

Supporting Information

Simple alcohols promoted direct C-H arylation of unactivated arenes with aryl halides

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General methods:

Aryl halides, alcohols, transition metal salts 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.

^1H 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:

1-Butanol, anhydrous, 99.8%, purchased from Sigma-Aldrich. 1-Propanol, ACS, 99.5+%, purchased from Alfa Aesar. 1-Hexanol, 99%, purchased from Alfa Aesar. 1-Decanol, 98+%, purchased from Alfa Aesar. Potassium ethoxide, 95%, purchased from Sigma-Aldrich. $\text{KO}t\text{-Bu}$ (99%, J&K) was sublimed before use and kept under nitrogen atmosphere. Unless otherwise stated, commercial reagents were used without purification.

General procedure for direct arylation of benzene with aryl halides:

A Schlenk tube was charged with $\text{KO}t\text{-Bu}$ (168 mg, 1.5 mmol) under an atmosphere of nitrogen at room temperature, and then benzene (4.0 mL), *n*-BuOH (14.8 mg, 0.2 mmol) and iodobenzene (102.0 mg, 0.5 mmol) were added. The resulting mixture was stirred at 80 °C for 12 h. After cooling to room temperature, the reaction mixture was quenched 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 (63.1 mg, 82% yield).

Table S1. Alcohols promoted direct arylation of benzene^a.

Entry	[Cat] (mol%)	Base (equiv)	<i>t</i> (h)	Yield (%) ^b
1	none	KO <i>t</i> -Bu (3.0)	12	0
2	(CH ₃) ₃ COH (50)	KO <i>t</i> -Bu (3.0)	12	trace
3	(CH ₃) ₃ COH (100)	KO <i>t</i> -Bu (3.0)	12	trace
4	(CH ₃) ₃ COH (50)	KO <i>t</i> -Bu (3.0)	24	trace
5	CH ₃ CH ₂ OH (50)	KO <i>t</i> -Bu (3.0)	24	70
6	CH ₃ (CH ₂) ₃ OH (50)	KO <i>t</i> -Bu (3.0)	24	90

^a Reactions conditions: **1a** (0.5 mmol), KO*t*-Bu (3.0 equiv), benzene (4.0 mL), 80 °C, N₂. ^b Calibrated GC yields of **3a** were reported using hexadecane as the internal standard.

Table S2. Alcohols promoted direct arylation of benzene^a.

Entry	[Cat] (mol%)	Base (equiv)	<i>t</i> (h)	Yield (%) ^b
1	CH ₃ (CH ₂) ₃ OH (40)	NaO <i>t</i> -Bu (3.0)	12	trace
2	CH ₃ (CH ₂) ₃ OH (40)	LiO <i>t</i> -Bu (3.0)	12	0
3	CH ₃ (CH ₂) ₃ OH (40)	K ₃ PO ₄ (3.0)	12	0
4	CH ₃ (CH ₂) ₃ OH (40)	K ₂ CO ₃ (3.0)	12	0
5	CH ₃ (CH ₂) ₃ OH (40)	KOH (3.0)	12	trace

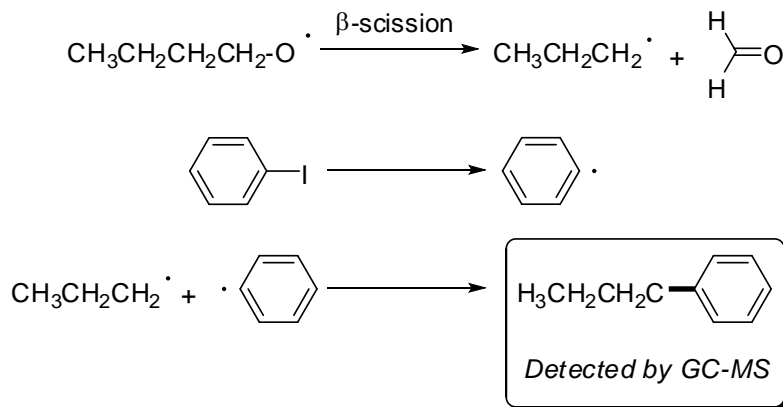
^a Reactions conditions: **1a** (0.5 mmol), *n*-BuOH (0.2 mmol), Base (3 equiv), benzene (4.0 mL), 80 °C, 12 h, N₂. ^b Calibrated GC yields of **3a** were reported using hexadecane as the internal standard.

Table S3. Controlled experiments for direct arylation of benzene^a.

Entry	[Cat] (mol%)	Base (equiv)	<i>t</i> (h)	Yield (%) ^b
1	none	KO <i>t</i> -Bu (3.0)	12	0
2	CH ₃ (CH ₂) ₂ COOH (20)	KO <i>t</i> -Bu (3.0)	12	trace
3	CH ₃ (CH ₂) ₂ COOH (40)	KO <i>t</i> -Bu (3.0)	12	trace
4	FeCl ₃ (20)	KO <i>t</i> -Bu (3.0)	12	0
5	CoCl ₂ (20)	KO <i>t</i> -Bu (3.0)	12	0
6	NiCl ₂ (20)	KO <i>t</i> -Bu (3.0)	12	0
7	CuCl ₂ (20)	KO <i>t</i> -Bu (3.0)	12	0
8	CuI (20)	KO <i>t</i> -Bu (3.0)	12	0
9	PdCl ₂ (20)	KO <i>t</i> -Bu (3.0)	12	0

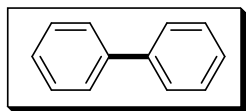
^a Reactions conditions: **1a** (0.5 mmol), Cat. (0.2 mmol), KO^t-Bu (3 equiv), benzene (4.0 mL), 80 °C, 12 h, N₂. ^b Calibrated GC yields of **3a** were reported using hexadecane as the internal standard.

Scheme S1. Plausible pathway for the formation of by-product via β-scission of alkoxy radical

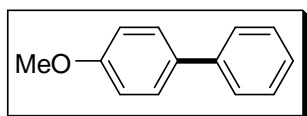


Compounds NMR Data:

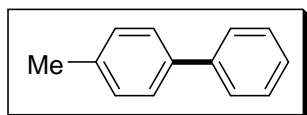
The spectroscopic data of all the products are presented below. All the known compounds gave satisfactory spectroscopic values and accorded to spectroscopic data reported in the literatures.



Biphenyl (3a)¹: ¹H NMR (300 MHz, CDCl₃) δ 7.63 (d, *J* = 7.2 Hz, 4H), 7.48 (t, *J* = 7.4 Hz, 4H), 7.33 (t, *J* = 7.4 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 141.2, 128.8, 127.3, 127.2.

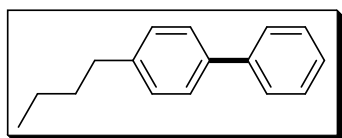


4-methoxybiphenyl (3b)¹: ¹H NMR (300 MHz, CDCl₃) δ 7.58-7.53 (m, 4H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 8.7 Hz, 1H), 6.99 (d, *J* = 6.6 Hz, 2H), 3.87 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 159.2, 140.9, 133.8, 128.7, 128.2, 126.8, 126.7, 114.2, 55.4.

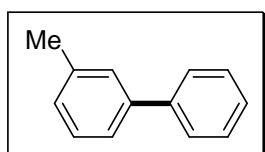


4-methylbiphenyl (3c)¹: ¹H NMR (300 MHz, CDCl₃) δ 7.66 (d, *J* = 7.2 Hz, 2H), 7.48 (d, *J* = 6.3 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 2H), 2.46 (s, 3H);

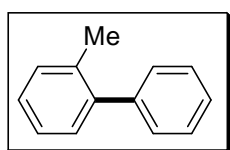
^{13}C NMR (75 MHz, CDCl_3) δ 141.2, 138.4, 137.1, 129.6, 128.8, 127.1, 21.2.



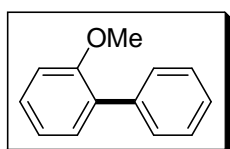
4-butylbiphenyl (3d)²: ^1H NMR (300 MHz, CDCl_3) δ 7.61 (d, $J = 7.5$ Hz, 2H), 7.54 (d, $J = 8.1$ Hz, 2H), 7.45 (t, $J = 7.5$ Hz, 2H), 7.35 (t, $J = 7.2$ Hz, 1H), 7.28 (d, $J = 8.1$ Hz, 2H), 2.68 (t, $J = 7.8$ Hz, 2H), 1.72-1.62 (m, 2H), 1.48-1.36 (m, 2H), 0.98 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 142.1, 141.2, 138.5, 128.8, 128.7, 127.0, 127.0, 127.0, 35.3, 33.7, 22.4, 14.0.



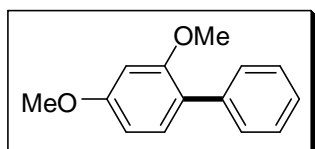
3-methylbiphenyl (3e)¹: ^1H NMR (300 MHz, CDCl_3) δ 7.65 (d, $J = 8.1$ Hz, 2H), 7.52-7.45 (m, 6H), 7.25 (d, $J = 8.7$ Hz, 1H), 2.49 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 141.4, 141.3, 138.4, 128.8, 128.7, 128.1, 128.0, 127.2, 124.3, 21.6.



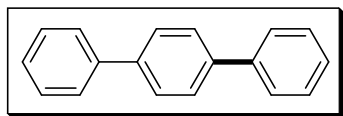
2-methylbiphenyl (3f)¹: ^1H NMR (300 MHz, CDCl_3) δ 7.47-7.27 (m, 9H), 2.31 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 141.9, 135.4, 130.3, 129.8, 129.2, 128.1, 127.3, 126.8, 125.8, 20.5.



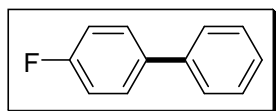
2-methoxybiphenyl (3g)³: ^1H NMR (300 MHz, CDCl_3) δ 7.58 (d, $J = 8.7$ Hz, 2H), 7.45 (t, $J = 8.0$ Hz, 2H), 7.39-7.33 (m, 3H), 7.10-7.00 (m, 2H), 3.84 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 155.4, 137.5, 129.8, 129.6, 128.5, 127.6, 126.9, 125.9, 119.8, 110.1, 54.5.



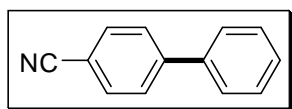
2,4-dimethoxybiphenyl (3h)⁴: ^1H NMR (300 MHz, CDCl_3) δ 7.41 (d, $J = 8.4$ Hz, 2H), 7.30 (t, $J = 7.5$ Hz, 2H), 7.22-7.12 (m, 2H), 6.50-6.43 (m, 2H), 3.75 (s, 3H), 3.70 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 160.3, 157.5, 138.4, 131.3, 129.5, 128.0, 126.5, 123.6, 104.6, 99.0, 55.6, 55.4.



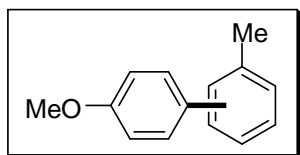
1,4-diphenylbenzene (3i)³: ¹H NMR (300 MHz, CDCl₃) δ 7.70-7.65 (m, 8H), 7.47 (t, *J* = 7.8 Hz, 4H), 7.38 (t, *J* = 7.4 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 140.7, 140.1, 128.8, 127.5, 127.4, 127.1.



