Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Alkoxy base-mediated transition-metal-free cross-coupling reactions of benzene with aryl halides

Wei Liu,* Lige Xu and Yanlan Bi
E-mail: liuwei307@hotmail.com

General methods:

Aryl halides and bases were purchased from commercial sources and used without prior treatments. Benzene was dried and distilled from sodium/benzophenone immediately prior to use under a nitrogen atmosphere. All other reagents and solvents were used as it from commercial sources. Unless noted below, all other compounds have been reported in the literatures or are commercially available. All reactions were performed in oven-dried glassware. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum ether.

^{1}H and ^{13}C NMR data were recorded in $CDCl_3$ solutions with Varian Mercury (300 MHz) spectrometers using tetramethylsilane (TMS) as the internal standard. Analytical gas chromatography (GC) was performed using an Aglient 6890 Gas Chromatography fitted with a flame ionization detector.

Reagents:

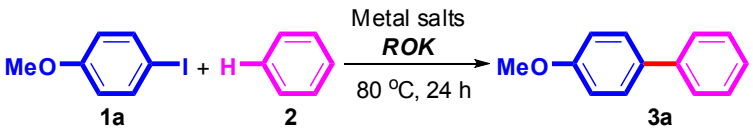
Potassium methoxide (MeOK), 95%, purchased from Sigma-Aldrich; Potassium ethoxide (EtOK), 95%, purchased from Sigma-Aldrich; Potassium *tert*-butoxide (*t*-BuOK), 99%, purchased from J&K Scientific Ltd.; Potassium *tert*-pentyloxide (*t*-AmOK), 25% w/w in toluene, purchased from Alfa Aesar, used after removing the toluene under reduced pressure. Unless otherwise stated, commercial reagents were used without purification.

General procedure for cross-coupling of benzene with 4-iodoanisole:

A Schlenk tube was charged with 4-iodoanisole (117 mg, 0.5 mmol), EtOK (42 mg, 0.5 mmol) and *t*-BuOK (168 mg, 1.5 mmol) under an atmosphere of nitrogen, and then benzene (4.0 mL) was added. The resulting mixture was stirred at 80 ^{o}C for 24 h. After cooling to room temperature, the reaction mixture was quenched with water and extracted with ethyl acetate (10 mL x 3). The organic layers were combined, dried over Na_2SO_4 and concentrated under reduced pressure, and then purified by silica gel chromatograph (petroleum ether) to yield the desired product as a white solid (70.8

mg, 77% yield).

Table S1. Alkoxy base promoted cross-coupling of benzene with 4-iodoanisole [a].



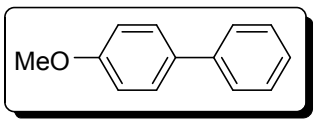
1a 2 3a

entry	Metal salts (mol%)	Base (equiv)	Yield (%)
1	$FeCl_3$ (10)	MeOK (3)	0
2	$CuCl_2$ (10)	MeOK (3)	0
3	$CoCl_2$ (10)	MeOK (3)	0
4	$NiCl_2$ (10)	MeOK (3)	0
5	$FeCl_3$ (10)	EtOK (3)	0
6	$CuCl_2$ (10)	EtOK (3)	0
7	$CoCl_2$ (10)	EtOK (3)	0
8	$NiCl_2$ (10)	EtOK (3)	0
9	$FeCl_3$ (10)	*t*-BuOK (3)	<5
10	$CuCl_2$ (10)	*t*-BuOK (3)	<5
11	$CoCl_2$ (10)	*t*-BuOK (3)	<5
12	$NiCl_2$ (10)	*t*-BuOK (3)	0
13	$FeCl_3$ (10)	*t*-AmOK (3)	<5
14	$CuCl_2$ (10)	*t*-AmOK (3)	0
15	$CoCl_2$ (10)	*t*-AmOK (3)	<5
16	$NiCl_2$ (10)	*t*-AmOK (3)	0

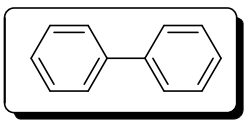
[a] Reactions conditions: **1a** (0.5 mmol), base (3.0 equiv), benzene (4.0 mL), 80 °C, 24 h, N_2. Calibrated GC yields of **3a** were reported using hexadecane as the internal standard.

Compounds NMR Data:

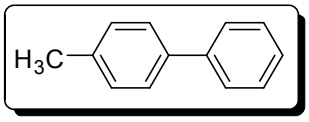
The spectroscopic data of all the products are presented below. All the known compounds gave satisfactory spectroscopic values and accorded to spectroscopic data reported in the literatures.



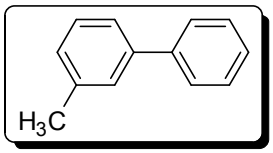
4-methoxybiphenyl (3a)[1]**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58-7.53 (m, 4H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 8.7 Hz, 1H), 6.99 (d, *J* = 6.6 Hz, 2H), 3.87 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.2, 140.9, 133.8, 128.7, 128.2, 126.8, 126.7, 114.2, 55.4.



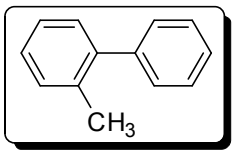
Biphenyl (3b) [1]**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.2Hz, 4H), 7.48 (t, *J* = 7.4 Hz, 4H), 7.33 (t, *J* = 7.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.2, 128.8, 127.3, 127.2.



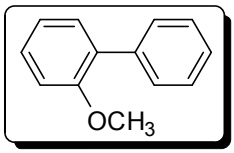
4-methylbiphenyl (**3c**) [1]**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.2 Hz, 2H), 7.48 (d, *J* = 6.3 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 2H), 2.46 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.2, 138.4, 137.1, 129.6, 128.8, 127.1, 21.2.



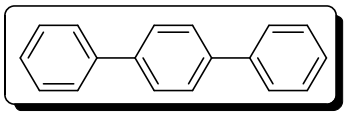
3-methylbiphenyl (**3d**)[1]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.1 Hz, 2H), 7.52-7.45 (m, 6H), 7.25 (d, *J* = 8.7 Hz, 1H), 2.49 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.4, 141.3, 138.4, 128.8, 128.7, 128.1, 128.0, 127.2, 124.3, 21.6.



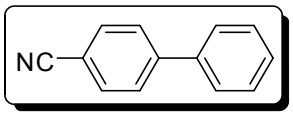
2-methylbiphenyl (**3e**)[1]**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47-7.27 (m, 9H), 2.31 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.9, 135.4, 130.3, 129.8, 129.2, 128.1, 127.3, 126.8, 125.8, 20.5.



2-methoxybiphenyl (**3f**)[2]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.7 Hz, 2H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.39-7.33 (m, 3H), 7.10-7.00 (m, 2H), 3.84 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.4, 137.5, 129.8, 129.6, 128.5, 127.6, 126.9, 125.9, 119.8, 110.1, 54.5.

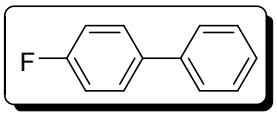


1,4-diphenylbenzene (**3g**) [2]**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70-7.65 (m, 8H), 7.47 (t, *J* = 7.8 Hz, 4H), 7.38 (t, *J* = 7.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.7, 140.1, 128.8, 127.5, 127.4, 127.1.



Biphenyl-4-carbonitrile (**3h**)[1]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76-7.69 (m, 4H), 7.60 (t, *J* = 6.0

Hz, 2H), 7.52-7.41 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.7, 139.2, 132.6, 129.1, 128.7, 127.7, 127.2, 119.1, 110.9.

