
O
O
2o-Bn
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
f1 (ppm)

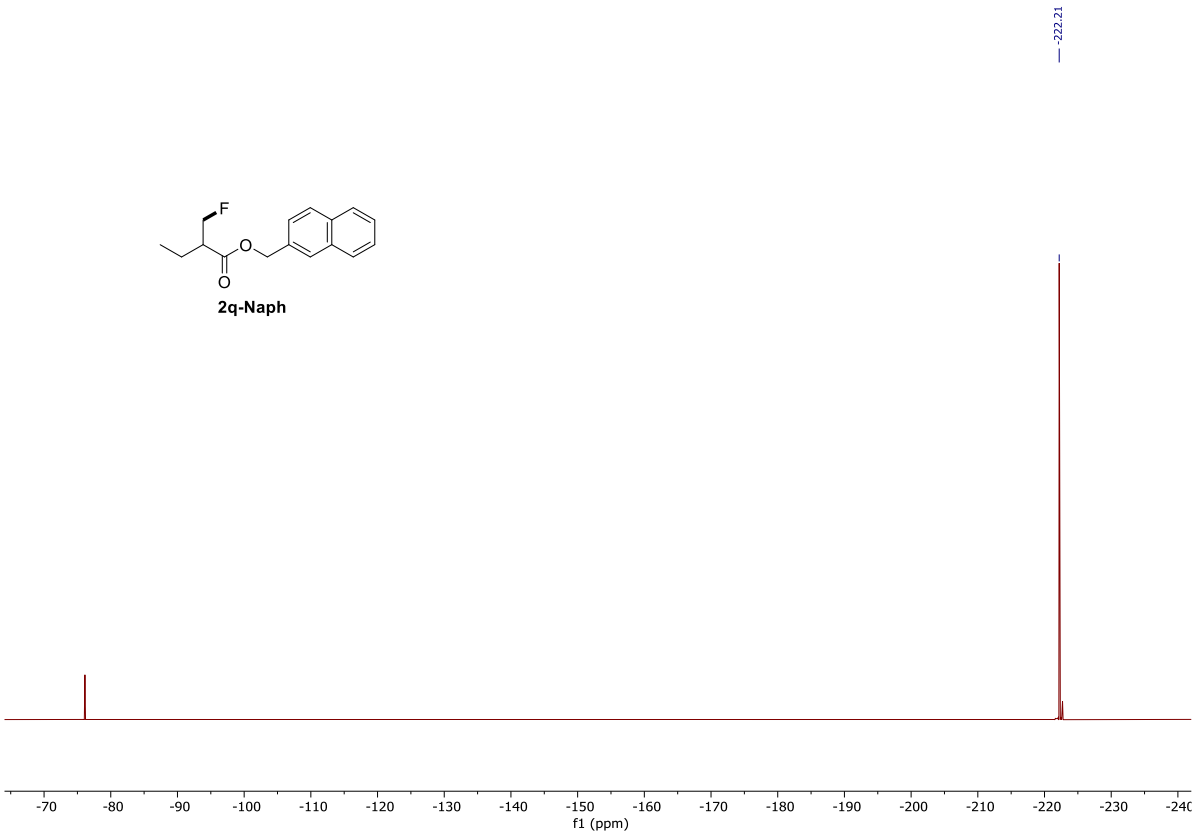

7.86
7.85
7.84
7.83
7.82
7.51
7.50
7.49
7.49
7.46
7.46
7.45
7.44
7.26 CDCl3
5.33
4.70
4.68
4.67
4.60
4.59
4.58
4.57
4.56
4.50
4.48
4.48
4.47
2.98
2.97
2.95
2.94
2.93
2.92
2.91
2.89
2.88
1.27
1.27
1.26
1.25
F
O
O
2p-Naph
2.34
4.70 4.65 4.60 4.55 4.50 4.45
f1 (ppm)
4.00
1.92
1.00
1.77
2.34
1.11
3.31
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

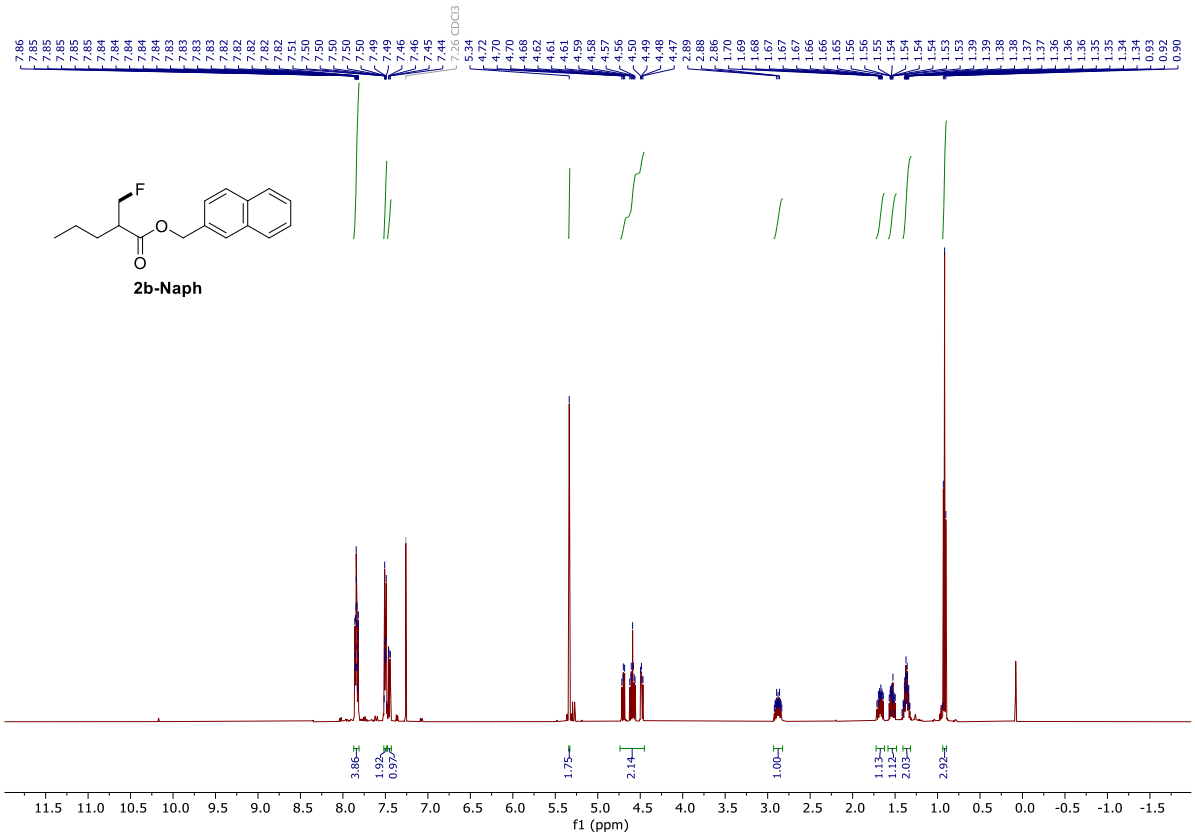

173.34
173.30
133.31
133.26
128.58
128.13
127.86
127.44
126.49
126.46
125.84
85.24
83.88
77.16 CDCl3
66.90
40.84
40.68
12.92
12.87
F
O
O
2p-Naph
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

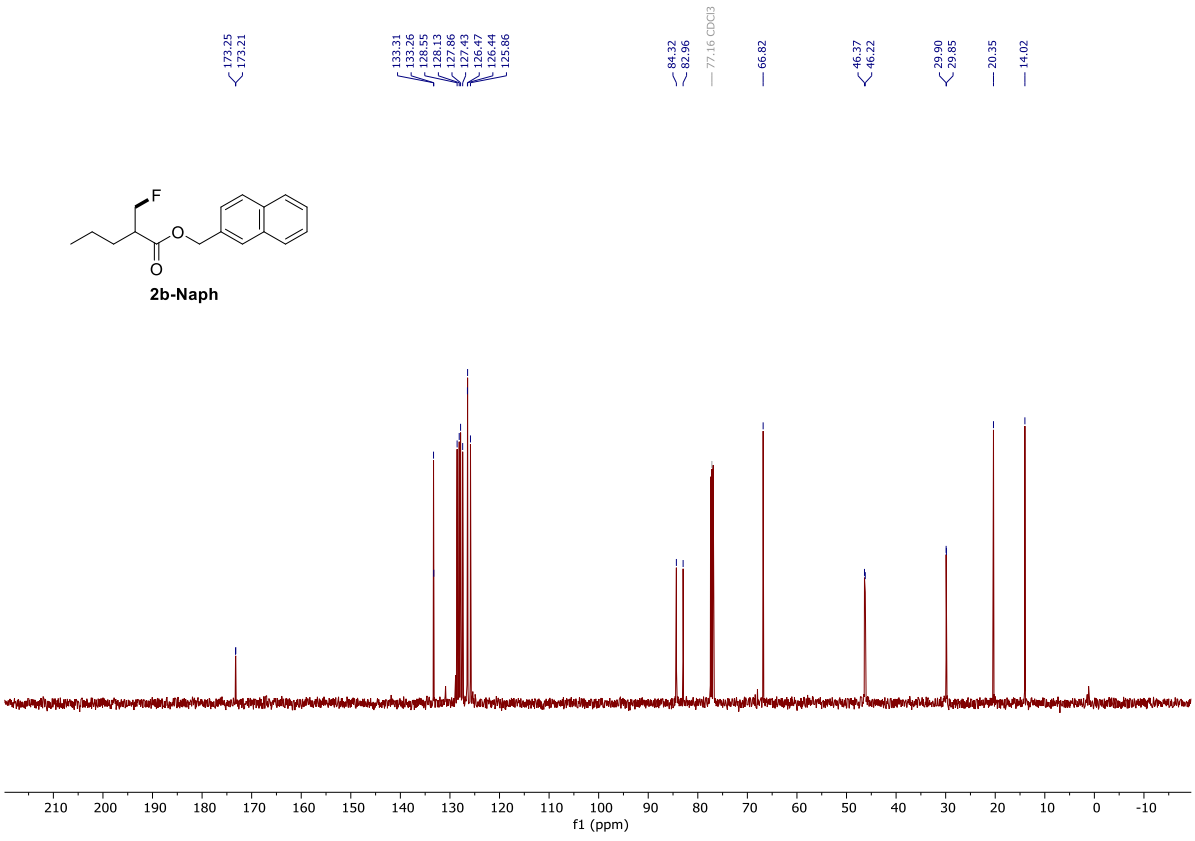

-222.03
F
O
O
2p-Naph
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
f1 (ppm)

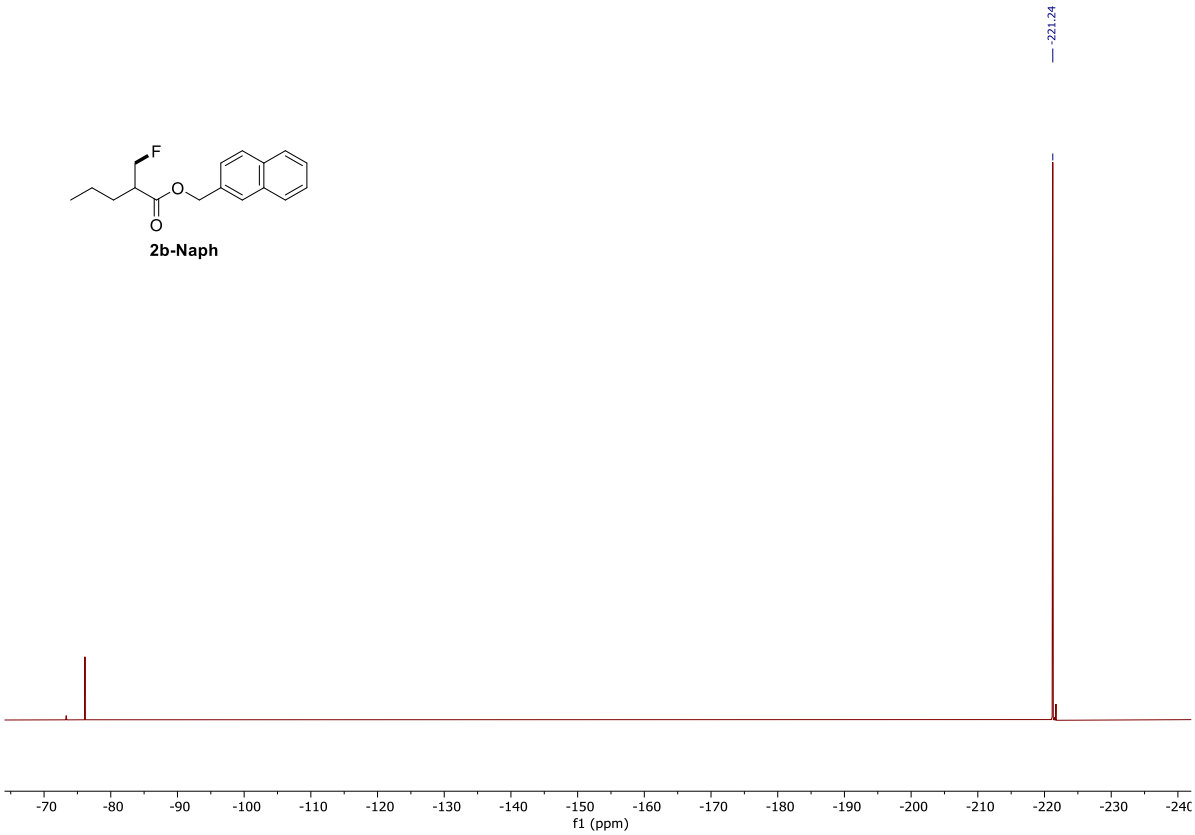

2q-Naph
f1 (ppm)

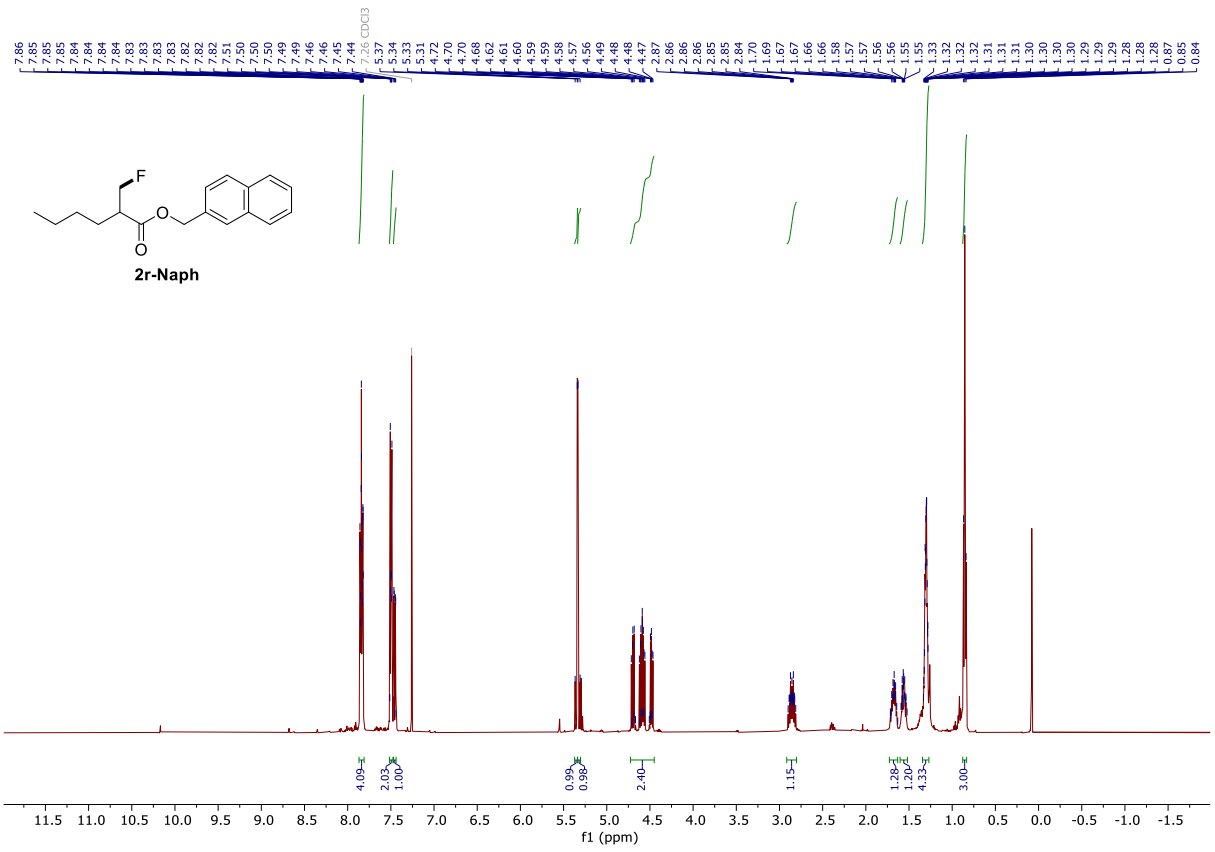

2q-Naph
f1 (ppm)

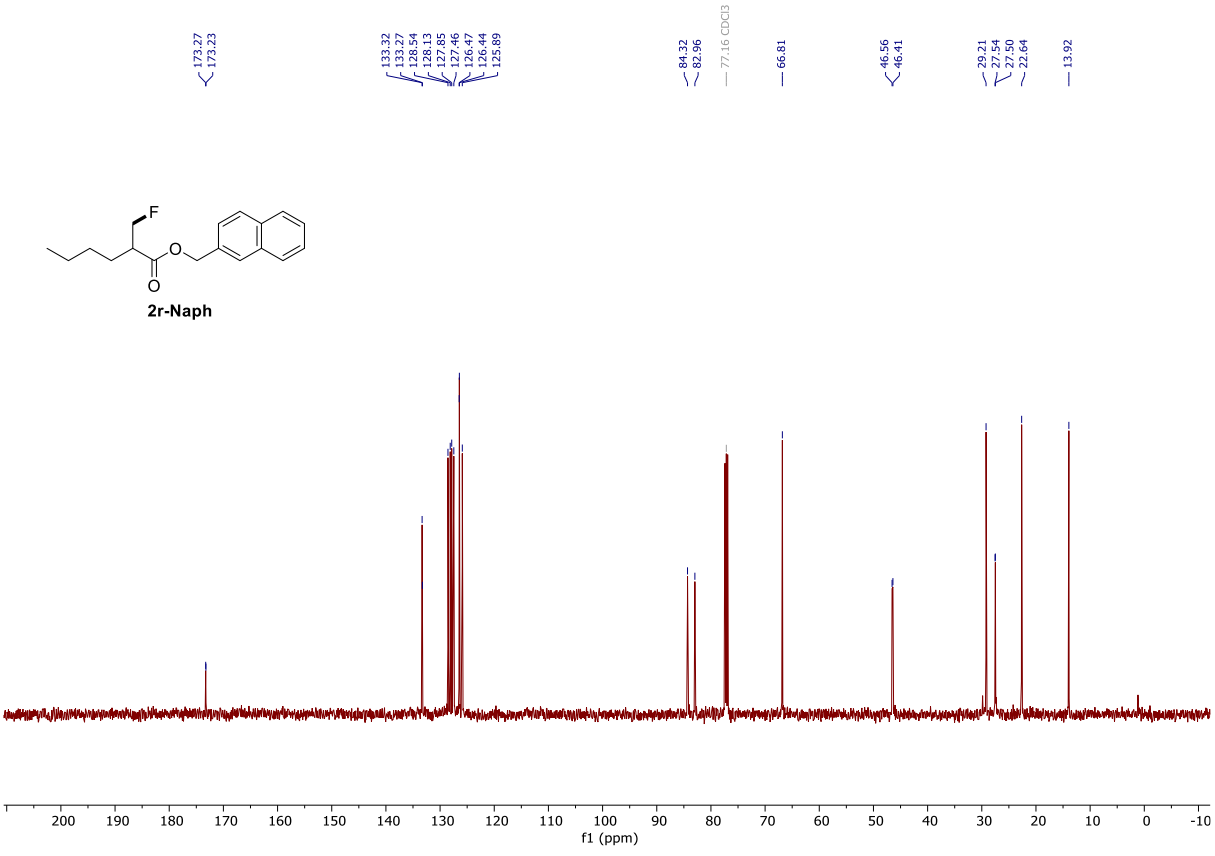

F
O
O
2q-Naph
-222.21
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
f1 (ppm)