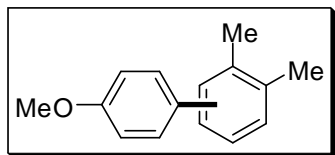
4-fluorobiphenyl (3j)⁵: ¹H NMR (300 MHz, CDCl₃) δ 7.63-7.56 (m, 4H), 7.51 (t, *J* = 8.4 Hz, 2H), 7.38 (t, *J* = 8.6 Hz, 1H), 7.16 (t, *J* = 7.8 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 164.1, 160.8, 140.2, 137.2, 128.8, 128.7, 128.6, 127.3, 127.0, 115.8, 115.5.



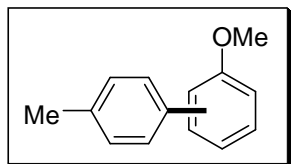
Biphenyl-4-carbonitrile (3k)¹: ¹H NMR (300 MHz, CDCl₃) δ 7.76-7.69 (m, 4H), 7.60 (t, *J* = 6.0 Hz, 2H), 7.52-7.41 (m, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 145.7, 139.2, 132.6, 129.1, 128.7, 127.7, 127.2, 119.1, 110.9.



3o³: The ratio of the regioisomers was determined by ¹H NMR (*o:m:p* = 3.7:1.7:1.0). ¹H NMR (300 MHz, CDCl₃) δ 7.60-7.35 (m, 3.6H), 7.35-7.22 (m, 5.3H), 7.04-6.98 (m, 3.6H), 3.88 (s, 2.9H), 3.83 (s, 0.6H), 3.81 (s, 0.5H), 2.46 (s, 1.4H), 2.43 (s, 0.8H), 2.33 (s, 3.0H).



3p⁶: The ratio of the regioisomers was determined by ¹H NMR (*o:m* = 1.6:1.0). ¹H NMR (300 MHz, CDCl₃) δ 7.54-7.17 (m, 9.8H), 7.00-6.87 (m, 6.0H), 6.85-6.80 (m, 7.1H), 6.55-6.51 (m, 5.1H), 3.88 (s, 2.9H), 3.82 (s, 1.9H), 2.38 (s, 3.0H), 2.36 (s, 1.9H), 2.33 (s, 1.9H), 2.20 (s, 3.0H).

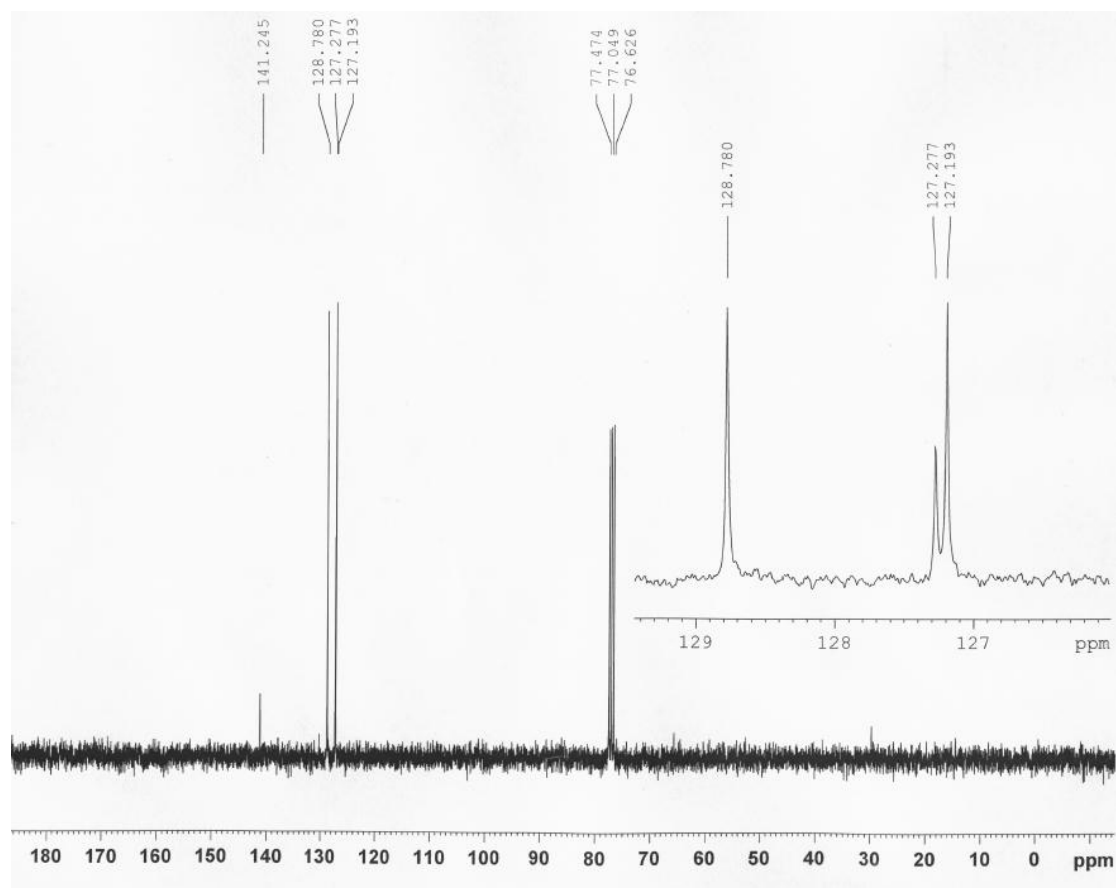
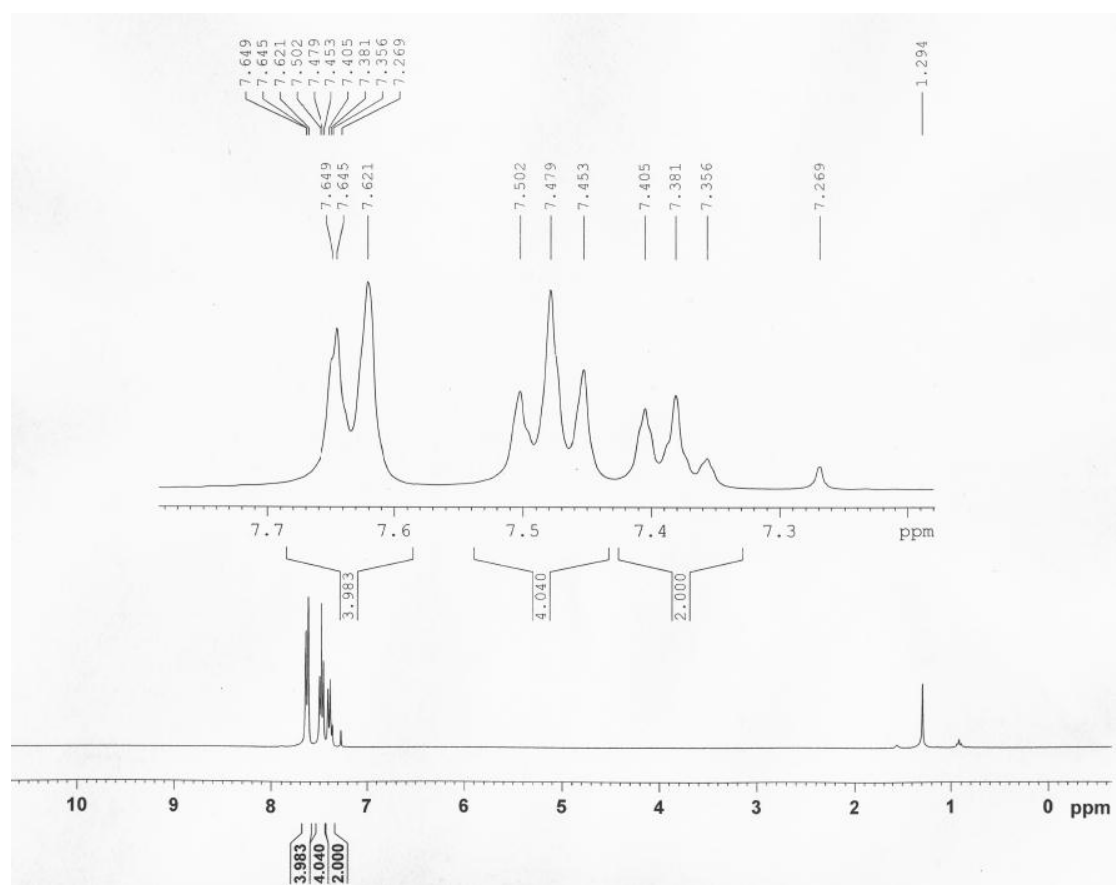


3q³: The ratio of the regioisomers was determined by ¹H NMR (*o:m:p* = 3.8:1.4:1.0). ¹H NMR (300 MHz, CDCl₃) δ 7.59-7.50 (m, 2.2H), 7.49-7.27 (m, 3.0H), 7.09-7.00 (m, 1.6H), 3.90 (s, 0.7H), 3.89 (s, 0.5H), 3.85 (s, 1.7H), 2.44 (s, 3.0H).

