Supporting Information

Nickel-Catalyzed Monofluoromethylation of (Hetero)aryl Bromides via Reductive Cross-coupling

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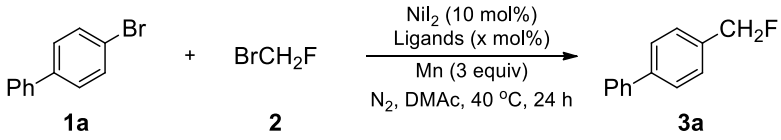
General Information

NMR spectra were recorded on Bruker-400 (400 MHz for ^{1}H, 101 MHz for ^{13}C and 376 MHz for ^{19}F {^{1}H, ^{13}C decoupled}) instruments internally referenced to $SiMe_4$ signal. High resolution mass spectra were recorded on P-SIMS-Gly of Bruker Daltonics Inc. using ESI-TOF (electrospray ionization-time of flight) or Micromass GCT using EI (electron impact). Anhydrous DMAc was obtained from Infsci. $BrCH_2F$ was obtained from ShangFluoro. NiI_2 was obtained from Strem. Substrates **1a** and **1c** were obtained from Adamas-beta. DMAP and substrate **1e** were obtained from SCR. Substrates **1d**, **1h** and **1m** were obtained from Accela. Substrates **1b**, **1f**, **1g**, **1u** and **1ac** were obtained from Energy. Substrates **1i**, **1k**, **1l**, **1p**, **1q**, **1s**, **1t**, **1v**, **1x** and **1aa** were obtained from Bidepharm. Substrates **1r** and **1z** were obtained from Leyan. Dtbpy and substrate **1n** were obtained from J&K. Substrate **1o** was obtained from Macklin. Mn powder and substrate **1ad** were obtained from Aladdin. Substrate **1y** was obtained from AikonChem. All reagents were used as received without further purification.

Tables of the Optimization of Reaction Conditions

Table S1. Ligands Screening[a]



Entry	Ligand (x mol%)	Yield(%)[b]	Entry	Ligands (x mol%)	Yield(%)[b]
1	None	0	11	dombpy(12)/DMAP(24)	76
2	dmbpy (12)	64	**12**	**dtbpy(12)/DMAP(24)**	**85(86)[c]**
3	dtbpy (12)	71	13	dmbpy(12)/DMAP(24)	72
4	dombpy (12)	79	14	phen(12)/DMAP(24)	69
5	phen (12)	52	15	bpy(12)/DMAP(24)	50
6	dppe (12)	12	16	dtbpy(12)/4-CN-Py(24)	74
7	DMAP (24)	15	17	dtbpy(12)/2,6-lutidine(24)	78
8	4-CN-Py (24)	0	18	dtbpy(12)/PPh_3(24)	50
9	2,6-lutidine (24)	0	19	dmbpy(12)/4-CN-Py(24)	0
10	PPh_3 (24)	0	20	dmbpy(12)/PPh_3(24)	64

[a] Reaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **2** (2.5 equiv), NiI_2 (10 mol%), ligands, Mn (200 mesh, 3.0 equiv), DMAc (1 mL), 40 °C, under N_2 atmosphere, 24 h. [b] Yields determined by ^{19}F NMR using $PhCF_3$ as an internal standard. [c] Isolated yield.

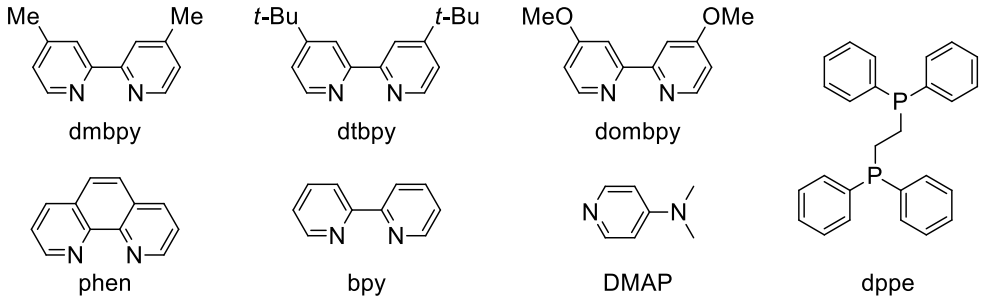
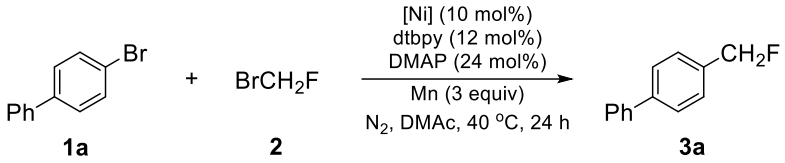


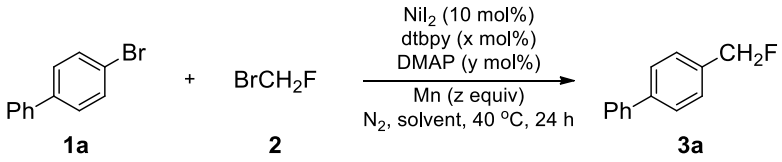
Table S2. Nickel Sources Screening [a]



Entry	[Ni]	Yield(%)[b]	Entry	[Ni]	Yield(%)[b]
1	None	0	5	$Ni(OAc)_2$	19
2	$NiCl_2$	39	6	$Ni(NO_3)_2{\cdot}6H_2O$	0
3	$NiBr_2$	<5	7	$Ni(acac)_2$	68
4	**NiI_2**	**86**[c]	8	$Ni(OTf)_2$	0

[a] Reaction conditions (unless otherwise specified): **1** (0.2 mmol, 1.0 equiv), **2** (2.5 equiv), [Ni] (10 mol%), dtbpy (12 mol%), DMAP (24 mol%), Mn (200 mesh, 3.0 equiv), DMAc (1 mL), 40 °C, under N_2 atmosphere, 24 h. [b] Yields determined by ^{19}F NMR using $PhCF_3$ as an internal standard. [c] Isolated yield.

Table S3. Optimization of Other Conditions [a]



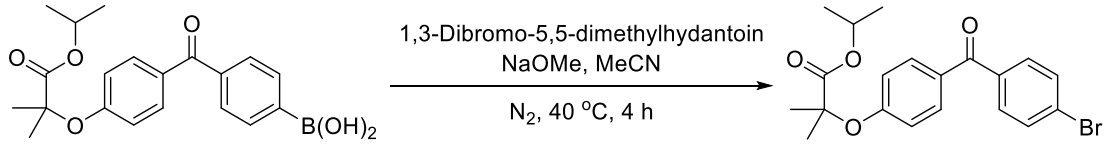
Entry	x	y	z	solvent	Yield(%)[b]
1	10	20	3.0	DMAc	80
2	12	24	3.0	DMF	0
3	12	24	3.0	MeCN	41
4	12	24	3.0	DMSO	0
5	12	24	2.0	DMAc	79
6[c]	12	24	3.0	DMAc	81
7[d]	12	24	3.0	DMAc	76

[a] Standard reaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **2** (2.5 equiv), NiI_2 (10 mol%), dtbpy (12 mol%),DMAP (24 mol%), Mn (200 mesh, 3.0 equiv), DMAc (1 mL), 40 °C, under N_2 atmosphere, 24 h. [b] Yields determined by ^{19}F NMR using $PhCF_3$ as an internal standard. [c] H_2O (3 equiv) was added. [d] 60 °C.

Preparation of Substrates

Substrates **1j**[1], **1w**[2] and **1ab**[3] were prepared in accordance with methods described in the references.

Synthesis of Fenofibrate bromide (1ae):



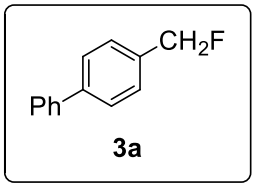
Fenofibrate boronic acid[4] (2 mmol, 0.74 g), 1,3-dibromo-5,5-dimethylhydantoin (2.2 mmol, 0.63 mg) and NaOMe (0.1 mmol, 5.4 mg) were added to a 50 mL Schlenk tube equipped with a magnetic stirring bar. The vessel was evacuated and backfilled with N_2 (repeated for 3 times). Acetonitrile (10 mL) were added to the tube at room temperature under a stream of nitrogen, and the tube was sealed and put into a pre-heated oil bath at 40 °C for 4 h under nitrogen atmosphere. After the resulting solution was cooled to room temperature, Na_2SO_3 (10% aq, ~20 mL) was added, and the aqueous layer was extracted with MTBE (3 × 15 mL). The combined organic phase was washed with NaOH (10% aq) and dried over anhydrous Na_2SO_4, filtrated and concentrated under vacuum. The residue was then purified by flash column chromatography (PE/EA = 5:1) to give the product as a white solid (> 80%). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.76–7.70 (m, 2H), 7.61 (s, 4H), 6.89–6.82 (m, 2H), 5.08 (hept, *J* = 6.3 Hz, 1H), 1.66 (s, 6H), 1.20 (d, *J* = 6.3 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-d) δ 194.51, 173.21, 159.88, 136.98, 132.09, 131.63, 131.41, 130.25, 127.03, 117.33, 79.53, 69.48, 25.49, 21.66. HRMS ESI (m/z): $[M+H]^+$ calcd. For $C_{20}H_{22}BrO_4$: 405.0701 found: 405.0685.

Preparation of $BrCH_2F$ Stock Solution[5]

Dry DMAc (~23 mL) was added to a Schlenk graduated cylinder under nitrogen. The vessel and solvent were weighed. Next, $BrCH_2F$ (~2mL) was added and the total volume of the solution reached approximately 25 mL. The vessel was sealed and weighed again. The concentration of the $BrCH_2F$ stock solution was calculated based on the mass of $BrCH_2F$ added and the total volume of the solution (~0.2 mol/L).

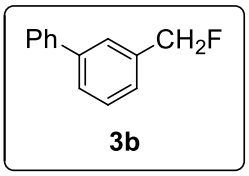
General Procedure for Nickel-Catalyzed Cross-Coupling between (Hetero)aryl Bromides and Bromofluoromethane

To a 5 mL of sealing tube were added NiI_2 (10 mol%), dtbpy (4,4'-Di-tert-butyl-2,2'-bipyridine, 12 mol%), DMAP (4-Dimethylaminopyridine, 24 mol%) and manganese powder (200 mesh, 3.0 equiv). The vessel was evacuated and backfilled with N_2 (repeated for 3 times), after that, aryl bromine **1** (0.2 mmol, 1.0 equiv) and dry DMAc (1 mL) were added. The solution then premix for 10 s before $BrCH_2F$ **2** (solution in DMAc, 2.5 equiv) was added. The tube was sealed with a Teflon lined cap and heated in a preheated oil bath at 40℃ for 24 h. The reaction mixture was then cooled to room temperature, diluted with EtOAc (~20 mL) and filtered through a pad of celite. The filtrate was added brine (30 mL) and extracted with EtOAc (2×15 mL), the combined organic layer was dried over Na_2SO_4, filtrated and concentrated under vacuum. The residue was then purified by flash column chromatography to give **3** as a colorless solid or oil.



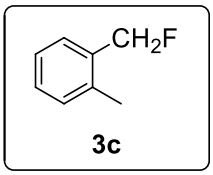
3a

4-(fluoromethyl)-1,1'-biphenyl (3a) was purified with silica gel chromatography (PE) as a white solid (86% yield). The compound is known[5]. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 (t, *J* = 8.5 Hz, 4H), 7.53-7.47 (m, 4H), 7.41 (t, *J* = 7.3 Hz, 1H), 5.46 (d, *J* = 47.9 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.83 (d, *J* = 3.3 Hz), 140.69 (d, *J* = 1.1 Hz), 135.23 (d, *J* = 17.0 Hz), 128.95, 128.19 (d, *J* = 5.7 Hz), 127.66, 127.47 (d, *J* = 1.4 Hz), 127.27, 84.51 (d, *J* = 166.0 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -206.03 (t, *J* = 47.8 Hz).



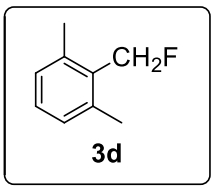
3b

3-(fluoromethyl)-1,1'-biphenyl (3b) was purified with silica gel chromatography (PE) as a colorless liquid (89% yield). The compound is known[6]. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67-7.60 (m, 4H), 7.53-7.45 (m, 3H), 7.43-7.36 (m, 2H), 5.48 (d, *J* = 47.8 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.79 (d, *J* = 1.0 Hz), 140.80, 136.85 (d, *J* = 17.1 Hz), 129.19, 128.95, 127.67, 127.65, 127.30, 126.43 (d, *J* = 2.0 Hz), 126.37 (d, *J* = 2.1 Hz), 84.72 (d, *J* = 166.6 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -207.15 (t, *J* = 47.8 Hz).



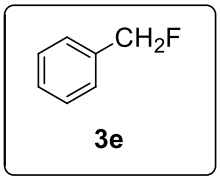
3c

1-(fluoromethyl)-2-methylbenzene (3c) due to the low boiling point of the product, the yield (74%) was determined by ^{19}F NMR using $PhCF_3$ as an internal standard. This compound is known[7]. The product was characterized by ^{19}F NMR and GC-MS analysis.



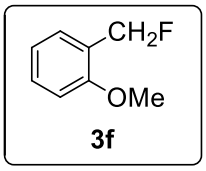
3d

2-(fluoromethyl)-1,3-dimethylbenzene (3d) due to the low boiling point of the product, the yield (76%) was determined by ^{19}F NMR using $PhCF_3$ as an internal standard. This compound is known[7]. The product was characterized by ^{19}F NMR and GC-MS analysis.



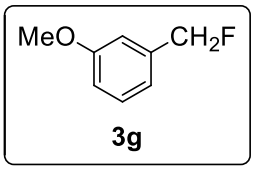
3e

(Fluoromethyl)benzene (3e) due to the low boiling point of the product, the yield (83%) was determined by ^{19}F NMR using $PhCF_3$ as an internal standard. This compound is known[6]. The product was characterized by ^{19}F NMR and GC-MS analysis.



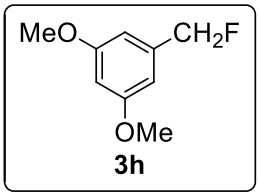
3f

1-(fluoromethyl)-2-methoxybenzene (3f) due to the low boiling point of the product, the yield (77%) was determined by ^{19}F NMR using $PhCF_3$ as an internal standard. This compound is known[6]. The product was characterized by ^{19}F NMR and GC-MS analysis.



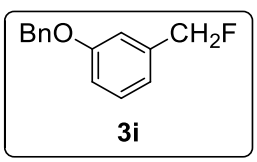
3g

1-(fluoromethyl)-3-methoxybenzene (3g) due to the low boiling point of the product, the yield (82%) was determined by ^{19}F NMR using $PhCF_3$ as an internal standard. This compound is known[6]. The product was characterized by ^{19}F NMR and GC-MS analysis.



3h

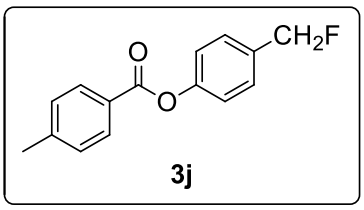
1-(fluoromethyl)-3,5-dimethoxybenzene (3h) was purified with silica gel chromatography (PE/EA = 20:1) as a colorless liquid (84% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 6.52 (t, *J* = 1.7 Hz, 2H), 6.45 (q, *J* = 2.1 Hz, 1H), 5.32 (d, *J* = 47.6 Hz, 2H), 3.80 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.13, 138.62 (d, *J* = 17.3 Hz), 105.03 (d, *J* = 6.5 Hz), 100.77 (d, *J* = 2.6 Hz), 84.60 (d, *J* = 167.5 Hz), 55.53. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -208.96 (t, *J* = 47.7 Hz). HRMS EI (m/z): $[M]^+$ calcd. For $C_9H_{11}FO_2$: 170.0743 found: 170.0739.



3i

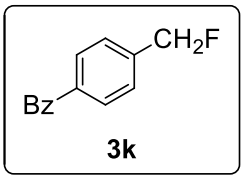
1-(benzyloxy)-3-(fluoromethyl)benzene (3i) was purified with silica gel chromatography (PE/EA = 20:1) as a white solid (94% yield). The compound is known[8]. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.53–7.39 (m, 4H), 7.39–7.29 (m, 2H), 7.04 (s,

1H), 6.99 (d, *J* = 7.7 Hz, 2H), 5.38 (d, *J* = 47.7 Hz, 2H), 5.10 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.11, 137.90 (d, *J* = 17.1 Hz), 136.91, 129.85, 128.73, 128.15, 127.61, 119.90 (d, *J* = 6.1 Hz), 115.30 (d, *J* = 2.8 Hz), 113.77 (d, *J* = 6.3 Hz), 84.54 (d, *J* = 166.9 Hz), 70.12. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -207.84 (t, *J* = 47.7 Hz).



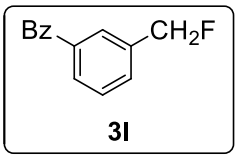
3j

4-(fluoromethyl)phenyl-4-methylbenzoate (3j) was purified with silica gel chromatography (PE/EA = 20:1) as a white solid (77% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 (d, *J* = 8.0 Hz, 2H), 7.45 (dd, *J* = 8.5, 1.9 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 5.40 (d, *J* = 47.8 Hz, 2H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.23 (d, *J* = 0.4 Hz), 151.42 (d, *J* = 3.3 Hz), 144.68, 133.87 (d, *J* = 17.5 Hz), 130.35, 129.44, 128.92 (d, *J* = 5.8 Hz), 126.73, 122.13 (d, *J* = 1.1 Hz), 84.13 (d, *J* = 166.6 Hz), 21.89. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -206.06 (t, *J* = 47.8 Hz). HRMS ESI (m/z): $[M+Na]^+$ calcd. For $C_{15}H_{13}FO_2Na$: 267.0797 found: 267.0792.



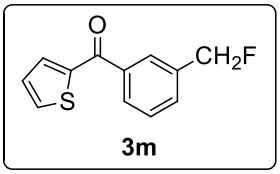
3k

(4-(fluoromethyl)phenyl)(phenyl)methanone (3k) was purified with silica gel chromatography (PE/EA = 15:1) as a pale yellow oil (95% yield). The compound is known[5]. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85-7.71 (m, 4H), 7.63–7.56 (m, 1H), 7.51-7.46 (m, 4H), 5.47 (d, *J* = 47.2 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.28, 140.72 (d, *J* = 17.2 Hz), 137.80 (d, *J* = 2.5 Hz), 137.51, 132.66, 130.41, 130.11, 128.44, 126.70 (d, *J* = 6.5 Hz), 83.83 (d, *J* = 168.4 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -212.32 (t, *J* = 47.2 Hz).



3l

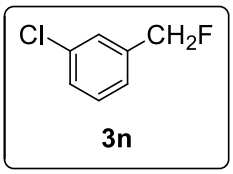
(3-(fluoromethyl)phenyl)(phenyl)methanone (3l) was purified with silica gel chromatography (PE/EA = 15:1) as a colorless liquid (83% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95–7.74 (m, 4H), 7.60 (t, *J* = 7.5 Hz, 2H), 7.57–7.44 (m, 3H), 5.44 (d, *J* = 47.5 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.38, 138.08, 137.41, 136.67 (d, *J* = 17.5 Hz), 132.74, 131.27 (d, *J* = 5.8 Hz), 130.44 (d, *J* = 2.6 Hz), 130.14, 128.81 (d, *J* = 6.2 Hz), 128.74, 128.49, 84.06 (d, *J* = 167.7 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -208.92 (t, *J* = 47.7 Hz). HRMS ESI (m/z): $[M+H]^+$ calcd. For $C_{14}H_{12}FO$: 215.0872 found: 215.0869.



3m

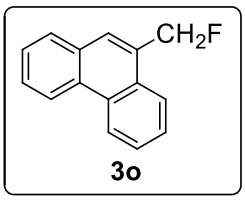
(3-(fluoromethyl)phenyl)(thiophen-2-yl)methanone (3m) was purified with silica gel chromatography (PE/EA = 5:1) as a colorless liquid (68% yield). ^{1}H NMR (400 MHz,

Chloroform-*d*) δ 7.91–7.81 (m, 2H), 7.74 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.64 (dd, *J* = 3.8, 1.1 Hz, 1H), 7.62-7.59 (m, 1H), 7.58–7.48 (m, 1H), 7.17 (dd, *J* = 4.9, 3.8 Hz, 1H), 5.46 (d, *J* = 47.5 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 187.85, 143.49, 138.62, 136.84 (d, *J* = 17.6 Hz), 135.08, 134.60, 131.04 (d, *J* = 5.9 Hz), 129.50 (d, *J* = 2.6 Hz), 128.88, 128.19, 127.95 (d, *J* = 6.3 Hz), 84.03 (d, *J* = 167.8 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -209.28 (t, *J* = 47.5 Hz). HRMS ESI (m/z): $[M+H]^+$ calcd. For $C_{12}H_{10}FOS$: 221.0436 found: 221.0429.



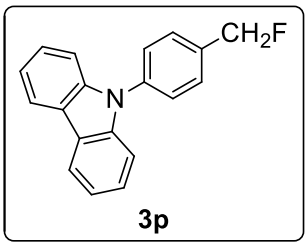
3n

1-chloro-3-(fluoromethyl)benzene (3n) due to the low boiling point of the product, the yield (78%) was determined by ^{19}F NMR using $PhCF_3$ as an internal standard. This compound is known[9]. The product was characterized by ^{19}F NMR and GC-MS analysis.



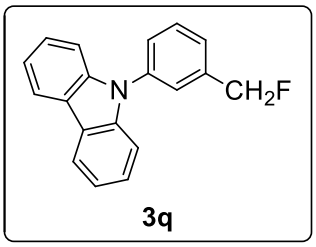
3o

9-(fluoromethyl)phenanthrene (3o) was purified with silica gel chromatography (PE) as a white solid (95% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.74 (dd, *J* = 7.3, 2.2 Hz, 1H), 8.69 (d, *J* = 8.3 Hz, 1H), 8.11 (dt, *J* = 6.6, 1.8 Hz, 1H), 7.91 (d, *J* = 7.7 Hz, 1H), 7.81 (d, *J* = 3.1 Hz, 1H), 7.70 (ddt, *J* = 10.8, 7.0, 3.4 Hz, 3H), 7.65 – 7.59 (m, 1H), 5.89 (d, *J* = 47.8 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 131.13 (d, *J* = 1.3 Hz), 131.03 (d, *J* = 1.8 Hz), 130.74, 130.36 (d, *J* = 15.2 Hz), 130.04 (d, *J* = 1.1 Hz), 129.08 (d, *J* = 1.4 Hz), 128.03 (d, *J* = 9.5 Hz), 127.51 (d, *J* = 1.1 Hz), 127.16, 127.01 (d, *J* = 0.6 Hz), 126.92, 124.37 (d, *J* = 1.3 Hz), 123.29, 122.70 (d, *J* = 1.0 Hz), 83.87 (d, *J* = 166.4 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -207.89 (t, *J* = 47.8 Hz). HRMS EI (m/z): $[M]^+$ calcd. For $C_{15}H_{11}F$: 210.0845 found: 210.0835.



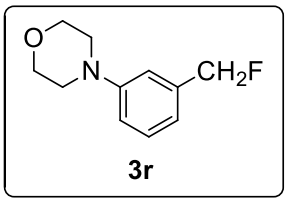
3p

9-(4-(fluoromethyl)phenyl)-9H-carbazole (3p) was purified with silica gel chromatography (PE/EA = 20:1) as a white solid (77% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.18 (dt, *J* = 7.7, 1.0 Hz, 2H), 7.63 (s, 4H), 7.47–7.40 (m, 4H), 7.36–7.28 (m, 2H), 5.52 (d, *J* = 47.7 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.84, 138.25 (d, *J* = 3.1 Hz), 135.43 (d, *J* = 17.4 Hz), 129.17 (d, *J* = 5.8 Hz), 127.33 (d, *J* = 0.9 Hz), 126.14, 123.57, 120.48, 120.22, 109.81, 84.21 (d, *J* = 167.0 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -207.06 (t, *J* = 47.7 Hz). HRMS ESI (m/z): $[M+H]^+$ calcd. For $C_{19}H_{15}FN$: 276.1189 found: 276.1180.



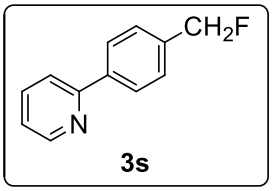
3q

9-(3-(fluoromethyl)phenyl)-9H-carbazole (3q) was purified with silica gel chromatography (PE/EA = 20:1) as a colorless liquid (93% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.20 (dt, *J* = 7.8, 1.0 Hz, 2H), 7.70–7.58 (m, 3H), 7.54–7.42 (m, 5H), 7.39-7.31 (m, 2H), 5.52 (d, *J* = 47.5 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.85, 138.42 (d, *J* = 17.5 Hz), 138.18, 130.29, 127.38 (d, *J* = 2.5 Hz), 126.25 (d, *J* = 6.0 Hz), 126.12, 125.89 (d, *J* = 6.3 Hz), 123.54, 120.46, 120.20, 109.78, 84.02 (d, *J* = 167.9 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -208.81 (t, *J* = 47.4 Hz). HRMS ESI (m/z): $[M+H]^+$ calcd. For $C_{19}H_{15}FN$: 276.1189 found: 276.1177.



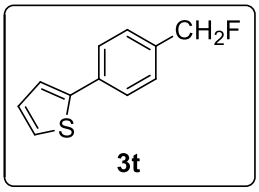
3r

4-(3-(fluoromethyl)phenyl)morpholine (3r) was purified with silica gel chromatography (PE/EA = 5:1) as a colorless liquid (93% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 (t, *J* = 7.8 Hz, 1H), 6.97–6.84 (m, 3H), 5.35 (d, *J* = 47.8 Hz, 2H), 3.91–3.81 (m, 4H), 3.24–3.13 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.66, 137.35 (d, *J* = 16.9 Hz), 129.56 (d, *J* = 0.8 Hz), 118.95 (d, *J* = 5.9 Hz), 116.02 (d, *J* = 2.9 Hz), 114.57 (d, *J* = 6.3 Hz), 84.97 (d, *J* = 166.5 Hz), 66.99, 49.31. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -207.25 (t, *J* = 47.8 Hz). HRMS EI (m/z): $[M]^+$ calcd. For $C_{11}H_{14}FNO$: 195.1059 found: 195.1050.



