Supporting Information

Sandmeyer Difluoromethylation of (Hetero-)Arenediazonium Salts

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General Methods

The reactions were performed in oven-dried glassware containing a Teflon-coated stirrer bar and septum under a nitrogen atmosphere. Dimethylformamid was dried by refluxing over CaH_2 and subsequent fractionally distillation. Three freeze-pump-thaw cycles were performed before the reagents were mixed. All reactions were monitored by GC and the yields were determined by ^{19}F NMR using trifluoroethanol as internal standard. GC analyses were carried out using a HP-5 capillary column (Phenyl Methyl Siloxane 30 m x 320 x 0.25) and a time program beginning with 2 min at 60 °C followed by 30 °C/min ramp to 300 °C, then 3 min at this temp. Column chromatography was performed using a Combi Flash Companion-Chromatography-System (Isco-Systems) and Grace Reveleris packed flash columns (12 g). NMR spectra were obtained on a Bruker AMX 400 system using chloroform-d_1, or methanol-d_4 as deuterated solvents, with proton, carbon and fluorine resonances at 400 MHz, 101 MHz and 375 MHz, respectively. Mass spectral data were acquired on a Varian Saturn 2100 T.

The diazonium salts were prepared from the corresponding anilines following the procedure below and were directly used. $TMSCF_2H$ was prepared from $TMSCF_3$ following the procedure below and was directly used. All other starting materials were commercially available. All the anilines and solvents were purified by distillation or sublimation prior to use. CsF was dried for 24 h at 200 °C in $1x10^{-3}$ mbar. The other chemicals were used without further purification.

Synthesis of Starting Materials

Synthesis of arenediazonium tetrafluoroborates

In a 50 mL round-bottom flask, the aniline (10 mmol) was dissolved in a mixture of absolute ethanol (3 mL) and an aqueous solution of HBF_4 (50%, 2.5 mL, 20 mmol) and *tert*-butyl nitrite (2.7 mL, 20 mmol) was added dropwise to the solution at 0 °C. The reaction was stirred at room temperature for 1 h and diethyl ether (20 mL) was added to precipitate the arenediazonium tetrafluoroborate that was filtered off and washed with diethyl ether (3 × 10 mL). The arenediazonium tetrafluoroborate was dried in vacuo (10^{-3} mbar) for 10 minutes and was then directly used without further purification.

Synthesis of difluoromethyltrimethylsilane

Trifluoromethyltrimethylsilane (22.3 mL, 139 mmol) was added dropwise to the stirred suspension of sodium borhydride (1.79 g, 46 mmol) in 40 mL of dry diglyme at 10 °C. The reaction mixture was stirred 12 h at room temperature and afterwards difluoromethyltrimethylsilane was isolated by distillation (b.p. 65-66 °C).[1]

Synthesis of difluoromethylarenes

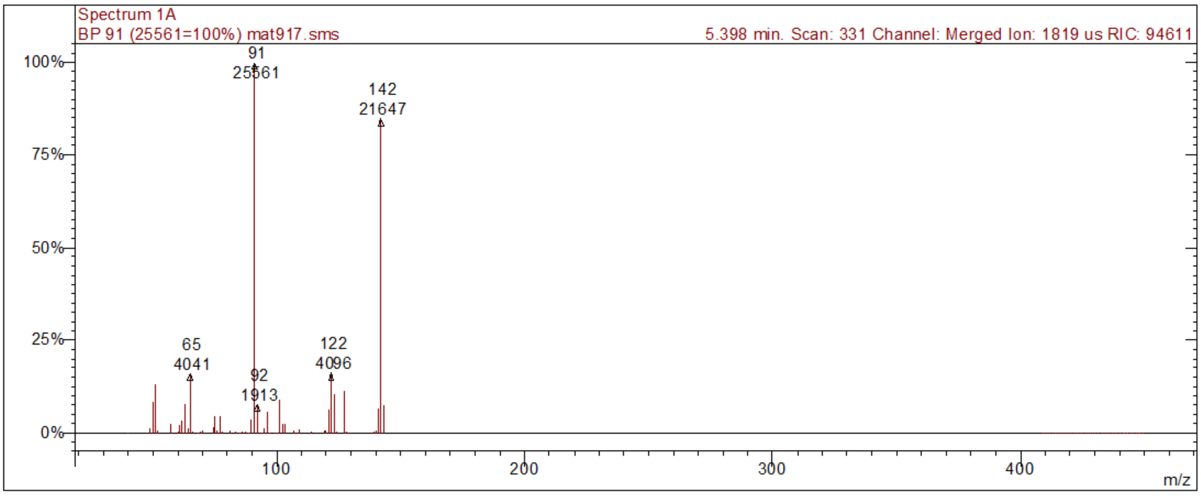
Standard procedure for the synthesis of difluoromethylarenes from the corresponding arenediazonium salts. An oven-dried 20 mL crimp cap vessel with Teflon-coated stirrer bar was charged with copper thiocyanate (122 mg, 1.00 mmol) and caesium fluoride (456 mg, 3.00 mmol) in DMF (2 mL) and difluoromethyltrimethylsilane (311 mg, 2.50 mmol) was added dropwise at 0 °C. The resulting suspension was stirred at 40 °C for 60 min and a solution of the arenediazonium tetrafluoroborate (1.00 mmol) in DMF (2 mL) was added dropwise via syringe at 0 °C. The suspension was stirred at room temperature for 12 h. The resulting mixture was filtered through a short pad of celite (5 g) and rinsed with diethyl ether (20 mL). The resulting organic solution was washed with water (2 × 10 mL) and brine (10 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated (700 mbar, 40 °C). The residue was further purified by flash chromatography (SiO_2, pentane/diethyl ether gradient), yielding the corresponding difluoromethylarenes.

Synthesis of 1-(difluoromethyl)-4-methoxybenzene (2) [CAS: 658-17-3]. Compound **2** was prepared following the standard procedure, starting from 4-methoxybenzenediazonium tetrafluoroborate [CAS: 459-64-3] (222 mg, 1.00 mmol). After purification, **2** was isolated as colorless liquid (109 mg, 0.69 mmol, 69%). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.45$ (d, $^3J = 8.7$ Hz, 2H), 6.96 (d, $^3J = 8.8$ Hz, 2H), 6.61 (t, $J = 56.8$ Hz, 1H), 3.85 ppm (s, 3H); ^{19}F NMR (375 MHz, $CDCl_3$): $\delta = -108.1$ ppm (d, $J = 57.1$ Hz); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 161.2$, 126.9 (t, ^3J(C,F) = 6.4 Hz, 2C), 126.7 (t, ^2J(C,F) = 22.7 Hz), 114.7 (t, ^1J(C,F) = 237.5 Hz), 113.8 (2C), 55.1 ppm; IR (neat): ν = 2962, 2845, 1610, 1498, 1468, 1386, 1290, 1256, 1059, 1025, 755 cm^{-1}; MS (Ion trap, EI, 70 eV): m/z (%) = 158 [M^+] (100), 157 (46), 139 (23), 127 (15), 108 (16); HRMS (EI-TOF) calcd for $C_8H_8OF_2$: 158.0543; found: 158.0545.

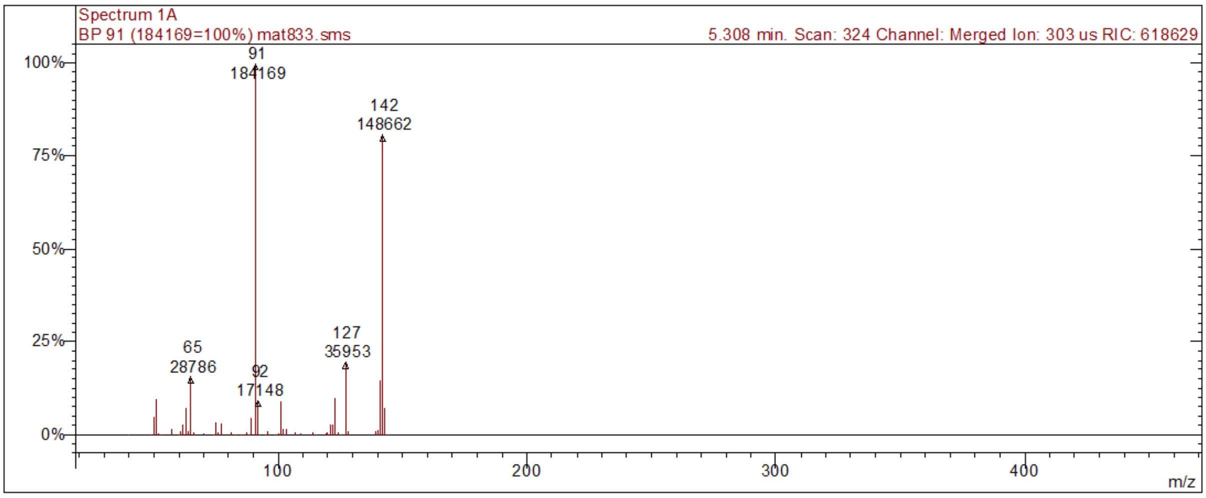
Synthesis of 1-(difluoromethyl)-2-methoxybenzene (3) [CAS: 1366392-20-2]. Compound **3** was prepared following the standard procedure, starting from 2-methoxybenzenediazonium tetrafluoroborate [CAS: 395-48-2] (222 mg, 1.00 mmol). After purification, **3** was isolated as colorless liquid (81 mg, 0.51 mmol, 51%). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.58$ (d, $^3J = 7.7$ Hz, 1H), 7.44 (t, $^3J = 8.0$ Hz, 1H), 7.04 (t, $^3J = 7.5$ Hz, 1H), 6.97 (t, $J = 55.7$ Hz, 1H), 6.95 (d, $^3J = 8.6$ Hz, 1H), 3.88 ppm (s, 3H); ^{19}F NMR (375 MHz, CDCl$_3$): δ = –115.4 ppm (d, J = 55.6 Hz); ^{13}C NMR (101 MHz, CDCl$_3$): δ = 157.2, 131.9, 126.2 (t, ^3J(C,F) = 6.0 Hz), 126.6 (t, ^2J(C,F) = 22.7 Hz), 120.5, 111.6 (t, ^1J(C,F) = 235.2 Hz), 110.8, 55.6 ppm; IR (neat): ν = 2962, 2845, 1610, 1498, 1468, 1386, 1290, 1256, 1059, 1025, 755 cm^{-1}; MS (Ion trap, EI, 70 eV): m/z (%) = 159 [M^++H] (10), 158 (100), 143 (33), 139 (23), 127 (16), 109 (13); HRMS (EI-TOF) calcd for $C_8H_8OF_2$: 158.0543; found: 158.0539.

Synthesis of 1-(difluoromethyl)-3-methoxybenzene (4) [CAS: 403648-71-5]. Compound **4** was prepared following the standard procedure, starting from 3-methoxybenzenediazonium tetrafluoroborate[2] (222 mg, 1.00 mmol). After purification, **4** was isolated as colorless liquid (100 mg, 0.63 mmol, 63%). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.38 (t, ^3J = 7.9 Hz, 1H), 7.10 (d, ^3J = 7.7 Hz, 1H), 7.05 (s, 1H), 7.03 (d, ^3J = 7.5 Hz, 1H), 6.63 (t, J = 56.4 Hz, 1H), 3.85 ppm (s, 3H); ^{19}F NMR (375 MHz, CDCl$_3$): δ = –110.6 ppm (d, J = 55.9 Hz); ^{13}C NMR (101 MHz, CDCl$_3$): δ = 159.8, 135.7 (t, ^2J(C,F) = 22.3 Hz), 129.9, 117.8 (t, ^3J = 6.6 Hz), 116.6 (t, ^3J(C,F) = 1.8 Hz), 114.6 (t, ^1J(C,F) = 238.8 Hz), 110.6 (t, ^3J = 5.9 Hz), 55.4 ppm; IR (neat): ν = 2962, 2845, 1610, 1498, 1468, 1386, 1290, 1256, 1059, 1025, 755 cm^{-1}; MS (Ion trap, EI, 70 eV): m/z (%) = 158 [M^+] (100), 139 (13), 128 (12), 127 (45), 115 (12), 109 (11), 108 (11), 95 (34), 77 (11), 75 (11), 63 (10), 51 (11); HRMS (EI-TOF) calcd for $C_8H_7OF_2$: 157.0465; found: 157.0455.

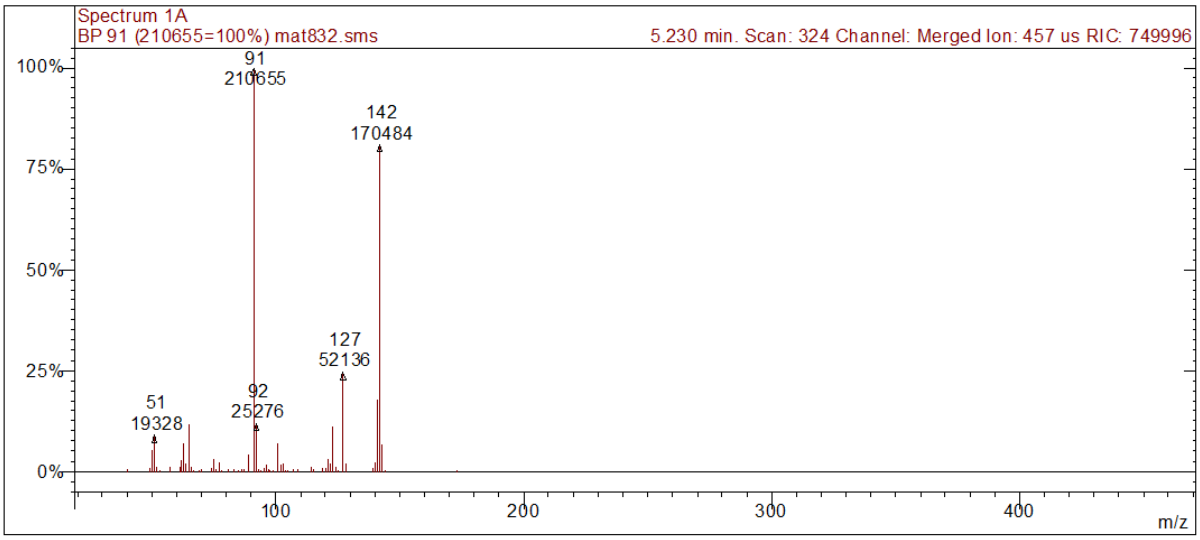
Synthesis of 1-(difluoromethyl)-2-methylbenzene (5) [CAS: 1222556-60-6]. Compound **5** was prepared following the standard procedure, starting from 2-methylbenzenediazonium tetrafluoroborate [CAS: 2093-46-1] (103 mg, 0.50 mmol). After the reaction, trifluoroethanol as internal standard (36 µL, 0.50 mmol) was added to the reaction mixture and the difluoromethylated product **5** was formed in 73% yield as determined by ^{19}F NMR spectroscopic analysis and confirmed by GC-MS analytics. ^{19}F NMR (375 MHz, DMSO-d_6): δ = –114.0 ppm.



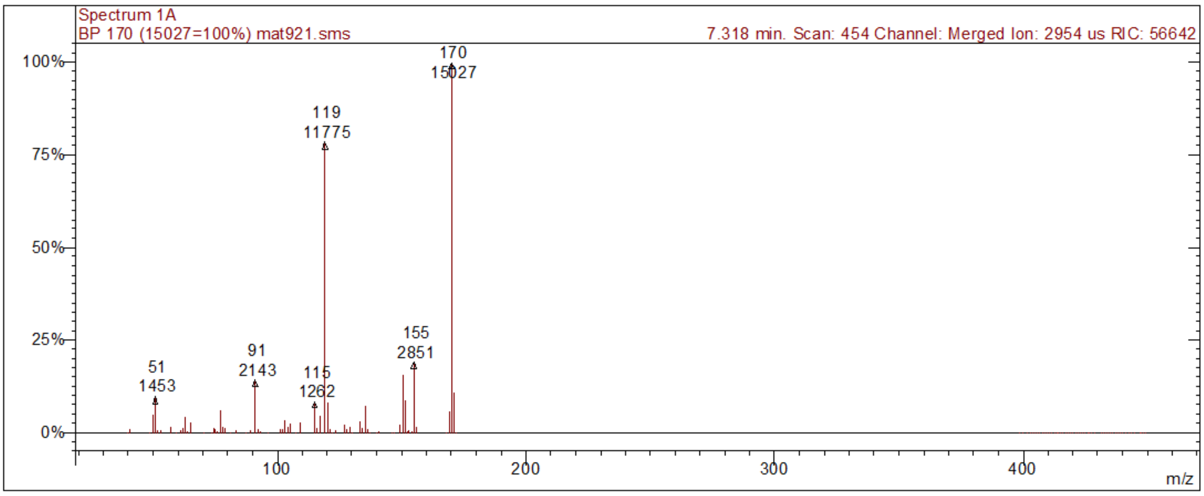
Synthesis of 1-(difluoromethyl)-3-methylbenzene (6). Compound **6** was prepared following the standard procedure, starting from 3-methylbenzenediazonium tetrafluoroborate [CAS: 1422-76-0] (103 mg, 0.50 mmol). After the reaction, trifluoroethanol as internal standard (36 µL, 0.50 mmol) was added to the reaction mixture and the difluoromethylated product **6** was formed in 86% yield as determined by ^{19}F NMR spectroscopic analysis and confirmed by GC-MS analytics. ^{19}F NMR (375 MHz, DMSO-d_6): δ = –110.9 ppm.



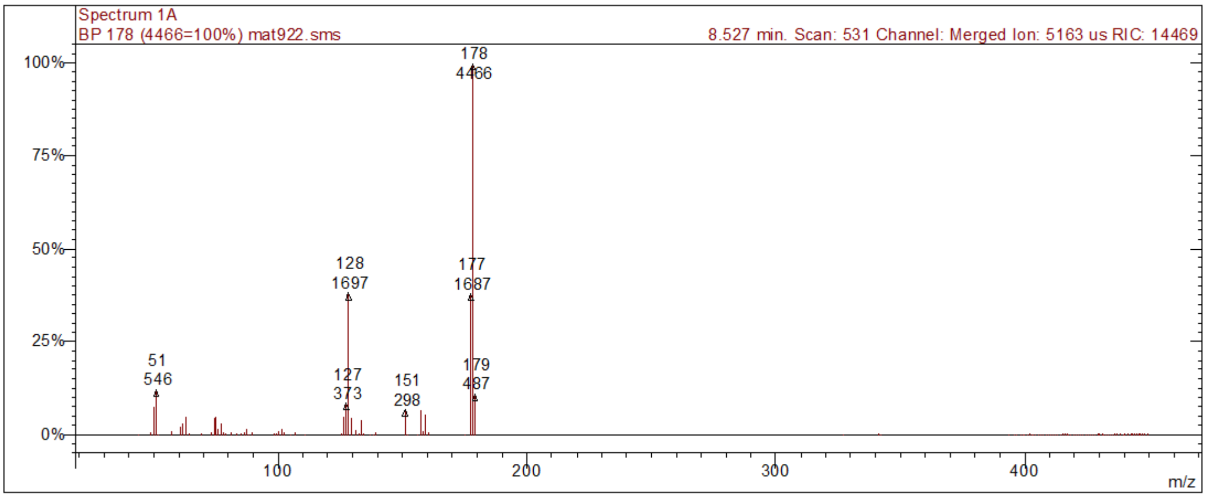
Synthesis of 1-(difluoromethyl)-4-methylbenzene (7) [CAS: 66865-75-6]. Compound **7** was prepared following the standard procedure, starting from 4-methylbenzenediazonium tetrafluoroborate [CAS: 459-44-9] (103 mg, 0.50 mmol). After the reaction, trifluoroethanol as internal standard (36 µL, 0.50 mmol) was added to the reaction mixture and the difluoromethylated product **7** was formed in 81% yield as determined by ^{19}F NMR spectroscopic analysis and confirmed by GC-MS analytics. ^{19}F NMR (375 MHz, DMSO-d_6): δ = –110.6 ppm.



Synthesis of 2-(difluoromethyl)-1,3,5-trimethylbenzene (8) [CAS: 103383-72-8]. Compound **8** was prepared following the standard procedure, starting from 1,3,5-trimethylbenzenediazonium tetrafluoroborate [3] (117 mg, 0.50 mmol). After the reaction, trifluoroethanol as internal standard (36 µL, 0.50 mmol) was added to the reaction mixture and the difluoromethylated product **8** was formed in 38% yield as determined by ^{19}F NMR spectroscopic analysis and confirmed by GC-MS analytics. ^{19}F NMR (375 MHz, DMSO-d_6): δ = –111.9 ppm.

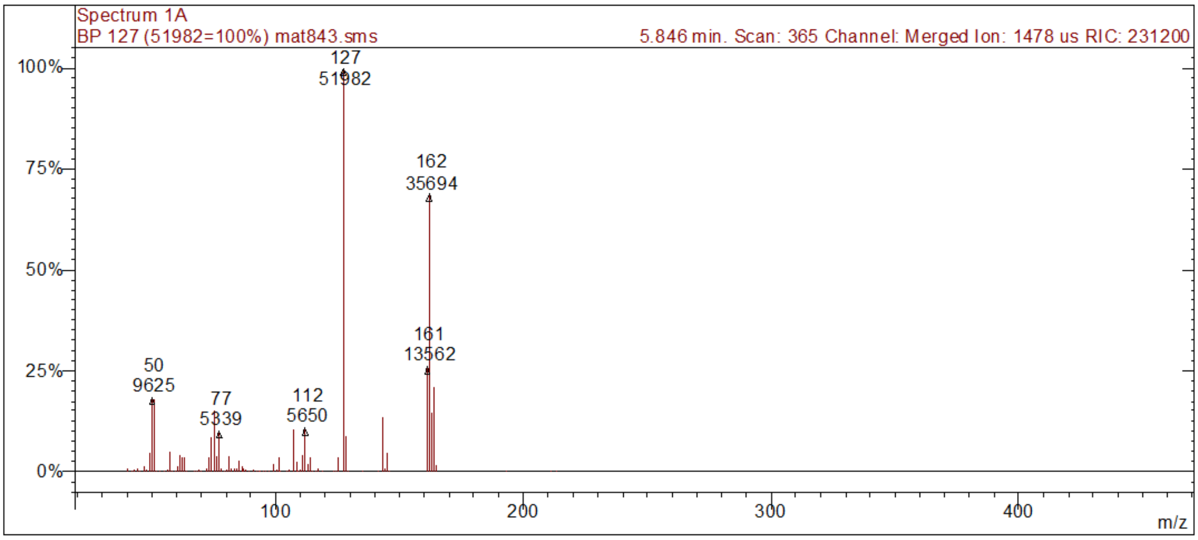


Synthesis of 1-(difluoromethyl)naphthalene (9) [CAS: 53731-26-3]. Compound **9** was prepared following the standard procedure, starting from α-naphthyldiazonium tetrafluoroborate [CAS: 28912-93-8] (121 mg, 0.50 mmol). After the reaction, trifluoroethanol as internal standard (36 µL, 0.50 mmol) was added to the reaction mixture and the difluoromethylated product **9** was formed in 51 % yield as determined by ^{19}F NMR spectroscopic analysis and confirmed by GC-MS analytics. ^{19}F NMR (375 MHz, DMSO-d_6): δ = –111.7 ppm.

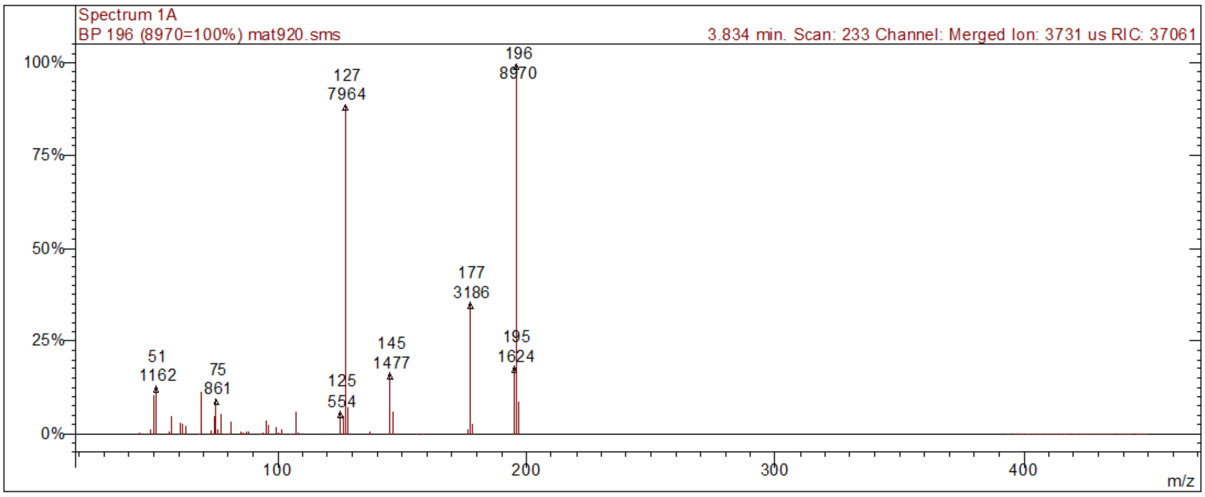


Synthesis of 4-(difluoromethyl)-1,1'-biphenyl (10) [CAS: 139219-68-4]. Compound **10** was prepared following the standard procedure, starting from [1,1'-biphenyl]-4-diazonium tetrafluoroborate[4] (267 mg, 1.00 mmol). After purification, **10** was isolated as white solid (165 mg, 0.81 mmol, 81%). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.70 (m, 2H), 7.61 (m, 4H), 7.48 (m, 2H), 7.41 (m, 1H), 6.72 ppm (t, J = 56.2 Hz, 1H); ^{19}F NMR (375 MHz, CDCl$_3$): δ = –110.3 ppm (d, J = 57.2 Hz); ^{13}C NMR (101 MHz, CDCl$_3$): δ = 143.7, 140.2, 133.2 (t, ^{2}J(C,F) = 22.7 Hz), 128.9 (2C), 127.9 (2C), 127.4 (2C), 127.2 (2C), 126.0 (t, ^{3}J(C,F) = 5.8 Hz), 114.7 ppm (t, ^{1}J(C,F) = 238.4 Hz); IR (neat): ν = 3060, 3037, 2966, 1614, 1487, 1412, 1376, 1315, 1223, 1199, 1072, 1021, 1006, 838, 764, 738, 691 cm^{-1}; MS (Ion trap, EI, 70 eV): m/z (%) = 204 [M^+] (100), 203 (28); m.p.: 69-70 °C; HRMS (EI-TOF) calcd for $C_{13}H_9F_2$: 203.0672; found: 203.0667.

Synthesis of 1-chloro-4-(difluoromethyl)benzene (11) [CAS: 43141-66-8]. Compound **11** was prepared following the standard procedure, starting from 4-chlorobenzenediazonium tetrafluoroborate [CAS: 673-41-6] (118 mg, 0.50 mmol). After the reaction, trifluoroethanol as internal standard (36 µL, 0.50 mmol) was added to the reaction mixture and the difluoromethylated product **11** was formed in 61 % yield as determined by ^{19}F NMR spectroscopic analysis and confirmed by GC-MS analytics. ^{19}F NMR (375 MHz, DMSO-d_6): δ = –111.2 ppm.



Synthesis of 1-(difluoromethyl)-4-(trifluoromethyl)benzene (12) [CAS: 2251-82-3]. Compound **12** was prepared following the standard procedure, starting from 4-(trifluoromethyl)benzenediazonium tetrafluoroborate[5] (130 mg, 0.50 mmol). After the reaction, trifluoroethanol as internal standard (36 µL, 0.50 mmol) was added to the reaction mixture and the difluoromethylated product **12** was formed in 74% yield as determined by ^{19}F NMR spectroscopic analysis and confirmed by GC-MS analytics. ^{19}F NMR (375 MHz, DMSO-d_6): $\delta = -113.1$ ppm.



Synthesis of 4-(difluoromethyl)benzonitrile (13) [CAS: 55805-10-2]. Compound **13** was prepared following the standard procedure, starting from 4-cyanobenzenediazonium tetrafluoroborate [CAS: 2252-32-6] (217 mg, 1.00 mmol). After purification, **13** was isolated as colorless oil (103 mg, 0.67 mmol, 67%). ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 7.78$ (d, ^3J(H,H) = 7.9 Hz, 2H), 7.65 (d, ^3J(H,H) = 8.0 Hz, 2H), 6.70 ppm (t, $J = 55.8$ Hz, 1H); ^{19}F NMR (375 MHz, CDCl$_3$): $\delta = -113.2$ (d, *J* = 55.9 Hz) ppm; ^{13}C NMR (101 MHz, CDCl$_3$): δ = 138.5 (t, ^2J(C,F) = 22.7 Hz), 132.6 (2C), 126.4 (t, ^3J(C,F) = 6.4 Hz, 2C), 117.9, 114.8, 113.3 ppm (t, ^1J(C,F) = 240.7 Hz); IR (neat): ν = 2962, 2845, 1610, 1498, 1468, 1386, 1290, 1256, 1059, 1025, 755 cm^{-1}; MS (Ion trap, EI, 70 eV): m/z (%) = 154 [M^++H] (14), 153 (88), 152 (100), 134 (17), 103 (59), 102 (13), 76 (18), 75 (18), 51 (21), 50 (18); HRMS (EI-TOF) calcd for $C_8H_5NF_2$: 153.0390; found: 153.0384.

Synthesis of 1-(difluoromethyl)-4-nitrobenzene (14) [CAS: 29848-57-5]. Compound **14** was prepared following the standard procedure, starting from 4-nitrobenzenediazonium tetrafluoroborate [CAS: 456-27-9] (237 mg, 1.00 mmol). After purification, **14** was isolated as light yellow oil (144 mg, 0.83 mmol, 83%). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.34 (d, ^3J(H,H) = 8.9 Hz, 2H), 7.73 (d, ^3J(H,H) = 8.3 Hz, 2H), 6.75 ppm (t, *J* = 55.8 Hz, 1H); ^{19}F NMR (375 MHz, CDCl$_3$): δ = –112.9 ppm (d, *J* = 55.9 Hz); ^{13}C NMR (101 MHz, CDCl$_3$): δ = 149.3, 140.2 (t, ^2J(C,F) = 22.7 Hz), 126.8 (t, ^3J(C,F) = 5.9 Hz, 2C), 124.0 (2C), 113.0 ppm (t, ^1J(C,F) = 240.9 Hz); IR (neat): ν = 3096, 2970, 1533, 1484, 1349, 1219, 1100, 1031, 940, 901, 808, 740, 707 cm^{-1}; MS (Ion trap, EI, 70 eV): m/z (%) = 174 [M^++H] (17), 173 (100), 157 (31), 154 (15), 143 (30), 127 (68), 115 (25), 107 (33), 101 (34), 95 (10), 77 (29), 75 (10), 57 (10), 51 (15), 50 (16), 46 (12); HRMS (EI-TOF) calcd for $C_7H_4NO_2F_2$: 172.0210; found: 172.0207.

Synthesis of *N,N*-dimethyl-4-(difluoromethyl)aniline (15) [CAS: 705-39-5]. Compound **15** was prepared following the standard procedure, starting from 4-(dimethylamino)benzenediazonium tetrafluoroborate [CAS: 24564-52-1] (235 mg, 1.00 mmol). After the aqueous workup and evaporation of the solvent, the resulting suspension was taken up in pentane and filtered. After evaporation of the pentane the crude mixture was purified by kugelrohr distillation and **15** was isolated as red solid (144 mg, 0.84 mmol, 84%). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.38 (d, ^3J(H,H) = 8.8 Hz, 2H), 6.74 (d, ^3J(H,H) = 8.8 Hz, 2H), 6.58 (t, *J* = 57.1 Hz, 1H), 3.01 ppm (s, 6H); ^{19}F NMR (375 MHz, CDCl$_3$): δ = –106.6 ppm; ^{13}C NMR (101 MHz, CDCl$_3$): δ = 151.9, 126.7 (t, ^3J(C,F) = 5.5 Hz, 2C), 121.7 (t, ^2J(C,F) = 22.7 Hz), 111.7 (t, ^1J(C,F) = 236.2 Hz), 111.6 (2C), 40.2 ppm (2C); IR (neat): ν = 2911, 2820, 1660, 1591, 1529, 1363, 1310, 1230, 1163, 1050, 987, 936, 813, 726 cm^{-1}; MS (Ion trap, EI, 70 eV): m/z (%) = 172 [M^{+}+H] (18), 171 (61), 170 (100), 118 (11); m.p.: 57-58 °C; HRMS (EI-TOF) calcd for $C_9H_{10}F_2N$: 170.0781; found: 170.0774.

Synthesis of methyl 4-(difluoromethyl)acetanilide (16) [CAS: 29848-60-0]. Compound **17** was prepared following the standard procedure, starting from 4-acetamidobenzenediazonium tetrafluoroborate [CAS: 19089-87-3] (249 mg, 1.00 mmol). After column chromatography, **16** and the protodediazotated compound were separated by precipitation of **16** from pentane and chloroform as colorless solid (141 mg, 0.76 mmol, 76%). ^{1}H NMR (400 MHz, MeOD-d$_4$): δ = 7.67 (d, ^{3}J(H,H) = 8.6 Hz, 2H), 7.46 (d, ^{3}J(H,H) = 8.5 Hz, 2H), 6.69 (t, J = 56.6 Hz, 1H), 2.13 ppm (s, 3H); ^{19}F NMR (375 MHz, $CDCl_3$): δ = –109.7 ppm (d, J = 55.9 Hz); ^{13}C NMR (101 MHz, MeOD-d$_4$): δ = 172.0, 142.4, 131.6 (t, ^{2}J(C,F) = 22.7 Hz, 2C), 127.5 (t, ^{3}J(C,F) = 6.4 Hz, 2C), 120.9 (2C), 116.4 (t, ^{1}J(C,F) = 236.2 Hz), 24.1 ppm; IR (neat): ν = 3267, 3203, 3137, 3083, 2972, 2872, 1670, 1609, 1545, 1520, 1413, 1374, 1324, 1270, 1219, 1065, 1014, 845, 807, 759 cm^{-1}; MS (Ion trap, EI, 70 eV): m/z (%) = 186 [M^{+}+H] (29), 185 (100), 143 (90), 142 (45), 124 (14), 93 (27), 43 (25); m.p.: 149-150 °C; HRMS (EI-TOF) calcd for $C_9H_9NOF_2$: 185.0652; found: 185.0647.

