Supporting Information

1,1-Difluoroethyl Chloride (CH_3CF_2Cl), A Novel Difluoroalkylating Reagent for 1,1-Difluoroethylation of Arylboronic Acids

Jianchang Liu,[a] Jida Zhang,[a] Chaolin Wu,[a] Hefu Liu,[a] Hui Liu,[a] Fenggang, Sun,[a] Yueyun Li,[a] Yuying Liu,[a] Yunhui Dong,[a] and Xinjin Li*[a,b]

[a] College of Chemistry and Chemical Engineering, Shandong University of Technology, 266 West Xincun Road, Zibo, 255000, China

[b]Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China

Table of Contents

1. General Information and Materials

General Information: ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a 400 MHz NMR spectrometer. ^{1}H NMR spectroscopy chemical shifts were determined relative to internal Me_4Si (TMS) at δ 0.0 or to the signal of the residual protonated solvent $CDCl_3$ δ 7.26, ^{13}C NMR spectroscopy chemical shifts were determined relative to internal TMS at δ 0.0. For the reaction mixtures, ^{19}F NMR spectroscopy chemical shifts were determined relative to $PhCF_3$ at δ –62.0. Data for ^{1}H, ^{13}C and ^{19}F NMR spectra are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, br = broad).

FT-IR spectra were obtained with a Nicolet 5700 spectrophotometer. GC-MS data were recorded on a Finnigan 4021 instrument and GCMS-QP2010. Melting points were recorded on a SGW X-4 melting point apparatus and are uncorrected. High resolution mass data were recorded on Waters Micromass GCT Premier and Bruker MicroTof Q II 10410.All reactions were monitored by TLC or ^{19}F NMR spectroscopy.

Materials: All reagents were used as received from commercial sources and used without further purification. DME, 1,4-dioxane, DMF, MeCN and DCE were distilled under reduced pressure from CaH_2, and stored over activated molecular sieve. THF and toluene were distilled from sodium and benzophenone immediately before use. The anhydrous K_2CO_3 was ground into a fine powder and was dried in vacuo. DMAP was recrystallized from toluene before used. All (hetero)arylboronic acids were used from commercial suppliers.

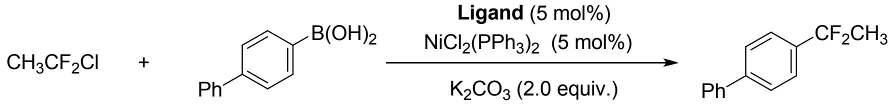
Preparation of CH_3CH_2Cl Stock Solution: DME was added to a Schlenk tube under N_2 atomosphere. CH_3CH_2Cl gas was then slowly bubbled through the DME until the total volume of the solution reach the maximum. The concentration of the CH_3CH_2Cl stock solution was determined by ^{19}F NMR using trifluorobenzene as an internal standard (generally 1.3 mol/L).

Preparation of $PhCF_2Cl$[1]: Into a round-bottom teflon flask, was added a magnetic stirrer and 20 g of Olah's reagent (HF 65-70%). Thereafter, 5g of $PhCl_3$ was slowly added to the HF-pyridine solution at 15°C, and then keep the reaction at 15-20 °C. A gas-outlet was placed on the top of the reaction flask for the purpose of HCl gas collection. The reaction mixture was stirred for 10 h and the progress of fluorination was monitored by GC-MS. After the reaction was finished, the reaction mixture was poured into iced water, and extracted with cold diethyl ether. The combined organic phase was washed with cold saturated $NaHCO_3$ aqueous solution and brine. After drying over $MgSO_4$ and solvent removal, the product was purified by distillation as a colorless oil (purity>95%, determined by ^{19}FNMR). The impurities were mainly $PhCF_3$ and $PhCFCl_2$. ^{19}F NMR (376 MHz, $CDCl_3$): δ –48.5 (s, 2F). GC-MS (*m*/*z*): 162 (M^+), 127 (M^+-Cl), 77 (M^+-CF_2Cl).

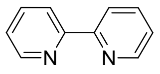
2. Optimization of Ni-Catalyzed Cross-Coupling of CH_3CH_2Cl with Aryl boronic Acids

General procedure of optimization of Ni-catalyzed cross-coupling of CH_3CH_2Cl with aryl boronic acid (2a): To a 10 mL of Schlenk tube were added 4-biphenylboronic acid (39.6 mg, 0.2 mmol, 1.0 equiv.), Nickel catalyst (1.5-7 mol%), ligand(1.5-7 mol%), base (1.5-4 equiv.) and additive (0.1-1.0 equiv.). The mixture was evacuated and backfilled with N_2 for three times, solvent (2 mL) and CH_3CF_2Cl (generally 1.3 mol/L in DME) were then added. The Schlenk tube was screw capped and put into a preheated oil bath (90-130 °C). After stirring for 5-12 h, the reaction mixture was cooled to room temperature and was purified with silica gel chromatography (petroleum ether) to give product **3a**.

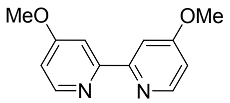
Table S1. Optimization of Ligands[a]



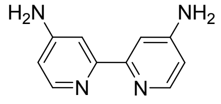
1a **2a** **3a**



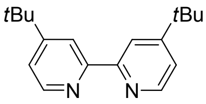
bpy



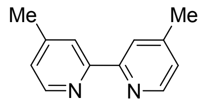
L1



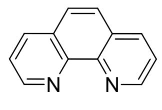
L2



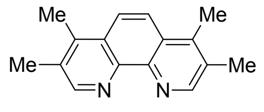
L3



L4



phen



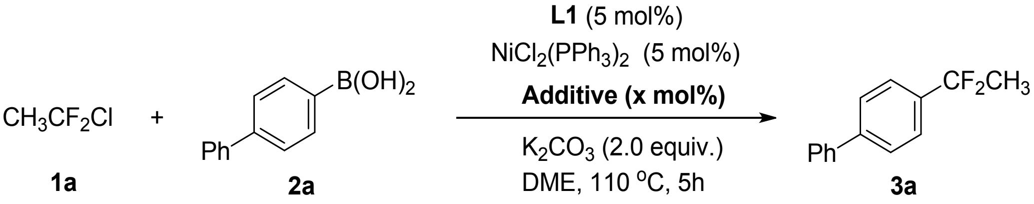
L5

Entry	Ligand	Yield[b] [%]
1	bpy	5
2	**L1**	15
3	**L2**	7
4	**L3**	7
5	**L4**	5
6	phen	trace
7	**L5**	trace

[a] Reaction conditions: **2a** (0.2 mmol, 1.0 equiv.), **1a** (2.6 mmol), DME (2 mL). [b] Isolated

yields.

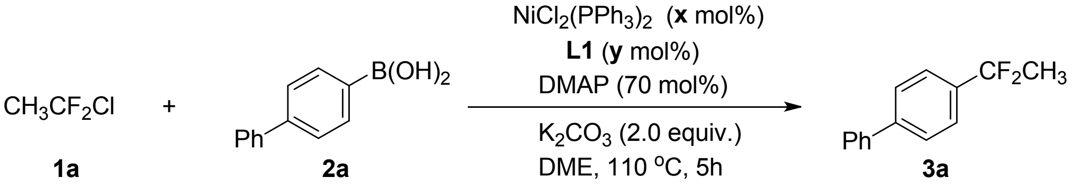
Table S2. Optimization of Additives[a]



Entry	Additive (x mol%)	Yield[b] [%]
1	none	15
2	DMAP(10)	30
3	DMAP(30)	42
4	DMAP(50)	49
5	DMAP(70)	61
6	DMAP(100)	59
7	Py (10)	trace
8	3-CNPy (10)	trace
9	4-CNPy (10)	trace
10	DMAP(70)+LiCl(1.0 eq.)	58

[a] Reaction conditions: **2a** (0.2 mmol,1.0 equiv.), **1a** (2.6 mmol), DME (2 mL). [b] Isolated yields.

Table S3. Optimization of Ratio of Nickel Catalyst and Ligand [a]

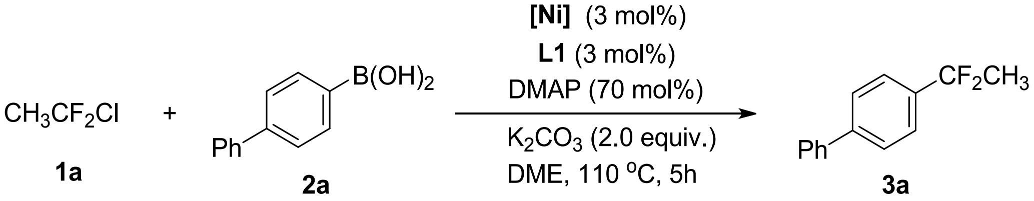


Entry	x/y	Yield[b][%]
1	7/7	43
2	5/5	61
3	3/3	70
4	1.5/1.5	63
5	0/3	0
6	3/0	trace

[a] Reaction conditions: **2a** (0.2 mmol, 1.0 equiv.), **1a** (2.6 mmol), DME (2 mL). [b] Isolated

yields.

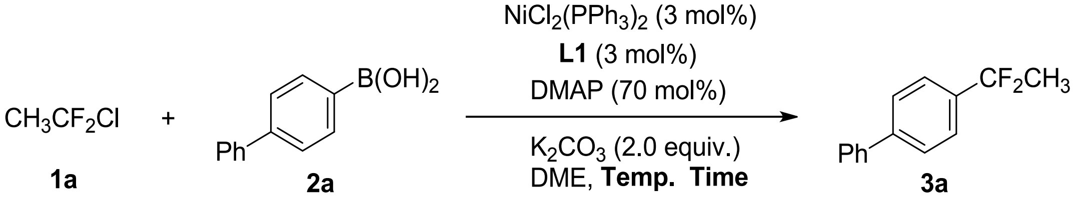
Table S4. Optimization of Nickel Catalyst[a]



Entry	[Ni]	Yield[b][%]
1	$NiCl_2(PPh_3)_2$	70
2	$NiCl_2\cdot dppe$	65
3	$NiCl_2\cdot DME$	49
4	$NiCl_2$	41
5	$NiCl_2(PCy_3)_2$	45
6	$Ni(NO_3)_2\cdot 6H_2O$	37

[a] Reaction conditions: **2a** (0.2 mmol,1.0 equiv.), **1a** (2.6 mmol), DME (2 mL). [b] Isolated yields.

Table S5. Optimization of Reaction Parameters [a]

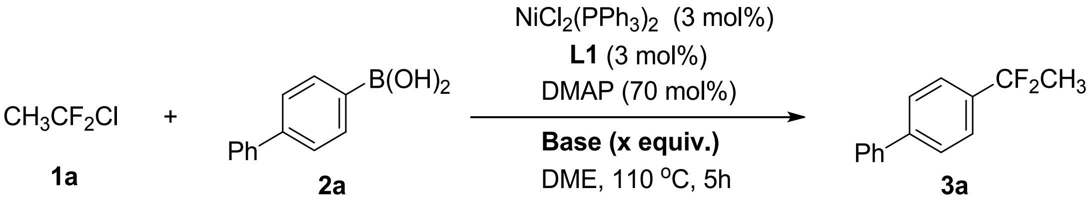


Entry	CF_2CH_3Cl (equiv.)	Temp (⁰C)	Time (h)	Yield[b] [%]
1	13	110	12	69
2	13	110	5	70
3	13	110	4	59
4	10	110	5	65
5	6	110	5	46
6	13	130	5	43

7	13	90	5	25
8	13	90	12	57

[a] Reaction conditions: **2a** (0.2 mmol,1.0 equiv.), **1a** (1.2-2.6 mmol), DME (2 mL). [b] Isolated yields.

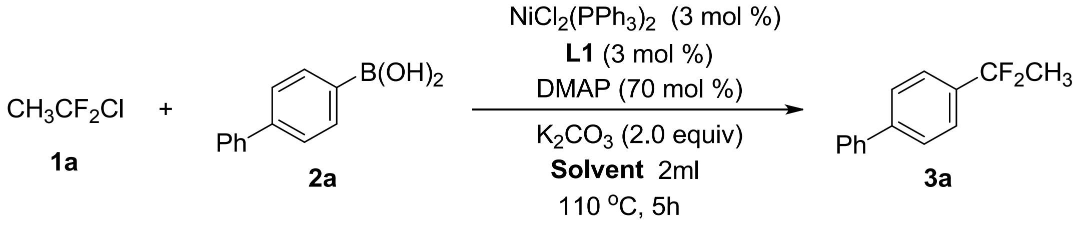
Table S6. Optimization of Bases[a]



Entry	Base(x equiv.)	Yield[b][%]
1	K_2CO_3 (1.5)	57
2	K_2CO_3 (2)	70
3	K_2CO_3 (3)	64
4	K_2CO_3 (4)	51
5	LiO^tBu (2)	33
6	NaO^tBu (2)	nd
7	K_3PO_4 (2)	29
8	Na_2CO_3 (2)	9
9	Cs_2CO_3 (2)	nd

[a] Reaction conditions: **2a** (0.2 mmol,1.0 equiv.), **1a** (2.6 mmol), DME (2 mL). [b] Isolated yields.

Table S7. Optimization of Solvents[a]

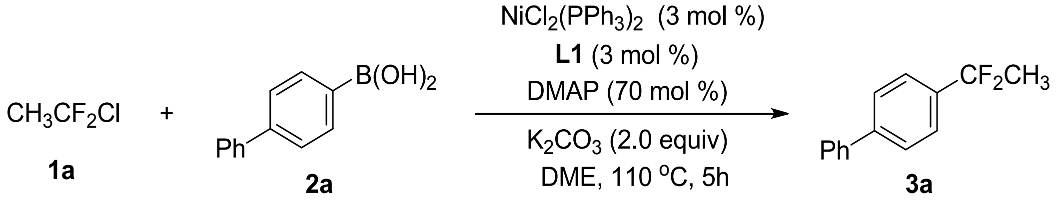


Entry	Solvent	Yield[b][%]
1	DME	70
2	triglyme	34
3	1,4-dioxane	31
4	THF	25
5	NMP	nd
6	DMSO	nd
7	DMF	21

8	DCE	trace
9	toluene	trace
10	tert-butanol	8
11	MeCN	23

[a] Reaction conditions: **2a** (0.2 mmol,1.0 equiv.), **1a** (2 mmol, 10 equiv.) [b] Isolated yields.

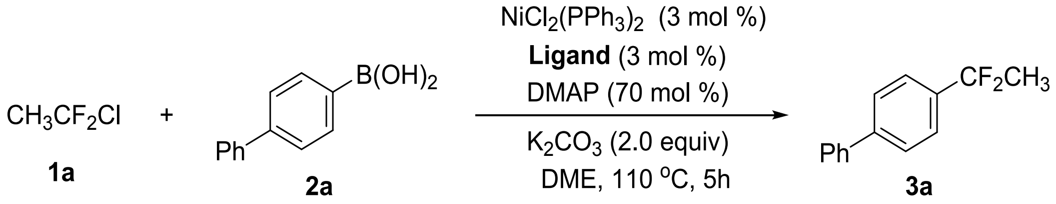
Table S8. The Effect of H_2O on the Ni-Catalyzed Reaction[a]

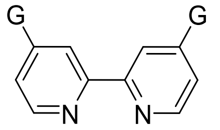


Entry	Solvent	Yield[b][%]
1	DME (without further purification)	70
2	DME (distilled from CaH_2)	69
3	Add H_2O(1.0 equiv.) to DME (without further purification)	66

[a] Reaction conditions: **2a** (0.2 mmol,1.0 equiv.), **1a** (2.6 mmol), DME (2 mL). [b] Isolated yields.

Table S9. The Effect of Ligands with DMAP[a]





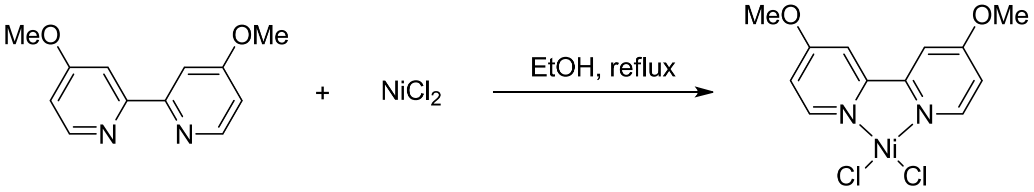
L1, G = OMe
L2, G = NH_2
L3, G = ^{t}Bu

Entry	Ligand	Yield[b][%]
1	**L1**	70
2	**L2**	24
3	**L3**	61

[a] Reaction conditions: **2a** (0.2 mmol,1.0 equiv.), **1a** (2.6 mmol), DME (2 mL). [b] Isolated yields.

3. The Role of DMAP

3.1 Preparation of $NiCl_2$(diOMebpy) and $NiCl_2(DMAP)_4$

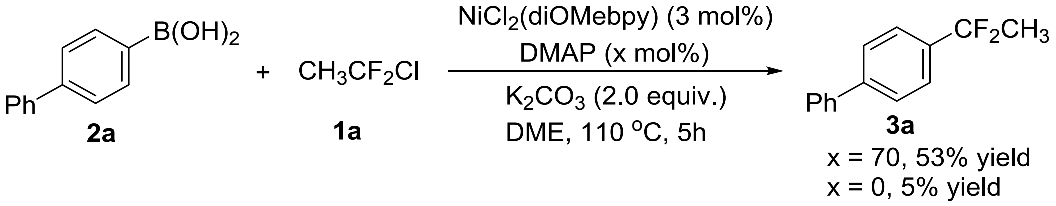


Preparation of $NiCl_2$(diOMebpy) [2]: To a solution of $NiCl_2$ (65 mg, 0.5 mmol) in ethanol (10 mL) was added a solution of 4,4′-diOMebpy (108 mg, 0.5 mmol) in ethanol (10 mL). The reaction mixture was refluxed with stirring for 10 h. The yellow solution slowly became green. The solution was filtrated and the filtrate was evaporated in vacuo to give a crude product $NiCl_2$(diOMebpy) 152mg (88% yield). The crude product was recrystallized from methanol.

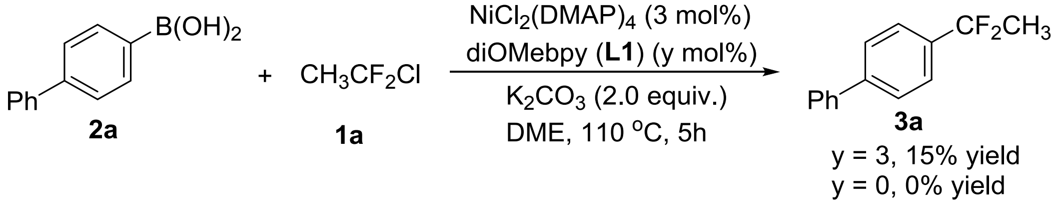
$$NiCl_2{\bullet}DME + DMAP \xrightarrow{\text{MeOH, rt.}} NiCl_2(DMAP)_4$$

Preparation of $NiCl_2(DMAP)_4$ [2]: To a stirring solution of DMAP (293 mg, 2.4 mmol) in MeOH (5 mL) was added dropwise a solution of $NiCl_2{\cdot}DME$ (66 mg, 0.3 mmol) in MeOH (5 mL). After the reaction mixture was stirred at room temperature for another 6 h, the solution was filtrated. The filtrate was evaporated in vacuo to give a blue solid $NiCl_2(DMAP)_4$ 172 mg (93% yield). The crude product was recrystallized from methanol.

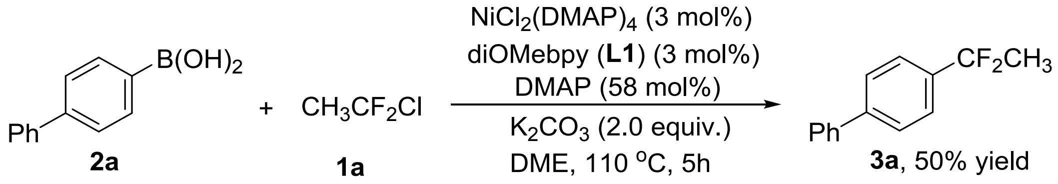
3.2 Reaction of Nickel complex with CH_3CF_2Cl



Procedure: To a 10 mL of Schlenk tube were added 4-biphenylboronic acid (39.6 mg, 0.2 mmol, 1.0 equiv.), $NiCl_2$(diOMebpy) (2 mg, 3 mol%) , K_2CO_3 (55.2 mg, 2.0 equiv.), DMAP(70 mol% or none). The mixture was evacuated and backfilled with N_2 for three times, DME (2 mL) and CH_3CF_2Cl (generally 1.3 mol/L in DME) were then added. The Schlenk tube was screw capped and put into a preheated oil bath (110 ^{o}C). After stirring for 5h, the reaction mixture was cooled to room temperature and was purified with silica gel chromatography (petroleum ether) to give product **3a**.



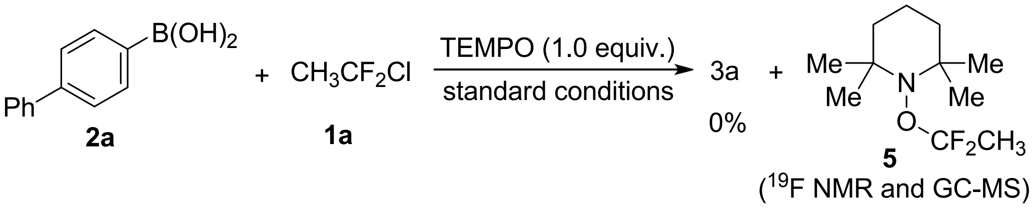
Procedure: To a 10 mL of Schlenk tube were added 4-biphenylboronic acid (39.6 mg, 0.2 mmol, 1.0 equiv.), NiCl$_2$(DMAP)$_4$ (3.7 mg, 3 mol%), **L1** (3 mol% or none), K$_2$CO$_3$ (55.2mg, 2.0 equiv.). The mixture was evacuated and backfilled with N$_2$ for three times, DME (2 mL) and CH$_3$CF$_2$Cl (generally 1.3 mol/L in DME) were then added. The Schlenk tube was screw capped and put into a preheated oil bath (110 ^{o}C). After stirring for 5h, the reaction mixture was cooled to room temperature and was purified with silica gel chromatography (petroleum ether) to give product **3a**.



Procedure: To a 10 mL of Schlenk tube were added 4-biphenylboronic acid (39.6 mg, 0.2 mmol, 1.0 equiv.), NiCl$_2$(DMAP)$_4$ (3.7 mg, 3 mol%), **L1** (1.3 mg, 3 mol%), K$_2$CO$_3$ (55.2 mg, 2.0 equiv.), DMAP(14.1mg, 58 mol%). The mixture was evacuated and backfilled with N$_2$ for three times, DME (2 mL) and CH$_3$CF$_2$Cl (generally 1.3 mol/L in DME) were then added. The Schlenk tube was screw capped and put into a preheated oil bath (110 ^{o}C). After stirring for 5h, the reaction mixture was cooled to room temperature and was purified with silica gel chromatography (petroleum ether) to give product **3a** 22mg (50% yield).

4. Radical Inhibition and Clock Experiments[a]

4.1 Radical inhibition experiment



Procedure: To a 10 mL of Schlenk tube were added 4-biphenylboronic acid (39.6 mg, 0.2 mmol, 1.0 equiv.), $NiCl_2(PPh_3)_2$ (3.9 mg, 3 mol%), **L1** (1.3 mg, 3 mol%), K_2CO_3 (55.2mg, 2.0 equiv.) DMAP (17.1 mg, 70 mol%) and TEMPO (31.2 mg, 1.0 equiv.). The mixture was evacuated and backfilled with N_2 for three times, DME (2 mL) and CH_3CF_2Cl (generally 1.3 mol/L in DME) were then added. The Schlenk tube was screw capped and put into a preheated oil bath (110 °C). After stirring for 5h, the reaction mixture was cooled to room temperature. The yield was determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard.

