Supporting Information (SI)

An *N*-Heterocyclic Carbene Functionalised Covalent Organic Framework: Atomically Dispersed Palladium Catalyst for Coupling Reactions under Mild Condition

Junjuan Yang[†,1], Yuanyuan Wu[†,1], Xiaowei Wu [2], Wenjing Liu [1], Yaofang Wang [1], Junwen Wang[,1]*

[1] Key Laboratory of Magnetic Molecules, Magnetic Information Materials Ministry of Education, School of Chemical and Material Science, Shanxi Normal University No. 1, Gongyuan Street, Linfen 041004, China; [2] School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing, Jiangsu 210094 (P. R. China).

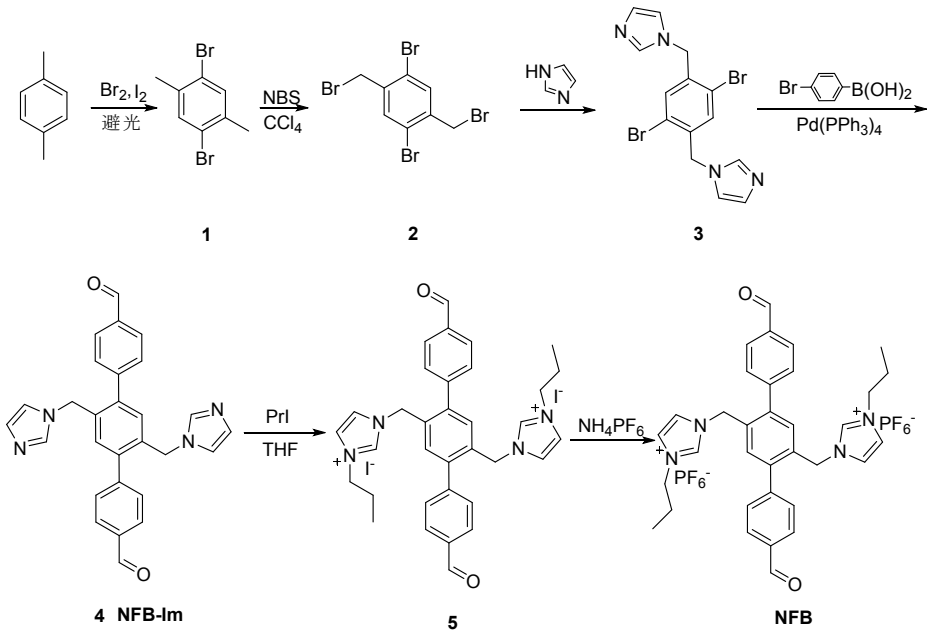
Table of Contents

Experimental Procedures

1.1. Materials and methods

All starting chemicals and reagents were purchased from commercial suppliers and used as received, unless otherwise mentioned. The design and preparation of bi-NHC substituted 1,4-di(4-formylbenzyl)benzene (NFB) monomer will be described later. Spectroscopic measurements were conducted under ambient conditions using dry solvents. The **FT-IR** spectra were recorded using KBr pellets in the range of 4000–400 cm^{-1} on a Varian 660-IR spectrometer. Nuclear magnetic resonance (**NMR**) spectra were obtained on a Bruker Avance III HD (600 MHz) spectrometer. The chemical shifts are expressed in parts per million (ppm) with TMS as internal standard. Solid-state cross-polarisation magicangle spinning (CP/MAS) ^{13}C NMR spectra were measured on an Agilent DD2 600 Solid NMR 3 System with 3.2mm zirconia rotors. The spinning rate was 15 kHz, and the contact time was 3 ms. Thermogravimetric analysis (**TGA**) measurements were carried out on a NETZSCH DSC 200F3 instrument equipped with an automatically programmed temperature controller. The TGA curves were measured in an air atmosphere by heating the samples from 25 °C to 800 °C at a rate of 10 °C min^{-1}.Powder X-ray diffraction (**PXRD**) measurements were carried out in reflection mode on a Rigaku Ultima IV–185 diffractometer with Cu-filtered Kα radiation (λ = 1.5404 Å) and a position-sensitive detector (LynxEye, step size: 0.02°, step time: 10s). The PXRD measurements of COF materials were performed by depositing the powder on a silicon wafer and applying a low scan speed and small angle increments (from 2θ = 1.5° up to 30° with 0.02° increment).Computational simulation and Pawley refinement were performed to obtain the probable structure of COF-NHC using Materials Studio software package.Scanning electron microscopy (**SEM**) images were recorded using a JEOL JSM-7500F instrument under an accelerating voltage of 20–30 kV. Transmission electron microscopy (**TEM**) images were obtainedon a JEOL JEM-2100 instrument. TheTEM samples were sonicated for 2.0 min in ethanol followed by drop casting on carbon-coated copper TEM grids. X-ray photoelectron spectroscopy (**XPS**) data were obtained using a Thermo K-Alpha^{+}scientific electron spectrometer using Al Kα radiation. Theamount of palladium was measured by inductively coupled plasma-mass spectrometry (**ICP-MS**, **Aglient 7800**).The **N_2 isotherm measurements** were carried out at 77 K in a liquid nitrogen bath. The samples were heated to 120 °C and kept at this temperature for at least 12 hours under vacuum for activation. The dry samples were thereafterloaded into sample tubes and activated under high vacuum (less than 10^{-5} Torr) at 200 °C. The apparent surface areas were calculated from nitrogen adsorption data by multipoint **BET** analysis. The apparent micropore distributions were calculated from nitrogen adsorption data by the NLDFT method.

1.2. Synthesis of bi-NHC monomer



Synthesis of bi-NHC substituted 1,4-di(4-formylbenzyl)benzene (NFB): The bi-NHC containing diformyl monomer was designed and prepared in six steps as follows. (Step 1) Bromine water (19.8 mL, 0.39 mmol) was dropped slowly into a mixture of p-xylene (23.1mL, 0.19 mol) and iodine (0.30 g, 1.18 mmol), and then the mixture was kept overnight in a 250-mL round bottom flask at 0 °C and stirred at 30 °C. The formed white precipitates were filtered and then recrystallised with ethanol to obtain the pure 1,4-dibromo-2,5-dimethylbenzene (compound **1**). ^{1}H NMR (DMSO-d_6): δ 2.32 (s,6H), 7.39 (s, 2H); ^{13}C NMR (DMSO-d_6): δ 22.1, 123.3, 133.9, 137.0 ppm[1].

(Step 2) Compound **1** (2.0 g, 7.57 mmol) was dissolved in CCl_4 (200 mL), then it was added with NBS (2.6 g, 15.2 mmol) initiated by benzoperoxide (0.04 g, 0.15 mmol) and stirred at 90 °C for 12 h. The insoluble substance was filtered to remove the solvent, and the crude product was recrystallised in ethanol to obtain the white pure 1,4-dibromo-2,5-bis(bromomethyl)benzene (compound **2**). ^{1}H NMR (DMSO-d_6): δ 4.44 (s, 4H), 7.59 (s, 2H) ppm; ^{13}C NMR (DMSO-d_6): 30.5, 122.3, 134.3, 138.0 ppm.

(Step 3) Imidazole (0.78 g, 11.5 mmol) was added to an anhydrous THF suspension of NaH in a 100 mL round bottom flask, after alternating treatments of degassing with N_2 and vacuum for three times [1]. The reaction mixture was stirred at 50 °C for 0.5 h, added with compound **2** (2.0 g, 4.75 mmol), and then heated to 60 °C and refluxed for 4.0 h. After removing most of the solvent, the reaction mixture was poured into H_2O, and the yellow solid precipitate was filtered to give the compound **3**, which was used without purification in the next step. ^{1}H NMR (DMSO-d_6): δ 5.27 (s, 4H), 6.96 (s, 2H), 7.21(s, 2H), 7.27 (s, 2H), 7.77 (s, 2H) ppm; ^{13}C NMR (DMSO-d_6): δ 49.3, 120.1, 122.3, 129.4, 133.5, 138.4, 139.1 ppm.

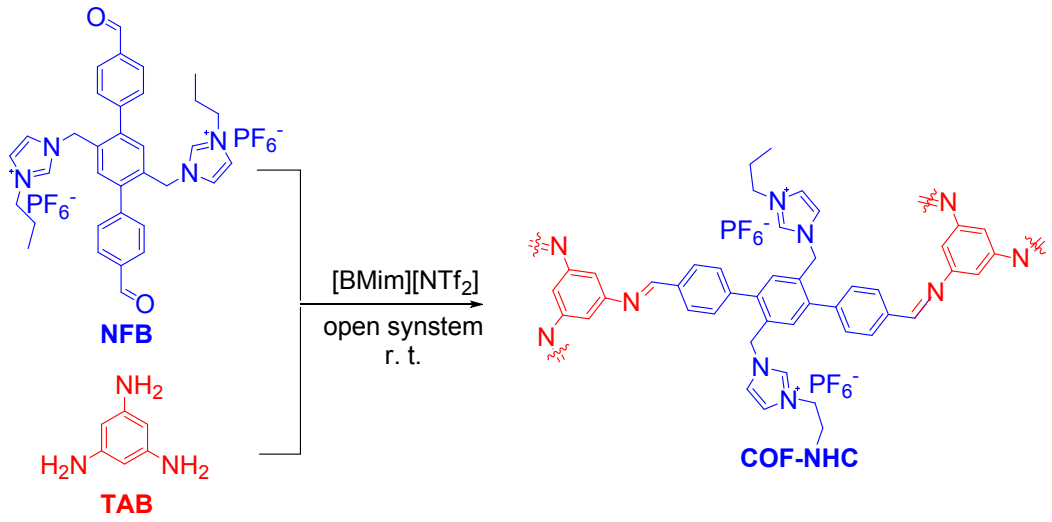
(Step 4) A mixture of **3** (1.0 g, 2.52 mmol), 4-formylphenylboronic acid (1.51 g, 10.08 mmol), K_2CO_3 (1.4 g, 10.08 mmol), and $Pd(PPh_3)_4$ (0.62 g, 0.53 mmol) in a mixed solvent of 1,4-dioxane and H_2O (v/v = 5:1) was heated at 90 °C overnight under N_2 protection. Then, $CHCl_3$ was added, the insoluble solid was removed, and washed with water. The aqueous phase was extracted with $CHCl_3$ and the combined organic phase was repeatedly washed and dried over $MgSO_4$. Compound**4** (**NFB-H**) was obtained as a brown solid after removing the organic solvents. This compound was used without purification in the fifth step. ^{1}H NMR (DMSO-d_6) δ 5.17 (s, 4H), 6.74 (s, 2H), 6.85 (s, 2H), 6.97 (s, 2H), 7.30

(s, 2H), 7.51 (d, *J*=8.08, 4H), 7.95 (d, *J*=8.16Hz, 4H), 10.03 (s, 2H) ppm; ^{13}C NMR (DMSO-d_6): δ 50.1 , 119.2, 128.1, 128.4, 130.4, 131.2, 132.4, 134.1, 135.8, 137.8, 143.7, 191.0 ppm.

(Step 5, 6) 1-Iodopropane (4.46 mmol) was added to **4** (1.0 g, 2.23 mmol) in THF, and the reaction mixture was stirred at room temperature for two days. The precipitated yellow solid was then filtered and recrystallised in diethyl ether to give the product **5**, followed by anion exchange with NH_4PF_6 to obtain the final product **NFB** (compound **6**) [2]. **NFB-Pr:** little yellow, ^{1}H NMR (DMSO-d_6) δ 0.74 (t, *J* = 7.3 Hz, 6H), 1.67 (q, *J* = 7.2Hz, 4H), 4.04 (t, *J* = 6.9 Hz, 4H), 5.58 (s, 4H),7.48 (d, *J* = 2.3Hz, 4H), 7.64 (d, *J*=7.9Hz, 4H), 7.69 (s, 2H), 8.01 (d, *J* = 8.0 Hz, 4H), 9.01 (s, 2H), 10.12 (s, 2H) ppm; ^{13}C NMR (DMSO-d_6) δ 10.8, 23.3, 50.5, 50.7, 123.0, 123.1, 130.0, 130.3, 132.5, 132.9, 136.0, 136.8, 141.0, 144.7, 193.4 ppm.

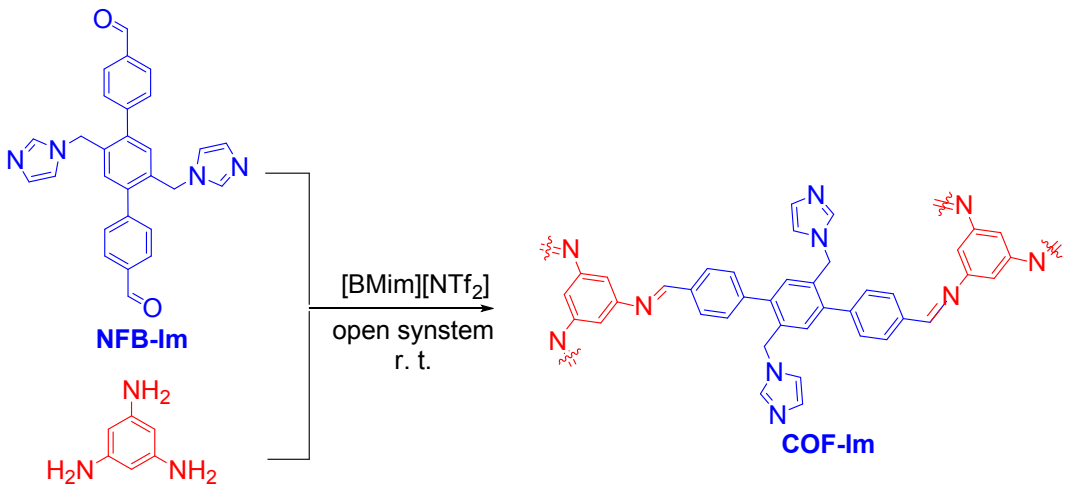
1.3. Synthesis of COF-NHC

1.3.1. Synthesis of COF-NHC



A round bottom centrifuge tube (1.5 mL) was charged with **TAB** (9.30 mg, 0.04 mmol) and **NFB** (49.33 mg, 0.06mmol) in 1-butyl-3-methylimidazoliumbis((trifluoromethyl)sulfonyl)imide ([BMIm][NTf_2], 100 μL). The reaction mixture was kept at room temperature for 3 h to afford a yellow-brown precipitate, which was isolated by centrifugation and washed with ethyl acetate (3*10 mL) and acetonitrile (3*10 mL). The solvent was removed under vacuum followed by dryingat 80 °C for 12 h to afford COF-NHC as a yellow powder (29.32 mg, 50% yield). IR (powder, cm^{-1}): 3405, 3325, 3212, 3051, 2923, 2850, 2601, 1651, 1547, 1539, 1418, 1330, 1129, 847, 662.

1.3.2. Synthesis of COF-Im



In a manner similar to the preparation of COF-NHC, a round bottom centrifuge tube (1.5 mL) was charged with **TAB** (9.30 mg, 0.04 mmol) and **NFB-Im** (27.79 mg, 0.06mmol) in 1-butyl-3-methylimidazoliumbis((trifluoromethyl)-sulfonyl)imide ([BMIm][NTf_2], 100 µL). The reaction mixture was kept at room temperature for 3 h to afford a grey-brown precipitate, which was isolated by centrifugation and washed with ethyl acetate (3×10 mL) and acetonitrile (3×10 mL). The solvent was removed under vacuum, and the product wasdried at 80 °C for 12 h to afford COF-Im as a yellow powder (33.38 mg, 90% yield). IR (powder, cm^{-1}): 3406, 2929, 2859, 2591, 1636, 1602, 1449, 1401, 1282, 1081, 830, 622.

1.4. Synthesis of Pd@COF-NHC

The heterogeneous catalyst Pd@COFs was prepared by post-synthesis of $Pd(OAc)_2$ into COFs. To a 25-mL two-necked round bottom flask, $Pd(OAc)_2$ (26.94 mg, 0.12 mmol) was dissolved in 10 mL of acetonitrile, and then one of the COFs (either COF-Im, 37.09 mg, 0.06 mmol orCOF-NHC, 58.63 mg, 0.06 mmol) was introduced. The reaction mixture was stirred at 75 °C for 3 h. The resulting solid was isolated by centrifugation, washed with acetonitrile using Soxhlet extraction for 24 h under an inert N_2 atmosphere, and then dried at 80 °C under vacuum for 12 h to give the Pd@COF-NHC and Pd@COF-Im. The products were both grey in colour.

1.5. General procedure for the Suzuki-Miyaura coupling reaction

In a typical activity test for the heterogeneous catalyst Pd@COFs, aryl halide (0.5 mmol), phenylboronic acid (0.55 mmol), a base (1.5 mmol), Pd@COFs (0.5 mol%), and 2.5 mL of solvent were added to 10 mL round bottom flask, and the reaction mixture was stirred at ambient temperature and atmosphere for 1.0 h. After the reaction was completed (monitored by TLC), the mixture was centrifuged and the solid was washed with water (3×5 mL) and acetonitrile (3×5 mL). The combined organic phase was washed with water (3×5 mL) to remove the base residue. Then, the organic phase was evaporated under vacuum leaving the crude product, which waspurified by column chromatography over silica gel to obtain the final product.

1.6. General procedure for the cross-coupling between triaylbismuths and aryl halide

In a typical run, a mixture of Pd@COF-NHC (2 mol%), triarylbismuths (1 mmol), aryl iodide (0.43 mmol), a base (4 mmol), and solvent (2.5 mL) was stirred at room temperature for 5.0 h under atmosphere. Afterwards, the content was centrifuged. The solid was washed with water and acetonitrile and used for the next round of reaction, while the liquid was extracted with dichloromethane. The combined organic extract was washed with brine (15mL), dried over

anhydrous $MgSO_4$, filtered, and concentrated under vacuum. The crude product was purified by column chromatography to afford biaryl compounds.

1.7. Recycle test

The recycle test used *p*-nitrobromobenzene (0.5 mmol) with phenylboronic acid (0.55mmol), potassium carbonate (207 mg, 1.5 mmol), and Pd@COF-NHC (0.5 mol%) in 2.5 mL aqueous solution. After each cycle, the catalyst was isolated by centrifugation, washed with water and acetonitrile, and then used directly without other post treatment.

Results and Discussion

2.1. FT-IR spectrum analysis

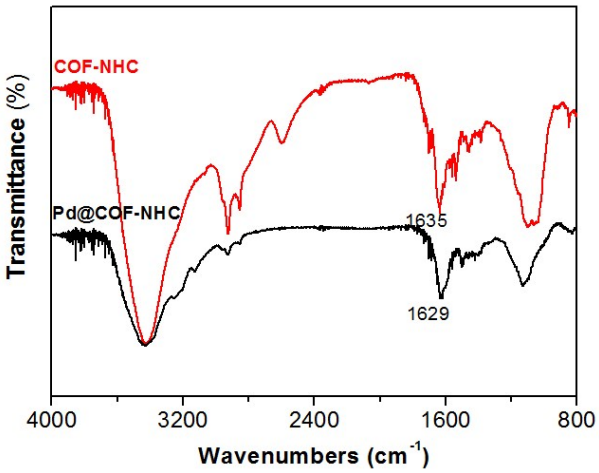


Figure S1FT-IR spectra of COF-NHC and Pd@COF-NHC.

2.2. ^{13}C CP/MAS NMR spectrum analysis

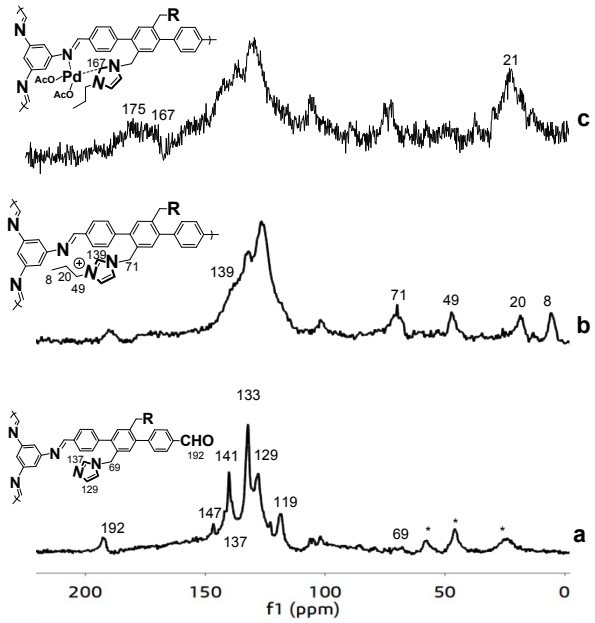


Figure S2^{13}C CP/MAS NMR spectra of COF-Im (a), COF-NHC (b) and Pd@COF-NHC (c). Asterisks denote spinning sidebands. The assignments of ^{13}C chemical shifts were indicated in the chemical structures.

