

SUPPORTING INFORMATION

Iron containing mesoporous aluminosilicate: A highly active and reusable heterogeneous catalyst for hydroarylation of styrenes

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General Information

All materials were purchased from commercial suppliers and used without further purification. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was purchased from Aldrich (Iron(III) chloride hexahydrate, reagent grade, $\geq 98\%$, purified lumps). The powder X-ray diffraction (XRD) patterns of the samples were recorded with X-Ray Diffractometer using Cu-K_α radiation. Prior to N_2 sorption experiments samples were outgassed at 125°C . All reactions were carried out in air, without any special precautions. Column chromatography was performed over silica gel (mesh 60-120) and hexane/ethyl acetate combination was used as the eluent. ^1H NMR and ^{13}C NMR spectra were recorded at ambient temperature in CDCl_3 with tetramethylsilane as internal standard. The chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. Gas chromatography was performed to identify and quantify the products of the reaction. Infra-red spectra were recorded using neat sample. HRMS measurements were performed on mass spectrometer by electron spray ionization method.

Synthesis of Al-MCM-41, Fe-Al-MCM-41 and their XRD study

Synthesis of Al-MCM-41. For the synthesis of the Al-MCM-41 (Si/Al=16) material, 22.3 ml (1 mol) of tetraethylorthosilicate was mixed with 0.68 g (0.033 mol) of aluminum isopropoxide (dissolved in 5 ml of distilled water). The mixture was stirred for 30 minutes and tetraethylammonium hydroxide solution (10% water) was added with continues stirring for another 30 minutes until the gel formation (pH = 11). After that, 7.2 g (0.2 mol) of cetyltrimethylammonium bromide was added drop wise (30 ml/h) so that the gel changed into suspension. After further stirring for 1 h the resulting synthesis gel of composition $1\text{SiO}_2:0.033\text{Al}_2\text{O}_3:0.2\text{CTMABr}:100\text{H}_2\text{O}$ was transferred into Teflon-line steel autoclave and heated to 150 °C for 48 h. After cooling to room temperature, the material was recovered by filtration, washed with deionized water and ethanol, dried in air at 100 °C for 1 h and finally calcined under flow of air at 540 °C for 6 h.

Synthesis of Fe-Al-MCM-41. Iron was incorporated into the mesoporous aluminosilicate (Al-MCM-41) using methanolic FeCl_3 solution. 0.5 g of Al-MCM-41 was added to 100 ml 0.001M methanolic solution of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and stirred vigorously for 12 h. The resultant solid was then filtered. To remove the excess FeCl_3 , it was washed with Soxhlet extraction using methanol. The resulting solid was dried in oven at 80 °C and characterized SAX and nitrogen sorption analysis.

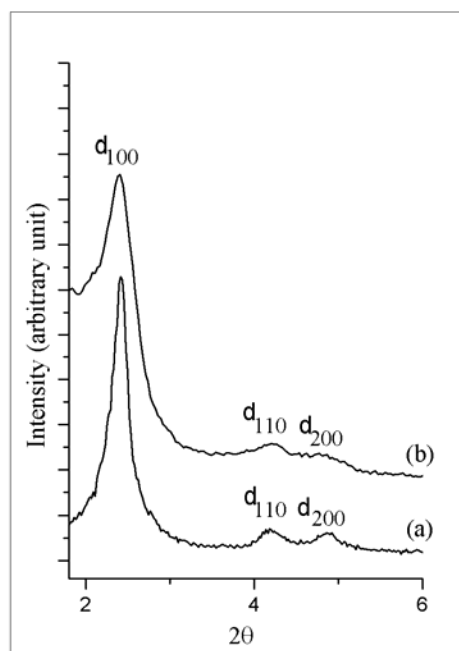


Figure S1. Small angle X-ray (SAX) diffraction patterns of (a) calcined Al-MCM-41, (b) Fe-Al-MCM-41.

Nitrogen sorption studies of Fe-Al-MCM-41

The nitrogen sorption experiments showed that the MCM-41 has the BET surface area (A_{SBET}) of $917 \text{ m}^2\text{g}^{-1}$. The average pore diameter is calculated to be 3.3 nm for Fe-Al-MCM-41.

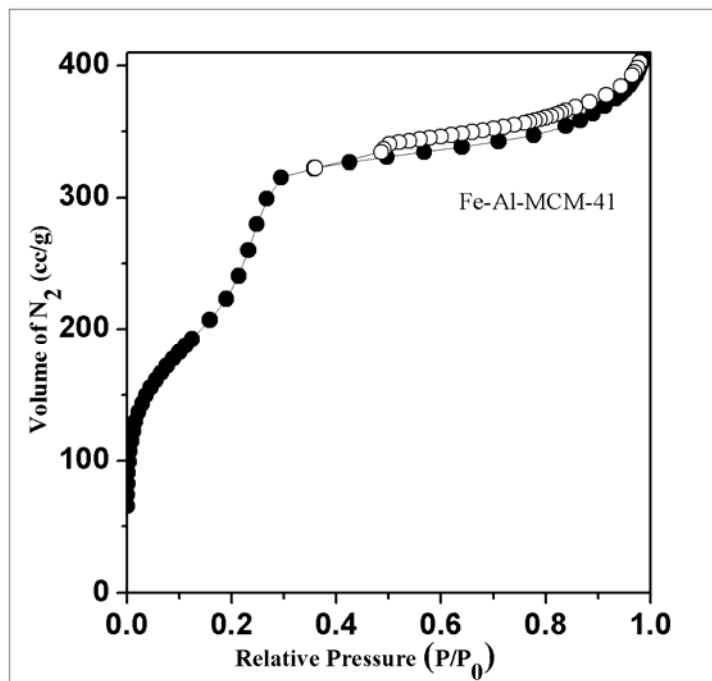


Figure S2. N₂ adsorption/desorption isotherms of Fe-Al-MCM-41. Adsorption points are marked by filled circles and desorption ones are by open circles

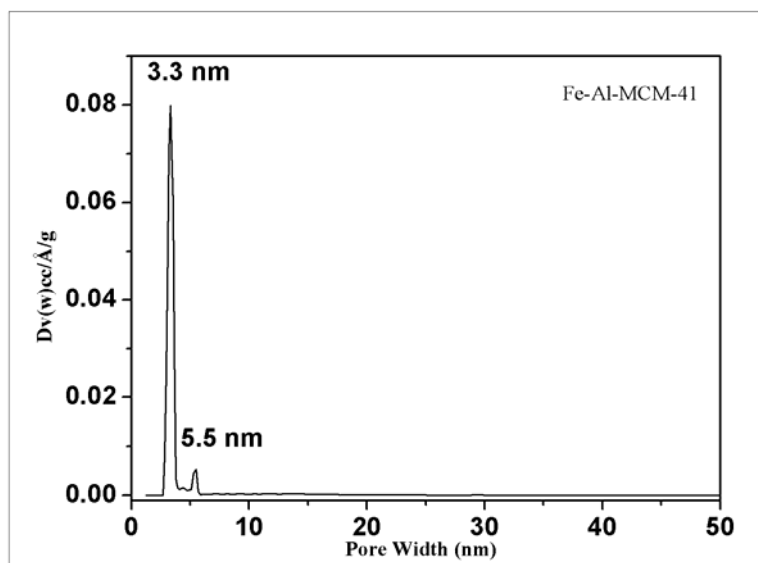


Figure S3. Pore Size Distribution Curve of Fe-Al-MCM-41

Mechanical stability of the catalyst Fe-Al-MCM-41

In order to test the mechanical stability of Fe-Al-MCM-41 X-ray diffraction of the recovered catalyst was measured. Details of the experiment given below:

Styrene (0.5 mmol) was added to a mixture of phenol (2 mmol) and Fe-Al-MCM-41 (0.065 g) in 5 ml of cyclohexane and the solution was stirred under 80 °C for 3 h with a stirring speed of 300 rpm. After the completion of the reaction, the mixture was allowed to cool down to room temperature. The catalyst was separated by filtration. This solid residue was washed with cyclohexane, methanol followed by dichloromethane and dried at 80 °C for 1h. This recovered Fe-Al-MCM-41 was subjected to XRD analysis [Fig S4(a)]. Then recovered Fe-Al-MCM-41 was re-calcined under flow of air at 540 °C for 6 h in order to remove any organic moiety that may be absorbed during reaction. XRD pattern of this re-calcined catalyst was also measured [Fig S4(b)]. It is clear from XRD patterns that the hexagonal pore structure of Al-MCM-41 was retained in both the cases. This indicates that the mechanical stability of the synthesized Fe-Al-MCM-41 is good enough to retain its mesoporosity during the course of the reaction.

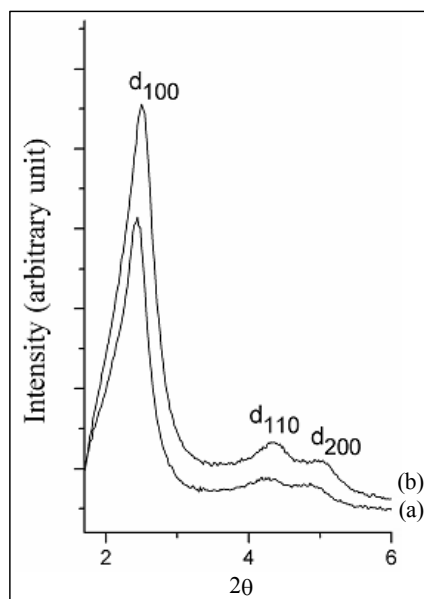


Figure S4. Small angle X-ray(SAX) diffraction patterns of (a) recovered Fe-Al-MCM-41, (b) recovered and re-calcined Fe-Al-MCM-41.

Influence of stirring speed in reactions

The effect of stirring speed was examined by varying the speed from 100 rpm to 1000 rpm. The results showed that the reaction is independent of stirring condition. Irrespective of the stirring speed the reactions were completed in 3 h in all cases.

