Supporting Information for

Direct Pd-catalyzed benzylation of highly electron-deficient perfluoroarenes

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General information: ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM300 and AM400 spectrometer. ^{19}F NMR was recorded on a Bruker AM300 spectrometer ($CFCl_3$ as outside standard and low field is positive). Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. NMR yield was determined by ^{19}F NMR using benzotrifluoride as an internal standard before working up the reaction.

Materials: All reagents were used as received from commercial sources, unless specified otherwise, or prepared as described in the literature. All reagents were weighed and handled in air, and refilled with an inert atmosphere of Ar at room temperature. DMF were distilled under reduced pressure from CaH_2. Toluene, Xylene, 1,4-Dioxane was distilled from sodium and benzophenone immediately before use. (4-(Chloromethyl)phenyl)(pyrrolidin-1-yl)methanone **2i** was prepared according to the literature procedure. [1]

Screens for Benzylation of Pentafluorobenzene 1 with Benzyl chloride 2a (Table 1). To a septum capped 25 mL of sealed tube were added Pd catalyst (10 mol%), and ligand (20 mol%), base (1.2 equiv) under Ar, followed by solvent (1.0 mL) with stirring. Pentafluorobenzene (0.4 mmol, 2.0 equiv) and benzyl chloride (0.2 mmol, 1.0 equiv) were then added subsequently. The sealed tube was screw capped and heated. After stirring for 12 h, the reaction mixture was cooled to room temperature and fluorobenzene (19 μL, 0.2 mmol) was added. The yield was determined by ^{19}F NMR before working up. If necessary, the reaction mixture was diluted with ethyl acetate, washed with water and brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified with silica gel chromatography to provide pure product.

General Procedure for Benzylation of Pentafluorobenzene 1 (Table 2).

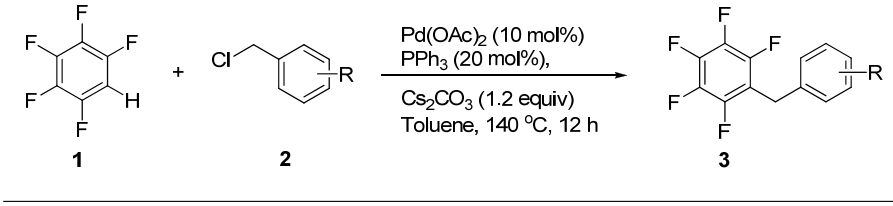
Method A: To a septum capped 25 mL of sealed tube were added $Pd(OAc)_2$ (10 mol%), and PPh_3 (20 mol%), Cs_2CO_3 (1.2 equiv) under Ar, followed by toluene (1.5

mL) with stirring. Pentafluorobenzene (1.2 mmol, 2.0 equiv) and benzyl chloride (0.6 mmol, 1.0 equiv) were then added subsequently. The sealed tube was screw capped and heated to 140 ^{o}C (oil bath). After stirring for 12 h, the reaction mixture was cooled to room temperature and diluted with ethyl acetate, washed with 1 N HCl and brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified with silica gel chromatography to provide pure product.

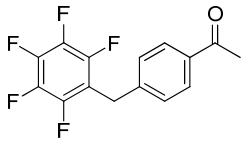
Method B: To a septum capped 25 mL of sealed tube were added $Pd(OAc)_2$ (10 mol%), and PPh_3 (20 mol%), Cs_2CO_3 (2.4 equiv) under Ar, followed by toluene (2.5 mL) with stirring. Pentafluorobenzene (1.2 mmol, 2.0 equiv), benzyl chloride (0.6 mmol, 1.0 equiv) and PivOH (1.2 equiv) were then added subsequently. The sealed tube was screw capped and heated to 140 ^{o}C (oil bath). After stirring for 12 h, the reaction mixture was cooled to room temperature and diluted with ethyl acetate, washed with 1 N HCl and brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified with silica gel chromatography to provide pure product.

Note: For compounds **3h**, **3j** and **3m**, the reaction was quenched by water, extracted with ethyl acetate, washed with brine, dried over Na_2SO_4, filtered and concentrated.

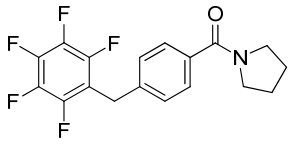
Table S1. Selected Results (3h-m) for Benzylation of Pentafluorobenzene 1 Using Method A[a]



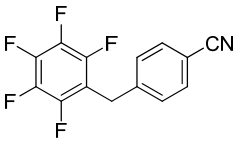
1 **2** **3**



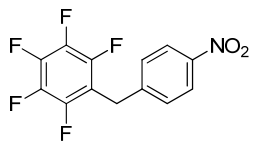
3h, 40%



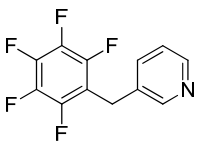
3i. 62%



3j, 74%

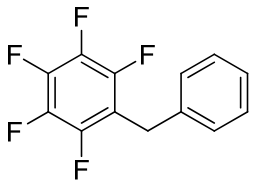


3k, 44%

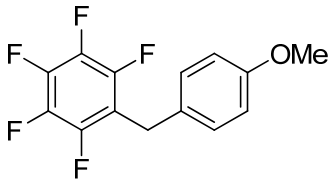


3m, 43%

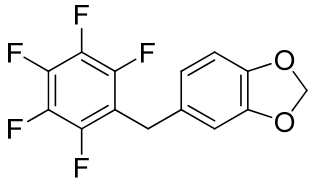
[a]Yield was determined by ^{19}F NMR using fluorobenzene as internal standard.



1-Benzyl-2,3,4,5,6-pentafluorobenzene (3a). Method A. The product (142 mg, 92% yield) as a white solid was purified with silica gel chromatography (Petroleum ether (100%)). This compound is known.[2] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32-7.23 (m, 5H), 4.01 (s, 2H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -143.7 (dd, *J* = 20.9 Hz, 7.3 Hz, 2F), -157.5 (td, *J* = 20.9, *J* = 7.3, Hz, 1F), -162.8 (tm, *J* = 20.9 Hz, 2F).

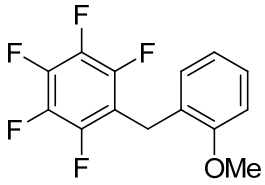


1,2,3,4,5-Pentafluoro-6-(4-methoxybenzyl)benzene (3b). Method A. The product (162 mg, 94% yield) as a white solid was purified with silica gel chromatography (Petroleum ether (100%)). This compound is known.[3] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16 (d, *J* = 8.7 Hz, 2 H), 6.81 (d, *J* = 8.7 Hz, 2 H), 3.94 (s, 2H), 3.76 (s, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 158.5, 144.9 (dm, *J* = 245.2 Hz), 139.8 (dm, *J* = 250.5 Hz), 137.5 (dm, *J* = 250.4 Hz), 129.5, 129.4, 114.9 (m), 114.1, 55.1, 27.2. ^{19}F NMR (282 MHz, $CDCl_3$) δ -144.1 (dd, *J* = 21.7 Hz, 7.9 Hz, 2F), -157.9 (t, *J* = 21.7 Hz, 1F), -162.9 (td, *J* = 21.7 Hz, 7.9 Hz, 2F). IR (thin film): ν_{max} 2969, 1660, 1531, 1504, 1246 cm^{-1}. MS (EI): *m/z* (%) 289 (M^++H^+), 288(M^+, 100), 121, 77.



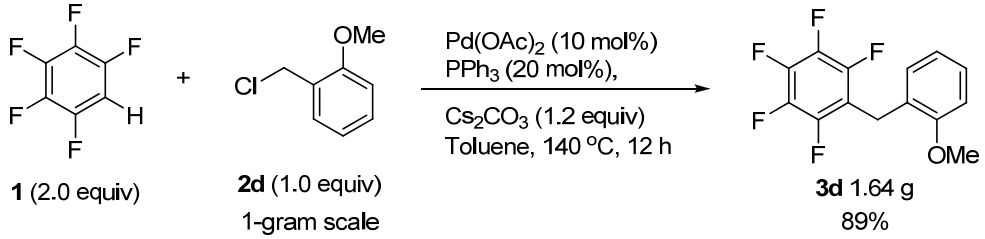
5-(Perfluorobenzyl)benzo[d][1,3]dioxole (3c). Method A. The product (145 mg, 80% yield) as a white solid (40 ^{o}C) was purified with silica gel chromatography (Petroleum ether /Ethyl acetate = 150:1).^{1}H NMR (300 MHz, $CDCl_3$) δ 6.72 (s, 3H), 5.92 (s, 2H), 3.92 (s, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 147.9, 146.5, 144.8(dm, *J* =

247.7 Hz), 139.8(dm, *J* = 251.8 Hz), 137.5 (dm, *J* = 252.6 Hz), 131.1, 121.4, 114.5 (m), 108.7, 108.4, 101.1, 27.7. ^{19}F NMR (282 MHz, $CDCl_3$) δ -144.0 (dd, *J* = 22.4 Hz, 9.1 Hz, 2F), -157.5 (t, *J* = 22.4 Hz, 1F), -162.6 (td, *J* = 22.4 Hz, 9.1 Hz, 2F). IR (thin film): ν_{max} 2989, 1655, 1521, 1503 cm^{-1}. MS (EI): *m/z* (%) 302 (M^+, 100), 244, 135. HRMS: Calculated for $C_{14}H_7O_2F_5$: 302.0366; Found: 302.0367.



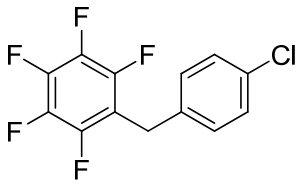
1,2,3,4,5-Pentafluoro-6-(2-methoxybenzyl)benzene (3d). Method A. The product (147 mg, 89% yield) as a white solid (64 °C) was purified with silica gel chromatography (Petroleum ether (100%)). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26-6.84 (m, 4H), 4.01 (s, 2H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 145.3 (dm, *J* = 245.0 Hz), 139.7 (dm, *J* = 248.2 Hz), 137.3 (dm, *J* = 258.1 Hz), 129.5, 128.2, 125.4, 120.4, 113.9 (m), 110.3, 55.2, 22.9. ^{19}F NMR (282 MHz, $CDCl_3$) δ -142.9 (dd, *J* = 21.7 Hz, 7.9 Hz, 2F), -158.1 (t, *J* = 19.8 Hz, 1F), -163.6 (td, *J* = 21.7 Hz, 5.9 Hz, 2F). IR (thin film): ν_{max} 2976, 1656, 1520, 1505 cm^{-1}. MS (EI): *m/z* (%) 288 (M^+, 100), 273, 237. HRMS: Calculated for $C_{14}H_9OF_5$: 288.0574; Found: 288.0570.

1-g-Scale Synthesis of 3d.

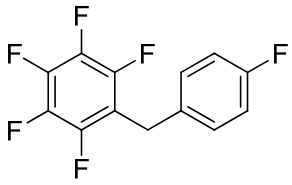


To a septum capped 100 mL of sealed tube were added $Pd(OAc)_2$ (143 mg, 0.64 mmol, 10 mol%), and PPh_3 (335 mg, 1.28 mmol, 20 mol%), Cs_2CO_3 (2.5 g, 7.67 mmol, 1.2 equiv) under Ar, followed by toluene (15 mL) with stirring. Pentafluorobenzene (1.42 mL, 12.8 mmol, 2.0 equiv) and benzyl chloride (1g, 6.4 mmol, 1.0 equiv) were then

added subsequently. The sealed tube was screw capped and heated to 140 ^{o}C (oil bath). After stirring for 12 h, the reaction mixture was cooled to room temperature and diluted with ethyl acetate, washed with 1 N HCl and brine, dried over Na_2SO_4, filtered and concentrated. The product (1.64 g, 89% yield) as a white solid (64 ^{o}C) was purified with silica gel chromatography (Petroleum ether (100%)).

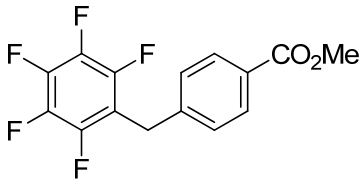


1-(4-Chlorobenzyl)-2,3,4,5,6-pentafluorobenzene (3e). Method A. The product (154 mg, 88% yield) as a white solid (42 ^{o}C) was purified with silica gel chromatography (Petroleum ether (100%)). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.4 Hz, 2H), 7.17 (t, *J* = 8.4 Hz, 2H), 3.98 (s, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 144.9 (dm, *J* = 251.7 Hz), 140.0 (dm, *J* = 252.5 Hz), 137.5 (dm, *J* = 246.8 Hz), 135.0, 132.9, 130.1, 128.9, 113.9 (m), 27.5. ^{19}F NMR (282 MHz, $CDCl_3$) δ -143.7 (dd, *J* = 21.1 Hz, 7.1 Hz, 2F), -156.9 (t, *J* = 18.9 Hz, 1F), -162.4 (td, *J* = 21.1 Hz, 8.1 Hz, 2F). IR (thin film): ν_{max} 2944, 1655, 1505 cm^{-1}. MS (EI): *m/z* (%) 425 ($M^+ + H^+$), 424 (M^+), 257 (100), 237. HRMS: Calculated for $C_{13}H_6F_5Cl$: 292.0078; Found: 292.0081.

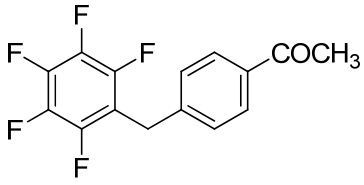


1,2,3,4,5-Pentafluoro-6-(4-fluorobenzyl)benzene (3f). Method A. The product (144 mg, 87% yield) as colorless oil was purified with silica gel chromatography (Petroleum ether (100%)). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22 (dd, *J* = 13.8 Hz, 6.0 Hz, 2H), 6.98 (t, *J* = 8.4 Hz, 2H), 3.99 (s, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 161.8 (d, *J* = 244.0 Hz), 144.9 (dm, *J* = 242.3 Hz), 140.1 (dm, *J* = 250.7 Hz), 137.6 (dm, *J* = 250.7 Hz), 133.1, 129.9 (d, *J* = 7.7 Hz), 115.6 (d, *J* = 21.7 Hz), 114.3, 27.3. ^{19}F NMR (282 MHz, $CDCl_3$) δ -116.1 (s, 1F), -144.0 (dd, *J* = 21.7 Hz, 7.6 Hz, 2F), -157.2 (t, *J*

= 21.7 Hz, 1F), -162.6 (td, *J* = 18.6 Hz, 5.6 Hz, 2F). IR (thin film): ν_{max} 1658, 1521, 1161 cm^{-1}. MS (EI): *m/z* (%) 277 ($M^+ + H^+$), 276 (M^+, 100), 255, 181, 109. HRMS: Calculated for $C_{13}H_6F_6$: 276.0374; Found: 276.0378.

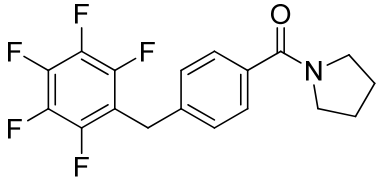


Methyl 4-(perfluorobenzyl)benzoate (3g). Method A. The product (161 mg, 85% yield) as a white solid (76 ^oC) was purified with silica gel chromatography (Petroleum ether /Ethyl acetate = 150:1). ^1H NMR (300 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.30 (t, *J* = 8.4 Hz, 2H), 4.07 (s, 2H), 3.90 (s, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 166.6, 146.4 (dm, *J* = 242.8 Hz), 142.4, 140.0 (dm, *J* = 252.6 Hz), 137.5 (dm, *J* = 252.6 Hz), 130.1, 128.9, 128.3, 113.5 (m), 52.1, 28.0. ^{19}F NMR (282 MHz, $CDCl_3$) δ -143.4 (dd, *J* = 23.0 Hz, 8.2 Hz, 2F), -156.6 (t, *J* = 21.7 Hz, 1F), -162.3 (td, *J* = 23.0 Hz, 8.2 Hz, 2F). IR (thin film): ν_{max} 2958, 1728, 1577 cm^{-1}. MS (EI): *m/z* (%) 317 ($M^+ + H^+$), 316 (M^+), 285 (100), 237. HRMS: Calculated for $C_{15}H_9O_2F_5$: 316.0523; Found: 316.0522.

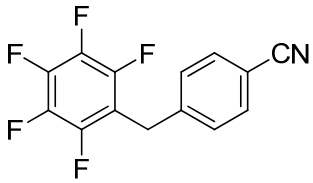


1-(4-(perfluorobenzyl)phenyl)ethanone (3h). Method B. The product (167 mg, 93% yield) as a white solid (81 ^oC) was purified with silica gel chromatography (Petroleum ether /Ethyl acetate = 80:1). ^1H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.1 Hz, 2H), 7.31 (t, *J* = 8.1 Hz, 2H), 4.06 (s, 2H), 2.56 (s, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 197.4, 144.9 (dm, *J* = 243.4 Hz), 142.6, 140.0 (dm, *J* = 252.7 Hz), 137.5 (dm, *J* = 252.1 Hz), 135.8, 128.8, 128.5, 113.3 (m), 28.0, 26.5. ^{19}F NMR (282 MHz, $CDCl_3$) δ -143.5 (dd, *J* = 21.7 Hz, 7.9 Hz, 2F), -156.7 (t, *J* = 21.7 Hz, 1F), -162.4 (td, *J* = 21.7 Hz, 7.9 Hz, 2F). IR (thin film): ν_{max} 2921, 1681, 1529 cm^{-1}. MS (EI): *m/z* (%)

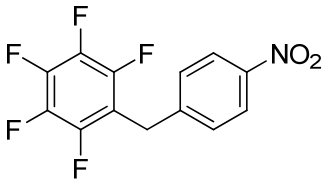
301 ($M^+ + H^+$), 300 (M^+), 285 (100). HRMS: Calculated for $C_{15}H_9OF_5$: 300.0574; Found: 300.0573.



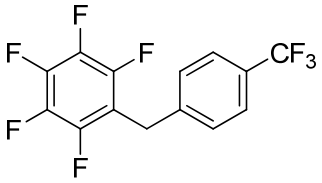
(4-(Perfluorobenzyl)phenyl)(pyrrolidin-1-yl)methanone (3i). Method A. The product (198 mg, 93% yield) as a white solid (103 ^oC) was purified with silica gel chromatography (Petroleum ether /Ethyl acetate = 4:1). ^1H NMR (300 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.1 Hz, 2H), 7.27 (t, *J* = 8.1 Hz, 2H), 4.04 (s, 2H), 3.52 (br, 4H), 1.91 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 144.7 (dm, *J* = 252.8 Hz), 139.8 (dm, *J* = 258.0 Hz), 138.9, 137.3 (dm, *J* = 263.1 Hz), 135.8, 128.0, 127.5, 113.8 (m), 49.4, 46.0, 27.8, 26.2, 24.3. ^{19}F NMR (282 MHz, $CDCl_3$) δ -143.5 (dd, *J* = 21.7 Hz, 7.9 Hz, 2F), -156.9 (t, *J* = 19.8 Hz, 1F), -162.4 (td, *J* = 21.7 Hz, 7.9 Hz, 2F). IR (thin film): ν_{max} 2951, 1655, 1501 cm^{-1}. MS (EI): *m/z* (%) 356 ($M^+ + H^+$), 355 (M^+), 285 (100), 237. HRMS: Calculated for $C_{18}H_{14}NOF_5$: 355.0996; Found: 355.0991.



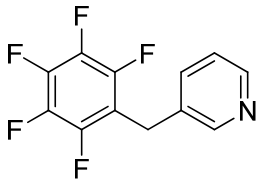
4-(Perfluorobenzyl)benzonitrile (3j). Method B. The product (139 mg, 82% yield) as a white solid (63 ^oC) was purified with silica gel chromatography (Petroleum ether /Ethyl acetate = 100:1). ^1H NMR (300 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.1 Hz, 2H), 7.37 (t, *J* = 8.1 Hz, 2H), 4.10 (s, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 144.8 (dm, *J* = 242.8 Hz), 142.6, 140.2 (dm, *J* = 253.3 Hz), 137.5 (dm, *J* = 253.1 Hz), 132.6, 129.1, 118.5, 112.7 (m), 111.0, 28.1. ^{19}F NMR (282 MHz, $CDCl_3$) δ -143.4 (dd, *J* = 24.0 Hz, 9.9 Hz, 2F), -156.0 (m, 1F), -161.9 (m, 2F). IR (thin film): ν_{max} 2230, 1655, 1523 cm^{-1}. MS (EI): *m/z* (%) 284 ($M^+ + H^+$), 283 (M^+, 100), 181. HRMS: Calculated for $C_{14}H_6NF_5$: 283.0420; Found: 283.0423.



1,2,3,4,5-Pentafluoro-6-(4-nitrobenzyl)benzene (3k). Method B. The product (134 mg, 74% yield) as a white solid (108 ^{o}C) was purified with silica gel chromatography (Petroleum ether /Ethyl acetate = 100:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.7 Hz, 2H), 7.42 (t, *J* = 8.7 Hz, 2H), 4.14 (s, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 147.0, 144.9 (dm, *J* = 250.3 Hz), 140.3 (dm, *J* = 254.1 Hz), 137.6 (dm, *J* = 253.3 Hz), 129.2, 124.4, 112.6 (m), 27.9. ^{19}F NMR (282 MHz, $CDCl_3$) δ -143.3 (dd, *J* = 20.6 Hz, 7.6 Hz, 2F), -155.6 (t, *J* = 20.0 Hz, 1F), -161.7 (td, *J* = 20.6 Hz, 7.9 Hz, 2F). IR (thin film): ν_{max} 3113, 1608, 1506 cm^{-1}. MS (EI): *m/z* (%) 304 ($M^+ + H^+$), 303 (M^+), 237 (100), 188. HRMS: Calculated for $C_{13}H_6NO_2F_5$: 303.0319; Found: 303.0320.



1,2,3,4,5-Pentafluoro-6-(4-(trifluoromethyl)benzyl)benzene (3l). Method B. The product (177 mg, 91% yield) as colorless oil was purified with silica gel chromatography (Petroleum ether (100%)). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.1 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 4.08 (s, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 145.0 (dm, *J* = 246.4 Hz), 141.4, 140.2 (dm, *J* = 252.9 Hz), 137.6 (dm, *J* = 252.7 Hz), 129.4 (q, *J* = 32.6 Hz), 128.7, 125.8 (q, *J* = 3.9 Hz), 124.0 (q, *J* = 271.7 Hz), 113.4 (m), 27.9. ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.1 (s, 3F), -143.6 (dd, *J* = 21.7 Hz, 7.9 Hz, 2F), -156.5 (t, *J* = 21.7 Hz, 1F), -162.2 (td, *J* = 21.7 Hz, 7.9 Hz, 2F). IR (thin film): ν_{max} 2936, 1574, 1521 cm^{-1}. MS (EI): *m/z* (%) 327 ($M^+ + H^+$), 326 (M^+), 257 (100), 255, 237. HRMS: Calculated for $C_{14}H_6F_8$: 326.0342; Found: 326.0344.

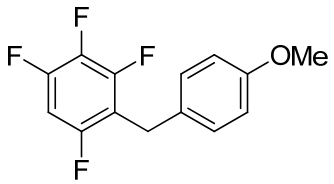


3-(Perfluorobenzyl)pyridine (3m). Method B. The product (117 mg, 75% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether /Ethyl acetate = 8:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.56-8.49 (m, 2H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.25 (dd, *J* = 7.5 Hz, 4.5 Hz, 1H), 4.04 (s, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 149.6, 148.4, 144.8 (dm, *J* = 246.3 Hz), 140.1 (dm, *J* = 253.0 Hz), 137.7 (dm, *J* = 252.7 Hz), 135.8, 133.0, 123.6, 113.1 (m), 25.4. ^{19}F NMR (282 MHz, $CDCl_3$) δ -143.6 (dd, *J* = 21.7 Hz, 7.9 Hz, 2F), -156.5 (t, *J* = 21.7 Hz, 1F), -162.2 (td, *J* = 21.7 Hz, 7.9 Hz, 2F). IR (thin film): ν_{max} 2946, 1656, 1506 cm^{-1}. MS (EI): *m/z* (%) 260 (M^+ + H^+), 259 (M^+, 100), 240. HRMS: Calculated for $C_{12}H_6NF_5$: 259.0420; Found: 259.0422.

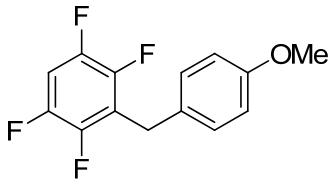
General Procedure for Benzylation of Fluoroarenes (Table 3).

To a septum capped 25 mL of sealed tube were added $Pd(OAc)_2$ (10 mol%), and PPh_3 (20 mol%), Cs_2CO_3 (2.4 equiv) under Ar, followed by toluene (2.5 mL) with stirring. Fluoroarene (2.0-3.0 equiv), benzyl chloride (0.6 mmol, 1.0 equiv) and PivOH (1.2 equiv) were then added subsequently. The sealed tube was screw capped and heated to 140 ^{o}C (oil bath). After stirring for 12 h, the reaction mixture was cooled to room temperature and diluted with ethyl acetate, washed with 1 N HCl and brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified with silica gel chromatography to provide pure product.

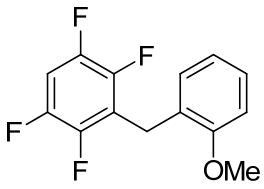
Note: For compound **5h**, the reaction was quenched by water, extracted with ethyl acetate, washed with brine, dried over Na_2SO_4, filtered and concentrated.



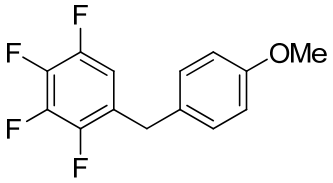
1,2,3,5-Tetrafluoro-4-(4-methoxybenzyl)benzene (5a). 3.0 equiv of fluoroarene was used. The product (138 mg, 85% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether /Ethyl ether = 200:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16 (d, *J* = 8.7 Hz, 2 H), 6.82 (d, *J* = 8.7 Hz, 2 H), 6.81-6.72 (m, 1H), 3.91 (s, 2H), 3.77 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 155.1 (dm, *J* = 243.4 Hz), 149.7 (dm, *J* = 246.8 Hz), 149.1 (dm, *J* = 249.8 Hz), 137.2 (dm, *J* = 252.4 Hz), 130.2, 129.3, 114.8 (m), 114.0, 100.6 (m), 55.2, 27.2. ^{19}F NMR (282 MHz, $CDCl_3$) δ -119.4 (t, *J* = 9.9 Hz, 1F), -135.7 (dm, *J* = 19.8 Hz, 1F), -136.6 (d, *J* = 20.0 Hz, 1F), -165.6 (m, 1F). IR (thin film): ν_{max} 2937, 1645, 1514, 1504 cm^{-1}. MS (EI): *m/z* (%) 271($M^+ + H^+$), 270 (M^+, 100), 121. HRMS: Calculated for $C_{14}H_{10}OF_4$: 270.0668; Found: 270.0669.



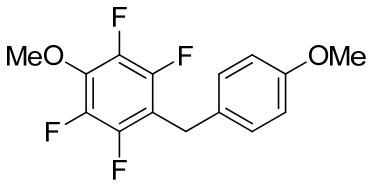
1,2,4,5-Tetrafluoro-3-(4-methoxybenzyl)benzene (5b). 3.0 equiv of fluoroarene was used. The product (151 mg, 93% yield) as a white solid (65 ^{o}C) was purified with silica gel chromatography (Petroleum ether /Ethyl ether = 200:1).^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.7 Hz, 2 H), 6.95-6.82 (m, 1H), 6.83 (d, *J* = 8.7 Hz, 2 H), 3.99 (s, 2H), 3.77 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 145.8 (dm, *J* = 246.6 Hz), 144.5(dm, *J* = 243.1 Hz), 129.7, 129.5, 120.8 (m), 114.0, 103.9 (m), 55.1, 27.8. ^{19}F NMR (282 MHz, $CDCl_3$) δ -139.9 (m, 2F), -144.6 (m, 2F). IR (thin film): ν_{max} 2968, 1609, 1513 cm^{-1}. MS (EI): *m/z* (%) 271 ($M^+ + H^+$), 270 (M^+, 100), 121. HRMS: Calculated for $C_{14}H_{10}OF_4$: 270.0668; Found: 270.0670.



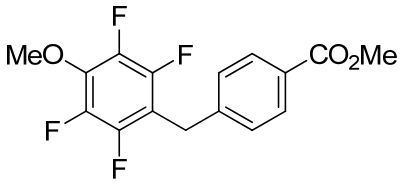
1,2,4,5-Tetrafluoro-3-(2-methoxybenzyl)benzene (5c). 3.0 equiv of fluoroarene was used. The product (135 mg, 83% yield) as a white solid (85 ^{o}C) was purified with silica gel chromatography (Petroleum ether /Ethyl ether = 250:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (t, *J* = 6.3 Hz, 1H), 7.05 (d, *J* = 7.2 Hz, 1H), 6.97-6.85 (m, 3 H), 4.06 (s, 2H), 3.84 (s, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 157.1, 145.7 (dm, *J* = 246.4 Hz), 145.0 (dm, *J* = 245.5 Hz), 129.4, 128.1, 125.6, 120.3, 119.7 (m), 110.2, 103.8 (m), 55.2, 23.4. ^{19}F NMR (282 MHz, $CDCl_3$) δ -140.6 (m 2F), -145.3 (m, 2F). IR (thin film): ν_{max} 2961, 1600, 1502 cm^{-1}. MS (EI): *m/z* (%) 271($M^+ + H^+$), 270 (M^+, 100), 255. HRMS: Calculated for $C_{14}H_{10}OF_4$: 270.0668; Found: 270.0667.