2.3. Morphology and composition

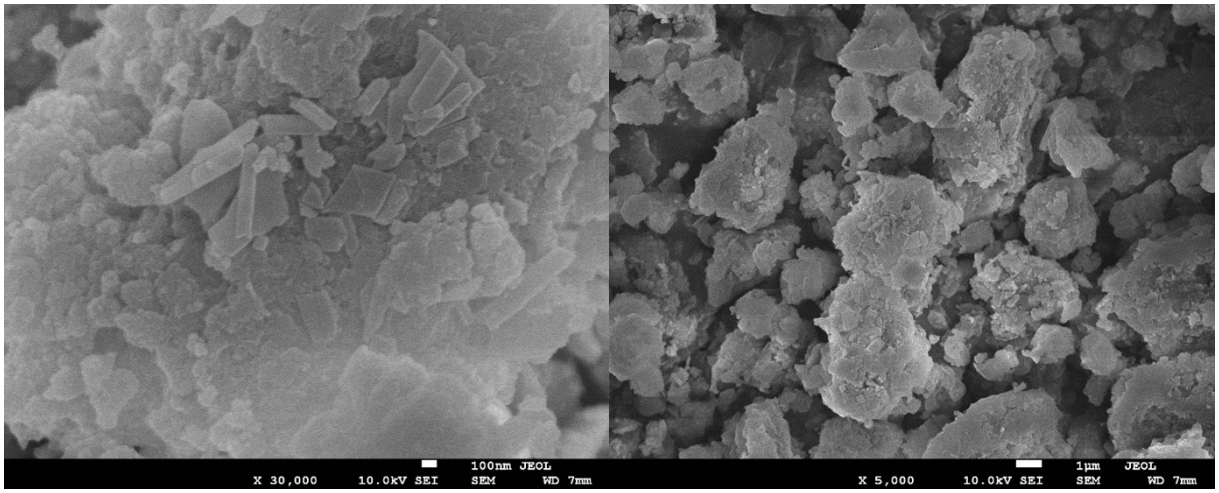


Figure S3 SEM images of COF-NHC.

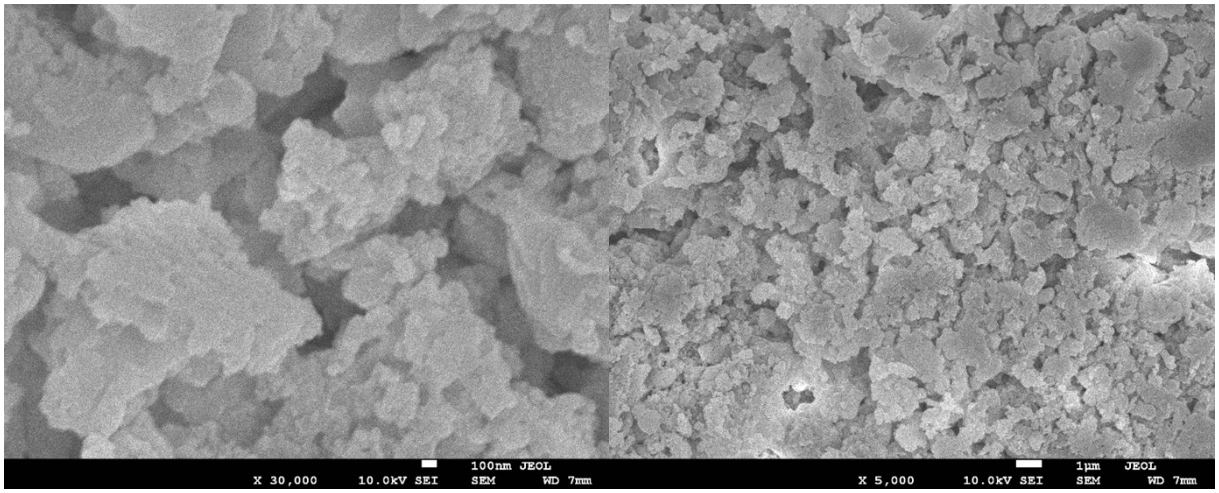


Figure S4 SEM images of Pd@COF-NHC.

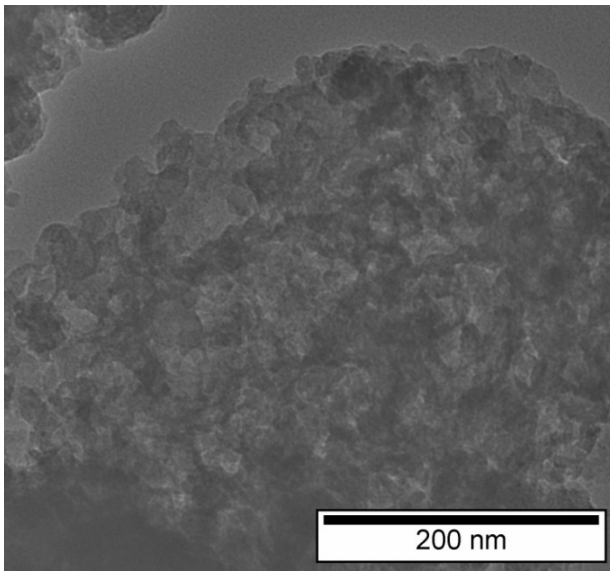


Figure S5 TEM images of COF-NHC.

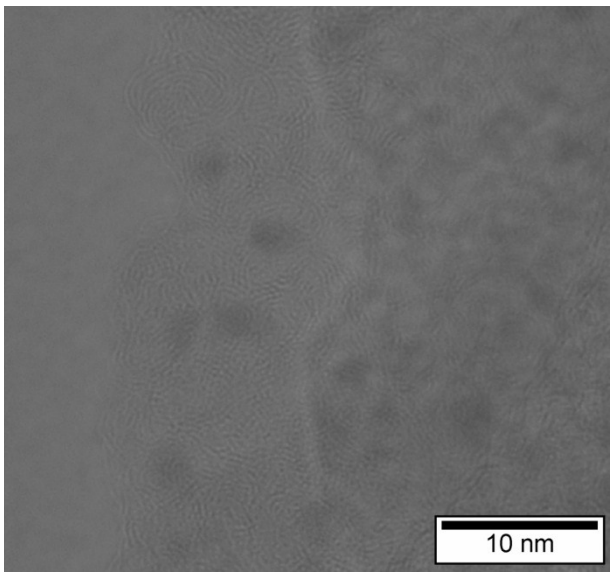


Figure S6 HRTEM images of COF-NHC.

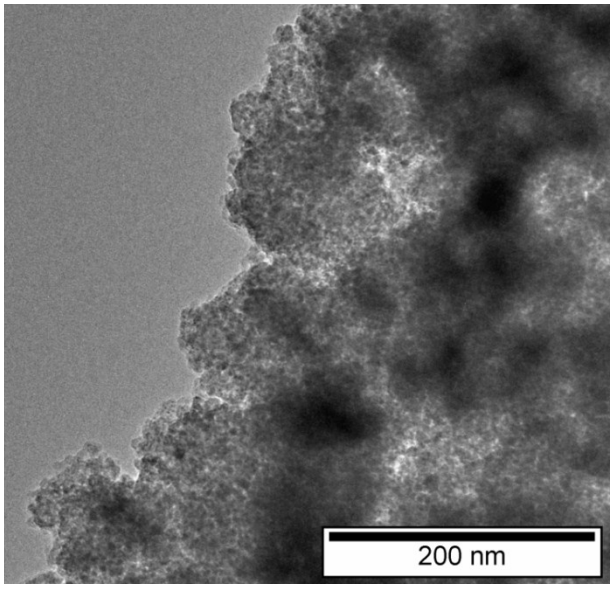


Figure S7 TEM of Pd@COF-NHC.

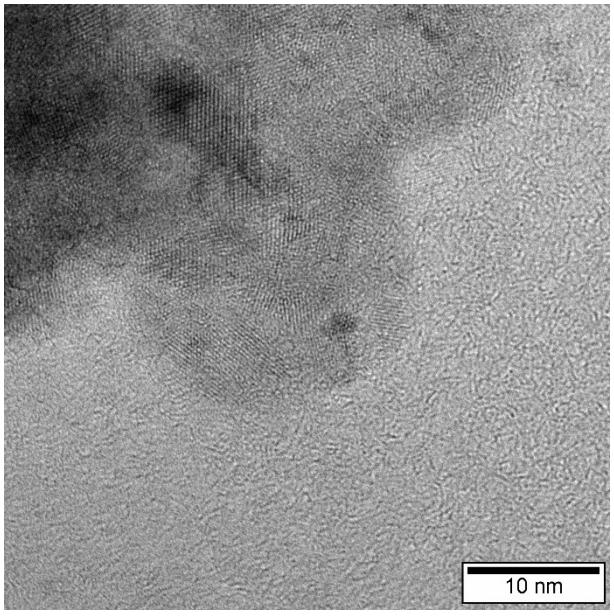


Figure S8 HRTEM images of Pd@COF-NHC.

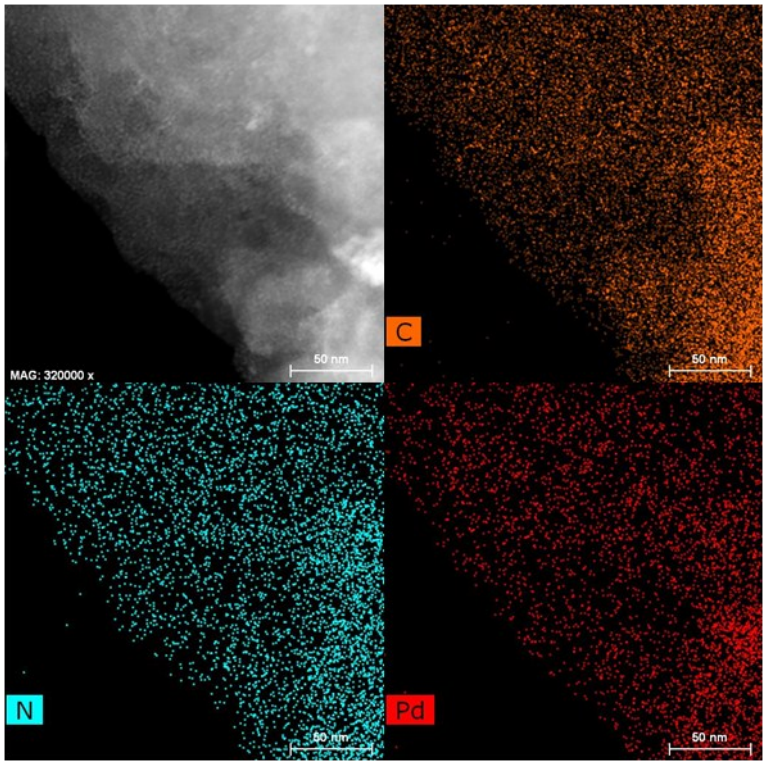


Figure S9 EDS mapping of composition elements C, N, and Pd.

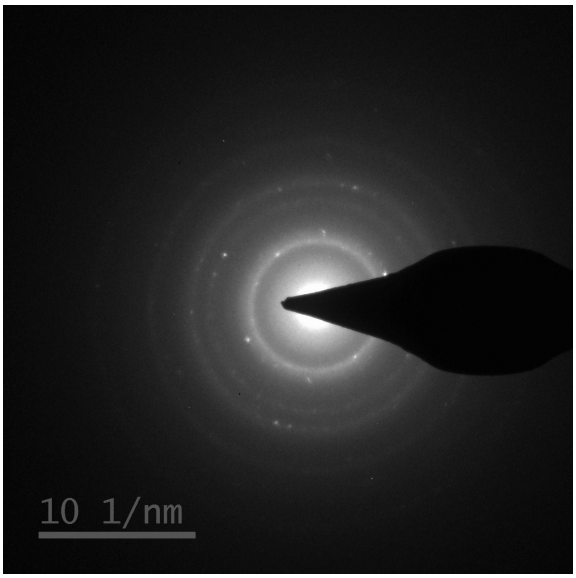


Figure S10 Selected area electron diffraction (SAED) pattern.

2.4. Powder X-ray diffraction Analysis

Molecular modeling of COFs was generated with the Materials Studio (ver. 8.0) suite of programs. Crystal structures models were built by using *Visualizer* module, unit cell dimension was set to the theoretical parameters. Pawley refinement was carried out by using *Reflex*, a software package for crystal determination from PXRD pattern. The Pawley refinement was performed to optimize the lattice parameters iteratively until the R_{wp} value converges and the overlay of the observed with refined profiles shows good agreement. The lattice models (cell parameters, atomic positions, and total energy) were then fully optimized using MS *Forcite* molecular dynamics module (universal force-field, Qeq, Ewald summations) method.

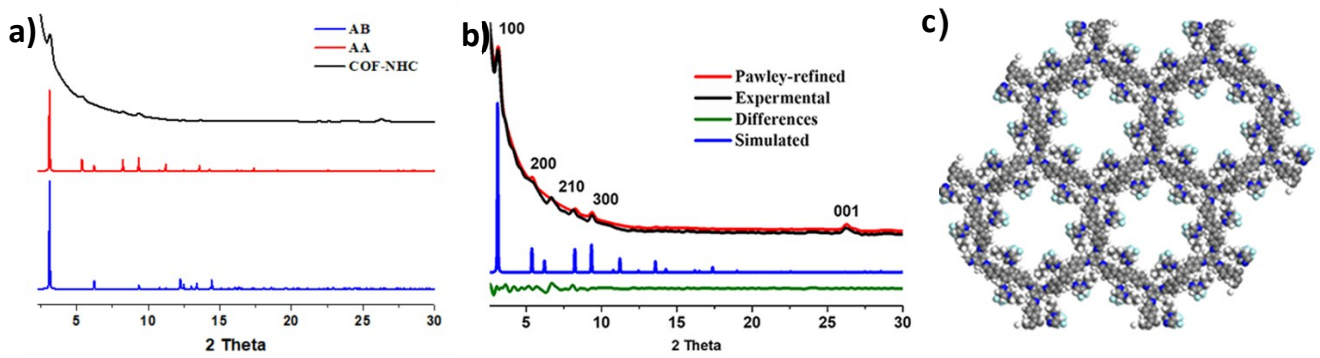


Figure S11 PXRD patterns of COF-NHC: (a) experimental (black), simulated PXRD patterns using AA (red) and staggered AB (blue) stacking modes; (b) Indexed experimental (black) and Pawly-refined (red) PXRD patterns with their difference (green) and the theoretical patterns for the eclipsed structures (blue, AA); (c) Eclipsed-stacked COF-NHC.

Table S1 Energy calculations

Staking models	Total energy (kcal/mol)
AA	2527.8
1 Å offset-AA	3679.9
2 Å offset-AA	3207.4
4 Å offset-AA	3377.7
AB	2728.3

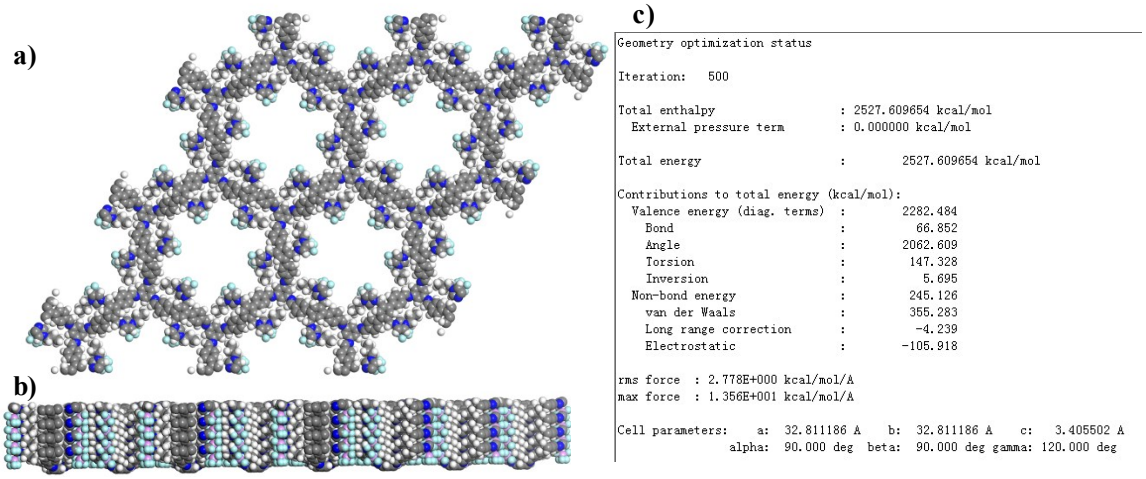
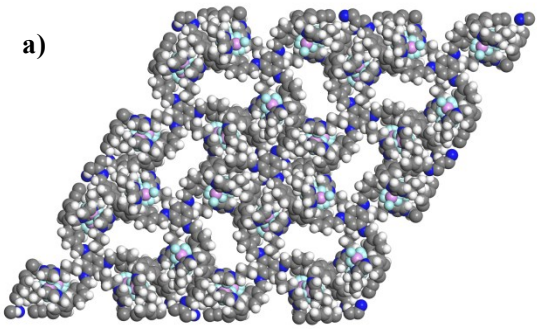
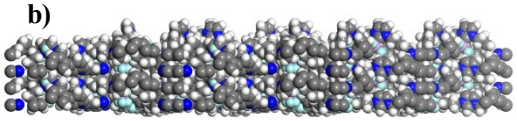


Figure S12 a) AA stacking structure; b) side view of idea AA stacking structure and c) the total energy after geometrical energy minimization of ideal AA stacking structure.

a)



b)



c)

```
Geometry optimization status

Iteration:   500

Total enthalpy                  : 2728.298011 kcal/mol
  External pressure term        : 0.000000 kcal/mol

Total energy                    :        2728.298011 kcal/mol

Contributions to total energy (kcal/mol):
  Valence energy (diag. terms)  :         3862.549
    Bond                        :           54.337
    Angle                       :         3533.392
    Torsion                     :          265.831
    Inversion                   :            8.990
  Non-bond energy               :        -1134.251
    van der Waals               :          -20.464
    Long range correction       :           -4.326
    Electrostatic               :        -1109.461

rms force  : 4.414E-004 kcal/mol/A
max force  : 3.018E-003 kcal/mol/A
rms stress : 7.945E-006 GPa
max stress : 1.946E-005 GPa

Cell parameters:    a:  32.740000 A    b:  32.740000 A    c:   7.884276 A
                 alpha:  90.000 deg  beta:  90.000 deg gamma: 120.000 deg
```

Figure S13 a) AB stacking structure; b) side view of idea AB stacking structure and c) the total energy after geometrical energy minimization of ideal AB stacking structure.

Table S2 Refined unit cell parameters and fractional atomic coordinates for **COF-NHC** using AA eclipsed stacking mode

COF-NHC : Space group: ***P6***			
a = b =32.81 Å, c = 3.41 Å			
α = β = 90°, γ= 120°			
Atom	x	y	z
C1	0.49407	0.45597	0.90547
C2	0.53924	0.49421	0.82575
C3	0.5442	0.53938	0.82409
C4	0.58519	0.58316	0.64294
C5	0.62419	0.51337	0.70138
C6	0.65508	0.50109	0.52344
C7	0.63704	0.45674	0.34797
C8	0.58868	0.42489	0.3657
C9	0.55875	0.43804	0.51468
C10	0.57511	0.48276	0.67986
C11	0.61875	0.32255	-0.17487
C12	0.6553	0.36873	-0.16116
N13	1.02511	1.39476	0.83938
C14	1.01116	1.35214	0.99578
C15	1.05046	1.34798	1.06346
N16	1.08856	1.38824	0.94663
C17	1.07201	1.41504	0.79996
C18	1.13621	1.39687	0.89084
C19	0.54722	0.72293	0.97686
C20	0.53583	0.76104	0.86249
N21	0.35506	0.59621	-0.03595
C22	0.33179	0.55819	0.16733
H23	0.48962	0.42197	0.96268
H24	0.56787	0.5864	0.39302
H25	0.61482	0.58081	0.51967
H26	0.63907	0.5454	0.87156
H27	0.69232	0.5255	0.53167
H28	0.57281	0.38923	0.25399
H29	0.5223	0.41198	0.48586
H30	0.58279	0.31503	-0.14411
H31	0.97513	1.32601	1.04669
H32	1.05094	1.31727	1.17312
H33	1.09291	1.44643	0.62932
H34	1.13914	1.38906	0.5946

H35	1.14225	1.37045	1.03979
H36	0.52166	0.68916	0.83839
H37	0.53858	0.71357	1.27503
H38	0.5637	0.78764	0.67376
H39	0.53321	0.78036	1.11291
H40	0.50141	0.7447	0.71107
H41	0.29593	0.54547	0.25691
F42	1.0247	1.39167	1.05449
P43	1.05143	1.37096	1.36832
F44	1.08249	1.35324	1.07672
F45	1.05239	1.41317	1.0593
F46	1.04783	1.32739	1.06443
F47	0.99825	1.32955	1.55845
F48	1.10482	1.41094	1.56529

2.5. Thermal gravimetric analysis

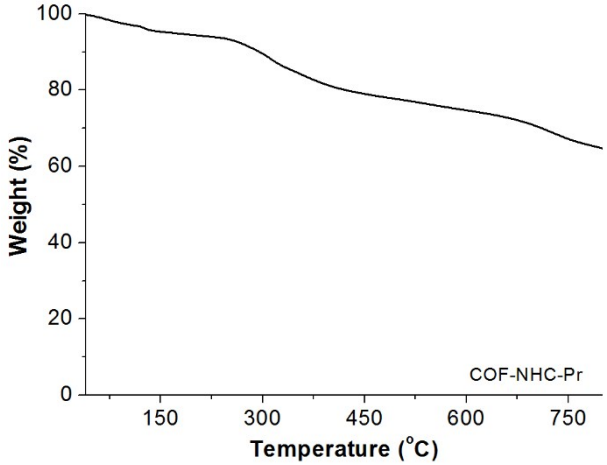


Figure S14 TGA curve of COF-NHC. The weight loss (8%) observed in the temperature of about 275 °C could be ascribed to the removal of [BMIm][NTF_2] in the pores of COF-NHC.