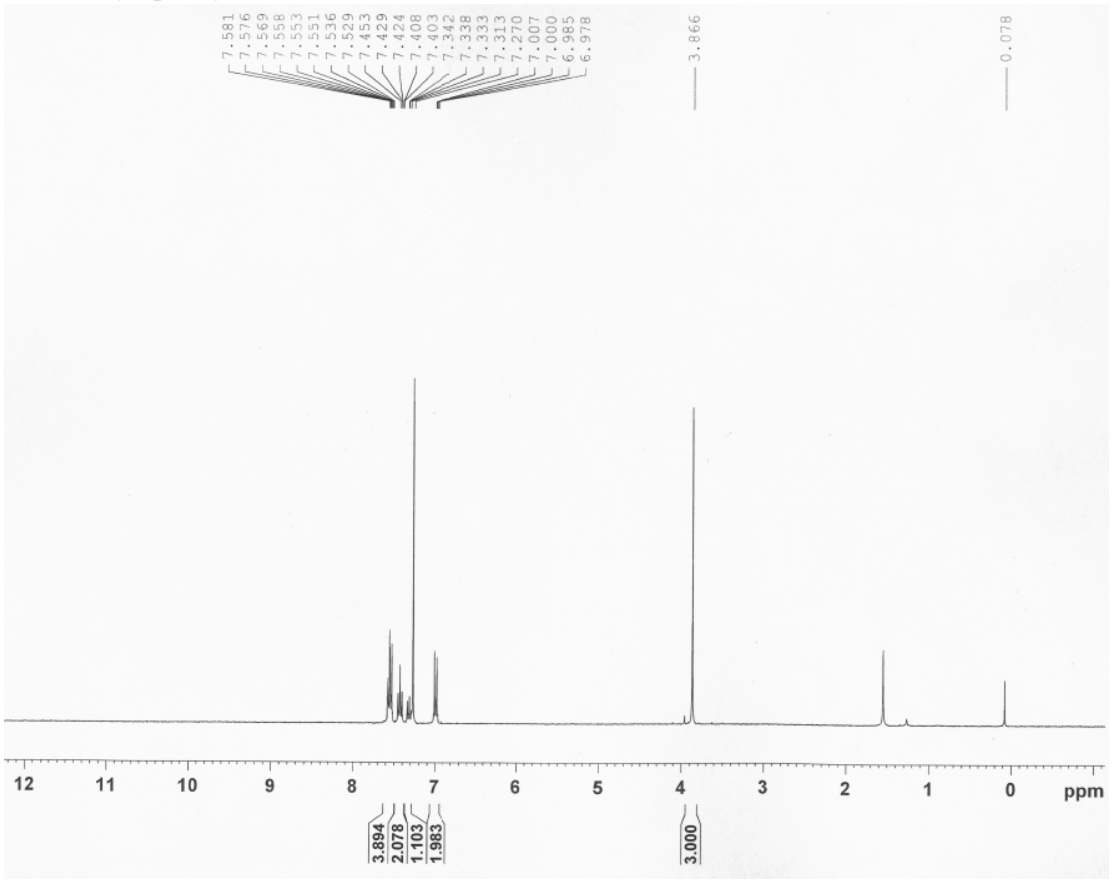


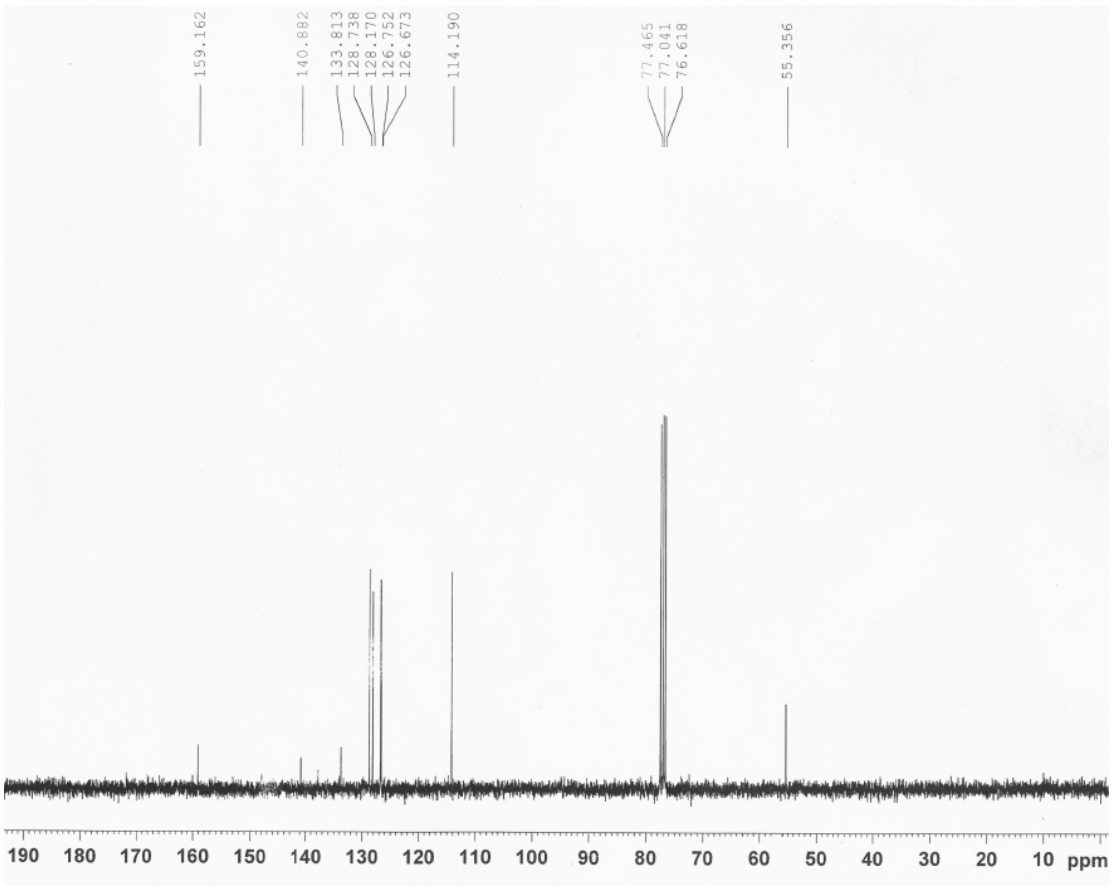
4-fluorobiphenyl (**3i**) [3]**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63-7.56 (m, 4H), 7.51 (t, *J* = 8.4 Hz, 2H), 7.38 (t, *J* = 8.6 Hz, 1H), 7.16 (t, *J* = 7.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.1, 160.8, 140.2, 137.2, 128.8, 128.7, 128.6, 127.3, 127.0, 115.8, 115.5.

REFERENCES

1. O. Kobayashi, D. Uraguchi and T. Yamakawa, *Org. Lett.,* 2009, ***11***, 2679.
2. G. –P. Yong, W. –L. She, Y. –M. Zhang and Y. –Z. Li, *Chem. Commun.,* 2011, ***47***, 11766.
3. C. L. Sun, H. Li, D. G. Yu, M. Yu, X. Zhou, X. Y. Lu, K. Huang, S. F. Zheng, B. J. Li and Z. J. Shi, *Nat. Chem.*, 2010, ***2***, 1044.

