Electronic supplementary information

Phosphine Ligand Triggered Oxidative Decarbonylative Homocoupling of Aromatic Aldehydes: Selectively Generating Biaryls and Diarylketones

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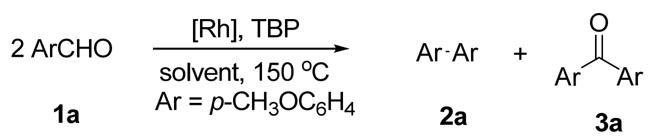
1. General information

Thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.25 mm) or Sorbent Silica Gel 60 F254 plates. The developed chromatography was analyzed by UV lamp (254 nm). GCMS analysis was conducted on an Agilent GCMS-6890N instrument equipped with a HP-5 column (30 m × 0.25 mm, Hewlett-Packard) and Agilent 5973 Mass Selective Detector. High-resolution mass spectra (HRMS) were obtained from a JEOL JMS-700 instrument (ESI). IR spectra were recorded by a Nexus 670 Avator FTIR spectrometer. Nuclear magnetic resonance (NMR) spectra were recorded on Varian MERCURY plus spectrometer (^{1}H 500 MHz, ^{13}C 125 MHz or ^{13}C 75 MHz) spectrometer. NMR yield was calculated based on the integration using nitromethane as internal standard. Chemical shifts for ^{1}H NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent resonance as the internal standard (chloroform: δ 7.26 ppm). Chemical shifts for ^{13}C NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent as the internal standard ($CDCl_3$: δ 77.23 ppm). Data are reported as following: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet, br = broad signal), coupling constant (Hz), and integration.

Reagents: Unless stated otherwise, liquid aromatic aldehydes were used after distillation under vacuum. Solid aromatic aldehydes, rhodium catalysts and phosphine ligands were used without further purification. Benzene was dried by sodium metal using benzophenone as the indicator.

2. The influence of solvents and concentrations to the homocoupling [a]

Table S1. Detailed Optimization of the Oxidative Decarbonylative Homocoupling

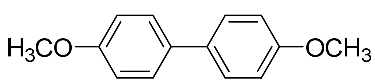


entry	Rh (mol%)	ligand (mol%)	Solvent /mL		Temp / °C	yield **2a** + **3a**	ratio[b] **2a** / **3a**
1	$[(CO)_2RhCl]_2$ (1.25)	PPh_3 (6)	PhCl	0.4	150	55	52 : 48
2	$[(CO)_2RhCl]_2$ (1.25)	PPh_3 (6)	dioxane	0.4	150	44	59 : 41
3	$[(CO)_2RhCl]_2$ (1.25)	PPh_3 (6)	DCE	0.4	150	69	62 : 38
4	$[(CO)_2RhCl]_2$ (1.25)	PPh_3 (6)	benzene	**0.8**	150	73	72 : 28
5	$[(CO)_2RhCl]_2$ (1.25)	PPh_3 (6)	benzene	0.4	**140**	76	84 : 16
6	$[(CO)_2RhCl]_2$ (1.25)	dppe (3)	PhCl	0.4	150	45	19 : 81
7	$[(CO)_2RhCl]_2$ (1.25)	dppe (3)	dioxane	0.4	150	33	<2 : 98
8	$[(CO)_2RhCl]_2$ (1.25)	dppe (3)	benzene	**0.8**	150	44	<2 : 98
9	$[(CO)_2RhCl]_2$ (1.25)	dppe (3)	benzene	0.4	**140**	56	<2 : 98
10	$[(CH_2{=}CH_2)_2RhCl]_2$ (1.25)	PPh_3 (6)	benzene	0.4	**150**	65	71 : 29
11	$[(CH_2{=}CH_2)_2RhCl]_2$ (1.25)	dppe (3)	benzene	0.4	**160**	58	57 : 43

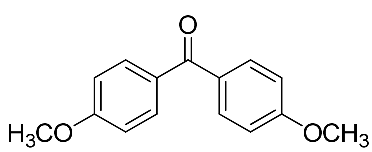
[a] Conditions: **1a** (0.2 mmol), [Rh], phosphine ligand, TBP (0.5 mmol) and solvent, sealed and stirred for 12 h under argon, unless otherwise noted. [b] Determined by 1H NMR analysis of the crude reaction mixture using an internal standard.

3. General experimental procedure for the oxidative decarbonylative homocoupling of aromatic aldehydes and characterization data

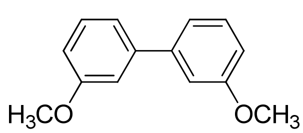
A general experimental procedure for the decarbonylative coupling is described as following: An oven-dried reaction vessel was charged with $[(CO)_2RhCl]_2$ (0.9 mg, 0.0025 mmol, 1.25 mol%), PPh_3 (0.9 mg, 0.012 mmol, 6.0 mol%) and benzene (dried over Na) (0.4 mL). After stirring the mixture at r.t. for 12 h under argon, 4-methoxybenzaldehyde **1a** (25 μL, 29.8 mg, 0.2 mmol) was added by syringe and the vessel was sealed and heated at 150 °C (oil bath temperature). After 12 h, the resulting mixture was cooled to room temperature, filtered through a short silica gel pad and washed by ethyl acetate. The above solution was evaporated under vacuum and the ratio of the two products was determined by ^1H NMR using nitromethane as the internal standard. Then the mixture was transferred to silica gel column directly and eluted with hexanes and ethyl acetate (90:10) to give products **2a** and **3a** (36 mg, 82% yield).



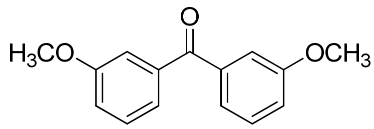
2a[1]: white solid, mp 160 °C; ^1H NMR (500 MHz, $CDCl_3$, TMS) δ (ppm) 7.48 (d, *J*=8.5 Hz, 4H), 6.96 (d, *J*=8.5 Hz, 4H), 3.85 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ (ppm) 158.9, 133.7, 128.0, 114.4, 55.6.



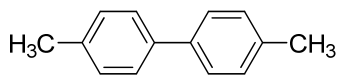
3a[6]: white solid, mp 142 °C; ^1H NMR (500 MHz, $CDCl_3$, TMS) δ (ppm) 7.79 (dt, *J*=3.0, 8.5 Hz, 4H), 6.96 (dt, *J*=3.0, 8.5 Hz, 4H), 3.88 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ (ppm) 194.7, 163.0, 132.4, 131.0, 113.6, 55.7.



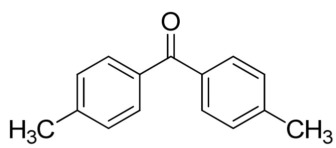
2b[2]: colorless oil; ^1H NMR (500 MHz, $CDCl_3$, TMS) δ (ppm) 7.35 (t, *J*=8.0 Hz, 2H), 7.18 (ddd, *J*=1.0, 1.5, 8.0 Hz, 2H), 7.12 (t, *J*=2.5 Hz, 2H), 6.91 (ddd, *J*=1.0, 3.0, 8.0 Hz, 4H), 3.87 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ (ppm) 160.1, 142.9, 129.9, 119.9, 113.2, 113.0, 55.5.



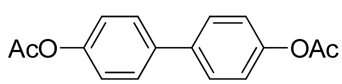
3b[10]: colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ (ppm) 7.39-7.33 (m, 6H), 7.13 (ddd, *J*=1.5, 3.0, 8.0 Hz, 2H), 3.86 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ (ppm) 195.5, 159.8, 139.1, 129.4, 123.1, 119.1, 114.5, 55.7.



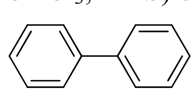
2c[1]: white solid, mp 116 °C; ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ (ppm) 7.48 (dt, *J*=2.0, 8.0 Hz, 4H), 7.24 (dt, *J*=2.0, 8.0 Hz, 4H), 2.39 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ (ppm) 138.5, 136.9, 129.6, 127.0, 21.3.



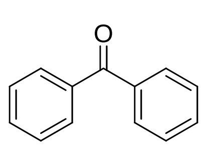
3c[6]: white solid, mp 92 °C; ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ (ppm) 7.70 (d, *J*=8.0 Hz, 4H), 7.28 (d, *J*=8.0 Hz, 4H), 2.44 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ (ppm) 196.3, 142.9, 135.2, 130.2, 128.9, 21.6.



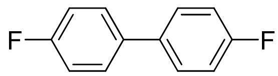
2d[4]: white solid, mp 150 °C; ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ (ppm) 7.55 (dt, *J*=2.5, 8.0 Hz, 4H), 7.16 (dt, *J*=2.5, 8.0 Hz, 4H), 2.33 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ (ppm) 169.8, 150.4, 138.4, 128.4, 122.1, 21.4.



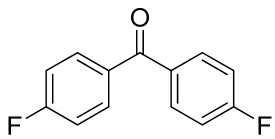
2e[1]: white solid, mp 70 °C; ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ (ppm) 7.59-7.61 (m, 4H), 7.43-7.46 (m, 4H), 7.34-7.37 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ (ppm) 141.5, 129.0, 127.5, 127.4.



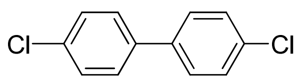
3e[6]: white solid, mp 48 °C; ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ (ppm) 7.80-7.82 (m, 4H), 7.57-7.61 (m, 2H), 7.47-7.50 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ (ppm) 196.9, 137.8, 132.6, 130.2, 128.4.



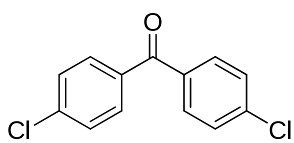
2f[1]: white solid, mp 86 °C; ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ (ppm) 7.48-7.50 (m, 4H), 7.10-7.14 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ (ppm) 162.6 (d, *J*=245.0 Hz), 136.6 (d, *J*=3.2 Hz), 128.8 (d, *J*=7.9 Hz), 115.9 (d, *J*=21.2 Hz).



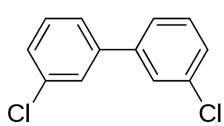
3f[7]: white solid, mp 104 °C; ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ (ppm) 7.80-7.84 (m, 4H), 7.15-7.20 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ (ppm) 194.0, 165.6 (d, *J*=253.5 Hz), 133.9 (d, *J*=3.2 Hz), 132.7 (d, *J*=9.2 Hz), 115.8 (d, *J*=21.8 Hz).



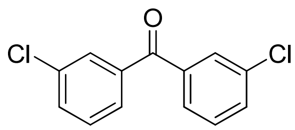
2g[3]: white solid, mp 145 °C; ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ (ppm) 7.56 (dt, *J*=2.0, 8.0 Hz, 4H), 7.42 (dt, *J*=2.0, 8.0 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ (ppm) 138.6, 134.0, 129.3, 128.4.



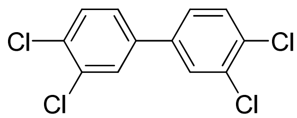
3g[11]: white solid, mp 144 °C; ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ (ppm) 7.73 (dt, *J*=2.0, 8.5 Hz, 4H), 7.47 (dt, *J*=2.0, 8.5 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ (ppm) 194.5, 135.7, 131.5, 129.0.



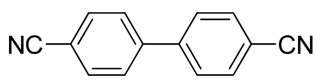
2h[3]: colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ (ppm) 7.55 (t, *J*=2.0Hz, 2H), 7.44 (dt, *J*=1.5, 8.0 Hz, 2H), 7.38 (t, *J*=8.0Hz, 2H), 7.35 (dt, *J*=1.5, 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ (ppm) 141.8, 135.0, 130.3, 128.1, 127.5, 125.5.



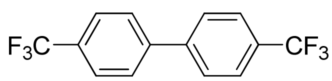
3h[8]: white solid, mp 170 °C; ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ (ppm) 7.74 (t, *J*=2.0Hz, 2H), 7.65 (dt, *J*=1.0, 8.0 Hz, 2H), 7.59 (ddd, *J*=1.0, 2.0, 8.0Hz, 2H), 7.35 (t, *J*=8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ (ppm) 194.0, 138.8, 135.0, 133.0, 130.05, 130.0, 128.3.



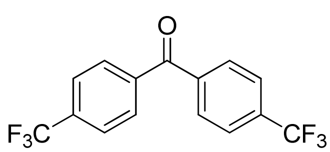
2i[5]: white solid, mp 170 °C; ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ (ppm) 7.62 (d, *J*=2.5Hz, 2H), 7.52 (d, *J*=8.5 Hz, 2H), 7.36 (dd, *J*=3.0, 11.0Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ (ppm) 138.9, 133.4, 132.7, 131.2, 129.0, 126.3.



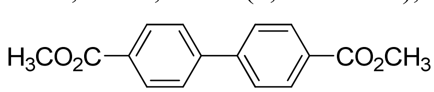
2j[1]: white solid, mp 220 °C; ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ (ppm) 7.78 (dt, *J*=2.0, 8.5Hz, 4H), 7.69 (dt, *J*=2.0, 8.5 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ (ppm) 143.7, 133.1, 128.2, 118.6, 112.7.



2k[2]: white solid, mp 80 °C; ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ (ppm) 7.74 (d, *J*=8.5Hz, 4H), 7.71 (d, *J*=8.5 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ (ppm) 143.5, 130.5 (d, *J*=32.3Hz), 127.9, 126.2 (q, *J*=3.6Hz), 124.3 (d, *J*=270.6Hz).

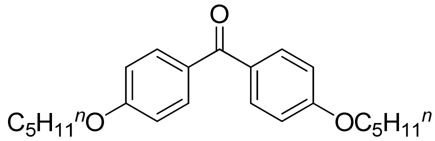


3k[10]: white solid, mp 110 °C; ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ (ppm) 7.91 (d, *J*=8.5Hz, 4H), 7.79 (d, *J*=8.5 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ (ppm) 194.6, 140.0, 134.6 (d, *J*=32.9Hz), 130.4, 125.8 (q, *J*=3.8Hz), 123.7 (d, *J*=271.1Hz).

