Supporting Information For

Preparation of Unsymmetrical Biaryls by Pd(II)-Catalyzed Cross-Coupling of Aryl Iodides

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General:

Unless otherwise indicated, all starting materials were obtained from commercial suppliers and were used without further purification. The purchased reagents are listed as follows:

Aryl Iodides:

Iodobenzene, 3-iodo-benzoic acid, 4-iodotoluene, 3-iodotoluene, 3-iodoanisole, 2-iodoanisole, 1-iodonaphthalene, 1-bromo-4-iodobenzene, 1-iodo-3-nitrobenzene, 1-chloro-3-iodobenzene, 1-chloro-4-iodobenzene.

Catalysts:

Palladium(II) acetate, palladium(II) chloride, palladium(II) on activated carbon, tetrakis(triphenylphosphine)palladium(0), tris(dibenzylidenacetone)dipalladium(0).

Solvents:

2,2,2-Trifluoroethanol (TFE), 1,2-dichloroethane, acetonitrile, phenetole, 2-butanone, ethanol, 3-pentanone, trifluoroacetic acid (TFA).

Base:

Potassium carbonate, anhydrous sodium carbonate, cesium carbonate.

Others:

Benzene, anisole, naphthalene, dichloromethane, acetone, petroleum ether, ethyl acetate, zinc powder, potassium iodide, *n*-hexane, chloroform-*d*, adamantane, sulphuric acid, *p*-xylene.

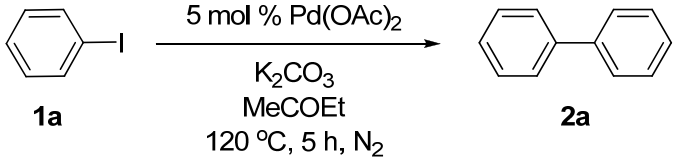
Previously reported compounds were characterized *via* ^{1}H NMR and m.p. and compared to literature values.

Instrumentation:

1. ^{1}H NMR spectra and ^{13}C NMR spectra were recorded on a Varian 400 MHz NMR system in $CDCl_3$ solvent with TMS internal standard unless otherwise specified.
2. TLC was run on 2 cm × 5 cm silica plate. Column chromatography was run on silica gel (300-400 mesh).
3. All GC analyses were performed on a GC9160 Gas-Chromatograph. The capillary column used was SE-54 (Length: 30 m, Column ID: 0.25 mm, Film Thickness: 0.25 um).
4. Melting points were measured with X-4 Microscopic Melting-point Detector are uncorrected.
5. EIMS and HRMS were performed at Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences.
6. FT-IR analyses were performed on a Avatar 360.

Procedure:

1. Typical procedure of Pd(II)-catalyzed homocoupling of aryl iodides, preparation of biphenyl (2a):



In a autoclave (10 mL), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), K_2CO_3 (331.7 mg, 2.4 mmol), MeCOEt (0.5 mL), **1a** (iodobenzene) (40.8 mg, 0.2 mmol) were mixed and stirred at 120 ^oC under N_2 for 5 h. The reaction propagation was monitored by GC and TLC analysis. Then the reaction mixture was diluted by CH_2Cl_2 and filtered. The organic layer was successively washed by water (3 × 10 mL) and dried over anhydrous $MgSO_4$. Then the solvent was evaporated. Coupling products were isolated by flash column chromatography on silica gel using petroleum ether as eluant. Yield of biphenyl (**2a**): 82% (13.9 mg). The products were characterized by their physical constants and spectral analysis.

2. Screening the reaction conditions

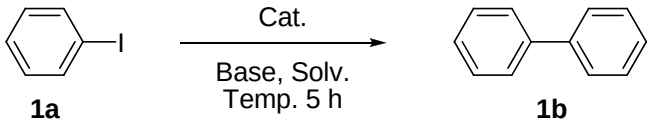


Table S-1 **Effects of catalyst** [a]

Entry	Cat.	Conv. [b] (%)	Yield [b] (%)
1	-	-	none
2	Pd/C	<5	<1
3	$Pd(PPh_3)_4$	51	8
4	$Pd_2(dba)_3$	36	9
5	$Pd(OAc)_2$	94	91(82) [c]
6	$PdCl_2$	62	17

[a] Conditions: **1a** 0.2 mmol, Cat. 0.01 mmol, K_2CO_3 2.4 mmol, MeCOEt 0.5 mL, 120 ^oC, 5 h, under N_2. [b] GC yield based on **1a** (Adamantane as internal standard). [c] Isolate yield in the parentheses.

Table S-2 **Effects of the amount of catalyst** [a]

Entry	$Pd(OAc)_2$ (mmol)	t	Conv. [b] (%)	Yield [b] (%)
1	0.01	5 h	94	91(82) [c]
2	0.002	7 days	71	64

[a] Conditions: **1a** 0.2 mmol, K_2CO_3 2.4 mmol, MeCOEt 0.5 mL, 120 °C, under N_2. (In the entry 2, 0.01 mmol $Pd(OAc)_2$ was put into a 5 mL flask, then o.1 mL TFA was added into the flask, and let the $Pd(OAc)_2$ dissolve in the solvent TFA well, finally 0.02 mL solution was drawoffed from the flask into a 10 mL autoclave.).
[b] GC yield based on **1a** (Adamantane as internal standard).
[c] Isolate yield in the parentheses.

Table S-3 **Effects of base** [a]

Entry	Base	Conv. [b] (%)	Yield [b] (%)
1	Na_2CO_3	10	6
2	K_2CO_3	94	91(82) [c]
3	Cs_2CO_3	>90	17

[a] Conditions: **1a** 0.2 mmol, $Pd(OAc)_2$ 0.01 mmol, base 2.4 mmol, MeCOEt 0.5 mL, 120 °C, 5 h, under N_2. [b] GC yield based on **1a** (Adamantane as internal standard). [c] Isolate yield in the parentheses.

Table S-4 **Effects of amount of base** [a]

Entry	K_2CO_3 (mmol)	Conv. [b] (%)	Yield [b] (%)
1	2.4	94	91(82) [c]
2	2.0	84	70
3	1.2	72	62
4	0.6	53	33
5	0.2	46	15

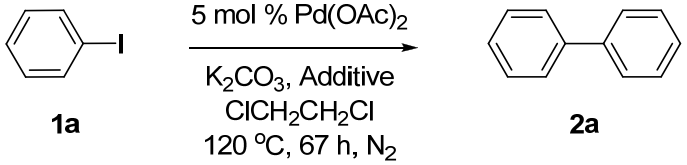
[a] Conditons: **1a** 0.2 mmol, $Pd(OAc)_2$ 0.01 mmol, MeCOEt 0.5 mL, 120 °C, 5 h, under N_2. [b] GC yield based on **1a** (Adamantane as internal standard). [c] Isolate yield in the parentheses.

Table S-5 **Effects of solvent and temperature** [a]

Entry	Solvent	T (^{o}C)	Conv. [b] (%)	Yield [b] (%)
1	TFE	120	82	25
2	EtOH	120	>99	11
3	MeCN	120	62	54
4	PhOEt	120	66	41
5	PhOMe	120	27	19
6	$ClCH_2CH_2Cl$	120	16	8
7	MeCOEt	120	94	91(82) [c]
8	MeCOEt	80	10	3
9 [d]	-	120	44	24
10	PhCOMe	120	51	34
11 [e]	MeCOEt	120	>99	79(72) [c]
12	EtCOEt	120	70 [f]	66 [f]

[a] Conditions: **1a** 0.2 mmol, $Pd(OAc)_2$ 0.01 mmol, K_2CO_3 2.4 mmol, solvent 0.5 mL, 120 ^{o}C, 5 h, under N_2. [b] Detected by GC, based on **1a** (Adamantane as internal standard). [c] Isolate yield in the parentheses. [d] **1a** (2 mmol), 6 days. [e] Under air. [f] Detected by ^{1}H NMR.

Table S-6 **Pd(II)-catalyzed homocoupling of iodobenzene in $ClCH_2CH_2Cl$** [a]

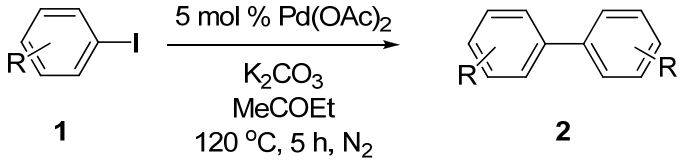


1a **2a**

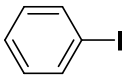
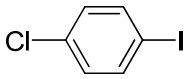
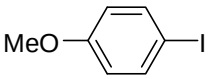
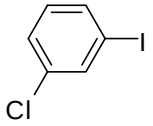
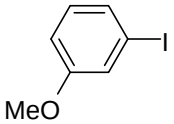
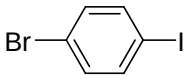
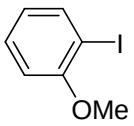
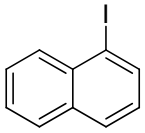
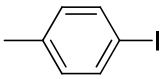
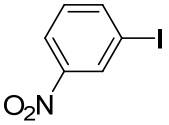
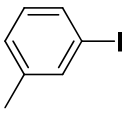
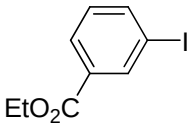
Entry [a]	Additive (mmol)	Yield [b] (%)
1	-	23
2	Benzene 0.6	49

[a] Conditions: **1a** 0.2 mmol, K_2CO_3 2.4 mmol, $ClCH_2CH_2Cl$ 0.5 mL, 120 ^{o}C, 67 h, under N_2.
[b] GC yield base on **1a** (Adamantane as internal standard).

3. Pd(II)-catalyzed homocoupling of aryl iodides [a]



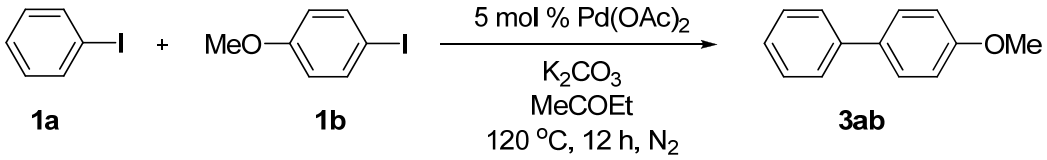
1 **2**

Entry	Ar-I 0.2 mmol	Yield [b] (%)	Entry	Ar-I 0.2 mmol	Yield [b] (%)
1	 **1a**	**2a** 82	7	 **1g**	**2g** 76
2	 **1b**	**2b** 88	8	 **1h**	**2h** 81
3	 **1c**	**2c** 78	9	 **1i**	**2i** 73
4	 **1d**	**2d** 69	10	 **1j**	**2j** 70
5	 **1e**	**2e** 72	11	 **1k**	**2k** 65
6	 **1f**	**2f** 76	12	 **1l**	**2l** 69

[a] Conditions: $Pd(OAc)_2$ 0.01 mmol, K_2CO_3 2.4 mmol, MeCOEt 0.5 mL, 120 °C, 5 h, under N_2.

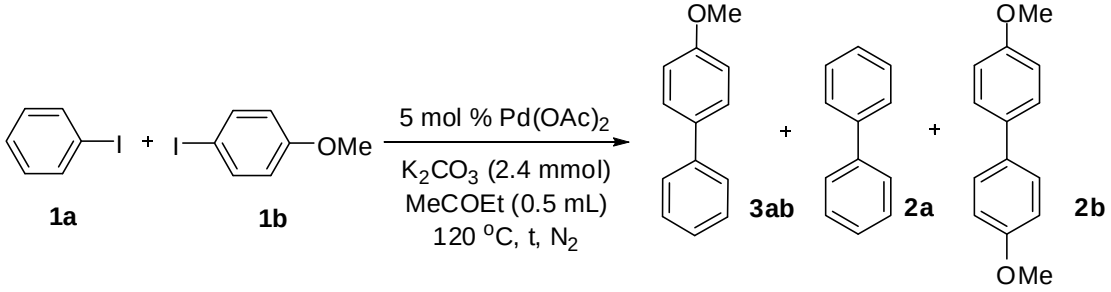
[b] Isolated yield.

4. Typical procedure of Pd(II)-catalyzed cross-coupling of aryl iodides, preparation of 4-methoxy-biphenyl (2ab):



In a autoclave (10 mL), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), K_2CO_3 (331.7 mg, 2.4 mmol), MeCOEt (0.5 mL), **1a** (iodobenzene) (81.6 mg, 0.4 mmol), **1b** (4-iodoanisole) (46.8 mg, 0.2 mmol) were mixed and stirred at 120 ^oC under N_2 for 12 h. The reaction propagation was monitored by GC and TLC analysis. Then the reaction mixture was diluted by CH_2Cl_2 and filtered. The organic layer was successively washed by water (3 × 10 mL) and dried over anhydrous $MgSO_4$. Then the solvent was evaporated. Coupling products were isolated by flash column chromatography on silica gel using *n*-hexane-ethyl actate (50:1, v/v) as eluant. Yield of 4-methoxy-biphenyl (**3ab**): 79% (29.1 mg). Yield of biphenyl (**2a**): 20% (13.0 mg). The products were characterized by their physical constants and spectral analysis.

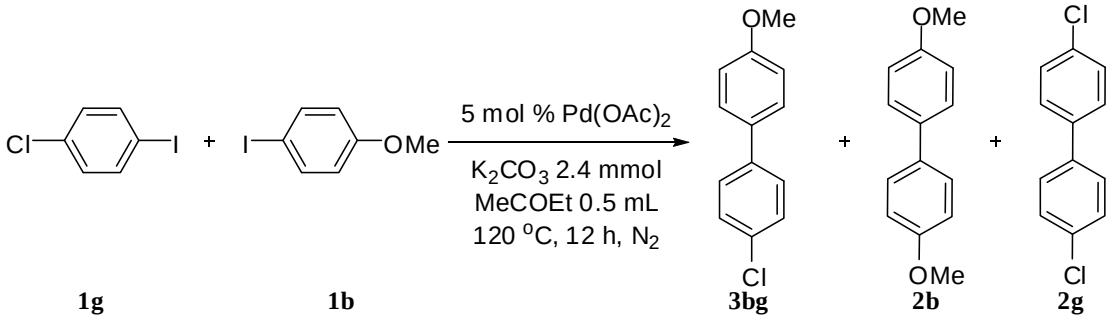
5. Effects of the ratio of 4-iodoanisole and iodobenzene



Entry	**1a** (mmol)	**1b** (mmol)	t (h)	Yield of **3ab** (%) [a]	Yield of **2a** (%) [b]	Yield of **2b** (%) [c]
1	0.40	0.20	12	79	20	<1
2	0.40	0.20	6	49	8	<1
3	0.34	0.20	12	68	15	<1
4	0.20	0.20	12	35	25	37
5	0.20	0.40	12	12	11	59

[a] Isolated yield based on the less aryl iodide. [b] GC yield based on **1a**. [c] GC yield based on **1b** (Adamantane as internal standard).

6. Effects of the ratio of 4-iodoanisole and 1-chloro-4-iodobenzene

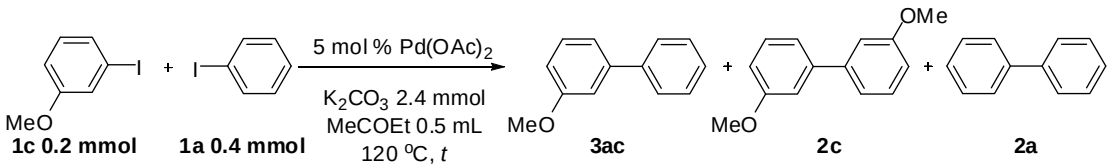


1g **1b** **3bg** **2b** **2g**

Entry	**1b** (mmol)	**1g** (mmol)	Yield of **3bg** (%) [a]	Yield of **2b** (%) [b]	Yield of **2g** (%) [c]
1	0.2	0.4	65	<1	20
2	0.2	0.3	70	<1	18
3	0.2	0.24	80	<1	14
4	0.2	0.2	61	11	19
5	0.2	0.16	55	32	20

[a] Isolated yield based on the less aryl iodide. [b] GC yield based on **1a**. [c] GC yield based on **1b** (Adamantane as internal standard).

7. Effects of the reaction time of coupling of 3-iodoanisole with 1-iodobenzene

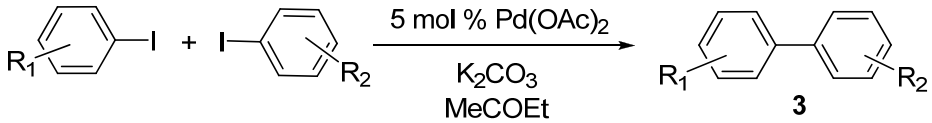


1c 0.2 mmol **1a 0.4 mmol** **3ac** **2c** **2a**

Entry	t (h)	Yield of **3ac** (%) [a]	Yield of **2a** (%) [a]	Yield of **2c** (%) [b]
1	1	21	none	<1
2	6	63	3	<1
3	12	75	18	<1

[a] Isolated yield based on **1c**. [b] GC yield based on **1c**. (Adamantane as internal standard).