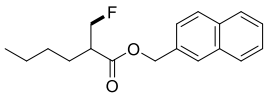

F
O
O
2b-Naph
f1 (ppm)


F
O
O
2b-Naph
f1 (ppm)


F
O
O
2b-Naph
-221.24
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
f1 (ppm)

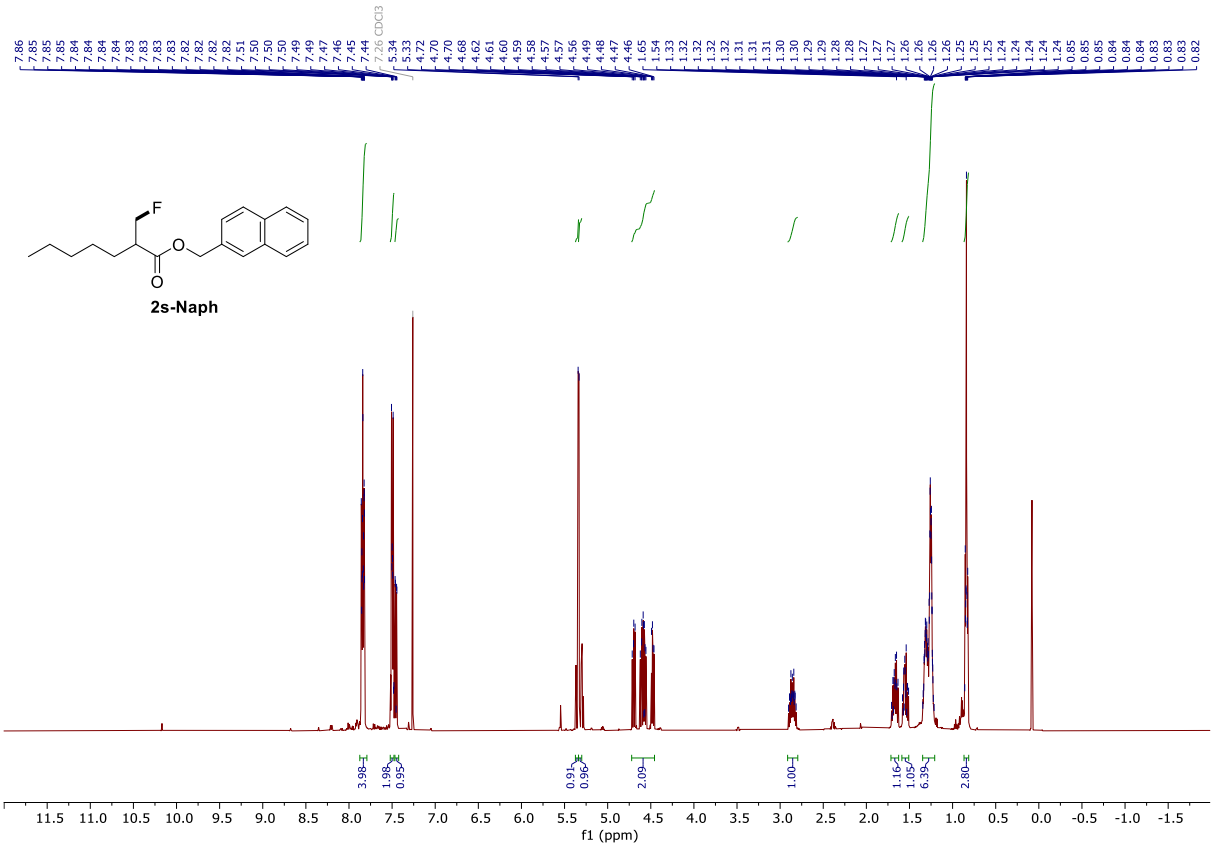

7.86 7.85 7.85 7.85 7.84 7.84 7.84 7.84 7.83 7.83 7.83 7.82 7.82 7.82 7.51 7.50 7.50 7.50 7.49 7.49 7.46 7.46 7.45 7.44 7.26 CDCl3 5.37 5.34 5.33 5.31 4.72 4.70 4.70 4.68 4.62 4.61 4.60 4.59 4.59 4.58 4.57 4.56 4.49 4.48 4.48 4.47 2.87 2.86 2.86 2.86 2.85 2.85 2.84 1.70 1.69 1.67 1.67 1.66 1.66 1.58 1.57 1.57 1.56 1.56 1.55 1.55 1.33 1.32 1.32 1.31 1.31 1.31 1.30 1.30 1.30 1.29 1.29 1.29 1.28 1.28 1.28 0.87 0.85 0.84
F
O
O
2r-Naph
4.09 2.03 1.00 0.99 0.98 2.40 1.15 1.28 1.20 4.33 3.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

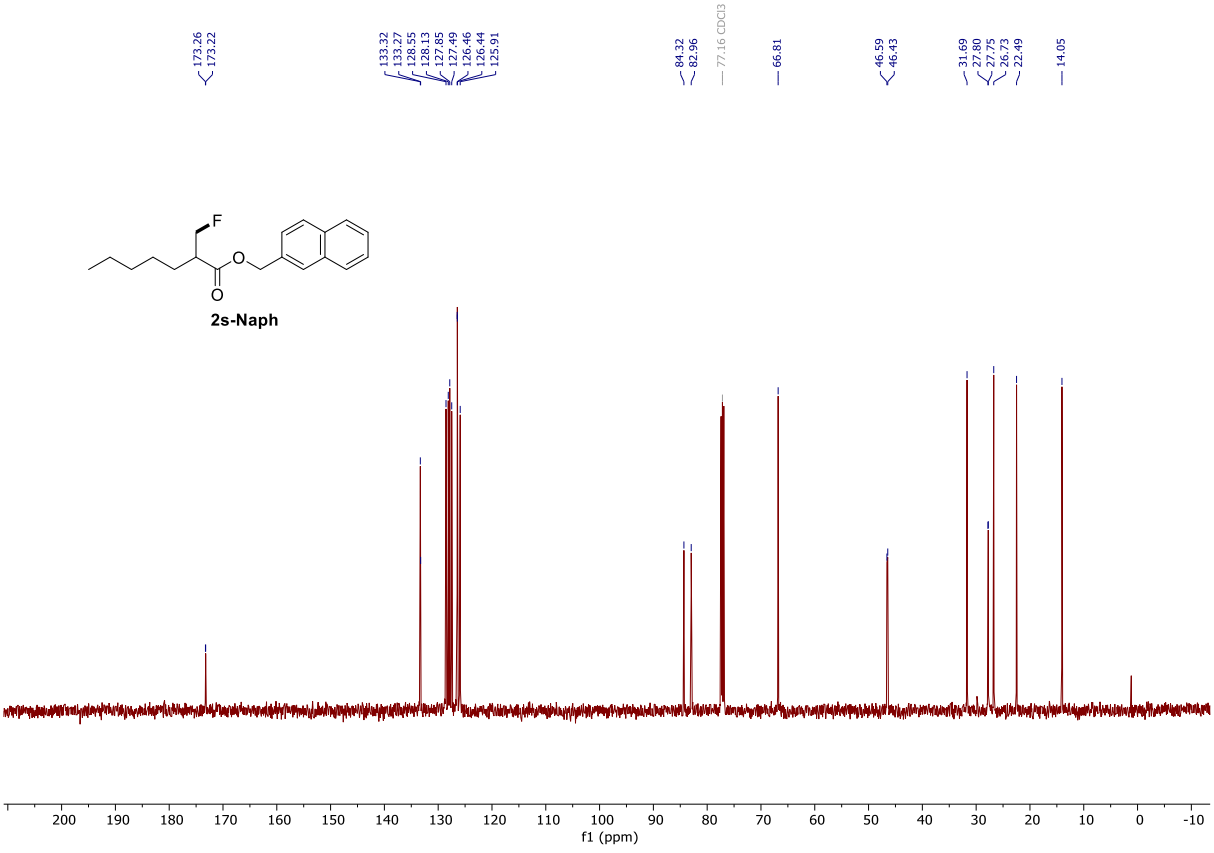

173.27 173.23 133.32 133.27 128.54 128.13 127.85 127.46 126.47 126.44 125.89 84.32 82.96 77.16 CDCl3 66.81 46.56 46.41 29.21 27.54 27.50 22.64 13.92
F
O
O
2r-Naph
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


F
O
O

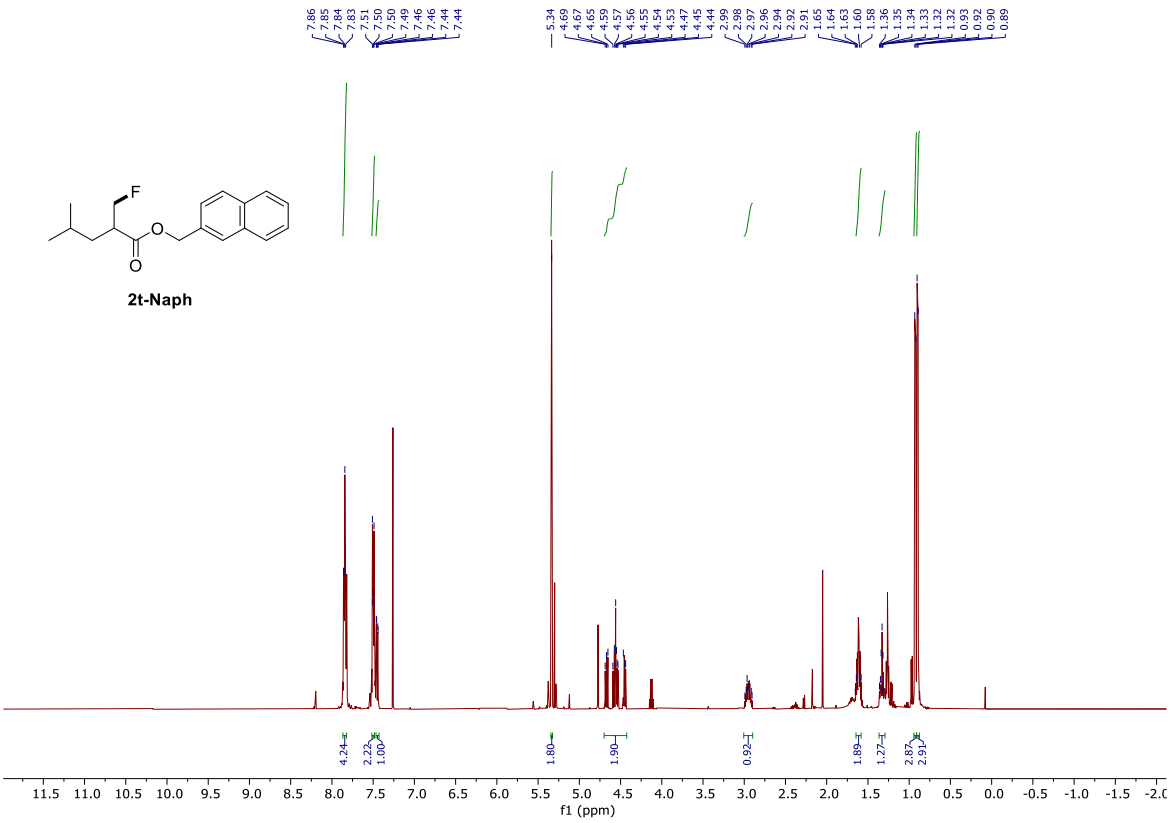
2r-Naph

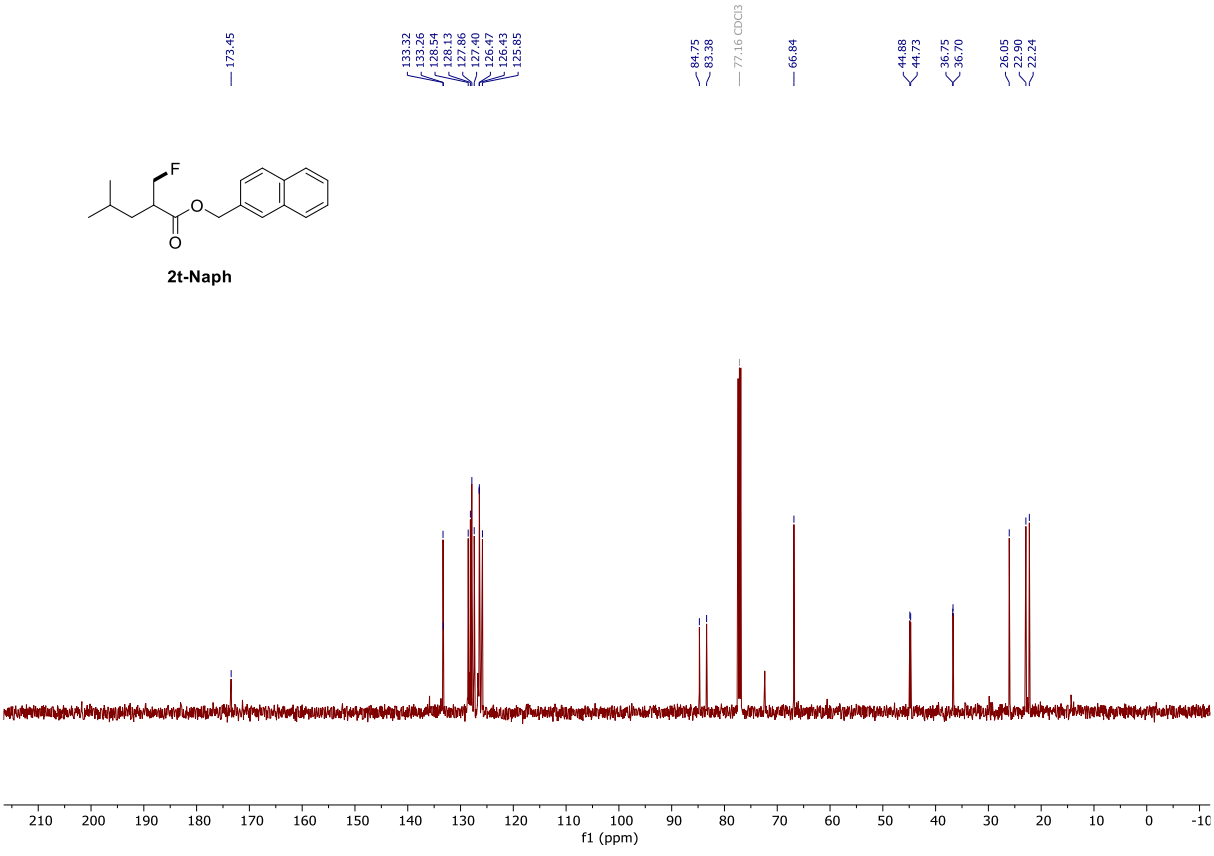
-221.23
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
f1 (ppm)

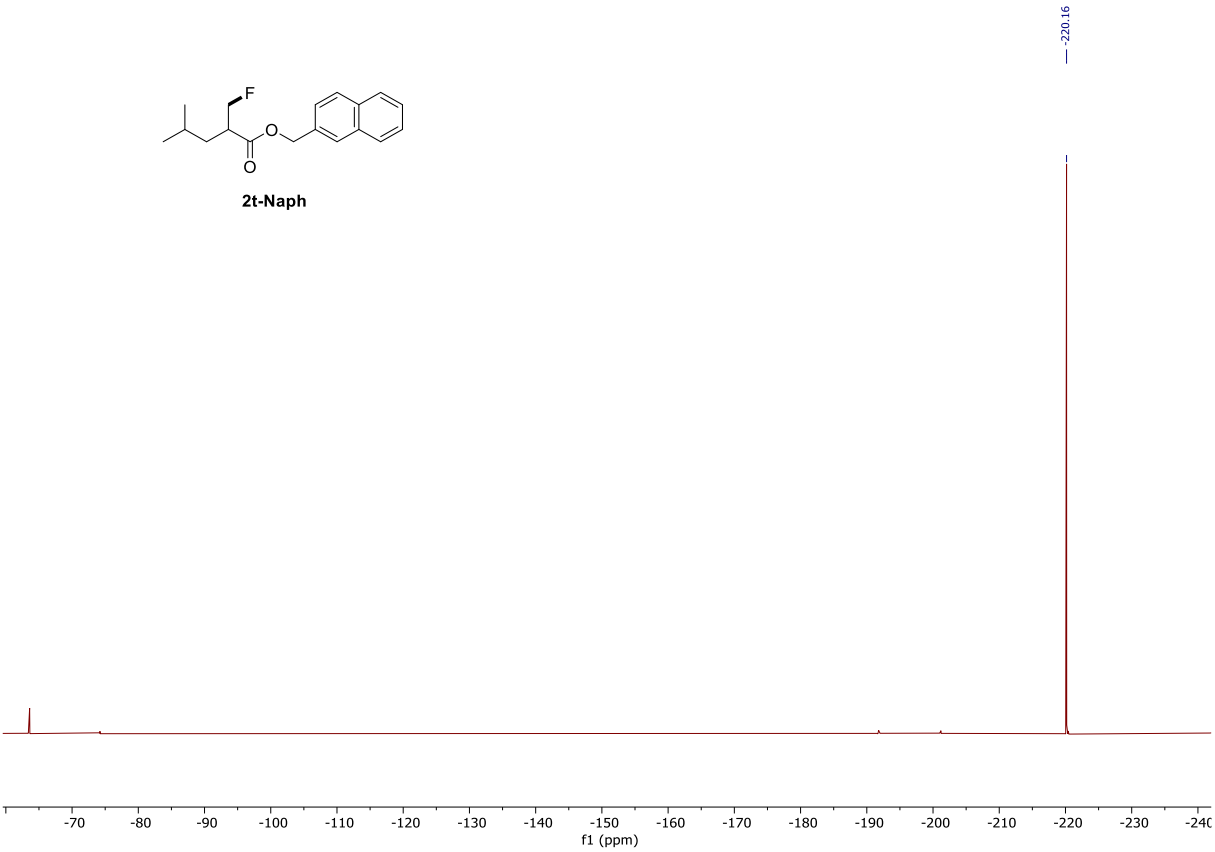

F
O
O
2s-Naph
f1 (ppm)