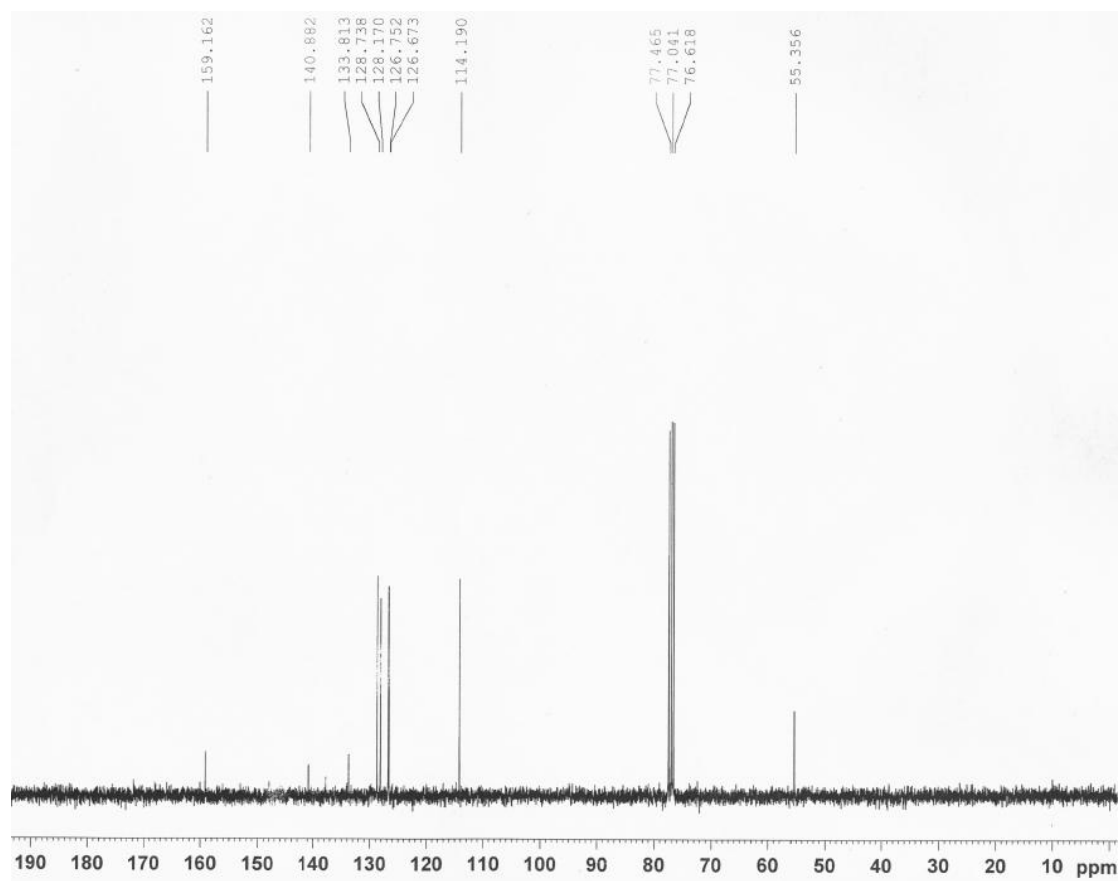
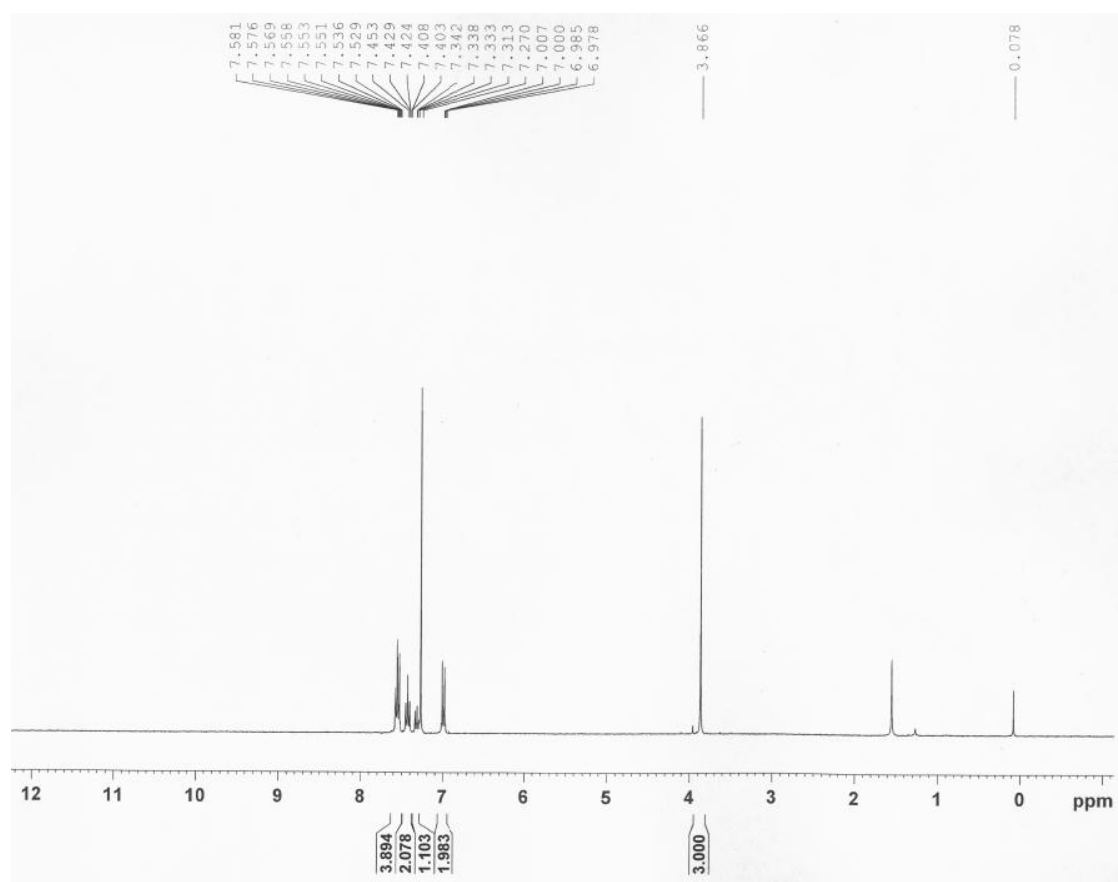
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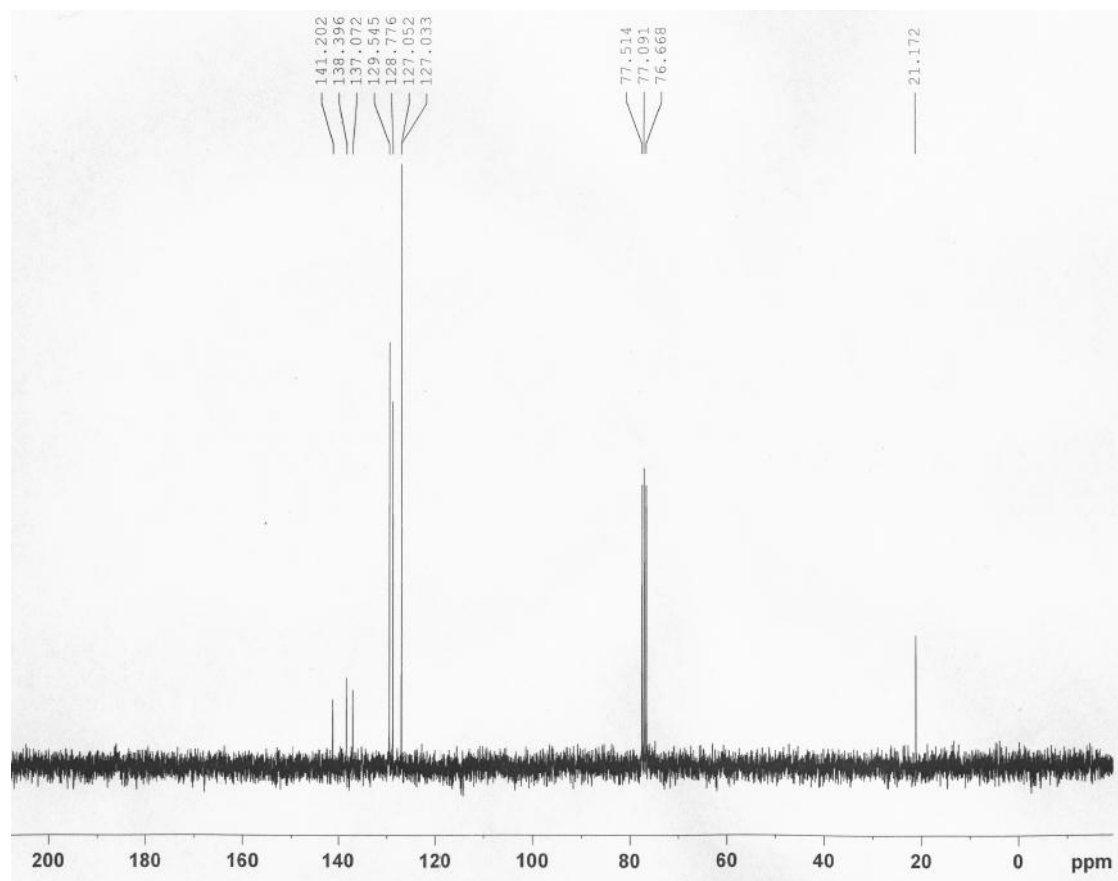
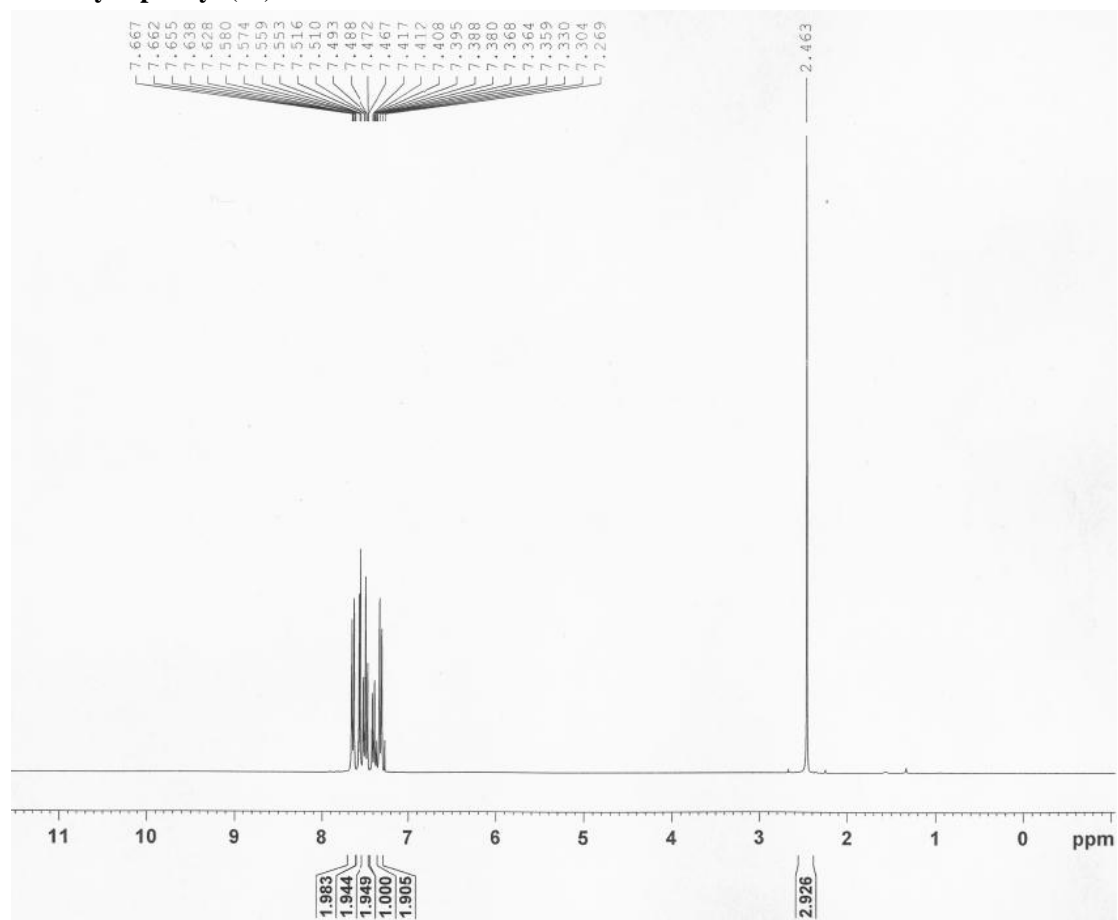
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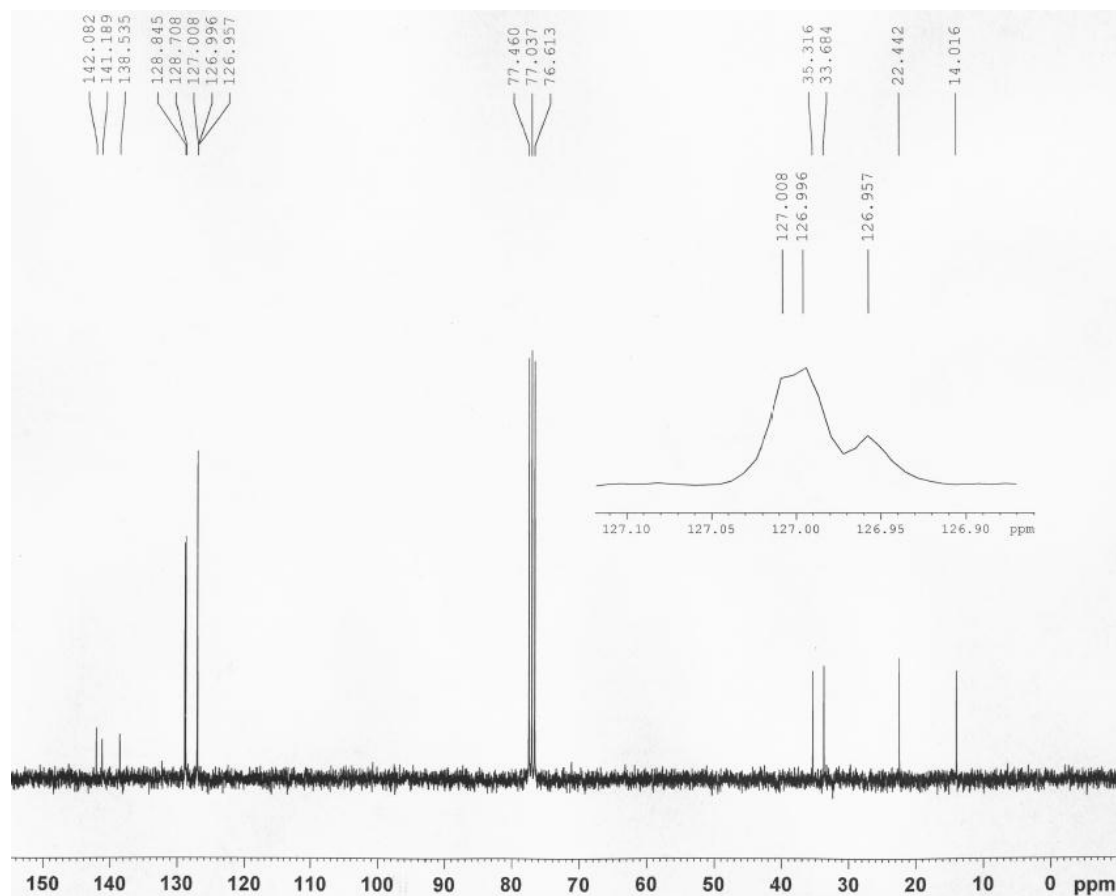
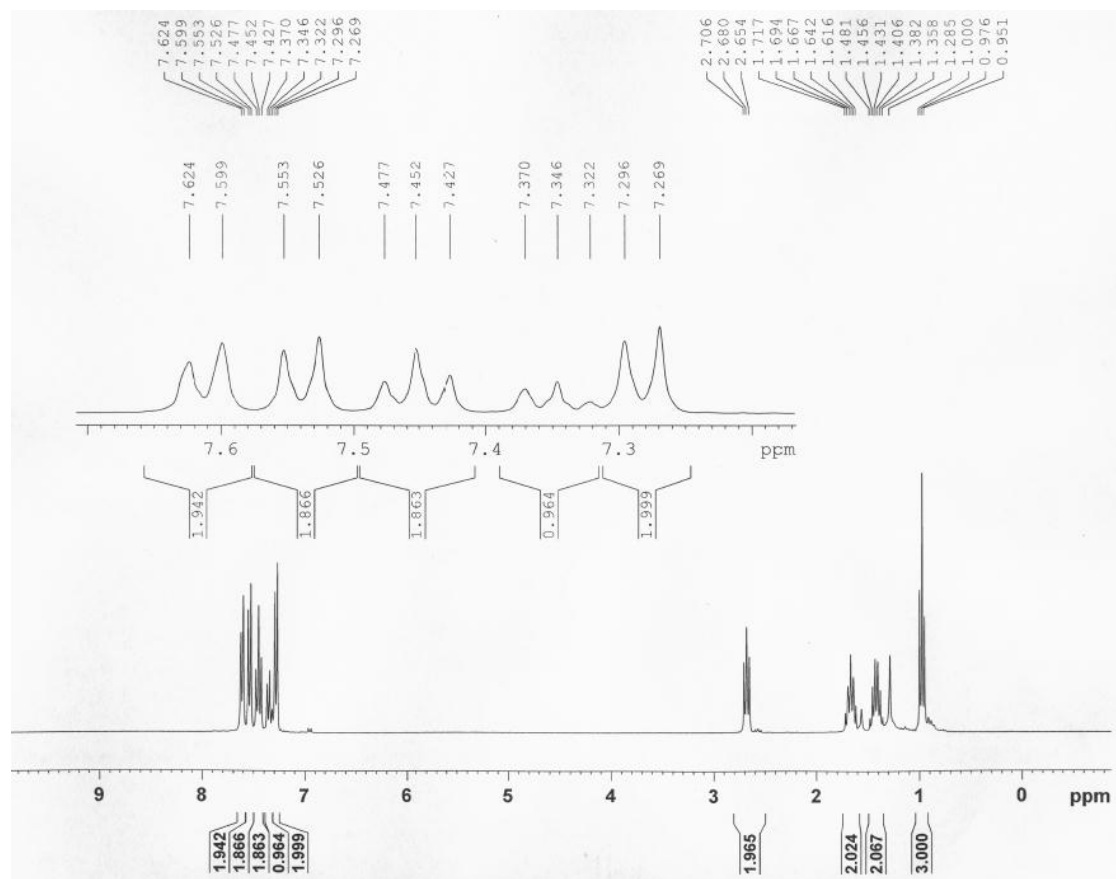
