Supporting Information

Trace amounts of palladium catalysed Suzuki-Miyaura reaction of deactivated and hindered aryl chlorides

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Contents

1. General Information

All reagents were obtained from commercial sources and used without further purification unless otherwise indicated. All experiments were conducted in the N_2. Silica gel for column chromatography was purchased from Qingdao Haiyang Chemical Co., Ltd. Column chromatography was performed on silica gel (240-400 mesh) with petroleum ether and ethyl acetate as eluent. Thin-layer chromatography (TLC) was used to monitor the reaction. ^{1}H NMR (400 MHz), ^{13}C NMR (101 MHz) and ^{19}F NMR (101 MHz) spectra were recorded with $CDCl_3$. Chemical shifts are reported downfield from TMS (=0) for ^{1}H NMR. For $^{13}C\{^1H\}$ NMR, chemical shifts are reported in the scale relative to $CDCl_3$ (=77.0).

2. Optimisation Study for Suzuki-Miyaura Cross-Coupling

Scheme S1. Screening of the catalyst systems.

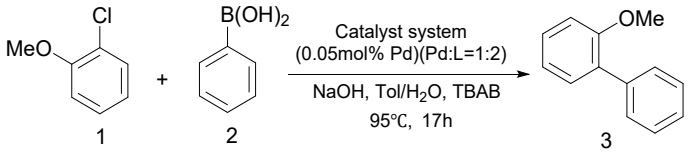


Table S1. Screening of the catalyst systems. [a]

Entry	catalytic system	Yield (%) [b]
1	**$Pd(PPh_3)_4 + PCy_3$**	**45**
2	$Pd(PPh_3)_4 + PMe_3$	4
3	$Pd(PPh_3)_4 + PPh_3$	11
4	$Pd(PPh_3)_4 + PMe(t\text{-}Bu)_2$	37
5	$Pd(PPh_3)_4$ + Sphos	33
6	$Pd(PPh_3)_4 + P(t\text{-}Bu)Cy_2$	48
7	$Pd(PPh_3)_4 + P(n\text{-}Bu)Ad_2$	40
8	$Pd(PPh_3)_4 + P(t\text{-}Bu)_3$	24
9	$(PCy_3)_2PdCl_2 + PCy_3$	38
10	$Pd(OAc)_2 + PCy_3$	40
11	$Pd_2(dba)_3 + PCy_3$	47

[a] Standard conditions: **1** (1.0 mmol), **2** (1.5 mmol), TBAB (0.2 equiv.), KOH (2.0 equiv.), The respective catalytic system (0.05 mol% Pd; Pd : L=1:2), N_2, Tol/H_2O (4:1, 5 ml), 95 °C, and 17 h. [b] Determined by HPLC analysis.

Scheme S2. Base screening.

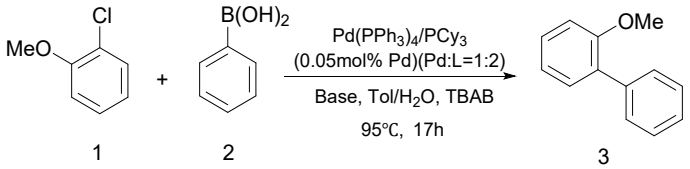


Table S2. Bases screening. [a]

Entry	Base	Yield (%) [b]
1	NaOH	45
2	K_3PO_4	n.d.
3	$NaCO_3$	n.d.
4	$CsCO_3$	11
5	KF	n.d.
6	**KOH**	**54**
7	KOH (1.0 equiv.)	n.d.
8	KOH (1.5 equiv.)	38
9	KOH (3.0 equiv.)	12

[a] Standard conditions: **1** (1.0 mmol), **2** (1.5 mmol), TBAB (0.2 equiv.), Base (2.0 equiv.), $Pd(PPh_3)_4$/ PCy_3 (0.05 mol% Pd; Pd : L=1:2), N_2, Tol/H_2O (4:1, 5 ml), 95 °C, and 17 h. [b] Determined by HPLC analysis.

Scheme S3. Solvent screening

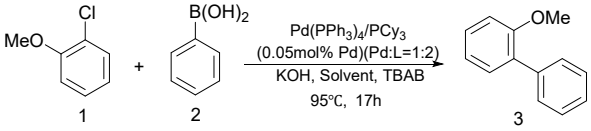


Table S3. Solvent screening. [a]

Entry	Solvent	Yield (%) [b]
1	Tol/H_2O	54
2	H_2O	n.d.
3	Dioxane	5
4	THF	8
5	Dioxane/H_2O =4/1	43
6	THF/H_2O =4/1	37
7	MeOH/H_2O =4/1	40
8	EtOH/H_2O =4/1	45
9	Tol/*i*-PrOH/H_2O =3/1/1	61
10	Tol/*i*-PrOH/H_2O =2/2/1	80
11	***i*-PrOH/H_2O =4/1**	**86**
12	*n*-BuOH/H_2O =4/1	82

[a] Standard conditions: **1** (1.0 mmol), **2** (1.5 mmol), TBAB (0.2 equiv.), KOH (2.0 equiv.), $Pd(PPh_3)_4$/ PCy_3 (0.05 mol% Pd; Pd : L=1:2), N_2, Solvent (5 ml), 95 °C, and 17 h. [b] Determined by HPLC analysis.

Scheme S4. Solvent amount screening

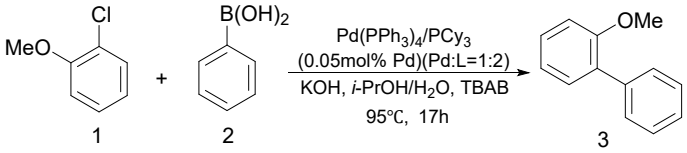


Table S4. Solvent amount screening. [a]

Entry	Solvent amount	Yield (%) [b]
1	*i*-PrOH/ H_2O =4/0.8 (4.8 ml)	86
2	*i*-PrOH/ H_2O =4/0.6 (4.6 ml)	82
3	*i*-PrOH/ H_2O =4/0.4 (4.4 ml)	74
4	*i*-PrOH/ H_2O =4/0.2 (4.2 ml)	71
5	*i*-PrOH/ H_2O =4/1 (2.5 ml)	75
6	*i*-PrOH/ H_2O =4/1 (5 ml)	86
7	***i*-PrOH/ H_2O =3/2 (5 ml)**	**92**
8	*i*-PrOH/ H_2O =1/1 (5 ml)	82

[a] Standard conditions: **1** (1.0 mmol), **2** (1.5 mmol), TBAB (0.2 equiv.), KOH (2.0 equiv.), $Pd(PPh_3)_4$/ PCy_3 (0.05 mol% Pd; Pd : L=1:2), N_2, Solvent, 95 °C, and 17 h. [b] Determined by HPLC analysis.

Scheme S5. Base screening under optimized conditions.

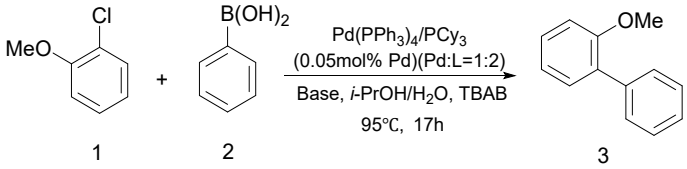


Table S5. Bases screening. [a]

Entry	Base	Yield (%) [b]
1	**KOH**	**92**
2	NaOH	87
3	$NaCO_3$	12
4	$CsCO_3$	13
5	KF	46

[a] Standard conditions: **1** (1.0 mmol), **2** (1.5 mmol), TBAB (0.2 equiv.), Base (2.0 equiv.), $Pd(PPh_3)_4$/ PCy_3 (0.05 mol% Pd; Pd : L=1:2), N_2, *i*-PrOH/H_2O (3:2, 5 ml), 95 °C, and 17 h. [b] Determined by HPLC analysis

Scheme S6. Ligand screening under optimized conditions.

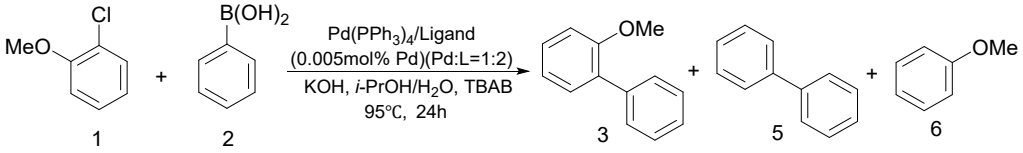


Table S6. Ligand screening. [a]

Entry	Ligand	%V_{bur}(min)	Yield (%) [b]
1	PMe_3	22.1	1 (2, 1)
2	P(*i*-Pr)$_3$	29	12 (13 9)
3	P(*t*-Bu)Ph_2	30.1	13 (11, 10)
4	PCy_3	30.2	89 (5, 5)
5	PMe(*t*-Bu)$_2$	31.5	82(8, 6)
6	Sphos	31.7	23 (14, 9)
7	**P(*t*-Bu)Cy_2**	**32**	**96 (3, 4)**
8	P(*n*-Bu)Ad_2	32.8	60 (7, 8)
9	P(*t*-Bu)$_3$	36.3	46 (3, 7)
10	P(*n*-Pr)$_3$	24.2	5
11	P(*n*-Bu)$_3$	24.2	2
12	PEt_3	24.4	1
13	P(OEt)$_3$	24.8	2
14	P(OEt)Ph_2	25.1	7
15	$PCyPh_2$	28	n.d.
16[c]	L_1	28	n.d.
17	PCy_2Ph	28.8	2
18	Ph_2P(*o*-Tol)	29	n.d.
19[c]	L_2	30	5
20	Cy-BippyPhos	30.1	10
21	Xphos	31.4	44
22	CyJohnPhos	31.8	4
23	P(*o*-Tol)$_3$	34.4	6
24	P(*t*-Bu)$_2$Ph	35.1	58
25	PAd_3	36.6	3
26[c]	L_3	44.1	59

[a] Standard conditions: **1** (1.0 mmol), **2** (1.5 mmol), TBAB (0.2 equiv.), KOH (2.0 equiv.), 10μL of the respective catalytic system (0.005 M in cyclohexane; Pd: L=1:2), N_2, *i*-PrOH/H_2O (3:2, 5 ml), 95 °C, and 24 h. [b] Determined by HPLC analysis, yields of 5 (left) and 6 (right). [c] L_1= Isopropyldiphenylphos-phine, L_2= Dicyclohexyl(o-tolyl)phos-phinee, L_3= Dicyclohexyl(2,4,6-triisopropylphenyl)phosphine.

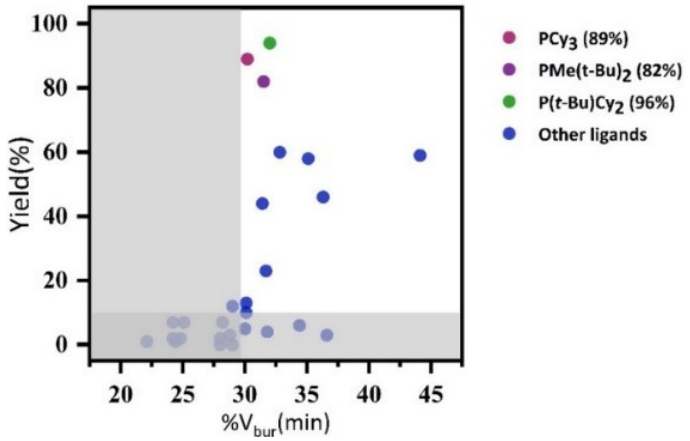


Figure S1. Screening of the ligands, yield vs descriptor plots for the model reaction of 27 phosphine ligands

Scheme S7. Screening of the palladium source under optimized conditions.

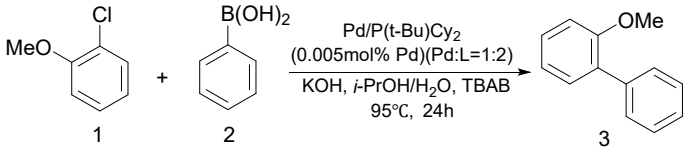


Table S7. Screening of the palladium source. [a]

Entry	catalytic system	Yield (%) [b]
1	**$Pd(PPh_3)_4$**	**96**
2	$PdCl_2$	70
3	$(PCy_3)_2PdCl_2$	75
4	$(PPh_3)_2PdCl_2$	85
5	$Pd(OAc)_2$	89
6	$Pd_2(dba)_3$	93
7	$(PPh_3)_2Pd(OAc)_2$	90
8	$PdCl_2(cod)$	72

[a] Standard conditions: **1** (1.0 mmol), **2** (1.5 mmol), TBAB (0.2 equiv.), KOH (2.0 equiv.), 10μL of the respective catalytic system (0.005 M in cyclohexane; Pd: L=1:2), N_2, *i*-PrOH/H_2O (3:2, 5 ml), 95 °C, and 24 h. [b] Determined by HPLC analysis.

Scheme S8. Screening of the ratio of Pd and L.

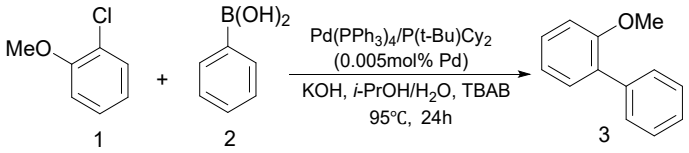


Table S8. Screening of the ratio of Pd and L. [a]

Entry	ratio of Pd and L	Yield (%) [b]
1	**Pd: L=1:2**	**96**
2	Pd: L=2:1	55
3	Pd: L=1:1	82
4	Pd: L=1:4	91
5	Pd: L=1:6	94

[a] Standard conditions: **1** (1.0 mmol), **2** (1.5 mmol), TBAB (0.2 equiv.), KOH (2.0 equiv.), 10μL of the $Pd(PPh_3)_4/P(t\text{-}Bu)Cy_2$ (0.005 M in cyclohexane), N_2, *i*-PrOH/H_2O (3:2, 5 ml), 95 °C, and 24 h. [b] Determined by HPLC analysis.

Scheme S9. Temperature screening

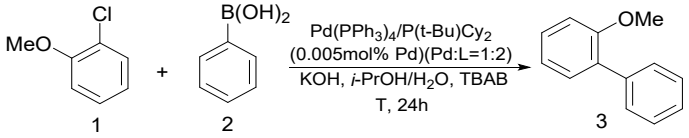


Table S9. Temperature screening. [a]

Entry	T(℃)	Yield (%) [b]
1	100	95
2	**95**	**96**
3	85	89
4	75	38
5	60	n.d.

[a] Standard conditions: **1** (1.0 mmol), **2** (1.5 mmol), TBAB (0.2 equiv.), KOH (2.0 equiv.), 10μL of the $Pd(PPh_3)_4/P(t\text{-}Bu)Cy_2$ (0.005 M in cyclohexane; Pd: L=1:2), N_2, *i*-PrOH/H_2O (3:2, 5 ml), T , and 24 h. [b] Determined by HPLC analysis.

Scheme S10. Surfactant screening

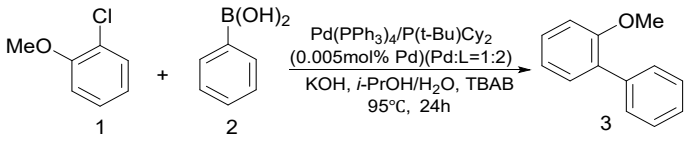


Table S10. Surfactant screening. [a]

Entry	Surfactant	Yield (%) [b]
1	No surfactant	78
2	TBAB (0.1 equiv.)	85
3	**TBAB (0.2 equiv.)**	**95**
4	TBAB (0.3 equiv.)	96

[a] Standard conditions: **1** (1.0 mmol), **2** (1.5 mmol), TBAB, KOH (2.0 equiv.), 10μL of the $Pd(PPh_3)_4$/P(*t*-Bu)Cy_2 (0.005 M in cyclohexane; Pd: L=1:2), N_2, *i*-PrOH/H_2O (3:2, 5 ml), 95℃ , and 24 h. [b] Determined by HPLC analysis.

Scheme S11. Catalyst loading screening

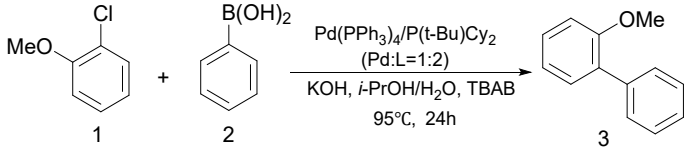


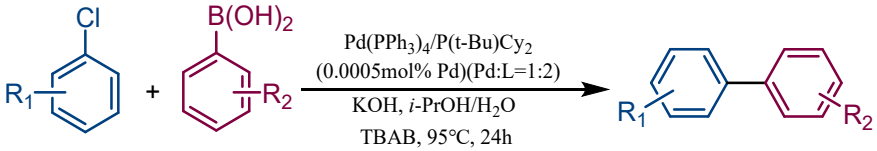
Table S11. Investigation on lower catalyst loading under the optimised conditions.

Entry	2-Chloroanisole	Phenylboronic acid	Catalyst loading (mol%)	Yield (%) [b]
1	1mmol	1.5 equiv.	0.005	95
2	1mmol	1.3 equiv.	0.005	91
3	1mmol	1.1 equiv.	0.005	83
4	1mmol	1.0 equiv.	0.005	65
5	1mmol	1.3 equiv.	0.001	83
6	1mmol	1.3 equiv.	0.0005	42
7	1.1 equiv.	1mmol	0.005	54
8	1.3 equiv.	1mmol	0.005	59
9	1.5 equiv.	1mmol	0.005	75
10	2.0 equiv.	1mmol	0.005	89
11[c]	3.0 equiv.	1mmol	0.005	94
12	3.0 equiv.	1mmol	0.001	96
13	**3.0 equiv.**	**1mmol**	**0.0005**	**95**
14[d]	3.0 equiv.	10mmol	0.00025	84
15[d]	3.0 equiv.	10mmol	0.000095	49

[a] Standard conditions: **1** (1.0 mmol), **2** (1.5 mmol), TBAB (0.2 equiv.), KOH (2.0 equiv.), $Pd(PPh_3)_4$/P(*t*-Bu)Cy_2, N_2, *i*-PrOH/H_2O (3:2, 5 ml), 95℃ , and 24 h. [b] Determined by HPLC analysis. [c] 16 instead of 24h. [d] 36 instead of 24h.

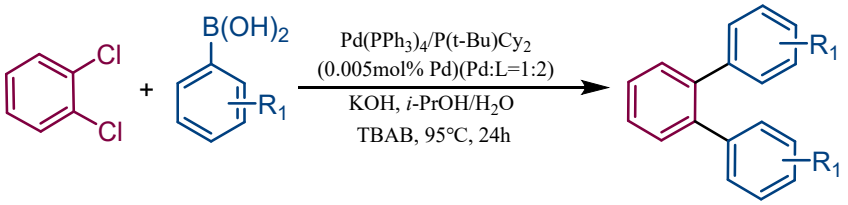
3. Suzuki-Miyaura Cross-Coupling of Aryl Chlorides at ppm Level

3.1 General Procedure for Suzuki-Miyaura Cross-Coupling (GP1)



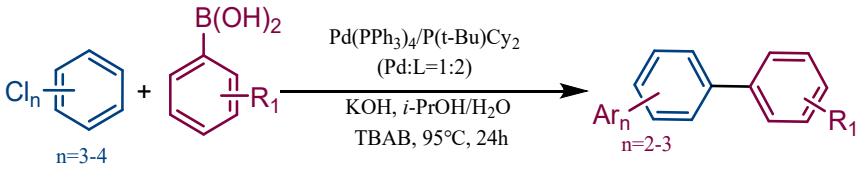
The reaction was carried out by using a glass vial equipped with a Teflon screw cap. Aryl boronic acid (10.0 mmol), aryl halide (30.0 mmol), KOH (840 mg 15.0 mmol), and TBAB (644 mg 2.0 mmol) were mixed in *i*-PrOH/H_2O (50.0 mL, 3:2, v/v) and stirred at room temperature until completely dissolved. The catalytic system (10μL of $Pd(PPh_3)_4$/P(t-Bu)Cy_2 (0.0005 mol% Pd: L=1:2) solution (0.005 M in cyclohexane) was then added, and the glass bottle was carefully evacuated and back-filled with nitrogen for three cycles. The reaction bottle was sealed and magnetically stirred in a preheated 95°C oil bath for 24 hours. After the reaction, the solvent and excess aryl halide were recovered through distillation under reduced pressure. The remaining crude product was added with ethyl acetate (10 ml) and water (10 ml), the aqueous layer was washed with ethyl acetate, the combined organic layers were dried ($MgSO_4$) and filtered, and the solvent was removed. The crude products were purified by column chromatography on silica gel to afford the desired product.

3.2 General Procedure for Suzuki-Miyaura Cross-Coupling (GP2)



The reaction was carried out by using a glass vial equipped with a Teflon screw cap. 1,2-dichlorobenzene (10.0 mmol), aryl boronic acid (25.0 mmol), KOH (1.68 g 30.0 mmol), and TBAB (644 mg 2.0 mmol) were mixed in *i*-PrOH/H_2O (50.0 mL, 3:2, v/v) and stirred at room temperature until completely dissolved. The catalytic system (10μL of $Pd(PPh_3)_4$/P(t-Bu)Cy_2 (0.005 mol% Pd Pd: L=1:2) solution (0.05 M in cyclohexane)) was then added, and the glass bottle was carefully evacuated and back-filled with nitrogen for three cycles. The reaction bottle was sealed and magnetically stirred in a preheated 95°C oil bath for 24 hours. After the reaction, the solvent was removed. The remaining crude product was added with ethyl acetate (15 ml) and water (15 ml), the aqueous layer was washed with ethyl acetate, the combined organic layers were dried ($MgSO_4$) and filtered, and the solvent was removed. The crude products were purified by column chromatography on silica gel to afford the desired product.

3.3 General Procedure for Suzuki-Miyaura Cross-Coupling (GP3)



The reaction was carried out by using a glass vial equipped with a Teflon screw cap. 1,3,5-trichlorobenzene (10.0 mmol), aryl boronic acid (35.0 mmol), KOH (2.24 g 40.0 mmol) (1,2,4,5-tetrachlorobenzene (10.0 mmol), aryl boronic acid (45.0 mmol), KOH (2.8 g 50.0 mmol)), and TBAB (644 mg 2.0 mmol) were mixed in *i*-PrOH/H_2O (50.0 mL, 3:2, v/v) and stirred at room temperature until completely dissolved. The catalytic system (0.0075 mol%Pd for 1,3,5-trichlorobenzene and 0.01 mol%Pd for 1,2,4,5-tetrachloro-benzene) was then added, and the glass bottle was carefully evacuated and back-filled with nitrogen for three cycles. The reaction bottle was sealed and magnetically stirred in a preheated 95°C oil bath for 24 hours. After the reaction, the reaction mixture is cooled to room temperature and then filtered. The filter cake was washed with isopropanol and dried to obtain the desired product.

(a) (b)

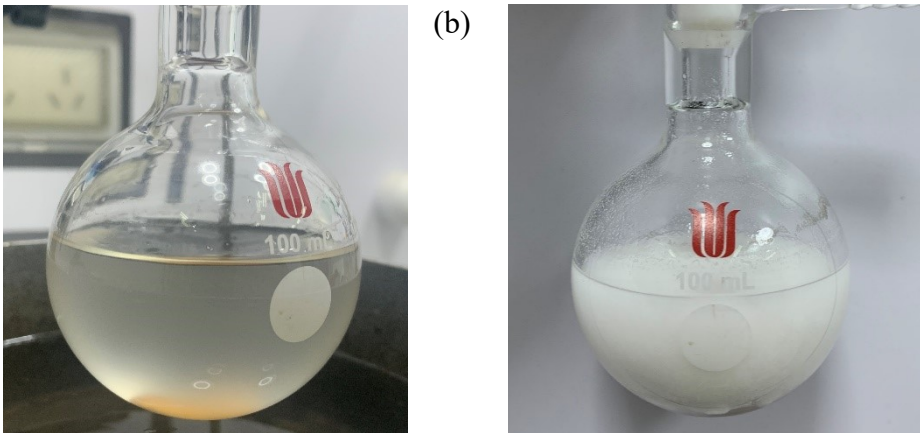
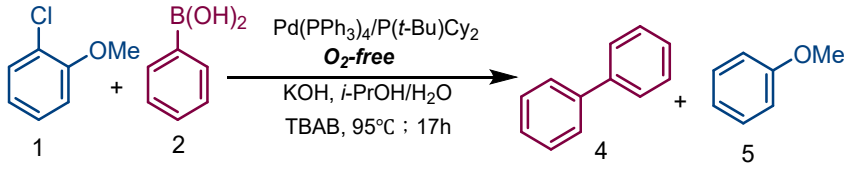


Figure S2. Reaction pictures of **4g:** a) before the reaction; b) after the reaction.

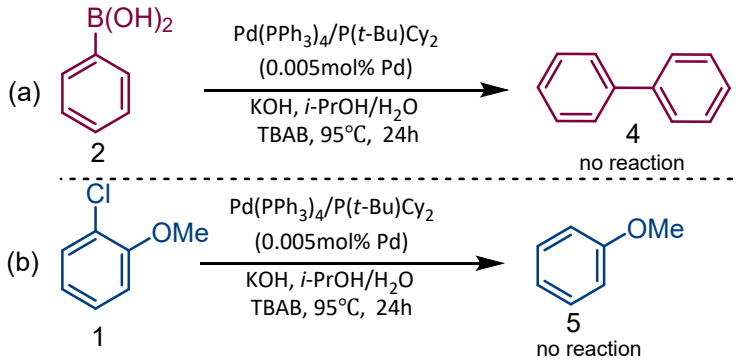
4. Control Experiments.

4.1 Control experiments with strictly anaerobic environment



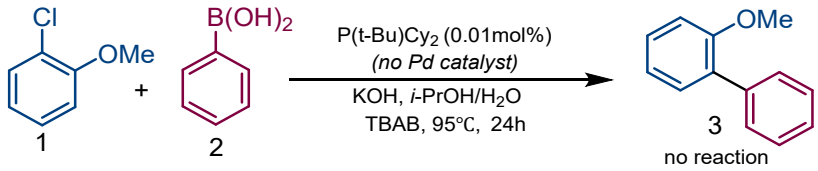
In a glovebox, a 100 ml glass vial was equipped with a magnetic stir bar, 1.22 g(10mmol) phenylboronic acid was added with 2-Chloroanisole (4.3 g 30 mmol), KOH (840 mg 15.0 mmol), TBAB (644 mg 2.0 mmol), 10μL of Pd(PPh3)4+P(t-Bu)Cy_2 solution (0.005 M in cyclohexane), and 50 ml i-PrOH/H2O(3:2, v/v), The vial was sealed and transferred outside the glovebox. The reaction bottle was sealed and magnetically stirred in a preheated 95°C oil bath for 24 hours. After the reaction, by-products were observed in the reaction by HPLC.

4.2 Controlled experiments on by-products [a]



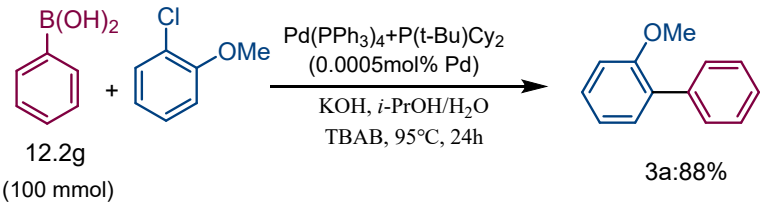
[a] The reaction proceeds without the addition of another feedstock (a: without 2-chloroanisole; b: without phenylboronic acid) according to the procedure (GP1) described before. After the reaction, by-products were observed in the reaction by HPLC.

4.3. Control experiments without catalyst [a]



[a] The experiment were done in a used pressure tube and using used magnetic stir bar according to the procedure (GP1) described before.

5. Scale-up Reaction



The reaction was carried out by using a 500 mL glass vial equipped with a Teflon screw cap. Phenylboronic acid (12.2 g 100 mmol), 2-Chloroanisole (42.7 g 300 mmol), KOH (8.4 g 150 mmol), and TBAB (6.4 g 20 mmol) were mixed in *i*-PrOH/H_2O (250 mL, 3:2, v/v) and stirred at room temperature until completely dissolved. The catalytic system (0.58 mg of $Pd(PPh_3)_4$ and 0.26 mg P(t-Bu)Cy_2) was then added, and the glass bottle was carefully evacuated and back-filled with nitrogen for three cycles. The reaction bottle was sealed and magnetically stirred in a preheated 95°C oil bath for 24 hours. After the reaction, the solvent was recovered through distillation under reduced pressure. The remaining crude product was added with ethyl acetate (100 ml) and water (100 ml), the aqueous layer was washed with ethyl acetate, the combined organic layers were dried ($MgSO_4$) and filtered, and the solvent was removed. The crude product underwent vacuum distillation at 100°C to recover 25.4 g 2-chloro-anisole (89% recovery rate). Elevating the temperature to 125°C allowed for the separation of homocoupling by-products, and further increasing the temperature to 140-150°C resulted in the attainment of the target product (16.2 g, 88%) with high purity (98.9%). The content of heavy metal Pd in the coupling product was detected using ICP-MS. The results showed that the palladium metal residue in the coupling product was 0.8 ppm.

(a)  (b) 

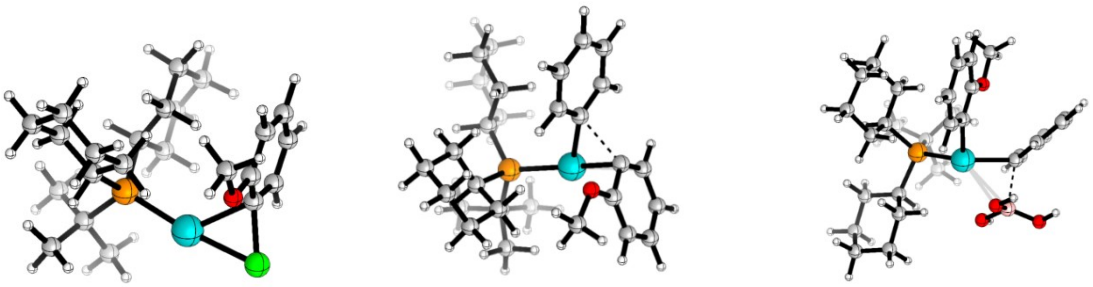
Figure S3. Reaction pictures of **3a:** a) before the reaction; b) after the reaction.

6. The Computational Calculations

6.1. Computational Details

Density functional theory (DFT) calculations were performed with Gaussian 16[1]. M06L functional[2] with a mixed basis set of SDD[3] for Pd and 6-31G(d) for other atoms was engaged in geometry optimizations. The energies were then refined by single-point calculations utilizing M06L functional and a mixed basis set of SDD for Pd and 6-311++G(d,p) for other atoms, in which the solvation effects were taken into consideration with the SMD model in the mixed solvent. The dielectric constant of mixed solvent was calculated based on the volume fractions of the mixed solvent according to an approach which has long been recognized[4]. Frequency calculations were also conducted at the same level of theory to obtain vibrational frequencies to determine the identity of stationary points as intermediates or transition states, as well as obtaining the thermal corrections to enthalpy ($H_{correction}$) and free energy ($G_{correction}$) at the temperature of 298 K. All DFT calculations were with an ultrafine integration grid. All structural figures were generated with CYLview[5]. Distances in structural figures are shown in Å and energies are in kcal/mol

6.2 The stereostructure of the transition state



TS^{OA} TS^{TM} TS^{RE}

Figure S4. The stereostructure of the transition state of SMC reactions in IPA/H_2O = 3:2.

6.3. Cartesian Coordinates and Energies of Calculated Structures

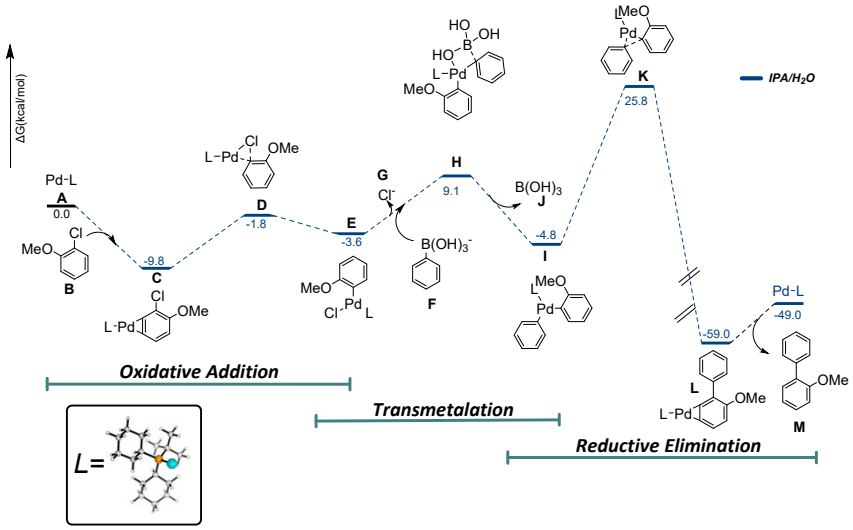


Figure S5 Calculated energy diagrams of SMC reactions in IPA/H_2O = 3:2.

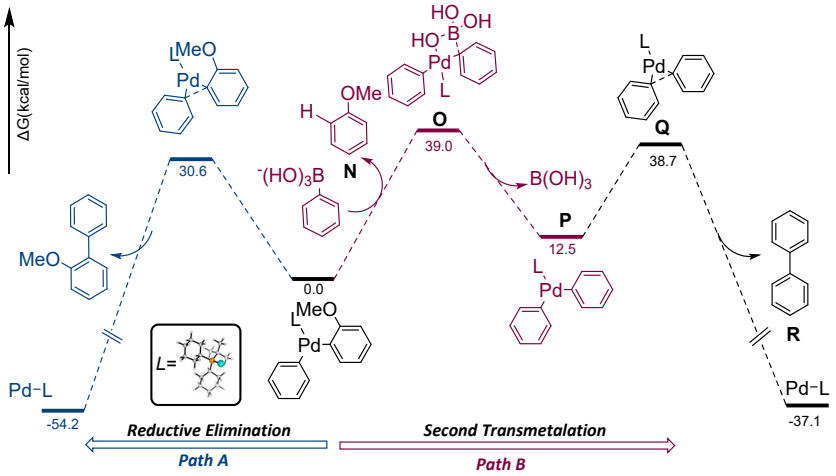


Figure S6 Calculated energy diagrams of SMC reactions in IPA/H_2O = 3:2.

Energies of Calculated Structures

(1) IPA/H_2O = 3:2

A (-1097.422333) B (-806.325611) C (-1903.763636) D (-1903.750797)

E (-1903.753619) F (-484.219512) G (-460.391774) H (-1927.561151)

I (-1675.066916) J (-252.533987) K (-1675.018109) L (-1675.153228)

M (-577.71537) N (-346.180777) O (-1813.03938) P (-1560.548084)

Q (-1560.506423) R (-463.205158)

(2) Tol/H_2O = 4:1

A (-1097.433437) B (-806.33195) C (-1903.78153) D (-1903.759889)

E (-1903.7654) F (-484.169526) G (-460.352272) H (-1927.561307)

I (-1675.086109) J (-252.516057) K (-1675.03799) L (-1675.175029)

M (-577.725947)

Cartesian Coordinates of Calculated Structures in IPA/H_2O (3:2)

A			
P	1.14357264	0.27545909	0.00000000
C	2.69018564	1.33036009	0.23912300
C	3.88186464	0.71851509	-0.50896000
C	5.18412364	1.42566709	-0.15230500
C	5.09652164	2.91991209	-0.43354900
C	3.88851064	3.53733709	0.25856400
C	2.59746164	2.81556109	-0.11944100
C	-0.27056736	1.48674209	0.22740900
C	-0.49532436	2.26544909	-1.07801600
C	-1.57713236	3.32785709	-0.92803100
C	-2.89546536	2.70535909	-0.49207100
C	-2.70751836	1.88459309	0.77490300
C	-1.60205236	0.84221609	0.62847000
H	2.90971364	1.28554709	1.31946600
H	3.96349164	-0.35788491	-0.31082200
H	3.68950764	0.81145909	-1.59144800
H	6.02149264	0.97723209	-0.70391100
H	5.39490264	1.26696109	0.91816300
H	6.01986464	3.42749109	-0.12362000
H	5.00430164	3.07513109	-1.52050900
H	3.80642064	4.60428709	0.01068200
H	4.02471564	3.47965509	1.35051200
H	1.74321764	3.29552609	0.37663800
H	2.43813164	2.92237509	-1.20410400
H	0.02096664	2.19401309	1.02358700
H	0.43217664	2.71941709	-1.44214400
H	-0.79812436	1.53692909	-1.85038600
H	-1.69973236	3.87312209	-1.87360900
H	-1.25417836	4.06963209	-0.17923800
H	-3.66191836	3.47756209	-0.34194700
H	-3.26464736	2.04916009	-1.29649700
H	-3.64610736	1.38997809	1.05922400
H	-2.44709236	2.55846309	1.60719400
H	-1.51337336	0.29200309	1.57010200
H	-1.88448536	0.10267909	-0.14113200
Pd	1.04584864	-0.89875491	-1.85174700
C	1.20179264	-0.76926591	1.59397900

C	0.18465064	-1.90856391	1.50010700
C	2.58178464	-1.42435991	1.69965700
C	0.96384364	0.06725009	2.85080400
H	-0.85149336	-1.56778591	1.41395400
H	0.39784564	-2.54267791	0.62824100
H	0.25289464	-2.53639691	2.40047500
H	3.38739664	-0.70203591	1.87831400
H	2.58013064	-2.12479191	2.54683700
H	2.82744664	-1.99837191	0.79510000
H	1.07707864	-0.56791091	3.74112100
H	1.68989264	0.88549909	2.94483900
H	-0.03921136	0.50619709	2.89091900

B			
C	-0.53022000	-0.63179500	-0.00001600
C	0.47493800	0.35001500	-0.00046200
C	-1.87537300	-0.29164400	0.00040900
C	0.08703700	1.69302400	-0.00056200
C	-2.24722500	1.05173900	0.00036400
H	-2.62411600	-1.07987300	0.00074400
C	-1.26361000	2.03512300	-0.00012000
H	0.84257300	2.47368200	-0.00093800
H	-3.30108600	1.31844000	0.00043100
H	-1.54131900	3.08691600	-0.00022800
O	1.76180800	-0.08076600	-0.00099300
C	2.77397600	0.92141400	0.00098600
H	3.72146800	0.38045900	0.00179100
H	2.71044900	1.55120000	-0.89488800
H	2.70818100	1.55011300	0.89744700
Cl	-0.06633800	-2.31776900	0.00000000

C			
Pd	-0.89315528	-0.25876460	0.00000000
C	0.89016572	-1.40687260	-2.74495000
C	1.10880672	-0.02079060	-2.74238100
C	1.30027072	0.66492840	-1.54455100
C	1.28332172	-0.06995360	-0.32014400

C	1.04397972	-1.46437960	-0.32660700
C	0.83611772	-2.12288060	-1.55953700
H	0.74810972	-1.91485260	-3.69686000
H	1.13030872	0.52359340	-3.68209800
H	1.18941372	-2.03400260	0.58873600
H	0.66417772	-3.19698560	-1.56122500
Cl	1.95622972	0.68936740	1.12768000
O	1.53400472	1.99689740	-1.44407200
C	1.43522372	2.75407940	-2.64675000
H	0.45623472	2.61331640	-3.12231000
H	1.55551872	3.79685940	-2.34902000
H	2.22792672	2.47774740	-3.35289400
P	-3.14309428	0.14997140	-0.26789600
C	-3.41018428	1.92058440	-0.80869500
C	-2.18906228	2.49399840	-1.54448900
C	-2.37559828	3.97641840	-1.84775100
C	-3.65918228	4.22715740	-2.62888300
C	-4.86544028	3.68489440	-1.87404200
C	-4.71052828	2.19819940	-1.56751700
C	-3.73525628	-0.91499460	-1.68799300
C	-2.96473428	-0.58415160	-2.97245000
C	-3.32385628	-1.51394860	-4.12628800
C	-3.12178528	-2.97448560	-3.75295300
C	-3.92502928	-3.31520460	-2.50690000
C	-3.55185528	-2.40028960	-1.34710300
H	-3.46129528	2.47196540	0.14334100
H	-1.28793428	2.33203440	-0.93196400
H	-2.01334028	1.95141340	-2.48615800
H	-1.50374728	4.35920740	-2.39651900
H	-2.41797428	4.53525440	-0.89879300
H	-3.78339528	5.29901740	-2.83326500
H	-3.59059728	3.72683540	-3.60877700
H	-5.78941128	3.85626340	-2.44260400
H	-4.97471028	4.23599240	-0.92567900
H	-5.57251528	1.84512740	-0.98548600
H	-4.72080728	1.63158440	-2.51169200
H	-4.80666928	-0.71496460	-1.85824600
H	-3.14490828	0.45504140	-3.27374000
H	-1.88255428	-0.66394160	-2.76050600
H	-2.72481528	-1.25071260	-5.00886700