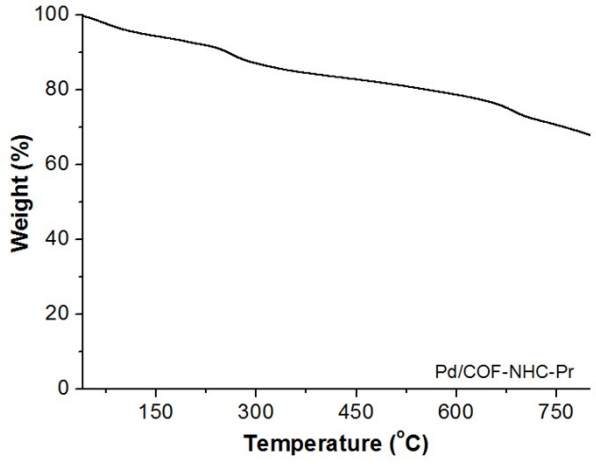


Figure S15 TGA curve of Pd@COF-NHC. The weight loss (9.7%) observed in the temperature of about 253 °C could be ascribed to the removal of [BMIm][NTF_2] and solvents in the pores of Pd@COF-NHC.

2.6. XPS analysis

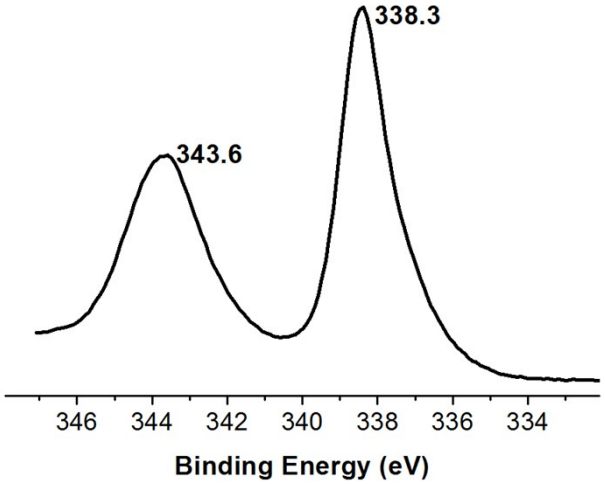
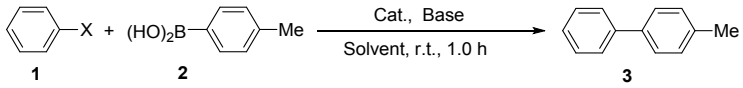


Figure S16 Pd 3d XPS spectra of free $Pd(OAc)_2$

2.7. Catalyst activity results of Pd@COF-NHC

2.7.1. Catalyst of Suzuki-Miyaua reaction

Table S3 Optimization Condition Studies of Suzuki-Miyaura Cross Coupling[a]

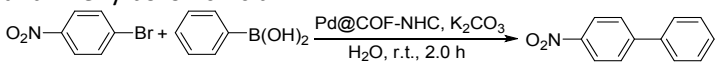


Entry	Catalyst ligand	Pd [b]	Pd content (mol %)	X	Solvent	Base	Yield(%)[c]
1	COF-Im	$Pd(OAc)_2$	1	Cl	MeOH	K_2CO_3	33
2	COF-NHC	$Pd(OAc)_2$	1	Cl	MeOH	K_2CO_3	78
3	Pd@COF-NHC		1	Cl	MeOH	K_2CO_3	79
4	Pd@COF-NHC		1	Br	MeOH	K_2CO_3	99
5	Pd@COF-NHC		1	I	MeOH	K_2CO_3	99
6	Pd@COF-NHC		0.5	Br	MeOH	K_2CO_3	99
7	Pd@COF-NHC		0.25	Br	MeOH	K_2CO_3	85
8	Pd@COF-NHC		0.5	Br	MeOH	KOH	94
9	Pd@COF-NHC		0.5	Br	MeOH	KOtBu	95
10	Pd@COF-NHC		0.5	Br	MeOH	K_3PO_4	98
11	Pd@COF-NHC		0.5	Br	MeOH	—	Trace
12	Pd@COF-NHC		0.5	Br	EtOH	K_2CO_3	99
13	Pd@COF-NHC		0.5	Br	THF	K_2CO_3	96
14	Pd@COF-NHC		0.5	Br	CH_3CN	K_2CO_3	91
15	Pd@COF-NHC		0.5	Br	Dioxane	K_2CO_3	80
16	Pd@COF-NHC		0.5	Br	DMF	K_2CO_3	55
17	Pd@COF-NHC		0.5	Br	NMP	K_2CO_3	87
18	Pd@COF-NHC		0.5	Br	MeOH:H_2O = 4:1	K_2CO_3	99
19	Pd@COF-NHC		0.5	Br	EtOH:H_2O = 4:1	K_2CO_3	99
20	Pd@COF-NHC		0.5	Br	H_2O	K_2CO_3	99

[a] Reaction condition: halobenzene (0.50 mmol), 4-methylphenylboronic acid (0.55 mmol), base (1.5 mmol), solvent (2.5 mL), room temperature for 1.0 h; [b] $Pd(OAc)_2$ (0.5 mol%); [c] Pd@COF-NHC (0.5 mol%); [d] Isolated yields.

2.7.2 Stability and reusability of Pd@COF-NHC

Table S4 Recycle test of Pd@COF-NHC in the Suzuki-Miyaura Cross Coupling Reaction of *p*-nitrobromobenzene and Phenylboronic Acid[a]



Entry	Yield (%) [b]
fresh	99
cycle 1	99
cycle 2	99
cycle 3	99
cycle 4	99
cycle 5	99
cycle 6	99
cycle 7	96

[a] Reaction condition: *p*-nitrobromobenzene (0.50 mmol), phenylboronic acid (0.55 mmol), K_2CO_3 (1.5 mmol), Pd@COF-NHC (0.5 mol%), solution (2.5 mL, H_2O), room temperature for 1.0 h; [b] Isolated yields.

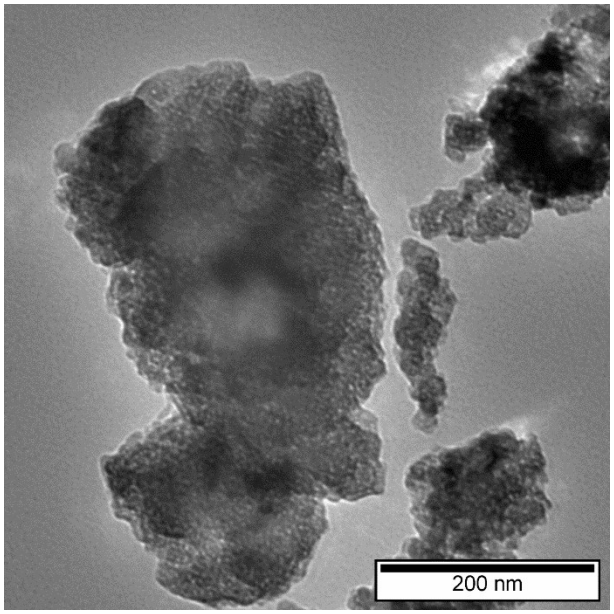


Figure S17 Representative TEM of recycled catalyst of Pd@COF-NHC

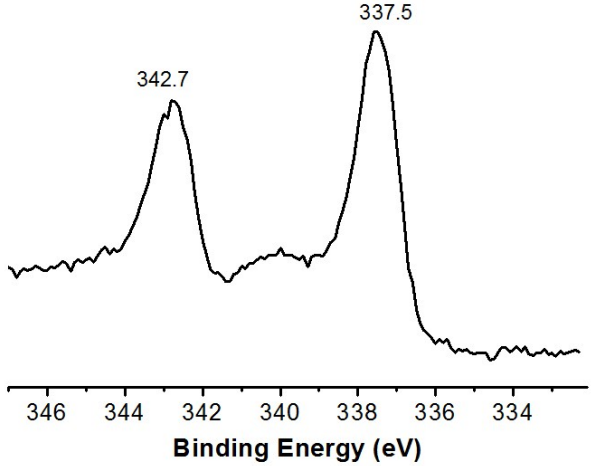
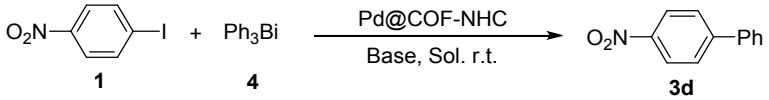


Figure S18 XPS spectra of the recycled catalyst of Pd@COF-NHC

2.7.3. Catalyst of carbon-carbon cross reaction

Table S5 Optimization Studies on the cross-coupling of 4-iodonirtobenzene with $BiPh_3$ [a]



1 **4** **3d**

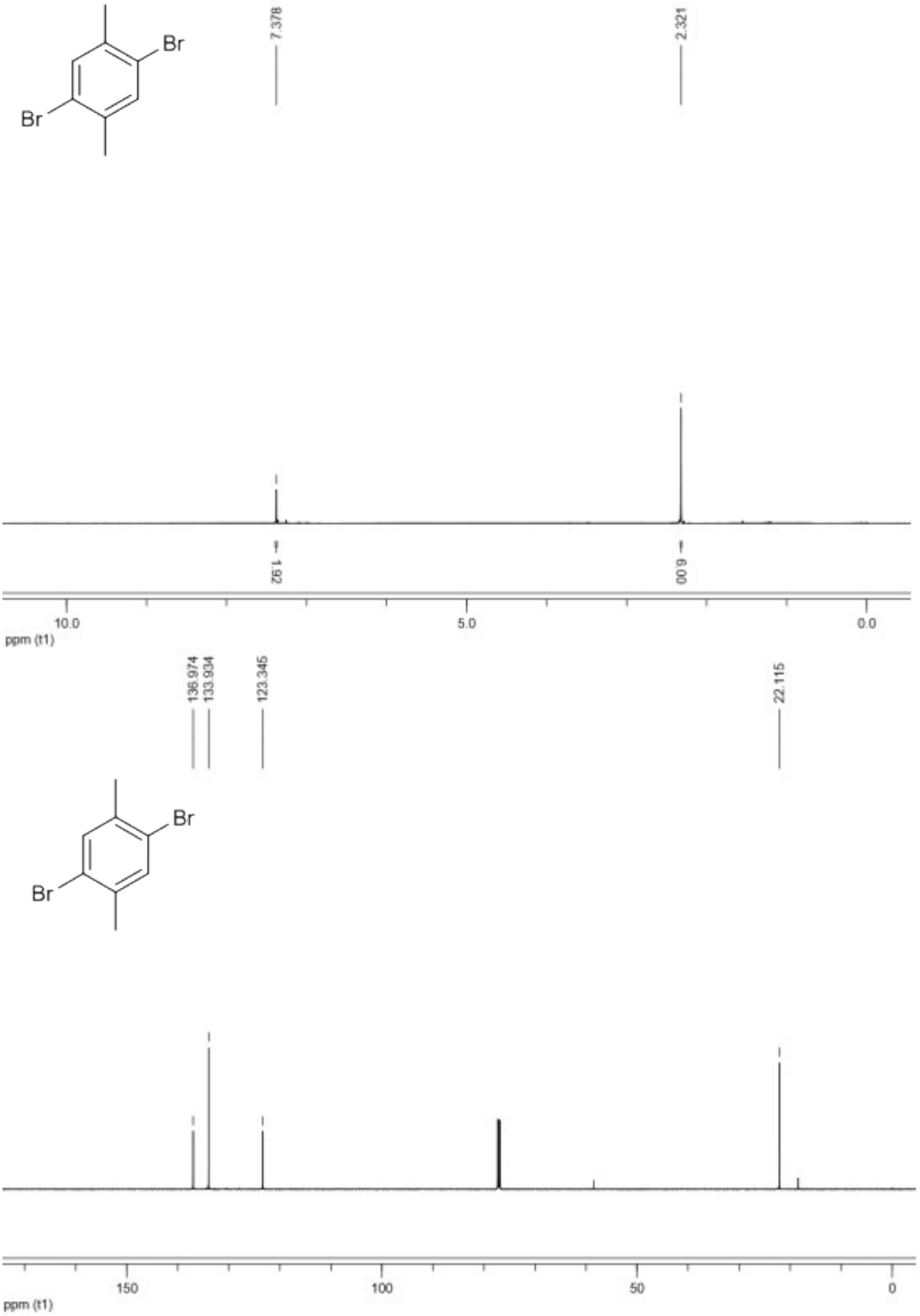
Entry	Solvent	Base	Time (h)	Yield (%)[b]
1	DMSO	K_2CO_3	5	56
2	DMSO	KOH	5	35
3	DMSO	KOAc	5	43
4	DMSO	K_3PO4	5	48
5	DMSO	KO^tBu	5	21
6	EtOH	K_2CO_3	5	93
7	H_2O	K_2CO_3	5	Trace
8	DMF	K_2CO_3	5	82

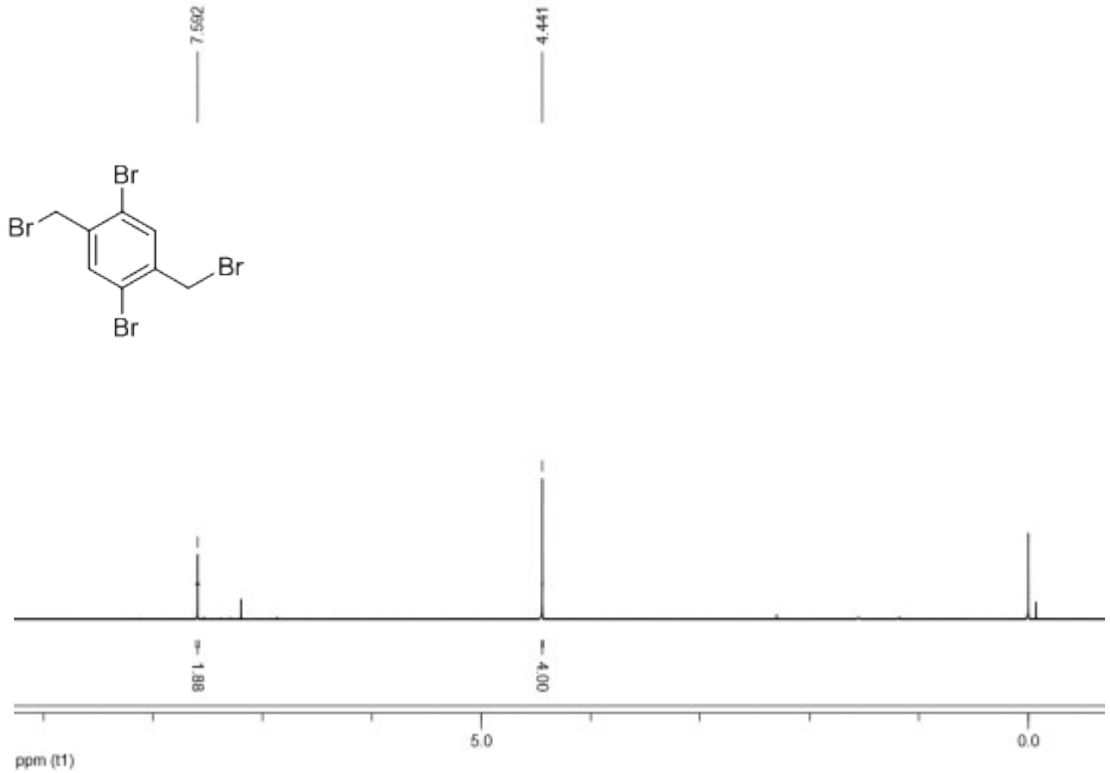
9	THF	K_2CO_3	5	43
10	CH_3CN	K_2CO_3	5	46
11	MeOH	K_2CO_3	5	97
12	1,4-dioxane	K_2CO_3	5	33
13	NMP	K_2CO_3	5	5
14	EtOH:H_2O=4:1	K_2CO_3	5	96
15	EtOH:H_2O=4:1	K_2CO_3	2	55
16	EtOH:H_2O=4:1	K_2CO_3	3	70
17	EtOH:H_2O=4:1	K_2CO_3	4	85
18	EtOH:H_2O=4:1	K_2CO_3	8	98

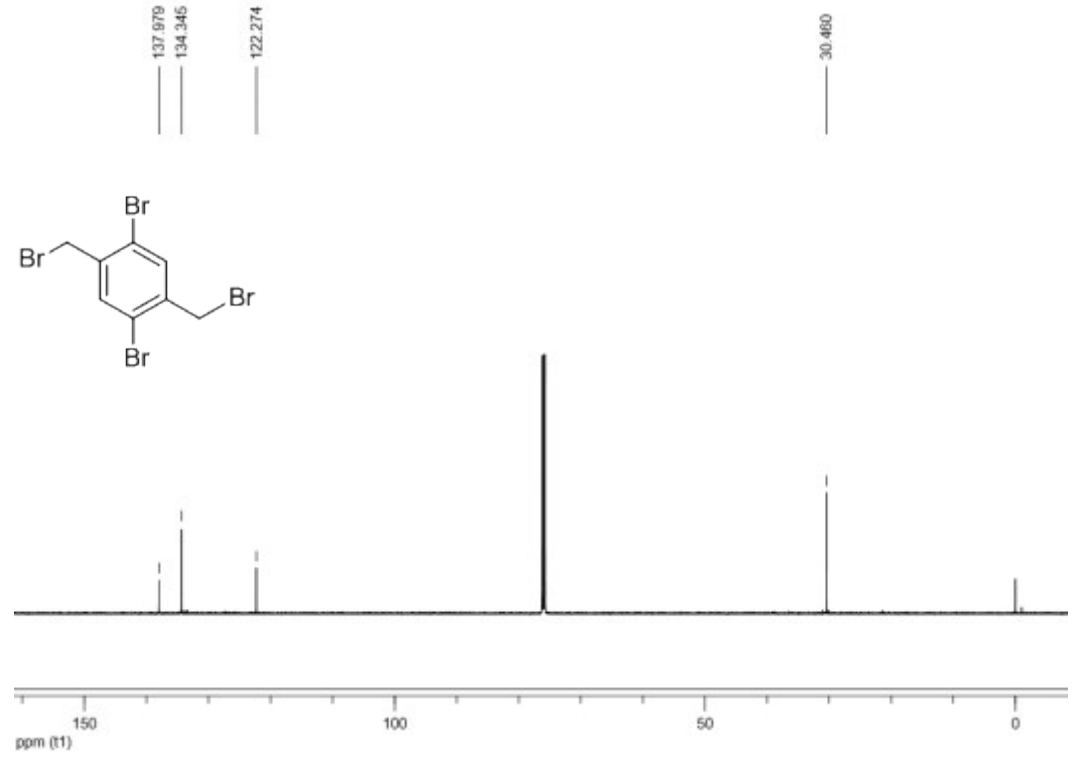
[a] Reactions condition: 4-iodonitrobenzene (1 mmol), triphenylbismuths (0.43 mmol), base (4 mmol), solvent (2.5 mL), Pd@COF-NHC (2 mol%) room temperature; [b] Isolated yields.