8. Pd(II)-catalyzed cross-coupling of aryl iodides [a]



Entry	R_1 (Ar') (1 eq)	R_2 (Ar) (2 eq)	Ar-Ar' [b] Yield (%)	Ar'-Ar' [c] Yield (%)	Ar-Ar [d] Yield (%)
1	4-OMe	H	**3ab** 79	<1	20
2	3-OMe	H	**3ac** 75	<1	18
3 [e]	3-OMe	H	**3ac** 63	<1	3
4	2-OMe	H	**3ad** 75	<1	18
5	4-OMe	4-Cl	**3bg** 65	<1	20
6 [f]	4-OMe	4-Cl	**3bg** 80	<1	14
7	4-OMe	4-Me	**3be** 68	<1	19
8	$C_{10}H_7I$	H	**3aj** 65	10	32
9	$C_{10}H_7I$	4-OMe	**3bj** 53	18	40
10	$C_{10}H_7I$	3-NO_2	**3jk** 57	32	11
11	$C_{10}H_7I$	4-Br	**3ij** 55	11	16
12	4-Me	4-Br	**3ei** 54	<1	17
13	4-Me	4-Cl	**3eg** 66	<1	21
14	H	3-CO_2Et	**3al** 69	<1	15
15	4-Br	3-CO_2Et	**3il** 70	<1	14
16 [f]	4-OMe	3-CO_2Et	**3bl** 82	<1	12

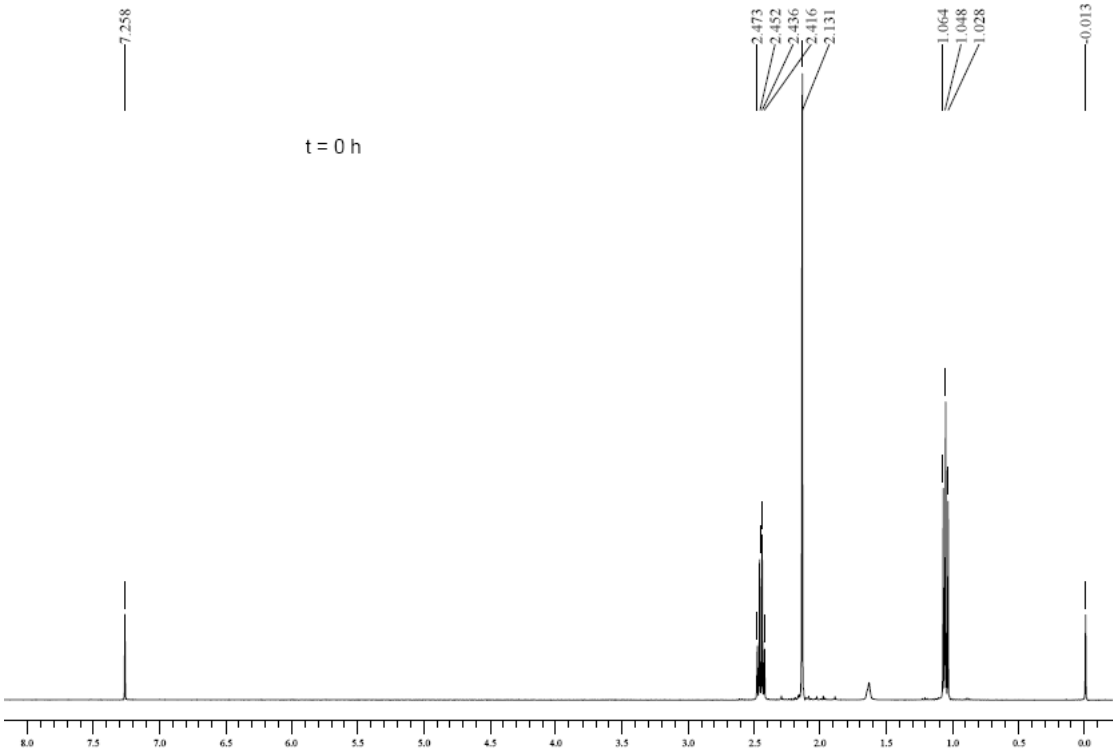
[a] Conditions: Ar'-I 0.2 mmol, Ar-I 0.4 mmol, $Pd(OAc)_2$ 0.01 mmol, K_2CO_3 2.4 mmol, MeCOEt 0.5 mL 120 °C, under N_2 . $C_{10}H_7I$ is 1-iodonaphthalene (entry 6-9). Ar'-I (0.5 mmol) (entry 10,11). [b] Isolated yield base on Ar-I. [c] GC yield based on Ar-I (Adamantane as internal standard). [d] GC yield based on Ar'-I (Adamantane as internal standard). [e] Reaction time (6 h). [f] Ar-I (0.24 mmol).

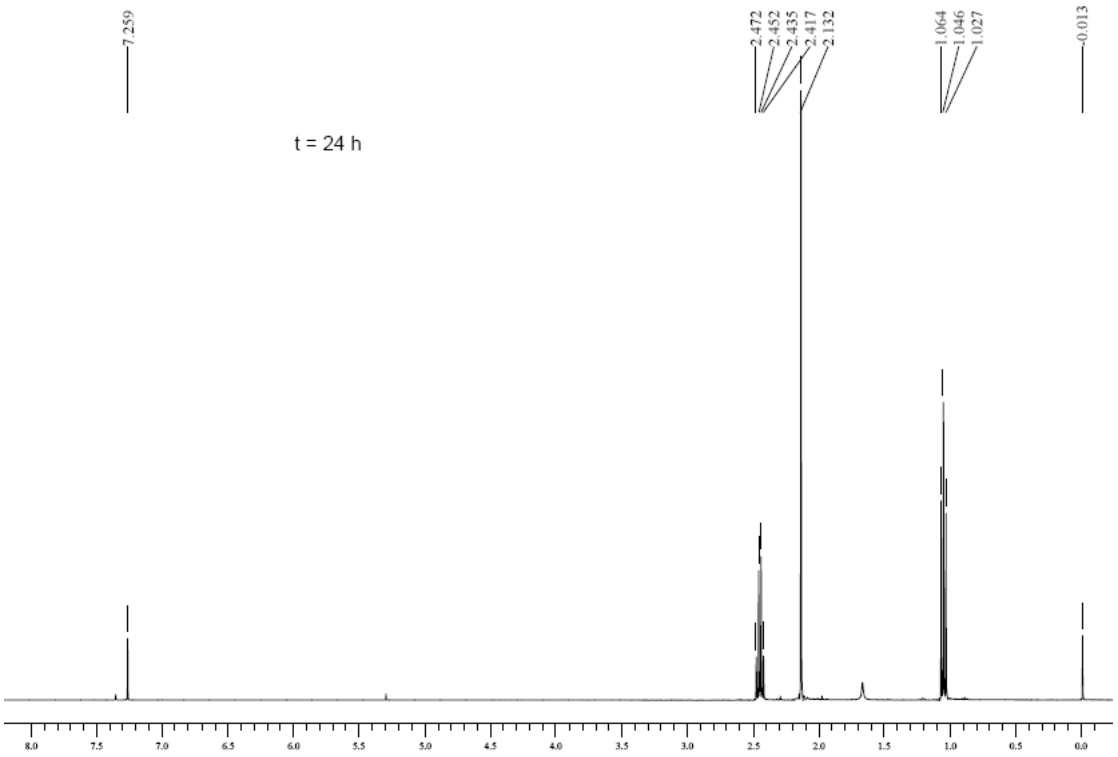
9. Reaction of $Pd(OAc)_2$ with MeCOEt

In a autoclave (10 mL), $Pd(OAc)_2$ (67.5 mg, 0.3 mmol), K_2CO_3 (145.1 mg, 1.0 mmol), MeCOEt (3 mmol) were mixed and stirred at 120 ^oC under N_2 for 24 h. Then 10 μL of the reaction mixture was drew out into the NMR tubes with 100 μL microliter syringe, and 0.6 mL of chloroform-*d* was added into the NMR tubes. The reaction mixture was characterized by ^1H NMR spectroscopy. No byproducts related MeCOEt were found.

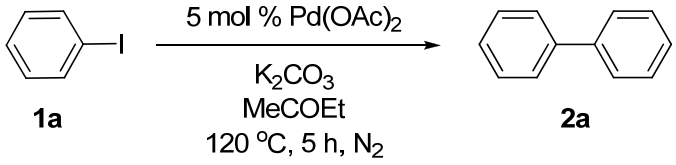
Before reaction starting,
^1H NMR data, (400 MHz, $CDCl_3$), δ, ppm:
2-Butone: 2.45 (q, CH_3CH_2-H), 2.13 (s, CH_3-H), 1.04 (t, CH_2CH_3-H). [20]

After 24 h,
^1H NMR data, (400 MHz, $CDCl_3$), δ, ppm:
2-Butone: 2.45 (q, CH_3CH_2-H), 2.13 (s, CH_3-H), 1.04 (t, CH_2CH_3-H).


7.258
2.473
2.452
2.436
2.416
2.131
1.064
1.048
1.028
-0.013
t = 0 h


7.259
2.472
2.452
2.435
2.417
2.132
1.064
1.046
1.027
-0.013
t = 24 h

10. Investigation of the role of MeCOEt in Pd(II)-catalyzed homocoupling of iodobenzene:



Test 1:

In a autoclave (10 mL), $Pd(OAc)_2$ (11.4 mg, 0.05 mmol), K_2CO_3 (334.7 mg, 2.4 mmol), MeCOEt (3.5 mmol), **1a** (iodobenzene, 1023.1 mg, 5.0 mmol) were mixed and stirred at 120 °C under N_2. After 17 h, *p*-xylene (36.7 mg, 0.35 mmol, as internal standard) was added into the reaction solution, and 10 μL of the reaction mixture was drew out into the NMR tubes with 100 μL microliter syringe, and 0.6 mL of chloroform-*d* was added into the NMR tubes. The reaction mixture was characterized by ^{1}H NMR spectroscopy. No byproducts related to MeCOEt were found.

Before reaction starting,
^{1}H NMR data, (400 MHz, $CDCl_3$), δ, ppm:
Iodobenzene: 7.69 (d, aryl(α)-H(2H)), 7.33-7.29 (m, aryl(γ)-H), 7.10-7.07 (m, aryl(β)-H).
2-Butone: 2.44 (q, CH_3CH_2-H), 2.12 (s, CH_3-H), 1.04 (t, CH_2CH_3-H).

After 17 h,
^{1}H NMR data, (400 MHz, $CDCl_3$), δ, ppm:
P-xylene: 7.05 (s, aryl-H(4H), 4H), 2.29 (s, CH_3(6H), 6H). [21]
Iodobenzene: 7.69 (d, aryl(α)-H(2H), 17.5H), 7.35-7.29 (m, aryl(γ)-H), 7.10-7.06 (m, aryl(β)-H). [1]
Biphenyl: 7.59 (d, aryl(α)-H(4H), 10.0H), 7.43 (t, aryl(β)-H). [2]
2-Butone: 2.44 (q, CH_3CH_2-H), 2.12 (s, CH_3-H), 1.04 (t, CH_2CH_3-H).

The amount of iodobenzene, (17.5/2)*0.35 = 3.03 mmol, the amount of biphenyl, (10.0/4)*0.35 = 0.86 mmol and the amount of MeCOEt, (28.1/3)*0.35 = 3.28 mmol.

Test 2:

In a autoclave (10 mL), $Pd(OAc)_2$ (12.0 mg, 0.05 mmol), K_2CO_3 (347.7 mg, 2.5 mmol), MeCOEt (3.5 mmol), **1a** (iodobenzene, 1038.1 mg, 5.1 mmol) were mixed and stirred at 120 °C under N_2. After 17 h, *p*-xylene (23.9 mg, 0.225 mmol, as internal standard) was added into the reaction solution, and 10 μL of the reaction mixture was drew out into the NMR tubes with 100 μL microliter syringe, and 0.6 mL of chloroform-*d* was added into the NMR tubes. The reaction mixture was characterized by ^{1}H NMR spectroscopy. No byproducts related to MeCOEt were found.

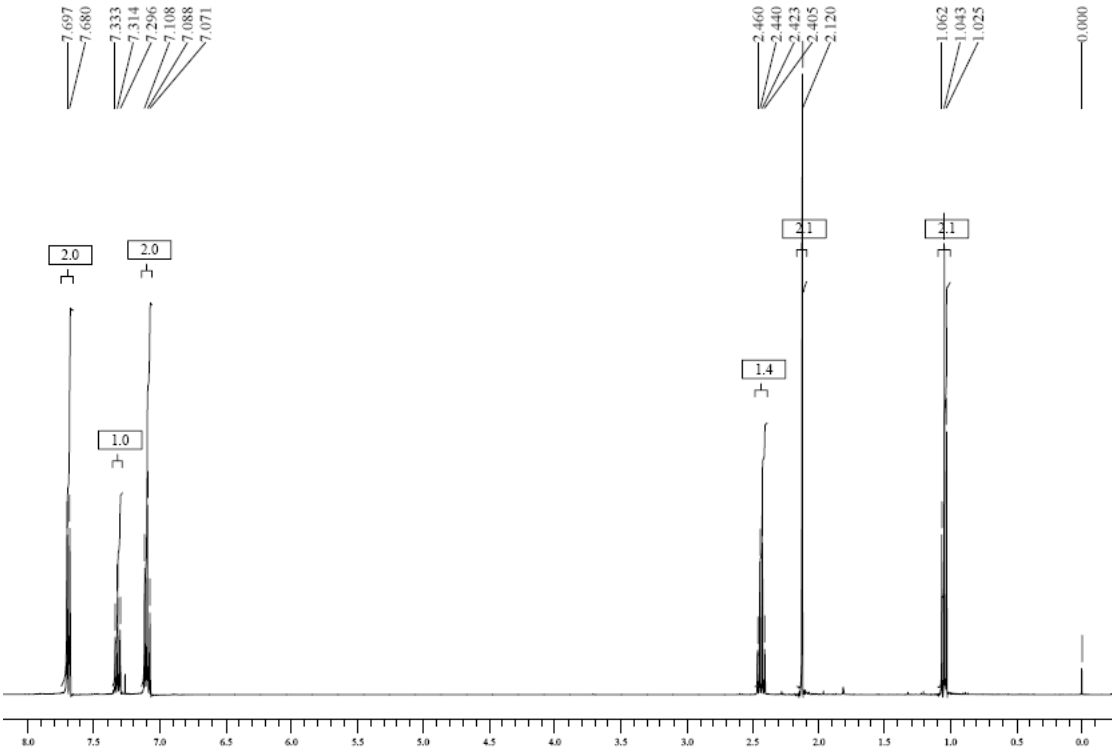
Before reaction starting,
^{1}H NMR data, (400 MHz, $CDCl_3$), δ, ppm:
Iodobenzene: 7.69 (d, aryl(α)-H(2H)), 7.33-7.29 (m, aryl(γ)-H), 7.10-7.07 (m, aryl(β)-H).
2-Butone: 2.44 (q, CH_3CH_2-H), 2.12 (s, CH_3-H), 1.04 (t, CH_2CH_3-H).

After 17 h,
^{1}H NMR data, (400 MHz, $CDCl_3$), δ, ppm:
P-xylene: 7.05 (s, aryl-H(4H), 4H), 2.29 (s, CH_3(6H), 6H). [21]
Iodobenzene: 7.70 (d, aryl(α)-H(2H), 17.5H), 7.35-7.29 (m, aryl(γ)-H), 7.10-7.07 (m, aryl(β)-H). [1]
Biphenyl: 7.59 (d, aryl(α)-H(4H), 10.0H), 7.43 (t, aryl(β)-H). [2]
2-Butone: 2.44 (q, CH_3CH_2-H), 2.12 (s, CH_3-H), 1.04 (t, CH_2CH_3-H).

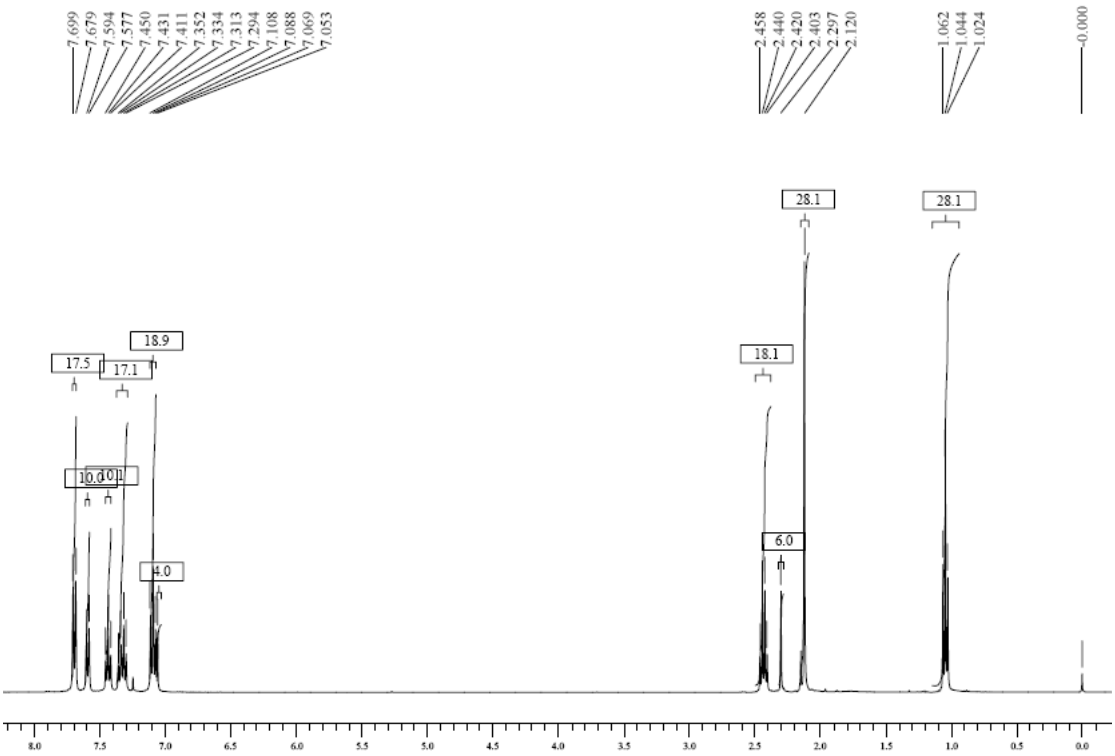
The amount of iodobenzene, (25.1/2)*0.225 = 2.83 mmol, the amount of biphenyl, (15.5/4)*0.225 = 0.87 mmol and the amount of MeCOEt, (45.2/3)*0.225 = 3.39 mmol.

Test 1:

Reaction time: t = 0 h.

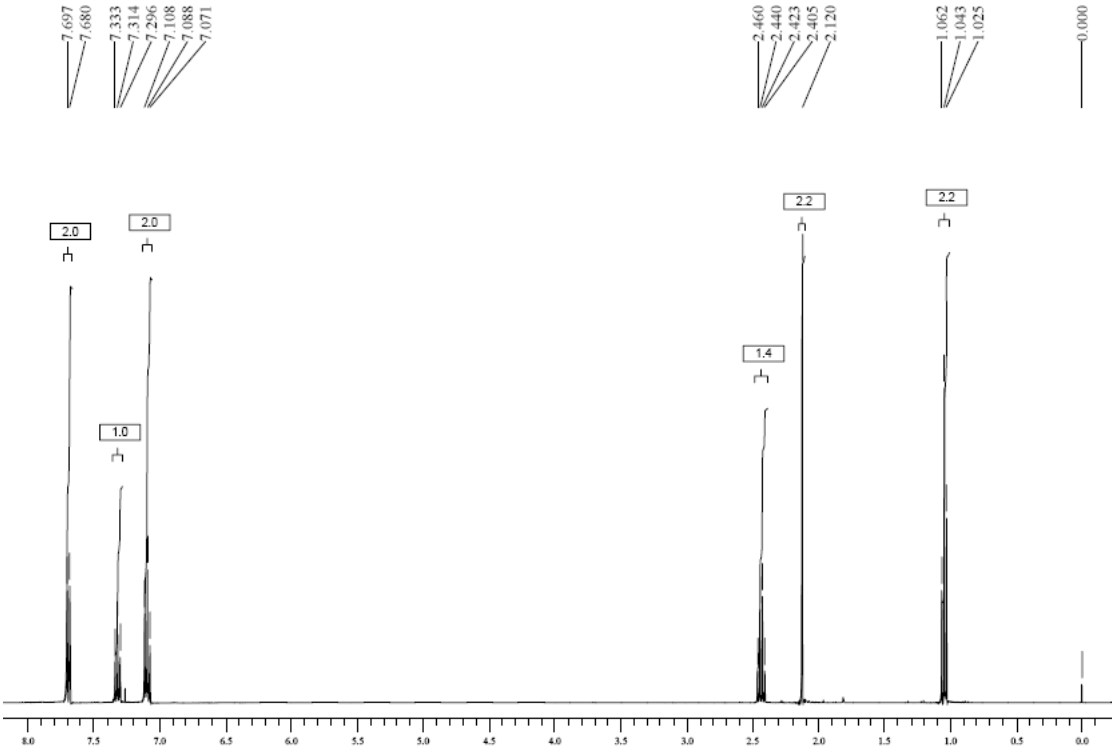


Reaction time: t = 17 h.