Synthesis of methyl 4-(difluoromethyl)benzoate (17) [CAS: 444915-76-8]. Compound **17** was prepared following the standard procedure, starting from 4-(methoxycarbonyl)benzenediazonium tetrafluoroborate[6] (222 mg, 1.00 mmol). After purification, **17** was isolated as colorless solid (134 mg, 0.72 mmol, 72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (d, ^{3}J(H,H) = 8.4 Hz, 2H), 7.60 (d, ^{3}J(H,H) = 8.2 Hz, 2H), 6.70 (t, J = 56.1 Hz, 1H), 3.95 ppm (s, 3H); ^{19}F NMR (375 MHz, $CDCl_3$): δ = –113.3 ppm (d, J = 55.9 Hz); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.2, 138.4 (t, ^{2}J(C,F) = 21.8 Hz), 132.3, 130.0 (2C), 125.6 (t, ^{3}J(C,F) = 5.8 Hz, 2C), 114.0 (t, ^{1}J(C,F) = 239.8 Hz), 52.4 ppm; IR (neat): ν = 3011, 2959, 2854, 1721, 1582, 1440, 1371, 1279, 1216, 1112, 1072, 1014, 958, 850, 770 cm^{-1}; MS (Ion trap, EI, 70 eV): m/z (%) = 186 [M^{+}] (12), 155 (100), 127 (33); HRMS (EI-TOF) calcd for $C_9H_8O_2F_2$: 186.0492; found: 186.0484.

Synthesis of (4-(difluoromethyl)phenyl)(phenyl)methanone (18) [CAS: 64747-73-5]. Compound **18** was prepared following the standard procedure, starting from 4-benzoylbenzenediazonium tetrafluoroborate [CAS: 32785-41-4] (296 mg, 1.00 mmol). After purification, **18** was isolated as yellow oil (164 mg, 0.71 mmol, 71%). ^{1}H NMR

(400 MHz, $CDCl_3$): $\delta = 7.89$ (d, ^3J(H,H) = 8.4 Hz, 2H), 7.82–7.80 (m, 2H), 7.66–7.63 (m, 3H), 7.53–7.49 (m, 2H), 6.74 ppm (t, $J = 56.2$ Hz, 1H); ^{19}F NMR (375 MHz, $CDCl_3$): $\delta = -112.0$ ppm (d, $J = 55.9$ Hz); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 195.9$, 139.7, 137.8 (t, ^2J(C,F) = 22.4 Hz), 137.0, 132.9 (2C), 130.2 (2C), 130.1 (2C), 128.4 (2C), 125.6 (t, ^3J(C,F) = 5.9 Hz), 114.0 ppm (t, ^1J(C,F) = 239.8 Hz); IR (neat): ν = 3063, 2971, 1649, 1597, 1418, 1369, 1309, 1278, 1217, 1122, 1070, 1016, 974, 939, 922, 841, 791, 748, 693, 658 cm^{-1}; MS (Ion trap, EI, 70 eV): m/z (%) = 233 [$M^+ + H$] (20), 232 (65), 181 (17), 155 (46), 127 (24), 105 (100), 77 (36), 51 (23), 50 (14); HRMS (EI-TOF) calcd for $C_{14}H_{10}OF_2$: 232.0700; found: 232.0701.

Synthesis of (2-(difluoromethyl)phenyl)(phenyl)methanone (19) [CAS: 1188475-55-9]. Compound **19** was prepared following the standard procedure, starting from 2-benzoylbenzenediazonium tetrafluoroborate [CAS: 342-62-1] (296 mg, 1.00 mmol). After purification, **19** was isolated as yellow oil (100 mg, 0.43 mmol, 43%). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.84$–7.81 (m, 3H), 7.65–7.62 (m, 2H), 7.49–7.47 (m, 4H), 7.07 ppm (t, $J = 55.8$ Hz, 1H); ^{19}F NMR (375 MHz, $CDCl_3$): $\delta = -112.3$ ppm (d, $J = 55.5$ Hz); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 196.6$, 137.3 (t, ^3J(C,F) = 5.1 Hz), 137.0, 134.0 (t, ^2J(C,F) = 22.3 Hz), 133.6, 131.0, 130.3 (2C), 129.7, 129.4, 128.5 (2C), 126.2 (t, ^3J(C,F) = 7.0 Hz), 112.3 ppm (t, ^1J(C,F) = 238.4 Hz); IR (neat): ν = 3063, 2970, 1649, 1597, 1418, 1368, 1309, 1277, 1216, 1122, 1070, 1016, 974, 939, 922, 842, 791, 748, 693, 658 cm^{-1}; MS (Ion trap, EI, 70 eV): m/z (%) = 233 [$M^+ + H$] (100), 231 (10), 213 (41), 212 (80), 211 (18), 155 (46), 127 (24), 107 (12), 105 (95), 77 (12), 51 (10); HRMS (EI-TOF) calcd for $C_{14}H_{10}OF_2$: 232.0700; found: 232.0711.

Synthesis of 1-(difluoromethyl)-3-nitrobenzene (20) [CAS: 403-25-8]. Compound **20** was prepared following the standard procedure, starting from 3-nitrobenzenediazonium tetrafluoroborate [CAS: 586-36-7] (237 mg, 1.00 mmol). After purification, **20** was isolated as light yellow oil (114 mg, 0.66 mmol, 66%). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.41$ (s, 1H), 8.37 (m, 1H), 7.88 (d, ^3J(H,H) = 7.8 Hz, 1H), 7.70 (t, ^3J(H,H) = 8.0 Hz, 1H), 6.76 ppm (t, $J = 55.9$ Hz, 1H); ^{19}F NMR (375 MHz, $CDCl_3$): $\delta = -112.1$ ppm (d, $J = 55.9$ Hz); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 148.3$, 136.1 (t, ^2J(C,F) = 23.6 Hz), 131.5 (t, ^3J(C,F) = 5.5 Hz), 130.1, 125.6, 121.0 (t, ^3J(C,F) = 6.4 Hz), 113.1 ppm (t, ^1J(C,F) = 241.1 Hz); IR (neat): ν = 3096, 2970, 1533, 1484, 1349, 1219, 1100, 1031, 940, 901, 808, 740, 707 cm^{-1}; MS (Ion trap, EI, 70 eV): m/z (%) = 173 [M^+] (100), 157 (14), 154 (21), 143 (39), 127 (78), 115 (11), 107 (29), 101 (32), 95 (13), 77 (30), 75 (13), 63 (10), 57 (14), 51 (21), 50 (22), 46 (15); HRMS (EI-TOF) calcd for $C_7H_5NO_2F_2$: 173.0288; found: 173.0281.

Synthesis of 2-(3-(difluoromethyl)phenyl)-1,1-difluoropropan-2-ol (21). Compound **21** was prepared following the standard procedure, starting from 3-acetylbenzenediazonium tetrafluoroborate[7] (234 mg, 1.00 mmol). After purification, **21** was isolated as colorless oil (75 mg, 0.34 mmol, 34%).^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (s, 1H), 7.65-7.63 (m, 1H), 7.51-7.49 (m, 2H), 6.68 (t, J = 56.3 Hz, 1H), 5.72 (t, J = 56.3 Hz, 1H), 1.69 ppm (s, 3H); ^{19}F NMR (375 MHz, $CDCl_3$): δ = –110.7 ppm (d, J = 55.9 Hz), –129.9 ppm (qd, ^1J = 277.9 Hz, ^2J = 55.9 Hz); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 141.0, 134.6 (t, ^2J(C,F) = 22.4 Hz), 128.9, 128.2, 125.3 (t, ^3J(C,F) = 6.2 Hz), 123.1 (t, ^3J(C,F) = 6.2 Hz), 116.6 (t, ^1J(C,F) = 249.4 Hz), 114.6 (t, ^1J(C,F) = 238.6 Hz), 74.1 (t, ^2J(C,F) = 22.0 Hz), 22.5 ppm (t, ^3J(C,F) = 2.2 Hz); IR (neat): ν = 3441, 2989, 1448, 1372, 1167, 1053, 805, 705 cm^{-1}; MS (Ion trap, EI, 70 eV): m/z (%) = 171 [M^++H] (100), 43 (61); HRMS (EI-TOF) calcd for $C_{10}H_9OF_4$: 221.0590; found: 221.0588.

Synthesis of 1-(6-(difluoromethyl)benzo[d][1,3]dioxol-5-yl)ethanone (22). Compound **22** was prepared following the standard procedure, starting from 6-acetylbenzo[d][1,3]dioxole-5-diazonium tetrafluoroborate (278 mg, 1.00 mmol). After purification, **22** was isolated as light yellow solid (88 mg, 0.41 mmol, 41%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 (t, J = 55.6 Hz, 1H), 7.29 (s, 1H), 7.28 (s, 1H), 6.12 (s, 2H), 2.58 ppm (s, 3H); ^{19}F NMR (375 MHz, $CDCl_3$): δ = –111.2 ppm (d, J = 55.9 Hz); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 198.2, 150.9, 148.9, 131.0, 130.5, 111.6 (t, ^1J(C,F) = 237.8 Hz), 109.7, 106.8 (t, ^3J(C,F) = 8.8 Hz), 102.5, 28.8 ppm; IR (neat): ν = 2916, 1683, 1617, 1509, 1493, 1392, 1363, 1266, 1241, 1116, 1068, 1036, 882 cm^{-1}; MS (Ion trap, EI, 70 eV): m/z (%) = 214 [M^+] (71), 159 (100), 171 (23), 115 (13), 63 (13); m.p.: 70-71 °C; HRMS (EI-TOF) calcd for $C_{10}H_8O_3F_2$: 214.0442; found: 214.0440.

Synthesis of 6-(difluoromethyl)quinoline (23) [CAS: 1416806-01-3]. Compound **23** was prepared following the standard procedure, starting from quinoline-6-diazonium tetrafluoroborate[6] (243 mg, 1.00 mmol). After purification, **23** was isolated as light yellow oil (86 mg, 0.48 mmol, 48%). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 9.00 (s, 1H), 8.22 (t, ^{3}J(H,H) = 9.2 Hz, 2H), 8.00 (s, 1H), 7.84 (d, ^{3}J(H,H) = 8.2 Hz, 1H), 7.51-7.47 (m, 1H), 6.84 ppm (t, J = 56.2 Hz, 1H); ^{19}F NMR (375 MHz, CDCl$_3$): δ = –111.4 ppm (d, J = 55.9 Hz); ^{13}C NMR (101 MHz, CDCl$_3$): δ = 151.8, 148.9, 136.6, 132.4 (t, ^{2}J(C,F) = 22.3 Hz, 1C), 130.5, 127.5, 125.8 (t, ^{3}J(C,F) = 5.5 Hz, 1C), 125.7, 121.9, 114.4 ppm (t, ^{1}J(C,F) = 239.4 Hz, 1C); IR (neat): ν = 2989, 2870, 1635, 1599, 1506, 1472, 1398, 1353, 1321, 1168, 1121, 1085, 1070, 1028, 895, 841, 794 cm^{-1}; MS (Ion trap, EI, 70 eV): m/z (%) = 180 [M^{+}+H] (17), 179 (100), 178 (31), 129 (36), 51 (11); HRMS (EI-TOF) calcd for $C_{10}H_7NF_2$: 179.0547; found: 179.0539.

Synthesis of 3-(difluoromethyl)quinoline (24) [CAS: 1186195-11-8]. Compound **24** was prepared following the standard procedure, starting from quinoline-3-diazonium tetrafluoroborate[7] (243 mg, 1.00 mmol). After purification, **24** was isolated as yellow oil (97 mg, 0.54 mmol, 54%). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 9.05 (s, 1H), 8.34 (s, 1H), 8.19 (d, ^{3}J(H,H) = 8.4 Hz, 1H), 7.92 (d, ^{3}J(H,H) = 8.2 Hz, 1H), 7.86–7.82 (m, 1H), 7.67–7.63 ppm (m, 1H), 6.91 ppm (t, J = 55.8 Hz, 1H); ^{19}F NMR (375 MHz, CDCl$_3$): δ = –111.6 ppm (d, J = 55.9 Hz); ^{13}C NMR (101 MHz, CDCl$_3$): δ = 148.9, 147.1 (t, ^{3}J(C,F) = 5.5 Hz), 134.0 (t, ^{3}J(C,F) = 6.4 Hz), 131.1, 129.4, 128.4, 127.7, 127.2, 126.9, 113.6 ppm (t, ^{1}J(C,F) = 239.4 Hz); IR (neat): ν = 2989, 2870, 1635, 1599, 1506, 1471, 1398, 1353, 1321, 1168, 1121, 1085, 1069, 1028, 895, 841, 794 cm^{-1}; MS (Ion trap, EI, 70 eV): m/z (%) = 180 [M^{+}+H] (64), 179 (100), 178 (24), 129 (27), 101 (10), 51 (10); HRMS (EI-TOF) calcd for $C_{10}H_7NF_2$: 179.0547; found: 179.0537.

Synthesis of 9-ethyl-3-(difluoromethyl)-9H-carbazole (25). Compound **25** was prepared following the standard procedure, starting from 9-ethyl-9*H*-carbazol-3-diazonium tetrafluoroborate[8] (309 mg, 1.00 mmol). After purification, **25** was isolated as yellow oil (191 mg, 0.78 mmol, 78%). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.27 (s, 1H), 8.14 (d, ^{3}J(H,H) = 7.8 Hz, 1H), 7.62 (d, ^{3}J(H,H) = 8.5 Hz, 1H), 7.53 (m, 1H), 7.46 (m, 2H), 7.30 (m, 1H), 6.87 (t, J = 57.0 Hz, 1H), 4.40 (q, ^{3}J(H,H) = 7.3 Hz, 2H), 1.46 ppm (t, ^{3}J(H,H) = 7.3 Hz, 3H); ^{19}F NMR (375 MHz, CDCl$_3$): δ = –106.7 ppm (d, J = 57.2 Hz); ^{13}C NMR (101 MHz, CDCl$_3$): δ = 141.0, 140.4, 126.3, 125.0 (t, ^{2}J(C,F) = 22.3 Hz), 122.9 (t, ^{3}J(C,F) = 5.5 Hz), 122.7 (t, ^{3}J(C,F) = 3.6 Hz), 120.6, 119.4, 118.2, 118.2, 115.9 (t, ^{1}J(C,F) = 237.1 Hz), 108.8, 108.6, 37.7, 13.8 ppm; IR (neat): ν = 2976, 2873, 1603, 1472, 1373, 1348, 1334, 1232, 1189, 1126, 1058, 1003, 890, 808, 770, 749, 730, 719 cm^{-1}; MS (Ion trap, EI, 70 eV): m/z (%) = 246 [M^++H] (14), 245 (79), 231 (15), 230 (100); HRMS (EI-TOF) calcd for $C_{15}H_{13}NF_2$: 245.1016; found: 245.1017.

Synthesis of 1-bromo-4-(difluoromethyl)naphthalene (26). Compound **26** was prepared following the standard procedure, starting from 4-bromonaphthalen-1-yldiazonium tetrafluoroborate [CAS: 341-89-9] (321 mg, 1.00 mmol). After purification, **26** was isolated as orange oil (144 mg, 0.56 mmol, 56%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.36 (m, 1H), 8.17 (m, 1H), 7.85 (d, ^3J(H,H) = 7.7 Hz, 1H), 7.68 (m, 2H), 7.56 (d, ^3J(H,H) = 7.7 Hz, 1H), 7.13 ppm (t, J = 56.2 Hz, 1H); ^{19}F NMR (375 MHz, $CDCl_3$): δ = –112.2 ppm (d, J = 55.9 Hz); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 132.2, 130.8 (t, ^3J(C,F) = 1.4 Hz), 129.4 (t, ^2J(C,F) = 21.4 Hz), 128.9, 128.1, 128.0, 127.8, 126.7, 124.9 (t, ^3J(C,F) = 9.1 Hz), 123.9, 114.7 ppm (t, ^1J(C,F) = 238.9 Hz); IR (neat): ν = 2962, 2845, 1610, 1498, 1468, 1386, 1290, 1256, 1059, 1025, 755 cm^{-1}; MS (Ion trap, EI, 70 eV): m/z (%) = 233 [M^++H] (100), 231 (10), 213 (41), 212 (80), 211 (18), 155 (46), 127 (24), 107 (12), 105 (95), 77 (12), 51 (10); HRMS (EI-TOF) calcd for $C_{11}H_7F_2Br$: 255.9699; found: 255.9710.

Synthesis of 5-(difluoromethyl)-1H-indole (27). Compound **27** was prepared following the standard procedure, starting from 1H-indole-5-diazonium tetrafluoroborate (231 mg, 1.00 mmol). After purification, **27** was isolated as colorless oil (59 mg, 0.35 mmol, 35%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.32 (s, 1H), 7.81 (s, 1H), 7.48 (d, ^3J(H,H) = 8.4 Hz, 1H), 7.37 (d, ^3J(H,H) = 8.4 Hz, 1H), 7.30 (t, ^3J(H,H) = 2.8 Hz, 1H), 6.77 (t, J = 56.9 Hz, 1H), 6.64 ppm (m, 1H); ^{19}F NMR (375 MHz, $CDCl_3$): δ = –105.9 ppm (d, J = 57.2 Hz); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 136.8, 127.4, 126.2 (t, ^2J(C,F) = 22.0 Hz), 125.4, 119.1 (t, ^3J(C,F) = 5.1 Hz), 118.8 (t, ^3J(C,F) = 6.9 Hz), 116.1 (t, ^1J(C,F) = 237.0 Hz), 111.4, 103.3 ppm; IR (neat): ν = 3416, 2971, 1382, 1325, 1230, 1217, 1076, 1001, 901, 820, 772, 741 cm^{-1}; MS (Ion trap, EI, 70 eV): m/z (%) = 168 [M^+] (12), 167 (100), 166 (77), 148 (30), 119 (10), 117 (30), 89 (17), 63 (15), 51 (13), 50 (12); HRMS (EI-TOF) calcd for $C_9H_7NF_2$: 167.0547; found: 167.0551.

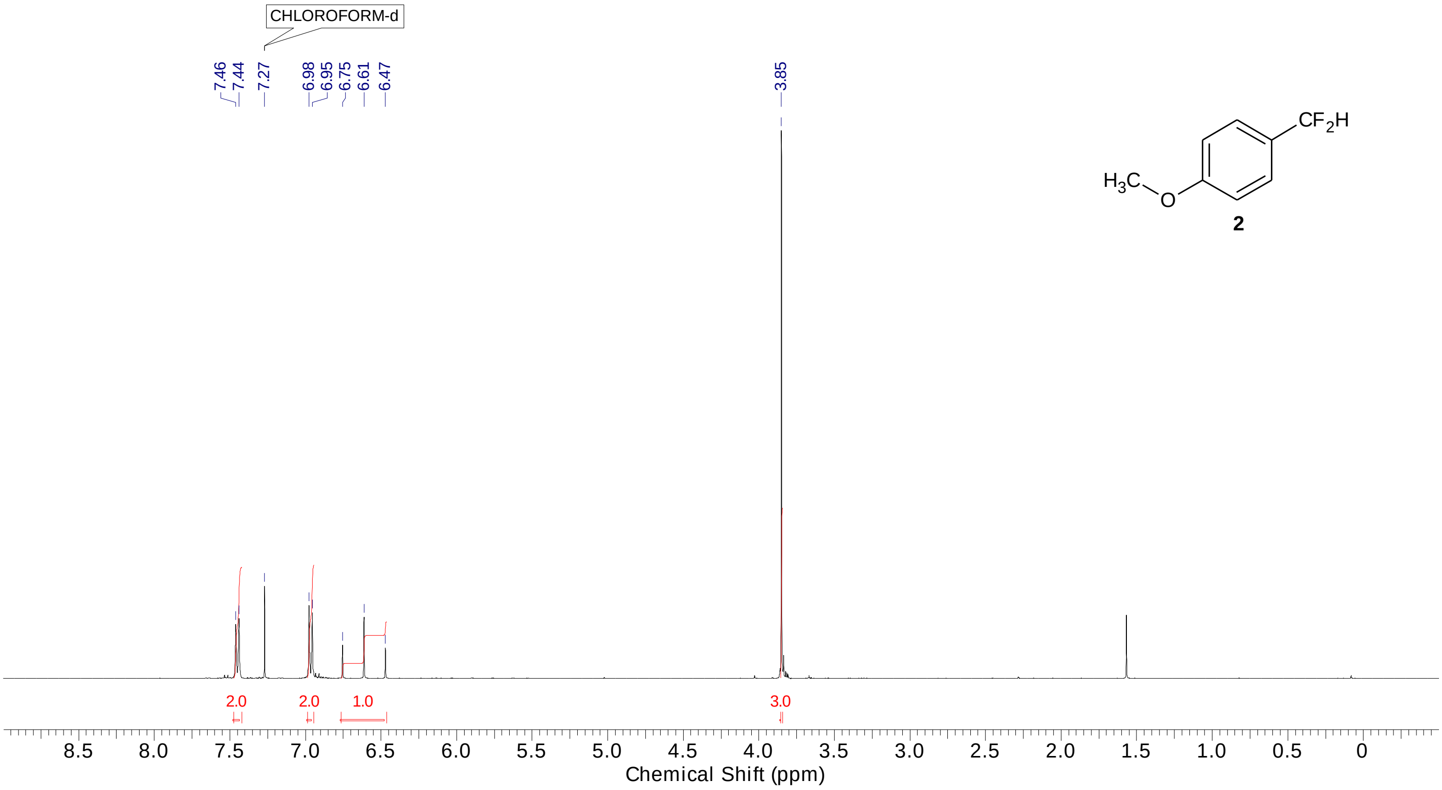
One-pot procedure:

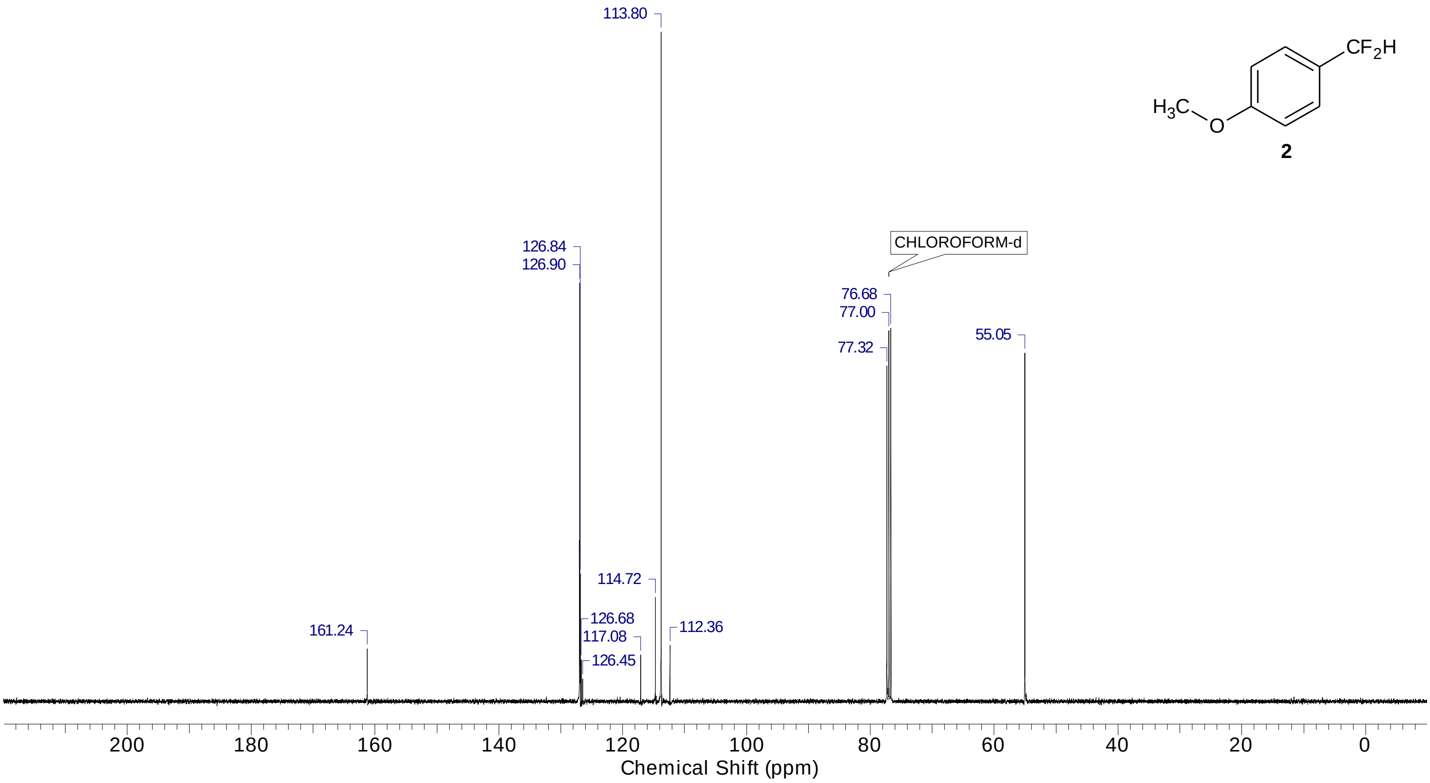
An oven-dried 20 mL crimp cap vessel with Teflon-coated stirrer bar was charged with 4-methoxyaniline (62 mg, 0.50 mmol), *p*-toluenesulfonic acid (129 mg, 0.75 mmol) and DMF (1 mL) under nitrogen. *t*-Butyl nitrite (67 µL, 0.50 mmol) was added dropwise via syringe. The resulting solution was stirred at room temperature for 30 minutes. An oven-dried 20 mL crimp cap vessel with Teflon-coated stirrer bar was charged with copper thiocyanate (61 mg, 0.50 mmol) and caesium fluoride (228 mg, 1.50 mmol) in DMF (1 mL) and difluoromethyltrimethylsilane (156 mg, 1.25 mmol) was added dropwise at 0 °C. The resulting suspension was stirred at 40 °C for 60 min. Afterwards the solution of the generated diazonium salt was added dropwise via syringe at 0 °C. The suspension was stirred at room temperature for 12 h.

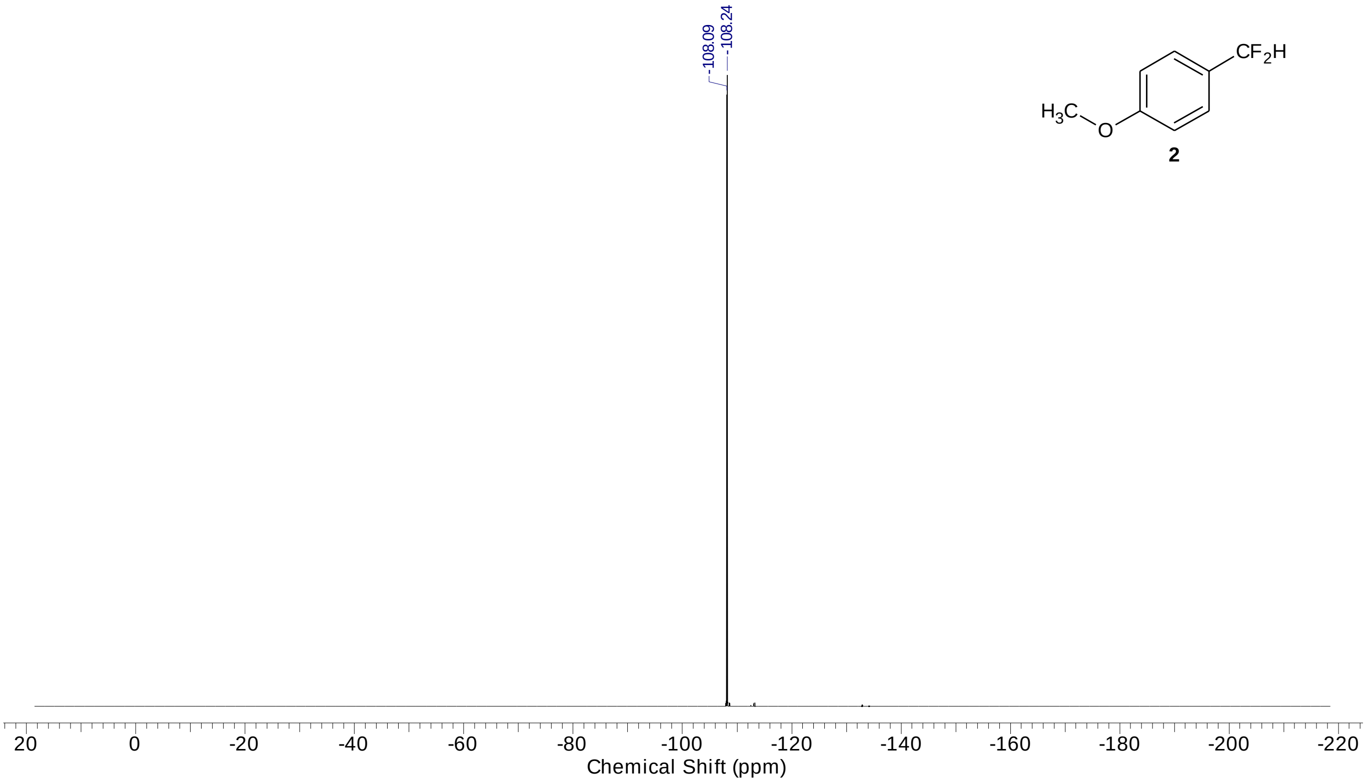
Radical trapping experiment:

Synthesis of 3-(2,2-difluoroethyl)-2,3-dihydrobenzofuran (29). Compound **29** was prepared following the standard procedure, starting from 2-(allyloxy)benzenediazonium salt [CAS: 341-89-9] (248 mg, 1.00 mmol). After purification, **29** was isolated as colorless oil (138 mg, 0.75 mmol, 75%). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.17 (m, 2H), 6.90 (t, ^3J(H,H) = 7.4 Hz, 1H), 6.84 (d, ^3J(H,H) = 7.8 Hz, 1H), 5.97 (tdd, ^3J = 56.1, 4.6 and 3.6 Hz, 1H), 4.72 (t, ^3J(H,H) = 9.0 Hz, 1H), 4.29 (dd, ^3J = 9.0 and 6.9 Hz, 1H), 3.73 (m, 1H), 2.36 (m, 1H), 2.14 ppm (m, 1H); ^{19}F NMR (375 MHz, CDCl$_3$): δ = –116.1 ppm (qm, J = 284.7 Hz); ^{13}C NMR (101 MHz, CDCl$_3$): δ = 159.7, 128.8 (2C), 124.1, 120.7, 116.0 (t, ^1J(C,F) = 239.5 Hz), 109.9, 76.6, 38.7 (t, ^2J(C,F) = 20.5 Hz), 36.1 ppm (t, ^3J(C,F) = 4.8 Hz); IR (neat): ν = 2978, 2893, 1598, 1482, 1461, 1234, 1122, 1075, 1017, 961, 844, 748 cm^{-1}; MS (Ion trap, EI, 70 eV): m/z (%) = 185 [M^++H] (11), 184 (88), 119 (100), 91 (43); HRMS (EI-TOF) calcd for $C_{10}H_9OF_2$: 183.0621; found: 183.0612.