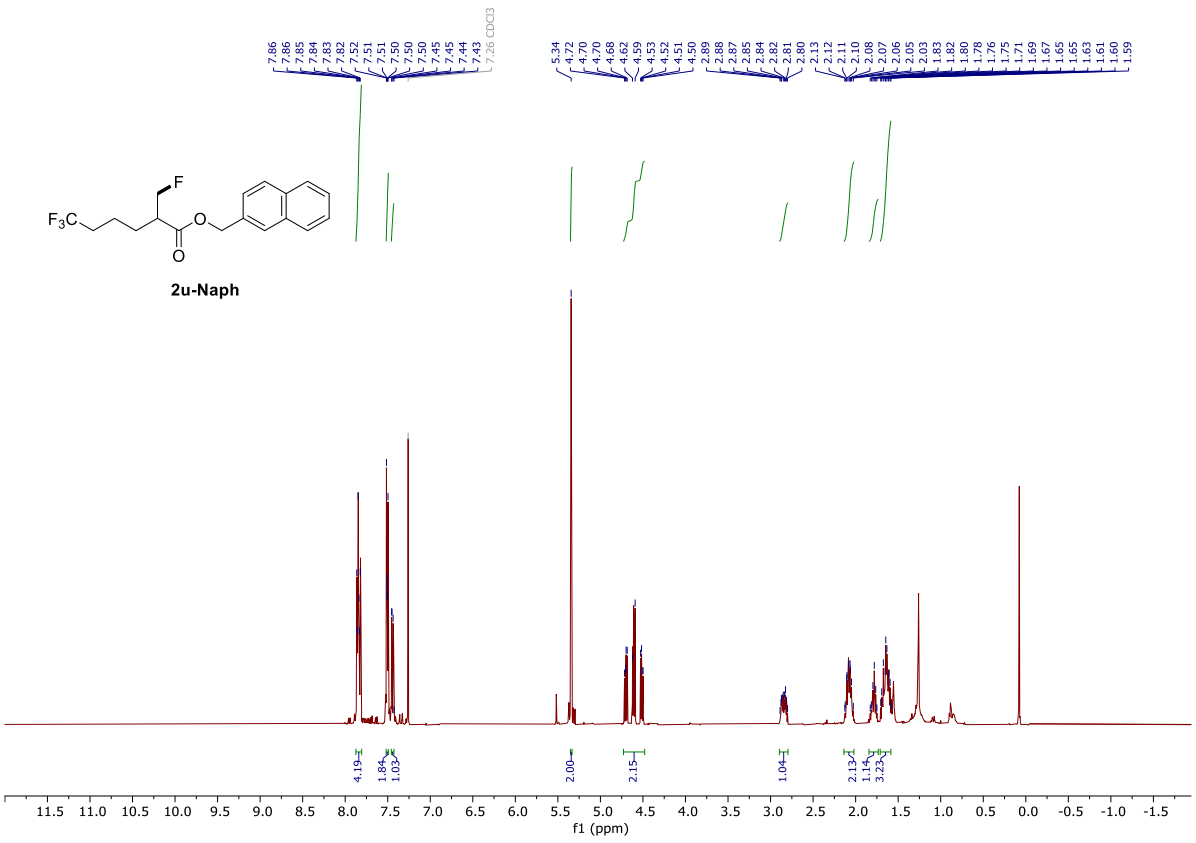

F
O
O
2s-Naph
f1 (ppm)


F
O
O
2s-Naph
-221.21
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
f1 (ppm)


F
O
O
2t-Naph
7.86
7.85
7.84
7.83
7.51
7.50
7.50
7.49
7.46
7.46
7.44
7.44
5.34
4.69
4.67
4.65
4.59
4.57
4.56
4.55
4.54
4.53
4.47
4.45
4.44
2.99
2.98
2.97
2.96
2.94
2.92
2.91
1.65
1.64
1.63
1.60
1.58
1.36
1.35
1.34
1.33
1.32
1.32
0.93
0.92
0.90
0.89
4.24
2.22
1.00
1.80
1.90
0.92
1.89
1.27
2.87
2.91
f1 (ppm)


F
O
O
2t-Naph
173.45
133.32
133.26
128.54
128.13
127.86
127.40
126.47
126.43
125.85
84.75
83.38
77.16 CDCl3
66.84
44.88
44.73
36.75
36.70
26.05
22.90
22.24
f1 (ppm)


F
O
O
2t-Naph
-220.16
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
f1 (ppm)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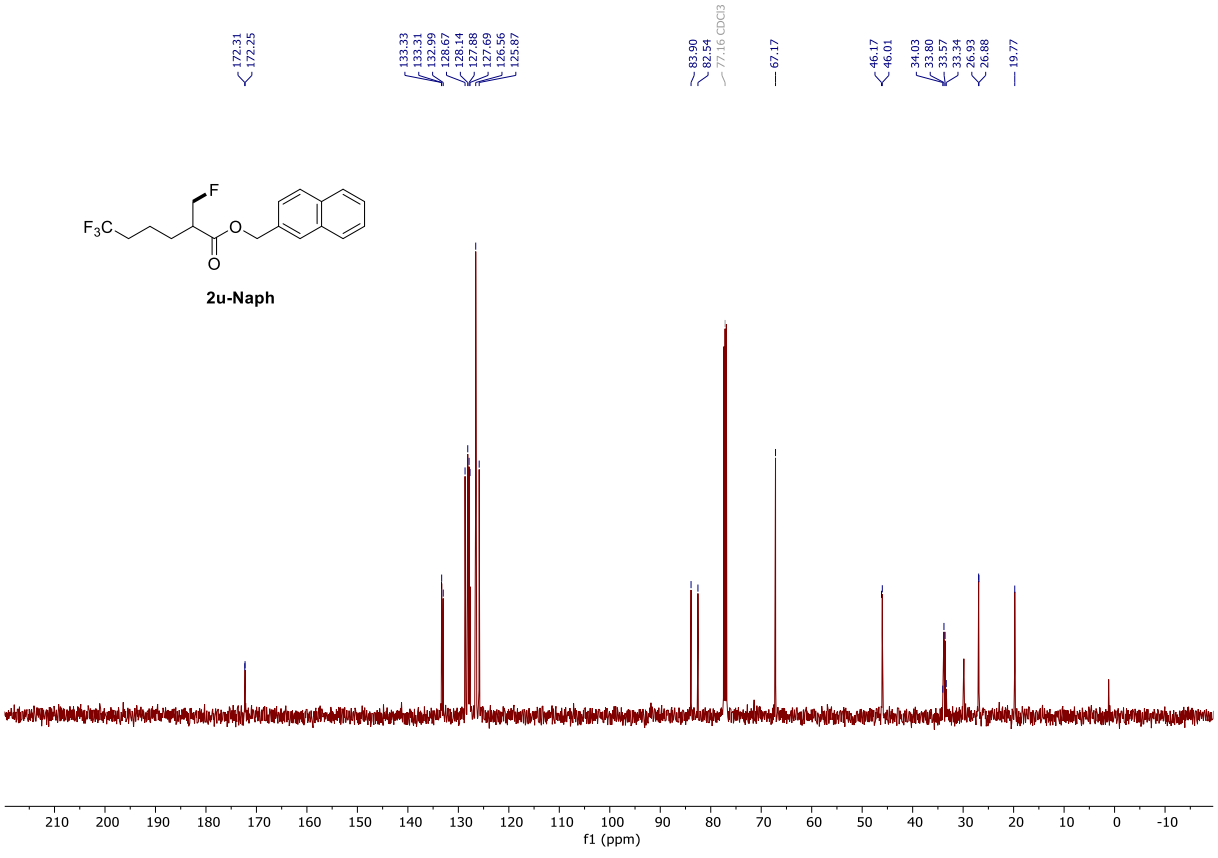
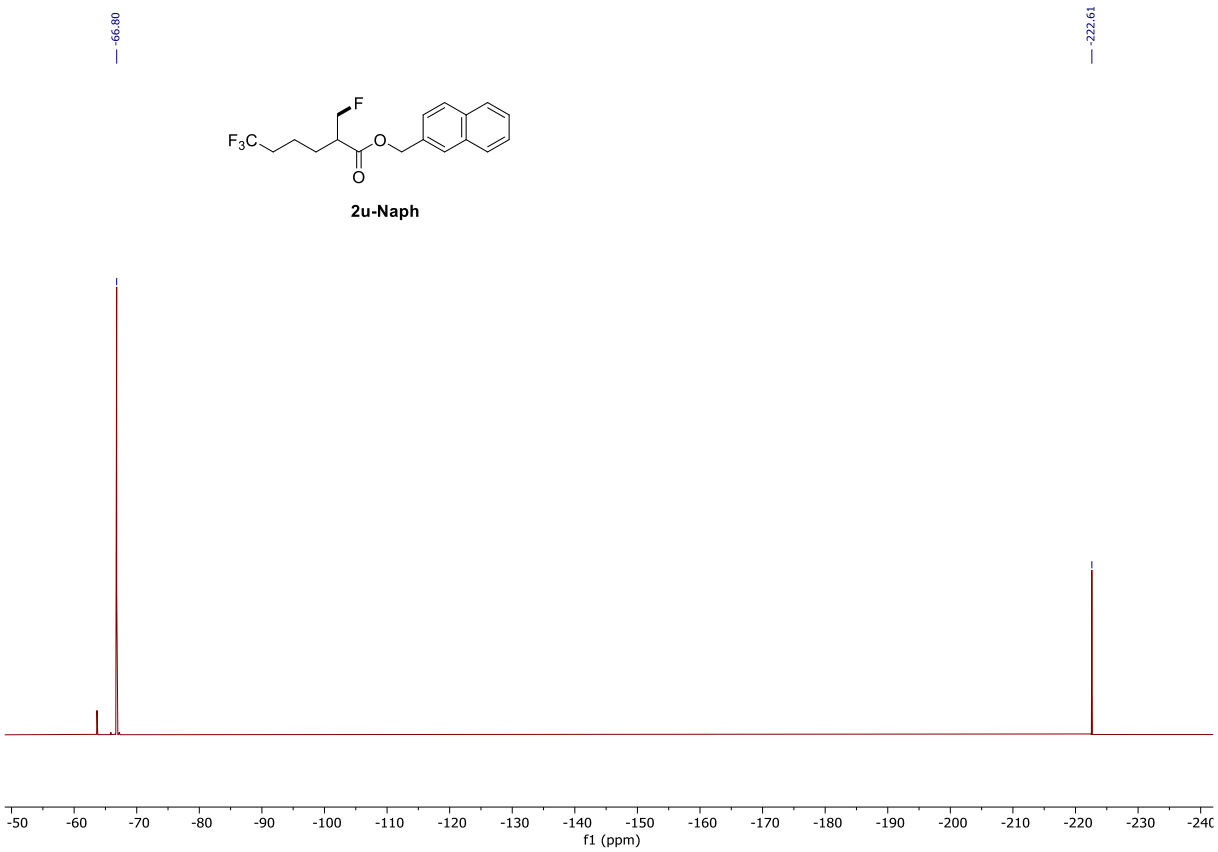
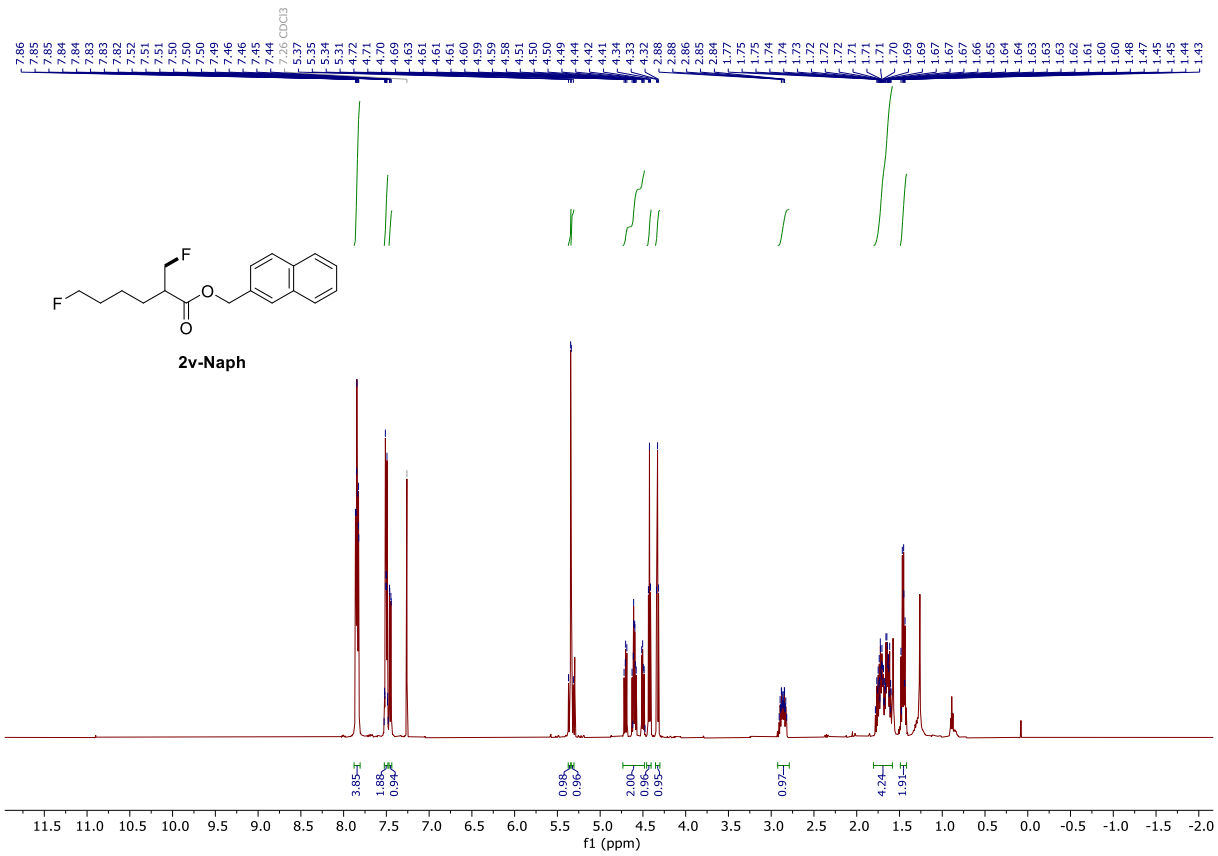
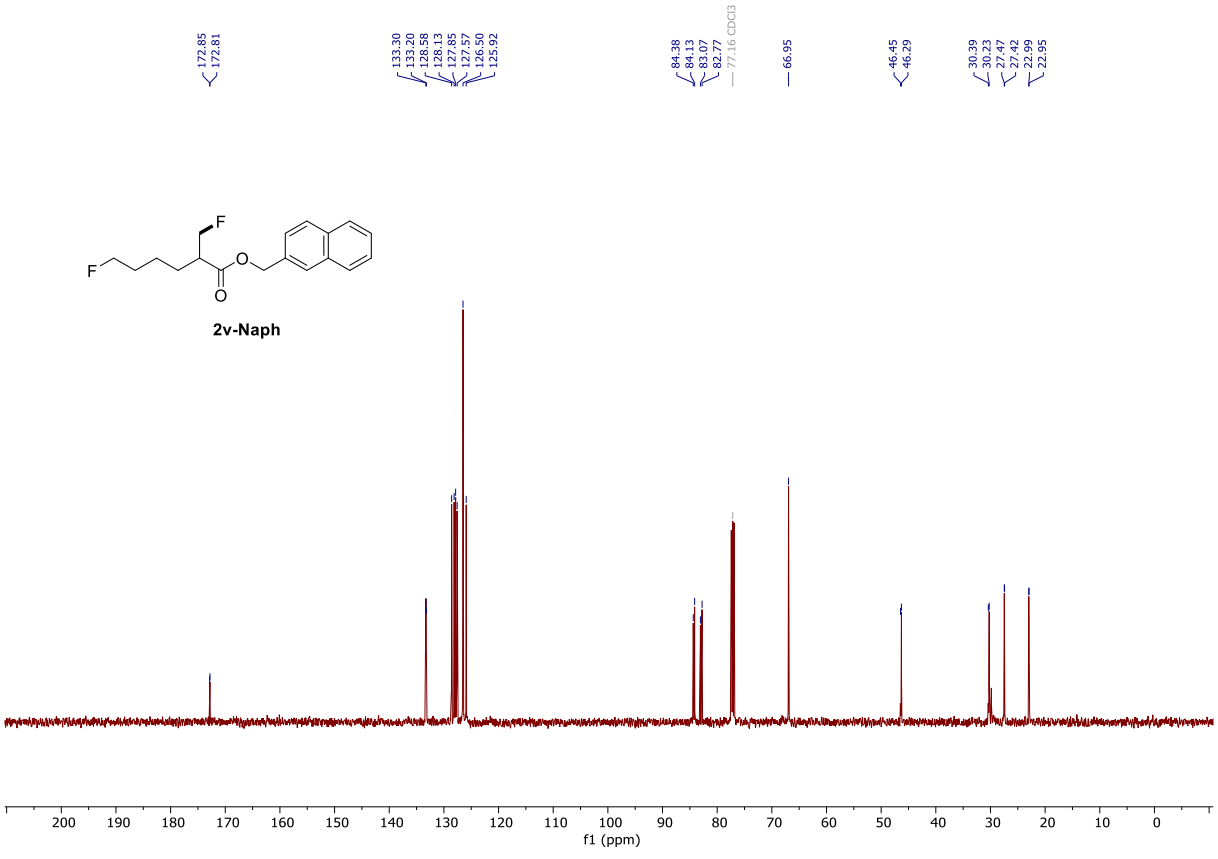
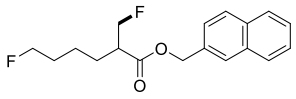
7.86
7.85
7.84
7.83
7.82
7.52
7.51
7.51
7.50
7.50
7.50
7.45
7.45
7.44
7.43
7.26 CDCl3
5.34
4.72
4.70
4.70
4.68
4.62
4.59
4.53
4.52
4.51
4.50
2.89
2.88
2.87
2.85
2.84
2.82
2.81
2.80
2.13
2.12
2.11
2.10
2.08
2.07
2.06
2.05
2.03
1.83
1.82
1.80
1.78
1.76
1.75
1.71
1.69
1.67
1.65
1.65
1.63
1.61
1.60
1.59
F
F3C
O
O
2u-Naph
4.19
1.84
1.03
2.00
2.15
1.04
2.13
1.14
3.23
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)


172.31
172.25
133.33
133.31
132.99
128.67
128.14
127.88
127.69
126.56
125.87
83.90
82.54
77.16 CDCl3
67.17
46.17
46.01
34.03
33.80
33.57
33.34
26.93
26.88
19.77
F
F3C
O
O
2u-Naph
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-66.80
-222.61
F
F3C
O
O
2u-Naph
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
f1 (ppm)