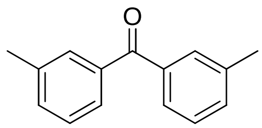


2l[1]: white solid, mp 210 °C; ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ (ppm) 8.13 (dt, *J*=2.0, 8.5Hz, 4H), 7.69 (dt, *J*=2.0, 8.5 Hz, 4H), 3.95 (s, 6H); ^{13}C NMR (125 MHz,

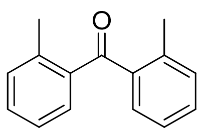
$CDCl_3$, TMS) δ (ppm) 167.0, 144.6, 130.4, 129.9, 127.5, 52.4.



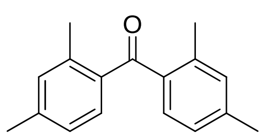
3m: colorless oil; ^1H NMR (500 MHz, $CDCl_3$, TMS) δ (ppm) 8.05 (dt, *J*=2.5, 9.5Hz, 4H), 6.93 (dt, *J*=2.5, 9.5 Hz, 4H), 4.03 (t, *J*=6.5 Hz, 4H), 1.80-1.84 (m, 4H), 1.37-1.47 (m, 8H), 0.94 (t, *J*=6.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ (ppm) 170.8, 163.9, 132.5, 121.4, 114.4, 68.5, 29.0, 28.3, 22.6, 14.2. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{30}O_3Na$, 377.2087; found: 377.2096.



3n[9]: colorless oil; ^1H NMR (500 MHz, $CDCl_3$, TMS) δ (ppm) 7.63 (s, 2H), 7.57 (d, *J*=7.5 Hz, 2H), 7.34-7.41 (m, 4H), 2.42 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ (ppm) 197.4, 138.3, 138.0, 133.3, 130.6, 128.2, 127.6, 21.6.



3o[9]: white solid, mp 64 °C; ^1H NMR (500 MHz, $CDCl_3$, TMS) δ (ppm) 7.39 (td, *J*=1.5, 7.5 Hz, 2H), 7.31 (dd, *J*=1.5, 7.5 Hz, 2H), 7.28 (dd, *J*=1.0, 7.5 Hz, 2H), 7.20 (td, *J*=1.0, 7.5 Hz, 2H), 2.44 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ (ppm) 201.0, 139.2, 138.4, 131.6, 131.3, 130.5, 125.6, 20.9.



3p: colorless oil; ^1H NMR (500 MHz, $CDCl_3$, TMS) δ (ppm) 7.21 (d, *J*=2.5Hz, 2H), 7.08 (s, 2H), 6.99 (d, *J*=2.5 Hz, 2H), 2.41 (s, 6H), 2.36 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ (ppm) 200.4, 141.3, 138.3, 136.5, 132.2, 130.6, 127.6. HRMS (ESI) m/z: $[M+1]^+$ calcd for $C_{17}H_{19}O$, 239.1430; found: 239.1433.

4. References

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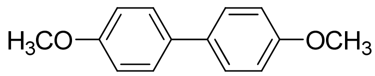
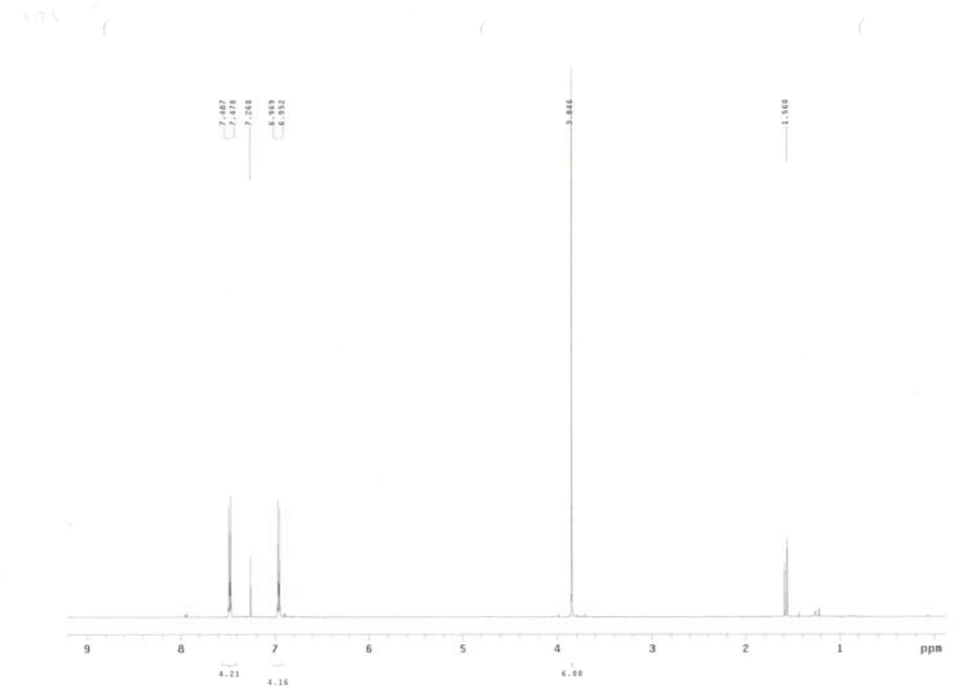
5. Copies of ^{1}H and ^{13}C NMR spectra of products 2a-6l, 3a-3c, 3d-3h, 3k, 3m-3p


H3CO
OCH3

2a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9
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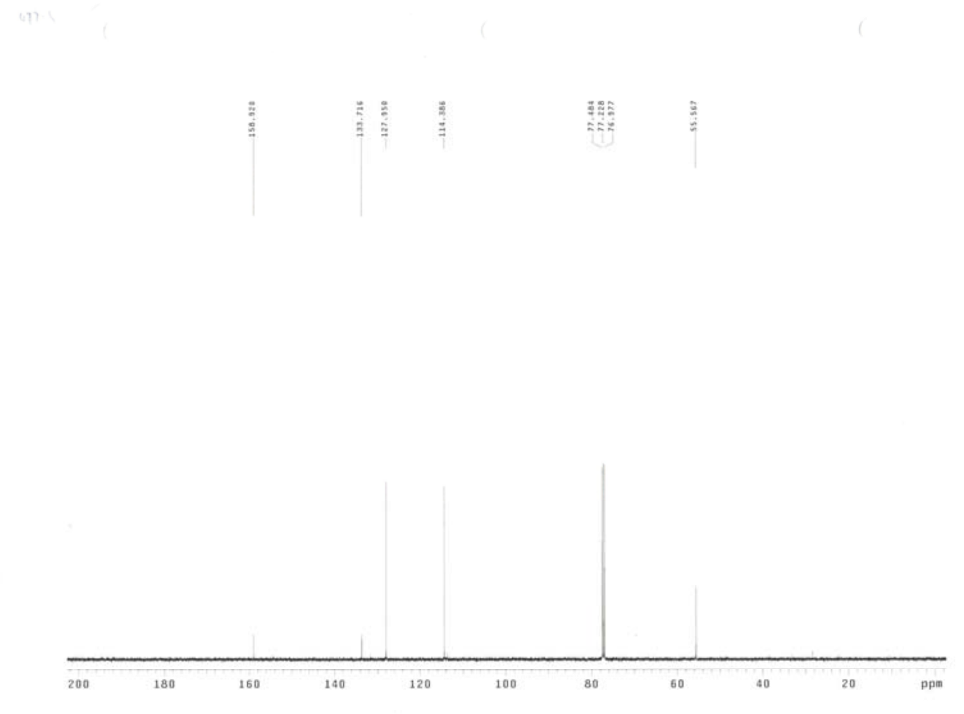
4.16
6.00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55.567
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80
60
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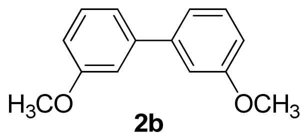
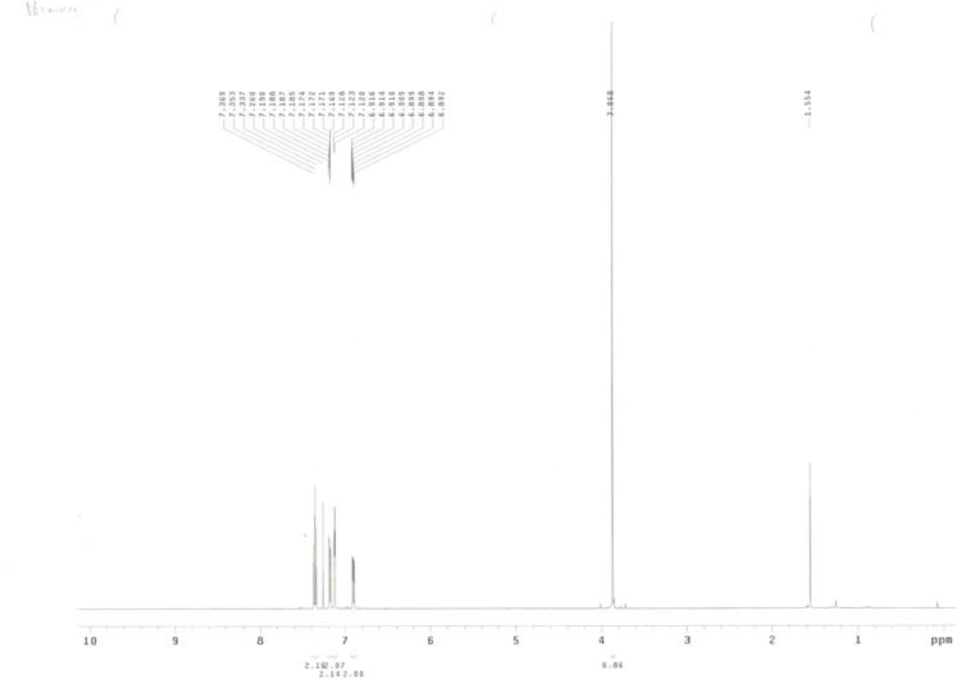
20
ppm


H3CO
OCH3

2b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9
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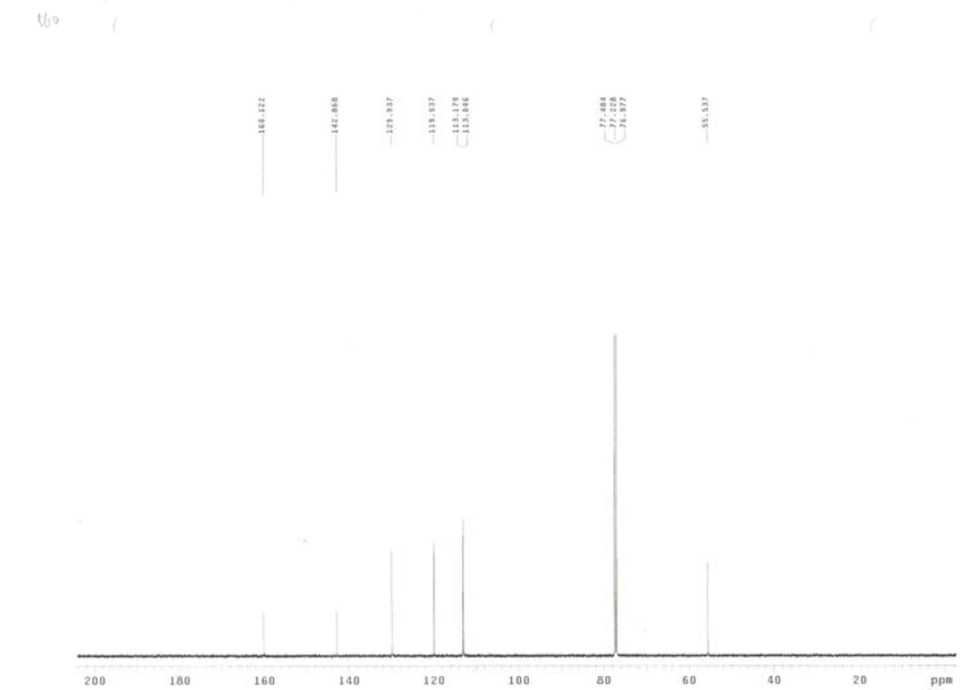
4
3
2
1
ppm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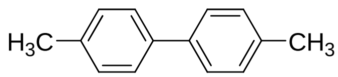
20
ppm



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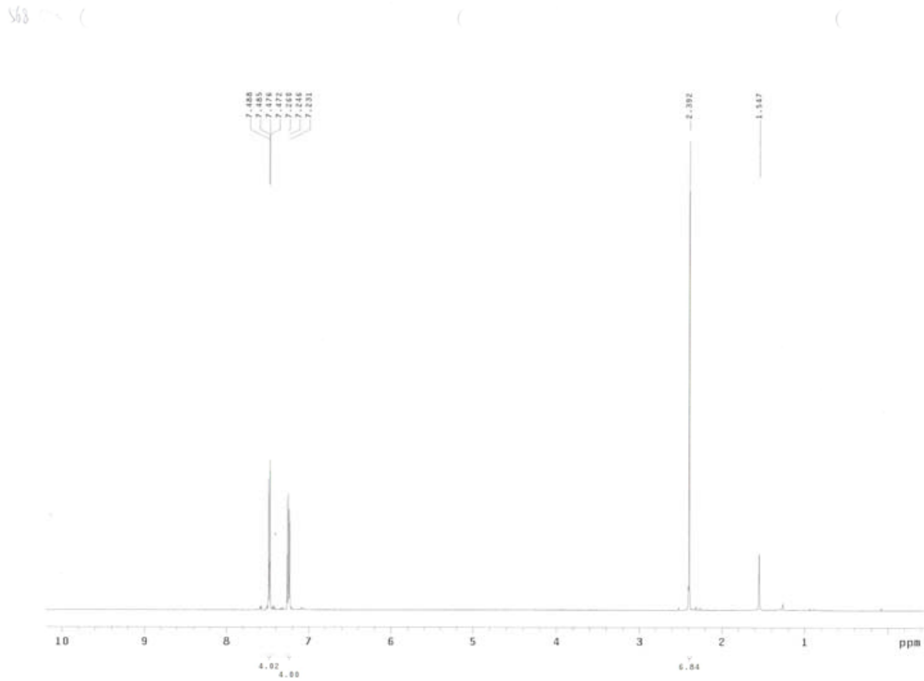

