Supporting Information for

Pd-Catalyzed Direct Cross-Coupling of Electron-Deficient Polyfluoroarenes with Heteroaromatic Tosylates

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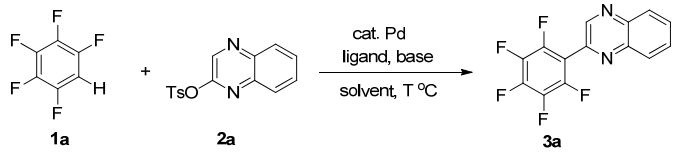
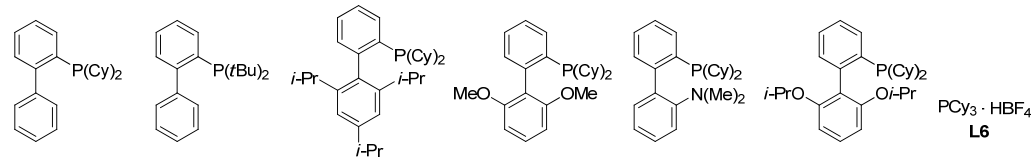
General information: ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM300 and AM400 spectrometer. ^{19}F NMR was recorded on a Bruker AM300 spectrometer ($CFCl_3$ as outside standard and low field is positive). Purification by reverse phase preparative HPLC was performed on a PerkinElmer 200 HPLC equipped with a PerkinElmer Series 200 UV/VIS detector and a Kromasil 100-5-C18 (250 x 10 mm) column. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. NMR yield was determined by ^{19}F NMR using fluorobenzene as an internal standard before working up the reaction.

Materials: All reagents were used as received from commercial sources, unless specified otherwise, or prepared as described in the literature. All reagents were weighed and handled in air, and refilled with an inert atmosphere of N_2 at room temperature. DMF and DMSO were distilled under reduced pressure from CaH_2. 1,4-Dioxane was distilled from sodium and benzophenone immediately before use. *t*BuOH was distilled from CaH_2. Compounds 2-phenylquinazolin-4-ol, 7-methyl-2-phenylquinazolin-4-ol, 7-fluoro-2-phenylquinazolin-4-ol were prepared according to literature.[1]

Screens for Pd-Catalyzed Direct Cross-Coupling of Pentafluorobenzene 1a with 2-Quinaxolinyl Tosylate 2a (Table S1). To a septum capped 25 mL of sealed tube were added Pd-catalyst (3-10 mol%), ligand (6-20 mol%), additive (1.2 equiv) and quinoxalin-2-yl-4-methylbenzenesulfonate **2a** (0.3 mmol, 1.0 euqiv) under N_2, followed by solvent (1.0 mL) with stirring. Pentafluorobenzene **1a** (2.0 equiv) was then added subsequently. The sealed tube was screw capped and heated to 60-120 ^{o}C (oil bath). After stirring for 12 h, the reaction mixture was cooled to room temperature and fluorobenzene (28.5 μL, 0.3 mmol) was added. The yield was determined by ^{19}F NMR before working up. If necessary, the reaction mixture was diluted with ethyl acetate, washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified with silica gel chromatography (Petroleum ether / Ethyl ether = 50:1) to provide pure product.

Table S1. Screens for Pd-catalyzed direct cross-coupling of pentafluorobenzene **1a** with 2-quinaxolinyl tosylate **2a**. [a]





L Cy-John-Phos **L1** John-Phos **L2** X-Phos **L3** S-Phos **L4** Dave-Phos **L5** Ru-Phos

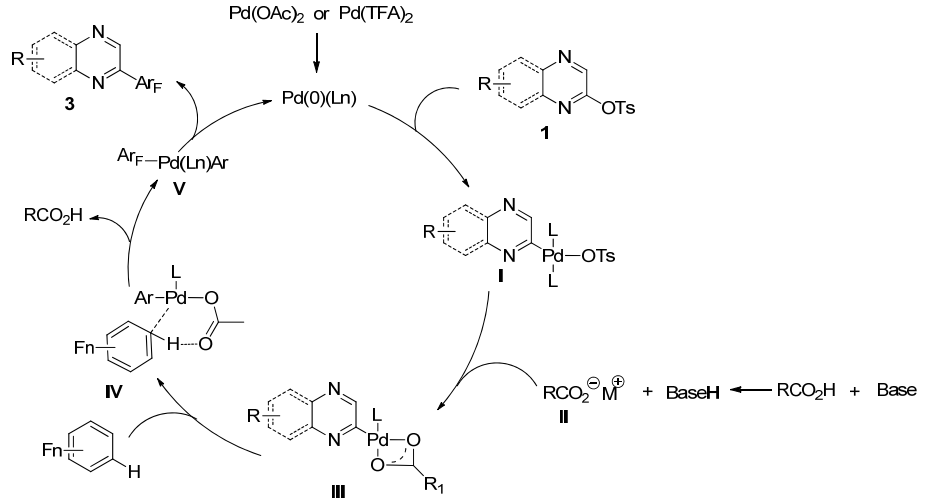
Entry	Pd (mol%)	Ligand (mol%)	Additvie (equiv)	Base (equiv)	Solvent	Temp (^{o}C)	Time (h)	Yield[b] (%)
1	$Pd(OAc)_2$(10)	PPh_3(20)	···	Cs_2CO_3 (1.2)	toluene	120	6	NR
2	$Pd(OAc)_2$(10)	PPh_3(20)	···	K_3PO_4 (1.2)	dioxane	120	6	trace
3	$Pd(OAc)_2$(10)	**L1** (20)	···	K_2CO_3 (1.2)	dioxane	120	6	NR
4	$Pd(OAc)_2$(10)	**L1** (20)	···	*t*-BuOLi (1.2)	dioxane	120	6	NR
5	$Pd(OAc)_2$(10)	**L1** (20)	···	K_3PO_4 (1.2)	dioxane	120	6	(3)
6	$Pd(OAc)_2$(10)	DPPE (20)	···	K_3PO_4 (1.2)	dioxane	120	6	11
7	$Pd(OAc)_2$(10)	**L2** (20)	···	K_3PO_4 (1.2)	dioxane	120	6	10
8	$Pd(OAc)_2$(10)	L3 (20)	···	K_3PO_4 (1.2)	dioxane	120	6	62
9	$Pd(OAc)_2$(10)	**L4** (20)	···	K_3PO_4 (1.2)	dioxane	120	6	trace
10	$Pd(OAc)_2$(10)	**L5** (20)	···	K_3PO_4 (1.2)	dioxane	120	6	36
11	$Pd(OAc)_2$(10)	**L6** (20)	···	K_3PO_4 (1.2)	dioxane	120	6	51
12	$Pd(OAc)_2$(10)	**L** (20)	···	K_3PO_4 (1.2)	dioxane	120	6	51
13	$Pd(OAc)_2$(10)	**L** (20)	···	K_3PO_4 (1.2)	dioxane	100	8	46
14	$Pd(OAc)_2$(10)	**L** (20)	···	K_3PO_4 (1.2)	dioxane	80	8	59
15	$Pd(OAc)_2$(10)	**L** (20)	···	K_3PO_4 (1.2)	dioxane	60	8	trace

16	$Pd(OAc)_2$(10)	**L3** (20)	···	K_3PO_4 (1.2)	dioxane	80	12	36
17	$Pd(OAc)_2$(10)	**L6** (20)	···	K_3PO_4 (1.2)	dioxane	80	12	NR
18	$Pd(OAc)_2$(10)	**L** (20)	···	K_3PO_4 (1.2)	dioxane	80	12	72
19	$Pd(OAc)_2$(10)	**L** (20)	···	K_3PO_4 (1.2)	DMF	80	12	18
20	$Pd(OAc)_2$(10)	**L** (20)	···	K_3PO_4 (1.2)	*t*-BuOH	80	12	72
21[c]	$Pd(OAc)_2$(10)	**L** (20)	···	K_3PO_4 (1.2)	DMF/ *t*-BuOH	80	12	33
22	$Pd(OAc)_2$(10)	**L** (20)	···	K_3PO_4 (1.2)	DMSO	80	12	trace
23	$Pd(OAc)_2$(5)	**L** (10)	···	K_3PO_4 (1.2)	dioxane	80	12	10
24	$Pd(OAc)_2$(5)	**L** (10)	···	K_3PO_4 (1.2)	*t*-BuOH	80	12	32
25	$Pd(OAc)_2$(5)	**L** (10)	PivOH (1.0)	K_3PO_4 (2.5)	dioxane	80	12	39
26	$Pd(OAc)_2$(5)	**L** (10)	PivOH (1.2)	K_3PO_4 (1.2)	*t*-BuOH	80	12	65
27	$Pd(OAc)_2$(5)	**L** (10)	AdOH (1.2)	K_3PO_4 (1.2)	*t*-BuOH	80	12	70
28	$Pd(OAc)_2$(3)	**L** (6)	PivOH (1.2)	K_3PO_4 (1.2)	*t*-BuOH	80	12	（51）
29	$Pd(OAc)_2$(3)	**L** (6)	AdOH (1.2)	K_3PO_4 (1.2)	*t*-BuOH	80	12	（60）
30	$Pd(TFA)_2$(3)	**L** (6)	AdOH (1.2)	K_3PO_4 (1.2)	*t*-BuOH	80	12	（68）
31	**$Pd(TFA)_2$(3)**	**L (6)**	**AdOH (1.2)**	**K_3PO_4 (1.2)**	***t*-BuOH**	**90**	**12**	**80(73)**
32	$Pd(TFA)_2$ (3)	---	AdOH (1.2)	K_3PO_4 (1.2)	*t*-BuOH	90	12	N.R.
33	$Pd(TFA)_2$ (3)	**L** (6)	AdOH (1.2)	K_2CO_3 (1.2)	*t*-BuOH	90	12	18
34	$Pd(TFA)_2$ (3)	**L** (6)	AdOH (1.2)	Cs_2CO_3 (1.2)	*t*-BuOH	90	12	N.R.
35	$Pd(TFA)_2$ (3)	**L** (6)	AdOH (1.2)	tBuOLi (1.2)	*t*-BuOH	90	12	30
36	$Pd(TFA)_2$ (3)	**L** (6)	AdOK (1.2)	---	*t*-BuOH	90	12	50

[a]Recation conditions unless otherwise specified: **1a** (2.0 equiv), **2a** (0.3 mmol) solvent (1.0 mL). [b]NMR yield determined by ^{19}F NMR using fluorobenzene as an internal standard (isolated yield in parentheses). [c]DMF/*t*BuOH = 4:1 (v/v).

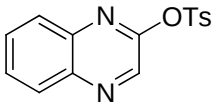
Considering that the phosphine-ligated arylpalladium carboxylates LPd(Ar)(OCOR) were typically proposed to react with arenes to form biarylpalladium complexes through a concerted metalation-deprotonation (CMD) pathway (*J. Am. Chem. Soc.* **2006**, *128*, 16496); the role of AdOH or PivOH was proposed to function as a proton shuttle during the aryl C-H cleavage step, a reaction mechanism for the cross-coupling of polyfluoroarenes with heteroaromatic tosylates was proposed as shown in Scheme S1.

Scheme S1. Proposed mechanism for the cross-coupling of polyfluoroarenes with heteroaromatic tosylates.

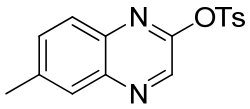


Typical Procedure for the Preparation of Heteroaromatic Tosylate 2.

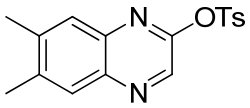
To a solution of quinoxalin-2(1*H*)-one (6.0 g, 34 mmol) in 100 mL of dichloromethane were added TsCl (7.13 g, 37.4 mmol) and DMAP (416 mg, 3.4 mmol), followed by Et_3N (7 mL, 48 mmol). The reaction mixture was stirred for 3 h at room temperature. The reaction mixture was diluted with ethyl acetate, washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified with silica gel chromatography (Petroleum ether / Ethyl ether = 6:1) to provide pure product **2a** (8.16 g, 91%).



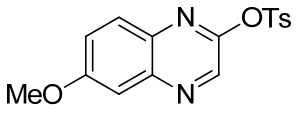
Quinoxalin-2-yl 4-methylbenzenesulfonate (2a). The product (83% yield) as a white solid was purified with silica gel chromatography (Petroleum ether / Ethyl ether = 5:1). This compound is known.[2] ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.66 (s, 1 H), 8.13-8.09 (m, 1 H), 8.03 (d, *J* = 8.4 Hz, 2 H), 7.92-7.89 (m, 1 H), 7.78-7.74 (m, 2 H), 7.39 (d, *J* = 8.4 Hz, 2 H), 2.47 (s, 3 H).



6-methylquinoxalin-2-yl 4-methylbenzenesulfonate (2b). The product (99% yield) as a white solid was purified with silica gel chromatography (Petroleum ether / Ethyl ether = 5:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.61 (s, 1 H), 8.01 (d, *J* = 8.7 Hz, 2 H), 7.88 (s, 1 H), 7.80 (d, *J* = 8.7 Hz, 1 H), 7.60 (d, *J* = 8.4 Hz, 1.5 Hz, 1 H), 7.38 (d, *J* = 8.1 Hz, 2 H), 2.58 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 150.3, 145.8, 141.1, 140.3, 138.8, 137.8, 133.2, 133.1, 129.7, 128.9, 127.9, 127.8, 21.6, 21.5.

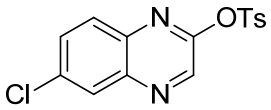


6,7-Dimethylquinoxalin-2-yl 4-methylbenzenesulfonate (2c). The product (67% yield) as a white solid was purified with silica gel chromatography (Petroleum ether / Ethyl ether = 10:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.54 (s, 1 H), 8.00 (d, *J* = 8.4 Hz, 2 H), 7.84 (s, 1 H), 7.65 (s, 1 H), 7.38 (d, *J* = 8.4 Hz, 2 H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 145.8, 141.9, 140.3, 140.1, 138.4, 137.9, 133.3, 129.7, 128.9, 128.1, 127.4, 21.7, 20.2, 20.1.

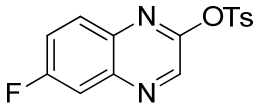


6-Methoxyquinoxalin-2-yl 4-methylbenzenesulfonate (2d). The product (81% yield) as a white solid was purified with silica gel chromatography (Petroleum ether / Ethyl

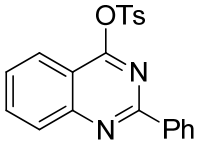
ether = 4:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.60 (s, 1 H), 7.98 (d, *J* = 8.1 Hz, 2 H), 7.78 (dd, *J* = 8.4 Hz, 1.2 Hz, 1 H), 7.44-7.37 (m, 4 H), 3.96 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 149.5, 145.8, 142.9, 139.1, 135.4, 133.2, 129.8, 129.3, 128.9, 124.2, 106.8, 55.8, 21.7.



6-Chloroquinoxalin-2-yl 4-methylbenzenesulfonate (2e). The product (92% yield) as a white solid was purified with silica gel chromatography (Petroleum ether / Ethyl ether = 6:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.65 (s, 1 H), 8.11 (d, *J* = 2.1 Hz, 1 H), 8.02 (d, *J* = 8.1 Hz, 2 H), 7.85 (d, *J* = 8.7 Hz, 1 H), 7.72 (dd, *J* = 9.0 Hz, 2.1 Hz, 1 H), 7.40 (d, *J* = 8.1 Hz, 2 H)), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 146.1, 141.3, 140.1, 138.2, 135.6, 133.1, 132.1, 129.8, 129.6, 129.0, 128.1, 21.8.

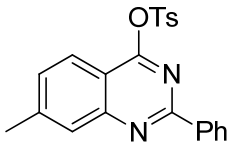


6-Fluoroquinoxalin-2-yl 4-methylbenzenesulfonate (2f). The product (84% yield) as a white solid was purified with silica gel chromatography (Petroleum ether / Ethyl ether = 6:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.66 (s, 1 H), 8.02 (d, *J* = 8.4 Hz, 2 H), 7.92 (dd, *J* = 9.3 Hz, 5.7 Hz, 1 H), 7.75 (dd, *J* = 9.0 Hz, 3.0 Hz, 1 H), 7.56 (dd, *J* = 8.1 Hz, 2.7 Hz, 1 H), 7.40 (d, *J* = 8.1 Hz, 2 H)), 2.48 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -104.8 (m, 1F). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 162.4 (d, *J* = 252.6), 150.5, 146.0, 141.8 (d, *J* = 13.0), 140.0, 136.6, 133.0, 130.3 (d, *J* = 9.9), 129.8, 128.9, 121.2 (d, *J* = 25.9), 112.9 (d, *J* = 22.0), 21.7.

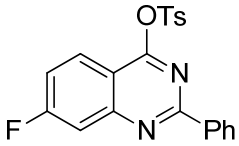


2-phenylquinazolin-4-yl 4-methylbenzenesulfonate (2g). The product (82% yield) as a white solid was purified with silica gel chromatography (Petroleum ether / Ethyl

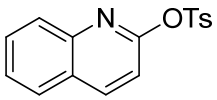
ether = 5:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.37-8.34 (s, 2 H), 8.20 (d, *J* = 7.5 Hz, 1 H), 8.13 (d, *J* = 8.4 Hz, 2 H), 8.08 (d, *J* = 8.4 Hz, 1 H), 7.92 (t, *J* = 8.1 Hz, 1 H), 7.63 (t, *J* = 7.8 Hz, 1 H), 7.52-7.47 (m, 3 H), 7.40 (d, *J* = 8.4 Hz, 2 H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 159.6, 153.3, 145.8, 136.9, 134.9, 134.2, 131.0, 129.8, 129.0, 128.7, 128.5, 128.3, 127.9, 123.3, 115.0, 21.8.



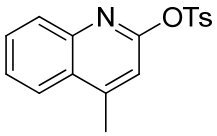
7-Methyl-2-phenylquinazolin-4-yl 4-methylbenzenesulfonate (2h). The product (70% yield) as a white solid was purified with silica gel chromatography (Petroleum ether / Ethyl ether = 10:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.34-8.31 (s, 2 H), 8.12 (d, *J* = 8.1 Hz, 2 H), 8.08 (d, *J* = 8.4 Hz, 1 H), 7.84 (s, 1 H), 7.49-7.44 (m, 4 H), 7.39 (d, *J* = 8.1 Hz, 2 H), 2.59 (s, 3 H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 159.6, 153.7, 146.1, 145.7, 137.0, 134.3, 130.9, 130.1, 129.7, 129.0, 128.6, 128.4, 127.4, 122.9, 112.9, 22.2, 21.7.



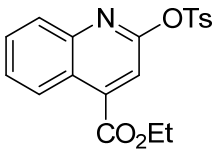
7-Fluoro-2-phenylquinazolin-4-yl 4-methylbenzenesulfonate (2i). The product (80% yield) as a white solid was purified with silica gel chromatography (Petroleum ether / Ethyl ether = 10:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.34 (dd, *J* = 7.8 Hz, 1.8 Hz, 2 H), 8.22 (dd, *J* = 9.6 Hz, 6.3 Hz, 1 H), 8.12 (d, *J* = 8.1 Hz, 2 H), 7.68 (dd, *J* = 9.6 Hz, 2.1 Hz, 1 H), 2.47 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -100.7 (m, 1F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4 (d, *J* = 255.8), 161.9, 160.8, 155.1 (d, *J* = 14.1), 145.9, 136.5, 134.0, 131.3, 129.8, 129.0, 128.8, 128.5, 126.1 (d, *J* = 10.7), 118.2 (d, *J* = 25.3), 112.4 (d, *J* = 21.0), 112.0, 21.8.



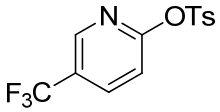
Quinolin-2-yl 4-methylbenzenesulfonate (2j). The product (82% yield) as a white solid was purified with silica gel chromatography (Petroleum ether / Ethyl ether = 10:1). This compound is known.[3] ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.7 Hz, 1 H), 8.02 (d, *J* = 8.4 Hz, 2 H), 7.86 (d, *J* = 8.4 Hz, 1 H), 7.80 (d, *J* = 8.4 Hz, 1 H), 7.69 (t, *J* = 7.8 Hz, 1 H), 7.53 (t, *J* = 7.8 Hz, 1 H), 7.18 (d, *J* = 8.4 Hz, 2 H), 2.45 (s, 3H).



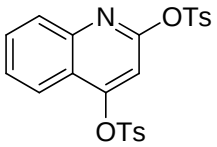
4-Methylquinolin-2-yl 4-methylbenzenesulfonate (2k). The product (83% yield) as a white solid was purified with silica gel chromatography (Petroleum ether / Ethyl ether = 10:1). This compound is known.[4] ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.4 Hz, 2 H), 7.94 (d, *J* = 8.1 Hz, 1 H), 7.84 (d, *J* = 8.4 Hz, 1 H), 7.67 (t, *J* = 6.9 Hz, 1 H), 7.53 (t, *J* = 7.5 Hz, 1 H), 7.35 (d, *J* = 8.1 Hz, 2 H), 2.68 (s, 3H), 2.44 (s, 3 H).



Ethyl 2-(tosyloxy)quinoline-4-carboxylate (2l). The product (95% yield) as a white solid was purified with silica gel chromatography (Petroleum ether / Ethyl ether = 10:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.74 (d, *J* = 8.7 Hz, 1 H), 8.04 (d, *J* = 8.4 Hz, 2 H), 7.91 (d, *J* = 8.4 Hz, 1 H), 7.75 (t, *J* = 7.2 Hz, 1 H), 7.71 (s, 1 H), 7.63 (t, *J* = 7.2 Hz, 1 H), 7.38 (d, *J* = 8.4 Hz, 2 H), 4.50 (q, *J* = 7.2 Hz, 2 H), 2.46 (s, 3H), 1.47 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 154.8, 147.0, 145.5, 139.8, 133.7, 130.7, 129.6, 129.1, 128.9, 128.0, 125.6, 124.2, 116.0, 62.2, 21.7, 14.2.



5-(Ttrifluoromethyl)pyridin-2-yl 4-methylbenzenesulfonate (2m). The product (88% yield) as a white solid was purified with silica gel chromatography (Petroleum ether / Ethyl ether = 15:1). This compound is known.[5] ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.55 (S, 1 H), 8.02 (d, *J* = 8.4 Hz, 1 H), 7.95 (d, *J* = 8.1 Hz, 2 H), 7.39 (d, *J* = 7.2 Hz, 2 H), 7.24 (d, *J* = 8.7 Hz, 1 H), 2.49 (s, 3 H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.5 (s, 3F).



Quinoline-2,4-diyl bis(4-methylbenzenesulfonate) (4). The product (92% yield) as a white solid was purified with silica gel chromatography (Petroleum ether / Ethyl ether = 2:1). This compound is known.[5] ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.4 Hz, 2 H), 7.90 (d, *J* = 8.4 Hz, 1 H), 7.83 (d, *J* = 8.4 Hz, 3 H), 7.70 (t, *J* = 7.5 Hz, 1 H), 7.49 (t, *J* = 7.5 Hz, 1 H), 7.36 (t, *J* = 8.4 Hz, 4 H), 7.01 (s, 1 H), 2.46 (s, 3 H), 2.45 (s, 3 H).

General Procedure for Pd-Catalyzed Direct Cross-Coupling of Fluoroarenes 1 with Various Heteroaromatic Tosylates 2. To a septum capped 25 mL of sealed tube were added $Pd(TFA)_2$ (5.0 mol%), **L** (10 mol%), K_3PO_4 (1.2 equiv), AdOH (1.2 equiv) and heteroaromatic tosylate **2** (0.3 mmol, 1.0 equiv) under N_2, followed by *t*-BuOH (1.5 mL) with stirring. Polyfluoroarene (0.6-0.9 mmol, 2.0-3.0 equiv) was then added subsequently. The sealed tube was screw capped and heated to 90 ^{o}C (oil bath). After stirring for 12 h, the reaction mixture was cooled to room temperature, and diluted with ethyl acetate, washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified with silica gel chromatography to provide pure product.

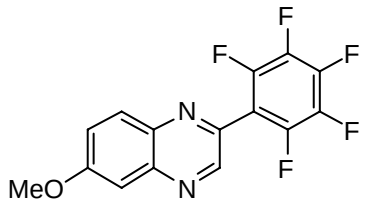
2-(Perfluorophenyl)quinoxaline (3a). 3 mol% of $Pd(TFA)_2$ and 6 mol% of **L** were used. The product (63 mg, 73% yield) as a white solid was purified with silica gel chromatography (Petroleum ether / Ethyl ether = 50:1). M.P. 138 ^oC; ^1H NMR (300 MHz, $CDCl_3$) δ 9.00 (s, 1H), 8.22-8.17 (m, 2H), 7.91-7.85 (m, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 145.4 (t, *J* = 2.3 Hz), 145.0 (dm, *J* = 252.4 Hz), 142.7 (m), 142.3, 141.8, 142.0 (dm, *J* = 257.2 Hz), 137.9 (dm, *J* = 254.9 Hz), 131.2, 130.9, 129.7, 129.3, 112.6 (t, *J* = 16.8 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ -142.8 (dd, *J* = 21.7 Hz, 7.9 Hz, 2F), -151.6 (t, *J* = 21.7 Hz, 1F), -161.0 (m, 2F). IR (KBr): ν_{max} 1652, 1523, 1498, 1029 cm^{-1}. MS (EI): *m/z* (%) 297 (M^++H^+), 296 (M^+), 76 (100). Anal. Calcd. for $C_{14}H_5F_5N_2$: N, 9.46; C, 56.77; H, 1.70; Found: N, 9.45; C, 56.91; H, 1.50.

6-Methyl-2-(perfluorophenyl)quinoxaline (3b). 3 mol% of $Pd(TFA)_2$ and 6 mol% of **L** were used. The product (86 mg, 92% yield) as a white solid was purified with silica gel chromatography (Petroleum ether / Ethyl ether = 50:1). M.P. 122 ^oC; ^1H NMR (300 MHz, $CDCl_3$) δ 8.94 (s, 1H), 8.06 (d, *J* = 8.7 Hz, 1H), 7.95 (s, 1H), 7.69 (d, *J* = 8.7 Hz, 1H), 2.65 (s, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 145.3, 144.9 (dm, *J* = 247.4 Hz), 142.2, 141.9, 141.8 (dm, *J* = 256.8 Hz), 141.7, 140.8, 137.9 (dm, *J* = 253.3 Hz), 133.2, 129.1, 128.1, 112.8 (m), 21.9. ^{19}F NMR (282 MHz, $CDCl_3$) δ -142.9 (dd, *J* = 21.7 Hz, 7.9 Hz, 2F), -152.0 (t, *J* = 21.7 Hz, 1F), -161.2 (td, *J* = 21.7 Hz, 7.9 Hz, 2F). IR (KBr): ν_{max} 1552, 1521, 1499 cm^{-1}. MS (EI): *m/z* (%) 311 (M^++H^+), 310 (M^+, 100), 89. Anal. Calcd. for $C_{15}H_7F_5N_2$: N, 7.52; C, 64.52; H, 2.44; Found: N, 7.49; C, 64.64; H, 2.48.

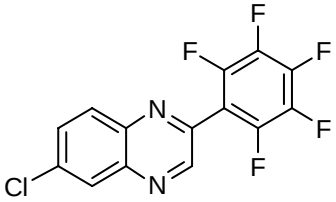
6,7-Dimethyl-2-(perfluorophenyl)quinoxaline (3c). 3 mol% of $Pd(TFA)_2$ and 6 mol% of **L** were used. The product (79 mg, 81% yield) as a white solid was purified with silica gel chromatography (Petroleum ether / Ethyl ether = 50:1). M.P. 192 ^oC; ^1H

NMR (400 MHz, $CDCl_3$) δ 8.79 (s, 1H), 7.83 (s, 1H), 7.82 (s, 1H), 2.46 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1 (dm, J = 250.4 Hz), 144.6, 142.0, 141.9 (dm, J = 255.1 Hz), 141.7, 141.55, 141.49, 141.0, 138.0 (dm, J = 252.1 Hz), 128.7, 128.4, 113.3 (m), 20.2, 20.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -142.6 (dd, J = 20.7 Hz, 8.3 Hz, 2F), -152.5 (t, J = 20.7 Hz, 1F), -161.4 (td, J = 20.7 Hz, 8.3 Hz, 2F). IR (KBr): ν_{max} 1651, 1548, 1496, 1418 cm^{-1}. MS (EI): *m/z* (%) 325 (M^++H^+), 324 (M^+, 100), 309. Anal. Calcd. for $C_{16}H_9F_5N_2$: N, 8.64; C, 59.27; H, 2.80; Found: N, 8.69; C, 59.48; H, 2.48.

6-Methoxy-2-(perfluorophenyl)quinoxaline (3d). 3 mol% of $Pd(TFA)_2$ and 6 mol% of **L** were used. The product (89 mg, 91% yield) as a white solid was purified with silica gel chromatography (Petroleum ether / Ethyl ether = 50:1). M.P. 133 ^oC; ^1H NMR (300 MHz, $CDCl_3$) δ 8.90 (s, 1H), 8.04 (d, J = 9.0 Hz, 1H), 7.51 (dd, J = 9.0 Hz, 2.7 Hz, 1H), 7.44 (d, J = 2.7 Hz, 1H), 4.03 (s, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 161.8, 145.4, 144.9 (dm, J = 251.5 Hz), 143.6, 141.7 (dm, J = 255.1 Hz), 139.8, 138.6, 137.9 (dm, J = 252.1 Hz), 130.6, 124.5, 112.9 (m), 106.3, 55.9. ^{19}F NMR (282 MHz, $CDCl_3$) δ -143.0 (dd, J = 21.7 Hz, 7.9 Hz, 2F), -152.2 (t, J = 21.7 Hz, 1F), -161.2 (td, J = 21.7 Hz, 7.9 Hz, 2F). IR (KBr): ν_{max} 1522, 1497, 1485 cm^{-1}. MS (EI): *m/z* (%) 327 (M^++H^+), 326 (M^+, 100), 106. HRMS: Calculated for $C_{15}H_7N_2OF_5$: 326.0479; Found: 326.0480.



6-Chloro-2-(perfluorophenyl)quinoxaline (3e). 3 mol% of $Pd(TFA)_2$ and 6 mol% of **L** were used. The product (43 mg, 43% yield) as a white solid was purified with silica gel chromatography (Petroleum ether / Ethyl ether = 50:1). M.P. 130 ^oC; ^1H NMR (300 MHz, $CDCl_3$) δ 9.00 (s, 1H), 8.18 (d, J = 2.1 Hz, 1H), 8.11 (d, J = 9.0 Hz, 1H), 7.81 (dd, J = 9.0 Hz, 2.1 Hz, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 146.3 (t, J = 9.3 Hz), 144.9 (dm, J = 252.4 Hz), 142.8 (m), 142.1 (dm, J = 257.6 Hz), 142.0, 140.8, 137.9 (dm, J = 255.2 Hz), 137.2, 132.0, 130.9, 128.2,

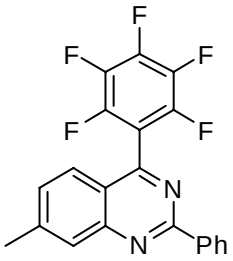


122.4 (m). ^{19}F NMR (282 MHz, $CDCl_3$) δ -142.8 (dd, *J* = 21.7 Hz, 7.9 Hz, 2F), -151.1 (t, *J* = 21.7 Hz, 1F), -160.8 (m, 2F). IR (KBr): ν_{max} 1657, 1551, 1521, 1499 cm^{-1}. MS (EI): *m/z* (%) 331 (M^++H^+), 330 (M^+, 100), 110. Anal. Calcd. for $C_{14}H_4ClF_5N_2$: N, 8.47; C, 50.86; H, 1.22; Found: N, 8.59; C, 51.11; H, 1.07.

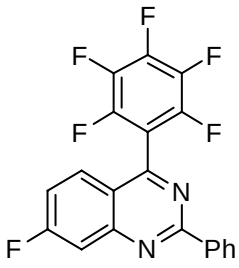
6-Fluoro-2-(perfluorophenyl)quinoxaline (3f). The product (72 mg, 76% yield) as a white solid (127 ^{o}C) was purified with silica gel chromatography (Petroleum ether / Ethyl ether = 50:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.00 (s, 1H), 8.20 (dd, *J* = 9.0 Hz, 5.4 Hz, 1H), 7.83 (dd, *J* = 9.0 Hz, 2.7 Hz, 1H), 7.66 (td, *J* = 8.4 Hz, 2.7 Hz, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 163.5 (d, *J* = 254.6 Hz), 146.2 (t, *J* = 9.3 Hz), 145.0 (dm, *J* = 256.3 Hz), 142.7 (d, *J* = 13.3 Hz), 142.04 (dm, *J* = 257.3 Hz), 142.03 (m), 139.6 (d, *J* = 1.0 Hz), 137.8 (dm, *J* = 254.6 Hz), 131.9 (d, *J* = 10.2 Hz), 121.5 (d, *J* = 26.2 Hz), 112.9 (d, *J* = 21.7 Hz), 112.4 (m). ^{19}F NMR (282 MHz, $CDCl_3$) δ -105.7 (dd, *J* = 13.8 Hz, 7.9 Hz, 1F), -142.9 (dd, *J* = 21.7 Hz, 7.9 Hz, 2F), -151.3 (t, *J* = 21.7 Hz, 1F), -160.8 (m, 2F). IR (KBr): ν_{max} 1653, 1557, 1521, 1499 cm^{-1}. MS (EI): *m/z* (%) 315 (M^++H^+), 314 (M^+), 94 (100). Anal. Calcd. for $C_{14}H_4F_6N_2$: N, 8.92; C, 53.52; H, 1.28; Found: N, 8.94; C, 53.43; H, 1.15.

4-(Perfluorophenyl)-2-phenylquinazoline (3g). The product (88 mg, 78% yield) as a white solid was purified with silica gel chromatography (Petroleum ether / Ethyl ether = 50:1). M.P. 197 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.63-8.61(m, 2H), 8.22 (d, *J* = 8.4 Hz, 1H), 7.97 (t, *J* = 8.1 Hz, 1H), 7.67-7.53 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 156.9, 151.6, 144.7 (dm, *J* = 246.6 Hz), 142.1 (dm, *J* = 256.1 Hz), 137.8 (dm, *J* = 249.4 Hz), 137.3, 134.6, 130.9, 129.3, 128.6, 127.9, 125.2, 122.6, 112.0 (m). ^{19}F NMR (282 MHz, $CDCl_3$) δ -139.9 (dd, *J* = 21.7 Hz, 7.9 Hz, 2F), -151.8 (t, *J* = 21.7 Hz, 1F), -160.8 (m, 2F). IR (KBr): ν_{max} 1565, 1521, 1499 cm^{-1}. MS (EI): *m/z* (%) 373 (M^++H^+), 372 (M^+, 100), 179. Anal. Calcd. for $C_{20}H_9F_5N_2$: N, 9.03; C, 58.07; H, 2.27; Found: N, 9.13; C, 58.15; H, 2.19.

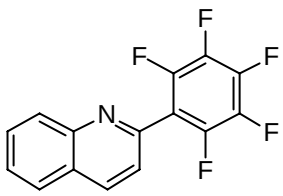
7-Methyl-4-(perfluorophenyl)-2-phenylquinazoline (3h). The product (106 mg, 95% yield) as a white solid was purified with silica gel chromatography (Petroleum ether / Ethyl ether = 50:1). M.P. 222 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.62-8.59 (m, 2H), 7.99 (s, 1H), 7.54-7.52 (m, 4H), 7.43 (d, *J* = 8.4 Hz, 1H), 2.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 156.3, 151.9, 145.9, 144.7 (dm, *J* = 250.4 Hz), 142.1 (dm, *J* = 255.2 Hz), 137.9 (dm, *J* = 253.4 Hz), 137.5, 130.8, 130.4, 128.7, 128.3, 124.9, 121.0, 112.3 (m), 22.3. ^{19}F NMR (282 MHz, $CDCl_3$) δ -140.0 (dd, *J* = 21.7 Hz, 5.9 Hz, 2F), -152.1 (t, *J* = 21.7 Hz, 1F), -161.0 (td, *J* = 21.7 Hz, 5.9 Hz, 2F). IR (KBr): ν_{max} 1655, 1566, 1521, 1499 cm^{-1}. MS (EI): *m/z* (%) 387 (M^++H^+), 386 (M^+, 100), 193. Anal. Calcd. for $C_{21}H_{11}F_5N_2$: N, 7.25; C, 65.29; H, 2.87; Found: N, 7.33; C, 65.43; H, 2.94.



7-Fluoro-4-(perfluorophenyl)-2-phenylquinazoline (3i). The reaction run at 80 ^{o}C for 24 h. The product (100 mg, 85% yield) as a white solid was purified with silica gel chromatography (Petroleum ether / Ethyl ether = 50:1). M.P. 208 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.63-8.59 (m, 2H), 7.84 (dd, *J* = 9.9 Hz, 2.4 Hz, 1H), 7.70-7.65 (m, 1H), 7.55-7.53 (m, 3H), 7.38 (td, *J* = 9.0 Hz, 2.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1 (d, *J* = 256.6 Hz), 161.6, 156.6, 153.5 (d, *J* = 14.2 Hz), 144.7 (dm, *J* = 251.1 Hz), 142.3 (dm, *J* = 251.1 Hz), 137.9 (dm, *J* = 255.5 Hz), 137.0, 131.3, 128.8 (d, *J* = 11.0 Hz), 128.0 (d, *J* = 10.7 Hz), 120.0, 118.7 (d, *J* = 25.6 Hz), 113.2 (d, *J* = 20.5 Hz), 111.9 (m). ^{19}F NMR (282 MHz, $CDCl_3$) δ -100.8 (dd, *J* = 14.1 Hz, 7.9 Hz, 1F), -139.9 (dd, *J* = 21.7 Hz, 7.9 Hz, 2F), -152.3 (t, *J* = 21.7 Hz, 1F), -161.5 (m, 2F). IR (KBr): ν_{max} 1572, 1521, 1499 cm^{-1}. MS (EI): *m/z* (%) 391 (M^++H^+), 390 (M^+, 100), 199. Anal. Calcd. for $C_{20}H_8F_6N_2$: N, 7.18; C, 61.55; H, 2.07; Found: N, 7.22; C, 61.42; H, 1.95.

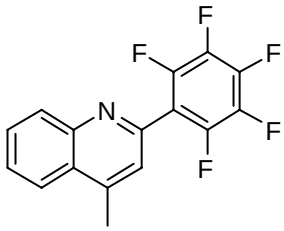


2-(Perfluorophenyl)quinoline (3j). The product (80 mg, 90% yield) as a white solid



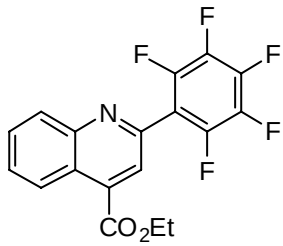
was purified with silica gel chromatography (Petroleum ether / Ethyl ether = 50:1). This compound is known.[6] M.P. 166 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.7 Hz, 1H), 8.17 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.81 (td, *J* = 6.9 Hz, 1.2 Hz, 1H), 7.65 (td, *J* = 8.1 Hz, 1.2 Hz, 1H), 7.55 (d, *J* = 8.7 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -143.1 (dd, *J* = 21.7 Hz, 7.9 Hz, 2F), -153.7(t, *J* = 21.7 Hz, 1F), -161.9 (td, *J* = 21.7 Hz, 7.9 Hz, 2F). Anal. Calcd. for $C_{15}H_6F_5N$: N, 4.74; C, 61.03; H, 2.05; Found: N, 4.75; C, 60.94; H, 1.80.

4-Methyl-2-(perfluorophenyl)quinoline (3k). The product (72 mg, 78% yield) as a



white solid was purified with silica gel chromatography (Petroleum ether / Ethyl ether = 50:1). M.P. 137 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.4 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.78 (t, *J* = 7.8 Hz, 1H), 7.65 (t, *J* = 7.8 Hz, 1H), 7.38 (s, 1H), 2.78 (s, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 147.8, 146.7, 145.5, 144.7 (dm, *J* = 246.0 Hz), 141.2 (dm, *J* = 254.9 Hz), 137.7 (dm, *J* = 253.0 Hz), 130.1, 129.8, 127.5, 127.3, 123.7, 123.3, 115.8 (m), 18.7. ^{19}F NMR (282 MHz, $CDCl_3$) δ -143.0 (dd, *J* = 21.7 Hz, 7.9 Hz, 2F), -154.1(t, *J* = 21.7 Hz, 1F), -162.1 (td, *J* = 21.7 Hz, 7.9 Hz, 2F). IR (KBr): ν_{max} 1653, 1523, 1507, 1494 cm^{-1}. MS (EI): *m/z* (%) 310 (M^++H^+), 309 (M^+, 100), 115.Anal. Calcd. for $C_{16}H_8F_5N$: N, 4.53; C, 62.14; H, 2.61; Found: N, 4.65; C, 62.34; H, 2.59.

Ethyl 2-(perfluorophenyl)quinoline-4-carboxylate (3l). The product (100 mg, 91%



yield) as a white solid was purified with silica gel chromatography (Petroleum ether / Ethyl ether = 50:1). M.P. 99 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.86 (d, *J* = 8.4 Hz, 1H), 8.22 (d, *J* = 8.4 Hz, 1H), 8.07 (s, 1H), 7.85 (t, *J* = 6.9Hz, 1H), 7.75 (t, *J* = 6.9 Hz, 1H), 4.54 (q, *J* = 7.2 Hz, 2H), 1.49 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 165.5, 149.1, 146.5, 144.8 (dm, *J* =

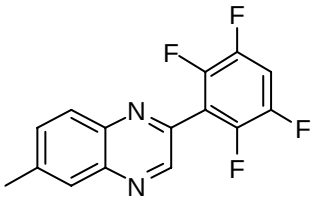
246.6 Hz), 141.4 (dm, J = 242.0 Hz), 137.8 (dm, J = 253.0 Hz), 136.1, 130.4, 130.2, 129.1, 125.0, 124.4, 123.7, 114.9 (m), 62.2, 14.2. ^{19}F NMR (282 MHz, $CDCl_3$) δ -142.9 (dd, J = 21.7 Hz, 7.9 Hz, 2F), -152.9 (t, J = 21.7 Hz, 1F), -161.6 (td, J = 21.7 Hz, 7.9 Hz, 2F). IR (KBr): ν_{max} 1723, 1653 cm^{-1}. MS (EI): *m/z* (%) 368 (M^++H^+), 367 (M^+), 309 (100). Anal. Calcd. for $C_{18}H_{10}F_5NO_2$: N, 3.81; C, 58.86; H, 2.74; Found: N, 4.06; C, 58.94; H, 2.66.

2-(Perfluorophenyl)-5-(trifluoromethyl)pyridine (3m). The reaction run at 80 °C for 36 h. The product as a colorless liquid was purified with silica gel chromatography (Petroleum ether / Ethyl ether = 50:1). Further purification by reverse phase preparative HPLC (MeOH/H_2O = 95:5) afforded pure product (66 mg, 70% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.05 (s, 1H), 8.11 (dd, J = 8.1 Hz, 1.8 Hz, 1H), 7.65 (d, J = 8.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 147.0 (q, J = 3.9 Hz), 144.7 (dm, J = 250.7 Hz), 144.0 (dm, J = 255.6 Hz), 137.9 (dm, J = 252.5 Hz), 134.0 (q, J = 3.2 Hz), 126.7 (q, J = 33.4 Hz), 125.7, 123.1 (q, J = 271.3 Hz), 114.2 (td, J = 15.7 Hz, 3.9 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.1 (s, 3F), -143.3 (dd, J = 21.7 Hz, 7.9 Hz, 2F), -152.4 (t, J = 21.7 Hz, 1F), -161.5 (m, 2F). IR (KBr): ν_{max} 2908, 1484, 1404 cm^{-1}. MS (EI): *m/z* (%) 314 (M^++H^+), 313 (M^+, 100), 294, 135. HRMS: Calculated for $C_{12}H_3F_8N$: 313.0138; Found: 313.0141.

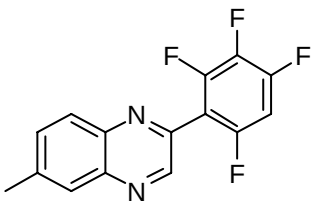
2-(2,3,5,6-Tetrafluorophenyl)quinoline (3n). The product (60 mg, 72% yield) as a white solid was purified with silica gel chromatography (Petroleum ether / Ethyl ether = 50:1). M.P. 109 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.31 (d, J = 8.7 Hz, 1H), 8.19 (d, J = 8.7 Hz, 1H), 7.90 (d, J = 7.8 Hz, 1H), 7.80 (t, J = 7.2 Hz, 1H), 7.64 (t, J = 7.2 Hz, 1H), 7.58 (d, J = 8.4 Hz, 1H), 7.27-7.13 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 147.8 (m), 146.1 (dm, J = 247.1 Hz), 144.3 (dm, J = 248.1 Hz), 136.7, 130.1, 129.6, 127.6, 127.5, 127.4, 122.6, 121.1 (t, J = 16.4 Hz), 106.1 (t, J = 22.4 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ -138.8 (m, 2F), -143.8 (m, 2F).

IR (KBr): ν_{max} 1490, 1484, 1425 cm^{-1}. MS (EI): *m/z* (%) 278 (M^++H^+), 277 (M^+, 100), 258. Anal. Calcd. for $C_{15}H_7F_4N$: N, 5.05; C, 64.99; H, 2.55; Found: N, 5.07; C, 65.17; H, 2.39.

6-Methyl-2-(2,3,5,6-tetrafluorophenyl)quinoxaline (3o). The product (50 mg, 57% yield) as a white solid was purified with silica gel chromatography (Petroleum ether / Ethyl ether = 50:1). M.P. 162 ^oC; ^1H NMR (300 MHz, $CDCl_3$) δ 8.98 (s, 1H), 8.08 (dd, *J* = 8.4 Hz, 4.5 Hz, 1H), 7.96 (d, *J* = 4.5 Hz, 1H), 7.70 (t, *J* = 6.6 Hz, 1H), 7.29-7.22 (m, 1H), 2.65 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.2 (dm, *J* = 247.9 Hz), 145.4 (t, *J* = 2.0 Hz), 144.5 (dm, *J* = 249.6 Hz), 142.5, 142.0, 141.9, 140.8, 133.1, 129.2, 128.1, 118.2 (t, *J* = 15.7 Hz), 107.1 (t, *J* = 22.4 Hz), 21.9. ^{19}F NMR (282 MHz, $CDCl_3$) δ -138.2 (m, 2F), -143.6 (m, 2F). IR (KBr): ν_{max} 1504, 1484, 1465 cm^{-1}. MS (EI): *m/z* (%) 293 (M^++H^+), 292 (M^+, 100), 89. HRMS: Calculated for $C_{15}H_8F_4N_2$: 292.0624; Found: 292.0632.



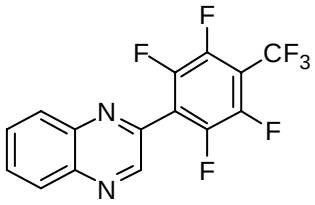
6-Methyl-2-(2,3,4,6-tetrafluorophenyl)quinoxaline (3p). The product (46 mg, 53% yield) as a white solid was purified with silica gel chromatography (Petroleum ether / Ethyl ether = 50:1). M.P. 149 ^oC; ^1H NMR (300 MHz, $CDCl_3$) δ 8.94 (s, 1H), 8.06 (d, *J* = 8.7 Hz, 1H), 7.94 (s, 1H), 7.68 (d, *J* = 8.7 Hz, 1H), 7.02-6.95 (m, 1H), 2.65 (s, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 155.0 (dm, *J* = 253.8 Hz), 151.2 (dm, *J* = 250.0 Hz), 149.7 (dm, *J* = 251.5 Hz), 145.6, 142.6, 141.8, 141.7, 140.8, 137.6 (dm, *J* = 250.1 Hz), 133.0, 129.1, 128.1, 113 (m), 101.5 (ddd, *J* = 28.0 Hz, 21.6 Hz, 4.1 Hz), 21.9. ^{19}F NMR (282 MHz, $CDCl_3$) δ -117.9 (t, *J* = 9.9 Hz, 1F), -129.6 (td, *J* = 17.8 Hz, 7.9 Hz, 1F), -135.1 (dd, *J* = 21.7 Hz, 7.9 Hz, 1F), -164.0 (m, 1F). IR (KBr): ν_{max} 1517, 1484, 1453 cm^{-1}. MS (EI): *m/z* (%) 293 (M^++H^+), 292 (M^+, 100), 89. HRMS: Calculated for $C_{15}H_8F_4N_2$: 292.0624; Found: 292.0629.



2-(2,3,5,6-Tetrafluoro-4-methoxyphenyl)quinoxaline (3q). The product (66 mg, 71% yield) as a white solid was purified with silica gel chromatography (Petroleum ether / Ethyl ether = 50:1). M.P. 95 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.00 (s, 1H), 8.20-8.16 (m, 2H), 7.87-7.84 (m, 2H), 2.94 (s, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 145.0 (dm, *J* = 249.0 Hz), 145.7 (m), 143.6 (m), 142.4, 142.3, 141.6, 141.0 (dm, *J* = 249.6 Hz), 130.8, 130.6, 129.6, 129.2, 125.2 (m), 110.5 (m), 62.2 (t, *J* = 3.9 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ -144.9 (dd, *J* = 21.7 Hz, 8.2 Hz, 2F), -157.5 (dd, *J* = 21.7 Hz, 9.9 Hz, 2F). IR (KBr): ν_{max} 1497, 1484, 1404 cm^{-1}. MS (EI): *m/z* (%) 309 (M^++H^+), 308 (M^+, 100), 76. HRMS: Calculated for $C_{15}H_8F_4N_2O$: 308.0573; Found: 308.0565.

2-(2,3,5,6-Tetrafluoro-4-methoxyphenyl)-5-(trifluoromethyl)pyridine (3r). The reaction run at 80 °C for 36 h. The product (58 mg, 60% yield) as a white solid was purified with silica gel chromatography (Petroleum ether / Ethyl ether = 50:1). M.P. 47 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.03 (s, 1 H), 8.08 (dd, *J* = 8.1 Hz, 1.8 Hz, 1H), 7.64 (d, *J* = 8.1 Hz, 1H), 4.16 (s, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 151.3, 146.8 (q, *J* = 3.9 Hz), 144.8 (dm, *J* = 249.3 Hz), 141.0 (dm, *J* = 247.4 Hz), 134.3 (m), 133.8 (q, *J* = 3.3 Hz), 126.2 (q, *J* = 33.4 Hz), 125.6, 123.2 (q, *J* = 272.3 Hz), 112.1 (t, *J* = 15.8 Hz), 62.1 (t, *J* = 4.0 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.9 (s, 3F), -145.4 (dd, *J* = 21.7 Hz, 7.9 Hz, 2F), -157.8 (dd, *J* = 21.7 Hz, 7.9 Hz, 2F). IR (KBr): ν_{max} 3012, 1652, 1472 cm^{-1}. MS (EI): *m/z* (%) 326 (M^++H^+), 325 (M^+, 100), 135. HRMS: Calculated for $C_{13}H_6F_7NO$: 325.0338; Found: 325.0336.

2-(2,3,5,6-Tetrafluoro-4-(trifluoromethyl)phenyl)quinoxaline (3s). The product (90 mg, 87% yield) as a white solid was purified with silica gel chromatography (Petroleum ether / Ethyl ether = 50:1). M.P. 137 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.04 (s, 1H), 8.24-8.17 (m, 2H), 7.94-7.86 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ



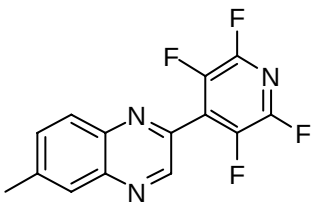
145.0 (m), 144.9 (dm, J = 252.9 Hz), 144.4 (dm, J = 260.1 Hz), 142.3, 142.1, 131.6, 131.1, 129.8, 129.4, 121.2 (m), 120.6 (q, J = 274.0 Hz), 110.6 (m). ^{19}F NMR (282 MHz, $CDCl_3$) δ -56.9 (t, J = 21.4, 3F), -139.7 (m, 2F), -141.1 (m, 2F). IR (KBr): ν_{max} 1660, 1499, 1343 cm^{-1}. MS (EI): *m/z* (%) 347 (M^++H^+), 346 (M^+, 100), 76. Anal. Calcd. for $C_{15}H_5F_7N_2$: N, 8.09; C, 52.04; H, 1.46; Found: N, 8.21; C, 52.36; H,1.32.

6-Methyl-2-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)quinoxaline (3t). The product (95 mg, 88% yield) as a white solid was purified with silica gel chromatography (Petroleum ether / Ethyl ether = 50:1). M.P. 98 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.98 (s, 1H), 8.07 (d, J = 8.4 Hz, 1H), 7.96 (s, 1H), 7.71 (d, J = 8.4 Hz, 1H), 2.66 (s, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 144.9 (t, J = 2.3 Hz), 144.8 (dm, J = 253.5 Hz), 144.6 (dm, J = 264.2 Hz), 142.7, 142.1, 141.1, 140.8, 133.4, 129.3, 128.1, 121.4 (t, J =16.0 Hz), 120.6 (q, J = 274.6 Hz), 110.3 (m), 21.7. ^{19}F NMR (282 MHz, $CDCl_3$) δ -56.8 (t, J = 21.7 Hz, 3F), -139.8 (m, 2F), -141.3 (m, 2F). IR (KBr): ν_{max} 1624, 1498 cm^{-1}. MS (EI): *m/z* (%) 361 (M^++H^+), 360 (M^+, 100), 90. Anal. Calcd. for $C_{16}H_7F_7N_2$: N, 7.78; C, 53.35; H, 1.96; Found: N, 7.72; C, 53.32; H,1.86.

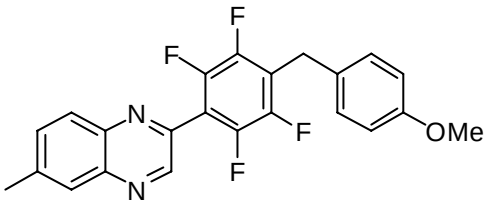
7-Methyl-4-(perfluoropyridin-4-yl)-2-phenylquinazoline (3u). The product (86 mg, 78% yield) as a white solid was purified with silica gel chromatography (Petroleum ether / Ethyl ether = 50:1). M.P. 211 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.62-8.59 (m, 2H), 8.03 (s, 1H), 7.56-7.45 (m, 5H), 2.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 155.2, 151.9, 146.3, 143.7 (dm, J = 246.3 Hz), 139.5 (dm, J = 262.8 Hz), 137.2, 131.0, 130.7, 129.7 (m), 128.7, 128.6, 128.4, 124.3, 120.0, 22.3. ^{19}F NMR (282 MHz, $CDCl_3$) δ -89.2 (m, 2F), -141.3 (m, 2F). IR (KBr): ν_{max} 1566, 1521, 1499 cm^{-1}. MS (EI): *m/z* (%) 370 (M^++H^+), 369 (M^+, 100), 219. Anal. Calcd. for

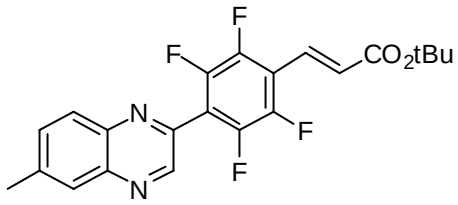
$C_{20}H_{11}F_4N_3$: N, 11.38; C, 65.04; H, 3.00; Found: N, 11.30; C, 65.07; H, 3.02.

6-Methyl-2-(perfluoropyridin-4-yl)quinoxaline (3v). The product (62 mg, 70% yield) as a white solid was purified with silica gel chromatography (Petroleum ether / Ethyl ether = 50:1). M.P. 106 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.03 (s, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 7.97 (s, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 2.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 143.9 (dm, *J* = 245.3 Hz), 143.0, 142.3, 140.7, 140.0 (dm, *J* = 261.8 Hz), 133.5, 129.7 (m), 129.3, 128.1, 21.9. ^{19}F NMR (282 MHz, $CDCl_3$) δ -89.5 (m, 2F), -144.3 (m, 2F). IR (KBr): ν_{max} 1645, 1497, 1471, 1406 cm^{-1}. MS (EI): *m/z* (%) 294 (M^++H^+, 100), 89. Anal. Calcd. for $C_{14}H_7F_4N_3$: N, 14.33; C, 57.35; H, 2.41; Found: N, 14.45; C, 57.42; H, 2.31.

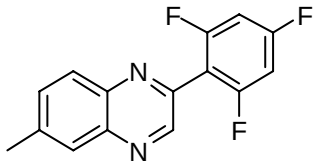


6-Methyl-2-(2,3,5,6-tetrafluoro-4-(4-methoxybenzyl)phenyl)quinoxaline (3w). 1.2 equiv of fluoroarene was used. The product (60 mg, 49% yield) as a white solid was purified with silica gel chromatography (Petroleum ether / Ethyl ether = 50:1). M.P. 100 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.94 (s, 1H), 8.06 (d, *J* = 8.7 Hz, 1H), 7.95 (s, 1H), 7.68 (d, *J* = 8.7 Hz, 1H), 7.24 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 4.09 (s, 2H), 3.79 (s, 3H), 2.64 (s, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 158.5, 145.6, 145.0 (dm, *J* = 245.1 Hz), 144.4 (dm, *J* = 239.3 Hz), 141.8 (m), 140.9, 133.1, 129.5, 129.4, 129.2, 128.1, 121.6 (t, *J* = 18.4 Hz), 115.4 (m), 114.1, 55.2, 28.0, 21.9. ^{19}F NMR (282 MHz, $CDCl_3$) δ -143.5 (dd, *J* = 21.7 Hz, 113.8 Hz, 2F), -144.3 (dd, *J* = 21.7 Hz, 11.8 Hz, 2F). IR (KBr): ν_{max} 1612, 1514 cm^{-1}. MS (EI): *m/z* (%) 413 (M^++H^+), 412 (M^+, 100), 206. HRMS: Calculated for $C_{23}H_{16}F_4N_2O$: 412.1199; Found: 412.1201.



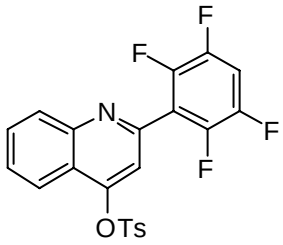
(*E*)-Tert-butyl 3-(2,3,5,6-tetrafluoro-4-(6-methylquinoxalin-2-yl)phenyl)acrylate (3x). 

1.2 equiv of fluoroarene was used. The product (100 mg, 80% yield) as a white solid was purified with silica gel chromatography (Petroleum ether / Ethyl ether = 50:1). M.P. 153 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.99 (s, 1H), 8.07 (d, *J* = 8.7 Hz, 1H), 7.95 (s, 1H), 7.69 (d, *J* = 16.5 Hz, 1H), 7.68 (s, 1H), 6.81 (d, *J* = 16.5 Hz, 1H), 2.65 (s, 3H), 1.57 (s, 9H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 165.2, 145.5 (dm, *J* = 255.3 Hz), 145.3 (m), 144.6 (dm, *J* = 256.3 Hz), 142.2, 141.9, 140.8, 133.2, 129.3, 129.2, 129.1, 127.6, 117.8 (t, *J* = 16.0 Hz), 115.6 (t, *J* = 13.5 Hz), 81.5, 28.0, 21.9. ^{19}F NMR (282 MHz, $CDCl_3$) δ -140.0 (dd, *J* = 21.7 Hz, 13.8 Hz, 2F), -143.9 (dd, *J* = 21.7 Hz, 13.8 Hz, 2F). IR (KBr): ν_{max} 1716, 1636 cm^{-1}. MS (EI): *m/z* (%) 419 (M^++H^+), 418 (M^+), 362 (100). Anal. Calcd. for $C_{22}H_{18}F_4N_2O_2$: N, 6.70; C, 63.16; H, 4.34; Found: N, 6.66; C, 63.27; H, 4.48.

6-Methyl-2-(2,4,6-trifluorophenyl)quinoxaline (3y). 10 mol% of $Pd(TFA)_2$ and 20 mol% of **L** were used. 

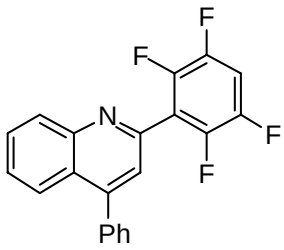
The product (22 mg, 27% yield) as a white solid was purified with silica gel chromatography (Petroleum ether / Ethyl ether = 50:1). M.P. 151 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.93 (s, 1H), 8.06 (d, *J* = 8.7 Hz, 1H), 7.93 (s, 1H), 7.66 (d, *J* = 8.1 Hz, 1H), 6.87 (t, *J* = 8.1 Hz, 1H), 2.63 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2 (dt, *J* = 251.0 Hz, 15.2 Hz), 161.2 (ddd, *J* = 251.7 Hz, 14.8 Hz, 9.3 Hz), 146.0, 143.6, 141.6, 141.3, 140.8, 132.8, 129.1, 128.0, 112.1 (m), 101.0 (m), 21.8. ^{19}F NMR (282 MHz, $CDCl_3$) δ -105.2 (m, 1F), -111.2 (t, *J* = 7.9 Hz, 2F). IR (KBr): ν_{max} 3047, 1643, 1599 cm^{-1}. MS (EI): *m/z* (%) 275 (M^++H^+), 274 (M^+, 100), 89. Anal. Calcd. for $C_{15}H_9F_3N_2$: N, 10.21; C, 65.69; H, 3.31; Found: N, 10.17; C, 65.71; H, 3.35.

2-(2,3,5,6-Tetrafluorophenyl)quinolin-4-yl-4-methylbenzenesulfonate (5). The product (74 mg, 55% yield) as a white solid was purified with silica gel chromatography (Petroleum ether / Ethyl ether = 50:1). M.P. 138 ^{o}C; ^{1}H NMR (300



MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.7 Hz, 1H), 8.00 (d, *J* = 8.7 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.79 (t, *J* = 8.4 Hz, 1H), 7.60 (t, *J* = 8.4 Hz, 1H), 7.47 (s, 1H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.23-7.15 (m, 1H), 2.43 (m, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 153.3, 149.7, 148.2 (m), 146.3, 146.1 (dm, *J* = 248.7 Hz), 144.2 (dm, *J* = 250.4 Hz), 131.6, 131.0, 130.0, 129.5, 128.4, 128.1, 121.5, 121.4, 120.2 (t, *J* = 16.1 Hz), 106.6 (t, *J* = 22.7 Hz), 21.6. ^{19}F NMR (282 MHz, $CDCl_3$) δ -138.5 (m, 2F), -143.6 (m, 2F). IR (KBr): ν_{max} 1613, 1595, 1497 cm^{-1}. MS (EI): *m/z* (%) 448 (M^++H^+), 447 (M^+), 91 (100). Anal. Calcd. for $C_{22}H_{13}F_4NO_3S$: N, 3.13; C, 59.06; H, 2.93; Found: N, 3.34; C, 59.24; H, 2.85.

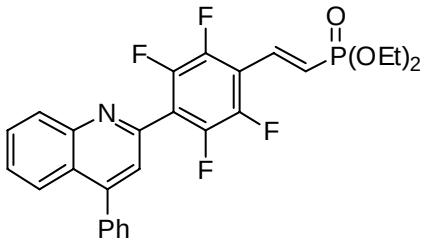
4-Phenyl-2-(2,3,5,6-tetrafluorophenyl)quinoline (6). To a septum capped 100 mL of



sealed tube were added $Pd(OAc)_2$ (13.8 mg, 0.06 mmol), X Phos (60 mg, 0.12 mmol), K_3PO_4 (764 mg, 3.6 mmol), 2-(2,3,5,6-Tetrafluorophenyl)quinolin-4-yl-4-methyl-benzenesulfonate **5** (552 mg, 1.2 mmol) and $PhB(OH)_2$ (294 mg, 2.4 mmol) under N_2, followed by THF (6 mL) with stirring. The sealed tube was screw capped and heated to 80 ^{o}C (oil bath). After stirring for 6 h, the reaction mixture was cooled to room temperature, and diluted with ethyl acetate, washed with brine, dried over Na_2SO_4, filtered and concentrated. The product (347 mg, 82% yield) as a white solid was purified with silica gel chromatography (Petroleum ether / Ethyl ether = 50:1). M.P. 152 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.7 Hz, 1H), 8.01 (d, *J* = 8.7 Hz, 1H), 7.83-7.78 (m, 1H), 7.62-7.53 (m, 7H), 7.21-7.15 (m, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 149.4, 148.6, 147.5 (m), 146.1 (dm, *J* = 248.7 Hz), 144.4 (dm, *J* = 249.4 Hz), 137.3, 130.1, 130.0, 129.5, 128.7, 128.6, 127.6, 126.0, 125.8, 122.9, 121.1(t, *J* = 16.3 Hz), 106.2 (t, *J* = 22.5 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ -138.5 (m, 2F), -143.6 (m, 2F). IR (KBr):

ν_{max} 1610, 1574, 1495 cm^{-1}. MS (EI): *m/z* (%) 354 (M^++H^+), 353 (M^+, 100), 352, 176. Anal. Calcd. for $C_{21}H_{11}F_4N$: N, 3.96; C, 71.39; H, 3.14; Found: N, 3.93; C, 71.33; H, 3.09.

(*E*)-Diethyl 2,3,5,6-tetrafluoro-4-(4-phenylquinolin-2-yl)styrylphosphonate (7).



To a septum capped 25 mL of sealed tube were added $Pd(OAc)_2$ (6.7 mg, 0.03 mmol), Ag_2CO_3 (158 mg, 0.9 mmol), and 4-phenyl-2-(2,3,5,6-tetrafluorophenyl)quinoline **6** (109 mg, 0.3 mmol), followed by DMF (1.5 mL), PivOH (92 mg, 0.9 mmol) and diethyl vinylphosphonate (148 mg, 0.9 mmol) with stirring. The sealed tube was screw capped and heated to 120 ^oC (oil bath). After stirring for 16 h, the reaction mixture was cooled to room temperature and diluted with ethyl acetate, washed with 1 N HCl, saturated $NaHCO_3$, and brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified with silica gel chromatography to provide pure product **7**. The product (118 mg, 76% yield) as a white solid was purified with silica gel chromatography (Petroleum ether / Ethyl ether = 2:1). M.P. 93 ^oC; ^1H NMR (300 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.1 Hz, 1H), 8.01 (d, *J* = 9.0 Hz, 1H), 7.82 (td, *J* = 6.9 Hz, 1.2 Hz, 1H), 7.64-7.50 (m, 8H), 6.77 (t, *J* = 17.7 Hz, 1H), 4.21 (q, *J* = 7.5 Hz, 2H), 4.18 (q, *J* = 7.5 Hz, 2H), 1.40 (t, *J* = 7.5 Hz, 6H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 149.4, 148.6, 146.8 (m), 145.3 (dm, *J* = 254.1 Hz), 144.5 (dm, *J* = 150.3 Hz), 137.2, 132.6 (m), 130.0, 129.4, 128.7, 128.6, 127.7, 126.0, 125.7, 124.7 (dt, *J* = 187.0 Hz, 8.4 Hz), 122.7, 121.1 (t, *J* = 16.7 Hz), 114.7 (m), 62.2, 62.1, 16.3, 16.2. ^{19}F NMR (282 MHz, $CDCl_3$) δ -141.6 (dd, *J* = 21.7 Hz, 14.1 Hz, 2F), -143.5 (m, 2F). ^{31}P NMR (121 MHz, $CDCl_3$) δ 17.4 (s). IR (KBr): ν_{max} 2982, 1623, 1590, 1425 cm^{-1}. MS (EI): *m/z* (%) 516 (M^++H^+), 515 (M^+), 376 (100). Anal. Calcd. for $C_{27}H_{22}F_4NO_3P$: N, 2.72; C, 62.92; H, 4.30; Found: N, 2.54; C, 62.88; H, 4.38.

2-(perfluorophenyl)quinolin-4-yl 4-methylbenzenesulfonate (8). To a septum capped 100 mL of sealed tube were added $Pd(OAc)_2$ (67 mg, 0.3 mmol), **L** (210 mg, 0.6 mmol), K_3PO_4 (1.52 g, 7.2 mmol), AdOH (1.3 g, 7.2 mmol) and quinoline-2,4-diyl-bis(4-methylbenzenesulfonate) **4** (2.9 g, 6.0 mmol) under N_2, followed by *t*-BuOH (30 mL) with stirring. Pentafluorobenzene (1.34 mL, 12 mmol) was then added subsequently. The sealed tube was screw capped and heated to 90 ^oC (oil bath). After stirring for 6 h, the reaction mixture was cooled to room temperature, and diluted with ethyl acetate, washed with brine, dried over Na_2SO_4, filtered and concentrated. The product (1.73 g, 62% yield) as a white solid was purified with silica gel chromatography (Petroleum ether / Ethyl ether = 60:1). M.P. 162 ^oC; ^1H NMR (300 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.80 (t, *J* = 7.2 Hz, 1H), 7.61 (t, *J* = 7.2 Hz, 1H), 7.45 (s, 1H), 7.34 (d, *J* = 8.4 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 153.5, 149.8, 147.3, 146.4, 144.7 (dm, *J* = 247.2 Hz), 141.6 (dm, *J* = 256.2 Hz), 137.8 (dm, *J* = 254.0 Hz), 131.7, 131.1, 130.1, 129.5, 128.4, 128.3, 121.6, 121.5, 114.9 (m), 113.9, 21.7. ^{19}F NMR (282 MHz, $CDCl_3$) δ -138.9 (dd, *J* = 21.9 Hz, 5.9 Hz, 2F), -148.8 (t, *J* = 19.7 Hz, 1F), -157.7 (m, 2F). IR (KBr): ν_{max} 1621, 1557, 1524 cm^{-1}. MS (EI): *m/z* (%) 466 (M^++H^+), 465 (M^+), 91 (100). Anal. Calcd. for $C_{22}H_{12}F_5NO_3S$: N, 3.01; C, 56.78; H, 2.60; Found: N, 2.83; C, 56.72; H, 2.66.

2-(perfluorophenyl)-4-phenylquinoline (9). To a septum capped 25 mL of sealed tube were added $Pd(OAc)_2$ (6.7 mg, 0.03 mmol), X Phos 30 mg, 0.06 mmol), K_3PO_4 (382 mg, 1.8 mmol), 2-(perfluorophenyl)quinolin-4-yl 4-methylbenzenesulfonate **8** (288 mg, 0.6 mmol) and $PhB(OH)_2$ (147 mg, 1.2 mmol) under N_2, followed by THF (3 mL) with stirring. The sealed tube was screw capped and heated to 80 ^oC (oil bath). After stirring for 6 h, the reaction mixture was cooled to room temperature, and diluted with ethyl acetate, washed with

brine, dried over Na_2SO_4, filtered and concentrated. The product (190 mg, 85% yield) as a white solid was purified with silica gel chromatography (Petroleum ether / Ethyl ether = 50:1). M.P. 113 ^oC; ^1H NMR (300 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.81 (t, *J* = 6.9 Hz, 1H), 7.60 (t, *J* = 6.9 Hz, 1H), 7.55-7.49 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 148.7, 146.6, 144.8 (dm, *J* = 249.1 Hz), 141.4 (dm, *J* = 253.8 Hz), 137.8 (dm, *J* = 251.6 Hz), 137.3, 130.1, 130.0, 129.5, 128.7, 128.6, 127.7, 126.1, 125.8, 122.9, 115.7 (t, *J* = 16.8 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ -142.9 (dd, *J* = 21.7 Hz, 7.9 Hz, 2F), -153.8 (t, *J* = 21.7 Hz, 1F), -162.0 (td, *J* = 21.7 Hz, 7.9 Hz, 2F). IR (KBr): ν_{max} 1551, 1524, 1457 cm^{-1}. MS (EI): *m/z* (%) 372 (M^++H^+), 371 (M^+, 100), 176. Anal. Calcd. for $C_{21}H_{10}F_5N$: N, 3.77; C, 67.93; H, 2.71; Found: N, 3.64; C, 68.20; H, 2.81.

References:

(1) Liu, X.; Fu, H.; Jiang, Y.; Zhao, Y. *Angew.Chem. Int. Ed.* **2009**, *48*, 348.

(2) Bhayana, B.; Fors, B.; Buchwald, S. L. *Org. Lett.*, **2009**, *11*, 3954.

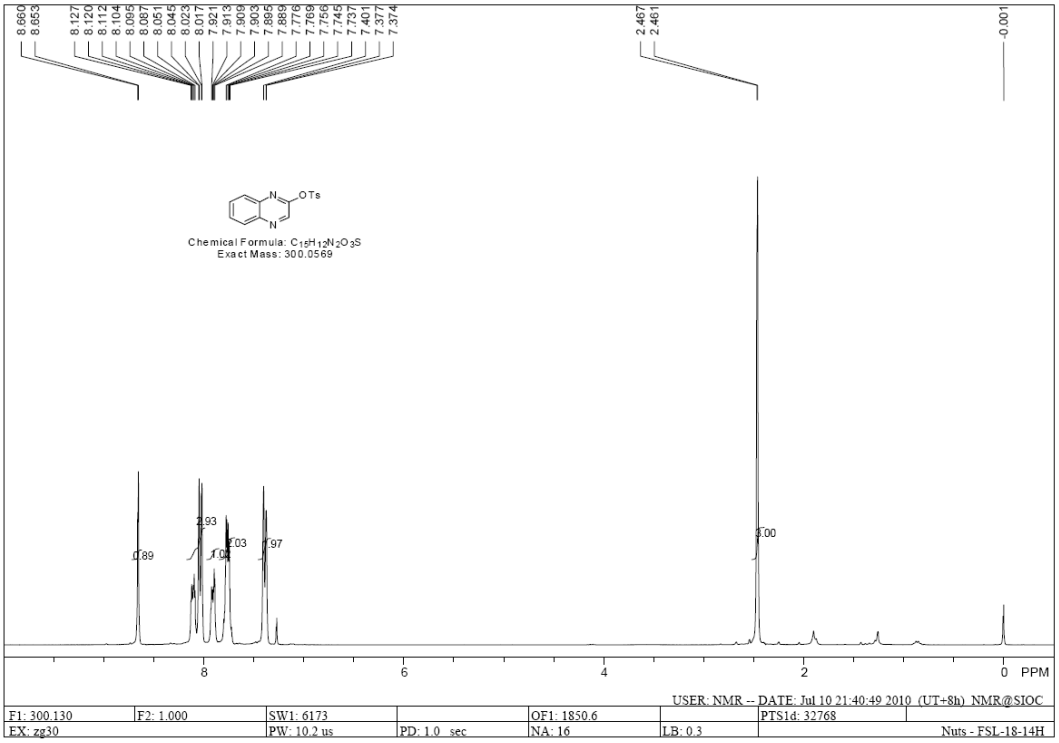
(3) Cavallito; Haskell. *J. Am. Chem. Soc.***1944,** *66*, 1927.

(4) Bunett; Basset. *J. Org. Chem.* ***1962****, 27,* 1887.

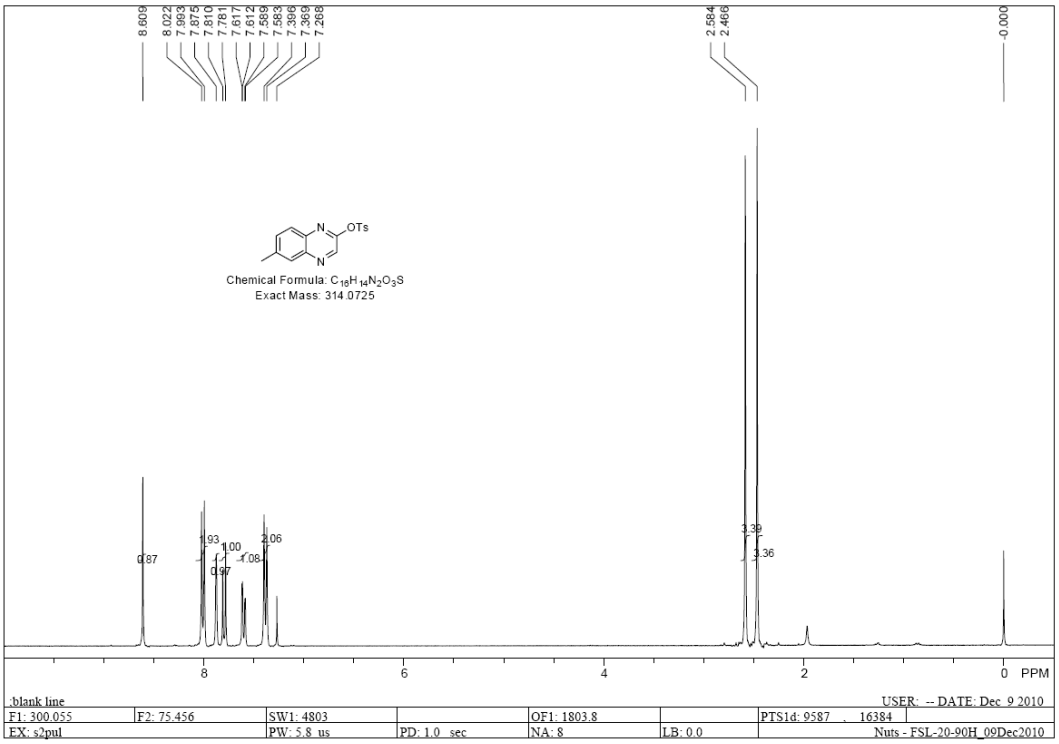
(5) Gogsig, T. M.; Lindhardt, A. T.; Grouleff, J.; Skrydstrup, T.; Dekhane, M. *Chem. Eur. J.*, **2009,** 15, 5950.

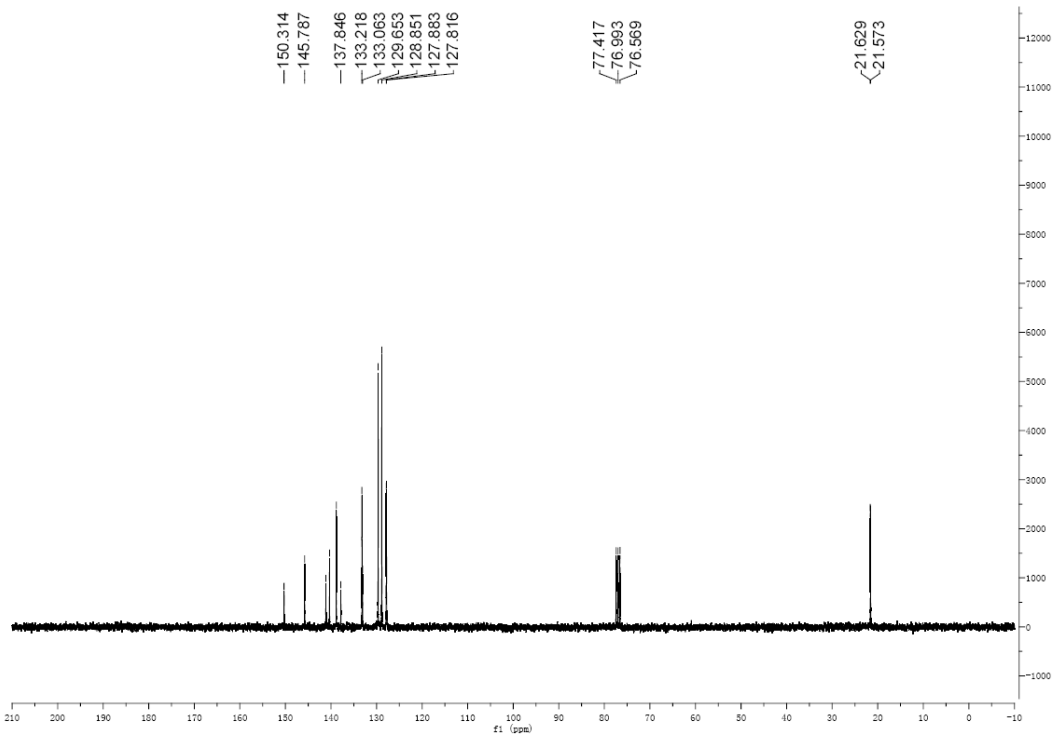
(6) Do, H.-Q.; Khan, R.; Daugulis, O. *J. Am. Chem. Soc.* **2008**, *130*, 15185.

Quinoxalin-2-yl 4-methylbenzenesulfonate (2a).

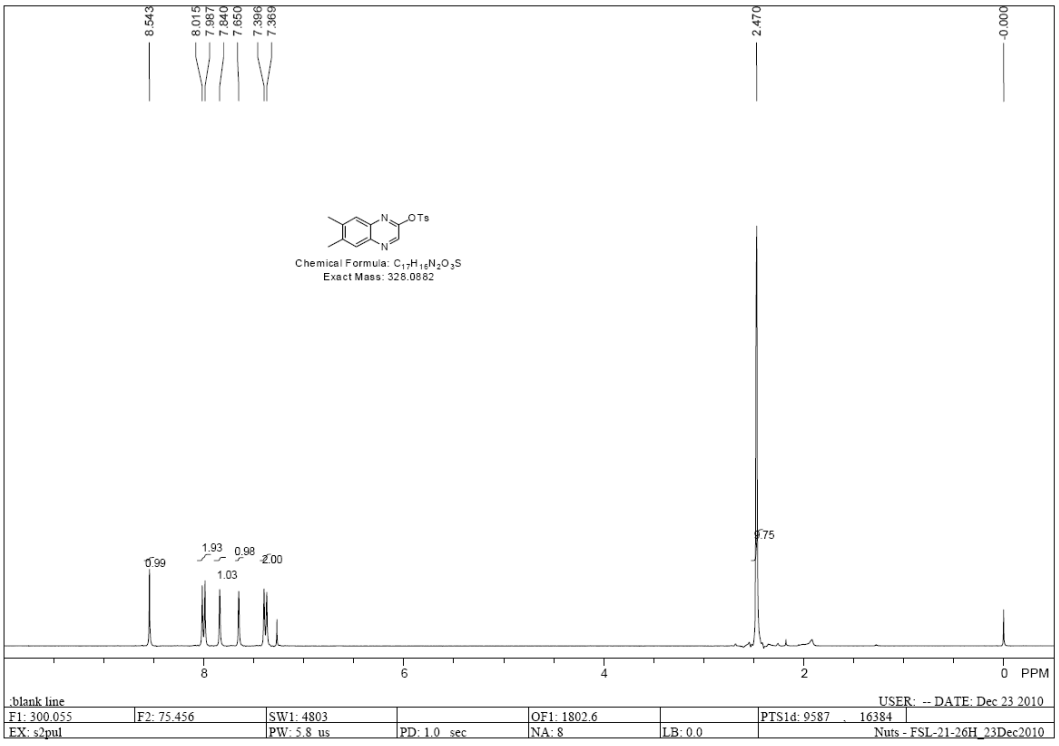


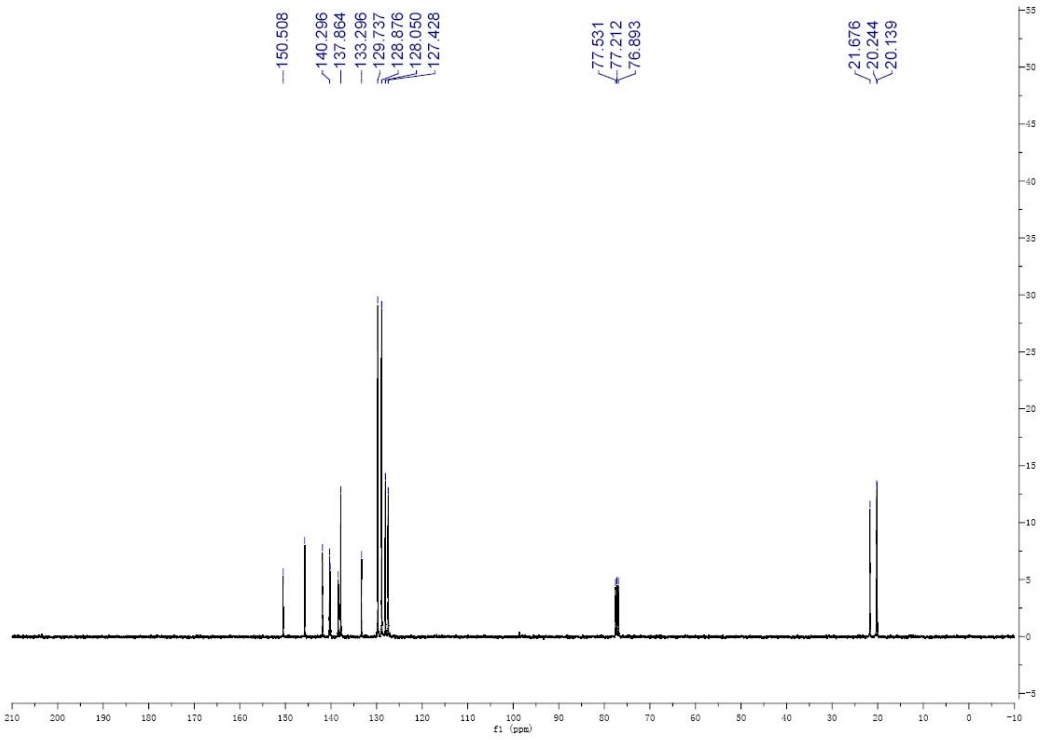
6-methylquinoxalin-2-yl 4-methylbenzenesulfonate (2b).



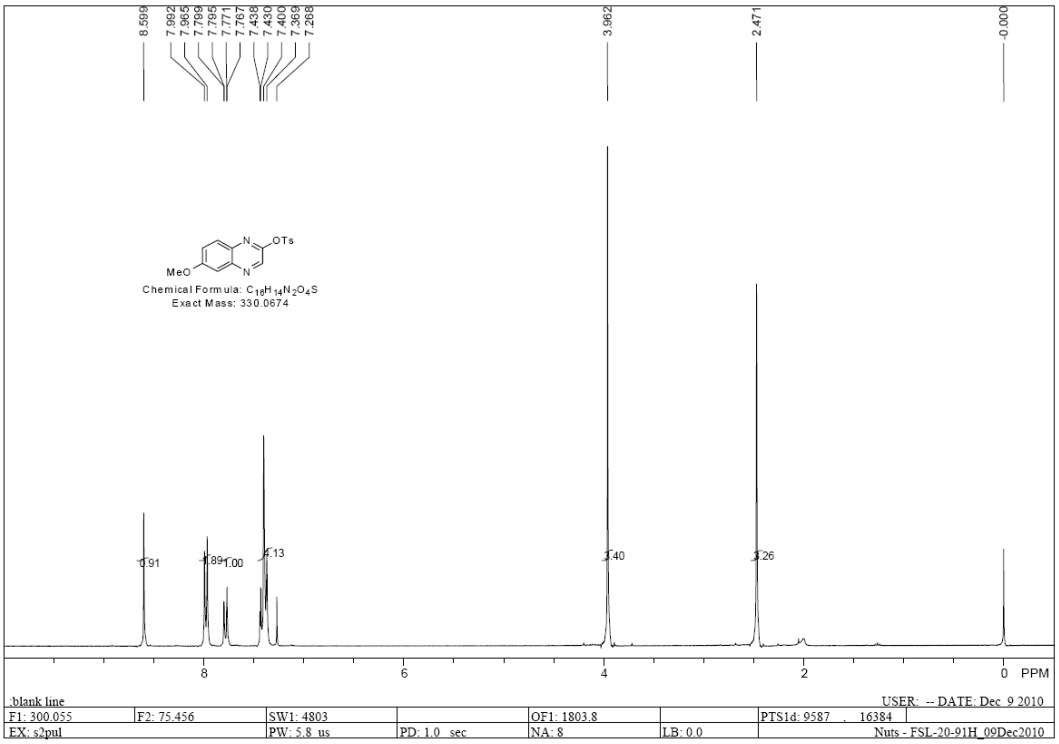


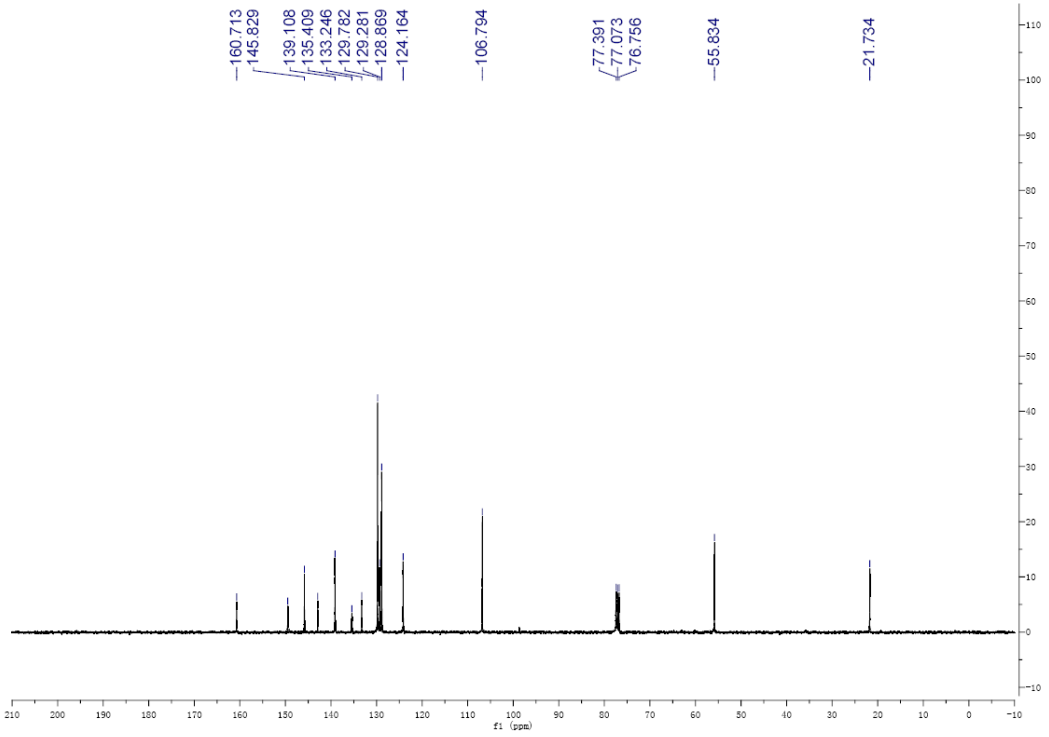
6,7-Dimethylquinoxalin-2-yl 4-methylbenzenesulfonate (2c).



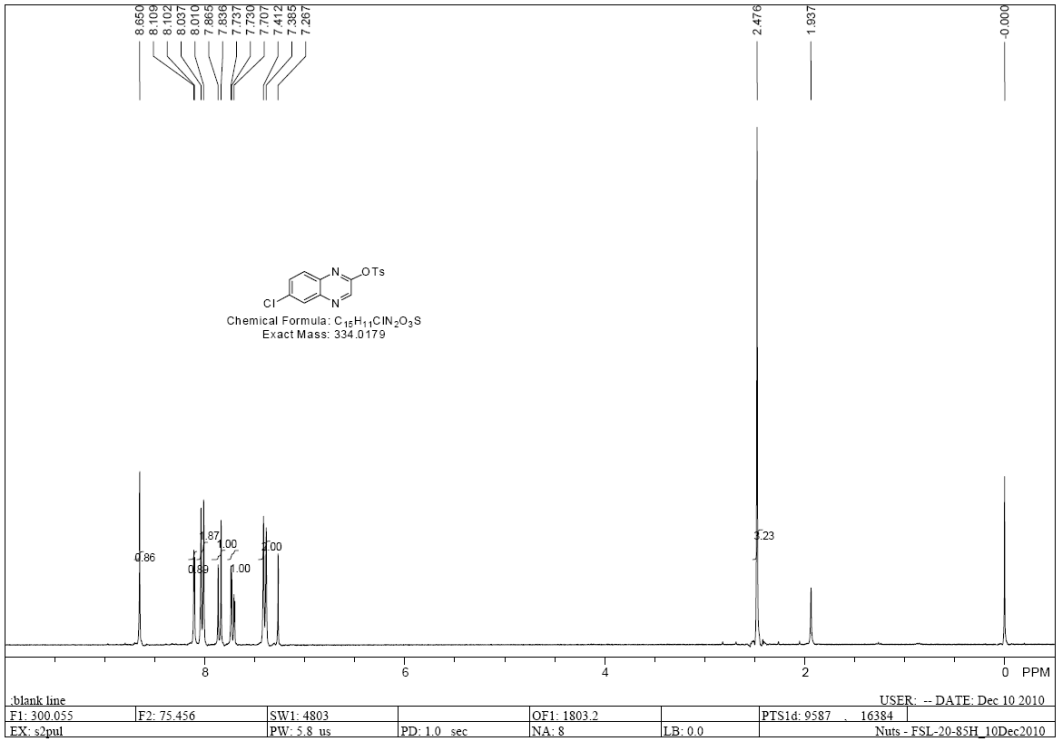


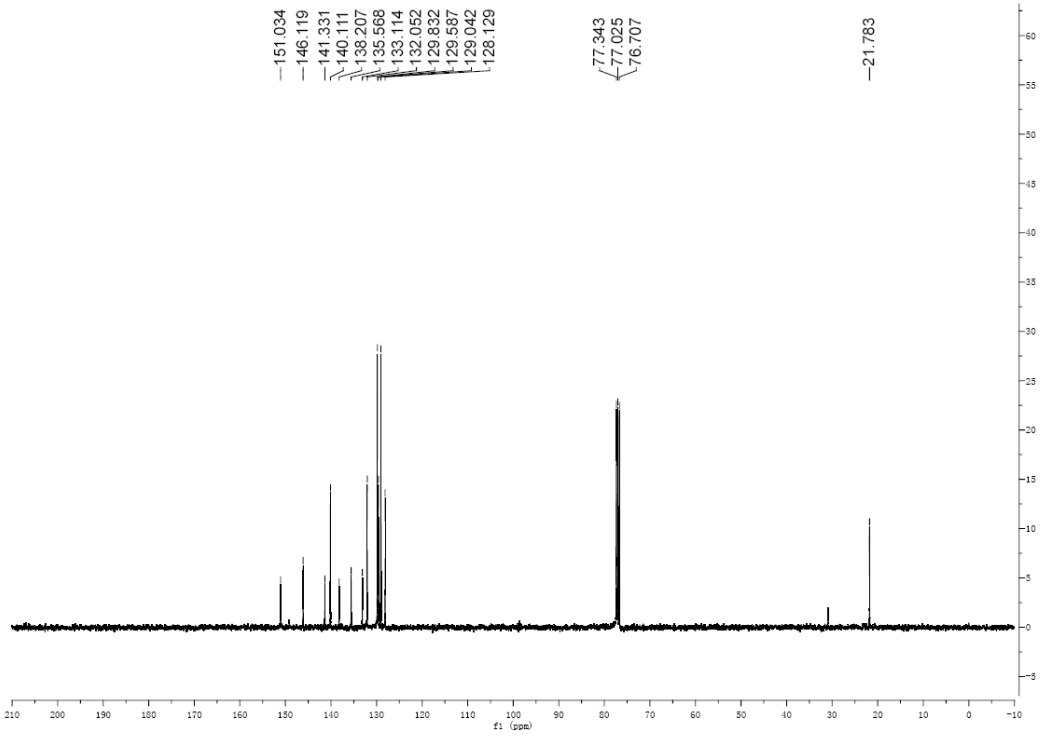
6-Methoxyquinoxalin-2-yl 4-methylbenzenesulfonate (2d).



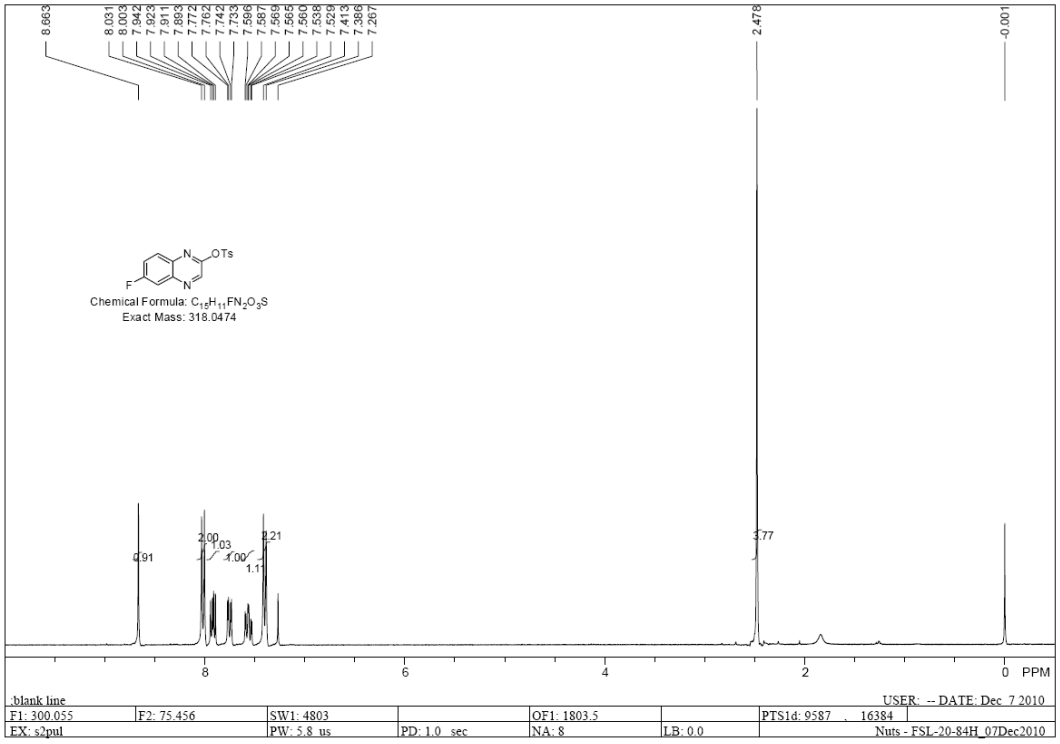


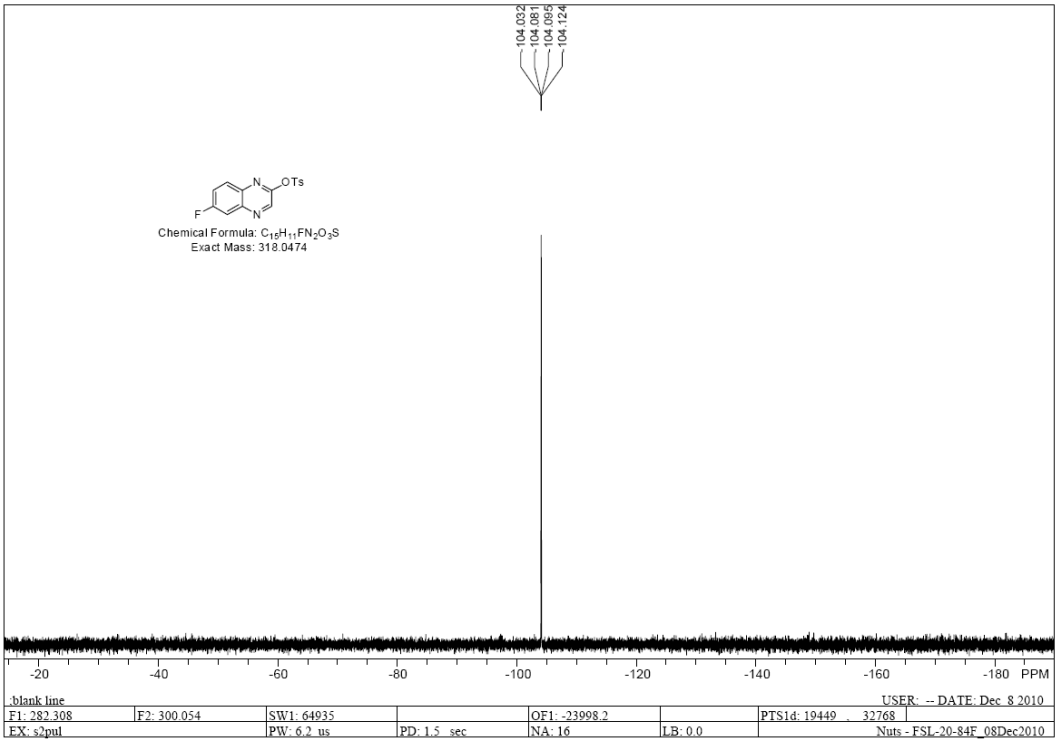
6-Chloroquinoxalin-2-yl 4-methylbenzenesulfonate (2e).





6-Fluoroquinoxalin-2-yl 4-methylbenzenesulfonate (2f).

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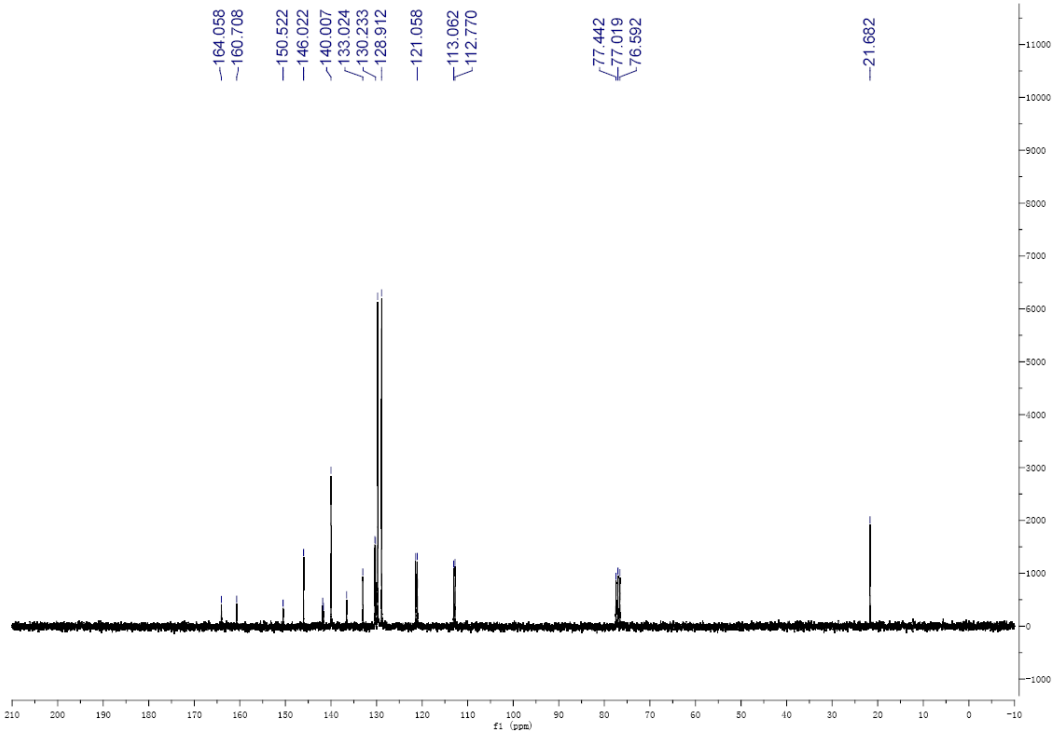
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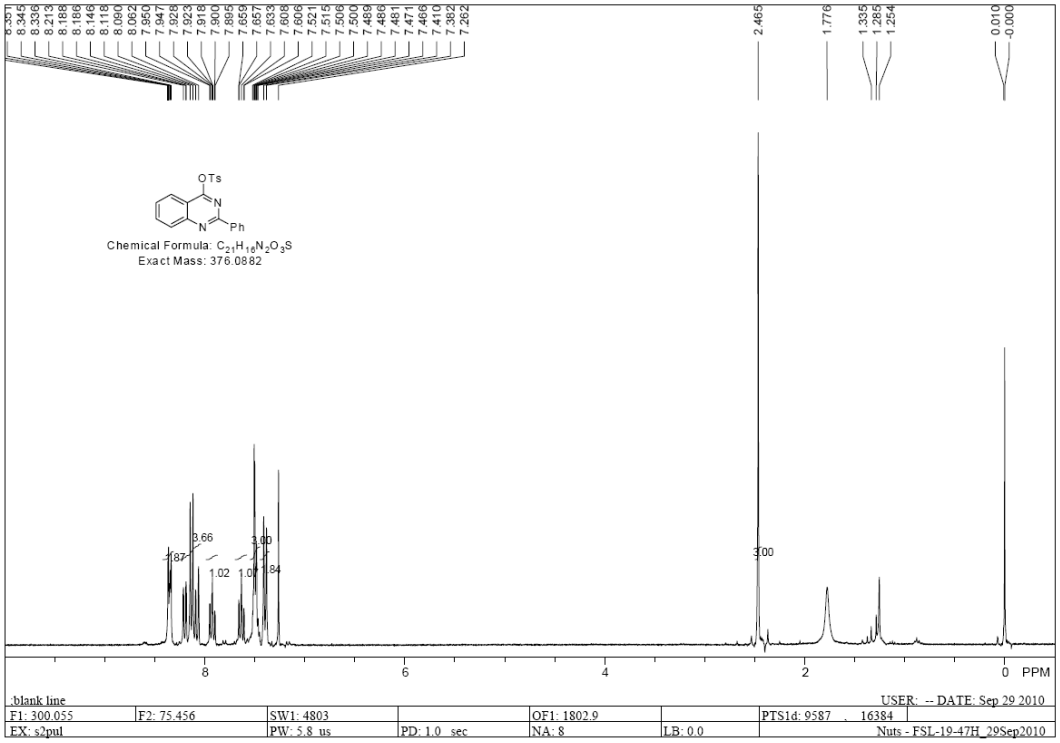
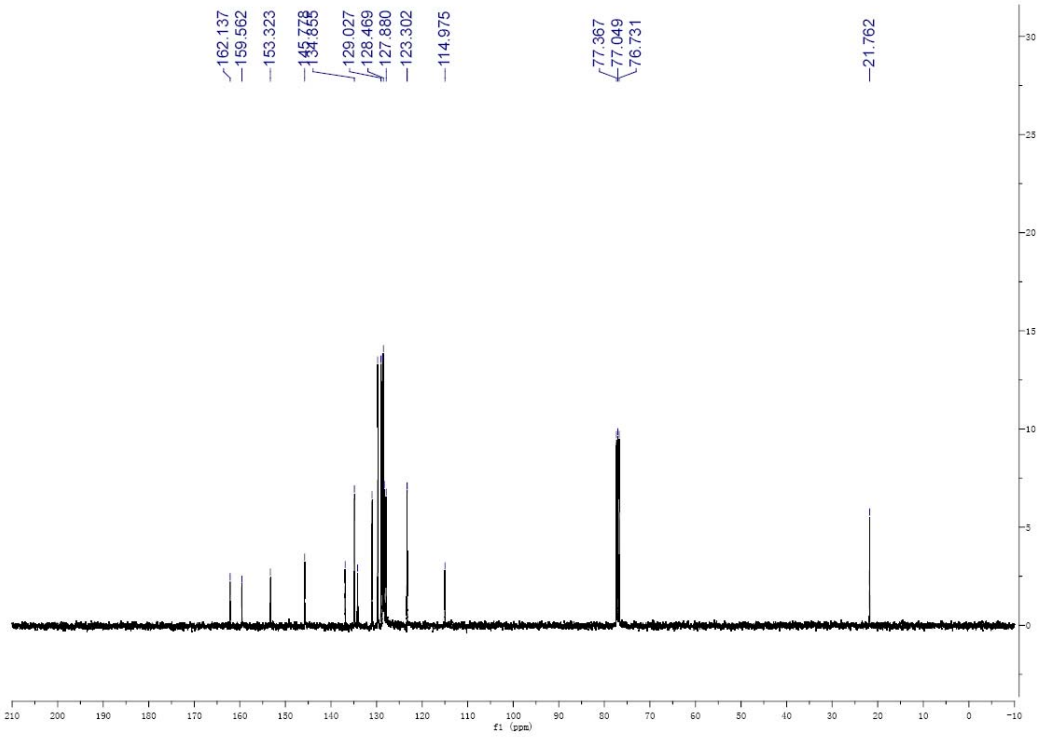
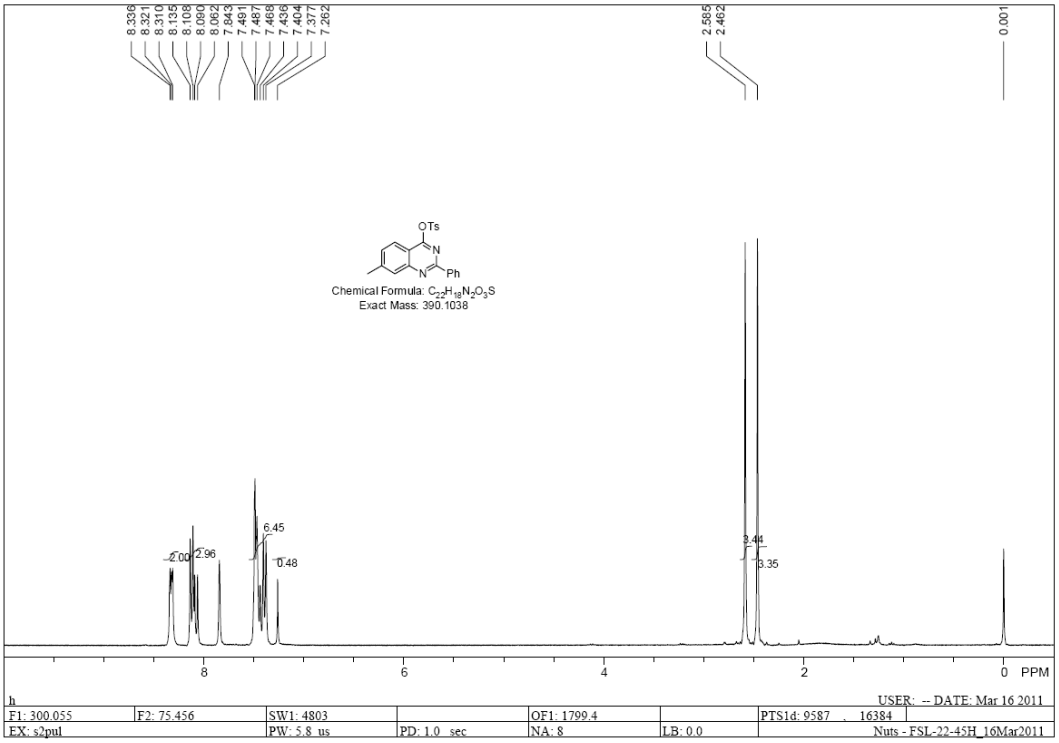
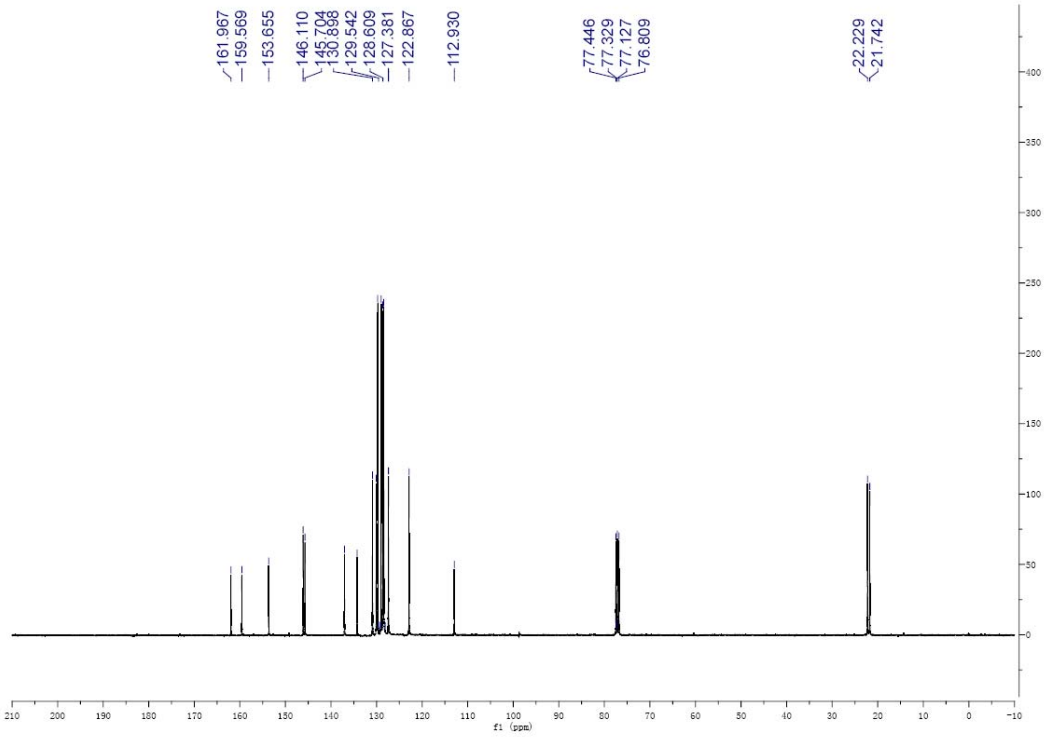
2-phenylquinazolin-4-yl 4-methylbenzenesulfonate (2g).



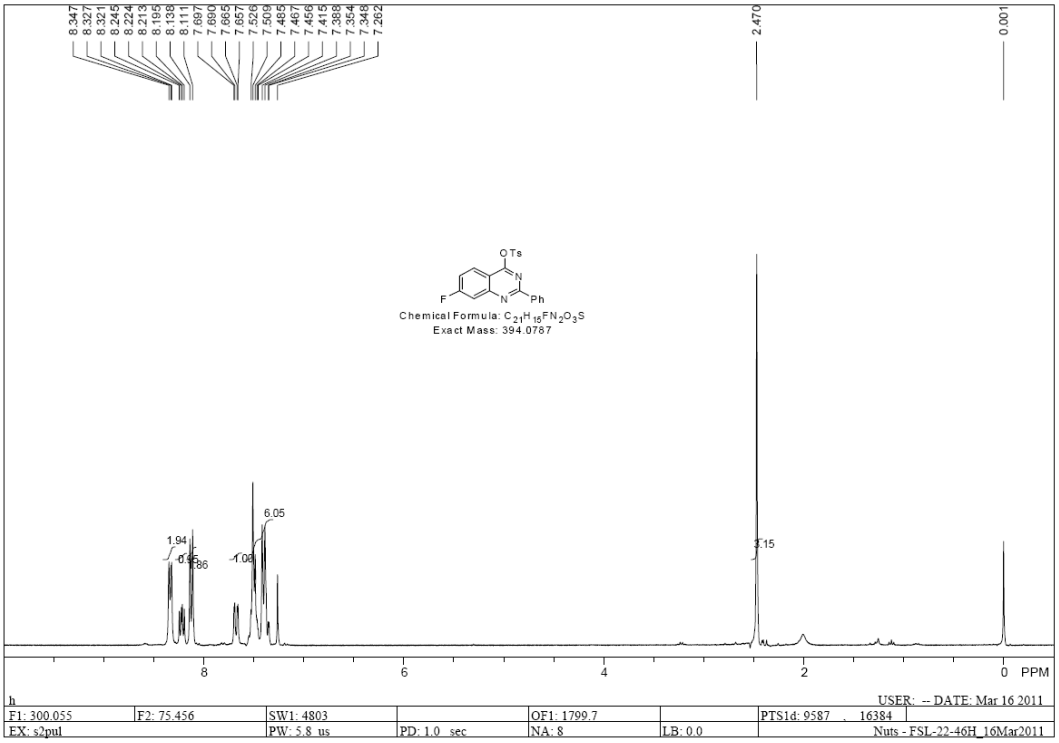


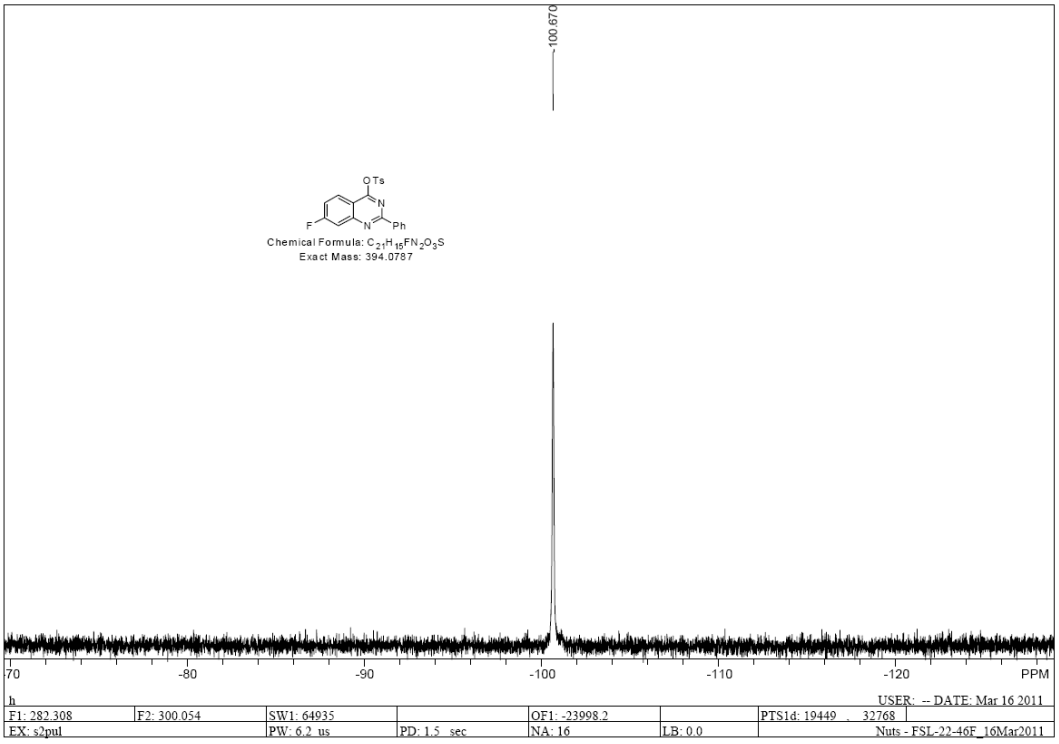
7-Methyl-2-phenylquinazolin-4-yl 4-methylbenzenesulfonate (2h).

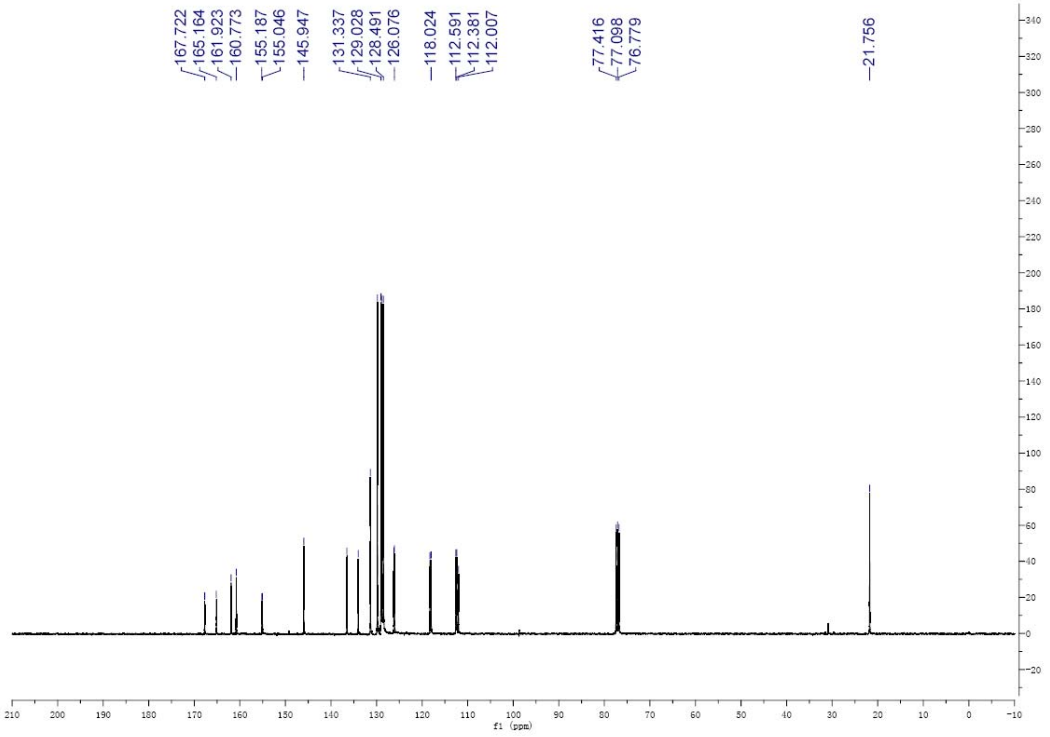




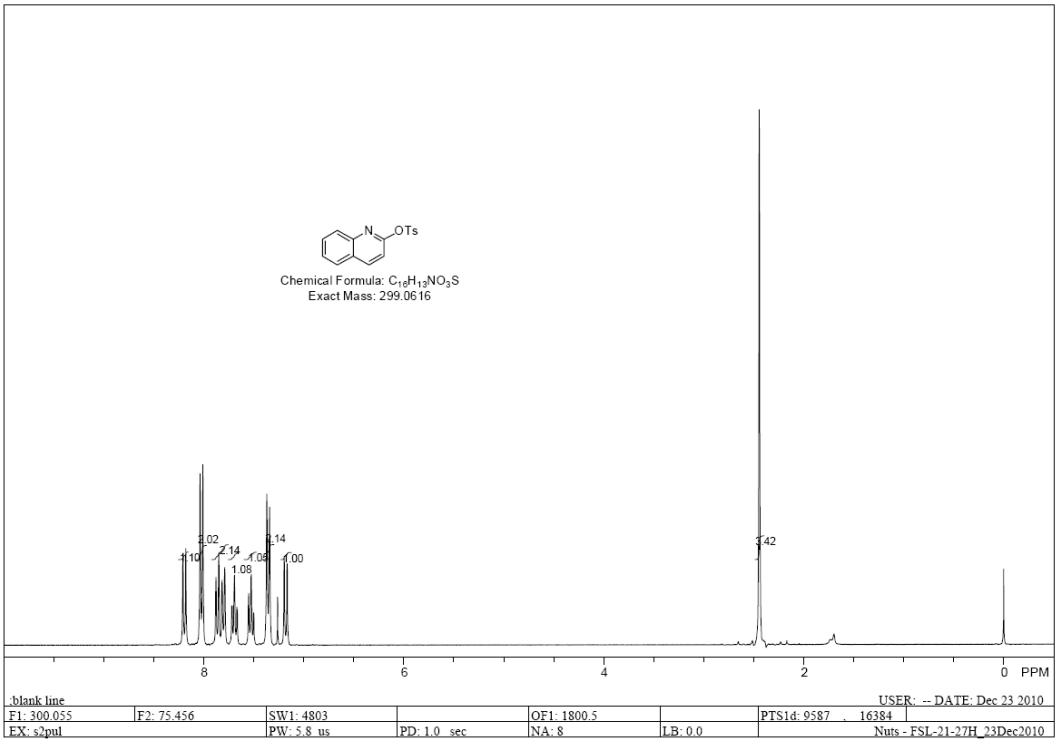
7-Fluoro-2-phenylquinazolin-4-yl 4-methylbenzenesulfonate (2i).



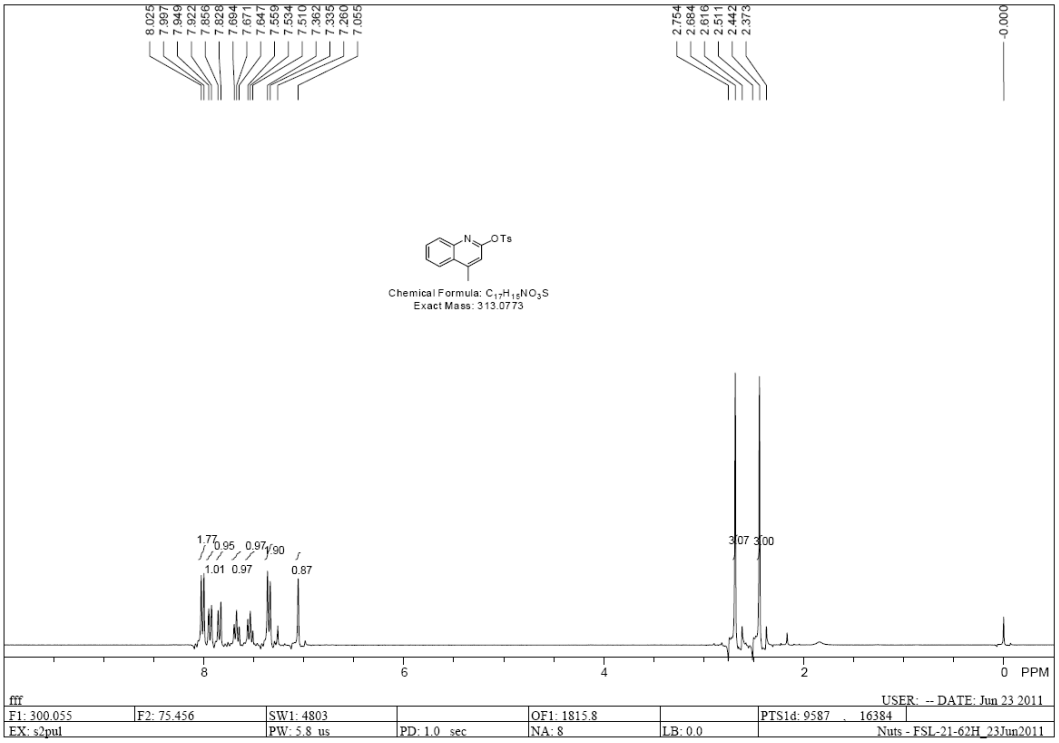




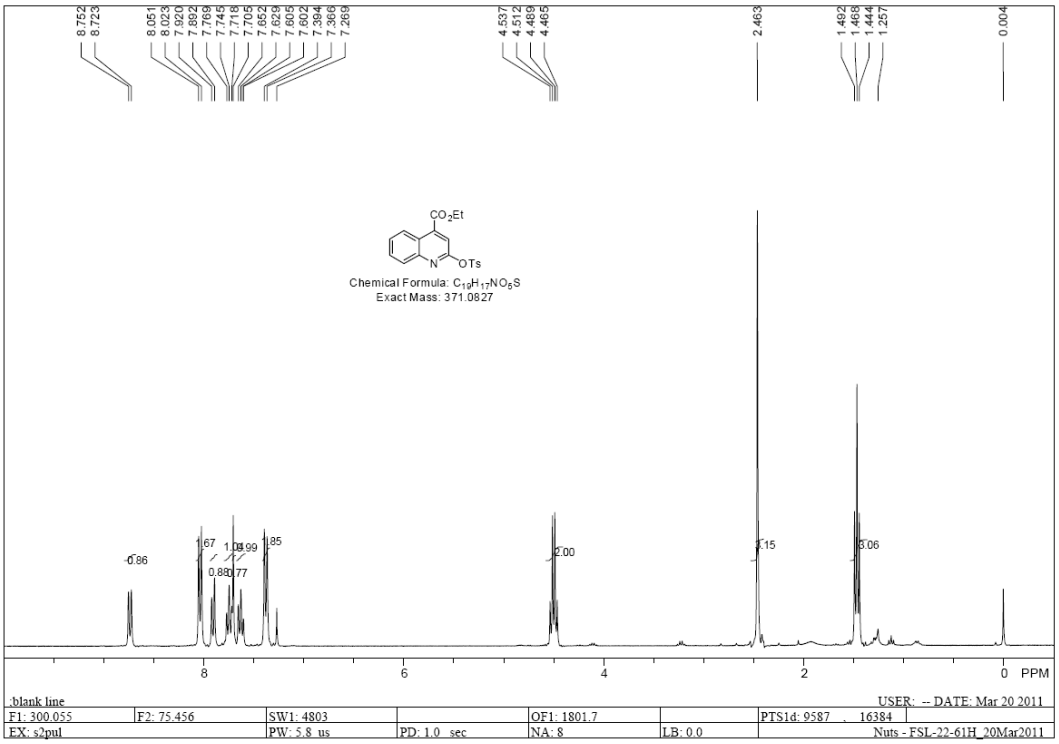
Quinolin-2-yl 4-methylbenzenesulfonate (2j).

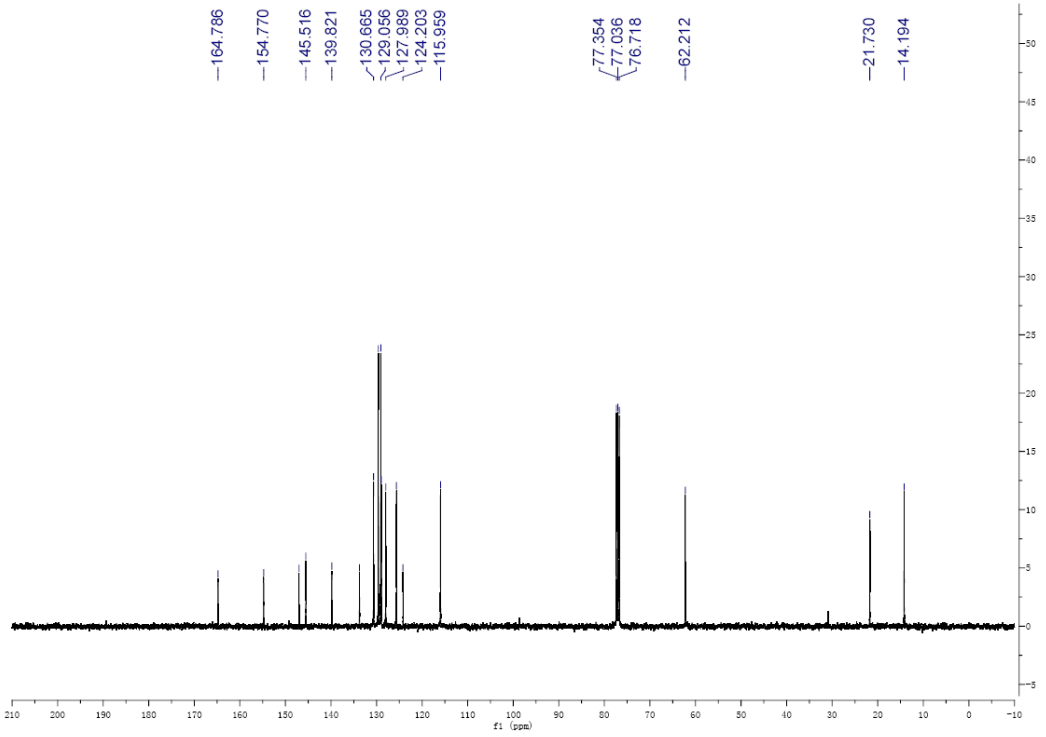


4-Methylquinolin-2-yl 4-methylbenzenesulfonate (2k).

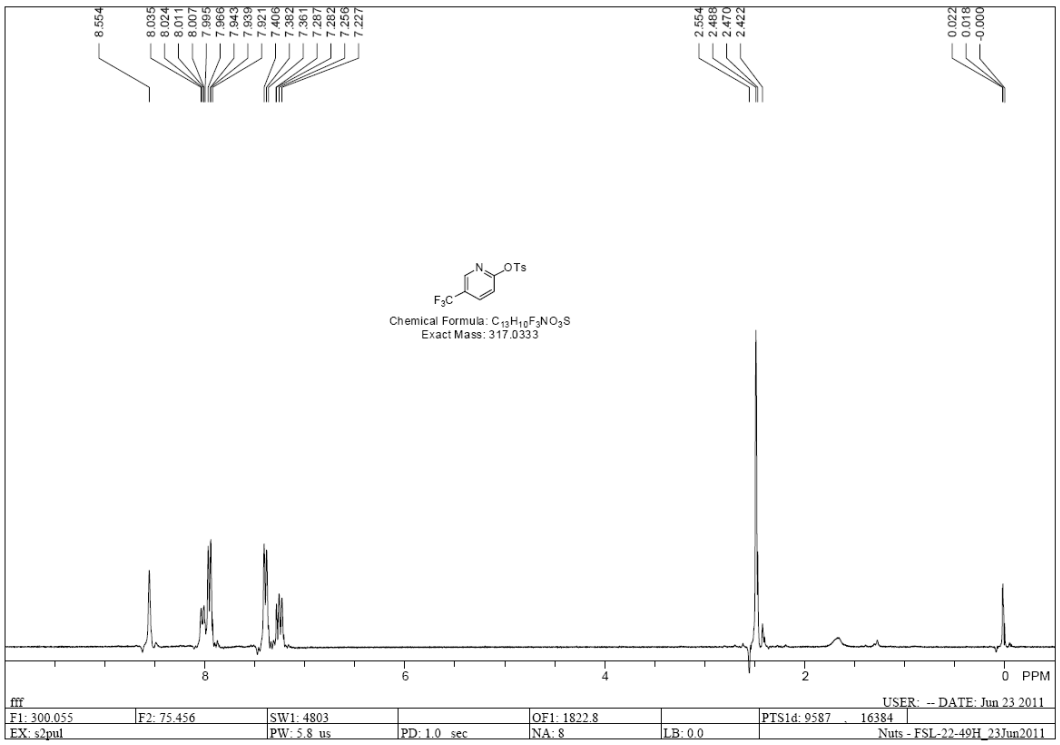


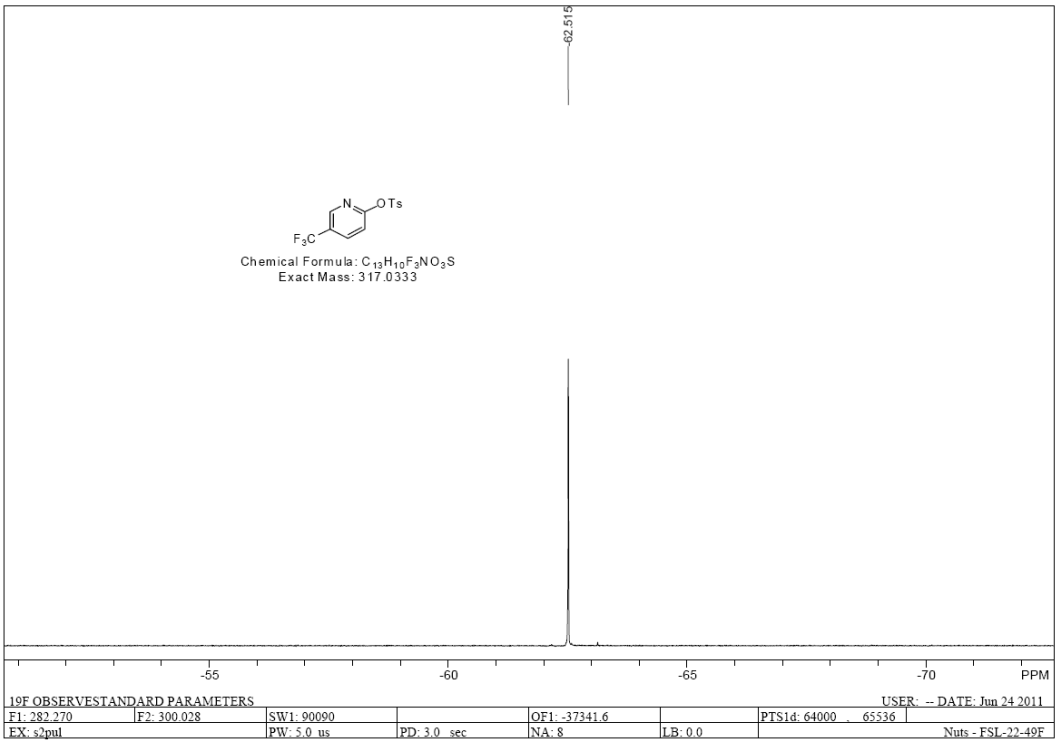
Ethyl 2-(tosyloxy)quinoline-4-carboxylate (2l).



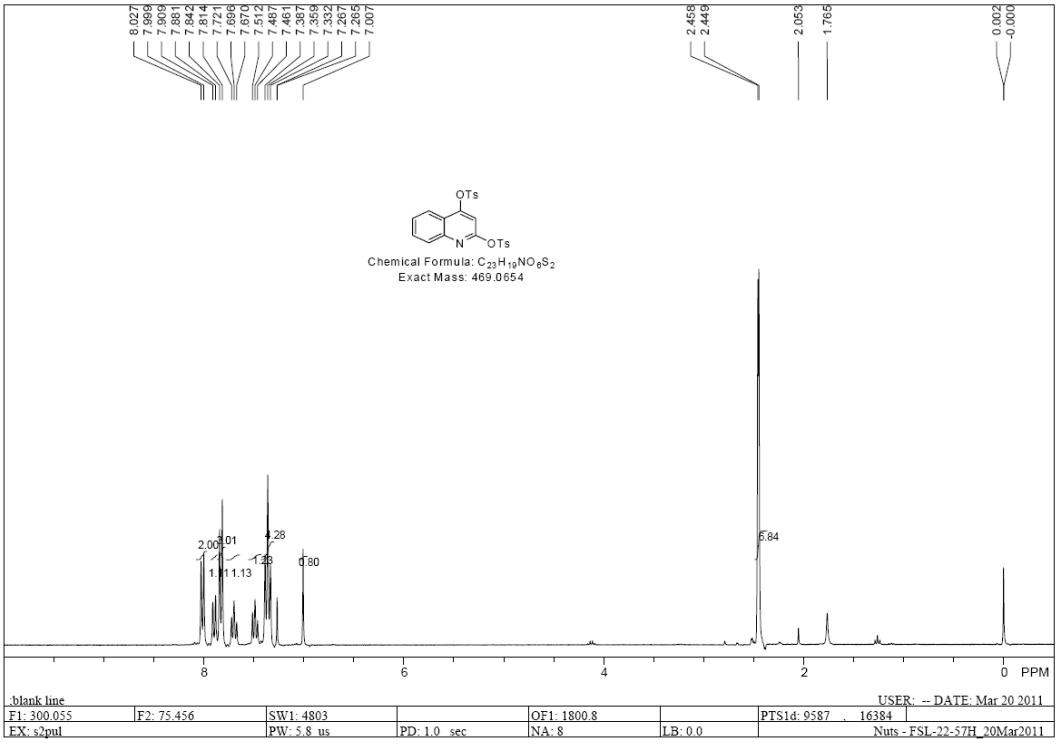


5-(Ttrifluoromethyl)pyridin-2-yl 4-methylbenzenesulfonate (2m).

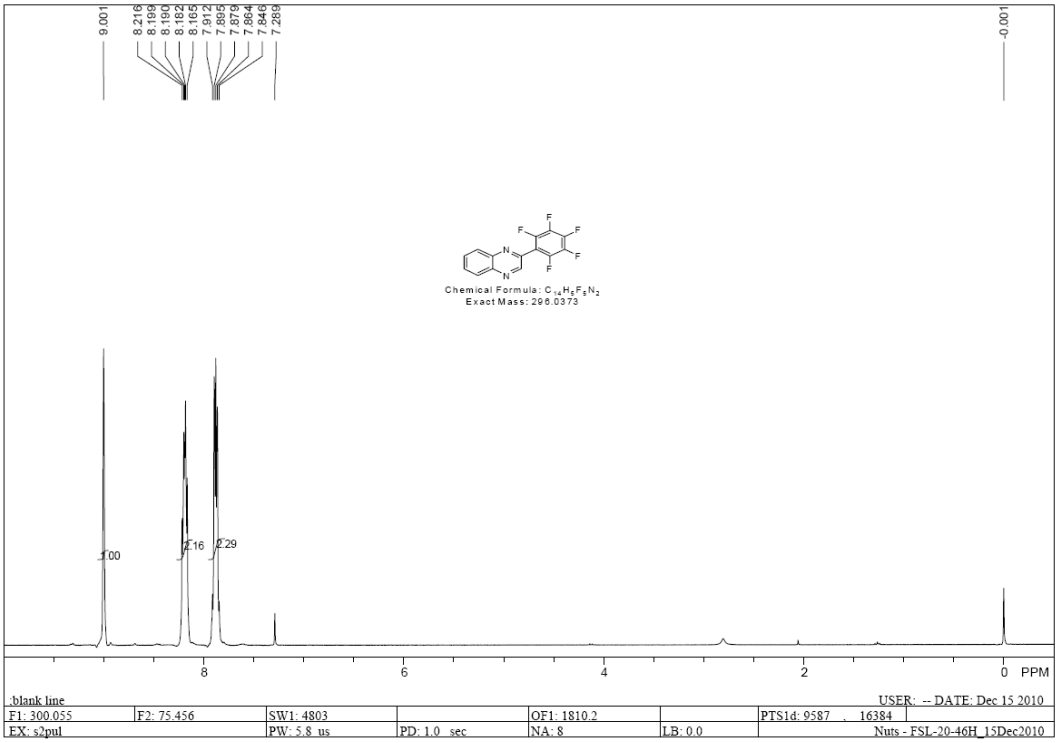


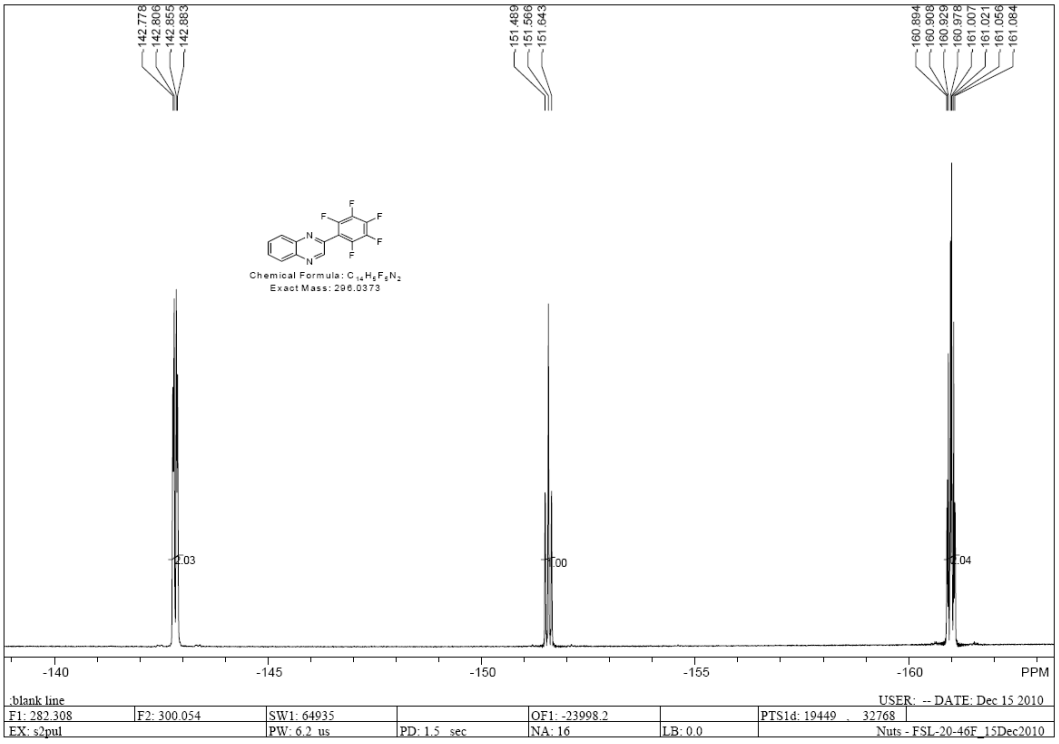


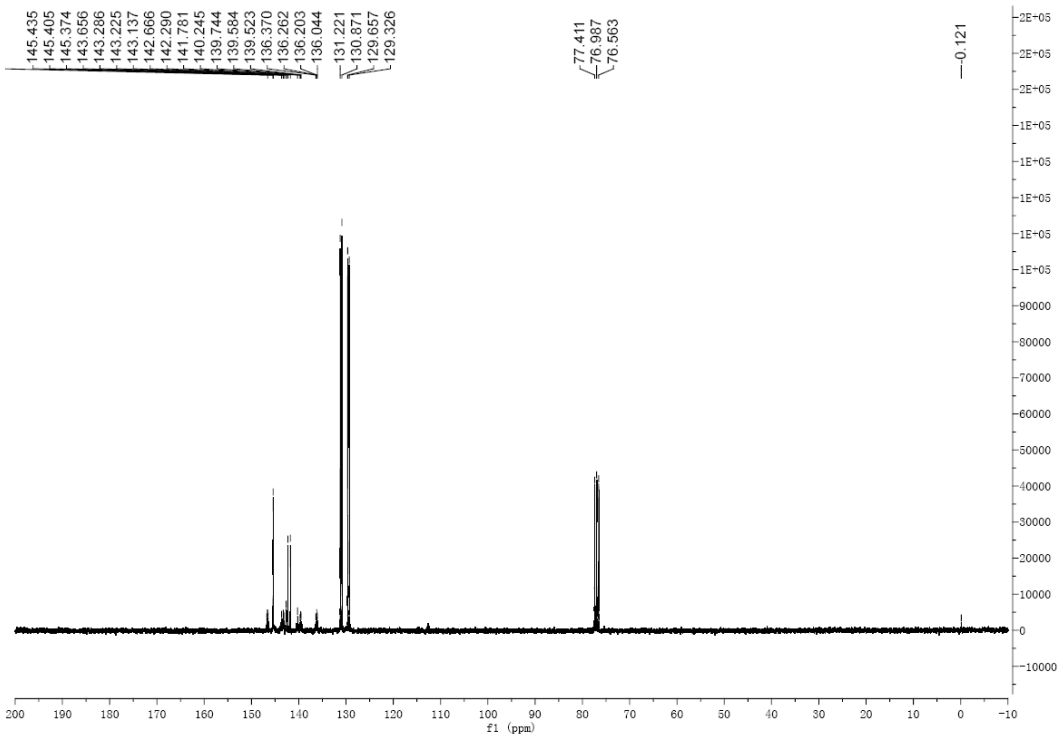
Quinoline-2,4-diyl bis(4-methylbenzenesulfonate) (4).



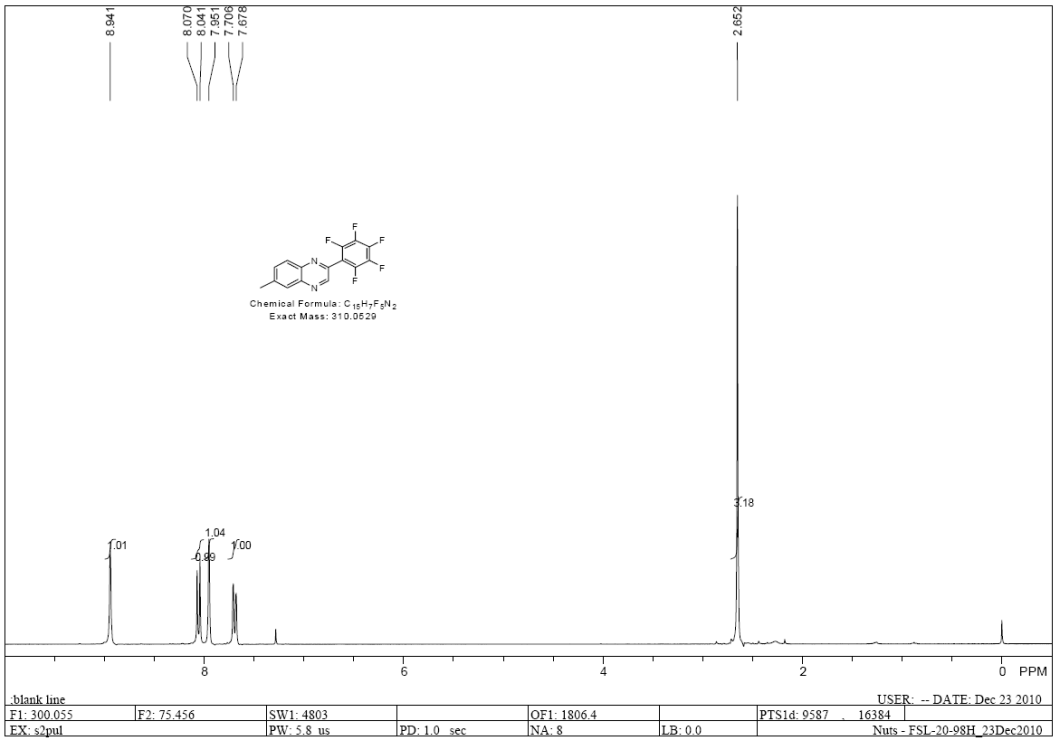
2-(Perfluorophenyl)quinoxaline (3a)

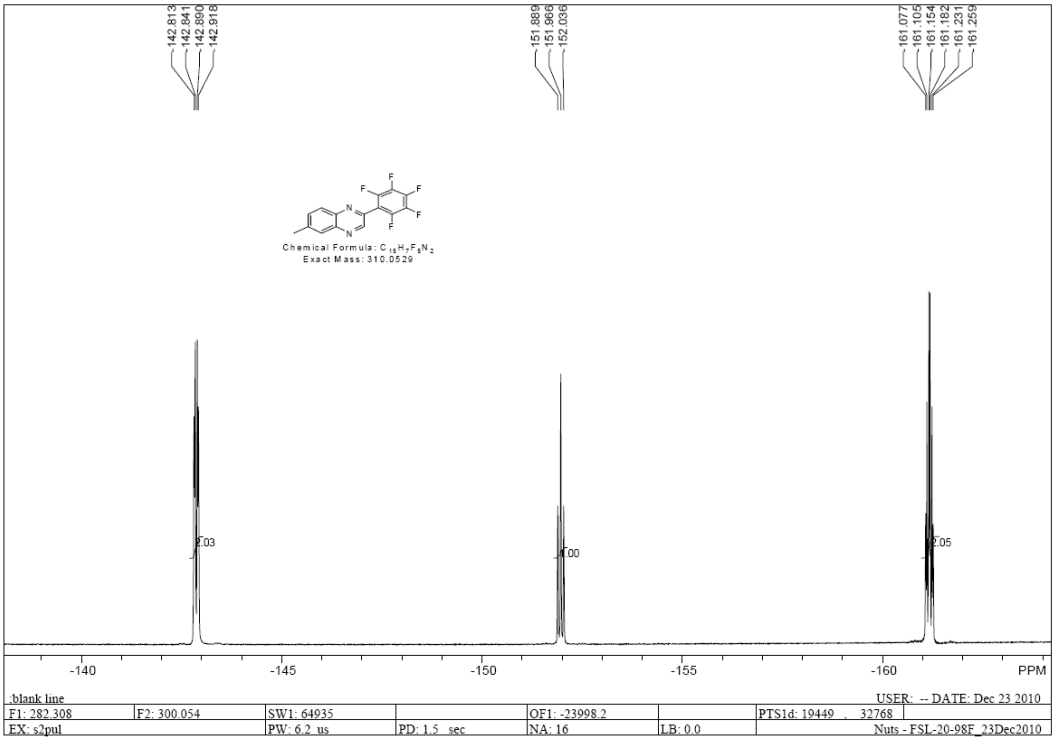






6-Methyl-2-(perfluorophenyl)quinoxaline (3b)

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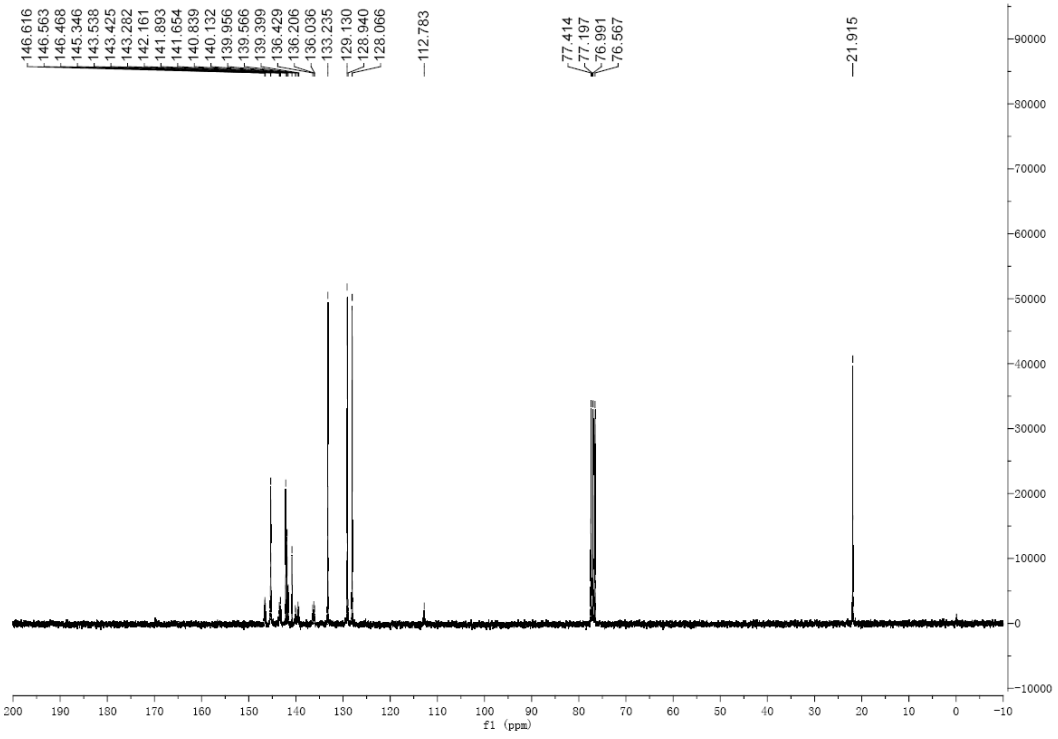
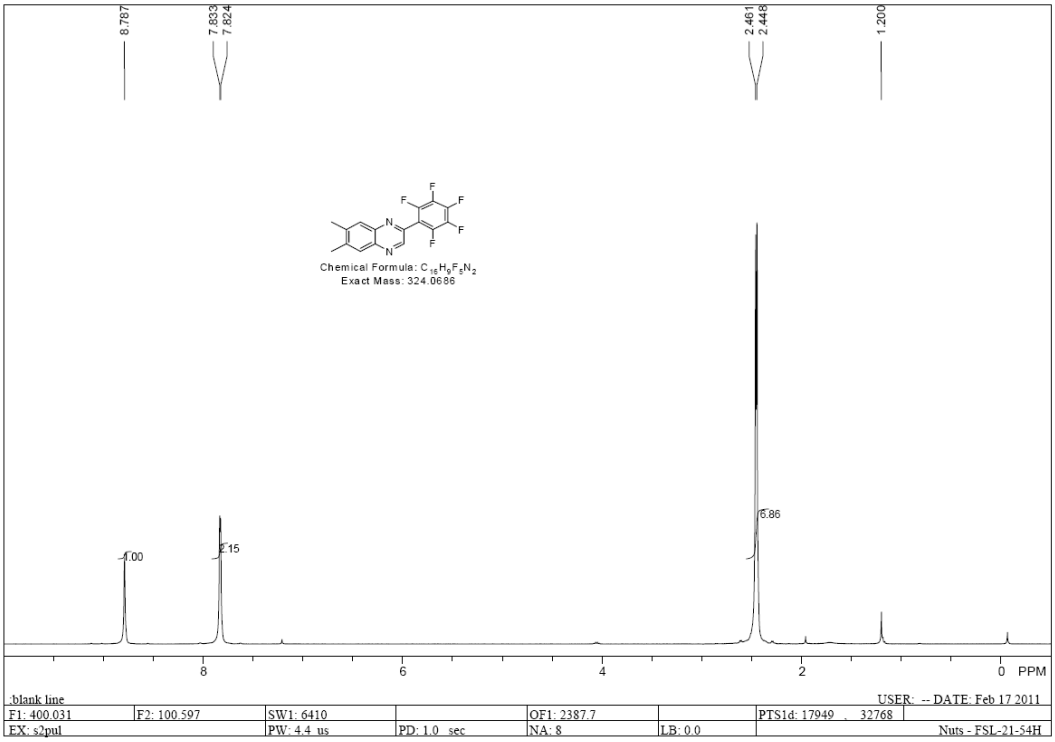
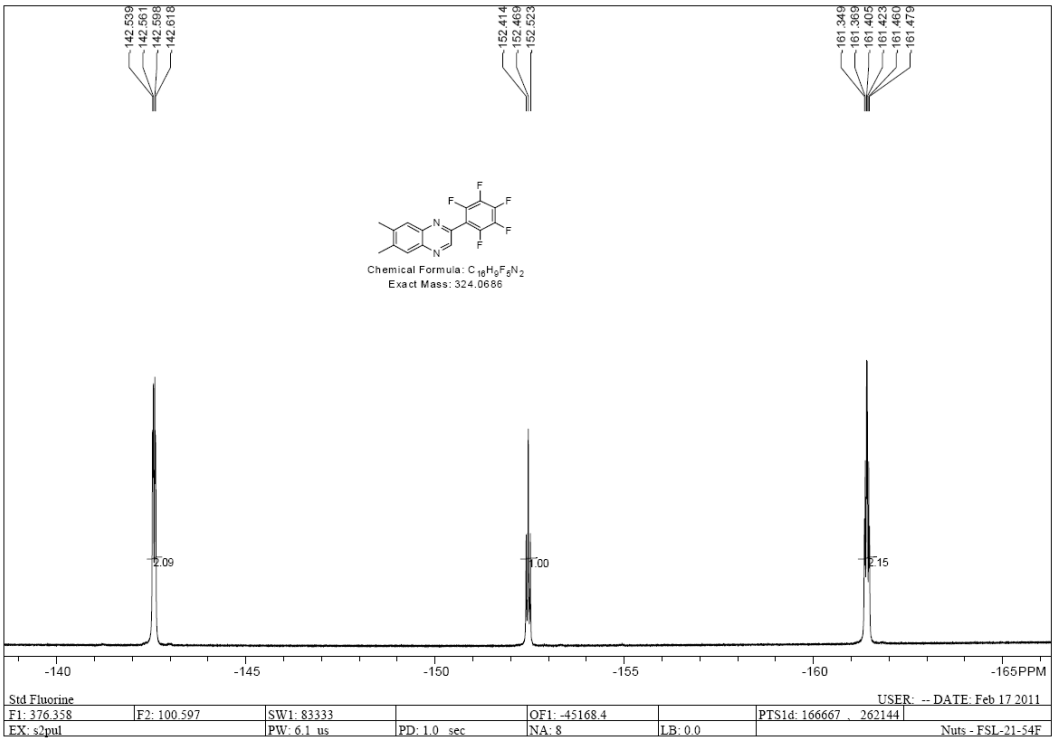
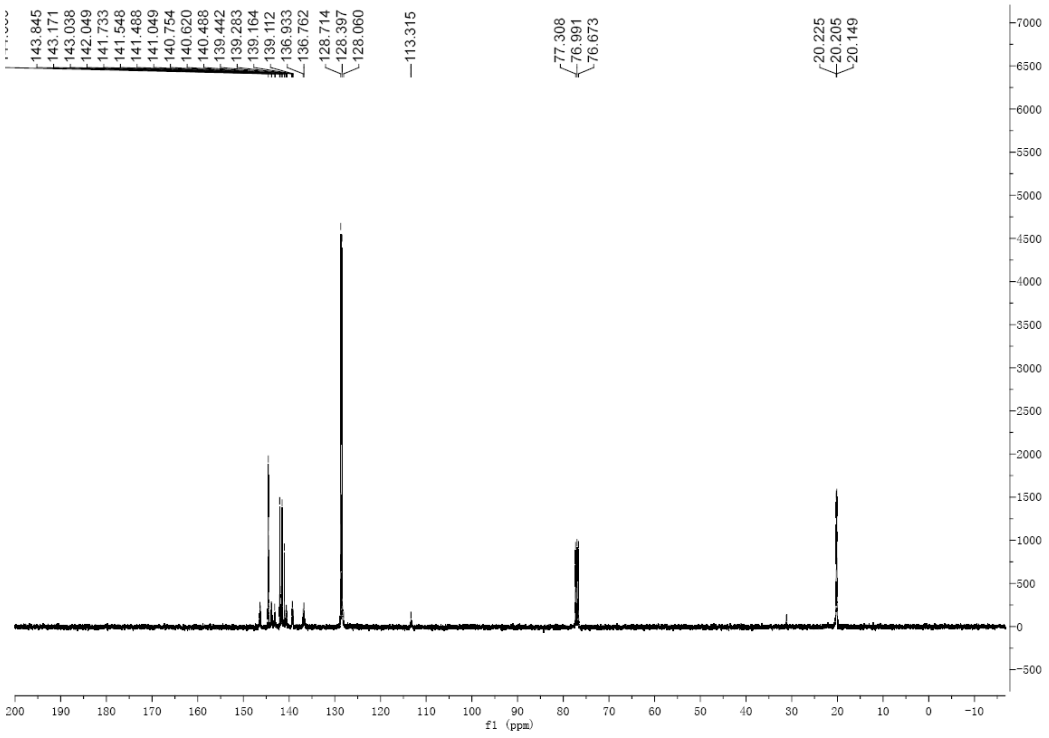
-155
-160
PPM
:blank line
USER: -- DATE: Dec 23 2010
F1: 282.308
F2: 300.054
SW1: 64935
OF1: -23998.2
PTS1d: 19449 , 32768
EX: s2pul
PW: 6.2 us
PD: 1.5 sec
NA: 16
LB: 0.0
Nuts - FSL-20-98F_23Dec2010


146.616
146.563
146.468
145.346
143.538
143.425
143.282
142.161
141.893
141.654
140.839
140.132
139.956
139.566
139.399
136.429
136.206
136.036
133.235
129.130
128.940
128.066
112.783
77.414
77.197
76.991
76.567
21.915
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

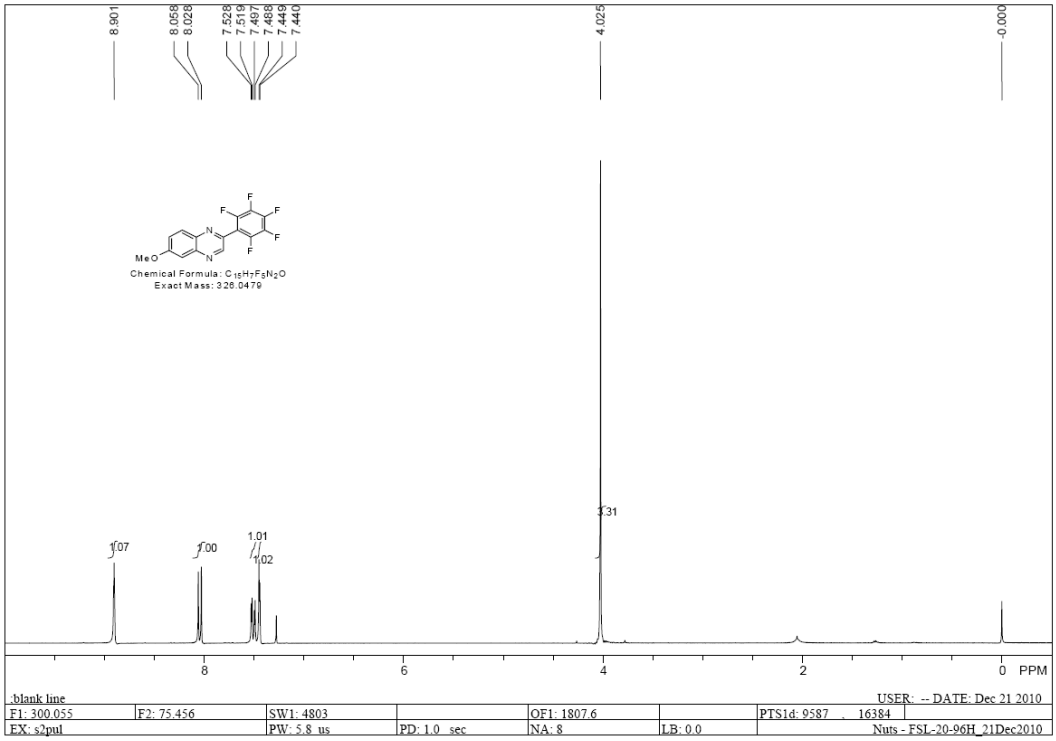
6,7-Dimethyl-2-(perfluorophenyl)quinoxaline (3c)

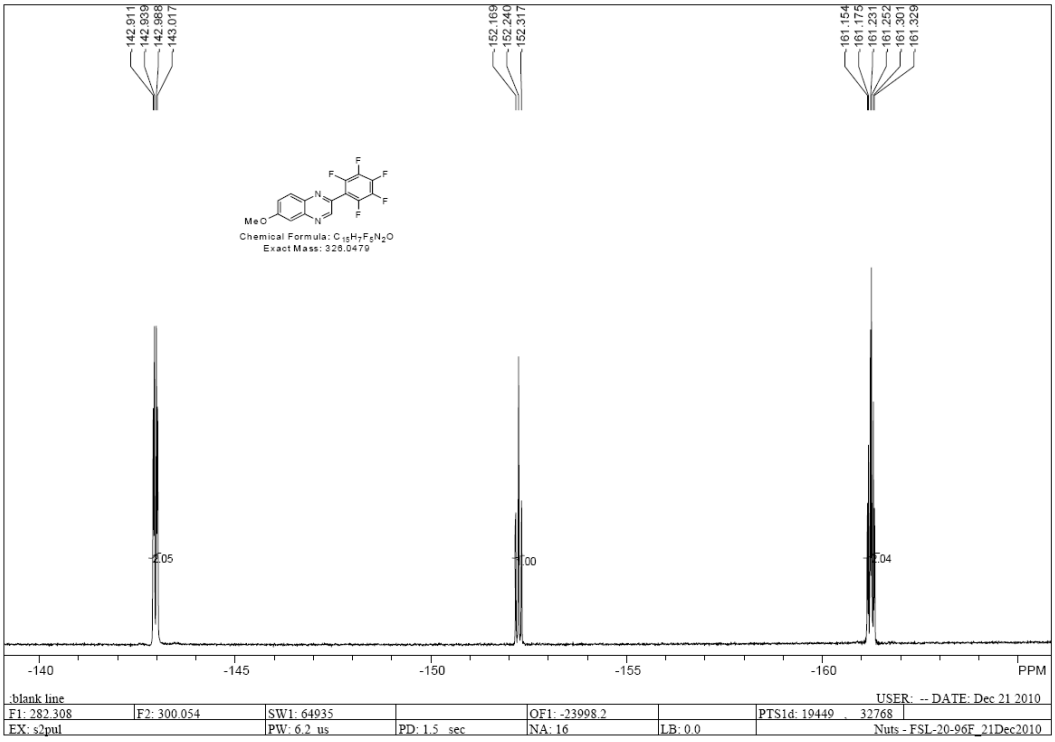


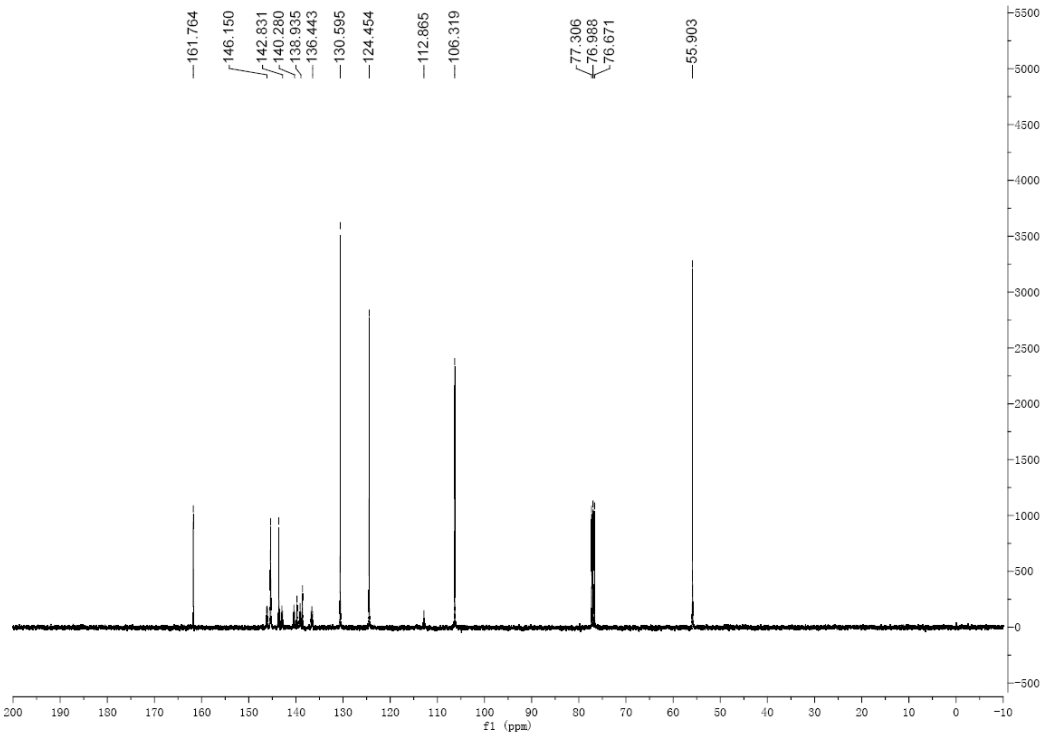




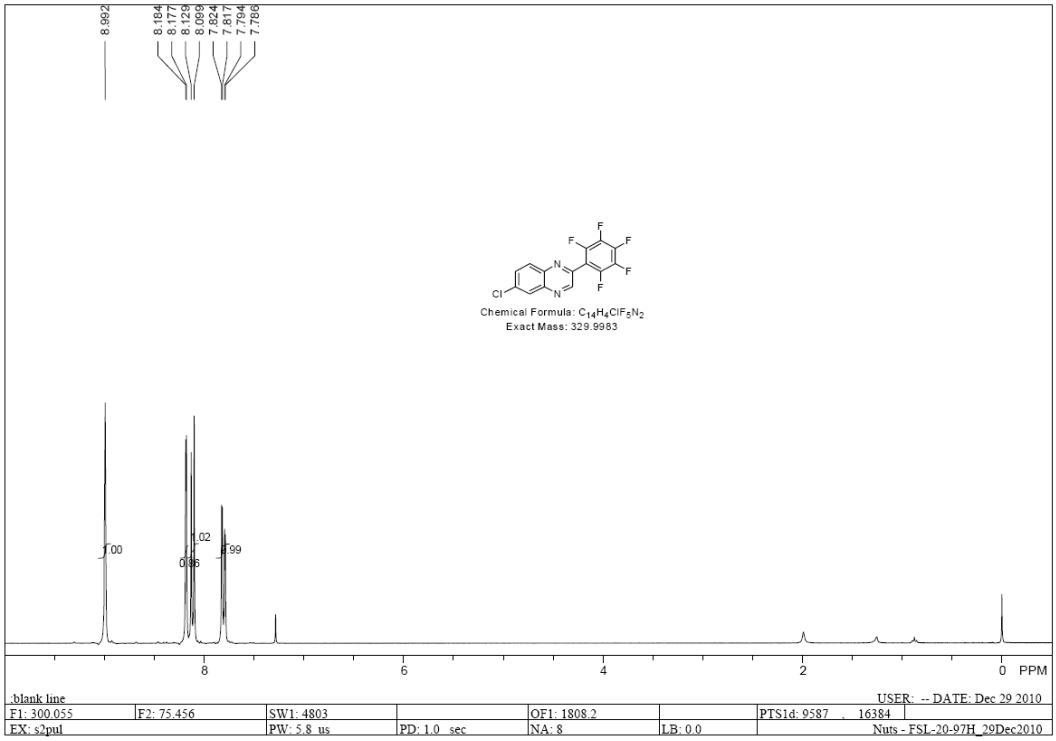
6-Methoxy-2-(perfluorophenyl)quinoxaline (3d)

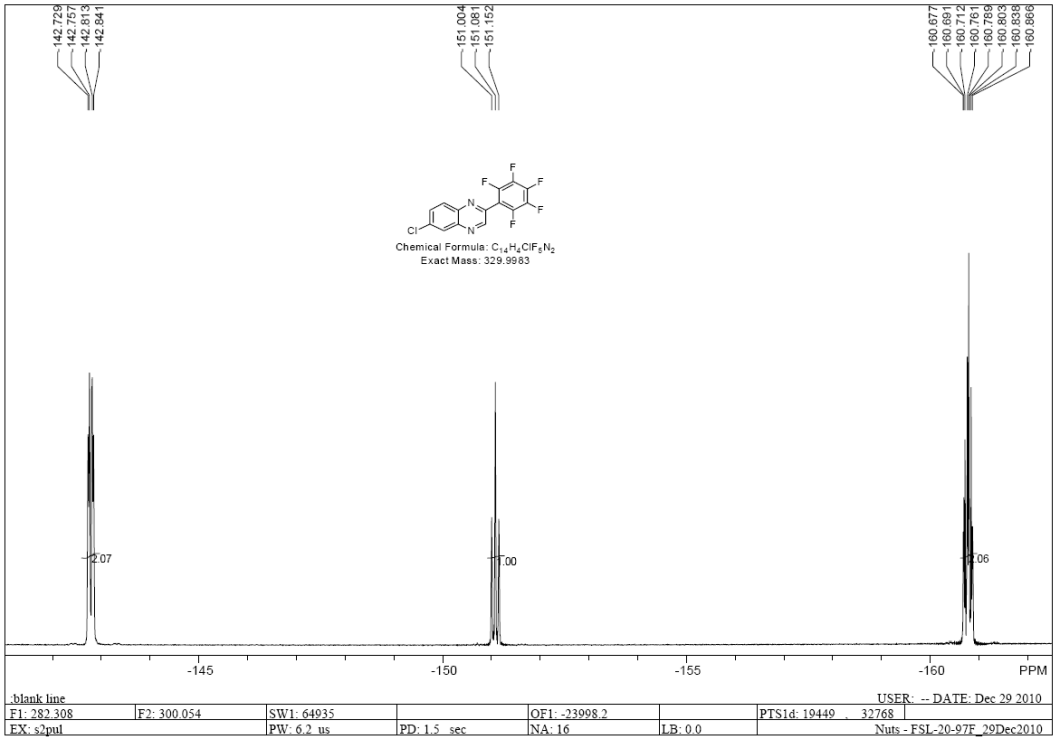


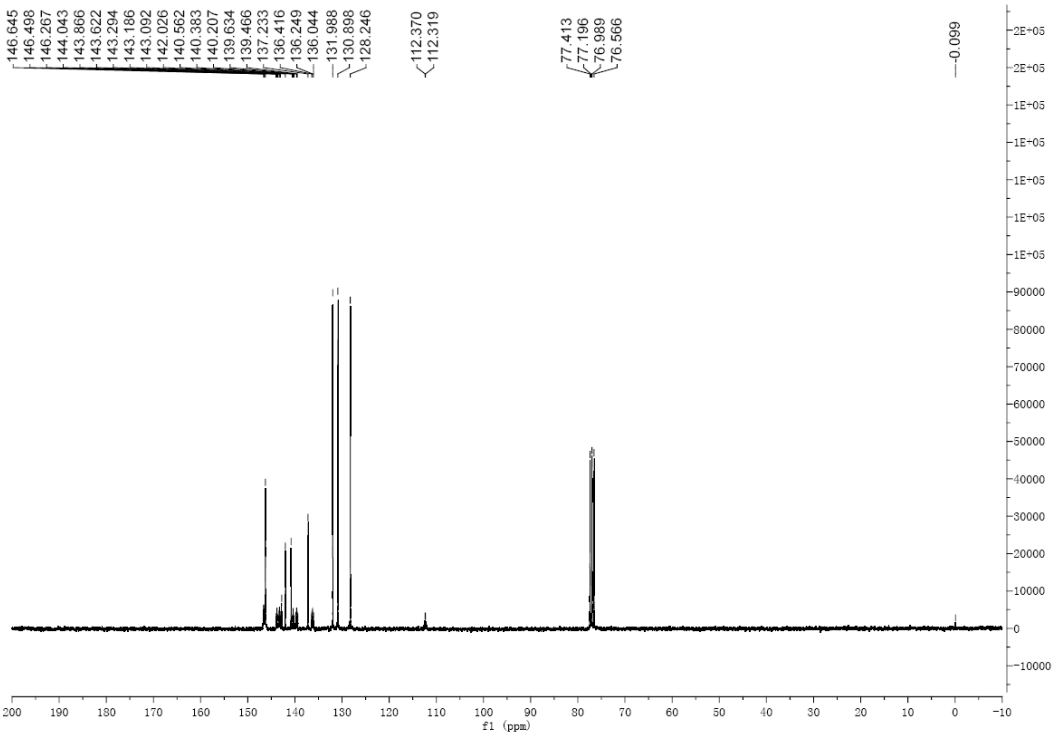

142.911
142.939
142.988
143.017
152.169
152.240
152.317
161.154
161.175
161.231
161.252
161.301
161.329
MeO
Chemical Formula: C16H7F5N2O
Exact Mass: 326.0479
2.05
1.00
2.04
-140
-145
-150
-155
-160
PPM
:blank line
USER: -- DATE: Dec 21 2010
F1: 282.308
F2: 300.054
SW1: 64935
OF1: -23998.2
PTS1d: 19449 , 32768
EX: s2pul
PW: 6.2 us
PD: 1.5 sec
NA: 16
LB: 0.0
Nuts - FSL-20-96F_21Dec2010


161.764
146.150
142.831
140.280
138.935
136.443
130.595
124.454
112.865
106.319
77.306
76.988
76.671
55.903
f1 (ppm)

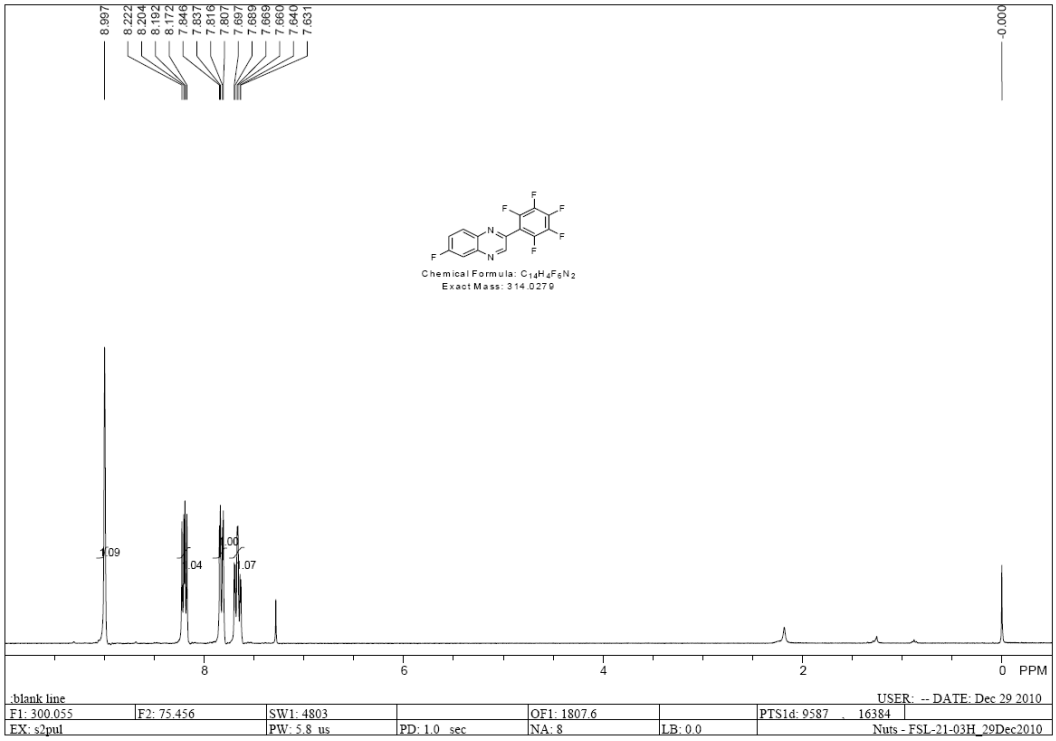
6-Chloro-2-(perfluorophenyl)quinoxaline (3e)

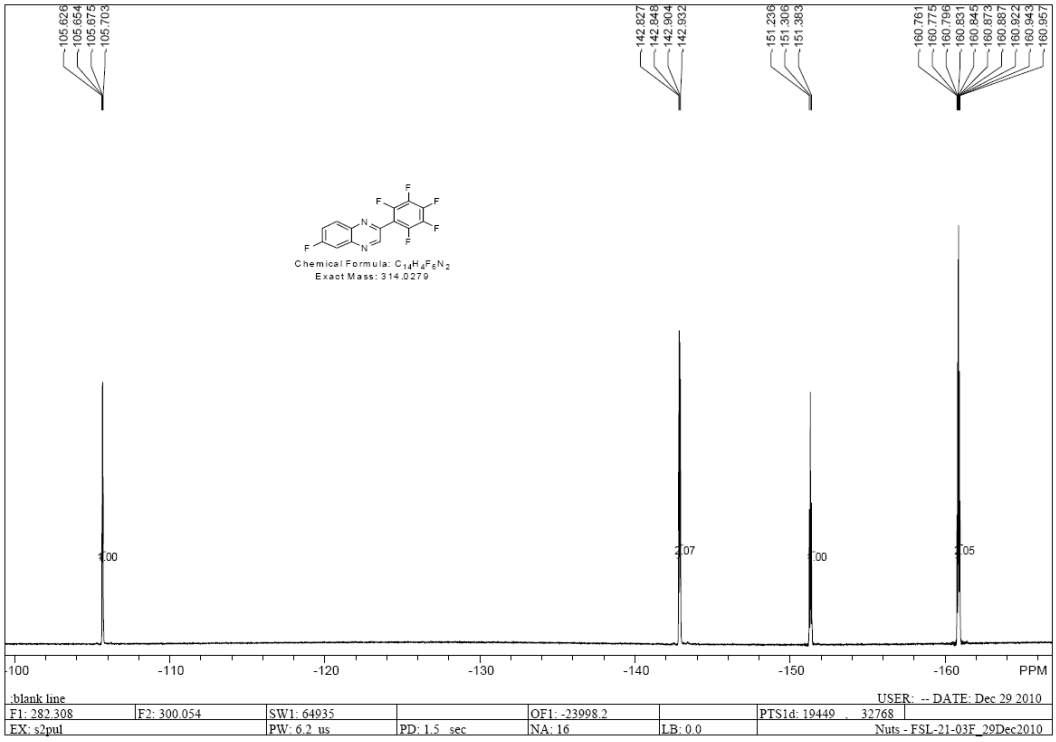


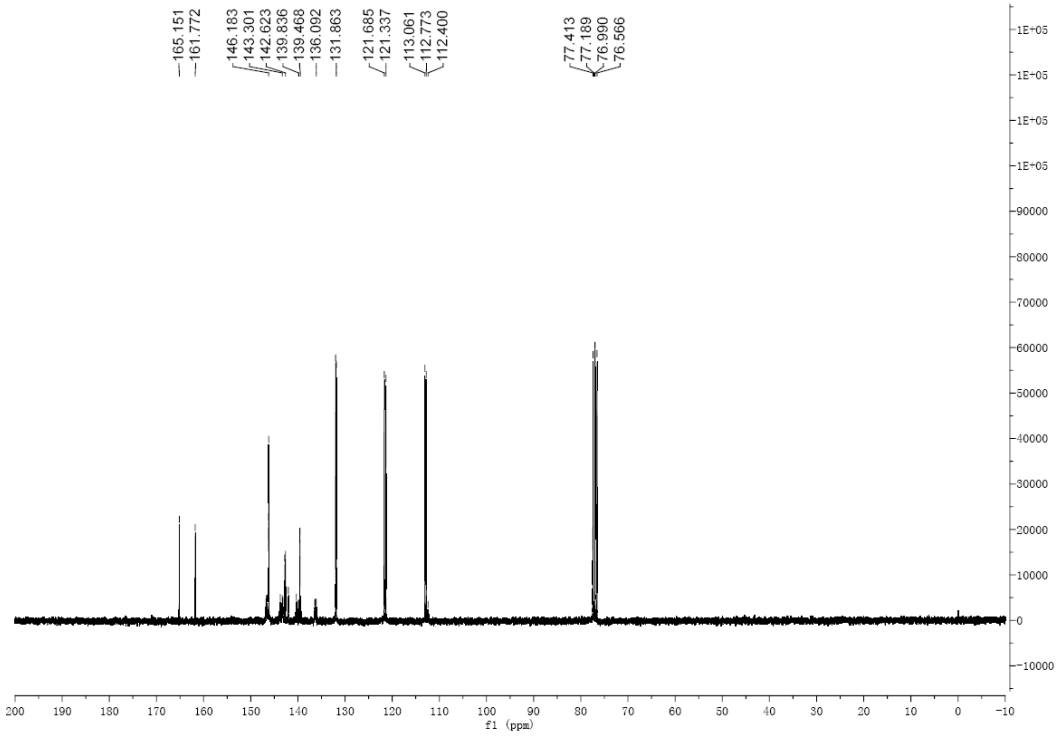




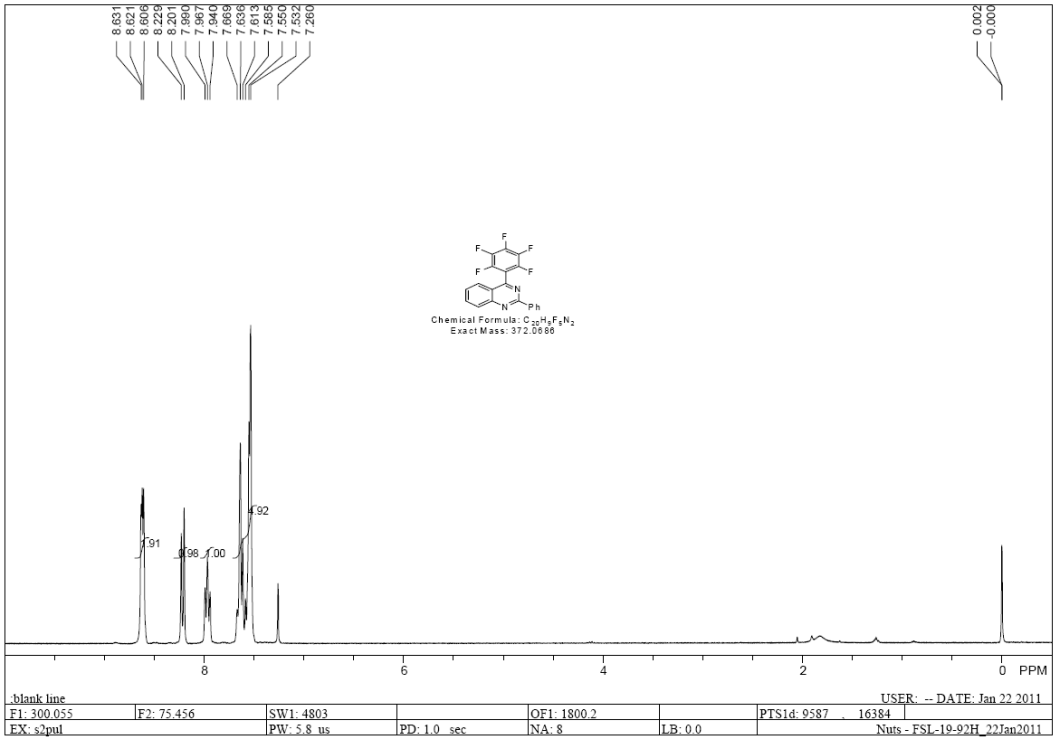
6-Fluoro-2-(perfluorophenyl)quinoxaline (3f)

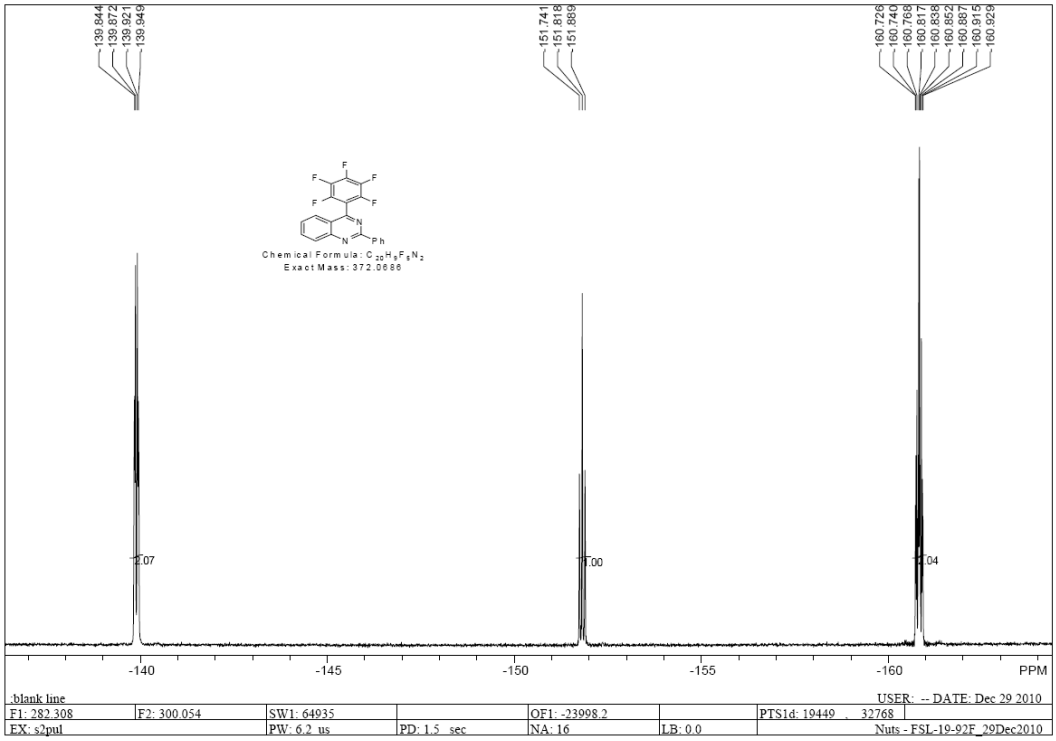


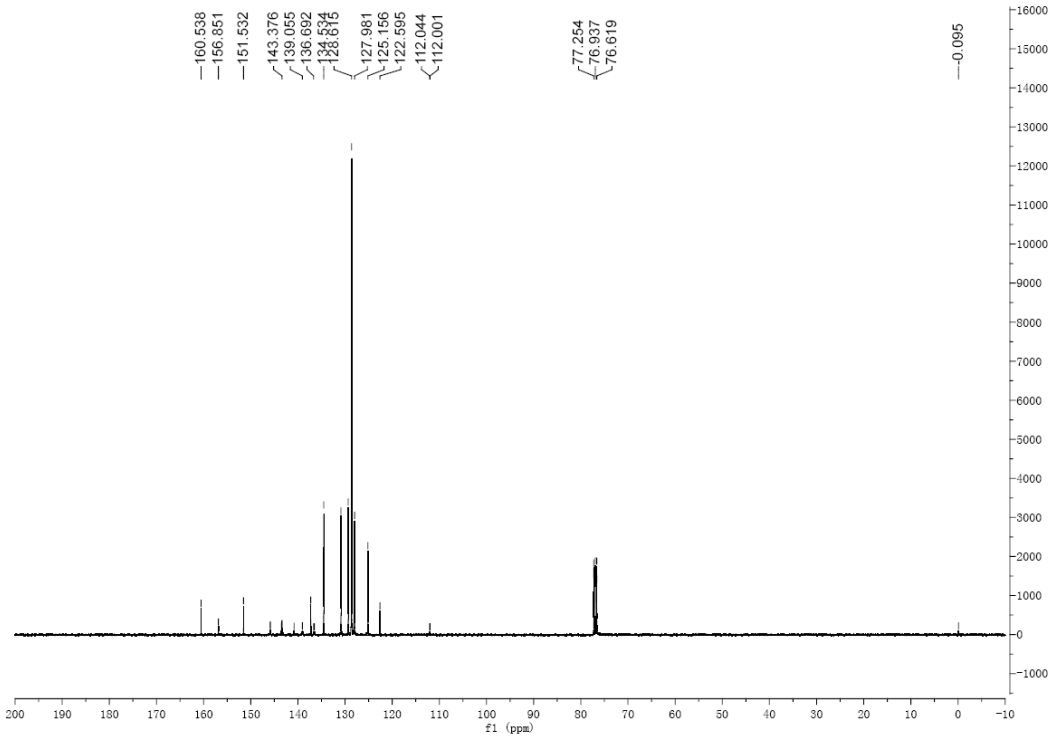

105.626
105.654
105.675
105.703
142.827
142.848
142.904
142.932
151.236
151.306
151.383
160.761
160.775
160.796
160.831
160.845
160.873
160.887
160.922
160.943
160.957
Chemical Formula: C14H4F6N2
Exact Mass: 314.0279
1.00
2.07
1.00
2.05
-100
-110
-120
-130
-140
-150
-160
PPM
;blank line
USER: -- DATE: Dec 29 2010
F1: 282.308
F2: 300.054
SW1: 64935
OF1: -23998.2
PTS1d: 19449 32768
EX: s2pul
PW: 6.2 us
PD: 1.5 sec
NA: 16
LB: 0.0
Nuts - FSL-21-03F_29Dec2010


165.151
161.772
146.183
143.301
142.623
139.836
139.468
136.092
131.863
121.685
121.337
113.061
112.773
112.400
77.413
77.189
76.990
76.566
f1 (ppm)

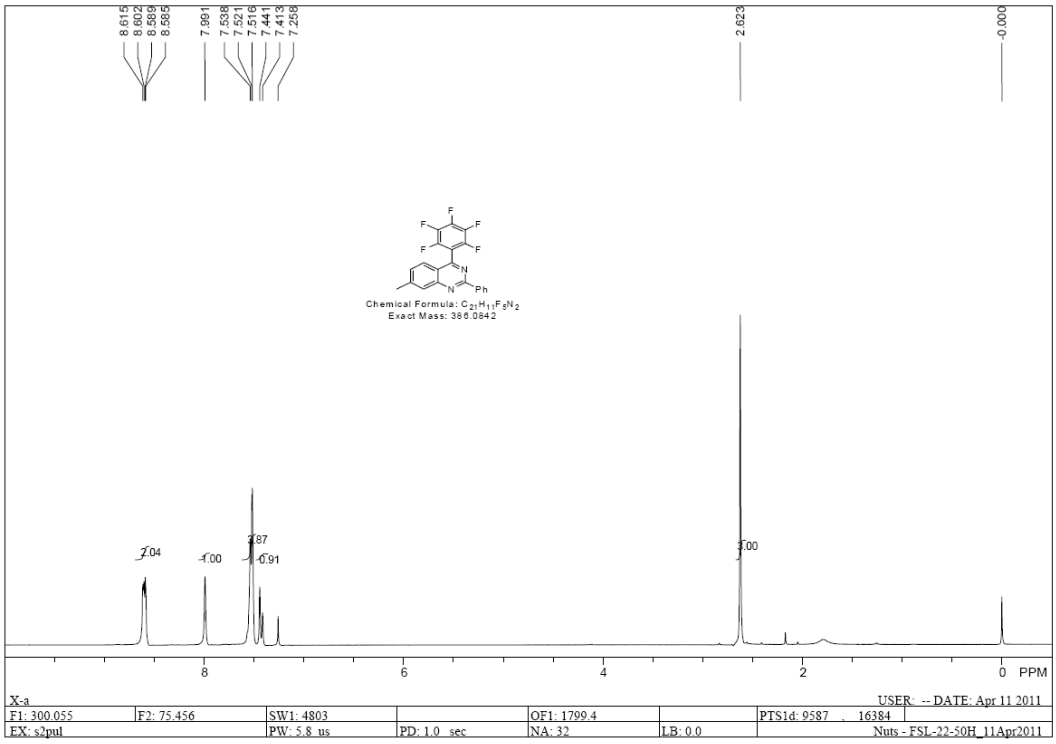
4-(Perfluorophenyl)-2-phenylquinazoline (3g)

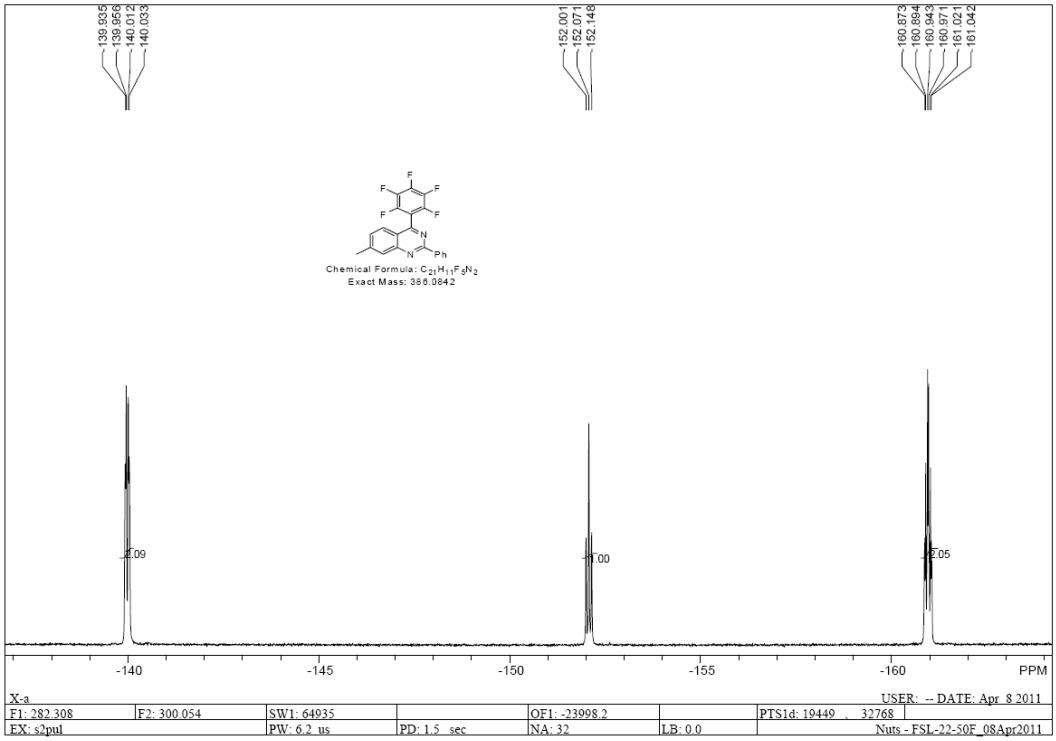


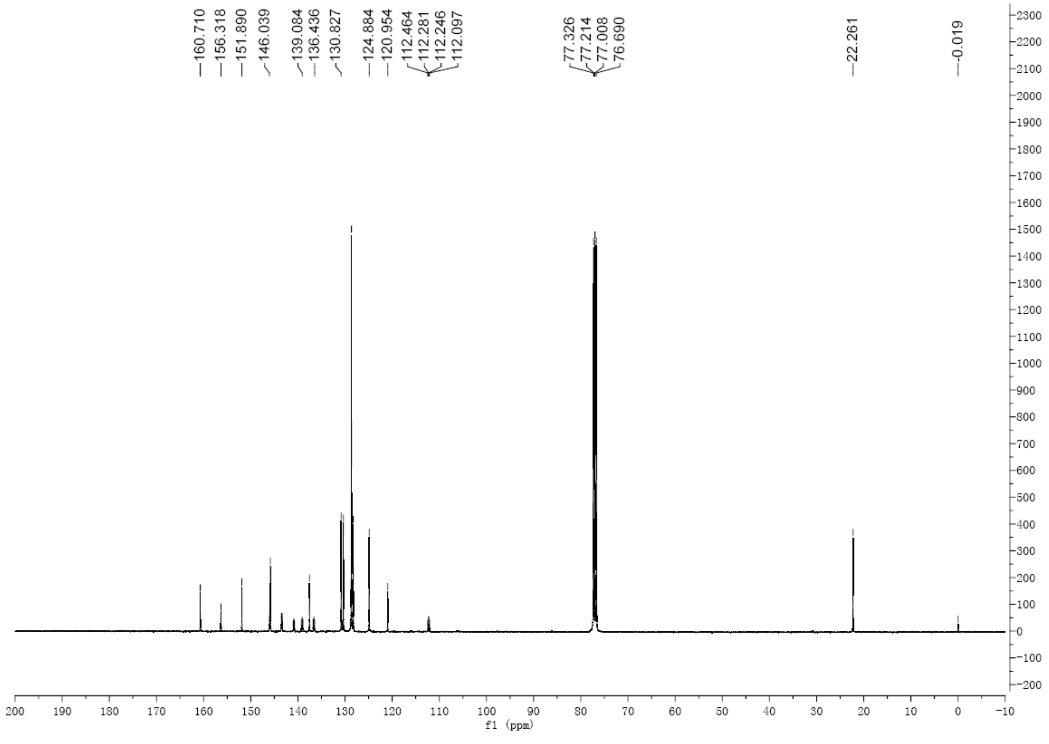




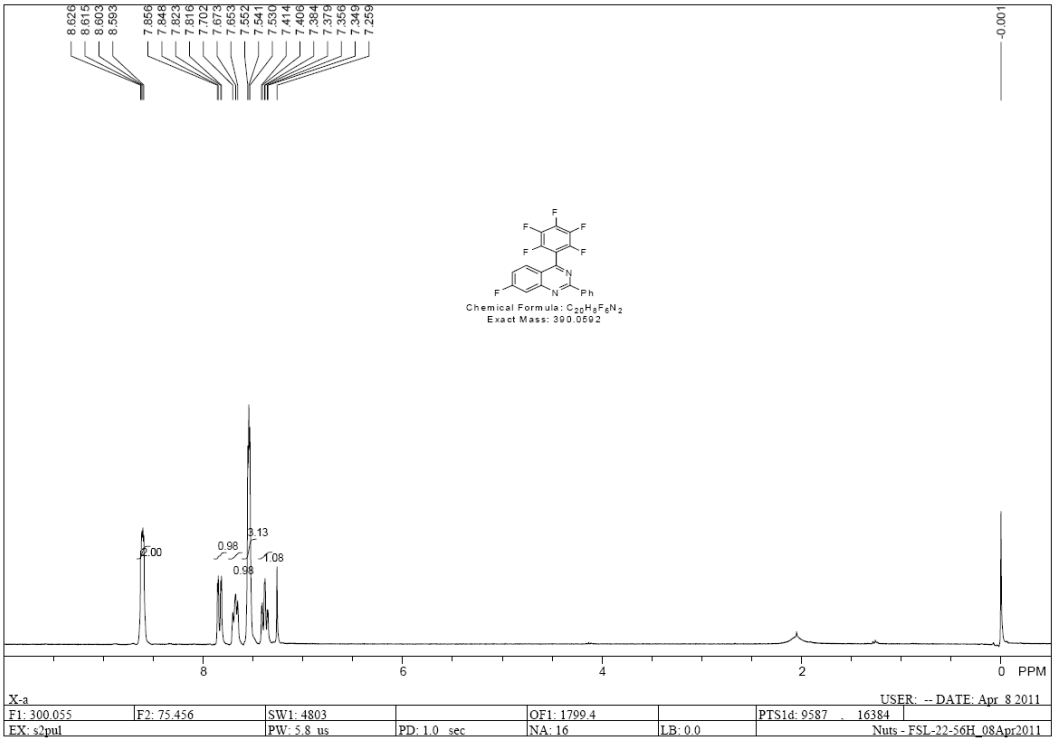
7-Methyl-4-(perfluorophenyl)-2-phenylquinazoline (3h)

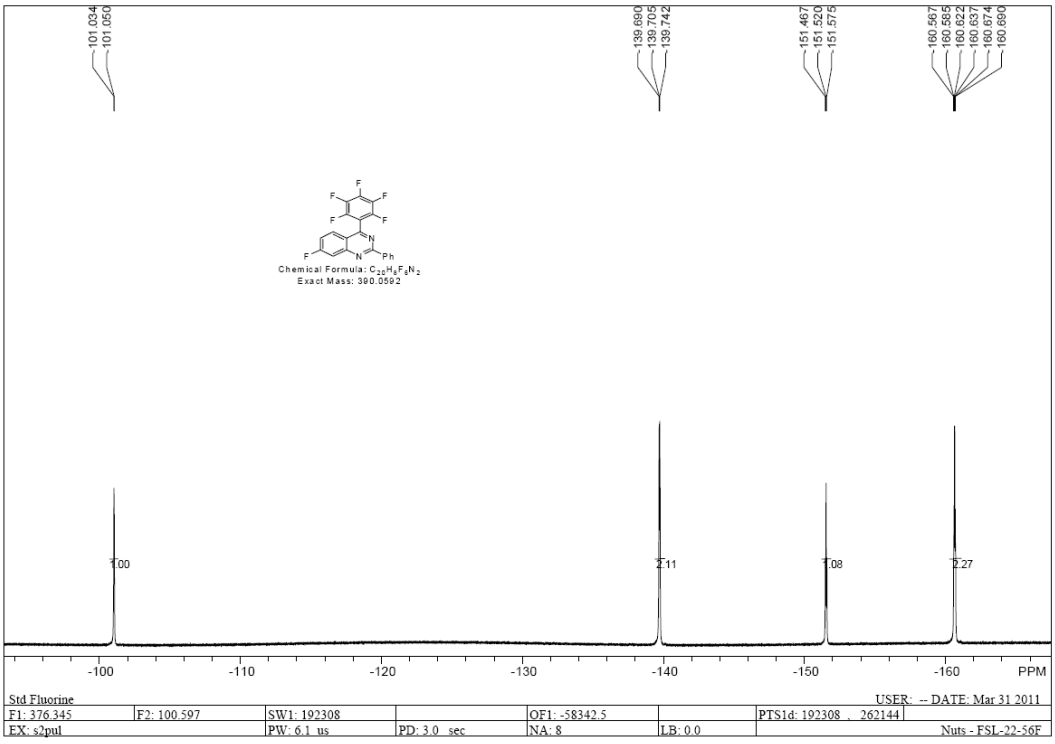


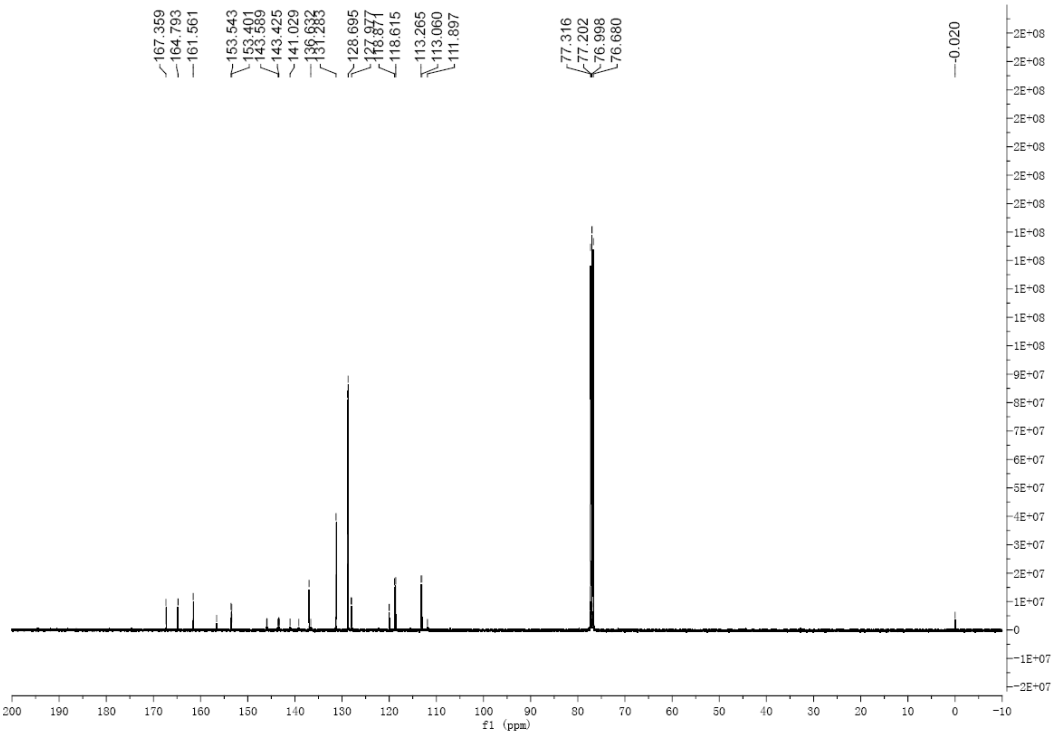

139.935
139.956
140.012
140.033
152.001
152.071
152.148
160.873
160.894
160.943
160.971
161.021
161.042
Chemical Formula: C21H11F5N2
Exact Mass: 386.0842
2.09
1.00
2.05
-140
-145
-150
-155
-160
PPM
X-a
USER: -- DATE: Apr 8 2011
F1: 282.308
F2: 300.054
SW1: 64935
OF1: -23998.2
PTS1d: 19449 32768
EX: s2pul
PW: 6.2 us
PD: 1.5 sec
NA: 32
LB: 0.0
Nuts - FSL-22-50F_08Apr2011


160.710
156.318
151.890
146.039
139.084
136.436
130.827
124.884
120.954
112.464
112.281
112.246
112.097
77.326
77.214
77.008
76.690
22.261
-0.019
f1 (ppm)

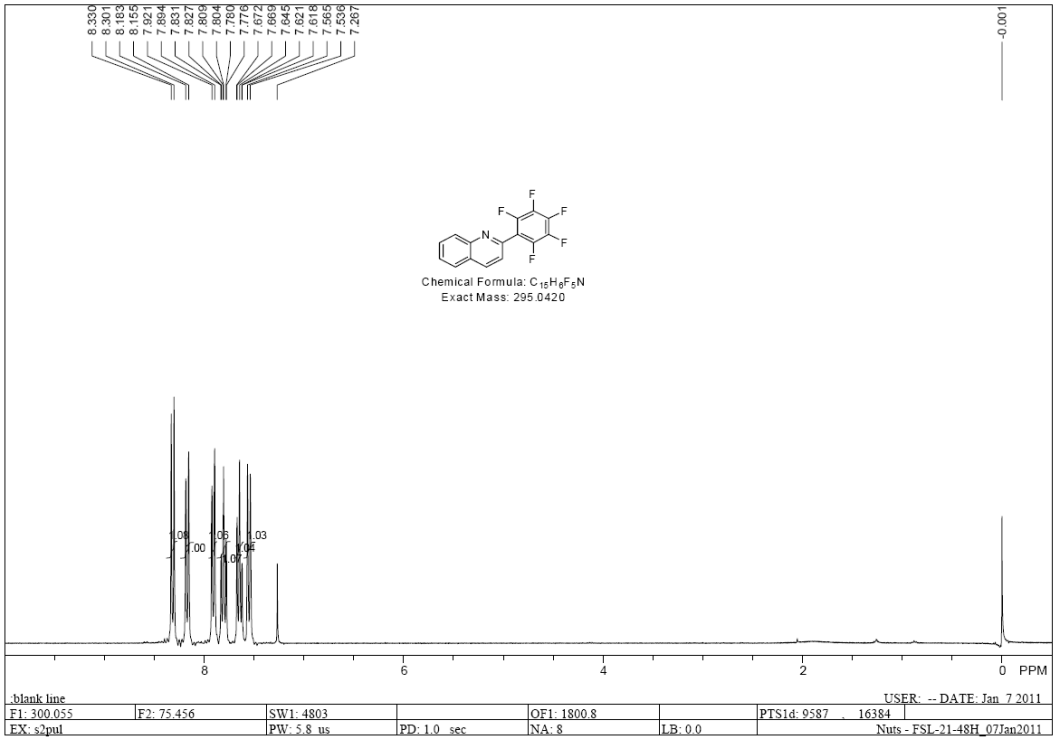
7-Fluoro-4-(perfluorophenyl)-2-phenylquinazoline (3i)

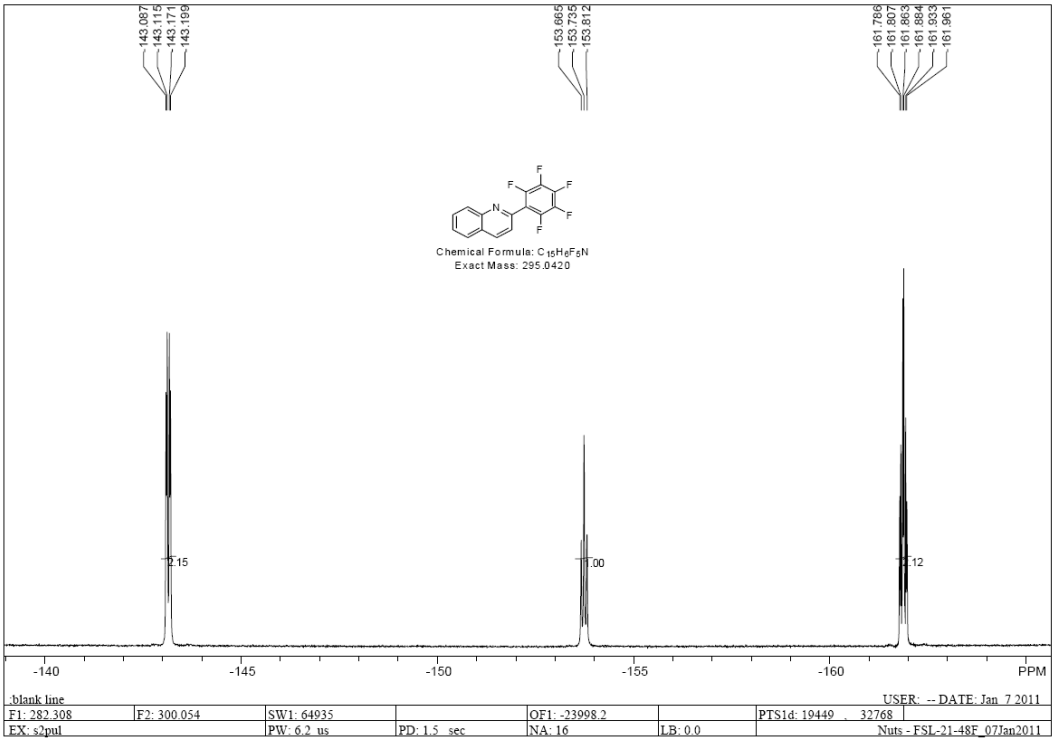




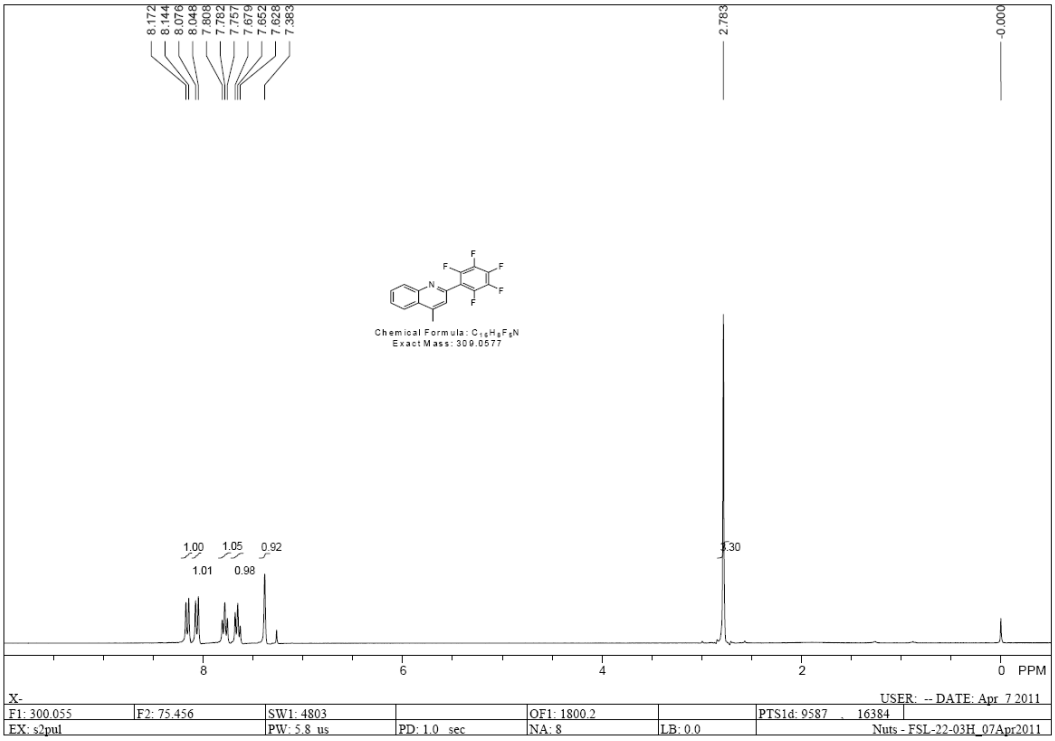


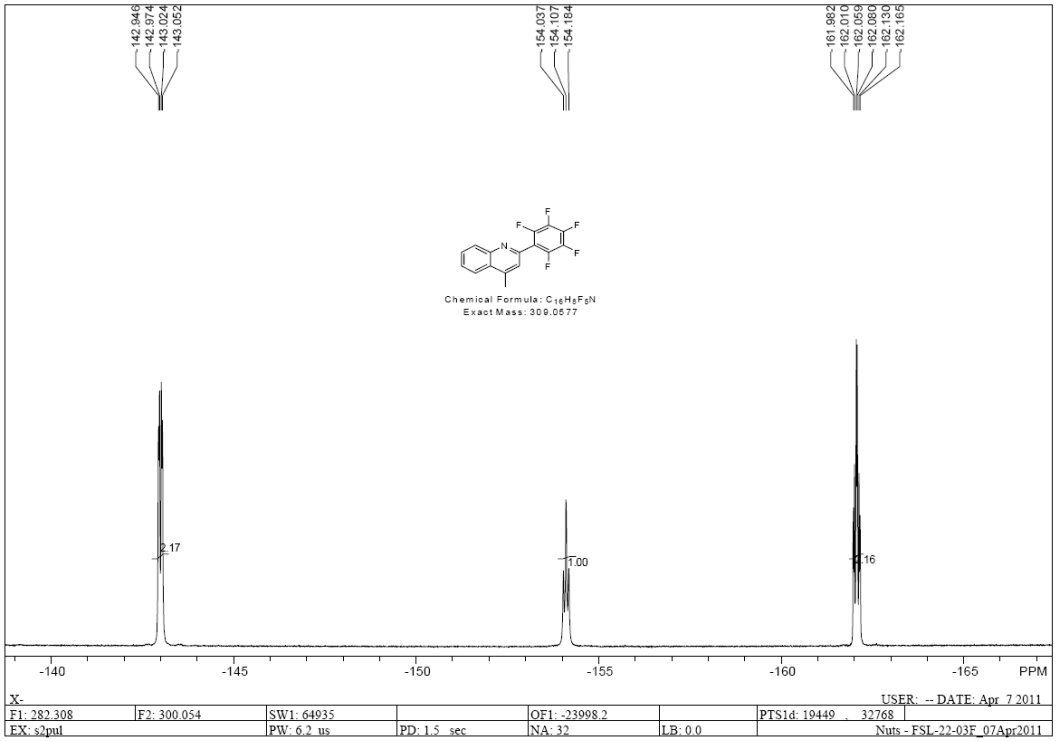
2-(Perfluorophenyl)quinoline (3j)

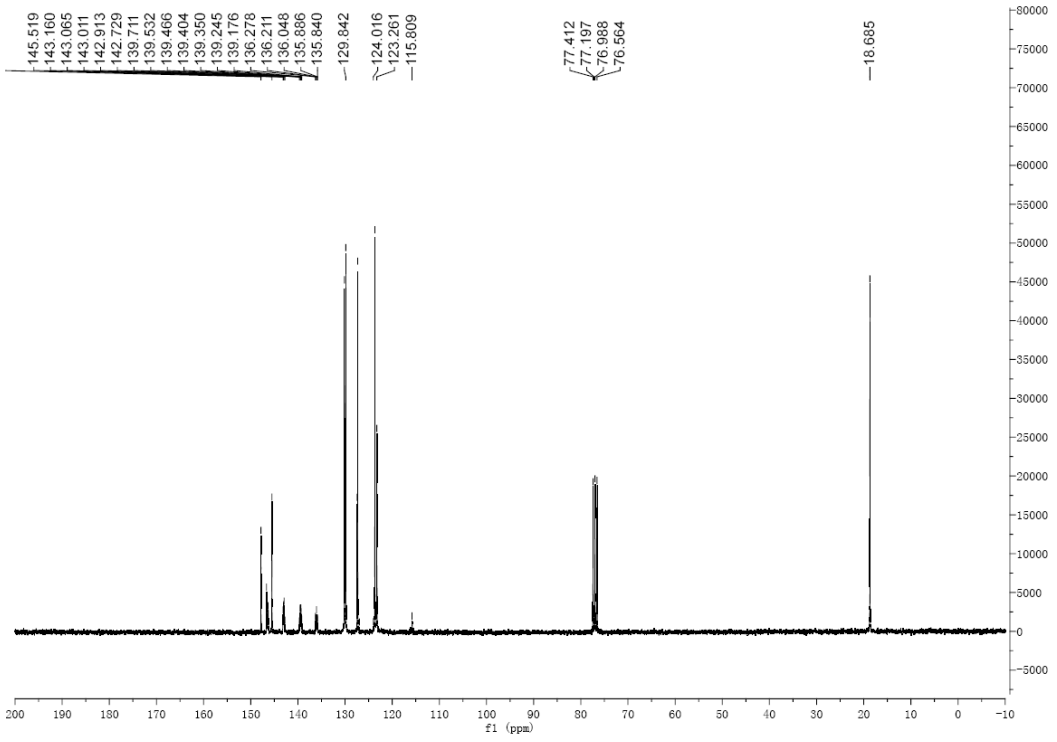




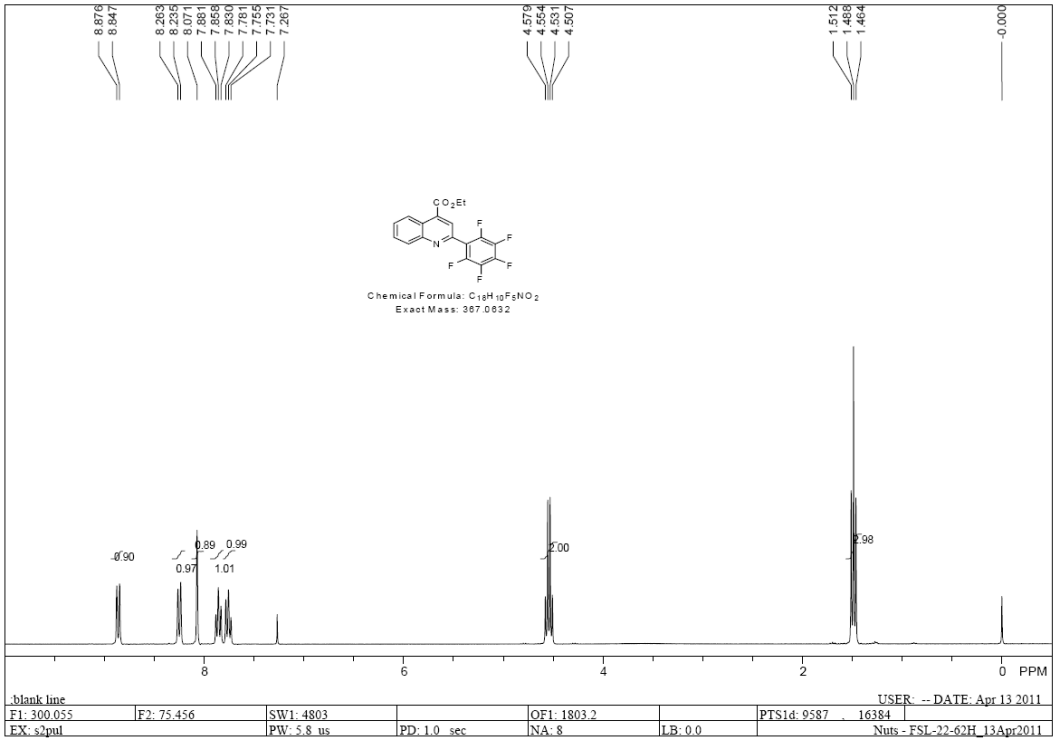
4-Methyl-2-(perfluorophenyl)quinoline (3k)

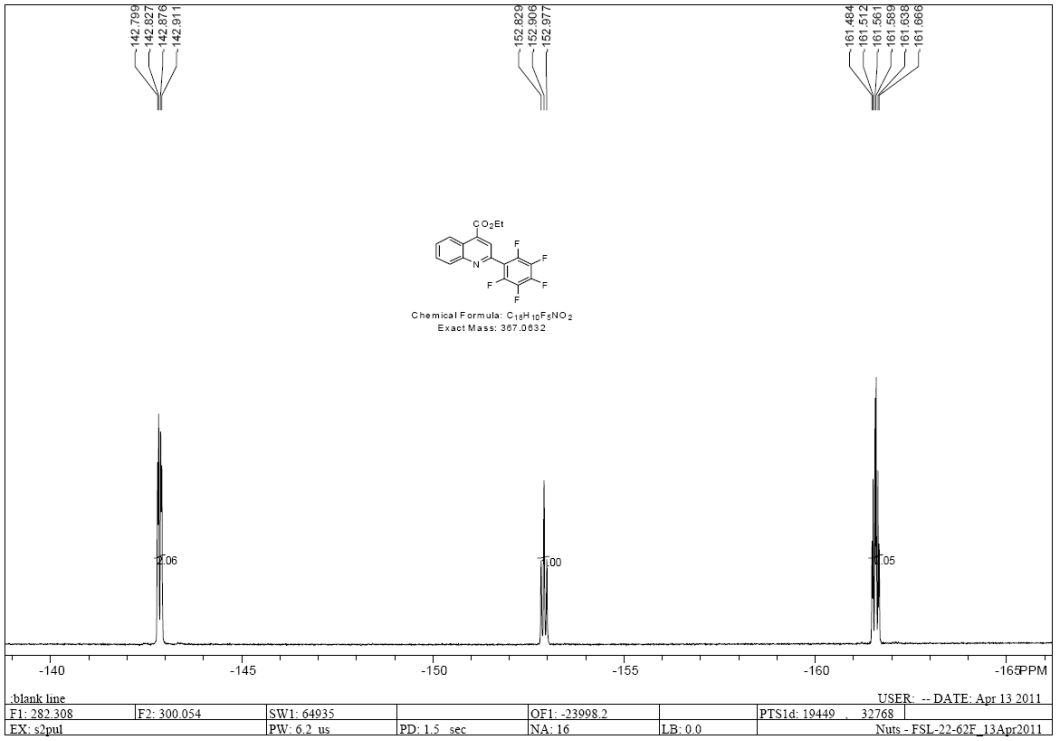


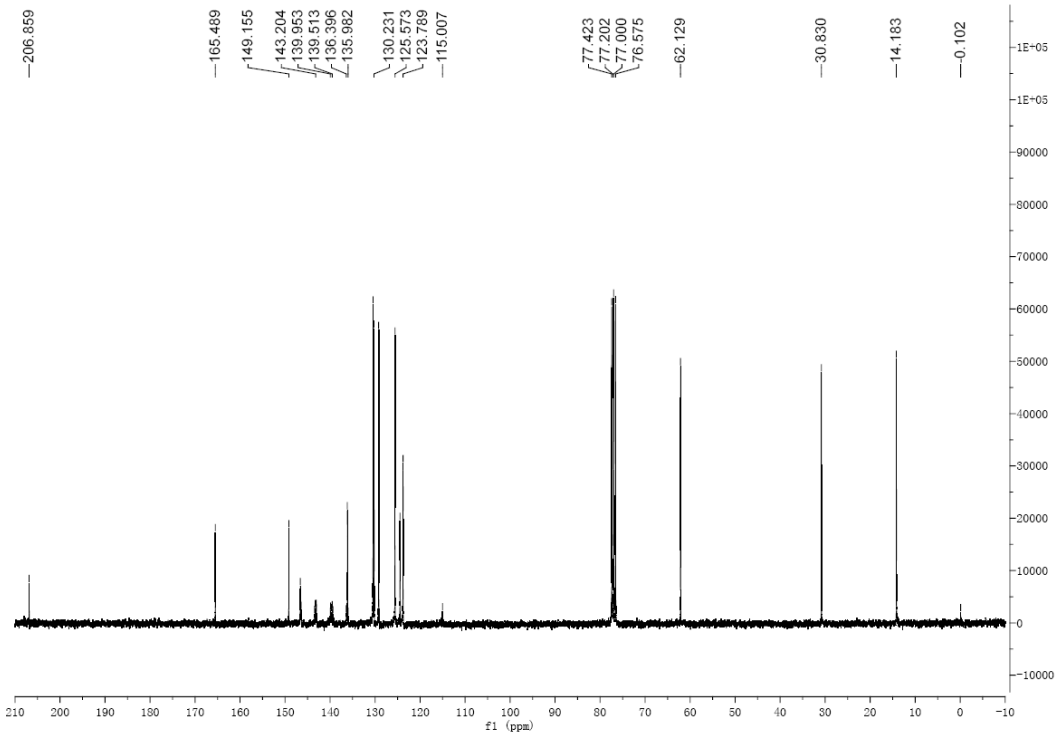

142.946
142.974
143.024
143.052
154.037
154.107
154.184
161.982
162.010
162.059
162.080
162.130
162.165
Chemical Formula: C15H6F5N
Exact Mass: 309.0577
2.17
1.00
2.16
-140
-145
-150
-155
-160
-165
PPM
X-
USER: -- DATE: Apr 7 2011
F1: 282.308
F2: 300.054
SW1: 64935
OF1: -23998.2
PTS1d: 19449 32768
EX: s2pul
PW: 6.2 us
PD: 1.5 sec
NA: 32
LB: 0.0
Nuts - FSL-22-03F_07Apr2011


145.519
143.160
143.065
143.011
142.913
142.729
139.711
139.532
139.466
139.404
139.350
139.245
139.176
136.278
136.211
136.048
135.886
135.840
129.842
124.016
123.261
115.809
77.412
77.197
76.988
76.564
18.685
f1 (ppm)

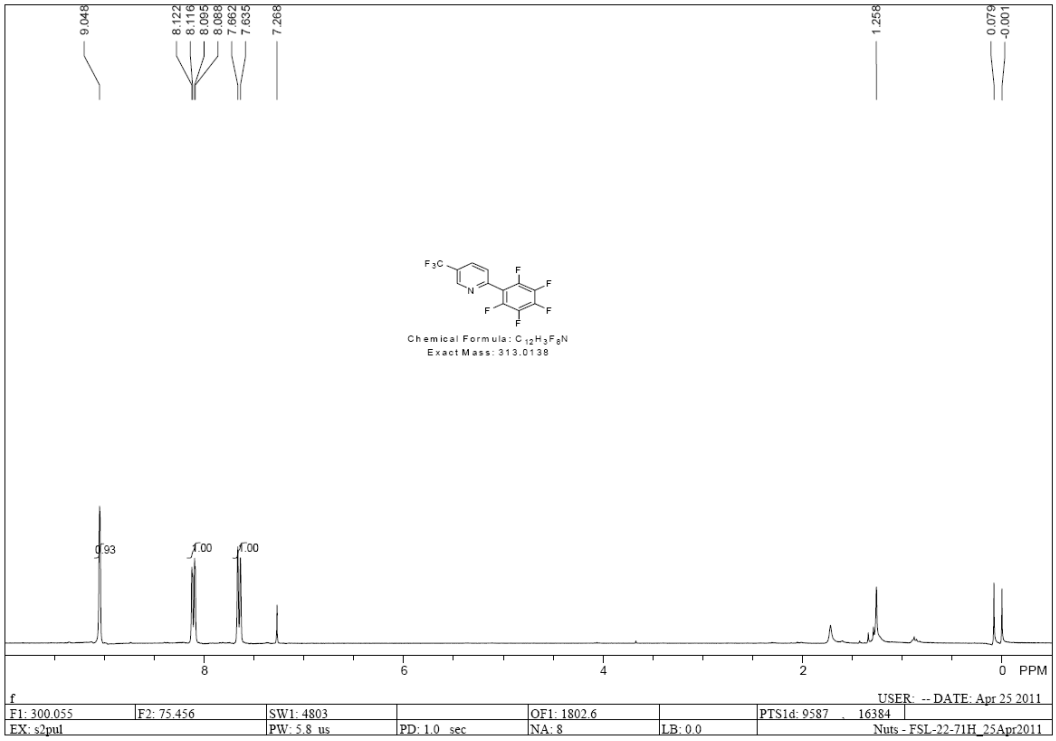
Ethyl 2-(perfluorophenyl)quinoline-4-carboxylate (3l)

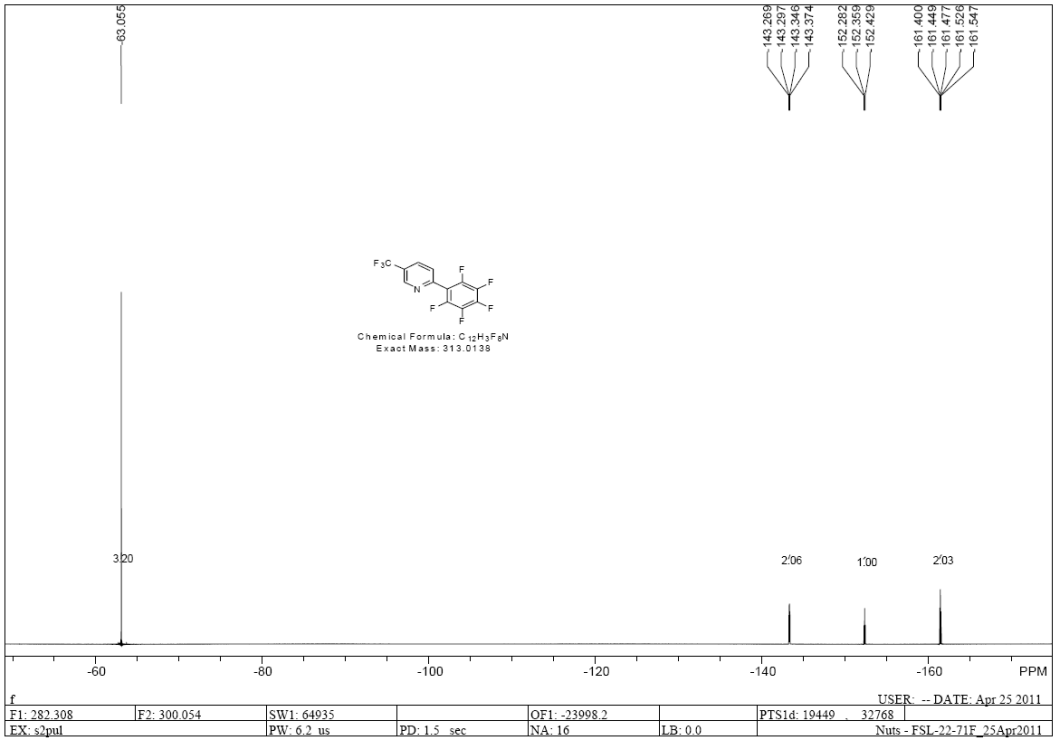


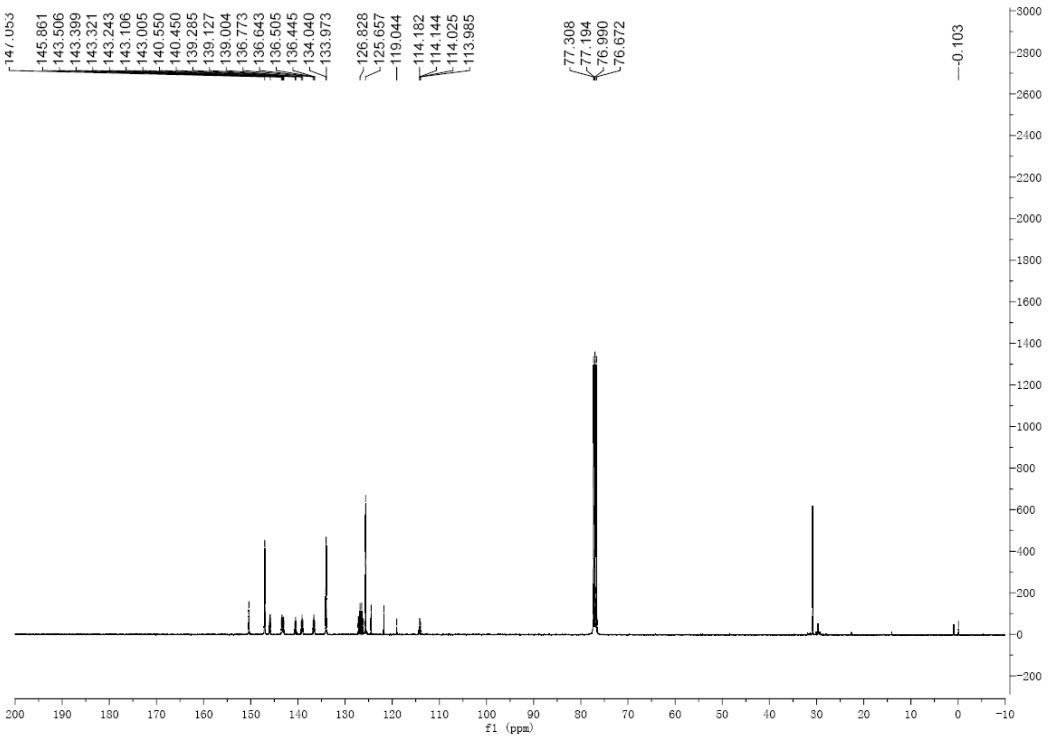




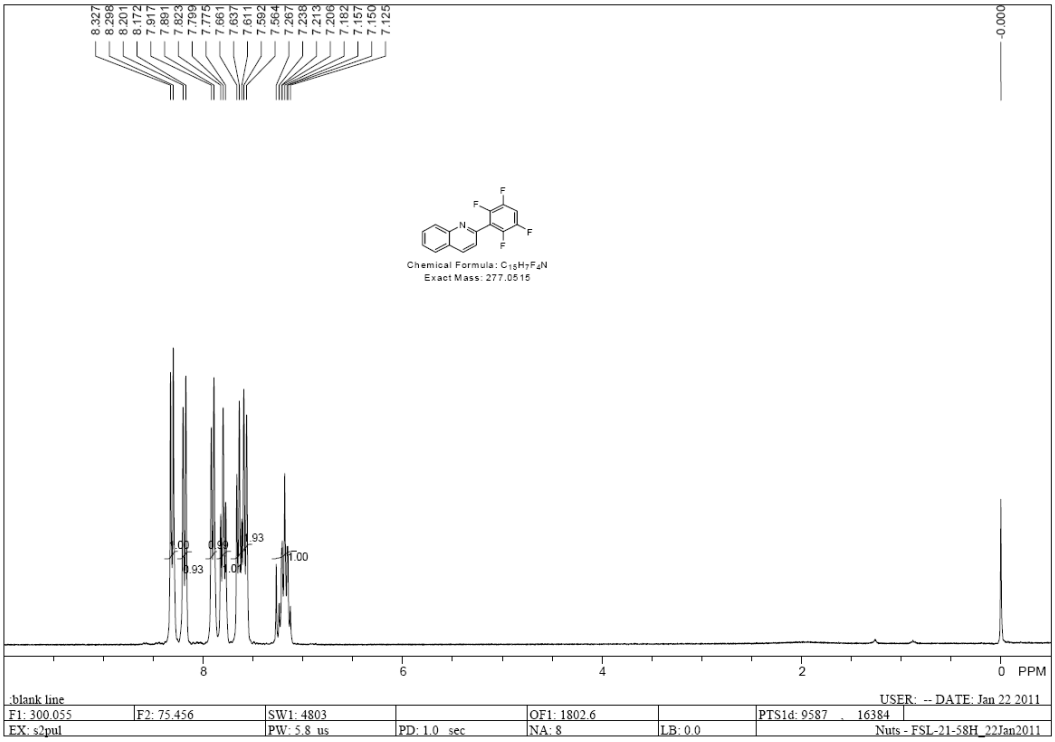
2-(Perfluorophenyl)-5-(trifluoromethyl)pyridine (3m)

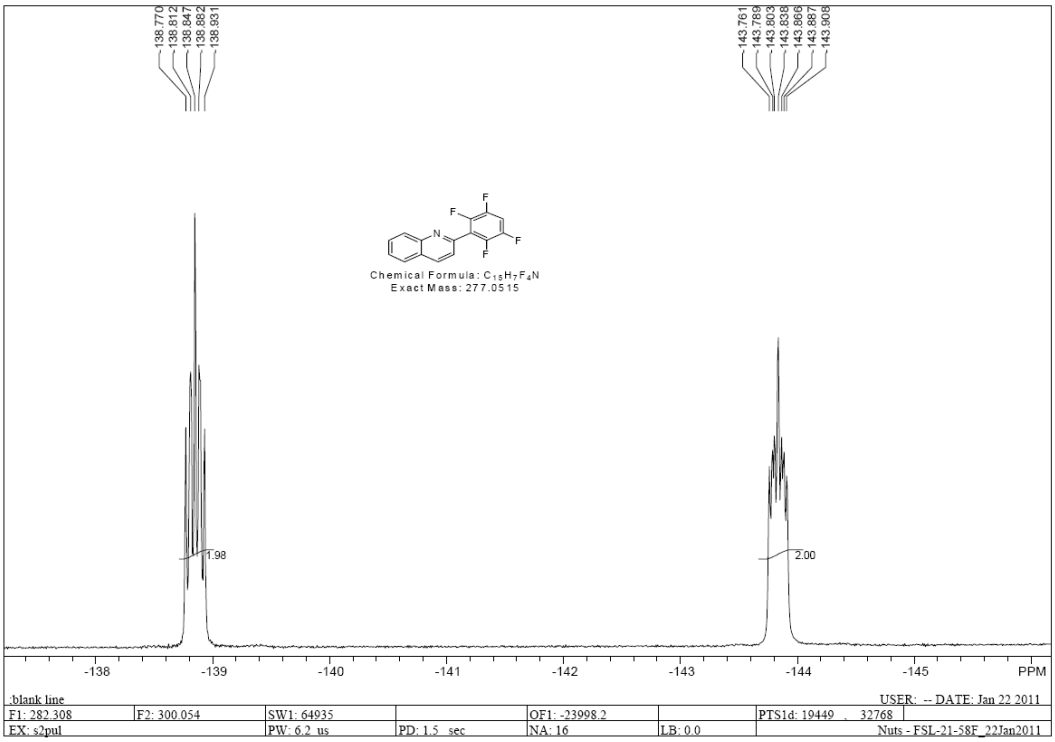


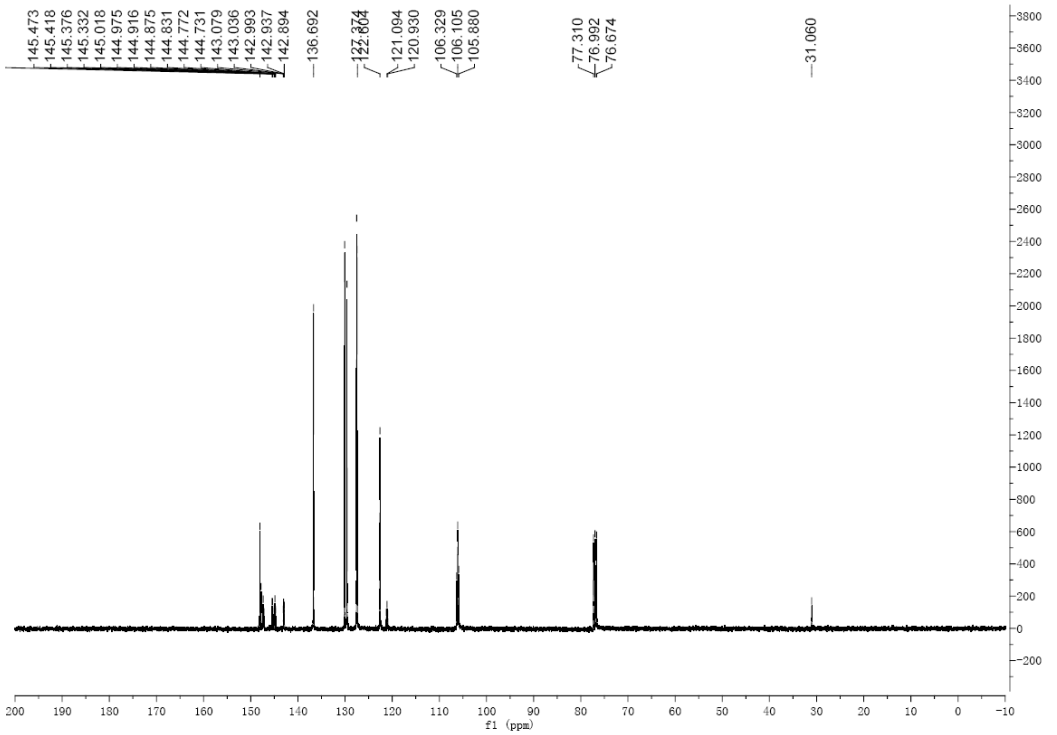

-63.055
-143.269
-143.297
-143.346
-143.374
-152.282
-152.369
-152.429
-161.400
-161.449
-161.477
-161.526
-161.547
Chemical Formula: C12H3F8N
Exact Mass: 313.0138
3.20
2.06
1.00
2.03
-60
-80
-100
-120
-140
-160
PPM
f
USER: -- DATE: Apr 25 2011
F1: 282.308
F2: 300.054
SW1: 64935
OF1: -23998.2
PTS1d: 19449 32768
EX: s2pul
PW: 6.2 us
PD: 1.5 sec
NA: 16
LB: 0.0
Nuts - FSL-22-71F_25Apr2011


145.861
143.506
143.399
143.321
143.243
143.106
143.005
140.550
140.450
139.285
139.127
139.004
136.773
136.643
136.505
136.445
134.040
133.973
126.828
125.657
119.044
114.182
114.144
114.025
113.985
77.308
77.194
76.990
76.672
-0.103
f1 (ppm)

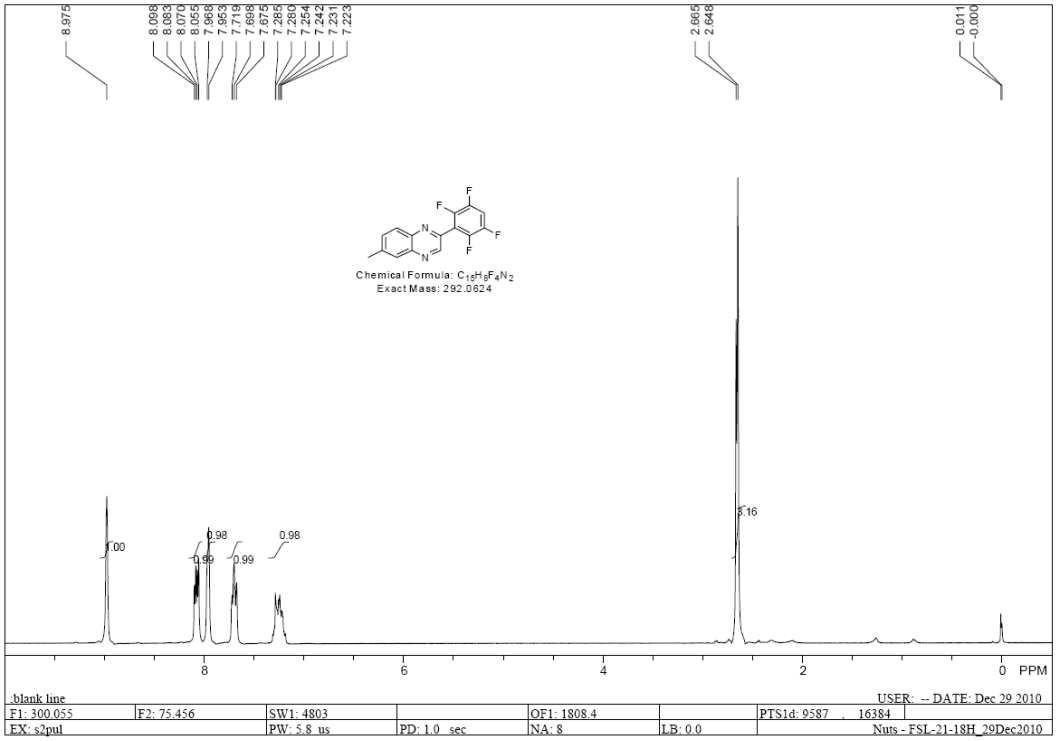
2-(2,3,5,6-Tetrafluorophenyl)quinoline (3n)

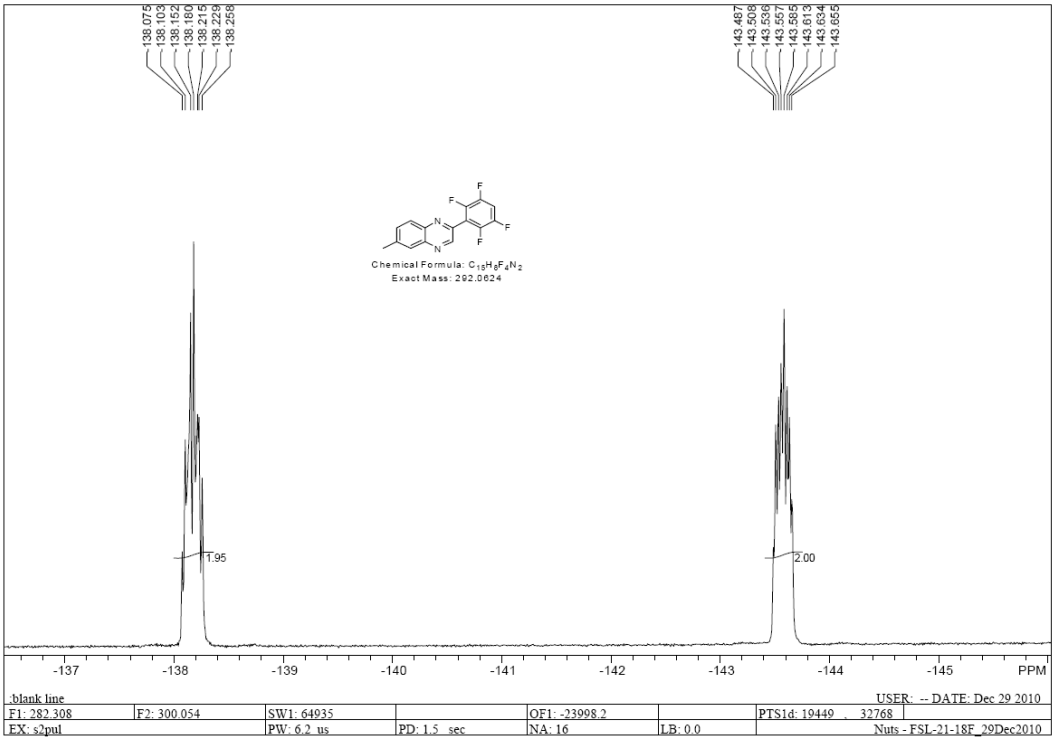


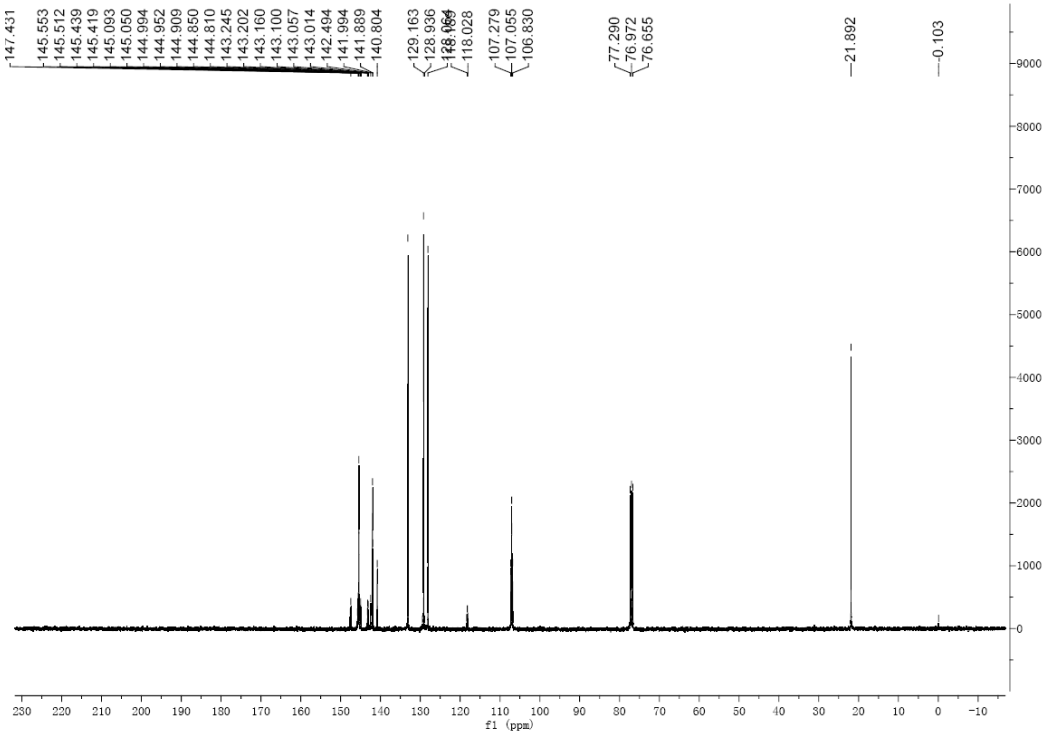




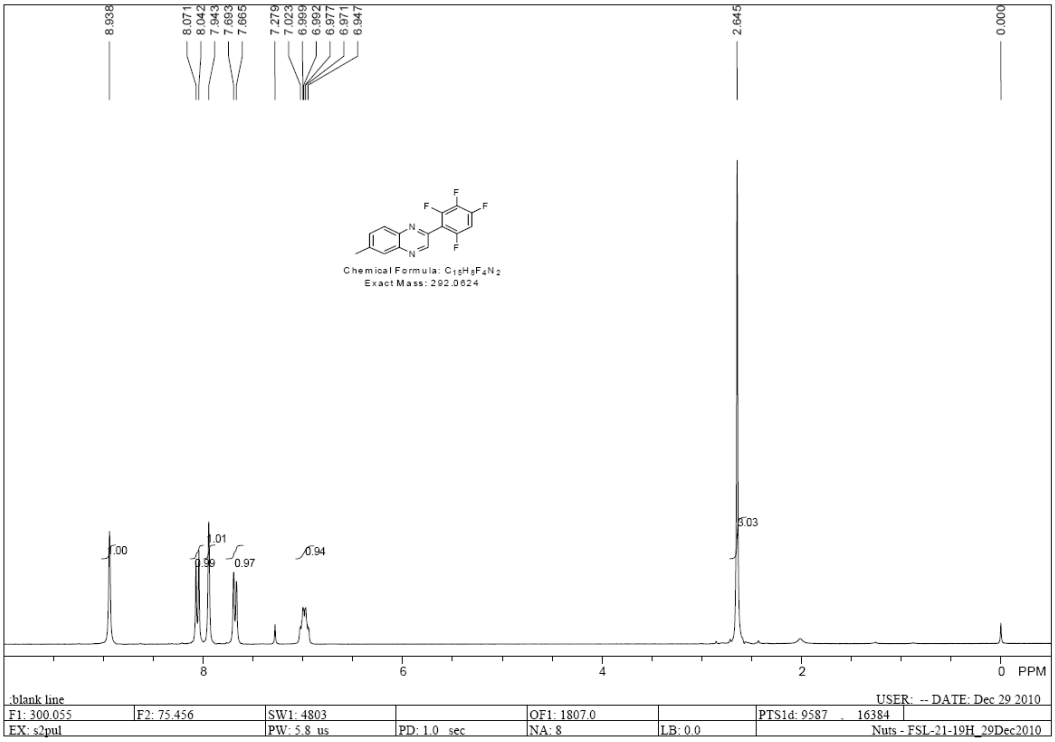
6-Methyl-2-(2,3,5,6-tetrafluorophenyl)quinoxaline (3o)

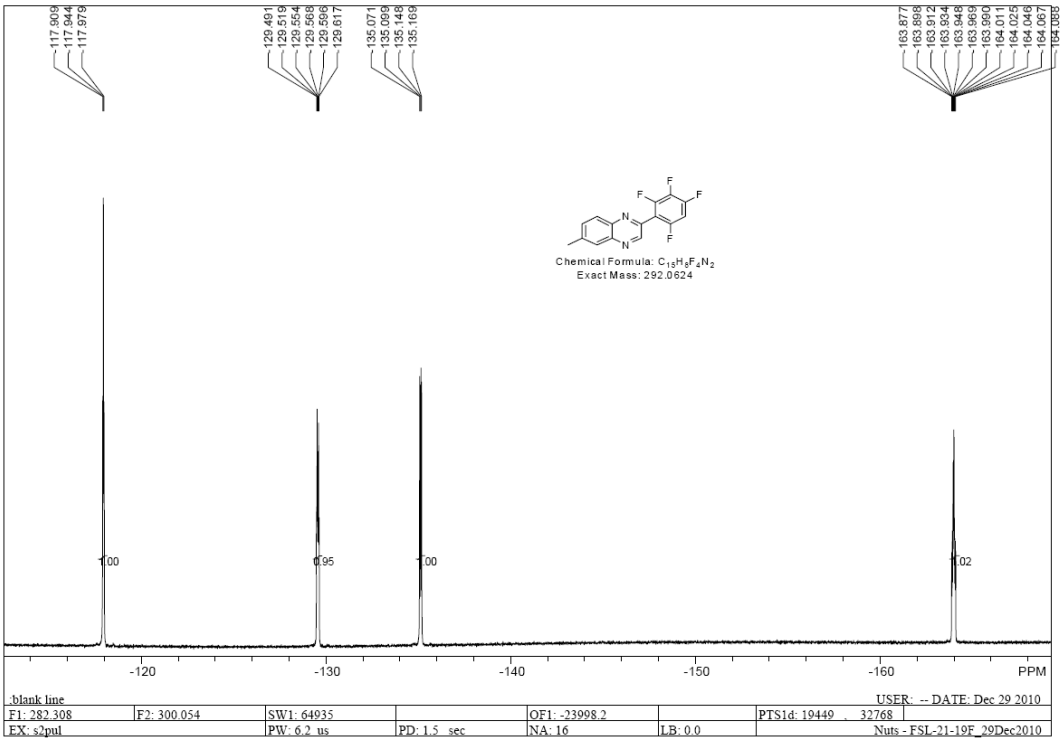


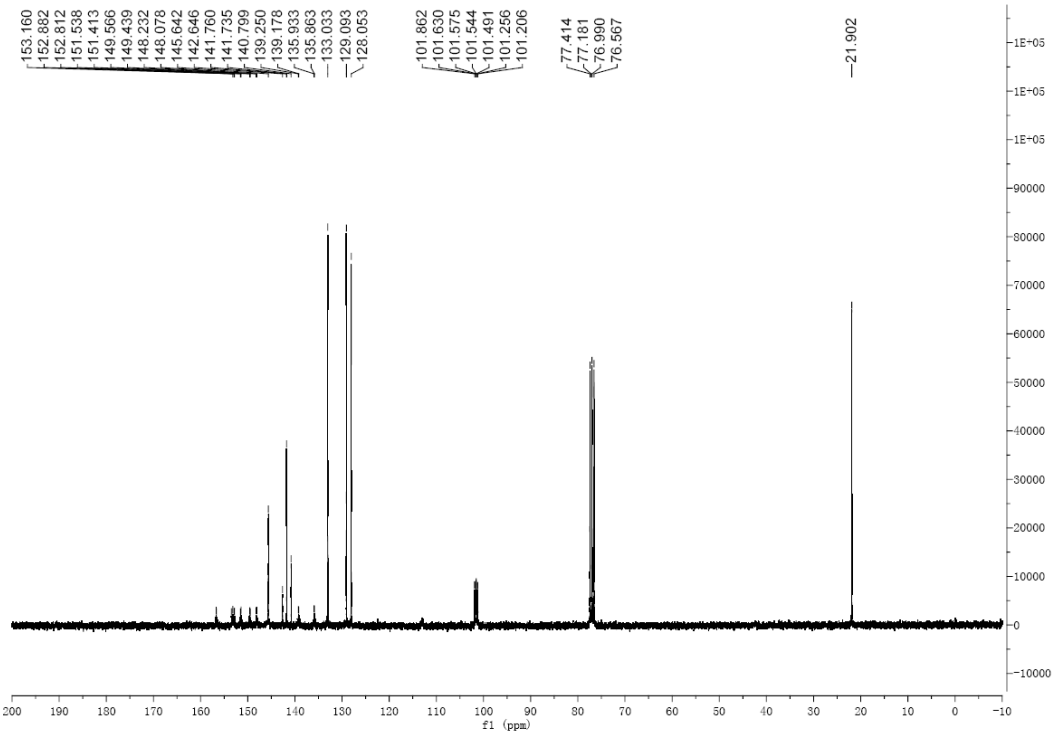

138.075
138.103
138.152
138.180
138.215
138.229
138.258
143.487
143.508
143.536
143.557
143.585
143.613
143.634
143.655
Chemical Formula: C15H8F4N2
Exact Mass: 292.0624
1.95
2.00
-137
-138
-139
-140
-141
-142
-143
-144
-145
PPM
:blank line
USER: -- DATE: Dec 29 2010
F1: 282.308
F2: 300.054
SW1: 64935
OF1: -23998.2
PTS1d: 19449 , 32768
EX: s2pul
PW: 6.2 us
PD: 1.5 sec
NA: 16
LB: 0.0
Nuts - FSL-21-18F_29Dec2010


147.431
145.553
145.512
145.439
145.419
145.093
145.050
144.994
144.952
144.909
144.850
144.810
143.245
143.202
143.160
143.100
143.057
143.014
142.494
141.994
141.889
140.804
129.163
128.936
118.028
107.279
107.055
106.830
77.290
76.972
76.655
21.892
0.103
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

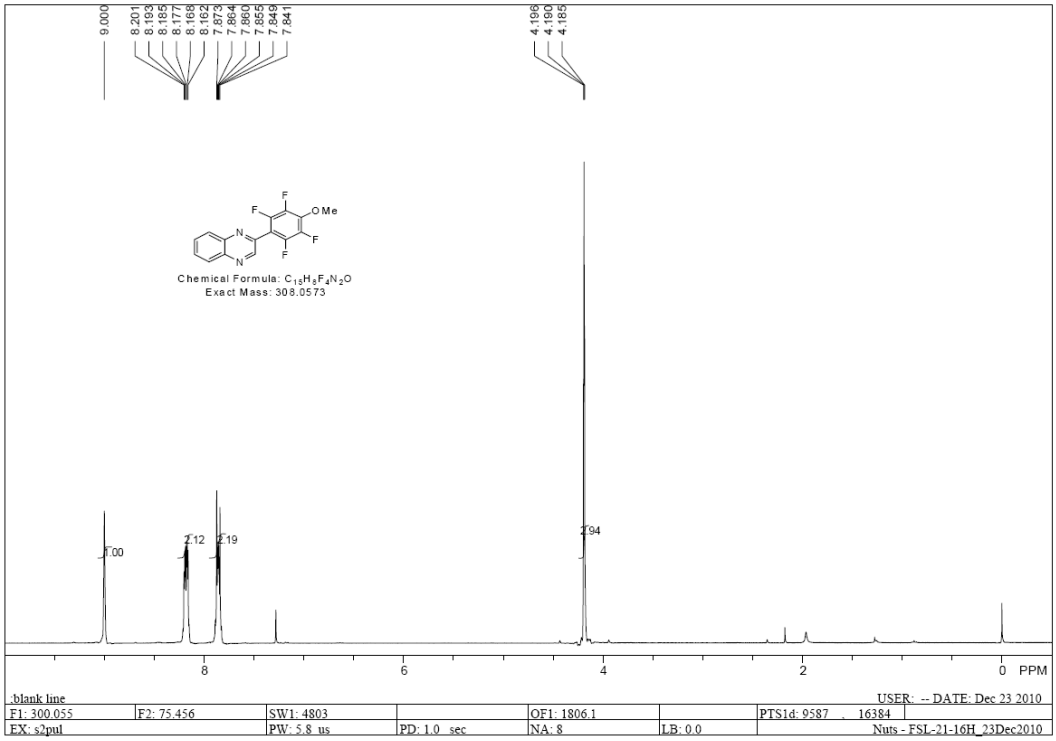
6-Methyl-2-(2,3,4,6-tetrafluorophenyl)quinoxaline (3p)

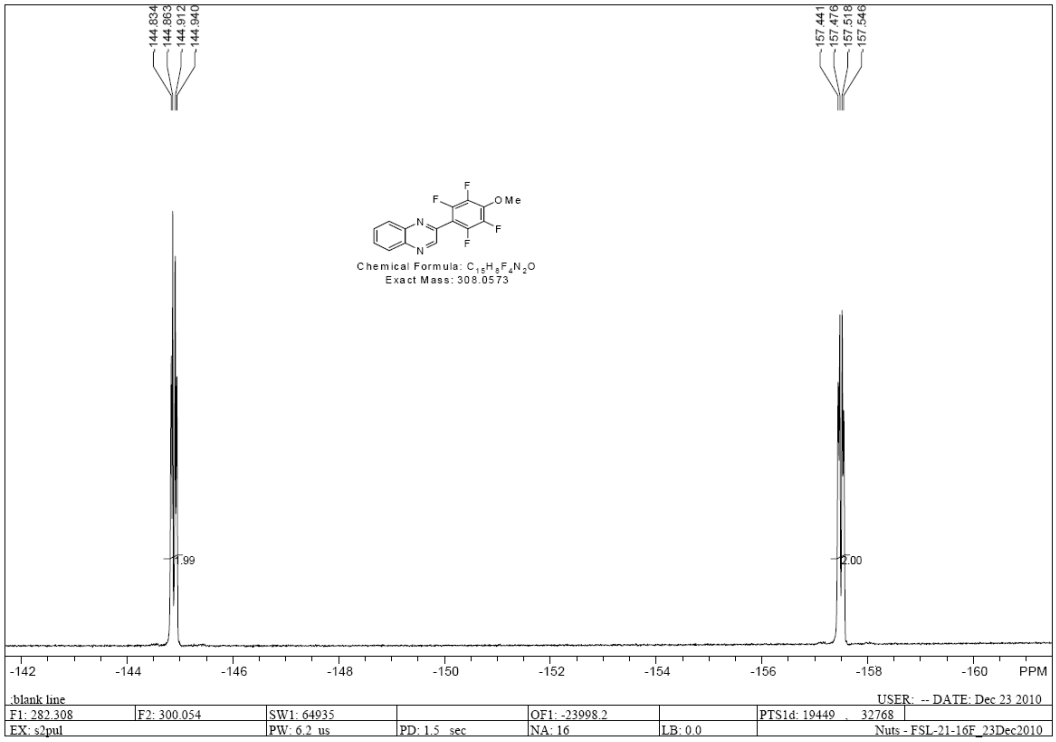


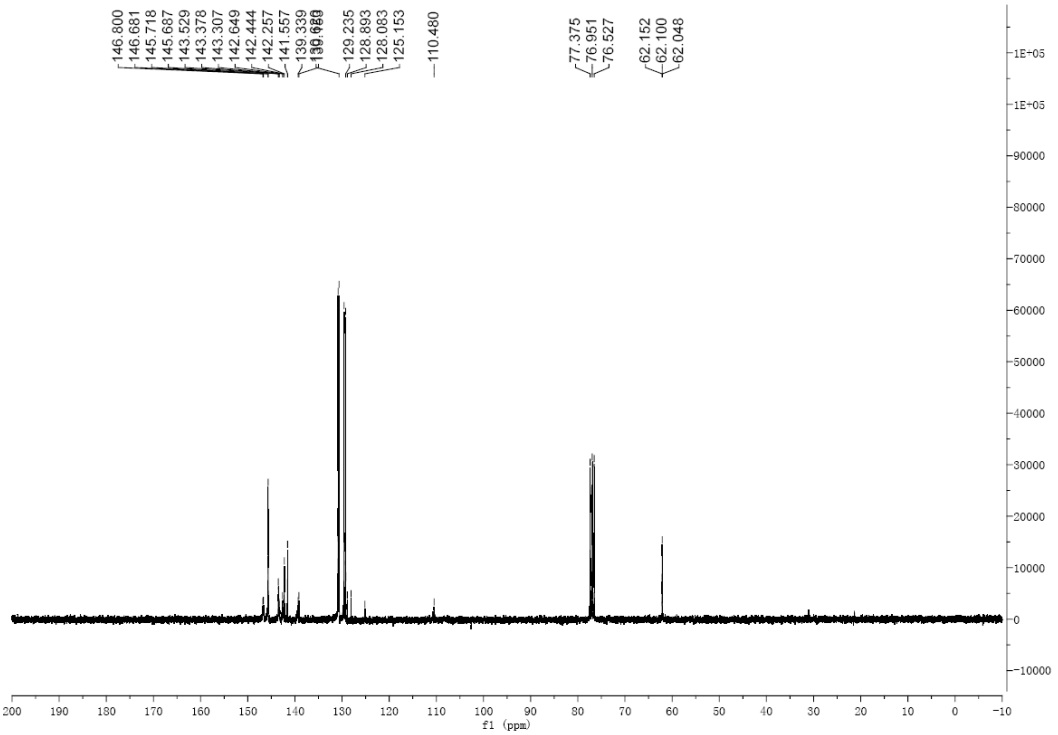




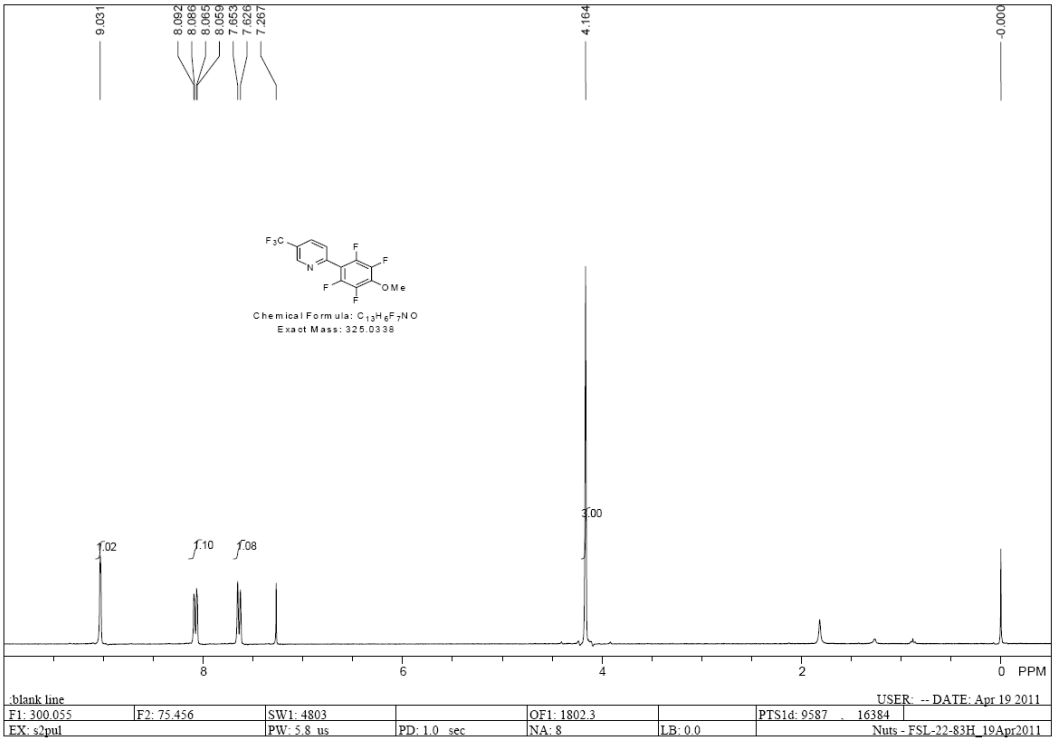
2-(2,3,5,6-Tetrafluoro-4-methoxyphenyl)quinoxaline (3q)

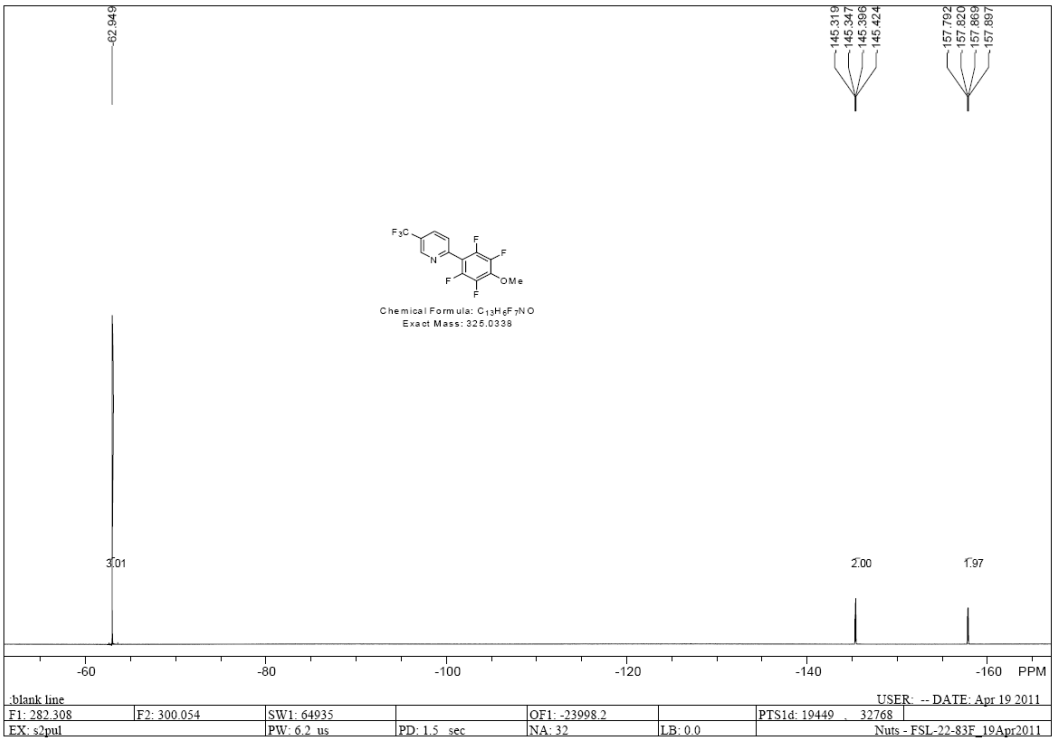


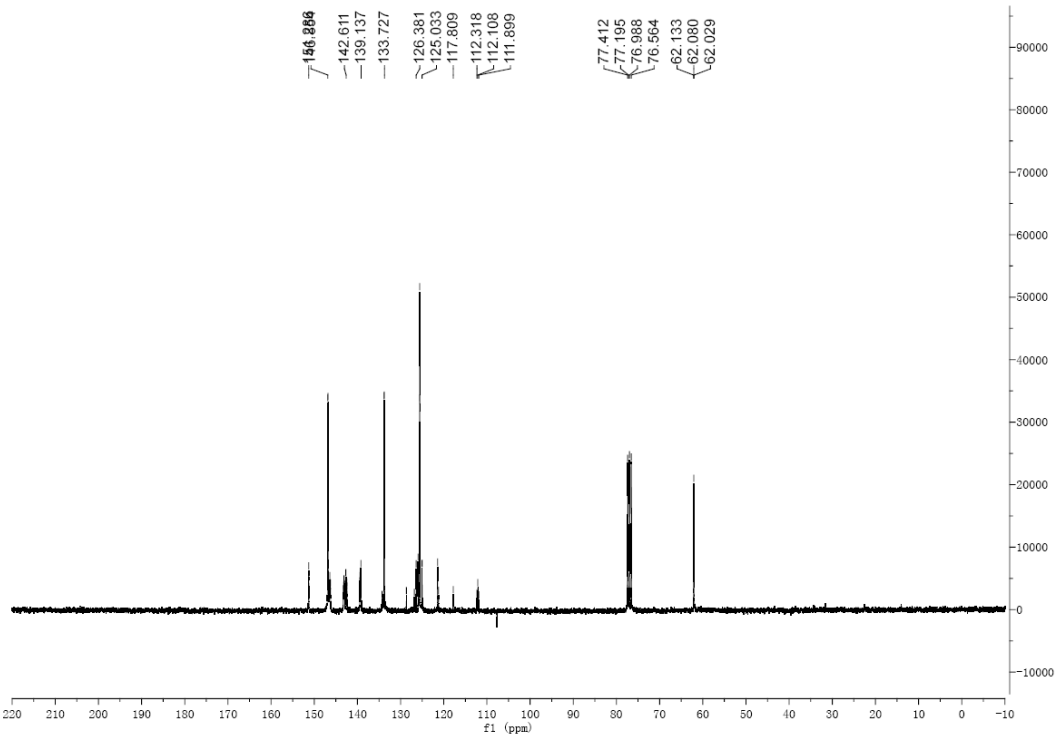

144.834
144.863
144.912
144.940
157.441
157.476
157.518
157.546
F
F
OMe
N
N
F
F
Chemical Formula: C15H8F4N2O
Exact Mass: 308.0573
1.99
2.00
-142
-144
-146
-148
-150
-152
-154
-156
-158
-160
PPM
:blank line
USER: -- DATE: Dec 23 2010
F1: 282.308
F2: 300.054
SW1: 64935
OF1: -23998.2
PTS1d: 19449 32768
EX: s2pul
PW: 6.2 us
PD: 1.5 sec
NA: 16
LB: 0.0
Nuts - FSL-21-16F_23Dec2010


146.800
146.681
145.718
145.687
143.529
143.378
143.307
142.649
142.444
142.257
141.557
139.339
129.235
128.893
128.083
125.153
110.480
77.375
76.951
76.527
62.152
62.100
62.048
1E+05
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

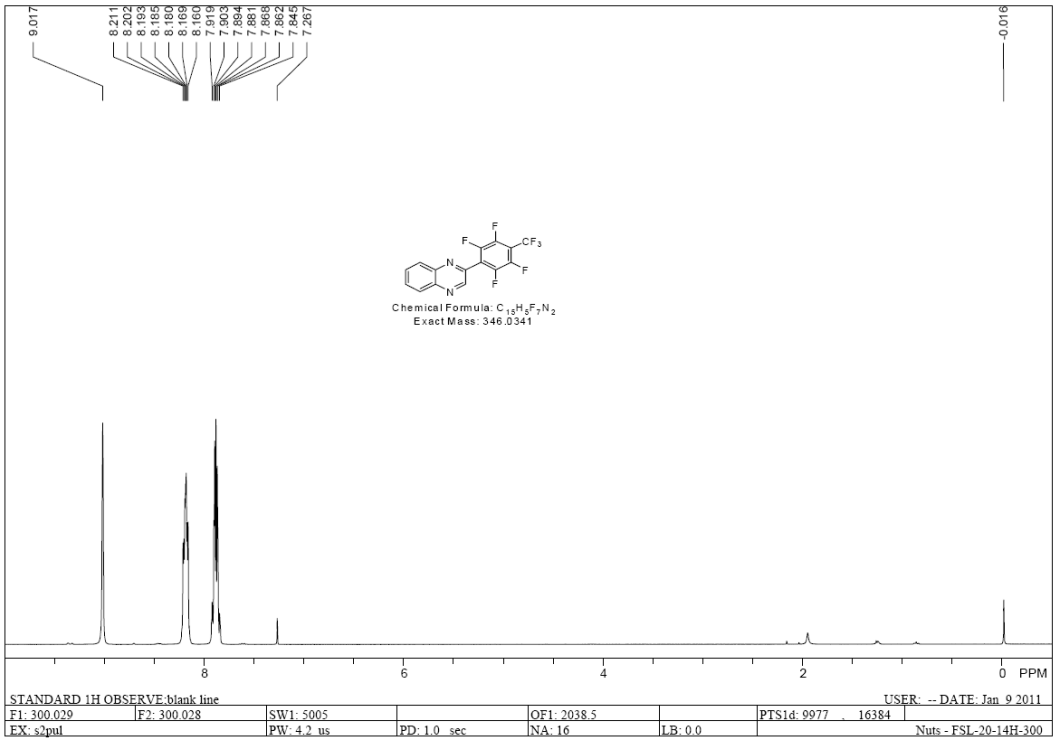
2-(2,3,5,6-Tetrafluoro-4-methoxyphenyl)-5-(trifluoromethyl)pyridine (3r)

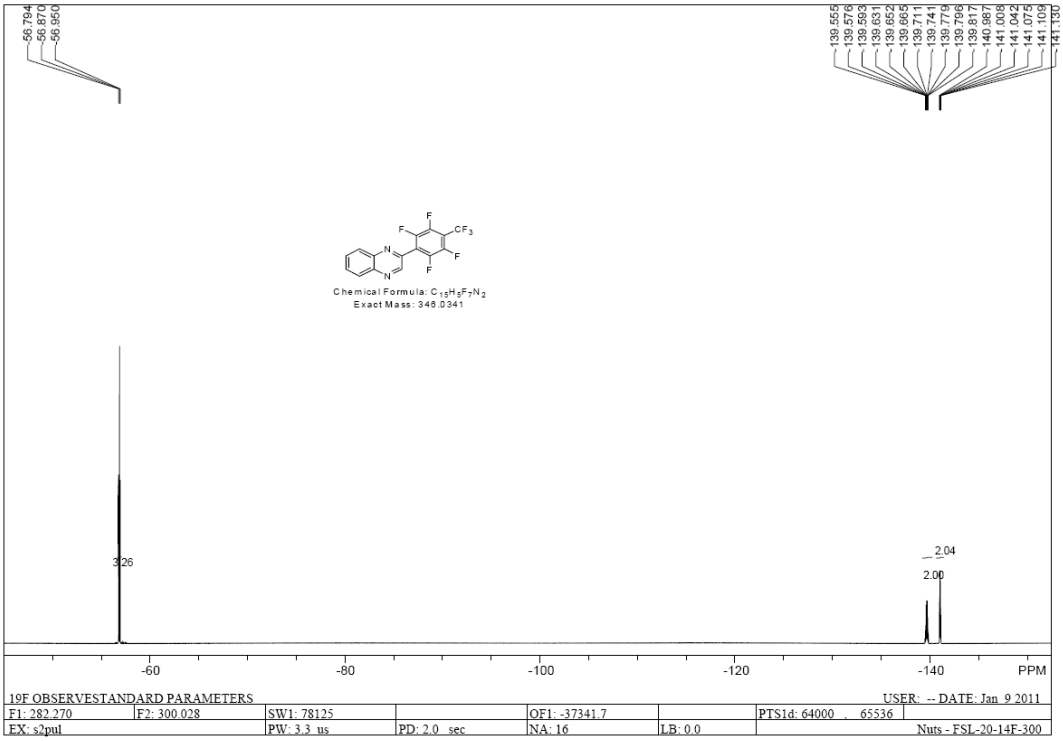


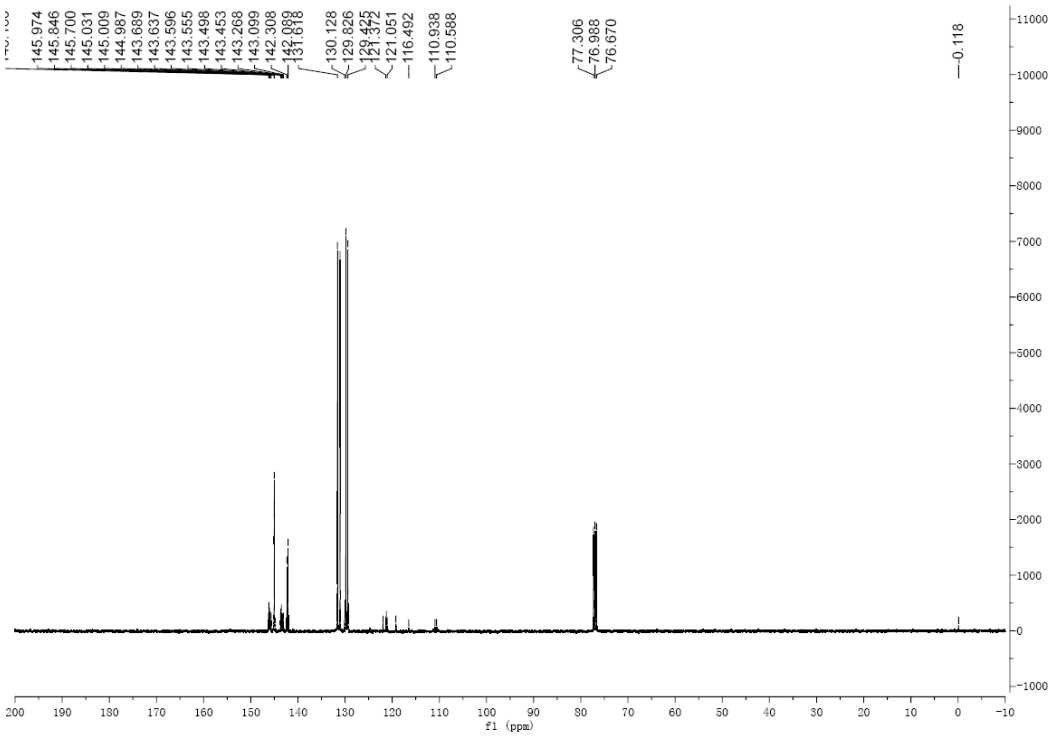




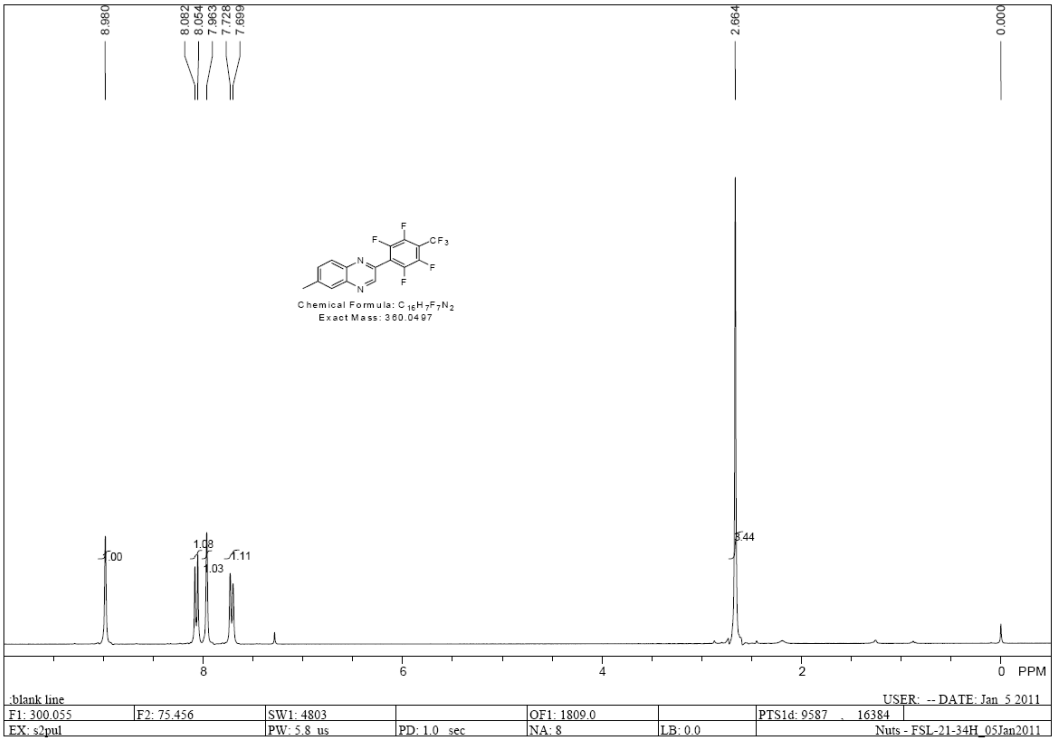
2-(2,3,5,6-Tetrafluoro-4-(trifluoromethyl)phenyl)quinoxaline (3s)

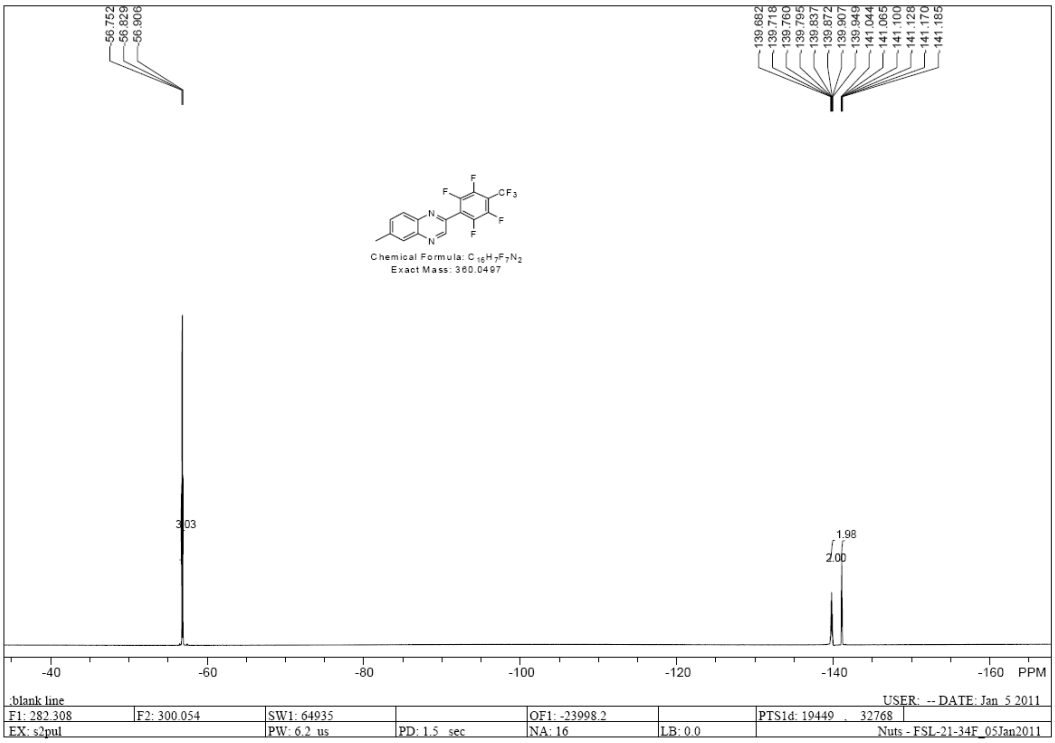


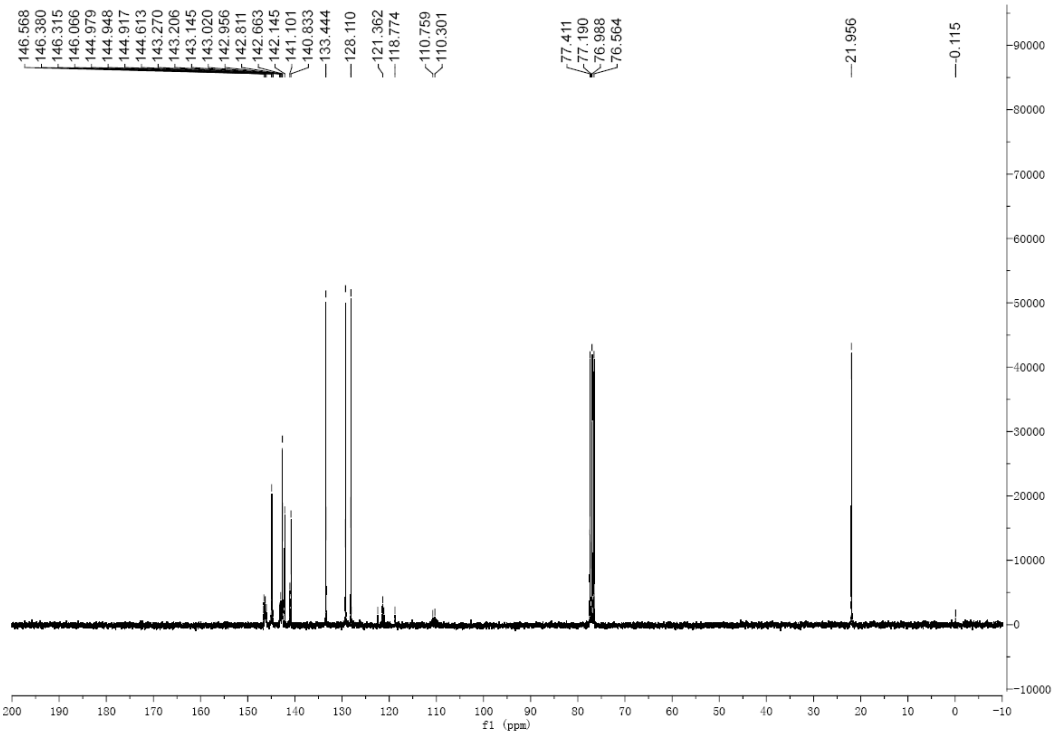

-56.794
-56.870
-56.950
139.555
139.576
139.593
139.631
139.652
139.665
139.711
139.741
139.779
139.796
139.817
140.987
141.008
141.042
141.075
141.109
141.130
Chemical Formula: C15H5F7N2
Exact Mass: 346.0341
3.26
2.04
2.00
-60
-80
-100
-120
-140
PPM
19F OBSERVESTANDARD PARAMETERS
USER: -- DATE: Jan 9 2011
F1: 282.270
F2: 300.028
SW1: 78125
OF1: -37341.7
PTS1d: 64000 , 65536
EX: s2pul
PW: 3.3 us
PD: 2.0 sec
NA: 16
LB: 0.0
Nuts - FSL-20-14F-300


145.974
145.846
145.700
145.031
145.009
144.987
143.689
143.637
143.596
143.555
143.498
143.453
143.268
143.099
142.308
142.089
131.618
130.128
129.826
129.425
121.332
121.051
116.492
110.938
110.588
77.306
76.988
76.670
-0.118
f1 (ppm)

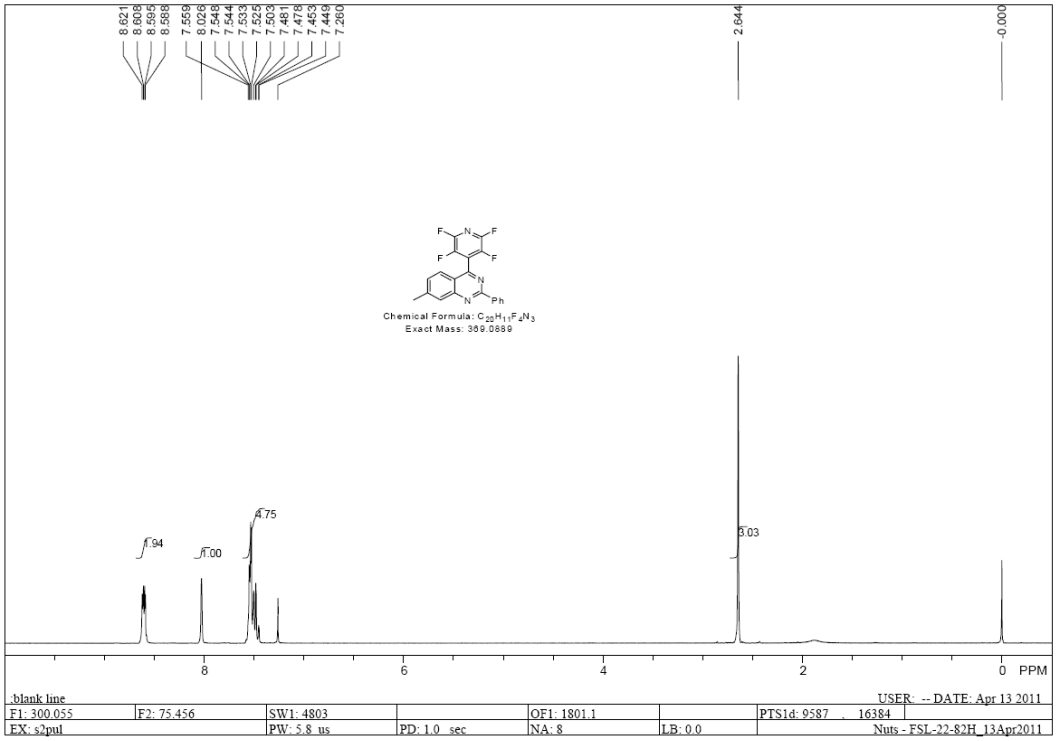
6-Methyl-2-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)quinoxaline (3t)

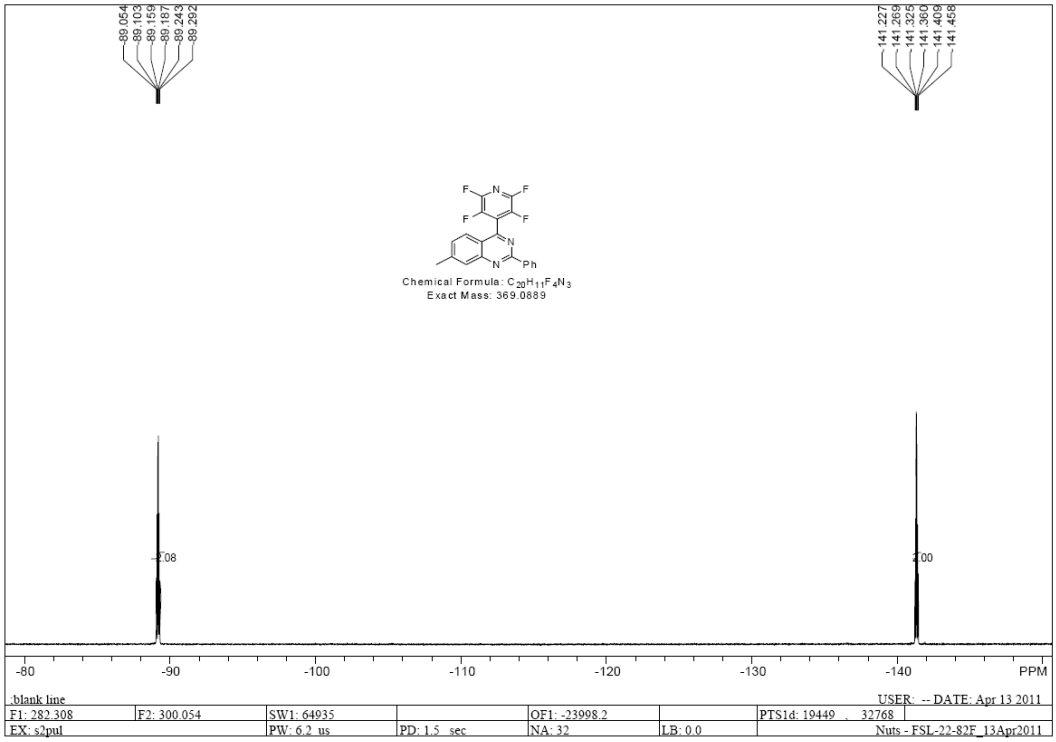


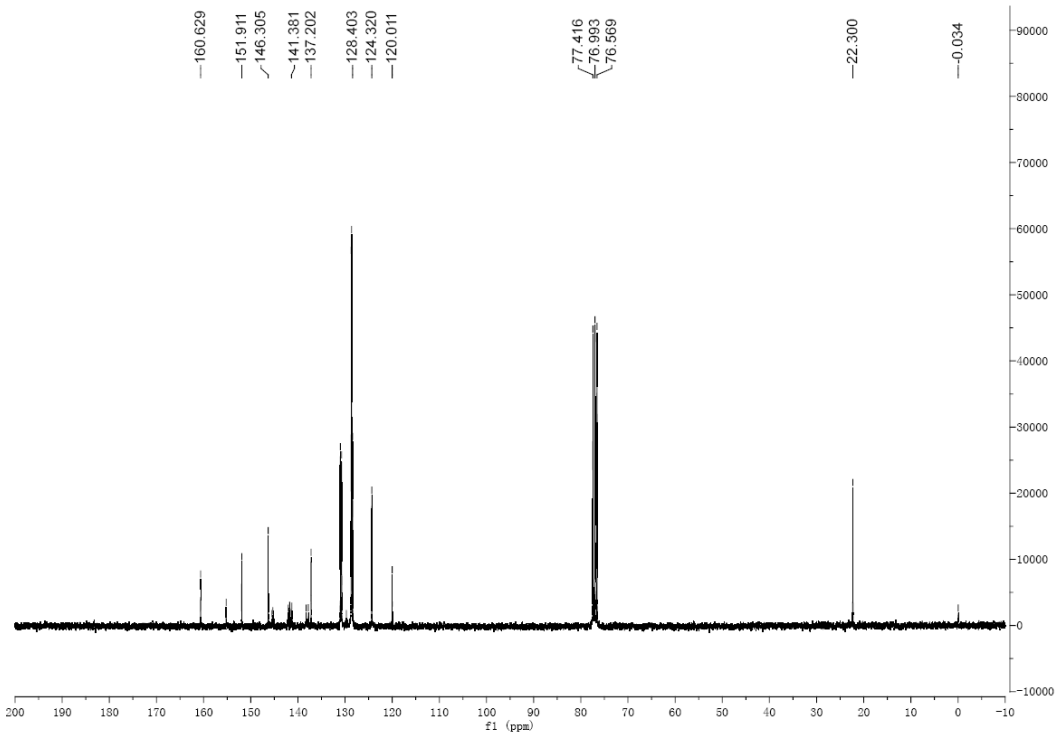




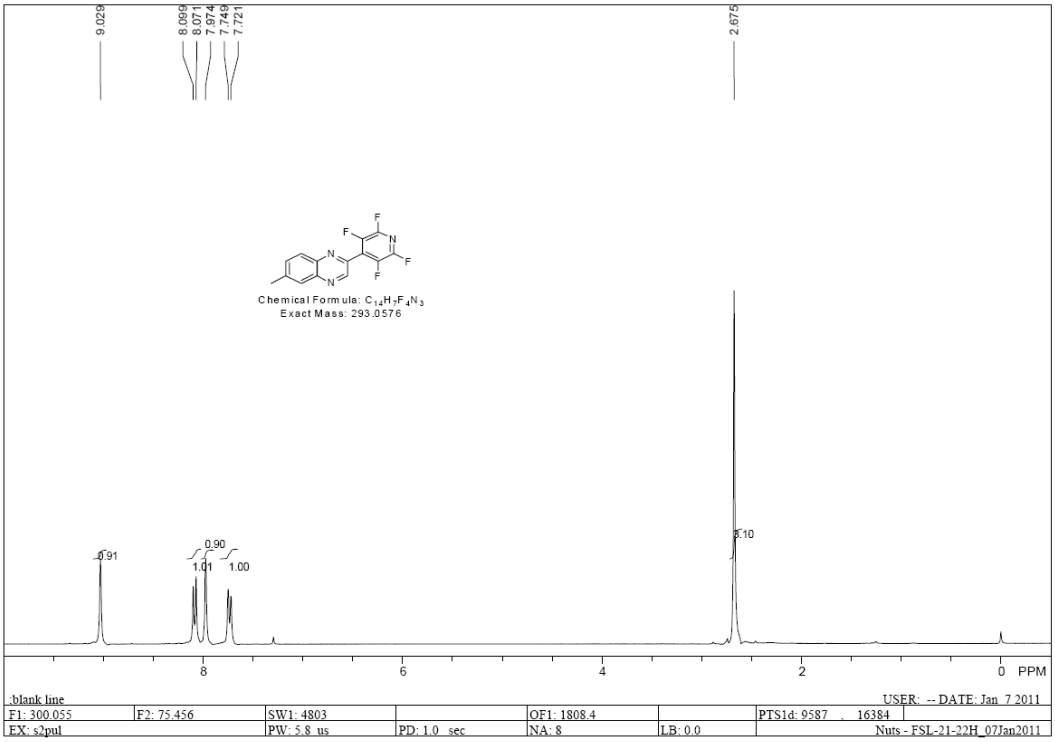
7-Methyl-4-(perfluoropyridin-4-yl)-2-phenylquinazoline (3u)

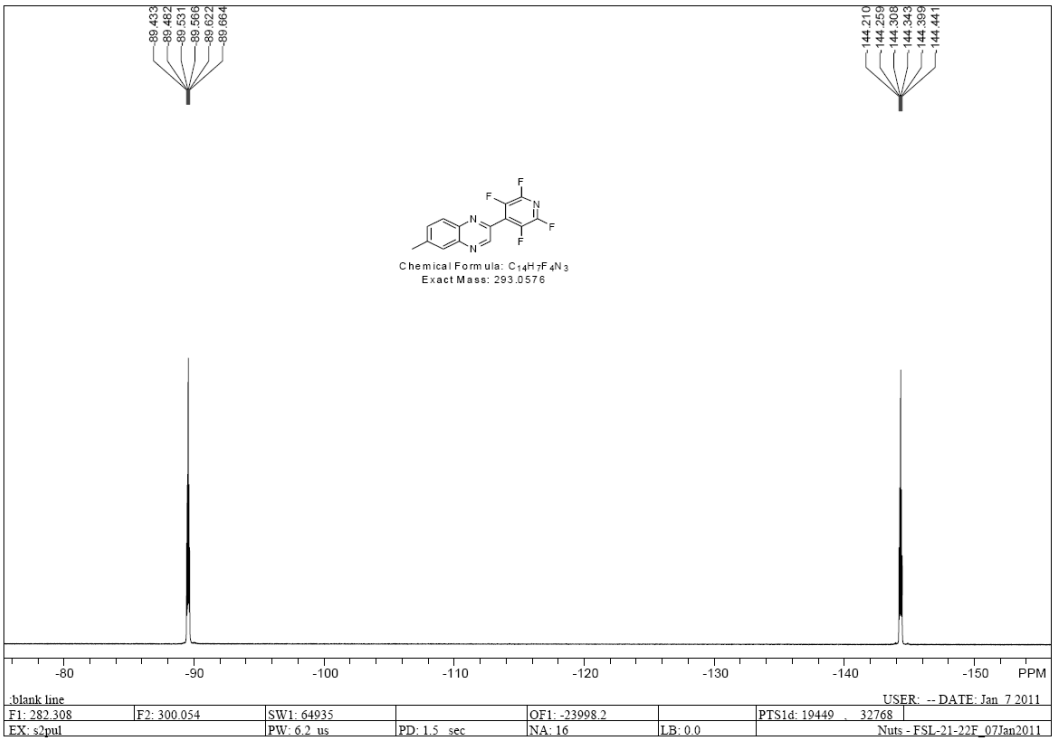


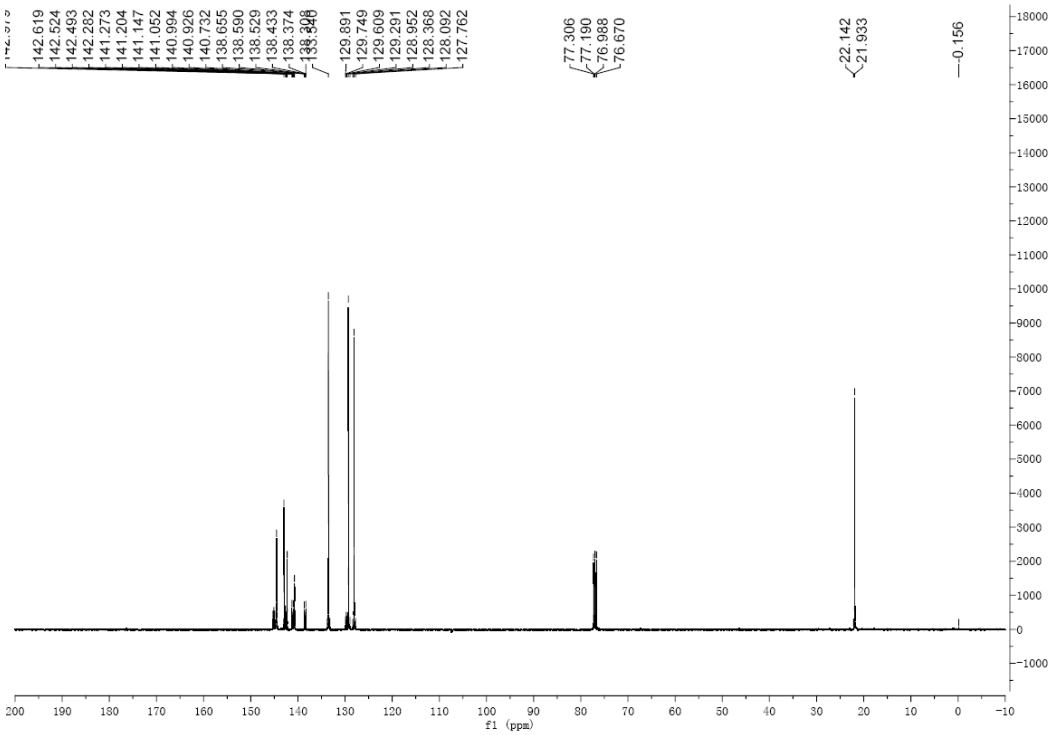

-89.054
-89.103
-89.159
-89.187
-89.243
-89.292
-141.227
-141.269
-141.325
-141.380
-141.409
-141.458
F
N
F
F
F
N
N
Ph
Chemical Formula: C20H11F4N3
Exact Mass: 369.0889
2.08
2.00
-80
-90
-100
-110
-120
-130
-140
PPM
:blank line
USER: -- DATE: Apr 13 2011
F1: 282.308
F2: 300.054
SW1: 64935
OF1: -23998.2
PTS1d: 19449 , 32768
EX: s2pul
PW: 6.2 us
PD: 1.5 sec
NA: 32
LB: 0.0
Nuts - FSL-22-82F_13Apr2011


160.629
151.911
146.305
141.381
137.202
128.403
124.320
120.011
77.416
76.993
76.569
22.300
-0.034
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

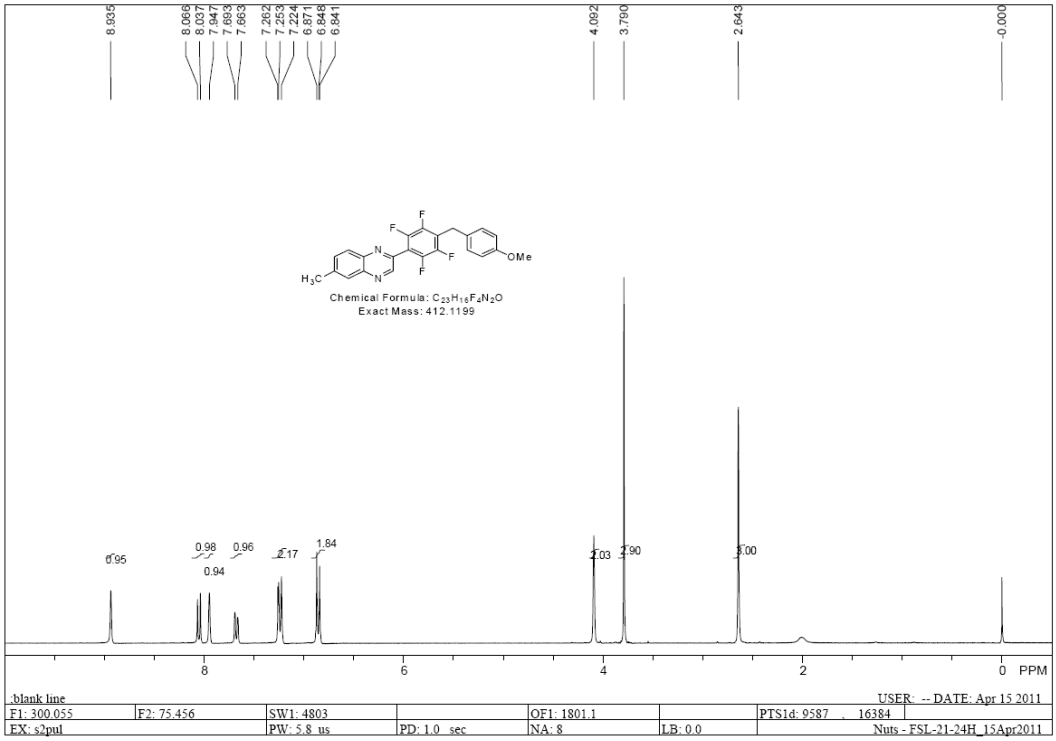
6-Methyl-2-(perfluoropyridin-4-yl)quinoxaline (3v)

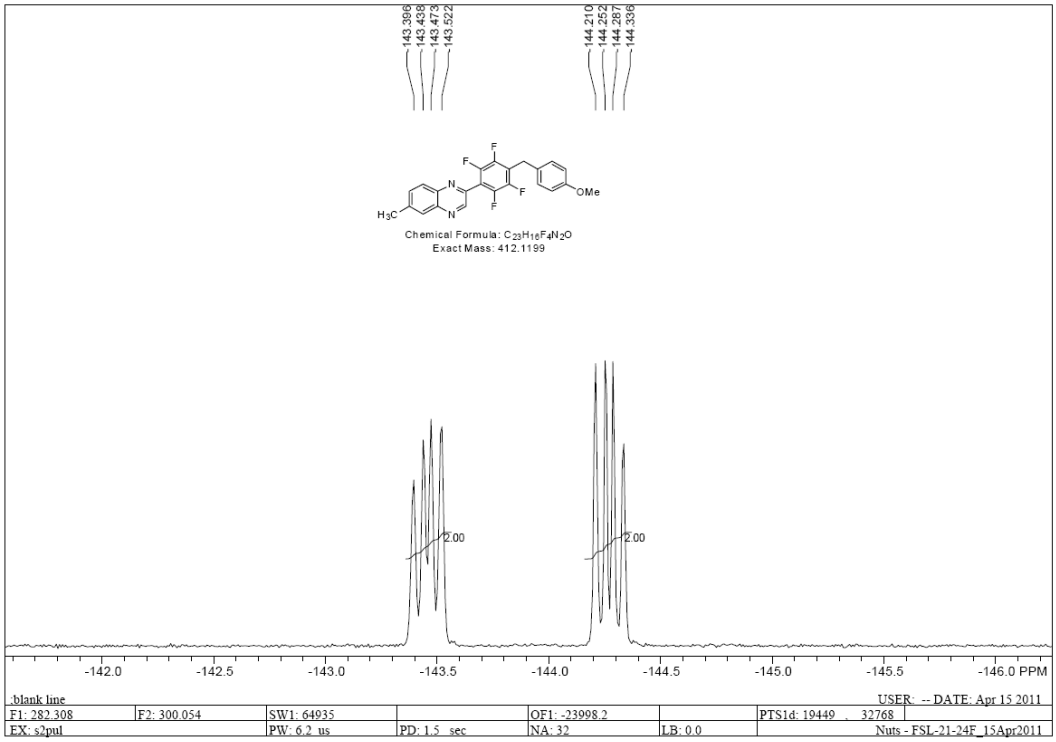


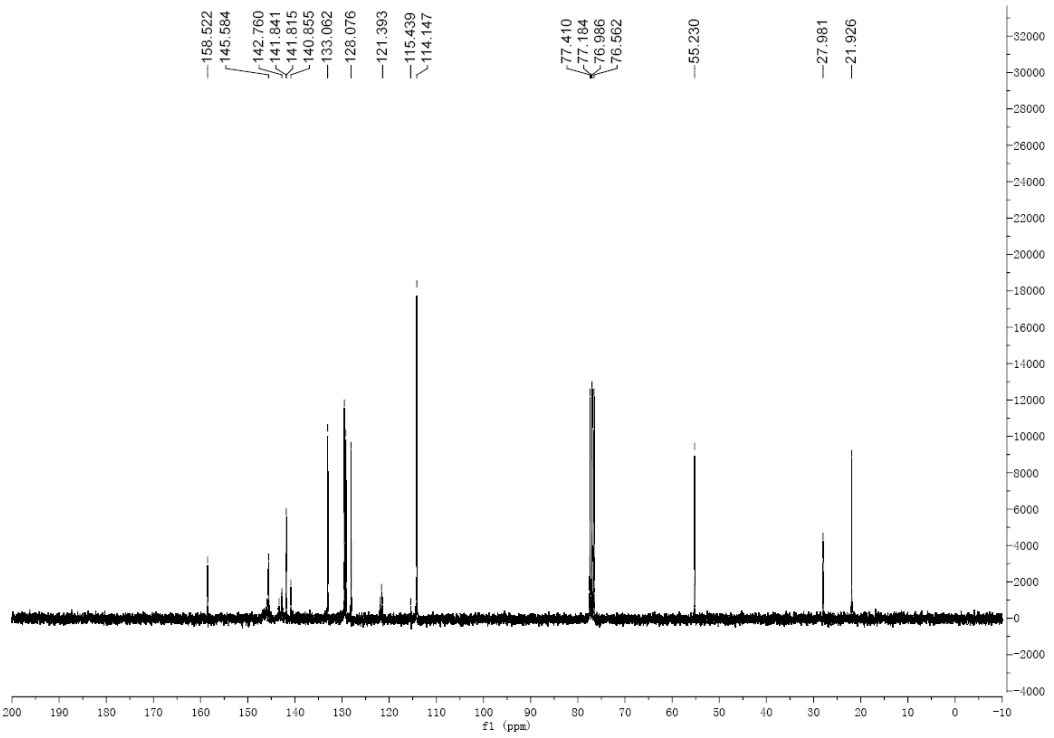




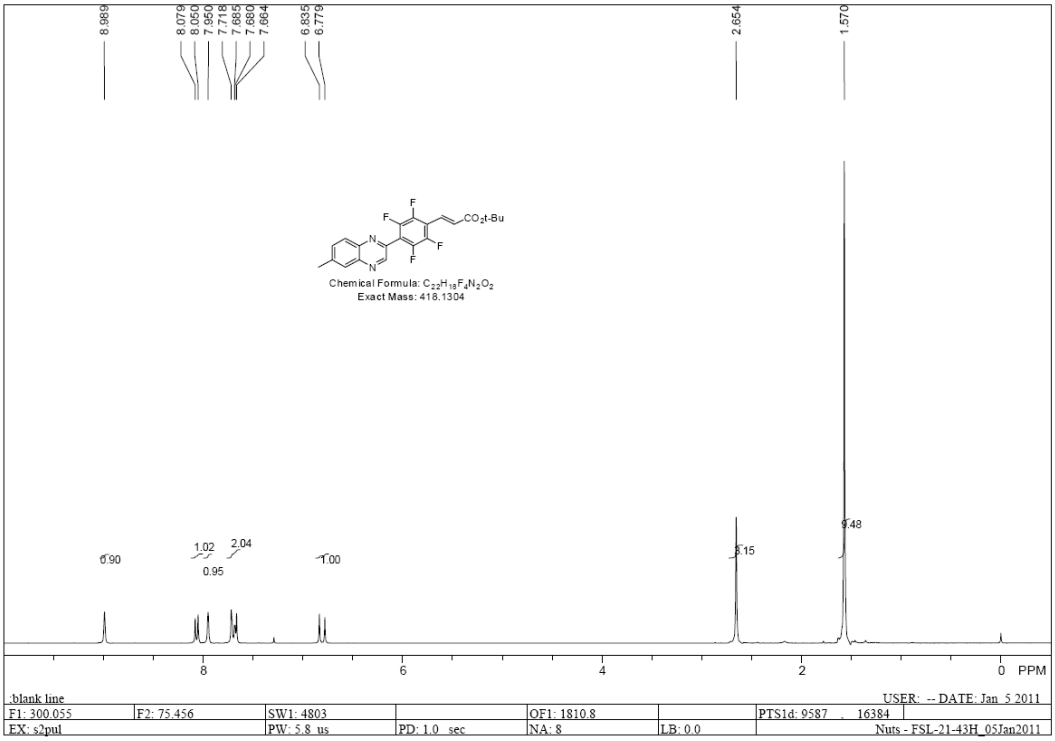
6-Methyl-2-(2,3,5,6-tetrafluoro-4-(4-methoxybenzyl)phenyl)quinoxaline (3w)

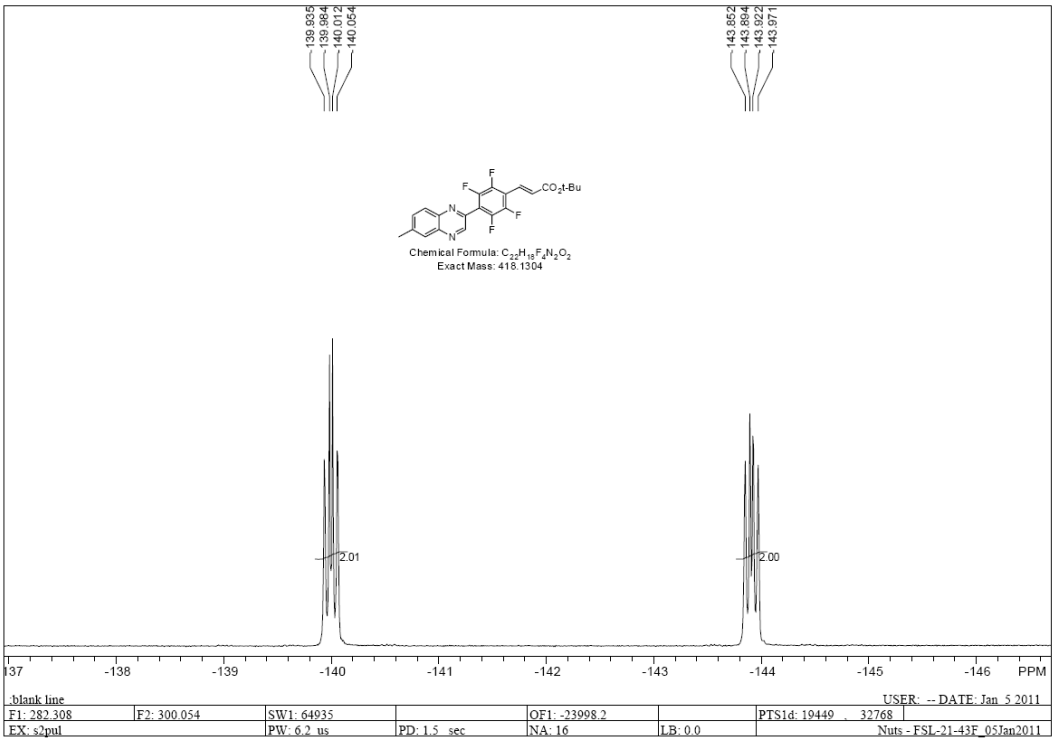


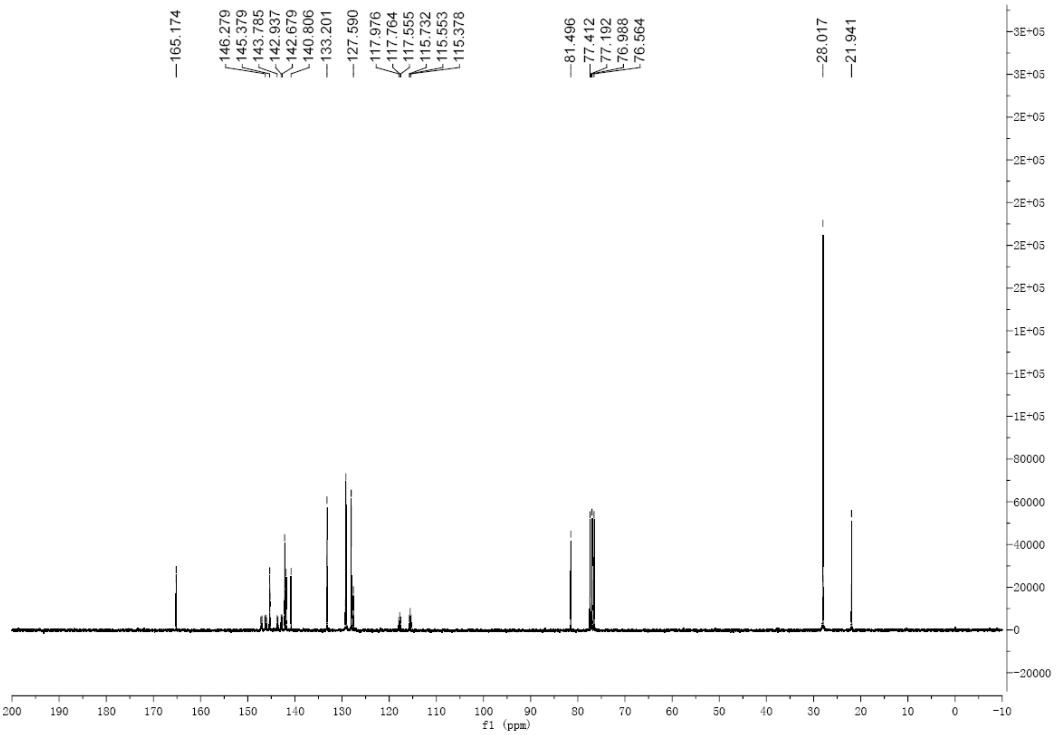

143.396
143.438
143.473
143.522
144.210
144.252
144.287
144.336
F
F
F
F
N
N
OMe
H3C
Chemical Formula: C23H16F4N2O
Exact Mass: 412.1199
2.00
2.00
-142.0
-142.5
-143.0
-143.5
-144.0
-144.5
-145.0
-145.5
-146.0 PPM
;blank line
USER: -- DATE: Apr 15 2011
F1: 282.308
F2: 300.054
SW1: 64935
OF1: -23998.2
PTS1d: 19449 , 32768
EX: s2pul
PW: 6.2 us
PD: 1.5 sec
NA: 32
LB: 0.0
Nuts - FSL-21-24F_15Apr2011


158.522
145.584
142.760
141.841
141.815
140.855
133.062
128.076
121.393
115.439
114.147
77.410
77.184
76.986
76.562
55.230
27.981
21.926
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
-4000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

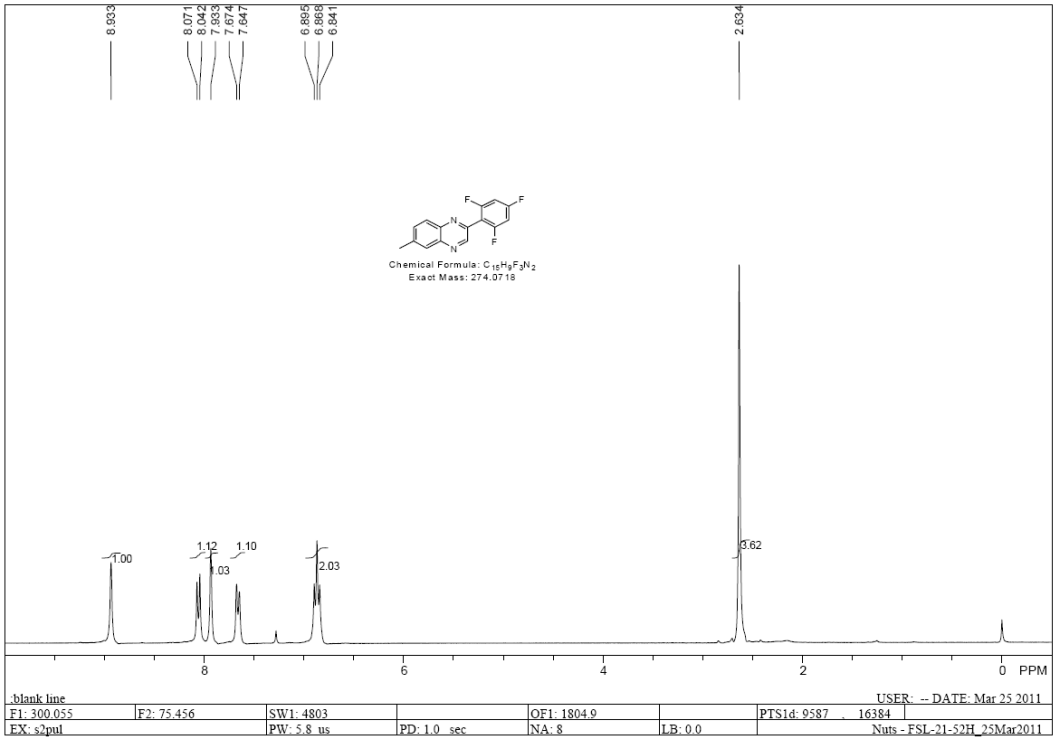
(*E*)-Tert-butyl 3-(2,3,5,6-tetrafluoro-4-(6-methylquinoxalin-2-yl)phenyl)acrylate (3x)

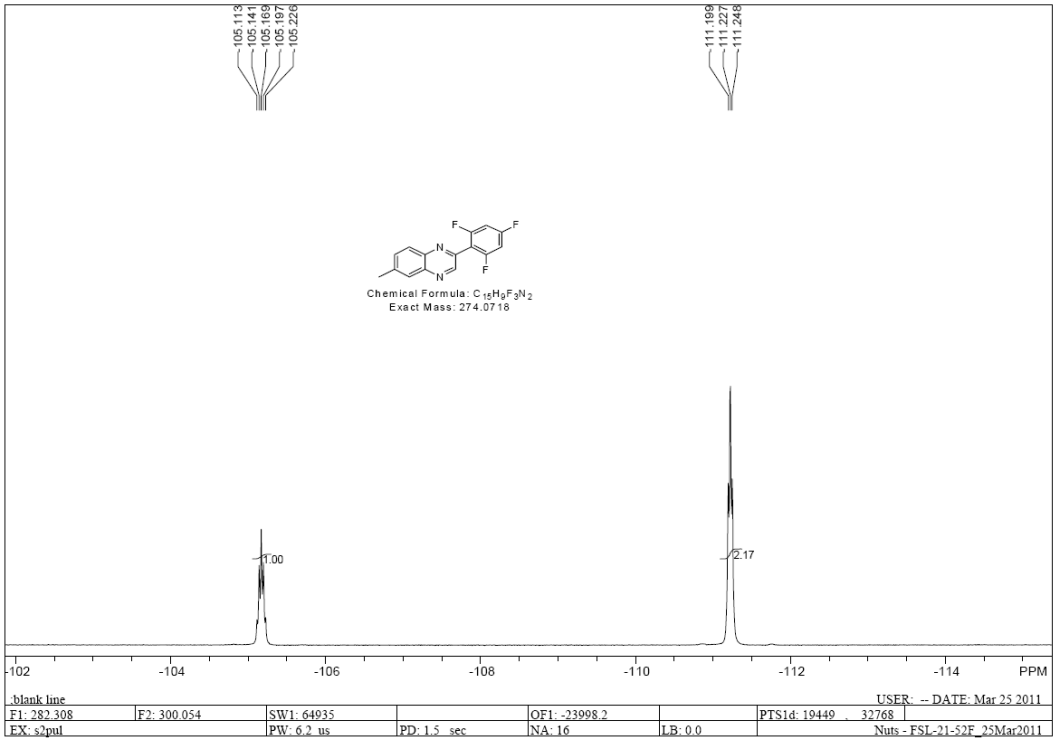


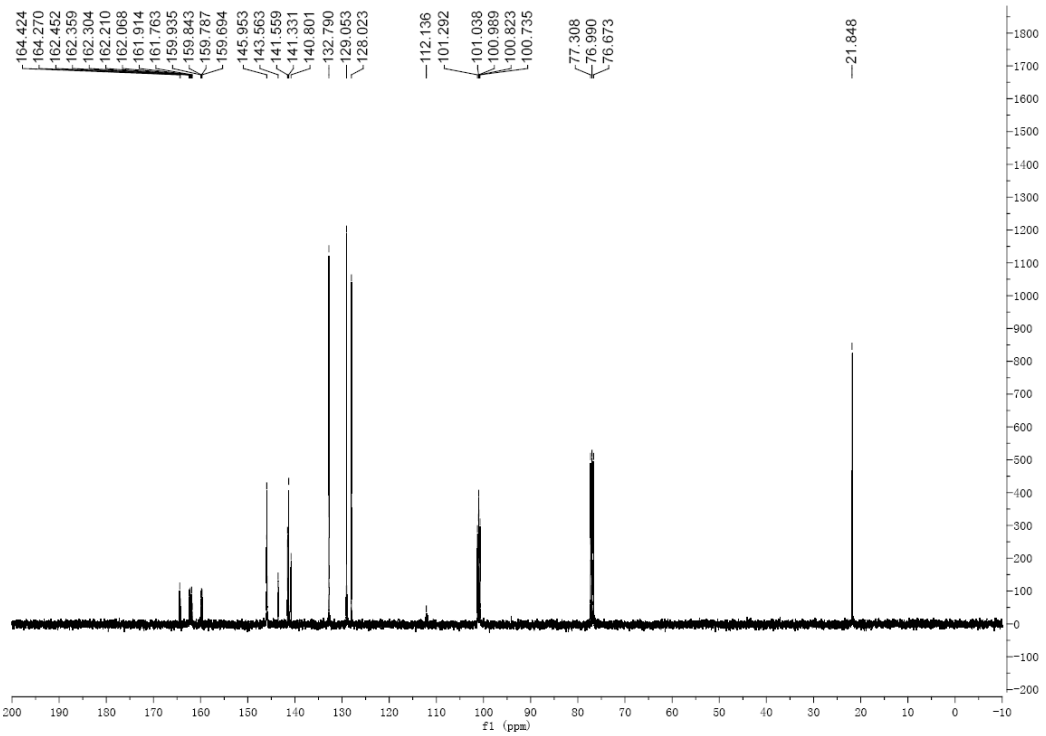




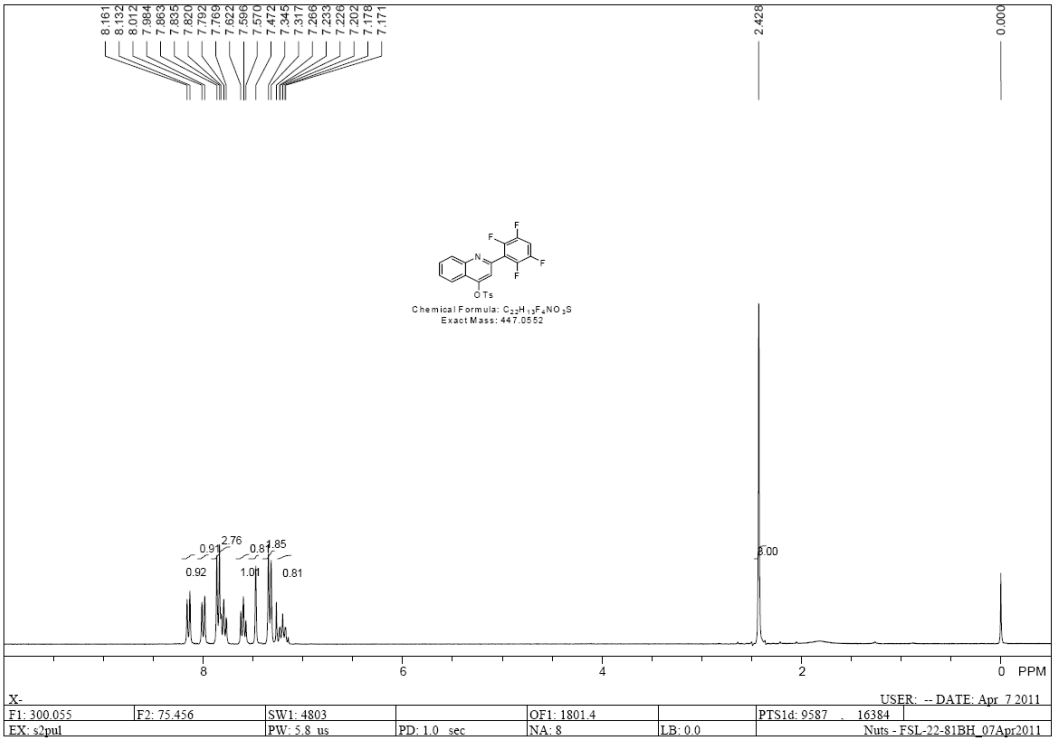
6-Methyl-2-(2,4,6-trifluorophenyl)quinoxaline (3y)

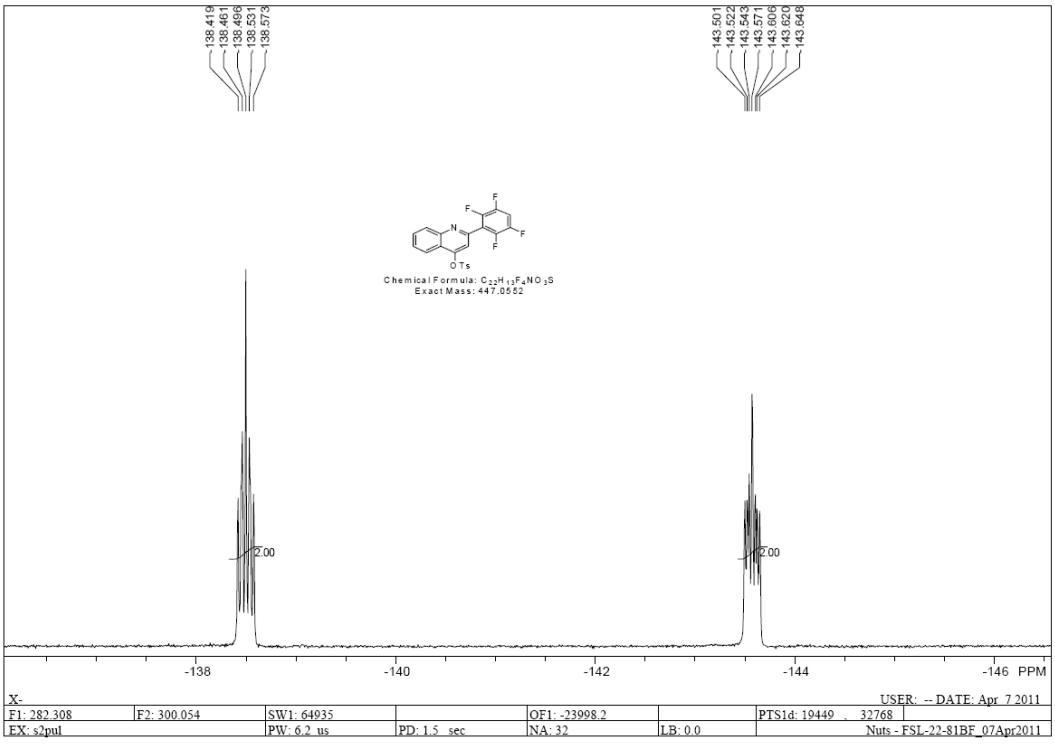


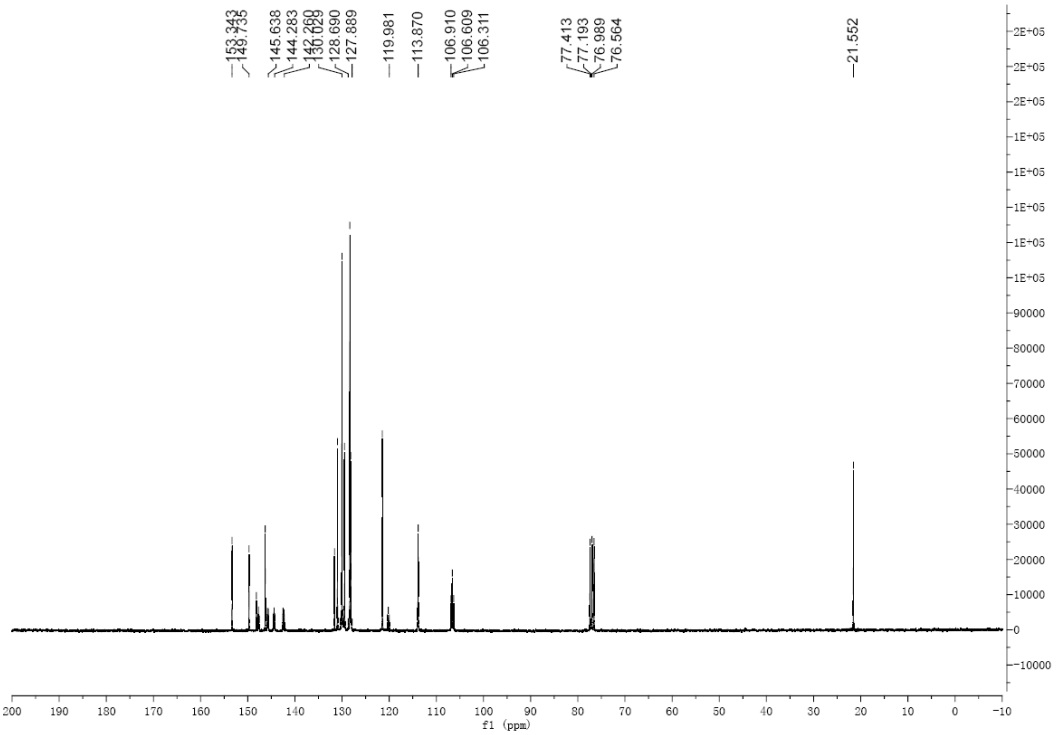

105.113
105.141
105.169
105.197
105.226
111.199
111.227
111.248
Chemical Formula: C15H9F3N2
Exact Mass: 274.0718
1.00
2.17
-102
-104
-106
-108
-110
-112
-114
PPM
:blank line
USER: -- DATE: Mar 25 2011
F1: 282.308
F2: 300.054
SW1: 64935
OF1: -23998.2
PTS1d: 19449 , 32768
EX: s2pul
PW: 6.2 us
PD: 1.5 sec
NA: 16
LB: 0.0
Nuts - FSL-21-52F_25Mar2011


164.424
164.270
162.452
162.359
162.304
162.210
162.068
161.914
161.763
159.935
159.843
159.787
159.694
145.953
143.563
141.559
141.331
140.801
132.790
129.053
128.023
112.136
101.292
101.038
100.989
100.823
100.735
77.308
76.990
76.673
21.848
f1 (ppm)

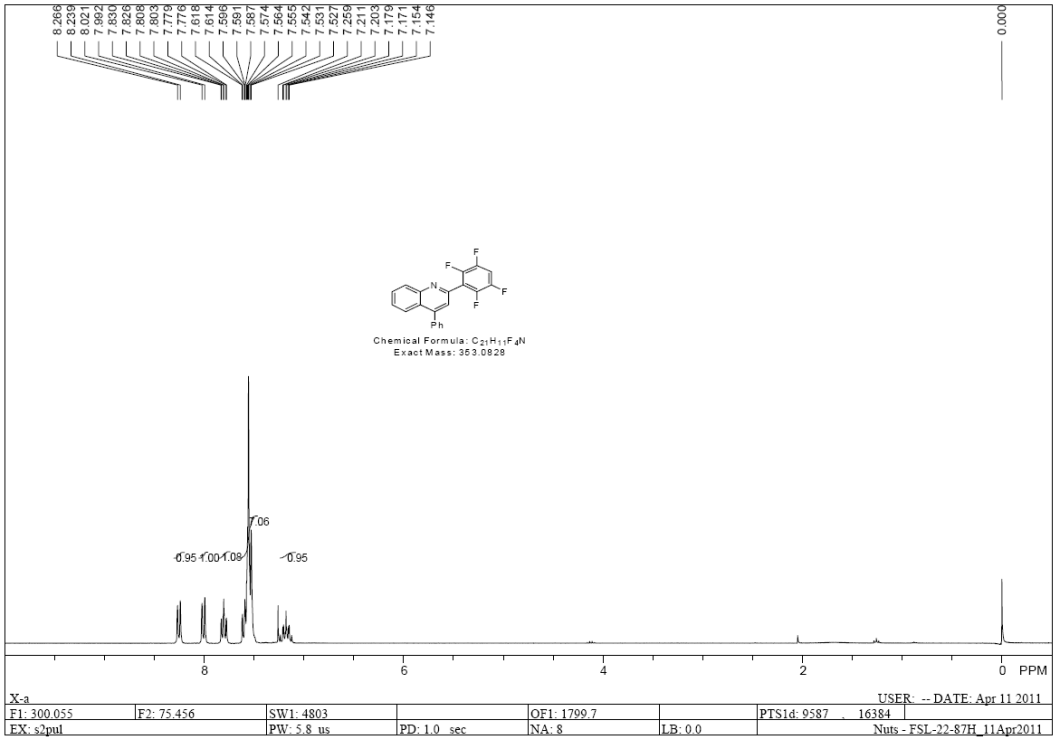
2-(2,3,5,6-Tetrafluorophenyl)quinolin-4-yl-4-methylbenzenesulfonate (5)

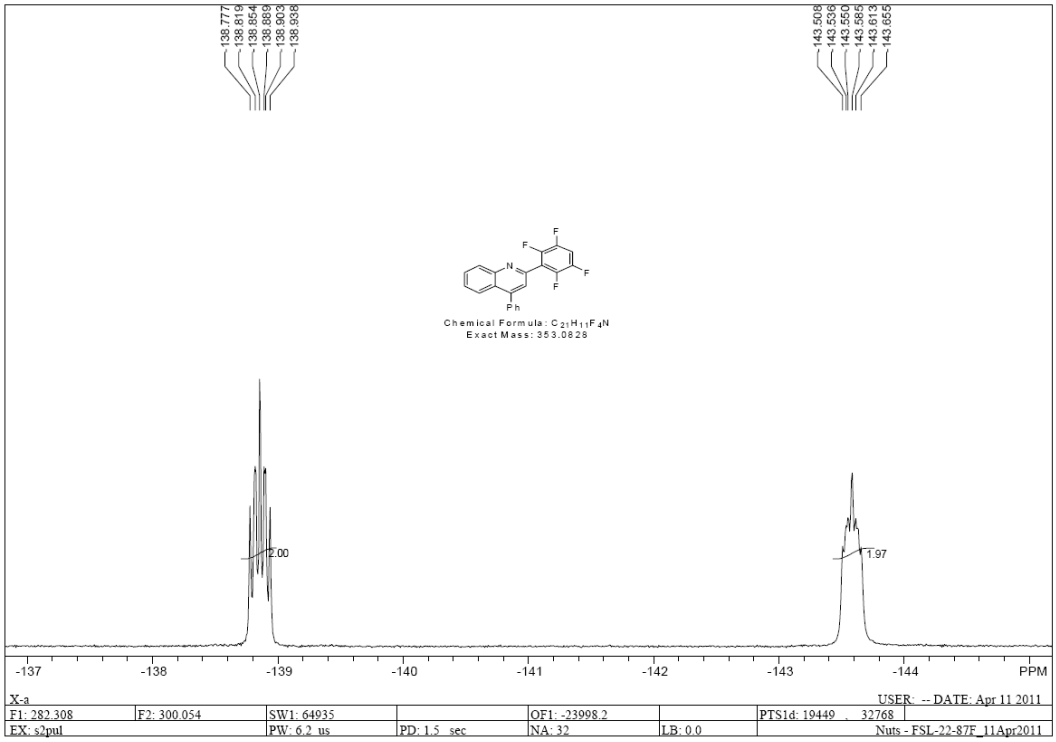


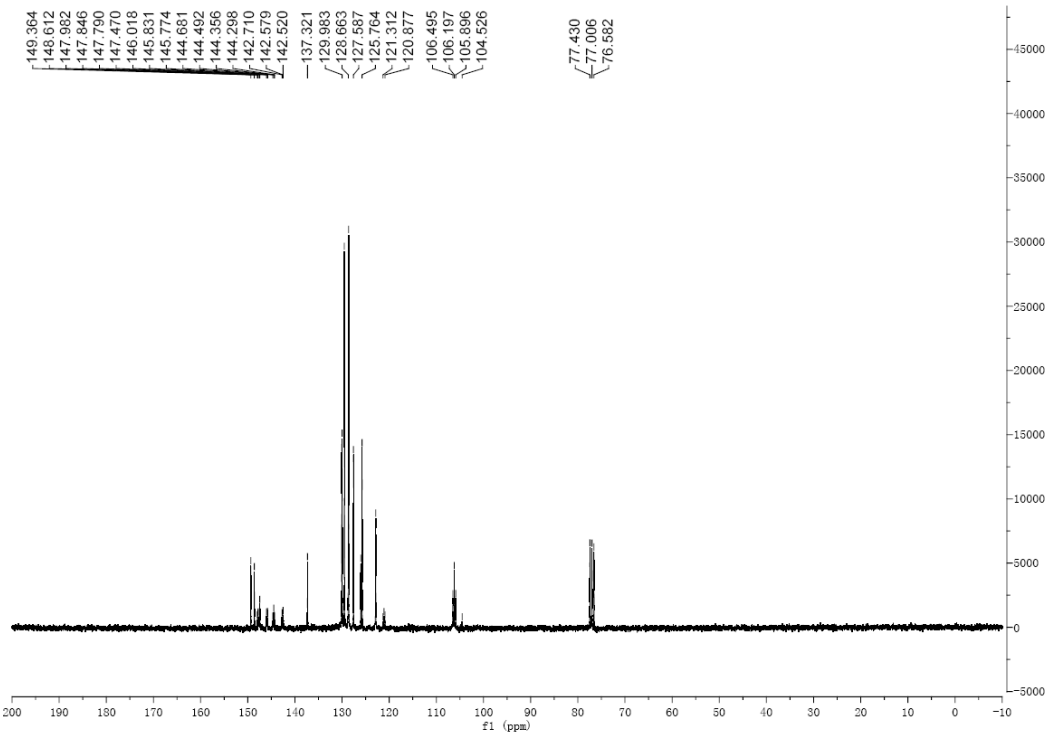




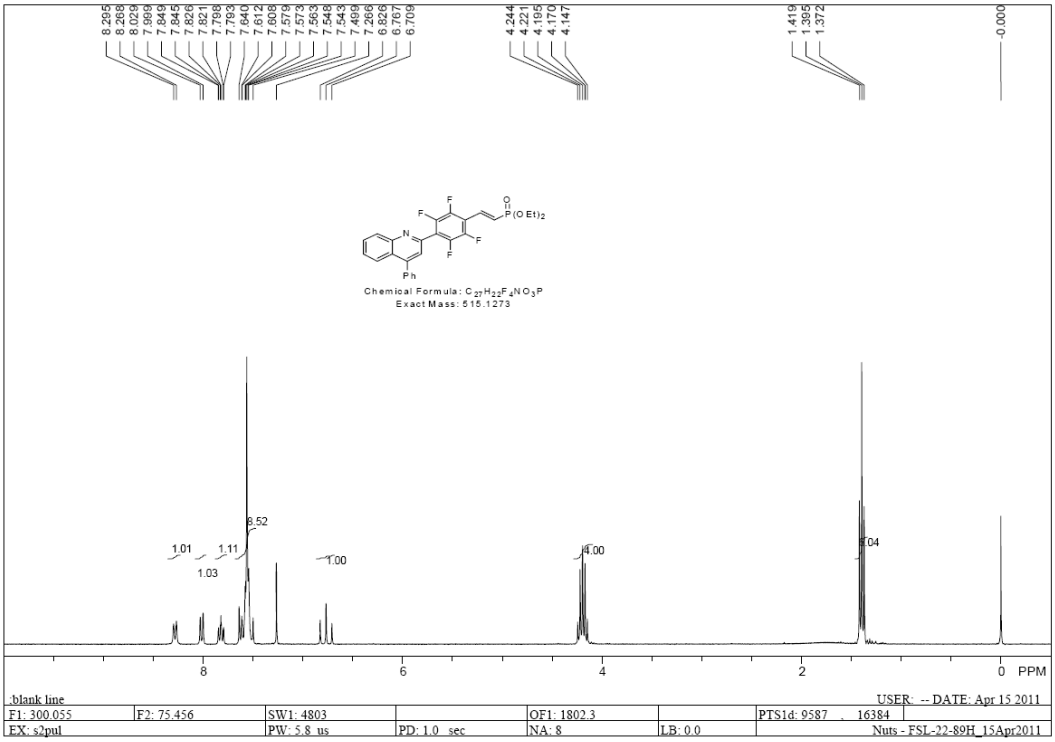
4-Phenyl-2-(2,3,5,6-tetrafluorophenyl)quinoline (6)

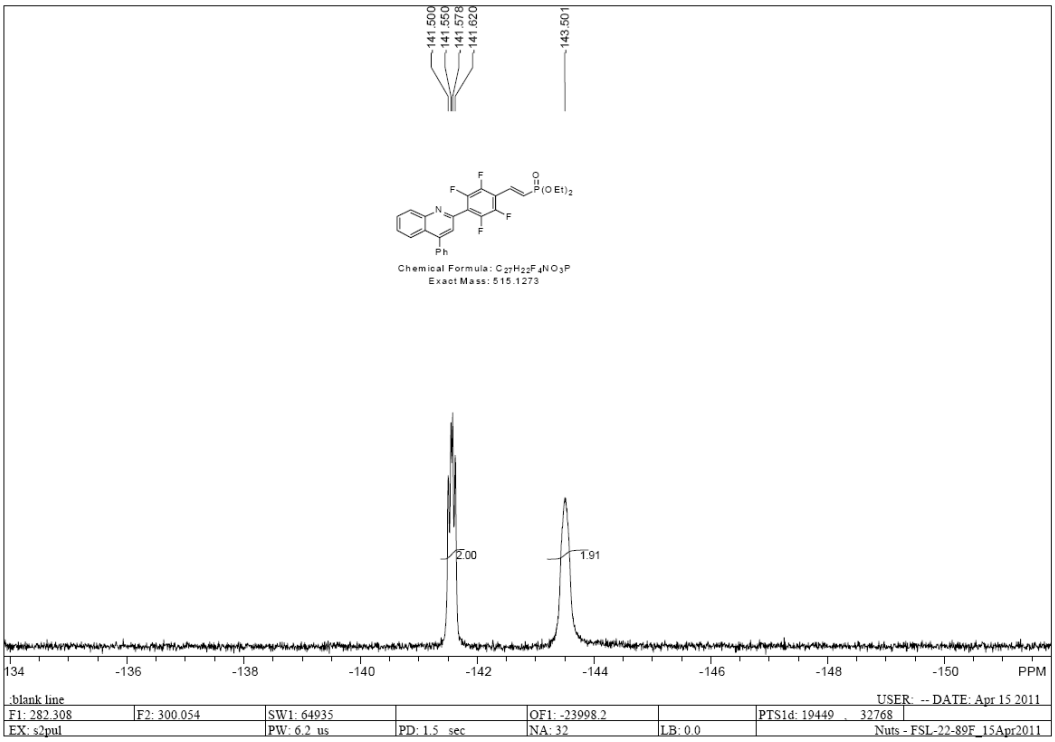


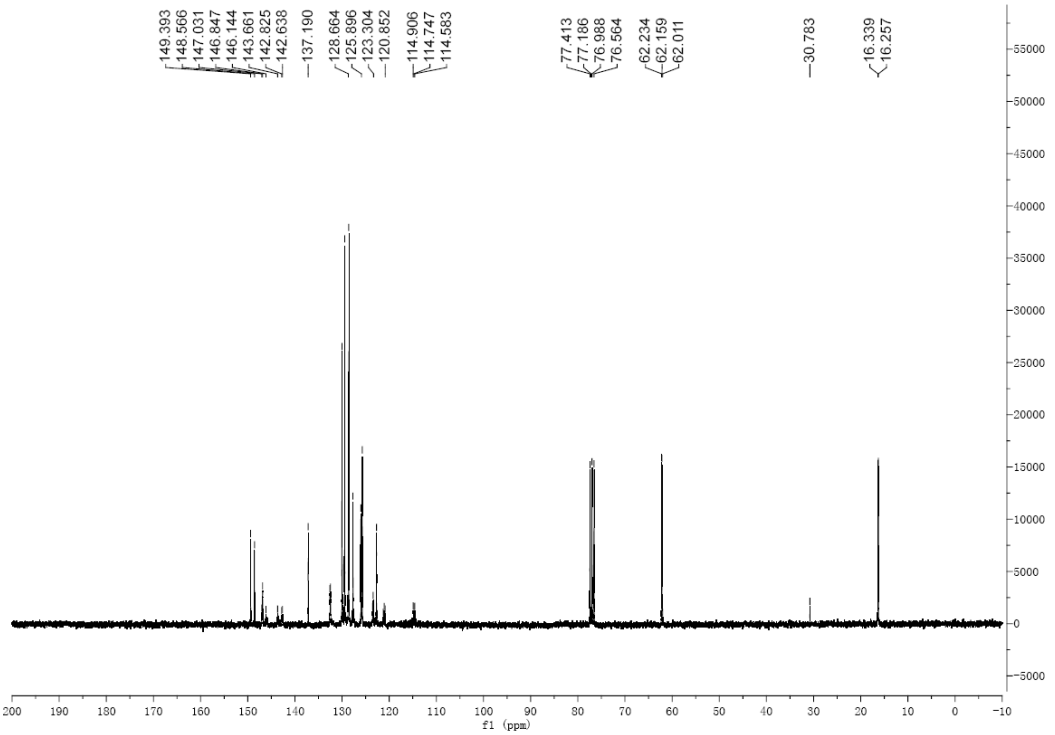

-138.777
-138.819
-138.854
-138.889
-138.903
-138.938
-143.508
-143.536
-143.550
-143.585
-143.613
-143.655
F
F
N
F
F
Ph
Chemical Formula: C21H11F4N
Exact Mass: 353.0828
2.00
1.97
-137
-138
-139
-140
-141
-142
-143
-144
PPM
X-a
USER: -- DATE: Apr 11 2011
F1: 282.308
F2: 300.054
SW1: 64935
OF1: -23998.2
PTS1d: 19449 , 32768
EX: s2pul
PW: 6.2 us
PD: 1.5 sec
NA: 32
LB: 0.0
Nuts - FSL-22-87F_11Apr2011

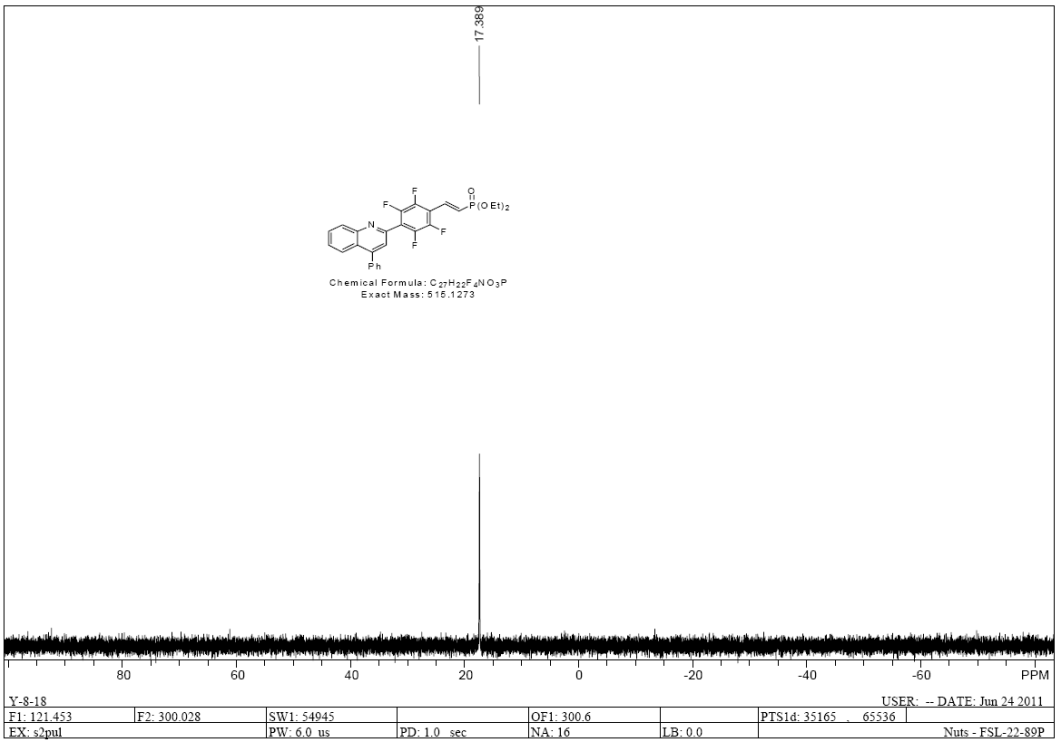

149.364
148.612
147.982
147.846
147.790
147.470
146.018
145.831
145.774
144.681
144.492
144.356
144.298
142.710
142.579
142.520
137.321
129.983
128.663
127.587
125.764
121.312
120.877
106.495
106.197
105.896
104.526
77.430
77.006
76.582
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

(*E*)-Diethyl 2,3,5,6-tetrafluoro-4-(4-phenylquinolin-2-yl)styrylphosphonate (7)

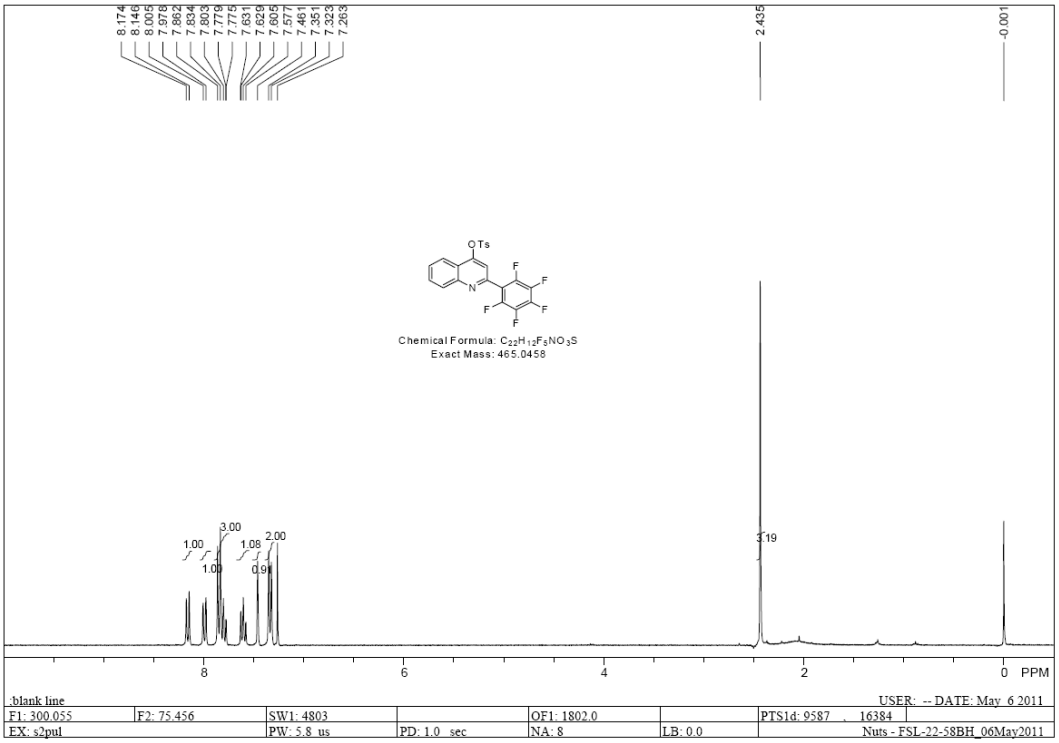


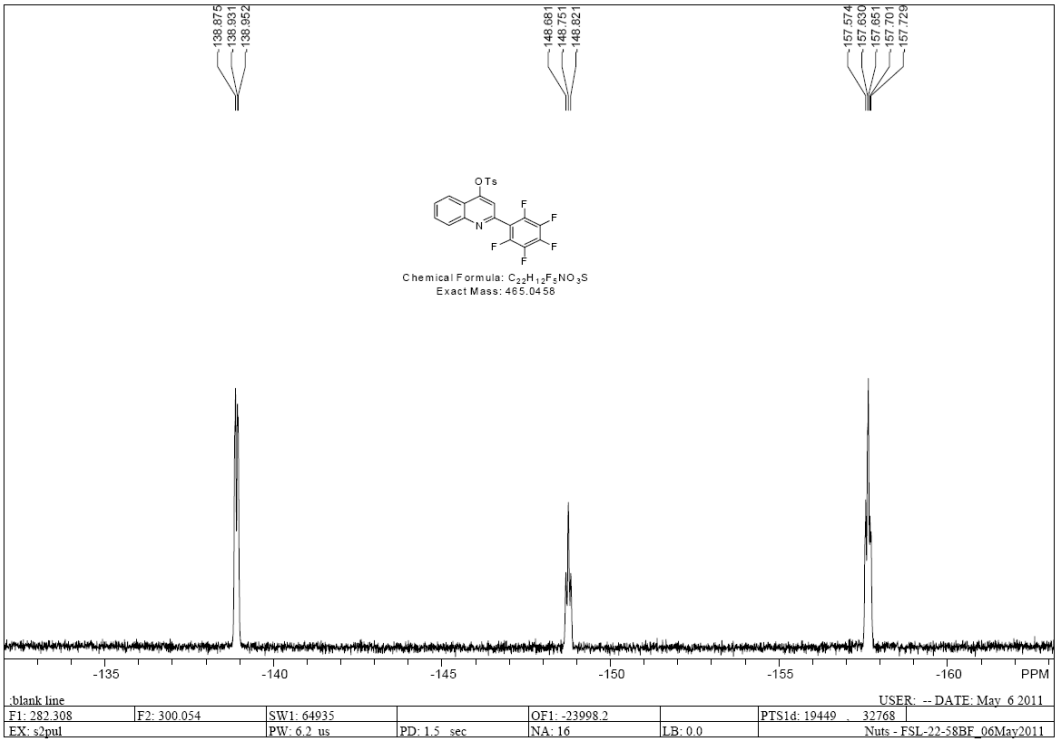


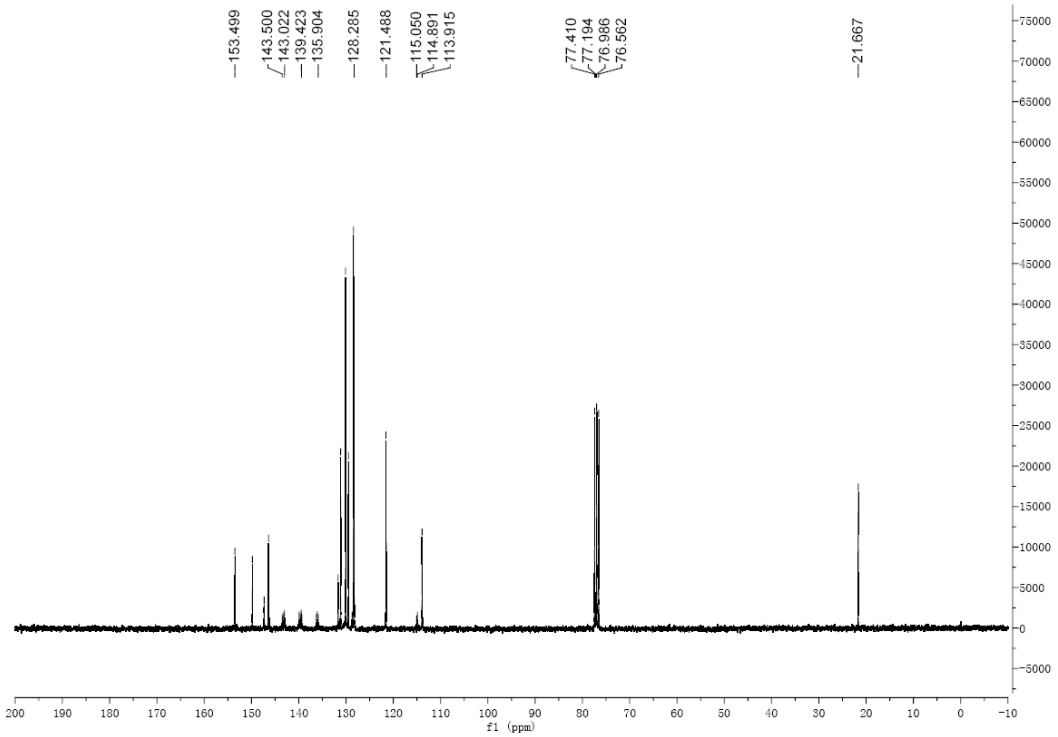

149.393
148.566
147.031
146.847
146.144
143.661
142.825
142.638
137.190
128.664
125.896
123.304
120.852
114.906
114.747
114.583
77.413
77.186
76.988
76.564
62.234
62.159
62.011
30.783
16.339
16.257
f1 (ppm)


17.389
Chemical Formula: C27H22F4NO3P
Exact Mass: 515.1273
PPM
Y-8-18
USER: -- DATE: Jun 24 2011
F1: 121.453
F2: 300.028
SW1: 54945
OF1: 300.6
PTS1d: 35165 , 65536
EX: s2pul
PW: 6.0 us
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - FSL-22-89P

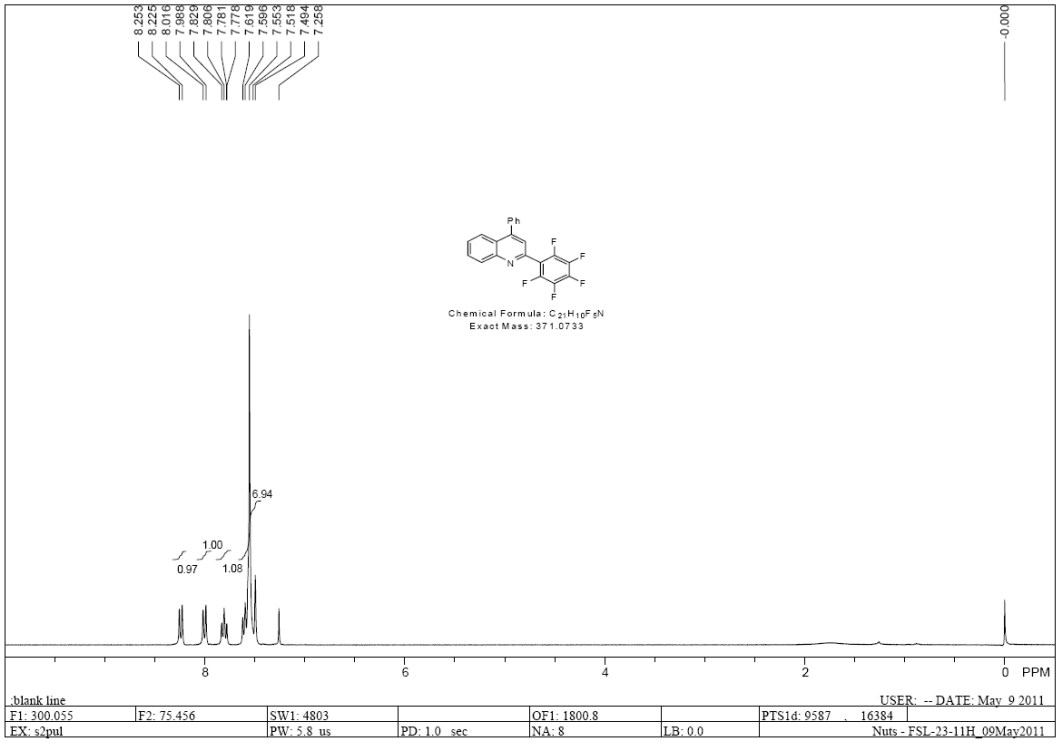
2-(perfluorophenyl)quinolin-4-yl 4-methylbenzenesulfonate (8)

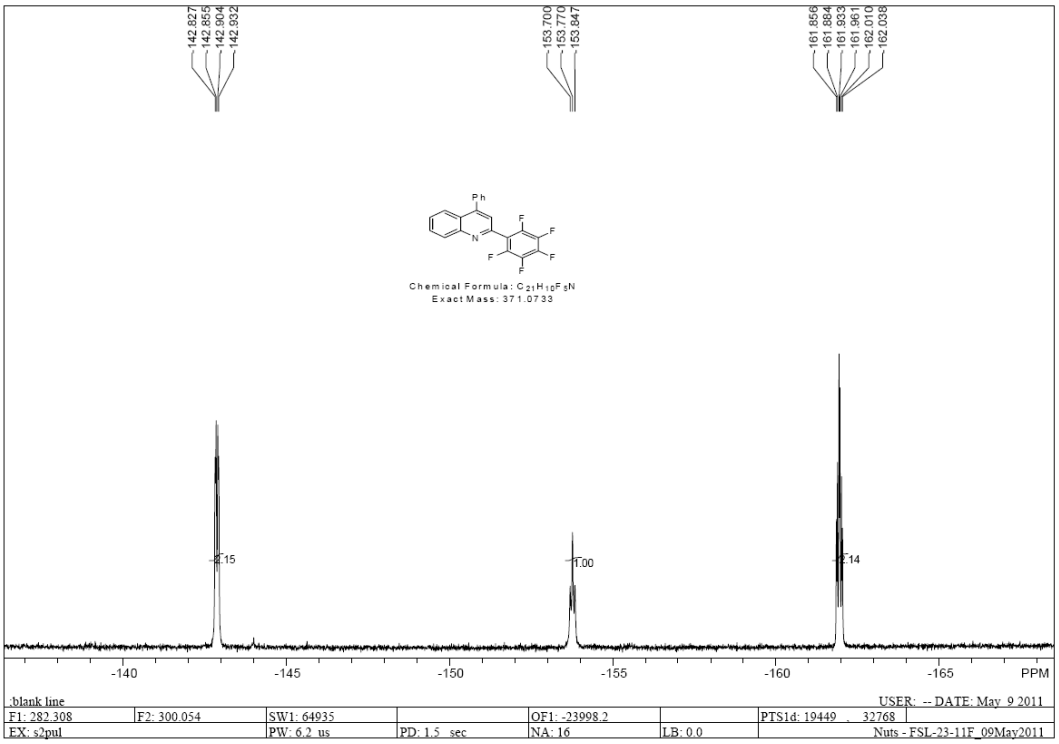


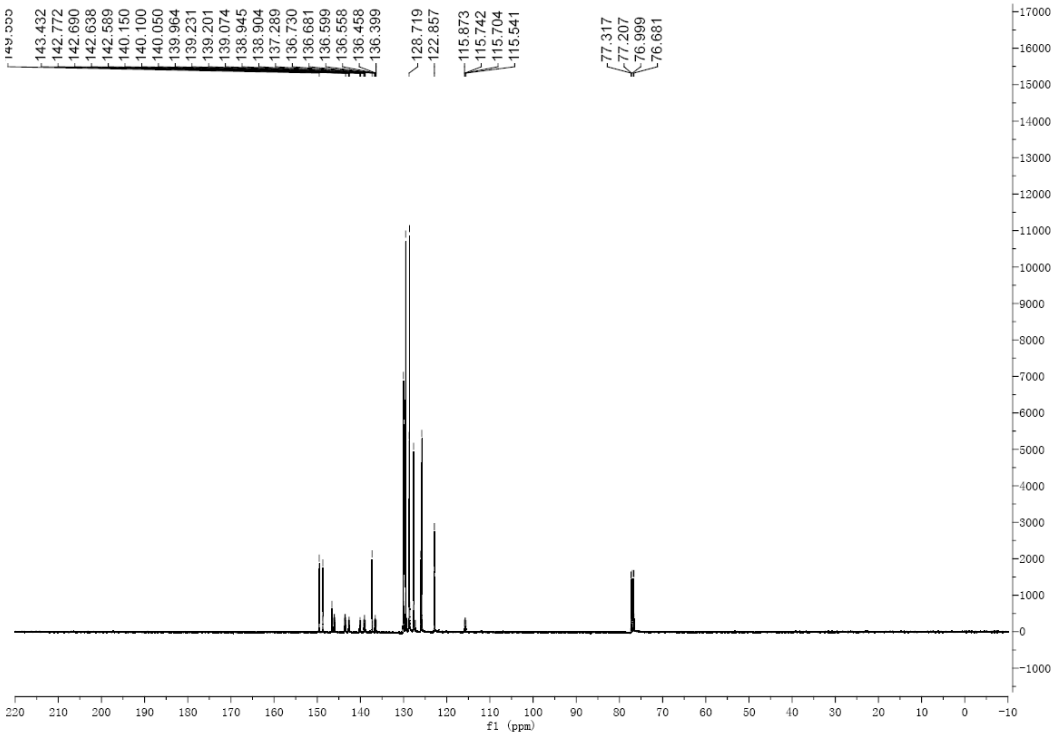




2-(perfluorophenyl)-4-phenylquinoline (9)




142.827
142.856
142.904
142.932
153.700
153.770
153.847
161.856
161.884
161.933
161.961
162.010
162.038
Ph
F
F
F
F
F
N
Chemical Formula: C21H10F5N
Exact Mass: 371.0733
2.15
1.00
2.14
-140
-145
-150
-155
-160
-165
PPM
blank line
USER: -- DATE: May 9 2011
F1: 282.308
F2: 300.054
SW1: 64935
OF1: -23998.2
PTS1d: 19449 . 32768
EX: s2pul
PW: 6.2 us
PD: 1.5 sec
NA: 16
LB: 0.0
Nuts - FSL-23-11F_09May2011


143.432
142.772
142.690
142.638
142.589
140.150
140.100
140.050
139.964
139.231
139.201
139.074
138.945
138.904
137.289
136.730
136.681
136.599
136.558
136.458
136.399
128.719
122.857
115.873
115.742
115.704
115.541
77.317
77.207
76.999
76.681
f1 (ppm)