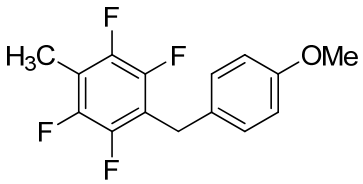
1,2,3,4-Tetrafluoro-5-(4-methoxybenzyl)benzene (5d). 3.0 equiv of fluoroarene was used. The product (111 mg, 69% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether /Ethyl ether = 200:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.4 Hz, 2 H), 6.87 (d, *J* = 8.4 Hz, 2 H), 6.70-6.67 (m, 1H), 3.90 (s, 2H), 3.80 (s, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 158.5, 146.8 (dm, *J* = 254.8 Hz), 145.4 (dm, *J* = 242.9 Hz), 140.6 (dm, *J* = 252.4 Hz), 138.8 (dm, *J* = 251.2 Hz), 129.8, 125.1 (m), 114.1, 111.3 (m), 55.1, 38.2. ^{19}F NMR (282 MHz, $CDCl_3$) δ -140.3 (m, 1F), -143.9 (m, 1F), -156.5 (t, *J* = 20.3 Hz, 1F), -159.3 (m, 1F). IR (thin film): ν_{max} 2937, 1650, 1513 cm^{-1}. MS (EI): *m/z* (%) 271($M^+ + H^+$), 270 (M^+, 100), 121. HRMS: Calculated for $C_{14}H_{10}OF_4$: 270.0668; Found: 270.0663.



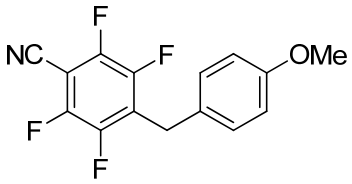
1,2,4,5-Tetrafluoro-3-methoxy-6-(4-methoxybenzyl)benzene (5e). 2.0 equiv of fluoroarene was used. The product (176 mg, 98% yield) as a white solid (47 ^{o}C) was purified with silica gel chromatography (Petroleum ether /Ethyl ether = 200:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.7 Hz, 2 H), 6.82 (d, *J* = 8.7 Hz, 2 H), 4.02 (s, 3H), 3.93 (s, 2H), 3.77 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 145.0 (dm, *J* = 238.3 Hz), 141.0 (dm, *J* = 245.4 Hz), 136.6 (m), 130.1, 129.4, 114.0, 113.3 (m), 62.1, 55.2, 27.2. ^{19}F NMR (282 MHz, $CDCl_3$) δ -145.8 (dd, *J* = 21.7 Hz, 10.6 Hz, 2F), -158.6 (dd, *J* = 21.7 Hz, 10.6 Hz, 2F). IR (thin film): ν_{max} 2968, 1658, 1513 cm^{-1}. MS (EI): *m/z* (%) 301 ($M^+ + H^+$), 300 (M^+, 100), 269. HRMS: Calculated for $C_{15}H_{12}O_2F_4$: 300.0773; Found: 300.0771.



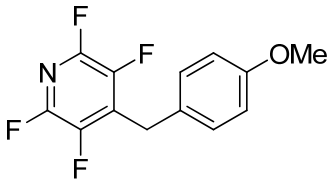
Methyl 4-(2,3,5,6-tetrafluoro-4-methoxybenzyl)benzoate (5f). 2.0 equiv of fluoroarene was used. The product (184 mg, 94% yield) as a white solid (86 ^{o}C) was purified with silica gel chromatography (Petroleum ether /Ethyl ether = 200:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.1 Hz, 2 H), 7.31 (d, *J* = 8.1 Hz, 2 H), 4.05 (s, 5H), 3.90 (s, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 166.7, 145.0 (dm, *J* = 244.6 Hz), 143.1, 140.8 (dm, *J* = 246.9 Hz), 137.0 (m), 129.9, 128.6, 128.3, 111.6 (m), 62.0, 52.0, 28.0. ^{19}F NMR (282 MHz, $CDCl_3$) δ -145.3 (dd, *J* = 21.7 Hz, 7.9 Hz, 2F), -158.3 (dd, *J* = 21.7 Hz, 7.9 Hz, 2F). IR (thin film): ν_{max} 2957, 1728, 1505 cm^{-1}. MS (EI): *m/z* (%) 329($M^+ + H^+$), 328(M^+), 297(100), 269. HRMS: Calculated for $C_{16}H_{12}O_3F_4$: 328.0723; Found: 328.0728.



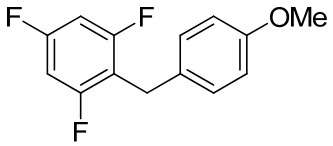
1,2,4,5-tetrafluoro-3-(4-methoxybenzyl)-6-methylbenzene (5g). 2.0 equiv of fluoroarene was used. The product (122 mg, 72% yield) as a white solid (70 ^{o}C) was purified with silica gel chromatography (Petroleum ether /Ethyl ether = 200:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.4 Hz, 2 H), 6.82 (d, *J* = 8.4 Hz, 2 H), 3.96 (s, 2H), 3.77 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 144.9 (dm, *J* = 242.4 Hz), 144.4(dm, *J* = 242.3 Hz), 130.2, 129.4, 117.0 (m), 114.0, 113.9 (m), 55.2, 27.6, 7.4. ^{19}F NMR (282 MHz, $CDCl_3$) δ -144.8 (dd, *J* = 22.2 Hz, 10.2 Hz, 2F), -146.2 (dd, *J* = 22.2 Hz, 12.1 Hz, 2F). IR (thin film): ν_{max} 2957, 1513, 1486 cm^{-1}. MS (EI): *m/z* (%) 285 ($M^+ + H^+$), 284 (M^+, 100), 121. HRMS: Calculated for $C_{15}H_{12}OF_4$: 284.0824; Found: 284.0814.



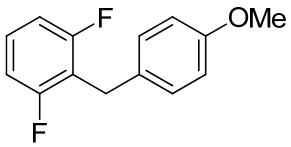
2,3,5,6-Tetrafluoro-4-(4-methoxybenzyl)benzonitrile (5h). 2.0 equiv of fluoroarene was used. The product (90 mg, 51% yield) as a white solid (111 ^{o}C) was purified with silica gel chromatography (Petroleum ether /Ethyl ether = 250:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17 (d, *J* = 8.4 Hz, 2 H), 6.82 (d, *J* = 8.4 Hz, 2 H), 4.04 (s, 2H), 3.77 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 147.1 (dm, *J* = 251.6 Hz), 144.5 (dm, *J* = 234.9 Hz), 143.3 (m), 129.6, 127.9, 127.4 (m), 107.5, 55.2, 28.4. ^{19}F NMR (282 MHz, $CDCl_3$) δ -133.0 (m, 2F), -140.6 (m, 2F). IR (thin film): ν_{max} 2943, 2246, 1656 cm^{-1}. MS (EI): *m/z* (%) 296($M^+ + H^+$), 296 (M^+, 100), 121. HRMS: Calculated for $C_{15}H_9NOF_4$: 295.0620; Found: 295.0622.



2,3,5,6-Tetrafluoro-4-(4-methoxybenzyl)pyridine (5i). 2.0 equiv of fluoroarene was used. The product (151 mg, 93% yield) as a pale yellow oil was purified with silica gel chromatography (Petroleum ether /Ethyl ether = 250:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.7 Hz, 2 H), 6.85 (d, *J* = 8.7 Hz, 2 H), 4.07 (s, 2H), 3.79 (s, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 158.8, 144.1 (dm, *J* = 244.2 Hz), 140.4 (dm, *J* = 256.3 Hz), 134.2 (m), 129.6, 127.6, 114.3, 55.1, 28.5. ^{19}F NMR (282 MHz, $CDCl_3$) δ -91.7 (m, 2F), -145.3 (m, 2F). IR (thin film): ν_{max} 2938, 1647, 1513 cm^{-1}. MS (EI): *m/z* (%) 272($M^+ + H^+$), 271(M^+, 100), 121. HRMS: Calculated for $C_{13}H_9NOF_4$: 271.0620; Found: 271.0619.



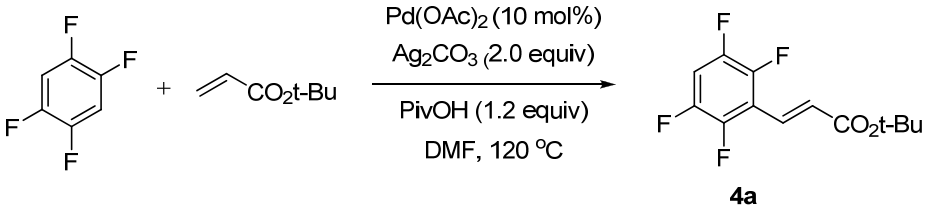
1,3,5-Prifluoro-2-(4-methoxybenzyl)benzene (5j). 3.0 equiv of fluoroarene was used. The product (110 mg, 73% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether /Ethyl ether = 250:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16 (d, *J* = 8.4 Hz, 2 H), 6.81 (d, *J* = 8.4 Hz, 2 H), 6.64 (t, *J* = 8.1 Hz, 2 H), 3.89 (s, 2H), 3.76 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2 (dm, *J* = 249.6 Hz), 158.1, 131.0, 129.3, 113.9, 100.0 (m), 55.2, 26.9. ^{19}F NMR (282 MHz, $CDCl_3$) δ -111.4 (m, 1F), -112.8 (t, *J* = 5.6 Hz, 2F). IR (thin film): ν_{max} 2937, 1660, 1513 cm^{-1}. MS (EI): *m/z* (%) 253 ($M^+ + H^+$), 252 (M^+, 100), 221. HRMS: Calculated for $C_{14}H_{11}OF_3$: 252.0762; Found: 252.0760.



1,3-Difluoro-2-(4-methoxybenzyl)benzene (5k). 3.0 equiv of fluoroarene was used.

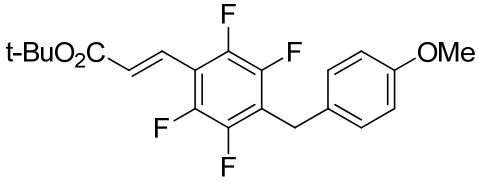
The product (67 mg, 48% yield) along with **5k'** (4%) as a colorless oil was purified with silica gel chromatography (Petroleum ether /Ethyl ether = 250:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.4 Hz, 2 H), 7.14-7.09 (m, 1 H), 6.87-6.78 (m, 4 H), 3.94 (s, 2H), 3.74 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3 (dd, *J* = 245.4 Hz, *J* = 8.1 Hz), 158.1, 131.3, 129.4, 127.7 (m), 117.2 (m), 113.8, 111.0(m), 55.1, 27.2. ^{19}F NMR (282 MHz, $CDCl_3$) δ -115.7 (m, 2F). IR (thin film): ν_{max} 2935, 1623, 1563 cm^{-1}. MS (EI): *m/z* (%) 235($M^+ + H^+$), 234(M, 100), 121. HRMS: Calculated for $C_{14}H_{12}OF_2$: 234.0856; Found: 234.0855.

Synthesis of 4a



4a

To a septum capped 25 mL of sealed tube were added $Pd(OAc)_2$ (10 mol%) and Ag_2CO_3 (2.0 equiv) under N_2, followed by DMF (2.4 mL) and PivOH (1.2 equiv) with stirring. 1,2,3,5-tetrafluorobenzene (4.0 equiv) and tert-butyl acrylate (0.6 mmol, 1.0 equiv) were added subsequently. The sealed tube was screw capped and heated to 120 °C (oil bath). After stirring for 18-24 h, the reaction mixture was cooled to room temperature and diluted with ethyl acetate, washed with 1 N HCl, saturated $NaHCO_3$ and brine, dried over Na_2SO_4, filtered and concentrated. The product (109 mg, 66% yield) was purified with silica gel chromatography (Petroleum ether /Ethyl ether = 150:1). This compound is known.[4]



(*E*)-*tert*-butyl 3-(2,3,5,6-tetrafluoro-4-(4-methoxybenzyl)phenyl)acrylate (5l). The product (174 mg, 73% yield) as a colorless oil was purified with silica gel

chromatography (Petroleum ether /Ethyl ether = 250:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, *J* = 16.5 Hz, 1 H), 7.20 (d, *J* = 8.7 Hz, 2 H), 6.83 (d, *J* = 8.7 Hz, 2 H), 6.67 (d, *J* = 16.5 Hz, 1 H), 4.00 (s, 2H), 3.77 (s, 3H), 1.54 (s, 9H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 165.5, 158.4, 145.0 (dm, *J* = 253.3 Hz), 144.6 (dm, *J* = 244.9 Hz), 129.4, 129.2, 128.1, 127.5 (t, *J* = 8.5 Hz), 121.1 (t, *J* = 18.7 Hz), 114.0, 112.4 (t, *J* = 13.4 Hz), 81.2, 55.1, 27.9. ^{19}F NMR (282 MHz, $CDCl_3$) δ -141.3 (m, 2F), -144.7 (dd, *J* = 21.7 Hz, 13.8 Hz, 2F). IR (thin film): ν_{max} 2978, 1714, 1513 cm^{-1}. MS (EI): *m/z* (%) 397($M^+ + H^+$), 396 (M^+), 340 (100), 323. HRMS: Calculated for $C_{21}H_{20}O_3F_4$: 396.1349; Found: 396.1359.

References:

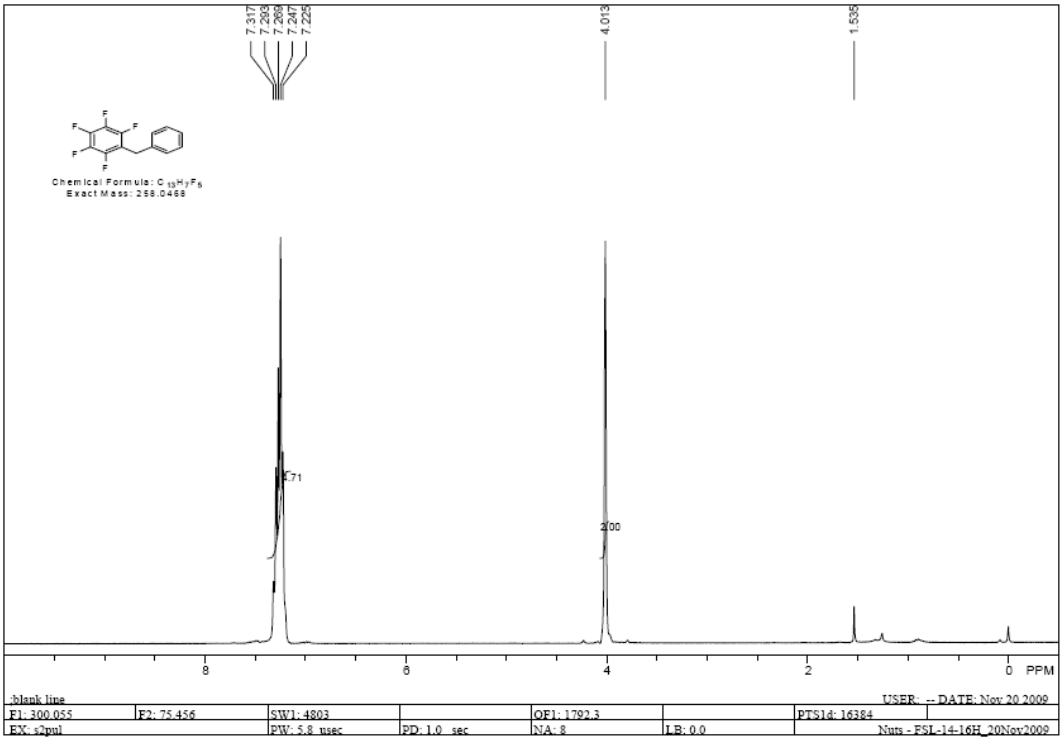
(1) Stoianova, D. S.; Yao, L.; Rolfe, A.; Samarakoon, T.; Hanson, P. R. *Tetrahedron Lett.* **2008**, *49*, 4553.

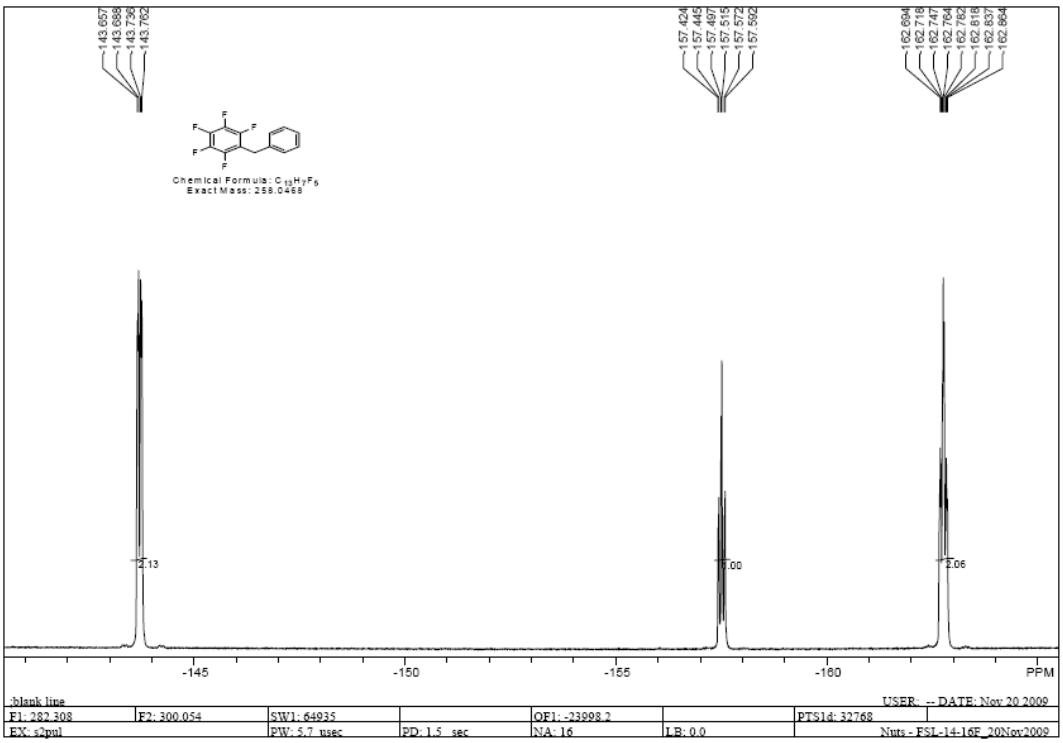
(2) Inaba, S.; Rieke, R. D. *J. Org. Chem.* **1985**, *50*, 1373.

(3) Park, S. Y.; Kang, M.; Yie, J. E.; Kim, J. M.; Lee, I.-M. *Tetrahedron Lett.* **2005**, *46*, 2849.

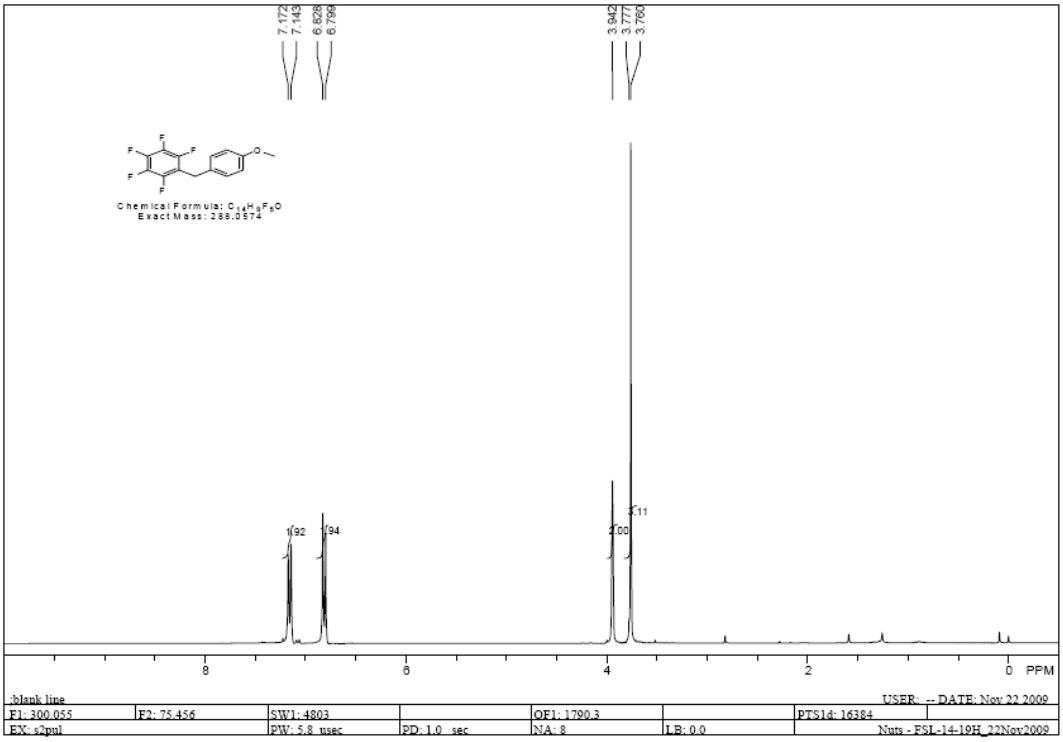
(4) Zhang, X.; Fan, S.; He, C.-H.; Wan, X.; Min, Q.-Q.; Yang, J.; Jiang, Z.-X. *J. Am. Chem. Soc.* **2010**, *132*, 4506.

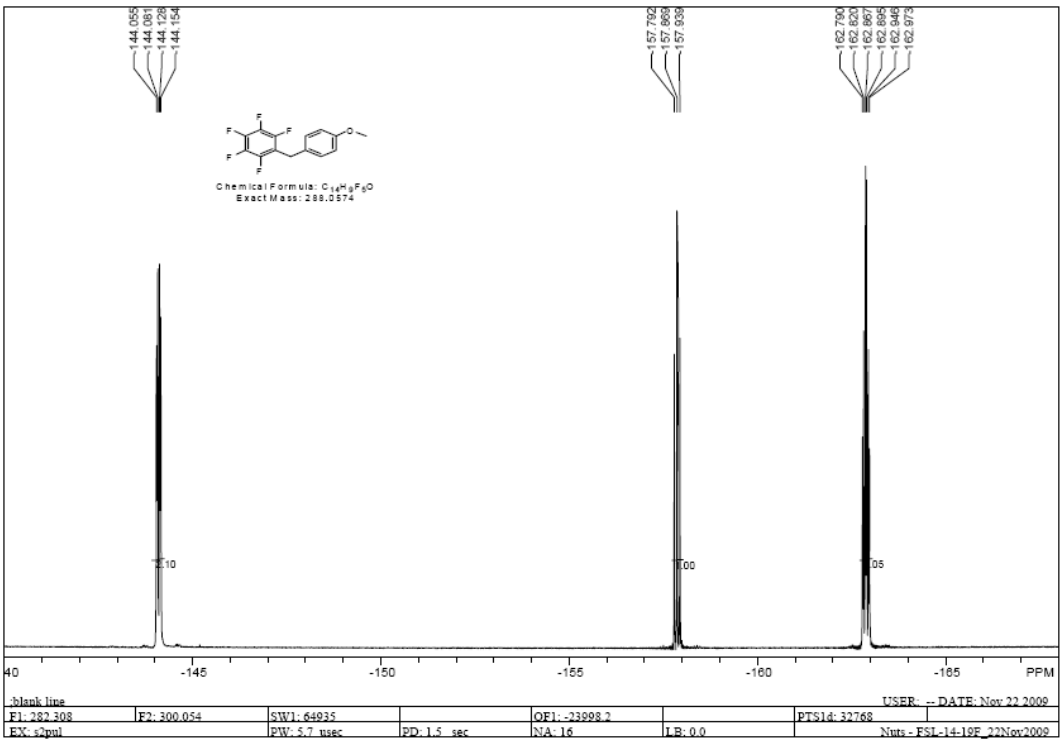
1-Benzyl-2,3,4,5,6-pentafluorobenzene (3a)

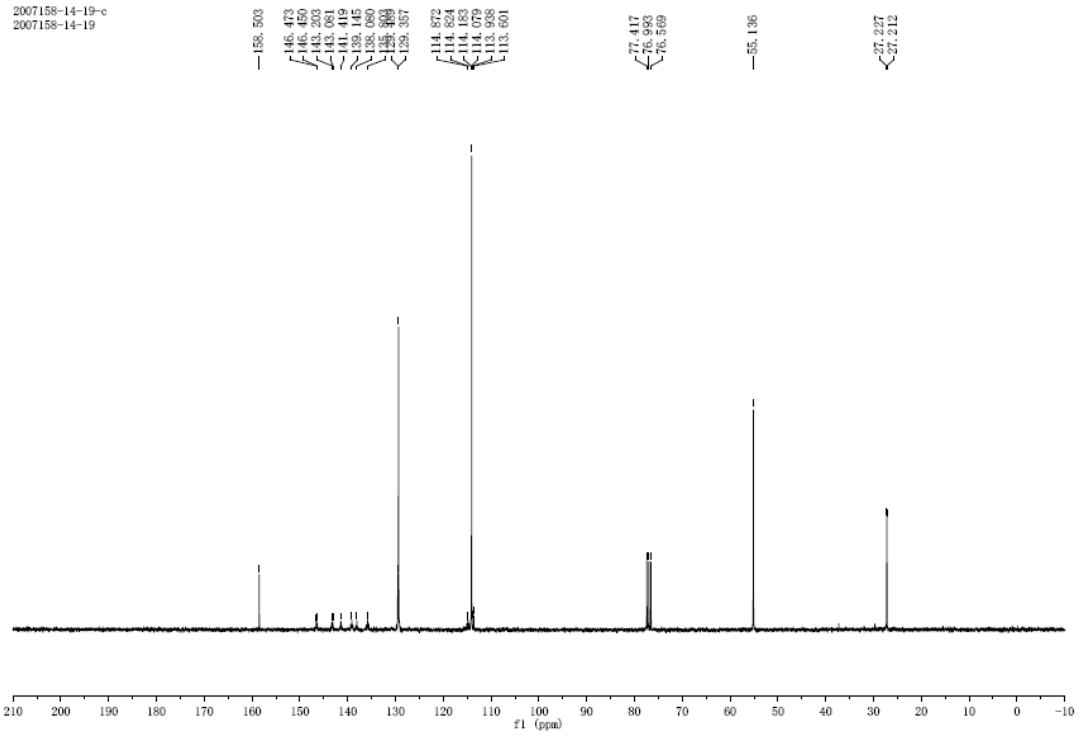




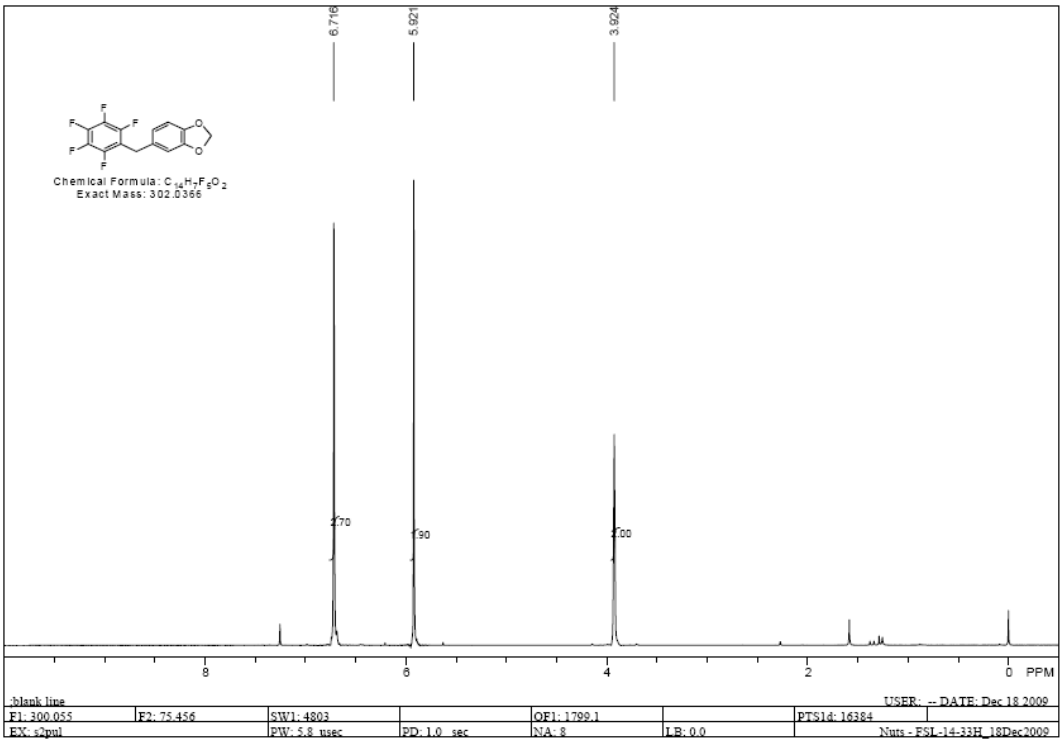
1,2,3,4,5-Pentafluoro-6-(4-methoxybenzyl)benzene (3b)

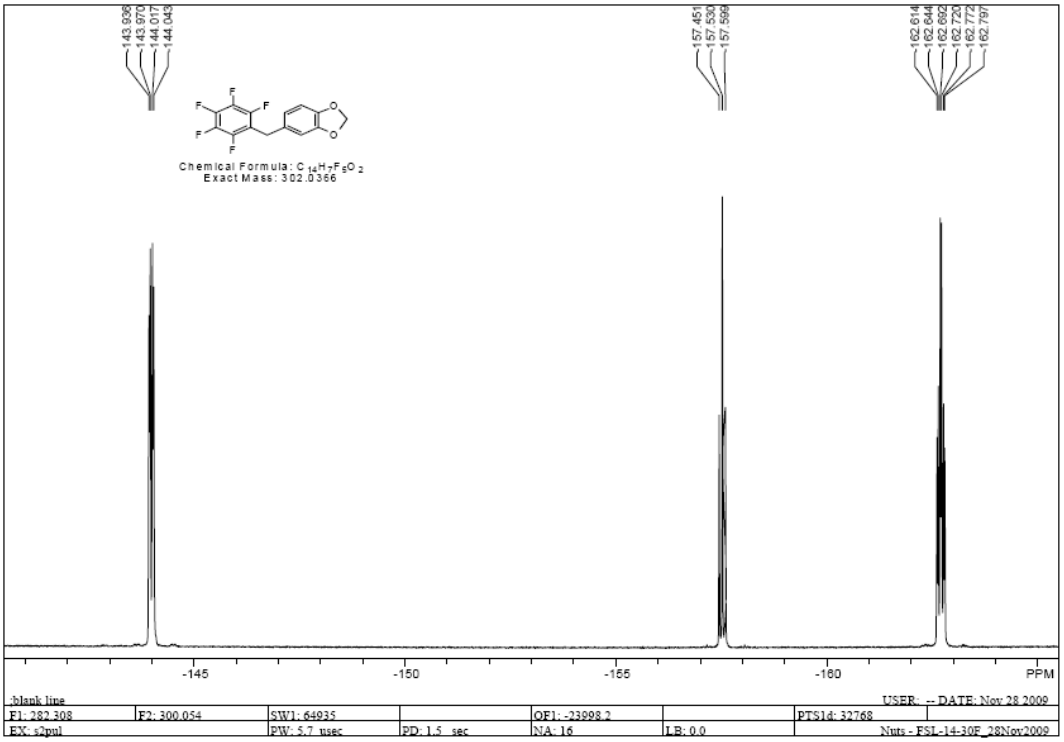






5-(Perfluorobenzyl)benzo[d][1,3]dioxole (3c)