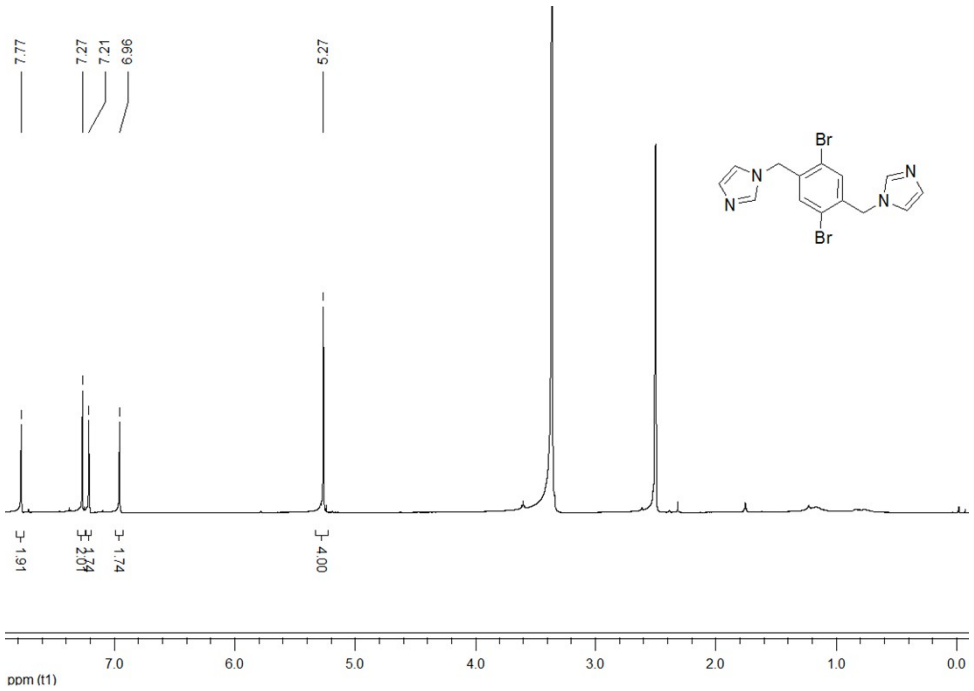
2.8. NMR spectra of compounds

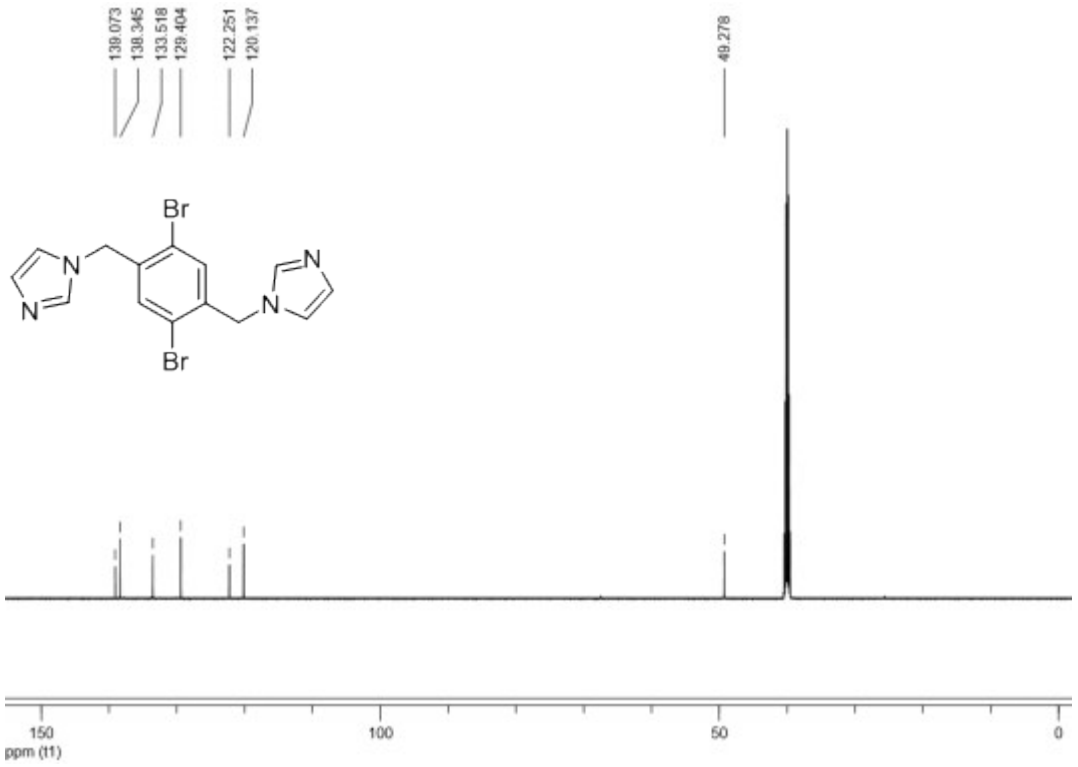
2.8.1. The spectra of synthesis NFB

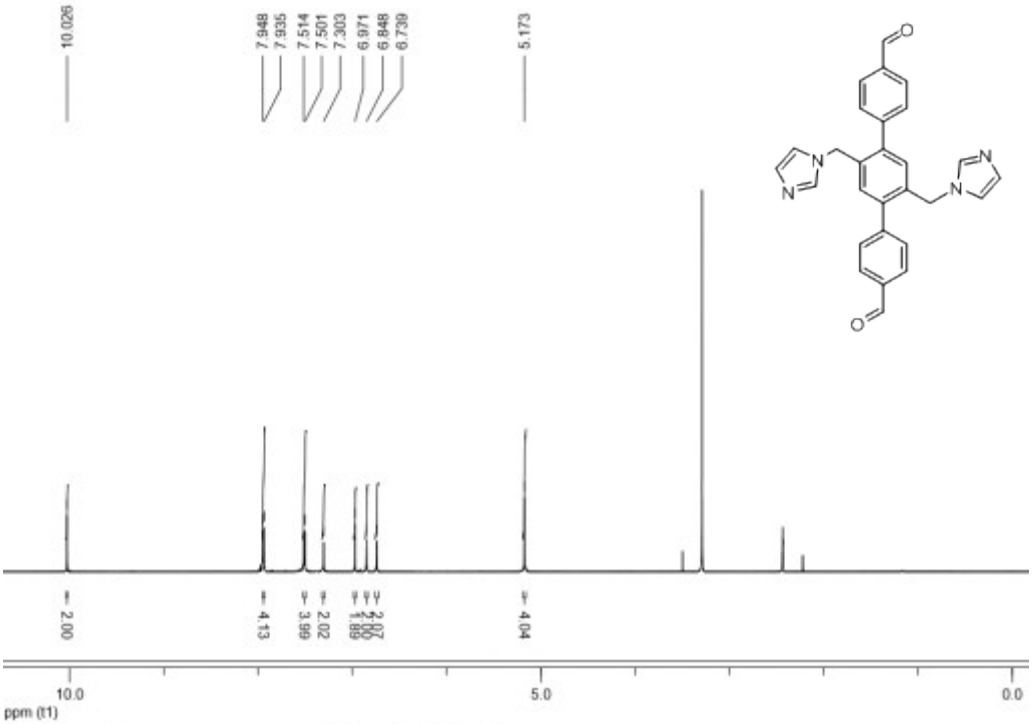


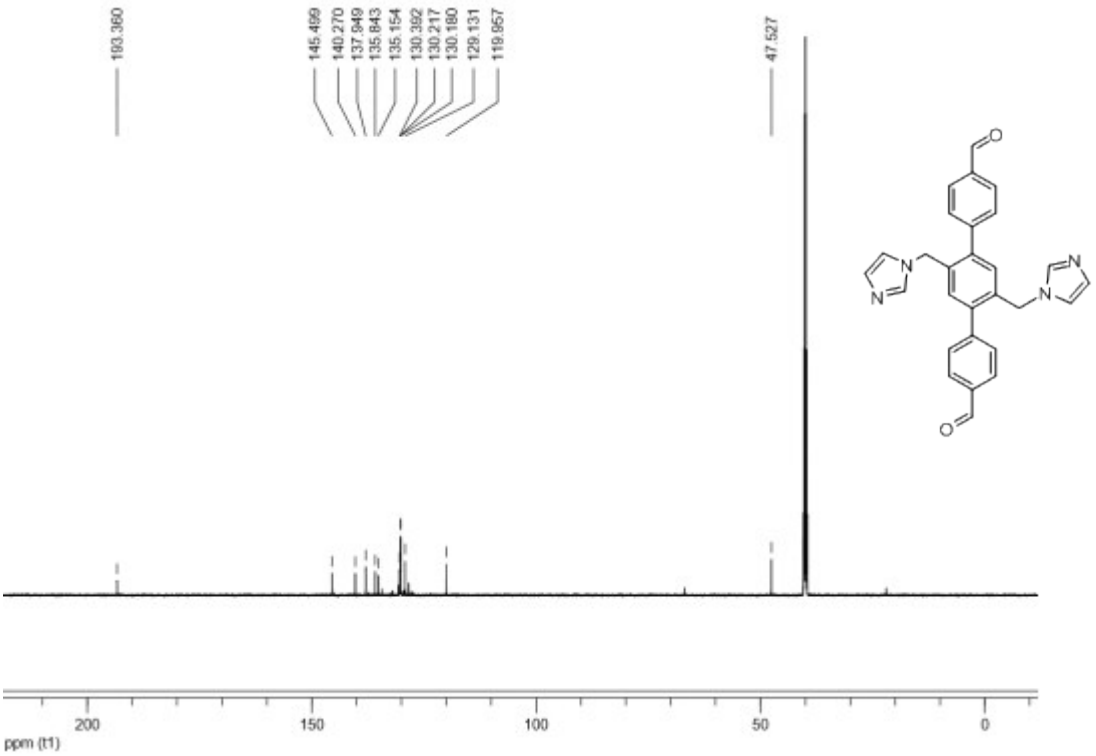

7.592
4.441
Br
Br
Br
Br
1.88
4.00
5.0
0.0
ppm (t1)

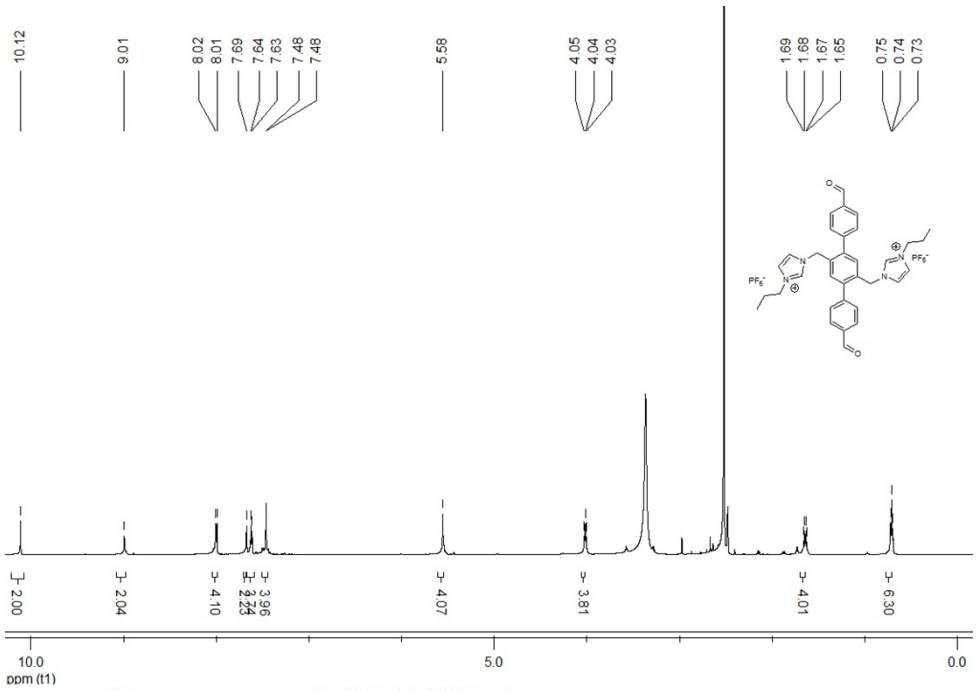

137.979
134.345
122.274
30.460
Br
Br
Br
Br
150
100
50
0
ppm (t1)

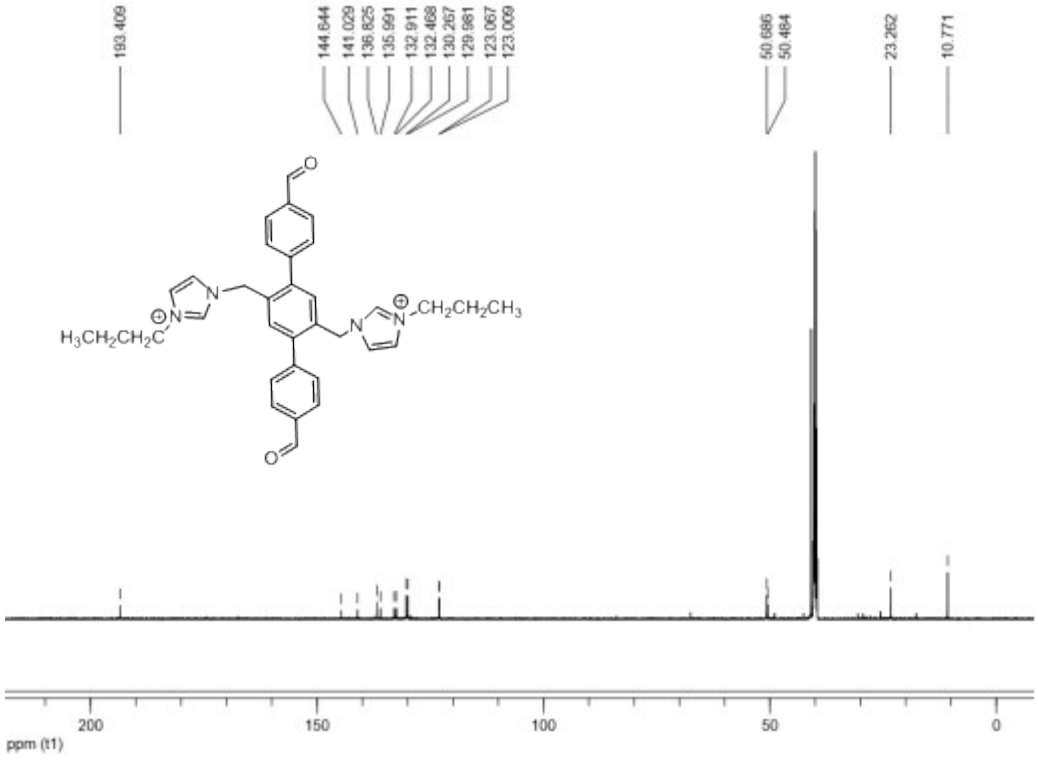

7.77
7.27
7.21
6.96
5.27
1.91
2.01
1.74
4.00
Br
Br
N
N
N
N
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


139.073
138.345
133.518
129.404
122.251
120.137
49.278
Br
Br
N
N
N
N
150
100
50
0
ppm (t1)


10.026
7.948
7.935
7.514
7.501
7.303
6.971
6.848
6.739
5.173
2.00
4.13
3.99
2.02
2.14
2.07
4.04
10.0
5.0
0.0
ppm (t1)

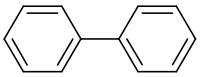

193.360
145.499
140.270
137.949
135.843
135.154
130.392
130.217
130.180
129.131
119.957
47.527
200
150
100
50
0
ppm (t1)


10.12
9.01
8.02
8.01
7.69
7.64
7.63
7.48
7.48
5.58
4.05
4.04
4.03
1.69
1.68
1.67
1.65
0.75
0.74
0.73
2.00
2.04
4.10
3.96
4.07
3.81
4.01
6.30
10.0
5.0
0.0
ppm (t1)

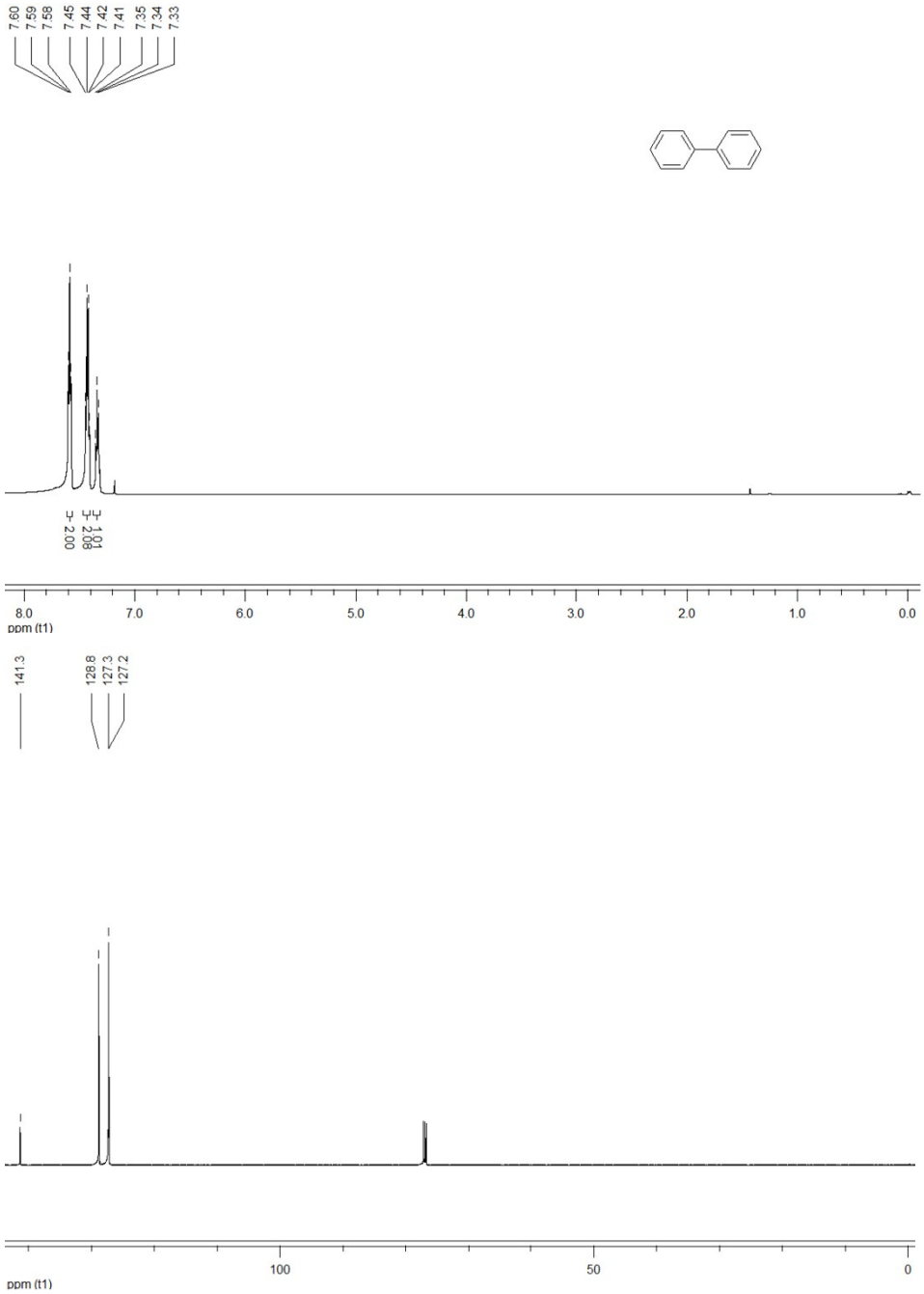

193.409
144.644
141.029
136.825
135.991
132.911
132.468
130.267
129.981
123.067
123.009
50.686
50.484
23.252
10.771
$H_3CH_2CH_2C$
$CH_2CH_2CH_3$
200
150
100
50
0
ppm (t1)

2.8.2 Spectra of compounds 3

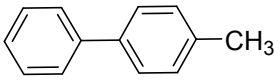
1,1'-biphenyl(3a)



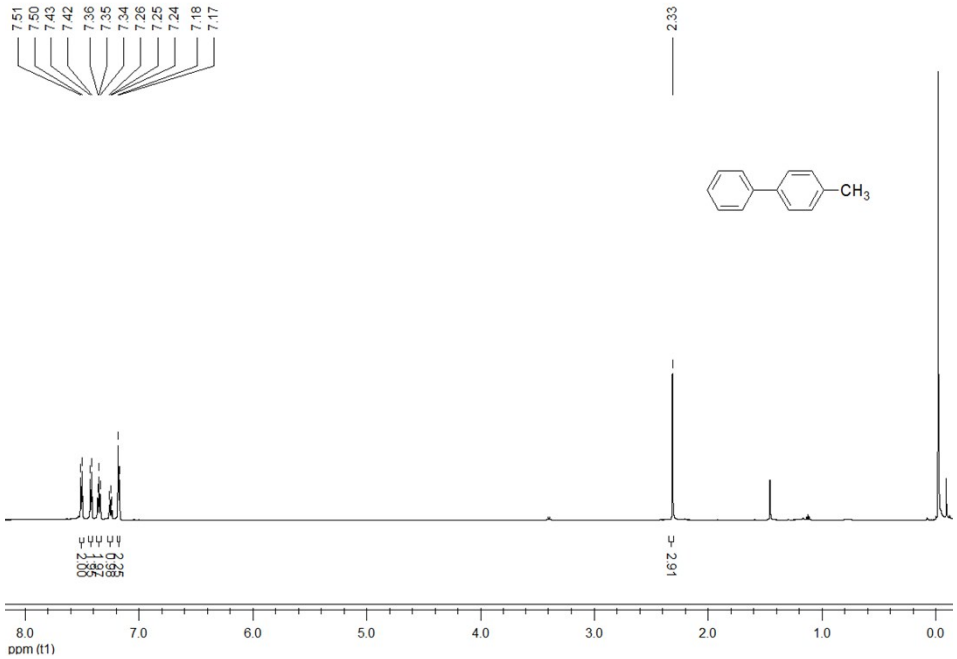
^{1}H NMR ($CDCl_3$):δ7.34 (t, *J*= 7.3 Hz, 4H), 7.41-7.45 (m, 4H), 7.59 (t, *J*=7.8Hz, 2H) ppm.^{13}C NMR ($CDCl_3$): δ 127.2, 127.3, 128.8, 141.3 ppm.