3s

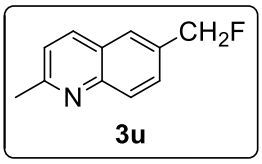
2-(4-(fluoromethyl)phenyl)pyridine (3s) was purified with silica gel chromatography (PE/EA = 5:1) as a colorless liquid (80% yield). The compound is known[10]. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.74 – 8.67 (m, 1H), 8.03 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.81–7.70 (m, 2H), 7.56–7.44 (m, 2H), 7.23 (ddd, *J* = 6.0, 4.8, 2.5 Hz, 1H), 5.43 (d, *J* = 47.7 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.90 (d, *J* = 1.4 Hz), 149.83, 139.87 (d, *J* = 3.0 Hz), 136.96 (d, *J* = 17.3 Hz), 136.89, 127.86 (d, *J* = 5.9 Hz), 127.20 (d, *J* = 1.3 Hz), 122.43, 120.66, 84.36 (d, *J* = 166.6 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -208.00 (t, *J* = 47.7 Hz).



3t

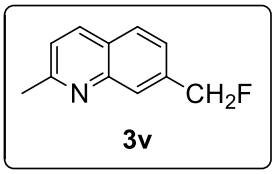
2-(4-(fluoromethyl)phenyl)thiophene (3t) was purified with silica gel chromatography (PE) as a white solid (75% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71–7.60 (m, 2H), 7.40 (ddd, *J* = 6.5, 2.8, 1.1 Hz, 2H), 7.35 (dd, *J* = 3.6, 0.8 Hz, 1H), 7.31 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.10 (dd, *J* = 5.1, 3.6 Hz, 1H), 5.40 (d, *J* = 47.8 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.85 (d, *J* = 1.5 Hz), 135.38 (d, *J* = 17.0 Hz), 135.00 (d,

J = 3.3 Hz), 128.31 (d, *J* = 5.8 Hz), 128.22, 126.19 (d, *J* = 1.3 Hz), 125.31, 123.60 (d, *J* = 0.5 Hz), 84.40 (d, *J* = 166.2 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -206.37 (t, *J* = 47.8 Hz). HRMS EI (m/z): $[M]^+$ calcd. For $C_{11}H_9FS$: 192.0409 found: 192.0398.



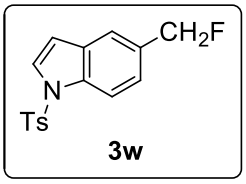
3u

6-(fluoromethyl)-2-methylquinoline (3u) was purified with silica gel chromatography (PE/EA = 4:1) as a white solid (72% yield). The compound is known[11]. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.75 (s, 1H), 7.65 (d, *J* = 8.6 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 1H), 5.52 (d, *J* = 47.6 Hz, 2H), 2.74 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.77 (d, *J* = 1.1 Hz), 147.93 (d, *J* = 2.1 Hz), 136.34 (d, *J* = 0.9 Hz), 133.64 (d, *J* = 17.1 Hz), 129.27, 128.52 (d, *J* = 4.8 Hz), 126.25 (d, *J* = 7.4 Hz), 126.24 (d, *J* = 1.0 Hz), 122.59, 84.38 (d, *J* = 167.2 Hz), 25.52. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -207.64 (t, *J* = 47.6 Hz).



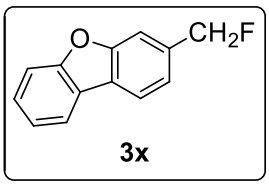
3v

7-(fluoromethyl)-2-methylquinoline (3v) was purified with silica gel chromatography (PE/EA = 4:1) as a white solid (79% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 8.4 Hz, 1H), 7.97 (s, 1H), 7.77 (d, *J* = 8.3 Hz, 1H), 7.47 (d, *J* = 8.3 Hz, 1H), 7.27 (d, *J* = 8.8 Hz, 1H), 5.55 (d, *J* = 47.4 Hz, 2H), 2.73 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.68, 147.73, 137.58 (d, *J* = 17.1 Hz), 136.01, 128.11, 127.10 (d, *J* = 7.3 Hz), 126.42 (d, *J* = 1.9 Hz), 124.54 (d, *J* = 5.3 Hz), 122.55, 84.43 (d, *J* = 167.6 Hz), 25.47. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -209.44 (t, *J* = 47.5 Hz). HRMS ESI (m/z): $[M+H]^+$ calcd. For $C_{11}H_{11}FN$: 176.0876 found: 176.0873.



3w

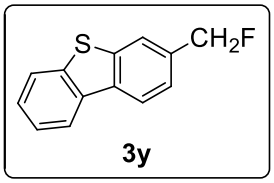
5-(fluoromethyl)-1-tosyl-1H-indole (3w) was purified with silica gel chromatography (PE/EA = 5:1) as a colorless liquid (87% yield). The compound is known[5]. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 8.5 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 3.7 Hz, 1H), 7.55 (t, *J* = 2.0 Hz, 1H), 7.34 (dt, *J* = 8.5, 1.7 Hz, 1H), 7.21 (d, *J* = 8.1 Hz, 2H), 6.66 (d, *J* = 3.6 Hz, 1H), 5.42 (d, *J* = 48.2 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.23, 135.22, 135.04 (d, *J* = 2.7 Hz), 131.36 (d, *J* = 17.2 Hz), 130.99 (d, *J* = 1.3 Hz), 130.03, 127.21, 126.89, 124.63 (d, *J* = 4.9 Hz), 121.21 (d, *J* = 6.1 Hz), 113.80 (d, *J* = 1.1 Hz), 109.10, 84.94 (d, *J* = 165.8 Hz), 21.65. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -201.63 (t, *J* = 48.2 Hz).



3x

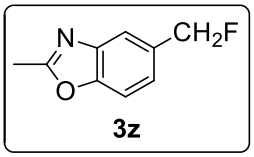
3-(fluoromethyl)dibenzo[*b*,*d*]furan (3x) was purified with silica gel chromatography (PE) as a white solid (93% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03–7.92 (m, 2H), 7.62–

7.56 (m, 2H), 7.49 (ddd, *J* = 8.4, 7.4, 1.3 Hz, 1H), 7.40–7.34 (m, 2H), 5.54 (d, *J* = 47.8 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.73 , 156.29 (d, *J* = 0.6 Hz), 135.59 (d, *J* = 17.1 Hz), 127.59, 124.78 (d, *J* = 2.7 Hz), 123.90 (d, *J* = 1.0 Hz), 122.99, 122.24 (d, *J* = 5.8 Hz), 120.91, 120.85 (d, *J* = 0.9 Hz), 111.89, 110.99 (d, *J* = 6.6 Hz), 84.76 (d, *J* = 167.3 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -204.77 (t, *J* = 47.8 Hz). HRMS EI (m/z): $[M]^+$ calcd. For $C_{13}H_9FO$: 200.0637 found: 200.0630.



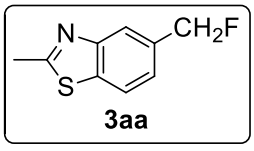
3y

3-(fluoromethyl)dibenzo[b,d]thiophene (3y) was purified with silica gel chromatography (PE) as a white solid (77% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21–8.09 (m, 2H), 7.87 (dtd, *J* = 6.6, 3.1, 1.7 Hz, 2H), 7.56–7.38 (m, 3H), 5.52 (d, *J* = 47.8 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.90 , 139.77 (d, *J* = 1.0 Hz), 135.96 (d, *J* = 2.7 Hz), 135.16 (d, *J* = 1.1 Hz), 134.90 (d, *J* = 17.1 Hz), 127.09, 124.60, 123.95 (d, *J* = 5.4 Hz), 122.97, 121.99 (d, *J* = 6.7 Hz), 121.86, 121.78 (d, *J* = 0.6 Hz), 84.67 (d, *J* = 167.2 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -205.39 (t, *J* = 47.8 Hz). HRMS EI (m/z): $[M]^+$ calcd. For $C_{13}H_9FS$: 216.0409 found: 216.0400.



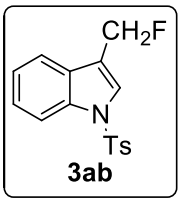
3z

5-(fluoromethyl)-2-methylbenzo[d]oxazole (3z) was purified with silica gel chromatography (PE/EA = 5:1) as a white solid (89% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 (s, 1H), 7.47 (d, *J* = 8.3 Hz, 1H), 7.32 (d, *J* = 8.3 Hz, 1H), 5.45 (d, *J* = 48.1 Hz, 2H), 2.64 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.79, 151.29 (d, *J* = 2.9 Hz), 141.90 (d, *J* = 1.0 Hz), 132.48 (d, *J* = 17.4 Hz), 124.62 (d, *J* = 5.4 Hz), 119.20 (d, *J* = 5.8 Hz), 110.41, 84.76 (d, *J* = 166.6 Hz), 14.69. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -201.70 (t, *J* = 48.1 Hz). HRMS ESI (m/z): $[M+H]^+$ calcd. For C_9H_9FNO: 166.0668 found: 166.0664.



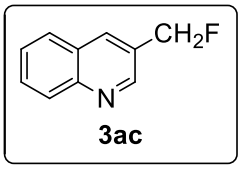
3aa

5-(fluoromethyl)-2-methylbenzo[d]thiazole (3aa) was purified with silica gel chromatography (PE/EA = 5:1) as a white solid (81% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (s, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.37 (d, *J* = 8.2 Hz, 1H), 5.49 (d, *J* = 47.9 Hz, 2H), 2.84 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.02, 153.62, 136.20 (d, *J* = 2.8 Hz), 134.41 (d, *J* = 17.3 Hz), 124.28 (d, *J* = 5.3 Hz), 121.73 (d, *J* = 0.8 Hz), 121.62 (d, *J* = 6.4 Hz), 84.60 (d, *J* = 167.0 Hz), 20.32. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -204.70 (t, *J* = 47.8 Hz). HRMS ESI (m/z): $[M+H]^+$ calcd. For C_9H_9FNS: 182.0440 found: 182.0435.



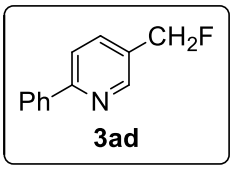
3ab

3-(fluoromethyl)-1-tosyl-1H-indole (3ab) was purified with silica gel chromatography (PE/EA = 5:1) as a white solid (65% yield). The compound is known[12]. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 8.3 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 4.7 Hz, 1H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.40–7.33 (m, 1H), 7.32–7.26 (m, 1H), 7.23 (d, *J* = 8.3 Hz, 2H), 5.52 (d, *J* = 48.4 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.38, 135.32, 135.18, 130.12, 129.36 (d, *J* = 0.9 Hz), 127.02, 125.97 (d, *J* = 9.3 Hz), 125.34, 123.71, 119.87, 117.78 (d, *J* = 19.7 Hz), 113.77, 76.52 (d, *J* = 162.9 Hz), 21.69. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -207.22 (td, *J* = 48.4, 4.8 Hz).



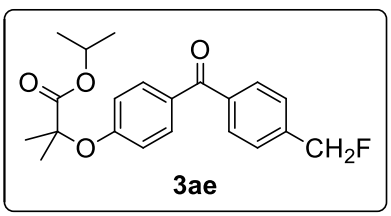
3ac

3-(fluoromethyl)quinoline (3ac) was purified with silica gel chromatography (PE/EA = 4:1) as a white solid (81% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.93 (s, 1H), 8.22–8.07 (m, 2H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.75 (t, *J* = 7.6 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 5.58 (d, *J* = 47.6 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.94 (d, *J* = 4.7 Hz), 148.31 (d, *J* = 2.2 Hz), 135.15 (d, *J* = 6.5 Hz), 130.19 (d, *J* = 1.0 Hz), 129.51 (d, *J* = 1.0 Hz), 128.91 (d, *J* = 17.3 Hz), 128.08 (d, *J* = 1.2 Hz), 127.62 (d, *J* = 0.9 Hz), 127.25 (d, *J* = 0.4 Hz), 82.55 (d, *J* = 167.7 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -208.67 (t, *J* = 47.6 Hz). HRMS ESI (m/z): $[M+H]^+$ calcd. For $C_{10}H_{19}FN$: 162.0719 found: 162.0716.



3ad

5-(fluoromethyl)-2-phenylpyridine (3ad) was purified with silica gel chromatography (PE/EA = 10:1) as a white solid (77% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.70 (s, 1H), 8.09–7.95 (m, 2H), 7.86–7.73 (m, 2H), 7.57–7.39 (m, 3H), 5.44 (d, *J* = 47.7 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.14 (d, *J* = 3.2 Hz), 149.09 (d, *J* = 6.0 Hz), 138.91, 136.49 (d, *J* = 4.8 Hz), 129.95 (d, *J* = 17.5 Hz), 129.39, 128.93, 127.10, 120.43, 82.25 (d, *J* = 167.0 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -208.42 (t, *J* = 47.8 Hz). HRMS ESI (m/z): $[M+H]^+$ calcd. For $C_{12}H_{11}FN$: 188.0876 found: 188.0872.



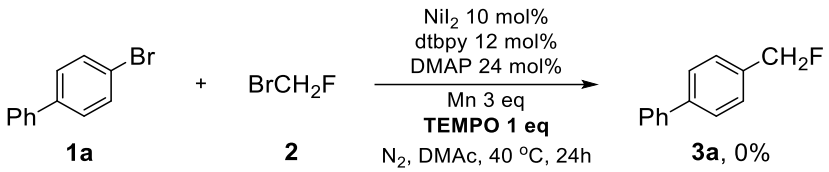
3ae

Isopropyl 2-(4-(4-(fluoromethyl)benzoyl)phenoxy)-2-methylpropanoate (3ae) was purified with silica gel chromatography (PE/EA = 5:1) as a white solid (81% yield). The compound is known[5]. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80-7.71 (m, 4H), 7.50–7.43 (m, 2H), 6.90–6.82 (m, 2H), 5.46 (d, *J* = 47.3 Hz, 2H), 5.08 (hept, *J* = 6.3 Hz, 1H),

1.66 (s, 6H), 1.20 (d, *J* = 6.3 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-d) δ 195.06, 173.19, 159.76, 140.20 (d, *J* = 17.2 Hz), 138.37 (d, *J* = 2.4 Hz), 132.11, 130.48, 130.07, 126.69 (d, *J* = 6.4 Hz), 117.28, 83.86 (d, *J* = 168.2 Hz), 79.47, 69.40, 25.44, 21.59. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -211.76 (t, *J* = 47.6 Hz).

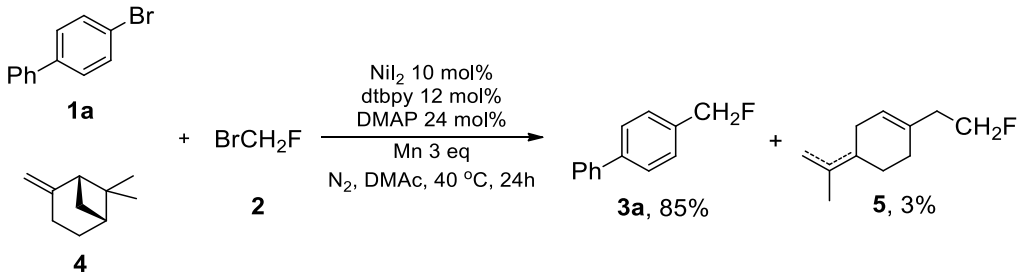
Mechanistic Studies

1. Radical Inhibition Experiment



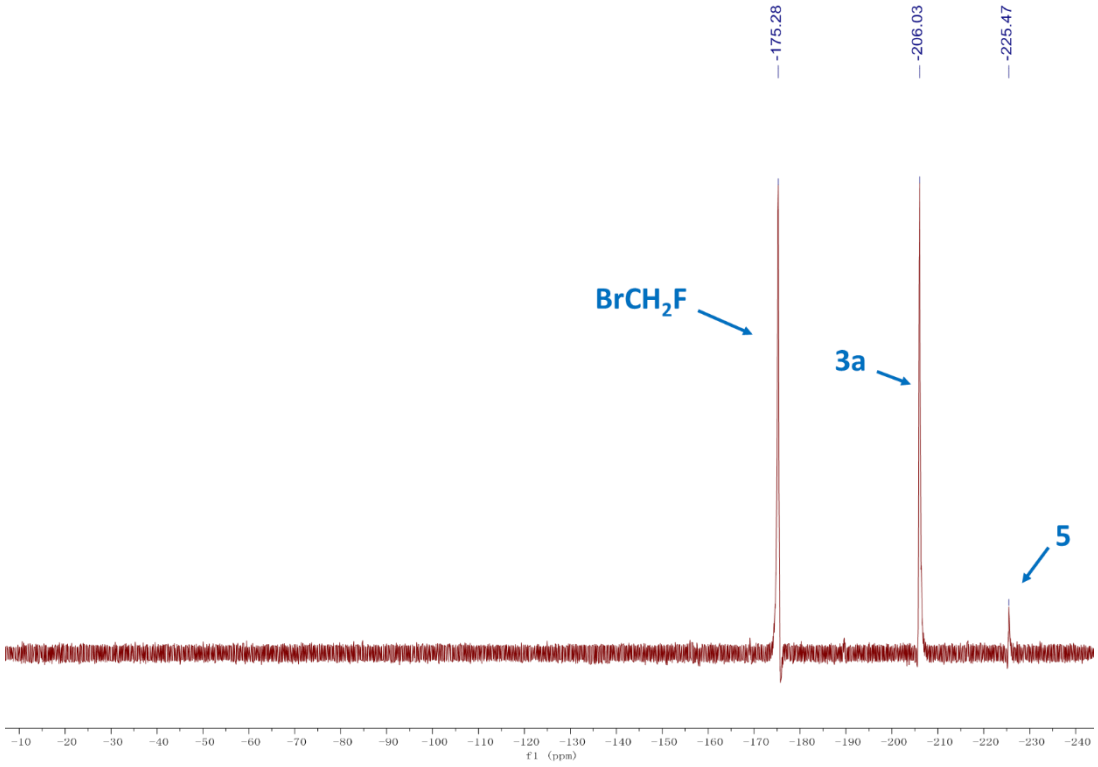
To a 5 mL of sealing tube were added aryl bromine **1** (0.2 mmol, 1.0 equiv), NiI_2 (10 mol%), dtbpy (12 mol%), DMAP (24 mol%) and Mn powder (200 mesh, 3.0 equiv). The mixture was added DMAc (1 mL), TEMPO (1 equiv) and **2** (2.5 equiv) under N_2 atmosphere. The tube was sealed with a Teflon lined cap and heated up into a preheated oil bath (40 ℃) for 48 h. Then the mixture was cooled to room temperature and diluted with ethyl acetate (2 mL) and filtered through a pad of silica gel. The mixture was detected by crude ^{19}F NMR and GC-MS. No product **3a** was found.

2. Radical Clock Experiment

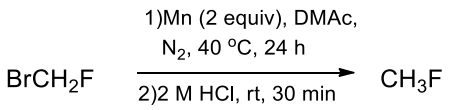


To a 5 mL of sealing tube were added aryl bromine **1** (0.2 mmol, 1.0 equiv), NiI_2 (10 mol%), dtbpy (12 mol%), DMAP (24 mol%) and Mn powder (200 mesh, 2.0 equiv). The mixture was added DMAc (1 mL), **4** (2 equiv) and **2** (2.5 equiv) under N_2 atmosphere. The tube was sealed with a Teflon lined cap and heated up into a preheated oil bath (40 ℃) for 24 h. Then the mixture was cooled to room temperature and diluted with ethyl acetate (2 mL) and filtered through a pad of silica gel. The mixture was then concentrated under vacuum and purified with silica gel chromatography to give product

3a in 85% yield and product **5** was yield by crude ^{19}F NMR and identified by GC-MS. HRMS EI (m/z): [M]+ calcd. For $C_{11}H_{17}F$: 168.1314 found: 168.1303.



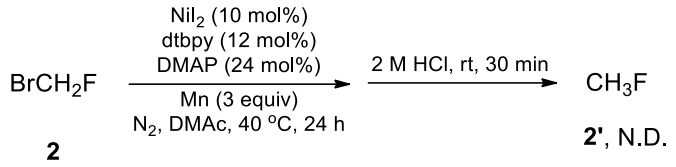
3. Direct Insertion of Bromofluoromethane (2) with Mn^0



2 **2'**, N.D.

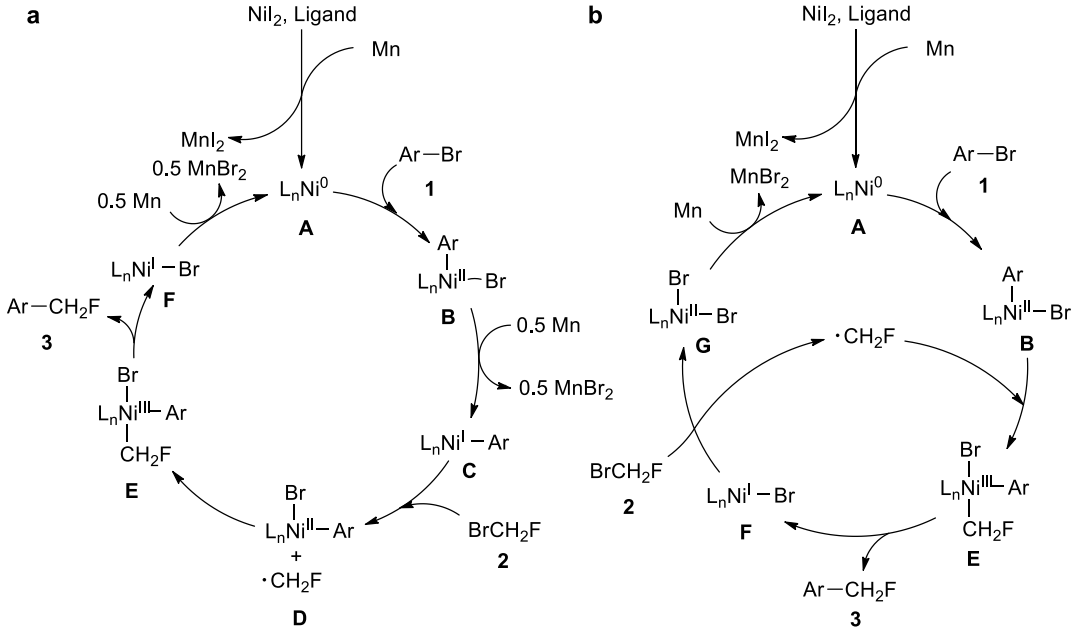
To a 5 mL of sealing tube was added Mn powder (3.0 equiv, 0.6 mmol) in air. The mixture was then added DMAc (1 mL) and **2** (2.5 equiv) under N_2 atmosphere. The tube was sealed with a Teflon lined cap and heated up into a preheated oil bath (40 ℃) for 24 h. After the mixture was cooled to room temperature, 2 M HCl (1 mL) was added via syringe and the reaction was stirred at room temperature for 30 min. No product **2'** was detected by crude ^{19}F NMR.

4. Direct Insertion of Bromofluoromethane (2) with Mn^0 at Standard Condition



To a 5 mL of sealing tube was added dtbpy (12 mol%, 0.024 mmol), DMAP (24 mol%), Mn powder (3.0 equiv) and NiI_2 (10 mol%). The mixture was then added DMAc (1 mL) and **2** (2.5 equiv) under N_2 atmosphere. The tube was sealed with a Teflon lined cap and heated up into a preheated oil bath (40 ℃) for 24 h. After the mixture was cooled to room temperature, 2 M HCl (1 mL) was added via syringe and the reaction was stirred at room temperature for 30 min. No product **2'** was detected by crude ^{19}F NMR.