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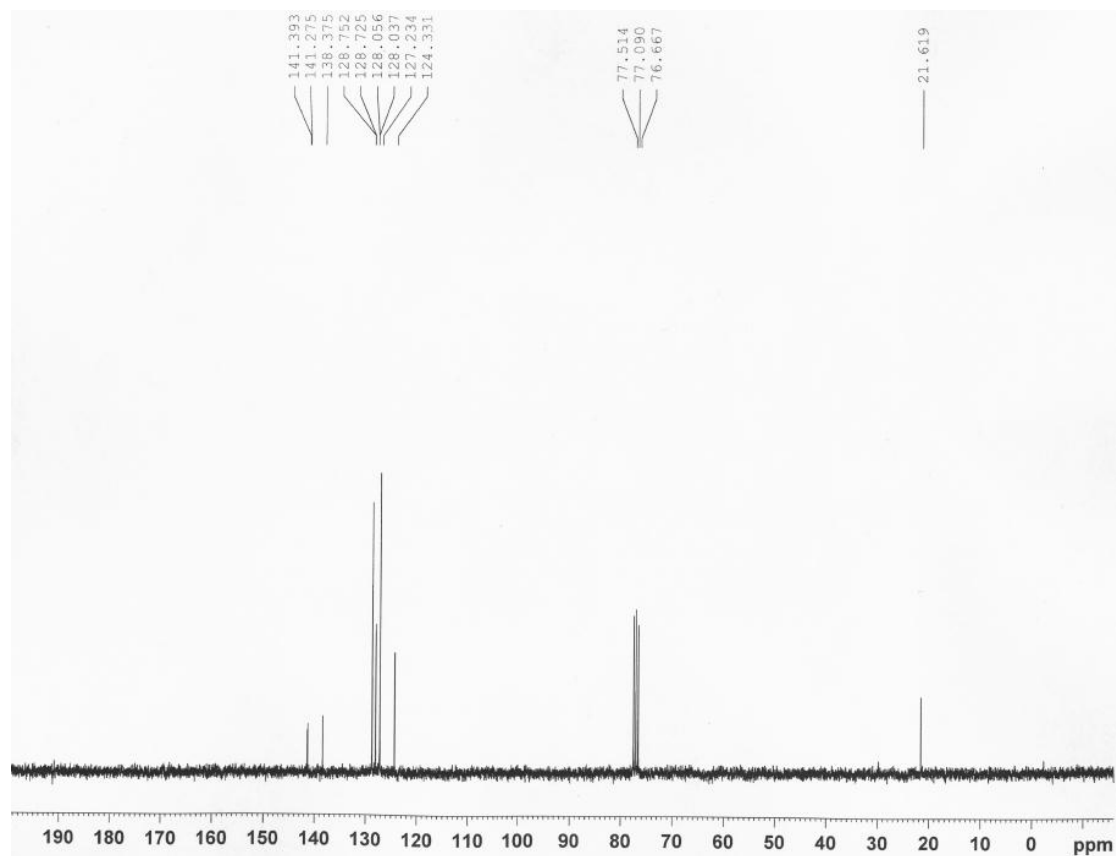
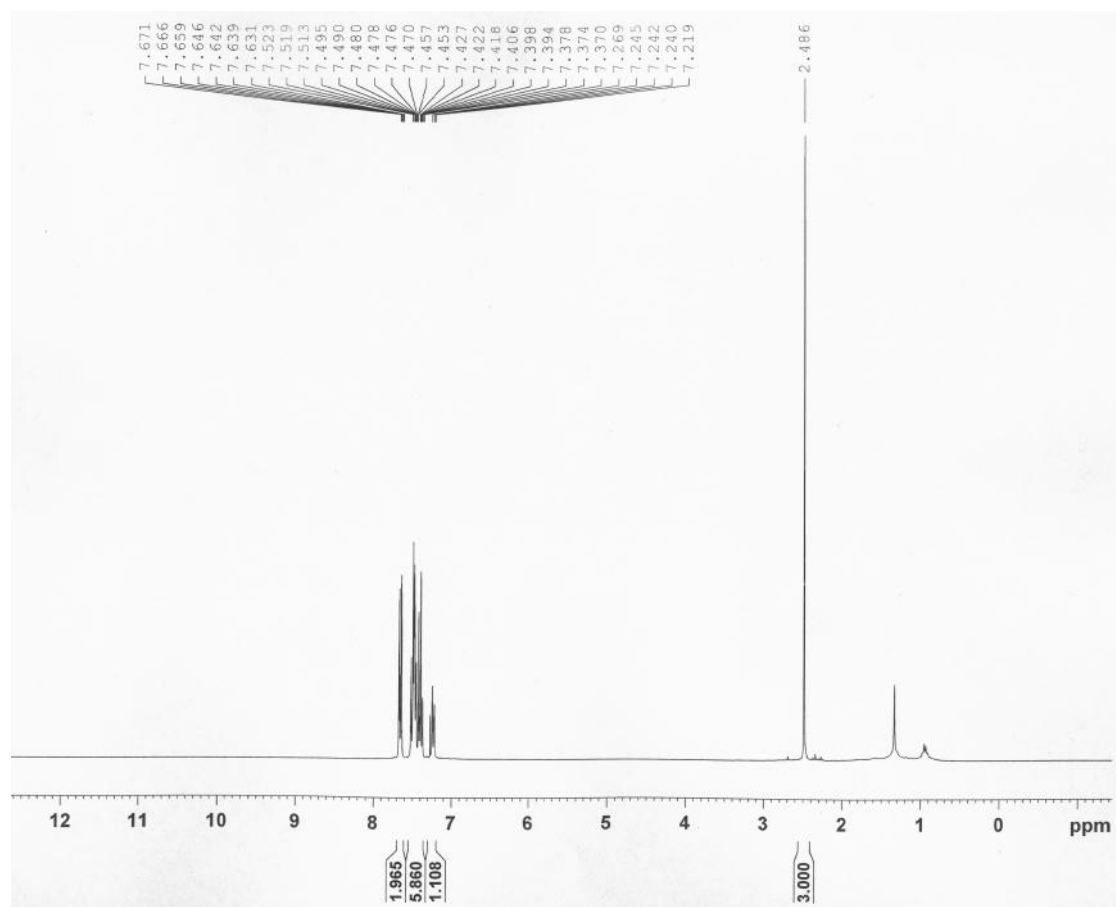
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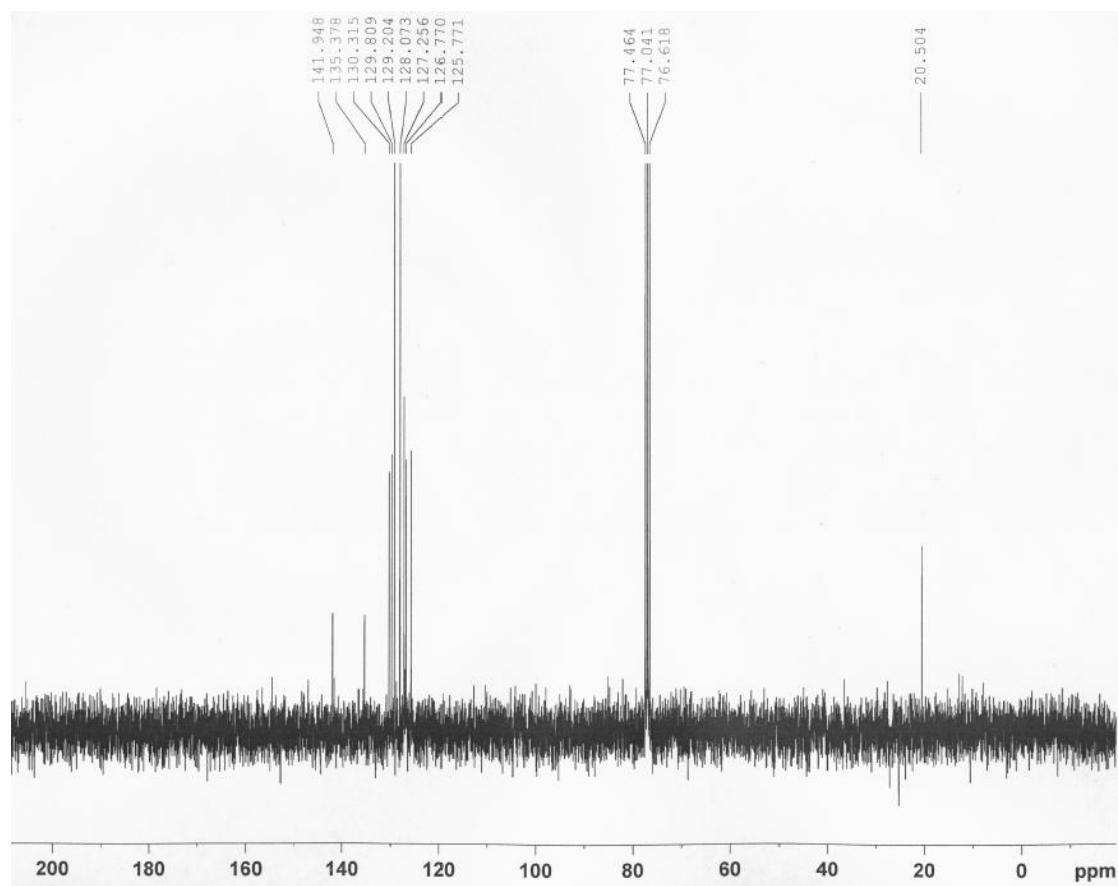
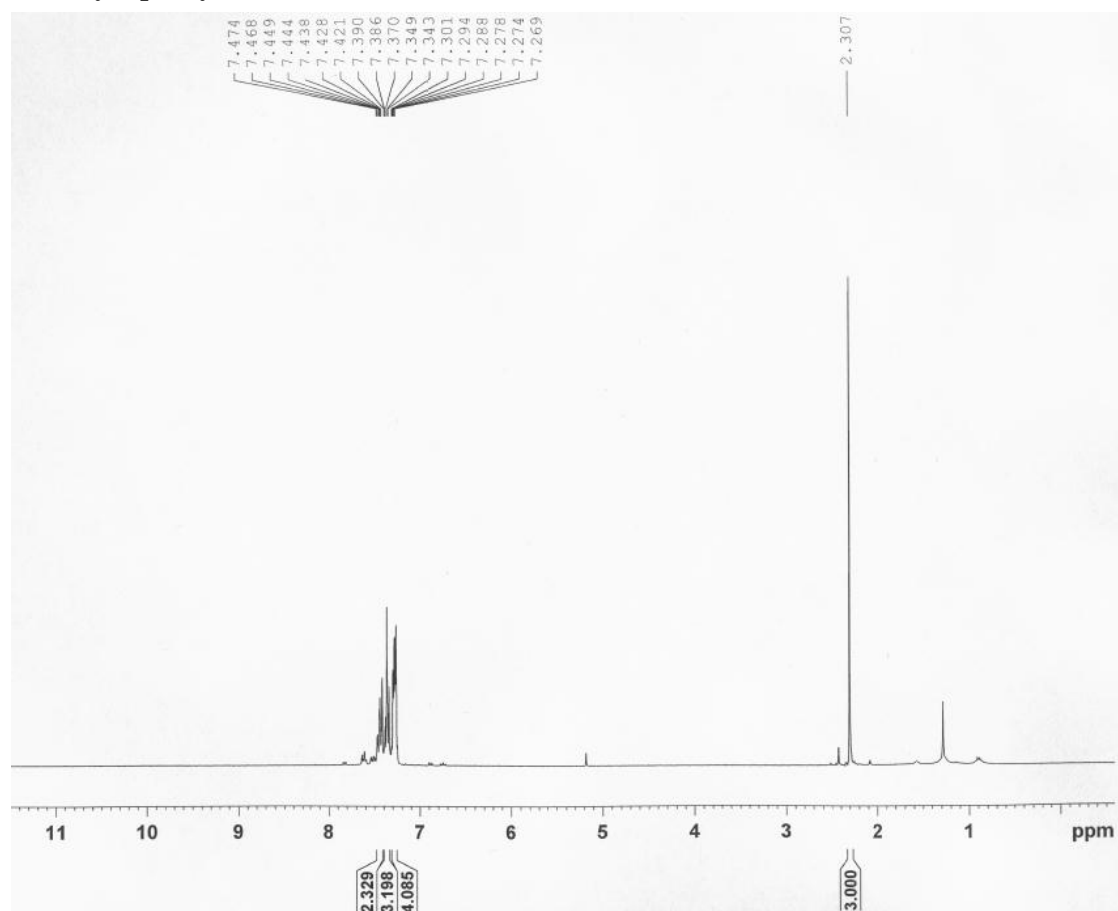
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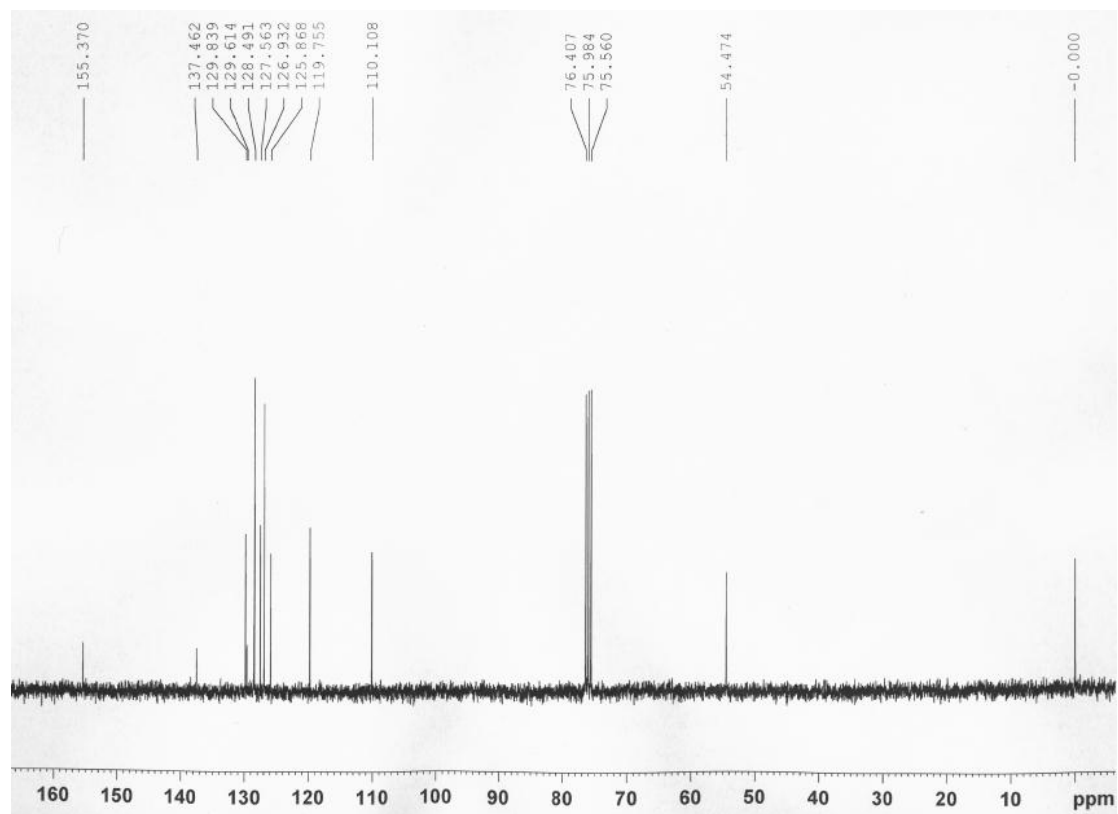