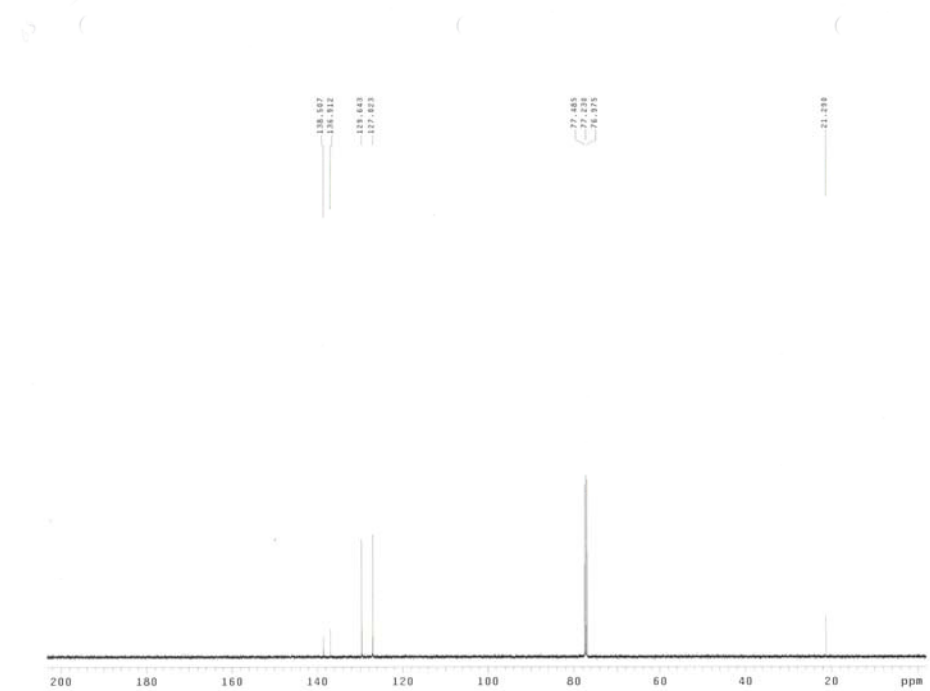

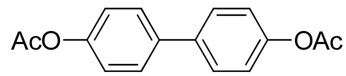

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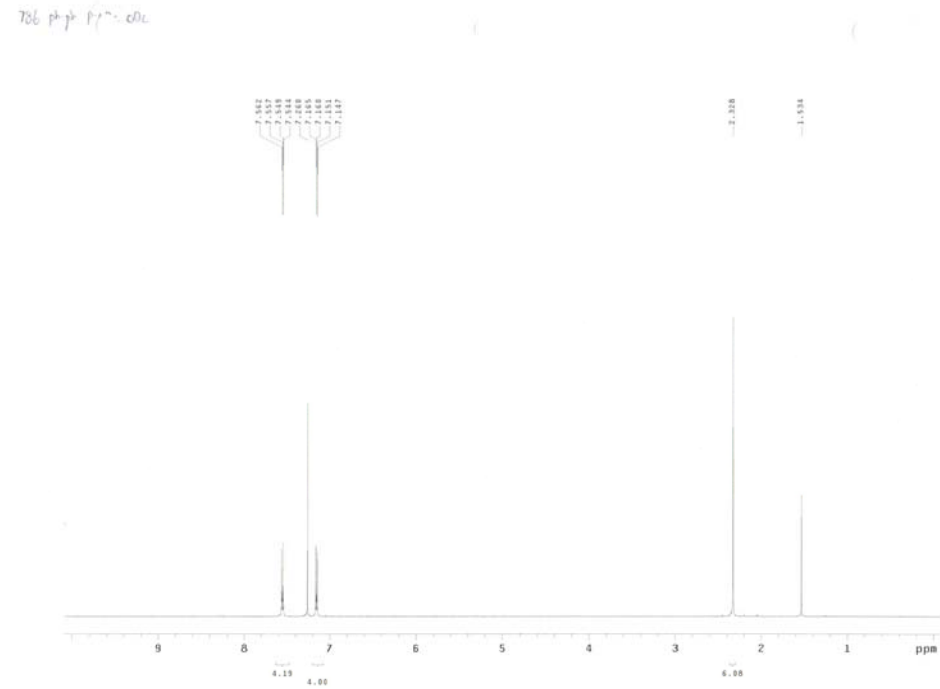

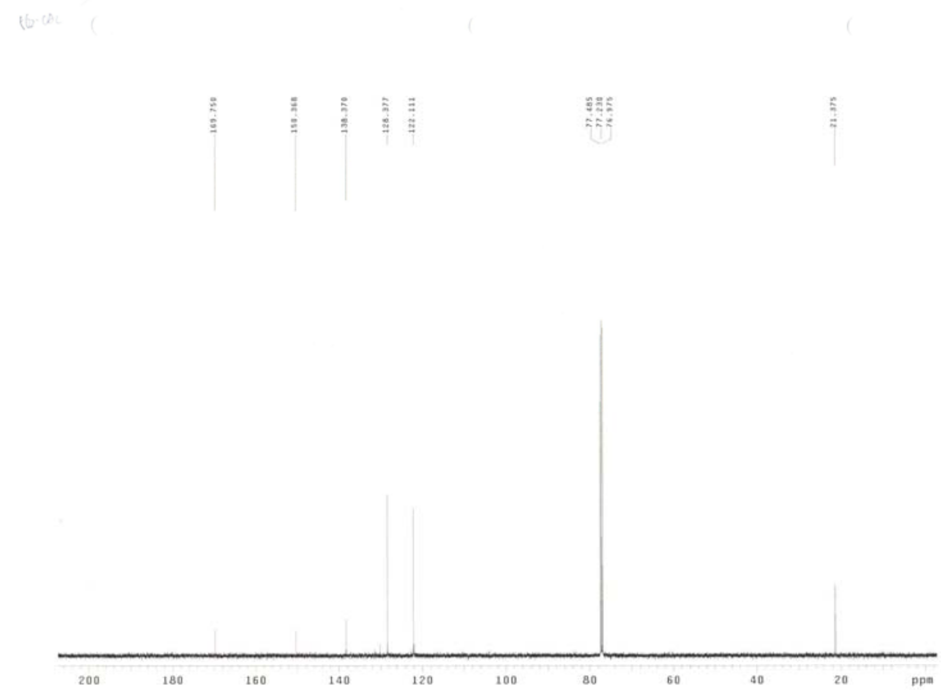

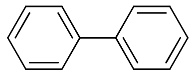

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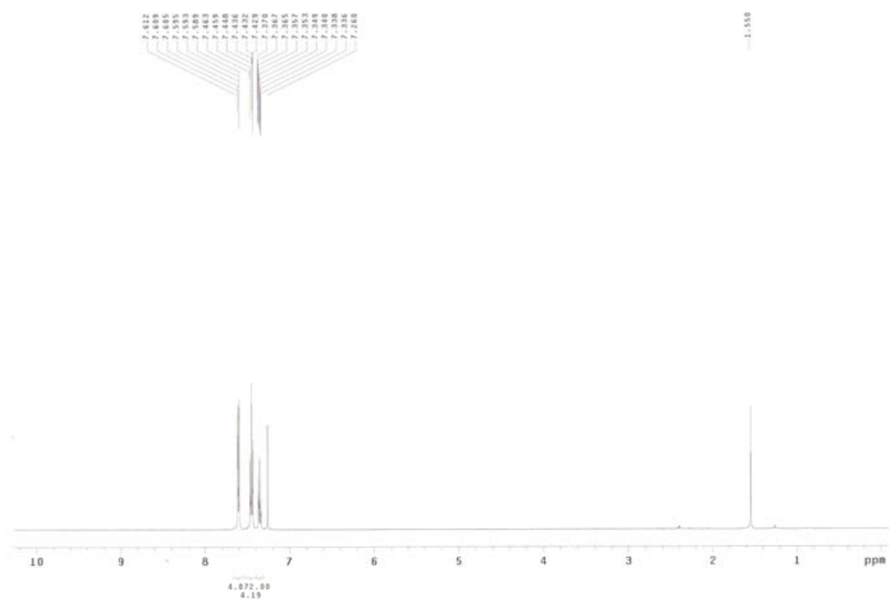