4-methoxybiphenyl (**3a**):





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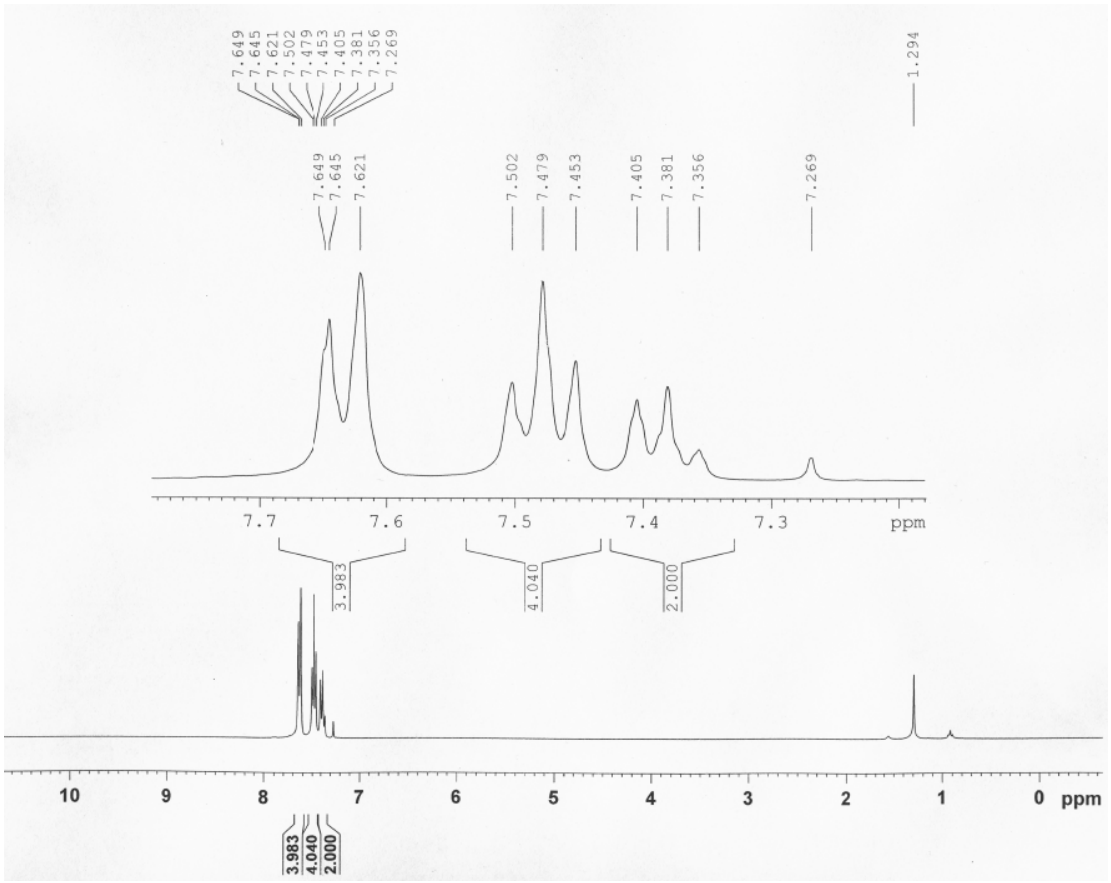
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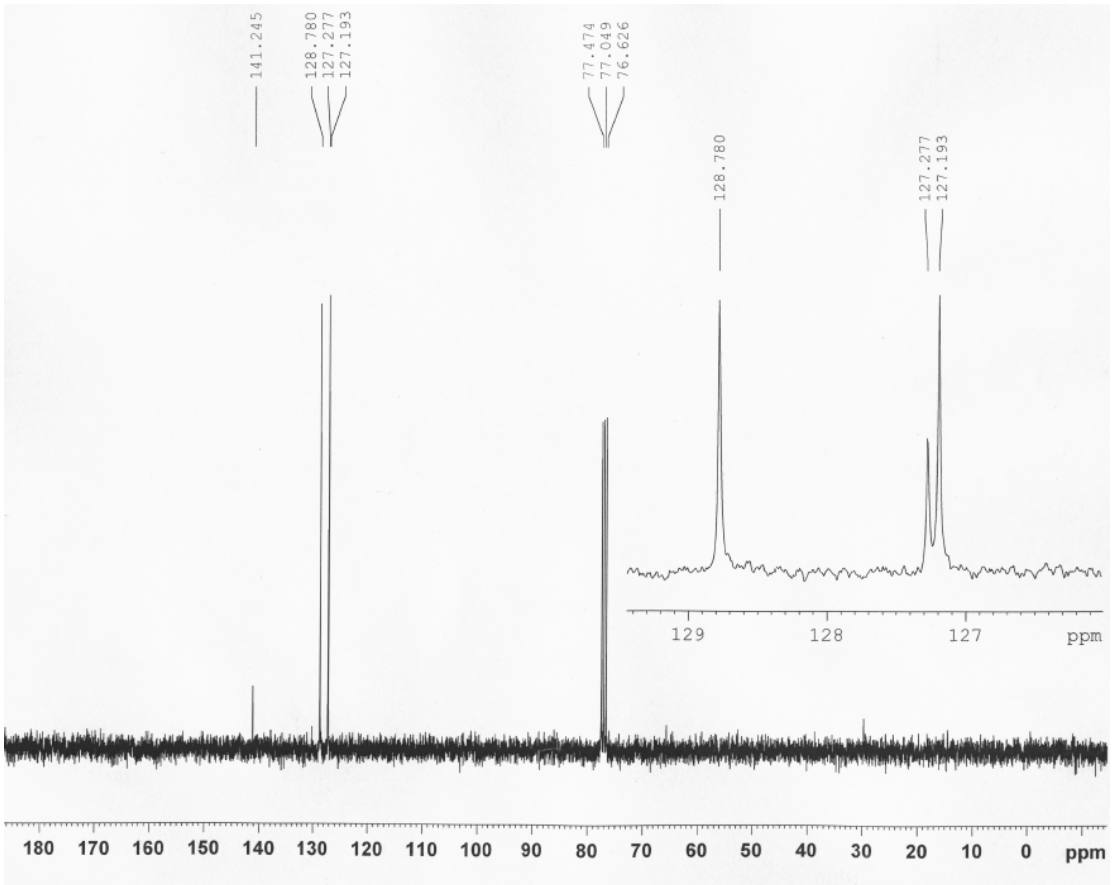
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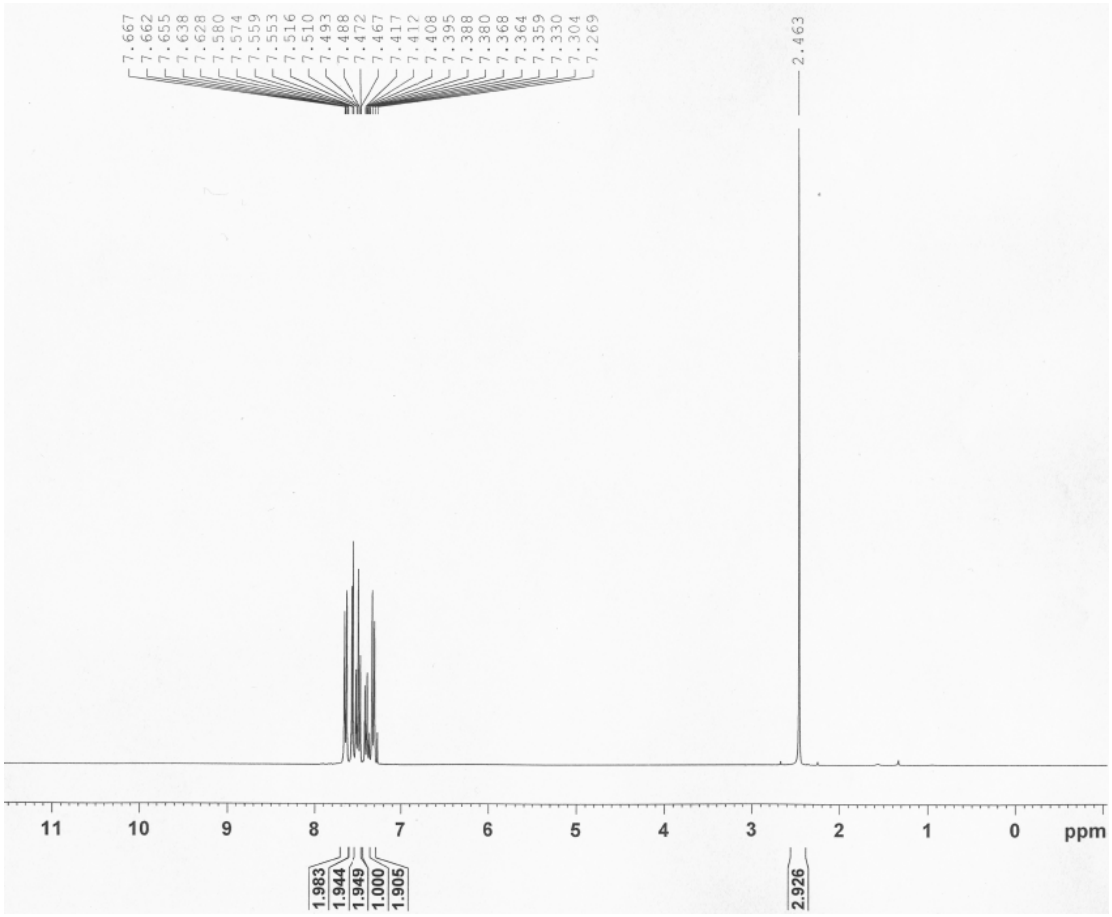

