Supporting Information

Pd-catalyzed *ortho* C-H Methylation and Fluorination of Benzaldehydes Using Orthanilic Acids as Transient Directing Groups

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General Information

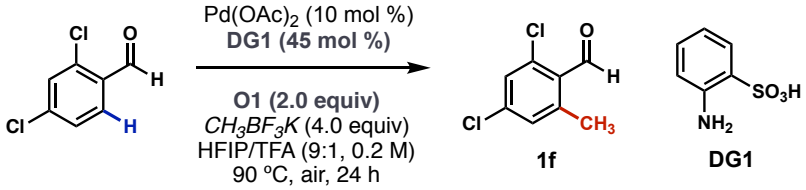
All commercially available reagents and solvents were purchased from Ark Pharm Inc., Chem-Impex Int'l. Inc., Combi-Blocks, Fisher Scientific, Oakwood Chemicals, Sigma Aldrich, Strem Chemicals and TCI America, and were used directly without further purifications. Reactions were monitored by thin layer chromatography (TLC) carried out on 250 μm Merck silica gel plates (60 F254) containing a fluorescent indicator (254 nm). Visualization of the developed TLC plate was performed by irradiation with UV light. Organic solvents were concentrated under reduced pressure on a Büchi rotary evaporator using a water bath (25 ^{o}C). Filtration was performed using either Celite® or Silicycle SiliaFlash P60 silica gel (60 Å pore size, 40 – 63 μm particle size, 230 – 400 mesh). Preparative thin layer chromatography was undertaken using Analtech Uniplate silica gel chromatography plates containing a fluorescent indicator (254 nm) (20x20 cm, 1000 micron). Flash column chromatography was performed using Silicycle SiliaFlash P60 silica gel (60 Å pore size, 40 – 63 μm particle size, 230 – 400 mesh).

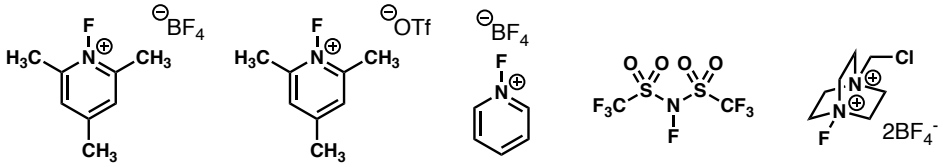
^{1}H NMR spectra were recorded on a Bruker 500 (500 MHz) and are referenced relative to residual $CHCl_3$ (in $CDCl_3$) proton signals at δ 7.26 ppm. Data for ^{1}H spectra are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad, ap = apparent), integration, coupling constant (Hz) and assignment. ^{13}C NMR spectra were recorded on a Bruker 500 (126 MHz) and are referenced relative to residual $CHCl_3$ (in $CDCl_3$) at δ 77.16 ppm. Data for ^{13}C NMR spectra are reported in terms of chemical shift and multiplicity where appropriate. ^{19}F NMR spectra were recorded on a Bruker 300 (282 MHz). Data for ^{19}F NMR spectra are reported in terms of chemical shift and multiplicity where appropriate. IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer with a 30000-200 cm^{-1} diamond and are reported in terms of frequency of absorption (cm^{-1}). High-resolution mass spectra were obtained from Princeton University Mass Spectrometry Facility using an Agilent 6210 TOF LC/MS (Electrospray Ionization). X-ray crystallographic analyses were performed using Bruker SMART APEX DUO diffractometer equipped with a copper or molybdenum X-ray tube on a Bruker Kappa APEX-II CCD diffractometer.

Experimental Procedures and Characterization Data

Benzaldehyde *ortho* C-H Methylation

Control experiments





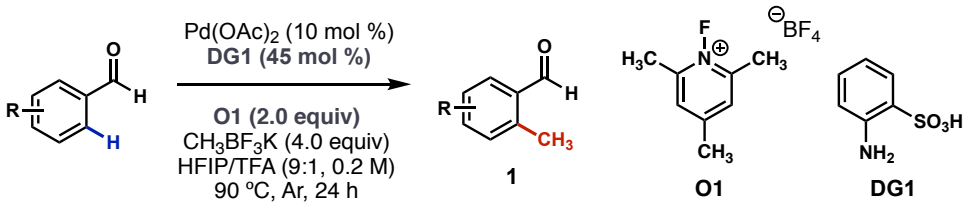
entry	variation from the standard condition	yield of **1f** (%)
1	none	60
2	no $Pd(OAc)_2$	0
3	no DG1	0
4	30 mol % DG1	54
5	60 mol % DG1	58
6	DG9 instead of DG1	20
7	DG10 instead of DG1	4
8	$Pd(TFA)_2$ instead of $Pd(OAc)_2$	58
9	$PdCl_2$ instead of $Pd(OAc)_2$	22
10	**O2** instead of **O1**	34
11	**O3** instead of **O1**	58
12	**O4** instead of **O1**	14
13	**O5** instead of **O1**	10
14	in HFIP/TFA (7:1, 0.2 M)	50
15	in HFIP/TFA (19:1, 0.2 M)	56
16	in HFIP/TFA (9:1, 0.1 M)	48
17	in HFIP/HOAc (9:1, 0.2 M)	10
18	in HFIP/*p*-TsOH (2.0 equiv, 0.2 M)	38
19	at 70 °C	54
20	at 100 °C	56
21	argon instead of air	**68**

Standard procedure for the control experiments

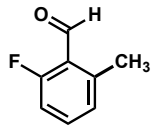
A 10-mL microwave-vial equipped with a stir bar was charged with $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 0.1 equiv), orthanilic acid (DG1) (7.8 mg, 0.045 mmol, 0.45 equiv), 1-fluoro-2,4,6-trimethylpyridinium tetrafluoroborate (O1) (45.4 mg, 0.20 mmol, 2.0 equiv), potassium methyl trifluoroborate (48.8 mg, 0.40 mmol, 4.0 equiv) and 2,4-dichlorobenzaldehyde (17.5 mg, 0.10 mmol, 1.0 equiv), followed by the addition of hexafluoroisopropanol (HFIP) (0.45 mL) and trifluoroacetic acid (TFA) (0.05 mL). The vial was sealed with a PTFE-lined aluminum cap, stirred at rt for 10 min before being heated in a pie-block at 90 °C under stirring for 24 h. After cooling to rt, the reaction mixture was filtered through a pad of Celite® and washed with EtOAc (10 mL). The filtrate was then concentrated *in vacuo* before CH_2Br_2 (6.95 µL, 0.1 mmol) was added. The yield of the desired product was determined by crude ^1H NMR using CH_2Br_2 as the internal standard.

Note: All control experiments were conducted on a 0.1 mmol scale, and changes were made based on the "standard condition" described above.

General procedure for the substrate scope experiments (using **1a** as an example)

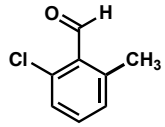


A 10-mL microwave-vial equipped with a stir bar was charged with $Pd(OAc)_2$ (6.7 mg, 0.03 mmol, 0.1 equiv), orthanilic acid (DG1**)** (23.5 mg, 0.135 mmol, 0.45 equiv), 1-fluoro-2,4,6-trimethylpyridinium tetrafluoroborate (O1) (136.2 mg, 0.60 mmol, 2.0 equiv), potassium methyl trifluoroborate (146.3 mg, 1.20 mmol, 4.0 equiv) and 2-fluorobenzaldehyde (31.6 µL, 0.30 mmol, 1.0 equiv), followed by the addition of hexafluoroisopropanol (HFIP) (1.35 mL) and trifluoroacetic acid (TFA) (0.15 mL). The vial was sealed with a PTFE-lined cap, sparged with argon gas and stirred at rt for 15 min before being heated in a pie-block at 90 °C under stirring for 24 h. After cooling to rt, the reaction mixture was filtered through a pad of silica gel and washed with hexane/EtOAc (1:1, 60 mL). The filtrate was then concentrated *in vacuo* and the resulting residue was purified by preparative thin layer chromatography using hexane/acetone (10:1) as the developing solvent.



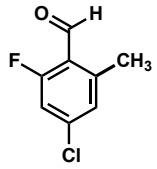
1a

This compound was synthesized from 2-fluorobenzaldehyde using the standard condition and purified by preparative thin layer chromatography using hexane/acetone (10:1) as the developing solvent. Light yellow liquid (29.4 mg, 71%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.55 (s, 1H), 7.43 (td, J = 8.3, 5.8 Hz, 1H), 7.08 – 6.98 (m, 2H), 2.62 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 189.42, 189.33, 167.49, 165.44, 142.68, 135.16, 135.08, 127.69, 127.67, 122.67, 122.63, 114.01, 113.83, 21.23, 21.21. ^{19}F NMR (282 MHz, $CDCl_3$): δ -121.81 (dd, J = 10.5, 5.8 Hz). MS-ESI m/z 137.0401 ($[M - H]^-$, C_8H_6FO, calc. 137.0408). IR (neat): 2967, 2928, 2878, 2778, 1698, 1613, 1575, 1473, 1413, 1382, 1296, 1246.



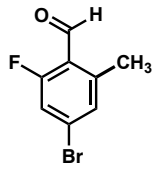
1b

This compound was synthesized from 2-chlorobenzaldehyde using the standard condition and purified by preparative thin layer chromatography using hexane/acetone (10:1) as the developing solvent. Off-white solid (28.3 mg, 61%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.65 (s, 1H), 7.35 (t, J = 7.7 Hz, 1H), 7.30 (dd, J = 8.0, 1.4 Hz, 1H), 7.17 – 7.14 (m, 1H), 2.58 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.66, 142.68, 139.22, 133.70, 130.86, 130.84, 128.46, 21.45. MS-ESI m/z 153.0108 ($[M - H]^-$, C_8H_6ClO, calc. 153.0113). IR (neat): 3064, 2967, 2929, 2868, 2768, 1697, 1591, 1565, 1455, 1401, 1382, 1282.



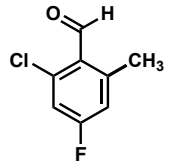
1c

This compound was synthesized from 4-chloro-2-fluorobenzaldehyde using the standard condition and purified by preparative thin layer chromatography using hexane/acetone (10:1) as the developing solvent. White solid (22.3 mg, 43%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.45 (s, 1H), 7.08 – 6.99 (m, 2H), 2.60 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.19, 188.10, 167.21, 165.14, 144.02, 144.01, 140.48, 140.38, 128.06, 128.03, 121.18, 121.13, 114.84, 114.64, 21.22, 21.20. ^{19}F NMR (282 MHz, $CDCl_3$): δ -119.41 (d, J = 10.4 Hz). MS-ESI m/z 171.0016 ($[M - H]^-$, C_8H_5ClFO, calc. 171.0018). IR (neat): 3084, 2930, 2878, 2780, 1698, 1603, 1565, 1446, 1401, 1382, 1294, 1266.



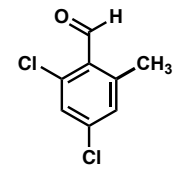
1d

This compound was synthesized from 4-bromo-2-fluorobenzaldehyde using the standard condition and purified by preparative thin layer chromatography using hexane/EtOAc (10:1) as the developing solvent. Yellow liquid (44.2 mg, 68%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.46 (s, 1H), 7.23 – 7.20 (m, 2H), 2.60 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.36, 188.27, 166.90, 164.82, 144.02, 144.01, 131.00, 130.97, 128.74, 128.64, 121.50, 121.46, 117.77, 117.58, 21.08, 21.06. ^{19}F NMR (282 MHz, $CDCl_3$): δ -116.81 – -122.94 (m). MS-ESI m/z 214.9509 ($[M - H]^-$, C_8H_5BrFO, calc. 214.9502). IR (neat): 3082, 2877, 2779, 1695, 1597, 1562, 1442, 1399, 1381, 1259.



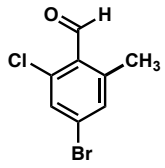
1e

This compound was synthesized from 2-chloro-4-fluorobenzaldehyde using the standard condition and purified by preparative thin layer chromatography using hexane/acetone (10:1) as the developing solvent. Light yellow solid (22.3 mg, 43%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.57 (s, 1H), 7.06 (dd, J = 8.0, 2.6 Hz, 1H), 6.89 (dd, J = 9.2, 2.6 Hz, 1H), 2.60 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.12, 165.31, 163.25, 145.88, 145.80, 141.11, 141.02, 127.54, 127.51, 118.20, 118.04, 116.02, 115.82, 21.84, 21.83. ^{19}F NMR (282 MHz, $CDCl_3$): δ -101.37 – -105.99 (m). MS-ESI m/z 173.0164 ($[M + H]^+$, C_8H_7ClFO, calc. 173.0164). IR (neat): 3079, 2893, 2781, 1693, 1594, 1575, 1461, 1429, 1394, 1381, 1290, 1260.



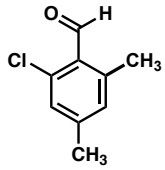
1f

This compound was synthesized from 2,4-chlorobenzaldehyde using the standard condition and purified by preparative thin layer chromatography using hexane/acetone (10:1) as the developing solvent. White solid (35.1 mg, 62%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.57 (s, 1H), 7.33 (d, J = 2.0 Hz, 1H), 7.18 – 7.15 (m, 1H), 2.57 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.49, 144.13, 139.98, 139.30, 131.00, 129.20, 128.28, 21.43. MS-ESI m/z 186.9724 ($[M - H]^-$, $C_8H_5Cl_2O$, calc. 186.9723). IR (neat): 3083, 2878, 1730, 1700, 1584, 1549, 1435, 1380, 1292.



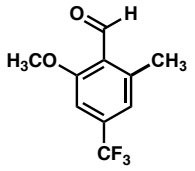
1g

This compound was synthesized from 4-bromo-2-chlorobenzaldehyde using the standard condition and purified by preparative thin layer chromatography using hexane/EtOAc (10:1) as the developing solvent. Light yellow solid (51.1 mg, 73%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.57 (s, 1H), 7.52 – 7.47 (m, 1H), 7.34 (s, 1H), 2.56 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 191.63, 144.11, 139.85, 133.95, 131.10, 129.60, 127.76, 21.31. MS-ESI m/z 230.9218 ([M − H]$^-$, C_8H_5BrClO, calc. 230.9218). IR (neat): 3071, 2934, 2876, 2772, 1698, 1576, 1544, 1429, 1374, 1277.



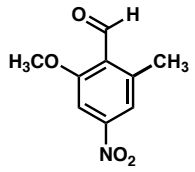
1h

This compound was synthesized from 2-chloro-4-methylbenzaldehyde using the standard condition and purified by preparative thin layer chromatography using hexane/EtOAc (10:1) as the developing solvent. White solid (32.7 mg, 65%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.60 (s, 1H), 7.13 (d, J = 1.5 Hz, 1H), 6.96 (d, J = 1.6 Hz, 1H), 2.56 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 192.31, 145.06, 142.67, 139.46, 131.79, 128.95, 128.28, 21.53, 21.51. MS-ESI m/z 169.0412 ([M + H]$^+$, $C_9H_{10}ClO$, calc. 169.0415). IR (neat): 2975, 2927, 2861, 2764, 1690, 1604, 1552, 1435, 1377.



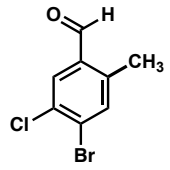
1i

This compound was synthesized from 2-methoxy-4-trifluoromethylbenzaldehyde using the standard condition and purified by preparative thin layer chromatography using hexane/acetone (10:1) as the developing solvent. White solid (26.2 mg, 40%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.64 (s, 1H), 7.07 (d, J = 1.6 Hz, 1H), 7.05 (s, 1H), 3.96 (s, 3H), 2.60 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 191.81, 163.00, 143.02, 135.70, 135.44, 135.18, 134.93, 126.70, 125.64, 124.53, 122.36, 120.84, 120.81, 120.78, 120.75, 120.19, 106.13, 106.10, 106.07, 106.03, 56.24, 21.61. ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.59. MS-ESI m/z 219.0617 ([M + H]$^+$, $C_{10}H_{10}F_3O_2$, calc. 219.0627). IR (neat): 2985, 2948, 2928, 1683, 1616, 1583, 1481, 1458, 1434, 1403, 1385, 1342, 1301.



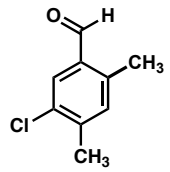
1j

This compound was synthesized from 2-methoxy-4-nitrobenzaldehyde using the standard condition and purified by preparative thin layer chromatography using hexane/EtOAc (5:1) as the developing solvent. Yellow solid (38.6 mg, 66%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.64 (s, 1H), 7.75 – 7.62 (m, 2H), 4.01 (s, 3H), 2.64 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 191.40, 163.15, 150.60, 143.63, 127.51, 118.76, 104.30, 56.62, 21.71. MS-ESI m/z 196.0594 ($[M + H]^+$, $C_9H_{10}NO_4$, calc. 196.0604). IR (neat): 3113, 2885, 1695, 1589, 1511, 1457, 1407, 1355, 1306, 1283.



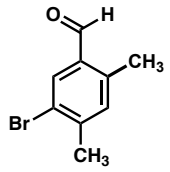
1k

This compound was synthesized from 4-bromo-3-chlorobenzaldehyde using the standard condition and purified by preparative thin layer chromatography using hexane/acetone (10:1) then hexane/DCM (1:1) as the developing solvent. White solid (35.7 mg, 51%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.16 (s, 1H), 7.83 (s, 1H), 7.56 (s, 1H), 2.61 (d, J = 0.8 Hz, 3H).^{13}C NMR (126 MHz, $CDCl_3$): δ 190.49, 139.98, 137.02, 134.22, 133.00, 132.78, 128.87, 18.69. MS-ESI m/z 230.9213 ($[M - H]^-$, C_8H_5BrClO, calc. 230.9218). IR (neat): 3080, 2867, 2759, 1689, 1577, 1543, 1447, 1378, 1357.



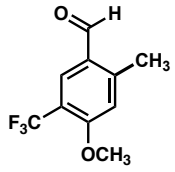
1l

This compound was synthesized from 3-chloro-4-methylbenzaldehyde using the standard condition and purified by preparative thin layer chromatography using hexane/acetone (10:1) then hexane/DCM (1:1) as the developing solvent. White solid (21.8 mg, 43%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.16 (s, 1H), 7.75 (s, 1H), 7.13 (s, 1H), 2.60 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 191.19, 142.52, 138.91, 134.49, 133.39, 132.62, 132.12, 20.45, 18.93. MS-ESI m/z 169.0407 ($[M + H]^+$, $C_9H_{10}ClO$, calc. 169.0415). IR (neat): 2976, 2922, 2878, 2766, 1682, 1600, 1485, 1458, 1439, 1403, 1384, 1368.



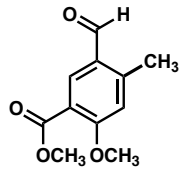
1m

This compound was synthesized from 3-bromo-4-methylbenzaldehyde using the standard condition and purified by preparative thin layer chromatography using hexane/acetone (10:1) then hexane/DCM (1:1) as the developing solvent. Off-white solid (25.6 mg, 40%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.14 (s, 1H), 7.92 (s, 1H), 7.13 (s, 1H), 2.58 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.01, 144.33, 139.55, 135.55, 134.32, 133.59, 122.53, 23.27, 19.02. MS-ESI m/z 212.9904 ($[M + H]^+$, $C_9H_{10}BrO$, calc. 212.9910). IR (neat): 2974, 2919, 2875, 2768, 1689, 1593, 1480, 1455, 1381, 1366, 1244.



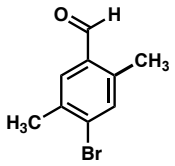
1n

This compound was synthesized from 4-methoxy-3-trifluoromethylbenzaldehyde using the standard condition and purified by preparative thin layer chromatography using hexane/EtOAc (5:1) as the developing solvent. Off-white solid (41.2 mg, 63%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.13 (s, 1H), 8.01 (s, 1H), 6.84 (s, 1H), 3.98 (s, 3H), 2.72 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 190.29, 160.99, 160.98, 160.97, 147.62, 131.90, 131.86, 131.82, 131.78, 126.89, 126.43, 124.27, 122.11, 119.94, 117.62, 117.37, 117.11, 116.86, 114.82, 56.40, 20.26. ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.64. MS-ESI m/z 219.0623 ($[M + H]^+$, $C_{10}H_{10}F_3O_2$, calc. 219.0627). IR (neat): 3076, 2963, 2927, 2854, 2746, 1696, 1621, 1561, 1510, 1471, 1426, 1392, 1311, 1268.



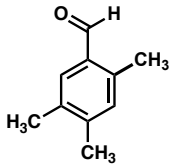
1o

This compound was synthesized from methyl 5-formyl-2-methoxybenzoate using the standard condition *with the exception of using EtOAc as the solvent in the filtration step*, and purified by preparative thin layer chromatography using hexane/acetone/DCM (2:1:1) as the developing solvent. White solid (23.7 mg, 38%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.10 (s, 1H), 8.29 (s, 1H), 6.82 (s, 1H), 3.98 (s, 3H), 3.90 (s, 3H), 2.71 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 190.89, 165.45, 162.81, 147.63, 137.73, 127.20, 117.91, 114.98, 56.49, 52.30, 20.65. MS-ESI m/z 209.0810 ($[M + H]^+$, $C_{11}H_{13}O_4$, calc. 209.0808). IR (neat): 2956, 2848, 2755, 1737, 1683, 1607, 1554, 1501, 1473, 1437, 1378, 1285, 1261.



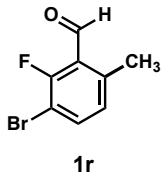
1p

This compound was synthesized from 4-bromo-3-methylbenzaldehyde using the standard condition and purified by preparative thin layer chromatography using hexane/acetone (10:1) then hexane/DCM (1:1) as the developing solvent. White solid (26.2 mg, 41%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.19 (s, 1H), 7.62 (s, 1H), 7.46 (s, 1H), 2.60 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 192.02, 139.43, 136.32, 135.61, 133.74, 133.20, 131.49, 22.41, 18.72. MS-ESI m/z 210.9765 ($[M - H]^-$, C_9H_8BrO, calc. 210.9764). IR (neat): 2923, 2863, 2723, 1687, 1595, 1547, 1479, 1445, 1383, 1284.



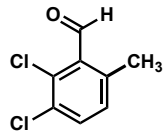
1q

This compound was synthesized from 3,4-dimethylbenzaldehyde using the standard condition and purified by preparative thin layer chromatography using hexane/EtOAc (10:1) as the developing solvent. Colorless liquid (16.4 mg, 37%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.19 (s, 1H), 7.55 (s, 1H), 7.03 (s, 1H), 2.60 (s, 3H), 2.29 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 192.73, 143.58, 138.23, 134.75, 133.30, 133.17, 132.22, 20.15, 19.24, 19.05. MS-ESI m/z 149.0953 ($[M + H]^+$, $C_{10}H_{13}O$, calc. 149.0961). IR (neat): 2925, 2865, 1694, 1613, 1558, 1503, 1452, 1385, 1259.



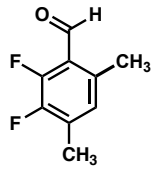
1r

This compound was synthesized from 3-bromo-2-fluorobenzaldehyde using the standard condition and purified by preparative thin layer chromatography using hexane/acetone (10:1) as the developing solvent. White solid (44.3 mg, 68%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.51 (d, J = 0.7 Hz, 1H), 7.63 (dd, J = 8.2, 7.1 Hz, 1H), 7.05 – 6.86 (m, 1H), 2.58 (d, J = 0.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 188.62, 188.54, 163.48, 161.43, 141.83, 138.05, 138.03, 128.61, 128.58, 123.71, 123.65, 107.00, 106.83, 20.96, 20.94. ^{19}F NMR (282 MHz, $CDCl_3$): δ -115.71 (d, J = 7.2 Hz). MS-ESI m/z 214.9496 ($[M - H]^-$, C_8H_5BrFO, calc. 214.9513). IR (neat): 2964, 2928, 2892, 2787, 1698, 1684, 1598, 1550, 1473, 1440, 1391, 1378, 1280.



1s

This compound was synthesized from 2,3-dichlorobenzaldehyde using the standard condition and purified by preparative thin layer chromatography using hexane/toluene (2:1) as the developing solvent. Light yellow solid (40.3 mg, 71%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.60 (s, 1H), 7.51 (d, J = 8.3 Hz, 1H), 7.12 (d, J = 8.2 Hz, 1H), 2.54 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 192.21, 140.63, 136.60, 133.93, 132.77, 131.63, 131.26, 20.99. MS-ESI m/z 186.9722 ($[M - H]^-$, $C_8H_5Cl_2O$, calc. 186.9723). IR (neat): 3073, 2929, 2877, 1687, 1548, 1446, 1377, 1359, 1272.

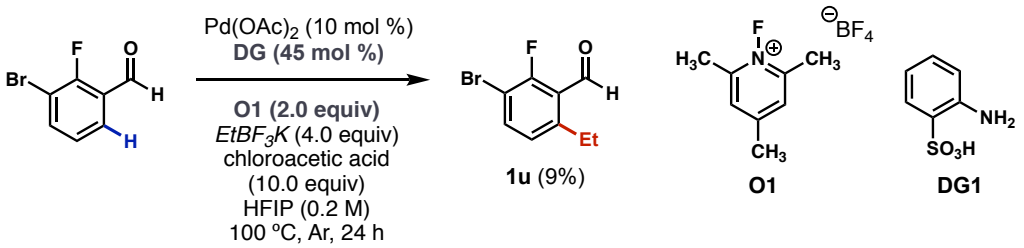


1t

This compound was synthesized from 2,3-difluoro-4-methylbenzaldehyde using the standard condition and purified by preparative thin layer chromatography using hexane/EtOAc (10:1) as the developing solvent. Yellow liquid (31.6 mg, 62%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.45 (s, 1H), 6.83 (d, J = 6.3 Hz, 1H), 2.53 (s, 3H), 2.33 (d, J = 2.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 187.85, 187.82, 187.77, 187.74, 154.90, 154.80, 152.85, 152.74, 147.99, 147.89, 146.04, 145.94, 135.82, 135.78, 133.15, 133.13, 133.04, 133.02, 128.50, 128.47, 128.45, 121.40, 121.38, 20.40, 20.38, 14.84, 14.82, 14.80. ^{19}F NMR (282 MHz, $CDCl_3$): δ -145.27 (dd, J = 19.8, 6.2 Hz), -147.73 (dd, J = 19.5, 2.3 Hz). MS-ESI m/z 171.0606 ($[M + H]^+$, $C_9H_9F_2O$, calc. 171.0616). IR (neat): 2930, 2887, 2781, 1694, 1633, 1570, 1501, 1402, 1387, 1317, 1292.

Preliminary studies on benzaldehyde *ortho* C-H alkylation

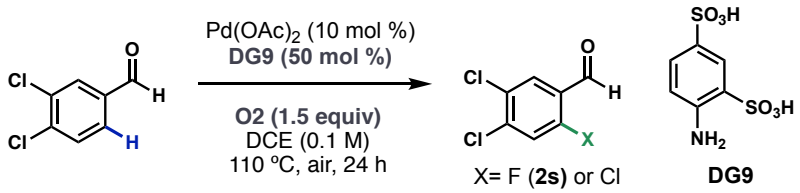
Initial attempts to perform *ortho* C-H alkylation of benzaldehydes using β-hydrogen-containing alkylating reagents were plagued by the rapid generation of Pd black upon stirring the reaction mixture at room temperature. This is presumably because Pd(II) quickly undergoes β-hydride elimination under such acidic conditions after transmetalating with potassium alkyl trifluoroborates. Replacing TFA with a milder acid, while successfully resolving this issue, was accompanied by the loss of catalytic turnover. As depicted below, the modified reaction with potassium ethyl trifluoroborate only gave the corresponding product in 9% yield. Further investigations are necessary to improve this process.

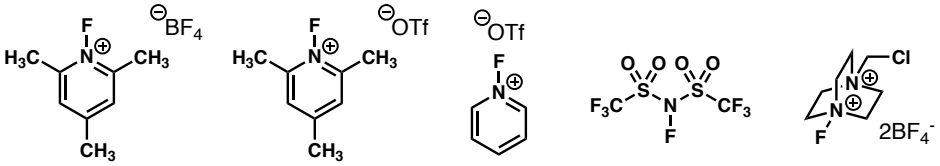


A 10-mL microwave-vial equipped with a stir bar was charged with $Pd(OAc)_2$ (6.7 mg, 0.03 mmol, 0.1 equiv), orthanilic acid (DG1**)** (23.5 mg, 0.135 mmol, 0.45 equiv), 1-fluoro-2,4,6-trimethylpyridinium tetrafluoroborate (O1) (136.2 mg, 0.60 mmol, 2.0 equiv), potassium ethyl trifluoroborate (163.2 mg, 1.20 mmol, 4.0 equiv), 3-bromo-2-fluorobenzaldehyde (60.9 mg, 0.30 mmol, 1.0 equiv) and chloroacetic acid (283.5 mg, 3.0 mmol, 10.0 equiv), followed by the addition of hexafluoroisopropanol (HFIP) (1.50 mL). The vial was sealed with a PTFE-lined cap, sparged with argon gas and stirred at rt for 15 min before being heated in a pie-block at 100 °C under stirring for 24 h. After cooling to rt, the reaction mixture was filtered through a pad of silica gel and washed with hexane/EtOAc (1:1, 60 mL). The filtrate was then concentrated *in vacuo* and the resulting residue was purified by preparative thin layer chromatography using hexane/EtOAc (10:1) as the developing solvent. Yellow liquid (6.2 mg, 9%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.50 (s, 1H), 7.66 (dd, J = 8.5, 7.1 Hz, 1H), 6.99 (d, J = 8.8 Hz, 1H), 2.99 (q, J = 7.7 Hz, 2H), 1.21 (t, J = 7.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 188.50, 188.41, 163.42, 161.37, 148.06, 138.34, 138.32, 127.11, 127.07, 123.32, 123.27, 107.08, 106.91, 26.62, 26.60, 15.39. ^{19}F NMR (282 MHz, $CDCl_3$): δ -114.83 (d, J = 7.1 Hz). MS-ESI m/z 230.9818 ($[M + H]^+$, C_9H_9BrFO, calc. 230.9815). IR (neat): 2972, 2932, 2875, 2778, 1704, 1598, 1557, 1473, 1401, 1262.

Benzaldehyde *ortho* C-H Fluorination

Control experiments





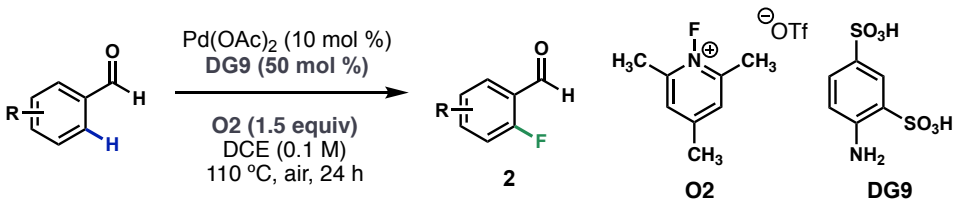
entry	variation from the standard condition	yield (%) X = F (2s)	yield (%) X = Cl
1	none	72	14
2	no $Pd(OAc)_2$	0	0
3	no DG9	0	0
4	30 mol % DG9	24	4
5	70 mol % DG9	52	22
6	$Pd(TFA)_2$ instead of $Pd(OAc)_2$	52	14
7	$Pd(NO_3)_2•2H_2O$ instead of $Pd(OAc)_2$	34	28
8	**O1** instead of **O2**	8	10
9	**O6** instead of **O2**	8	10
10	**O4** instead of **O2**	0	2
11	**O5** instead of **O2**	0	0
12	with TfOH (50 mol %)	30	38
13	$PhCF_3$ instead of DCE	2	0
14	trichloroethylene instead of DCE	0	62
15	chloroform instead of DCE	8	22
16	0.15 M	50	22
17	at 100 °C	44	12
18	at 120 °C	42	20

Standard procedure for the control experiments

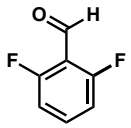
A 10-mL microwave-vial equipped with a stir bar was charged with $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 0.1 equiv), aniline-2,4-disulfonic acids (DG9) (12.7 mg, 0.05 mmol, 0.5 equiv), 1-fluoro-2,4,6-trimethylpyridinium triflate (O2) (43.4 mg, 0.15 mmol, 1.5 equiv) and 3,4-dichlorobenzaldehyde (17.5 mg, 0.10 mmol, 1.0 equiv), followed by the addition of dichloroethane (DCE) (1.0 mL). The vial was sealed with a PTFE-lined aluminum cap, stirred at rt for 10 min before being heated in a pie-block at 110 °C under stirring for 24 h. After cooling to rt, the reaction mixture was filtered through a pad of Celite® and washed with EtOAc (10 mL). The filtrate was then concentrated *in vacuo* before CH_2Br_2 (6.95 μL, 0.1 mmol) was added. The yield of the desired product was determined by crude ^1H NMR using CH_2Br_2 as the internal standard.

Note: All control experiments were conducted on a 0.1 mmol scale, and changes were made based on the "standard condition" described above.

General procedure for the substrate scope experiments (using **2a** as an example)

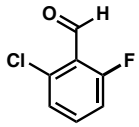


A 10-mL microwave-vial equipped with a stir bar was charged with $Pd(OAc)_2$ (6.7 mg, 0.03 mmol, 0.1 equiv), aniline-2,4-disulfonic acids (DG9**)** (38.0 mg, 0.15 mmol, 0.5 equiv), 1-fluoro-2,4,6-trimethylpyridinium triflate (O2) (130.2 mg, 0.45 mmol, 1.5 equiv) and 2-fluorobenzaldehyde (31.6 μL, 0.30 mmol, 1.0 equiv), followed by the addition of DCE (3.0 mL). The vial was sealed with a PTFE-lined cap, stirred at rt for 10 min before being heated in a pie-block at 110 °C under stirring for 24 h. After cooling to rt, the reaction mixture was filtered through a pad of Celite® and washed with EtOAc (30 mL). The filtrate was then concentrated *in vacuo* and the resulting residue was purified by preparative thin layer chromatography using hexane/EtOAc (5:1) as the developing solvent.



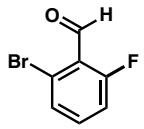
2a

This compound was synthesized from 2-fluorobenzaldehyde using the standard condition and purified by preparative thin layer chromatography using hexane/EtOAc (5:1) as the developing solvent. Colorless liquid (29.4 mg, 69%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.37 (s, 1H), 7.56 (tt, J = 9.0, 6.3 Hz, 1H), 7.00 (t, J = 8.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 184.79, 184.75, 184.72, 164.39, 164.35, 162.30, 162.26, 136.46, 136.37, 136.28, 112.75, 112.71, 112.58, 112.55. ^{19}F NMR (282 MHz, $CDCl_3$): δ -114.77 (dd, J = 8.9, 6.2 Hz). MS-ESI m/z 141.0159 ($[M - H]^-$, $C_7H_3F_2O$, calc. 141.0157). IR (neat): 3102, 2926, 1707, 1622, 1577, 1471, 1411, 1240.



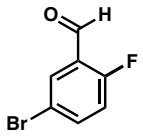
2b

This compound was synthesized from 2-chlorobenzaldehyde using the standard condition and purified by preparative thin layer chromatography using hexane/EtOAc (5:1) as the developing solvent. White solid (36.1 mg, 75%). ^{1}H NMR (500 MHz, $CDCl_3$): 10.45 (d, J = 1.1 Hz, 1H), 7.48 (td, J = 8.5, 5.7 Hz, 1H), 7.29 – 7.27 (m, 1H), 7.13 – 7.07 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 187.09, 187.06, 164.43, 162.32, 137.25, 137.22, 135.36, 135.27, 126.93, 126.90, 121.96, 121.88, 115.87, 115.70. ^{19}F NMR (282 MHz, $CDCl_3$): δ -114.38 (dd, J = 10.1, 5.7 Hz). MS-ESI m/z 156.9867 ($[M - H]^-$, C_7H_3ClFO, calc. 156.9862). IR (neat): 3089, 2895, 1701, 1600, 1574, 1454, 1409, 1292.



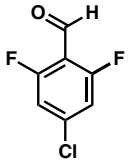
2c

This compound was synthesized from 2-bromobenzaldehyde using the standard condition and purified by preparative thin layer chromatography using hexane/EtOAc (5:1) as the developing solvent. Light yellow solid (32.9 mg, 54%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.35 (d, J = 1.1 Hz, 1H), 7.48 (dt, J = 8.1, 1.1 Hz, 1H), 7.40 (td, J = 8.3, 5.6 Hz, 1H), 7.14 (ddd, J = 9.8, 8.5, 1.1 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 188.65, 188.63, 164.32, 162.20, 135.60, 135.52, 130.24, 130.21, 125.50, 125.48, 122.96, 122.89, 116.57, 116.40. ^{19}F NMR (282 MHz, $CDCl_3$): δ -113.96 (dd, J = 10.3, 5.5 Hz). MS-ESI m/z 200.9351 ($[M - H]^-$, C_7H_3BrFO, calc. 200.9357). IR (neat): 3095, 3076, 2881, 2772, 1693, 1598, 1566, 1450, 1401, 1249.



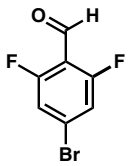
2d

This compound was synthesized from 3-bromobenzaldehyde using the standard condition and purified by preparative thin layer chromatography using hexane/EtOAc (5:1) as the developing solvent. Light yellow liquid (39.6 mg, 65%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.29 (s, 1H), 7.97 (dd, J = 6.1, 2.7 Hz, 1H), 7.70 (ddd, J = 9.0, 4.7, 2.7 Hz, 1H), 7.09 (t, J = 9.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 185.85, 185.80, 164.74, 162.68, 139.11, 139.04, 131.43, 131.41, 125.52, 125.45, 118.76, 118.59, 117.81, 117.79. ^{19}F NMR (282 MHz, $CDCl_3$): δ -124.03 (dt, J = 10.4, 5.5 Hz). MS-ESI m/z 200.9358 ($[M - H]^-$, C_7H_3BrFO, calc. 200.9357). IR (neat): 3095, 2872, 2761, 1708, 1602, 1579, 1475, 1393, 1256.



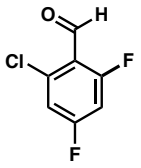
2e

This compound was synthesized from 4-chloro-2-fluorobenzaldehyde using the standard condition and purified by preparative thin layer chromatography using hexane/EtOAc (5:1) as the developing solvent. Off-white solid (23.8 mg, 45%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.28 (s, 1H), 7.09 – 7.01 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 183.52, 183.49, 183.45, 164.23, 164.17, 162.12, 162.06, 142.07, 141.96, 141.85, 114.00, 113.98, 113.95, 113.81, 113.79, 113.77, 113.05. ^{19}F NMR (282 MHz, $CDCl_3$): δ -112.95 (d, J = 8.6 Hz). MS-ESI m/z 174.9765 ($[M - H]^-$, $C_7H_2ClF_2O$, calc. 174.9768). IR (neat): 3092, 2921, 1693, 1617, 1572, 1430, 1305.



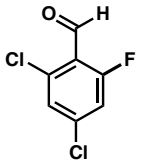
2f

This compound was synthesized from 4-bromo-2-fluorobenzaldehyde using the standard condition and purified by preparative thin layer chromatography using hexane/EtOAc (5:1) as the developing solvent. White solid (39.8 mg, 60%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.28 (d, J = 1.1 Hz, 1H), 7.24 – 7.18 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 183.66, 183.63, 183.59, 164.01, 163.96, 161.89, 161.84, 129.65, 129.54, 129.44, 116.90, 116.88, 116.85, 116.71, 116.69, 116.67, 113.34. ^{19}F NMR (282 MHz, $CDCl_3$): δ -113.23 (d, J = 8.3 Hz). MS-ESI m/z 218.9259 ($[M - H]^-$, $C_7H_2BrF_2O$, calc. 218.9263). IR (neat): 3080, 2893, 1694, 1611, 1568, 1424, 1408, 1299.



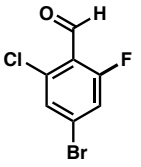
2g

This compound was synthesized from 2-chloro-4-fluorobenzaldehyde using the standard condition and purified by preparative thin layer chromatography using hexane/EtOAc (5:1) as the developing solvent. White solid (29.1 mg, 55%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.37 (d, J = 1.2 Hz, 1H), 7.05 (dt, J = 8.1, 2.1 Hz, 1H), 6.86 (ddd, J = 10.7, 8.4, 2.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 185.64, 185.62, 166.32, 166.20, 165.57, 165.46, 164.24, 164.13, 163.45, 163.34, 139.13, 139.08, 139.02, 138.98, 119.01, 118.98, 118.94, 118.91, 115.11, 115.08, 114.92, 114.89, 104.83, 104.63, 104.43. ^{19}F NMR (282 MHz, $CDCl_3$): δ -98.36 (dt, J = 12.4, 8.4 Hz), -106.80 – -112.03 (m). MS-ESI m/z 174.9770 ($[M - H]^-$, $C_7H_2ClF_2O$, calc. 174.9768). IR (neat): 3087, 2908, 1693, 1600, 1580, 1462, 1434, 1405, 1303.



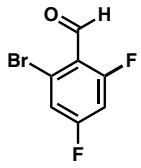
2h

This compound was synthesized from 2,4-dichlorobenzaldehyde using the standard condition and purified by preparative thin layer chromatography using hexane/EtOAc (5:1) as the developing solvent. Light yellow solid (43.4 mg, 75%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.38 (d, J = 1.1 Hz, 1H), 7.31 (t, J = 1.8 Hz, 1H), 7.14 (dd, J = 10.0, 2.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 185.89, 185.87, 164.28, 162.15, 140.97, 140.86, 138.04, 138.00, 127.20, 127.17, 120.53, 120.46, 116.86, 116.66. ^{19}F NMR (282 MHz, $CDCl_3$): δ -112.57 (d, J = 10.0 Hz). MS-ESI m/z 190.9471 ($[M - H]^-$, $C_7H_2Cl_2FO$, calc. 190.9472). IR (neat): 3080, 2881, 1697, 1593, 1551, 1408, 1390, 1236.



2i

This compound was synthesized from 4-bromo-2-chlorobenzaldehyde using the standard condition and purified by preparative thin layer chromatography using hexane/EtOAc (5:1) as the developing solvent. Pale yellow solid (35.6 mg, 50%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.38 (d, J = 1.1 Hz, 1H), 7.47 (t, J = 1.7 Hz, 1H), 7.30 (dd, J = 9.7, 1.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 186.03, 186.01, 164.01, 161.88, 137.99, 137.96, 129.99, 129.96, 128.75, 128.66, 120.86, 120.79, 119.77, 119.57. ^{19}F NMR (282 MHz, $CDCl_3$): δ -112.76 (d, J = 9.7 Hz). MS-ESI m/z 236.9125 ($[M + H]^+$, $C_7H_4BrClFO$, calc. 236.9113). IR (neat): 3076, 2879, 1698, 1588, 1407, 1387.



2j

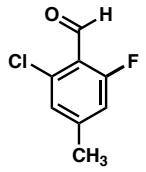
This compound was synthesized from 2-bromo-4-fluorobenzaldehyde using the standard condition and purified by preparative thin layer chromatography using hexane/EtOAc (5:1) as the developing solvent. White solid (35.1 mg, 53%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.27 (d, J = 1.2 Hz, 1H), 7.26 (dt, J = 7.8, 2.1 Hz, 1H), 6.91 (ddd, J = 10.7, 8.4, 2.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 187.23, 187.21, 166.36, 166.25, 165.43, 165.32, 164.28, 164.17, 163.29, 163.19, 126.82, 126.79, 126.72, 126.69, 119.93, 119.90, 119.86, 119.83, 118.38, 118.35, 118.19, 118.15, 105.41, 105.22, 105.01. ^{19}F NMR (282 MHz, $CDCl_3$): δ -98.89 (dt, J = 12.4, 8.1 Hz), -108.04 – -111.77 (m). MS-ESI m/z 218.9256 ($[M - H]^-$, $C_7H_2BrF_2O$, calc. 218.9263). IR (neat): 3087, 2884, 1693, 1601, 1574, 1457, 1424, 1398, 1300, 1282.

2k

This compound was synthesized from 2-bromo-4-chlorobenzaldehyde using the standard condition and purified by preparative thin layer chromatography using hexane/EtOAc (5:1) as the developing solvent. Pale yellow solid (52.0 mg, 73%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.27 (d, J = 1.1 Hz, 1H), 7.51 (t, J = 1.7 Hz, 1H), 7.18 (dd, J = 10.0, 2.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 187.40, 187.38, 164.08, 161.95, 141.13, 141.03, 130.32, 130.29, 125.94, 125.91, 121.50, 121.43, 117.46, 117.26. ^{19}F NMR (282 MHz, $CDCl_3$): δ -112.36 (d, J = 10.4 Hz). MS-ESI m/z 234.8961 ($[M - H]^-$, $C_7H_2BrClFO$, calc. 234.8967). IR (neat): 3075, 2879, 1693, 1589, 1560, 1408, 1388, 1231.

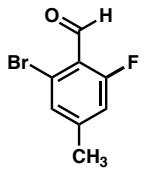
2l

This compound was synthesized from 2-fluoro-4-methoxybenzaldehyde using the standard condition and purified by preparative thin layer chromatography using hexane/EtOAc (3:1) as the developing solvent. Pale yellow solid (17.0 mg, 33%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.19 (s, 1H), 6.56 – 6.40 (m, 2H), 3.87 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 183.65, 183.62, 183.58, 166.00, 165.88, 165.81, 163.81, 163.74, 108.40, 108.31, 108.22, 98.96, 98.92, 98.77, 98.73, 56.44. ^{19}F NMR (282 MHz, $CDCl_3$): δ -112.96 (d, J = 10.7 Hz). MS-ESI m/z 173.0407 ($[M + H]^+$, $C_8H_7F_2O_2$, calc. 173.0409). IR (neat): 3093, 2994, 2896, 2851, 1688, 1623, 1571, 1428, 1350, 1310, 1212.



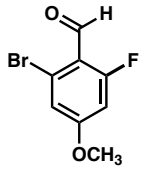
2m

This compound was synthesized from 2-chloro-4-methylbenzaldehyde using the standard condition and purified by preparative thin layer chromatography using hexane/EtOAc (5:1) as the developing solvent. Yellow solid (29.0 mg, 56%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.38 (d, J = 2.0 Hz, 1H), 7.08 (s, 1H), 6.89 (d, J = 11.2 Hz, 1H), 2.38 (d, J = 2.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 186.85, 186.83, 164.42, 162.32, 147.62, 147.54, 137.04, 137.01, 127.51, 127.48, 119.39, 119.31, 116.38, 116.21, 21.79, 21.77. ^{19}F NMR (282 MHz, $CDCl_3$): δ -115.33 (d, J = 11.2 Hz). MS-ESI m/z 171.0011 ($[M - H]^-$, C_8H_5ClFO, calc. 171.0018). IR (neat): 3079, 2873, 2775, 1705, 1616, 1561, 1451, 1400, 1300, 1203.



2n

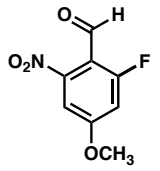
This compound was synthesized from 2-bromo-4-methylbenzaldehyde using the standard condition and purified by preparative thin layer chromatography using hexane/EtOAc (5:1) as the developing solvent. Light yellow solid (41.0 mg, 63%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.29 (d, J = 1.1 Hz, 1H), 7.29 (s, 1H), 6.93 (dd, J = 11.3, 1.5 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 188.43, 188.41, 164.29, 162.18, 147.83, 147.75, 130.86, 130.83, 125.44, 125.41, 120.34, 120.27, 117.09, 116.92, 21.61, 21.60. ^{19}F NMR (282 MHz, $CDCl_3$): δ -114.99 (d, J = 11.2 Hz). MS-ESI m/z 214.9507 ($[M - H]^-$, C_8H_5BrFO, calc. 214.9513). IR (neat): 3066, 2875, 2768, 1697, 1608, 1553, 1446, 1399, 1267, 1205.



2o

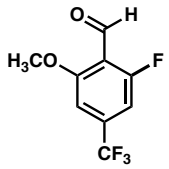
This compound was synthesized from 2-bromo-4-methoxybenzaldehyde using the standard condition and purified by preparative thin layer chromatography using hexane/EtOAc (5:1) as the developing solvent. White solid (50.3 mg, 72%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.21 (d, J = 1.3 Hz, 1H), 6.99 (dd, J = 2.5, 1.4 Hz, 1H), 6.62 (dd, J = 12.4, 2.4 Hz, 1H), 3.86 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 187.67, 187.65, 165.96, 164.79, 164.68, 163.85, 127.11, 127.06, 116.38, 116.36, 116.22, 116.15, 102.43, 102.23, 56.36. ^{19}F NMR (282 MHz, $CDCl_3$): δ -111.83 (d, J = 12.4 Hz). MS-ESI m/z 232.9598 ($[M + H]^+$, $C_8H_7BrFO_2$, calc. 232.9608). IR (neat): 3085, 2873, 1684, 1603, 1563,

1477, 1436, 1404, 1332, 1280, 1203.



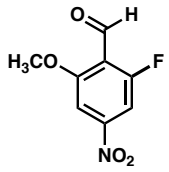
2p

This compound was synthesized from 4-methoxy-2-nitrobenzaldehyde using the standard condition and purified by preparative thin layer chromatography using hexane/EtOAc (2:1) as the developing solvent. Yellow solid (36.4 mg, 61%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.14 (s, 1H), 7.16 (dd, J = 2.4, 1.4 Hz, 1H), 6.90 (dd, J = 11.5, 2.4 Hz, 1H), 3.94 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 183.29, 183.26, 164.68, 164.24, 164.14, 162.60, 112.32, 112.20, 106.99, 106.96, 106.03, 105.82, 56.88. ^{19}F NMR (282 MHz, $CDCl_3$): δ -112.31 (d, J = 11.5 Hz). MS-ESI m/z 200.0344 ($[M + H]^+$, $C_8H_7FNO_4$, calc. 200.0354). IR (neat): 3098, 2877, 1704, 1623, 1537, 1485, 1340, 1292.



2q

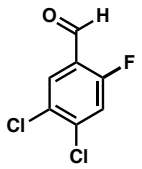
This compound was synthesized from 2-methoxy-4-trifluoromethylbenzaldehyde using the standard condition and purified by preparative thin layer chromatography using hexane/EtOAc (3:1) as the developing solvent. Pale yellow solid (46.0 mg, 69%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.42 (d, J = 1.2 Hz, 1H), 7.00 (d, J = 9.1 Hz, 2H), 4.00 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 186.48, 186.46, 164.11, 162.43, 162.39, 162.01, 137.71, 137.61, 137.44, 137.35, 137.17, 137.08, 136.90, 136.81, 125.94, 123.77, 123.74, 121.60, 121.57, 119.43, 116.25, 116.18, 106.58, 106.55, 106.52, 106.49, 106.38, 106.35, 106.32, 106.29, 104.58, 104.55, 104.52, 104.49, 104.46, 56.89. ^{19}F NMR (282 MHz, $CDCl_3$): δ -63.91, -111.91 (d, J = 10.0 Hz). MS-ESI m/z 221.0234 ($[M - H]^-$, $C_9H_5F_4O_2$, calc. 221.0231). IR (neat): 3085, 2953, 2916, 1706, 1629, 1589, 1467, 1428, 1357, 1257.



2r

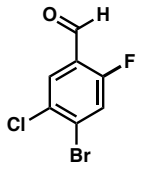
This compound was synthesized from 2-methoxy-4-nitrobenzaldehyde following the standard condition and purified by preparative thin layer chromatography using hexane/EtOAc (2:1) as the developing solvent. Yellow solid (37.0 mg, 62%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.43 (d, J = 1.2 Hz, 1H), 7.66 (t, J = 1.7 Hz, 1H), 7.59 (dd, J = 9.9, 2.0 Hz, 1H), 4.06 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 185.97, 185.95, 163.85, 162.41, 162.36, 161.74, 151.80, 151.70, 117.99, 117.91, 105.02,

104.81, 102.94, 102.91, 57.27. ^{19}F NMR (282 MHz, $CDCl_3$): δ -109.85 (d, J = 9.8 Hz). MS-ESI m/z 200.0343 ([M + H]$^-$, $C_8H_7FNO_4$, calc. 200.0354). IR (neat): 3116, 3097, 2897, 1705, 1614, 1533, 1470, 1427, 1401, 1355, 1208.



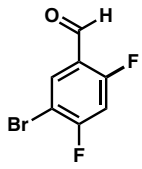
2s

This compound was synthesized from 3,4-dichlorobenzaldehyde using the standard condition and purified by preparative thin layer chromatography using hexane/EtOAc (10:1) as the developing solvent. White solid (40.0 mg, 69%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.26 (s, 1H), 7.95 (d, J = 6.6 Hz, 1H), 7.37 (d, J = 9.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 184.97, 184.92, 163.33, 161.26, 140.27, 140.18, 129.72, 129.70, 123.71, 123.63, 119.34, 119.14. ^{19}F NMR (282 MHz, $CDCl_3$): δ -122.50 (dd, J = 9.4, 6.7 Hz). MS-ESI m/z 190.9474 ([M − H]$^-$, $C_7H_2Cl_2FO$, calc. 190.9472). IR (neat): 3086, 1686, 1600, 1455, 1411, 1378, 1234.



2t

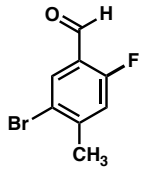
This compound was synthesized from 4-bromo-3-chlorobenzaldehyde using the standard condition and purified by preparative thin layer chromatography using hexane/EtOAc (10:1) as the developing solvent. Off-white solid (49.9 mg, 70%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.26 (s, 1H), 7.93 (d, J = 6.6 Hz, 1H), 7.54 (d, J = 9.1 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 185.16, 185.11, 163.00, 160.91, 131.75, 131.72, 130.44, 130.36, 129.34, 129.32, 124.21, 124.13, 122.56, 122.37. ^{19}F NMR (282 MHz, $CDCl_3$): δ -122.95 (dd, J = 9.1, 6.5 Hz). MS-ESI m/z 234.8960 ([M − H]$^-$, $C_7H_2BrClFO$, calc. 234.8967). IR (neat): 3084, 1684, 1592, 1565, 1451, 1410, 1369, 1232.



2u

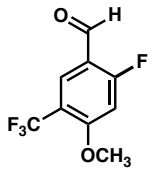
This compound was synthesized from 3-bromo-4-fluorobenzaldehyde using the standard condition and purified by preparative thin layer chromatography using hexane/EtOAc (10:1) as the developing solvent. White solid (31.2 mg, 47%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.23 (s, 1H), 8.11 (t, J = 7.5 Hz, 1H), 7.02 (dd, J = 9.8, 8.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 184.57, 184.56, 184.52, 184.51, 165.35, 165.26, 164.18, 164.08, 163.27, 163.18, 162.12, 162.02, 133.54, 133.51, 133.49,

122.13, 122.10, 122.05, 122.02, 106.37, 106.17, 106.01, 105.98, 105.96, 105.84, 105.81. ^{19}F NMR (282 MHz, $CDCl_3$): δ -91.32 (dt, J = 12.3, 7.8 Hz), -118.66 (ddd, J = 12.3, 9.8, 7.2 Hz). MS-ESI m/z 218.9263 ([M − H]$^-$, $C_7H_2BrF_2O$, calc. 218.9263). IR (neat): 3047, 2867, 1706, 1604, 1587, 1478, 1446, 1412, 1400, 1276.



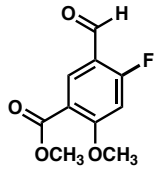
2v

This compound was synthesized from 3-bromo-4-methylbenzaldehyde using the standard condition and purified by preparative thin layer chromatography using hexane/EtOAc (10:1) as the developing solvent. Off white solid (45.6 mg, 70%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.23 (s, 1H), 7.98 (d, J = 6.6 Hz, 1H), 7.07 (d, J = 10.6 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 185.69, 185.64, 164.45, 162.39, 147.72, 147.65, 131.98, 131.97, 123.41, 123.34, 120.34, 120.31, 118.87, 118.70, 23.89, 23.87. ^{19}F NMR (282 MHz, $CDCl_3$): δ -124.47 (dd, J = 10.5, 6.5 Hz). MS-ESI m/z 214.9506 ([M − H]$^-$, C_8H_5BrFO, calc. 214.9513). IR (neat): 3068, 2918, 2868, 2765, 1694, 1677, 1608, 1565, 1471, 1401, 1374, 1251.



2w

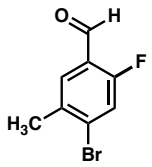
This compound was synthesized from 4-methoxy-3-trifluoromethylbenzaldehyde using the standard condition and purified by preparative thin layer chromatography using hexane/EtOAc (5:1) as the developing solvent. Off-white solid (56.0 mg, 84%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.20 (s, 1H), 8.21 – 7.99 (m, 1H), 6.77 (d, J = 11.8 Hz, 1H), 3.99 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 184.87, 184.83, 169.06, 166.96, 163.85, 163.84, 163.76, 163.75, 128.58, 128.54, 128.50, 125.92, 123.75, 121.59, 119.42, 116.79, 116.71, 116.62, 116.59, 116.36, 116.34, 100.59, 100.39, 56.99. ^{19}F NMR (282 MHz, $CDCl_3$): δ -62.66, -112.61 (dd, J = 12.0, 7.9 Hz). MS-ESI m/z 223.0378 ([M + H]$^+$, $C_9H_7F_4O_2$, calc. 223.0377). IR (neat): 3069, 2954, 2933, 2893, 2842, 1677, 1623, 1583, 1501, 1472, 1316, 1266, 1239.



2x

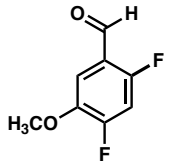
This compound was synthesized from methyl 5-formyl-2-methoxybenzoate using the standard

condition and purified by preparative thin layer chromatography using hexane/EtOAc (1:1) as the developing solvent. Pale yellow solid (32.5 mg, 51%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.18 (s, 1H), 8.38 (d, *J* = 8.2 Hz, 1H), 6.73 (d, *J* = 12.3 Hz, 1H), 3.97 (s, 3H), 3.88 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 185.24, 185.20, 168.85, 166.75, 165.63, 165.54, 164.61, 133.70, 133.66, 117.38, 117.35, 117.10, 117.02, 100.35, 100.15, 56.99, 52.41. ^{19}F NMR (282 MHz, $CDCl_3$): δ -112.00 (dd, *J* = 12.4, 8.2 Hz). MS-ESI m/z 213.0551 ($[M + H]^+$, $C_{10}H_{10}FO_4$, calc. 213.0558). IR (neat): 3090, 2958, 2871, 1696, 1612, 1573, 1493, 1467, 1436, 1291, 1260, 1200.



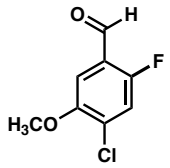
2y

This compound was synthesized from 4-bromo-3-methylbenzaldehyde using the standard condition and purified by preparative thin layer chromatography using hexane/EtOAc (10:1) as the developing solvent. Pale yellow solid (37.1 mg, 57%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.29 (s, 1H), 7.71 (d, *J* = 7.2 Hz, 1H), 7.42 (d, *J* = 9.6 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 186.62, 186.57, 163.30, 161.23, 135.13, 135.10, 132.58, 132.50, 129.55, 129.53, 123.10, 123.03, 120.87, 120.84, 120.68, 22.21. ^{19}F NMR (282 MHz, $CDCl_3$): δ -125.01 – -125.10 (m). MS-ESI m/z 214.9502 ($[M - H]^-$, C_8H_5BrFO, calc. 214.9513). IR (neat): 3094, 2931, 2876, 2775, 1694, 1599, 1477, 1411, 1388, 1255.



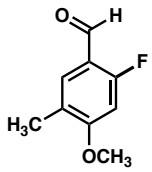
2z

This compound was synthesized from 4-fluoro-3-methoxybenzaldehyde using the standard condition and purified by preparative thin layer chromatography using hexane/EtOAc (5:1) as the developing solvent. White solid (32.0 mg, 62%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.28 (s, 1H), 7.41 (dd, *J* = 9.3, 6.3 Hz, 1H), 6.96 (t, *J* = 10.0 Hz, 1H), 3.91 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 185.80, 185.79, 185.75, 185.74, 160.56, 160.47, 158.53, 158.44, 157.76, 157.66, 155.69, 155.59, 145.45, 145.43, 145.36, 145.34, 120.22, 120.19, 120.15, 120.12, 110.59, 110.57, 110.56, 110.53, 105.93, 105.75, 105.72, 105.54, 56.72. ^{19}F NMR (282 MHz, $CDCl_3$): δ -118.22 (td, *J* = 9.9, 7.2 Hz), -128.62 (dt, *J* = 9.7, 6.9 Hz). MS-ESI m/z 171.0265 ($[M - H]^-$, $C_8H_5F_2O_2$, calc. 171.0263). IR (neat): 3057, 2882, 1690, 1677, 1618, 1606, 1500, 1426, 1409, 1348, 1292, 1279, 1211.



2aa

This compound was synthesized from 4-chloro-3-methoxybenzaldehyde using the standard condition and purified by preparative thin layer chromatography using hexane/EtOAc (5:1) as the developing solvent. Off white solid (41.3 mg, 73%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.29 (s, 1H), 7.34 (d, J = 5.8 Hz, 1H), 7.26 (d, J = 9.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 186.15, 186.10, 159.74, 157.72, 152.31, 152.29, 130.87, 130.79, 122.84, 122.76, 118.96, 118.76, 108.91, 108.89, 56.84. ^{19}F NMR (282 MHz, $CDCl_3$): δ -131.22 (dd, J = 9.2, 5.9 Hz). MS-ESI m/z 186.9957 ([M − H]$^-$, $C_8H_5ClFO_2$, calc. 186.9968). IR (neat): 3076, 2885, 1683, 1599, 1479, 1459, 1395, 1265.

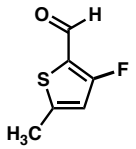


2bb

This compound was synthesized from 4-methoxy-3-methylbenzaldehyde using the standard condition and purified by preparative thin layer chromatography using hexane/EtOAc (5:1) as the developing solvent. Light yellow solid (8.1 mg, 16%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.20 (s, 1H), 7.71 – 7.57 (m, 1H), 6.57 (d, J = 12.3 Hz, 1H), 3.90 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 186.32, 186.28, 166.37, 164.34, 164.33, 164.26, 129.46, 129.43, 123.73, 123.71, 116.89, 116.83, 98.28, 98.08, 56.18, 15.66. ^{19}F NMR (282 MHz, $CDCl_3$): δ -122.20 (dd, J = 12.3, 8.0 Hz). MS-ESI m/z 169.0658 ([M + H]$^+$, $C_9H_{10}FO_2$, calc. 169.0659). IR (neat): 3018, 2957, 2861, 1733, 1677, 1616, 1586, 1506, 1439, 1341, 1273, 1243.

2cc

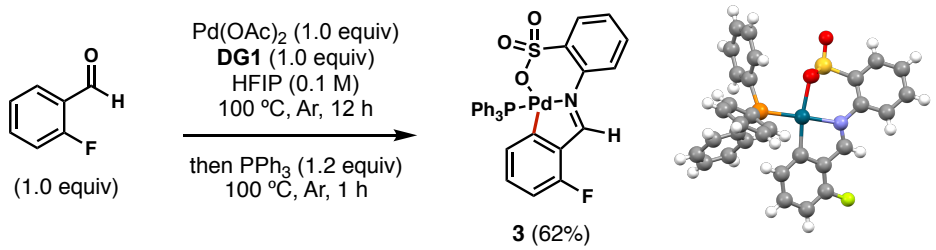
This compound was synthesized from 2-bromo-3-fluorobenzaldehyde using the standard condition and purified by preparative thin layer chromatography using hexane/EtOAc (5:1) as the developing solvent. Light-yellow solid (45.7 mg, 69%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.32 (s, 1H), 7.34 (ddd, J = 9.3, 7.4, 4.5 Hz, 1H), 7.15 (td, J = 9.4, 4.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 187.56, 187.54, 187.52, 160.37, 160.35, 158.29, 158.27, 156.81, 156.78, 154.86, 154.83, 123.51, 123.42, 121.82, 121.74, 121.62, 121.54, 117.16, 117.11, 116.97, 116.91, 112.30, 112.28, 112.11, 112.09. ^{19}F NMR (282 MHz, $CDCl_3$): δ -109.75 (ddd, J = 15.6, 7.5, 4.0 Hz), -120.08 (ddd, J = 15.5, 9.5, 4.6 Hz). MS-ESI m/z 218.9246 ([M − H]$^-$, $C_7H_2BrF_2O$, calc. 218.9263). IR (neat): 3094, 2875, 1700, 1602, 1584, 1467, 1401, 1381, 1293, 1242.



2dd

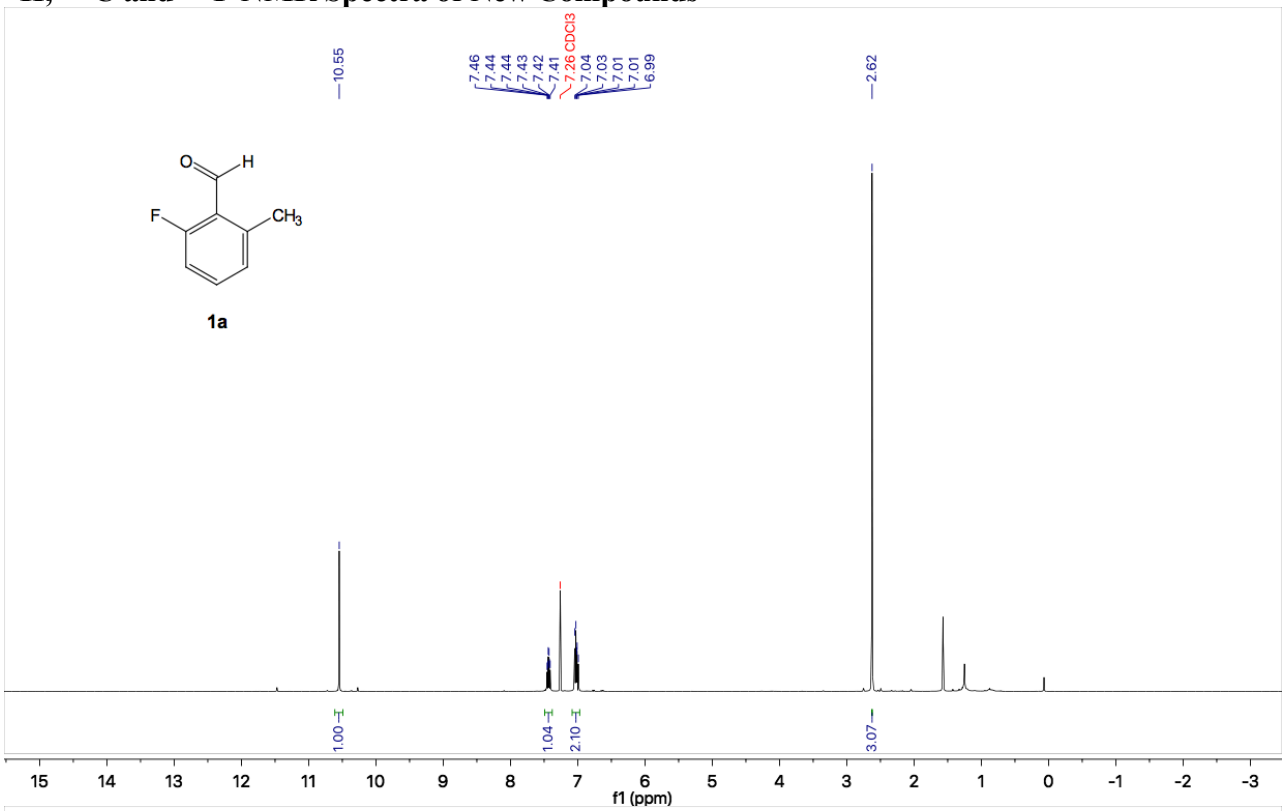
This compound was synthesized from 5-methyl-2-thiophenecarboxaldehyde using the standard condition and purified by preparative thin layer chromatography using hexane/Et_2O (4:1) as the developing solvent. Light yellow liquid (16.0 mg, 37%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.93 (s, 1H), 6.62 (s, 1H), 2.51 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 179.45, 179.44, 163.83, 161.62, 150.74, 150.66, 121.06, 120.99, 116.76, 116.57, 17.42, 17.41. ^{19}F NMR (282 MHz, $CDCl_3$): δ -118.93. MS-ESI m/z 145.0120 ($[M + H]^+$, C_6H_6FOS, calc. 145.0118). IR (neat): 3087, 2926, 2858, 2820, 2732, 1720, 1664, 1557, 1476, 1411, 1376, 1238.

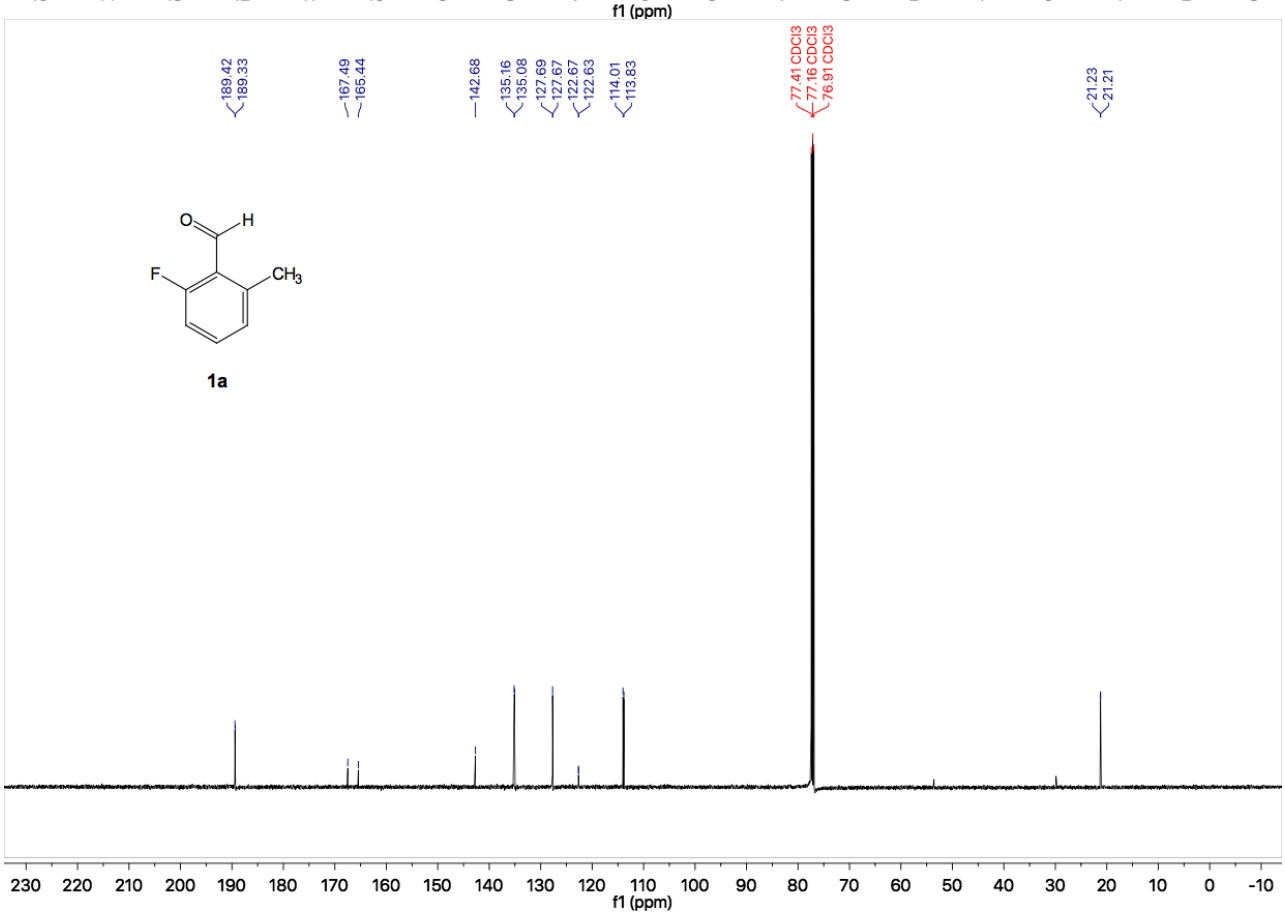
Synthesis and Isolation of Palladacycle 3

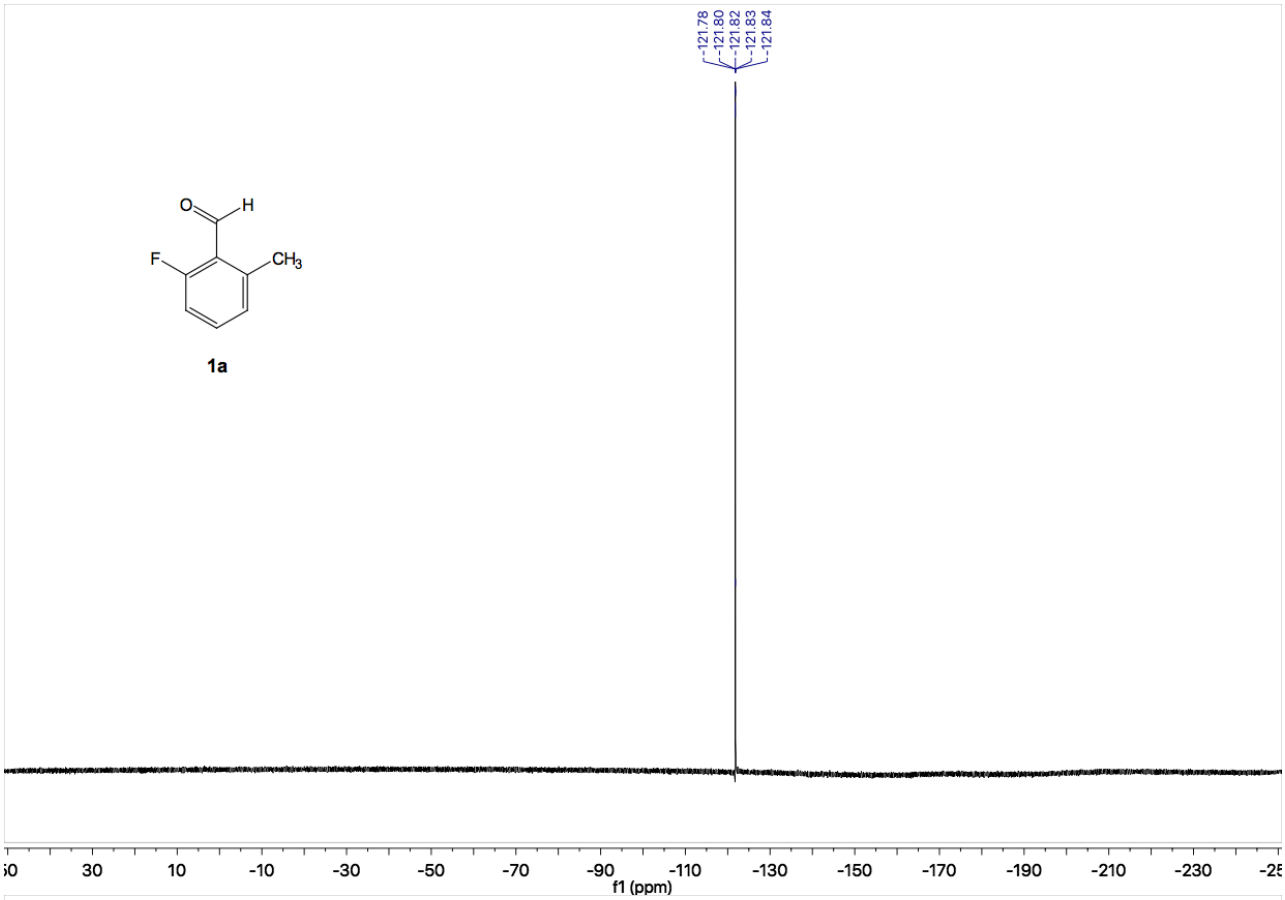


Following a previously reported procedure,[1] a 10-mL microwave vial equipped with a stir bar was charged with $Pd(OAc)_2$ (67.4 mg, 0.30 mmol, 1.0 equiv), orthanilic acid (DG1**)** (52.0 mg, 0.30 mmol, 1.0 equiv), 2-fluorobenzaldehyde (31.6 µL, 0.30 mmol, 1.0 equiv) and HFIP (3.0 mL). The vial was sealed with a PTFE-lined aluminum cap, sparged with argon gas and stirred at rt for 15 mins before being heated in a pie-block at 100 ºC for 12 h. After cooling to rt, the vial was decapped and triphenylphosphine (94.4 mg, 0.36 mmol, 1.2 equiv) was quickly added. The vial was re-sealed with a PTFE-lined aluminum cap and heated with stirring at 100 ºC for 1 h. After cooling to rt, the reaction was filtered through a pad of Celite®, washed with DCM (30 mL) and the filtrate concentrated *in vacuo*. The residue was purified by preparative thin layer chromatography using DCM/MeOH (20:1) as the developing solvent to yield the desired palladacycle **3** as a yellow solid (120.0 mg, 62%). Single crystal was obtained by slow diffusion of hexane to a solution of palladacycle **3** in DCM at -20 ºC.[2] ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.87 (d, J = 6.4 Hz, 1H), 8.04 (d, J = 8.3 Hz, 1H), 7.75 (dd, J = 12.1, 8.3 Hz, 6H), 7.53 – 7.36 (m, 12H), 6.72 – 6.62 (m, 2H), 6.20 (t, J = 6.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 166.28, 166.27, 166.25, 166.23, 162.55, 160.46, 155.90, 155.87, 155.84, 143.94, 137.49, 135.31, 135.22, 135.01, 135.00, 134.97, 134.95, 134.45, 134.42, 134.36, 134.34, 134.00, 133.95, 133.93, 133.89, 131.91, 131.64, 131.62, 129.09, 128.78, 128.69, 128.59, 128.52, 128.17, 120.06, 120.04, 111.83, 111.68. ^{19}F NMR (282 MHz, $CDCl_3$): δ -109.37 (dd, J = 9.2, 6.8 Hz). MS-ESI m/z 646.0219 ($[M + H]^+$, $C_{31}H_{24}FNO_3PPdS$, calc. 646.0228). IR (neat): 3055, 1601, 1574, 1555, 1454, 1434, 1264, 1240.