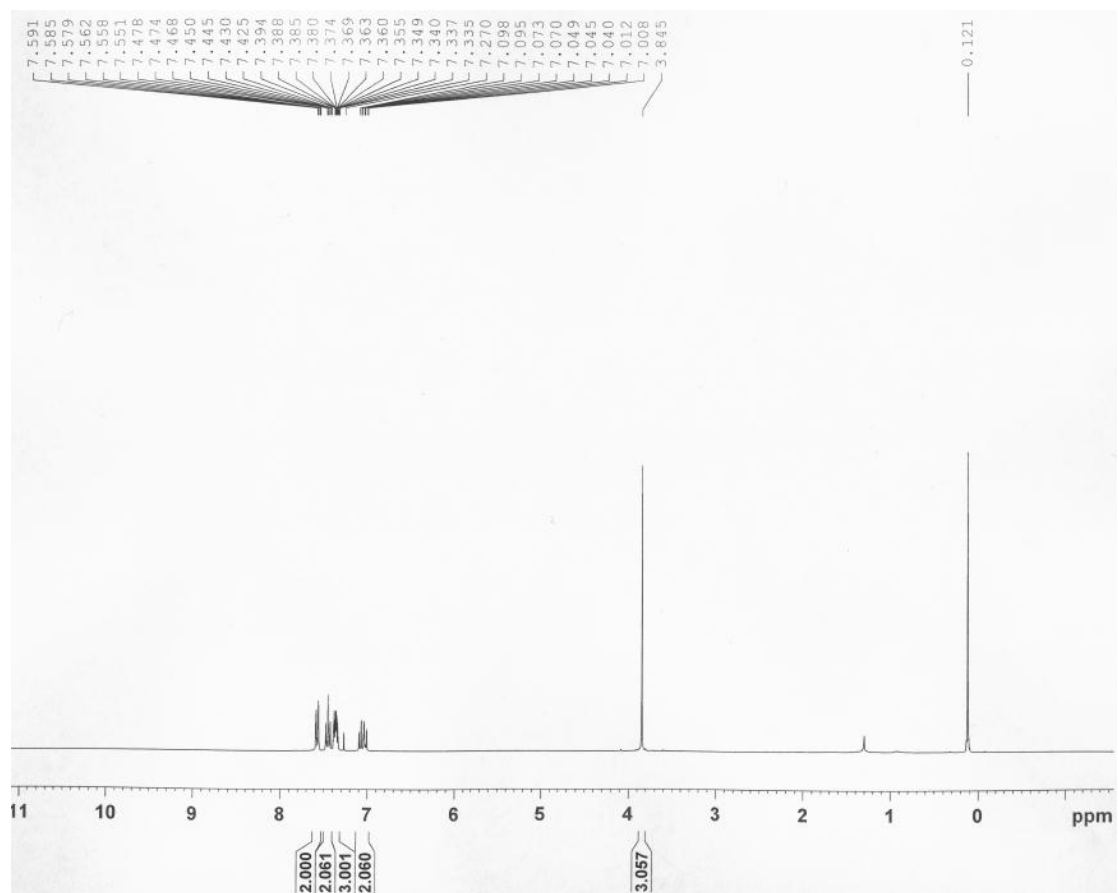
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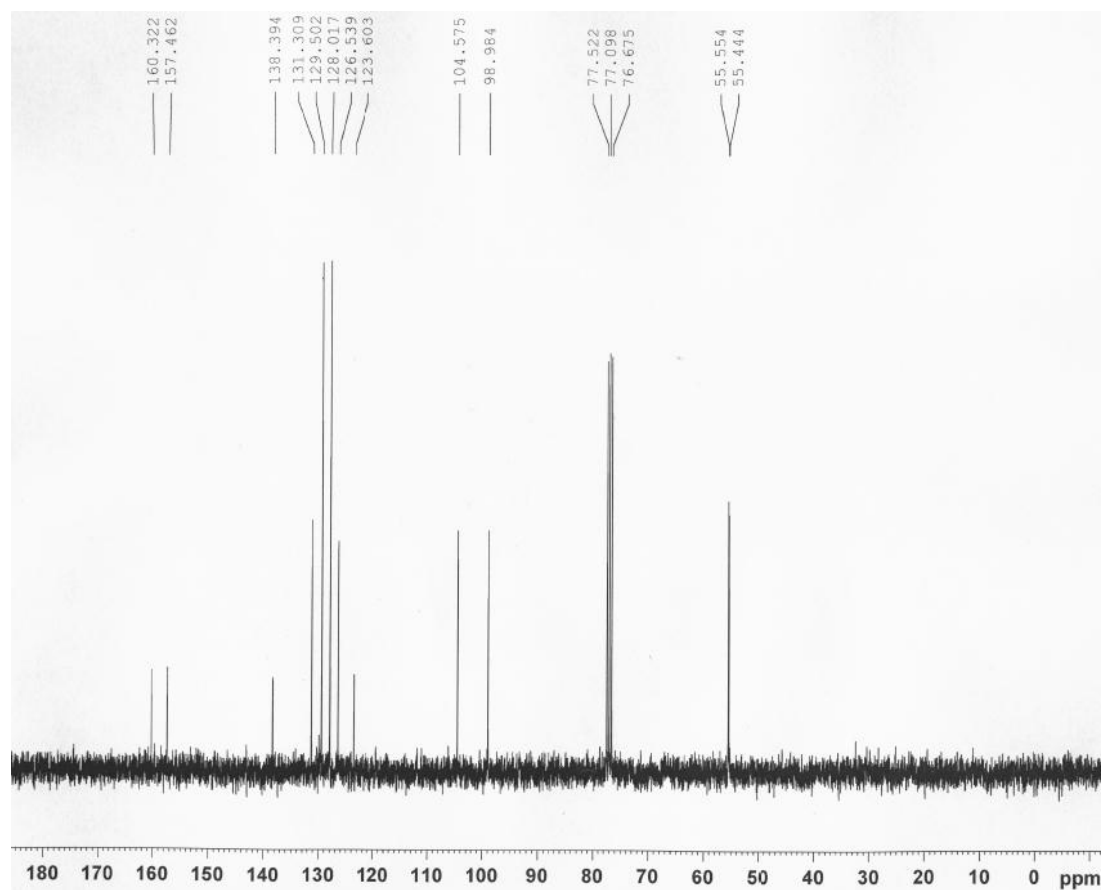
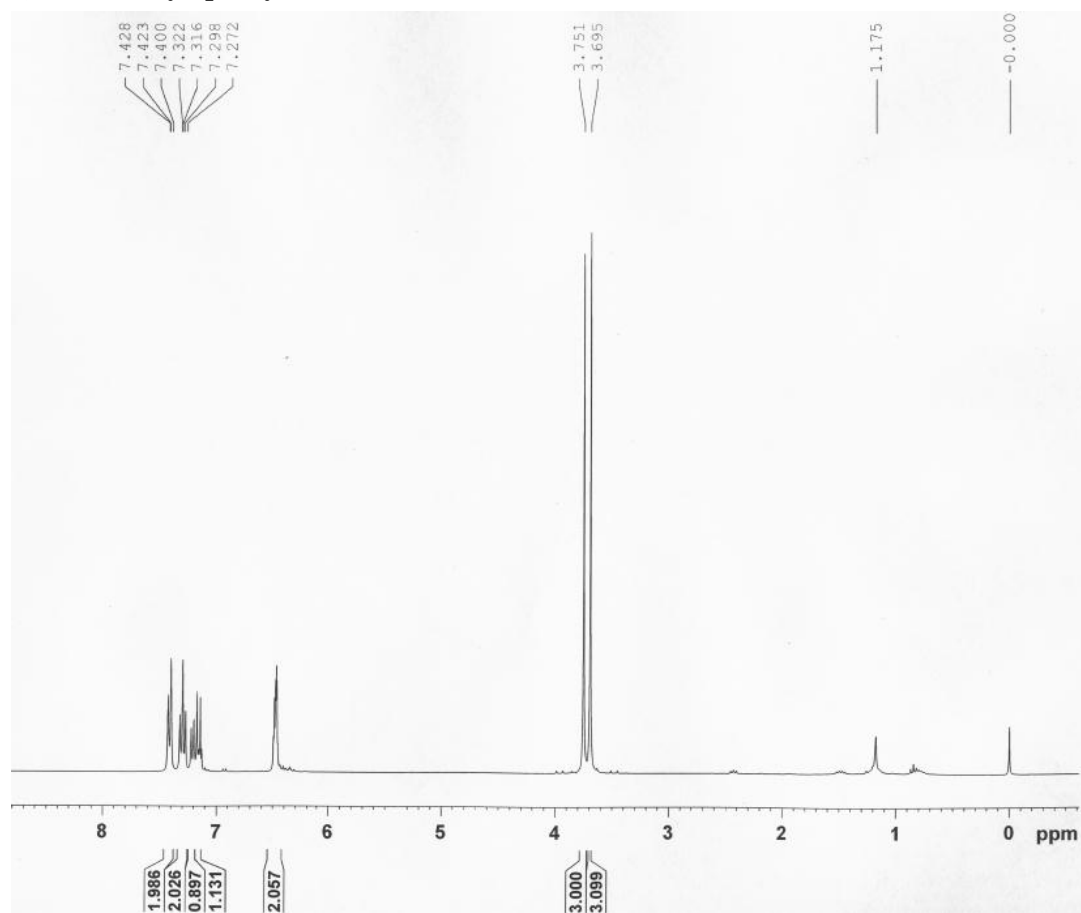
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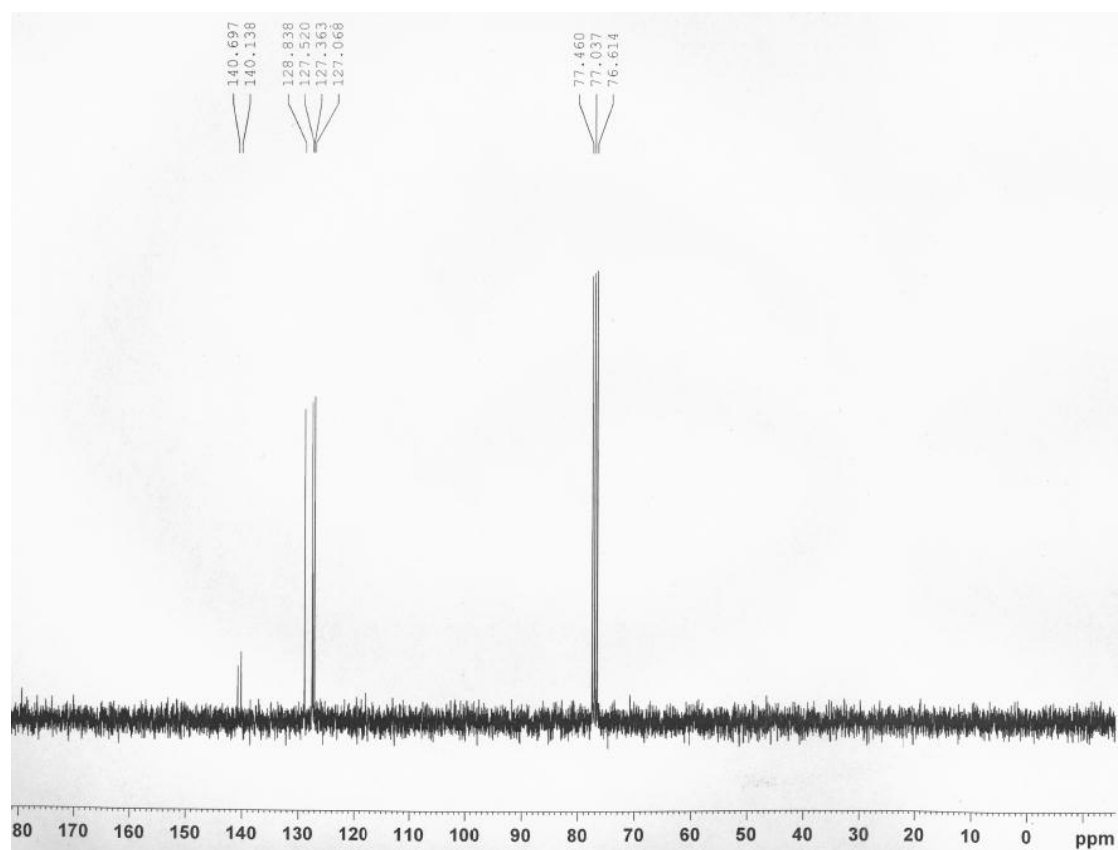
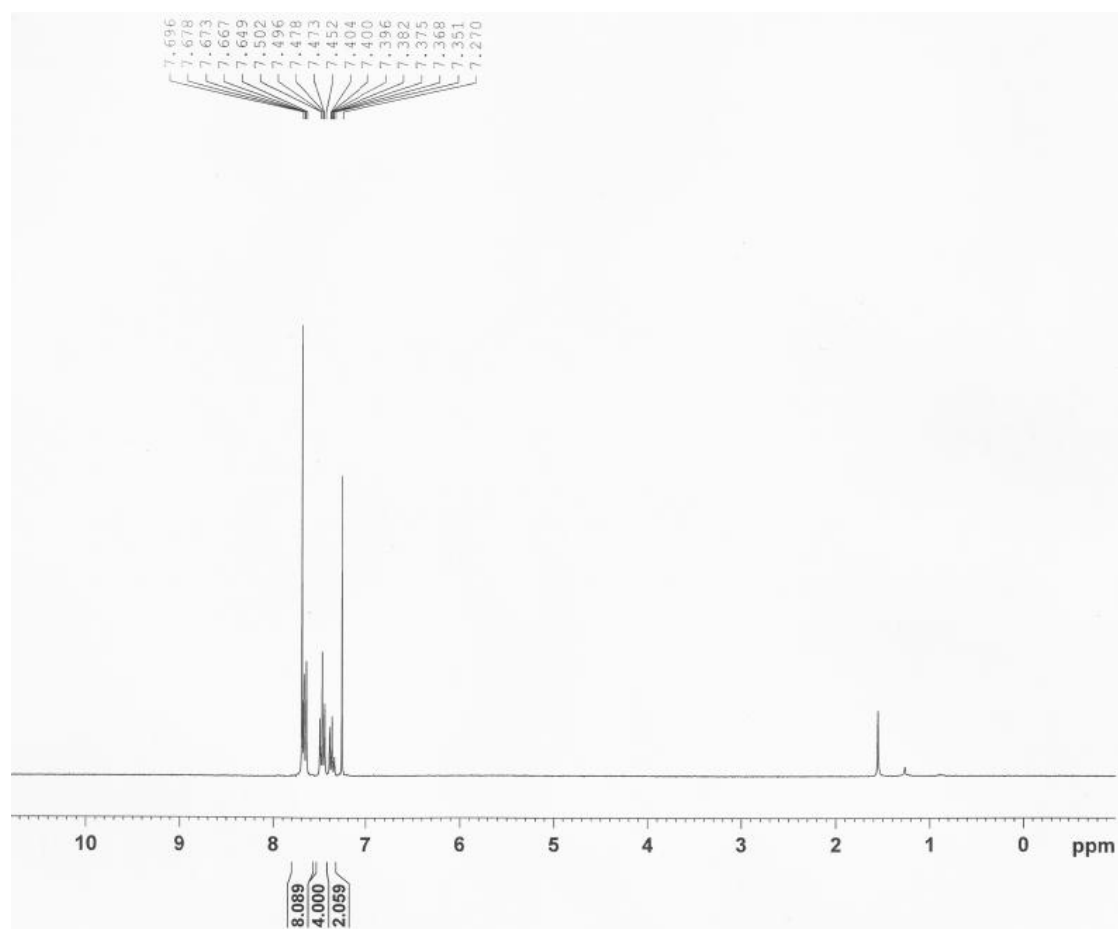
2-methoxybiphenyl (3g):