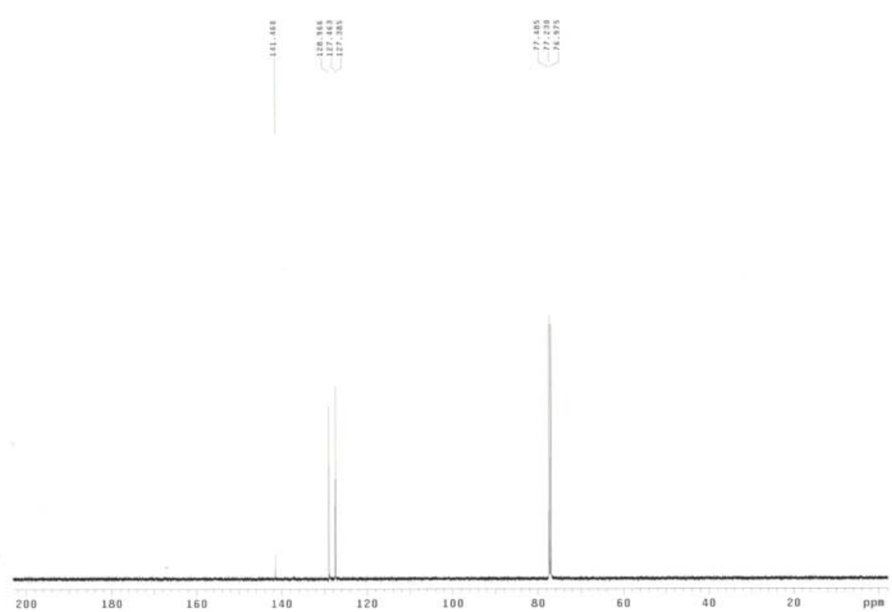

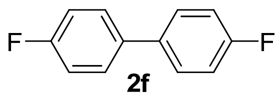

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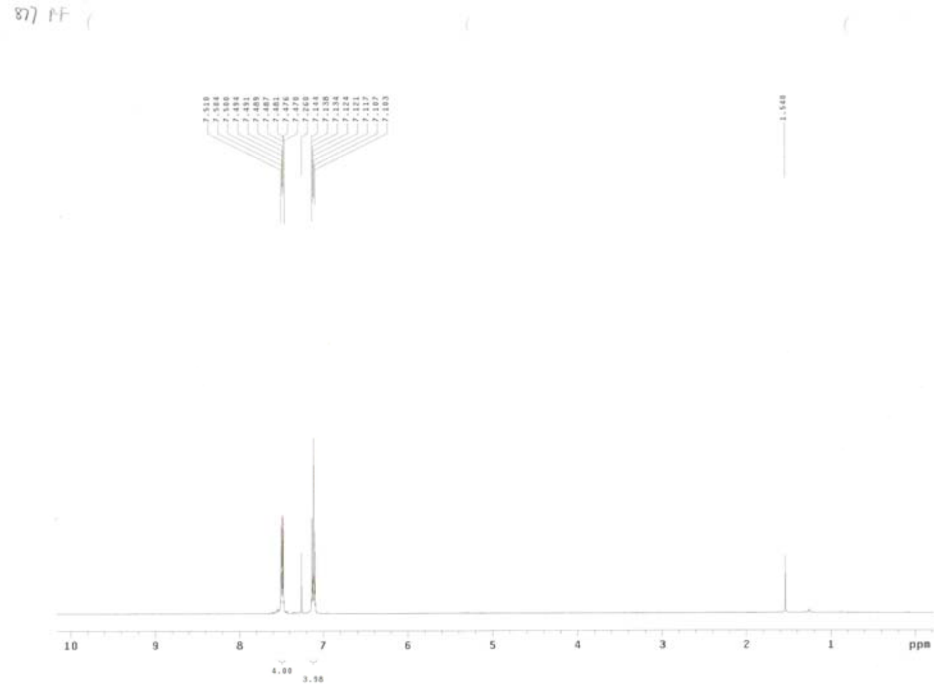
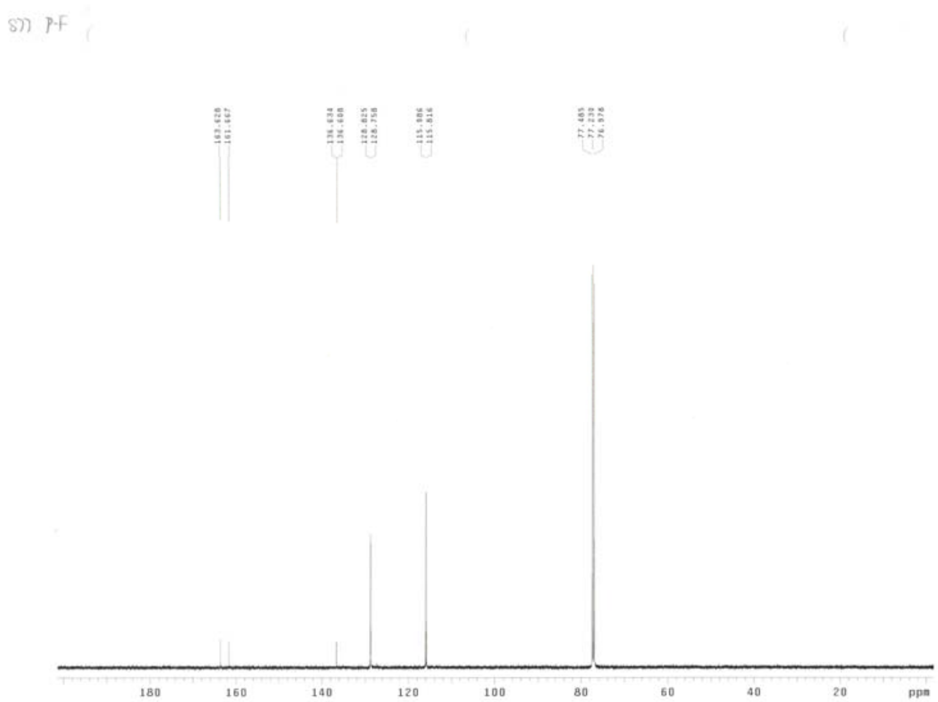
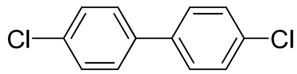
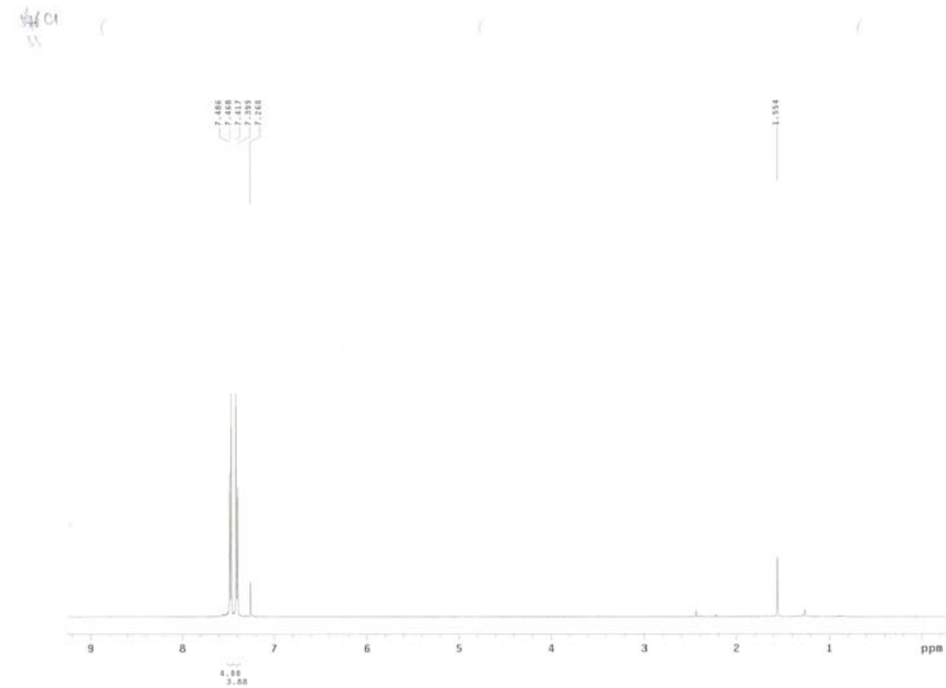
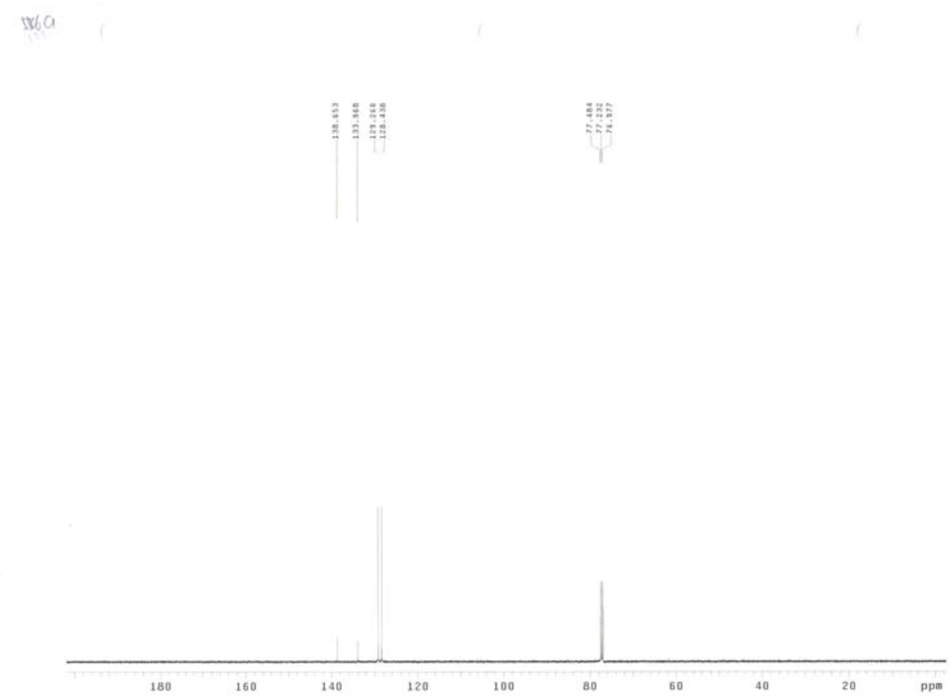


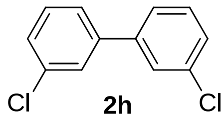




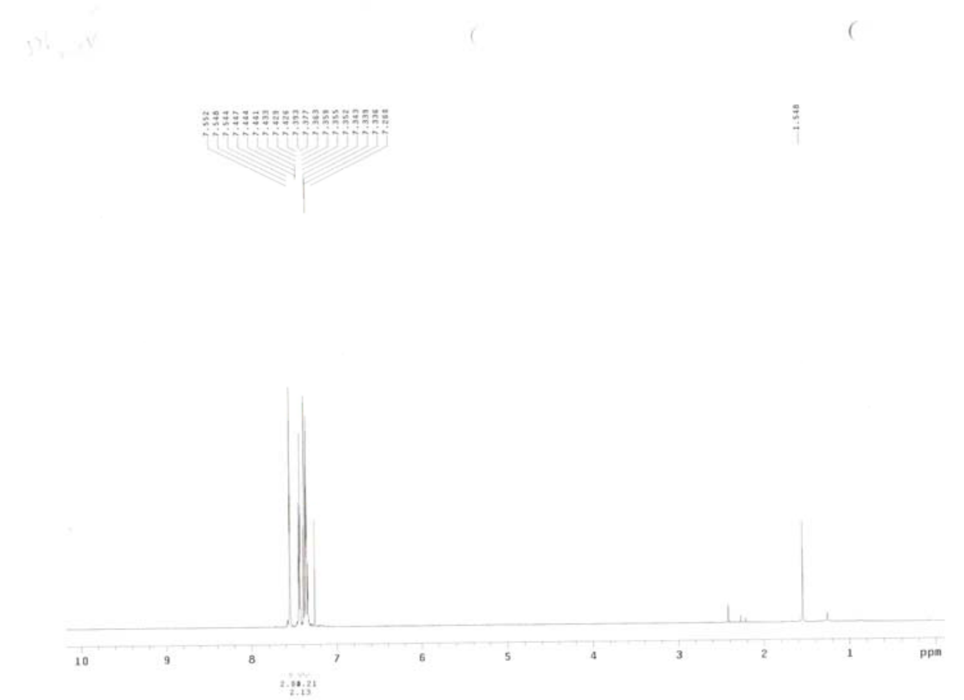
2g

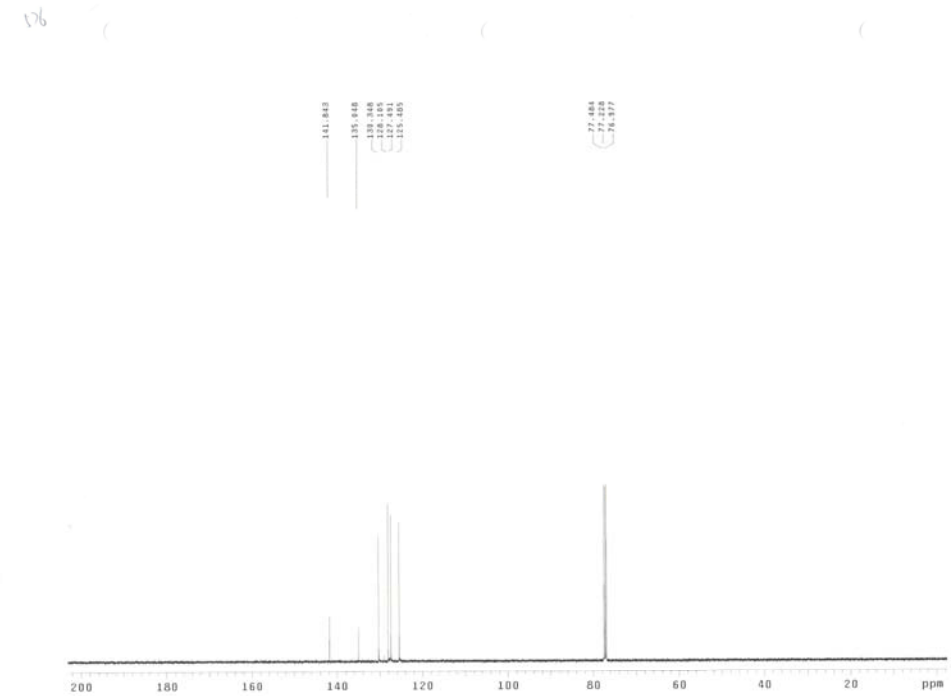




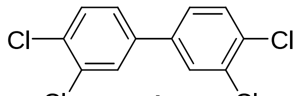


2h





Supplementary Material (ESI) for Chemical Communications



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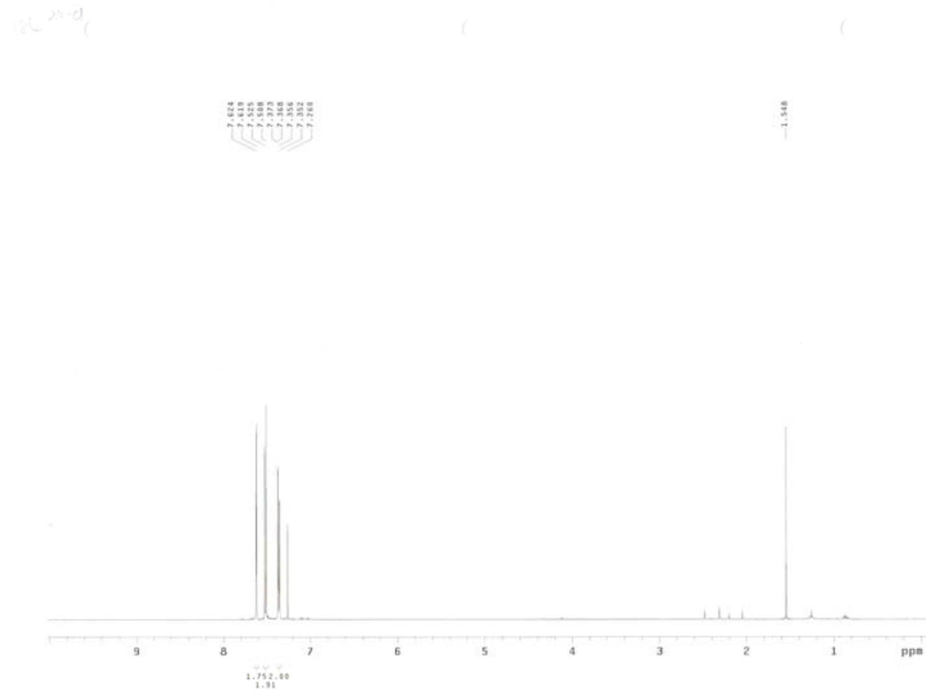