^{1}H, ^{13}C and ^{19}F NMR Spectra of New Compounds



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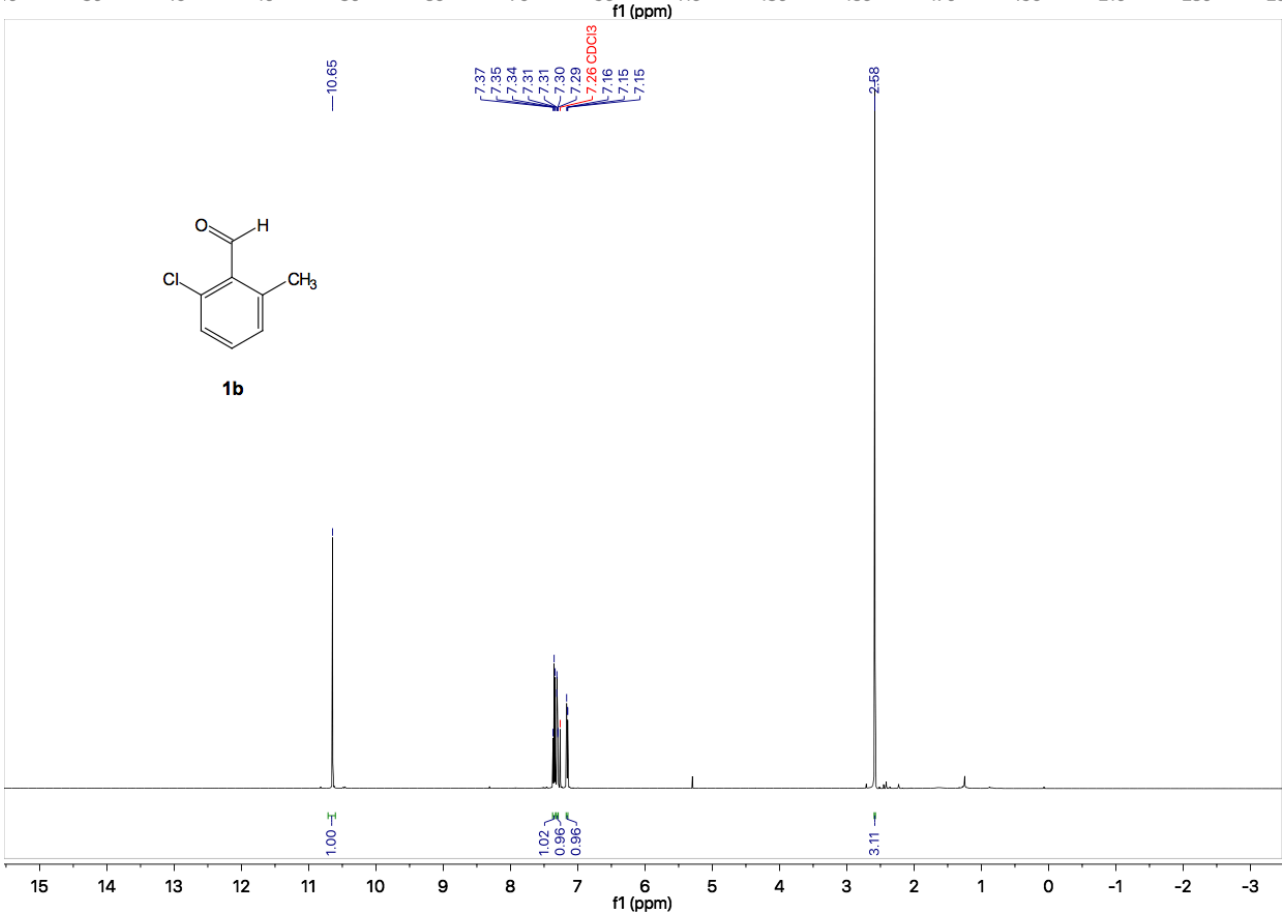
-121.83
-121.84
O
H
F
CH3
1a
f1 (ppm)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7.34
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7.31
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7.29
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7.15
7.15
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O
H
Cl
CH3
1b
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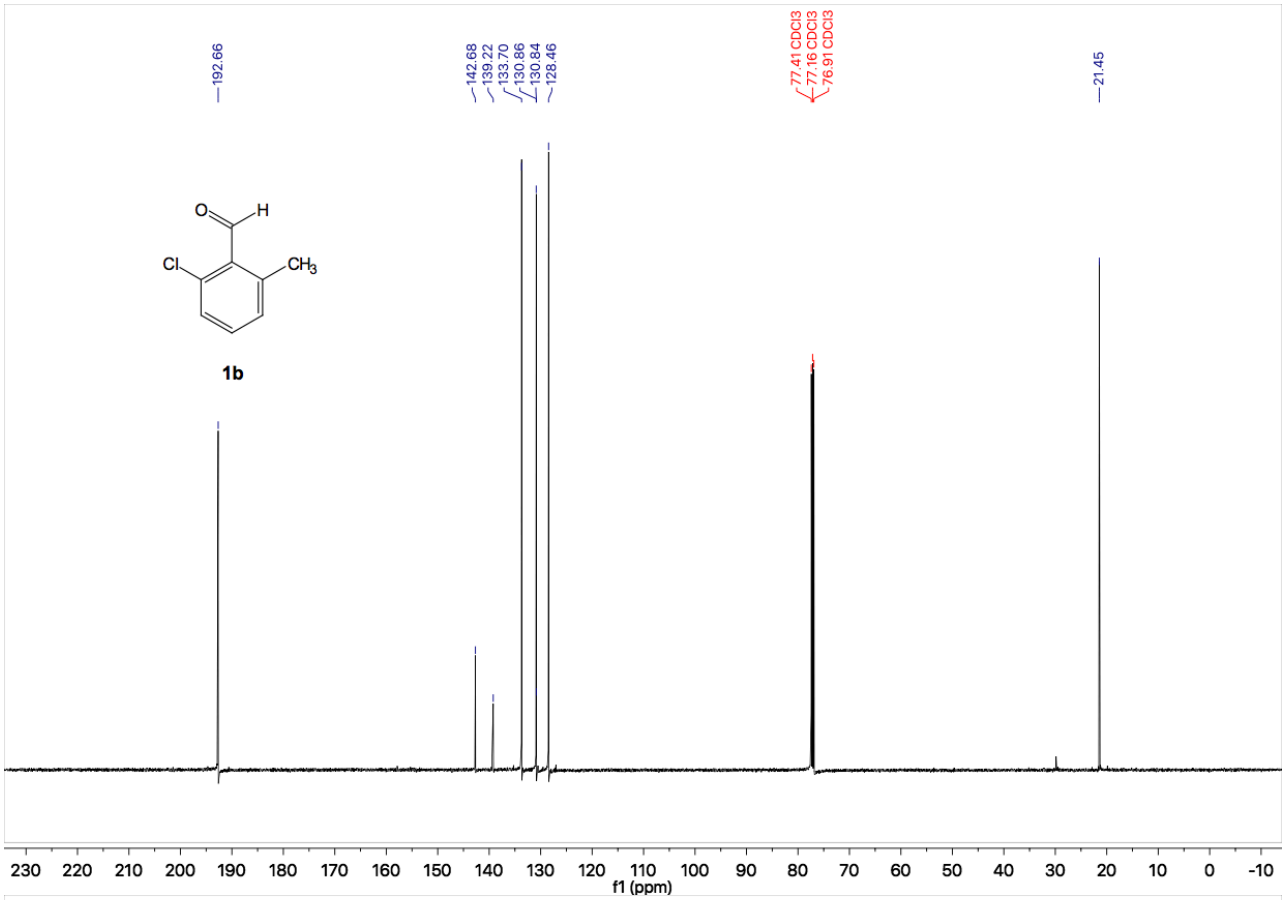
1.02
0.96
0.96
3.11
f1 (ppm)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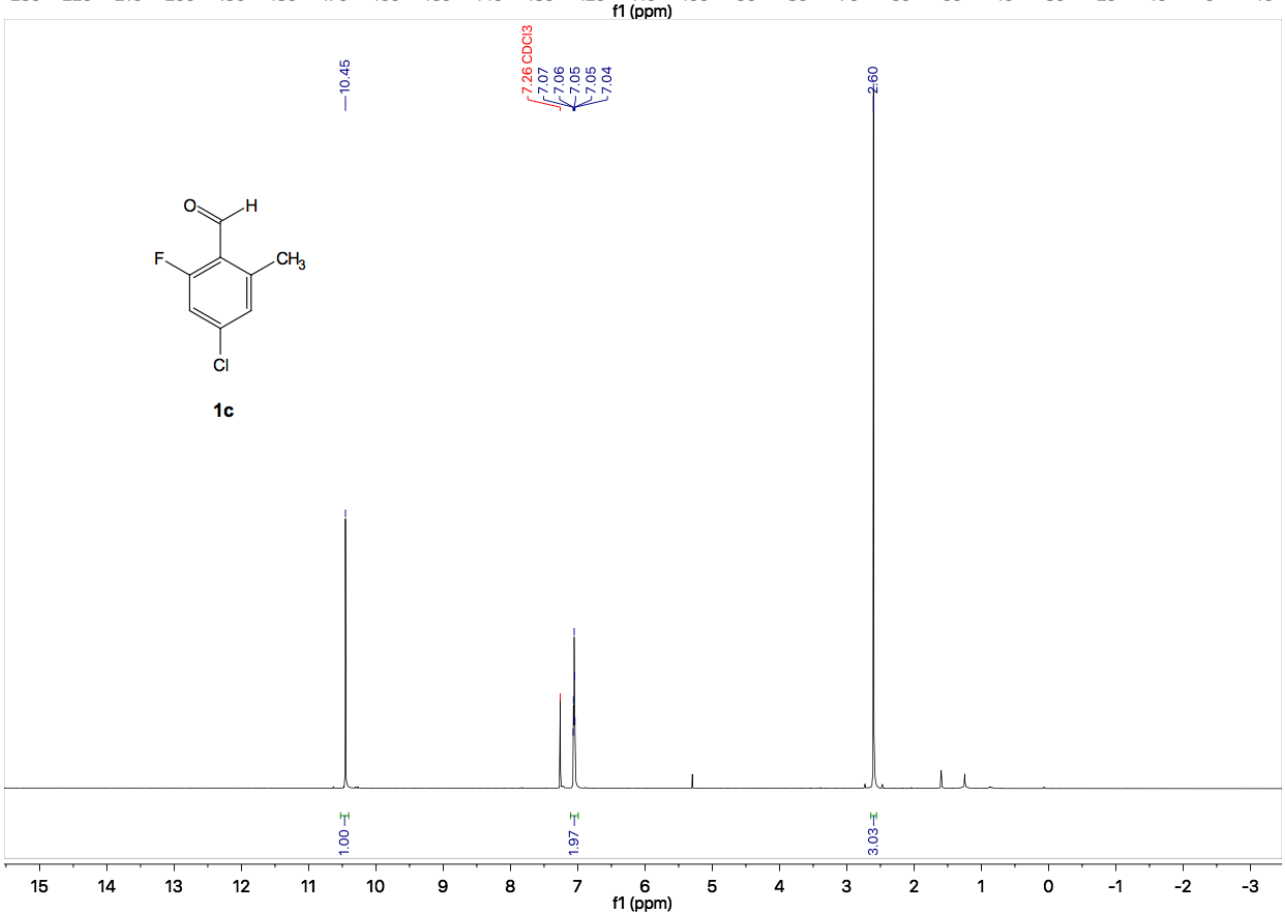
77.16 CDCl3
76.91 CDCl3
21.45
O
H
Cl
CH3
1b
f1 (ppm)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7.05
7.04
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H
F
CH3
Cl
1c
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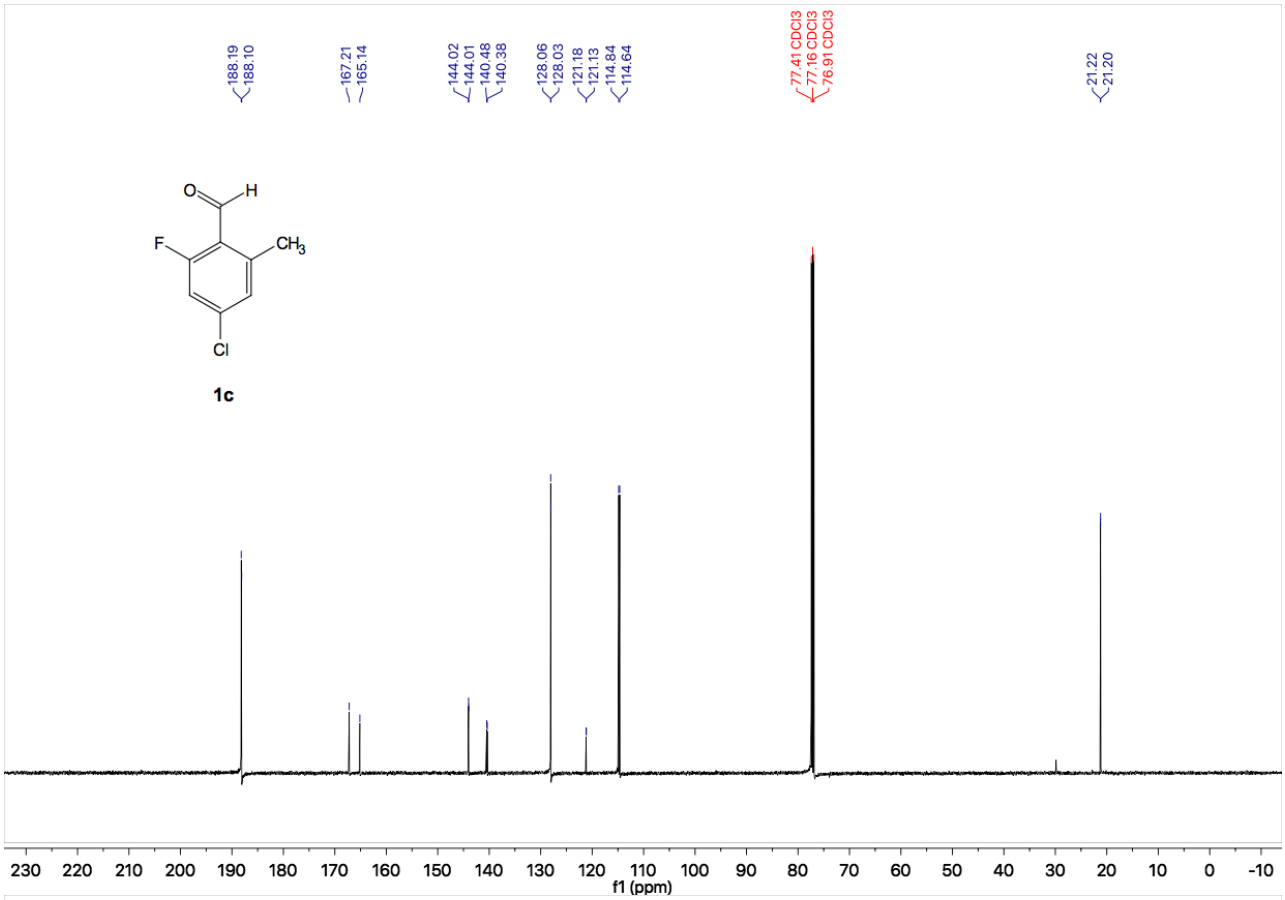
3.03
f1 (ppm)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188.10
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165.14
144.02
144.01
140.48
140.38
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128.03
121.18
121.13
114.84
114.64
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
21.22
21.20
O
H
F
CH3
Cl
1c
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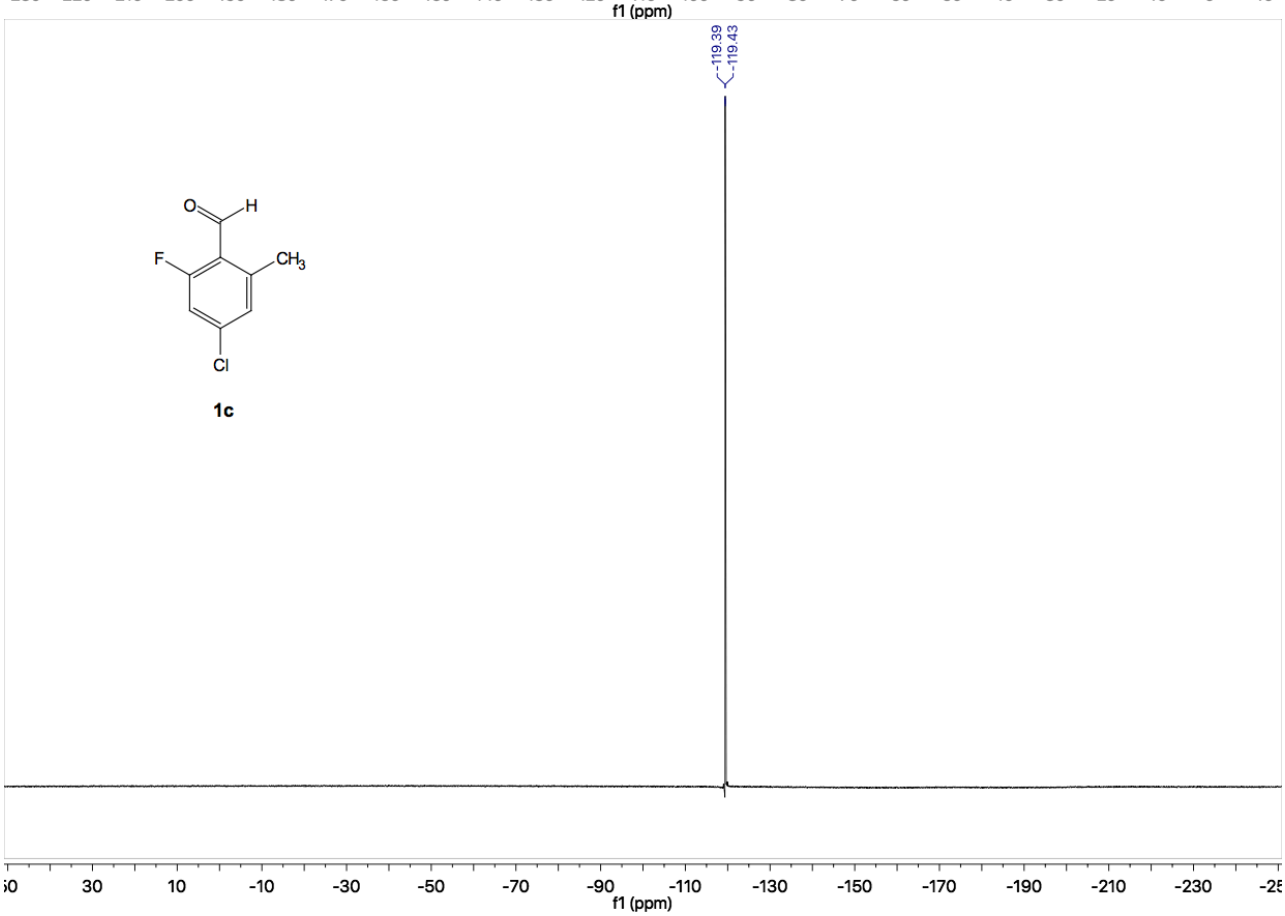
f1 (ppm)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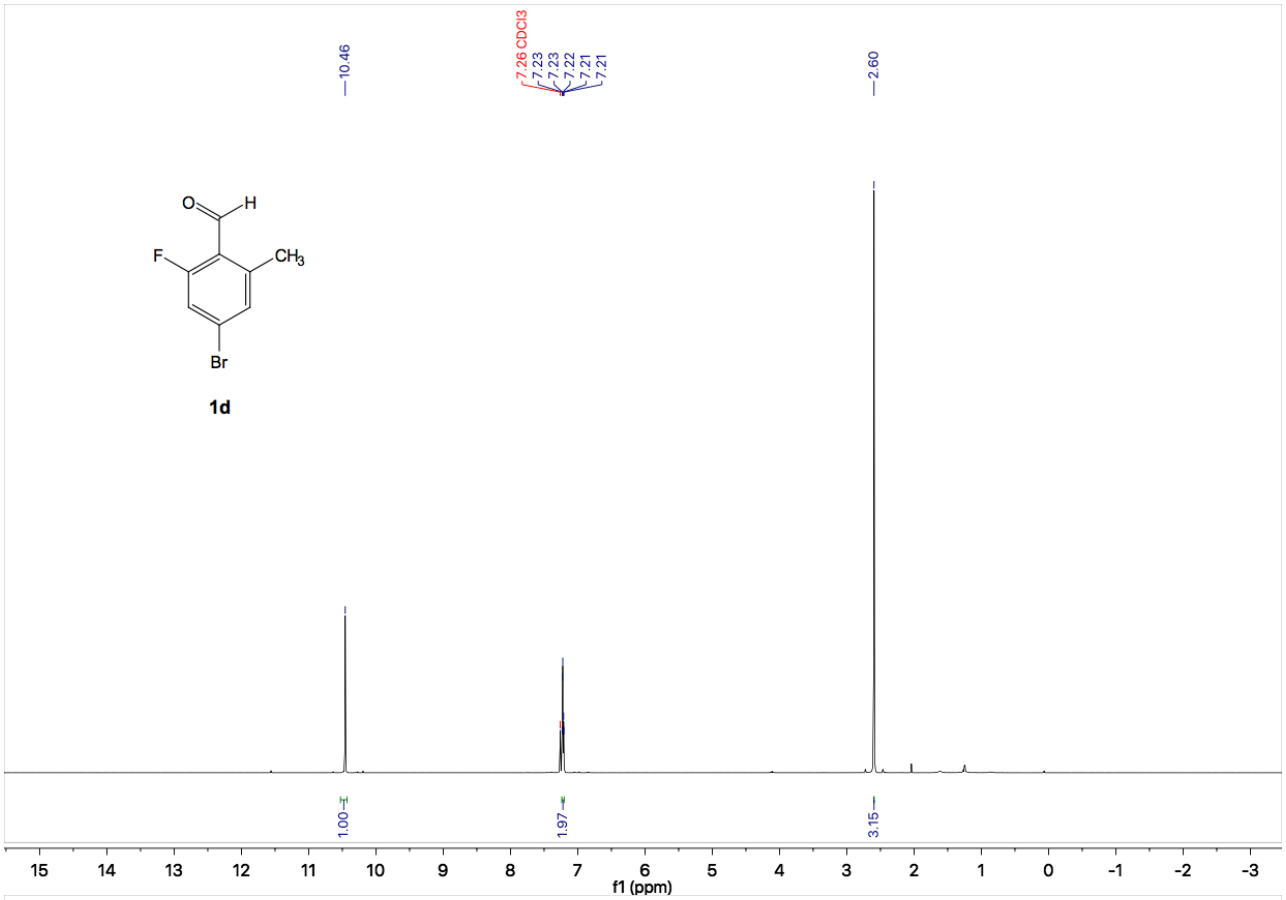
H
F
CH3
Cl
1c
30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)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7.22
7.21
7.21
2.60
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H
F
CH3
Br
1d
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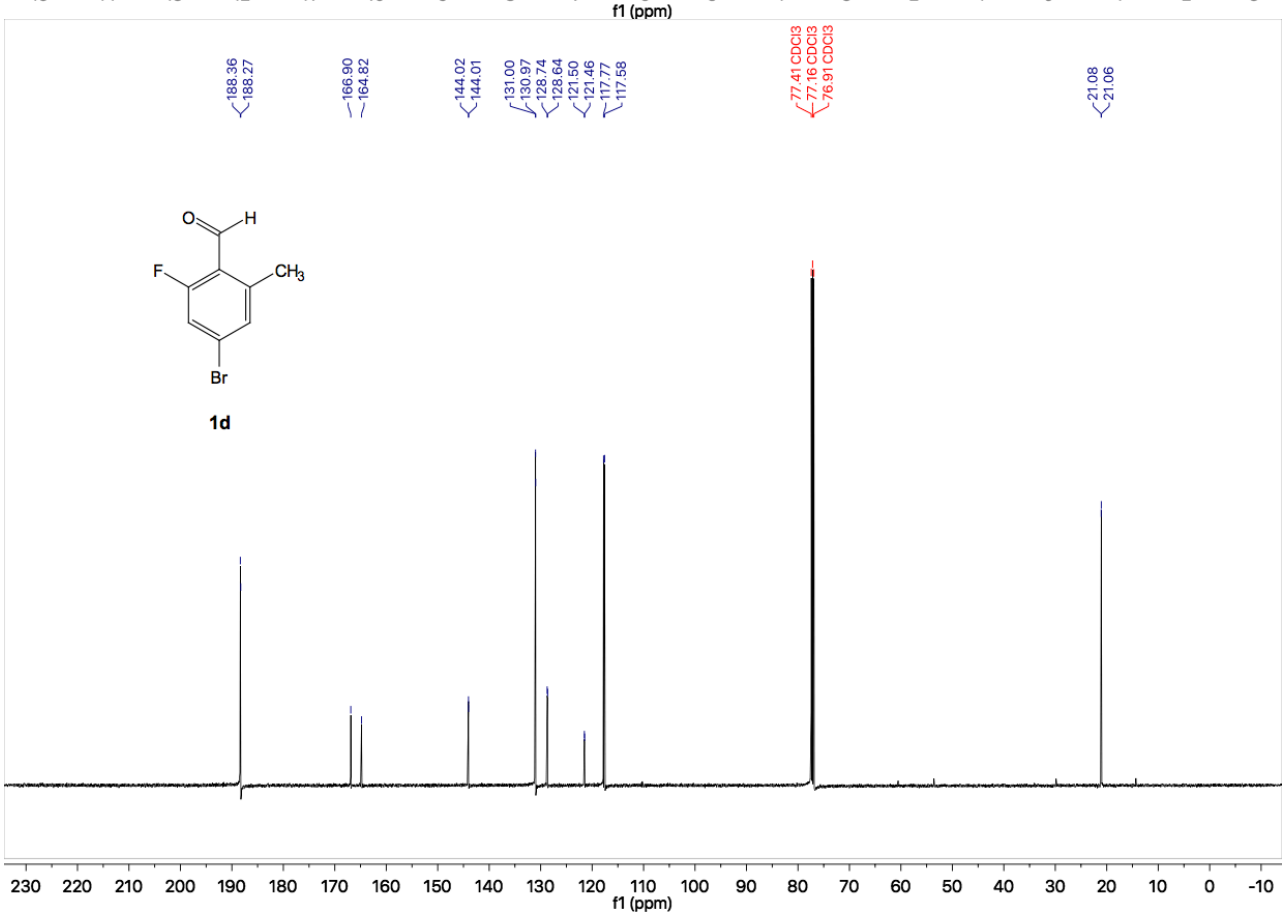
1.97
3.15
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)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130.97
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121.50
121.46
117.77
117.58
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
21.08
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O
H
F
CH3
Br
1d
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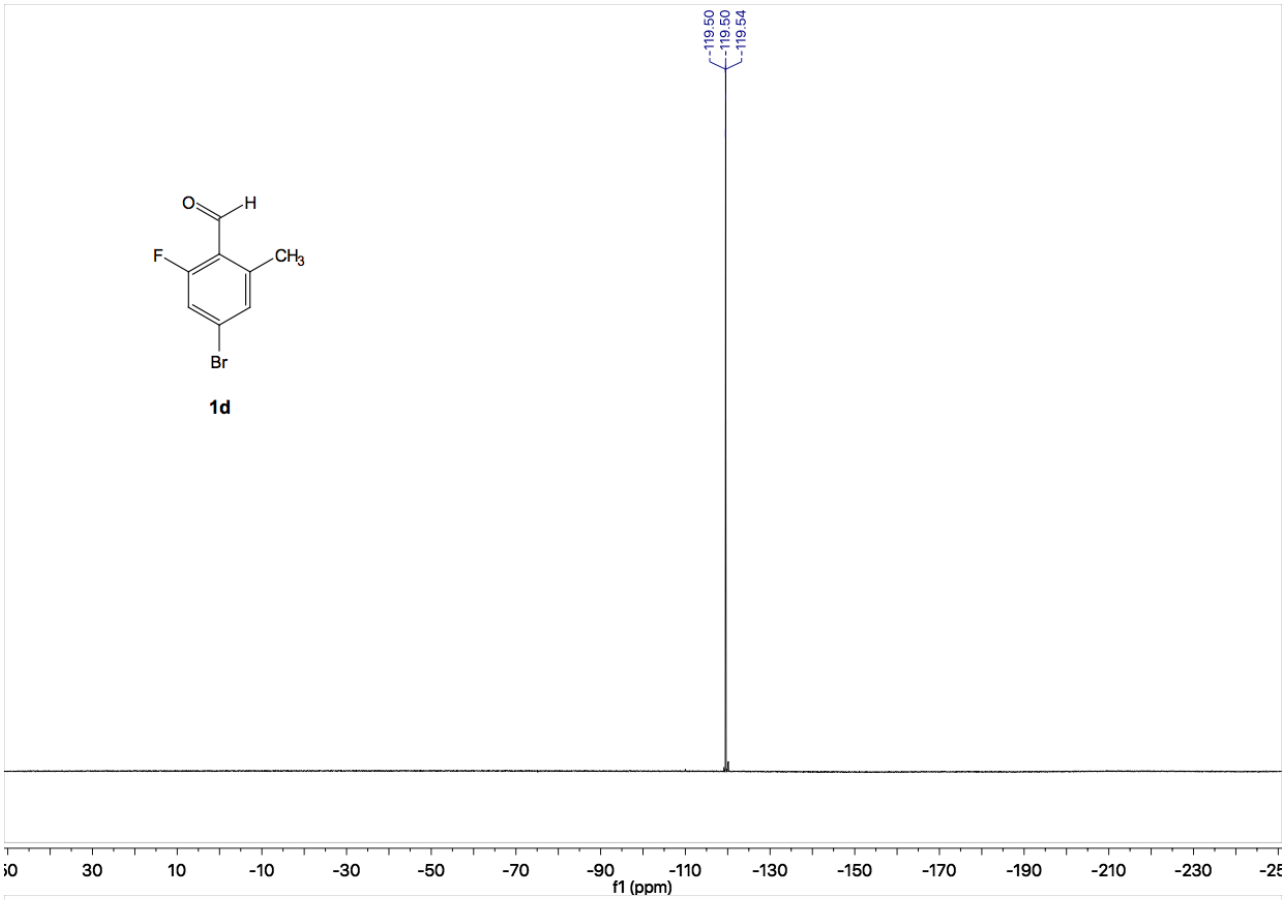
f1 (ppm)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-119.50
-119.54
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H
F
CH3
Br
1d
30
10
-10
-30
-50
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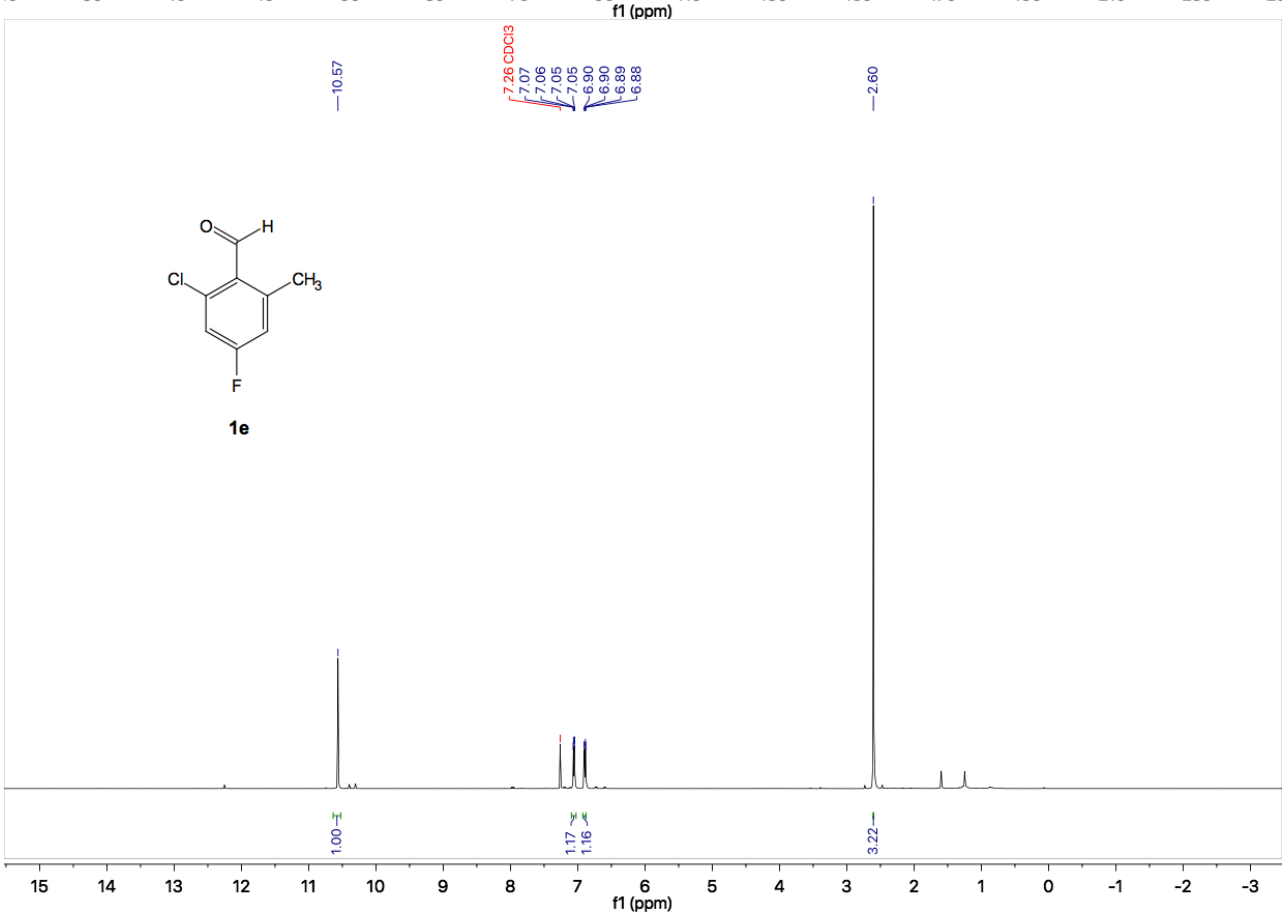
-150
-170
-190
-210
-230
f1 (ppm)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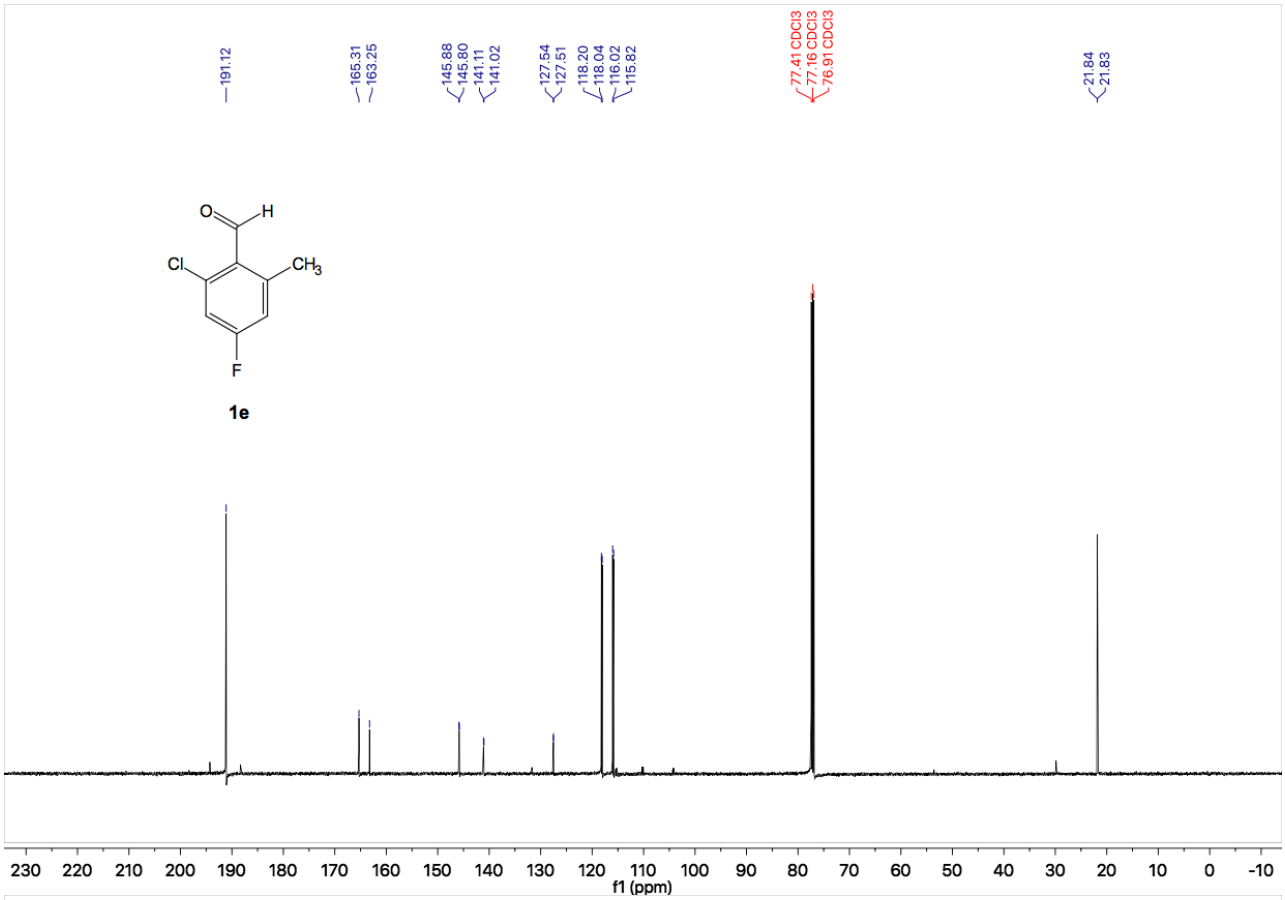
Cl
CH3
F
1e
1.00
1.17
1.16
3.22
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)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77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
21.84
21.83
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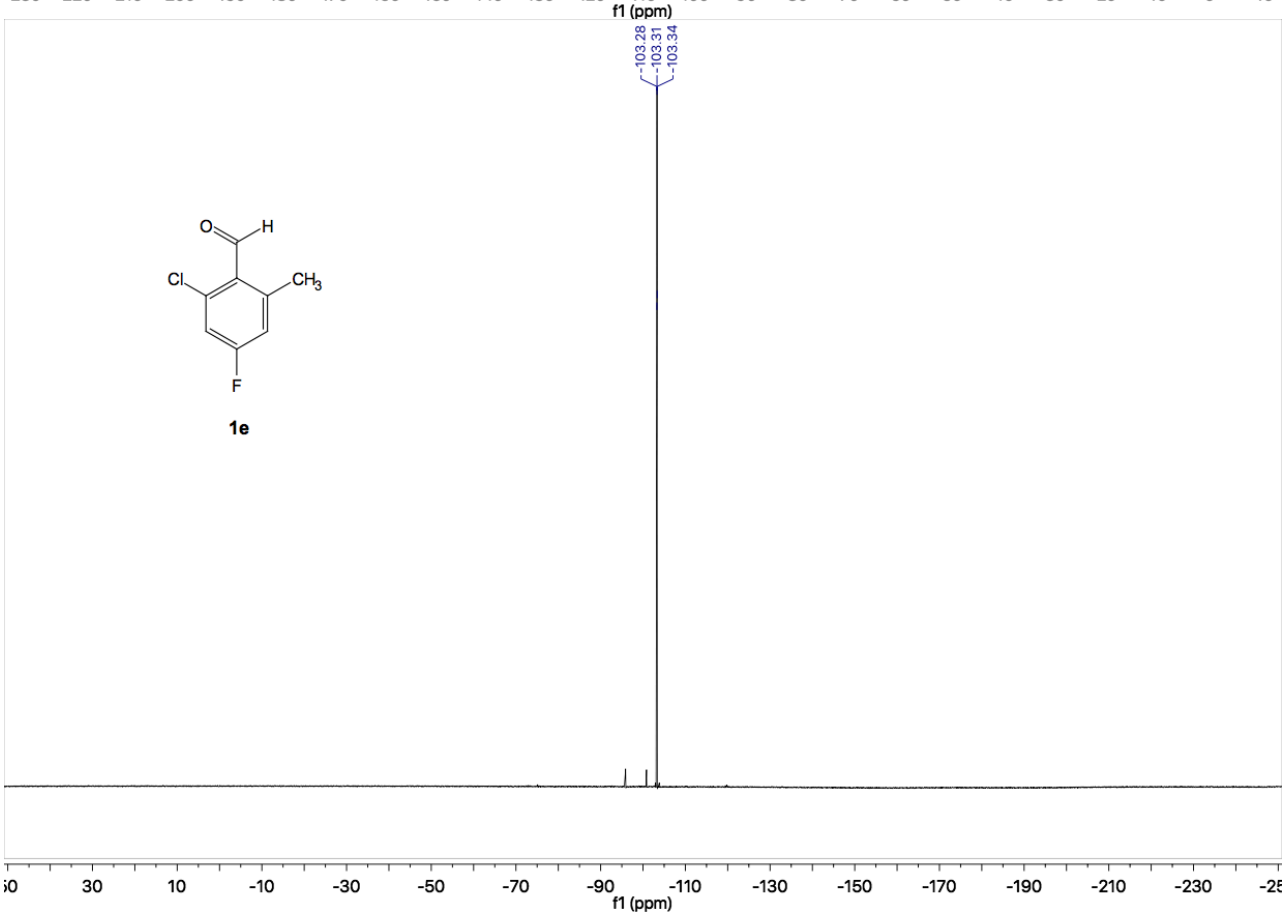
Cl
CH3
F
1e
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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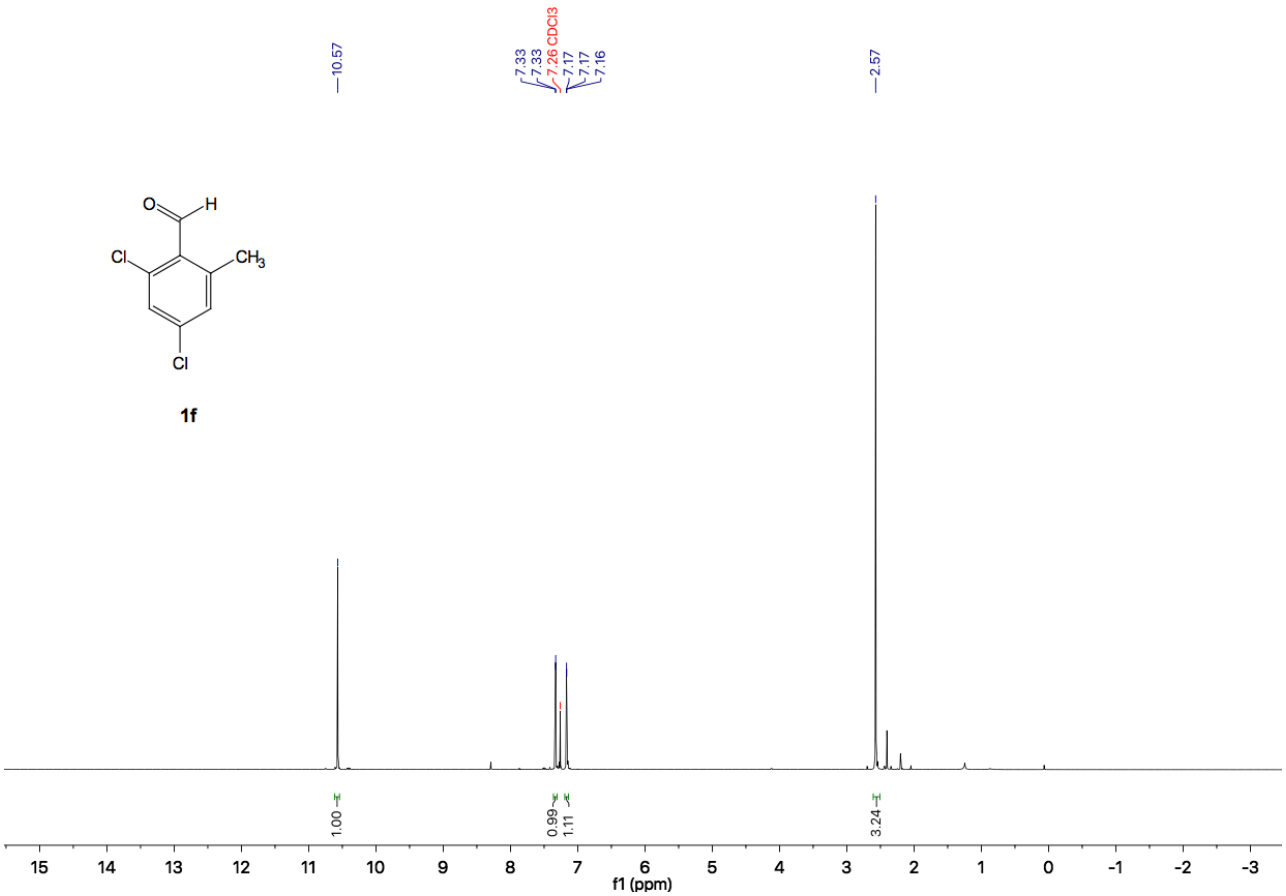
H
Cl
CH3
F
1e
30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)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H
Cl
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3.24
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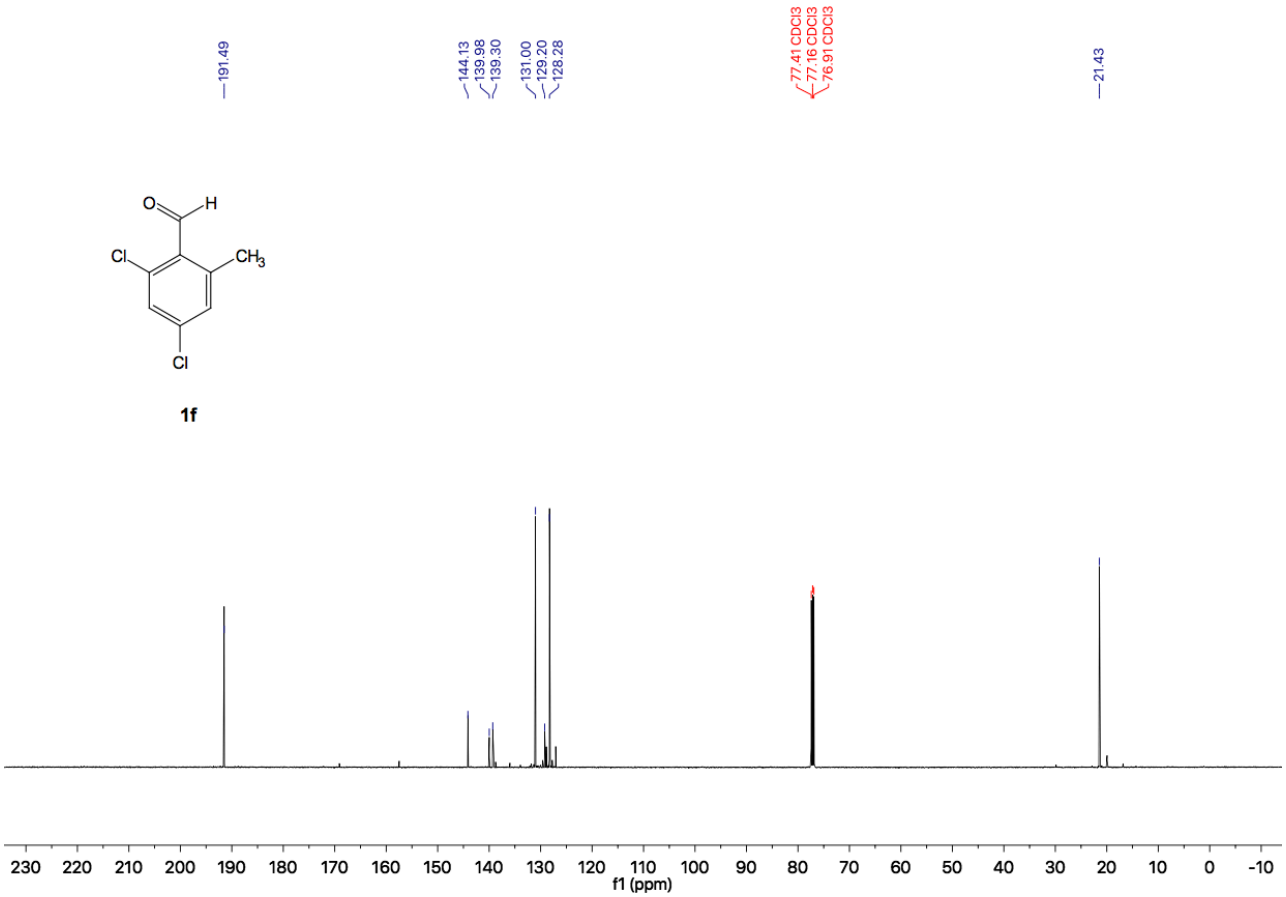
f1 (ppm)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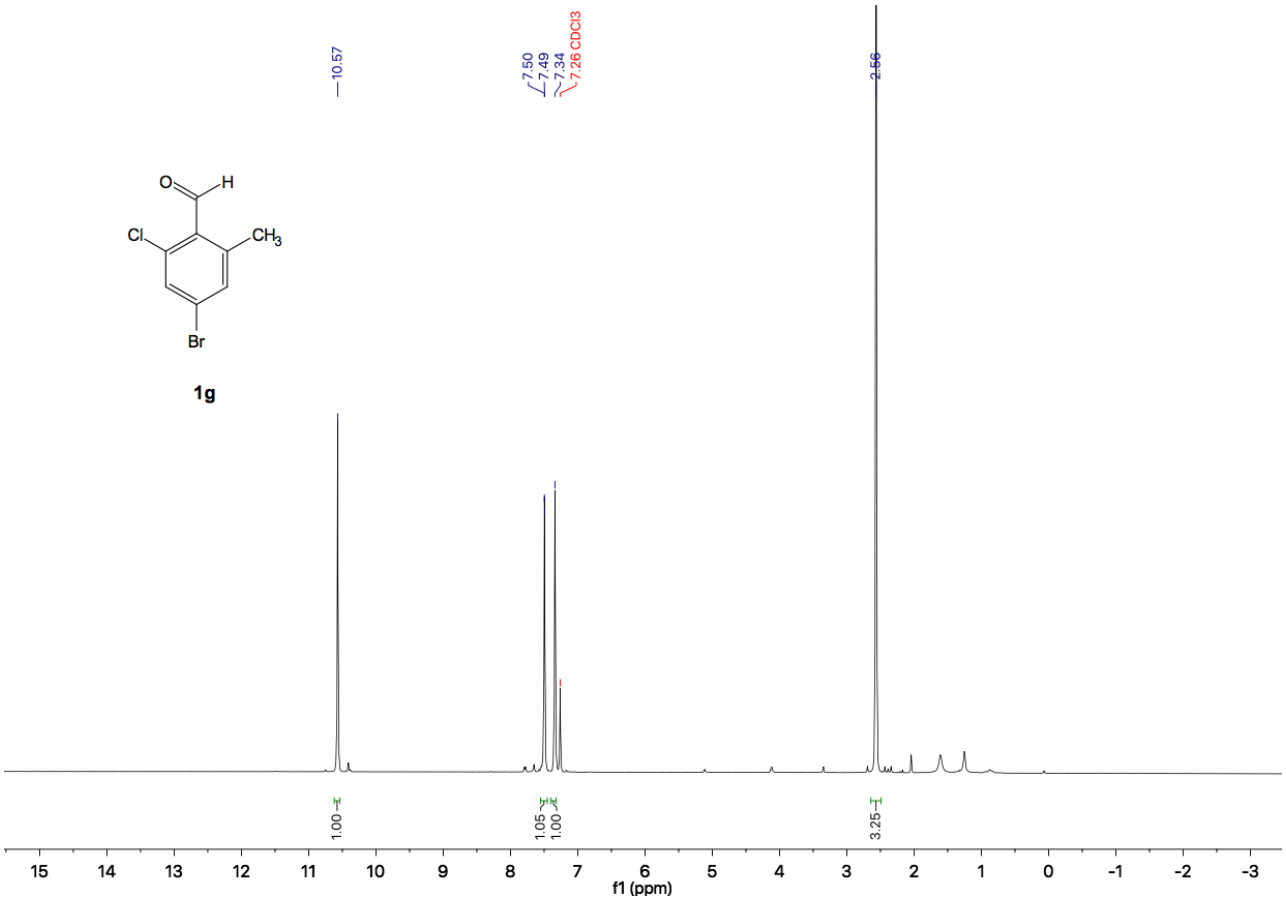
f1 (ppm)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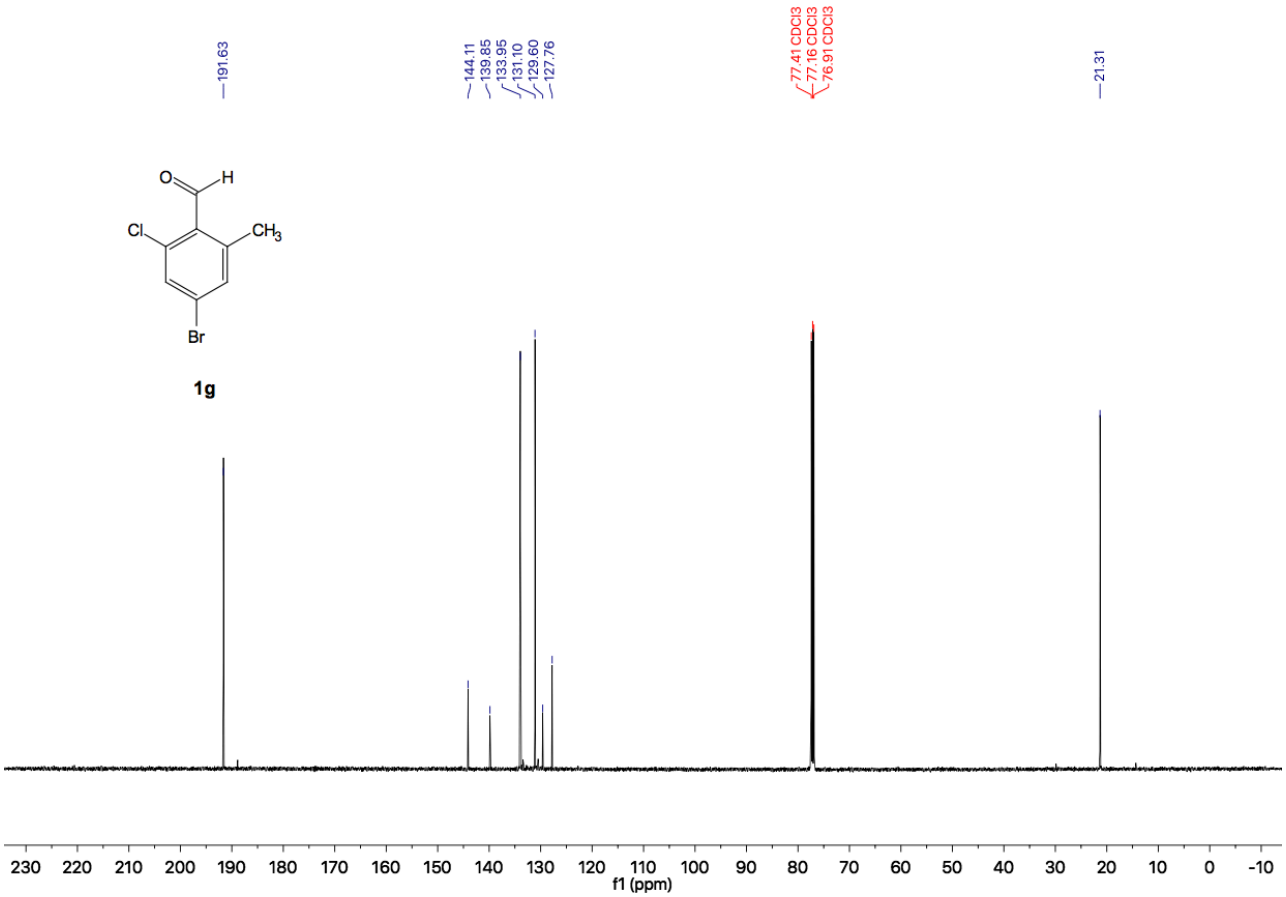
f1 (ppm)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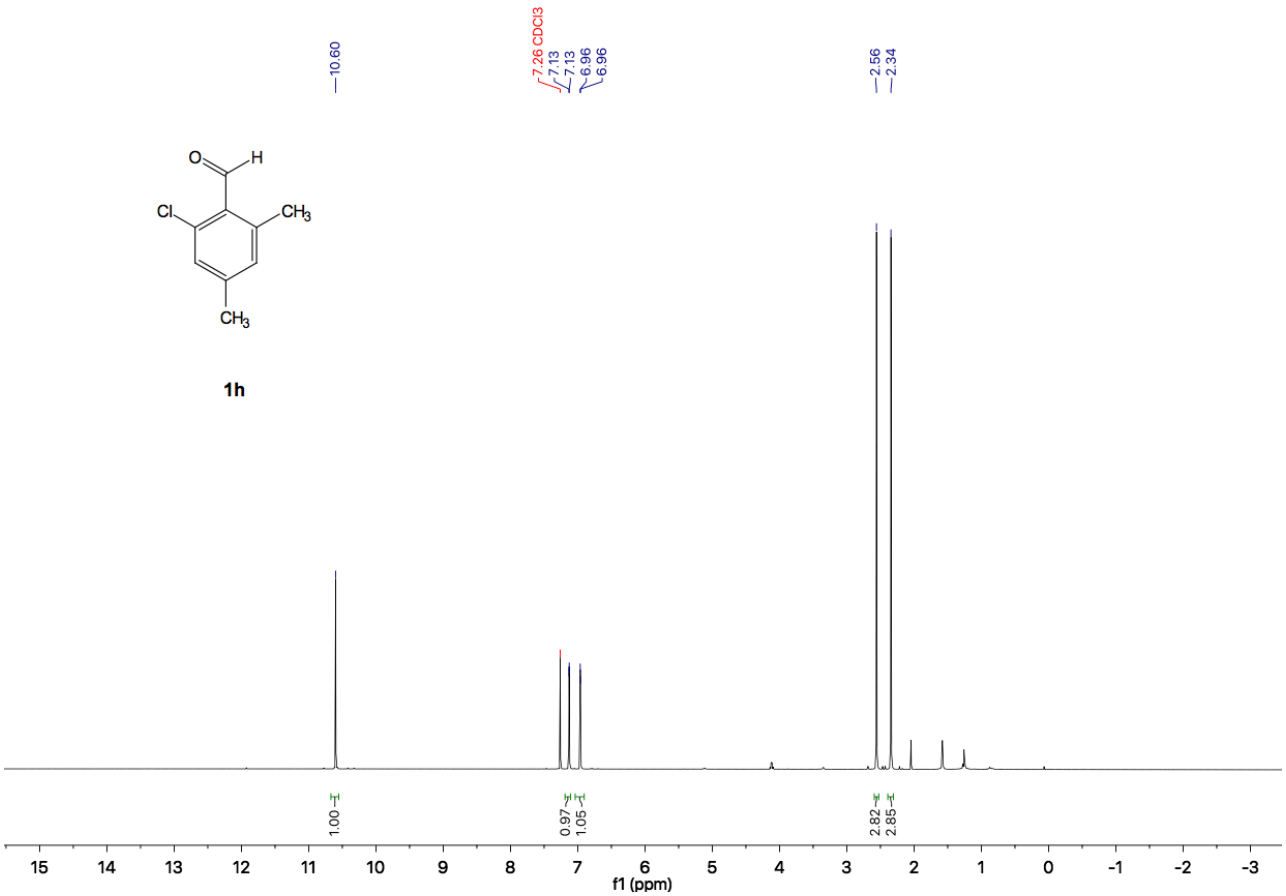
O
H
Cl
CH3
Br
1g
f1 (ppm)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H
Cl
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CH3
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1.05
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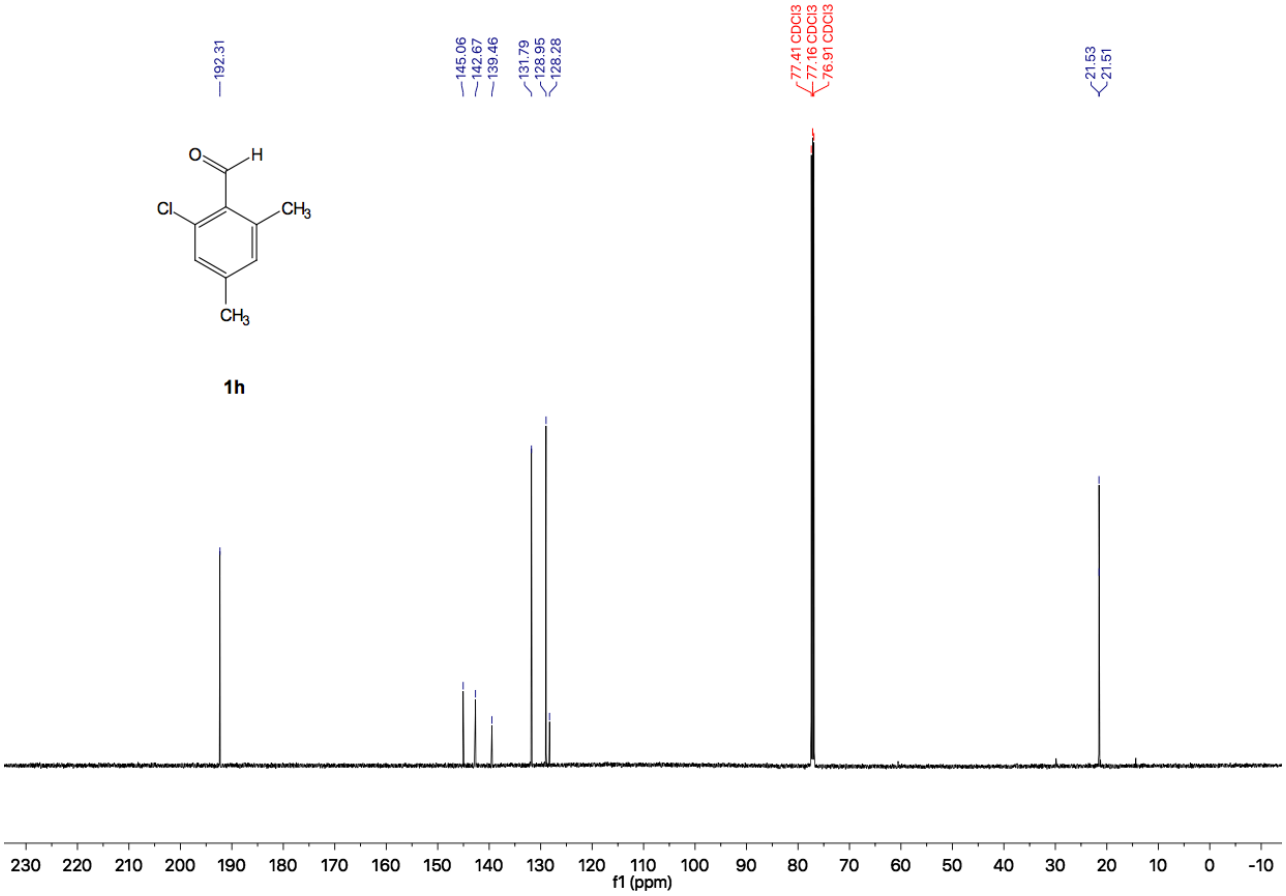
2.85
f1 (ppm)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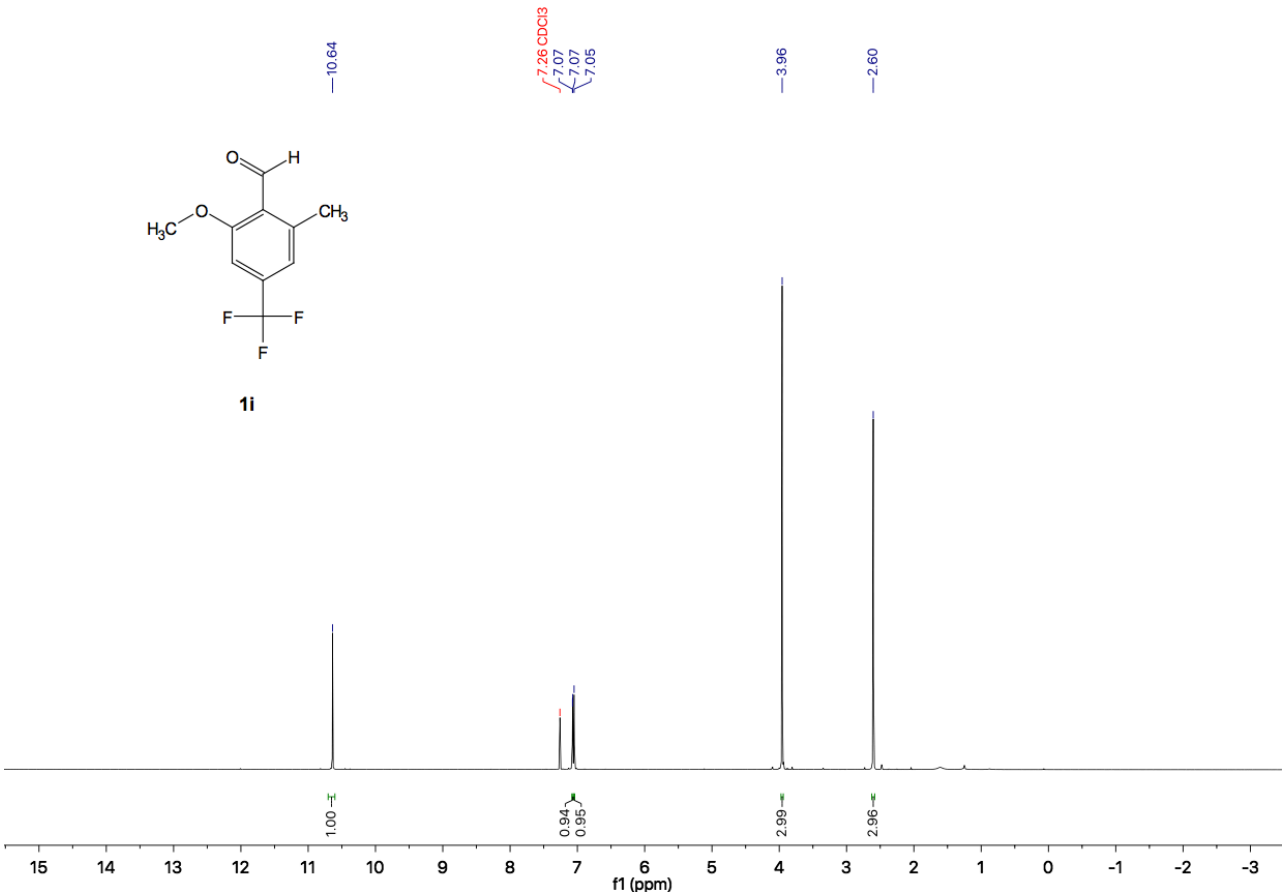
O
H
Cl
CH3
CH3
1h
f1 (ppm)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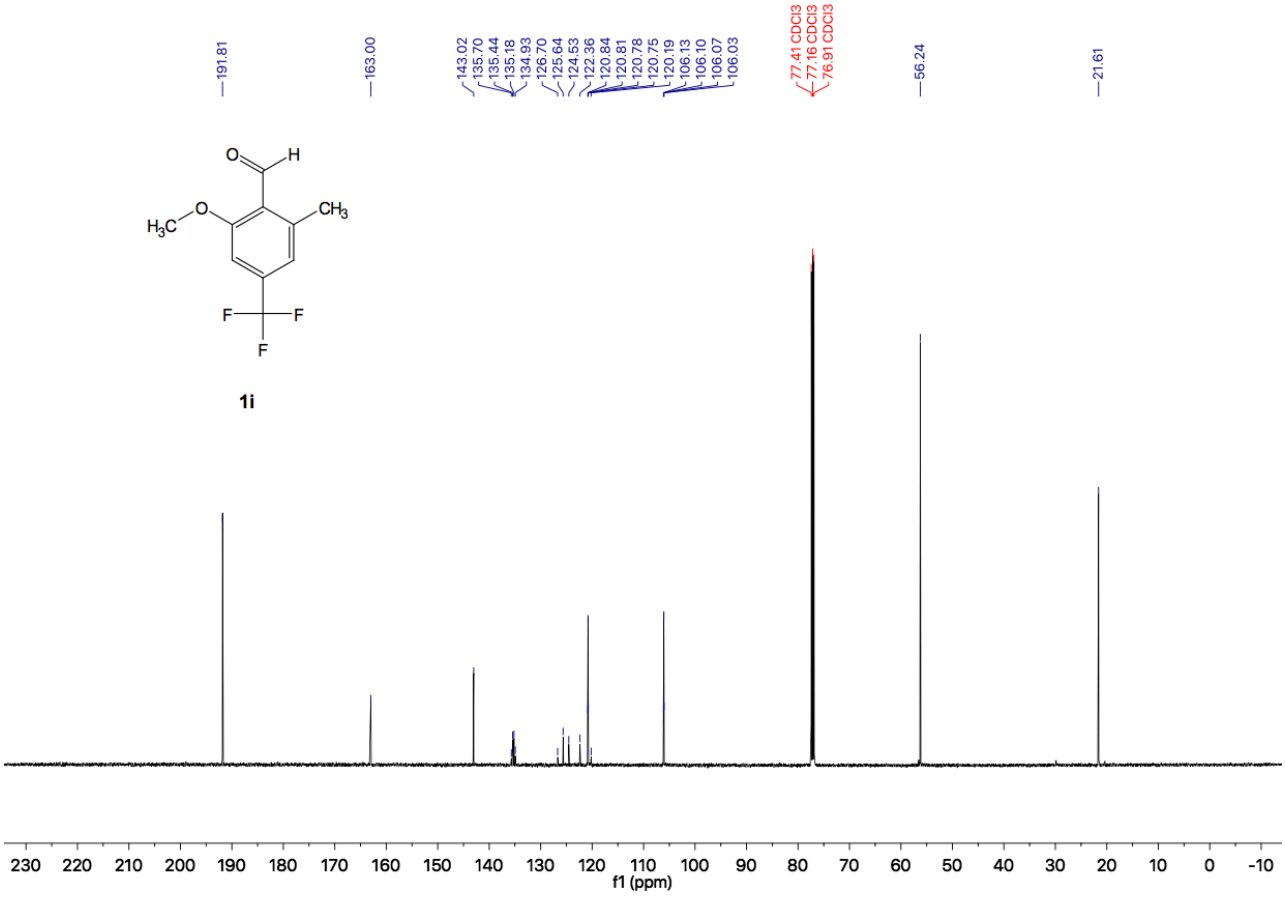
2.96
f1 (ppm)