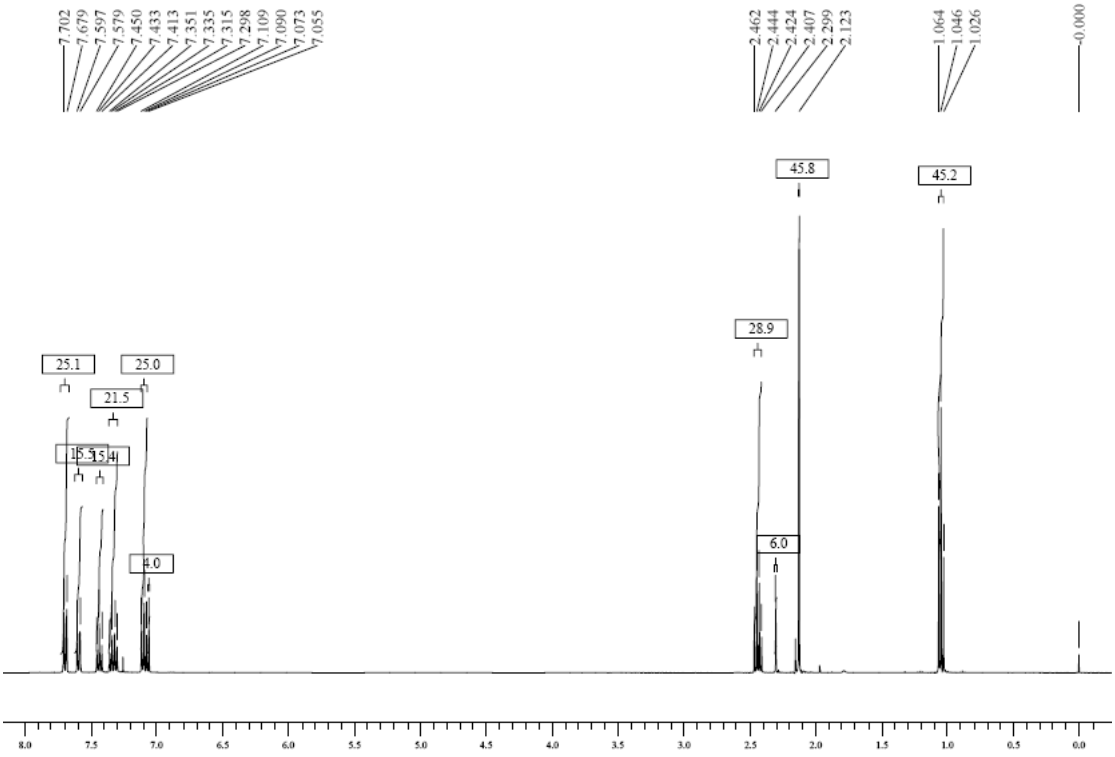


Test 2:

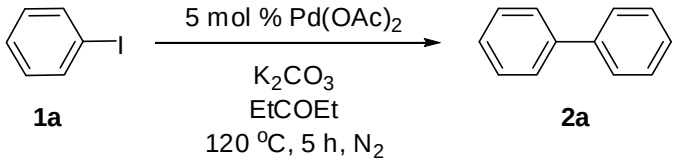
Reaction time: t = 0 h.



Reaction time: t = 17 h.



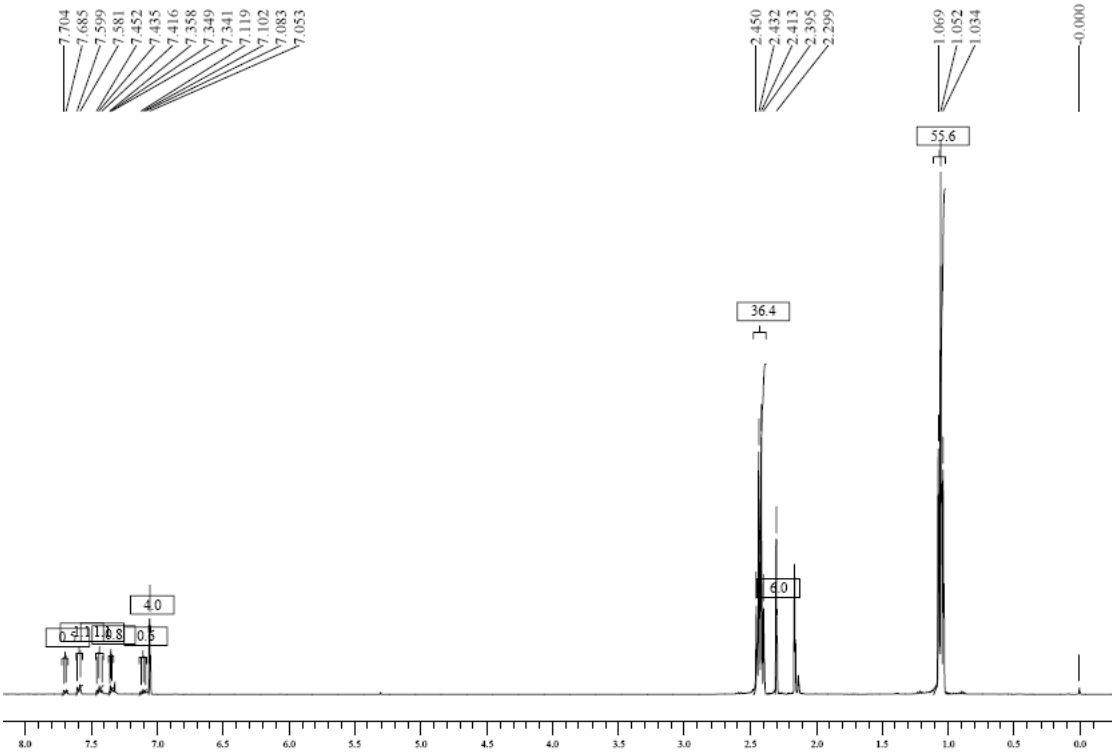
11. Pd(II)-catalyzed homocoupling of iodobenzene in 3-pentanone:



In a autoclave (10 mL), $Pd(OAc)_2$ (11.2 mg, 0.01 mmol), K_2CO_3 (331.7 mg, 2.4 mmol), EtCOEt (3-pentanone, 0.5 mL), **1a** (iodobenzene, 40.8 mg, 0.2 mmol) were mixed and stirred at 120 ^oC under N_2 for 5 h. Then *p*-xylene (25.5 mg, 0.24 mmol, as internal standard) was added into the reaction solution, then 10 μL of the reaction mixture was drew out into the NMR tubes with 100 μL microliter syringe, 0.6 mL of chloroform-*d* was added into the NMR tubes. The reaction mixture was characterized by ^1H NMR spectroscopy.

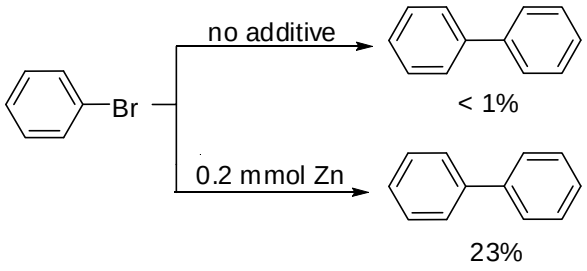
According to the following data:
^1H NMR data, (400 MHz, $CDCl_3$), δ, ppm:
P-xylene: 7.05 (s, aryl-H(4H), 4H), 2.29 (s, CH_3(6H), 6H). [20]
Iodobenzene: 7.70 (d, α-H, 0.5H).
Biphenyl: 7.59 (d, α-H, 1.1H).
3-Pentanone: 2.43(q, CH_3CH_2-H), 1.05 (t, CH_2CH_3-H). [23]

The amount of biphenyl is (1.1/4)*0.24 = 0.066 mmol (yield 66%) and the amount of iodobenzene is (0.5/2)*0.24 = 0.06 mmol. The conversion of 1-iodobenzene was 70%.



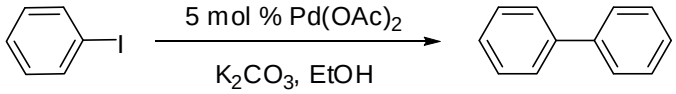
12. Pd(II)-catalyzed couplings of bromobenzene in MeCOEt:

In a autoclave (10 mL), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), Zn powder (13.1 mg, 0.2 mmol), K_2CO_3 (331.7 mg, 2.4 mmol), MeCOEt (0.5 mL), bromobenzene (34.6 mg, 0.22 mmol) were mixed and stirred at 120 ^oC under N_2 for 23 h. The biphenyl product is in the yield of 23% based on bromobenzene detected by GC (adamantine as internal standard).



Conditions: PhBr (0.2 mmol), 5 mol% $Pd(OAc)_2$, K_2CO_3 (2.4mmol), MeCOEt (0.5 mL), 120 ^oC, 23 h, N_2. GC yield based on PhBr. (Adamantane as internal standard)

13. Pd(II)-catalyzed homocoupling of iodobenzene in EtOH:

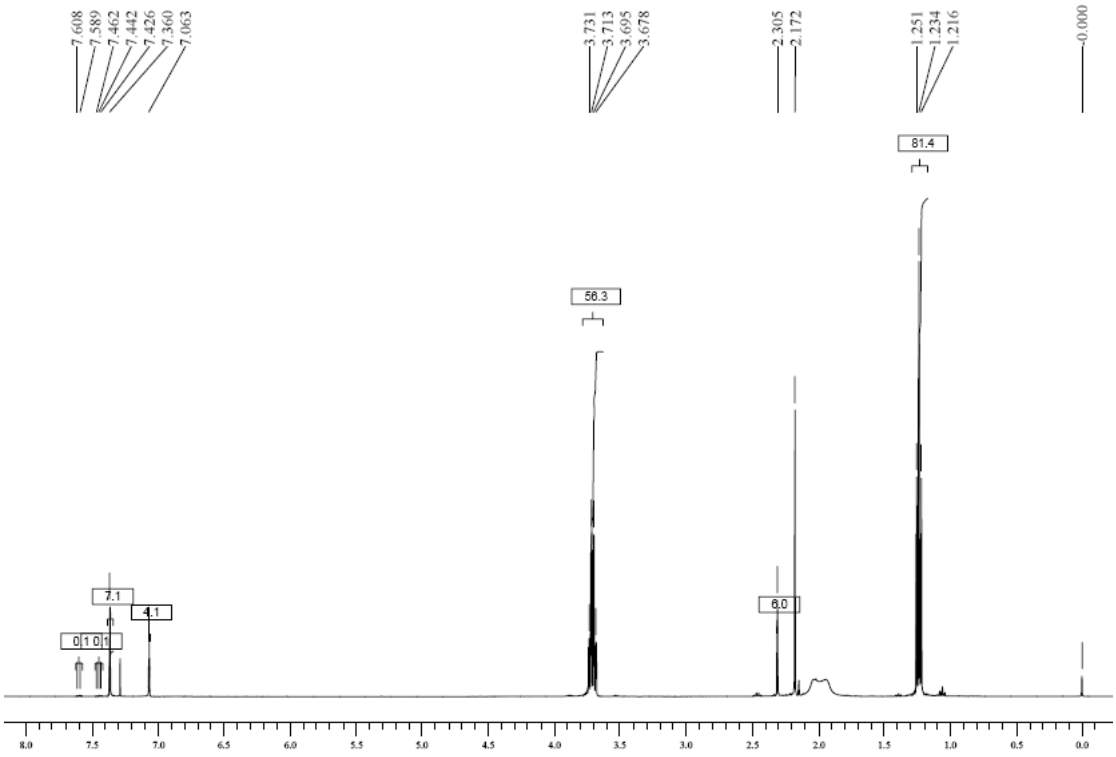


1a **2a**

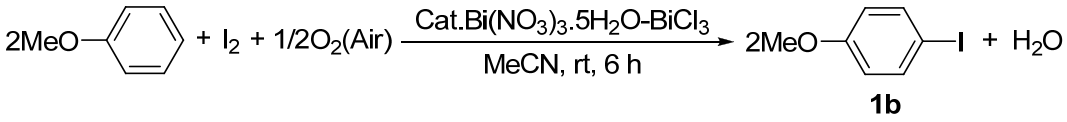
In a autoclave (10 mL), $Pd(OAc)_2$ (11.2 mg, 0.01 mmol), K_2CO_3 (331.7 mg, 2.4 mmol), EtOH (0.5 mL), **1a** (iodobenzene, 40.8 mg, 0.2 mmol) were mixed and stirred at 120 ^oC under N_2 for 5 h. Then *p*-xylene (14.9 mg, 0.14 mmol, as internal standard) was added into the reaction solution, then 10 μL of the reaction mixture was drew out into the NMR tubes with 100 μL microliter syringe, simultaneously 0.6 mL of Chloroform-*d* was added into the NMR tubes. The reaction mixture was characterized by ^1H NMR spectroscopy.

According to the following data:
^1H NMR data, (400 MHz, $CDCl_3$), δ, ppm:
Benzene: 7.36 (s, 7.1H) [22].
Biphenyl: 7.60 (d, aryl(α)-H(4H), 0.1H)
EtOH: 3.71 (q, CH_2-H, 49.5H), 1.23 (t, CH_3-H, 72.3H).
P-xylene: 7.06 (s, aryl-H(4H), 4H), 2.30 (s, CH_3(6H), 6H). [21]

The amount of biphenyl is (0.1/4)*0.14 = 0.0035 mmol (Yield 3.5%) and the amount of benzene is (7.1/6)*0.14 = 0.166 mmol.


7.608
7.589
7.462
7.442
7.426
7.360
7.063
3.731
3.713
3.695
3.678
2.305
2.172
1.251
1.234
1.216
0.000
81.4
56.3
7.1
4.1
6.0
0.10
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

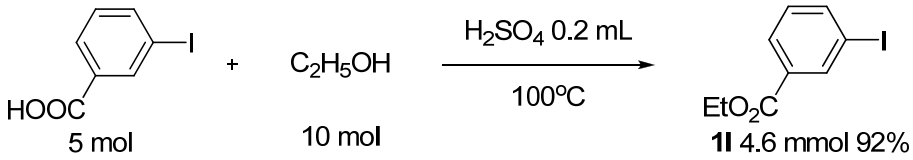
14. Preparation of 4-iodoanisole:



1b

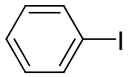
Anisole (108.2 mg, 1.0 mmol), I_2 (126.9 mg, 0.5 mmol), BNP (12.1 mg, 0.025 mmol, 2.5 mol %), $BiCl_3$ (7.8 mg, 0.025 mmol, 2.5 mol %), MeCN (1.0 mL) and a magnetic stir bar were placed in a dried flask. The mixture was stirred at room temperature under air for 6 h. The reaction propagation was monitored by GC and TLC analysis (see the preliminary study of our group) [18]. Then the reaction mixture was desorbed by dichloromethane (3 × 10 mL). The organic extracts were successively washed with aq. $Na_2S_2O_3$ solution, dried over anhydrous $MgSO_4$ and then evaporated under reduced pressure. The crude product was purified by column chromatography on silica using petroleum ether as eluant to furnish the pure iodides. Yield of **1b** (4-iodoanisole): 82% (191.9 mg).

15. Preparation of 3-Iodo-benzoic acid ethyl ester:



3-Iodo-benzoic acid (1240.1 mg, 5 mmol), ethanol (460.7 mg, 10 mol) and a magnetic stir bar were placed in a dried flask, and the sulphuric acid (0.2 mL) was injected slowly. Then the mixture was stirred at 100 ^oC (the reflux temperature) under air for 3 h. The reaction propagation was monitored by GC and TLC analysis. The reaction mixture was washed with saturated $NaHCO_3$ solution, then desorbed by dichloromethane (3 × 10 mL). The organic extracts were dried over anhydrous $MgSO_4$ and then evaporated. The crude product was purified by column chromatography on silica using petroleum ether-ethyl actate (50:1, v/v) as eluant to furnish the pure iodides. Yield of **1l** (3-Iodo-benzoic acid ethyl ester): 92% (1269.9 mg). The product was characterized by ^1H NMR analysis.

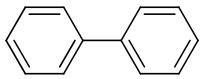
Characterization of the Products:



Iodobenzene (1a): [1]

Liquid.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.72 (d, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.13-7.09 (m, 2H).

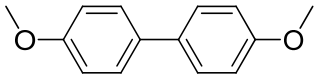


Biphenyl (2a): [2]

White solid. m.p. 69-70 ^{o}C (Lit. 67-69 ^{o}C).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.61 (d, *J* = 7.6 Hz, 4H), 7.47 (m, 4H), 7.35 (t, *J* = 7.6 Hz, 2H).

IR (cm $^{-1}$, KBr): 3034, 1571, 1482, 1182, 753, 697.

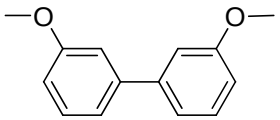


4,4'-Dimethoxy-biphenyl (2b): [2]

White solid. m.p. 178-181 ^{o}C (Lit. 178-179 ^{o}C).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.49 (d, *J* = 8.8 Hz, 4H), 6.97 (d, *J* = 8.8 Hz, 4H), 3.84 (s, 6H).

IR (cm $^{-1}$, KBr): 3034, 3009, 2957, 2915, 2833, 1607, 1497, 1275, 1244, 1177, 1040, 1010, 821, 808, 549, 513.

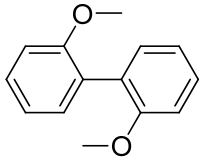


3,3'-Dimethoxy-biphenyl (2c): [2]

Colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.38-7.34 (m, 2H), 7.19 (d, *J* = 7.6 Hz, 2H), 7.12 (s, 2H), 6.92 (d, *J* = 8.0 Hz, 2H), 3.87 (s, 6H).

IR (cm $^{-1}$): 3055, 3000, 2957, 2936, 2833, 1598, 1571, 1476, 1412, 1272, 1232, 1202, 1031, 851, 772, 693, 616.