5. Proposed mechanism: a) Radical-cage-rebound process; b) A radical chain process



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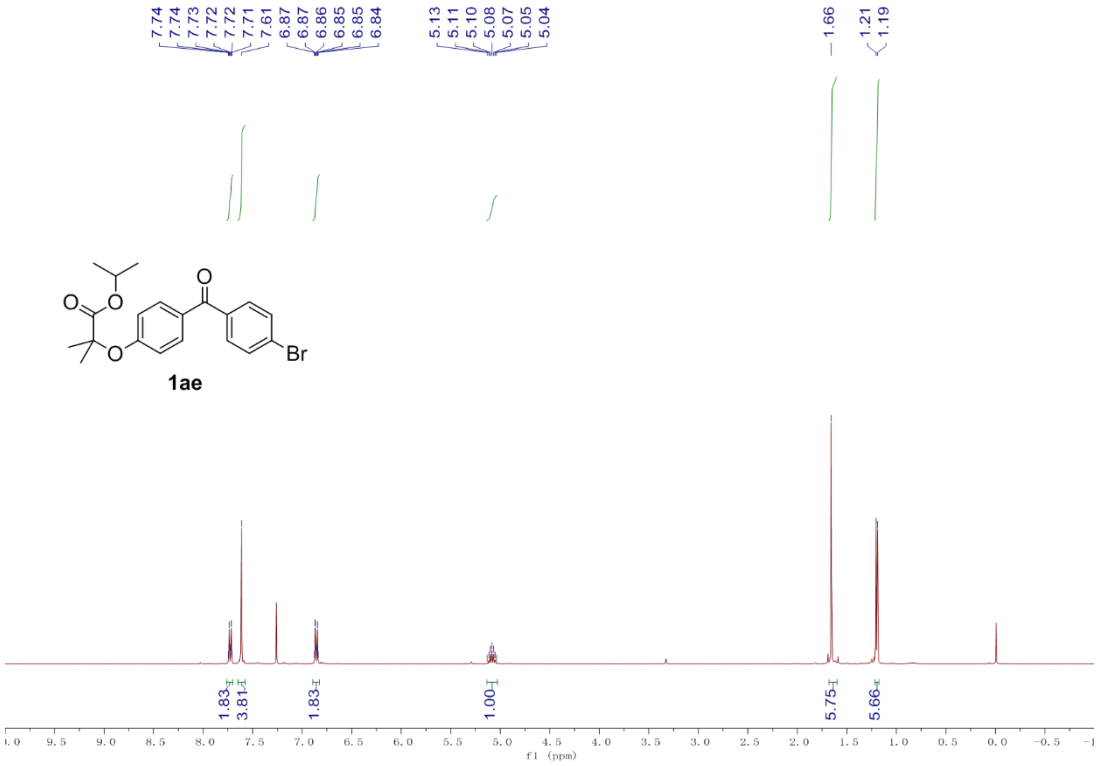
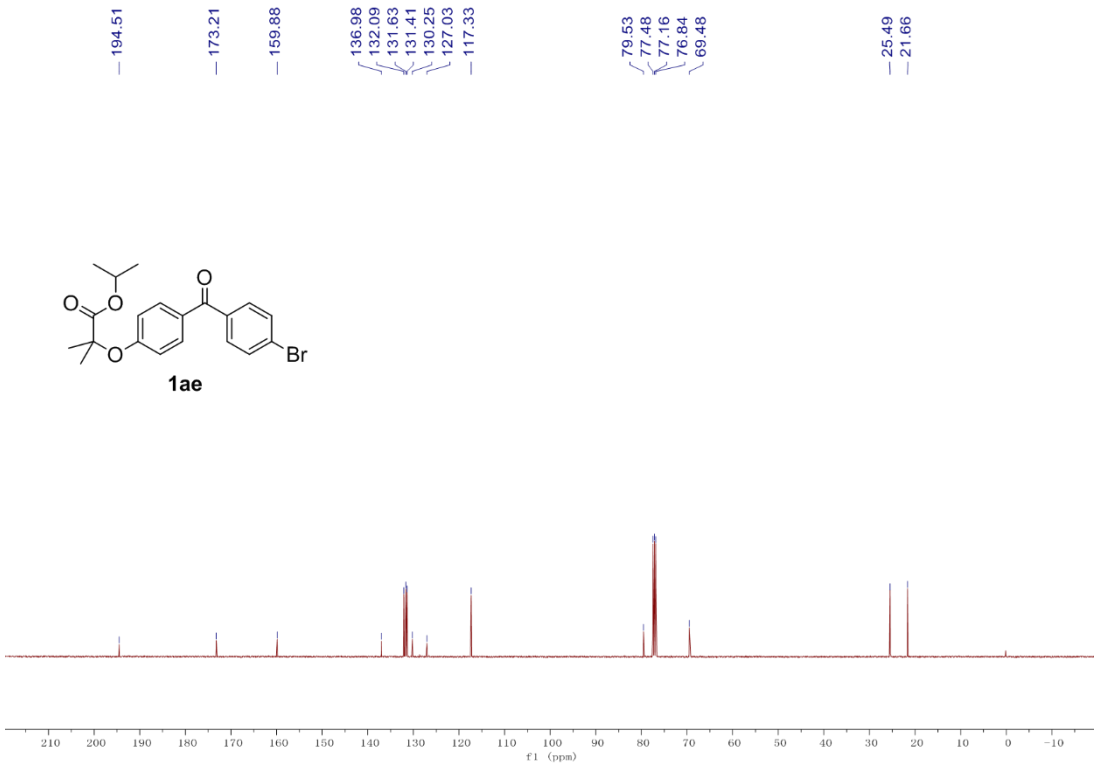
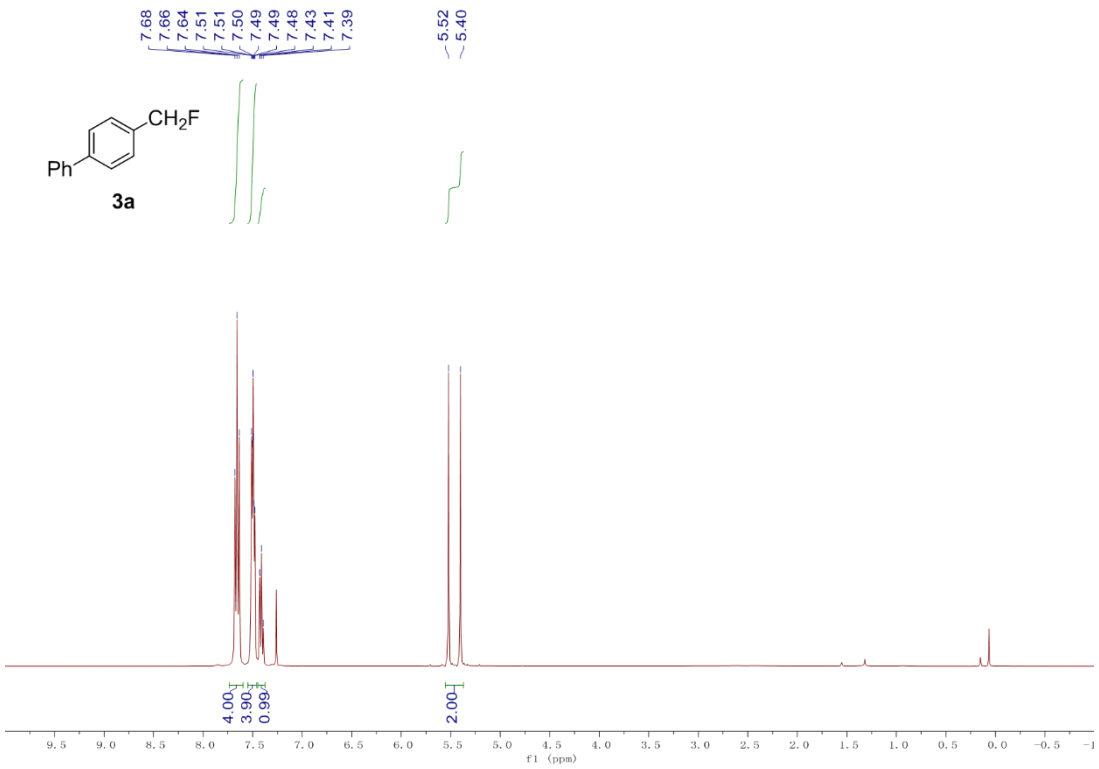
^{1}H, ^{19}F, and ^{13}C NMR Spectra



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5.40
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Ph
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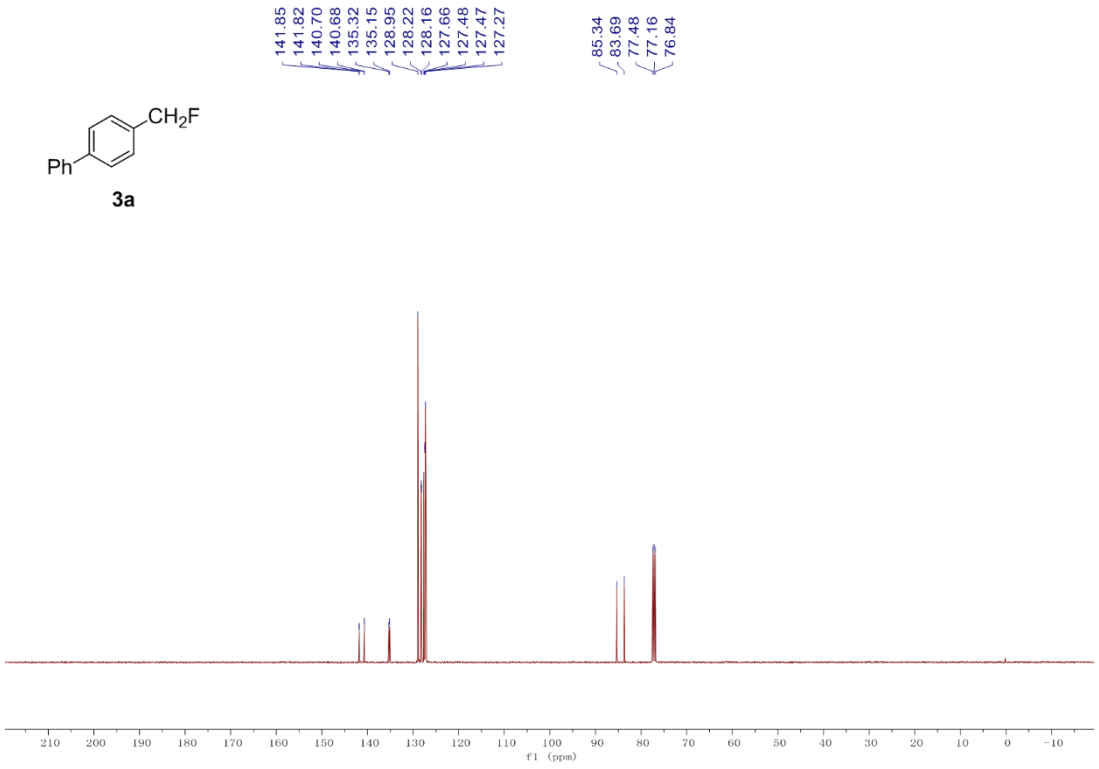
0.99
2.00
f1 (ppm)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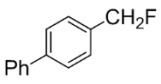
CH2F
Ph
3a
f1 (ppm)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Ph

3a

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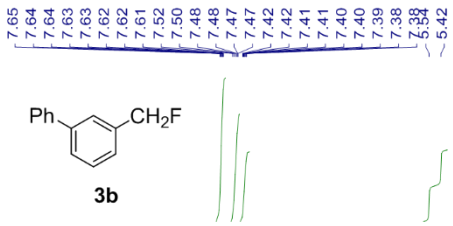
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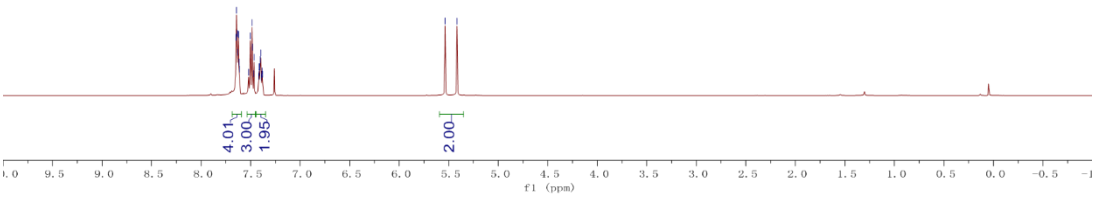
7.38
5.42

Ph
CH2F

3b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2.00
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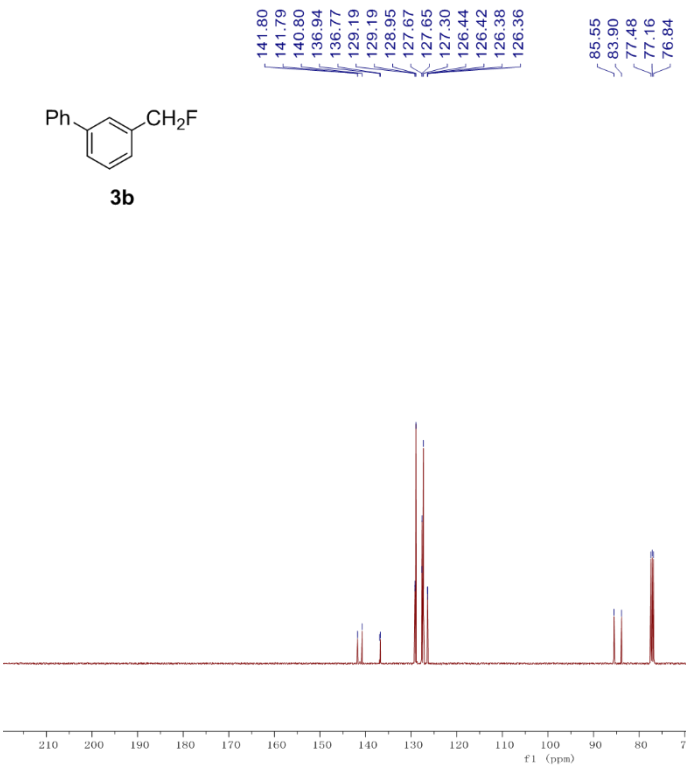
f1 (ppm)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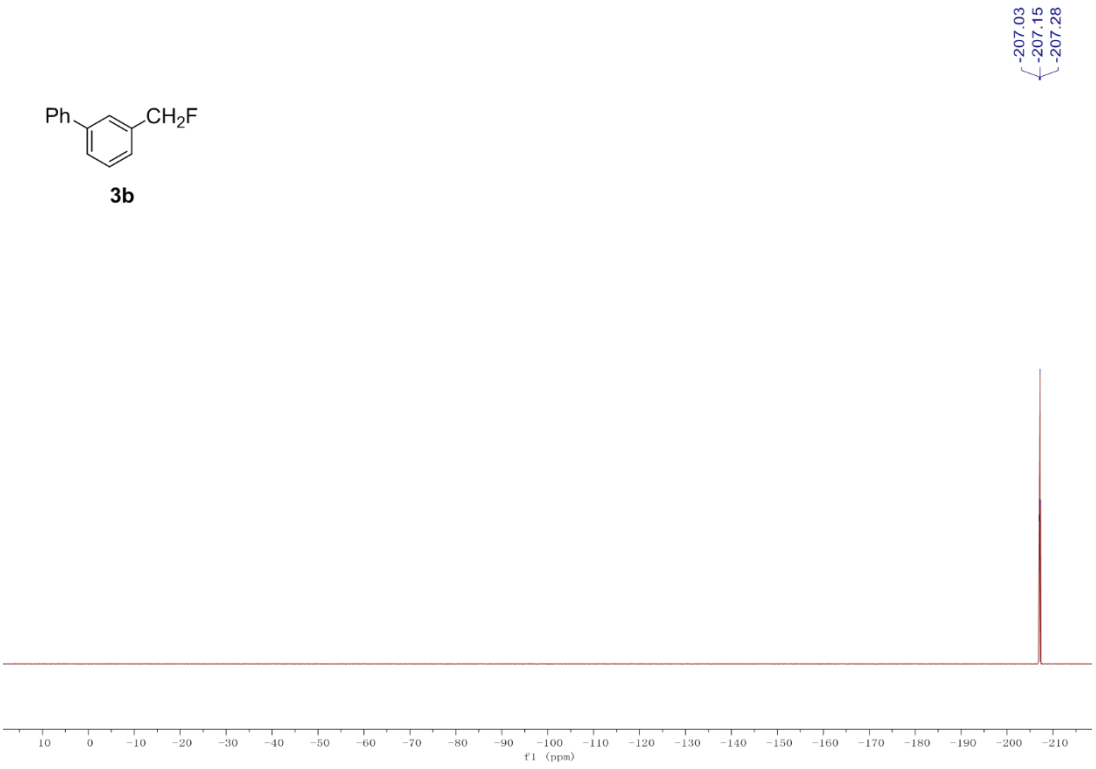
Ph
CH2F
3b
f1 (ppm)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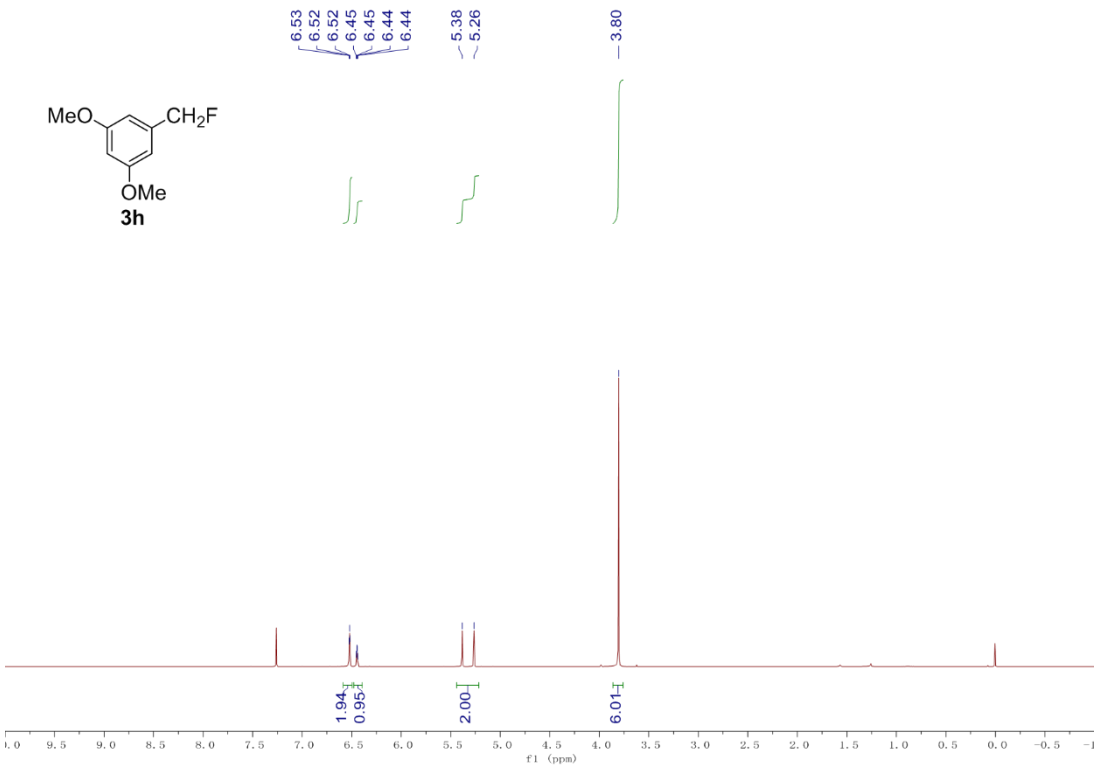
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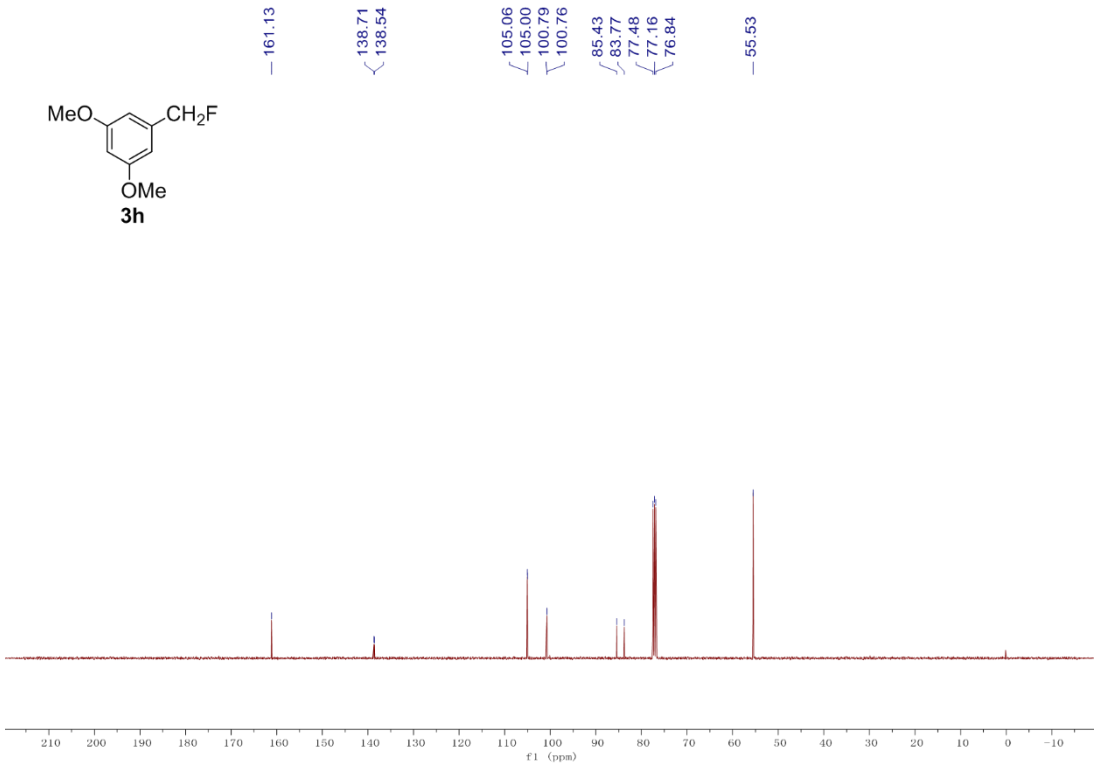
6.01
f1 (ppm)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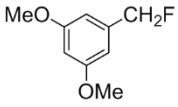
OMe
3h
f1 (ppm)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OMe

3h


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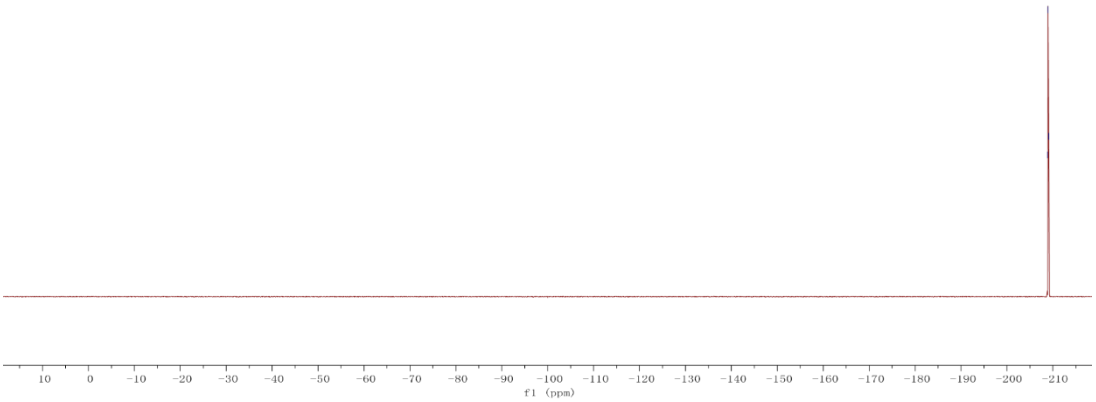
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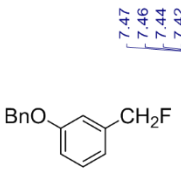
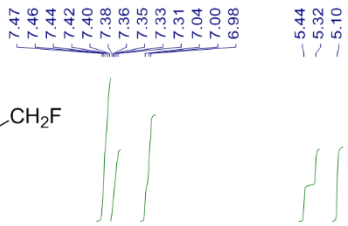

BnO
CH2F

3i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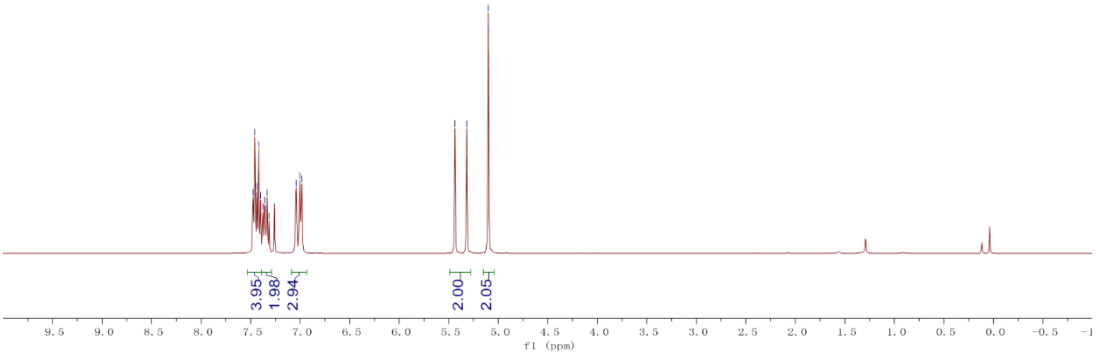
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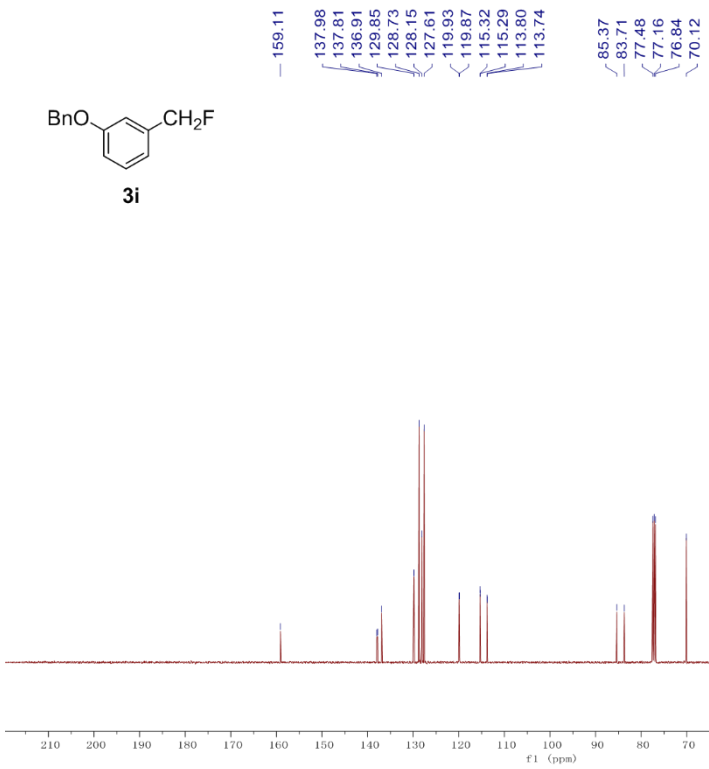
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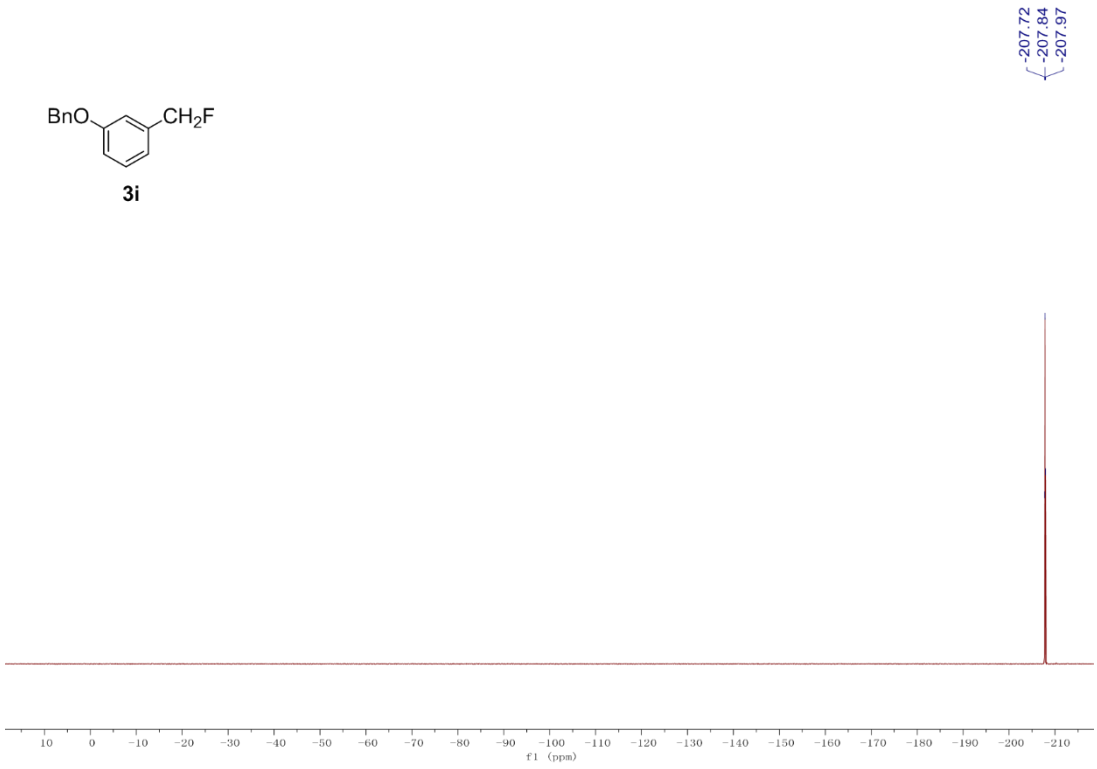
f1 (ppm)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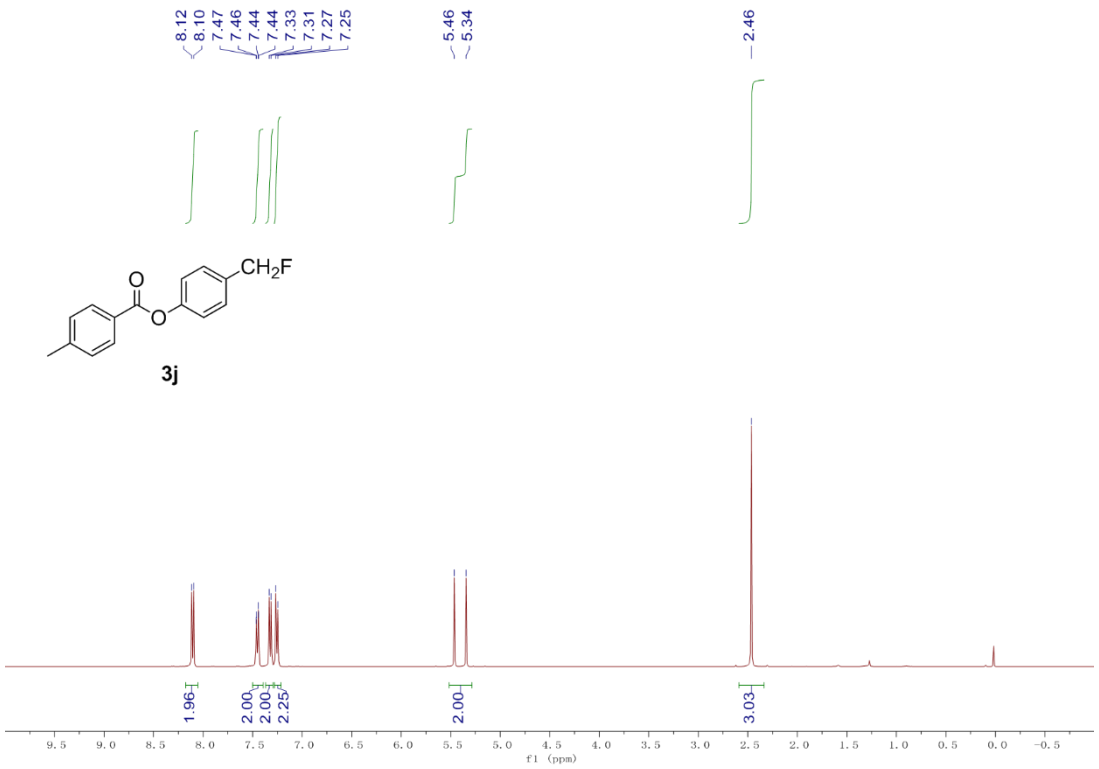
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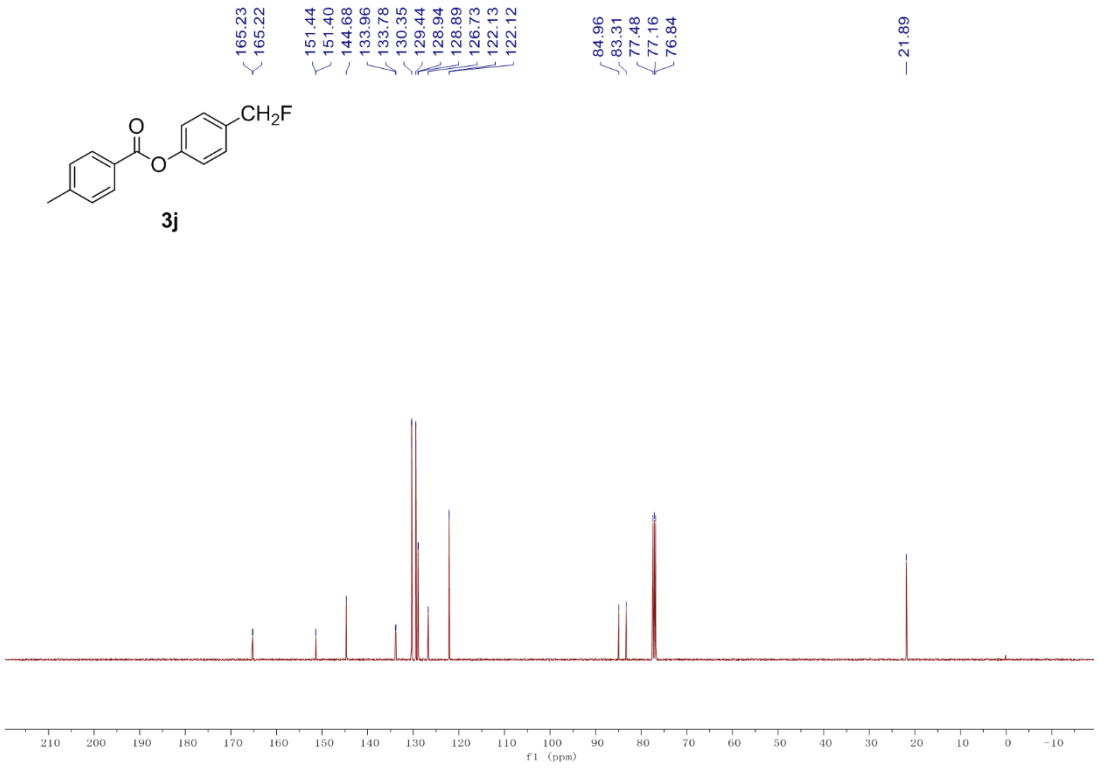
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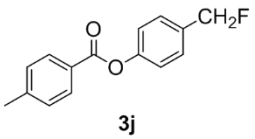
f1 (ppm)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3j