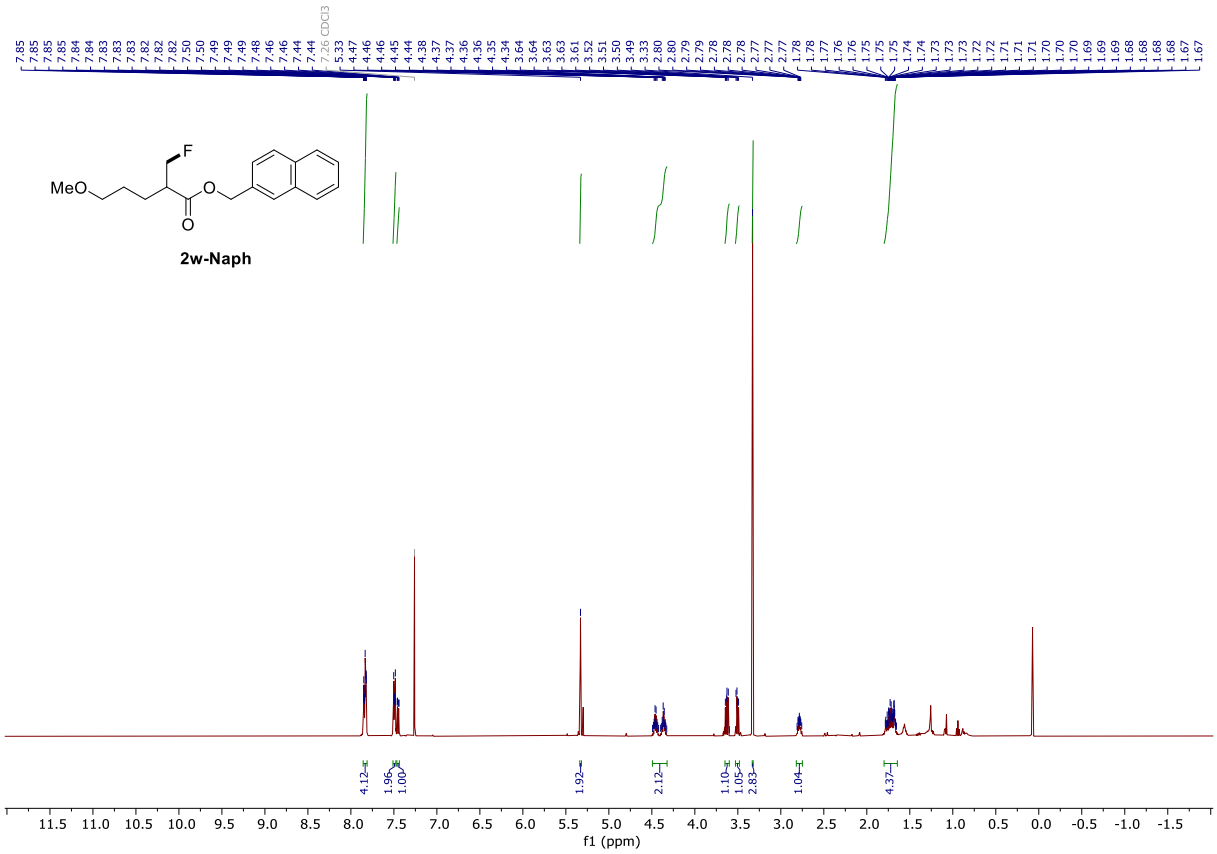

7.26 CDCl3
F
F
O
O
2v-Naph
3.85
1.88
0.94
0.98
0.96
2.00
0.96
0.95
0.97
4.24
1.91
f1 (ppm)

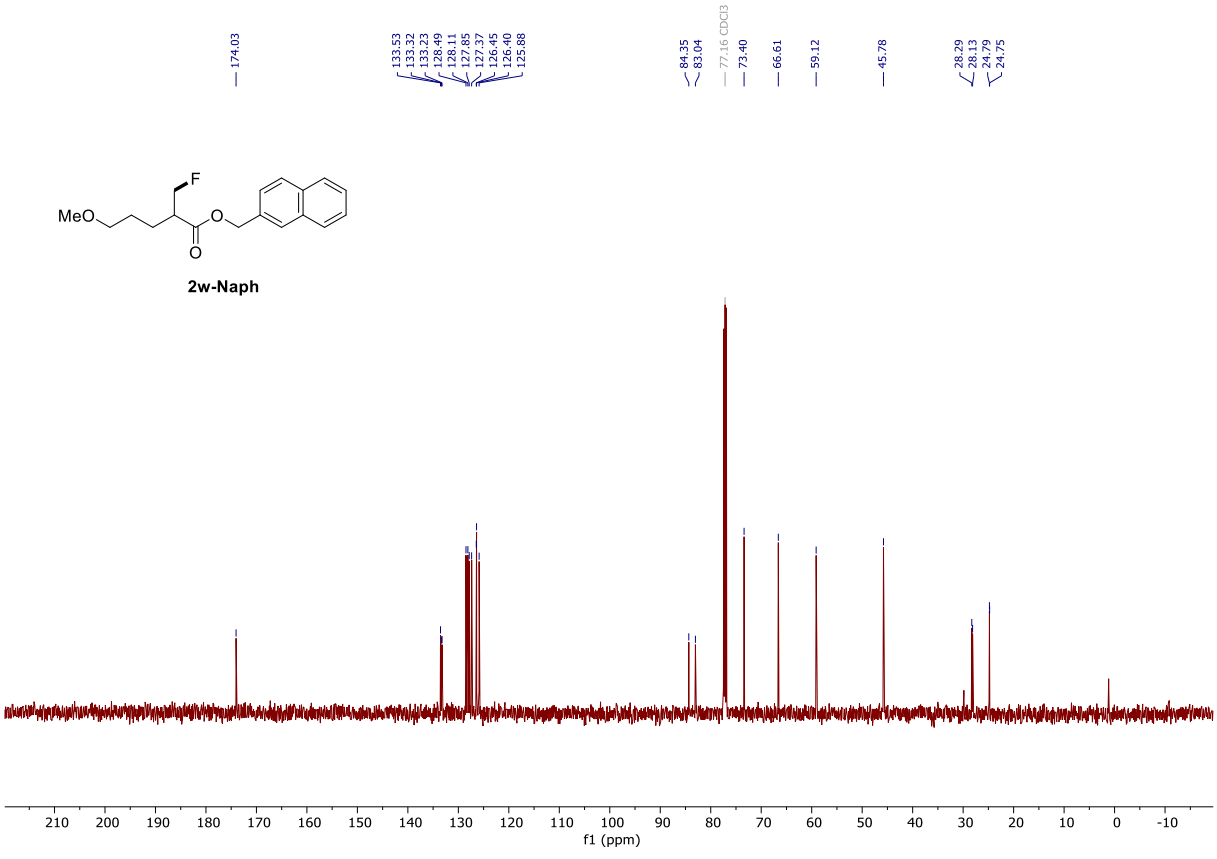

172.85
172.81
133.30
133.20
128.58
128.13
127.85
127.57
126.50
125.92
84.38
84.13
83.07
82.77
77.16 CDCl3
66.95
46.45
46.29
30.39
30.23
27.47
27.42
22.99
22.95
F
F
O
O
2v-Naph
f1 (ppm)

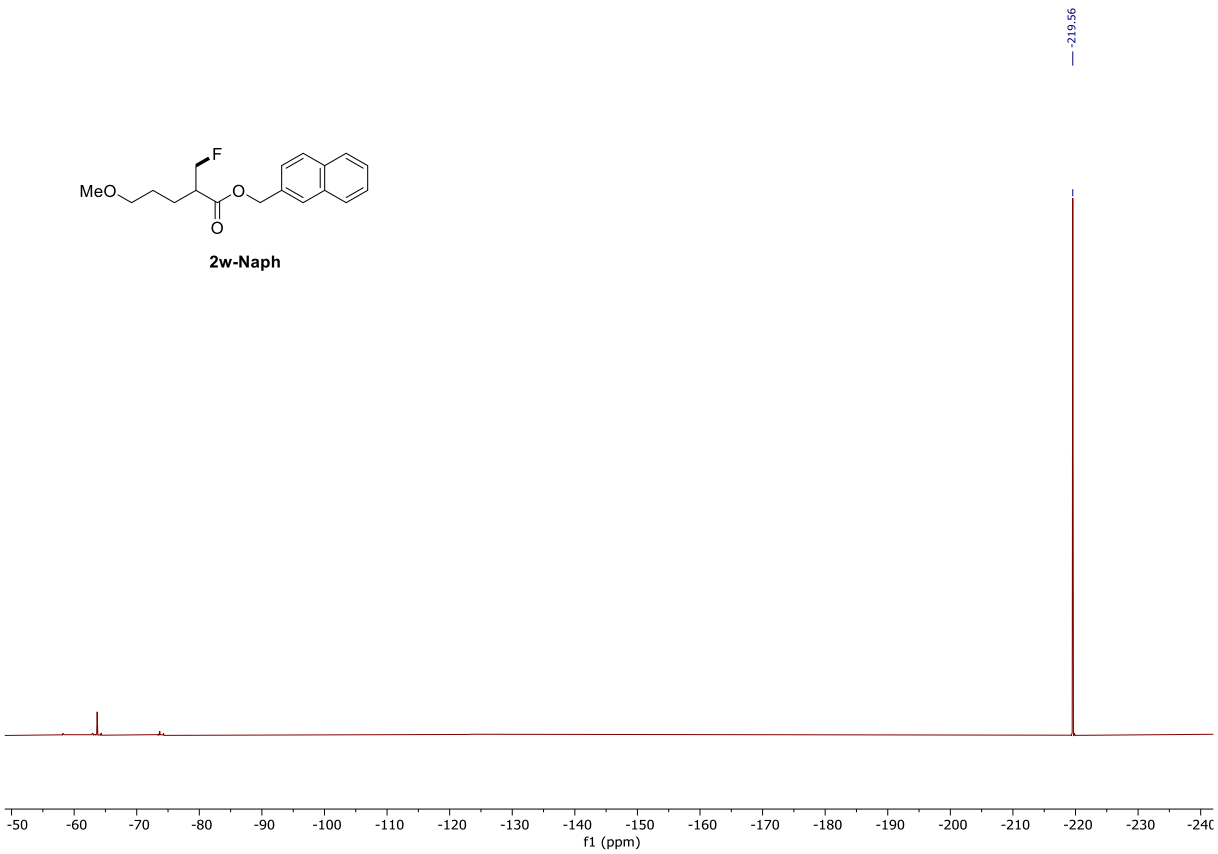

F
F
O
O

2v-Naph

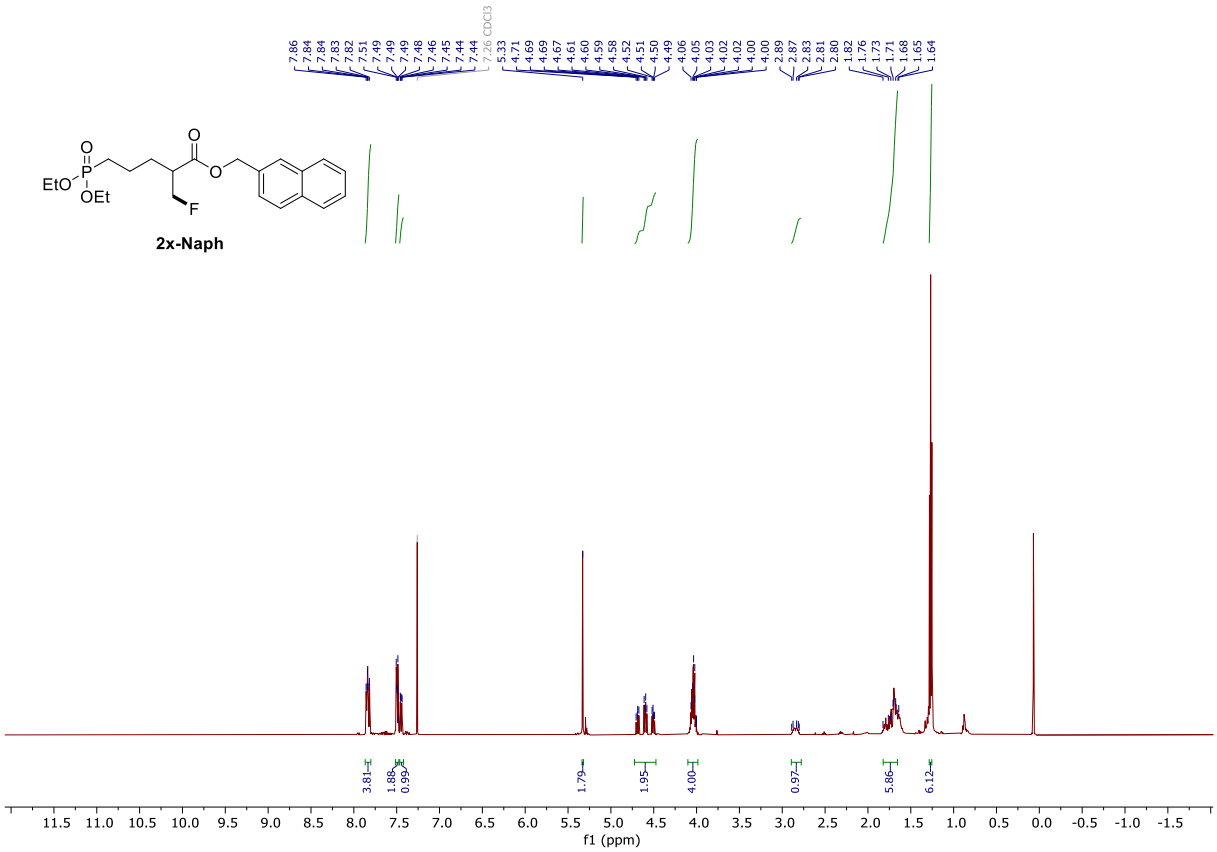
-219.08
-221.85
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
f1 (ppm)

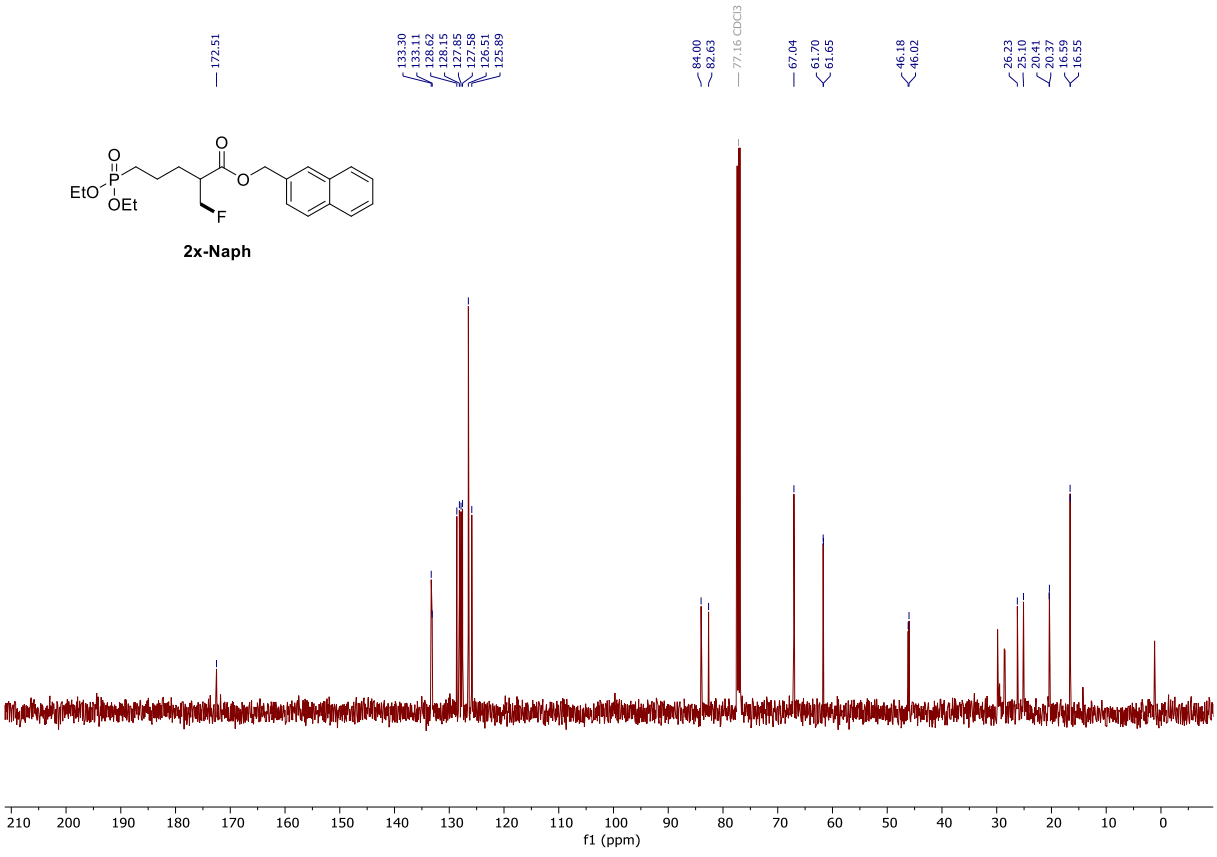

MeO
F
O
O
2w-Naph
f1 (ppm)

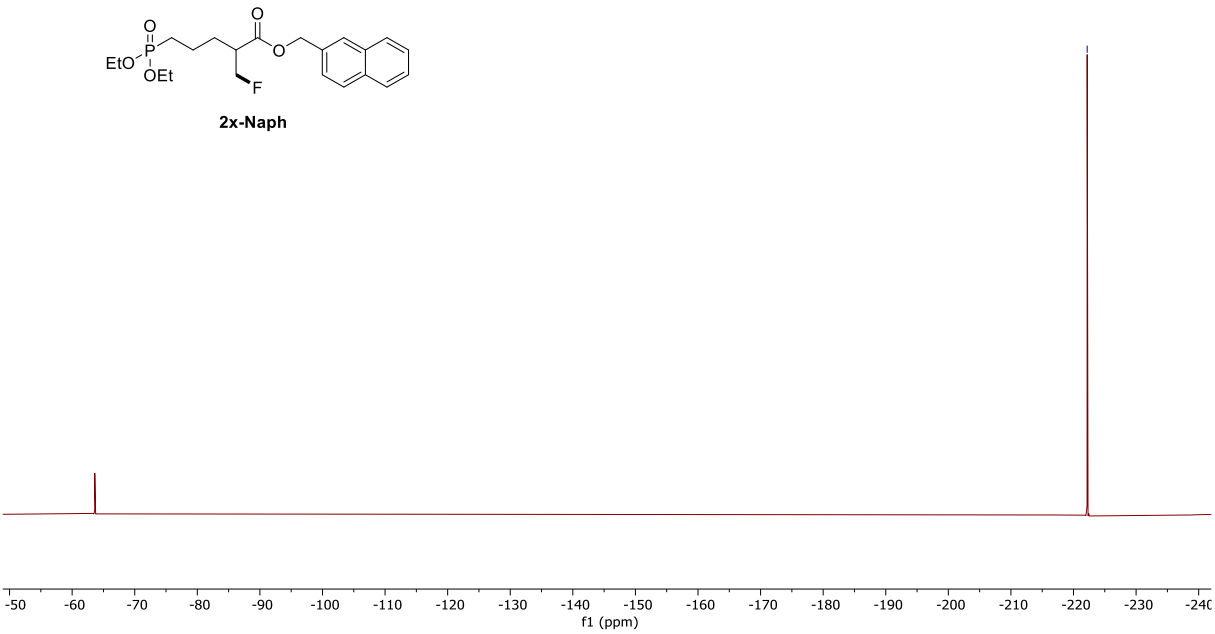

MeO
F
O
O
2w-Naph
f1 (ppm)


-219.56
F
MeO
O
O
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
f1 (ppm)