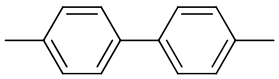


2,2'-Dimethoxy-biphenyl (2d): [2]

White solid. m.p. 156-157 ^{o}C (Lit. 155-156 ^{o}C).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.32-7.36 (m, 2H), 7.25-7.27 (m, 2H), 6.98-7.04 (m, 4H), 3.78 (s, 6H).

IR (cm $^{-1}$, KBr): 3058, 3025, 2957, 2924, 2833, 1586, 1500, 1479, 1427, 1281, 1238, 1162, 1110, 1052, 1019, 997, 933, 784, 763, 613, 546.

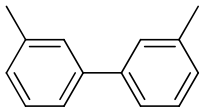


4,4'-Dimethyl-biphenyl (2e): [3]

White solid. m.p. 120-122 ^{o}C (Lit. 121.5-122.0 ^{o}C).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.48 (d, J = 8.4 Hz, 4H), 7.25 (d, J = 7.6 Hz, 4H), 2.39 (s, 6H).

IR (cm $^{-1}$, KBr): 3045, 3031, 2918, 2851, 1500, 1446, 1110, 1001, 805, 723, 549, 504.

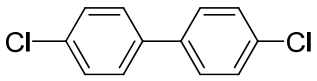


3,3'-Dimethyl-biphenyl (2f): [3]

Colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.40-7.38 (m, 4H), 7.34-7.31 (m, 2H), 7.17 (d, J = 7.2 Hz, 2H), 2.42 (s, 6H).

IR (cm $^{-1}$): 3034, 2957, 2915, 2848, 1464, 1378, 1254, 1095, 1025, 772, 693.

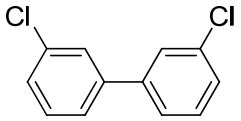


4,4'-Dichloro-biphenyl (2g): [4]

White solid. m.p. 141-142 ^{o}C (Lit. 139.5-143.6 ^{o}C).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.48 (d, J = 8.8 Hz, 4H), 7.41 (d, J = 8.8 Hz, 4H).

IR (cm $^{-1}$, KBr): 3052, 3028, 2917, 1900, 1473, 1385, 1089, 1022, 1007, 848, 815, 723, 699.

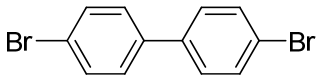


3,3'-Dichloro-biphenyl (2h): [5]

Viscous colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.54 (s, 2H), 7.45-7.33 (m, 6H).

IR (cm $^{-1}$): 3067, 2921, 2874, 1595, 1561, 1464, 1394, 1101, 1043, 879, 775, 717, 687.

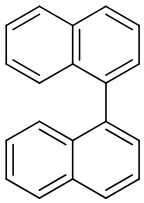


4,4'-Dibromo-biphenyl (2i): [6]

White solid. m.p. 168-171 ^{o}C (Lit. 168-169 ^{o}C). [7]

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.57 (d, *J* = 7.2 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 2H).

IR (cm $^{-1}$, KBr): 3046, 2915, 2848, 1903, 1467, 1382, 1061, 997, 845, 805, 717, 671, 540, 501.

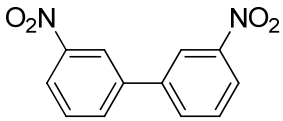


1,1'-Bisnaphthalene (2j): [2]

White solid. m.p. 148-150 ^{o}C (Lit. 150-160 ^{o}C).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.97 (d, *J* = 4.0 Hz, 1H), 7.95 (d, *J* = 4.0 Hz, 1H), 7.62-7.58 (m, 1H), 7.51-7.46 (m, 2H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.31-7.27 (m, 1H).

IR (cm $^{-1}$, KBr): 3043, 1500, 1378, 1254, 1010, 802, 781, 665.

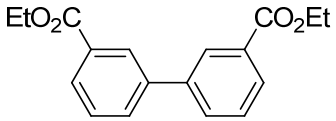


3,3'-Dinitro-biphenyl (2k): [8]

Yellow solid. m.p. 178-180 ^{o}C (Lit. 177.2-179.8 ^{o}C).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.49 (s, 2H), 8.31 (d, *J* = 8.0 Hz, 2H), 7.98 (d, *J* = 7.6 Hz, 2H), 7.72 (m, 2H).

IR (cm $^{-1}$, KBr): 3079, 1522, 1351, 1263, 1101, 1080, 890, 857, 799, 726, 699, 674.

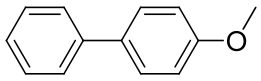


3,3'-dicarbethoxybiphenyl (2l): [9]

White solid. m.p. 69-70 ^{o}C (Lit. 68-69 ^{o}C).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.29 (s, 2H), 8.06 (d, *J* = 7.6 Hz, 2H), 7.81 (d, *J* = 7.6 Hz, 2H), 7.55-7.51 (m, 2H), 4.42 (q, *J* = 7.2 Hz, 4H), 1.42 (t, *J* = 7.2 Hz, 6H).

IR (cm $^{-1}$, KBr): 3058, 3000, 2982, 2918, 1723, 1589, 1473, 1385, 1360, 1308, 1238, 1107, 1083, 1016, 897, 738, 693, 680, 619.

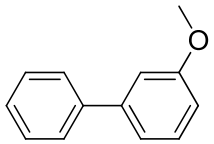


4-Methoxy-biphenyl (3ab): [10]

White solid. m.p. 85-87 ^{o}C (Lit. 85.3-85.7 ^{o}C).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.56-7.52 (m, 4H), 7.44-7.40 (m, 2H), 7.30 (t, *J* = 8.0 Hz, 1H), 6.99 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H).

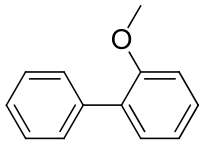
IR (cm $^{-1}$, KBr): 3067, 3034, 3003, 2957, 2836, 1604, 1522, 1488, 1461, 1436, 1287, 1269, 1199, 1183, 1031, 833, 757, 687, 568.



3-Methoxy-biphenyl (3ac): [10]

Colourless oil.

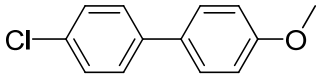
^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.60 (d, *J* = 8.0 Hz, 2H), 7.44 (t, *J* = 7.2 Hz, 2H), 7.38-7.34 (m, 2H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.13-7.12 (m, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 3.87 (s, 3H).



2-Methoxy-biphenyl (3ad): [11]

Yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.56-7.53 (m, 2H), 7.44-7.40 (m, 2H), 7.35-7.32 (m, 3H), 7.06-7.02 (m, 1H), 7.01-6.99 (m, 1H), 3.82 (s, 3H).

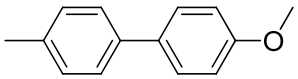


4-Chloro-4'-methoxy-biphenyl (3bg): [11]

White solid. m.p. 110-112 ^{o}C (Lit. 111.1-111.3 ^{o}C).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.50-7.46 (m, 4H), 7.38 (d, *J* = 8.8 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H).

IR (cm $^{-1}$, KBr): 3009, 2964, 2921, 2848, 1601, 1522, 1482, 1461, 1397, 1287, 1263, 1196, 1177, 1098, 1037, 1010, 808, 732, 498.

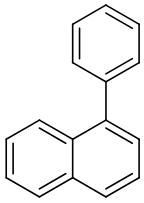


4-Methoxy-4'-methyl-biphenyl (3be): [11]

White solid. m.p. 105-107 ^{o}C (Lit. 107.9-108.1 ^{o}C).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.52 (d, *J* = 9.6 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 7.6 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 3.85 (s, 3H), 2.38 (s, 3H).

IR (cm $^{-1}$, KBr): 3022, 2961, 2918, 2848, 1610, 1500, 1281, 1250, 1186, 1037, 839, 808, 491.

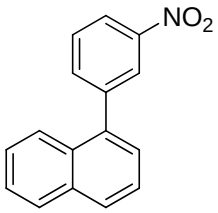


1-Phenyl-naphthalene (3aj): [10]

Yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.91-7.89 (m, 2H), 7.87-7.85 (m, 1H), 7.55-7.47 (m, 6H), 7.45-7.38 (m, 3H).

IR (cm $^{-1}$): 3058, 1488, 1394, 1263, 1034, 1019, 799, 781, 760, 702.

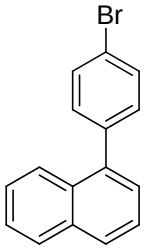


1-(3-nitro-phenyl)-naphthalene (3jk): [12]

Pale yellow solid. m.p. 129-130 ^{o}C (Lit. 131-132 ^{o}C).

^{1}H NMR (400 MHz, $CDCl_3$ δ): 8.38 (s, 1H), 8.31 (d, *J* = 7.2 Hz, 1H), 7.96-7.92 (m, 2H), 7.85 (d, *J* = 7.2 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.69-7.65 (m, 1H), 7.58-7.52 (m, 2H), 7.50-7.43 (m, 2H).

IR (cm $^{-1}$, KBr): 3064, 3043, 1528, 1348, 1101, 802, 775, 732, 690.

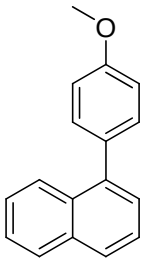


1-(4-Bromo-phenyl)-naphthalene (3ij): [13]

Pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.92-7.83 (m, 3H), 7.63 (d, *J* = 7.2 Hz, 2H), 7.54-7.48 (m, 2H), 7.46-7.42 (m, 1H), 7.39-7.36 (m, 3H).

IR (cm $^{-1}$): 3055, 3046, 2927, 2845, 1485, 1400, 1077, 1004, 799, 778.

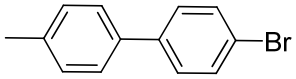


1-(4-Methoxy-phenyl)-naphthalene (3bj): [14]

White solid. m.p. 116-117 ^{o}C (Lit. 115-116 ^{o}C).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.96-7.90 (m, 2H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.54-7.41 (m, 6H), 7.06 (d, *J* = 8.8 Hz, 2H), 3.91 (s, 3H).

IR (cm $^{-1}$, KBr): 3058, 3040, 2991, 2957, 2918, 2848, 1607, 1500, 1391, 1275, 1241, 1174, 1043, 821, 805, 781, 583, 571, 552.

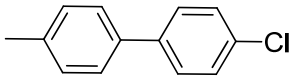


4-Bromo-4'-methyl-biphenyl (3ei): [15]

White solid. m.p. 130-131 ^{o}C (Lit. 129-131 ^{o}C).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.55 (d, *J* = 8.8 Hz, 2H), 7.46-7.42 (m, 4H), 7.25 (d, *J* = 7.2 Hz, 2H), 2.39 (s, 3H).

IR (cm $^{-1}$, KBr): 3022, 2915, 2848, 1476, 1388, 1071, 1001, 805, 720, 543, 501.

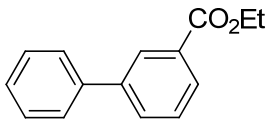


4-Chloro-4'-methyl-biphenyl (3eg): [16]

White solid. m.p. 123-124 ^{o}C (Lit. 122-123 ^{o}C).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.51 (d, *J* = 8.8 Hz, 2H), 7.46 (d, *J* = 7.6 Hz, 2H), 7.40 (d, *J* = 8.8 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 2.40 (s, 3H).

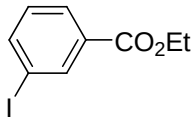
IR (cm $^{-1}$, KBr): 3049, 3031, 2918, 1476, 1388, 1086, 1004, 848, 805, 723, 543, 498.



Biphenyl 3-carboxylic acid ethyl ester (3al): [17]

Colorless oil.

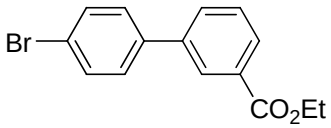
^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.28 (s, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.53-7.49 (m, 1H), 7.48-7.44 (m, 2H), 7.39-7.36 (m, 1H), 4.42 (q, *J* = 7.2 Hz, 2H), 1.41 (t, *J* = 6.8 Hz, 3H).



3-Iodobenzoic acid ethyl ester (1l): [19]

Pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.36(s, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.18 (m, 1H), 4.37 (q, *J* = 7.2 Hz, 2H), 1.38 (t, *J* = 7.2 Hz, 3H).



4'-Bromo-biphenyl-2-carboxylic acid ethyl ester (3il):

Pale yellow oil.

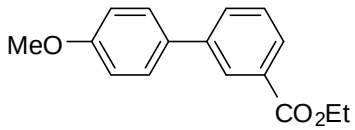
^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.23 (s, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.53-7.48 (m, 3H), 4.42 (q, *J* = 7.2 Hz, 2H), 1.41 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ): 166.6, 140.4, 139.3, 132.2, 131.4, 131.3, 129.1, 128.9, 128.8, 128.2, 122.2, 61.3, 14.5.

EIMS (m/z): M^+304, 289, 276, 259, 231, 152, 76.

HRMS (m/z): Calc for $C_{15}H_{13}BrO_2$, 304.0099; found, 304.0100.

IR (cm $^{-1}$): 3061, 3055, 2982, 2930, 2900, 1717, 1586, 1470, 1436, 1360, 1299, 1263, 1238, 1125, 1037, 1004, 842, 815, 757, 717, 687, 495.



4'-Methoxy-biphenyl-3-carboxylic acid ethyl ester (3bl): [24]

Pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.23 (s, 1H), 7.98 (d, *J* = 7.6 Hz, 1H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 8.8 Hz, 2H), 7.50-7.46 (m, 1H), 7.00 (d, *J* = 8.8 Hz, 2H), 4.41 (q, *J* = 7.2 Hz, 2H), 3.86 (d, 3H), 1.41 (t, *J* = 7.2 Hz, 3H).

IR (cm $^{-1}$): 3037, 2957, 2927, 2842, 1717, 1610, 1516, 1436, 1366, 1296, 1247, 1177, 1046, 842, 754.