Table S1. Reaction of Phenol and Styrene under different stirring speed ^a

Entry	Stirring speed (rpm)	Time [h]	Conversion [%] ^b	Yield [%] ^c
1	100	3	100	95
2	300	3	100	96
3	600	3	100	95
4	1000	3	100	94

^aReaction condition: 0.5 mmol of styrene, 2 mmol of phenol, 5 ml of cyclohexane, 65 mg Fe-Al-MCM-41, 80°C.

^bGC conversion of styrene. ^cGC yield of arylated products.

Reaction of Phenol and Styrene using different iron doped cheap aluminosilicates

Commercially available cheap aluminosilicates NaX and NaY were also used as supports. Reaction was performed using this modified aluminosilicates. To study the progress of the reaction the products were collected at different time intervals and identified and quantified by Gas Chromatograph. The results are given in Table S1 below:

Table S2. Reaction of Phenol and Styrene using iron containing microporous solids.^a

Entry	Catalyst	Time [h]	Conversion[%] ^b	Yield [%] ^c
1	Fe-NaX	24	3	0
2	Fe-NaY	24	4	0

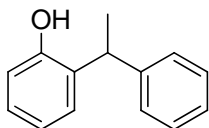
^aReaction conditions: 0.5 mmol of styrene, 2 mmol of phenol, 65 mg of catalyst, 5 ml cyclohexane, 80°C.

^bGC conversion of styrene. ^cGC yield of arylated products.

General experimental procedure of organic reaction and spectral data

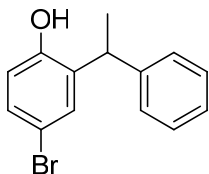
Styrene (0.5 mmol) was added to a mixture of phenol (2 mmol) and Fe-Al-MCM-41 (0.065 g) in 5 ml of cyclohexane. The solution was stirred under 80 °C for 4 h and the progress of the reaction at different time intervals were identified and quantified by Gas Chromatography. After completion of the reaction, the solution was cooled down and the catalyst was removed by filtration. The resulting crude mixture was gently evaporated under vacuo and purified by column chromatography on silica gel using appropriate solvent.

2-(1-Phenylethyl)phenol (3a):



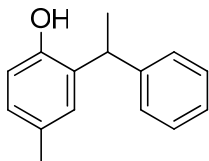
^1H NMR (300 MHz, CDCl_3) δ 7.34 -7.19 (m, 6H; CH), 7.17 -7.11 (m, 1H; CH), 6.98 -6.93 (m, 1H; CH), 6.78 -6.75 (m, 1H; CH), 4.69 (s, 1H; OH), 4.39 (q, J (H,H) = 7.2 Hz, 1H; CHCH₃), 1.64 (d, J (H,H) = 7.2 Hz, 3H; CH₃CH); ^{13}C NMR (75 MHz, CDCl_3) δ 152.7, 144.8, 131.4, 128.1, 127.4, 126.9, 125.9, 120.3, 115.4, 38.2, 20.4.

4-bromo-2-(1-phenylethyl)phenol (3b):



^1H NMR (300 MHz, CDCl_3) δ 7.34-7.20 (m, 7 H; CH), 6.64 (d, J (H, H) = 8.5 Hz, 1 H; CH), 4.74 (s, 1 H; OH), 4.32 (q, J (H,H) = 7.2 Hz, 1 H; CHCH₃), 1.60 (d, J (H,H) = 7.2 Hz, 3 H; CH₃CH); ^{13}C NMR (75 MHz, CDCl_3) δ 152.6, 144.5, 134.4, 130.7, 130.2, 128.8, 127.5, 126.7, 117.7, 113.1, 38.7, 20.9

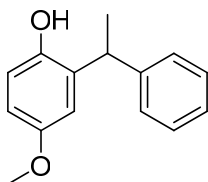
4-Methyl-2-(1-phenylethyl)phenol (3d):



^1H NMR (300 MHz, CDCl_3) δ 7.36-7.23 (m, 5 H; CH), 7.08 (d, J (H,H) = 1.8 Hz, 1 H; CH), 6.96 (dd, J

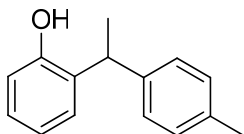
(H,H) = 8.0, 1.9 Hz, 1 H; *CH*), 6.67 (d, *J* (H,H) = 8.1 Hz, 1 H; *CH*), 4.69 (s, 1 H; *OH*), 4.40 (q, *J* (H,H) = 7.2 Hz, 1 H; *CHCH*₃), 2.33 (s, 3H; Ar*CH*₃), 1.67 (d, *J* (H,H) = 7.1 Hz, 3 H; *CH*₃*CH*); ¹³C NMR (75 MHz, CDCl₃) δ 151.0, 145.5, 131.7, 129.9, 128.6, 128.5, 127.8, 127.5, 126.3, 115.8, 38.7, 21.0, 20.7.

4-methoxy-2-(1-phenylethyl)phenol (3e):



¹H NMR (300 MHz, CDCl₃) δ 7.32-6.67 (m, 8 H; *CH*), 4.37-4.33 (m, 2H), 3.77 (s, 3 H; O*CH*₃), 1.62 (d, *J* (H, H) = 7.2 Hz, 3 H; *CH*₃*CH*); ¹³C NMR (75 MHz, CDCl₃) δ 153.8, 147.2, 145.0, 133.3, 128.7, 127.4, 126.4, 116.6, 114.3, 111.5, 55.7, 38.9, 21.9.

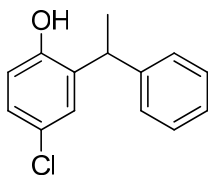
2-[1-(4-methylphenyl)ethyl]phenol (3h):



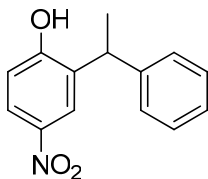
¹H NMR (300 MHz, CDCl₃) δ 7.32-6.96 (m, 7 H; *CH*), 6.78 (dd, *J* (H,H) = 7.9 Hz, 1 H; *CH*), 4.99 (s, 1 H; *OH*), 4.39 (q, *J* (H,H) = 7.2 Hz, 1 H; *CHCH*₃), 1.69 (d, *J* (H,H) = 7.8 Hz, 3 H; *CH*₃*CH*); ¹³C NMR (75 MHz, CDCl₃) δ 153.4, 142.3, 136.0, 132.2, 129.4, 129.0, 128.0, 127.5, 120.8, 116.0, 38.4, 21.1, 21.0.

New Products

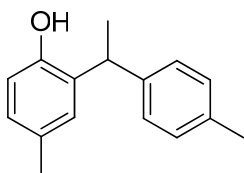
4-chloro-2-(1-phenylethyl)phenol (3c):



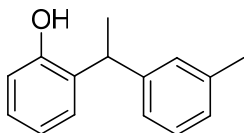
¹H NMR (300 MHz, CDCl₃) δ 7.34-7.23 (m, 6 H; *CH*), 7.08 (d, *J* (H,H) = 8.4 Hz, 1 H; *CH*), 6.68 (d, *J* (H,H) = 8.3 Hz, 1 H; *CH*), 4.32 (q, *J* (H,H) = 7.0 Hz, 1 H; *CHCH*₃), 1.61 (d, *J* (H,H) = 7.2 Hz, 3H; *CH*₃*CH*); ¹³C NMR (75 MHz, CDCl₃) δ 151.9, 144.6, 133.9, 128.8, 127.9, 127.5, 127.2, 126.7, 125.7, 117.2, 38.7, 20.9; IR(neat, liquid): ν_{max} = 1600, 1493, 1451, 1413, 1267, 1163, 1116, 812, 700 cm⁻¹; HRMS (ESI-TOF) (m/z): [M+Na]⁺, calcd. for C₁₄H₁₃ClONa : 255.0553, found 255.0545

4-nitro-2-(1-phenylethyl)phenol (3g):

^1H NMR (500 MHz, CDCl_3) δ 8.23 (d, J (H,H) = 3 Hz, 1 H; CH), 8.08 (dd, J (H,H) = 8.75 Hz, 1 H; CH), 7.36-7.25 (m, 5 H; CH), 6.85 (d, J (H,H) = 8.5 Hz, 1 H; CH), 4.40 (q, J (H,H) = 7.0 Hz, 1 H; CHCH₃), 1.70 (d, J (H,H) = 7 Hz, 3H; CH₃CH); ^{13}C NMR (126 MHz, CDCl_3) δ 159.2, 143.7, 141.9, 133.0, 129.2, 127.5, 127.2, 124.3, 124.2, 116.3, 38.9, 21.0; IR(neat, liquid): ν_{max} = 1588, 1514, 1484, 1323, 1274, 915, 793, 699 cm^{-1} ; HRMS (ESI-TOF) (m/z): $[\text{M}+\text{Na}]^+$, calcd. for $\text{C}_{14}\text{H}_{13}\text{NO}_3\text{Na}$: 266.0793, found 266.0791

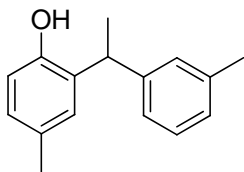
4-Methyl-2-[1-(4-methylphenyl)ethyl]phenol (3i):

^1H NMR (300 MHz, CDCl_3) δ 7.17-7.05 (m, 6 H; CH), 6.66 (d, J (H,H) = 8.1 Hz, 1 H; CH), 4.54 (s, 1 H; OH), 4.29 (q, J (H,H) = 7.2 Hz, 1 H; CHCH₃), 2.34 (s, 3 H; ArCH₃), 2.30 (s, 3 H; ArCH₃), 1.61 (d, J (H,H) = 7.2 Hz, 3 H; CH₃CH); ^{13}C NMR (75 MHz, CDCl_3) δ 151.1, 142.2, 136.0, 131.7, 129.9, 129.4, 128.4, 127.8, 127.3, 115.9, 38.5, 21.0, 20.9, 20.7; IR(neat, liquid): ν_{max} = 1609, 1509, 1453, 1258, 1185, 1119, 816 cm^{-1} ; HRMS (ESI-TOF) (m/z): $[\text{M}+\text{Na}]^+$, calcd. for $\text{C}_{16}\text{H}_{18}\text{ONa}$: 249.1255, found 249.1254