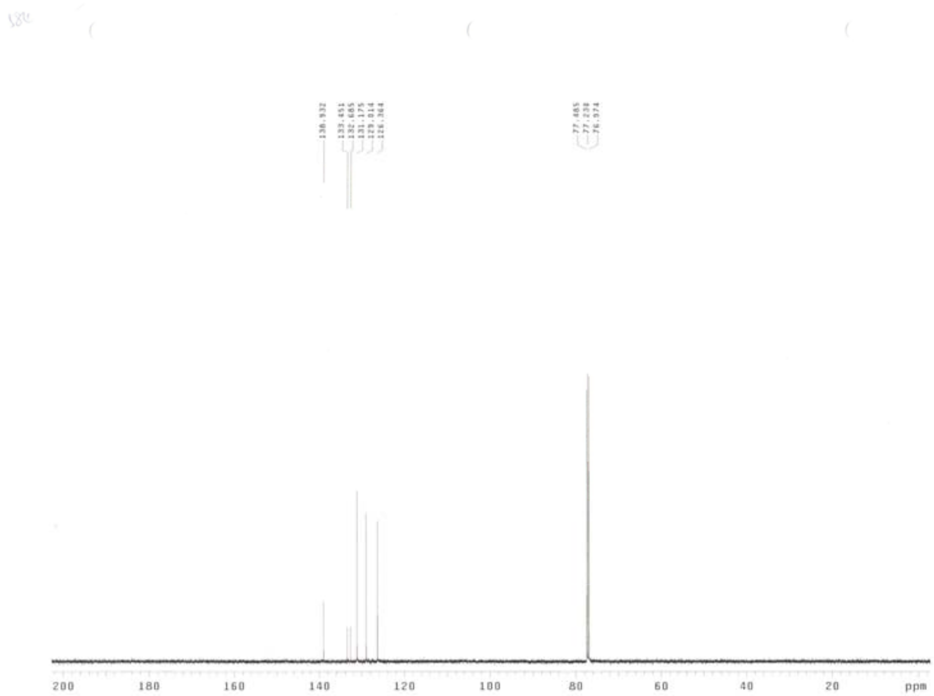

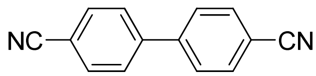

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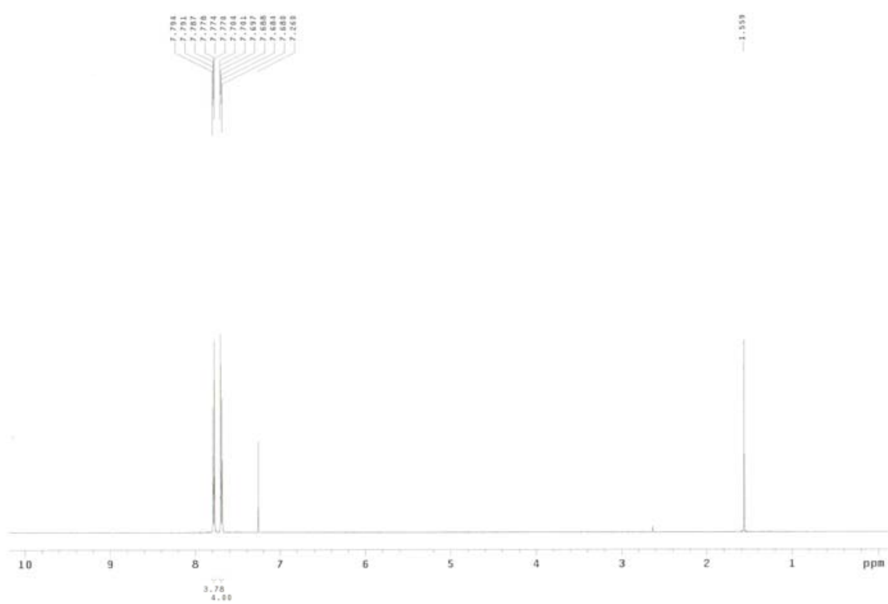
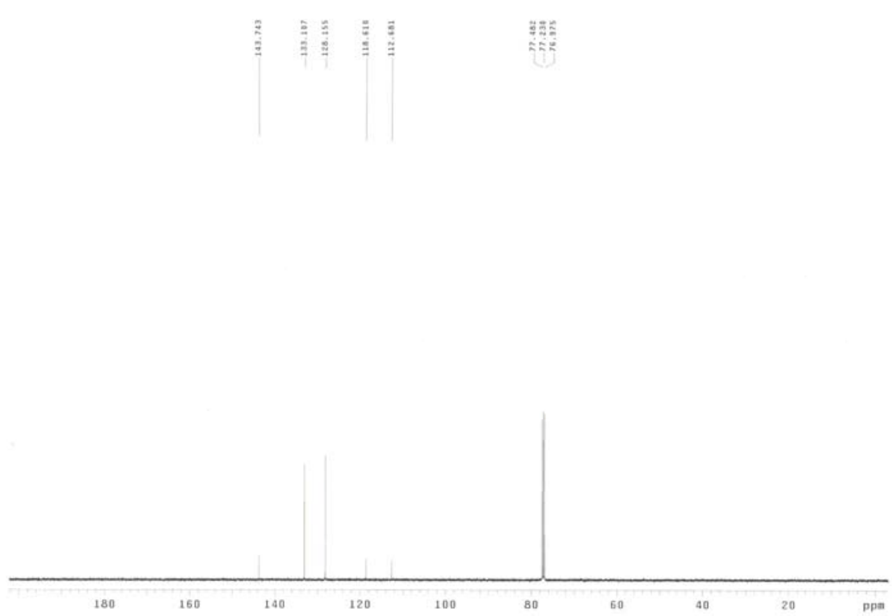
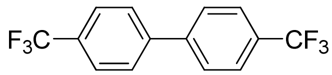
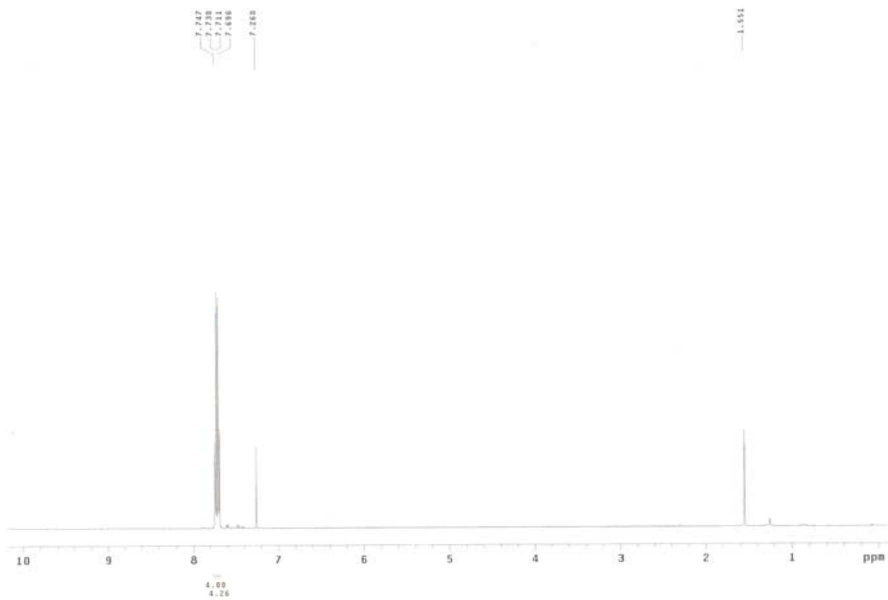





F3C
CF3

2k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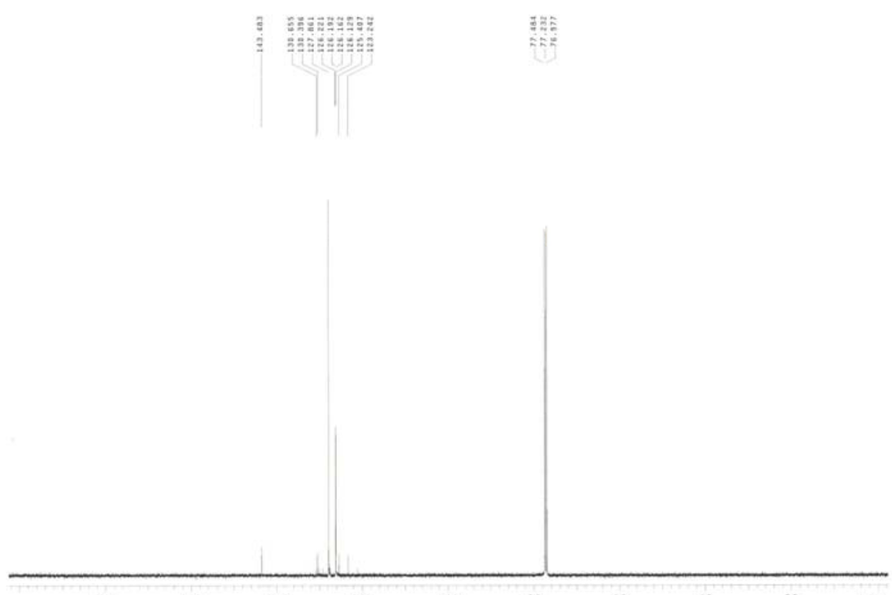
7.730
7.711
7.690
7.268
1.551
10 9 8 7 6 5 4 3 2 1 ppm
4.00
4.26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130.655
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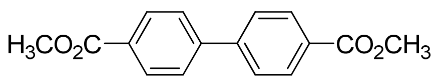
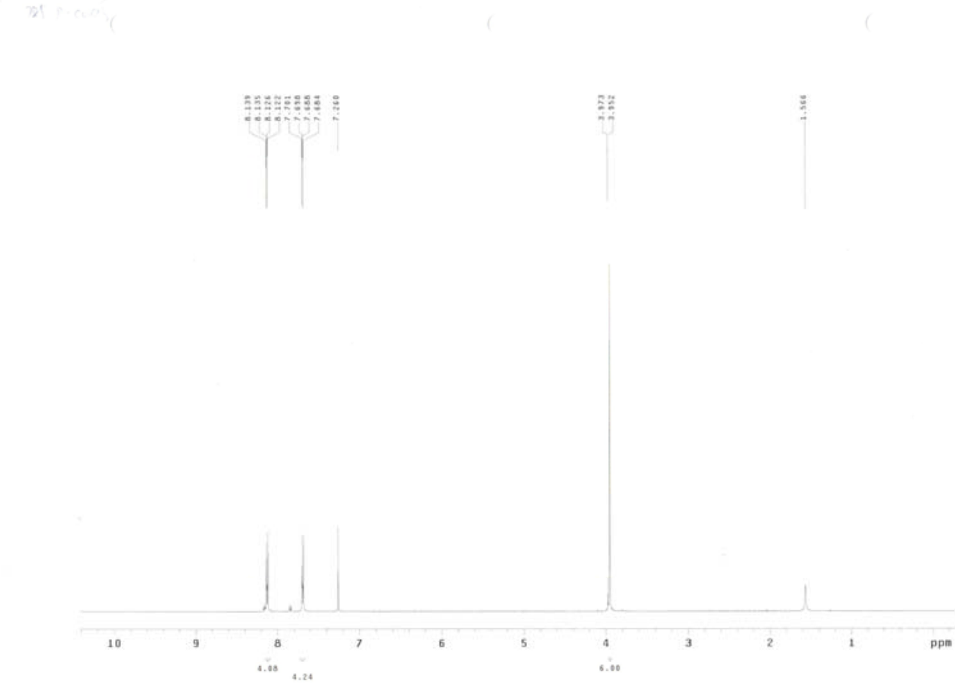
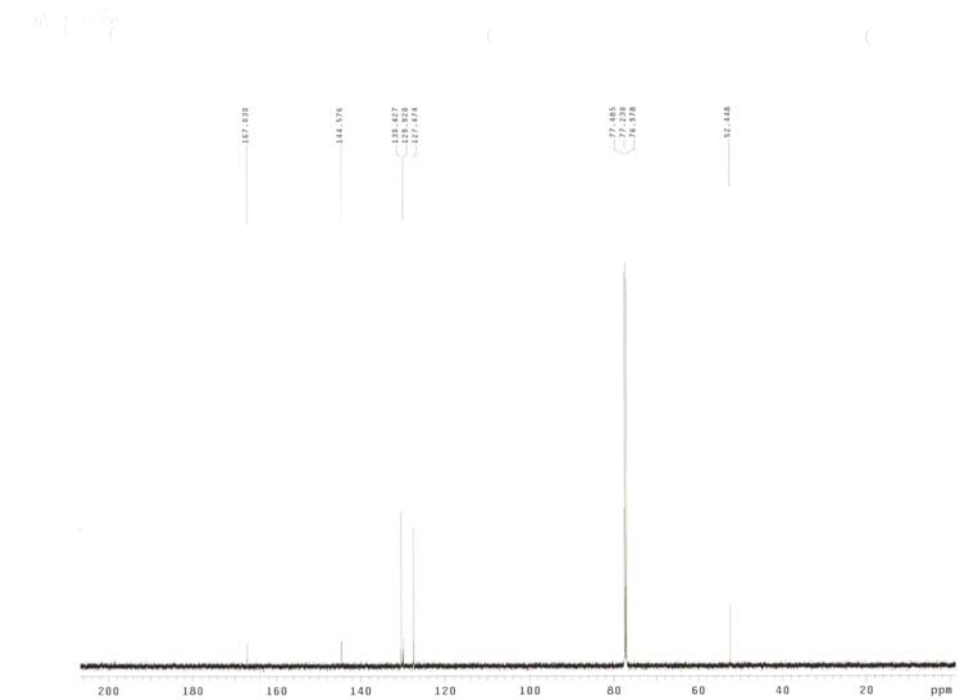
180 160 140 120 100 80 60 40 20 ppm


H3CO2C
CO2CH3

2l


10
9
8
7
6
5
4
3
2
1
ppm


200
180
160
140
120
100
80
60
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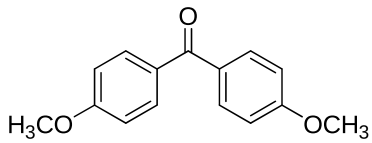
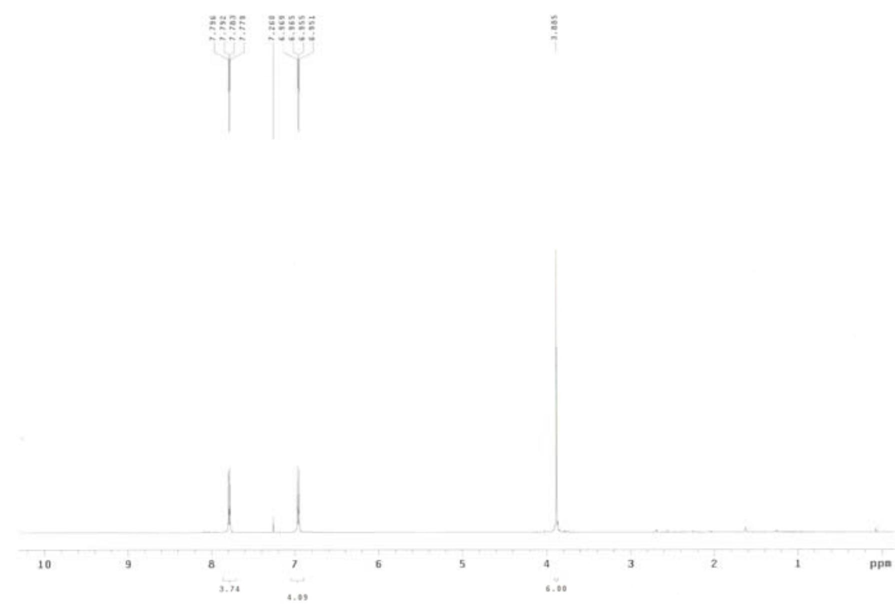
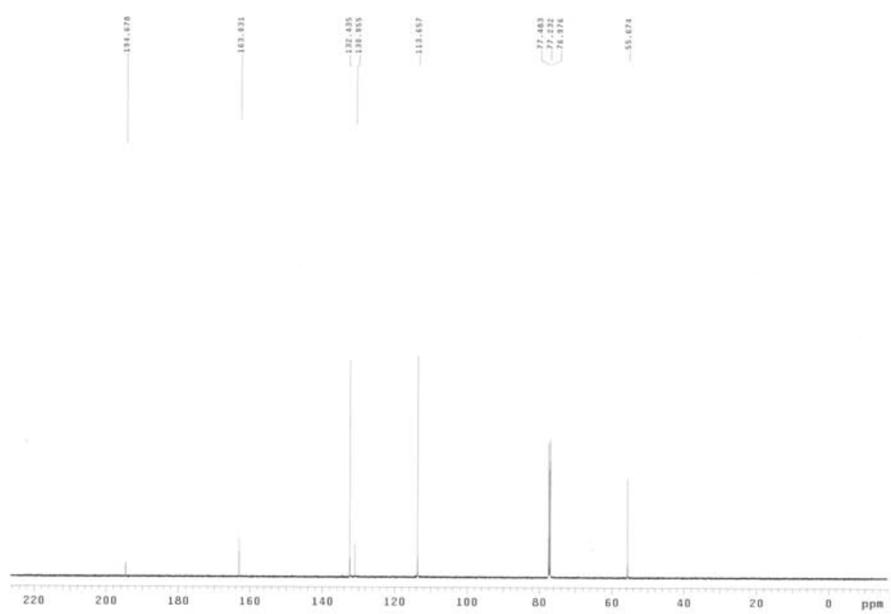
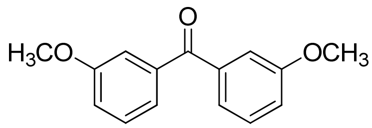
20
ppm



