Supporting Information

Direct Monofluoromethylation of *O*-, *S*-, *N*-, and *P*-Nucleophiles with PhSO(NTs)CH_2F: Accelerating Effect of α-Fluorine Substitution

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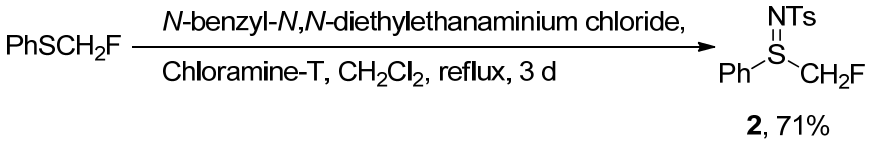
General Methods:

N-Tosyl-*S*-methyl-*S*-phenylsulfoximine[1] and *N*-Tosyl-*S*-trifluoromethyl-*S*-phenylsulfoximine[2] were prepared via the literature procedures. Unless otherwise mentioned, solvents and reagents were purchased from commercial sources and used as received. THF was distilled over sodium. CH_3CN, NMP, DMF, and DMSO were distilled over CaH_2. ^1H, ^{13}C and ^{19}F NMR spectra were recorded on a 500 MHz, 400 MHz or 300 MHz NMR spectrometer. ^1H NMR chemical shifts were determined relative to internal $(CH_3)_4Si$ (TMS) at δ 0.0 or to the signal of a residual protonated solvent: $CDCl_3$ δ 7.26. ^{13}C NMR chemical shifts were determined relative to internal TMS at δ 0.0. ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ at δ 0.0. Mass spectra were obtained on a mass spectrometer. High-resolution mass data were recorded on a high-resolution mass spectrometer in the EI or ESI mode. Melting points (open or sealed capillaries) are reported without correction.

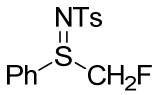
Preparation of *N*-Tosyl-*S*-fluoromethyl-*S*-phenylsulfilimine (2).



2, 71%

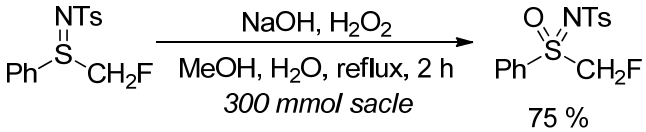
Under N_2 atmosphere, a mixture of $PhSCH_2F$ (364 mmol), *N*-benzyl-*N*,*N*-diethylethanaminium chloride (3 g, 13 mmol), Chloramine-T•$3H_2O$ (120 g, 427 mmol) in CH_2Cl_2 (250 mL) was refluxed for 3 days, after which the reaction was quenched by adding excess amount of water, followed by extraction with CH_2Cl_2. The organic phase was washed with brine and then dried over anhydrous $MgSO_4$. After the solution was filtered and the solvent was evaporated under vacuum, the residue was recrystallized in anhydrous EtOH, giving white crystal product **2** (80 g, 71%).

N-Tosyl-S-fluoromethyl-S-phenylsulfilimine (2)



White solid. ^1H NMR (300 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.0 Hz, 4H), 7.70 – 7.50 (m, 3H), 7.20 (d, *J* = 8.0 Hz, 2H), 5.37 (dd, *J* = 46.2, 7.1 Hz, 1H), 5.14 (dd, *J* = 46.9, 7.0 Hz, 1H), 2.37 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -205.31 (t, *J* = 46.5 Hz). ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.15, 140.86, 133.44, 130.20, 129.35, 127.01, 126.26, 94.05 (d, *J* = 231.9 Hz), 21.41. Anal. Calcd. for $C_{14}H_{14}FNO_2S_2$: C, 54.00; H, 4.53; N, 4.50; Found: C, 53.88; H, 4.43; N, 4.39.

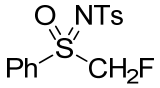
Preparation of *N*-Tosyl-*S*-fluoromethyl-*S*-phenylsulfoximine (1).



75 %

To a solution of *N*-Tosyl-*S*-fluoromethyl-*S*-phenylsulfilimine (93.3 g, 300 mmol) in 500 mL MeOH, was added NaOH/H_2O (25 g/100 mL) at rt. H_2O_2 (30%, 67 mL) was added in several portions, and the solution was kept in reflux. 2 hours later, the solution was allowed to rt and extracted with CH_2Cl_2. The organic phase was washed with brine and then dried over anhydrous $MgSO_4$. After the solution was filtered and the solvent was evaporated under vacuum, the residue was recrystallized in anhydrous EtOH/EA/PE, giving colourless white crystal product (73.5g, 75%).

*N-Tosyl-S-fluoromethyl-S-phenylsulfoximine (**1**)*

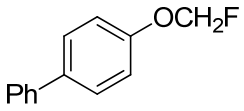


White solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.03 (d, *J* = 7.8 Hz, 2H), 7.90 (d, *J* = 8.3 Hz, 2H), 7.77 (t, *J* = 7.4 Hz, 1H), 7.64 (t, *J* = 7.7 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 5.74 (dd, *J* = 47.1, 9.1 Hz, 1H), 5.52 (dd, *J* = 47.1, 9.7 Hz, 1H), 2.41 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ –205.84 (t, *J* = 46.7 Hz). ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.42, 140.12, 135.40, 133.10, 129.81, 129.46, 129.10, 126.74, 92.79 (d, *J* = 227.6 Hz), 21.54. MS (ESI, m/z): 345.0 ($M+NH_4^+$). Anal. calcd. For $C_{14}H_{14}FNO_3S_2$: C, 51.36; H, 4.31; N, 4.28; Found: C, 51.65; H, 4.53; N, 3.88.

Typical Experimental Procedure for the Monofluoromethylation of *O*–, *S*–, *N*–, and *P*–Nucleophiles with $PhSO(NTs)CH_2F$ (1).

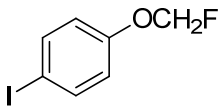
Under N_2 atmosphere, to a solution of [1,1'-biphenyl]-4-ol (51 mg, 0.3 mmol) in 1.5 mL DMSO, was added NaH (15 mg, 60% purity, 0.375 mmol) at rt. After 30 min, *N*-Tosyl-*S*-fluoromethyl-*S*-phenylsulfoximine (128 mg, 0.39 mmol), DMSO (0.5 mL) was added successively. The solution was allowed to 80 °C, and stirred for 4 h, after which the reaction was quenched by adding excess amount of saturated NH_4Cl aqueous solution, followed by extraction with ethyl ether. The organic phase was washed with brine and then dried over anhydrous $MgSO_4$. After the solution was filtered and the solvent was evaporated under vacuum, the residue was subjected to silica gel column chromatography using petroleum ether as eluent to give product **4a** (58 mg, 95%). In general, 4 h was used for the reaction of phenols and thiols, 6 h was used for the *P*-nucleophile, 8~71 h for *N*-nucleophiles and the reaction of acid were performed at 100°C for 12h.

*4-(fluoromethoxy)biphenyl(**4a**)*[3]



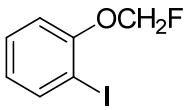
White solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.49 (d, *J* = 8.4 Hz, 4H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 2H), 5.69 (d, *J* = 54.6 Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -148.88 (t, *J* = 54.7 Hz). MS (EI, m/z): 202 (M^+, 100.0), 169 (55.5), 141(42.3), 115 (38.7).

*1-(fluoromethoxy)-4-iodobenzene (**4b**)*[4]



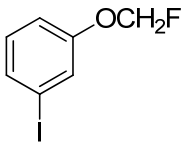
Colourless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55 (d, *J* = 7.8 Hz, 2H), 6.79 (d, *J* = 8.1 Hz, 2H), 5.61 (d, *J* = 54.4 Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -149.05 (t, *J* = 54.3 Hz). MS (EI, m/z): 252 (M^+, 100.0), 219 (35.3), 92(22.5), 64 (22.0), 63 (21.7).

*1-(fluoromethoxy)-2-iodobenzene (**4c**)*[4]



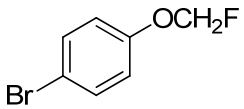
Colourless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.81 (d, *J* = 7.8 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.13 (d, *J* = 8.2 Hz, 1H), 6.87 (t, *J* = 7.6 Hz, 1H), 5.74 (d, *J* = 54.1 Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -149.20 (t, *J* = 54.2 Hz). MS (EI, m/z): 252 (M^+).

*1-(fluoromethoxy)-3-iodobenzene (**4d**)*



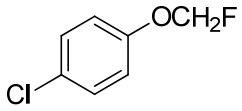
Colourless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50 – 7.41 (m, 2H), 7.11 – 7.03 (m, 2H), 5.69 (d, *J* = 54.3 Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -149.03 (t, *J* = 54.8 Hz). ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.20, 132.75, 131.05, 125.99, 116.16, 100.50 (d, *J* = 220.1 Hz), 94.16. IR: 2956, 2924, 2854, 1460, 1377, 1261, 1096, 1020, 802 cm^{-1}. MS (EI, m/z,%): 252 (M^+,100.0), 77 (35.3), 92(31.9) , 125 (27.0), 64 (25.2)，63(24.9), 95(19.4), 76(10.5). HRMS (EI) Calcd. for : C_7H_6FIO: 251.9447; Found 251.9445.

*1-bromo-4- (fluoromethoxy)benzene (**4e**)*[4]



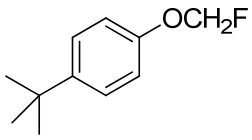
Colourless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44 (d, *J* = 8.7 Hz, 2H), 6.97 (d, *J* = 8.7 Hz, 2H), 5.68 (d, *J* = 54.4 Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -148.96 (t, *J* = 54.4 Hz). MS (EI, m/z): 204 (M^+, 29.8), 56 (100), 57 (53.7), 152 (42.7), 122 (36.5).

*1-chloro-4-(fluoromethoxy)benzene (**4f**)*[4]



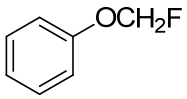
Colourless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.29 (d, *J* = 6.9 Hz, 2H), 7.02 (d, *J* = 7.0 Hz, 2H), 5.68 (d, *J* = 54.4Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -148.82 (t, *J* = 54.5 Hz).

*1-tert-butyl-4-(fluoromethoxy)benzene (**4g**)*[3]



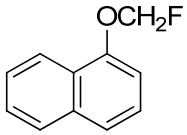
Colourless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34 (d, *J* = 8.8 Hz, 2H), 7.02 (d, *J* = 8.9 Hz, 2H), 5.70 (d, *J* = 54.9 Hz, 2H), 1.31 (s, 9H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -148.39 (t, *J* = 54.9 Hz). MS (EI, m/z, %): 182 (M^+, 17.1), 167 (100%).

*(fluoromethoxy)benzene (**4h**)*[5]



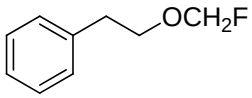
Volatile compound. ^{19}F NMR (282 MHz, DMSO): δ -151.8 (t, *J* = 55 Hz).

*1-(fluoromethoxy) naphthalene (**4i**)*[3]



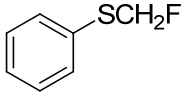
Colourless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.30 – 8.12 (m, 1H), 7.92 – 7.77 (m, 1H), 7.60 (d, *J* = 8.2 Hz, 1H), 7.54 – 7.48 (m, 2H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.18 (d, *J* = 7.7 Hz, 1H), 5.93 (d, *J* = 54.4 Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -148.68 (t, *J* = 54.5 Hz). MS (EI, m/z): 176 (M^+, 100.0), 91 (70.8).

*(2-(fluoromethoxy)ethyl)benzene(**4j**)*



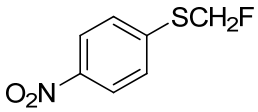
^{19}F NMR (282 MHz, DMSO): δ -150.9 (t, *J* = 55 Hz). No ^{19}F NMR of compound **4j** was reported in the literature. Based on the fact that the ^{19}F NMR signals of aryl monofluoromethyl ethers in this study are at -148 ~ -152 ppm and the coupling constants are ranging from 54-55 Hz, we assign the signal at -150.9 (t, *J* = 55 Hz) as that of compound **4j** (trace amount of **4j** was observed by ^{19}F NMR in our reaction).