2-[1-(3-methylphenyl)ethyl]phenol (3j):

^1H NMR (300 MHz, CDCl_3) δ 7.28-6.94 (m, 7 H; CH), 6.77 (d, J (H,H) = 7.8 Hz, 1 H; CH), 4.78 (s, 1 H; OH), 4.34 (q, J (H,H) = 7.0 Hz, 1 H; CHCH₃), 2.33 (s, 3 H; ArCH₃), 1.64 (d, J (H,H) = 7.1 Hz, 3H; CH₃CH); ^{13}C NMR (75 MHz, CDCl_3) δ 153.4, 145.2, 138.4, 132.0, 128.7, 128.3, 127.9, 127.5, 127.3, 124.5, 120.9, 116.1, 38.8, 21.5, 21.1.; IR(neat, liquid): ν_{max} = 1605, 1505, 1454, 1257, 1189, 810, 705 cm^{-1} ; HRMS (ESI-TOF) (m/z): $[\text{M}+\text{Na}]^+$, calcd. for $\text{C}_{15}\text{H}_{16}\text{ONa}$: 235.1099, found 235.1097

4-Methyl-2-[1-(3-methylphenyl)ethyl]phenol (3k):

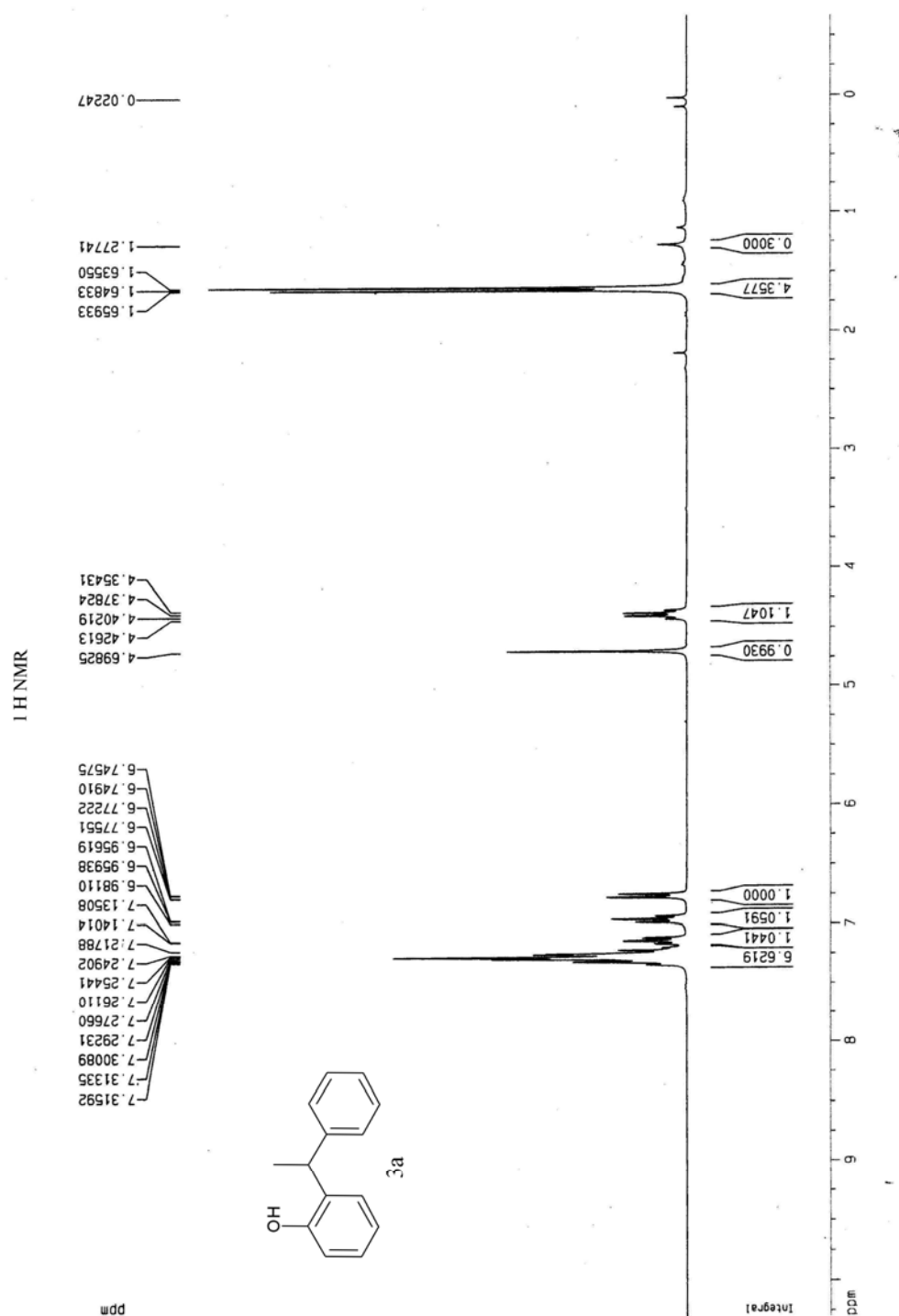


^1H NMR (300 MHz, CDCl_3) δ 7.20-6.91 (m, 6 H; CH), 6.67 (d, J (H,H) = 8.1 Hz, 1 H; CH), 4.55 (s, 1 H; OH), 4.28 (q, J (H,H) = 7.2 Hz, 1 H; CHCH_3), 2.33 (s, 3 H; ArCH_3), 2.31 (s, 3 H; ArCH_3), 1.62 (d, J (H,H) = 7.2 Hz, 3 H; CH_3CH); ^{13}C NMR (75 MHz, CDCl_3) δ 150.6, 144.7, 137.8, 131.1, 129.4, 128.0, 127.9, 127.7, 127.3, 126.7, 123.9, 115.4, 38.3, 20.9, 20.5, 20.2; IR(neat, liquid): ν_{max} = 1605, 1505, 1454, 1257, 1189, 810, 705 cm^{-1} ; HRMS (ESI-TOF) (m/z): $[\text{M}+\text{Na}]^+$, calcd. for $\text{C}_{16}\text{H}_{18}\text{ONa}$: 249.1255, found 249.1257

References of known compounds

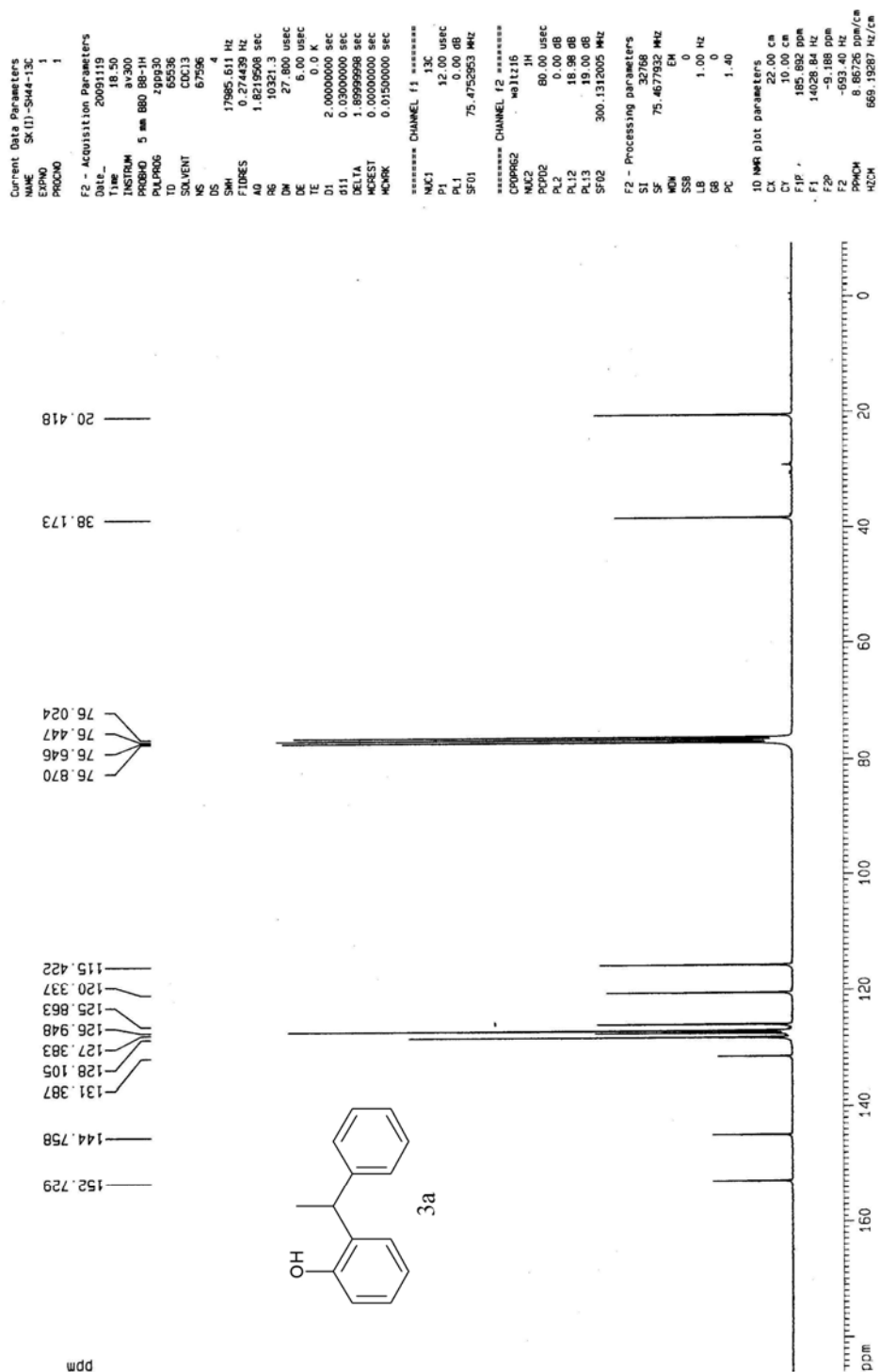
- 2-(1-Phenylethyl)phenol (3a): Sun, G.; Sun, H.; Wang, Z.; Zhou, M.-M. *Synlett*, **2008**, 1096-1100.
- 4-Methyl-2-(1-phenylethyl)phenol (3d): Sun, G.; Sun, H.; Wang, Z.; Zhou, M.-M. *Synlett*, **2008**, 1096-1100.
- 4-methoxy-2-(1-phenylethyl)phenol (3e): Jovel, I.; Mertins, K.; Kischel, J.; Zapf, A.; Beller, M. *Angew. Chem., Int. Ed.* **2005**, 44, 3913-3917.
- 4-bromo-2-(1-phenylethyl)phenol (3b): Jovel, I.; Mertins, K.; Kischel, J.; Zapf, A.; Beller, M. *Angew. Chem., Int. Ed.* **2005**, 44, 3913-3917.
- 2-[1-(4-methylphenyl)ethyl]phenol (3h): Das, B.; Krishnaiah, M.; Laxminarayana, K.; Damodar, K.; Kumar, D. N. *Chem. Lett.* **2009**, 38, 42-43.

¹H-NMR and ¹³C-NMR charts for all compounds

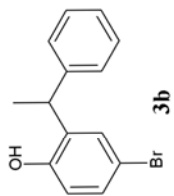


¹H-NMR of 2-(1-Phenylethyl)phenol (3a)

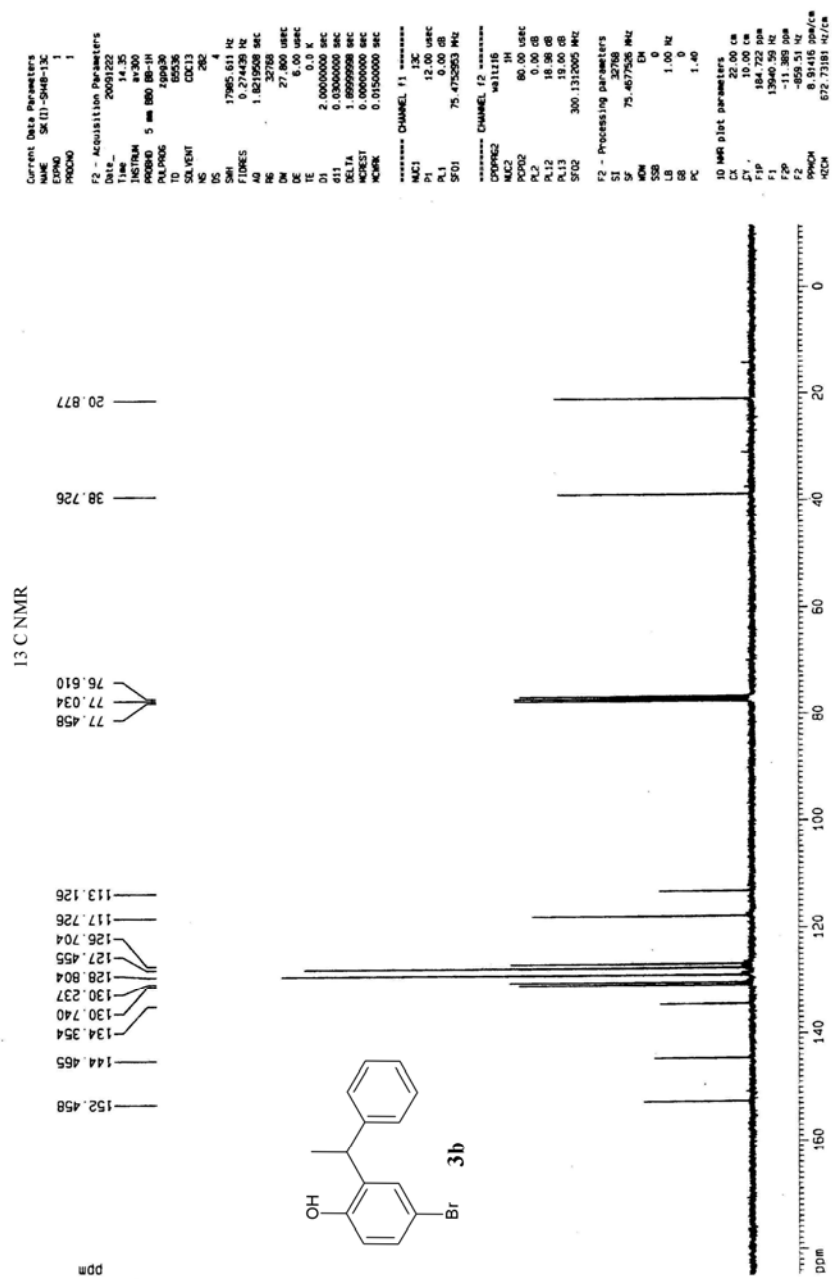
¹³C NMR



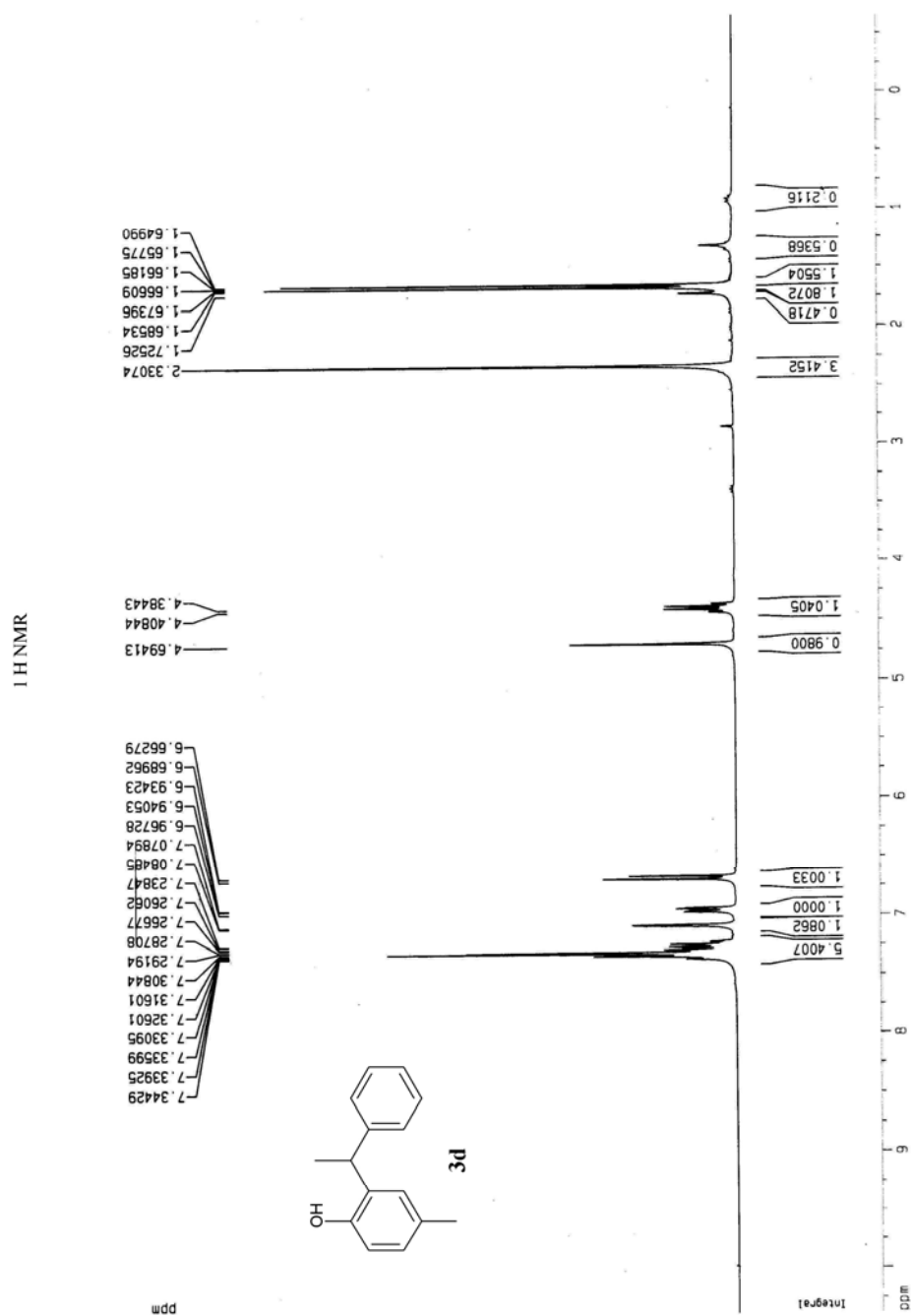
¹³C-NMR of 2-(1-Phenylethyl)phenol (3a)



S13



¹³C-NMR of 4-bromo-2-(1-phenylethyl)phenol (**3b**)

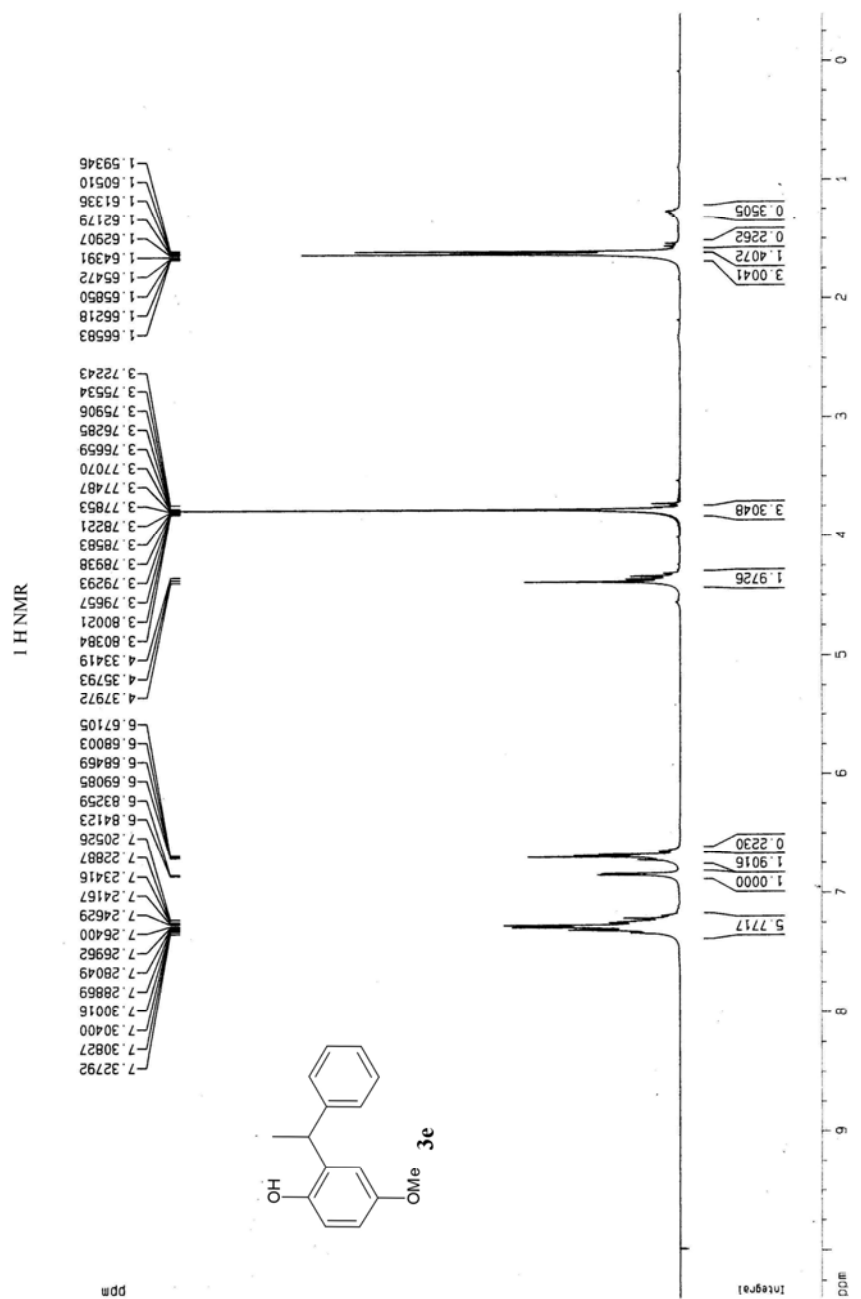


¹H-NMR of 4-Methyl-2-(1-phenylethyl)phenol (3d)

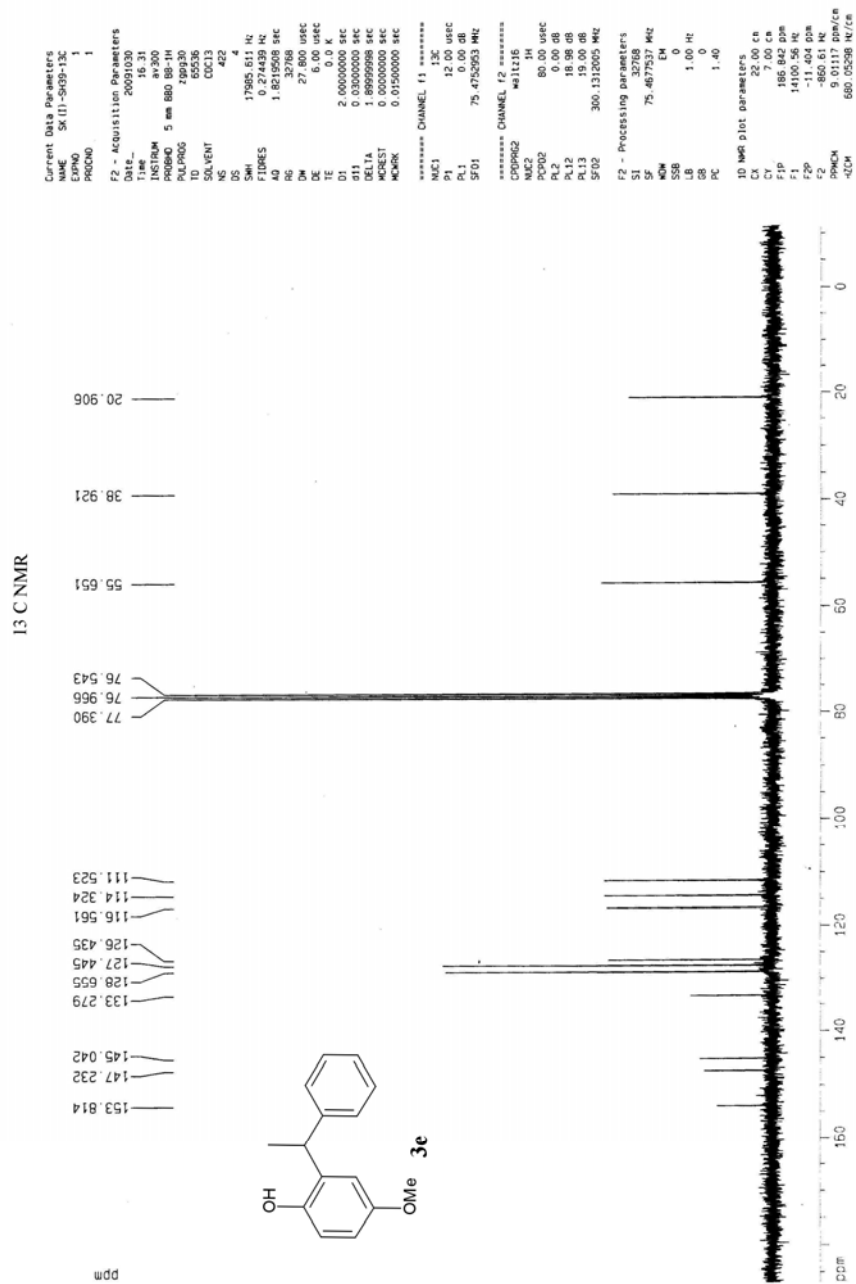
Chemical structure of **3d**: CC1=CC=C(C=C1)C(=C2C=CC(=C2)C=C2C=CC(=C2)C)C

Chemical Shift (ppm)	Integration
7.74	1.00
7.45	1.00
7.26	1.00
7.03	1.00
6.88	1.00
6.85	1.00
6.82	1.00
6.79	1.00
6.76	1.00
6.73	1.00
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5.95	1.00
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5.53	1.00
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5.02	1.00
4.99	1.00
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4.87	1.00
4.84	1.00
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4.78	1.00
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3.31	1.00
3.28	1.00
3.25	1.00
3.22	1.00
3.19	1.00
3.16	1.00
3.13	1.00
3.10	1.00
3.07	1.00
3.04	1.00
3.01	1.00
2.98	1.00
2.95	1.00
2.92	1.00
2.89	1.00
2.86	1.00
2.83	1.00
2.80	1.00
2.77	1.00
2.74	1.00
2.71	1.00
2.68	1.00
2.65	1.00
2.62	1.00
2.59	1.00
2.56	1.00
2.53	1.00
2.50	1.00
2.47	1.00
2.44	1.00
2.41	1.00
2.38	1.00
2.35	1.00
2.32	1.00
2.29	1.00
2.26	1.00
2.23	1.00
2.20	1.00
2.17	1.00
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2.08	1.00
2.05	1.00
2.02	1.00
1.99	1