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Addendum

Figure S-1 **Iodobenzene (1a)**

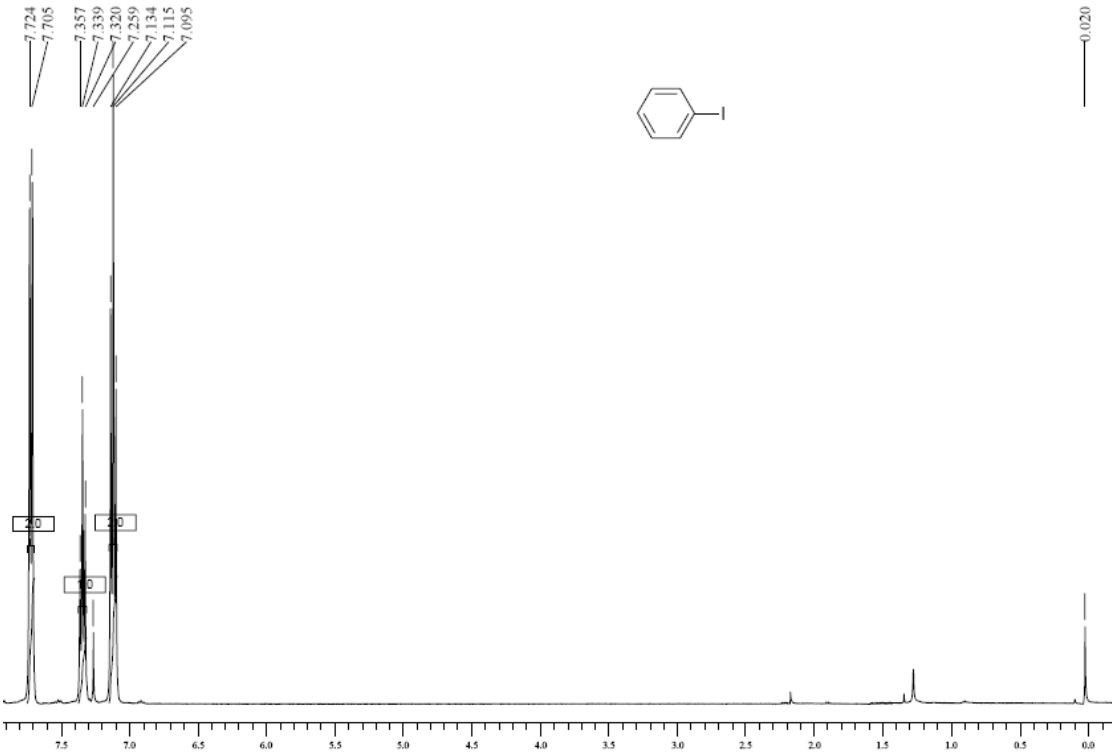

Figure S-2 **Biphenyl (2a)**

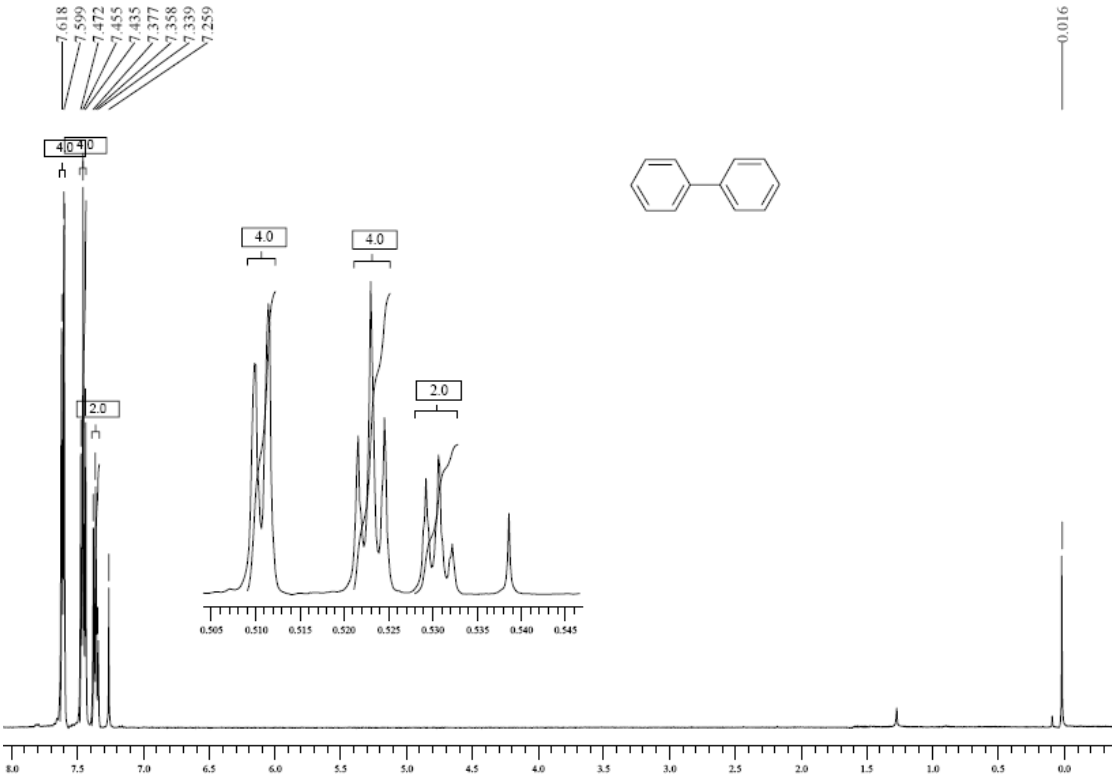

Figure S-3 **4,4'-Dimethoxy-biphenyl (2b)**

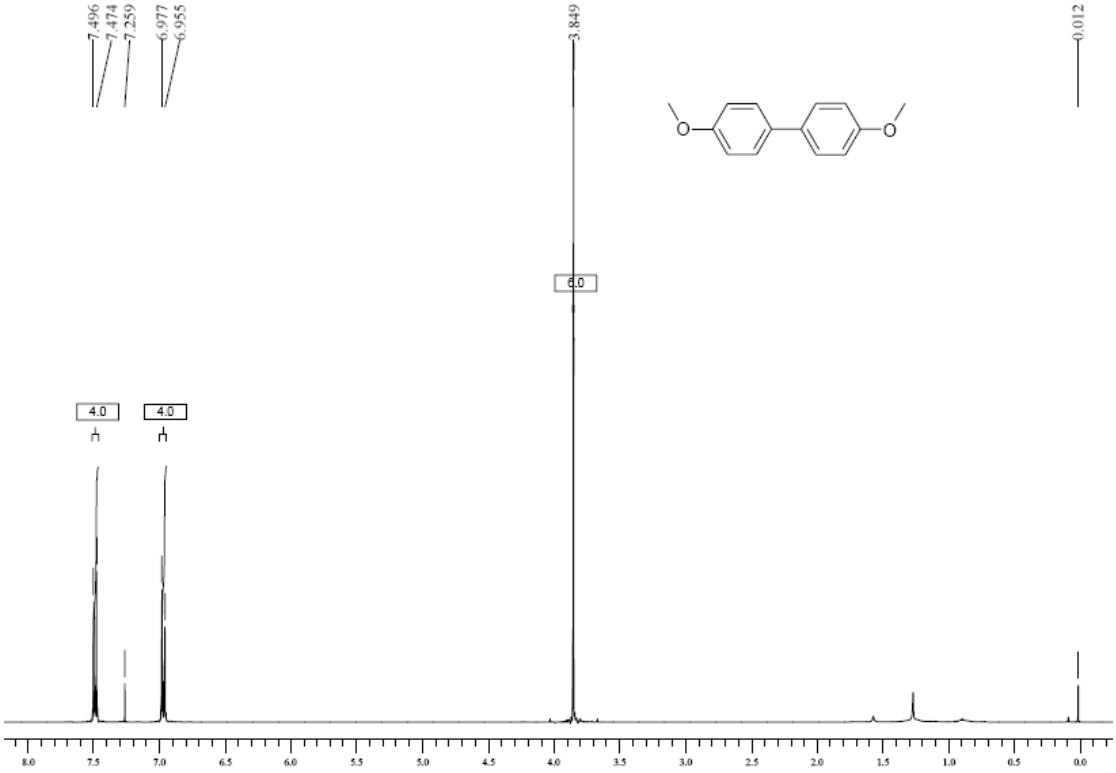

Figure S-4 **3,3'-Dimethoxy-biphenyl (2c)**

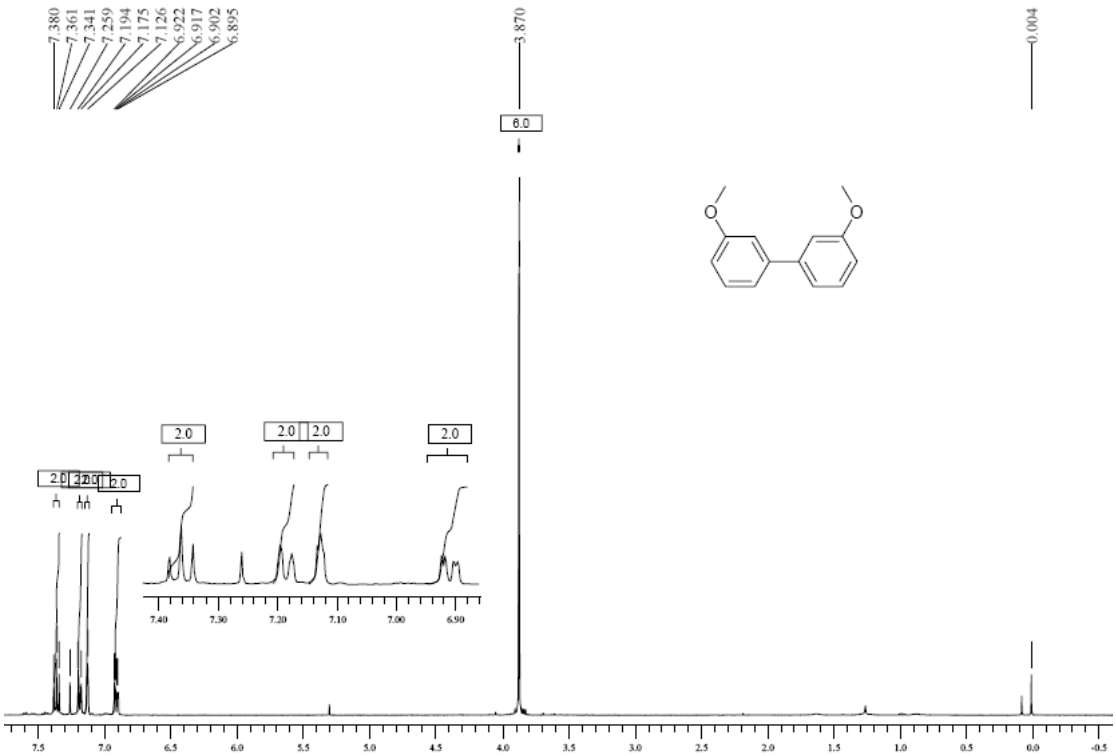

Figure S-5 **2,2'-Dimethoxy-biphenyl (2d)**

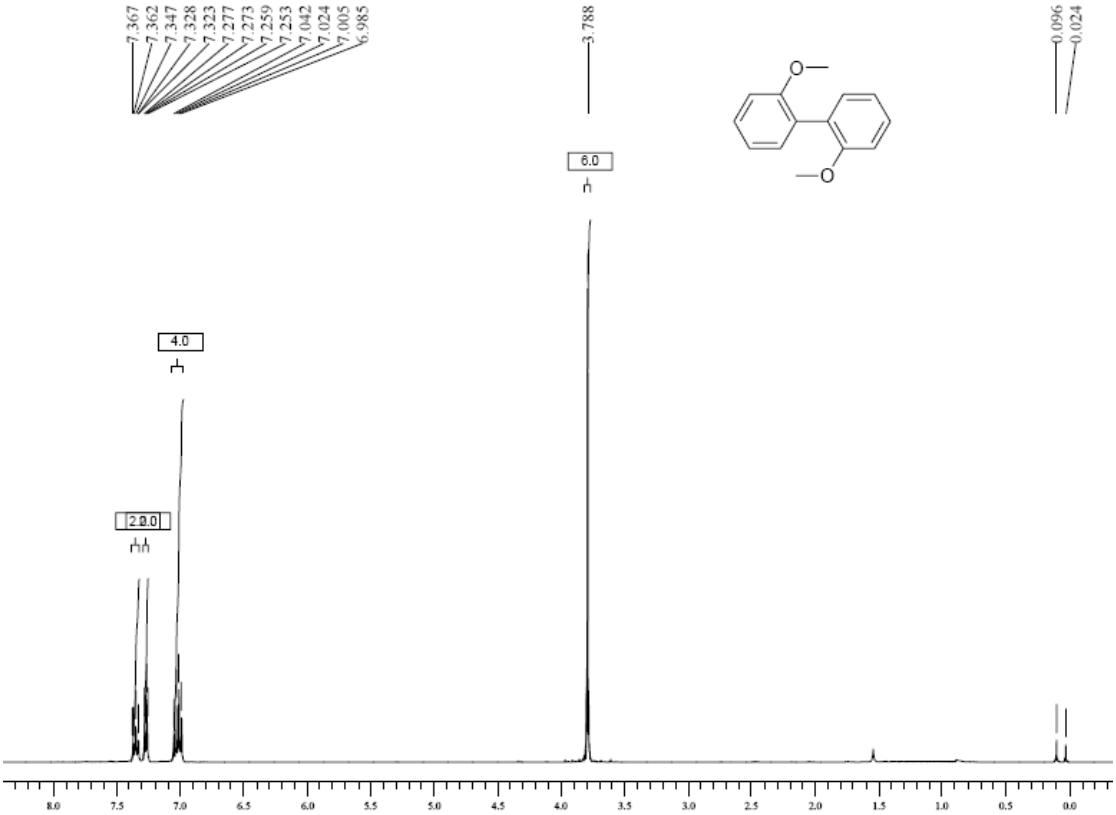

Figure S-6 **4,4'-Dimethyl-biphenyl (2e)**

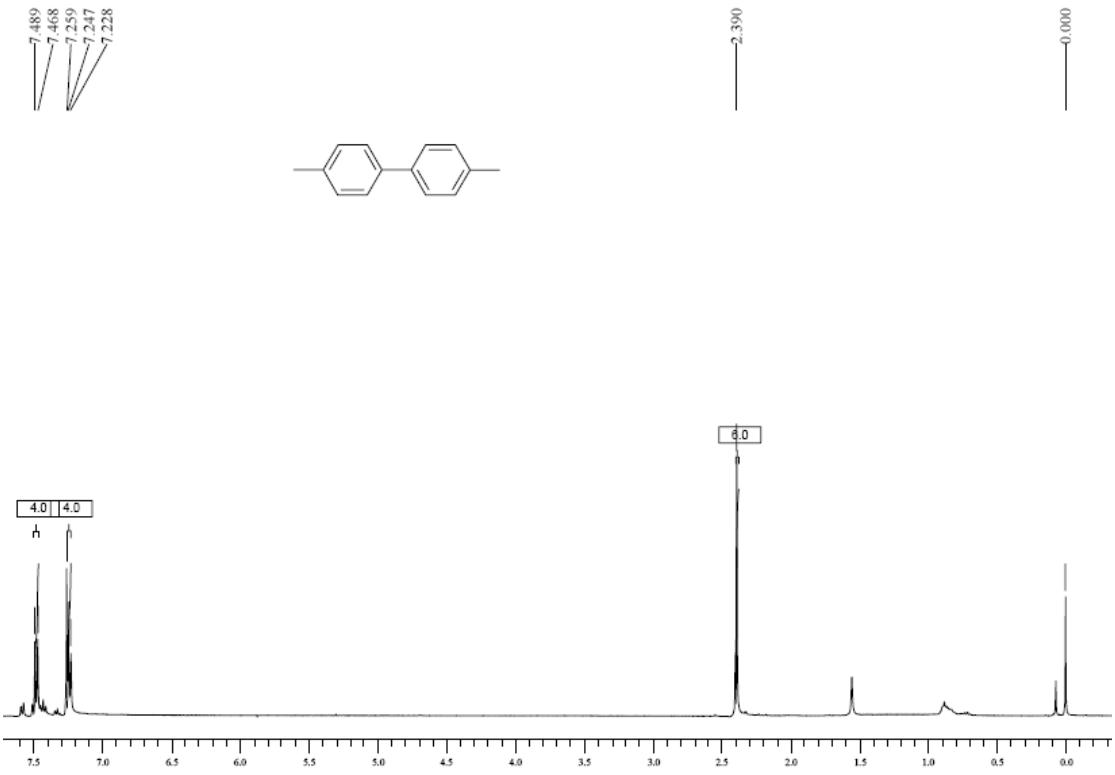

Figure S-7 **3,3'-Dimethyl-biphenyl (2f)**

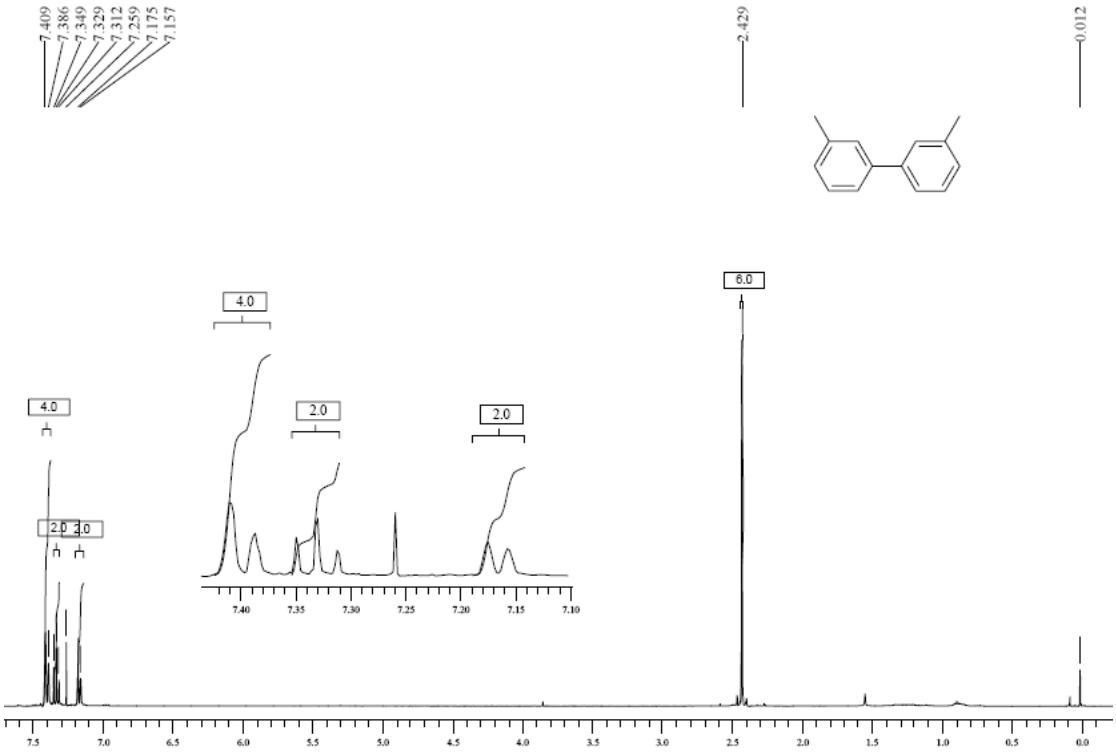

Figure S-8 **4,4'-Dichloro-biphenyl (2g)**