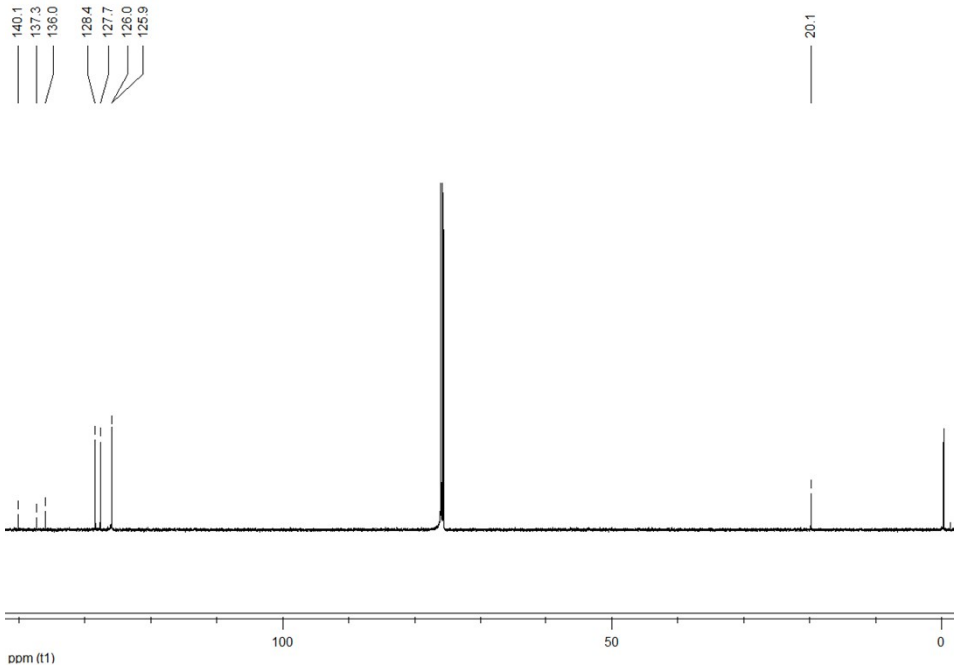


4-methyl-1,1'-biphenyl (3b)

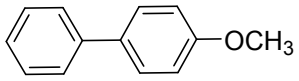


^{1}H NMR ($CDCl_3$): δ 2.33 (s, 3H), 7.18 (d, *J* = 6.0Hz, 2H), 7.25 (t, *J* = 6.7 Hz, 1H), 7.35 (t, *J* = 6.8 Hz, 2H), 7.42 (d, *J* = 7.9 Hz, 2H), 7.51 (d, *J* = 7.9 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$): δ 20.1, 125.9, 126.0, 127.7, 128.4, 136.0, 137.3, 140.11 ppm.

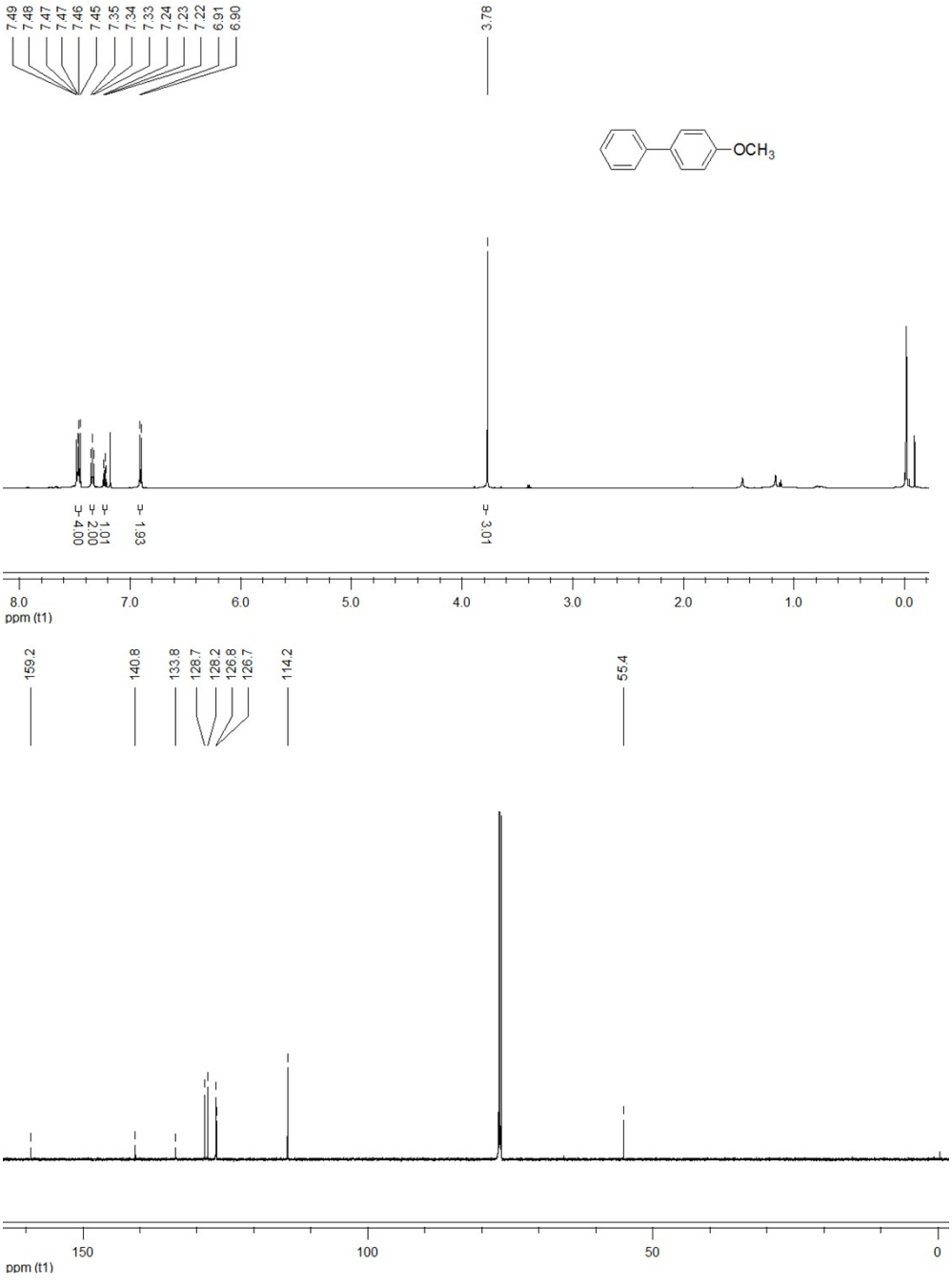




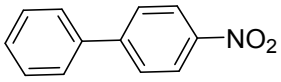
4-methoxy-1,1'-biphenyl (3c)



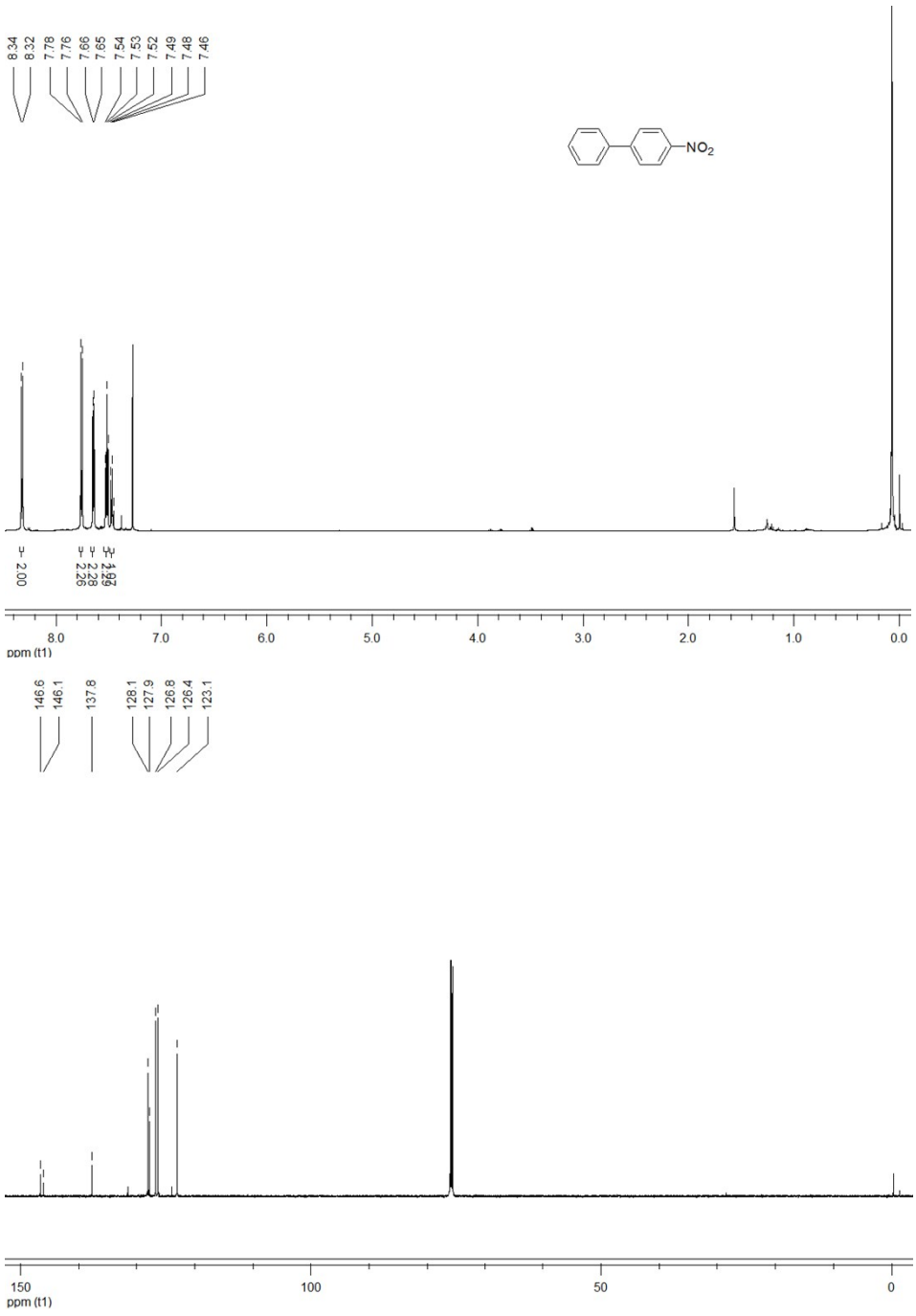
^{1}H NMR ($CDCl_3$): δ 3.78 (s, 3H), 6.91 (d, *J* = 8.8 Hz, 2H), 7.23 (t, *J* = 6.2 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.45-7.49 (m, 4H) ppm; ^{13}C NMR ($CDCl_3$): δ 55.4, 114.2, 126.7, 126.8, 128.2, 128.7, 133.8, 140.8, 159.2 ppm.



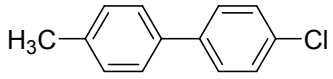
4-nitro-1,1'-biphenyl (3d)



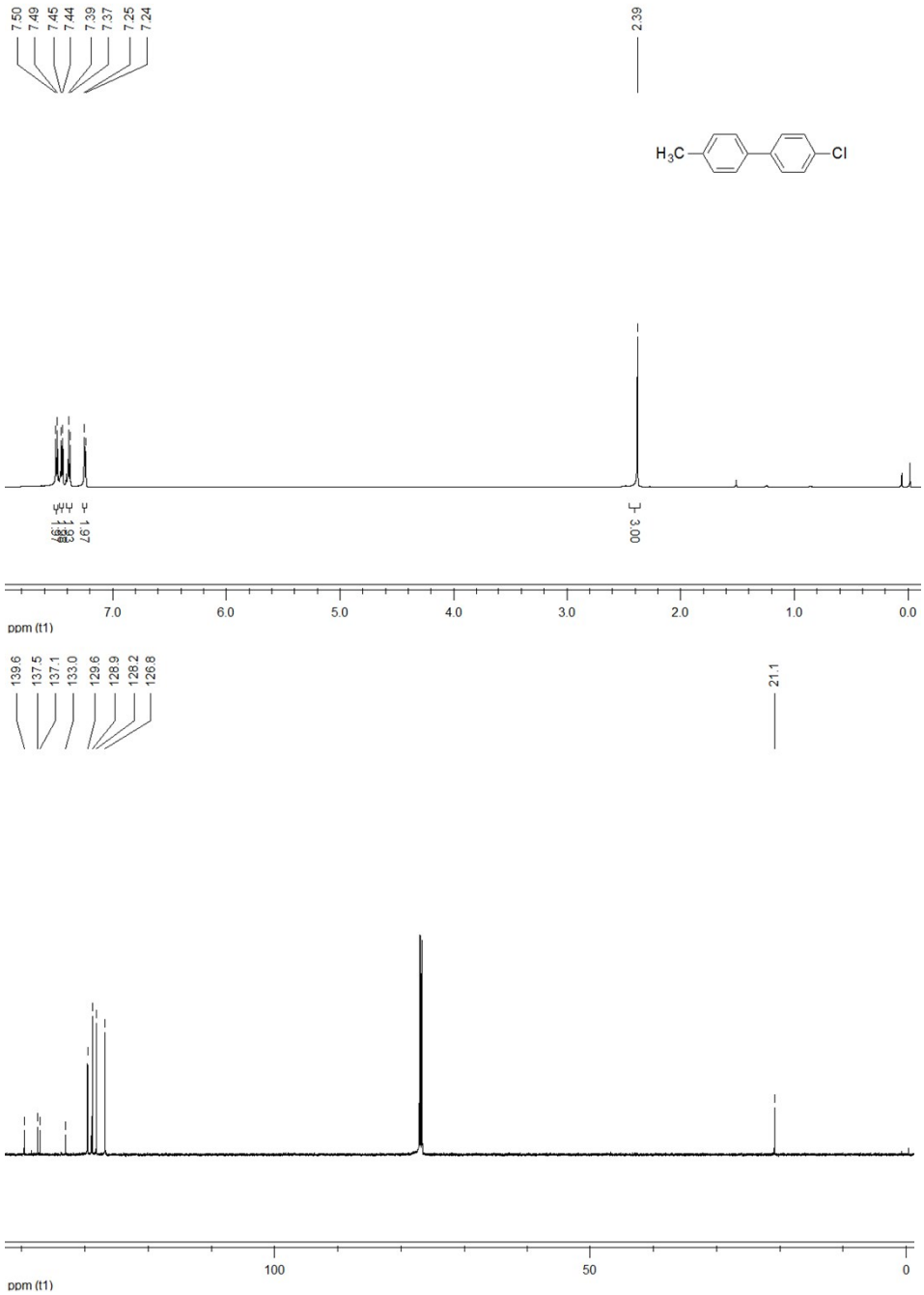
^{1}H NMR ($CDCl_3$): δ7.48 (t, *J* = 7.36 Hz, 1H), 7.53 (d, *J* = 7.15 Hz, 2H), 7.66 (d, *J* = 7.19 Hz, 2H), 7.77 (d, *J* = 8.83 Hz, 2H), 8.33 (d, *J* = 8.83 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$): δ 124.1, 127.4, 127.8, 128.9, 129.1, 138.8, 147.1, 147.6 ppm.



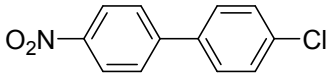
4-chloro-4'-methyl-1,1'-biphenyl (3e)



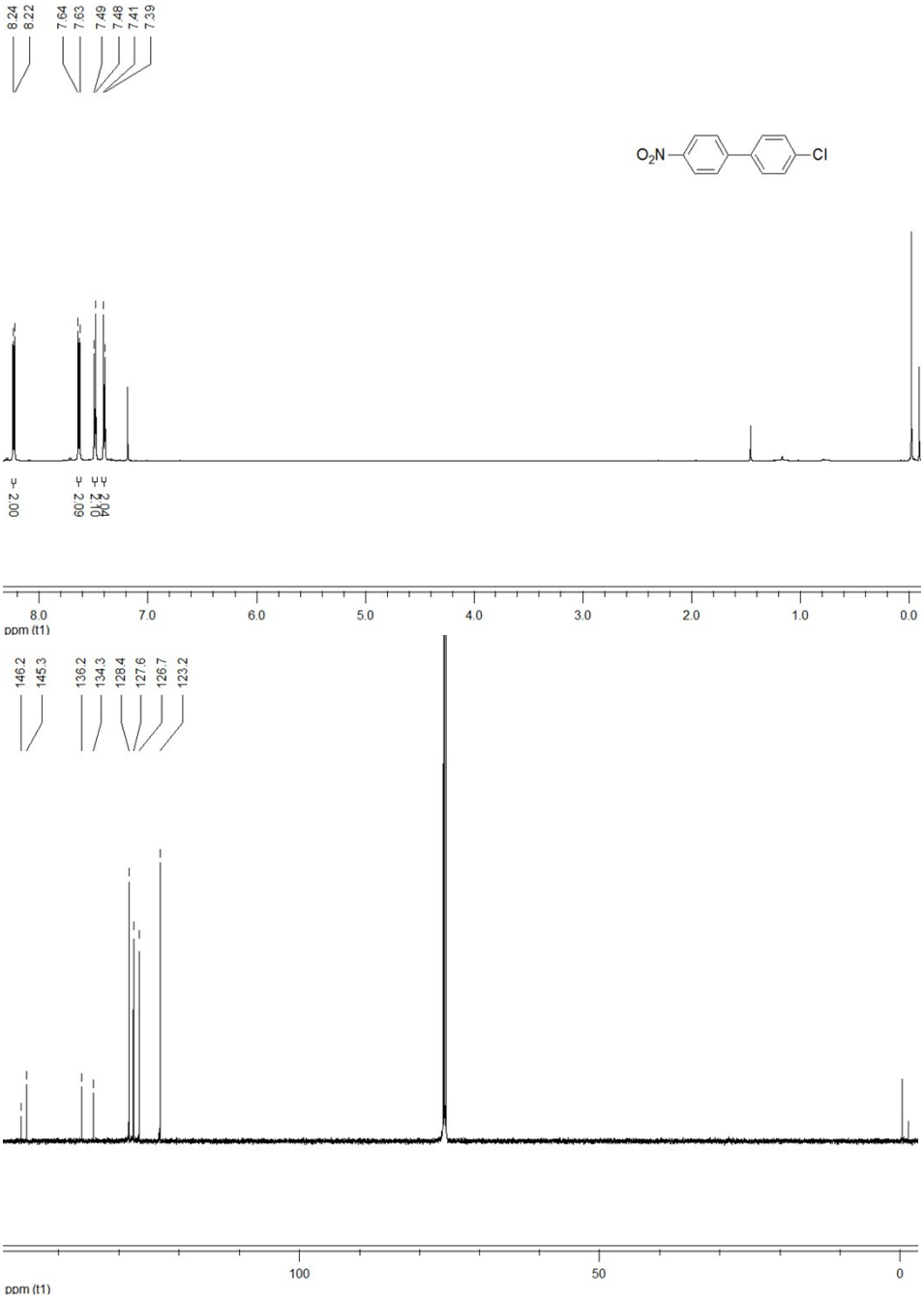
^{1}H NMR ($CDCl_3$): δ 2.39 (s, 3H), 7.24 (d, *J* = 7.5 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$): δ 21.1, 126.8, 128.2, 128.9, 129.6, 133.0, 137.1, 137.5, 139.6 ppm.