*(fluoromethyl)(phenyl)sulfane(**4k**)*[3]



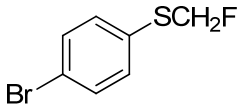
Unstable compound, which decomposes gradually during or after the silica gel column chromatography. ^{19}F NMR (282 MHz, DMSO): δ -181.8 (t, *J* = 52 Hz).

*(fluoromethyl)(4-nitrophenyl)sulfane (**4l**)*[3]



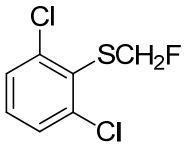
Yellow solid.[1]H NMR (300 MHz, $CDCl_3$): δ 8.20 (d, *J* = 8.8 Hz, 2H), 7.58 (d, *J* = 8.8 Hz, 2H), 5.84 (d, *J* = 52.2 Hz, 2H). [19]F NMR (282 MHz, $CDCl_3$): δ -184.70 (t, *J* = 52.2 Hz). MS (EI, m/z): 187 (M^+, 100), 157 (43.6), 108 (36.4), 69 (26.3), 45 (21.6).

*(4-bromophenyl)(fluoromethyl)sulfane(**4m**)*



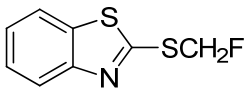
Unstable compound, which decomposes gradually during or after the silica gel column chromatography. [19]F NMR (282 MHz, DMSO) δ -186.3 (t, *J* = 52 Hz). No [19]F NMR of compound **4m** was reported in the literature. Based on the fact that the [19]F NMR signals of aryl monofluoromethyl sulfanes in this study are mostly around -184 ~ -187 ppm and the coupling constants are ranging from 50~52 Hz, we assign the signal at -186.3 (t, *J* = 52 Hz) as that of compound **4m**.

*(2,6-dichlorophenyl)(fluoromethyl)sulfane (**4n**)*[3]



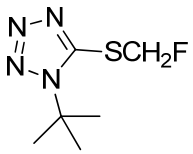
Colourless liquid. [1]H NMR (300 MHz, $CDCl_3$): δ 7.44 (d, *J* = 7.8 Hz, 2H), 7.26 (t, *J* = 7.8 Hz, 1H), 5.69 (d, *J* = 52.1 Hz, 2H). [19]F NMR (282 MHz, $CDCl_3$): δ -185.38 (t, *J* = 52.1 Hz). MS (EI, m/z): 210 (M^+, 100), 177 (89.7), 142 (77.9), 212 (67.4), 179 (57.9), 144 (29.1), 107(19.6), 69(14.5).

*2-(fluoromethylthio)benzo[d]thiazole (**4o**)*[3]



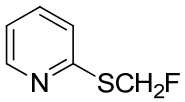
White solid. [1]H NMR (300 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 7.7 Hz, 1H), 7.47 (t, *J* = 7.2 Hz, 1H), 7.36 (t, *J* = 6.9 Hz, 1H), 6.15 (d, *J* = 51.0 Hz, 2H). [19]F NMR (282 MHz, $CDCl_3$): δ -186.46 (t, *J* = 51.0 Hz). MS (EI, *m/z*, %): 135 (M^+-SCH_2F, 100), 199 (M^+, 89.4), 108 (59.4) , 166 (58.1), 179(35.0).

*1-tert-butyl-5-(fluoromethylthio)-1H-tetrazole (**4p**)*[3]



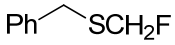
White solid. [1]H NMR (300 MHz, $CDCl_3$): δ 6.21 (d, *J* = 50.0 Hz, 2H), 1.75 (s, 9H). [19]F NMR (282 MHz, $CDCl_3$): δ -187.76 (t, *J* = 50.0 Hz). MS (EI, *m/z*, %): 190 (M^+, 9), 57 (100).

*2-(fluoromethylthio)pyridine (**4q**)*[6]



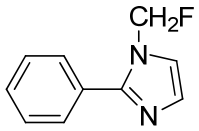
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.52 (s, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 8.3 Hz, 1H), 7.11 (s, 1H), 6.15 (d, *J* = 51.7 Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -187.32 (t, *J* = 51.6 Hz). MS (EI, *m/z*, %): 143 (M^+, 31.5), 79 (100).

*benzyl(fluoromethyl)sulfane(**4r**)*[3]



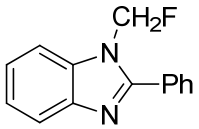
Unstable compound, which decomposes gradually during or after the silica gel column chromatography.^{19}F NMR (282 MHz, DMSO): δ -188.0 (t, *J* = 52 Hz).

*1-(fluoromethyl)-2-phenyl-1H-imidazole (**4s**)*[3]



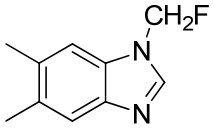
Yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.83 – 7.62 (m, 2H), 7.60 – 7.41 (m, 3H), 7.20 (s, 2H), 5.89 (d, *J* = 52.7 Hz, 2H).^{19}F NMR (282 MHz, $CDCl_3$): δ -157.08 (t, *J* = 52.7 Hz). MS (EI, *m/z*, %): 176 (M^+).

*1-(fluoromethyl)-2-phenyl-1H-benzo[d]imidazole (**4t**)*



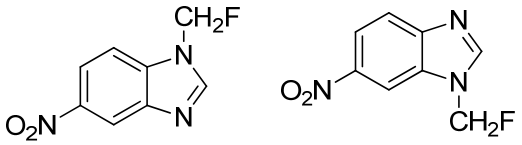
White solid. 128-129°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.88 – 7.77 (m, 3H), 7.60 – 7.48 (m, 4H), 7.43 – 7.32 (m, 2H), 6.12 (d, *J* = 53.6 Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -161.78 (t, *J* = 53.6 Hz). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.14, 143.09, 135.43, 130.57, 129.54, 129.06, 128.95, 124.06, 123.83, 120.38, 109.53, 81.74 (d, *J* = 198.6 Hz). IR: 3048, 1925, 1616, 1525, 1479, 1458, 1380, 1368, 1252, 1080, 977, 818, 780, 745, 701, 592, 430. MS (EI, *m/z*, %): 226 (M^+, 87.95), 225 (100). HRMS(EI, *m/z*): m/z calcd. For $C_{14}H_{11}FN_2$ 226.0906, found 226.0909.

*1-(fluoromethyl)-5,6-dimethyl-1H-benzo[d]imidazole (**4u**)*



White solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91 (s, 1H), 7.58 (s, 1H), 7.29 (s, 1H), 6.11 (d, *J* = 53.7 Hz, 2H), 2.41 (s, 3H), 2.38 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -163.07 (t, *J* = 53.7 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.66, 142.38, 133.58, 132.45, 131.67, 120.77, 109.69, 81.76 (d, *J* = 200.6 Hz), 20.52, 20.22. MS (EI, *m/z*, %): 178 (M^+, 100), 163 (69.4), 177(58.5).

1-(fluoromethyl)-5-nitro-1H-benzo[d]imidazole (***4va***)[3]
1-(fluoromethyl)-6-nitro-1H-benzo[d]imidazole (***4vb***)[3]



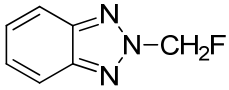
mixture

Yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.76 (s, 1H), 8.52 (s, 1H), 8.32 – 8.29 (m, 3H), 8.23 (s, 1H), 7.94 (d, *J* = 8.9 Hz, 1H), 7.64 (d, *J* = 8.9 Hz, 1H), 6.26 (d, *J* = 52.5 Hz, 2H), 6.24 (d, *J* = 52.8 Hz, 2H). ^{19}F NMR (282 MHz, CDCl3): δ -164.78 (t, *J* = 52.5 Hz), -165.23 (t, *J* = 52.5 Hz). MS (EI, *m/z*, %): 195 (M^+, 100.00), 165(33.28).

1-(fluoromethyl)-1H-benzo[d][1,2,3]triazole (**4wa**)

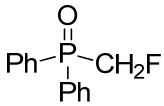
White solid. Mp: 106-107 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.13 (d, *J* = 8.4 Hz, 1H), 7.71-7.56 (m, 2H), 7.47 (t, *J* = 7.5 Hz, 1H), 6.60 (d, *J* = 52.5 Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -167.84 (t, *J* = 52.5 Hz). ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.31, 132.72, 128.83, 124.88, 120.33, 109.02, 83.36 (d, *J* = 204.2 Hz). IR (film): 3026, 2922, 1617, 1455, 1278, 1171, 989, 766, 616, 427 cm^{-1}. MS (EI, *m/z*, %): 151(M^+, 100), 122(77.4). HRMS (EI, *m/z*): calcd. For $C_7H_6FN_3$ (M^+) 151.0546, Found 151.0544.

2-(fluoromethyl)-2H-benzo[d][1,2,3]triazole (**4wa**)



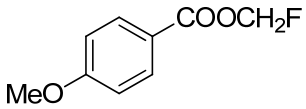
White solid. Mp: 40-41°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.44 (dd, *J* = 6.7, 3.0 Hz, 2H), 6.54 (d, *J* = 50.4 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -168.74 (t, *J* = 50.4 Hz). ^{13}C NMR (101 MHz, $CDCl_3$): δ 145.46, 127.98, 118.80, 90.31 (d, *J* = 208.7 Hz). IR (film): 3048, 2994, 1560, 1455, 1339, 1273, 1019, 858, 750 cm^{-1}. MS (EI, *m/z*, %): 151 (M^+, 100). HRMS (EI, *m/z*): calcd. For $C_7H_6FN_3$ (M^+) 151.0546, Found 151.0543.

(fluoromethyl)diphenylphosphine oxide (***6***)[7]



White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 – 7.78 (m, 4H), 7.61 – 7.57 (m, 2H), 7.53 – 7.49 (m, 4H), 5.16 (dd, *J* = 47.1, 3.4 Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -241.81 (q, 47.4 Hz). MS (ESI, *m/z*, %): 235($M+H^+$).

fluoromethyl 4-methoxybenzoate (***8***)[8]

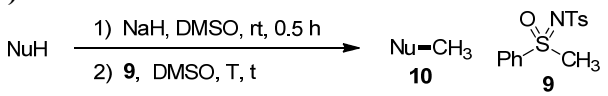


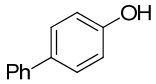
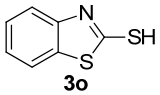
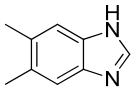
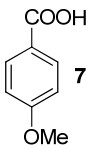
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 5.93 (d, *J* = 51.0 Hz, 2H), 3.88 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -156.99 (t, *J* = 51.0 Hz). MS (EI, *m/z*, %): 135 (100.00), 184(M^+, 36.70).

Typical Experimental Procedure for the Methylation of *O*–, *S*–, *N*–, *P*–Nucleophiles with PhSO(NTs)CH_3 (9)

Under N_2 atmosphere, to a solution of [1,1'-biphenyl]-4-ol (85 mg, 0.5 mmol) in 2.5 mL DMSO, was added NaH (25 mg, 60% purity, 0.625 mmol) slowly at rt. After 30 min, *N*-Tosyl-*S*-methyl-*S*-phenylsulfoximine (201 mg, 0.65 mmol), DMSO (0.5 mL) was added successively. The solution was allowed to 80 °C, and stirred for 4 h, after which the reaction was quenched by adding excess amount of saturated NH_4Cl aqueous solution, followed by extraction with ethyl ether. The organic phase was washed with brine and then dried over anhydrous $MgSO_4$. After the solution was filtered and the solvent was evaporated under vacuum, the residue was subjected to silica gel column chromatography using petroleum ether as eluent to give product (3 mg, 3%). When the reaction was performed at 120 °C for 6 h, 75% yield was given.

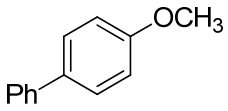
Table S-1. Direct Methylation of Some *O*–, *S*–, *N*–, *P*–Nucleophiles with PhSO(NTs)CH_3 (9)



Entry	NuH	T (°C)	t (h)	Product	Yield (%)[a]
1	 **3a**	80	4	**10a**	3
2		120	6	**10a**	75
3	 **3o**	80	4	**10b**	10
4		120	6	**10b**	73
5	 **3u**	80	8.5	**10c**	8[b]
6		120	6	**10c**	79[b]
7	Ph_2PH **5**	80	6	**10d**	28[c]
8	 **7**	100	12	**10e**	12
9		120	6	**10e**	69

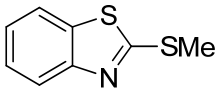
[a] Isolated yield. [b] Mixtures of **10c** and remained **3u** was obtained, and the yield of **10c** was calculated based on the ratio of **10c/3u**. [c] H_2O_2 (30%, 0.1mL) was added to quench the reaction, and the yield refers to the isolated yield of Ph_2POCH_3.