1i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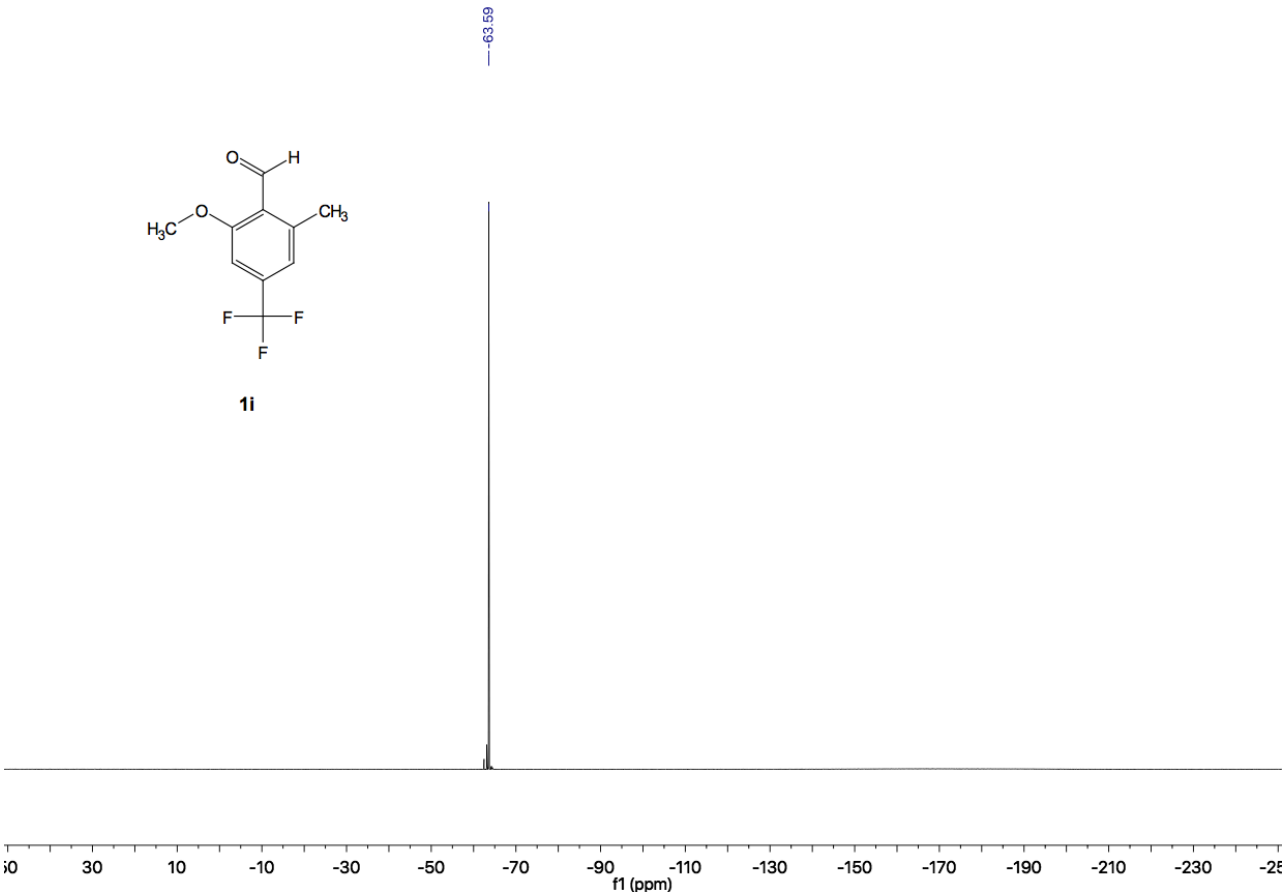
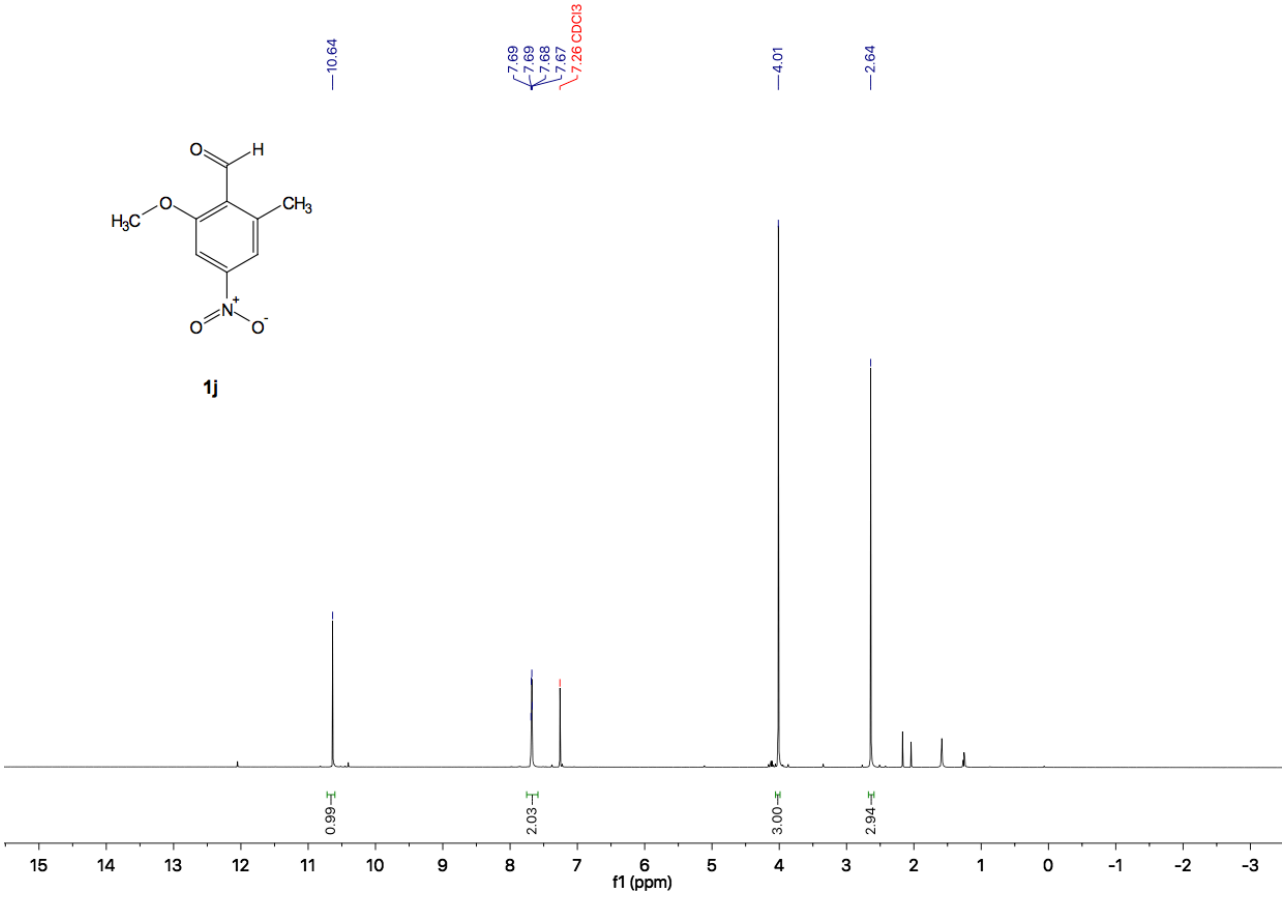
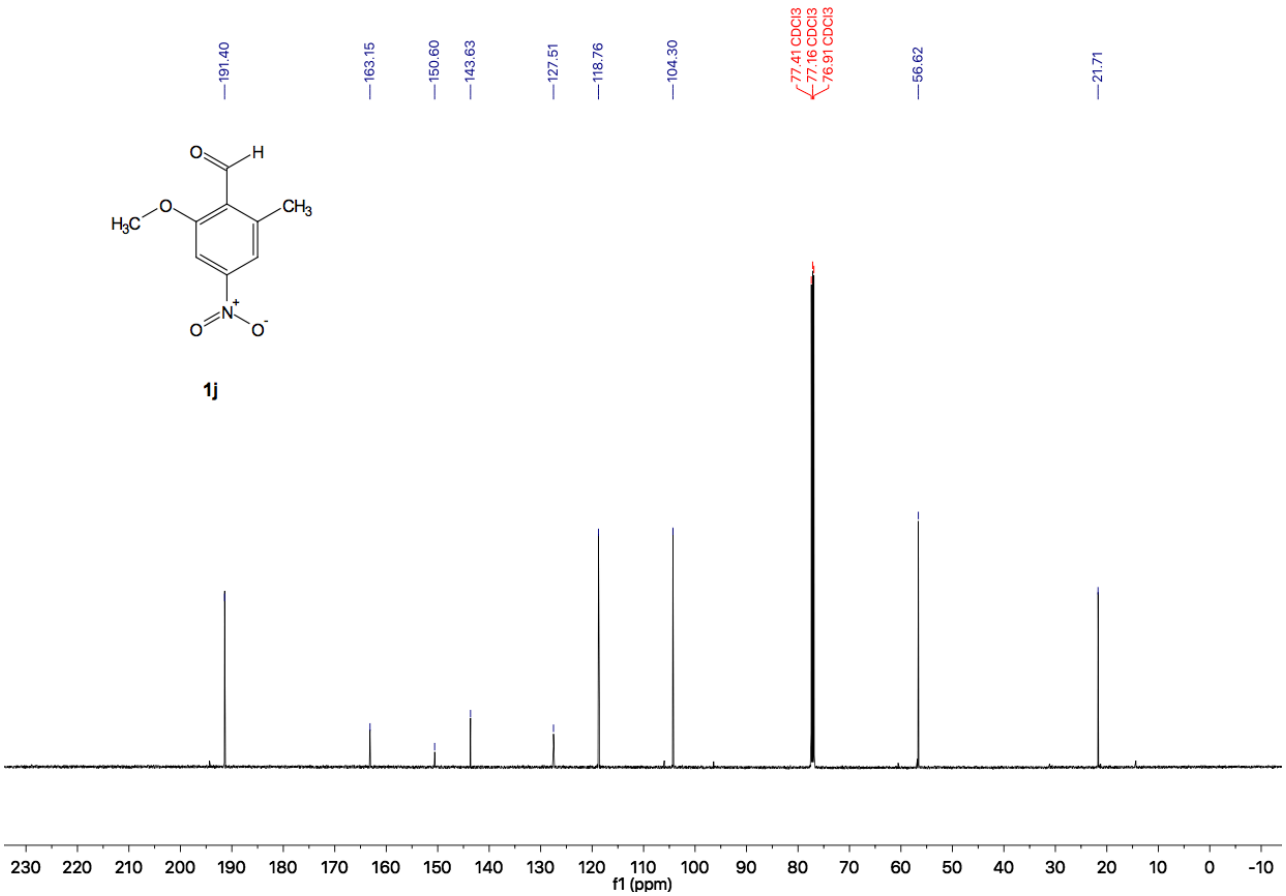
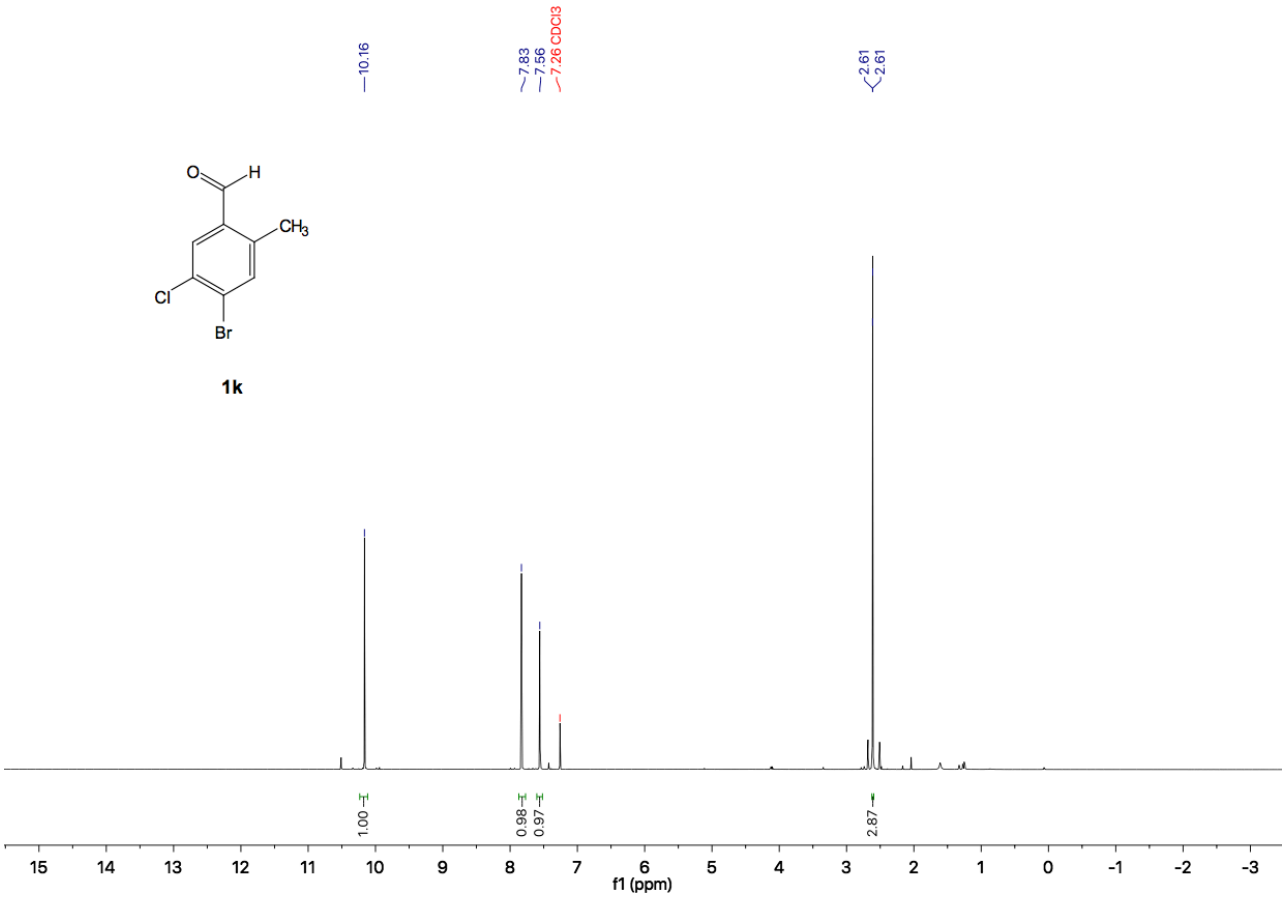
120.78
120.75
120.19
106.13
106.10
106.07
106.03
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
56.24
21.61
f1 (ppm)

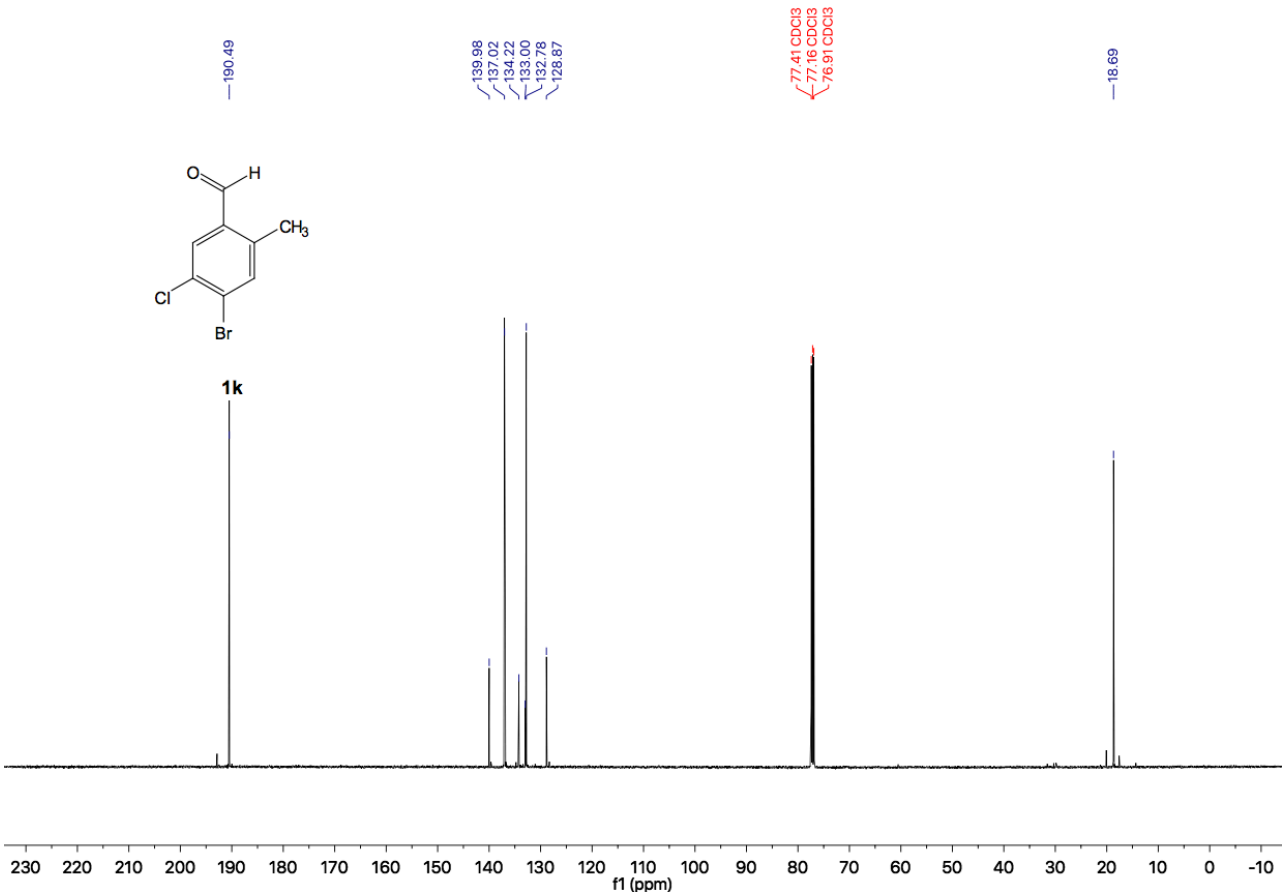
1i

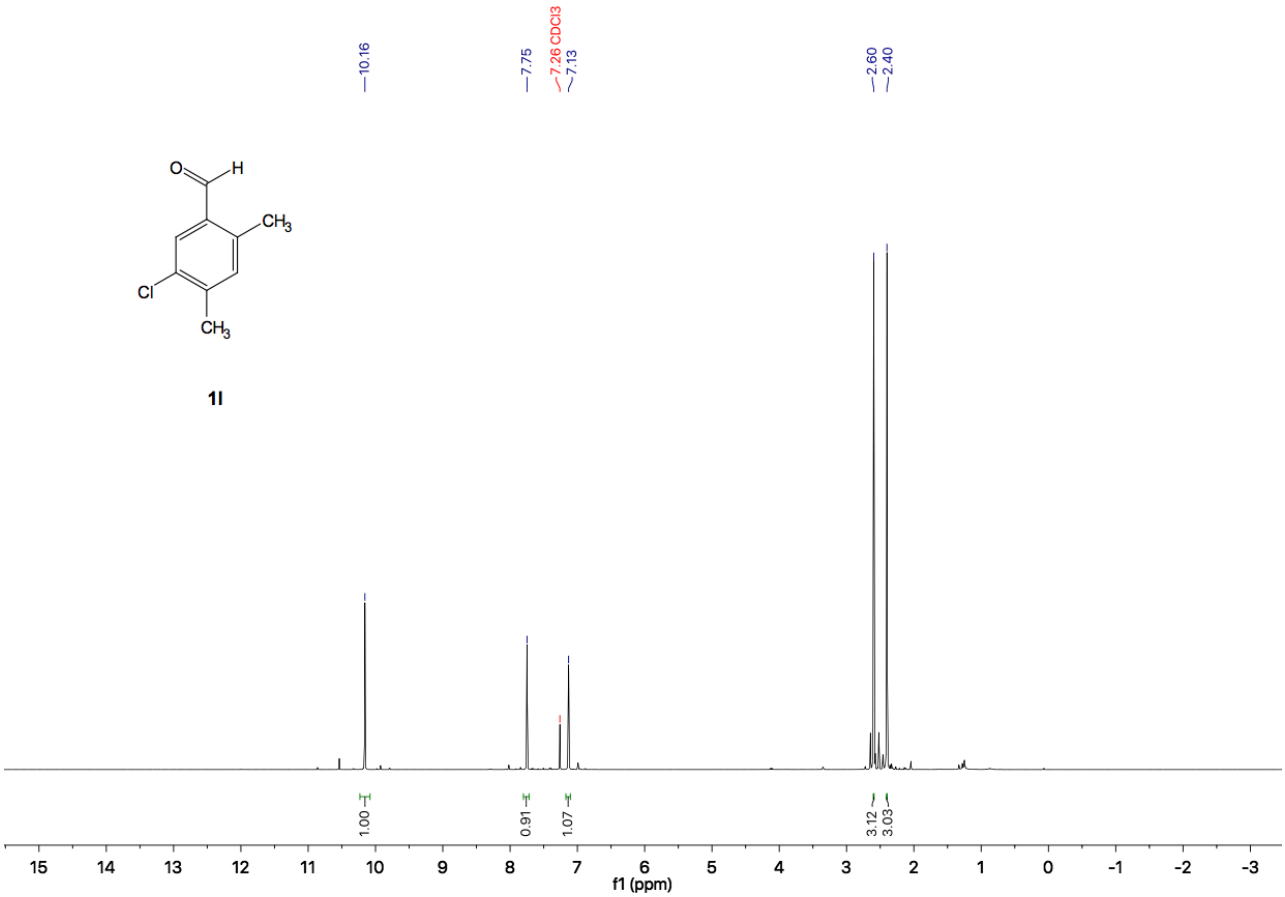

-63.59
O
H
H3C
O
CH3
F
F
F
1i
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

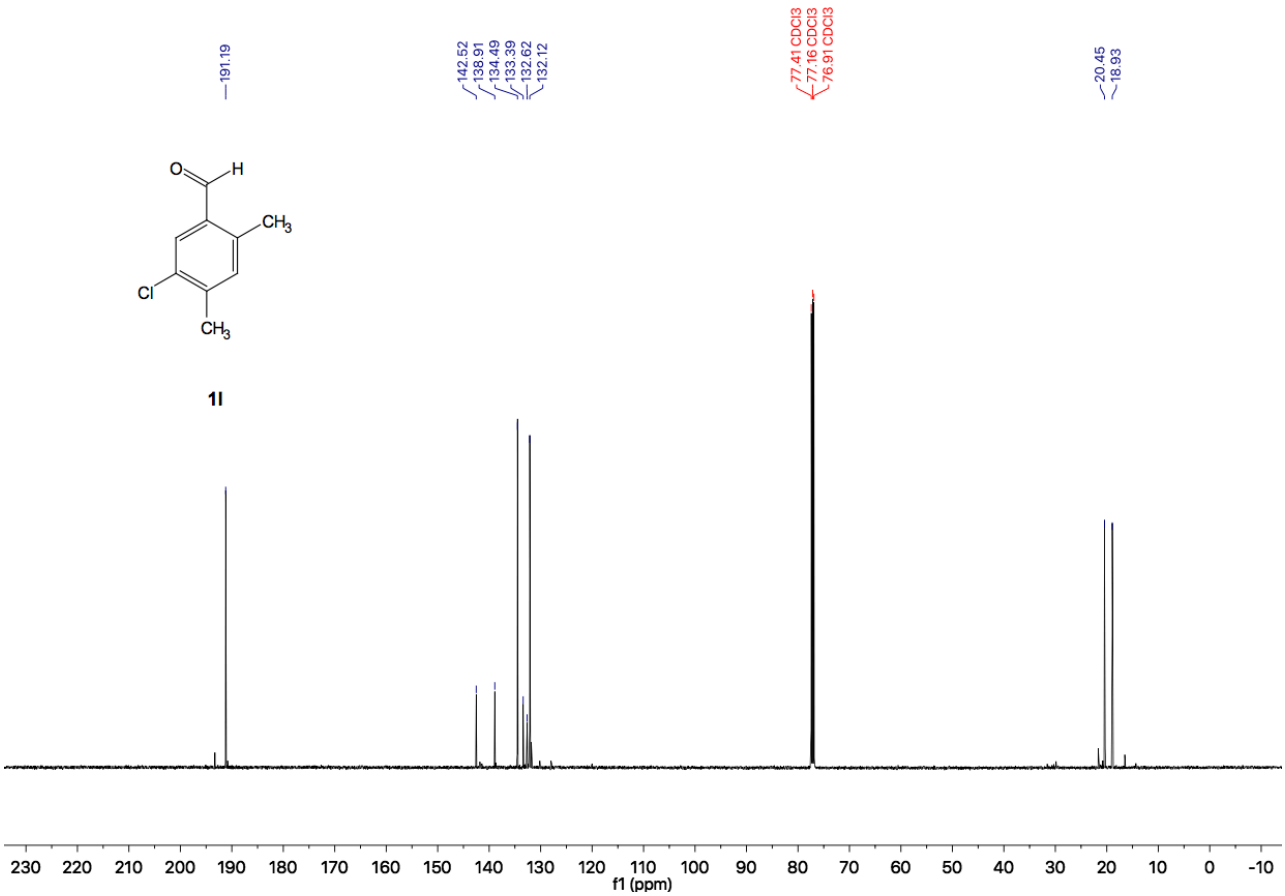

10.64
7.69
7.69
7.68
7.67
7.26 CDCl3
4.01
2.64
O
H
H3C
O
CH3
N+
O
O-
1j
0.99
2.03
3.00
2.94
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

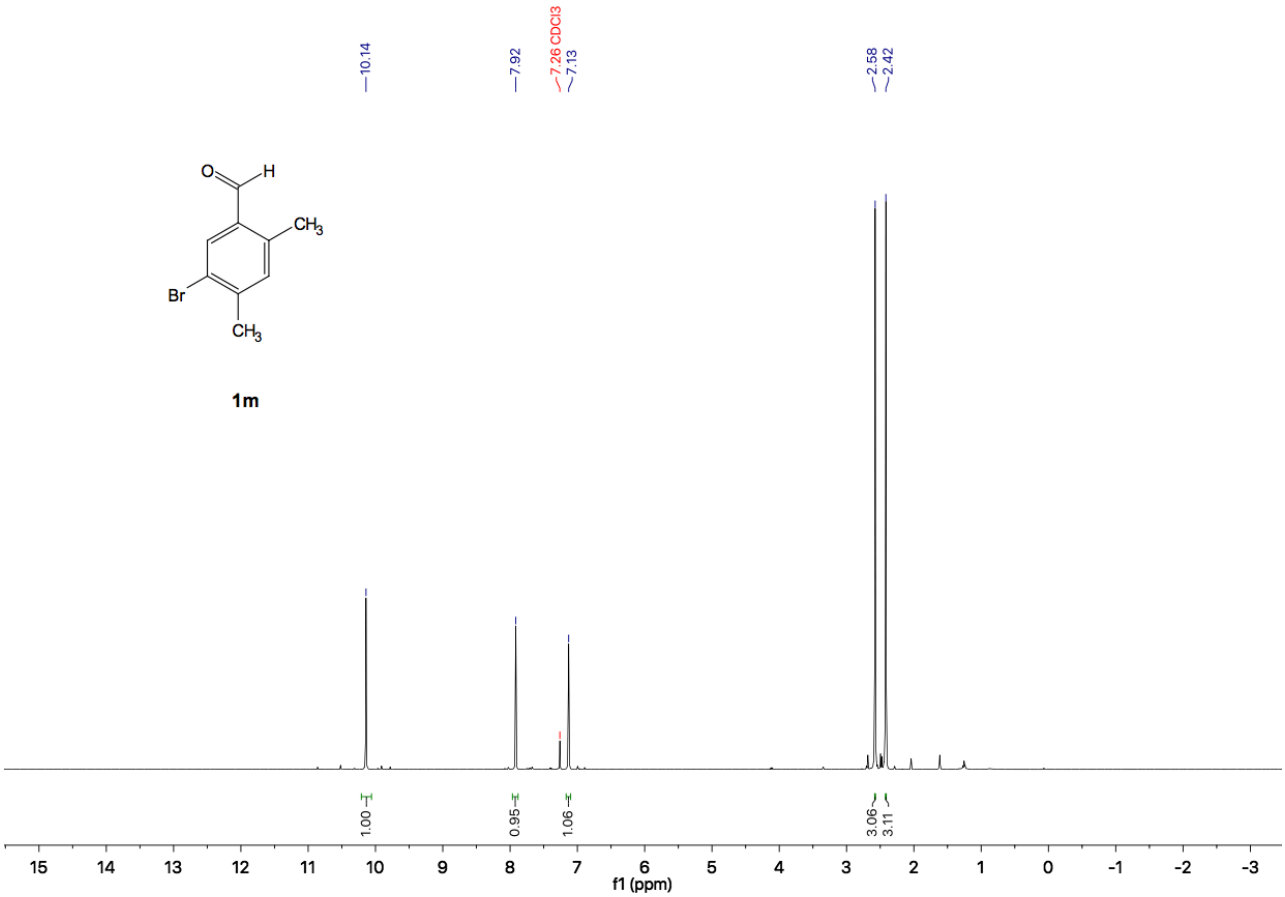

191.40
163.15
150.60
143.63
127.51
118.76
104.30
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
56.62
21.71
O
H
H3C
O
CH3
O
N+
O
O-
1j
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

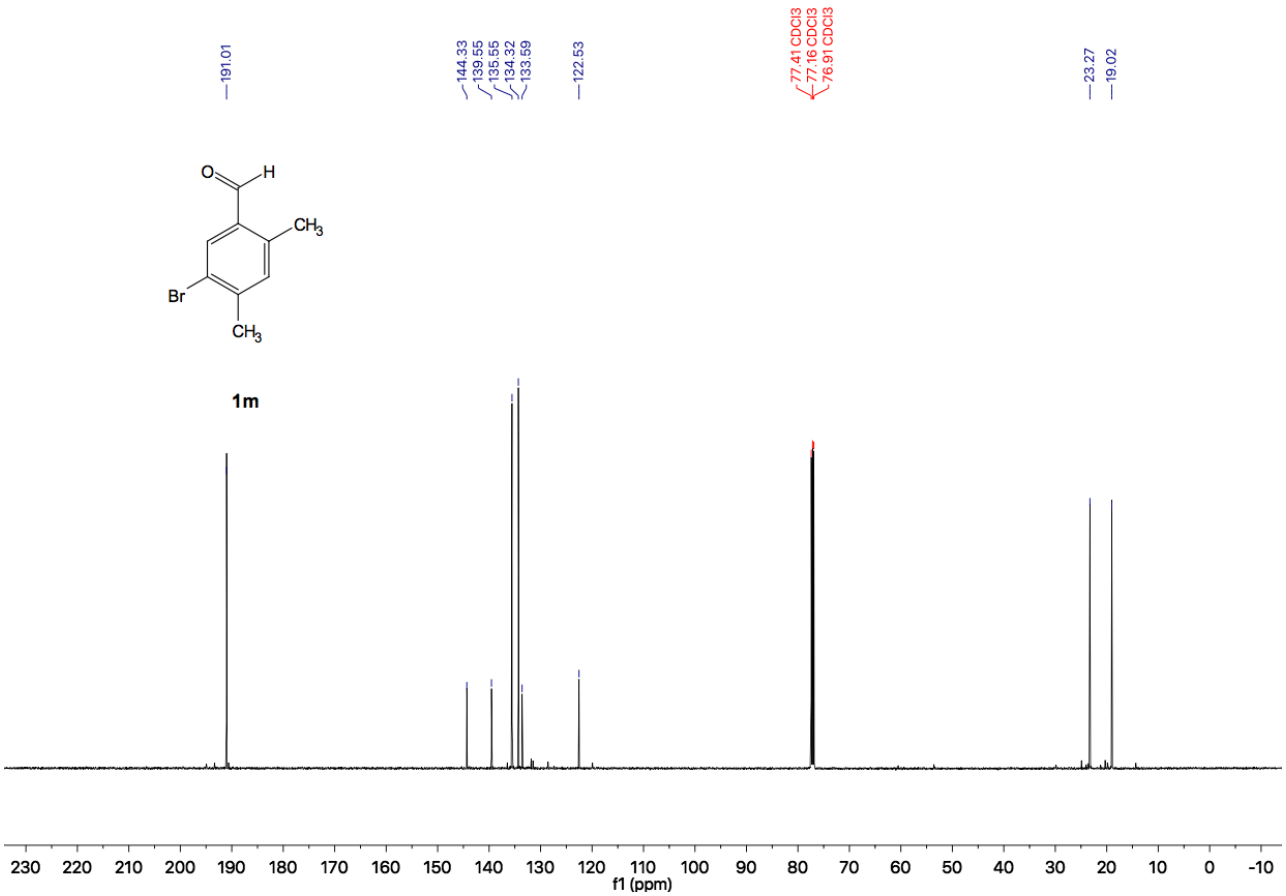

10.16
7.83
7.56
7.26 CDCl3
2.61
2.61
O
H
CH3
Cl
Br
1k
1.00
0.98
0.97
2.87
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

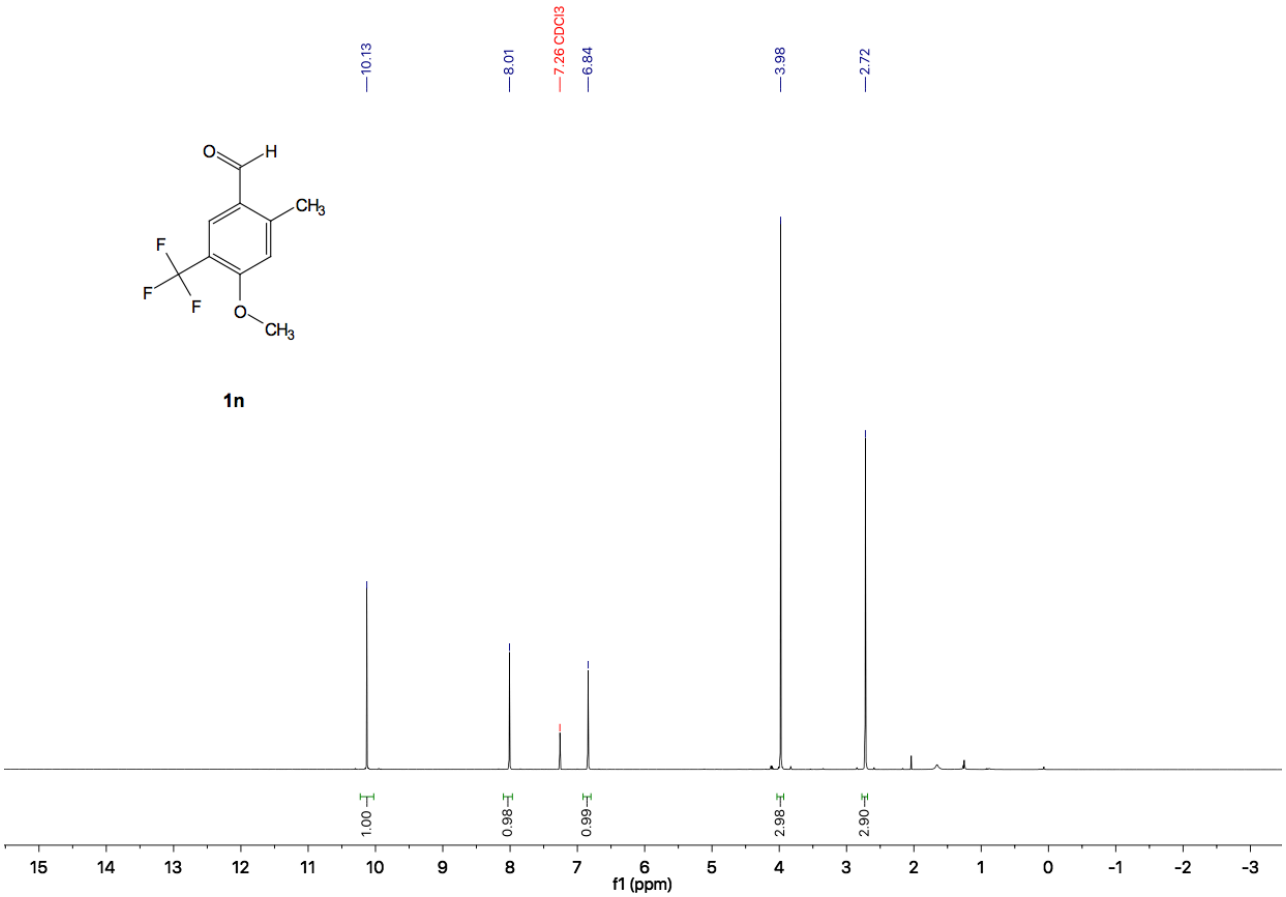

190.49
139.98
137.02
134.22
133.00
132.78
128.87
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
18.69
O
H
CH3
Cl
Br
1k
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

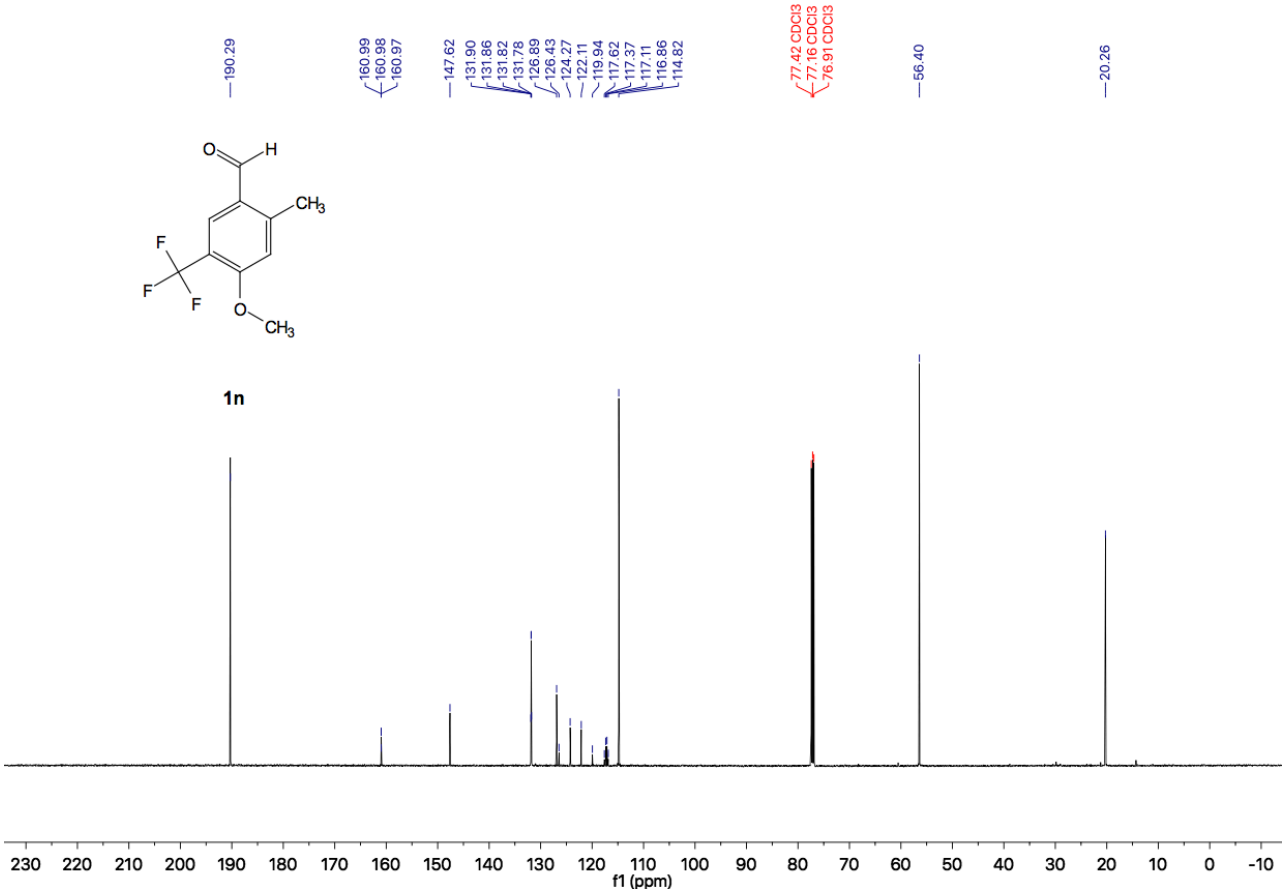

10.16
7.75
7.26 CDCl3
7.13
2.60
2.40
O
H
CH3
Cl
CH3
1l
1.00
0.91
1.07
3.12
3.03
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

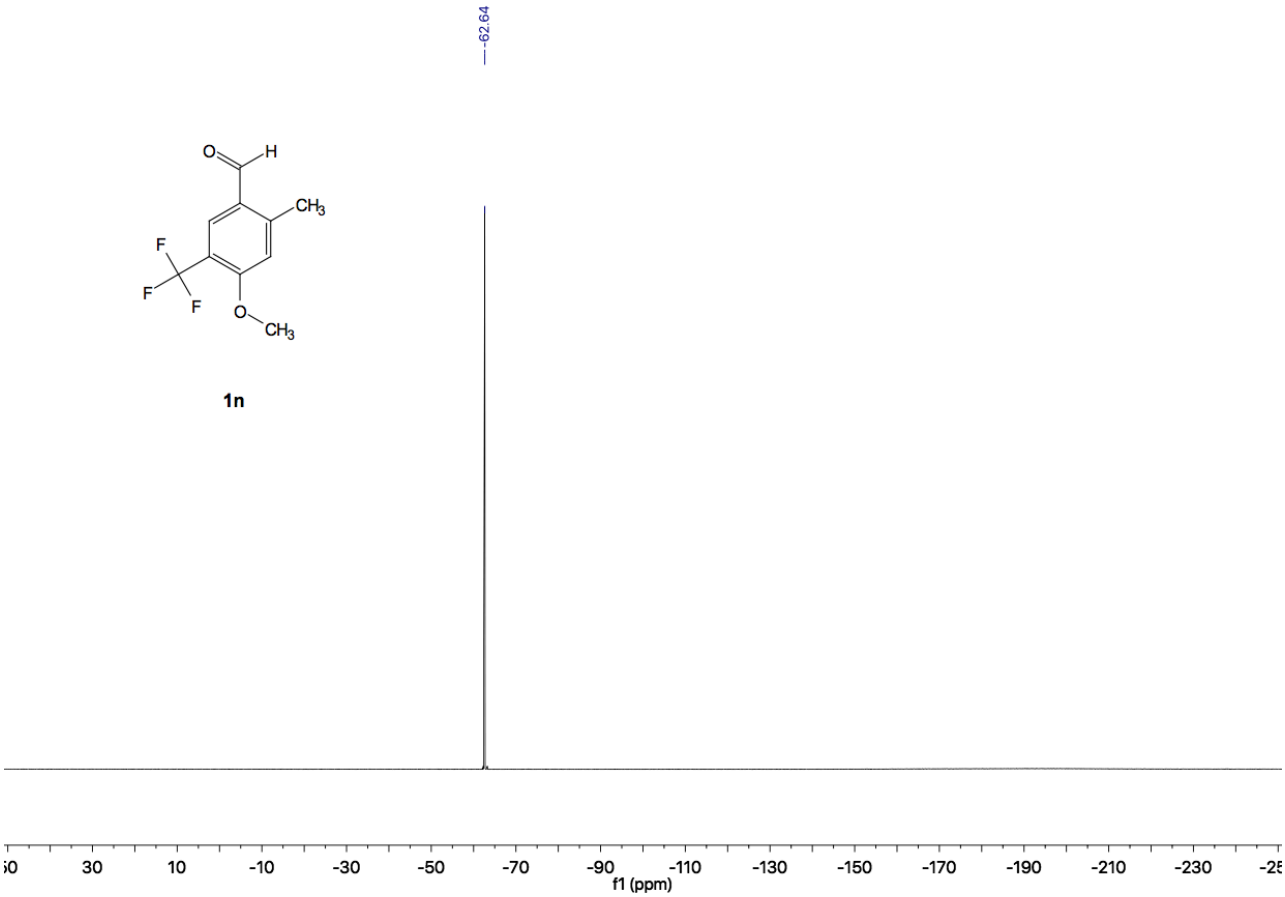

191.19
142.52
138.91
134.49
133.39
132.62
132.12
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
20.45
18.93
O
H
CH3
Cl
CH3
1l
f1 (ppm)

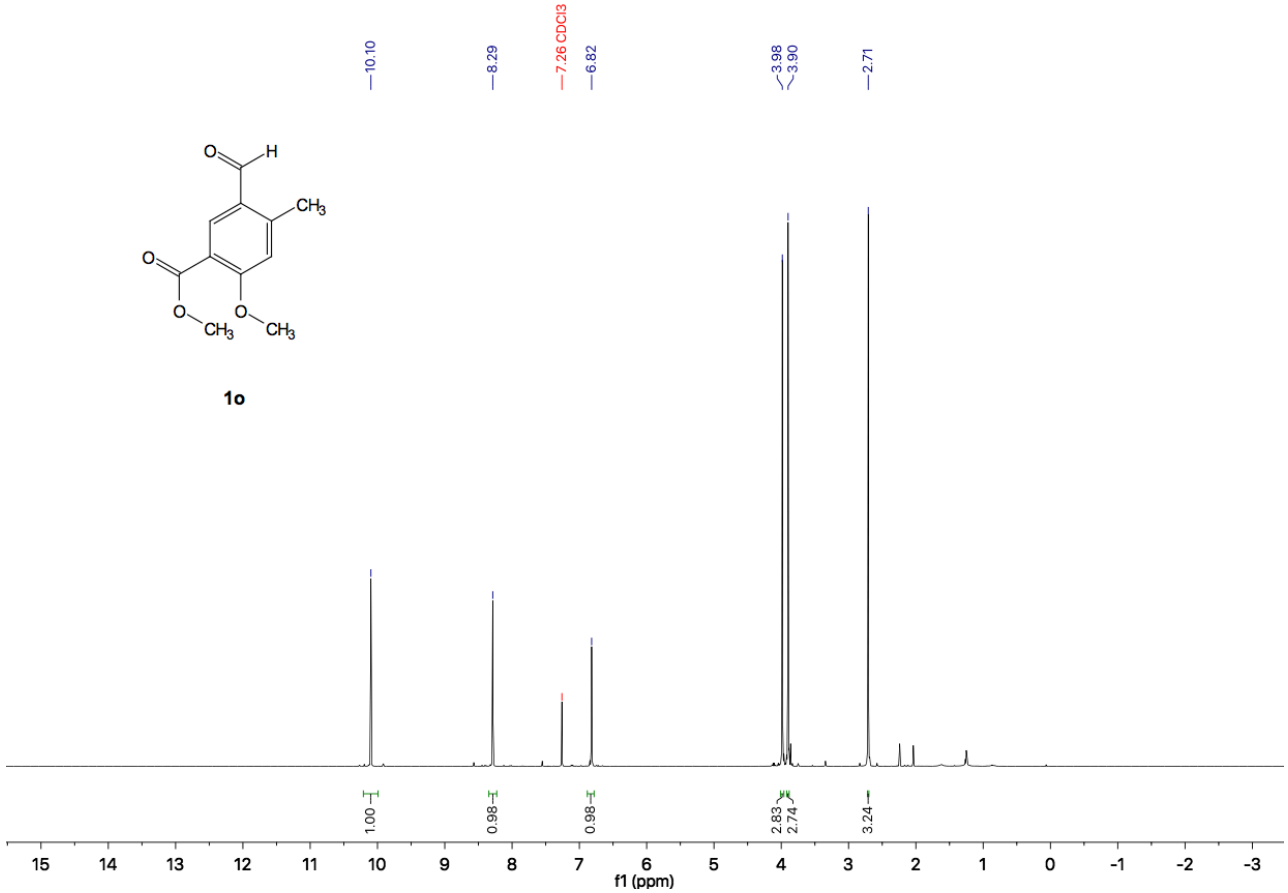

10.14
7.92
7.26 CDCl3
7.13
2.58
2.42
O
H
CH3
Br
CH3
1m
1.00
0.95
1.06
3.06
3.11
f1 (ppm)


191.01
144.33
139.55
135.55
134.32
133.59
122.53
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
23.27
19.02
O
H
CH3
Br
CH3
1m
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

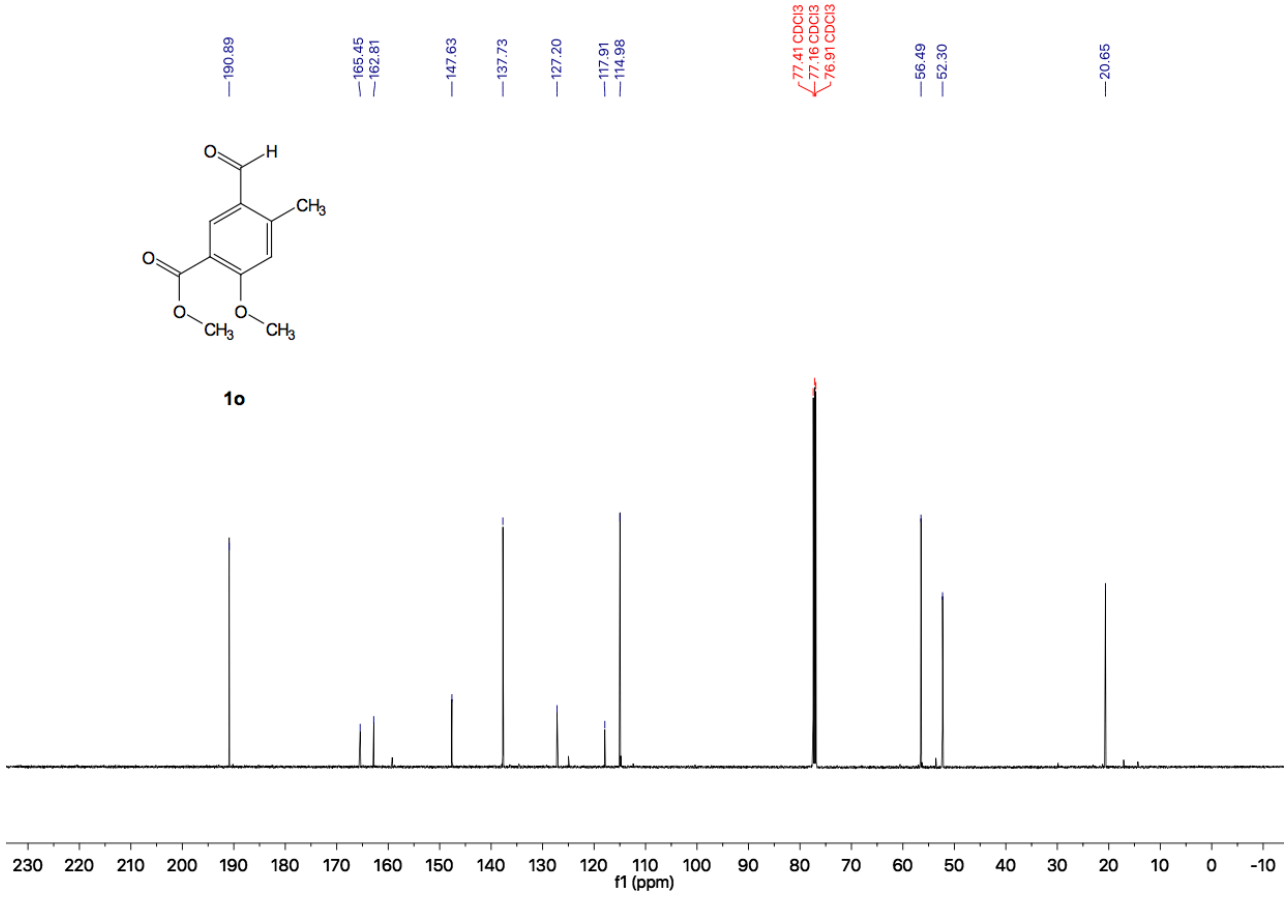

10.13
8.01
7.26 CDCl3
6.84
3.98
2.72
O
H
CH3
F
F
F
O
CH3
1n
1.00
0.98
0.99
2.98
2.90
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


190.29
160.99
160.98
160.97
147.62
131.90
131.86
131.82
131.78
126.89
126.43
124.27
122.11
119.94
117.62
117.37
117.11
116.86
114.82
77.42 CDCl3
77.16 CDCl3
76.91 CDCl3
56.40
20.26
O
H
CH3
F
F
F
O
CH3
1n
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

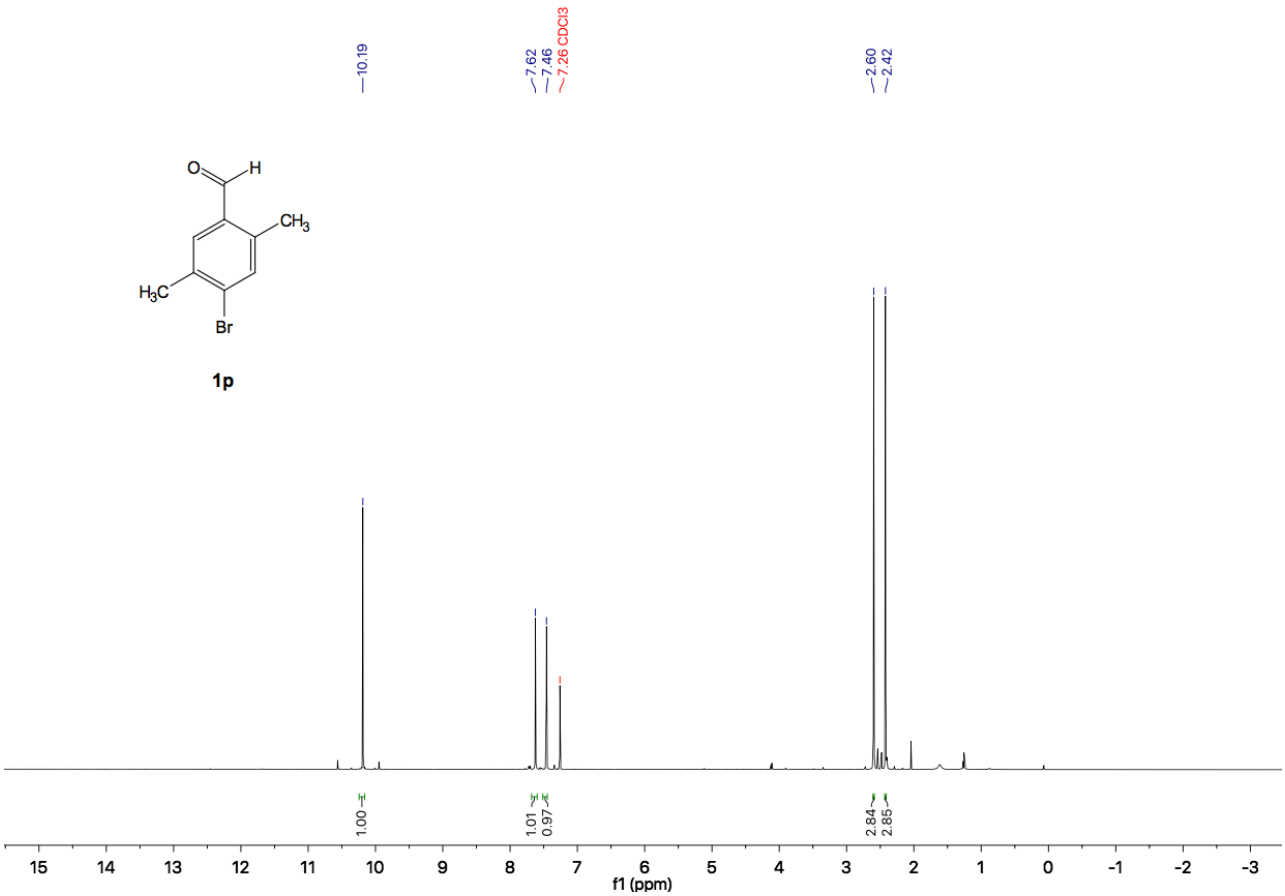

-62.64
O
H
CH3
F
F
F
O
CH3
1n
50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -25
f1 (ppm)

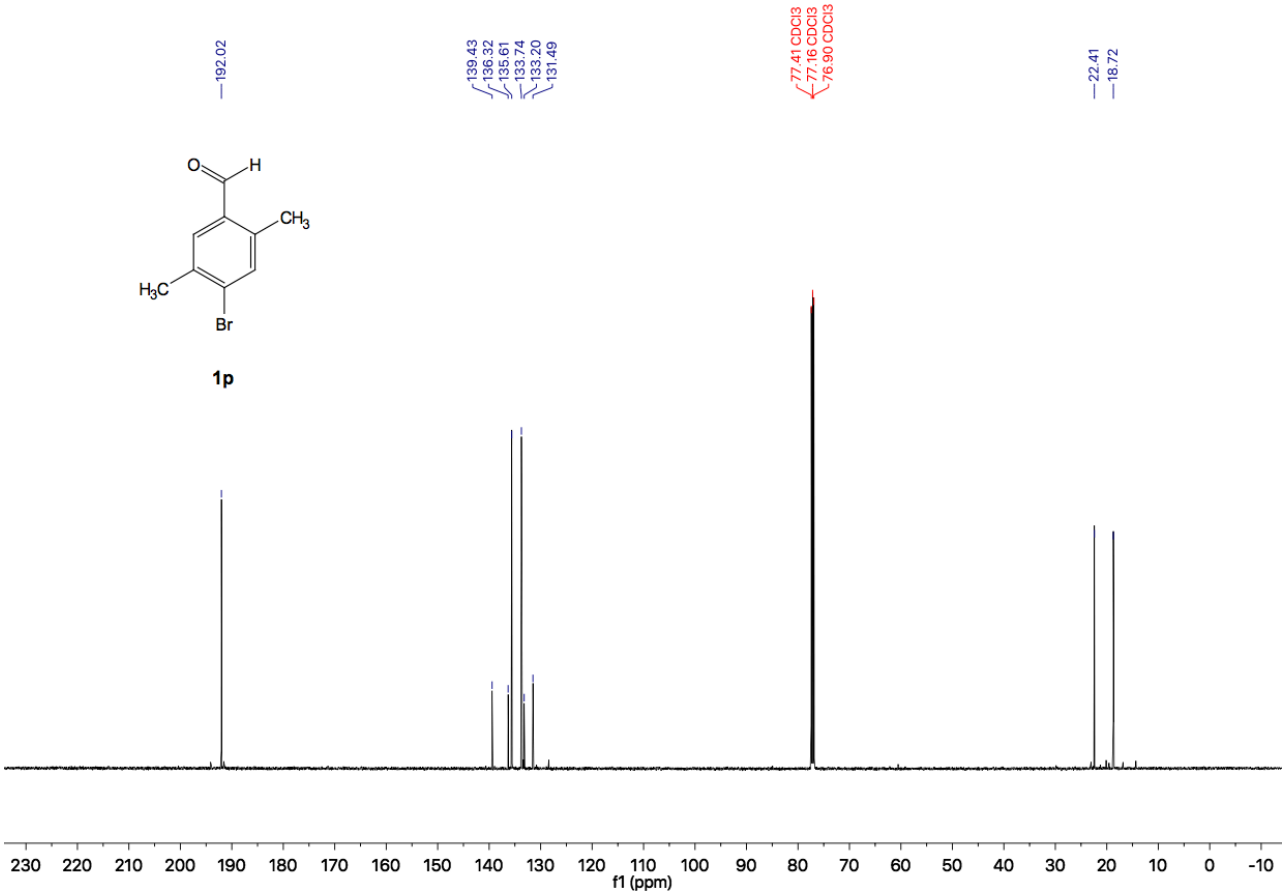

10.10
8.29
7.26 CDCl3
6.82
3.98
3.90
2.71
1.00
0.98
0.98
2.83
2.74
3.24
f1 (ppm)

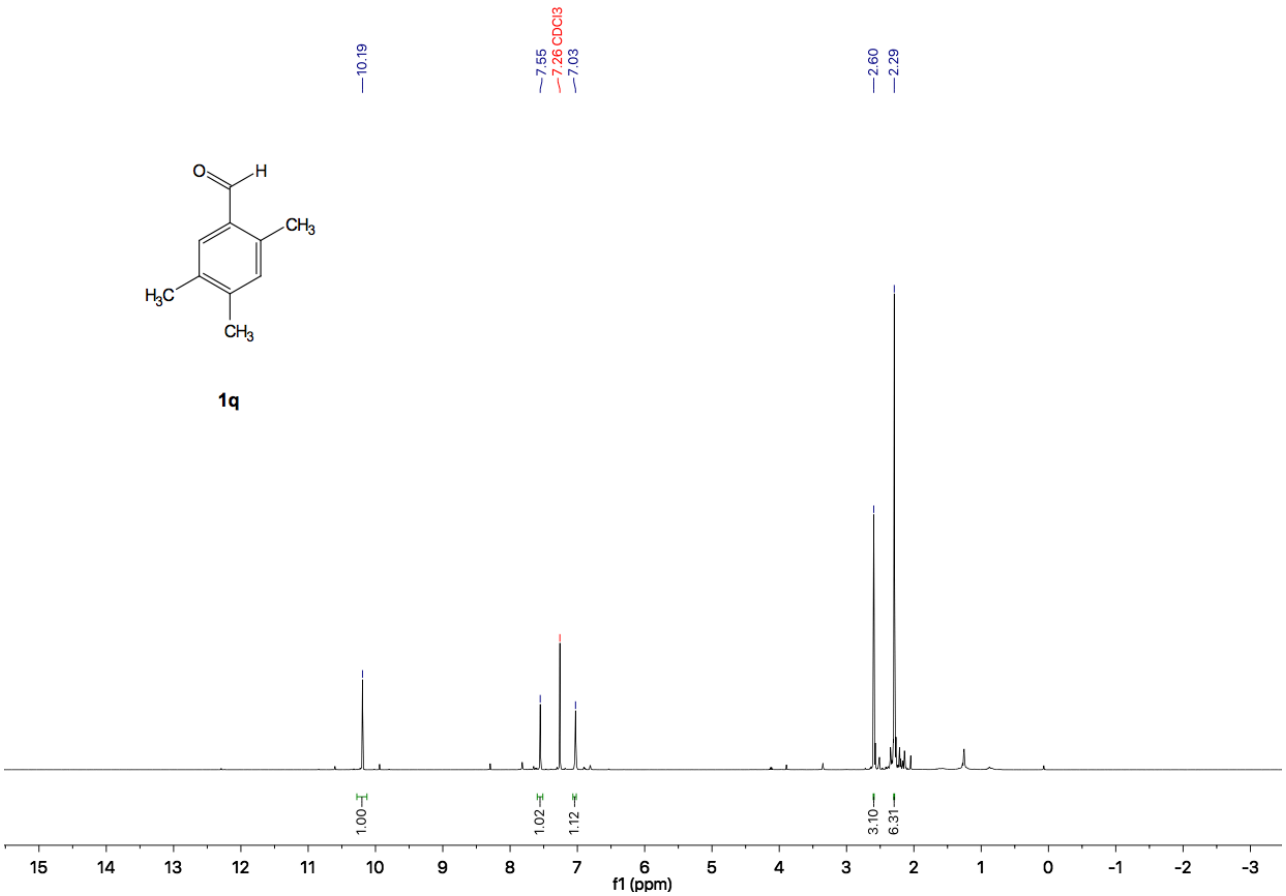
1o


190.89
165.45
162.81
147.63
137.73
127.20
117.91
114.98
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
56.49
52.30
20.65
f1 (ppm)

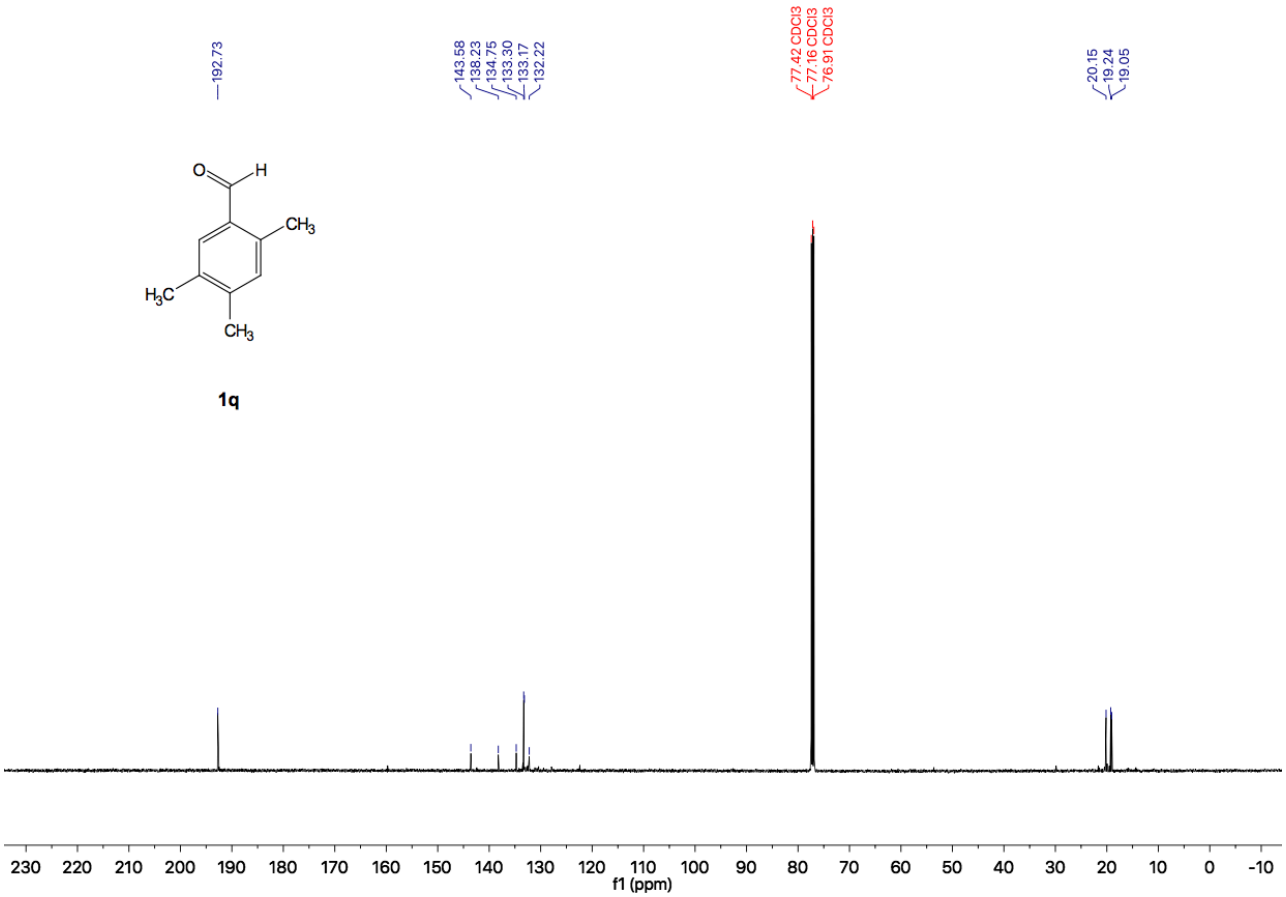
1o


10.19
7.62
7.46
7.26 CDCl3
2.60
2.42
O
H
CH3
H3C
Br
1p
1.00
1.01
0.97
2.84
2.85
f1 (ppm)

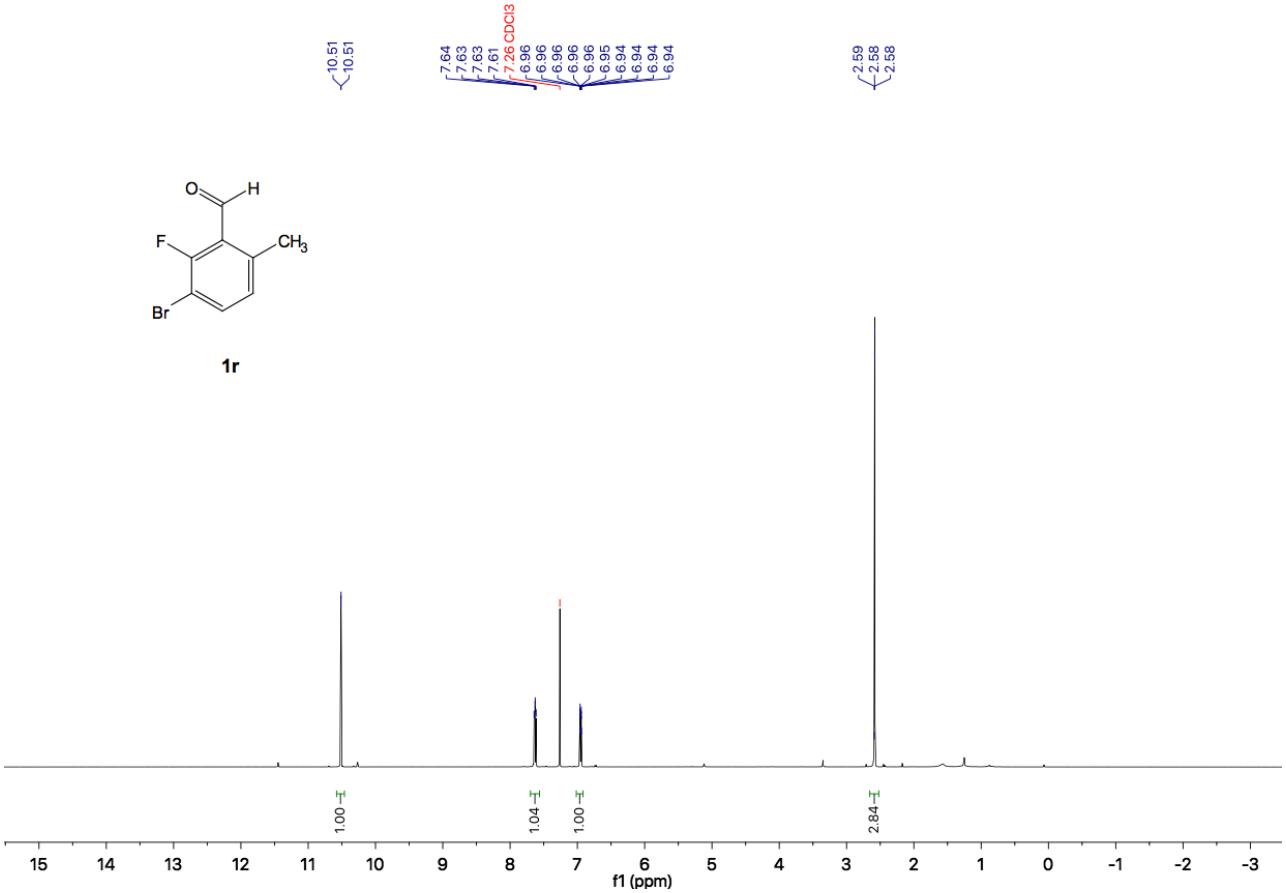

192.02
139.43
136.32
135.61
133.74
133.20
131.49
77.41 CDCl3
77.16 CDCl3
76.90 CDCl3
22.41
18.72
O
H
CH3
H3C
Br
1p
f1 (ppm)

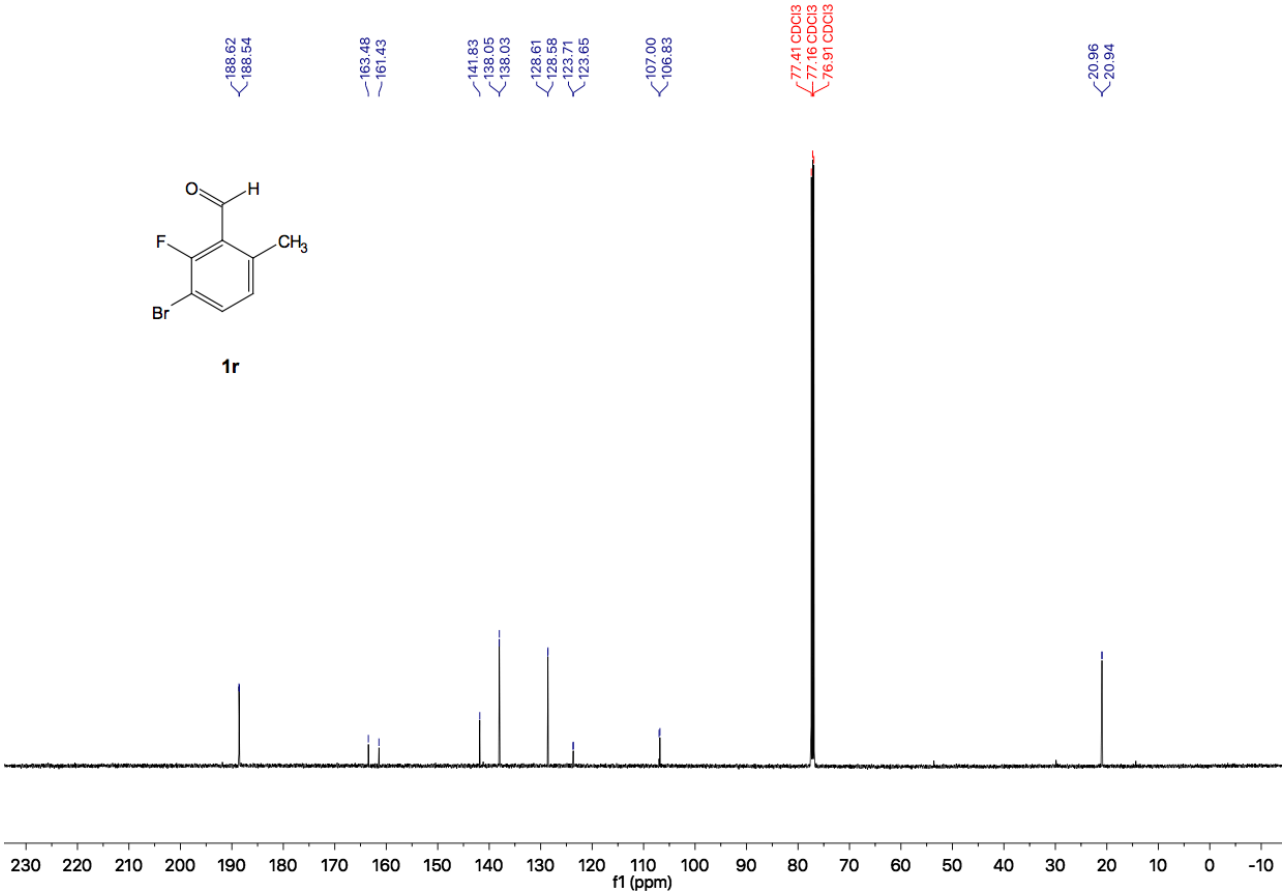

10.19
7.55
7.26 CDCl3
7.03
2.60
2.29
1.00
1.02
1.12
3.10
6.31
f1 (ppm)

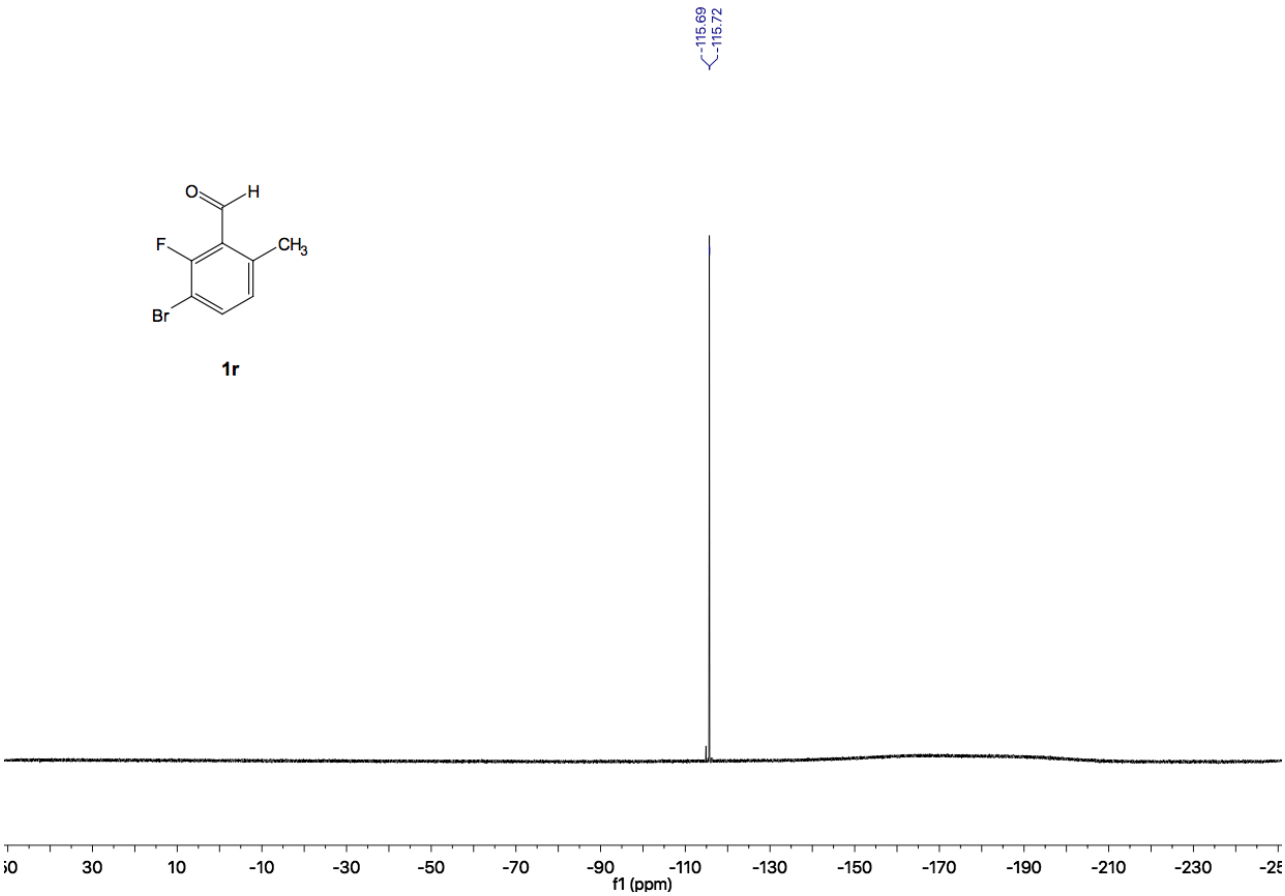
1q

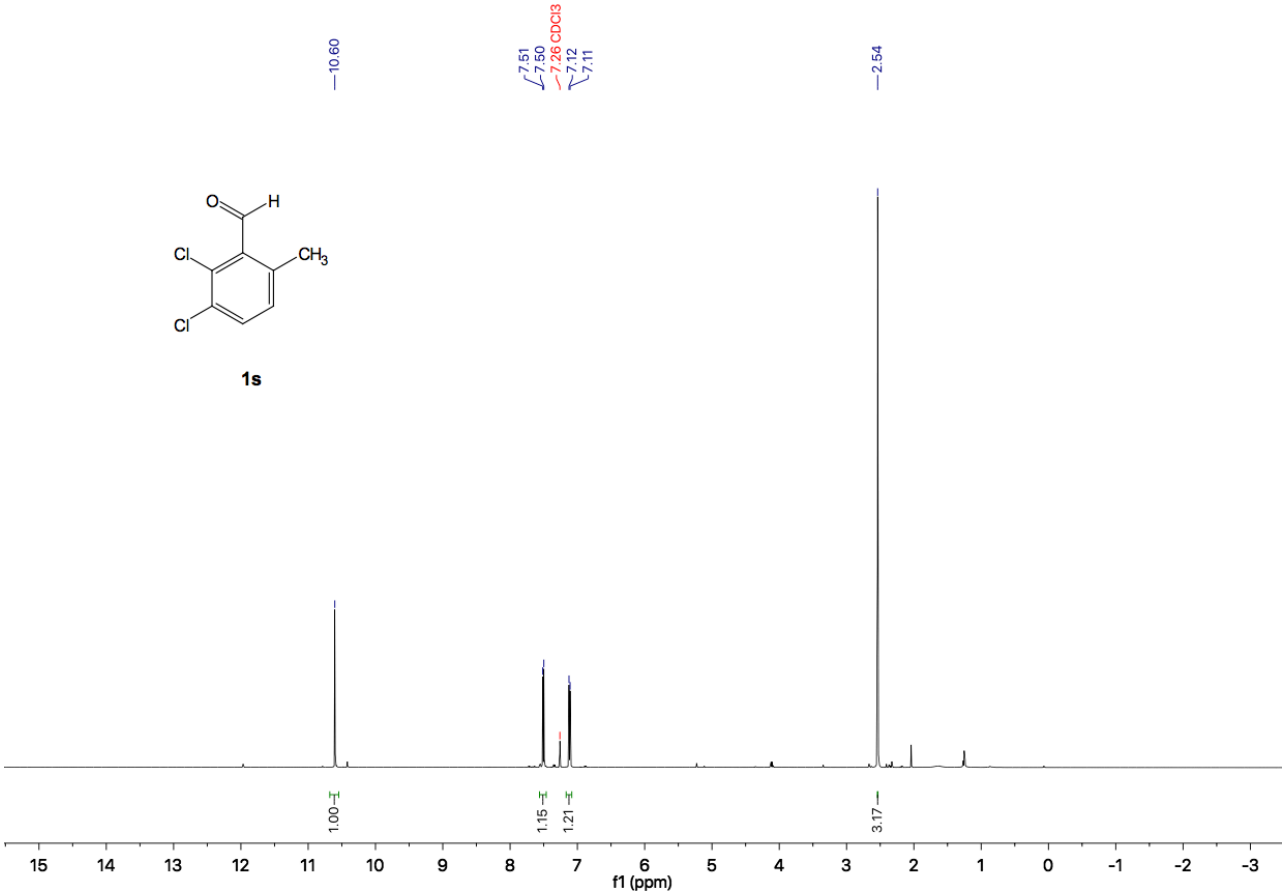

192.73
143.58
138.23
134.75
133.30
133.17
132.22
77.42 CDCl3
77.16 CDCl3
76.91 CDCl3
20.15
19.24
19.05
f1 (ppm)

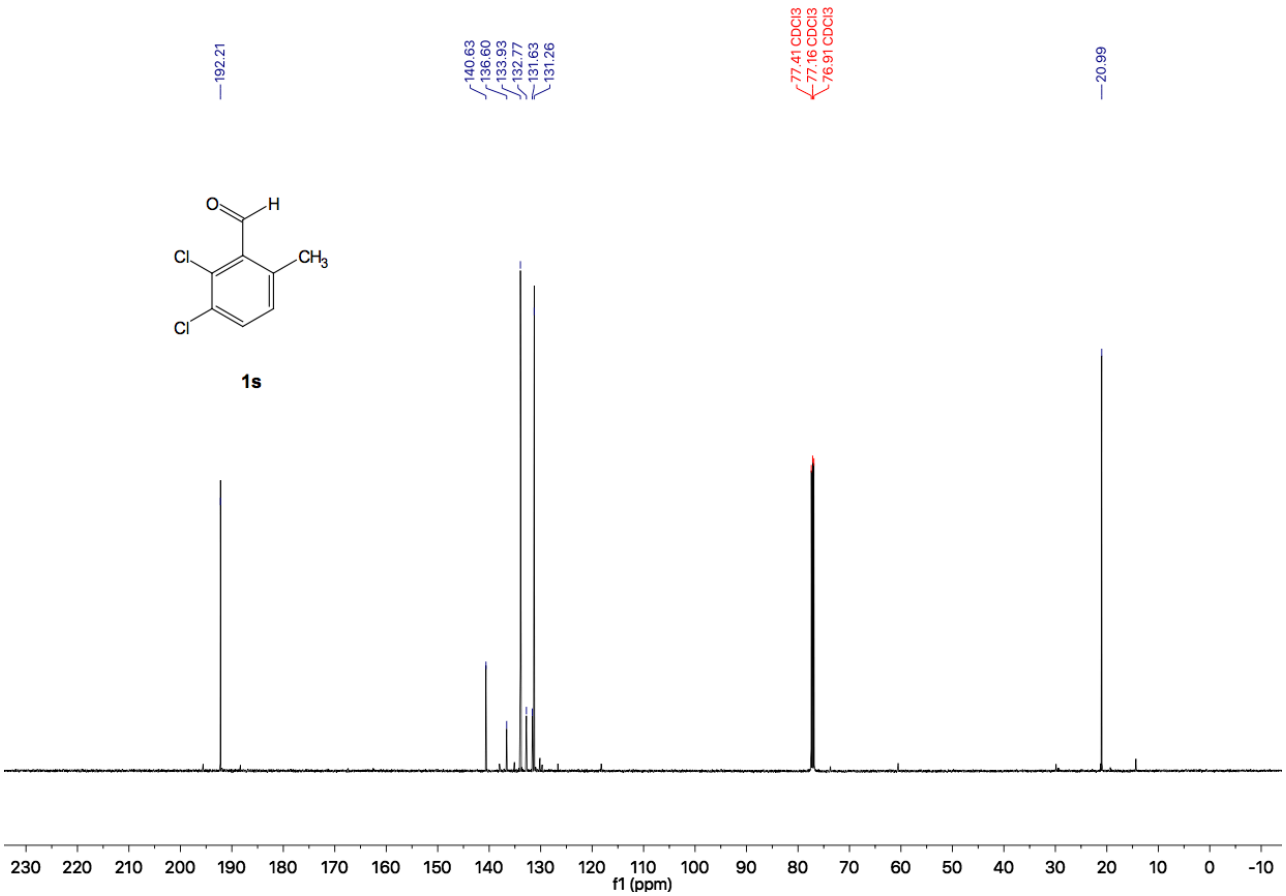
1q

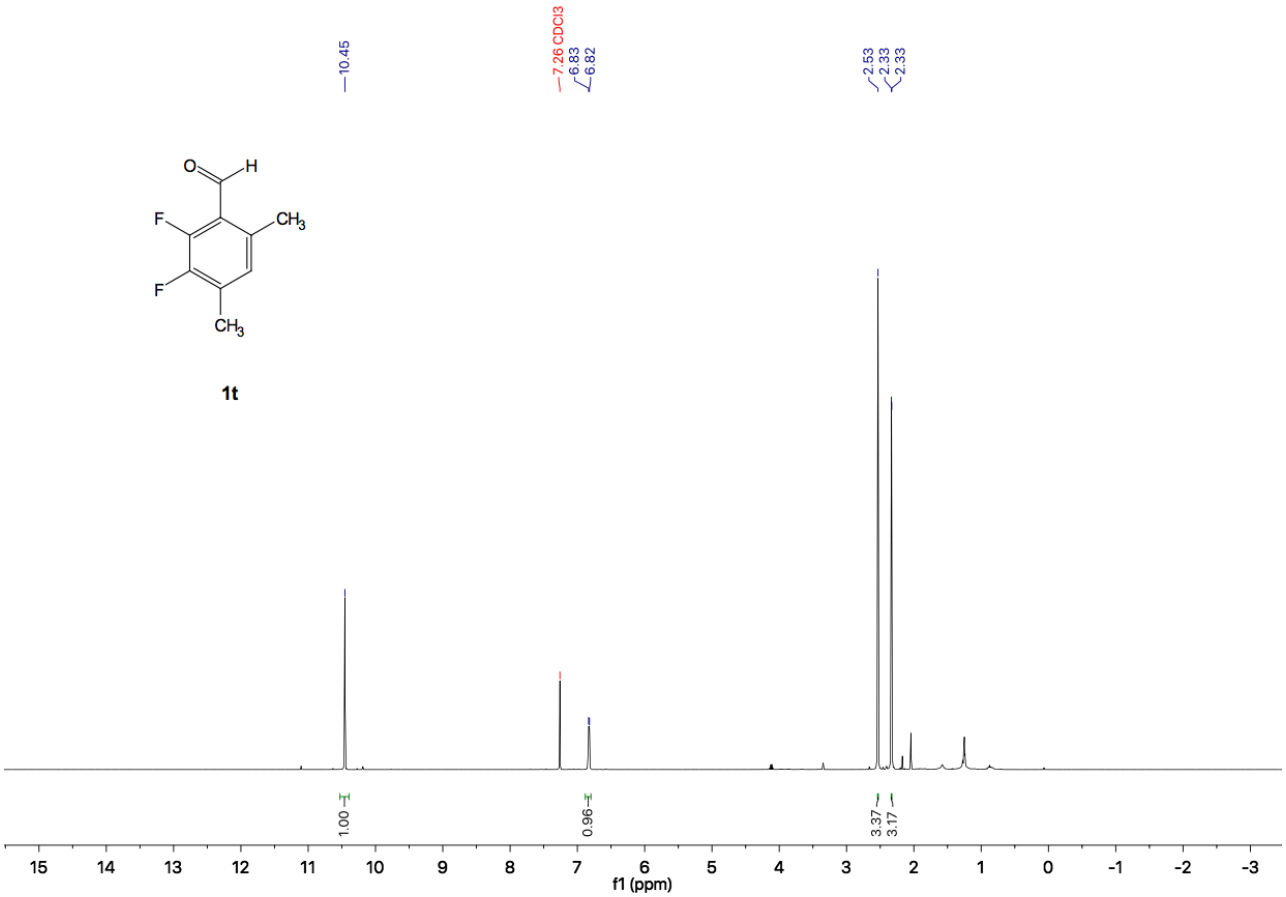

10.51
10.51
7.64
7.63
7.63
7.61
7.26 CDCl3
6.96
6.96
6.96
6.96
6.96
6.95
6.94
6.94
6.94
6.94
2.59
2.58
2.58
O
H
F
CH3
Br
1r
1.00
1.04
1.00
2.84
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

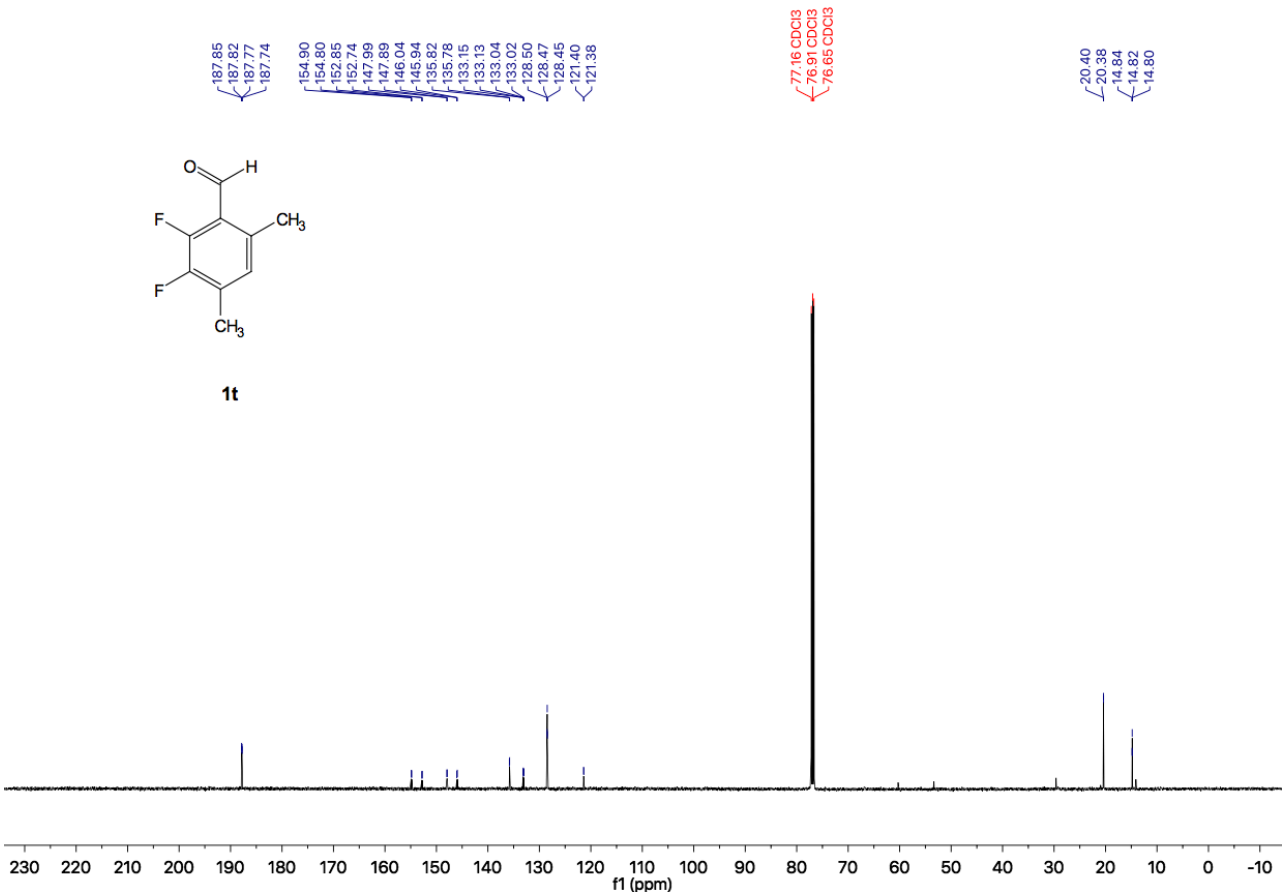

188.62
188.54
163.48
161.43
141.83
138.05
138.03
128.61
128.58
123.71
123.65
107.00
106.83
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
20.96
20.94
O
H
F
CH3
Br
1r
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

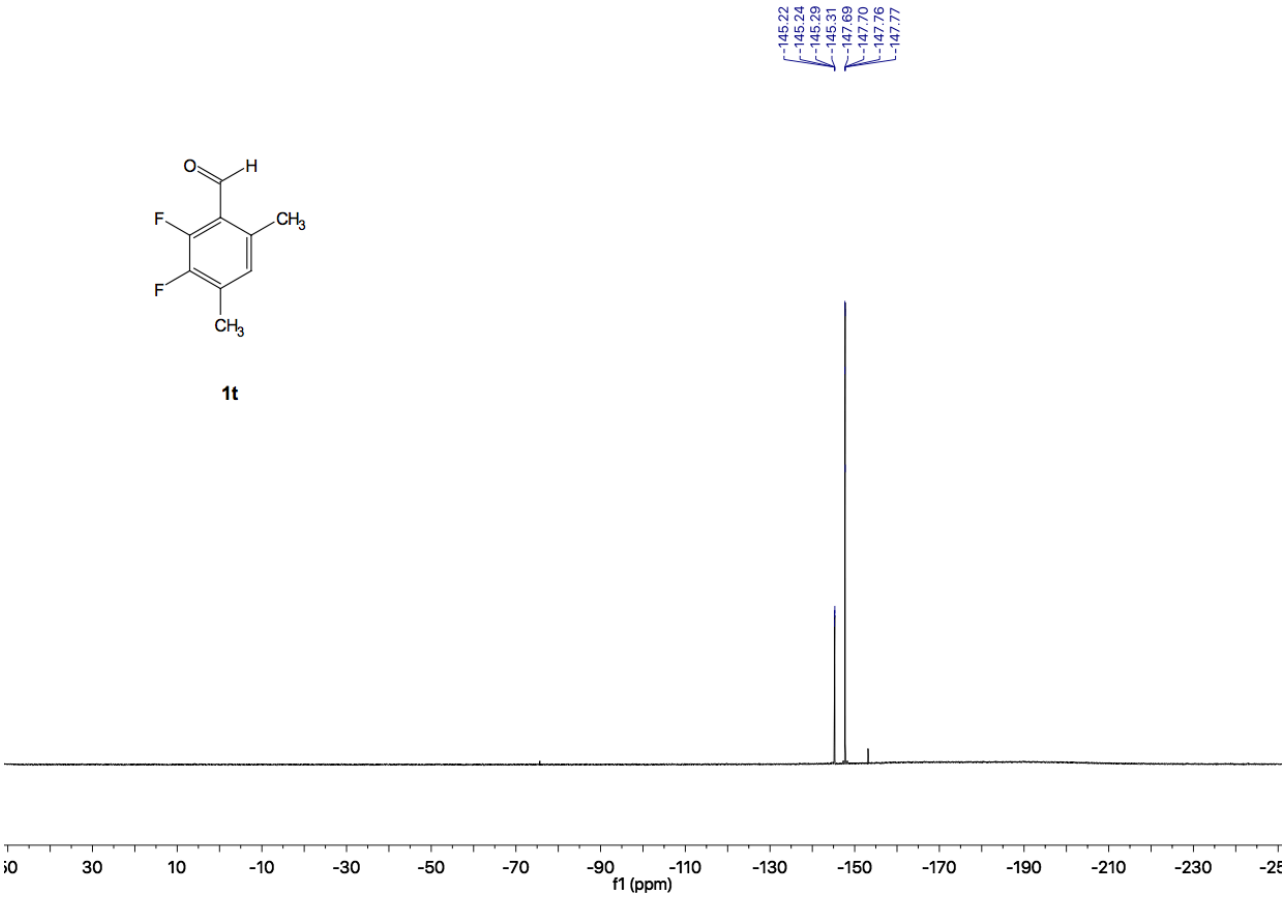

-115.69
-115.72
O
H
F
CH3
Br
1r
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

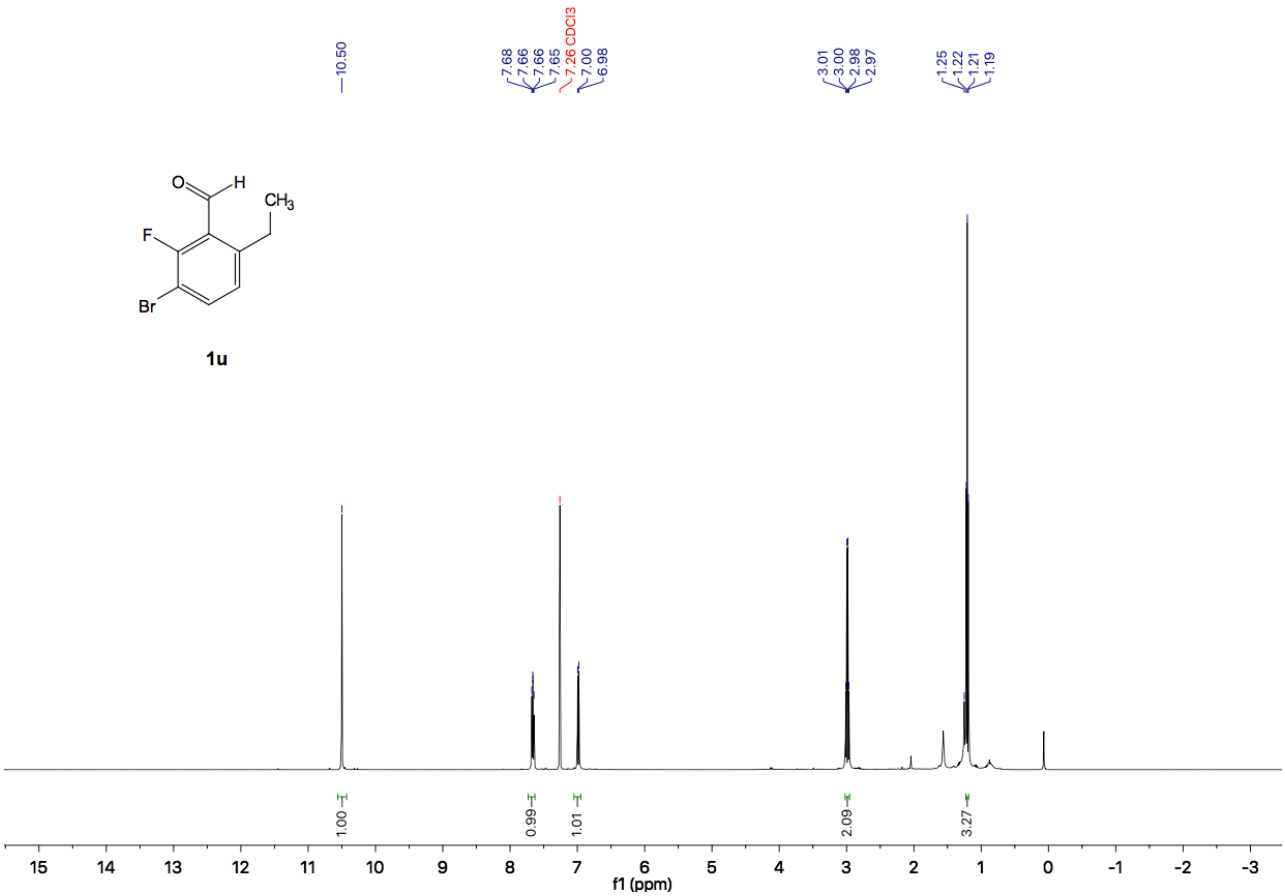

10.60
7.51
7.50
7.26 CDCl3
7.12
7.11
2.54
O
H
Cl
CH3
Cl
1s
1.00
1.15
1.21
3.17
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

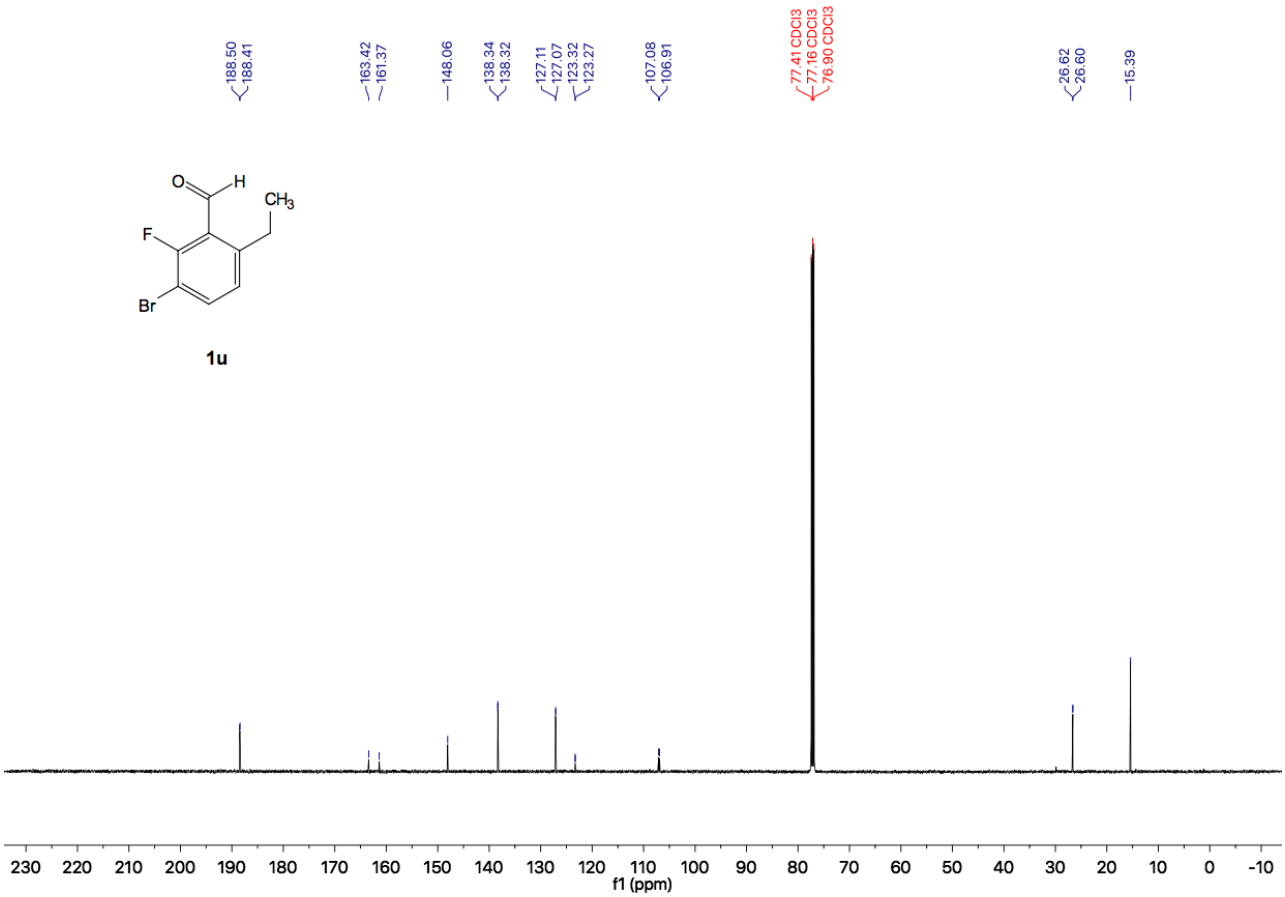

192.21
140.63
136.60
133.93
132.77
131.63
131.26
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
20.99
O
H
Cl
CH3
Cl
1s
f1 (ppm)

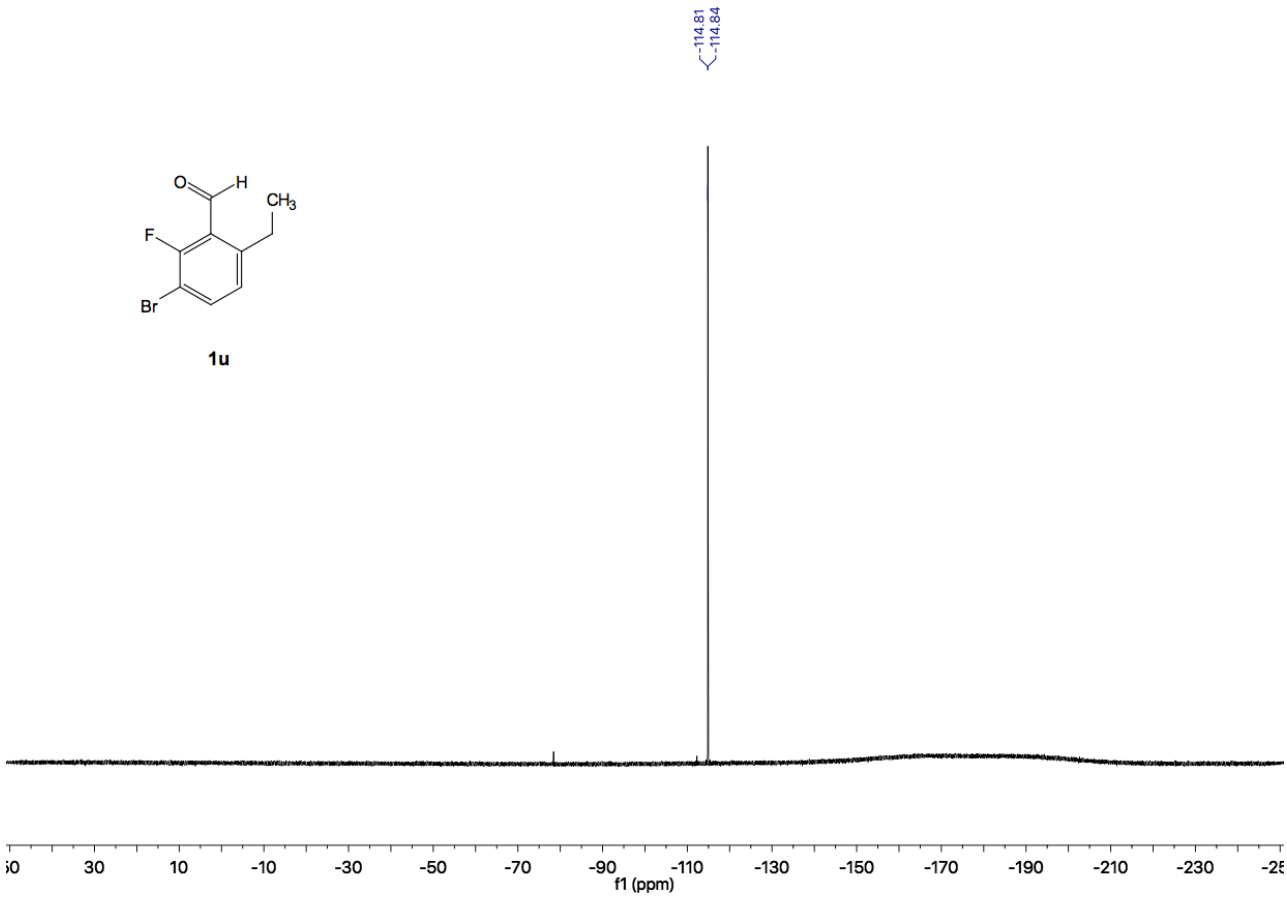

10.45
7.26 CDCl3
6.83
6.82
2.53
2.33
2.33
O
H
F
CH3
F
CH3
1t
1.00
0.96
3.37
3.17
f1 (ppm)

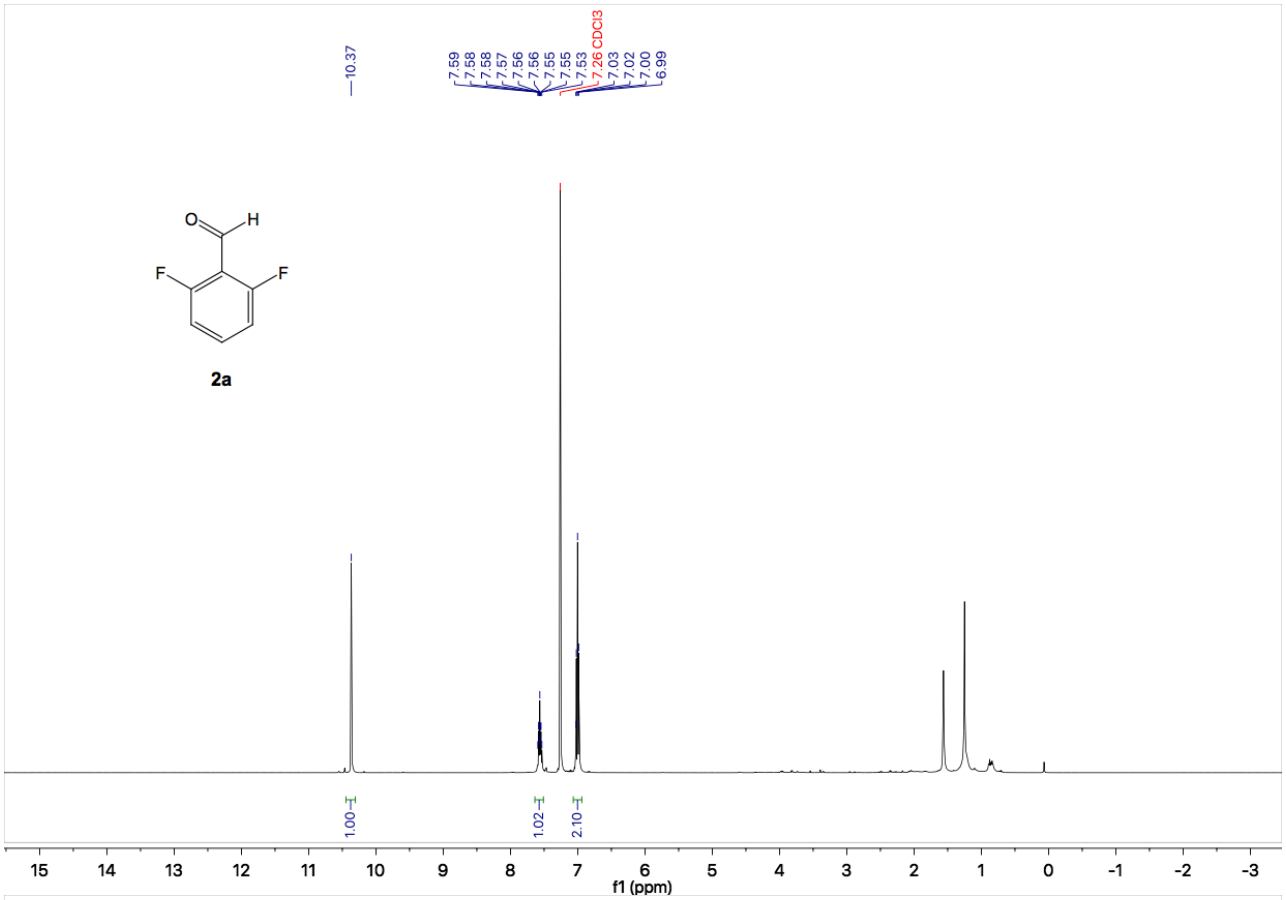

187.85
187.82
187.77
187.74
154.90
154.80
152.85
152.74
147.99
147.89
146.04
145.94
135.82
135.78
133.15
133.13
133.04
133.02
128.50
128.47
128.45
121.40
121.38
77.16 CDCl3
76.91 CDCl3
76.65 CDCl3
20.40
20.38
14.84
14.82
14.80
O
H
F
CH3
F
CH3
1t
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

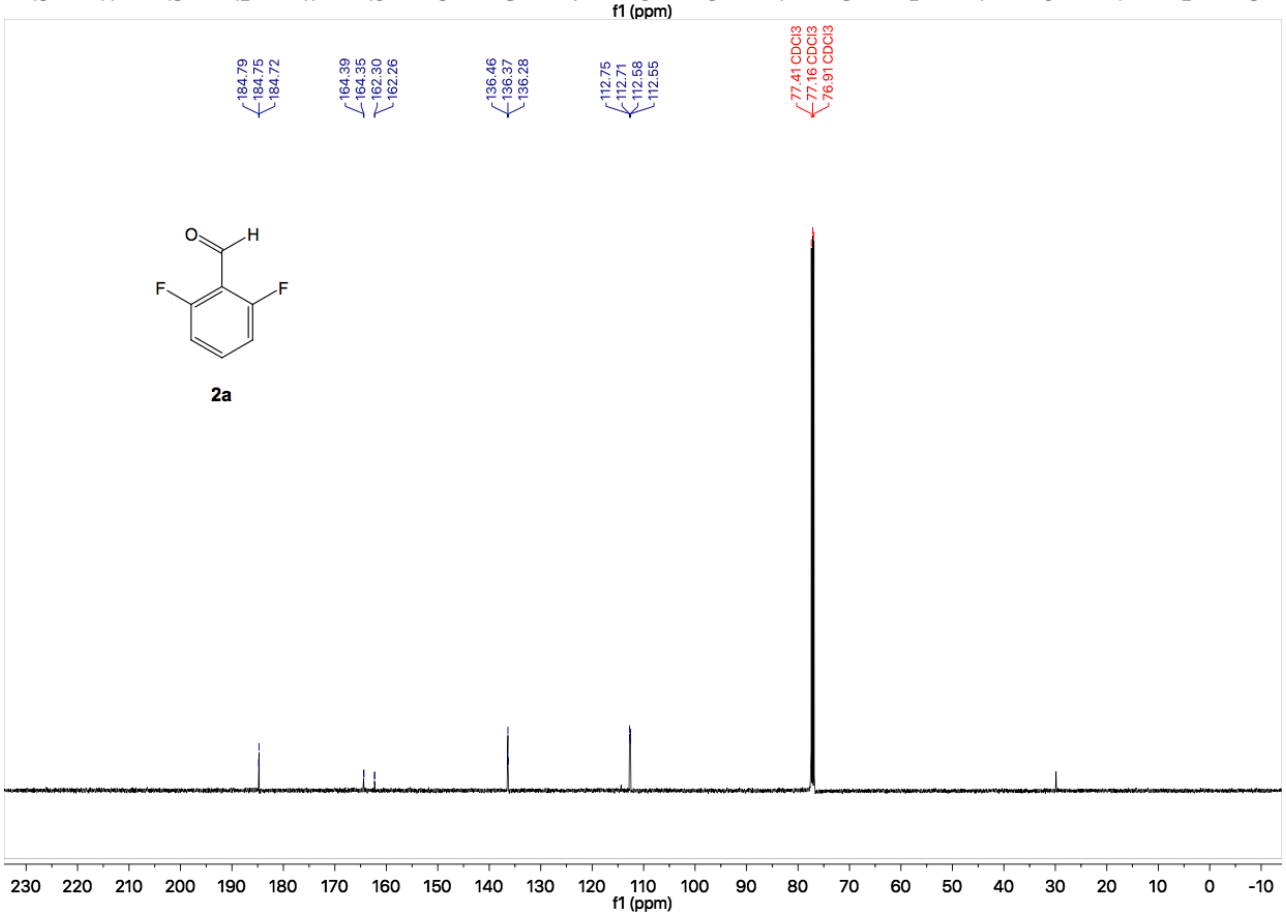

-145.22
-145.24
-145.29
-145.31
-147.69
-147.70
-147.76
-147.77
O
H
F
CH3
F
CH3
1t
30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

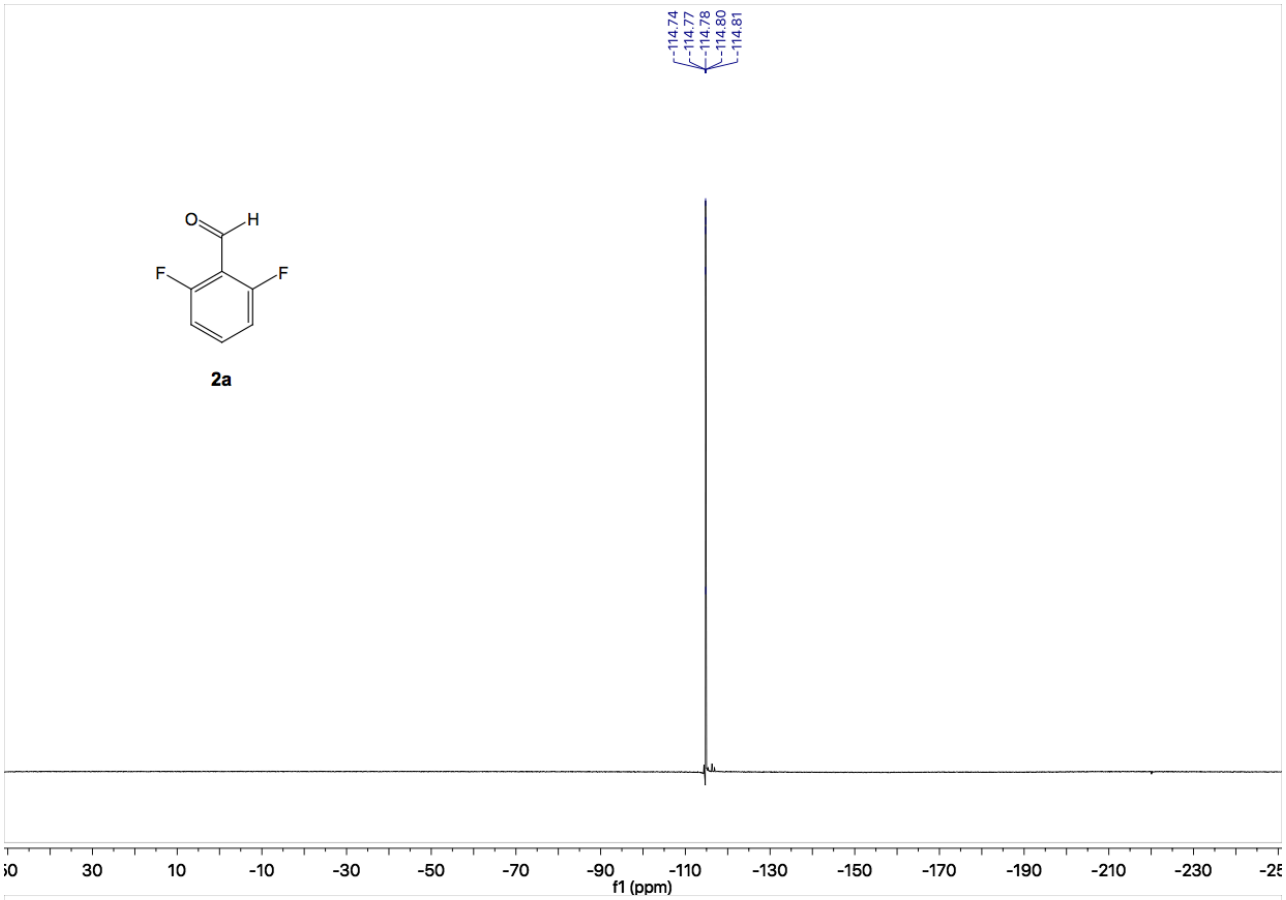

10.50
7.68
7.66
7.66
7.65
7.26 CDCl3
7.00
6.98
3.01
3.00
2.98
2.97
1.25
1.22
1.21
1.19
O
H
CH3
F
Br
1u
1.00
0.99
1.01
2.09
3.27
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

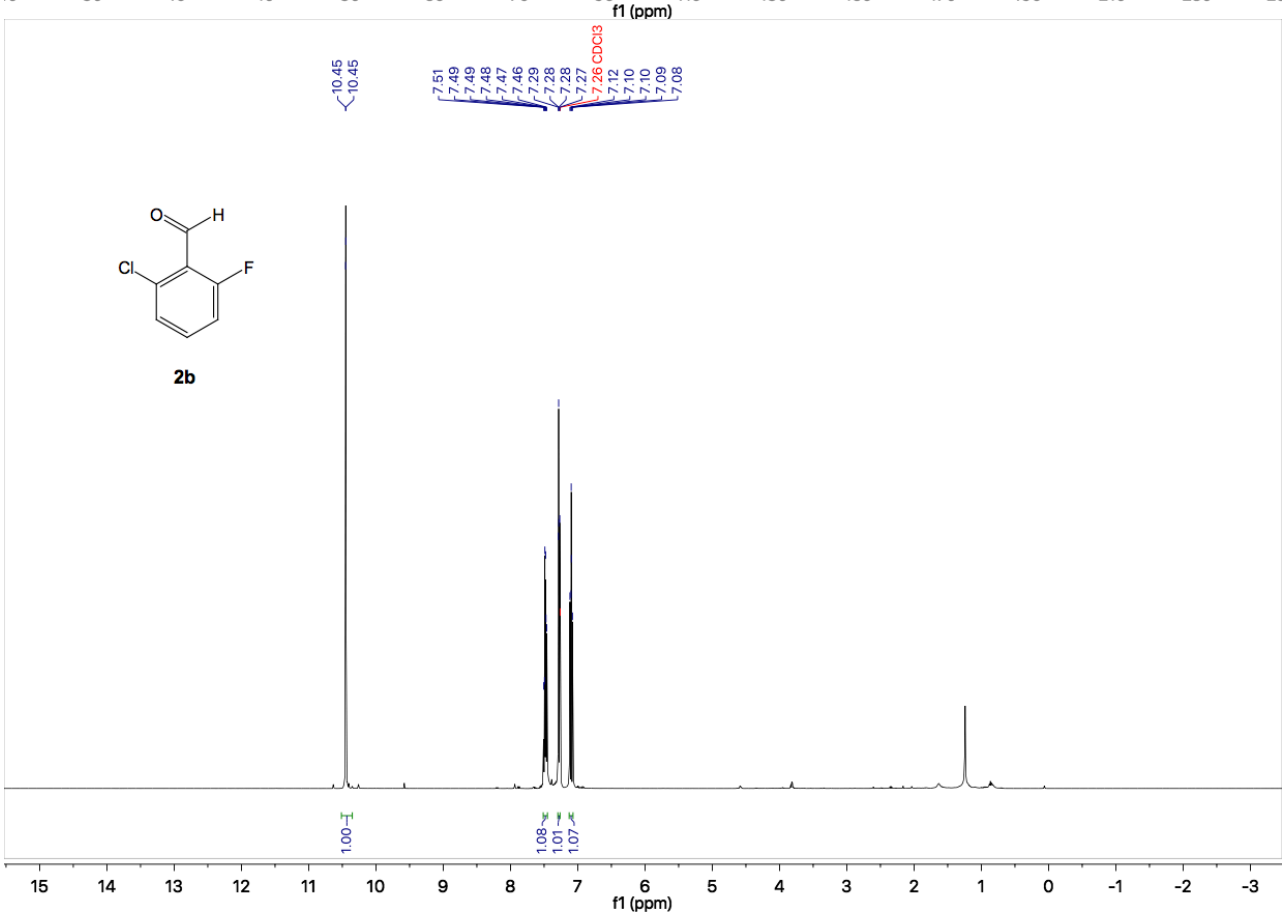

188.50
188.41
163.42
161.37
148.06
138.34
138.32
127.11
127.07
123.32
123.27
107.08
106.91
77.41 CDCl3
77.16 CDCl3
76.90 CDCl3
26.62
26.60
15.39
O
H
CH3
F
Br
1u
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-114.81
-114.84
O
H
CH3
F
Br
1u
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)


10.37
7.59
7.58
7.58
7.57
7.56
7.56
7.55
7.55
7.53
7.26 CDCl3
7.03
7.02
7.00
6.99
O
H
F
F
2a
1.00
1.02
2.10
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


184.79
184.75
184.72
164.39
164.35
162.30
162.26
136.46
136.37
136.28
112.75
112.71
112.58
112.55
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
O
H
F
F
2a
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-114.74
-114.77
-114.78
-114.80
-114.81
O
H
F
F
2a
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)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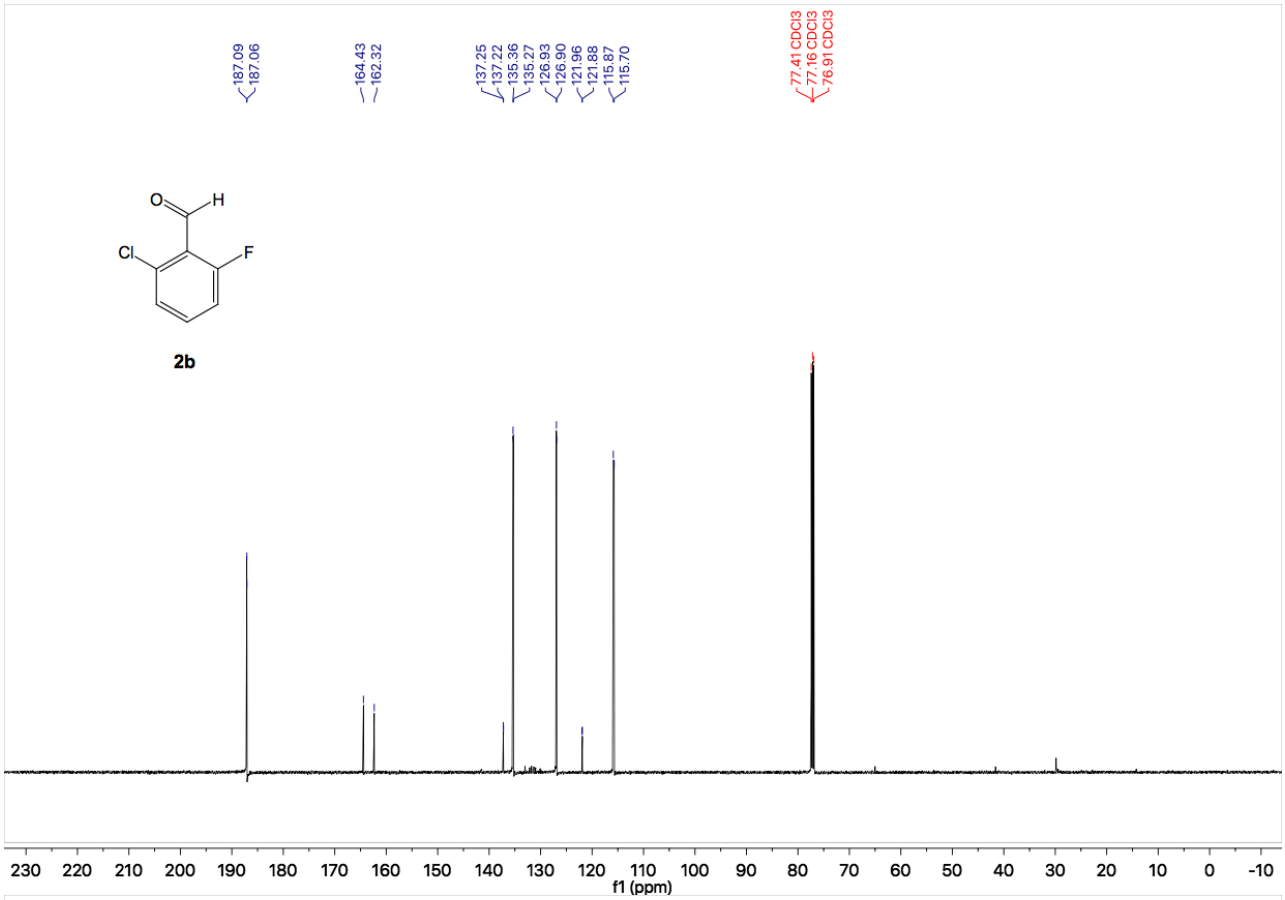
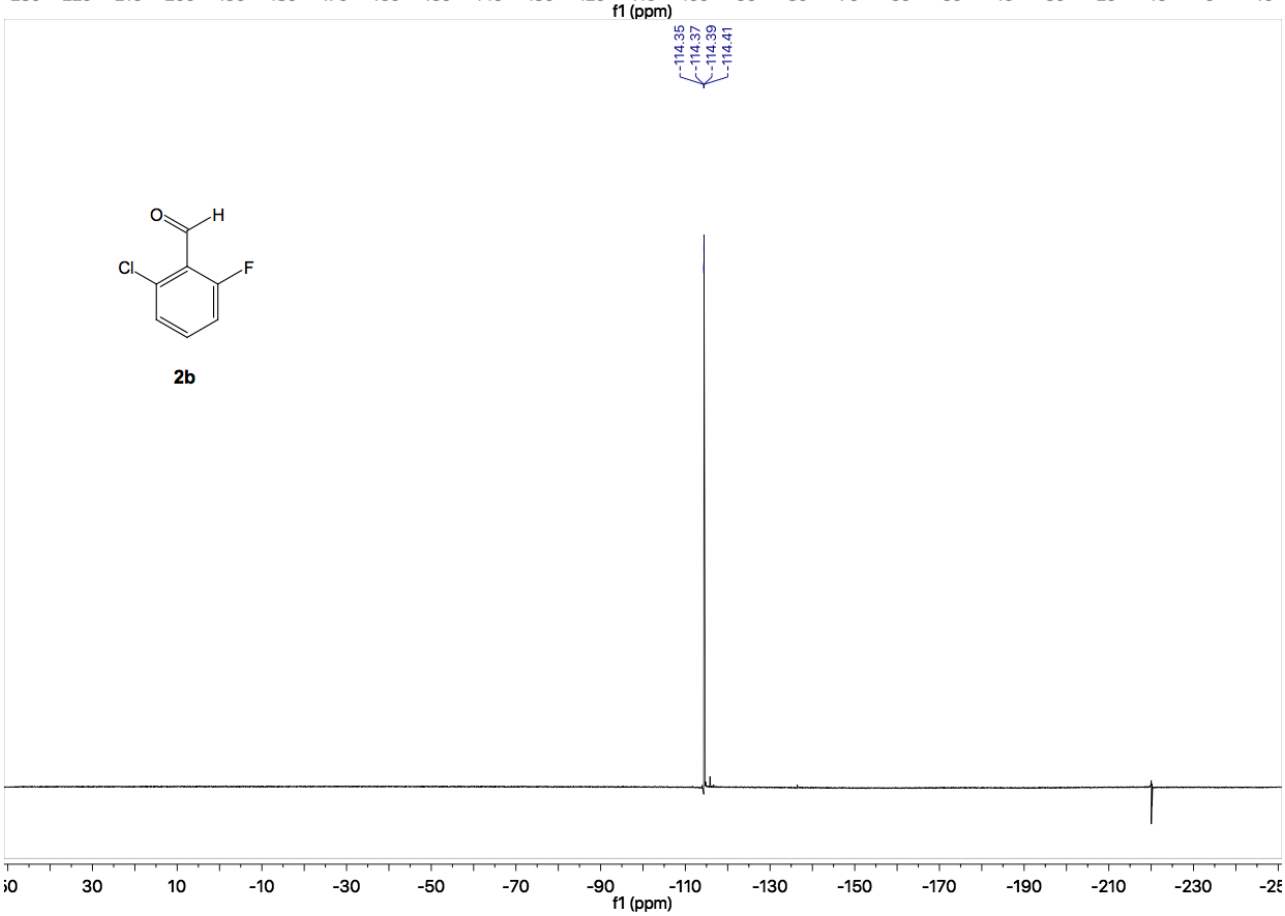
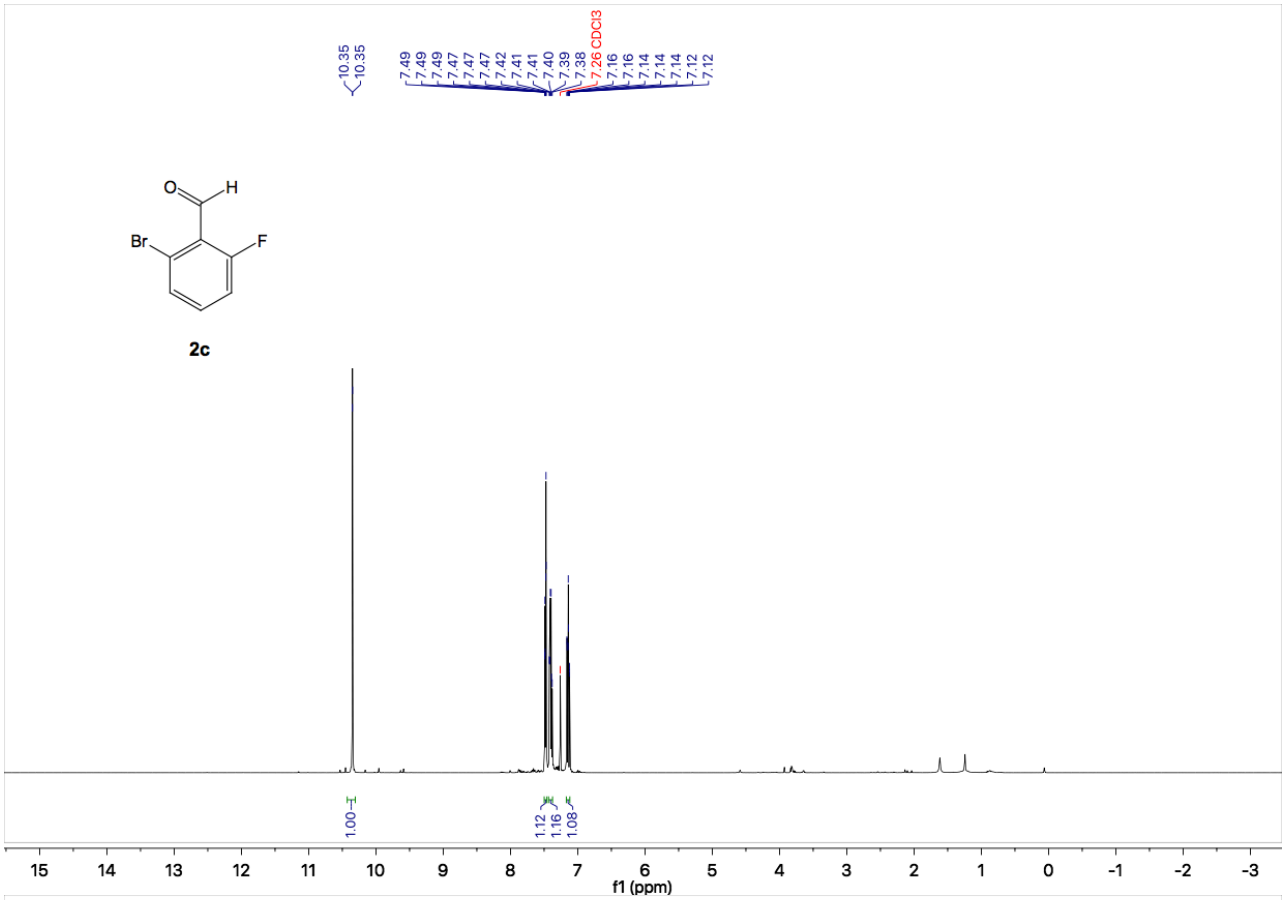
10.45
7.51
7.49
7.49
7.48
7.47
7.46
7.29
7.28
7.28
7.27
7.26 CDCl3
7.12
7.10
7.10
7.09
7.08
O
H
Cl
F
2b
1.00
1.08
1.01
1.07
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)


187.09
187.06
164.43
162.32
137.25
137.22
135.36
135.27
126.93
126.90
121.96
121.88
115.87
115.70
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
O
H
Cl
F
2b
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-114.35
-114.37
-114.39
-114.41
O
H
Cl
F
2b
30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)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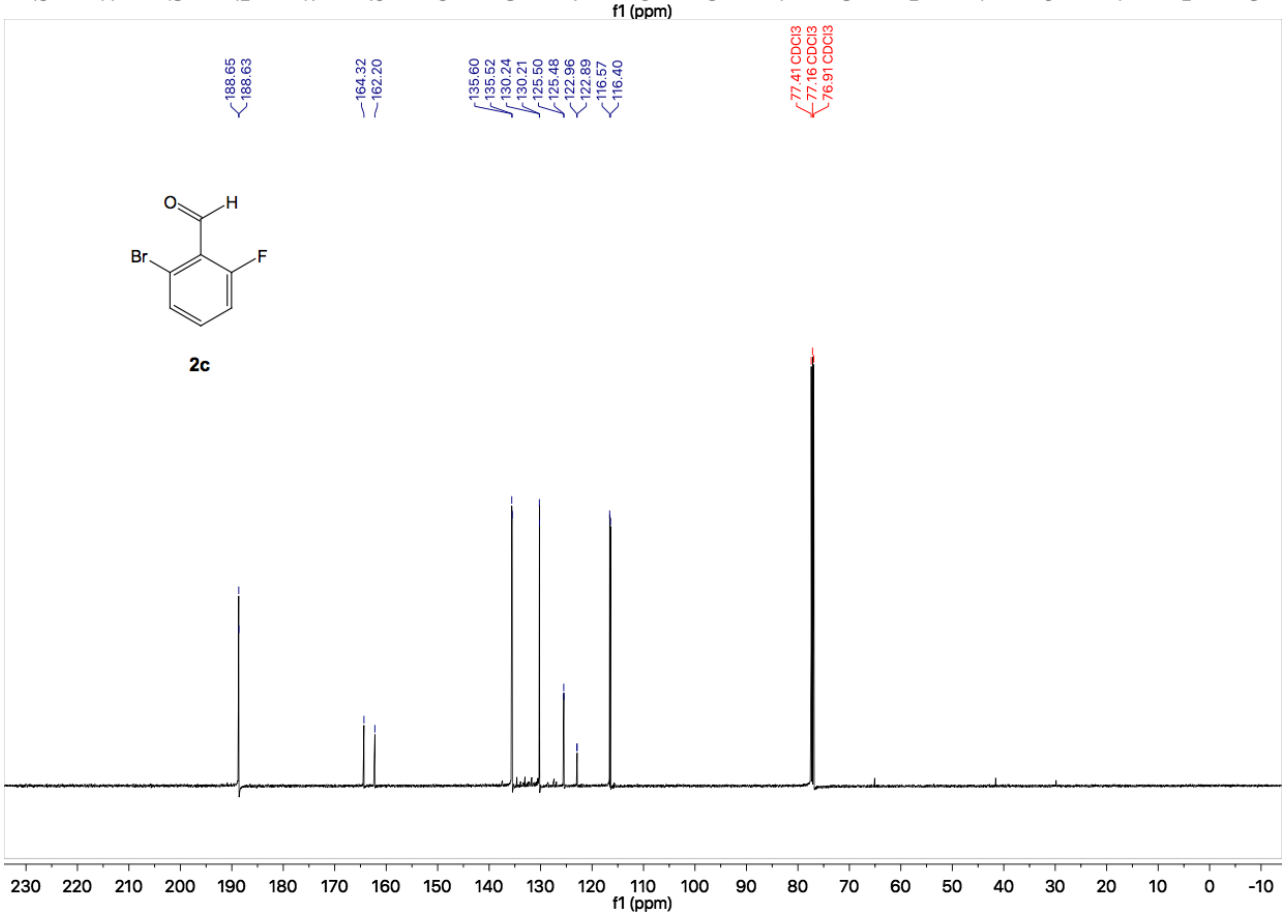
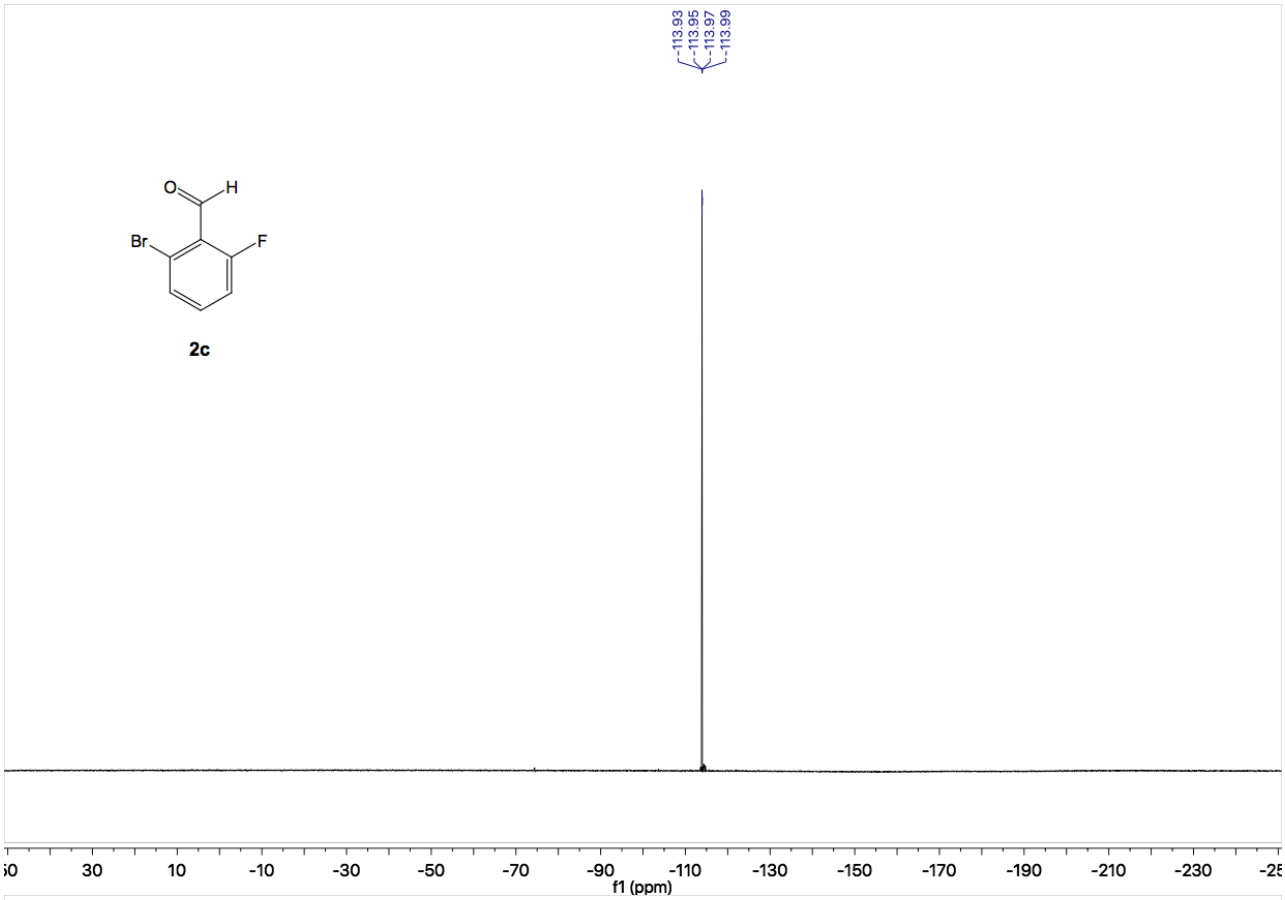
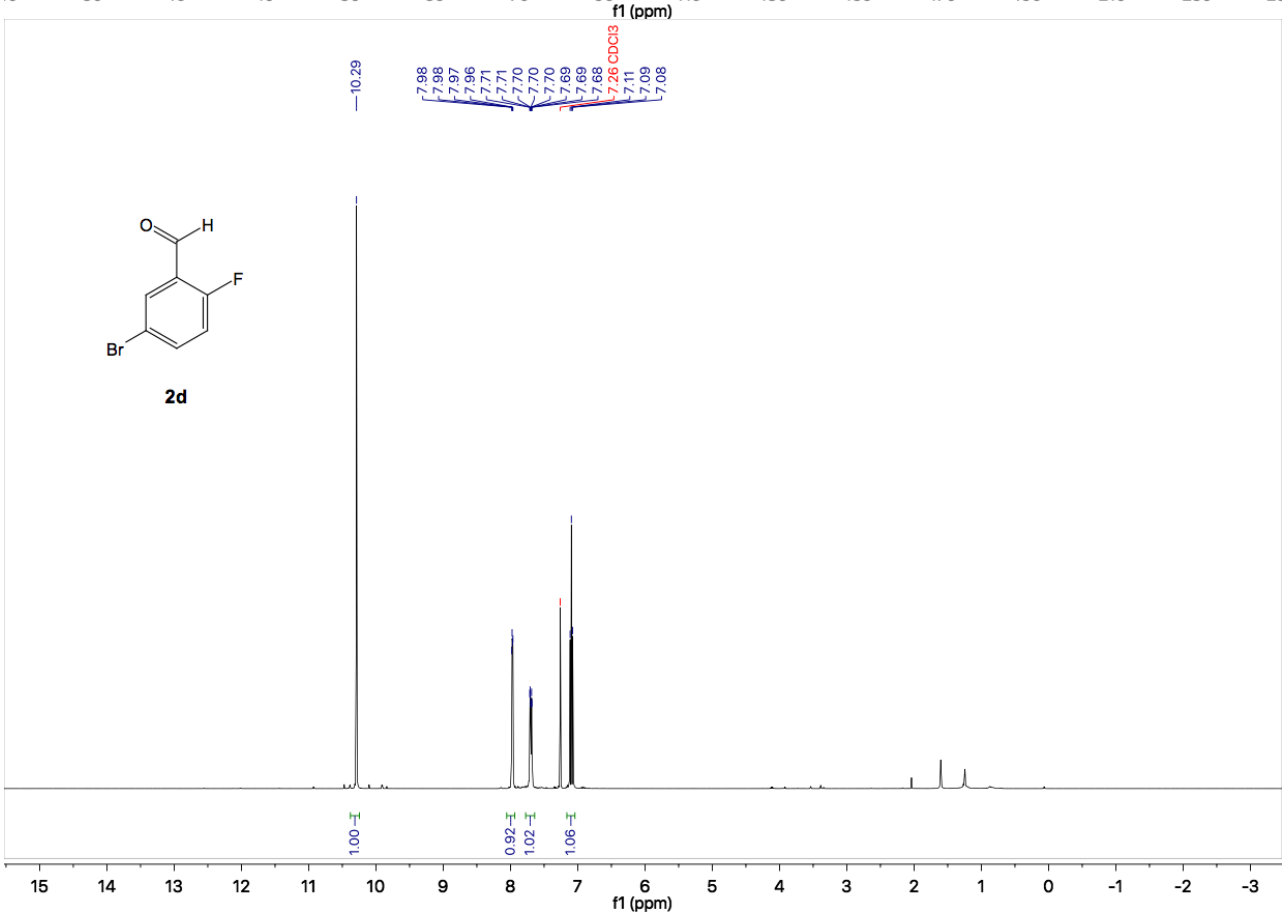
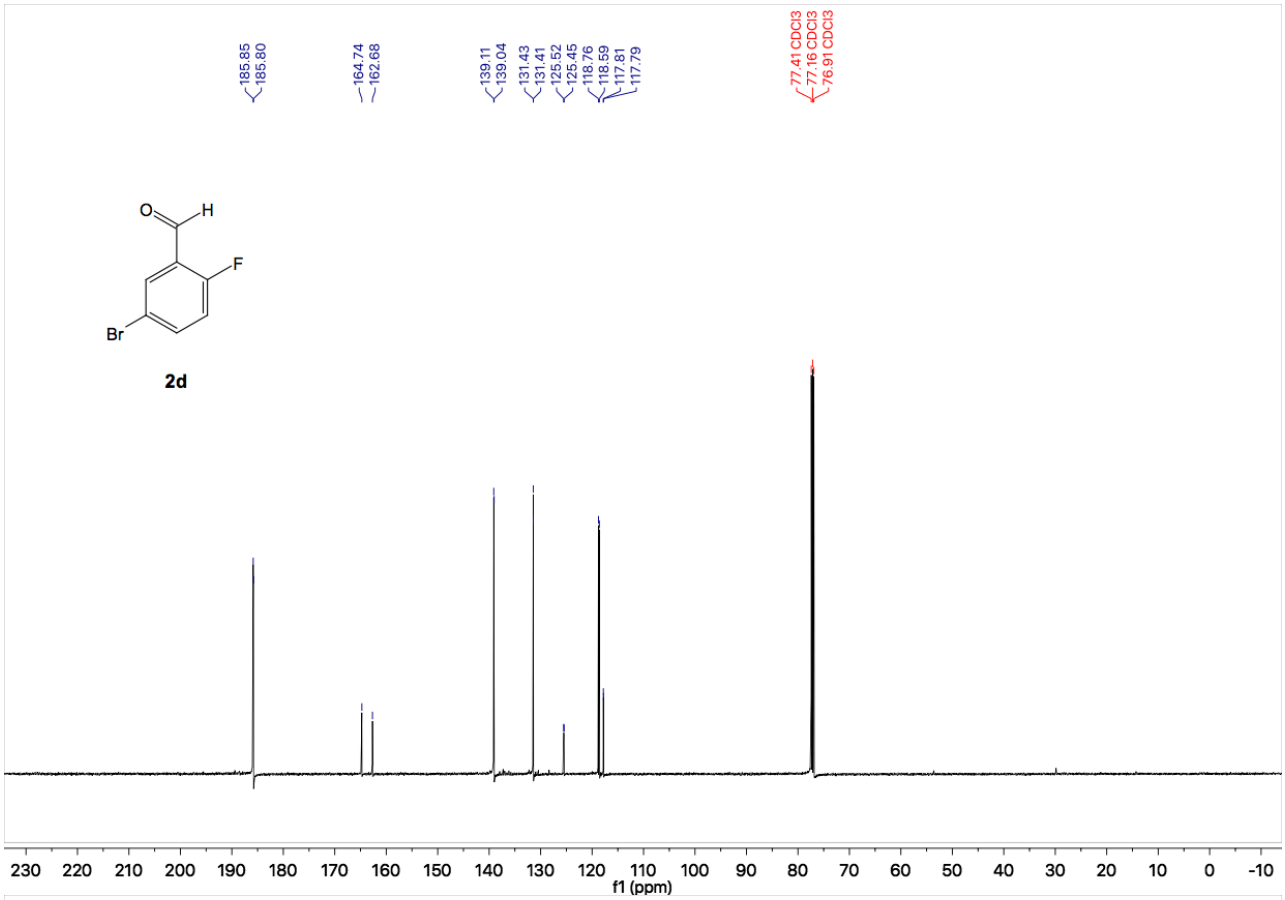
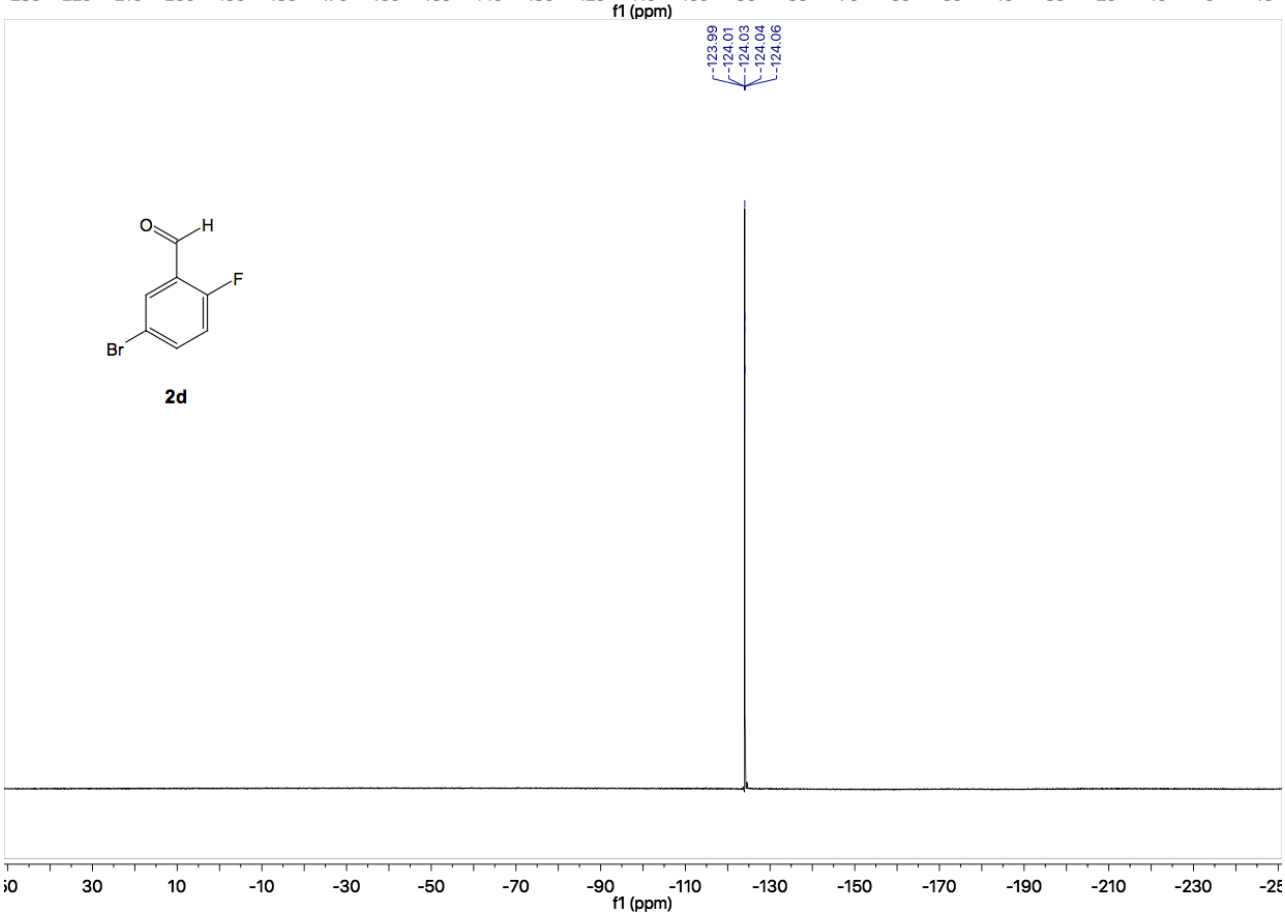
10.35
7.49
7.49
7.49
7.47
7.47
7.47
7.42
7.41
7.41
7.40
7.39
7.38
7.26 CDCl3
7.16
7.16
7.14
7.14
7.14
7.12
7.12
O
H
Br
F
2c
1.00
1.12
1.16
1.08
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

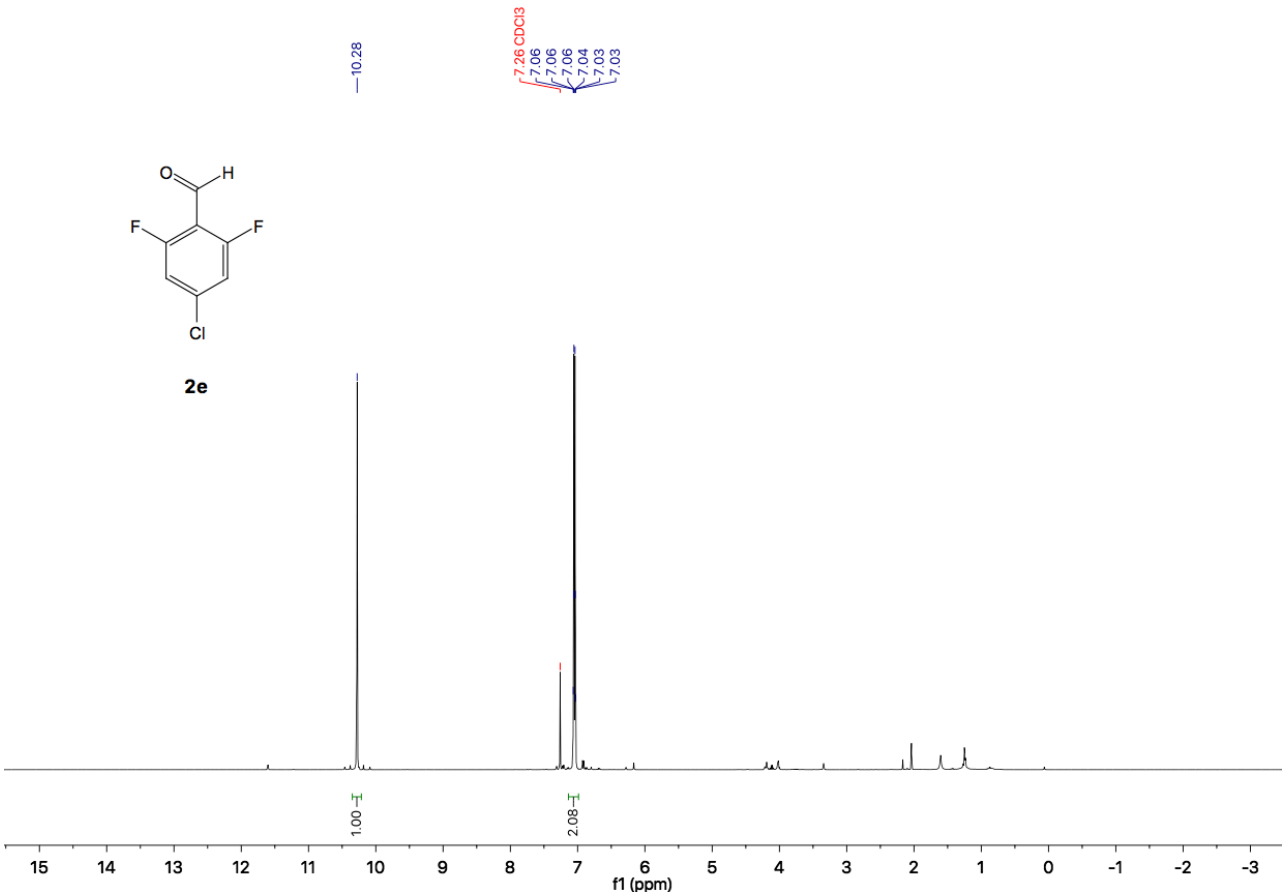

188.65
188.63
164.32
162.20
135.60
135.52
130.24
130.21
125.50
125.48
122.96
122.89
116.57
116.40
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
O
H
Br
F
2c
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

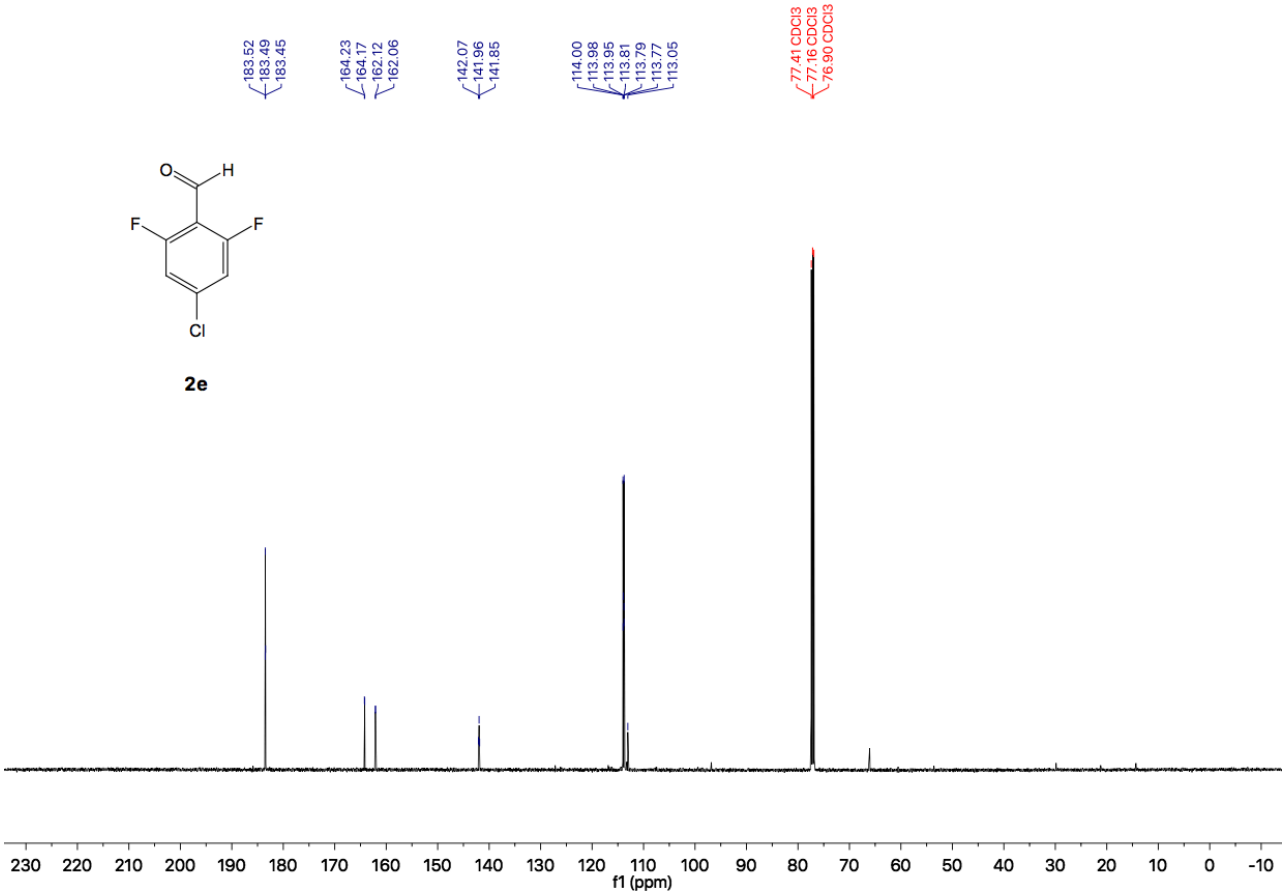

-113.93
-113.95
-113.97
-113.99
O
H
Br
F
2c
f1 (ppm)

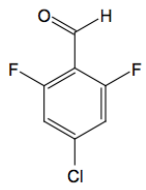

10.29
7.98
7.98
7.97
7.96
7.71
7.71
7.70
7.70
7.70
7.69
7.69
7.68
7.26 CDCl3
7.11
7.09
7.08
O
H
F
Br
2d
1.00
0.92
1.02
1.06
f1 (ppm)


185.85
185.80
164.74
162.68
139.11
139.04
131.43
131.41
125.52
125.45
118.76
118.59
117.81
117.79
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
O
H
F
Br
2d
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-123.99
-124.01
-124.03
-124.04
-124.06
O
H
F
Br
2d
30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

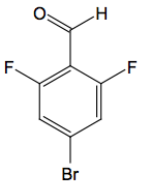

10.28
7.26 CDCl3
7.06
7.06
7.06
7.04
7.03
7.03
O
H
F
F
Cl
2e
1.00
2.08
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


183.52
183.49
183.45
164.23
164.17
162.12
162.06
142.07
141.96
141.85
114.00
113.98
113.95
113.81
113.79
113.77
113.05
77.41 CDCl3
77.16 CDCl3
76.90 CDCl3
O
H
F
F
Cl
2e
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
H
F
F
Cl

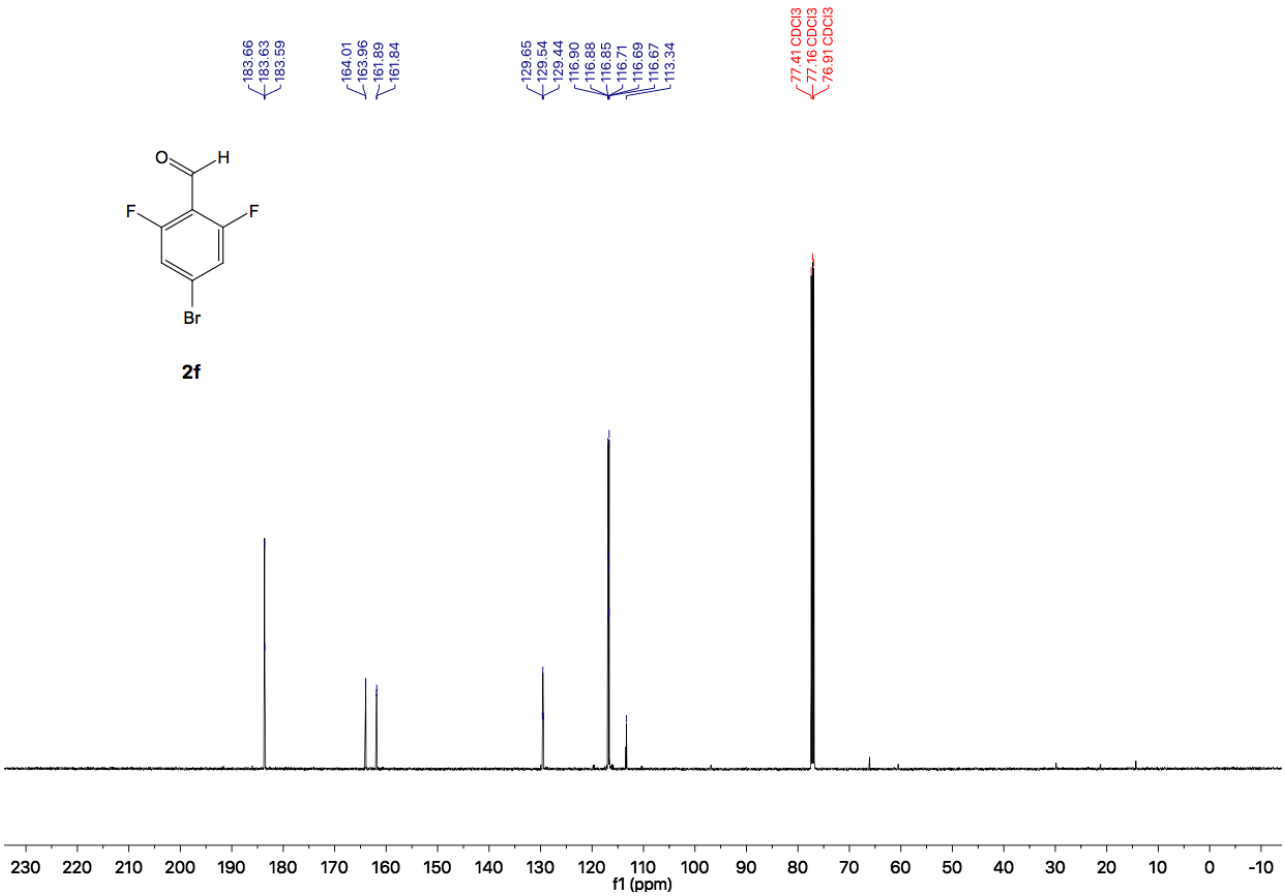
2e

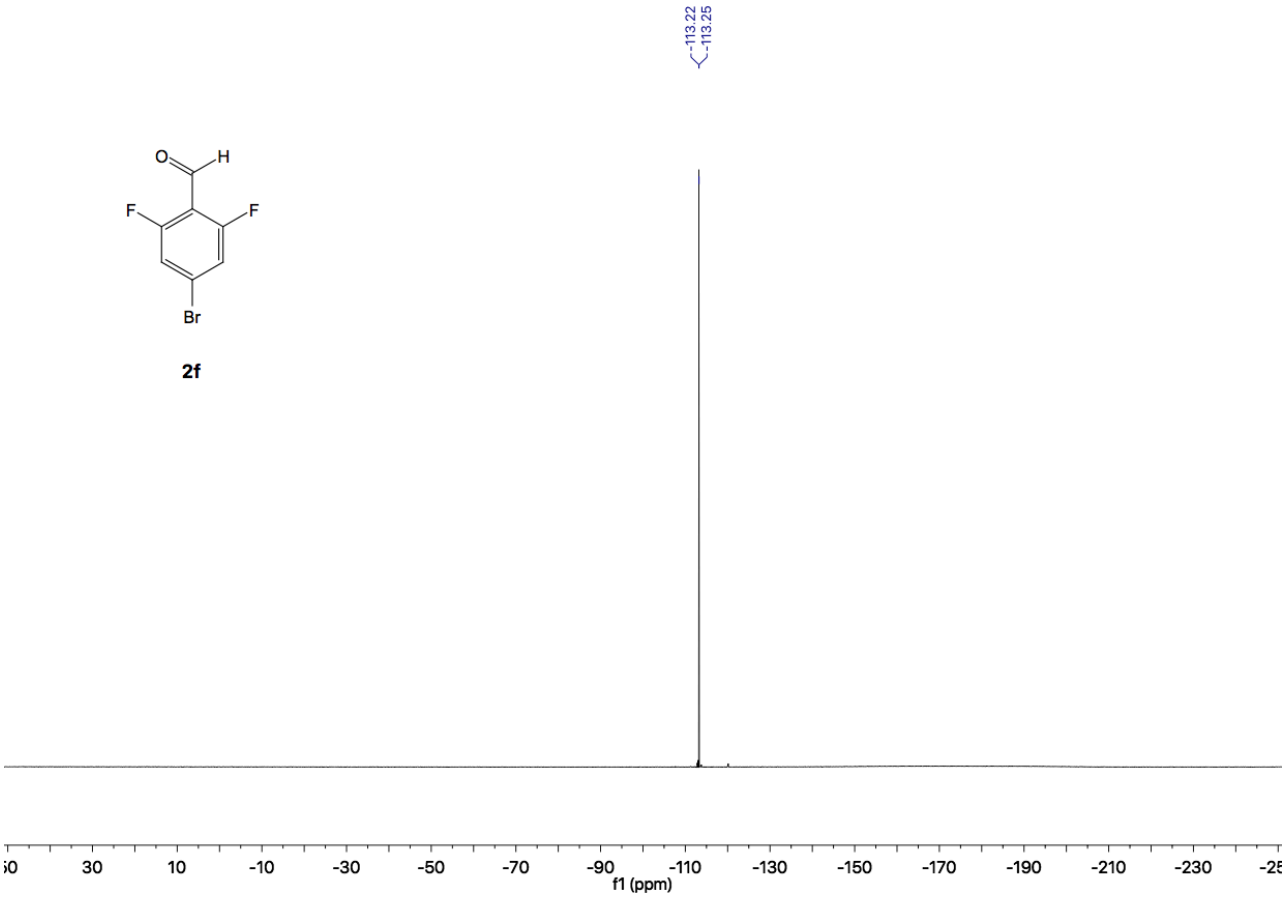
-112.94
-112.97
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

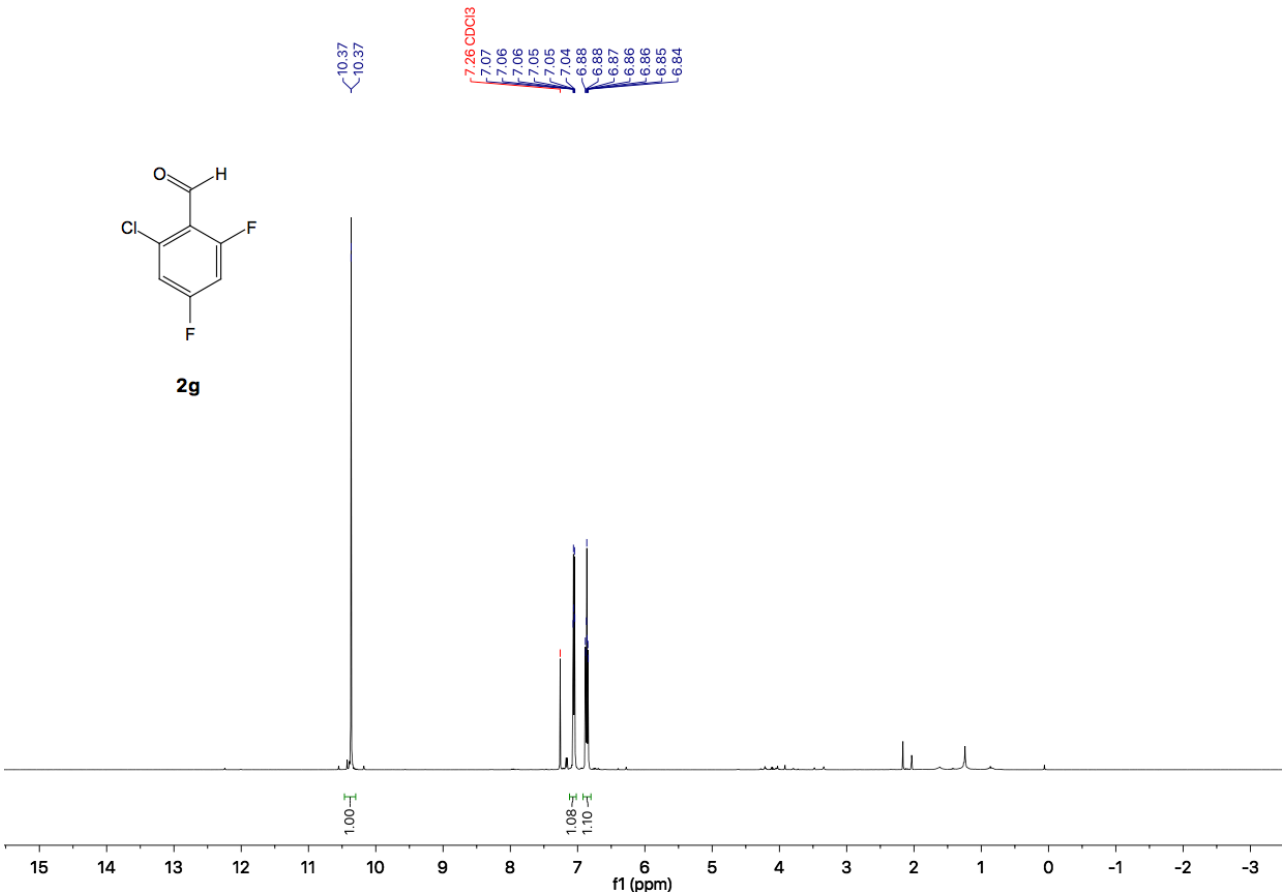

O
H
F
F
Br

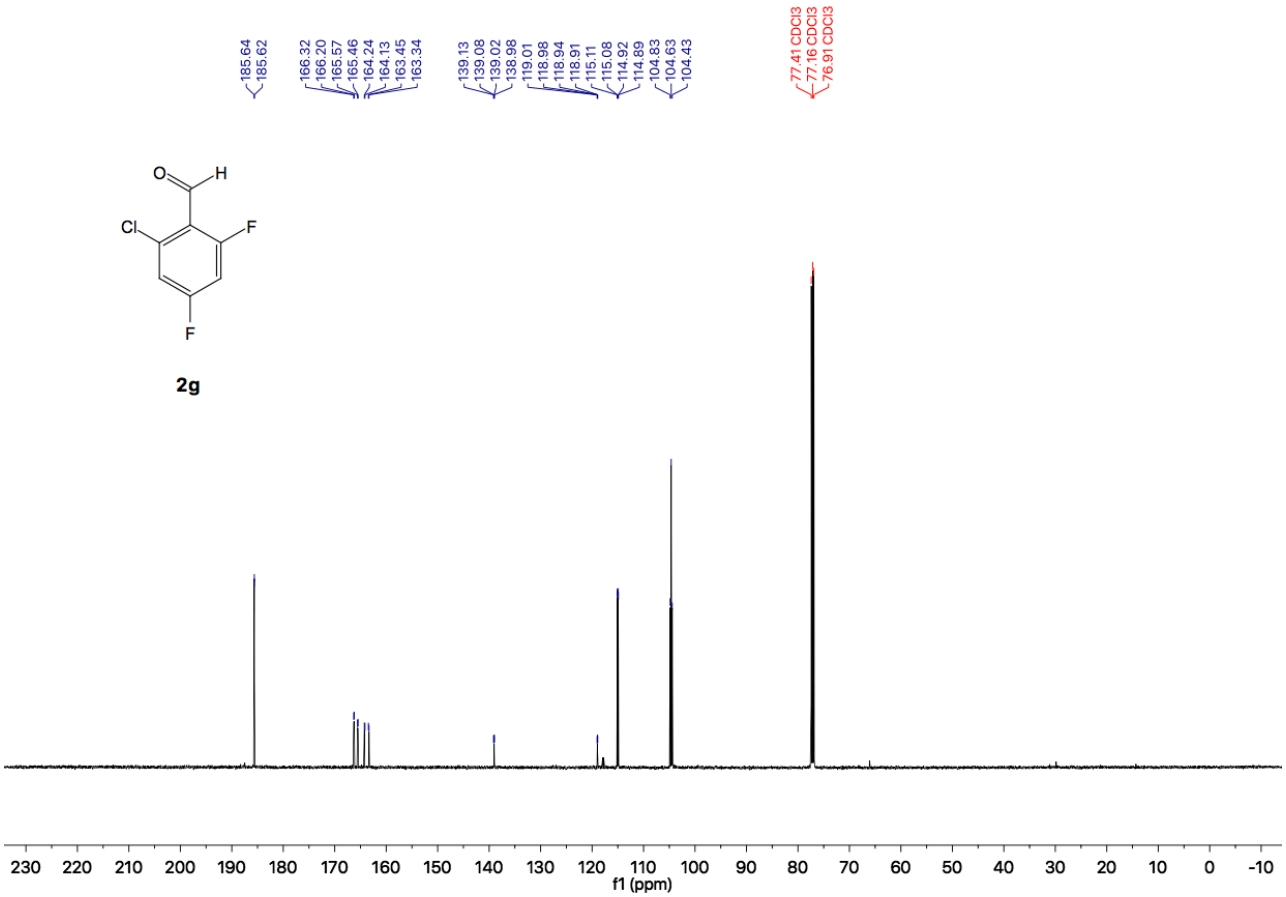
2f

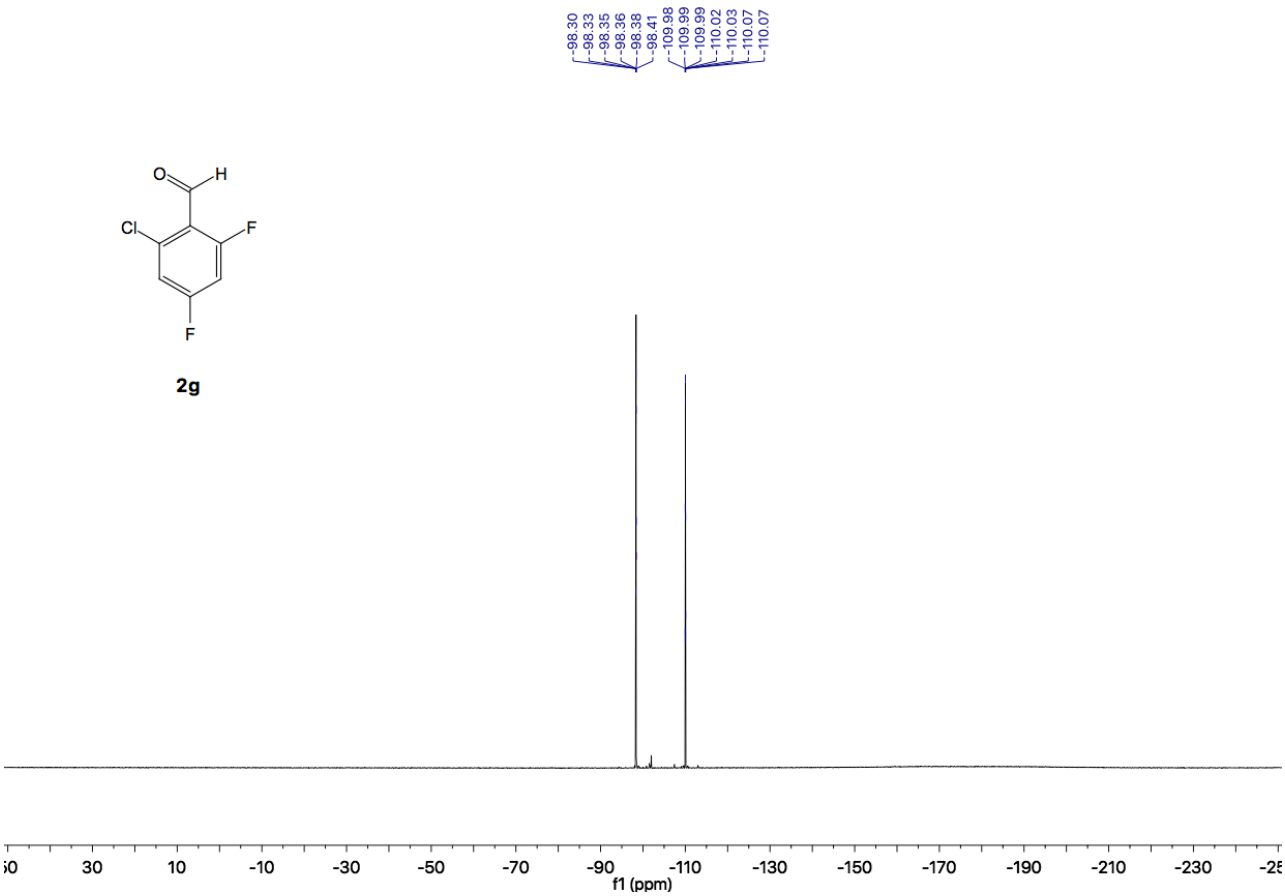
10.28
10.28
10.28
7.26 CDCl3
7.22
7.20
7.20
1.00
1.83
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)

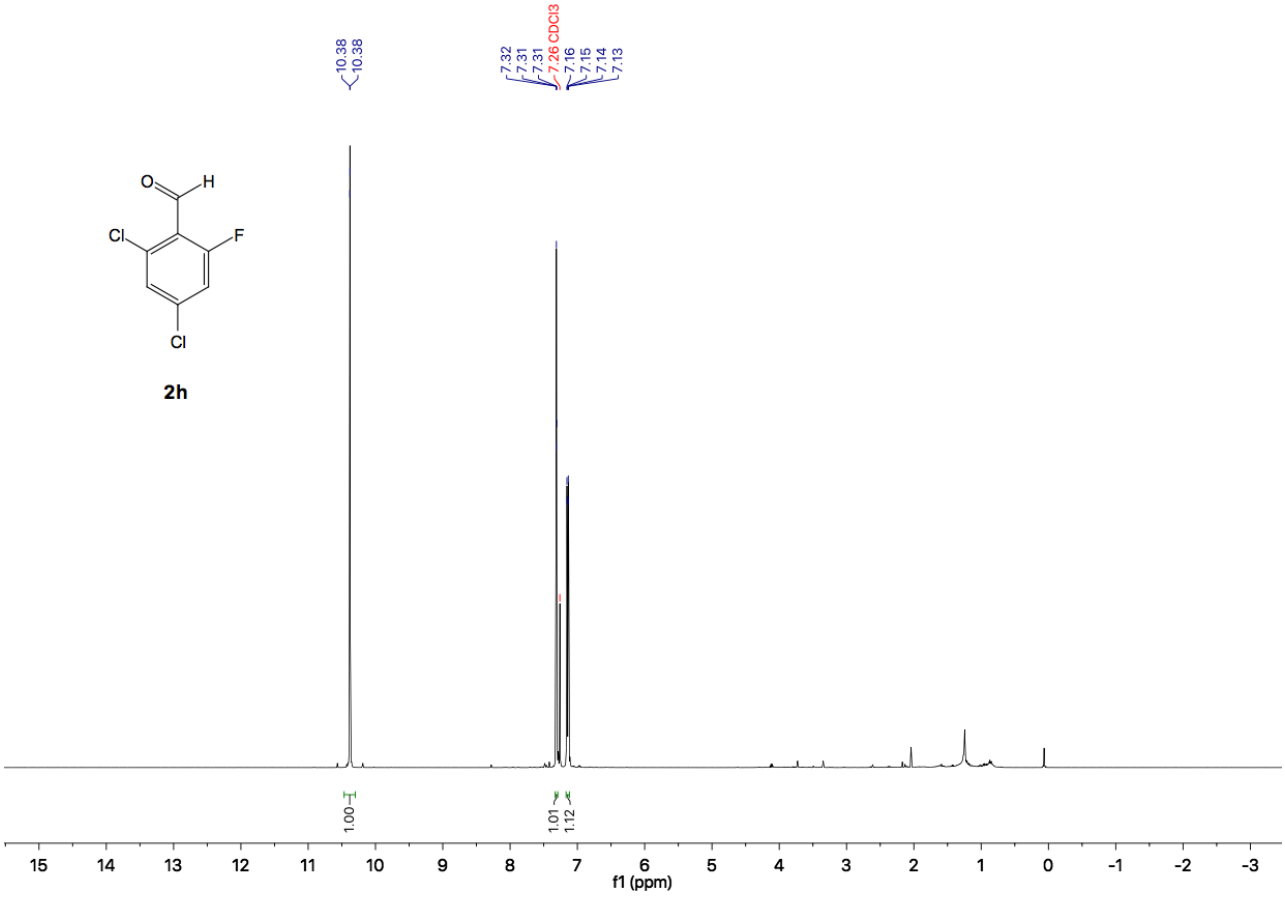

183.66
183.63
183.59
164.01
163.96
161.89
161.84
129.65
129.54
129.44
116.90
116.88
116.85
116.71
116.69
116.67
113.34
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
O
H
F
F
Br
2f
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

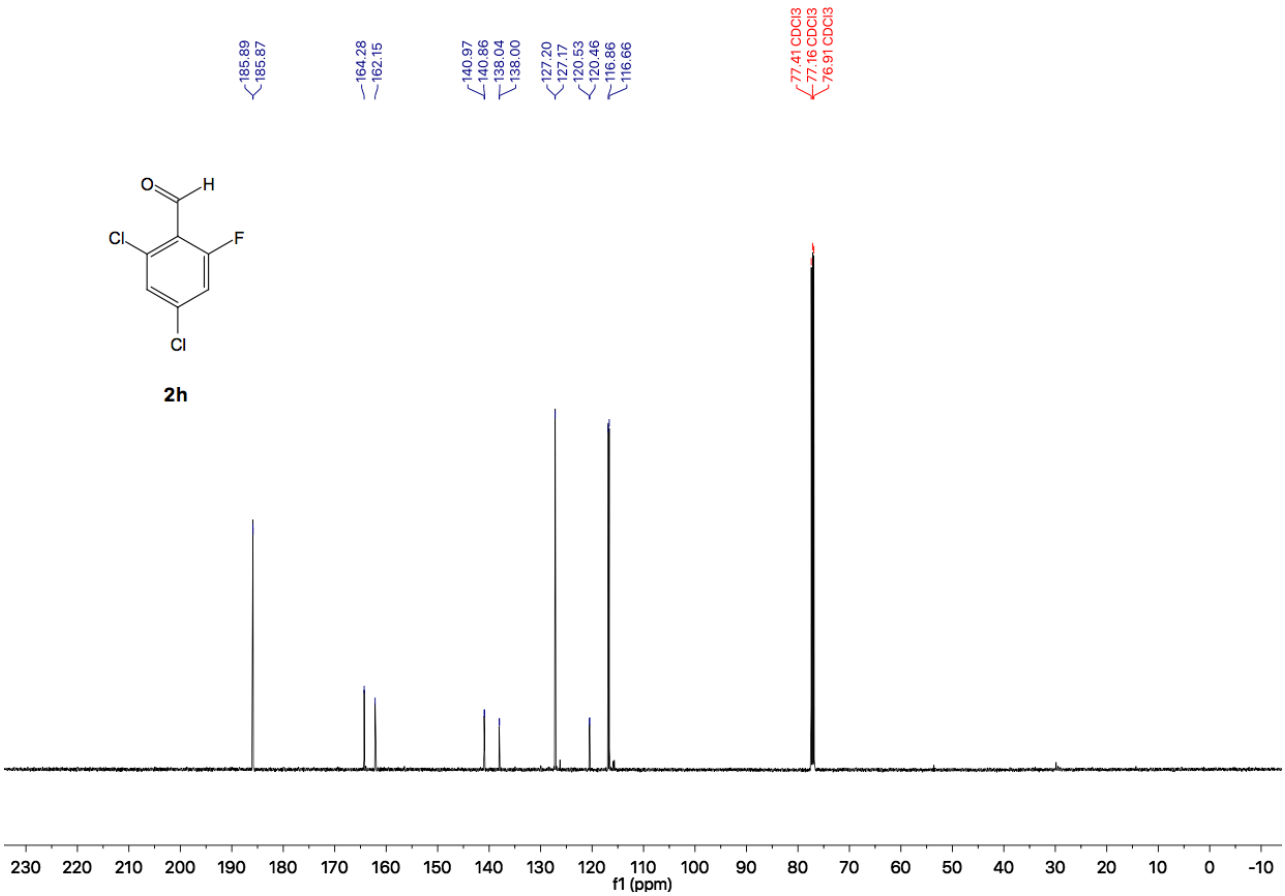

-113.22
-113.25
O
H
F
F
Br
2f
30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)


10.37
10.37
7.26 CDCl3
7.07
7.06
7.06
7.05
7.05
7.04
6.88
6.88
6.87
6.86
6.86
6.85
6.84
O
H
Cl
F
F
2g
1.00
1.08
1.10
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


185.64
185.62
166.32
166.20
165.57
165.46
164.24
164.13
163.45
163.34
139.13
139.08
139.02
138.98
119.01
118.98
118.94
118.91
115.11
115.08
114.92
114.89
104.83
104.63
104.43
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
O
H
Cl
F
F
2g
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-98.30
-98.33
-98.35
-98.36
-98.38
-98.41
-109.98
-109.99
-109.99
-110.02
-110.03
-110.07
-110.07
O
H
Cl
F
F
2g
f1 (ppm)


10.38
10.38
7.32
7.31
7.31
7.26 CDCl3
7.16
7.15
7.14
7.13
O
H
Cl
F
Cl
2h
1.00
1.01
1.12
f1 (ppm)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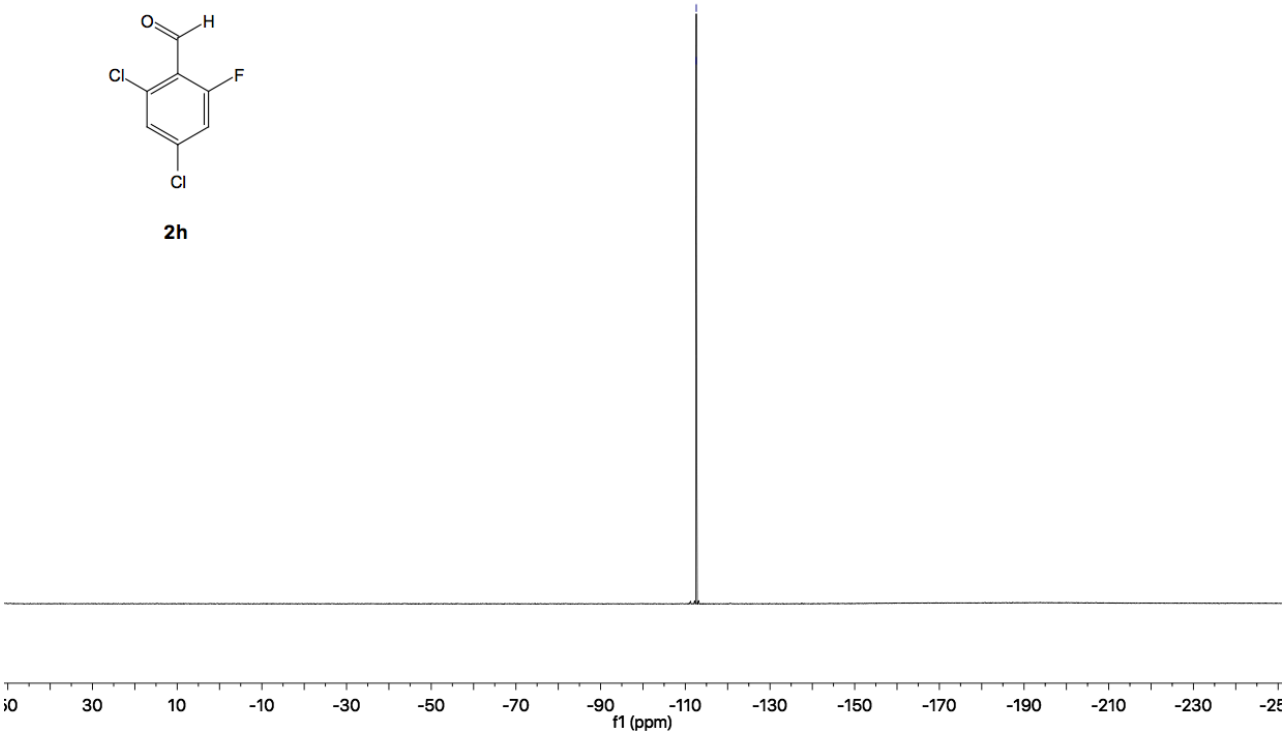
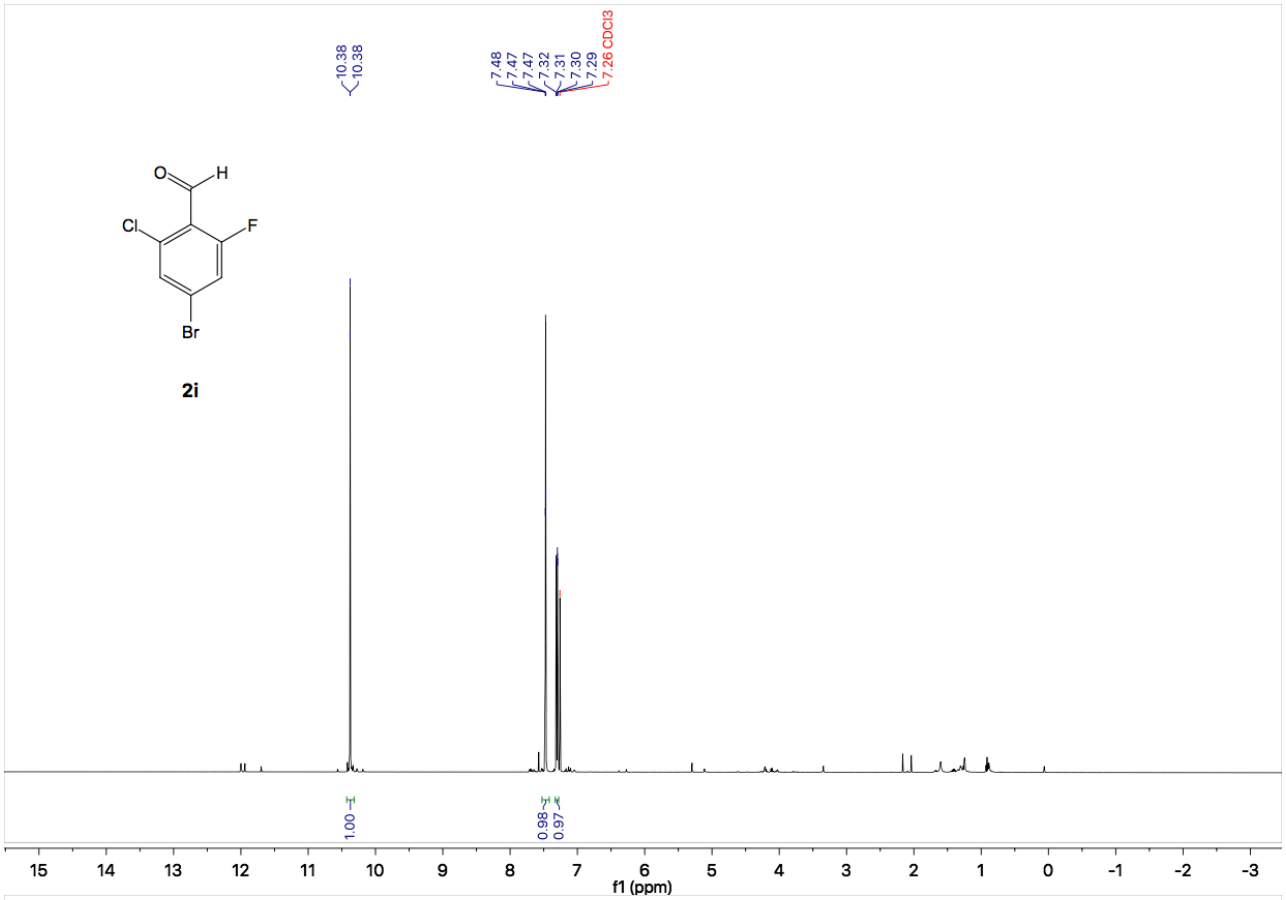
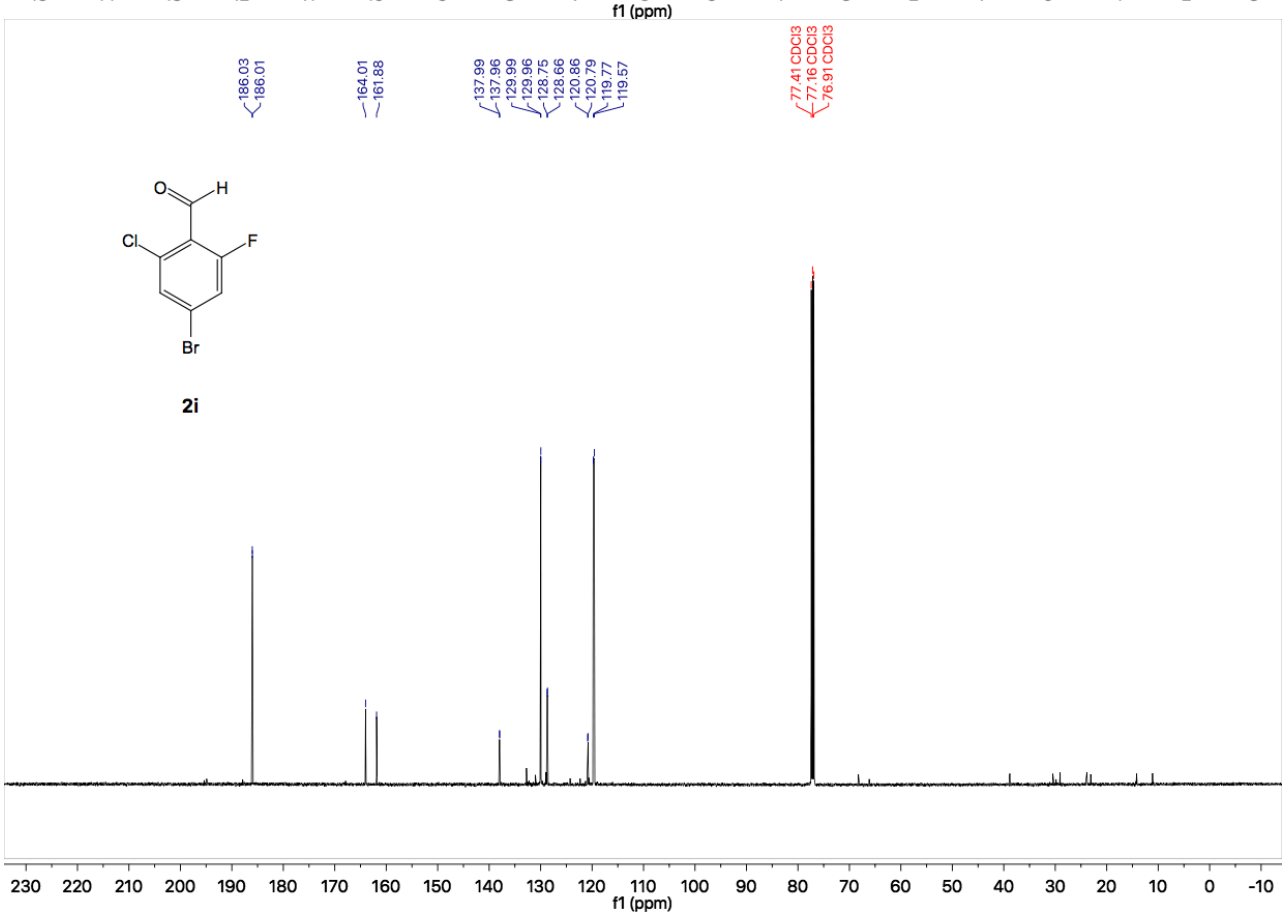
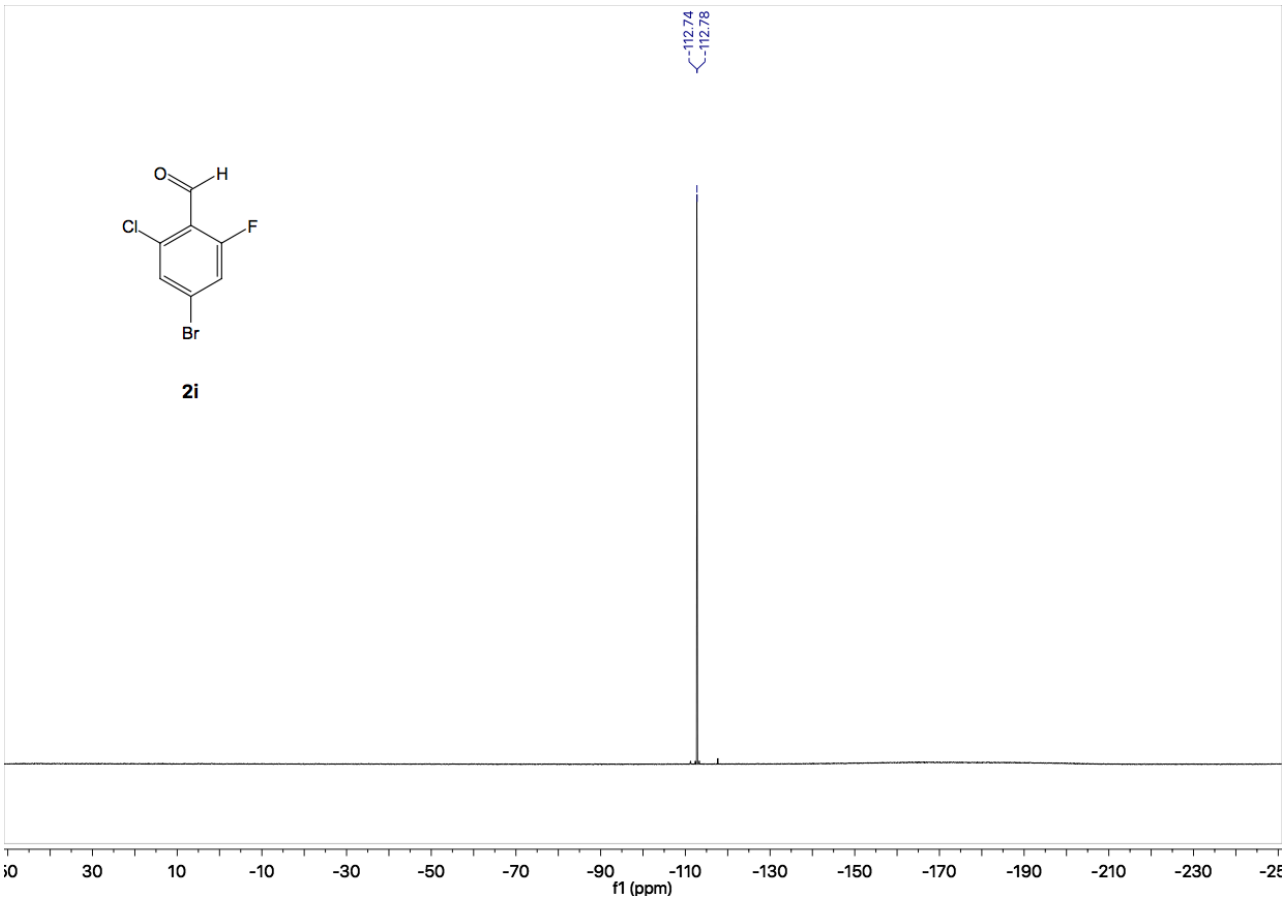
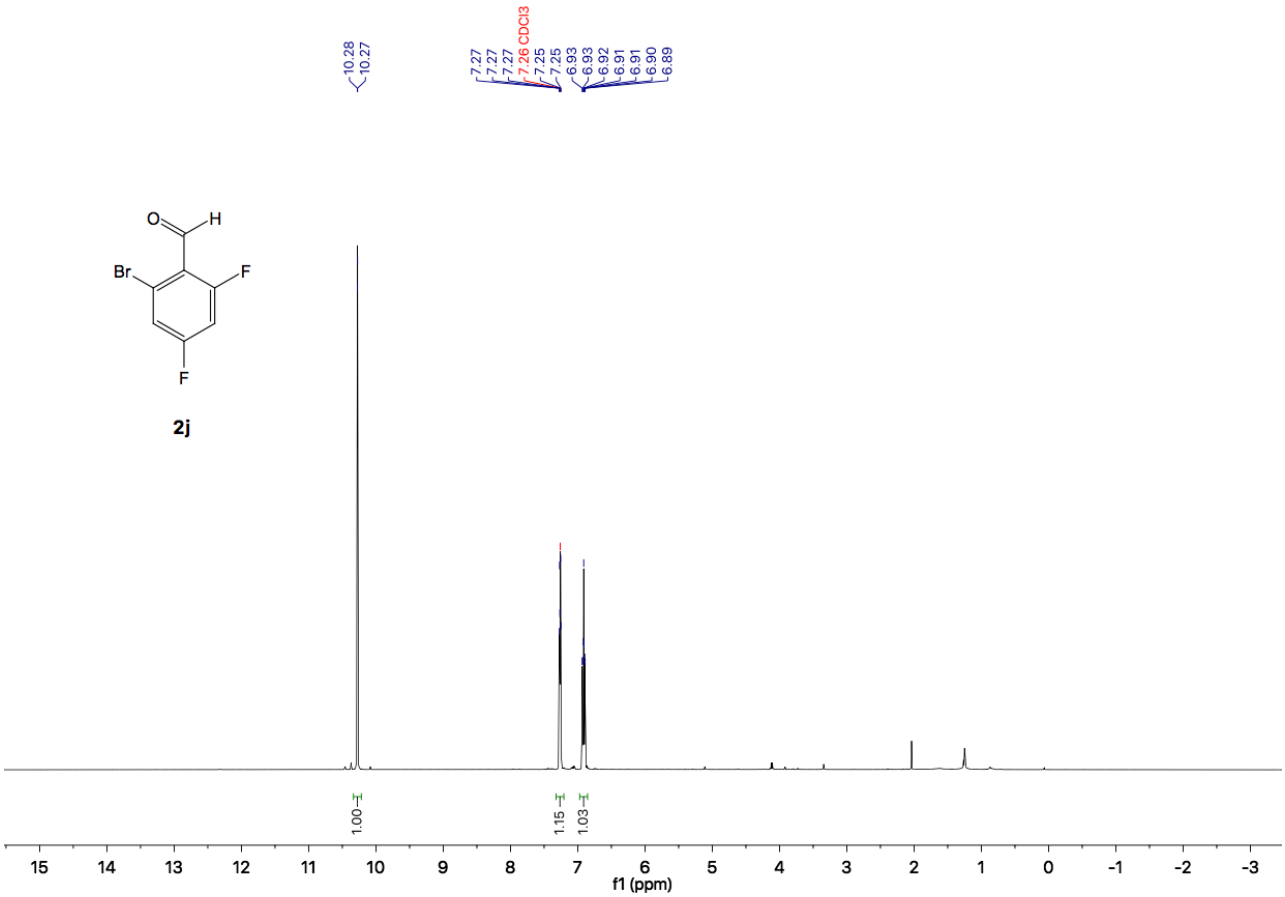
185.87
164.28
162.15
140.97
140.86
138.04
138.00
127.20
127.17
120.53
120.46
116.86
116.66
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
O
H
Cl
F
Cl
2h
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

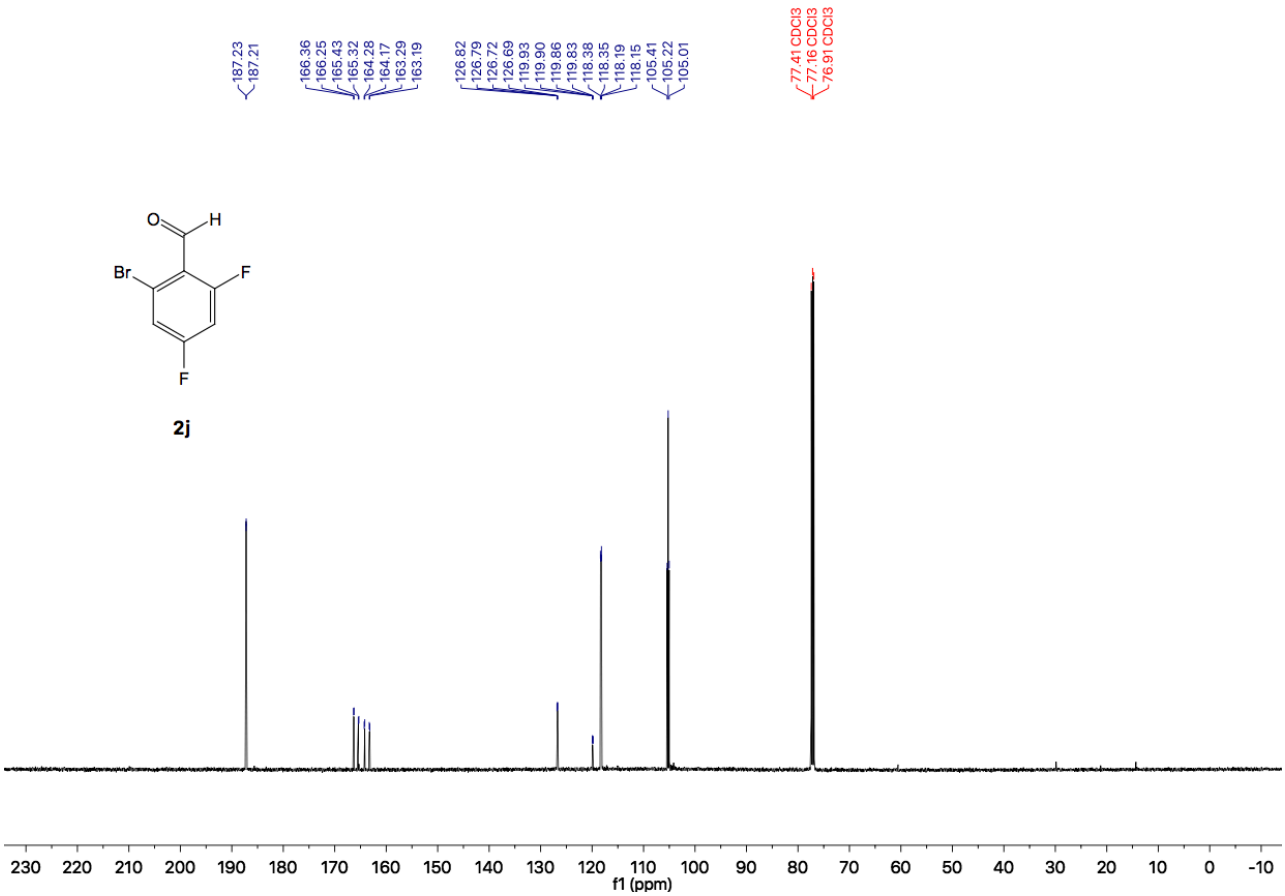

112.56
112.59
O
H
Cl
F
Cl
2h
30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

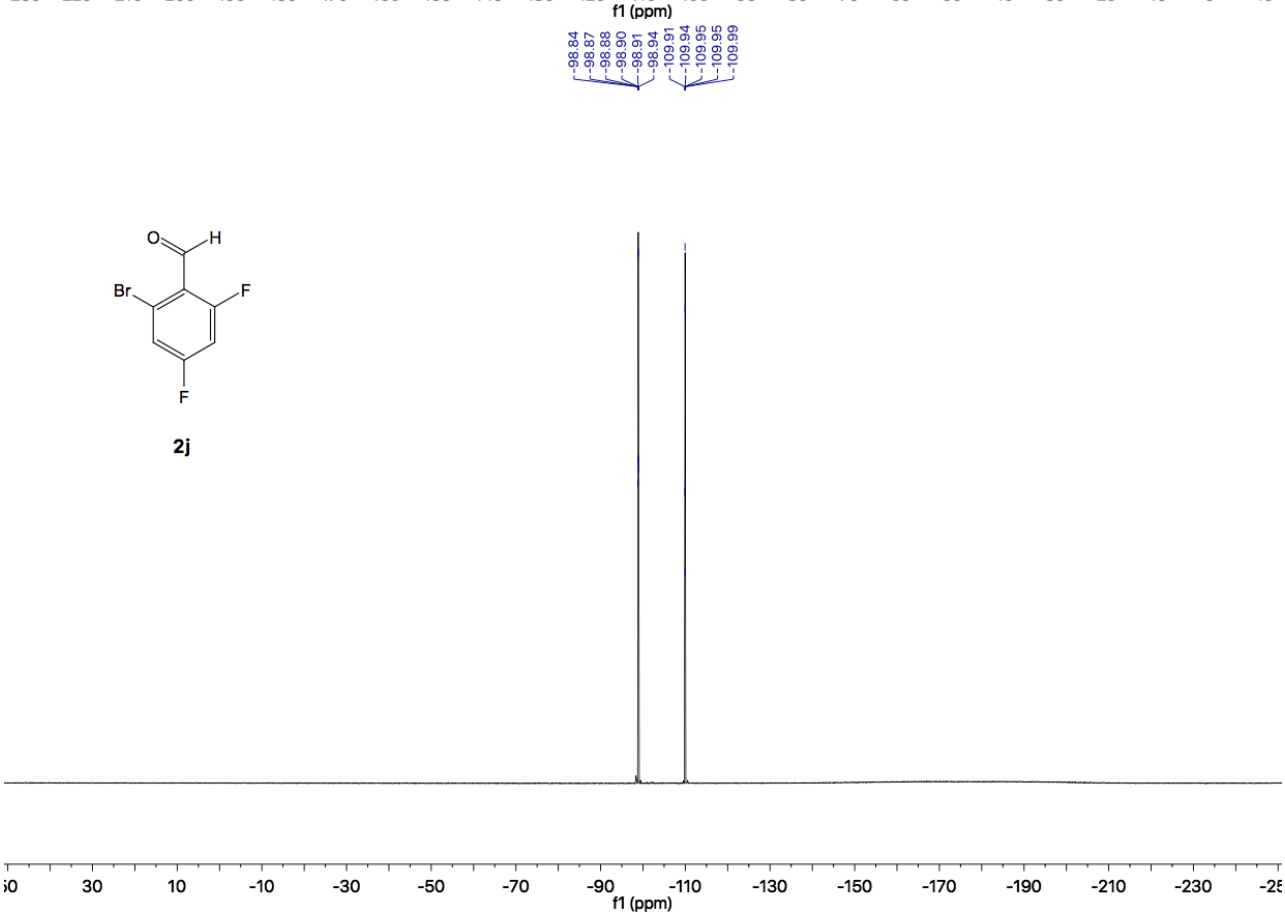

10.38
10.38
7.48
7.47
7.47
7.32
7.31
7.30
7.29
7.26 CDCl3
O
H
Cl
F
Br
2i
1.00
0.98
0.97
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

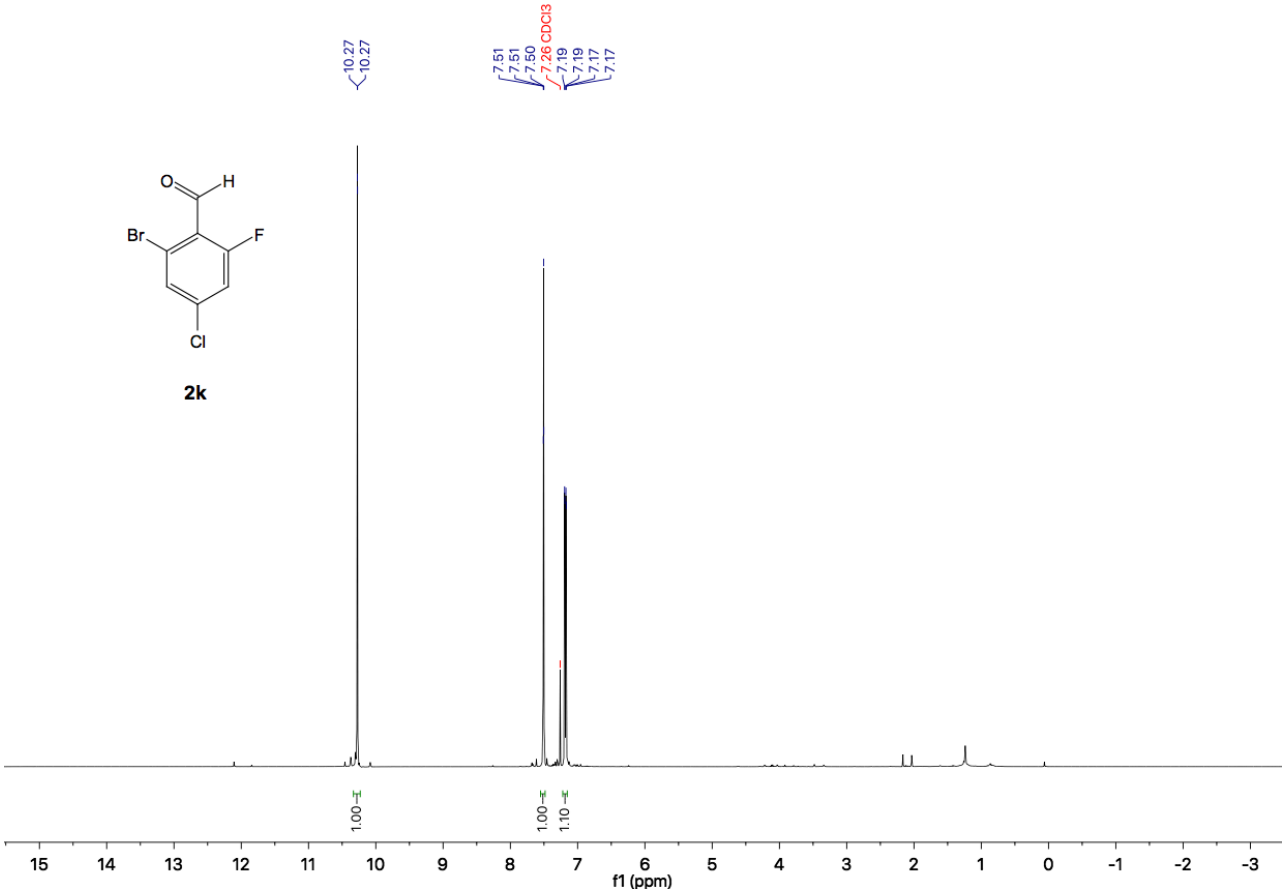

186.03
186.01
164.01
161.88
137.99
137.96
129.99
129.96
128.75
128.66
120.86
120.79
119.77
119.57
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
O
H
Cl
F
Br
2i
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

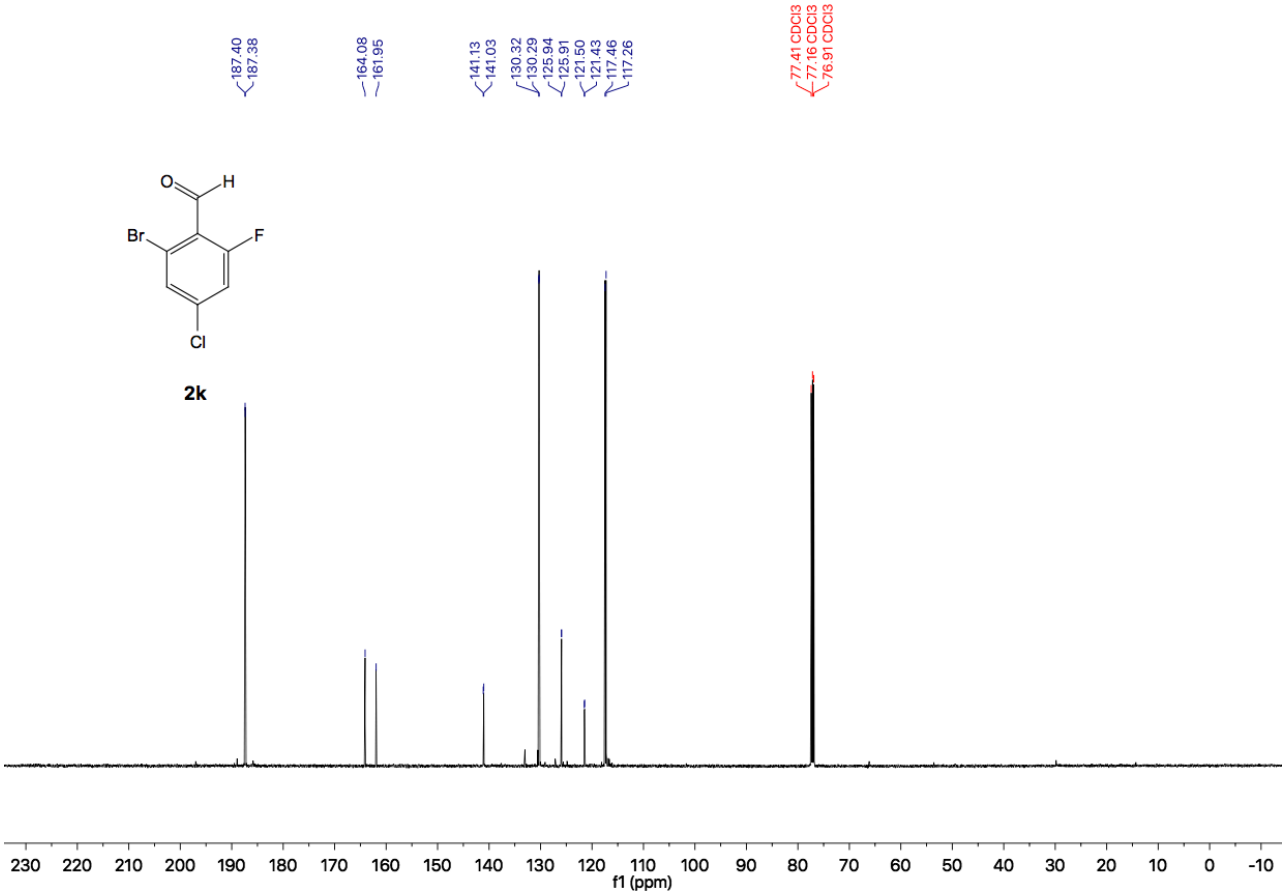

-112.74
-112.78
O
H
Cl
F
Br
2i
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

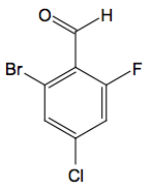

10.28
10.27
7.27
7.27
7.27
7.26 CDCl3
7.25
7.25
6.93
6.93
6.92
6.91
6.91
6.90
6.89
O
H
Br
F
F
2j
1.00
1.15
1.03
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)


187.23
187.21
166.36
166.25
165.43
165.32
164.28
164.17
163.29
163.19
126.82
126.79
126.72
126.69
119.93
119.90
119.86
119.83
118.38
118.35
118.19
118.15
105.41
105.22
105.01
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
O
H
Br
F
F
2j
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-98.84
-98.87
-98.88
-98.90
-98.91
-98.94
-109.91
-109.94
-109.95
-109.95
-109.99
O
H
Br
F
F
2j
50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -25
f1 (ppm)

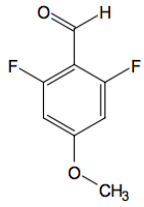

10.27
10.27
7.51
7.51
7.50
7.26 CDCl3
7.19
7.19
7.17
7.17
O
H
Br
F
Cl
2k
1.00
1.00
1.10
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


187.40
187.38
164.08
161.95
141.13
141.03
130.32
130.29
125.94
125.91
121.50
121.43
117.46
117.26
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
O
H
Br
F
Cl
2k
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
H
Br
F
Cl

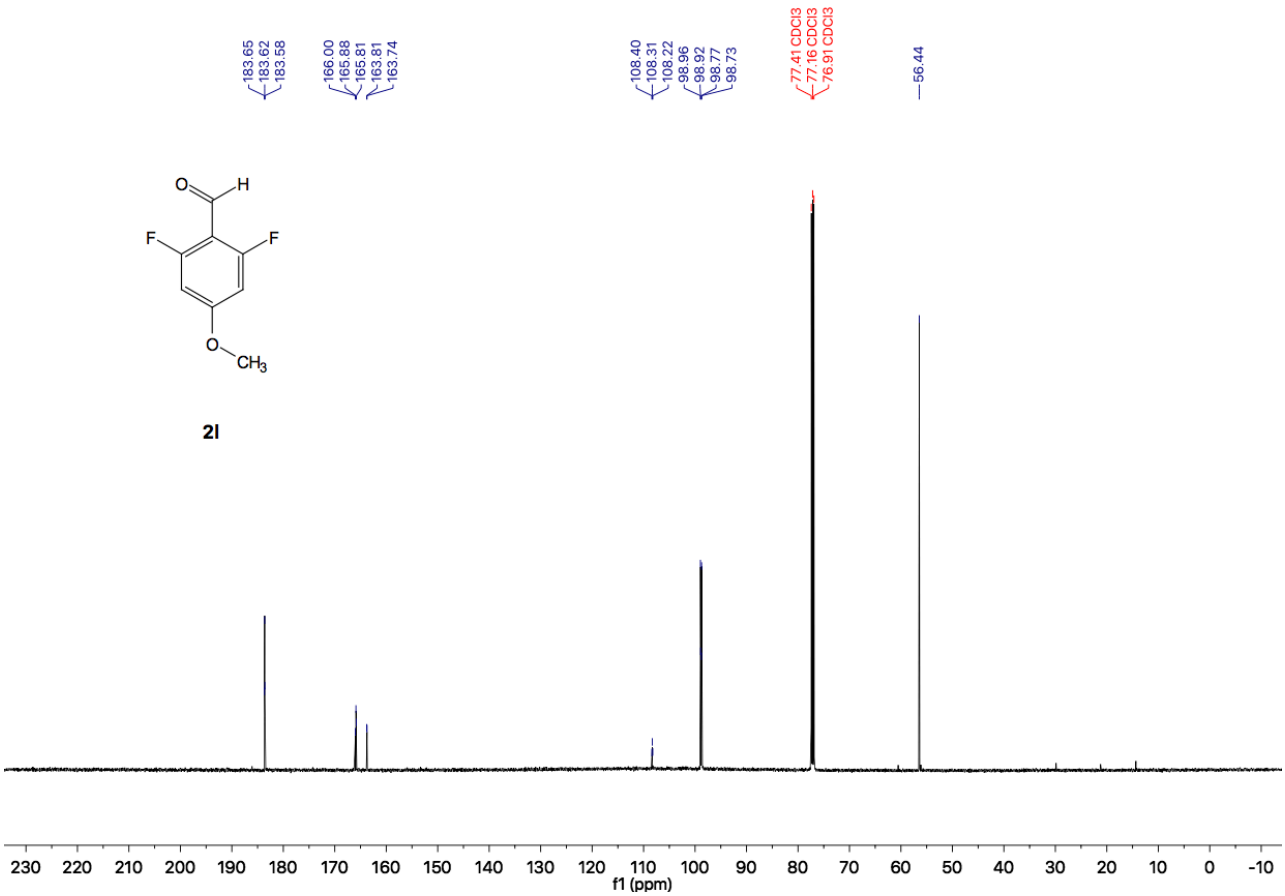
2k

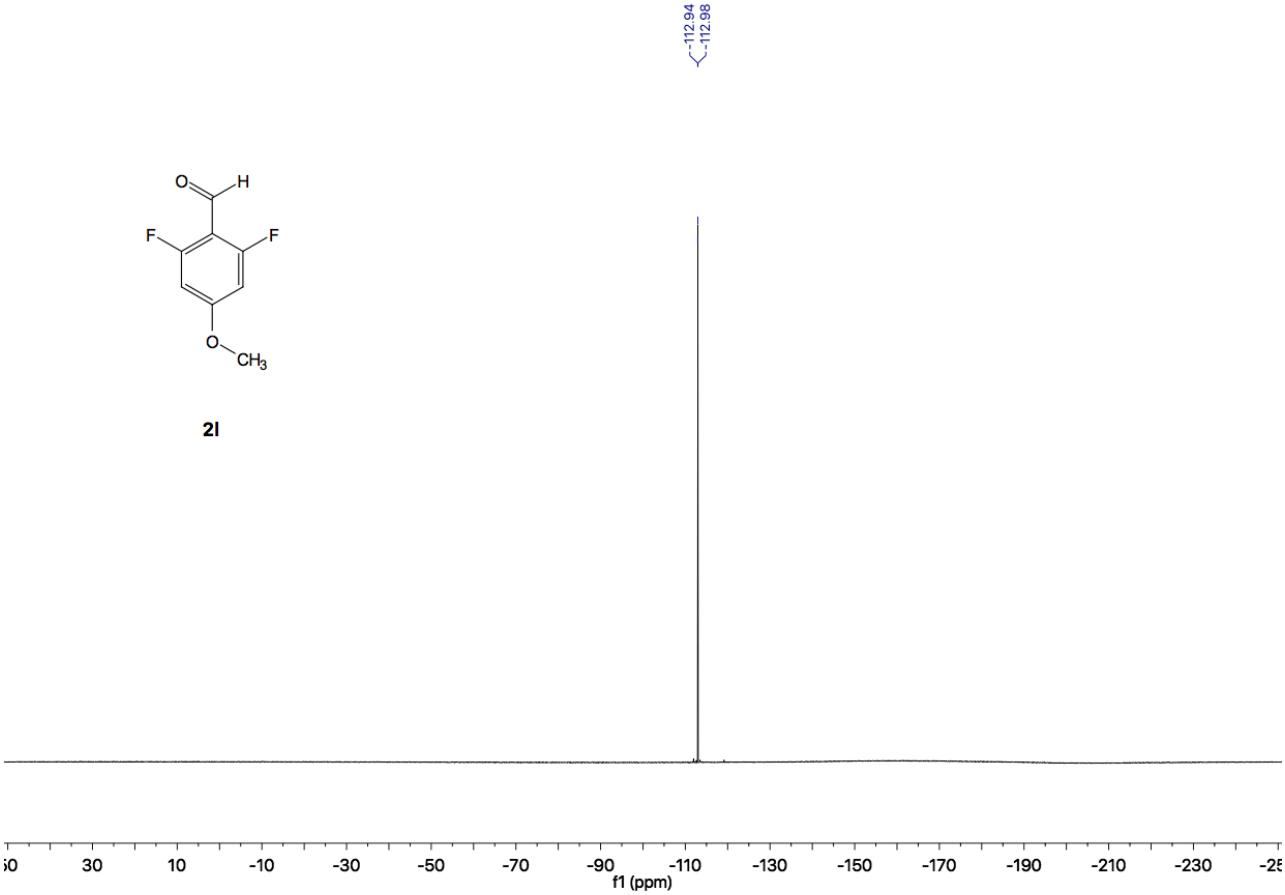
-112.34
-112.38
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

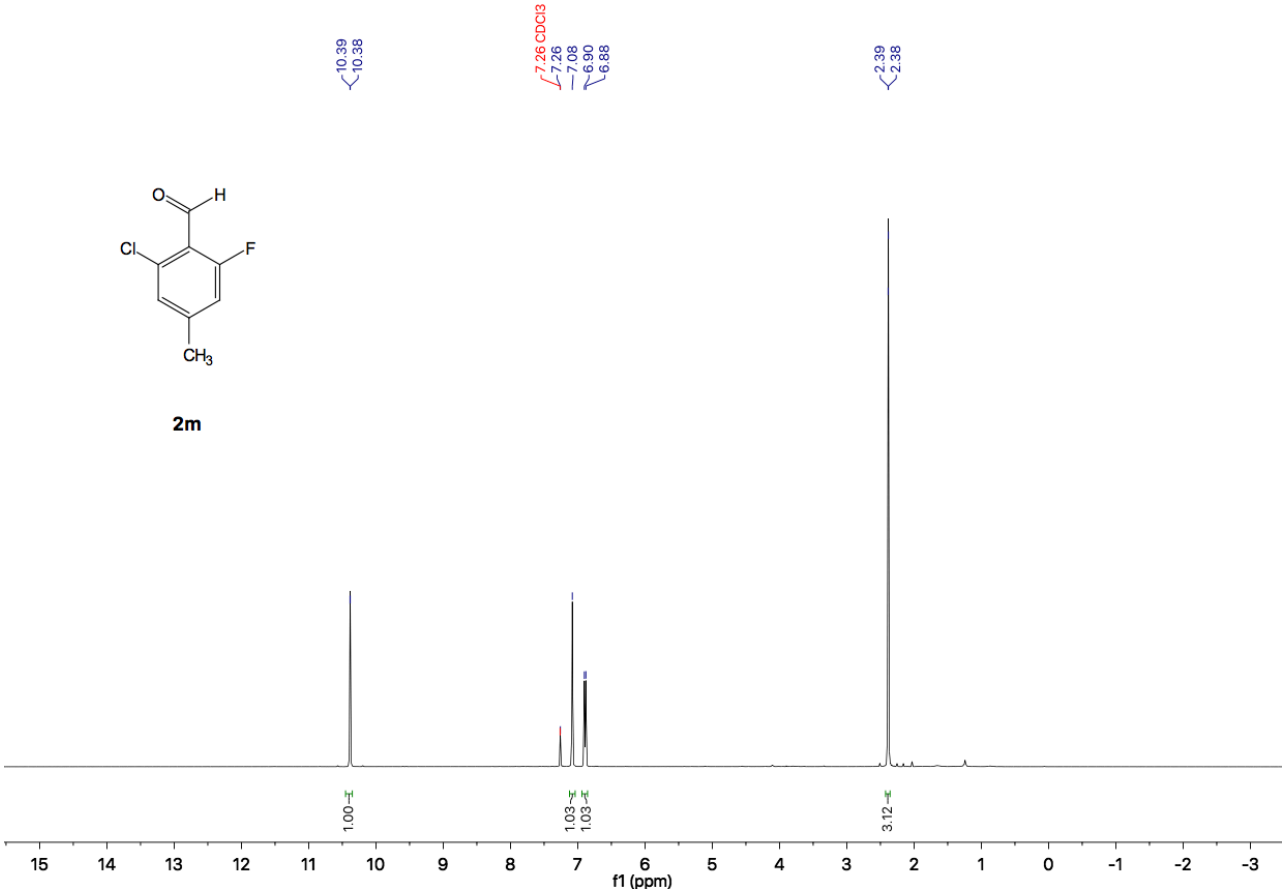

O
H
F
F
O
CH3

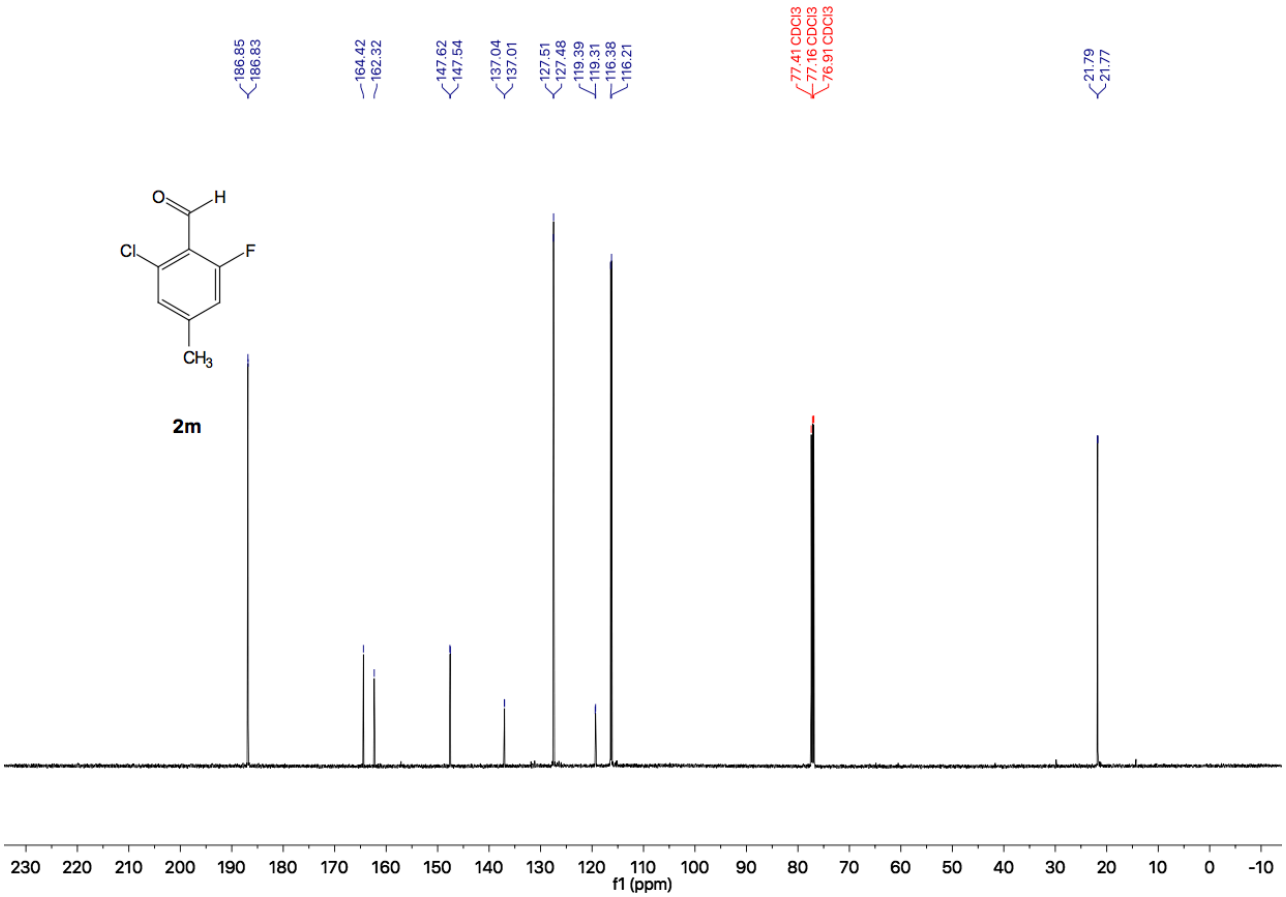
2l

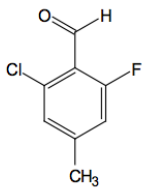
10.19
7.26 CDCl3
6.50
6.48
6.48
3.87
3.86
1.00
1.87
2.91
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)


183.65
183.62
183.58
166.00
165.88
165.81
163.81
163.74
108.40
108.31
108.22
98.96
98.92
98.77
98.73
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
56.44
O
H
F
F
O
CH3
2l
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


112.94
112.98
O
H
F
F
O
CH3
2l
50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -25
f1 (ppm)

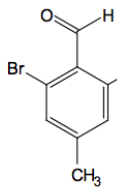

10.39
10.38
7.26 CDCl3
7.26
7.08
6.90
6.88
2.39
2.38
O
H
Cl
F
CH3
2m
1.00
1.03
1.03
3.12
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


186.85
186.83
164.42
162.32
147.62
147.54
137.04
137.01
127.51
127.48
119.39
119.31
116.38
116.21
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
21.79
21.77
O
H
Cl
F
CH3
2m
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
H
Cl
F
CH3

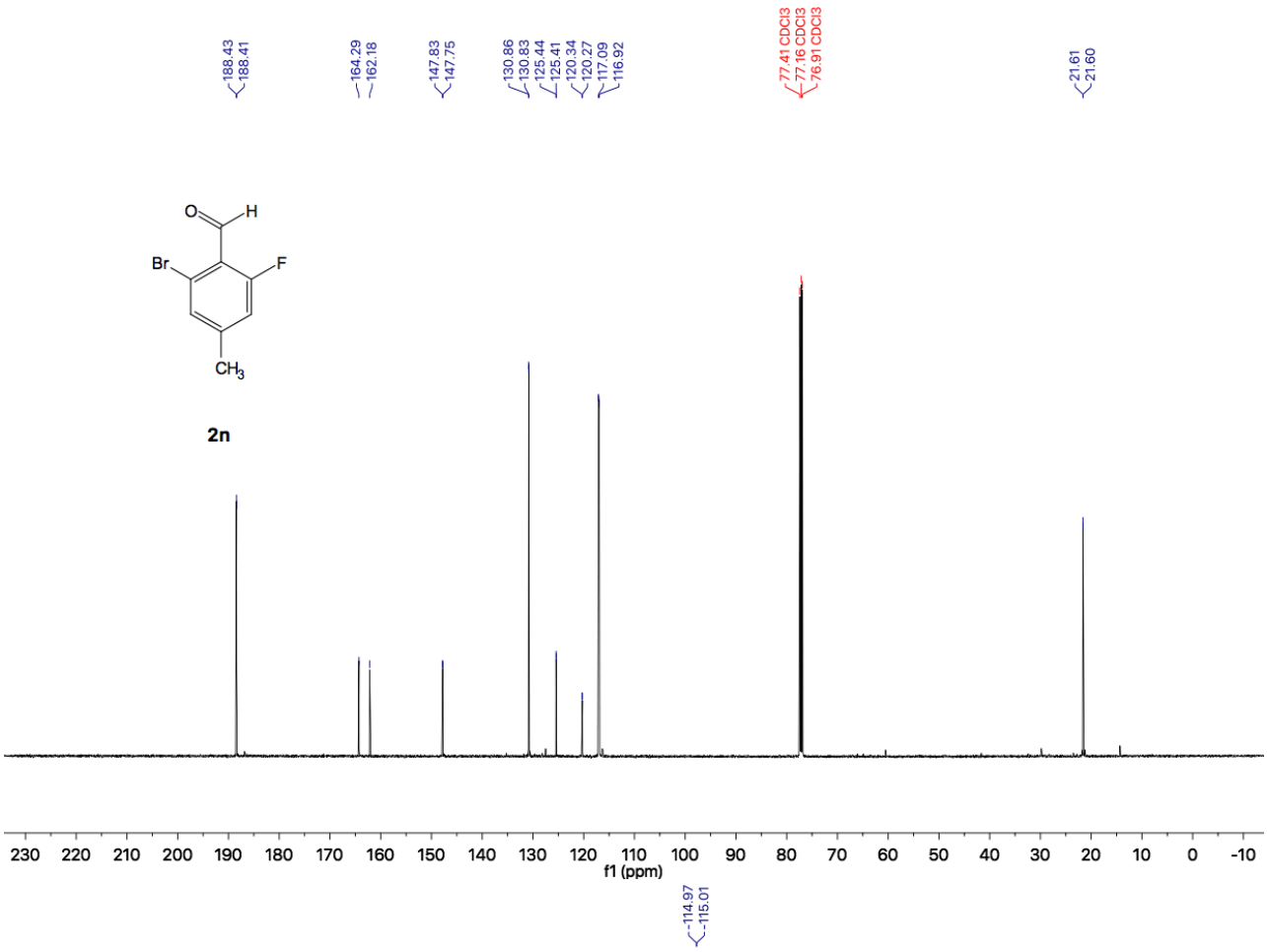
2m

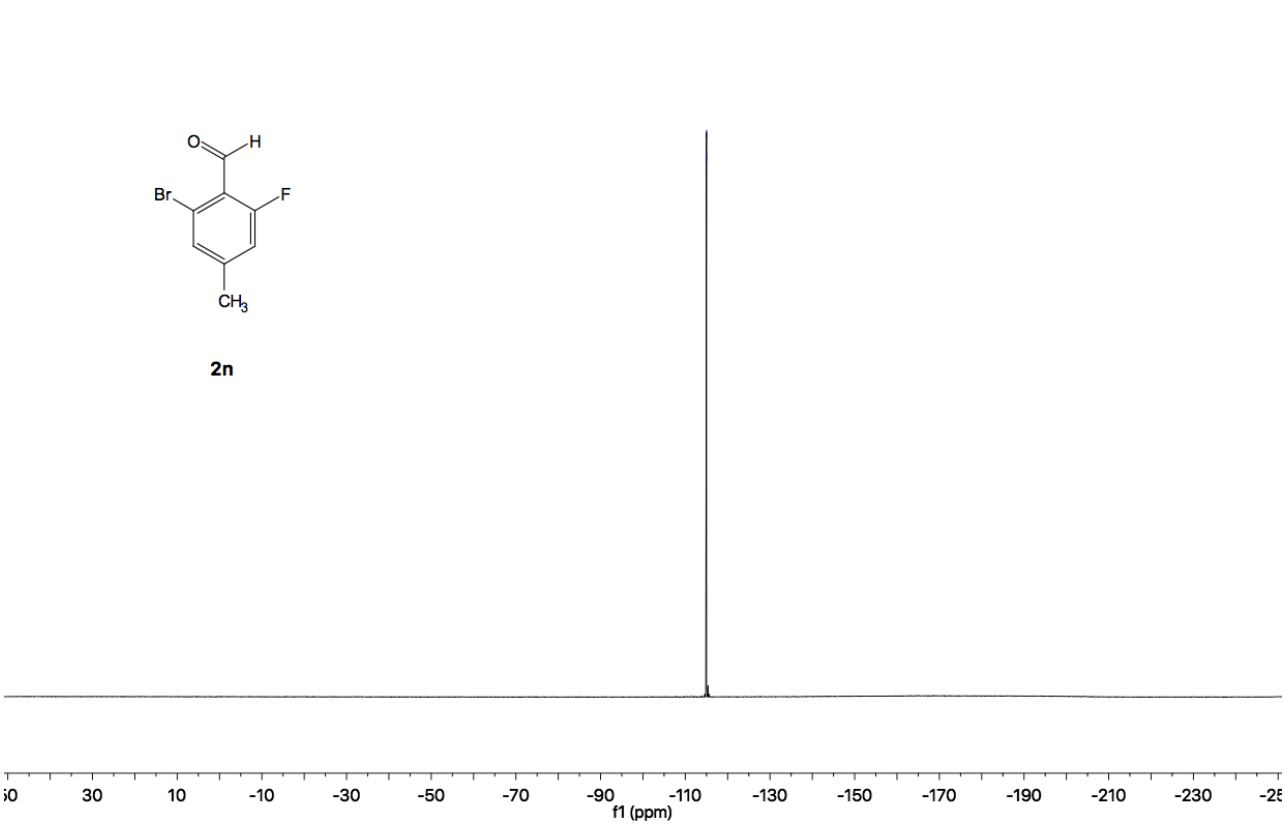
-115.31
-115.35
f1 (ppm)

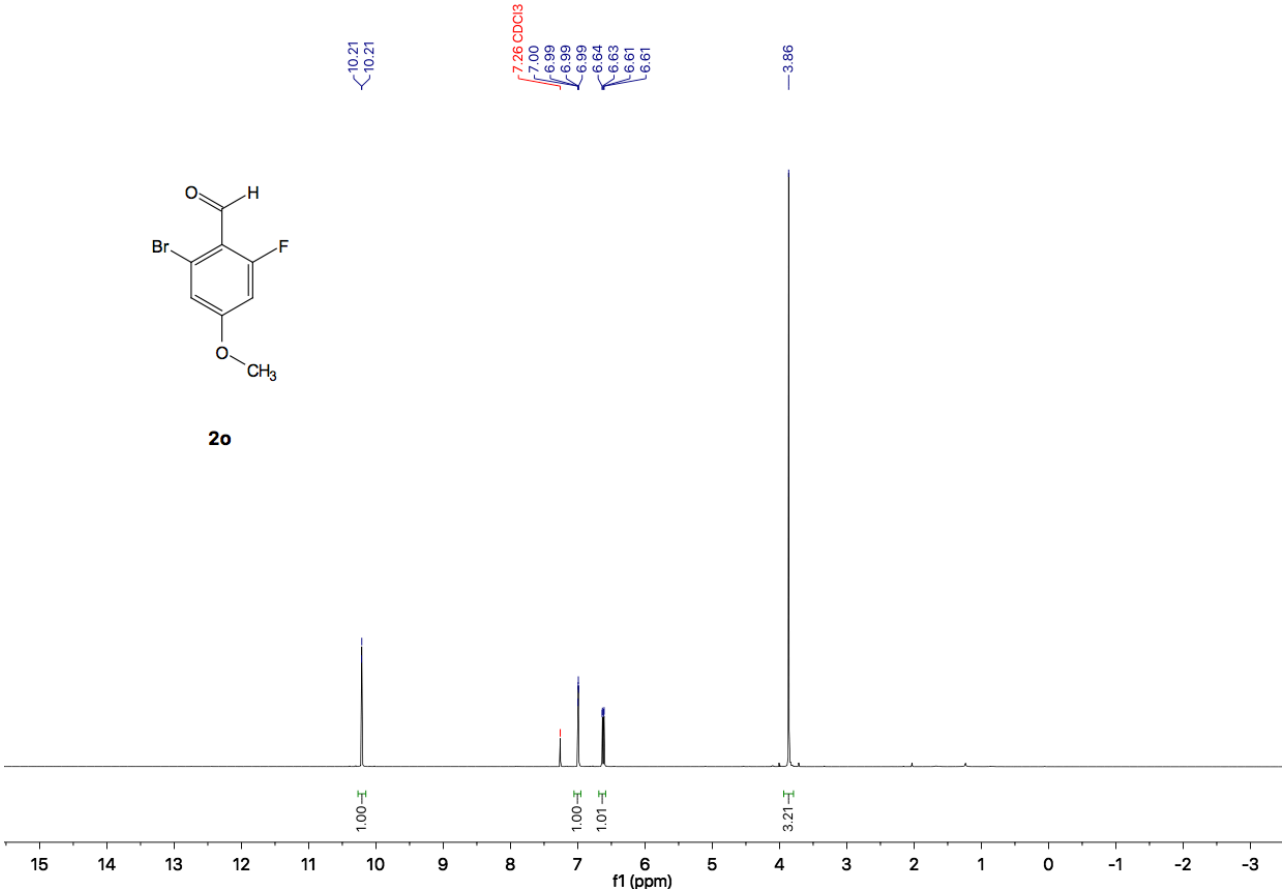

O
H
Br
F
CH3

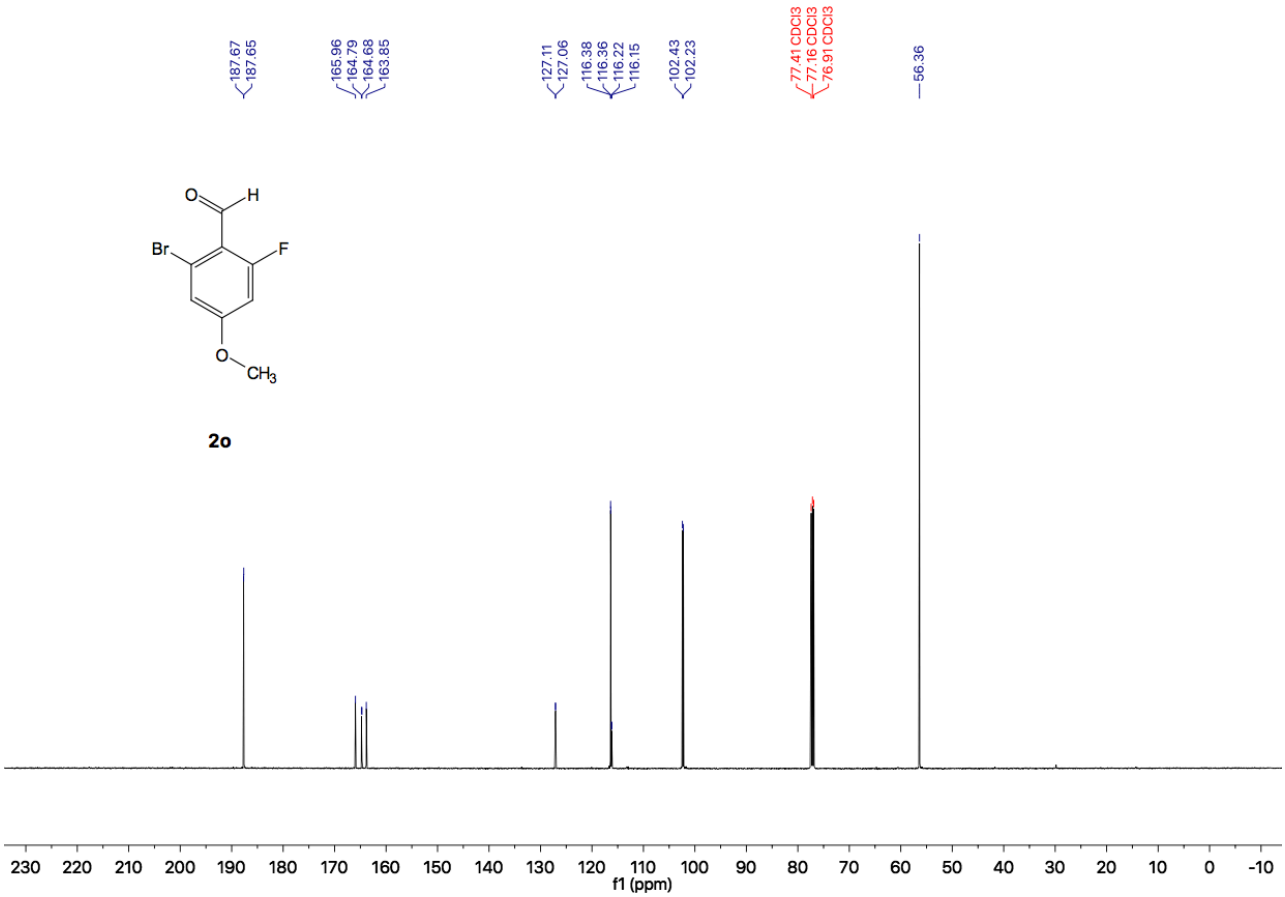
2n

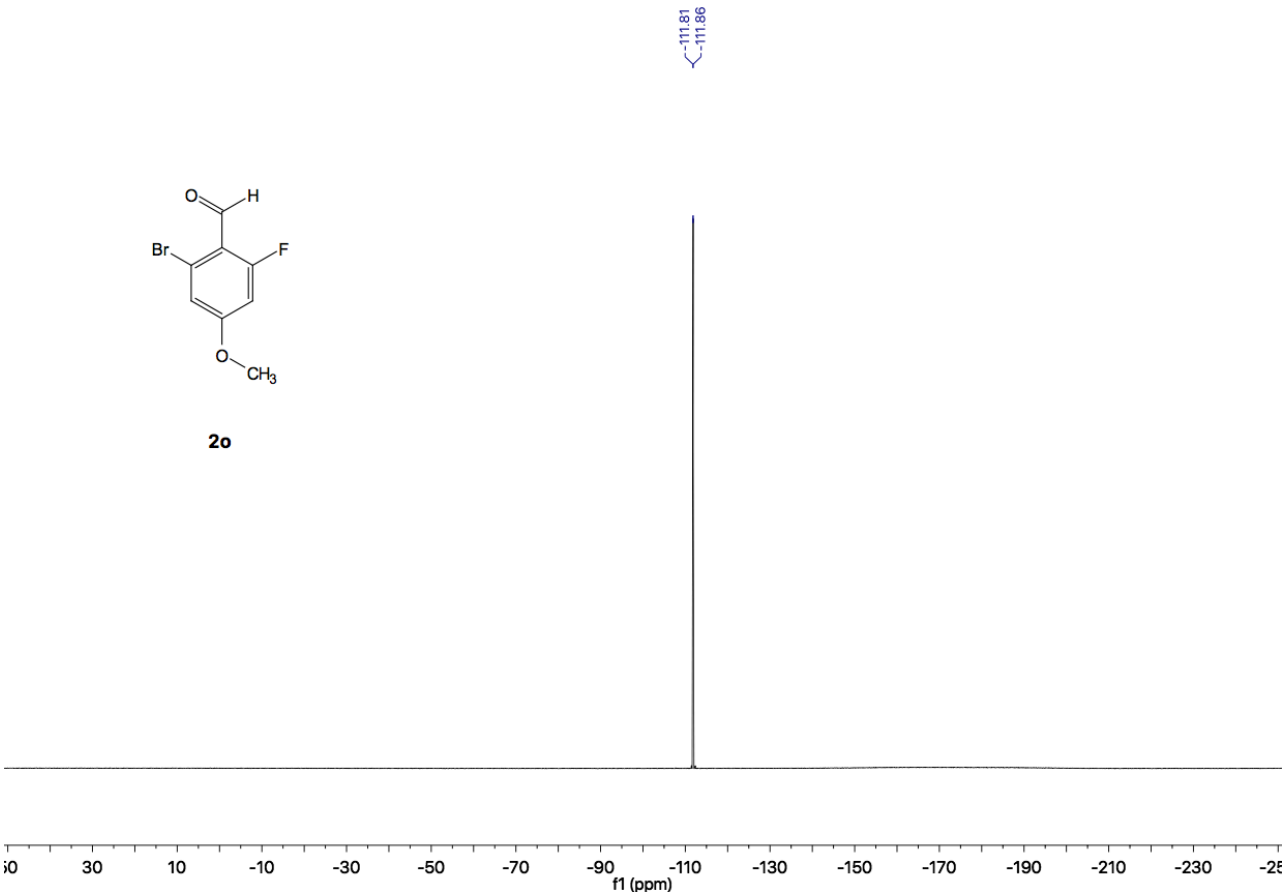
10.29
10.29
7.29
7.26 CDCl3
6.95
6.94
6.92
6.92
2.38
1.00
0.95
1.03
2.90
f1 (ppm)


188.43
188.41
164.29
162.18
147.83
147.75
130.86
130.83
125.44
125.41
120.34
120.27
117.09
116.92
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
21.61
21.60
O
H
Br
F
CH3
2n
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

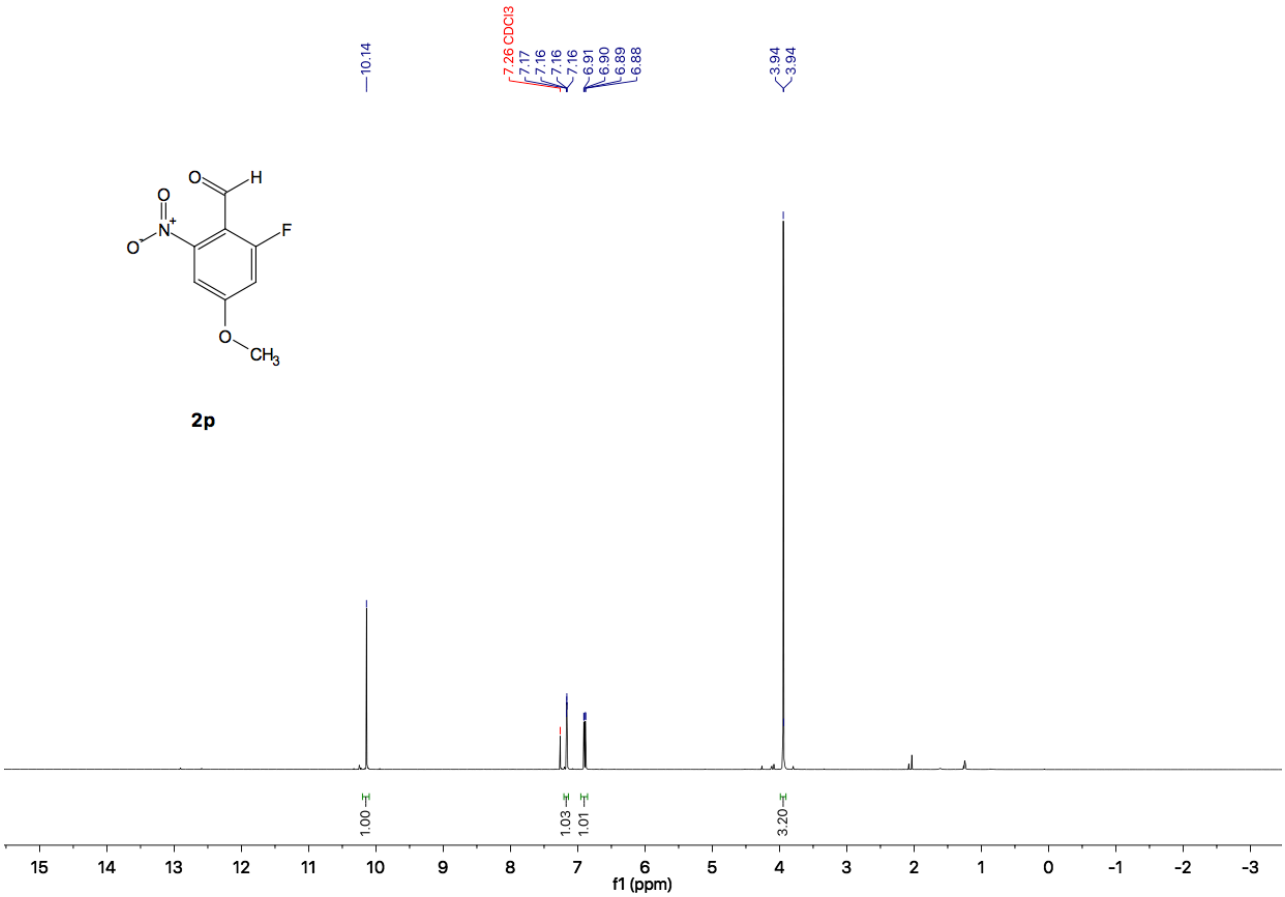

114.97
115.01
O
H
Br
F
CH3
2n
30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)


10.21
10.21
7.26 CDCl3
7.00
6.99
6.99
6.99
6.64
6.63
6.61
6.61
3.86
O
H
Br
F
O
CH3
2o
1.00
1.00
1.01
3.21
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

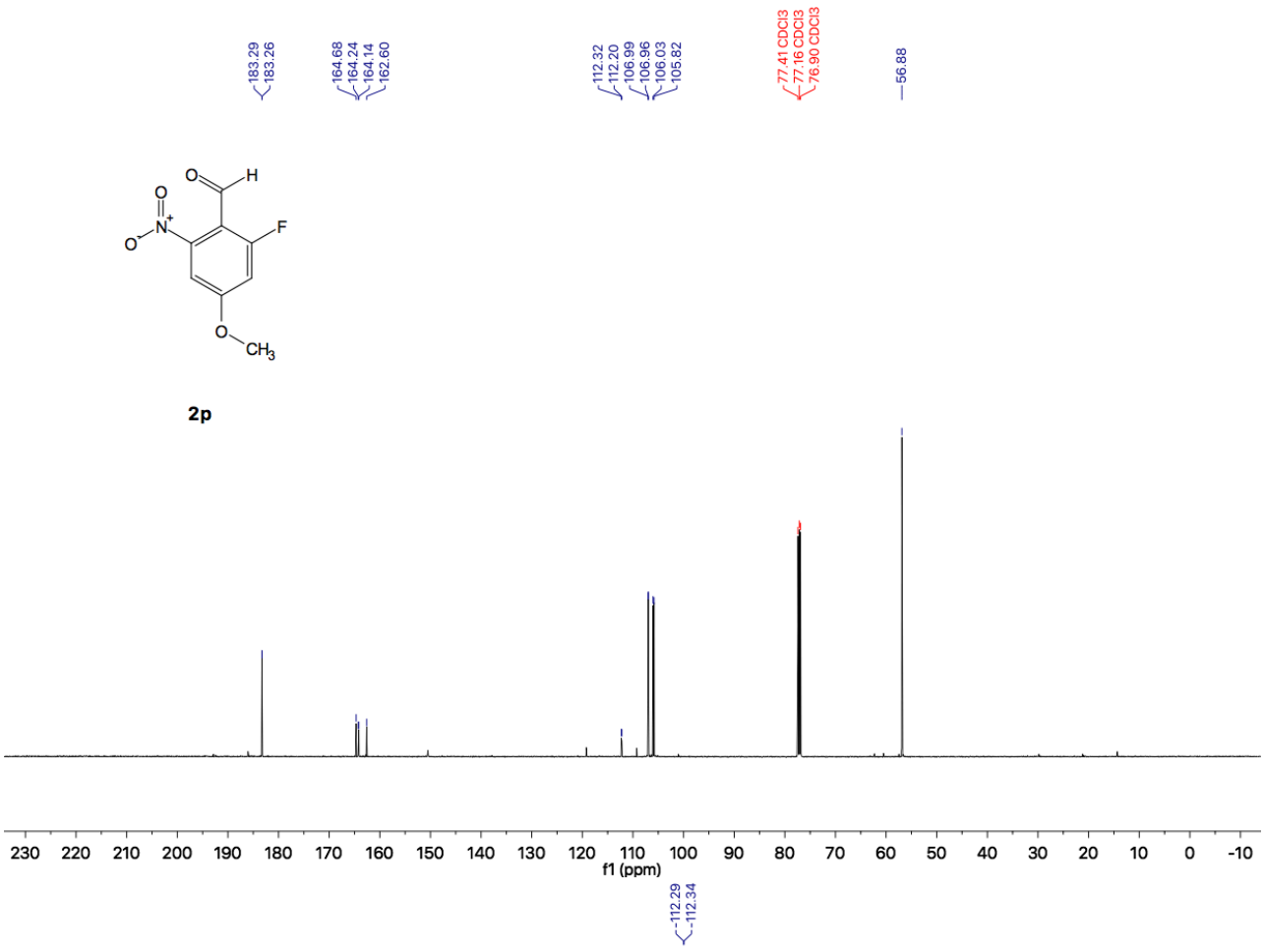

187.67
187.65
165.96
164.79
164.68
163.85
127.11
127.06
116.38
116.36
116.22
116.15
102.43
102.23
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
56.36
O
H
Br
F
O
CH3
2o
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

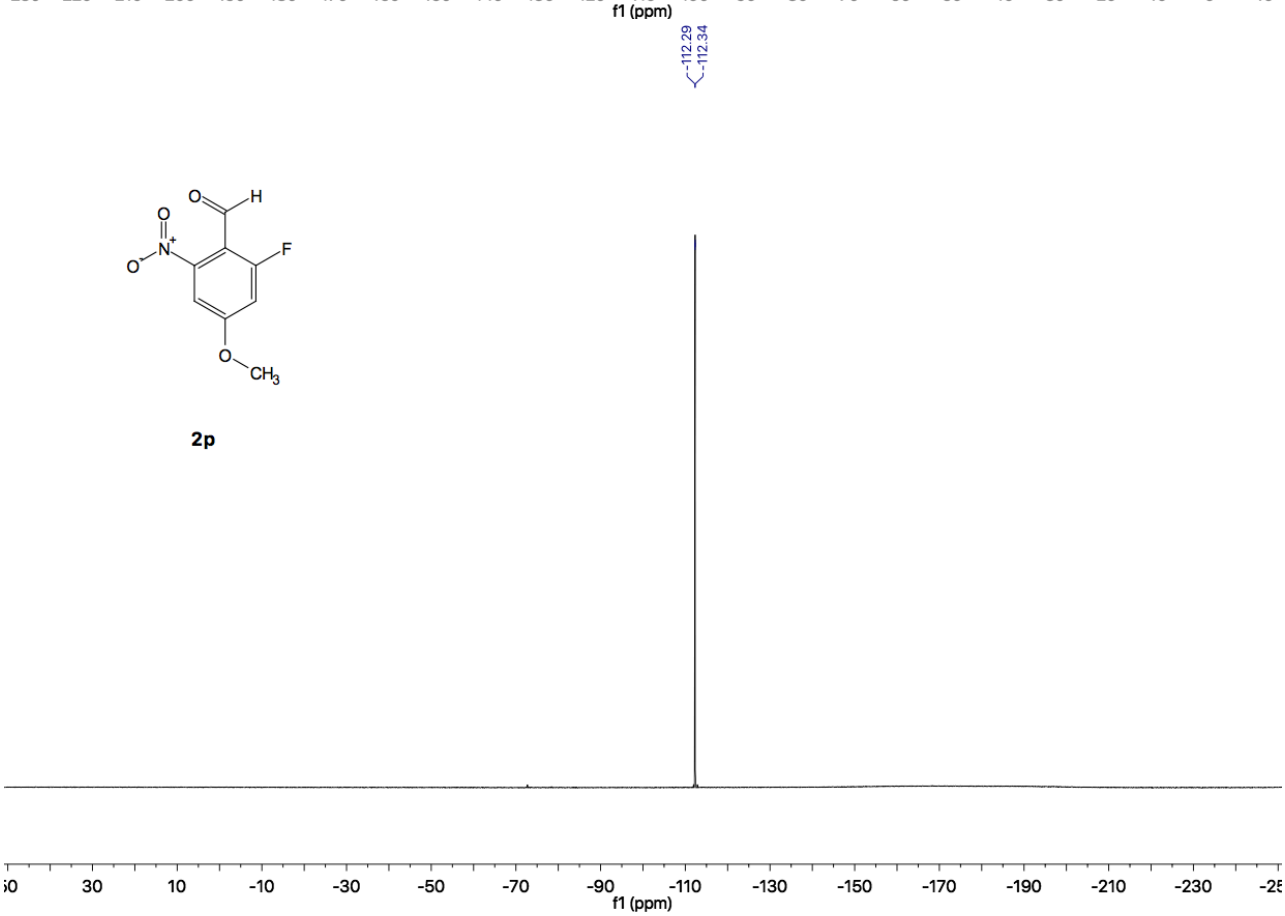

-111.81
-111.86
O
H
Br
F
O
CH3
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

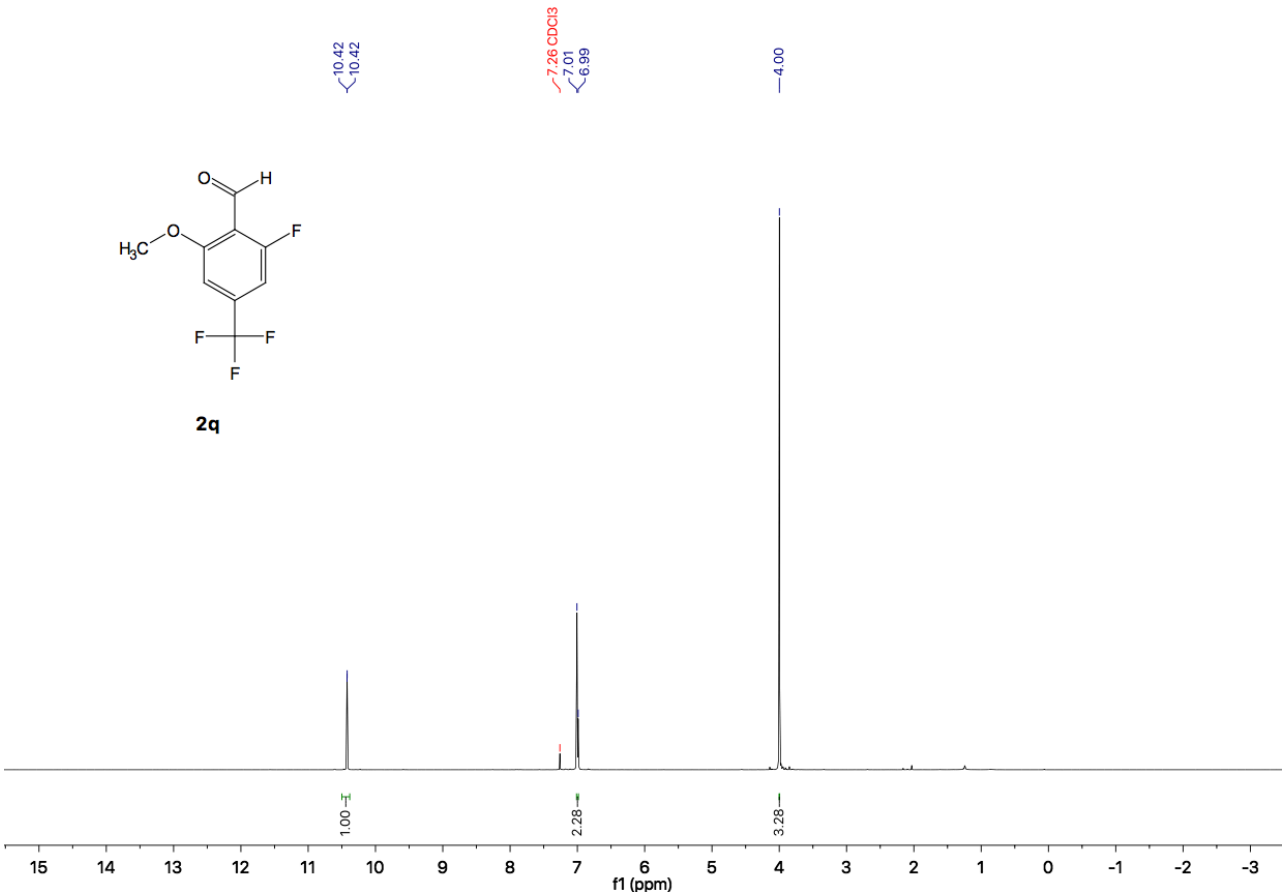
2o

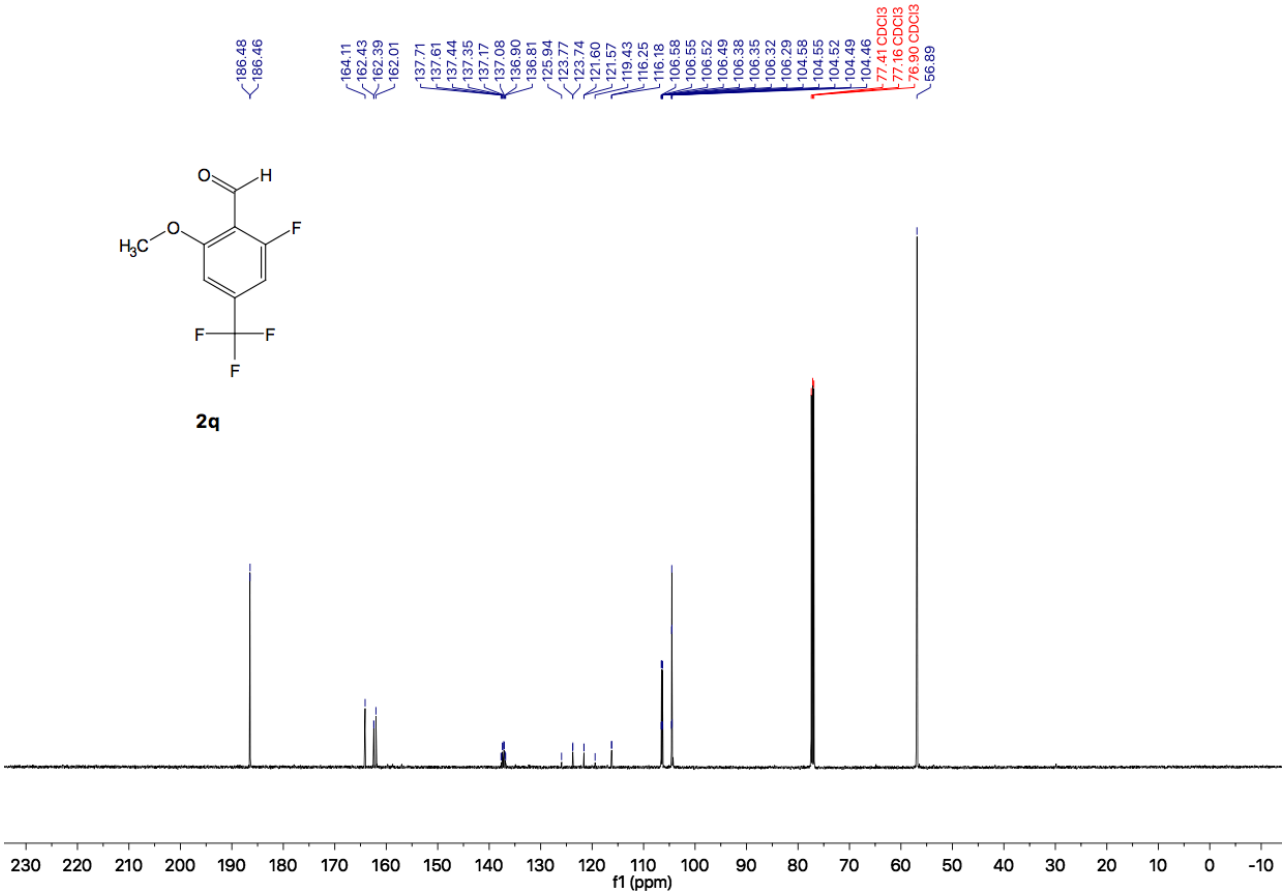

10.14
7.26 CDCl3
7.17
7.16
7.16
7.16
6.91
6.90
6.89
6.88
3.94
3.94
O
H
O
N+
O-
F
O
CH3
1.00
1.03
1.01
3.20
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

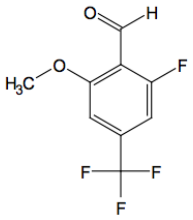
2p


183.29
183.26
164.68
164.24
164.14
162.60
112.32
112.20
106.99
106.96
106.03
105.82
77.41 CDCl3
77.16 CDCl3
76.90 CDCl3
56.88
O
H
O
N+
O-
F
O
CH3
2p
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


112.29
112.34
O
H
O
N+
O-
F
O
CH3
2p
30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

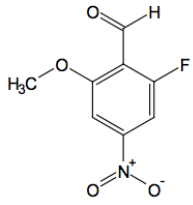

10.42
10.42
7.26 CDCl3
7.01
6.99
4.00
O
H
O
F
H3C
F
F
F
2q
1.00
2.28
3.28
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


186.48
186.46
164.11
162.43
162.39
162.01
137.71
137.61
137.44
137.35
137.17
137.08
136.90
136.81
125.94
123.77
123.74
121.60
121.57
119.43
116.25
116.18
106.58
106.55
106.52
106.49
106.38
106.35
106.32
106.29
104.58
104.55
104.52
104.49
104.46
77.41 CDCl3
77.16 CDCl3
76.90 CDCl3
56.89
O
H
O
F
H3C
F
F
F
2q
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



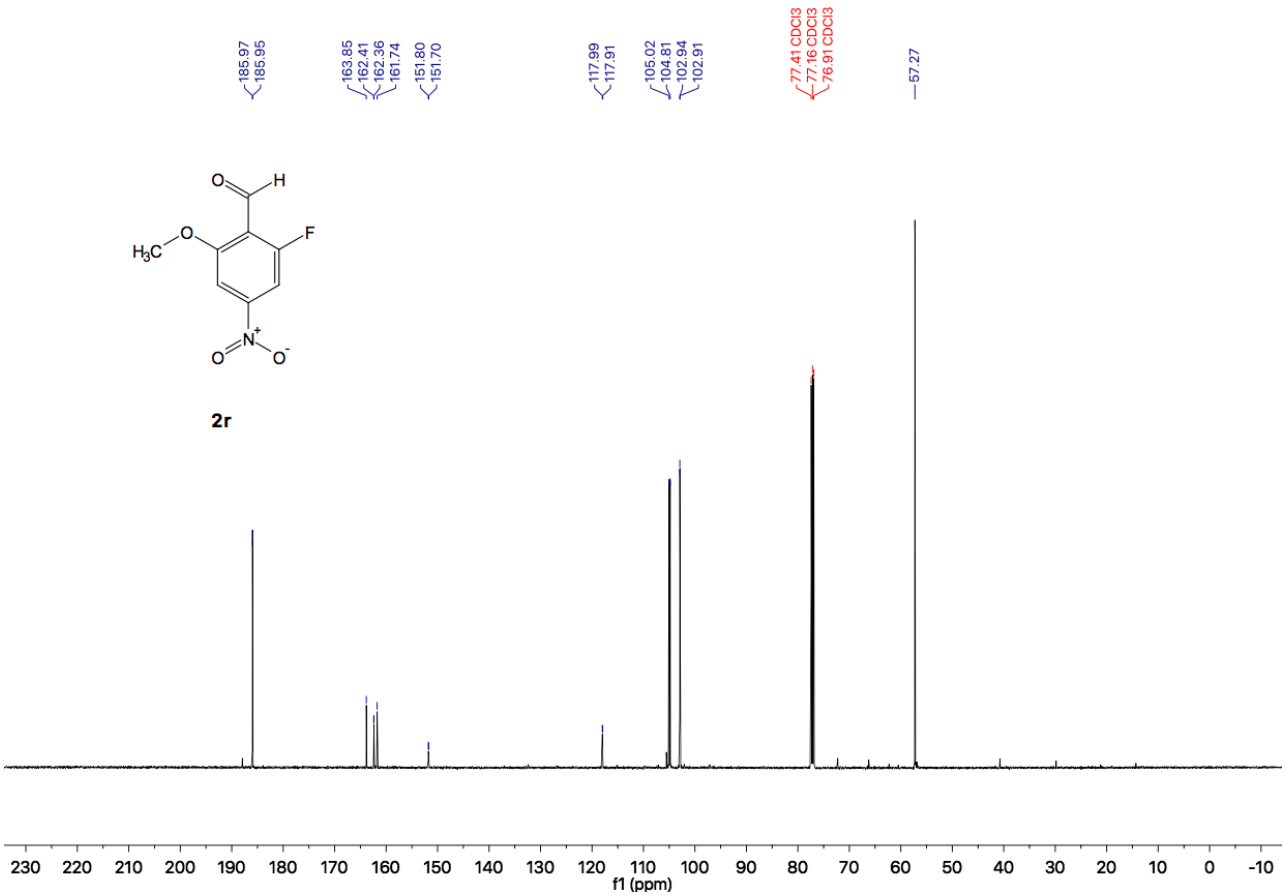
2q

-63.91
-111.89
-111.93
f1 (ppm)

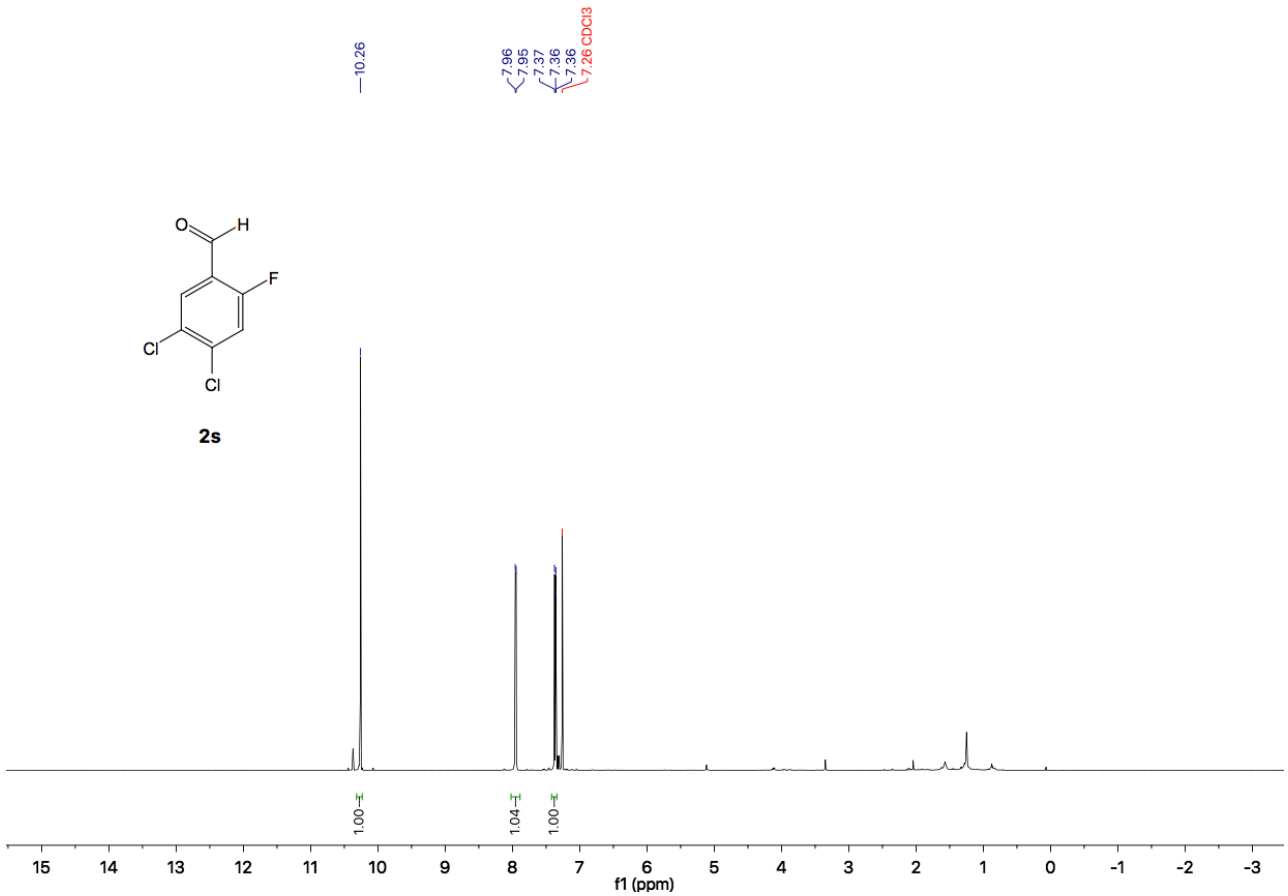


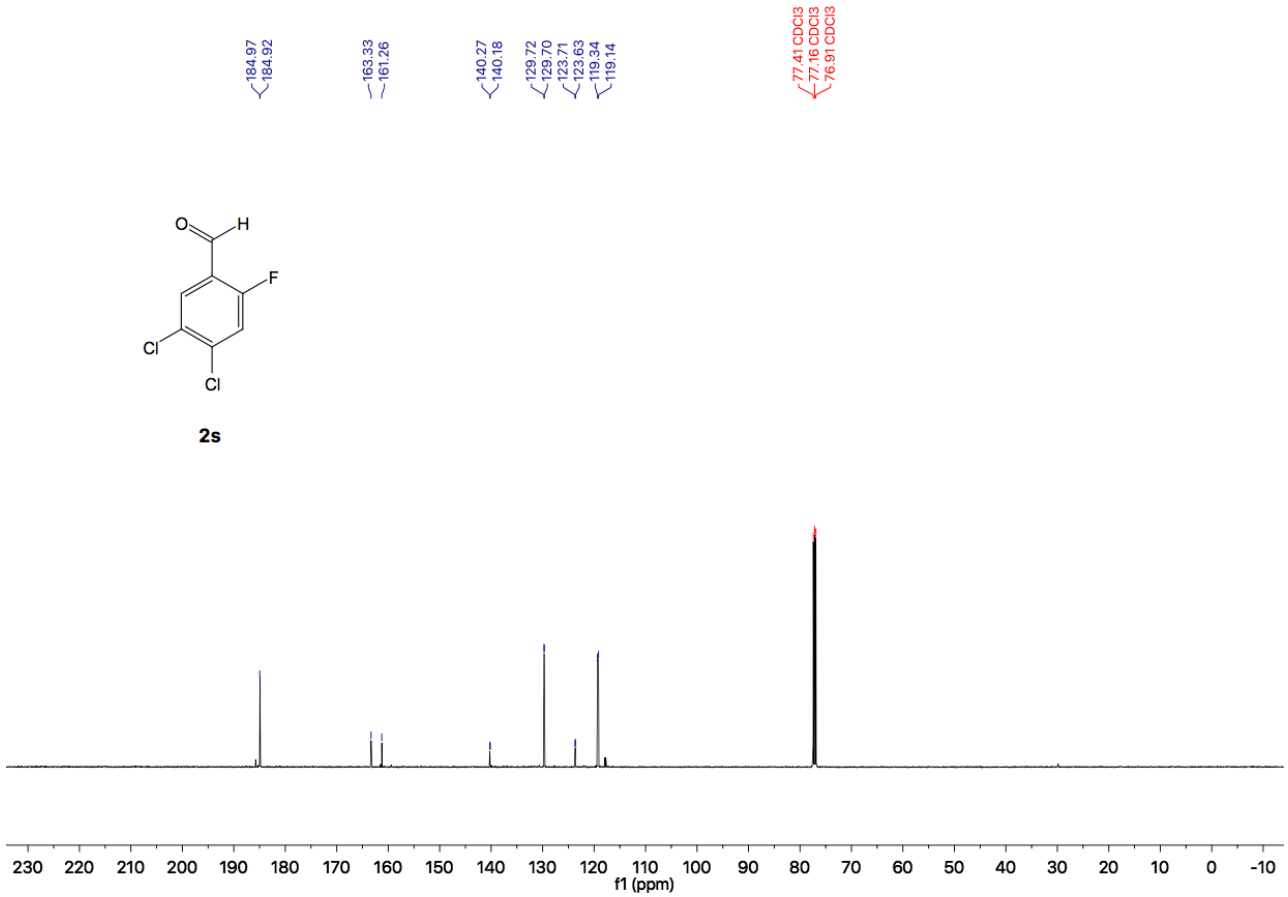
2r

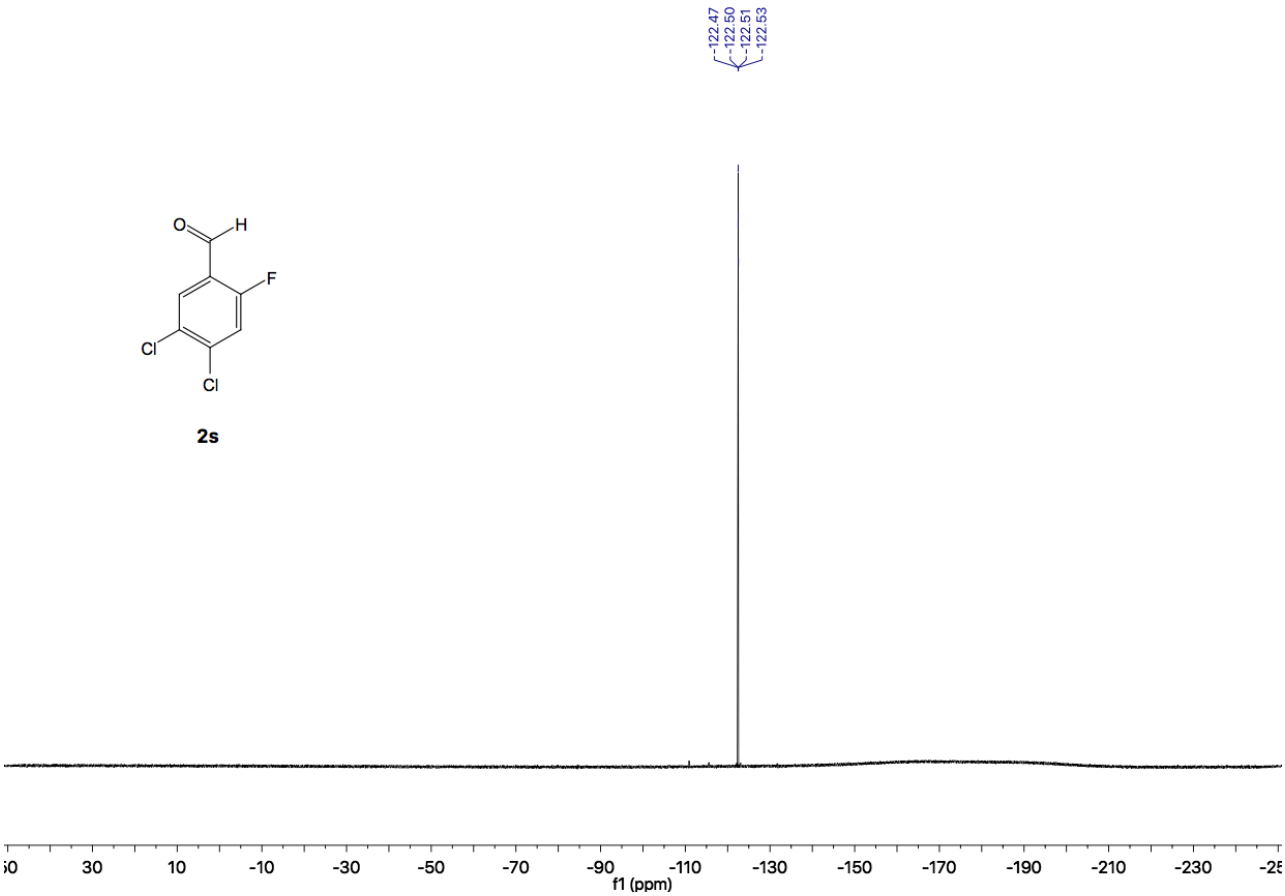
10.43
10.43
7.66
7.66
7.65
7.61
7.60
7.59
7.58
7.26 CDCl3
4.06
1.00
0.93
0.96
3.21
f1 (ppm)

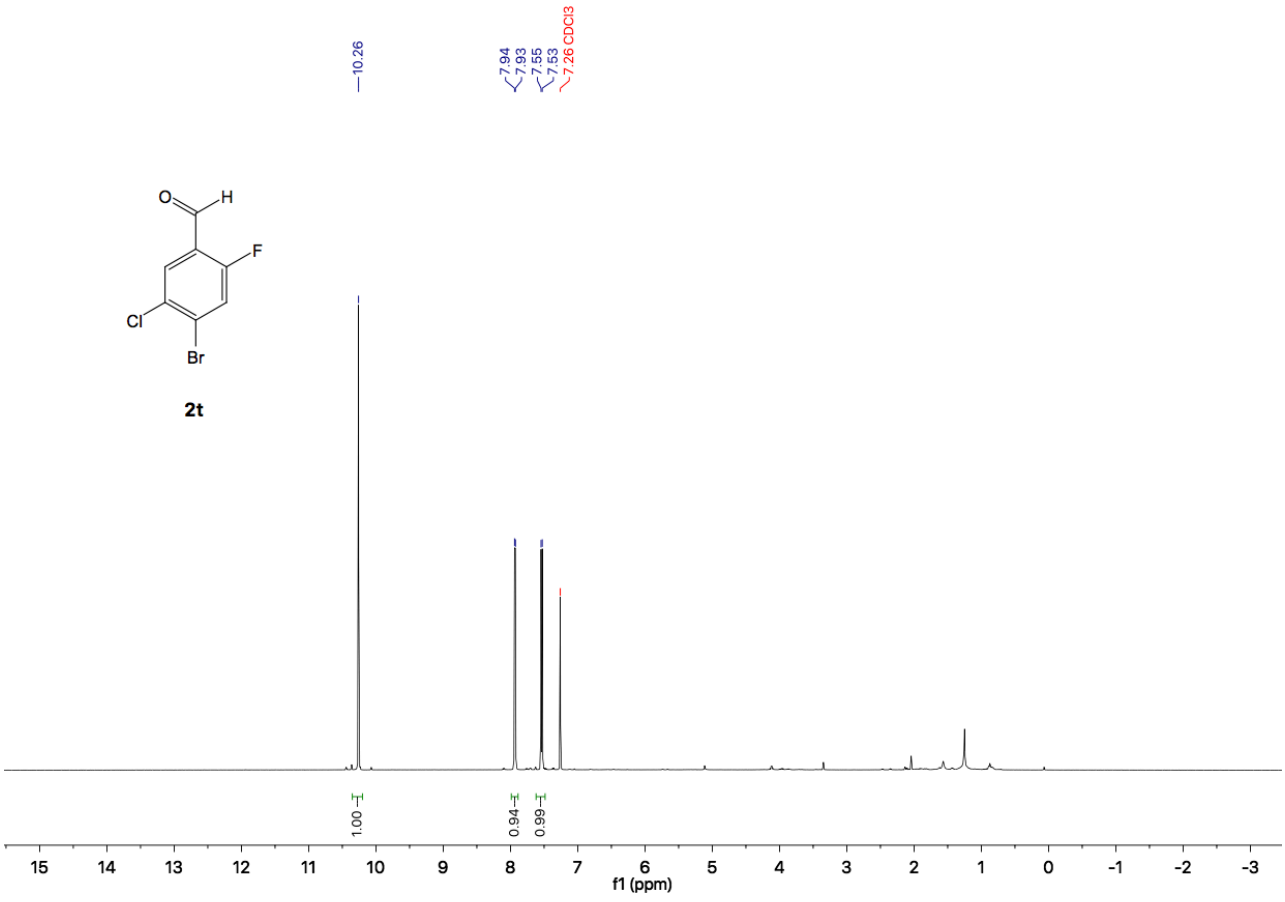

185.97
185.95
163.85
162.41
162.36
161.74
151.80
151.70
117.99
117.91
105.02
104.81
102.94
102.91
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
57.27
O
H
H3C
O
F
O
N+
O-
2r
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

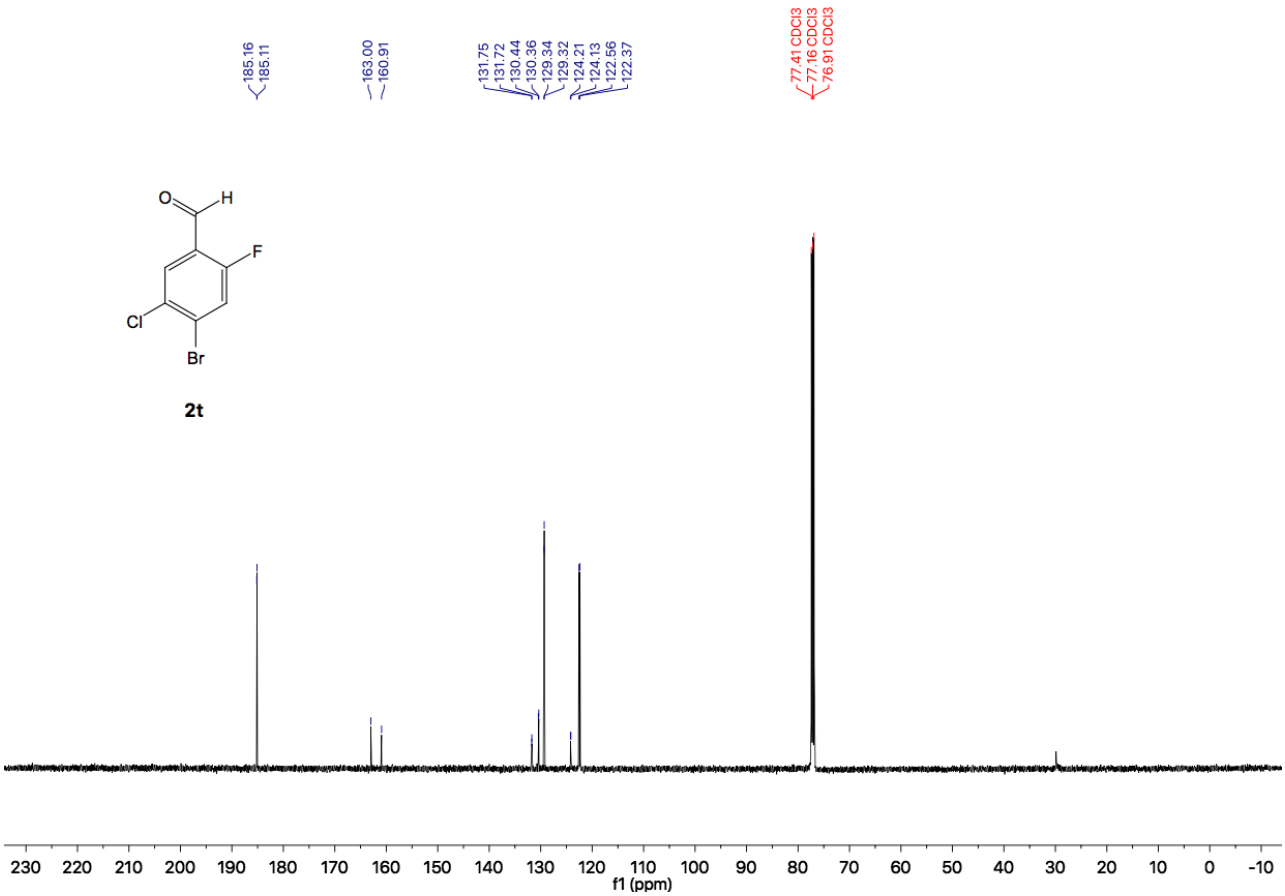

-109.83
-109.86
O
H
H3C
O
F
O
N+
O-
2r
30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

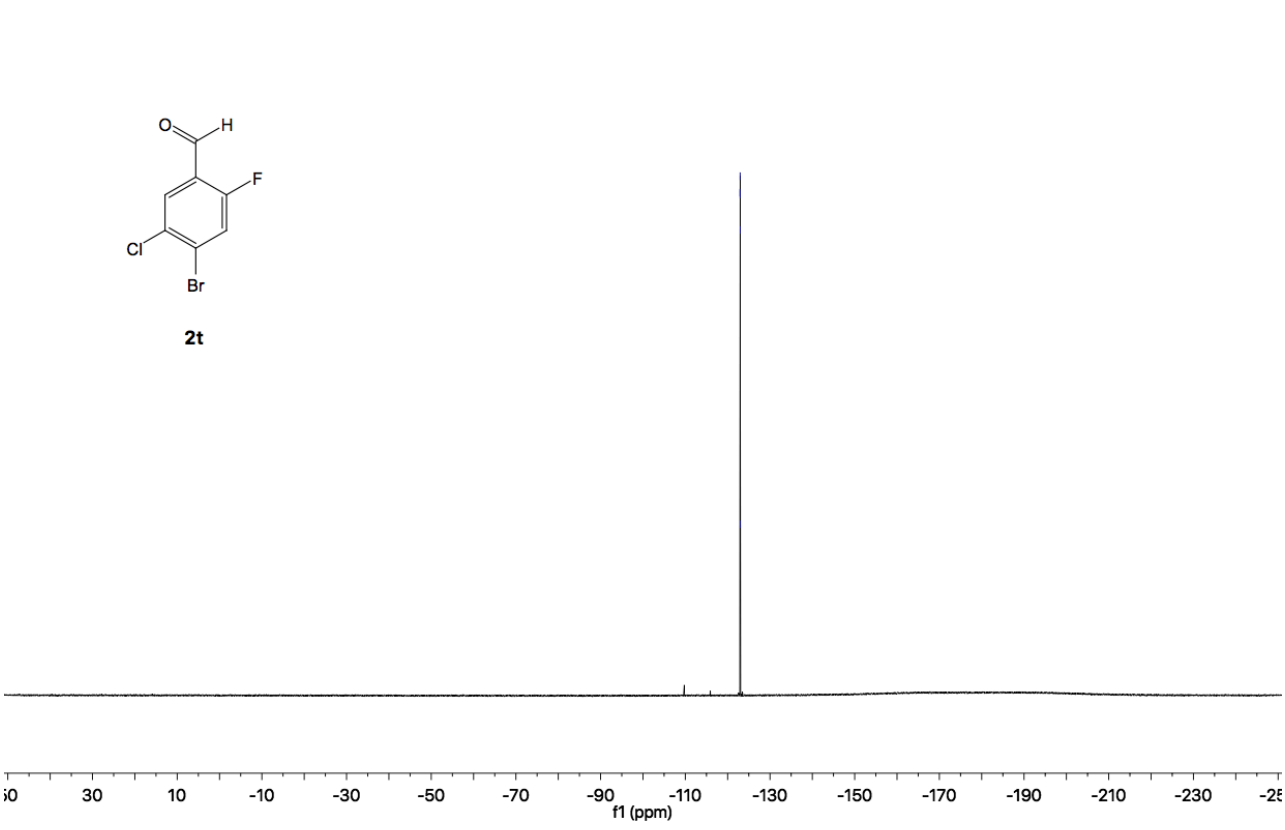

10.26
7.96
7.95
7.37
7.36
7.36
7.26 CDCl3
O
H
F
Cl
Cl
2s
1.00
1.04
1.00
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

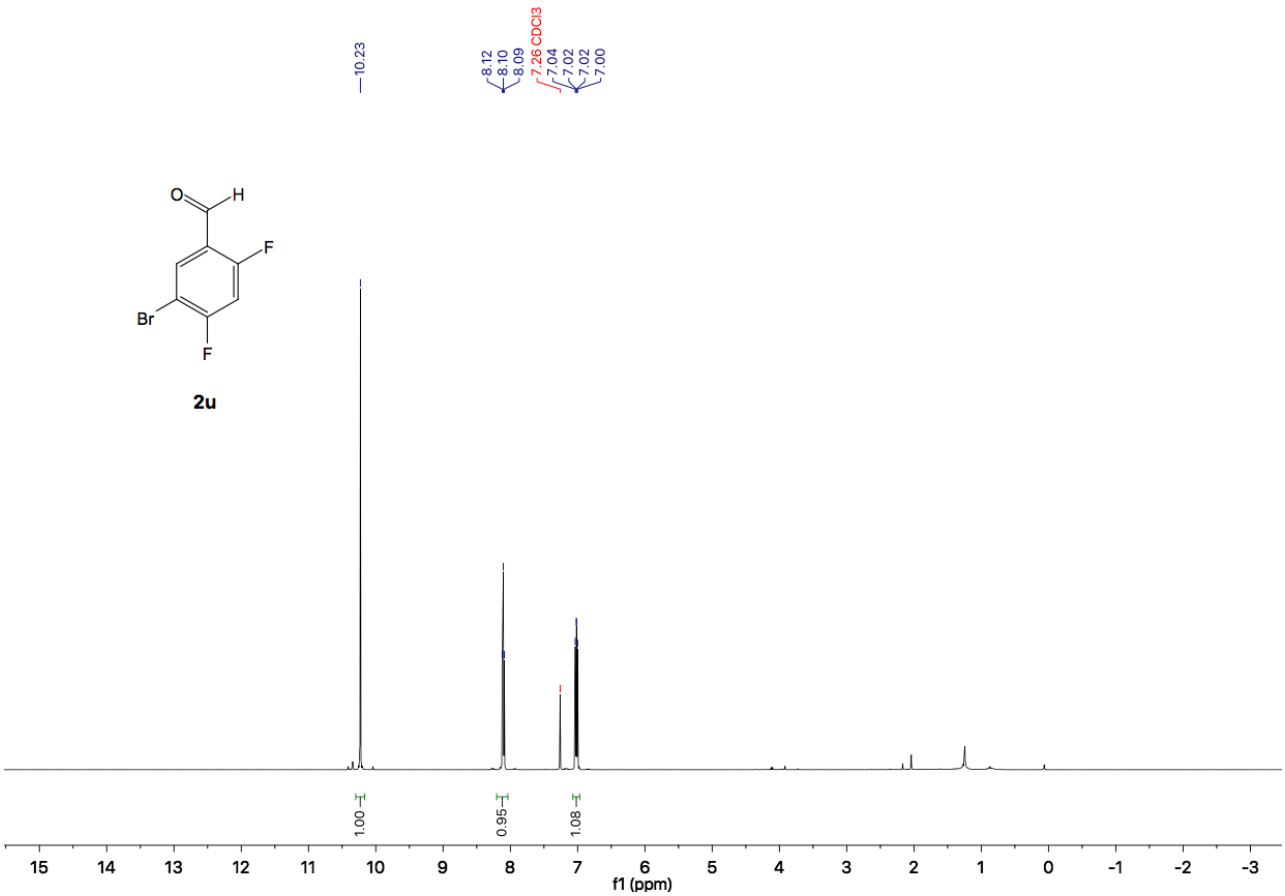

184.97
184.92
163.33
161.26
140.27
140.18
129.72
129.70
123.71
123.63
119.34
119.14
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
O
H
F
Cl
Cl
2s
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

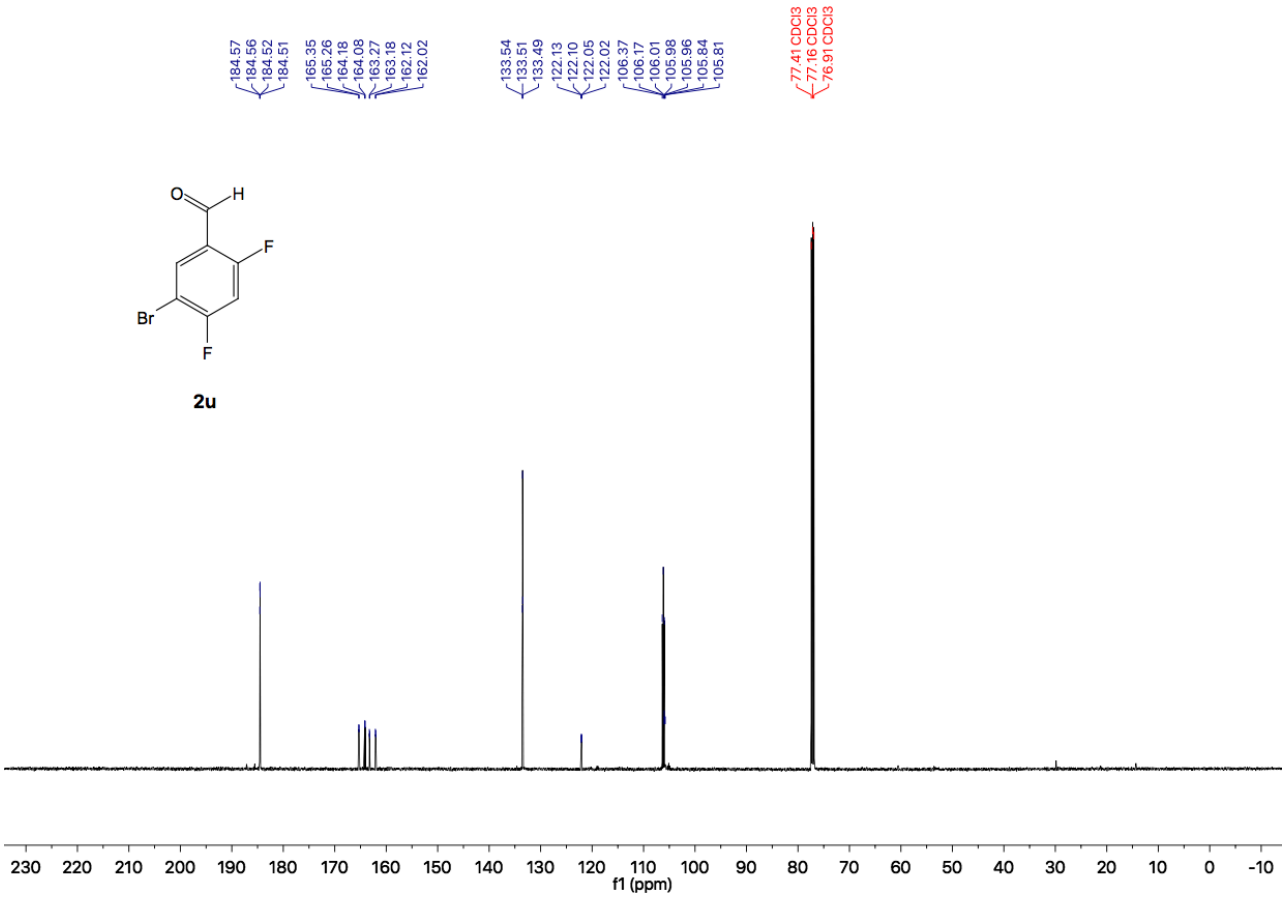

122.47
122.50
122.51
122.53
O
H
F
Cl
Cl
2s
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

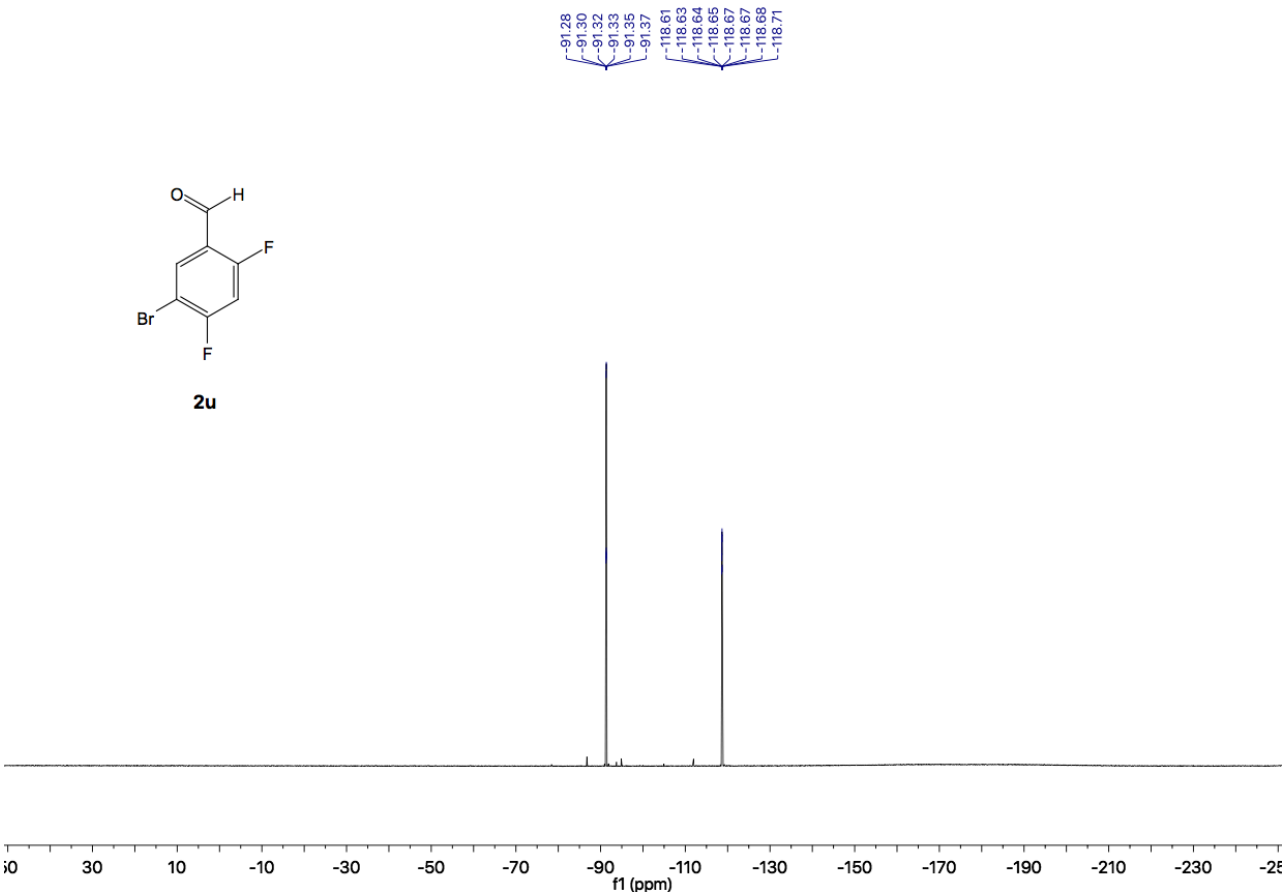

10.26
7.94
7.93
7.55
7.53
7.26 CDCl3
O
H
F
Cl
Br
2t
1.00
0.94
0.99
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

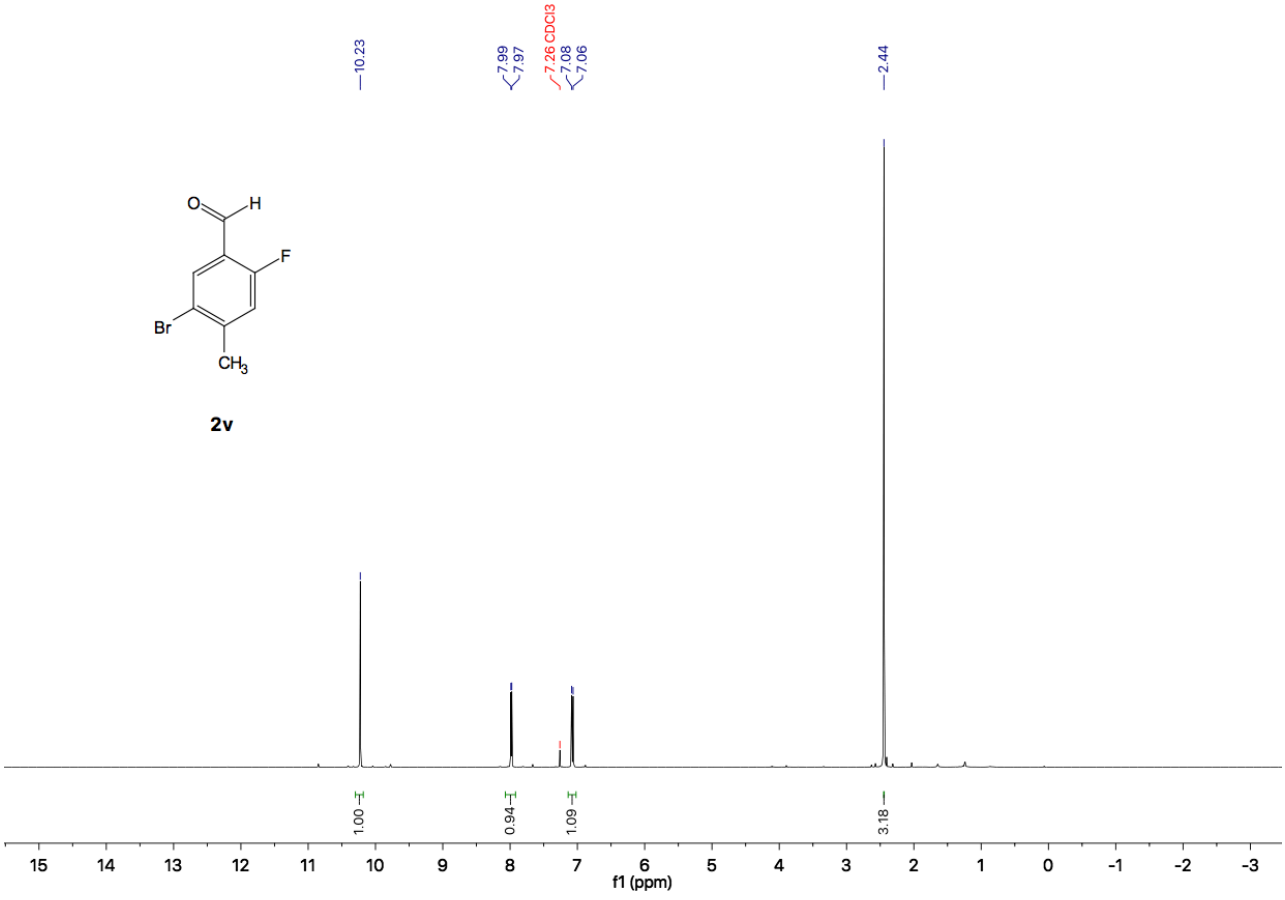

185.16
185.11
163.00
160.91
131.75
131.72
130.44
130.36
129.34
129.32
124.21
124.13
122.56
122.37
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
O
H
F
Cl
Br
2t
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

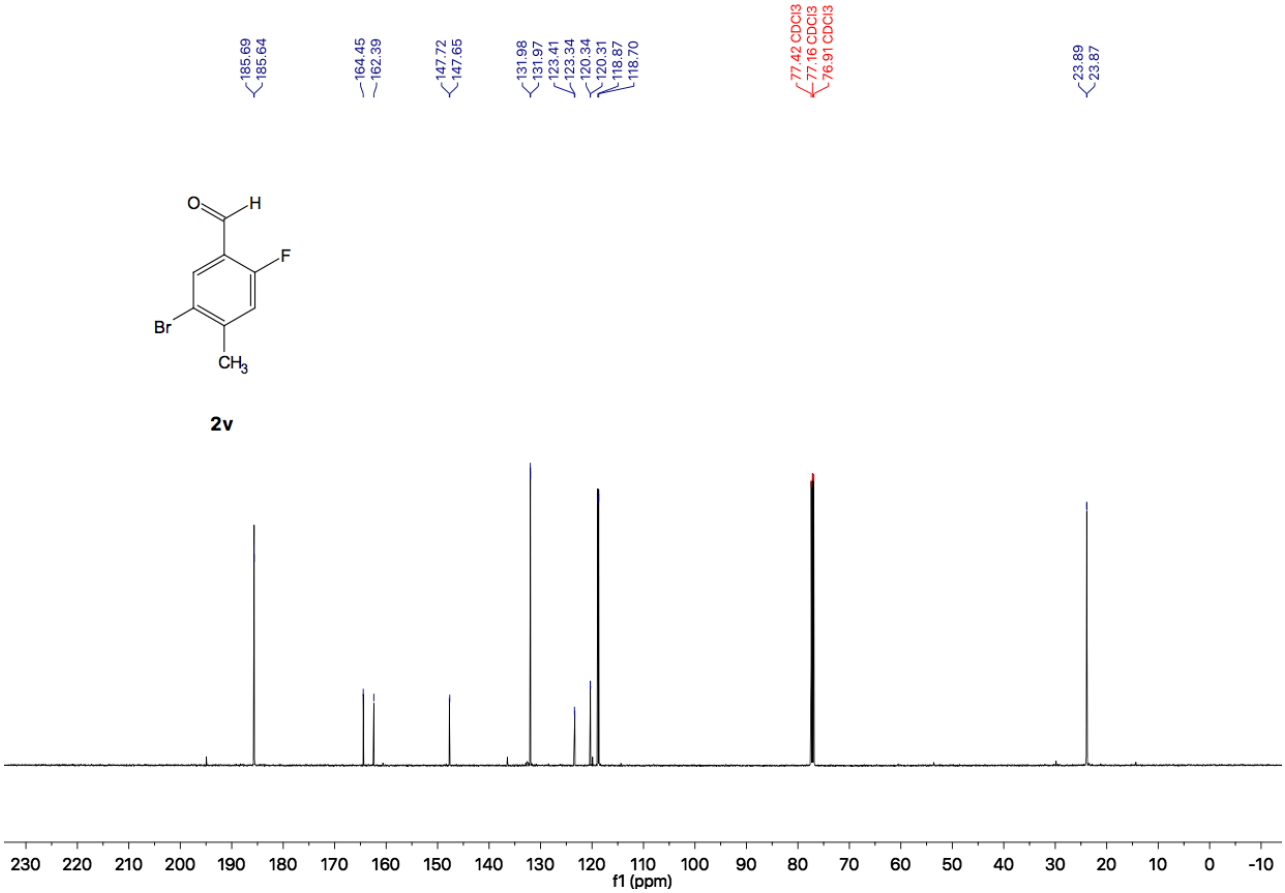

-122.93
-122.95
-122.96
-122.98
-122.99
O
H
F
Cl
Br
2t
30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

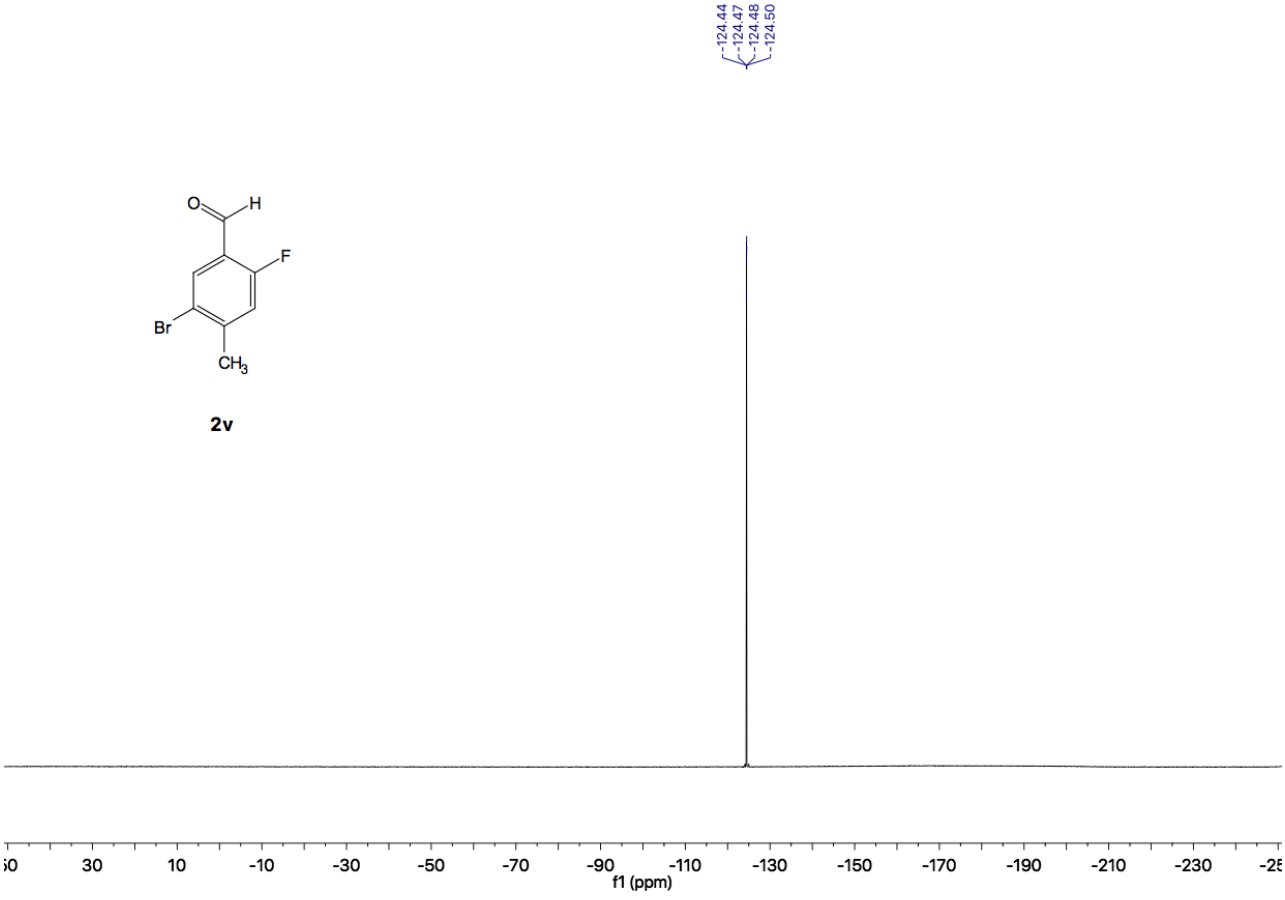

10.23
8.12
8.10
8.09
7.26 CDCl3
7.04
7.02
7.02
7.00
O
H
F
Br
F
2u
1.00
0.95
1.08
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

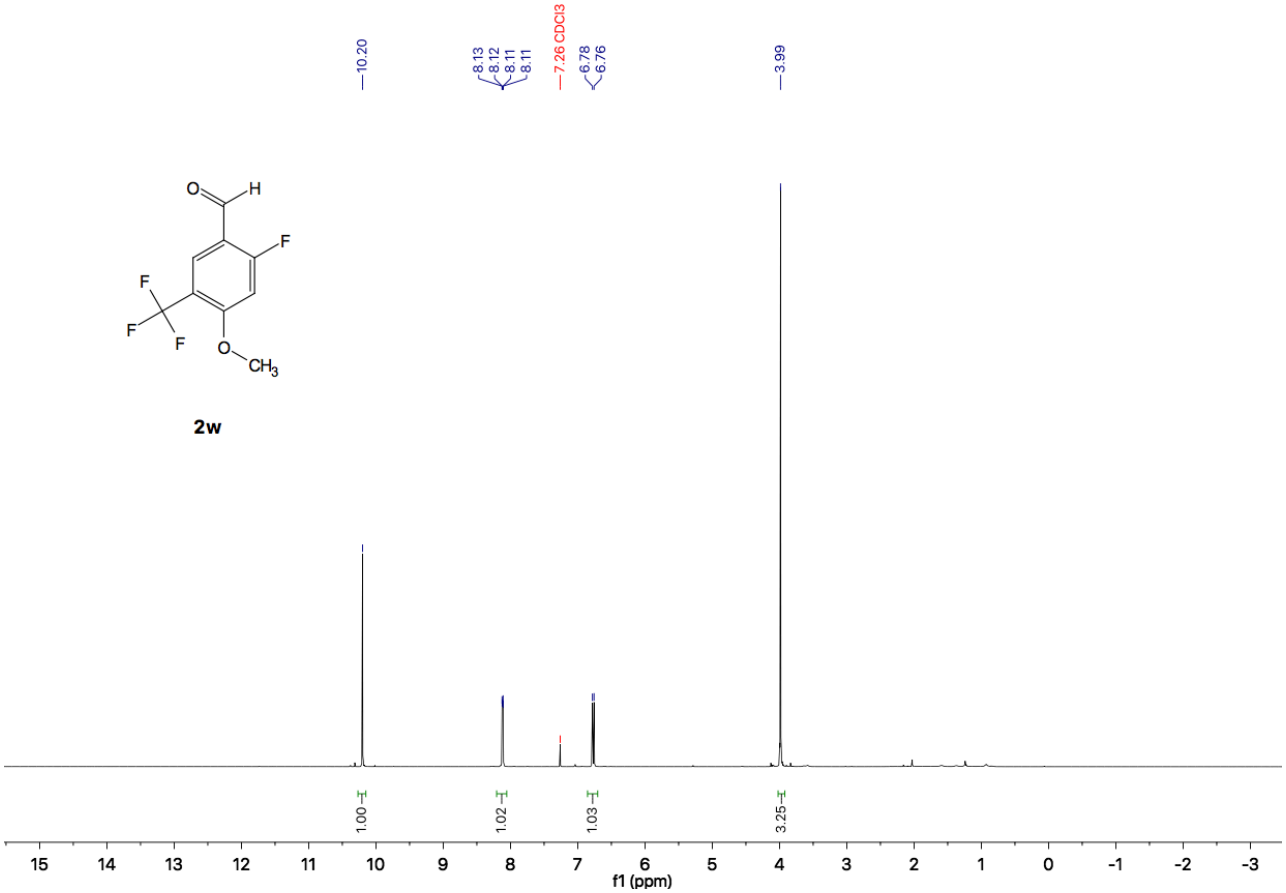

184.57
184.56
184.52
184.51
165.35
165.26
164.18
164.08
163.27
163.18
162.12
162.02
133.54
133.51
133.49
122.13
122.10
122.05
122.02
106.37
106.17
106.01
105.98
105.96
105.84
105.81
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
O
H
F
Br
F
2u
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

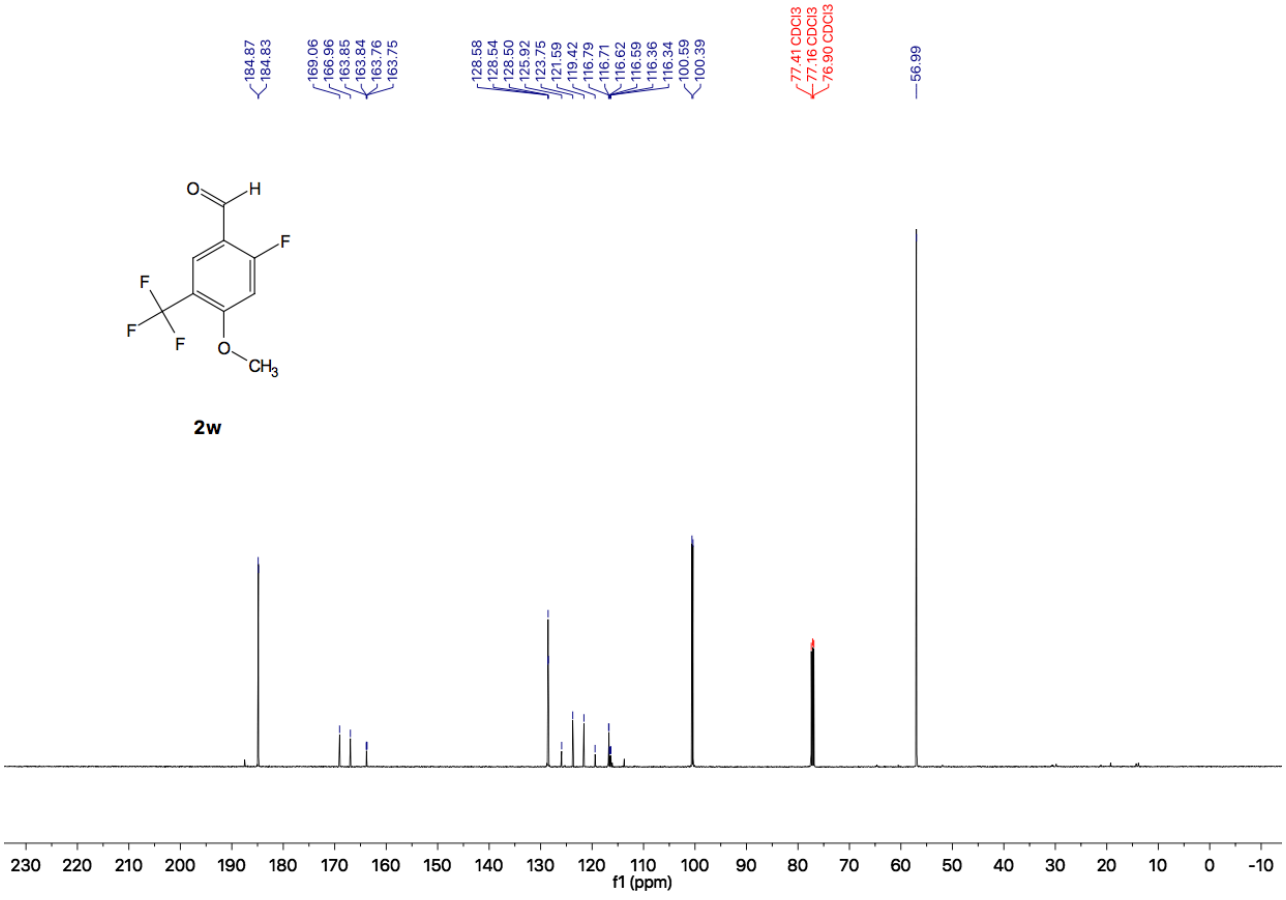

-91.28
-91.30
-91.32
-91.33
-91.35
-91.37
-118.61
-118.63
-118.64
-118.65
-118.67
-118.67
-118.67
-118.68
-118.71
O
H
F
Br
F
2u
f1 (ppm)


10.23
7.99
7.97
7.26 CDCl3
7.08
7.06
2.44
O
H
F
Br
CH3
2v
1.00
0.94
1.09
3.18
f1 (ppm)


185.69
185.64
164.45
162.39
147.72
147.65
131.98
131.97
123.41
123.34
120.34
120.31
118.87
118.70
77.42 CDCl3
77.16 CDCl3
76.91 CDCl3
23.89
23.87
O
H
F
Br
CH3
2v
f1 (ppm)


-124.44
-124.47
-124.48
-124.50
O
H
F
Br
CH3
2v
f1 (ppm)


10.20
8.13
8.12
8.11
8.11
7.26 CDCl3
6.78
6.76
3.99
O
H
F
F
F
F
O
CH3
2w
1.00
1.02
1.03
3.25
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)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163.75
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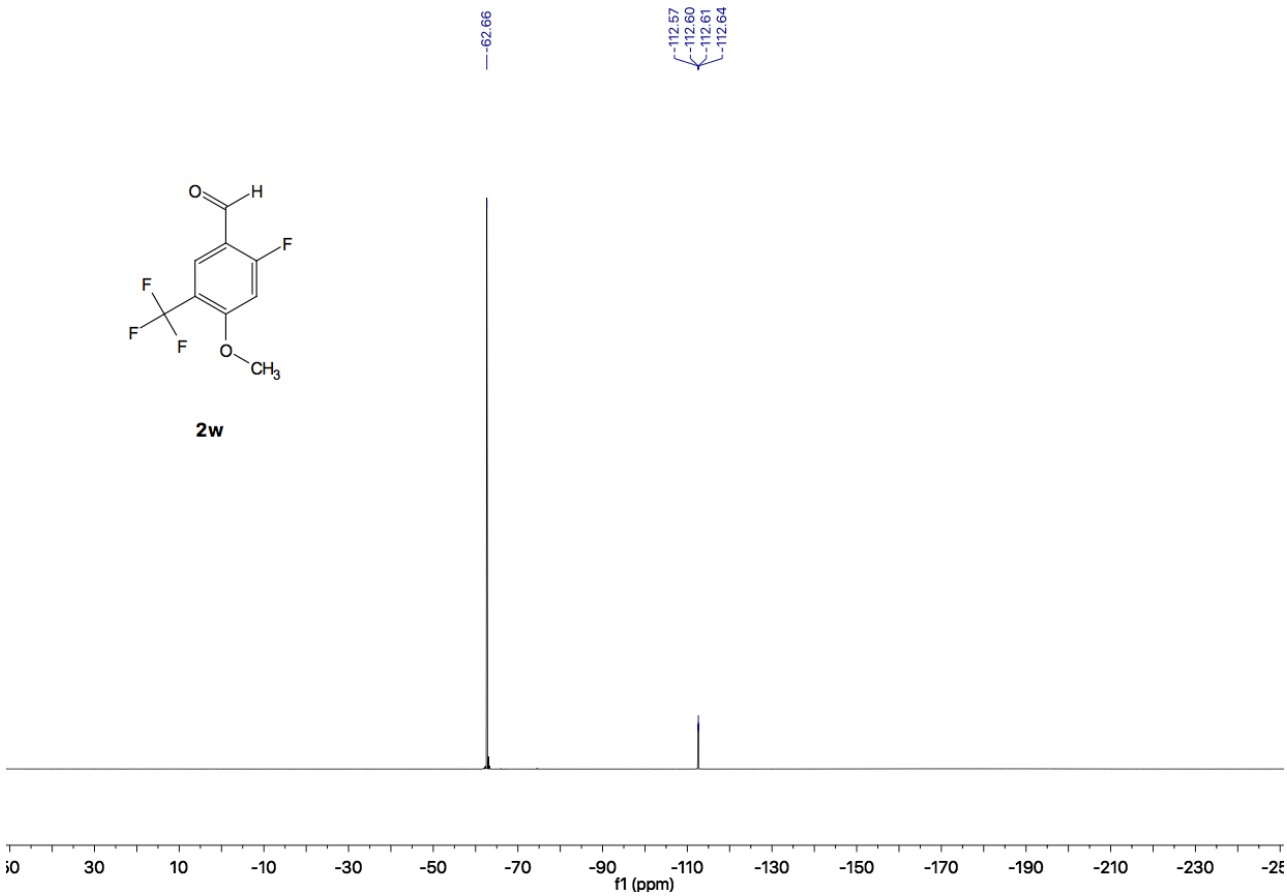
121.59
119.42
116.79
116.71
116.62
116.59
116.36
116.34
100.59
100.39
77.41 CDCl3
77.16 CDCl3
76.90 CDCl3
56.99
O
H
F
F
F
F
O
CH3
2w
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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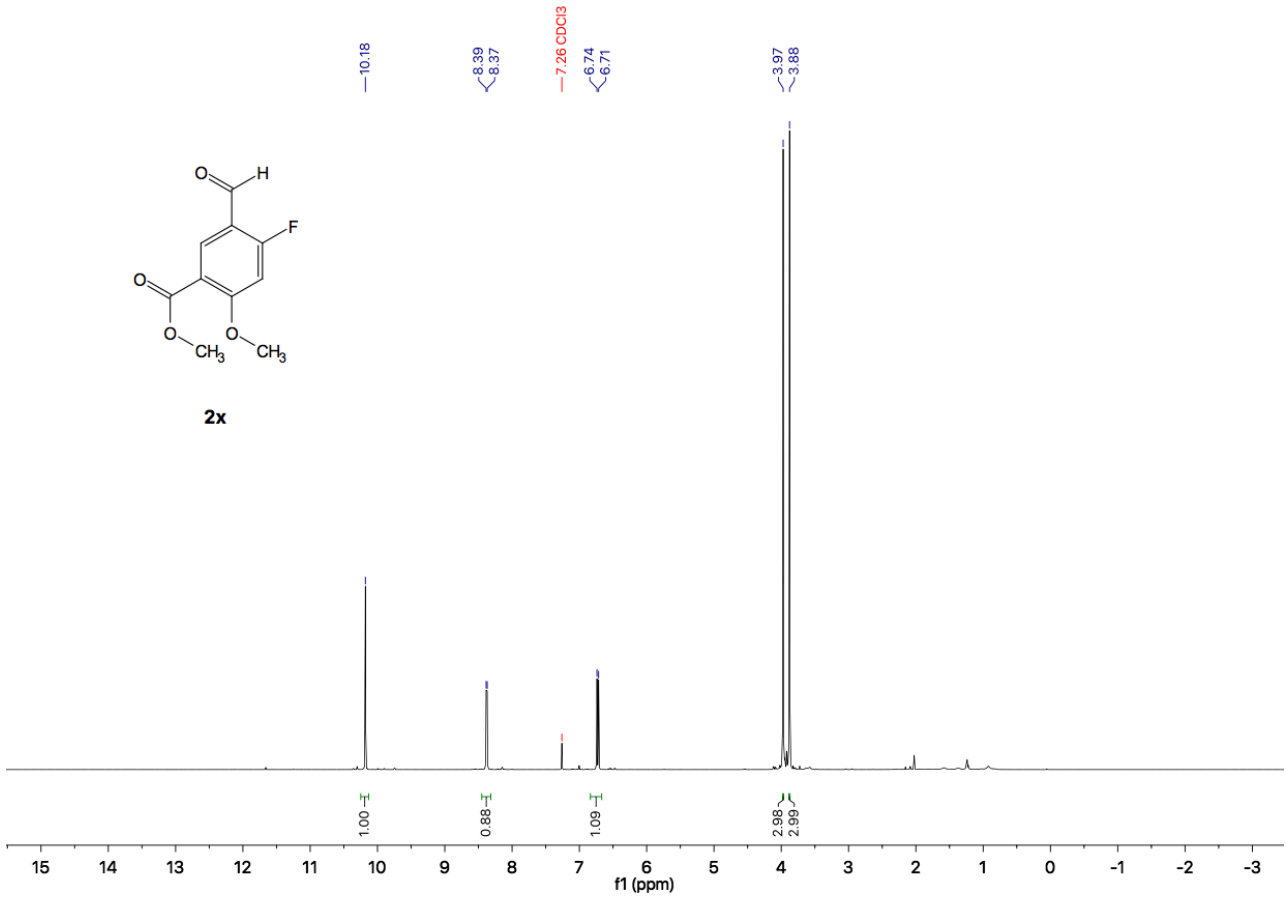
-112.61
-112.64
O
H
F
F
F
F
O
CH3
f1 (ppm)

2w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8.39
8.37
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6.74
6.71
3.97
3.88
O
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F
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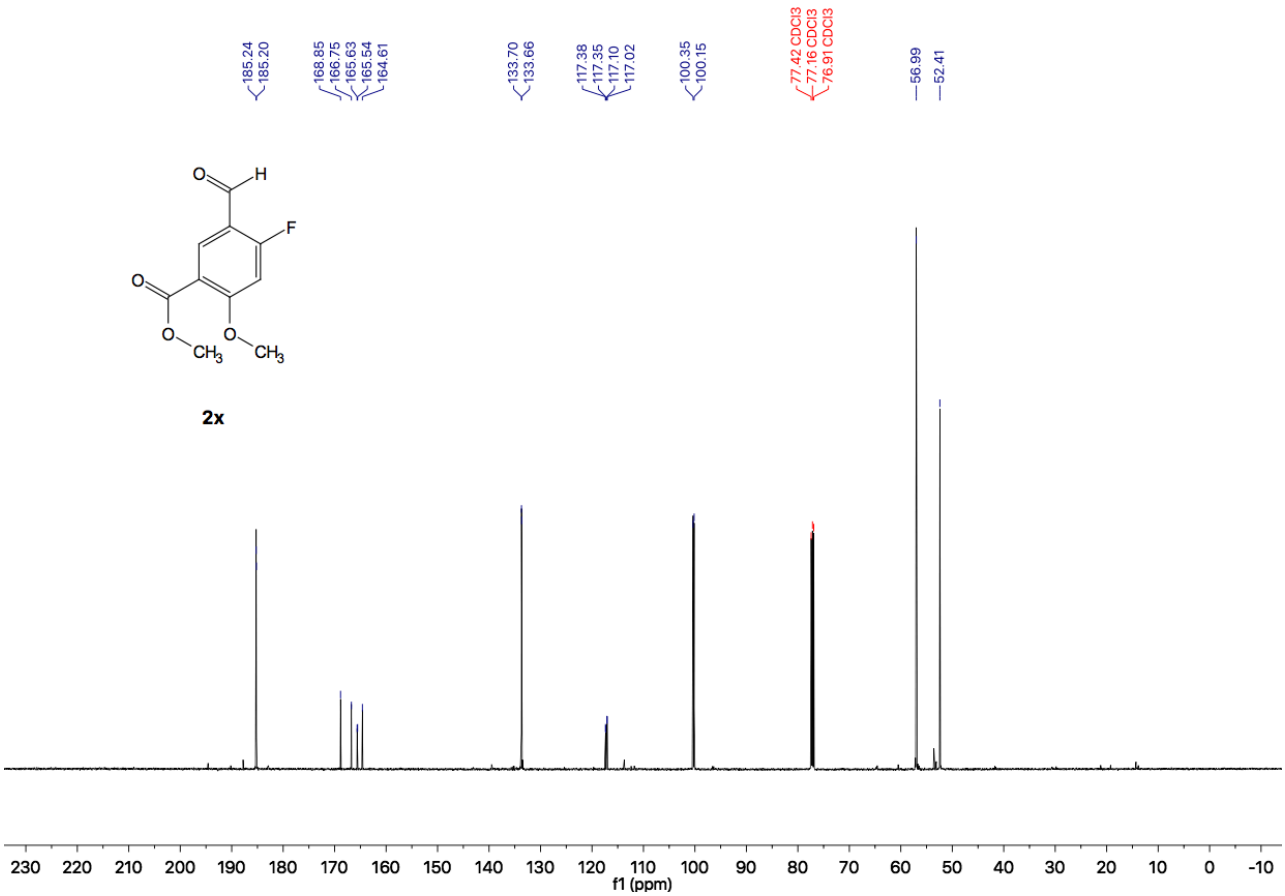
O
CH3
O
CH3
1.00
0.88
1.09
2.98
2.99
f1 (ppm)

2x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117.02
100.35
100.15
77.42 CDCl3
77.16 CDCl3
76.91 CDCl3
56.99
52.41
O
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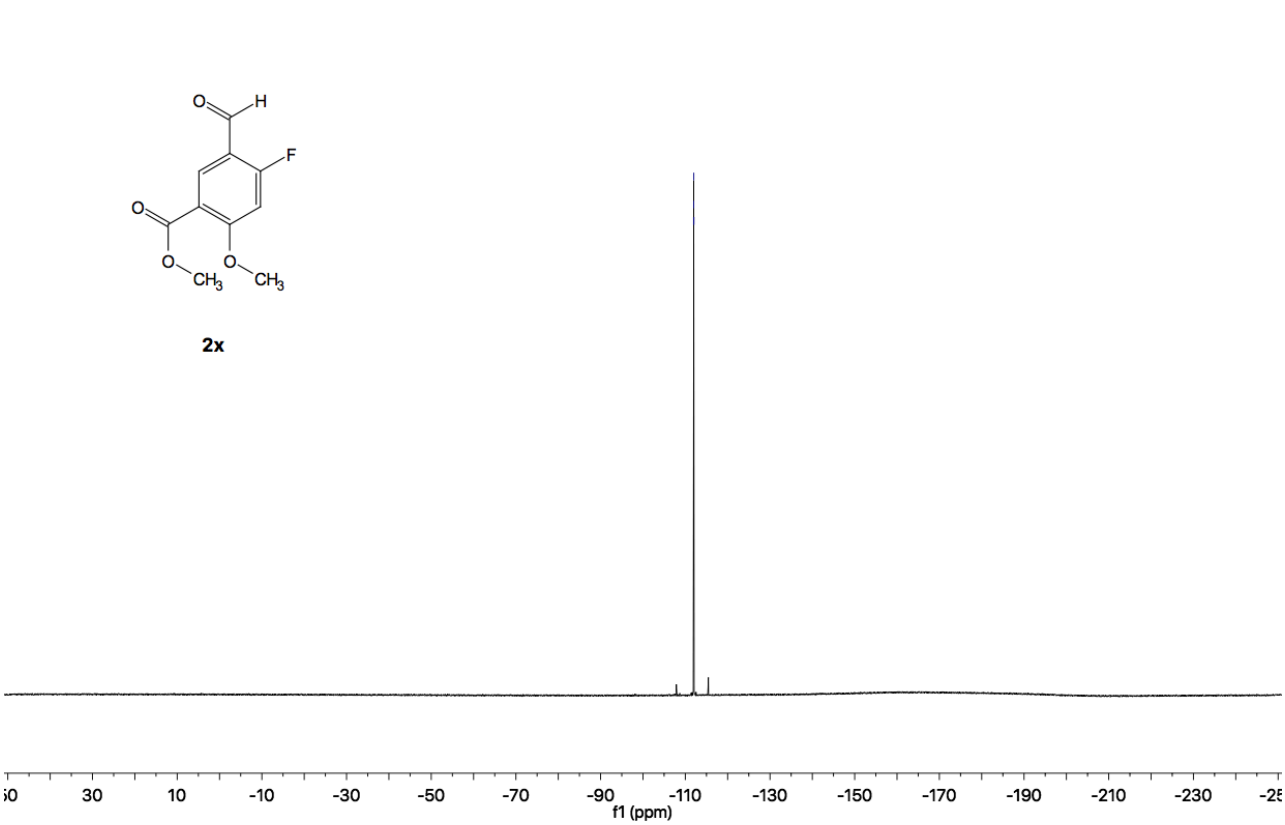
F
O
O
CH3
O
CH3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

2x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111.99
112.01
112.04
O
H
F
O
O
CH3
O
CH3
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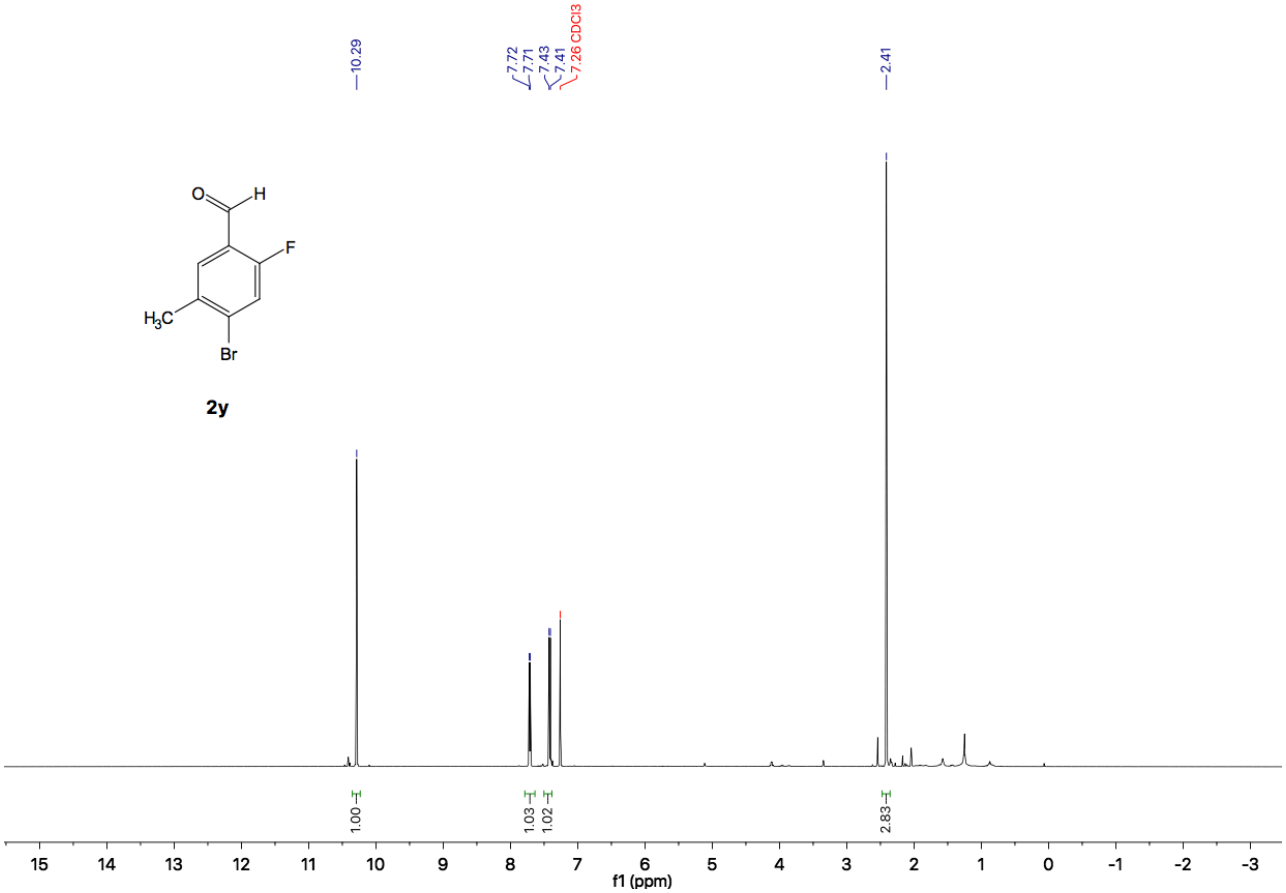
f1 (ppm)

2x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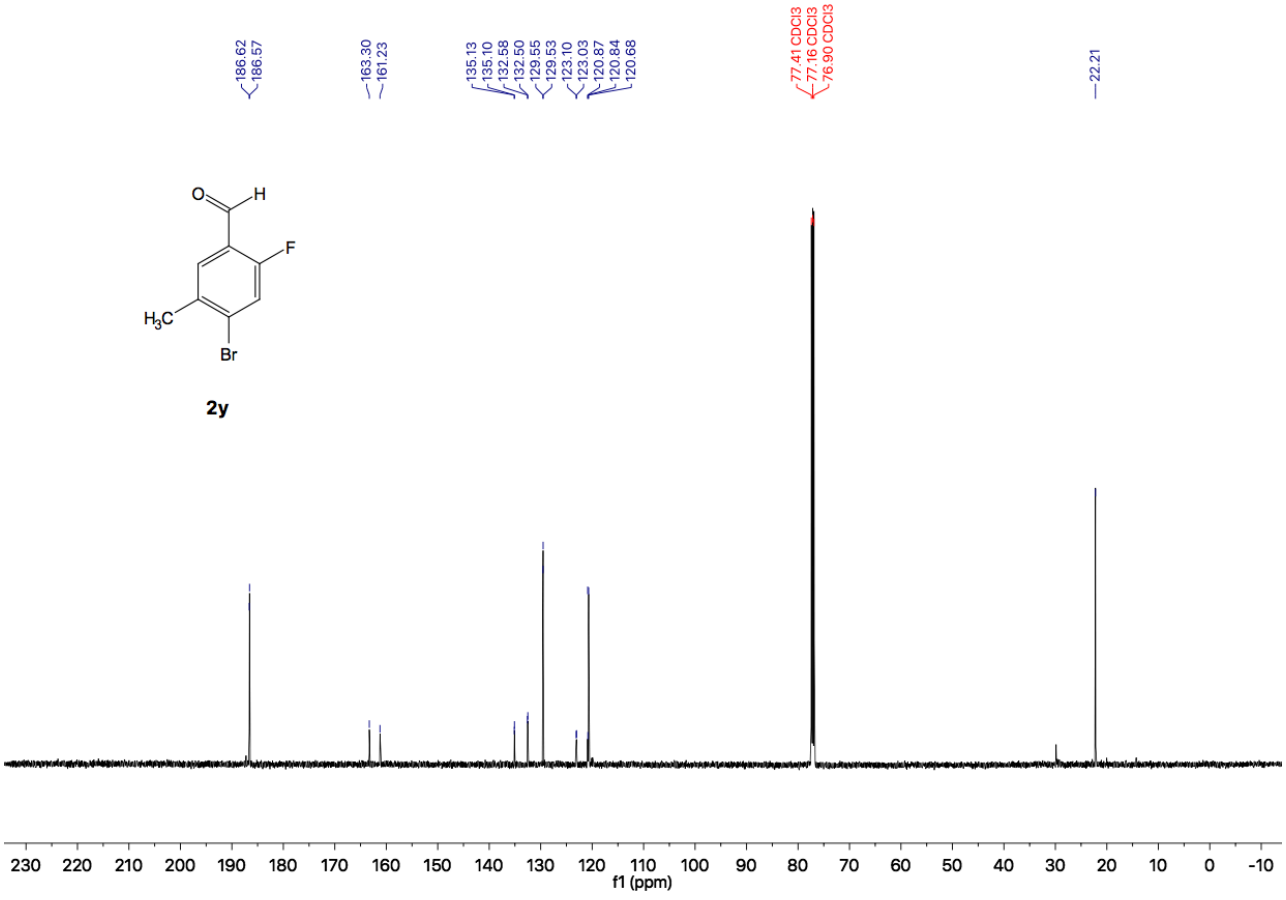
7.71
7.43
7.41
7.26 CDCl3
2.41
O
H
F
H3C
Br
2y
1.00
1.03
1.02
2.83
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)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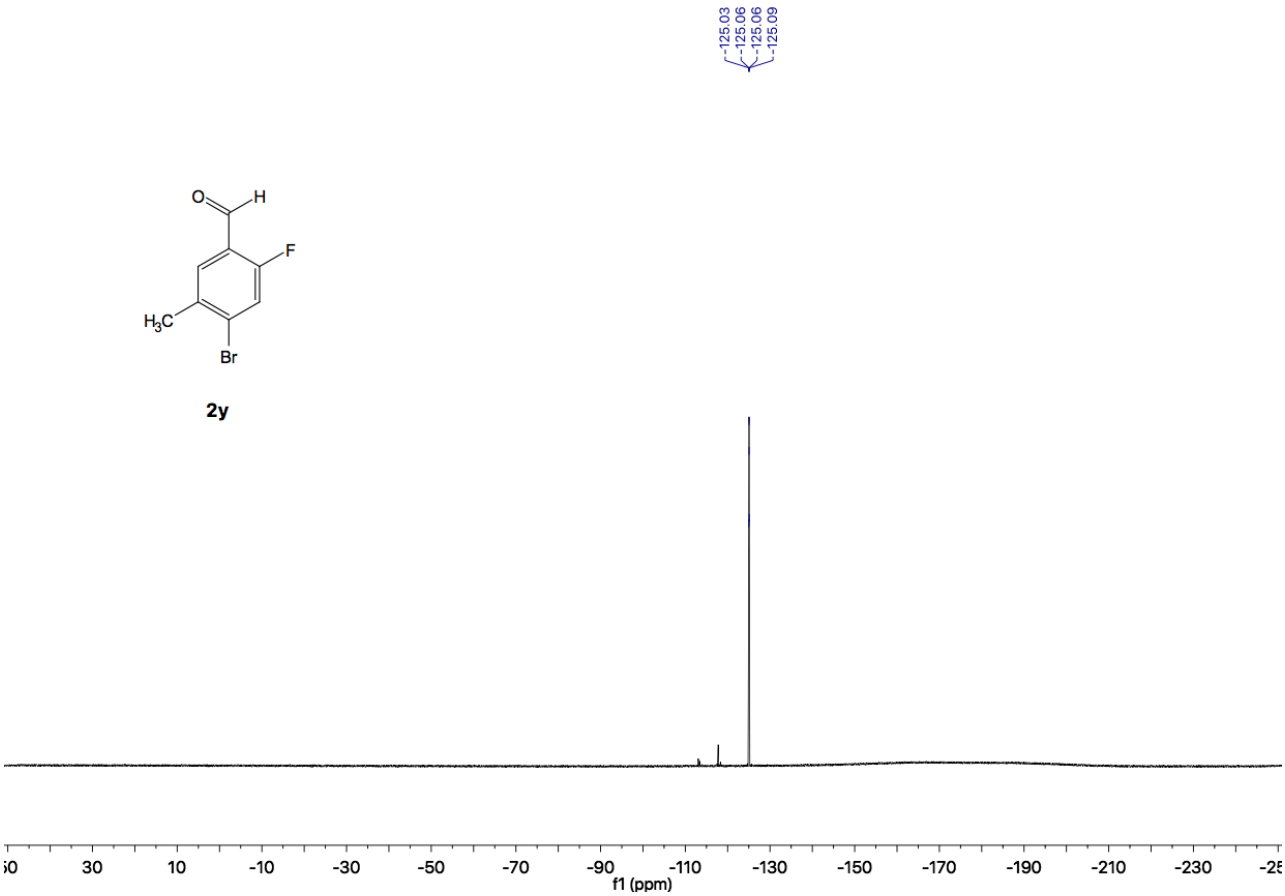
123.10
123.03
120.87
120.84
120.68
77.41 CDCl3
77.16 CDCl3
76.90 CDCl3
22.21
O
H
F
H3C
Br
2y
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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-125.06
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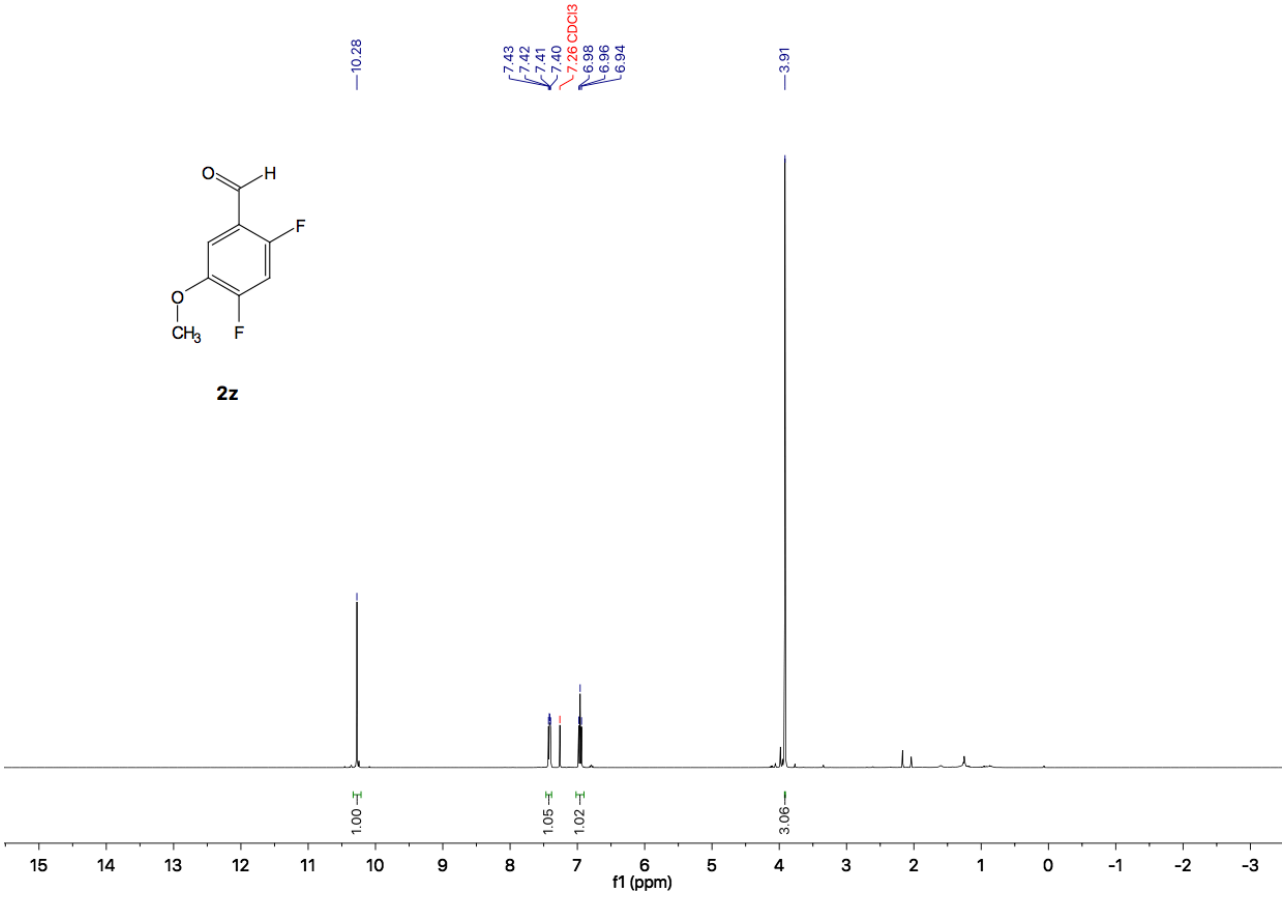
O
H
F
H3C
Br
2y
f1 (ppm)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7.43
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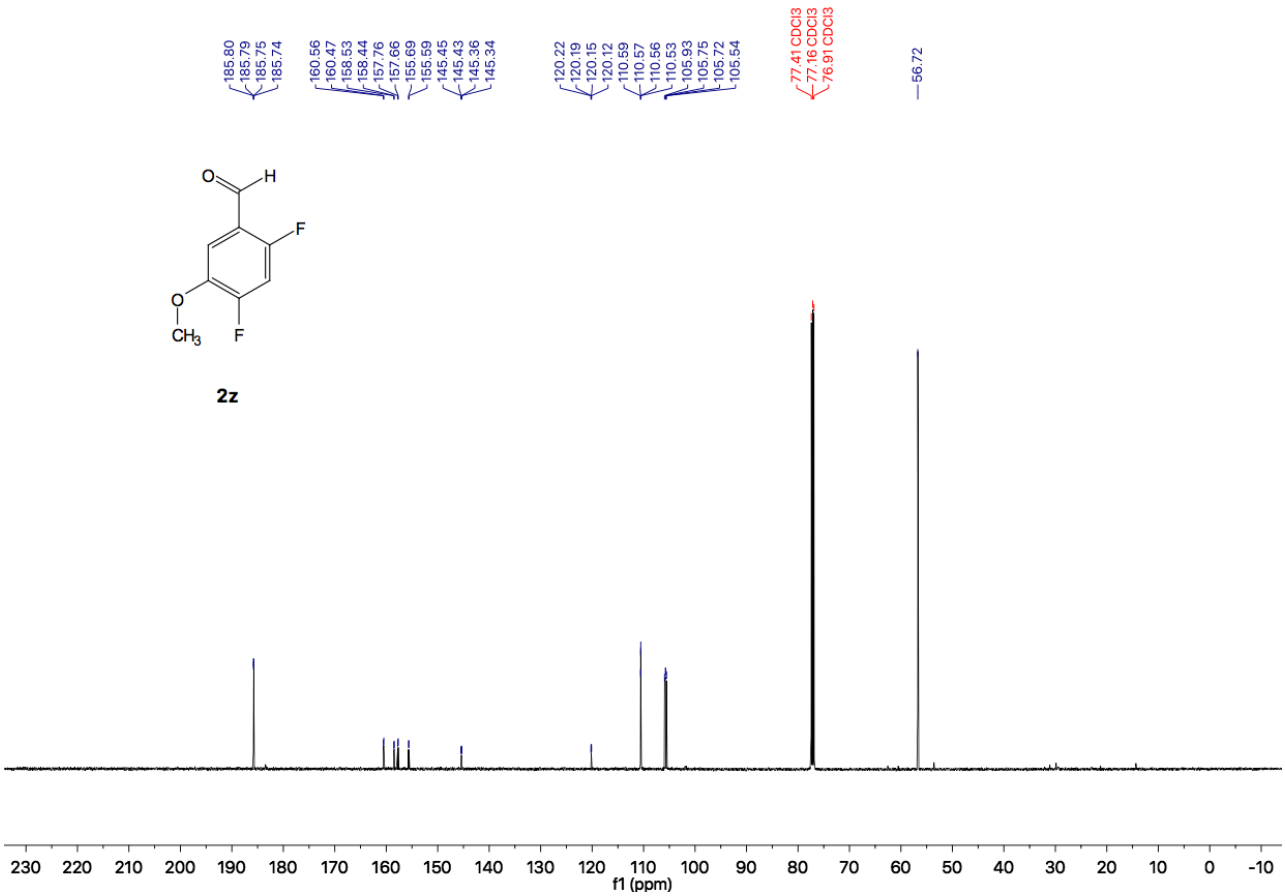
7.40
7.26 CDCl3
6.98
6.96
6.94
3.91
O
H
F
O
CH3
F
2z
1.00
1.05
1.02
3.06
f1 (ppm)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158.44
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157.66
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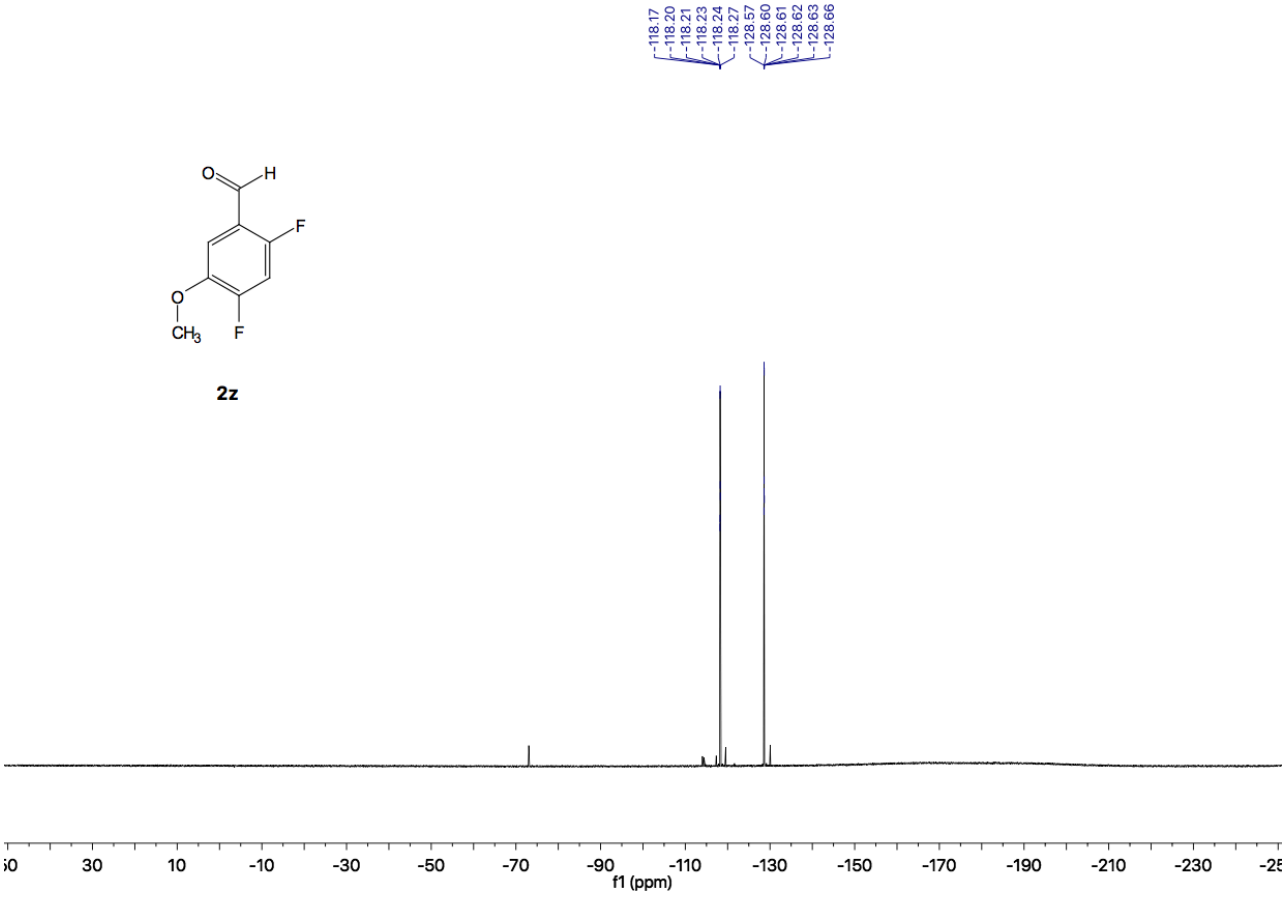
145.45
145.43
145.36
145.34
120.22
120.19
120.15
120.12
110.59
110.57
110.56
110.53
105.93
105.75
105.72
105.54
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
56.72
O
H
F
O
CH3
F
2z
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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-118.20
-118.21
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-128.57
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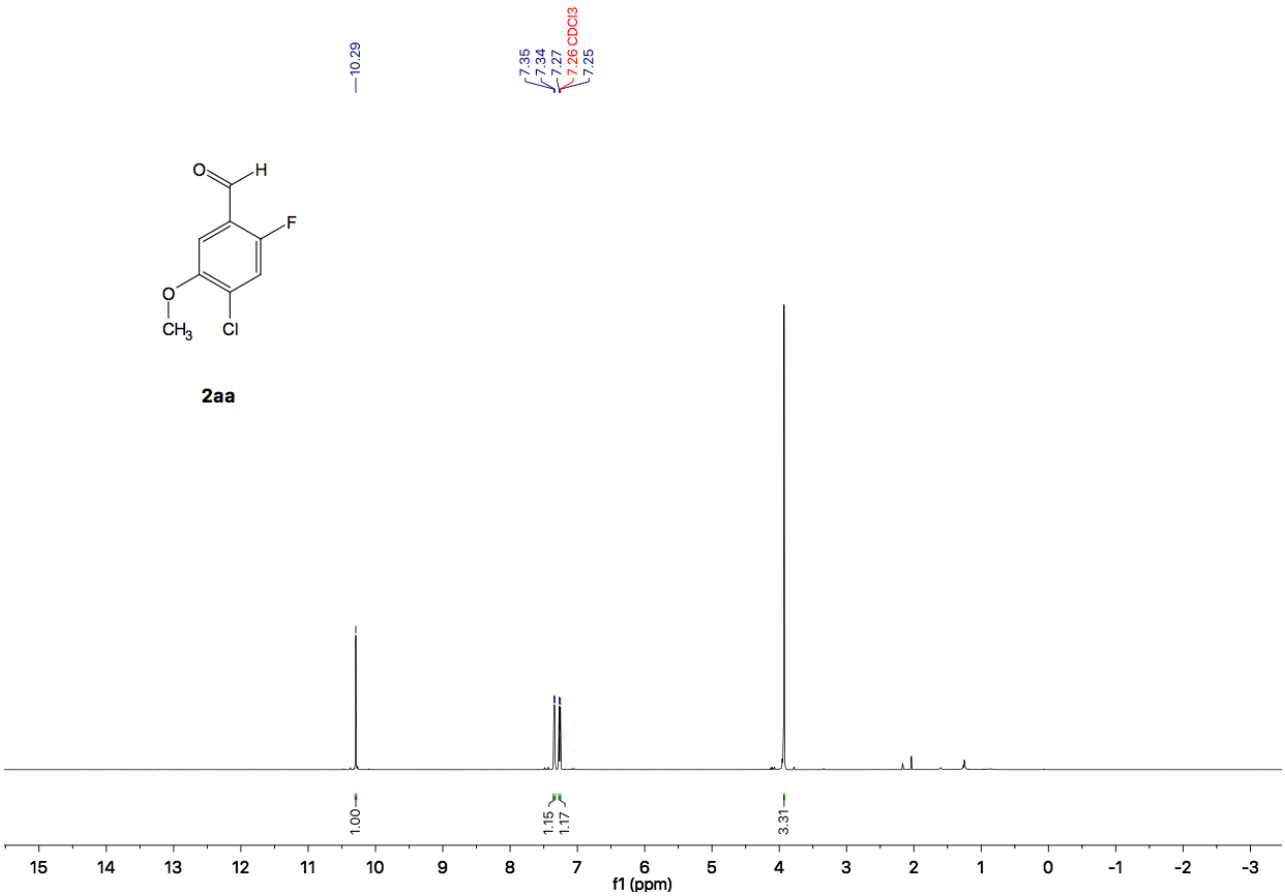
-128.61
-128.62
-128.63
-128.66
O
H
F
O
CH3
F
2z
50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -25
f1 (ppm)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7.26 CDCl3
7.25
O
H
F
O
CH3
Cl
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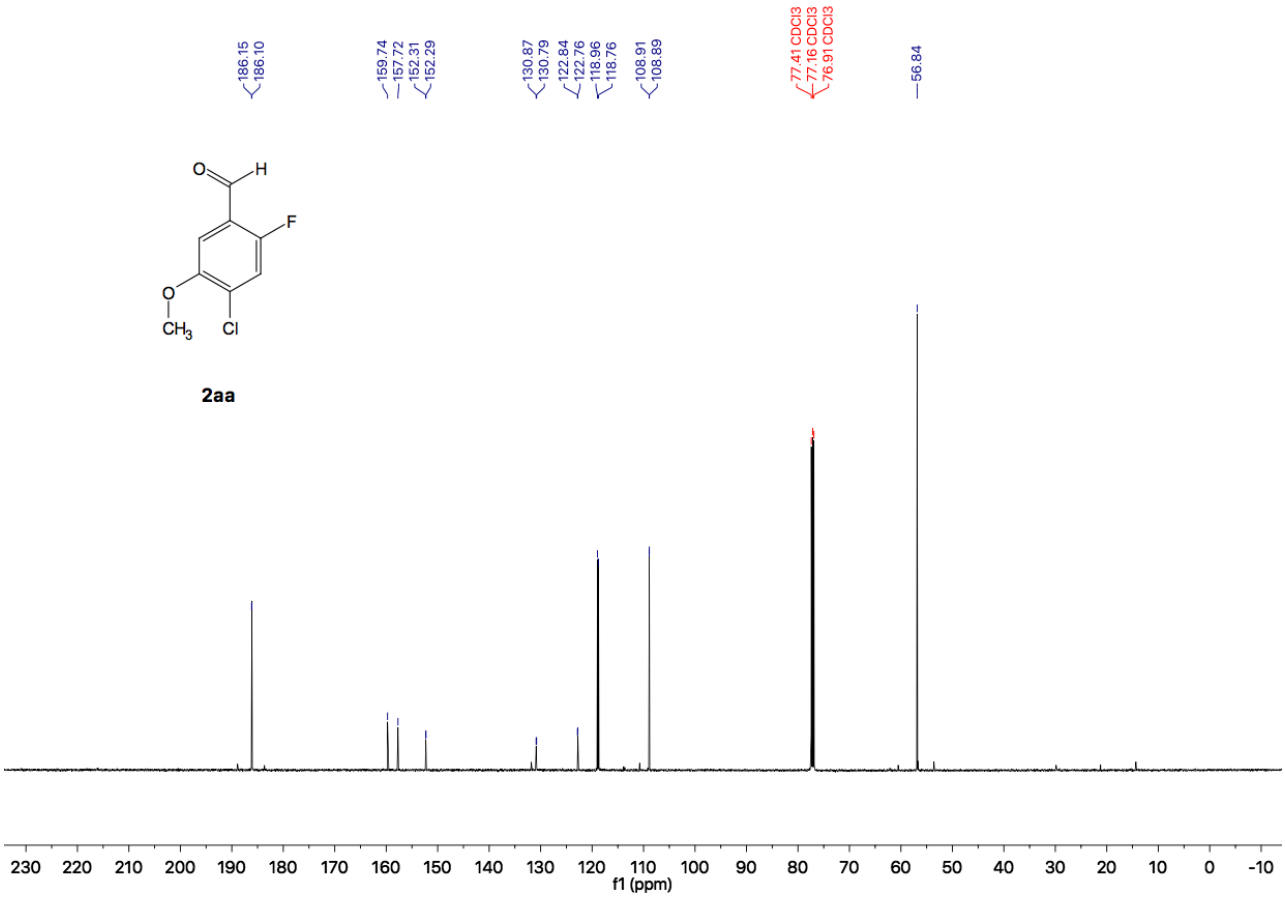
1.15
1.17
3.31
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)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130.87
130.79
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122.76
118.96
118.76
108.91
108.89
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
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F
O
CH3
Cl
2aa
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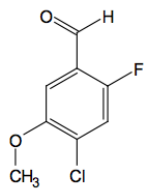
f1 (ppm)


O
H
F
O
CH3
Cl

2aa

-131.19
-131.22
-131.23
-131.25
30
10
-10
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-50
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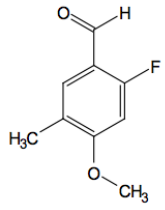
-150
-170
-190
-210
-230
f1 (ppm)


O
H
F
H3C
O
CH3

2bb

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7.63
7.61
7.61
7.26 CDCl3
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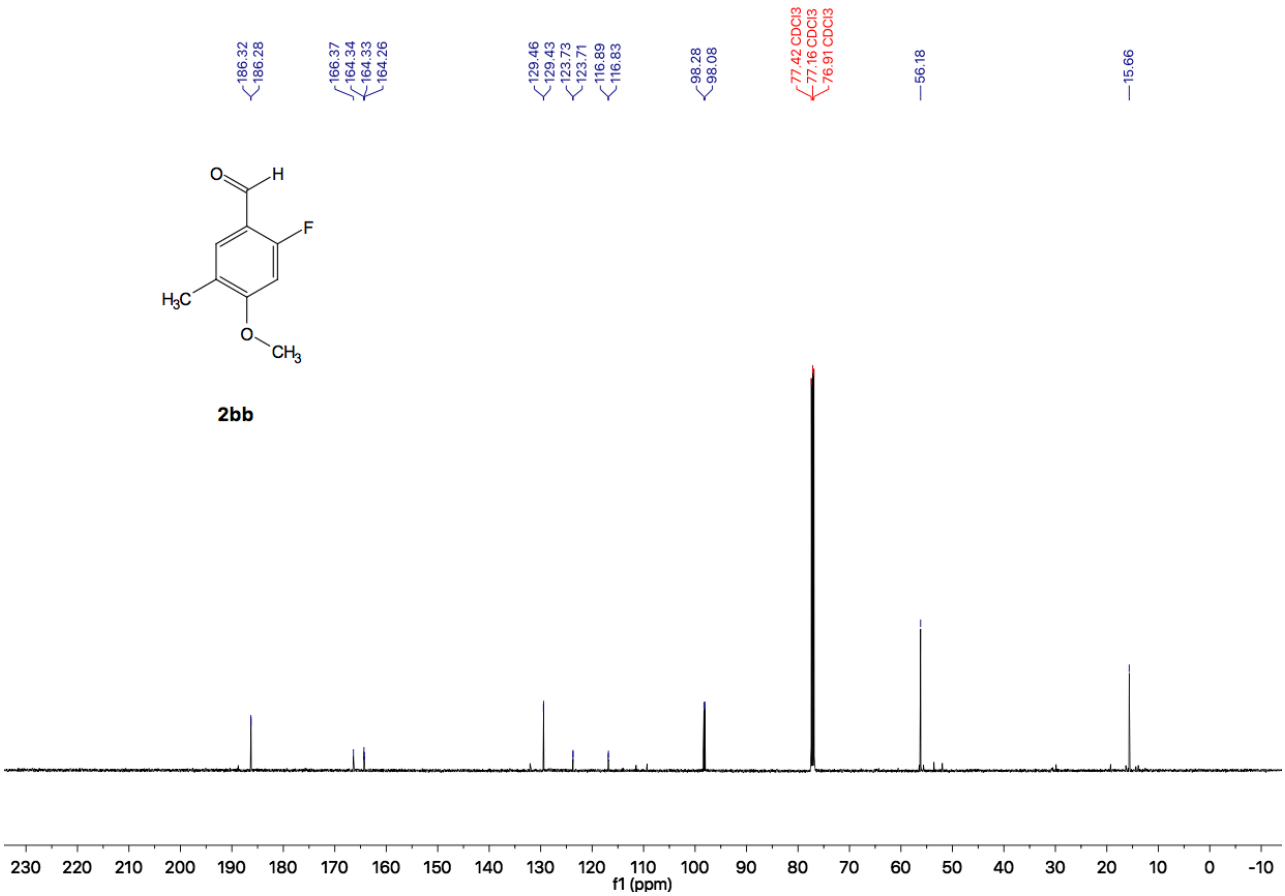
2.17
1.00
1.02
1.05
3.13
3.25
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)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123.71
116.89
116.83
98.28
98.08
77.42 CDCl3
77.16 CDCl3
76.91 CDCl3
56.18
15.66
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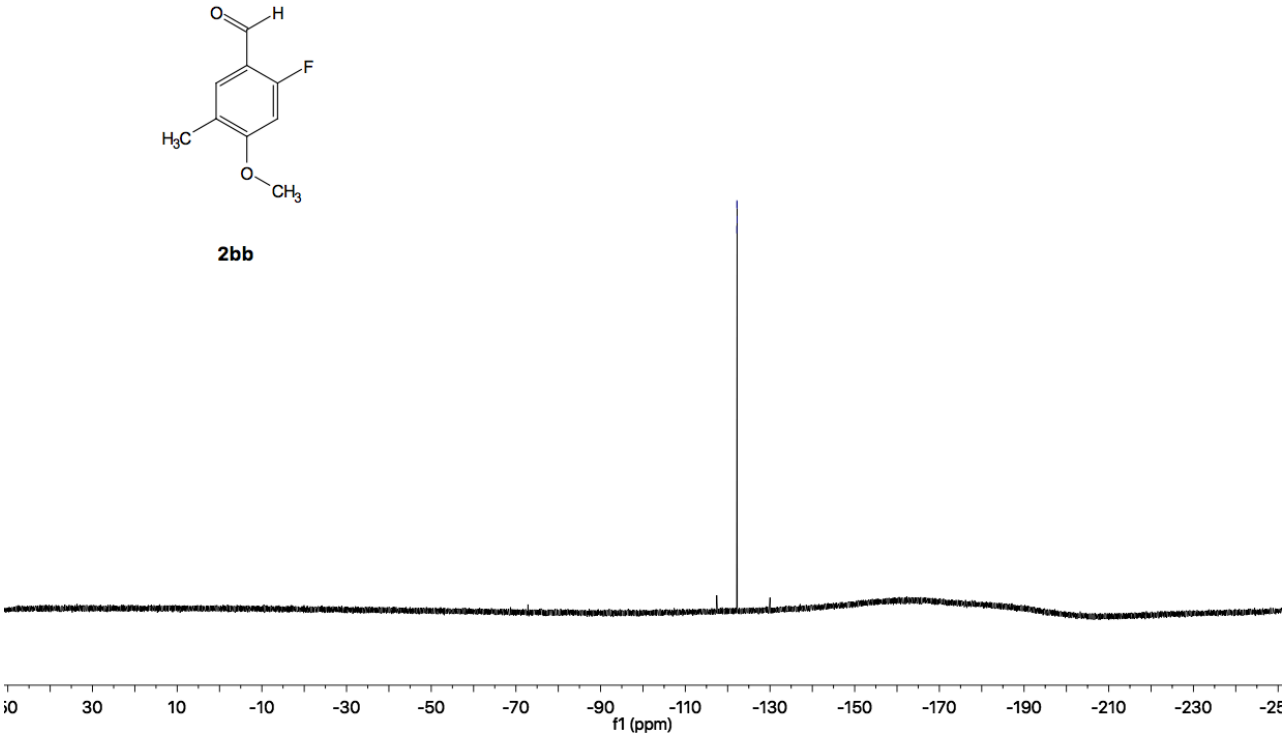
f1 (ppm)


-122.17
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-122.21
-122.24
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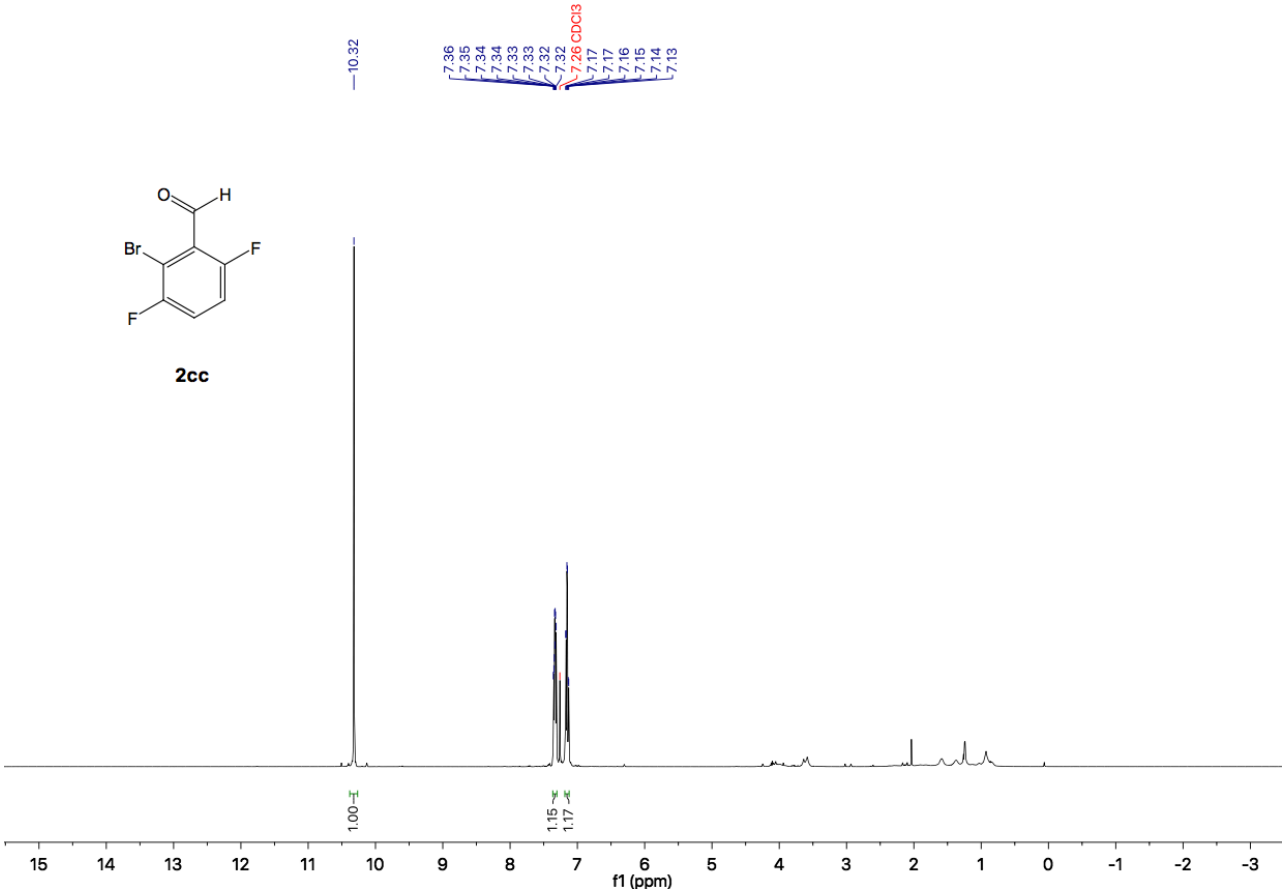
H
F
H3C
O
CH3
2bb
30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)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7.32
7.32
7.26 CDCl3
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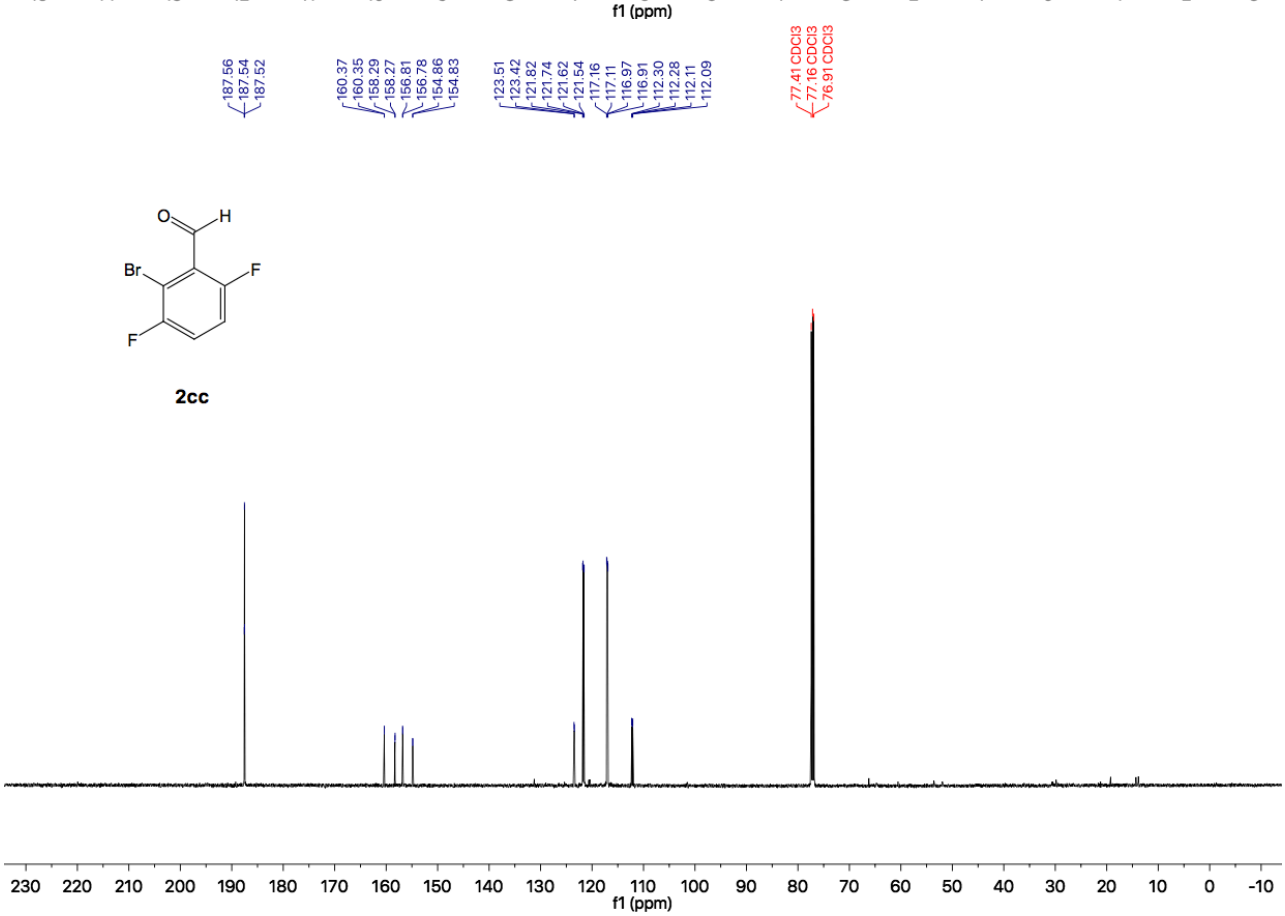
7.17
7.16
7.15
7.14
7.13
O
H
Br
F
F
2cc
1.00
1.15
1.17
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)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123.42
121.82
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121.62
121.54
117.16
117.11
116.97
116.91
112.30
112.28
112.11
112.09
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
O
H
Br
F
F
2cc
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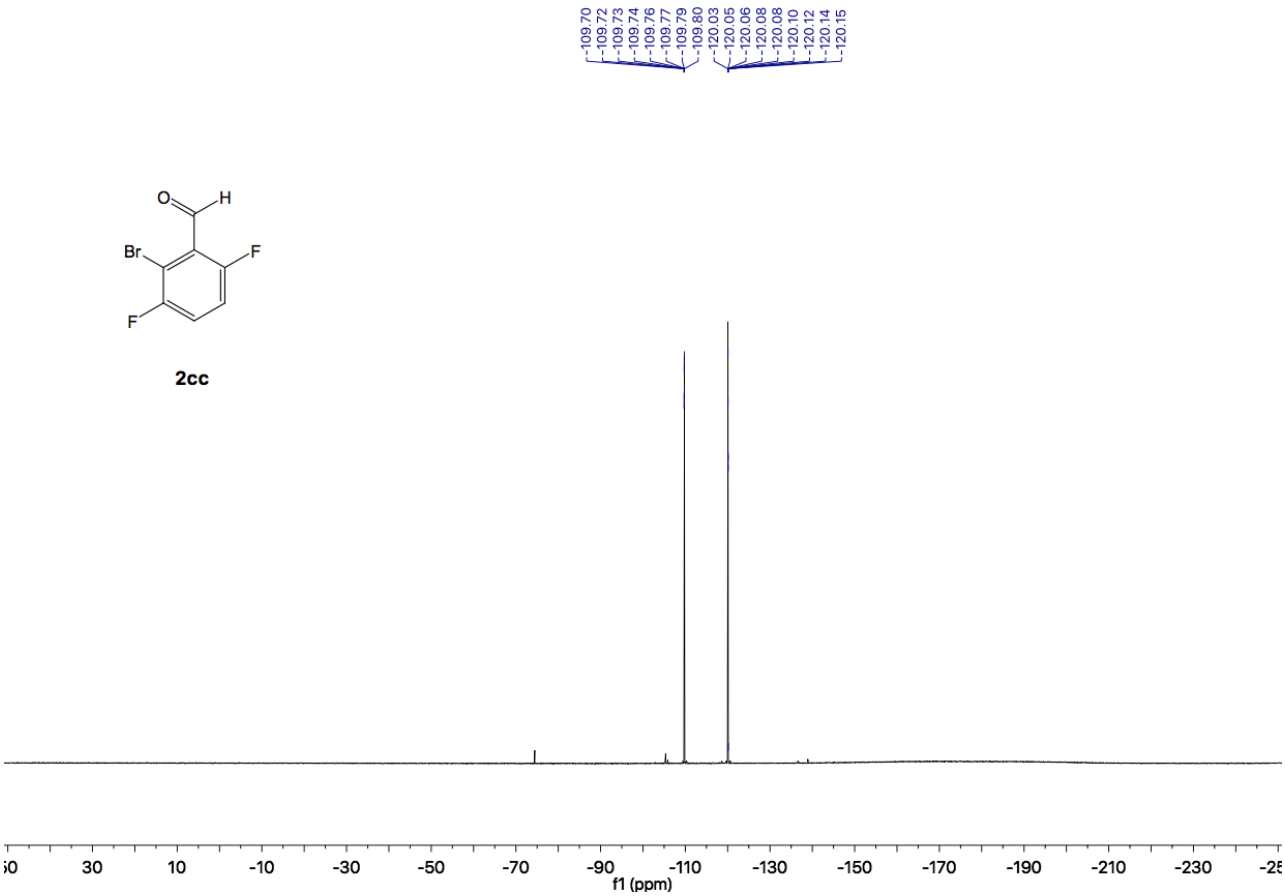
f1 (ppm)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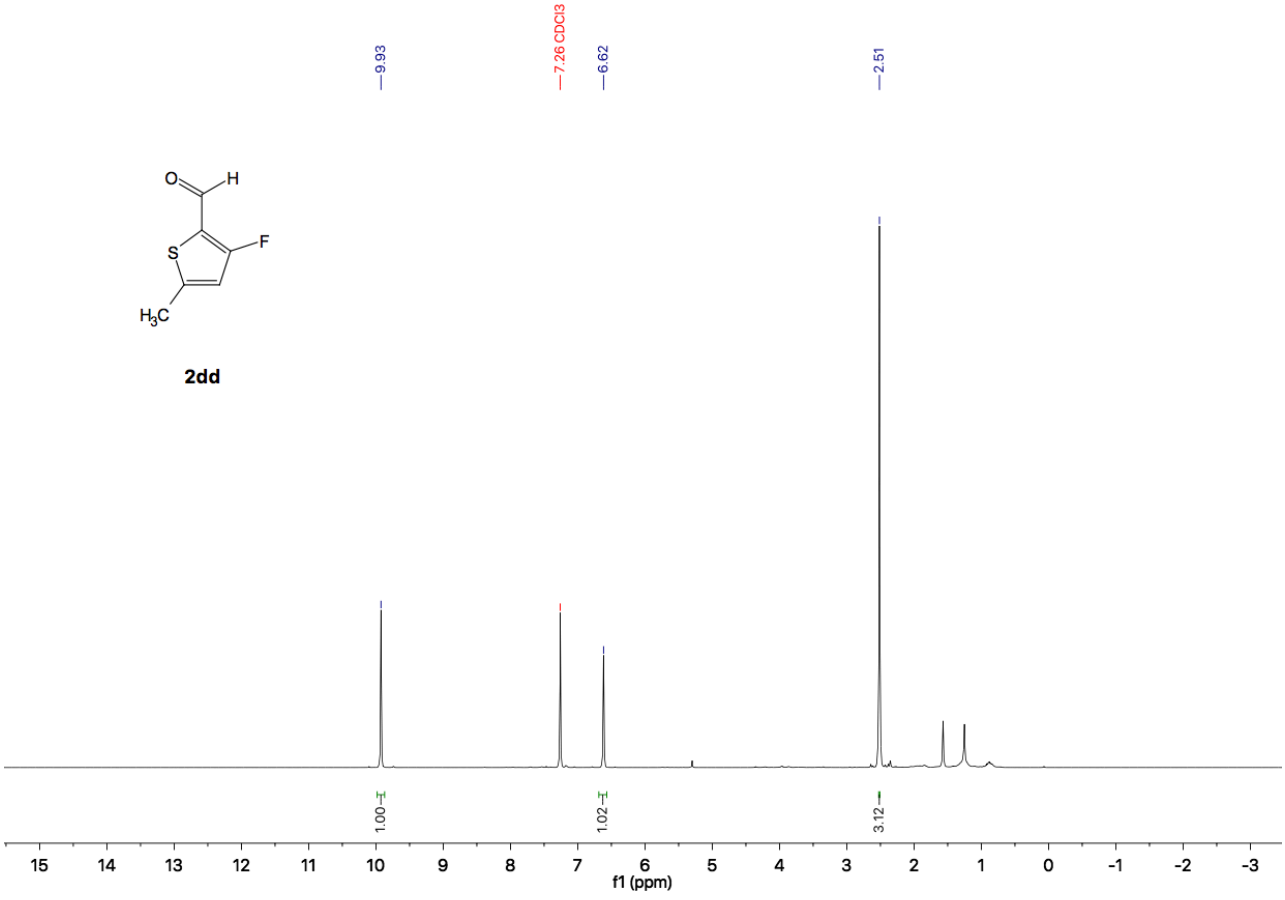
O
H
Br
F
F
2cc
f1 (ppm)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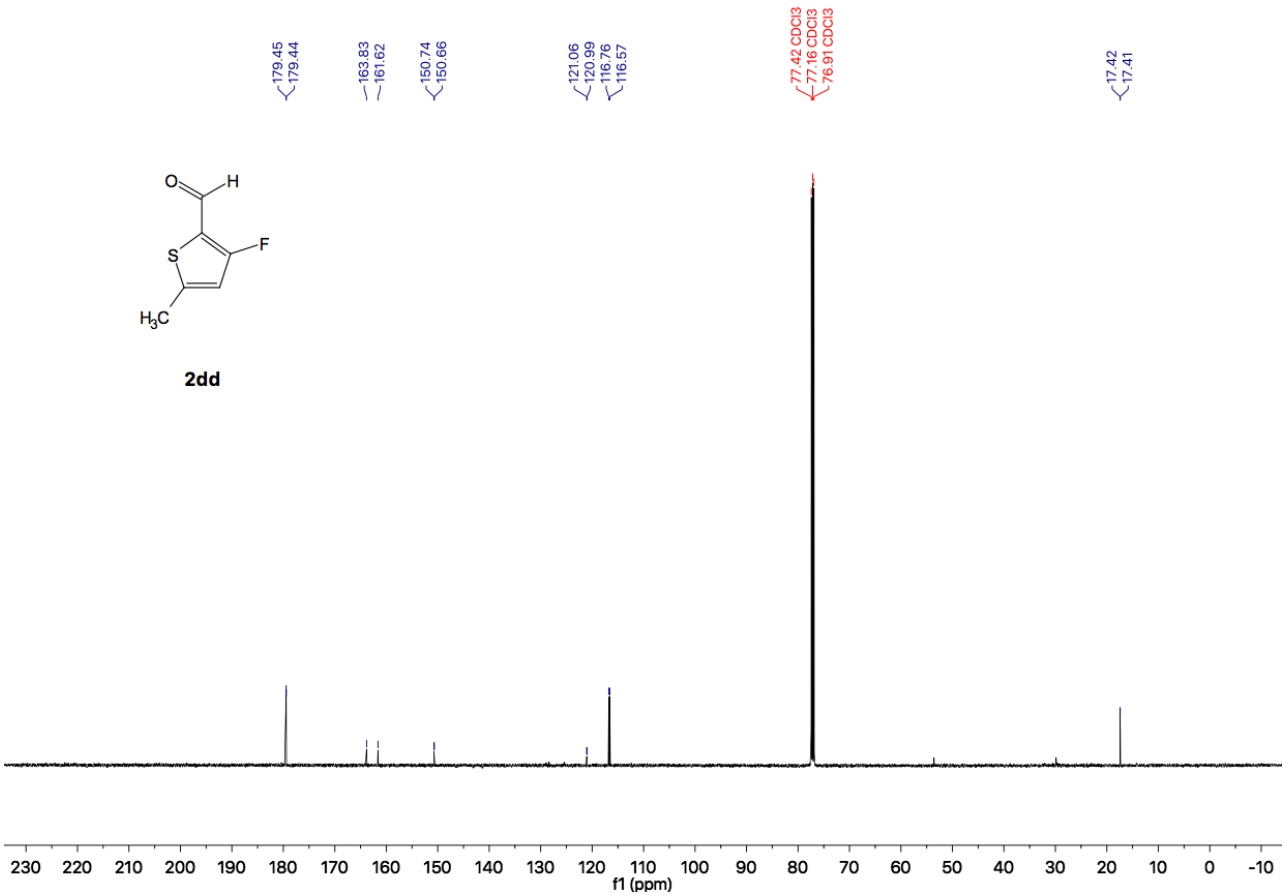
S
F
H3C
2dd
1.00
1.02
3.12
f1 (ppm)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179.44
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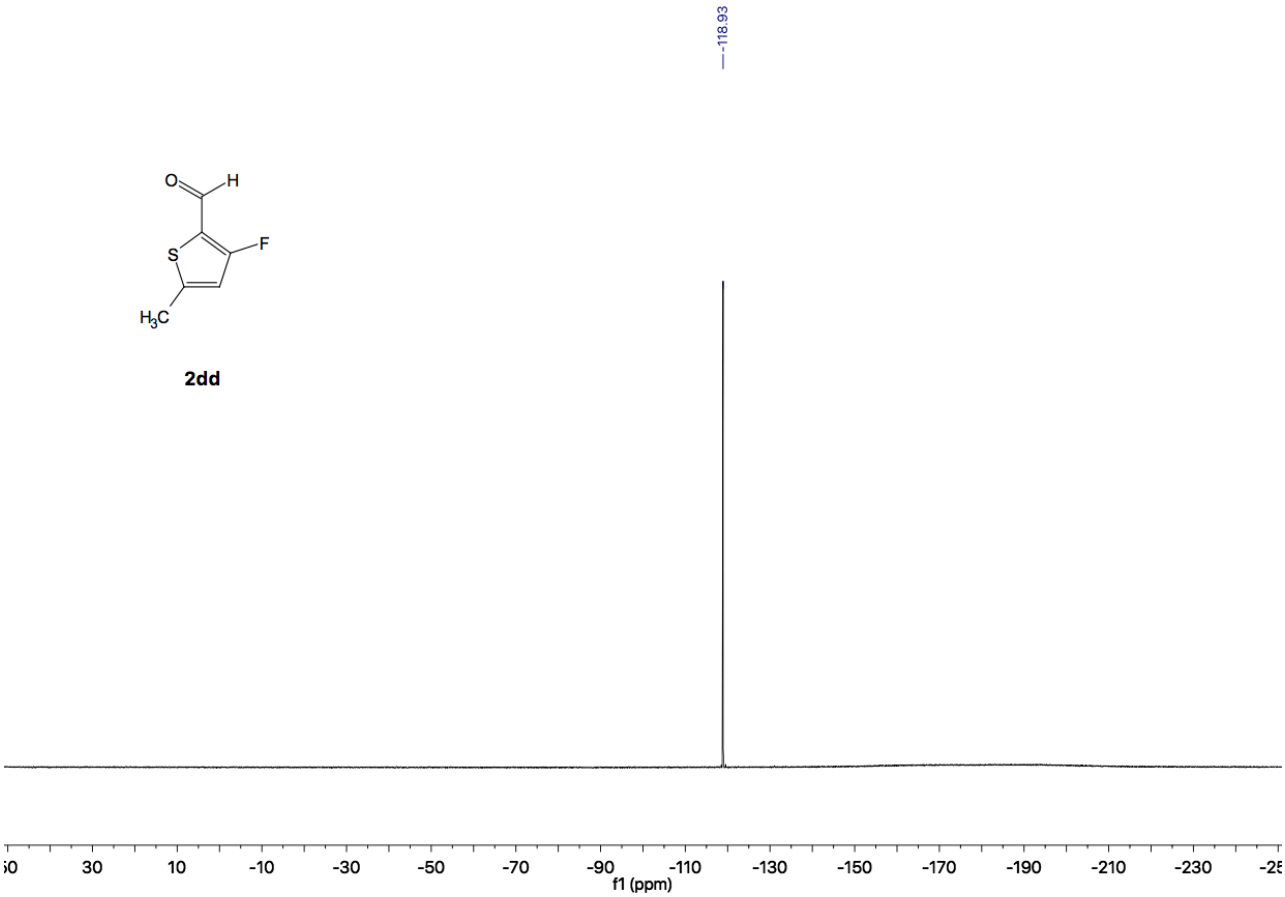
150.74
150.66
121.06
120.99
116.76
116.57
77.42 CDCl3
77.16 CDCl3
76.91 CDCl3
17.42
17.41
O
H
S
F
H3C
2dd
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


118.93
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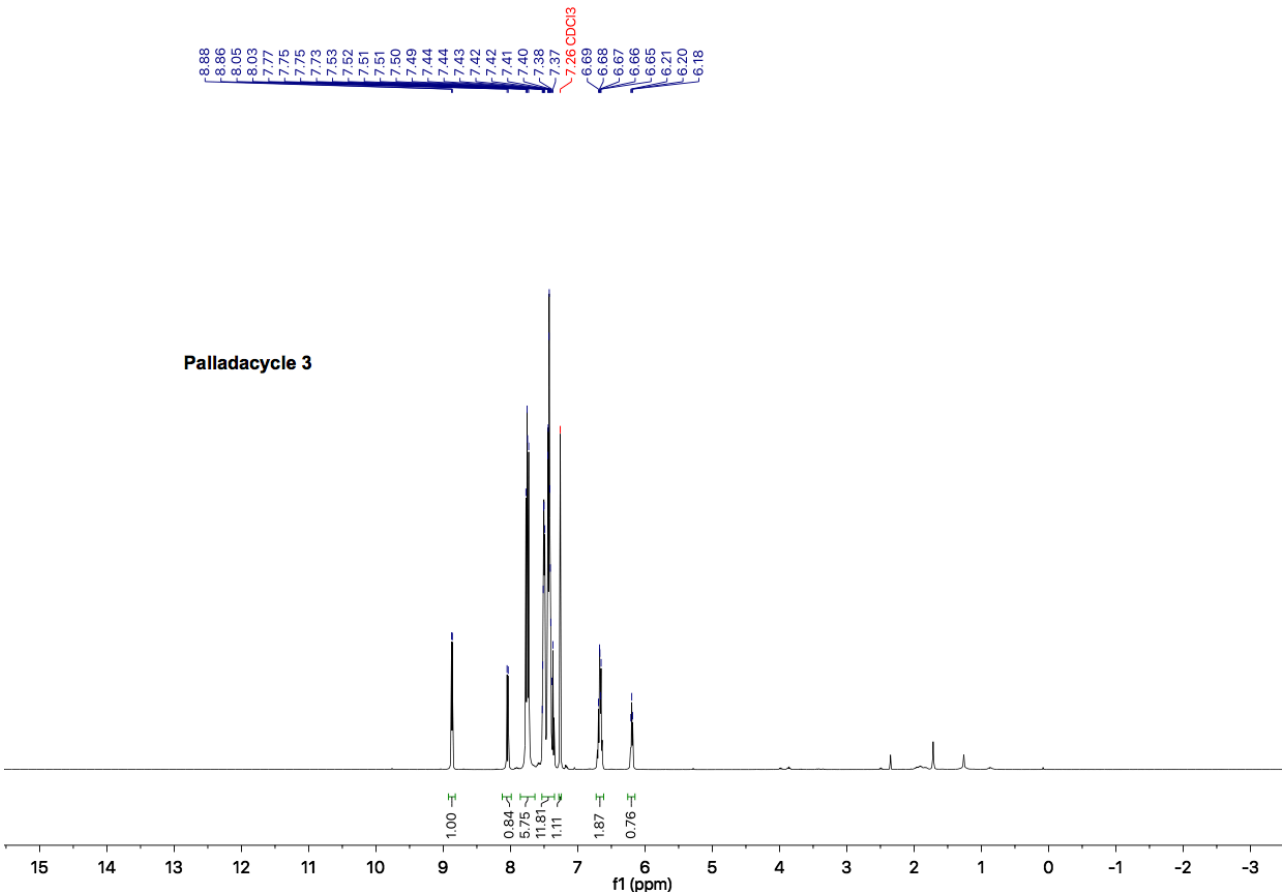
H
S
F
H3C
2dd
50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -25
f1 (ppm)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7.50
7.49
7.44
7.44
7.43
7.42
7.42
7.41
7.40
7.38
7.37
7.26 CDCl3
6.69
6.68
6.67
6.66
6.65
6.21
6.20
6.18
Palladacycle 3
1.00
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5.75
11.81
1.11
1.87
0.76
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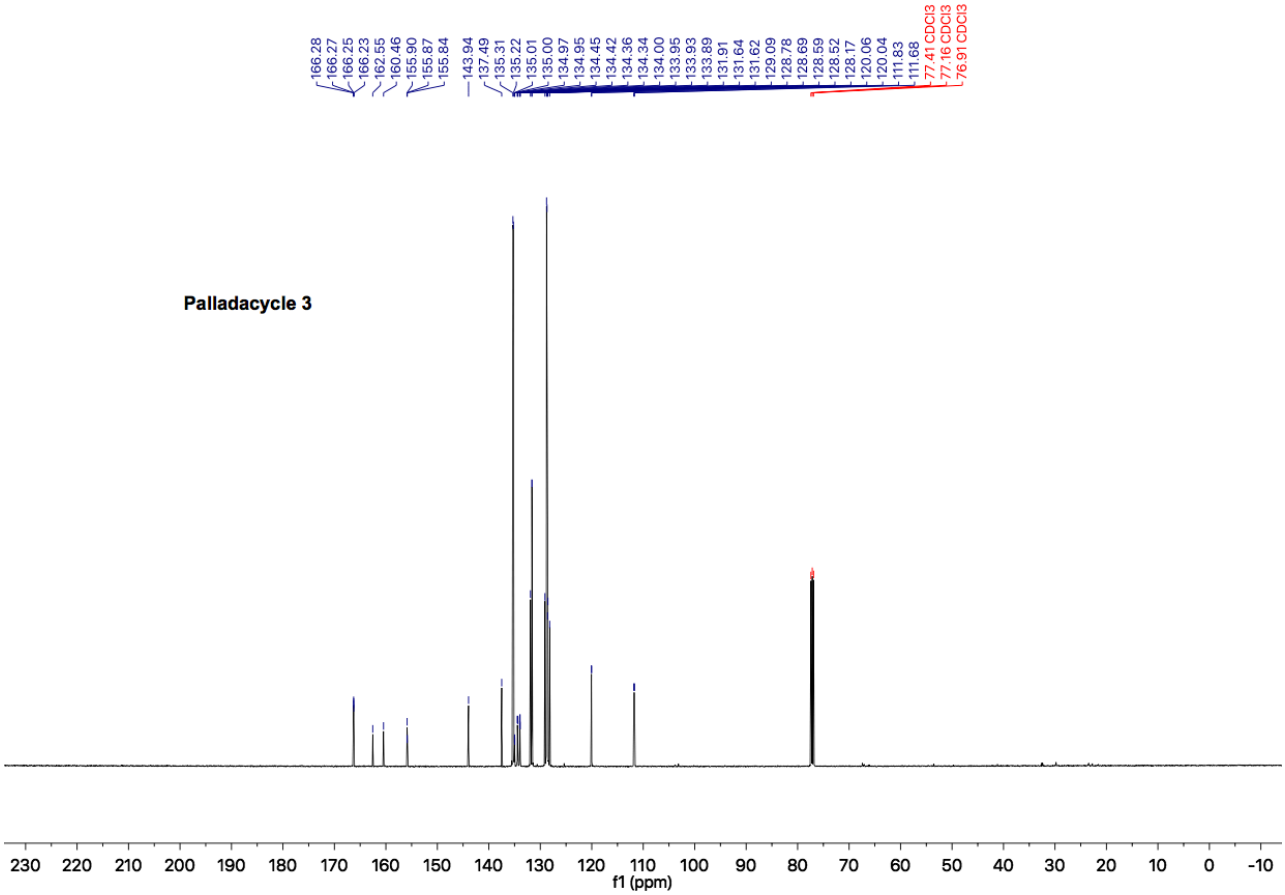
f1 (ppm)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135.00
134.97
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134.36
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128.69
128.59
128.52
128.17
120.06
120.04
111.83
111.68
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
Palladacycle 3
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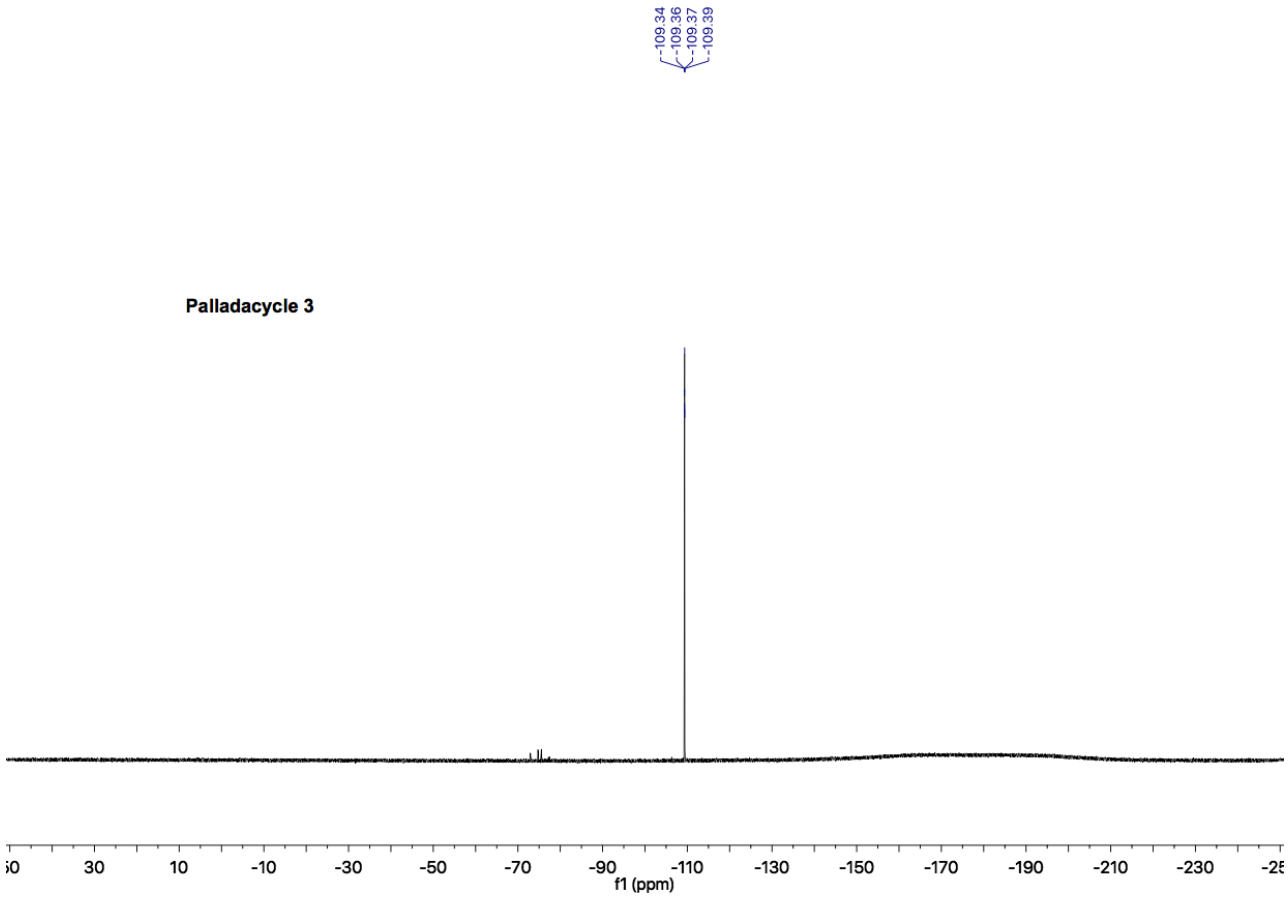
f1 (ppm)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109.37
109.39
Palladacycle 3
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

X-ray Crystallography Data

A translucent pale-yellow prism-like specimen of $C_{32}H_{25}Cl_2FNO_3PPdS$, approximate dimensions 0.192 mm x 0.277 mm x 0.471 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

Table 1: Data collection details for PDJXC4.

Axis	dx/mm	2θ/°	ω/°	φ/°	χ/°	Width/°	Frames	Time/s	Wavelength/Å	Voltage/kV	Current/mA	Temperature/K
Phi	49.991	0.00	0.00	0.00	54.74	1.00	180	2.00	0.71073	50	1.0	n/a
Omega	33.991	35.93	-130.07	-54.00	54.74	0.50	303	10.00	0.71073	50	1.0	n/a
Omega	33.991	35.93	-130.07	51.00	54.74	0.50	303	10.00	0.71073	50	1.0	n/a
Omega	33.991	35.93	-130.07	-105.00	54.74	0.50	303	10.00	0.71073	50	1.0	n/a
Omega	33.991	35.93	-130.07	0.00	54.74	0.50	303	10.00	0.71073	50	1.0	n/a
Omega	33.991	35.93	-130.07	-156.00	54.74	0.50	303	10.00	0.71073	50	1.0	n/a
Omega	33.991	35.93	-130.07	102.00	54.74	0.50	303	10.00	0.71073	50	1.0	n/a

A total of 1998 frames were collected. The total exposure time was 5.15 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 118216 reflections to a maximum θ angle of 39.38° (0.56 Å resolution), of which 17723 were independent (average redundancy 6.670, completeness = 99.9%, R_{int} = 3.63%, R_{sig} = 2.36%) and 15393 (86.85%) were greater than $2\sigma(F^2)$. The final cell constants of a = 12.7112(5) Å, b = 14.8397(6) Å, c = 15.9385(6) Å, β = 98.6077(13)°, volume = 2972.6(2) $Å^3$, are based upon the refinement of the XYZ-centroids of 9747 reflections above 20 σ(I) with 5.676° < 2θ < 80.63°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.893. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6580 and 0.8360.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/c 1, with Z = 4 for the formula unit, $C_{32}H_{25}Cl_2FNO_3PPdS$. The final anisotropic full-matrix least-squares refinement on F^2 with 407 variables converged at R1 = 3.14%, for the observed data and wR2 = 7.81% for all data. The goodness-of-fit was 1.089. The largest peak in the final difference electron density synthesis was 1.480 $e^-/Å^3$ and the largest hole was -0.619 $e^-/Å^3$ with an RMS deviation of 0.121 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.633 g/cm^3 and F(000), 1472 e^-.

Table 2. Sample and crystal data for PDJXC4.

Identification code	PDJXC4	
Chemical formula	$C_{32}H_{25}Cl_2FNO_3PPdS$	
Formula weight	730.86 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.192 x 0.277 x 0.471 mm	
Crystal habit	translucent pale yellow prism	
Crystal system	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 12.7112(5) Å	α = 90°
	b = 14.8397(6) Å	β = 98.6077(13)°
	c = 15.9385(6) Å	γ = 90°
Volume	2972.6(2) $Å^3$	
Z	4	
Density (calculated)	1.633 g/cm^3	
Absorption coefficient	0.970 mm^{-1}	
F(000)	1472	

Table 3. Data collection and structure refinement for PDJXC4.

Theta range for data collection	2.12 to 39.38°	
Index ranges	-22<=h<=22, -26<=k<=26, -28<=l<=28	
Reflections collected	118216	
Independent reflections	17723 [R(int) = 0.0363]	
Coverage of independent reflections	99.9%	
Absorption correction	multi-scan	
Max. and min. transmission	0.8360 and 0.6580	
Structure solution technique	direct methods	
Structure solution program	SHELXT (Sheldrick, 2016)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	17723 / 3 / 407	
Goodness-of-fit on F^2	1.089	
Δ/σ_{max}	0.005	
Final R indices	15393 data; I>2σ(I)	R1 = 0.0314, wR2 = 0.0736
	all data	R1 = 0.0397, wR2 = 0.0781

Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0321P)^2+2.5718P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	1.480 and -0.619 eÅ^{-3}
R.M.S. deviation from mean	0.121 eÅ^{-3}

Table 4. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for PDJXC4.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
Pd1	0.76337(2)	0.54706(2)	0.33872(2)	0.00813(2)
S1	0.85557(2)	0.67186(2)	0.21708(2)	0.01023(4)
P1	0.67363(2)	0.43633(2)	0.26275(2)	0.00913(4)
F1	0.97554(6)	0.52672(5)	0.63852(5)	0.01542(12)
O1	0.75084(7)	0.63659(6)	0.23341(5)	0.01249(13)
N1	0.86049(7)	0.64215(6)	0.41048(5)	0.00933(13)
C1	0.89382(8)	0.75006(7)	0.30111(6)	0.00991(14)
O2	0.84305(8)	0.72476(6)	0.14000(5)	0.01633(15)
C2	0.92861(9)	0.83503(7)	0.27990(7)	0.01273(16)
O3	0.93633(7)	0.60262(6)	0.22372(6)	0.01587(14)
C3	0.95414(10)	0.90136(8)	0.34148(8)	0.01550(18)
C4	0.94074(10)	0.88301(8)	0.42492(8)	0.01635(19)
C5	0.90793(9)	0.79809(7)	0.44760(7)	0.01355(17)
C6	0.88832(8)	0.73001(7)	0.38654(6)	0.01001(14)
C7	0.90125(8)	0.61008(7)	0.48361(6)	0.01048(15)
C8	0.86353(8)	0.52325(7)	0.50674(6)	0.00995(14)
C9	0.89904(9)	0.48353(7)	0.58506(6)	0.01116(15)
C10	0.85945(9)	0.40301(8)	0.61045(7)	0.01329(17)
C11	0.77856(10)	0.36250(8)	0.55438(7)	0.01435(17)
C12	0.74174(9)	0.39971(7)	0.47464(7)	0.01259(16)
C13	0.78513(8)	0.47922(7)	0.44775(6)	0.01001(14)
C14	0.68368(8)	0.44847(7)	0.15079(7)	0.01109(15)
C15	0.62161(10)	0.51256(8)	0.10186(7)	0.01442(17)
C16	0.63549(11)	0.52693(9)	0.01797(7)	0.01716(19)
C17	0.71097(11)	0.47798(9)	0.98240(8)	0.0183(2)
C18	0.77273(11)	0.41408(10)	0.03073(8)	0.0203(2)
C19	0.75946(10)	0.39935(9)	0.11478(7)	0.01630(19)
C20	0.53266(8)	0.43643(7)	0.27073(7)	0.01134(15)
C21	0.45747(9)	0.39344(8)	0.21072(7)	0.01448(17)
C22	0.35077(9)	0.39149(9)	0.22191(8)	0.0175(2)
C23	0.31876(10)	0.43305(9)	0.29203(9)	0.0190(2)
C24	0.39264(10)	0.47707(9)	0.35122(9)	0.0180(2)
C25	0.49954(9)	0.47885(8)	0.34066(8)	0.01419(17)

	x/a	y/b	z/c	U(eq)
C26	0.72158(8)	0.32254(7)	0.28676(7)	0.01109(15)
C27	0.83004(9)	0.31087(8)	0.31628(8)	0.01454(17)
C28	0.87176(10)	0.22507(9)	0.33251(8)	0.01699(19)
C29	0.80540(11)	0.15025(8)	0.31904(8)	0.0189(2)
C30	0.69759(11)	0.16134(8)	0.29036(9)	0.0191(2)
C31	0.65520(10)	0.24736(8)	0.27409(8)	0.01556(18)
C32A	0.3939(14)	0.2602(16)	0.4557(11)	0.047(5)
Cl1A	0.3848(5)	0.2903(3)	0.5614(6)	0.0451(11)
Cl2A	0.5234(9)	0.2243(8)	0.4441(8)	0.067(2)
C32B	0.4131(3)	0.2572(3)	0.4417(3)	0.0248(6)
Cl1B	0.37192(11)	0.30654(17)	0.53127(17)	0.0457(4)
Cl2B	0.54021(7)	0.20874(6)	0.46657(8)	0.0260(2)

Table 5. Bond lengths (Å) for PDJXC4.

Pd1-C13	1.9915(10)	Pd1-N1	2.0979(9)
Pd1-O1	2.1280(8)	Pd1-P1	2.2481(3)
S1-O3	1.4451(9)	S1-O2	1.4466(9)
S1-O1	1.4891(9)	S1-C1	1.7838(11)
P1-C20	1.8153(11)	P1-C26	1.8164(11)
P1-C14	1.8170(11)	F1-C9	1.3543(13)
N1-C7	1.2933(13)	N1-C6	1.4181(13)
C1-C2	1.3944(15)	C1-C6	1.4057(14)
C2-C3	1.3936(17)	C2-H2	0.95
C3-C4	1.3927(18)	C3-H3	0.95
C4-C5	1.3921(16)	C4-H4	0.95
C5-C6	1.3991(15)	C5-H5	0.95
C7-C8	1.4419(15)	C7-H7	0.95
C8-C9	1.3931(14)	C8-C13	1.4225(15)
C9-C10	1.3805(16)	C10-C11	1.3936(17)
C10-H10	0.95	C11-C12	1.4005(16)
C11-H11	0.95	C12-C13	1.3967(15)
C12-H12	0.95	C14-C15	1.3968(16)
C14-C19	1.3979(16)	C15-C16	1.3910(16)
C15-H15	0.95	C16-C17	1.3902(18)
C16-H16	0.95	C17-C18	1.3884(19)
C17-H17	0.95	C18-C19	1.3923(17)
C18-H18	0.95	C19-H19	0.95
C20-C25	1.3986(16)	C20-C21	1.4007(16)
C21-C22	1.3945(16)	C21-H21	0.95
C22-C23	1.390(2)	C22-H22	0.95
C23-C24	1.3905(19)	C23-H23	0.95

C24-C25	1.3942(16)	C24-H24	0.95
C25-H25	0.95	C26-C31	1.3951(16)
C26-C27	1.3993(16)	C27-C28	1.3887(17)
C27-H27	0.95	C28-C29	1.392(2)
C28-H28	0.95	C29-C30	1.388(2)
C29-H29	0.95	C30-C31	1.3948(17)
C30-H30	0.95	C31-H31	0.95
C32A-Cl1A	1.765(14)	C32A-Cl2A	1.765(14)
C32A-H32A	0.99	C32A-H32B	0.99
C32B-Cl1B	1.753(4)	C32B-Cl2B	1.759(4)
C32B-H32C	0.99	C32B-H32D	0.99

Table 6. Bond angles (°) for PDJXC4.

C13-Pd1-N1	82.57(4)	C13-Pd1-O1	171.18(4)
N1-Pd1-O1	88.77(3)	C13-Pd1-P1	95.37(3)
N1-Pd1-P1	174.31(3)	O1-Pd1-P1	93.41(2)
O3-S1-O2	115.77(6)	O3-S1-O1	112.41(5)
O2-S1-O1	110.58(5)	O3-S1-C1	107.27(5)
O2-S1-C1	105.52(5)	O1-S1-C1	104.35(5)
C20-P1-C26	106.84(5)	C20-P1-C14	106.50(5)
C26-P1-C14	103.20(5)	C20-P1-Pd1	112.85(4)
C26-P1-Pd1	116.03(4)	C14-P1-Pd1	110.60(4)
S1-O1-Pd1	113.20(5)	C7-N1-C6	119.90(9)
C7-N1-Pd1	111.56(7)	C6-N1-Pd1	128.45(7)
C2-C1-C6	119.33(10)	C2-C1-S1	117.83(8)
C6-C1-S1	122.82(8)	C3-C2-C1	121.11(10)
C3-C2-H2	119.4	C1-C2-H2	119.4
C4-C3-C2	119.05(10)	C4-C3-H3	120.5
C2-C3-H3	120.5	C5-C4-C3	120.61(11)
C5-C4-H4	119.7	C3-C4-H4	119.7
C4-C5-C6	120.15(10)	C4-C5-H5	119.9
C6-C5-H5	119.9	C5-C6-C1	119.43(9)
C5-C6-N1	120.16(9)	C1-C6-N1	120.39(9)
N1-C7-C8	117.11(9)	N1-C7-H7	121.4
C8-C7-H7	121.4	C9-C8-C13	119.93(9)
C9-C8-C7	122.12(9)	C13-C8-C7	117.92(9)
F1-C9-C10	118.96(9)	F1-C9-C8	117.99(9)
C10-C9-C8	123.05(10)	C9-C10-C11	116.86(10)
C9-C10-H10	121.6	C11-C10-H10	121.6
C10-C11-C12	121.75(10)	C10-C11-H11	119.1
C12-C11-H11	119.1	C13-C12-C11	121.19(10)
C13-C12-H12	119.4	C11-C12-H12	119.4

C12-C13-C8	117.06(9)	C12-C13-Pd1	133.24(8)
C8-C13-Pd1	109.68(7)	C15-C14-C19	119.49(10)
C15-C14-P1	119.94(8)	C19-C14-P1	120.36(8)
C16-C15-C14	119.92(11)	C16-C15-H15	120.0
C14-C15-H15	120.0	C17-C16-C15	120.43(11)
C17-C16-H16	119.8	C15-C16-H16	119.8
C18-C17-C16	119.86(11)	C18-C17-H17	120.1
C16-C17-H17	120.1	C17-C18-C19	120.08(12)
C17-C18-H18	120.0	C19-C18-H18	120.0
C18-C19-C14	120.21(11)	C18-C19-H19	119.9
C14-C19-H19	119.9	C25-C20-C21	119.55(10)
C25-C20-P1	118.31(8)	C21-C20-P1	122.11(9)
C22-C21-C20	119.97(11)	C22-C21-H21	120.0
C20-C21-H21	120.0	C23-C22-C21	120.07(11)
C23-C22-H22	120.0	C21-C22-H22	120.0
C22-C23-C24	120.32(11)	C22-C23-H23	119.8
C24-C23-H23	119.8	C23-C24-C25	119.90(12)
C23-C24-H24	120.1	C25-C24-H24	120.1
C24-C25-C20	120.18(11)	C24-C25-H25	119.9
C20-C25-H25	119.9	C31-C26-C27	119.59(10)
C31-C26-P1	122.43(9)	C27-C26-P1	117.94(8)
C28-C27-C26	120.38(11)	C28-C27-H27	119.8
C26-C27-H27	119.8	C27-C28-C29	119.81(11)
C27-C28-H28	120.1	C29-C28-H28	120.1
C30-C29-C28	120.14(11)	C30-C29-H29	119.9
C28-C29-H29	119.9	C29-C30-C31	120.31(12)
C29-C30-H30	119.8	C31-C30-H30	119.8
C30-C31-C26	119.77(11)	C30-C31-H31	120.1
C26-C31-H31	120.1	Cl1A-C32A-Cl2A	111.8(9)
Cl1A-C32A-H32A	109.2	Cl2A-C32A-H32A	109.2
Cl1A-C32A-H32B	109.2	Cl2A-C32A-H32B	109.2
H32A-C32A-H32B	107.9	Cl1B-C32B-Cl2B	111.3(2)
Cl1B-C32B-H32C	109.4	Cl2B-C32B-H32C	109.4
Cl1B-C32B-H32D	109.4	Cl2B-C32B-H32D	109.4
H32C-C32B-H32D	108.0		

Table 7. Anisotropic atomic displacement parameters (Å^2) for PDJXC4.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd1	0.00857(3)	0.00879(3)	0.00698(3)	0.00045(2)	0.00101(2)	-0.00135(2)
S1	0.01225(10)	0.01079(9)	0.00778(9)	0.00111(7)	0.00191(7)	-0.00055(7)
P1	0.00843(10)	0.01015(10)	0.00867(10)	-0.00031(8)	0.00086(7)	-0.00097(8)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F1	0.0191(3)	0.0156(3)	0.0102(3)	-0.0006(2)	-0.0026(2)	-0.0005(2)
O1	0.0120(3)	0.0150(3)	0.0099(3)	0.0030(2)	-0.0001(2)	-0.0025(3)
N1	0.0111(3)	0.0094(3)	0.0076(3)	0.0010(2)	0.0016(2)	-0.0016(2)
C1	0.0100(3)	0.0096(3)	0.0103(4)	0.0009(3)	0.0020(3)	-0.0004(3)
O2	0.0216(4)	0.0181(4)	0.0093(3)	0.0047(3)	0.0021(3)	-0.0027(3)
C2	0.0130(4)	0.0111(4)	0.0146(4)	0.0030(3)	0.0037(3)	-0.0004(3)
O3	0.0176(4)	0.0137(3)	0.0168(4)	-0.0014(3)	0.0041(3)	0.0030(3)
C3	0.0157(4)	0.0107(4)	0.0202(5)	0.0014(3)	0.0028(4)	-0.0023(3)
C4	0.0200(5)	0.0110(4)	0.0177(5)	-0.0021(3)	0.0016(4)	-0.0025(3)
C5	0.0172(4)	0.0113(4)	0.0120(4)	-0.0018(3)	0.0017(3)	-0.0021(3)
C6	0.0110(4)	0.0095(3)	0.0097(3)	-0.0002(3)	0.0018(3)	-0.0013(3)
C7	0.0119(4)	0.0105(4)	0.0088(3)	-0.0003(3)	0.0009(3)	-0.0010(3)
C8	0.0122(4)	0.0096(3)	0.0082(3)	0.0008(3)	0.0022(3)	0.0000(3)
C9	0.0128(4)	0.0128(4)	0.0078(3)	-0.0005(3)	0.0014(3)	0.0012(3)
C10	0.0175(4)	0.0134(4)	0.0094(4)	0.0031(3)	0.0033(3)	0.0017(3)
C11	0.0180(4)	0.0131(4)	0.0126(4)	0.0033(3)	0.0043(3)	-0.0018(3)
C12	0.0148(4)	0.0127(4)	0.0106(4)	0.0014(3)	0.0033(3)	-0.0028(3)
C13	0.0114(4)	0.0104(3)	0.0085(3)	0.0003(3)	0.0023(3)	-0.0007(3)
C14	0.0112(4)	0.0125(4)	0.0093(3)	-0.0008(3)	0.0008(3)	-0.0013(3)
C15	0.0176(4)	0.0146(4)	0.0109(4)	0.0013(3)	0.0017(3)	0.0021(3)
C16	0.0220(5)	0.0173(5)	0.0117(4)	0.0018(4)	0.0009(4)	0.0028(4)
C17	0.0218(5)	0.0226(5)	0.0106(4)	0.0007(4)	0.0031(4)	0.0005(4)
C18	0.0195(5)	0.0293(6)	0.0129(4)	0.0005(4)	0.0049(4)	0.0062(4)
C19	0.0152(4)	0.0222(5)	0.0116(4)	-0.0001(4)	0.0022(3)	0.0043(4)
C20	0.0094(4)	0.0116(4)	0.0129(4)	0.0004(3)	0.0013(3)	-0.0005(3)
C21	0.0109(4)	0.0174(4)	0.0145(4)	0.0000(3)	0.0001(3)	-0.0019(3)
C22	0.0112(4)	0.0196(5)	0.0208(5)	0.0025(4)	-0.0010(4)	-0.0032(4)
C23	0.0102(4)	0.0215(5)	0.0256(6)	0.0036(4)	0.0037(4)	0.0001(4)
C24	0.0135(4)	0.0203(5)	0.0212(5)	0.0000(4)	0.0062(4)	0.0022(4)
C25	0.0118(4)	0.0143(4)	0.0167(4)	-0.0016(3)	0.0030(3)	0.0004(3)
C26	0.0125(4)	0.0104(4)	0.0105(4)	0.0003(3)	0.0022(3)	0.0002(3)
C27	0.0123(4)	0.0156(4)	0.0158(4)	0.0001(3)	0.0027(3)	0.0015(3)
C28	0.0169(5)	0.0189(5)	0.0159(4)	0.0022(4)	0.0049(4)	0.0069(4)
C29	0.0267(6)	0.0143(4)	0.0176(5)	0.0020(4)	0.0092(4)	0.0067(4)
C30	0.0254(6)	0.0109(4)	0.0216(5)	-0.0007(4)	0.0052(4)	-0.0003(4)
C31	0.0168(4)	0.0122(4)	0.0176(5)	-0.0003(3)	0.0022(4)	-0.0018(3)
C32A	0.040(8)	0.051(9)	0.047(9)	0.031(7)	-0.003(6)	-0.005(6)
Cl1A	0.0456(18)	0.0386(14)	0.056(3)	-0.0028(16)	0.025(2)	0.0137(12)
Cl2A	0.078(4)	0.064(3)	0.074(4)	-0.039(3)	0.056(3)	-0.050(3)
C32B	0.0271(12)	0.0189(10)	0.0277(11)	0.0026(9)	0.0023(9)	0.0062(9)
Cl1B	0.0347(4)	0.0505(7)	0.0555(8)	-0.0220(6)	0.0180(5)	0.0055(4)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl2B	0.0168(3)	0.0200(3)	0.0429(4)	0.0001(2)	0.0104(2)	-0.0006(2)

Table 8. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for PDJXC4.

	x/a	y/b	z/c	U(eq)
H2	0.9350	0.8479	0.2225	0.015
H3	0.9803	0.9583	0.3267	0.019
H4	0.9541	0.9289	0.4667	0.02
H5	0.8988	0.7863	0.5047	0.016
H7	0.9538	0.6423	0.5205	0.013
H10	0.8861	0.3765	0.6636	0.016
H11	0.7476	0.3082	0.5707	0.017
H12	0.6863	0.3703	0.4382	0.015
H15	0.5700	0.5463	0.1258	0.017
H16	0.5931	0.5705	-0.0152	0.021
H17	0.7203	0.4882	-0.0749	0.022
H18	0.8241	0.3804	0.0064	0.024
H19	0.8020	0.3558	0.1478	0.02
H21	0.4791	0.3656	0.1624	0.017
H22	0.2999	0.3617	0.1815	0.021
H23	0.2461	0.4314	0.2996	0.023
H24	0.3703	0.5059	0.3988	0.022
H25	0.5500	0.5090	0.3811	0.017
H27	0.8754	0.3619	0.3253	0.017
H28	0.9454	0.2175	0.3527	0.02
H29	0.8339	0.0915	0.3295	0.023
H30	0.6525	0.1101	0.2818	0.023
H31	0.5814	0.2547	0.2545	0.019
H32A	0.3742	0.3126	0.4182	0.056
H32B	0.3428	0.2110	0.4377	0.056
H32C	0.4144	0.3036	0.3972	0.03
H32D	0.3614	0.2101	0.4189	0.03

References:

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