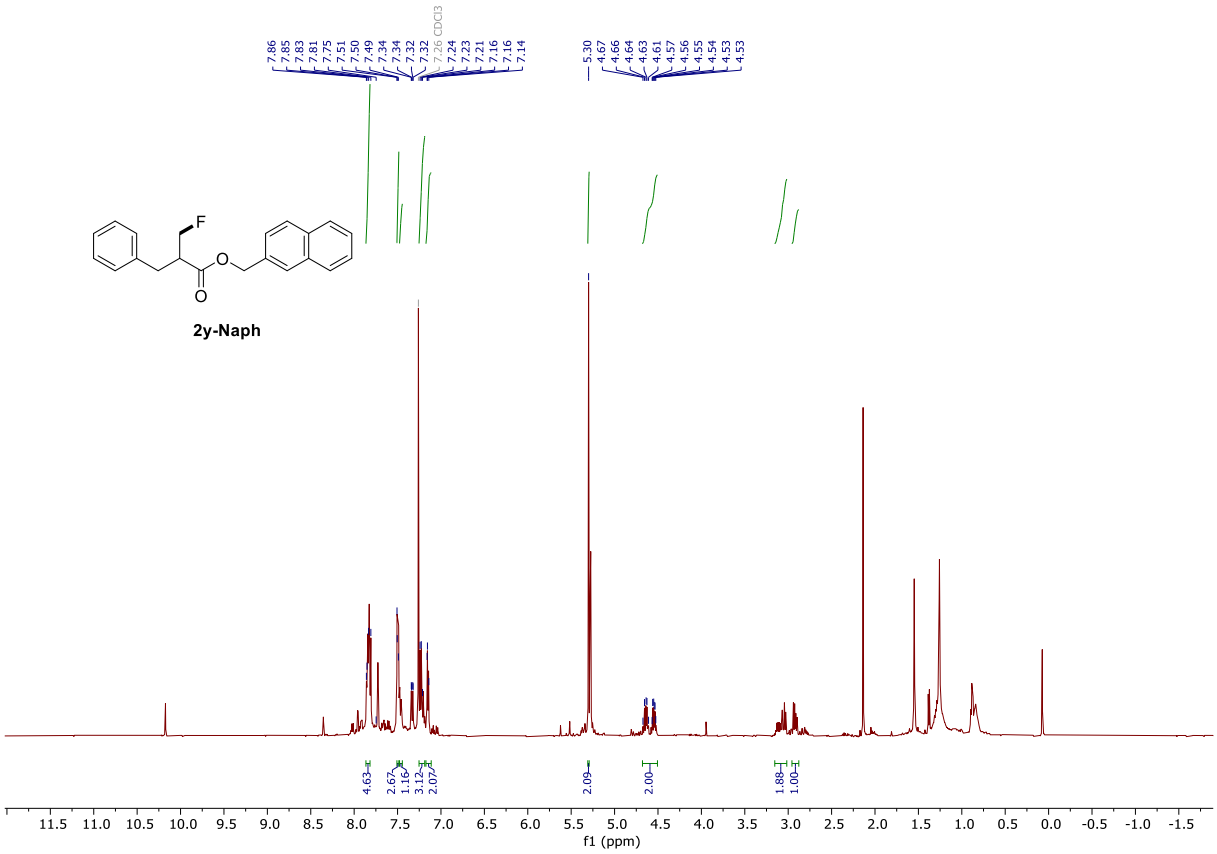
2w-Naph

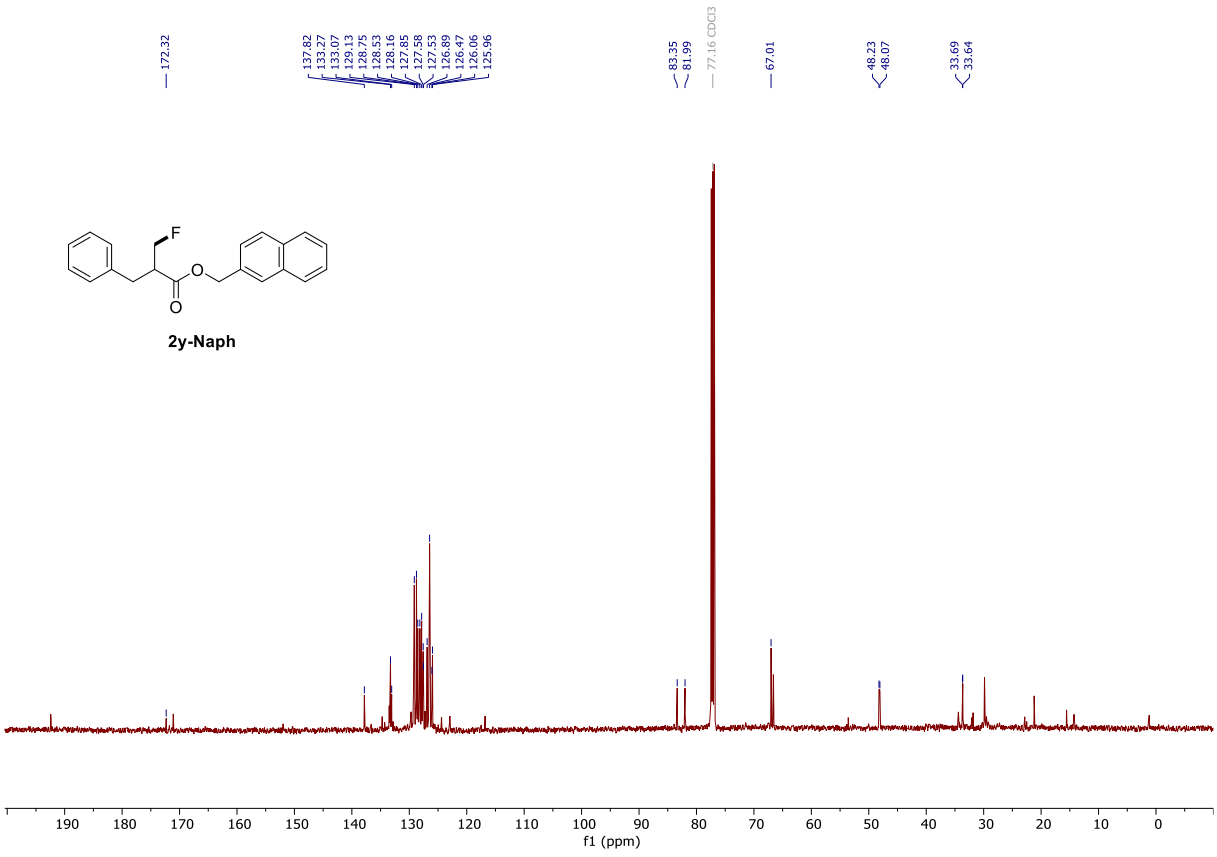

7.86
7.84
7.84
7.83
7.82
7.51
7.49
7.49
7.49
7.48
7.46
7.45
7.44
7.26 CDCl3
5.33
4.71
4.69
4.69
4.67
4.61
4.60
4.59
4.58
4.52
4.51
4.50
4.49
4.06
4.05
4.03
4.02
4.02
4.00
4.00
2.89
2.87
2.83
2.81
2.80
1.82
1.76
1.73
1.71
1.68
1.65
1.64
EtO
OEt
F
2x-Naph
3.81
1.88
0.99
1.79
1.95
4.00
0.97
5.86
6.12
f1 (ppm)

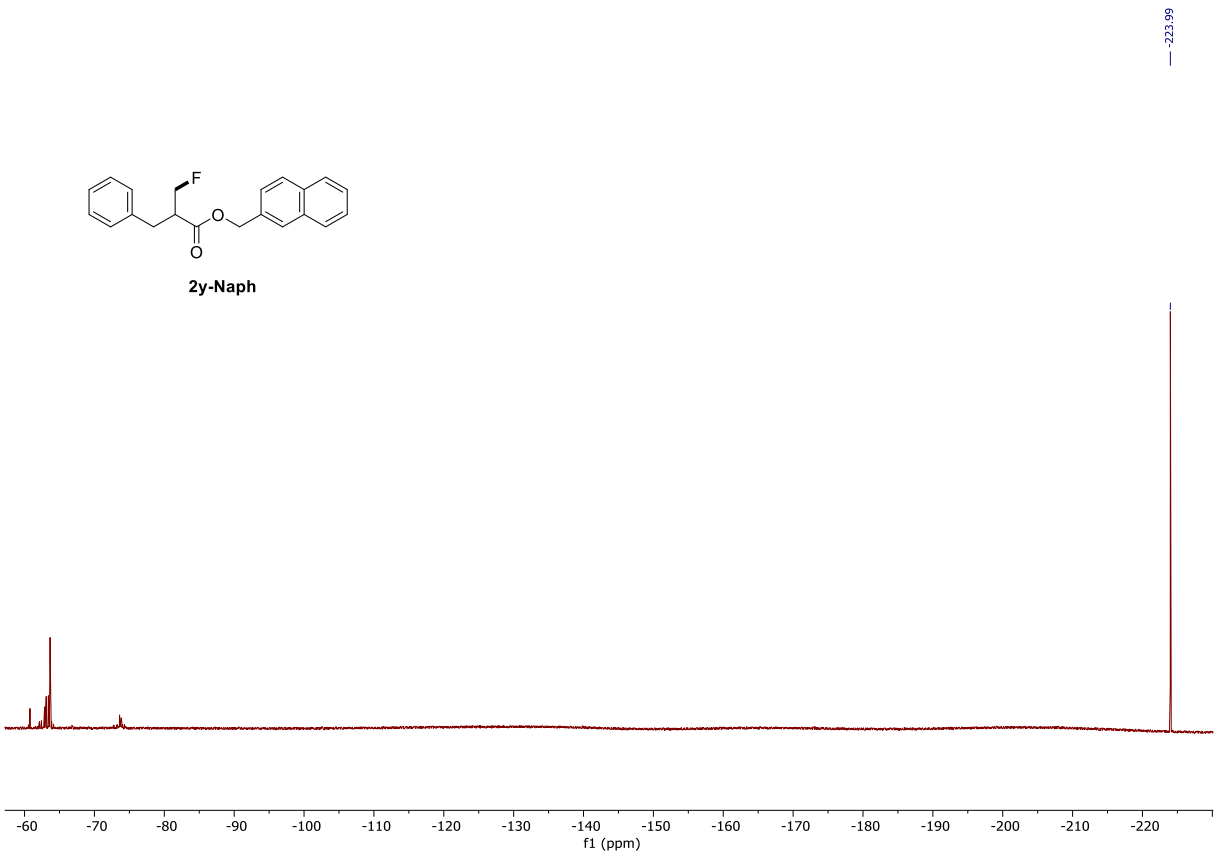

172.51
133.30
133.11
128.62
128.15
127.85
127.58
126.51
125.89
84.00
82.63
77.16 CDCl3
67.04
61.70
61.65
46.18
46.02
26.23
25.10
20.41
20.37
16.59
16.55
EtO
OEt
F
2x-Naph
f1 (ppm)

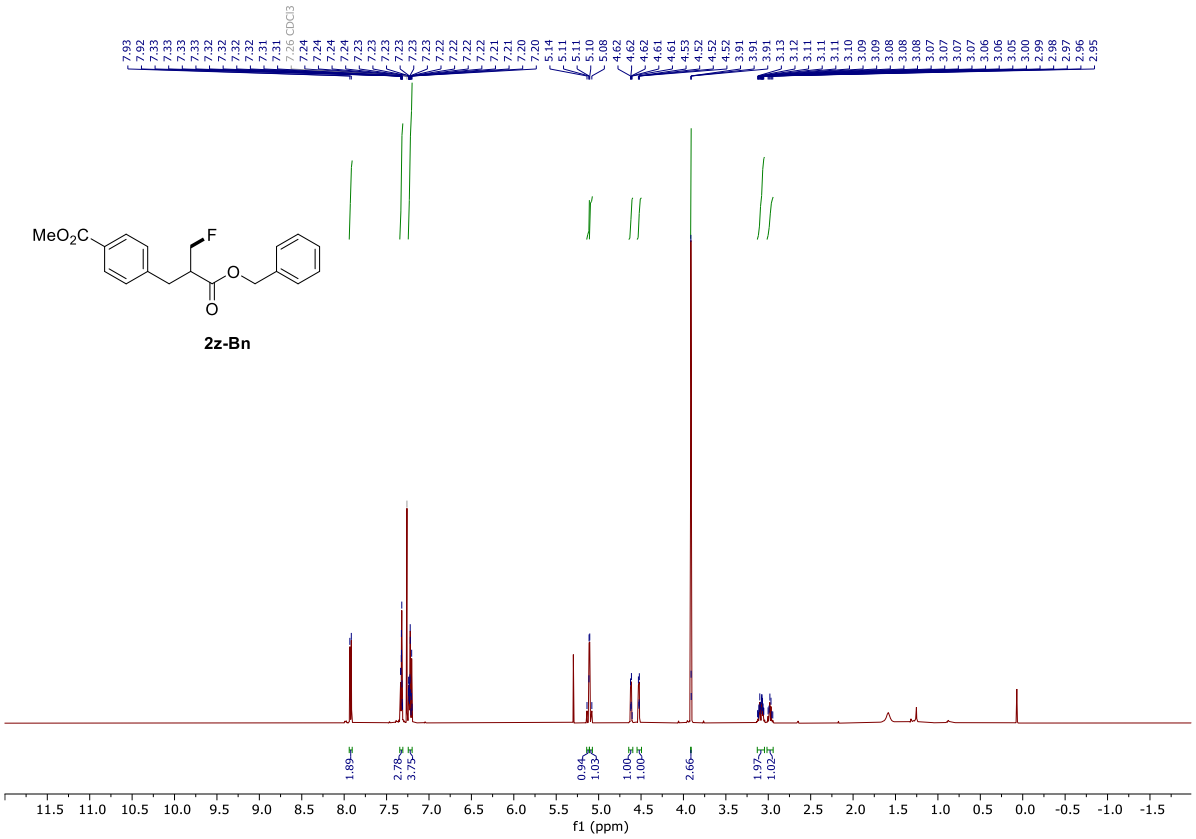

-222.18
EtO
OEt
O
P
O
O
F
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
f1 (ppm)

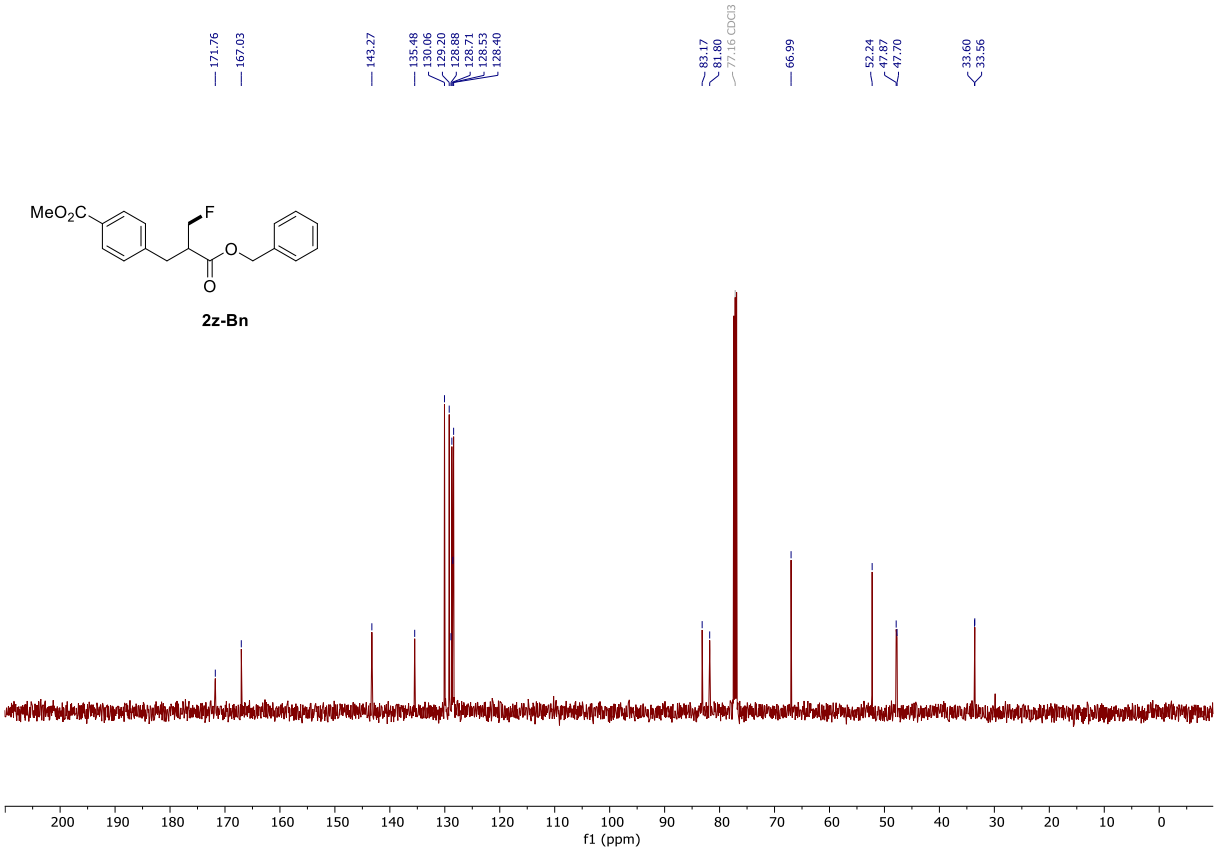
2x-Naph

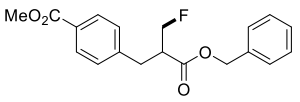

7.86
7.85
7.83
7.81
7.75
7.51
7.50
7.49
7.34
7.34
7.32
7.32
7.26 CDCl3
7.24
7.23
7.21
7.16
7.16
7.14
5.30
4.67
4.66
4.64
4.63
4.61
4.57
4.56
4.55
4.54
4.53
4.53
F
O
O
2y-Naph
4.63
2.67
1.16
3.12
2.07
2.09
2.00
1.88
1.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)


172.32
137.82
133.27
133.07
129.13
128.75
128.53
128.16
127.85
127.58
127.53
126.49
126.06
125.96
83.35
81.99
77.16 CDCl3
67.01
48.23
48.07
33.69
33.64
F
O
O
2y-Naph
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-223.99
F
O
O
2y-Naph
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
f1 (ppm)

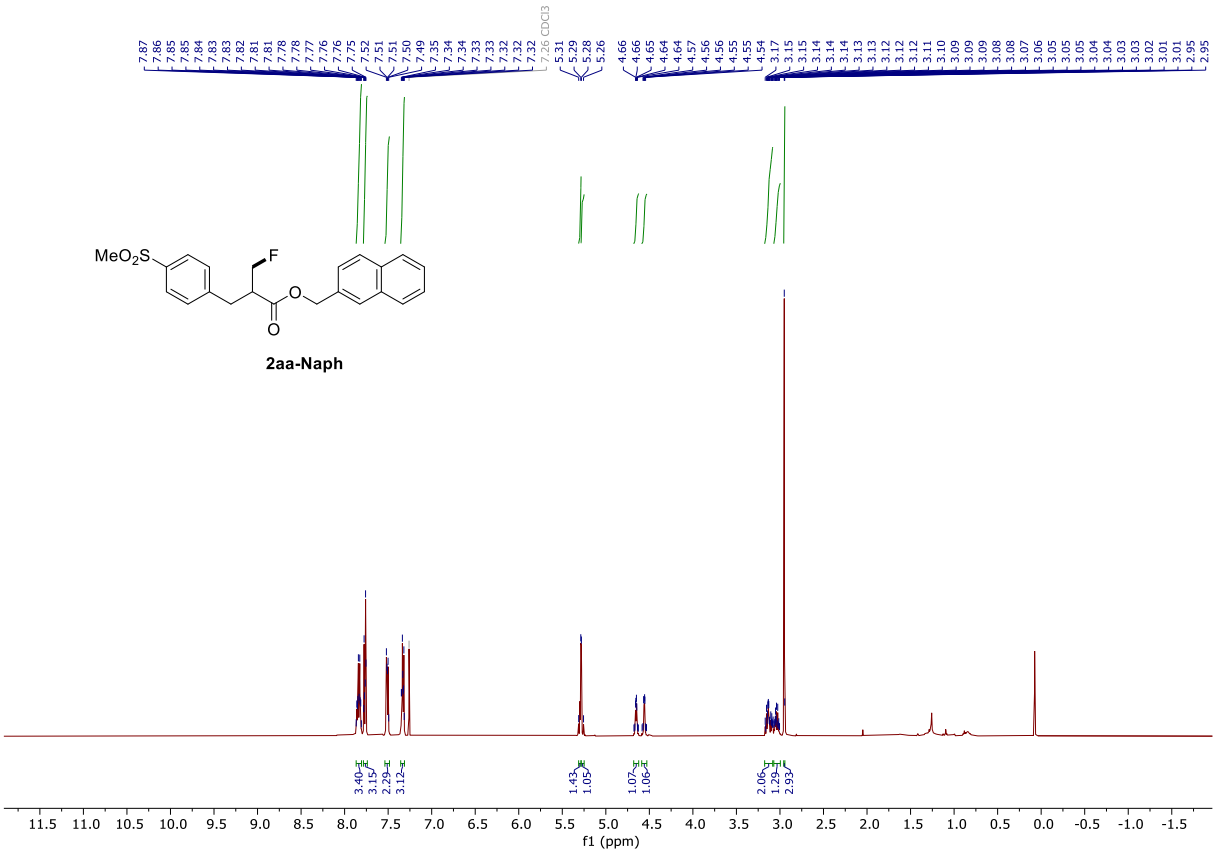

MeO2C
F
O
O
2z-Bn
f1 (ppm)