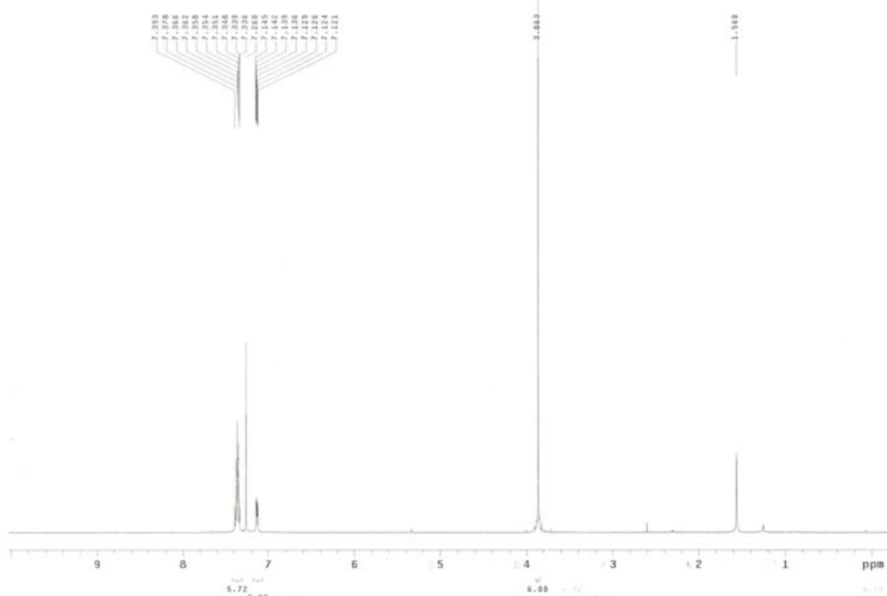
3a






O
H3CO
OCH3

3b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1
ppm
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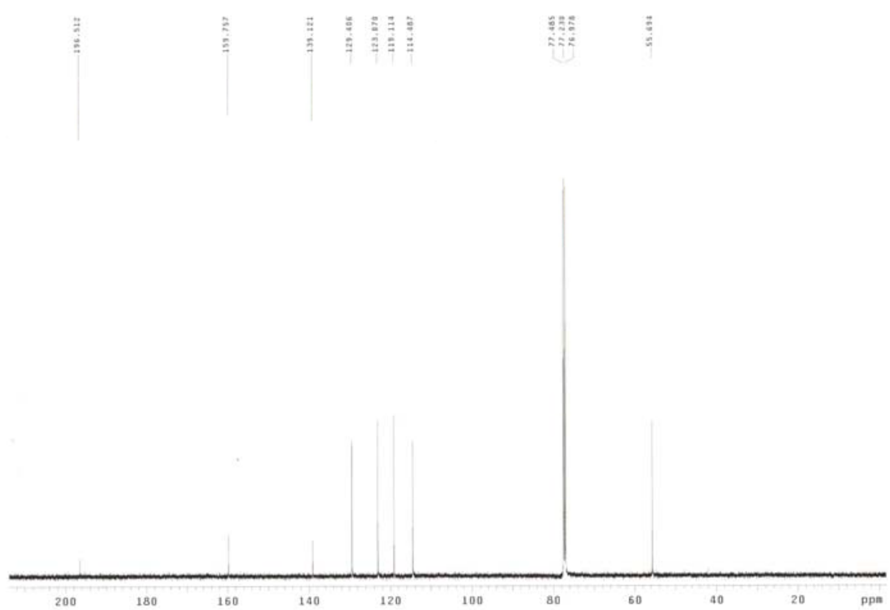
6.00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139.121
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40
20
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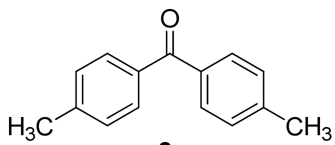
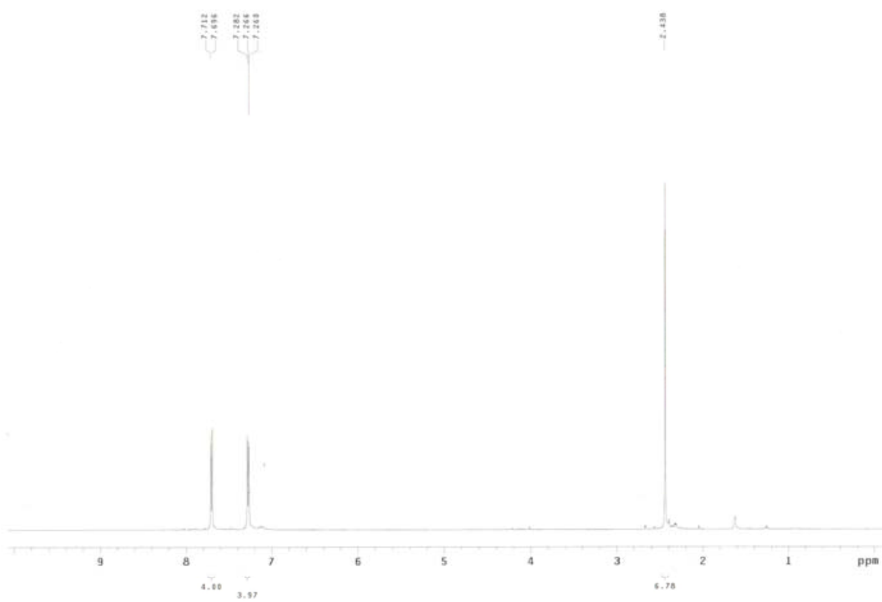

O
H3C
CH3

3c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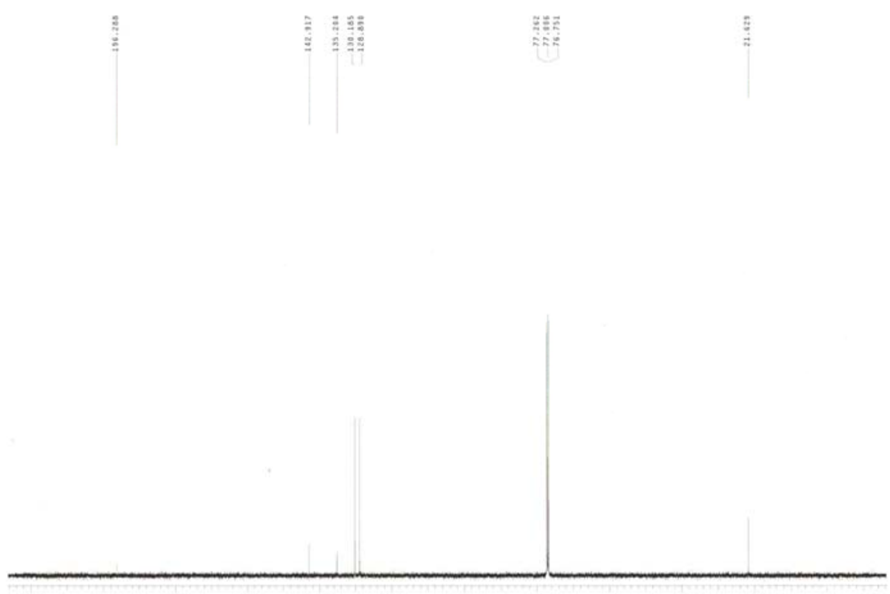
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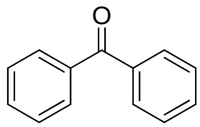
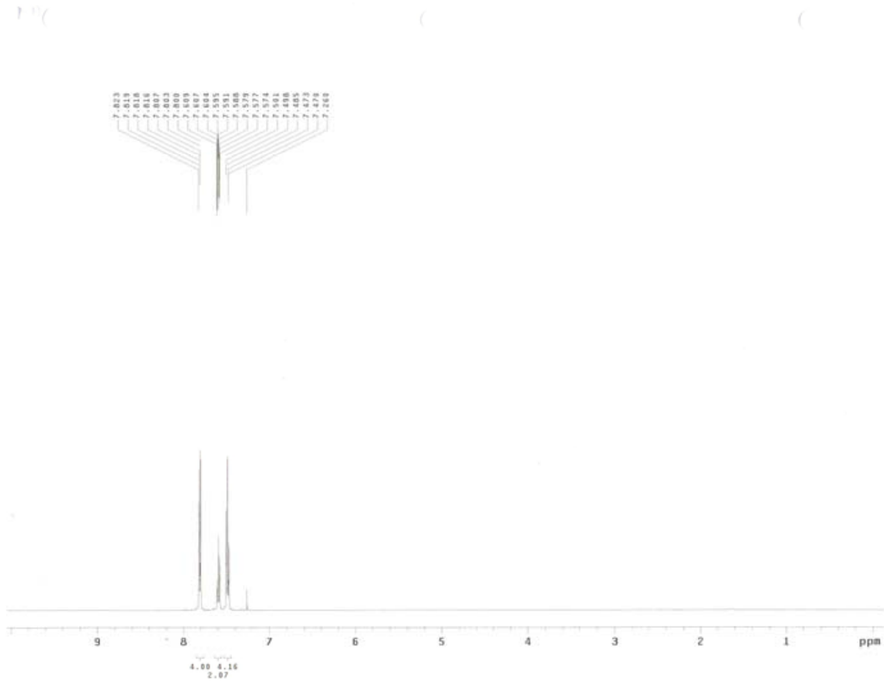
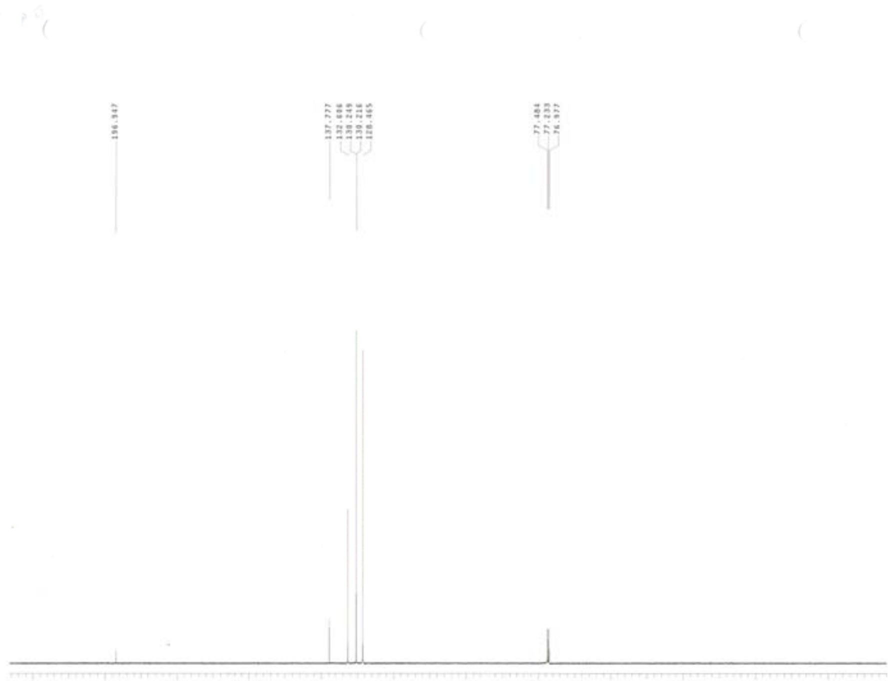

O

3e


9
8
7
6
5
4
3
2
1
ppm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120
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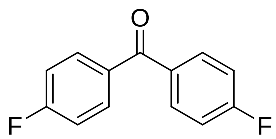
ppm



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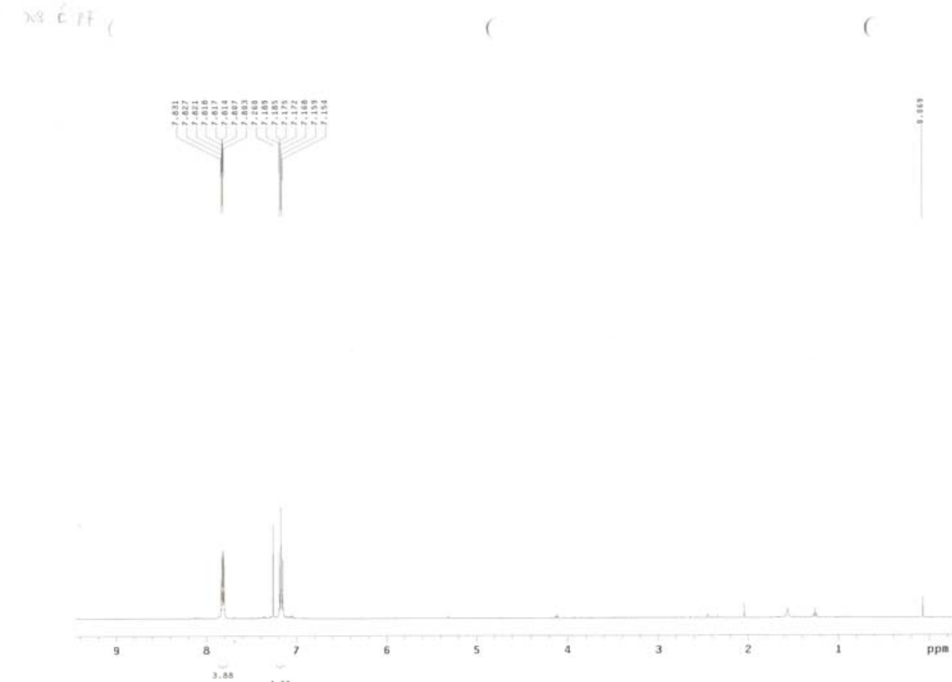

