Pd-catalyzed Divergent Trifluoroethylation and Arylation of Arylboronic Acids by Aryl(2,2,2-trifluoroethyl)iodonium Triflates

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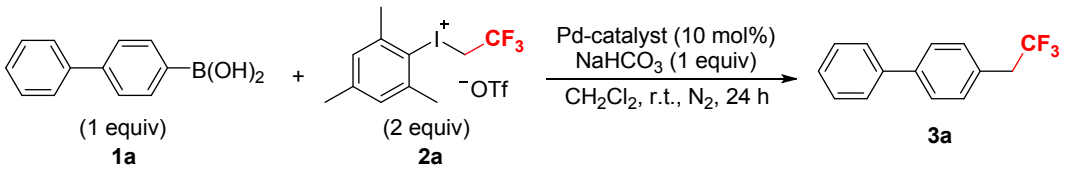
1. General considerations

All reactions were carried out under a nitrogen atmosphere. Unless otherwise specified, NMR spectra were recorded in $CDCl_3$ on a 500 or 400 MHz (for ^1H), 471 or 376 MHz (for ^{19}F), or 126 or 100 MHz (for ^{13}C) spectrometer. All chemical shifts were reported in ppm relative to TMS (0 ppm) for ^1H NMR and $PhCF_3$ (-63.5 ppm) for ^{19}F NMR as internal or external standards. The HPLC experiments were carried out on a Waters e2695 instrument (column: J&K, RP-C18, 5 μm, 4.6 × 150 mm), and the yields of the products were determined by using the corresponding pure compounds as the external standards. Melting points of the products were measured and uncorrected. Trifluoroethylation reagents **2a**,[1] **2b**,[1] **2c**,[2] and **2d**[3] were synthesized according to the literatures.[1-3] Arylboronic acids and other reagents were all purchased from commercial sources and used without further purification.

2. Screening the optimized reaction conditions for Pd-catalyzed trifluoroethylation of arylboronic acids with aryl(trifluoroethyl)iodonium triflate

Table 1 Trifluoroethylation of **1a** by **2a** in the presence of various Pd-catalysts at room temperature using $NaHCO_3$ as the base and CH_2Cl_2 as the solvent.[a]



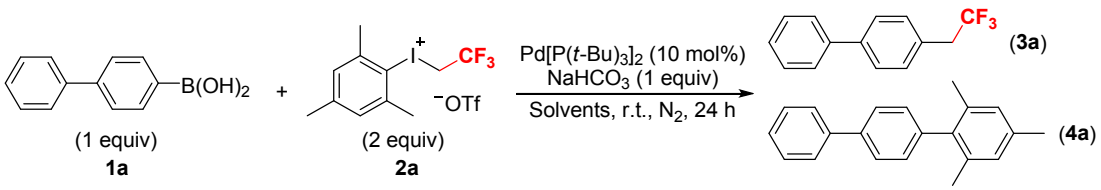
(1 equiv) **1a** (2 equiv) **2a** **3a**

Entry	Pd-catalyst	Yield (**3a**, %)[b]
1	$(CH_3CN)_2PdCl_2$	0.4
2	$PdCl_2$	1
3	$Pd(PCy_3)_2$	3
4	$Pd(OAc)_2$	2
5	**$Pd(dba)_2$**	**9**
6	**$Pd_2(dba)_3$**	**6**

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), $NaHCO_3$ (0.1 mmol), Pd-

catalyst (0.01 mmol), CH_2Cl_2 (2 mL), r.t., N_2, 24 h. [b] The yields were determined by HPLC using 4-(2,2,2-trifluoroethyl)-1,1'-biphenyl (**3a**) as the external standard (t_R = 6.7 min, λ_{max} = 250.0 nm, water/methanol = 20 : 80 (v / v)).

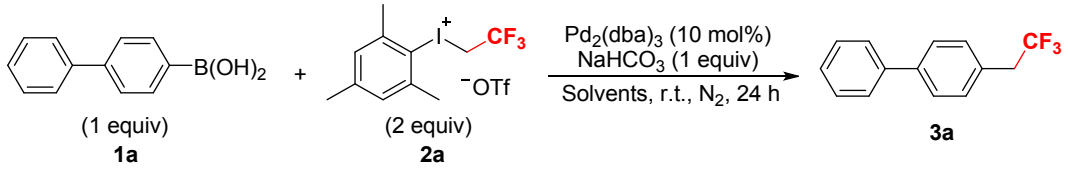
Table 2-1 The solvent effects on the reaction of **1a** and **2a** at room temperature using $Pd[P(t\text{-}Bu)_3]_2$ as the catalyst and $NaHCO_3$ as the base.[a]



Entry	Solvent	Yield (**3a**, %)[b]	Yield (**4a**, %)[b]
1	DMF	2%	19%
2	CH_2Cl_2	3%	2%
3	1,4-dioxane	5%	10%

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), $Pd[P(t\text{-}Bu)_3]_2$ (0.01 mmol), $NaHCO_3$ (0.1 mmol), solvent (2 mL), r.t., N_2, 24 h. [b] The yields were determined by HPLC using **3a** and 2,4,6-trimethyl-1,1':4',1''-terphenyl (**4a**) as the external standards, respectively (**3a**: t_R = 6.5 min, λ_{max} = 250.0 nm; **4a**: t_R = 13.9 min, λ_{max} = 257.1 nm; gradient elution: eluent A: water/methanol = 20 : 80 (v / v), eluent B: water/methanol = 5 : 95 (v / v); 0-6 min, eluent A; 6-10 min, from eluent A to eluent B; 10-15 min, eluent B).

Table 2-2 The solvent effects on the reaction of **1a** and **2a** at room temperature using $Pd_2(dba)_3$ as the catalyst and $NaHCO_3$ as the base.[a]

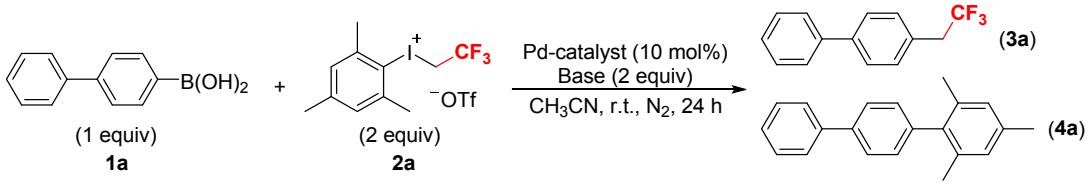


Entry	Solvent	Yield (**3a**, %)[b]
1	CH_2Cl_2	6

2[c]	CH_2Cl_2	11
3	1,4-dioxane	8
4	**CH_3CN**	**15**
5	toluene	2
6	DMF	trace
7	DMSO	0
8	THF	3

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), $NaHCO_3$ (0.1 mmol), $Pd_2(dba)_3$ (10 mol%), solvent (2 mL), r.t., N_2, 24 h. [b] The yields were determined by HPLC using **3a** as the external standard (t_R = 6.7 min, λ_{max} = 250.0 nm, water/methanol = 20 : 80 (v / v)). The byproduct **4a** was not tested. [c] $NaHCO_3$ (0.2 mmol) was used.

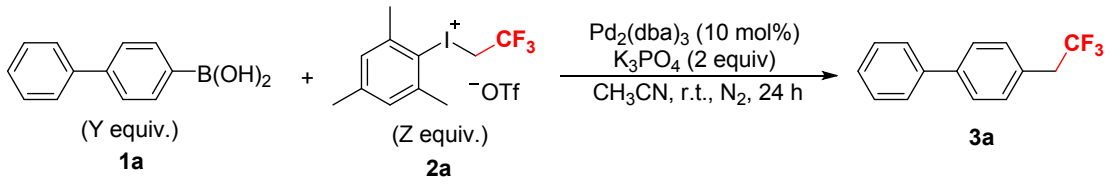
Table 3 Trifluoroethylation of **1a** with **2a** in the presence of different bases. [a]



Entry	Pd-catalyst	Base	Yield (**3a**, %)	Yield (**4a**, %)
1[b]	$Pd_2(dba)_3$	$NaHCO_3$	26	0
2[b]	$Pd_2(dba)_3$	K_2CO_3	25	2
3[b]	**$Pd_2(dba)_3$**	**K_3PO_4**	**52**	**1**
4[b]	$Pd_2(dba)_3$	Cs_2CO_3	2	19
6[c]	$Pd_2(dba)_3$	NaOAc	10	–
7[c]	$Pd_2(dba)_3$	t-BuOK	12	–
8[c]	$Pd_2(dba)_3$	KF	16	–
9[b]	$Pd_2(dba)_3$	CsF	29	0
10[c]	$Pd(dba)_2$	$NaHCO_3$	30	–
11[c]	$Pd(dba)_2$	K_2CO_3	47	–
12[c]	$Pd(dba)_2$	K_3PO_4	45	–
13[c]	$Pd(dba)_2$	Cs_2CO_3	9	–
14 c	$Pd(dba)_2$	CsF	12	–

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), base (0.2 mmol), catalyst (0.01 mmol), CH_3CN (2 mL), r.t., N_2, 24 h. [b] The yields were determined by HPLC using **3a** and **4a** as the external standards, respectively (**3a**: t_R = 6.5 min, λ_{max} = 250.0 nm; **4a**: t_R = 13.9 min, λ_{max} = 257.1 nm; gradient elution: eluent A: water/methanol = 20 : 80 (v / v), eluent B: water/methanol = 5 : 95 (v / v); 0-6 min, eluent A; 6-10 min, from eluent A to eluent B; 10-15 min, eluent B). [c] The yields were determined by HPLC using **3a** as the external standard (t_R = 6.7 min, λ_{max} = 250.0 nm, water/methanol = 20 : 80 (v / v)). "–": Not tested.

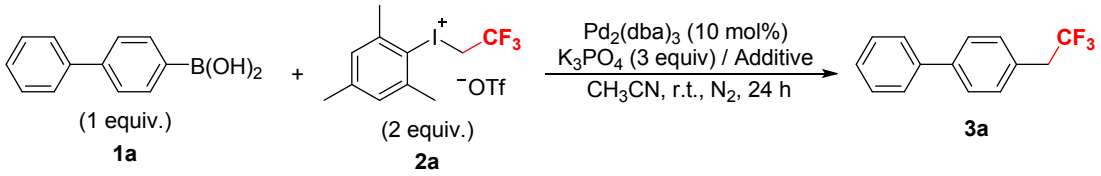
Table 4 The influence of the molar ratio of **1a** and **2a** on the reaction.[a]



Entry	Y : Z	Yield (**3a**, %)[b]
1	1.2 : 1	31
2[c]	1.2 : 1	34
3	1.5 : 1	29
4	1 : 1.2	42
5	1 : 1.5	48
6	**1 : 2**	**52**

[a] Reaction conditions: **1a** (0.1, 0.12 or 0.15 mmol), **2a** (0.1, 0.12, 0.15 or 0.2 mmol), K_3PO_4 (0.2 mmol), $Pd_2(dba)_3$ (0.01 mmol), CH_3CN (2 mL), r.t., N_2, 24 h. [b] The yields were determined by HPLC using **3a** as the external standard (t_R = 6.7 min, λ_{max} = 250.0 nm, water/methanol = 20 : 80 (v / v)). The byproduct **4a** was not tested. [c] 0.1 mmol of $K_3PO_4$was used.

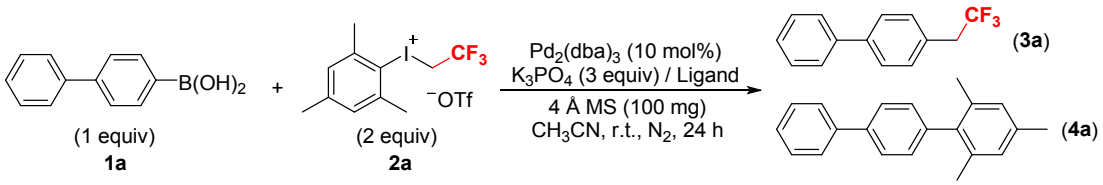
Table 5 The choice of additives for Pd-catalyzed trifluoroethylation of **1a** with **2a**.[a]



Entry	Additive	Yield (**3a**, %)[b]
1	H_2O (1.8 mmol, 18 equiv)	42
2	4 Å MS (30 mg)	60
3	**4 Å MS (100 mg)**	**67**
4 [c]	**4 Å MS (100 mg)**	**67**
6	Na_2SO_4 (100 mg)	59
8	$CaSO_4$ (100 mg)	64
9	Allochroic silicagel (100 mg)	64

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), $Pd_2(dba)_3$ (0.01 mmol), K_3PO_4 (0.3 mmol), CH_3CN (2 mL), r.t., N_2, 24 h. MS: molecular sieves. [b] The yields were determined by HPLC using **3a** as the external standard (t_R = 6.7 min, λ_{max} = 250.0 nm, water/methanol = 20 : 80 (v / v)). The byproduct **4a** was not tested. [c] 0.3 mmol of **2a** was used.

Table 6 Screening the ligands for Pd-catalyzed trifluoroethylation of **1a** with **2a**.[a]

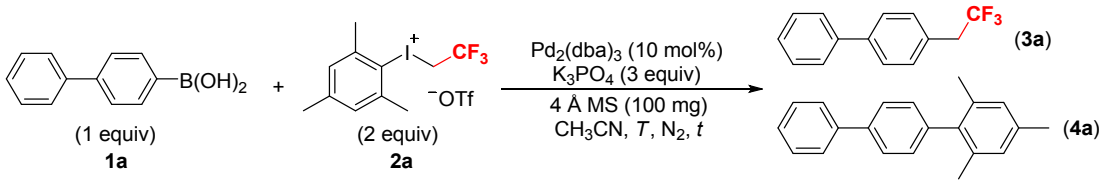


Entry	Ligand (12%)	Yield (**3a**, %)[b]	Yield (**4a**, %)[b]
1	DavePhos	58	< 1
2	tBuMePhos	51	< 1
3	TrixiePhos	38	< 1
4	BrettPhos	56	< 1
5	tBuDavePhos	35	< 1
6	PhDavePhos	50	< 1

7	JohnPhos	47	< 1
8	CyJohnPhos	60	< 1
9	MePhos	51	< 1
10	RuPhos	63	< 1
11[c]	RuPhos	56	< 1

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), $Pd_2(dba)_3$ (0.01mmol), ligand (0.012 mmol), K_3PO_4 (0.3 mmol), 4 Å MS (100 mg), CH_3CN (2 mL), r.t., N_2, 24 h. MS: molecular sieves. [b] The yields were determined by HPLC using **3a** and **4a** as the external standards, respectively (**3a**: t_R = 6.5 min, λ_{max} = 250.0 nm; **4a**: t_R = 13.9 min, λ_{max} = 257.1 nm; gradient elution: eluent A: water/methanol = 20 : 80 (v / v), eluent B: water/methanol = 5 : 95 (v / v); 0-6 min, eluent A; 6-10 min, from eluent A to eluent B; 10-15 min, eluent B). [c] 0.02 mmol of RuPhos was used.

Table 7 Screening the reaction time and temperature.[a]

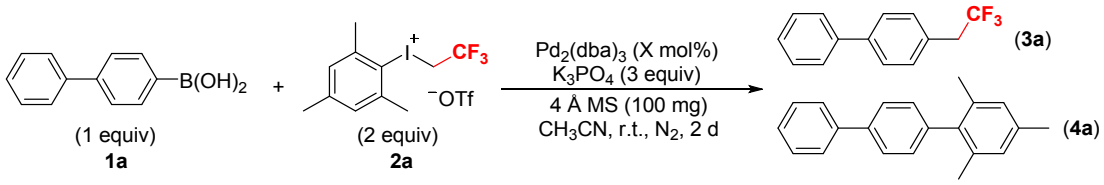


Entry	*T* (°C)	*t* (d)	Yield (**3a**, %) [b]	Yield (**4a**, %) [b]
1 [c]	r.t.	1	67	–
2 [d]	r.t.	2	78	< 1
3	**r.t.**	**2**	**80**	**< 1**
4	r.t.	3	78	< 1
5	r.t.	5	74	< 1
6	30	1	72	< 1
7	50	1	59	6

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), $Pd_2(dba)_3$ (0.01 mmol), K_3PO_4 (0.3 mmol), 4 Å MS (100 mg), CH_3CN (2 mL), N_2. MS: molecular sieves. [b] The yields were determined by HPLC using **3a** and **4a** as the external standards, respectively (**3a**: t_R = 6.5 min, λ_{max} = 250.0 nm; **4a**: t_R = 13.9 min, λ_{max} = 257.1 nm;

gradient elution: eluent A: water/methanol = 20 : 80 (v / v), eluent B: water/methanol = 5 : 95 (v / v); 0-6 min, eluent A; 6-10 min, from eluent A to eluent B; 10-15 min, eluent B). [c] "–": Not tested. [d] 0.2 mmol of K_3PO_4 was used.

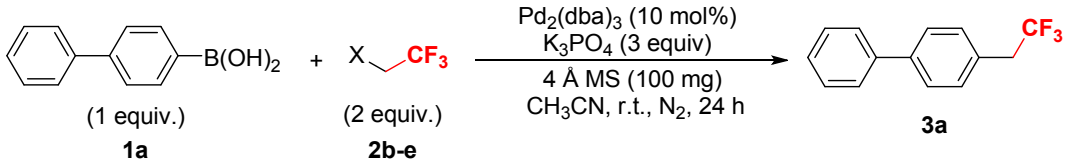
Table 8 Screening the catalyst loading of $Pd_2(dba)_3$.[a]



Entry	X	Additive	Yield (**3a**, %)[b]	Yield (**4a**, %)[b]
1	10	4 Å MS (100 mg)	80	< 1
2	7.5	4 Å MS (100 mg)	76	< 1
3	5	4 Å MS (100 mg)	70	< 1
4	10	–	58	< 1

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), $Pd_2(dba)_3$ (X mol%), K_3PO_4 (0.3 mmol), CH_3CN (2 mL), r.t., N_2, 2 days. MS: molecular sieves. [b] The yields were determined by HPLC using **3a** and **4a** as the external standards, respectively (**3a**: t_R = 6.5 min, λ_{max} = 250.0 nm; **4a**: t_R = 13.9 min, λ_{max} = 257.1 nm; gradient elution: eluent A: water/methanol = 20 : 80 (v / v), eluent B: water/methanol = 5 : 95 (v / v); 0-6 min, eluent A; 6-10 min, from eluent A to eluent B; 10-15 min, eluent B).

Table 9 Pd-catalyzed trifluoroethylation of **1a** by other "CH_2CF_3" reagents at room temperature.[a]

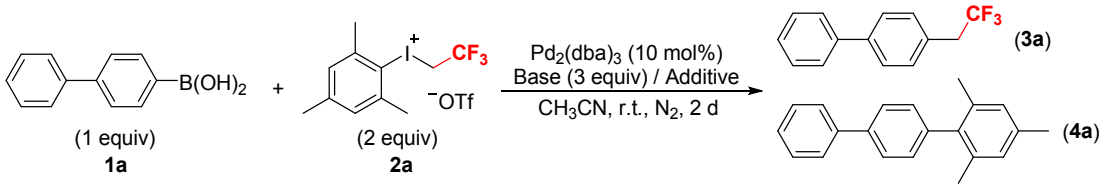


Entry	CF_3CH_2X	Yield (**3a**, %)[b]
1	$[CF_3CH_2IC_6H_5][OTf]$ (**2b**)	69[c] (50[d])
2	$TfOCH_2CF_3$ (**2c**)	0 (0[d])

3	$TsOCH_2CF_3$ (**2d**)	0 (0[d])
4	CF_3CH_2I (**2e**)	0 (0[d])

[a] Reaction conditions: **1a** (0.1 mmol), **2b-e** (0.2 mmol), K_3PO_4 (0.3 mmol), $Pd_2(dba)_3$ (10 mol%), 4 Å MS (100 mg), CH_3CN (2 mL), r.t., N_2, 24 h. MS: molecular sieves. [b] The yields were determined by HPLC using **3a** as the external standard (t_R = 6.7 min, λ_{max} = 250.0 nm, water/methanol = 20 : 80 (v / v)). The byproduct **4a** was not tested. [c] 48 h. [d] Yields without using 4 Å MS (100 mg).

Table 10 The Pd-catalyzed trifluoroethylation in the absence of base and/or additive.[a]

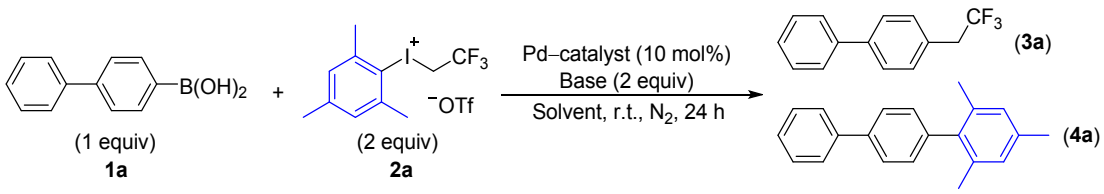


Entry	Base	Additive	Yield (**3a**, %)[b]	Yield (**4a**, %)[b]
1	–	4 Å MS (100 mg)	39	< 1
2	–	–	0	0
3	K_3PO_4	4 Å MS (100 mg)	80	< 1

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), K_3PO_4 (0.3 mmol), $Pd_2(dba)_3$ (10 mol%), 4 Å MS (100 mg), CH_3CN (2 mL), r.t., N_2, 2 d. MS: molecular sieves. [b] The yields were determined by HPLC using **3a** and **4a** as the external standards, respectively (**3a**: t_R = 6.5 min, λ_{max} = 250.0 nm; **4a**: t_R = 13.9 min, λ_{max} = 257.1 nm; gradient elution: eluent A: water/methanol = 20 : 80 (v / v), eluent B: water/methanol = 5 : 95 (v / v); 0-6 min, eluent A; 6-10 min, from eluent A to eluent B; 10-15 min, eluent B).

3. Screening the optimized reaction conditions for Pd-catalyzed arylation of arylboronic acids with aryl(trifluoroethyl)iodonium triflate

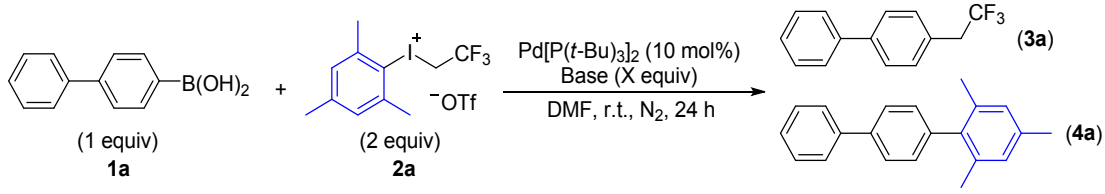
Table 1 Arylation of **1a** by **2a** in the presence of diverse Pd-catalysts, bases and solvents



Entry	Pd-catalyst	Base	Solvent	Yield (**3a**, %)[b]	Yield (**4a**, %)[b]
1	$Pd(PPh_3)_4$	Na_2CO_3	DCE	4	5
2	$Pd(PPh_3)_4$	Na_2CO_3	DMF	< 1	3
3	$Pd(PPh_3)_4$	Na_2CO_3	DME	1	2
4	$Pd(OAc)_2$	Na_2CO_3	DCE	2	7
5	$Pd(OAc)_2$	Na_2CO_3	DMF	< 1	21
6	$Pd(OAc)_2$	Na_2CO_3	DME	3	3
7	$Pd_2(dba)_3$	Cs_2CO_3	DMF	2	28

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), base (0.2 mmol), Pd-catalyst (0.01 mmol), solvent (2 mL), r.t., N_2, 24 h. [b] The yields were determined by HPLC using **3a** and **4a** as the external standards, respectively (**3a**: t_R = 6.5 min, λ_{max} = 250.0 nm; **4a**: t_R = 13.9 min, λ_{max} = 257.1 nm; gradient elution: eluent A: water/methanol = 20 : 80 (v / v), eluent B: water/methanol = 5 : 95 (v / v); 0-6 min, eluent A; 6-10 min, from eluent A to eluent B; 10-15 min, eluent B).

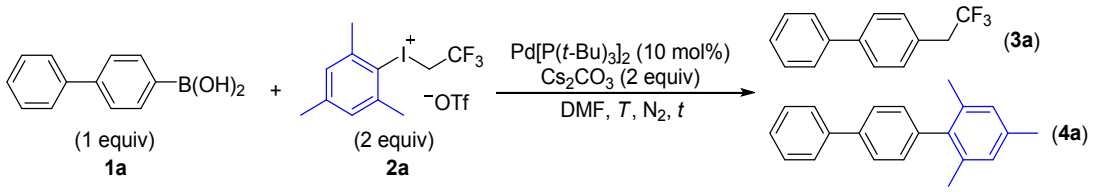
Table 2 Arylation of **1a** by **2a** in the presence of different bases and equivalents.[a]



Entry	Base	X	Yield (**3a**, %)[b]	Yield (**4a**, %)[b]
1	Cs_2CO_3	2	2	75
2	Cs_2CO_3	3	2	71
3	$NaHCO_3$	2	2	34
4	$NaHCO_3$	3	2	46
5	K_3PO_4	2	2	55
6	K_3PO_4	3	3	74

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), base (0.2 or 0.3 mmol), Pd[P(*t*-Bu)$_3$]$_2$ (0.01 mmol), DMF (2 mL), r.t., N_2, 24 h. [b] The yields were determined by HPLC using **3a** and **4a** as the external standards, respectively (**3a**: t_R = 6.5 min, λ_{max} = 250.0 nm; **4a**: t_R = 13.9 min, λ_{max} = 257.1 nm; gradient elution: eluent A: water/methanol = 20 : 80 (v / v), eluent B: water/methanol = 5 : 95 (v / v); 0-6 min, eluent A; 6-10 min, from eluent A to eluent B; 10-15 min, eluent B).

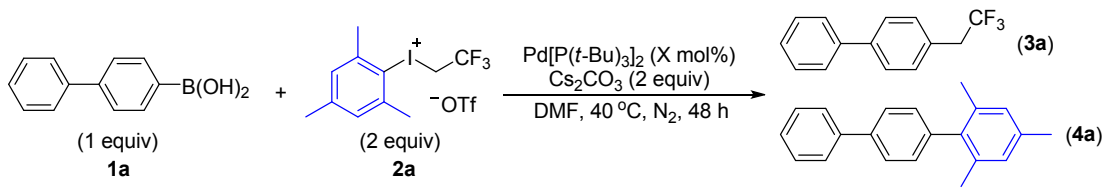
Table 3 Screening the reaction time and temperature.[a]



Entry	*T* (°C)	*t* (h)	Yield (**3a**, %) [b]	Yield (**4a**, %) [b]
1	r.t.	24	2	75
2	r.t.	36	2	87
3	r.t.	48	2	86
4	40	24	2	91
5	40	48	1	96 (84)
6 [c]	40	48	1	49

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), Cs_2CO_3 (0.2 mmol), Pd[P(*t*-Bu)$_3$]$_2$ (0.01 mmol), DMF (2 mL), N_2. [b] The yields were determined by HPLC using **3a** and **4a** as the external standards, respectively (**3a**: t_R = 6.5 min, λ_{max} = 250.0 nm; **4a**: t_R = 13.9 min, λ_{max} = 257.1 nm; gradient elution: eluent A: water/methanol = 20 : 80 (v / v), eluent B: water/methanol = 5 : 95 (v / v); 0-6 min, eluent A; 6-10 min, from eluent A to eluent B; 10-15 min, eluent B). Isolated yield is depicted in the parentheses. [c] DMSO was used as the solvent.

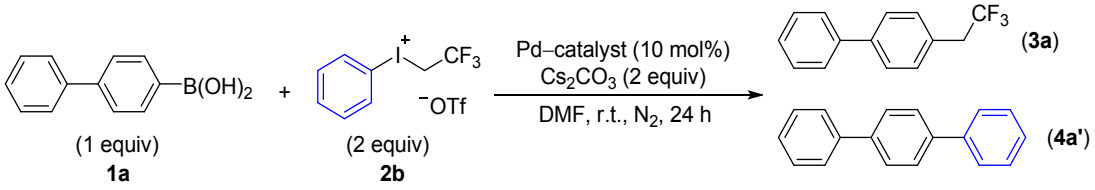
Table 4 Screening the catalyst loading of Pd[P(*t*-Bu)$_3$]$_2$.[a]



Entry	X	Yield (**3a**, %)[b]	Yield (**4a**, %)[b]
1	10	1	96 (84)
2	7.5	1	94 (81)
3	5	< 1	91

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), Cs_2CO_3 (0.2 mmol), Pd[P(*t*-Bu)$_3$]$_2$ (X mol%), DMF (2 mL), 40 °C, N_2, 48 h. [b] The yields were determined by HPLC using **3a** and **4a** as the external standards, respectively (**3a**: t_R = 6.5 min, λ_{max} = 250.0 nm; **4a**: t_R = 13.9 min, λ_{max} = 257.1 nm; gradient elution: eluent A: water/methanol = 20 : 80 (v / v), eluent B: water/methanol = 5 : 95 (v / v); 0-6 min, eluent A; 6-10 min, from eluent A to eluent B; 10-15 min, eluent B). Isolated yield is depicted in the parentheses.

Table 5 Arylation of **1a** by $[C_6H_5ICH_2CF_3]^+[OTf]^-$ (**2b**) in the presence of different Pd-catalysts.[a]

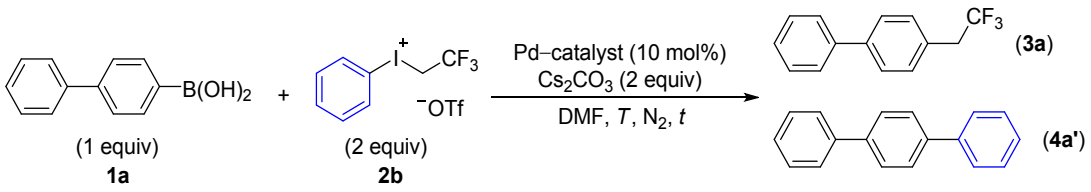


Entry	Pd-catalyst	Yield (**3a**, %)[b]	Yield (**4a'**, %)[b]
1	$Pd_2(dba)_3$	1	77
2 [c]	$Pd_2(dba)_3$	< 1	42
3 [d]	Pd[P(*t*-Bu)$_3$]$_2$	4	48
4	Pd[P(*t*-Bu)$_3$]$_2$	2	84
5	$Pd(OAc)_2$	2	65
6	$Pd(PPh_3)_4$	1	9
7	$Pd(PCy_3)_2$	< 1	19

8	$Pd(PPh_3)_2Cl_2$	< 1	43

[a] Reaction conditions: **1a** (0.1 mmol), **2b** (0.2 mmol), Cs_2CO_3 (0.2 mmol), Pd-catalyst (0.01 mmol), DMF (2 mL), r.t., N_2, 24 h. [b] The yields were determined by HPLC using **3a** and **4a'** as the external standards, respectively (**3a**: t_R = 6.5 min, λ_{max} = 250.0 nm; **4a'**: t_R = 11.7 min, λ_{max} = 278.0 nm; gradient elution: eluent A: water/methanol = 20 : 80 (v / v), eluent B: water/methanol = 5 : 95 (v / v); 0-6 min, eluent A; 6-10 min, from eluent A to eluent B; 10-15 min, eluent B). [c] DMSO was used as the solvent. [d] 0.2 mmol of $NaHCO_3$ was used.

Table 6 Screening the reaction time and temperature.[a]



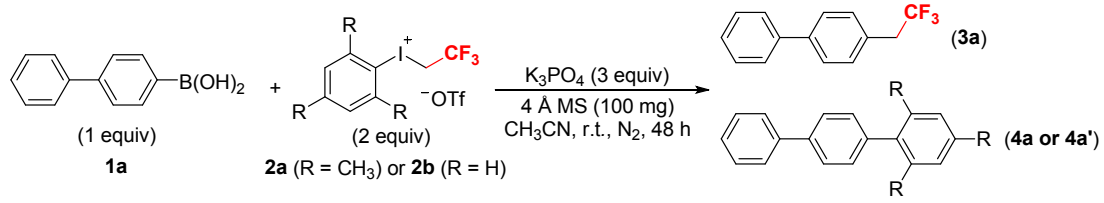
(1 equiv) **1a** (2 equiv) **2b**

Entry	*T* (°C)	*t* (h)	Yield (**3a**, %) [b]	Yield (**4a'**, %) [b]
1	r.t.	24	2	84
2	r.t.	48	2	83
3	40	48	2	93

[a] Reaction conditions: **1a** (0.1 mmol), **2b** (0.2 mmol), Cs_2CO_3 (0.2 mmol), Pd[P(*t*-Bu)$_3$]$_2$ (0.01 mmol), DMF (2 mL), N_2. [b] The yields were determined by HPLC using **3a** and **4a'** as the external standards, respectively (**3a**: t_R = 6.5 min, λ_{max} = 250.0 nm; **4a'**: t_R = 11.7 min, λ_{max} = 278.0 nm; gradient elution: eluent A: water/methanol = 20 : 80 (v / v), eluent B: water/methanol = 5 : 95 (v / v); 0-6 min, eluent A; 6-10 min, from eluent A to eluent B; 10-15 min, eluent B).

4. The control experiments for Pd-catalyzed trifluoroethylation and arylation of arylboronic acids with aryl(trifluoroethyl)iodonium triflate

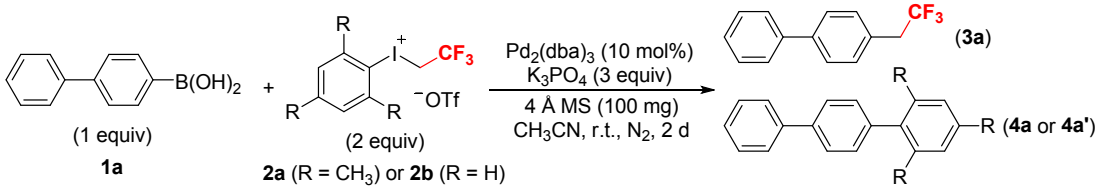
Table 1 Trifluoroethylation of **1a** by **2a** or **2b** without Pd-catalysts.[a]



Entry	R	Yield (**3a**, %)[b]	Yield (**4a** or **4a'**, %)[b]
1	CH_3	0	0
2	H	0	0

[a] Reaction conditions: **1a** (0.1 mmol), **2a** or **2b** (0.2 mmol), K_3PO_4 (0.3 mmol), 4 Å MS (100 mg), CH_3CN (2 mL), r.t., N_2, 2 d. [b] The yields were determined by HPLC using **3a** and **4a or 4a'** as the external standards, respectively (**3a**: t_R = 6.5 min, λ_{max} = 250.0 nm; **4a**: t_R = 13.9 min, λ_{max} = 257.1 nm or **4a'**: t_R = 11.7 min, λ_{max} = 278.0 nm; gradient elution: eluent A: water/methanol = 20 : 80 (v / v), eluent B: water/methanol = 5 : 95 (v / v); 0-6 min, eluent A; 6-10 min, from eluent A to eluent B; 10-15 min, eluent B).

Table 2 Trifluoroethylation of **1a** by **2a** or **2b** in the presence of different additives.[a]

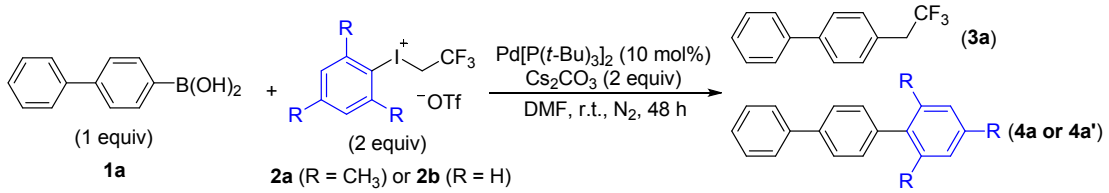


Entry	R	Additive	Yield (**3a**, %)[b]	Yield (**4a** or **4a'**, %)[b]
1	CH_3	none	80	< 1
2	H	none	69	7
3	CH_3	TEMPO	< 1	10
4	H	TEMPO	< 1	16
5	CH_3	styrene	84	0
6	H	styrene	79	0

[a] Reaction conditions: **1a** (0.1 mmol), **2a** or **2b** (0.2 mmol), K_3PO_4 (0.3 mmol), $Pd_2(dba)_3$ (10 mol%), 4 Å MS (100 mg), additive (2 equiv), CH_3CN (2 mL), r.t., N_2, 2 d. [b] The yields were determined by HPLC using **3a** and **4a** or **4a'** as the external standards, respectively (**3a**: t_R = 6.5 min, λ_{max} = 250.0 nm; **4a**: t_R = 13.9 min, λ_{max} = 257.1 nm or **4a'**: t_R = 11.7 min, λ_{max} = 278.0 nm; gradient elution: eluent A:

water/methanol = 20 : 80 (v / v), eluent B: water/methanol = 5 : 95 (v / v); 0-6 min, eluent A; 6-10 min, from eluent A to eluent B; 10-15 min, eluent B).

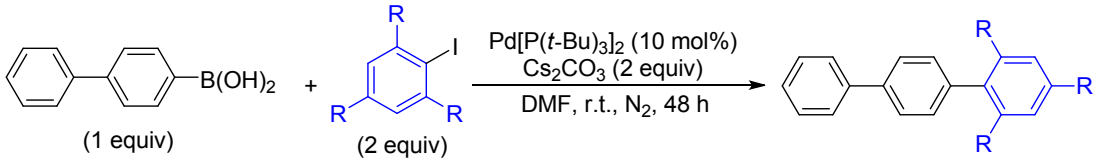
Table 3 Arylation of **1a** by **2a** or **2b** in the presence of different additives.[a]



Entry	R	Additive	Yield (**3a**, %)[b]	Yield (**4a** or **4a'**, %)[b]
1	CH_3	none	2	86
2	H	none	2	83
3	CH_3	TEMPO	0	67
4	H	TEMPO	< 1	96
5	CH_3	Styrene	0	44
6	H	Styrene	0	71
7[c]	CH_3	none	1	96
8[c]	H	none	2	93
9[c]	CH_3	H_2O (0.1 mL)	1	77
10[c]	H	H_2O (0.1 mL)	2	71

[a] Reaction conditions: **1a** (0.1 mmol), **2a** or **2b** (0.2 mmol), Cs_2CO_3 (0.2 mmol), Pd[P(*t*-Bu)$_3$]$_2$ (10 mol%), additive (2 equiv), DMF (2 mL), r.t., N_2, 48 h. [b] The yields were determined by HPLC using **3a** and **4a** or **4a'** as the external standards, respectively (**3a**: t_R = 6.5 min, λ_{max} = 250.0 nm; **4a**: t_R = 13.9 min, λ_{max} = 257.1 nm; **4a'**: t_R = 11.7 min, λ_{max} = 278.0 nm; gradient elution: eluent A: water/methanol = 20 : 80 (v / v), eluent B: water/methanol = 5 : 95 (v / v); 0-6 min, eluent A; 6-10 min, from eluent A to eluent B; 10-15 min, eluent B). [c] 40 °C.