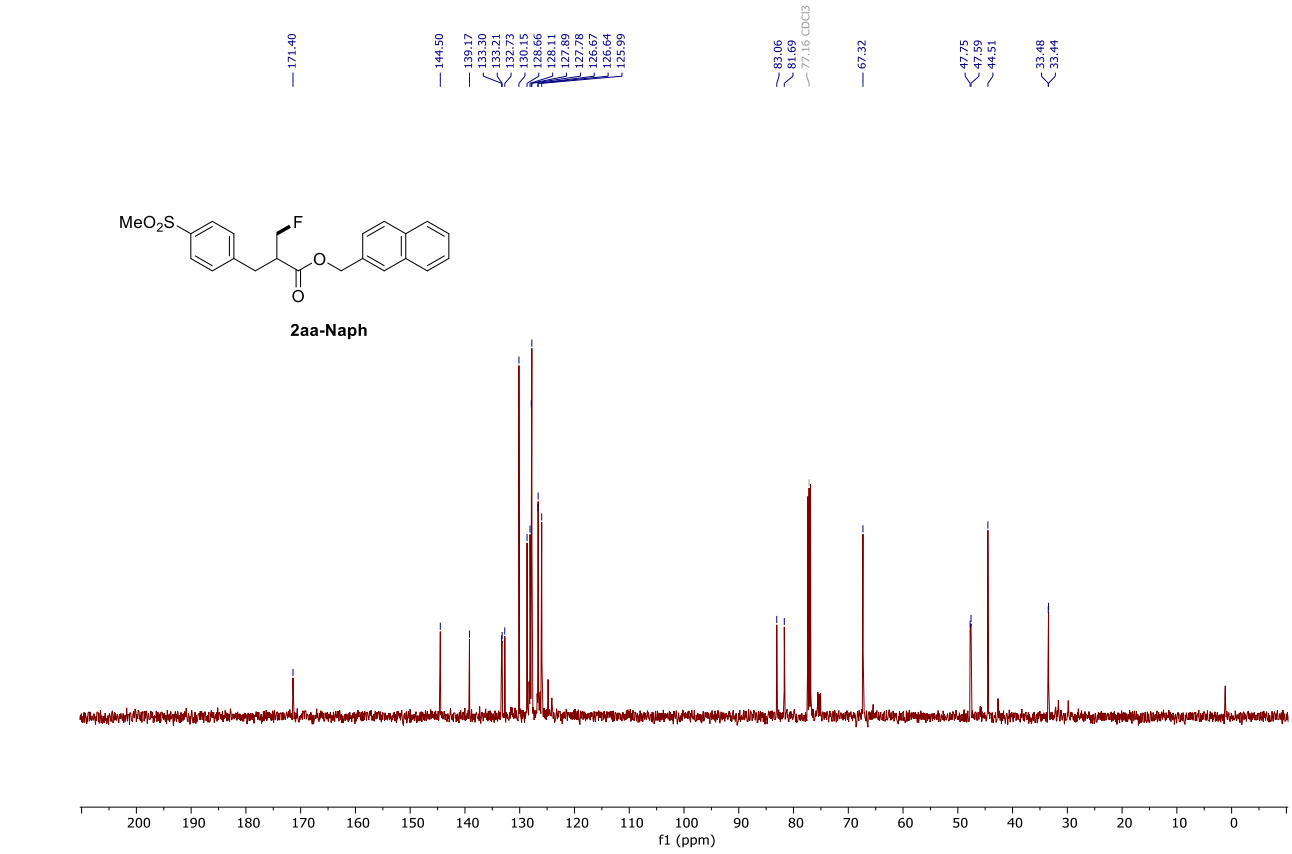

MeO2C
F
O
O
2z-Bn
f1 (ppm)

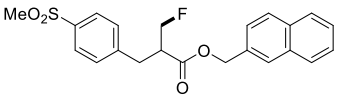

MeO2C
F
O
O

2z-Bn

-224.27
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
f1 (ppm)

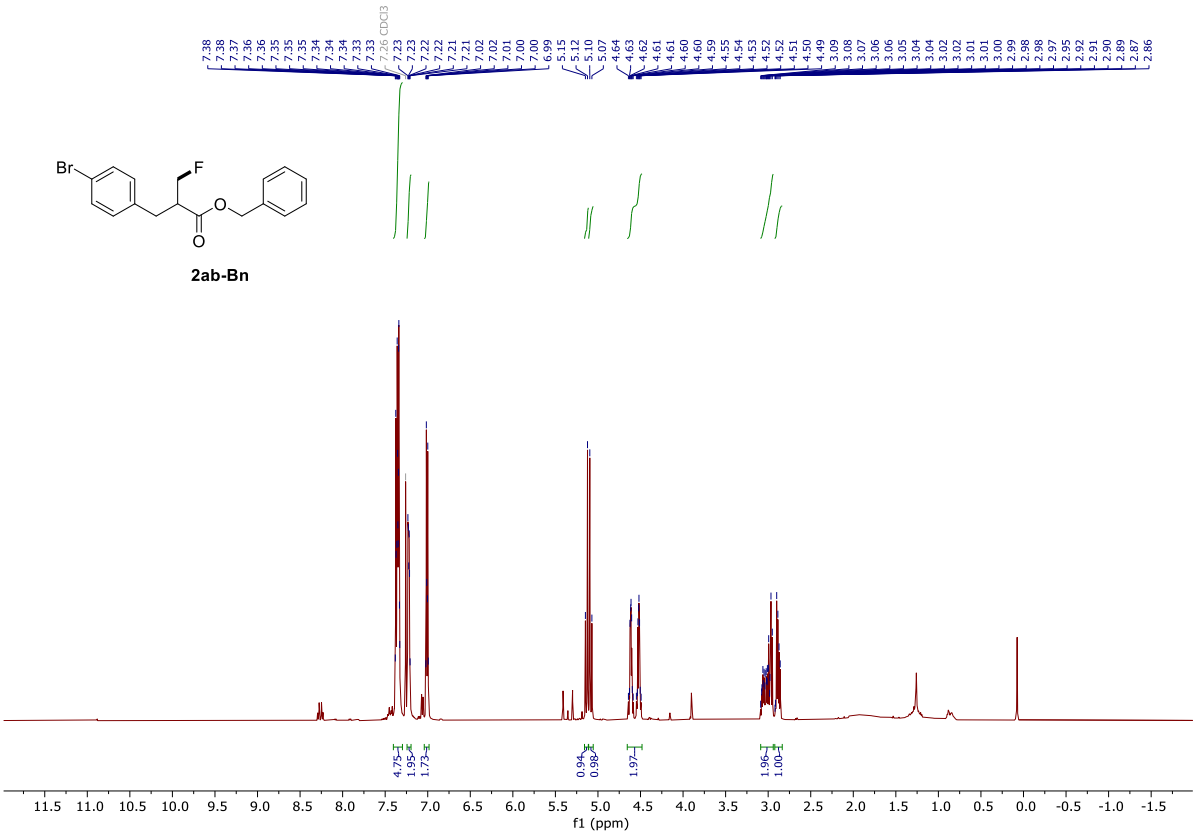

MeO2S
F
O
O
2aa-Naph
f1 (ppm)

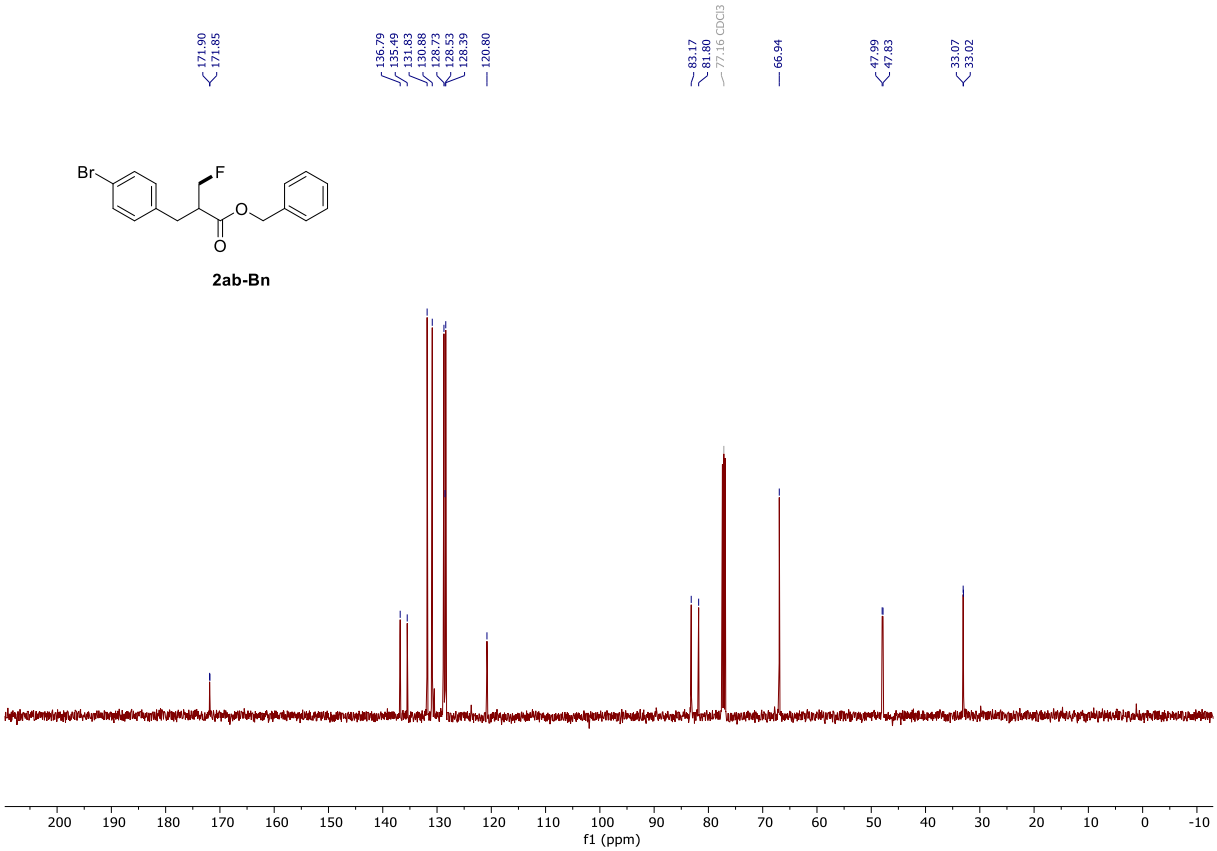

MeO2S
F
O
O
2aa-Naph
f1 (ppm)


MeO2S
F
O
O

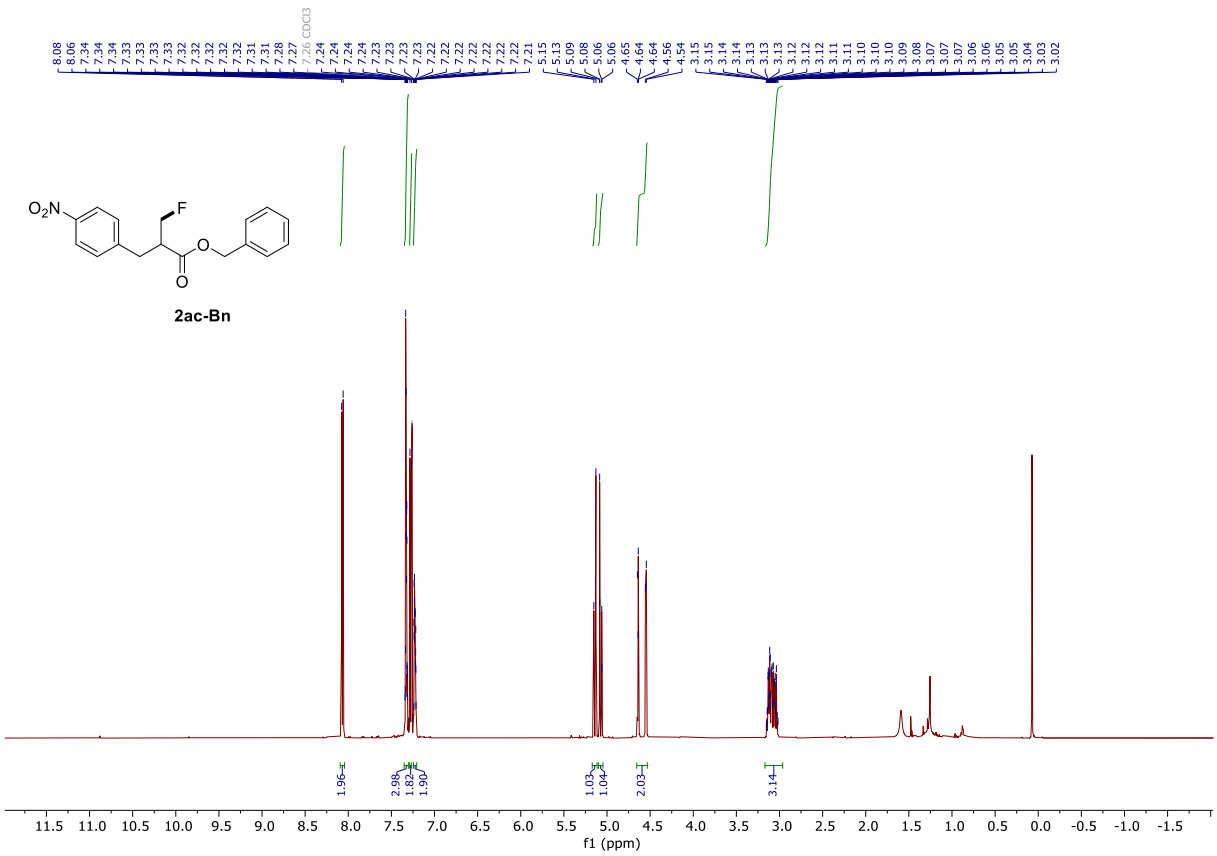
2aa-Naph

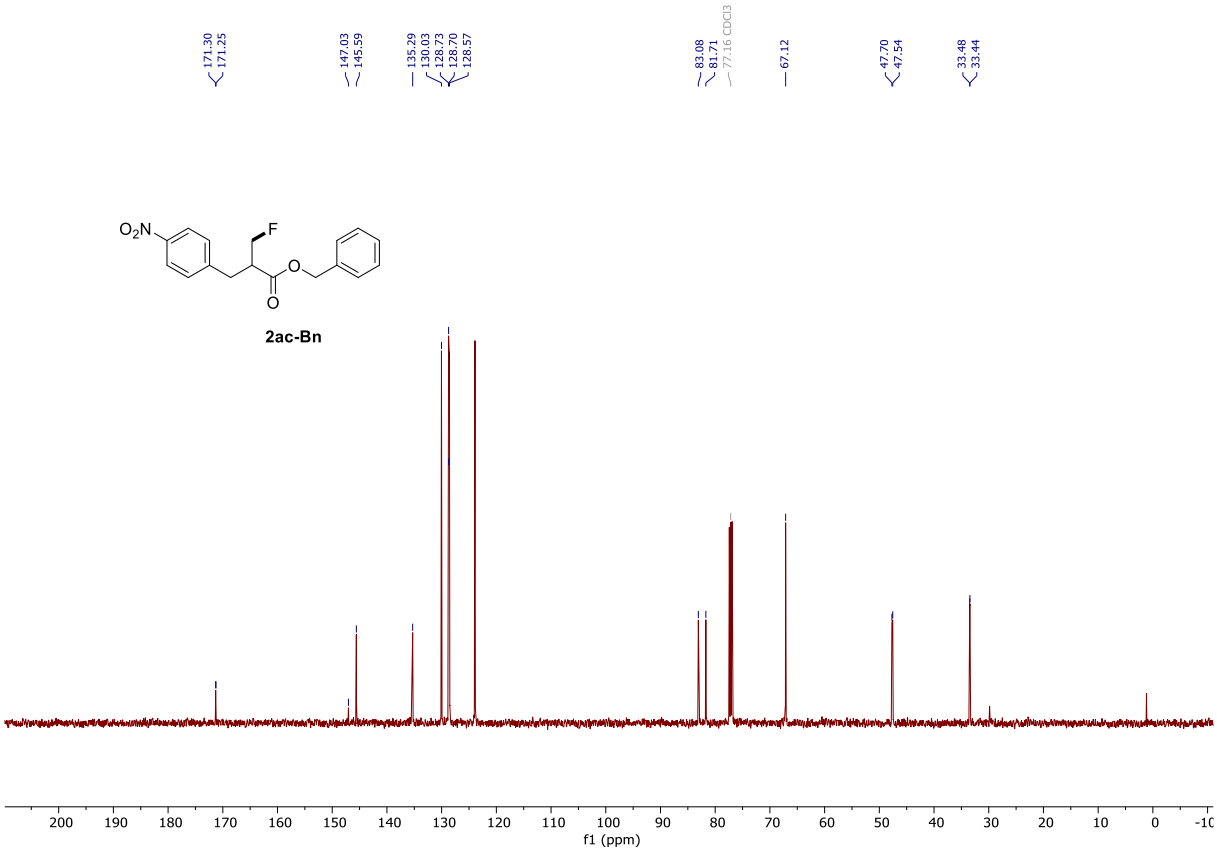
-224.38
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
f1 (ppm)