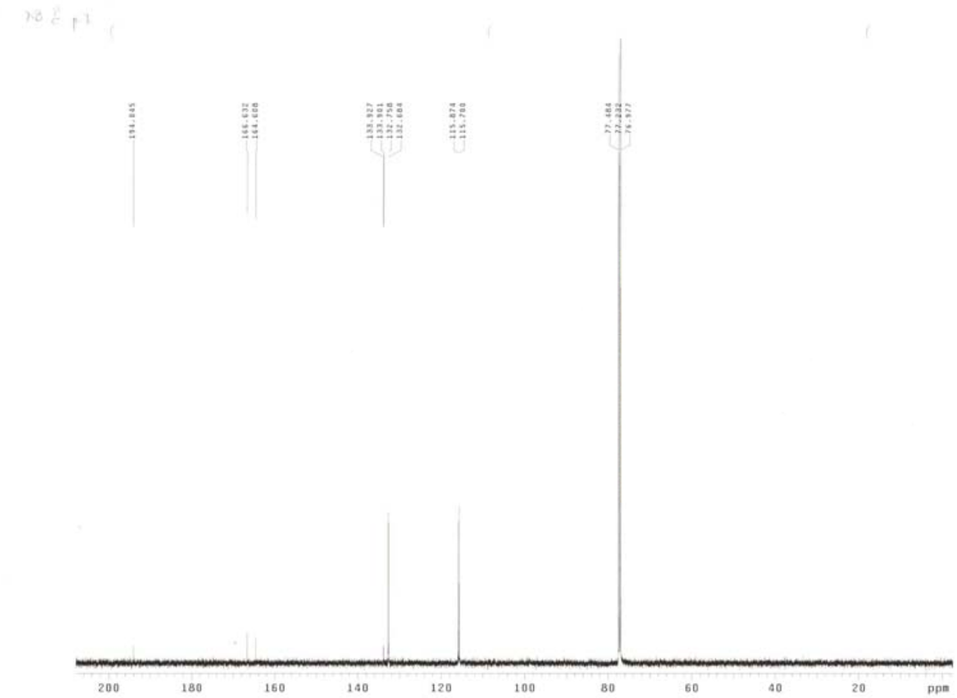

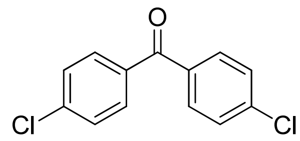

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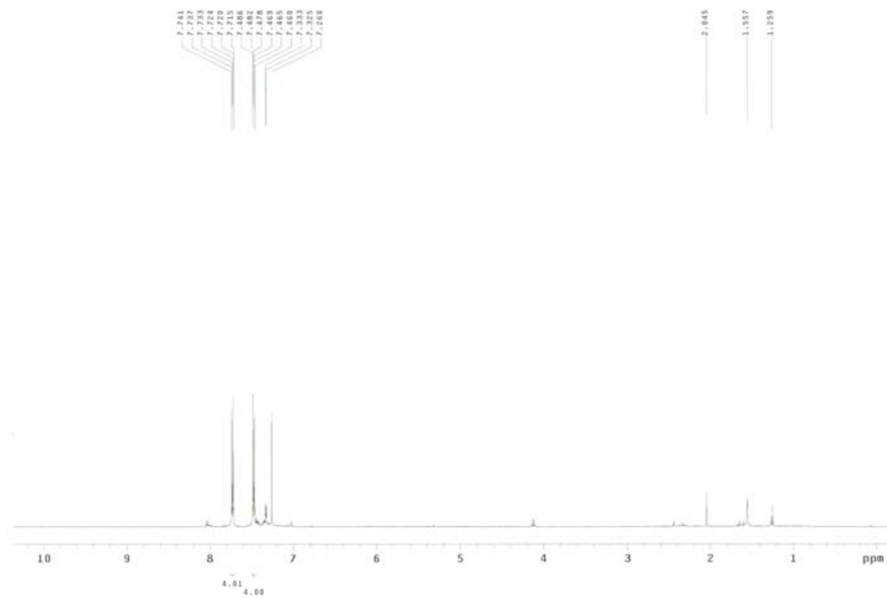

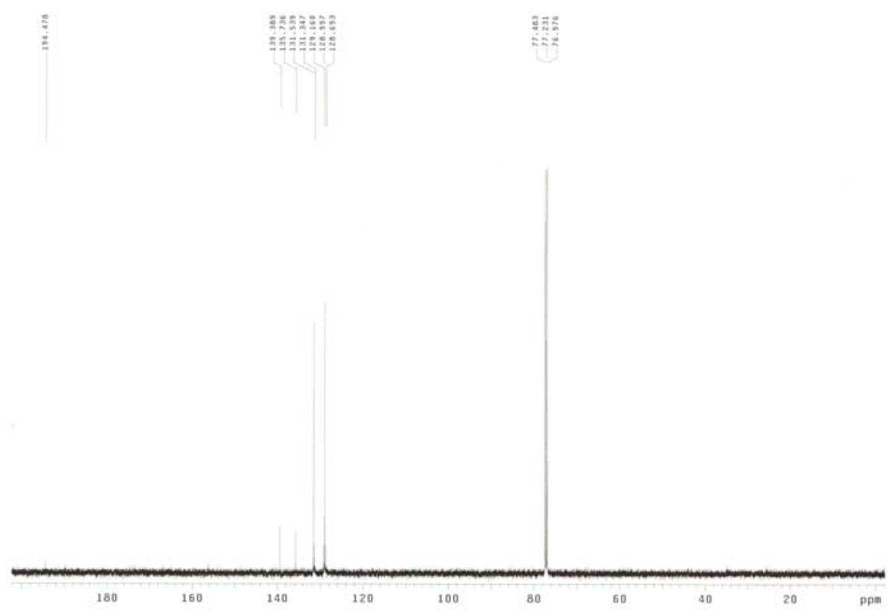

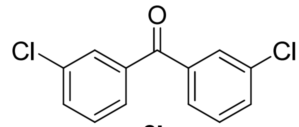

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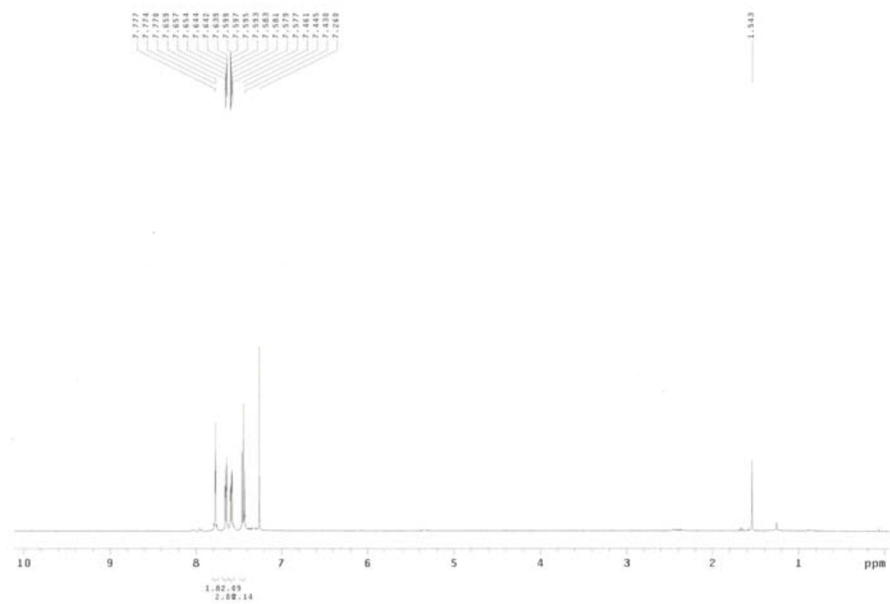

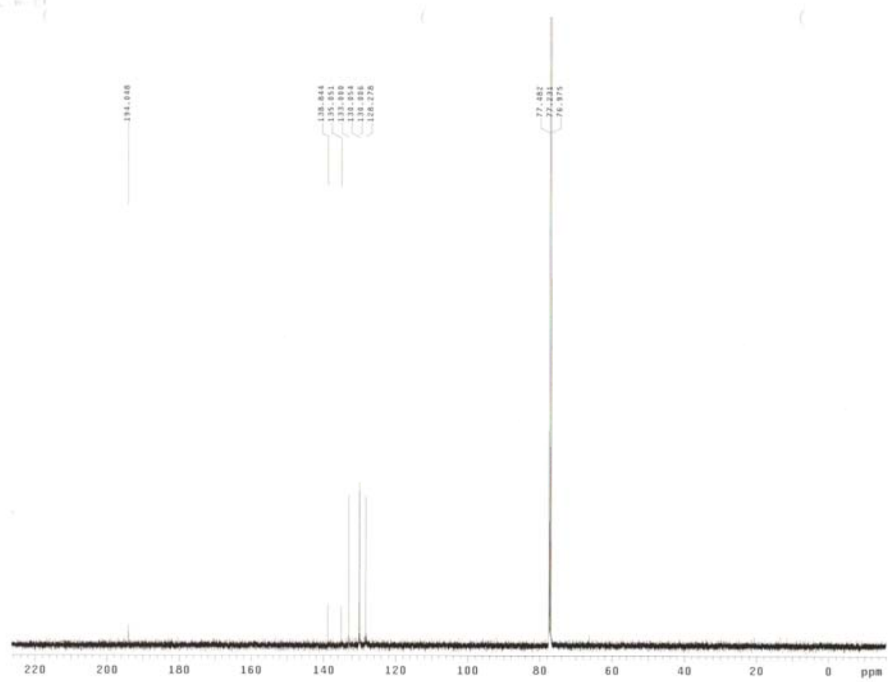

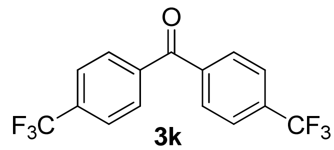

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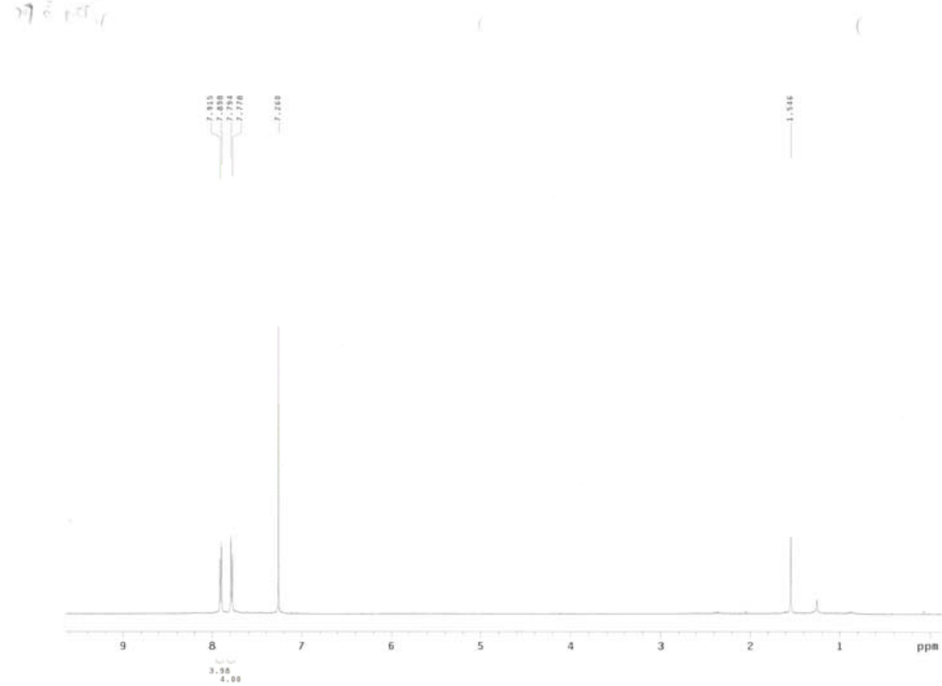