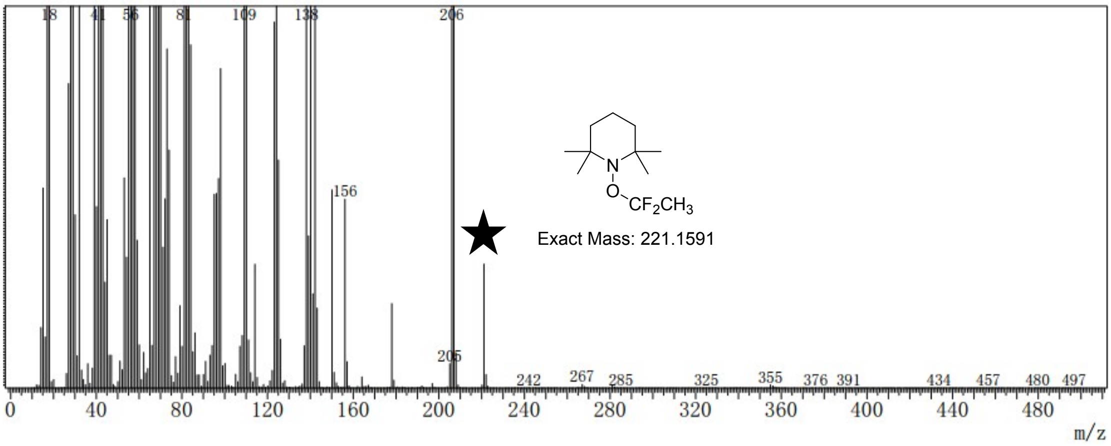


Figure S1. GC-MS analysis of adding TEMPO to Standard reaction conditions

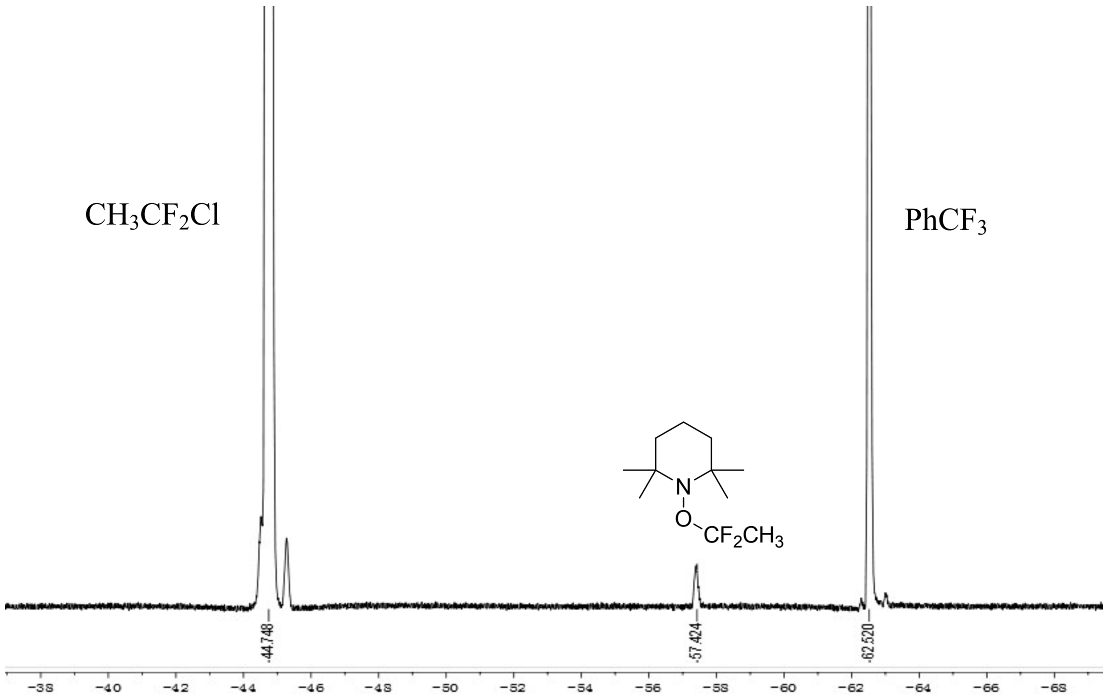
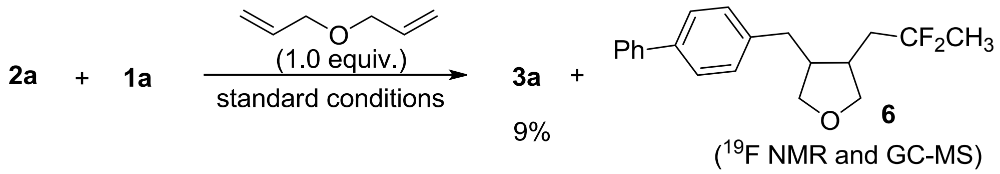


Figure S2. ^{19}F NMR analysis of adding TEMPO to standard reaction conditions

4.2 Radical clock experiment



Procedure: To a 10 mL of Schlenk tube were added 4-biphenylboronic acid (39.6 mg, 0.2 mmol, 1.0 equiv.), $NiCl_2(PPh_3)_2$ (3.9 mg, 3 mol%), **L1** (1.3 mg, 3 mol%), K_2CO_3 (55.2 mg, 2.0 equiv.), DMAP(17.1 mg, 70 mol%) and allyl ether (19.6 mg, 1.0 equiv.). The mixture was evacuated and backfilled with N_2 for three times, DME (2 mL) and CH_3CF_2Cl (generally 1.3 mol/L in DME) were then added. The Schlenk tube was screw capped and put into a preheated oil bath (110 ^{o}C). After stirring for 5h, the reaction mixture was cooled to room temperature. The yield was determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard.

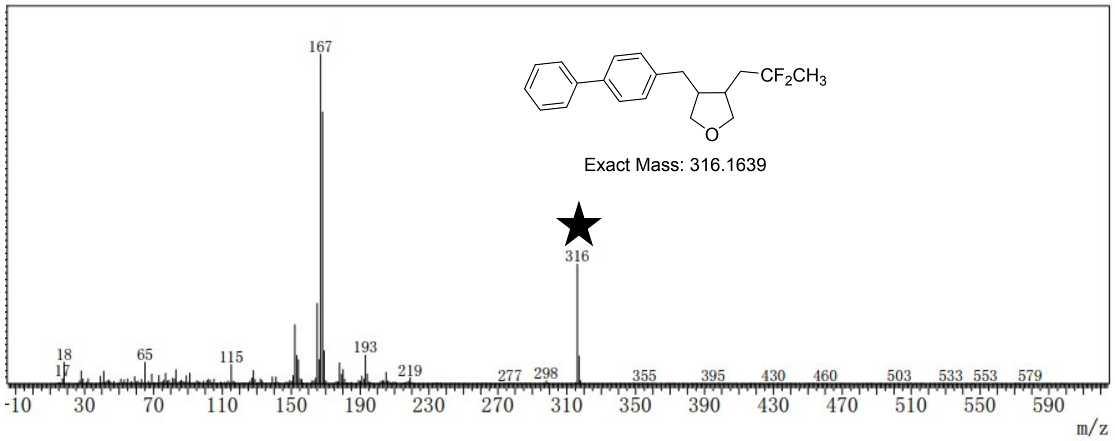


Figure S3. GC-MS analysis of adding allyl ether to standard reaction conditions

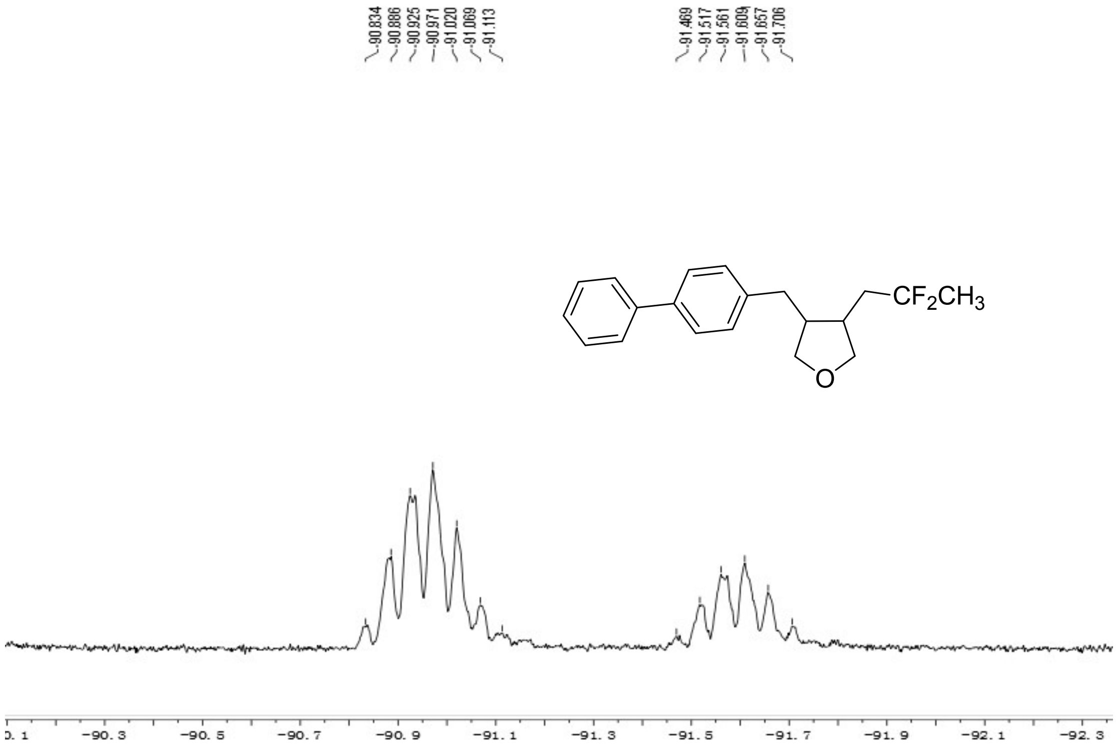
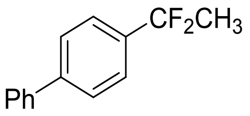


Figure S4. ^{19}F NMR analysis of adding allyl ether to standard reaction conditions

5. Experimental Procedures and Characterization Data

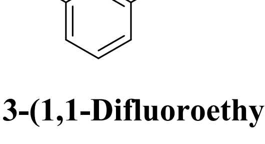
5.1 Ni-catalyzed cross-coupling of arylboronic acids with CH_3CF_2Cl.

Typical Experiment Procedure: To a 10 mL of Schlenk tube were added arylboronic acid (0.2 mmol, 1.0 equiv.), $NiCl_2(PPh_3)_3$ (3.9 mg, 3 mol%), **L1** (1.3 mg, 3 mol%), K_2CO_3 (55.2 mg, 2.0 equiv.), DMAP(17.1 mg, 70 mol%). The mixture was evacuated and backfilled with N_2 for three times, DME (2 mL) and CH_3CF_2Cl (generally 1.3 mol/L in DME) were then added. The Schlenk tube was screw capped and put into a preheated oil bath (110 °C). After stirring for 5 h, the reaction mixture was cooled to room temperature and purified by silica gel chromatography to give product.



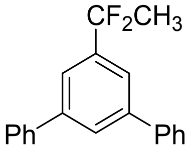
4-(1,1-Difluoroethyl)-1,1'-biphenyl (3a)[3]

For 0.2 mmol scale, the standard procedure of method was followed to provide **3a** by column chromatography on silica gel (petroleum ether) as a white solid (31 mg, 70%). M.p.: 62–64 °C. IR (KBr): 3080, 3032, 3006 , 1680, 1488, 1388, 1305, 1166, 1112, 921, 766, 692, 581 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.65-7.57 (m, 6H), 7.45 (t, J = 7.2 Hz, 2H), 7.40-7.36 (m, 1H),1.96 (t, J = 18.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): -87.2 (q, J = 18.0 Hz, 2F). GC-MS (*m*/*z*): 218 (M^+), 203 ($M^+–CH_3$), 153 ($M^+–CF_2–CH_3$).



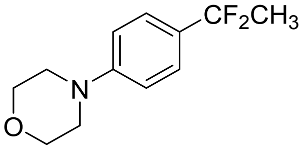
3-(1,1-Difluoroethyl)-1,1'-biphenyl (3b)[3]

For 0.2 mmol scale, the standard procedure of method was followed to provide **3b** by column chromatography on silica gel (petroleum ether) as a colorless oil (24 mg, 54%). IR (thin film): 3061, 3003, 2927, 1483, 1384, 1316, 1178, 929, 759, 704, 599cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (s, 1H), 7.64-7.63 (m, 1H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.49-7.43 (m, 4H), 7.37 (t, *J* = 7.4 Hz, 1H), 1.96 (t, *J* = 18.2Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -87.6 (q, *J* = 18.0 Hz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.6, 140.5, 138.7 (t, $^2J_{C\text{-}F}$ = 26.4 Hz), 129.0, 128.9, 128.5, 127.7, 127.3, 123.52 (t, $^3J_{C\text{-}F}$ = 6.2 Hz), 123.48 (t, $^3J_{C\text{-}F}$ = 5.8 Hz), 121.9 (t, $^1J_{C\text{-}F}$ = 237.7 Hz), 26.1 (t, $^2J_{C\text{-}F}$ = 29.7 Hz).



5'-(1,1-Difluoroethyl)-1,1':3',1''-terphenyl (3c)

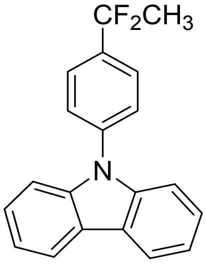
For 0.2 mmol scale, the standard procedure of method was followed to provide **3c** by column chromatography on silica gel (petroleum ether) as a colorless oil (23 mg, 39%). IR (thin film): 3061, 3037, 2854, 1599, 1433, 1254, 1179, 1144, 930, 759, 698 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (s, 1H), 7.71 (s, 2H), 7.67, (d, *J* = 7.2 Hz, 4H), 7.49 (t, *J* = 7.2 Hz, 4H), 7.41 (t, *J* = 7.2 Hz, 2H), 2.00 (t, *J* = 18.0 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -87.6 (q, *J* = 18.2 Hz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.3, 140.5, 139.3 (t, $^2J_{C\text{-}F}$ = 26.3 Hz), 128.9, 127.9 127.4, 127.3, 122.4 (t, $^3J_{C\text{-}F}$ = 6.0 Hz), 121.9 (t, $^1J_{C\text{-}F}$ = 238.0 Hz), 26.2 (t, $^2J_{C\text{-}F}$ = 29.7). GC-MS (*m*/*z*): 294 (M^+), 279 ($M^+{-}CH_3$). HRMS (EI): calcd. For $C_{20}H_{16}F_2$ (M^+): 294.1220, found: 294.1223.



4-(4-(1,1-Difluoroethyl)phenyl)morpholine (3h)

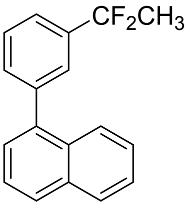
For 0.2 mmol scale, the standard procedure of method was followed to provide **3h** by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) as a white solid (12 mg, 28%). M.p.: 56-58 °C. IR (KBr): 2965, 2861, 1615, 1521, 1385, 1239, 1115, 925, 828, 622, 579 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 3.87 (t, *J* = 4.8 Hz, 4H), 3.2 (t, *J* = 5.0 Hz, 4H), 1.91 (t,

J = 18.0 Hz, 3H). ^{19}F NMR (376 MHz, CDCl$_3$): δ -85.4 (q, J = 18.0 Hz, 2F). ^{13}C NMR (100 MHz, CDCl$_3$): δ 152.1 129.1 (t, $^2J_{C\text{-}F}$ = 26.9 Hz), 125.8 (t, $^3J_{C\text{-}F}$ = 5.9 Hz), 122.1 (t, $^1J_{C\text{-}F}$ = 236.2 Hz), 114.8, 66.8, 48.7, 25.8 (t, $^2J_{C\text{-}F}$ = 30.3 Hz). GC-MS (*m*/*z*): 227 (M$^+$), 65 (CF$_2$CH$_3$$^+$). HRMS (EI): calcd. For $C_{12}H_{15}F_2NO$ (M$^+$): 227.1122, found: 227.1128.



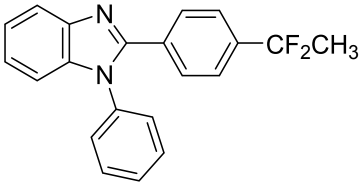
9-(4-(1,1-Difluoroethyl)phenyl)-9H-carbazole (3j)

For 0.2 mmol scale, the standard procedure of method was followed to provide **3j** by column chromatography on silica gel (petroleum ether) as a white solid (38 mg, 62%). M.p.: 150–152 °C. IR (KBr): 3250, 3003, 1610, 1517, 1453, 1295, 1232, 1175, 907, 752, 628, 570 cm^{-1}.^{1}H NMR (400 MHz, CDCl$_3$): δ 8.17 (d, J = 7.6 Hz, 2H), 7.76 (d, J = 8.4 Hz, 2H), 7.66 (d, J = 8.4 Hz, 2H), 7.46-7.41 (m, 4H), 7.34-7.30 (m, 2H), 2.05 (t, J = 18.2 Hz, 3H). ^{19}F NMR (376 MHz, CDCl$_3$): δ -87.2 (q, J = 18.2 Hz, 2F). ^{13}C NMR (100 MHz, CDCl$_3$): δ 140.6, 139.1, 137.1 (t, $^2J_{C\text{-}F}$ = 26.9 Hz), 127.0, 126.4 (t, $^3J_{C\text{-}F}$ = 5.9 Hz), 126.1, 123.6, 121.7 (t, $^1J_{C\text{-}F}$ = 237.6 Hz), 120.4, 120.3, 109.7, 26.0 (t, $^2J_{C\text{-}F}$ = 29.7 Hz). GC-MS (*m*/*z*): 307 (M$^+$), 292 (M$^+$–CH$_3$), 242 (M$^+$–CF$_2$–CH$_3$), 65 (CF$_2$CH$_3$$^+$). HRMS (ESI): calcd. For $C_{20}H_{16}F_2N$ (M+H)$^+$: 308.1251, found: 308.1254.



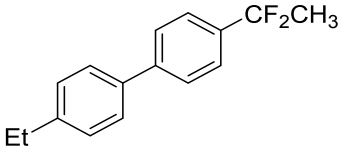
1-(3-(1,1-Difluoroethyl)phenyl)naphthalene (3k)

For 0.2 mmol scale, the standard procedure of method was followed to provide **3k** by column chromatography on silica gel (petroleum ether) as a colorless oil (12 mg, 26%). IR (thin film): 3060, 2927, 1591, 1509, 1394, 1313, 1180, 1083, 928, 798, 708, 601 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94-7.84 (m, 3H), 7.65 (s, 1H), 7.60-7.43 (m, 7H), 1.99 (t, J = 18.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -87.3 (q, J = 18.2 Hz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.1, 139.4, 138.3 (t, $^2J_{C-F}$ = 26.4 Hz), 133.8, 131.5, 131.4, 128.5, 128.4, 128.1, 127.1, 126.3 (t, $^3J_{C-F}$ = 5.9 Hz), 126.0, 125.7, 125.4, 123.5 (t, $^3J_{C-F}$ = 5.9 Hz), 121.9 (t, $^1J_{C-F}$ = 237.6 Hz), 26.1 (t, $^2J_{C-F}$ = 29.7 Hz). GC-MS (*m/z*): 268 (M^+), 203 (M^+–CF_2–CH_3). HRMS (EI): calcd. For $C_{18}H_{14}F_2$ (M^+): 268.1064, found: 268.1071.



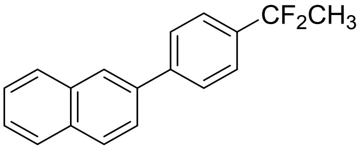
2-(4-(1,1-Difluoroethyl)phenyl)-1-phenyl-1H-benzo[d]imidazole (3l)

For 0.2 mmol scale, the standard procedure of method was followed to provide **3l** by column chromatography on silica gel (DCM) as a white solid (11 mg, 16%). M.p.: 98-100 °C. IR (KBr): 3060, 2927, 1509, 1394, 1266, 1180, 1083, 928, 798, 779, 708, 601 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, J = 7.6 Hz, 1H), 7.63 (d, J = 8.4 Hz, 2H), 7.55-7.50 (m, 3H), 7.44 (d, J = 8.4 Hz, 2H), 7.38-7.25 (m, 5H), 1.90 (t, J = 18.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -88.0 (q, J = 18.2 Hz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$): 151.3, 142.9, 139.0 (t, $^2J_{C-F}$ = 26.7 Hz), 137.3, 136.8, 131.4, 130.0, 129.5, 128.8, 127.4, 124.7 (t, $^3J_{C-F}$ = 5.9 Hz), 123.7, 123.2, 121.6 (t, $^1J_{C-F}$ = 237.8 Hz), 120.0, 110.6, 25.9 (t, $^2J_{C-F}$ = 29.5 Hz). GC-MS (*m/z*): 334 (M^+) . HRMS (ESI): calcd. For $C_{21}H_{17}F_2N_2$ $(M+H)^+$: 335.1360, found: 335.1371.



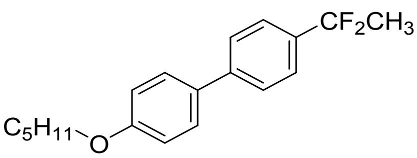
4-(1,1-Difluoroethyl)-4'-ethyl-1,1'-biphenyl (3m)

For 0.2 mmol scale, the standard procedure of method was followed to provide **3m** by column chromatography on silica gel (petroleum ether) as a white solid (30 mg, 61%). M.p.: 107–109 °C. IR (KBr):2966, 2931, 2874, 1613, 1501, 1398, 1300, 1176, 1124, 918, 821, 651, 573 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.63 (d, *J* = 8.4 Hz, 2H), 7.58-7.52 (m, 4H), 7.30 (d, *J* = 8.4 Hz, 2H), 2.71 (q, *J* = 7.6 Hz, 2H), 1.96 (t, *J* = 18.0 Hz, 3H), 1.29 (t, *J* = 7.6 Hz, 3H). ^{19}F NMR (376 MHz, CDCl$_3$): δ -87.2 (q, *J* = 18.2 Hz, 2F). ^{13}C NMR (100 MHz, CDCl$_3$): δ 144.0, 142.6, 137.6, 136.7 (t, $^2J_{C-F}$ = 26.6 Hz), 128.4, 127.1, 127.0, 125.1 (t, $^3J_{C-F}$ = 5.9 Hz), 122.0 (t, $^1J_{C-F}$ = 237.2 Hz), 28.6, 26.0 (t, $^2J_{C-F}$ = 29.9 Hz), 15.6. GC-MS (*m/z*): 246 (M$^+$), 231 (M$^+$–CH$_3$), 181 (M$^+$–CF$_2$–CH$_3$), 65 (CF$_2$CH$_3^+$). HRMS (EI): calcd. For $C_{16}H_{16}F_2$ (M$^+$): 246.1220, found: 246.1221.



2-(4-(1,1-Difluoroethyl)phenyl)naphthalene (3n)

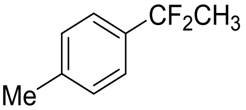
For 0.2 mmol scale, the standard procedure of method was followed to provide **3n** by column chromatography on silica gel (petroleum ether) as a white solid (29 mg, 55%). M.p.: 115–117 °C. IR (KBr): 3056, 2925, 1734, 1388, 1304, 1111, 922, 818, 748, 585, 477 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.07 (s, 1H), 7.96-7.88 (m, 3H), 7.79-7.74, (m, 3H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.56–7.50 (m, 2H), 2.00 (t, *J* = 18.2 Hz, 3H). ^{19}F NMR (376 MHz, CDCl$_3$): δ -87.3 (q, *J* = 18.0 Hz, 2F). ^{13}C NMR (100 MHz, CDCl$_3$): δ 142.6, 137.6, 137.1 (t, $^2J_{C-F}$ = 26.6 Hz), 133.6, 132.8, 128.6, 128.3, 127.7, 127.5, 126.5, 126.3, 126.1, 125.4, 125.2 (t, $^3J_{C-F}$ = 5.8 Hz), 122.0 (t, $^1J_{C-F}$ = 237.3 Hz), 26.0 (t, $^2J_{C-F}$ = 29.8 Hz). GC-MS (*m/z*): 268 (M$^+$), 253(M$^+$–CH$_3$), 65 (CF$_2$CH$_3^+$). HRMS (EI): calcd. For $C_{18}H_{14}F_2$ (M$^+$): 268.1064, found: 268.1068.



4-(1,1-Difluoroethyl)-4'-(pentyloxy)-1,1'-biphenyl (3o)

For 0.2 mmol scale, the standard procedure of method was followed to provide **3o** by column chromatography on silica gel (petroleum ether) as a white solid (31 mg, 51%). M.p.: 117–119 °C. IR (KBr): 2957, 2875, 1606, 1501, 1385, 1305, 1171, 1130, 1051, 922, 820, 604, 536 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61-7.51 (m, 6H), 6.98 (d, J = 8.8 Hz, 2H), 4.01 (t, J = 6.6 Hz, 2H), 1.96 (t, J = 18.0 Hz, 3H), 1.86-1.79 (m, 2H), 1.51-1.36 (m, 4H), 0.95 (t, J = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -87.1 (q, J = 18.0 Hz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.1, 142.3, 136.3 (t, $^{2}J_{C\text{-}F}$ = 26.6 Hz), 132.5, 128.2, 126.7, 125.1 (t, $^{3}J_{C\text{-}F}$ = 5.9 Hz), 122.0 (t, $^{1}J_{C\text{-}F}$ = 237.1 Hz), 114.9, 68.1, 29.0, 28.2, 26.0 (t, $^{2}J_{C\text{-}F}$ = 29.9 Hz), 22.5, 14.1. GC-MS (*m/z*): 304 (M^+), 233 ($M^+–C_5H_{11}$). HRMS (EI): calcd. For $C_{20}H_{16}F_2$ (M^+): 304.1639, found: 304.1635.

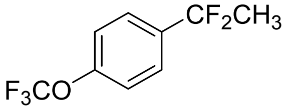
Typical Experiment Procedure for highly volatile products: To a 10 mL of Schlenk tube were added arylboronic acid (0.2 mmol, 1.0 equiv.), $NiCl_2(PPh_3)_3$ (3.9 mg, 3 mol%), **L1** (1.3 mg, 3 mol%), K_2CO_3 (55.2 mg, 2.0 equiv.), DMAP(17.1 mg, 70 mol%). The mixture was evacuated and backfilled with N_2 for three times, DME (2 mL) and CH_3CF_2Cl (generally 1.3 mol/L in DME) were then added. The Schlenk tube was screw capped and put into a preheated oil bath (110 °C). After stirring for 5h, the reaction mixture was cooled to room temperature. The yield was determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard.



1-(1,1-difluoroethyl)-4-methylbenzene (3d)[4]

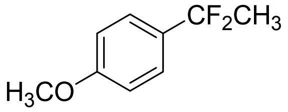
For 0.2 mmol scale, the yield (34%) was determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard. Characterization of **3d** in reaction solution: ^{19}F NMR (376 MHz, $CDCl_3$): δ -86.1 (q, J = 17.9 Hz, 2F). GC-MS (*m/z*):156 (M^+), 141

($M^+–CH_3$), 91 ($M^+–CF_2–CH_3$), 65 ($CF_2CH_3^+$)



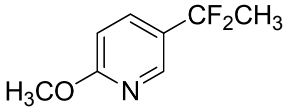
1-(1,1-difluoroethyl)-4-(trifluoromethoxy)benzene (3g)

For 0.2 mmol scale, the yield (35%) was determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard. Characterization of **3g** in reaction solution: ^{19}F NMR (376 MHz, $CDCl_3$): δ -57.2 (s, 3F), -86.7 (q, J = 18.2 Hz, 2F). GC-MS (*m*/*z*): 226 (M^+), 211 ($M^+–CH_3$).