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-143.970
-144.017
-144.043
-157.451
-157.530
-157.599
-162.614
-162.644
-162.692
-162.720
-162.772
-162.797
Chemical Formula: C14H7F5O2
Exact Mass: 302.0366
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-150
-155
-160
PPM
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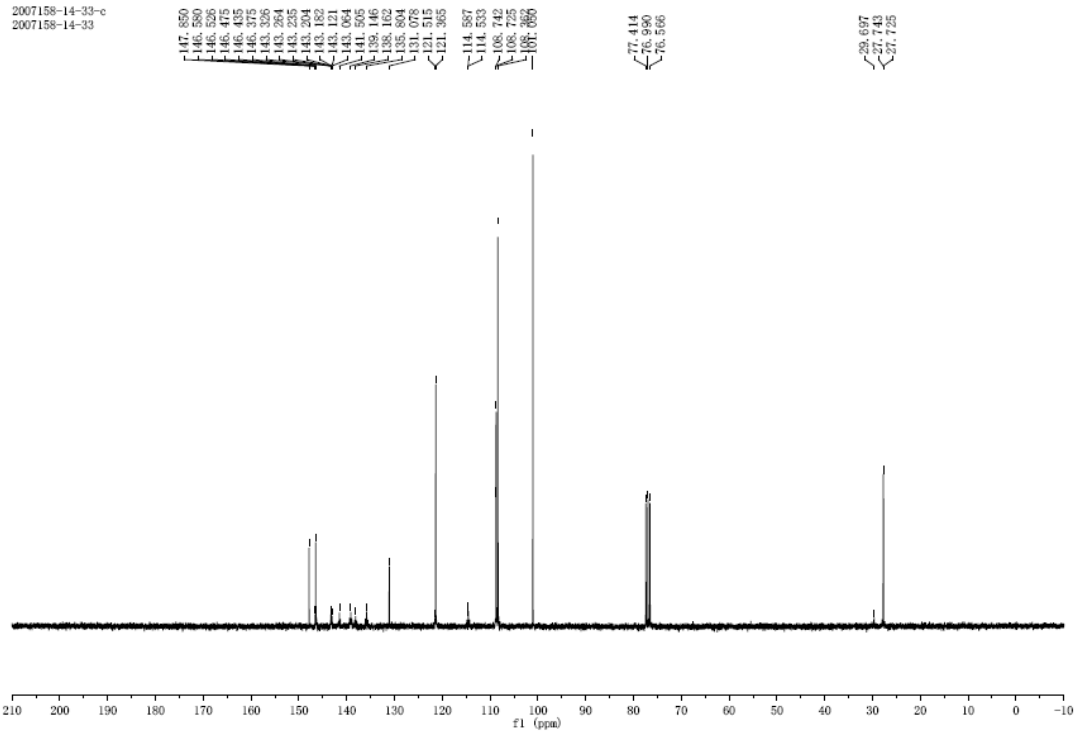
USER: -- DATE: Nov 28 2009
F1: 282.308
F2: 300.054
SW1: 64935
OF1: -23998.2
PTS1d: 32768
EX: s2pul
PW: 5.7 usec
PD: 1.5 sec
NA: 16
LB: 0.0
Nuts - FSL-14-30F_28Nov2009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2007158-14-33
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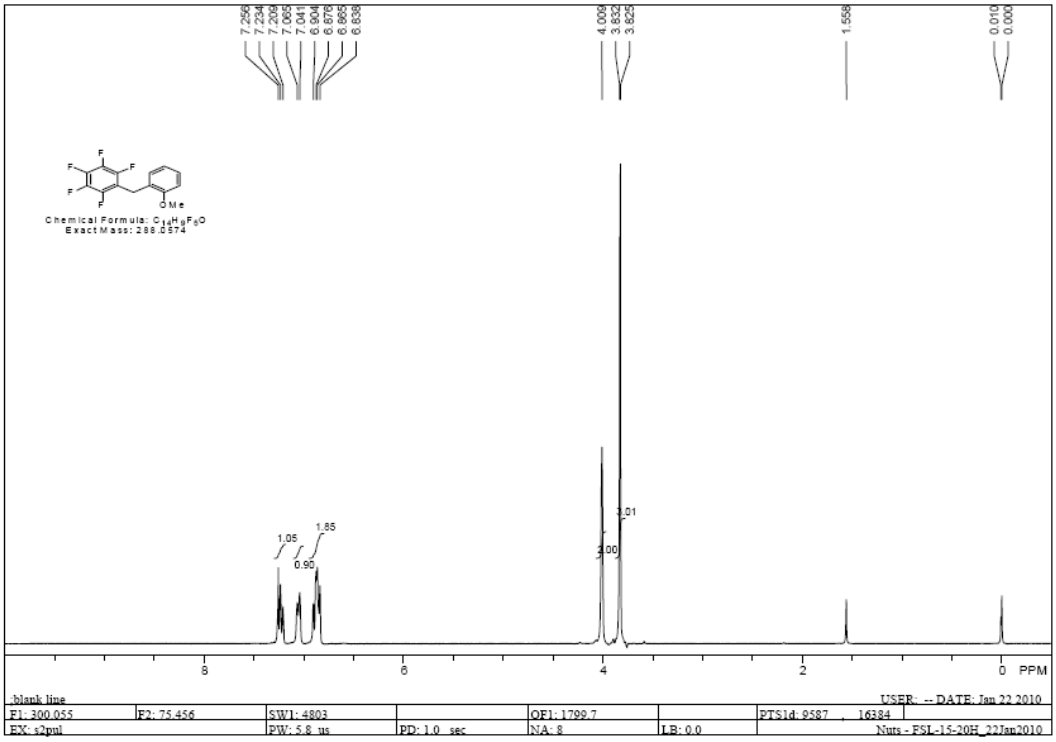
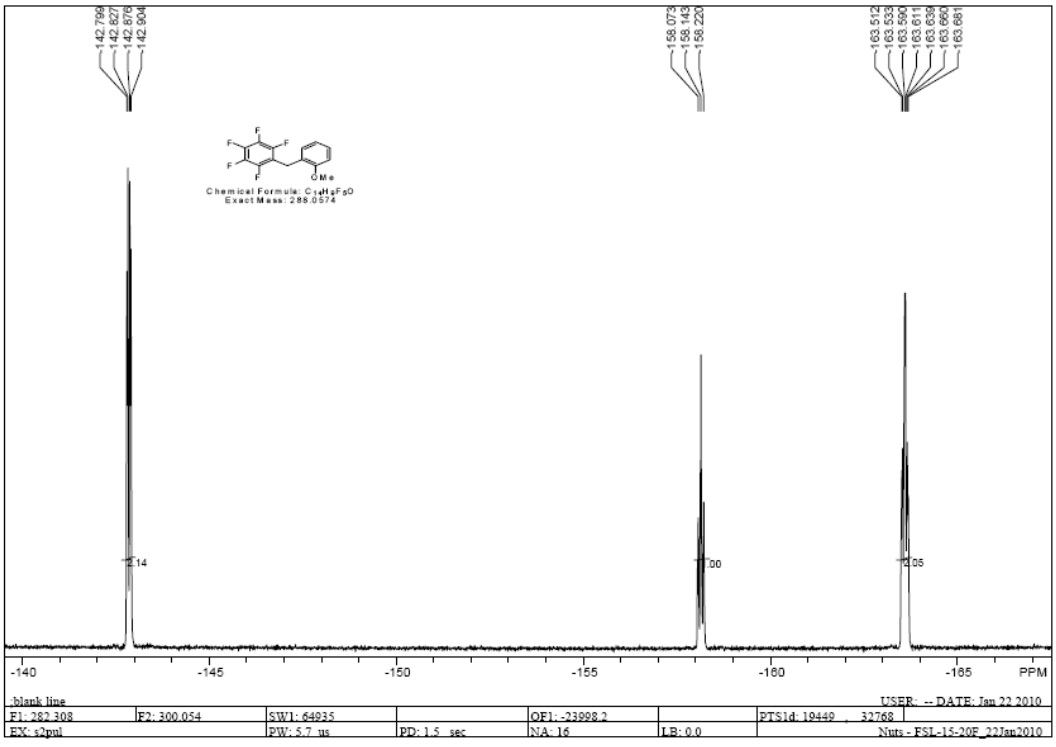
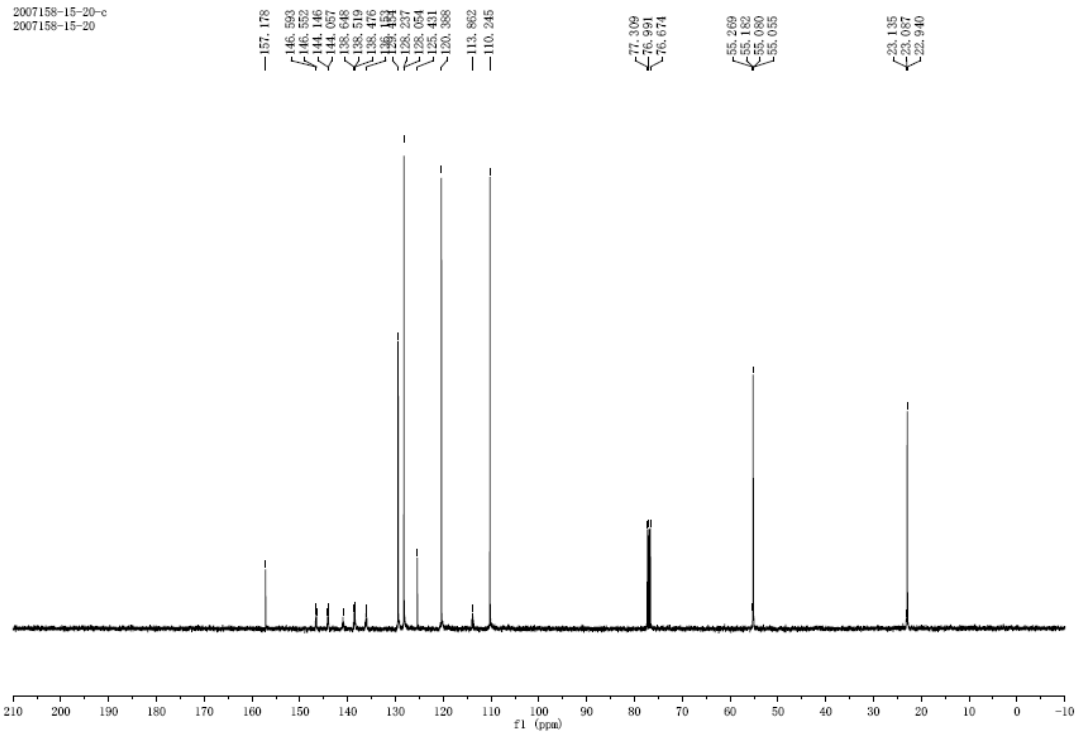
146.580
146.526
146.475
146.435
146.375
143.326
143.264
143.235
143.204
143.162
143.121
143.064
141.595
139.146
138.162
135.804
131.078
121.515
121.365
114.587
114.533
108.742
108.725
108.362
101.086
77.414
76.990
76.566
29.697
27.743
27.715
27.725
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

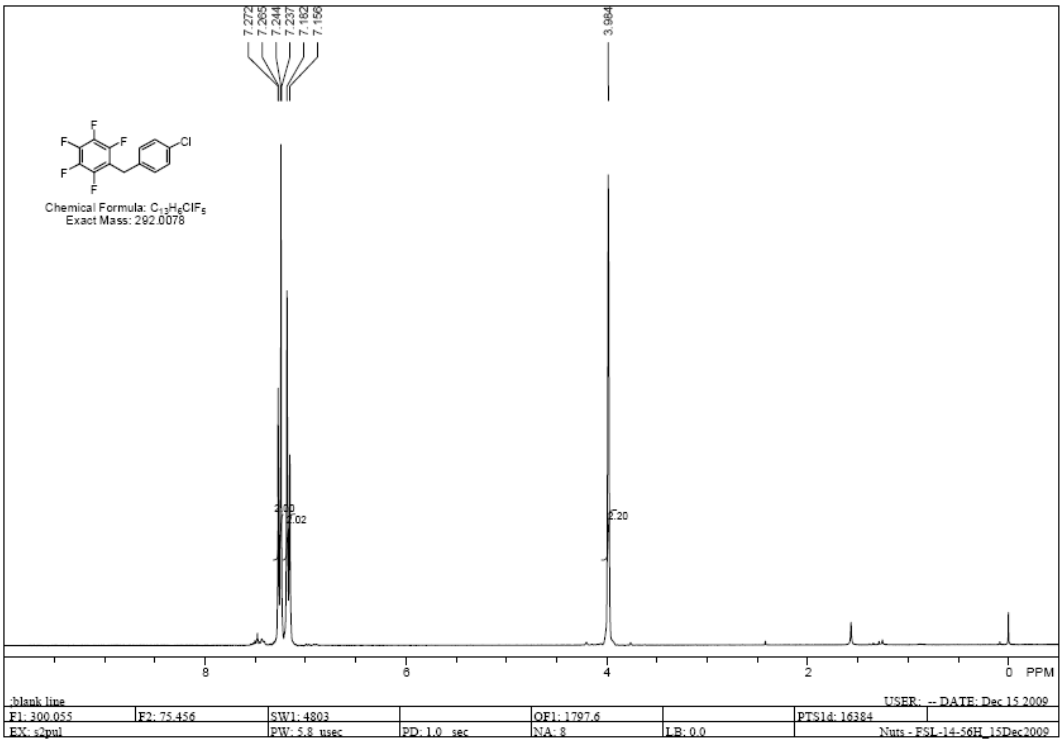
1,2,3,4,5-Pentafluoro-6-(2-methoxybenzyl)benzene (3d)

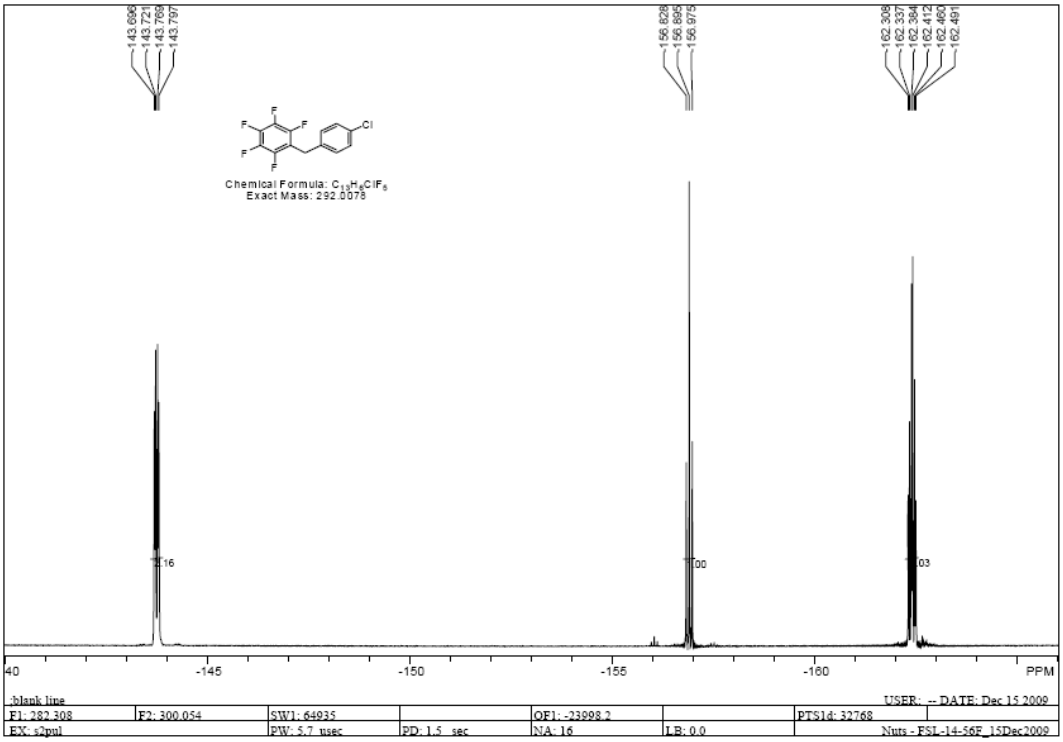






1-(4-Chlorobenzyl)-2,3,4,5,6-pentafluorobenzene (3e)




143.696
143.721
143.769
143.797
156.828
156.895
156.975
162.308
162.337
162.364
162.412
162.460
162.491
Cl
Chemical Formula: C13H6ClF5
Exact Mass: 292.0078
16
00
03
40
-145
-150
-155
-160
PPM
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USER: -- DATE: Dec 15 2009
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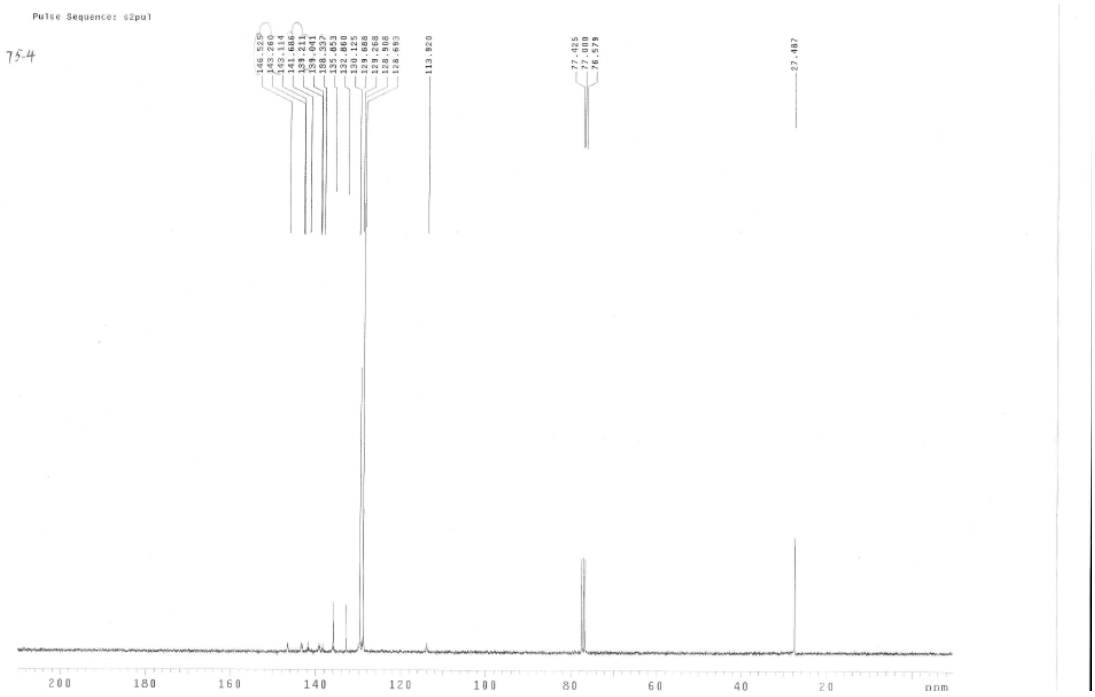
F2: 300.054
SW1: 64935
OF1: -23998.2
PTS1d: 32768
EX: s2pul
PW: 5.7 usec
PD: 1.5 sec
NA: 16
LB: 0.0
Nuts - FSL-14-56F_15Dec2009


Pulse Sequence: s2pul
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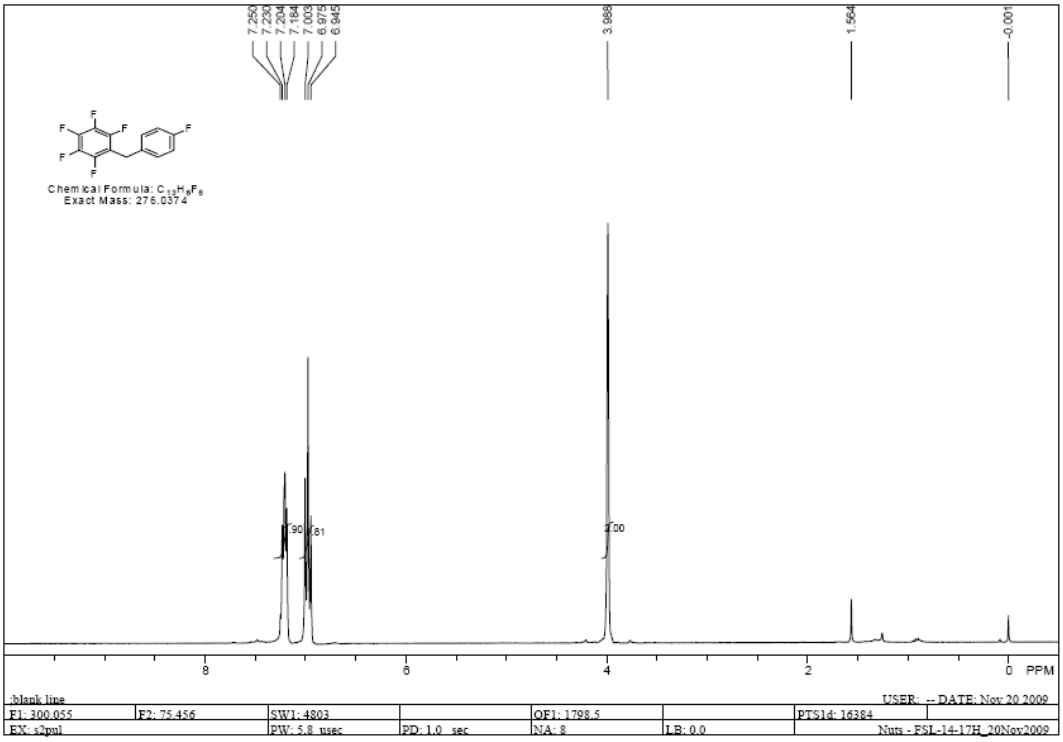
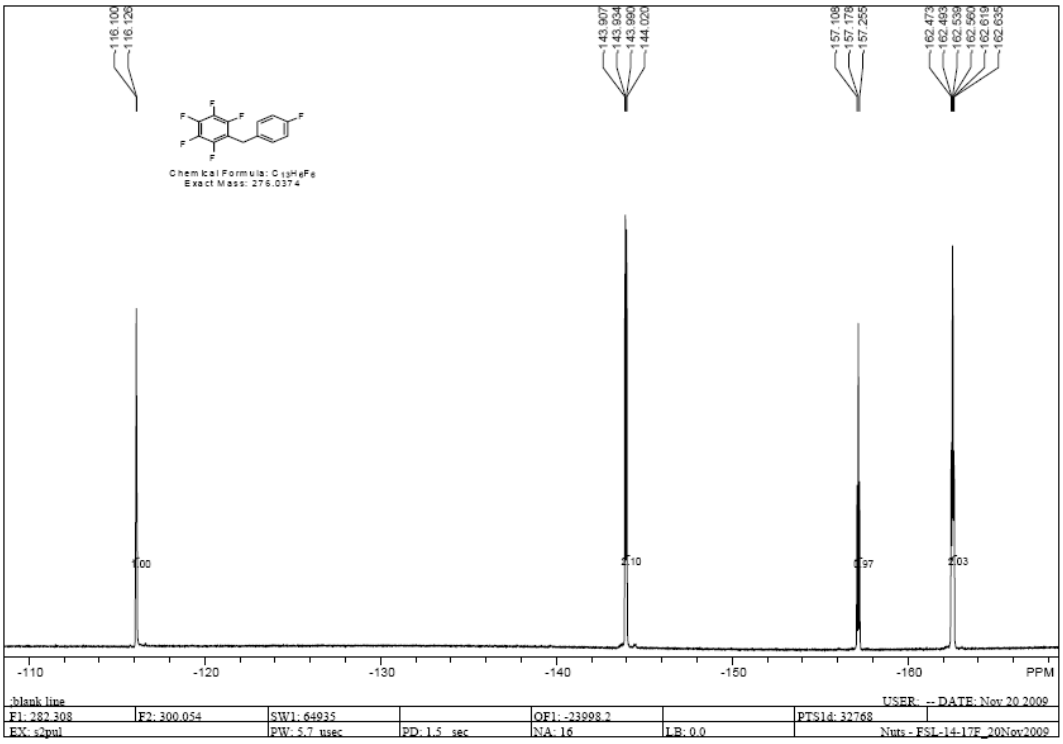
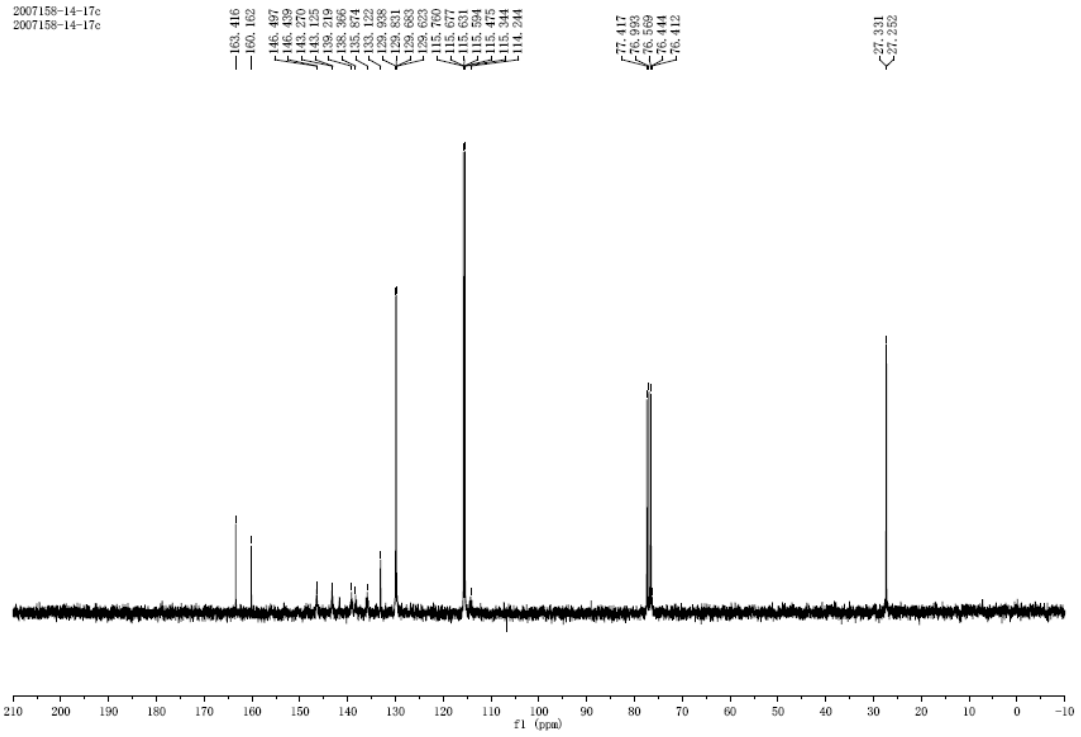
143.114
141.646
139.211
139.041
138.337
135.463
132.860
130.125
129.688
129.558
128.508
128.493
113.820
77.425
77.108
76.579
27.487
200
180
160
140
120
100
80
60
40
20
ppm

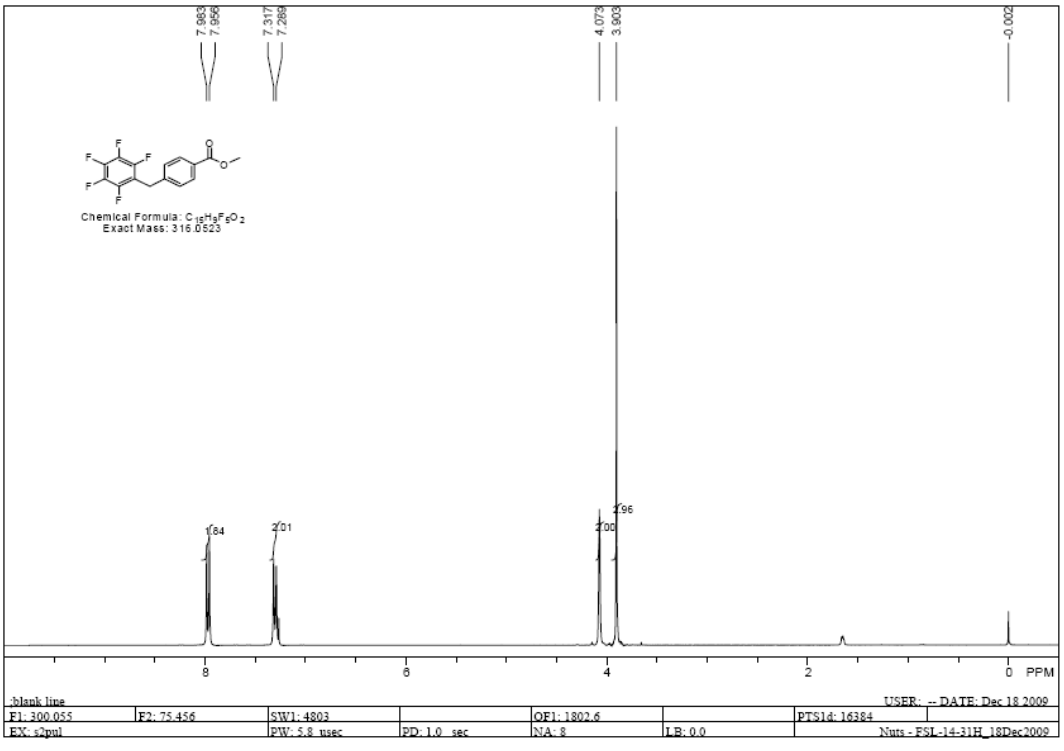
1,2,3,4,5-Pentafluoro-6-(4-fluorobenzyl)benzene (3f)