*4-methoxy-1,1'-biphenyl (**10a**)*[9]



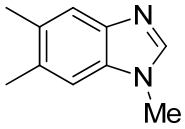
White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (t, *J* = 8.2 Hz, 4H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 6.9 Hz, 1H), 6.98 (d, *J* = 8.3 Hz, 2H), 3.85 (s, 3H). MS (EI, *m/z*, %): 184 (M^+, 100.00).

*2-(methylthio)benzo[d]thiazole(**10b**)*[10]



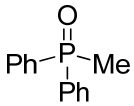
Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 1H), 7.28(d, *J* = 7.9 Hz, 1H), 2.79 (s, 3H). MS (EI, *m/z*, %): 181(M^+, 100.00).

*1,5,6-trimethyl-1H-benzo[d]imidazole(**10c**)*



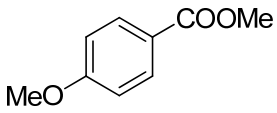
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (s, 1H), 7.55 (s, 1H), 7.15 (s, 1H), 3.79 (s, 3H), 2.40 (s, 3H), 2.37 (s, 3H). MS (EI, *m/z*, %): 160(M^+, 100.00).

*methyldiphenylphosphine oxide(**10d**)* [11]



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 – 7.61 (m, 4H), 7.56 – 7.37 (m, 6H), 2.00 (d, *J* = 13.2 Hz, 3H). MS (EI, *m/z*, %): 216(M^+, 36.32), 215(M-H^+, 100.00).

*methyl 4-methoxybenzoate(**10e**)*[12]

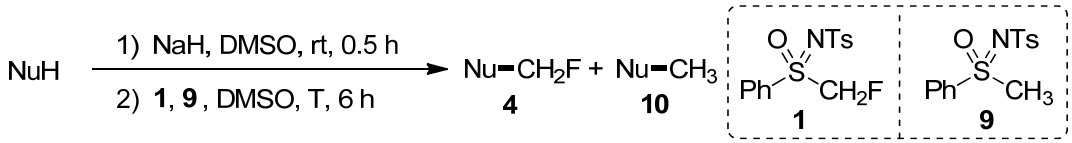


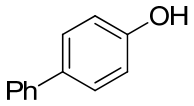
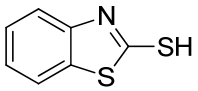
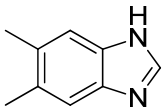
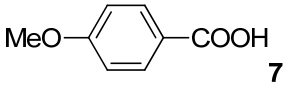
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.9 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 3.88 (s, 3H), 3.85 (s, 3H). MS (EI, *m/z*, %): 166(M^+, 34.13), 135(M-OMe^+, 100.00).

Competitive Reactions of $PhSO(NTS)CH_2F$ (1) and $PhSO(NTS)CH_3$ (9) with Phenol 3a, Thiol 3o, Imidazole 3u, Diphenylphosphine 5, and Acid 7.

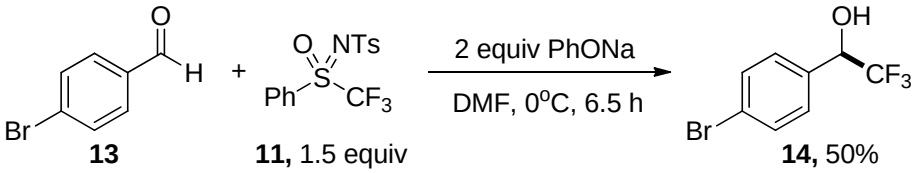
Typical Experimental Procedure: Under N_2 atmosphere, to a solution of 5,6-dimethyl-1H-benzo[*d*]imidazole (**3u**) (73 mg, 0.5 mmol) in 3 mL DMSO, was added NaH (25 mg, 60% purity, 0.625 mmol) at rt. After 30 min, compound **1** (213 mg, 0.65 mmol) and compound **9** (201 mg, 0.65 mmol) was added successively. The solution was allowed to 120 °C, and stirred for 4 h, after which the reaction was quenched by adding excess amount of saturated NH_4Cl aqueous solution, followed by extraction with ethyl ether. The organic phase was washed with brine and then dried over anhydrous $MgSO_4$. After the solution was filtered and the solvent was evaporated under vacuum, the residue was solved in CH_2Cl_2, $PhCF_3$ (25 mg) was added as standard to determine the yield of product **4u**. And then, the CH_2Cl_2 was evaporated under vacuum, the residue was solved in $CDCl_3$. The total yield and the ratio of monofluoromethylation product to methylation product was determined according to the analysis of the characteristic peak (N-CH_2F and N-Me). In all cases, monofluoromethylation product was given as the major product while methylation product was afforded as the minor product. The results reveal that α-fluorinated sulfoximine **1** has higher reactivity than the non-fluorinated sulfoximine **9** under the current conditions.

Table S-2 Competitive Reactions of $PhSO(NTS)CH_2F$ (1) and $PhSO(NTS)CH_3$ (9) with Phenol 3a, Thiol 3o, Imidazole 3u, Diphenylphosphine 5, and Acid 7.



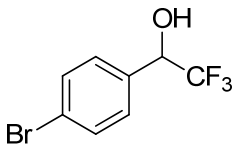
Entry	NuH		T (°C)	Yield (4+10)	4/10
1		**3a**	120	89	145/1
2		**3o**	120	99	90/10
3		**3u**	120	92	97/3
4	Ph_2PH	**5**	80	98	89/11
5		**7**	120	95	100/1

Nucleophilic Trifluoromethylation of 4-Bromobenzaldehyde (13) with PhSO(NTs)CF_3 (11).



Under N_2 atmosphere, to a solution of 4-bromobenzaldehyde (56 mg, 0.3 mmol) and PhSO(NTs)CF_3 (164 mg, 0.45 mmol) in DMF (3 mL), was added PhONa (70 mg, 0.6 mmol) in DMF (1.5 mL) slowly at 0°C in 3 min. After 6.5 h, the reaction was quenched by adding excess amount of water, followed by extraction with ethyl ether. The organic phase was washed with water, brine and then dried over anhydrous $MgSO_4$. After the solution was filtered and the solvent was evaporated under vacuum, the residue was subjected to silica gel column chromatography using petroleum ether as eluent to give product **14** (38 mg, 50%).

1-(4-bromophenyl)-2,2,2-trifluoroethanol (***14***)[13]

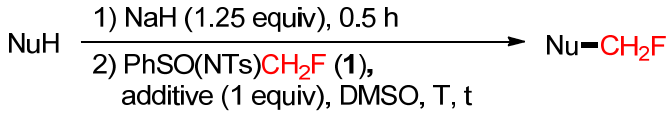


Colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 5.28 – 4.65 (m, 1H), 2.61 (d, *J* = 3.5 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -78.39 (d, *J* = 6.5 Hz). MS (EI, *m/z*, %): 77 (100.00), 254(M^+, 0.96), 256(0.96).

Radical Inhibition Experiments with NuH as Substates

*Experimental procedure for the reaction of [1,1'-biphenyl]-4-ol (**3a**) and PhSO(NTs)CH_2F (**1**) with 1,4-dinitrobenzene as the radical inhibitor:*

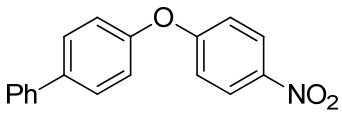
Under N_2 atmosphere, NaH (60% purity, 25 mg, 0.625 mmol) was added to the solution of [1,1'-biphenyl]-4-ol (85 mg, 0.5 mmol) in DMSO (2 mL). 0.5 h later, sulfoximine **1** (213 mg, 0.65 mmol) and1,4-dinitrobenzene (89 mg, 0.5 mmol) was added simultaneously followed by adding DMSO (1 mL). After stirring for 4 h at 80℃, the reaction mixture was detected by ^{19}F NMR by using $PhCF_3$ as the internal standard. The results are shown in the table below. The reaction was quenched by adding excess amount of water, followed by extraction with ethyl ether. The organic phase was washed with water, brine and then dried over anhydrous $MgSO_4$. After the solution was filtered and the solvent was evaporated under vacuum, the residue was subjected to silica gel column chromatography using PE/EA (v/v=100/1) as eluent to give 4-(4-nitrophenoxy)-1,1'-biphenyl (114 mg, 78%).



entry	NuH	additive	T (°C)	t (h)	yield (%)	unreacted **1** (%)[e]
1	**3a**	nitrobenzene	80	4	72	47
2[b]	**3a**	1,4-dinitrobenzene	80	4	0	120
3[c]	**3a**	benzoquinone	80	4	5	110
4	**3a**	benzoquinone	80	8	35	94
5	**3o**	benzoquinone	80	4	7	120
6	**3u**	benzoquinone	80	8.5	0	71
7	**5**	benzoquinone	80	6	20	60
8	**7**	benzoquinone	100	12	52	54
9[d]	**3a**	benzoquinone	120	6	25	ND

[a] Yield was determined by ^{19}F NMR. [b] 4-(4-nitrophenoxy)-1,1'-biphenyl was isolated in 78% yield. [c] **3a** was recovered in 87% yield. [d] **9** was used instead of **1**, the yield of methylation product refers to the isolated yield, and the yield of remained **9** was not determined (ND). [e] 130% of **1** (based on the amount of NuH) was added as starting material.

4-(4-nitrophenoxy)-1,1'-biphenyl[14]

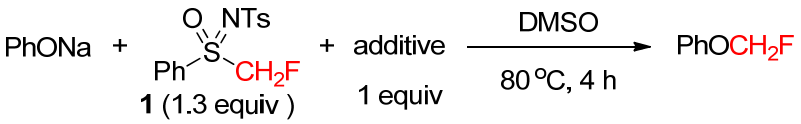


^1H NMR (400 MHz,$CDCl_3$): δ 8.21 (d, *J* = 9.1 Hz, 2H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.58 (d, *J* = 7.7 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 9.1 Hz, 2H). MS (EI, *m/z*, %): 291(M^+, 100).

Radical Inhibition Experiments with Sodium Phenolate as the Substate

Under N_2 atmosphere, compound **1** (127 mg, 0.39 mmol), and additive (0.3 mmol) was added to the sodium phenolate (35 mg, 0.3 mmol) in DMSO (3 ml). After stirring for 4 h at 80℃, the reaction mixture was detected by ^{19}F NMR. The results are shown in the table below. When no additive was added, $PhOCH_2F$ was obtaiend in 95% yield. When nitrobenzene was added as a radical scavenger, the yield decreased to 68%, and when benzoquinone was added, a yield of 16% was given, when 1,4-dinitrobenzene was added, no monofluoromethylation product was afforded.