H	-4.37794728	-1.35472460	-4.40562300
H	-3.39895228	-3.63113660	-4.58840700
H	-2.05172228	-3.15209160	-3.55231900
H	-3.76979328	-4.36290160	-2.21631900
H	-4.99984828	-3.20723460	-2.72548200
H	-4.13296028	-2.67345460	-0.45748300
H	-2.49039528	-2.56026560	-1.08284500
C	-4.40119528	-0.14030460	1.13313600
C	-3.83281928	-1.23363660	2.04319900
C	-4.53939328	1.13523840	1.96424800
C	-5.78541528	-0.56233160	0.64156900
H	-3.66638928	-2.17974860	1.51395700
H	-2.87360728	-0.92694760	2.48074900
H	-4.53472828	-1.43186960	2.86617900
H	-5.07984428	1.92517340	1.42779600
H	-5.10746528	0.91072540	2.87772800
H	-3.56407128	1.53547940	2.27378500
H	-6.45503128	-0.68004260	1.50565500
H	-6.23828828	0.18232840	-0.02357500
H	-5.77038628	-1.52169760	0.11125000

D			
Pd	0.72379363	-0.10815308	0.00000000
C	3.39051463	-0.18627408	-3.73973700
C	3.09990863	1.06242092	-3.18171800
C	2.78674963	1.17960892	-1.82850500
C	2.69700863	0.00021092	-1.05192300
C	3.05165563	-1.23913108	-1.59570800
C	3.37105963	-1.33226308	-2.94944800
H	3.64620963	-0.24979008	-4.79514000
H	3.12712763	1.95243892	-3.80515600
H	3.05034363	-2.11983208	-0.95794600
H	3.61213663	-2.30432208	-3.37450700
Cl	2.98398163	0.19202292	0.83460300
O	2.52330363	2.35320092	-1.19262700
C	2.49495663	3.52546292	-1.99942700
H	1.75741463	3.43311892	-2.80699800
H	2.20783463	4.33816892	-1.32994200
H	3.48302863	3.73262092	-2.42942700

P	-1.31583937	-0.23323008	-1.03092400
C	-1.96625537	1.43656492	-1.56143700
C	-0.83501837	2.40709192	-1.92950300
C	-1.37947537	3.79947792	-2.22791700
C	-2.45059137	3.75943392	-3.31020300
C	-3.58393537	2.82367392	-2.91245800
C	-3.06961337	1.41658192	-2.62319100
C	-1.22962437	-1.25504608	-2.59021600
C	-0.32282237	-0.59430208	-3.63416000
C	-0.19714537	-1.43619908	-4.89973100
C	0.28238463	-2.84821608	-4.59761800
C	-0.61366537	-3.51067508	-3.56161300
C	-0.70914437	-2.66746008	-2.29546000
H	-2.40794237	1.84188892	-0.63739100
H	-0.10979637	2.44284992	-1.10315100
H	-0.27571737	2.04164992	-2.80522600
H	-0.55755137	4.46919992	-2.51729200
H	-1.81587937	4.21967492	-1.30719200
H	-2.83619237	4.76833892	-3.50880300
H	-2.00139437	3.40413192	-4.25213200
H	-4.35231437	2.78746292	-3.69638400
H	-4.07665937	3.21787892	-2.00870000
H	-3.89964337	0.77589692	-2.29646400
H	-2.68573537	0.97544192	-3.55608700
H	-2.24889137	-1.33053608	-3.00604100
H	-0.69402837	0.40254792	-3.90066100
H	0.67438663	-0.44683308	-3.18559600
H	0.48269063	-0.93902508	-5.60581800
H	-1.18022737	-1.48516908	-5.39558700
H	0.32421363	-3.44753008	-5.51700600
H	1.31099963	-2.80175108	-4.20414300
H	-0.24395937	-4.51460908	-3.31349700
H	-1.62383337	-3.64453008	-3.98182500
H	-1.33998437	-3.17799608	-1.55724900
H	0.29266863	-2.57590408	-1.83718100
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C	-2.07717237	-1.99743908	0.98144000
C	-3.41537537	0.07534592	0.81360800
C	-3.76352637	-1.74791308	-0.84101300
H	-1.52406537	-2.79888008	0.47671400

H	-1.37458237	-1.48383308	1.65212900
H	-2.85804337	-2.46720708	1.59703800
H	-4.02814337	0.73648892	0.18832900
H	-4.08481137	-0.39714508	1.54569300
H	-2.70100637	0.69507392	1.37302600
H	-4.55009837	-2.13437708	-0.17713700
H	-4.24814537	-1.09311708	-1.57471800
H	-3.34527037	-2.60604208	-1.37992400

E			
Pd	-0.69282138	0.04173623	0.00000000
C	-5.06202638	-0.36057077	2.03111500
C	-4.61328538	0.91006023	1.66573100
C	-3.40970138	1.03931323	0.96791300
C	-2.63541438	-0.09540877	0.65877200
C	-3.11711538	-1.35695677	1.01968600
C	-4.32501838	-1.49771677	1.71059400
H	-6.00340838	-0.45372077	2.56975900
H	-5.20585438	1.78518623	1.92220000
H	-2.53567138	-2.24829677	0.77727100
H	-4.68126538	-2.48633477	1.99479900
Cl	0.15510562	0.63930523	-2.22086800
O	-2.90126238	2.24136523	0.55763800
C	-3.57401338	3.41631623	0.98684200
H	-3.60672538	3.47443723	2.08330400
H	-2.99438838	4.25368923	0.59225900
H	-4.59587338	3.46369523	0.58928000
P	1.10424062	0.92551123	1.31692900
C	1.45497662	2.70174823	0.89806000
C	0.19681262	3.46384423	0.46348400
C	0.56218662	4.82525123	-0.11636700
C	1.38869762	5.65032023	0.86111300
C	2.62238162	4.88304323	1.31754400
C	2.24674362	3.53168723	1.91877500
C	2.65694762	0.02956023	0.82229200
C	3.99661962	0.66642623	1.20981200
C	5.15464162	-0.10773577	0.58337500
C	5.11491362	-1.58651777	0.94224200
C	3.78081262	-2.20459577	0.54614200

C	2.62178562	-1.45513677	1.19212900
H	2.08786562	2.58781623	-0.00117800
H	-0.36115338	2.87142923	-0.27400700
H	-0.46843538	3.59751023	1.33103000
H	-0.35025338	5.36488023	-0.40440100
H	1.14019562	4.67158923	-1.04217000
H	1.67686562	6.60850423	0.40881400
H	0.77130062	5.89233423	1.74109900
H	3.19310962	5.46819323	2.05074800
H	3.29154662	4.71807223	0.45755700
H	3.14607462	3.00443023	2.25670500
H	1.62898162	3.69919523	2.81324100
H	2.58205262	0.09262723	-0.27895000
H	4.03646062	1.70938423	0.87178700
H	4.10681762	0.67828723	2.30462900
H	6.10714462	0.34241723	0.89279400
H	5.09958662	-0.00171177	-0.51174400
H	5.94531162	-2.11950777	0.46071900
H	5.25654962	-1.70120577	2.02897200
H	3.74368962	-3.26466177	0.82932100
H	3.67047362	-2.16620277	-0.54929600
H	1.65766162	-1.89728277	0.89710000
H	2.69922462	-1.55997477	2.28526200
C	0.66857462	0.70423323	3.13364100
C	-0.41544938	1.73171423	3.47161400
C	0.06200462	-0.68981877	3.32380000
C	1.86838262	0.85827623	4.06593500
H	-0.04919038	2.76373223	3.43699800
H	-1.27664238	1.65049123	2.79255900
H	-0.77712638	1.54260623	4.49152200
H	0.77617662	-1.49567177	3.12692600
H	-0.26924138	-0.78922677	4.36678400
H	-0.81367238	-0.84031977	2.67768400
H	1.52895362	0.73615423	5.10448000
H	2.62844862	0.09042723	3.87713800
H	2.34508562	1.84085223	3.98772600

F			
C	-0.42570952	-0.30884808	0.00000000
C	-1.18637152	0.86973292	0.00342700
C	-2.58223652	0.85801792	0.01049100
C	-3.26931552	-0.35470108	0.01479700
C	-2.54457952	-1.54678208	0.01197400
C	-1.15080652	-1.51260008	0.00482600
H	-0.66831652	1.83021192	-0.00175200
H	-3.13706252	1.79659592	0.01183100
H	-4.35857852	-0.37186308	0.01951900
H	-3.06967652	-2.50227208	0.01410800
H	-0.60264052	-2.45794908	-0.00073500
B	1.19367248	-0.32372008	0.00781700
O	1.64824448	-1.18077708	-1.13060400
H	2.61255548	-1.23535508	-1.07556700
O	1.63754748	-0.91391408	1.30997900
H	2.60481848	-0.88831708	1.31639500
O	1.69330048	1.07031192	-0.14066200
H	2.65885048	1.02652292	-0.15574800

G			
Cl	-1.84474127	1.27712853	0.00000000

H			
P	-0.64273791	0.94323872	0.00000000
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C	1.76252109	-1.14809028	-2.75119100
C	3.16555909	-0.76879428	-2.29437100
C	3.22538909	-0.61726328	-0.78064500
C	2.18246109	0.37182172	-0.26637500
C	-0.15046891	2.74229972	-0.08311000
C	0.14120009	3.15894072	-1.53105300
C	0.38590409	4.65674272	-1.67512400
C	-0.76504791	5.47027872	-1.10520000
C	-0.96818491	5.11933172	0.35984100
C	-1.23592791	3.63030272	0.53987600

H	0.58069209	-1.04972128	-0.35356700
H	-0.27358391	-0.41681528	-2.59883400
H	0.95388409	0.83927972	-2.71592600
H	1.71973209	-1.22447128	-3.84584900
H	1.50437909	-2.14412828	-2.35554300
H	3.89771209	-1.51318828	-2.63460500
H	3.44890009	0.18673472	-2.76452100
H	4.22787709	-0.30178328	-0.46170700
H	3.04181809	-1.59737828	-0.31104200
H	2.23597709	0.42279672	0.82766600
H	2.41286609	1.38226972	-0.64096400
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H	1.01569509	2.61390872	-1.90513100
H	-0.71050991	2.86750772	-2.16937900
H	0.55263209	4.89755072	-2.73348900
H	1.31298609	4.92561172	-1.14349400
H	-0.57903791	6.54560572	-1.22701200
H	-1.68831691	5.24205572	-1.66546100
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H	-0.06898491	5.40557472	0.92896500
H	-1.34860991	3.40934472	1.60770000
H	-2.19726891	3.38633872	0.06932800
Pd	-2.49807791	0.39409872	-1.47979900
C	-3.50809891	2.18401672	-1.95839200
C	-3.35848791	2.76316172	-3.22093400
C	-4.30712791	2.86760872	-1.02267400
C	-3.96252391	3.98393772	-3.55449900
H	-2.74162091	2.26112372	-3.97134000
C	-4.90867691	4.09104572	-1.32925900
C	-4.73197591	4.64296672	-2.60187300
O	-3.14236391	-1.20925828	-3.31163200
B	-3.18150991	-2.07898728	-2.17236100
H	-4.02800291	-1.08327628	-3.68398000
O	-4.00597591	-3.21952328	-2.17508800
H	-4.87663891	-3.00861328	-2.54018900
C	-6.43680791	-1.00941028	0.91601000
C	-5.21168391	-1.49101128	1.37702700
C	-4.09228991	-1.45537428	0.54551900
C	-4.16099791	-0.93914328	-0.75840300
C	-5.41323891	-0.47103328	-1.20361700

C	-6.53940291	-0.51260328	-0.38517100
H	-3.14447591	-1.84948828	0.91907900
H	-5.50689091	-0.05727628	-2.21051500
O	-1.87146591	-2.27696028	-1.66798000
H	-1.90223391	-2.82451128	-0.86991000
H	-5.51056991	4.62093172	-0.59378400
H	-5.20412991	5.59547272	-2.83764700
H	-3.82528891	4.41256372	-4.54659100
H	-7.49708191	-0.14769128	-0.75602900
H	-7.31073591	-1.02703928	1.56522900
H	-5.12753591	-1.89132228	2.38733000
C	-0.69188991	0.50967072	1.84901900
C	0.30590309	1.30091872	2.69662000
H	0.22084909	0.96695472	3.74053300
H	1.34569409	1.14742272	2.38940500
H	0.10505109	2.37841972	2.68566400
C	-0.40142691	-0.98493528	1.99719100
H	-0.63400491	-1.29871028	3.02386000
H	-1.00900591	-1.59872328	1.31719900
H	0.65421609	-1.21946228	1.81098500
C	-2.10336291	0.79257672	2.37430800
H	-2.86912491	0.25006772	1.80976800
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H	-2.35767691	1.85754072	2.34061900
O	-4.42480091	2.26667372	0.20868600
C	-5.16076391	2.95132772	1.20534900
H	-6.20586291	3.10519672	0.90262900
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I			
P	-1.26043408	0.30884808	0.00000000
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C	-5.43211608	0.78300908	0.04439700
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C	-4.59643608	1.77693808	2.19162600
C	-3.24090008	1.10963008	1.97327700
C	-0.10831808	0.83923508	1.36889200

C	-0.25209808	-0.13170892	2.55193800
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C	2.07124392	0.37738208	3.34324300
C	2.24341492	1.31635608	2.15899200
C	1.37306292	0.90637508	0.97397100
H	-2.99330008	1.97512408	0.03993900
H	-3.88982508	-0.07859492	-1.21467600
H	-4.07854608	-0.85907392	0.34789800
H	-6.21766208	0.17036308	-0.41856500
H	-5.44275808	1.75428908	-0.47688100
H	-6.68223408	1.50328608	1.66699700
H	-5.80937908	0.00875408	2.01215400
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H	-1.29719608	-0.24352392	2.85864000
H	0.07042692	-1.12607492	2.20551400
H	0.46758092	-0.42736892	4.56325500
H	0.26192292	1.26527508	4.11168000
H	2.68680992	0.70609308	4.19112700
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H	3.29437892	1.35538208	1.84320200
H	1.97092992	2.33943308	2.46466100
H	1.53799992	1.61119808	0.15288400
H	1.69360692	-0.08414192	0.60939700
Pd	-1.07684208	-2.03032592	-0.37453900
C	-2.48107608	-2.97744292	0.88239900
C	-3.71556508	-3.34752692	0.31833700
C	-2.32672908	-3.15372792	2.25870600
C	-4.75908108	-3.85183992	1.09703000
C	-3.35489408	-3.66965592	3.05854900
H	-1.38399008	-2.87167092	2.73449000
C	-4.56936308	-4.01011192	2.47272400
H	-5.71358708	-4.12312392	0.65078100
H	-3.20526408	-3.79583392	4.13010700
C	0.93835992	-2.61119492	-0.19351000
C	1.43246592	-3.10037492	1.02583000
C	1.84429292	-2.47691392	-1.25837200

C	2.78100592	-3.42847492	1.18388800
H	0.75910692	-3.22677692	1.87727800
C	3.19423992	-2.80577992	-1.10521400
H	1.50634992	-2.10186792	-2.22635900
C	3.66852192	-3.27500492	0.11895600
H	-5.38302508	-4.40375192	3.07972400
O	-3.82969108	-3.14668392	-1.04524600
C	-5.12300108	-3.29558692	-1.61056400
H	-5.03078508	-2.99866892	-2.65737000
H	-5.47087308	-4.33583692	-1.55852800
H	-5.85417008	-2.64699092	-1.10809600
H	3.13869992	-3.80220192	2.14364000
H	4.72150192	-3.52357592	0.24129500
H	3.87740092	-2.69010092	-1.94700900
C	-0.85812808	1.33255908	-1.54061900
C	0.34450392	0.70915608	-2.25226300
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H	-1.75558908	1.75554508	-3.44763600
H	-2.30278808	0.21866508	-2.75618100
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K			
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C	-3.02718742	3.60599800	1.31873900
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C	-2.95057442	1.81279500	-1.00655500
H	-0.87358442	-1.35679800	1.60339300
H	1.57940658	-1.24534700	0.91352400
H	1.74009558	0.20506800	1.88639900
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H	0.91330458	-2.55722500	2.93405600
H	1.07167958	-1.51552200	5.18675000
H	1.51609658	0.02897300	4.45849800
H	-0.89710242	0.03375800	5.03526000
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H	-2.72544342	4.53081000	1.82920000
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H	-4.76082042	4.46967100	0.33731500
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H	-4.86997542	2.03276200	-0.06678900
H	-3.26605842	0.91190200	-1.54179200
H	-2.29412842	2.37343300	-1.69338800
Pd	1.29770258	1.54289400	-0.64448600
C	3.31124458	2.43950500	-0.45382100
C	4.04858258	1.35948100	0.09490900

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C	3.79894058	1.60578300	-2.69582000
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C	4.53833958	0.56579500	-2.14525300
H	5.24076758	-0.38603400	-0.33819500
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C	1.63955458	3.28393200	0.60747300
C	1.79386158	3.24988600	2.01801700
C	1.42552858	4.56224700	0.02536100
C	1.78593358	4.41237400	2.78176600
H	1.91302358	2.29059600	2.52589700
C	1.41248558	5.72327500	0.78905000
H	1.26487858	4.64144800	-1.05243200
C	1.59585658	5.65817100	2.17483600
H	5.02914958	-0.16073500	-2.78935300
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C	4.69490158	0.14842100	2.03166300
H	4.53930358	0.23970400	3.10931100
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C	-2.44263942	-1.63774700	-0.71676800
H	-1.84882142	0.21396100	-2.78710900
H	-0.12077042	-0.16915300	-2.85549200
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H	-0.21878742	-2.88744900	-1.72169300
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H	2.47980291	-0.63659489	4.00189600
H	0.29598191	-0.04808589	5.03134600
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H	-3.77950309	3.74358611	-1.00059800
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Pd	1.58497791	0.92165811	-1.04752400
C	3.77460391	1.64319311	-0.52993300
C	4.41561091	0.45697411	-0.06199000
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C	3.83199791	0.67515711	-2.80090700
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C	4.45853091	-0.46183089	-2.30618800
H	5.26682891	-1.45405589	-0.57616700
H	3.61506791	0.77545811	-3.86201800
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H	4.12764391	4.25433011	-1.13714800
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M

C	0.22537563	-0.27545909	0.00000000
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C	-2.07843637	-0.86601109	-0.74166700
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H	-1.17151237	1.74898291	1.22565200
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H	-4.09195737	-1.34559609	-1.32120000
H	-3.60998537	2.10873791	1.19403700
H	-5.09088037	0.56877491	-0.08081600

N			
C	-0.39612673	-0.84507041	0.00000000
C	-1.79689973	-0.65342141	-0.00001000
C	-2.11770973	0.71118659	-0.00008400
C	-1.20942873	1.78030459	-0.00014600
C	0.15568127	1.50228959	-0.00000500
C	0.57221427	0.17061759	0.00004300
H	-0.00231373	-1.87420641	-0.00009000
H	-1.56742073	2.81299659	-0.00021800
H	0.87961327	2.31784659	0.00003000
H	1.63894827	-0.06711641	0.00018900
O	-3.45373673	1.16182259	0.00026300

C	-4.45156573	0.16224859	-0.00010900
H	-4.38979673	-0.48697441	0.88483000
H	-5.40906473	0.69418559	-0.00027800
H	-4.38914473	-0.48680841	-0.88504100

O			
P	1.24119710	-0.33450704	0.00000000
C	2.13435010	-1.83517104	-0.65375400
C	1.86614110	-2.05828704	-2.14851200
C	2.41213510	-3.40910304	-2.59494800
C	3.90014410	-3.52879804	-2.29097200
C	4.17824510	-3.29249004	-0.81190600
C	3.62804310	-1.94856004	-0.34075600
C	2.40523010	1.10263496	-0.24141600
C	2.76026510	1.27919096	-1.72351900
C	3.67558410	2.47690696	-1.95348900
C	3.07366710	3.75875296	-1.39847000
C	2.75496410	3.59447996	0.07968000
C	1.82566010	2.40969996	0.31723800
H	1.62032210	-2.66355804	-0.13919500
H	0.78831210	-1.99311104	-2.34255200
H	2.33971210	-1.26661704	-2.74703400
H	2.22287510	-3.55670804	-3.66672300
H	1.86586010	-4.20812404	-2.06687100
H	4.28059010	-4.51171304	-2.59956900
H	4.44907010	-2.78032804	-2.88534900
H	5.25569810	-3.34961004	-0.60651200
H	3.70462210	-4.09481804	-0.22298600
H	3.80984910	-1.82791804	0.73522700
H	4.17356810	-1.13362204	-0.84311400
H	3.33395510	0.86738196	0.30825100
H	3.24484310	0.37553596	-2.11125900
H	1.83034010	1.41143296	-2.30219000
H	3.88854910	2.57690396	-3.02617500
H	4.64251510	2.28838196	-1.45930200
H	3.75226210	4.60716196	-1.55878800
H	2.14356110	3.98982096	-1.94419800
H	2.29580310	4.50716396	0.48314100
H	3.69207610	3.44043996	0.63919400

H	1.61900710	2.31918896	1.39025900
H	0.85879410	2.60704196	-0.17065300
Pd	-1.07572390	-0.32493204	-0.79843900
C	-1.32181090	1.73619996	-1.32621500
C	-0.82647490	2.27063296	-2.51972100
C	-1.90879490	2.60509096	-0.39839600
C	-0.88997890	3.64542396	-2.77154000
H	-0.36257090	1.61715696	-3.26377400
C	-1.96875090	3.98034296	-0.64169600
H	-2.31858890	2.21295196	0.53790600
C	-1.45149290	4.50459796	-1.82703900
O	-1.49632290	-1.30504804	-2.93863900
B	-2.26735290	-2.25428504	-2.18100500
H	-2.07676790	-0.66595204	-3.38361300
O	-3.43741390	-2.81054804	-2.70999400
H	-3.93772690	-2.15788304	-3.21937000
C	-5.54065490	-0.42481804	0.72510900
C	-4.58172590	-1.28021304	1.26424600
C	-3.41309790	-1.55869604	0.54916700
C	-3.16498690	-0.97253404	-0.70549600
C	-4.15159190	-0.11544104	-1.22728800
C	-5.32684690	0.15203996	-0.53055200
H	-2.68414290	-2.25392304	0.97470900
H	-3.99167690	0.35705696	-2.20083400
O	-1.43152290	-3.12414904	-1.46080200
H	-1.96993690	-3.78824104	-1.00664600
H	-2.42043890	4.64375996	0.09653900
H	-1.49303890	5.57598196	-2.01663800
H	-0.49187990	4.04572796	-3.70472800
H	-6.07708290	0.81689896	-0.95869200
H	-6.45499690	-0.21064004	1.27616100
H	-4.74854990	-1.74215504	2.23739500
C	1.11547510	-0.57949804	1.88203700
C	2.37022610	-0.16859404	2.65075000
H	2.21949210	-0.37106504	3.72081400
H	3.25700810	-0.72957904	2.33410900
H	2.59452410	0.89993396	2.55284700
C	0.81280710	-2.05133104	2.16614600
H	0.52796110	-2.16453904	3.22122600
H	-0.02410790	-2.42336704	1.55584500

H	1.68098910	-2.69797004	1.98839800
C	-0.07869490	0.24544296	2.38031100
H	-1.02201990	-0.10500904	1.93440400
H	-0.16717690	0.13989196	3.47109100
H	0.01485410	1.31480596	2.15679100

P			
P	-1.92781678	0.00000000	0.00000000
C	-0.13212778	-0.39447500	0.38304000
C	0.82366322	0.58225100	-0.31694000
C	2.26536122	0.10045800	-0.20974500
C	2.67347622	-0.06447500	1.24822500
C	1.70574222	-0.98016000	1.98624100
C	0.26437522	-0.49320000	1.85854300
C	-2.91066678	-0.65626400	1.44535300
C	-2.82700878	0.34476800	2.60918400
C	-3.55482378	-0.16013700	3.84860700
C	-5.01609578	-0.45032500	3.54122800
C	-5.12915178	-1.42677600	2.38062100
C	-4.39020478	-0.92816700	1.14178300
H	0.02236922	-1.39678800	-0.05402200
H	0.54445422	0.73881400	-1.36665900
H	0.73302922	1.56360900	0.17232400
H	2.93513422	0.80465200	-0.72106100
H	2.36596022	-0.86504200	-0.73228000
H	3.70004322	-0.44678100	1.32460000
H	2.66990922	0.92614100	1.73257600
H	1.97845322	-1.05536400	3.04730200
H	1.77805322	-1.99823300	1.57128900
H	-0.40693378	-1.16344900	2.41142800
H	0.18462522	0.50204600	2.32472100
H	-2.43938878	-1.60792200	1.74940700
H	-1.78875778	0.58770000	2.85648700
H	-3.28992678	1.28685500	2.27412300
H	-3.46508178	0.57866700	4.65619700
H	-3.06475178	-1.07946100	4.20877200
H	-5.53255178	-0.84089300	4.42813400
H	-5.52069978	0.49225400	3.27079300
H	-6.18181178	-1.61047500	2.12774200

H	-4.70614378	-2.39875600	2.68186700
H	-4.50549478	-1.66552800	0.34115600
H	-4.86133978	0.00278300	0.78428100
Pd	-2.48567678	2.26677900	-0.46439600
C	-1.03526478	3.49769700	0.42000700
C	-0.22012278	4.29882900	-0.39651900
C	-0.73462078	3.43473500	1.78957500
C	0.87115522	4.99263300	0.13385000
C	0.35346622	4.12820400	2.32324100
H	-1.34506378	2.81959100	2.45519500
C	1.16436622	4.90446700	1.49420900
H	1.49557222	5.60157100	-0.52034400
H	0.57264522	4.05745900	3.38895800
C	-4.53604378	2.57194000	-0.11722100
C	-4.98563878	3.03092900	1.13088700
C	-5.50172878	2.27044100	-1.09128500
C	-6.34852878	3.16717400	1.40458700
H	-4.26500678	3.28326300	1.91244000
C	-6.86642178	2.40669700	-0.82111300
H	-5.19854278	1.91114800	-2.07670600
C	-7.29421578	2.84801300	0.43023400
H	2.01783922	5.43979200	1.90716700
H	-6.67137578	3.52124200	2.38395700
H	-8.35731378	2.94688700	0.64364500
H	-7.59680678	2.16290100	-1.59296000
C	-2.26630078	-1.11289200	-1.49446000
C	-3.58279278	-0.67967400	-2.14323700
C	-1.16507678	-0.89524500	-2.53532300
C	-2.28908678	-2.59201200	-1.11158700
H	-4.44701578	-0.74236200	-1.47428200
H	-3.51050878	0.35909400	-2.49480600
H	-3.78767678	-1.31676300	-3.01514400
H	-0.18500378	-1.25703900	-2.20243900
H	-1.42672678	-1.45481200	-3.44392700
H	-1.06931278	0.16245600	-2.81512200
H	-2.43037478	-3.19854800	-2.01718400
H	-1.34308178	-2.90900000	-0.65340600
H	-3.09839178	-2.84540400	-0.41860800
H	-0.42036578	4.37752700	-1.46710900

Q			
P	-0.64260559	-0.61619717	0.00000000
C	-0.86125859	-1.05750717	1.81110100
C	0.42065141	-1.68911917	2.37561900
C	0.20596541	-2.20703917	3.79276500
C	-0.27845959	-1.09813117	4.71680500
C	-1.52448159	-0.42773717	4.15428800
C	-1.28995959	0.08504583	2.73642300
C	-1.87402959	0.75418083	-0.31840400
C	-1.28545159	2.09895483	0.13758300
C	-2.30517259	3.22484883	0.02640900
C	-2.79895259	3.36750683	-1.40613300
C	-3.33034659	2.04065683	-1.92752700
C	-2.31450059	0.91032183	-1.77925800
H	-1.66321659	-1.81601417	1.83977400
H	0.79317441	-2.49178417	1.72802300
H	1.20829441	-0.91765517	2.37774300
H	1.13505641	-2.65110017	4.17452800
H	-0.54123959	-3.01728417	3.76940300
H	-0.47123659	-1.48888517	5.72482400
H	0.51883541	-0.34375617	4.81984600
H	-1.84263859	0.40094383	4.80087200
H	-2.35469059	-1.15206617	4.14176600
H	-2.19529259	0.58300883	2.36481900
H	-0.49314259	0.84651583	2.76265000
H	-2.77026759	0.52636183	0.28498900
H	-0.88180759	2.04752383	1.15502900
H	-0.42414059	2.32355483	-0.51207000
H	-1.86000759	4.16527483	0.37852700
H	-3.15690659	3.01184583	0.69291800
H	-3.56965859	4.14645583	-1.47886900
H	-1.96056059	3.69540883	-2.04128700
H	-3.62960759	2.13025283	-2.98033000
H	-4.24002759	1.76931883	-1.36790300
H	-2.75735359	-0.01065517	-2.16977900
H	-1.42744859	1.12113683	-2.40033600
Pd	1.58064141	-0.12945717	-0.44161000
C	3.71429141	0.38175283	-0.21198700
C	4.19045741	-0.65178717	0.61993200

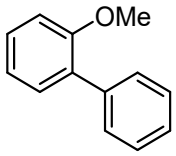
C	3.68006341	0.22050183	-1.61345900
C	4.66753341	-1.82503017	0.04133600
C	4.15927841	-0.98025417	-2.16984200
H	3.38886641	1.04365083	-2.26690000
C	4.66667741	-1.98867017	-1.35208600
H	5.05672941	-2.61765917	0.68035500
H	4.16977141	-1.09519117	-3.25354800
C	2.18888141	1.68409983	0.57612700
C	2.37182941	1.78236383	1.97863500
C	2.26613141	2.89443783	-0.16197100
C	2.67368141	2.99451283	2.59165300
H	2.28752141	0.88692283	2.60005800
C	2.56593441	4.10566683	0.45135000
H	2.09393841	2.87699283	-1.24099400
C	2.77475141	4.16531883	1.83375900
H	5.05405041	-2.90473417	-1.79274100
H	2.81451841	3.03446383	3.67236500
H	2.99959041	5.11505383	2.31598700
H	2.62142641	5.01665883	-0.14542100
C	-1.29815559	-2.17556817	-0.86638600
C	-0.92736759	-2.12018117	-2.35001000
C	-0.58481559	-3.39599217	-0.28016500
C	-2.80298459	-2.35673417	-0.67284400
H	-1.37280759	-1.27694617	-2.88605100
H	0.16377341	-2.05288917	-2.47125600
H	-1.26348459	-3.04246917	-2.84440900
H	-0.86065559	-3.58893417	0.76354200
H	-0.86784259	-4.28401617	-0.86218200
H	0.50875741	-3.29561817	-0.33992600
H	-3.12142159	-3.29586217	-1.14714400
H	-3.07080959	-2.42465417	0.38952800
H	-3.39739159	-1.55053517	-1.11579500
H	4.21234641	-0.52070617	1.70249300

R			
C	-0.73830600	-0.00000100	0.00000000
C	-1.46092400	-1.16033000	-0.31958400
C	-2.85203000	-1.16045100	-0.31960600
C	-3.55498800	0.00000100	0.00000000

C	-2.85202800	1.16045200	0.31960600
C	-1.46092200	1.16032900	0.31958400
C	0.73830600	-0.00000100	0.00000000
C	1.46092400	-1.16033000	0.31958400
C	2.85203000	-1.16045100	0.31960600
C	3.55498800	0.00000100	0.00000000
C	2.85202800	1.16045200	-0.31960600
C	1.46092200	1.16032900	-0.31958400
H	-0.92476200	-2.06739500	-0.59527200
H	-3.38999500	-2.07065000	-0.57874600
H	-4.64328900	0.00000200	-0.00000100
H	-3.38999200	2.07065200	0.57874600
H	-0.92475900	2.06739200	0.59527400
H	0.92476200	-2.06739500	0.59527200
H	3.38999500	-2.07065000	0.57874700
H	4.64328900	0.00000200	0.00000100
H	3.38999200	2.07065200	-0.57874800
H	0.92475900	2.06739300	-0.59527300

7. Characterization data for coupling products

2-methoxy-1,1'-biphenyl (compound 3a)[6]



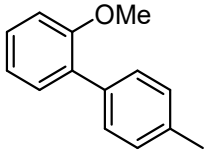
Prepared from phenylboronic acid (1.22 g, 10.0 mmol) and 1-chloro-2-methoxybenzene (4.26 g, 30.0 mmol 3.0 equiv.) according to **GP1**. The title compound 2-methoxy-1,1'-biphenyl (3a, 1.65 g, 90%) was obtained as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.56 (m, 4H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.38 – 7.32 (m, 1H), 7.05 – 6.99 (m, 2H), 3.89 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.19, 140.86, 133.82, 128.75, 128.18, 126.77, 126.68, 114.24, 55.37.

HRMS (EI) for $C_{13}H_{12}O^+$ [M^+]: calculated 184.0888, found 184.0886.

2-methoxy-4'-methyl-1,1'-biphenyl (compound 3b)[7]



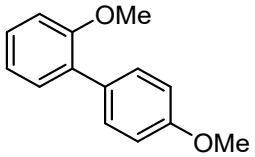
Prepared from p-tolylboronic acid (1.36 g, 10.0 mmol) and 1-chloro-2-methoxybenzene (4.26 g, 30.0 mmol 3.0 equiv.) according to **GP1**. The title compound 2-methoxy-4'-methyl-1,1'-biphenyl (3b, 1.74 g, 88%) was obtained as a light yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.1 Hz, 2H), 7.35 (t, *J* = 7.3 Hz, 2H), 7.26 (d, *J* = 7.3 Hz, 2H), 7.12 – 6.98 (m, 2H), 3.85 (s, 3H), 2.44 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.54, 136.62, 135.63, 130.83, 130.74, 129.43, 128.77, 128.40, 120.83, 111.22, 55.56, 21.24.

HRMS (EI) for $C_{14}H_{14}O^+$ [M^+]: calculated 198.1045, found 198.1044.

2,4'-dimethoxy-1,1'-biphenyl (compound 3c)[7]



Prepared from (4-methoxyphenyl)boronic acid (1.52 g, 10.0 mmol) and 1-chloro-2-methoxybenzene (4.26 g, 30.0 mmol 3.0 equiv.) according to **GP1**. The title compound 2,4'-dimethoxy-1,1'-biphenyl (3c, 1.95 g, 91%) was obtained as a white solid.

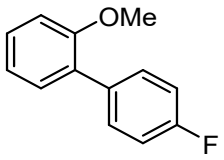
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.6 Hz, 2H),7.36-7.31 (m, 2H), 7.08 –

7.01 (m, 2H), 7.00 (d, *J* = 8.6 Hz, 2H), 3.88 (s, 3H), 3.85 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.68, 156.49, 130.94, 130.71, 130.62, 130.38, 128.19, 120.85, 113.52, 111.24, 55.57, 55.29.

HRMS (EI) for $C_{14}H_{14}O_2^+$ [M^+]: calculated 214.0994, found 214.0992.

4'-fluoro-2-methoxy-1,1'-biphenyl (compound 3d)[8]



Prepared from (4-fluorophenyl)boronic acid (1.40 g, 10.0 mmol) and 1-chloro-2-methoxybenzene (4.26 g, 30.0 mmol 3.0 equiv.) according to **GP1**. The title compound 4'-fluoro-2-methoxy-1,1'-biphenyl (3d, 1.79 g, 89%) was obtained as a white solid.

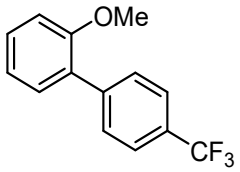
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.50 (m, 2H), 7.39 – 7.31 (m, 2H), 7.16 – 7.00 (m, 4H), 3.85 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.01 (d, *J* = 245.7 Hz), 156.38, 134.43 (d, *J* = 3.3 Hz), 131.12 (d, *J* = 8.0 Hz), 130.78, 129.67, 128.75, 120.89, 114.88 (d, *J* = 21.2 Hz), 111.24, 55.56.

^{19}F NMR (376 MHz, $CDCl_3$) δ -115.94 (m).

HRMS (EI) for $C_{13}H_{11}FO^+$ [M^+]: calculated 202.0794, found 202.0794.

2-methoxy-4'-(trifluoromethyl)-1,1'-biphenyl (compound 3e)[9]



Prepared from (4-(trifluoromethyl)phenyl)boronic acid (1.90 g, 10.0 mmol) and 1-chloro-2-methoxybenzene (4.26 g, 30.0 mmol 3.0 equiv.) according to **GP1**. The title compound 2-methoxy-4'-(trifluoromethyl)-1,1'-biphenyl (3e, 1.42 g, 56%) was obtained as a light yellow oil.

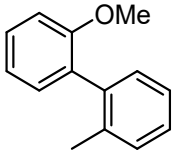
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74–7.66 (m, 4H), 7.41 (t, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.13 – 7.02 (m, 2H), 3.86 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.42, 142.24, 130.79, 129.85, 129.50, 129.22, 128.9 (q, *J* = 32.6 Hz), 124.91 (q, *J* = 3.8 Hz) , 124.4 (q, *J* = 272.2 Hz) , 121.00, 111.31, 55.56.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.38.

HRMS (EI) for $C_{14}H_{11}F_3O^+$ [M^+]: calculated 252.0762, found 252.0758.

2-methoxy-2'-methyl-1,1'-biphenyl (compound 3f)[6]



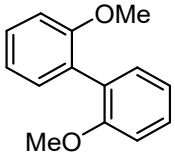
Prepared from o-tolylboronic acid (1.36 g, 10.0 mmol) and 1-chloro-2-methoxybenzene (4.26 g, 30.0 mmol 3.0 equiv.) according to **GP1**. The title compound 2-methoxy-2'-methyl-1,1'-biphenyl (3f, 1.72 g, 87%) was obtained as a light yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.37 (m, 1H), 7.31 – 7.20 (m, 4H), 7.18 (dd, *J* = 7.4, 1.8 Hz, 1H), 7.04 (td, *J* = 7.4, 1.1 Hz, 1H), 6.99 (dd, *J* = 8.3, 1.1 Hz, 1H), 3.79 (s, 3H), 2.17 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.65, 138.68, 136.86, 131.05, 130.91, 130.04, 129.61, 128.59, 127.33, 125.48, 120.48, 110.70, 55.43, 19.96.

HRMS (EI) for $C_{14}H_{14}O^+$ [M^+]: calculated 198.1045, found 198.1043.

2,2'-dimethoxy-1,1'-biphenyl (compound 3g)[7]



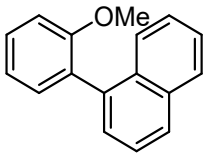
Prepared from (2-methoxyphenyl)boronic acid (1.52 g, 10.0 mmol) and 1-chloro-2-methoxybenzene (4.26 g, 30.0 mmol 3.0 equiv.) according to **GP1**. The title compound 2,2'-dimethoxy-1,1'-biphenyl (3 g, 1.82 g, 85%) was obtained as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (t, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 6.7 Hz, 2H), 7.10 – 6.95 (m, 4H), 3.81 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.05, 131.49, 128.64, 127.82, 120.37, 111.11, 55.72.

HRMS (EI) for $C_{14}H_{14}O_2^+$ [M^+]: calculated 214.0994, found 214.0994.

1-(2-methoxyphenyl)naphthalene (compound 3h)[7]



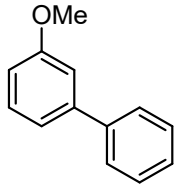
Prepared from naphthalen-1-ylboronic acid (1.72 g, 10.0 mmol) and 1-chloro-2-methoxybenzene (4.26 g, 30.0 mmol 3.0 equiv.) according to **GP1**. The title compound 1-(2-methoxyphenyl)naphthalene (3h, 1.78 g, 76%) was obtained as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (t, *J* = 9.2 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.58 (td, *J* = 7.6, 2.0 Hz, 1H), 7.55 – 7.40 (m, 4H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.20 – 7.06 (m, 2H), 3.74 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.28, 137.02, 133.50, 132.19, 131.99, 129.58, 129.04, 128.17, 127.70, 127.34, 126.48, 125.69, 125.60, 125.41, 120.60, 111.02, 55.59.

HRMS (EI) for $C_{17}H_{14}O^+$ [M^+]: calculated 234.1045, found 234.1043.

3-methoxy-1,1'-biphenyl (compound 3i) [10]



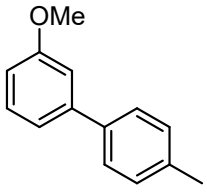
Prepared from phenylboronic acid (1.22 g, 10.0 mmol) and 1-chloro-3-methoxybenzene (4.26 g, 30.0 mmol 3.0 equiv.) according to **GP1**. The title compound 2-methoxy-1,1'-biphenyl (3i, 1.67 g, 91%) was obtained as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.60 (m, 2H), 7.51 – 7.46 (m, 2H), 7.43 – 7.37 (m, 2H), 7.23 (ddd, *J* = 7.6, 1.7, 1.0 Hz, 1H), 7.18 (dd, *J* = 2.5, 1.6 Hz, 1H), 6.95 (ddd, *J* = 8.2, 2.6, 0.9 Hz, 1H), 3.91 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.97, 142.81, 141.14, 129.79, 128.77, 127.45, 127.24, 119.72, 112.93, 55.33.

HRMS (EI) for $C_{13}H_{12}O^+$ [M^+]: calculated 184.0888, found 184.0885.