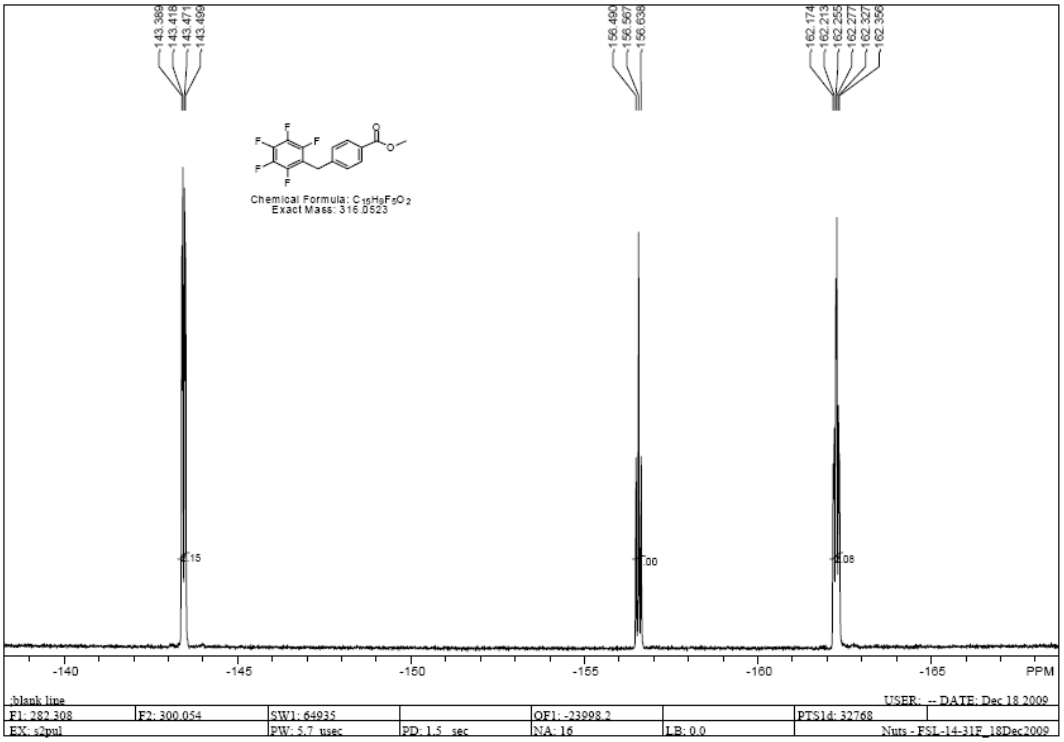






Methyl 4-(perfluorobenzyl)benzoate (3g)




143.399
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143.471
143.488
156.490
156.567
156.638
162.174
162.213
162.255
162.277
162.327
162.356
Chemical Formula: C15H8F5O2
Exact Mass: 316.0523
1.15
1.00
2.08
-140
-145
-150
-155
-160
-165
PPM
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USER: -- DATE: Dec 18 2009
F1: 282.308
F2: 300.054
SW1: 64935
OF1: -23998.2
PTS1d: 32768
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PW: 5.7 usec
PD: 1.5 sec
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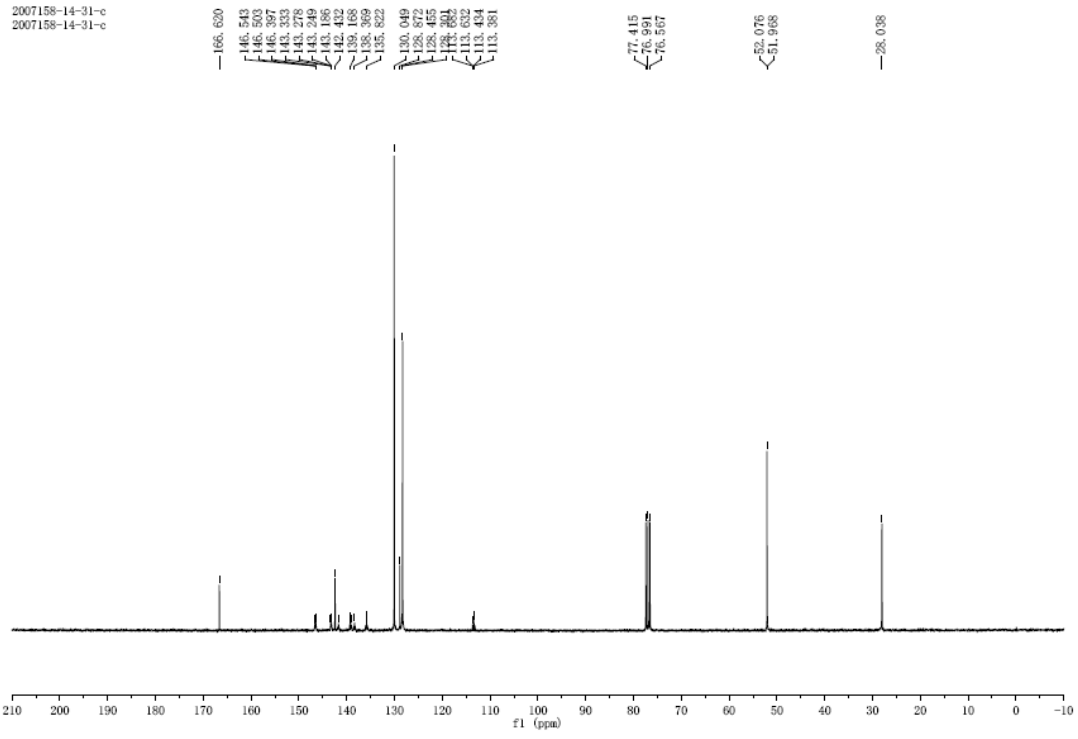
LB: 0.0
Nuts - FSL-14-31F_18Dec2009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2007158-14-31-c
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146.397
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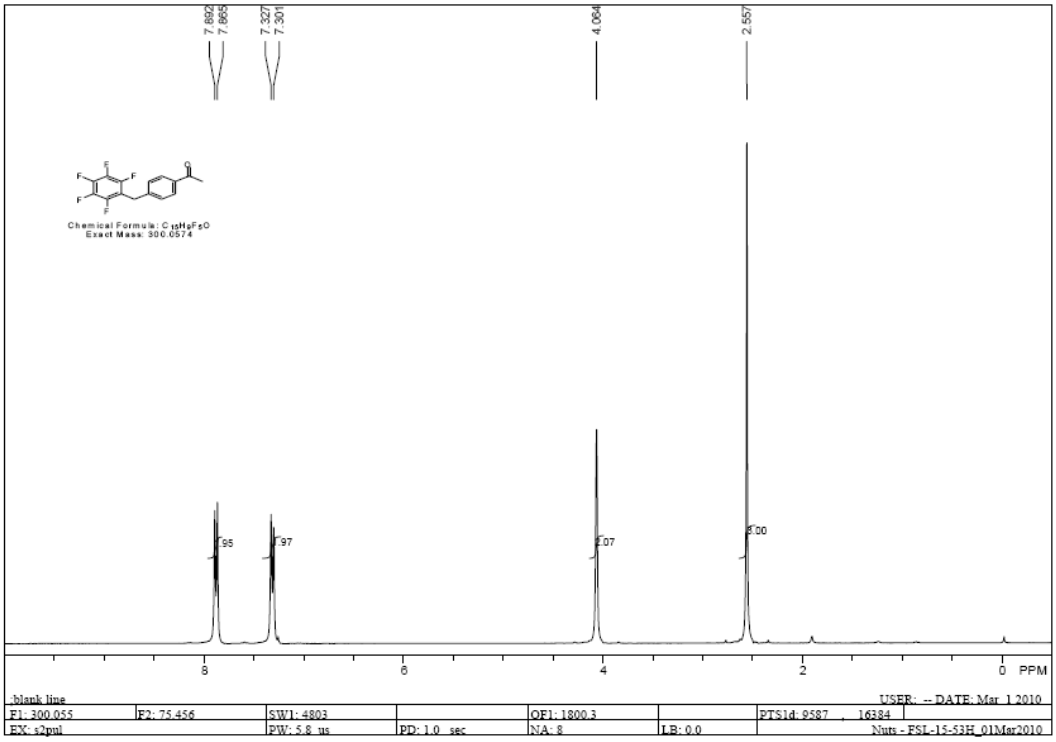
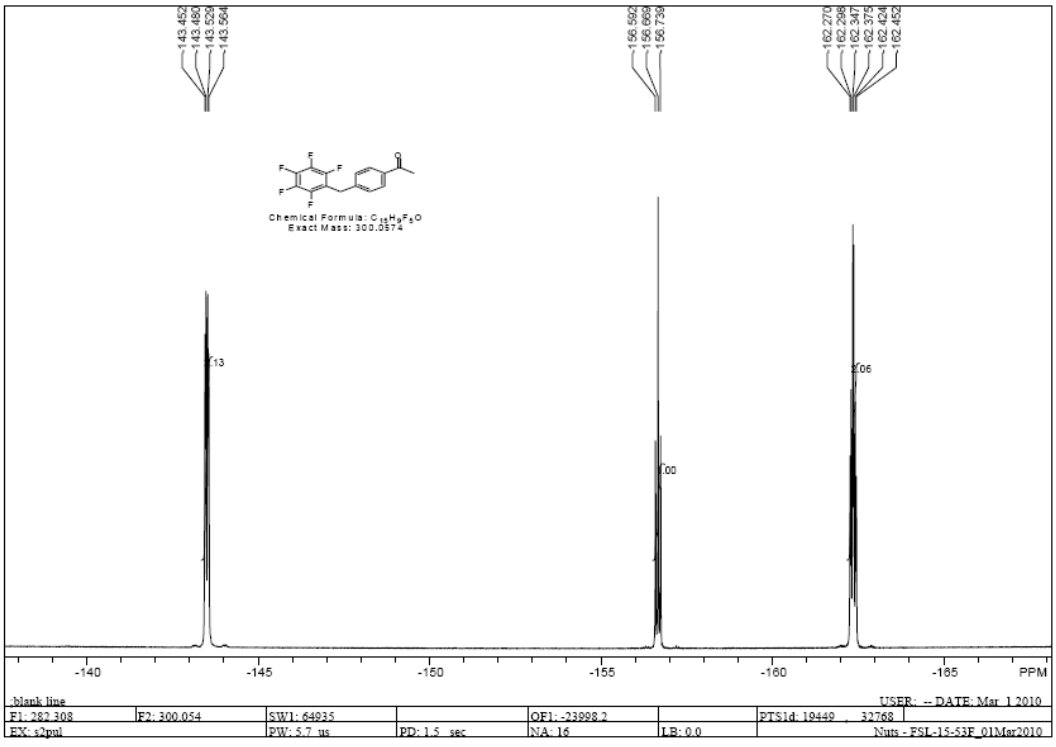
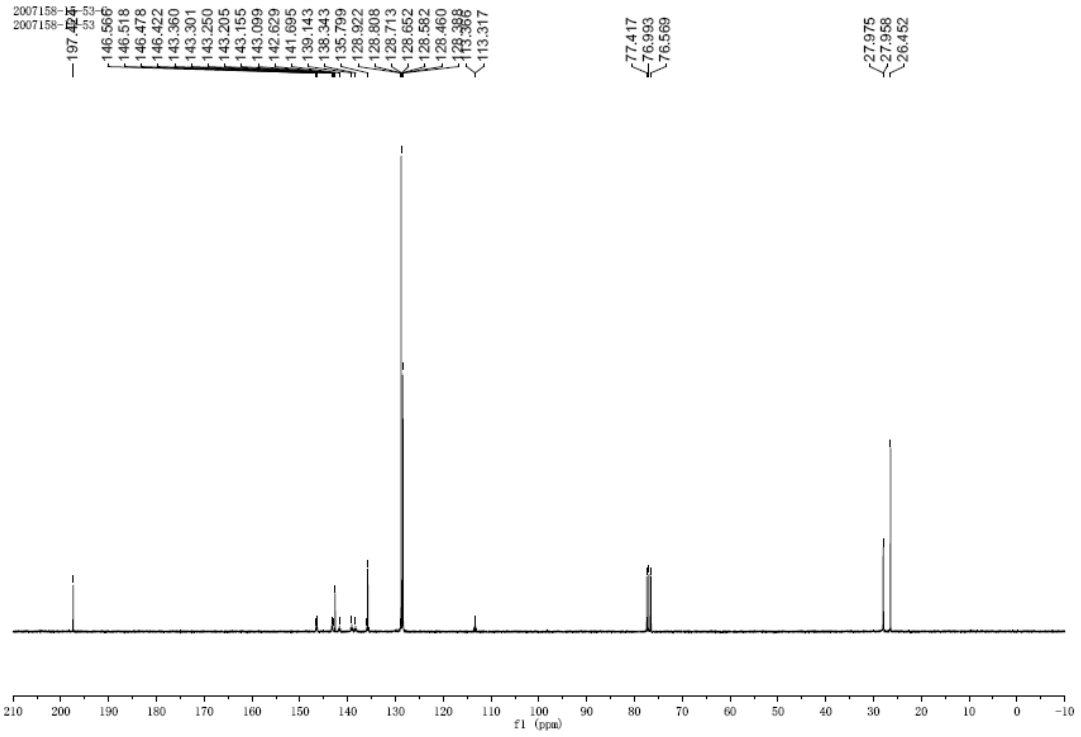
143.278
143.249
143.186
142.432
139.168
138.369
135.822
130.049
128.672
128.455
113.632
113.434
113.381
77.415
76.991
76.567
52.076
51.968
28.038
f1 (ppm)

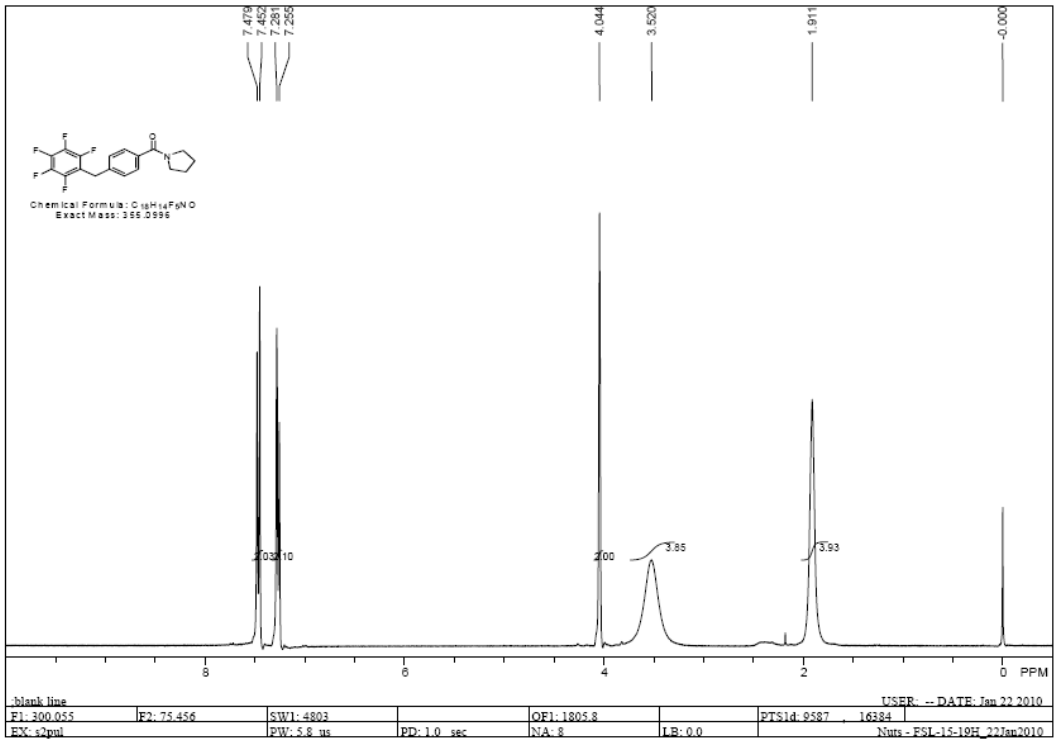
1-(4-(perfluorobenzyl)phenyl)ethanone (3h)

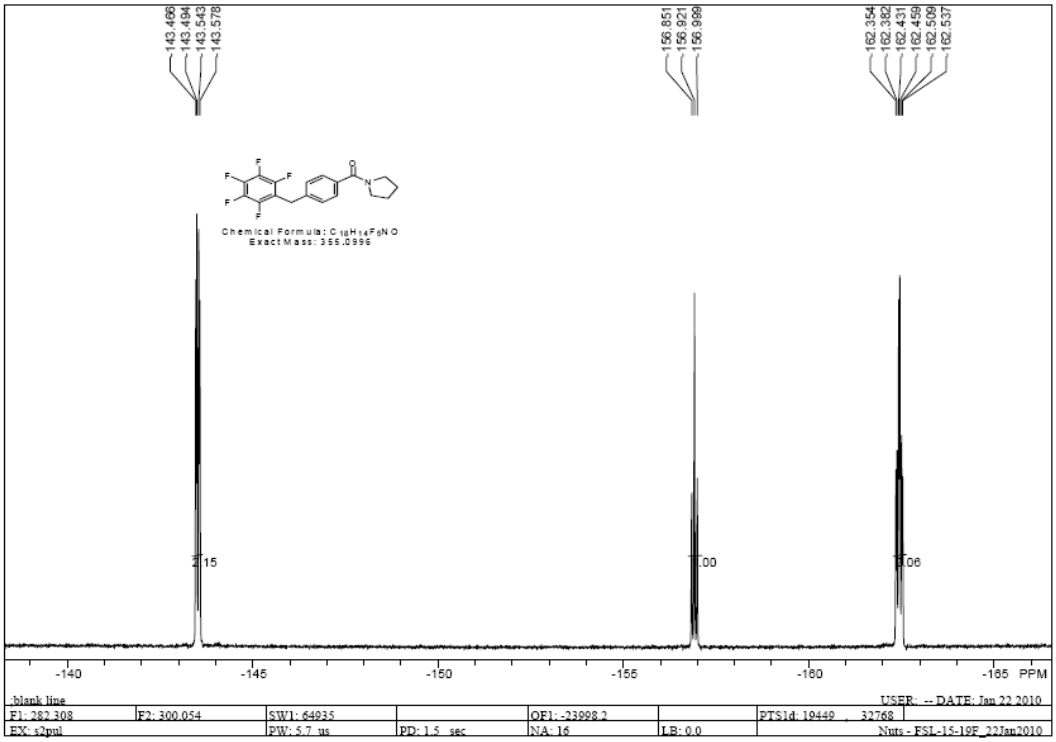






(4-(Perfluorobenzyl)phenyl)(pyrrolidin-1-yl)methanone (3i)

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143.494
143.543
143.578
156.851
156.921
156.999
162.354
162.382
162.431
162.459
162.509
162.537
Chemical Formula: C18H14F6NO
Exact Mass: 355.0996
1.15
1.00
1.06
-140
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-150
-155
-160
-165 PPM
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F1: 282.308
F2: 300.054
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OF1: -23998.2
PTS1d: 19449 , 32768
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PD: 1.5 sec
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LB: 0.0
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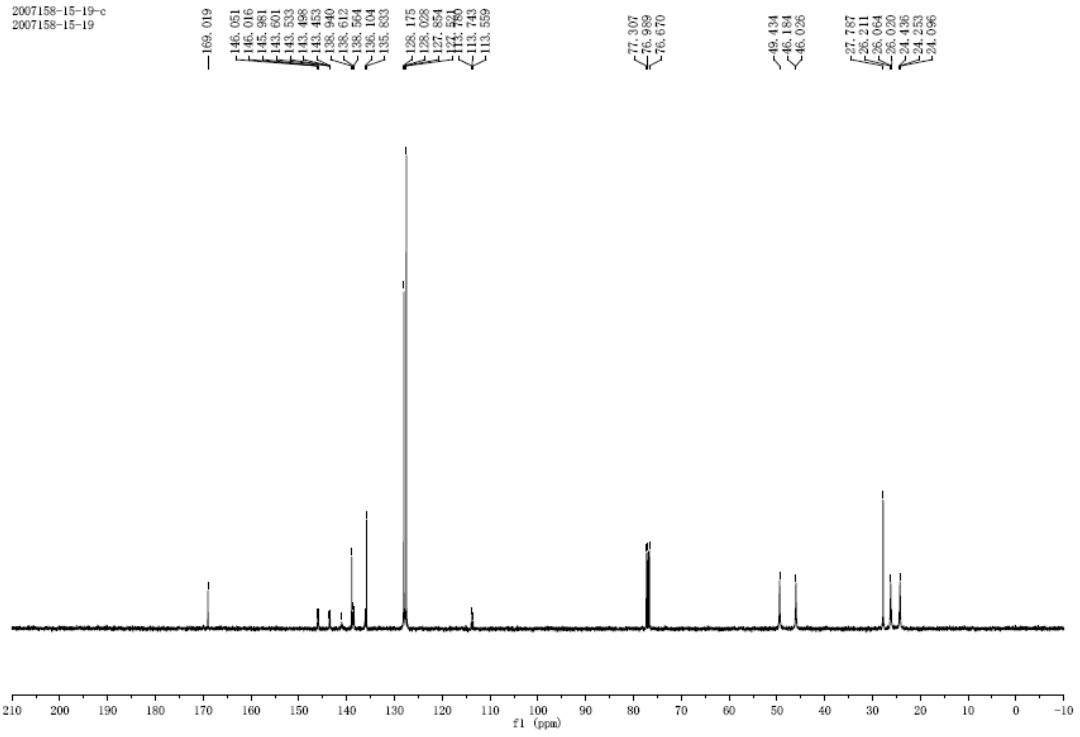
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2007158-15-19
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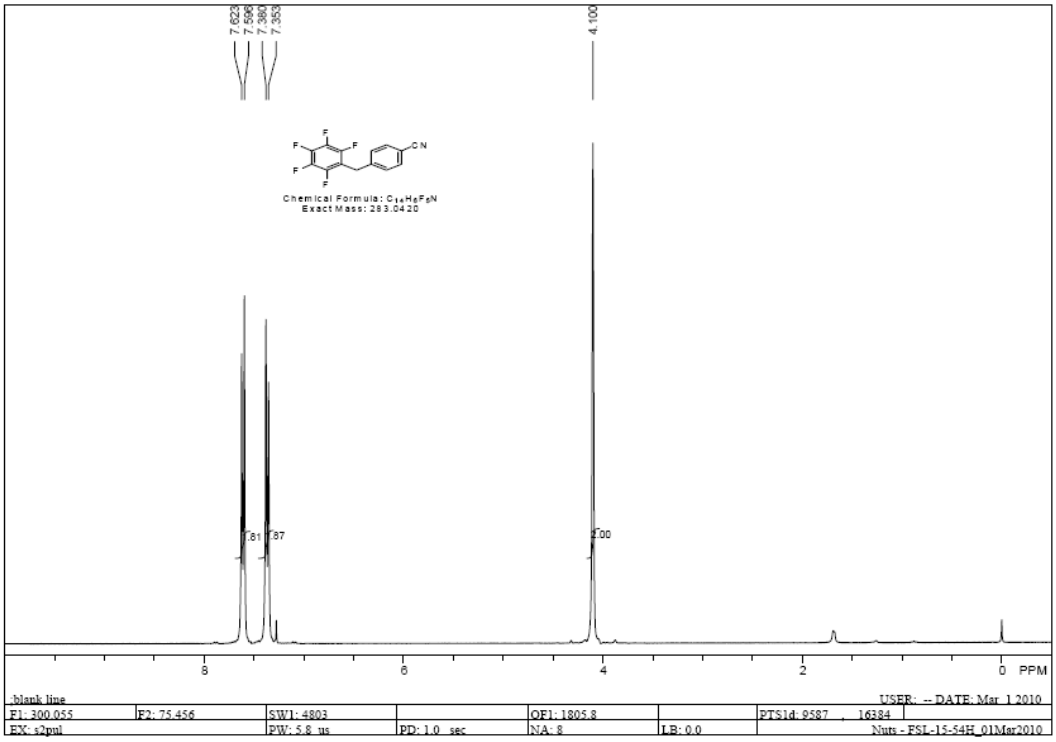
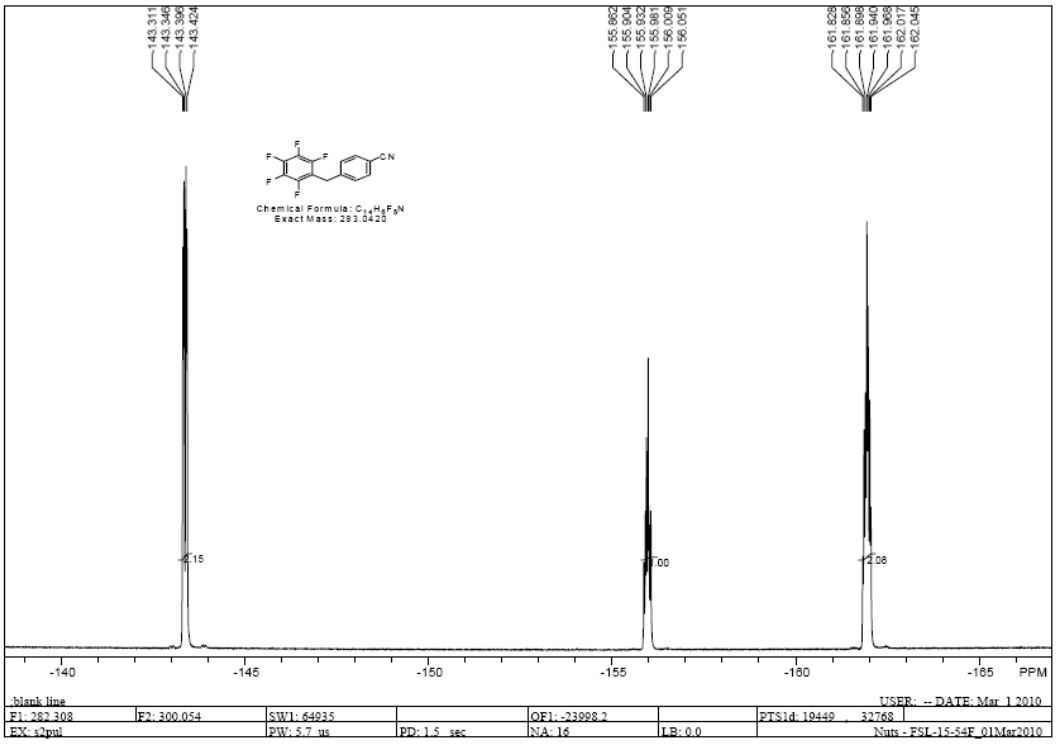
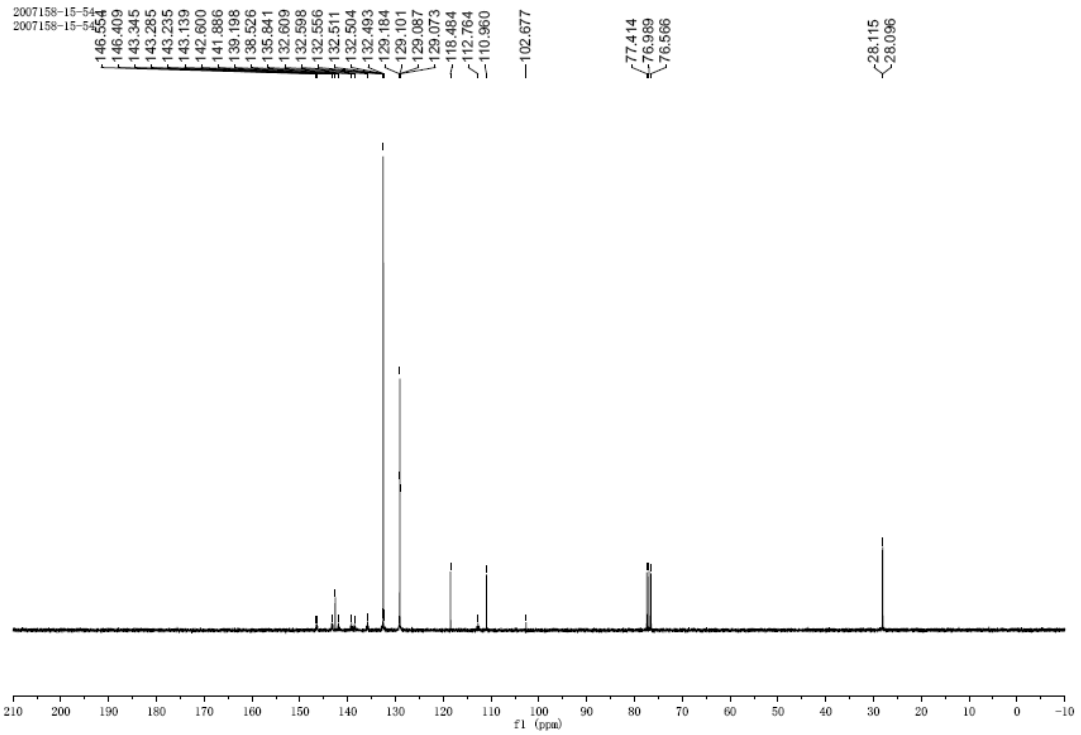
143.498
143.453
138.940
138.612
138.564
136.104
135.833
128.175
128.028
127.854
77.307
76.989
76.670
49.434
46.184
46.026
27.787
26.211
26.044
26.020
24.436
24.253
24.096
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