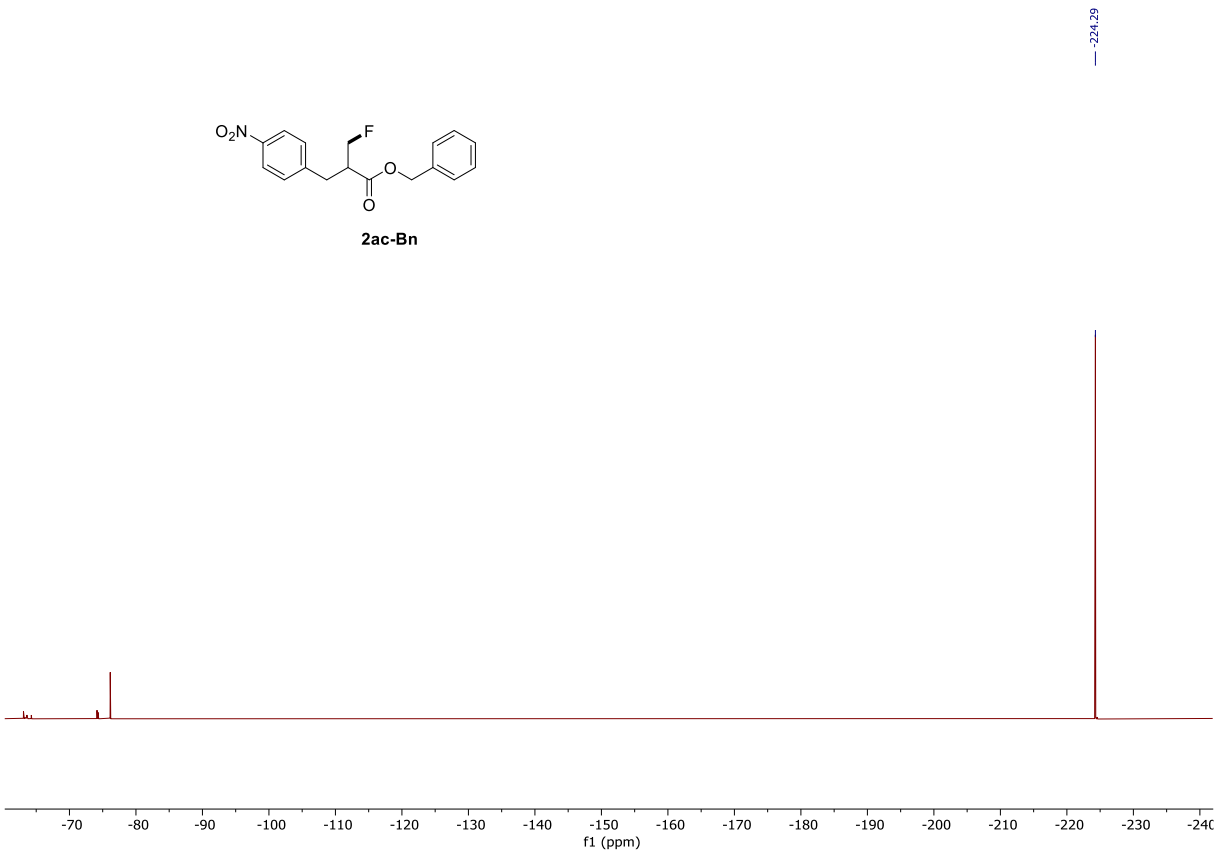

Br
F
O
O
2ab-Bn
f1 (ppm)

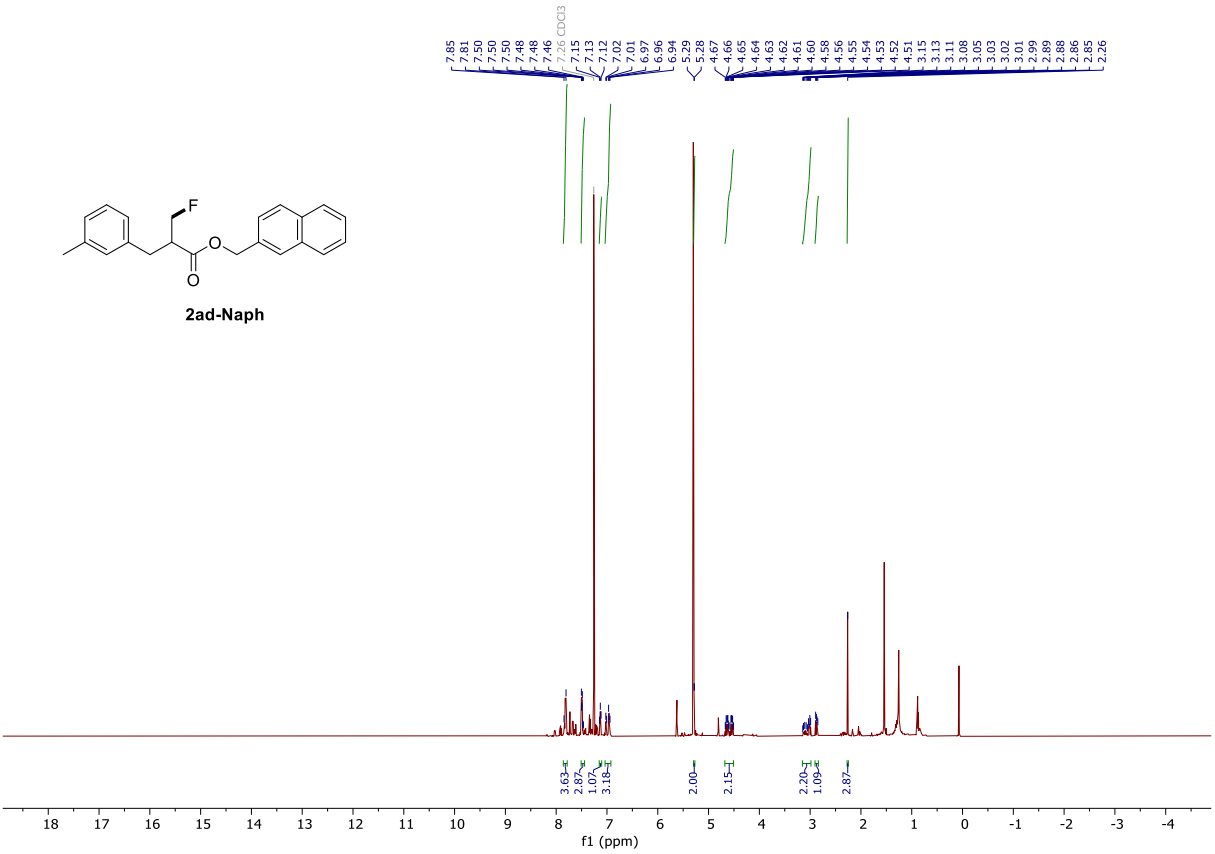

Br
F
O
O
2ab-Bn
f1 (ppm)

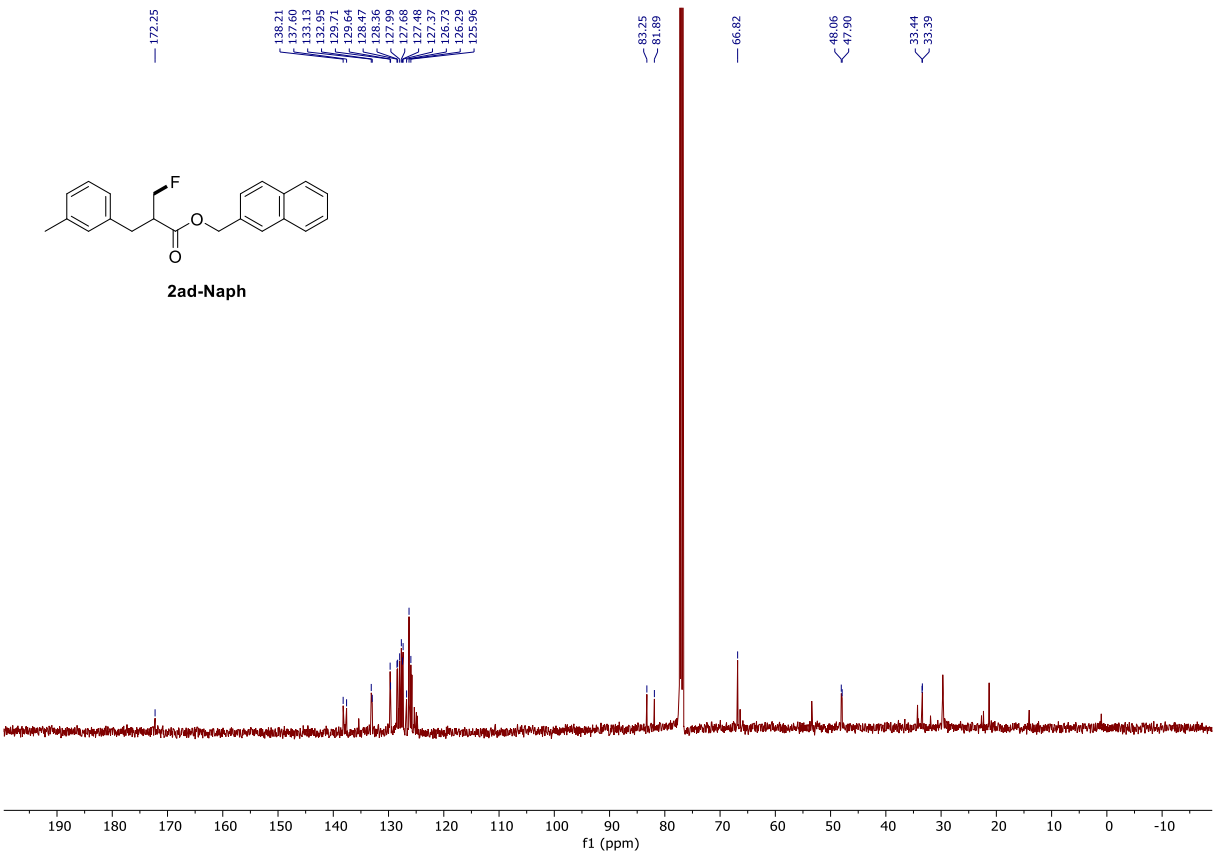

Br
F
O
O
2ab-Bn
-224.22
1.00
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
f1 (ppm)

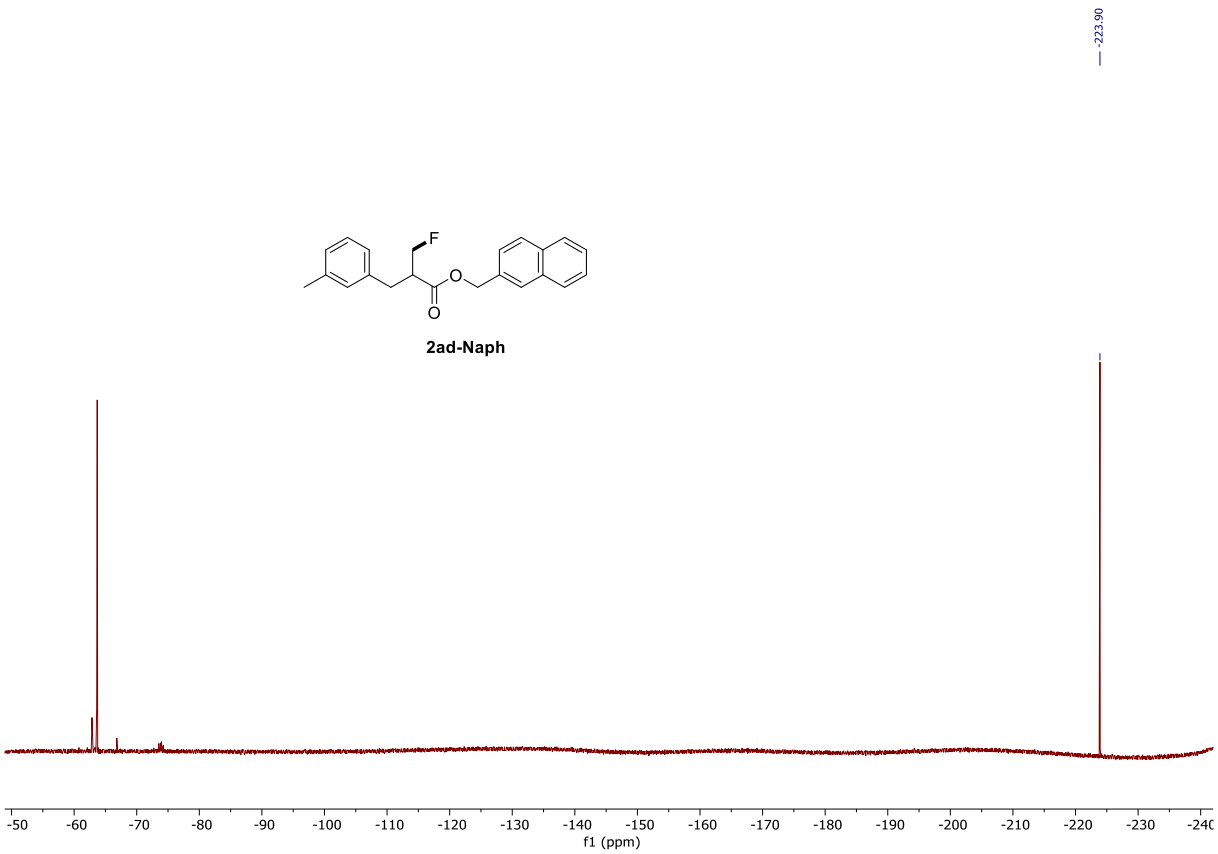

2ac-Bn
f1 (ppm)

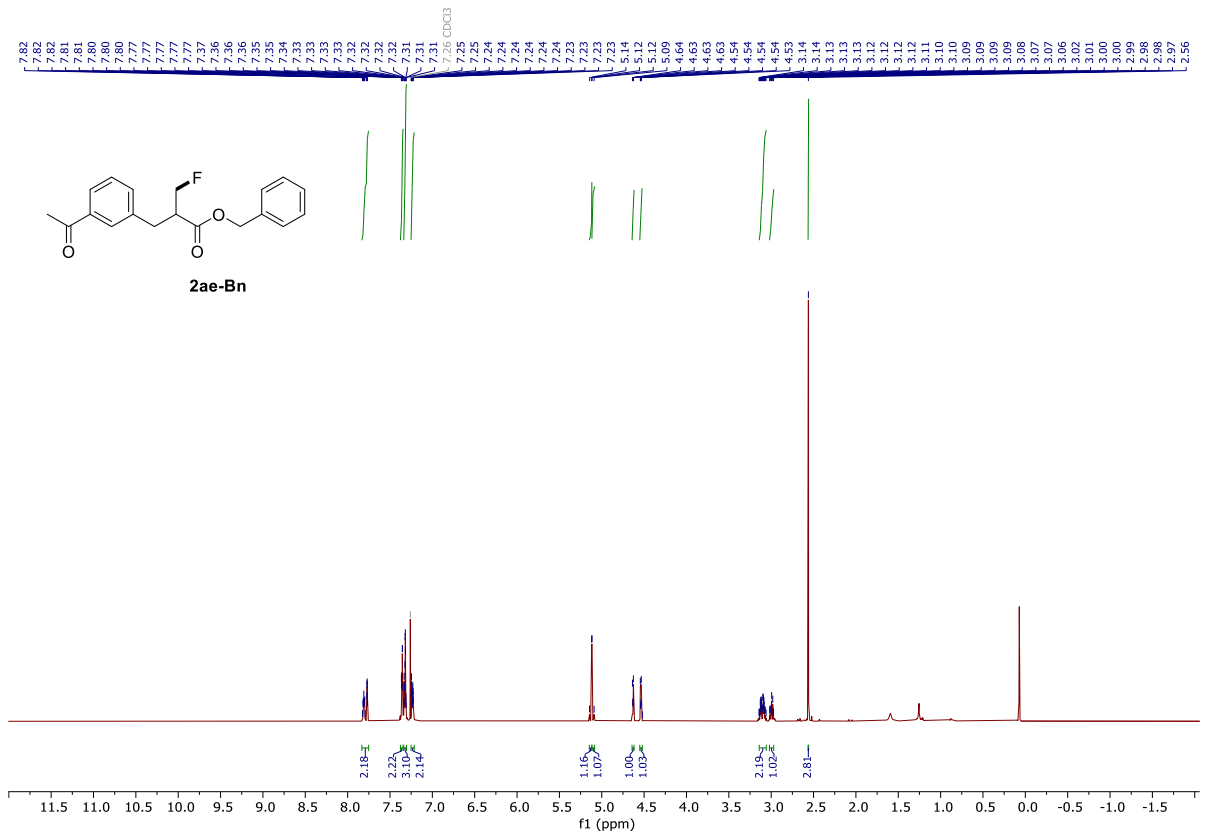

2ac-Bn
f1 (ppm)

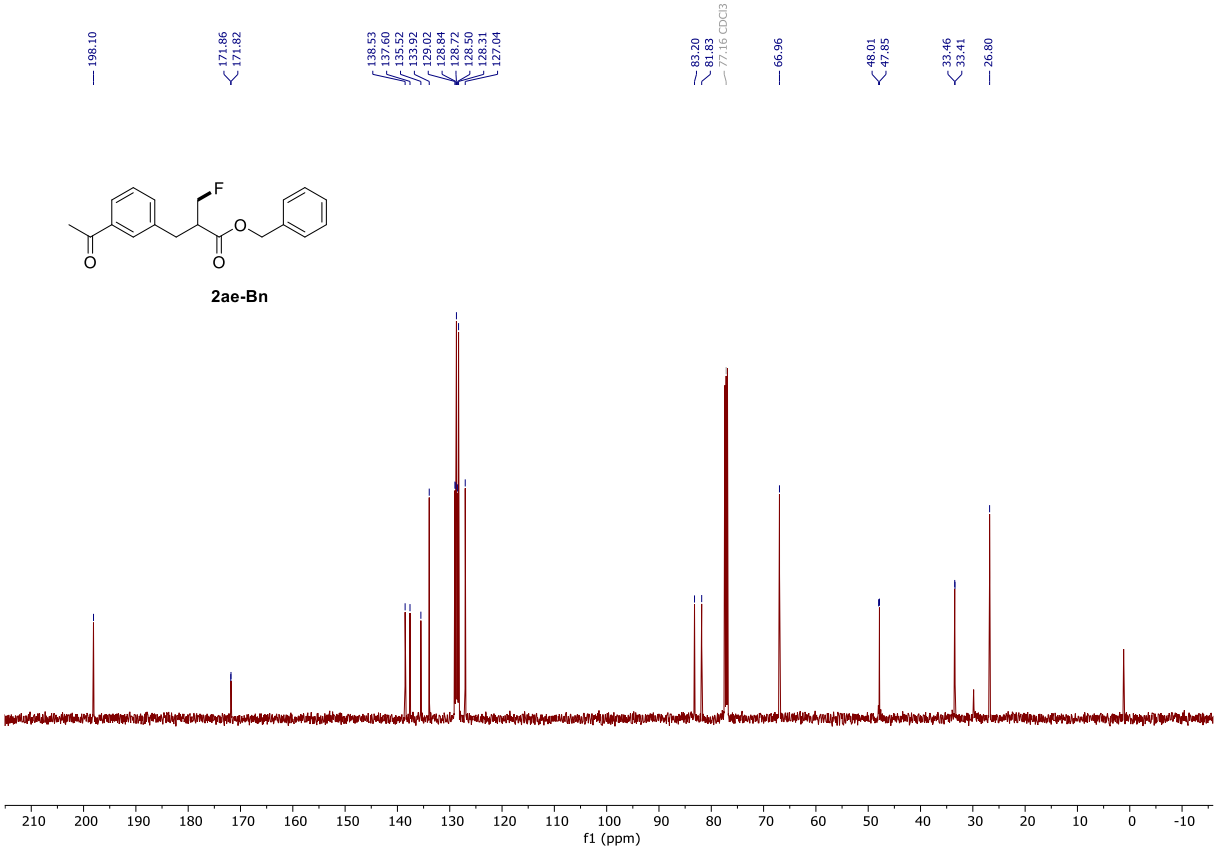

-224.29
O2N
F
O
O
2ac-Bn
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
f1 (ppm)