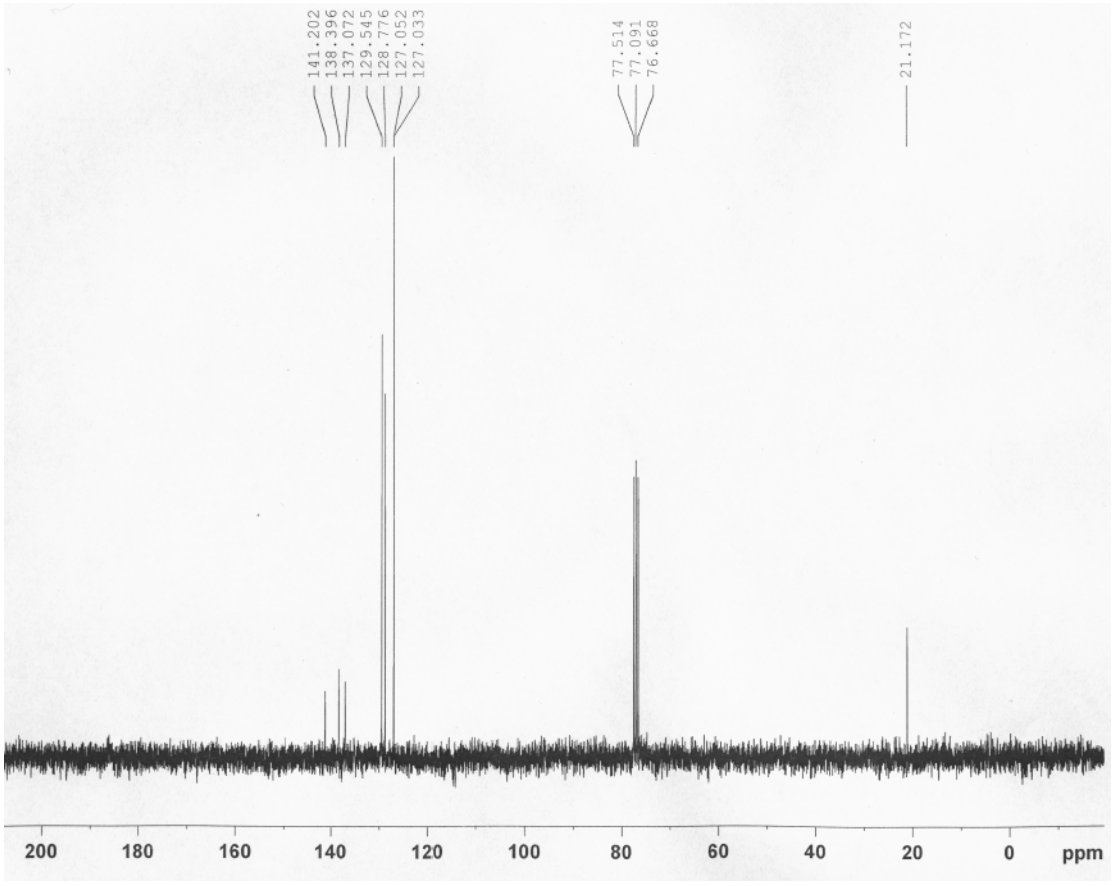

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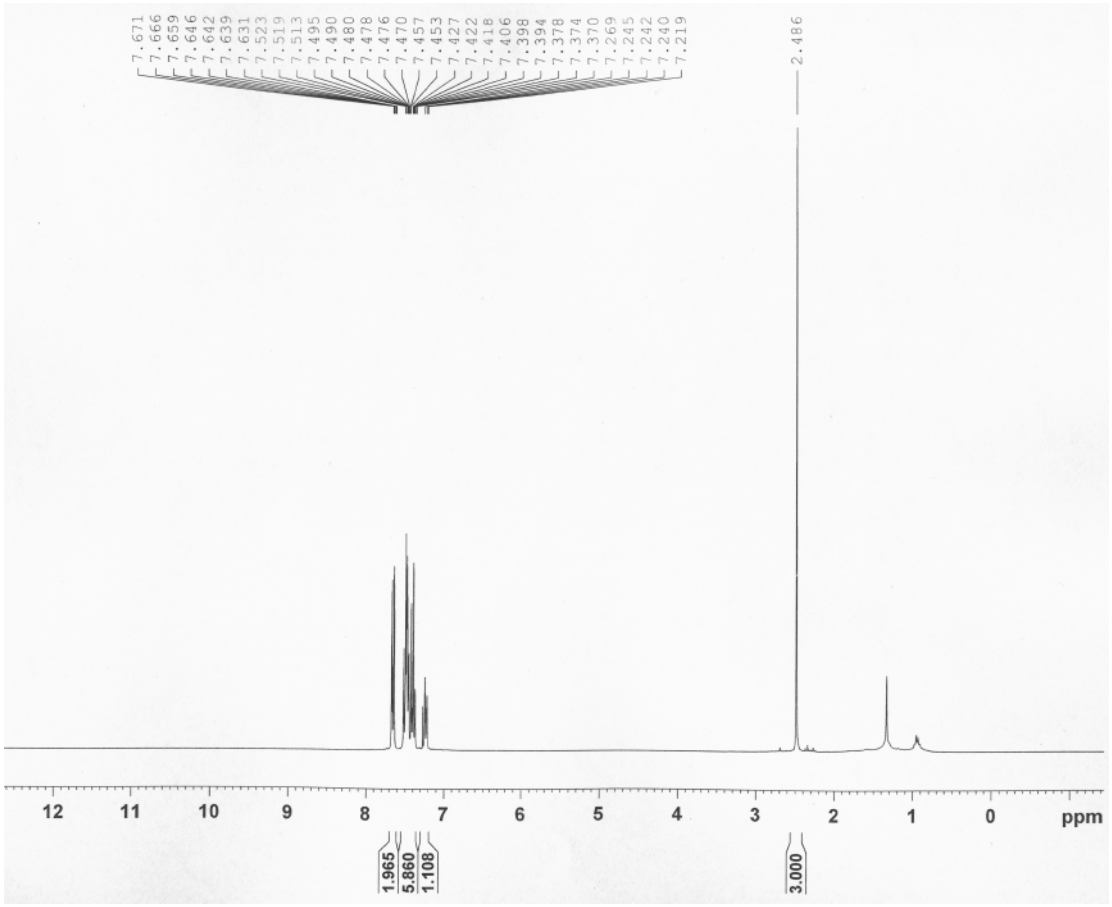