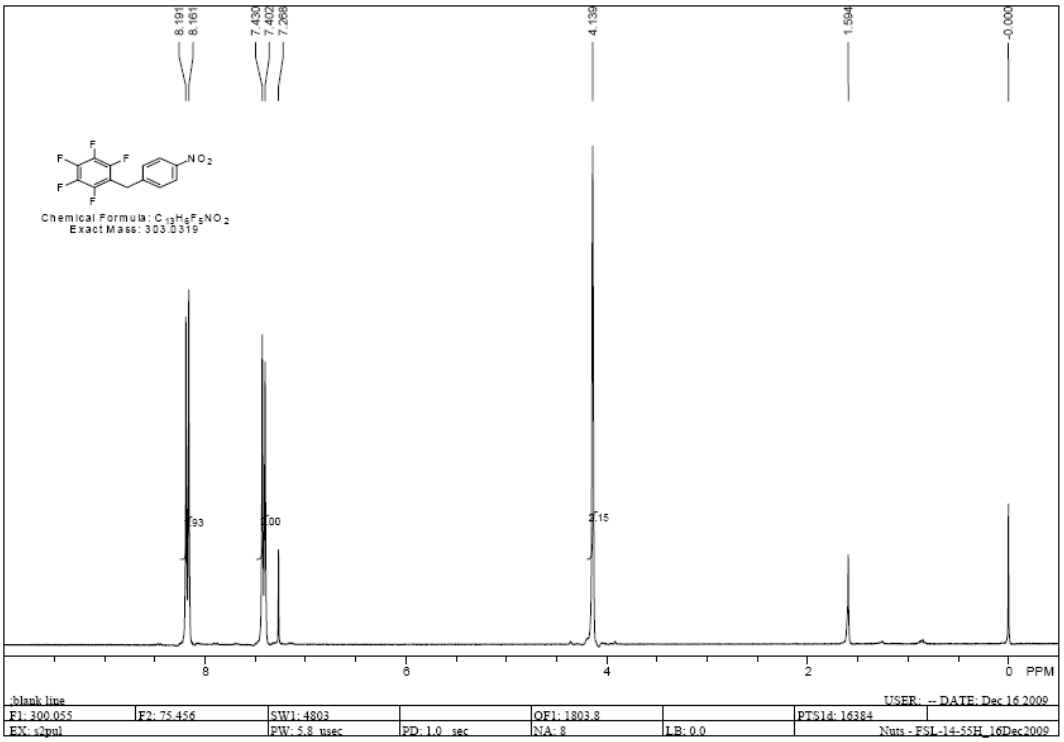
4-(Perfluorobenzyl)benzonitrile (3j)

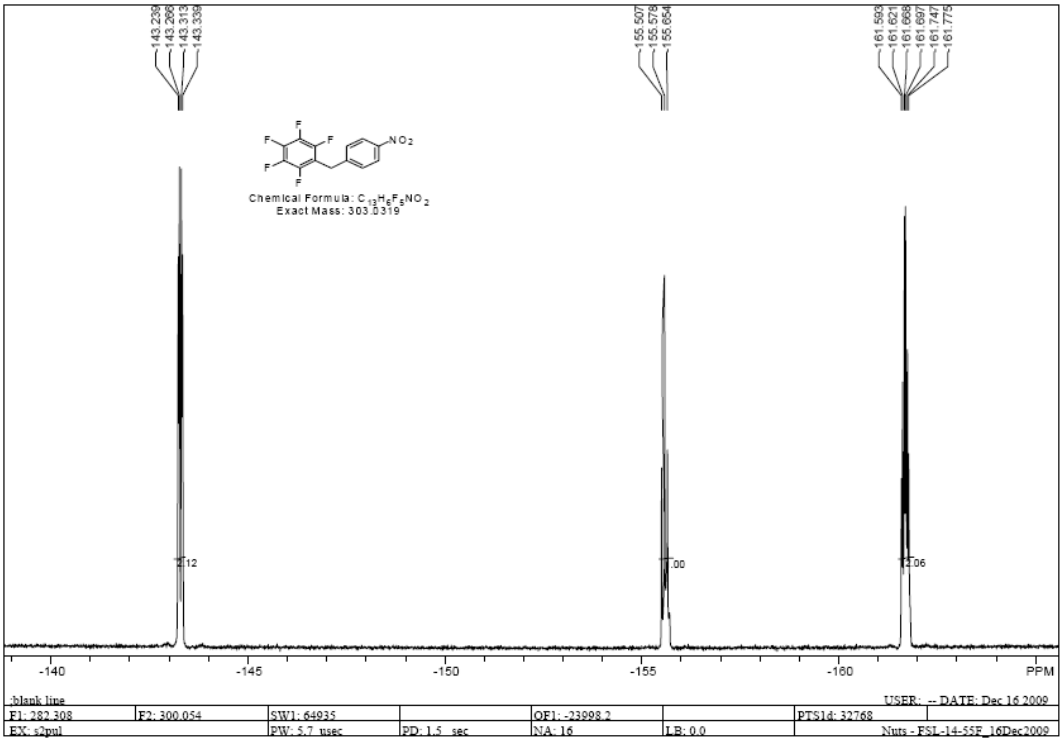






1,2,3,4,5-Pentafluoro-6-(4-nitrobenzyl)benzene (3k)




143.239
143.266
143.313
143.339
155.507
155.578
155.654
161.593
161.621
161.668
161.697
161.747
161.775
Chemical Formula: C13H6F5NO2
Exact Mass: 303.0319
1.12
1.00
1.06
-140
-145
-150
-155
-160
PPM
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USER: -- DATE: Dec 16 2009
F1: 282.308
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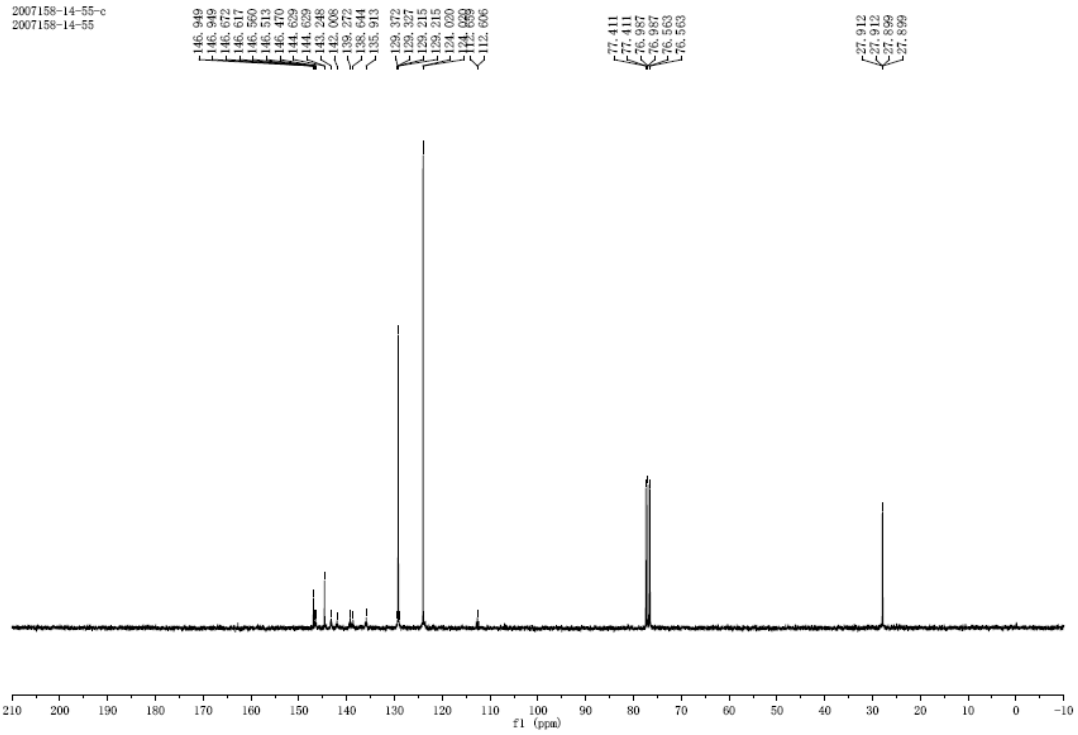
SW1: 64935
OF1: -23998.2
PTS1d: 32768
EX: s2pul
PW: 5.7 usec
PD: 1.5 sec
NA: 16
LB: 0.0
Nuts - FSL-14-55F_16Dec2009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2007158-14-55
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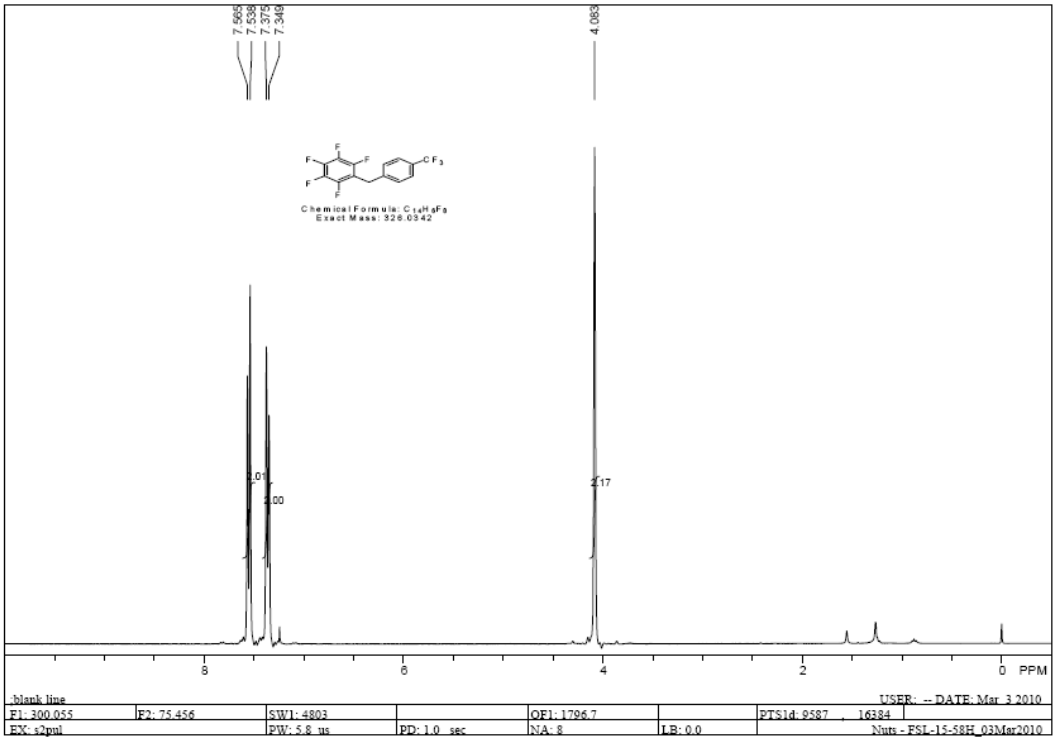
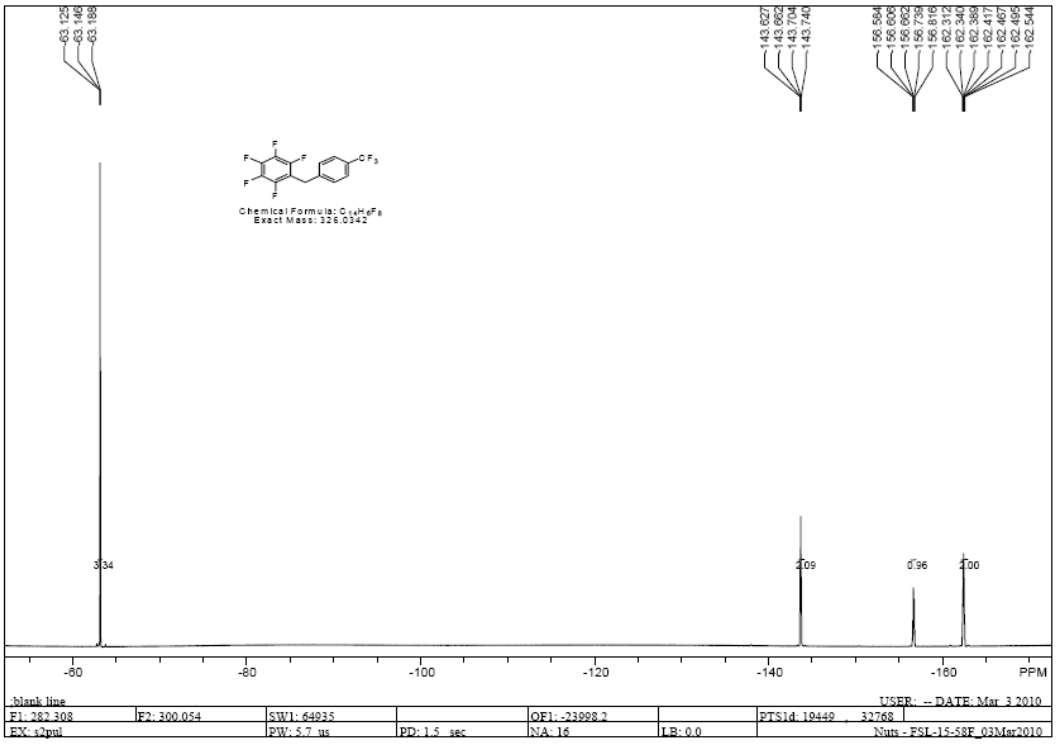
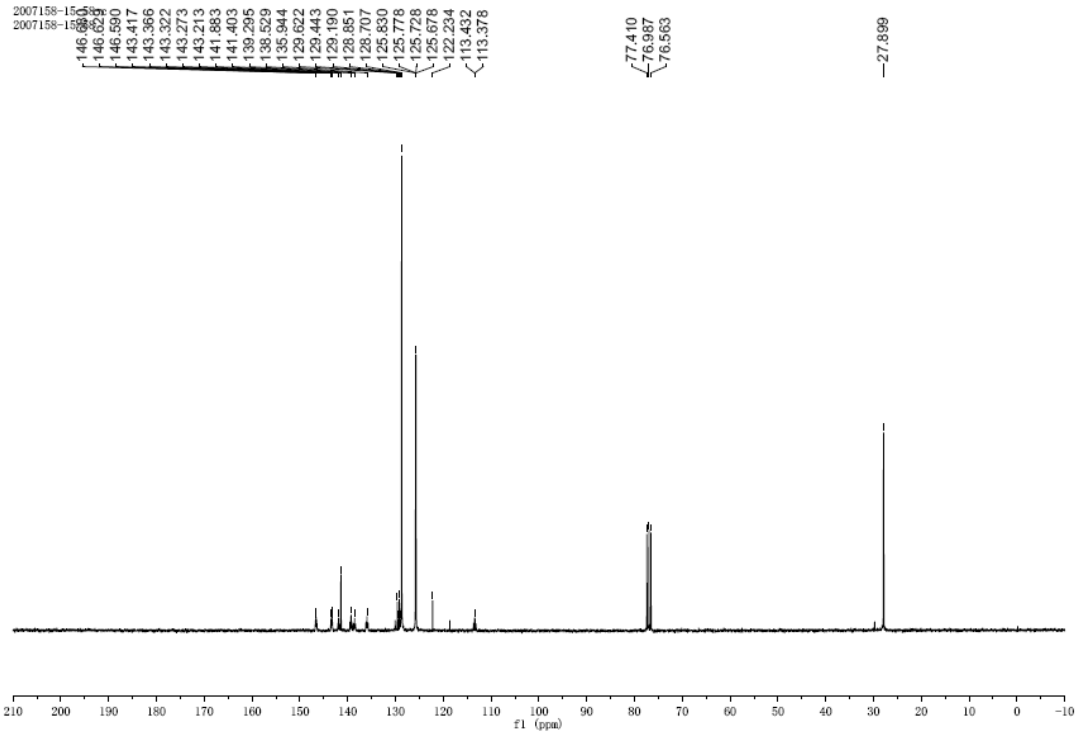
144.629
143.248
142.006
139.272
138.644
135.913
129.372
129.327
129.215
129.215
124.020
112.606
77.411
77.411
76.957
76.957
76.563
76.563
27.912
27.912
27.899
27.899
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

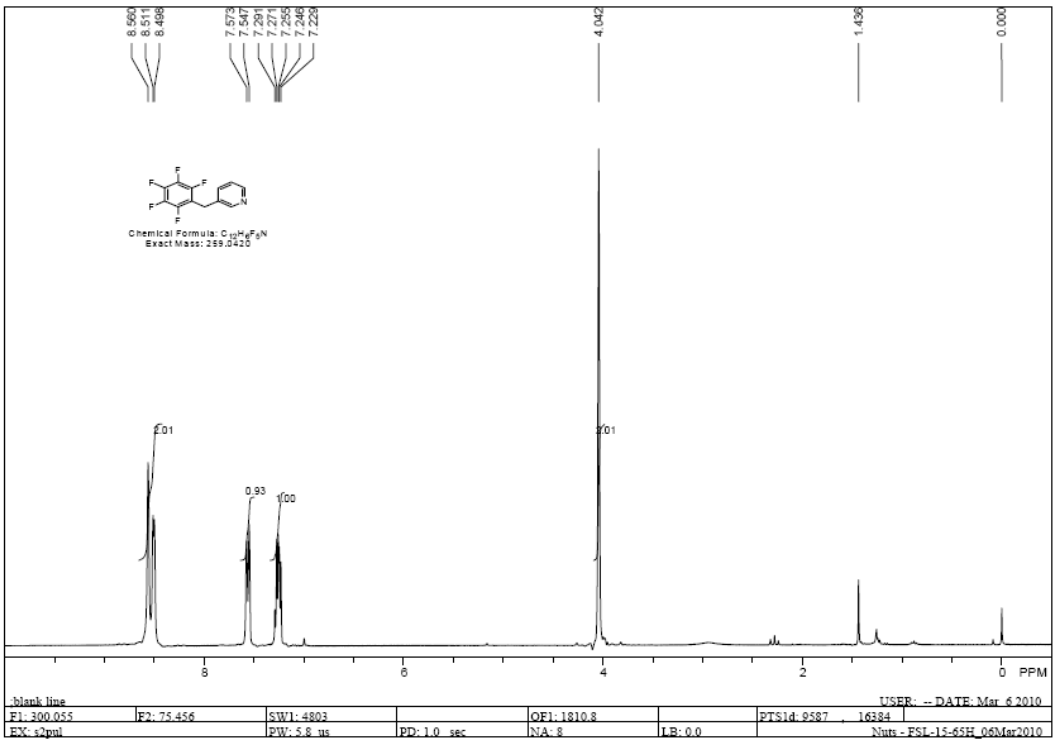
\1,2,3,4,5-Pentafluoro-6-(4-(trifluoromethyl)benzyl)benzene (3l)

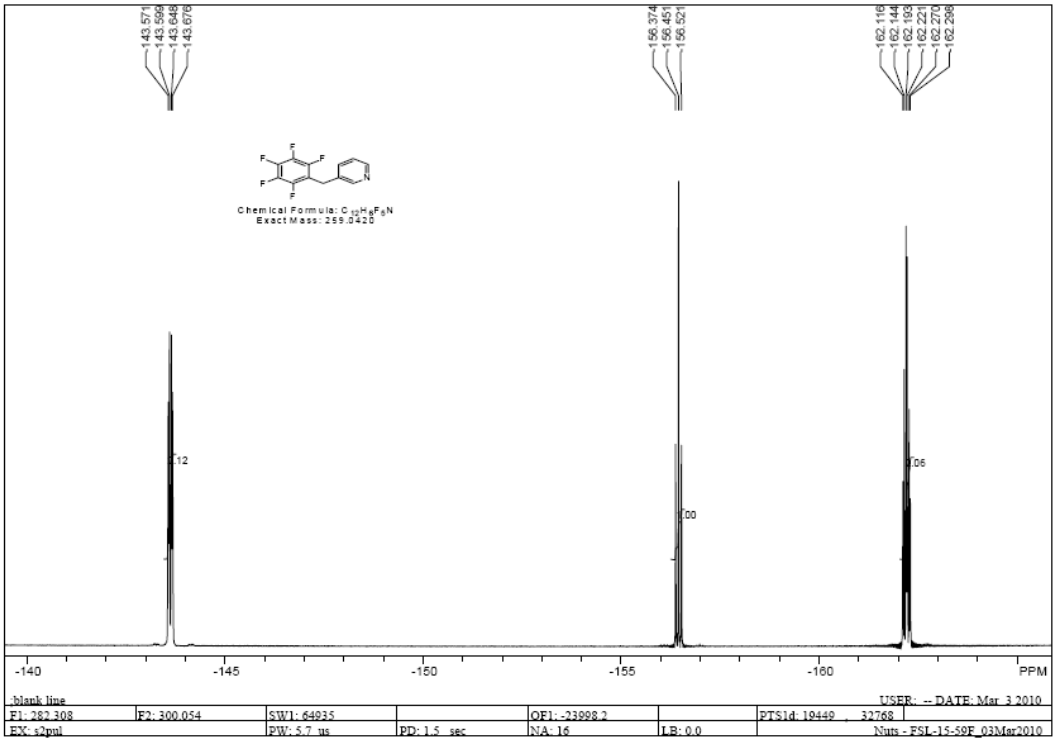






3-(Perfluorobenzyl)pyridine (3m)

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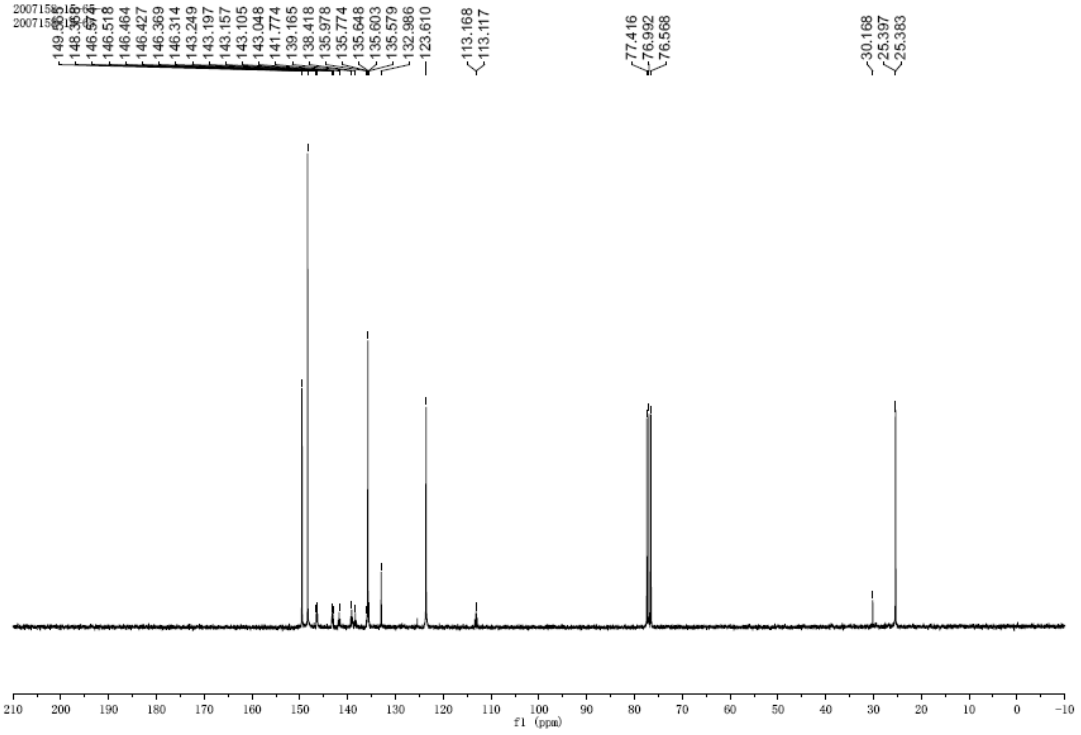
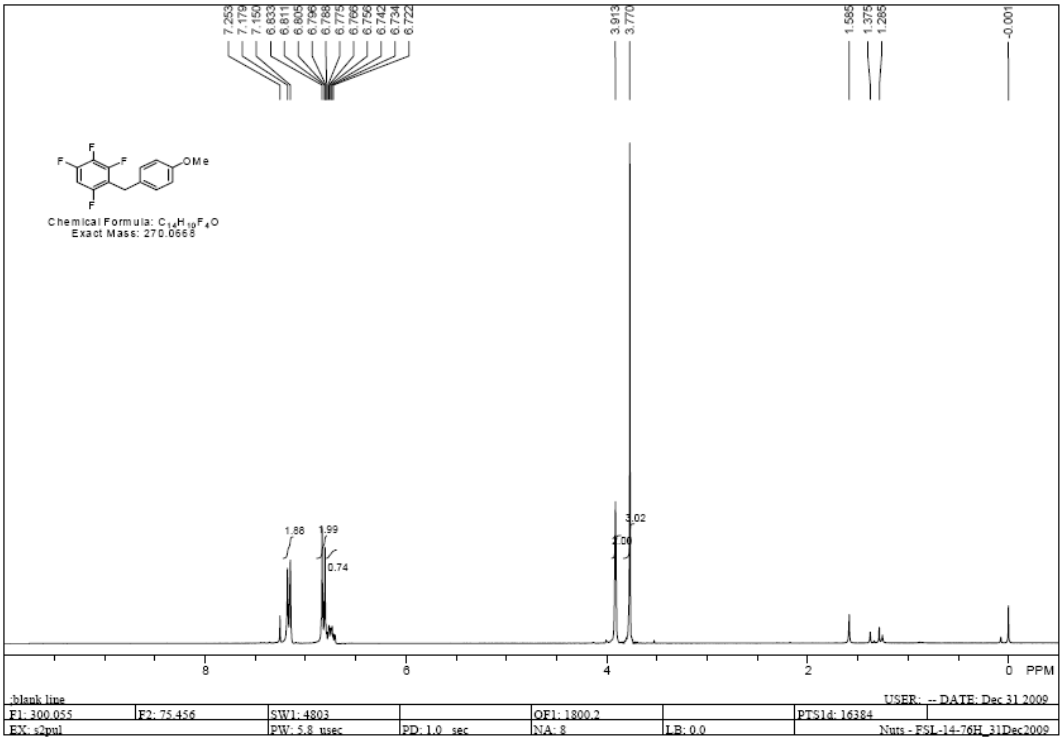
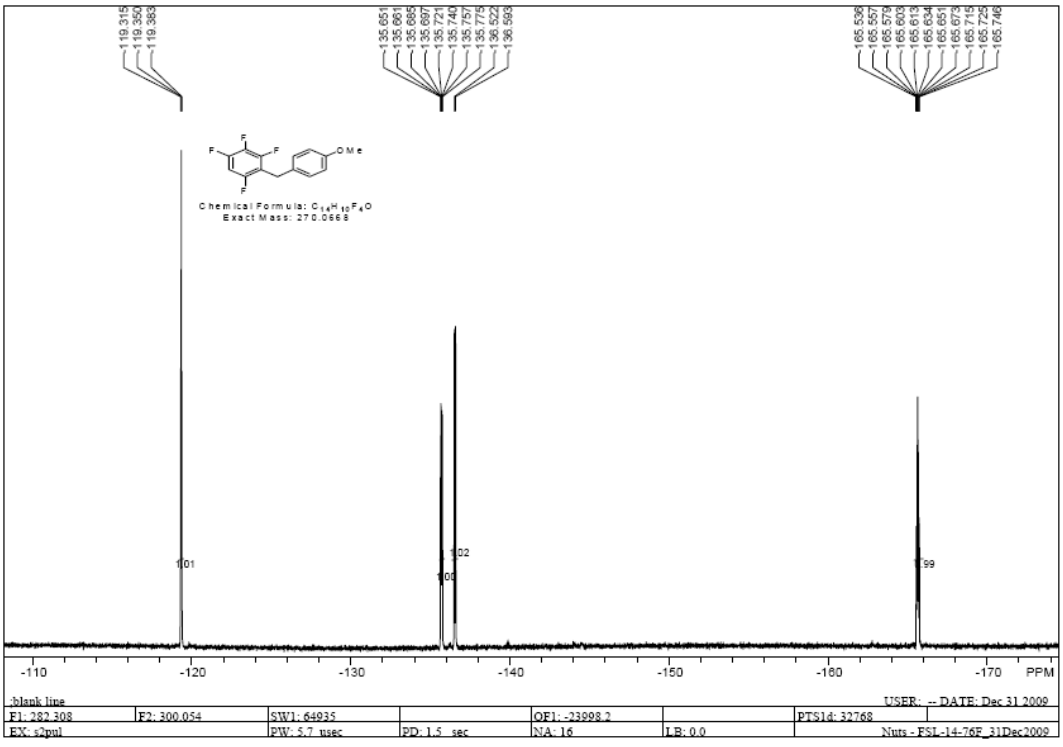
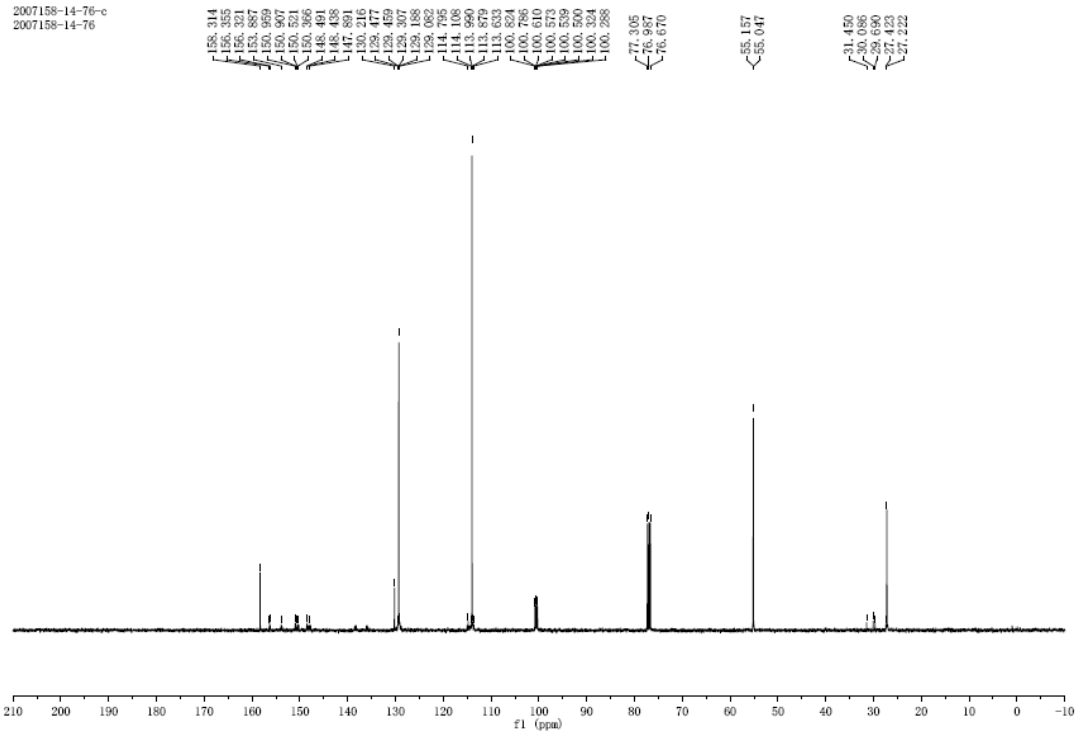
143.599
143.648
143.676
156.374
156.451
156.521
162.116
162.144
162.193
162.221
162.270
162.298
Chemical Formula: C12H5F5N
Exact Mass: 259.0420
1.12
1.00
1.06
-140
-145
-150
-155
-160
PPM
blank line
USER: -- DATE: Mar 3 2010
F1: 282.308
F2: 300.054
SW1: 64935
OF1: -23998.2
PTS1d: 19449 32768
EX: s2pul
PW: 5.7 us
PD: 1.5 sec
NA: 16
LB: 0.0
Nuts - FSL-15-59F_03Mar2010


149.360
148.357
146.574
146.518
146.464
146.427
146.369
146.314
143.249
143.197
143.157
143.105
143.048
141.774
139.165
138.418
135.978
135.774
135.648
135.603
135.579
132.986
123.610
113.168
113.117
77.416
76.992
76.568
30.168
25.397
25.383
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)

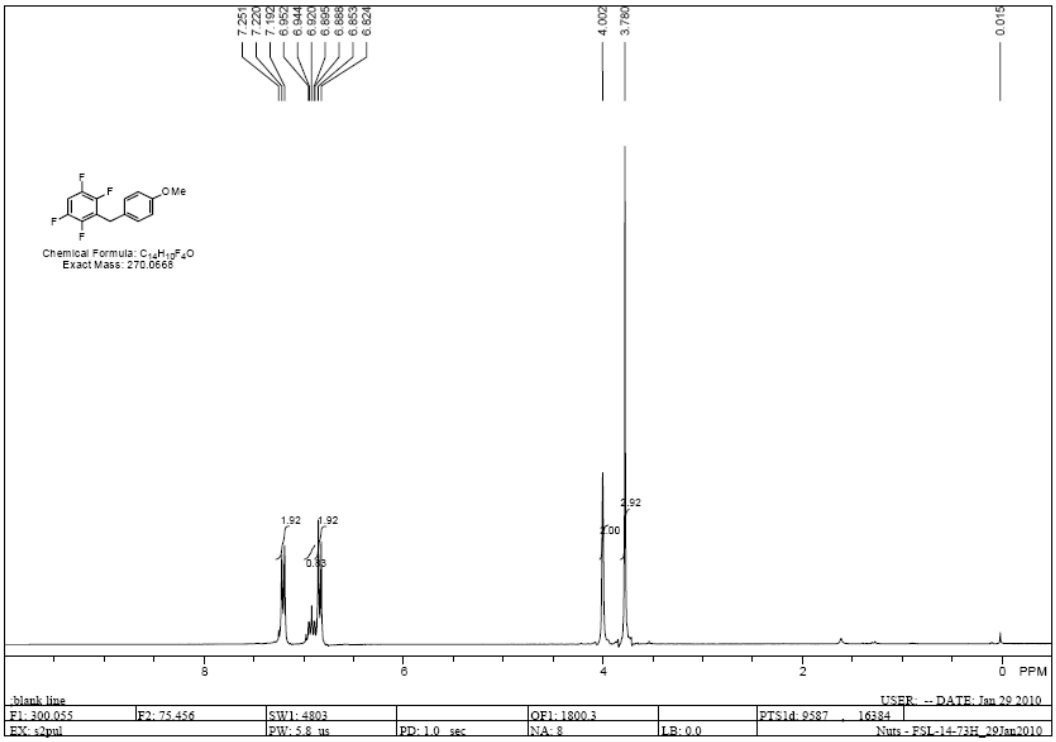
1,2,3,5-Tetrafluoro-4-(4-methoxybenzyl)benzene (5a).