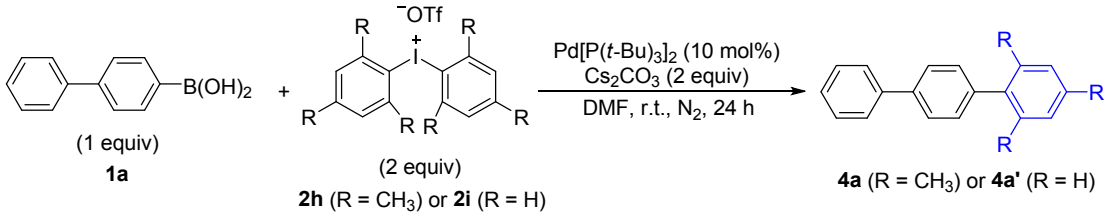
Table 4 Pd-catalyzed arylation of **1a** by **2f** or **2g** in the presence of diverse additives.[a]



Entry	R	Additive	Yield (**4a** or **4a'**, %)[b]
1	CH_3	none	20
2	H	none	49
3	CH_3	TEMPO	31
4	H	TEMPO	53
5	CH_3	Styrene	18
6	H	Styrene	65
7[c]	CH_3	none	95
8[c]	H	none	97
9[c]	CH_3	H_2O (0.1 mL)	67
10[c]	H	H_2O (0.1 mL)	76

[a] Reaction conditions: **1a** (0.1 mmol), **2f** or **2g** (0.2 mmol), Cs_2CO_3 (0.2 mmol), $Pd[P(t\text{-}Bu)_3]_2$ (10 mol%), additive (2 equiv), DMF (2 mL), r.t., N_2, 48 h. [b] The yields were determined by HPLC using **4a** or **4a'** as the external standard (**4a**: t_R = 13.9 min, λ_{max} = 257.1 nm or **4a'**: t_R = 11.7 min, λ_{max} = 278.0 nm; gradient elution: eluent A: water/methanol = 20 : 80 (v / v), eluent B: water/methanol = 5 : 95 (v / v); 0-6 min, eluent A; 6-10 min, from eluent A to eluent B; 10-15 min, eluent B). [c] 40 ^oC.

Table 5 Pd-catalyzed arylation of **1a** by **2h** or **2i** at room temperature.[a]

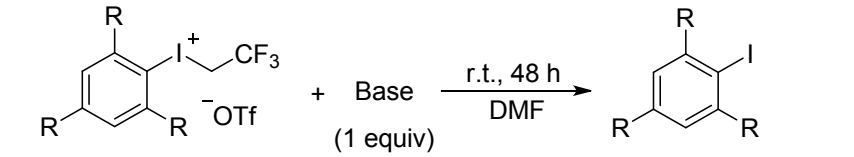


Entry	R	Yield (**4a** or **4a'**, %)[b]
1	CH_3	99

2	H	96

[a] Reaction conditions: **1a** (0.1 mmol), **2h** or **2i** (0.2 mmol), Cs_2CO_3 (0.2 mmol), $Pd[P(t\text{-}Bu)_3]_2$ (10 mol%), DMF (2 mL), r.t., N_2, 24 h. [b] The yield was determined by HPLC using **4a** or **4a'** as the external standard (**4a**: t_R = 13.9 min, λ_{max} = 257.1 nm or **4a'**: t_R = 11.7 min, λ_{max} = 278.0 nm; gradient elution: eluent A: water/methanol = 20 : 80 (v / v), eluent B: water/methanol = 5 : 95 (v / v); 0-6 min, eluent A; 6-10 min, from eluent A to eluent B; 10-15 min, eluent B).

Table 6 Decomposition of **2a** or **2b** by bases.[a]



(1 equiv)
2a (R = CH_3) or **2b** (R = H)

2f (R = CH_3) or **2g** (R = H)

Entry	R	Base	Yield (**2f** or **2g**, %)[b]
1	CH_3	K_3PO_4	92
2	CH_3	Cs_2CO_3	96
3	H	K_3PO_4	96
4	H	Cs_2CO_3	98

[a] Reaction conditions: **2a** or **2b** (0.1 mmol), base (0.1 mmol), DMF (1 mL), r.t., N_2, 48 h. [b] The yields were determined by HPLC using **2f** or **2g** as the external standard, respectively (**2f**: t_R = 11.2 min, λ_{max} = 230.0 nm or **2g**: t_R = 4.9 min, λ_{max} = 226.4 nm; gradient elution: eluent A: water/methanol = 20 : 80 (v / v), eluent B: water/methanol = 5 : 95 (v / v); 0-6 min, eluent A; 6-10 min, from eluent A to eluent B; 10-15 min, eluent B). [c] 40 °C.

Figure 1. ^{19}F NMR spectrum of the reaction mixture of **1a** (0.1 mmol), **2a** (0.2 mmol), K_3PO_4 (0.3 mmol), $Pd_2(dba)_3$ (10 mol%), TEMPO (0.2 mmol), 4 Å MS (100 mg), and CH_3CN (2 mL) at room temperature under N_2 for 2 days.

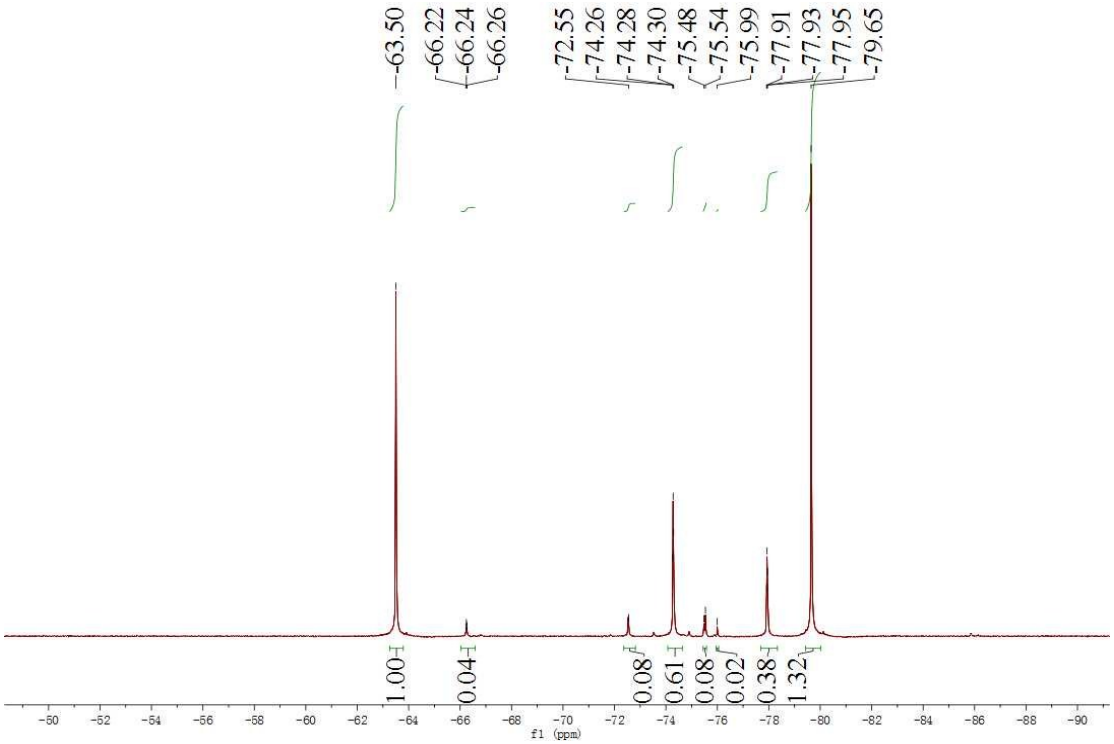


Figure 2. The combined ^{19}F NMR spectra of the reactions of **2a** (0.2 mmol) and TEMPO in the presence or absence of additives at room temperature under N_2 for 1 day. (***2a*** *was decomposed in the presence of TEMPO without substrate and catalyst*)

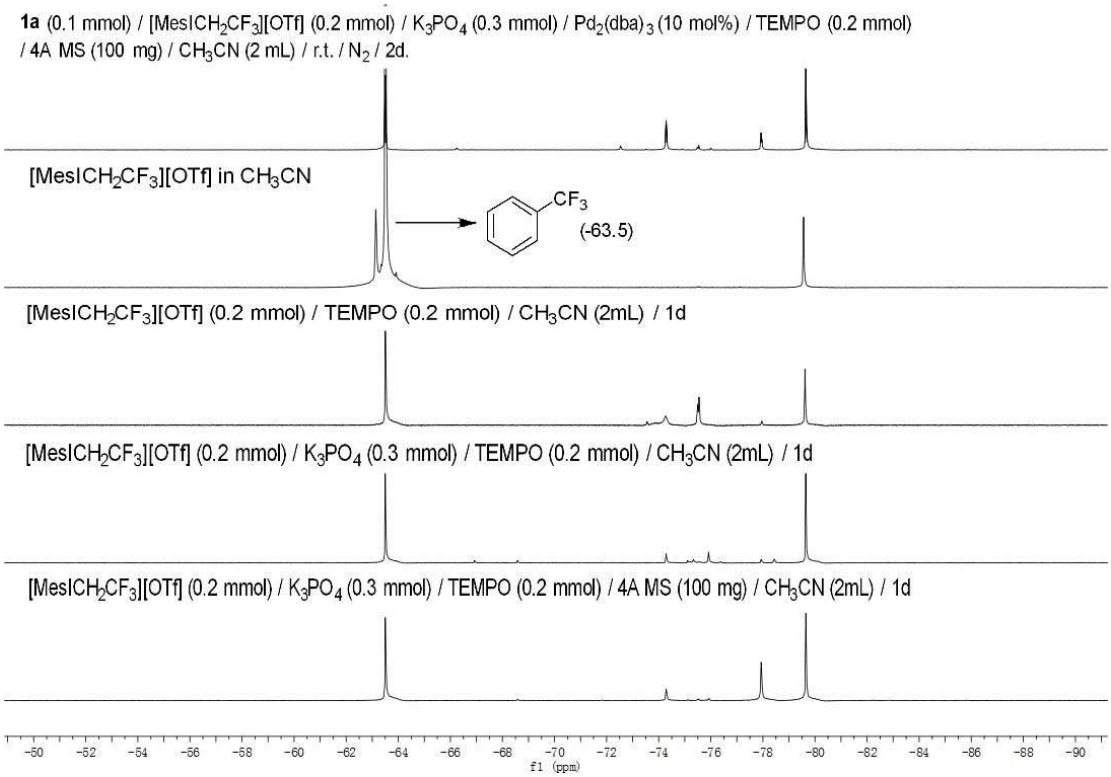


Figure 3. ^{19}F NMR spectrum of the reaction mixture of **1a** (0.1 mmol), **2a** (0.2 mmol), K_3PO_4 (0.3 mmol), $Pd_2(dba)_3$ (10 mol%), Styrene (0.2 mmol), 4 Å MS (100 mg), and CH_3CN (2 mL) at room temperature under N_2 for 2 days.

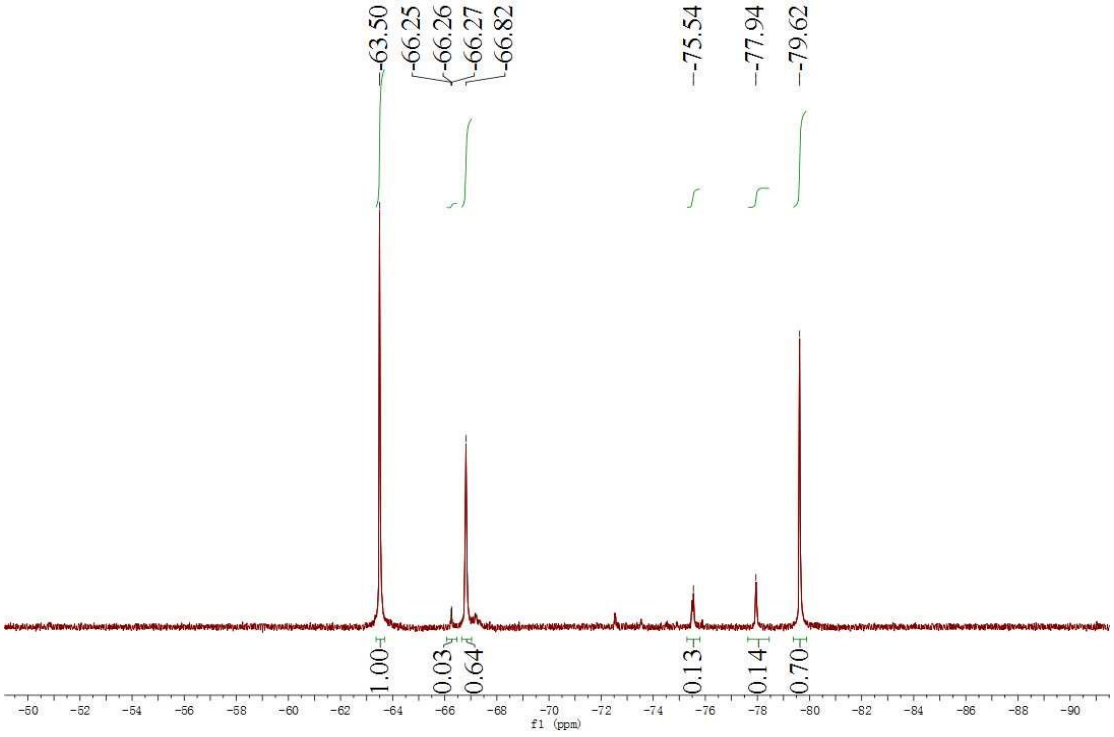


Figure 4. ^{19}F NMR spectrum of CF_3CH_2I in CH_3CN

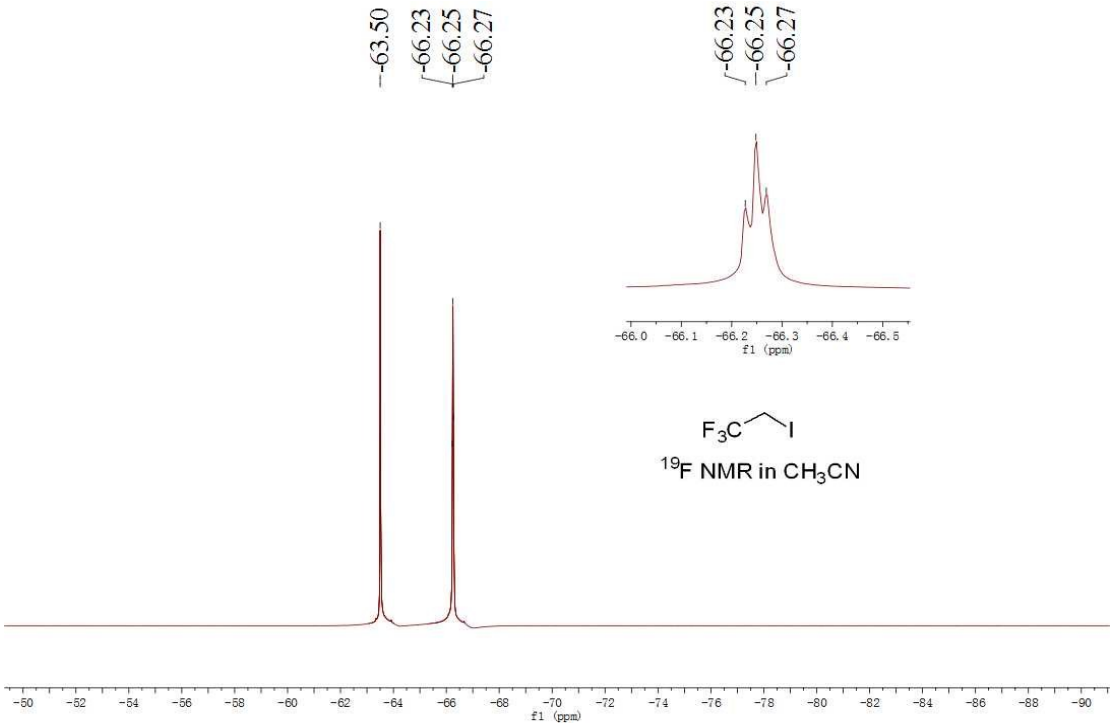


Figure 5. ^{19}F NMR spectrum of the reaction mixture of **1a** (0.1 mmol), **2a** (0.2 mmol), Cs_2CO_3 (0.2 mmol), $Pd[P(t\text{-}Bu)_3]_2$ (10 mol%), and DMF (2 mL) at 40 °C under N_2 for 2 days.

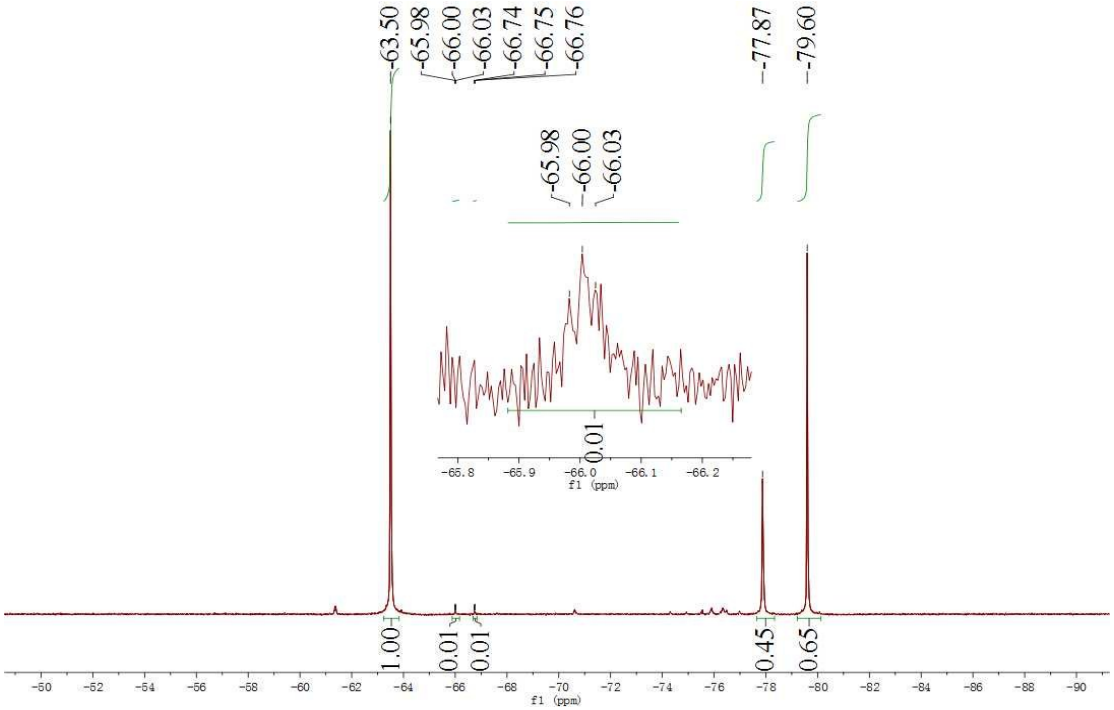


Figure 6. ^{19}F NMR spectrum of CF_3CH_2I in DMF

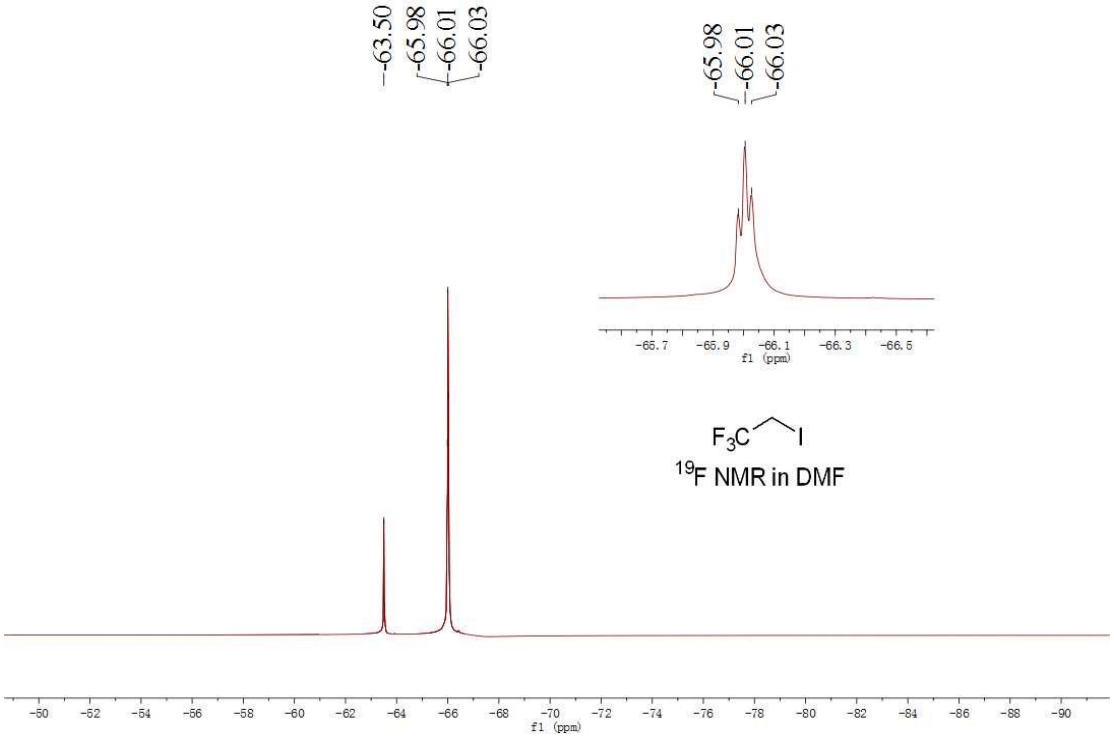
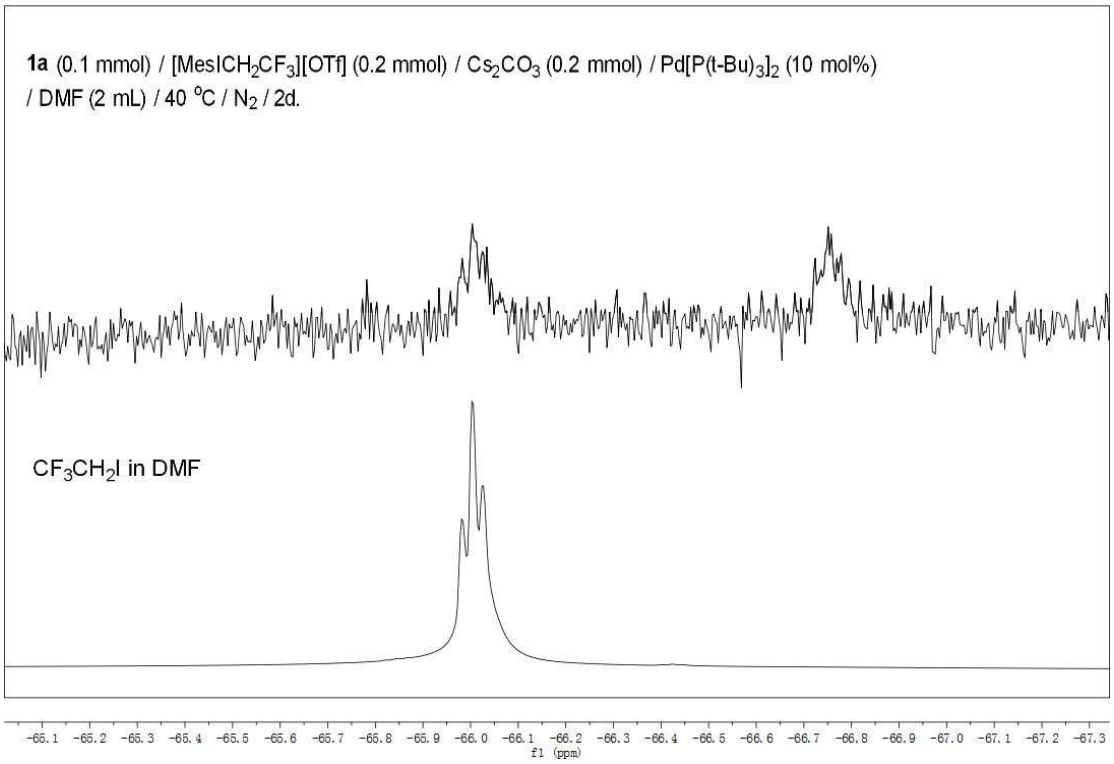


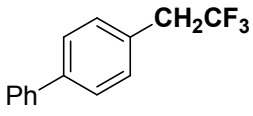
Figure 7. The combination of **Figure 4** and **Figure 5**



5. General procedure for Pd-catalyzed trifluoroethylation of arylboronic acids with aryl(trifluoroethyl)iodonium triflate.

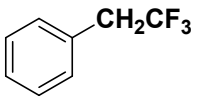
In a nitrogen-filled glovebox, a sealed tube was charged with arylboronic acid (**1**, 0.4 mmol), $[ArICH_2CF_3]^+[OTf]^-$ (**2**, 0.8 mmol), $Pd_2(dba)_3$ (0.04 mmol), 4 Å MS (400 mg), K_3PO_4 (1.2 mmol), and CH_3CN (8 mL) with stirring. The mixture was reacted at room temperature for 48 h, filtered, and washed with CH_3CN for three times. The combined solution was concentrated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel using petroleum ether or a mixture of petroleum ether and ethyl acetate as eluents to give the trifluoroethylated product (**3**).

4-(2,2,2-Trifluoroethyl)-1,1'-biphenyl (**3a**).[4]



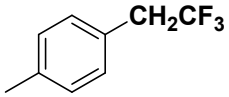
White solid, 68.9 mg, 73% yield, petroleum ether as the eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, J = 7.7 Hz, 4H), 7.48 (t, J = 7.4 Hz, 2H), 7.42−7.38 (m, 3H), 3.45 (q, J = 10.8 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -66.4 (t, J = 11.3 Hz, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.1 (s), 140.5 (s), 130.6 (s), 129.1 (q, J = 2.8 Hz), 128.8 (s), 127.5 (s), 127.4 (s), 127.1 (s), 125.8 (q, J = 276.4 Hz), 39.9 (q, J = 29.7 Hz).

2,2,2-Trifluoroethylbenzene (**3b**).[5]



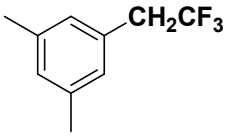
47% or 48% ^{19}F NMR yield using $C_6H_5CF_3$ as an internal standard. GC-MS (*m/z*): 160.0 (M^+). ^{19}F NMR (471 MHz) δ -66.9 (t, J =11.2 Hz, 3F).

1-Methyl-4-(2,2,2-trifluoroethyl)benzene (**3c**).[6]



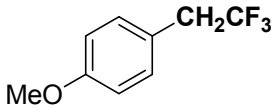
55% ^{19}F NMR yield using $C_6H_5CF_3$ as an internal standard. GC-MS (*m/z*): 174.0 (M^+). ^{19}F NMR (471 MHz) δ -67.1 (t, J = 11.2 Hz, 3F).

1,3-Dimethyl-5-(2,2,2-trifluoroethyl)benzene (**3d**).[7]



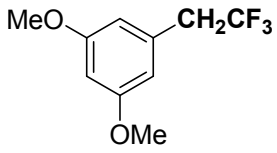
68% ^{19}F NMR yield using $C_6H_5CF_3$ as an internal standard. GC-MS (*m/z*): 188.1 (M^+). ^{19}F NMR (471 MHz) δ -66.8 (t, J = 11.2 Hz, 3F).

1-Methoxy-4-(2,2,2-trifluoroethyl)benzene (**3e**).[7]



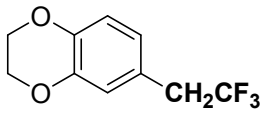
67% ^{19}F NMR yield using $C_6H_5CF_3$ as an internal standard. GC-MS (*m/z*): 190.0 (M^+). ^{19}F NMR (471 MHz) δ -67.3 (t, *J* = 11.2 Hz, 3F).

1,3-Dimethoxy-5-(2,2,2-trifluoroethyl)benzene (**3f**).[8]



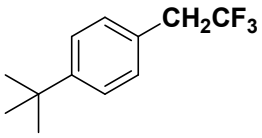
27% ^{19}F NMR yield using $C_6H_5CF_3$ as an internal standard. GC-MS (*m/z*): 220.1 (M^+). ^{19}F NMR (471 MHz) δ -66.6 (t, *J* = 11.2 Hz, 3F).

6-(2,2,2-Trifluoroethyl)-2,3-dihydrobenzo[b][1,4]dioxine (**3g**).[9]



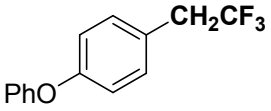
70% ^{19}F NMR yield using $C_6H_5CF_3$ as an internal standard. GC-MS (*m/z*): 217.9 (M^+). ^{19}F NMR (471 MHz) δ -67.2 (t, *J* = 11.2 Hz, 3F).

1-(*Tert*-butyl)-4-(2,2,2-trifluoroethyl)benzene (**3h**).[9]



70% ^{19}F NMR yield using $C_6H_5CF_3$ as an internal standard. GC-MS (*m/z*): 215.9 (M^+). ^{19}F NMR (471 MHz) δ -66.9 (t, *J* = 11.2 Hz, 3F).

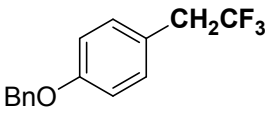
1-Phenoxy-4-(2,2,2-trifluoroethyl)benzene (**3i**).[9]



Colorless oil, 53.3 mg, 53% yield, petroleum ether as the eluent for column chromatography. ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.8 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.12 (t, *J* = 7.4 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 3.33 (q, *J* = 10.8 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.2 (t, *J* = 10.8 Hz,

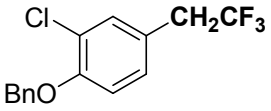
3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.4 (s), 156.8 (s), 131.5 (s), 129.8 (s), 125.8 (q, *J* = 276.5 Hz), 124.7 (q, *J* = 2.9 Hz), 123.6 (s), 119.2 (s), 118.7 (s), 39.5 (q, *J* = 29.8 Hz).

1-(Benzyloxy)-4-(2,2,2-trifluoroethyl)benzene (**3j**).[9]



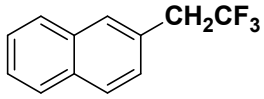
White solid, 87.5 mg, 82% yield, petroleum ether / ethyl acetate = 40 : 1 (v / v) as the eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47−7.35 (m, 5H), 7.25 (d, *J* = 8.1 Hz, 2H), 7.00 (d, *J* = 8.2 Hz, 2H), 5.10 (s, 2H), 3.33 (q, *J* = 10.8 Hz, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -66.3 (t, *J* = 10.8 Hz, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.8 (s), 136.9 (s), 131.3 (s), 128.6 (s), 128.1 (s), 127.5 (s), 125.9 (q, *J* = 276.8), 122.5 (q, *J* = 2.9 Hz), 115.0 (s), 70.1 (s), 39.4 (q, *J* = 29.8 Hz).

1-Benzyloxy-2-chloro-4-(2,2,2-trifluoroethyl)benzene (**3k**).[10]



Light yellow solid, 81.7 mg, 68% yield, petroleum ether / ethyl acetate = 20 : 1 (v / v) as the eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.4 Hz, 2H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.39−7.36 (m, 2H), 7.15 (d, *J* = 8.3 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 5.19 (s, 2H), 3.31 (q, *J* = 10.7 Hz, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -66.2 (t, *J* = 10.7 Hz, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.2 (s), 136.3 (s), 132.0 (s), 129.5 (s), 128.7 (s), 128.1 (s), 127.1 (s), 125.6 (q, *J* = 277.1 Hz), 123.5 (q, *J* = 3.0 Hz), 123.4 (s), 114.0 (s), 70.9 (s), 39.2 (q, *J* = 30.1 Hz).

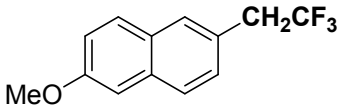
2-(2,2,2-Trifluoroethyl)naphthalene (**3l**).[9]



White solid, 57.3 mg, 68% yield, petroleum ether as the eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89−7.87 (m, 3H), 7.81 (s, 1H),

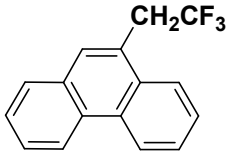
7.55−7.53 (m, 2H), 7.44 (d, *J* = 8.3 Hz, 1H), 3.57 (q, *J* = 10.8 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.6 (t, *J* = 10.8 Hz, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.3 (s), 132.9 (s), 129.5 (s), 128.4 (s), 127.8 (s), 127.7 (s), 127.6 (s), 127.6 (m), 126.4 (s), 126.4 (s), 125.9 (q, *J* = 277.4 Hz), 40.4 (q, *J* = 29.7 Hz).

2-Methoxy-6-(2,2,2-trifluoroethyl)naphthalene (**3m**).[9]



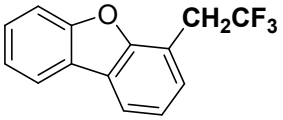
White solid, 54.4 mg, 57% yield, petroleum ether as the eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 3.2 Hz, 1H), 7.75 (d, *J* = 3.8 Hz, 1H), 7.71 (s, 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.20 (m, 1H), 7.16 (d, *J* = 1.2 Hz, 1H), 3.95 (s, 3H), 3.52 (q, *J* = 10.8 Hz, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -65.8 (t, *J* = 10.9 Hz, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.1 (s), 134.1 (s), 129.3 (s), 129.3 (s), 128.8 (s), 128.1 (s), 127.2 (s), 126.0 (q, *J* = 277.6 Hz), 125.2 (q, *J* = 3.0 Hz), 119.3 (s), 105.6 (s), 55.3 (s), 40.2 (q, *J* = 29.6 Hz).

9-(2,2,2-Trifluoroethyl)phenanthrene (**3n**).[9]



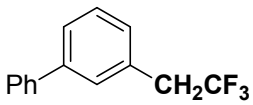
White solid, 51.6 mg, 50% yield, petroleum ether as the eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.79 (d, *J* = 7.3 Hz, 1H), 8.72 (d, *J* = 8.3 Hz, 1H), 8.10 (d, *J* = 7.6 Hz, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.80 (s, 1H), 7.75−7.70 (m, 3H), 7.65 (t, *J* = 7.4 Hz, 1H), 3.94 (q, *J* = 10.5 Hz, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -64.3 (t, *J* = 10.5 Hz, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 131.1 (s), 130.9 (s), 130.8 (s), 130.6 (s), 130.5 (s), 128.6 (s), 127.2 (s), 126.9 (s), 126.7 (s), 126.2 (q, *J* = 277.6 Hz), 124.9 (q, *J* = 3.0 Hz), 124.4 (s), 123.3 (s), 122.6 (s), 37.2 (q, *J* = 30.0 Hz).

4-(2,2,2-Trifluoroethyl)dibenzodibenzofuran (**3o**).



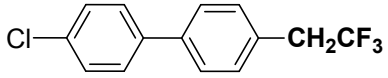
White solid, 44.1 mg, 44% yield, petroleum ether as the eluent for column chromatography. M.p.: 73−74 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99−7.95 (m, 2H), 7.63 (d, *J* = 8.2 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 1H), 7.45 (d, *J* = 7.4 Hz, 1H), 7.41−7.36 (m, 2H), 3.83 (q, *J* = 10.7 Hz, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -65.3 (t, *J* = 10.7 Hz, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.1 (s), 155.2 (s), 128.8 (s), 127.5 (s), 125.8 (q, *J* = 277.7 Hz), 124.5 (s), 124.2 (s), 123.0 (s), 122.9 (s), 120.8 (s), 120.7 (s), 114.3 (q, *J* = 2.9 Hz), 111.8 (s), 34.4 (q, *J* = 31.0 Hz). IR (KBr): 3436, 1450, 1427, 1359, 1261, 1213, 1192, 1168, 1138, 1099, 934, 893, 795, 753, 717, 678, 642, 605 cm^{-1}. HRMS-EI (m/z) calcd for $C_{14}H_9F_3O$ (M^+): 250.0605; Found: 250.0608.

3-(2,2,2-trifluoroethyl)-1,1’-biphenyl (**3p**).[9]



White solid, 55.3 mg, 59% yield, petroleum ether as the eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63−7.60 (m, 3H), 7.55 (s, 1H), 7.50−7.45 (m, 3H), 7.40 (t, *J* = 7.2 Hz, 1H), 7.32 (d, *J* = 7.4 Hz, 1H), 3.47 (q, *J* = 10.8 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.8 Hz (t, *J* = 10.7 Hz, 3F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8 (s), 140.7 (s), 130.7 (q, *J* = 3.0 Hz), 129.1 (s), 129.1 (s), 129.0 (s), 128.9 (s), 127.6 (s), 127.2 (s), 127.0 (s), 125.8 (q, *J* = 277.9 Hz), 40.3 (q, *J* = 29.7 Hz).