Table S-3. Radical Inhibition Experiments with Sodium Phenolate as the Substate

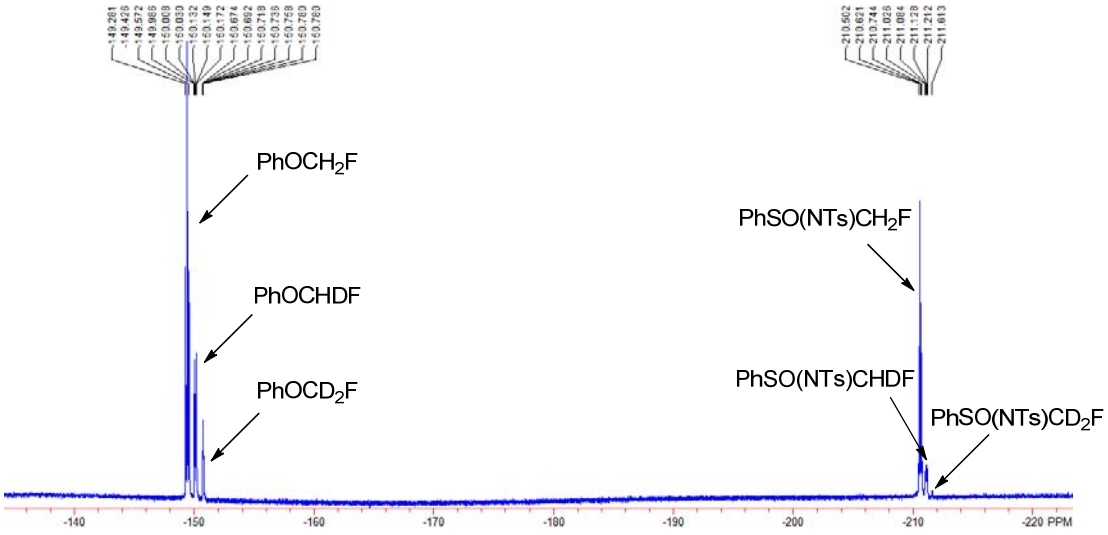


entry	additive	yield (%)[a]	recoverd **1** (%)
1	null	95	31
2	nitrobenzene	68	55
3	benzoquinone	16	114
4	1,4-dinitrobenzene	0	128

[a] Yield was determined by ^{19}F NMR by using $PhCF_3$ as standard

Monofluoromethylation of Sodium Phenolate With Reagent 1 By Added 10 Equivalents of D_2O:

Under N_2 atmosphere, compound **1** (127 mg, 0.39 mmol), and D_2O (54 μl, 3 mmol) was added to the sodium phenolate (35 mg, 0.3 mmol) in DMSO (3 ml). After stirring for 4 h at 80℃, the reaction mixture was detected by ^{19}F NMR: $PhOCH_2F$: -149.4 (t, J = 52.4 Hz), 45% yield; PhOCHDF: -150.1 (dt, J = 54.0, 8.0 Hz), 30% yield; PhOCHDF: -150.7 (heptet, 8.2 Hz), 10% yield; $PhSO(NTs)CH_2F$: -210.6 (t, J = 45.1 Hz), 32% yield; PhSO(NTs)CHDF -211.0 ~ -211.3 (m), a mixture of two diastereoisomers, 11% yield; $PhSO(NTs)CD_2F$: -211.5 ~ -211.7 (m), 1% yield. Although excess D_2O was added, non-deuterated product $PhOCH_2F$ was given as the major product, indicating that monofluorocarbene mechanism is not likely to be the major pathway for the current monofluoromethylation reaction.



References

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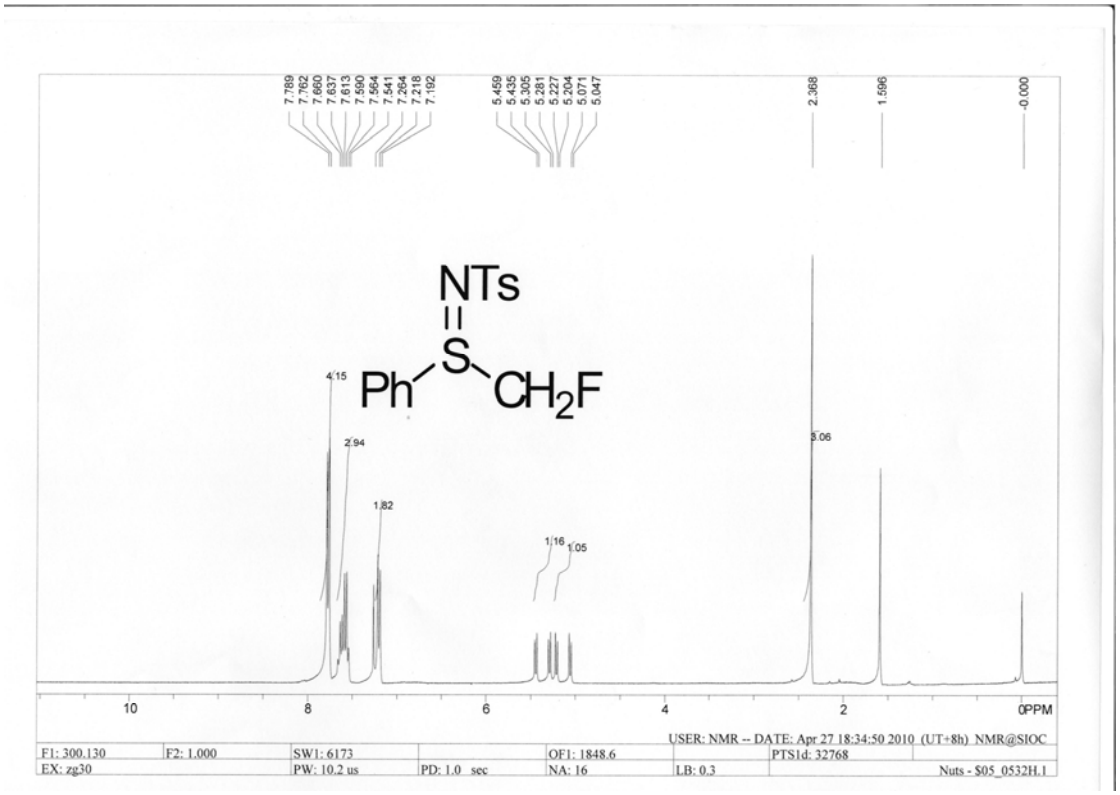
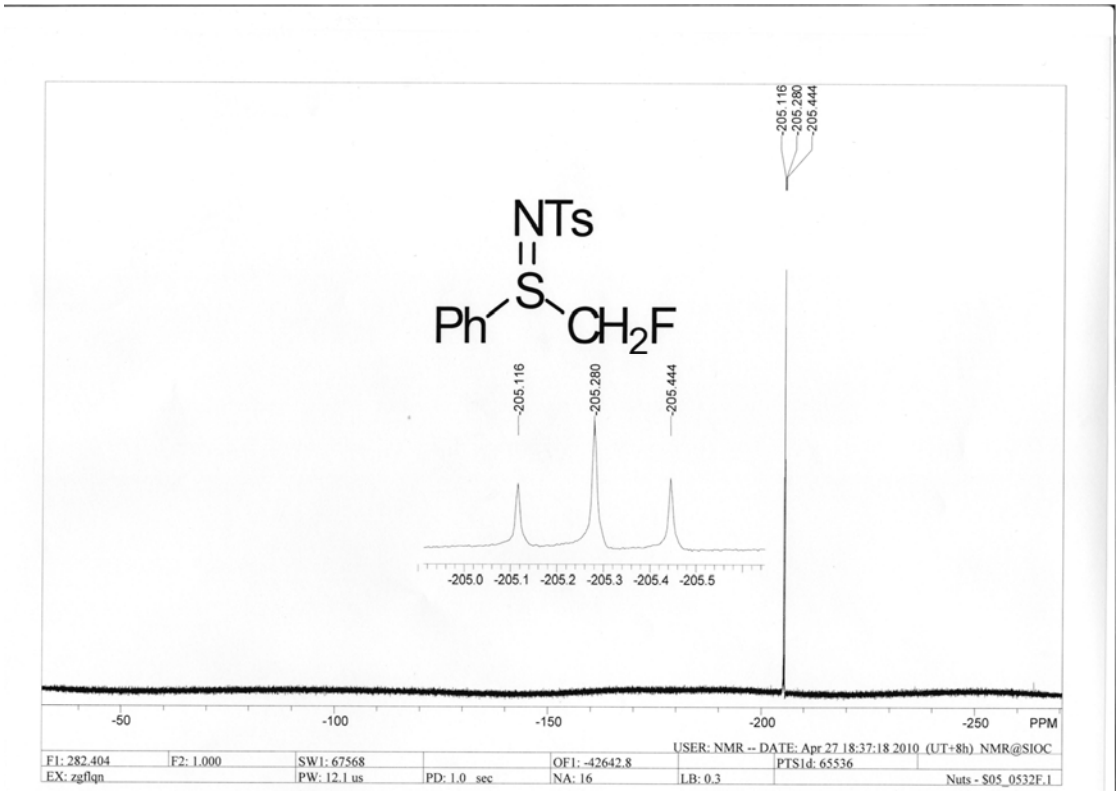
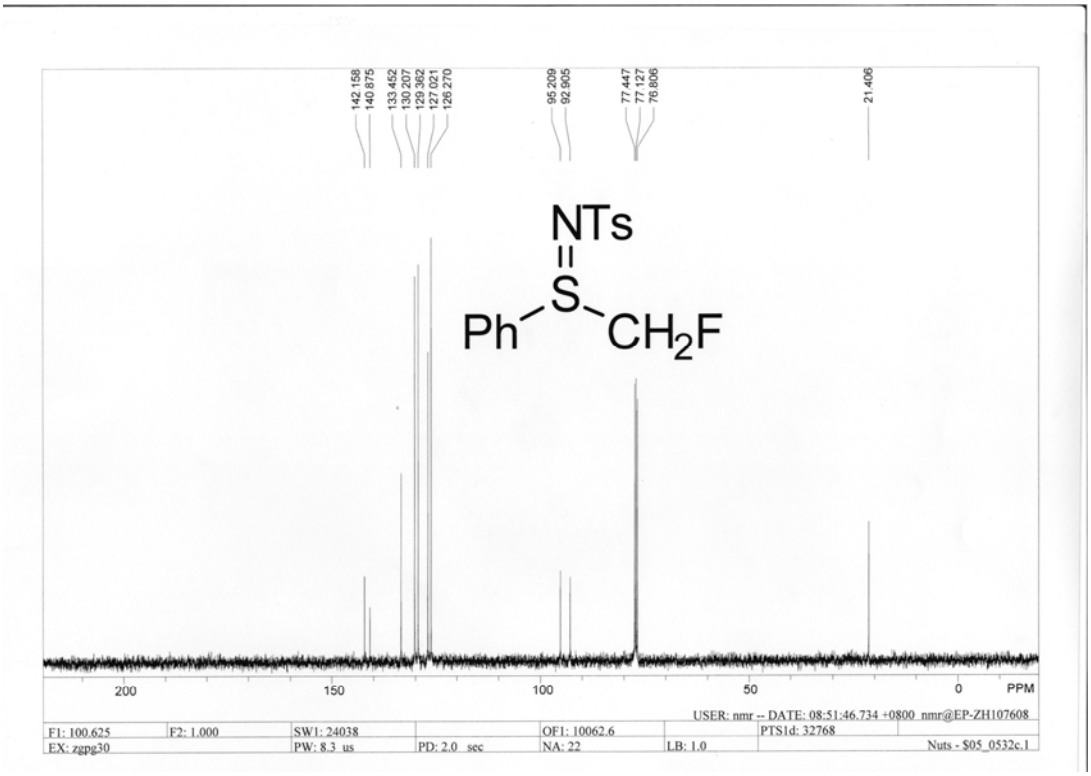
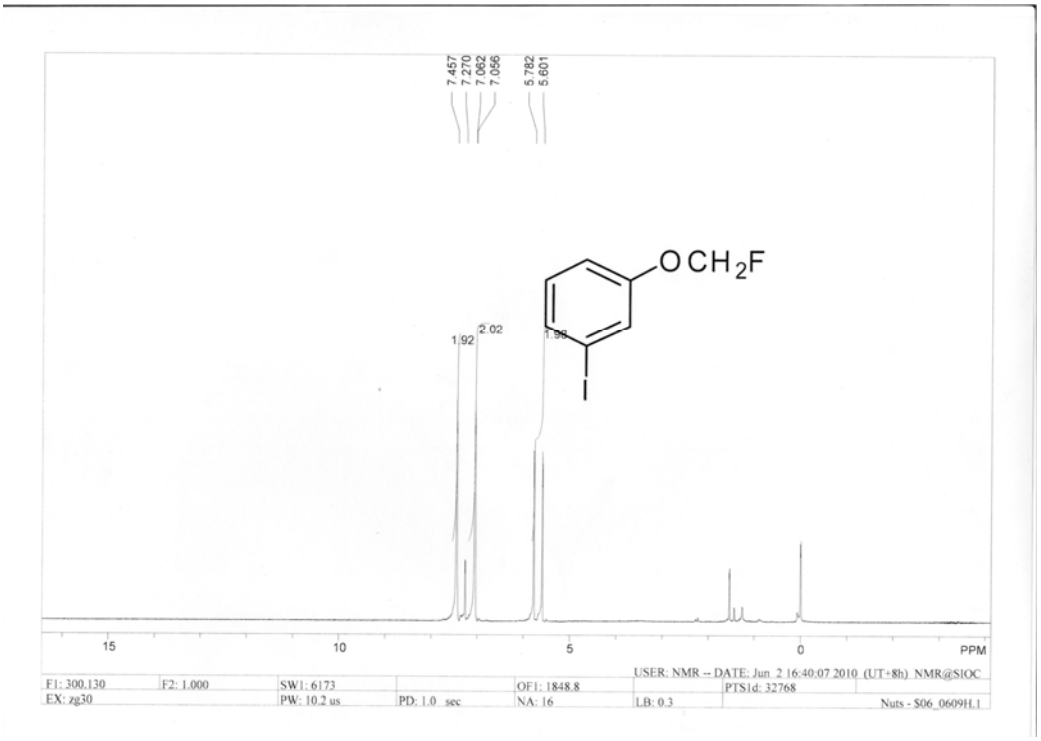
NMR Spectra of New Compounds






142.158
140.875
133.452
130.207
129.382
127.021
126.270
95.209
92.905
77.447
77.127
76.806
21.406
NTs
S
Ph
CH2F
200
150
100
50
0
PPM
USER: nmr -- DATE: 08:51:46.734 +0800 nmr@EP-ZH107608
F1: 100.625
F2: 1.000
SW1: 24038
OF1: 10062.6
PTS1d: 32768
EX: zgpg30
PW: 8.3 us
PD: 2.0 sec
NA: 22
LB: 1.0
Nuts - S05_0532c.1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7.270
7.062
7.056
5.782
5.601
OCH2F
1.92
2.02
1.98
I
15
10
5
0
PPM
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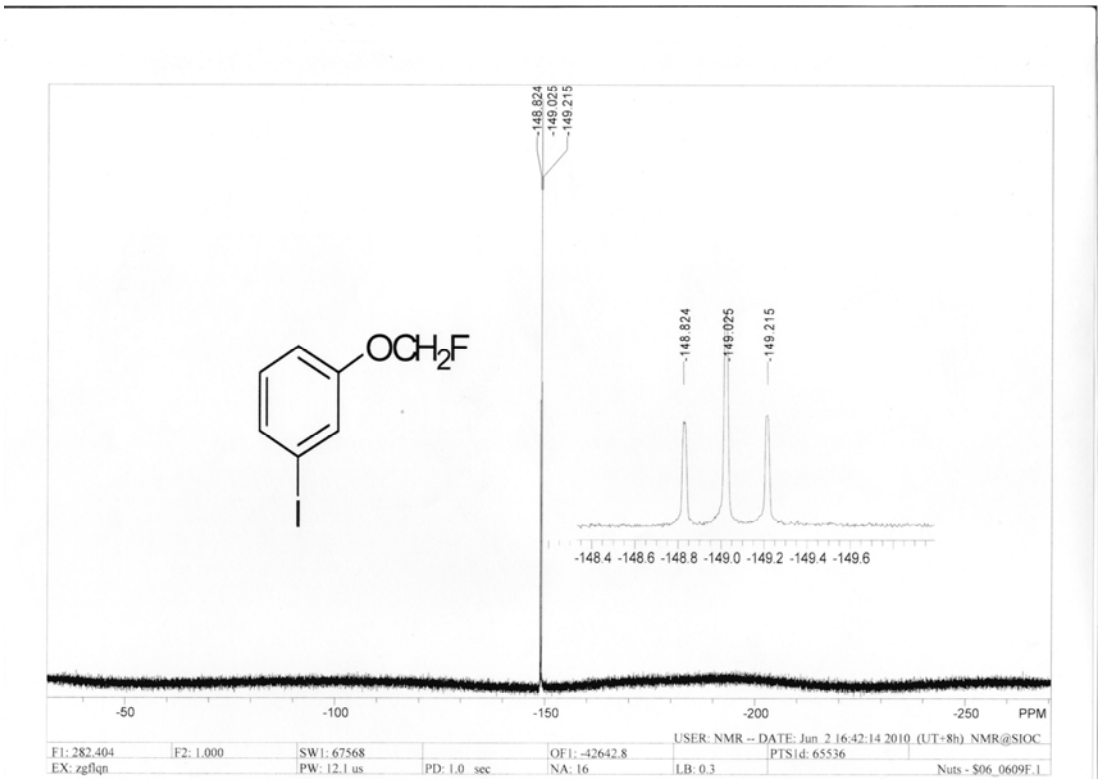
F1: 300.130
F2: 1.000
SW1: 6173
OF1: 1848.8
PTS1d: 32768
EX: zg30
PW: 10.2 us
PD: 1.0 sec
NA: 16
LB: 0.3
Nuts - S06_0609H.1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-149.215
OCH2F
-148.824
-149.025
-149.215
-148.4 -148.6 -148.8 -149.0 -149.2 -149.4 -149.6
-50
-100
-150
-200
-250
PPM
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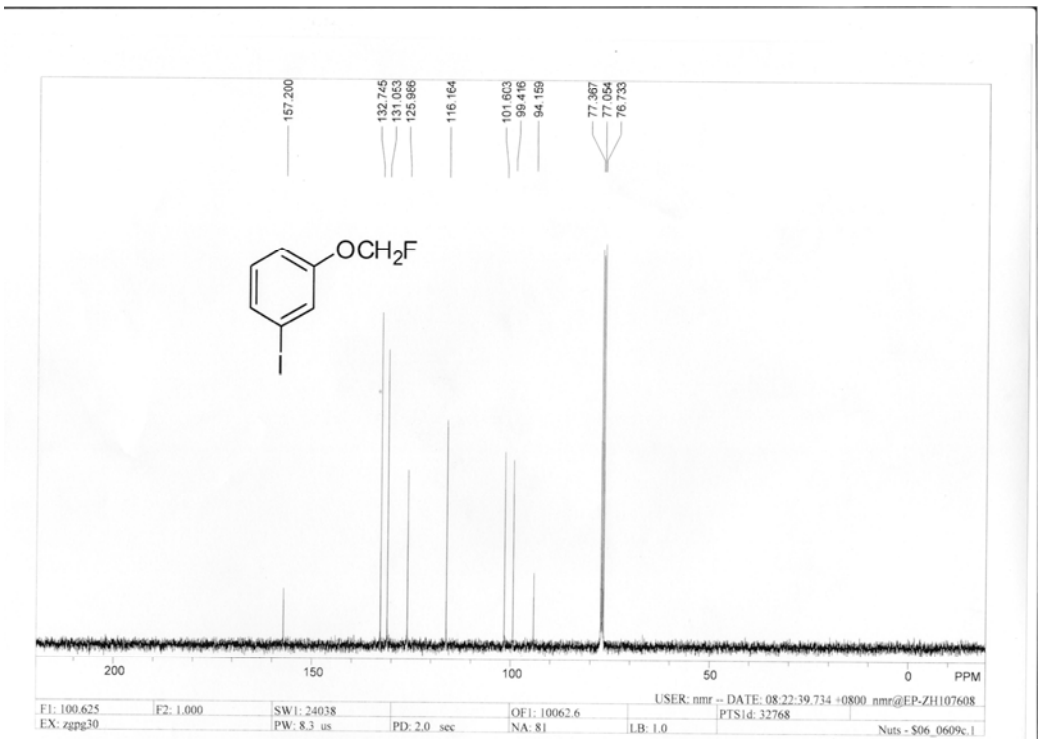
SW1: 67568
OF1: -42642.8
PTS1d: 65536
EX: zgflqn
PW: 12.1 us
PD: 1.0 sec
NA: 16
LB: 0.3
Nuts - $06_0609F.1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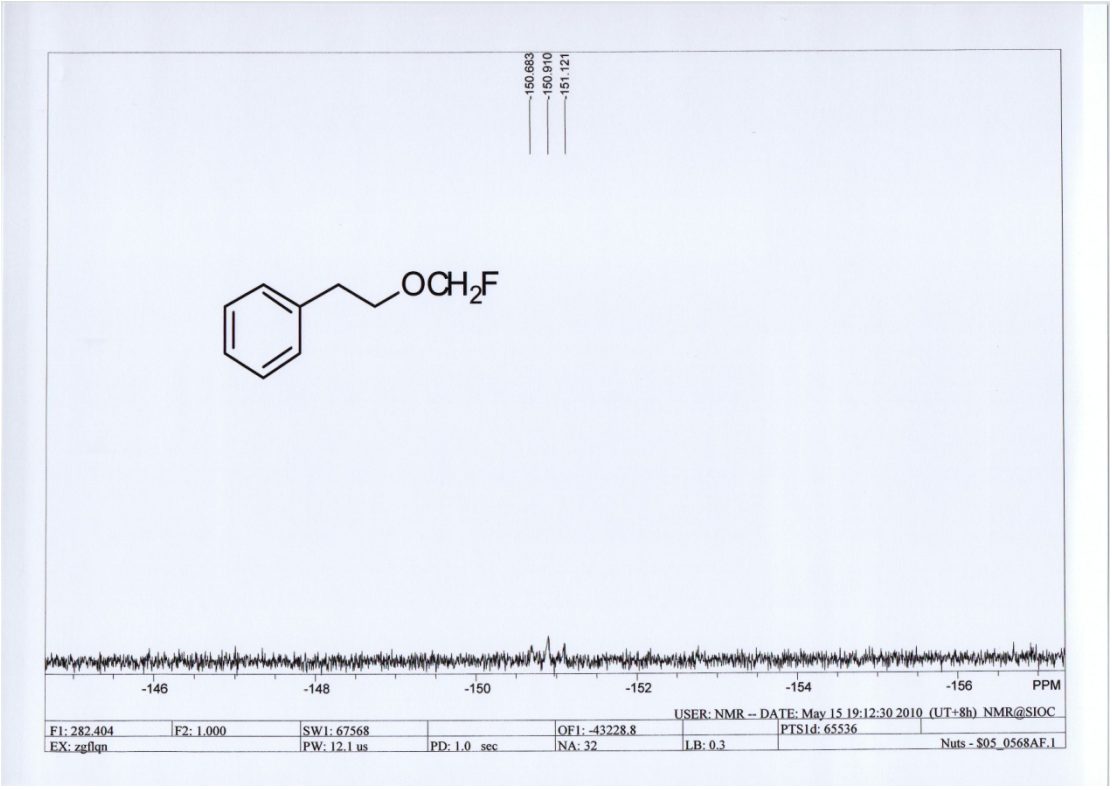
131.053
125.986
116.164
101.603
99.416
94.159
77.387
77.054
76.733
OCH2F
200
150
100
50
0
PPM
USER: nmr -- DATE: 08:22:39.734 +0800 nmr@EP-ZH107608
F1: 100.625
F2: 1.000
SW1: 24038
OF1: 10062.6
PTS1d: 32768
EX: zgpg30
PW: 8.3 us
PD: 2.0 sec
NA: 81
LB: 1.0
Nuts - $06_0609c.1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-151.121
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-148
-150
-152
-154
-156
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PTS1d: 65536
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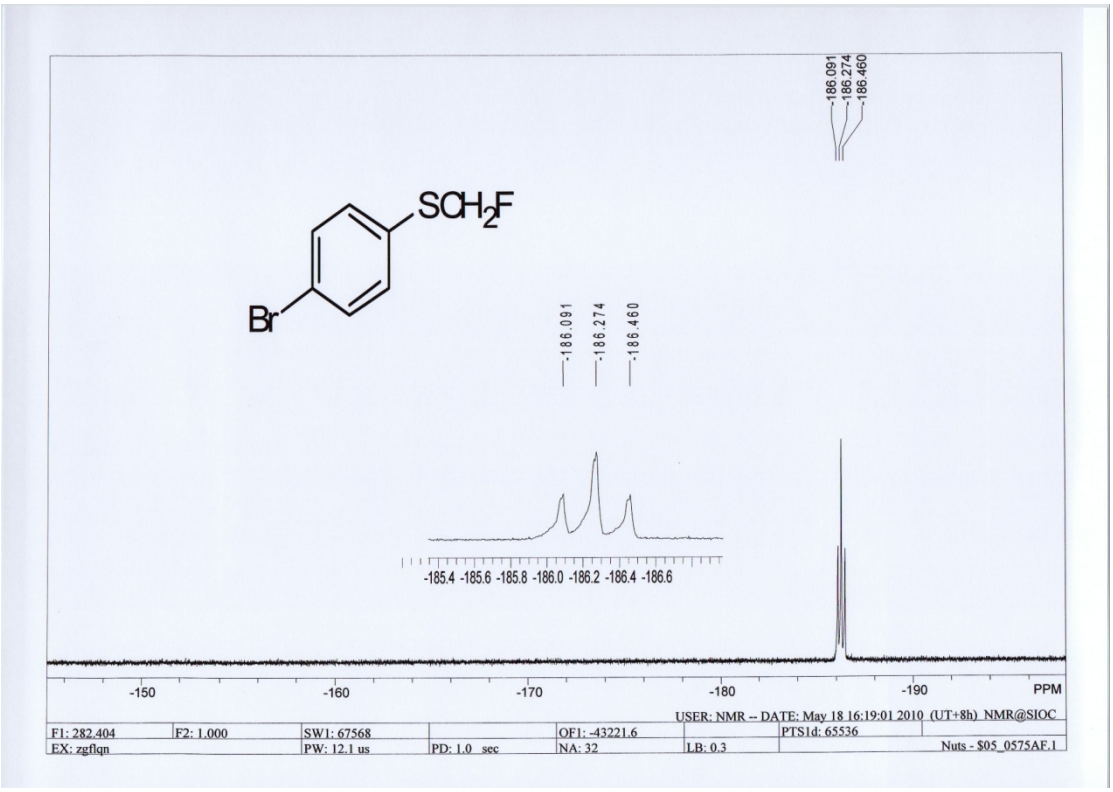
NA: 32
LB: 0.3
Nuts - $05_0568AF.1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-186.274
-186.460
SCH2F
Br
-186.091
-186.274
-186.460
-185.4 -185.6 -185.8 -186.0 -186.2 -186.4 -186.6
-150
-160
-170
-180
-190
PPM
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OF1: -43221.6
PTS1d: 65536
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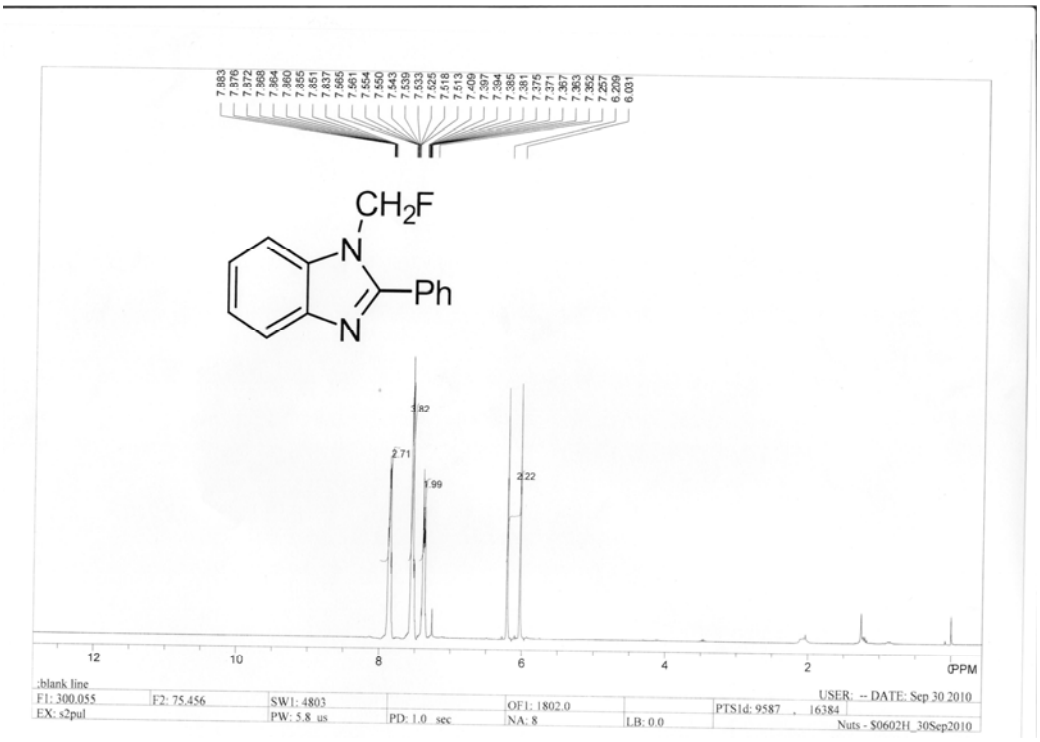
PD: 1.0 sec
NA: 32
LB: 0.3
Nuts - $05_0575AF.1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7.876
7.872
7.868
7.864
7.860
7.855
7.851
7.837
7.665
7.661
7.654
7.650
7.645
7.539
7.533
7.525
7.518
7.513
7.409
7.397
7.394
7.385
7.381
7.375
7.371
7.367
7.363
7.352
7.257
6.209
6.031
CH2F
N
Ph
N
3.82
2.71
1.99
2.22
12
10
8
6
4
2
PPM
:blank line
F1: 300.055
F2: 75.456
SW1: 4803
PW: 5.8 us
PD: 1.0 sec
OF1: 1802.0
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LB: 0.0
PTS1d: 9587 , 16384
USER: -- DATE: Sep 30 2010
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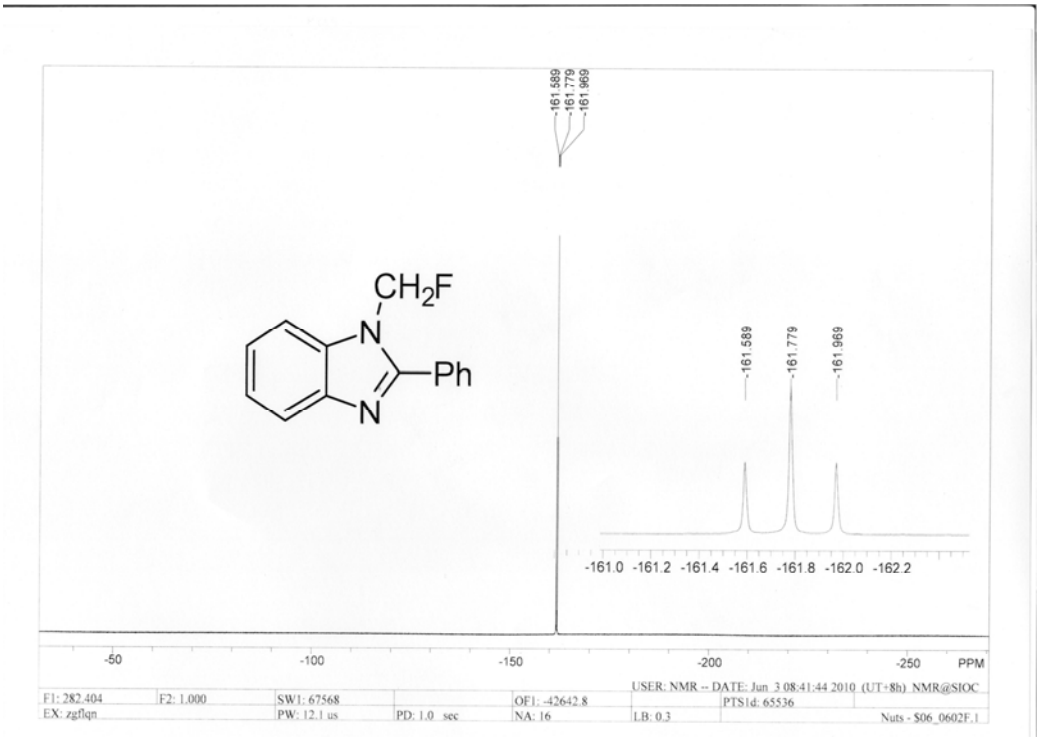
Nuts - S0602H_30Sep2010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-161.779
-161.969
CH2F
N
Ph
N
-161.589
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-161.969
-161.0 -161.2 -161.4 -161.6 -161.8 -162.0 -162.2
-50
-100
-150
-200
-250
PPM
F1: 282.404
F2: 1.000
SW1: 67568
PW: 12.1 us
PD: 1.0 sec
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NA: 16
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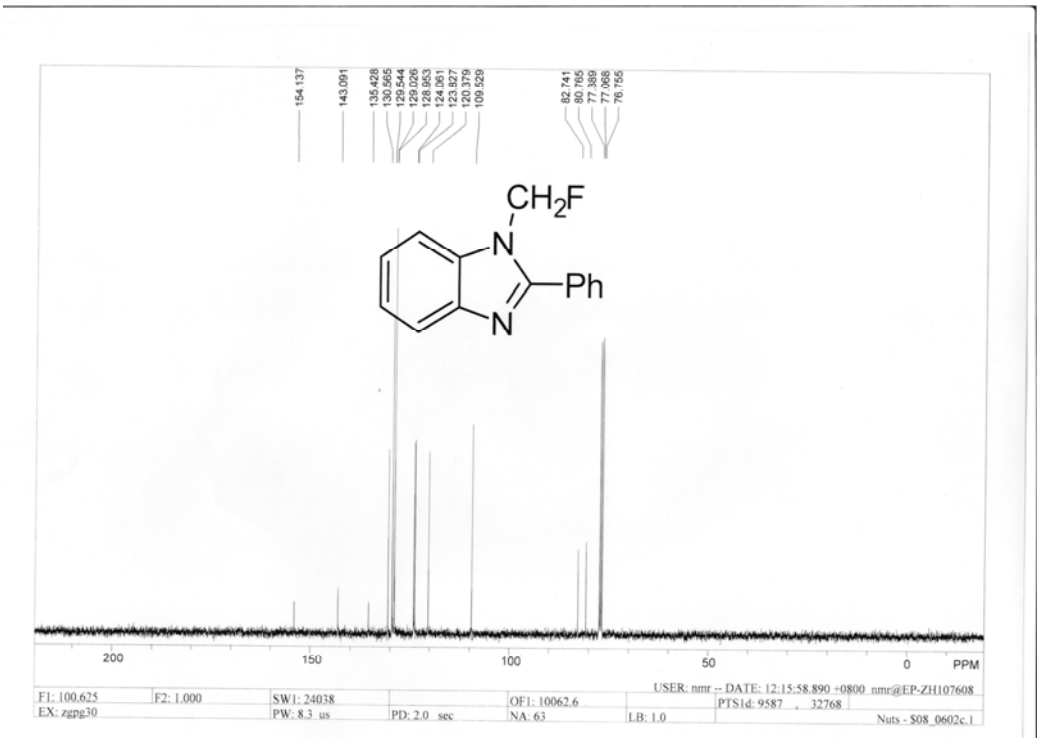
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135.428
130.565
129.544
129.026
128.863
124.061
123.827
120.379
109.329
82.741
80.765
77.389
77.068
76.156
CH2F
N
Ph
N
200
150
100
50
0
PPM
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F1: 100.625
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SW1: 24038
OF1: 10062.6
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EX: zgpg30
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PD: 2.0 sec
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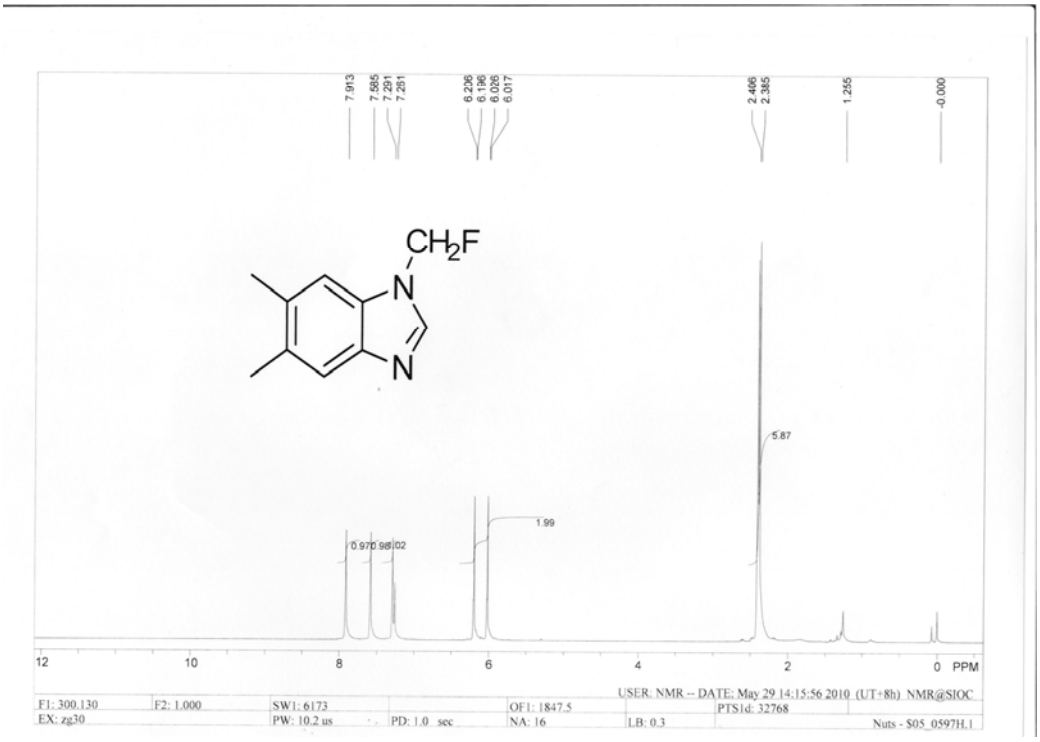
LB: 1.0
Nuts - S08_0602c.1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7.585
7.291
7.281
6.206
6.196
6.026
6.017
2.406
2.385
1.255
-0.000
CH2F
N
N
5.87
1.99
0.97 0.98 2.02
12
10
8
6
4
2
0
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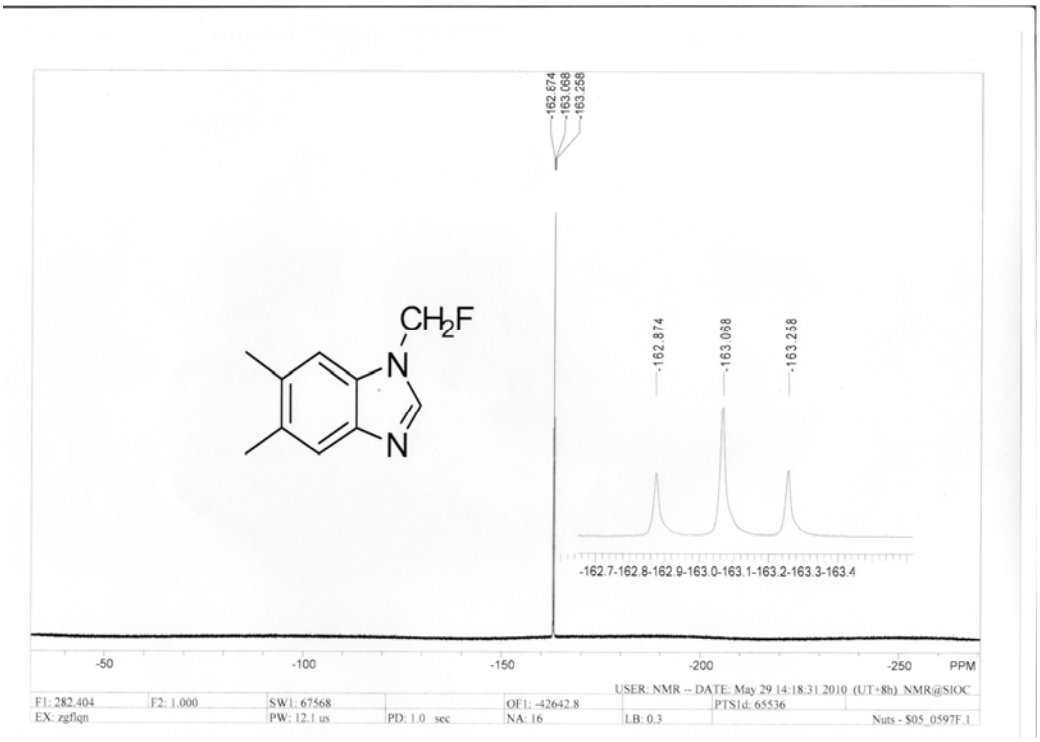
SW1: 6173
OF1: 1847.5
PTS1d: 32768
EX: zg30
PW: 10.2 us
PD: 1.0 sec
NA: 16
LB: 0.3
Nuts - S05_0597H.1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-163.258
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N
N
-162.874
-163.068
-163.258
-162.7-162.8-162.9-163.0-163.1-163.2-163.3-163.4
-50
-100
-150
-200
-250
PPM
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F1: 282.404
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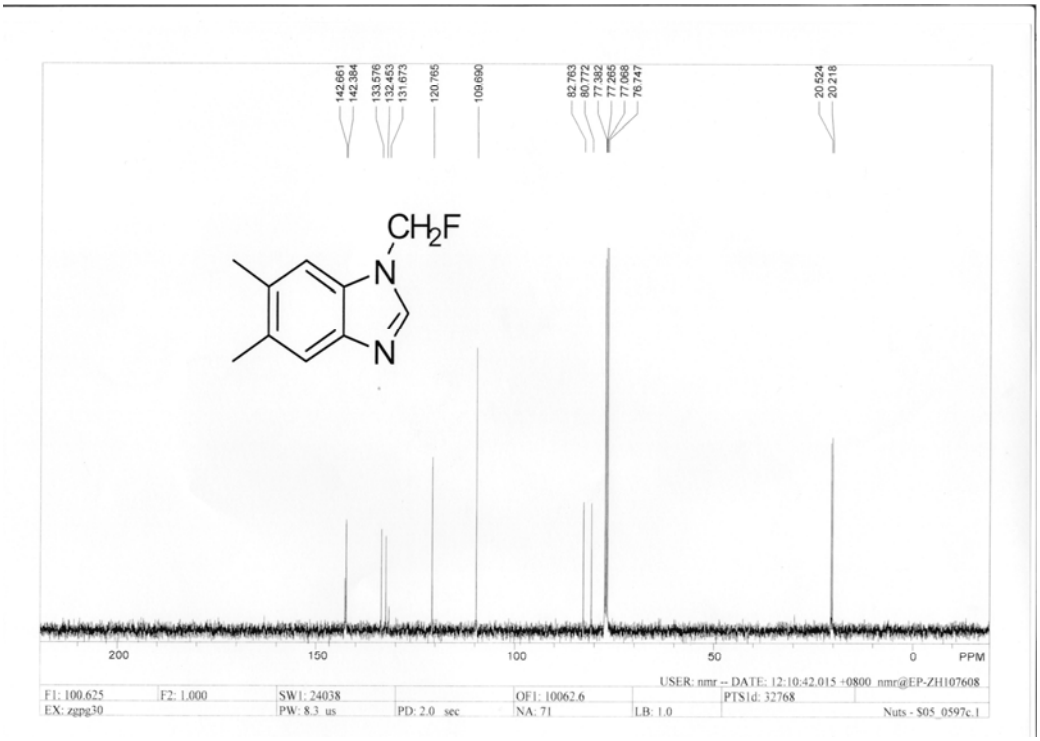
SW1: 67568
OF1: -42642.8
PTS1d: 65536
EX: zgflqn
PW: 12.1 us
PD: 1.0 sec
NA: 16
LB: 0.3
Nuts - S05_0597F.1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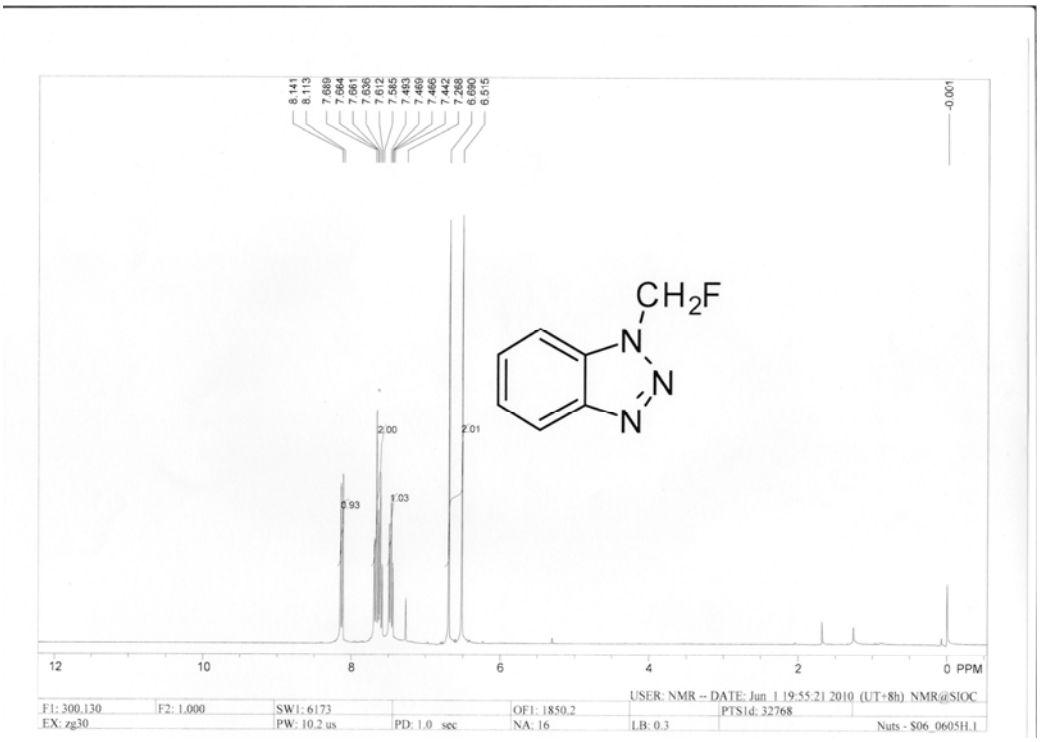
133.576
132.453
131.673
120.765
109.690
82.763
80.772
77.382
77.265
77.068
76.747
20.524
20.218
CH2F
N
N
200
150
100
50
0
PPM
USER: nmr -- DATE: 12:10:42.015 +0800 nmr@EP-ZH107608
F1: 100.625
F2: 1.000
SW1: 24038
OF1: 10062.6
PTS1d: 32768
EX: zgpg30
PW: 8.3 us
PD: 2.0 sec
NA: 71
LB: 1.0
Nuts - S05_0597c.1


8.141
8.113
7.669
7.664
7.661
7.636
7.612
7.545
7.465
7.469
7.466
7.442
7.268
6.690
6.515
-0.001
CH2F
N
N
N
2.00
2.01
1.03
0.93
12
10
8
6
4
2
0 PPM
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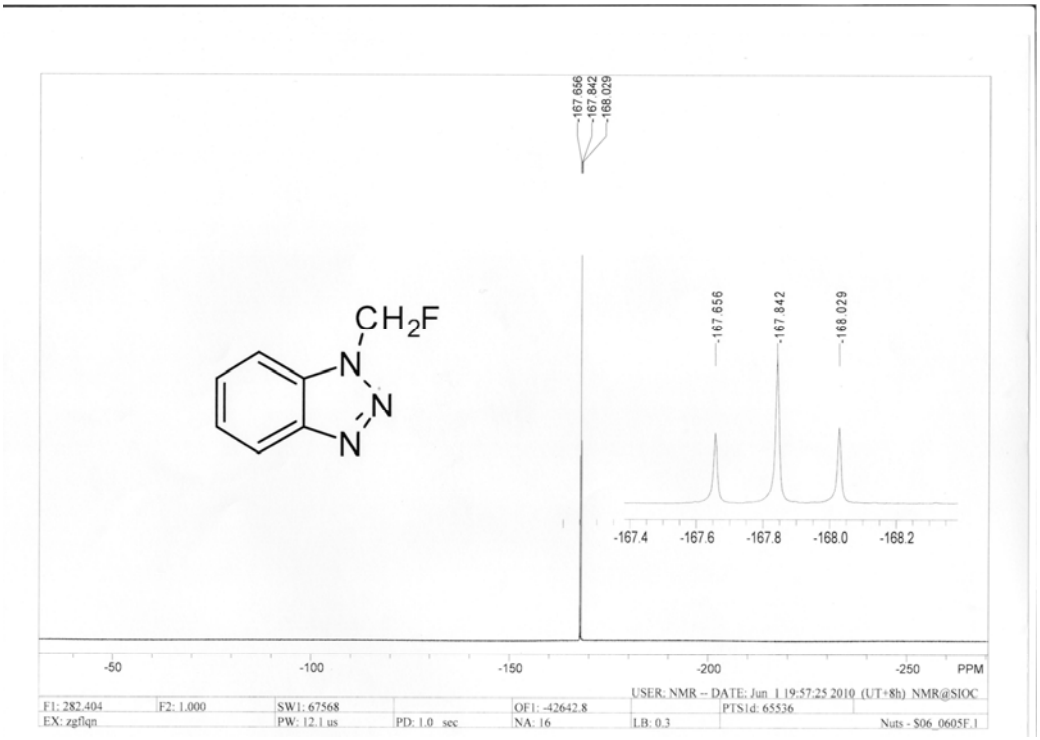
OF1: 1850.2
PTS1d: 32768
EX: zg30
PW: 10.2 us
PD: 1.0 sec
NA: 16
LB: 0.3
Nuts - S06_0605H.1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-168.029
CH2F
N
N
N
-167.656
-167.842
-168.029
-167.4
-167.6
-167.8
-168.0
-168.2
-50
-100
-150
-200
-250
PPM
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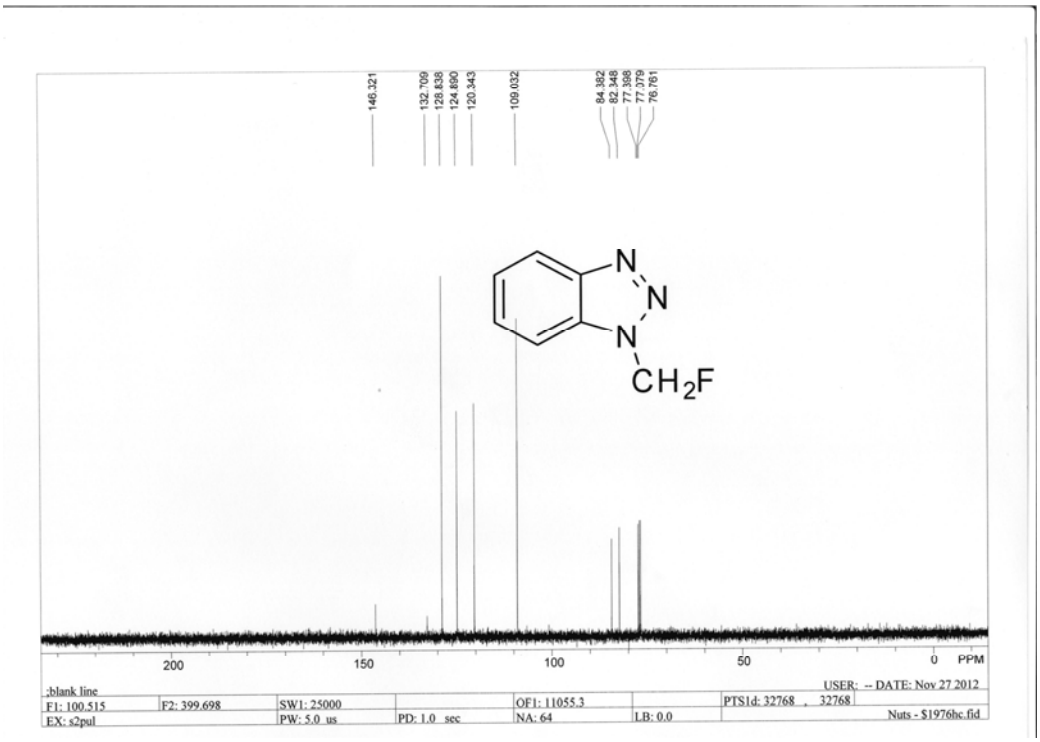
F2: 1.000
SW1: 67568
OF1: -42642.8
PTS1d: 65536
EX: zgflqn
PW: 12.1 us
PD: 1.0 sec
NA: 16
LB: 0.3
Nuts - S06_0605F.1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124.890
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109.032
84.382
82.348
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77.379
76.761
N
N
N
CH2F
200
150
100
50
0 PPM
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F2: 399.698
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PD: 1.0 sec
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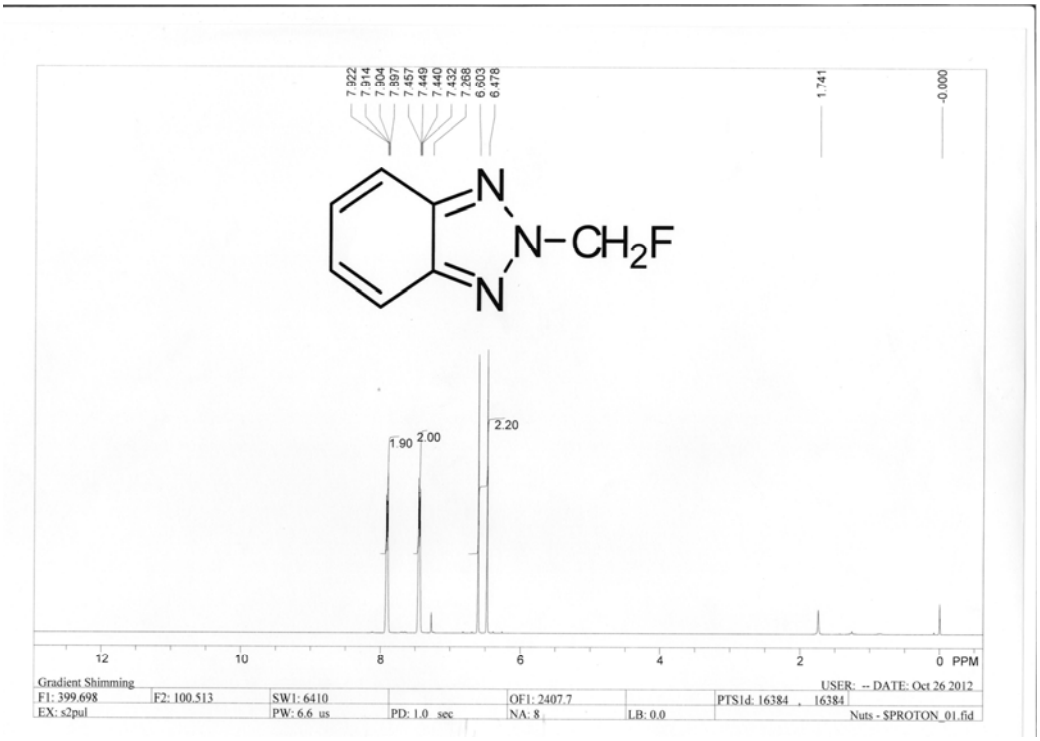
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7.457
7.449
7.440
7.432
7.268
6.603
6.478
1.741
-0.000
N
N-CH2F
N
1.90
2.00
2.20
12
10
8
6
4
2
0 PPM
Gradient Shimming
F1: 399.698
F2: 100.513
SW1: 6410
PW: 6.6 us
PD: 1.0 sec
OF1: 2407.7
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LB: 0.0
PTS1d: 16384 , 16384
USER: -- DATE: Oct 26 2012
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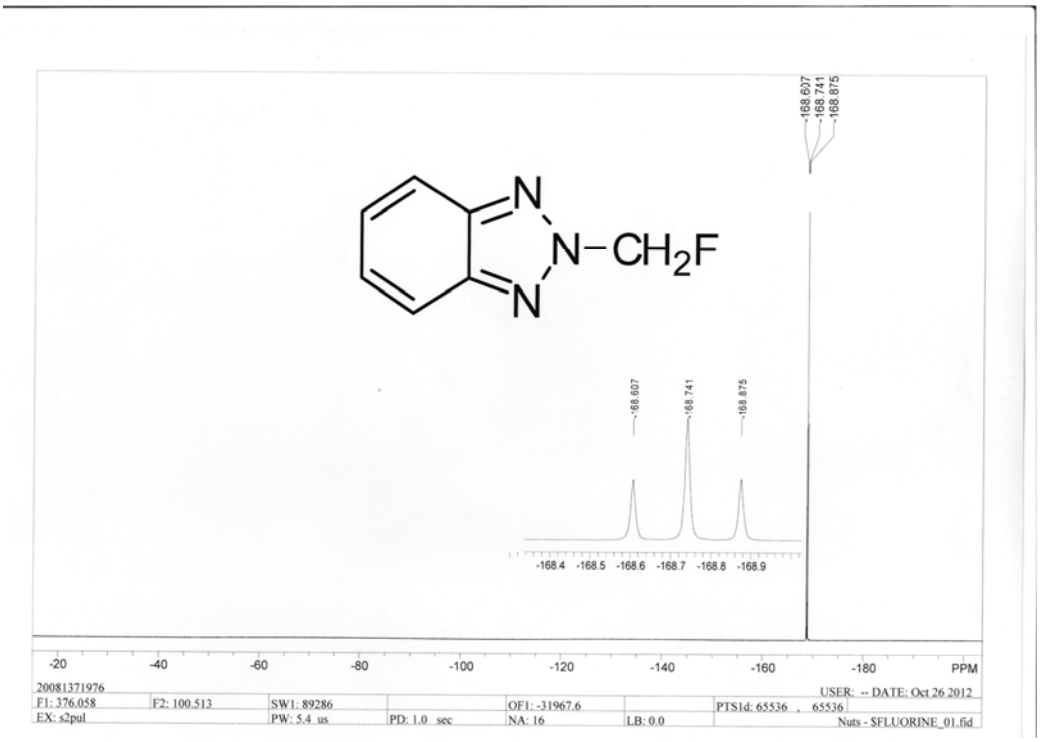
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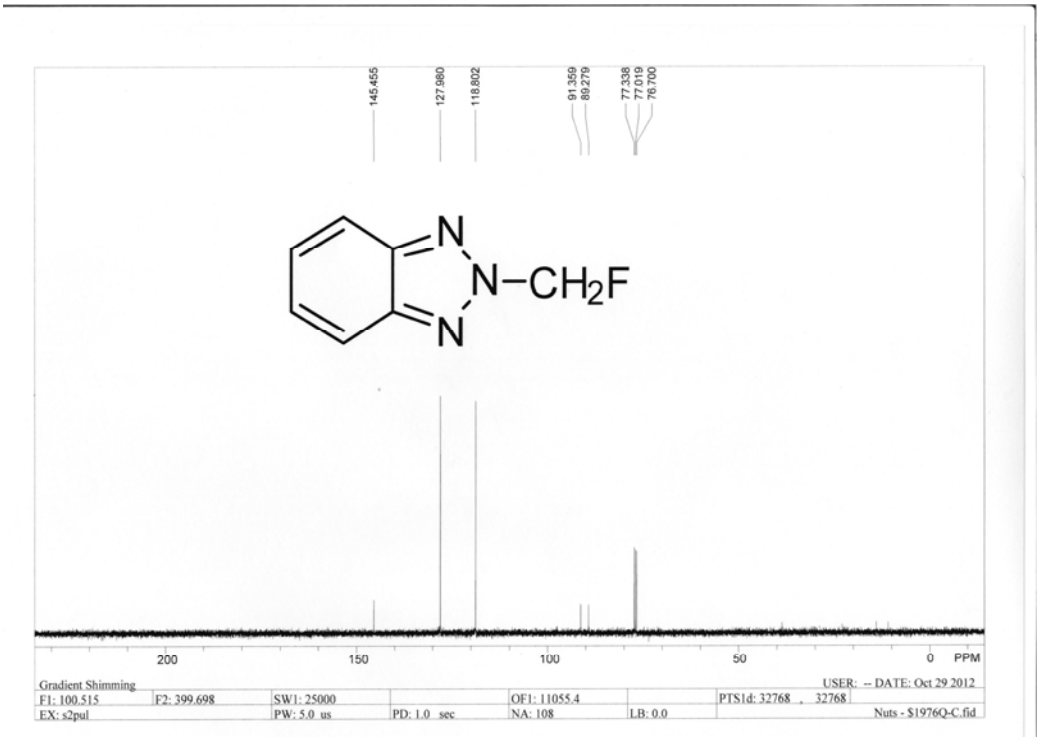
-168.741
-168.875
N
N
N
N−CH2F
-168.607
-168.741
-168.875
-168.4 -168.5 -168.6 -168.7 -168.8 -168.9
-20 -40 -60 -80 -100 -120 -140 -160 -180 PPM
20081371976
USER: -- DATE: Oct 26 2012
F1: 376.058 F2: 100.513 SW1: 89286 OF1: -31967.6 PTS1d: 65536 , 65536
EX: s2pul PW: 5.4 us PD: 1.0 sec NA: 16 LB: 0.0 Nuts - $FLUORINE_01.fid


145.455
127.980
118.802
91.359
89.279
77.338
77.019
76.700
N
N
N
N−CH2F
200 150 100 50 0 PPM
Gradient Shimming
USER: -- DATE: Oct 29 2012
F1: 100.515 F2: 399.698 SW1: 25000 OF1: 11055.4 PTS1d: 32768 , 32768
EX: s2pul PW: 5.0 us PD: 1.0 sec NA: 108 LB: 0.0 Nuts - $1976Q-C.fid