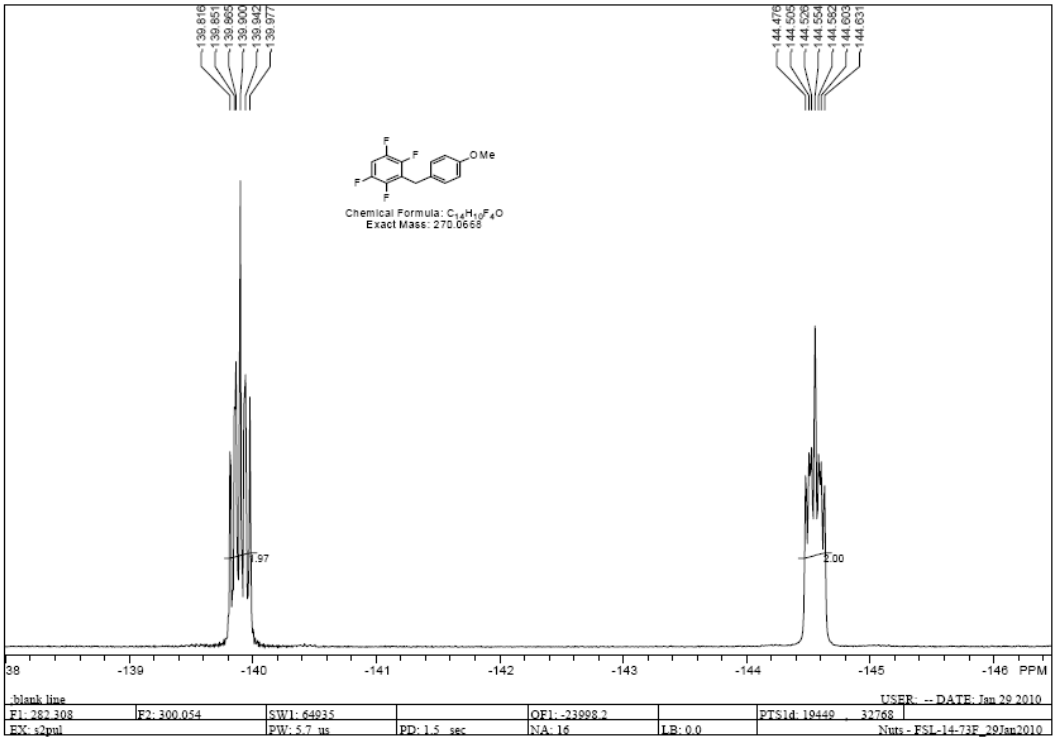


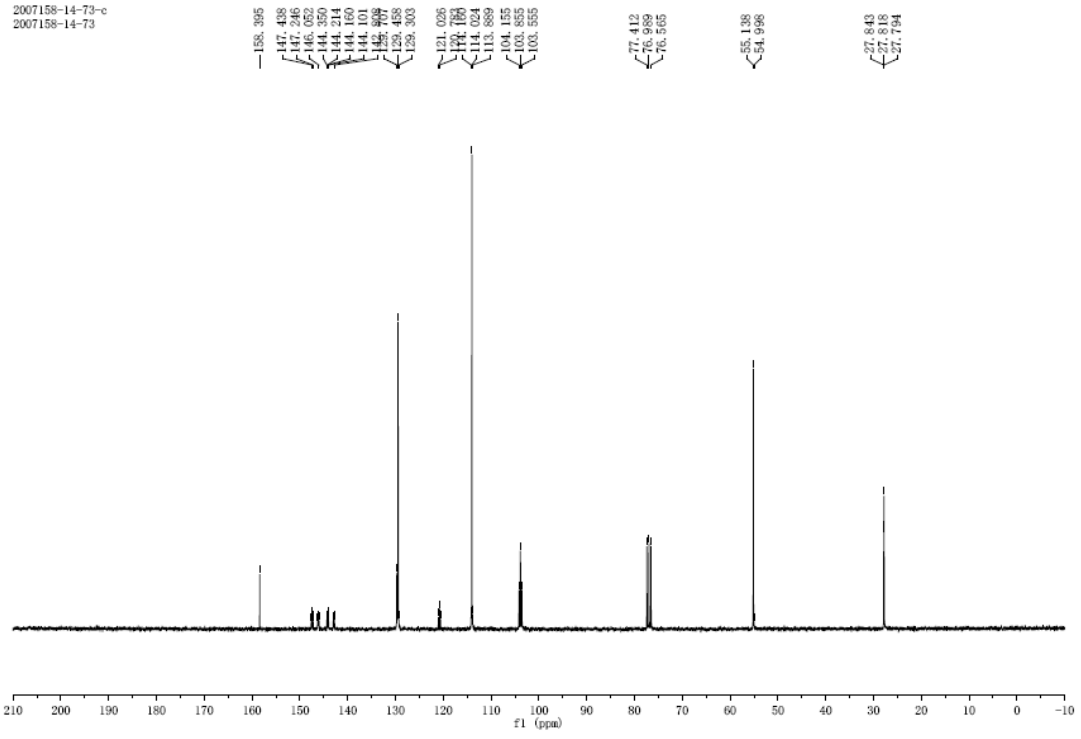




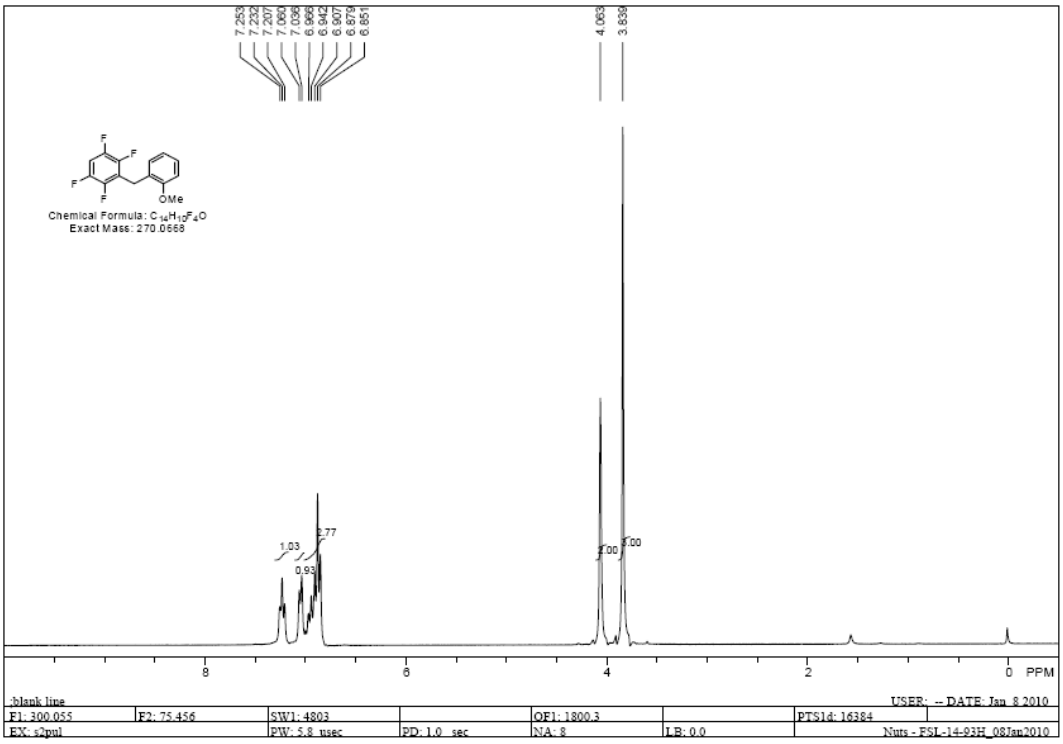
1,2,4,5-Tetrafluoro-3-(4-methoxybenzyl)benzene (5b)

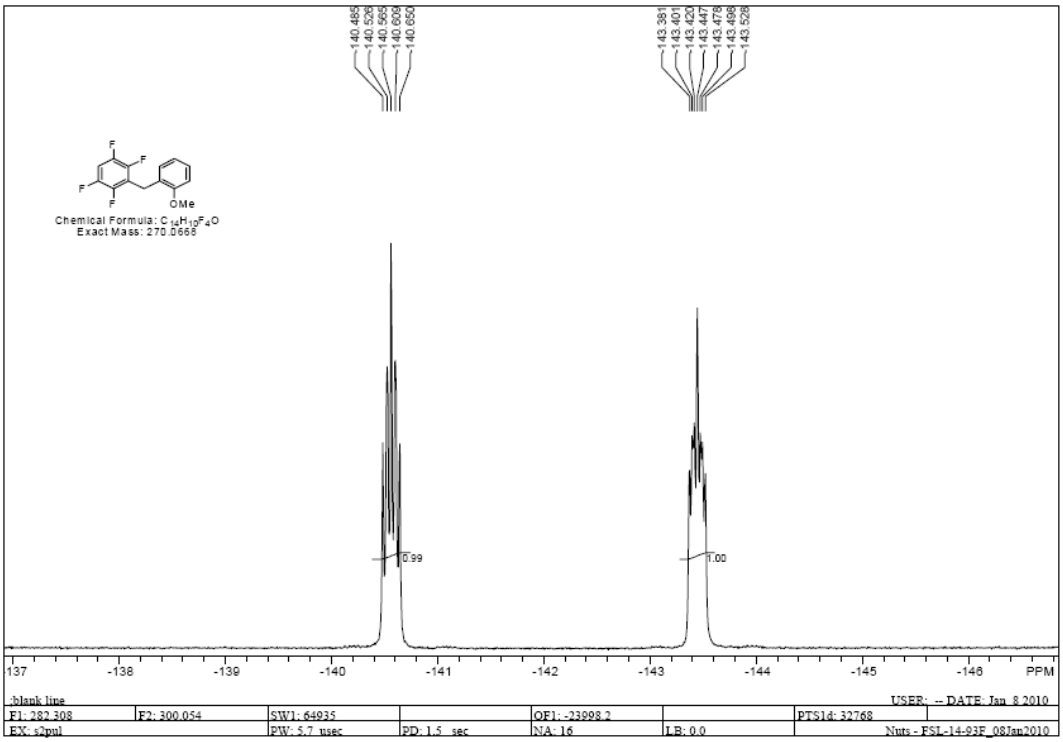


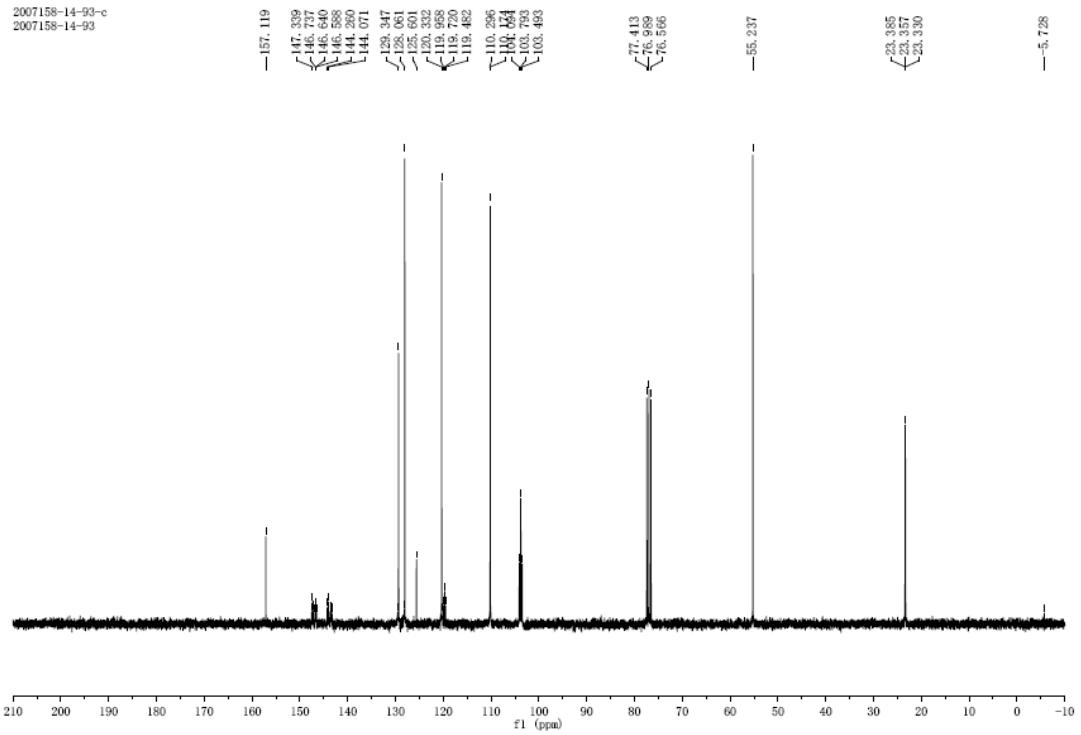

139.816
139.851
139.865
139.900
139.942
139.977
144.476
144.505
144.526
144.554
144.582
144.603
144.631
F
F
F
F
OMe
Chemical Formula: C14H10F4O
Exact Mass: 270.0668
1.97
2.00
38
-139
-140
-141
-142
-143
-144
-145
-146 PPM
blank line
USER: -- DATE: Jan 29 2010
F1: 282.308
F2: 300.054
SW1: 64935
OF1: -23998.2
PTS1d: 19449 , 32768
EX: s2pul
PW: 5.7 us
PD: 1.5 sec
NA: 16
LB: 0.0
Nuts - FSL-14-73F_29Jan2010


2007158-14-73-c
2007158-14-73
158.395
147.438
147.246
146.052
144.350
144.214
144.160
144.101
129.458
129.303
121.026
114.024
113.869
104.155
103.855
103.555
77.412
76.989
76.565
55.138
54.996
27.843
27.818
27.794
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)

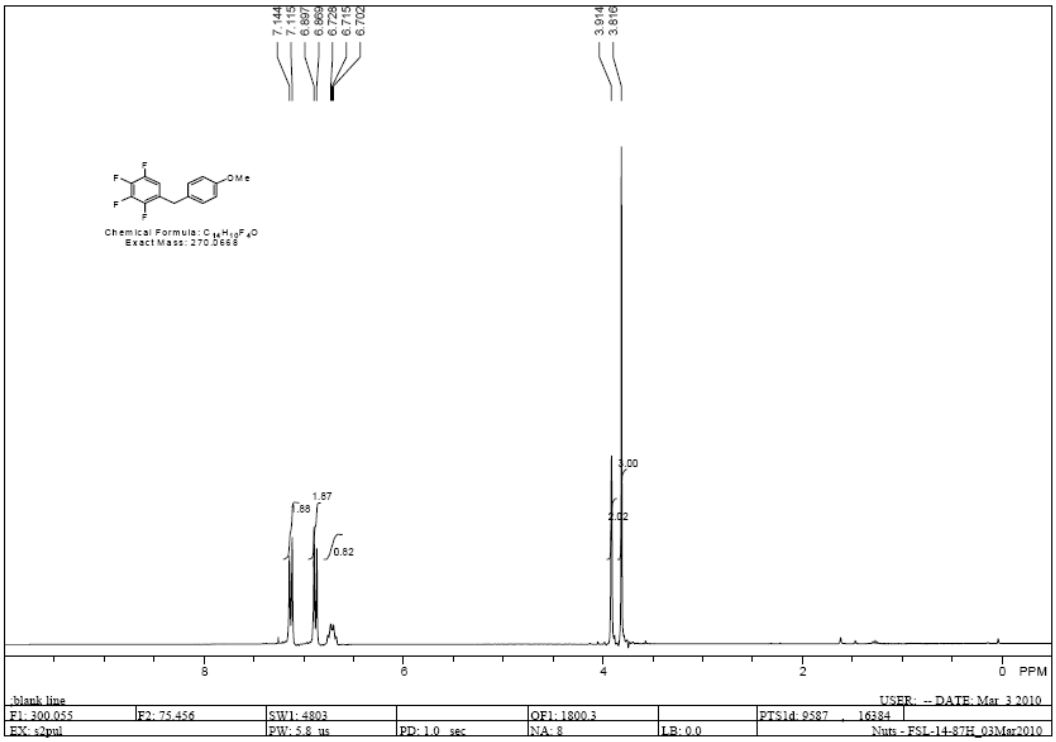
1,2,4,5-Tetrafluoro-3-(2-methoxybenzyl)benzene (5c)

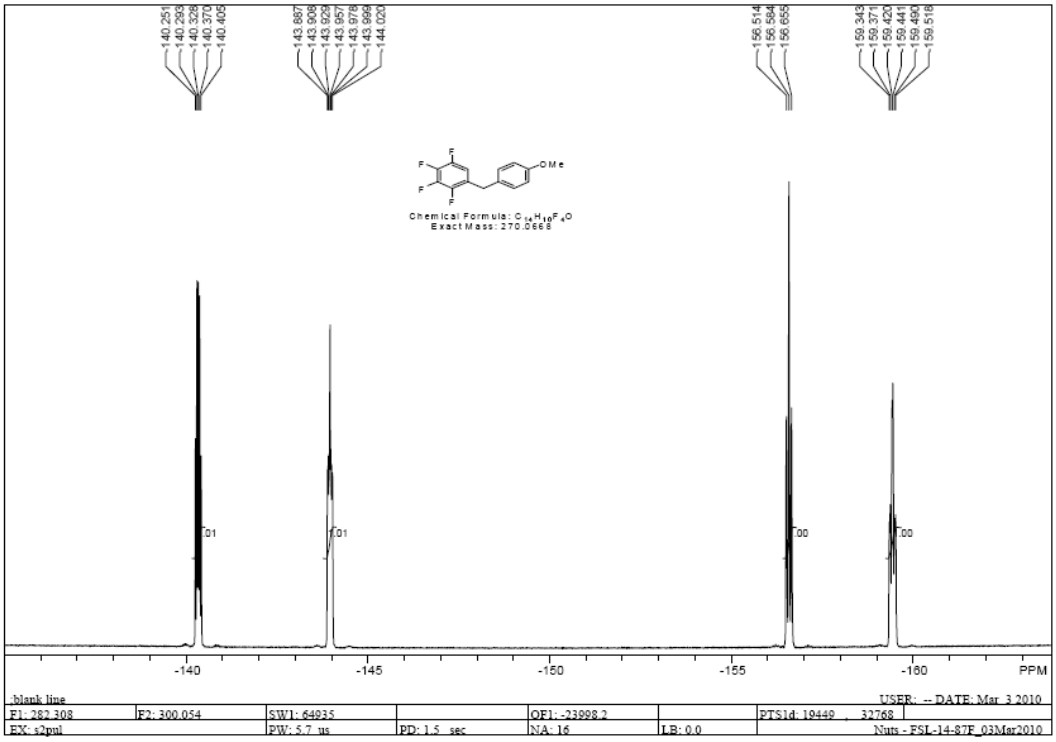


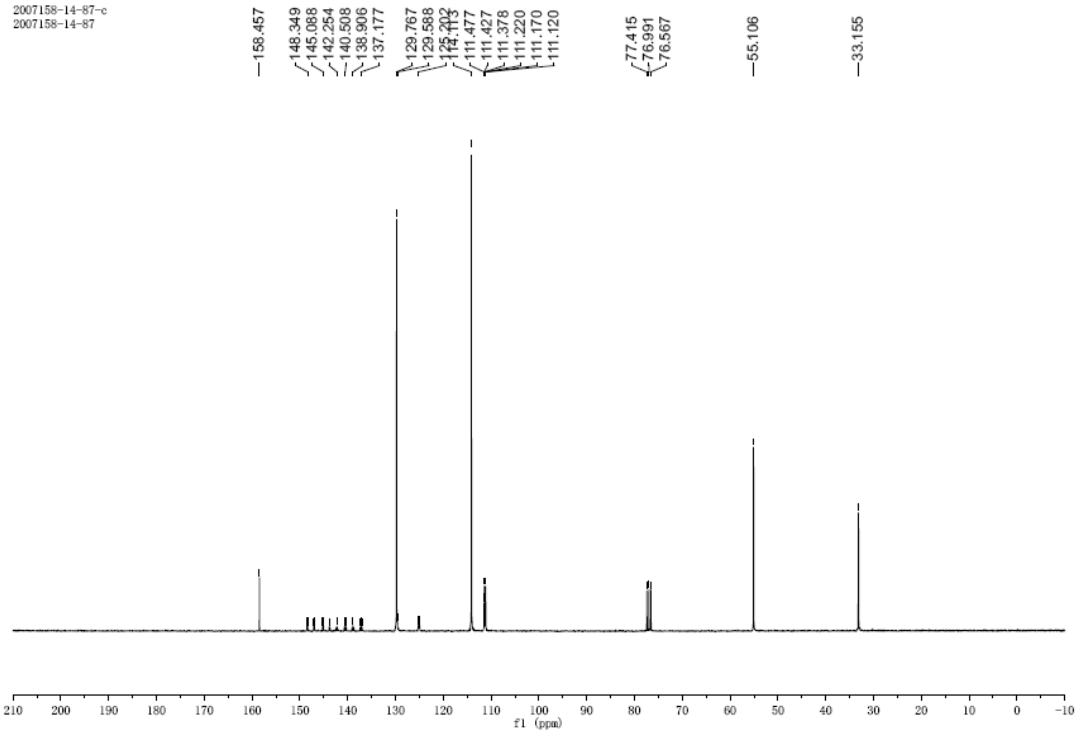




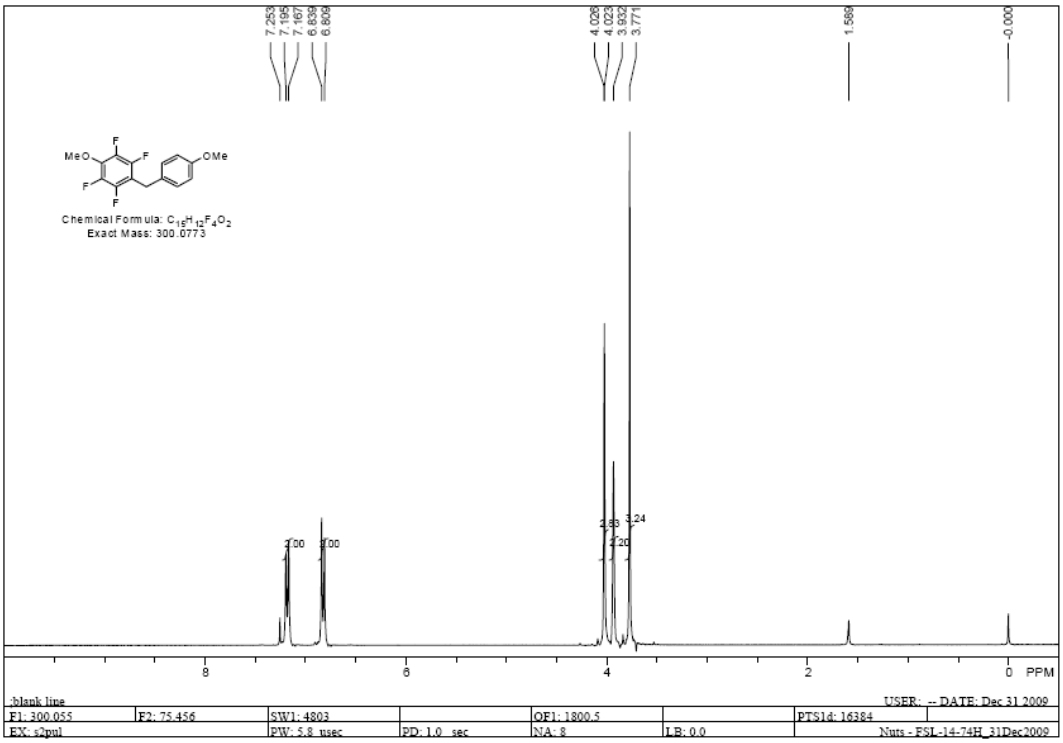
1,2,3,4-Tetrafluoro-5-(4-methoxybenzyl)benzene (5d)

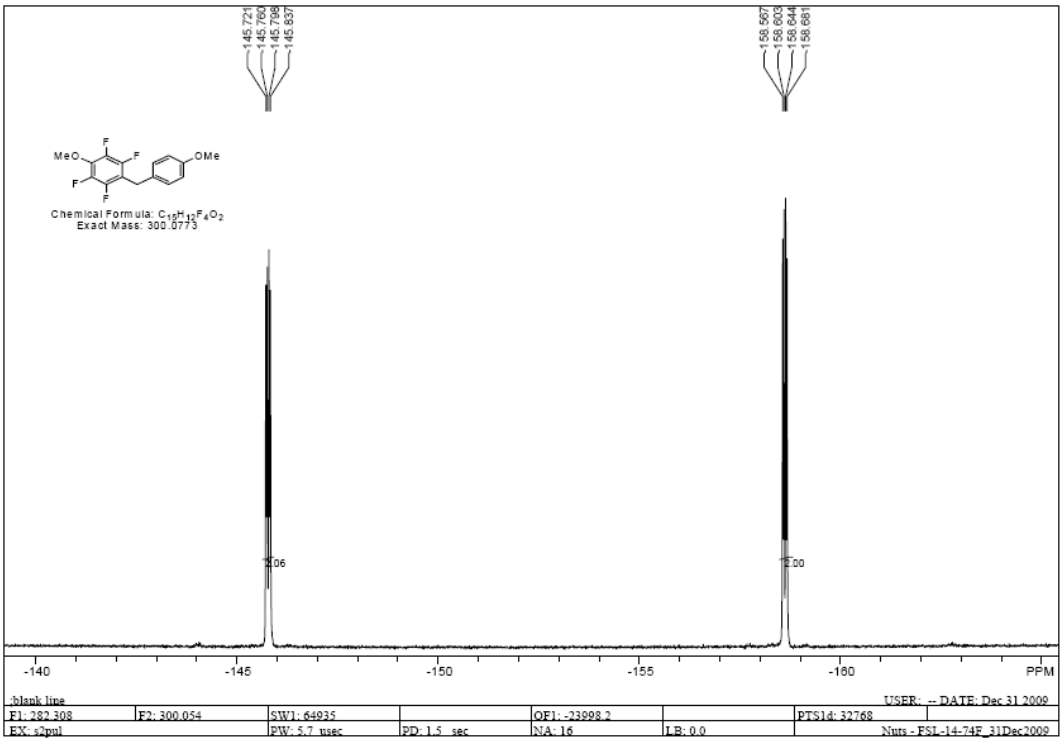


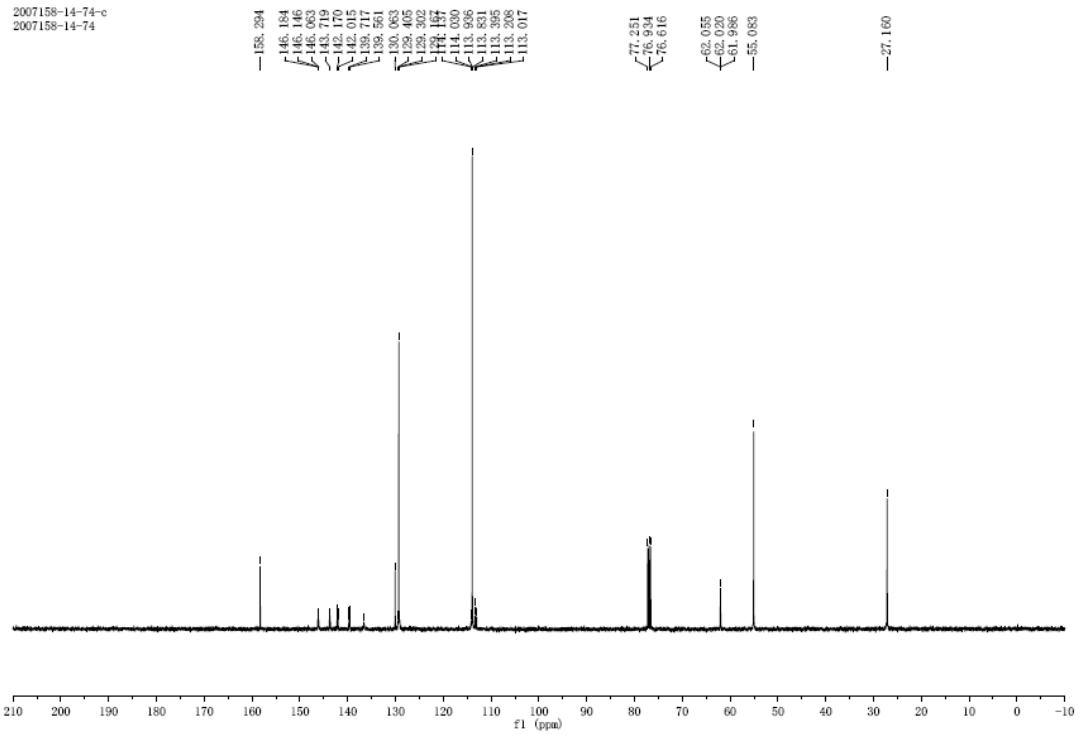

140.251
140.293
140.328
140.370
140.405
143.887
143.908
143.929
143.957
143.978
143.999
144.020
156.514
156.584
156.655
159.343
159.371
159.420
159.441
159.490
159.518
F
F
F
F
OMe
Chemical Formula: C14H10F4O
Exact Mass: 270.0668
1.01
1.01
1.00
1.00
-140
-145
-150
-155
-160
PPM
blank line
USER: -- DATE: Mar 3 2010
F1: 282.308
F2: 300.054
SW1: 64935
OF1: -23998.2
PTS1d: 19449 , 32768
EX: s2pul
PW: 5.7 us
PD: 1.5 sec
NA: 16
LB: 0.0
Nuts - FSL-14-87F_03Mar2010