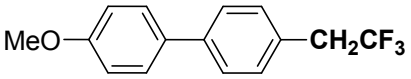
4-Chloro-4'-(2,2,2-trifluoroethyl)-1,1’-biphenyl (**3r**)



White solid, 67.3 mg, 62% yield, petroleum ether as the eluent for column chromatography. M.p.: 66−68 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.7 Hz, 2H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 7.7 Hz, 2H), 3.44 (q, *J* = 10.8 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.8 (t, *J* = 10.8 Hz, 3F). ^{13}C

NMR (126 MHz, $CDCl_3$) δ 139.9 (s), 138.9 (s), 133.7 (s), 130.7 (s), 129.5 (q, J = 3.1 Hz), 129.0 (s), 128.4 (s), 127.3 (s), 125.7 (q, J = 277.6 Hz), 39.9 (q, J = 29.8 Hz). IR (KBr): 3480, 3410, 2952, 1654, 1484, 1433, 1366, 1258, 1137, 1068, 907, 863, 802, 760, 664, 632 cm^{-1}. HRMS-EI (m/z) calcd for $C_{14}H_{10}ClF_3$ (M^+): 270.0423; Found: 270.0418.

4-Methoxy-4'-(2,2,2-trifluoroethyl)-1,1'-biphenyl (**3s**)

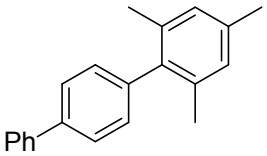


White solid, 78.0 mg, 73% yield, petroleum ether as the eluent for column chromatography. M.p.: 98−100 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 7.58-7.55 (m, 4H), 7.37 (d, J = 7.7 Hz, 2H), 7.01 (d, J = 8.0 Hz, 2H), 3.88 (s, 3H), 3.43 (q, J = 10.8 Hz, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -65.9 (t, J = 10.8 Hz, 3F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4 (s), 140.7 (s), 133.0 (s), 130.5 (s), 128.5 (q, J = 3.2 Hz), 128.1 (s), 127.0 (s), 125.8 (q, J = 277.0 Hz), 114.3 (s), 55.4 (s), 39.9 (q, J = 29.7 Hz). IR (KBr): 3450, 2967, 2840, 1640, 1501, 1459, 1368, 1278, 1153, 1073, 911, 831, 796, 739, 651, 642 cm^{-1}. HRMS-EI (m/z) calcd for $C_{15}H_{13}F_3O$ (M^+): 266.0918; Found: 266.0920.

6. General procedure for Pd-catalyzed arylation of arylboronic acids with aryl(trifluoroethyl)iodonium triflate.

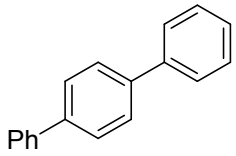
In a nitrogen-filled glovebox, a sealed tube was charged with arylboronic acid (**1**, 0.4 mmol), $[ArICH_2CF_3]^+[OTf]^-$ (**2**, 0.8 mmol), $Pd[P(t\text{-}Bu)_3]_2$ (0.02, 0.03, or 0.04 mmol), Cs_2CO_3 (0.8 mmol), and DMF (4 mL) with stirring. The mixture was reacted at 40 °C for 48 h and extracted with ethyl acetate (3 times). The organic solution was washed by water, dried over anhydrous Na_2SO_4, and concentrated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel using petroleum ether or a mixture of petroleum ether and ethyl acetate as eluents to give the arylation product (**4**).

2,4,6-Trimethyl[1,1';4',1"]terphenyl (**4a**).[11a]



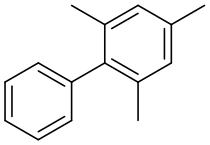
White solid, 88.2 mg, 81% yield (7.5 mol% Pd[P(*t*-Bu)$_3$]$_2$), petroleum ether as the eluent for colunm chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72−7.69 (m, 4H), 7.51 (t, *J* = 7.4 Hz, 2H), 7.40 (t, *J* = 7.2 Hz, 1H), 7.26 (d, *J* = 7.8 Hz, 2H), 7.01 (s, 2H), 2.39 (s, 3H), 2.11 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0 (s), 140.1 (s), 139.3 (s), 138.7 (s), 136.7 (s), 136.1 (s), 129.8 (s), 128.8 (s), 128.1 (s), 127.2 (s), 127.1 (s), 21.1 (s), 20.9 (s).

1,1':4',1''-Terphenyl (**4a'**)[11b]



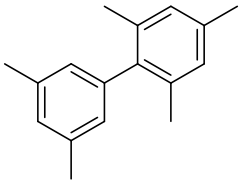
White solid, 75.1mg, 82% yield (10 mol% Pd[P(*t*-Bu)$_3$]$_2$), petroleum ether as the eluent for colunm chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72-7.67 (m, 8H), 7.50 (t, *J* = 7.5 Hz, 4H), 7.40 (t, *J* = 7.4 Hz, 2H).

2,4,6-Trimethyl-1,1'-biphenyl (**4b**).[12]



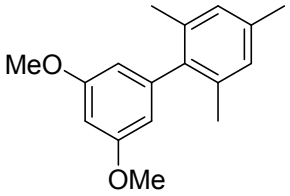
Colorless oil, 51.4 mg, 66% yield (10 mol% Pd[P(*t*-Bu)$_3$]$_2$), petroleum ether as the eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (t, *J* = 7.4 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 1H), 7.19 (d, *J* = 7.4 Hz, 2H), 7.00 (s, 2H), 2.39 (s, 3H), 2.06 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1 (s), 139.1 (s), 136.6 (s), 136.0 (s), 129.3 (s), 128.4 (s), 128.1 (s), 126.5 (s), 21.1 (s), 20.8 (s).

2,3',4,5',6-Pentamethyl-1,1'-biphenyl (**4d**).[13]



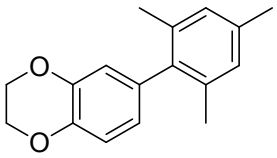
Colorless oil, 56.9 mg, 64% yield (5 mol% Pd[P(*t*-Bu)$_3$]$_2$), petroleum ether as the eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.01 (s, 1H), 6.98 (s, 2H), 6.80 (s, 2H), 2.39 (s, 6H), 2.38 (s, 3H), 2.06 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0 (s), 139.3 (s), 137.7 (s), 136.3 (s), 135.9 (s), 128.1 (s), 128.0 (s), 127.0 (s), 21.4 (s), 21.0 (s), 20.8 (s).

3',5'-Dimethoxy-2,4,6-trimetheyl-1,1'-biphenyl (**4f**).[14]



Yellow solid, 73.6 mg, 72% yield (7.5 mol% Pd[P(*t*-Bu)$_3$]$_2$), petroleum ether / ethyl acetate = 20 : 1 (v / v) as the eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.97 (s, 2H), 6.48 (s, 1H), 6.34 (s, 2H), 3.83 (s, 6H), 2.36 (s, 3H), 2.09 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.8 (s), 143.2 (s), 139.0 (s), 136.6 (s), 135.9 (s), 128.0 (s), 107.3 (s), 98.7 (s), 55.3 (s), 21.0 (s), 20.5 (s).

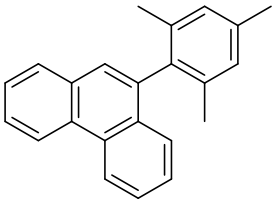
6-Mesityl-2,3-dihydrobenzo[b][1,4]dioxine (**4g**)



Yellow oil, 77.4mg, 76% yield (7.5 mol% Pd[P(*t*-Bu)$_3$]$_2$), petroleum ether as the eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.95 (s, 2H), 6.93 (d, *J* = 8.8 Hz, 1H), 6.69 (s, 1H), 6.63 (d, *J* = 8.2 Hz, 1H), 4.34 (s, 4H), 2.35 (s, 3H), 2.07 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.4 (s), 142.2 (s), 138.5 (s), 136.5 (s), 136.3 (s), 134.4 (s), 128.0 (s), 122.5 (s), 118.0 (s), 117.1 (s), 64.5 (s), 64.4 (s), 21.0 (s), 20.7 (s). IR (KBr): 2973, 2921, 2875, 1611, 1580, 1511, 1479, 1457, 1360, 1284,

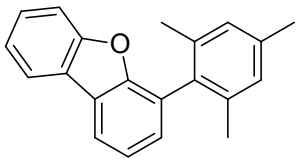
1243, 1220, 1122, 1069, 1055, 1021, 932, 892, 851, 816, 758, 732, 689, 650 cm^{-1}. HRMS-EI (m/z) calcd for $C_{17}H_{18}O_2$ (M^+): 254.1307; Found: 254.1308.

9-Mesitylphenanthrene (**4n**).[15]



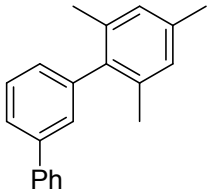
White solid, 92.2 mg, 78% yield (7.5 mol% Pd[P(*t*-Bu)$_3$]$_2$), petroleum ether as the eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.82 (d, *J* = 8.4 Hz, 1H), 8.79 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 7.7 Hz, 1H), 7.73−7.64 (m, 3H), 7.59 (s, 1H), 7.52−7.46 (m, 2H), 7.08 (s, 2H), 2.45 (s, 3H), 1.98 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.4 (s), 137.1 (s), 137.0 (s), 136.6 (s), 132.0 (s), 131.4 (s), 130.6 (s), 130.0 (s), 128.6 (s), 128.2 (s), 127.3 (s), 126.8 (s), 126.7 (s), 126.5 (s), 126.4 (s), 126.2 (s), 122.9 (s), 122.6 (s), 21.2 (s), 20.3 (s).

4-Mesityldibenzo[b,d]furan (**4o**)



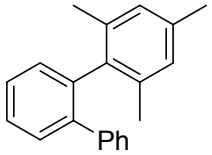
Colorless oil, 98.0 mg, 86% yield (7.5 mol% Pd[P(*t*-Bu)$_3$]$_2$), petroleum ether as the eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.6 Hz, 1H), 8.01 (d, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.49−7.44 (m, 2H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.30 (d, *J* = 7.5 Hz, 1H), 7.09 (s, 2H), 2.44 (s, 3H), 2.09 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.3 (s), 153.9 (s), 137.6 (s), 136.9 (s), 133.0 (s), 128.6 (s), 128.3 (s), 127.1 (s), 125.0 (s), 124.5 (s), 124.3 (s), 122.9 (s), 122.7 (s), 120.7 (s), 119.4 (s), 112.0 (s), 21.2 (s), 20.5 (s). IR (KBr): 3052, 2950, 2918, 2856, 1612, 1584, 1450, 1420, 1376, 1312, 1274, 1218, 1121, 1097, 1057, 1014, 932, 845, 799, 753, 684, 592 cm^{-1}. HRMS-EI (m/z) calcd for $C_{21}H_{18}O$ (M^+): 286.1358; Found: 286.1354.

2,4,6-Trimethyl[1,1':3',1"]terphenyl (**4p**).[16]



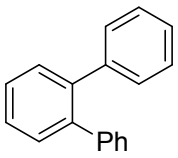
Colorless oil, 90.3 mg, 83% yield (7.5 mol% Pd[P(*t*-Bu)$_3$]$_2$), petroleum ether as the eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.6 Hz, 2H), 7.63 (d, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.50−7.47 (m, 3H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.19 (d, *J* = 7.4 Hz, 1H), 7.02 (s, 2H), 2.40 (s, 3H), 2.11 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6 (s), 141.2 (s), 141.1 (s), 139.0 (s), 136.7 (s), 136.0 (s), 128.9 (s), 128.8 (s), 128.3 (s), 128.2 (s), 128.1 (s), 127.3 (s), 127.1 (s), 125.3 (s), 21.1 (s), 20.9 (s).

2,4,6-Trimethyl[1,1':2',1"]terphenyl (**4q**).[17]



Colorless oil, 23.2 mg, 21% yield (7.5 mol% Pd[P(*t*-Bu)$_3$]$_2$), petroleum ether as the eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.4 Hz, 1H), 7.47−7.41 (m, 2H), 7.21−7.20 (m, 4H), 7.15 (m, 2H), 6.83 (s, 2H), 2.30 (s, 3H), 1.95 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5 (s), 141.0 (s), 139.1 (s), 137.9 (s), 136.3 (s), 135.9 (s), 130.7 (s), 130.2 (s), 128.8 (s), 128.0 (s), 127.6 (s), 127.3 (s), 127.3 (s), 126.5 (s), 21.1 (s), 20.7 (s).

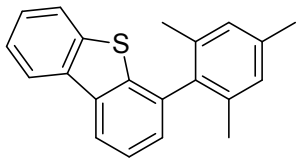
2-Phenylbiphenyl (**4q'**).[12]



Colorless oil, 85.7 mg, 93% yield (7.5 mol% Pd[P(*t*-Bu)$_3$]$_2$) or 77.8 mg, 85% (10 mol% Pd[P(*t*-Bu)$_3$]$_2$), petroleum ether as the eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50−7.45 (m, 4H), 7.28−7.22 (m, 6H), 7.20−7.19 (m, 4H). ^{13}C

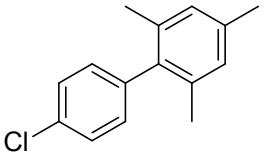
NMR (100 MHz, $CDCl_3$) δ 141.6 (s), 140.6 (s), 130.6 (s), 129.9 (s), 127.9 (s), 127.5 (s), 126.5 (s).

4-Mesityldibenzo[b,d]thiophene (**4t**)



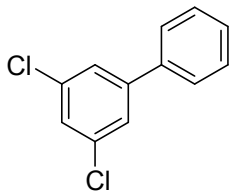
Colorless oil, 101.5 mg, 84% yield (7.5 mol% Pd[P(*t*-Bu)$_3$]$_2$), petroleum ether as the eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, *J* = 7.6 Hz, 1H), 8.19 (d, *J* = 7.8 Hz, 1H), 7.81 (d, *J* = 7.5 Hz, 1H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.52–7.45 (m, 2H), 7.29 (d, *J* = 6.8 Hz, 1H), 7.06 (s, 2H), 2.43 (s, 3H), 2.04 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.1 (s), 139.8 (s), 137.6 (s), 136.7 (s), 136.3 (s), 136.2 (s), 136.1 (s), 135.7 (s), 128.4 (s), 127.3 (s), 126.7 (s), 125.0 (s), 124.3 (s), 122.9 (s), 121.8 (s), 120.1 (s), 21.2 (s), 20.0 (s). IR (KBr): 3059, 2950, 2917, 2854, 1611, 1572, 1450, 1384, 1323, 1301, 1250, 1182, 1100, 1042, 1023, 1003, 851, 812, 751, 725, 587 cm^{-1}. HRMS-EI (m/z) calcd for $C_{21}H_{18}S$ (M^+): 302.1129; Found: 302.1134.

4-Chloro-2',4',6'-trimetheylbiphenyl (**4u**).[16]



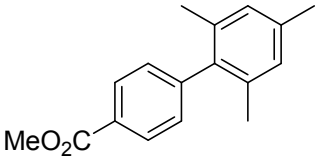
White solid, 69.8 mg, 76% yield (10 mol% Pd[P(*t*-Bu)$_3$]$_2$), petroleum ether as the eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.6 Hz, 2H), 7.12 (d, *J* = 7.5 Hz, 2H), 6.98 (s, 2H), 2.37 (s, 3H), 2.03 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.5 (s), 137.8 (s), 137.0 (s), 135.9 (s), 132.5 (s), 130.8 (s), 128.7 (s), 128.2 (s), 21.0 (s), 20.7 (s).

3,5-Dichlorobiphenyl (**4v'**).[18]



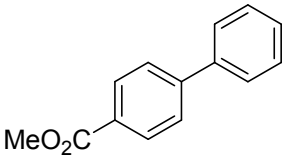
Colorless liquid, 86.1 mg, 97% yield (7.5 mol% Pd[P(*t*-Bu)$_3$]$_2$) or 85.7 mg, 96% yield (10 mol% Pd[P(*t*-Bu)$_3$]$_2$), petroleum ether as the eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.0 Hz, 2H), 7.49−7.47 (m, 4H), 7.43 (d, J = 7.4 Hz, 1H), 7.37 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.2 (s), 138.5 (s), 135.3 (s), 129.1 (s), 128.5 (s), 127.2 (s), 127.1 (s), 125.7 (s).

Methyl 2',4',6'-trimethyl-[1,1'-biphenyl]-4-carboxylate (**4w**).[19]



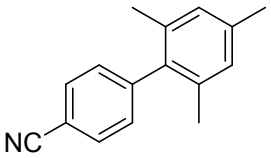
Light yellow solid, 59.2 mg, 58% (7.5 mol% Pd[P(*t*-Bu)$_3$]$_2$), petroleum ether / ethyl acetate = 40 : 1 (v / v) as the eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.7 Hz, 2H), 7.26 (d, *J* = 7.7 Hz, 2H), 6.98 (s, 2H), 3.98 (s, 3H), 2.37 (s, 3H), 2.01 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.2 (s), 146.3 (s), 138.0 (s), 137.1 (s), 135.5 (s), 129.8 (s), 129.5 (s), 128.6 (s), 128.2 (s), 52.1 (s), 21.0 (s), 20.6 (s).

Methyl [1,1'-biphenyl]-4-carboxylate (**4w'**).[19]



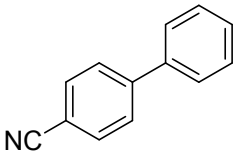
White solid, 73.0 mg, 86% yield (7.5 mol% Pd[P(*t*-Bu)$_3$]$_2$) or 73.5 mg, 87% (10 mol% Pd[P(*t*-Bu)$_3$]$_2$), petroleum ether / ethyl acetate = 40 : 1 (v / v) as the eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.1 Hz, 2H), 7.69 (d, *J* = 8.1 Hz, 2H), 7.65 (d, *J* = 7.2 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 1H), 3.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.4 (s), 167.0 (s), 145.7 (s), 140.0 (s), 130.1 (s), 128.9 (s), 128.2 (s), 127.3 (s), 127.1 (s), 52.1 (s).

2',4',6'-Trimethyl-[1,1'-biphenyl]-4-carbonitrile (**4x**).[20]



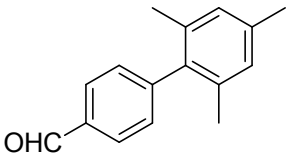
White solid, 44.6 mg, 50% yield (7.5 mol% Pd[P(*t*-Bu)$_3$]$_2$) or 64.2 mg, 73% yield (10 mol% Pd[P(*t*-Bu)$_3$]$_2$), petroleum ether / ethyl acetate = 40 : 1 (v / v) as the eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.7 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 6.99 (s, 2H), 2.37 (s, 3H), 2.00 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.5 (s), 137.6 (s), 137.2 (s), 135.3 (s), 132.3 (s), 130.4 (s), 128.4 (s), 119.0 (s), 110.7 (s), 21.0 (s), 20.6 (s).

[1,1'-Biphenyl]-4-carbonitrile (**4x'**).[20]



White solid, 71.2 mg, 99% yield (7.5 mol% Pd[P(*t*-Bu)$_3$]$_2$), petroleum ether / ethyl acetate = 40 : 1 (v / v) as the eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74−7.67 (m, 4H), 7.59 (d, *J* = 7.3 Hz, 2H), 7.51−7.41 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7 (s), 139.2 (s), 132.6 (s), 129.1 (s), 128.7 (s), 127.8 (s), 127.3 (s), 119.0 (s), 110.9 (s).

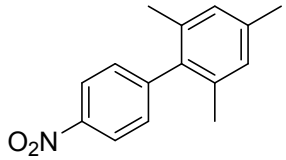
2',4',6'-Trimethyl-[1,1'-biphenyl]-4-carbaldehyde (**4y**).[21]



Yellow oil, 54.5 mg, 61% yield (7.5 mol% Pd[P(*t*-Bu)$_3$]$_2$) or 75.3 mg, 84% yield (10 mol% Pd[P(*t*-Bu)$_3$]$_2$), petroleum ether / ethyl acetate = 40 : 1 (v / v) as the eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.1 (s, 1H), 7.98 (d, *J* = 7.5 Hz, 2H), 7.36 (d, *J* = 7.6 Hz, 2H), 6.99 (s, 2H), 2.37 (s, 3H), 2.02 (s, 6H). ^{13}C NMR

(126 MHz, $CDCl_3$) δ 192.1 (s), 148.2 (s), 137.8 (s), 137.3 (s), 135.4 (s), 135.0 (s), 130.2 (s), 129.9 (s), 128.3 (s), 21.0 (s), 20.6 (s).

2,4,6-Trimethyl-4'-nitro-1,1'-biphenyl (**4z**).[22]



Yellow solid, 73.4 mg, 76% yield (7.5 mol% $Pd[P(t\text{-}Bu)_3]_2$), petroleum ether / ethyl acetate = 20 : 1 (v / v) as the eluent for column chromatography. ^1H NMR (500 MHz, $CDCl_3$) δ 8.32 (d, J = 7.8 Hz, 2H), 7.36 (d, J = 7.8 Hz, 2H), 6.99 (s, 2H), 2.37 (s, 3H), 2.01 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6 (s), 146.9 (s), 137.7 (s), 136.8 (s), 135.3 (s), 130.5 (s), 128.4 (s), 123.8 (s), 21.0 (s), 20.6 (s).

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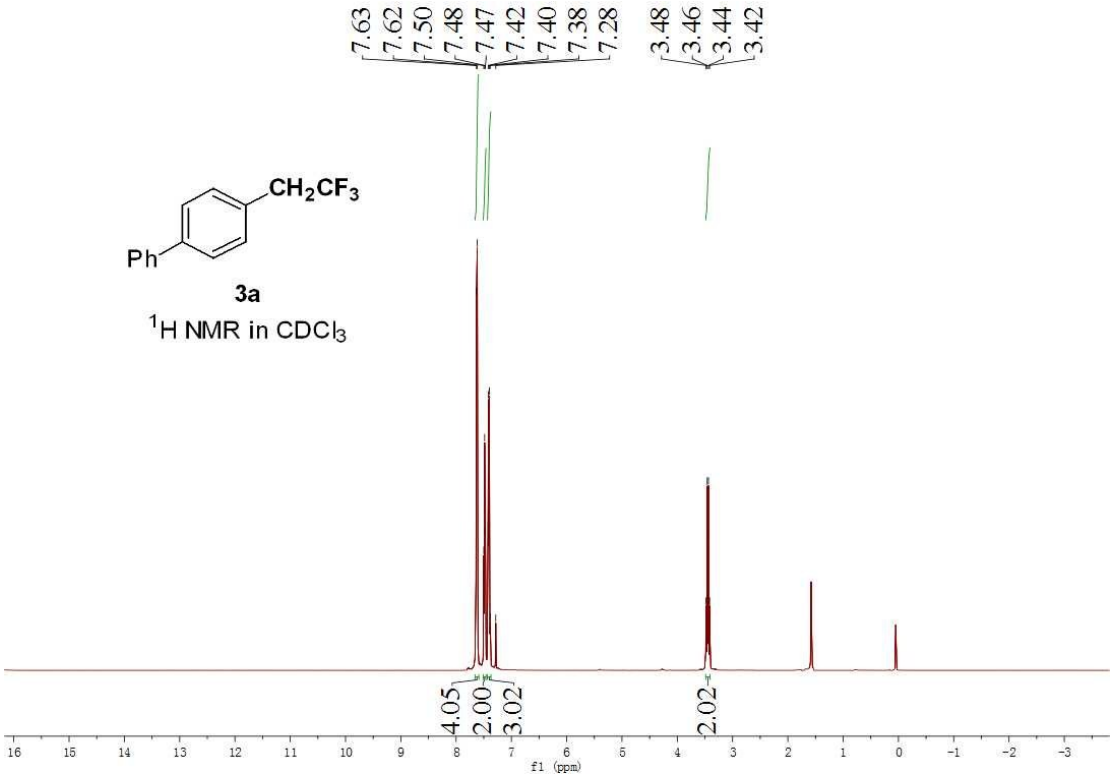
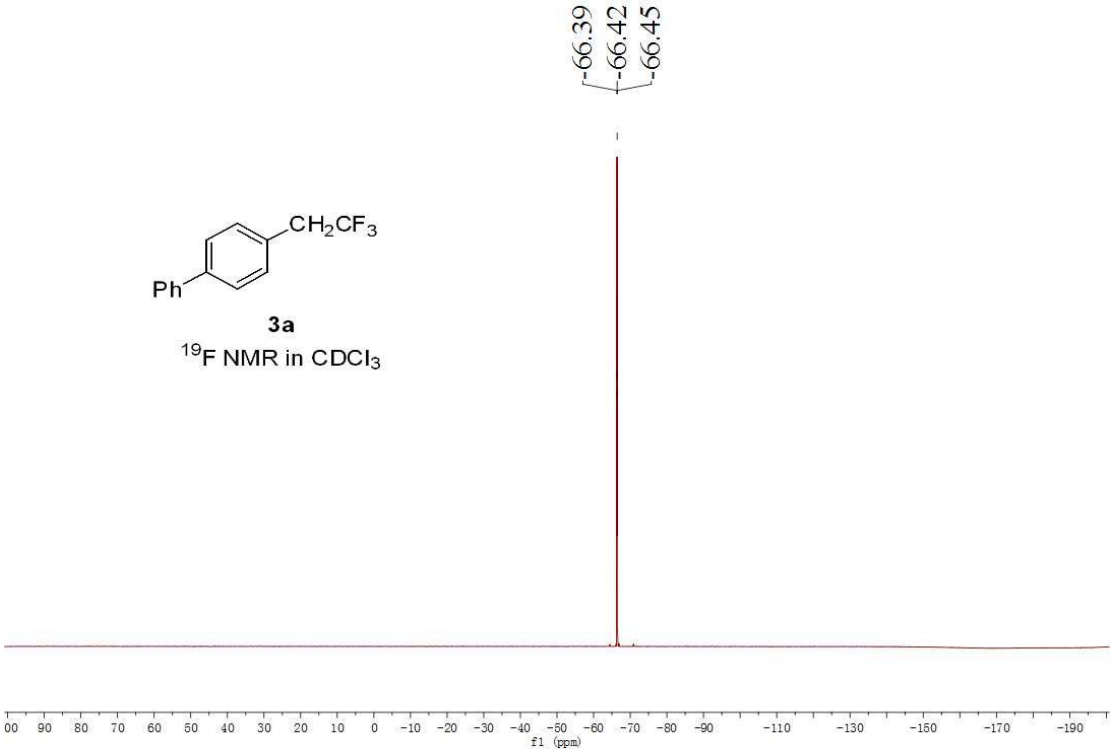
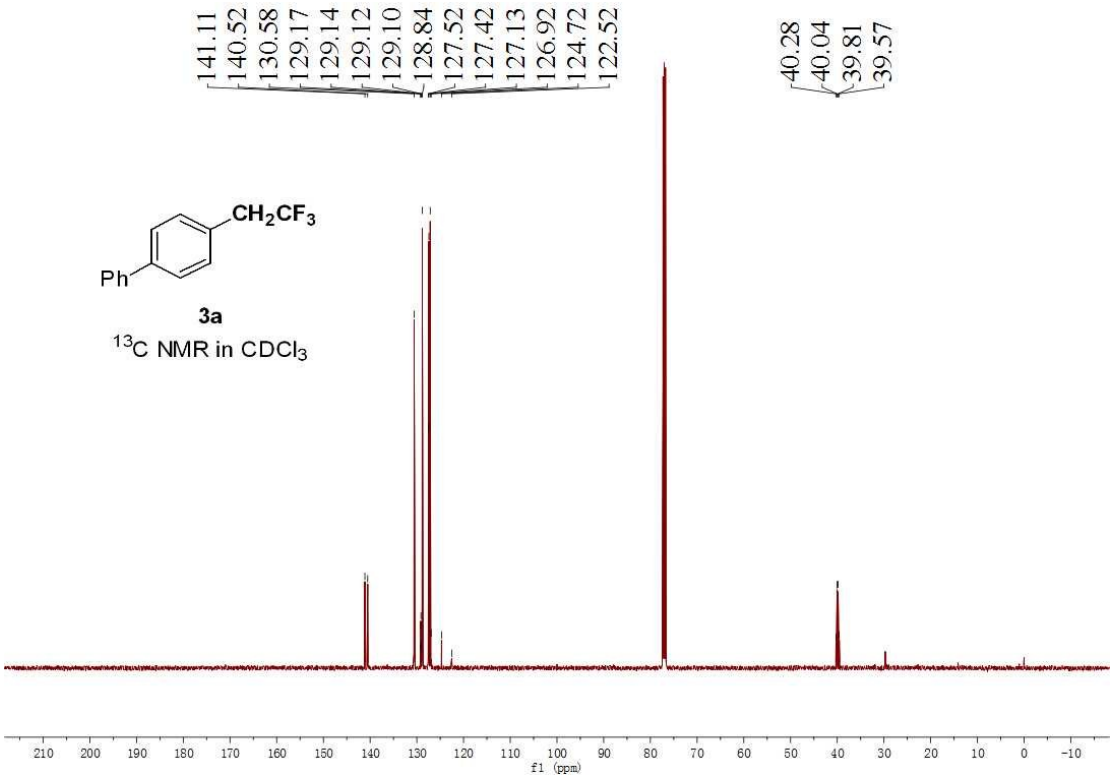
7. The NMR spectra of 3 and 4.



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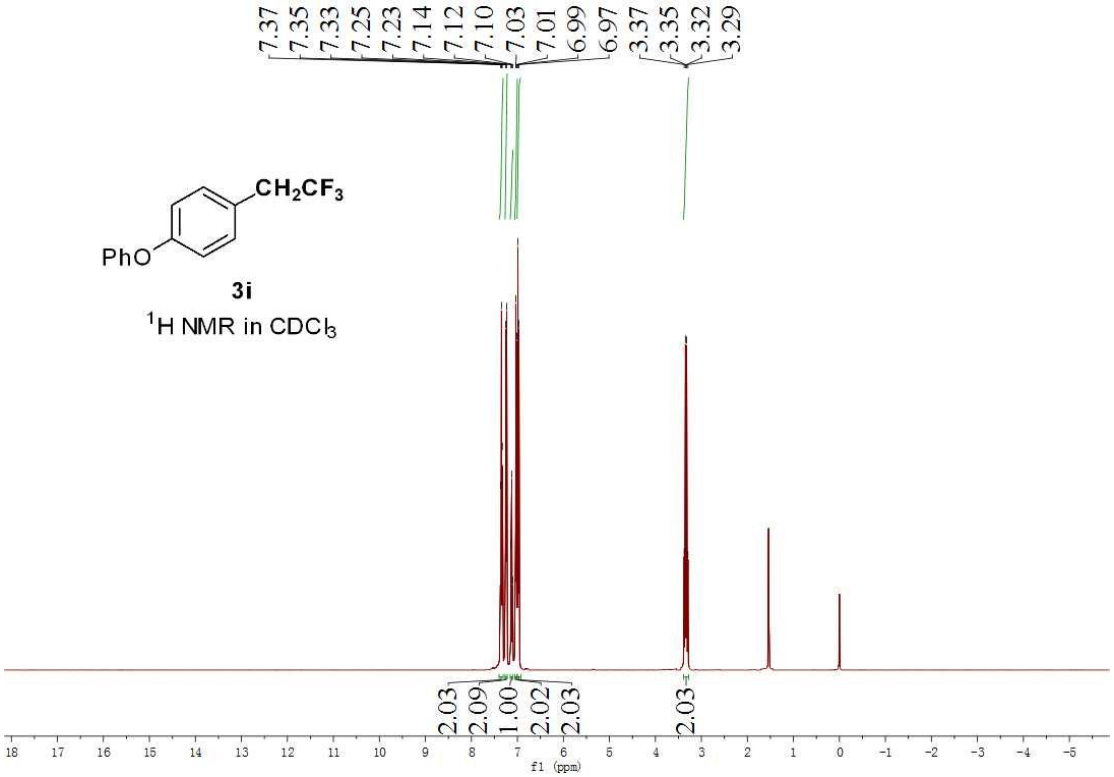
CH2CF3
Ph
3a
13C NMR in CDCl3
f1 (ppm)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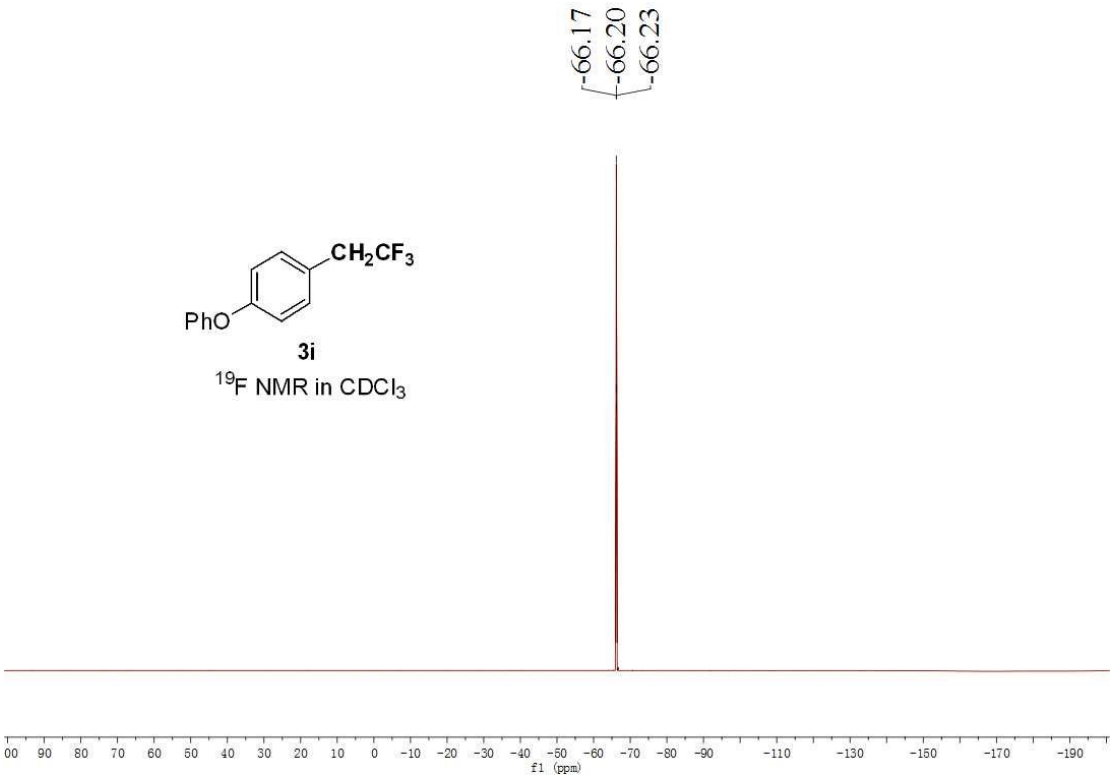
7.25
7.23
7.14
7.12
7.10
7.03
7.01
6.99
6.97
3.37
3.35
3.32
3.29
CH2CF3
PhO
3i
1H NMR in CDCl3
2.03
2.09
1.00
2.02
2.03
2.03
f1 (ppm)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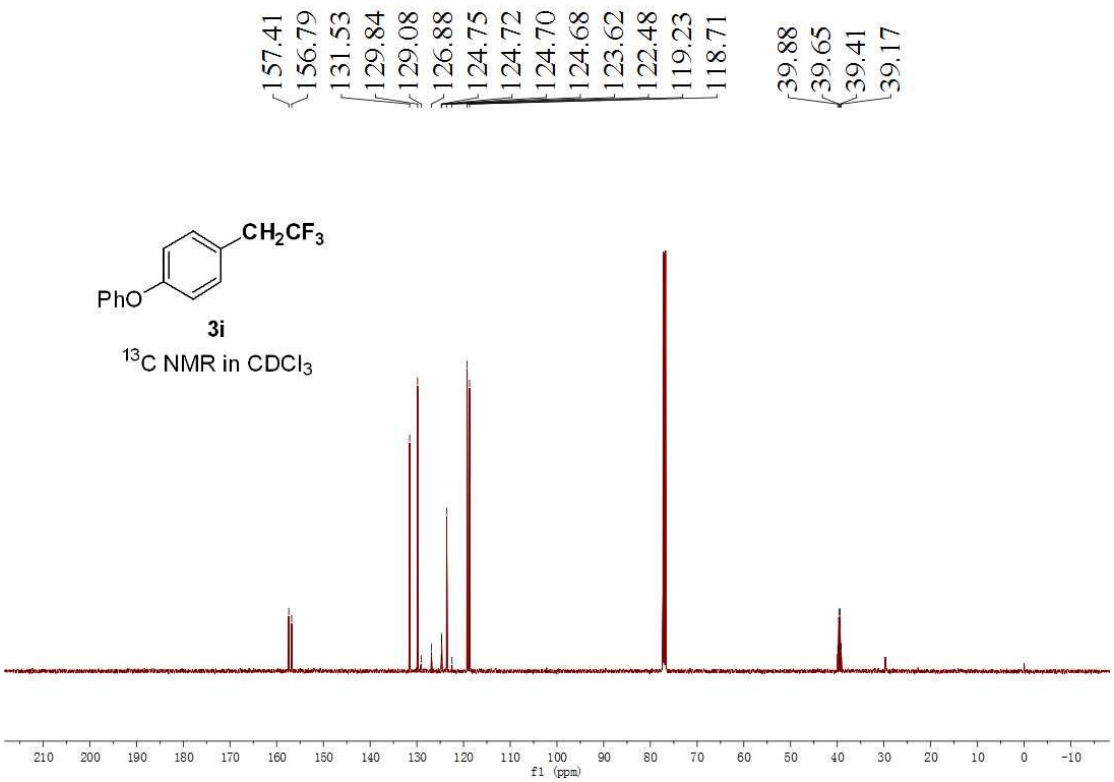
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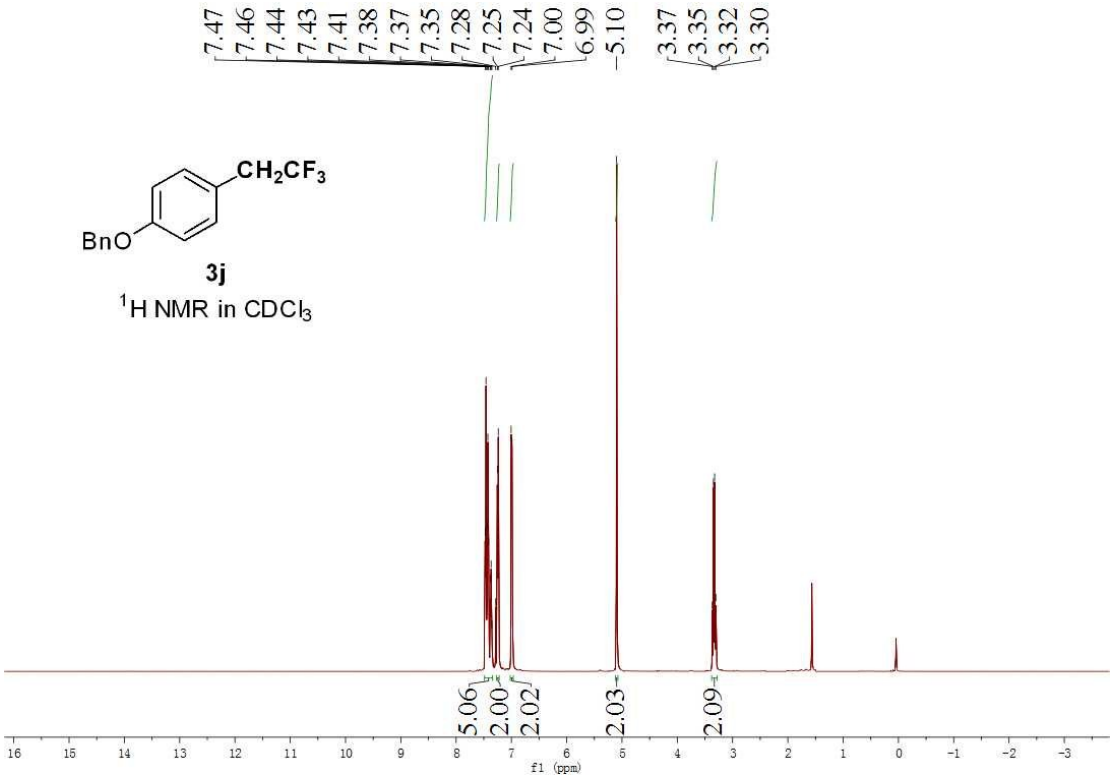
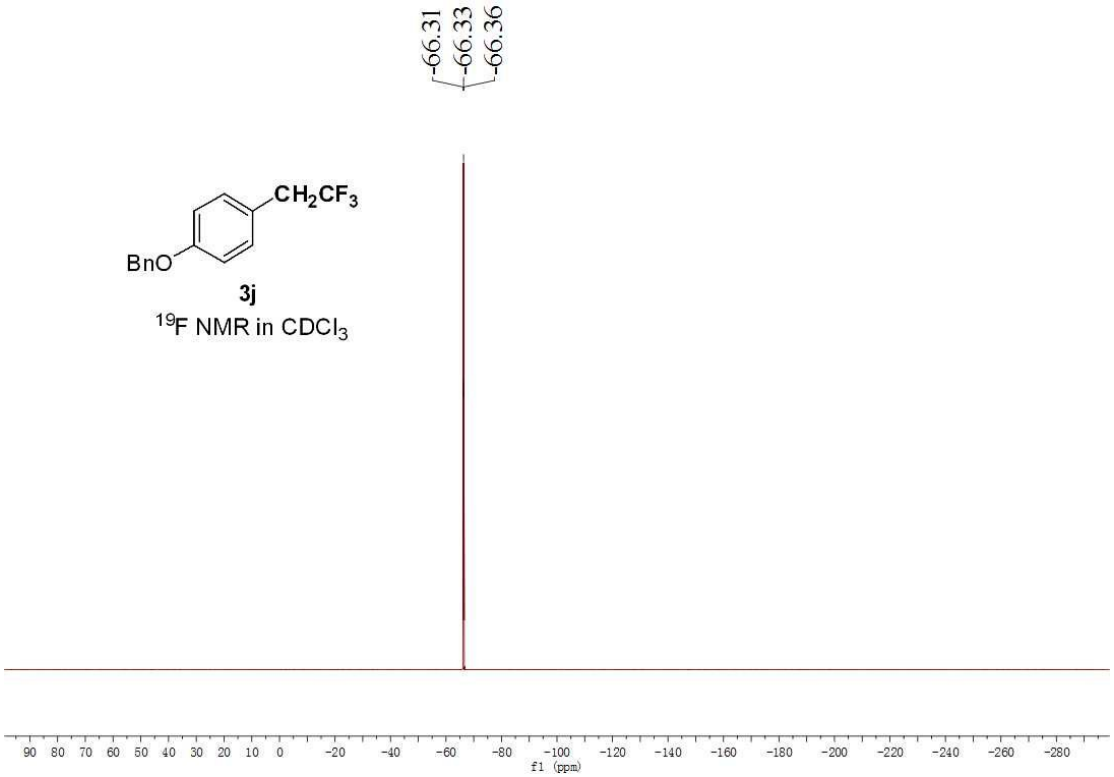
13C NMR in CDCl3
f1 (ppm)