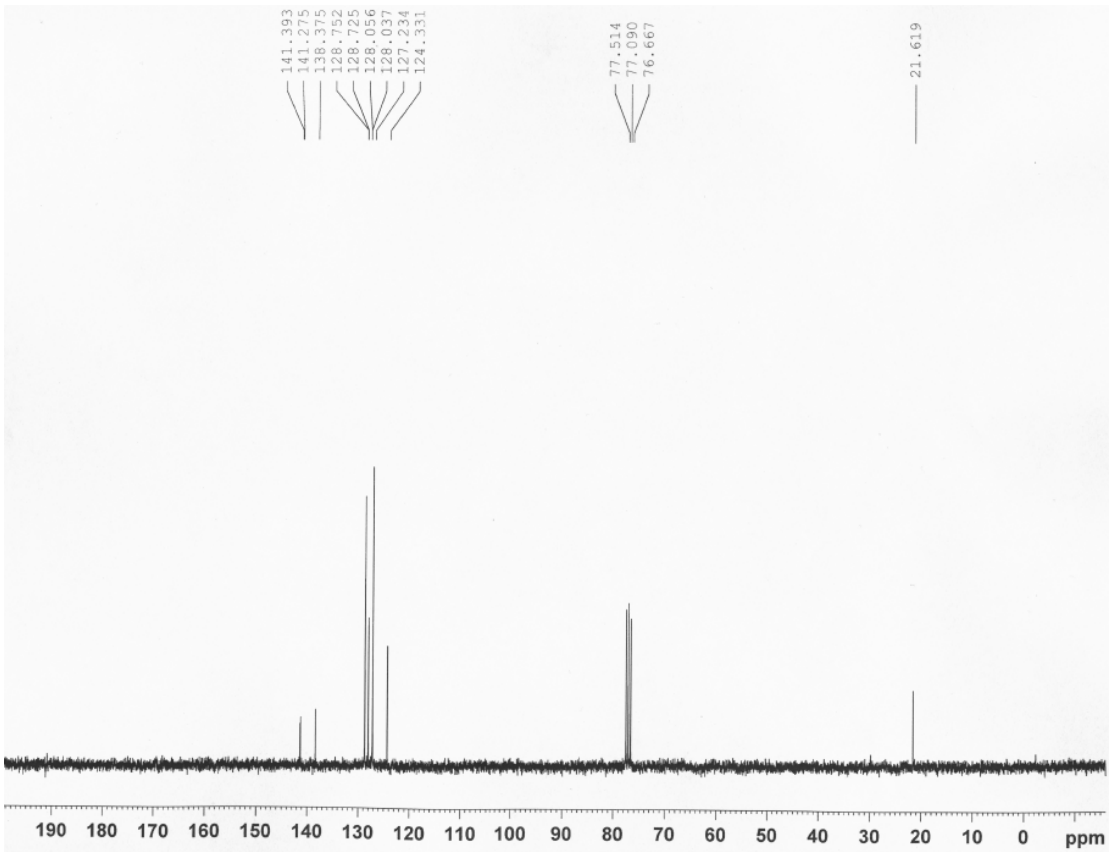
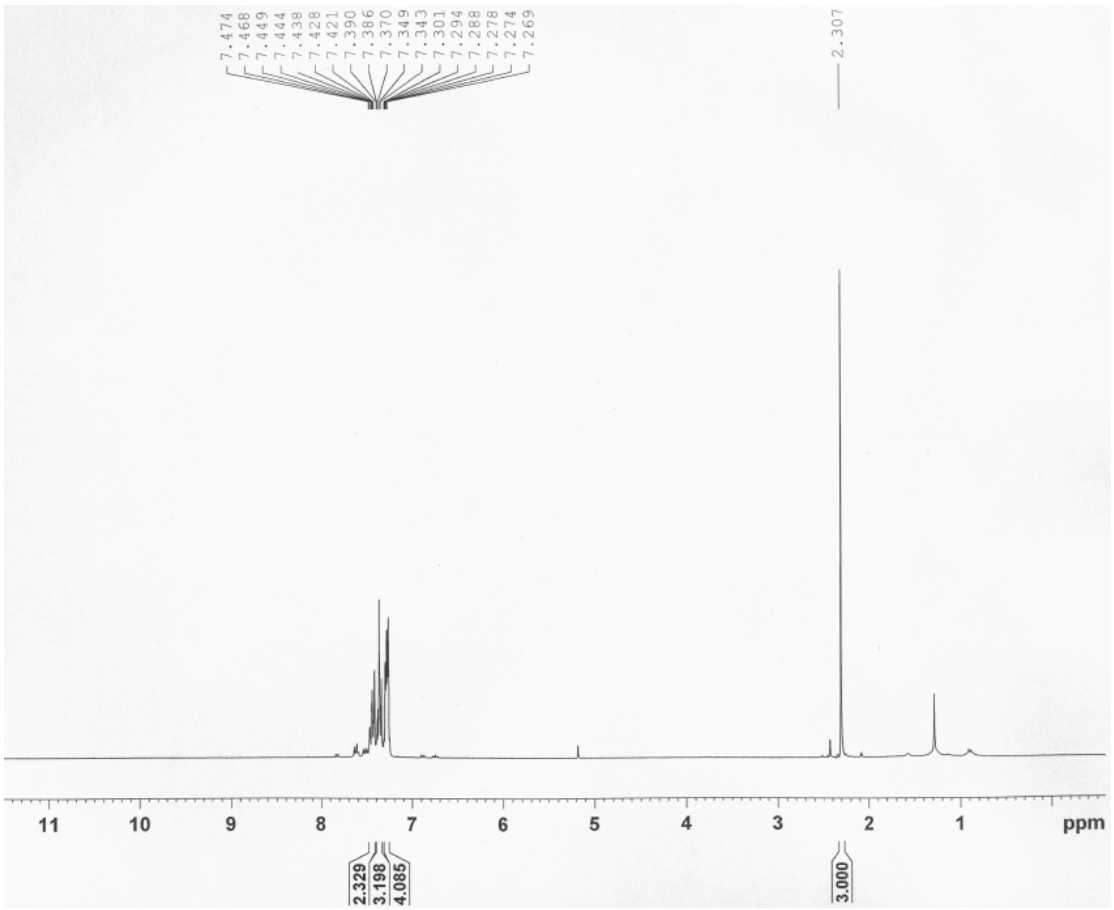
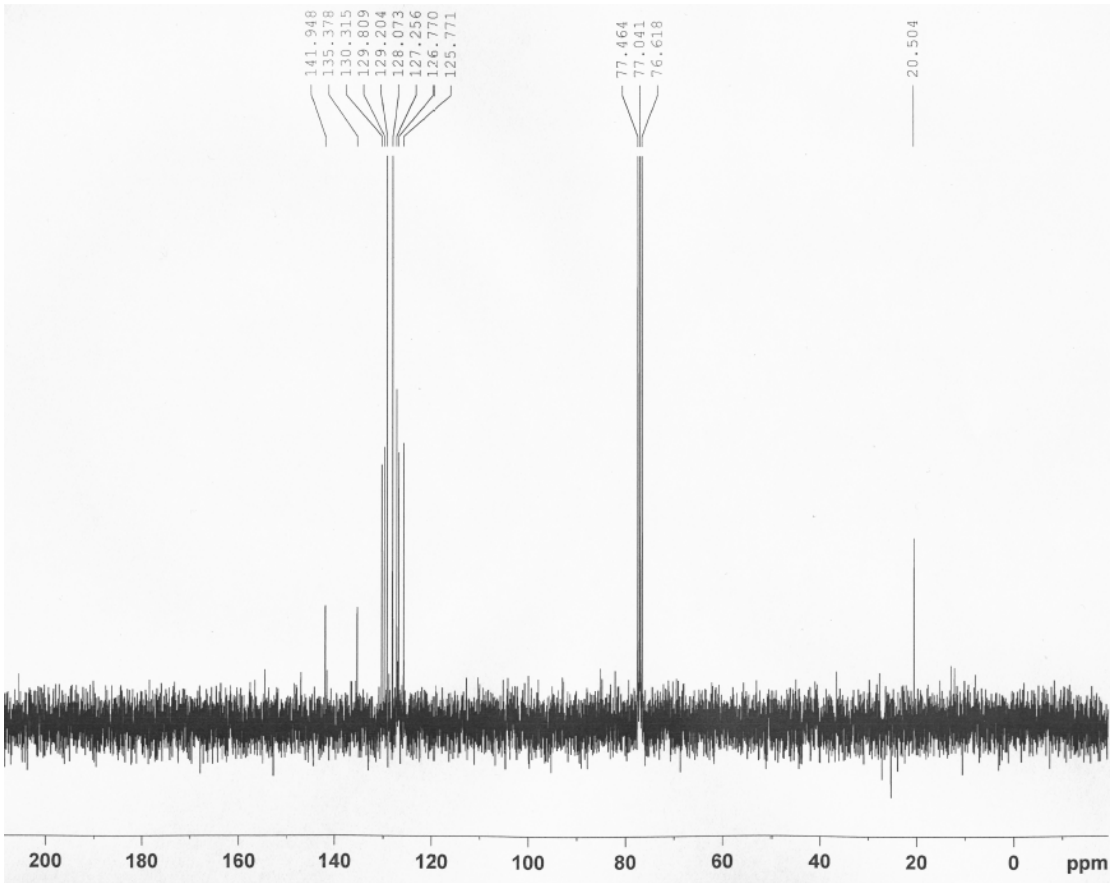