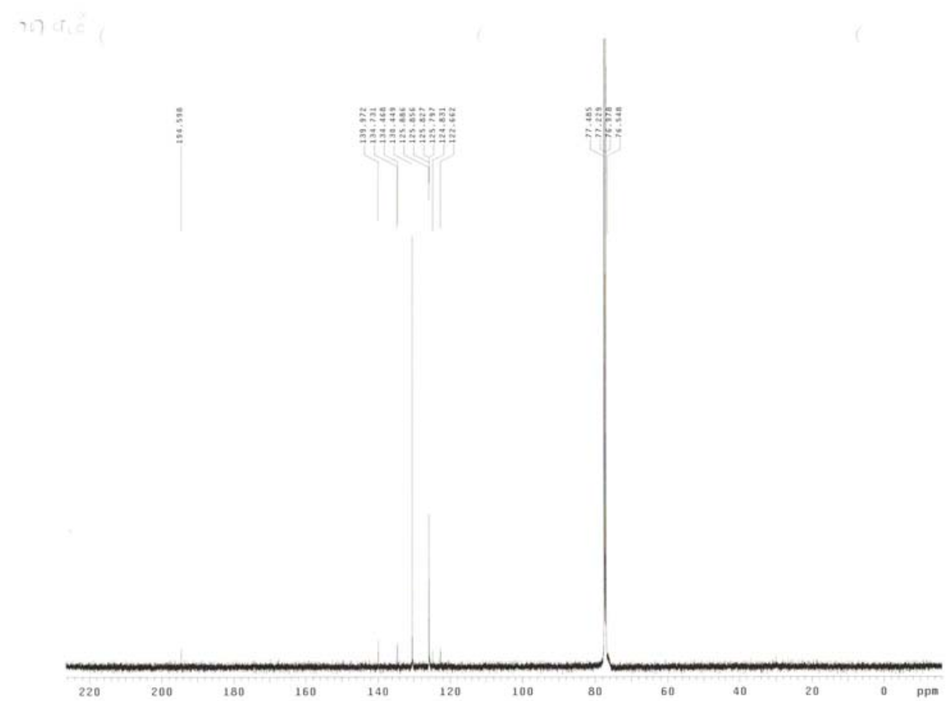

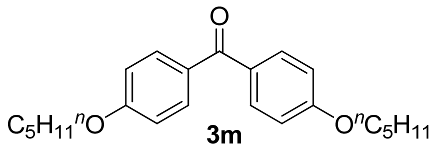

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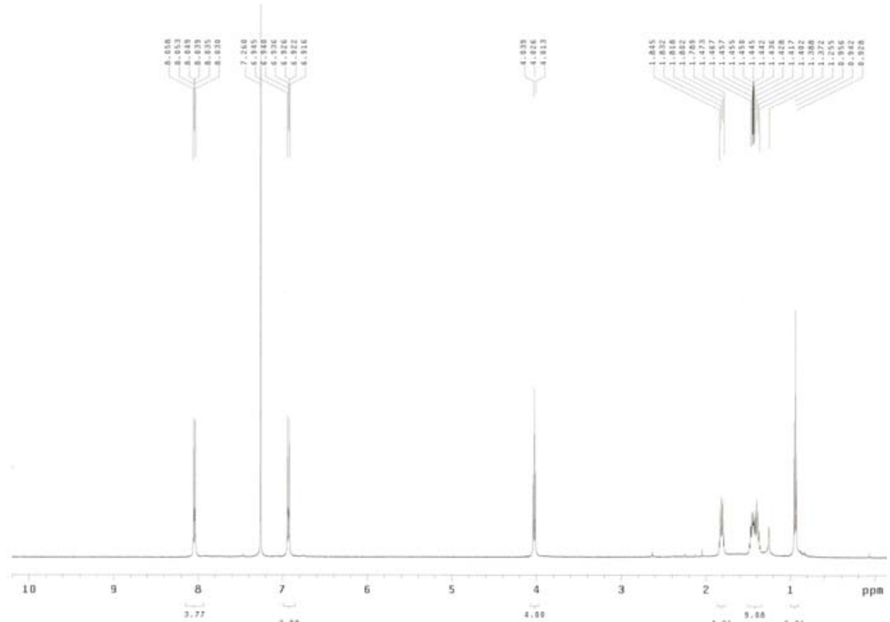

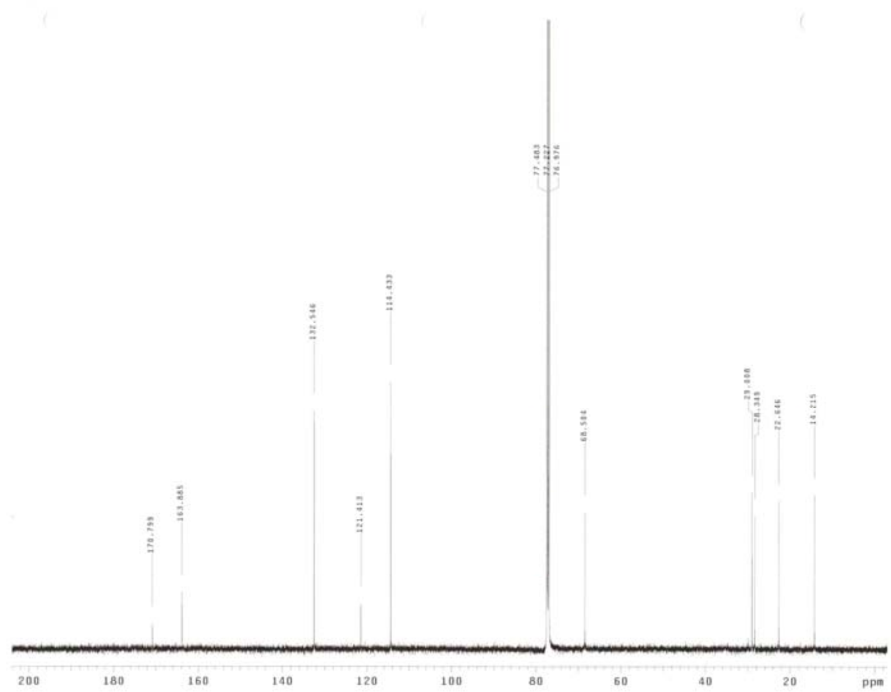

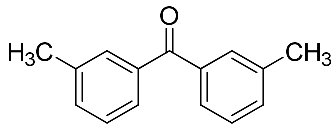

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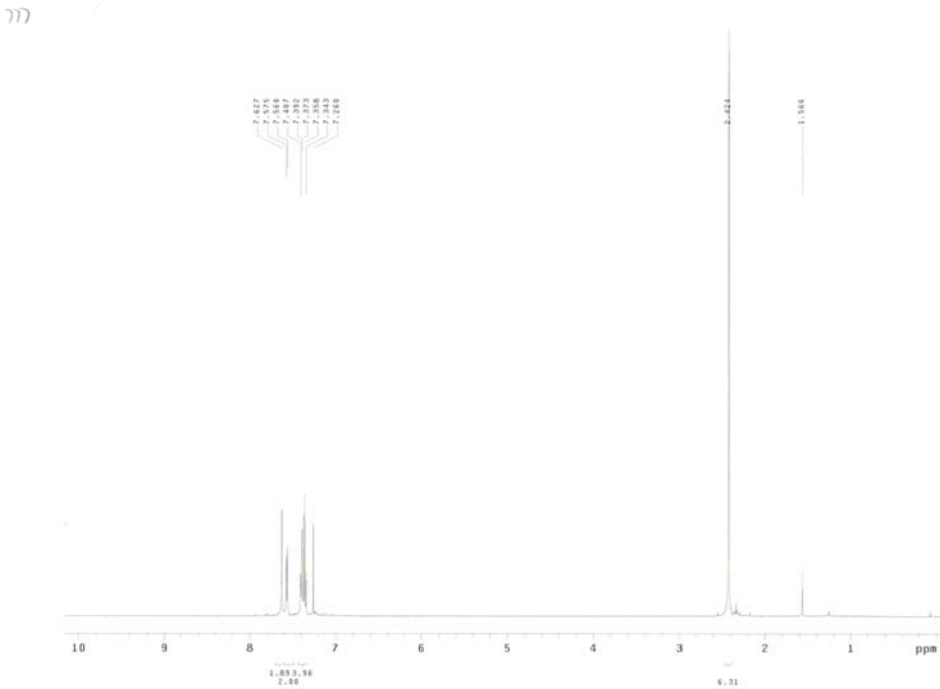

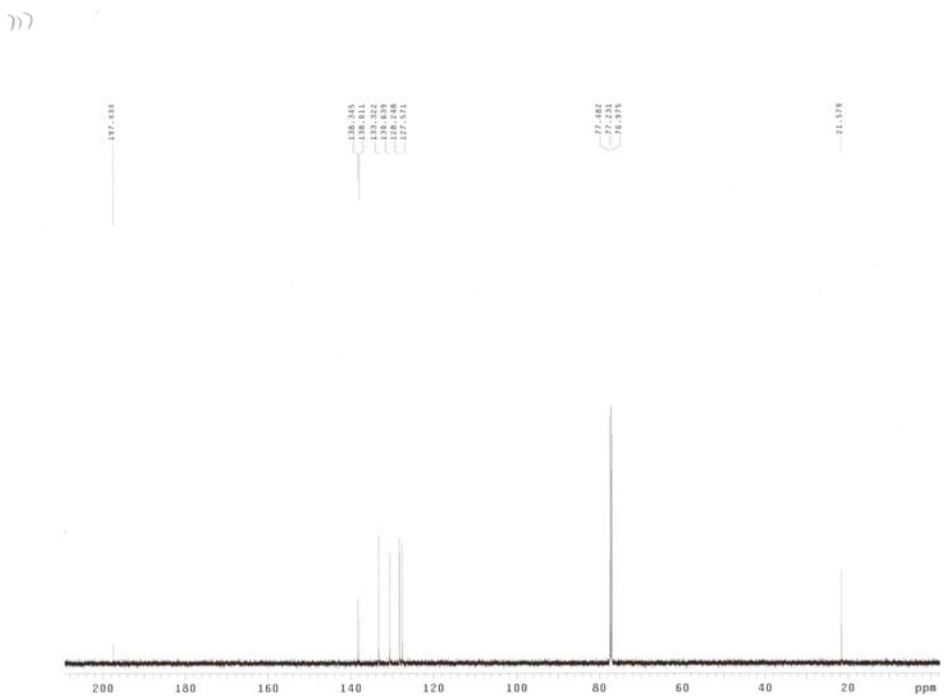

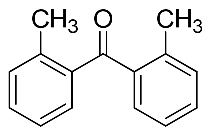

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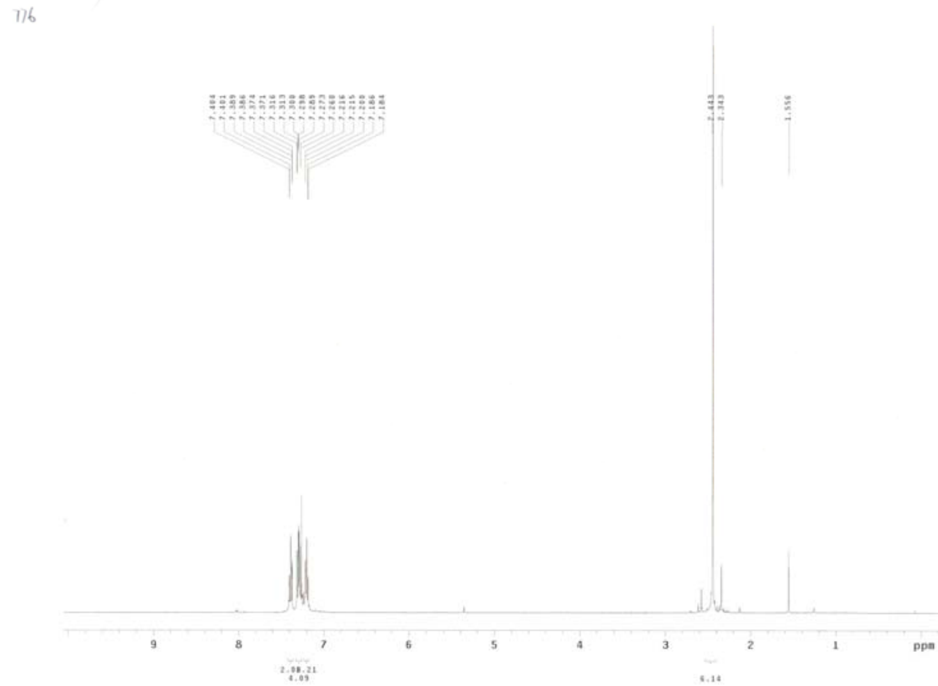

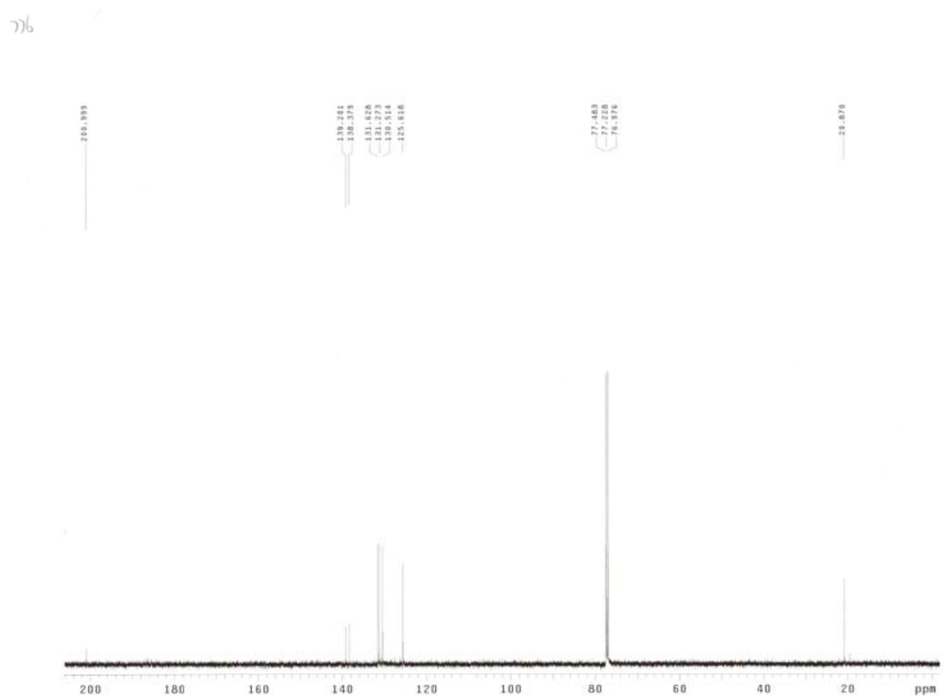

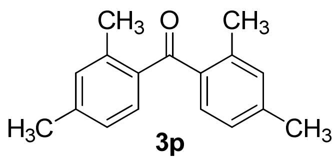

3p