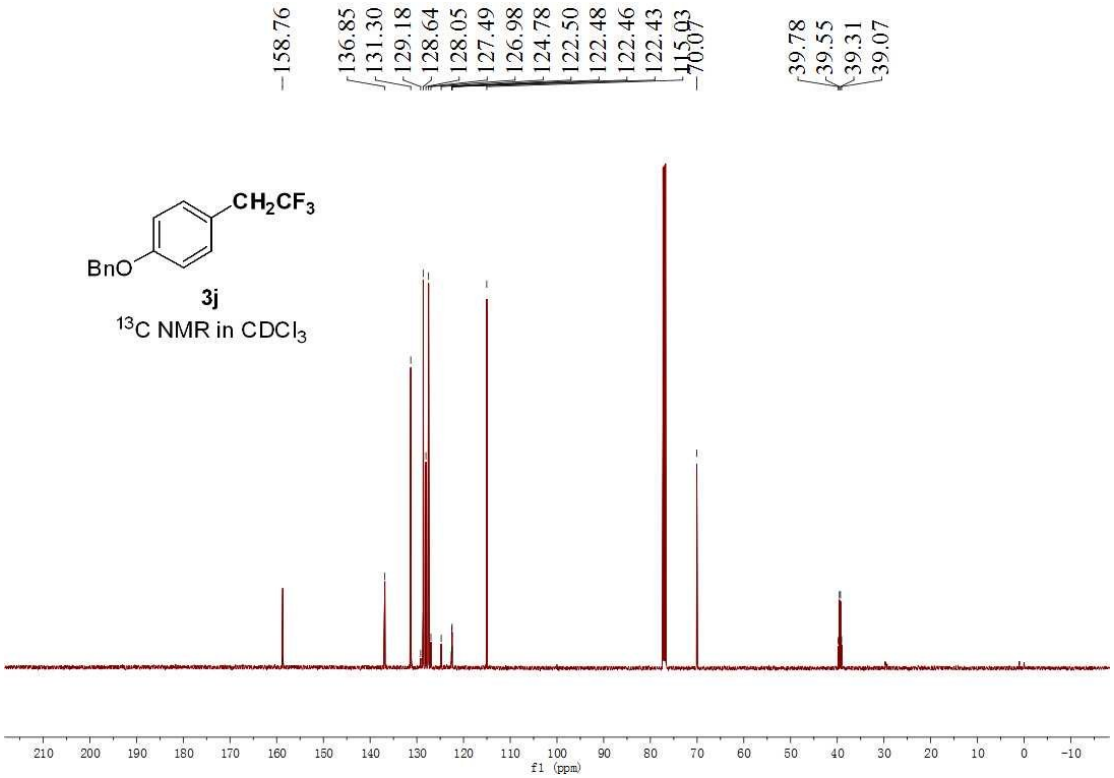
3j

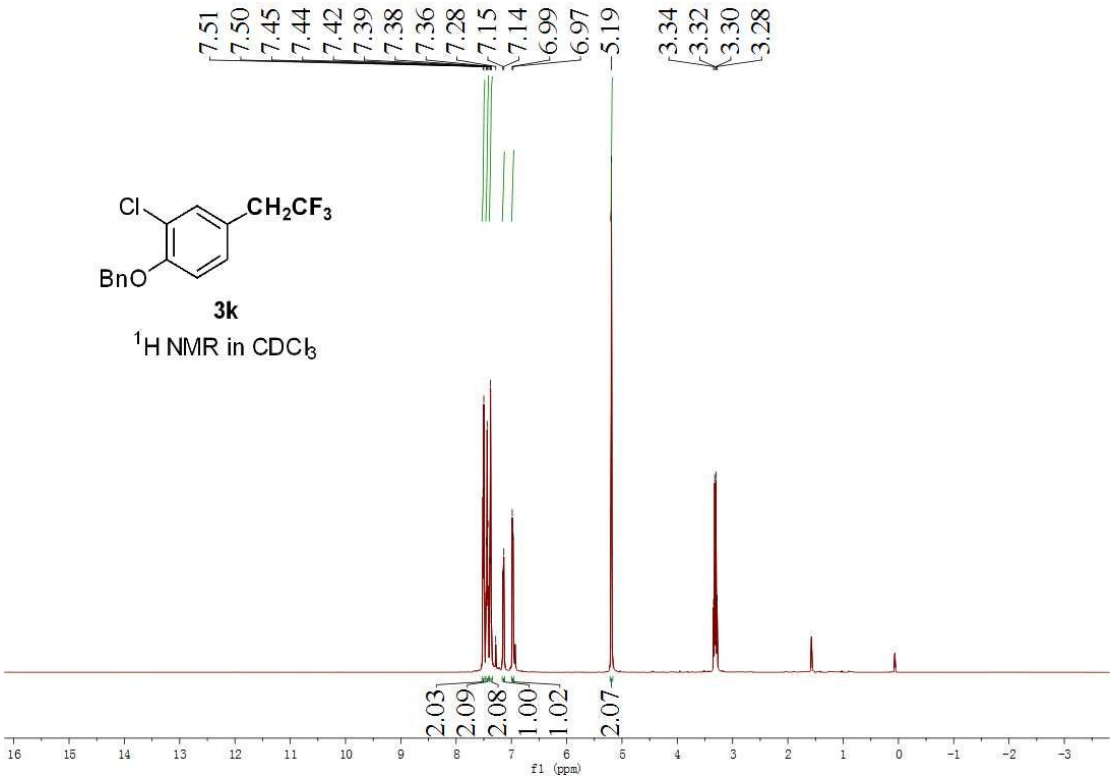
^{1}H NMR in $CDCl_3$

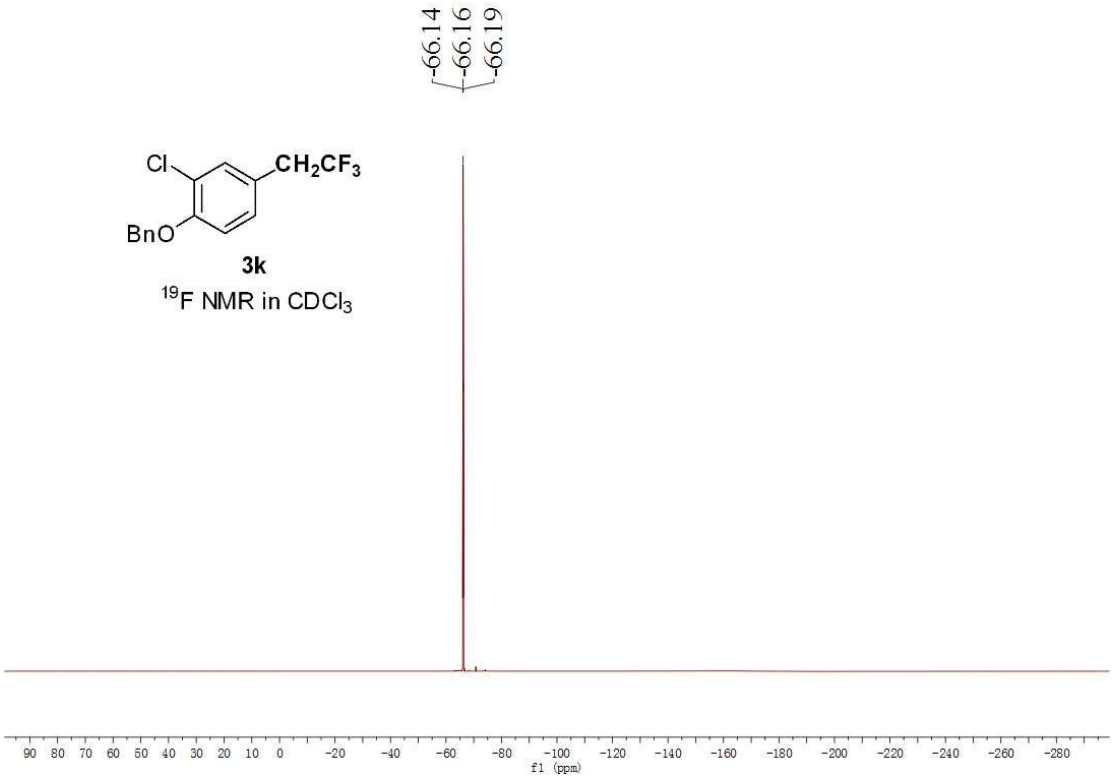


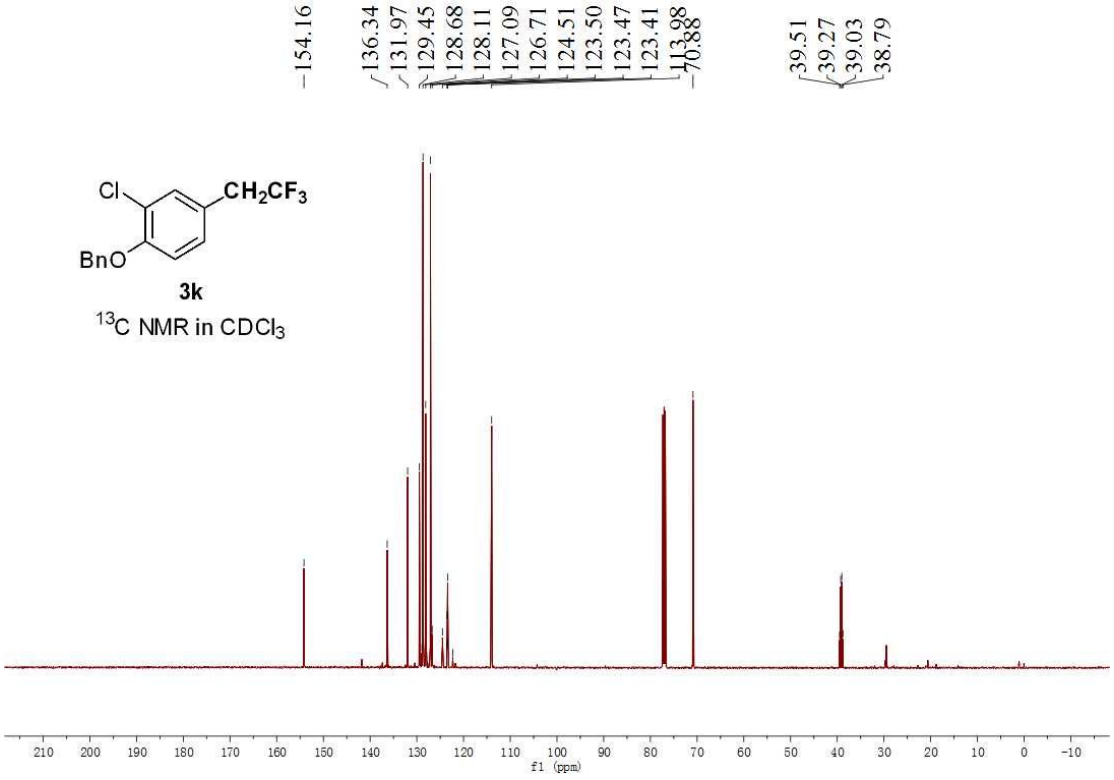
3j

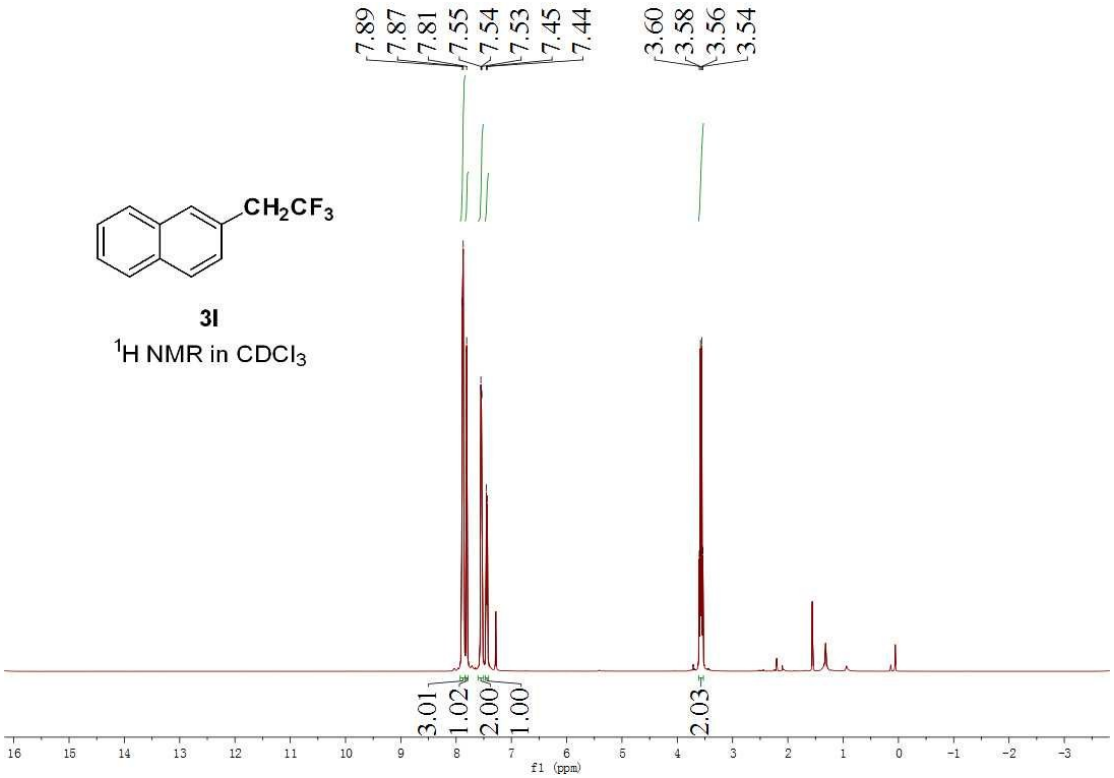
^{19}F NMR in $CDCl_3$


158.76
136.85
131.30
129.18
128.64
128.05
127.49
126.98
124.78
122.50
122.48
122.46
122.43
115.03
70.07
39.78
39.55
39.31
39.07
CH2CF3
BnO
3j
13C NMR in CDCl3
f1 (ppm)


7.51
7.50
7.45
7.44
7.42
7.39
7.38
7.36
7.28
7.15
7.14
6.99
6.97
5.19
3.34
3.32
3.30
3.28
Cl
CH2CF3
BnO
3k
1H NMR in CDCl3
2.03
2.09
2.08
1.00
1.02
2.07
f1 (ppm)

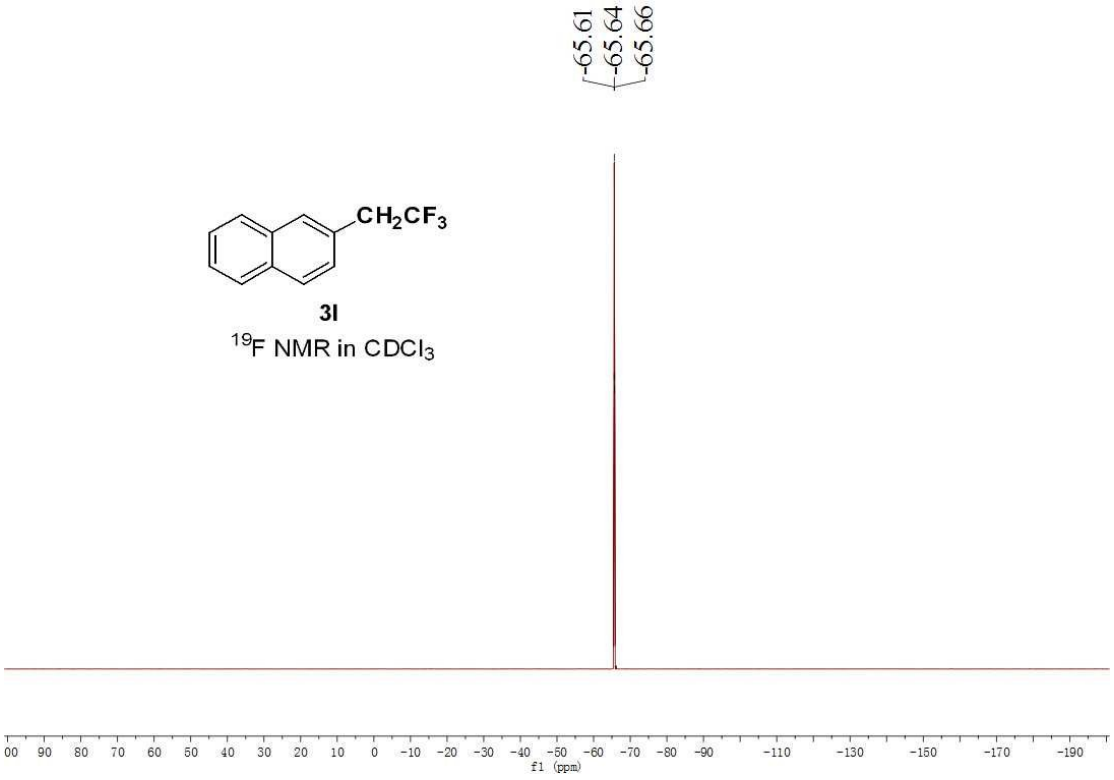

-66.14
-66.16
-66.19
Cl
CH2CF3
BnO
3k
19F NMR in CDCl3
f1 (ppm)


154.16
136.34
131.97
129.45
128.68
128.11
127.09
126.71
124.51
123.50
123.47
123.41
113.98
70.88
39.51
39.27
39.03
38.79
Cl
CH2CF3
BnO
3k
13C NMR in CDCl3
f1 (ppm)



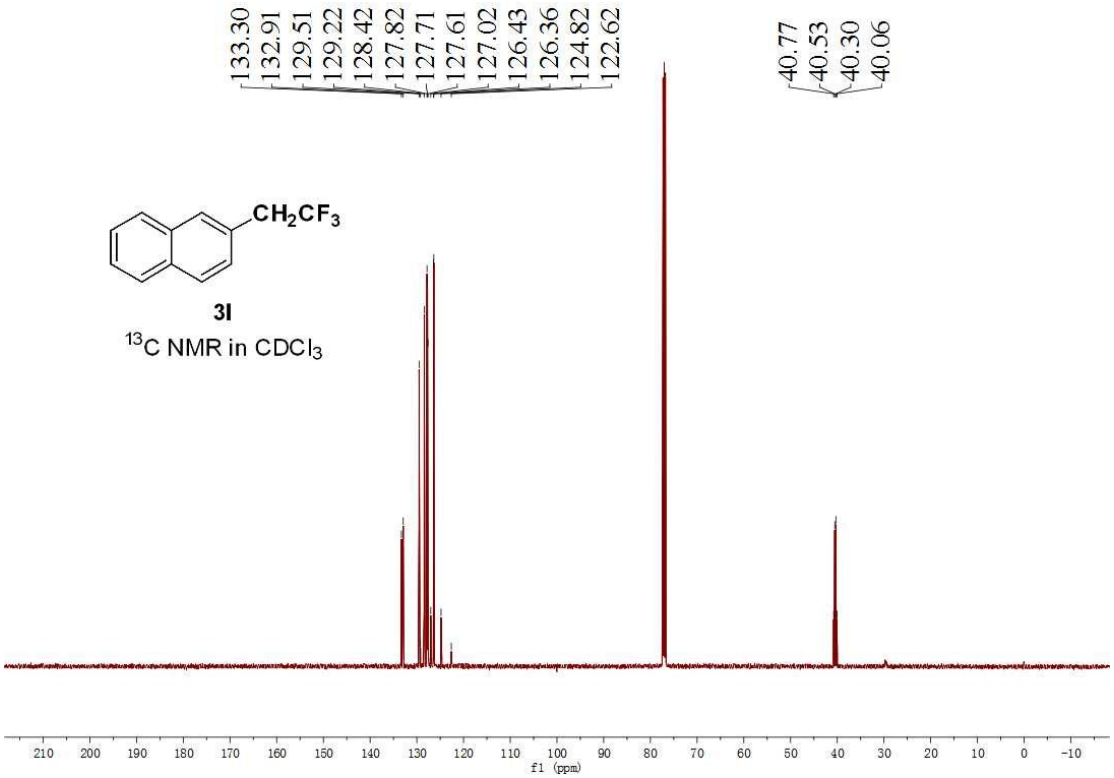
3l

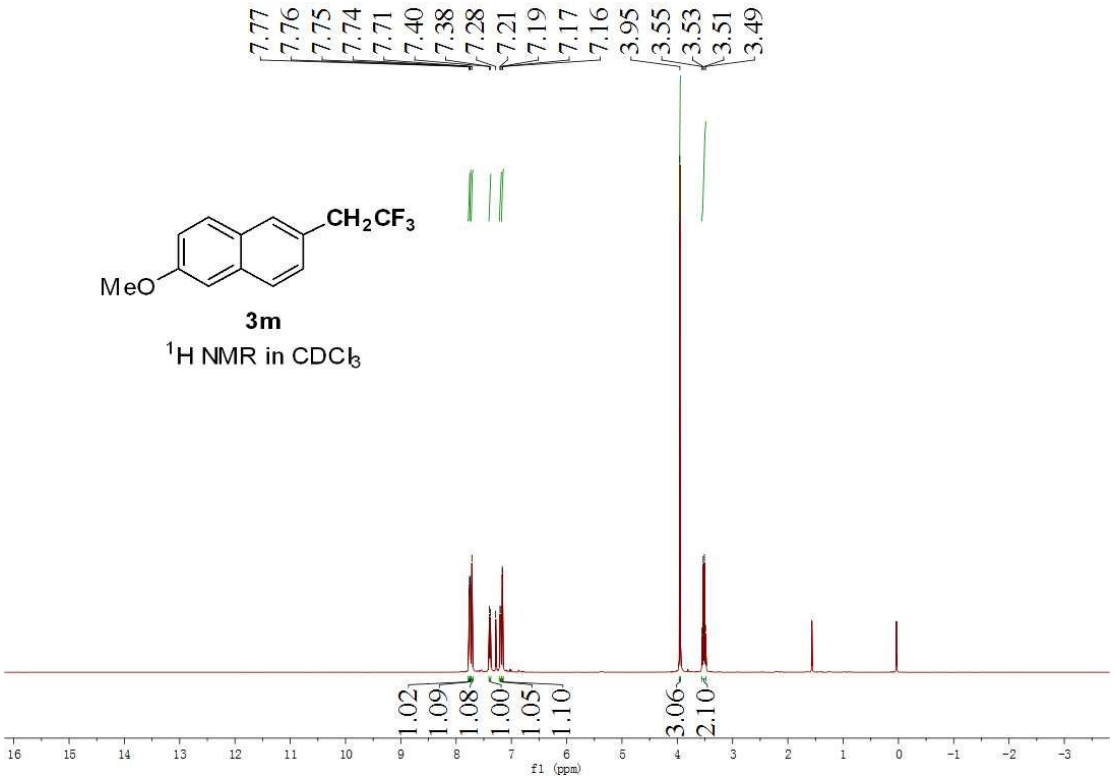
^{1}H NMR in $CDCl_3$

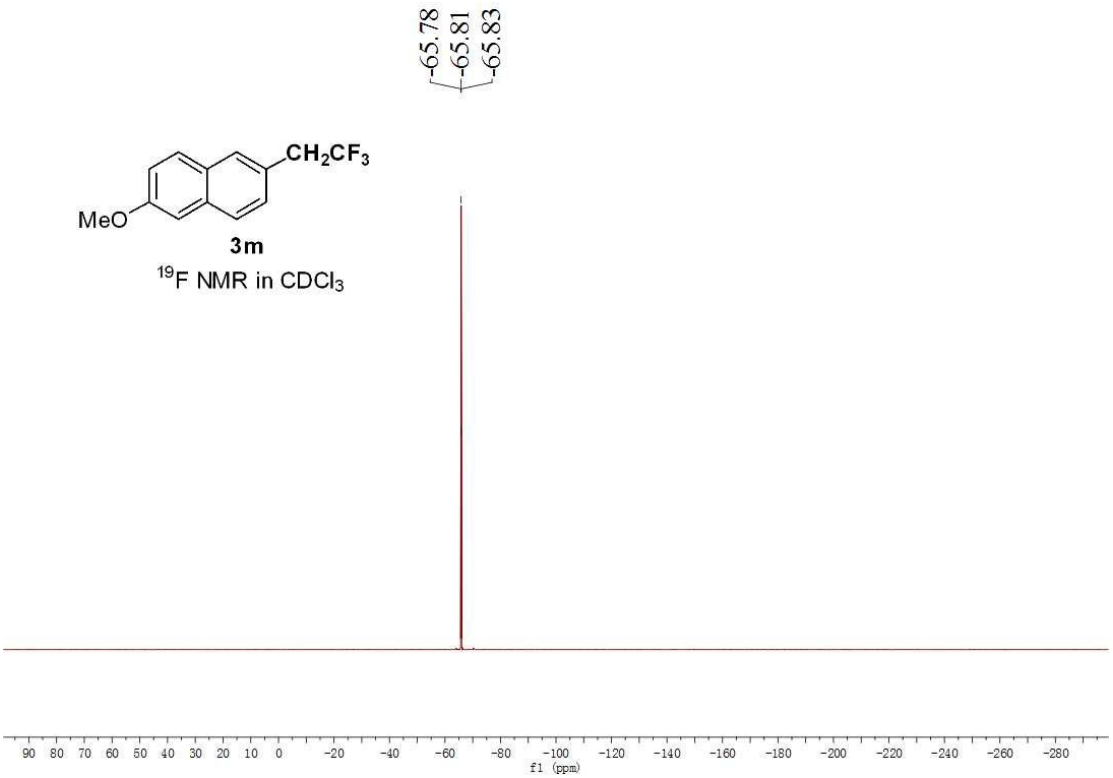


3l

^{19}F NMR in $CDCl_3$


133.30
132.91
129.51
129.22
128.42
127.82
127.71
127.61
127.02
126.43
126.36
124.82
122.62
40.77
40.53
40.30
40.06
CH2CF3
3l
13C NMR in CDCl3
f1 (ppm)


7.77
7.76
7.75
7.74
7.71
7.40
7.38
7.28
7.21
7.19
7.17
7.16
3.95
3.55
3.53
3.51
3.49
CH2CF3
MeO
3m
1H NMR in CDCl3
1.02
1.09
1.08
1.00
1.05
1.10
3.06
2.10
f1 (ppm)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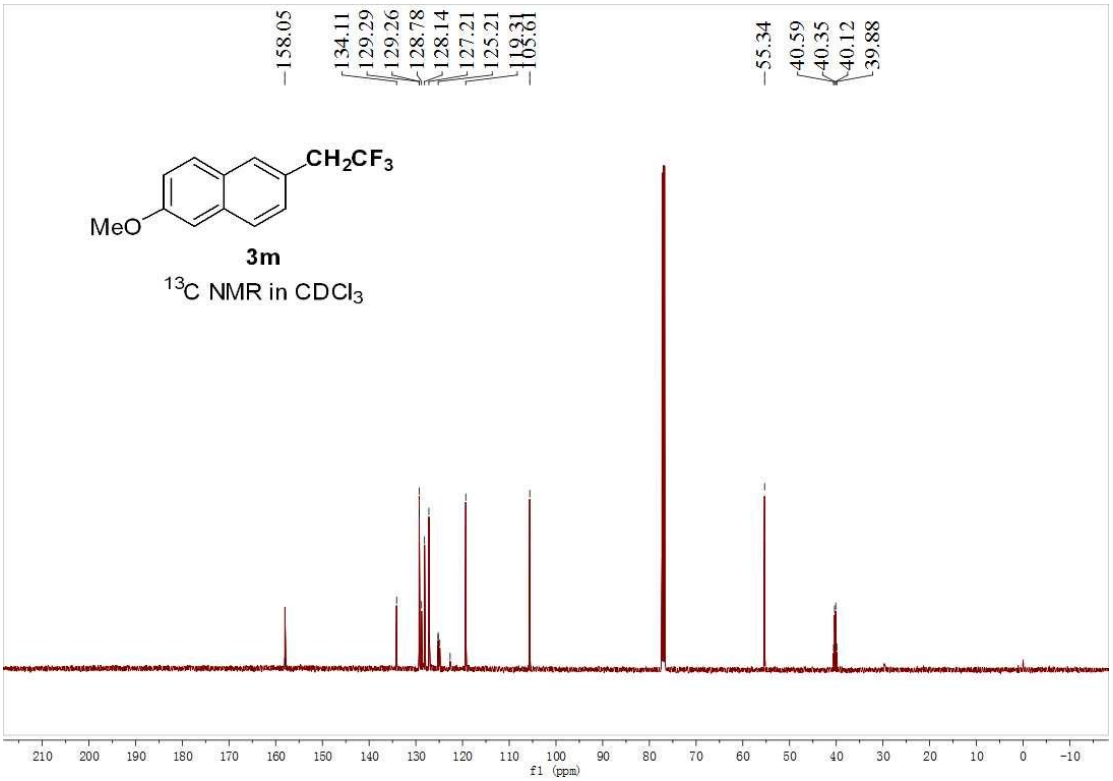
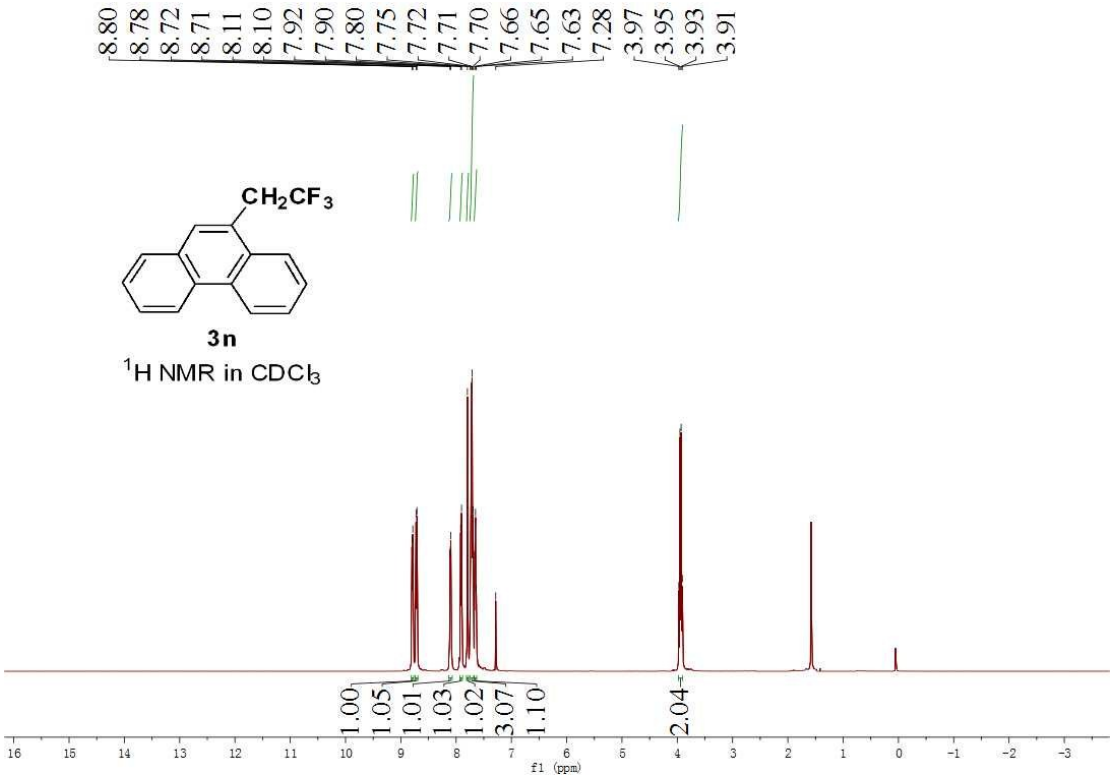
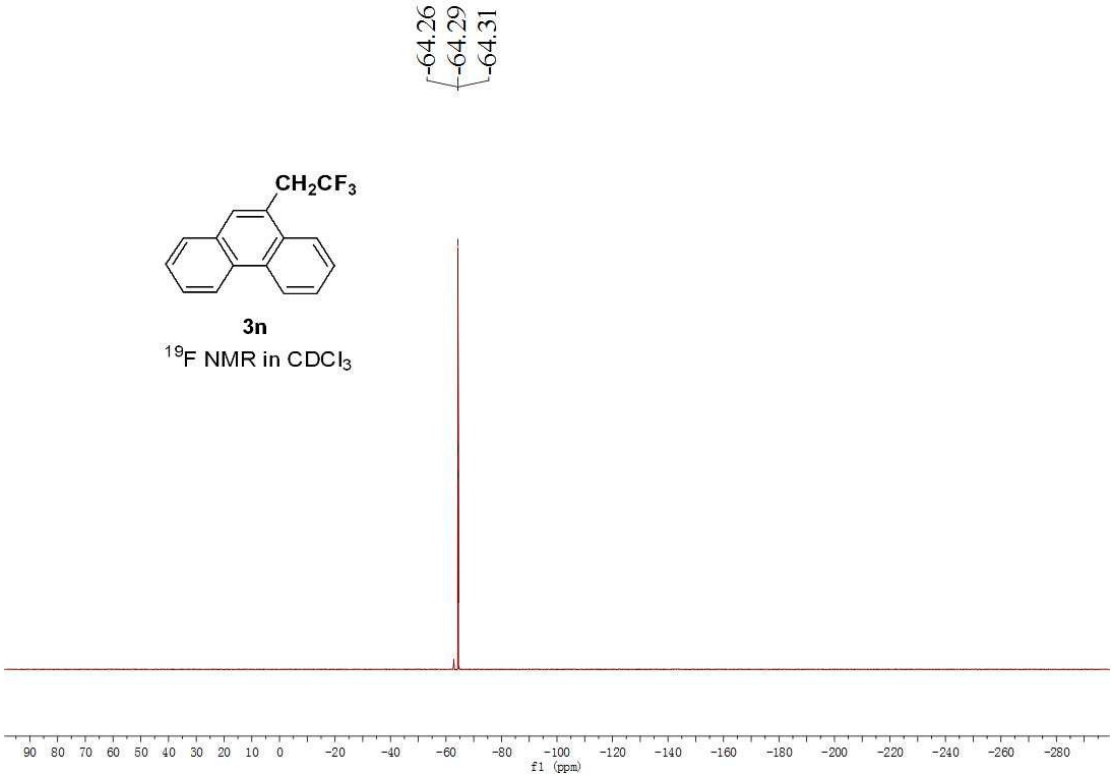
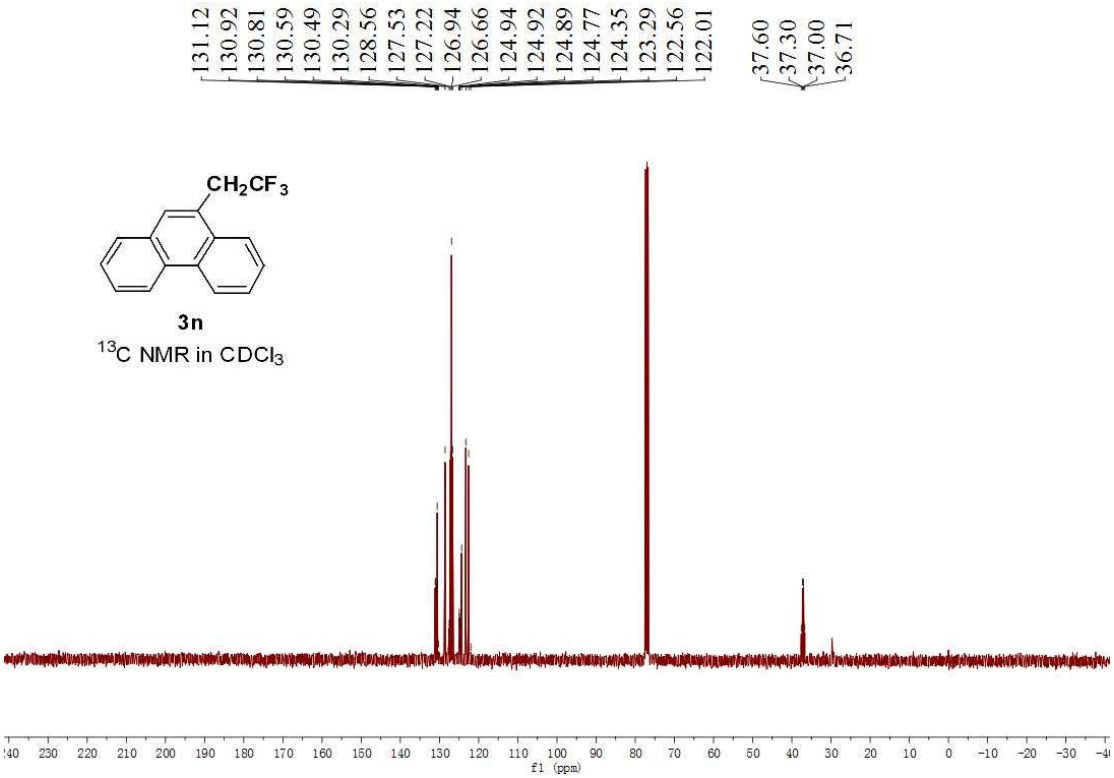
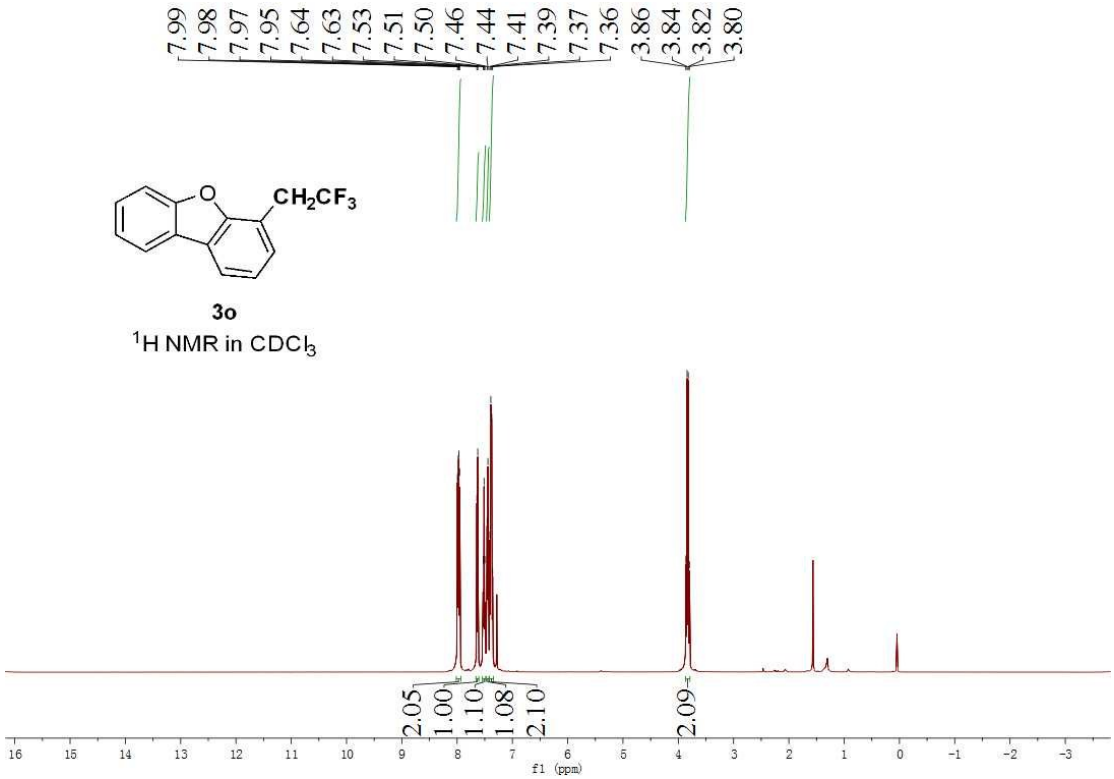
-65.83
CH2CF3
MeO
3m
19F NMR in CDCl3
f1 (ppm)