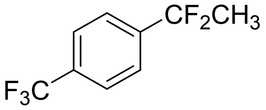
1-(1,1-difluoroethyl)-4-methoxybenzene (3e) [4]

For 0.2 mmol scale, the yield (33%) was determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard. Characterization of **3e** in reaction solution: ^{19}F NMR (376 MHz, $CDCl_3$): δ -84.8 (q, J = 17.9 Hz, 2F). GC-MS (*m*/*z*): 172 (M^+), 65 ($CF_2CH_3^+$).



5-(1,1-difluoroethyl)-2-methoxypyridine (3i)

For 0.2 mmol scale, the yield (27%) was determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard. Characterization of **3i** in reaction solution: ^{19}F NMR (376 MHz, $CDCl_3$): δ -86.3 (q, J = 18.4 Hz, 2F). GC-MS (*m*/*z*): 173 (M^+), 158 ($M^+–CH_3$).

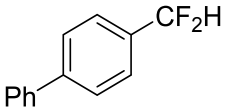


1-(1,1-difluoroethyl)-4-(trifluoromethyl)benzene (3f) [4]

For 0.2 mmol scale, the yield (40%) was determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard. Characterization of **3f** in reaction solution: ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.2 (s, 3F), -87.7 (q, *J* = 18.2 Hz, 2F). GC-MS (*m*/*z*): 210 (M^+), 195 ($M^+–CH_3$), 145 ($M^+–CF_2–CH_3$).

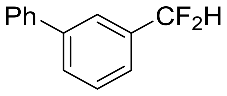
5.2 Ni-catalyzed cross-coupling of arylboronic acids with alkyl halides.

Procedure: To a 10 mL of Schlenk tube were added arylboronic acid (0.2 mmol, 1.0 equiv.), $NiCl_2(PPh_3)_3$ (3.9 mg, 3 mol%), **L1** (1.3 mg, 3 mol%), K_2CO_3 (55.2 mg, 2.0 equiv.), DMAP (17.1 mg, 70 mol%). The mixture was evacuated and backfilled with N_2 for three times, DME (2 mL) and CF_2HCl (generally 10.0 equiv) were then added. The Schlenk tube was screw capped and put into a preheated oil bath (110 °C). After stirring for 5 h, the reaction mixture was cooled to room temperature and purified by silica gel chromatography to give product.



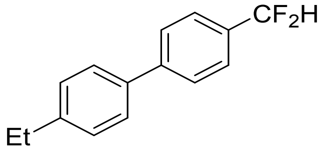
4-(Difluoromethyl)-1,1'-biphenyl (4a)[3]

For 0.2 mmol scale, the standard procedure of method was followed to provide **4a** by column chromatography on silica gel (petroleum ether) as a white solid (20 mg, 50%). M.p:70-72 °C. IR (KBr): 3059, 2965, 1614, 1488, 1380, 1226, 1077, 1025,839 766, 694 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.60 (t, *J* = 7.2 Hz, 4H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 1H), 6.71, (t, *J* = 56.6 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -110.3 (d, *J* = 56.4 Hz, 2F). GC-MS (*m*/*z*): 204 (M^+), 127 (M^+-Ph).



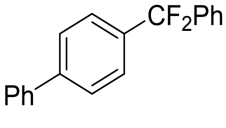
3-(Difluoromethyl)-1,1'-biphenyl (4b) [3]

For 0.2 mmol scale, the standard procedure of method was followed to provide **4b** by column chromatography on silica gel (petroleum ether) as a colorless oil (12 mg, 29%). IR (thin film): 3359, 3063, 2921, 1481, 1370, 1120, 1030, 899, 804, 759, 700, 615, 550 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73-7.72 (m, 2H), 7.61 (d, *J* = 7.6 Hz, 2H), 7.56-7.45 (m, 4H), 7.39 (t, *J* = 7.4 Hz, 1H), 6.72 (t, *J* = 56.6 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -110.6 (d, *J* = 56.4 Hz, 2F). GC-MS (*m/z*): 204 (M^+), 153(M^+-CF_2H), 127 (M^+-Ph),



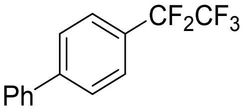
4-(Difluoromethyl)-4'-ethyl-1,1'-biphenyl (4c)

For 0.2 mmol scale, the standard procedure of method was followed to provide **4c** by column chromatography on silica gel (petroleum ether) as a white solid (21 mg, 46%). M.p.:102-104 °C. IR (KBr):3031, 2970, 2878, 1611, 1500, 1402, 1075, 1026, 818, 730, 552, 521 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.60-7.54 (m, 4H), 7.33 (*J* = 8.0 Hz, 2H), 6.71 (t, *J* = 56.6 Hz, 1H), 2.74 (q, *J* = 7.6 Hz, 2H), 1.31 (t, *J* = 7.6 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -110.2 (d, *J* = 56.6 Hz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.2, 143.7, 137.5, 132.9 (t, $^2J_{C\text{-}F}$ = 22.3 Hz), 128.5, 127.3, 127.2, 126.0 (t, $^3J_{C\text{-}F}$ = 5.9 Hz), 114.8 (t, $^1J_{C\text{-}F}$ = 236.9 Hz), 28.6, 15.6. GC-MS (*m/z*): 232 (M^+), 217 (M^+-CH_3), 181 (M^+-CF_2H). HRMS (EI): calcd. For $C_{15}H_{14}F_2$ (M^+): 232.1064, found: 232.1067.



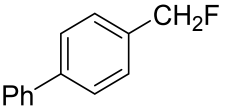
4-(Difluoro(phenyl)methyl)-1,1'-biphenyl (4d)[5]

To a 10 mL of Schlenk tube were added 4-biphenylboronic acid (39.6 mg, 0.2 mmol, 1.0 equiv.), $NiCl_2(PPh_3)_3$ (3.9 mg, 3 mol%), **L1** (1.3 mg, 3 mol%), K_2CO_3 (55.2 mg, 2.0 equiv.), DMAP (17.1 mg, 70 mol%). The mixture was evacuated and backfilled with N_2 for three times, DME (2 mL) and $PhCF_2Cl$ (162 mg, 175 μl 5.0 equiv.) were then added. The Schlenk tube was screw capped and put into a preheated oil bath (110 °C). After stirring for 5h, the reaction mixture was cooled to room temperature and purified by column chromatography on silica gel (petroleum ether) to product **4d** that a white solid (6 mg, 11%). M.p.: 78-80 °C. IR (KBr): 3450, 3345, 3064, 2922, 2851, 1450, 1272, 1236, 1047, 961, 838, 755, 696, 607 cm^{-1}.^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, J = 8.4 Hz, 2H), 7.60-7.55 (m, 6H), 7.48-7.44 (m, 5H), 7.38 (t, J = 7.2 Hz, 1H), ^{19}F NMR (376 MHz, $CDCl_3$): δ -88.6 (s, 2F). GC-MS (*m*/*z*): 280 (M^+), 203 (M^+-Ph), 127($PhCF_2^+$).



4-(Perfluoroethyl)-1,1'-biphenyl (4e)[6]

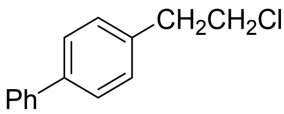
To a 10 mL of Schlenk tube were added 4-biphenylboronic acid (39.6 mg, 0.2 mmol, 1.0 equiv.), $NiCl_2(PPh_3)_3$ (3.9 mg, 3 mol%), **L1** (1.3 mg, 3 mol%), K_2CO_3 (55.2 mg, 2.0 equiv.), DMAP (17.1 mg, 70 mol%). The mixture was evacuated and backfilled with N_2 for three times, DME (2 mL) and CF_3CF_2Cl (generally 10.0 equiv) were then added. The Schlenk tube was screw capped and put into a preheated oil bath (110 °C). After stirring for 5h, the reaction mixture was cooled to room temperature and purified by column chromatography on silica gel (petroleum ether) to product **4e** that a white solid (10 mg, 19%). M.p.:68-70 °C. IR (KBr): 3358, 2923, 2852, 1407, 1292, 1205, 1114, 1093, 974, 841, 739, 691 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.7 (q, J = 8.8 Hz, 4H), 7.61 (d, J = 7.6 Hz, 2H), 7.48 (t, J = 7.6 Hz, 2H), 7.41 (t, J = 7.2 Hz, 1H), ^{19}F NMR (376 MHz, $CDCl_3$): δ -84.7 (s, 3F), -114.7 (s, 2F). GC-MS (*m*/*z*): 272 (M^+), 203 (M^+-CF_3).



4-(Fluoromethyl)-1,1'-biphenyl (4f)[7]

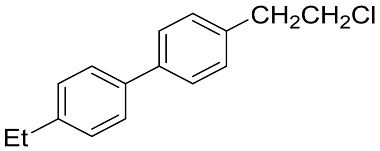
To a 10 mL of Schlenk tube were added 4-biphenylboronic acid (39.6 mg, 0.2

mmol, 1.0 equiv.), $NiCl_2(PPh_3)_3$ (3.9 mg, 3 mol%), **L1** (1.3 mg, 3 mol%), K_2CO_3 (55.2 mg, 2.0 equiv.), DMAP (17.1 mg, 70 mol%). The mixture was evacuated and backfilled with N_2 for three times, DME (2 mL) and CH_2FCl (generally 10.0 equiv.) were then added. The Schlenk tube was screw capped and put into a preheated oil bath (110 °C). After stirring for 5h, the reaction mixture was cooled to room temperature and purified by column chromatography on silica gel (petroleum ether) to product **4f** that a white solid (9 mg, 25%).GC-MS (*m*/*z*): 186 (M^+), 109 (M^+-Ph), 153 (M^+-CH_2F).



4-(2-Chloroethyl)-1,1'-biphenyl (4g)[8]

To a 10 mL of Schlenk tube were added 4-biphenylboronic acid (39.6 mg, 0.2 mmol, 1.0 equiv.), $NiCl_2(PPh_3)_3$ (3.9 mg, 3 mol%), **L1** (1.3 mg, 3 mol%), K_2CO_3 (55.2 mg, 2.0 equiv.), DMAP (17.1 mg, 70 mol%). The mixture was evacuated and backfilled with N_2 for three times, DME (2 mL) and $ClCH_2CH_2Cl$ (98 mg, 78 µl, 5.0 equiv) were then added. The Schlenk tube was screw capped and put into a preheated oil bath (110 °C). After stirring for 5h, the reaction mixture was cooled to room temperature and purified by column chromatography on silica gel (petroleum ether) to product **4g** that a white solid (34 mg, 79%).M.p.:25-27 °C. IR (KBr): 3401, 3029, 2927, 1601, 1487, 1246, 1108, 825, 748, 698 503 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.60-7.55 (m, 4H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.37-7.30 (m, 3H), 3.76 (t, *J* = 7.4 Hz, 2H), 3.12 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.8, 139.9, 137.1, 129.3, 128.8, 127.3, 127.2, 127.1, 44.9, 38.8. GC-MS (*m*/*z*): 216 (M^+), 167 (M^+-CH_2Cl)



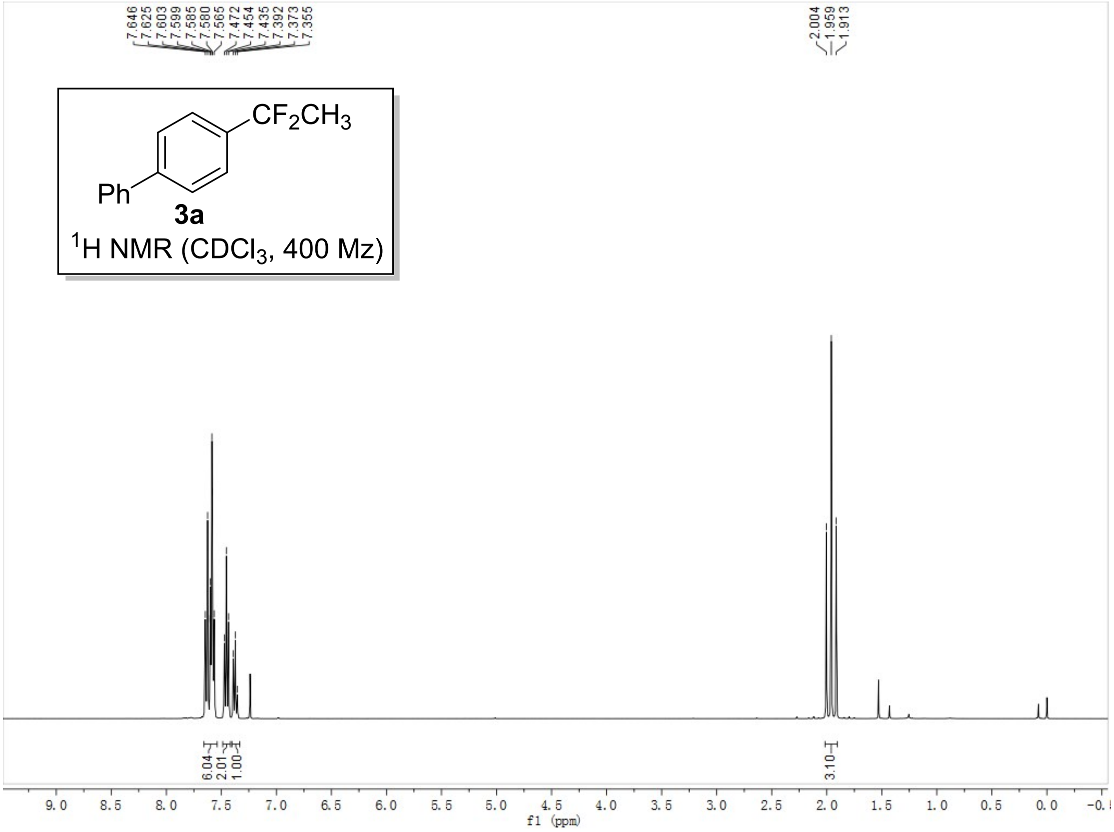
4-(2-Chloroethyl)-4'-ethyl-1,1'-biphenyl (4h)

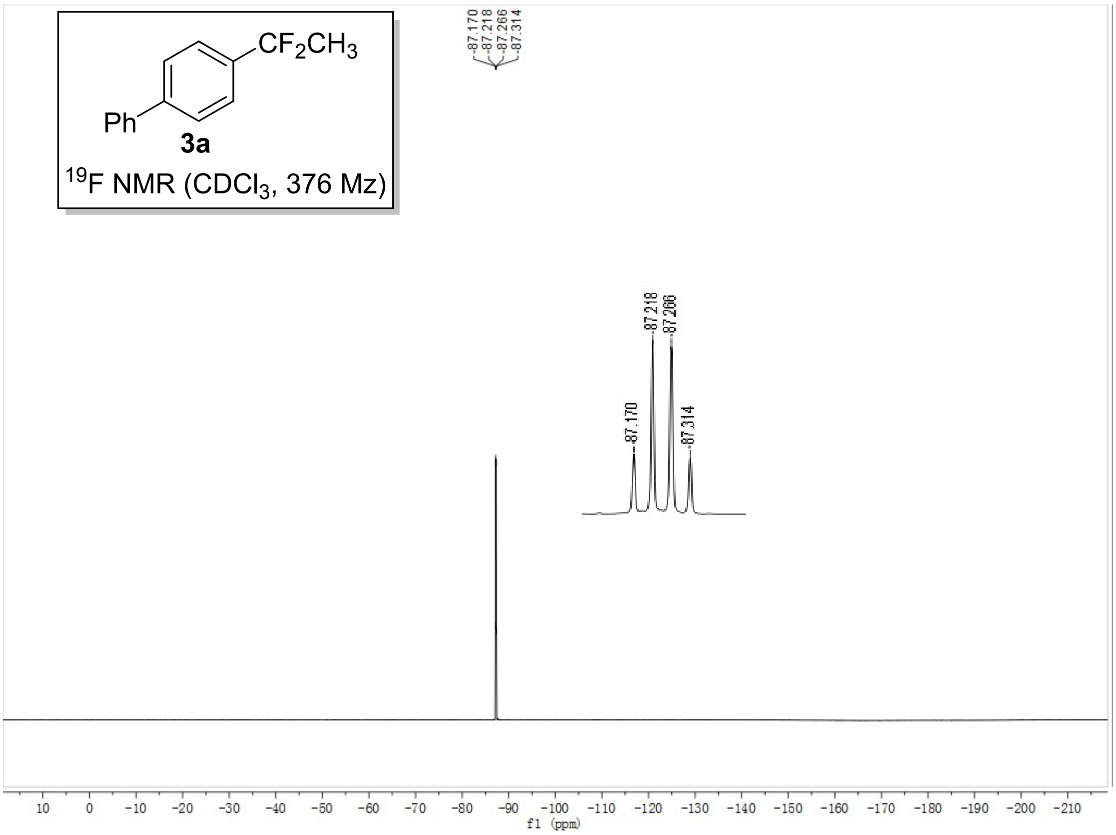
To a 10 mL of Schlenk tube were added (4'-Ethyl[1,1'-biphenyl]-4-yl)-boronic (0.2 mmol, 1.0 equiv.), $NiCl_2(PPh_3)_3$ (3.9 mg, 3 mol%), **L1** (1.3 mg, 3 mol%), K_2CO_3 (55.2 mg, 2.0 equiv.), DMAP (17.1 mg, 70 mol%). The mixture was evacuated and backfilled with N_2 for three times, DME (2 mL) and $ClCH_2CH_2Cl$ (98 mg, 78 μl, 5.0 equiv) were then added. The Schlenk tube was screw capped and put into a preheated oil bath (110 ^oC). After stirring for 5h, the reaction mixture was cooled to room temperature and purified by column chromatography on silica gel (petroleum ether) to product **4h** that a white solid (31 mg, 64%). M.p.:83-85 ^oC. IR (KBr): 3027, 2961, 2868, 1497, 1400, 1245, 1144, 1004, 814, 747, 707, 499 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.58-7.52 (m, 4H), 7.30 (d, *J* = 7.6 Hz, 4H), 3.77 (t, *J* = 7.4 Hz, 2H), 3.13 (t, *J* = 7.4 Hz, 2H), 2.72 (q, 2.72, *J* = 7.6 Hz, 2H), 1.31 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.4, 139.9, 138.2, 136.8, 129.2, 128.3, 127.2, 127.0, 45.00, 38.9, 28.6, 15.7. GC-MS (*m/z*): 244 (M^+), 229 (M^+-CH_3), 195 (M^+-CH_2Cl). HRMS (EI): calcd. For $C_{16}H_{17}Cl$ (M^+): 244.1019, found: 244.1013.

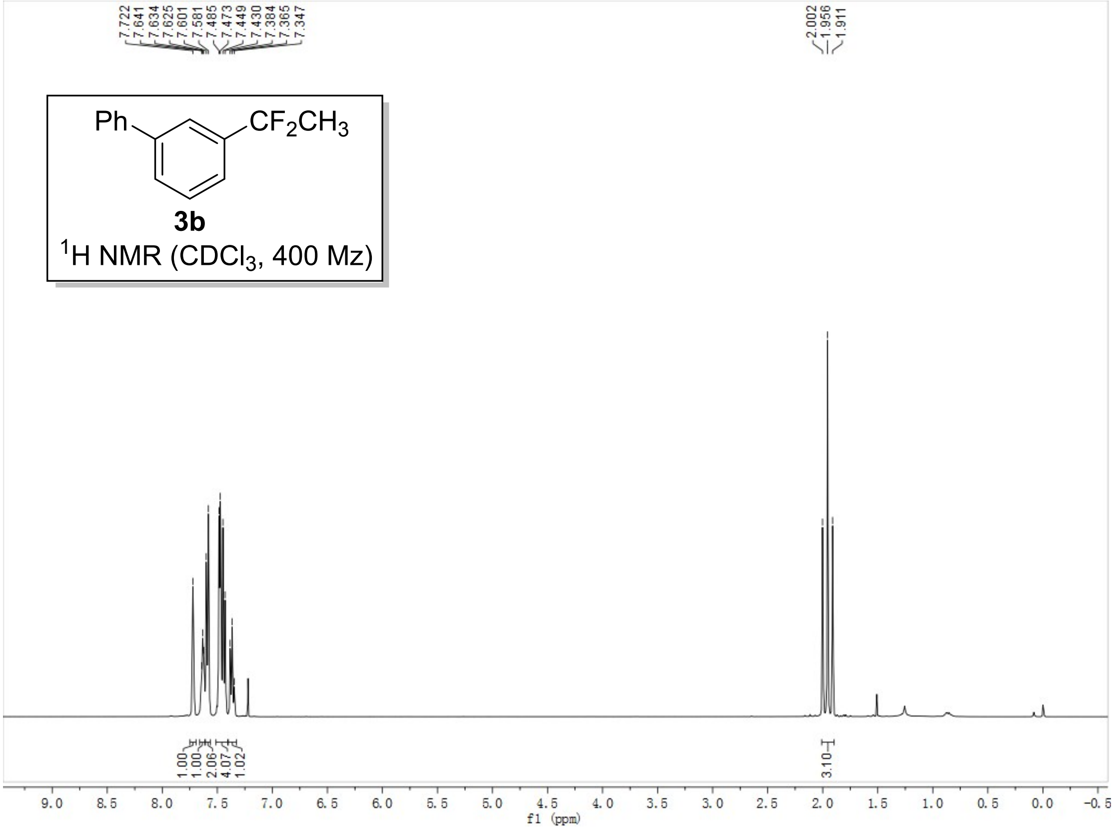
6. References

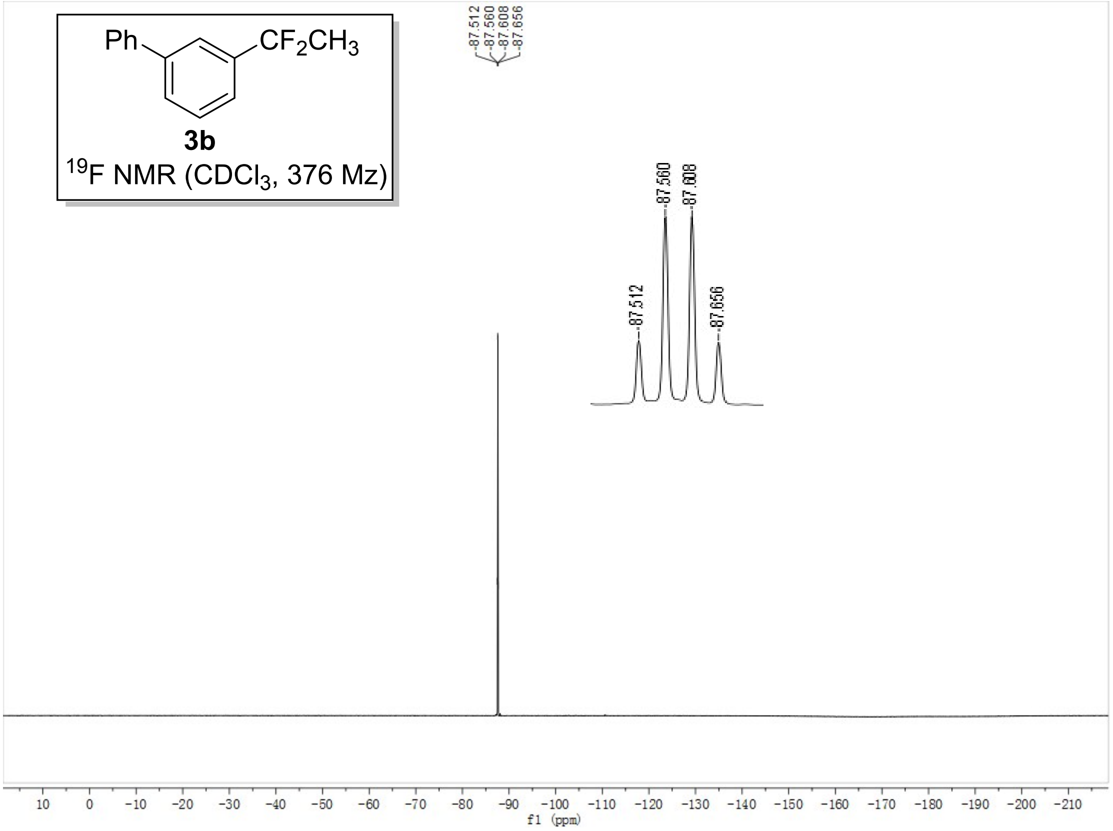
1. Saint-Jalmes, L. *J. Fluorine Chem*. **2006**, *127*, 85–90.
2. Xiao, Y.; Min, Q.; Xu, C.; Wang, R.; Zhang, X. *Angew. Chem., Int. Ed.* **2016,** *55*, 5837-5841.
3. An, L.; Xiao, Y.-L.; Zhang, S.; Zhang, X. *Angew. Chem., Int. Ed.* **2018**, *57*, 6921–6925.
4. Li, X.; Zhao, J.; Wang, Y.; Rong, J.; Hu, M.; Chen, D.; Hu, J. *Chem. — Asian J.* **2016**, *11*, 1789–1792.
5. Gu, J.; Guo, W.; Zhang, X. *Org. Chem. Front.* **2015**, *2*, 38–41.
6. Li, L.; Ni, C.; Xie, Q.; Hu, M.; Wang, F.; Hu, J. *Angew. Chem., Int. Ed.* **2017**, *56*, 9971–9975.
7. Pan, F.; Boursalian, G.; Ritter, T. *Angew. Chem., Int. Ed.* **2018**, *57*, 16871–16876.
8. Yang, Y.; Cai, J.; Luo, G.; Tong, X.; Su, Y.; Jiang, Y ; Li, C. .*Tetrahedron.* **2019**, *60*, 1130–1134.

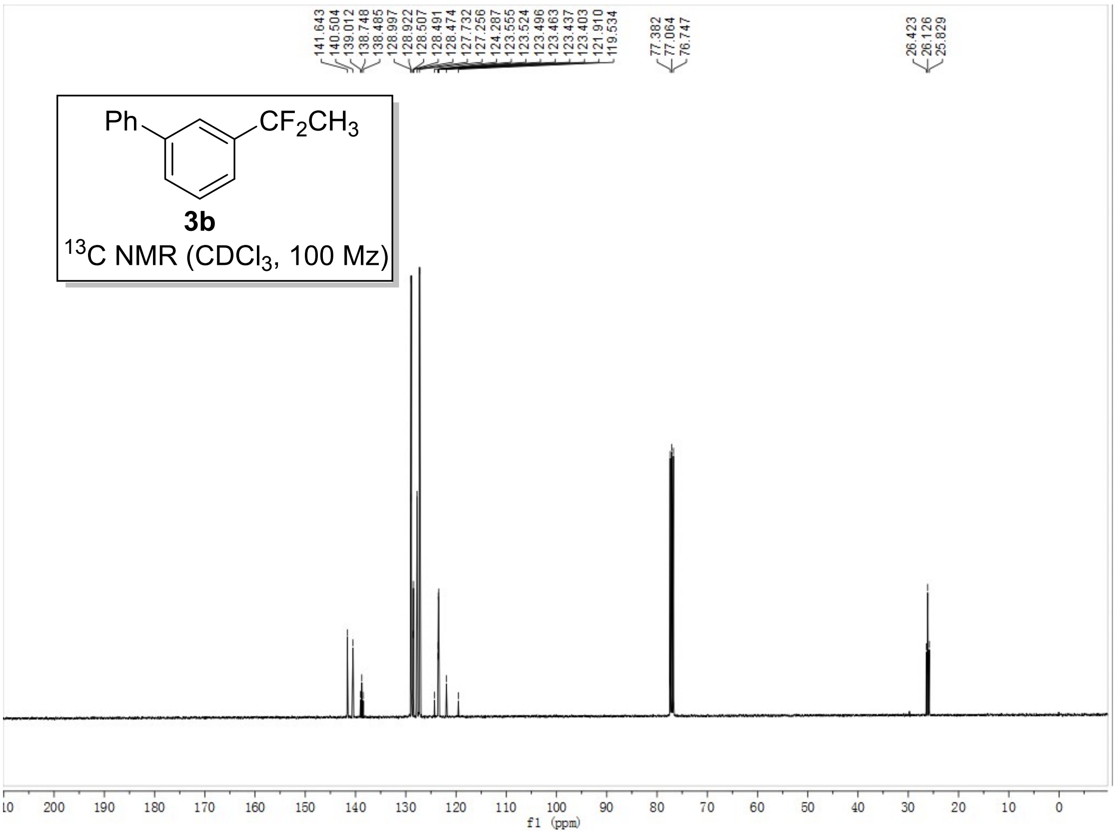
7. ^{1}H, ^{19}F and ^{13}C NMR Spectra of Isolated Products

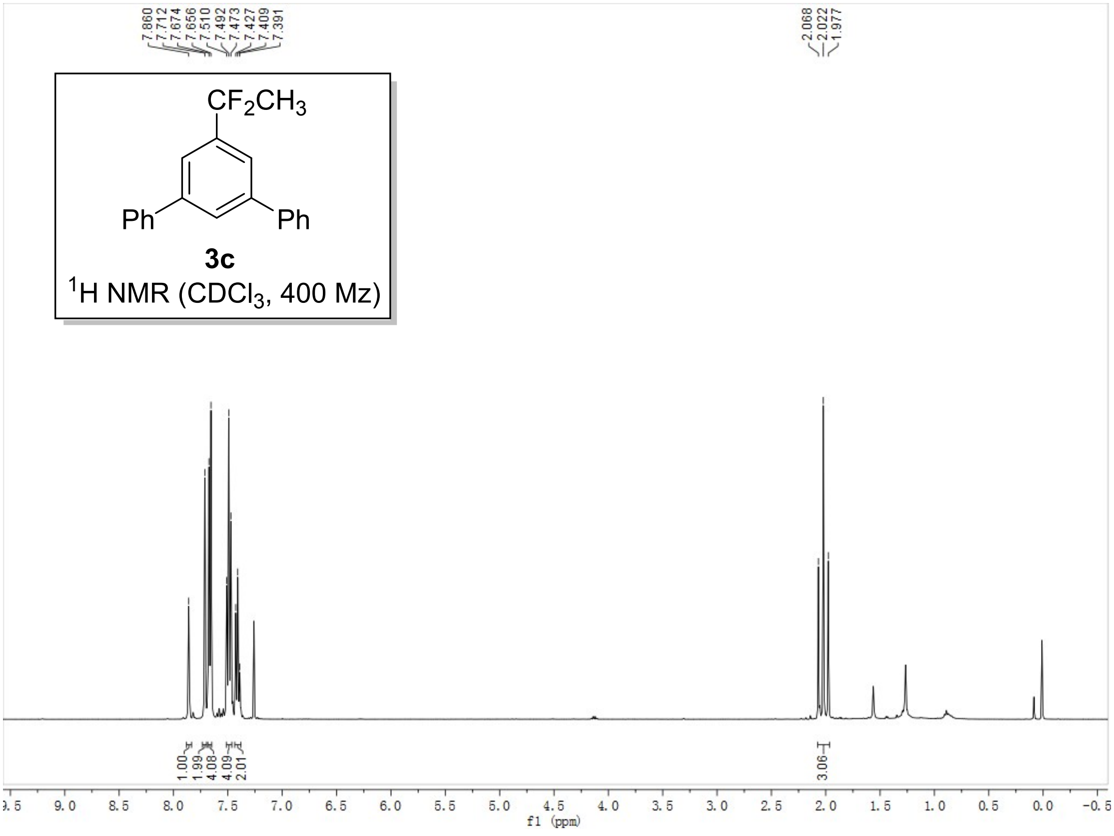


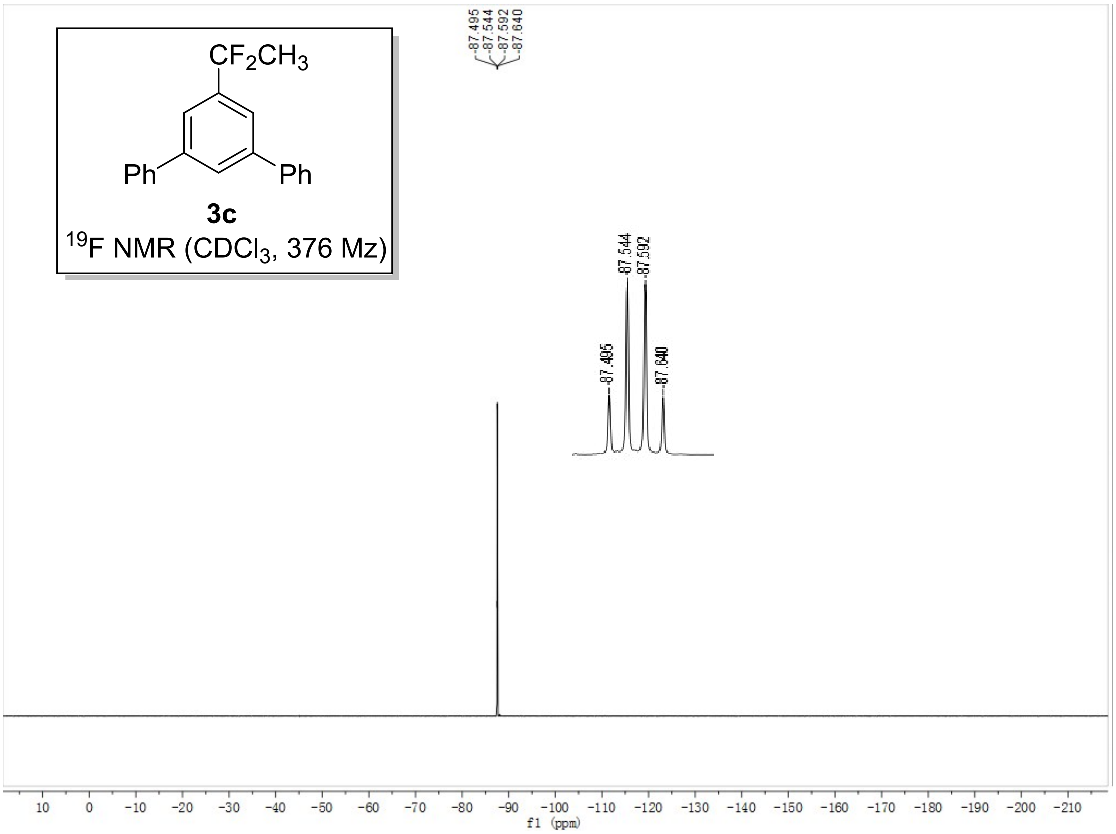


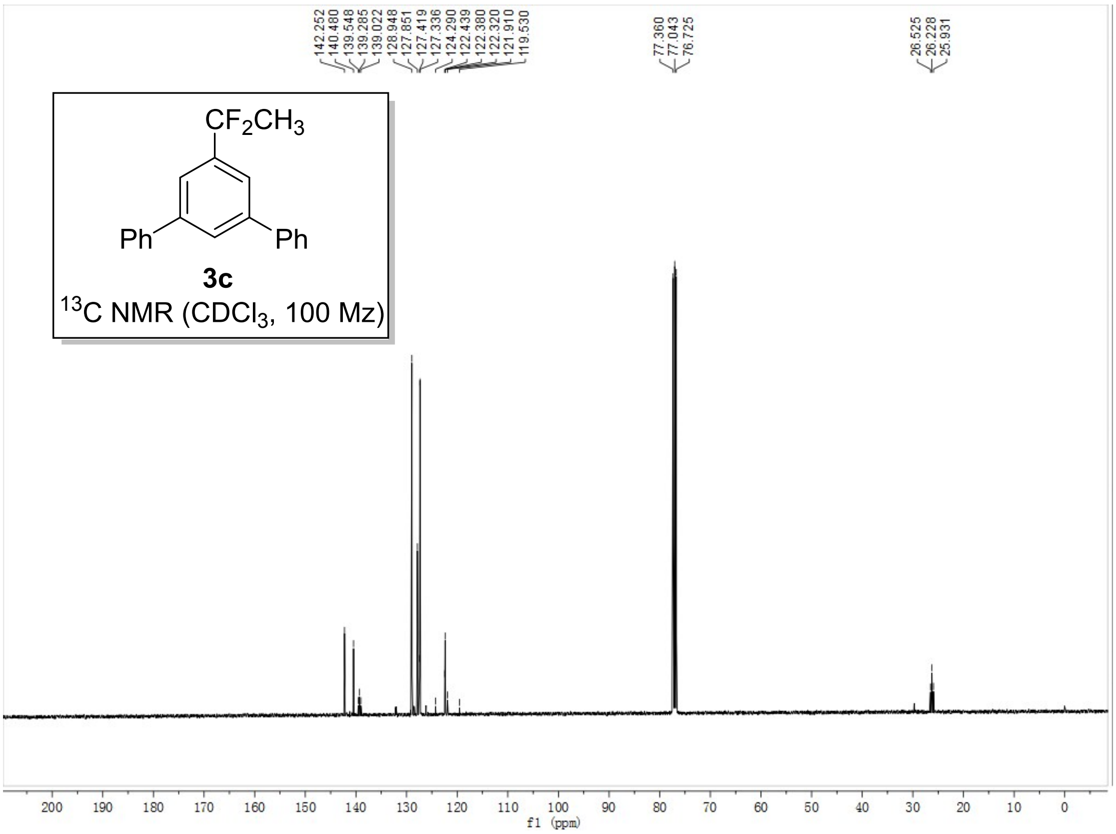

7.722
7.641
7.634
7.625
7.601
7.581
7.485
7.473
7.449
7.430
7.384
7.365
7.347
2.002
1.956
1.911
Ph
CF2CH3
3b
1H NMR (CDCl3, 400 Mz)
1.00
1.00
2.06
4.07
1.02
3.10
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

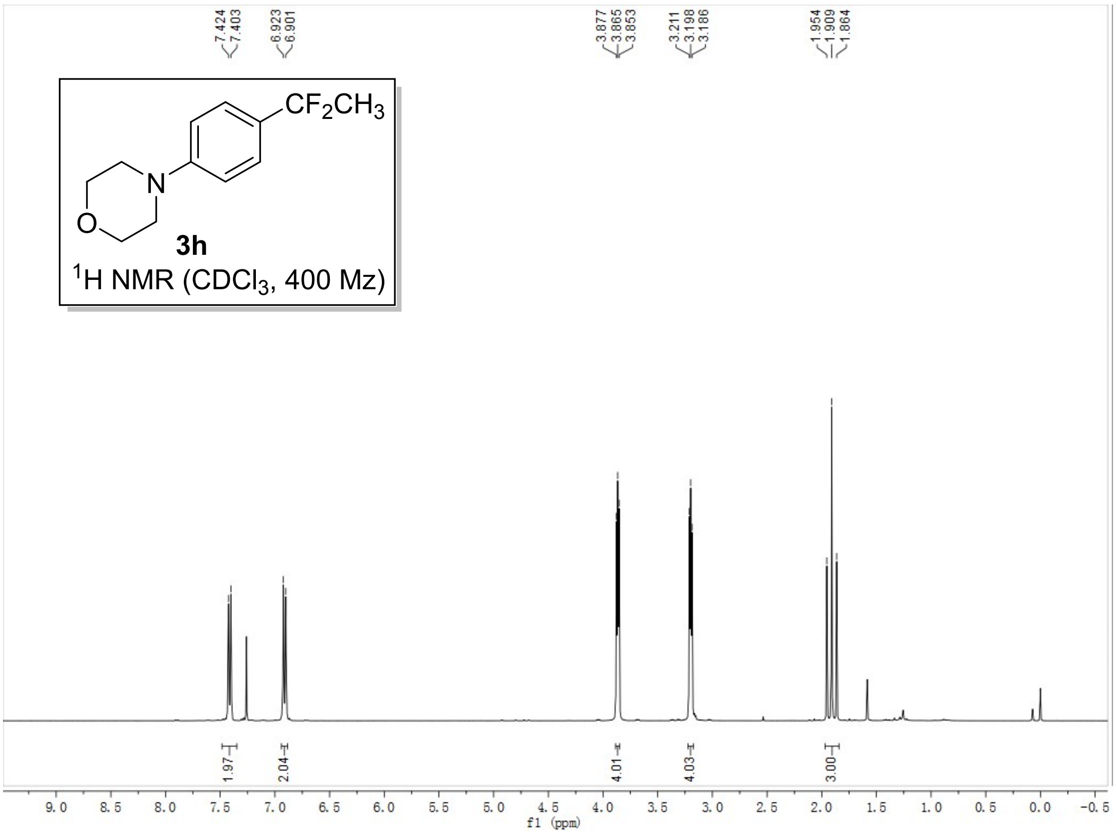

Ph
CF2CH3
3b
19F NMR (CDCl3, 376 Mz)
-87.512
-87.560
-87.608
-87.656
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

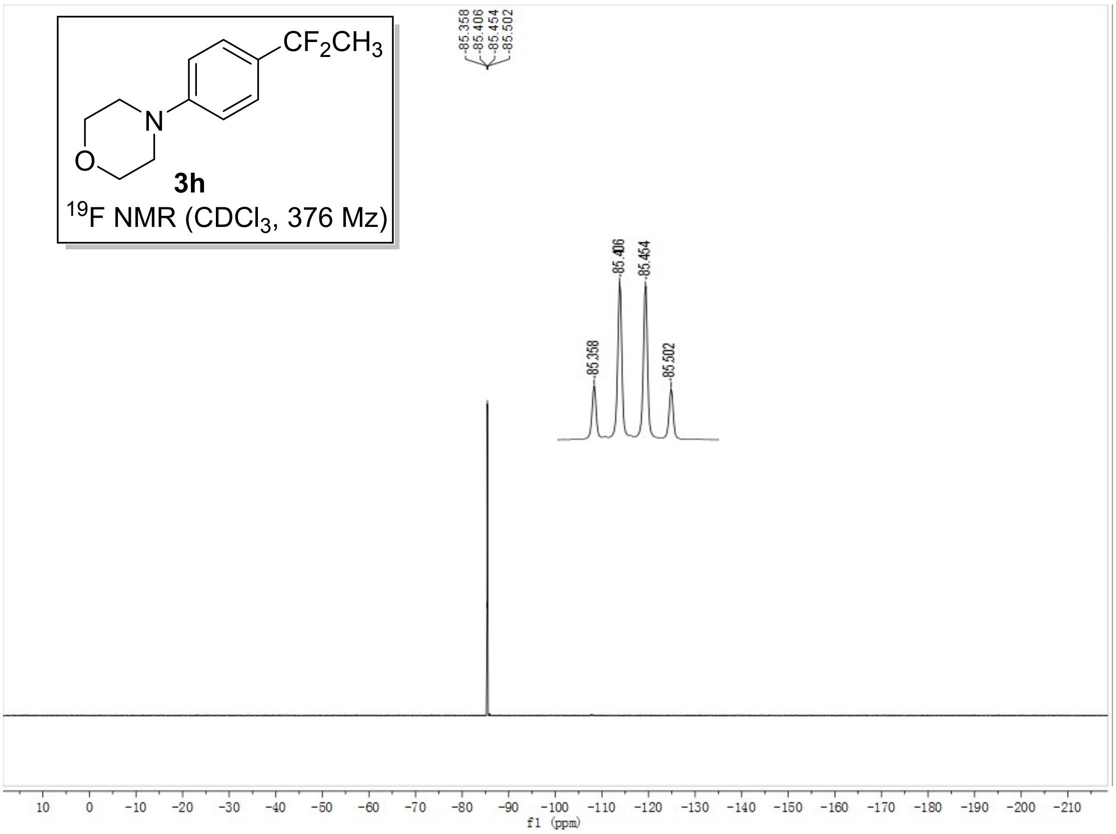

141.643
140.504
139.012
138.748
138.485
128.997
128.922
128.507
128.491
128.474
127.732
127.256
124.287
123.555
123.524
123.496
123.463
123.437
123.403
121.910
119.534
77.382
77.064
76.747
26.423
26.126
25.829
Ph
CF2CH3
3b
13C NMR (CDCl3, 100 Mz)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

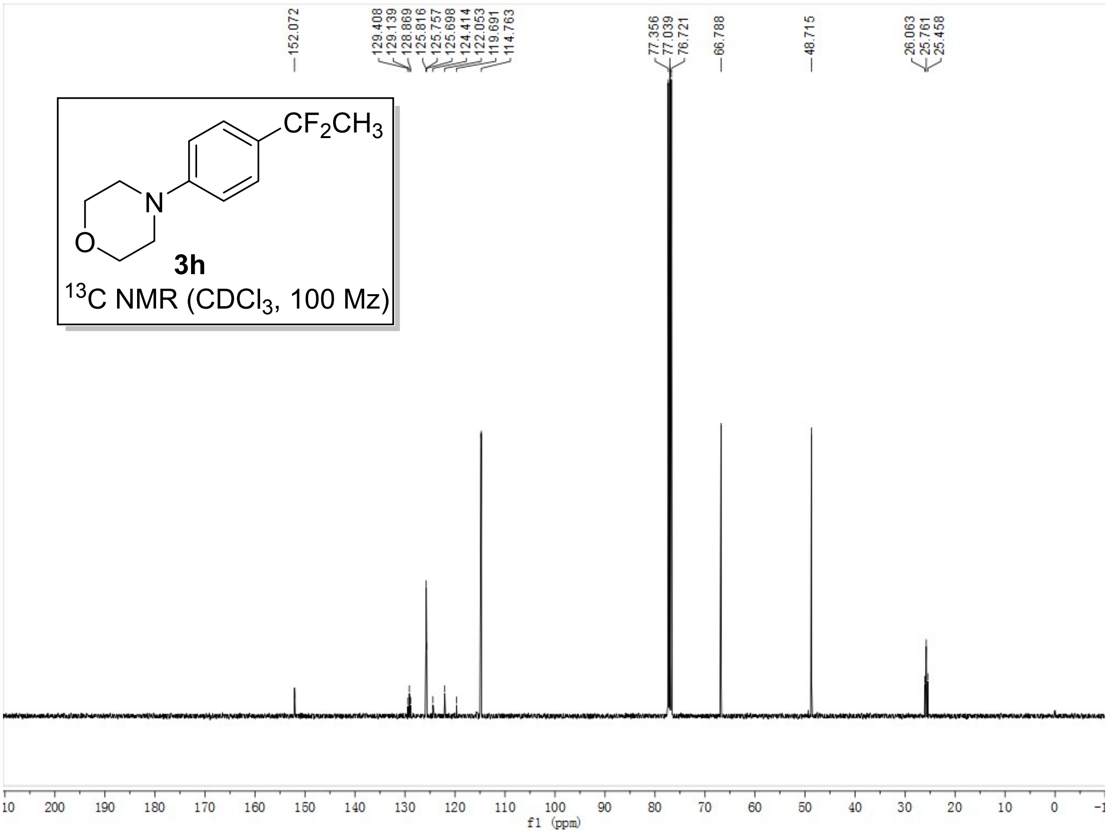

7.860
7.712
7.674
7.656
7.510
7.492
7.473
7.427
7.409
7.391
2.068
2.022
1.977
CF2CH3
Ph
Ph
3c
1H NMR (CDCl3, 400 Mz)
1.00
1.99
4.08
4.09
2.01
3.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

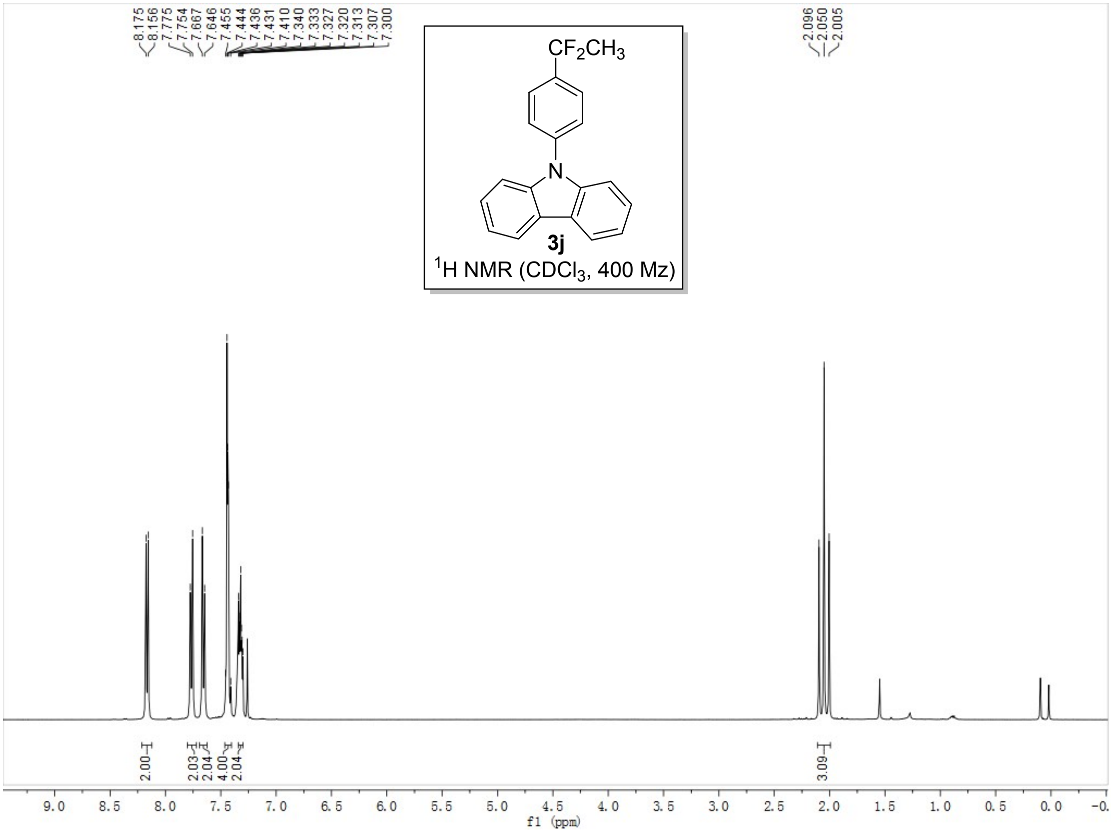

-87.495
-87.544
-87.592
-87.640
CF_2CH_3
Ph
Ph
3c
^{19}F NMR ($CDCl_3$, 376 Mz)
-87.495
-87.544
-87.592
-87.640
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

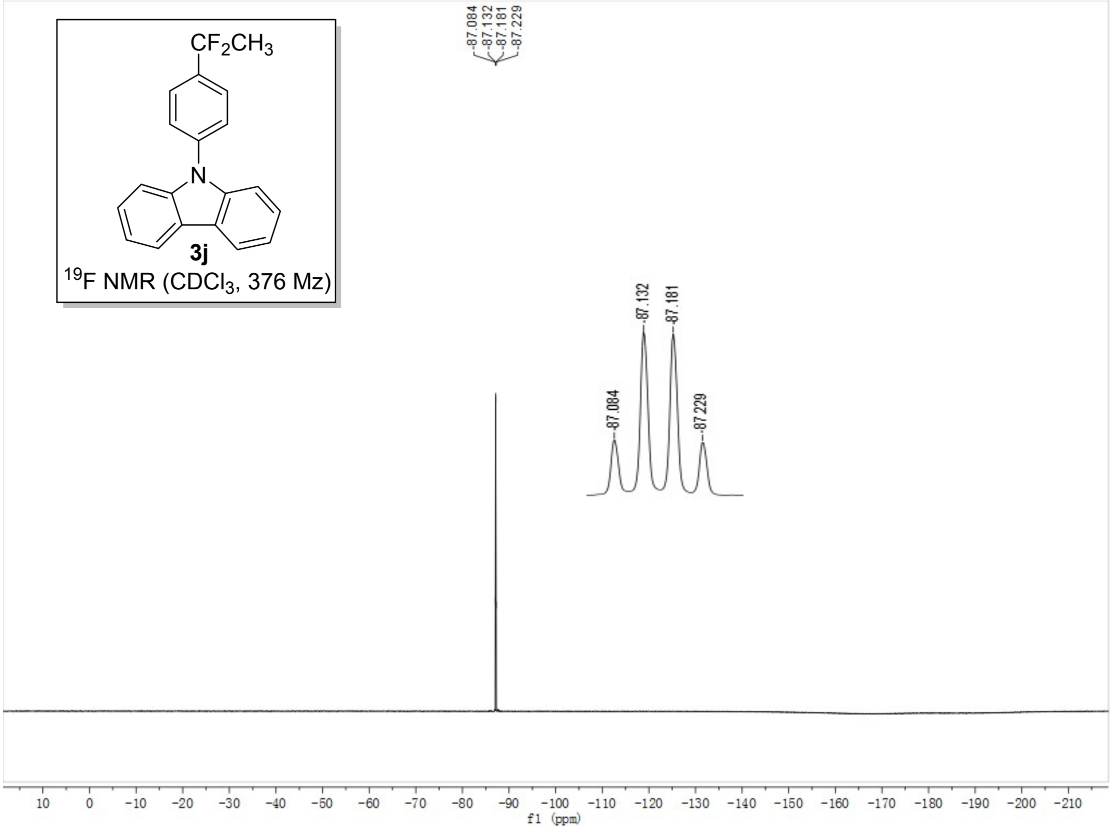

142.252
140.480
139.548
139.285
139.022
128.948
127.851
127.419
127.336
124.290
122.439
122.380
122.320
121.910
119.530
77.360
77.043
76.725
26.525
26.228
25.931
CF_2CH_3
Ph
Ph
3c
^{13}C NMR ($CDCl_3$, 100 Mz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

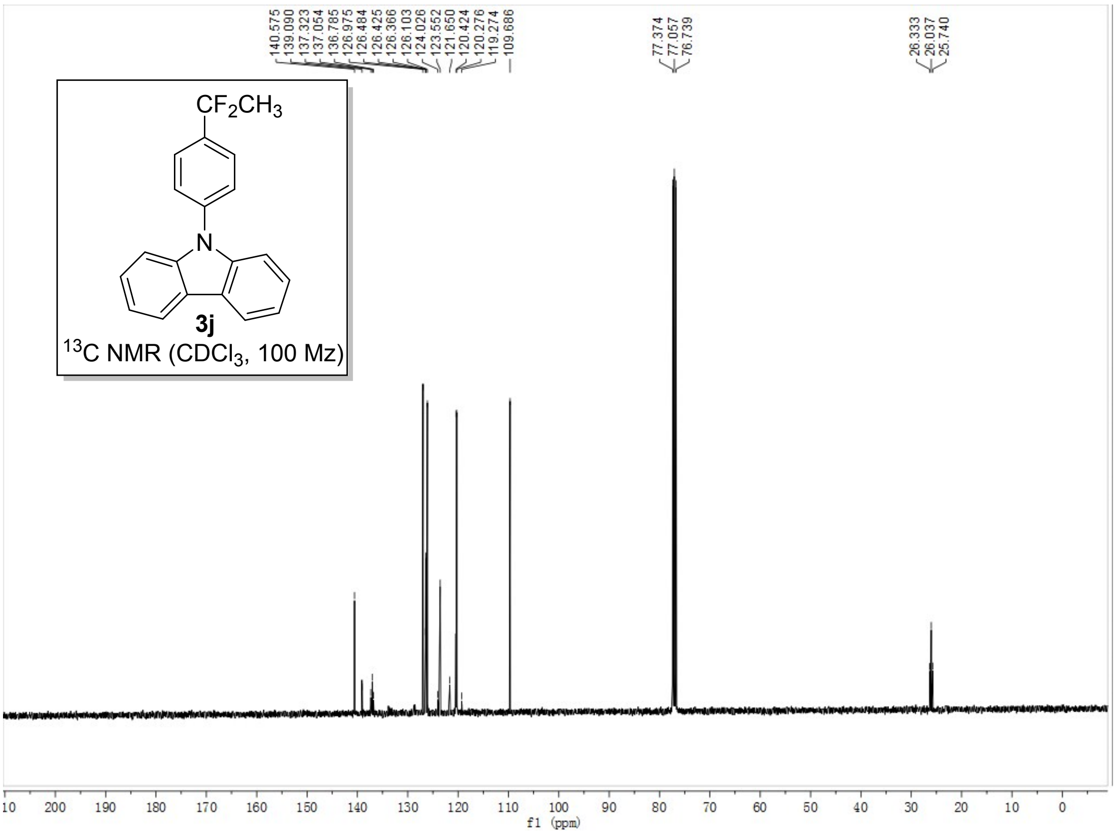

7.424
7.403
6.923
6.901
3.877
3.865
3.853
3.211
3.198
3.186
1.954
1.909
1.864
CF2CH3
N
O
3h
1H NMR (CDCl3, 400 Mz)
1.97
2.04
4.01
4.03
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

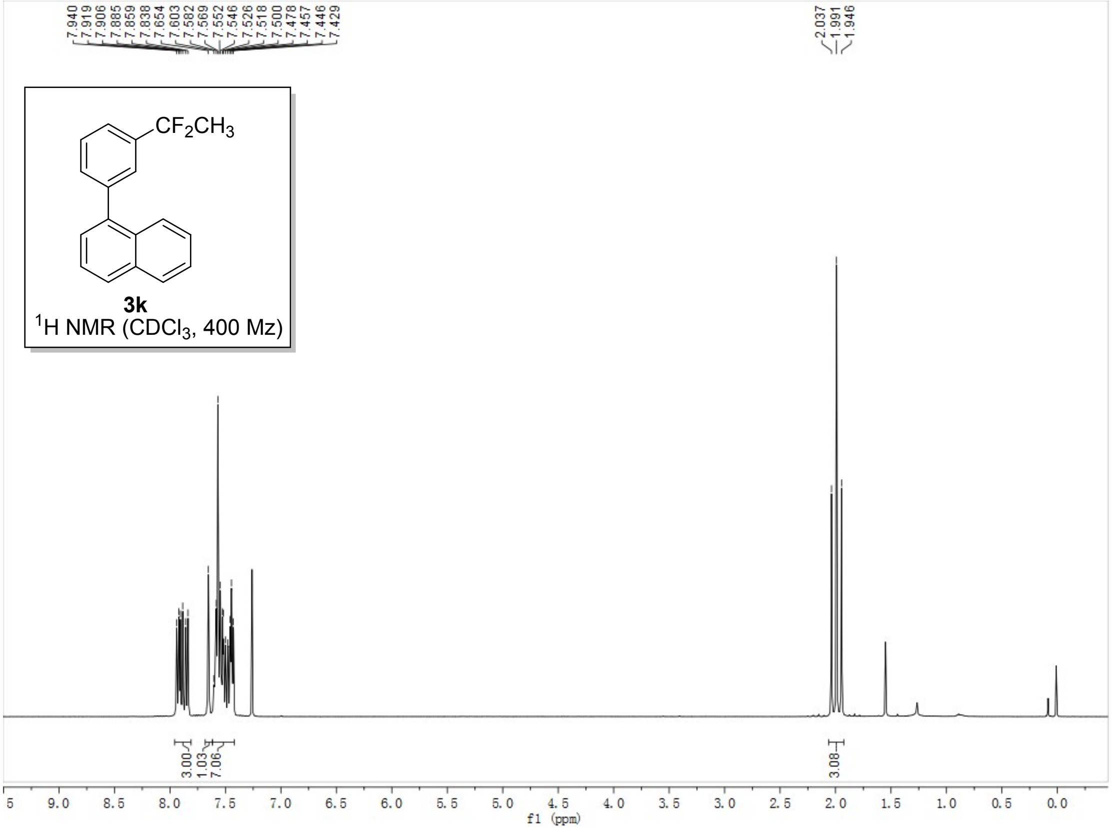

-85.358
-85.406
-85.454
-85.502
CF2CH3
N
O
3h
19F NMR (CDCl3, 376 Mz)
-85.358
-85.406
-85.454
-85.502
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

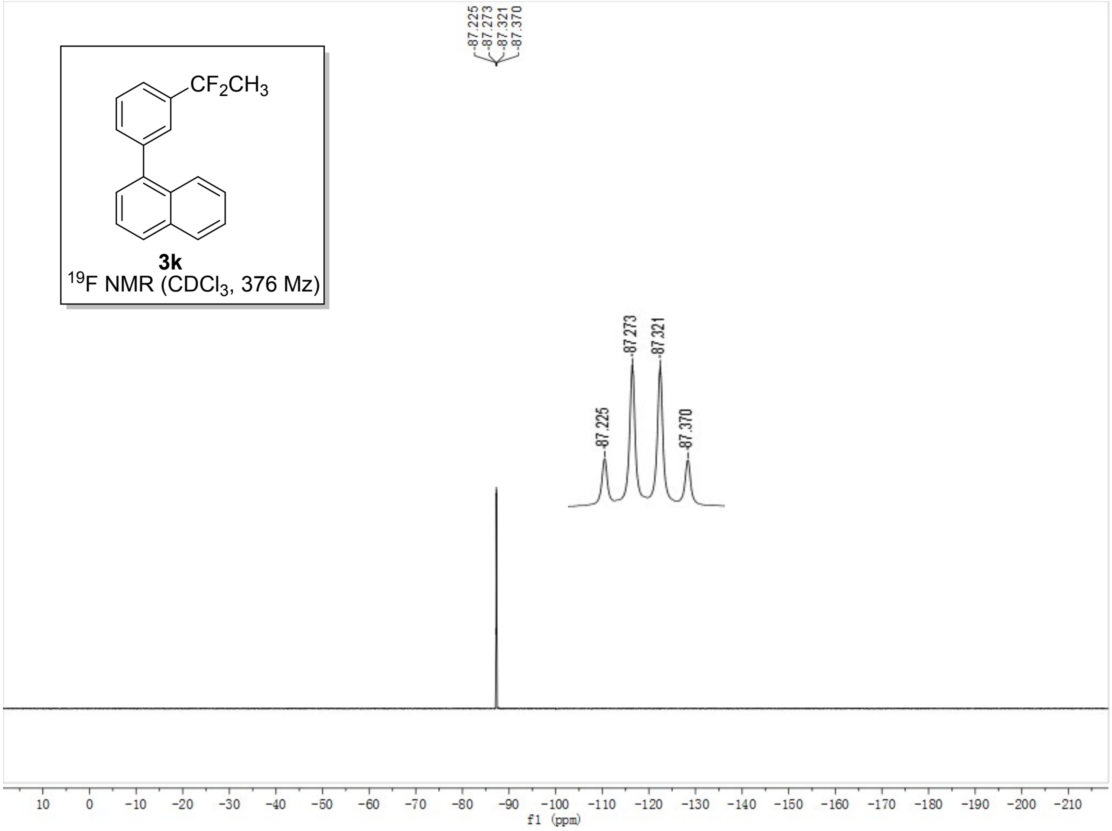

152.072
129.408
129.139
128.869
125.816
125.757
125.698
124.414
122.053
119.691
114.763
77.356
77.039
76.721
66.788
48.715
26.063
25.761
25.458
CF2CH3
N
O
3h
13C NMR (CDCl3, 100 Mz)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

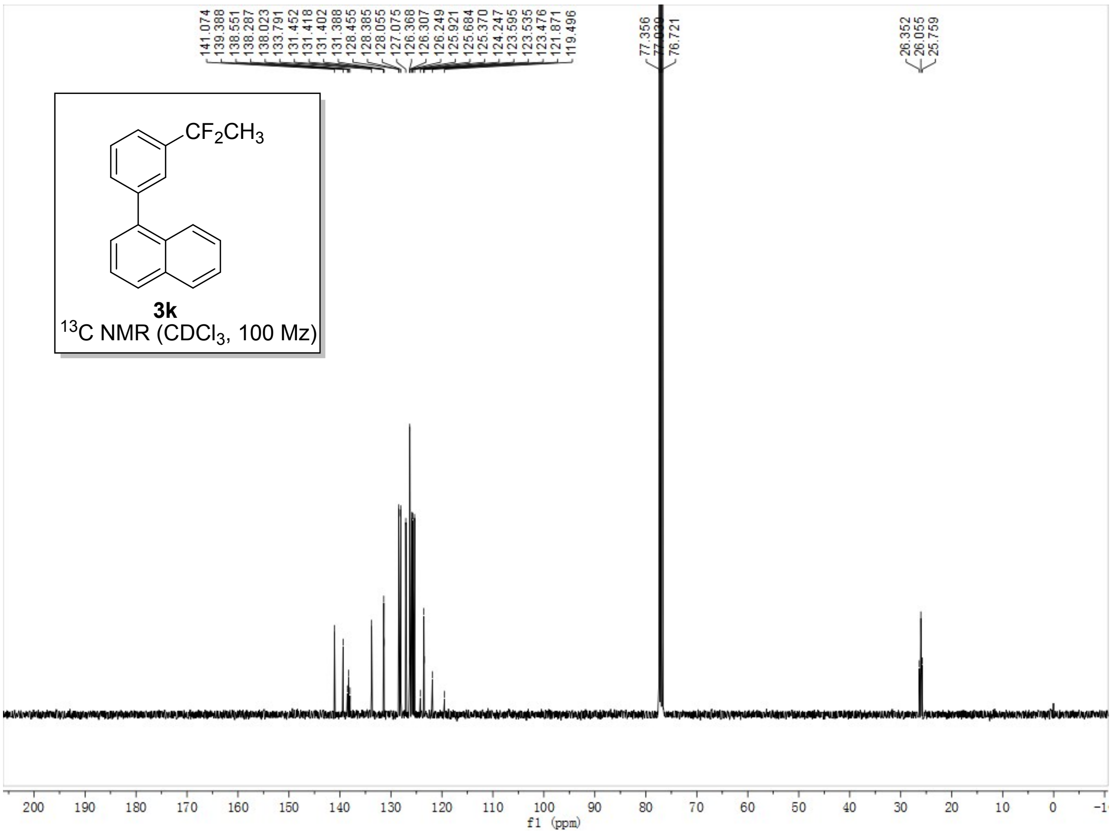

8.175
8.156
7.775
7.754
7.667
7.646
7.455
7.444
7.436
7.431
7.410
7.340
7.333
7.327
7.320
7.313
7.307
7.300
2.096
2.050
2.005
CF2CH3
N
3j
1H NMR (CDCl3, 400 Mz)
2.00
2.03
2.04
4.00
2.04
3.09
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)


-87.084
-87.132
-87.181
-87.229
CF_2CH_3
N
3j
^{19}F NMR ($CDCl_3$, 376 Mz)
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

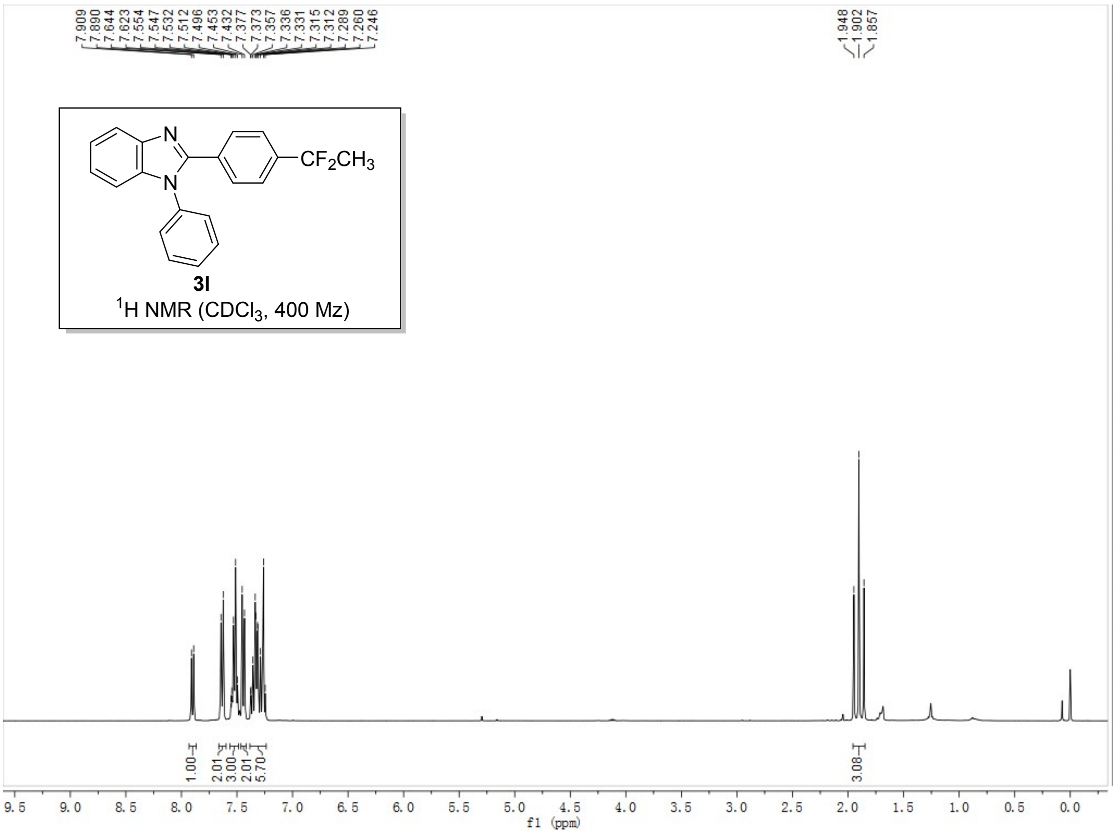

140.575
139.090
137.323
137.054
136.785
126.975
126.484
126.425
126.366
126.103
124.026
123.552
121.650
120.424
120.276
119.274
109.686
77.374
77.057
76.739
26.333
26.037
25.740
CF_2CH_3
N
3j
^{13}C NMR ($CDCl_3$, 100 Mz)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.940
7.919
7.906
7.885
7.859
7.838
7.654
7.603
7.582
7.569
7.552
7.546
7.526
7.518
7.500
7.478
7.457
7.446
7.429
2.037
1.991
1.946
CF$_2$CH$_3$
3k
^{1}H NMR (CDCl$_3$, 400 Mz)
3.00
1.03
7.06
3.08
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

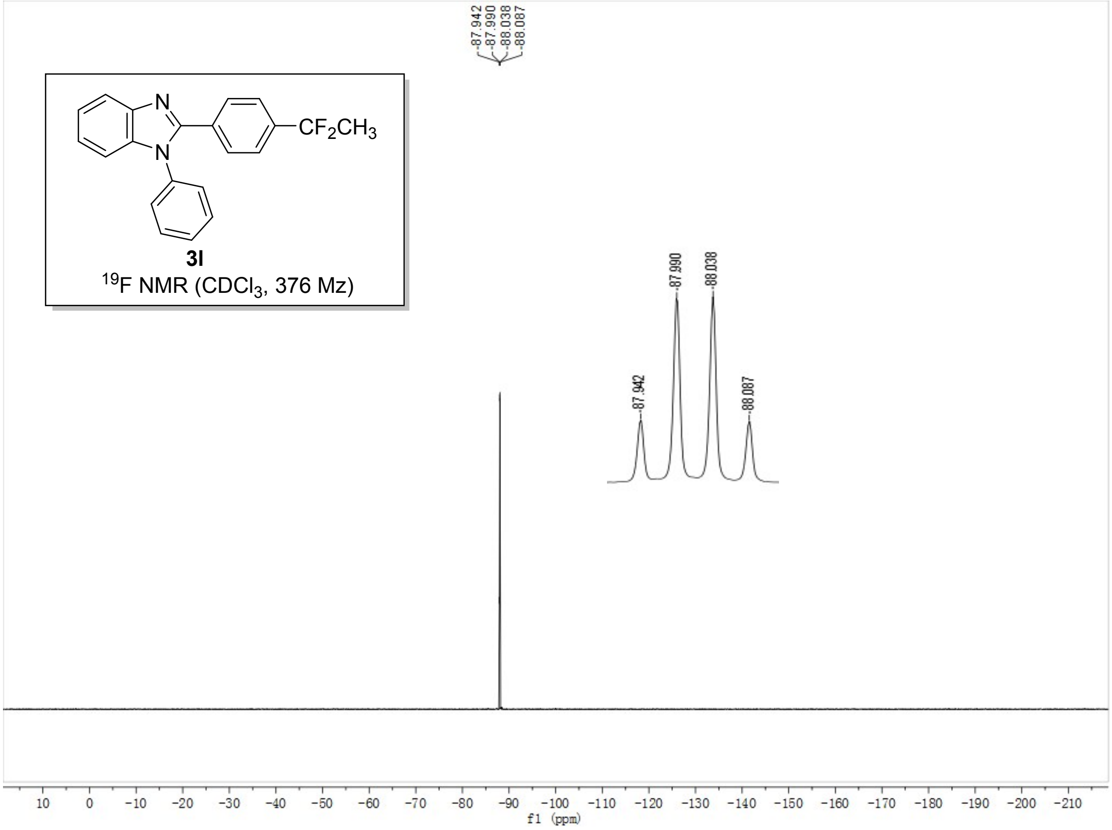

-87.225
-87.273
-87.321
-87.370
CF$_2$CH$_3$
3k
^{19}F NMR (CDCl$_3$, 376 Mz)
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)



3k
^{13}C NMR ($CDCl_3$, 100 Mz)

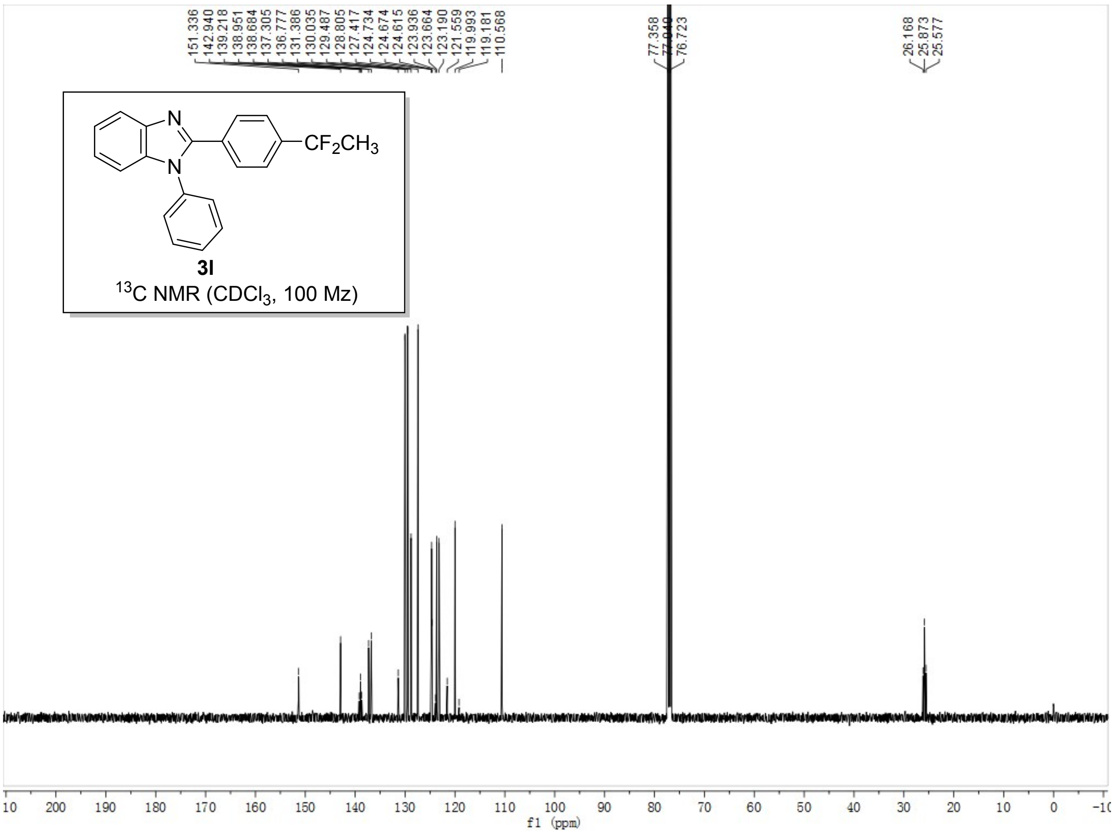


3l
^{1}H NMR ($CDCl_3$, 400 Mz)



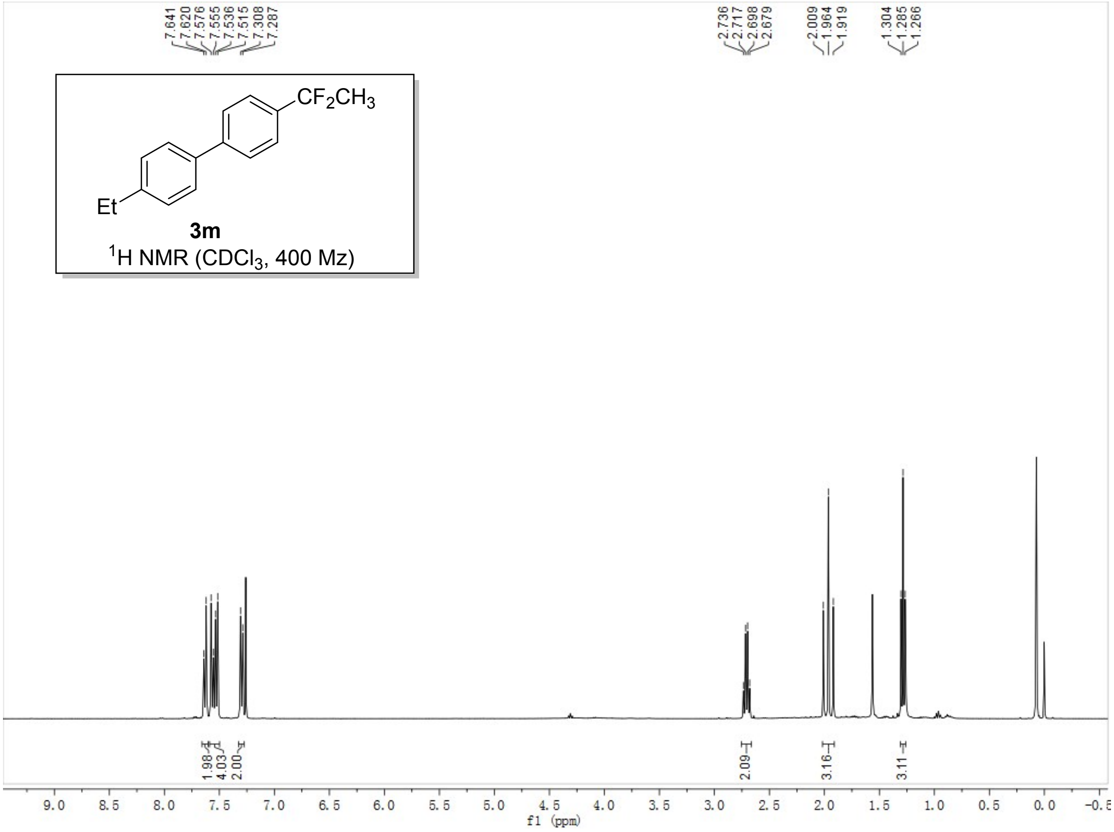
3l

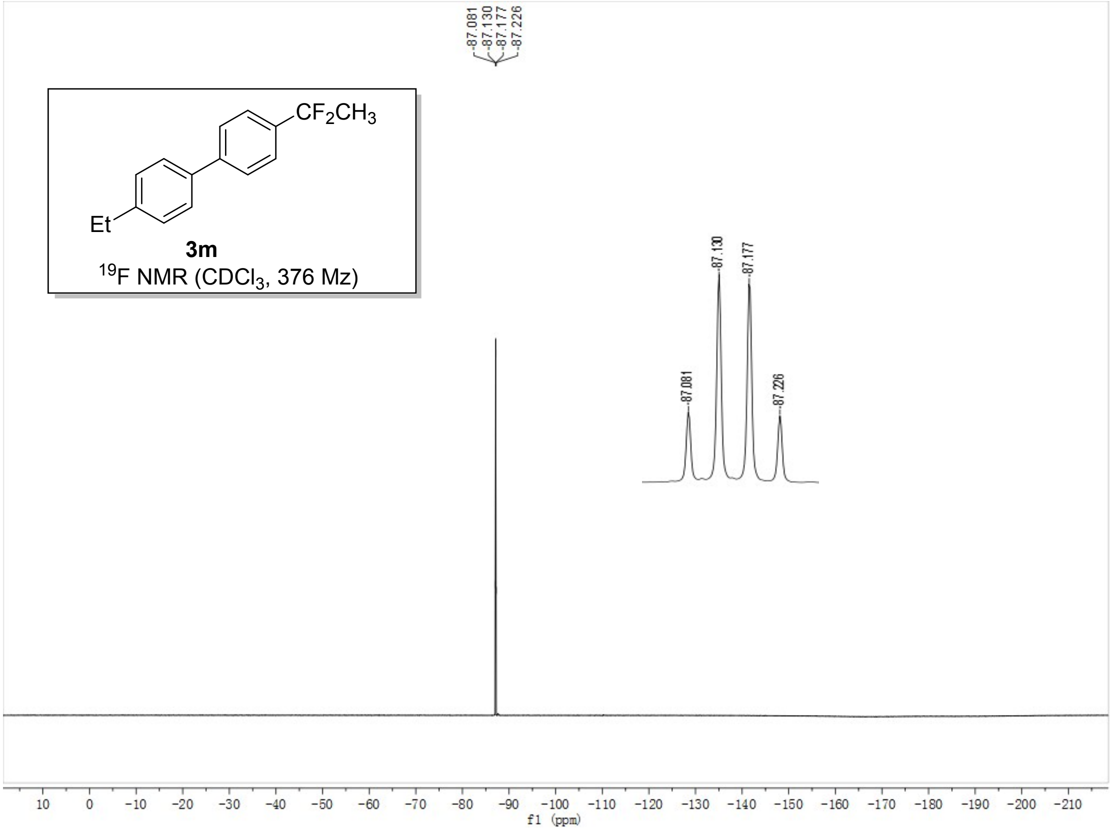
^{19}F NMR (CDCl$_3$, 376 Mz)

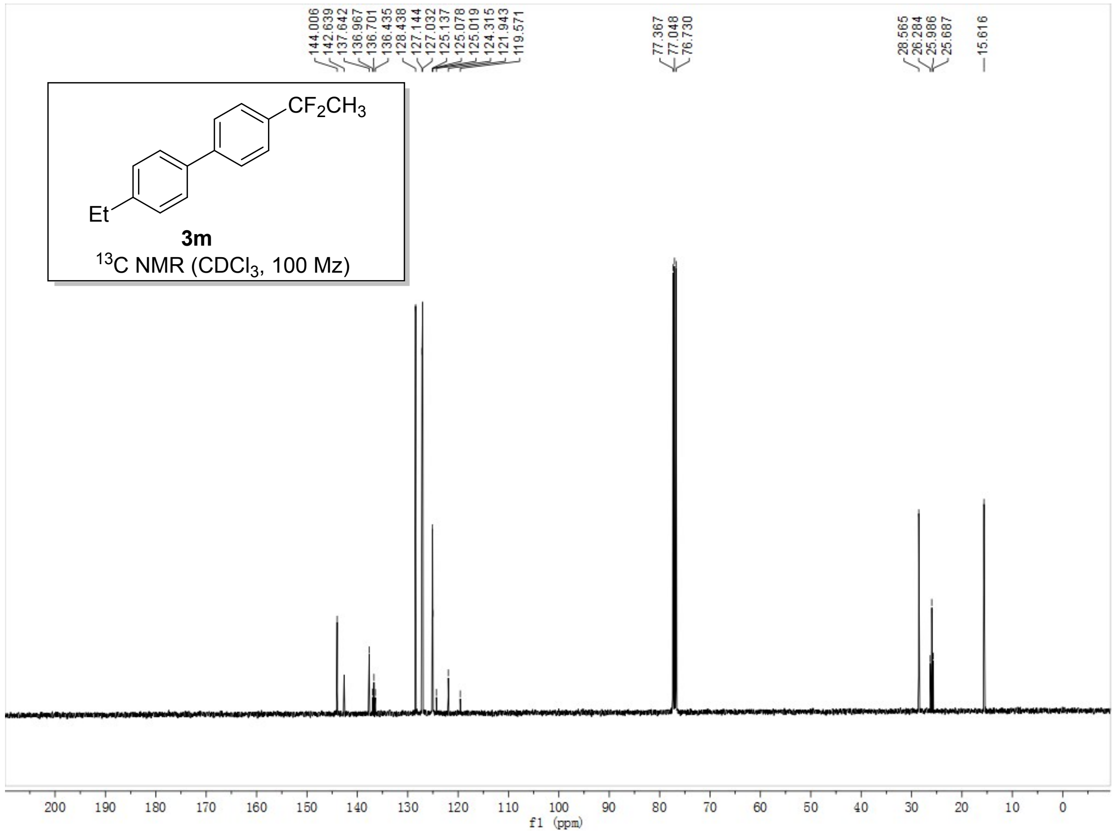


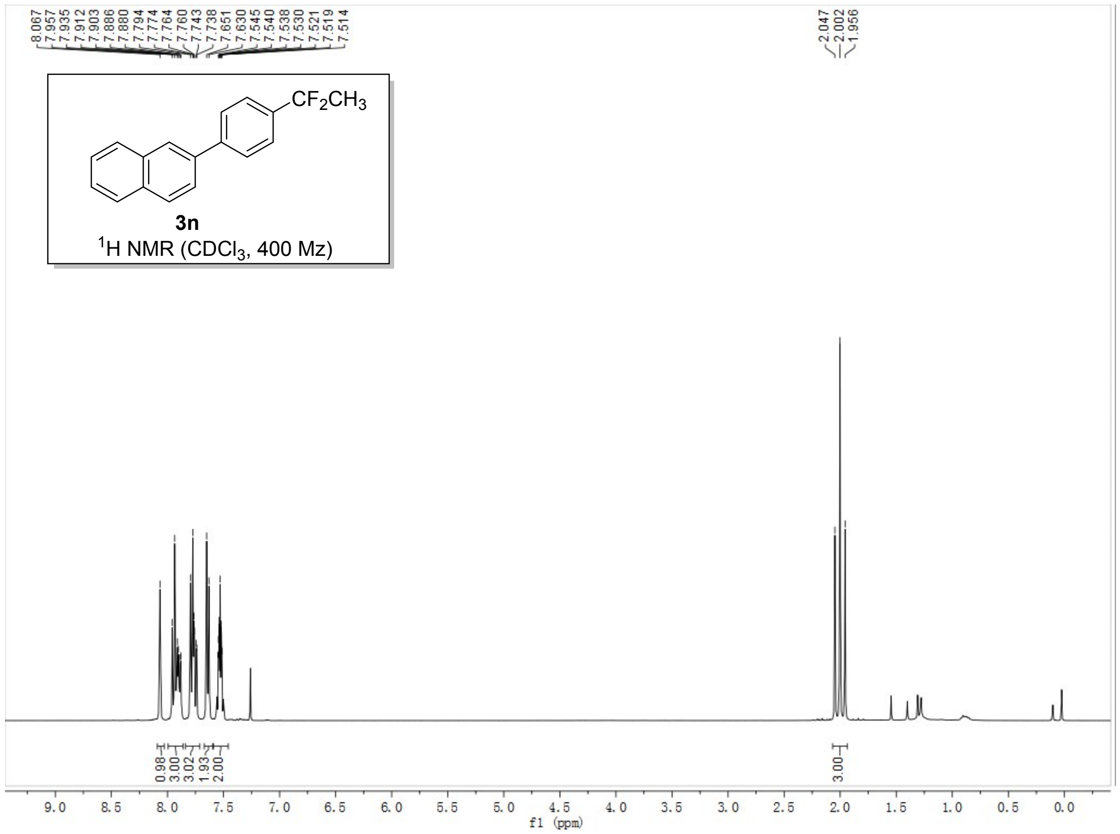
3l

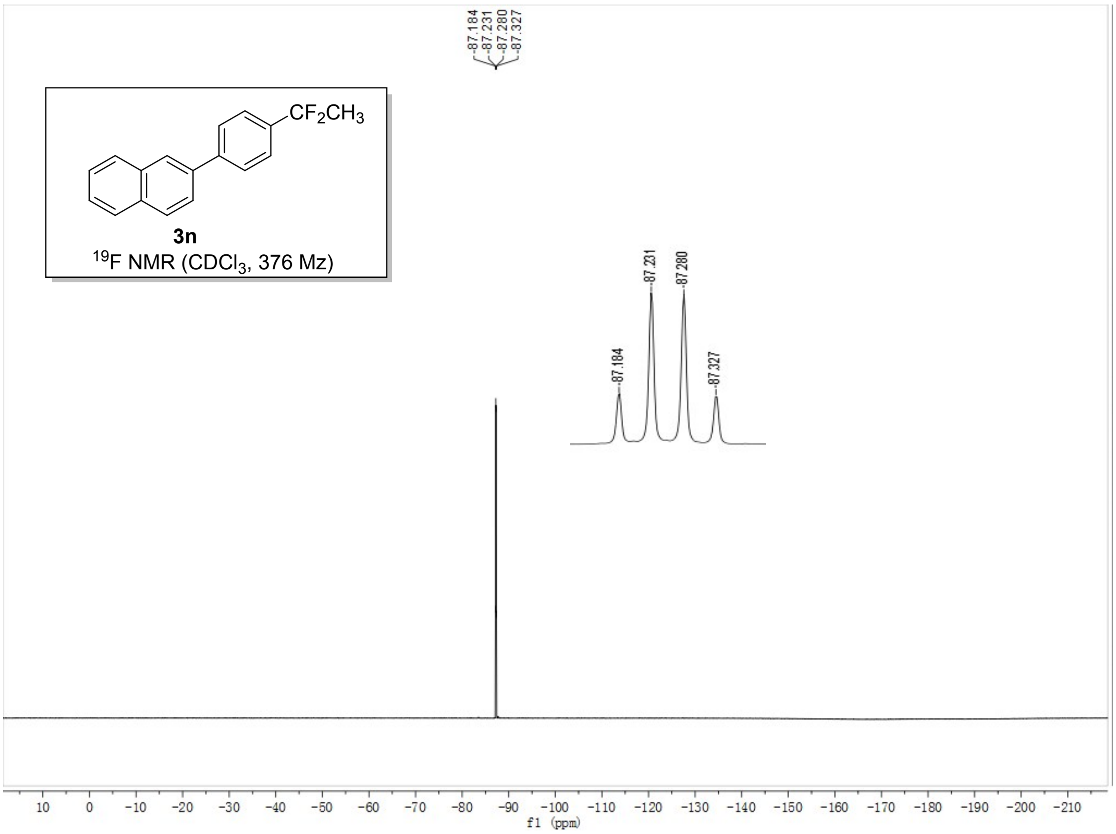
^{13}C NMR (CDCl$_3$, 100 Mz)

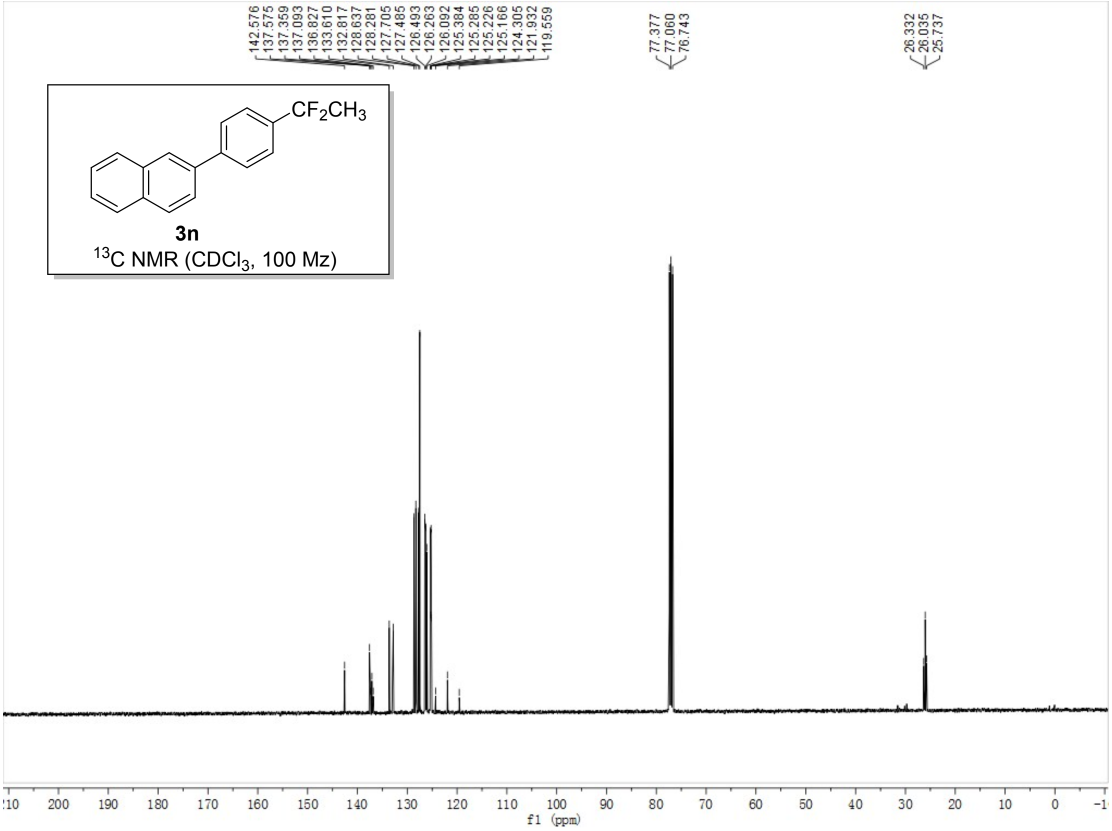

7.641
7.620
7.576
7.555
7.536
7.515
7.308
7.287
2.736
2.717
2.698
2.679
2.009
1.964
1.919
1.304
1.285
1.266
CF2CH3
Et
3m
1H NMR (CDCl3, 400 Mz)
1.98
4.03
2.00
2.09
3.16
3.11
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

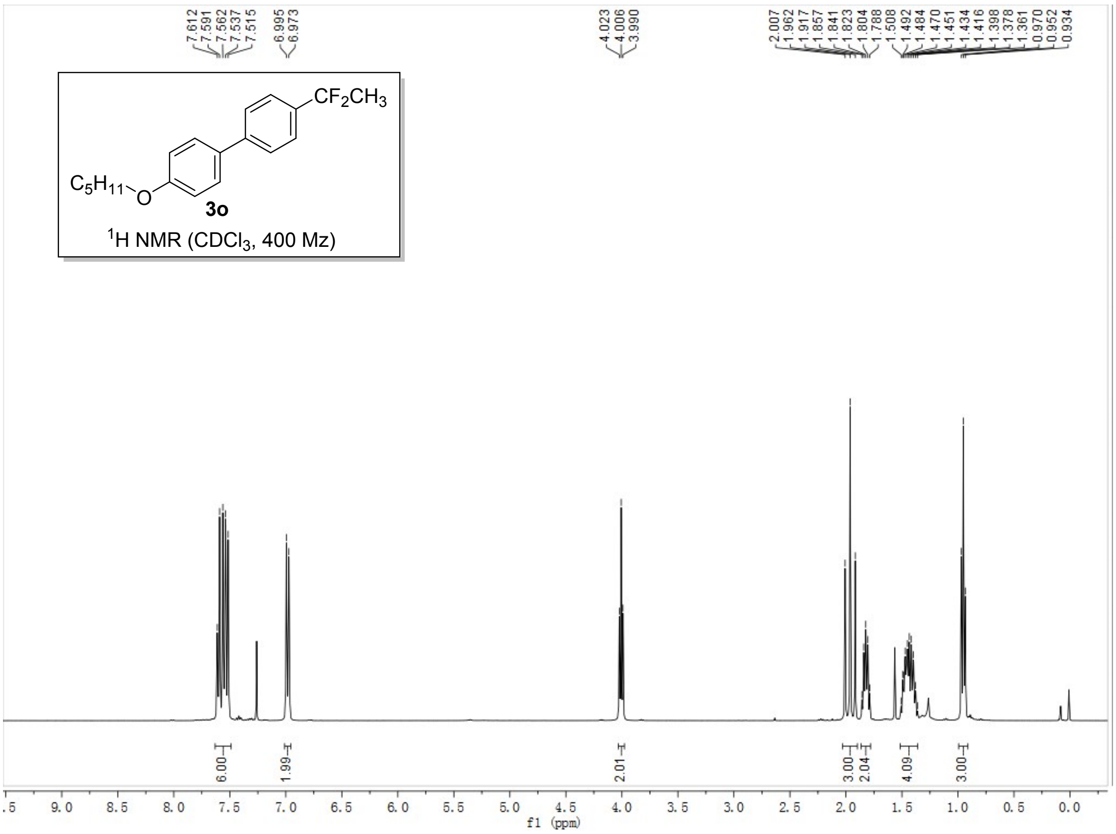

-87.081
-87.130
-87.177
-87.226
CF2CH3
Et
3m
19F NMR (CDCl3, 376 Mz)
-87.081
-87.130
-87.177
-87.226
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


144.006
142.639
137.642
136.967
136.701
136.435
128.438
127.144
127.032
125.137
125.078
125.019
124.315
121.943
119.571
77.367
77.048
76.730
28.565
26.284
25.986
25.687
15.616
CF2CH3
Et
3m
13C NMR (CDCl3, 100 Mz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.067
7.957
7.935
7.912
7.903
7.886
7.880
7.794
7.774
7.764
7.760
7.743
7.738
7.651
7.630
7.545
7.540
7.538
7.530
7.521
7.519
7.514
2.047
2.002
1.956
CF2CH3
3n
1H NMR (CDCl3, 400 Mz)
0.98
3.00
3.02
1.93
2.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

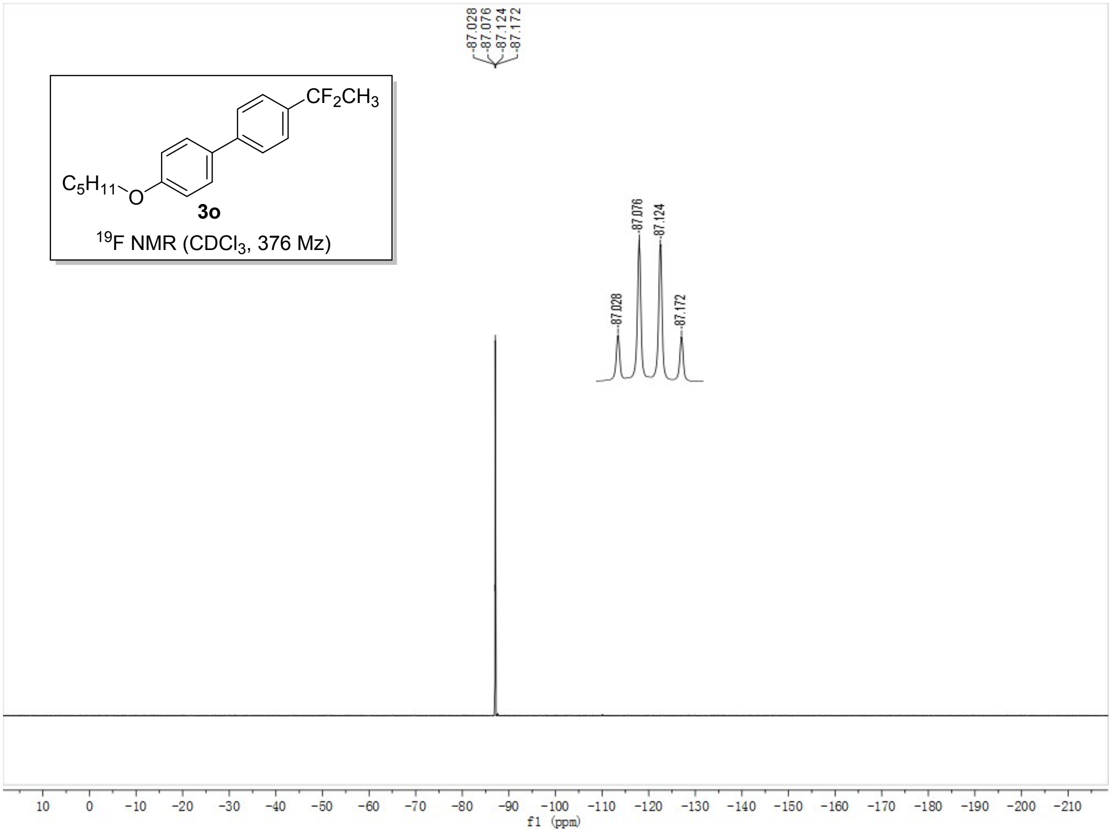

-87.184
-87.231
-87.280
-87.327
CF2CH3
3n
19F NMR (CDCl3, 376 Mz)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


142.576
137.575
137.359
137.093
136.827
133.610
132.817
128.637
128.281
127.705
127.485
126.493
126.263
126.092
125.384
125.285
125.226
125.166
124.305
121.932
119.559
77.377
77.060
76.743
26.332
26.035
25.737
CF2CH3
3n
13C NMR (CDCl3, 100 Mz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



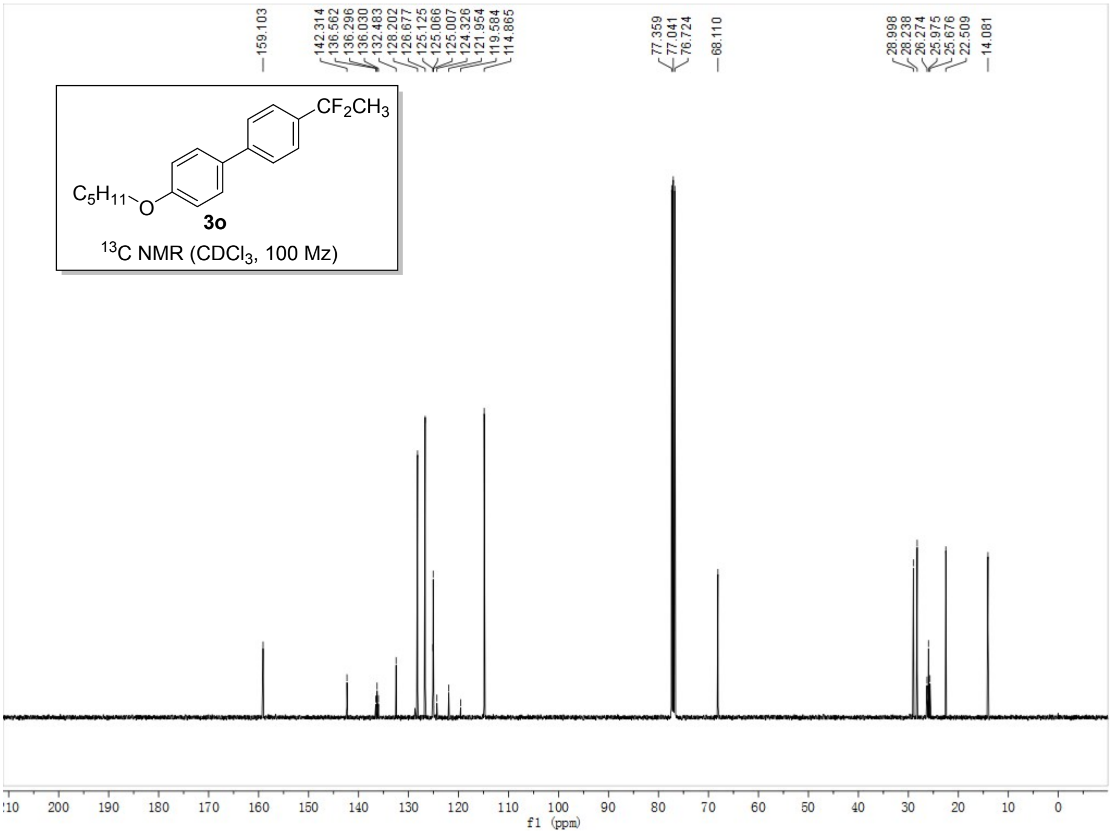
3o

^{1}H NMR (CDCl$_3$, 400 Mz)



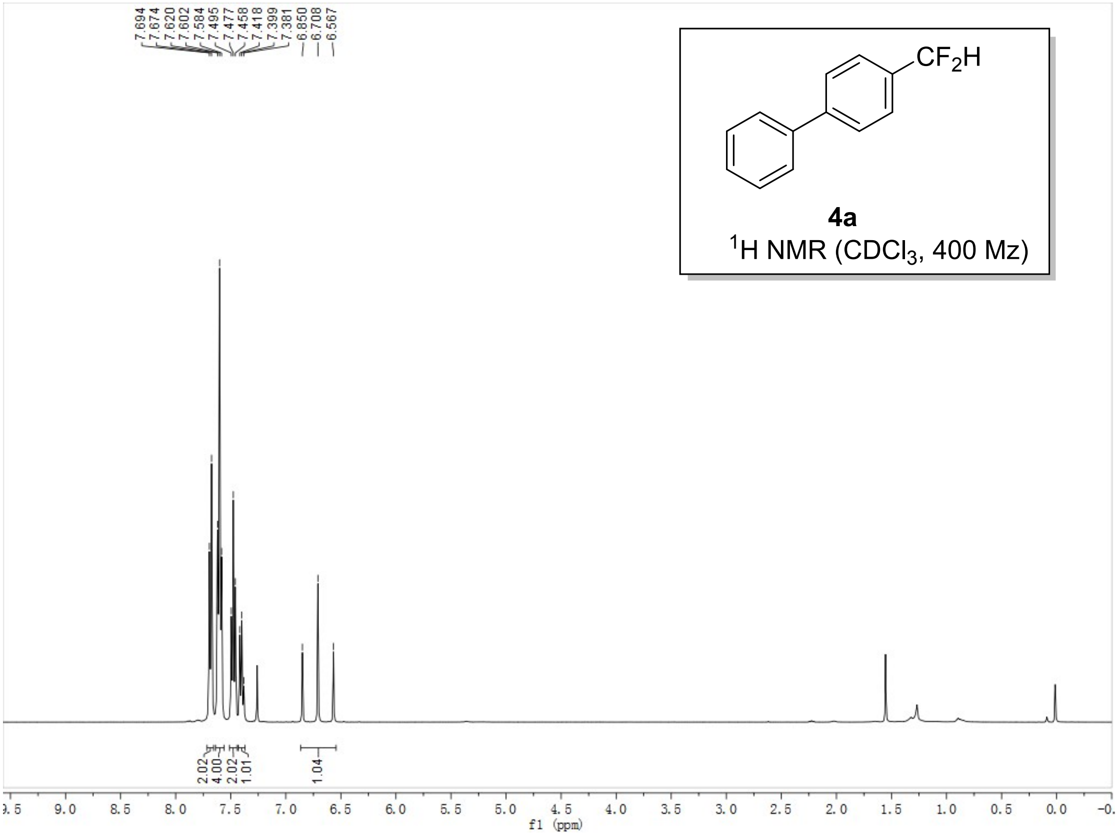
3o

^{19}F NMR (CDCl$_3$, 376 Mz)



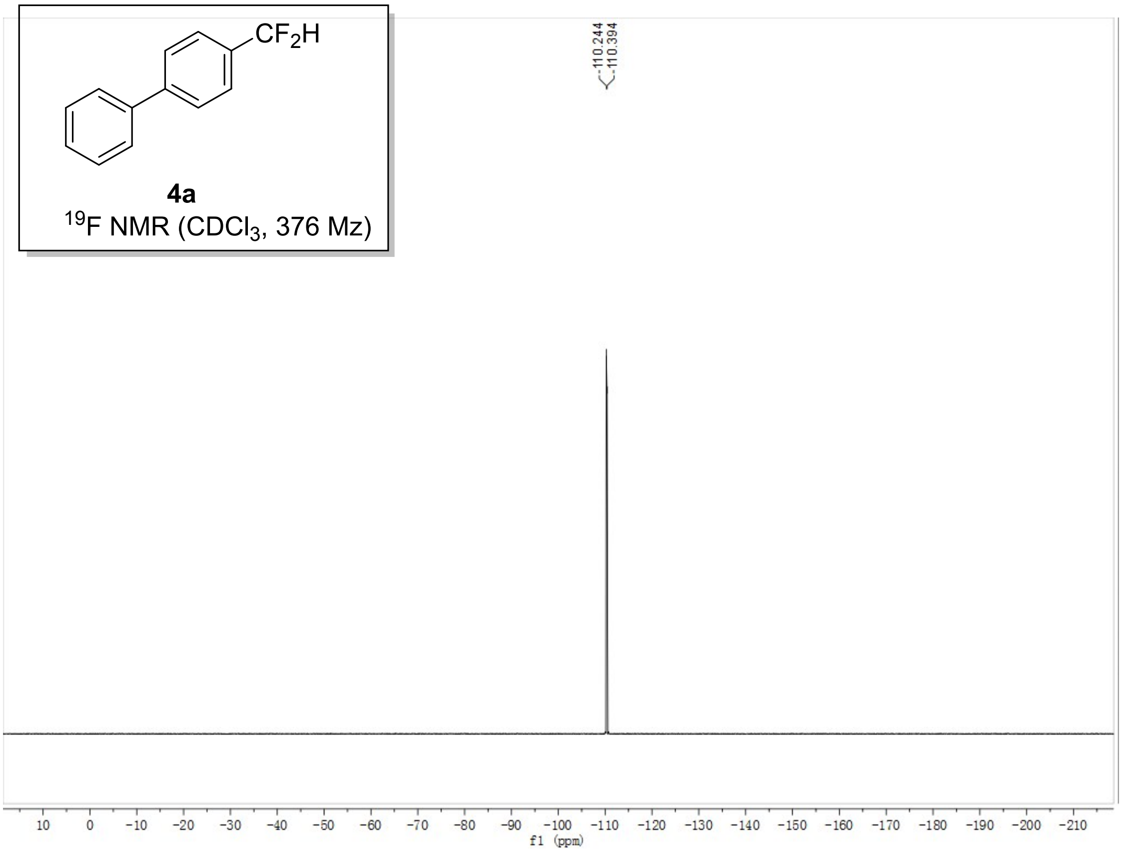
3o

^{13}C NMR (CDCl$_3$, 100 Mz)



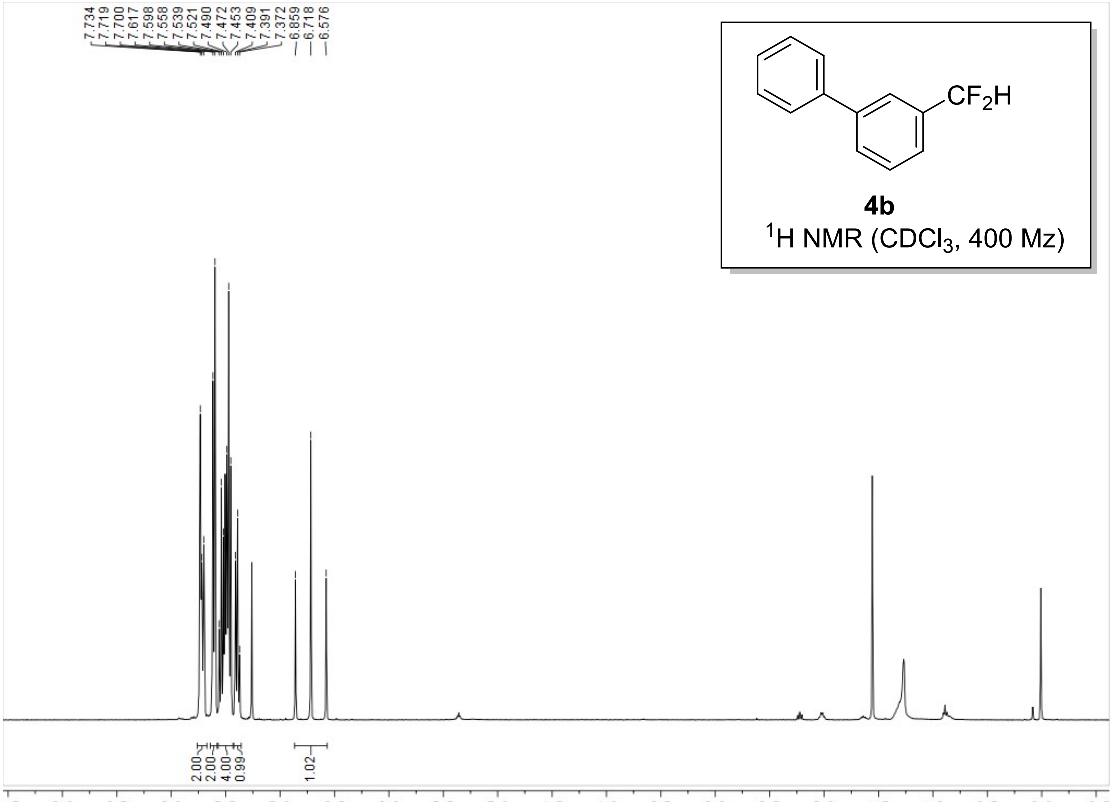
4a

^{1}H NMR (CDCl$_3$, 400 Mz)



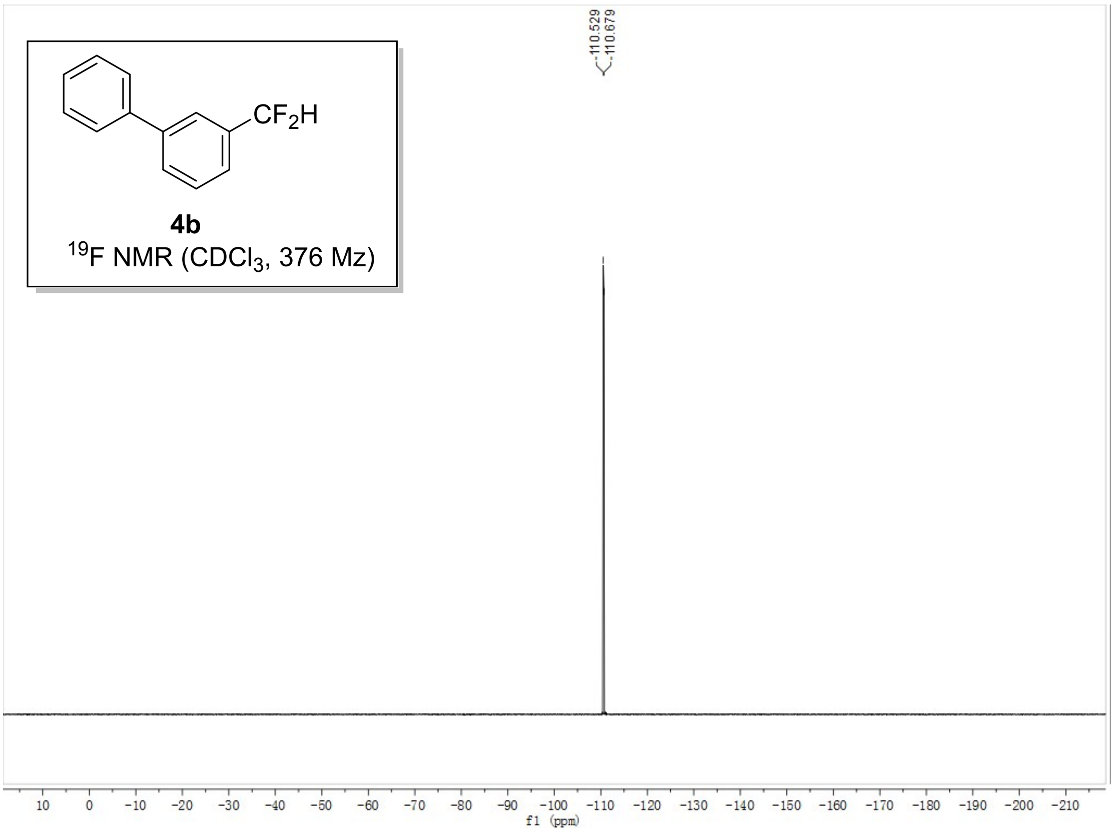
4a

^{19}F NMR (CDCl$_3$, 376 Mz)



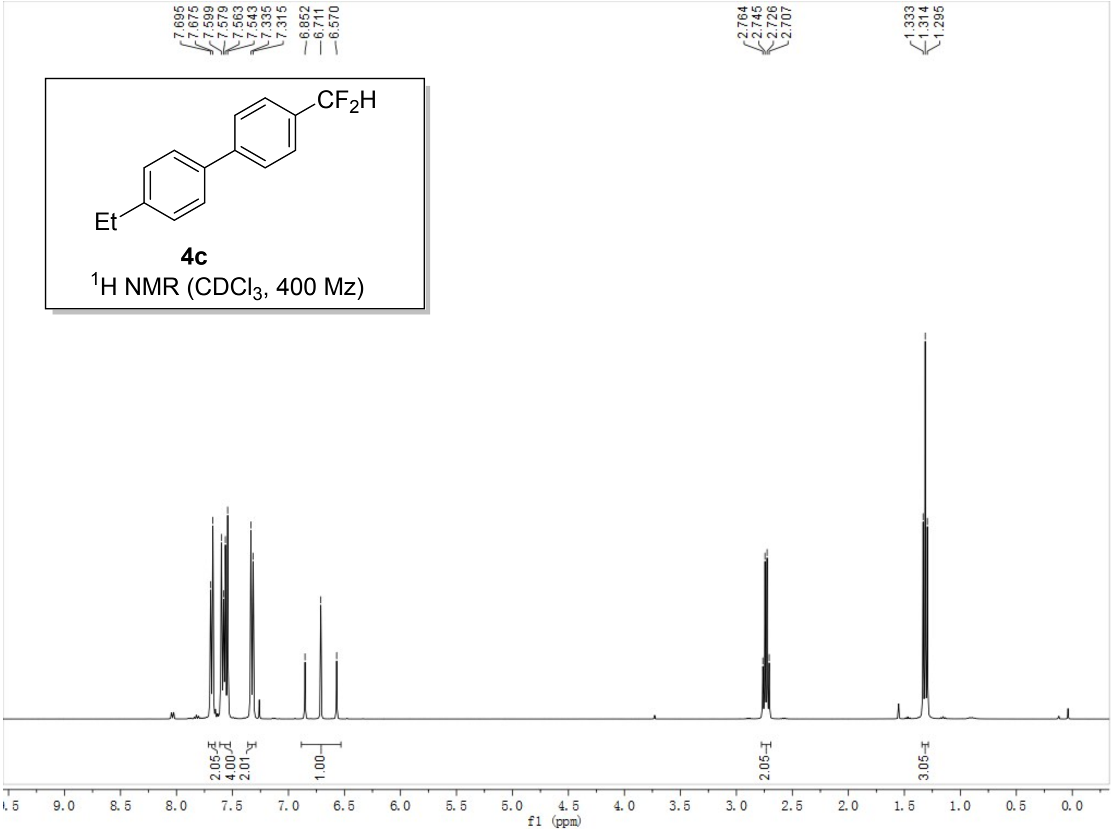
4b

^{1}H NMR (CDCl$_3$, 400 Mz)



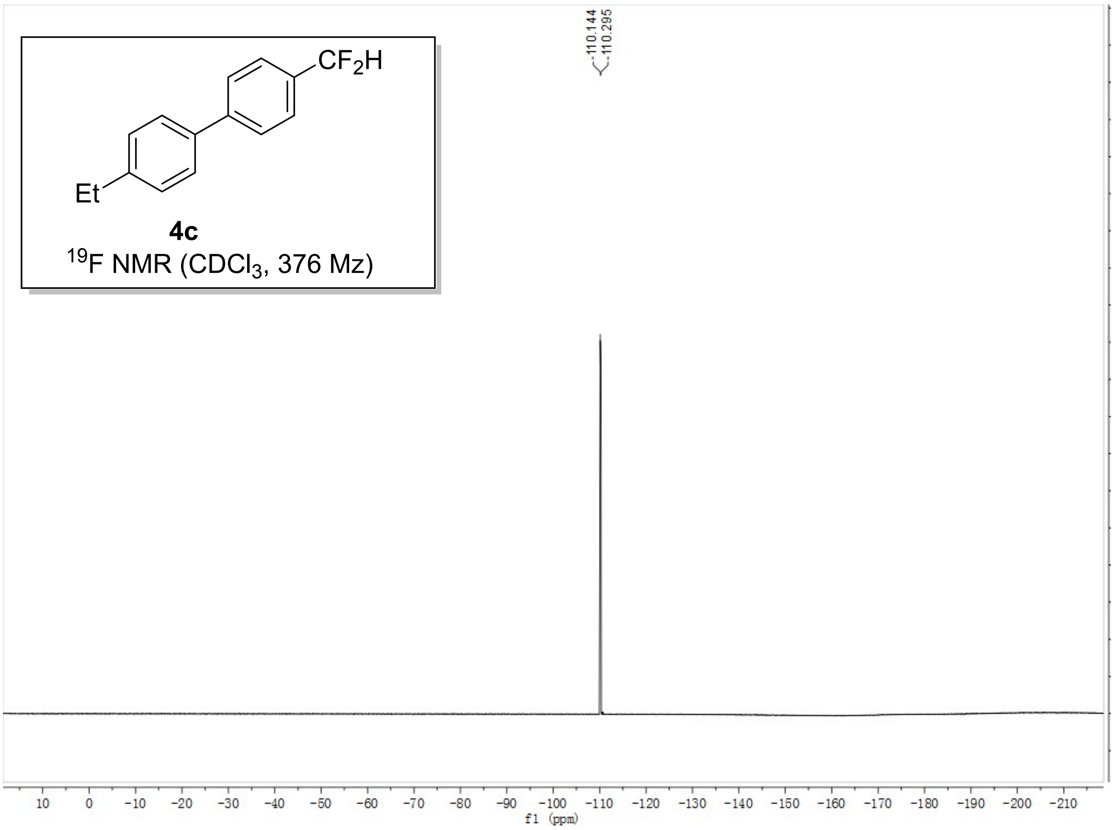
4b

^{19}F NMR ($CDCl_3$, 376 Mz)



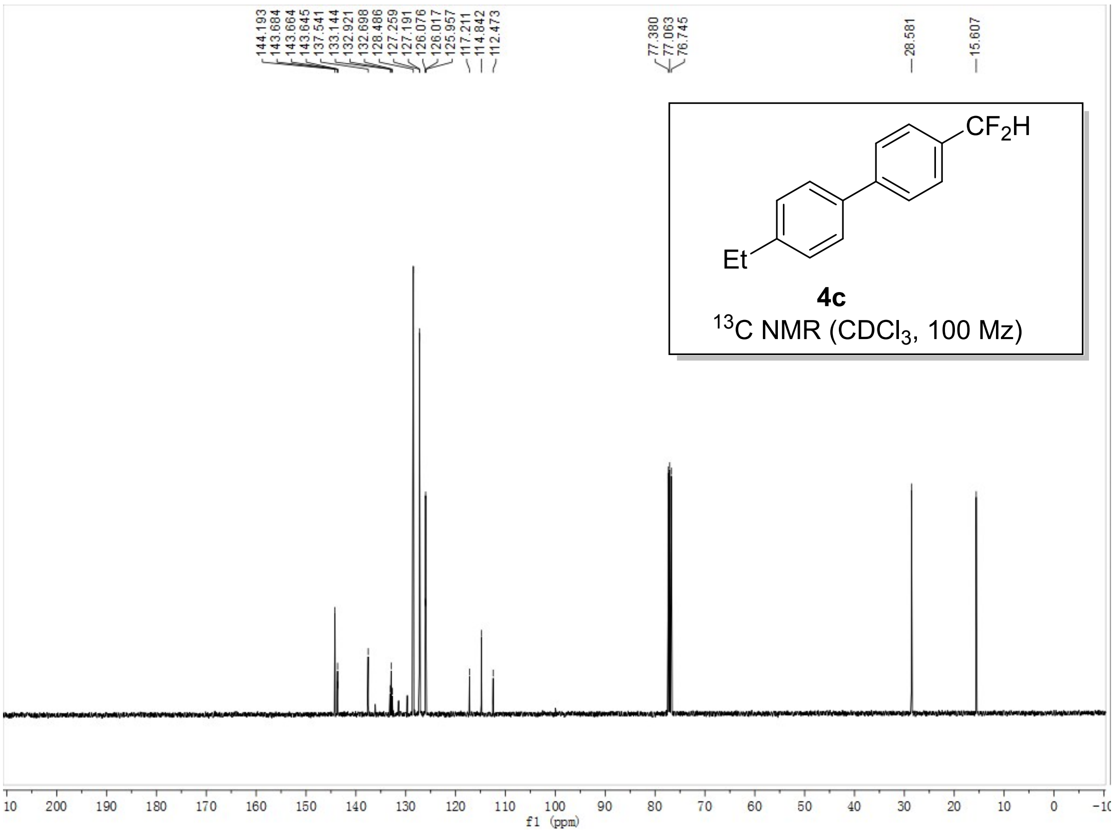
4c

^{1}H NMR ($CDCl_3$, 400 Mz)