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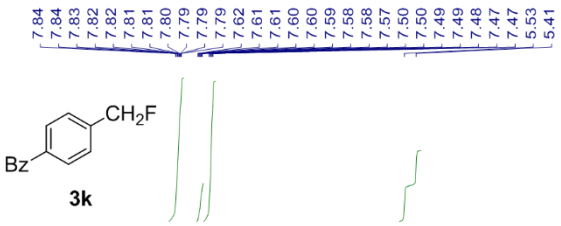
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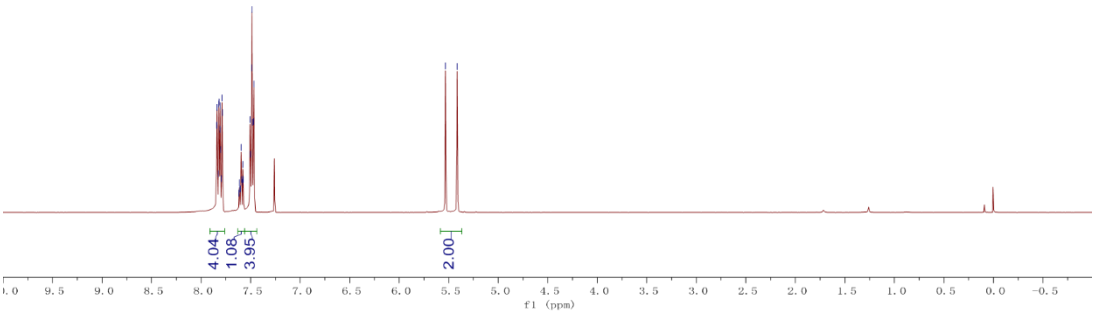
Bz

3k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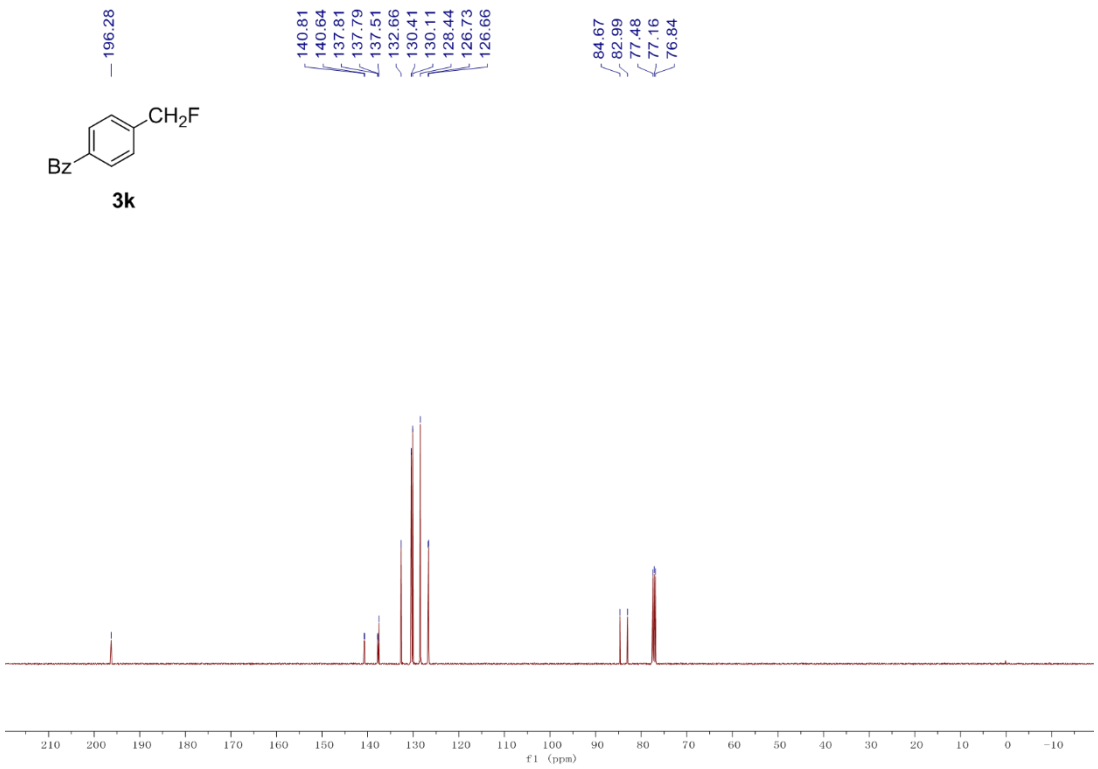
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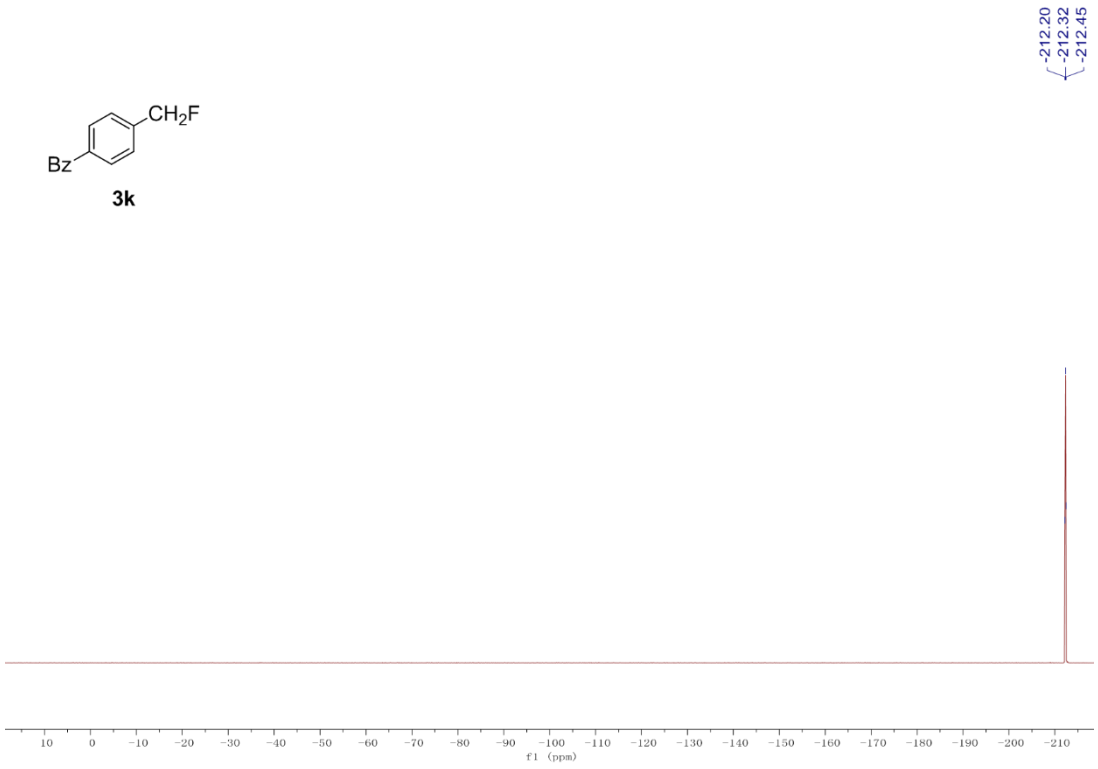
76.84
CH2F
Bz
3k
f1 (ppm)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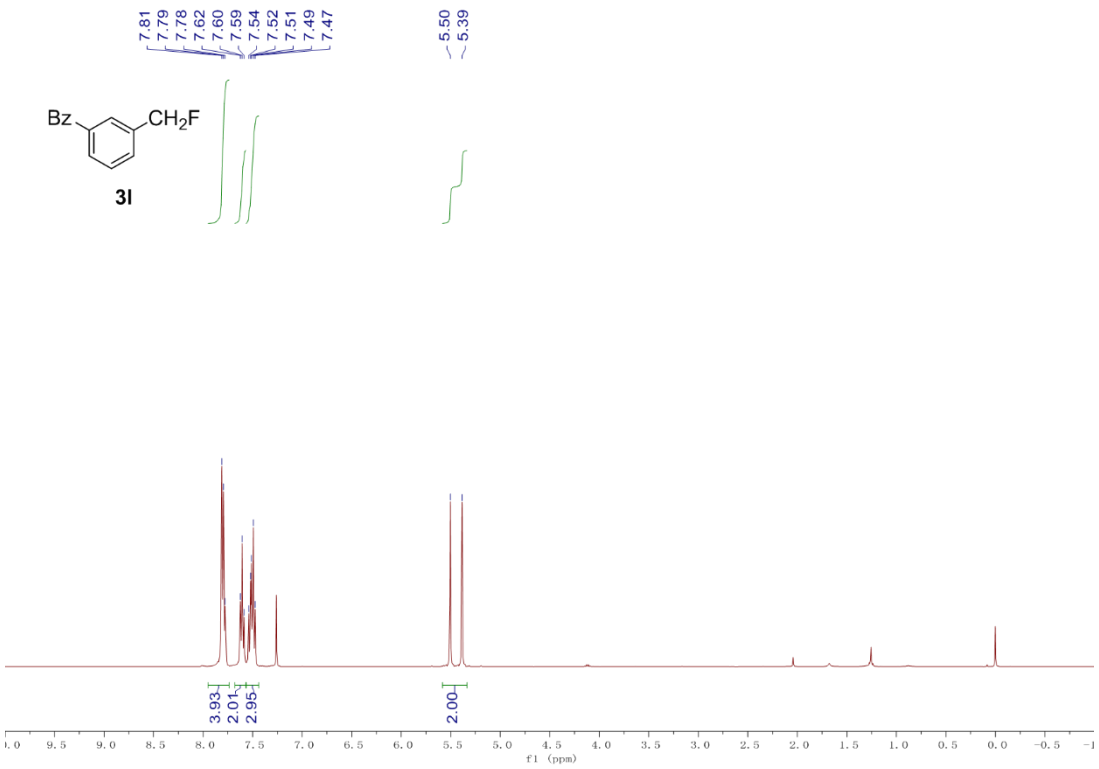
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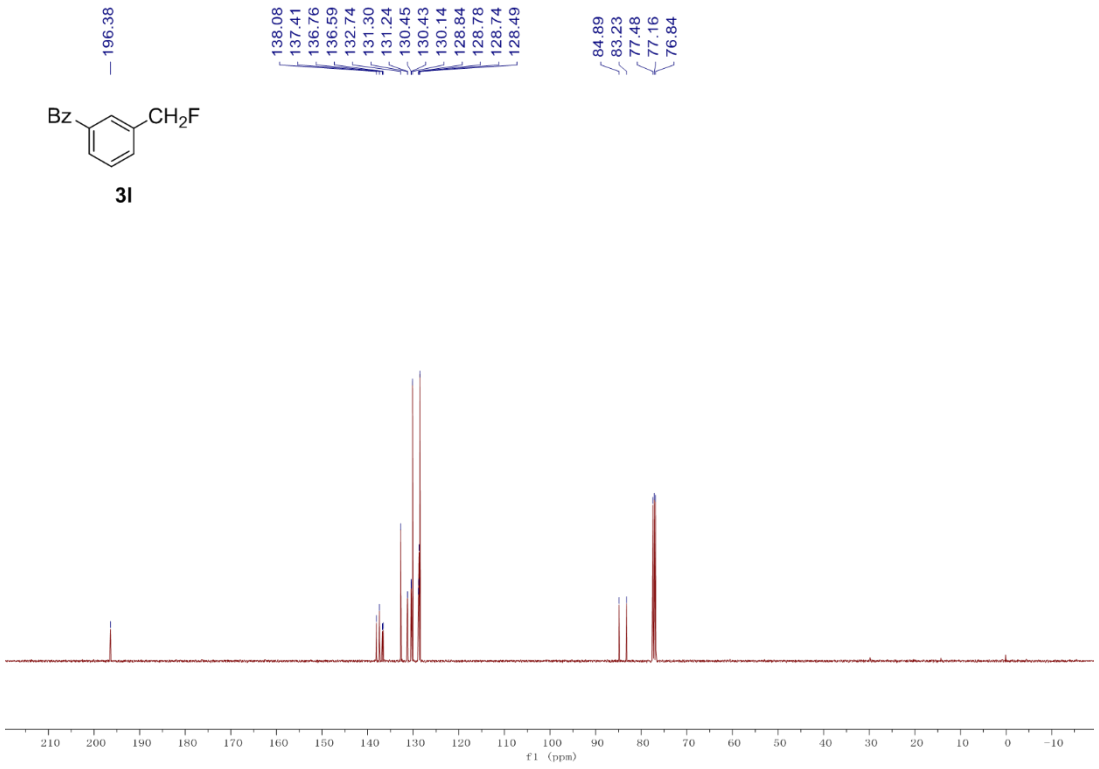
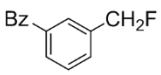
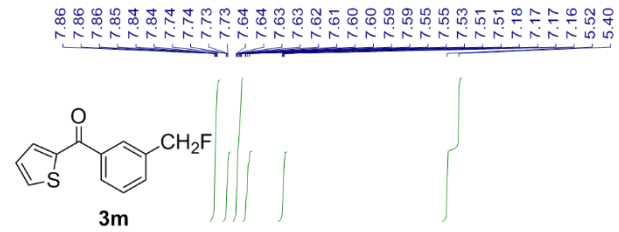

196.38
138.08
137.41
136.76
136.59
132.74
131.30
131.24
130.45
130.43
130.14
128.84
128.78
128.74
128.49
84.89
83.23
77.48
77.16
76.84
Bz
CH2F
3l
f1 (ppm)

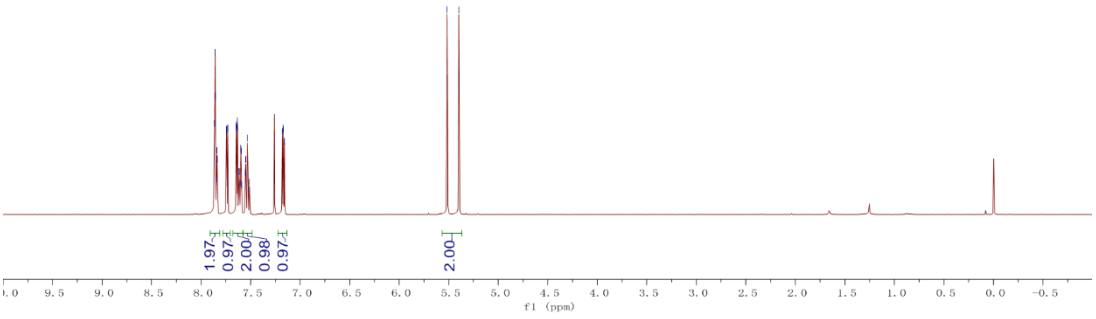

Bz
CH2F

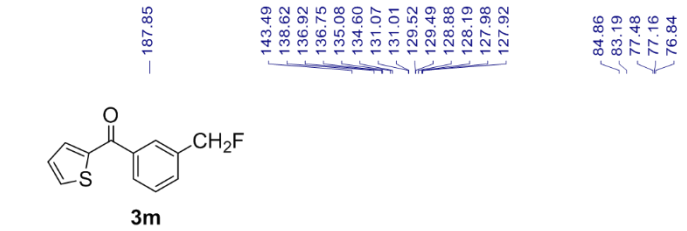
3l

-208.79
-208.92
-209.04
f1 (ppm)

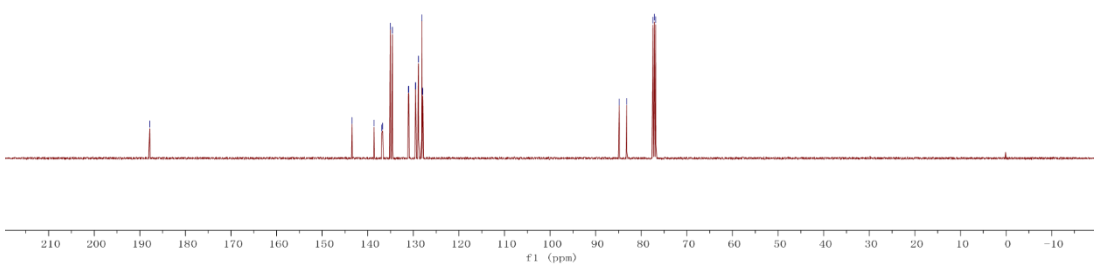

7.86
7.86
7.86
7.85
7.84
7.84
7.74
7.74
7.73
7.73
7.64
7.64
7.63
7.63
7.62
7.61
7.60
7.60
7.59
7.59
7.55
7.55
7.53
7.51
7.51
7.18
7.17
7.17
7.16
5.52
5.40
O
CH2F
S

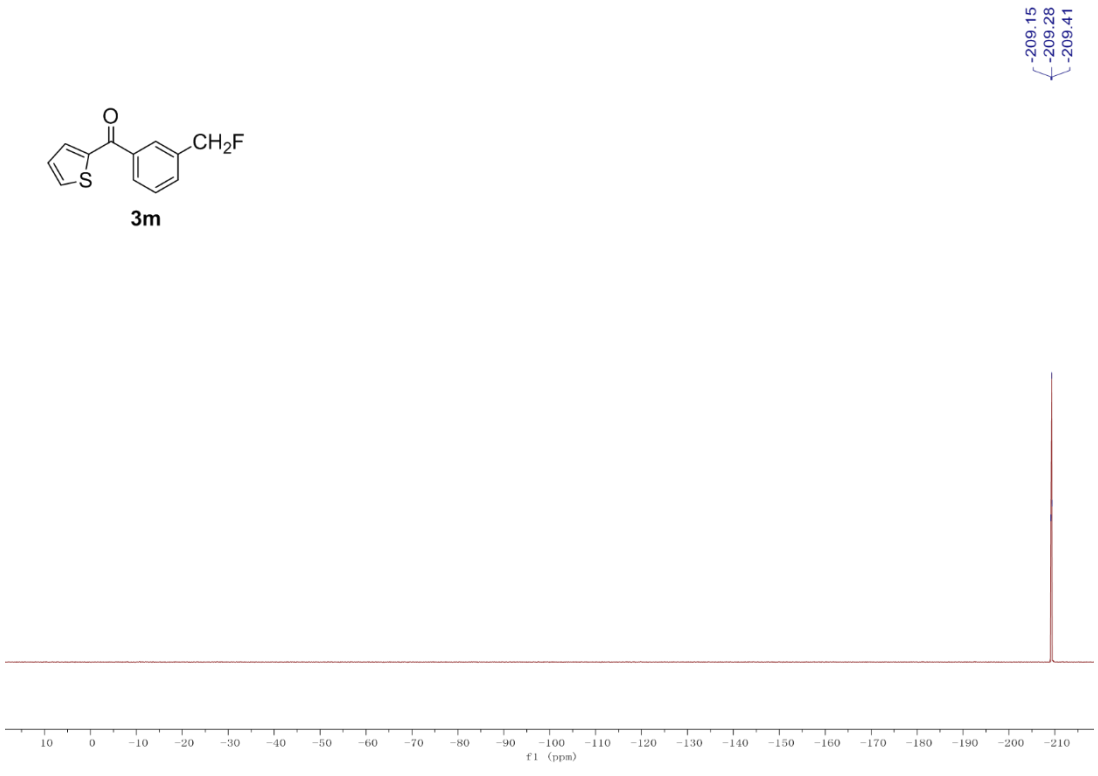
3m


1.97
0.97
2.00
0.98
0.97
2.00
f1 (ppm)

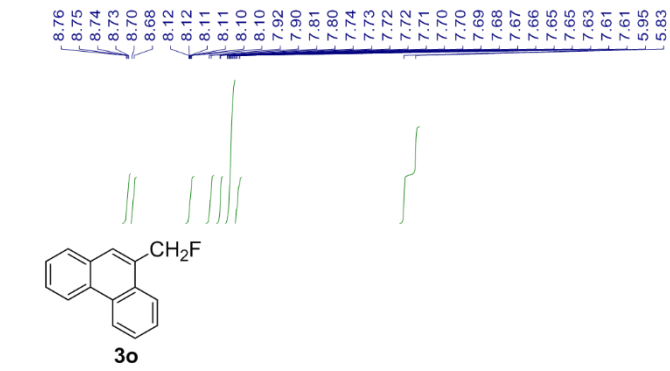

187.85
143.49
138.62
136.92
136.75
135.08
134.60
131.07
131.01
129.52
129.49
128.88
128.19
127.98
127.92
84.86
83.19
77.48
77.16
76.84
O
S
CH2F

3m

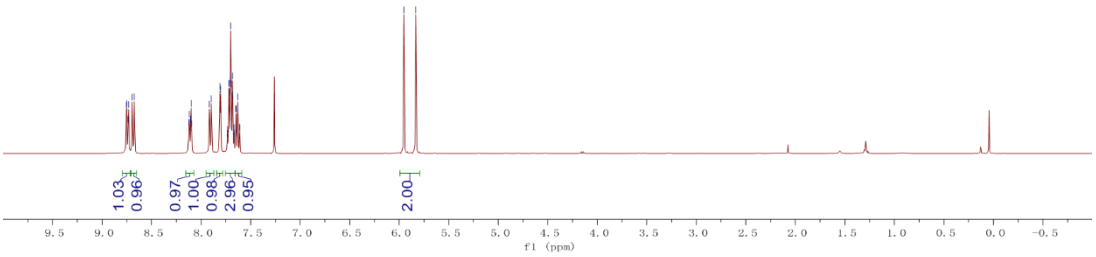

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

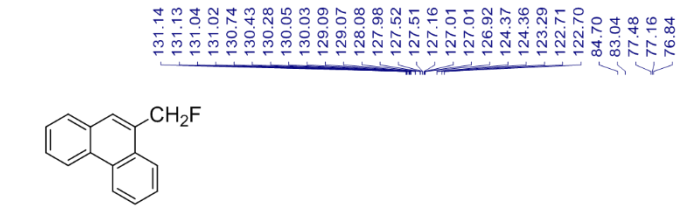

-209.15
-209.28
-209.41
O
S
CH2F
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