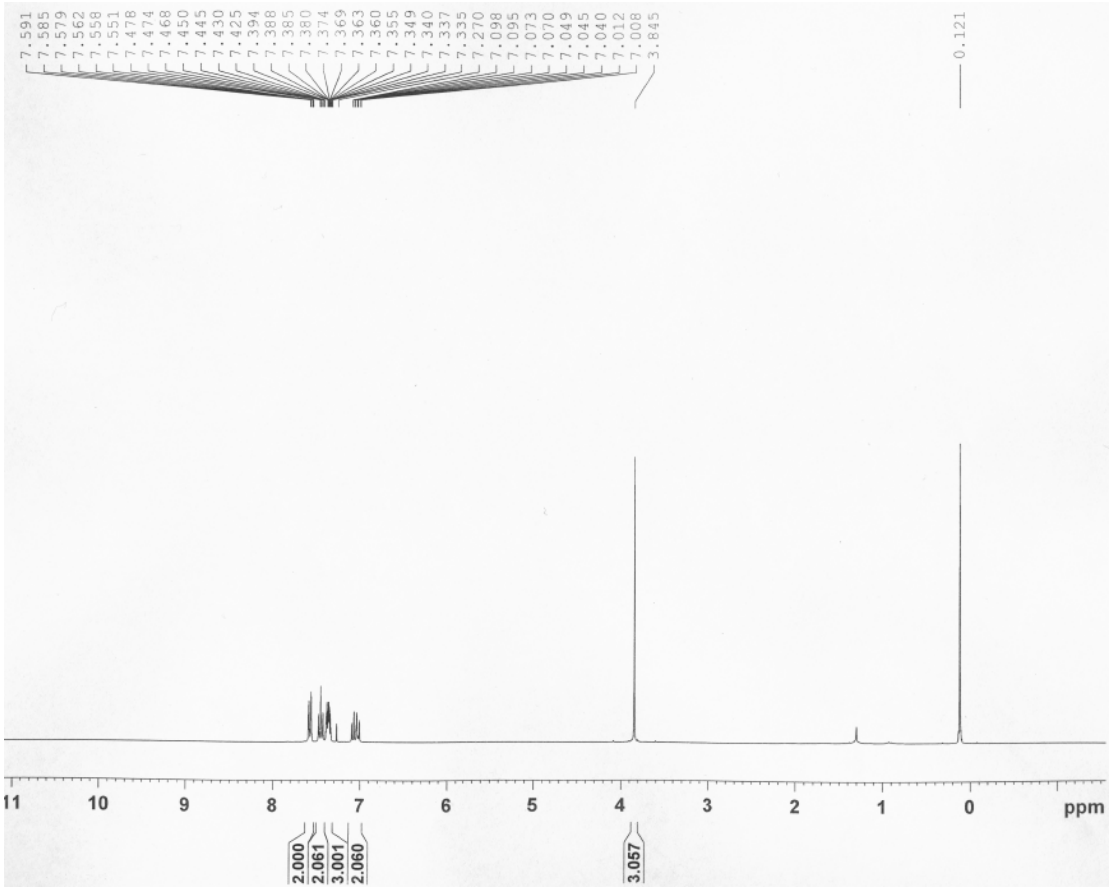


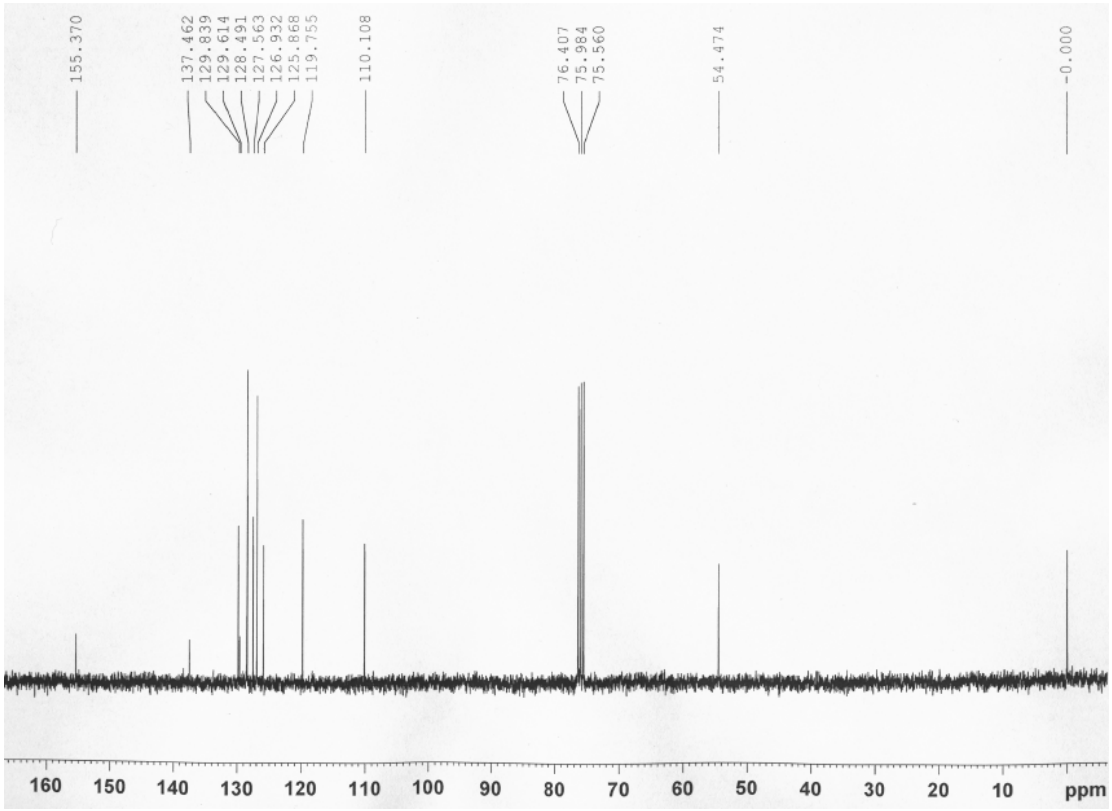
2-methylbiphenyl (**3e**):