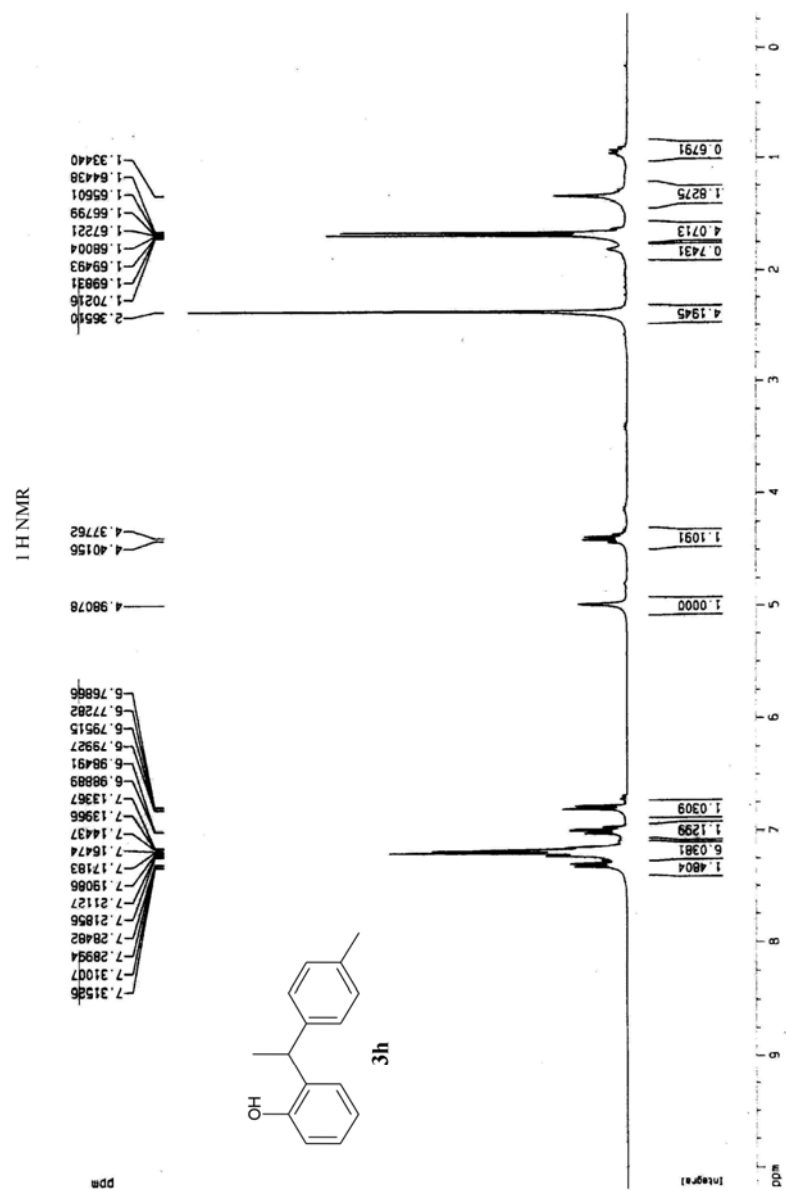
S16



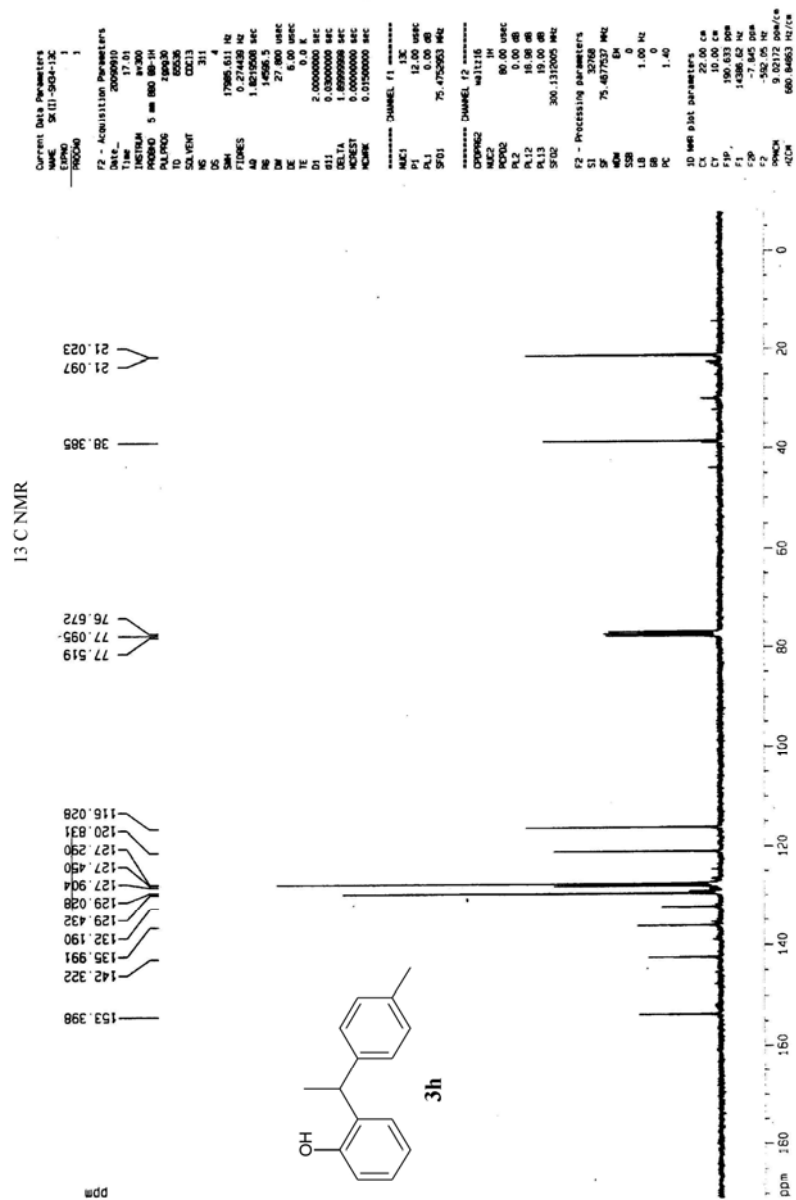
¹H-NMR of 4-methoxy-2-(1-phenylethyl)phenol (**3e**)



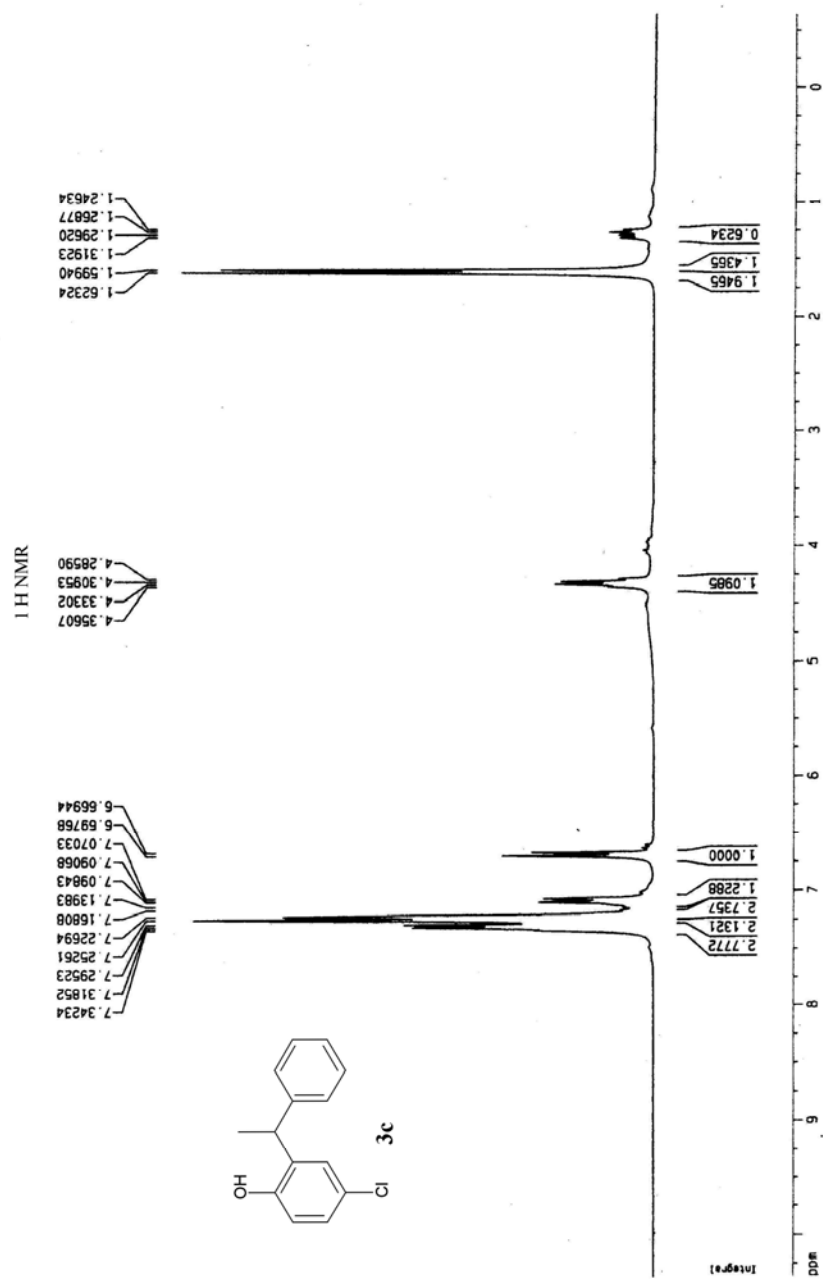
¹³C-NMR of 4-methoxy-2-(1-phenylethyl)phenol (3e)



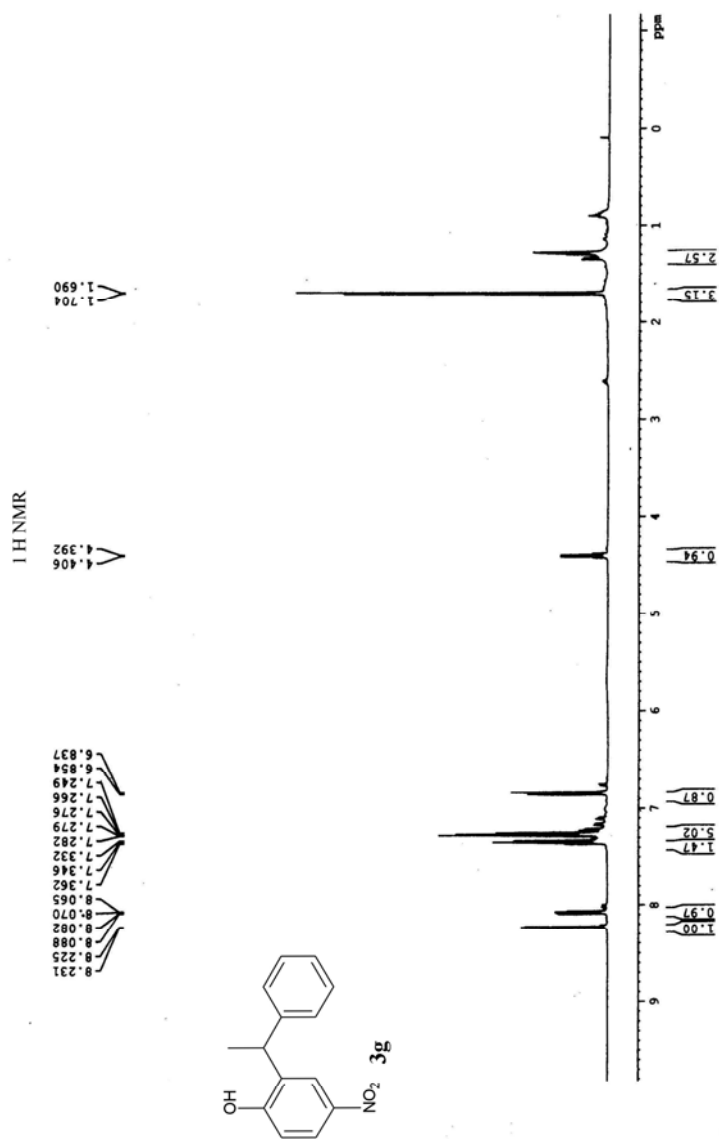
¹H-NMR of 2-[1-(4-methylphenyl)ethyl]phenol (3h)