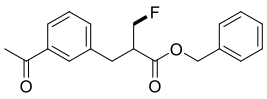

F
O
O
2ad-Naph
7.85
7.81
7.50
7.50
7.50
7.50
7.48
7.48
7.46
7.26 CDCl3
7.15
7.13
7.12
7.02
7.01
6.97
6.96
6.94
5.29
5.28
4.67
4.66
4.65
4.64
4.63
4.62
4.61
4.60
4.58
4.56
4.55
4.54
4.53
4.52
4.51
3.15
3.13
3.11
3.08
3.05
3.03
3.02
3.01
2.99
2.89
2.88
2.86
2.85
2.26
3.63
2.87
1.07
3.18
2.00
2.15
2.20
1.09
2.87
f1 (ppm)


172.25
138.21
137.60
133.13
132.95
129.71
129.64
128.47
128.36
127.99
127.68
127.48
127.37
126.73
126.29
125.96
83.25
81.89
66.82
48.06
47.90
33.44
33.39
F
O
O
2ad-Naph
f1 (ppm)


-223.90
F
O
O
2ad-Naph
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
f1 (ppm)

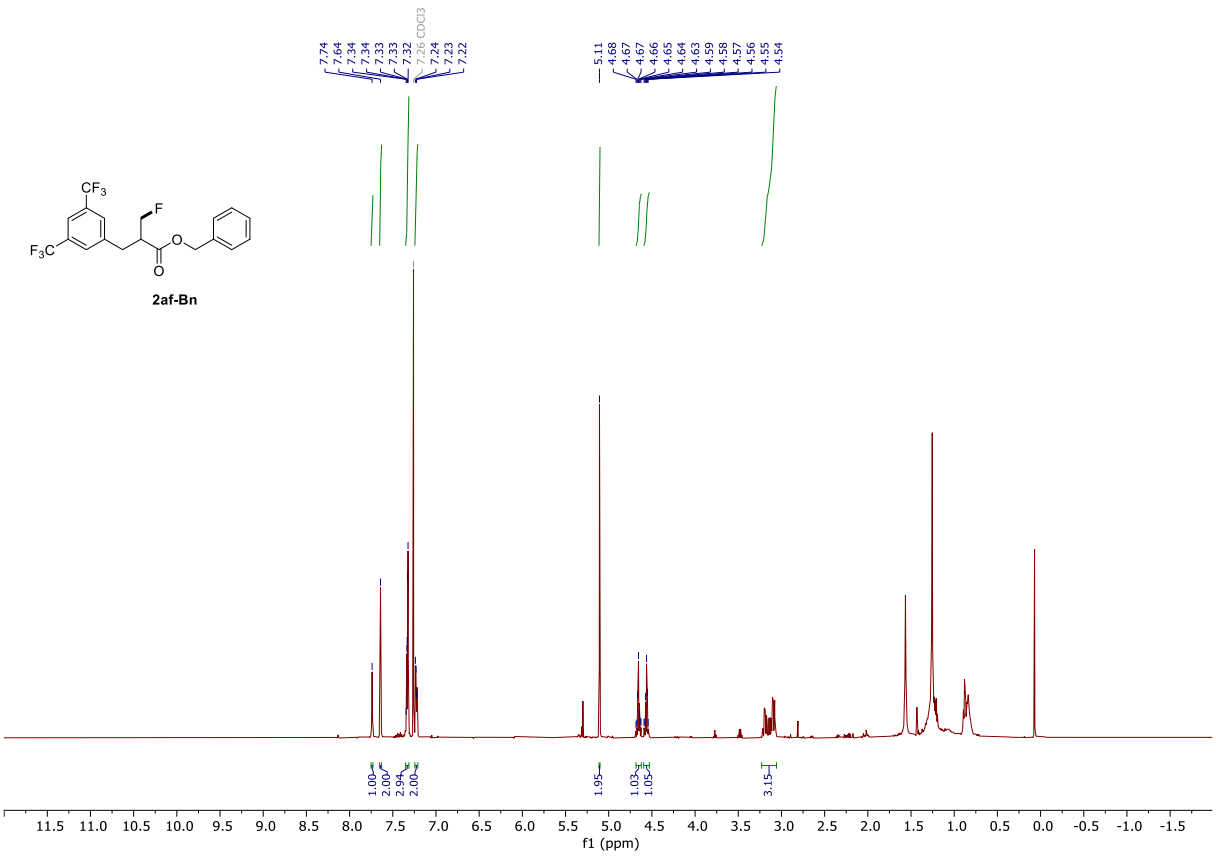

F
O
O
O
2ae-Bn
f1 (ppm)

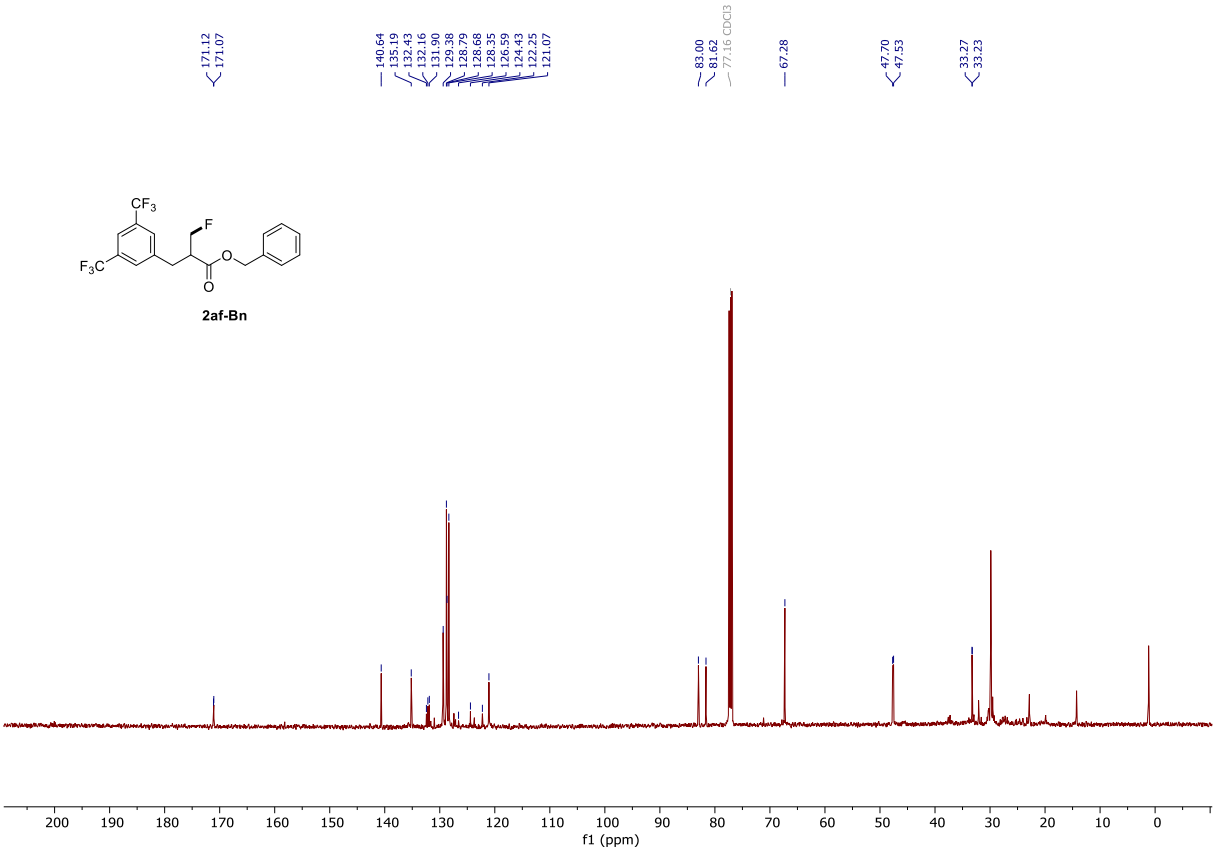

F
O
O
O
2ae-Bn
f1 (ppm)

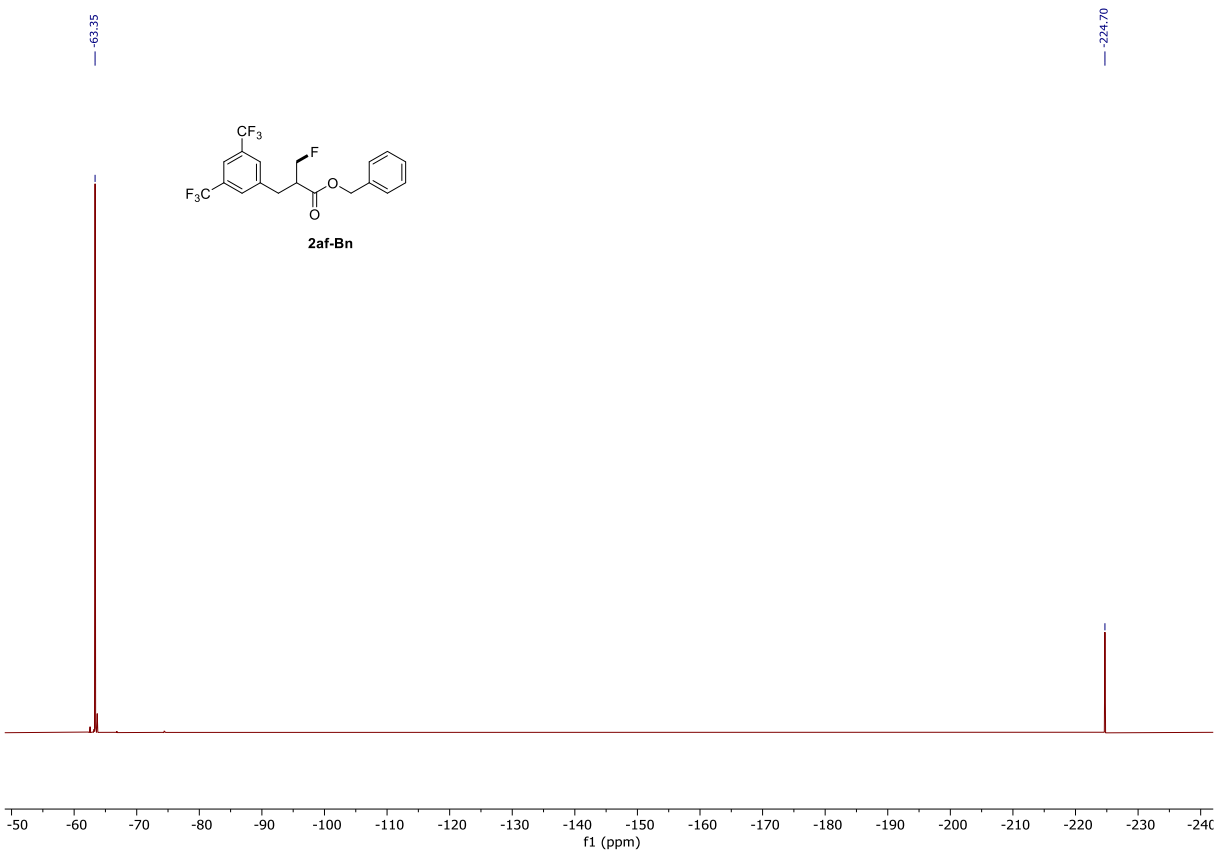

F
O
O

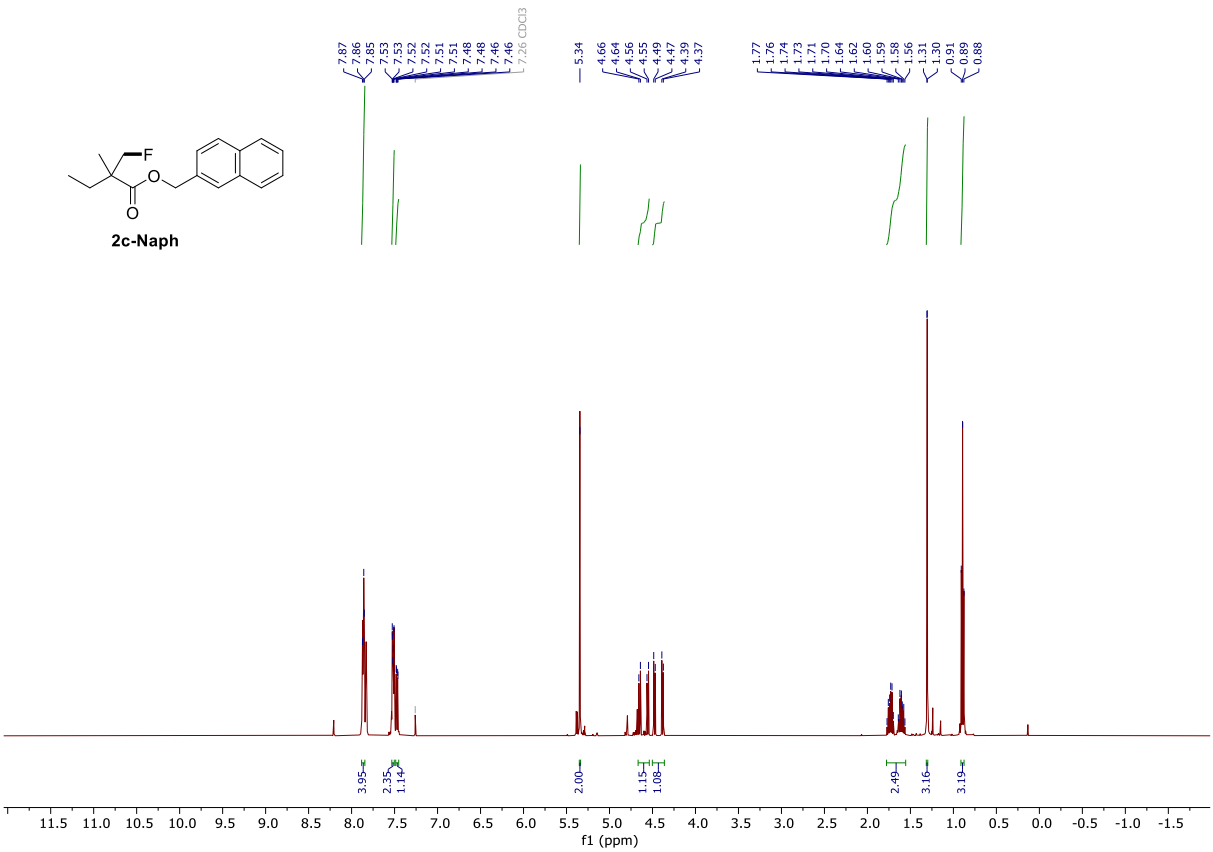
2ae-Bn

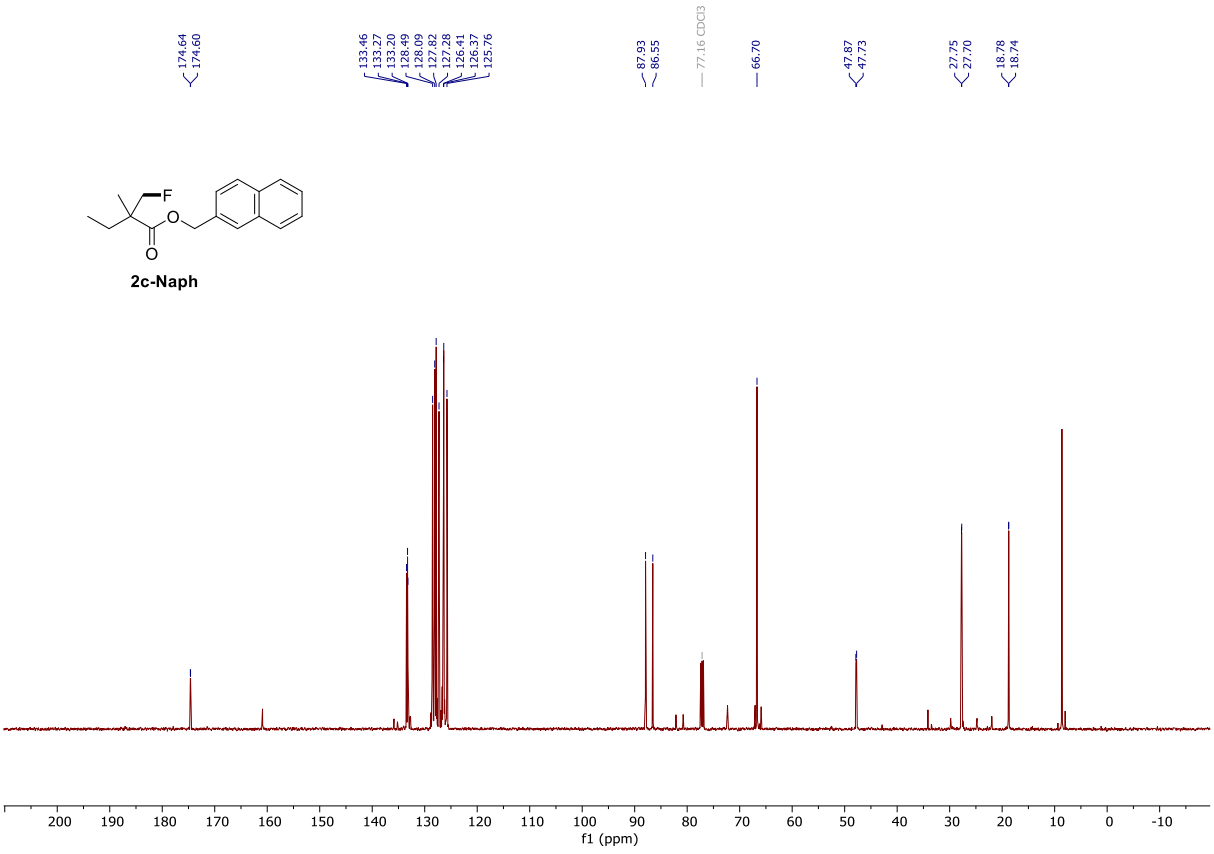
-224.16
-224.26
-224.30
-224.36
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
f1 (ppm)

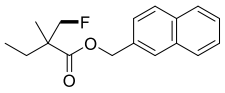

7.74
7.64
7.34
7.34
7.33
7.33
7.32
7.26 CDCl3
7.24
7.23
7.22
5.11
4.68
4.67
4.67
4.66
4.65
4.64
4.63
4.59
4.58
4.57
4.56
4.55
4.54
CF3
F
F3C
O
O
2af-Bn
1.00
2.00
2.94
2.00
1.95
1.03
1.05
3.15
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)


171.12
171.07
140.64
135.19
132.43
132.16
131.90
129.38
128.79
128.68
128.35
126.59
124.43
122.25
121.07
83.00
81.62
77.16 CDCl3
67.28
47.70
47.53
33.27
33.23
CF3
F
F3C
O
O
2af-Bn
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-63.35
-224.70
CF3
F
F3C
O
O
2af-Bn
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
f1 (ppm)


7.87
7.86
7.85
7.53
7.53
7.52
7.52
7.51
7.51
7.48
7.48
7.46
7.46
7.26 CDCl3
5.34
4.66
4.64
4.56
4.55
4.49
4.47
4.39
4.37
1.77
1.76
1.74
1.73
1.71
1.70
1.64
1.62
1.60
1.59
1.58
1.56
1.31
1.30
0.91
0.89
0.88
F
O
O
2c-Naph
3.95
2.35
1.14
2.00
1.15
1.08
2.49
3.16
3.19
f1 (ppm)


174.64
174.60
133.46
133.27
133.20
128.49
128.09
127.82
127.28
126.41
126.37
125.76
87.93
86.55
77.16 CDCl3
66.70
47.87
47.73
27.75
27.70
18.78
18.74
F
O
O
2c-Naph
f1 (ppm)


F
O
O

2c-Naph

-225.87
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
f1 (ppm)