3-methoxy-4'-methyl-1,1'-biphenyl (compound 3j)[11]



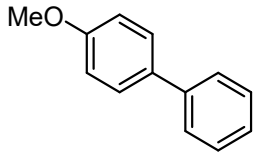
Prepared from phenylboronic acid (1.22 g, 10.0 mmol) and 1-chloro-3-methoxybenzene (4.26 g, 30.0 mmol 3.0 equiv.) according to **GP1**. The title compound 2-methoxy-1,1'-biphenyl (3j, 1.61 g, 88%) was obtained as a light yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.51 (m, 2H), 7.38 (t, *J* = 7.9 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 2H), 7.24 – 7.18 (m, 1H), 7.20 – 7.11 (m, 1H), 6.92 (ddd, *J* = 8.2, 2.6, 1.0 Hz, 1H), 3.90 (s, 3H), 2.44 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.94, 142.73, 138.24, 137.25, 129.73, 129.48, 127.06, 119.54, 112.74, 112.40, 55.31, 21.14.

HRMS (EI) for $C_{14}H_{14}O^+$ [M^+]: calculated 198.1045, found 198.1040.

4-methoxy-1,1'-biphenyl (compound 3k)[6]



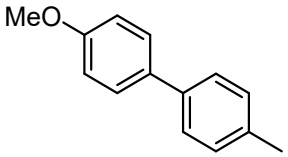
Prepared from phenylboronic acid (1.22 g, 10.0 mmol) and 1-chloro-4-methoxybenzene (4.26 g, 30.0 mmol 3.0 equiv.) according to **GP1**. The title compound 4-methoxy-1,1'-biphenyl (3k, 1.66 g, 90%) was obtained as a light yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.54 (m, 4H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 8.7 Hz, 2H), 3.88 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.15, 140.84, 133.79, 128.74, 128.18, 126.76, 126.67, 114.21, 55.37.

HRMS (EI) for $C_{13}H_{12}O^+$ [M^+]: calculated 184.0888, found 184.0881.

4-methoxy-4'-methyl-1,1'-biphenyl (compound 3l)[11]



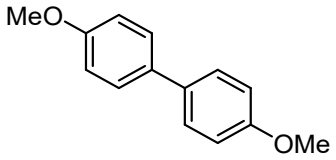
Prepared from p-tolylboronic acid (1.36 g, 10.0 mmol) and 1-chloro-4-methoxybenzene (4.26 g, 30.0 mmol 3.0 equiv.) according to **GP1**. The title compound 4-methoxy-4'-methyl-1,1'-biphenyl (3l, 1.72 g, 87%) was obtained as a light yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 24.4, 8.5 Hz, 4H), 7.26 (d, *J* = 7.9 Hz, 2H), 7.00 (d, *J* = 8.7 Hz, 2H), 3.88 (s, 3H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.95, 137.99, 136.36, 133.77, 129.45, 127.97, 126.60, 114.17, 55.36, 21.06.

HRMS (EI) for $C_{14}H_{14}O^+$ [M^+]: calculated 198.1045, found 198.1043.

4,4'-dimethoxy-1,1'-biphenyl (compound 3m)[10]



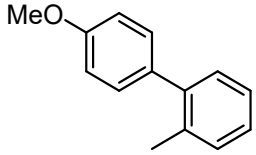
Prepared from (4-methoxyphenyl)boronic acid (1.52 g, 10.0 mmol) and 1-chloro-4-methoxybenzene (4.26 g, 30.0 mmol 3.0 equiv..) according to **GP1**. The title compound 4,4'-dimethoxy-1,1'-biphenyl (3m, 1.75 g, 82%) was obtained as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.2 Hz, 4H), 6.99 (d, *J* = 8.2 Hz, 4H), 3.87 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.70, 133.50, 127.75, 114.18, 55.37.

HRMS (EI) for $C_{14}H_{14}O_2^+$ [M^+]: calculated 214.0994, found 214.0992.

4'-methoxy-2-methyl-1,1'-biphenyl (compound 3n)[12]



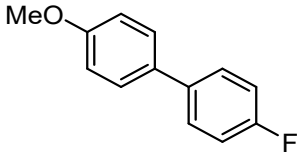
Prepared from o-tolylboronic acid (1.36 g, 10.0 mmol) and 1-chloro-4-methoxybenzene (4.26 g, 30.0 mmol 3.0 equiv..) according to **GP1**. The title compound 4'-methoxy-2-methyl-1,1'-biphenyl (3n, 1.68 g, 85%) was obtained as a light yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.22 (m, 6H), 7.04-6.97 (m, 2H), 3.89 (s, 3H), 2.32 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.53, 141.58, 135.52, 134.40, 130.33, 130.28, 129.94, 127.01, 125.79, 113.51, 55.31, 20.59.

HRMS (EI) for $C_{14}H_{14}O^+$ [M^+]: calculated 198.1045, found 198.1038.

4-fluoro-4'-methoxy-1,1'-biphenyl (compound 3o)[13]



Prepared from (4-fluorophenyl)boronic acid (1.40 g, 10.0 mmol) and 1-chloro-4-methoxybenzene (4.26 g, 30.0 mmol 3.0 equiv.) according to **GP1**. The title compound 4-fluoro-4'-methoxy-1,1'-biphenyl (3o, 1.66 g, 82%) was obtained as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.48 (m, 4H), 7.13 (t, *J* = 8.7 Hz, 2H), 7.00 (d, *J* = 8.7 Hz, 2H), 3.88 (s, 3H).

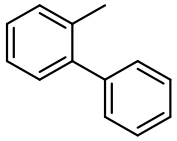
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.12 (d, *J* = 245.5 Hz), 159.13, 136.99 (d, *J* = 3.2

Hz), 132.86, 128.23 (d, J = 8.0 Hz), 128.05, 115.54 (d, J = 21.3 Hz), 114.27, 55.37

^{19}F NMR (376 MHz, $CDCl_3$) δ -116.74.

HRMS (EI) for $C_{13}H_{11}FO^+$ [M^+]: calculated 202.0783, found 202.0789.

2-methyl-1,1'-biphenyl (compound 3p)[6]



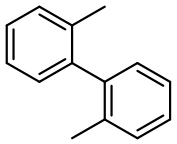
Prepared from phenylboronic acid (1.22 g, 10.0 mmol) and 1-chloro-2-methylbenzene (3.78 g, 30.0 mmol 3.0 equiv.) according to **GP1**. The title compound 2-methyl-1,1'-biphenyl (3p, 1.43 g, 85%) was obtained as a Colorless transparent oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.43 (m, 2H), 7.41 – 7.35 (m, 3H), 7.33 – 7.27 (m, 4H), 2.33 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.00, 141.97, 135.37, 130.32, 129.82, 129.22, 128.08, 127.26, 126.78, 125.78, 20.48.

HRMS (EI) for $C_{13}H_{12}^+$ [M^+]: calculated 168.0939, found 168.0936.

2,2'-dimethyl-1,1'-biphenyl (compound 3q)[9]



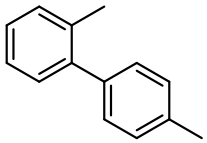
Prepared from o-tolylboronic acid (1.36 g, 10.0 mmol) and 1-chloro-2-methylbenzene (3.78 g, 30.0 mmol 3.0 equiv.) according to **GP1**. The title compound 2,2'-dimethyl-1,1'-biphenyl (3q, 1.58 g, 87%) was obtained as a Colorless transparent oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.30 (m, 4H), 7.29 – 7.24 (m, 2H), 7.17 – 7.14 (m, 2H), 2.11 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.62, 135.84, 129.83, 129.31, 127.18, 125.57, 19.86.

HRMS (EI) for $C_{14}H_{14}^+$ [M^+]: calculated 182.1096, found 182.1094.

2,4'-dimethyl-1,1'-biphenyl (compound 3r)[14]



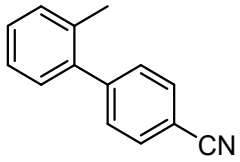
Prepared from p-tolylboronic acid (1.36 g, 10.0 mmol) and 1-chloro-2-methylbenzene (3.78 g, 30.0 mmol 3.0 equiv.) according to **GP1**. The title compound 2,4'-dimethyl-1,1'-biphenyl (3r, 1.51 g, 83%) was obtained as a Colorless transparent oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 8H), 2.46 (s, 3H), 2.34 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.90, 139.06, 136.41, 135.43, 130.32, 129.89, 129.11, 128.81, 127.10, 125.78, 21.22, 20.56.

HRMS (EI) for $C_{14}H_{14}^+$ [M^+]: calculated 182.1096, found 182.1093.

2'-methyl-[1,1'-biphenyl]-4-carbonitrile (compound 3s)[15]



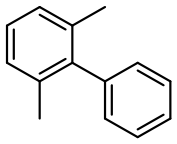
Prepared from (4-cyanophenyl)boronic acid (1.47 g, 10.0 mmol) and 1-chloro-2-methylbenzene (3.78 g, 30.0 mmol 3.0 equiv.) according to **GP1**. The title compound 2'-methyl-[1,1'-biphenyl]-4-carbonitrile (3s, 1.25 g, 65%) was obtained as a light yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.72 (m, 2H), 7.49 – 7.45 (m, 2H), 7.35 – 7.29 (m, 3H), 7.22 (d, *J* = 7.3 Hz, 1H), 2.29 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.81, 140.01, 135.06, 132.00, 130.69, 130.02, 129.44, 128.32, 126.12, 118.99, 110.73, 20.34.

HRMS (EI) for $C_{14}H_{11}N^+$ [M^+]: calculated 193.0891, found 193.0889.

2,6-dimethyl-1,1'-biphenyl (compound 3t)[16]



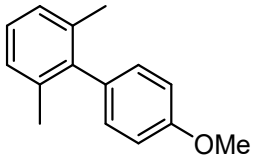
Prepared from phenylboronic acid (1.22 g, 10.0 mmol) and 2-chloro-1,3-dimethylbenzene (4.20 g, 30.0 mmol 3.0 equiv.) according to **GP1**. The title compound 2,6-dimethyl-1,1'-biphenyl (3t, 1.62 g, 89%) was obtained as a Colorless transparent oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (t, *J* = 7.4 Hz, 2H), 7.41 – 7.36 (m, 1H), 7.25 – 7.12 (m, 5H), 2.08 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.90, 141.11, 136.10, 129.05, 128.45, 127.30, 127.05, 126.64, 20.89.

HRMS (EI) for $C_{14}H_{14}^+$ [M^+]: calculated 182.1096, found 182.1099.

4'-methoxy-2,6-dimethyl-1,1'-biphenyl (compound 3u)[12]



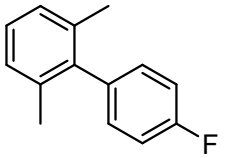
Prepared from (4-methoxyphenyl)boronic acid (1.22 g, 10.0 mmol) and 2-chloro-1,3-dimethylbenzene (4.20 g, 30.0 mmol 3.0 equiv.) according to **GP1**. The title compound 4'-methoxy-2,6-dimethyl-1,1'-biphenyl (3u, 1.74 g, 82%) was obtained as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.08 (m, 5H), 7.04 – 6.97 (m, 2H), 3.90 (s, 3H), 2.09 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.27, 141.54, 136.56, 133.33, 130.09, 127.27, 126.91, 113.82, 55.23, 20.95.

HRMS (EI) for $C_{15}H_{16}O^+$ [M^+]: calculated 212.1201, found 212.1204.

4'-fluoro-2,6-dimethyl-1,1'-biphenyl (compound 3v)[16]



Prepared from (4-fluorophenyl)boronic acid (1.40 g, 10.0 mmol) and 2-chloro-1,3-dimethylbenzene (4.20 g, 30.0 mmol 3.0 equiv.) according to **GP1**. The title compound 4'-fluoro-2,6-dimethyl-1,1'-biphenyl (3v, 1.74 g, 87%) was obtained as a white solid.

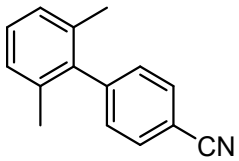
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.13 (m, 7H), 2.06 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.76 (d, J = 245.0 Hz), 140.82, 136.27, 130.60 (d, J = 7.8 Hz), 128.60 (d, J = 8.1 Hz), 127.37, 127.25, 115.39 (d, J = 21.1 Hz), 20.86.

^{19}F NMR (376 MHz, $CDCl_3$) δ -116.26.

HRMS (EI) for $C_{14}H_{13}F^+$ [M^+]: calculated 200.1001, found 200.1003.

2',6'-dimethyl-[1,1'-biphenyl]-4-carbonitrile (compound 3w)[17]



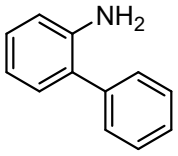
Prepared from (4-cyanophenyl)boronic acid (1.47 g, 10.0 mmol) and 2-chloro-1,3-dimethylbenzene (4.20 g, 30.0 mmol 3.0 equiv.) according to **GP1**. The title compound 2',6'-dimethyl-[1,1'-biphenyl]-4-carbonitrile (3w, 1.57 g, 76%) was obtained as a light yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.2 Hz, 2H), 7.34 – 7.29 (m, 2H), 7.24 (dd, J = 8.4, 6.6 Hz, 1H), 7.15 (d, J = 7.5 Hz, 2H), 2.03 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.33, 139.94, 135.43, 132.41, 130.10, 127.91, 127.61, 118.99, 110.80, 20.74.

HRMS (EI) for $C_{15}H_{13}N^+$ [M^+]: calculated 207.1048, found 207.1046.

[1,1'-biphenyl]-2-amine (compound 3y)[18]



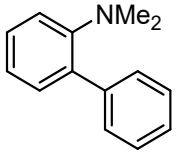
Prepared from phenylboronic acid (1.22g, 10.0 mmol) and 2-chloroaniline (3.81g, 30.0 mmol 3.0 equiv) according to **GP1**. The title compound [1,1'-biphenyl]-2-amine (3y, 1.44g,85%) was obtained as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.36 (m, 5H), 7.23-7.16 (m, 2H), 6.92 – 6.78 (m, 2H), 3.72 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.35, 139.50, 130.49, 129.13, 128.84, 128.53, 127.76, 127.21, 118.79, 115.72.

HRMS (EI) for $C_{12}H_{11}N^+$ [M^+]: calculated 169.0891, found 169.0893.

***N,N*-dimethyl-[1,1'-biphenyl]-2-amine (compound 3z)[18]**



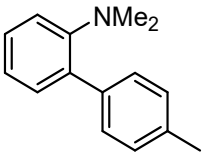
Prepared from phenylboronic acid (1.22 g, 10.0 mmol) and 2-chloro-N,N-dimethylaniline (4.65 g, 30.0 mmol 3.0 equiv.) according to **GP1**. The title compound *N,N*-dimethyl-[1,1'-biphenyl]-2-amine (3z, 1.38 g, 70%) was obtained as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 7.5 Hz, 2H), 7.44 (t, J = 7.5 Hz, 2H), 7.36 – 7.25 (m, 3H), 7.07 (d, J = 7.1 Hz, 2H), 2.59 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.26, 142.01, 134.17, 131.75, 128.70, 128.33, 128.10, 126.51, 121.48, 117.59, 43.39.

HRMS (EI) for $C_{14}H_{15}N^+$ [M^+]: calculated 197.1204, found 197.1206.

***N,N*,4'-trimethyl-[1,1'-biphenyl]-2-amine (compound 3aa)[18]**



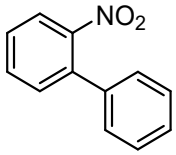
Prepared from p-tolylboronic acid (1.36 g, 10.0 mmol) and 2-chloro-N,N-dimethylaniline (4.65 g, 30.0 mmol 3.0 equiv.) according to **GP1**. The title compound *N,N*,4'-trimethyl-[1,1'-biphenyl]-2-amine (3aa, 1.52 g, 72%) was obtained as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 2H), 7.33 – 7.22 (m, 4H), 7.06 (q, *J* = 7.4 Hz, 2H), 2.59 (s, 6H), 2.44 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.31, 139.07, 136.09, 134.19, 131.69, 129.04, 128.53, 127.87, 121.48, 117.56, 43.39, 21.27.

HRMS (EI) for $C_{15}H_{17}N^+$ [M^+]: calculated 211.1361, found 211.1364.

2-nitro-1,1'-biphenyl (compound 3bb)[19]



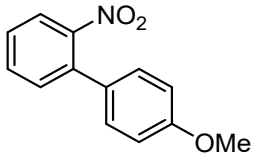
Prepared from phenylboronic acid (1.22 g, 10.0 mmol) and 1-chloro-2-nitrobenzene (4.71 g, 30.0 mmol 3.0 equiv.) according to **GP1**. The title compound N,N,4'-trimethyl-2-nitro-1,1'-biphenyl (3bb, 1.79 g, 90%) was obtained as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.55-7.40 (m, 5H), 7.38-7.32 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.41, 136.36, 132.31, 131.99, 128.72, 128.26, 128.19, 127.91, 124.10.

HRMS (EI) for $C_{12}H_9NO_2^+$ [M^+]: calculated 199.0633, found 199.0630.

4'-methyl-2-nitro-1,1'-biphenyl (compound 3cc)[19]



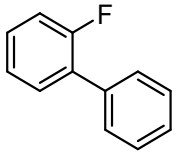
Prepared from p-tolylboronic acid (1.36 g, 10.0 mmol) and 1-chloro-2-nitrobenzene (4.71 g, 30.0 mmol 3.0 equiv.) according to **GP1**. The title compound 4'-methyl-2-nitro-1,1'-biphenyl (3cc, 1.83, 86%) was obtained as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.64 – 7.58 (m, 1H), 7.46 (td, *J* = 7.5, 1.0 Hz, 2H), 7.31 – 7.26 (m, 2H), 7.03 – 6.95 (m, 2H), 3.87 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.72, 135.87, 132.15, 131.94, 129.51, 129.15, 127.74, 124.01, 114.24, 55.32.

HRMS (EI) for $C_{13}H_{11}NO_3^+$ [M^+]: calculated 229.0739, found 229.0742.

2-fluoro-1,1'-biphenyl (compound 3dd)[6]



Prepared from phenylboronic acid (1.22 g, 10.0 mmol) and 1-chloro-2-fluorobenzene

(3.90 g, 30.0 mmol 3.0 equiv.) according to **GP1**. The title compound 2-fluoro-1,1'-biphenyl (3dd, 1.39 g, 81%) was obtained as a Colorless transparent oil.

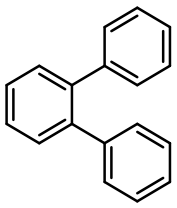
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dt, *J* = 8.1, 1.6 Hz, 2H), 7.51 – 7.45 (m, 3H), 7.43 – 7.32 (m, 2H), 7.25 (td, *J* = 7.5, 1.3 Hz, 1H), 7.22 – 7.15 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.79 (d, *J* = 247.7 Hz), 135.85, 130.80 (d, *J* = 3.5 Hz), 129.06 (d, *J* = 3.0 Hz), 128.97 (d, *J* = 8.1 Hz), 128.45, 127.67, 124.35 (d, *J* = 3.7 Hz), 116.11 (d, *J* = 22.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -118.05.

HRMS (EI) for $C_{12}H_9F^+$ [M^+]: calculated 172.0688, found 172.0686.

1,1':2',1''-terphenyl (compound 4a)[20]



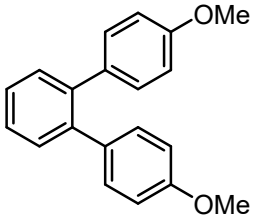
Prepared from 1,2-dichlorobenzene (1.46 g, 10.0 mmol 3.0 equiv.) and phenylboronic acid (3.05 g, 25.0 mmol) according to **GP2**. The title compound 1,1':2',1''-terphenyl (4a, 2.0 g, 89%) was obtained as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.44 (m, 4H), 7.28 – 7.14 (m, 10H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.55, 140.61, 130.64, 129.93, 127.89, 127.51, 126.48.

HRMS (EI) for $C_{18}H_{14}^+$ [M^+]: calculated 230.1096, found 230.1098.

4,4''-dimethoxy-1,1':2',1''-terphenyl (compound 4b)[21]



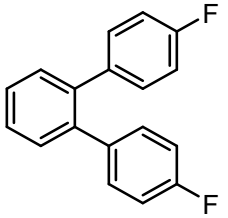
Prepared from 1,2-dichlorobenzene (1.46 g, 10.0 mmol) and (4-methoxyphenyl) boronic acid (3.80 g, 25.0 mmol 2.5 equiv.) according to **GP2**. The title compound 4,4''-dimethoxy-1,1':2',1''-terphenyl (4b, 1.97 g, 68%) was obtained as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.38 (m, 4H), 7.13 – 7.08 (m, 4H), 6.83 – 6.78 (m, 4H), 3.82 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.24, 140.07, 134.12, 130.92, 130.58, 127.16, 113.39, 55.19.

HRMS (EI) for $C_{20}H_{18}O_2^+$ [M^+]: calculated 290.1307, found 290.1310.

4,4''-difluoro-1,1':2',1''-terphenyl (compound 4c)[20]



Prepared from 1,2-dichlorobenzene (1.46 g, 10.0 mmol) and (4-fluorophenyl)boronic acid (3.50 g, 25.0 mmol 2.5 equiv.) according to **GP2**. The title compound 4,4''-difluoro-1,1':2',1''-terphenyl (4c, 1.94 g,73%) was obtained as a white solid.

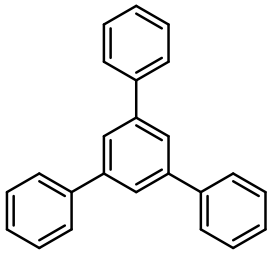
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.39 (m, 4H), 7.15 – 7.07 (m, 4H), 6.95 (t, *J* = 8.7 Hz, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.78 (d, *J* = 246.0 Hz), 139.55, 137.28, 131.37 (d, *J* = 8.1 Hz), 130.56, 127.71, 114.95 (d, *J* = 21.3 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -116.06.

HRMS (EI) for $C_{18}H_{12}F_2^+$ [M^+]: calculated 266.0907, found 266.0905.

5'-phenyl-1,1':3',1''-terphenyl (compound 4d)[22]



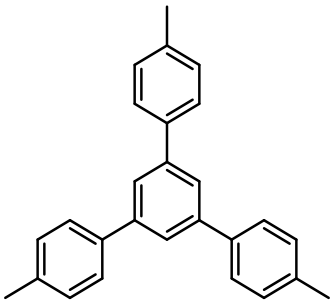
Prepared from 1,3,5-trichlorobenzene (1.80 g, 10.0 mmol) and phenylboronic acid (4.27 g, 35.0 mmol 3.5 equiv.) according to **GP3**. The title compound 5'-phenyl-1,1':3',1''-terphenyl (4d, 2.82 g,92%) was obtained as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 3H), 7.78 – 7.73 (m, 6H), 7.53 (dd, *J* = 8.3, 6.7 Hz, 6H), 7.47 – 7.41 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.39, 141.19, 128.90, 127.60, 127.41, 125.23.

HRMS (EI) for $C_{24}H_{18}^+$ [M^+]: calculated 306.1409, found 306.1411.

4,4''-dimethyl-5'-(p-tolyl)-1,1':3',1''-terphenyl (compound 4e)[22]



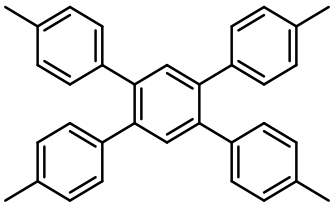
Prepared from 1,3,5-trichlorobenzene (1.80 g, 10.0 mmol) and p-tolylboronic acid (4.76 g, 35.0 mmol 3.5 equiv.) according to **GP3**. The title compound 4,4''-dimethyl-5'-(p-tolyl)-1,1':3',1''-terphenyl (4e, 3.03 g,87%) was obtained as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 3H), 7.65 (d, *J* = 8.1 Hz, 6H), 7.34 (d, *J* = 7.9 Hz, 6H), 2.47 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.21, 138.44, 137.32, 129.59, 127.23, 124.62, 21.19.

HRMS (EI) for $C_{27}H_{24}^+$ [M^+]: calculated 348.1878, found 348.1876.

4,4''-dimethyl-4',5'-di-p-tolyl-1,1':2',1''-terphenyl (compound 4f)[23]



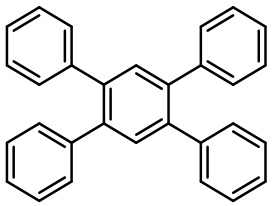
Prepared from 1,2,4,5-tetrachlorobenzene (2.14 g, 10.0 mmol) and p-tolylboronic acid (6.12 g, 45.0 mmol 4.5 equiv.) according to **GP3**. The title compound 4,4''-dimethyl-4',5'-di-p-tolyl-1,1':2',1''-terphenyl (4f, 3.90 g, 89%) was obtained as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (s, 2H), 7.17 (d, *J* = 8.1 Hz, 8H), 7.10 (d, J = 8.0 Hz, 8H), 2.37 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.28, 138.24, 136.16, 133.11, 129.77, 128.74, 21.19.

HRMS (EI) for $C_{34}H_{30}^+$ [M^+]: calculated 438.2348, found 438.2344.

4',5'-diphenyl-1,1':2',1''-terphenyl (compound 4g) [22]



Prepared from 1,2,4,5-tetrachlorobenzene (2.14 g, 10.0 mmol) and p-tolylboronic acid (5.49 g, 45.0 mmol 4.5 equiv.) according to **GP3**. The title compound 4',5'-diphenyl-

1,1':2',1"-terphenyl (4 g, 3.48 g, 91%) was obtained as a white solid.

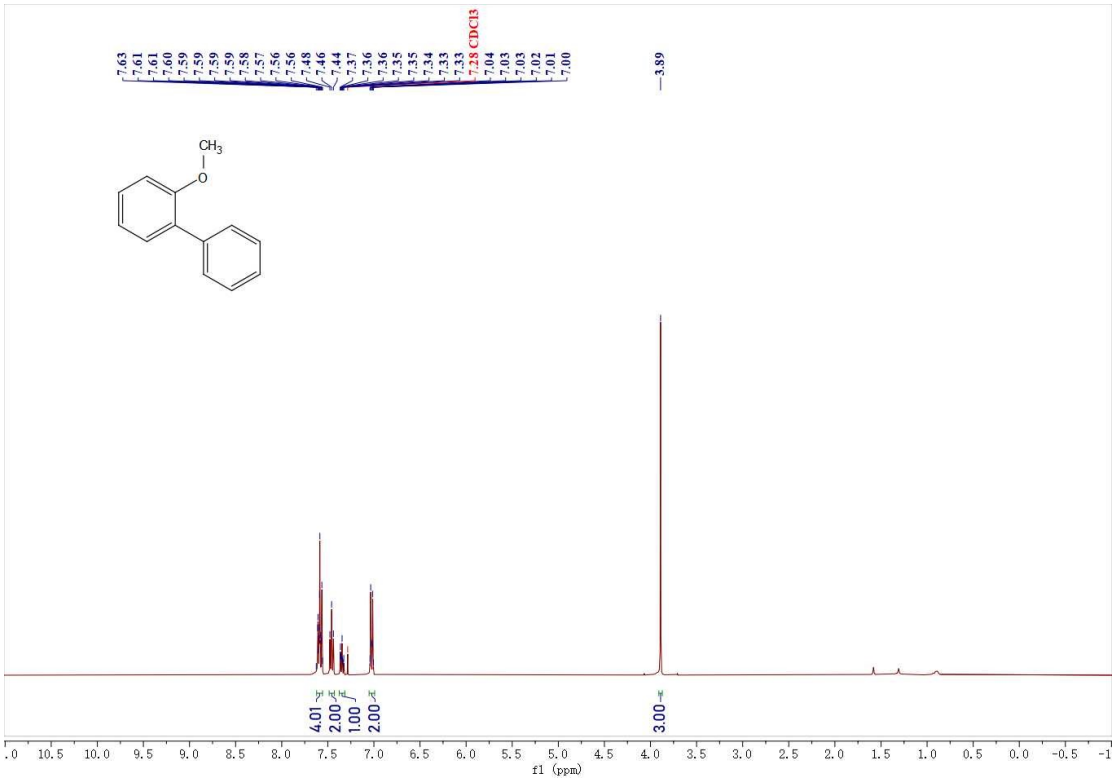
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 2H), 7.28-7.24(m, 20H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.96, 139.66, 133.01, 129.93, 127.99, 126.66.

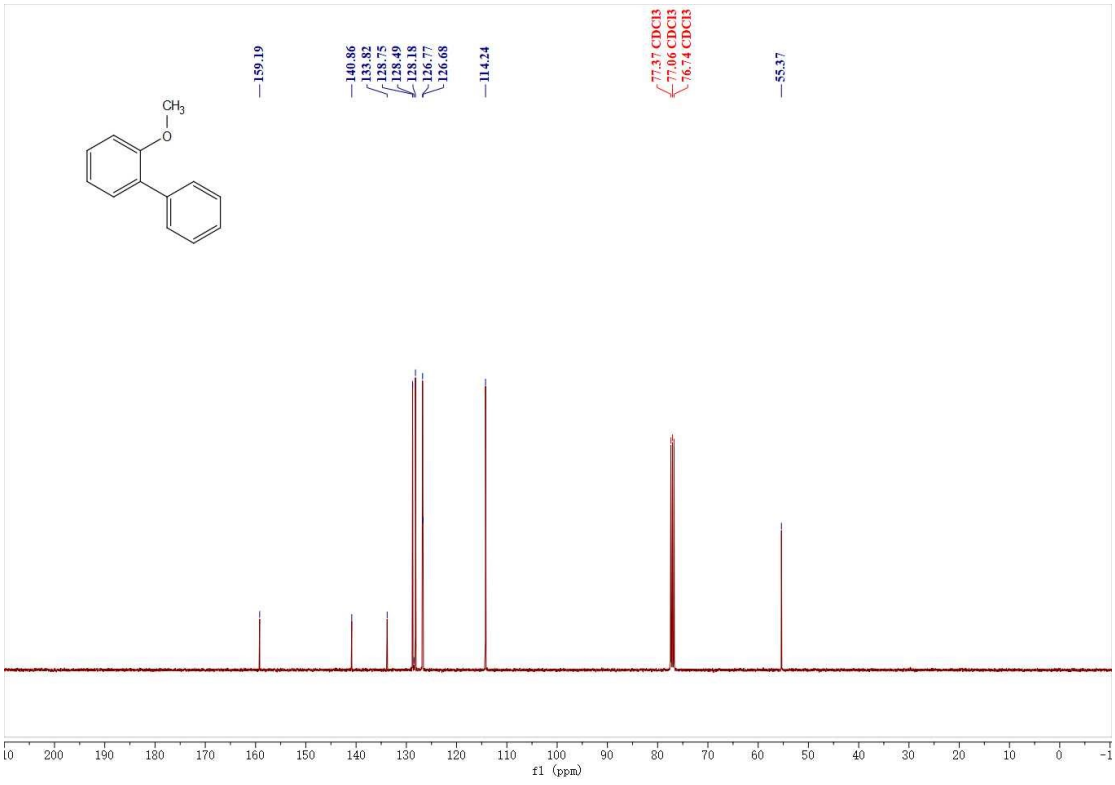
HRMS (EI) for $C_{30}H_{22}^{+}$ [M^{+}]: calculated 382.1722, found 382.1713.

8. ^{1}H, ^{13}C, ^{19}F, NMR Spectra

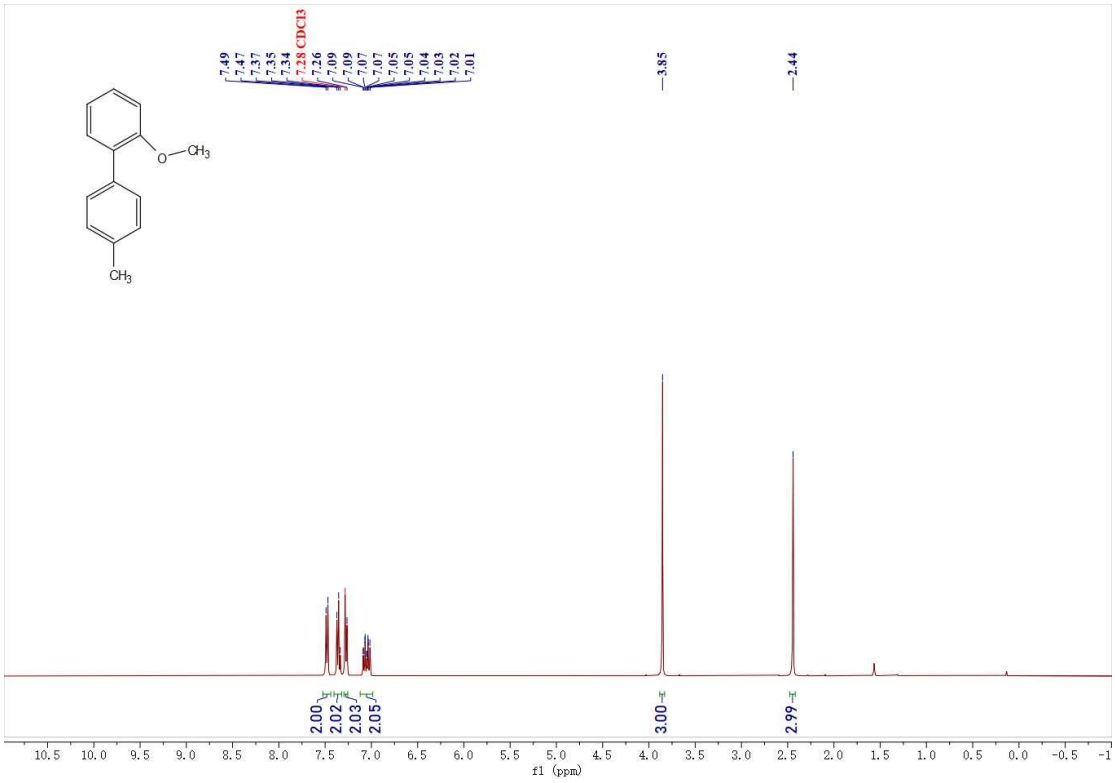
^{1}H NMR spectra of the compound 3a (400 MHz, $CDCl_3$)



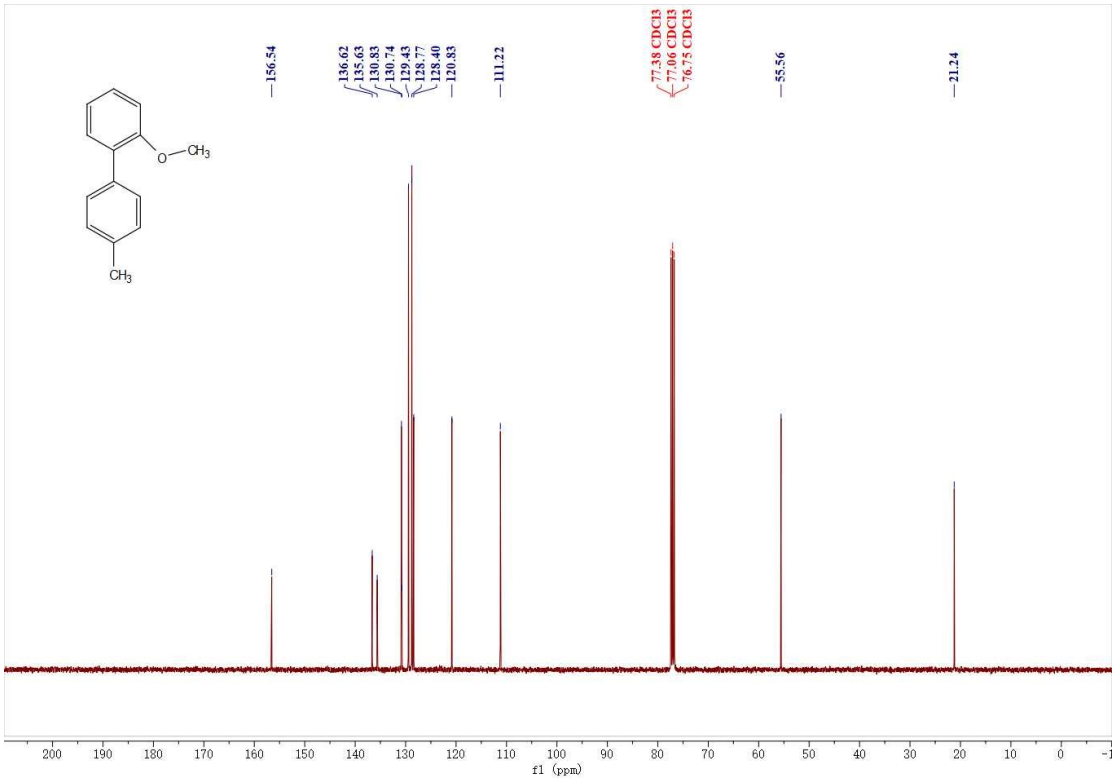
^{13}C NMR spectra of the compound 3a (101 MHz, $CDCl_3$)



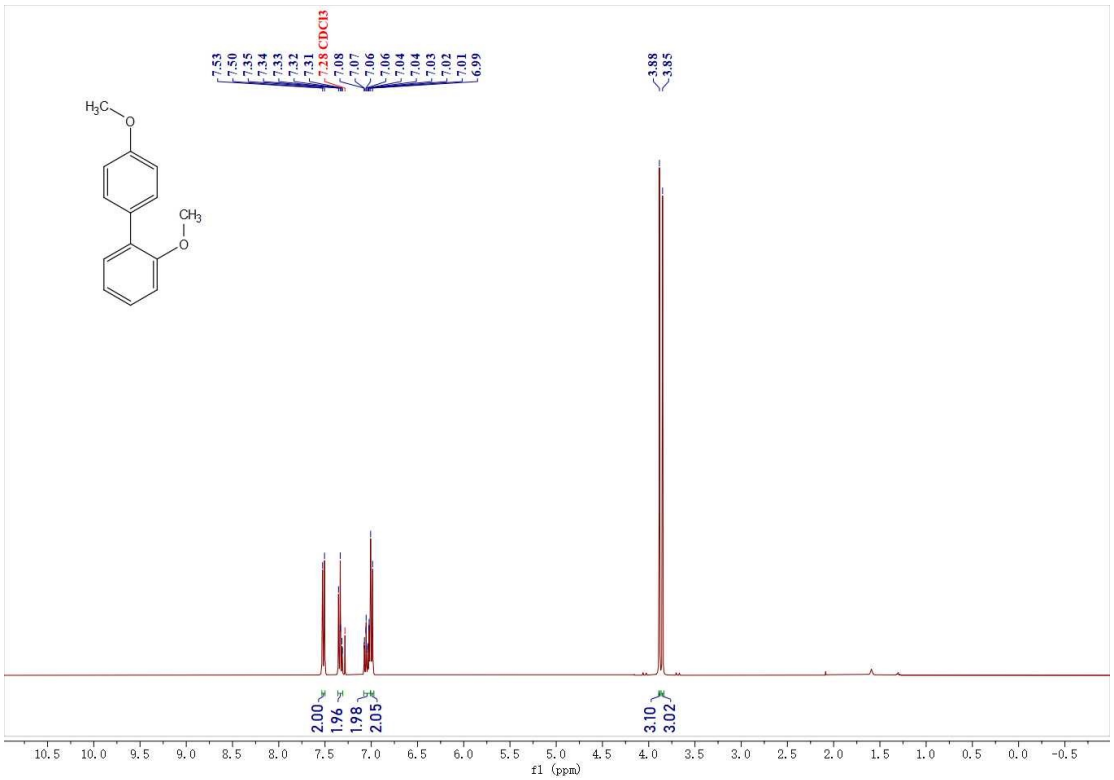
^{1}H NMR spectra of the compound 3b (400 MHz, $CDCl_3$)



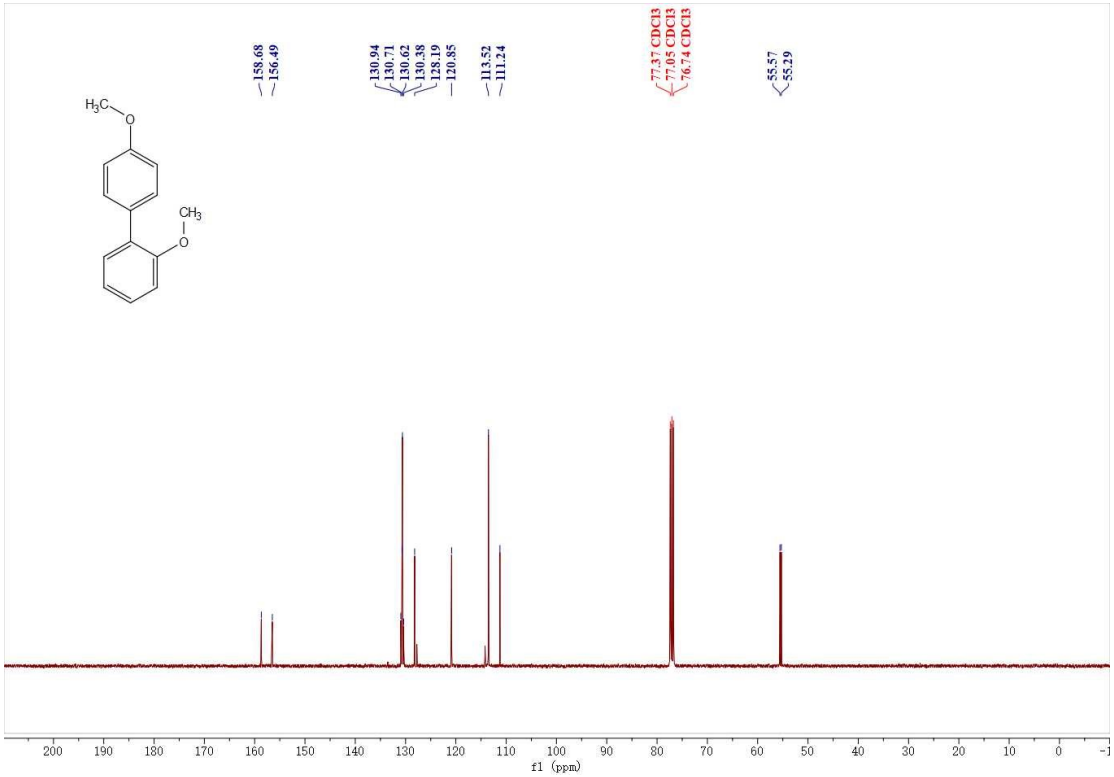
^{13}C NMR spectra of the compound 3b (101 MHz, $CDCl_3$)