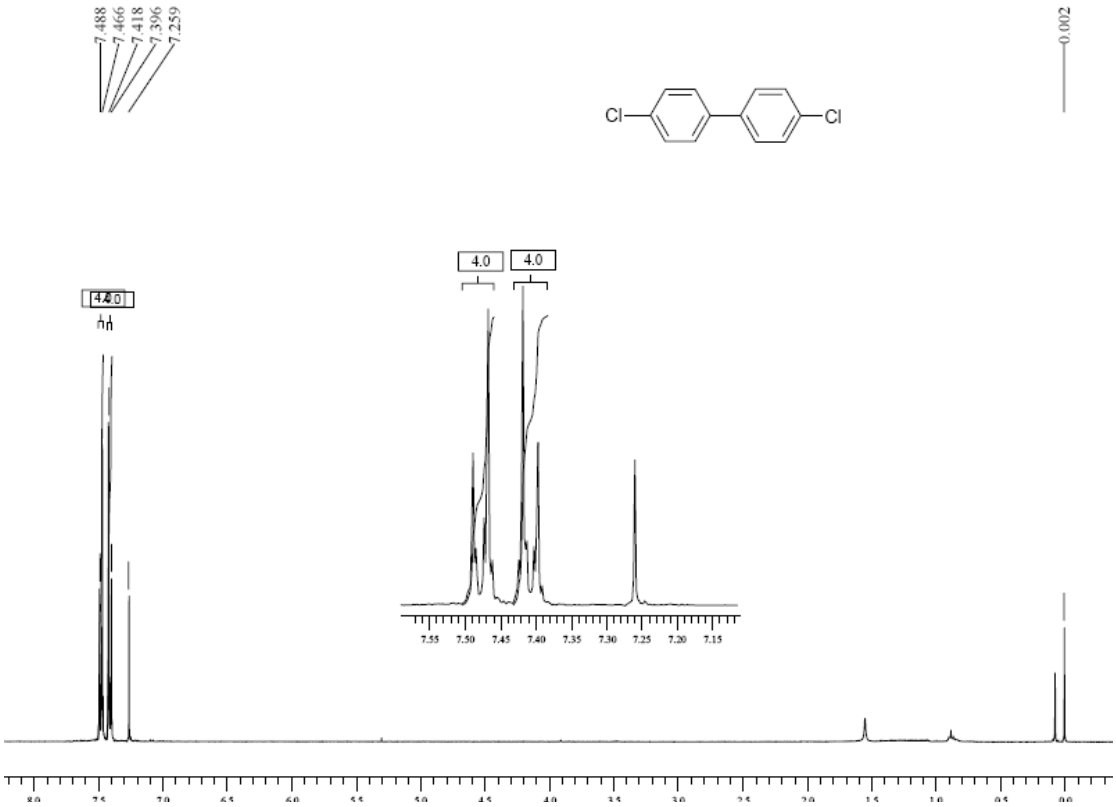

Figure S-9 **3,3'-Dichloro-biphenyl (2h)**

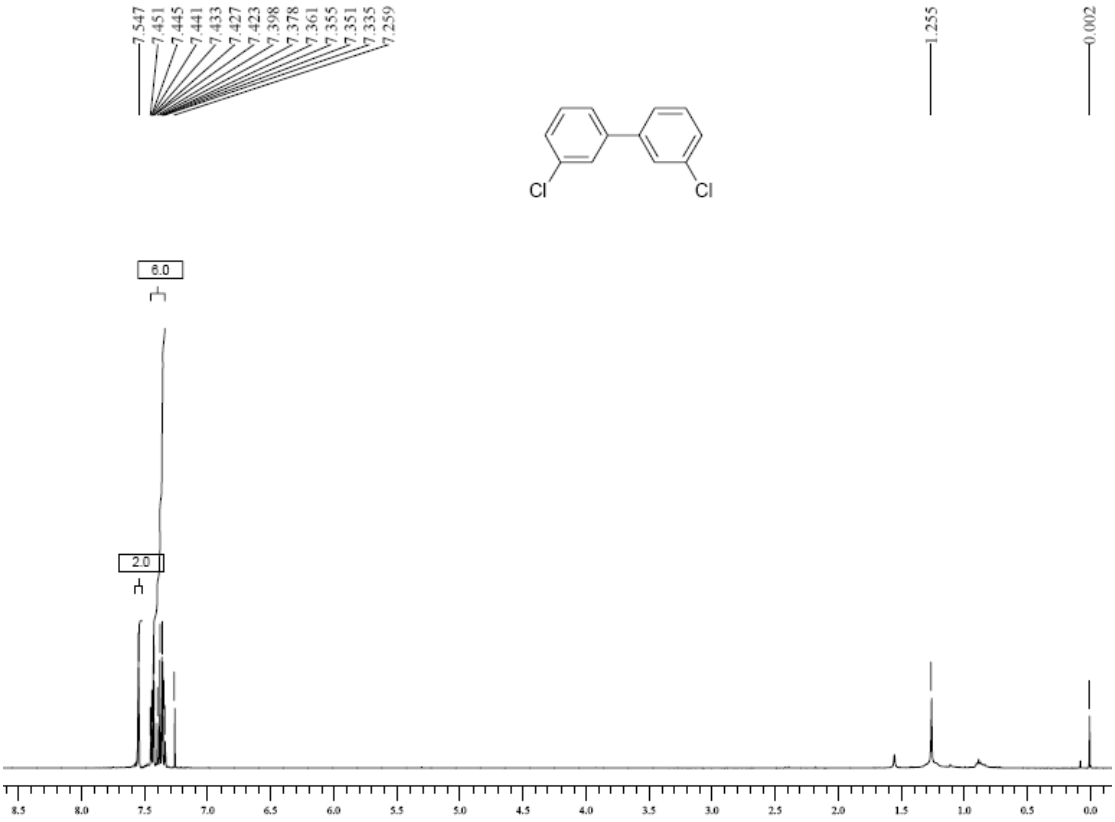

Figure S-10 **4,4'-Dibromo-biphenyl (2i)**

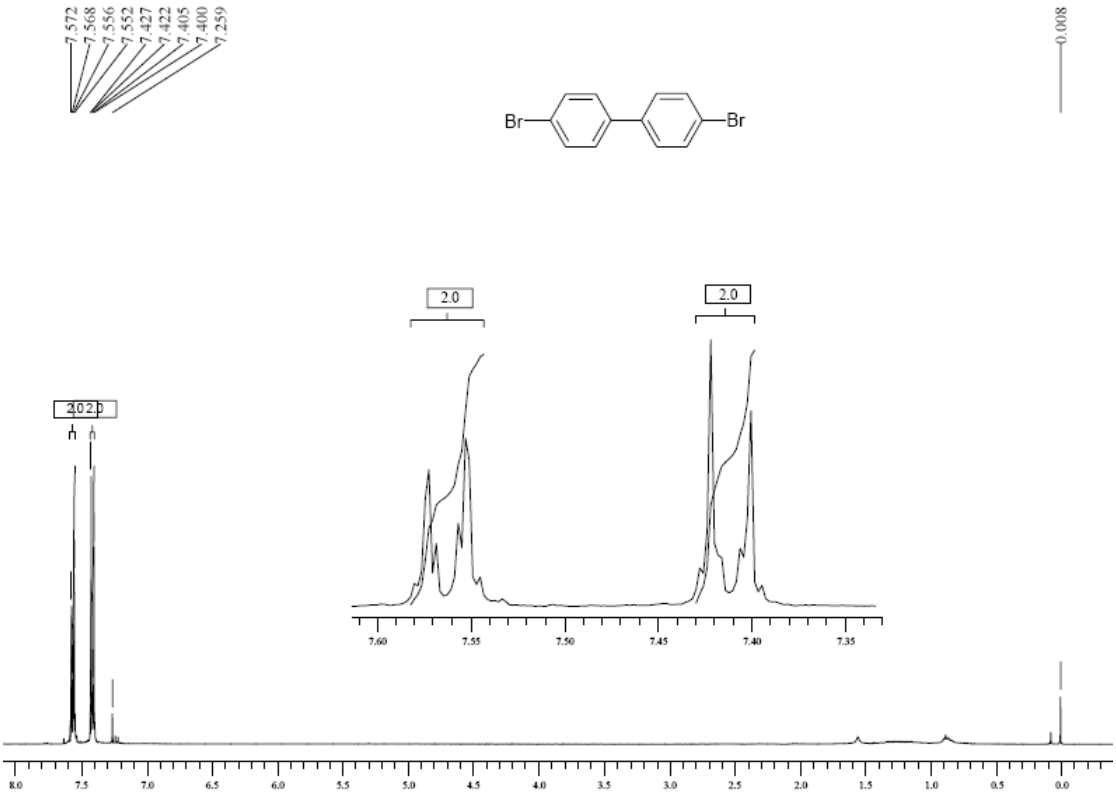

Figure S-11 **1,1'-Bisnaphthalene (2j)**

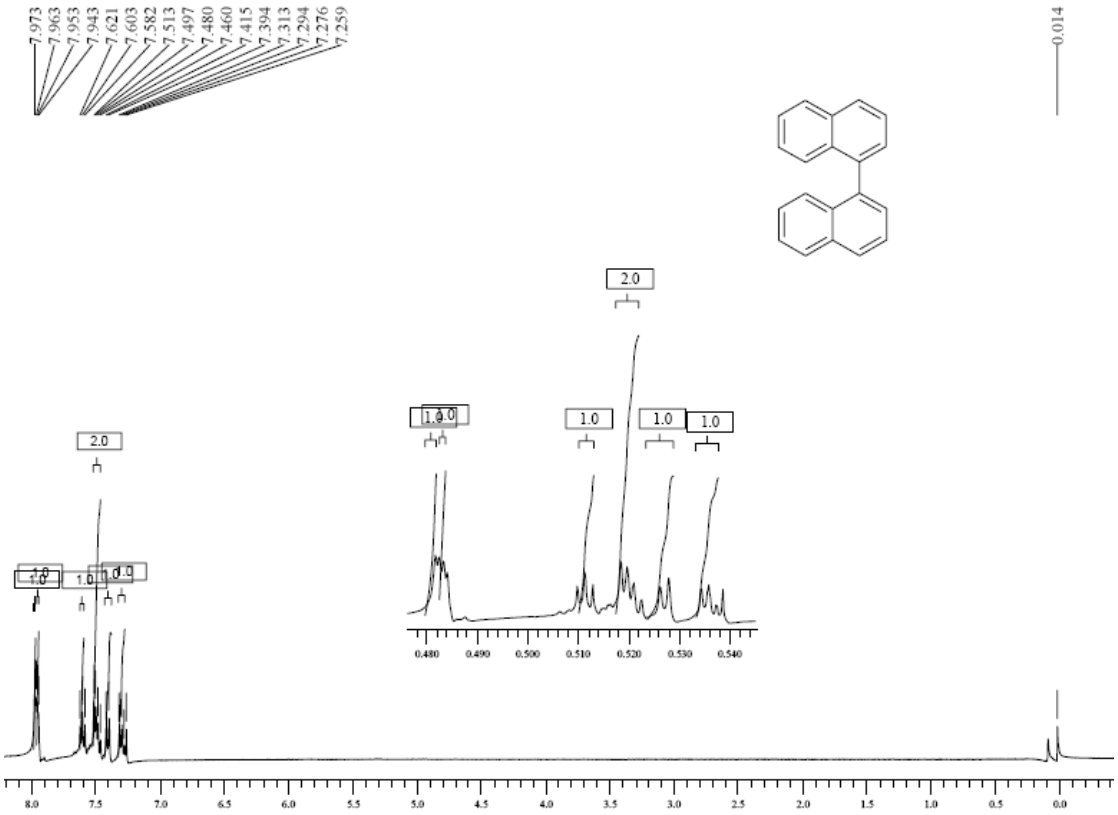

Figure S-12 **3,3'-Dinitro-biphenyl (2k)**

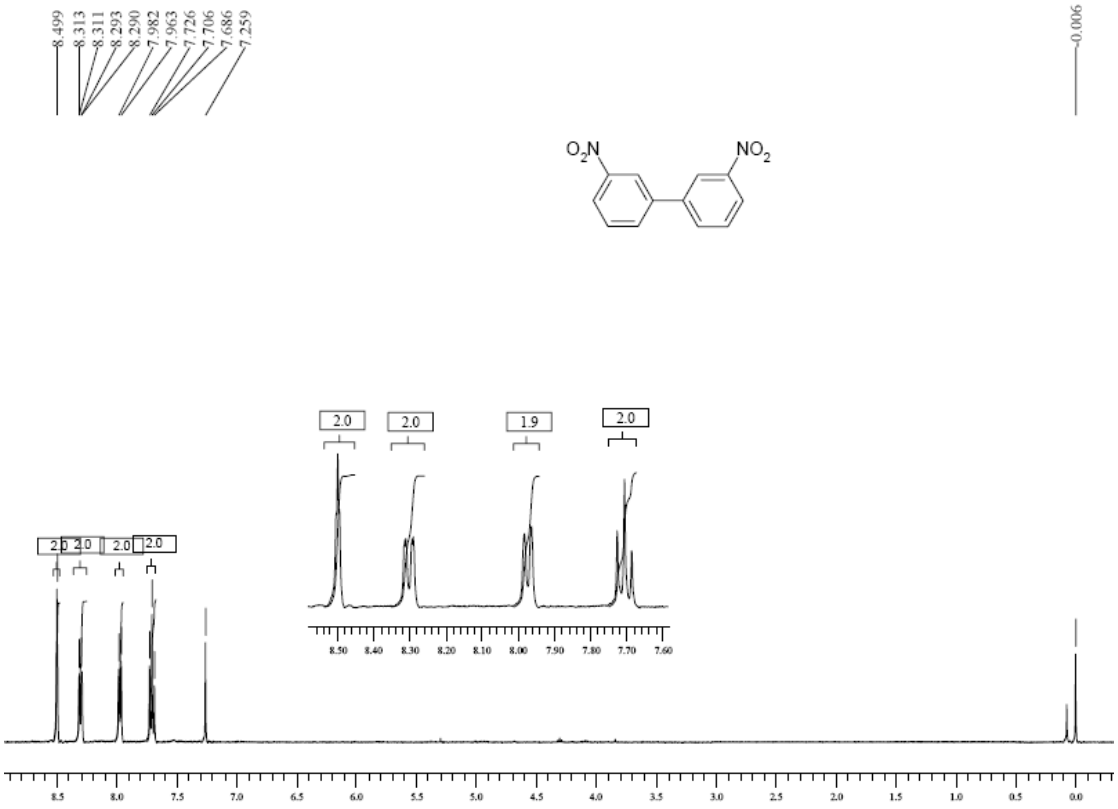

Figure S-13 **3,3'-dicarbethoxybiphenyl (2l)**

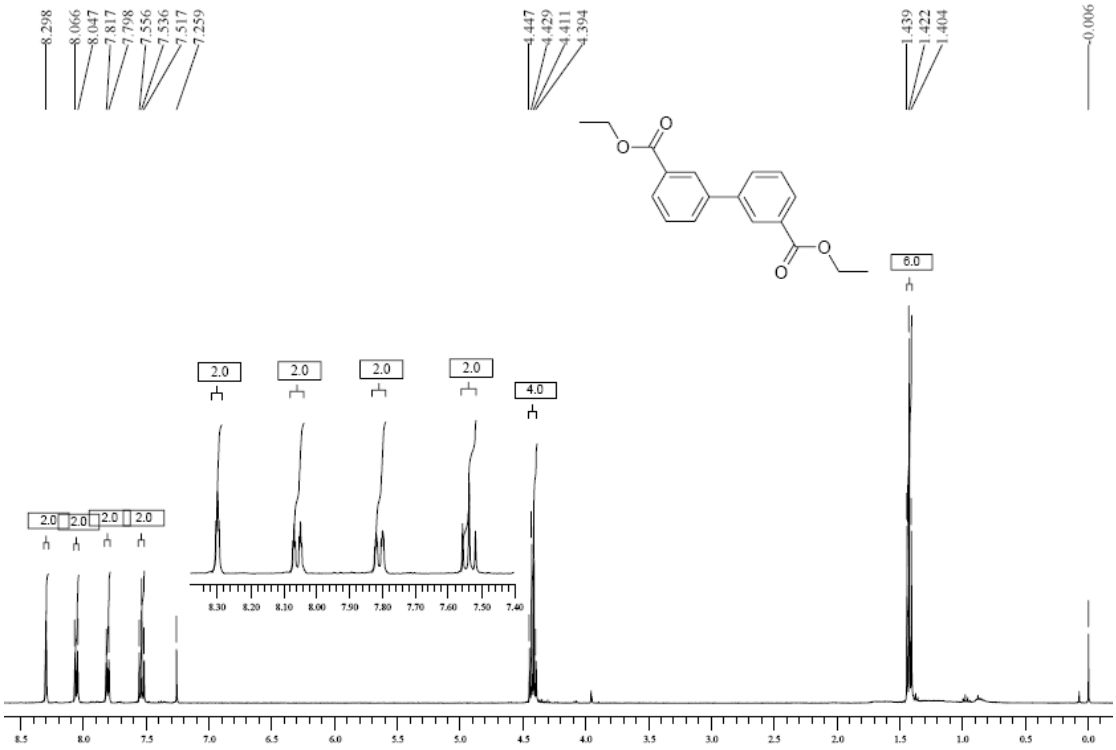

Figure S-14 **4-Methoxy-biphenyl (3ab)**

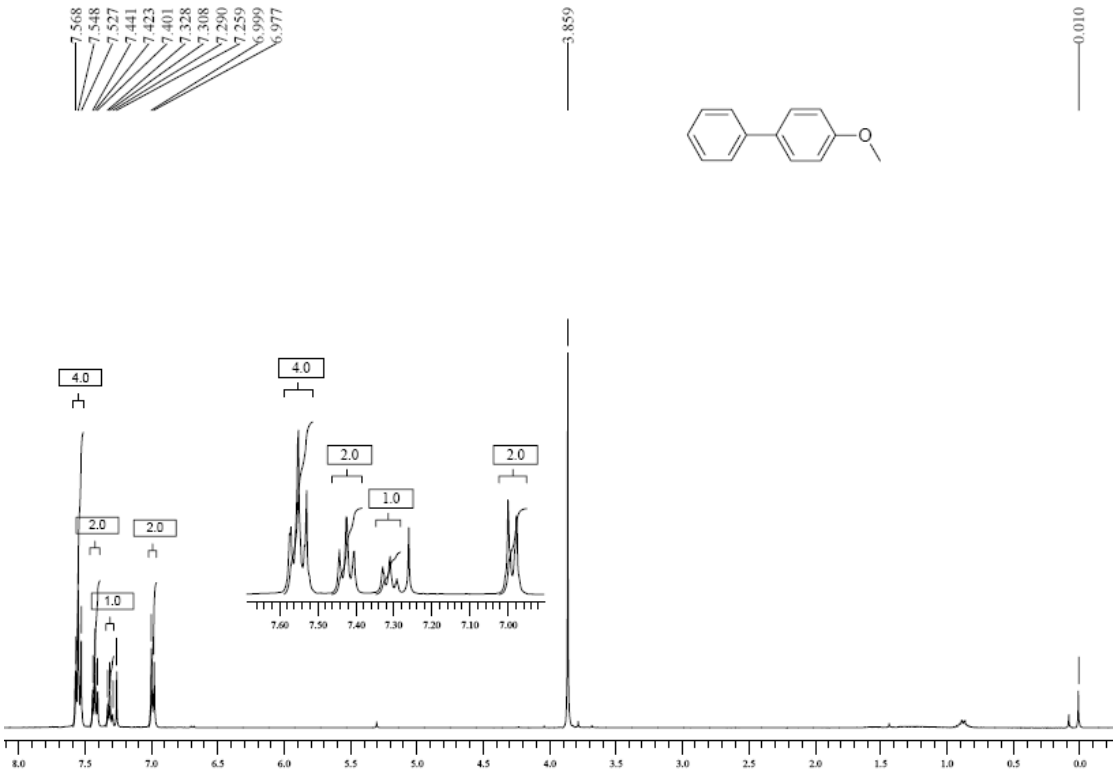

Figure S-15 **3-Methoxy-biphenyl (3ac)**

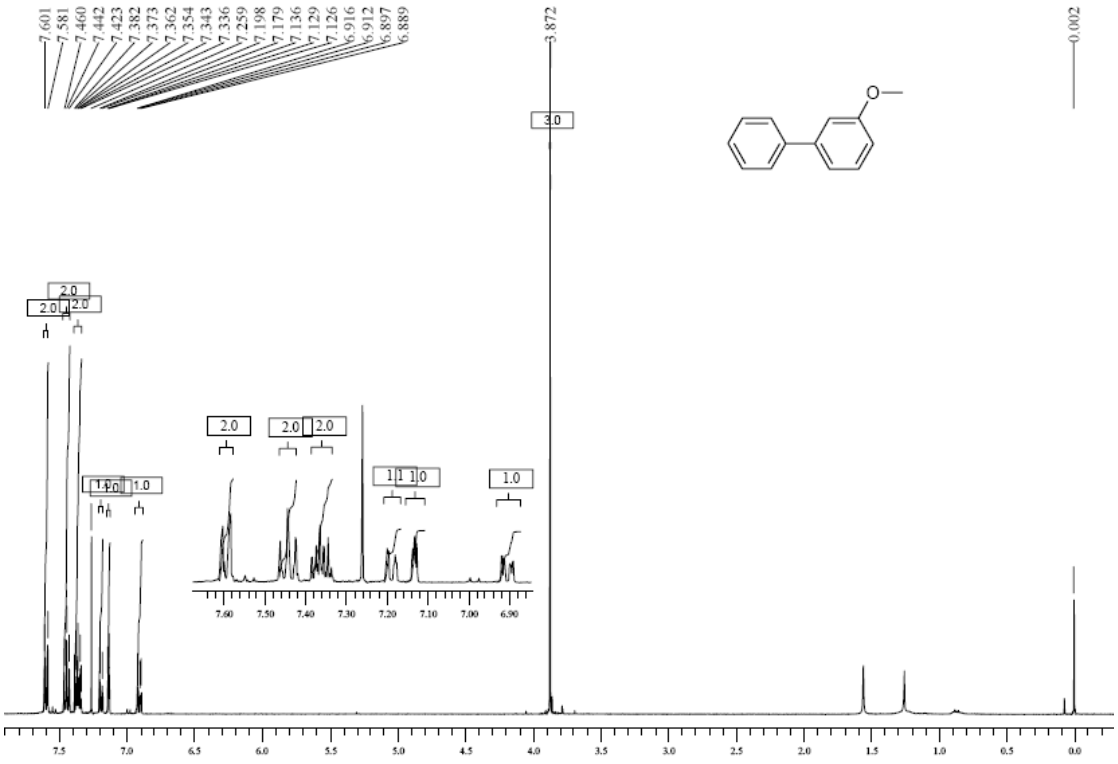