2007158-14-87-c
2007158-14-87
158.457
148.349
145.088
142.254
140.508
138.906
137.177
129.767
129.588
125.202
114.113
111.477
111.427
111.378
111.220
111.170
111.120
77.415
76.991
76.567
55.106
33.155
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)

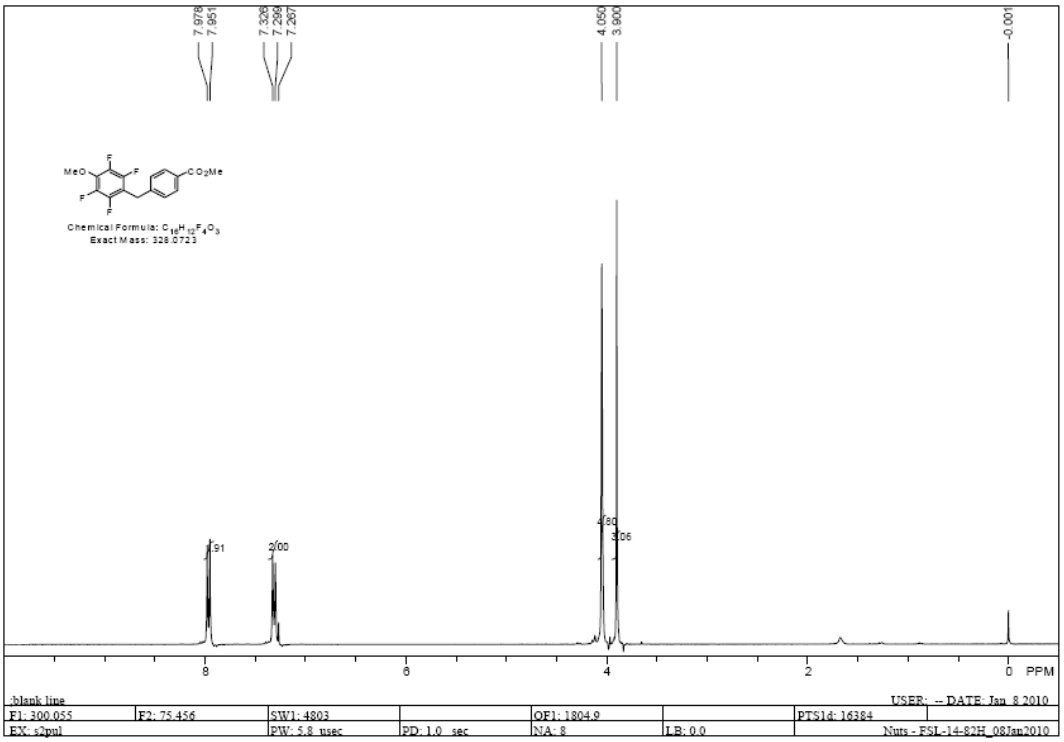
1,2,4,5-Tetrafluoro-3-methoxy-6-(4-methoxybenzyl)benzene (5e)

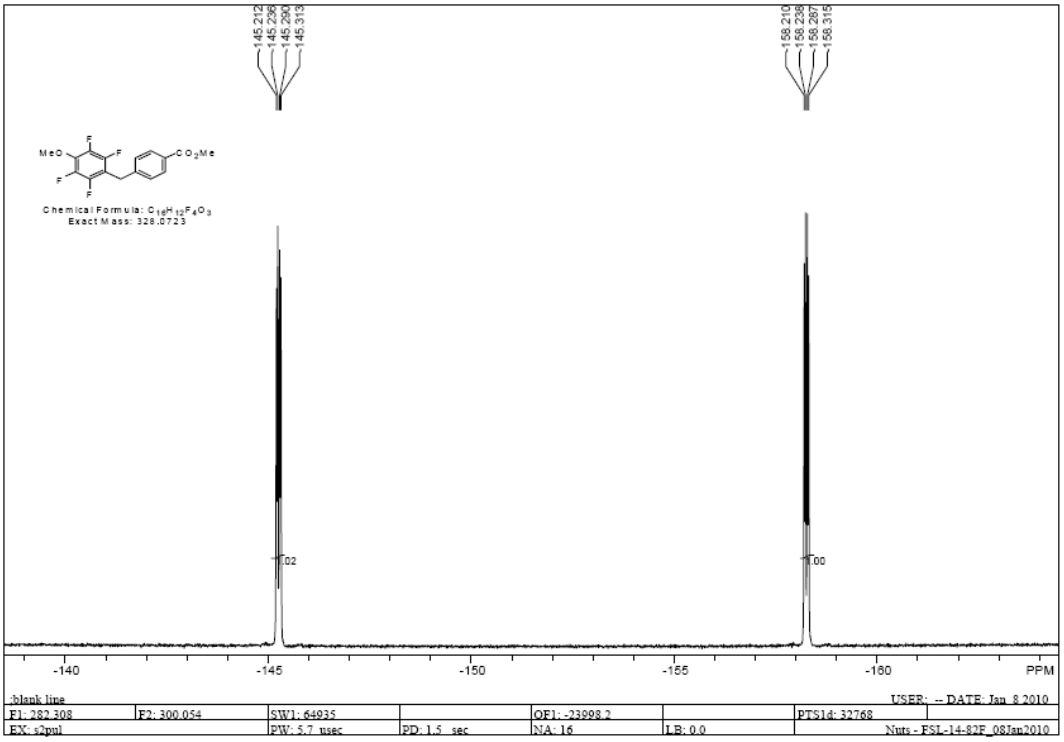


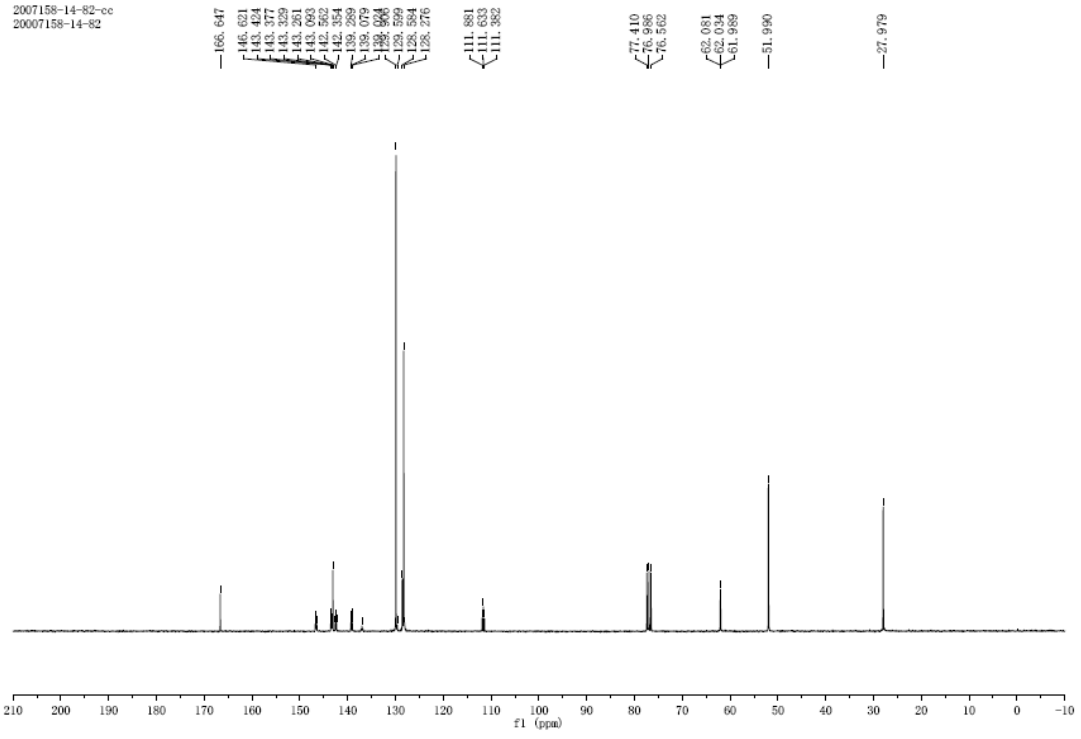




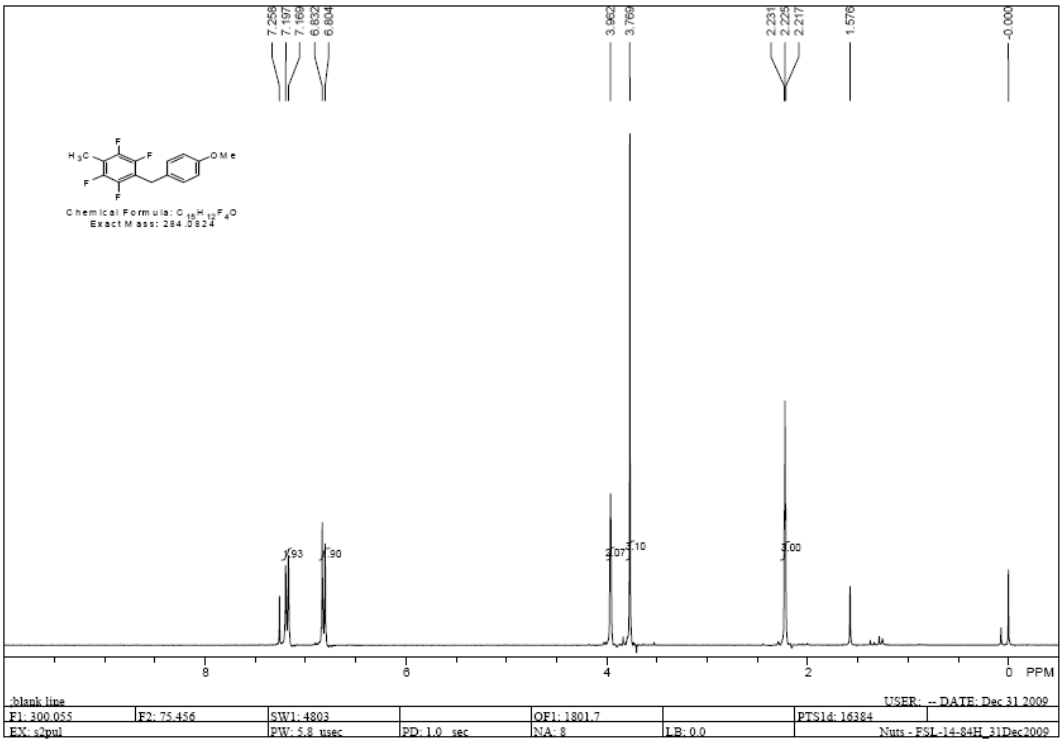
Methyl 4-(2,3,5,6-tetrafluoro-4-methoxybenzyl)benzoate (5f)

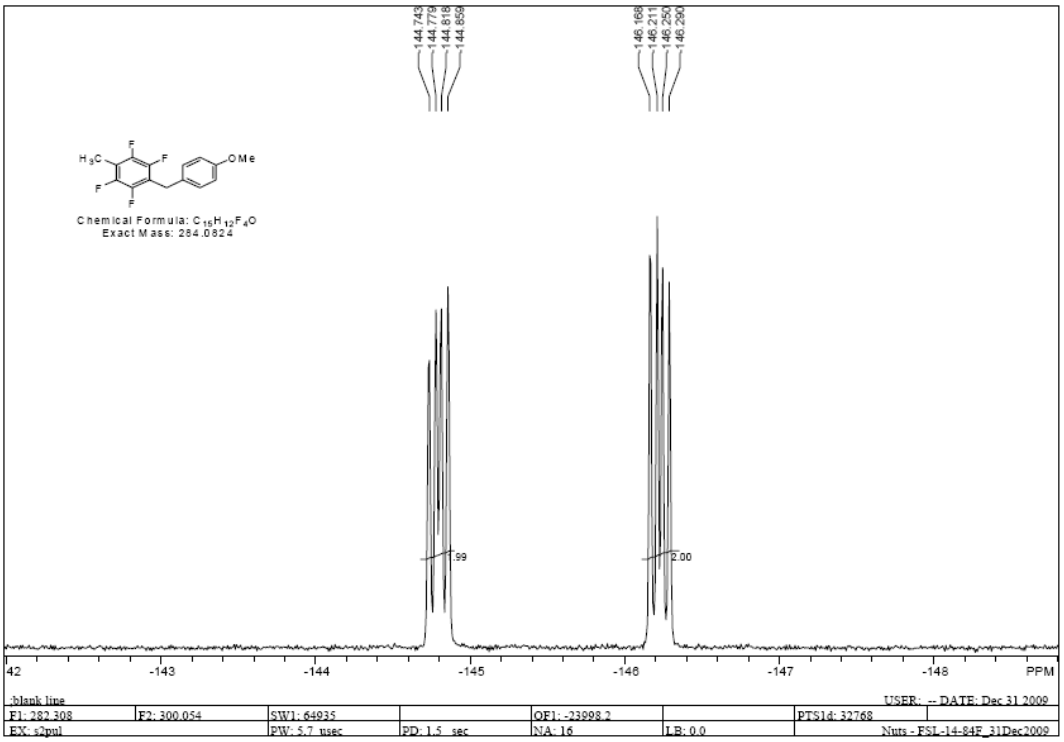


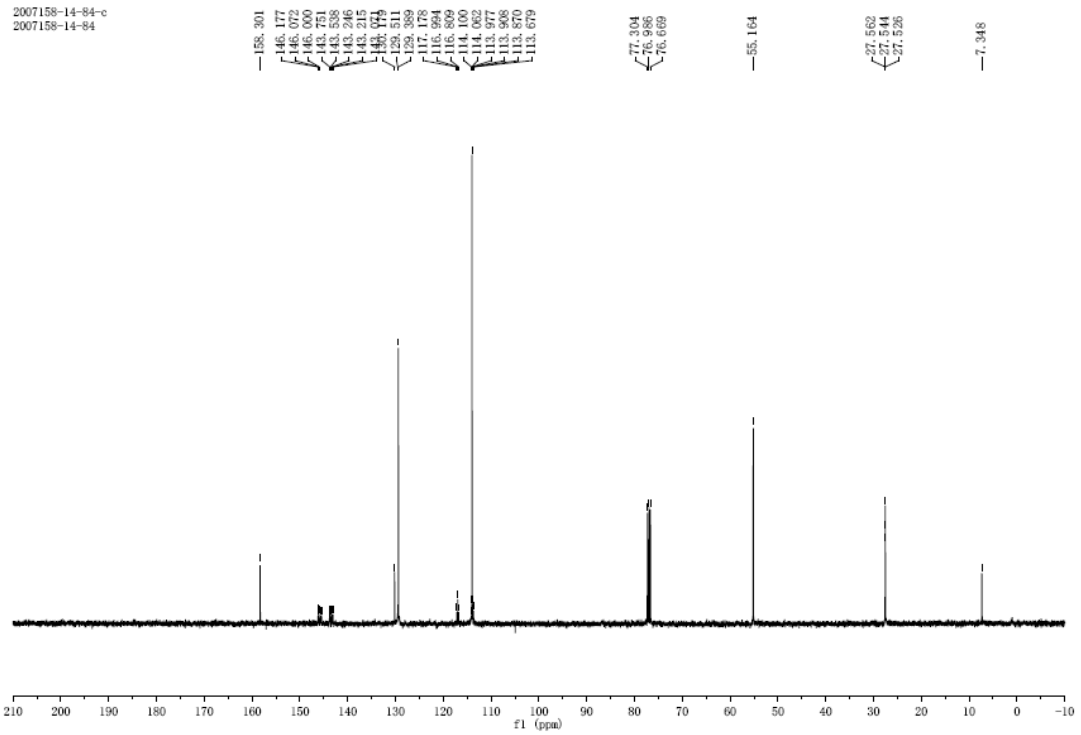

145.212
145.236
145.260
145.313
158.210
158.238
158.267
158.315
MeO
F
F
F
F
CO2Me
Chemical Formula: C18H12F4O3
Exact Mass: 328.0723
1.02
1.00
-140
-145
-150
-155
-160
PPM
;blank line
USER: -- DATE: Jan 8 2010
F1: 282.308
F2: 300.054
SW1: 64935
OF1: -23998.2
PTS1d: 32768
EX: s2pul
PW: 5.7 usec
PD: 1.5 sec
NA: 16
LB: 0.0
Nuts - FSL-14-82F_08Jan2010


2007158-14-82-cc
20007158-14-82
166.647
146.621
143.424
143.377
143.329
143.261
143.093
142.562
142.354
139.269
139.079
129.599
128.584
128.276
111.881
111.633
111.382
77.410
76.986
76.562
62.081
62.034
61.989
51.990
27.979
f1 (ppm)

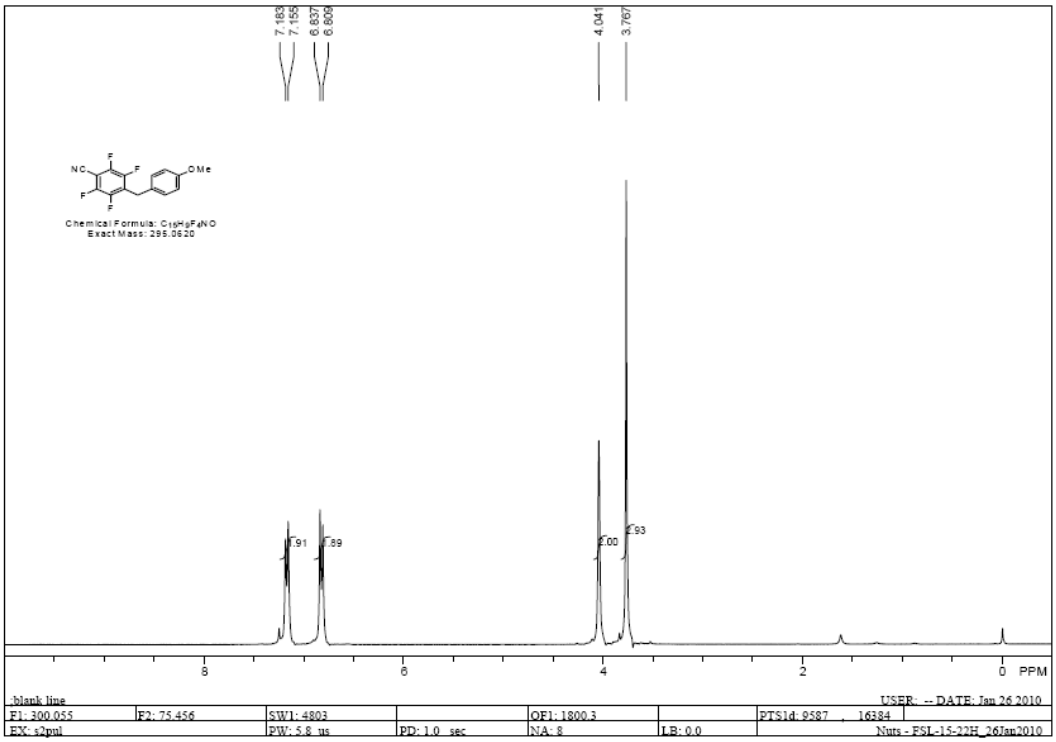
1,2,4,5-tetrafluoro-3-(4-methoxybenzyl)-6-methylbenzene (5g)

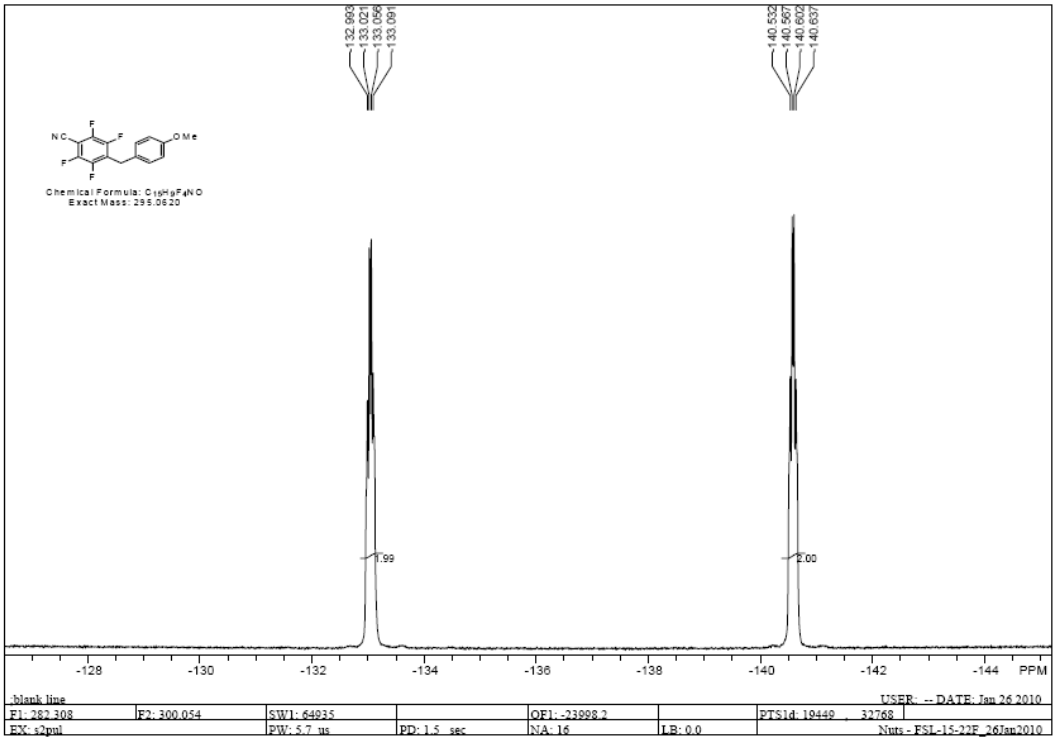


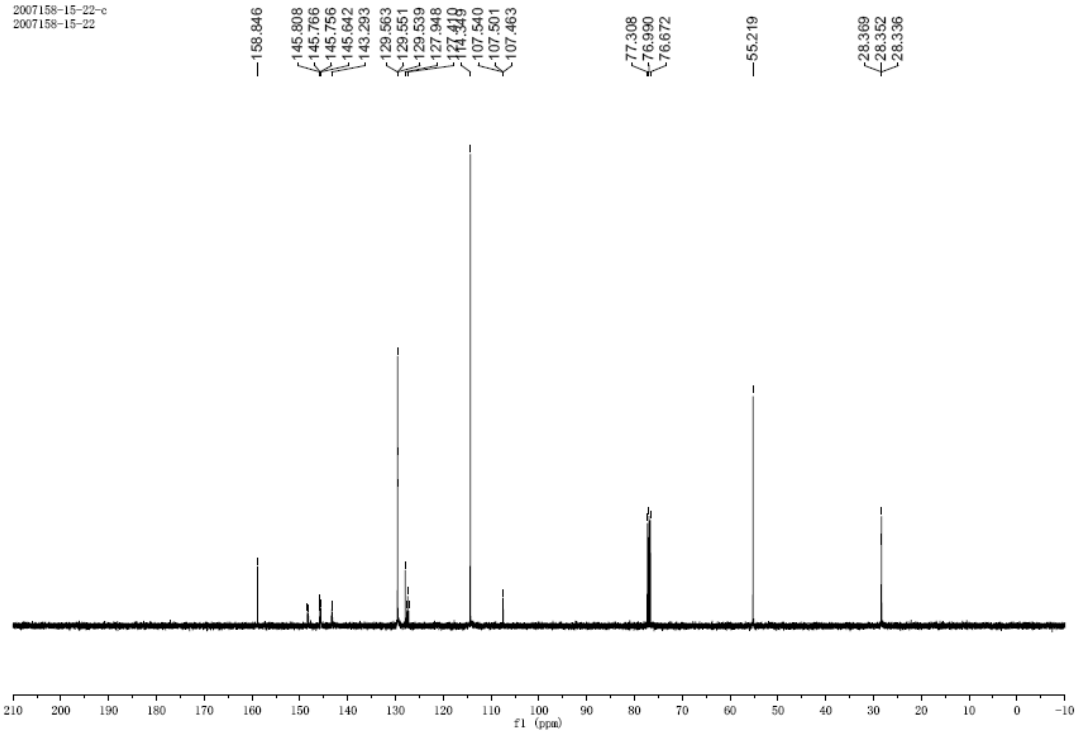




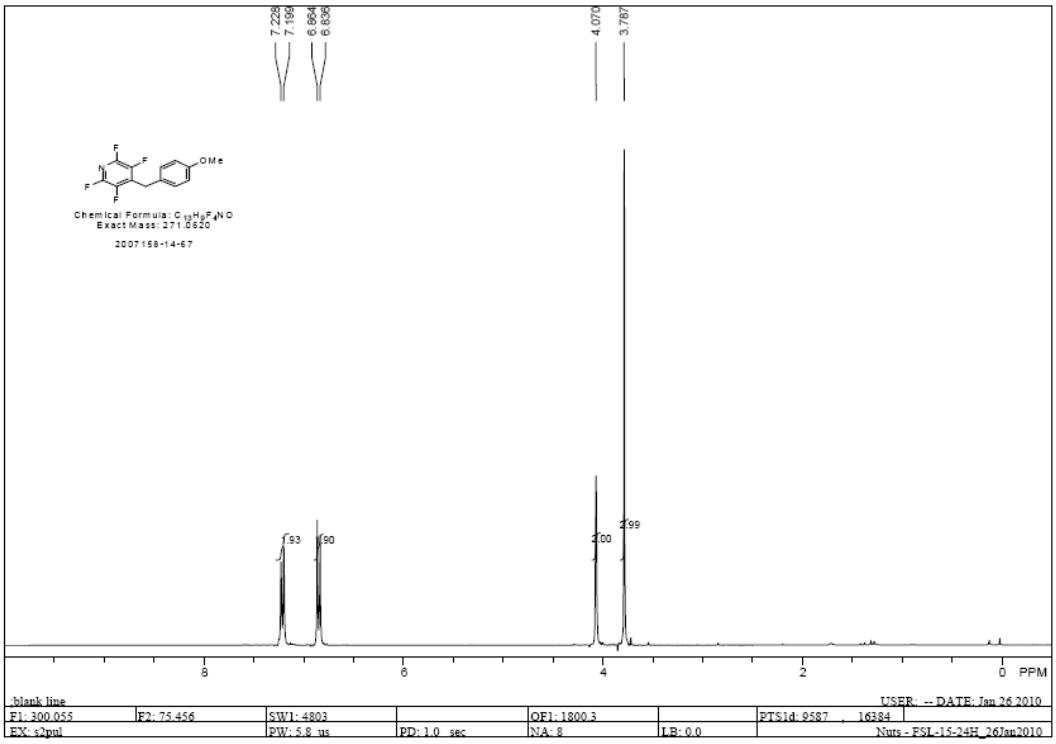
2,3,5,6-Tetrafluoro-4-(4-methoxybenzyl)benzonitrile (5h)