158.05
134.11
129.29
129.26
128.78
128.14
127.21
125.21
119.31
105.01
55.34
40.59
40.35
40.12
39.88
CH2CF3
MeO
3m
13C NMR in CDCl3
f1 (ppm)


8.80
8.78
8.72
8.71
8.11
8.10
7.92
7.90
7.80
7.75
7.72
7.71
7.70
7.66
7.65
7.63
7.28
3.97
3.95
3.93
3.91
CH2CF3
3n
1H NMR in CDCl3
1.00
1.05
1.01
1.03
1.02
3.07
1.10
2.04
f1 (ppm)


-64.26
-64.29
-64.31
CH2CF3
3n
19F NMR in CDCl3
f1 (ppm)


131.12
130.92
130.81
130.59
130.49
130.29
128.56
127.53
127.22
126.94
126.66
124.94
124.92
124.89
124.77
124.35
123.29
122.56
122.01
37.60
37.30
37.00
36.71
CH2CF3
3n
13C NMR in CDCl3
f1 (ppm)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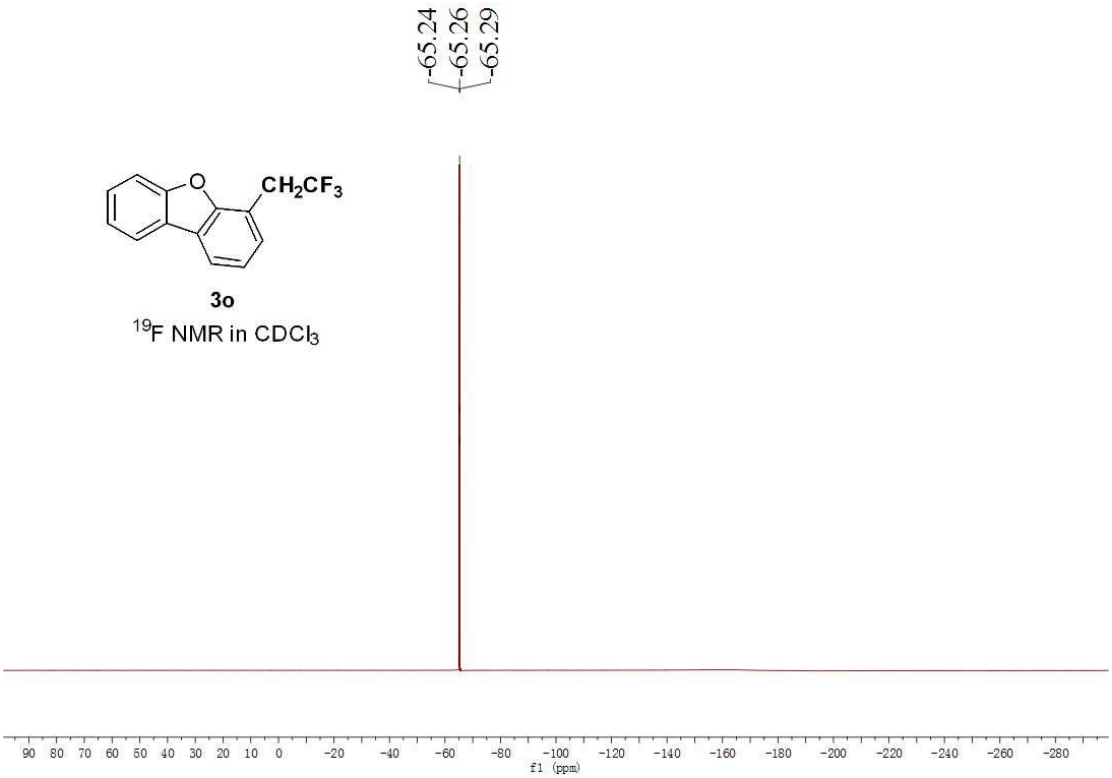
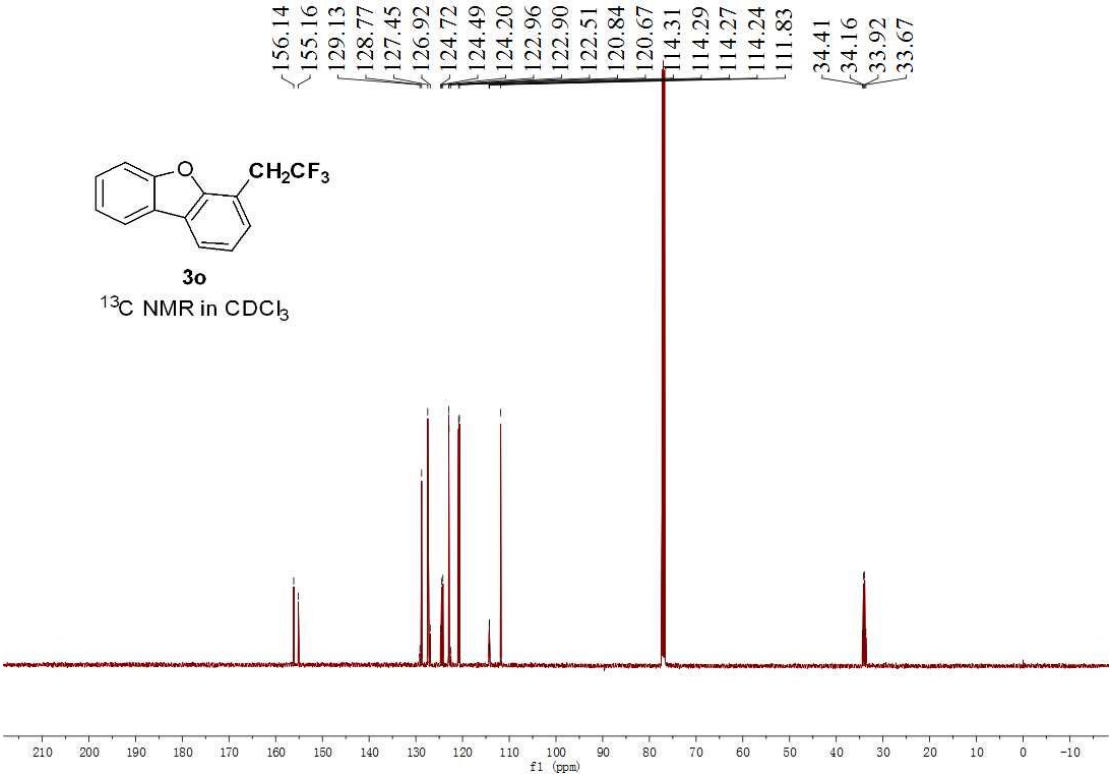
7.98
7.97
7.95
7.64
7.63
7.53
7.51
7.50
7.46
7.44
7.41
7.39
7.37
7.36
3.86
3.84
3.82
3.80
CH2CF3
3o
1H NMR in CDCl3
2.05
1.00
1.10
1.08
2.10
2.09
f1 (ppm)



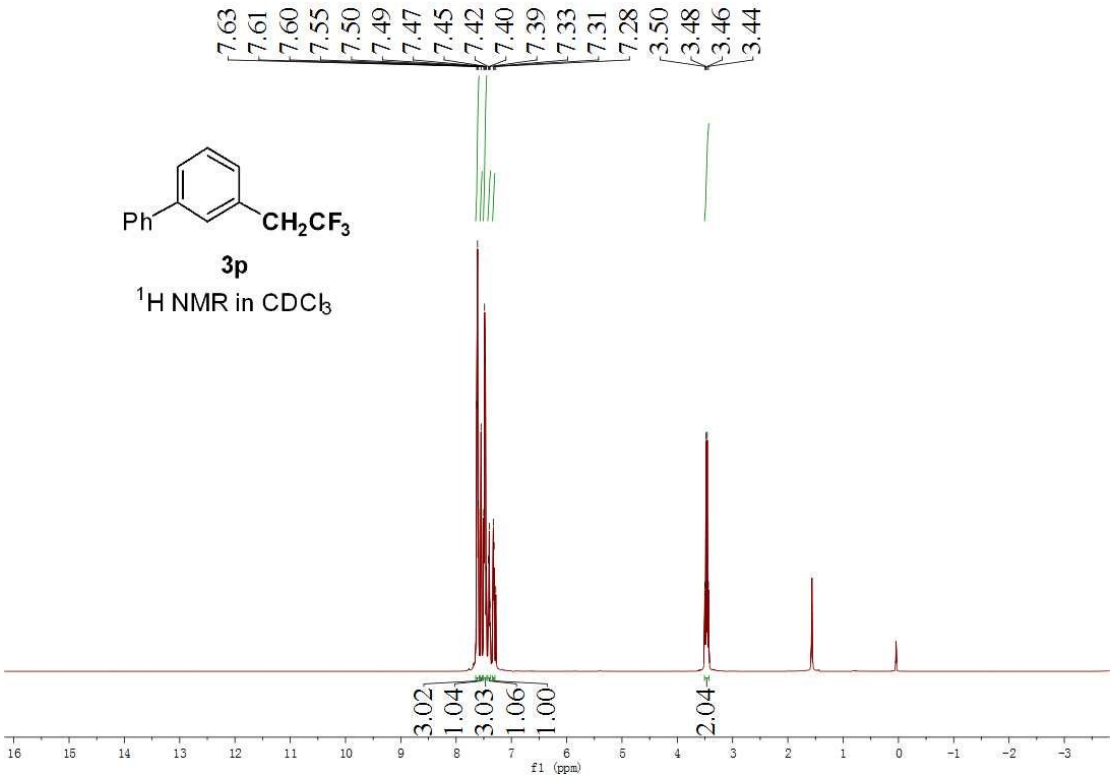
3o

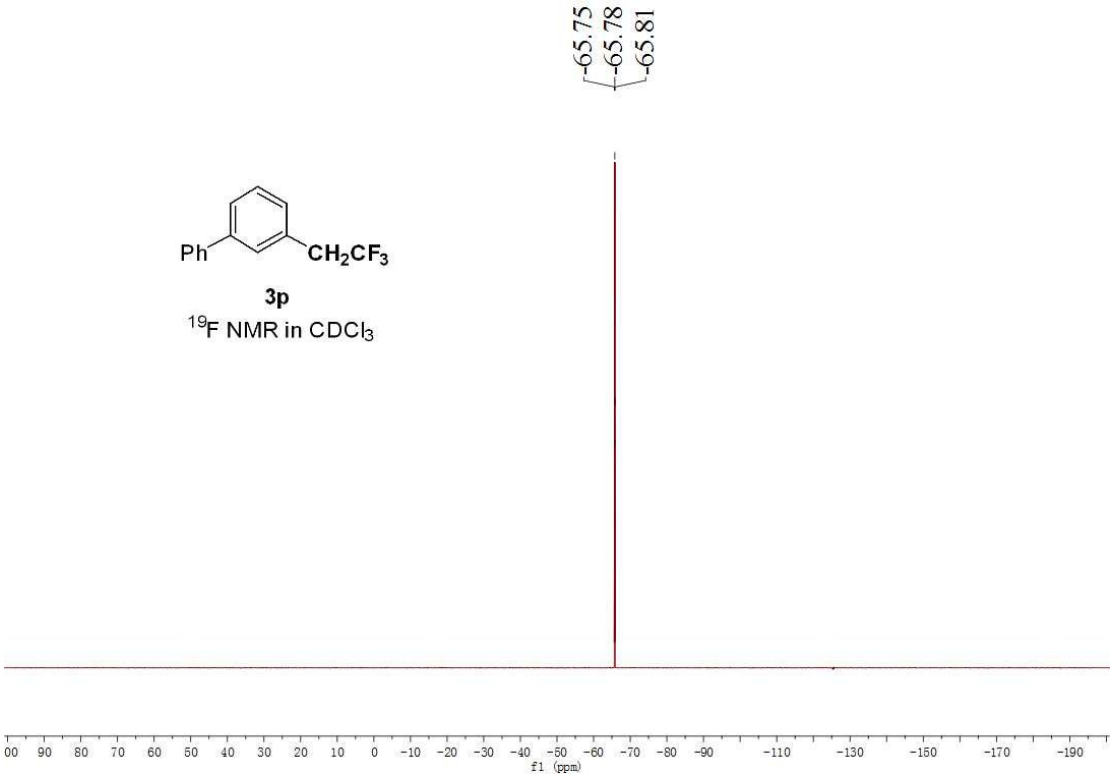
^{19}F NMR in $CDCl_3$

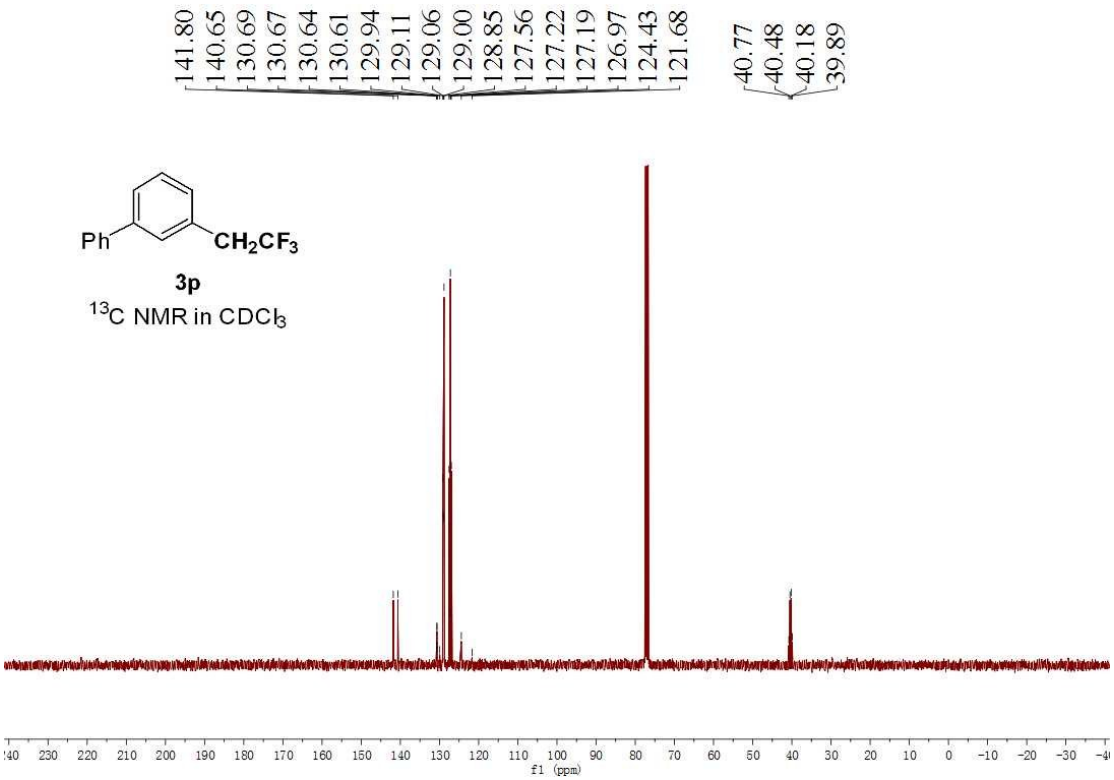


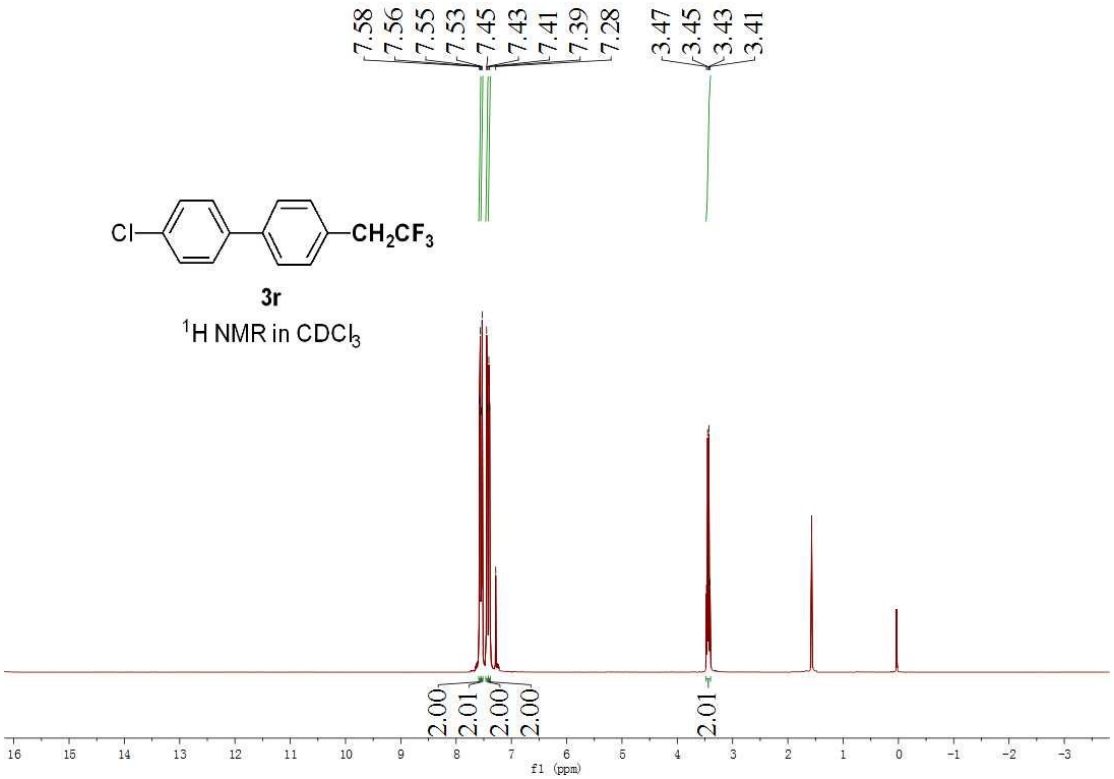
3o

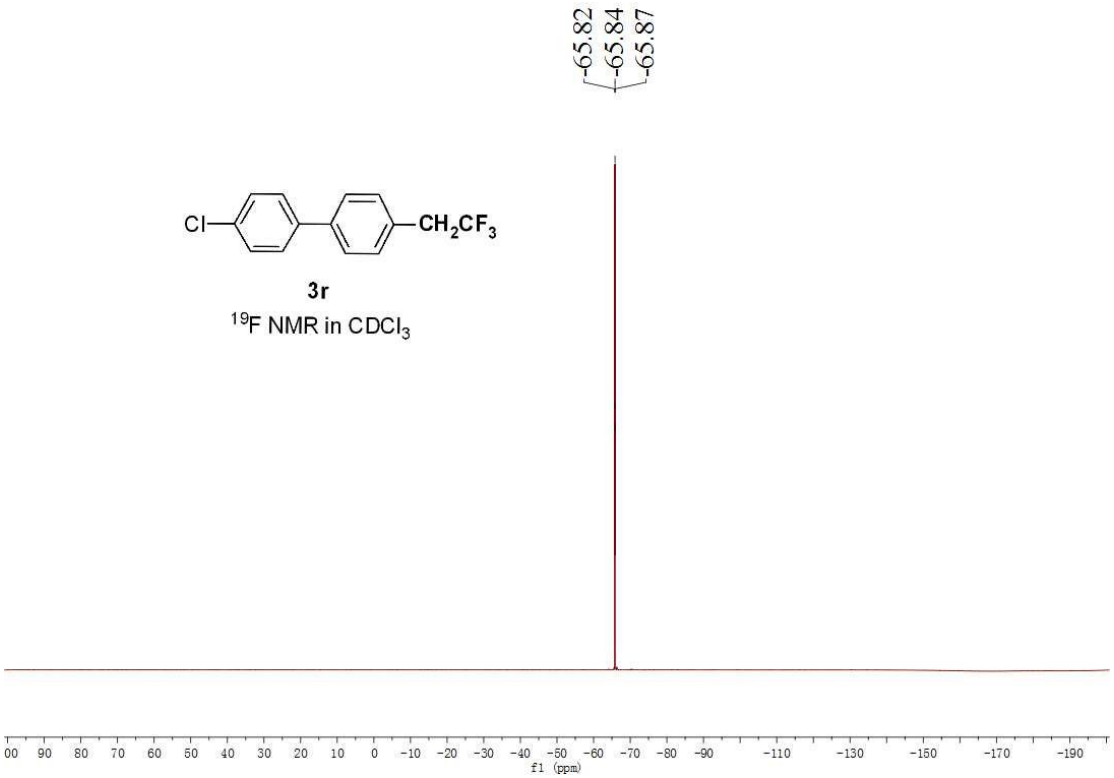
^{13}C NMR in $CDCl_3$

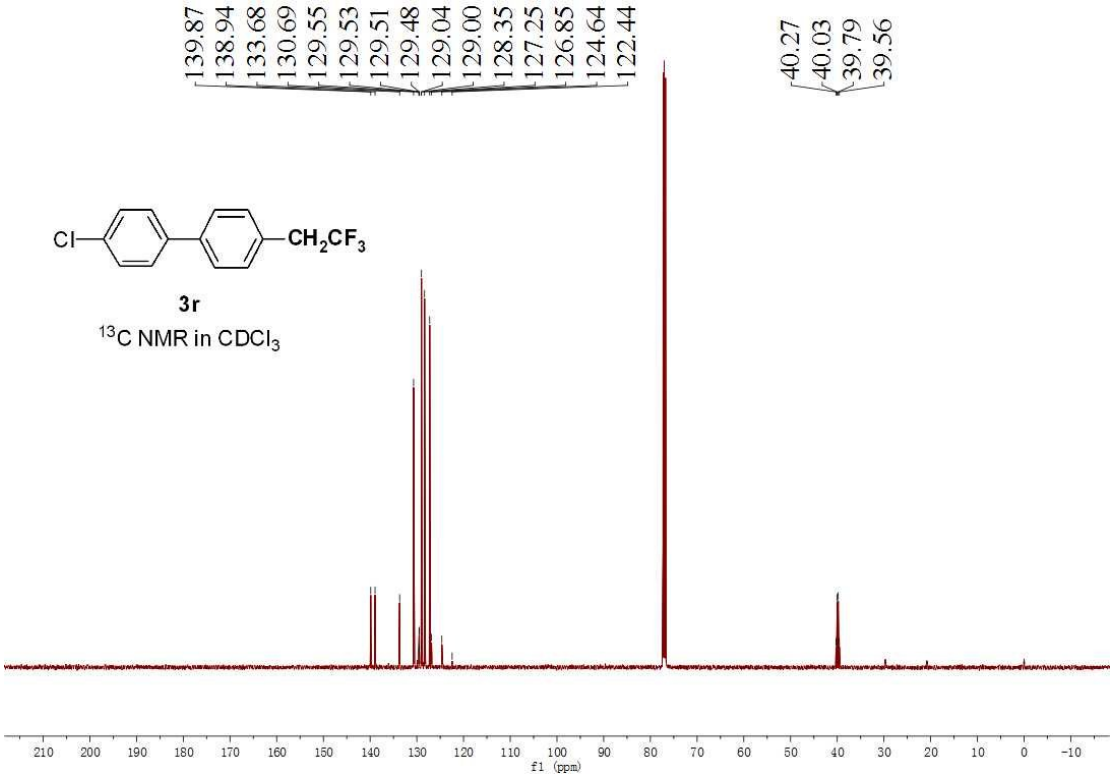

7.63
7.61
7.60
7.55
7.50
7.49
7.47
7.45
7.42
7.40
7.39
7.33
7.31
7.28
3.50
3.48
3.46
3.44
Ph
CH2CF3
3p
1H NMR in CDCl3
3.02
1.04
3.03
1.06
1.00
2.04
f1 (ppm)

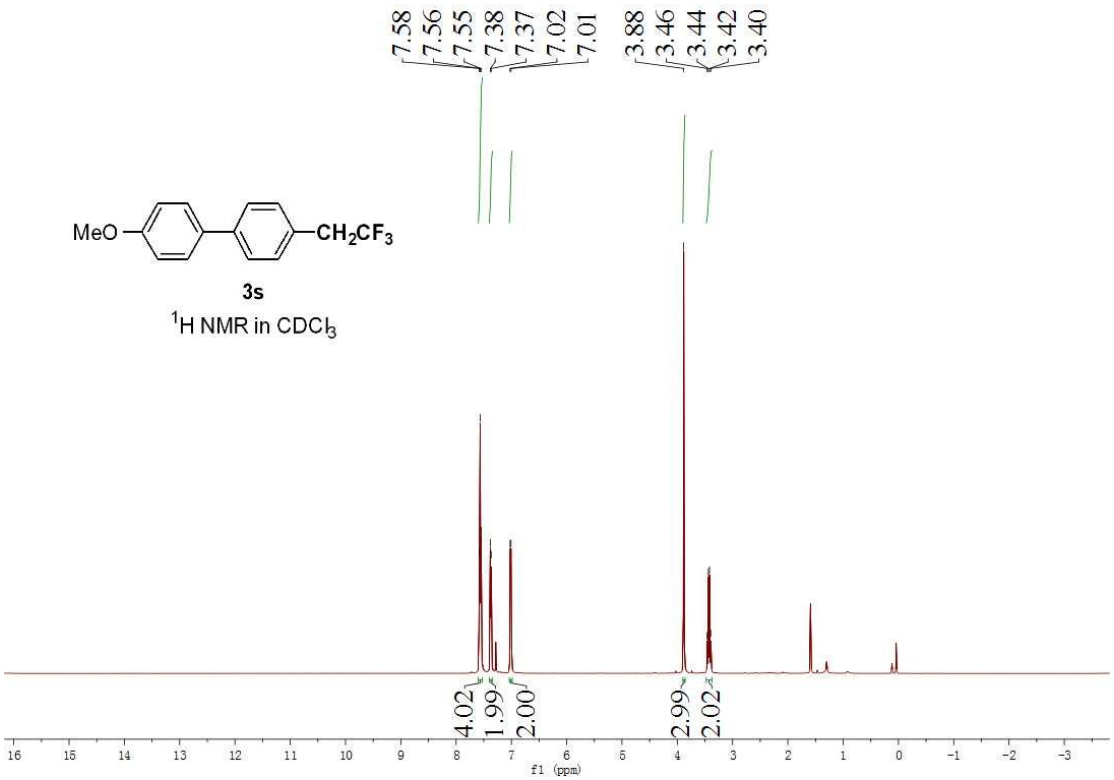

-65.75
-65.78
-65.81
Ph
CH2CF3
3p
19F NMR in CDCl3
f1 (ppm)


141.80
140.65
130.69
130.67
130.64
130.61
129.94
129.11
129.06
129.00
128.85
127.56
127.22
127.19
126.97
124.43
121.68
40.77
40.48
40.18
39.89
Ph
CH2CF3
3p
13C NMR in CDCl3
f1 (ppm)


7.58
7.56
7.55
7.53
7.45
7.43
7.41
7.39
7.28
3.47
3.45
3.43
3.41
Cl
CH2CF3
3r
1H NMR in CDCl3
2.00
2.01
2.00
2.00
2.01
f1 (ppm)

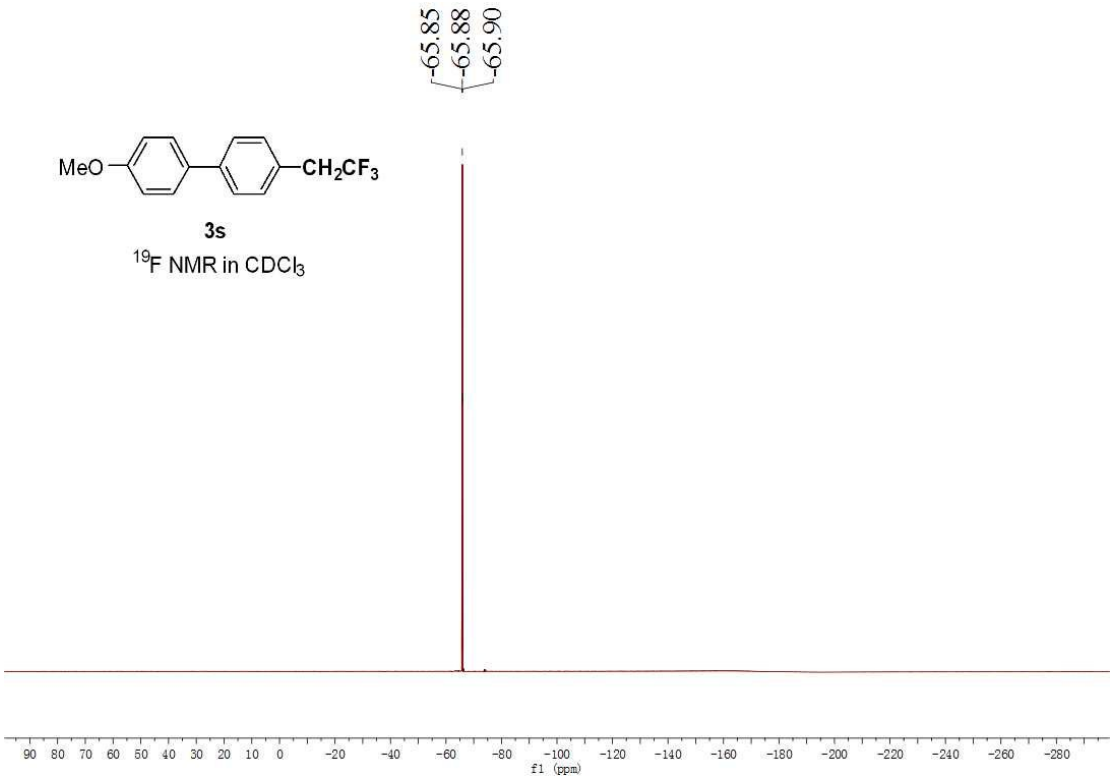

-65.82
-65.84
-65.87
Cl
CH2CF3
3r
19F NMR in CDCl3
f1 (ppm)


139.87
138.94
133.68
130.69
129.55
129.53
129.51
129.48
129.04
129.00
128.35
127.25
126.85
124.64
122.44
40.27
40.03
39.79
39.56
Cl
CH2CF3
3r
13C NMR in CDCl3
f1 (ppm)