Figure S-16 **2-Methoxy-biphenyl (3ad)**

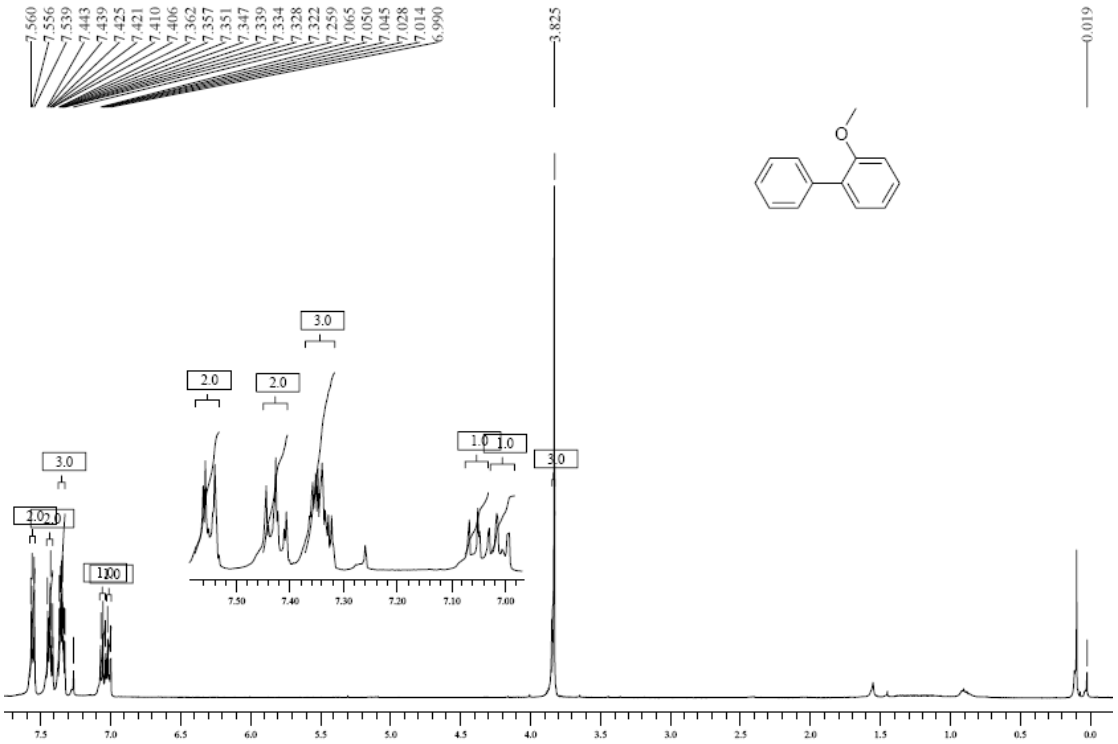

Figure S-17 **4-Chloro-4'-methoxy-biphenyl (3bg)**

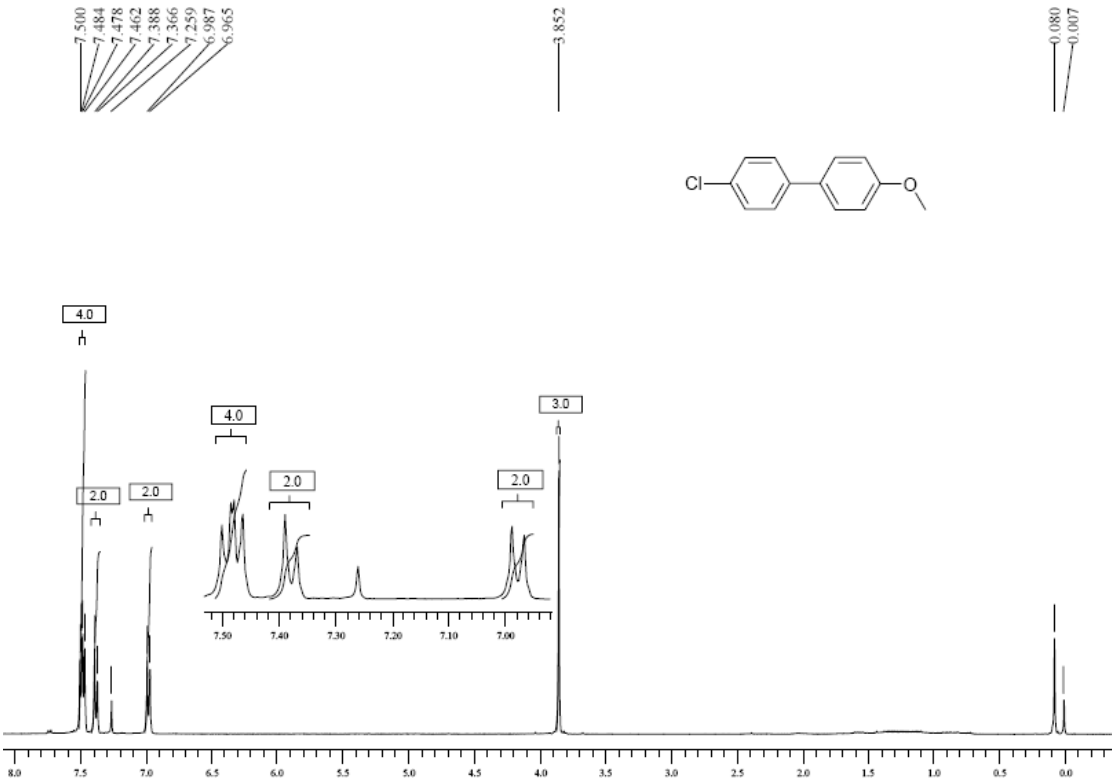

Figure S-18 **4-Methoxy-4'-methyl-biphenyl (3be)**

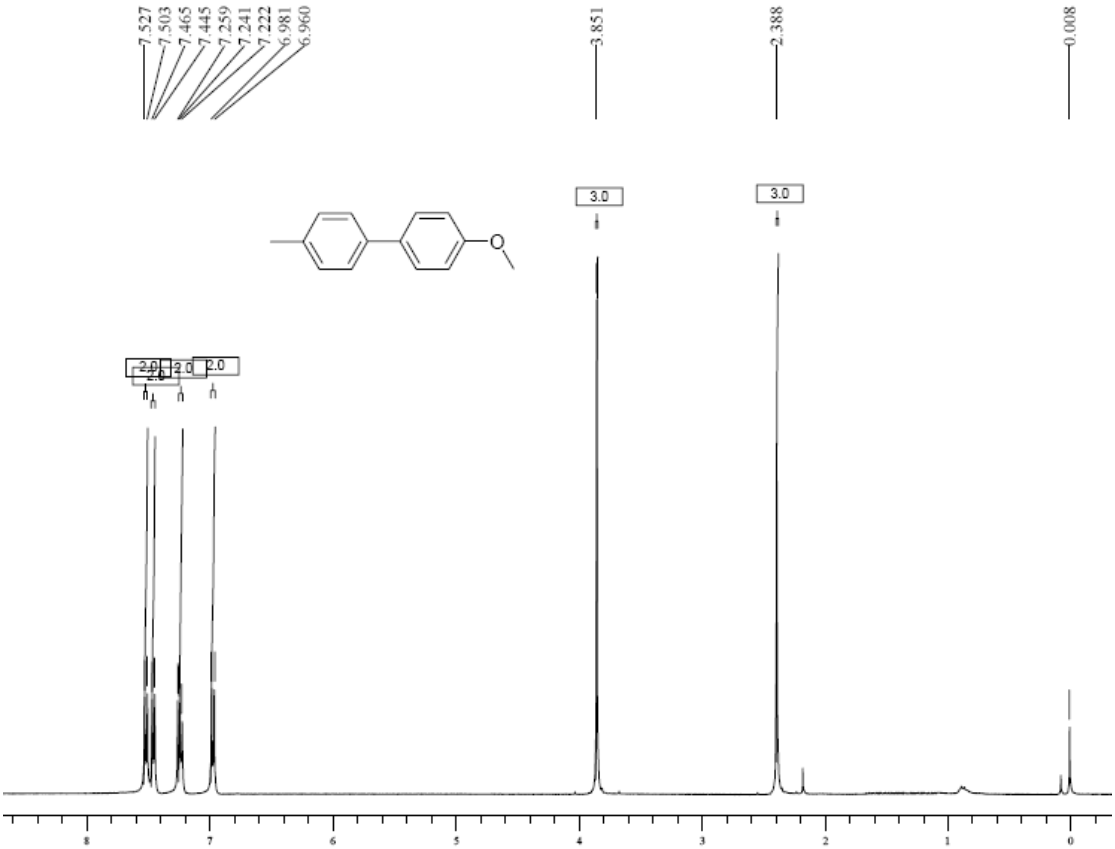

Figure S-19 **1-Phenyl-naphthalene (3aj)**

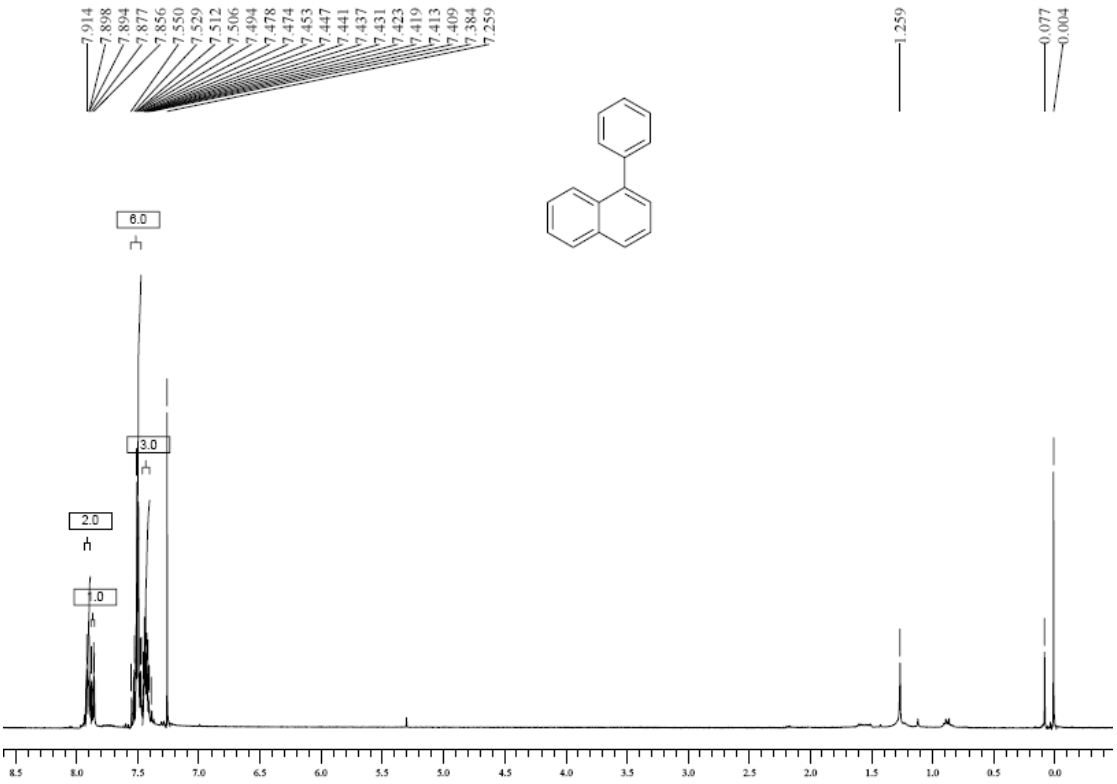

Figure S-20 **1-(3-nitro-phenyl)-naphthalene (3jk)**

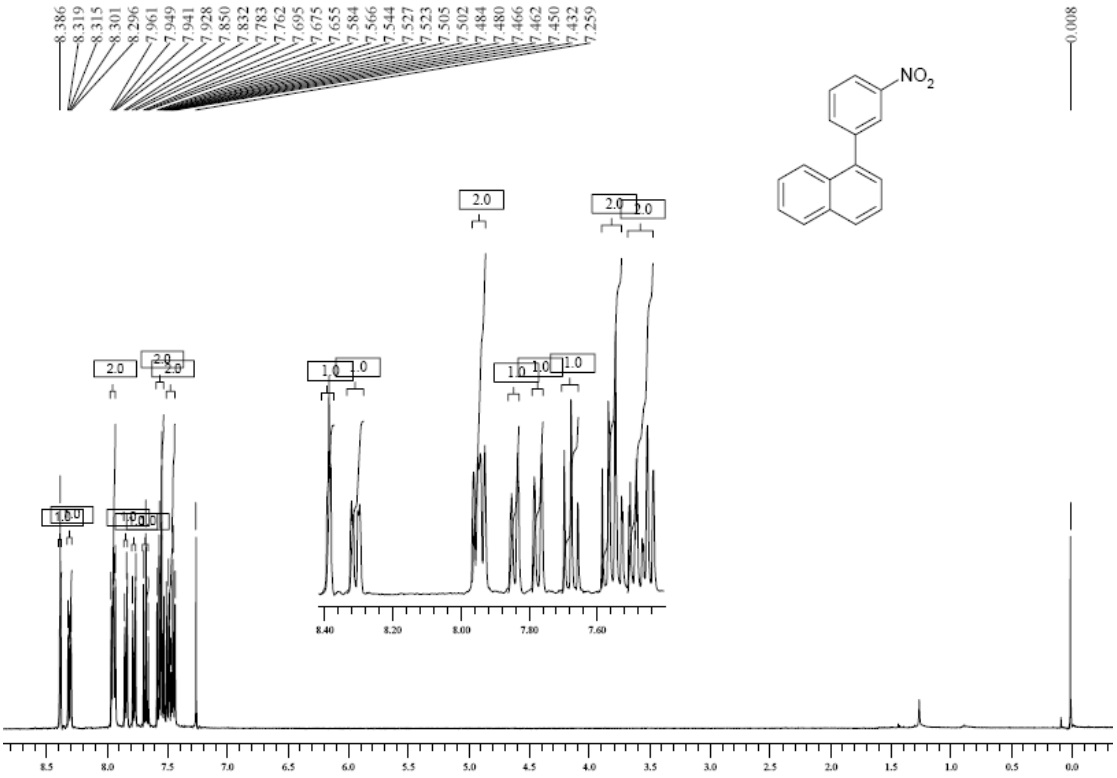

Figure S-21 **1-(4-Bromo-phenyl)-naphthalene (3ij)**

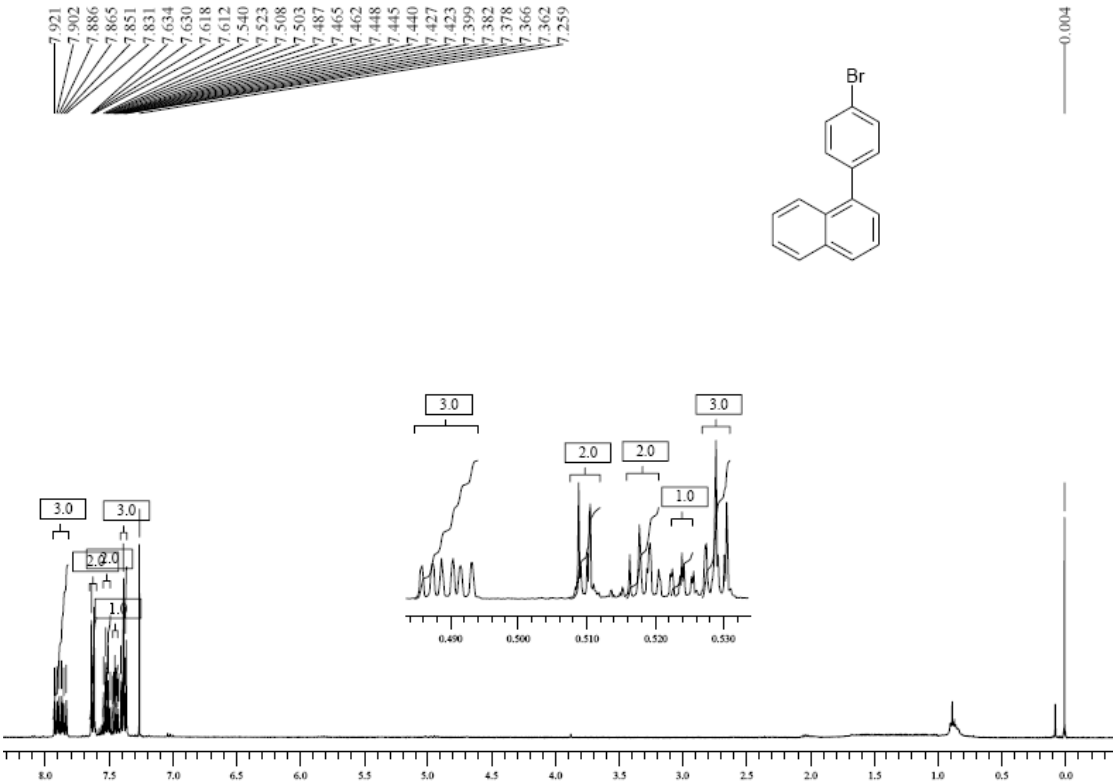

Figure S-22 **4-Chloro-4'-methyl-biphenyl (3eg)**

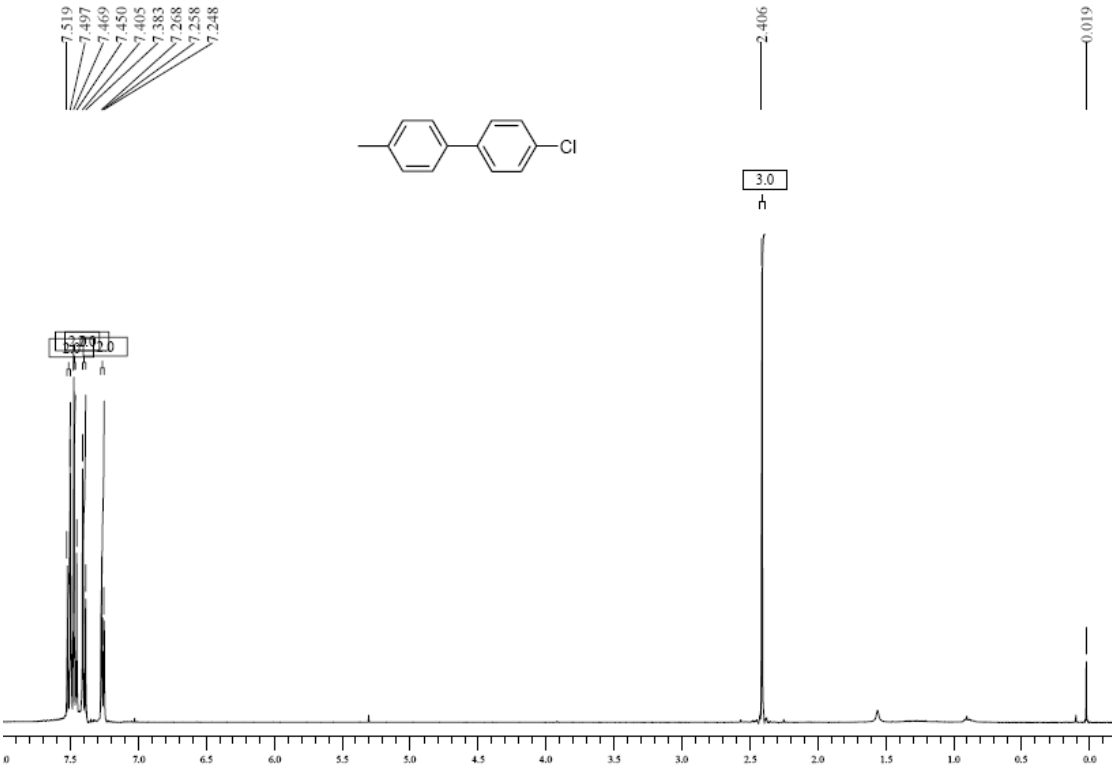

Figure S-23 **1-(4-Methoxy-phenyl)-naphthalene (3bj)**