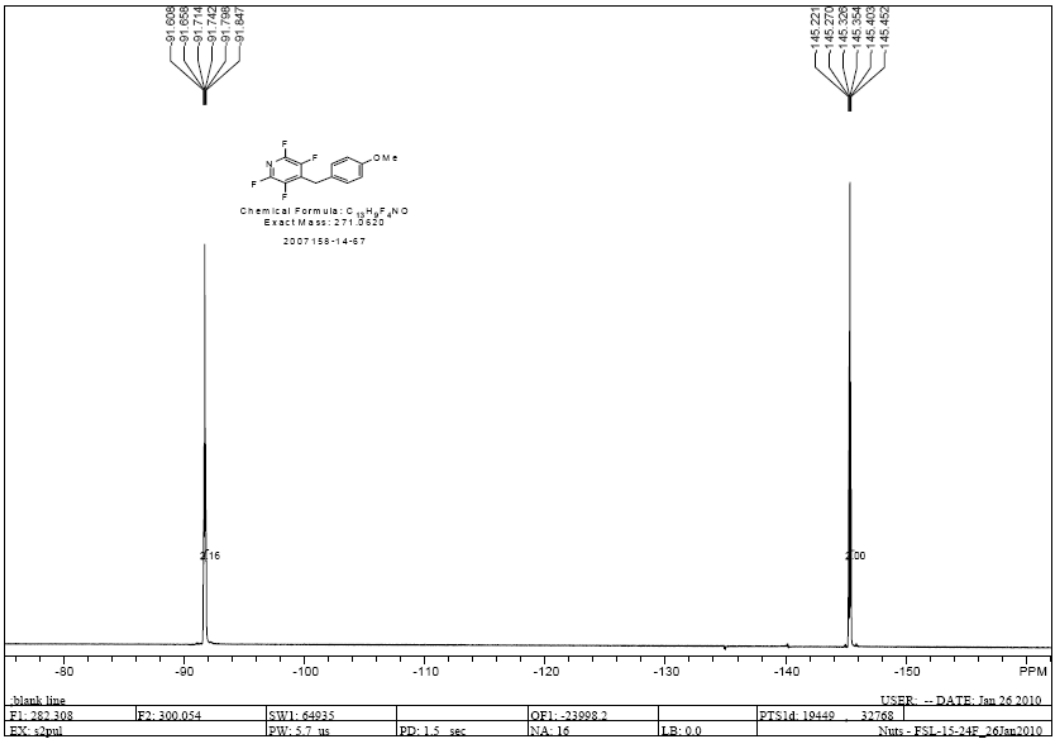


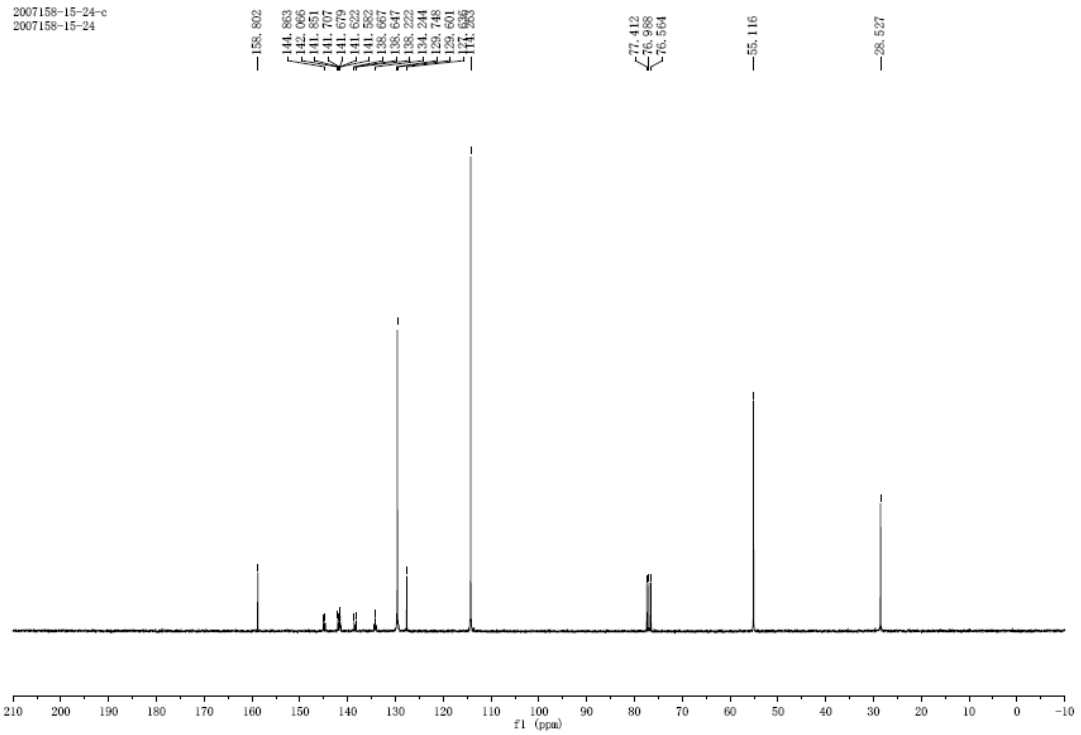

132.993
133.021
133.056
133.091
140.532
140.567
140.602
140.637
Chemical Formula: C15H9F4NO
Exact Mass: 295.0620
1.99
2.00
-128
-130
-132
-134
-136
-138
-140
-142
-144
PPM
;blank line
USER: -- DATE: Jan 26 2010
F1: 282.308
F2: 300.054
SW1: 64935
OF1: -23998.2
PTS1d: 19449 , 32768
EX: s2pul
PW: 5.7 us
PD: 1.5 sec
NA: 16
LB: 0.0
Nuts - FSL-15-22F_26Jan2010


2007158-15-22-c
2007158-15-22
158.846
145.808
145.766
145.756
145.642
143.293
129.563
129.551
129.539
127.948
127.410
114.349
107.540
107.501
107.463
77.308
76.990
76.672
55.219
28.369
28.352
28.336
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)

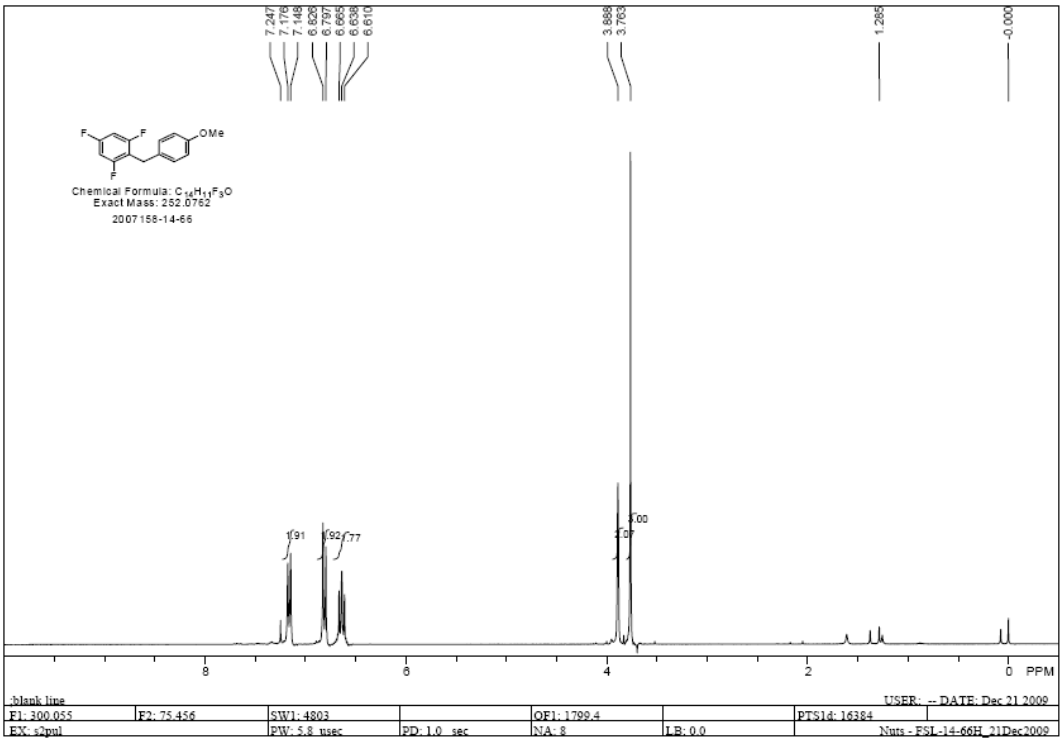
2,3,5,6-Tetrafluoro-4-(4-methoxybenzyl)pyridine (5i)

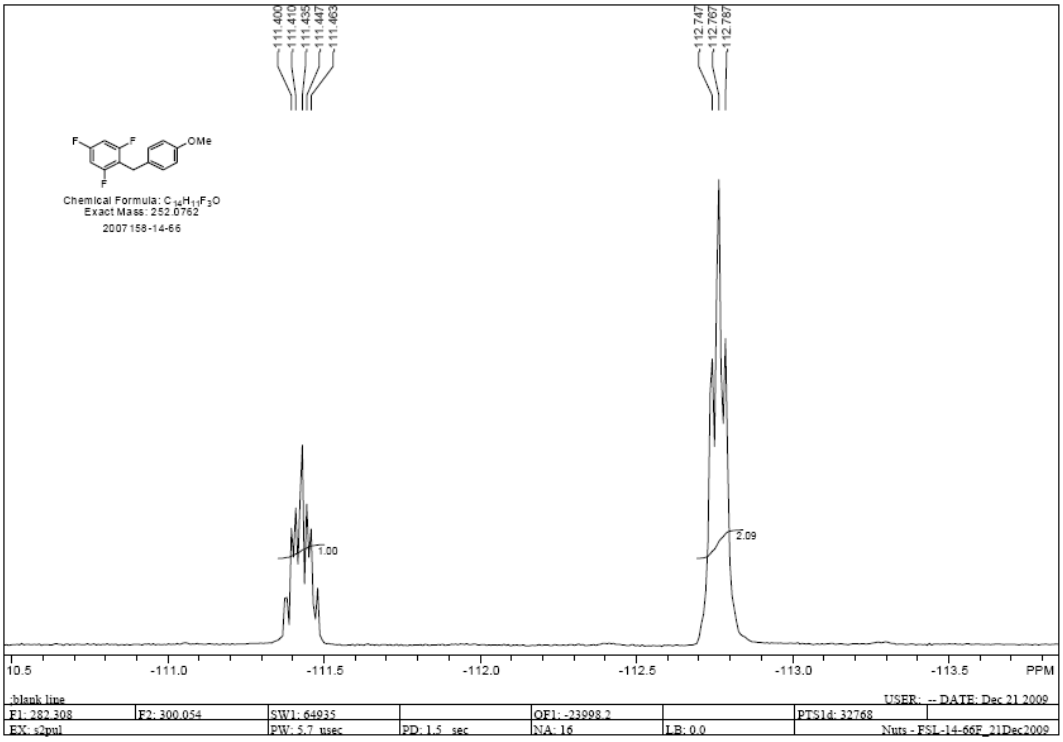


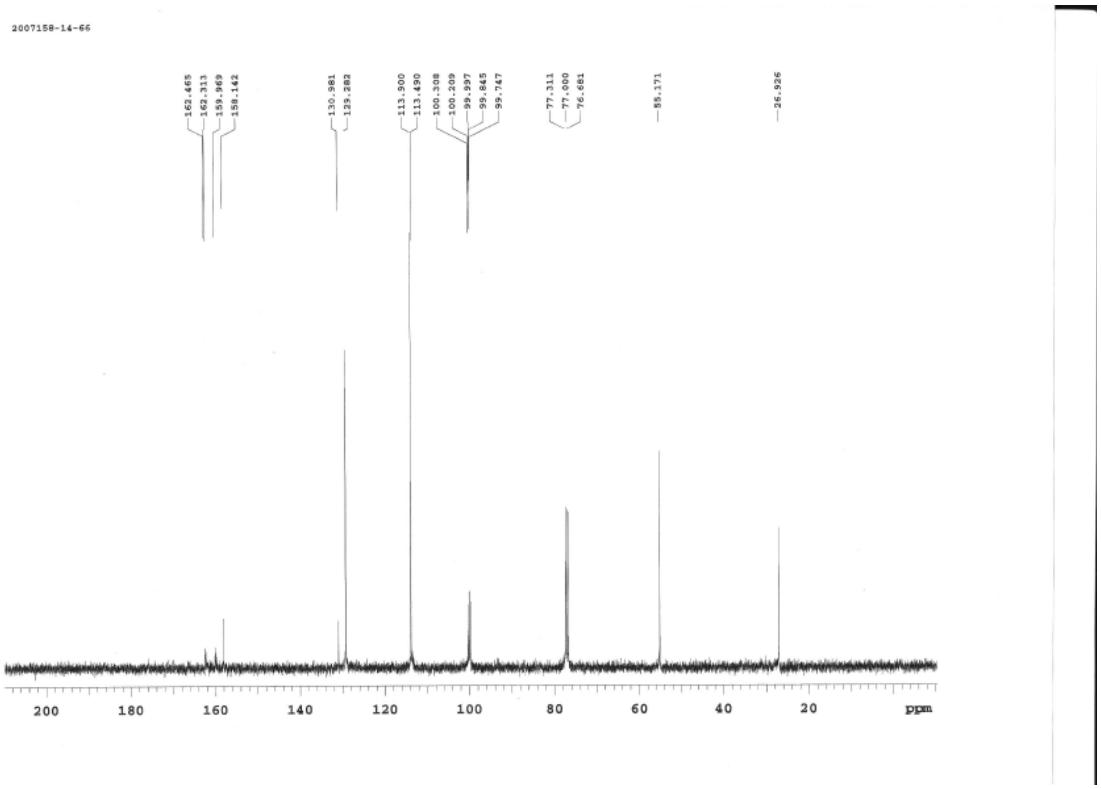




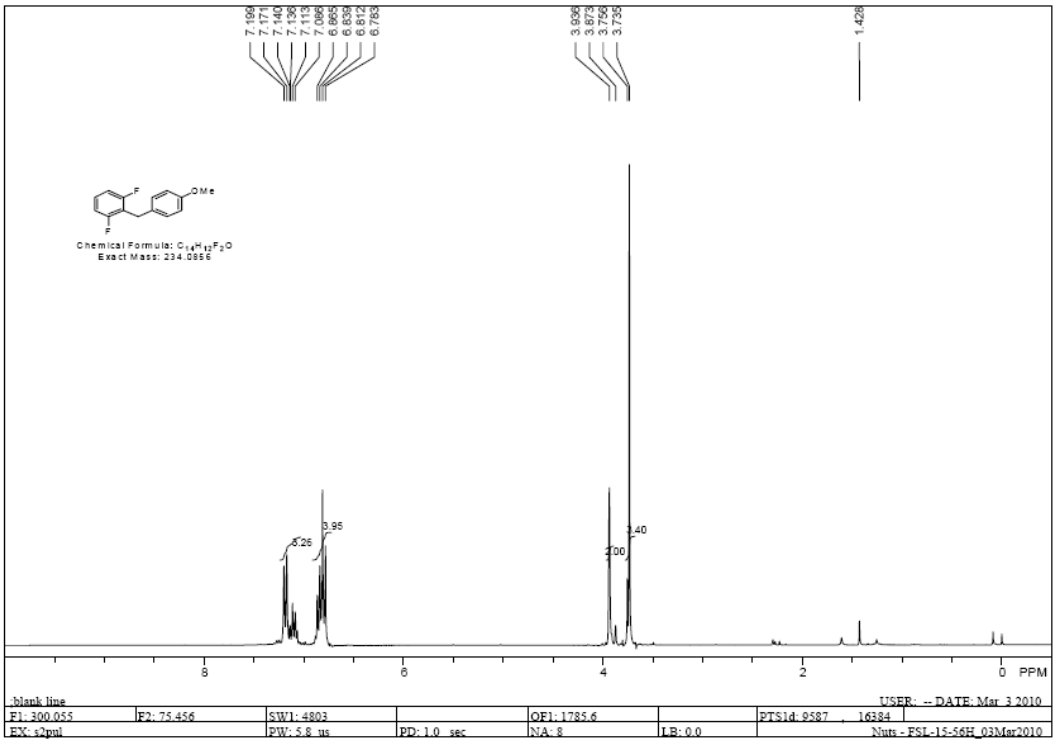
1,3,5-Prifluoro-2-(4-methoxybenzyl)benzene (5j)

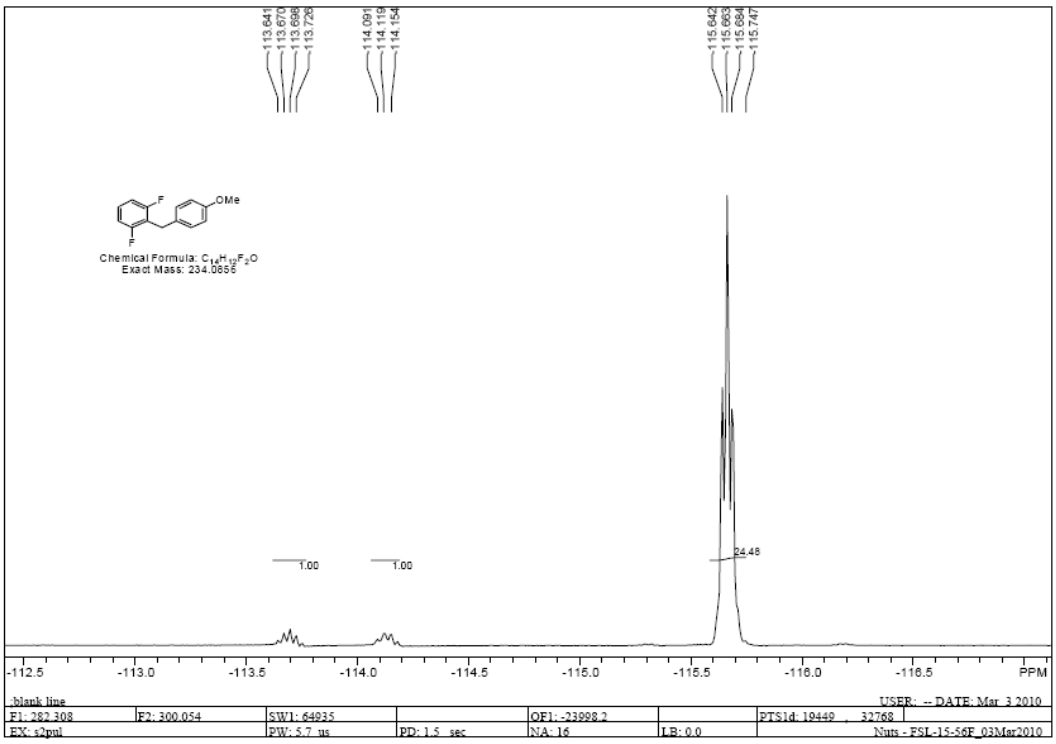


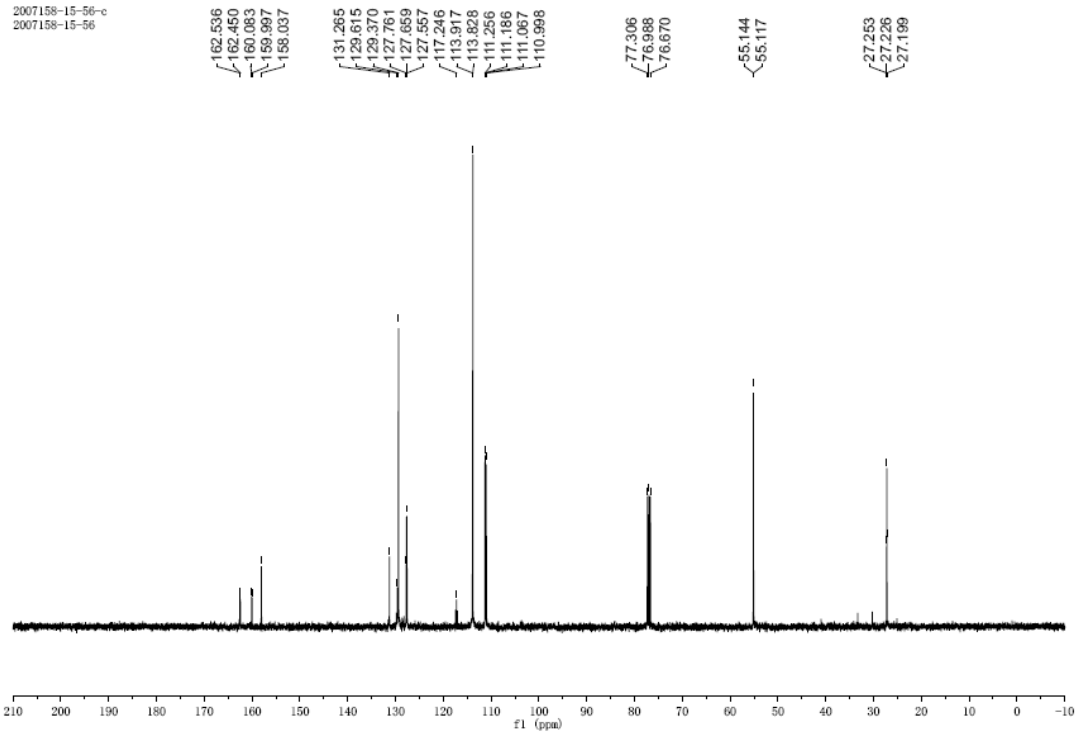

111.400
111.410
111.435
111.447
111.463
112.747
112.767
112.787
F
F
F
OMe
Chemical Formula: C14H11F3O
Exact Mass: 252.0762
2007158-14-66
1.00
2.09
10.5
-111.0
-111.5
-112.0
-112.5
-113.0
-113.5
PPM
;blank line
USER: -- DATE: Dec 21 2009
F1: 282.308
F2: 300.054
SW1: 64935
OF1: -23998.2
PTS1d: 32768
EX: s2pul
PW: 5.7 usec
PD: 1.5 sec
NA: 16
LB: 0.0
Nuts - FSL-14-66F_21Dec2009


2007158-14-66
162.465
162.313
159.969
159.142
130.981
129.282
113.900
113.490
100.308
100.209
99.997
99.845
99.747
77.311
77.000
76.681
55.171
26.926
200
180
160
140
120
100
80
60
40
20
ppm

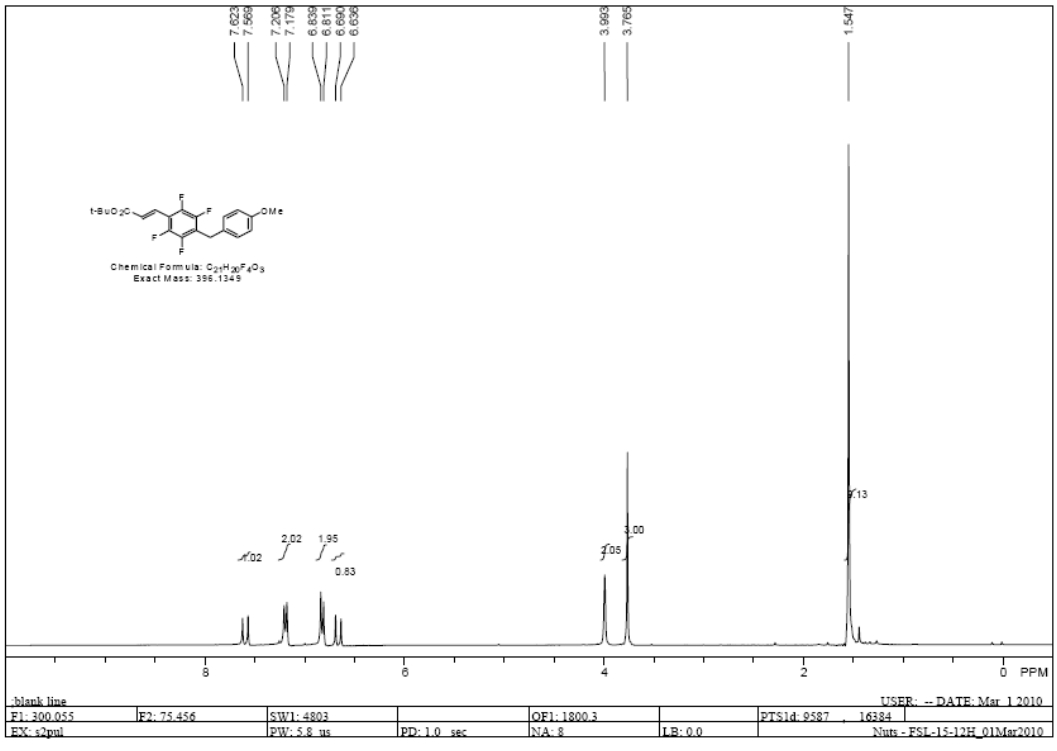
1,3-Difluoro-2-(4-methoxybenzyl)benzene (5k)

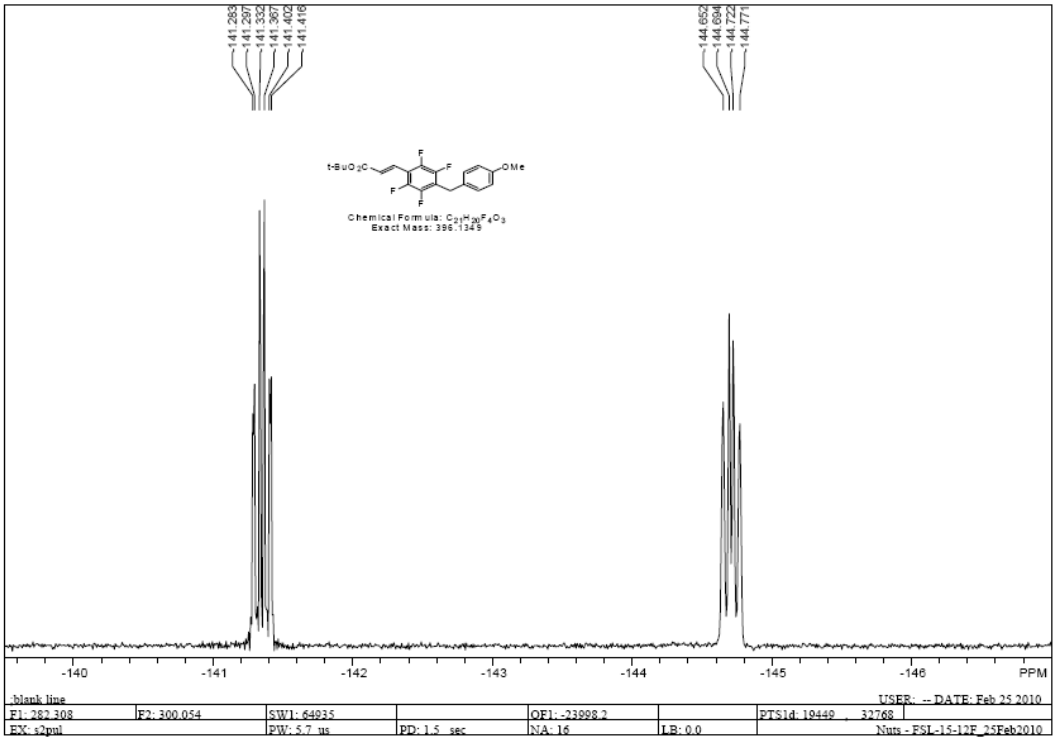


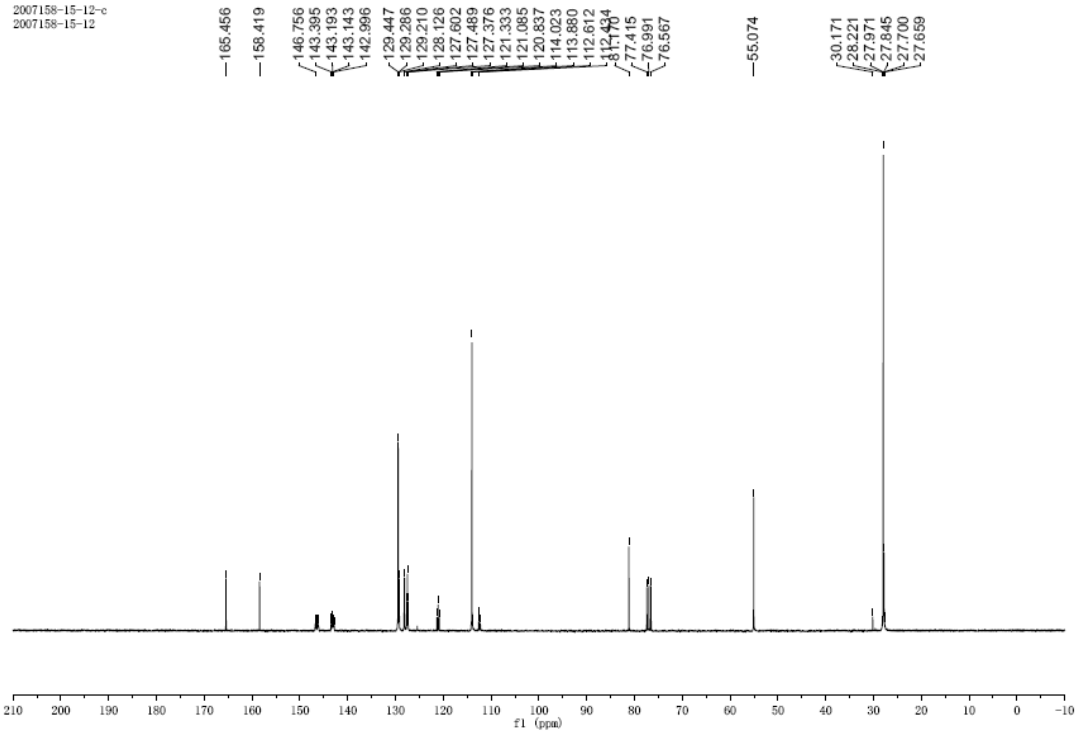




(*E*)-*tert*-butyl 3-(2,3,5,6-tetrafluoro-4-(4-methoxybenzyl)phenyl)acrylate (5l)




141.283
141.297
141.332
141.367
141.402
141.416
144.652
144.694
144.722
144.771
t-BuO2C
F
F
F
F
OMe
Chemical Formula: C21H20F4O3
Exact Mass: 396.1349
-140
-141
-142
-143
-144
-145
-146
PPM
blank line
USER: -- DATE: Feb 25 2010
F1: 282.308
F2: 300.054
SW1: 64935
OF1: -23998.2
PTS1d: 19449 , 32768
EX: s2pul
PW: 5.7 us
PD: 1.5 sec
NA: 16
LB: 0.0
Nuts - FSL-15-12F_25Feb2010


2007158-15-12-c
2007158-15-12
165.456
158.419
146.756
143.395
143.193
143.143
142.996
129.447
129.286
129.210
128.126
127.602
127.489
127.376
121.333
121.085
120.837
114.023
113.880
112.612
112.434
81.170
77.415
76.991
76.567
55.074
30.171
28.221
27.971
27.845
27.700
27.659
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)