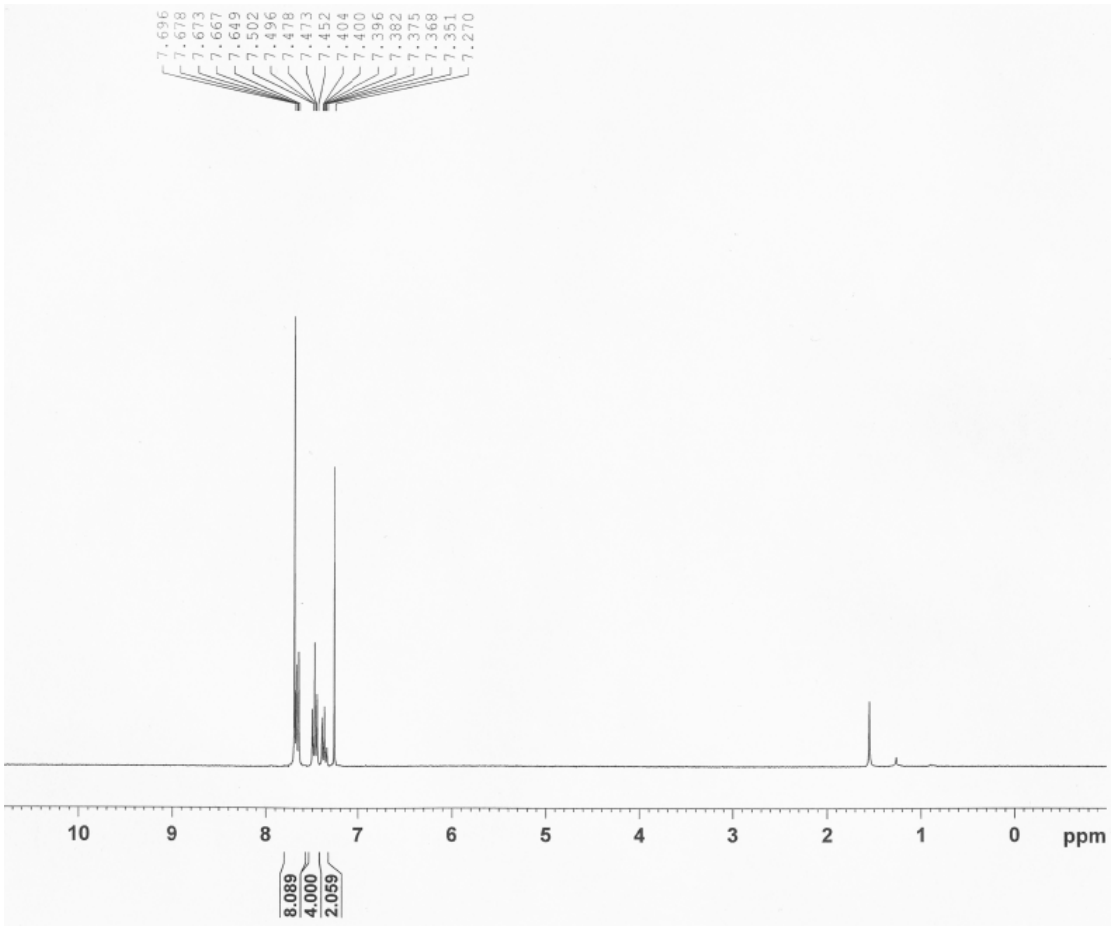


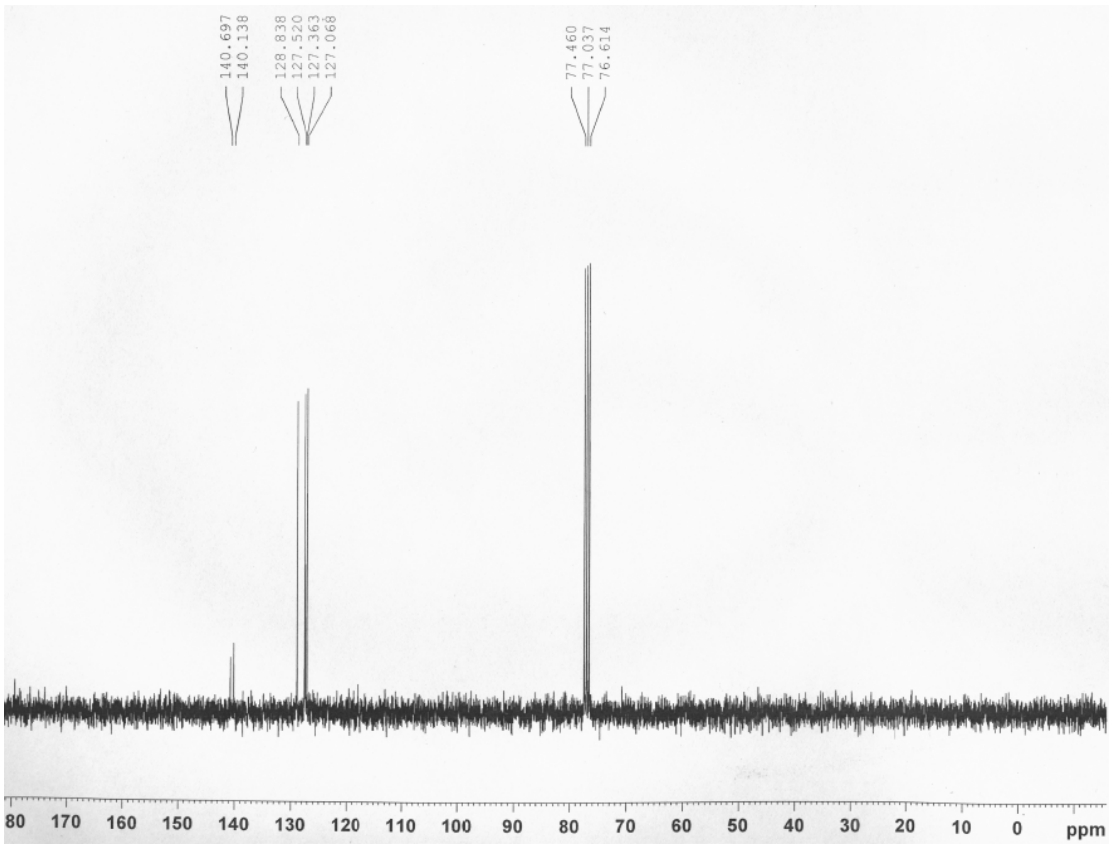
2-methoxybiphenyl (3f):