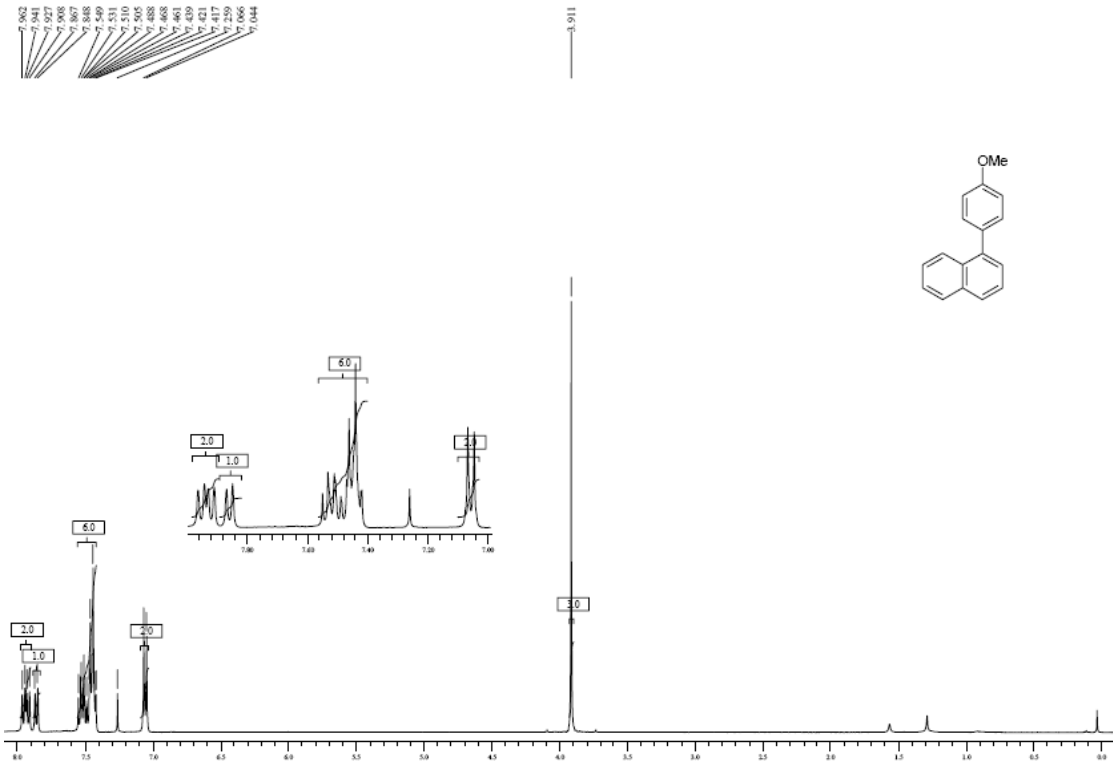

Figure S-24 **4-Bromo-4'-methyl-biphenyl (3ei)**

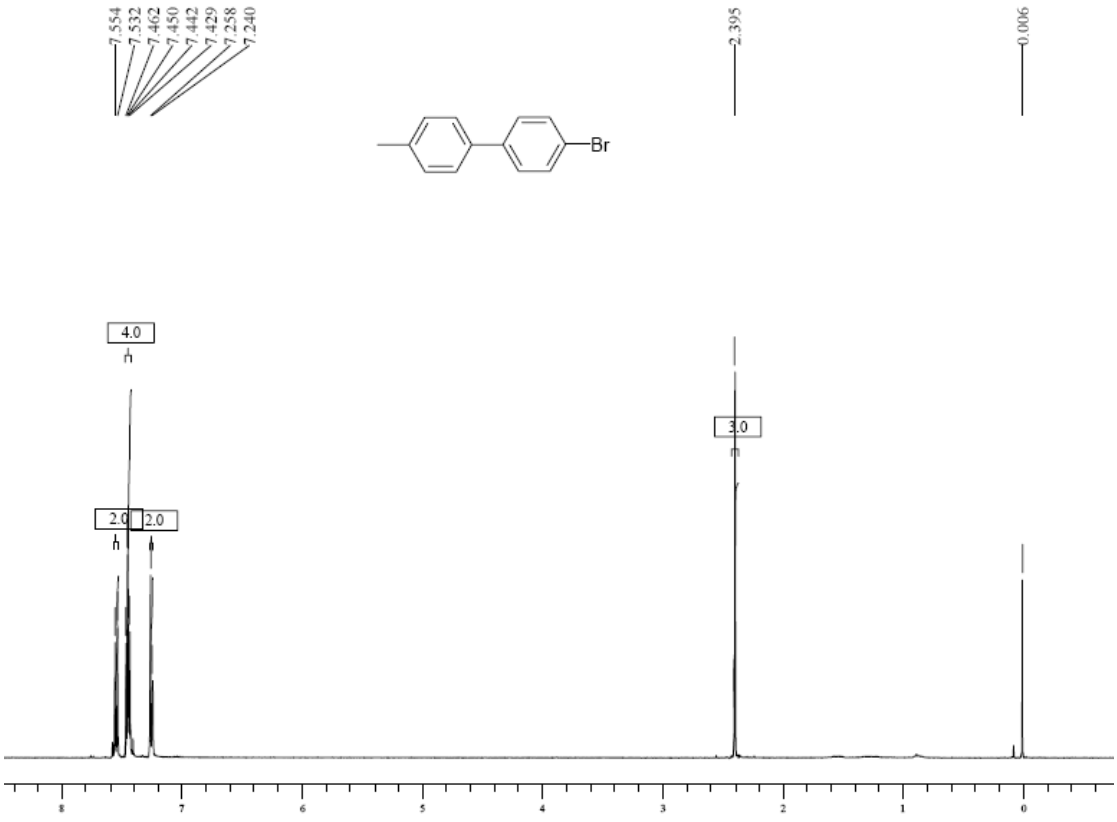

Figure S-25 **Biphenyl 3-carboxylic acid ethyl ester (3al)**

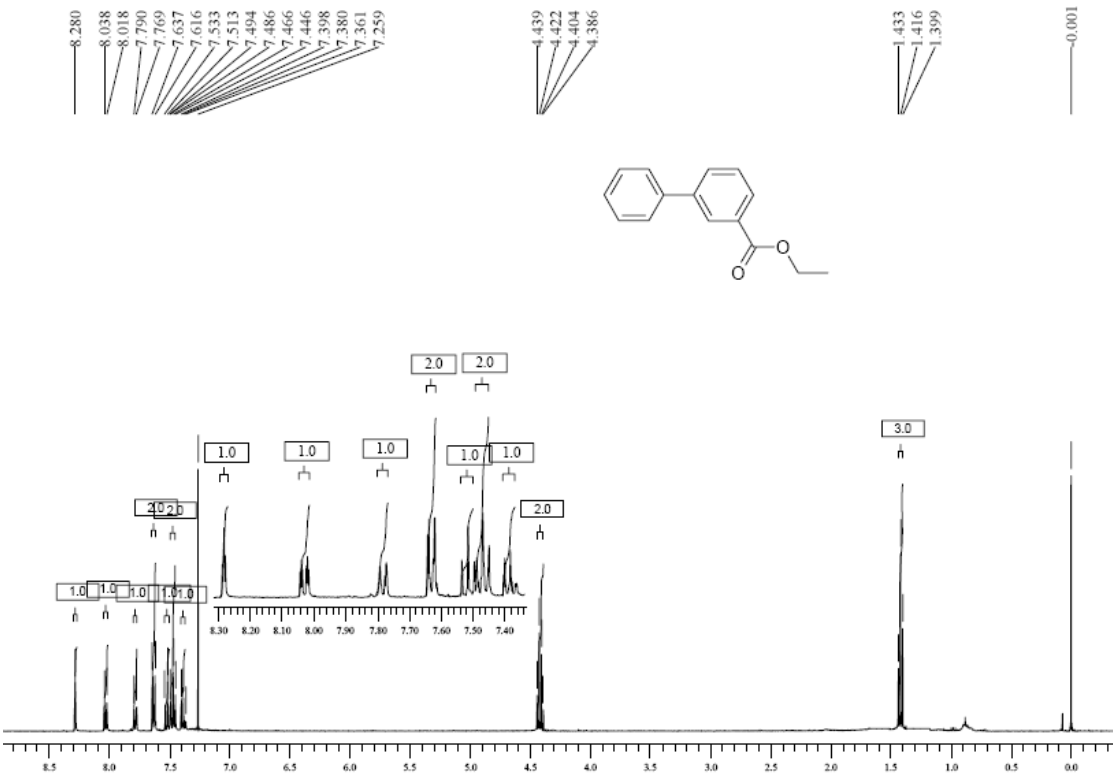

Figure S-26 **3-Iodobenzoic acid ethyl ester (1l)**

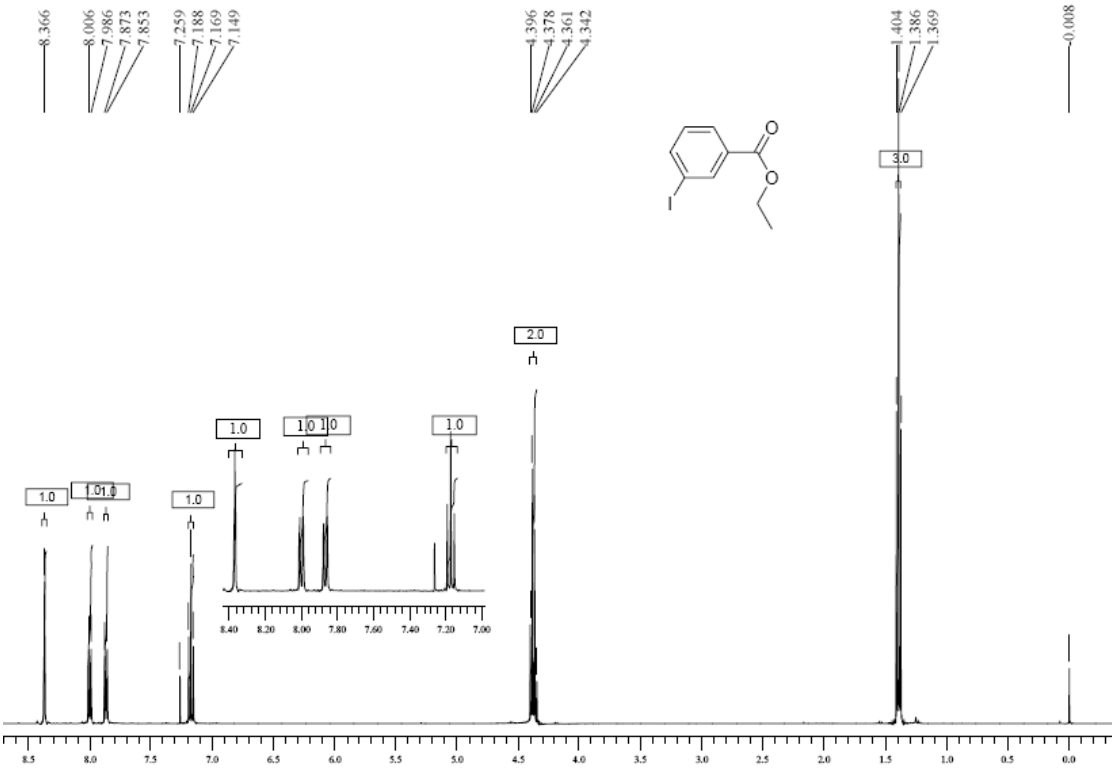

Figure S-27 **4'-Bromo-biphenyl-2-carboxylic acid ethyl ester (3il) (^{1}H NMR)**

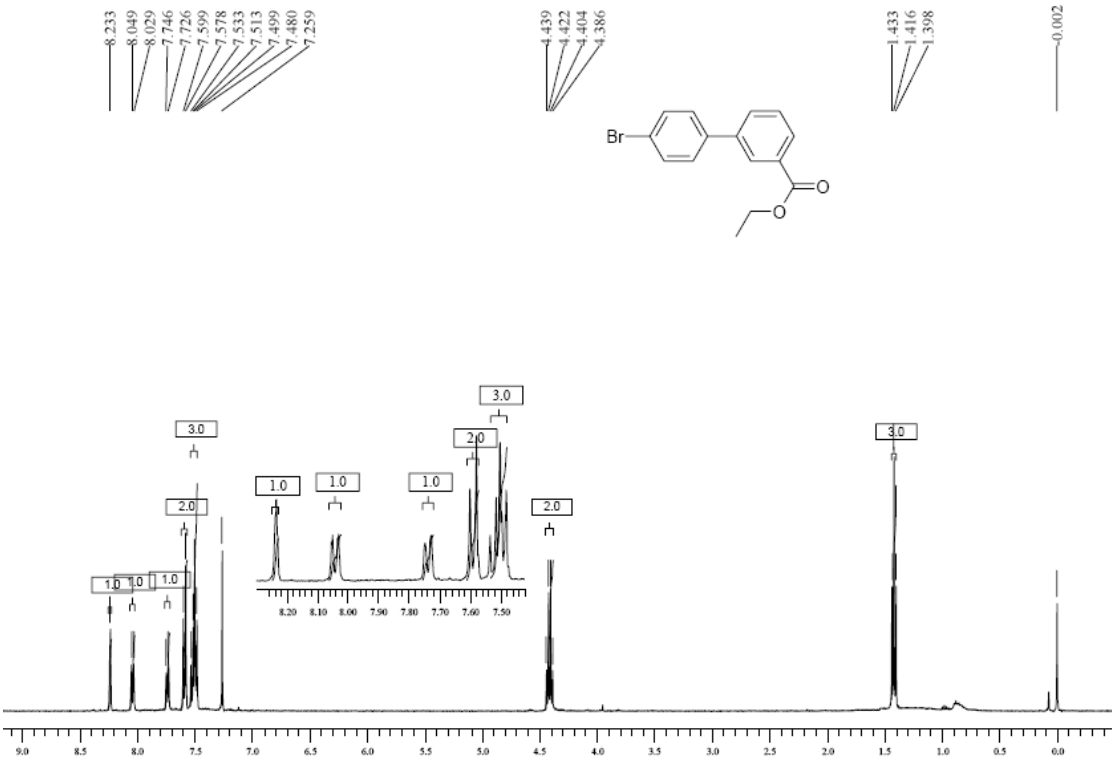

Figure S-28 **4'-Bromo-biphenyl-2-carboxylic acid ethyl ester (3il) (^{13}C NMR)**

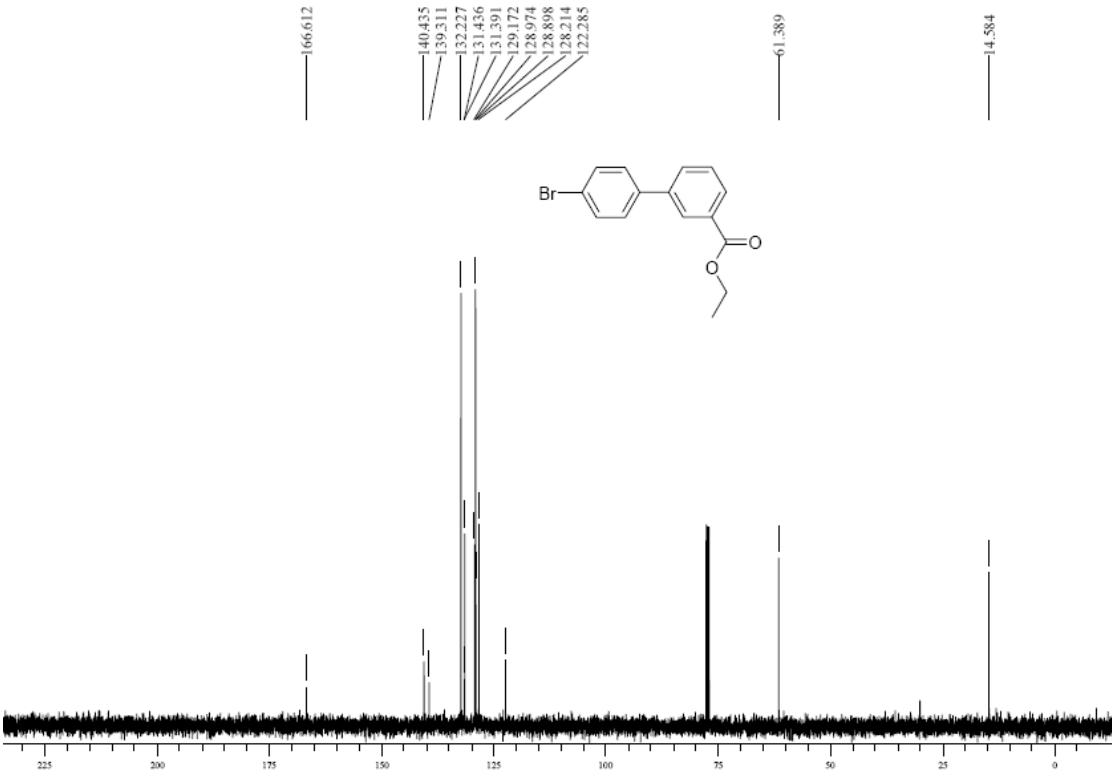

Figure S-29 **4'-Methoxy-biphenyl-3-carboxylic acid ethyl ester (3bl):**