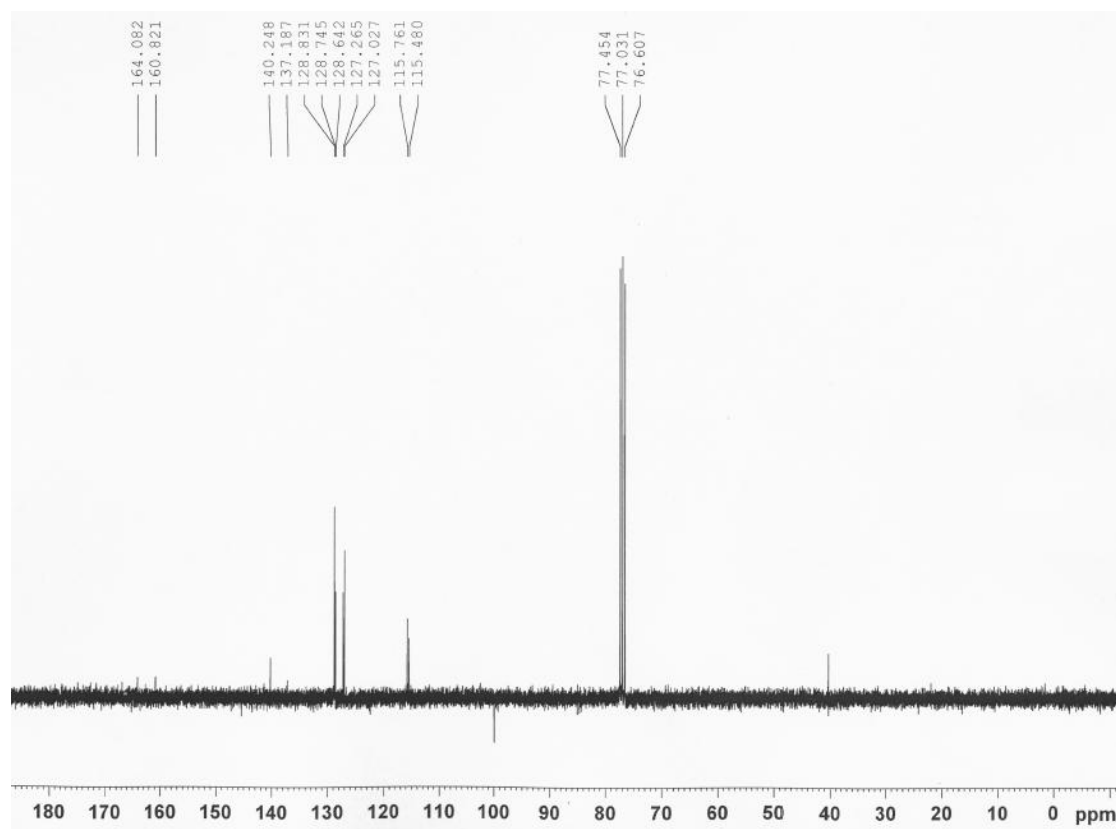
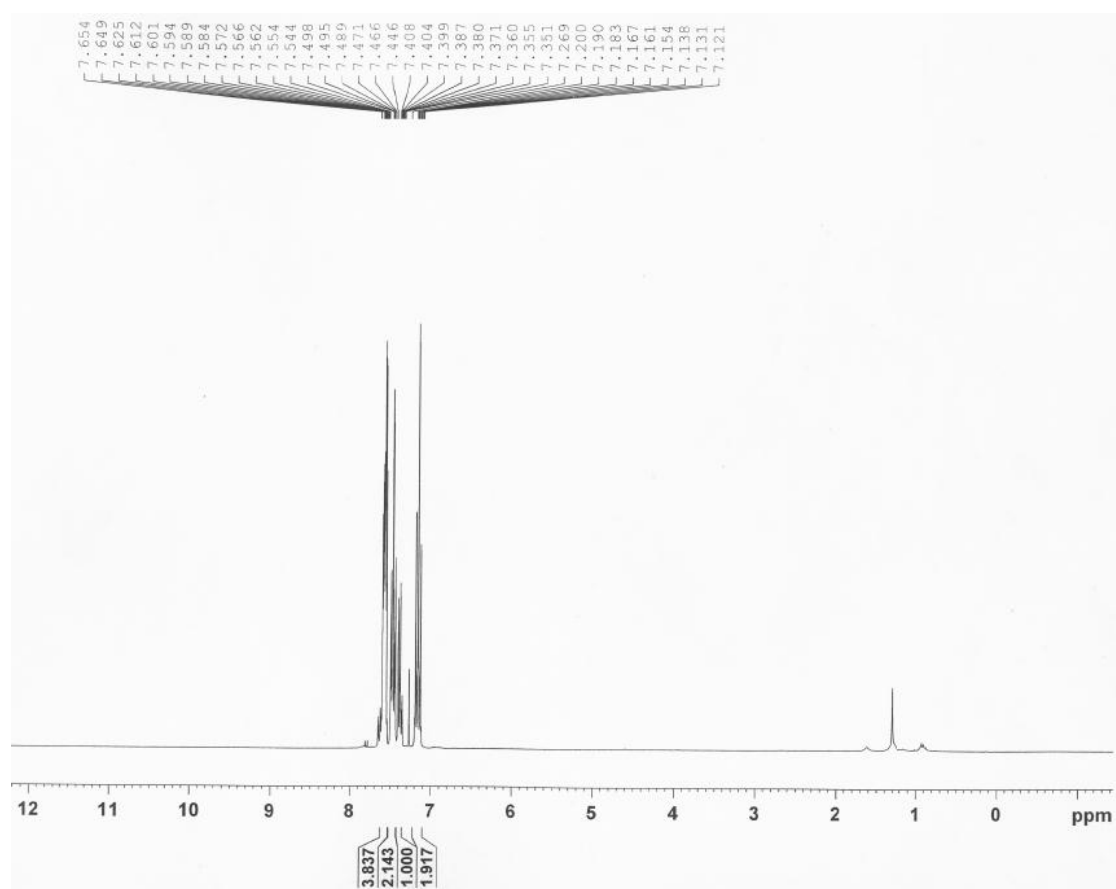
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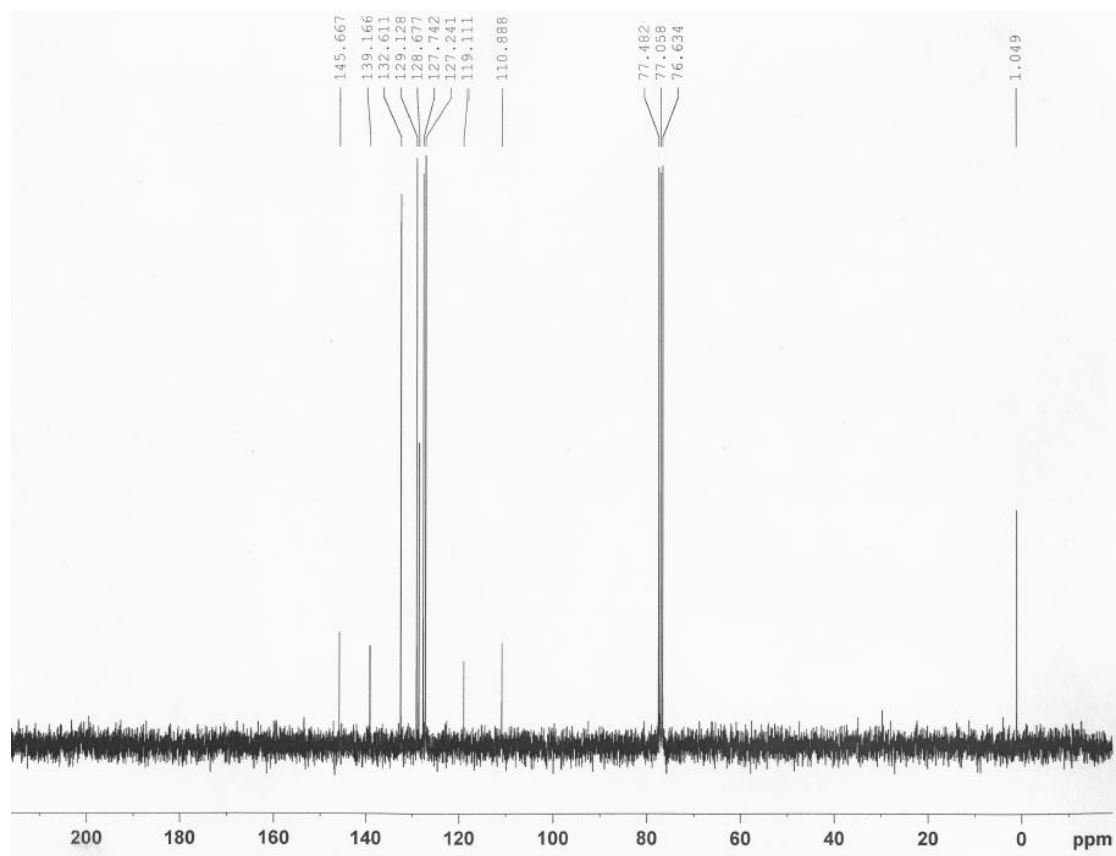
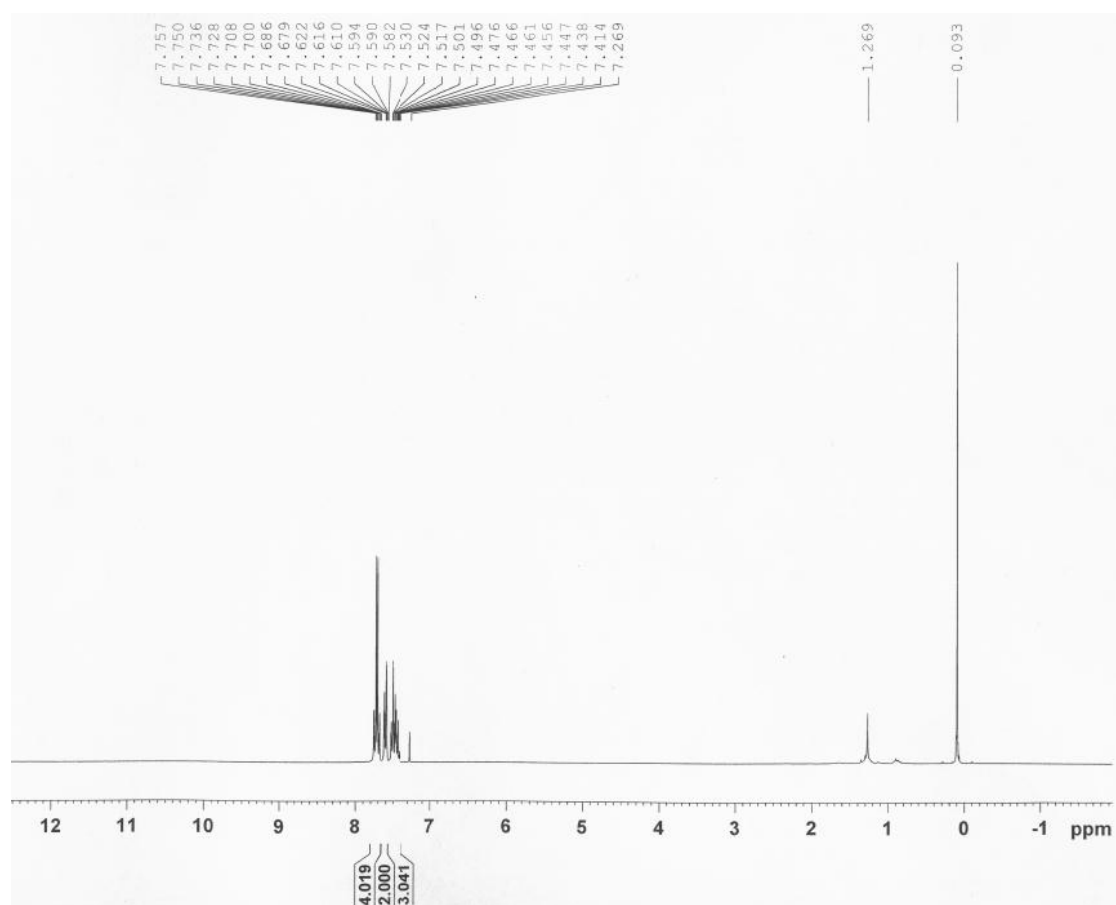
1,4-diphenylbenzene (3i):