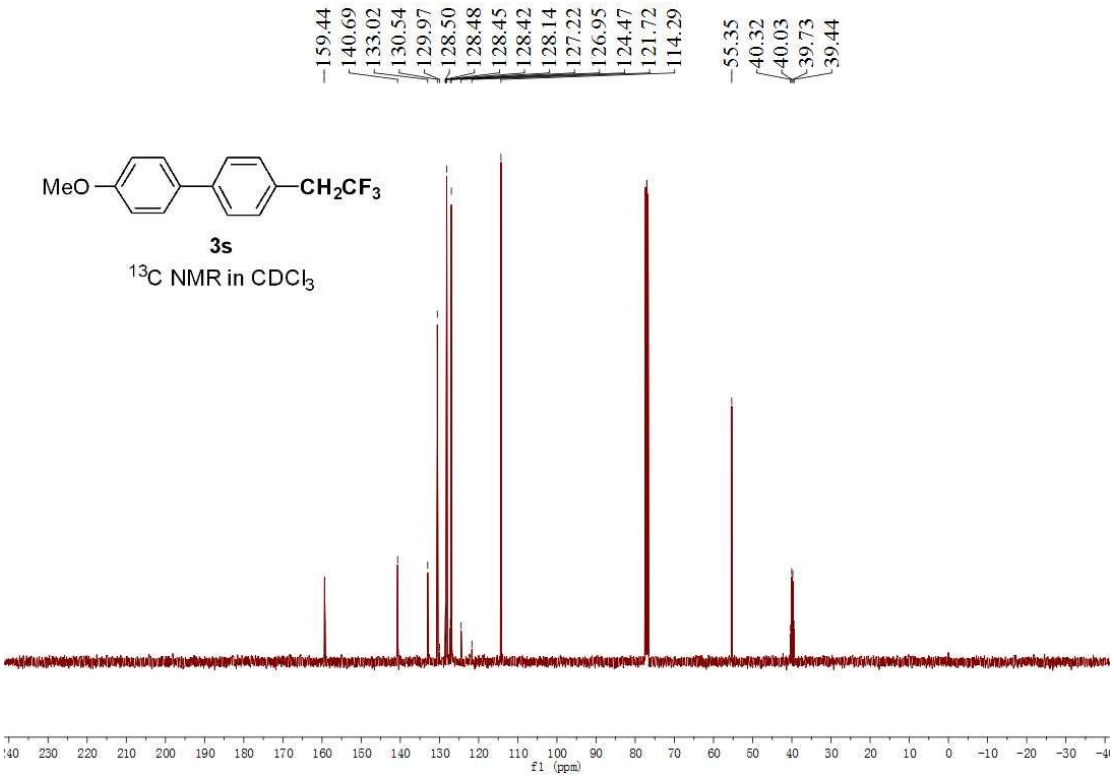
3s

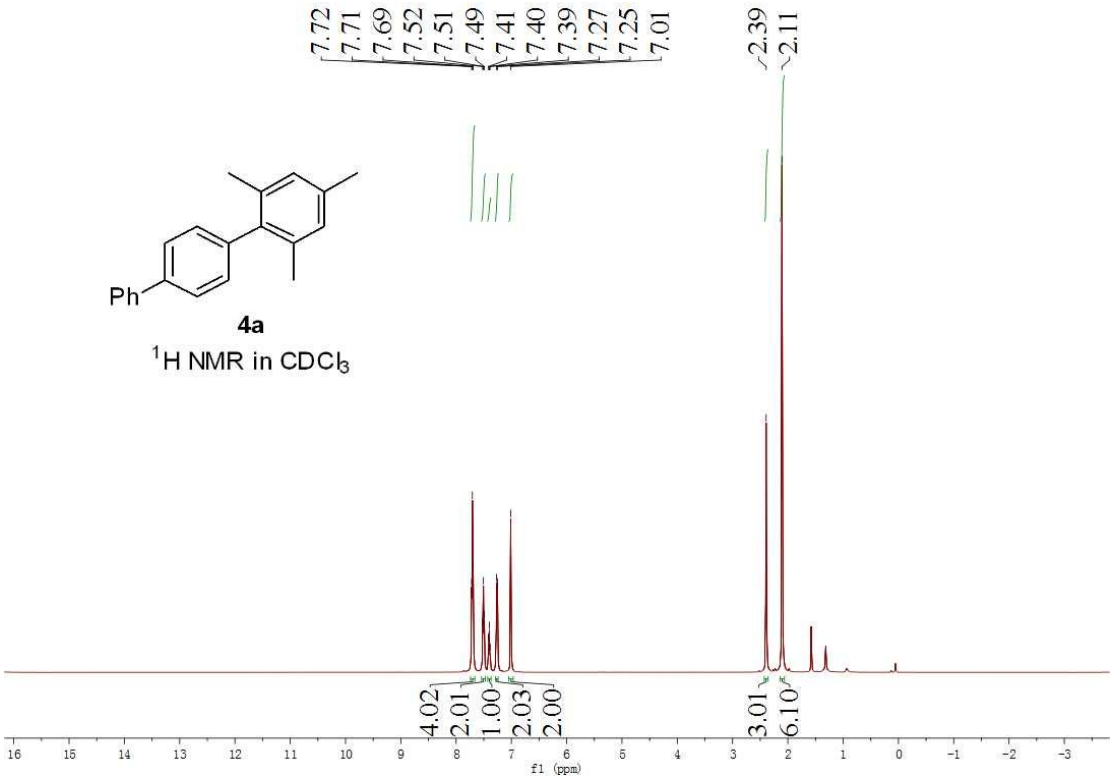
^{1}H NMR in $CDCl_3$

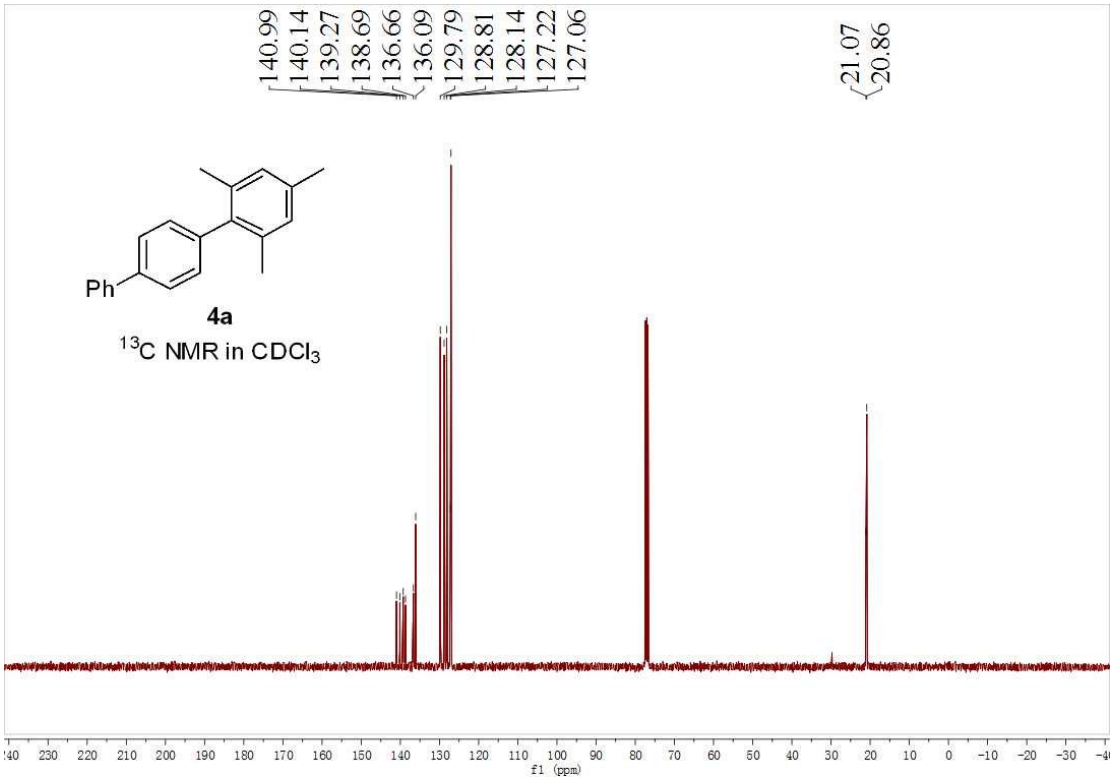


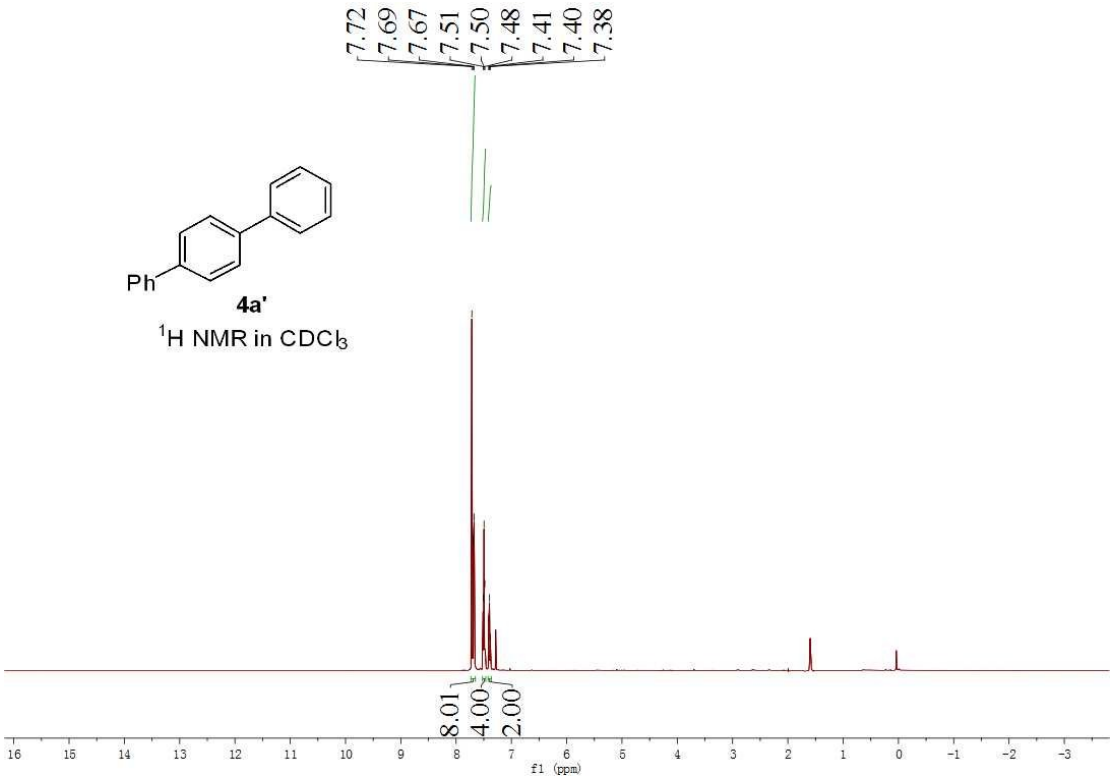
3s

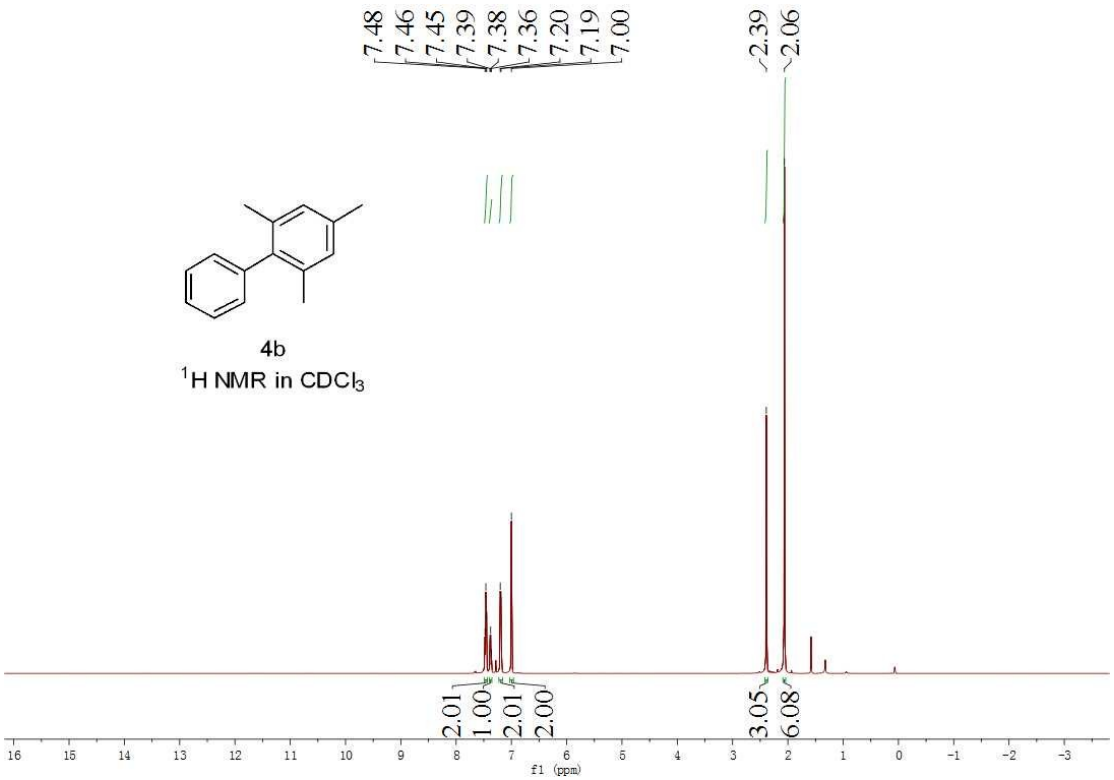
^{19}F NMR in $CDCl_3$


159.44
140.69
133.02
130.54
129.97
128.50
128.48
128.45
128.42
128.14
127.22
126.95
124.47
121.72
114.29
55.35
40.32
40.03
39.73
39.44
MeO
CH2CF3
3s
13C NMR in CDCl3
f1 (ppm)


7.72
7.71
7.69
7.52
7.51
7.49
7.41
7.40
7.39
7.27
7.25
7.01
2.39
2.11
Ph
4a
1H NMR in CDCl3
4.02
2.01
1.00
2.03
2.00
3.01
6.10
f1 (ppm)

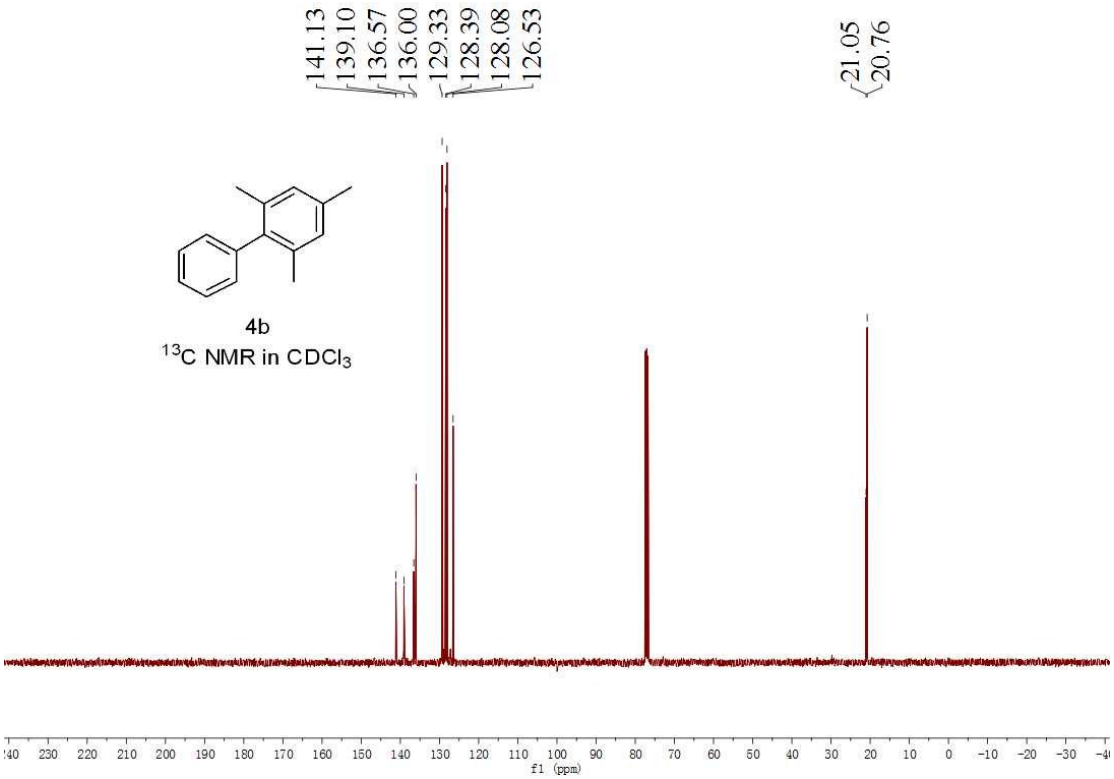

140.99
140.14
139.27
138.69
136.66
136.09
129.79
128.81
128.14
127.22
127.06
21.07
20.86
Ph
4a
13C NMR in CDCl3
f1 (ppm)


7.72
7.69
7.67
7.51
7.50
7.48
7.41
7.40
7.38
Ph
4a'
1H NMR in CDCl3
8.01
4.00
2.00
f1 (ppm)



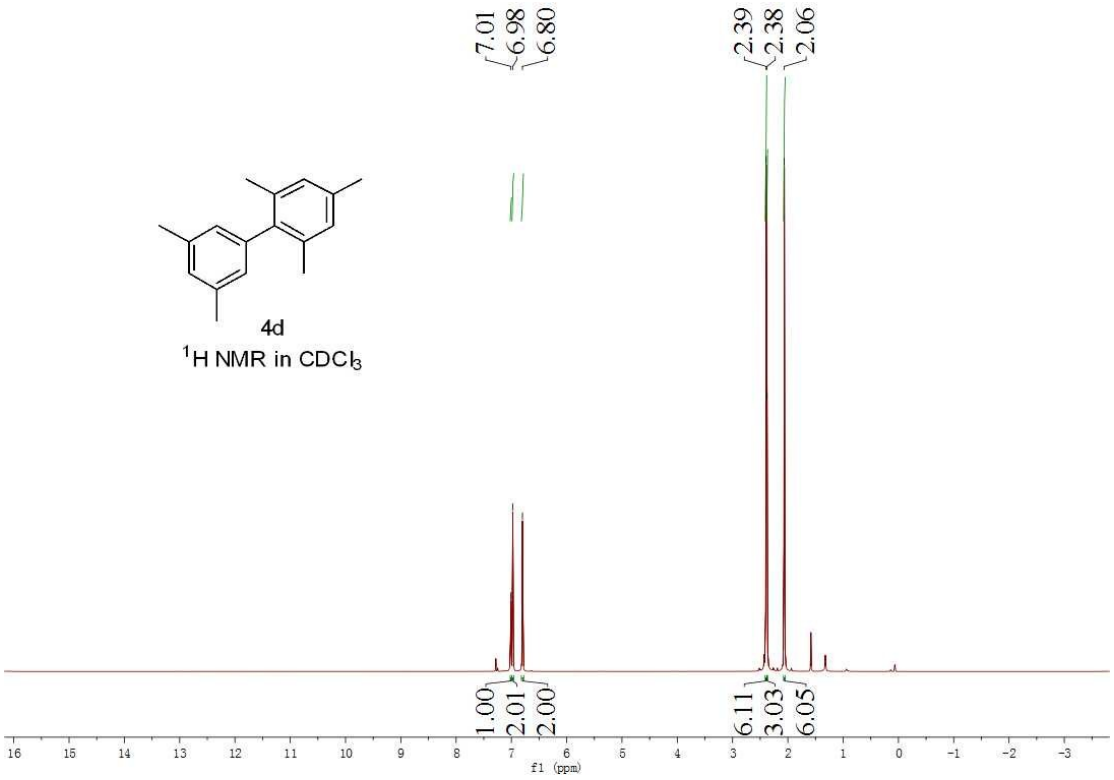
4b

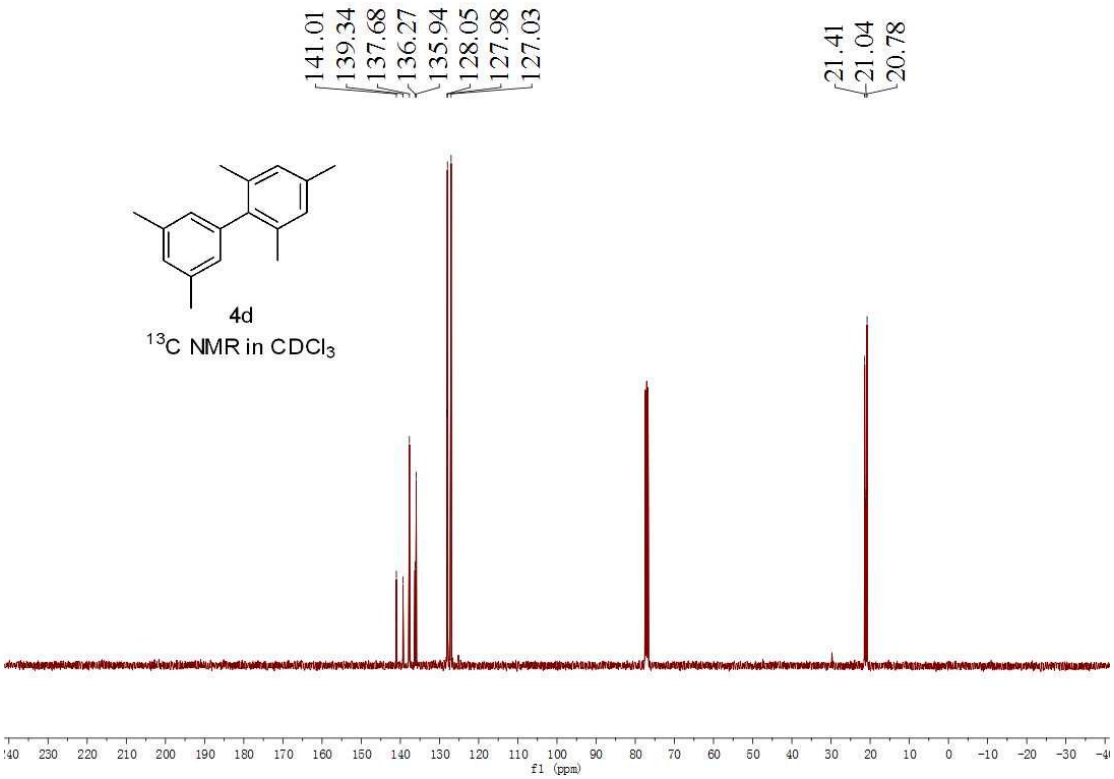
^{1}H NMR in $CDCl_3$

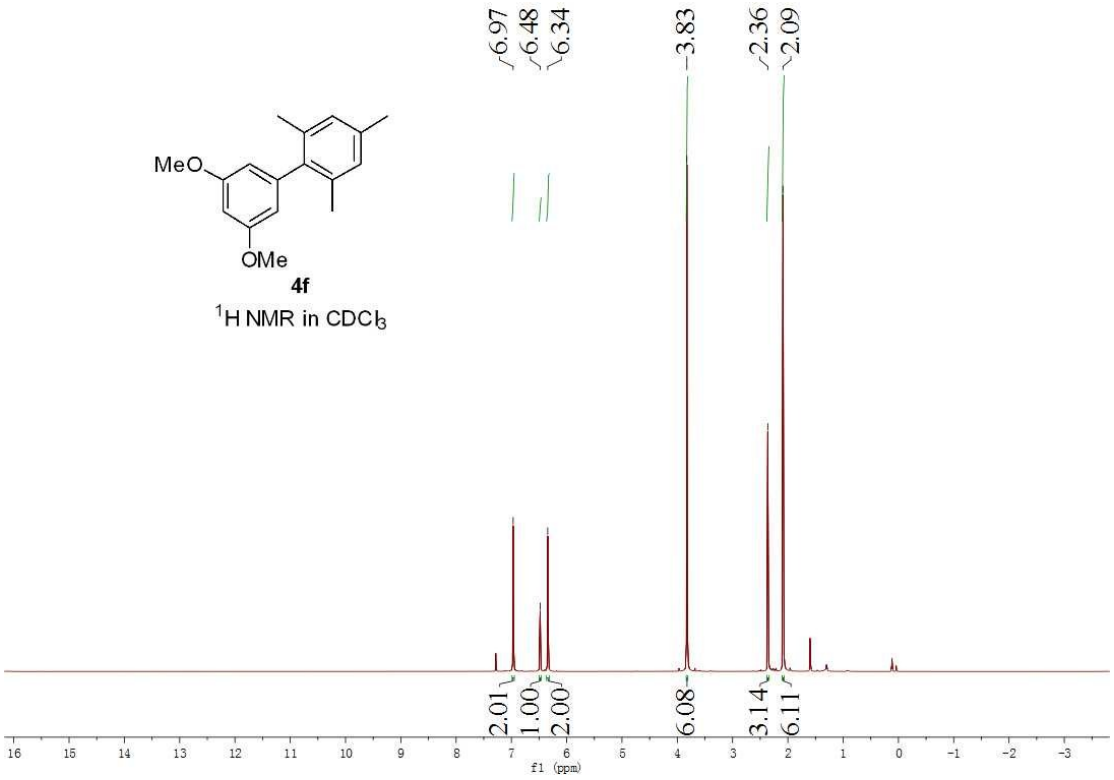


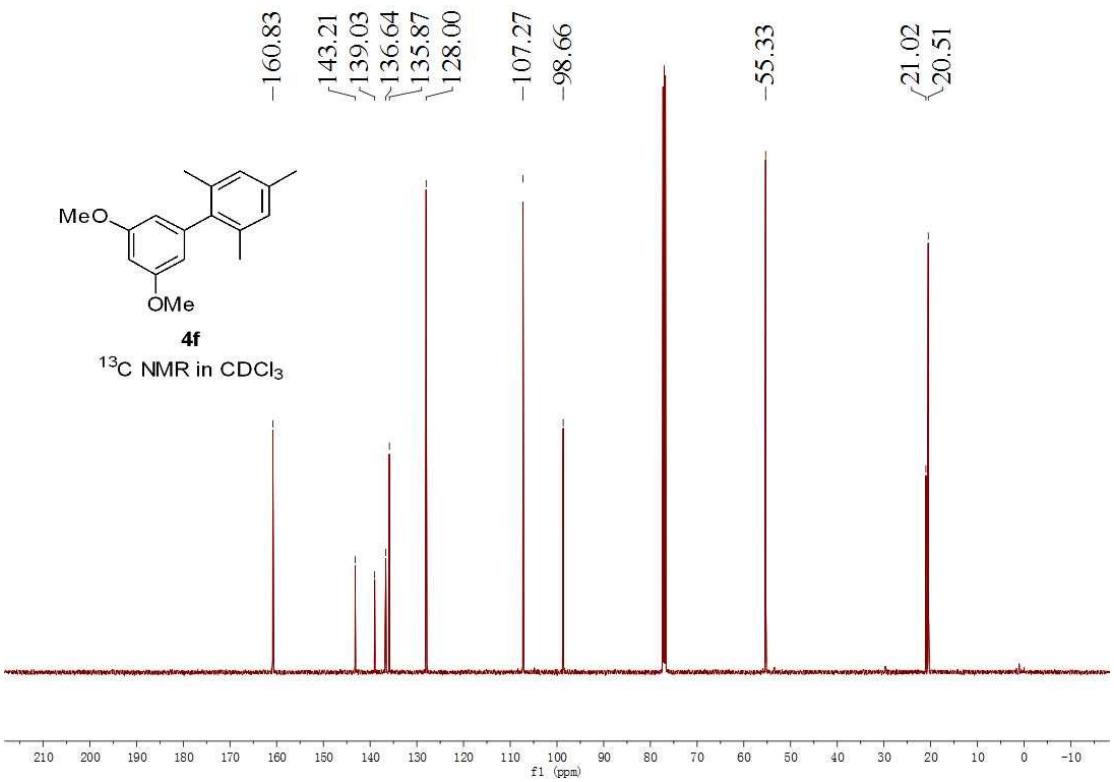
4b

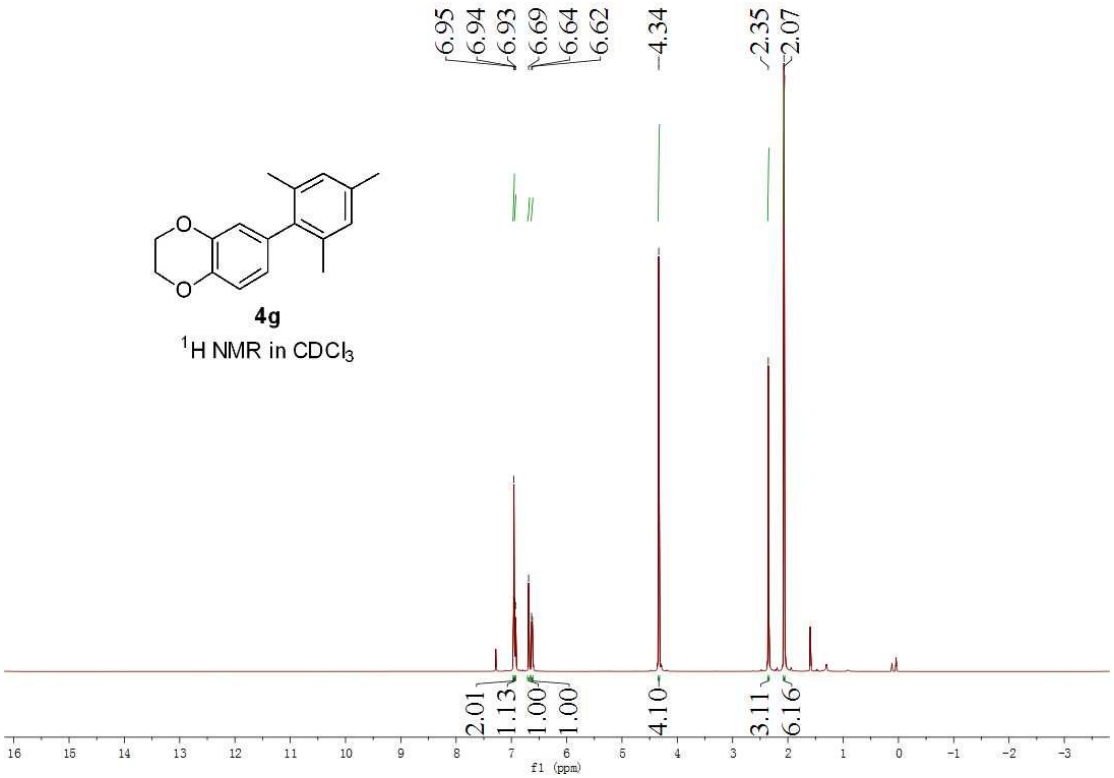
^{13}C NMR in $CDCl_3$


7.01
6.98
6.80
2.39
2.38
2.06
4d
^{1}H NMR in CDCl$_3$
1.00
2.01
2.00
6.11
3.03
6.05
f1 (ppm)


141.01
139.34
137.68
136.27
135.94
128.05
127.98
127.03
21.41
21.04
20.78
4d
^{13}C NMR in CDCl$_3$
f1 (ppm)

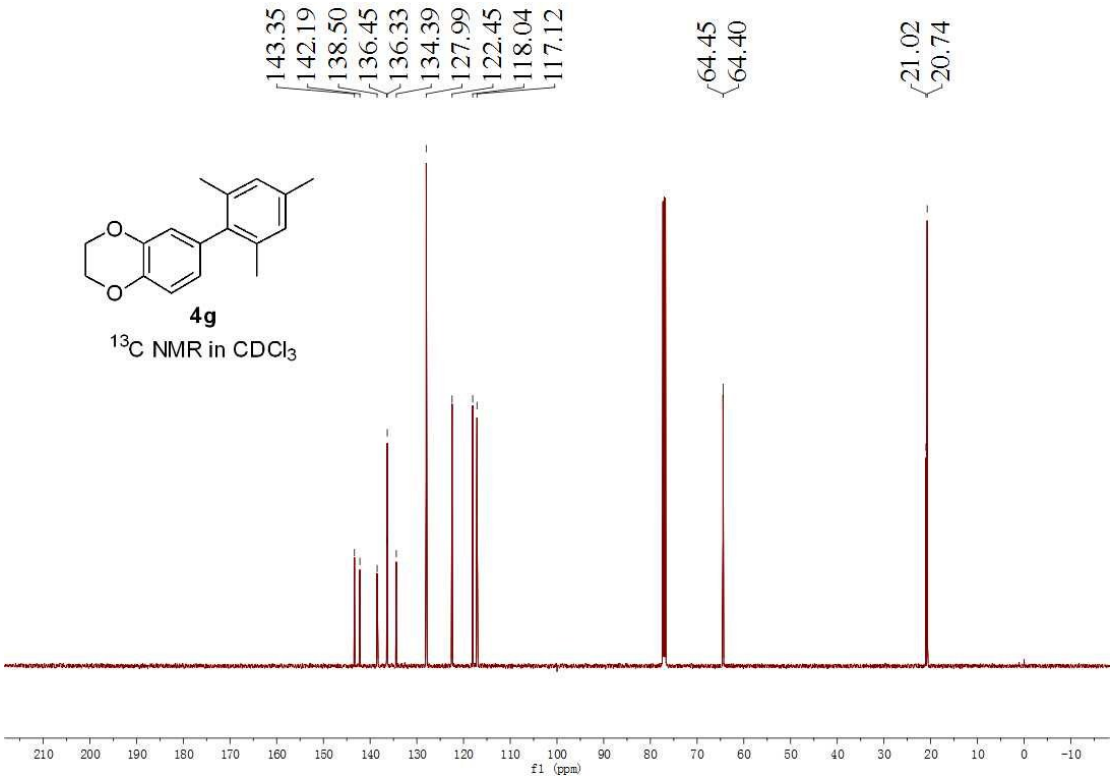

MeO
OMe
4f
^{1}H NMR in CDCl$_3$
6.97
6.48
6.34
3.83
2.36
2.09
2.01
1.00
2.00
6.08
3.14
6.11
f1 (ppm)


MeO
OMe
4f
^{13}C NMR in CDCl$_3$
160.83
143.21
139.03
136.64
135.87
128.00
107.27
98.66
55.33
21.02
20.51
f1 (ppm)



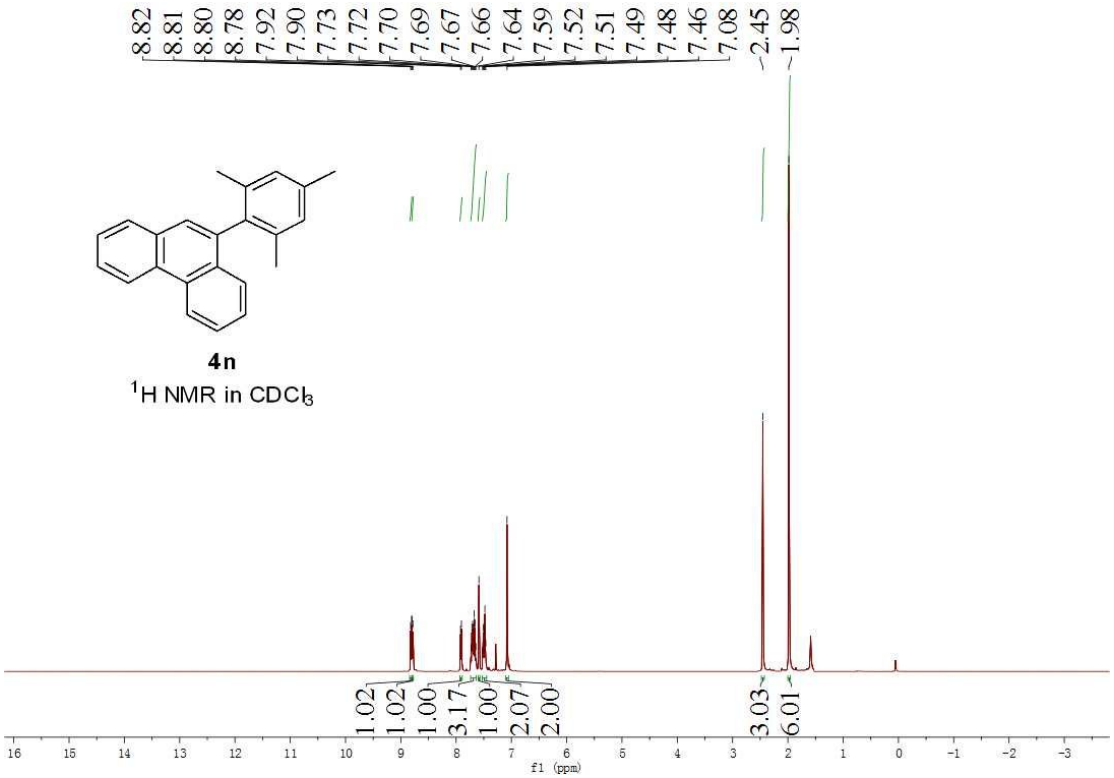
4g

^{1}H NMR in $CDCl_3$



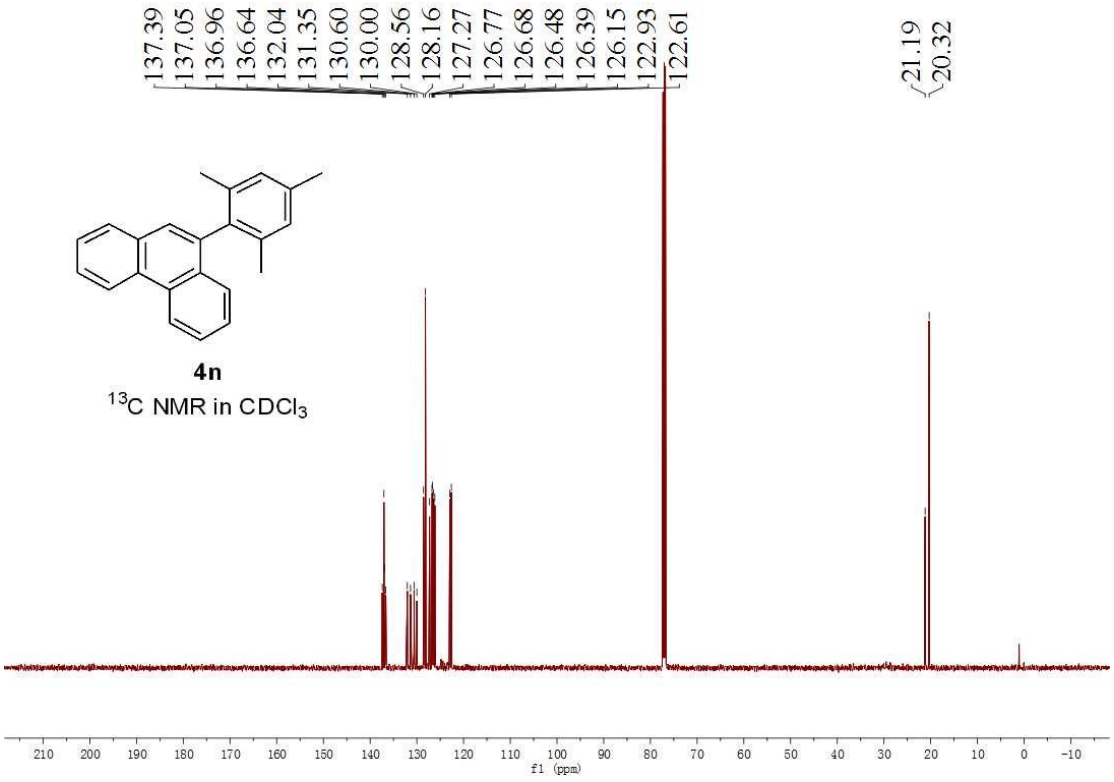
4g

^{13}C NMR in $CDCl_3$



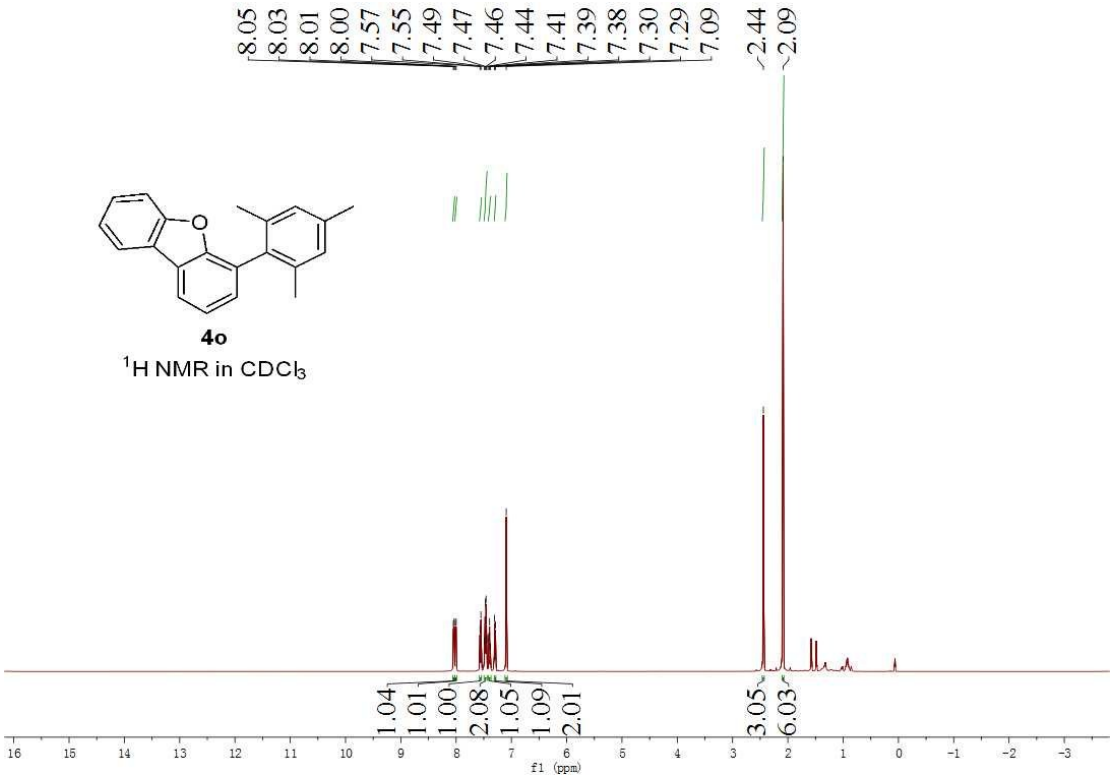
4n

^{1}H NMR in $CDCl_3$



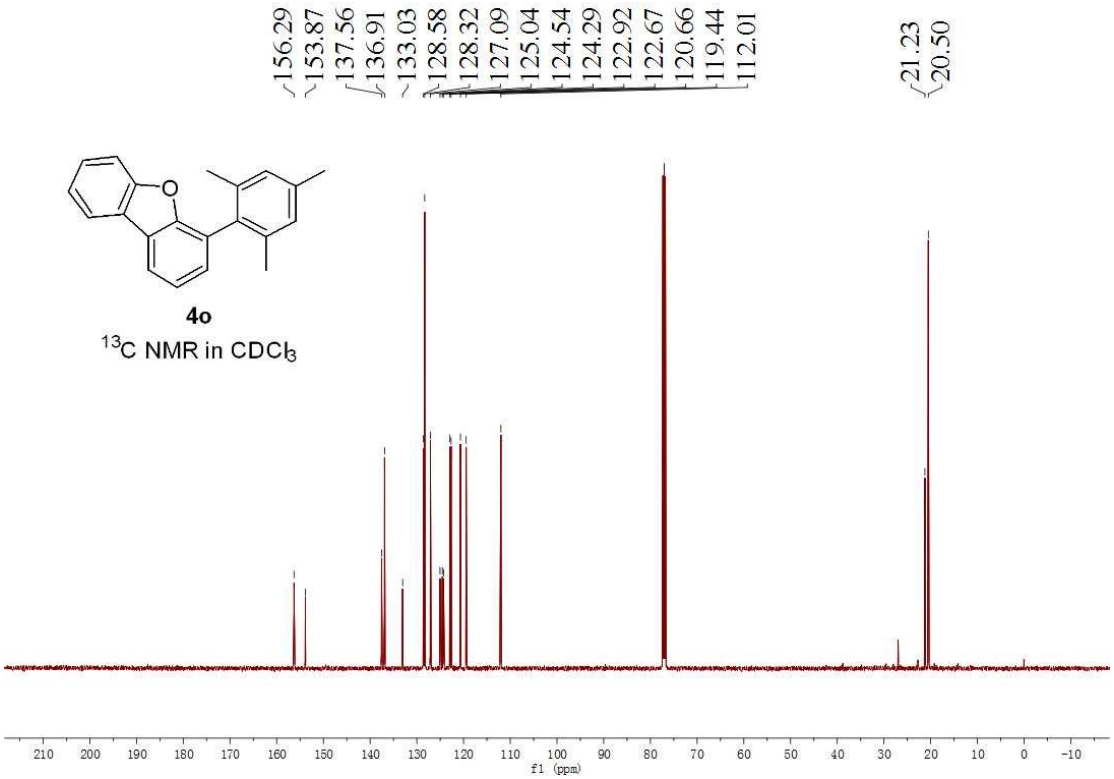
4n

^{13}C NMR in $CDCl_3$



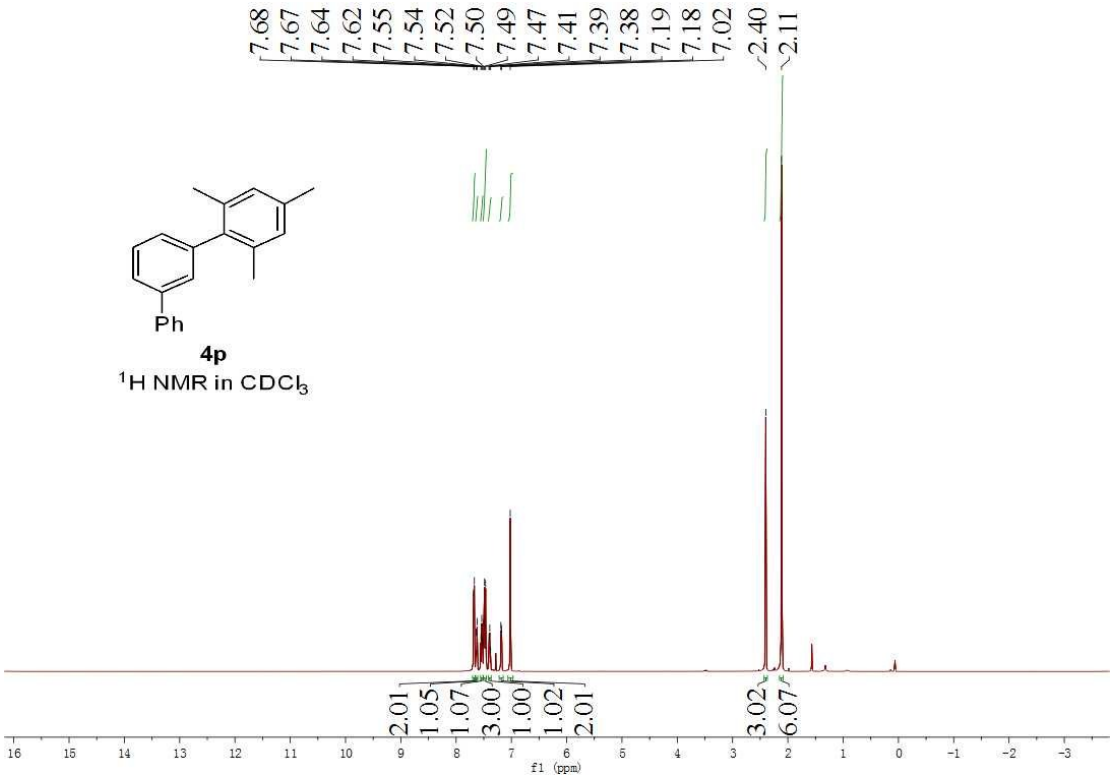
4o

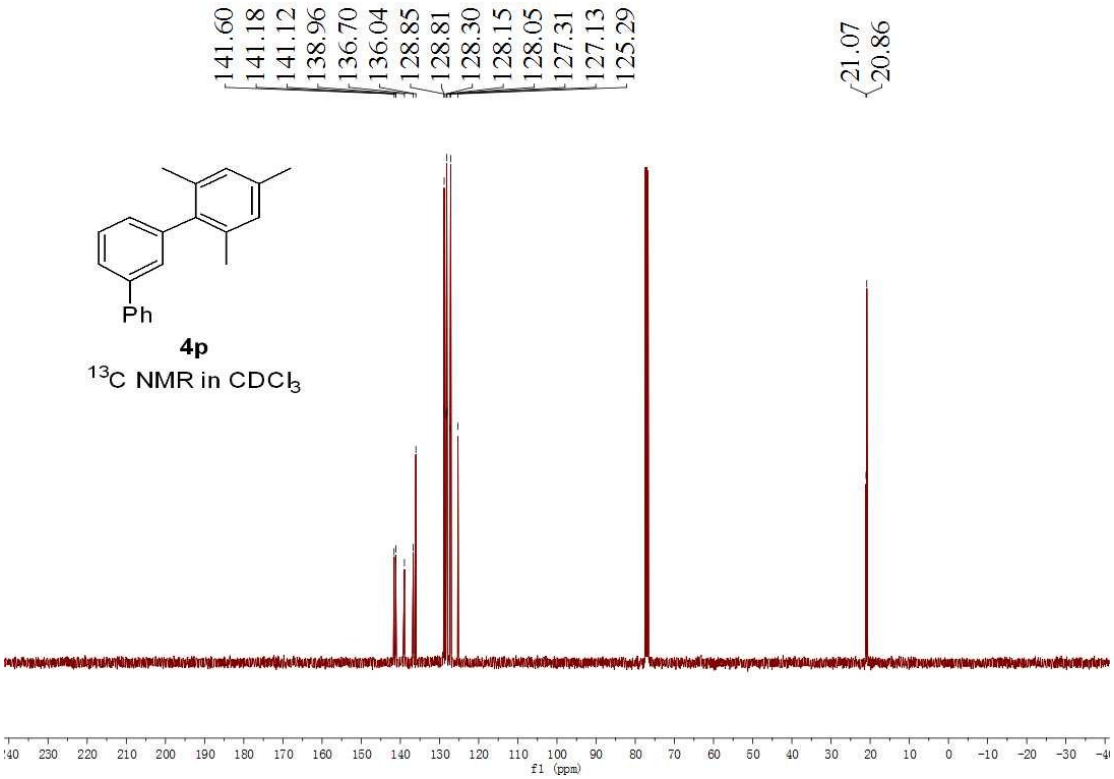
^{1}H NMR in $CDCl_3$

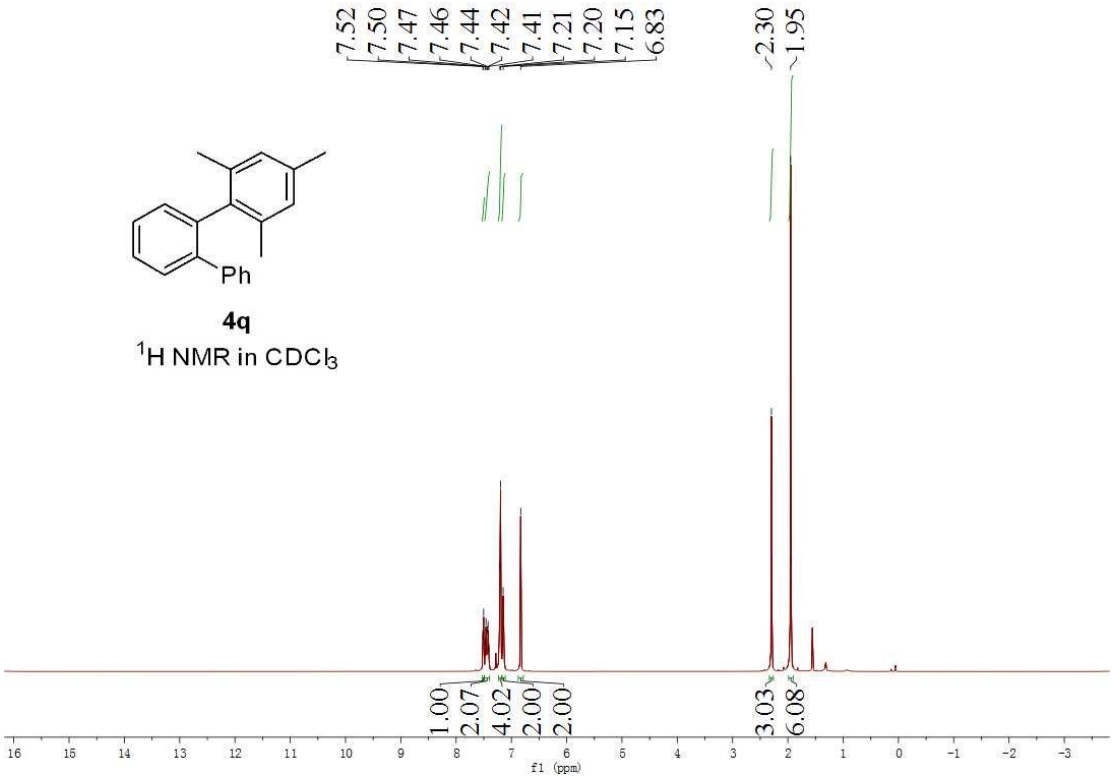


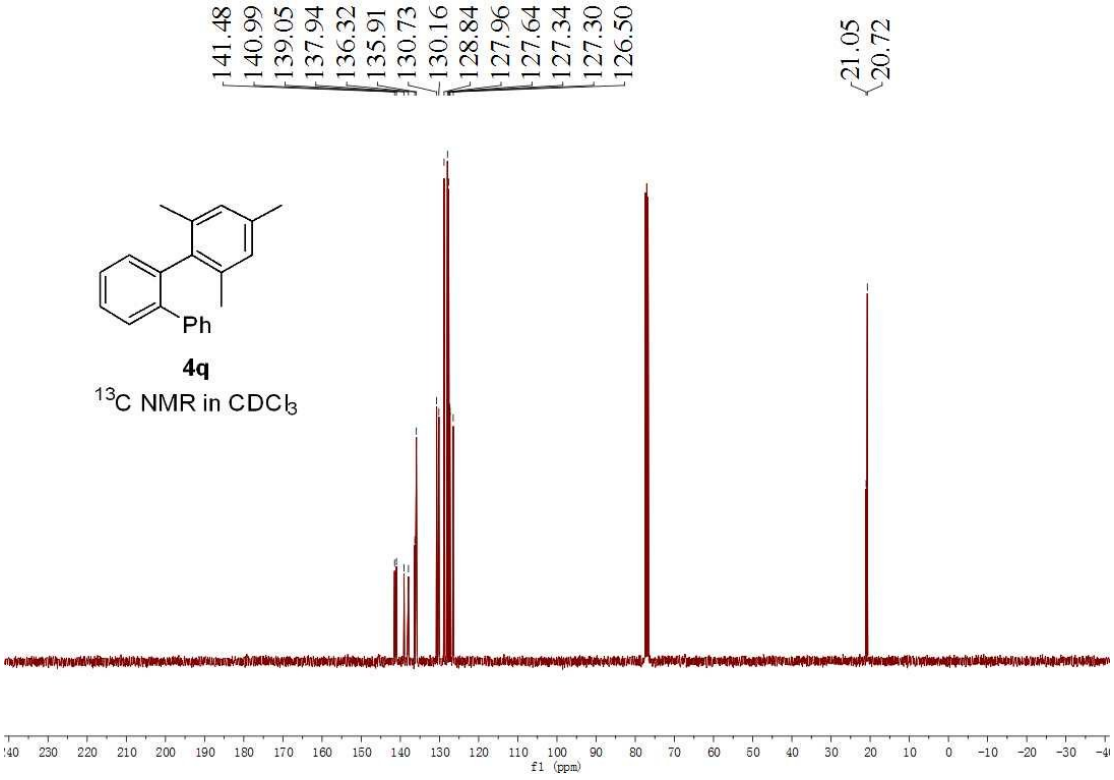
4o

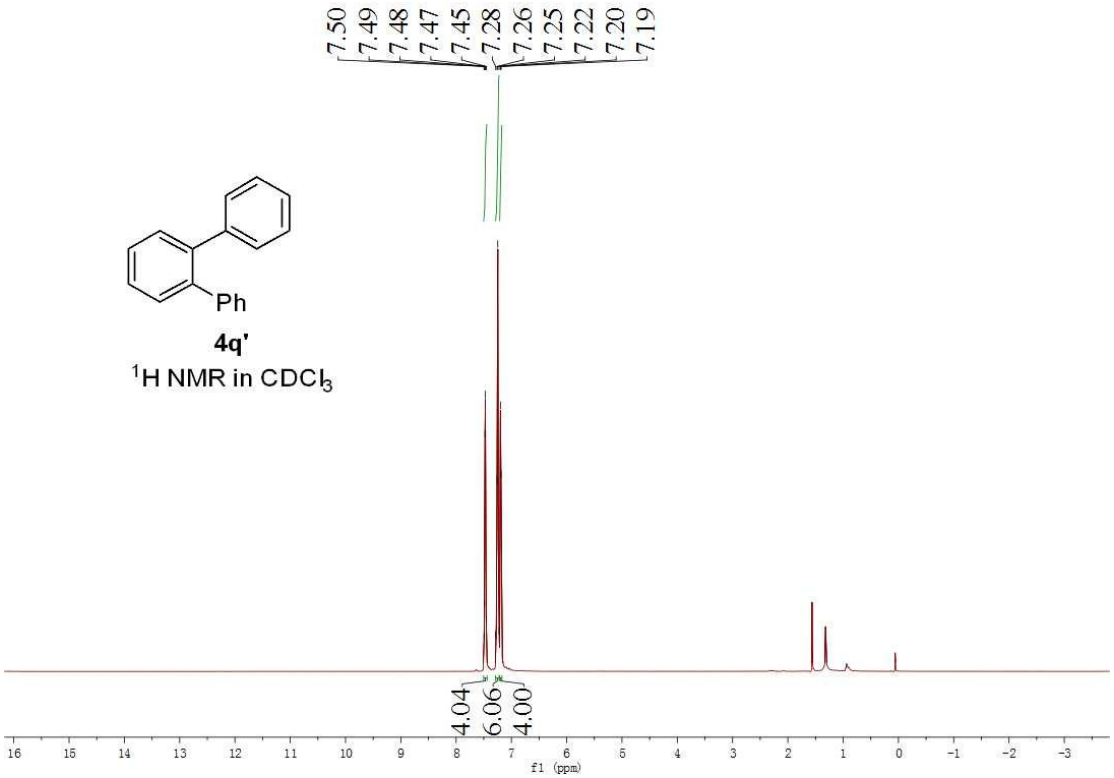
^{13}C NMR in $CDCl_3$

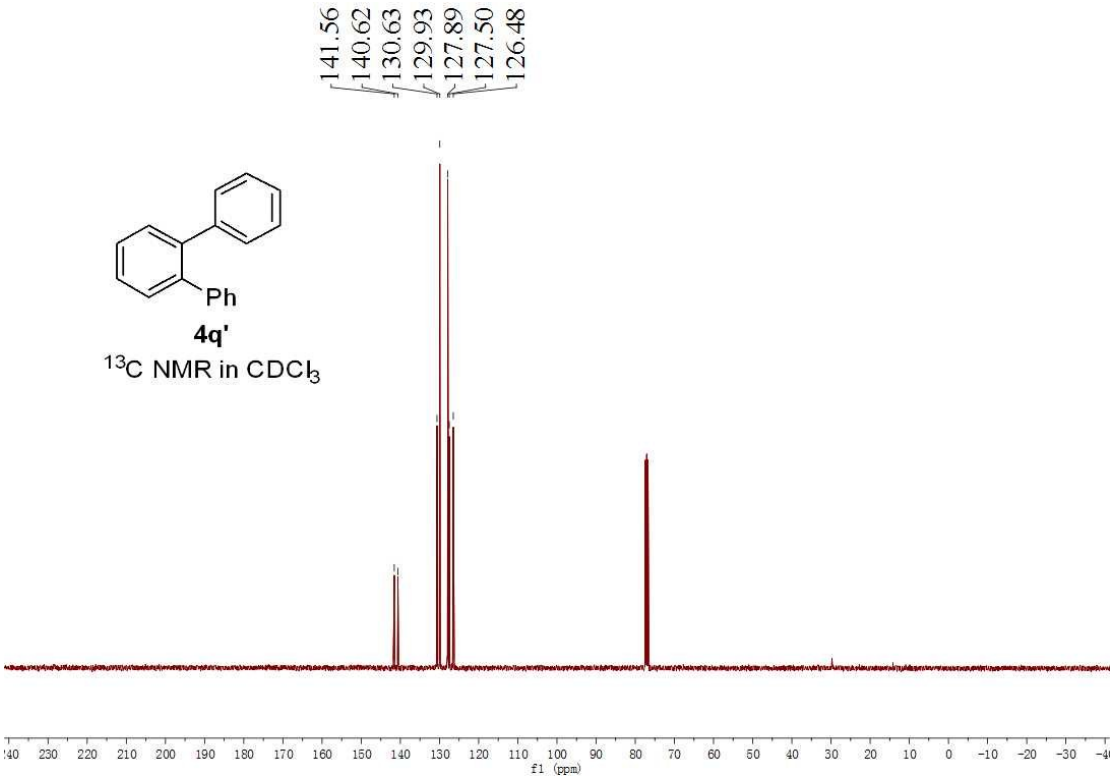

7.68
7.67
7.64
7.62
7.55
7.54
7.52
7.50
7.49
7.47
7.41
7.39
7.38
7.19
7.18
7.02
2.40
2.11
Ph
4p
1H NMR in CDCl3
2.01
1.05
1.07
3.00
1.00
1.02
2.01
3.02
6.07
f1 (ppm)

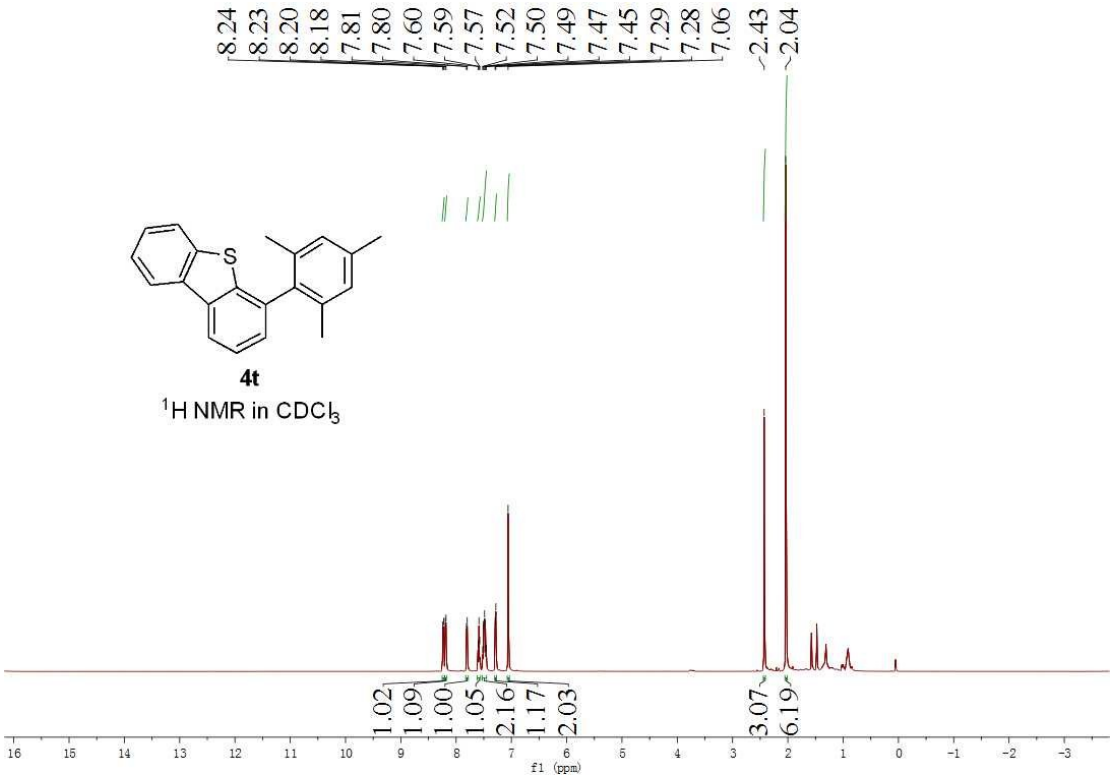

141.60
141.18
141.12
138.96
136.70
136.04
128.85
128.81
128.30
128.15
128.05
127.31
127.13
125.29
21.07
20.86
Ph
4p
13C NMR in CDCl3
f1 (ppm)


7.52
7.50
7.47
7.46
7.44
7.42
7.41
7.21
7.20
7.15
6.83
2.30
1.95
Ph
4q
1H NMR in CDCl3
1.00
2.07
4.02
2.00
2.00
3.03
6.08
f1 (ppm)


141.48
140.99
139.05
137.94
136.32
135.91
130.73
130.16
128.84
127.96
127.64
127.34
127.30
126.50
21.05
20.72
Ph
4q
13C NMR in CDCl3
f1 (ppm)

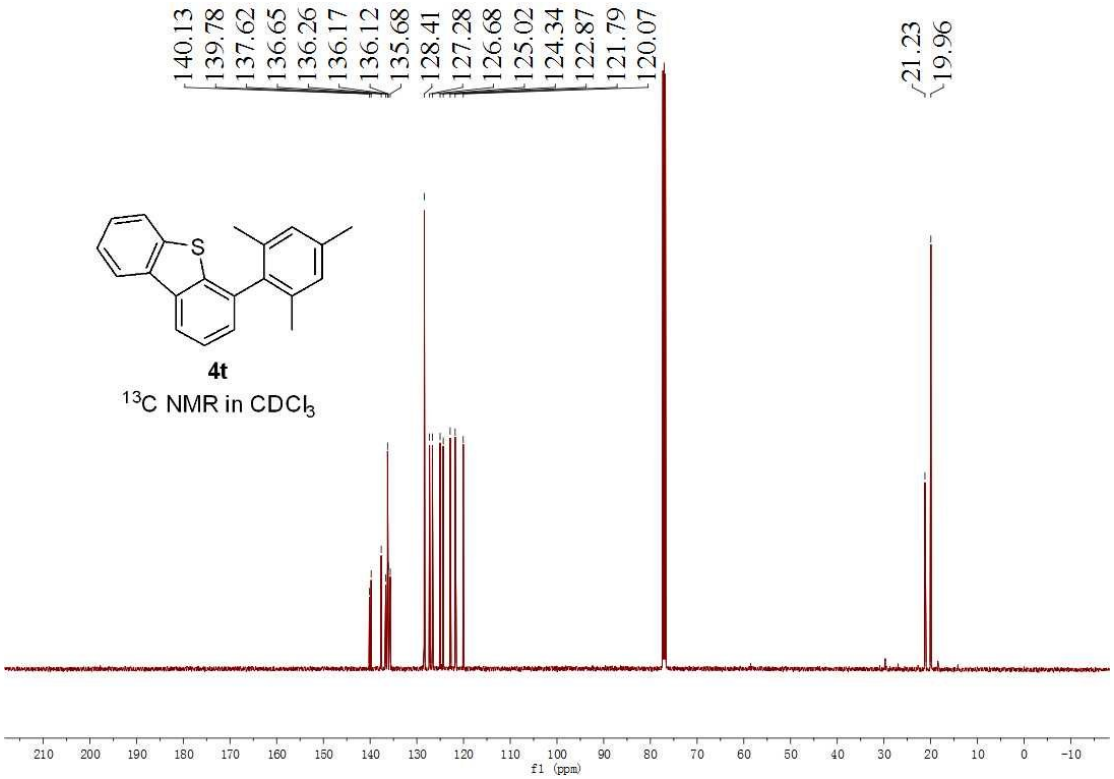

7.50
7.49
7.48
7.47
7.45
7.28
7.26
7.25
7.22
7.20
7.19
Ph
4q'
1H NMR in CDCl3
4.04
6.06
4.00
f1 (ppm)


141.56
140.62
130.63
129.93
127.89
127.50
126.48
Ph
4q'
13C NMR in CDCl3
f1 (ppm)



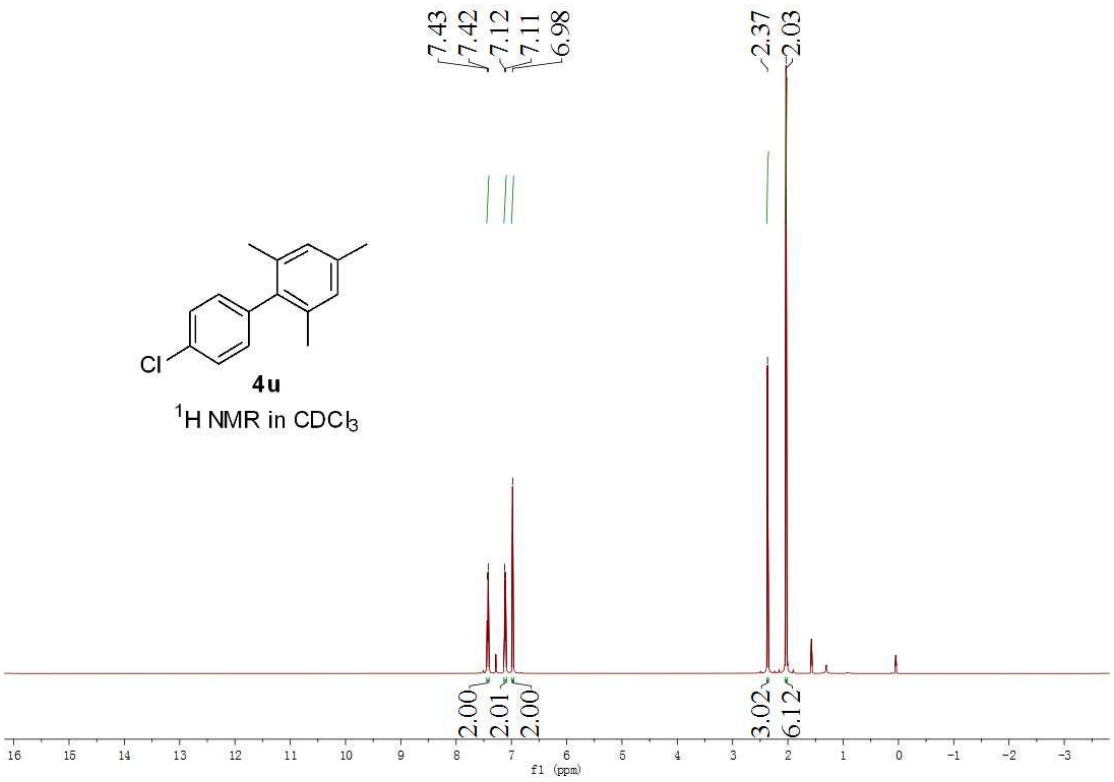
4t

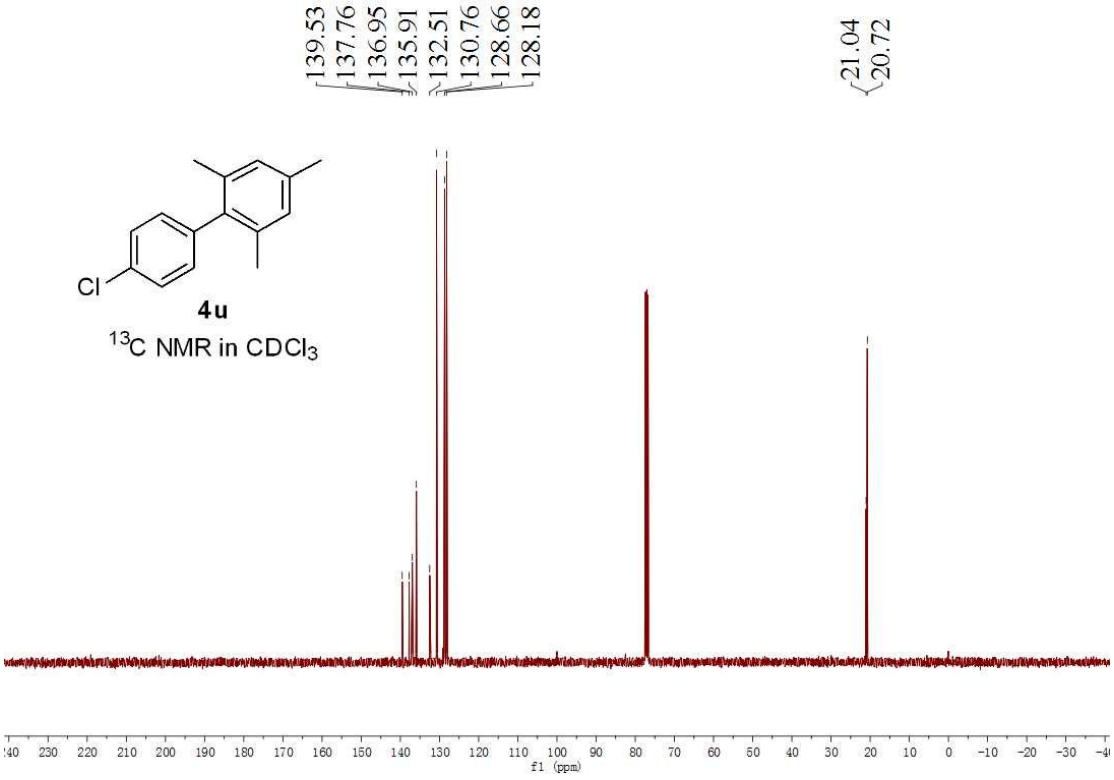
^{1}H NMR in $CDCl_3$

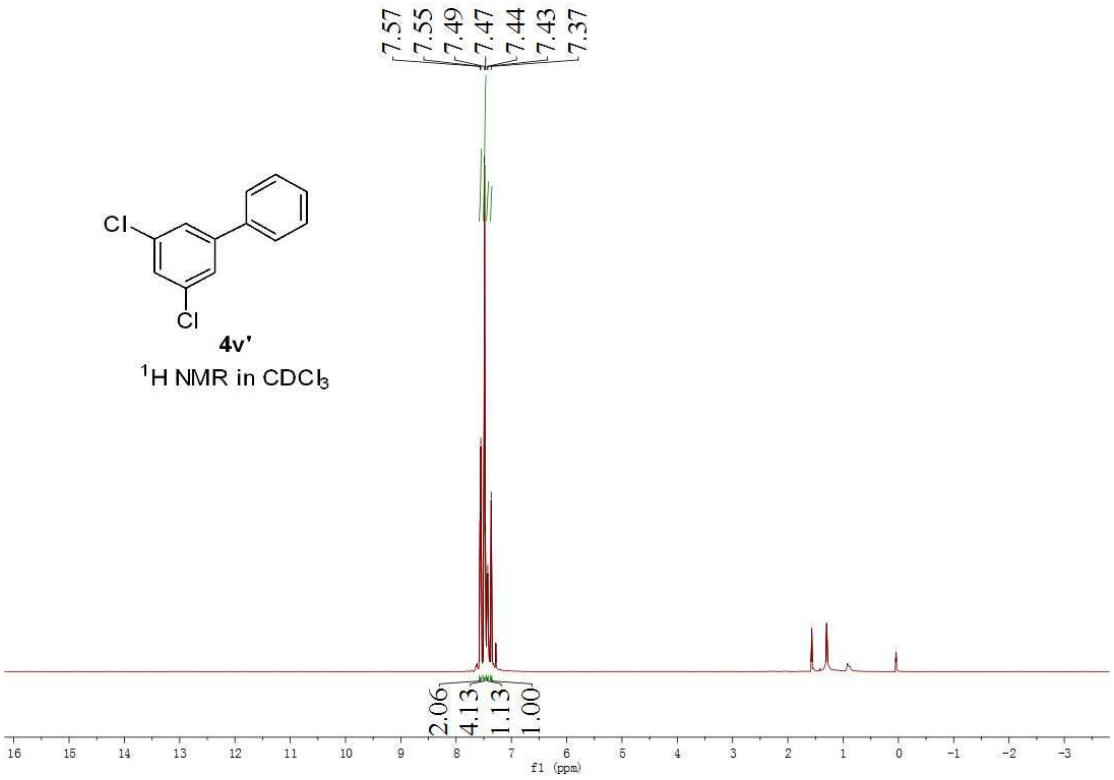


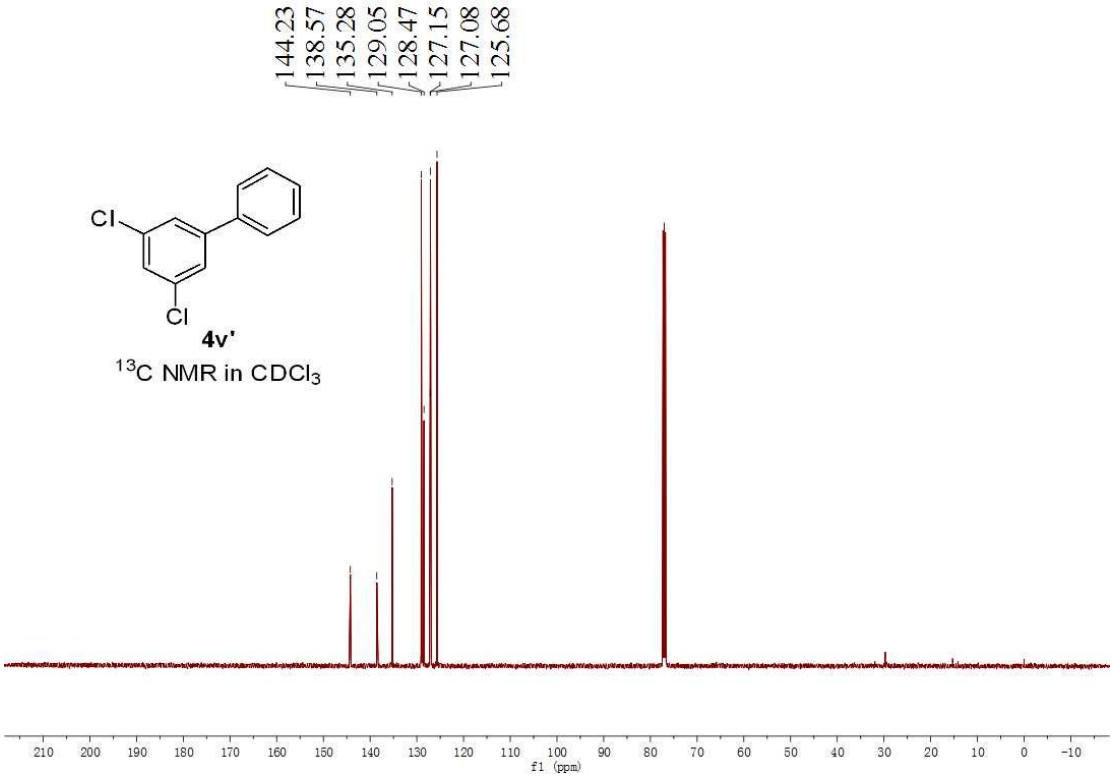
4t

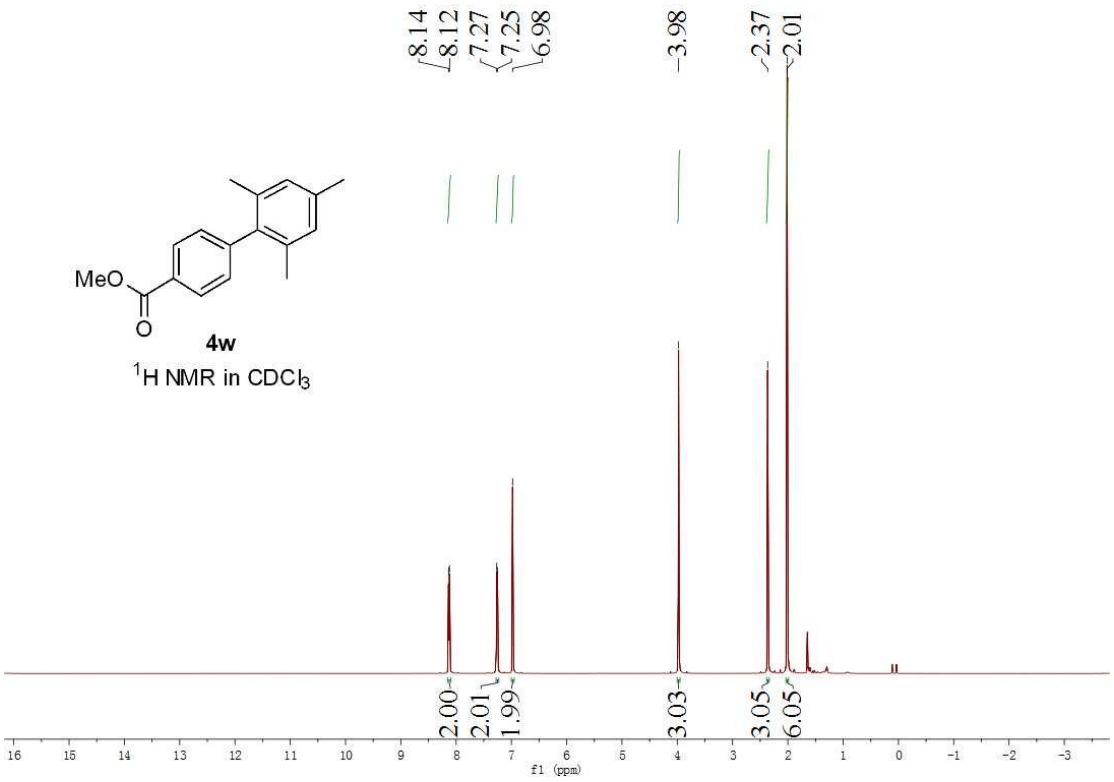
^{13}C NMR in $CDCl_3$

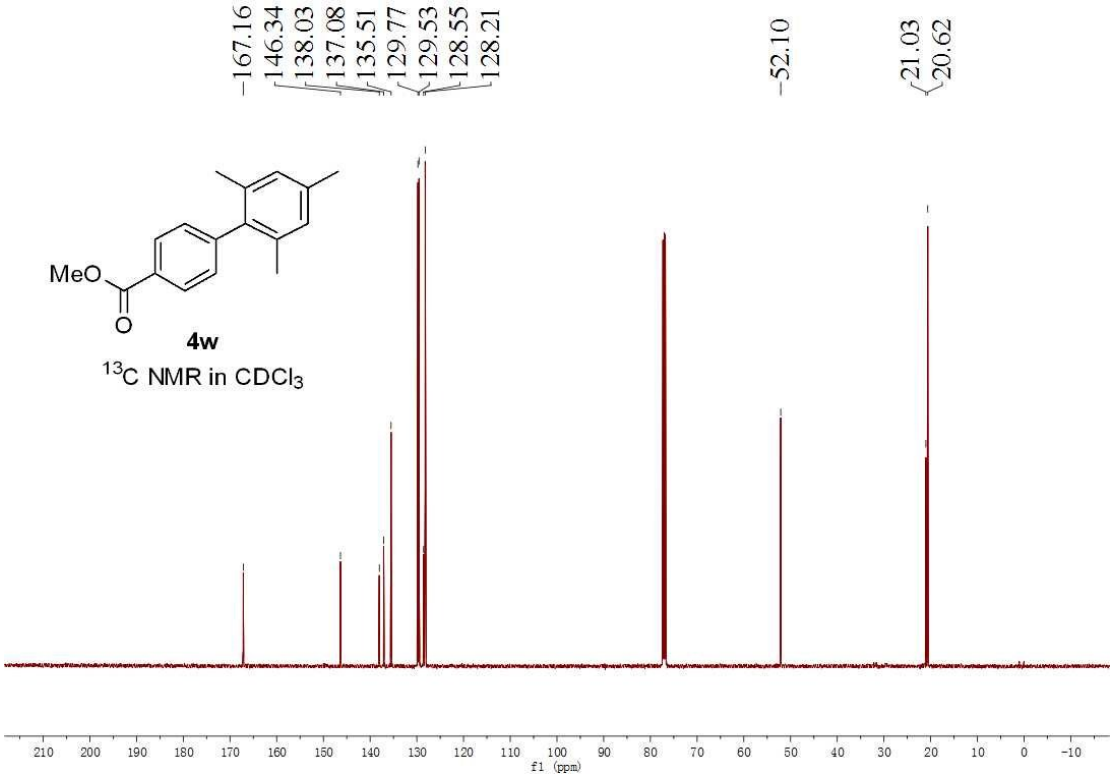

7.43
7.42
7.12
7.11
6.98
2.37
2.03
Cl
4u
1H NMR in CDCl3
2.00
2.01
2.00
3.02
6.12
f1 (ppm)

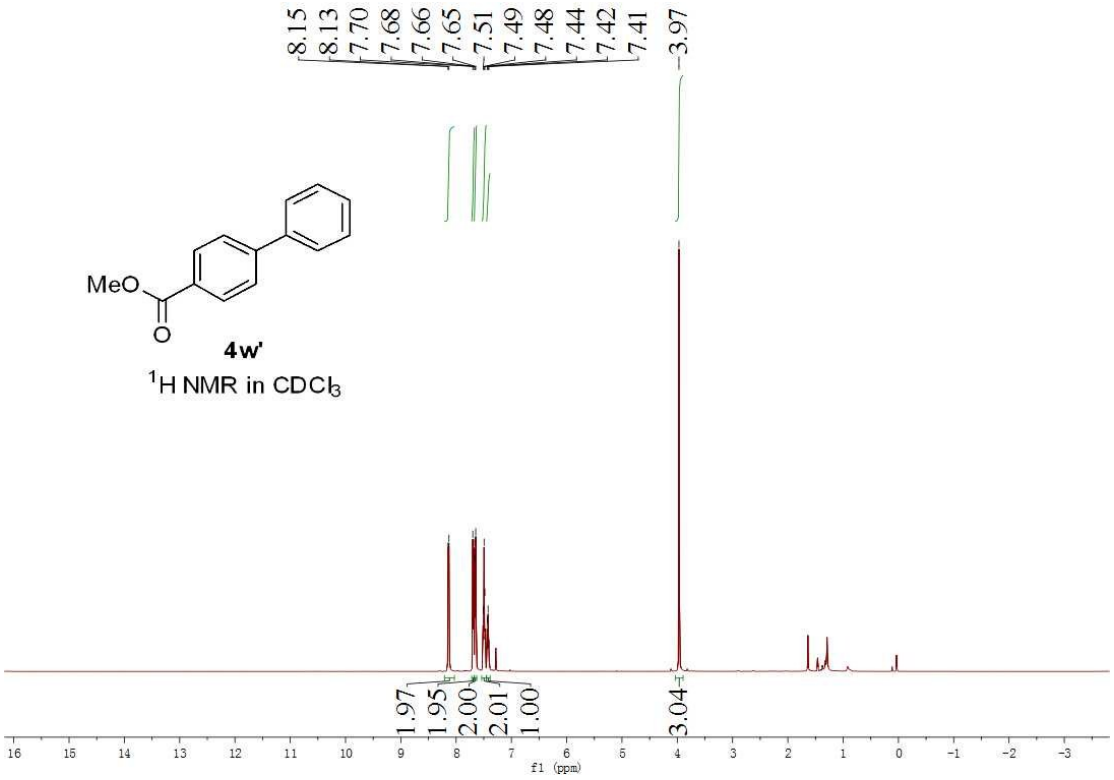

139.53
137.76
136.95
135.91
132.51
130.76
128.66
128.18
21.04
20.72
Cl
4u
13C NMR in CDCl3
f1 (ppm)

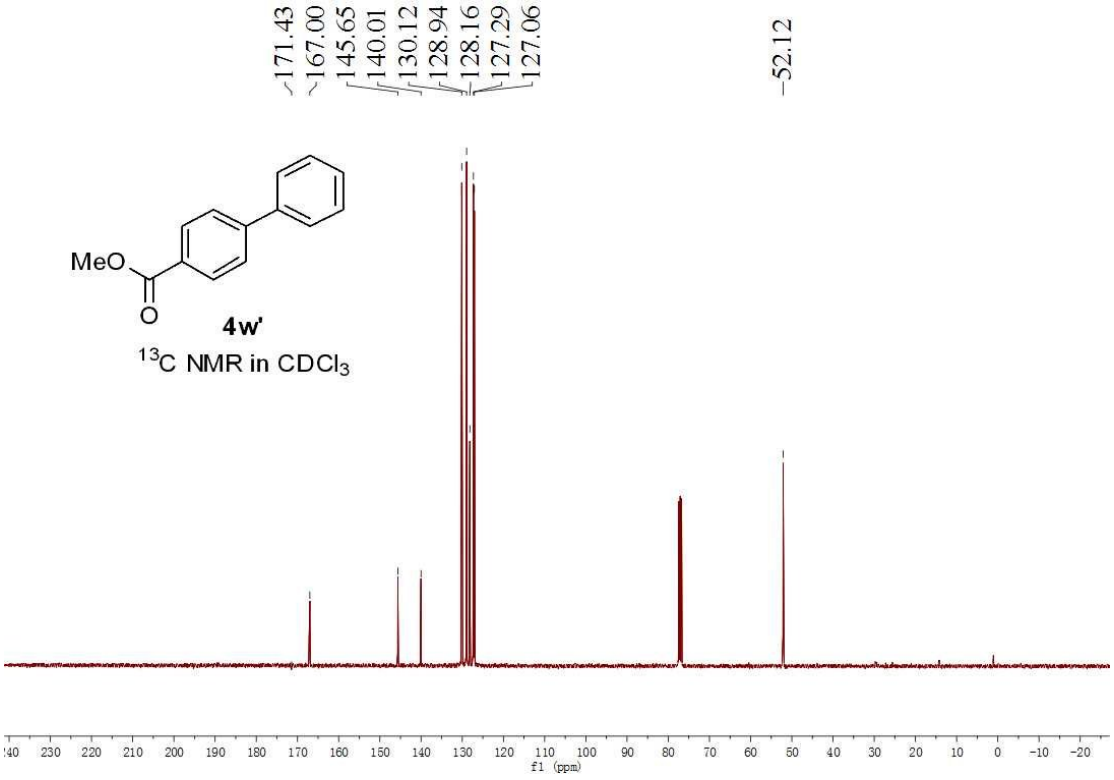

7.57
7.55
7.49
7.47
7.44
7.43
7.37
Cl
Cl
4v'
^{1}H NMR in CDCl$_3$
2.06
4.13
1.13
1.00
f1 (ppm)

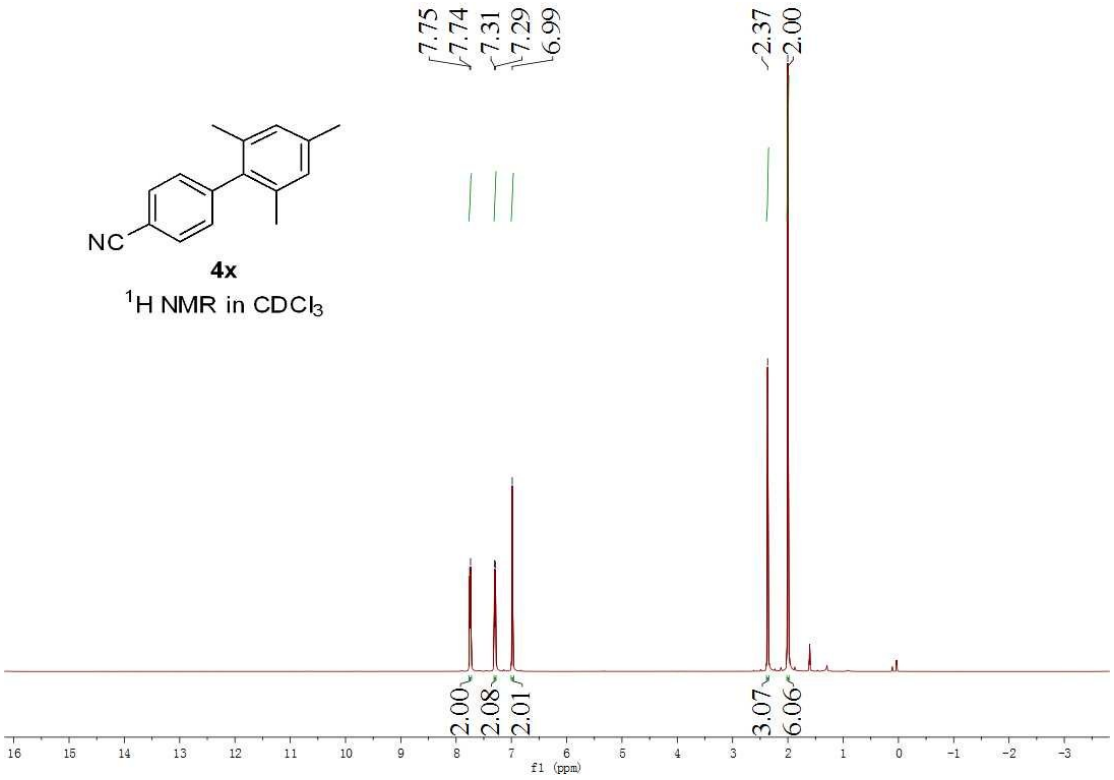

144.23
138.57
135.28
129.05
128.47
127.15
127.08
125.68
Cl
Cl
4v'
^{13}C NMR in CDCl$_3$
f1 (ppm)

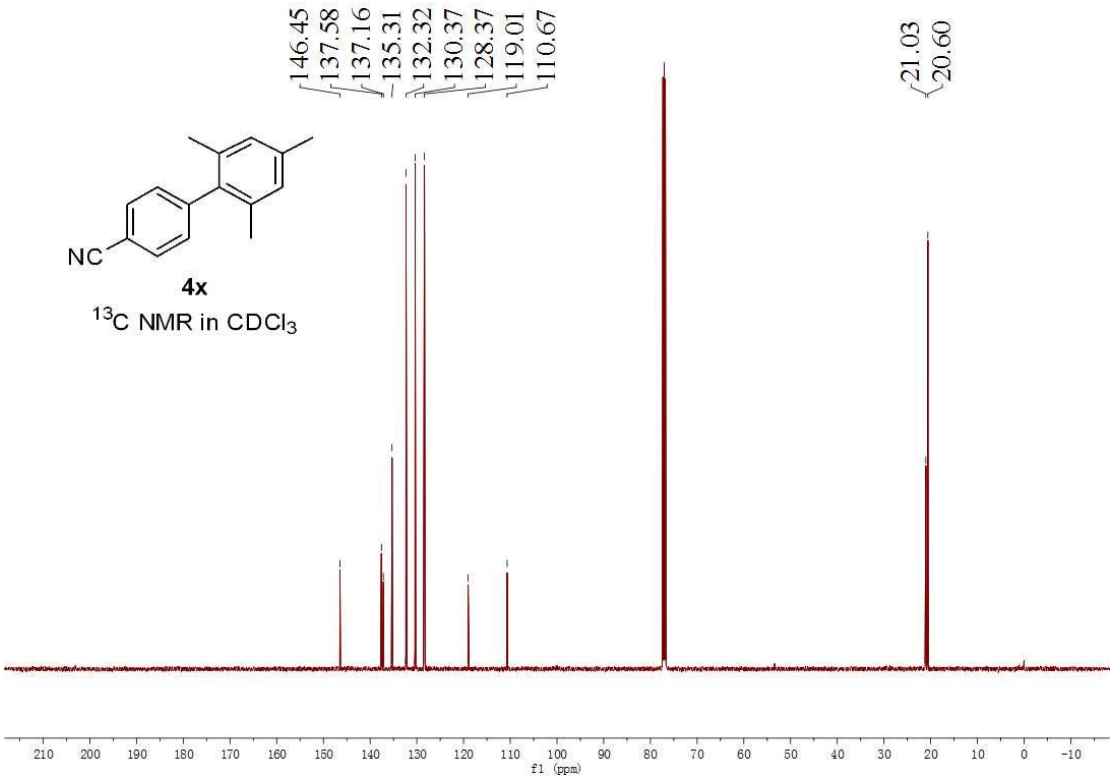

8.14
8.12
7.27
7.25
6.98
3.98
2.37
2.01
MeO
O
4w
^{1}H NMR in CDCl$_3$
2.00
2.01
1.99
3.03
3.05
6.05
f1 (ppm)

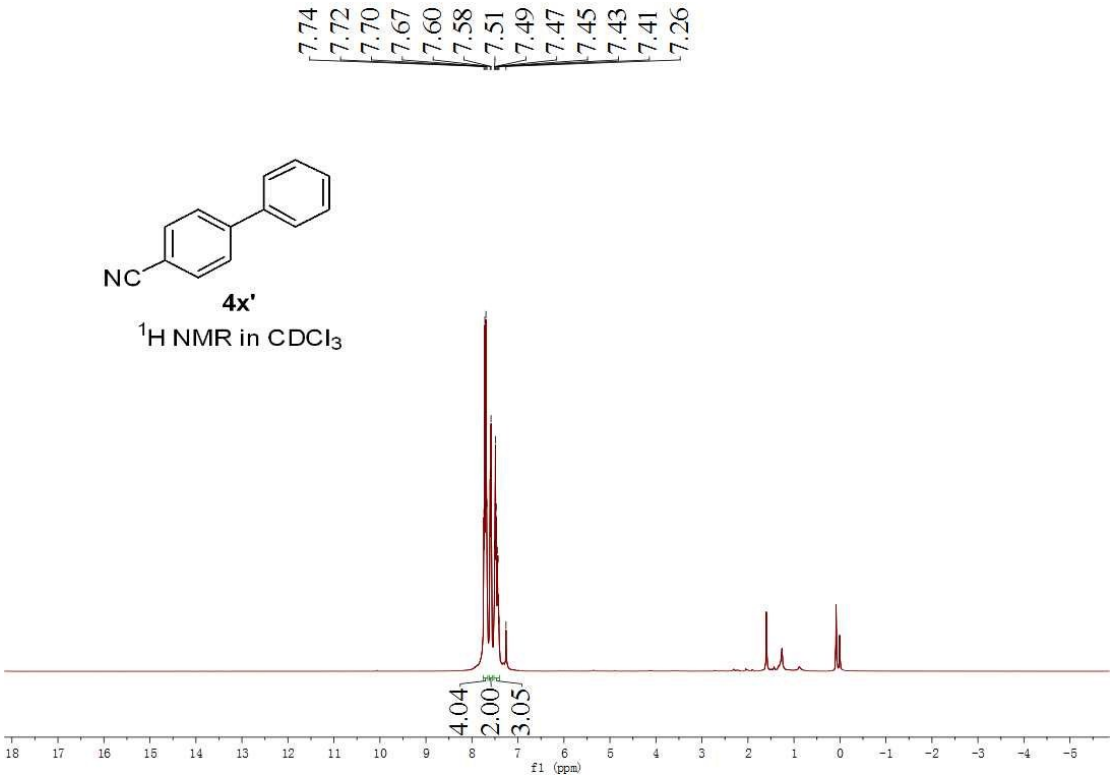

167.16
146.34
138.03
137.08
135.51
129.77
129.53
128.55
128.21
52.10
21.03
20.62
MeO
O
4w
^{13}C NMR in CDCl$_3$
f1 (ppm)

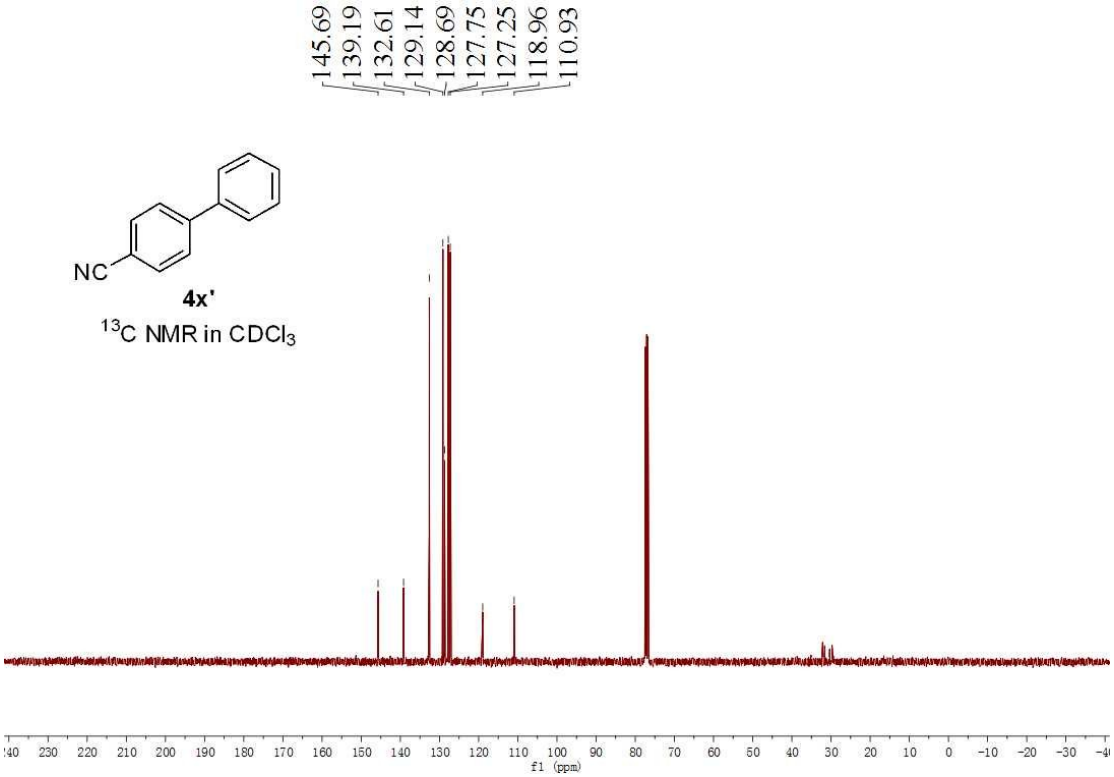

8.15
8.13
7.70
7.68
7.66
7.65
7.51
7.49
7.48
7.44
7.42
7.41
3.97
MeO
O
4w'
1H NMR in CDCl3
1.97
1.95
2.00
2.01
1.00
3.04
f1 (ppm)

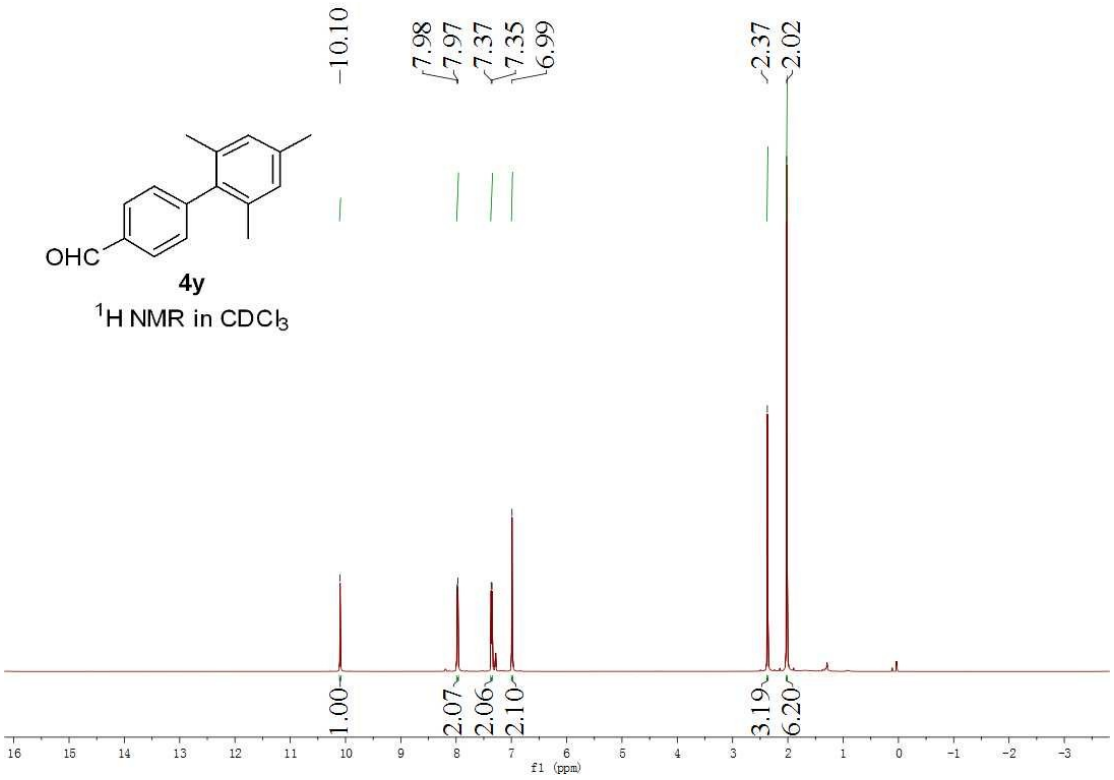

171.43
167.00
145.65
140.01
130.12
128.94
128.16
127.29
127.06
52.12
MeO
O
4w'
13C NMR in CDCl3
f1 (ppm)

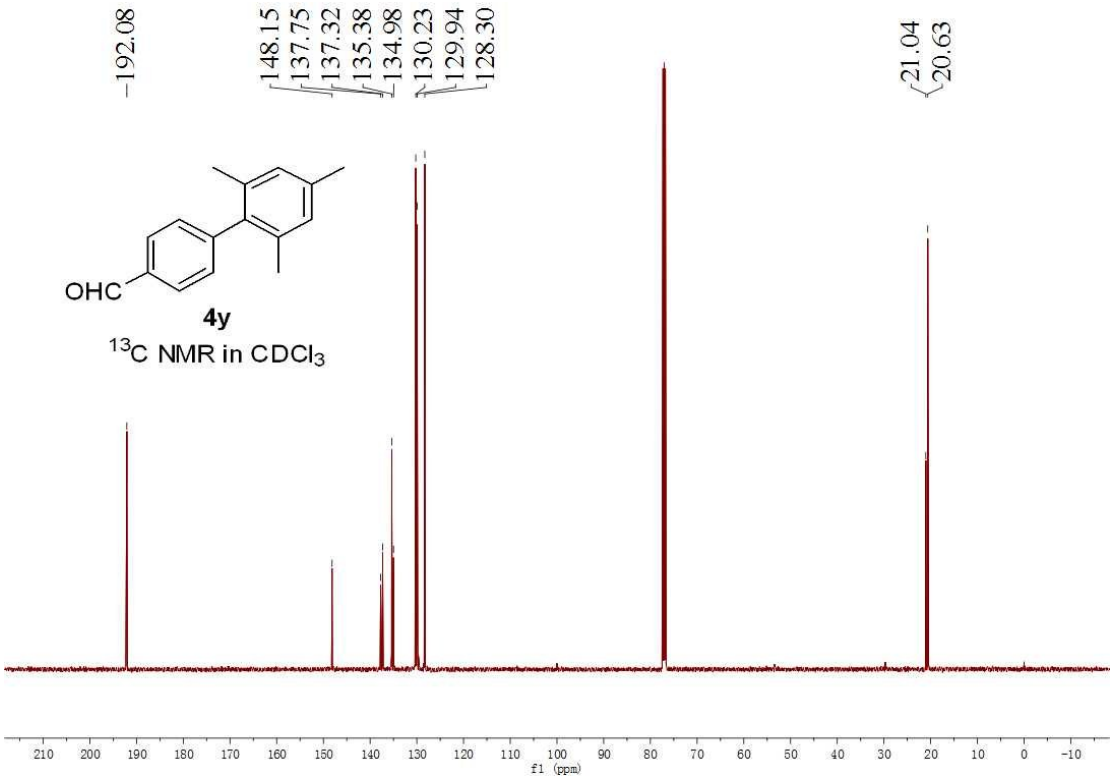

7.75
7.74
7.31
7.29
6.99
2.37
2.00
NC
4x
^{1}H NMR in CDCl$_3$
2.00
2.08
2.01
3.07
6.06
f1 (ppm)

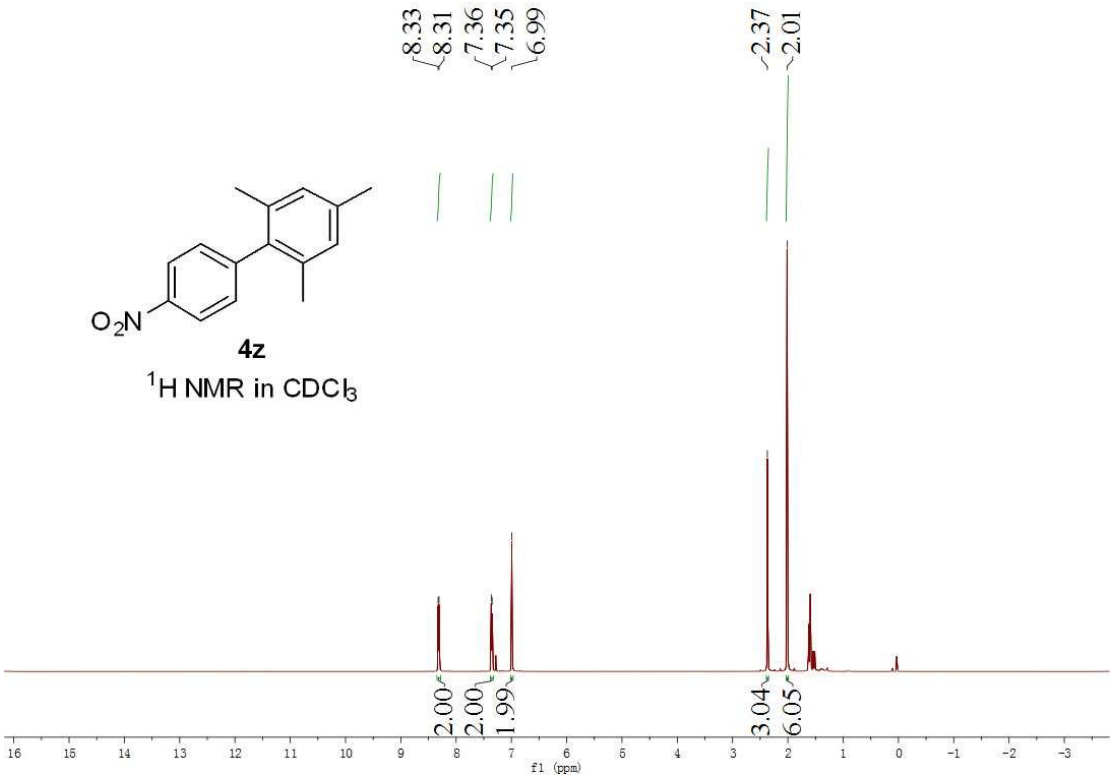

146.45
137.58
137.16
135.31
132.32
130.37
128.37
119.01
110.67
21.03
20.60
NC
4x
^{13}C NMR in CDCl$_3$
f1 (ppm)

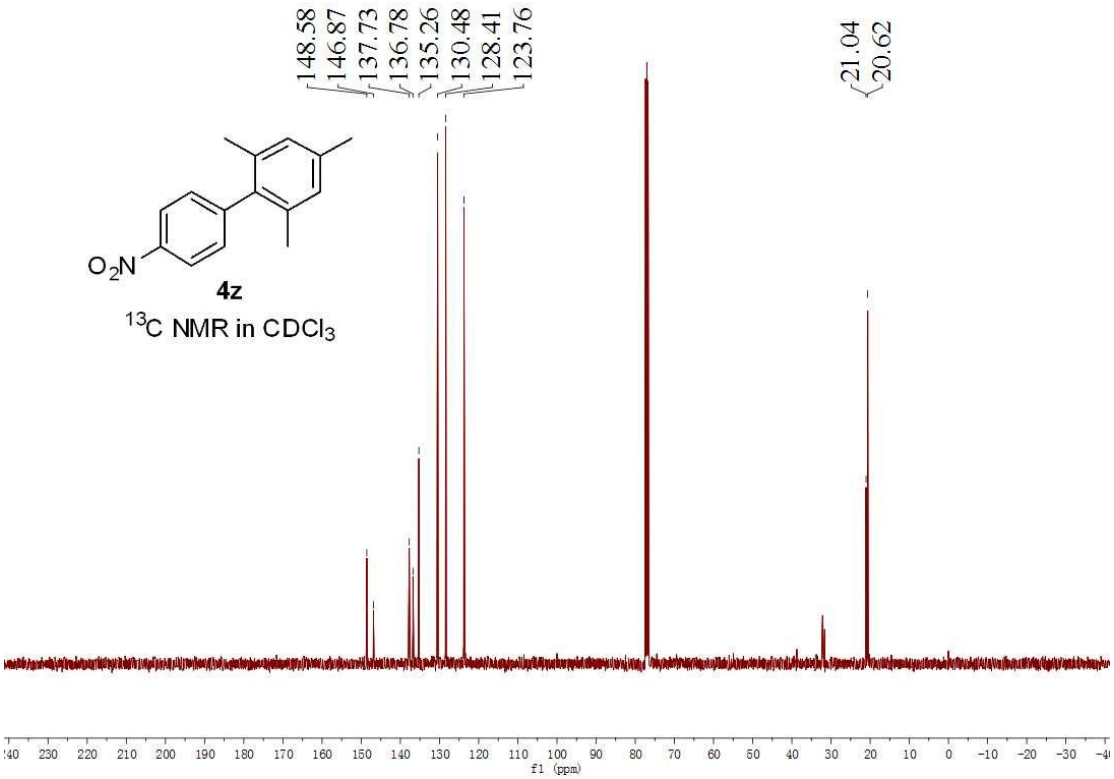

7.74
7.72
7.70
7.67
7.60
7.58
7.51
7.49
7.47
7.45
7.43
7.41
7.26
NC
4x'
1H NMR in CDCl3
4.04
2.00
3.05
f1 (ppm)


145.69
139.19
132.61
129.14
128.69
127.75
127.25
118.96
110.93
NC
4x'
13C NMR in CDCl3
f1 (ppm)


10.10
7.98
7.97
7.37
7.35
6.99
2.37
2.02
OHC
4y
1H NMR in CDCl3
1.00
2.07
2.06
2.10
3.19
6.20
f1 (ppm)


192.08
148.15
137.75
137.32
135.38
134.98
130.23
129.94
128.30
21.04
20.63
OHC
4y
13C NMR in CDCl3
f1 (ppm)


8.33
8.31
7.36
7.35
6.99
2.37
2.01
O2N
4z
1H NMR in CDCl3
2.00
2.00
1.99
3.04
6.05
f1 (ppm)


148.58
146.87
137.73
136.78
135.26
130.48
128.41
123.76
21.04
20.62
O2N
4z
13C NMR in CDCl3
f1 (ppm)