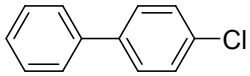
4-chloro-4'-nitro-1,1'-biphenyl (3f)



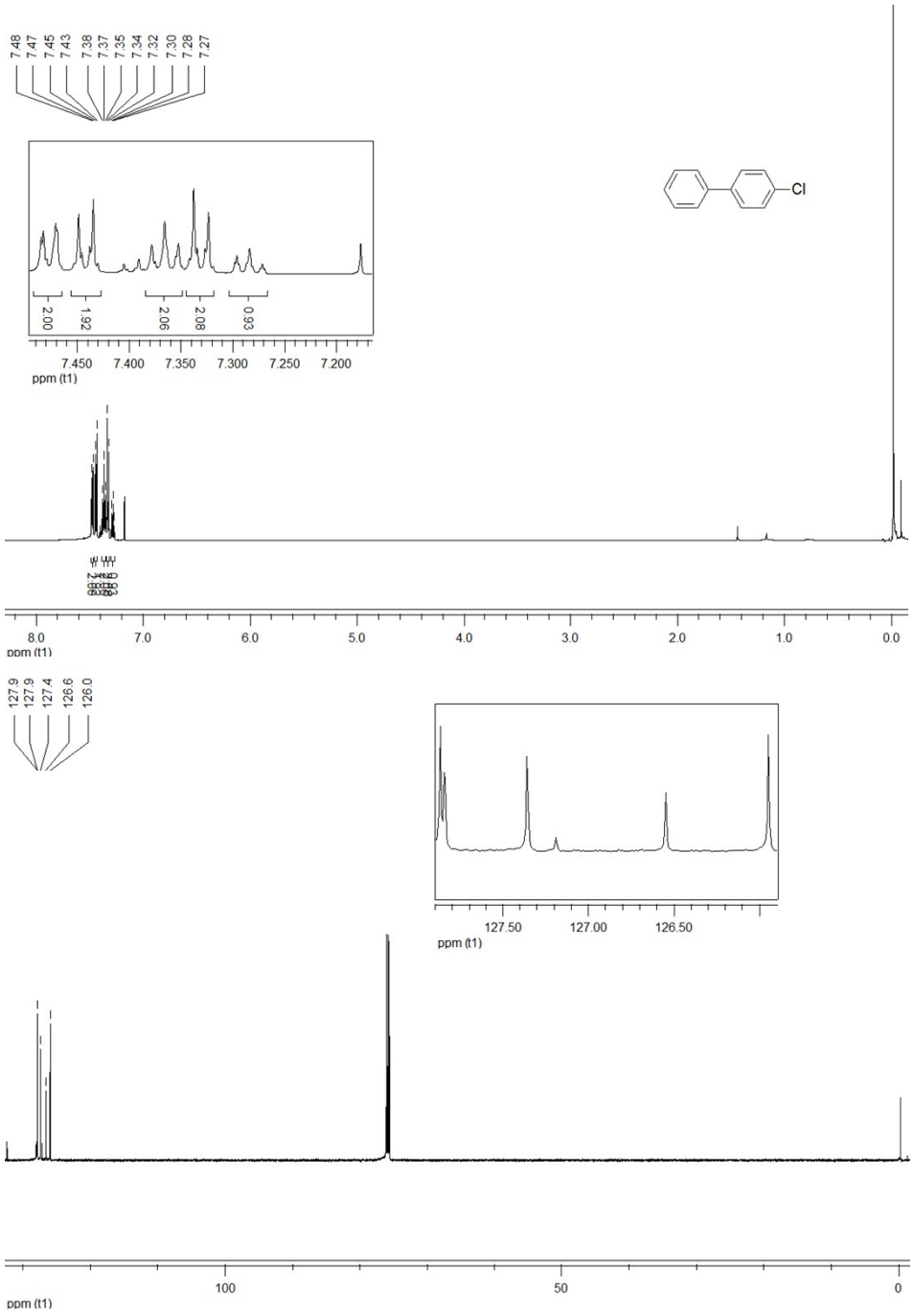
^{1}H NMR ($CDCl_3$): δ 7.40 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.63 (d, *J* = 8.8 Hz, 2H), 8.23 (d, *J* = 8.8 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$): δ 123.2, 126.7, 127.6, 128.4, 134.3, 136.2, 145.3, 146.2, ppm.



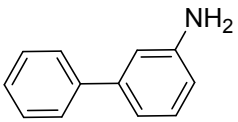
4-chloro-1,1'-biphenyl (3g)



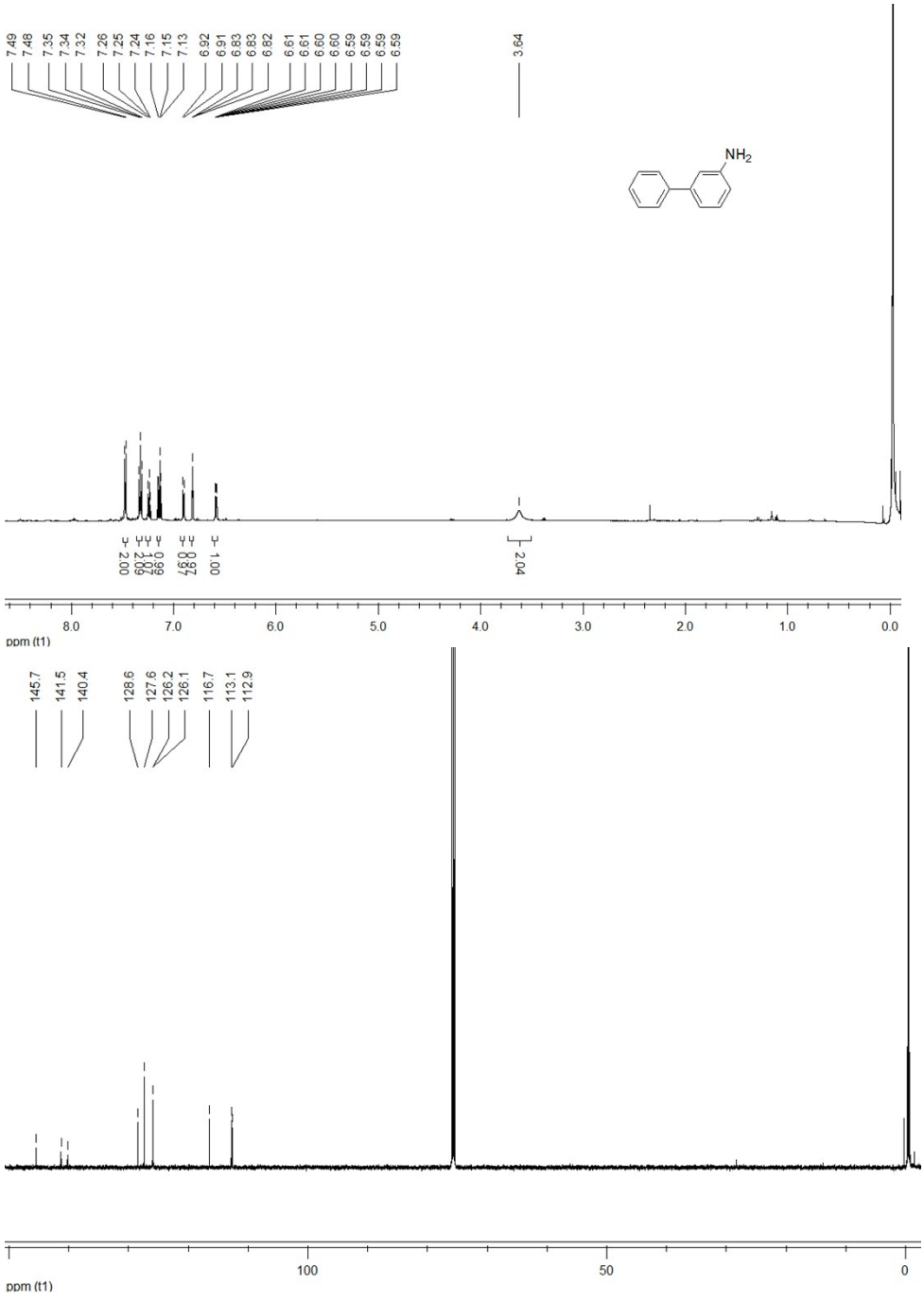
^{1}H NMR ($CDCl_3$): δ7.29 (t, *J* = 7.3 Hz, 1H), 7.33 (d, *J* = 8.6 Hz, 2H), 7.36 (t, *J* = 7.9 Hz, 2H), 7.44 (d, *J* =8.6Hz, 2H), 7.48 (d, *J* = 7.1Hz,2H)ppm; ^{13}C NMR ($CDCl_3$): δ126.0, 126.6, 127.4, 127.9, 127.9 ppm.



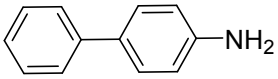
[1,1'-biphenyl]-3-amine (3h)



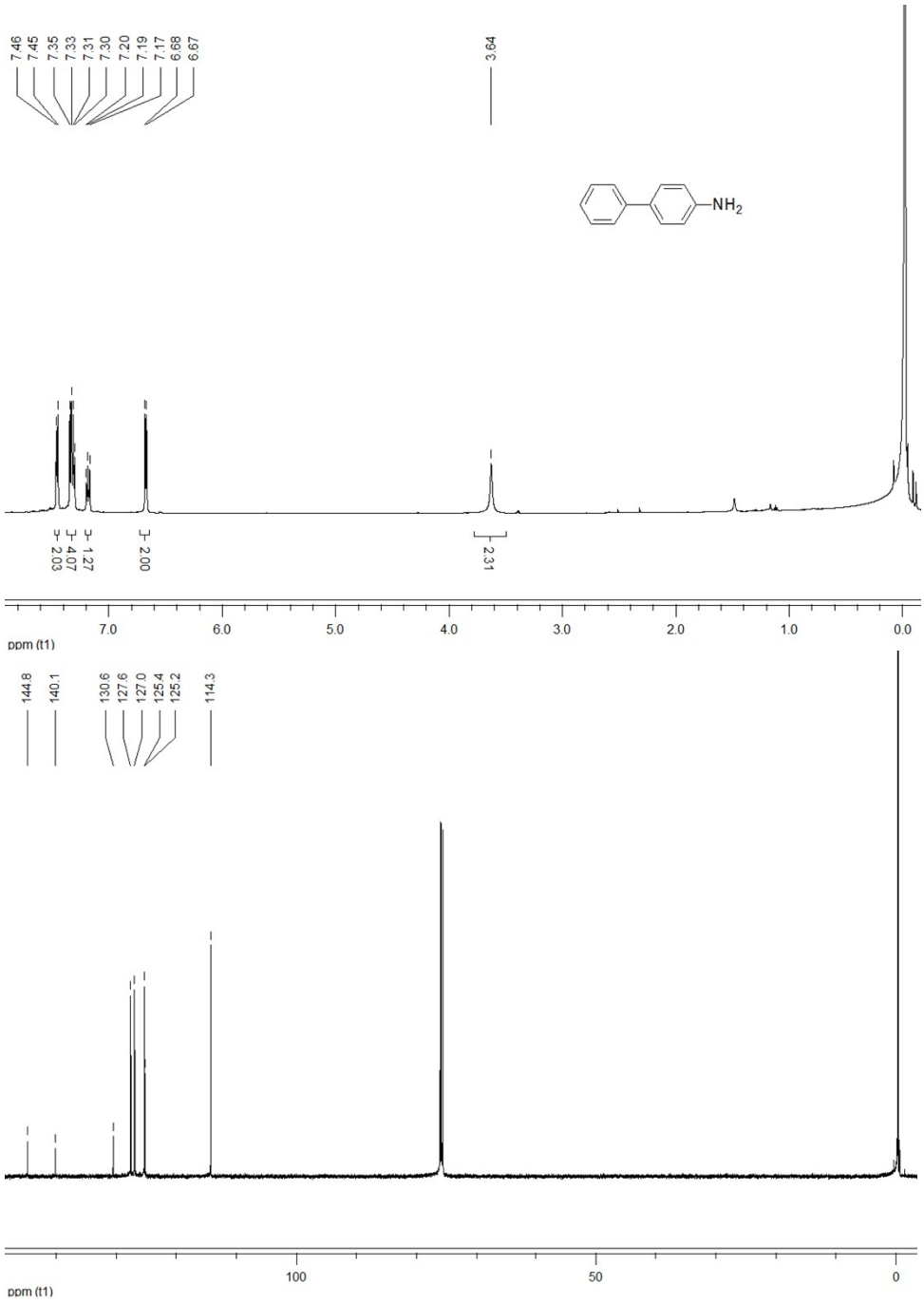
^{1}H NMR ($CDCl_3$): δ 3.64 (s, 2H), 6.59-6.61 (m, 1H), 6.83 (t, *J* = 2.0 Hz, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 7.14 (t, *J* = 7.8 Hz, 1H), 7.26 (t, *J* = 7.4 Hz, 1H), 7.33 (t, *J* = 7.9 Hz, 2H), 7.48 (d, *J* = 8.1 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$): δ 112.9, 113.1, 116.7, 126.1, 126.2, 127.6, 128.6, 140.4, 141.5, 145.7 ppm.



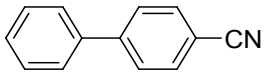
[1,1'-biphenyl]-4-amine (3i)



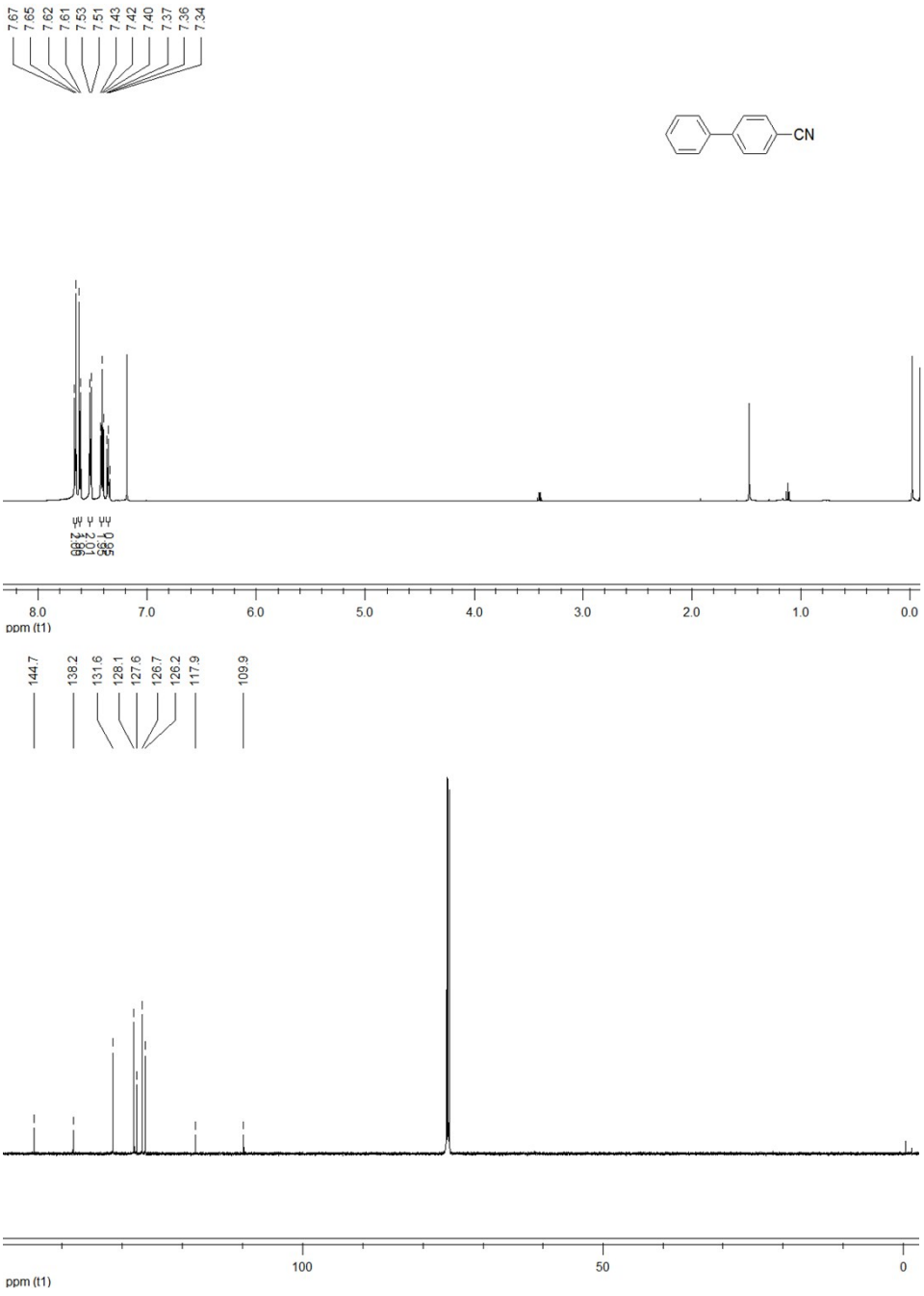
^{1}H NMR ($CDCl_3$): δ 3.64 (s, 2H), 6.68 (d, *J* = 8.3 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.30-7.35 (m, 2H), 7.46 (d, *J* = 7.8 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$): δ 114.3, 125.2, 125.4, 127.0, 127.6, 130.6, 140. 1, 144.8 ppm.



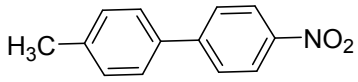
[1,1'-biphenyl]-4-carbonitrile (3j)



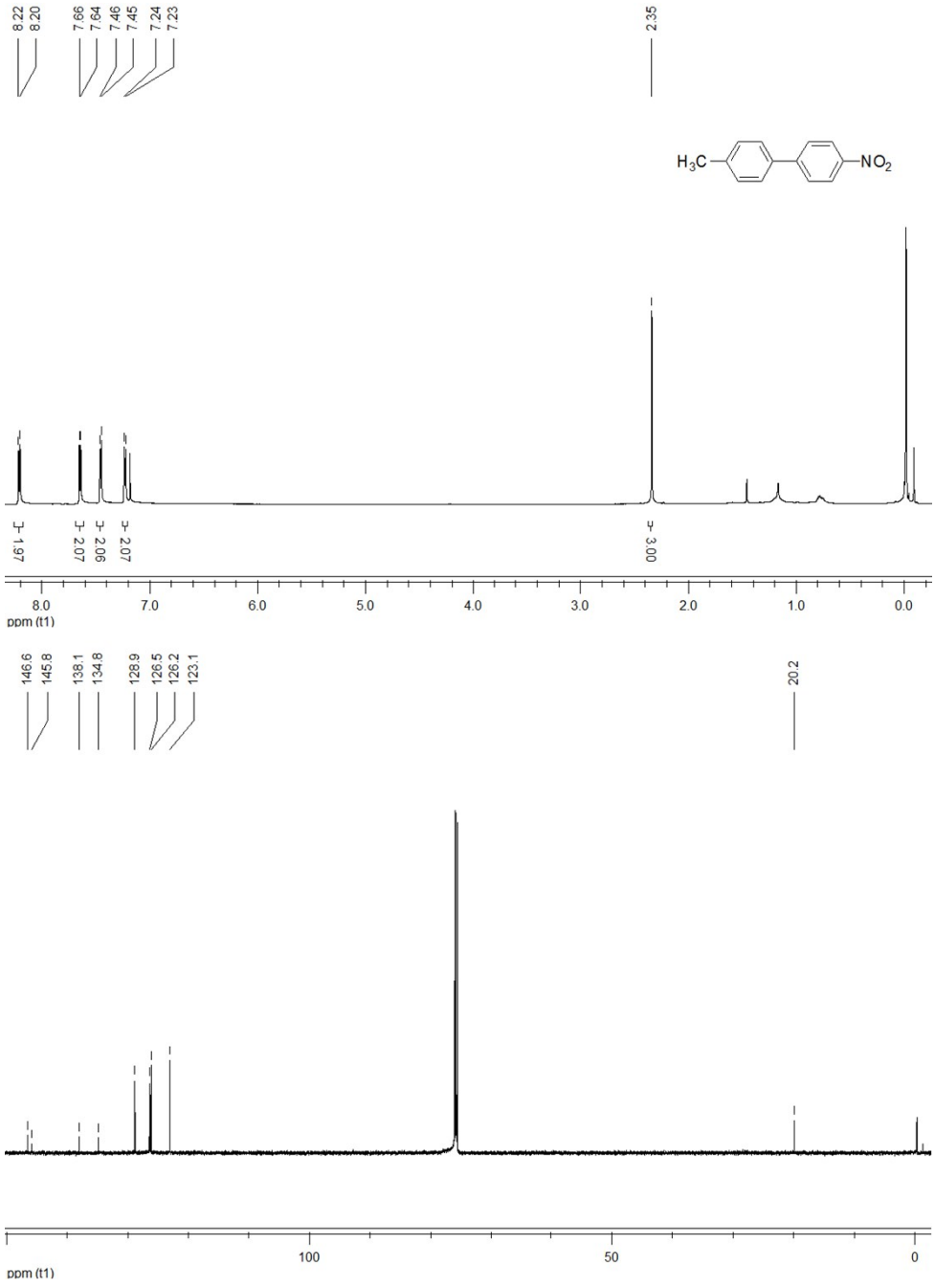
^{1}H NMR ($CDCl_3$): δ7.36 (t, *J* = 7.5Hz, 1H), 7.42 (t, *J* = 7.2 Hz, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.62（d, *J* = 8.6 Hz, 2H）, 7.66 (d, *J* = 8.6 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$): δ 109.9, 117.9, 126.2, 126.7, 127.6, 128.1, 131.6, 138.2, 144.7 ppm.