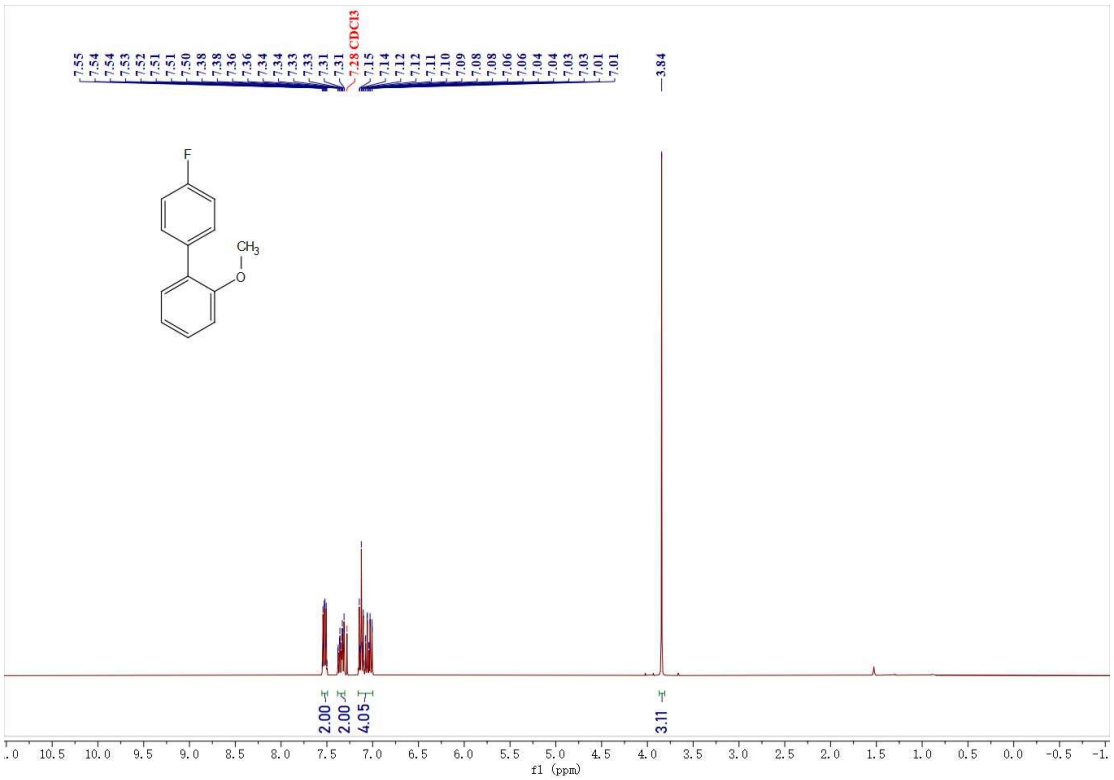
^{1}H NMR spectra of the compound 3c (400 MHz, $CDCl_3$)



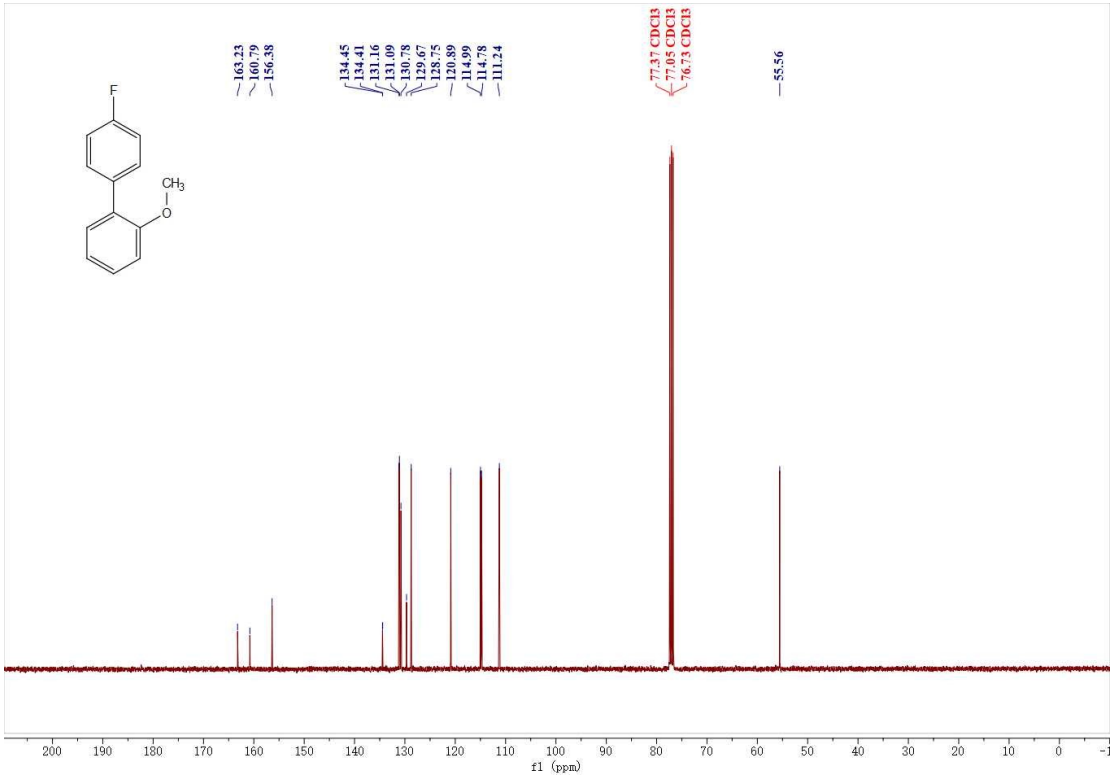
^{13}C NMR spectra of the compound 3c (101 MHz, $CDCl_3$)



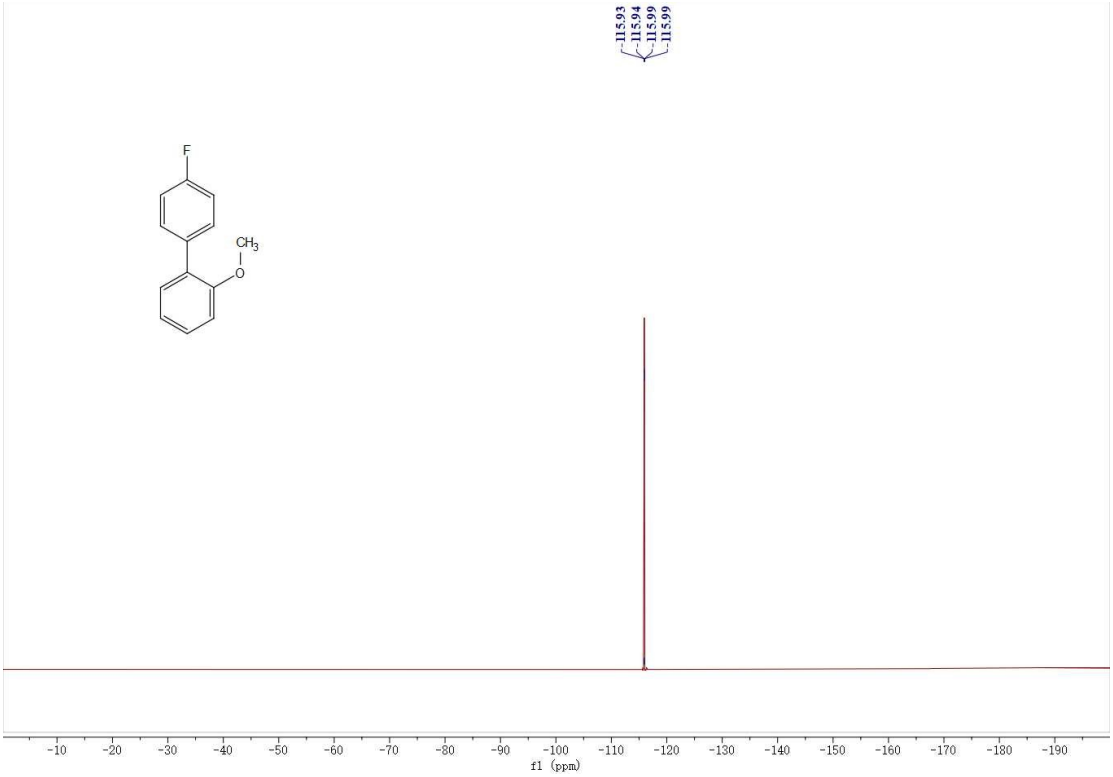
^{1}H NMR spectra of the compound 3d (400 MHz, $CDCl_3$)



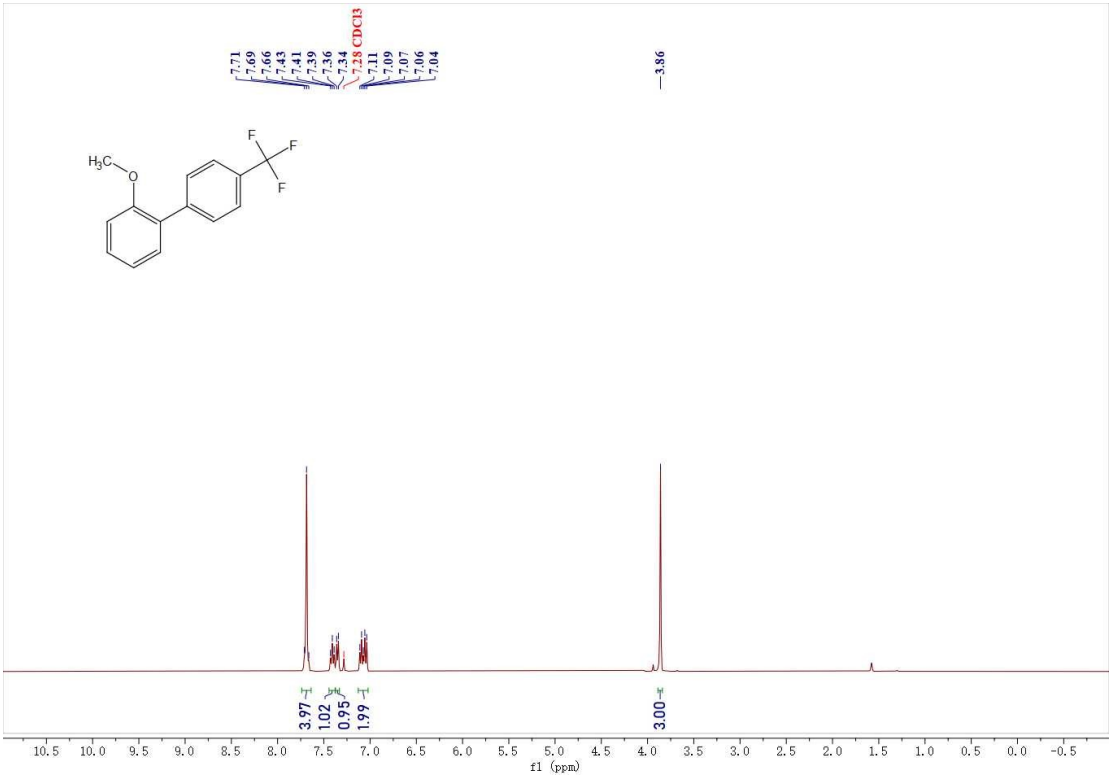
^{13}C NMR spectra of the compound 3d (101 MHz, $CDCl_3$)



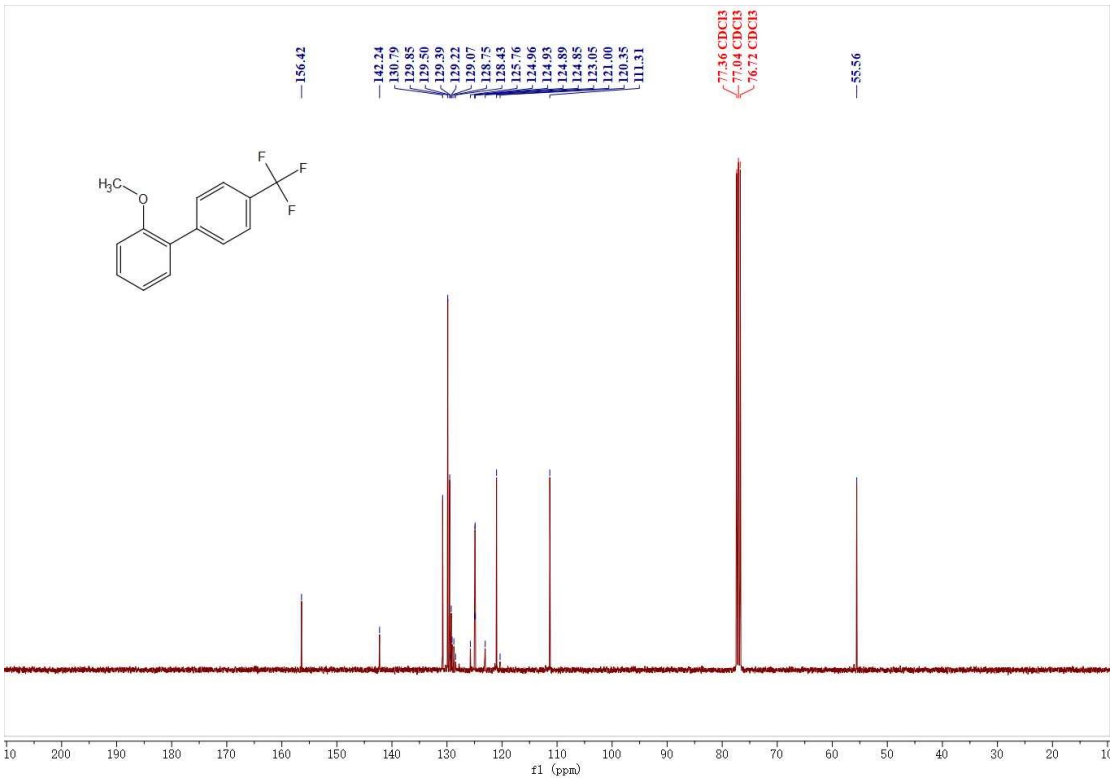
^{19}F spectra of the compound 3d (101 MHz, $CDCl_3$)



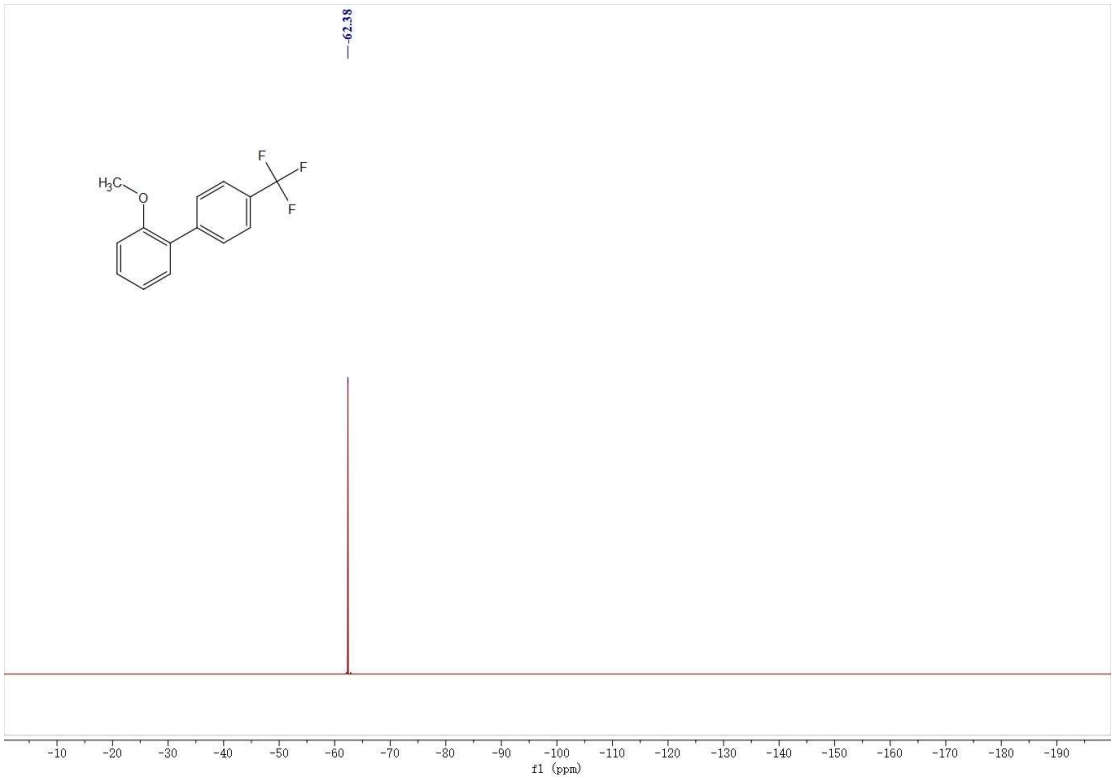
^{1}H NMR spectra of the compound 3e (400 MHz, $CDCl_3$)



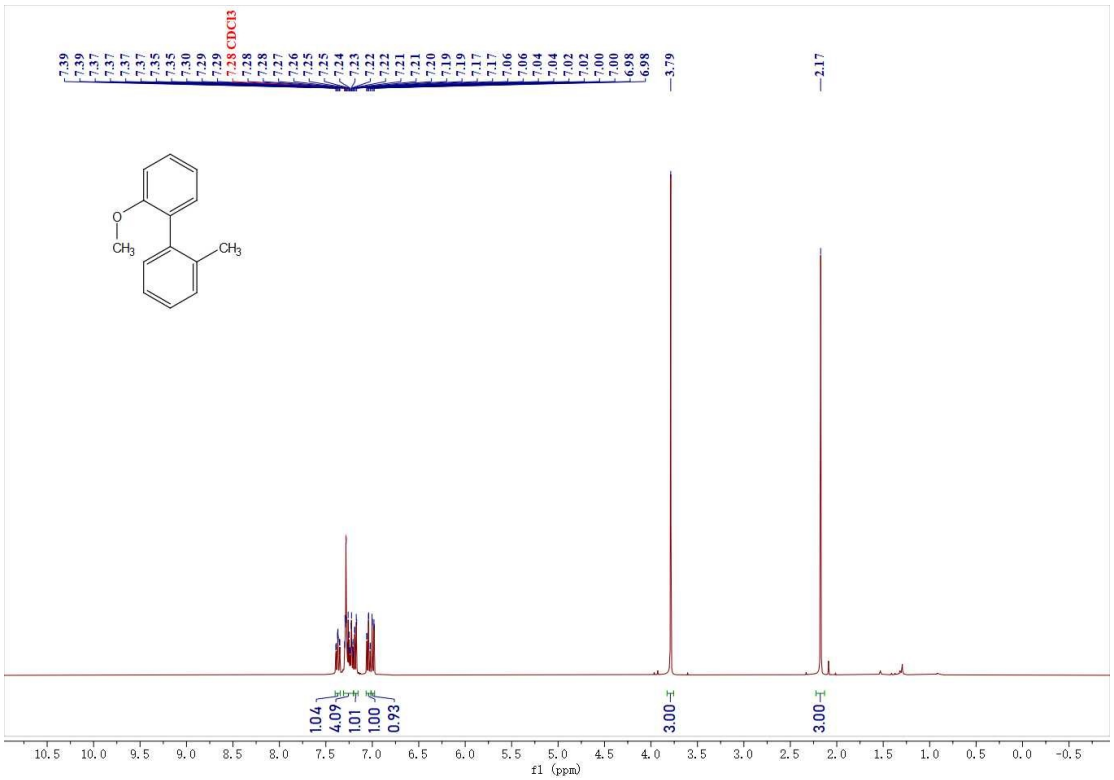
^{13}C NMR spectra of the compound 3e (101 MHz, $CDCl_3$)



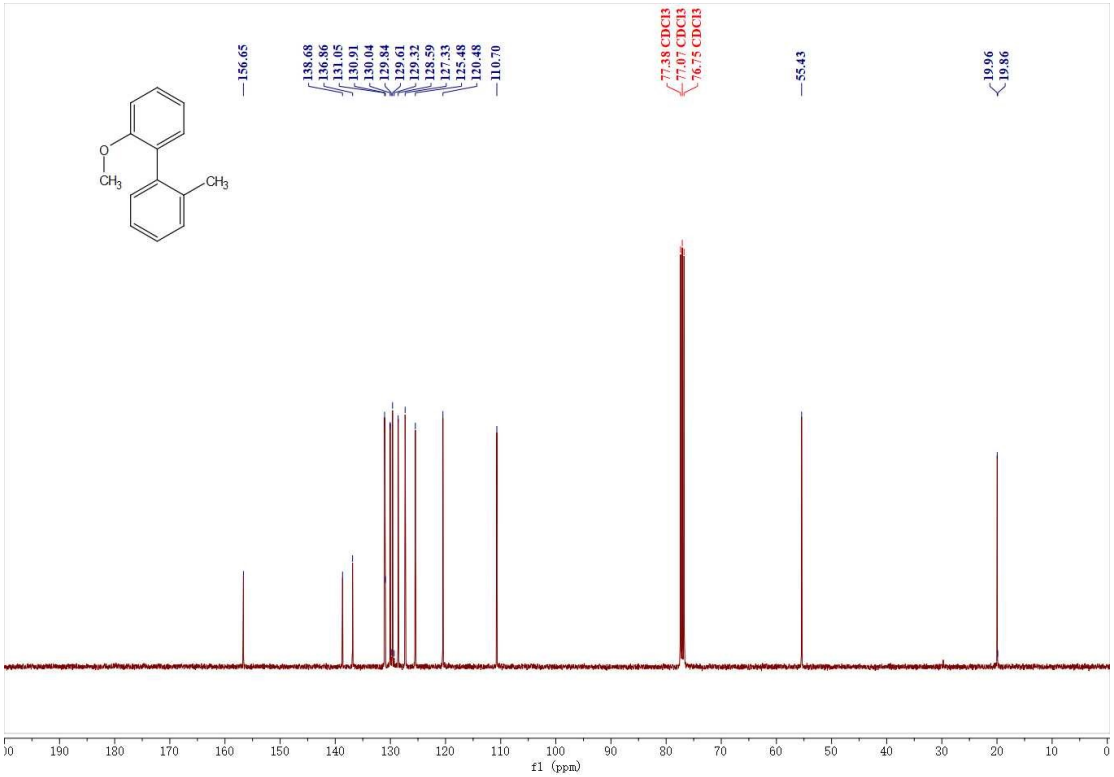
^{19}F spectra of the compound 3e (101 MHz, $CDCl_3$)



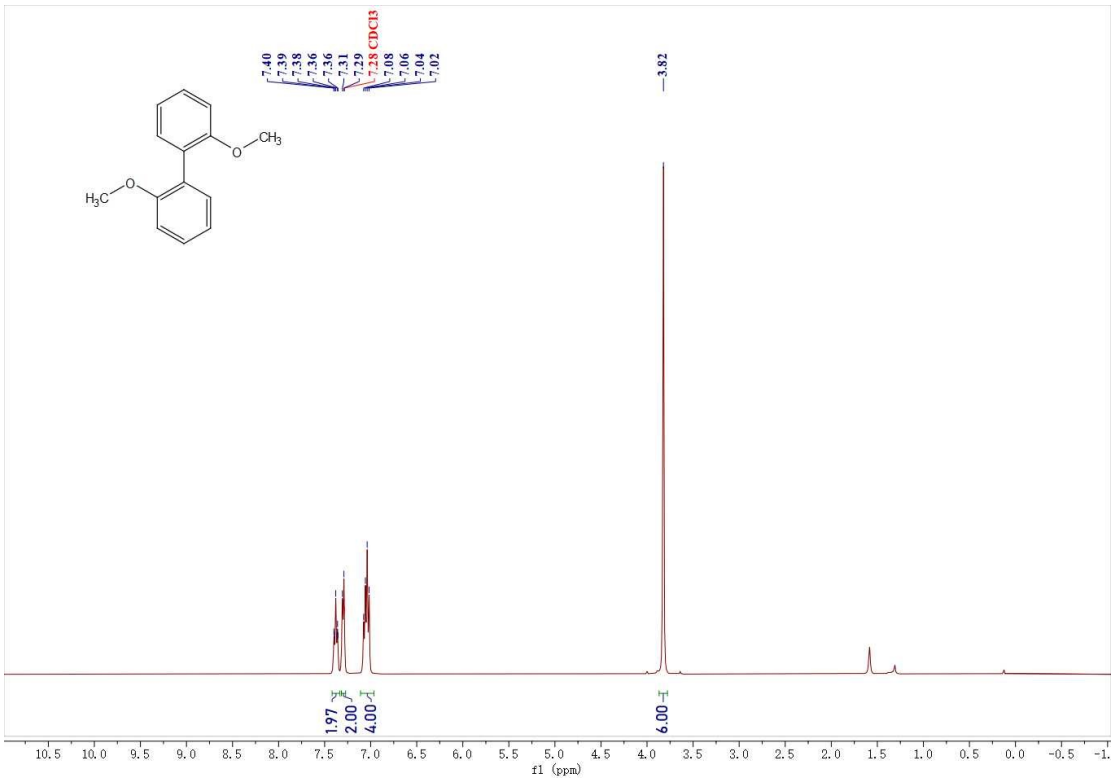
^{1}H NMR spectra of the compound 3f (400 MHz, $CDCl_3$)



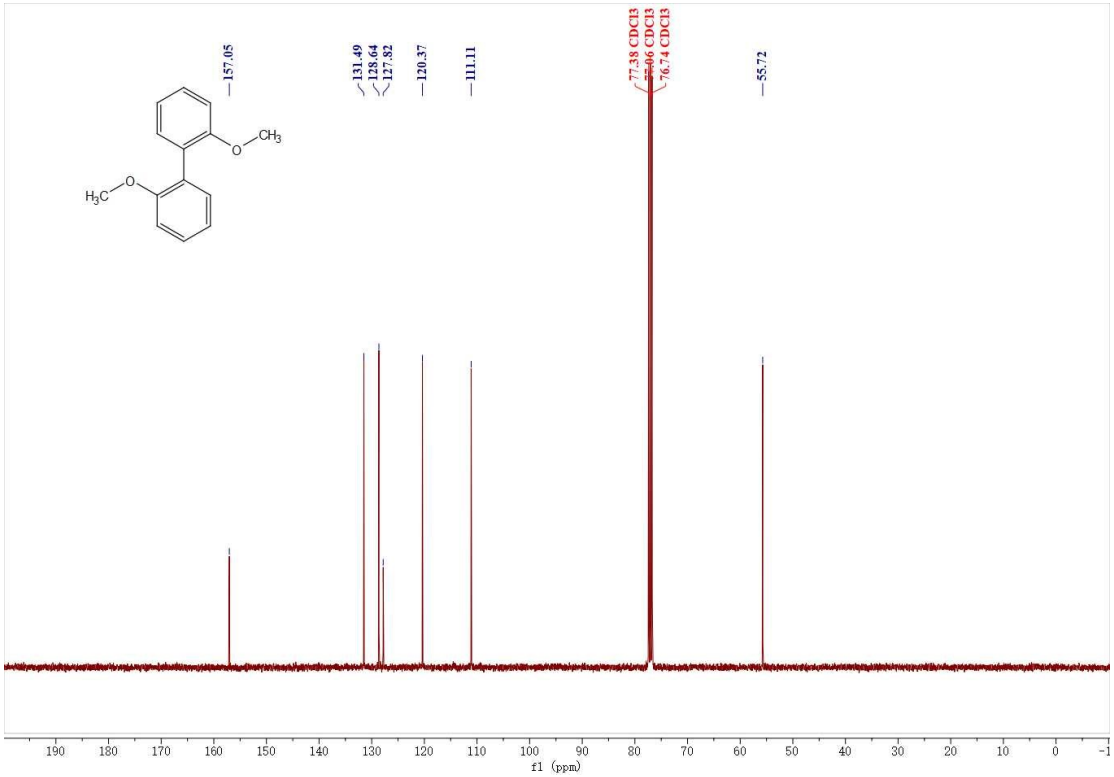
^{13}C NMR spectra of the compound 3f (101 MHz, $CDCl_3$)



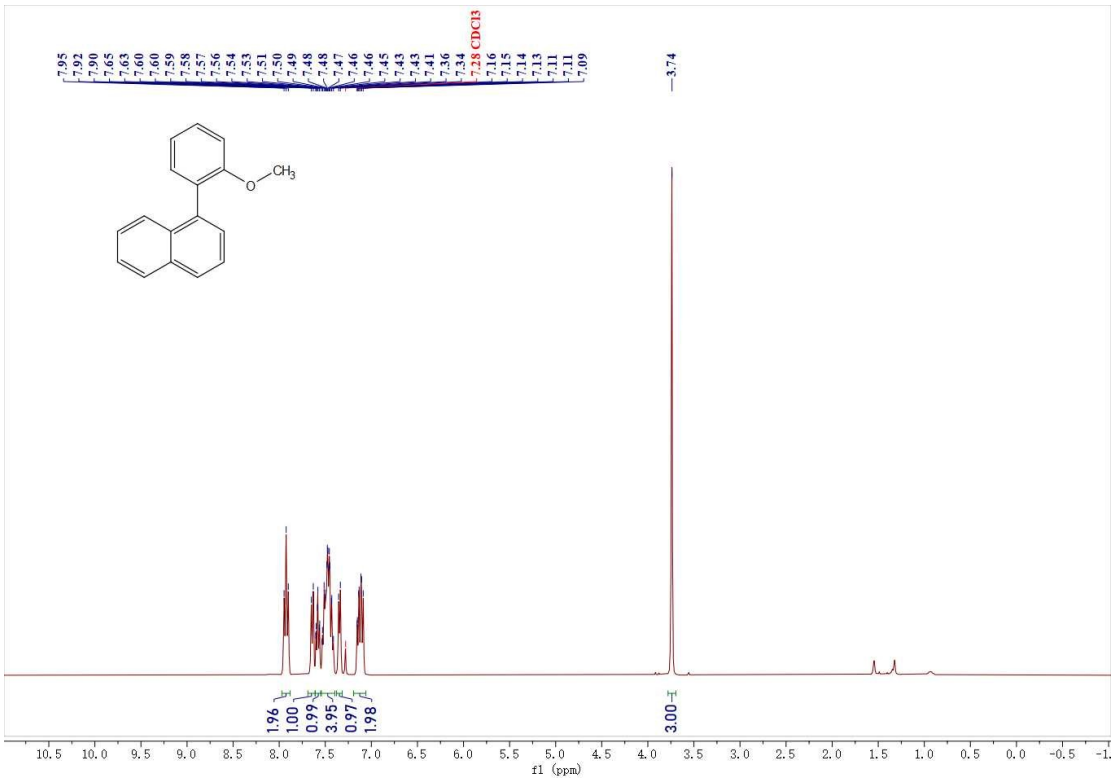
^{1}H NMR spectra of the compound 3g (400 MHz, $CDCl_3$)



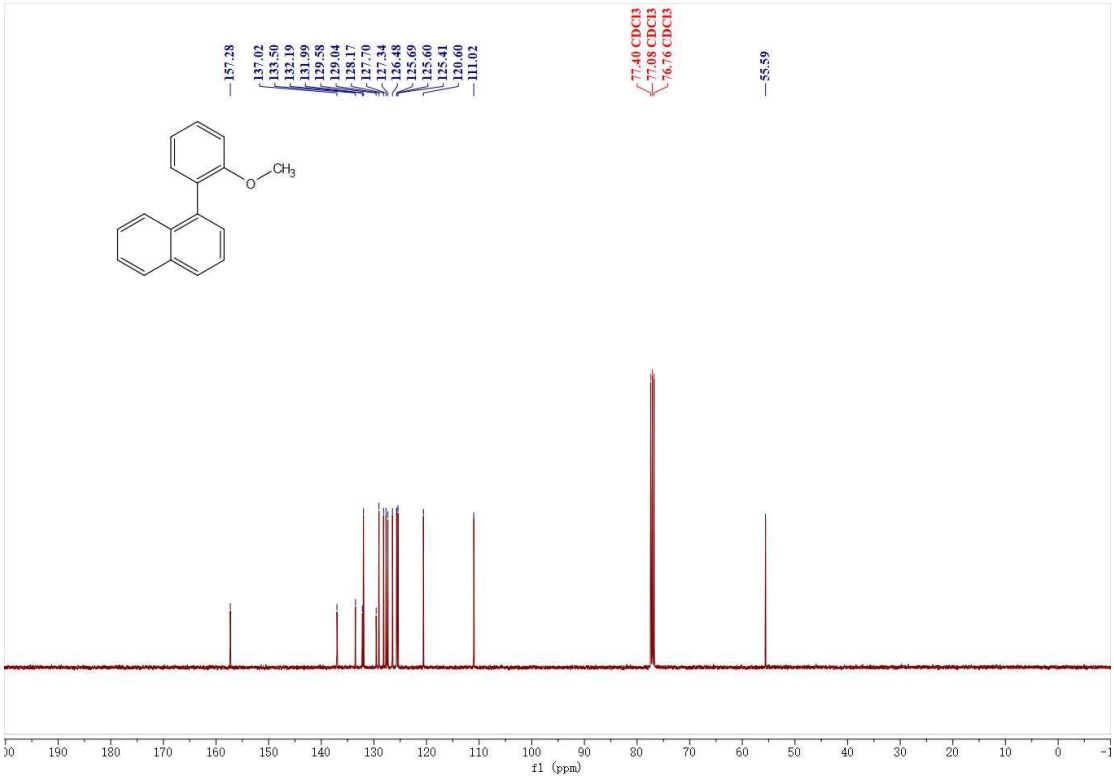
^{13}C NMR spectra of the compound 3g (101 MHz, $CDCl_3$)



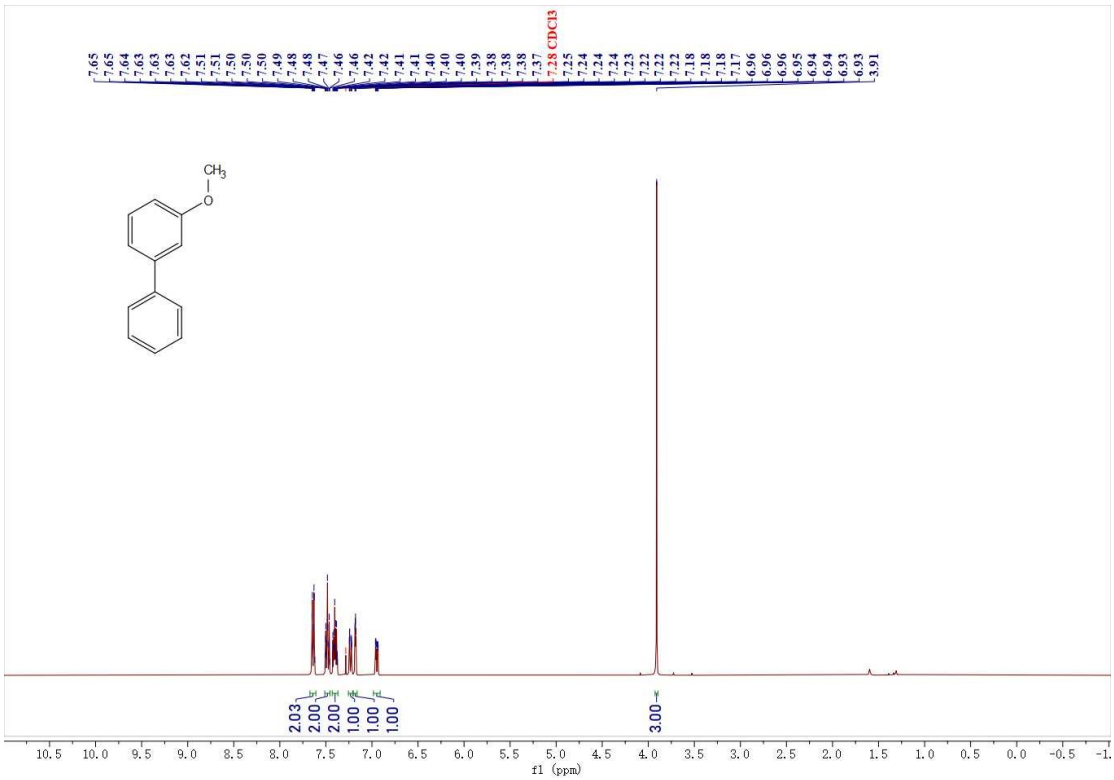
^{1}H NMR spectra of the compound 3h (400 MHz, $CDCl_3$)



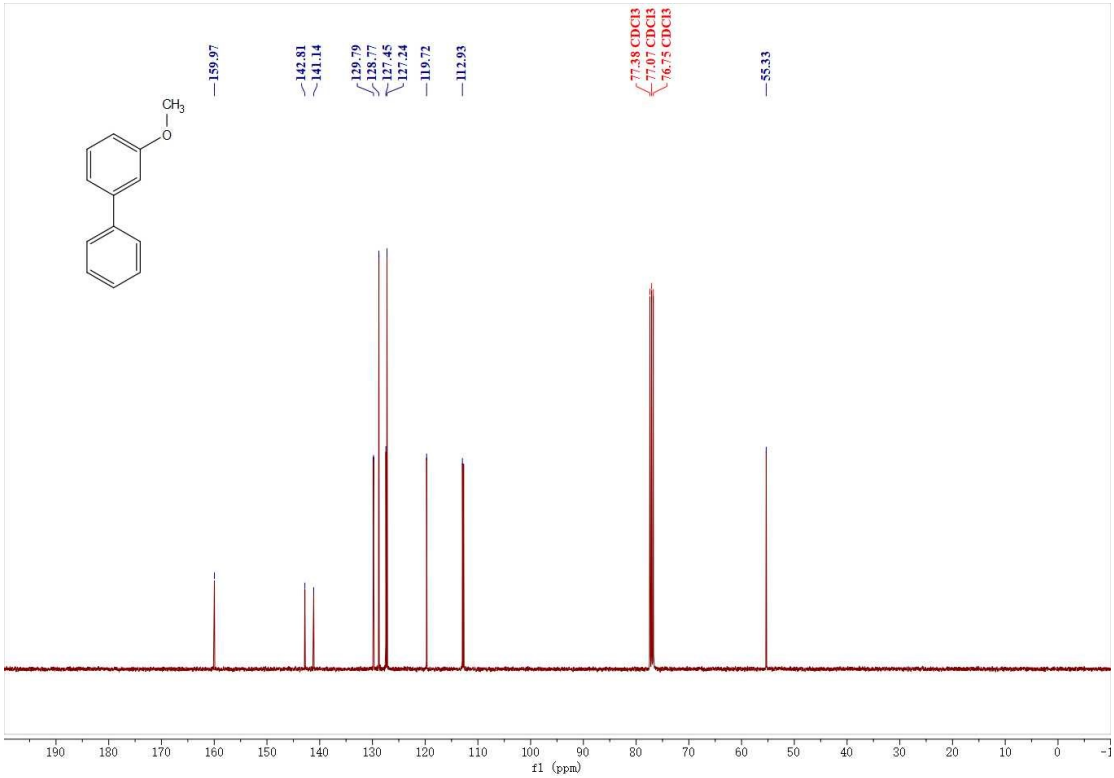
^{13}C NMR spectra of the compound 3h (101 MHz, $CDCl_3$)



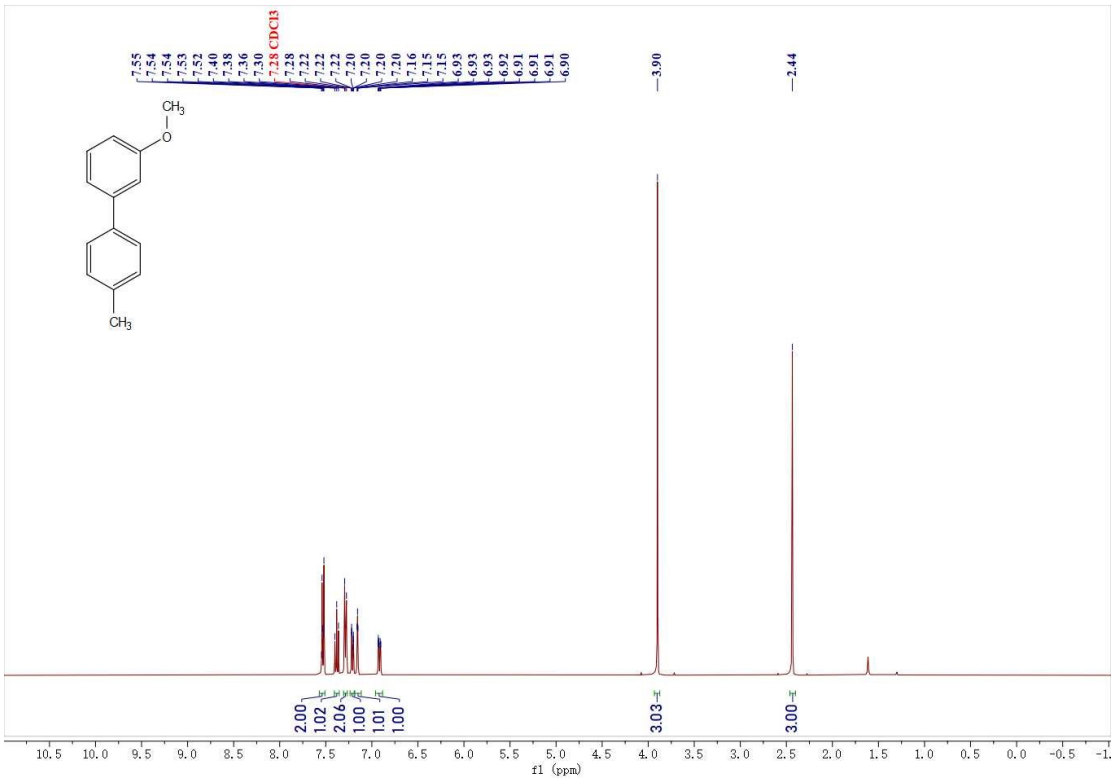
^{1}H NMR spectra of the compound 3i (400 MHz, $CDCl_3$)



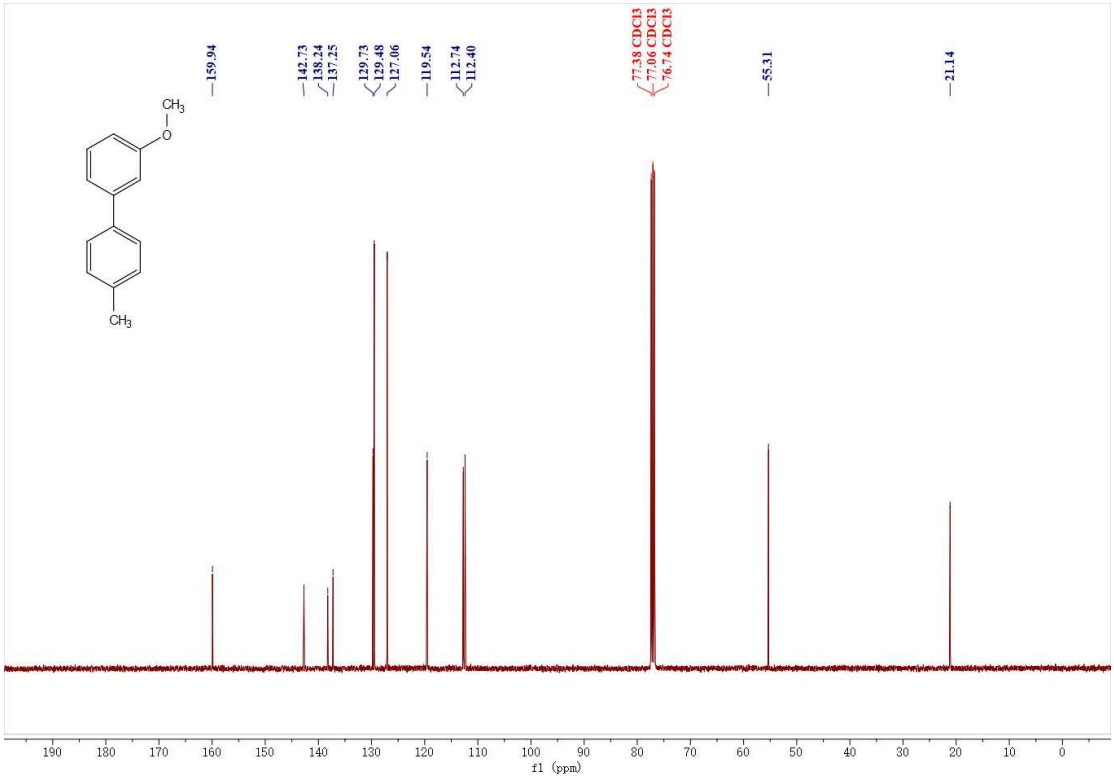
^{13}C NMR spectra of the compound 3i (101 MHz, $CDCl_3$)



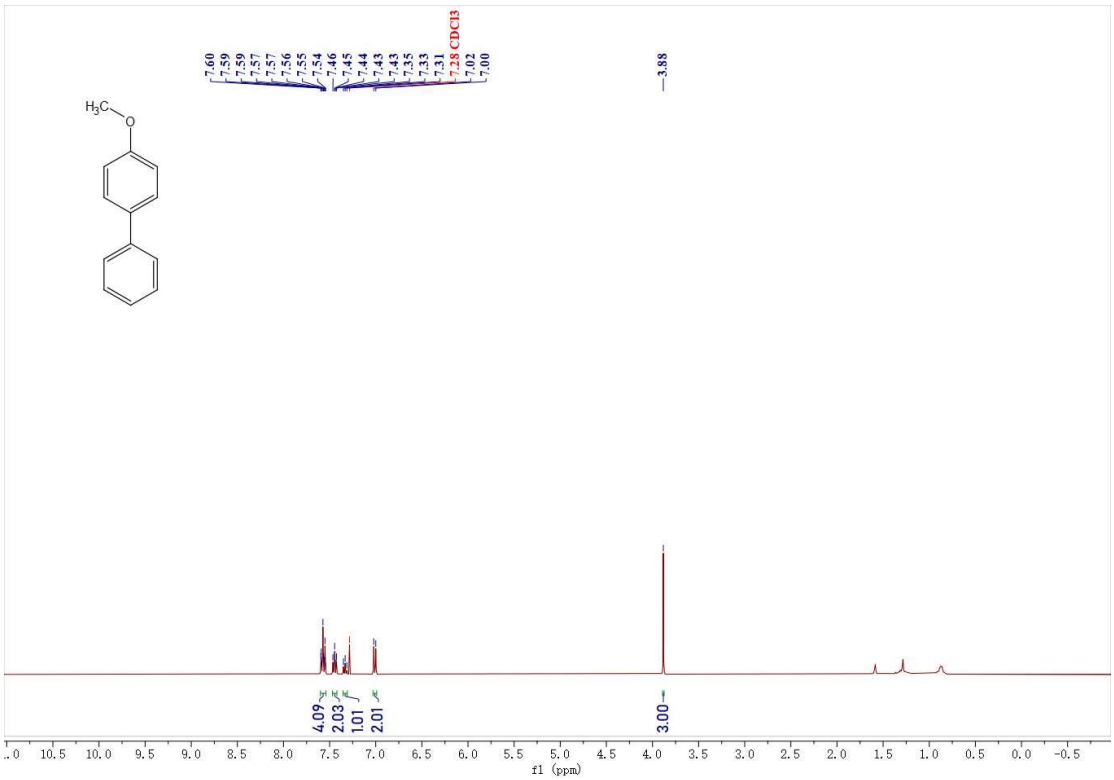
^{1}H NMR spectra of the compound 3j (400 MHz, $CDCl_3$)



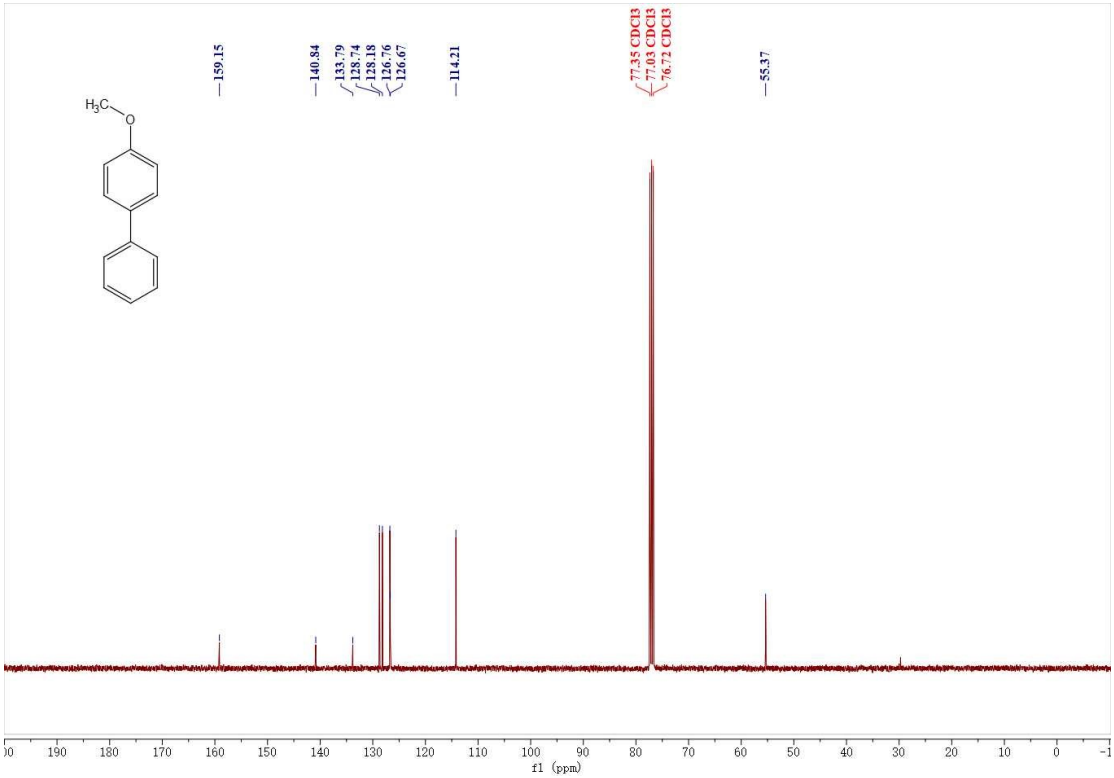
^{13}C NMR spectra of the compound 3j (101 MHz, $CDCl_3$)



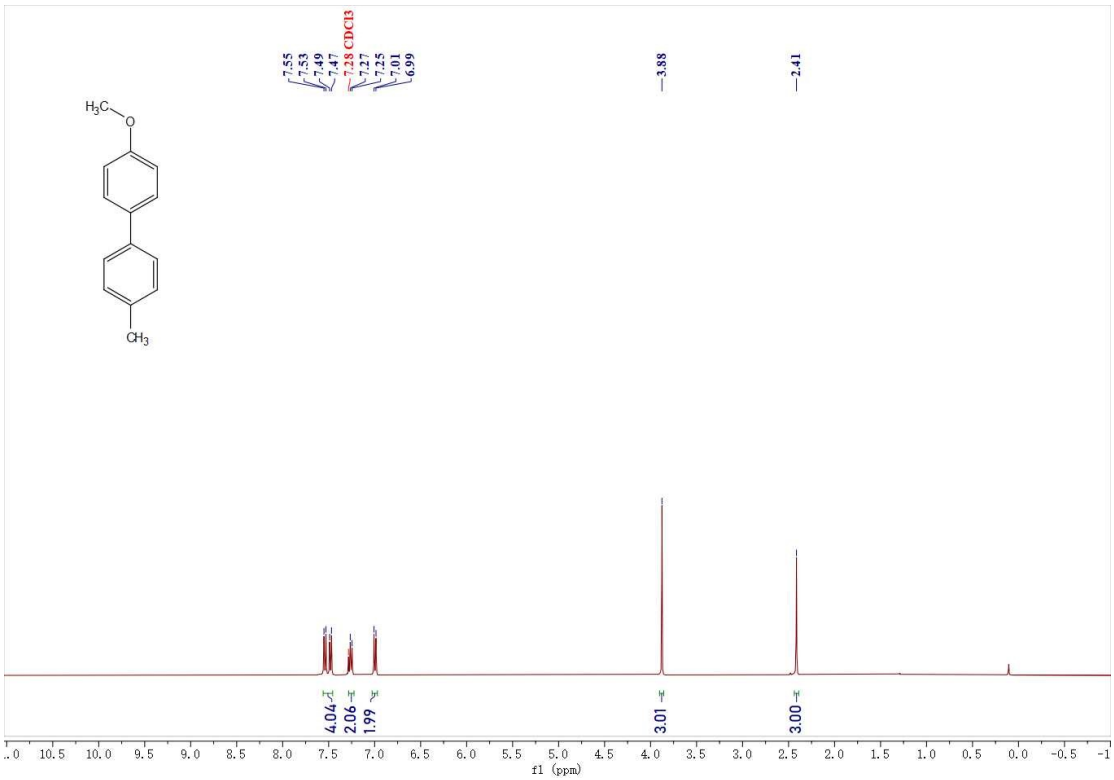
^{1}H NMR spectra of the compound 3k (400 MHz, $CDCl_3$)



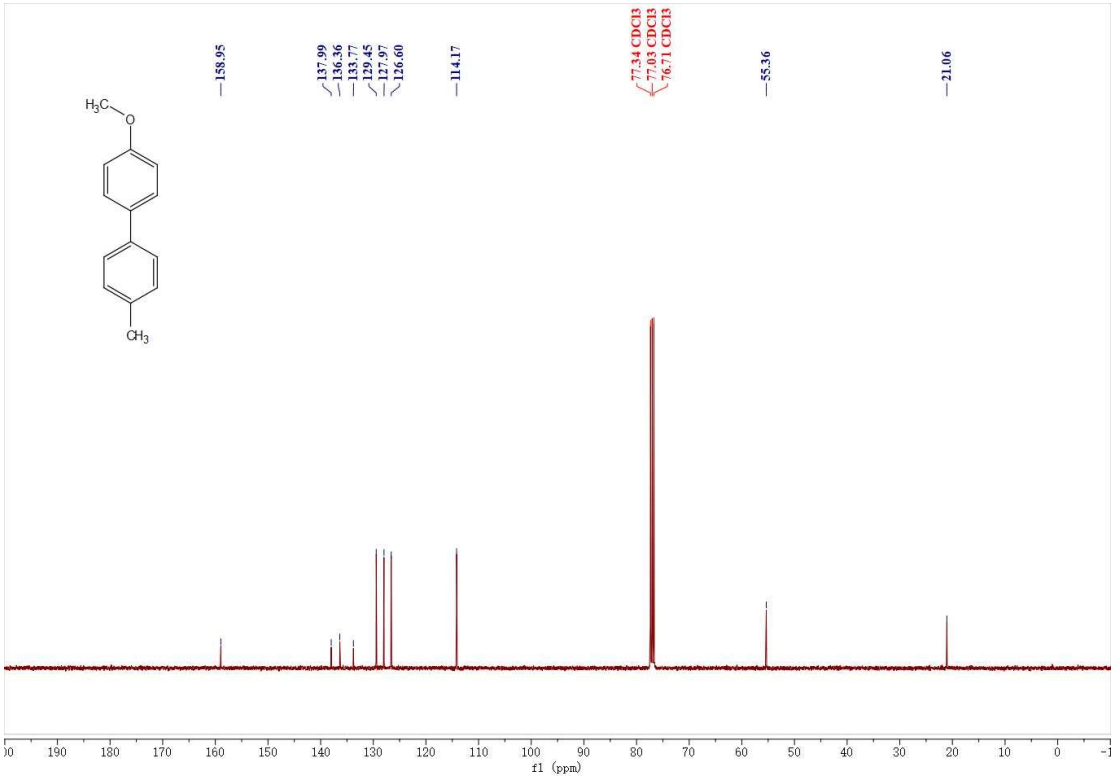
^{13}C NMR spectra of the compound 3k (101 MHz, $CDCl_3$)



^{1}H NMR spectra of the compound 3l (400 MHz, $CDCl_3$)

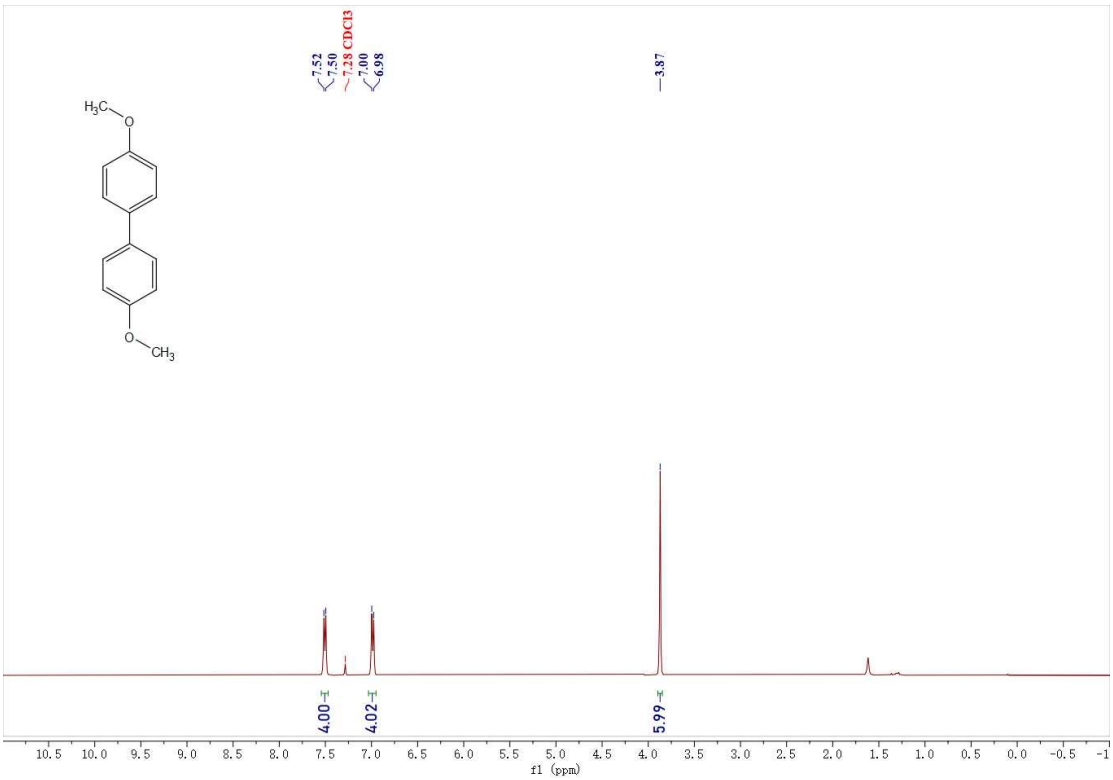


^{13}C NMR spectra of the compound 3l (101 MHz, $CDCl_3$)

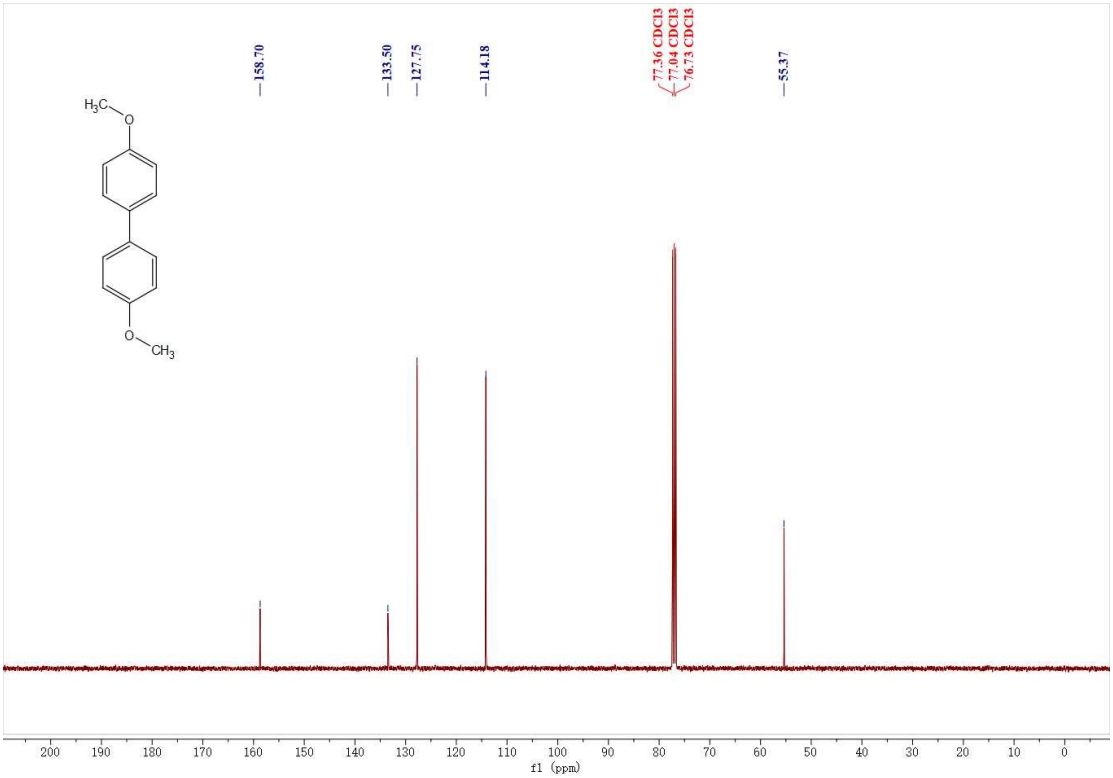


c

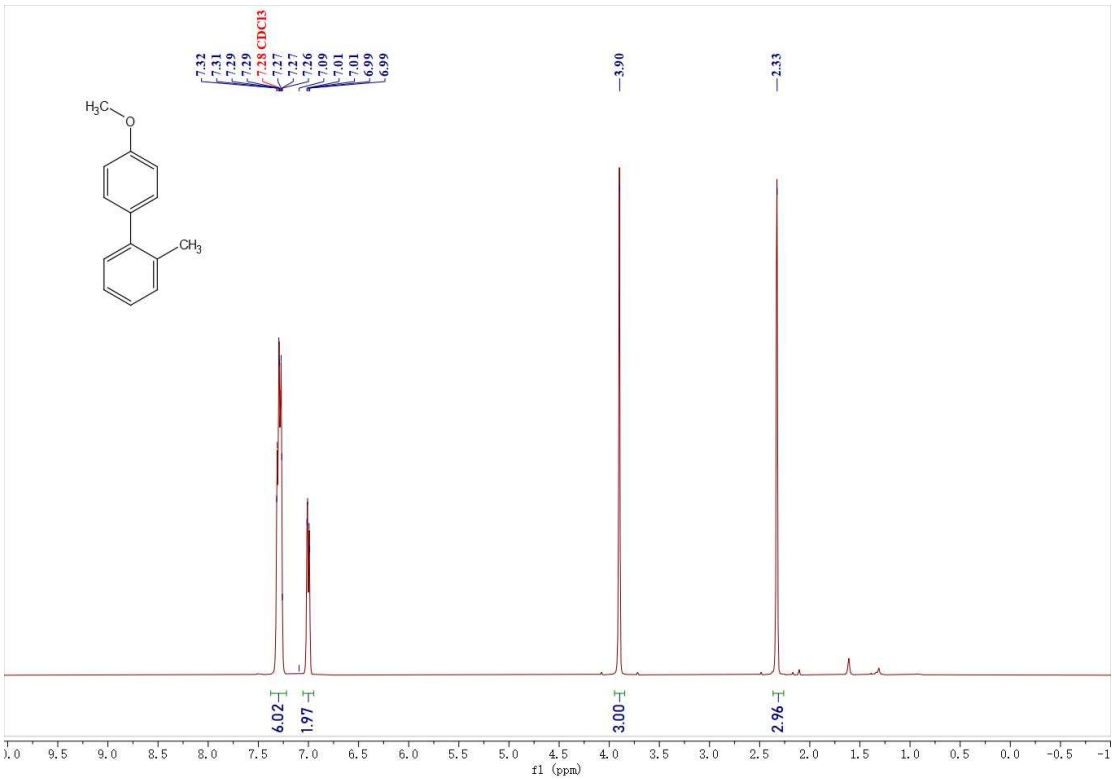
^{1}H NMR spectra of the compound 3m (400 MHz, $CDCl_3$)



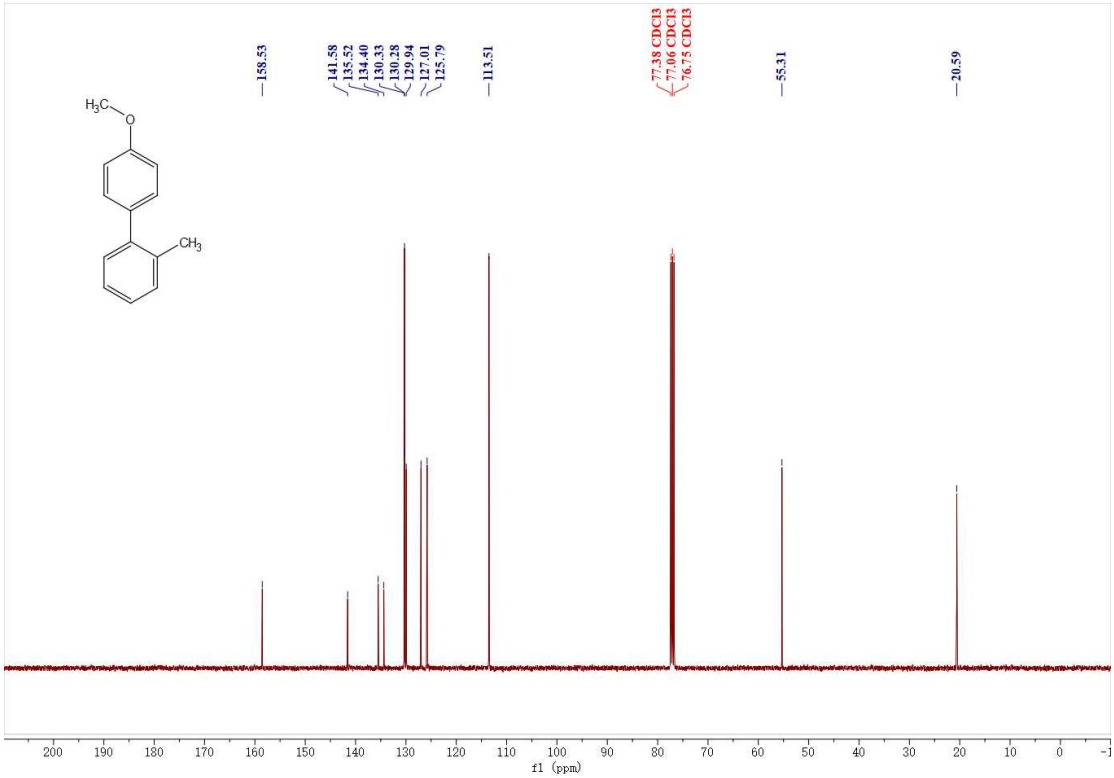
^{13}C NMR spectra of the compound 3m (101 MHz, $CDCl_3$)



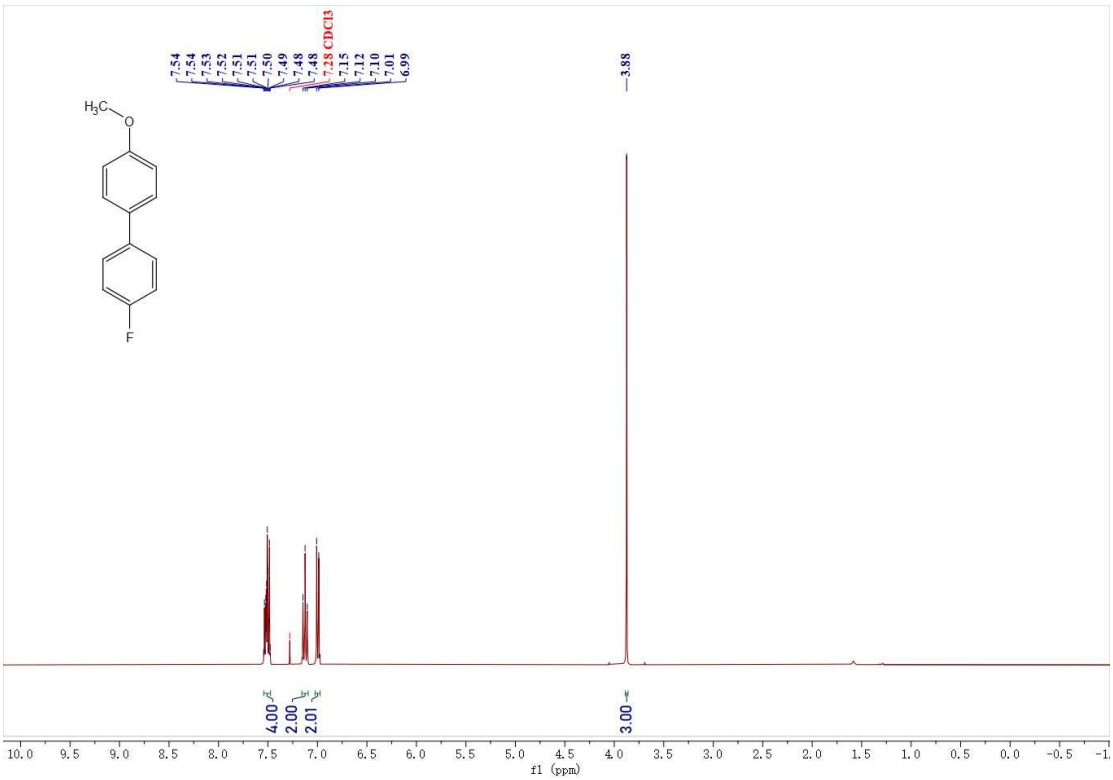
^{1}H NMR spectra of the compound 3n (400 MHz, $CDCl_3$)



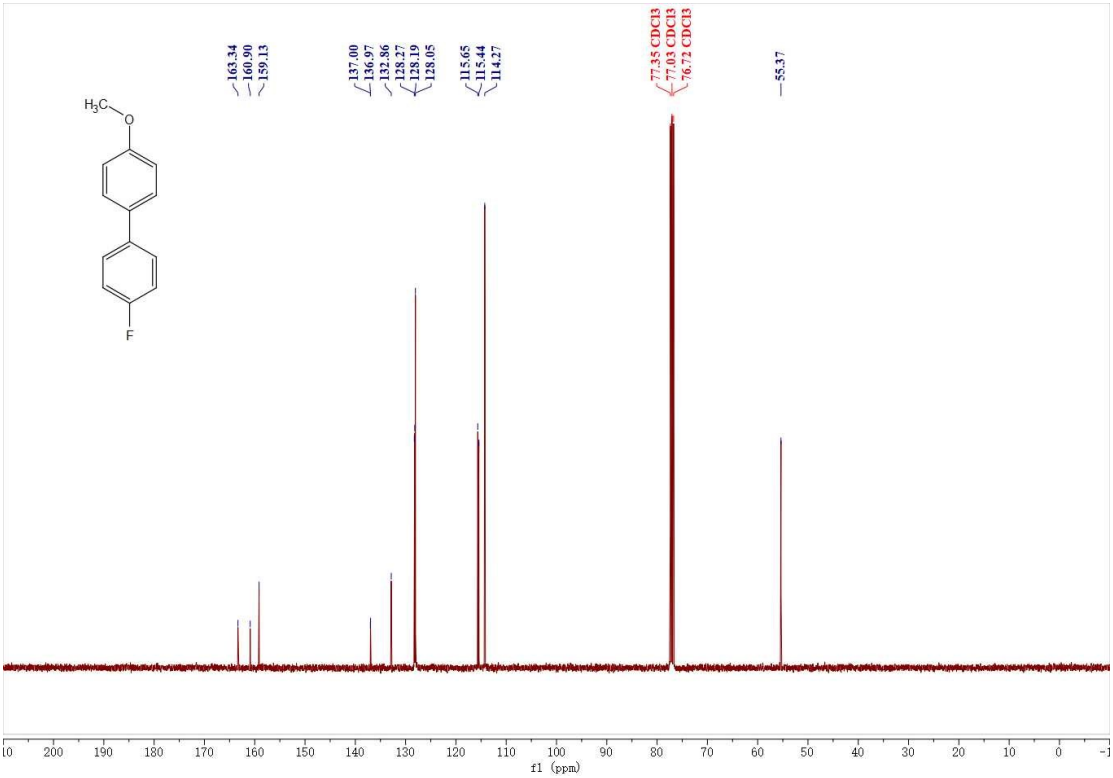
^{13}C NMR spectra of the compound 3n (101 MHz, $CDCl_3$)



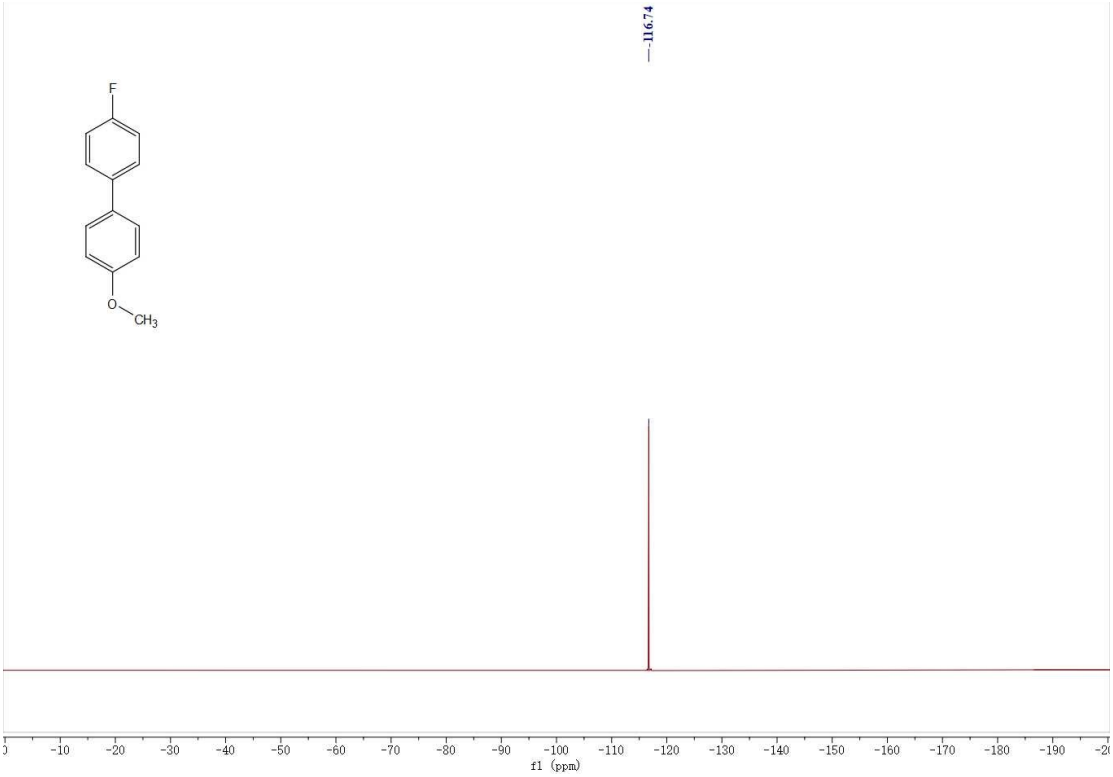
^{1}H NMR spectra of the compound 3o (400 MHz, $CDCl_3$)



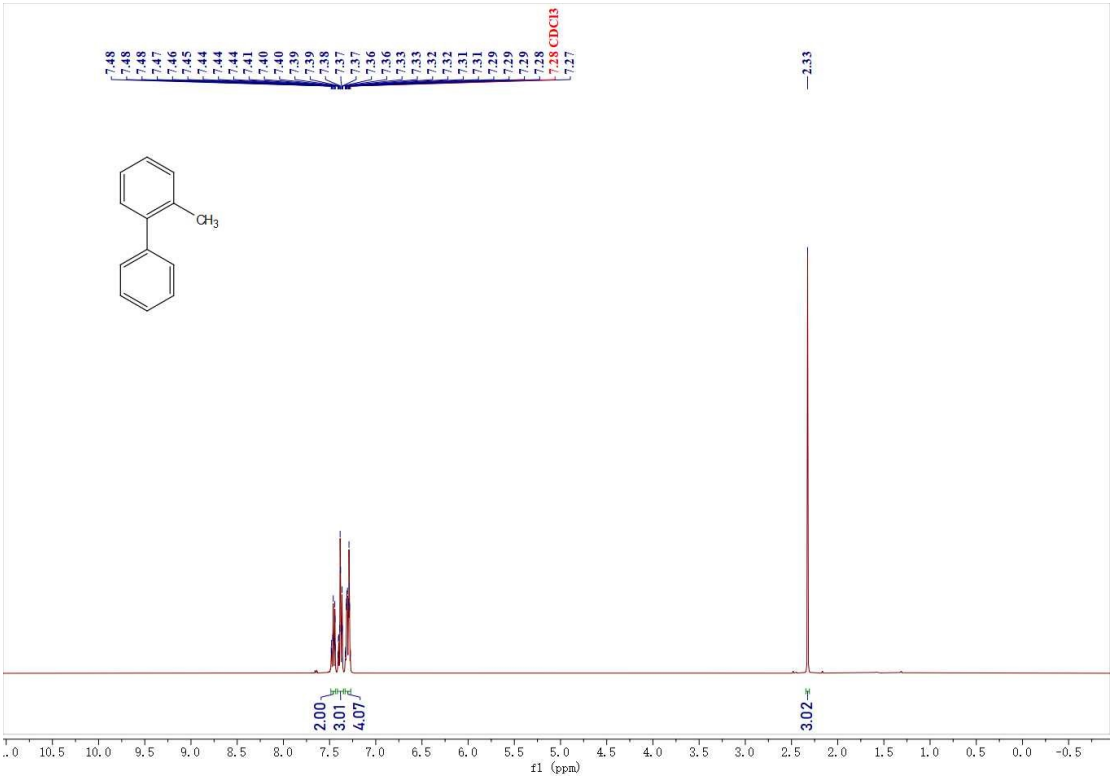
^{13}C NMR spectra of the compound 3o (101 MHz, $CDCl_3$)



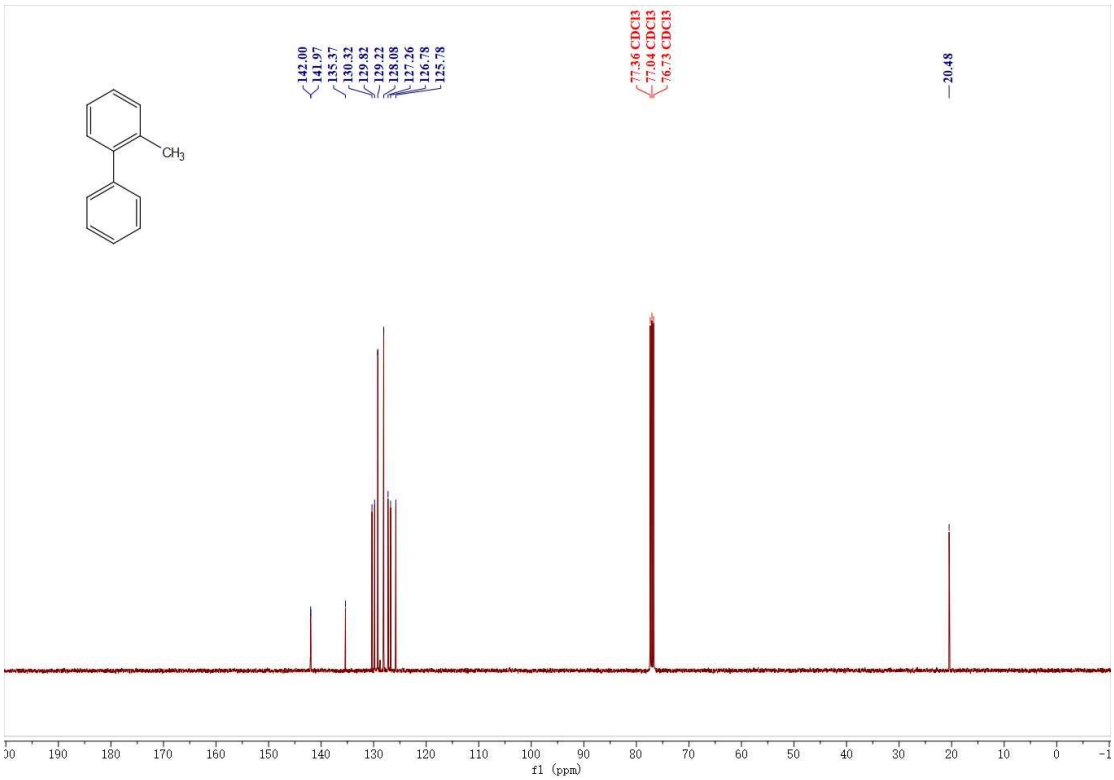
^{19}F spectra of the compound 3o (101 MHz, $CDCl_3$)



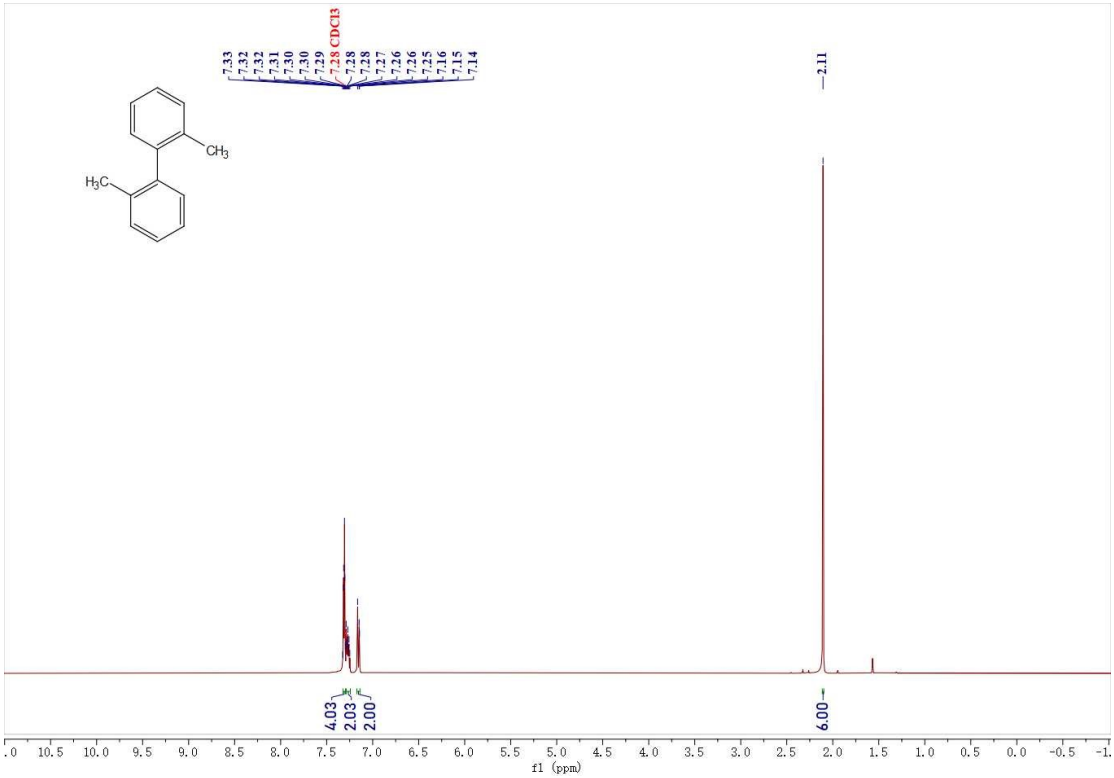
^{1}H NMR spectra of the compound 3p (400 MHz, $CDCl_3$)



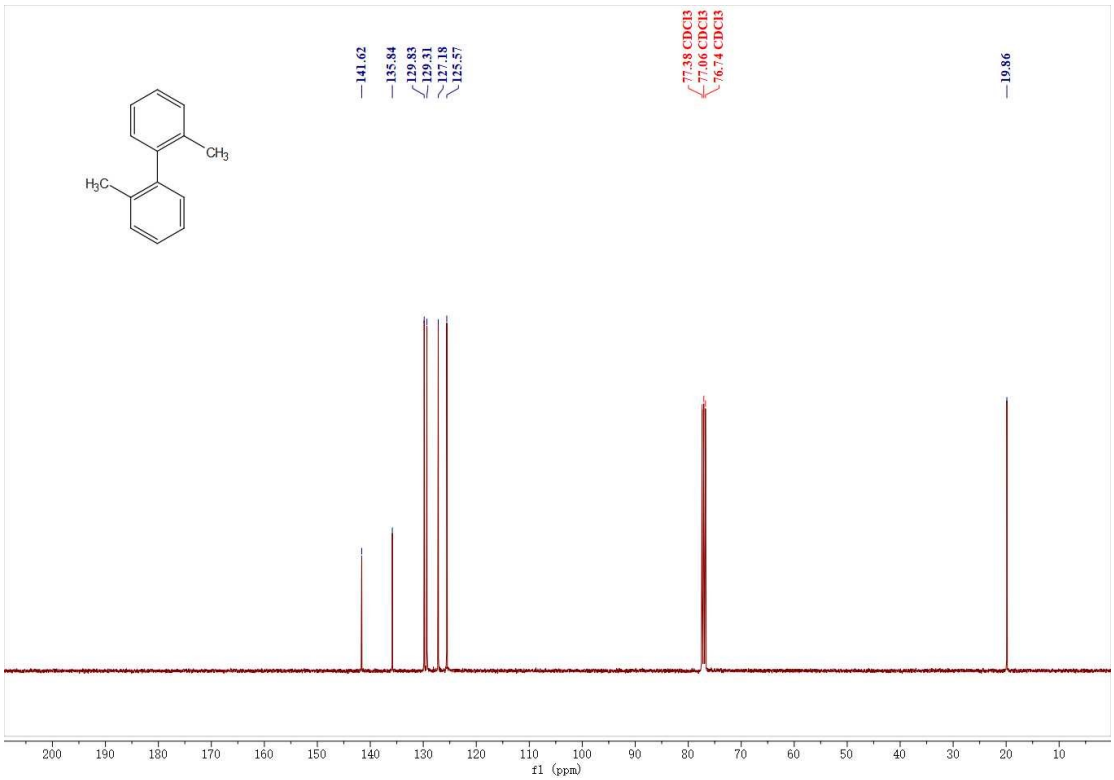
^{13}C NMR spectra of the compound 3p (101 MHz, $CDCl_3$)



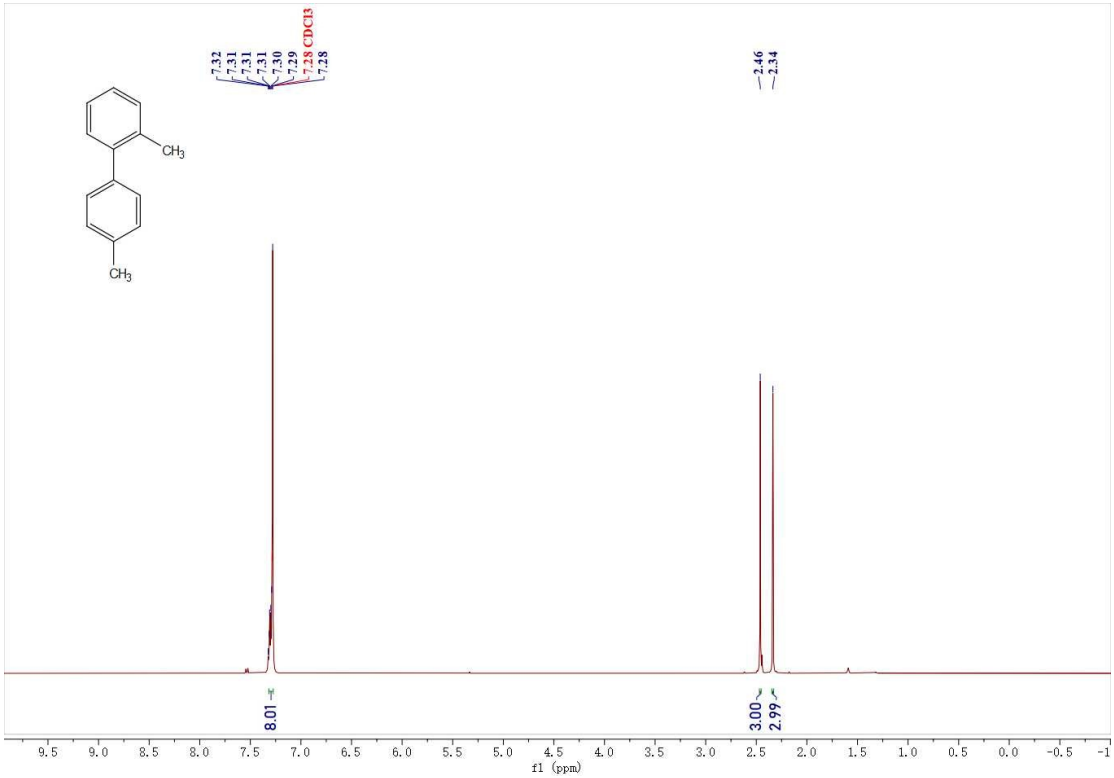
^{1}H NMR spectra of the compound 3q (400 MHz, $CDCl_3$)



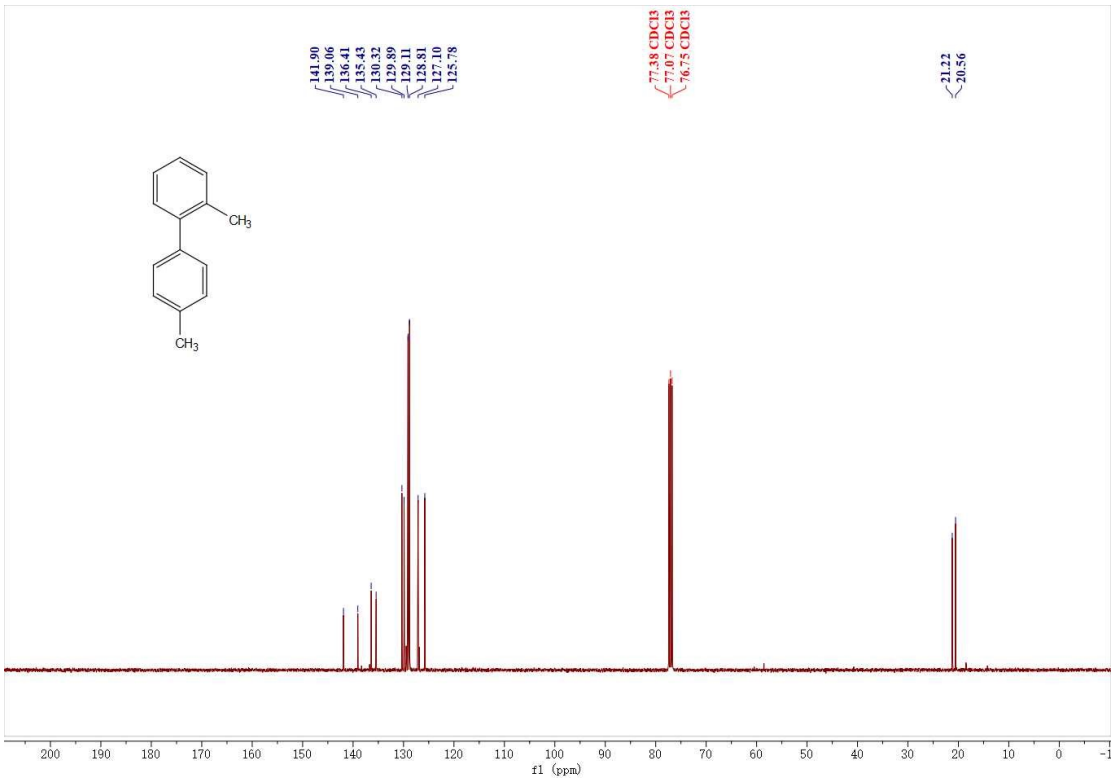
^{13}C NMR spectra of the compound 3q (101 MHz, $CDCl_3$)



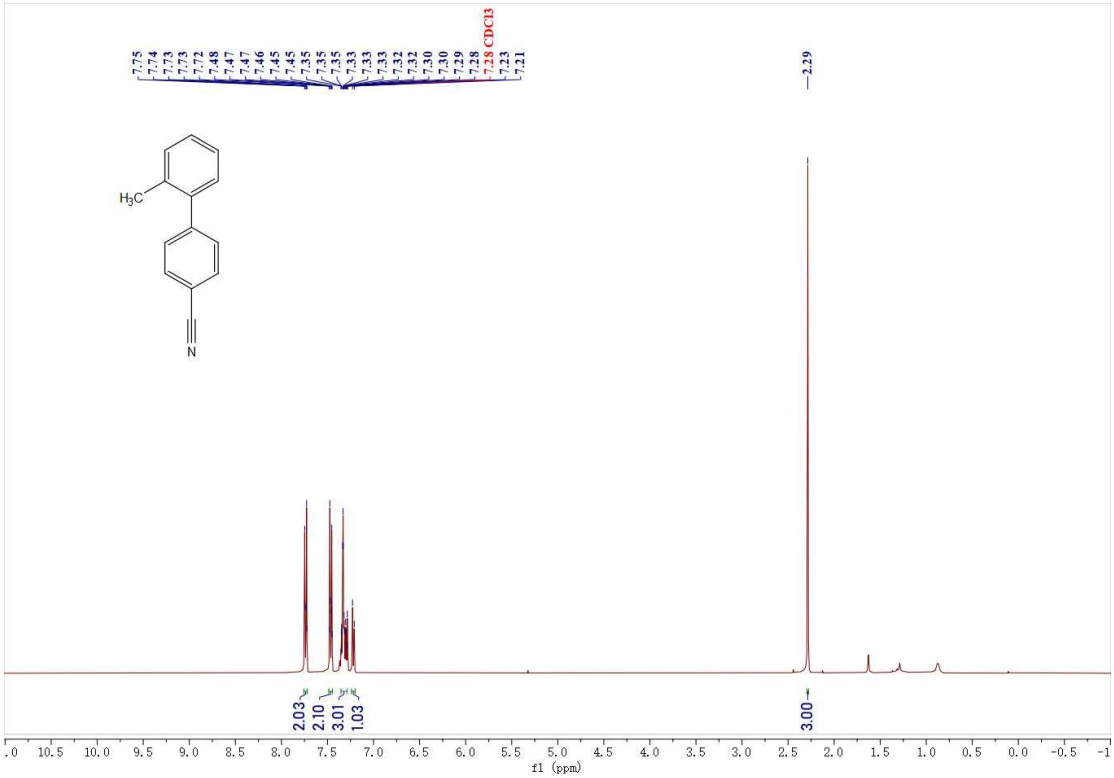
^{1}H NMR spectra of the compound 3r (400 MHz, $CDCl_3$)



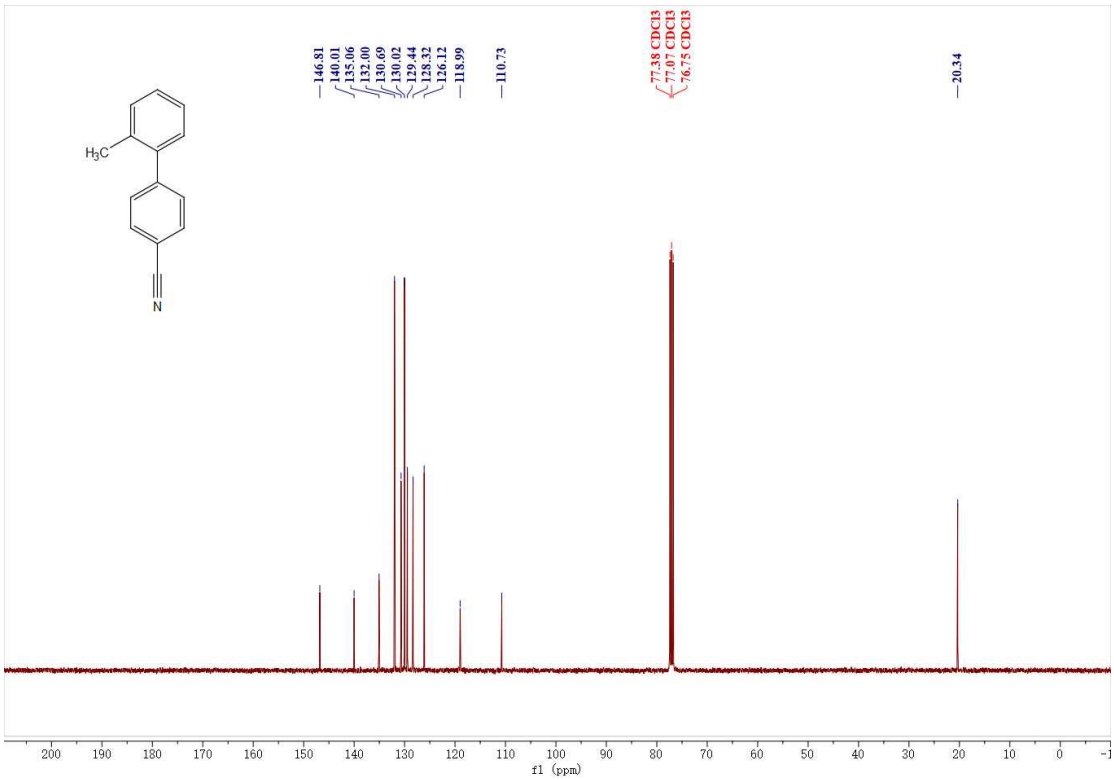
^{13}C NMR spectra of the compound 3r (101 MHz, $CDCl_3$)



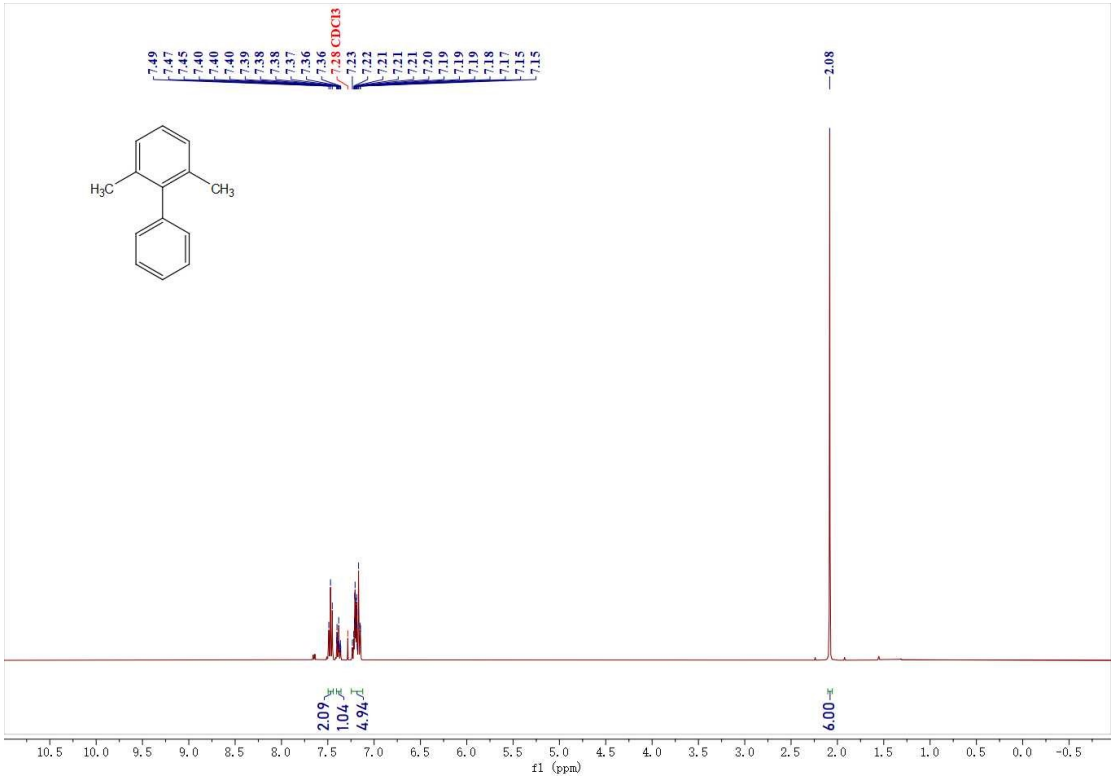
^{1}H NMR spectra of the compound 3s (400 MHz, $CDCl_3$)



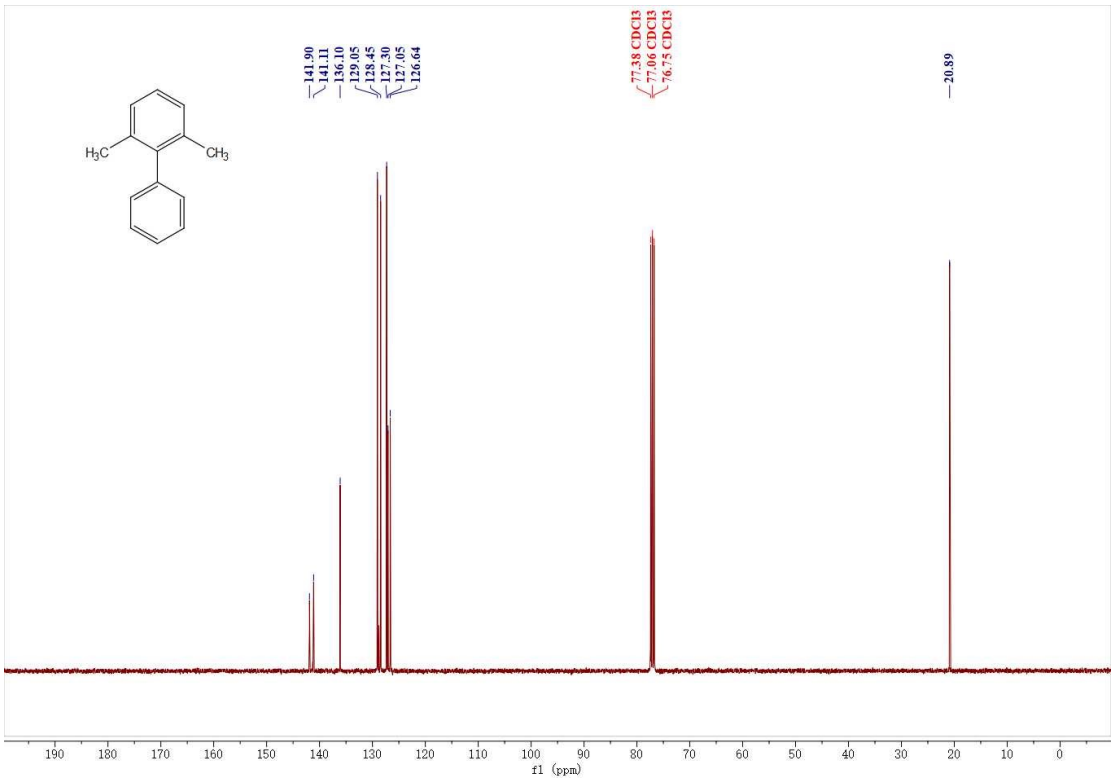
^{13}C NMR spectra of the compound 3s (101 MHz, $CDCl_3$)



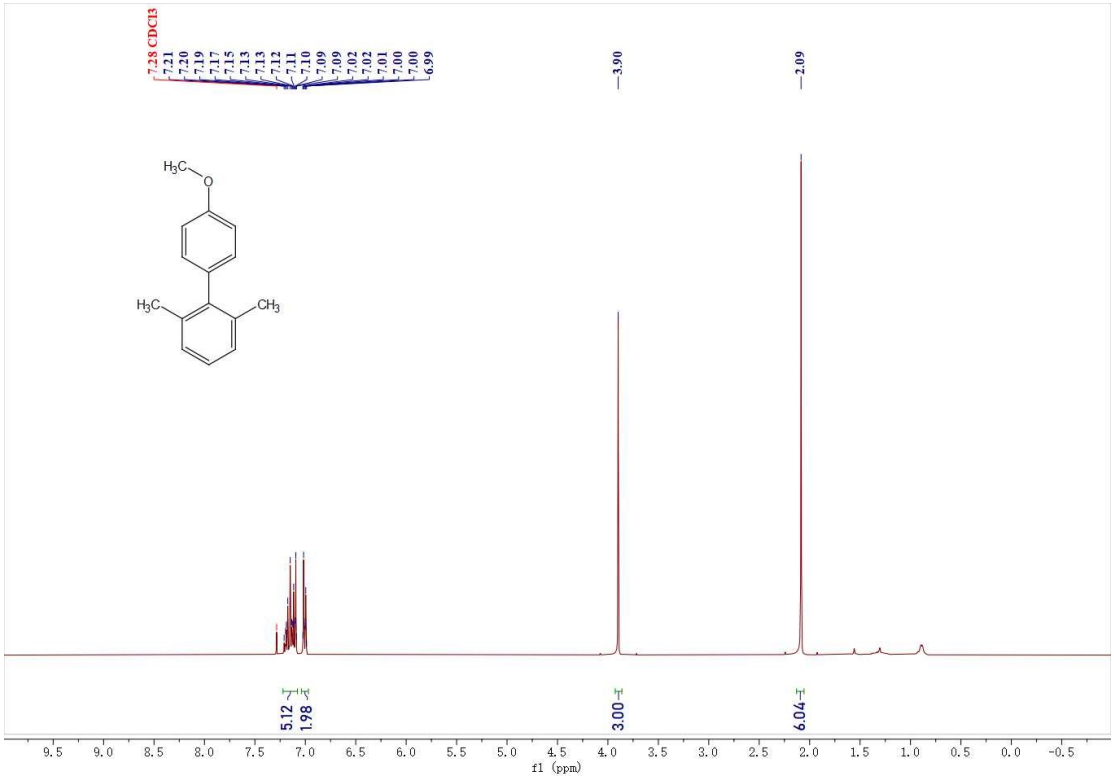
^{1}H NMR spectra of the compound 3t (400 MHz, $CDCl_3$)



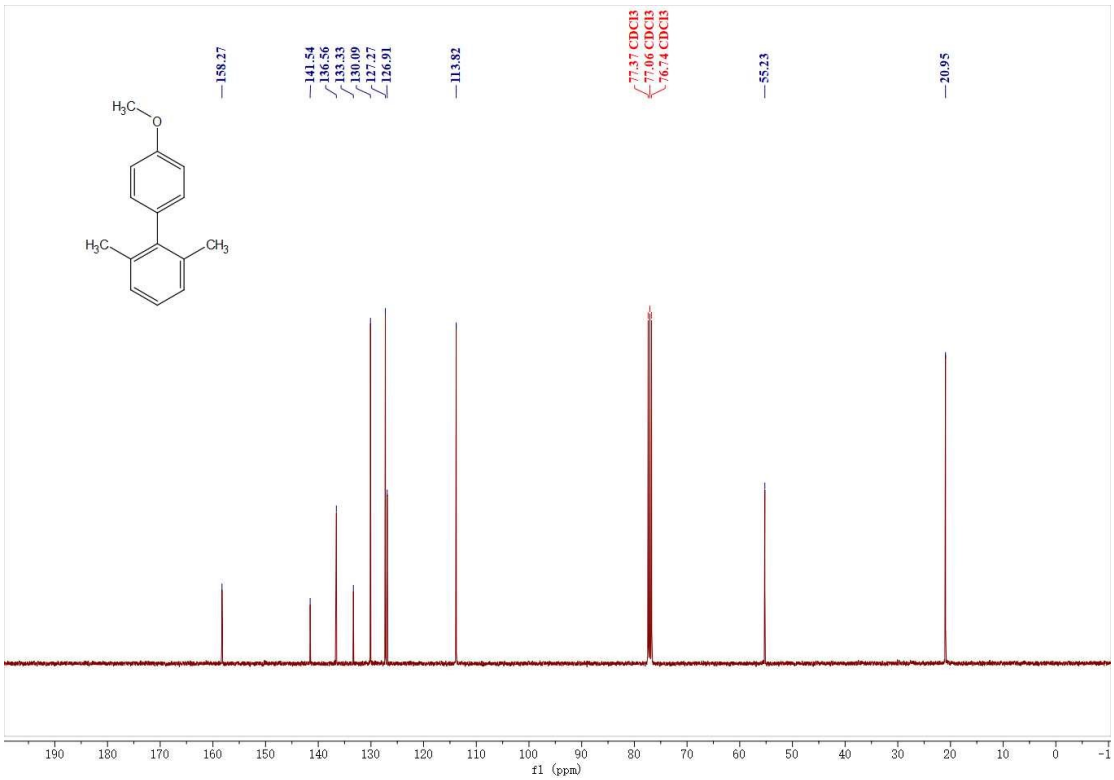
^{13}C NMR spectra of the compound 3t (101 MHz, $CDCl_3$)



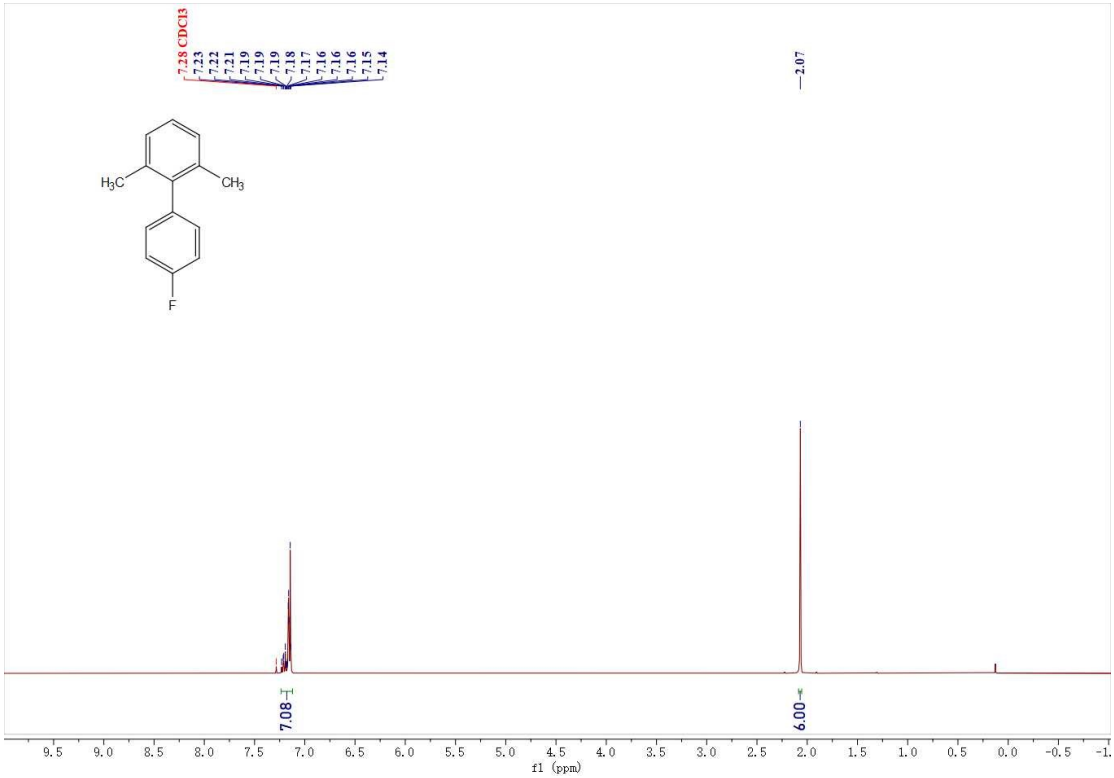
^{1}H NMR spectra of the compound 3u (400 MHz, $CDCl_3$)



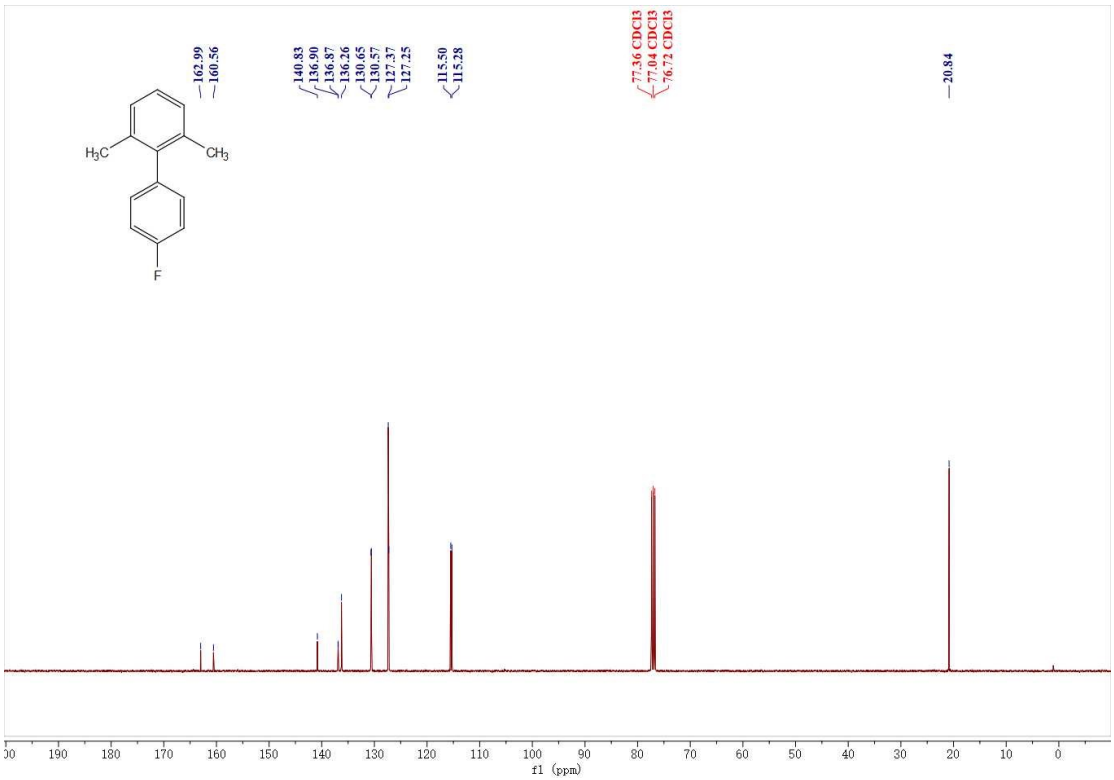
^{13}C NMR spectra of the compound 3u (101 MHz, $CDCl_3$)



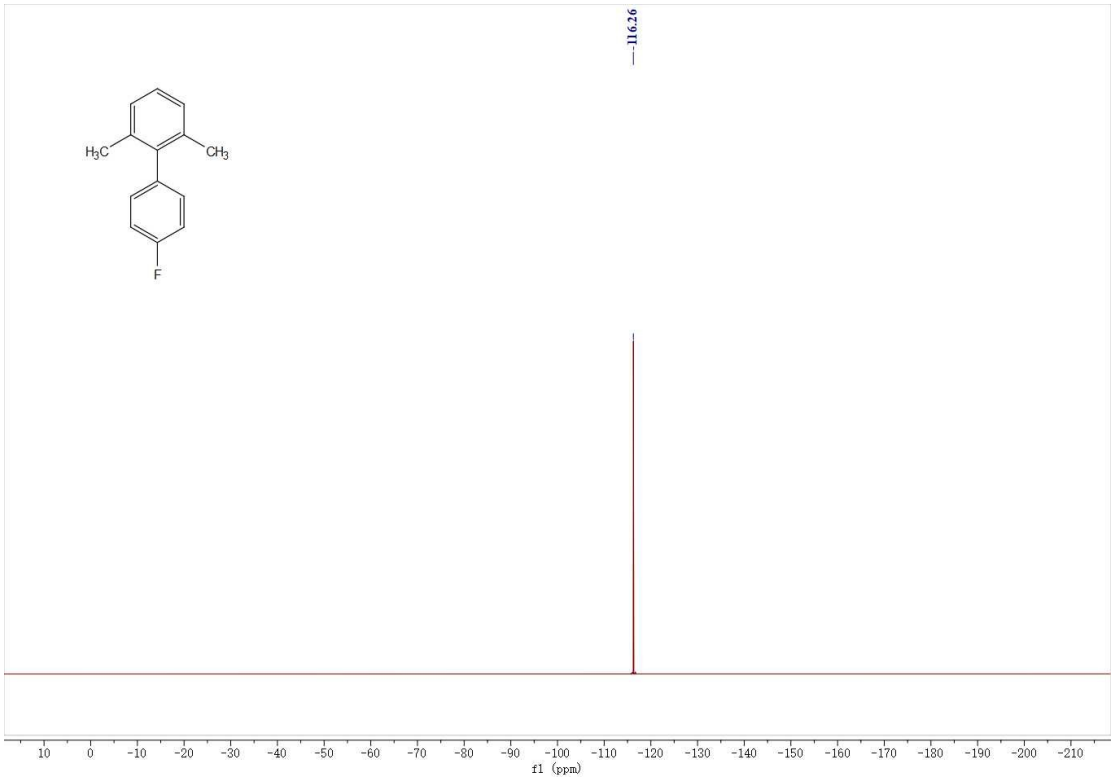
^{1}H NMR spectra of the compound 3v (400 MHz, $CDCl_3$)



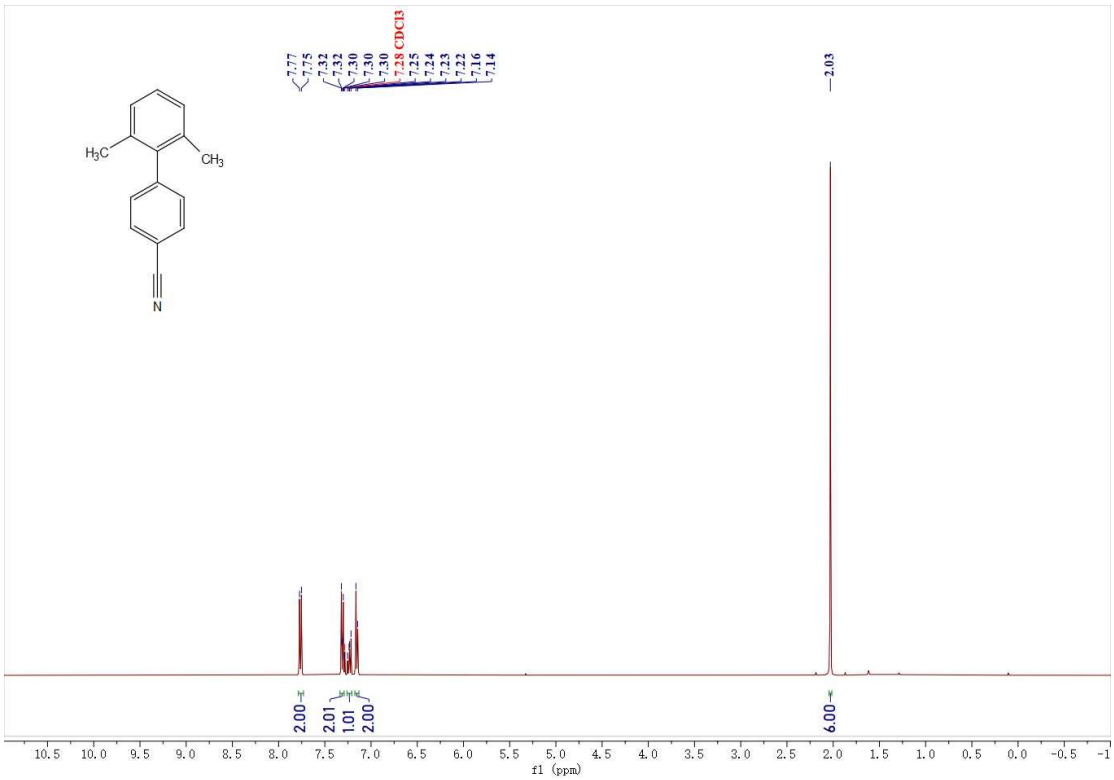
^{13}C NMR spectra of the compound 3v (101 MHz, $CDCl_3$)



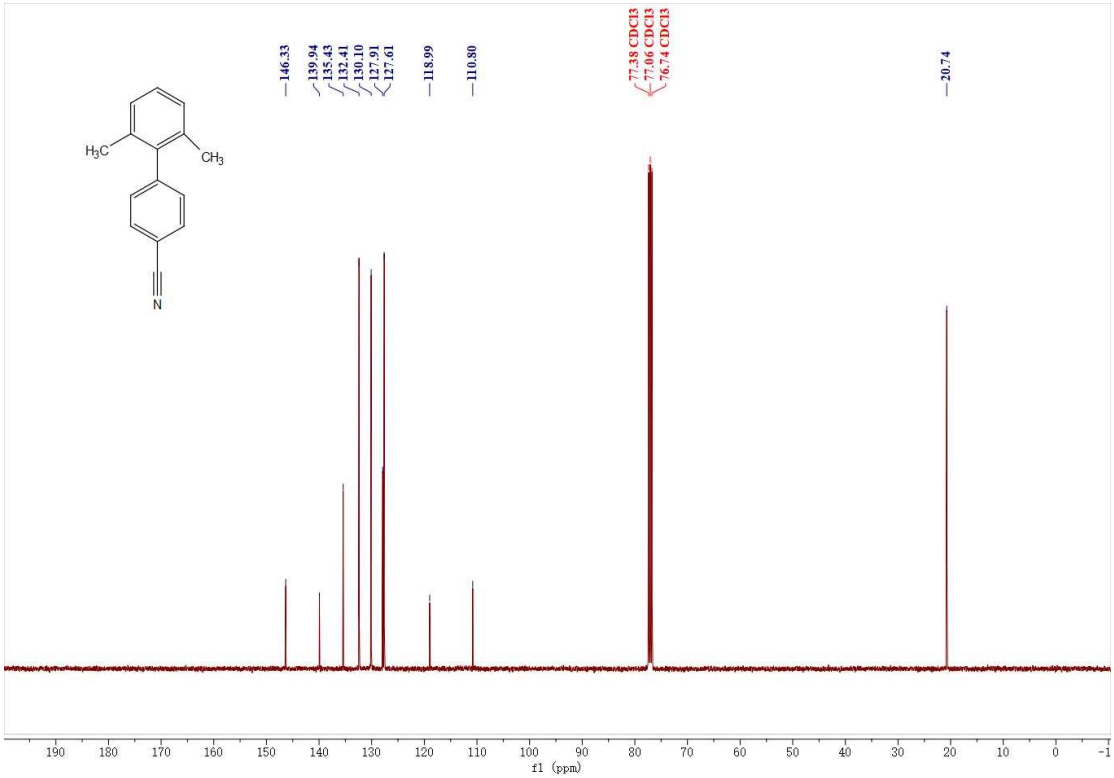
^{19}F spectra of the compound 3e (101 MHz, $CDCl_3$)



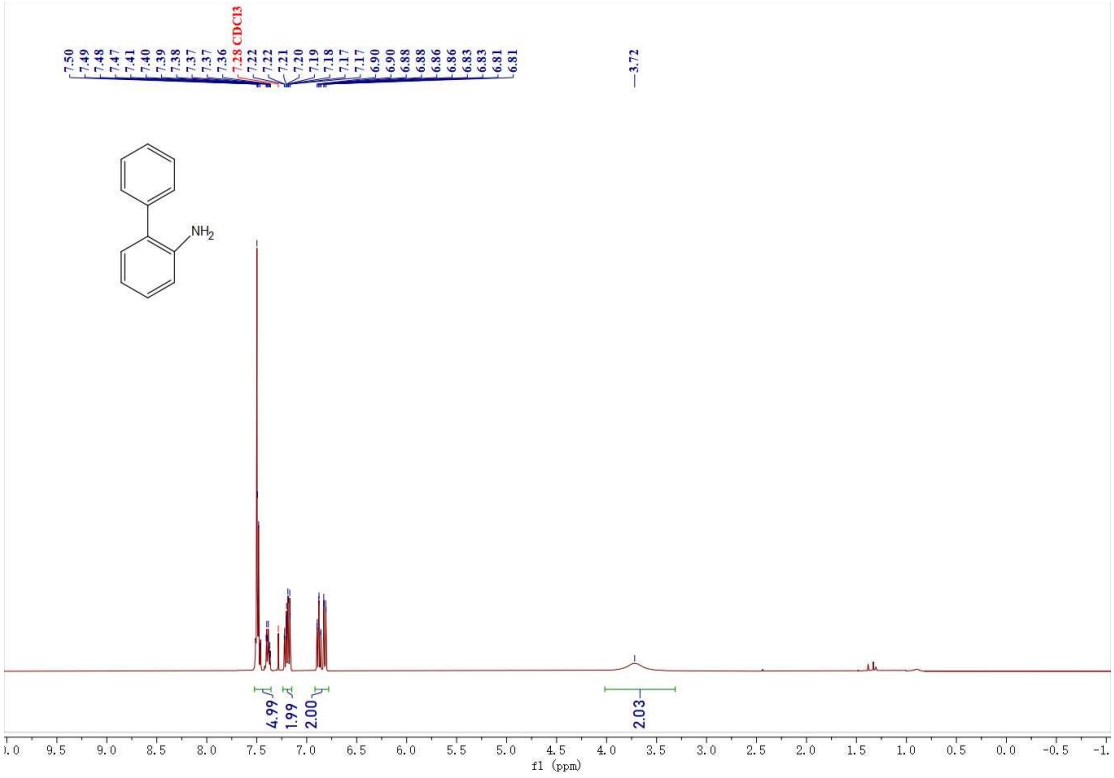
^{1}H NMR spectra of the compound 3w (400 MHz, $CDCl_3$)



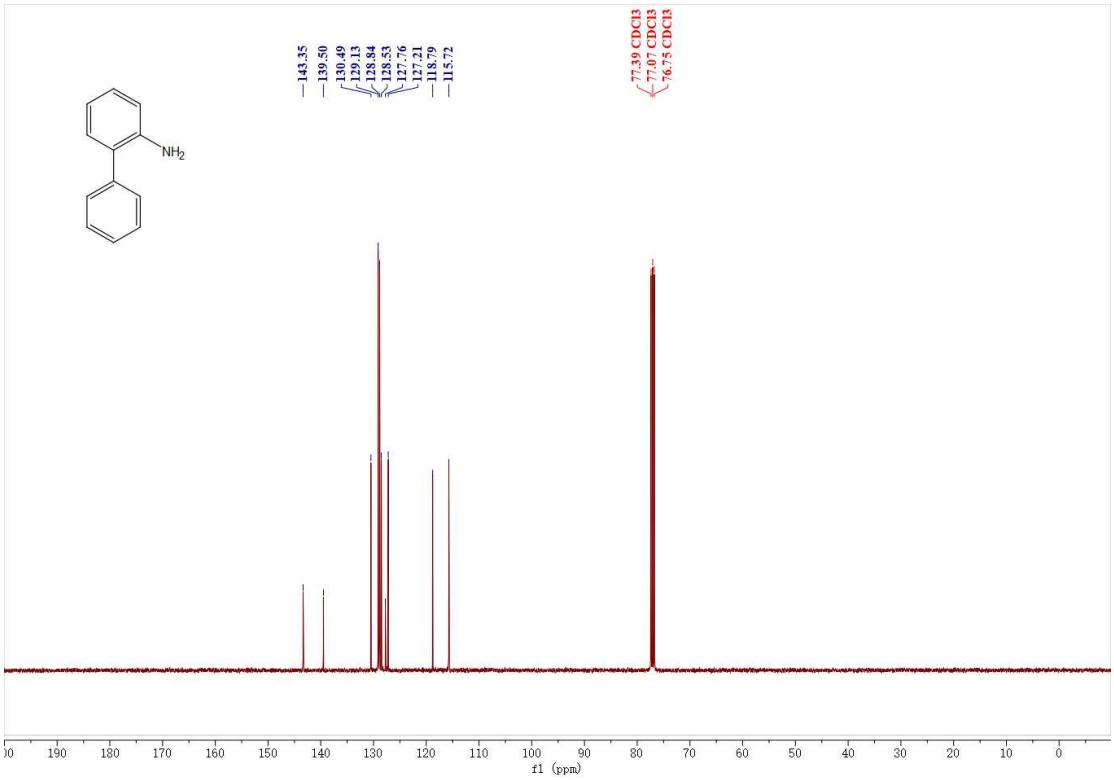
^{13}C NMR spectra of the compound 3w (101 MHz, $CDCl_3$)



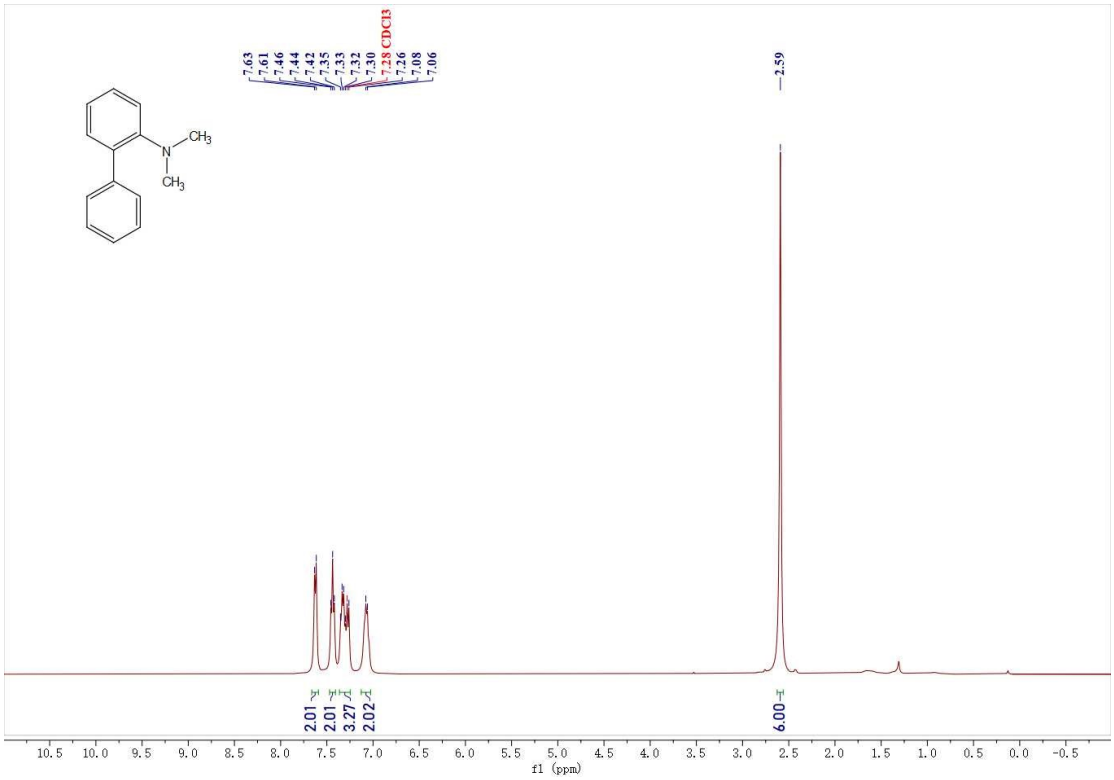
^{1}H NMR spectra of the compound 3y (400 MHz, $CDCl_3$)



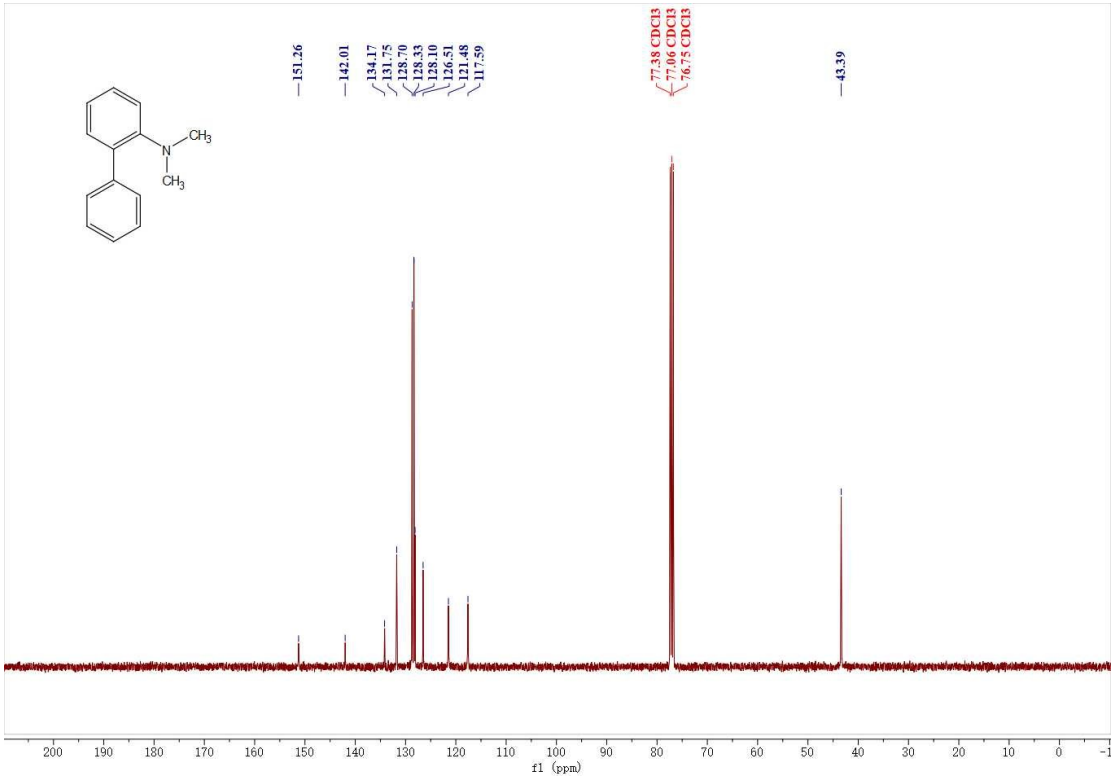
^{13}C NMR spectra of the compound 3y (101 MHz, $CDCl_3$)



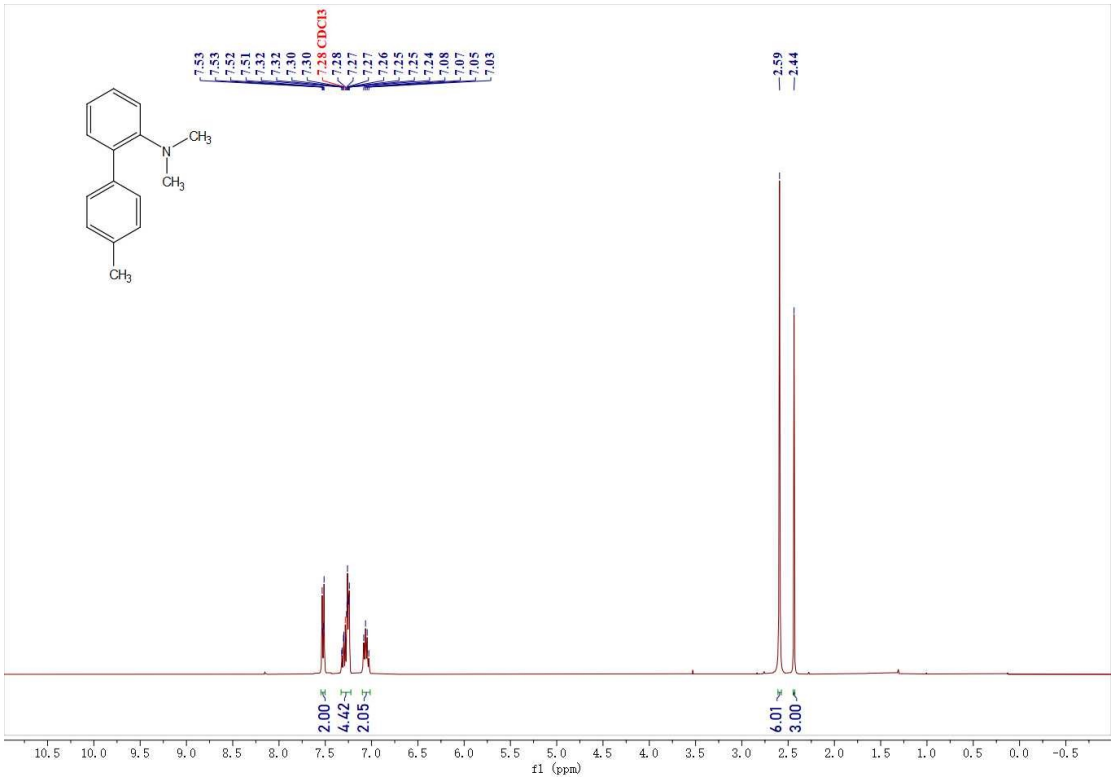
^{1}H NMR spectra of the compound 3z (400 MHz, $CDCl_3$)



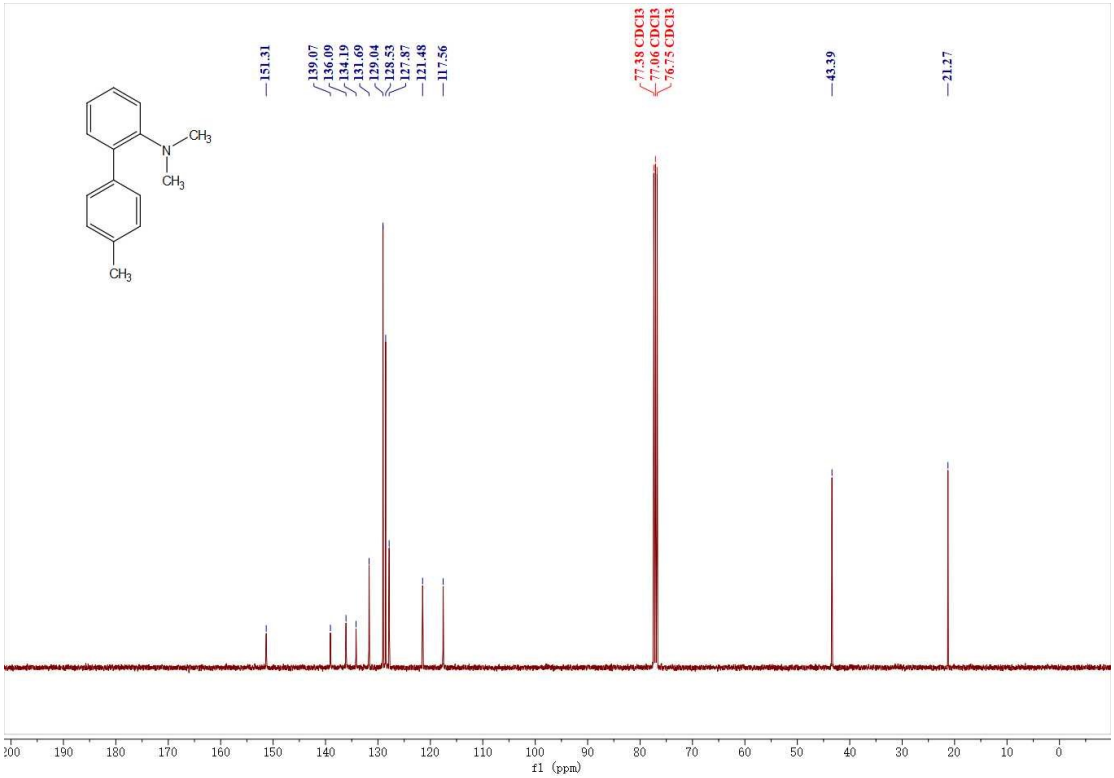
^{13}C NMR spectra of the compound 3z (101 MHz, $CDCl_3$)



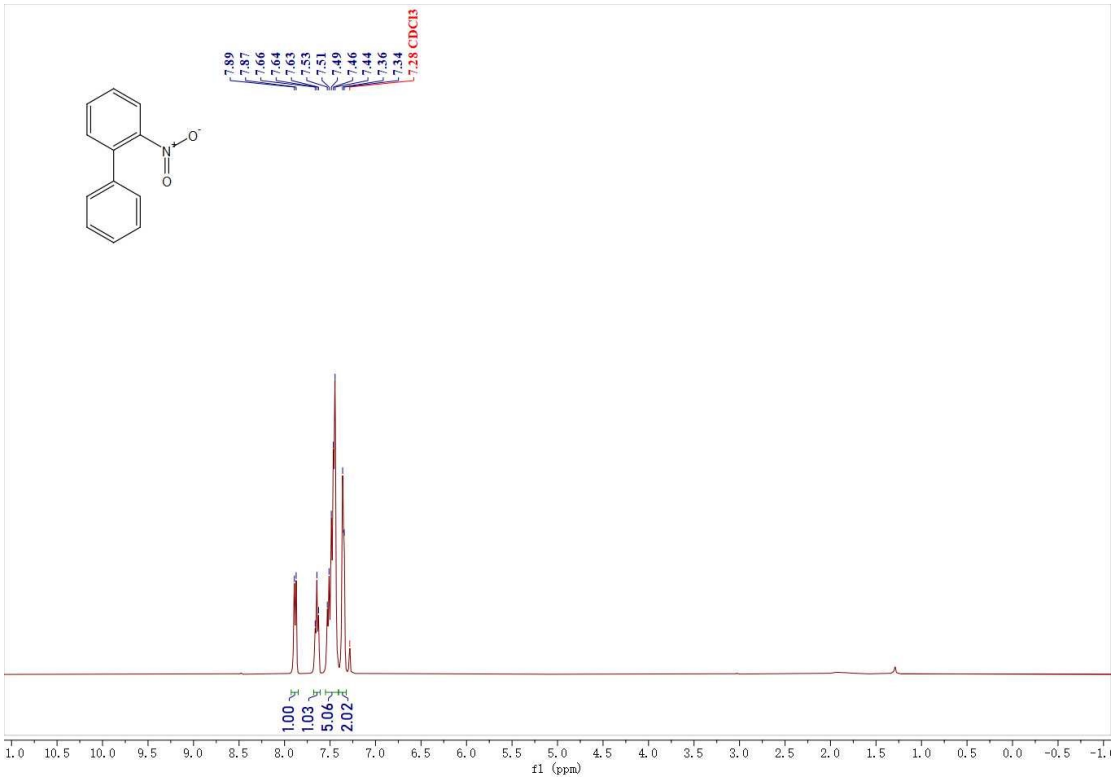
^{1}H NMR spectra of the compound 3aa (400 MHz, $CDCl_3$)



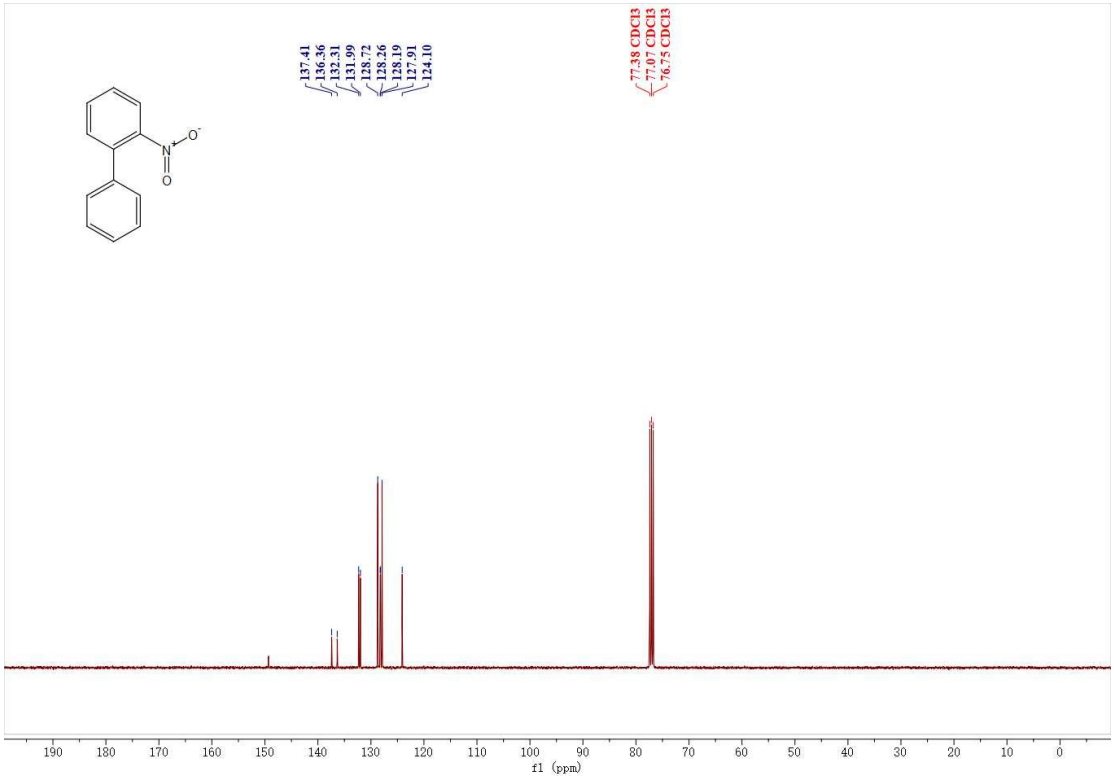
^{13}C NMR spectra of the compound 3aa (101 MHz, $CDCl_3$)



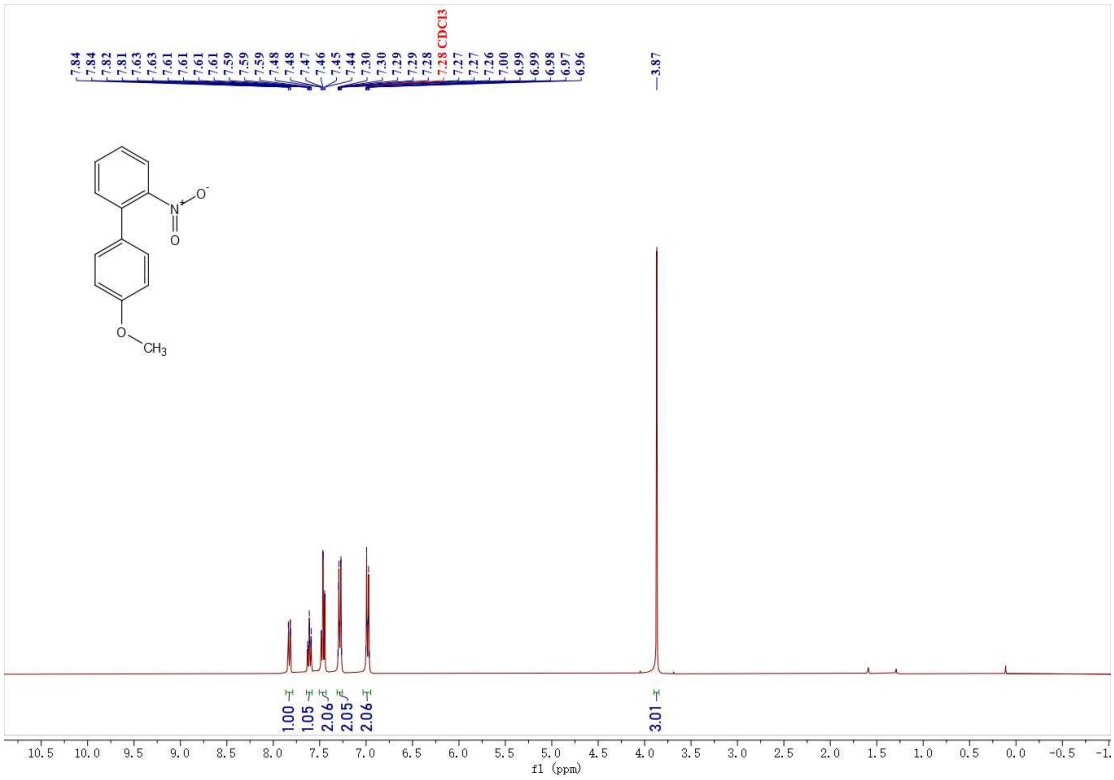
^{1}H NMR spectra of the compound 3bb (400 MHz, $CDCl_3$)



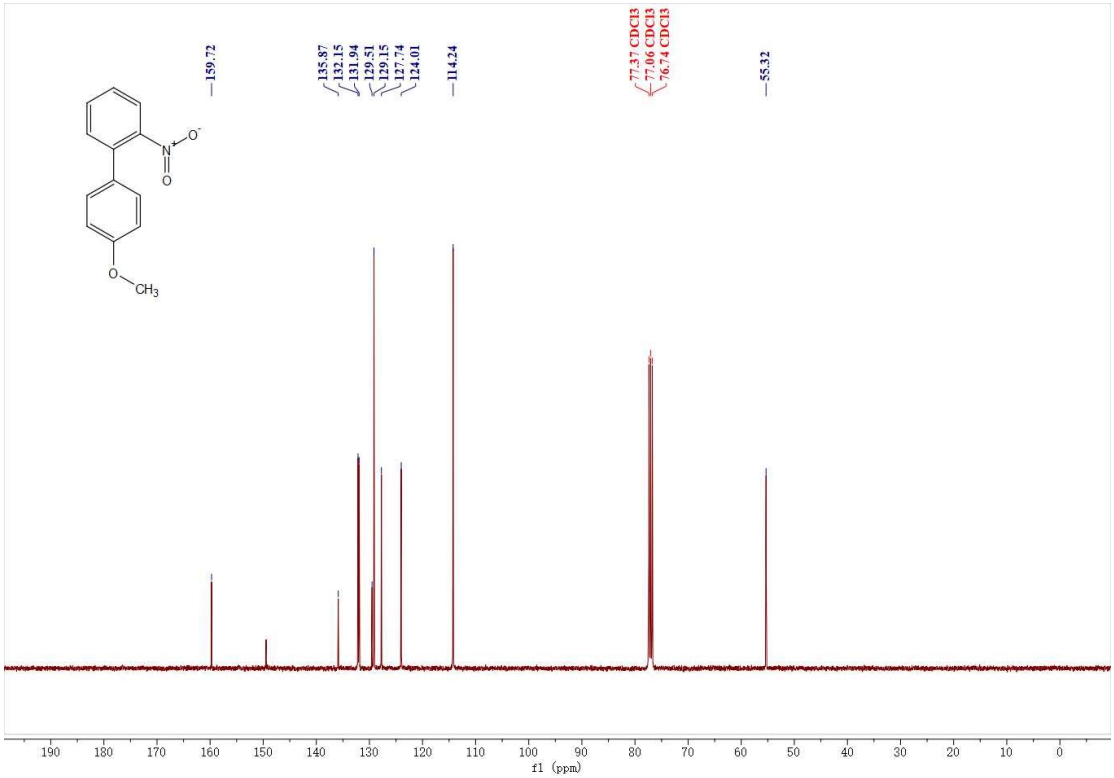
^{13}C NMR spectra of the compound 3bb (101 MHz, $CDCl_3$)



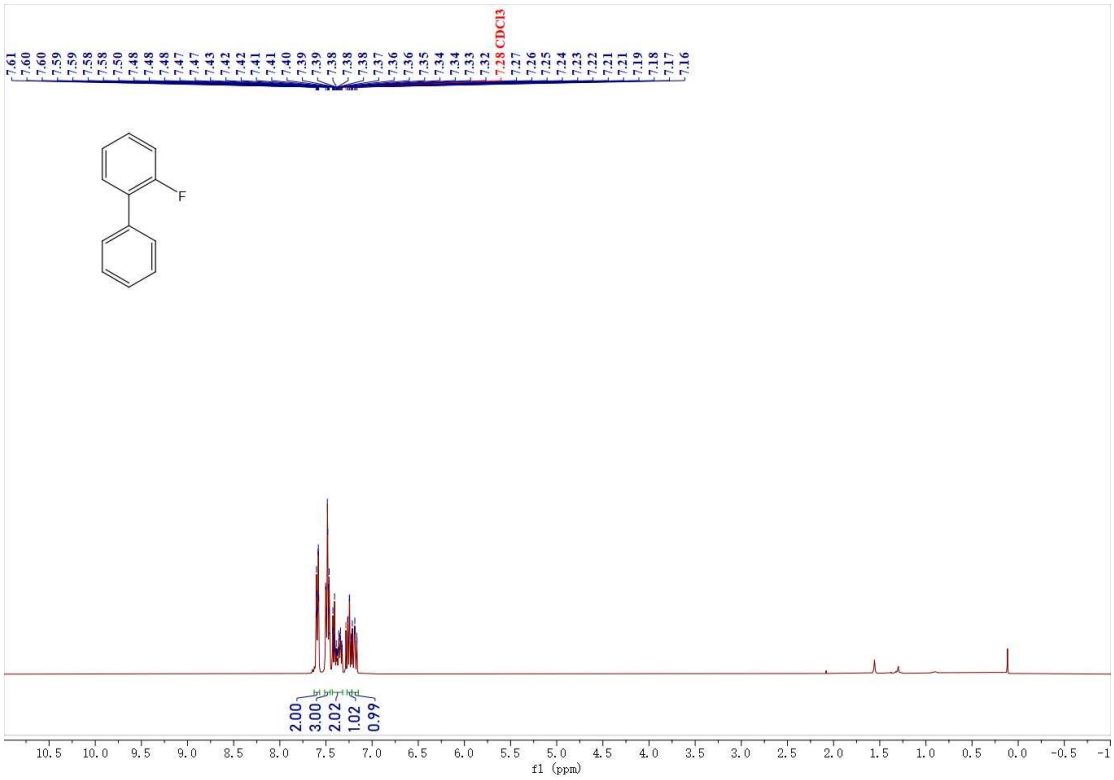
^{1}H NMR spectra of the compound 3cc (400 MHz, $CDCl_3$)



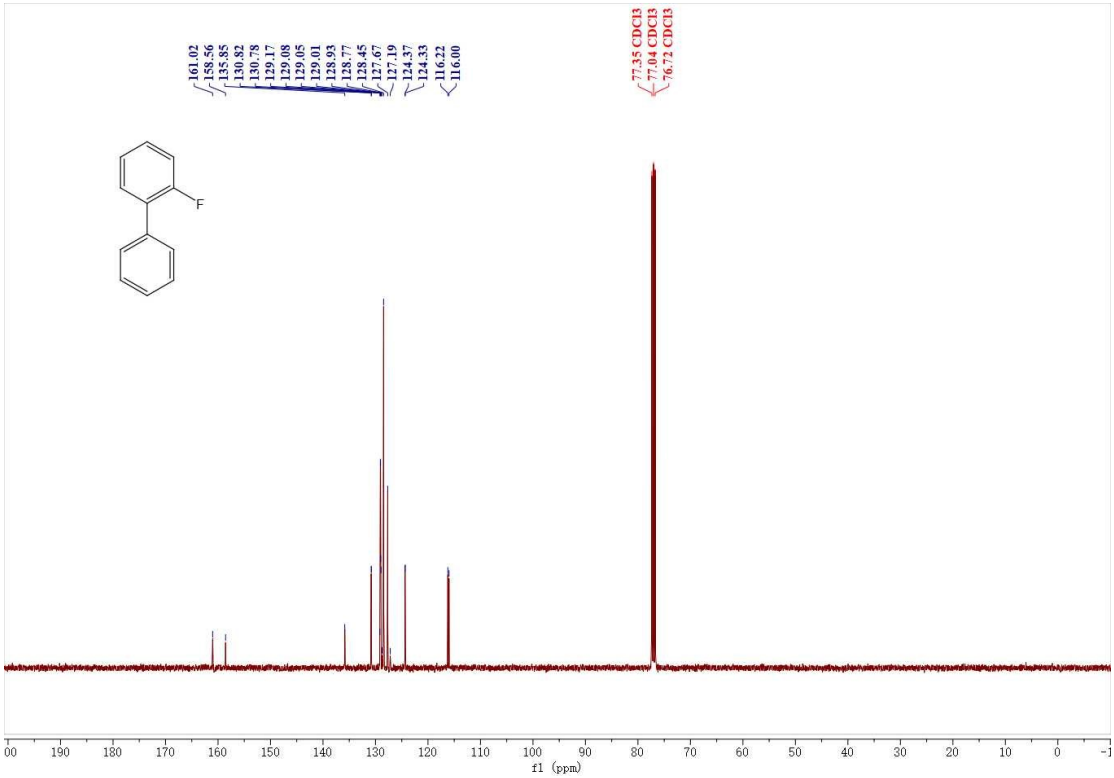
^{13}C NMR spectra of the compound 3cc (101 MHz, $CDCl_3$)



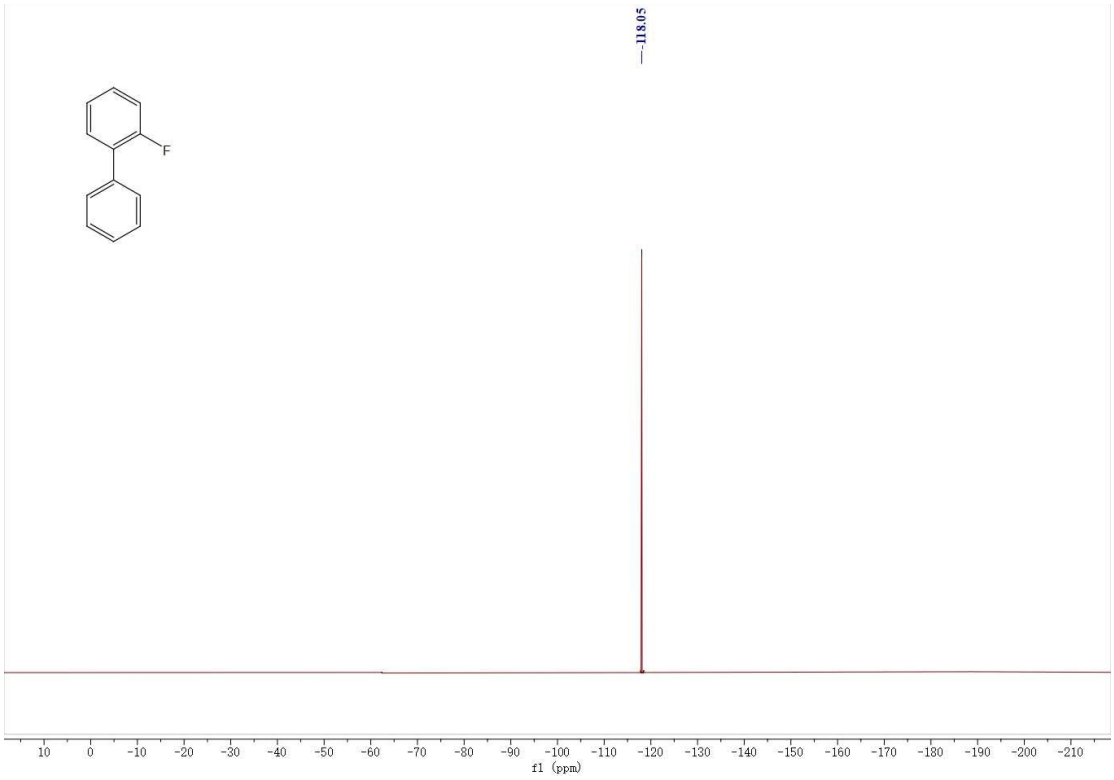
^{1}H NMR spectra of the compound 3dd (400 MHz, $CDCl_3$)



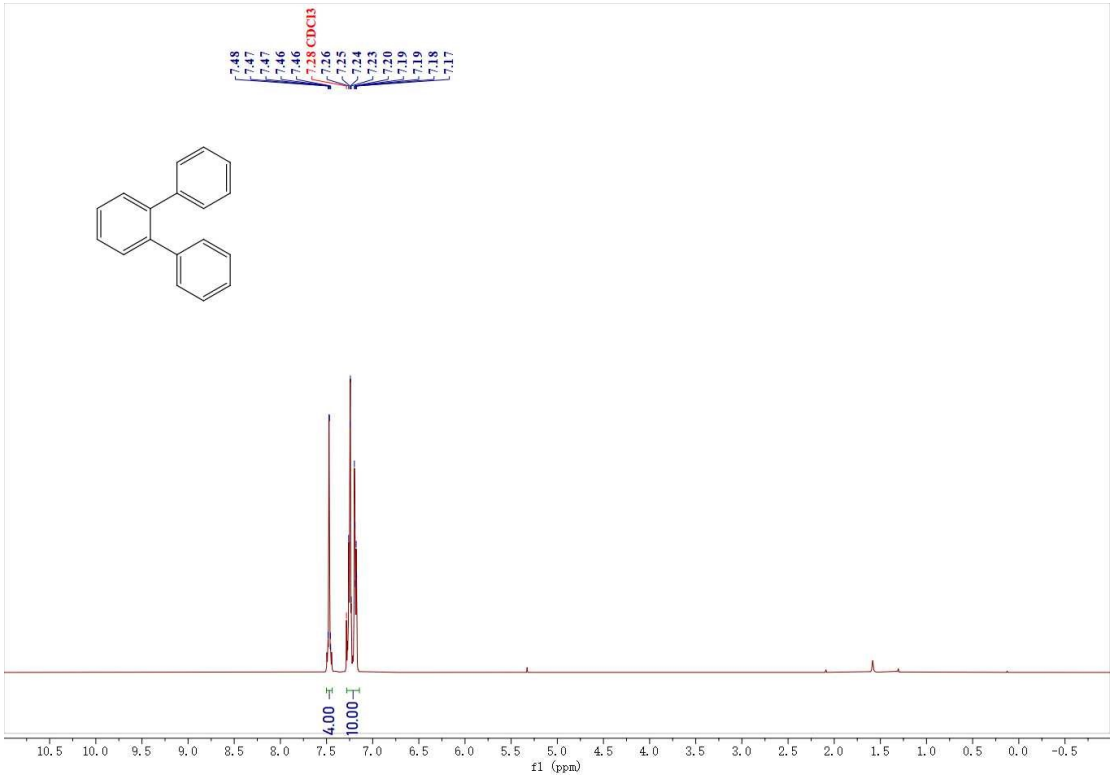
^{13}C NMR spectra of the compound 3dd (101 MHz, $CDCl_3$)



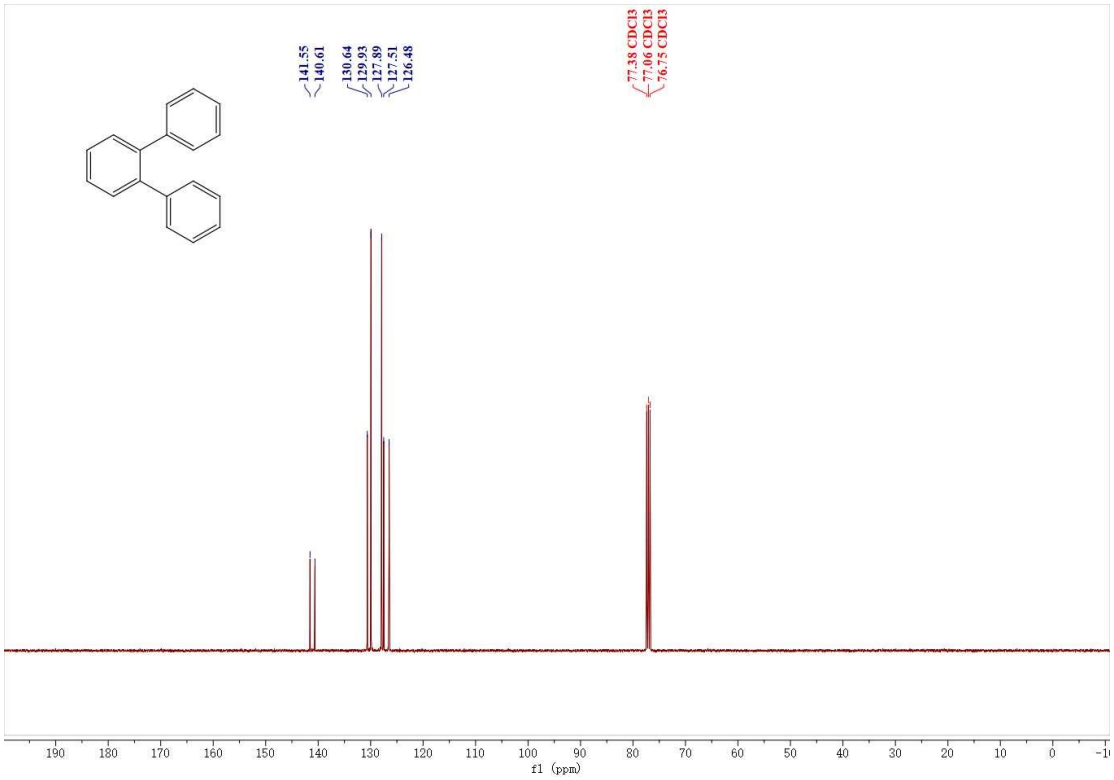
^{19}F spectra of the compound 3dd (101 MHz, $CDCl_3$)



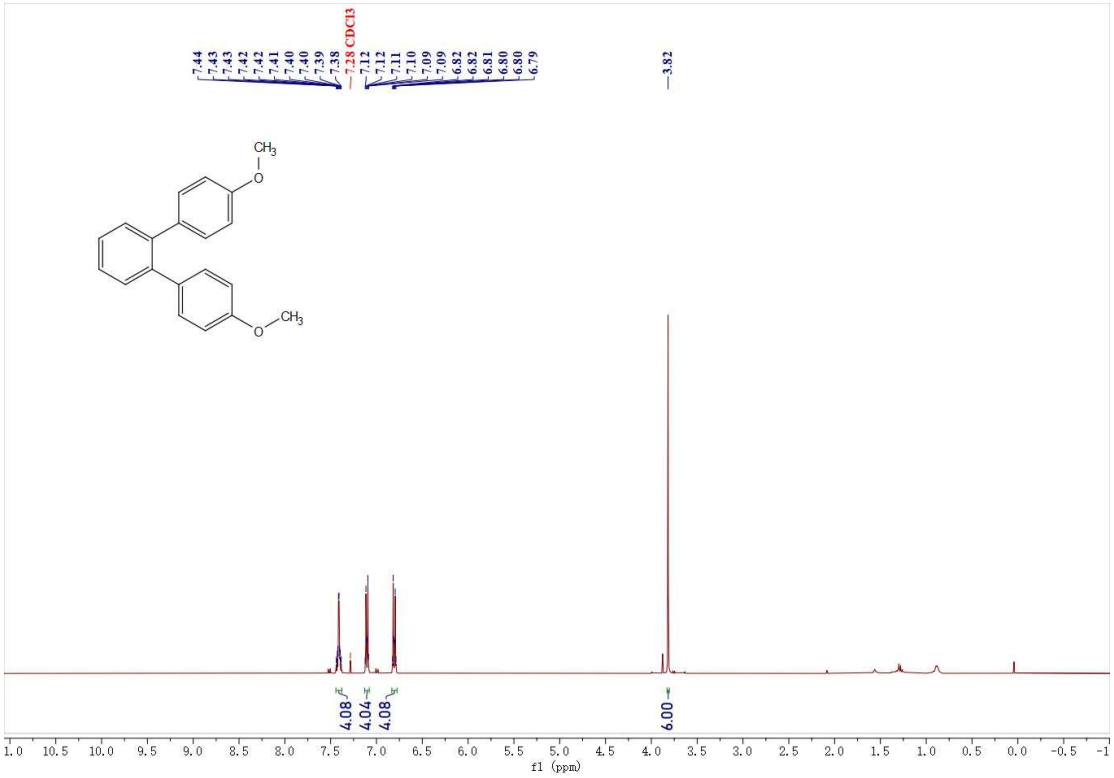
^{1}H NMR spectra of the compound 4a (400 MHz, $CDCl_3$)



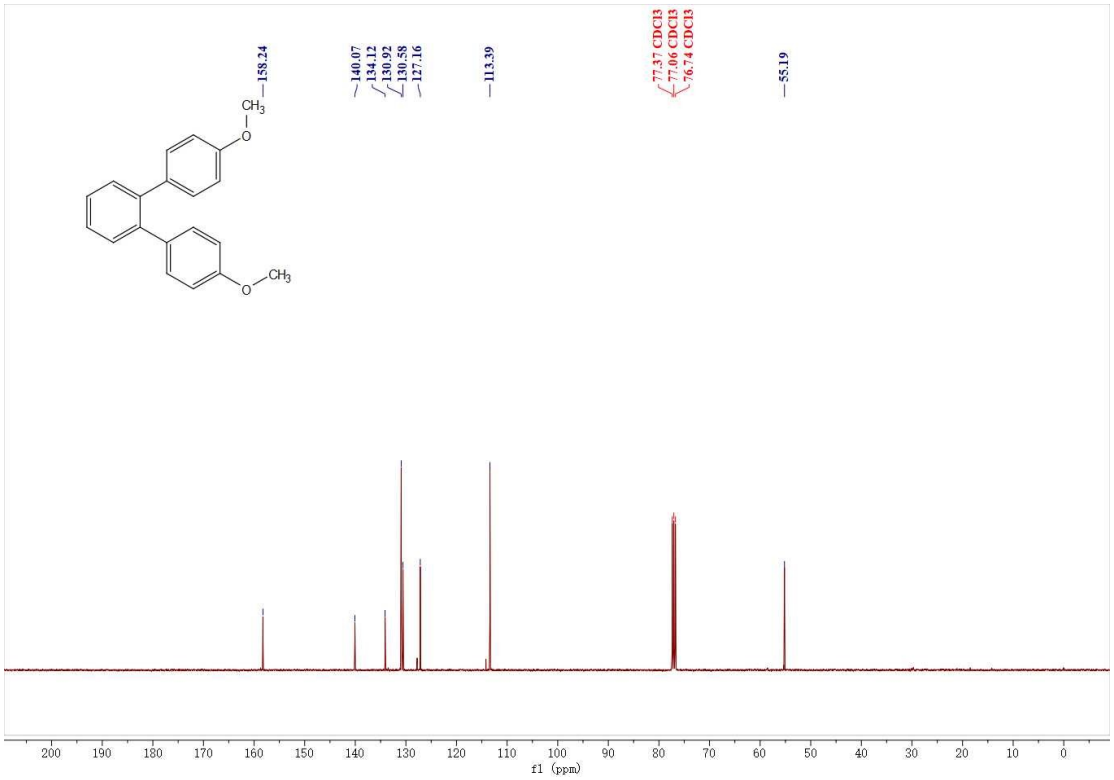
^{13}C NMR spectra of the compound 4a (101 MHz, $CDCl_3$)



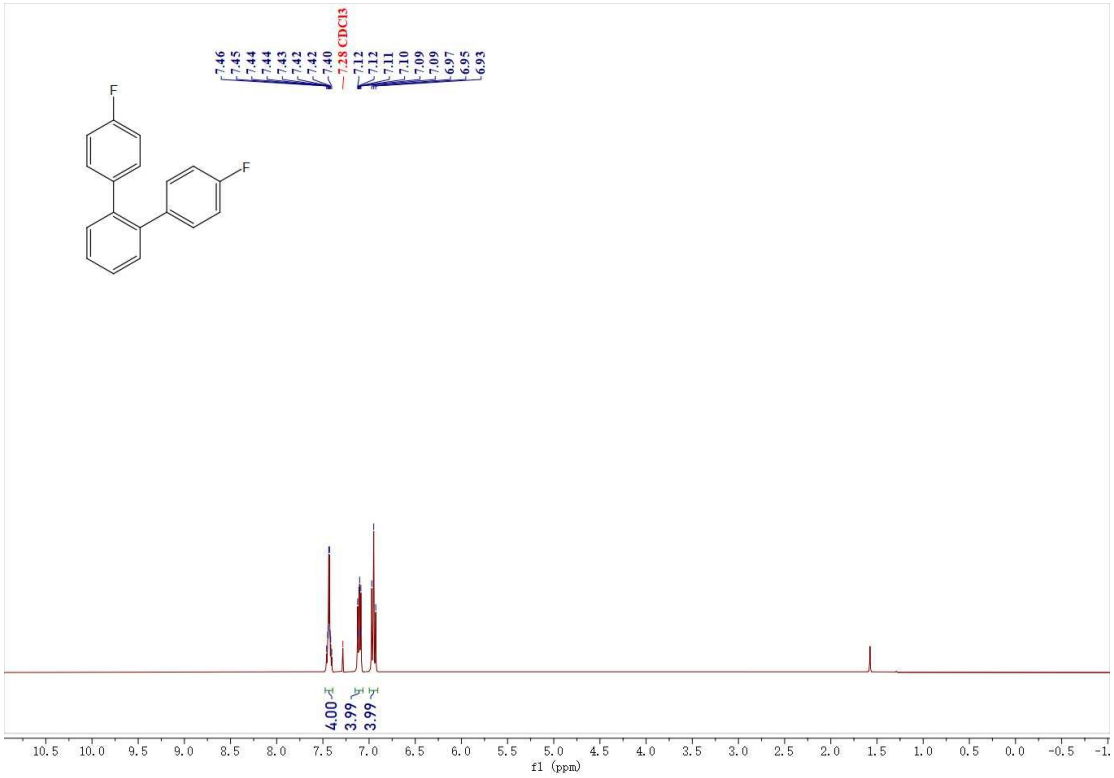
^{1}H NMR spectra of the compound 4b (400 MHz, $CDCl_3$)



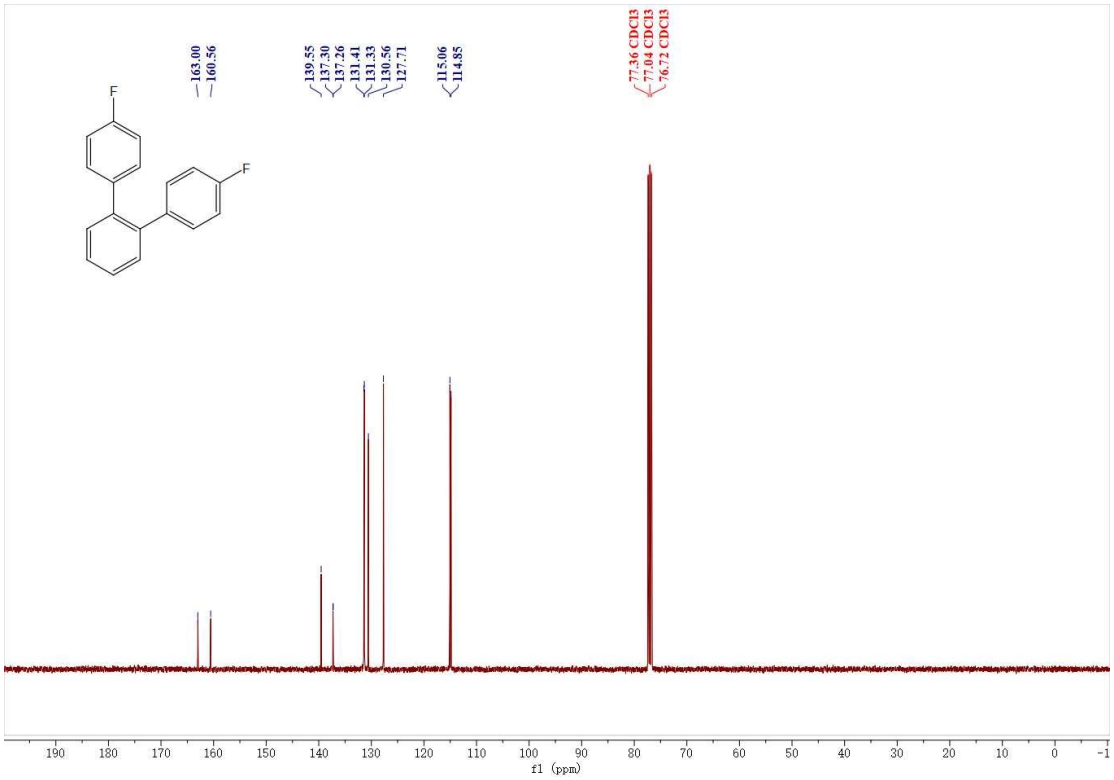
^{13}C NMR spectra of the compound 4b (101 MHz, $CDCl_3$)



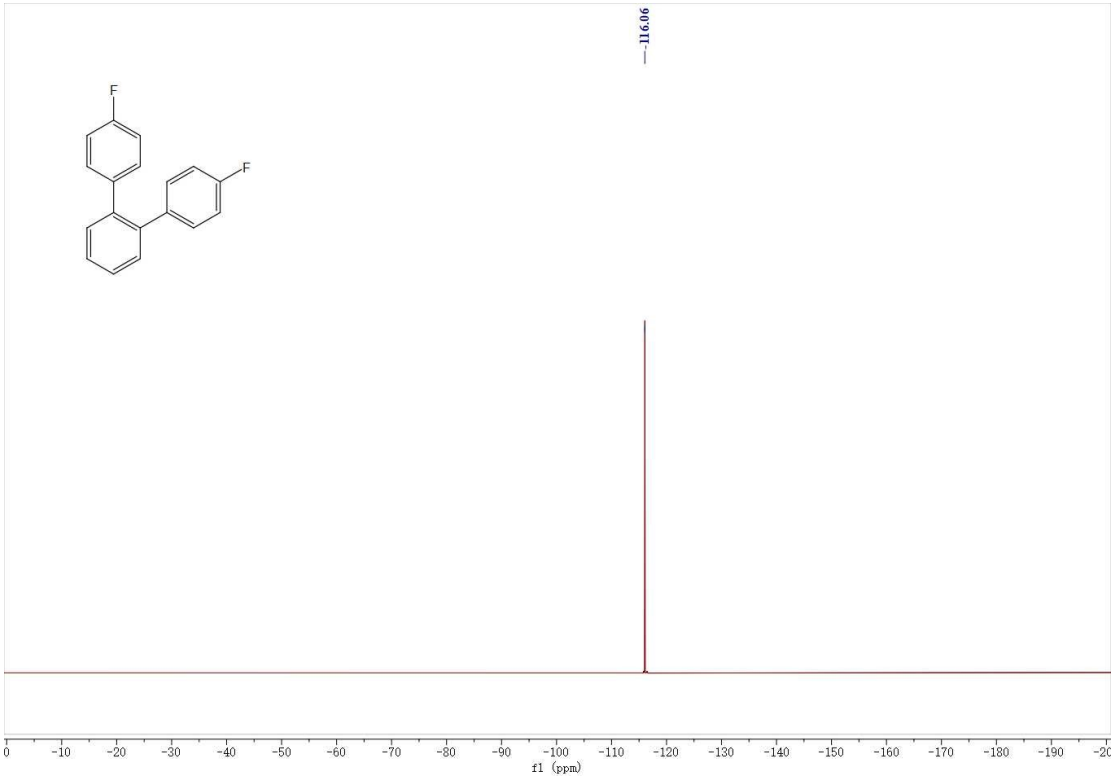
^{1}H NMR spectra of the compound 4c (400 MHz, $CDCl_3$)



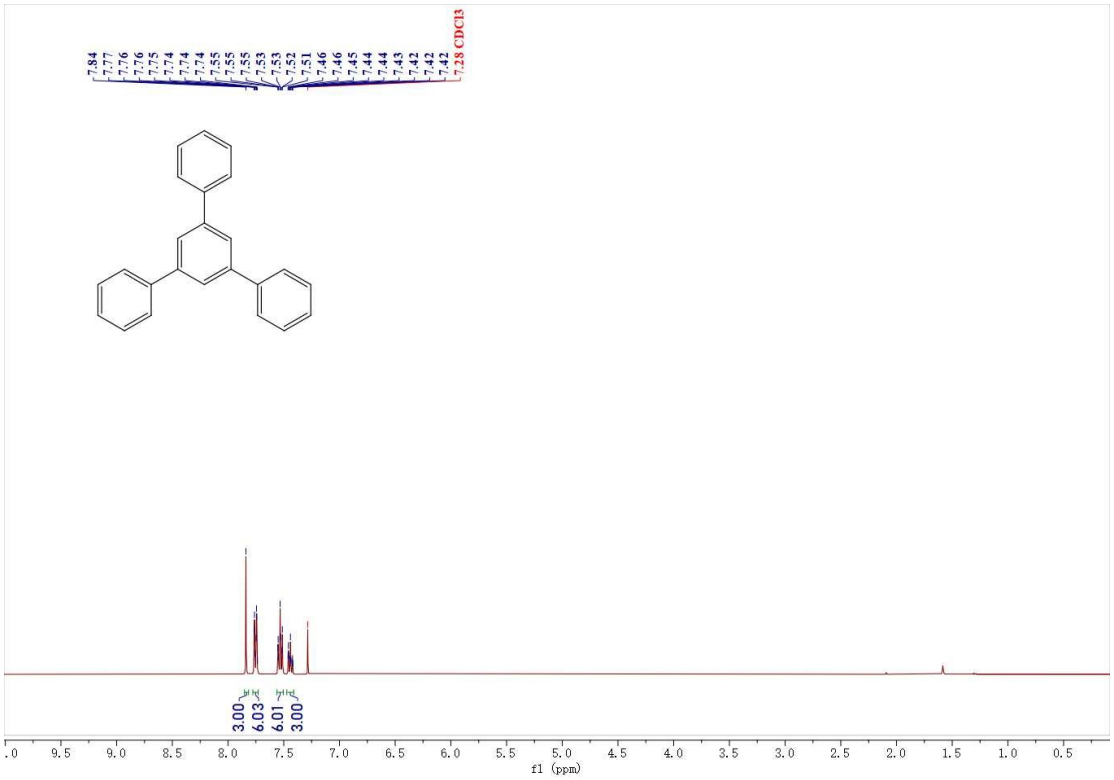
^{13}C NMR spectra of the compound 4c (101 MHz, $CDCl_3$)



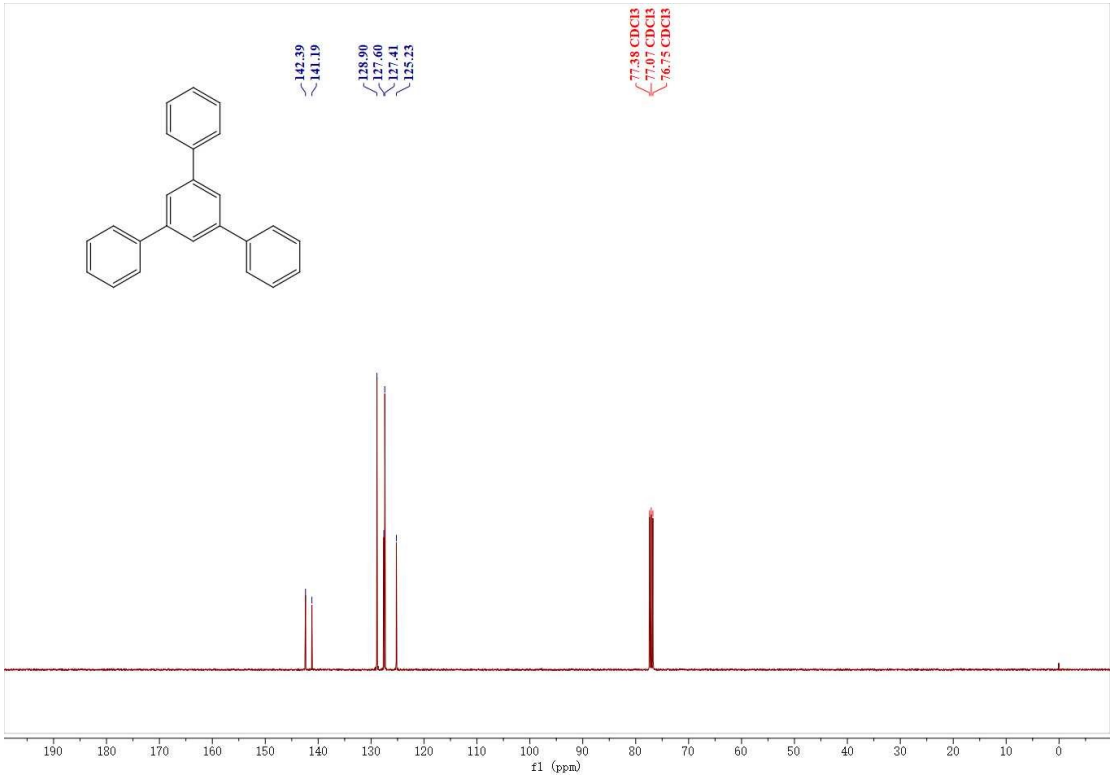
^{19}F spectra of the compound 4c (101 MHz, $CDCl_3$)



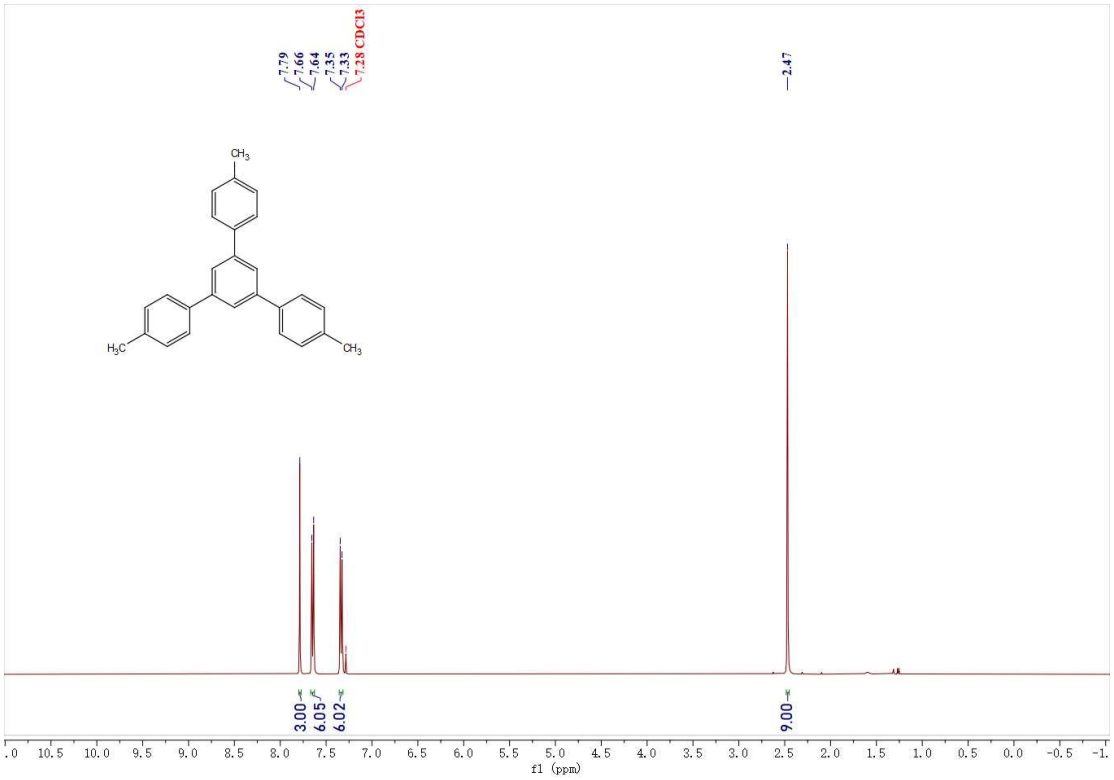
^{1}H NMR spectra of the compound 4d (400 MHz, $CDCl_3$)



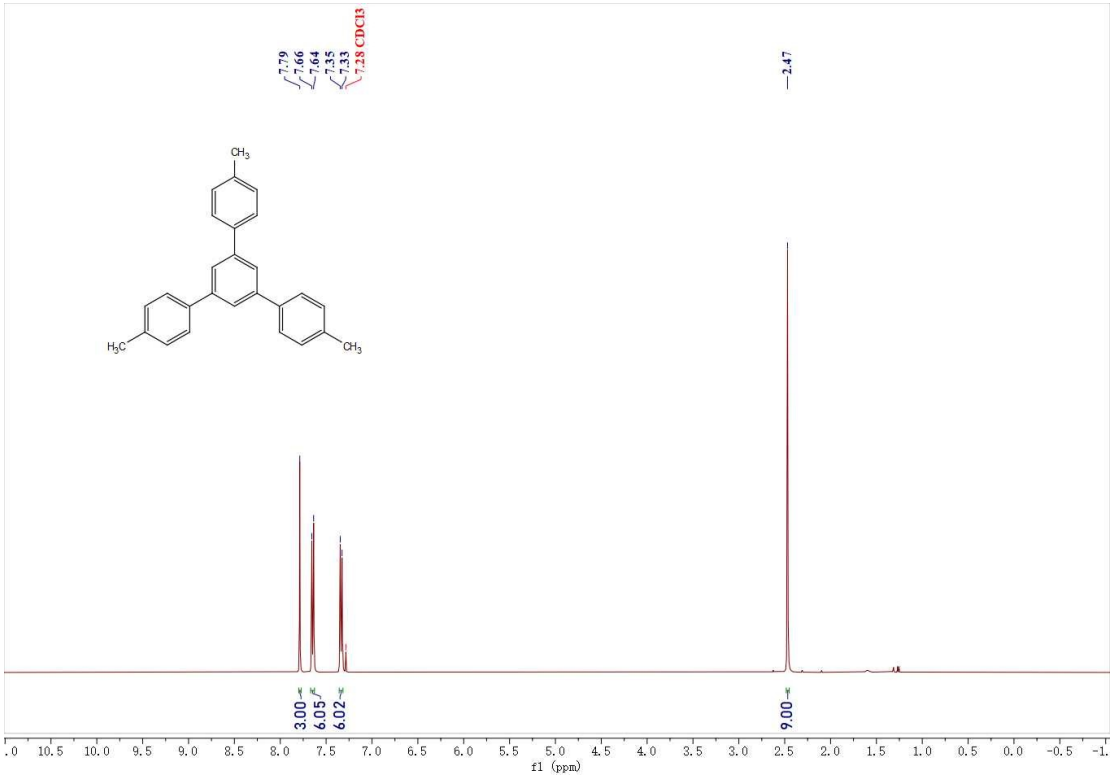
^{13}C NMR spectra of the compound 4d (101 MHz, $CDCl_3$)



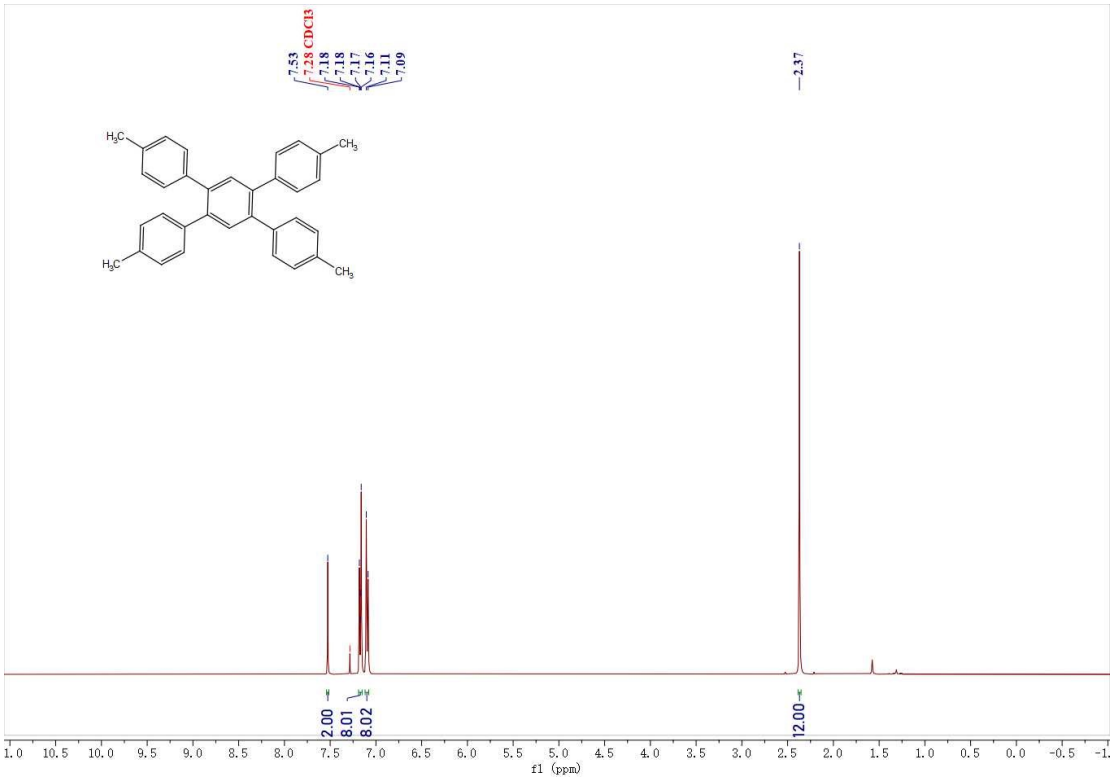
^{1}H NMR spectra of the compound 4e (400 MHz, $CDCl_3$)



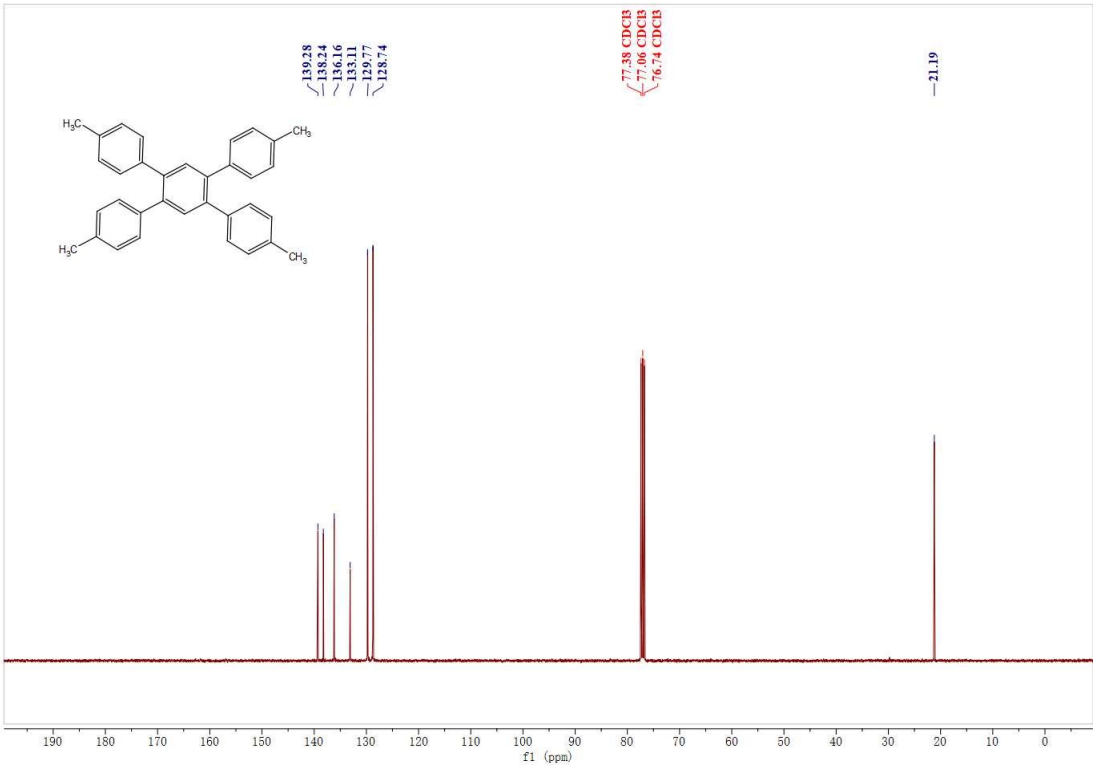
^{13}C NMR spectra of the compound 4e (101 MHz, $CDCl_3$)



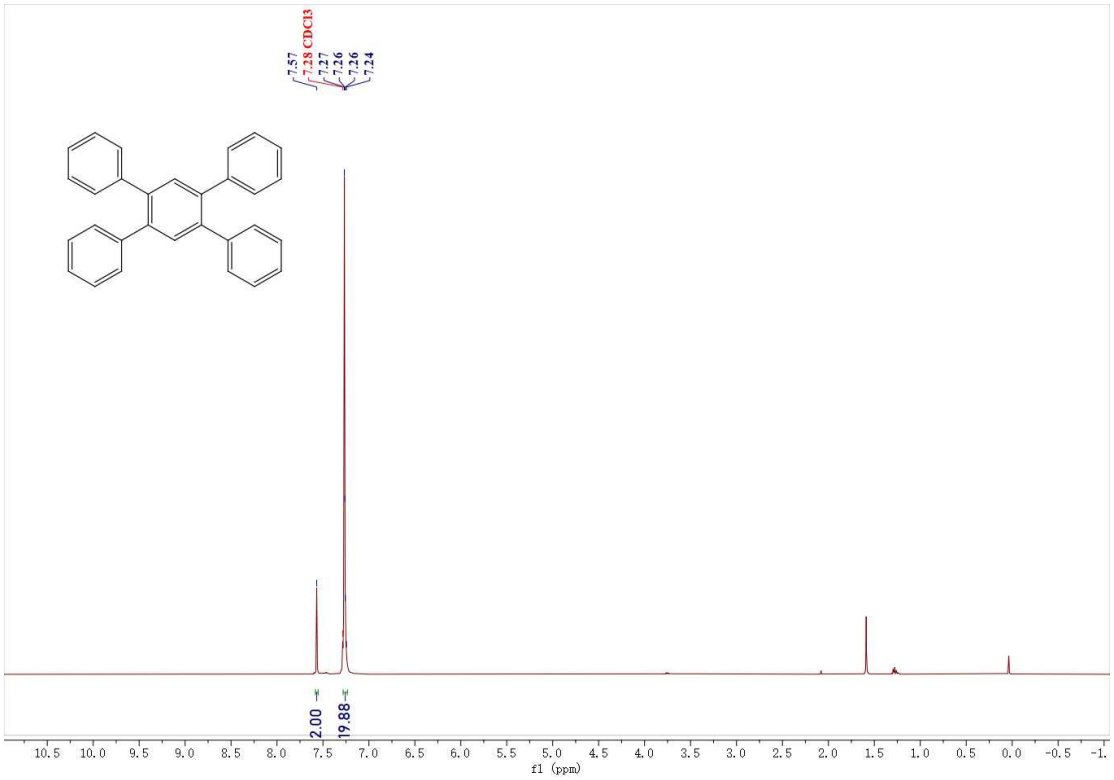
^{1}H NMR spectra of the compound 4f (400 MHz, $CDCl_3$)



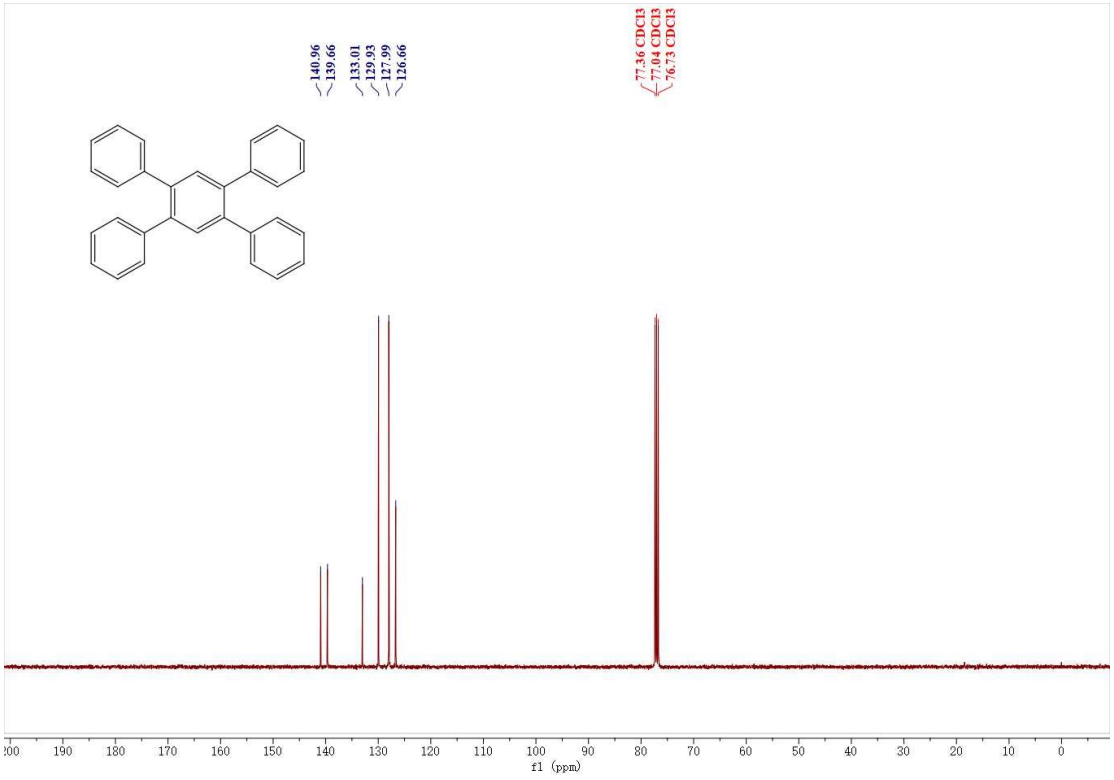
^{13}C NMR spectra of the compound 4f (101 MHz, $CDCl_3$)



^{1}H NMR spectra of the compound 4g (400 MHz, $CDCl_3$)



^{13}C NMR spectra of the compound 4g (101 MHz, $CDCl_3$)



9. References

1. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2019.

2.(a) Y. Zhao and D. G. Truhlar, *J. Chem. Phys.*, 2006, **125**, 194101−194118**.** (b) T. Sperger, I. A. Sanhueza, I. Kalvet and F. Schoenebeck, *Chem Rev.*, 2015, **115**, 9532-9586.

3. L. E. Roy, P. J. Hay and R. L. Martin, *J. Chem. Theory Comput.*, 2008, **4**, 1029-1031.

4. (a) W. E. Moore, *J. Am. Pharm. Assoc.*, 1958, **47**, 855-857. (b) Y. Xu, D. Zheng, W. Ji, N. Abu-Zahra and D. Qu, *Compos Part B-eng.*, 2021, **206,** 108531.

5. Legault, C. Y. CYLview, 1.0b; Universite′ de Sherbrooke, 2009; http://www.cylview.org.

6. S. B. Hong and L. C. Liang, *RSC Adv.*, 2022, **12**, 28862-28866.

7. J.-S. Ouyang, Y.-F. Li, F.-D. Huang, D.-D. Lu and F.-S. Liu, *ChemCatChem.*, 2018, **10**, 371-375.

8. C. M. Zinser, K. G. Warren, R. E. Meadows, F. Nahra, A. M. Al-Majid, A. Barakat, M. S. Islam, S. P. Nolan and C. S. J. Cazin, *Green Chem.*, 2018, **20**, 3246-3252.

9. Y. Li, Y. Dong, Y.-L. Wei, J.-J. Jv, Y.-Q. Chen, J.-P. Ma, J.-J. Yao and Y.-B. Dong, *Organometallics.*, 2018, **37**, 1645-1648.

10. X.-J. Wei, B. Xue, J. Handelmann, Z. Hu, H. Darmandeh, V. H. Gessner and L. J. Gooßen, *Adv Synth Catal.*, 2022, **364**, 3336-3341.

11. Z.-J. Jiang, Z.-H. Li, J.-B. Yu and W.-K. Su, *J. Org. Chem.*, 2016, **81**, 10049-10055.

12. J.-Y. Lee, R.-J. Tzeng, M.-C. Wang and H. M. Lee, *Inorg Chim Acta.*, 2017, **464**,

74-80.
13. Y. Liu, V. A. Voloshkin, T. Scattolin, M. Peng, K. Van Hecke, S. P. Nolan and C. S. J. Cazin, *Eur. J. Org. Chem.*, 2022, **2022**, e202200309.
14. P. Y. Choy, O. Y. Yuen, M. P. Leung, W. K. Chow and F. Y. Kwong, *Eur. J. Org. Chem.*, 2020, **2020**, 2846-2853.
15. M. Akkoç, N. Buğday, S. Altın, İ. Özdemir and S. Yaşar, *Catal. Lett.*, 2021, **152**, 1621-1638.
16. Y. Zhang, R. Zhang, C. Ni, X. Zhang, Y. Li, Q. Lu, Y. Zhao, F. Han, Y. Zeng and G. Liu, *Tetrahedron Lett.*, 2020, **61**, 151541.
17. S. Teo, Z. Weng and T. S. A. Hor, *J Organomet Chem.*, 2011, **696**, 2928-2934.
18. J. Zhang, H. Jung, D. Kim, S. Park and S. Chang, *Angew. Chem. Int. Ed.*, 2019, **58**, 7361-7365.
19. P. Orecchia, D. S. Petkova, R. Goetz, F. Rominger, A. S. K. Hashmi and T. Schaub, *Green Chem.*, 2021, **23**, 8169-8180.
20. G. Wang, Z. Wu, Y. Liang, W. Liu, H. Zhan, M. Song and Y. Sun, *J Catal.*, 2020, **384**, 177-188.
21. D.-H. Lee and M.-J. Jin, *Org. Lett.*, 2011, **13**, 252-255.
22. S. Reimann, P. Ehlers, M. Sharif, A. Spannenberg and P. Langer, *Tetrahedron.*, 2016, **72**, 1083-1094.
23. J. Zhang, T. Li, X. Li, G. Zhang, S. Fang, W. Yan, X. Li, X. Yang, Y. Ma and M. Szostak, *ChemComm.,* 2022, **58**, 7404-7407.