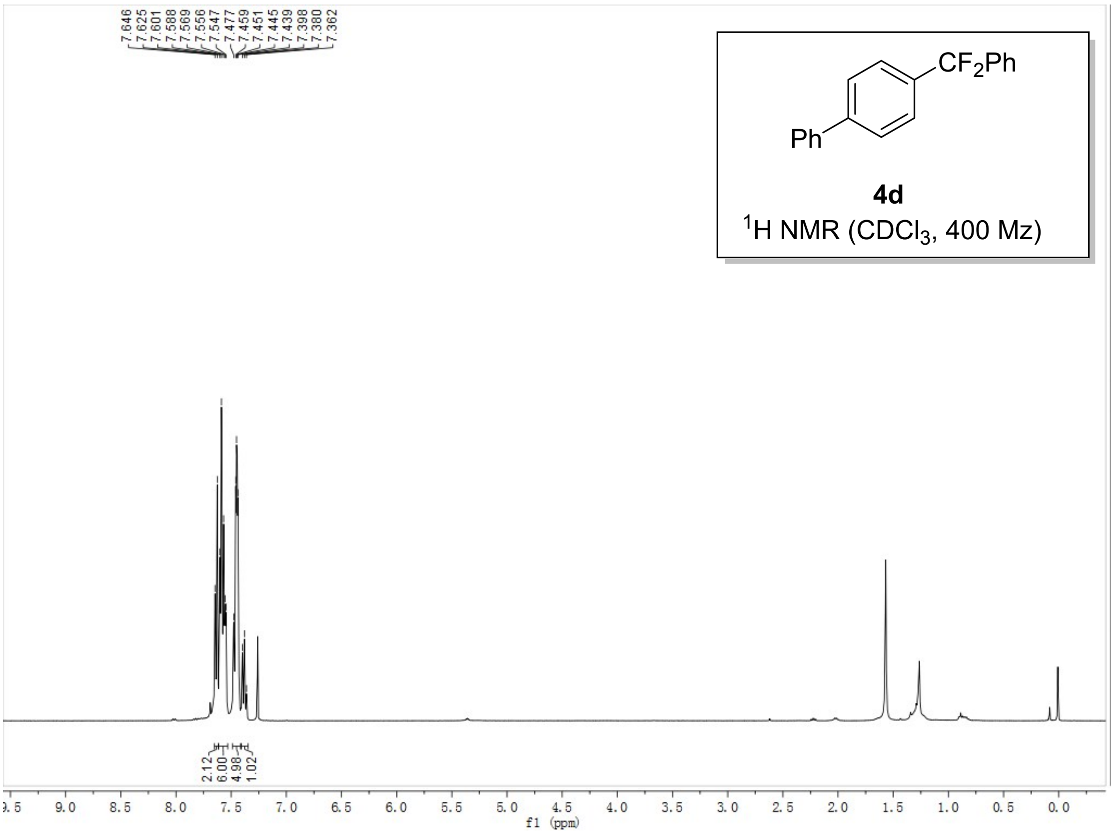
4c

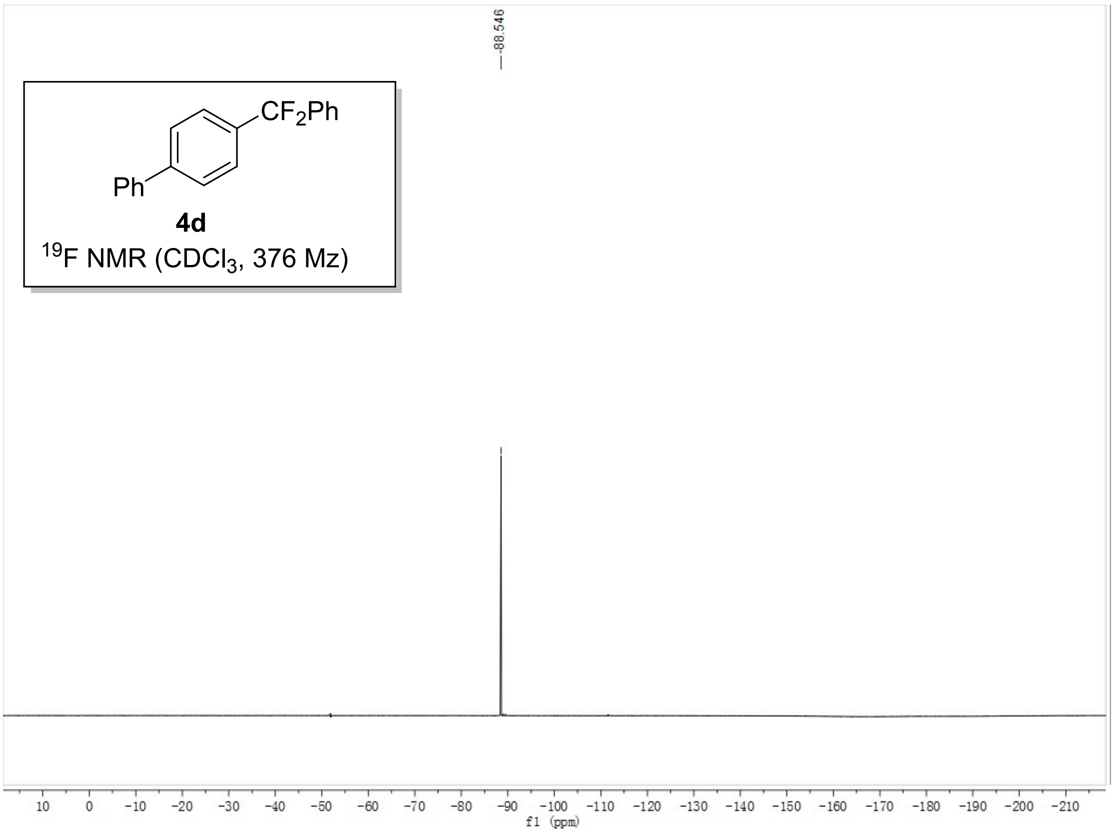
^{19}F NMR (CDCl$_3$, 376 Mz)

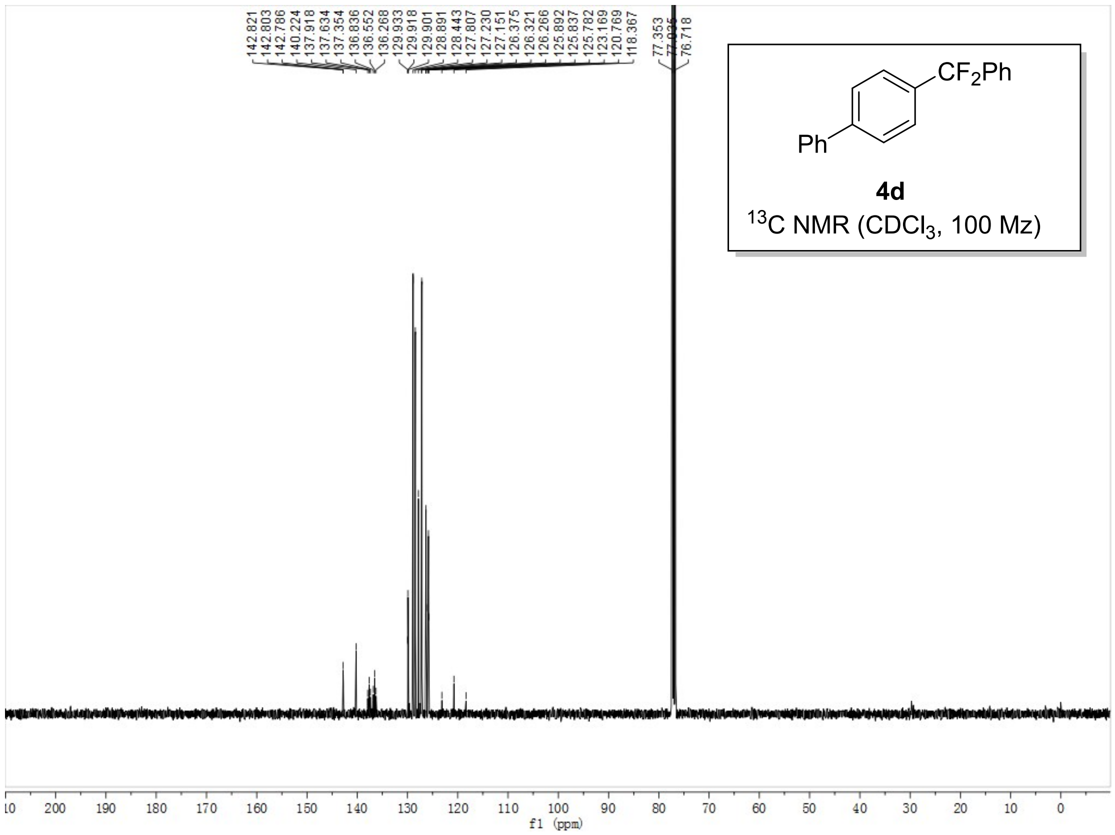


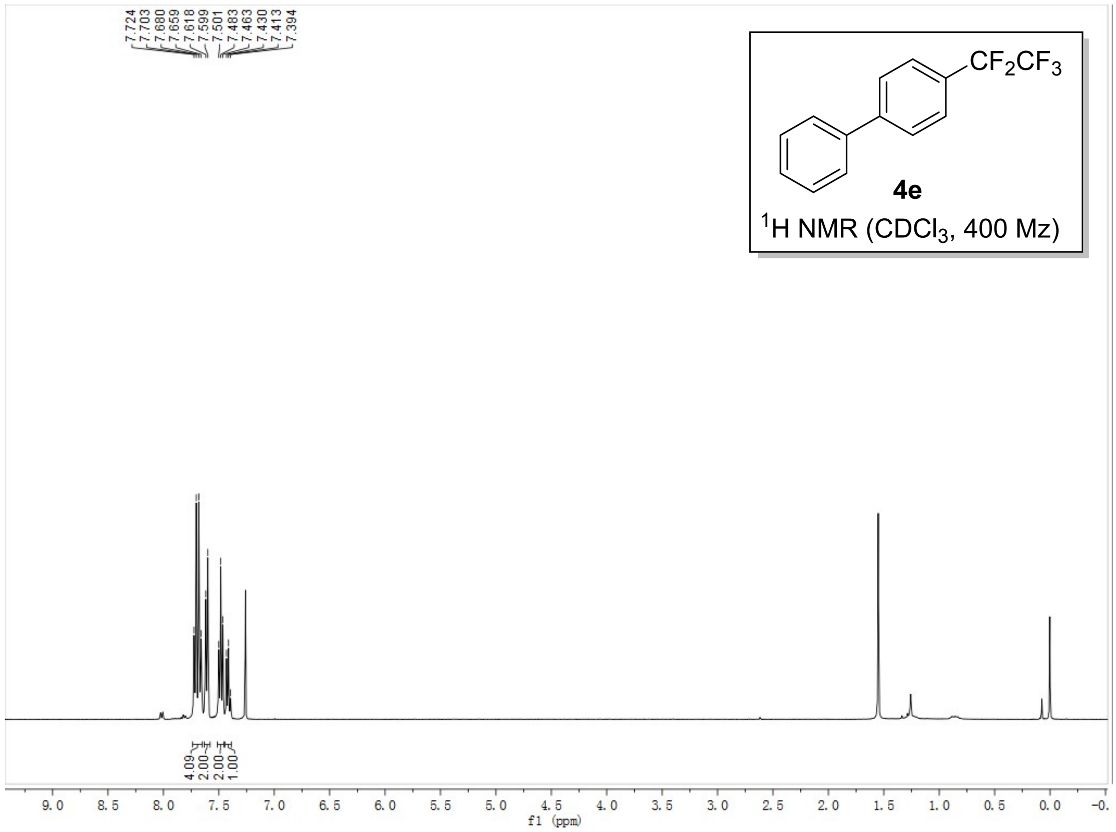
4c

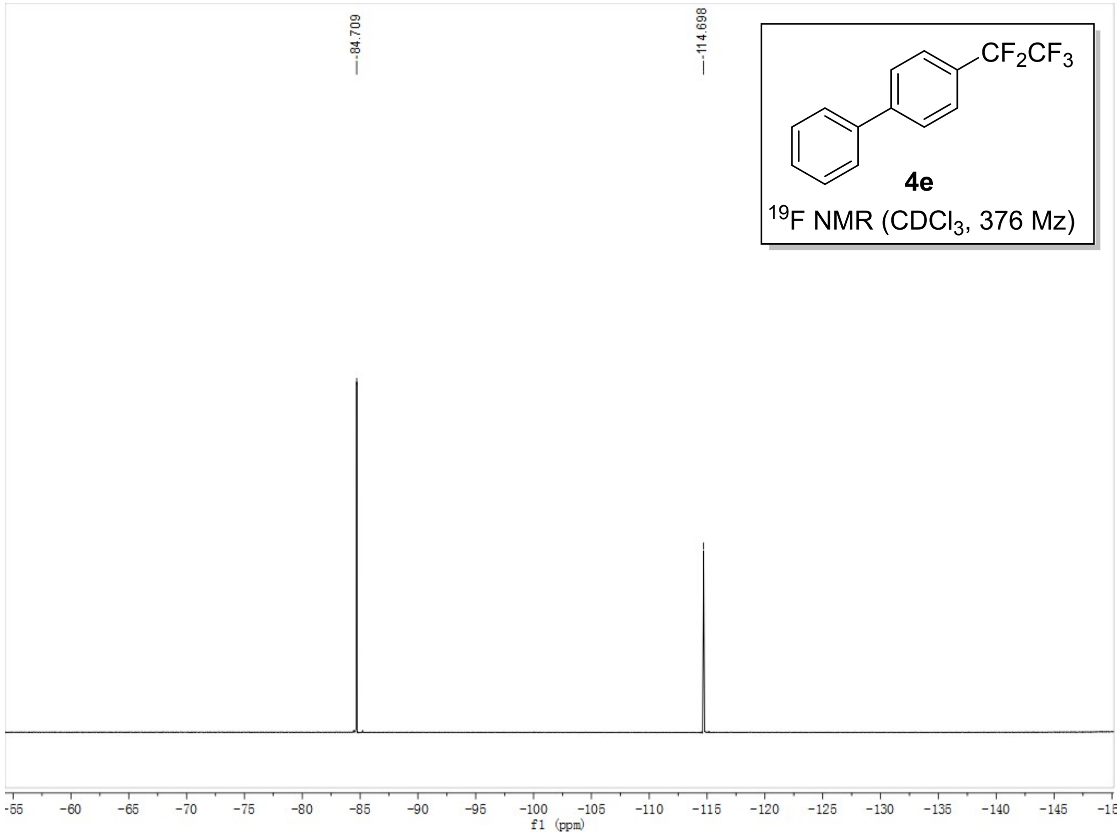
^{13}C NMR (CDCl$_3$, 100 Mz)


7.646
7.625
7.601
7.588
7.569
7.556
7.547
7.477
7.459
7.451
7.445
7.439
7.398
7.380
7.362
CF2Ph
Ph
4d
1H NMR (CDCl3, 400 Mz)
2.12
6.00
4.98
1.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


-88.546
CF2Ph
Ph
4d
19F NMR (CDCl3, 376 Mz)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

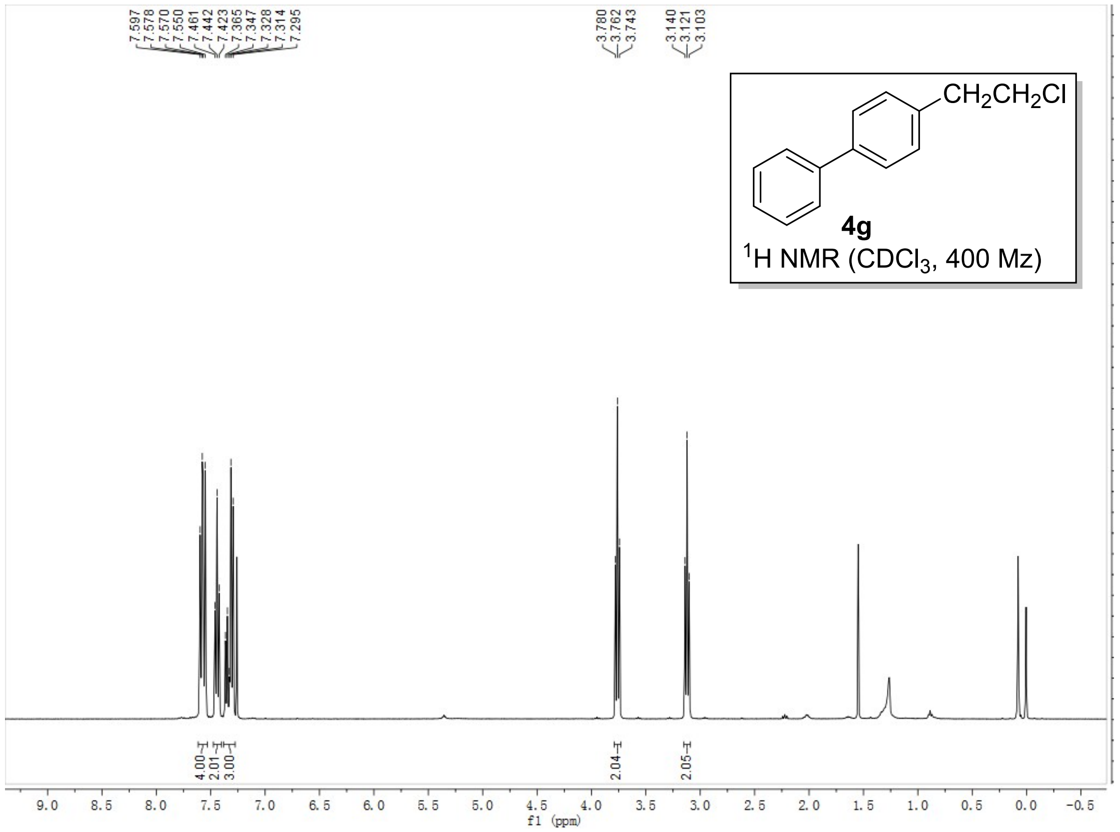

142.821
142.803
142.786
140.224
137.918
137.634
137.354
136.836
136.552
136.268
129.933
129.918
129.901
128.891
128.443
127.807
127.230
127.151
126.375
126.321
126.266
125.892
125.837
125.782
123.169
120.769
118.367
77.353
77.035
76.718
CF2Ph
Ph
4d
13C NMR (CDCl3, 100 Mz)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.724
7.703
7.680
7.659
7.618
7.599
7.501
7.483
7.463
7.430
7.413
7.394
CF2CF3
4e
1H NMR (CDCl3, 400 Mz)
4.09
2.00
2.00
1.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)



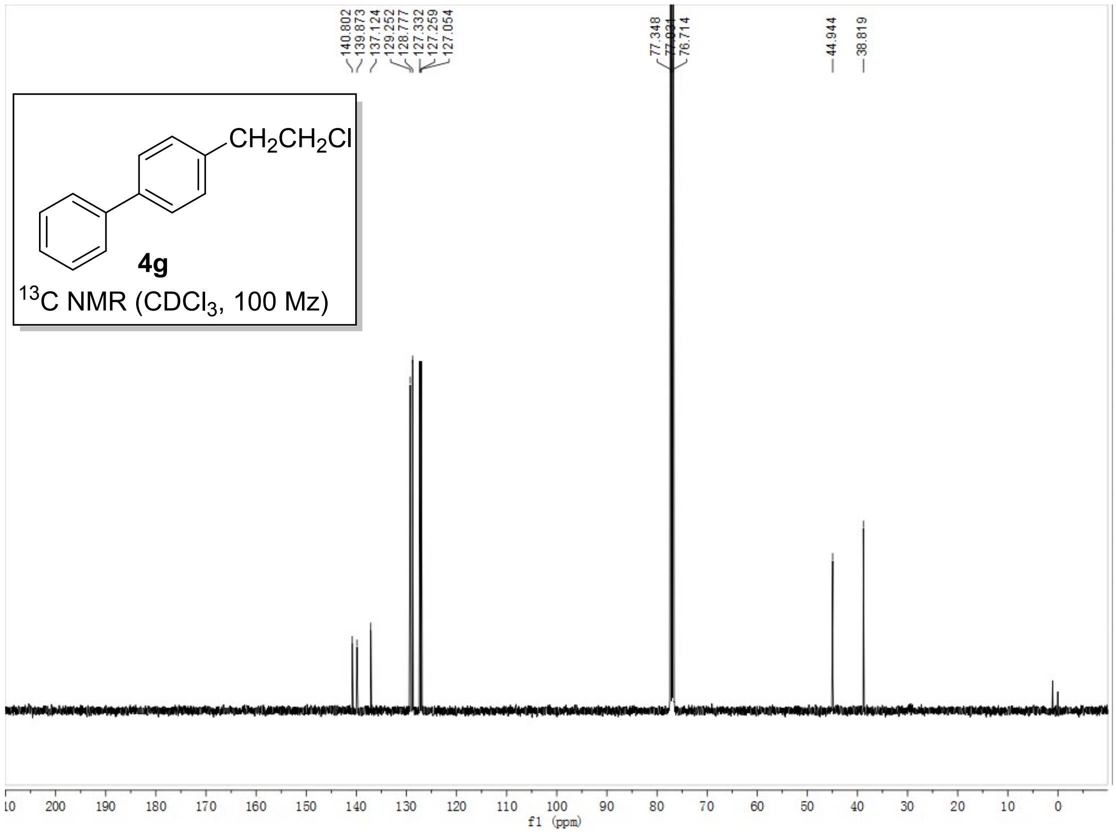
4e

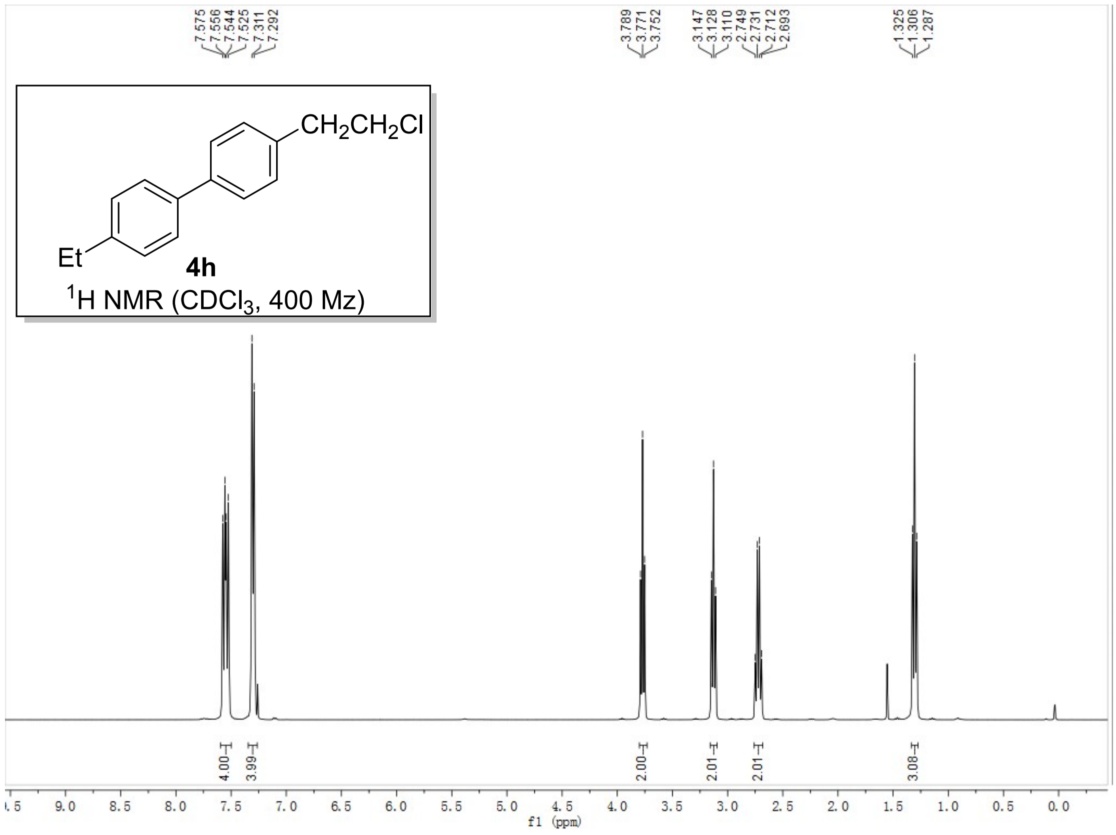
^{19}F NMR (CDCl$_3$, 376 Mz)

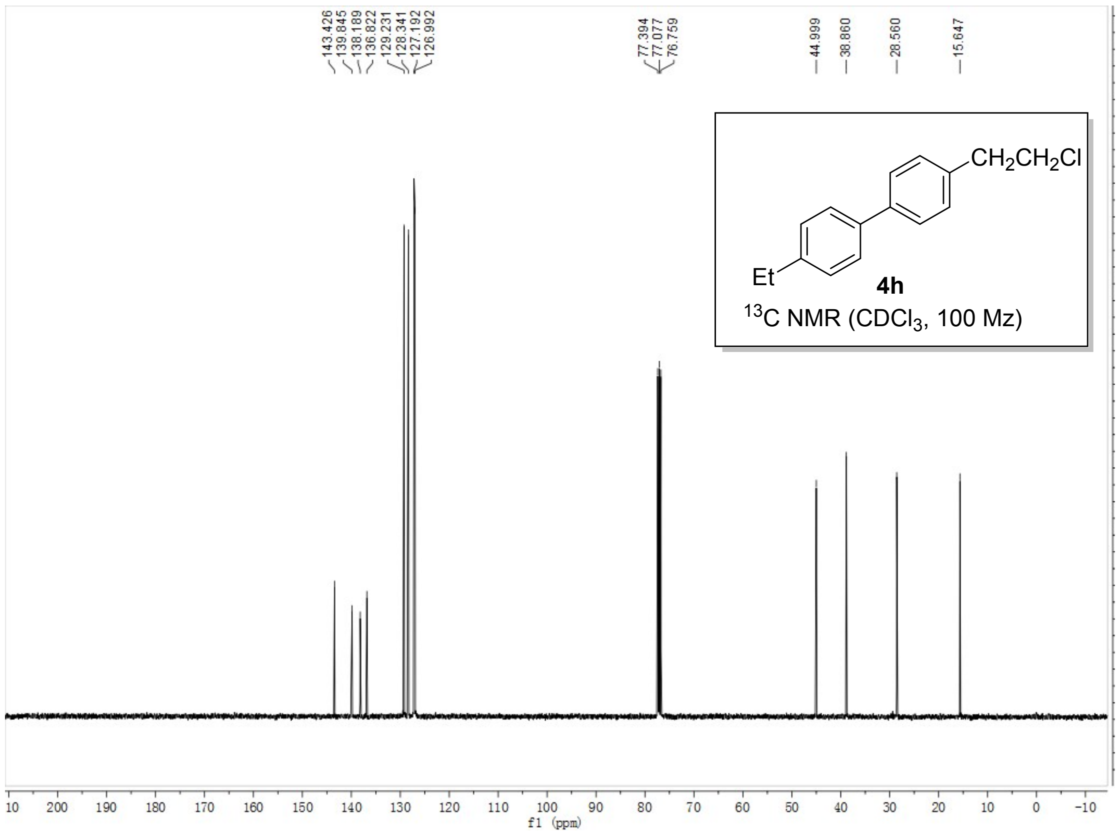


4g

^{1}H NMR (CDCl$_3$, 400 Mz)


140.802
139.873
137.124
129.252
128.777
127.332
127.259
127.054
77.348
77.031
76.714
44.944
38.819
CH_2CH_2Cl
4g
^{13}C NMR ($CDCl_3$, 100 Mz)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.575
7.556
7.544
7.525
7.311
7.292
3.789
3.771
3.752
3.147
3.128
3.110
2.749
2.731
2.712
2.693
1.325
1.306
1.287
CH_2CH_2Cl
Et
4h
^1H NMR ($CDCl_3$, 400 Mz)
4.00
3.99
2.00
2.01
2.01
3.08
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


143.426
139.845
138.189
136.822
129.231
128.341
127.192
126.992
77.394
77.077
76.759
44.999
38.860
28.560
15.647
CH_2CH_2Cl
Et
4h
^{13}C NMR ($CDCl_3$, 100 Mz)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)