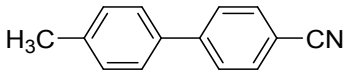
4-methyl-4'-nitro-1,1'-biphenyl (3k)



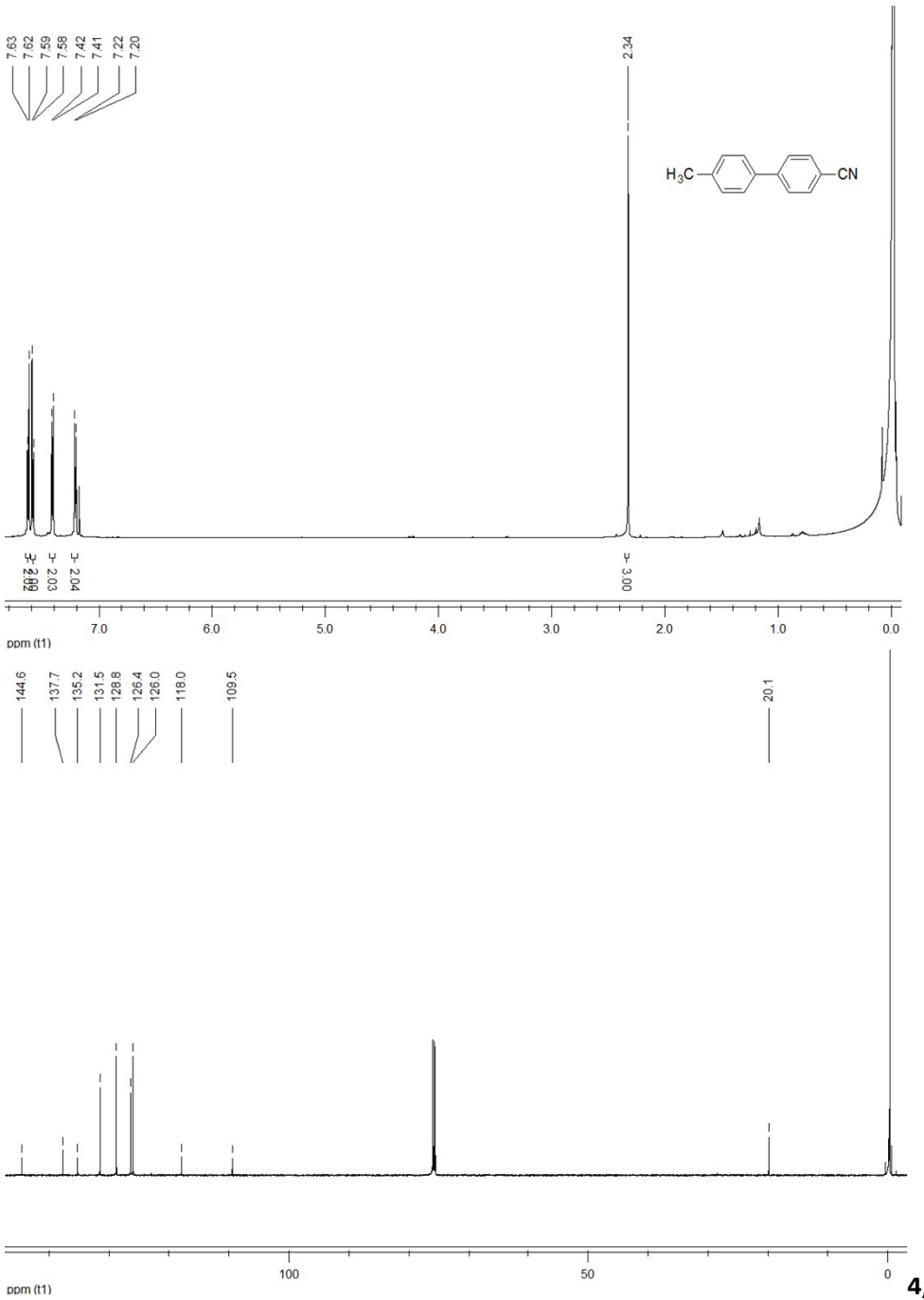
^{1}H NMR ($CDCl_3$): δ 2.35 (s, 3H), 7.23 (d, *J* = 7.7 Hz, 2H), 7.46 (d, *J* = 7.8 Hz, 2H), 7.65 (d, *J* = 8.6 Hz, 2H), 8.21 (d, *J* = 8.6 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$): δ 20.2, 123.1, 126.2, 126.5, 128.9, 134.8, 138.1, 145.8, 146.6 ppm.



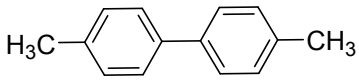
4'-methyl-[1,1'-biphenyl]-4-carbonitrile (3l)



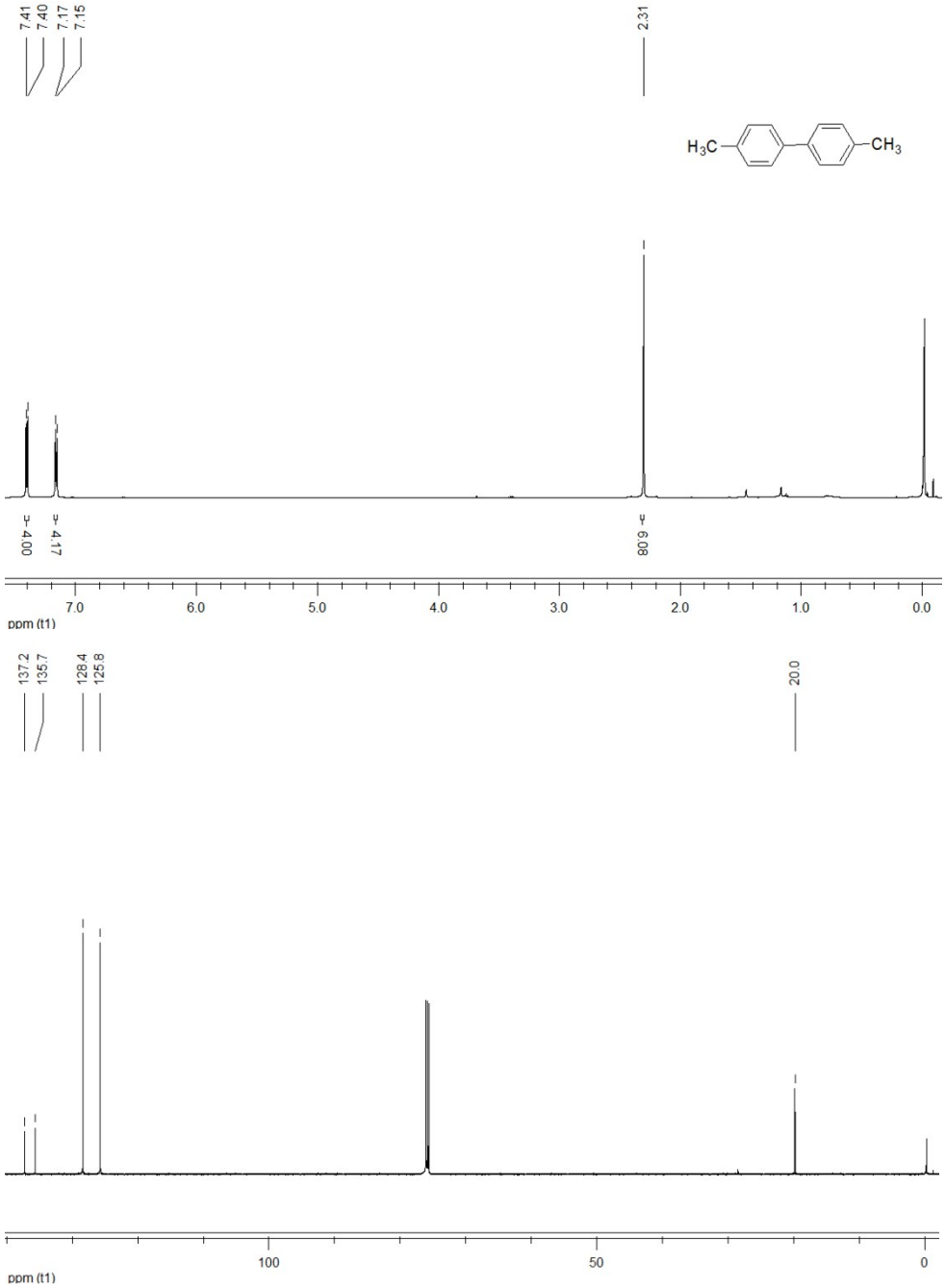
^{1}H NMR ($CDCl_3$): δ 2.34(s, 3H), 7.21 (d, *J* = 7.9 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$): δ 20.1, 109.5, 118.0, 126.0, 126.4, 126.8, 131.5, 135.2, 137.7, 144.6 ppm.



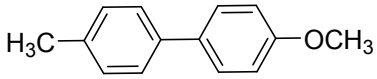
4,4'-dimethyl-1,1'-biphenyl (3m)



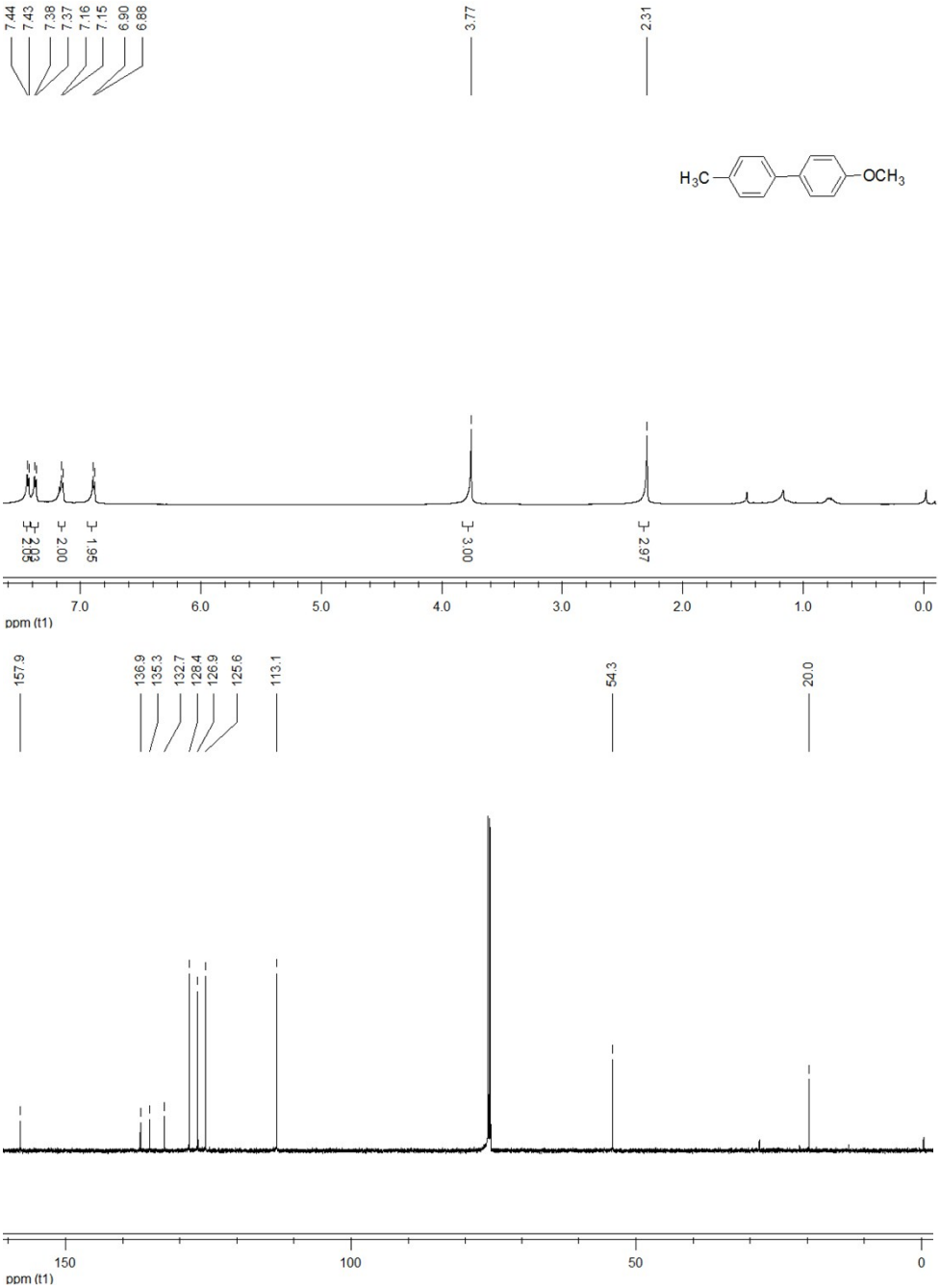
^{1}H NMR ($CDCl_3$): δ 2.31 (s, 6H), 7.16 (d, *J* = 7.9 Hz, 4H), 7.40 (d, *J* = 8.1 Hz, 4H) ppm; ^{13}C NMR ($CDCl_3$): δ 20.0, 125.8, 128.4, 135.7, 137.2 ppm.



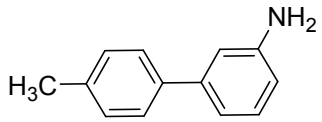
4-methoxy-4'-methyl-1,1'-biphenyl (3n)



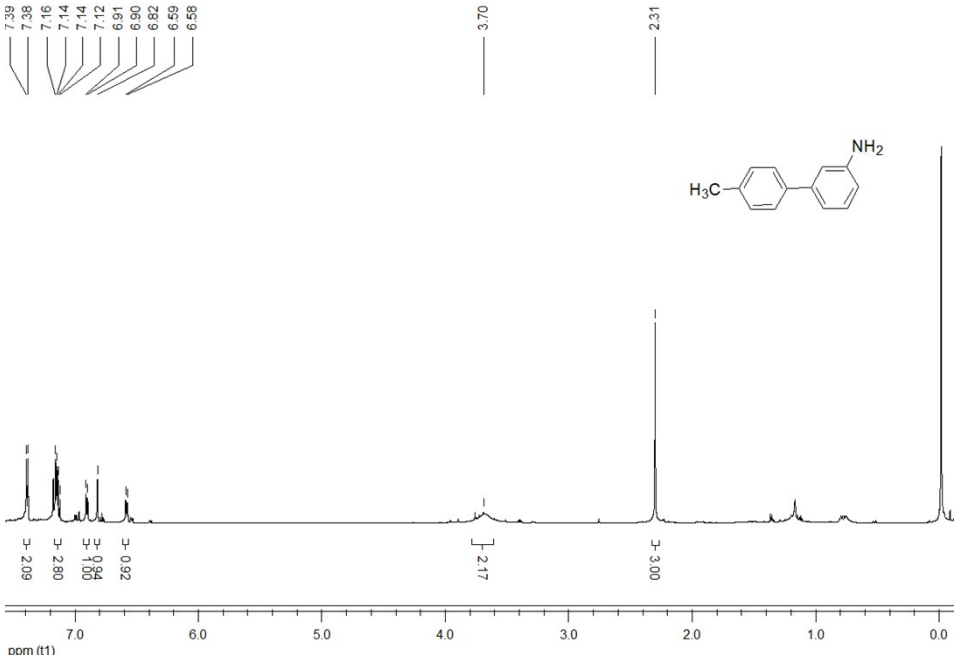
^{1}H NMR ($CDCl_3$): δ 2.31 (s, 3H), 3.77 (s, 3H), 6.89 (d, *J* = 8.3 Hz, 2H), 7.15 (d, *J* = 7.5 Hz, 2H), 7.45 (d, *J* = 7.6Hz, 2H), 7.52 (d, *J* = 8.3Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$): δ 20.0, 54.3, 113.1, 125.6, 126.9, 128.4, 132.7, 135.3, 136.9, 157.9 ppm.

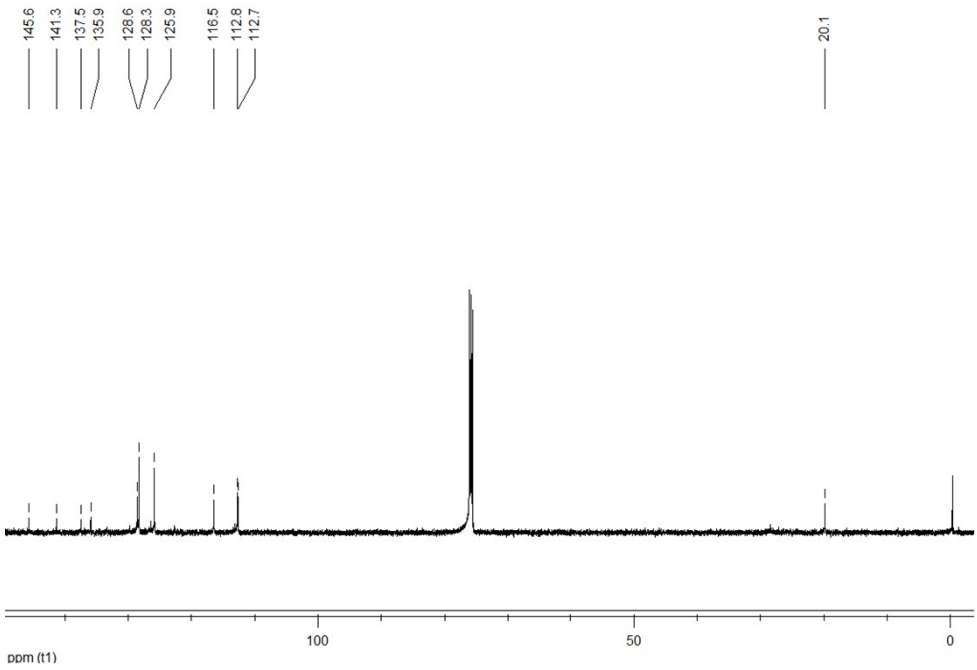


4'-methyl-[1,1'-biphenyl]-3-amine (3o)

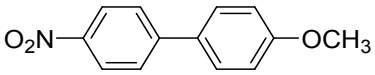


^{1}H NMR ($CDCl_3$): δ 2.31 (s, 3H), 3.70 (s, 2H), 6.58 (d, *J* = 7.9 Hz, 1H), 6.82 (s, 1H), 6.91 (d, *J* = 7.7 Hz, 1H), 7.12-7.16 (m, 3H), 7.39 (d, *J* = 8.0 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$): δ 20.1, 112.7, 112.8, 116.5, 125.9, 128.3, 128.6, 135.9, 137.5, 141.3, 145.6 ppm.