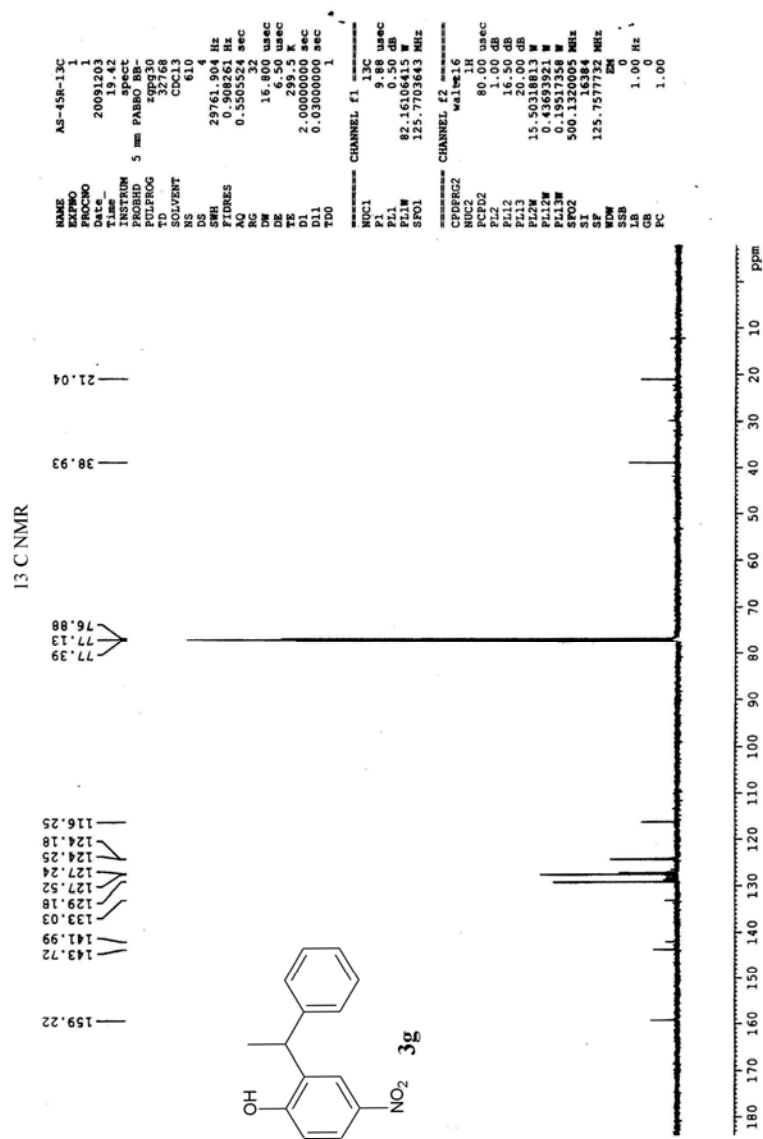
¹³C-NMR of 2-[1-(4-methylphenyl)ethyl]phenol (3h)



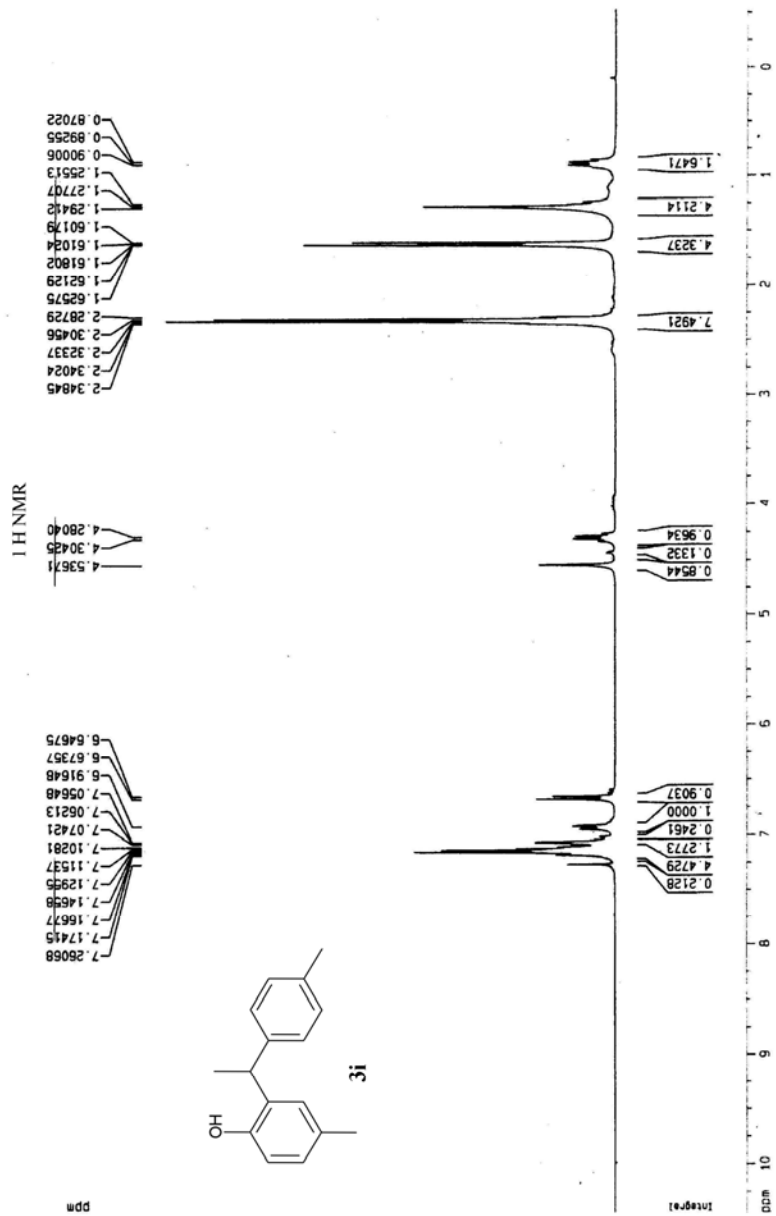
¹H-NMR of 4-chloro-2-(1-phenylethyl)phenol (3c)



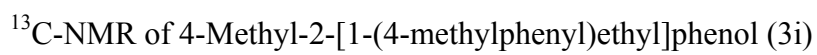
¹H-NMR of 4-nitro-2-(1-phenylethyl)phenol (3g)

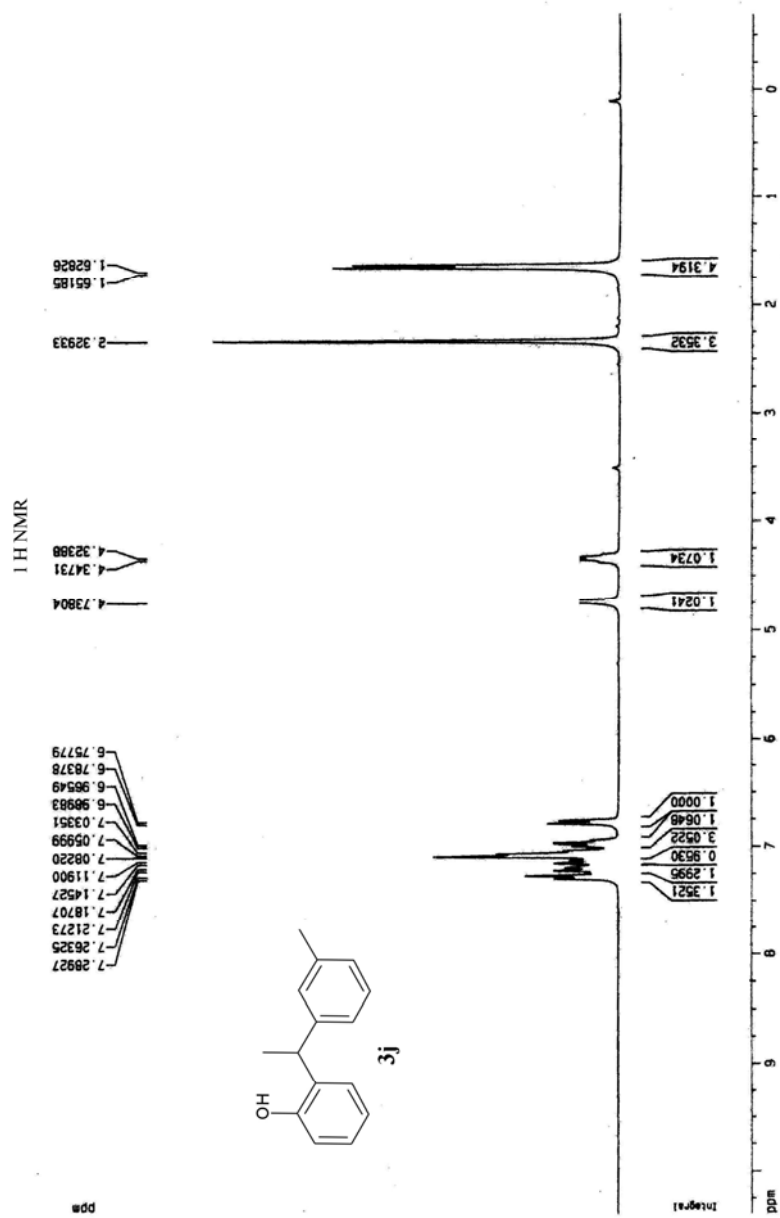


¹³C-NMR of 4-nitro-2-(1-phenylethyl)phenol (3g)