Spectroscopic data



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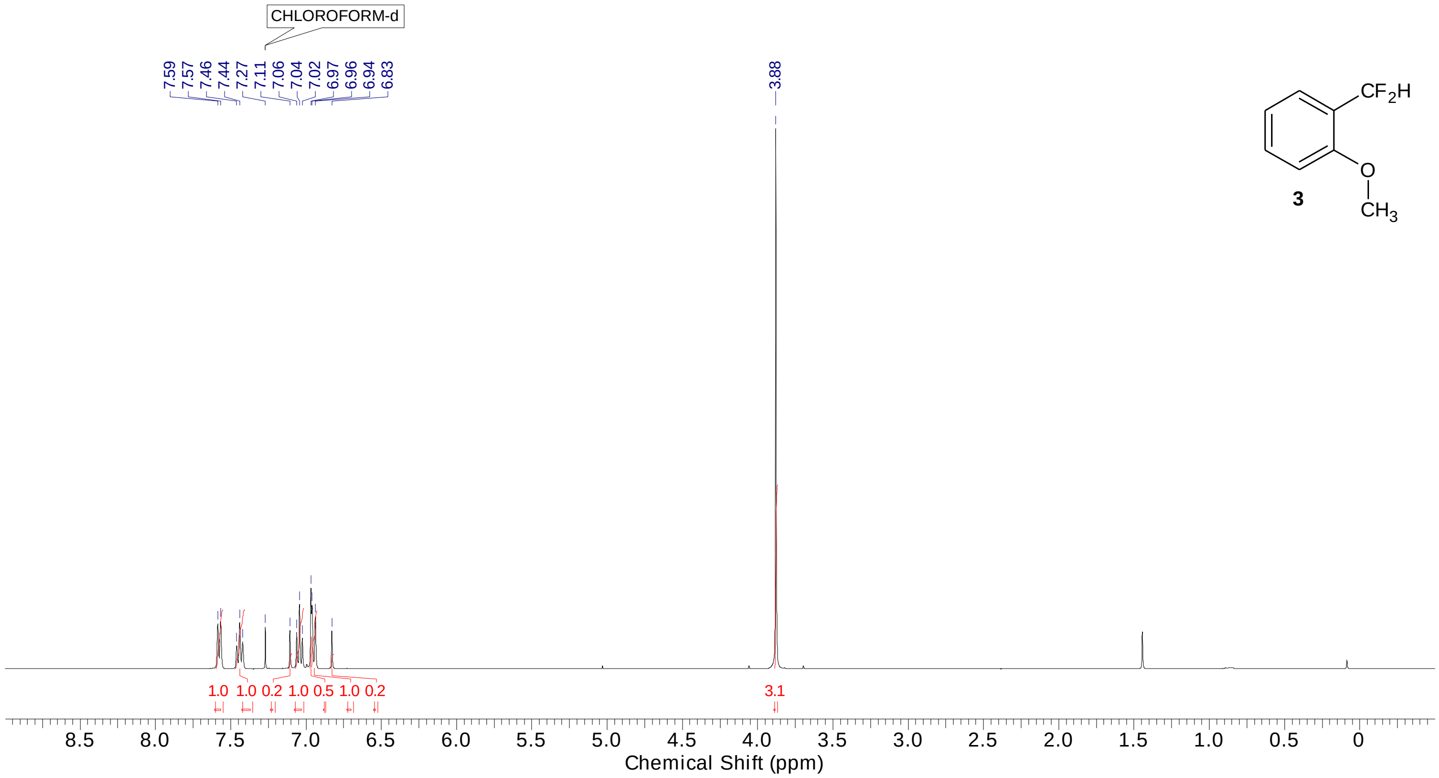
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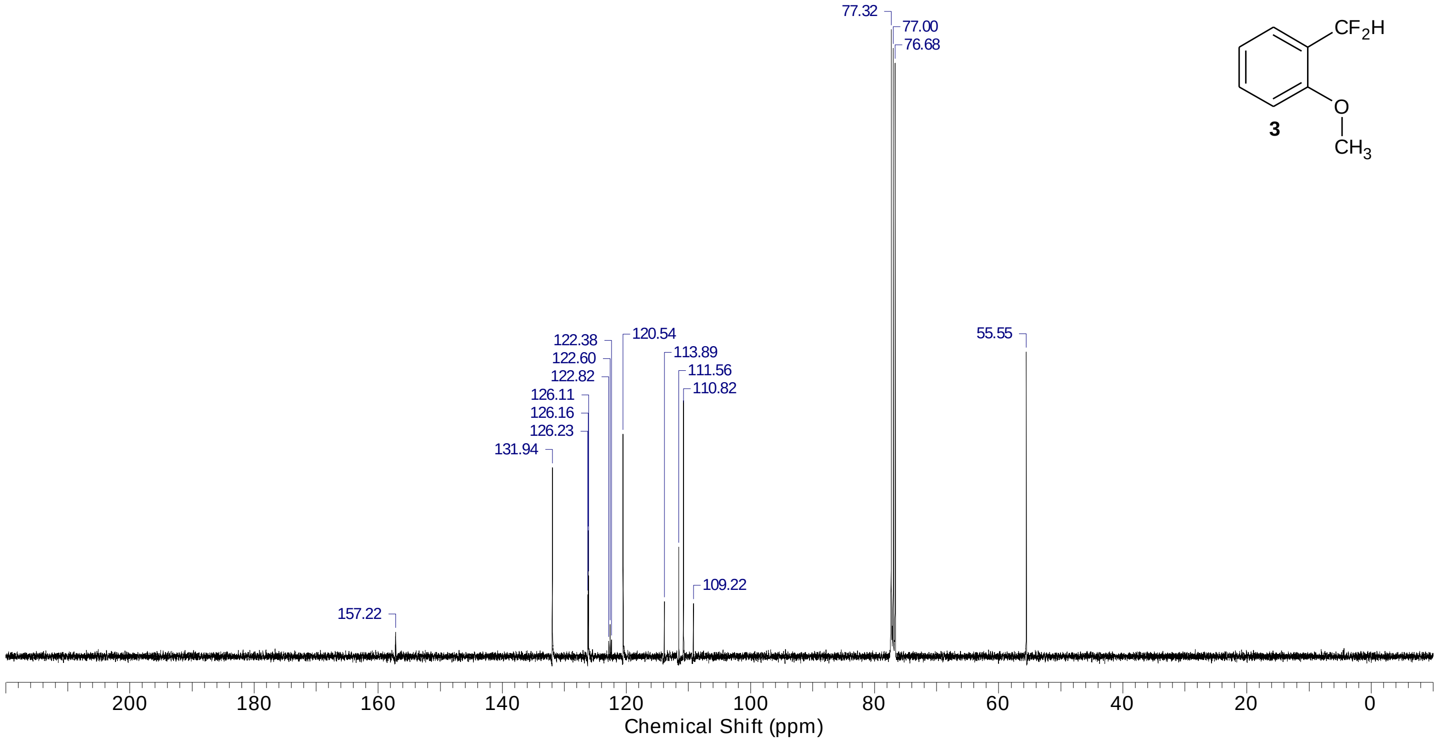
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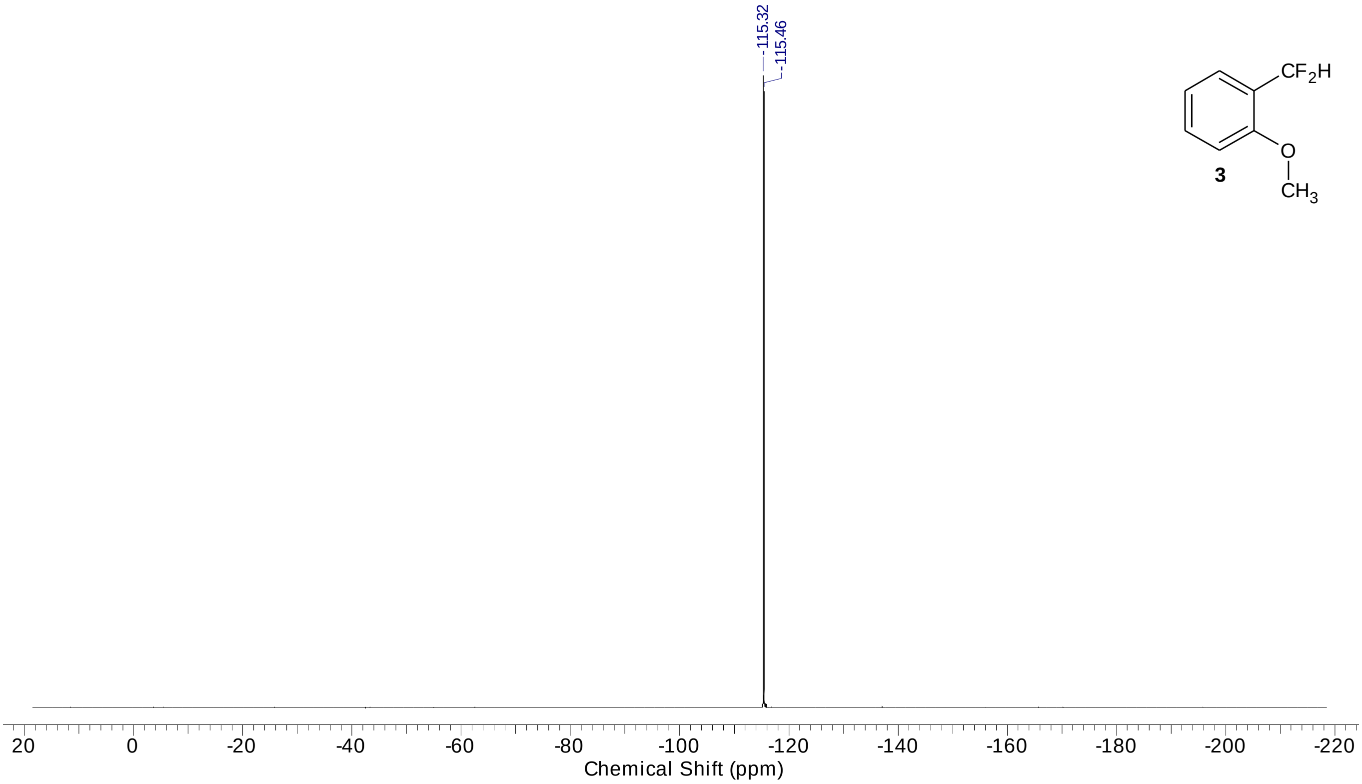
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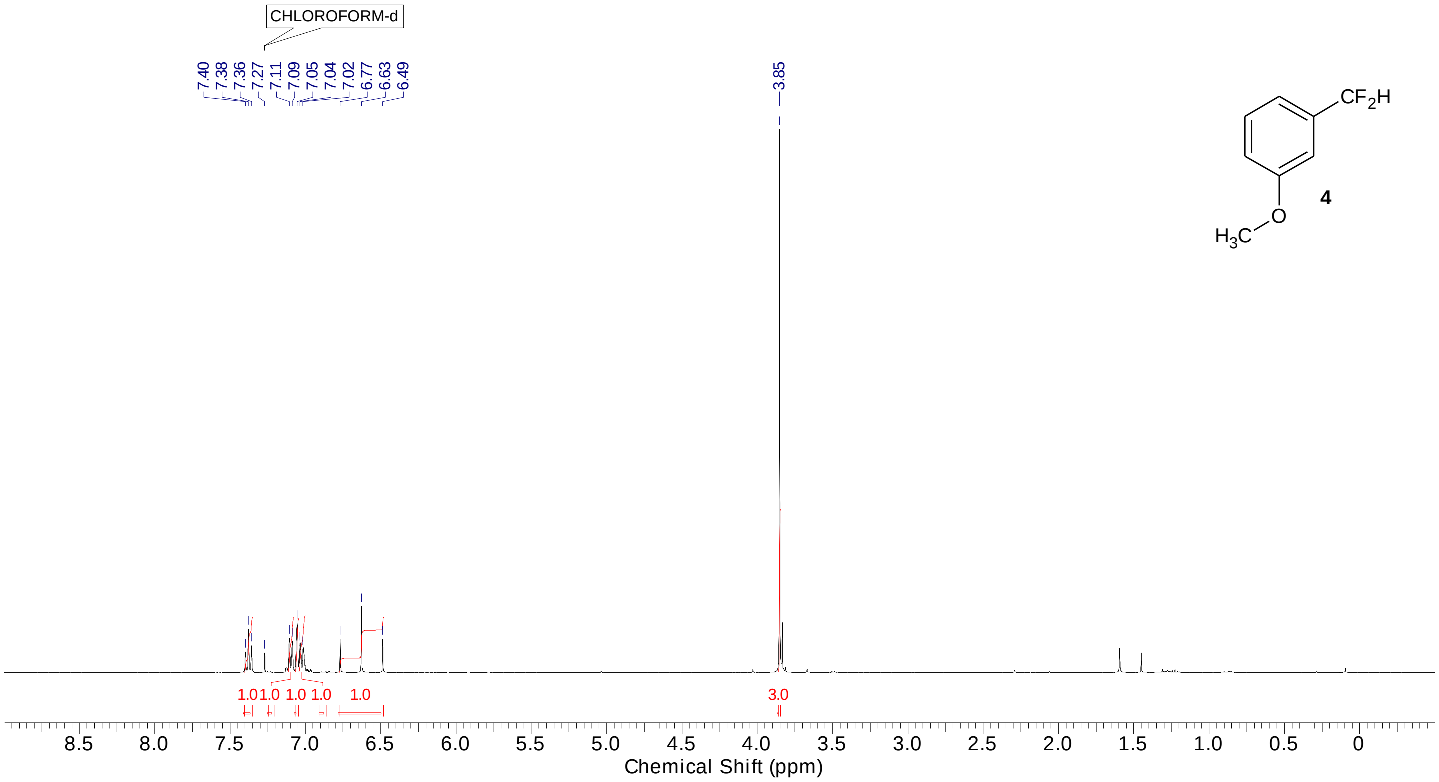
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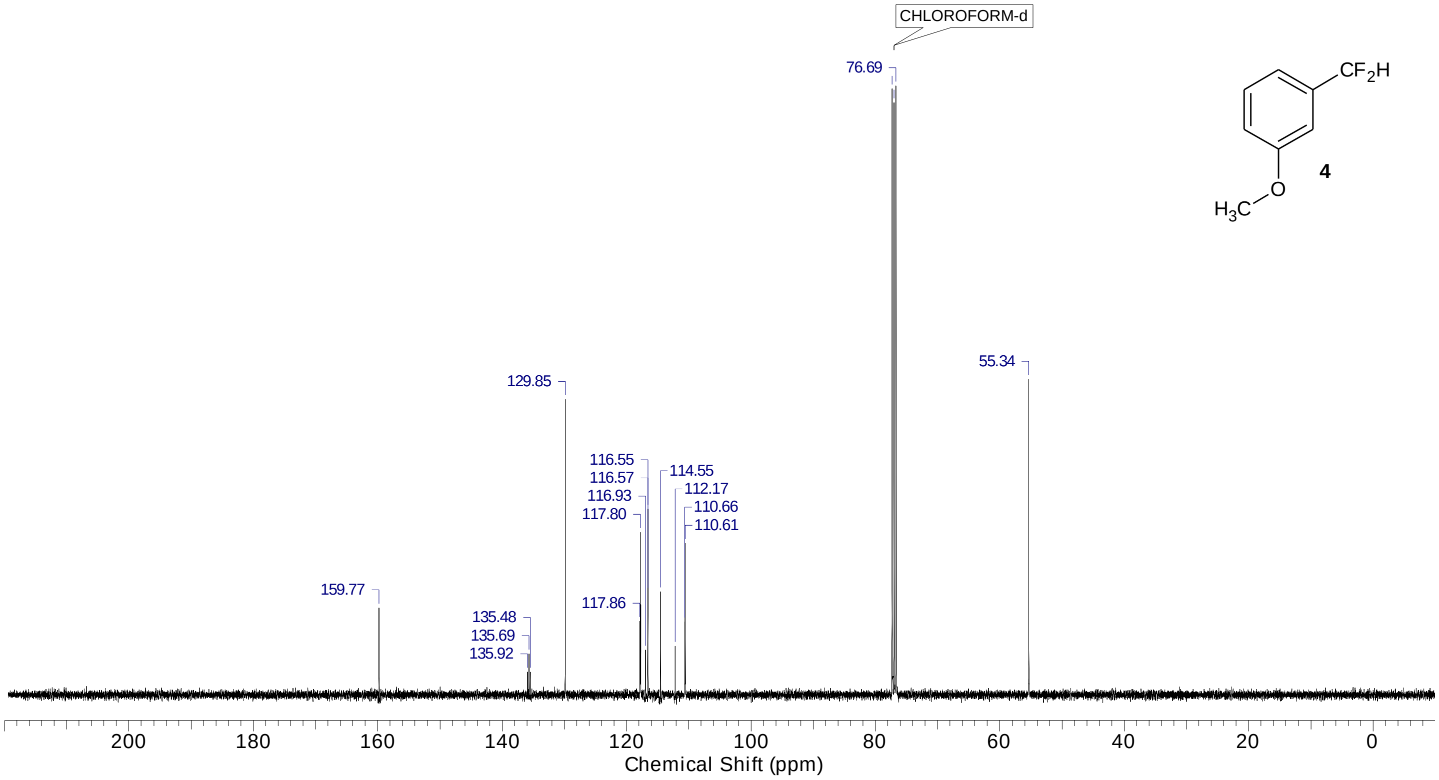
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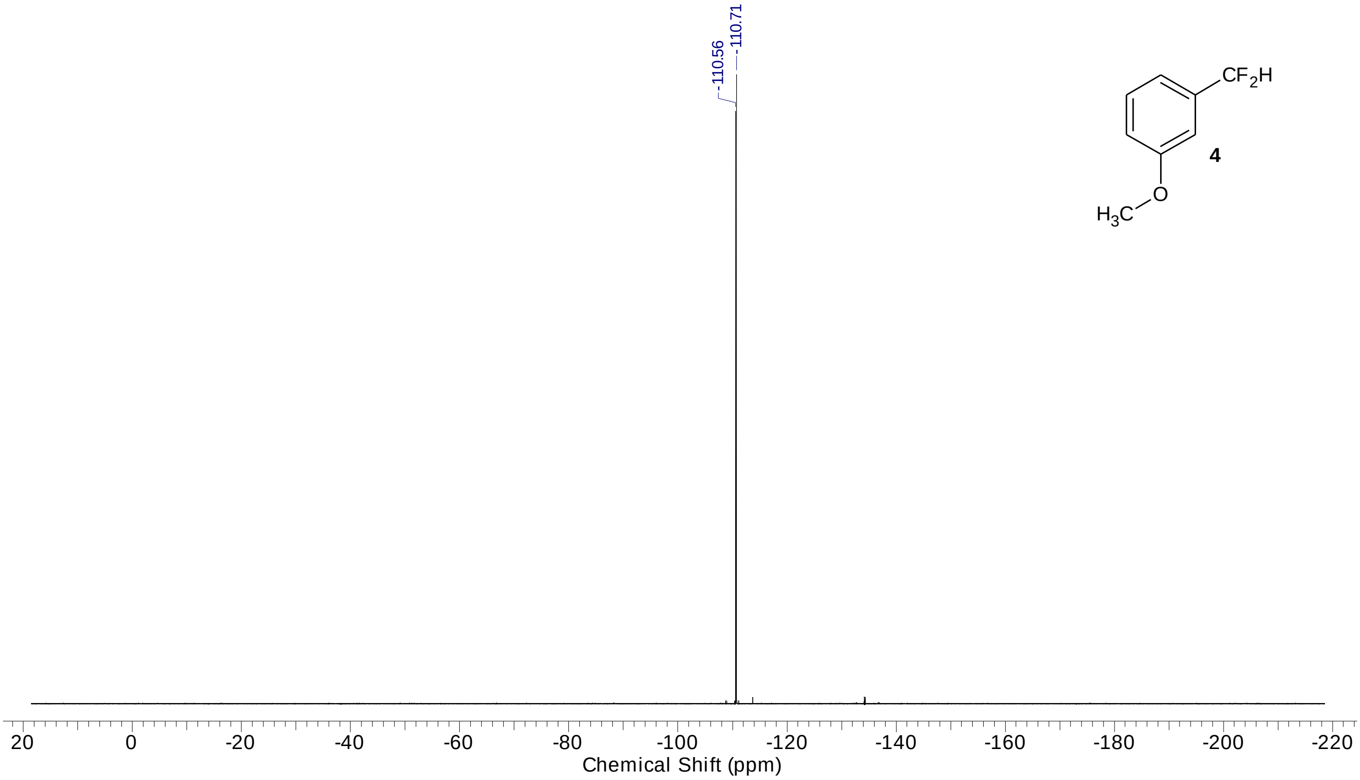
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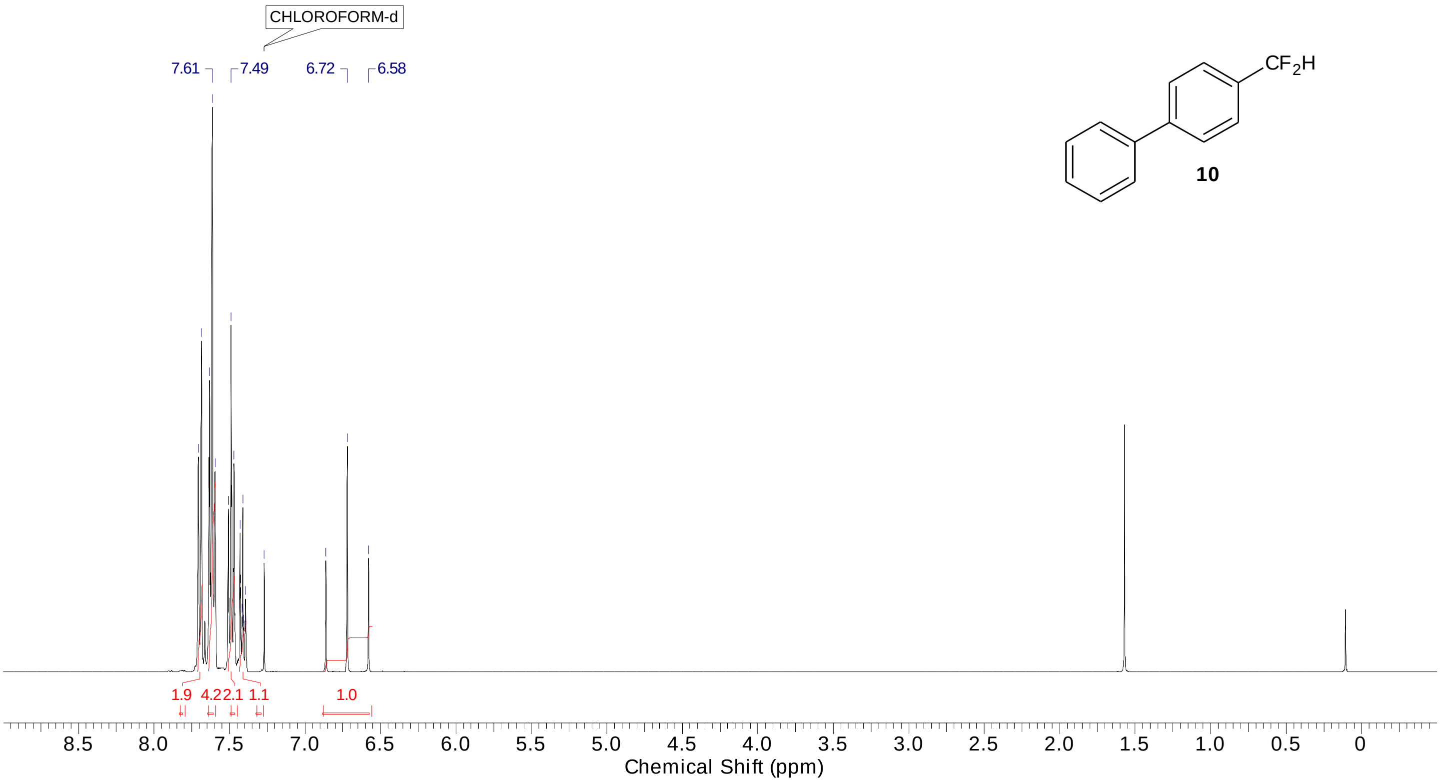
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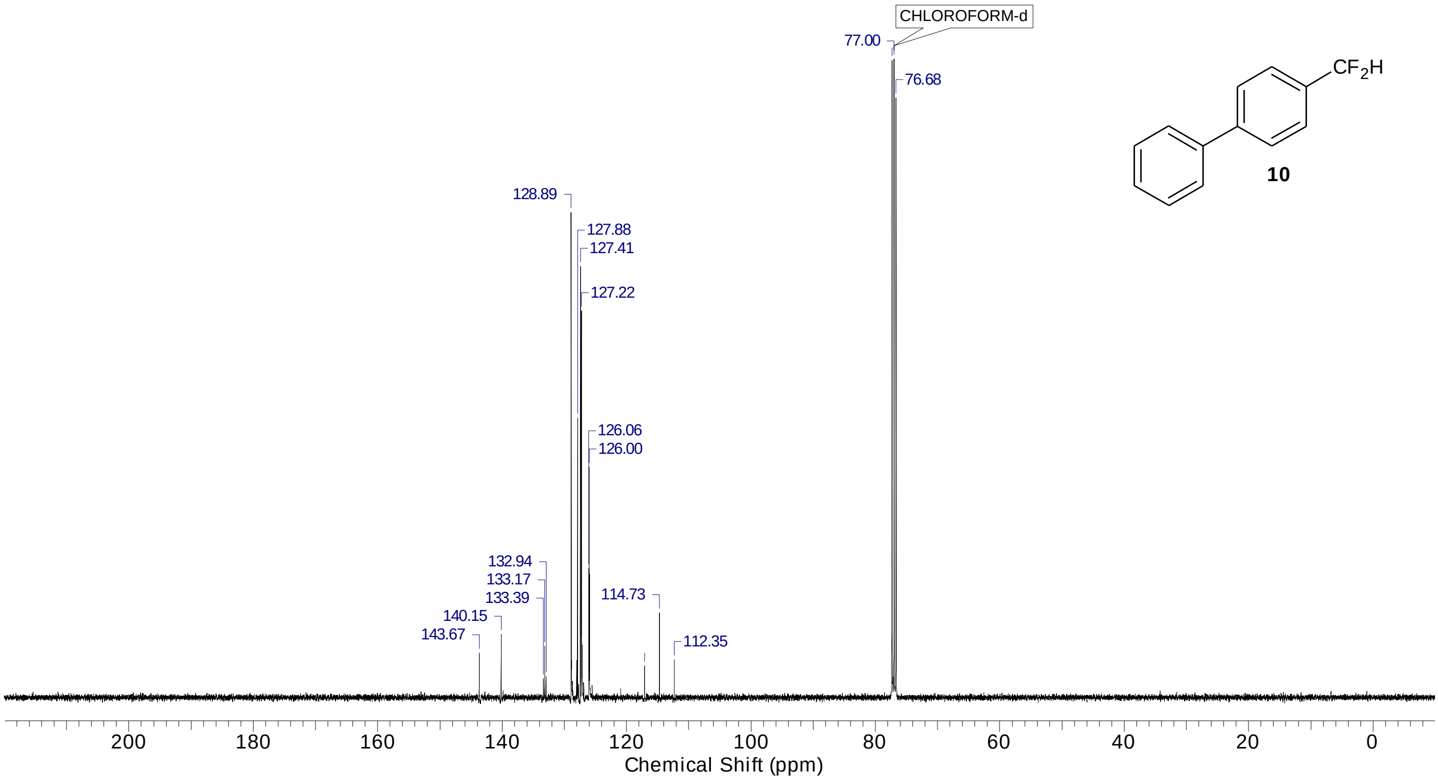
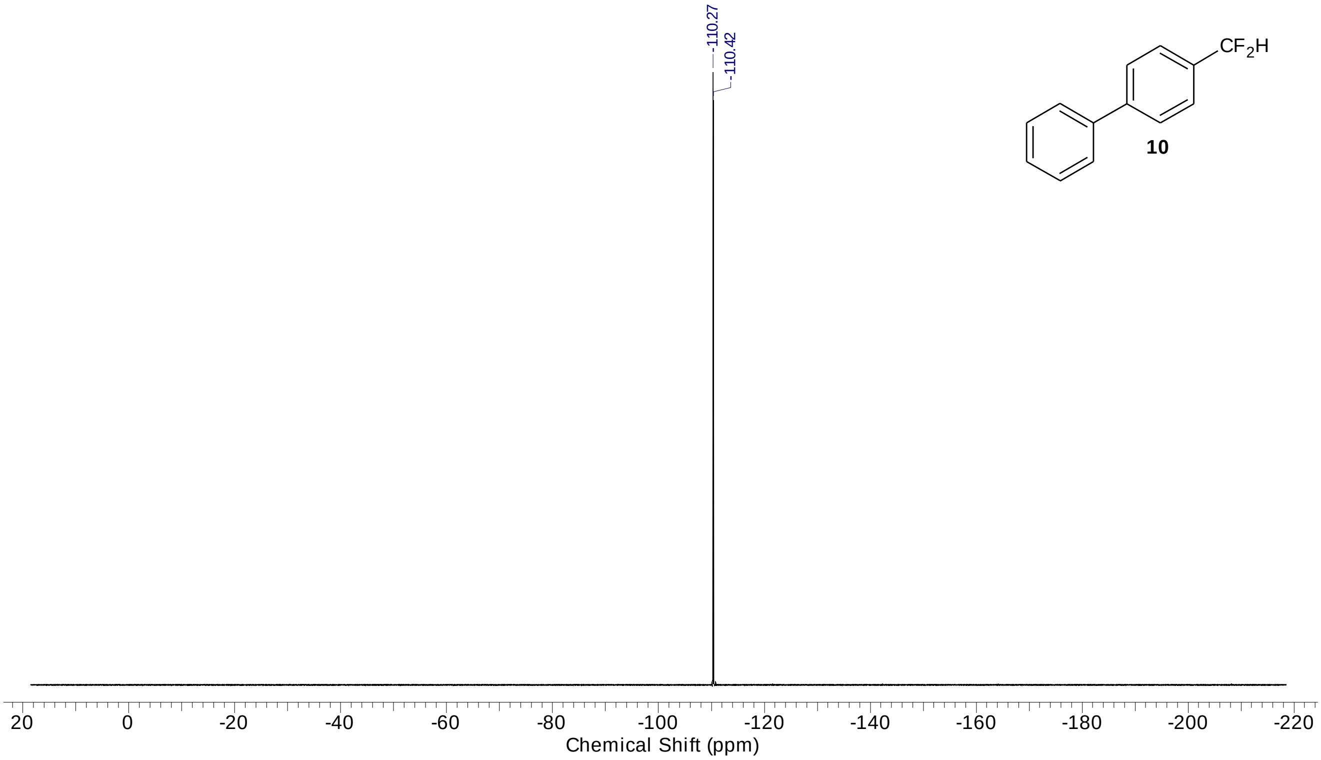
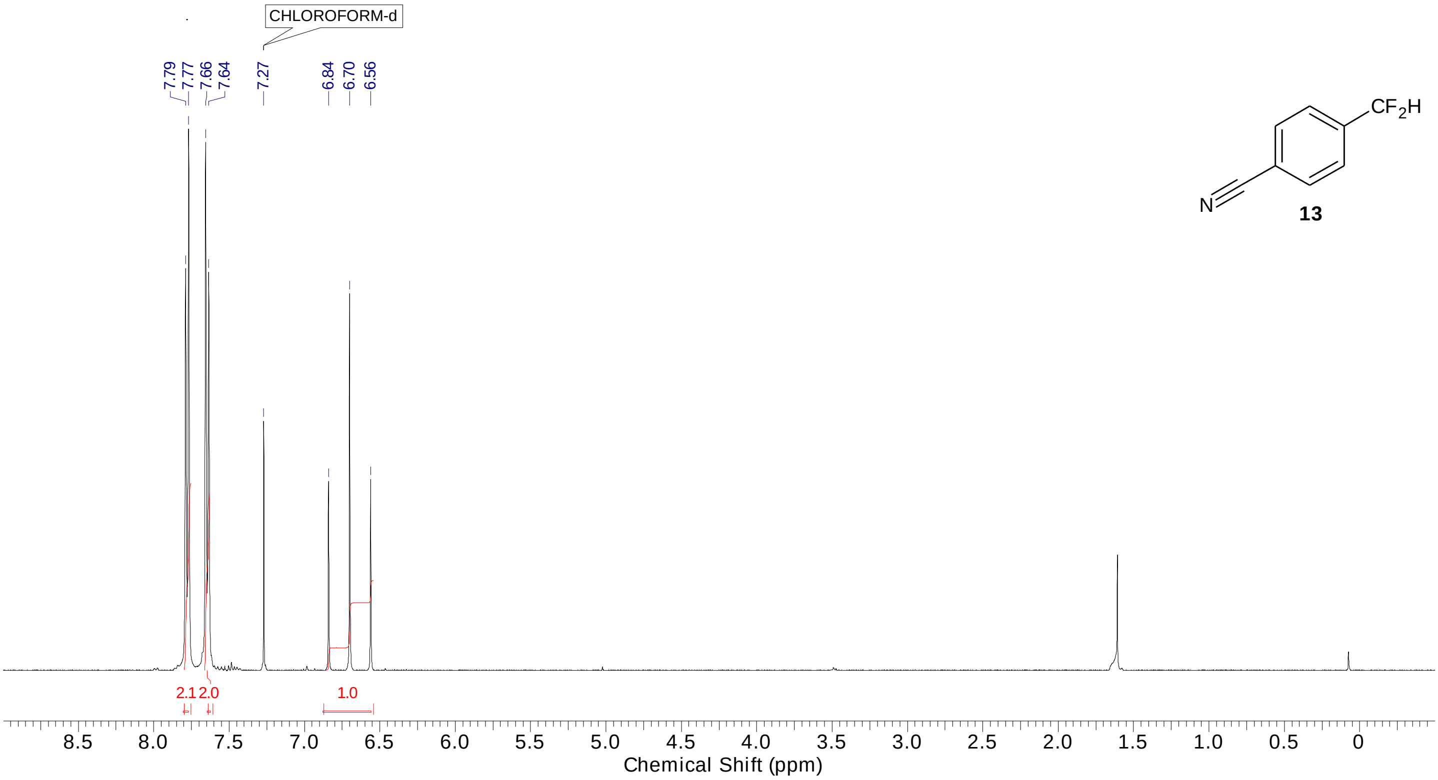
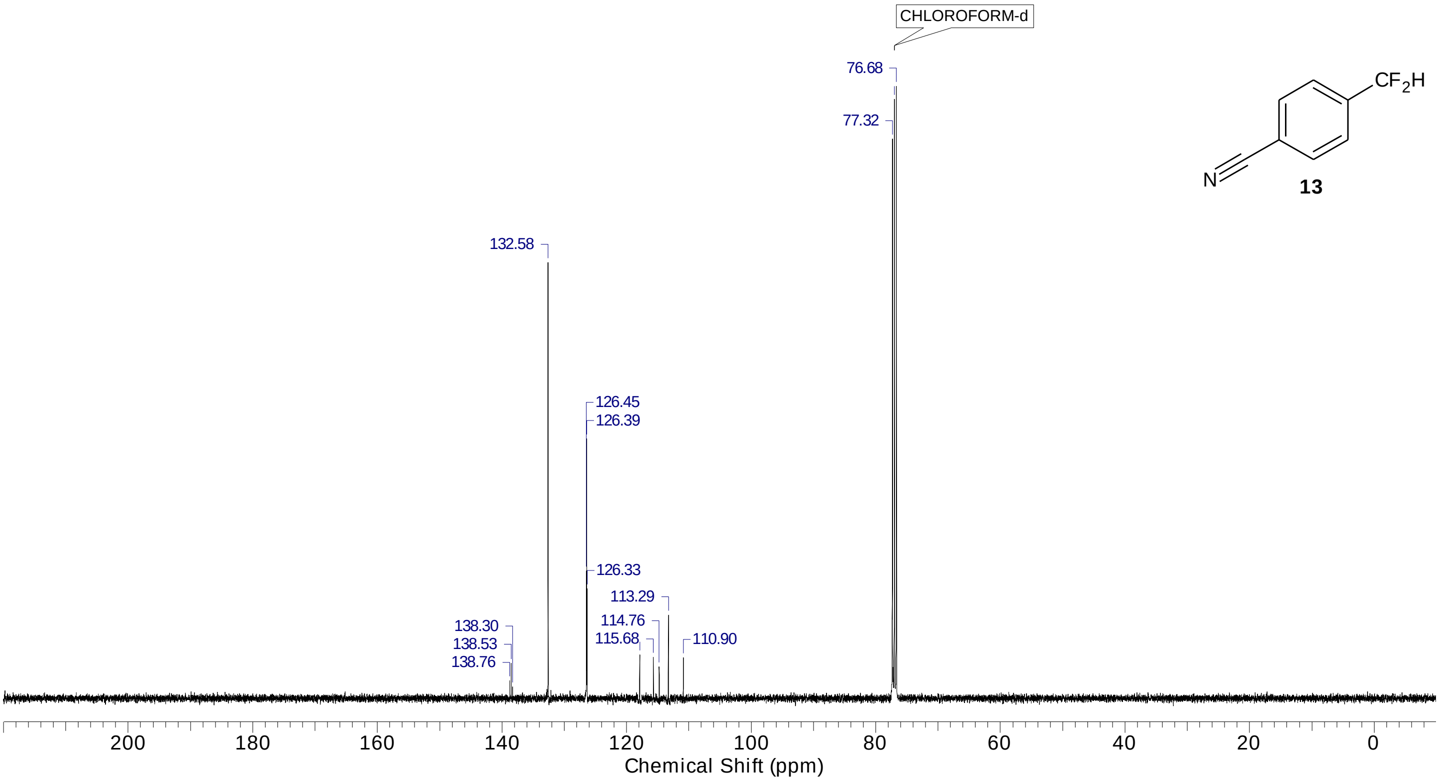

CHLOROFORM-d
77.00
76.68
128.89
127.88
127.41
127.22
126.06
126.00
132.94
133.17
133.39
140.15
143.67
114.73
112.35
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)
CF2H
10

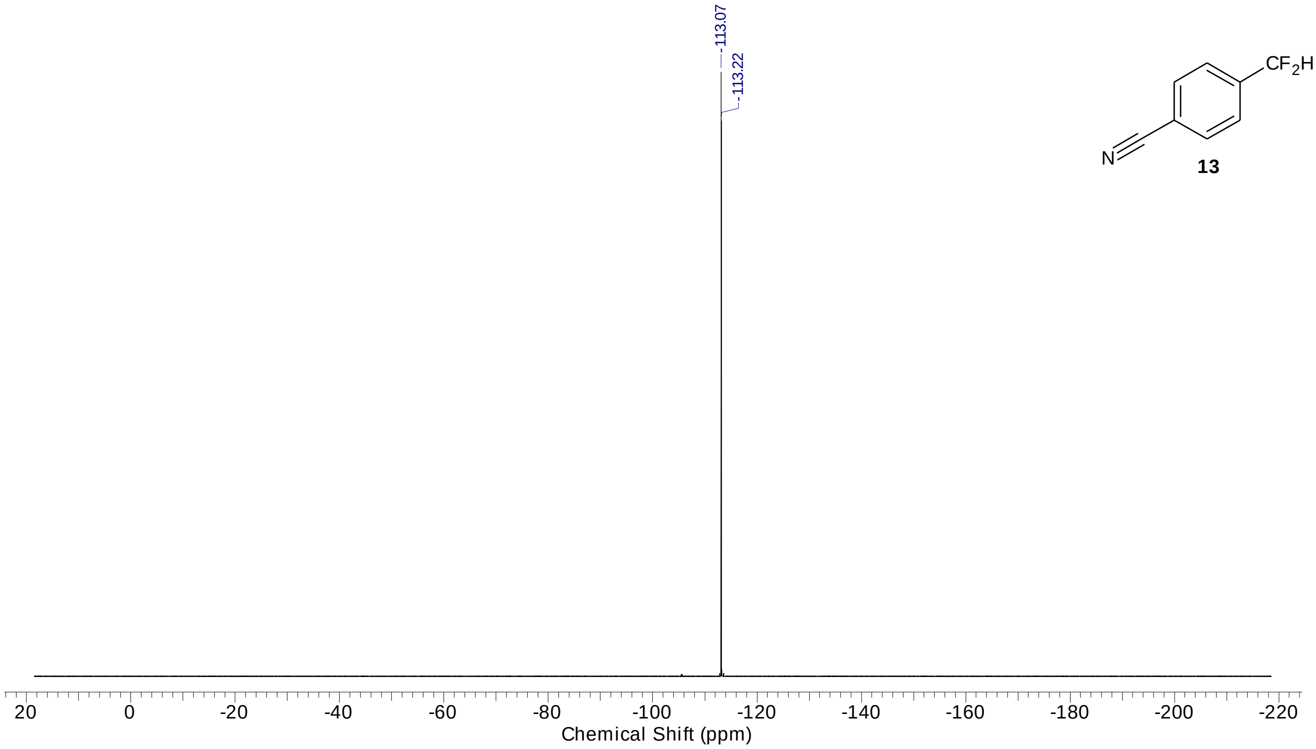

-110.27
-110.42
CF2H
10
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
Chemical Shift (ppm)

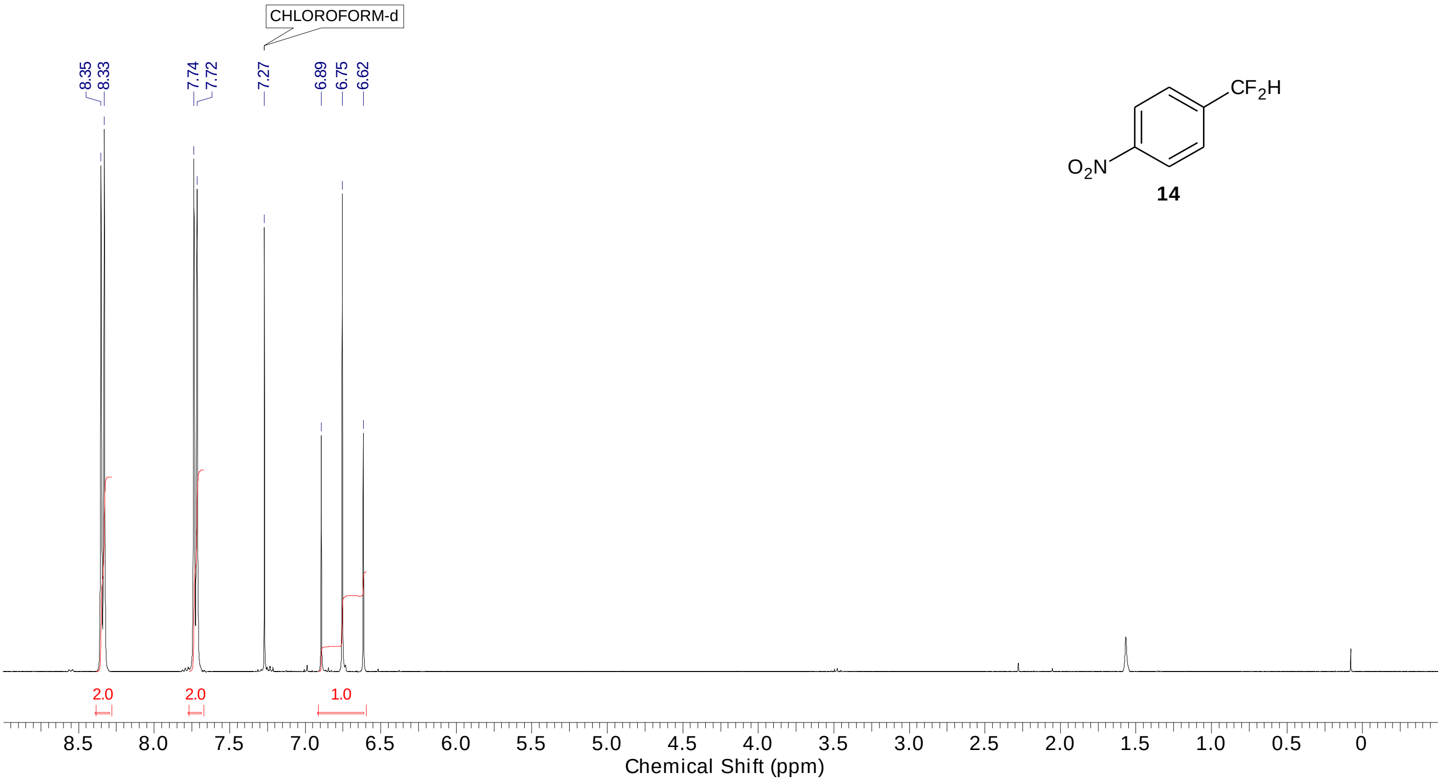

CHLOROFORM-d
7.79
7.77
7.66
7.64
7.27
6.84
6.70
6.56
2.1
2.0
1.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)
CF_2H
N

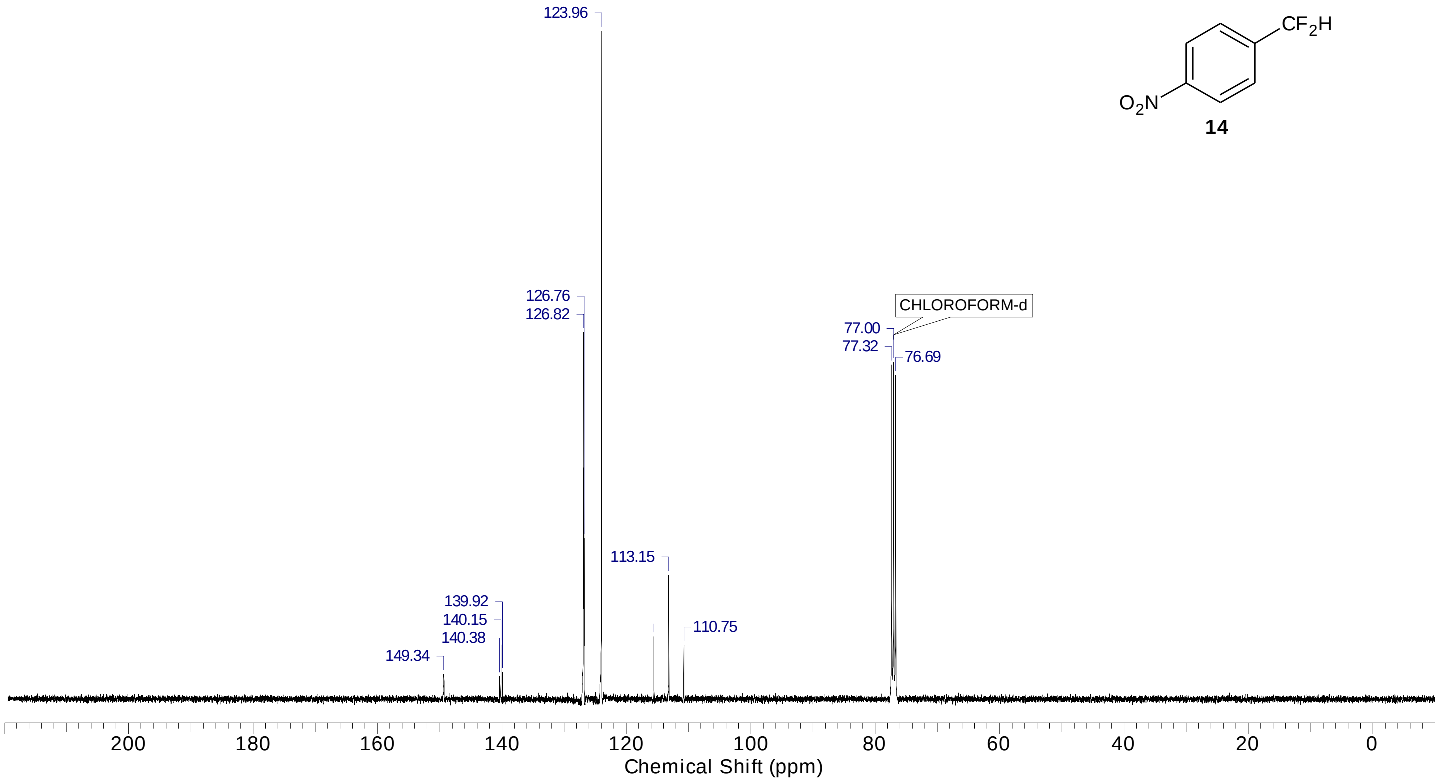
13

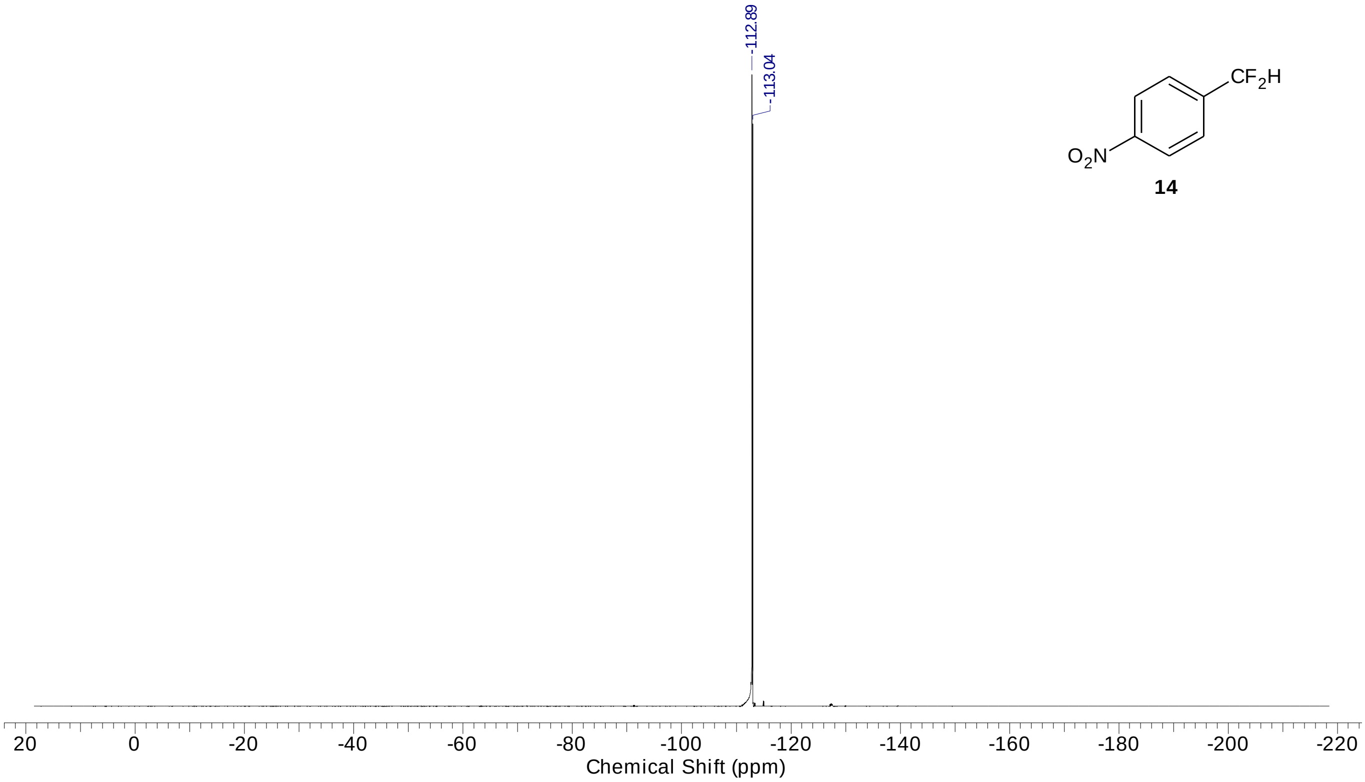

CHLOROFORM-d
76.68
77.32
132.58
126.45
126.39
126.33
113.29
114.76
115.68
110.90
138.30
138.53
138.76
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)
CF_2H
N

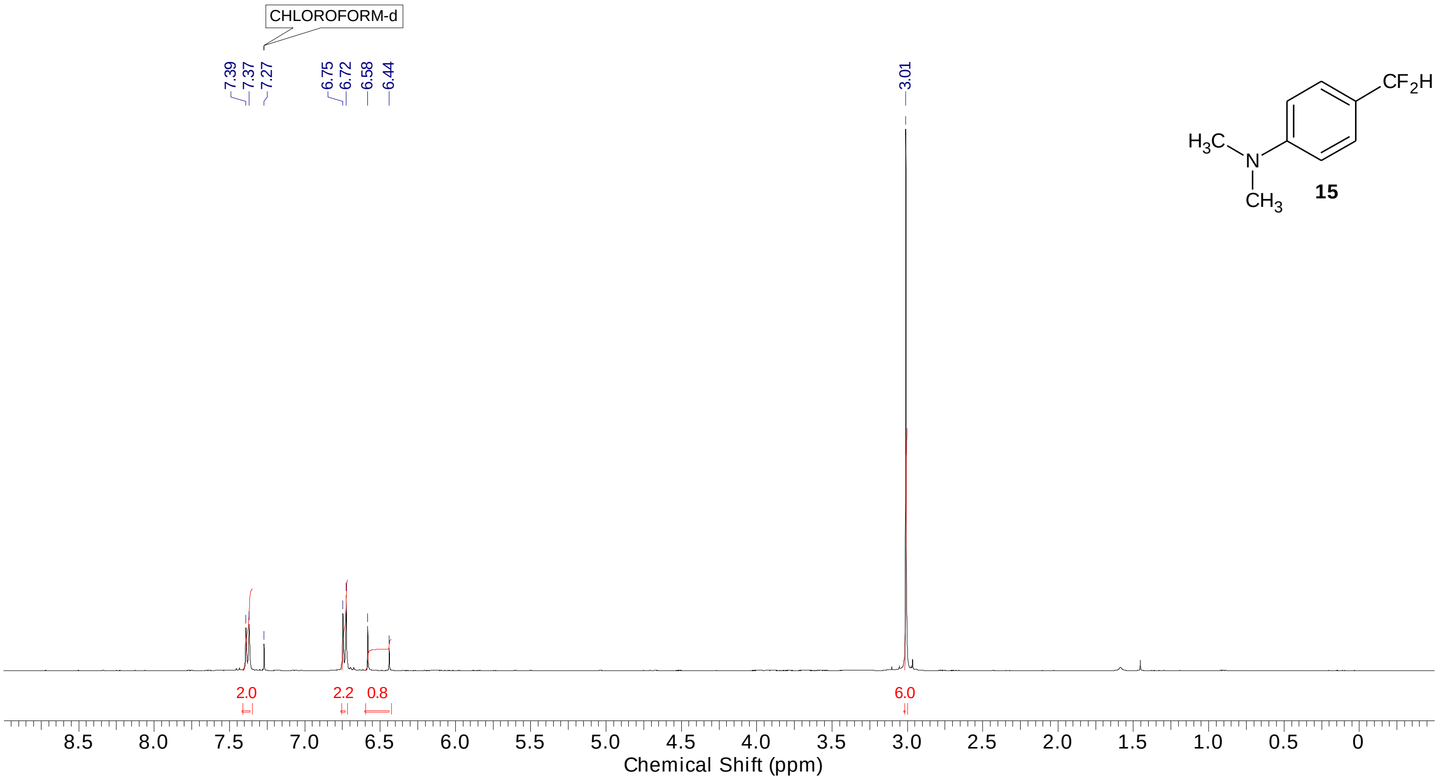
13

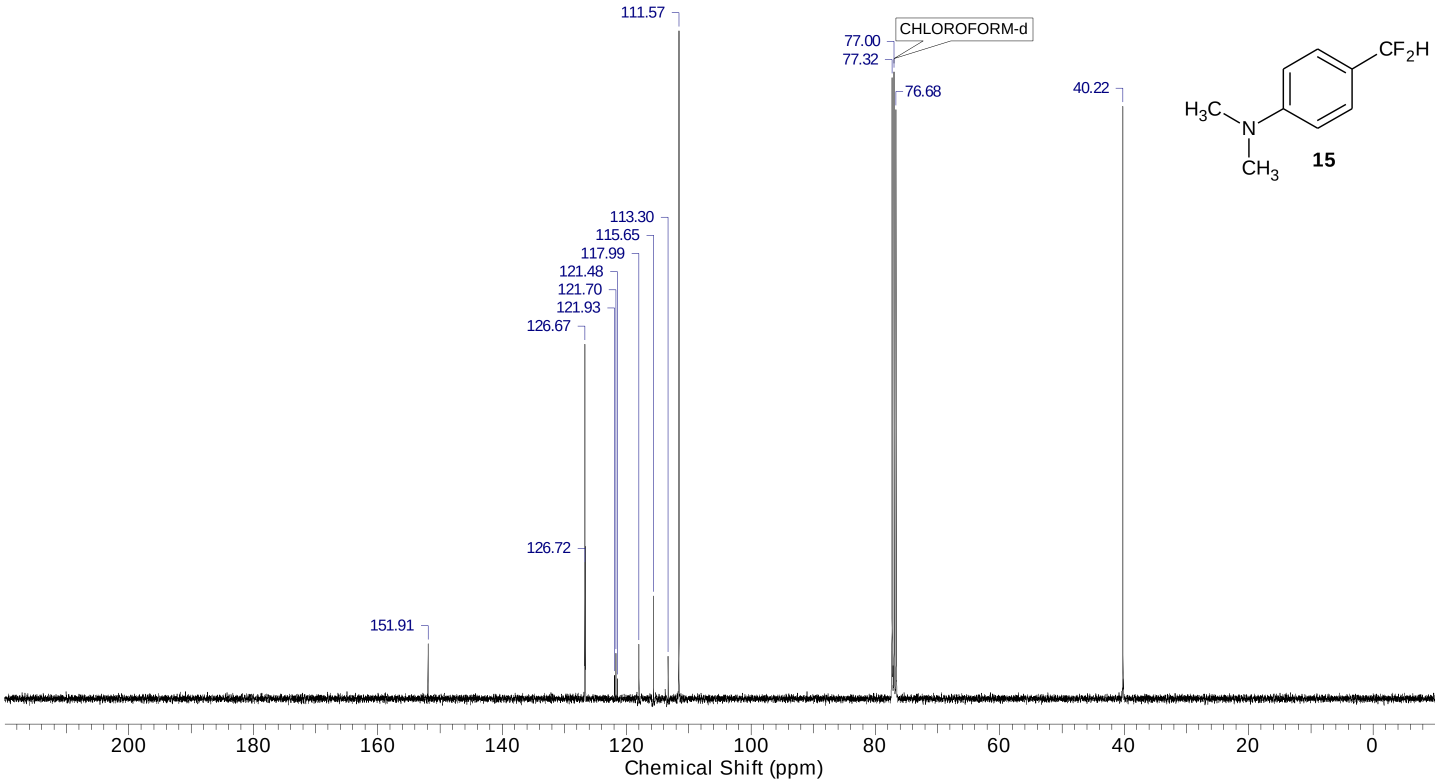

-113.07
-113.22
CF$_2$H
N
13
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
Chemical Shift (ppm)

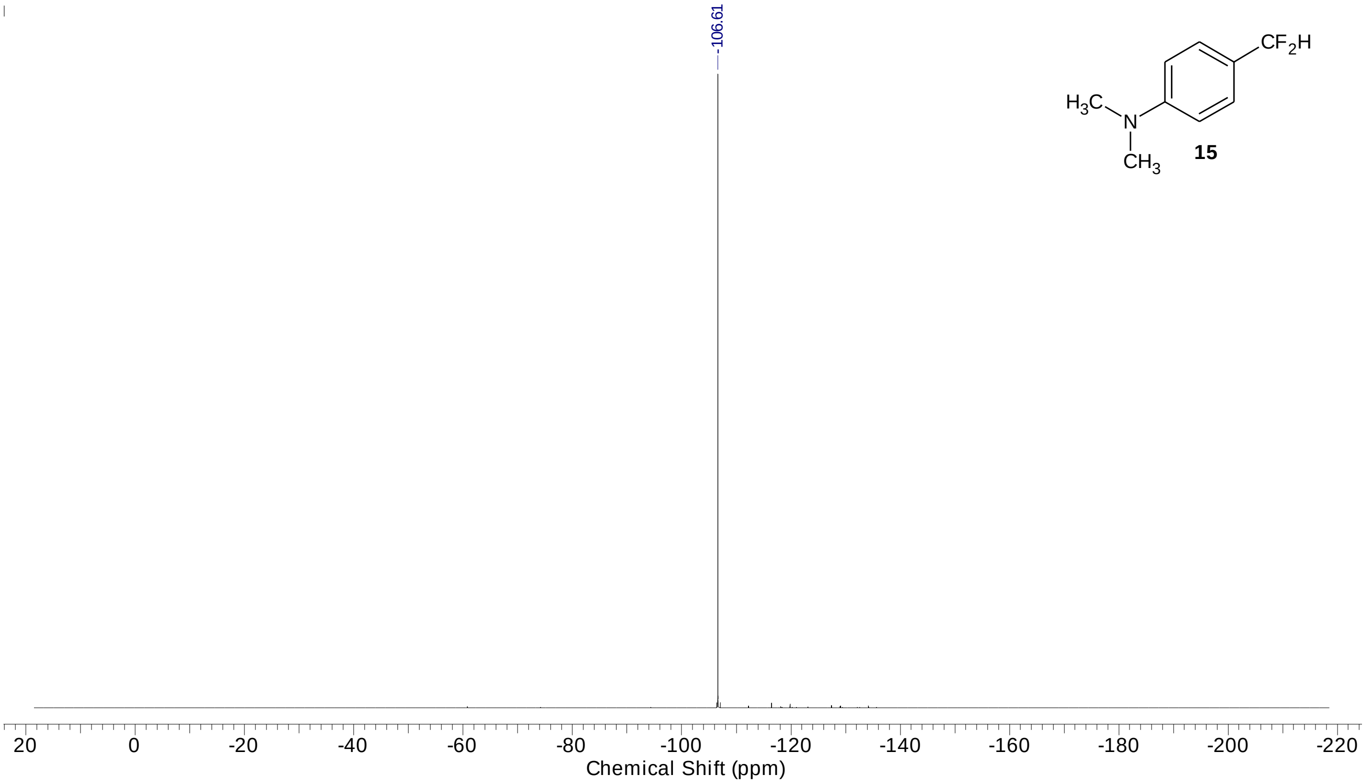

CHLOROFORM-d
8.35
8.33
7.74
7.72
7.27
6.89
6.75
6.62
CF$_2$H
O$_2$N
14
2.0
2.0
1.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

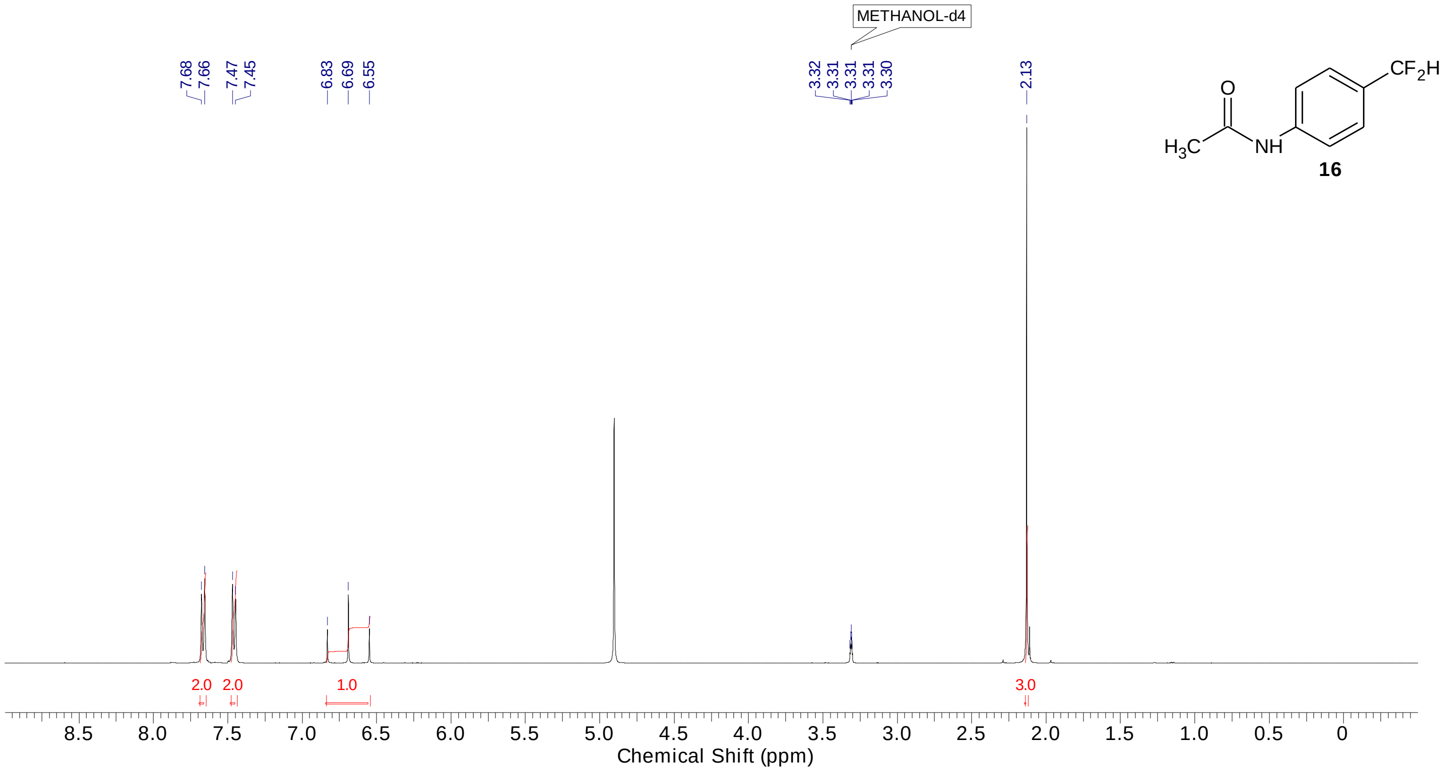

123.96
CF$_2$H
O$_2$N
14
126.76
126.82
CHLOROFORM-d
77.00
77.32
76.69
113.15
139.92
140.15
140.38
110.75
149.34
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

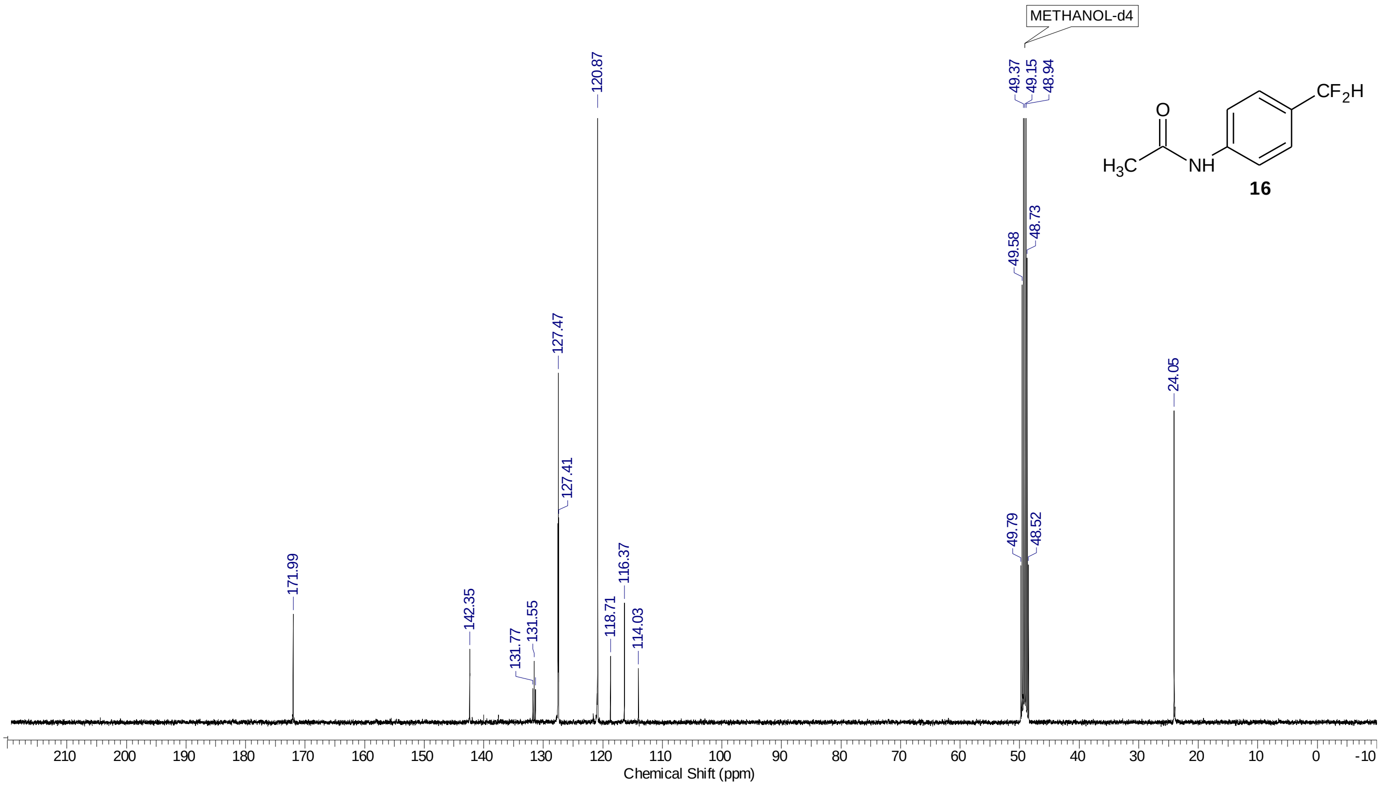

-112.89
-113.04
CF$_2$H
O$_2$N
14
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
Chemical Shift (ppm)

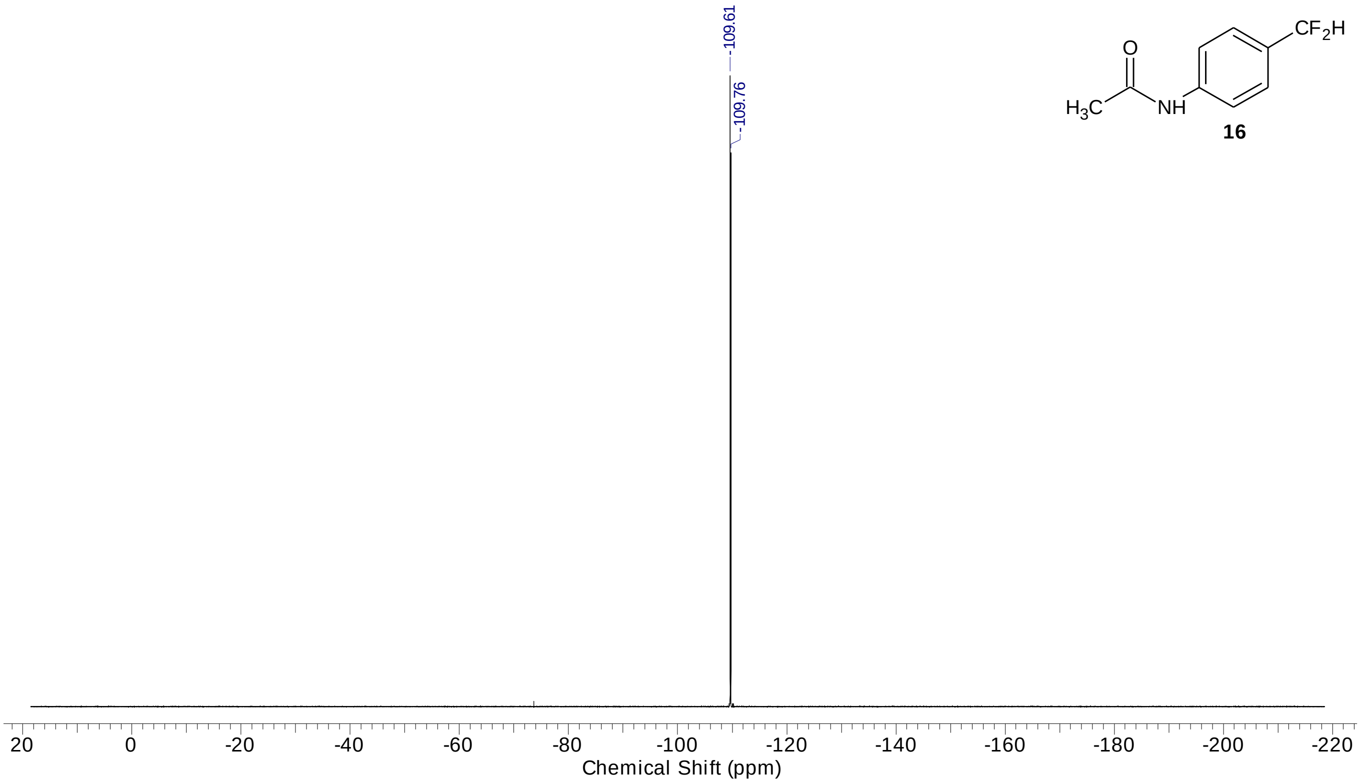

CHLOROFORM-d
7.39
7.37
7.27
6.75
6.72
6.58
6.44
3.01
CF$_2$H
H$_3$C
N
CH$_3$
15
2.0
2.2
0.8
6.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

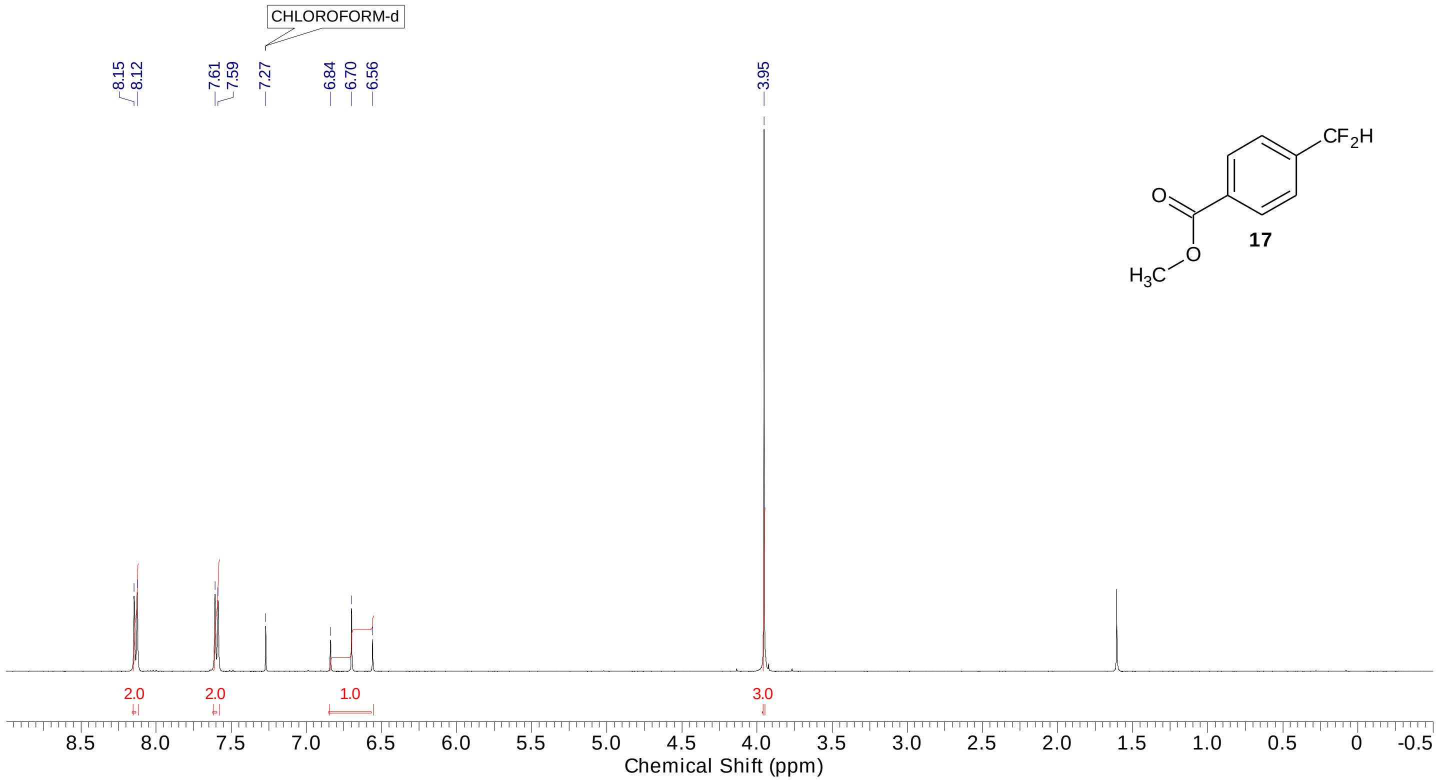

111.57
77.00
77.32
CHLOROFORM-d
76.68
40.22
CF$_2$H
H$_3$C
N
CH$_3$
15
113.30
115.65
117.99
121.48
121.70
121.93
126.67
126.72
151.91
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

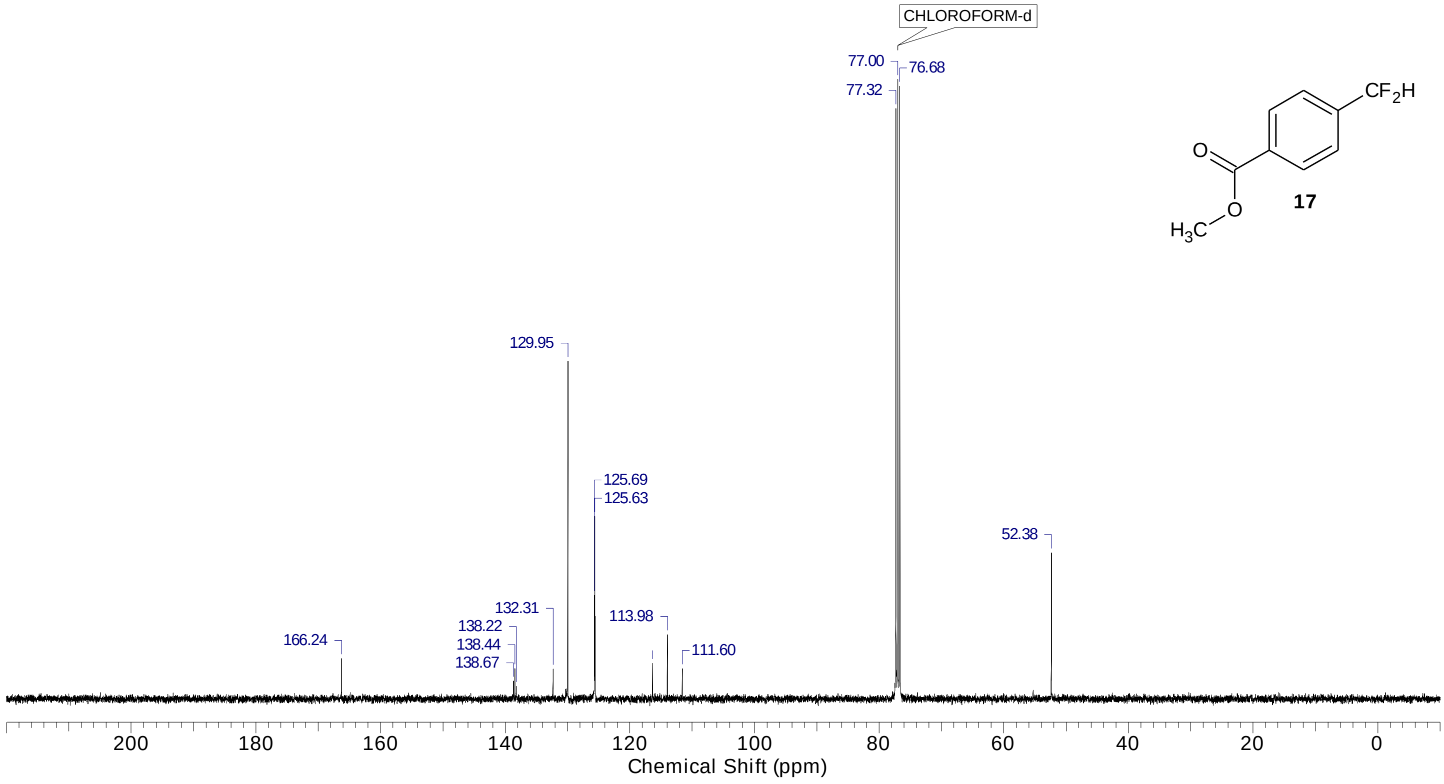

-106.61
CF2H
H3C
N
CH3
15
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
Chemical Shift (ppm)

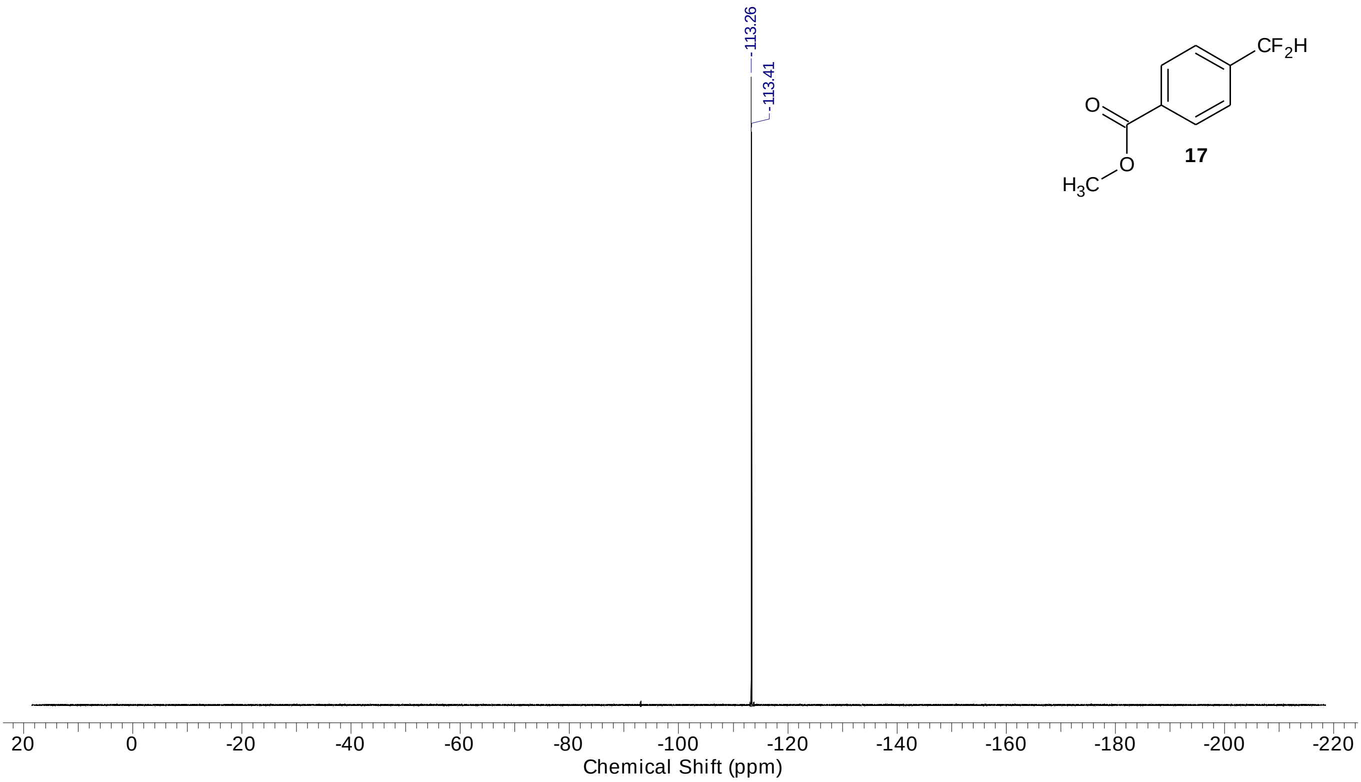

METHANOL-d4
7.68
7.66
7.47
7.45
6.83
6.69
6.55
3.32
3.31
3.31
3.31
3.30
2.13
2.0
2.0
1.0
3.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)
O
H_3C
NH
CF_2H
16

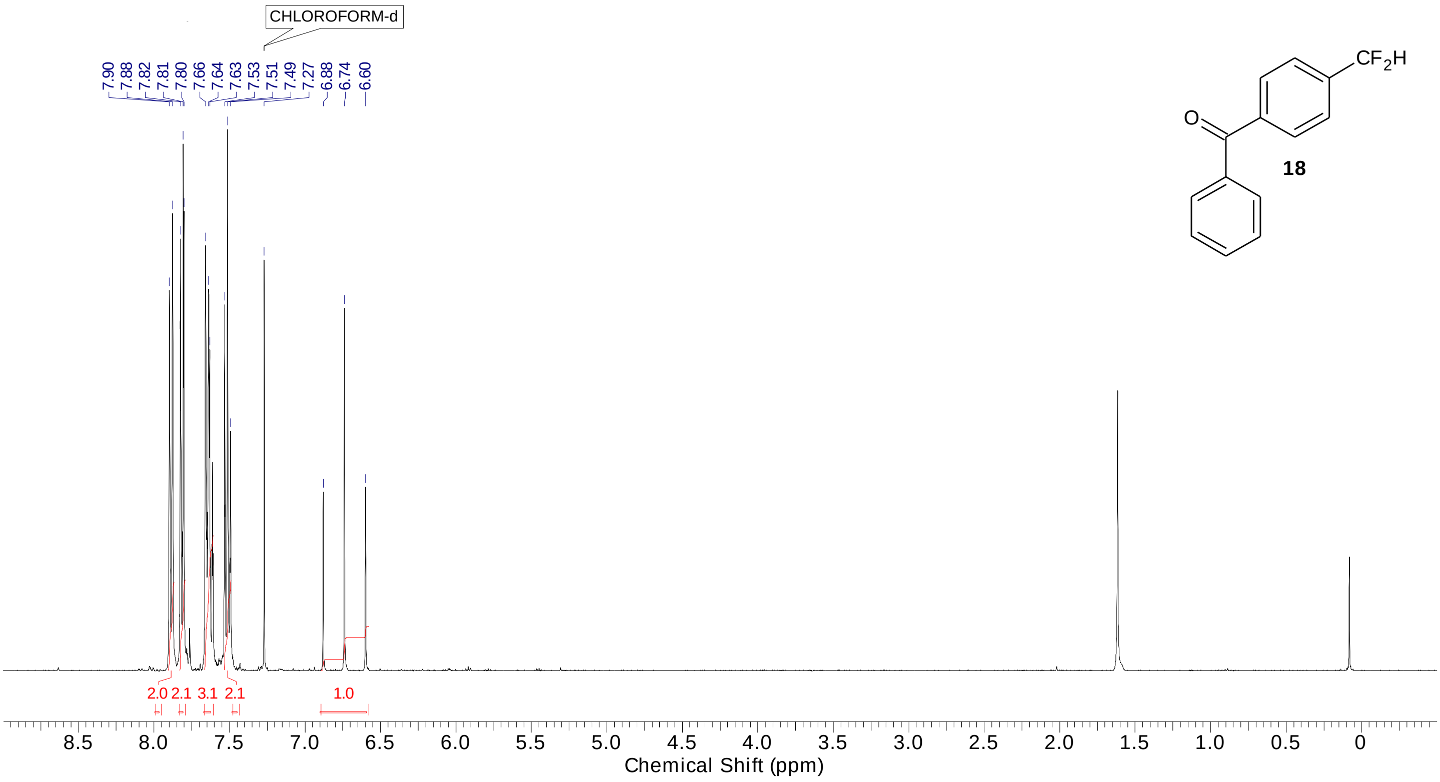

METHANOL-d4
171.99
142.35
131.77
131.55
127.47
127.41
120.87
118.71
116.37
114.03
49.37
49.15
48.94
49.58
48.73
49.79
48.52
24.05
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
Chemical Shift (ppm)
O
H_3C
NH
CF_2H
16

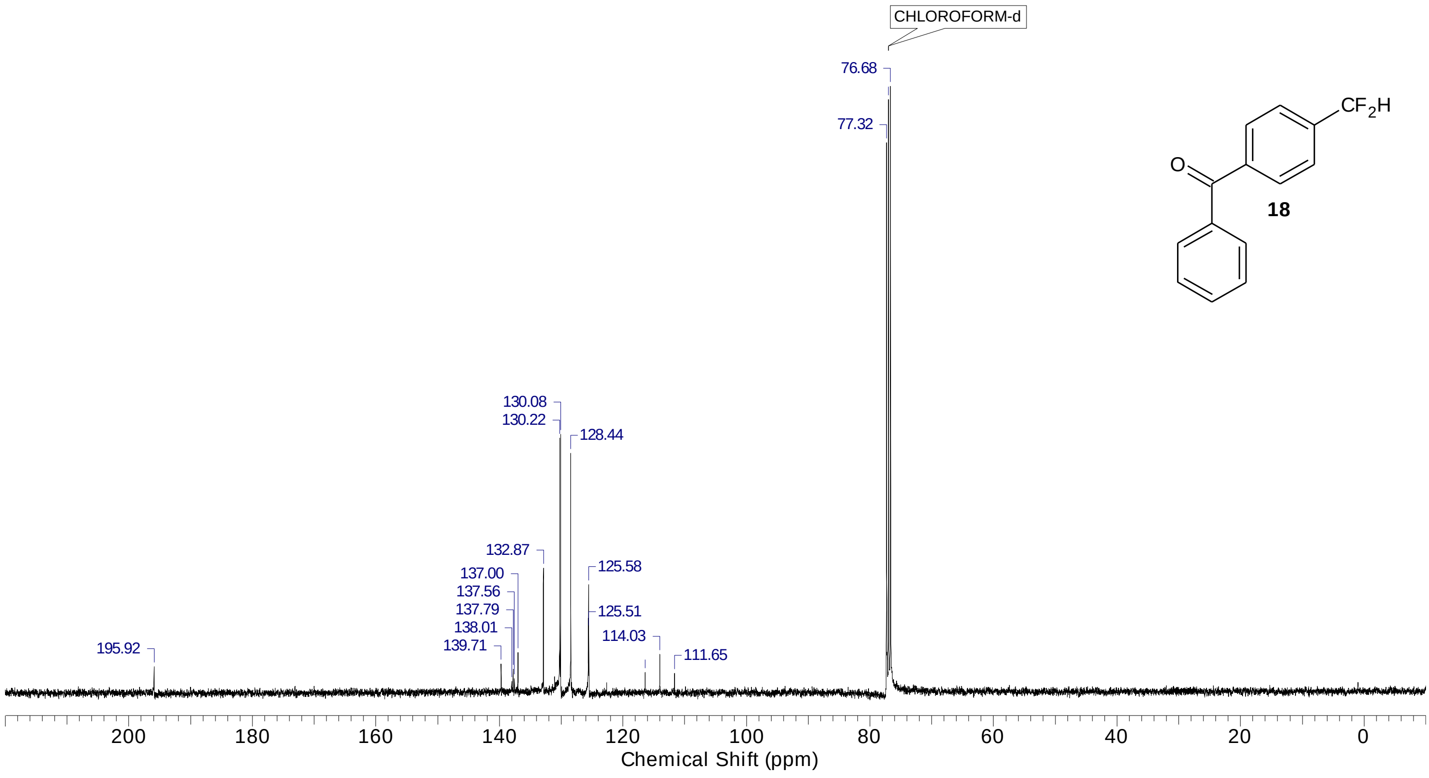

-109.61
-109.76
O
H_3C
NH
CF_2H
16
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
Chemical Shift (ppm)

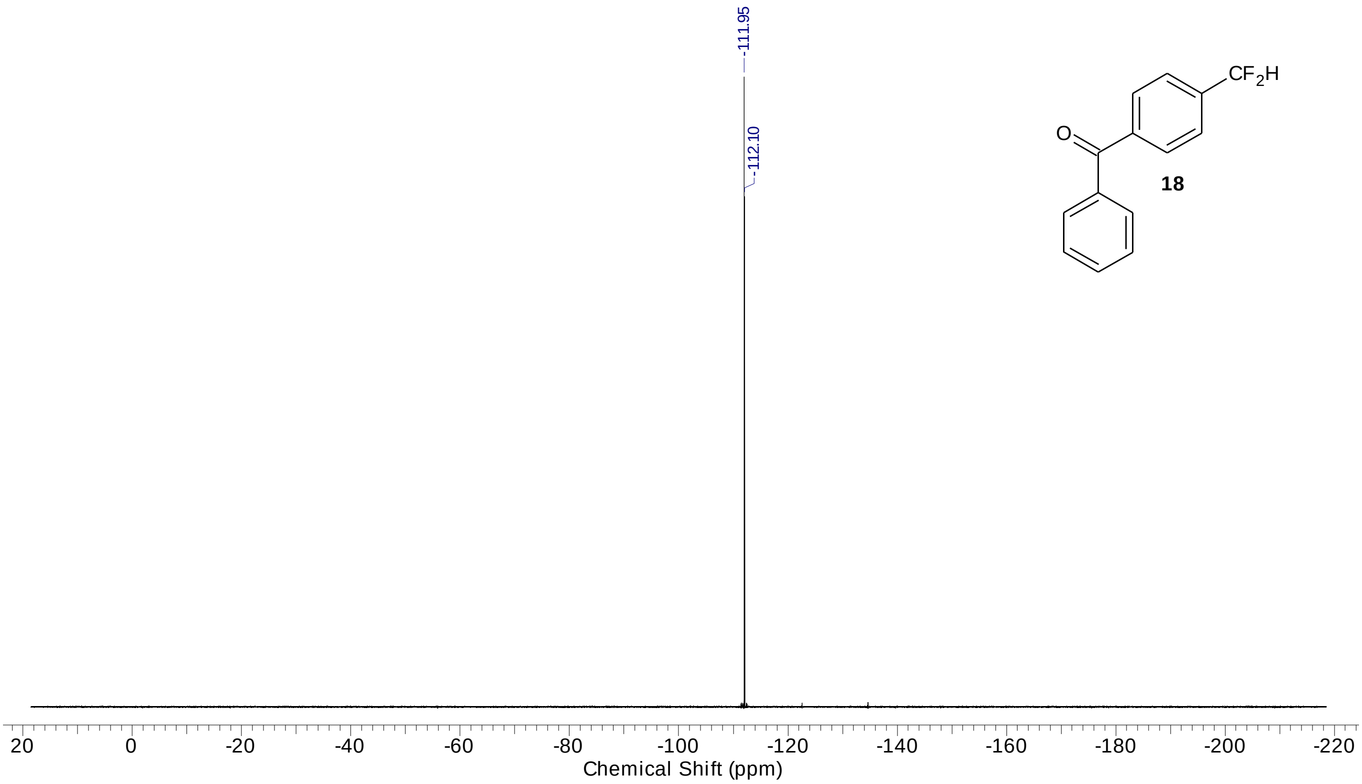

CHLOROFORM-d
8.15
8.12
7.61
7.59
7.27
6.84
6.70
6.56
3.95
CF$_2$H
O
O
H$_3$C
17
2.0
2.0
1.0
3.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
-0.5
Chemical Shift (ppm)

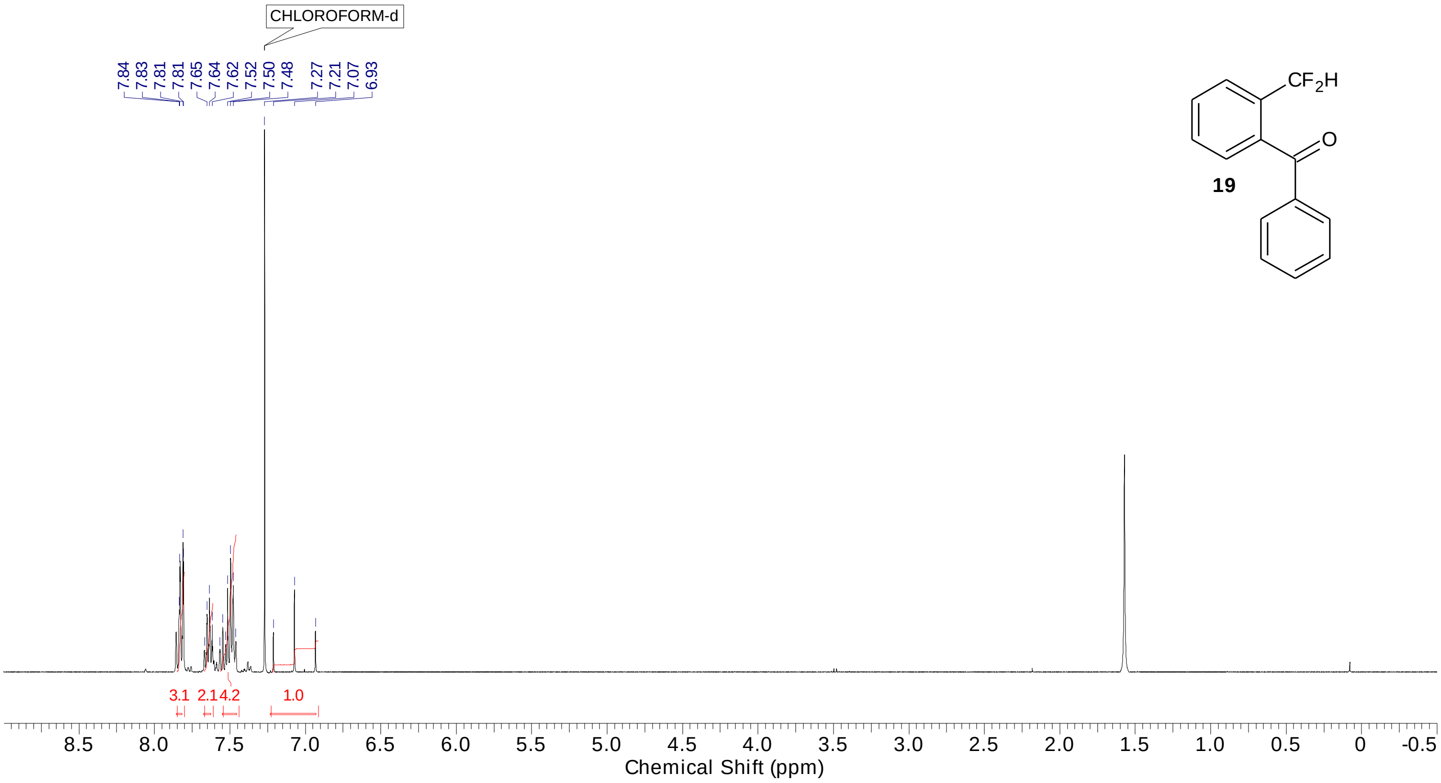

CHLOROFORM-d
77.00
76.68
77.32
CF$_2$H
O
O
H$_3$C
17
129.95
125.69
125.63
52.38
132.31
138.22
138.44
138.67
166.24
113.98
111.60
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

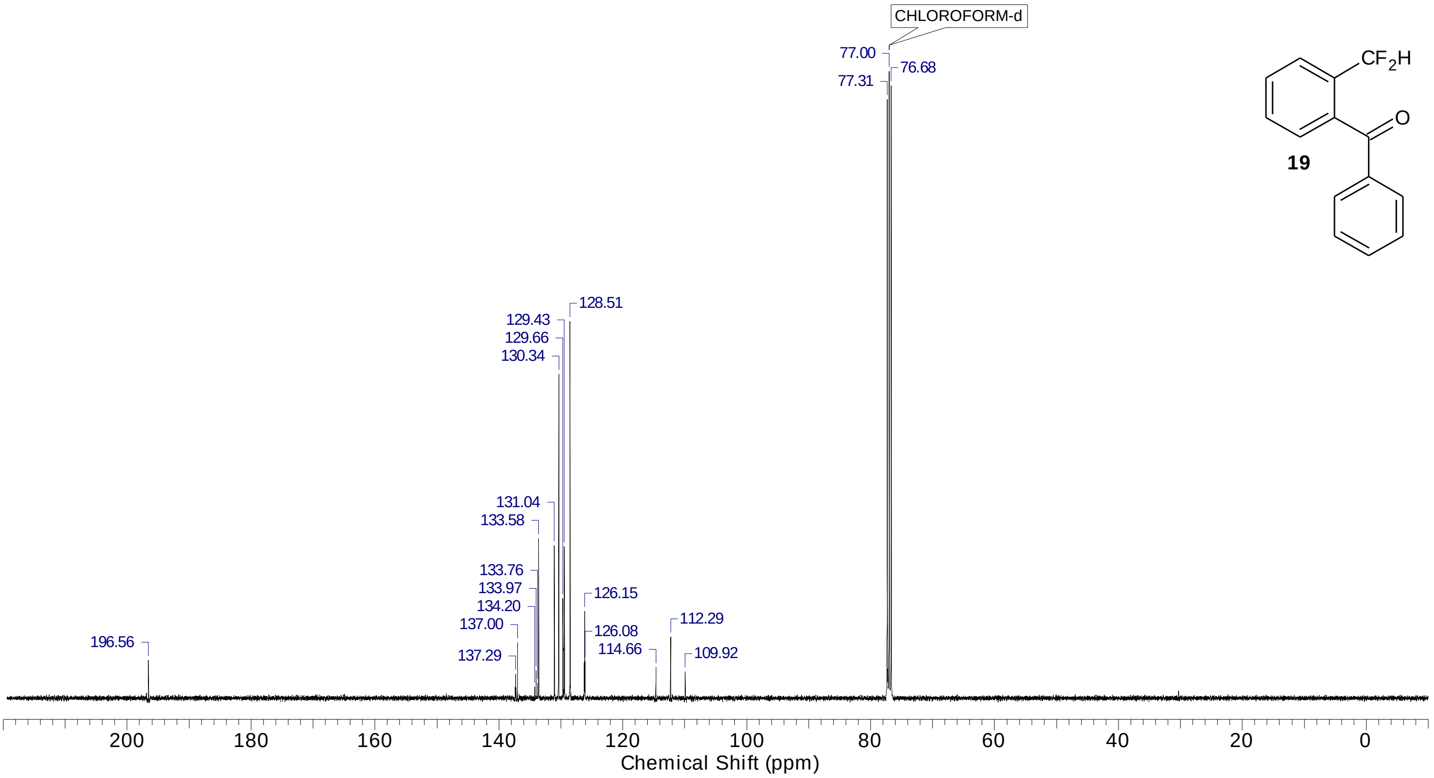

-113.26
-113.41
CF_2H
O
O
H_3C
17
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
Chemical Shift (ppm)

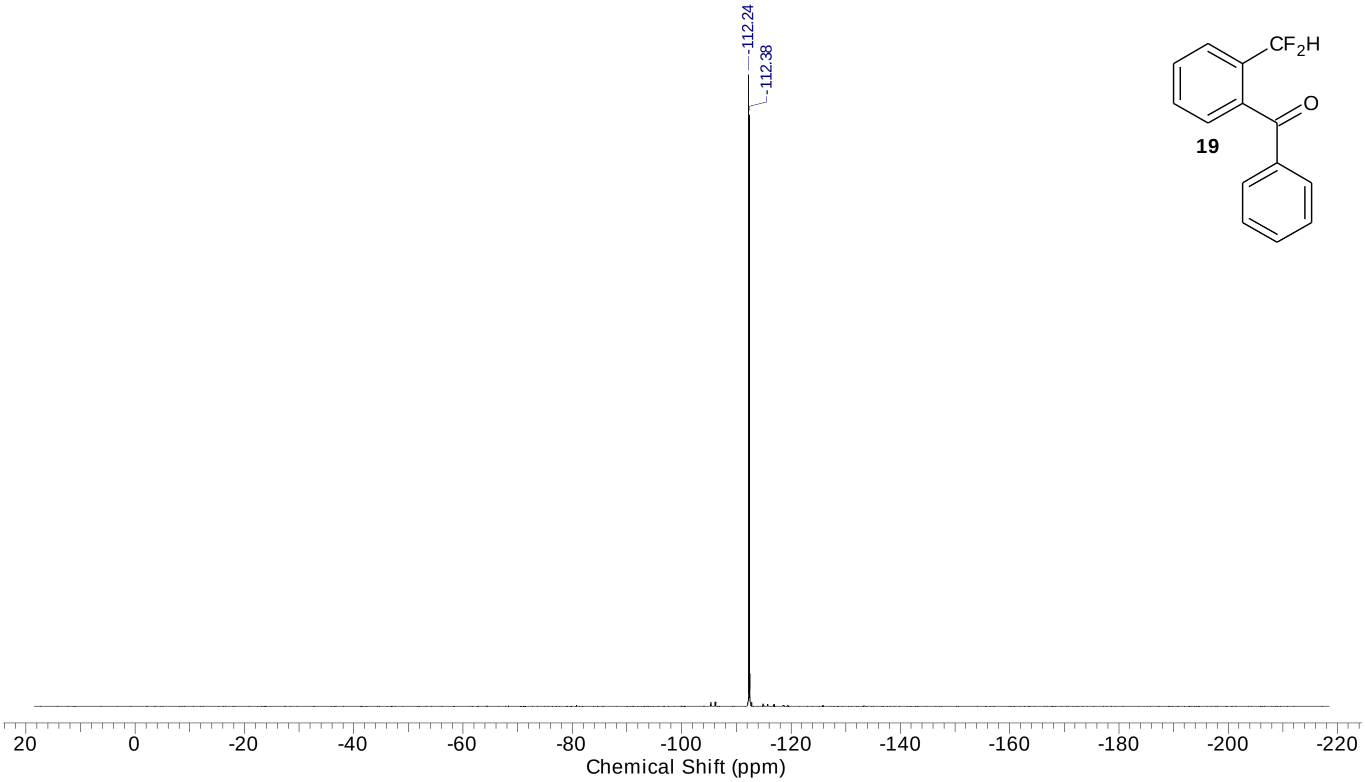

CHLOROFORM-d
7.90
7.88
7.82
7.81
7.80
7.66
7.64
7.63
7.53
7.51
7.49
7.27
6.88
6.74
6.60
2.0
2.1
3.1
2.1
1.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)
CF$_2$H
O
18


CHLOROFORM-d
76.68
77.32
130.08
130.22
128.44
132.87
137.00
137.56
137.79
138.01
139.71
125.58
125.51
114.03
111.65
195.92
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)
CF$_2$H
O
18


-111.95
-112.10
CF$_2$H
O
18
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
Chemical Shift (ppm)

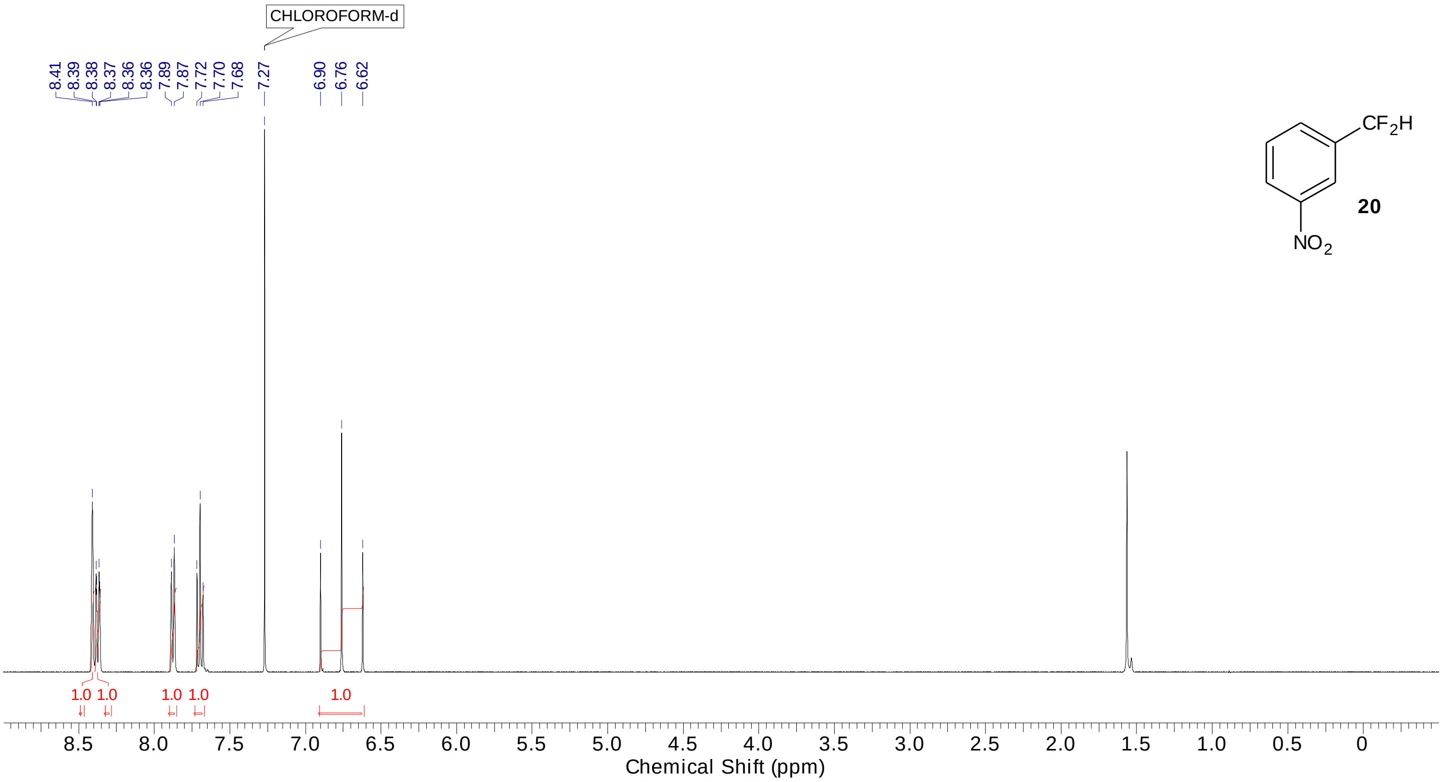

CHLOROFORM-d
7.84
7.83
7.81
7.81
7.65
7.64
7.62
7.52
7.50
7.48
7.27
7.21
7.07
6.93
CF2H
O
19
3.1
2.1
4.2
1.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
-0.5
Chemical Shift (ppm)

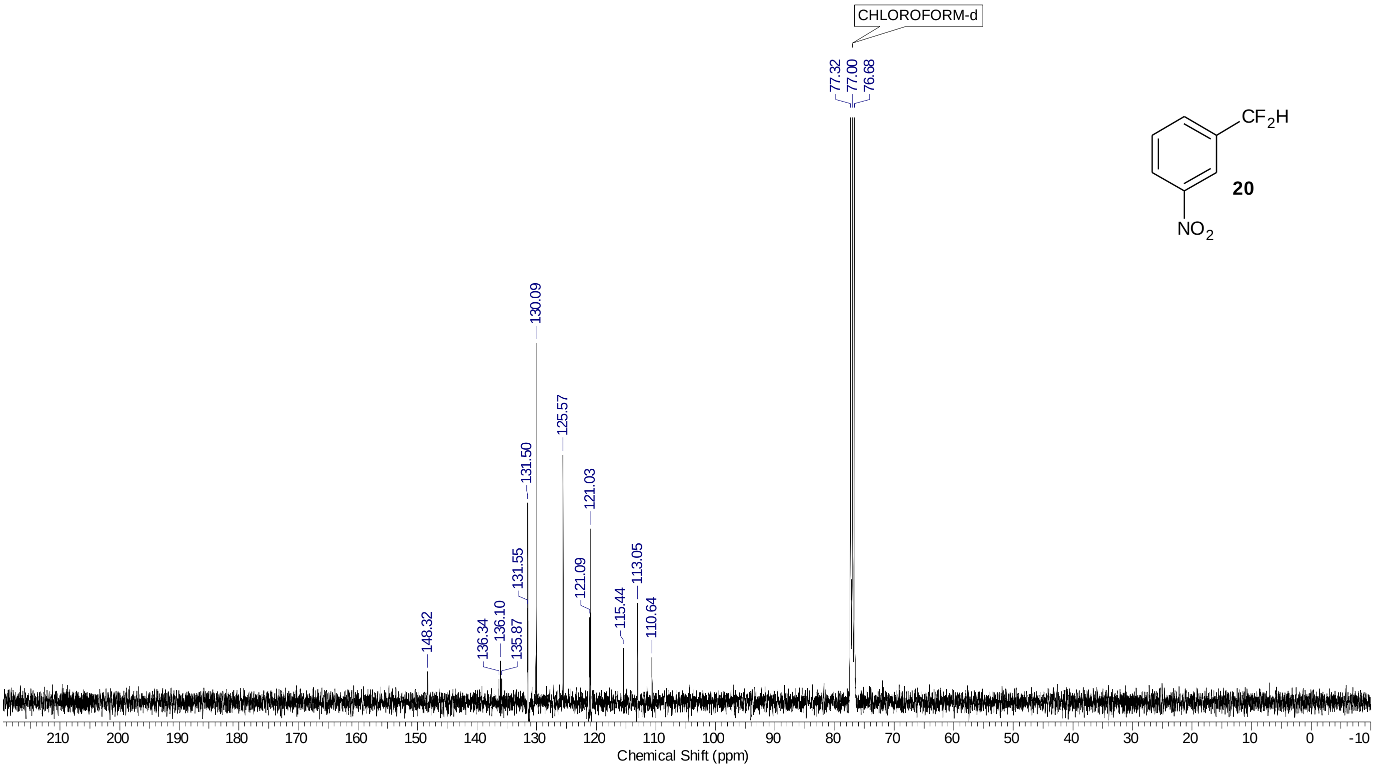

CHLOROFORM-d
77.00
77.31
76.68
CF2H
O
19
128.51
129.43
129.66
130.34
131.04
133.58
133.76
133.97
134.20
137.00
137.29
126.15
126.08
114.66
112.29
109.92
196.56
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

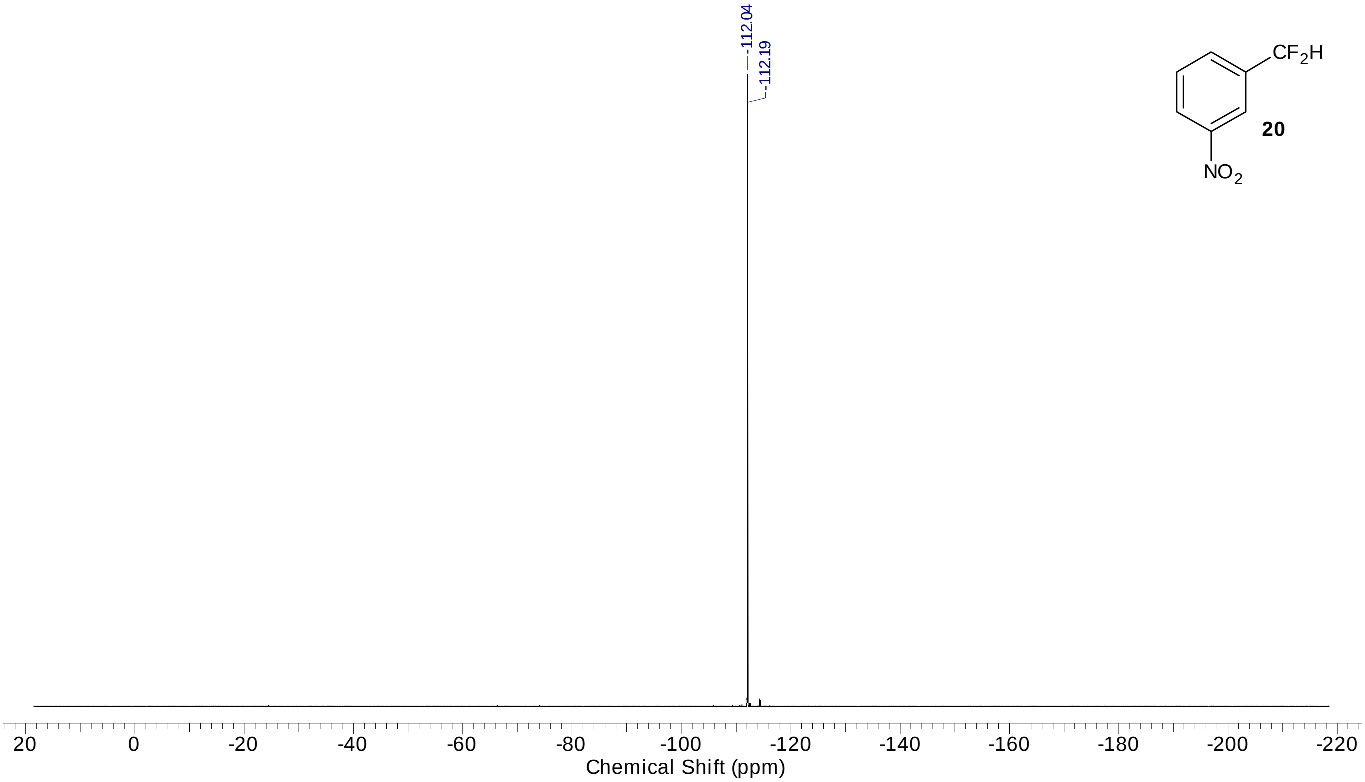


-112.24
-112.38
CF$_2$H
O
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
Chemical Shift (ppm)

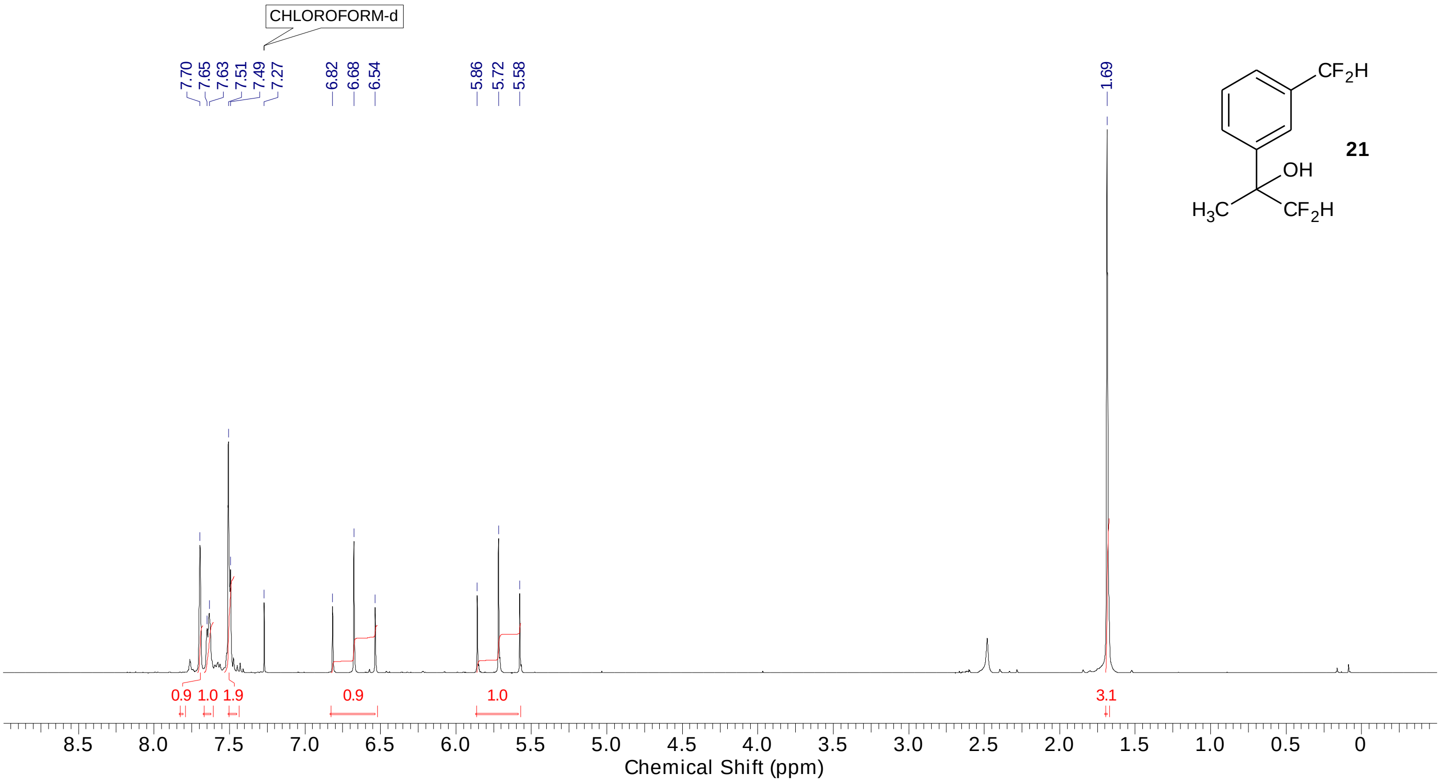
19

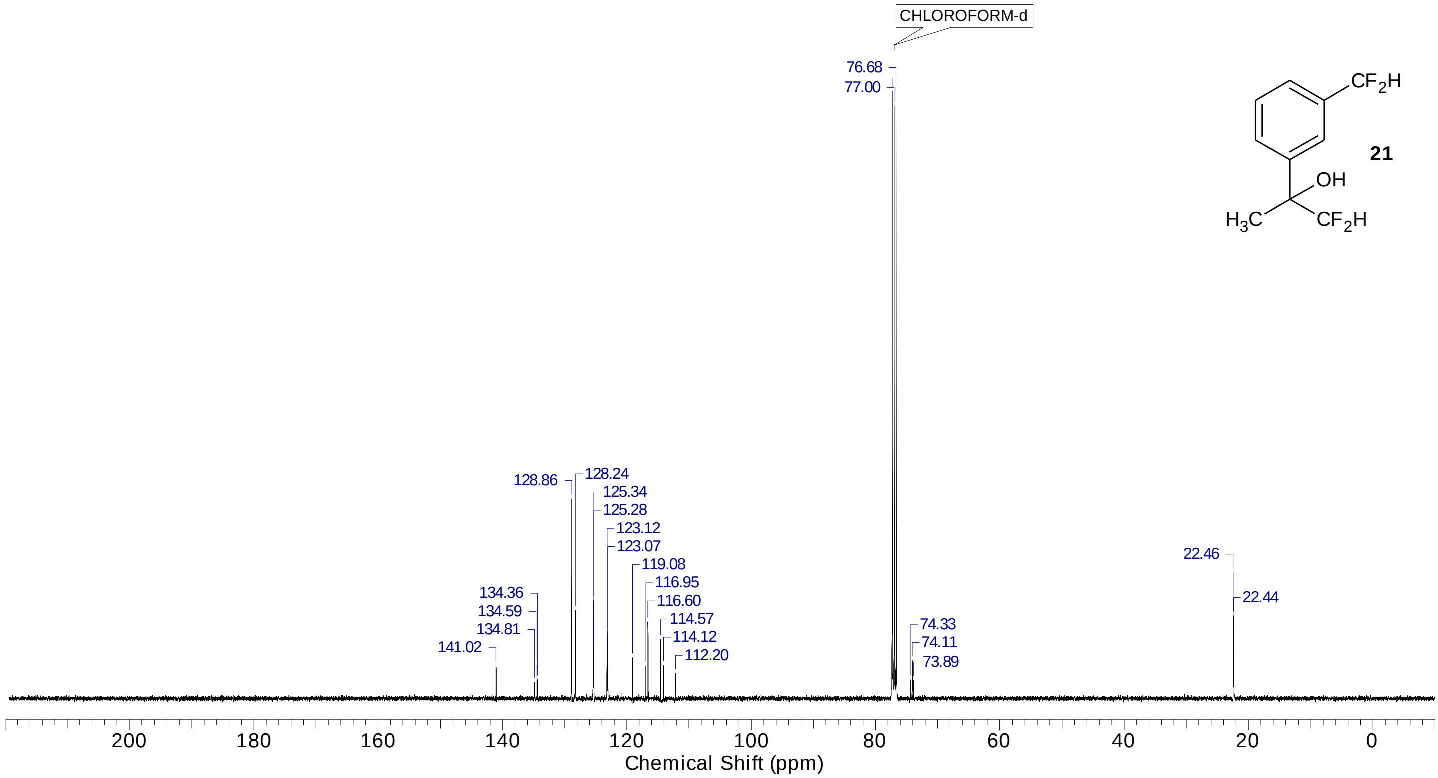

CHLOROFORM-d
8.41
8.39
8.38
8.37
8.36
8.36
7.89
7.87
7.72
7.70
7.68
7.27
6.90
6.76
6.62
CF2H
NO2
20
1.0
1.0
1.0
1.0
1.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

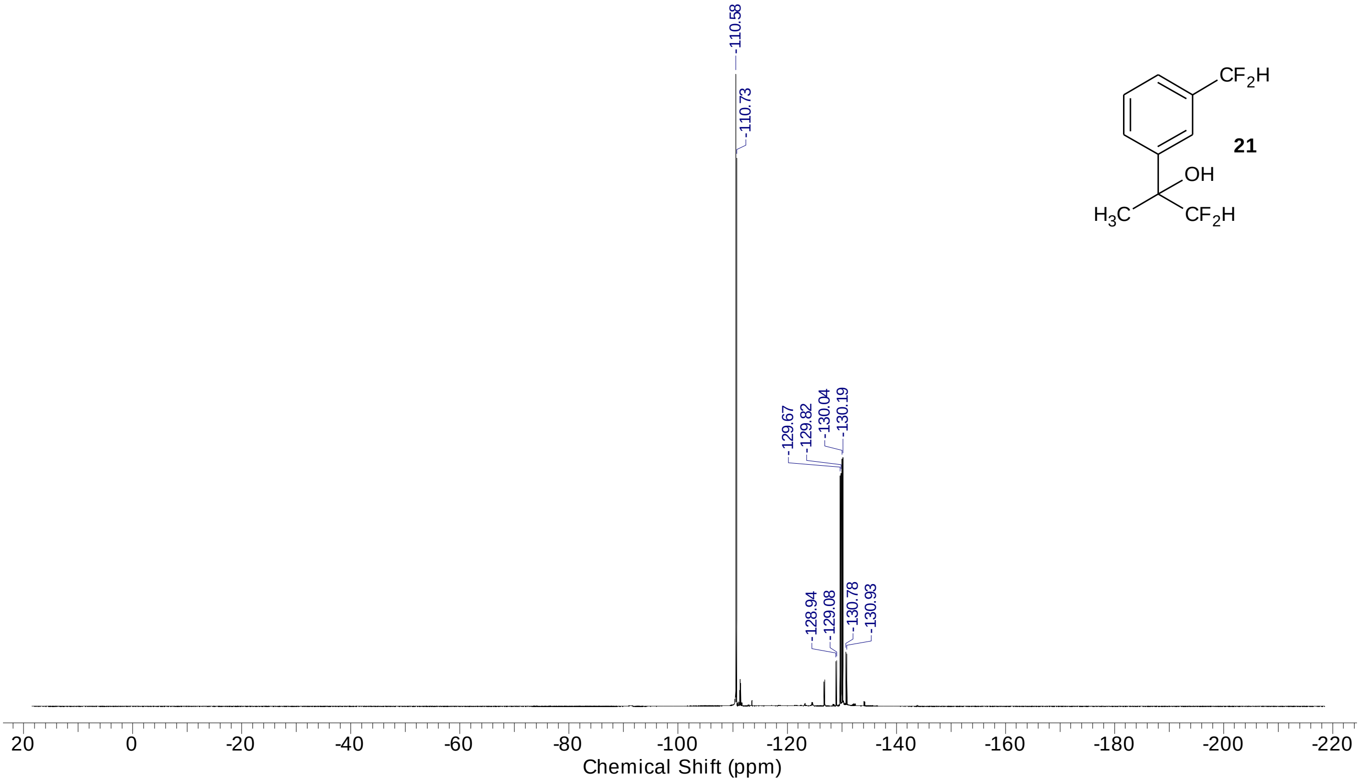

CHLOROFORM-d
77.32
77.00
76.68
CF2H
NO2
20
130.09
125.57
131.50
121.03
131.55
121.09
113.05
115.44
110.64
148.32
136.34
136.10
135.87
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
Chemical Shift (ppm)

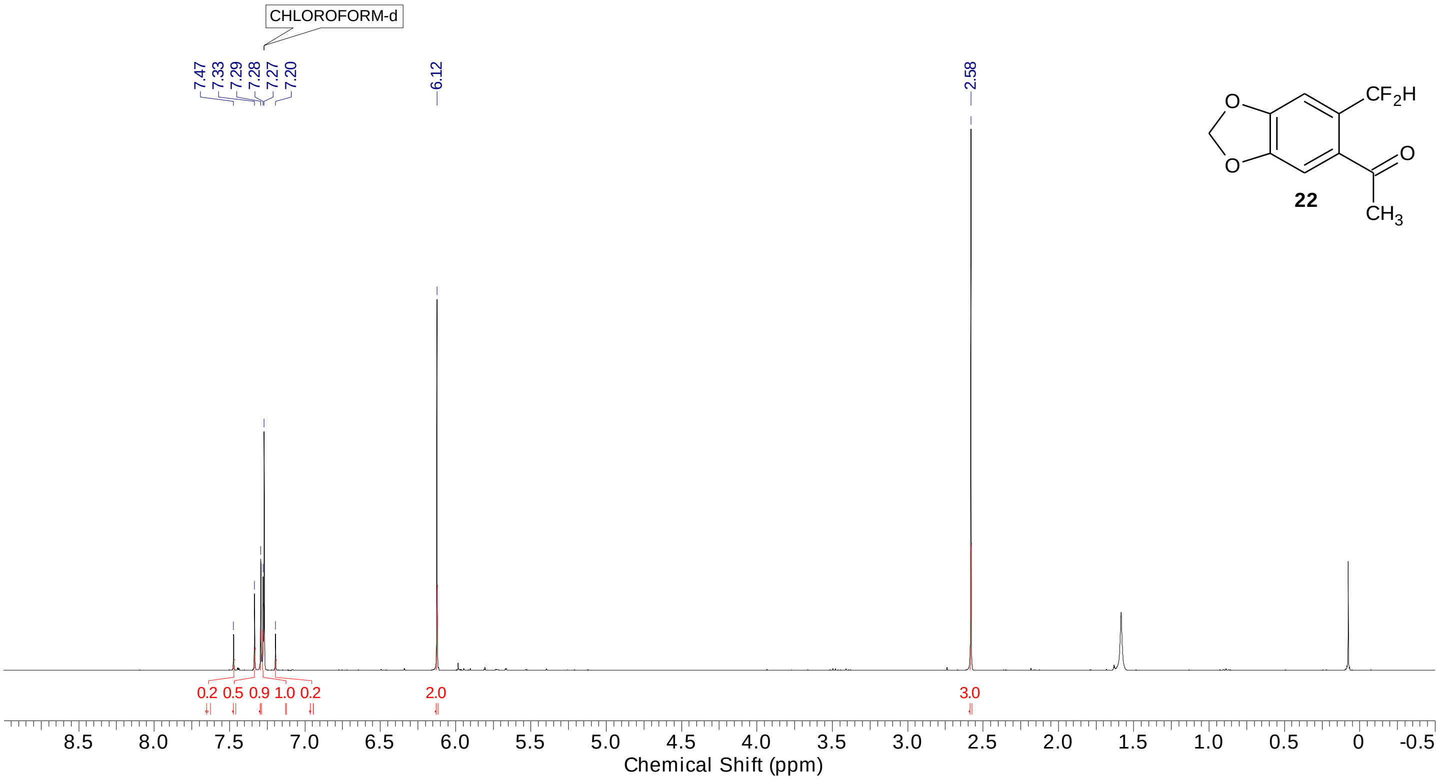

-112.04
-112.19
CF2H
NO2
20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220
Chemical Shift (ppm)

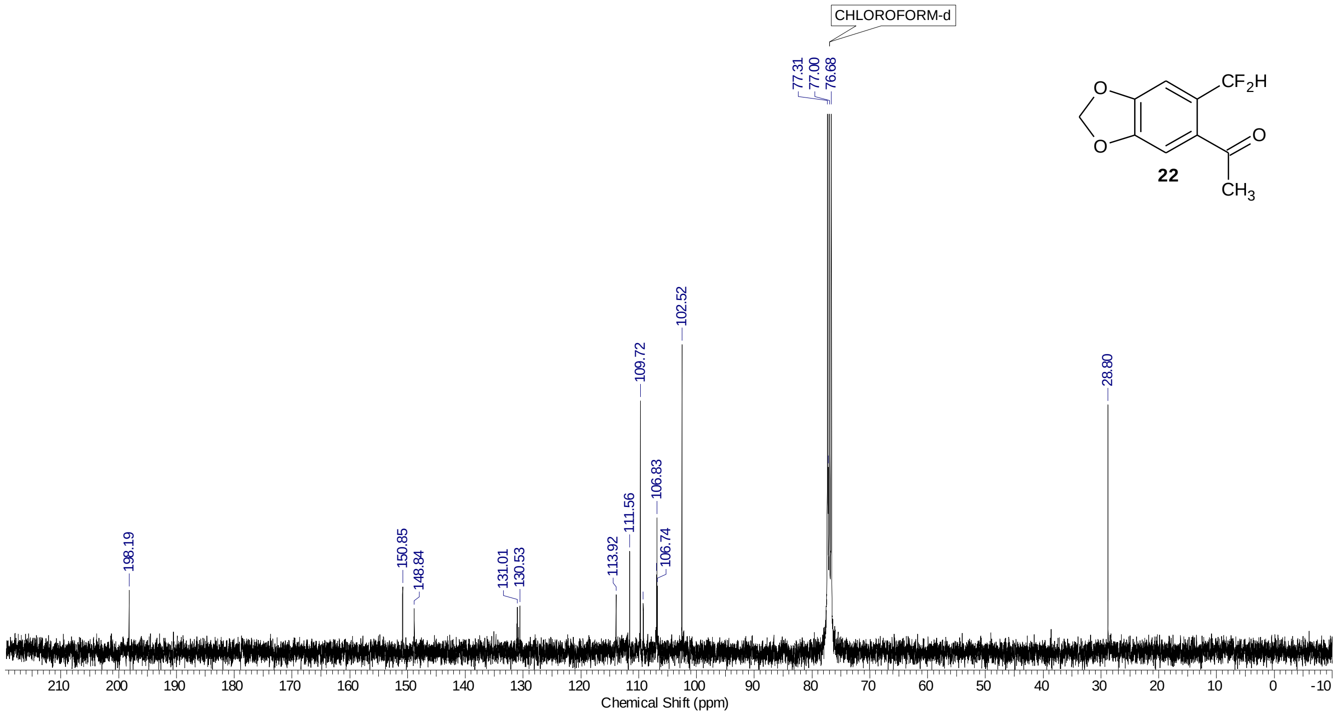
20

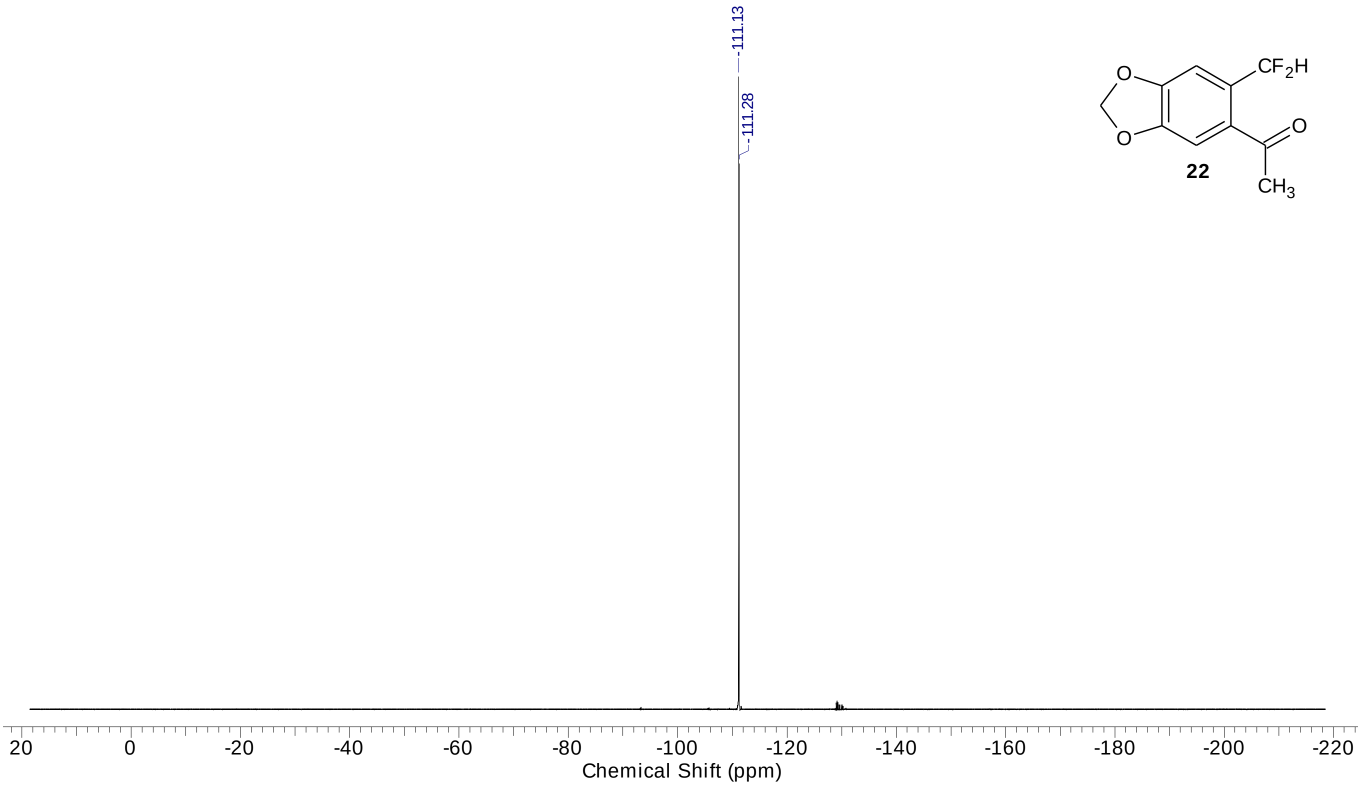

CHLOROFORM-d
7.70
7.65
7.63
7.51
7.49
7.27
6.82
6.68
6.54
5.86
5.72
5.58
1.69
0.9
1.0
1.9
0.9
1.0
3.1
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)
CF2H
21
OH
H3C
CF2H

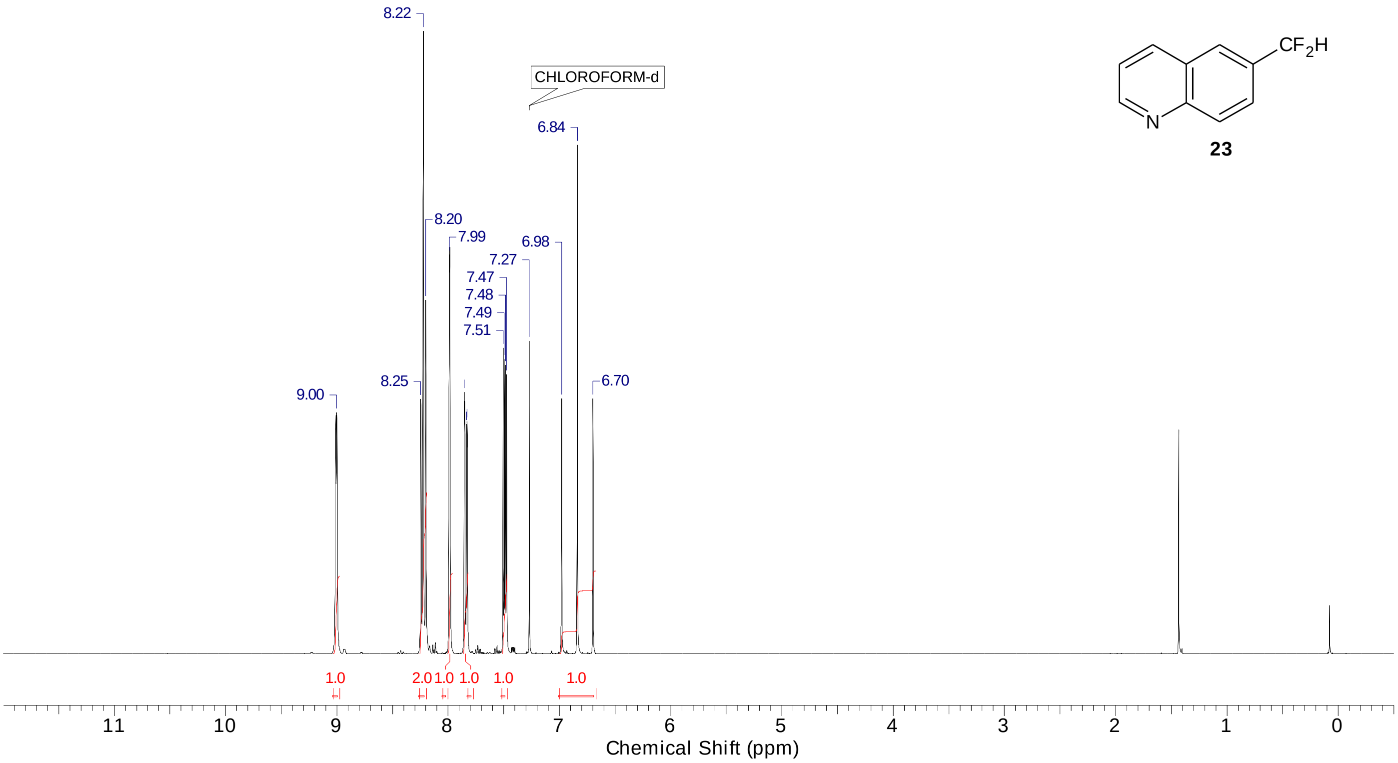

CHLOROFORM-d
76.68
77.00
128.86
128.24
125.34
125.28
123.12
123.07
119.08
116.95
116.60
114.57
114.12
112.20
134.36
134.59
134.81
141.02
74.33
74.11
73.89
22.46
22.44
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)
CF2H
21
OH
H3C
CF2H

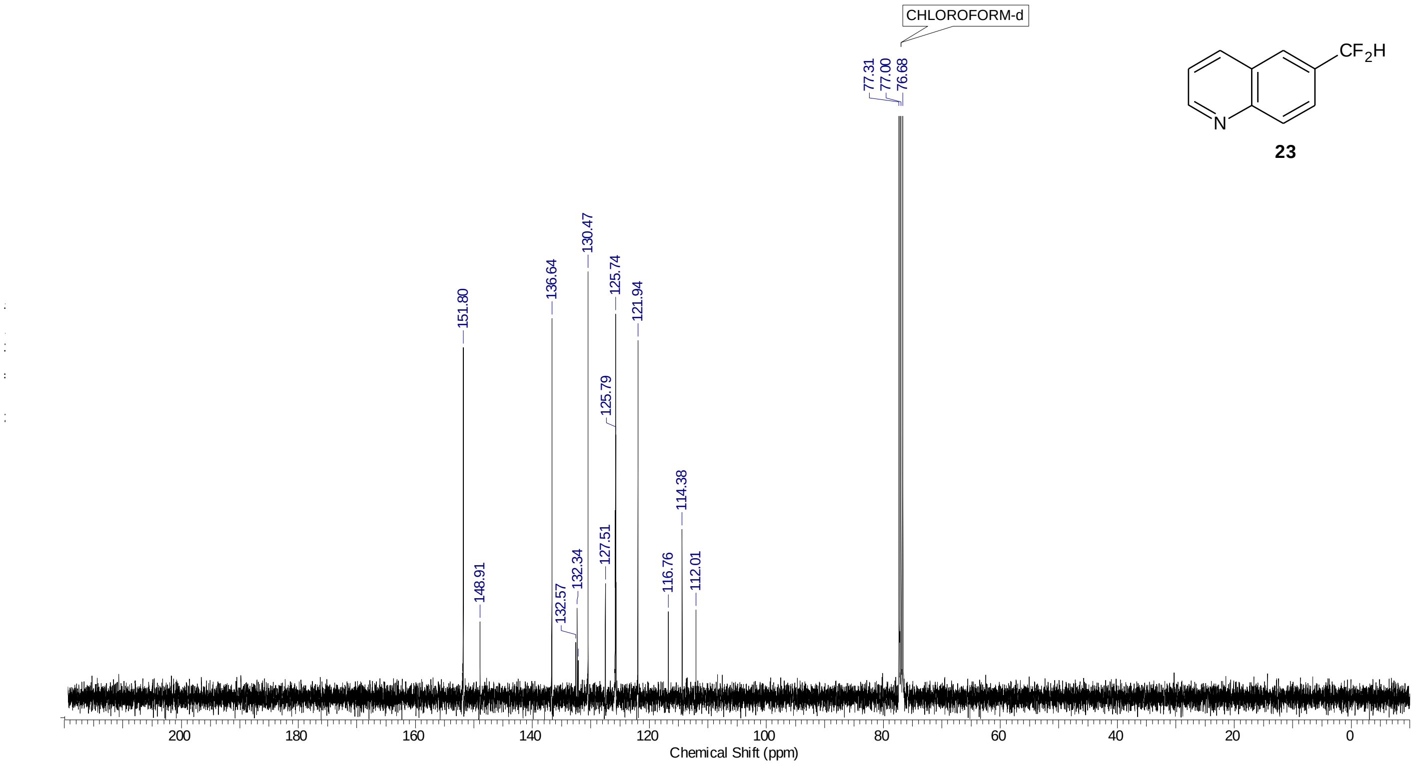

-110.58
-110.73
-129.67
-129.82
-130.04
-130.19
-128.94
-129.08
-130.78
-130.93
CF2H
21
OH
H3C
CF2H
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
Chemical Shift (ppm)

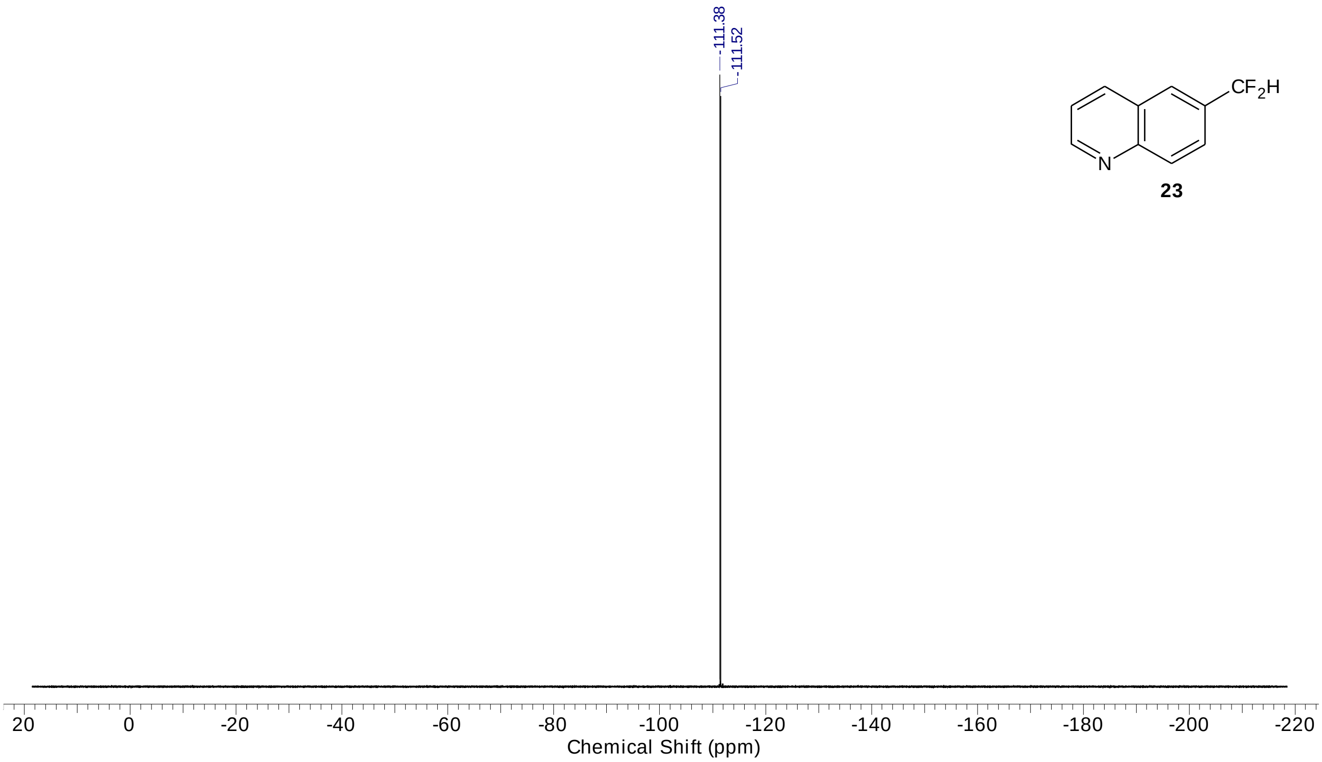

CHLOROFORM-d
7.47
7.33
7.29
7.28
7.27
7.20
6.12
2.58
0.2
0.5
0.9
1.0
0.2
2.0
3.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
-0.5
Chemical Shift (ppm)
O
O
CF2H
O
22
CH3


CHLOROFORM-d
77.31
77.00
76.68
102.52
109.72
28.80
111.56
106.83
113.92
106.74
198.19
150.85
148.84
131.01
130.53
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
Chemical Shift (ppm)
O
O
CF2H
O
22
CH3

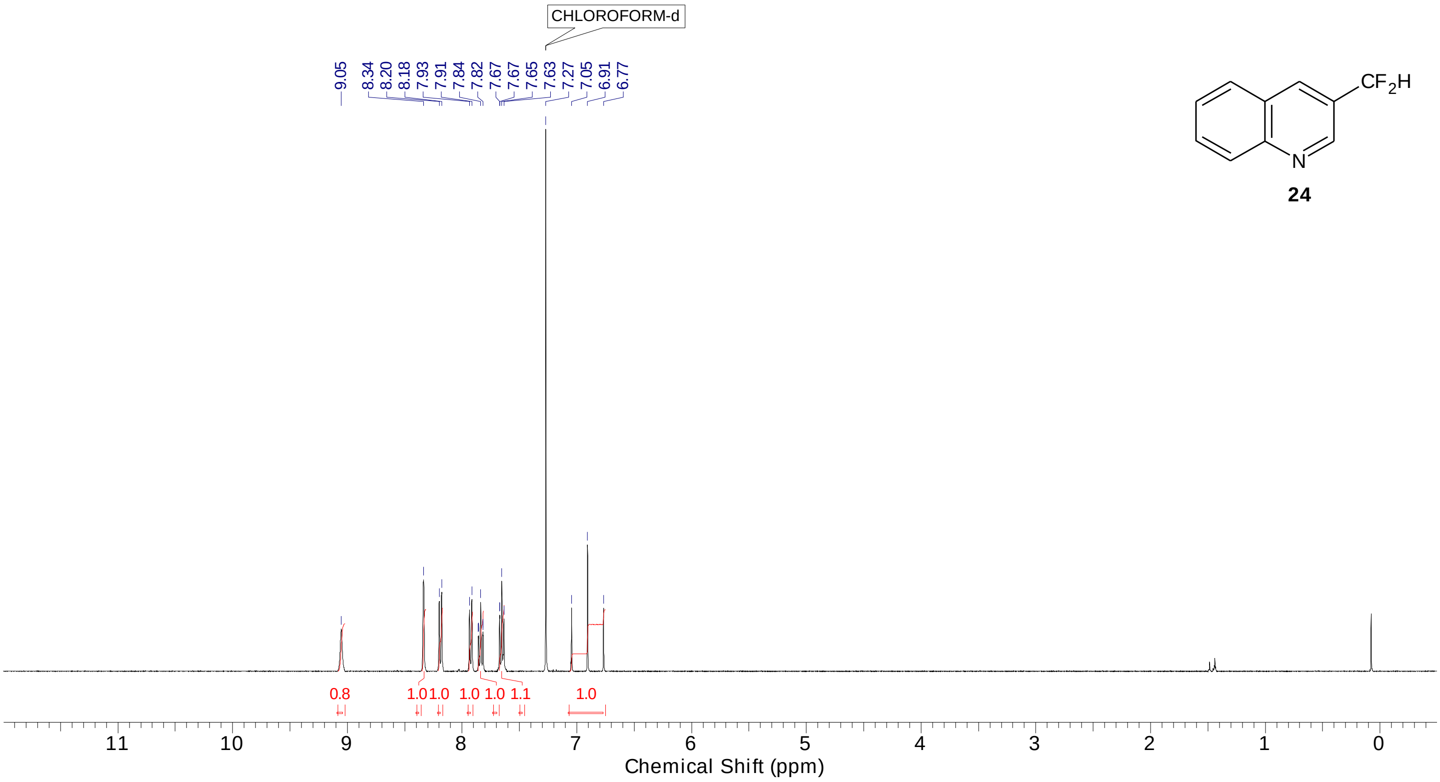

-111.13
-111.28
CF2H
O
O
O
CH3
22
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
Chemical Shift (ppm)


8.22
8.20
7.99
CHLOROFORM-d
6.84
6.98
7.27
7.47
7.48
7.49
7.51
9.00
8.25
6.70
1.0
2.0
1.0
1.0
1.0
1.0
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)
CF$_2$H
N
23

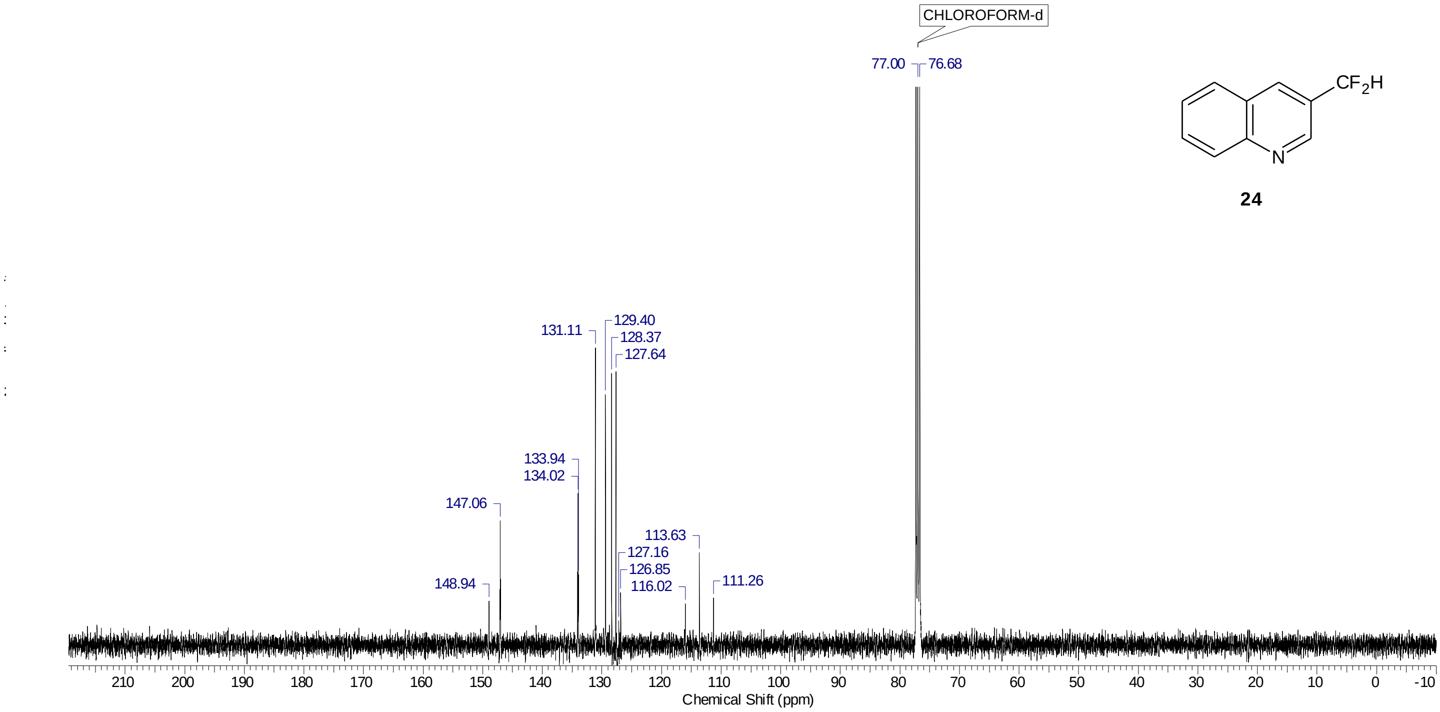

CHLOROFORM-d
77.31
77.00
76.68
CF$_2$H
N
23
130.47
136.64
125.74
151.80
121.94
125.79
114.38
127.51
132.34
148.91
116.76
112.01
132.57
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


-111.38
-111.52
CF2H
N
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
Chemical Shift (ppm)

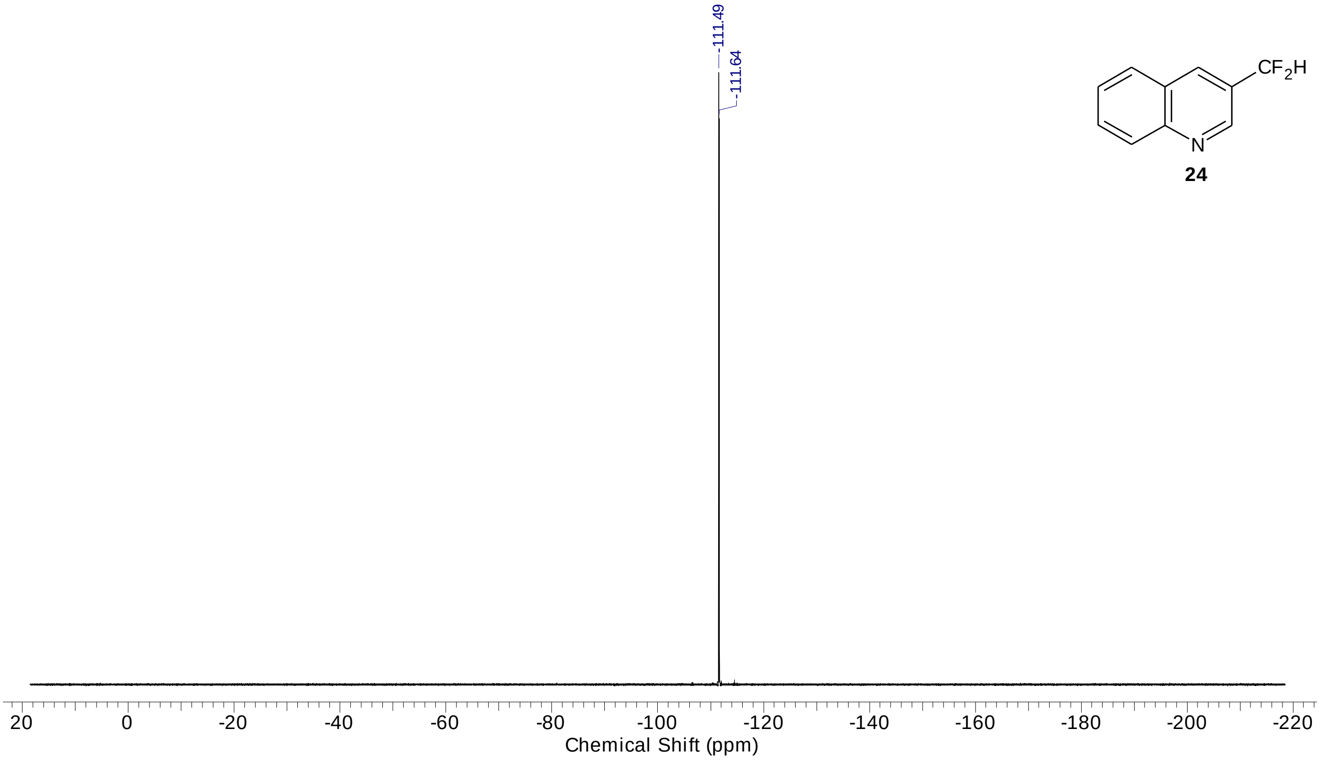
23


CHLOROFORM-d
9.05
8.34
8.20
8.18
7.93
7.91
7.84
7.82
7.67
7.67
7.65
7.63
7.27
7.05
6.91
6.77
0.8
1.0
1.0
1.0
1.0
1.1
1.0
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)
CF_2H
N

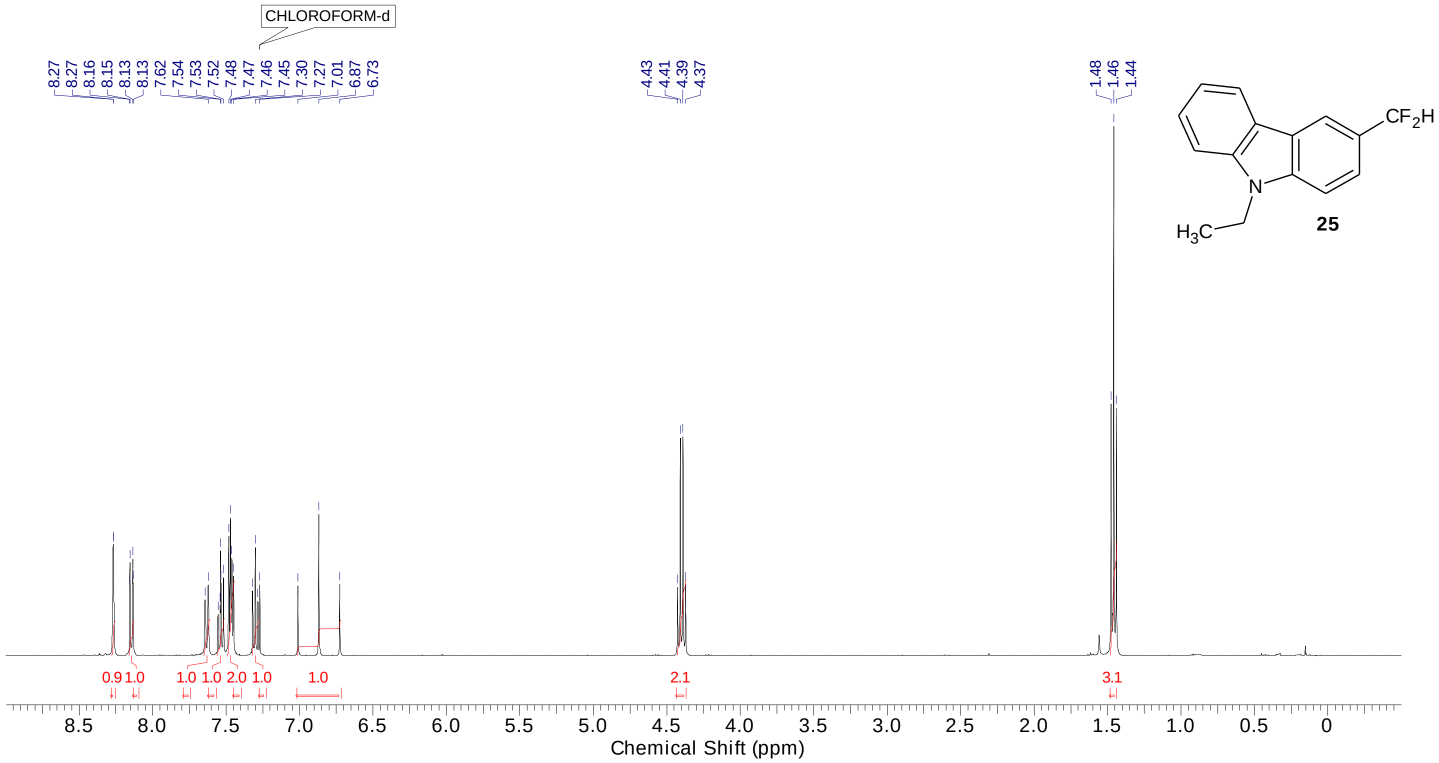
24

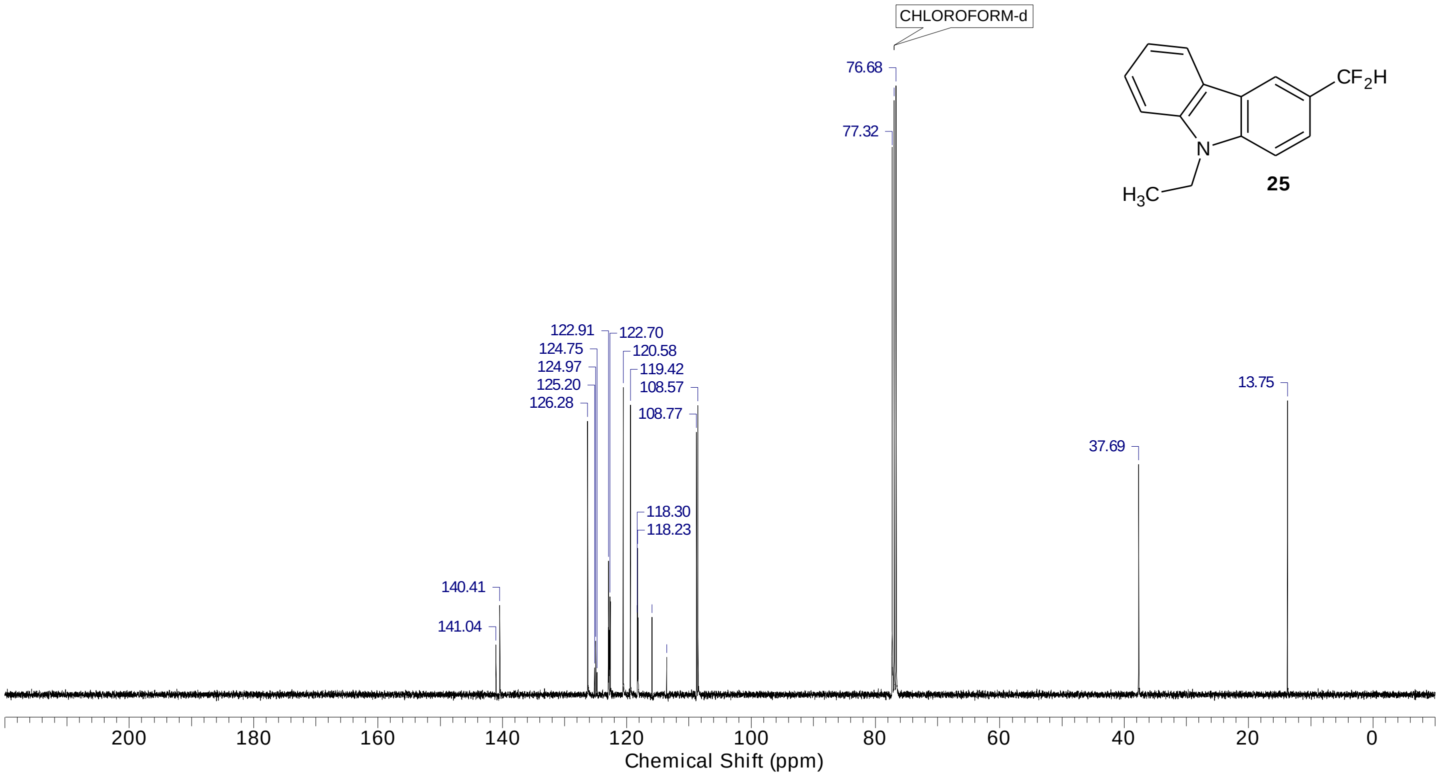

CHLOROFORM-d
77.00
76.68
131.11
129.40
128.37
127.64
133.94
134.02
147.06
113.63
127.16
126.85
116.02
111.26
148.94
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
Chemical Shift (ppm)
CF_2H
N

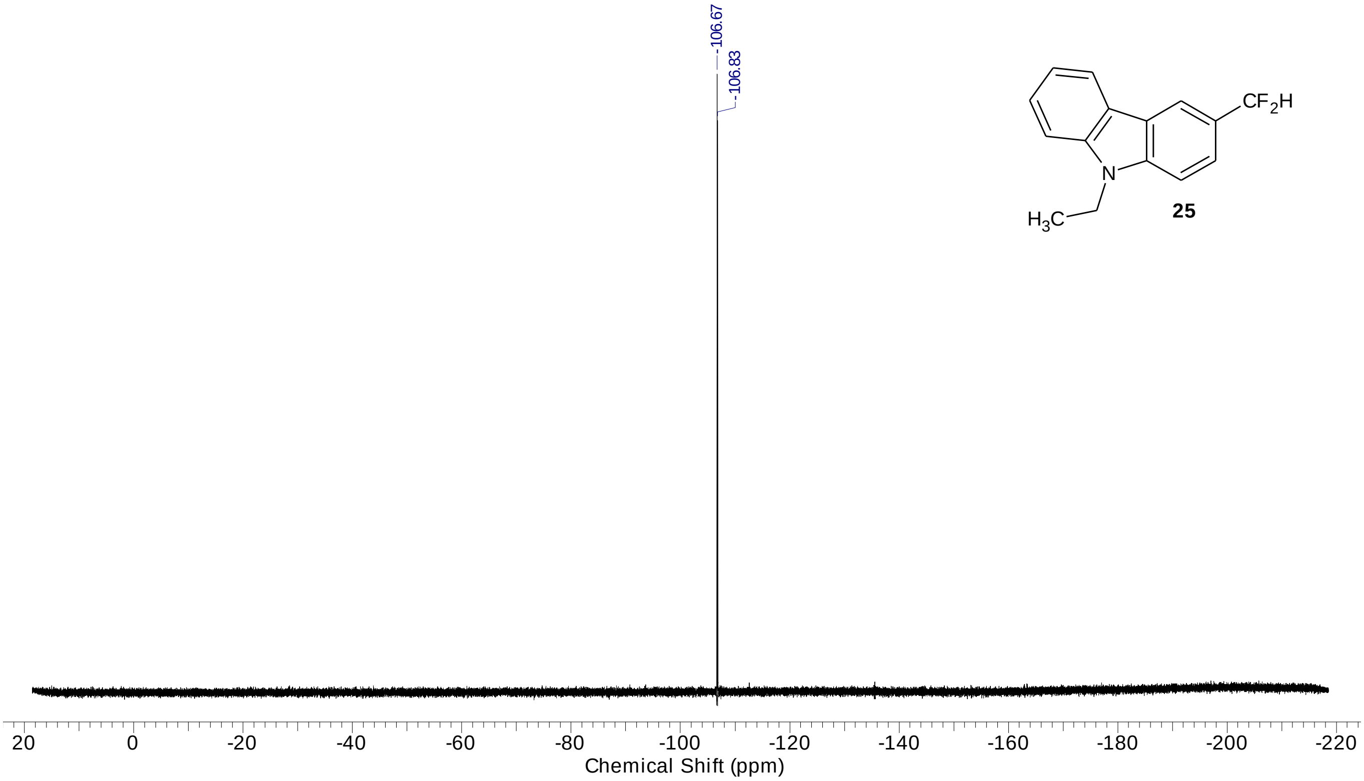
24

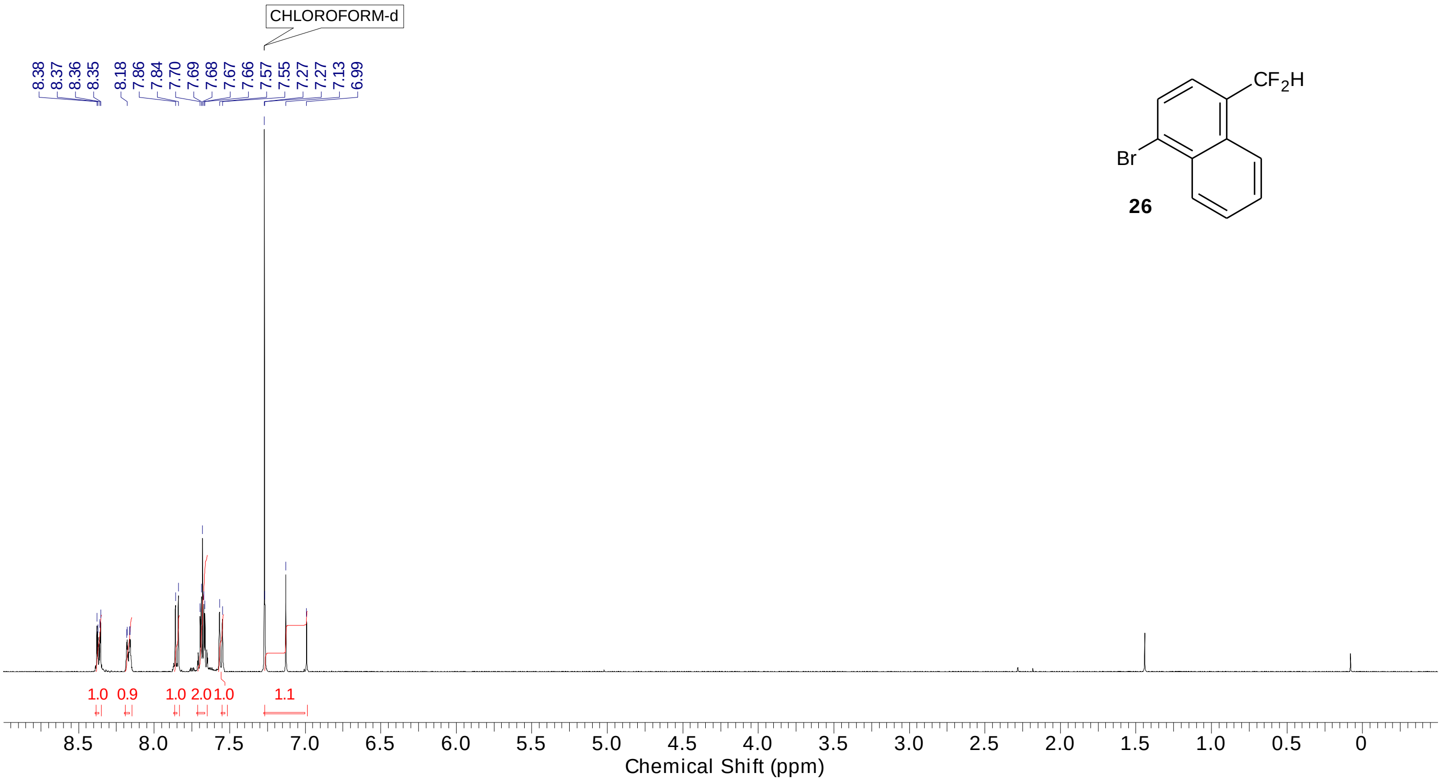

-111.49
-111.64
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
Chemical Shift (ppm)
CF2H
N

24

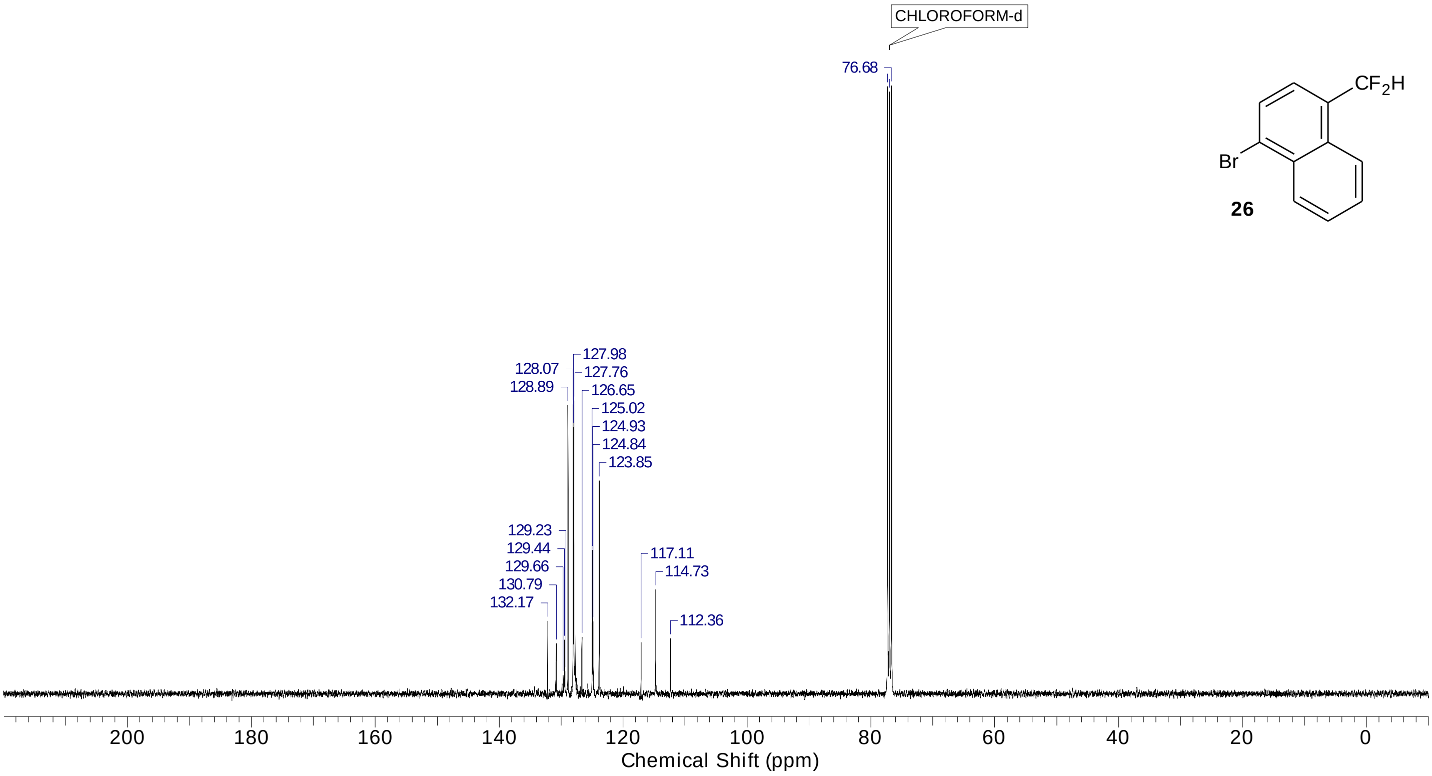

CHLOROFORM-d
8.27
8.27
8.16
8.15
8.13
8.13
7.62
7.54
7.53
7.52
7.48
7.47
7.46
7.45
7.30
7.27
7.01
6.87
6.73
4.43
4.41
4.39
4.37
1.48
1.46
1.44
CF$_2$H
N
H$_3$C
25
0.9
1.0
1.0
1.0
2.0
1.0
1.0
2.1
3.1
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


CHLOROFORM-d
76.68
77.32
CF$_2$H
N
H$_3$C
25
122.91
124.75
124.97
125.20
126.28
122.70
120.58
119.42
108.57
108.77
13.75
37.69
118.30
118.23
140.41
141.04
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

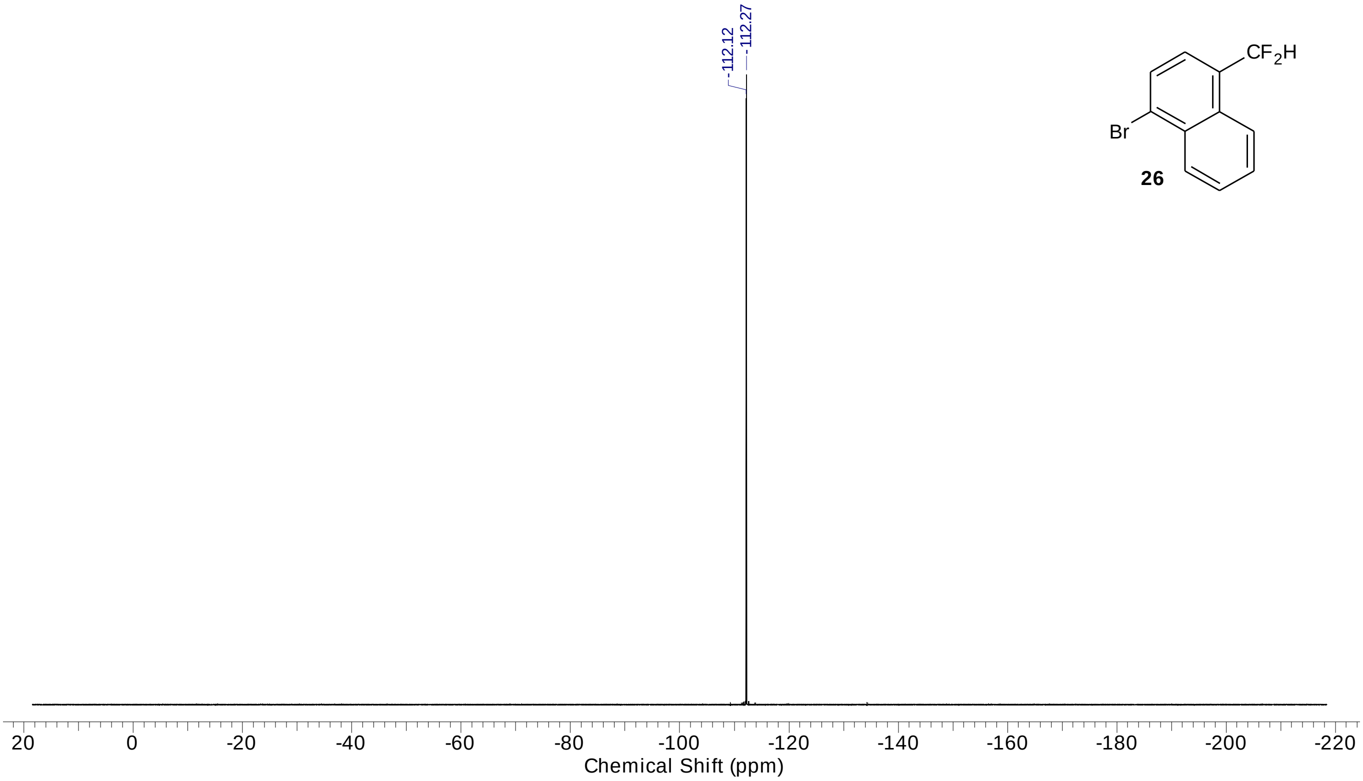

-106.67
-106.83
CF2H
N
H3C
25
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
Chemical Shift (ppm)

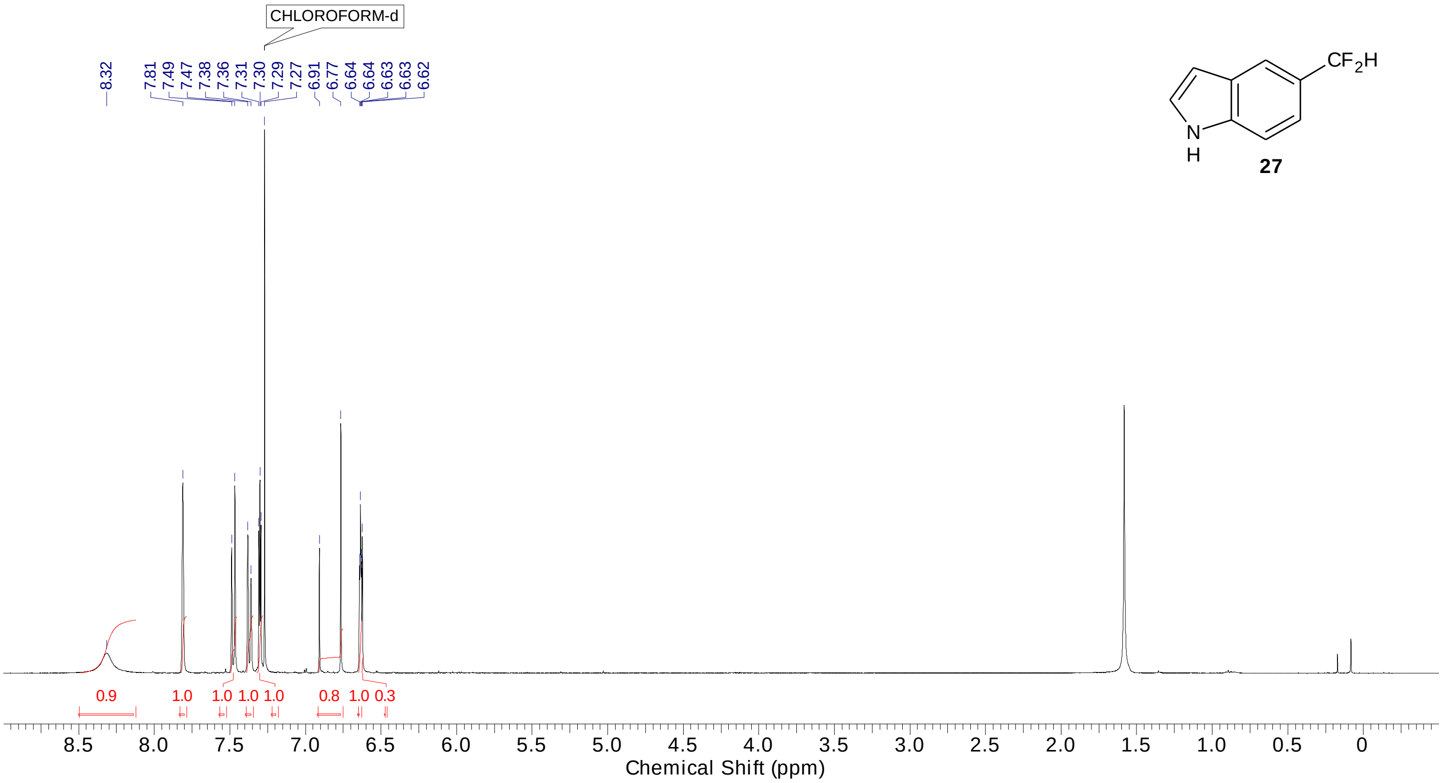

CHLOROFORM-d
8.38
8.37
8.36
8.35
8.18
7.86
7.84
7.70
7.69
7.68
7.67
7.66
7.57
7.55
7.27
7.27
7.13
6.99
1.0
0.9
1.0
2.0
1.0
1.1
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)
CF$_2$H
Br

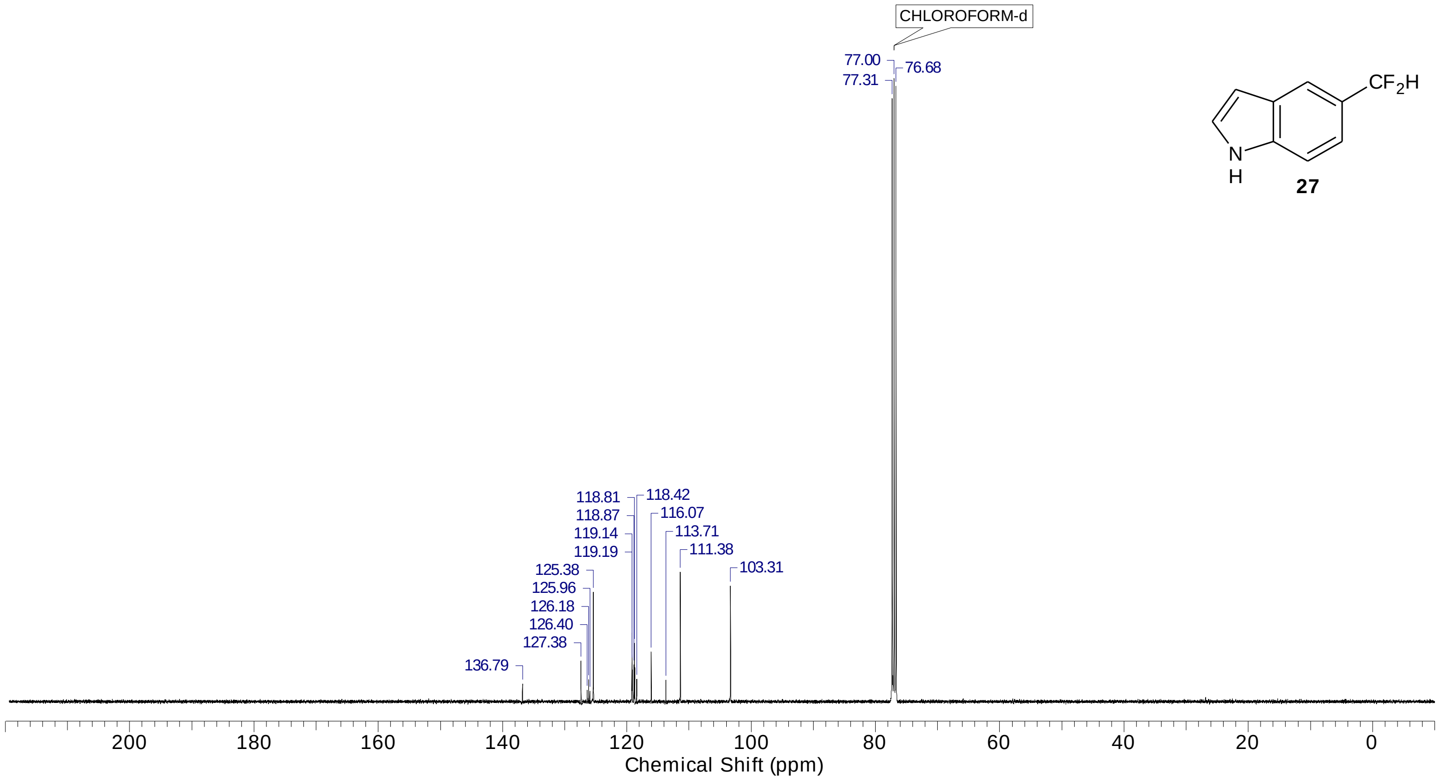
26

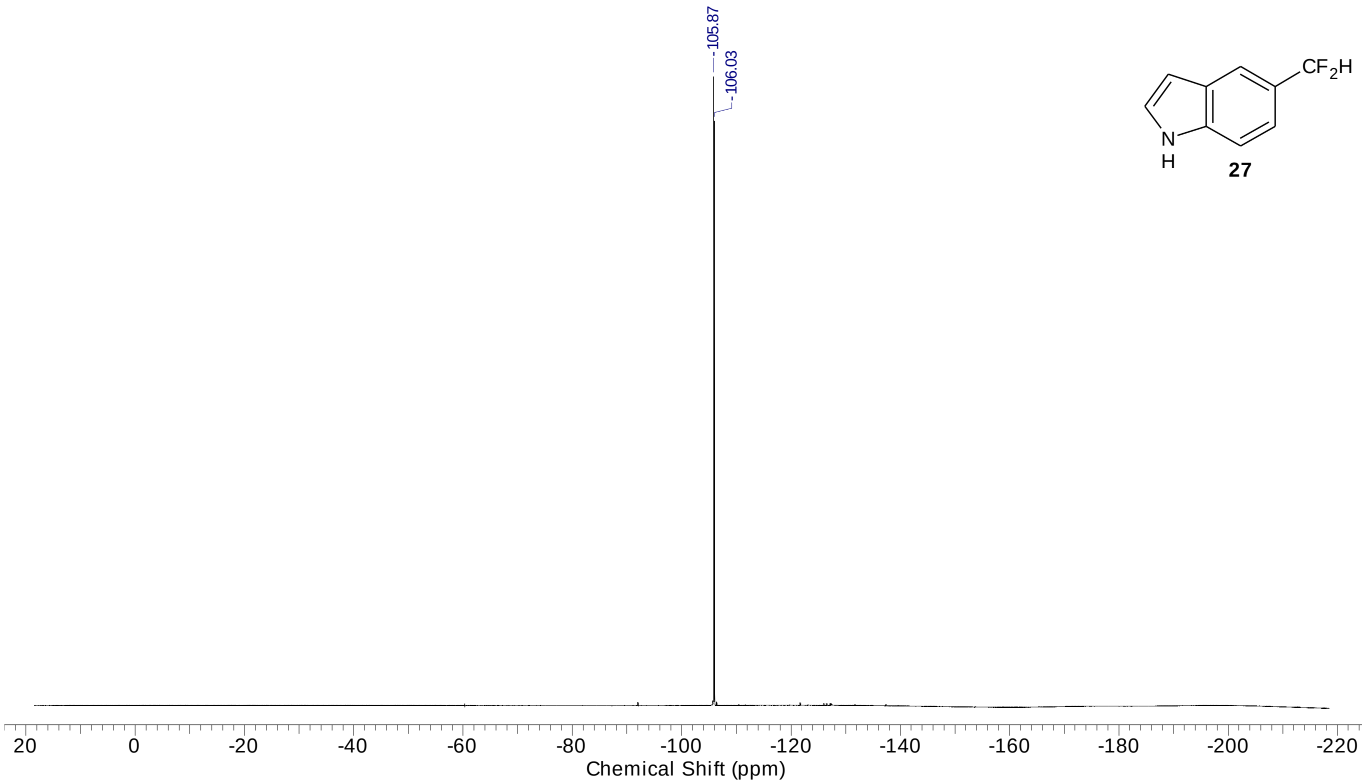

CHLOROFORM-d
76.68
127.98
127.76
126.65
125.02
124.93
124.84
123.85
128.07
128.89
129.23
129.44
129.66
130.79
132.17
117.11
114.73
112.36
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)
CF$_2$H
Br

26

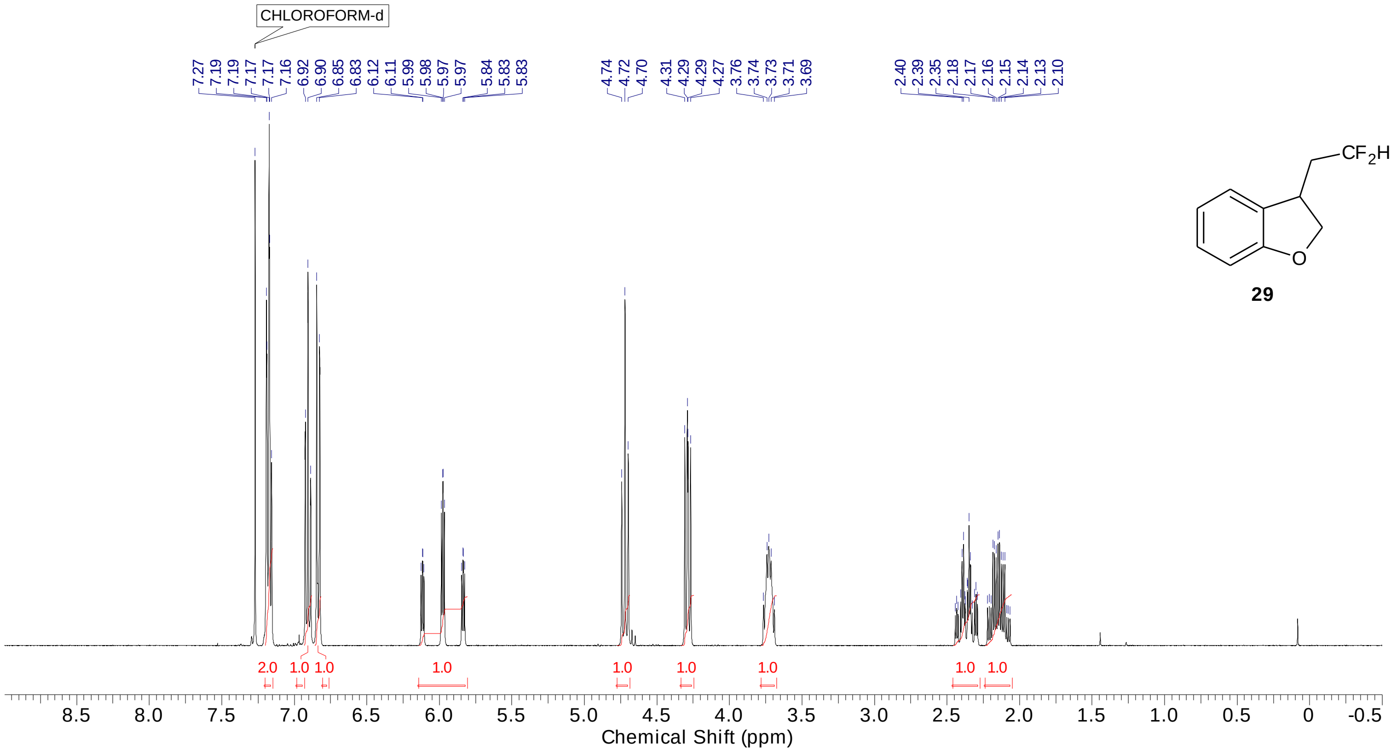

-112.12
-112.27
CF2H
Br
26
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
Chemical Shift (ppm)

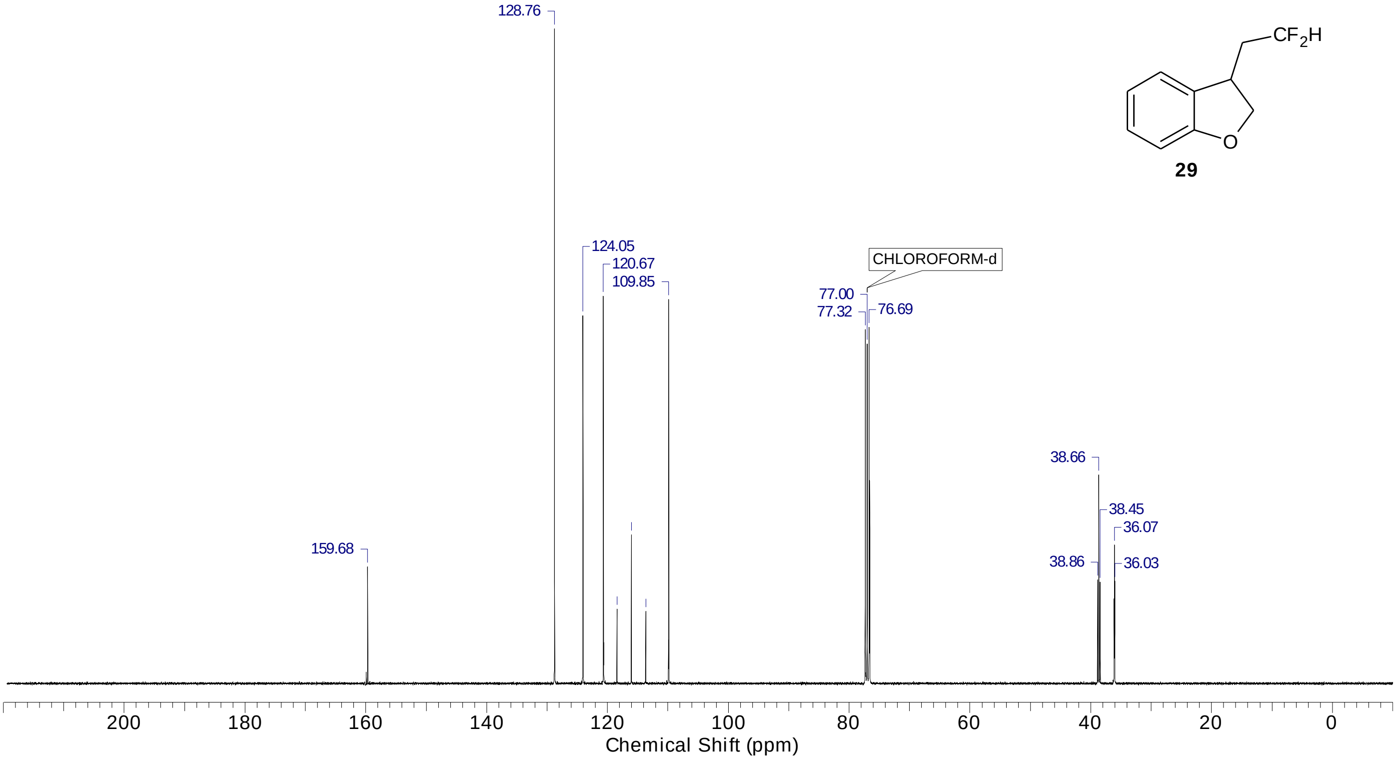

CHLOROFORM-d
8.32
7.81
7.49
7.47
7.38
7.36
7.31
7.30
7.29
7.27
6.91
6.77
6.64
6.64
6.63
6.63
6.62
0.9
1.0
1.0
1.0
1.0
0.8
1.0
0.3
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)
CF2H
N
H
27

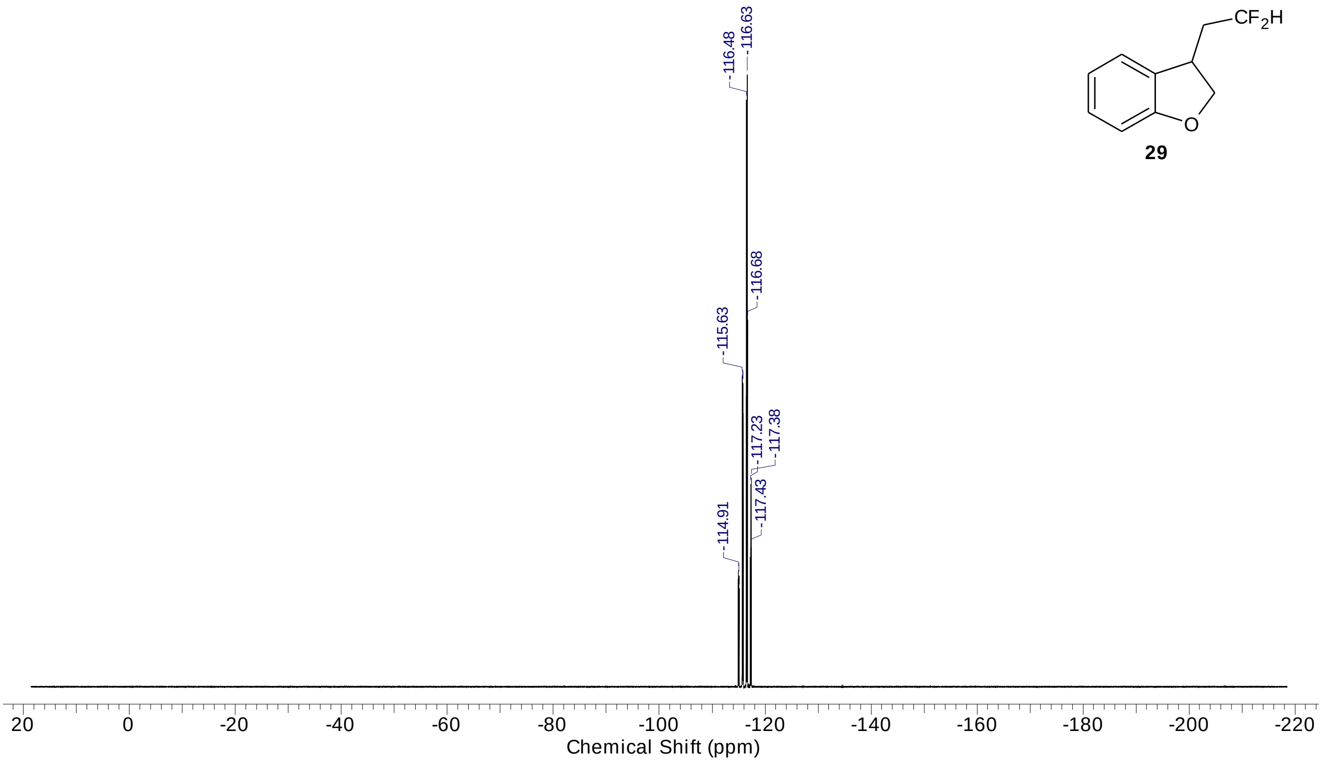

CHLOROFORM-d
77.00
77.31
76.68
118.81
118.87
119.14
119.19
125.38
125.96
126.18
126.40
127.38
136.79
118.42
116.07
113.71
111.38
103.31
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)
CF2H
N
H
27


-105.87
-106.03
CF2H
N
H
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
Chemical Shift (ppm)

27


CHLOROFORM-d
7.27
7.19
7.19
7.17
7.17
7.16
6.92
6.90
6.85
6.83
6.12
6.11
5.99
5.98
5.97
5.97
5.84
5.83
5.83
4.74
4.72
4.70
4.31
4.29
4.29
4.27
3.76
3.74
3.73
3.71
3.69
2.40
2.39
2.35
2.18
2.17
2.16
2.15
2.14
2.13
2.10
CF2H
O
29
2.0
1.0
1.0
1.0
1.0
1.0
1.0
1.0
1.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
-0.5
Chemical Shift (ppm)


128.76
124.05
120.67
109.85
CHLOROFORM-d
77.00
77.32
76.69
159.68
38.66
38.45
36.07
38.86
36.03
CF2H
O
29
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)



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