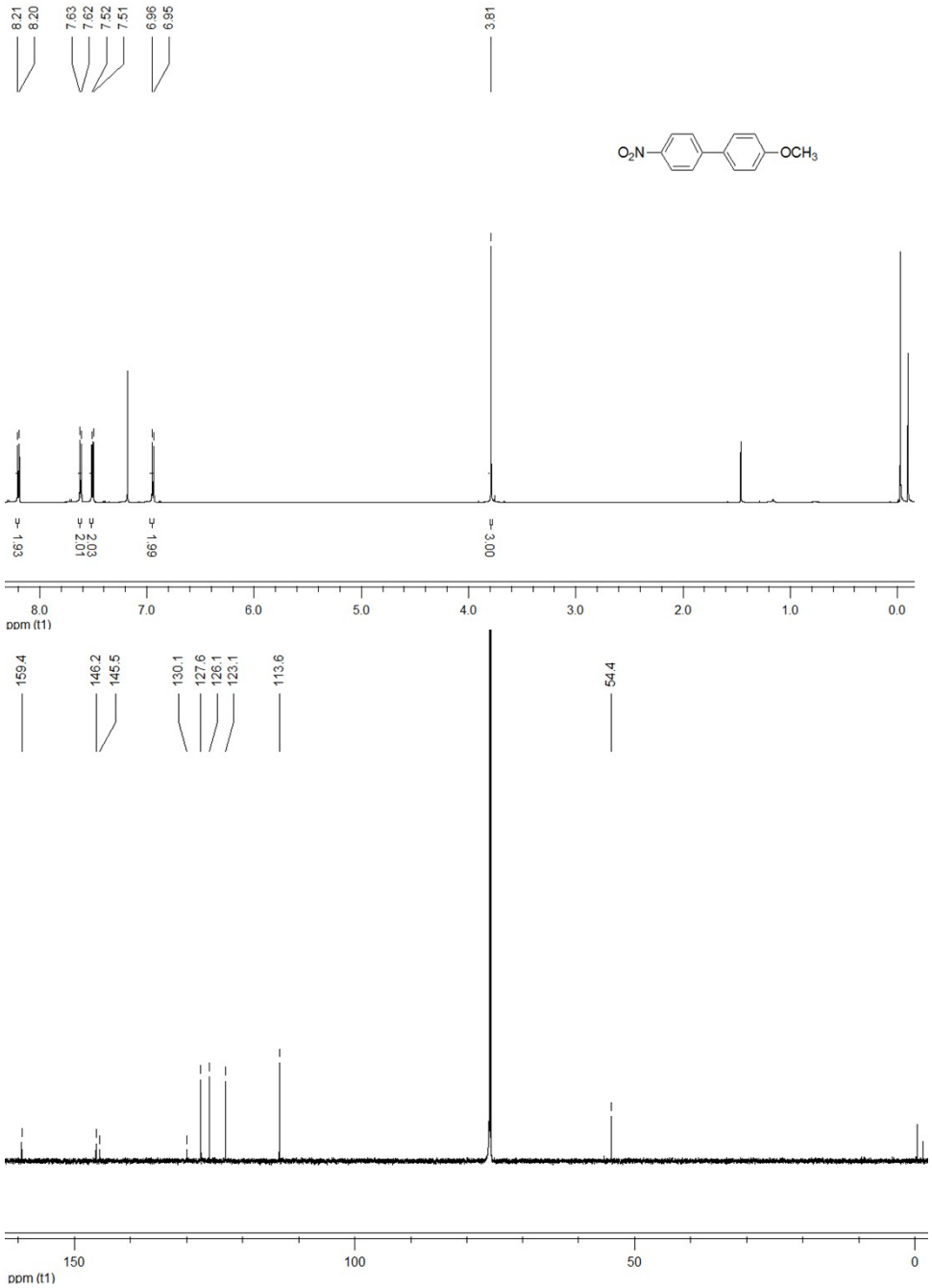




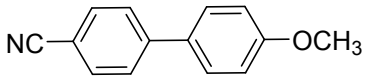
4-methoxy-4'-nitro-1,1'-biphenyl (3p)



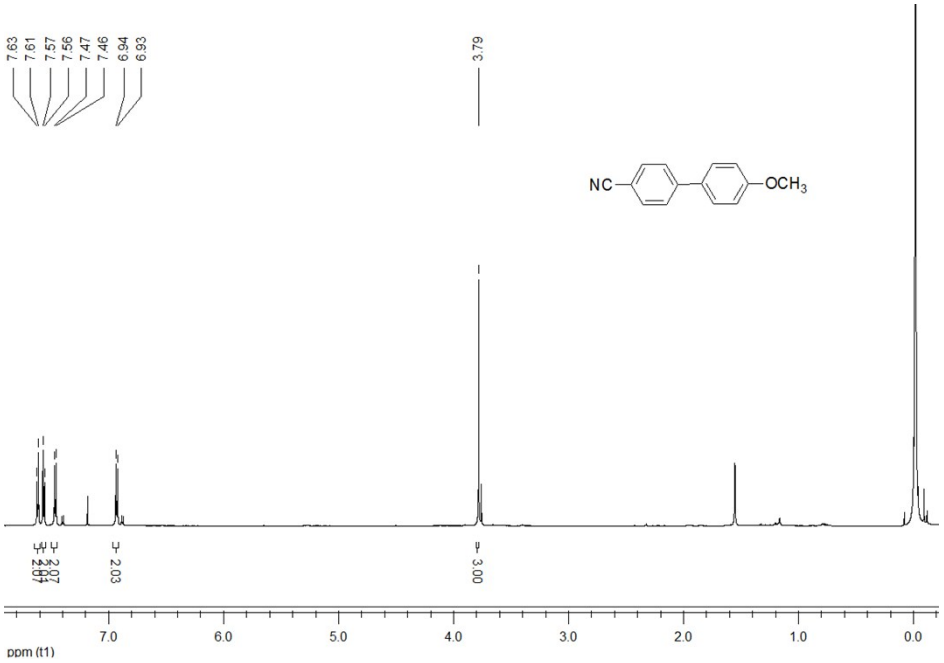
^{1}H NMR ($CDCl_3$): δ 3.81 (s, 3H), 6.95 (d, *J* = 8.8 Hz, 2H), 7.52 (d, *J* = 8.8 Hz, 2H), 7.63 (d, *J* = 8.9 Hz, 2H), 8.21 (d, *J* = 8.9 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$): δ 54.4, 113.6, 123.1, 126.1, 127.6, 130.1, 145.5, 146.2, 159.4 ppm.

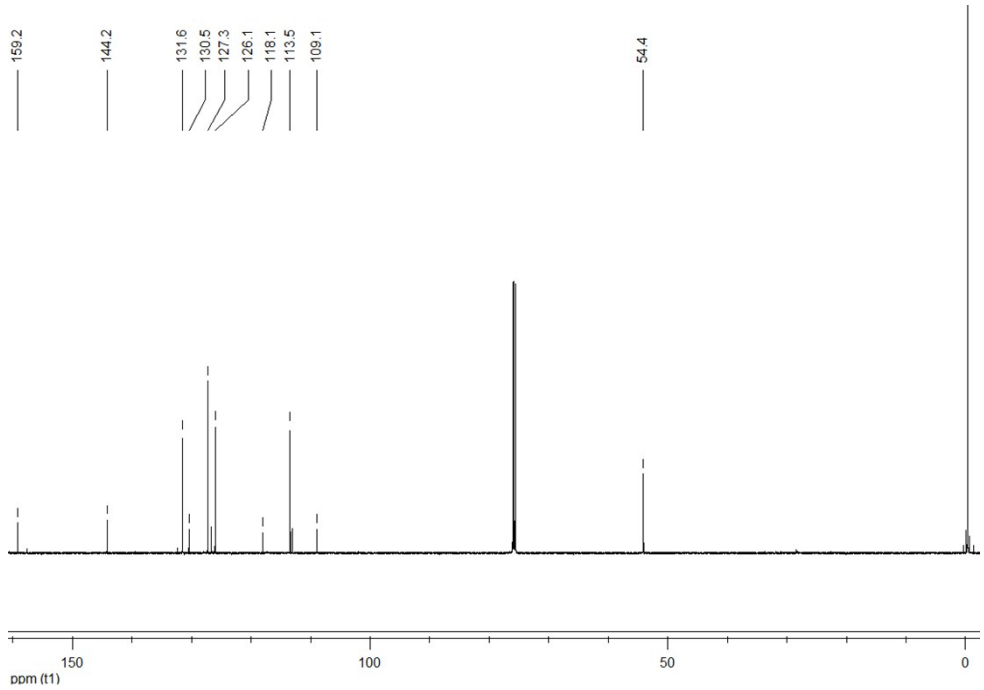


4'-methoxy-[1,1'-biphenyl]-4-carbonitrile (3q)

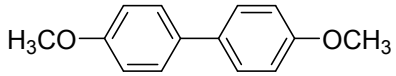


^{1}H NMR ($CDCl_3$): δ3.79(s, 3H), 6.93 (d, *J* = 8.8 Hz, 2H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.62 (d, *J* = 8.5 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$): δ 54.4, 109.1, 113.5, 118.1, 126.1, 127.3, 130.5, 131.6, 144.2, 159.2 ppm.

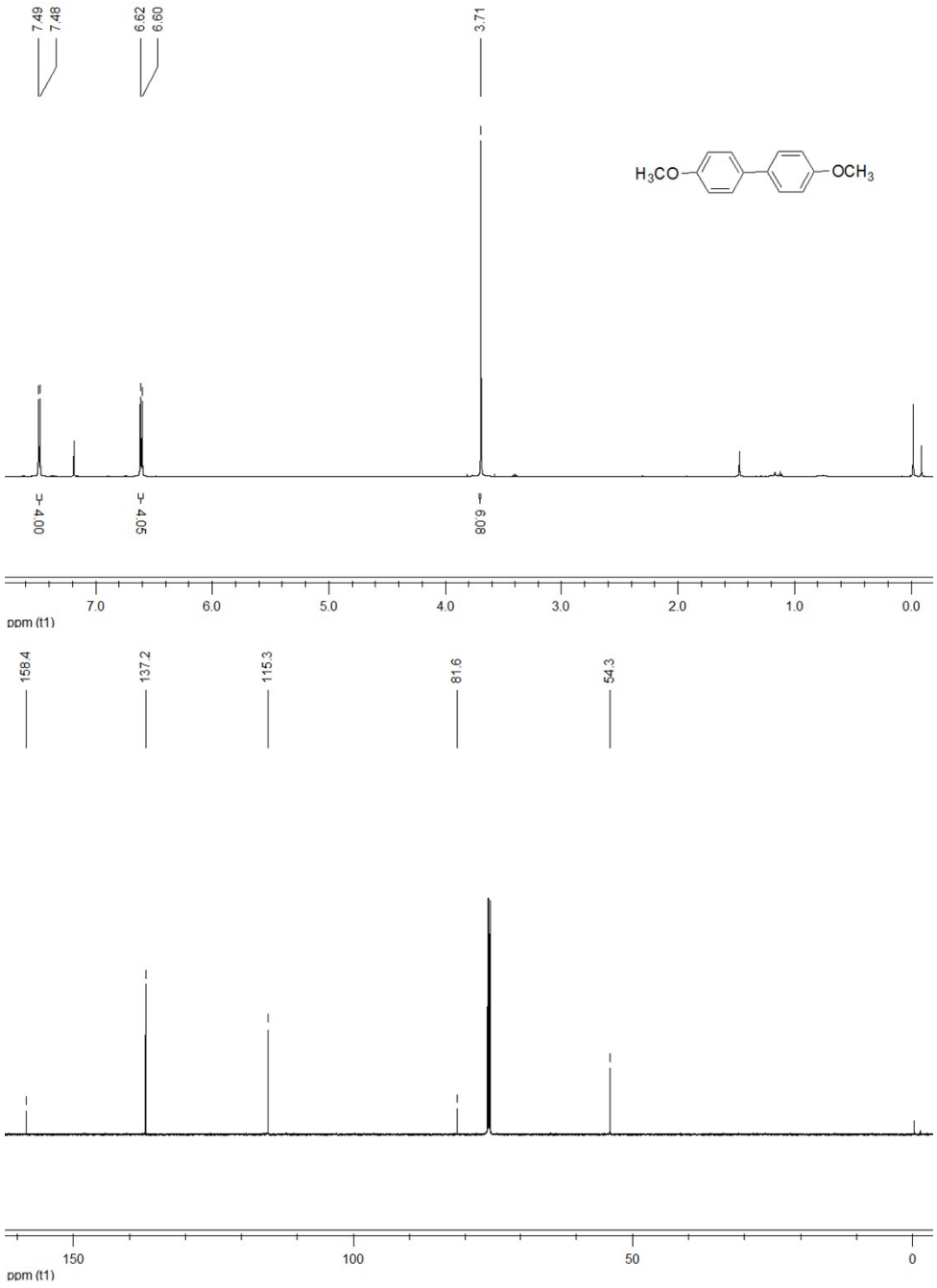




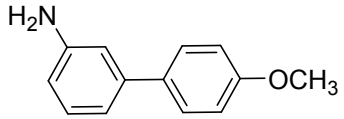
4,4'-dimethoxy-1,1'-biphenyl (3r)



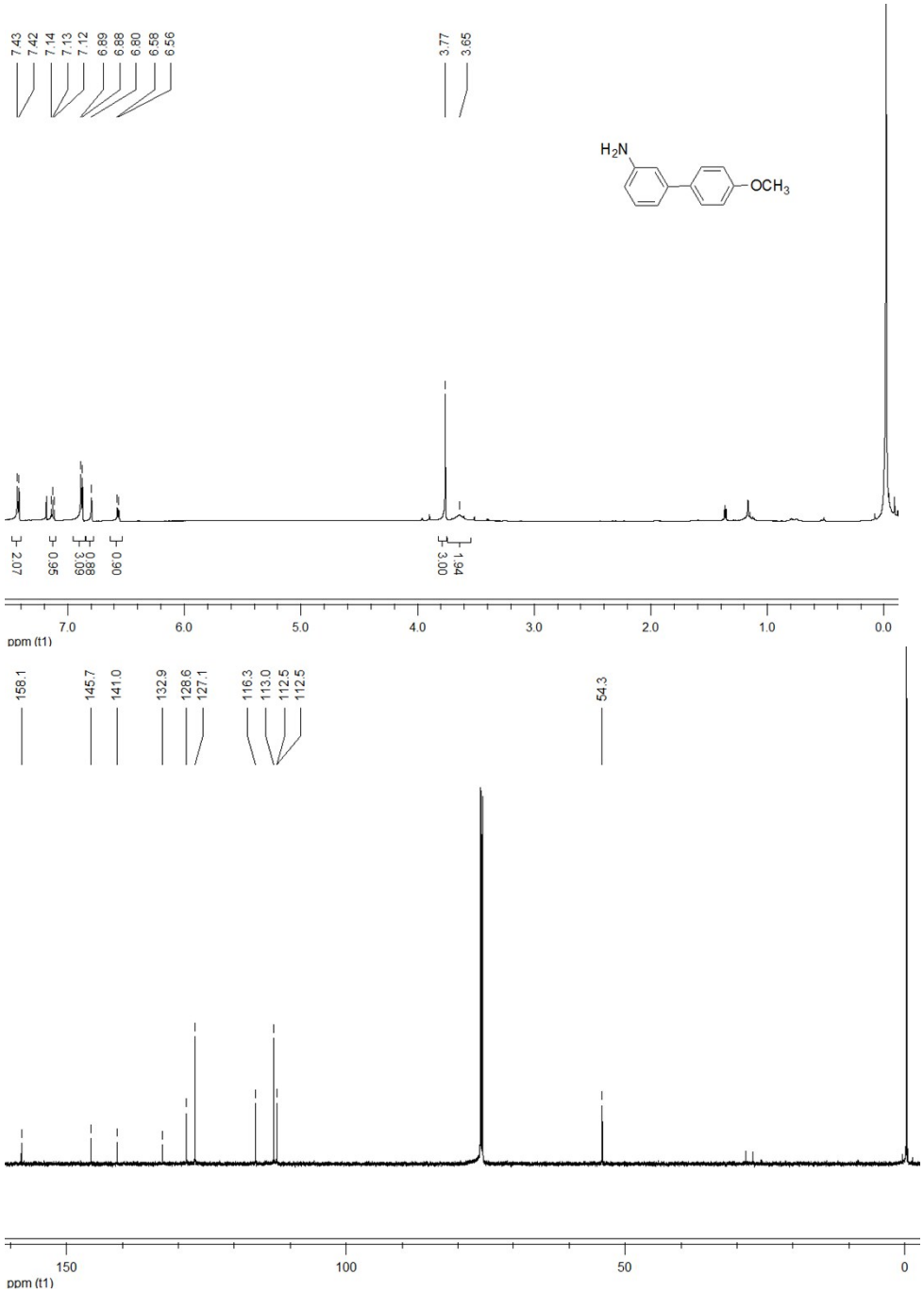
^{1}H NMR ($CDCl_3$): δ 3.71 (s, 6H), 6.61 (d, *J* = 8.9 Hz, 4H), 7.48 (d, *J* = 8.9 Hz, 4H) ppm; ^{13}C NMR ($CDCl_3$): δ 54.3, 81.6, 115.3, 137.2, 158.4 ppm.



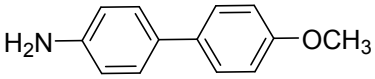
4'-methoxy-[1,1'-biphenyl]-3-amine (3s)



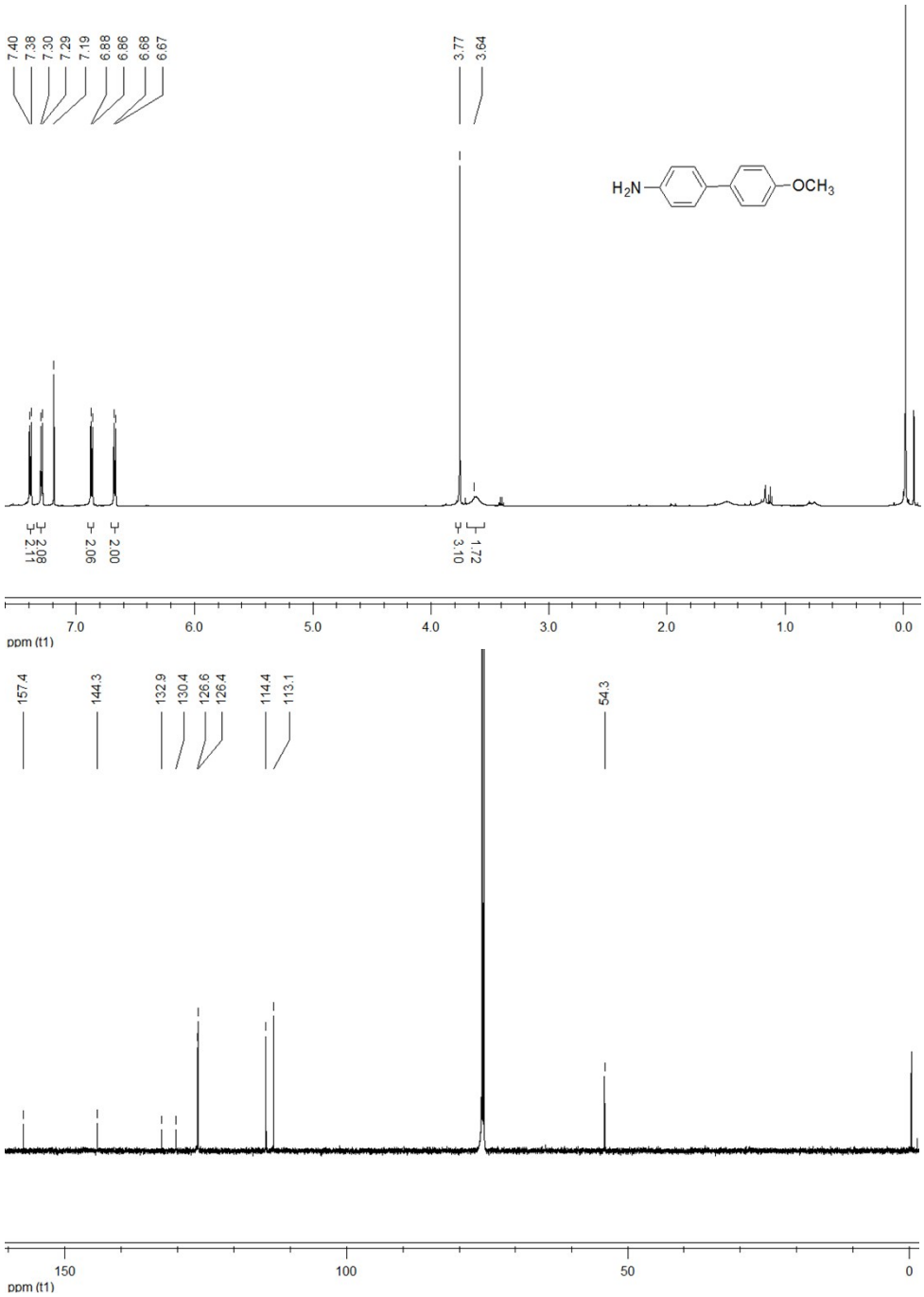
^{1}H NMR ($CDCl_3$): δ 3.65 (s, 2H), 3.77 (s, 3H), 6.57 (d, *J* = 7.9 Hz, 1H), 6.80 (s, 1H), 6.88 (d, *J* = 8.4 Hz, 3H), 7.13 (t, *J* = 7.8 Hz, 1H), 7.43 (d, *J* = 8.5 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$): δ 54.3, 112.5, 112.5, 113.0, 116.3, 127.1, 128.6, 132.9, 141.0, 145.7, 158.1 ppm.



4'-methoxy-[1,1'-biphenyl]-4-amine (3t)



^{1}H NMR ($CDCl_3$): δ 3.64 (s, 2H), 3.77 (s, 3H), 6.68 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$): δ 54.3, 113.1, 114.4, 126.4, 126.6, 130.4, 132.9, 144.3, 157.4 ppm.



References

S1 T. Takagi ;T.Miwa; H.Masu, Synthesis and Optical Properties of π-Conjugated Polymers Containing Fused Imidazole Skeleton. *Macromolecules*, 2016. **49**, 8879.

S2 J.Wang;H. Song ;Q. Li;F. Xu; Z. Zhang, Macrocyclic dinuclear gold(I) and silver(I) NHCs complexes. *Inorg. Chim. Acta*, 2005. **358**, 3653.