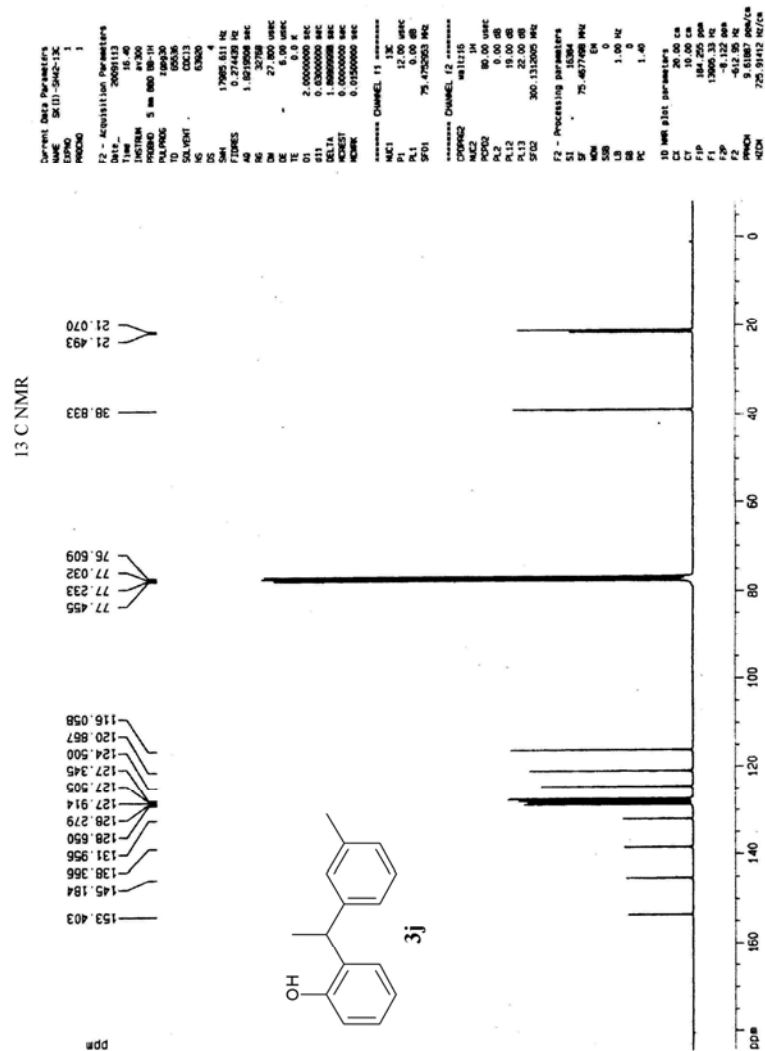


¹H-NMR of 4-Methyl-2-[1-(4-methylphenyl)ethyl]phenol (3i)

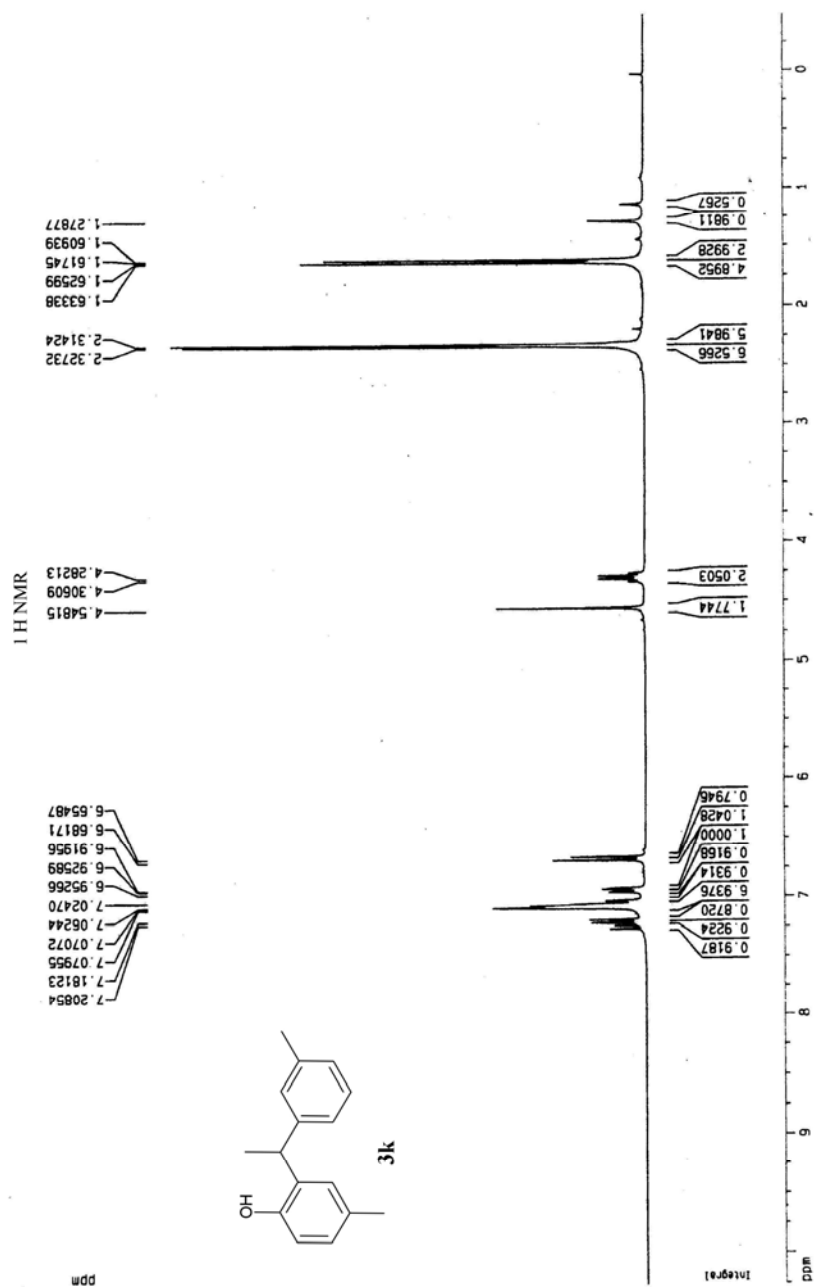




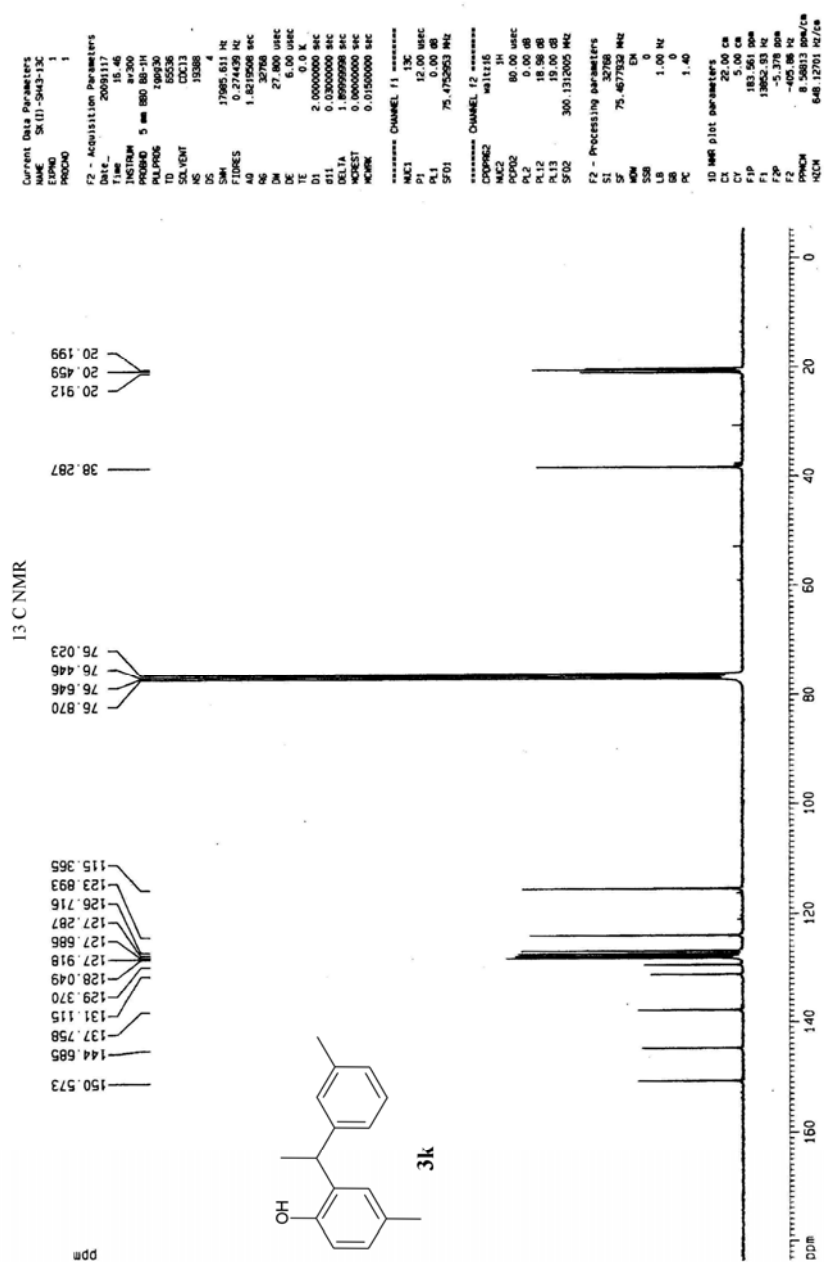
¹H-NMR of 2-[1-(3-methylphenyl)ethyl]phenol (3j)



¹³C-NMR of 2-[1-(3-methylphenyl)ethyl]phenol (3j)



¹H-NMR of 4-Methyl-2-[1-(3-methylphenyl)ethyl]phenol (3k)



¹³C-NMR of 4-Methyl-2-[1-(3-methylphenyl)ethyl]phenol (3k)