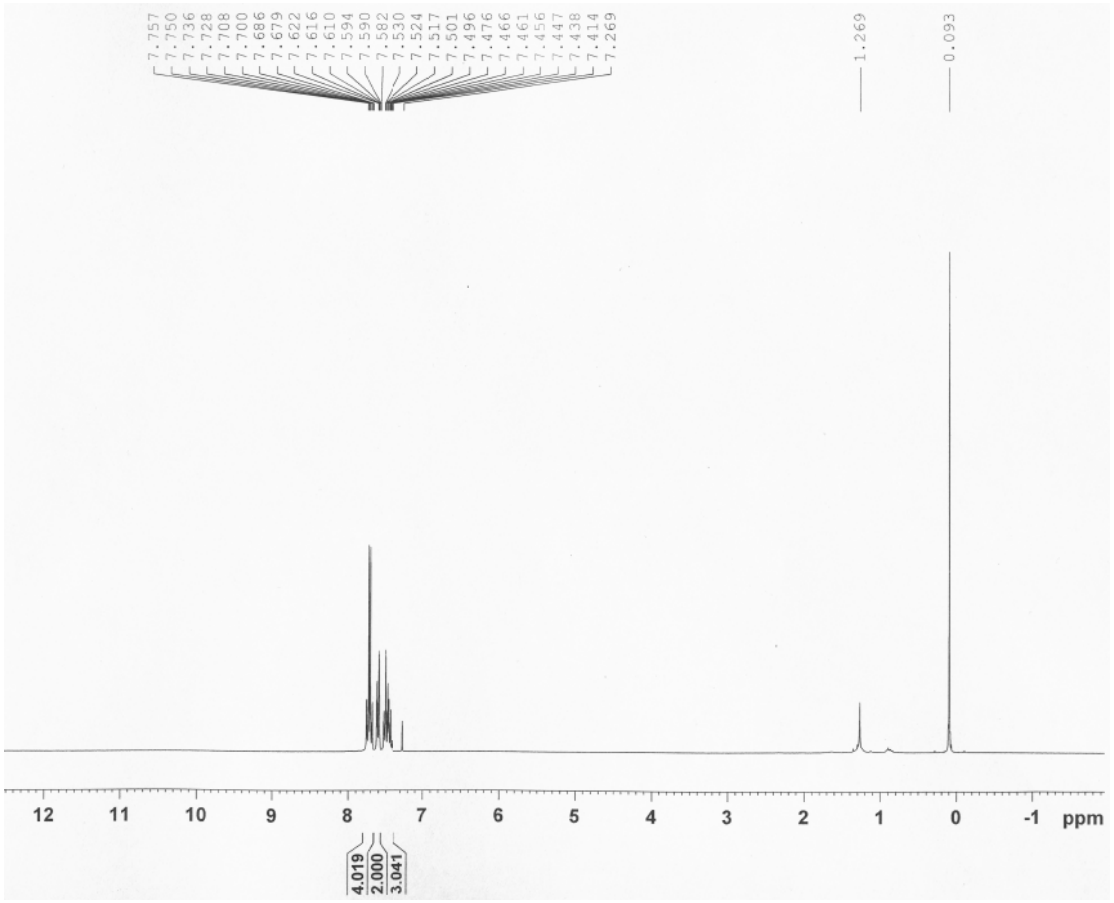


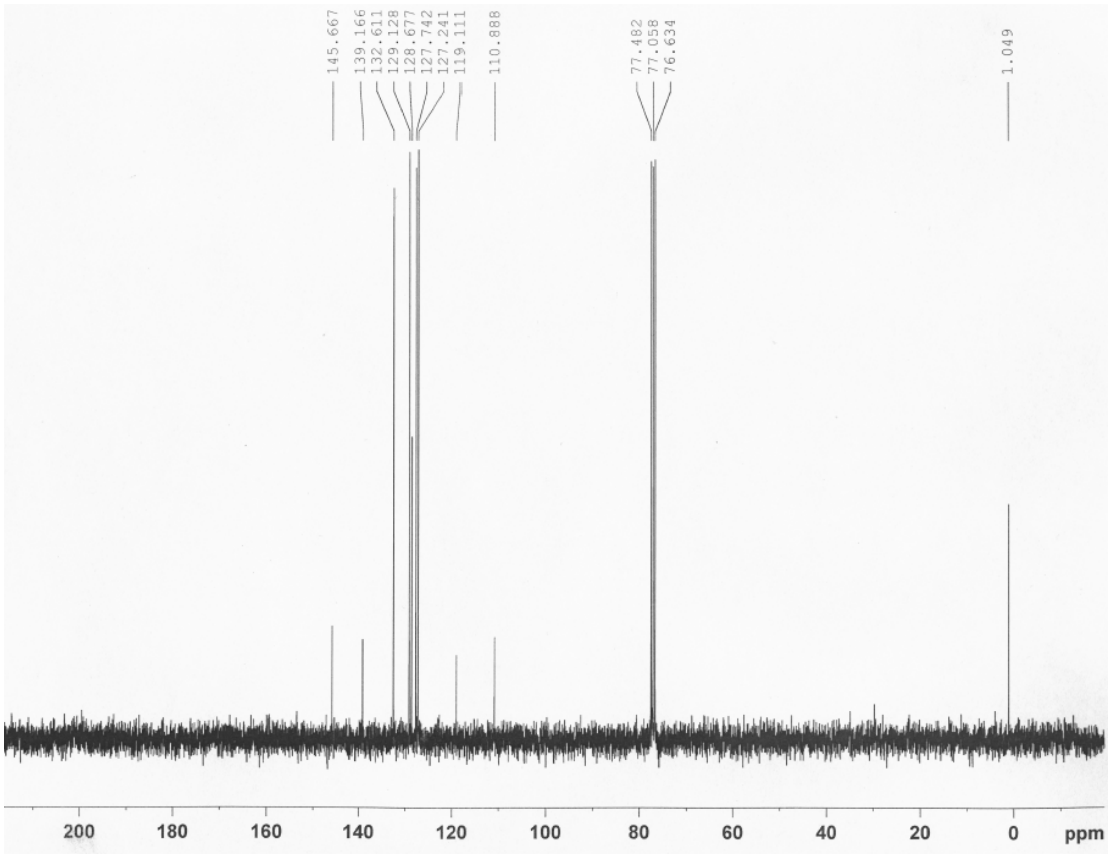
1,4-diphenylbenzene (**3g**):





Biphenyl-4-carbonitrile (**3h**):





4-fluorobiphenyl (**3i**):