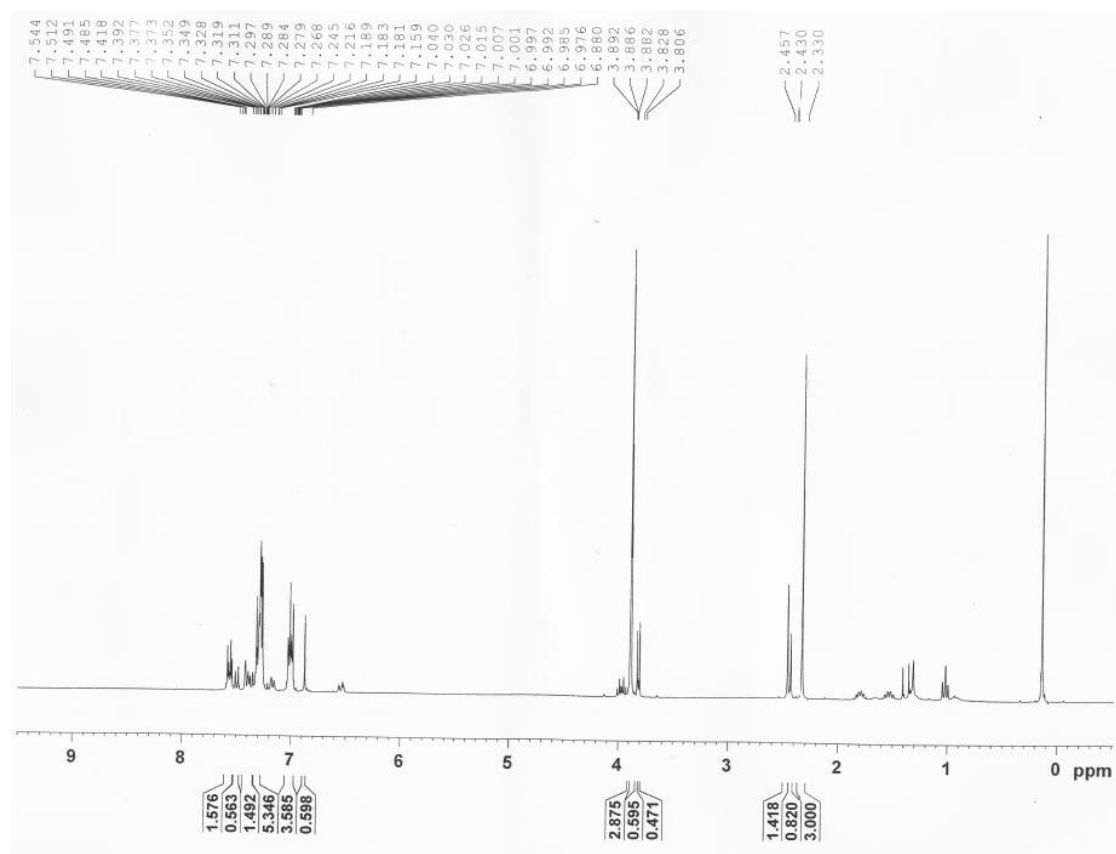
4-fluorobiphenyl (3j):