3m

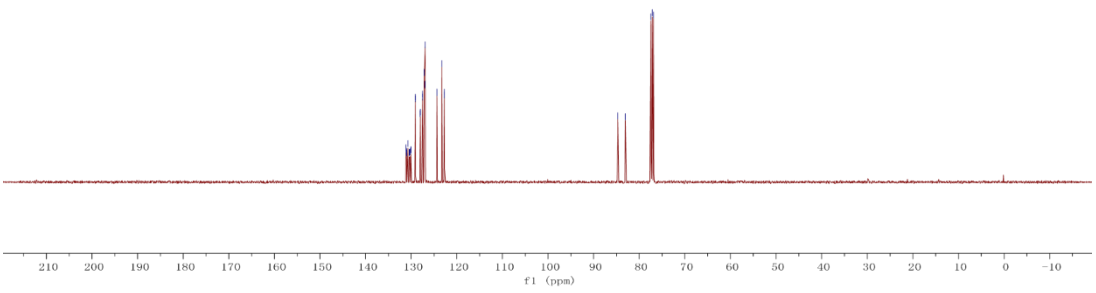

8.76
8.75
8.74
8.73
8.70
8.68
8.12
8.12
8.11
8.11
8.10
8.10
7.92
7.90
7.81
7.80
7.74
7.73
7.72
7.72
7.71
7.70
7.70
7.69
7.68
7.67
7.66
7.65
7.65
7.63
7.61
7.61
5.95
5.83
CH2F

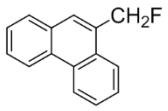
3o


1.03
0.96
0.97
1.00
0.98
2.96
0.95
2.00
f1 (ppm)


131.14
131.13
131.04
131.02
130.74
130.43
130.28
130.05
130.03
129.09
129.07
128.08
127.98
127.52
127.51
127.16
127.01
127.01
126.92
124.37
124.36
123.29
122.71
122.70
84.70
83.04
77.48
77.16
76.84
CH2F

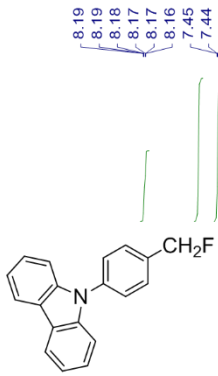
3o


f1 (ppm)


CH2F

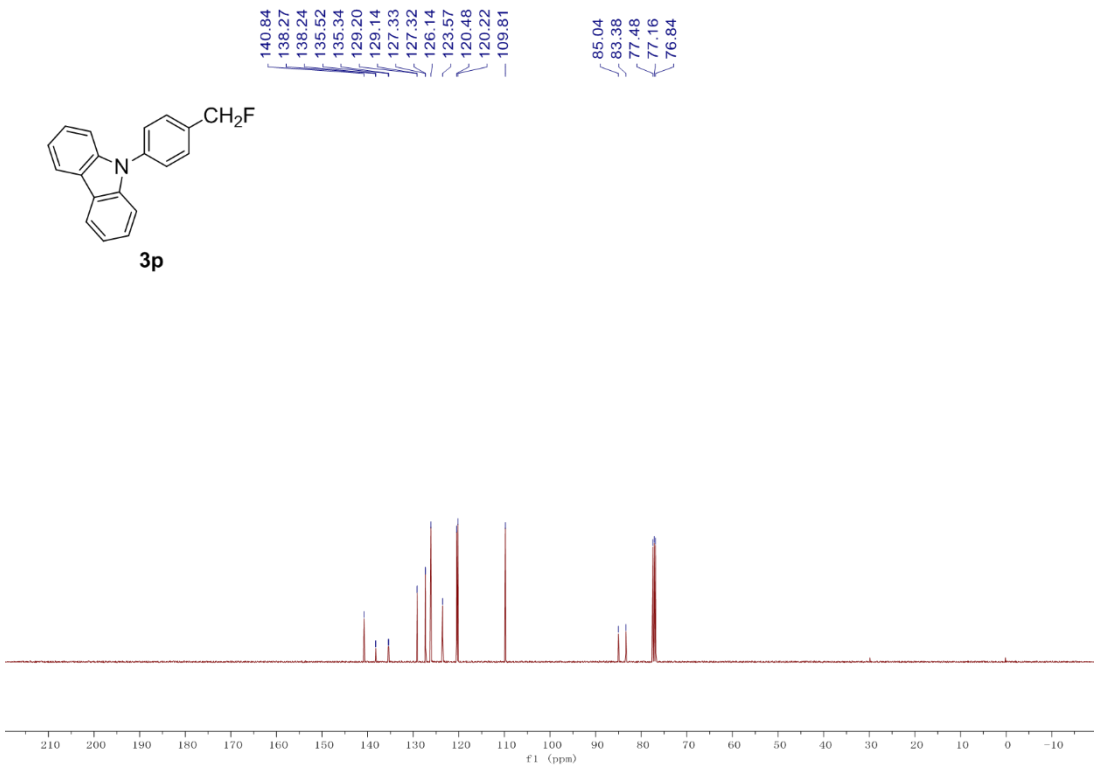
3o

-207.77
-207.89
-208.02
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


CH2F
N

3p

8.19
8.19
8.18
8.17
8.17
8.16
7.45
7.44
7.44
7.43
7.43
7.36
7.34
7.34
7.33
7.32
7.31
7.30
7.29
5.58
5.46
1.97
3.99
4.00
2.00
2.00
f1 (ppm)


140.84
138.27
138.24
135.52
135.34
129.20
129.14
127.33
127.32
126.14
123.57
120.48
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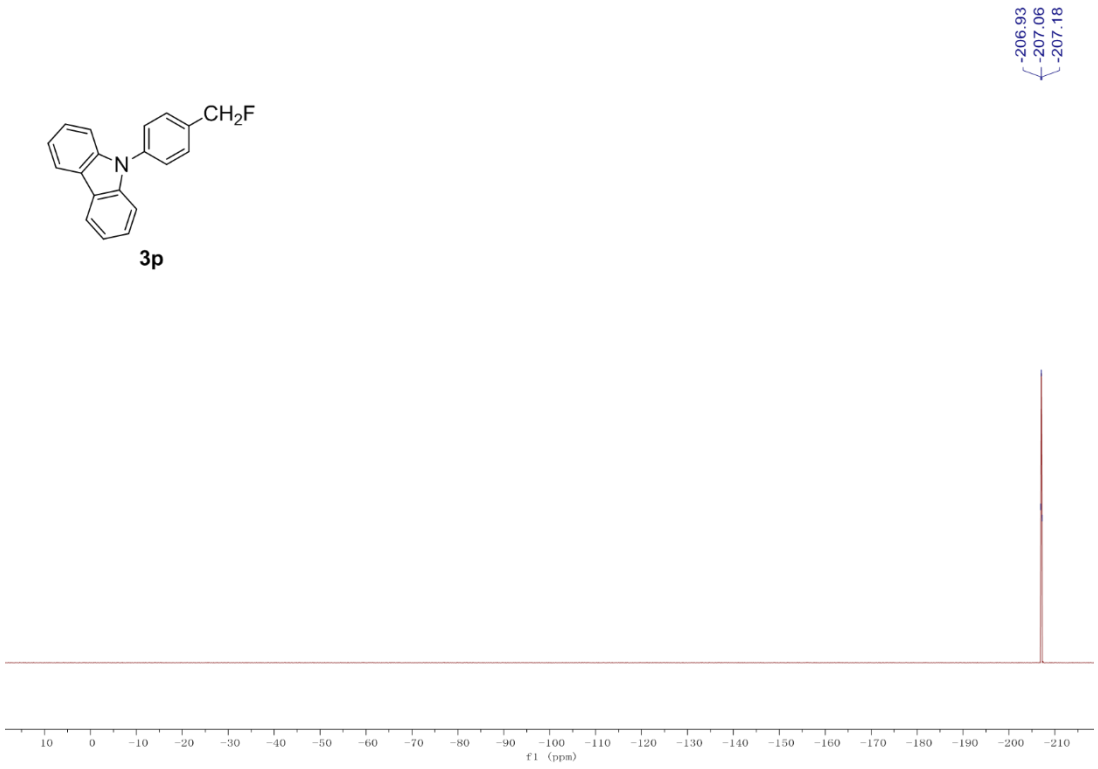
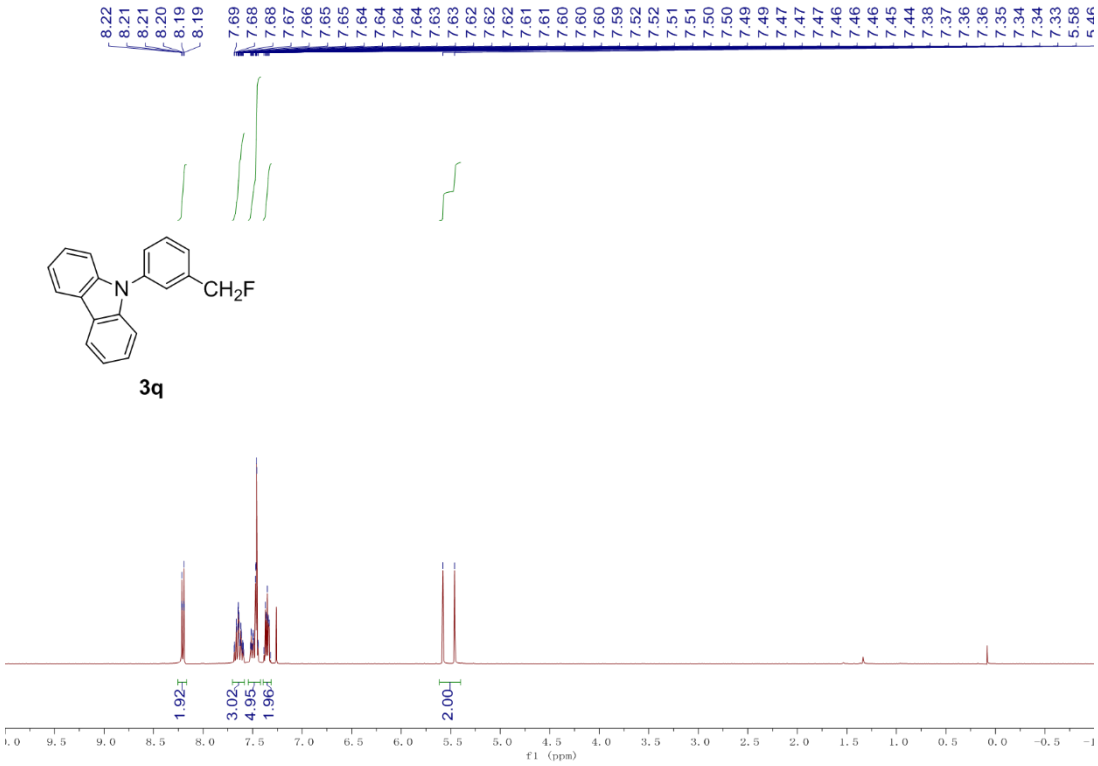
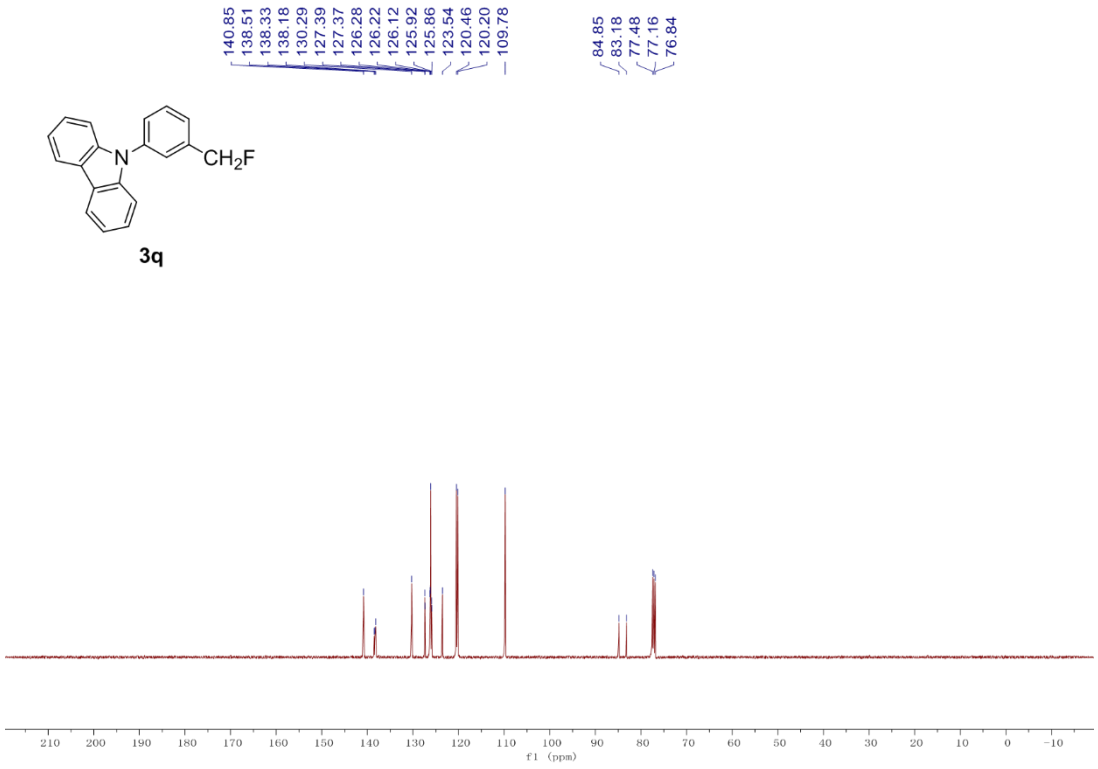
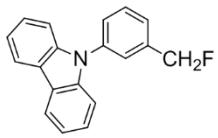
85.04
83.38
77.48
77.16
76.84
CH2F
N
3p
f1 (ppm)


-206.93
-207.06
-207.18
CH2F
N
3p
f1 (ppm)

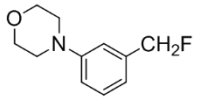

8.22 8.21 8.21 8.20 8.19 8.19
7.69 7.68 7.68 7.67 7.66 7.65 7.65 7.64 7.64 7.64 7.64 7.63 7.63 7.62 7.62 7.62 7.61 7.61 7.60 7.60 7.60 7.59 7.52 7.52 7.51 7.51 7.50 7.50 7.49 7.49 7.47 7.47 7.47 7.46 7.46 7.46 7.45 7.44 7.38 7.37 7.36 7.36 7.35 7.34 7.34 7.33 5.58
N
CH2F
3q
1.92
3.02
4.95
1.96
2.00
f1 (ppm)


140.85 138.51 138.33 138.18 130.29 127.39 127.37 126.28 126.22 126.12 125.92 125.86 123.54 120.46 120.20 109.78
84.85 83.18 77.48 77.16 76.84
N
CH2F
3q
f1 (ppm)


N
CH2F

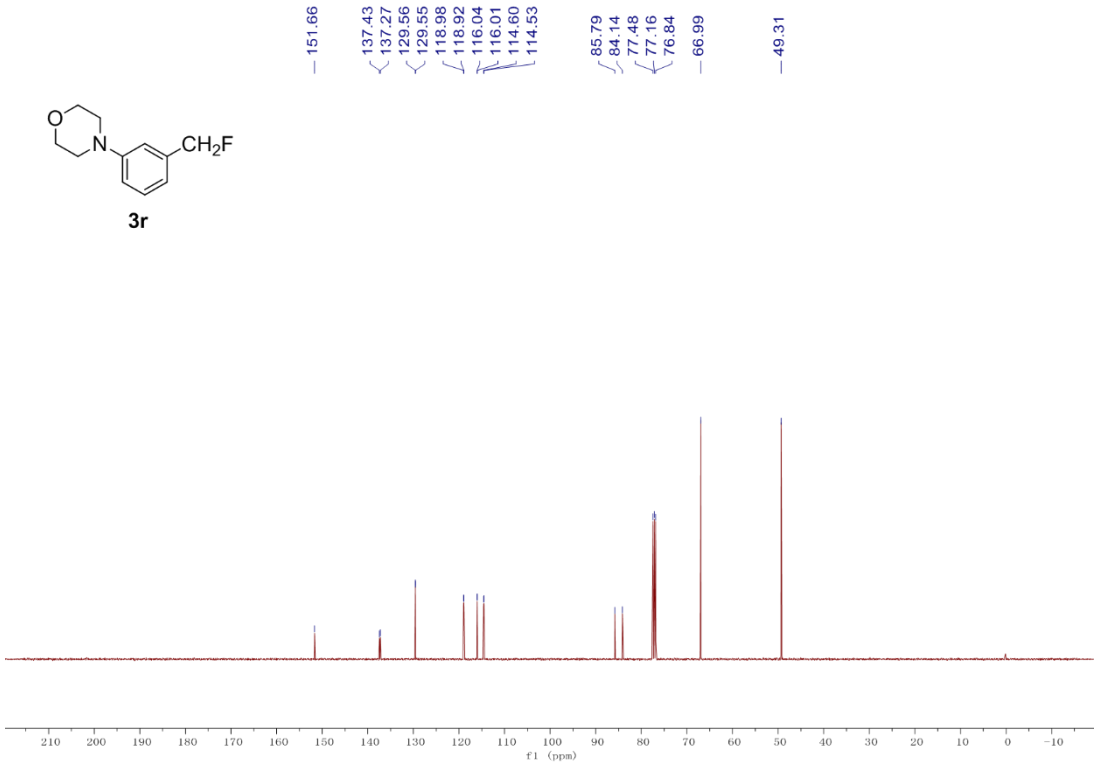
3q

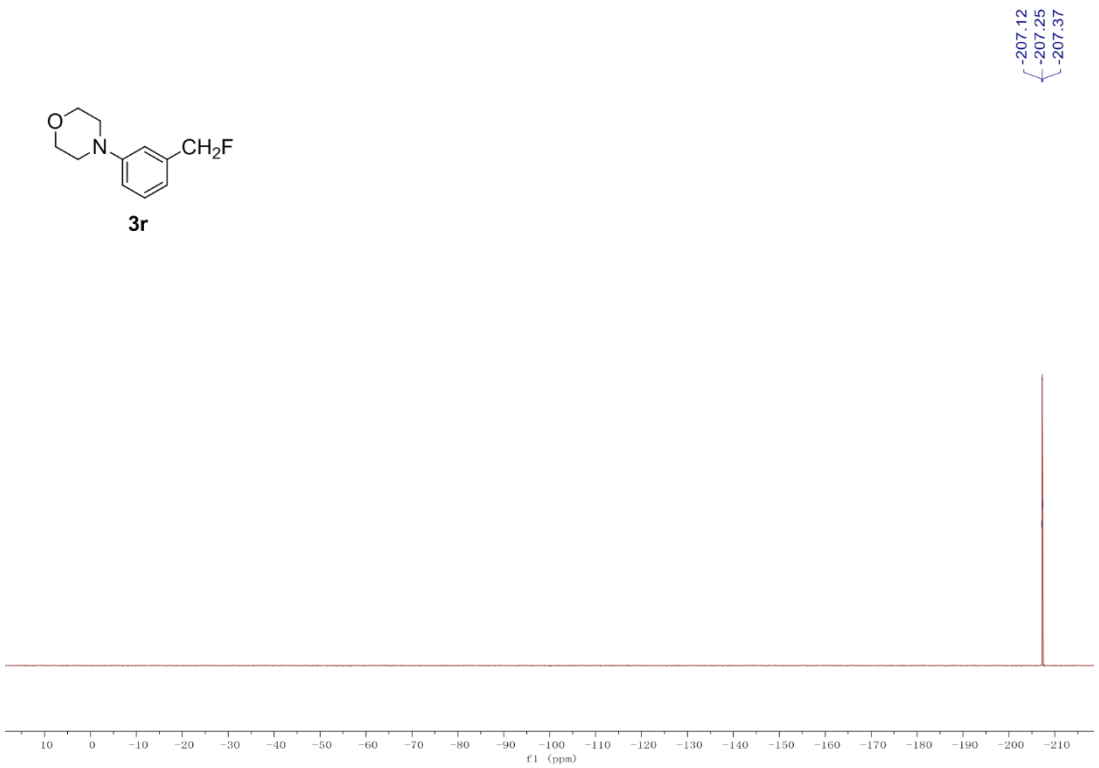
-208.69
-208.81
-208.94
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

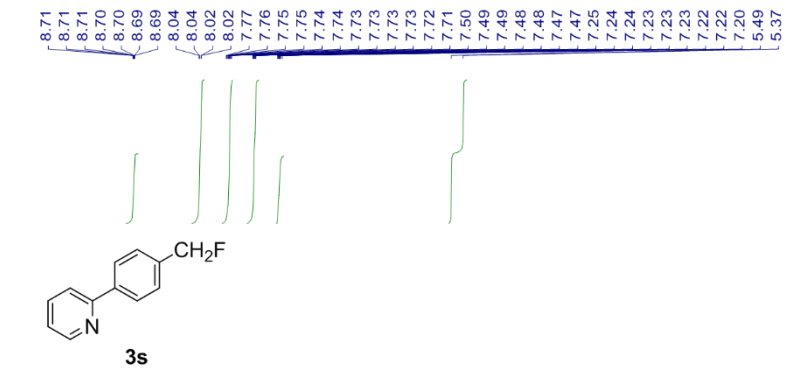

O
N
CH2F

3r

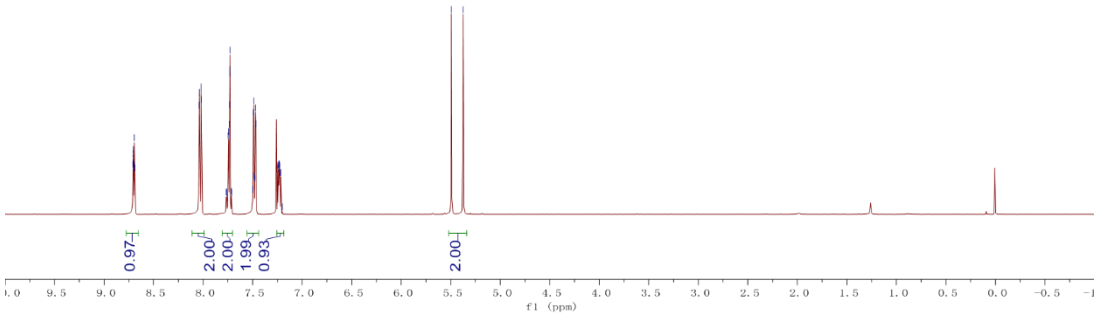
7.32
7.30
7.28
6.94
6.94
6.93
6.93
6.93
6.92
6.91
6.90
6.90
6.89
6.89
6.89
6.88
6.88
6.87
6.87
5.41
5.29
3.88
3.87
3.87
3.86
3.86
3.20
3.19
3.18
3.18
3.17
1.00
3.01
2.00
4.09
4.10
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

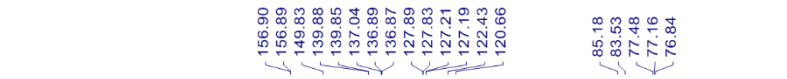

151.66
137.43
137.27
129.56
129.55
118.98
118.92
116.04
116.01
114.60
114.53
85.79
84.14
77.48
77.16
76.84
66.99
49.31
O
N
CH2F
3r
f1 (ppm)

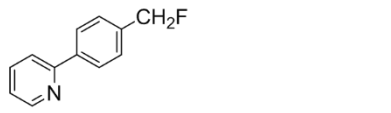

-207.12
-207.25
-207.37
O
N
CH2F
3r
f1 (ppm)


8.71
8.71
8.71
8.70
8.70
8.69
8.69
8.04
8.04
8.02
8.02
7.77
7.76
7.75
7.75
7.74
7.74
7.73
7.73
7.73
7.72
7.71
7.50
7.49
7.49
7.48
7.48
7.47
7.47
7.25
7.24
7.24
7.23
7.23
7.22
7.22
7.20
5.49
5.37
CH2F
N

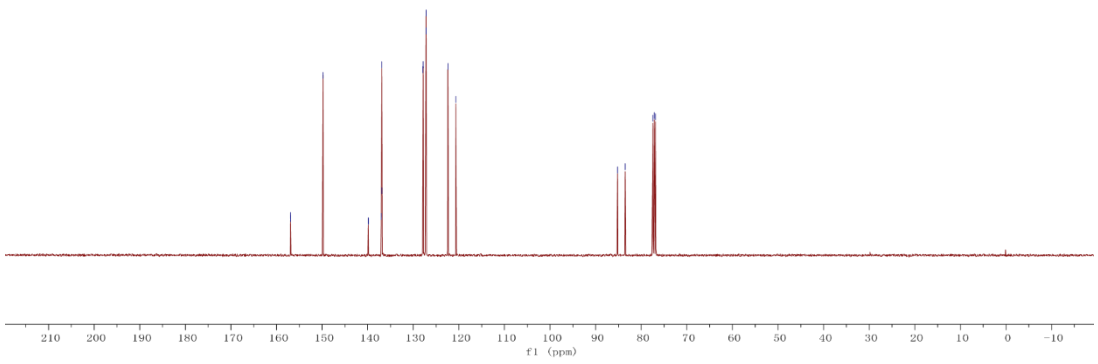
3s

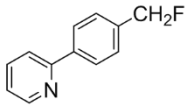

0.97
2.00
2.00
1.99
0.93
2.00
f1 (ppm)


156.90
156.89
149.83
139.88
139.85
137.04
136.89
136.87
127.89
127.83
127.21
127.19
122.43
120.66
85.18
83.53
77.48
77.16
76.84


CH2F
N

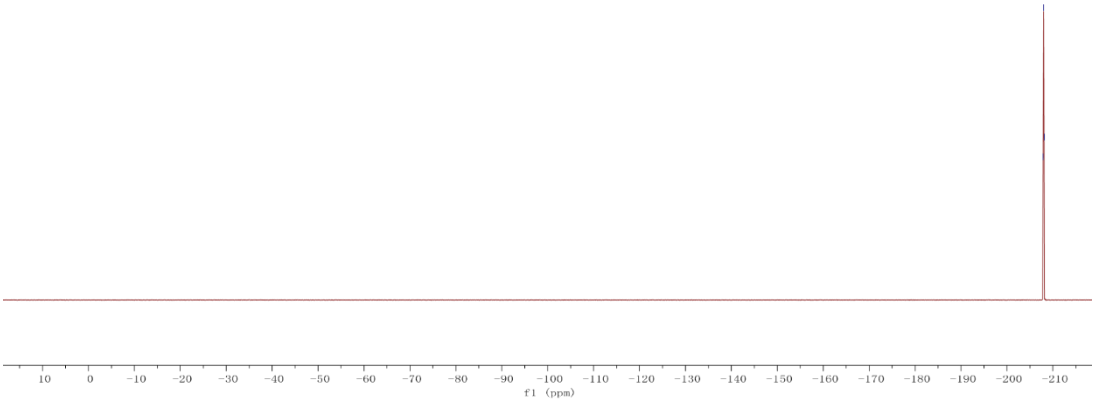
3s

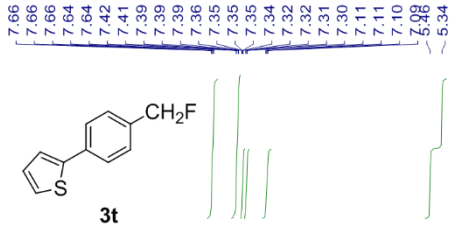

f1 (ppm)


CH2F
N

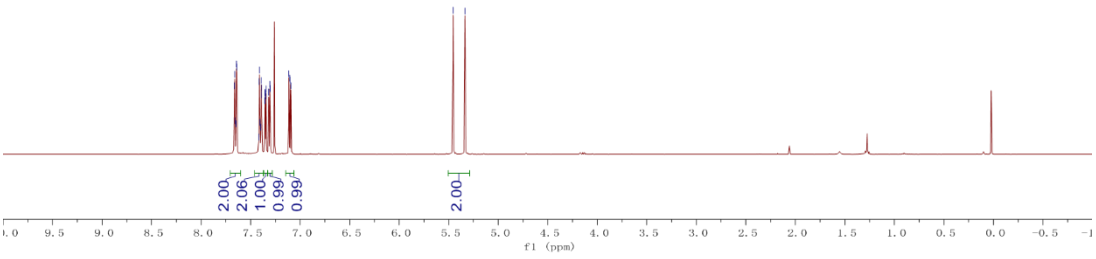
3s

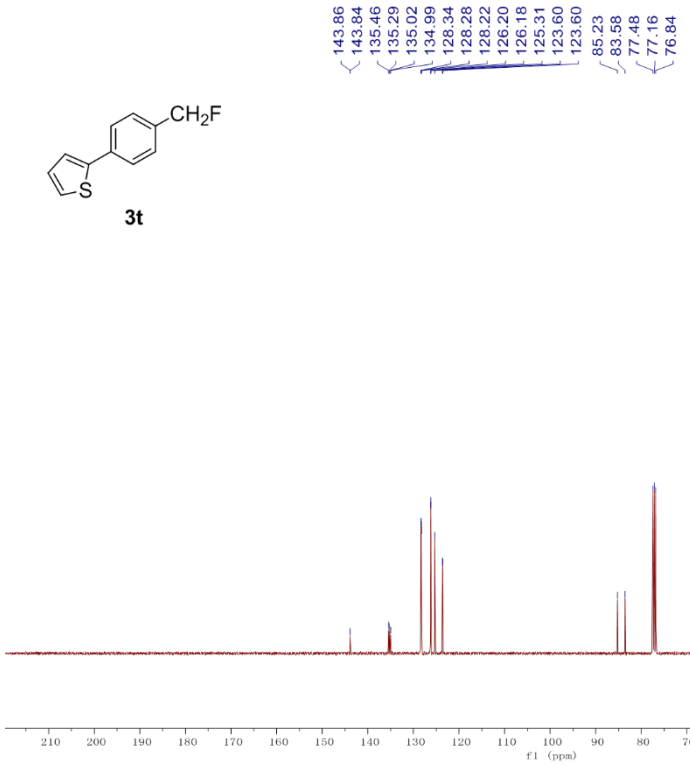

-207.87
-208.00
-208.13

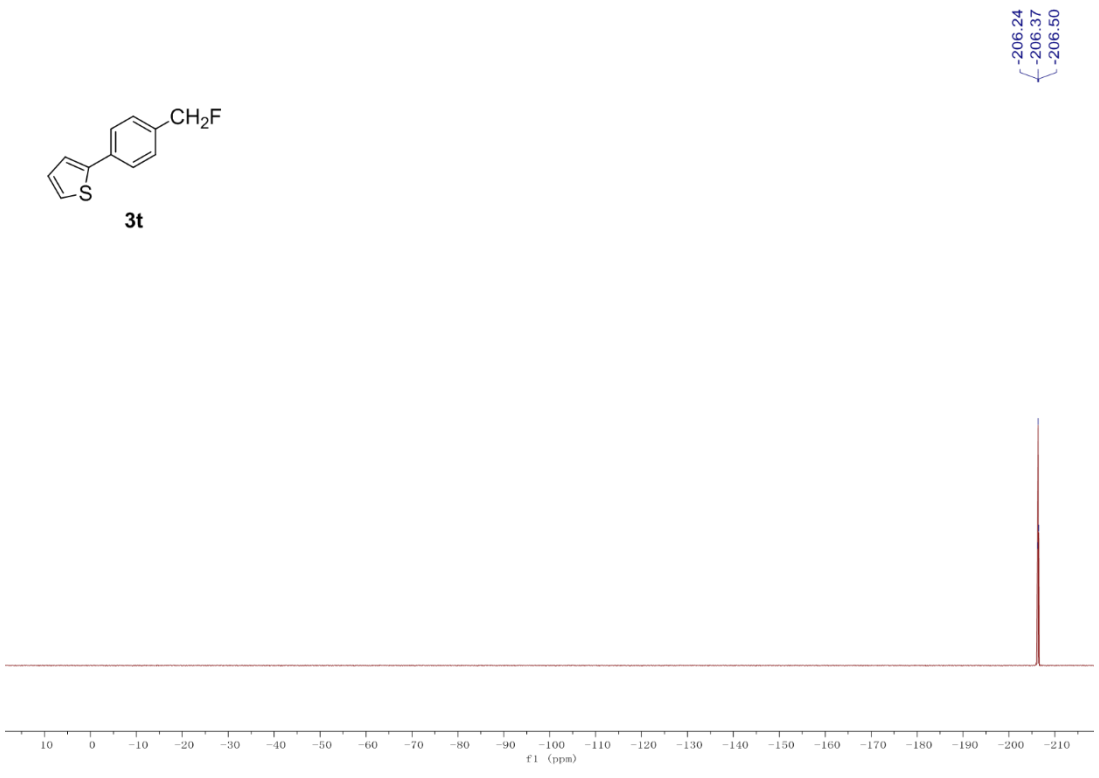

10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

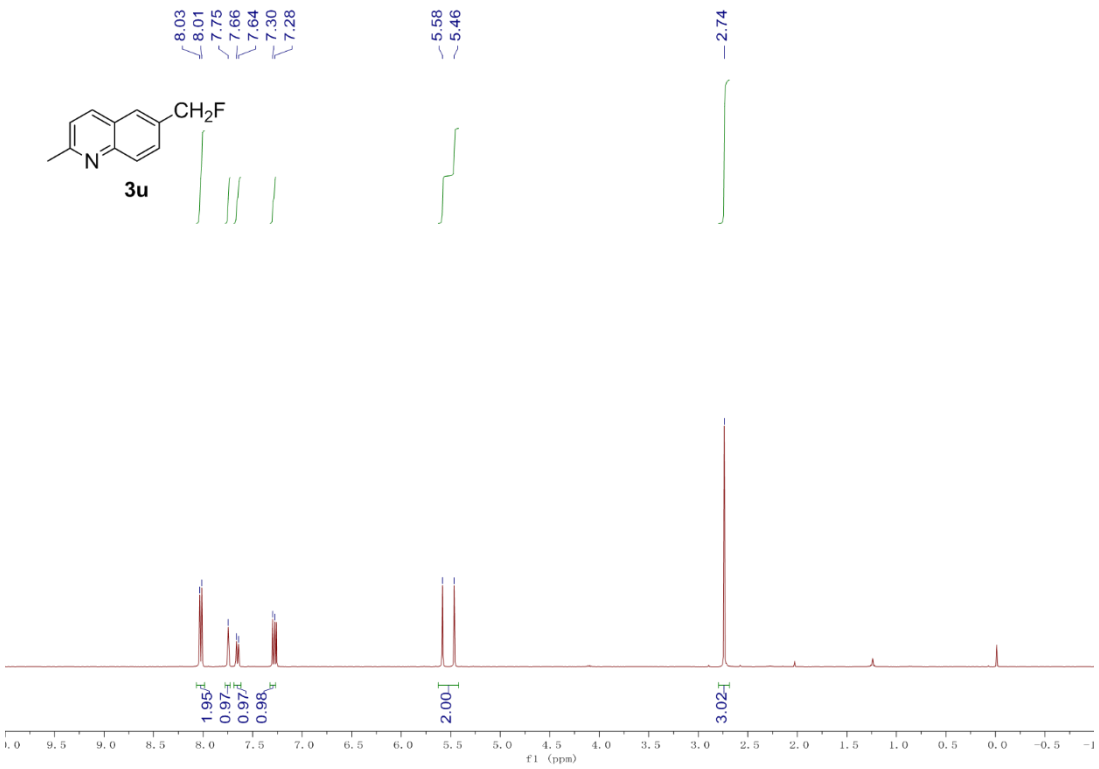

7.66
7.66
7.66
7.64
7.64
7.42
7.41
7.39
7.39
7.39
7.36
7.35
7.35
7.35
7.34
7.32
7.32
7.31
7.30
7.11
7.11
7.10
7.09
5.48
5.34
CH2F
S

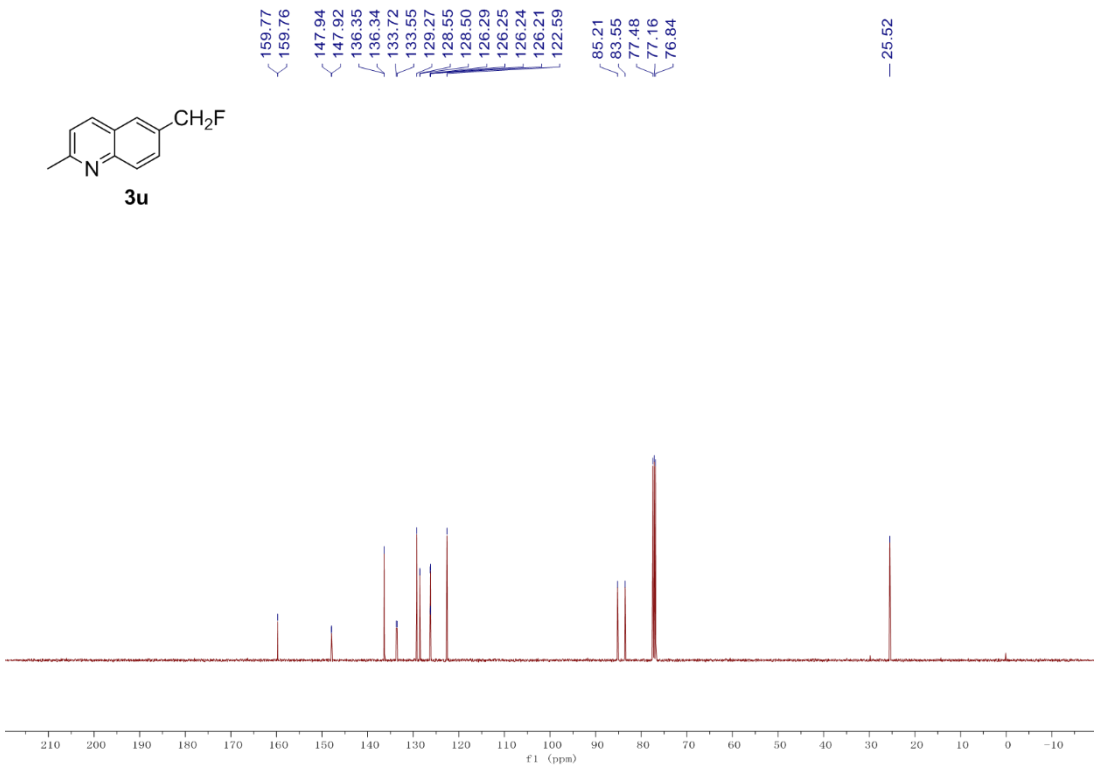
3t

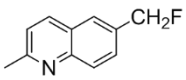

2.00
2.06
1.00
0.99
0.99
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


143.86
143.84
135.46
135.29
135.02
134.99
128.34
128.28
128.22
126.20
126.18
125.31
123.60
123.60
85.23
83.58
77.48
77.16
76.84
CH2F
S
3t
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)


-206.24
-206.37
-206.50
CH2F
S
3t
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

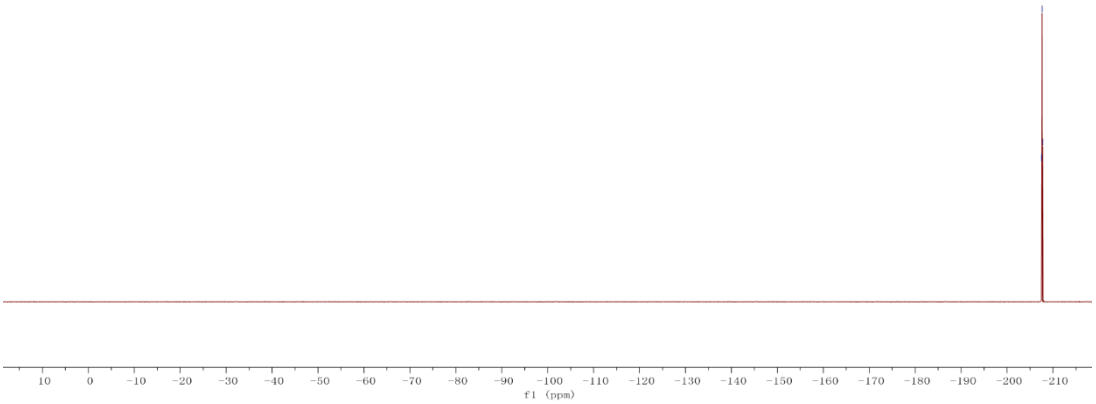

8.03
8.01
7.75
7.66
7.64
7.30
7.28
5.58
5.46
2.74
CH2F
N
3u
1.95
0.97
0.97
0.98
2.00
3.02
f1 (ppm)

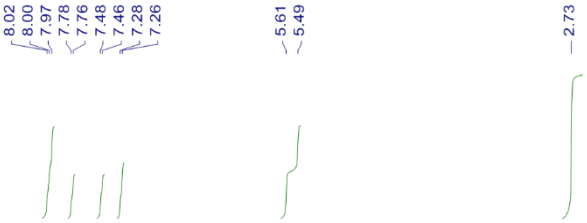

159.77
159.76
147.94
147.92
136.35
136.34
133.72
133.55
129.27
128.55
128.50
126.29
126.25
126.24
126.21
122.59
85.21
83.55
77.48
77.16
76.84
25.52
CH2F
N
3u
f1 (ppm)

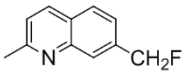


3u

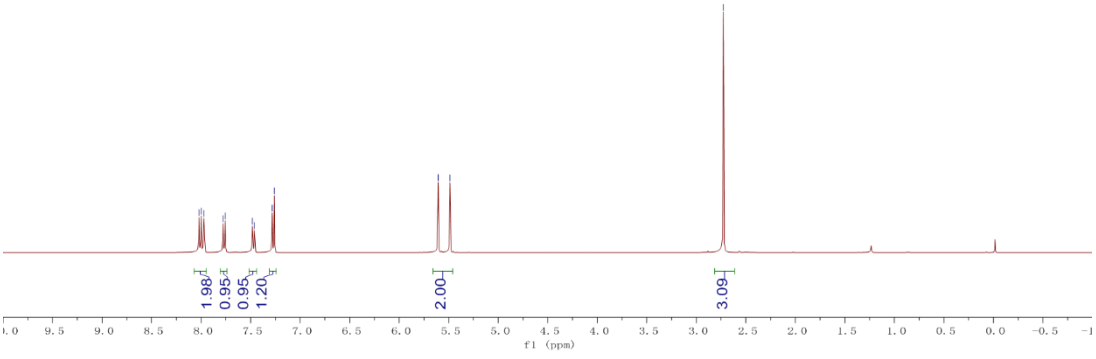

-207.51
-207.64
-207.77

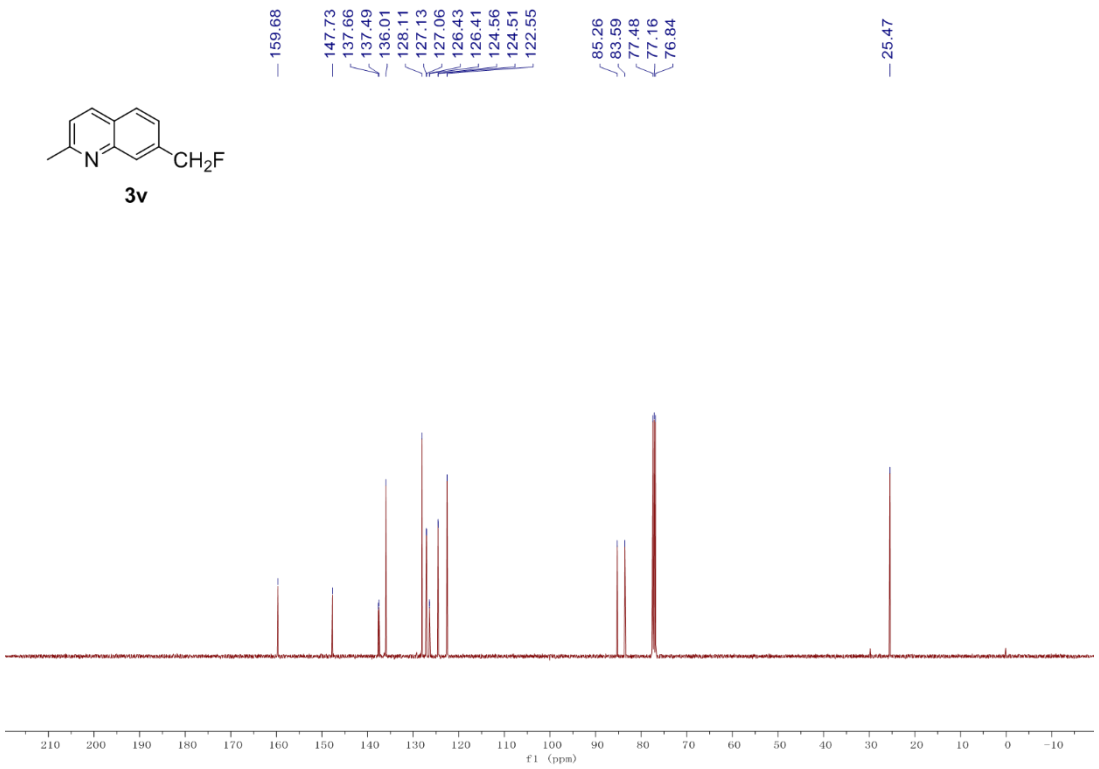

10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

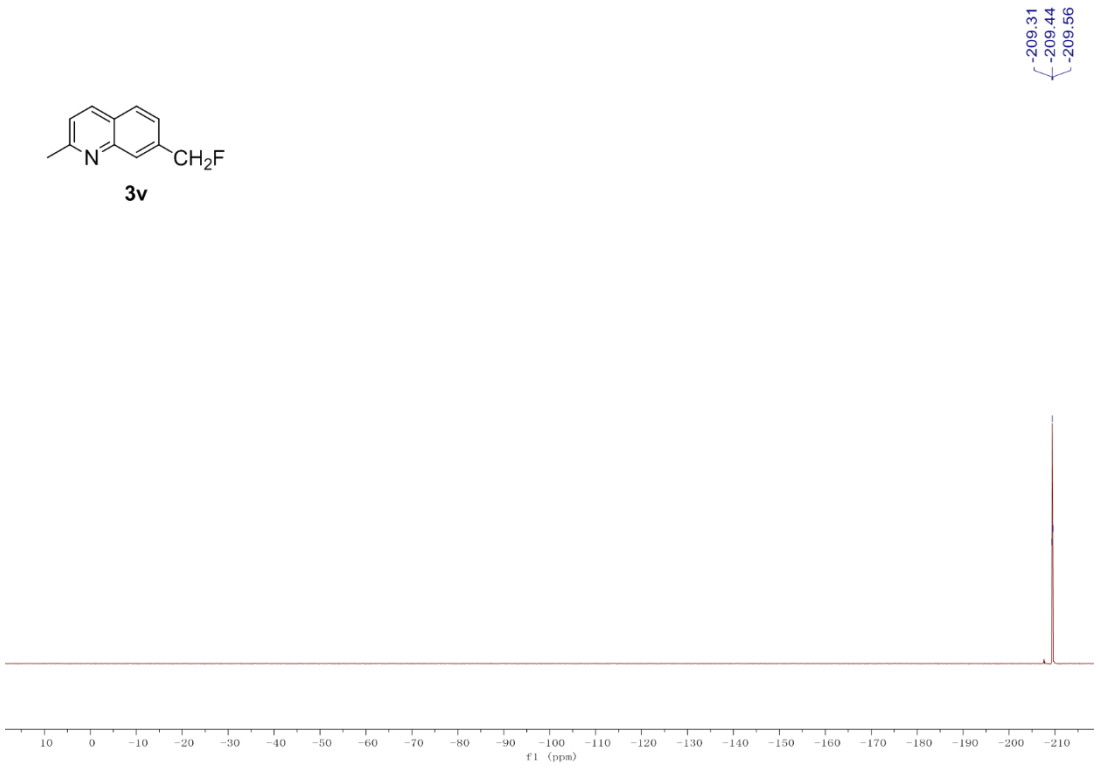

8.02
8.00
7.97
7.78
7.76
7.48
7.46
7.28
7.26
5.61
5.49
2.73

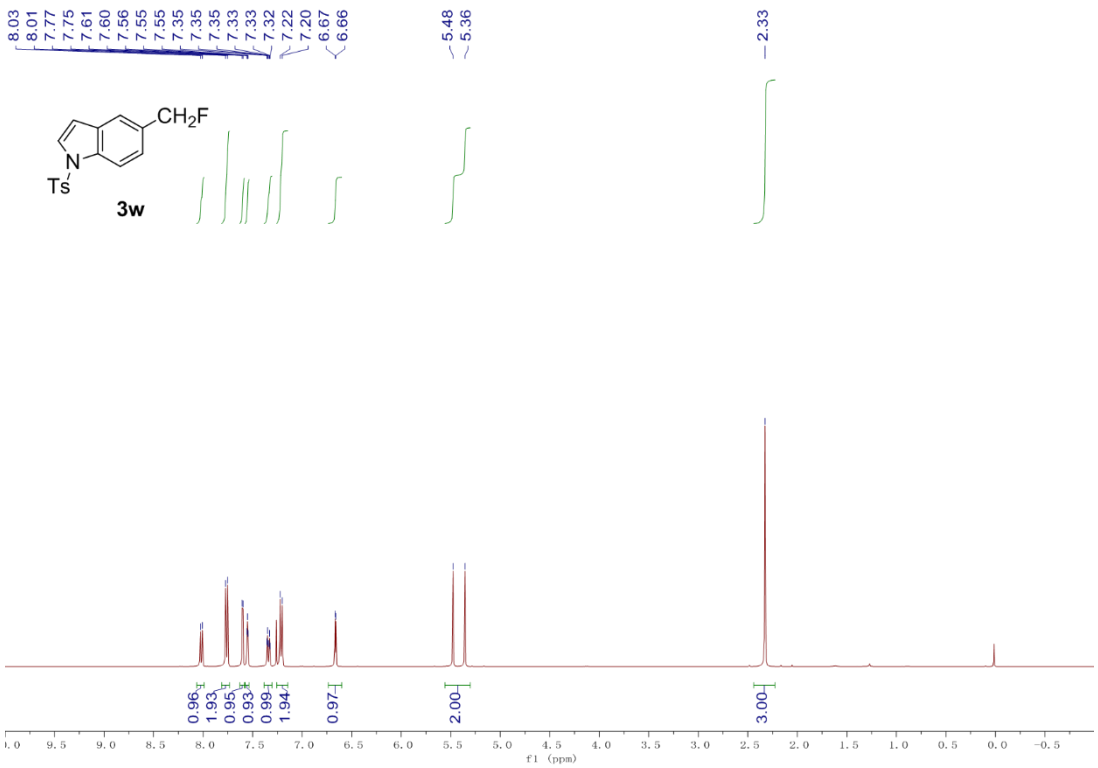


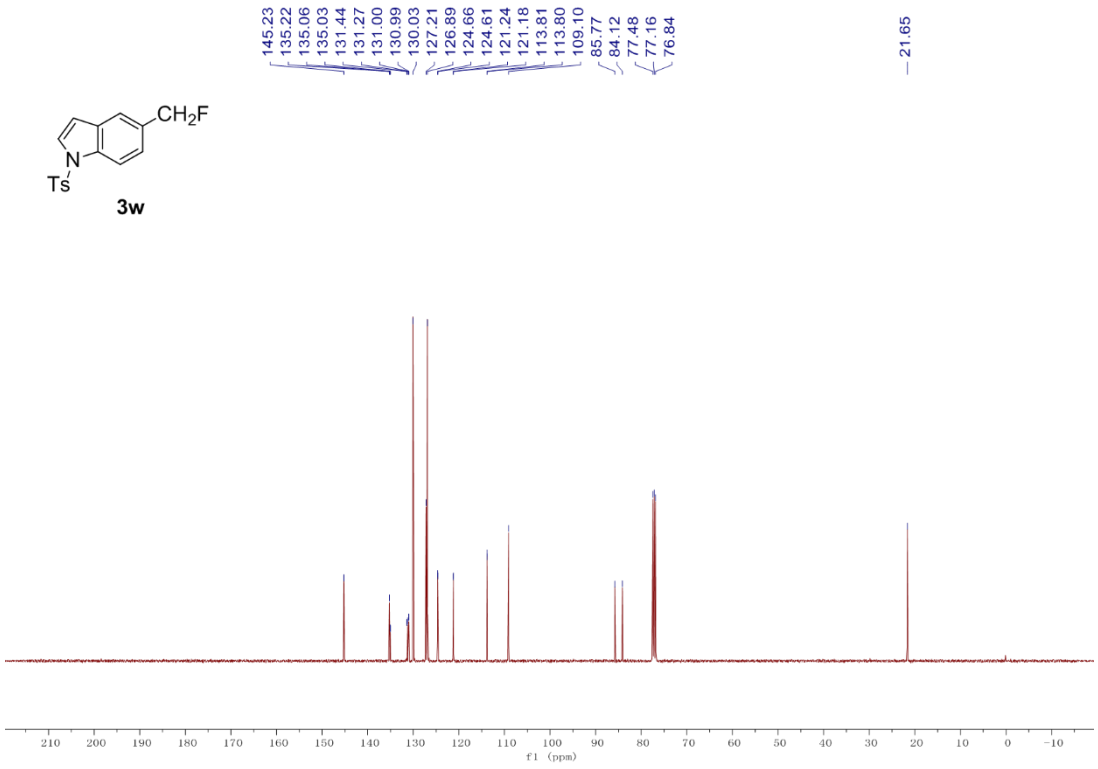
3v


1.98
0.95
0.95
1.20
2.00
3.09
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


159.68
147.73
137.66
137.49
136.01
128.11
127.13
127.06
126.43
126.41
124.56
124.51
122.55
85.26
83.59
77.48
77.16
76.84
25.47
N
CH2F
3v
f1 (ppm)


-209.31
-209.44
-209.56
N
CH2F
3v
f1 (ppm)


8.03
8.01
7.77
7.75
7.61
7.60
7.56
7.55
7.55
7.35
7.35
7.35
7.33
7.33
7.32
7.22
7.20
6.67
6.66
5.48
5.36
2.33
CH2F
N
Ts
3w
0.96
1.93
0.95
0.93
0.99
1.94
0.97
2.00
3.00
f1 (ppm)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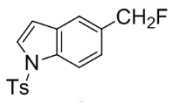
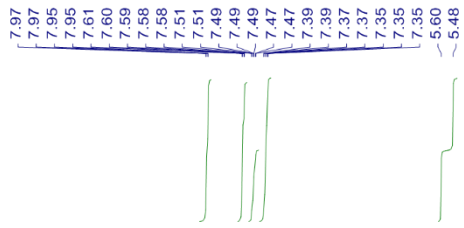
135.22
135.06
135.03
131.44
131.27
131.00
130.99
130.03
127.21
126.89
124.66
124.61
121.24
121.18
113.81
113.80
109.10
85.77
84.12
77.48
77.16
76.84
21.65
CH2F
N
Ts
3w
f1 (ppm)


CH2F
N
Ts

3w

-201.50
-201.63
-201.76
f1 (ppm)


7.97
7.97
7.95
7.95
7.61
7.60
7.59
7.58
7.58
7.51
7.51
7.49
7.49
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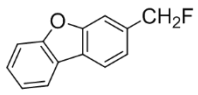
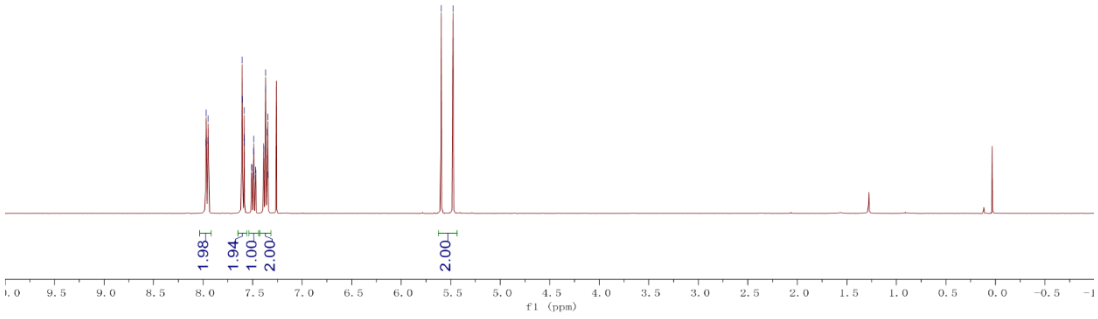
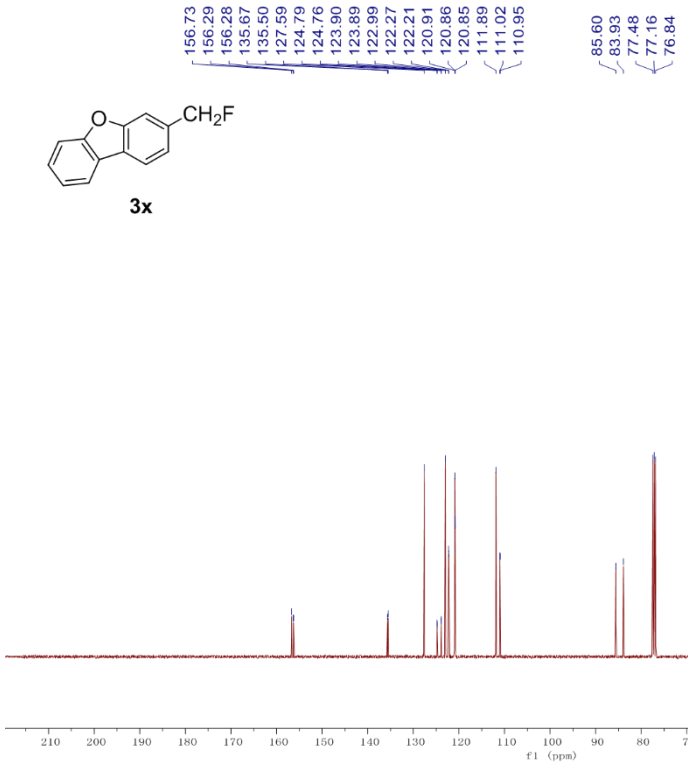
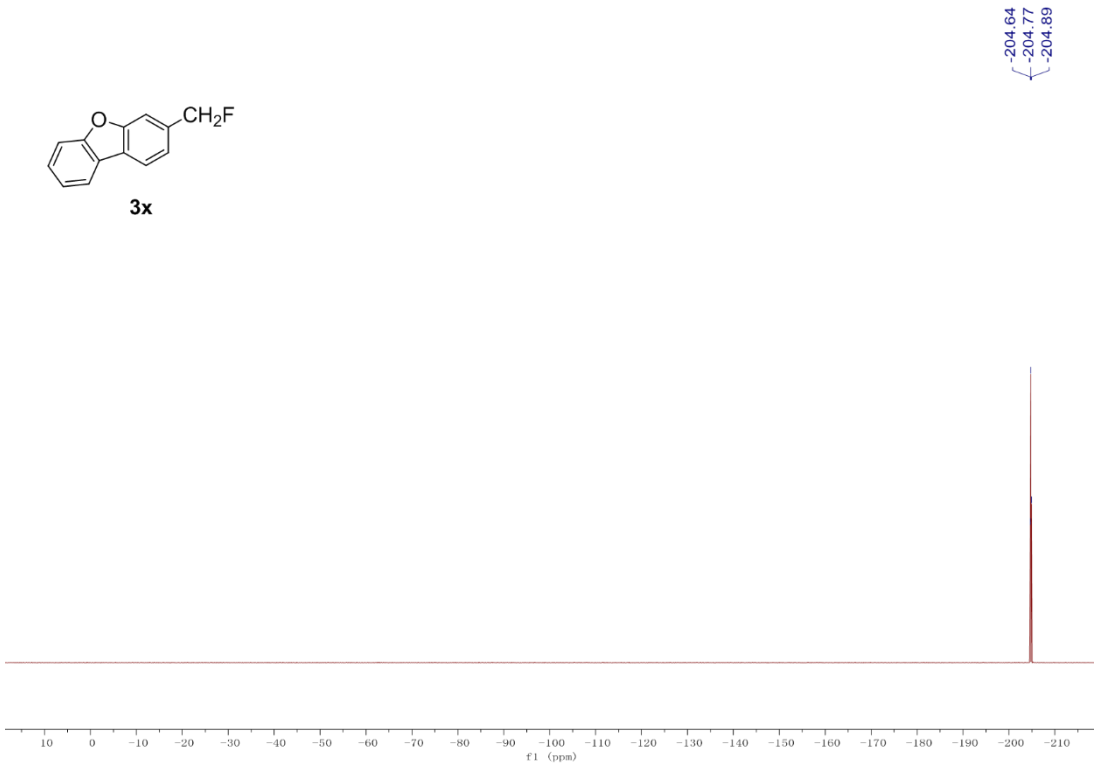
7.37
7.35
7.35
7.35
5.60
5.48

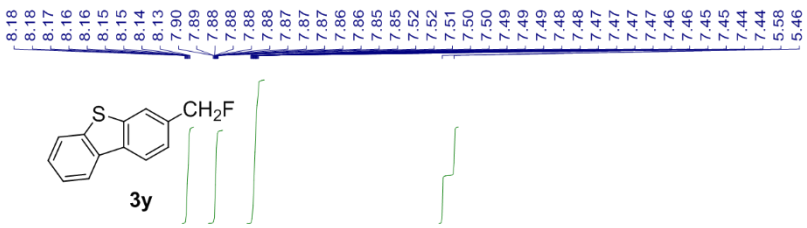

O
CH2F

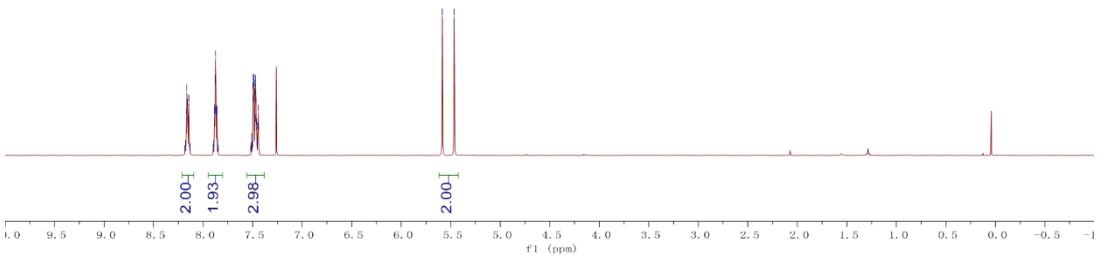
3x

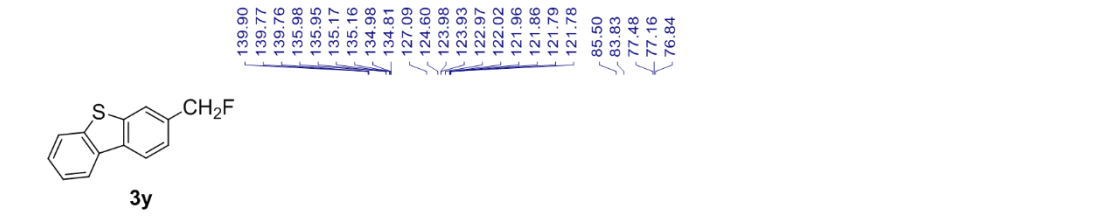

1.98
1.94
1.00
2.00
2.00
f1 (ppm)

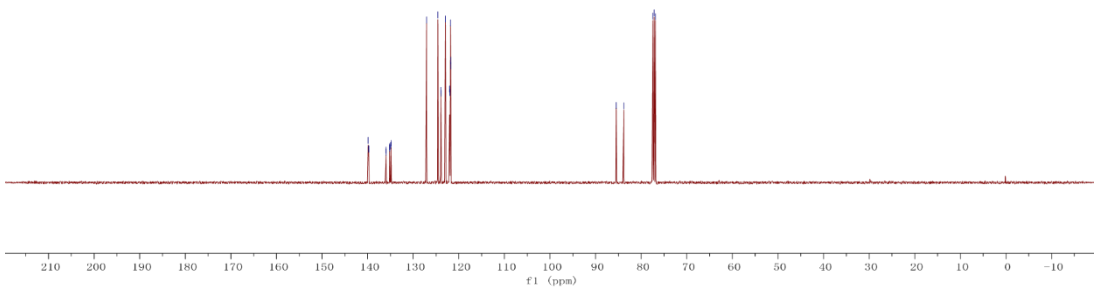

156.73
156.29
156.28
135.67
135.50
127.59
124.79
124.76
123.90
123.89
122.99
122.27
122.21
120.91
120.86
120.85
111.89
111.02
110.95
85.60
83.93
77.48
77.16
76.84
O
CH2F
3x
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

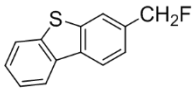

-204.64
-204.77
-204.89
O
CH2F
3x
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


8.18
8.18
8.17
8.16
8.16
8.15
8.15
8.14
8.13
7.90
7.89
7.88
7.88
7.88
7.88
7.87
7.87
7.87
7.86
7.86
7.85
7.85
7.52
7.51
7.50
7.50
7.49
7.49
7.49
7.48
7.48
7.47
7.47
7.47
7.47
7.46
7.46
7.45
7.45
7.44
7.44
5.58
5.46
S
CH2F
3y


2.00
1.93
2.98
2.00
f1 (ppm)

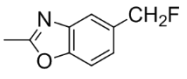

139.90
139.77
139.76
135.98
135.95
135.17
135.16
134.98
134.81
127.09
124.60
123.98
123.93
122.97
122.02
121.96
121.86
121.79
121.78
85.50
83.83
77.48
77.16
76.84
S
CH2F
3y


f1 (ppm)


S
CH2F

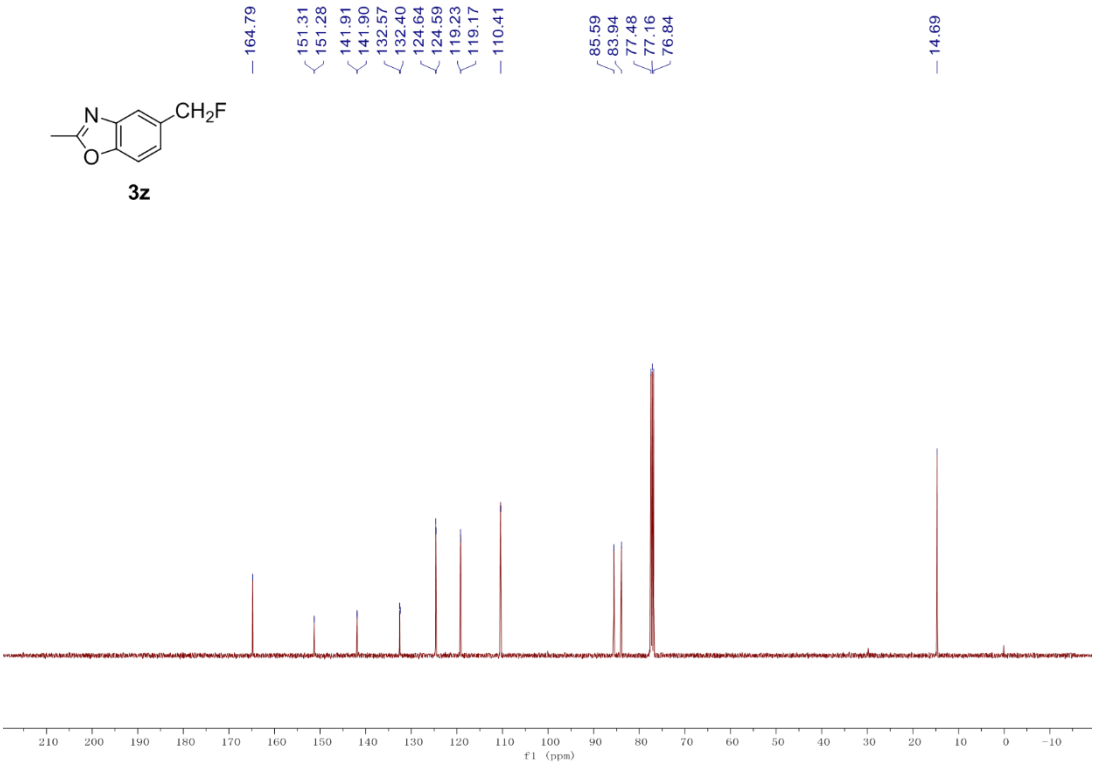
3y

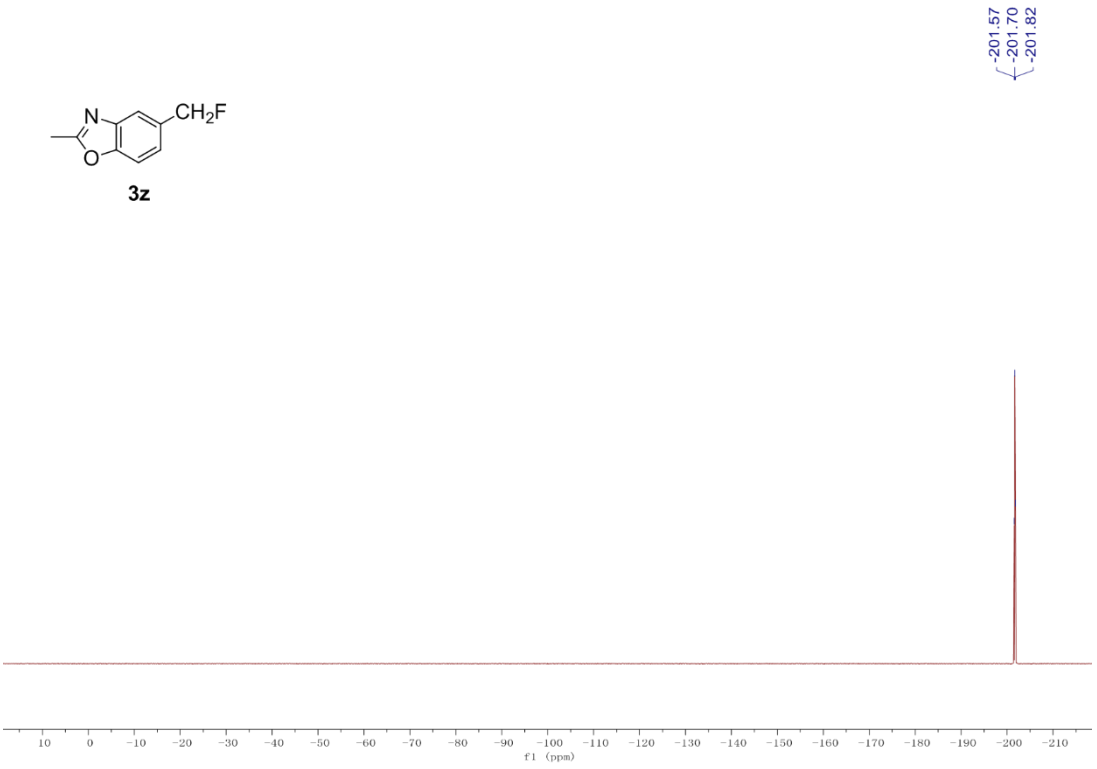
-205.27
-205.39
-205.52
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

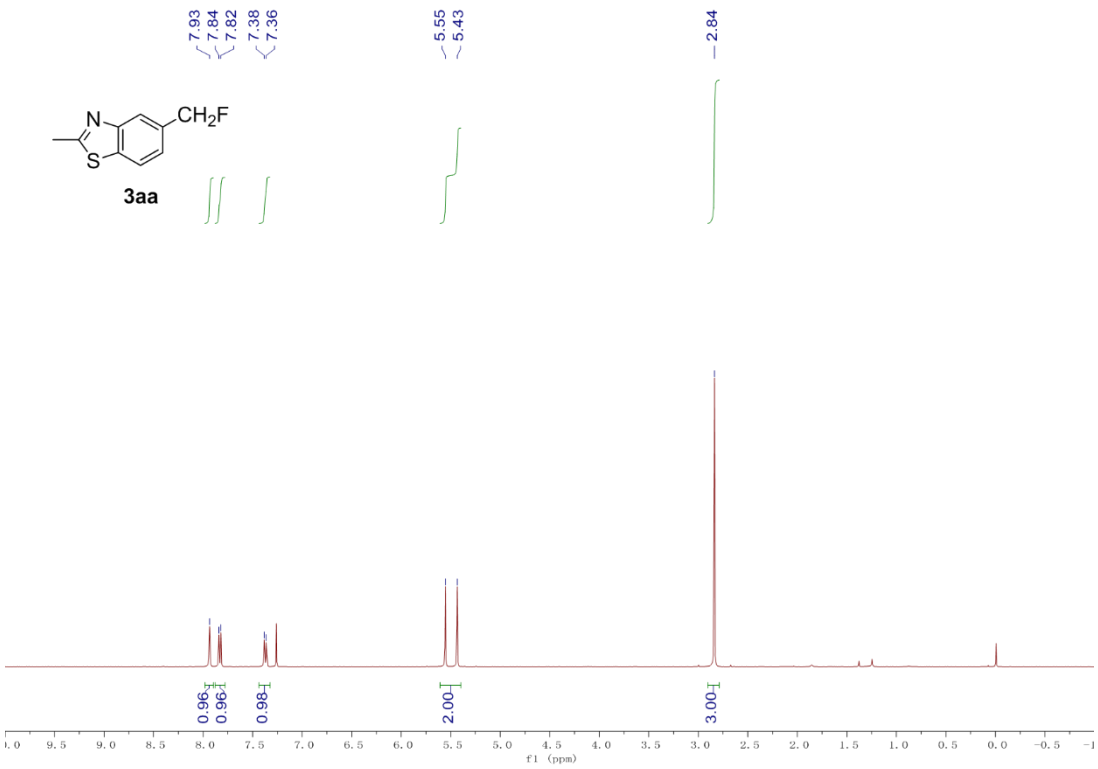

N
O
CH2F

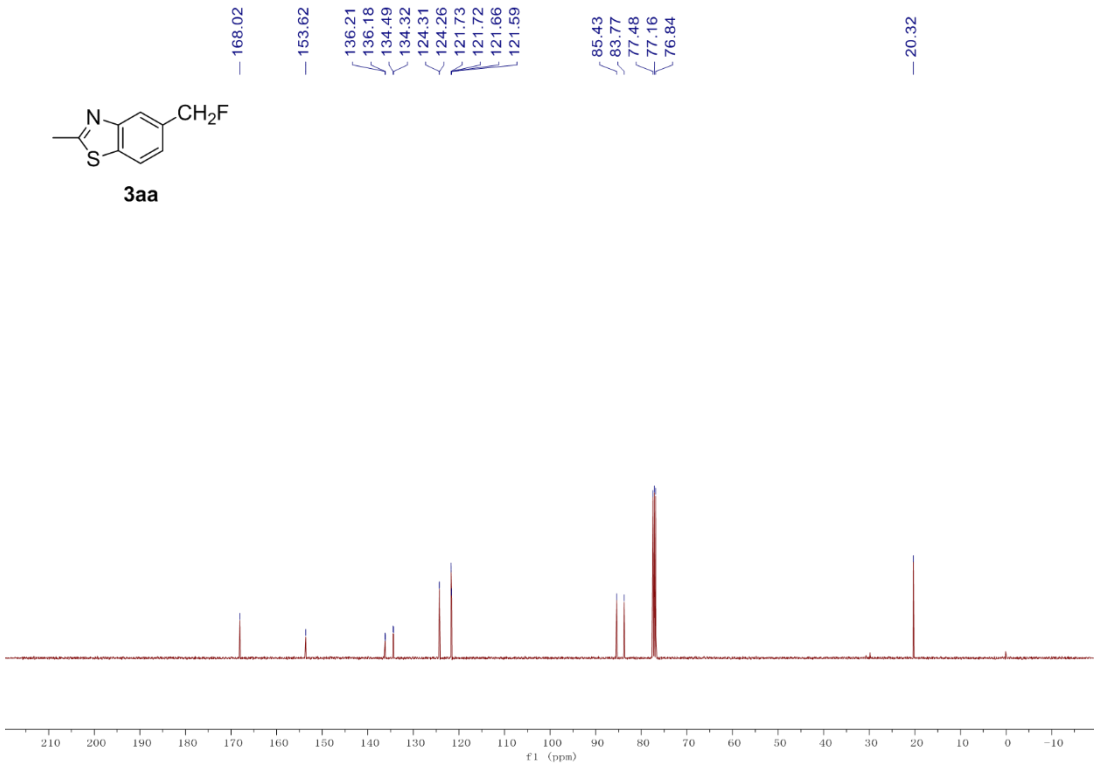
3z

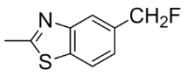
7.66
7.48
7.46
7.33
7.31
5.51
5.39
2.64
1.01
0.99
0.96
2.00
3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


164.79
151.31
151.28
141.91
141.90
132.57
132.40
124.64
124.59
119.23
119.17
110.41
85.59
83.94
77.48
77.16
76.84
14.69
N
O
CH2F
3z
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)


-201.57
-201.70
-201.82
N
O
CH2F
3z
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

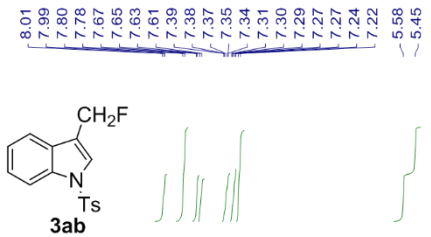

7.93
7.84
7.82
7.38
7.36
5.55
5.43
2.84
N
S
CH2F
3aa
0.96
0.96
0.98
2.00
3.00
f1 (ppm)


168.02
153.62
136.21
136.18
134.49
134.32
124.31
124.26
121.73
121.72
121.66
121.59
85.43
83.77
77.48
77.16
76.84
20.32
N
S
CH2F
3aa
f1 (ppm)

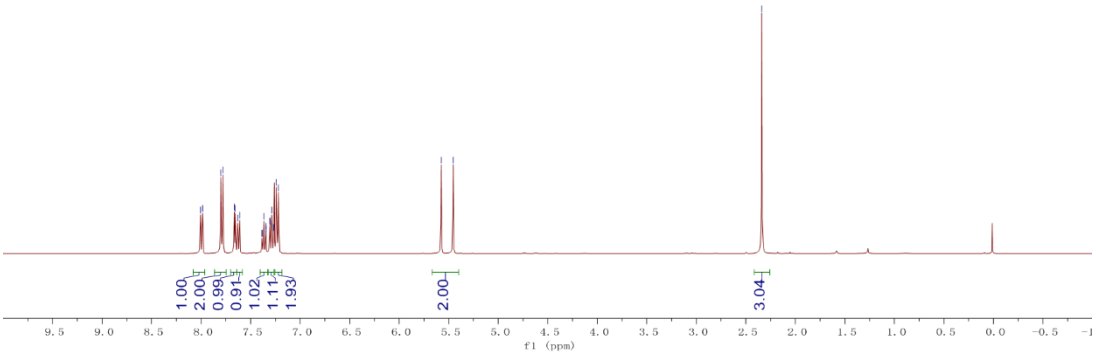

N
S
CH2F

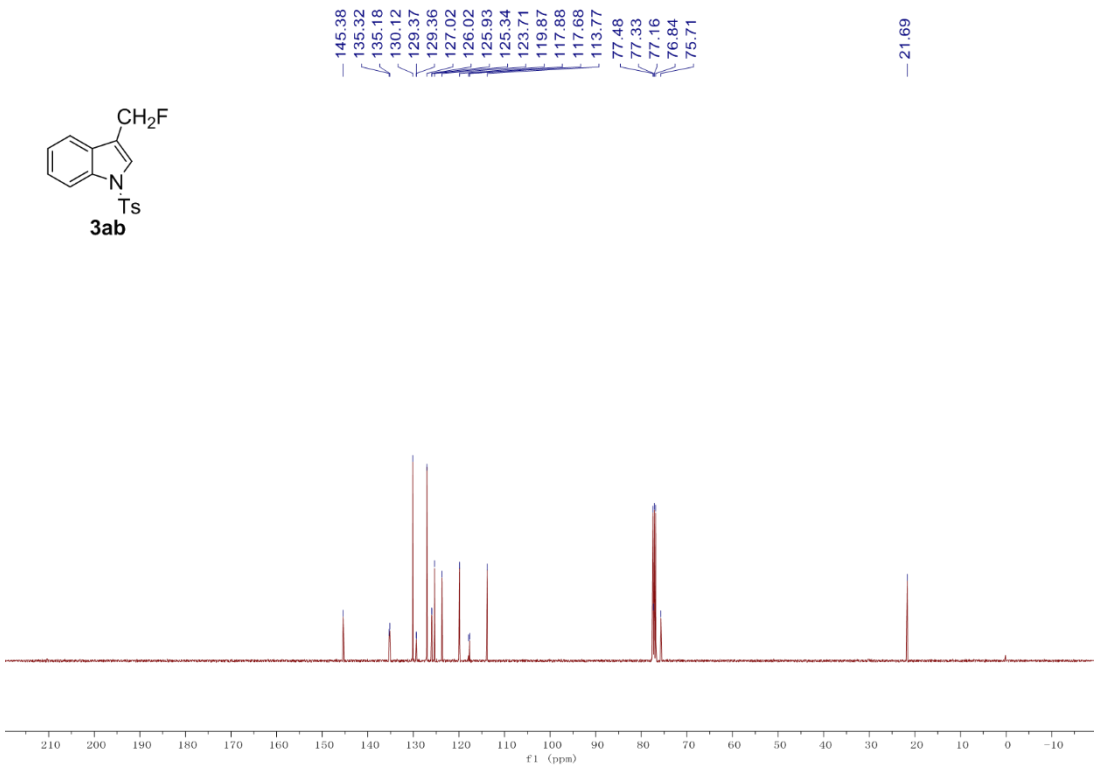
3aa

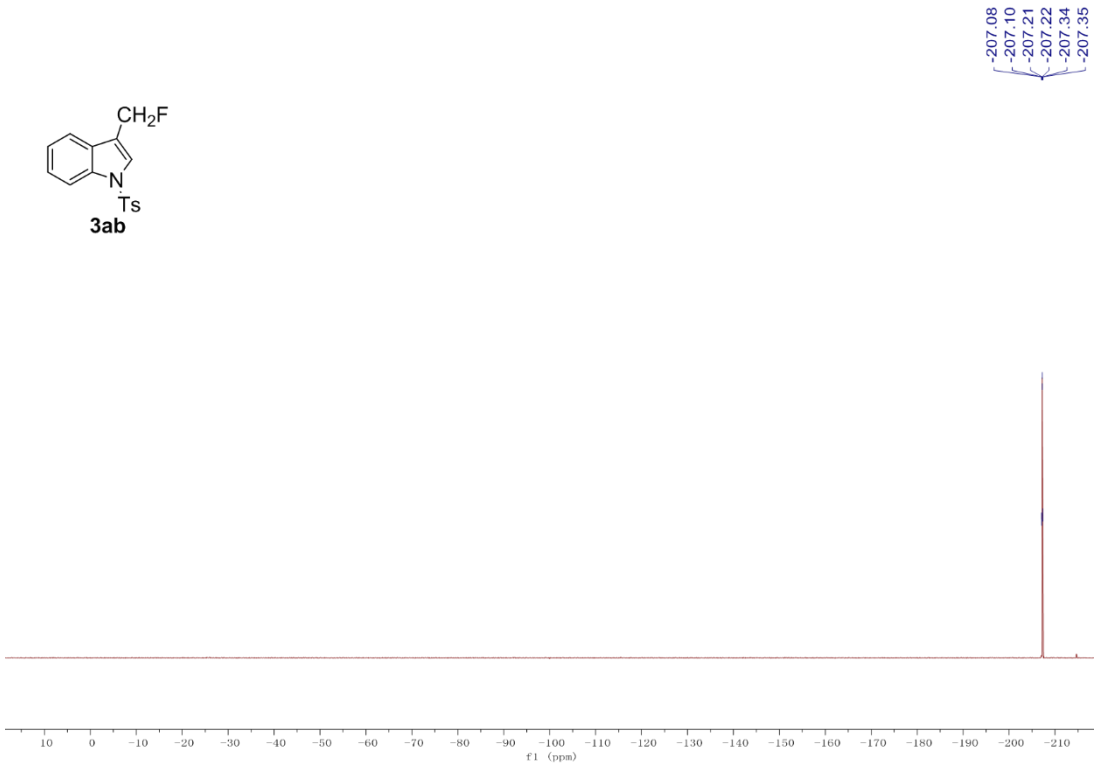
-204.57
-204.70
-204.83
f1 (ppm)

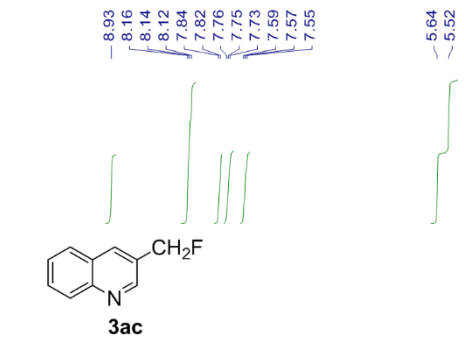

8.01
7.99
7.80
7.78
7.67
7.65
7.63
7.61
7.39
7.38
7.37
7.35
7.34
7.31
7.30
7.29
7.27
7.27
7.24
7.22
5.58
5.45
2.34
CH2F
N
Ts

3ab

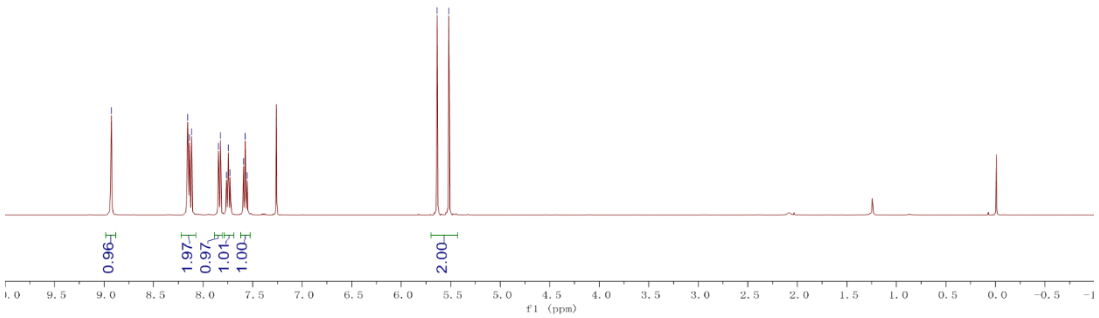

1.00
2.00
0.99
0.91
1.02
1.11
1.93
2.00
3.04
f1 (ppm)

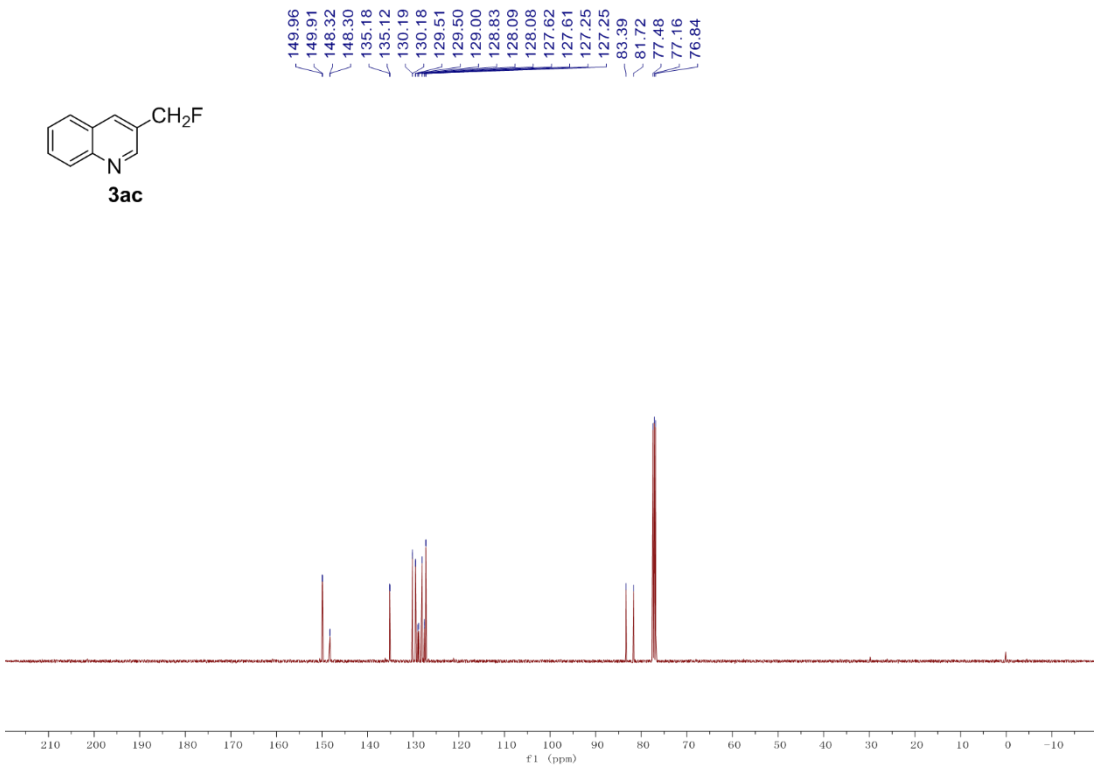

145.38
135.32
135.18
130.12
129.37
129.36
127.02
126.02
125.93
125.34
123.71
119.87
117.88
117.68
113.77
77.48
77.33
77.16
76.84
75.71
21.69
CH2F
N
Ts
3ab
f1 (ppm)


-207.08
-207.10
-207.21
-207.22
-207.34
-207.35
CH2F
N
Ts
3ab
f1 (ppm)


8.93
8.16
8.14
8.12
7.84
7.82
7.76
7.75
7.73
7.59
7.57
7.55
5.64
5.52
CH2F
N

3ac


0.96
1.97
0.97
1.01
1.00
2.00
f1 (ppm)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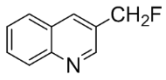
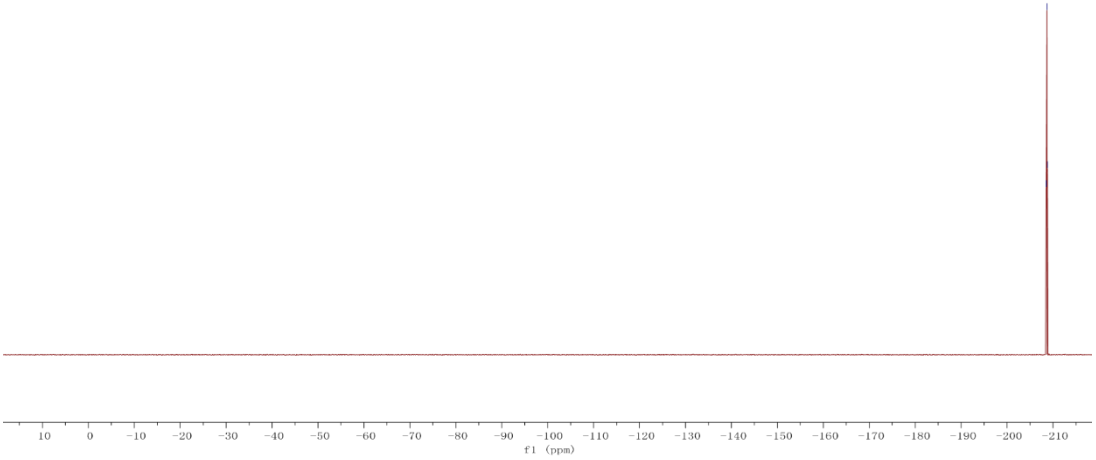
149.91
148.32
148.30
135.18
135.12
130.19
130.18
129.51
129.50
129.00
128.83
128.09
128.08
127.62
127.61
127.25
127.25
83.39
81.72
77.48
77.16
76.84
CH2F
N
f1 (ppm)

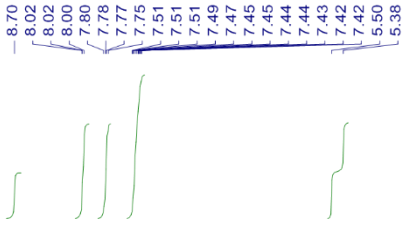
3ac


CH2F
N

3ac


-208.54
-208.67
-208.79


10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


8.70
8.02
8.02
8.00
7.80
7.78
7.77
7.75
7.51
7.51
7.51
7.49
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7.45
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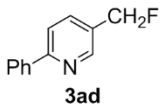
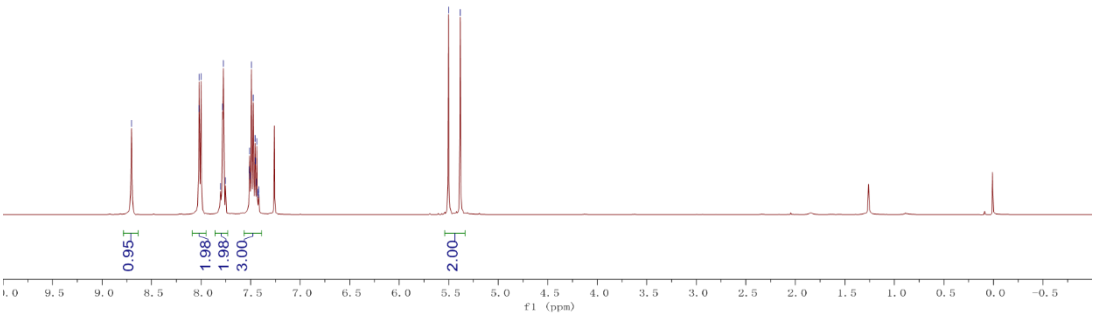
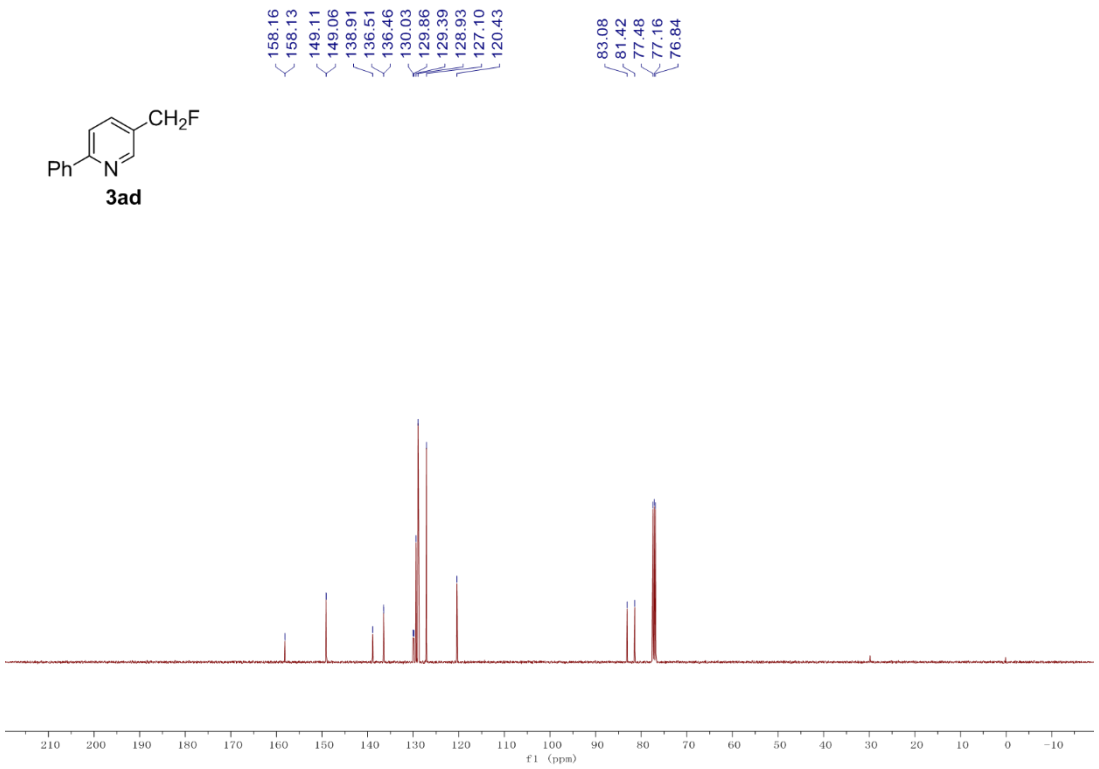
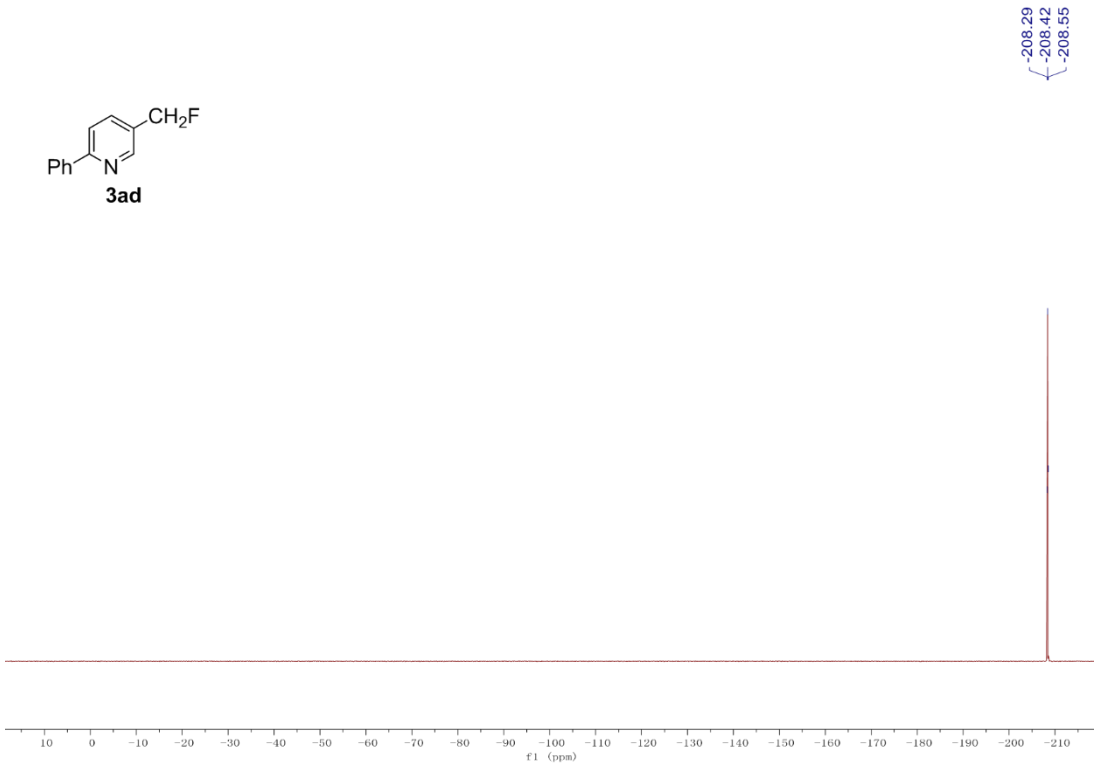
7.44
7.44
7.43
7.42
7.42
5.50
5.38

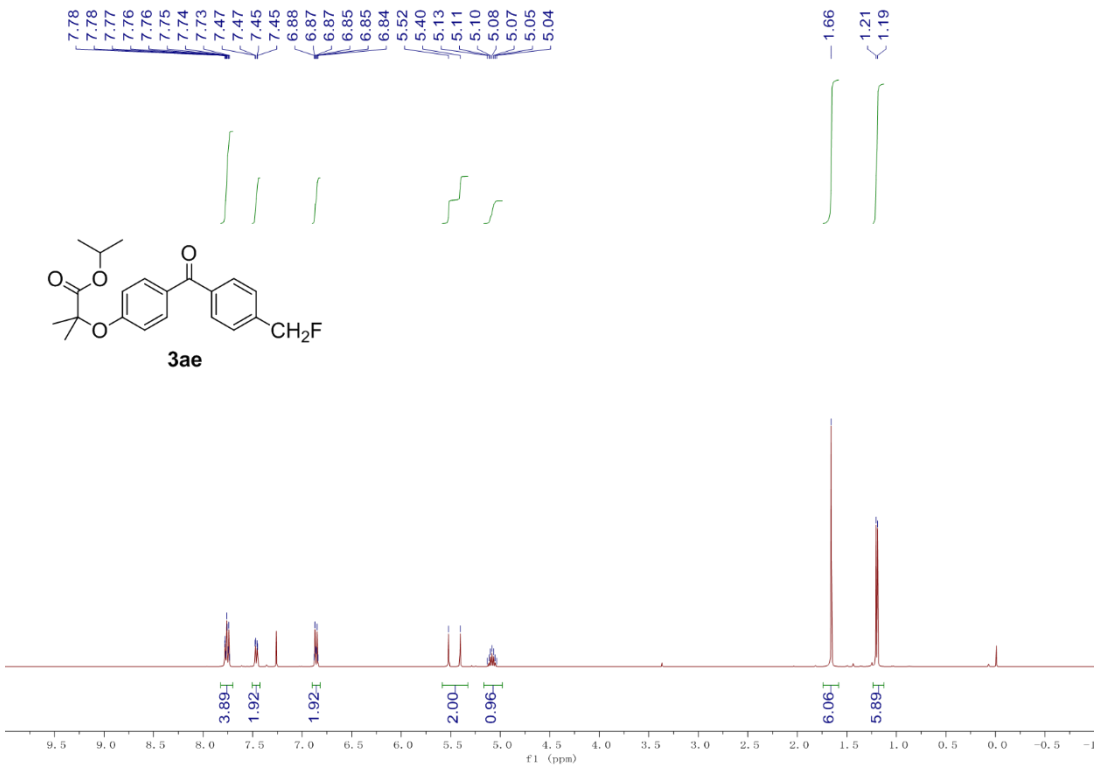

CH2F
Ph
N

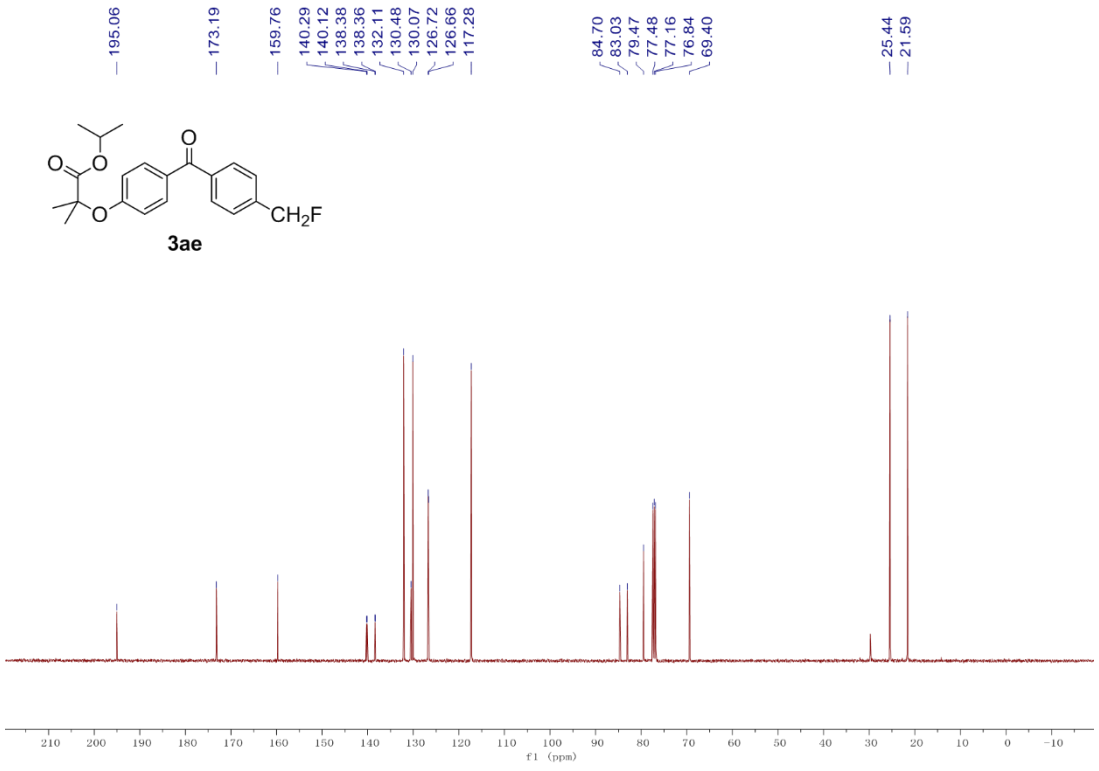
3ad

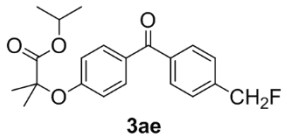

0.95
1.98
1.98
3.00
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


158.16
158.13
149.11
149.06
138.91
136.51
136.46
130.03
129.86
129.39
128.93
127.10
120.43
83.08
81.42
77.48
77.16
76.84
CH2F
Ph
N
3ad
f1 (ppm)


-208.29
-208.42
-208.55
CH2F
Ph
N
3ad
f1 (ppm)


7.78
7.78
7.77
7.76
7.76
7.75
7.74
7.73
7.47
7.47
7.45
7.45
6.88
6.87
6.87
6.85
6.85
6.84
5.52
5.40
5.13
5.11
5.10
5.08
5.07
5.05
5.04
1.66
1.21
1.19
O
O
O
O
CH2F
3ae
3.89
1.92
1.92
2.00
0.96
6.06
5.89
f1 (ppm)


195.06
173.19
159.76
140.29
140.12
138.38
138.36
132.11
130.48
130.07
126.72
126.66
117.28
84.70
83.03
79.47
77.48
77.16
76.84
69.40
25.44
21.59
O
O
O
O
CH2F
3ae
f1 (ppm)


O
O
O
O
CH2F

3ae

-211.63
-211.76
-211.88
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)