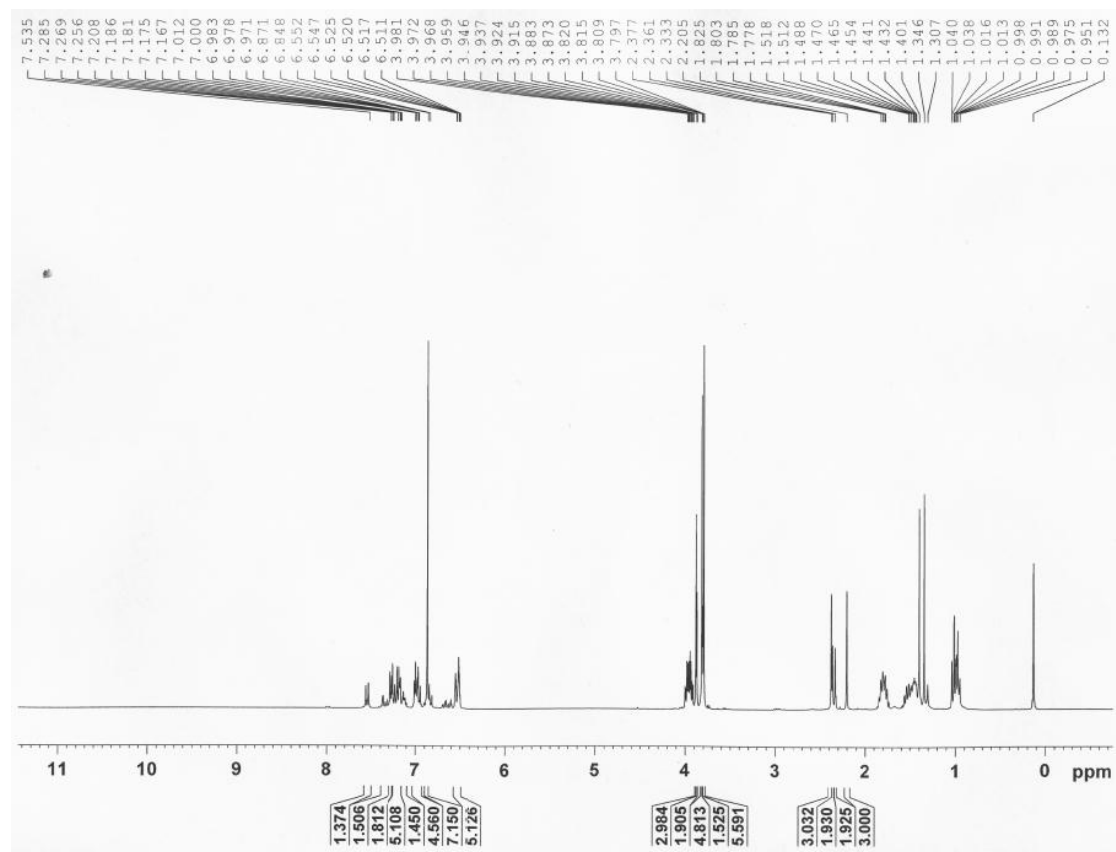
Biphenyl-4-carbonitrile (3k):



3o:



3p:



3q:

