Electronic Supplementary Information (ESI)

Reaction-activated Palladium Catalyst for Dehydrogenation of Substituted Cyclohexanones to Phenols and H_2 without Oxidants and Hydrogen Acceptors

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1. General specifications

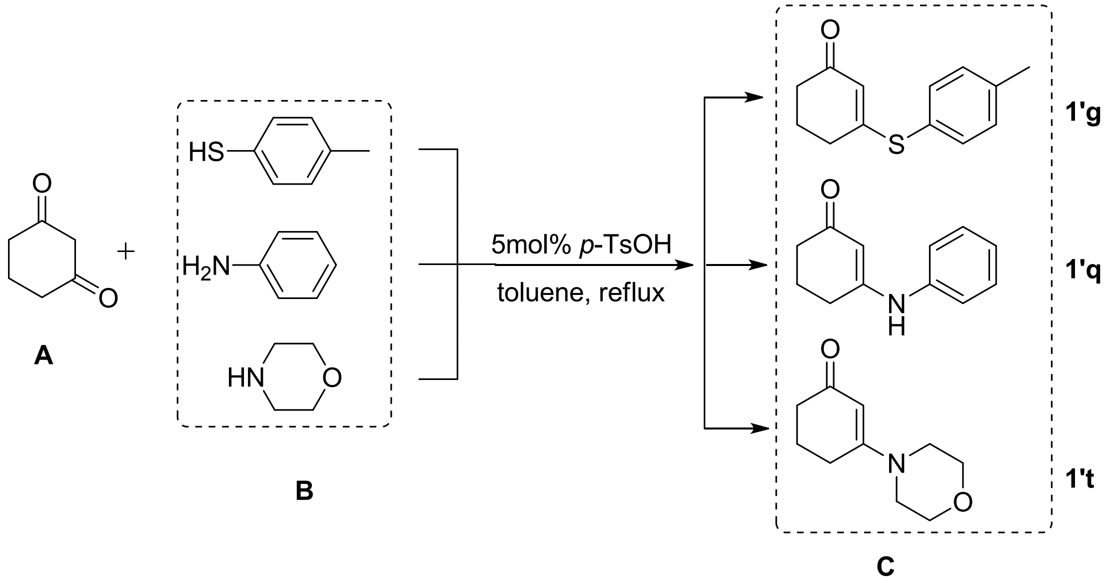
The Pd/C was first washed with acetone and then was dried under reduced pressure at 100℃ before used. Solvents were purified prior to use by refluxing and distilling over CaH_2 under an argon atmosphere. All the other chemical reagents were obtained from commercial sources and used without further purification. Melting points were measured in open glass capillaries on a Temperature Apparatus and are uncorrected. The purification of compounds was accomplished by chromatography with petroleum ether and ethyl acetate as eluents. ^1H NMR (400MHz) and ^{13}C NMR (100 MHz) spectra were obtained on a Bruker DRX-400 NMR as solutions in $CDCl_3$.Chemical shifts are reported in parts per million and coupling constants are in hertz. The reaction mixture was filtered through 300-400 mesh silica gel and then injected into the GC equipped with FID detector (Agilent Technologies, GC7890A) for analysis. General GC conditions: HP-5 column, 30 m×0.32 mm (id); FID detector; injection: 0.2 μL; carrier gas: N_2; carrier gas rate: 1.2 mL/min; area normalization. The reaction was detected under the conditions: column temperature: 75 °C for 2 min, rising to 300 °C at a rate of 10 °C/min. The detection of H_2 was carried out with GC with TCD detector (Shimadzu GC-2014C, stationary phase: AE5A MS 3m*3mm（OD）).The chemical structures of products were confirmed by GC-MS (Agilent Technologies, GC7683B, MS5973) and ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz).

2. General procedure for the dehydrogenation of cyclic ketones to the phenols and H_2

To a two-necks flask loaded with a stir bar was added the cyclic ketone (0.5 mmol), K_2CO_3 (0.1 mmol), Pd/C (26.5 mg, 0.025 mmol Pd) and DMA (1 ml). The flask was first degassed and then sealed with a gas mixture (30 vol% H_2 and 70 vol% N_2) balloon. The reaction was heated in an oil bath to 150 °C with vigorous stirring for an appropriate time (the specific reaction time see table 2-3). The reaction was detected by GC. After the reaction was completed, Pd/C was filtrated. Then 2 ml water was added to the filtrate and a certain amount of acid was also added to neutralize the filtrate. Then the filtrate was extracted with EtOAc (3 ml ×3) and the combined organic layer was dried over anhydrous Na_2SO_4. After that the solvent evaporated under reduced pressure. The residue was loaded onto a silica gel column and purified by flash chromatography (hexanes/EtOAc mixture, gradient from 0–30%) to afford the pure product.

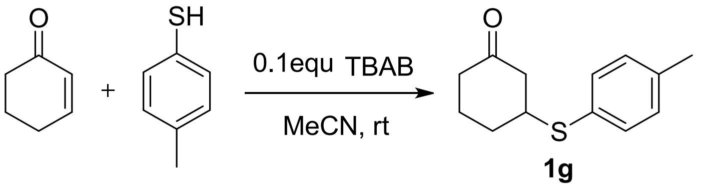
3. General Procedure for Synthesis of substrates

Synthesis of 3 - substituted cyclohexenone compounds



Dehydrated to form compounds C.[1] A mixture of cyclohexane-1,3-dione (11.2 g, 0.1 mol) and **B** (0.11 mol，1.1eq) in toluene (150 ml) was refluxed at a Dean-Stark trap until the separation of H_2O had finished (ca. 3 h).The solvent was removed in vacuo and the residual solid or viscous oil was triturated (EtOAc) to give **C** [**1′ g**(19.g, 91% yield)，**1′ q**(17.4g, 93%yield)，**1′ t**(15.7, 87%yield)]as a crystalline solid. If not, the crude product was further purified by silica gel chromatography.

Synthesis of 1g.[2,3]



A mixture of cyclohexenone (96.1 mg, 10 mmol) and *p*-thiocresol (1.37 g, 11 mmol) in MeCN (20 ml) was stirred at room temperature. Then tetrabutyl ammonium bromide(TBAB)(32.2 mg, 1 mmol) was added. The reaction mixture was stirred at ambient temperature for an appropriate reaction time as monitored by TLC After the reaction was completed, 10ml water was added. Then the mixture was extracted 3 times with EtOAc. The organic layer was dried with anhydrous Na_2SO_4. After the solvent was removed under reduced pressure, the crude product was purified by silica

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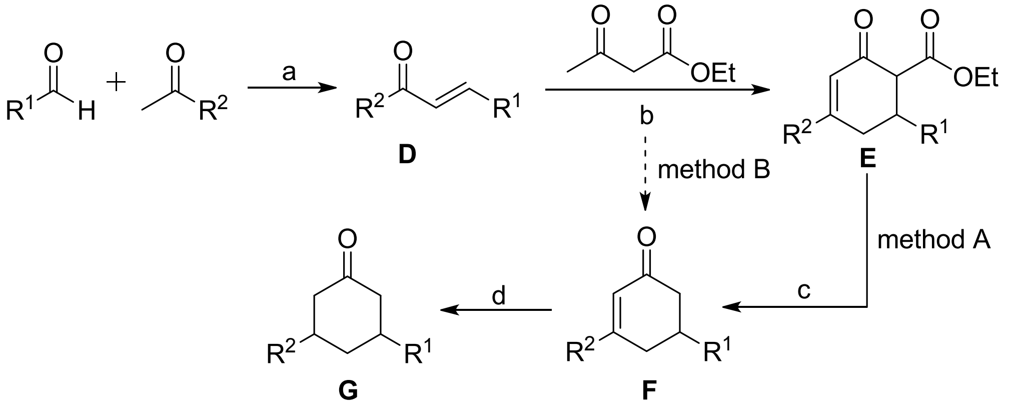
[1] Hemmerling, H.-J.; Reiss, G. *Synthesis* **2009**, 6, 0985-0999.

gel chromatography to provide **1g** (light yellow oil, 1.76g, 80% yield). ^{1}H NMR (400MHz, $CDCl_3$) δ 7.34(d, J=8.0Hz, 2H), 7.14(d, J=8.0Hz, 2H), 3.32-3.39(m, 1H), 2.67(dd, J=4.4, 14.4Hz, 1H), 2.38(d, J=10.8Hz, 1H), 2.35(s, 3H), 2.29-2.33(m, 2H), 2.09-2.18(m, 2H).

General Procedure for Synthesis of G



Reaction conditions:(a) NaOH, EtOH/H_2O(1:1), rt. (b) NaOH, EtOH, reflux. (c).NaOH, EtOH/H_2O=1:1,reflux. (d) Pd/C, H_2, MeOH.

Aldol condensation to form D.[4] A mixture of aldehyde (0.1 mol) and methyl ketone (0.11 mol) in 150 ml EtOH/H_2O (1:1) was stirred at room temperature for about 5min. Then NaOH (5.2 g, 0.13 mol) was slowly added. The mixture was stirred for an appropriate reaction time as monitored by TLC. After the reaction was completed, a large amount of solids would be precipitated. Then the reaction mixture was filtrated and the solid filtered out is the desired product. Without any purification, in most cases, the purity of the products was found to be >99 %. Products are directly used in the next reaction. If there was no solids precipitate, then the mixture was neutralized with 1N HCl. The mixture was extracted 3 times with EtOAc. The organic layer was dried with Na_2SO_4. After the solvent was removed under reduced pressure, the crude product was purified by silica gel chromatography to provide D.

Robinson annulation to form E.[5] To a 250 mL three-necked, round-bottomed flask was added chalcone (D, 0.05 mol), ethyl acetoacetate (7.8 g, 0.06 mol), NaOH (2.88 g, 0.072 mol), and anhydrous ethanol (80 ml). The reaction was heated in an oil bath to

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[2] Ménand, M.; Dalla, V. *Synthesis* **2005**, 1, 0095-0098.

[3] Chen, C.; Lin, Y.; Liu, C. *Tetrahedron* **2009**, 65, 10470-10476.

[4] Srinivasan, B.; Johnson, T. E.; Lad, R.; Xing, C. *J. Med. Chem.* **2009**, 52,7228-7235.

[5] Li, J. T.; Cui, Y.; Chen, G. F.; Cheng, Z. L. *Syn. Commun.* **2003***,* 33, 353-359 .

reflux with vigorous stirring for an appropriate time (the reaction was continued until crystals were appeared or chalcone was disappeared indicated by TLC). After cooling a period of time, the precipitate was isolated by filtration, washed with cool water to neutral, dried, and crystallized from ethanol. The authenticity of the products was confirmed by NMR.

Decarboxylation to form F.[6]

Method A: To a 100ml three-necked, round-bottomed flask was added 10mmol E, NaOH (2.0 g, 0.05 mol) and 60ml ethanol/H_2O (1:1). The reaction was heated in an oil bath to reflux with vigorous stirring for an appropriate time as monitored by TLC. After the reaction had finished (ca. 3 h).The solvent was removed in vacuo and the residual solid or viscous oil was triturated (EtOAc) to give **F** as a crystalline solid. If not, the crude product was further purified by silica gel chromatography to afford the pure product.

Method B: In the reaction of synthesis of E, when chalcone was disappeared indicated by TLC, 80 ml water was added. Then NaOH(14.4 g, 0.36 mol) was following added and continued to reflux. Pure product was isolated by using the same procedure as described in method A.

Hydrogenation to form G.[7] Compound F(5 mmol) were placed in a 50 ml flask and immersed in 30 ml methanol, followed by Pd/C (10% wt). The reaction mixture was stirred at ambient temperature with hydrogen at atmospheric pressure (using hydrogen filled balloons). On completion, the reaction mixture was filtered. The solvent was removed in vacuo and the residual solid or viscous oil was triturated (EtOAc) to give **G**. If not, the crude product was further purified by silica gel chromatography.

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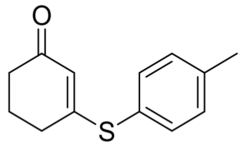
[6] Qi, S.; Shi, K.; Gao, H.; Liu, Q.; Wang, H. *Molecules* **2007**, 12, 988-996.

[7] Hossain, S.; Jin, M. J.; Park, J.; Yingjie, Q.; Yang, D. A. *Catal Lett.* **2013**, 143, 122-

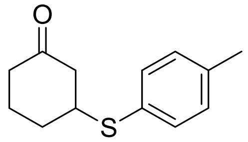
125.

4. Characterization Data of Compounds



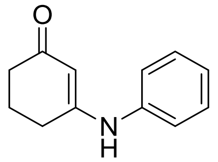
1'g: *3-(p-tolylthio)cyclohex-2-enone*

Yellow solid. Yield 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 7.90 Hz, 2H), 7.22 (d, J = 7.82 Hz, 2H), 5.45 (s, 1H), 2.53 (t, J = 6.01 Hz, 2H), 2.37 (d, J = 9.47 Hz, 5H), 2.05 (m, 2H).



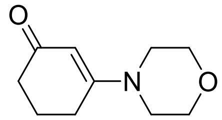
1g: *3-(p-tolylthio)cyclohexanone*

Yellow oil. Yield 80%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34(d, *J*=8.0Hz, 2H), 7.14(d, J=8.0Hz, 2H), 3.32-3.39(m, 1H), 2.67(dd, J=4.4Hz, 14.4Hz, 1H), 2.29-2.39(m, 6H), 2.09-2.19(m, 2H), 1.67-1.74(m, 2H).



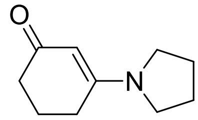
1'q: *3-phenylamino-2-cyclohexenone*

Yellow solid. Yield 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33(t, 2H), 7.17(t, 3H), 6.76(s, 1H), 5.58(s, 1H), 2.52(t, 2H), 2.36(t, 2H), 2.0-2.06(m,2H).



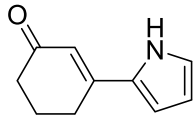
1' t: *3-morpholinocyclohex-2-enone*

Yellow oil. Yield 87%. ^{1}H NMR (400 MHz,$CDCl_3$) δ 5.28(s, 1H), 3.75(t, *J*=4.8Hz, 4H), 3.32(t, *J*=5.2Hz, 4H), 2.42(t, *J*=6.4Hz, 2H), 2.31(t, *J*=6.4Hz, 2H), 2.01(m, 2H).



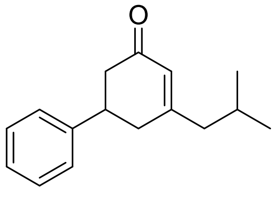
1'r: *3-(pyrrolidin-1-yl)cyclohex-2-enone*

Gray solid. Yield 76%. ^{1}H NMR (400 MHz,$CDCl_3$) δ 5.05(s, 1H), 3.45(t, *J*=5.6Hz, 2H), 3.23(m, 2H), 2.46(t, *J*=6.4Hz, 2H), 2.29(t, *J*=6.4Hz, 2H), 2.00(m, 6H).



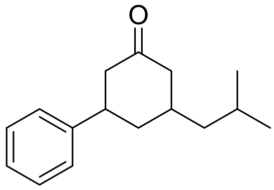
1's: *3-(1H-pyrrol-2-yl)cyclohex-2-enone*

Yellow solid. Yield 78%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.77(s, 1H), 7.07(s, 1H), 6.67(s, 1H), 6.39(s, 1H), 6.32(q, *J*=3.6Hz, 6.0Hz, 1H), 2.74(t, *J*=6.0Hz, 2H), 2.47(t, *J*=6.4Hz, 2H), 2.11(m, 2H).



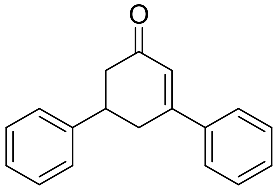
1'k: *5-phenyl-3-isobuty-2-cyclohexen-1-one*

Yellow solid. Yield 66%.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37(t, J=7.2Hz, 2H), 7.30(m, 3H), 5.98(s, 1H), 3.29-3.37(m, 1H), 2.52- 2.72(m, 4H), 2.11-2.22(m, 2H), 1.86-1.98(m, 1H), 0.95(dd, J= 10Hz, 6H).



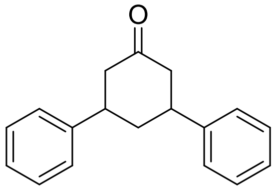
1k: *3-isobutyl-5-phenyl-cyclohexanone*

White solid. Yield 87%.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34(t, *J*= 7.2Hz, 2H), 7.22-7.25(m, 3H), 2.93-3.01(m, 1H), 2.45-2.60 (m, 3H), 1.90-2.11(m, 3H), 1.61-1.73(m, 1H), 1.49-1.58(m, 1H), 1.19-1.32(m, 2H), 0.88(d, *J*=6.8Hz, 6H).



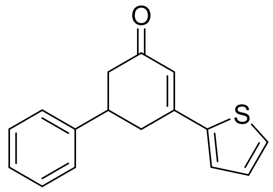
1'h: *3,5-diphenyl-2-cyclohexen-1-one*

Yellow solid. Yield 73%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.60(m, 2H), 7.39-7.45(m, 5H), 7.30-7.35(m, 3H), 6.55(d, J=2Hz, 1H), 3.45-3.54(m, 1H), 3.07-3.13(m, 1H), 2.93-3.0(m, 1H), 2.72-2.84(m, 2H).



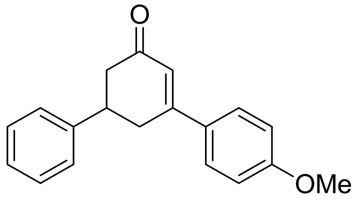
1h: *3,5-diphenyl-cyclohexanone*

White solid. Yield 91%.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34(t, *J*=7.6Hz, 4H), 7.22-7.27(m, 6H), 3.09-3.17(m, 2H), 2.58-2.71(m, 4H), 2.27-2.31(m, 1H), 2.05-2.14(m, 1H).



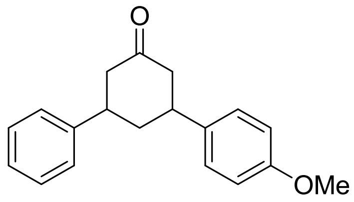
1'w: *5-phenyl-3-(2-thienyl)- 2-cyclohexen-1-one*

Brown solid. Yield 57%.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 5.04 Hz, 1H), 7.37 (dd, J = 9.50, 5.47 Hz, 3H), 7.33-7.25 (m, 3H), 7.08 (t, J = 4.33 Hz, 1H), 6.51 (s, 1H), 3.50-3.36 (m, 1H), 3.09 (dd, J = 17.47, 4.25 Hz, 1H), 2.93-2.81 (m, 1H), 2.71 (m, 2H).



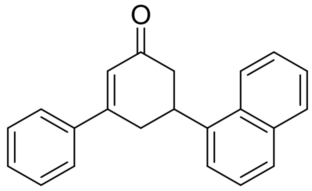
1'o: *3-(4-methoxyphenyl)-5-phenyl-2-cyclohexen-1-one*

Yellow solid. Yield 64%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.56 (m, 2H), 7.38(t, J=7.6Hz, 2H), 7.27-7.32(m, 3H), 6.91-6.95 (m, 2H), 6.49(d, *J*=2Hz, 1H), 3.85(s, 3H), 3.40-3.49(m, 1H), 3.04-3.10(m, 1H), 2.84-2.92(m, 1H), 2.67-2.79(m, 2H).



1o: *3-(4-methoxyphenyl)-5-phenyl-cyclohexanone*

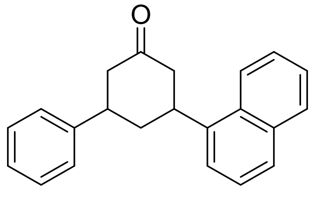
White solid. Yield 77%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14-7.32 (m, 7H), 6.84(d, *J*=7.6Hz, 2H), 3.78(s, 3H), 2.71-2.80(m, 2H), 2.24(d, *J*=7.2Hz, 2H), 2.01(d, J=12.4Hz, 1H), 1.46-1.58(m, 3H).



1'n: *3-phenyl-5-naphthalen-1-yl-2-cyclohexen-1-one*

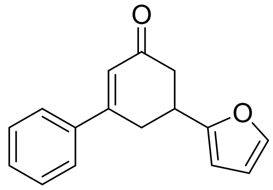
Yellow solid. Yield 59%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.36 Hz, 1H), 7.86 (dd, J = 9.36, 7.74 Hz, 1H), 7.81-7.74 (m, 1H), 7.49 (ddd, J = 19.96, 11.67, 5.96 Hz, 6H), 7.36 (dd, J = 9.85, 4.92 Hz, 3H), 6.58 (s, 1H), 4.36-4.20 (m, 1H), 3.20 (dd, J

= 17.70, 3.98 Hz, 1H), 2.94 (m, 3H).



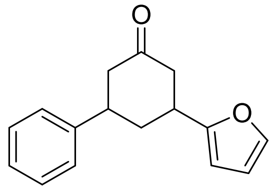
1n:*3-(naphthalen-1-yl)-5-phenyl-cyclohexanone*

White solid. Yield 72%. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.06 (d, J = 8.39 Hz, 1H), 7.87 (d, J = 8.00 Hz, 1H), 7.76 (dd, J = 5.88, 3.25 Hz, 1H), 7.50 (ddd, J = 12.91, 10.44, 5.14 Hz, 4H), 7.29 (tdd, J = 21.03, 14.16, 7.06 Hz, 5H), 4.04-3.89 (m, 1H), 3.30 (tt, J = 12.66, 3.33 Hz, 1H), 2.77 (tdd, J = 26.99, 22.34, 7.70 Hz, 4H), 2.44 (d, J = 13.19 Hz, 1H), 2.25 (q, J = 12.44 Hz, 1H).



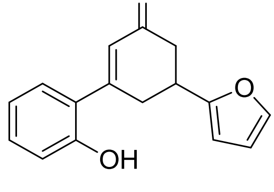
1'i: *5-(2-furanyl)-3-phenyl-2-cyclohexen-1-one*

Light yellow solid. Yield 66%. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.53 (dd, J = 12.68, 9.20 Hz, 2H), 7.44-7.36 (m, 3H), 7.34 (s, 1H), 6.45 (s, 1H), 6.31 (s, 1H), 6.10 (d, J = 2.53 Hz, 1H), 3.59-3.46 (m, 1H), 3.12 (dd, J = 17.74, 4.40 Hz, 1H), 2.93 (dd, J = 17.72, 9.77 Hz, 1H), 2.81 (dd, J = 16.52, 4.21 Hz, 1H), 2.66 (dd, J = 16.48, 11.77 Hz, 1H).



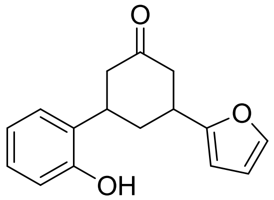
1r: *3-(furan-2-yl)-5-phenyl-cyclohexanone*

White solid. Yield 78%.^{1}H NMR (400 MHz, CDCl$_3$) δ 7.35-7.28 (m, 3H), 7.25-7.19 (m, 3H), 6.30-6.26 (m, 1H), 6.03 (d, J = 2.97 Hz, 1H), 3.20 (tt, J = 12.81, 3.54 Hz, 1H), 3.05 (tt, J = 12.79, 3.52 Hz, 1H), 2.81-2.71 (m, 1H), 2.59 (m, 3H), 2.40 (dd, J = 18.44, 7.00 Hz, 1H), 2.00 (q, J = 12.58 Hz, 1H).



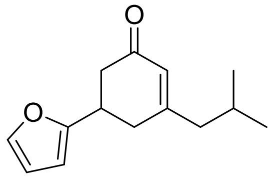
1'm: *5-(2-furanyl)-3-(2-hydroxyphenyl)-2-cyclohexen-1-one*

Orange solid. Yield 58%. ^{1}HNMR [400 MHz, $(CD_3)_2SO$] δ 10.02 (s, 1H), 7.57 (s, 1H), 7.24 (dd, J = 15.46, 7.73 Hz, 2H), 6.93 (d, J = 8.09 Hz, 1H), 6.85 (t, J = 7.48 Hz, 1H), 6.39 (s, 1H), 6.29-6.18 (m, 2H), 3.59-3.50 (m, 1H), 3.12 (dd, J = 17.74, 4.25 Hz, 1H), 2.96 (dd, J = 17.74, 9.37 Hz, 1H), 2.67 (m, 2H).



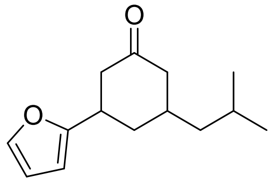
1m: *3-(furan-2-yl)-5-(2-hydroxyphenyl)-cyclohexanone*

White solid. Yield 75%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 10.76 Hz, 1H), 7.18 (d, J = 7.55 Hz, 1H), 7.10 (t, J = 7.44 Hz, 1H), 6.90 (t, J = 7.46 Hz, 1H), 6.82 (d, J = 7.94 Hz, 1H), 6.53 (s, 1H), 6.30 (s, 1H), 6.05 (d, J = 2.83 Hz, 1H), 3.47 (dd, J = 17.83, 7.83 Hz, 1H), 3.32-3.18 (m, 1H), 2.80 (d, J = 13.93 Hz, 2H), 2.58 (td, J = 22.02, 13.69 Hz, 2H), 2.40 (d, J = 13.01 Hz, 1H), 2.13 (q, J = 12.58 Hz, 1H).



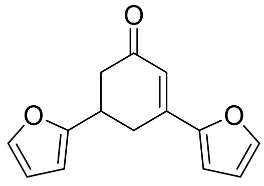
1'l: *5-(2-furanyl)-3-isobuty -2-cyclohexen-1-one*

Red-brown oil, Yield 62%.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J*=1.2Hz, 1H), 6.30-6.31(m, 1H), 6.05(d, *J*=3.2Hz, 1H), 5.91(s, 1H), 3.38-3.45(m, 1H), 2.71-2.76(m, 1H), 2.48-2.66 (m, 3H), 2.07-2.18(m, 2H), 1.84-1.94(m, 1H), 0.90(dd, *J*=6.4Hz, 18.4Hz, 6H).



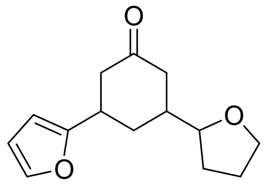
1l: *3-(furan-2-yl)-5-isobutyl-cyclohexanone*

White solid. Yield 76%.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32(s, 1H), 6.29(s,1H), 6.01(s,1H), 3.07(t, *J*=12.4Hz, 1H), 2.67(d, *J*= 13.6Hz, 1H), 2.45(t, *J*=12.8Hz, 2H), 2.23(d, *J*=9.6Hz, 1H), 1.91-2.03(m, 2H), 1.66-1.71(m, 1H), 1.45(q, *J*=12Hz,24Hz, 1H), 1.18-1.32(m, 2H), 0.89(d, J=6.4Hz, 6H).



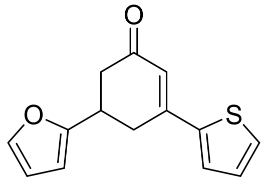
1'j: *3,5-di(furan-2-yl)-2-cyclohexen-1-one*

Light yellow solid. Yield 69%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57(d, *J*=1.6Hz, 1H), 7.39(d, *J*=1.2Hz, 1H), 6.81(d, *J*=3.2Hz, 1H), 6.54-6.56(m, 2H), 6.34-6.35(m, 1H), 6.13(d, *J*=3.2Hz, 1H), 3.53-3.60(m, 1H), 3.07-3.13(m, 1H), 2.80-2.87(m, 2H), 2.66-2.73(m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 156.3,152.0, 145.5, 145.4, 141.8, 120.9, 113.1, 112.6, 110.3, 105.0, 41.8, 34.0, 30.5.



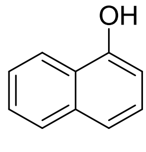
1j: *3-(furan-2-yl)-5-(tetrahydrofuran-2-yl)-cyclohexanone*

White solid. Yield 66%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32(d, *J* =1.2Hz, 1H), 6.29-6.30(m, 1H), 6.03(d, *J*=3.2Hz,1H), 3.82- 3.87(m, 1H), 3.73-3.78(m,1H), 3.65-3.70(m, 1H), 3.02-3.11 (m, 1H), 2.68-2.73(m,1H), 2.38-2.50(m, 3H), 2.19(t, *J*=13.2Hz, 1H), 1.85-2.0(m, 4H), 1.52-1.63(m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.4,157.2, 141.3, 110.0, 103.8, 82.5, 68.0, 45.8, 44.2, 42.6, 36.6, 33.2, 29.1, 25.9.



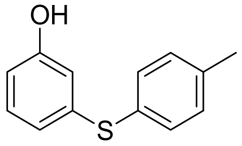
1'v: *5-(furan-2-yl)-3-(thiophen-2-yl)-2-cyclohexen-1-one*

Light yellow solid. Yield 56%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.47 (m, 1H), 7.43(d, *J*=3.6Hz, 1H), 7.38(d, *J*=1.2Hz, 1H), 6.48(d, *J*=2Hz, 1H), 6.33-6.34(m, 1H), 6.12(d, *J*=3.2Hz, 1H), 3.54-3.62(m, 1H), 3.19-3.24(m, 1H), 2.91-2.99(m, 1H), 2.80-2.86(m, 1H), 2.65-2.73(m, 1H).



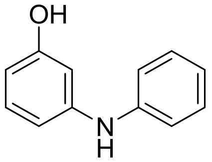
2p: *1-Naphthol*

Light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21-8.12 (m, 1H), 7.84-7.74 (m, 1H), 7.44 (td, J = 15.03, 7.03 Hz, 3H), 7.25 (t, J = 7.85 Hz, 1H), 6.72 (d, J = 7.44 Hz, 1H), 5.45 (s, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 151.5, 134.9, 127.8, 126.6, 126.0, 125.4, 124.5, 121.7, 120.8, 108.7.



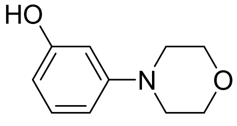
2g: *3-(p-tolylthio)phenol*

Colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.36(d, *J*=8Hz, 2H), 7.16(dd, *J*=8.0, 17.6Hz, 3H), 6.84(d, *J*=8.4Hz, 1H), 6.85-6.89(m, 2H), 4.98(s, 1H), 2.38(s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 154.9, 138.1, 137.1, 132.0, 129.3, 129.1, 129.0, 120.4, 114.7, 112.3, 20.1. HRMS: m/z (ESI) calculated [M - H]$^-$ 216.0609, measured 216.0610.



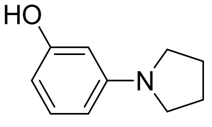
2q: *3-(phenylamino)phenol*

Yellow solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.26-7.30(m, 3H), 7.11(t, *J* =8Hz,3H), 6.96(t, *J*=7.4Hz, 1H), 6.61(dd, *J*=1.6, 8Hz, 1H), 6.57(t, *J*= 2.4Hz, 1H), 6.38(dd, *J*=2.0, 8.0Hz, 1H), 5.69(s, 1H), 4.69(s, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 156.6, 145.0, 142.5, 130.4, 129.4, 121.5, 118.7, 110.0, 107.6, 103.9.



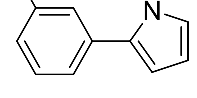
2t: *3-morpholino-phenol*

White soild. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.12(t, *J*=8.0Hz, 1H), 6.50(dd, *J*=2.4, 8.4Hz, 1H), 6.39(t, *J*=2.0Hz, 1H), 6.34(dd, *J*=2.0, 7.6Hz, 1H), 4.96(s, 1H), 3.85(t, *J*=4.8Hz, 4H), 3.14(t, *J*=4.8Hz,4H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 156.7, 152.8, 130.1, 108.2, 107.1, 102.9, 66.8, 49.2.



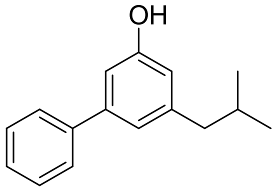
2r: *3-(pyrrolidin-1-yl)phenol*

White soild. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.06(t, *J*=8.0Hz, 1H), 6.15(m, 2H), 6.05(t, *J*=2.4Hz, 1H), 4.67(s, 1H), 3.25(t, *J*=6.4Hz, 4H), 1.98(m, 4H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 156.6, 149.5, 130.0, 104.8, 102.5, 98.6, 47.6, 25.4.



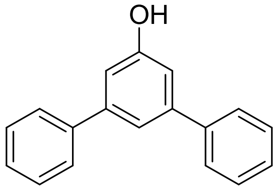
2s: *3-(1H-pyrrol-2-yl)phenol*

White soild. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.37(s, 1H), 7.15(m, 1H), 6.96(d, *J*=7.6Hz, 1H), 6.86(s, 1H), 6.74(s, 1H), 6.60(d, *J*=8.0Hz, 1H), 6.12(s, 1H), 6.21(s, 1H), 3.62(s, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 156.1, 134.4, 131.7, 130.2, 119.1, 116.4, 113.3, 110.8, 110.1, 106.3.



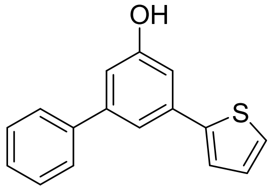
2k: *3-phenyl-5-isobutyl-phenol*

Brown solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.61-7.63(m, 2H), 7.47(t, *J*=7.4Hz, 2H), 7.39(t, *J*=7.4Hz, 1H), 7.04(s, 1H), 6.97(t, *J*=1.8Hz, 1H), 6.70(s, 1H), 5.55(s, 1H), 2.53(d, *J*=7.2Hz, 2H), 1.90-2.00(m, 1H), 0.99(d, *J*=6.8Hz,6H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 155.6, 144.1, 142.6, 141.0, 128.8, 127.4, 127.2, 120.9, 115.1, 111.6, 77.4, 77.1, 76.8, 45.5, 30.2 22.5. HRMS: m/z (ESI) calculated [M - H]$^-$ 226.1358, measured 226.1359.



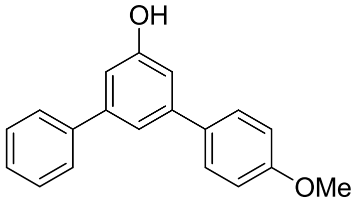
2h: *3,5-diphenyl-phenol*

White solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.65-7.67(m,4H), 7.48(t, *J*=7.4Hz, 4H), 7.39-7.43(m, 3H), 7.12(d, *J*=1.6Hz, 2H), 6.13(s, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 156.5, 143.4, 140.9, 128.8, 127.6, 127.3, 118.8, 113.2.



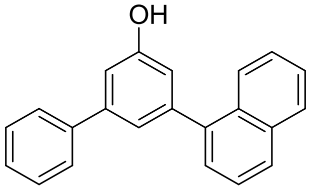
2w: *3-phenyl-5-(thiophen-2-yl)phenol*

Brown solid. ^{1}H NMR (400 nnMHz, CDCl$_3$) δ 7.47(d, *J*=7.2Hz, 2H), 7.11-7.34(m, 6H), 6.94-6.98(m, 2H), 6.87(s, 1H), 5.51(s, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 156.3, 143.9, 143.7, 140.5, 136.3, 128.9, 128.1, 127.8, 127.2, 125.2, 123.6, 117.8, 113.5, 111.9. HRMS: m/z (ESI) calculated [M - H]$^-$ 252.0609, measured 252.0607.



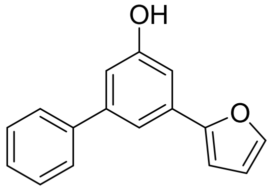
2o: *3-(4-methoxyphenyl)-5-phenyl-phenol*

White solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.68 (dd, J = 17.83, 7.83 Hz, 2H), 7.63-7.56 (m, 2H), 7.49 (ddd, J = 16.61, 7.63, 2.48 Hz, 4H), 7.14 (d, J = 8.48 Hz, 2H), 7.08-7.00 (m, 2H), 6.63-6.31 (m, 1H), 3.90 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 158.2, 155.2, 142.3, 141.9, 139.8, 132.3, 127.7, 127.2, 126.5, 126.1, 117.4, 113.2, 111.6, 111.5, 54.3.



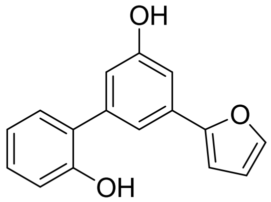
2n: *3-(naphthalen-1-yl)-5-phenyl-phenol*

White solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.92 (d, J = 8.47 Hz, 1H), 7.81 (d, J = 8.16 Hz, 1H), 7.76 (d, J = 8.11 Hz, 1H), 7.50 (d, J = 7.61 Hz, 2H), 7.38 (t, J = 7.56 Hz, 2H), 7.29 (m, 6H), 7.12-7.03 (m, 1H), 6.86 (s, 1H), 5.79 (s, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 155.8, 142.9, 140.6, 139.8, 133.9, 131.6, 128.9, 128.4, 128.0, 127.7, 127.3, 126.9, 126.3, 126.1, 126.0, 125.5, 121.8, 116.1, 113.1. HRMS: m/z (ESI) calculated [M - H]$^-$ 296.1201, measured 296.1203.



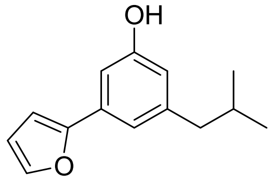
2i: *3-(furan-2-yl)-5-phenyl-phenol*

Yellow solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.63-7.65(m, 2H), 7.46-7.52(m, 4H), 7.38-7.42(m, 1H), 7.00(t, *J*=1.8Hz, 1H), 6.72(d, *J*=3.2Hz, 1H), 6.52(dd, *J*=1.6, 3.2Hz, 1H), 5.00(s, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 156.2, 153.5, 143.5, 142.3, 140.6, 132.7, 128.8, 127.7, 127.2, 115.5, 113.3, 111.7, 109.6, 105.7. HRMS: m/z (ESI) calculated [M - H]$^-$ 236.0837, measured 236.0838.



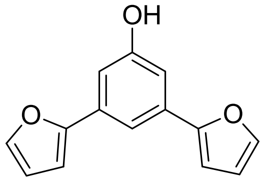
2m: *3-(furan-2-yl)-5-(2-hydroxyphenyl)-phenol*

Brown oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.43(d, *J*=1.2Hz, 1H), 7.31(t, *J*=1.6Hz, 1H), 7.23-7.27(m, 2H), 7.14(dd, *J*=1.2, 2.4Hz, 1H), 6.96-6.99(m, 2H), 6.81(dd, *J*=1.2, 2.4Hz, 1H), 6.63(d, J=3.2Hz, 1H), 6.44(dd, *J*=1.6,3.2Hz, 1H), 5.77(s, 1H), 5.52(s, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 156.5, 153.0, 152.3, 142.5, 139.1, 133.2, 130.1, 129.4, 127.6, 121.0, 117.0, 116.0, 115.0, 111.8, 110.1, 106.1. HRMS: m/z (ESI) calculated [M - H]$^-$ 252.0786, measured 252.0787.



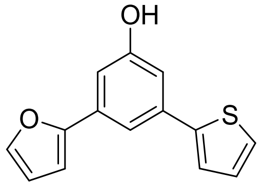
2l: *3-(furan-2-yl)-5-isobutyl-phenol*

White solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.13(s, 1H), 7.05(s, 1H), 6.99(s, 1H), 6.60(s, 1H), 6.55(s, 1H), 6.44(s, 1H), 5.42(s, 1H), 2.43 (d, *J*=6.8Hz, 2H), 1.84-1.91(m, 1H), 0.90(d, *J*=6.4Hz, 6H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 155.7, 153.9, 144.1, 142.0, 132.0, 117.3, 115.3, 111.6, 108.2, 105.2, 45.4, 20.1, 22.4. HRMS: m/z (ESI) calculated [M - H]$^-$ 216.1150, measured 216.1152.



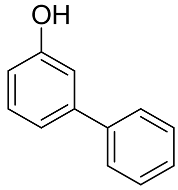
2j: *3,5-di(furan-2-yl)phenol*

White solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.58(s, 1H), 7.47(d, *J*=1.2Hz, 2H), 7.06(d, *J*=1.2Hz, 2H), 6.69(d, *J*=3.6Hz, 2H), 6.48(dd, *J*=1.6, 3.2Hz, 2H), 4.95(s, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 156.1, 153.3, 142.3, 132.7, 112.2, 111.7, 109.7, 105.8. HRMS: m/z (ESI) calculated [M - H]$^-$ 226.0630, measured 226.0631.



2v:*3-(furan-2-yl)-5-(thiophen-2-yl)phenol*

White solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.50(s, 1H), 7.48(s, 1H), 7.34(d, J=3.2Hz, 1H), 7.29(d, J=4.8Hz, 1H), 7.09(s, 2H), 7.00(s, 1H), 6.68(d, J=2.8Hz, 1H), 6.48(s, 1H), 5.18(s, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 156.2, 153.2, 143.7, 142.4, 136.4, 132.9, 128.0, 125.2, 123.7, 114.3, 111.9, 111.8, 109.8, 105.9. HRMS: m/z (ESI) calculated [M - H]$^-$ 242.0402, measured 242.0403.



2u: *3-hydroxybiphenyl*

White solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.45(d, *J*=7.6Hz, 2H), 7.32(t, *J*=6.0Hz, 2H), 7.18-7.26(m, 2H), 7.08(d, *J*=8Hz, 1H), 6.96(s, 1H), 6.72(dd, *J*=2.0Hz, 8.0Hz, 1H), 5.19(s, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 156.0, 143.0, 140.8, 130.0, 128.8, 128.7, 127.5, 127.1, 126.6, 119.7, 114.2, 114.1.

5. ^{1}H NMR and ^{13}C NMR spectra of phenols and substrates

Figure 1. ^{1}H NMR spectrum of 1’g in $CDCl_3$.

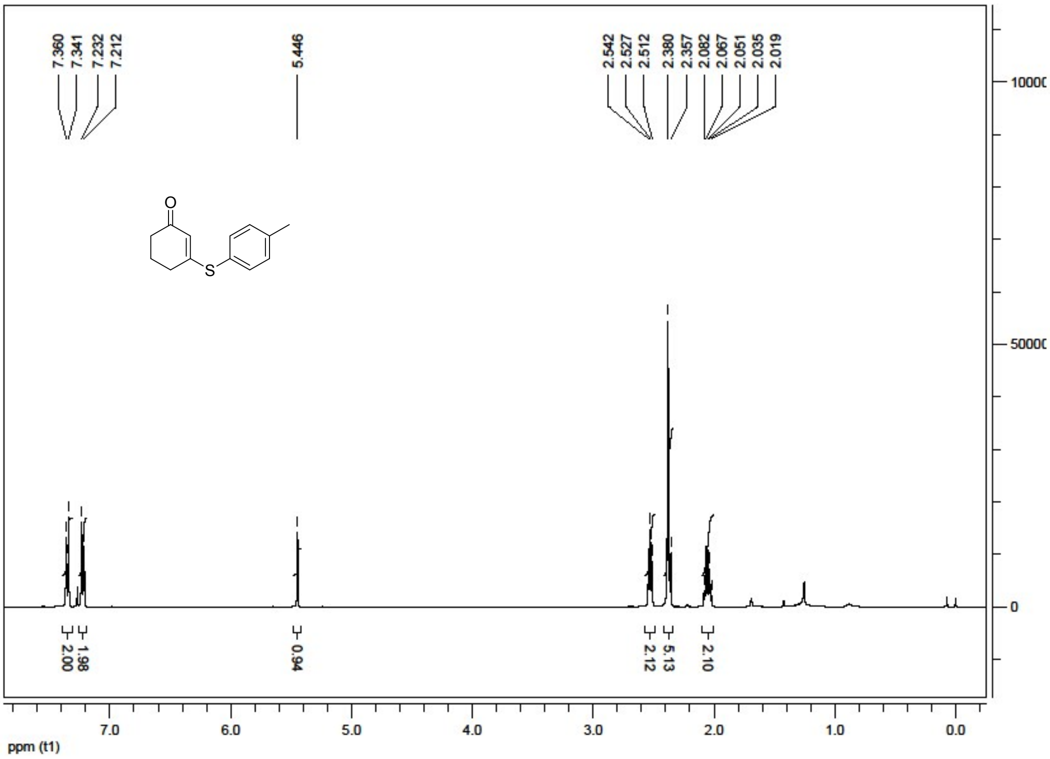


Figure 2. ^{1}H NMR spectrum of 1g in $CDCl_3$.

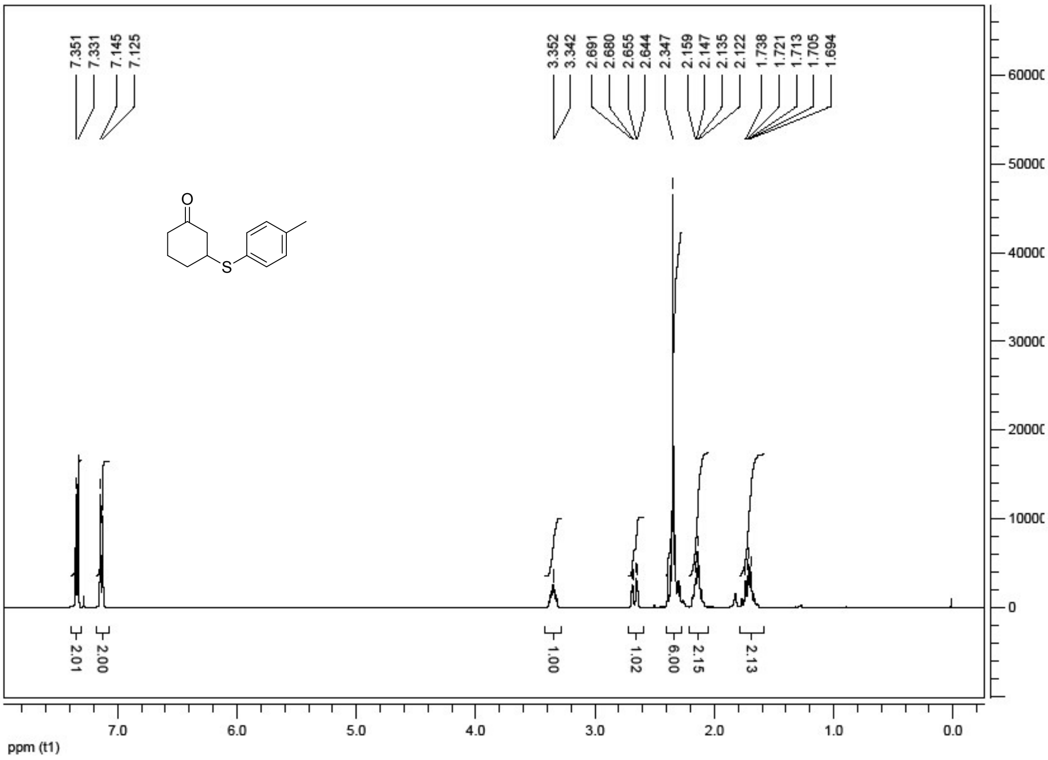


Figure 3. ^{1}H NMR spectrum of 1’q in $CDCl_3$.

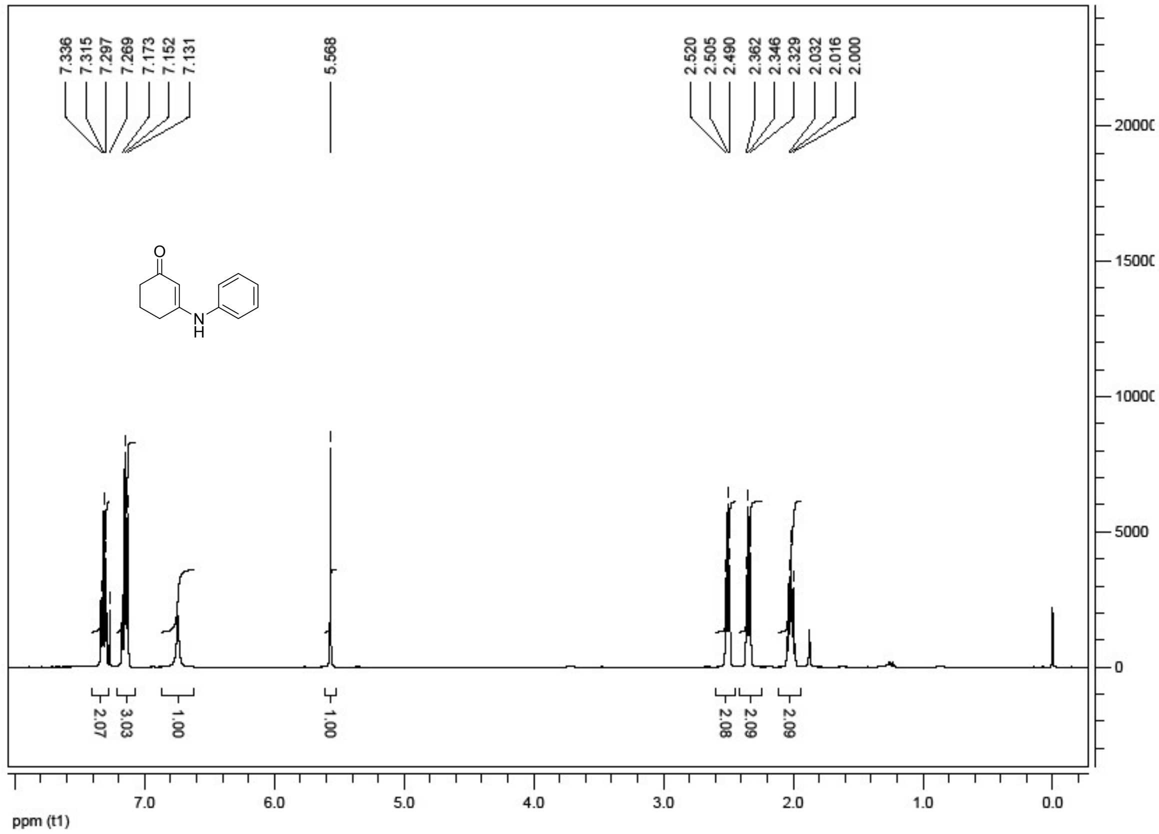


Figure 4. ^{1}H NMR spectrum of 1’t in $CDCl_3$.

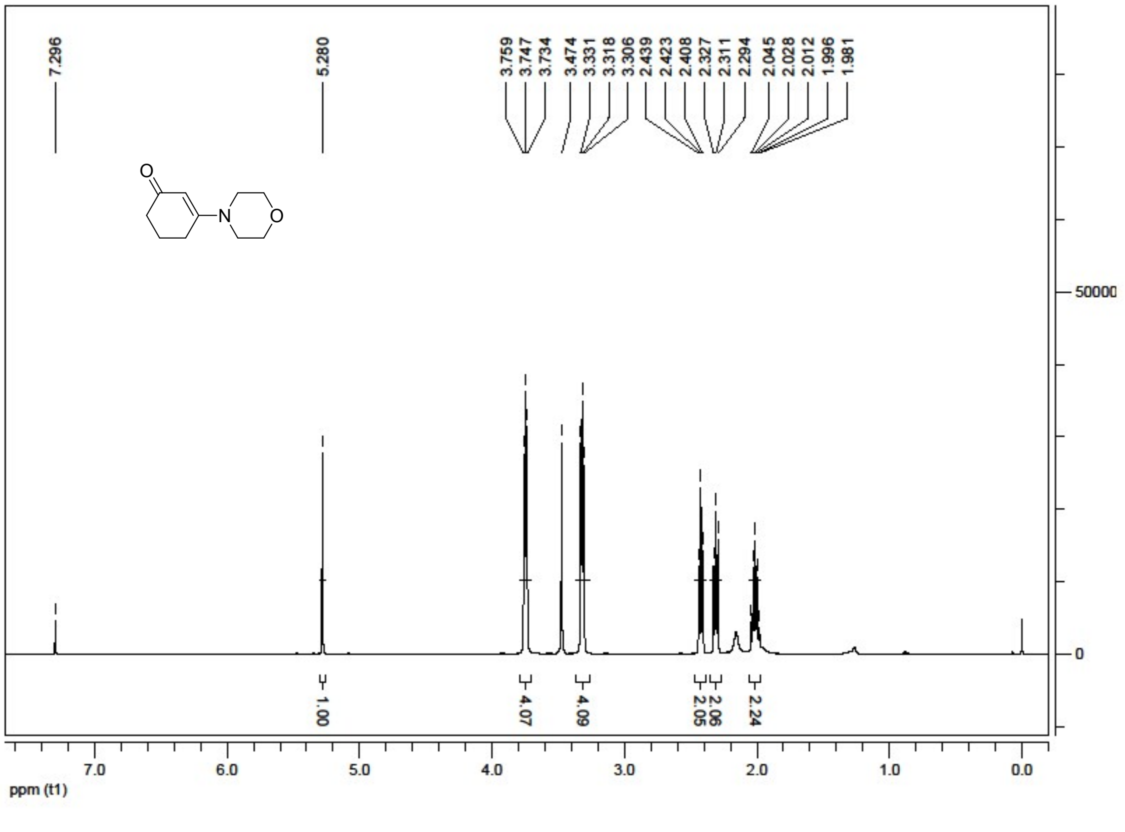


Figure 5. ^{1}H NMR spectrum of 1’r in CDCl$_3$.

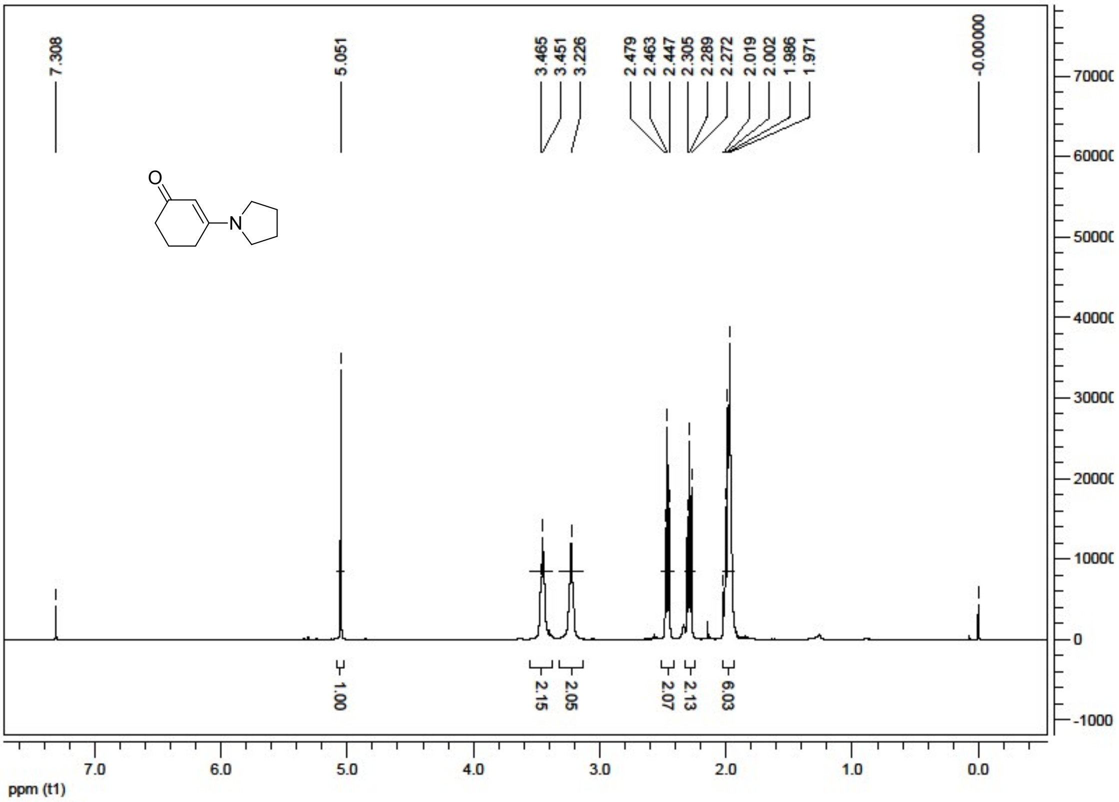


Figure 6. ^{1}H NMR spectrum of 1’s in CDCl$_3$.

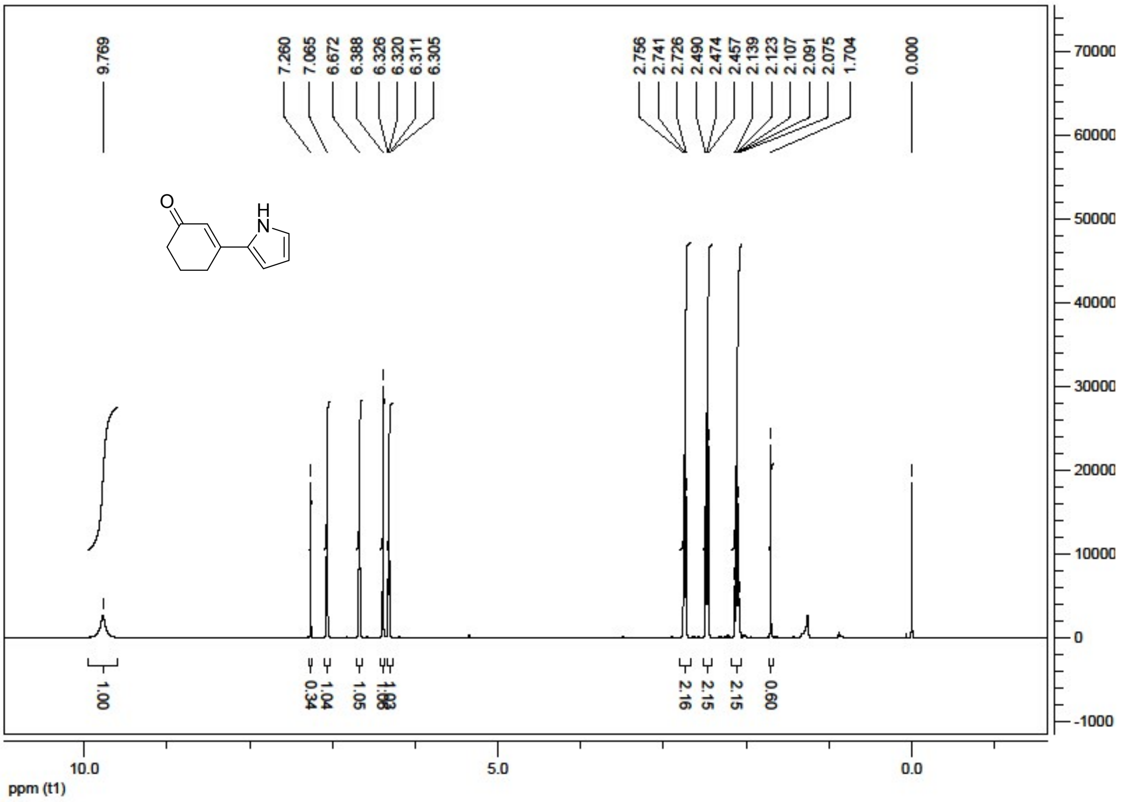


Figure 7. ^{1}H NMR spectrum of 1'k in CDCl$_3$.

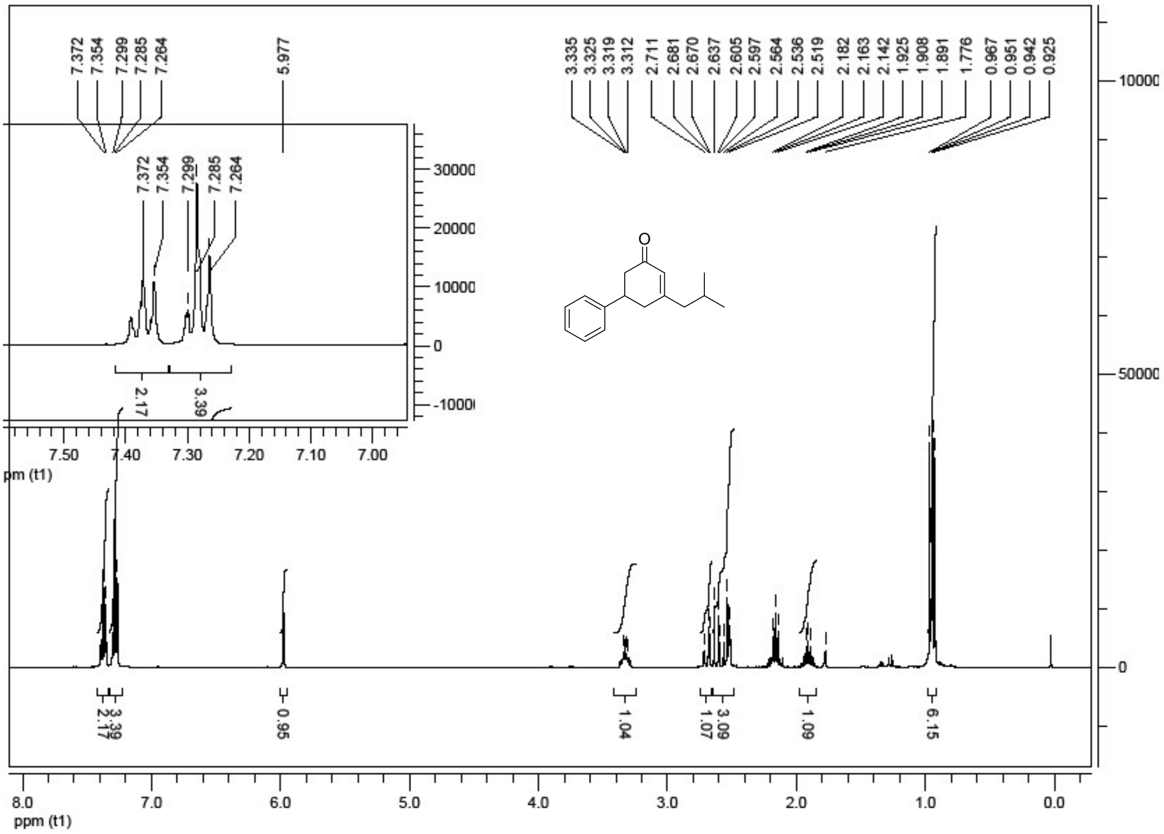


Figure 8. ^{1}H NMR spectrum of 1k in CDCl$_3$.

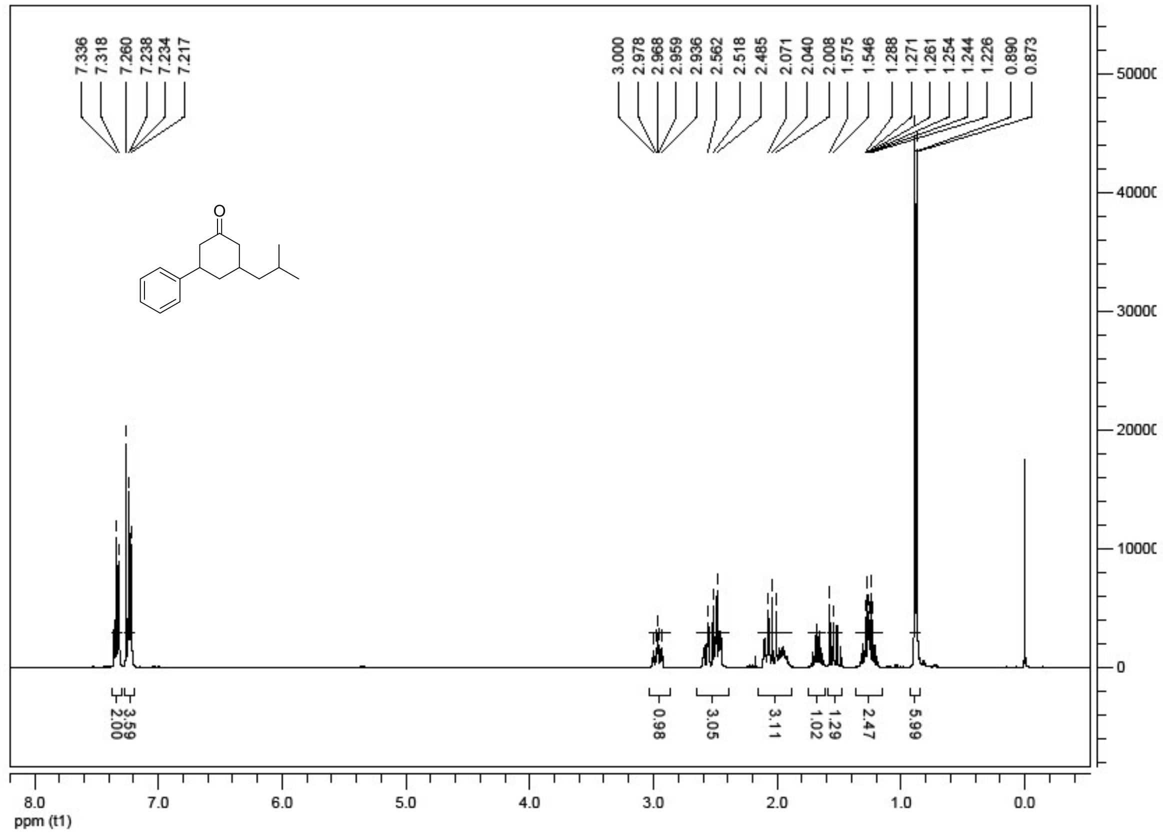


Figure 9. ^{1}H NMR spectrum of 1’h in CDCl$_3$.

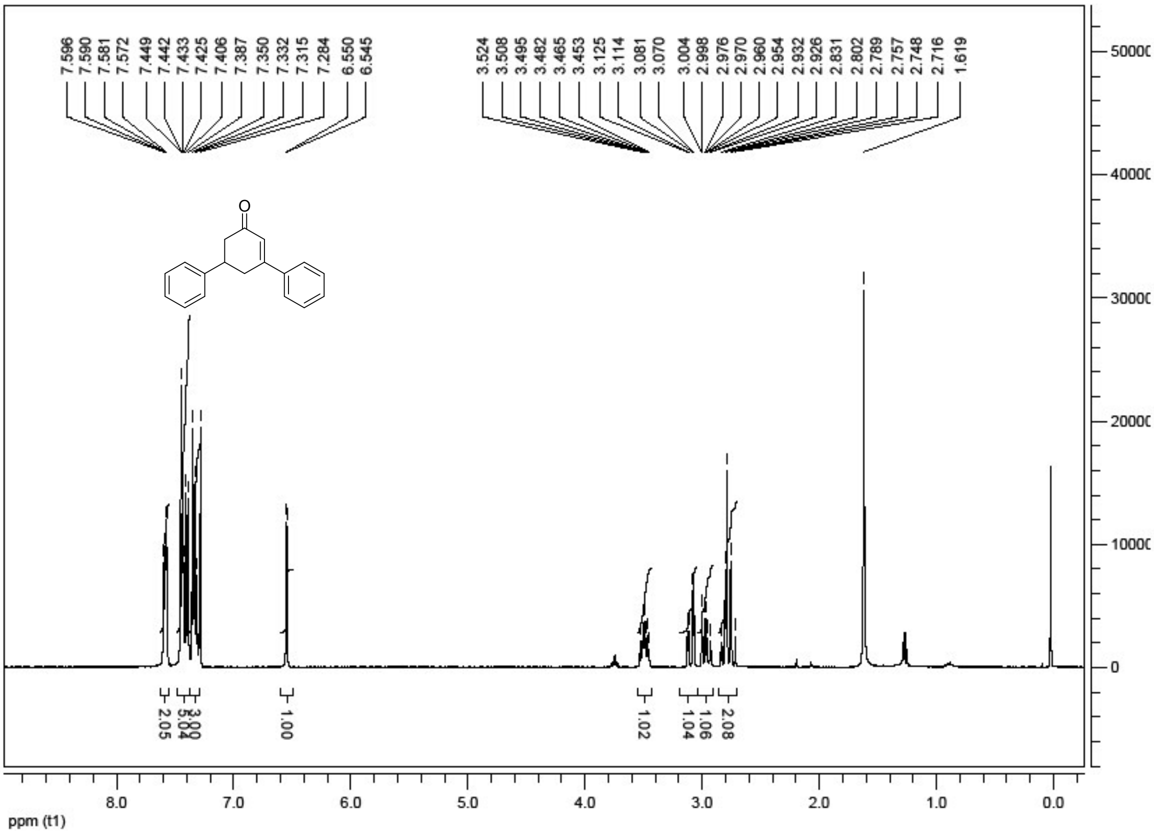


Figure 10. ^{1}H NMR spectrum of 1h in CDCl$_3$.

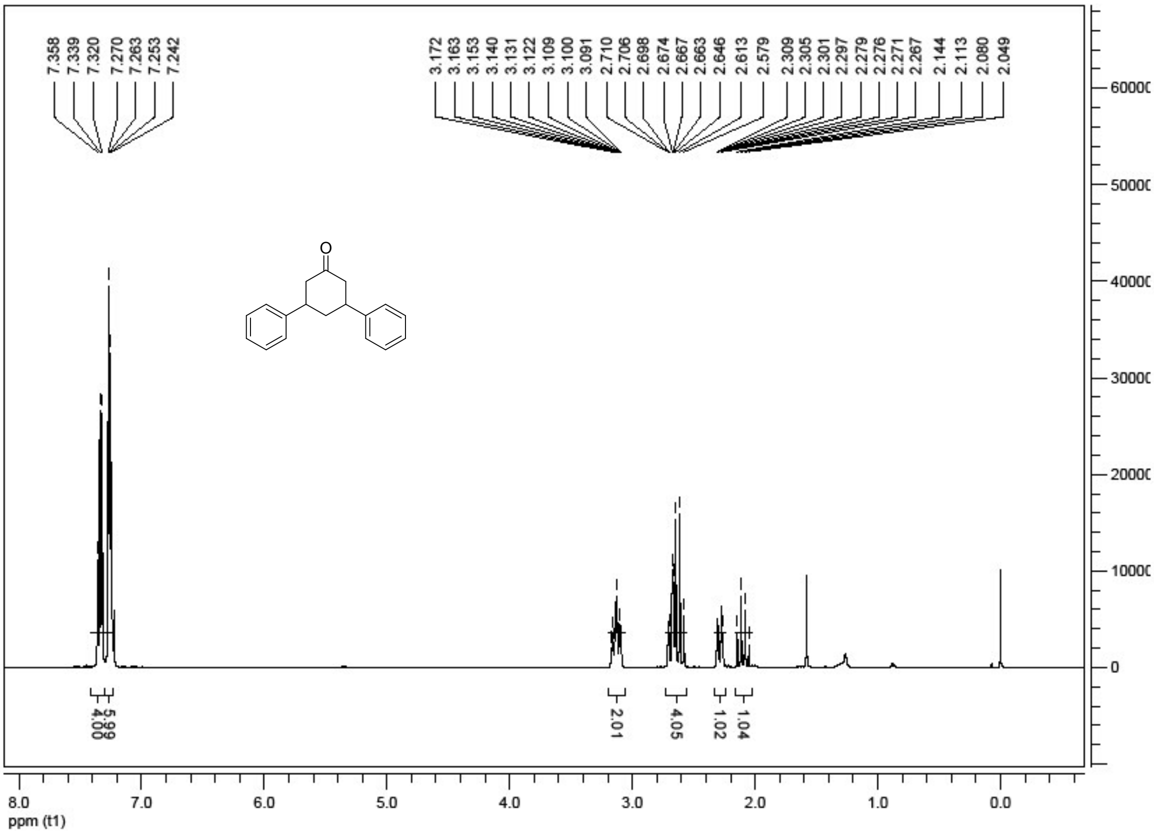


Figure 11. ^1H NMR spectrum of 1’w in $CDCl_3$.

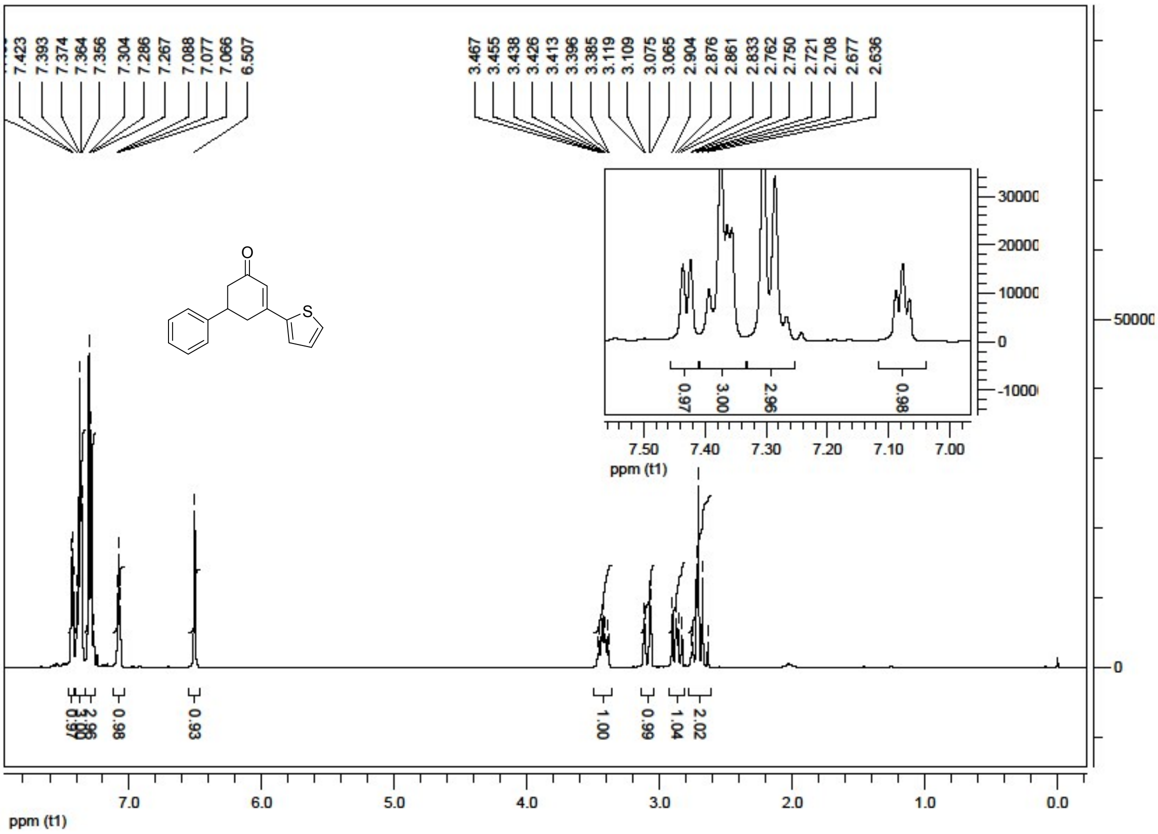


Figure 12. ^1H NMR spectrum of 1’o in $CDCl_3$.

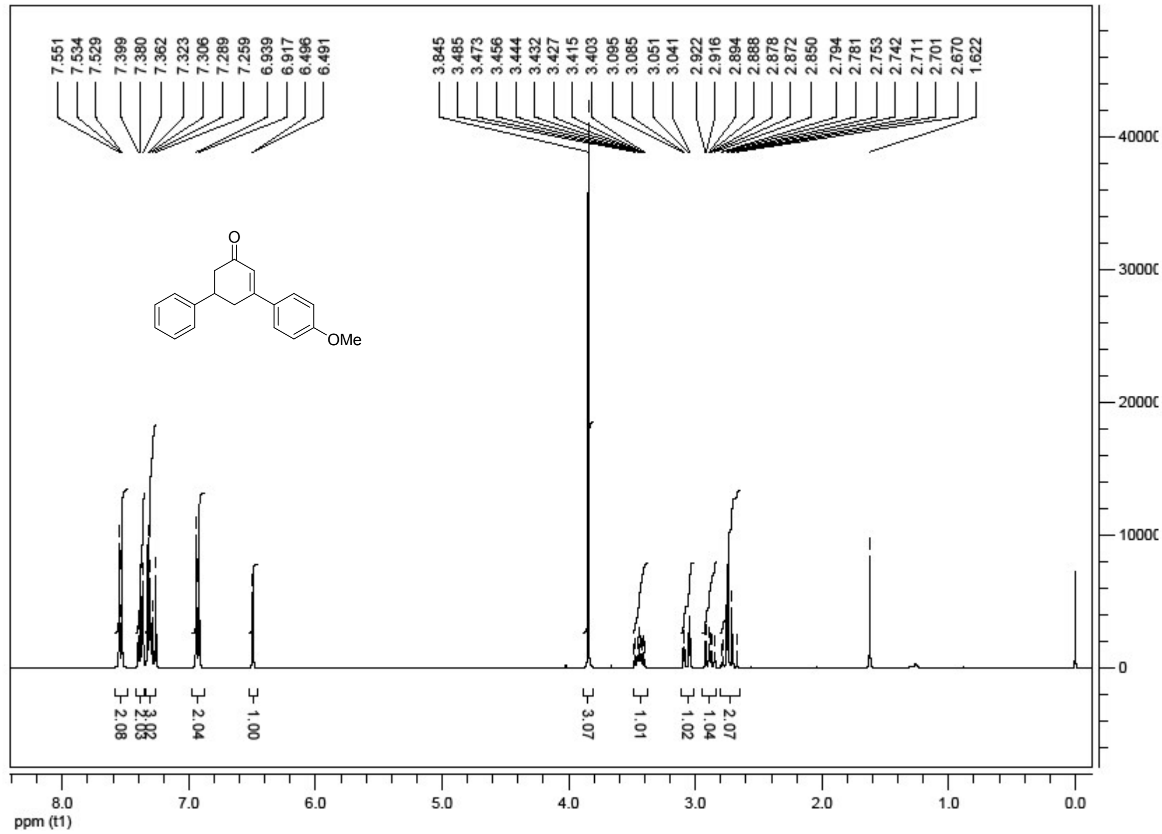


Figure 13. ^{1}H NMR spectrum of 1o in $CDCl_3$.

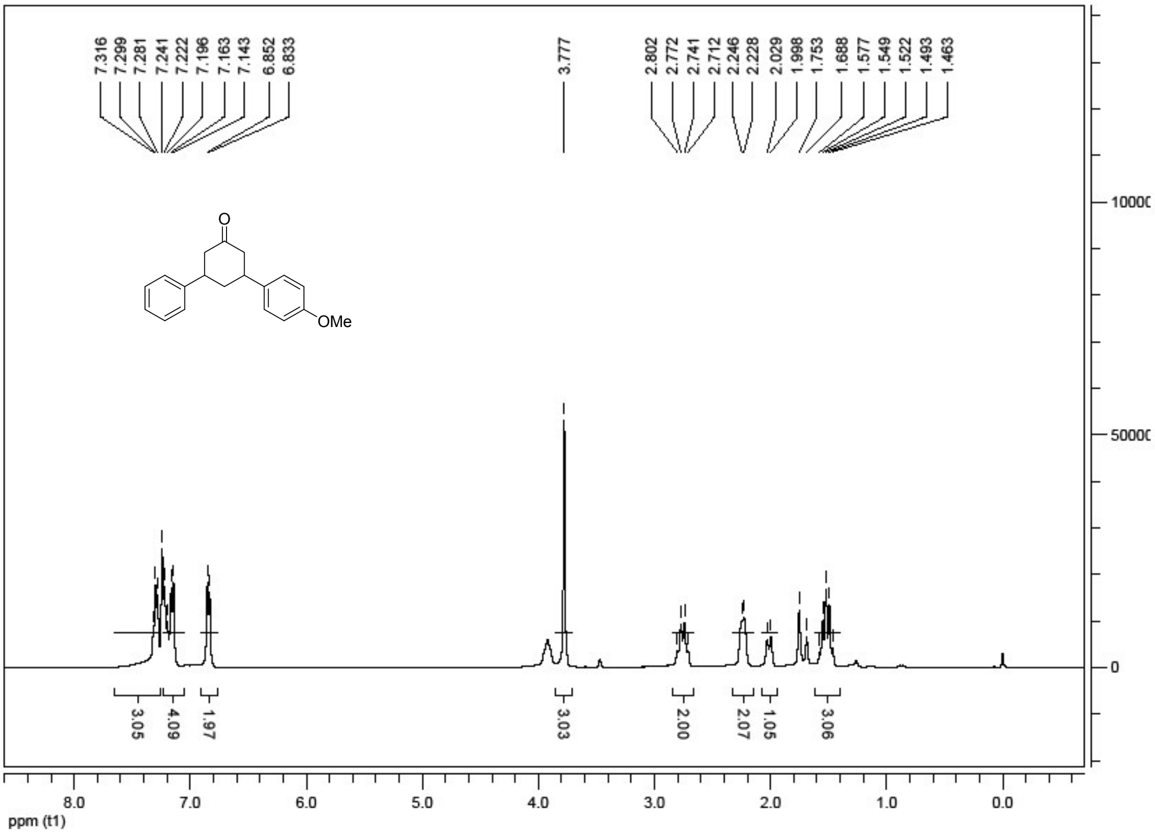


Figure 14. ^{1}H NMR spectrum of 1'n in $CDCl_3$.

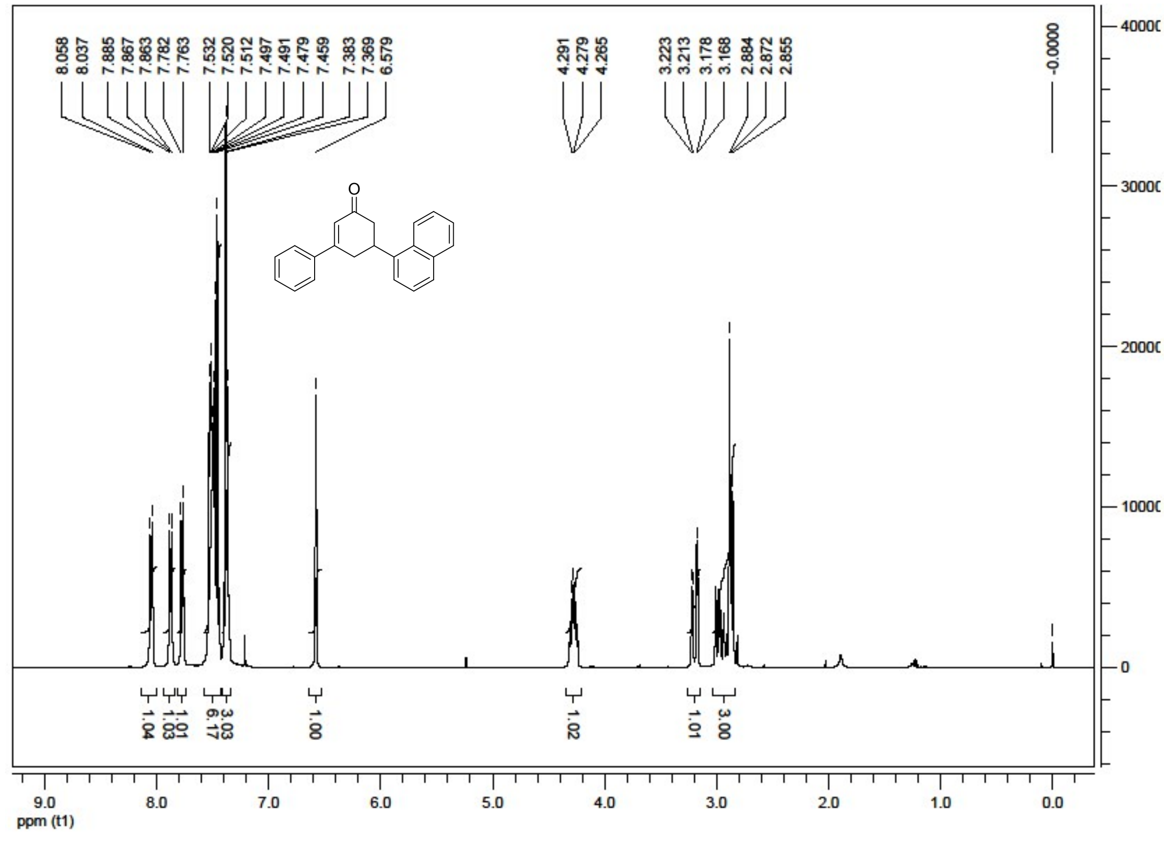


Figure 15. ^{1}H NMR spectrum of 1n in CDCl$_3$.

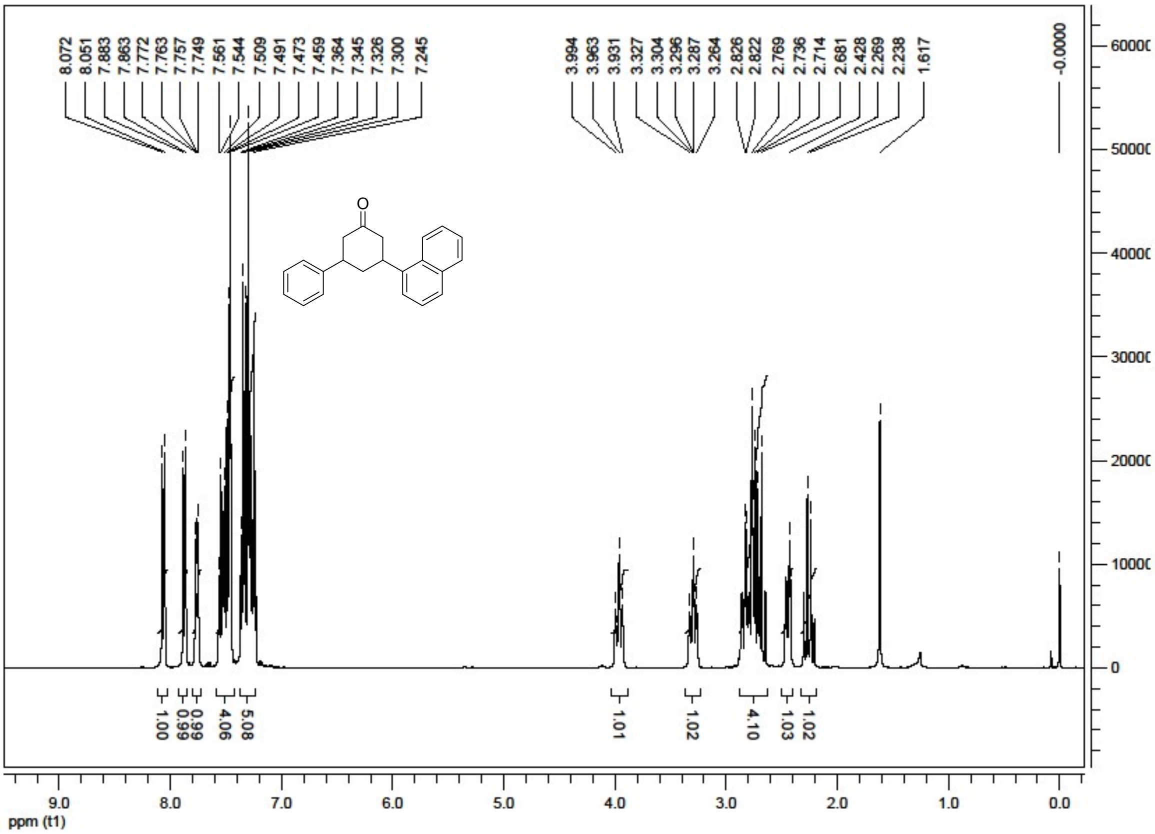


Figure 16. ^{1}H NMR spectrum of 1’i in CDCl$_3$.

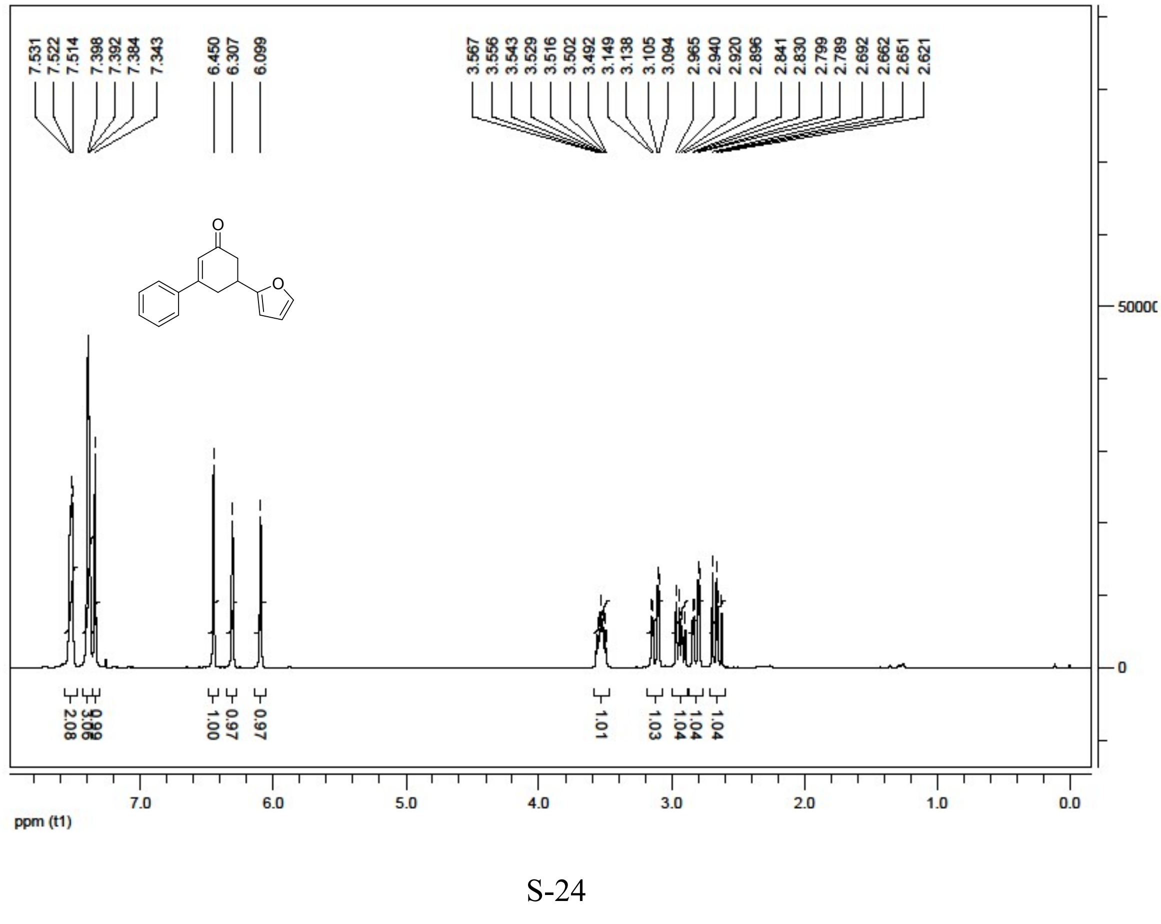


Figure 17. ${}^1H$ NMR spectrum of 1i in $CDCl_3$.

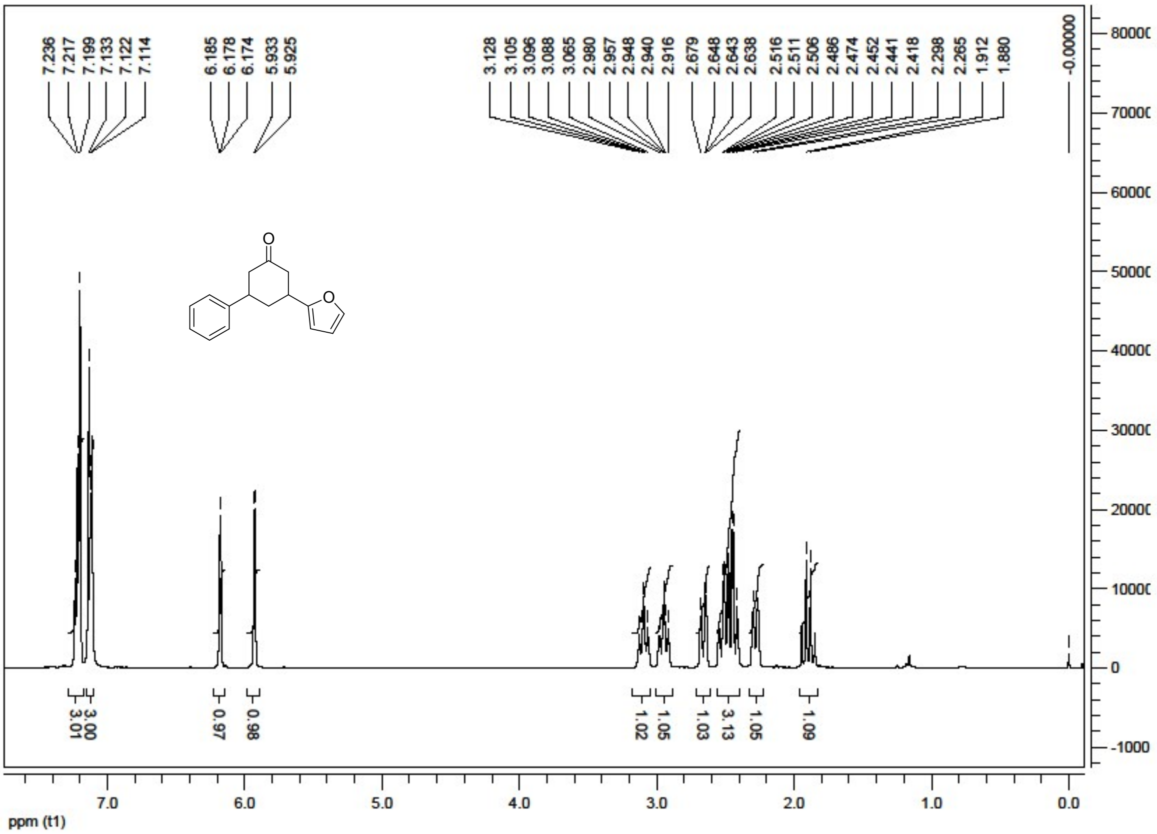


Figure 18. ${}^1H$ NMR spectrum of 1'm in $(CD_3)_2SO$.

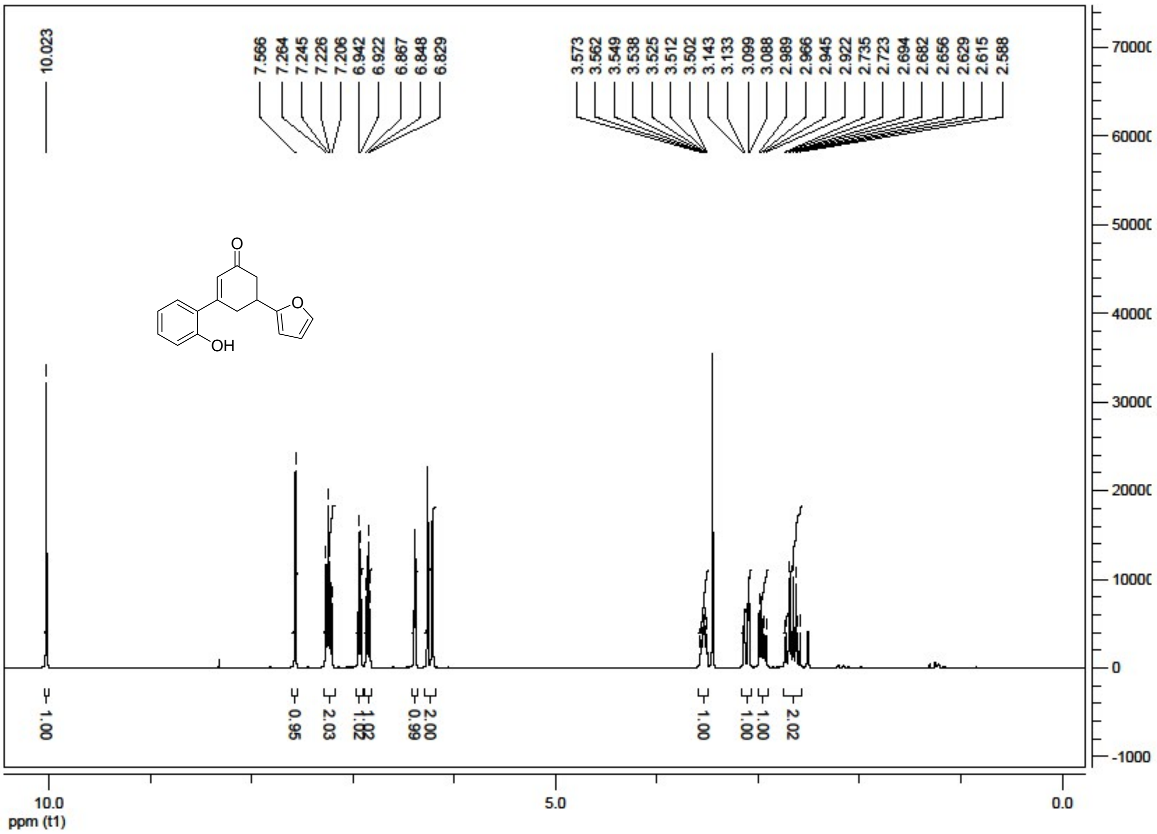


Figure 19. ^{1}H NMR spectrum of 1m in CDCl$_3$.

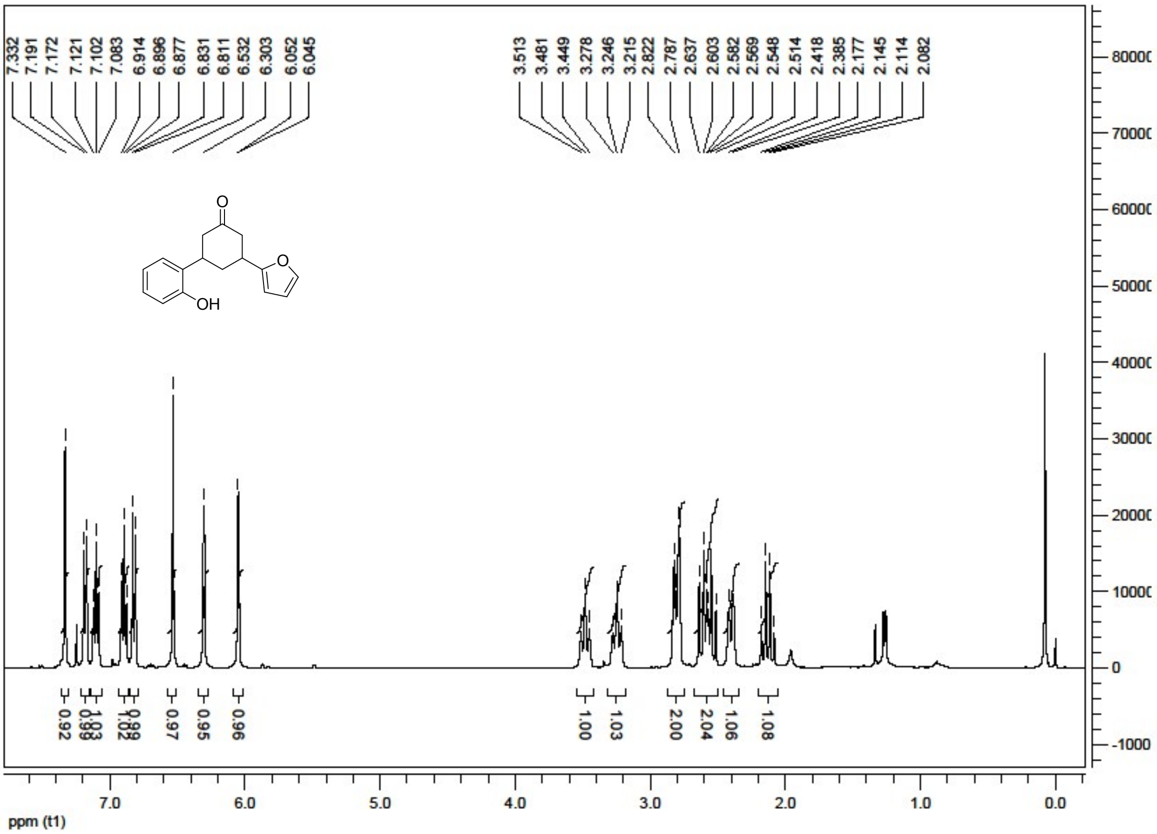


Figure 20. ^{1}H NMR spectrum of 1’l in CDCl$_3$.

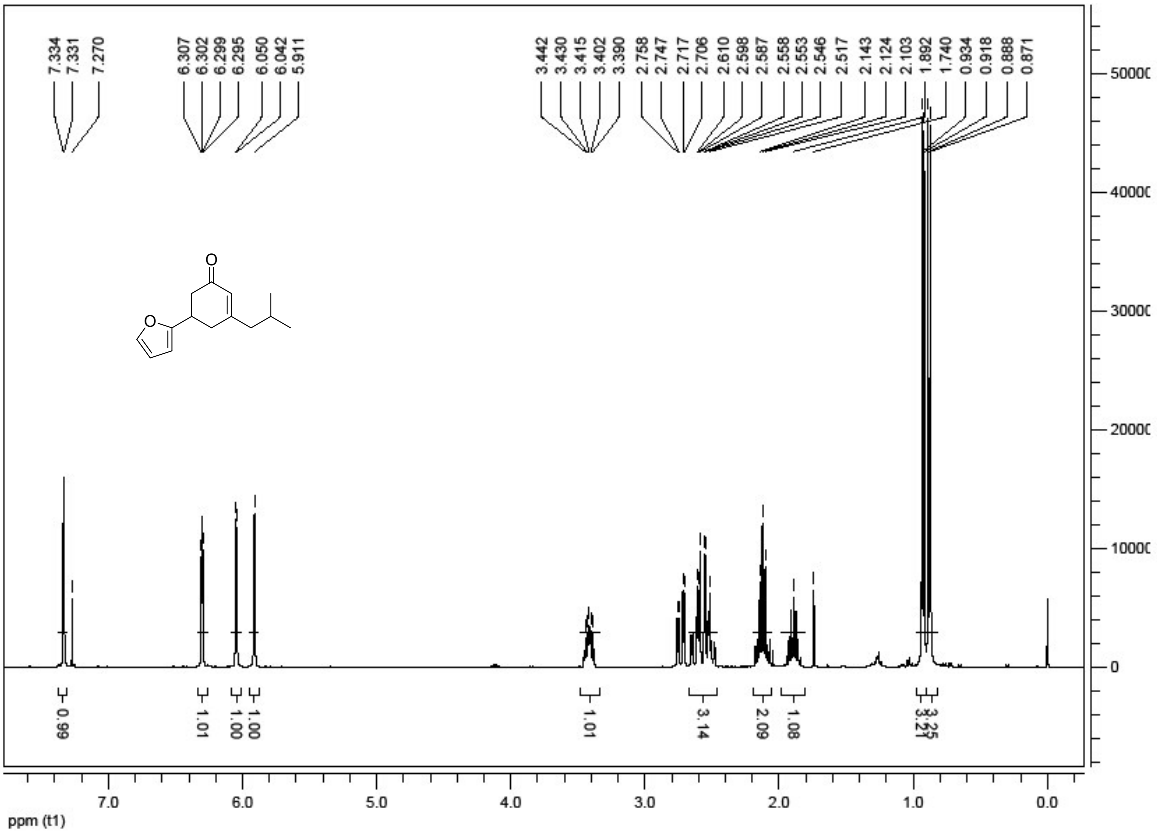


Figure 21. ^{1}H NMR spectrum of 1l in CDCl$_3$.

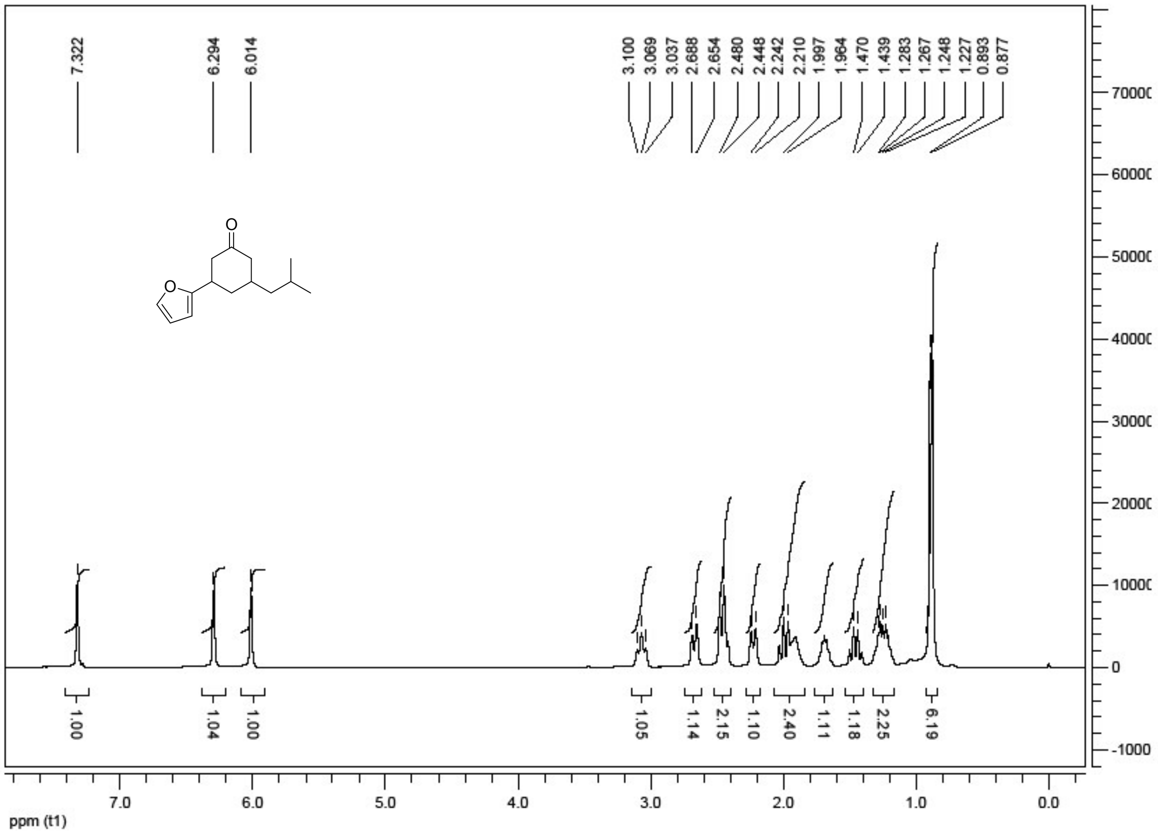


Figure 22. ^{1}H NMR spectrum of 1'j in CDCl$_3$.

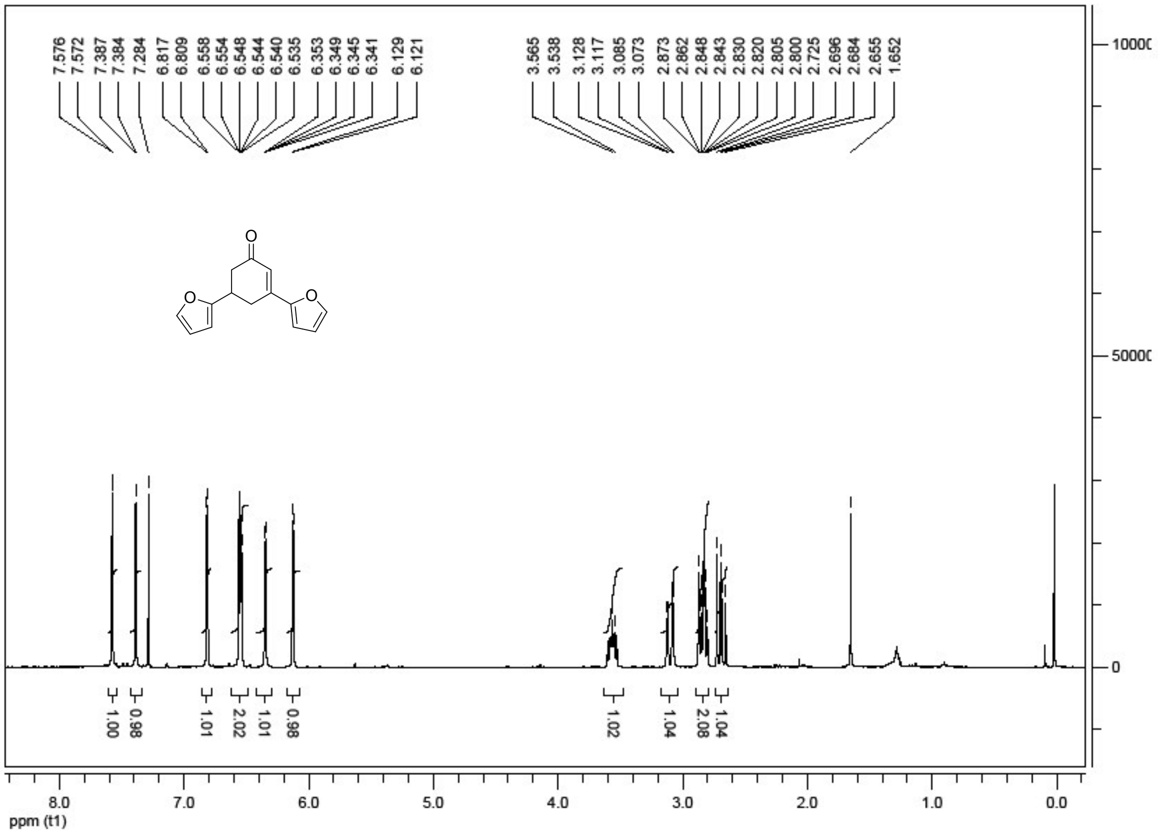


Figure 23. ^{13}C NMR spectrum of 1'j in $CDCl_3$.

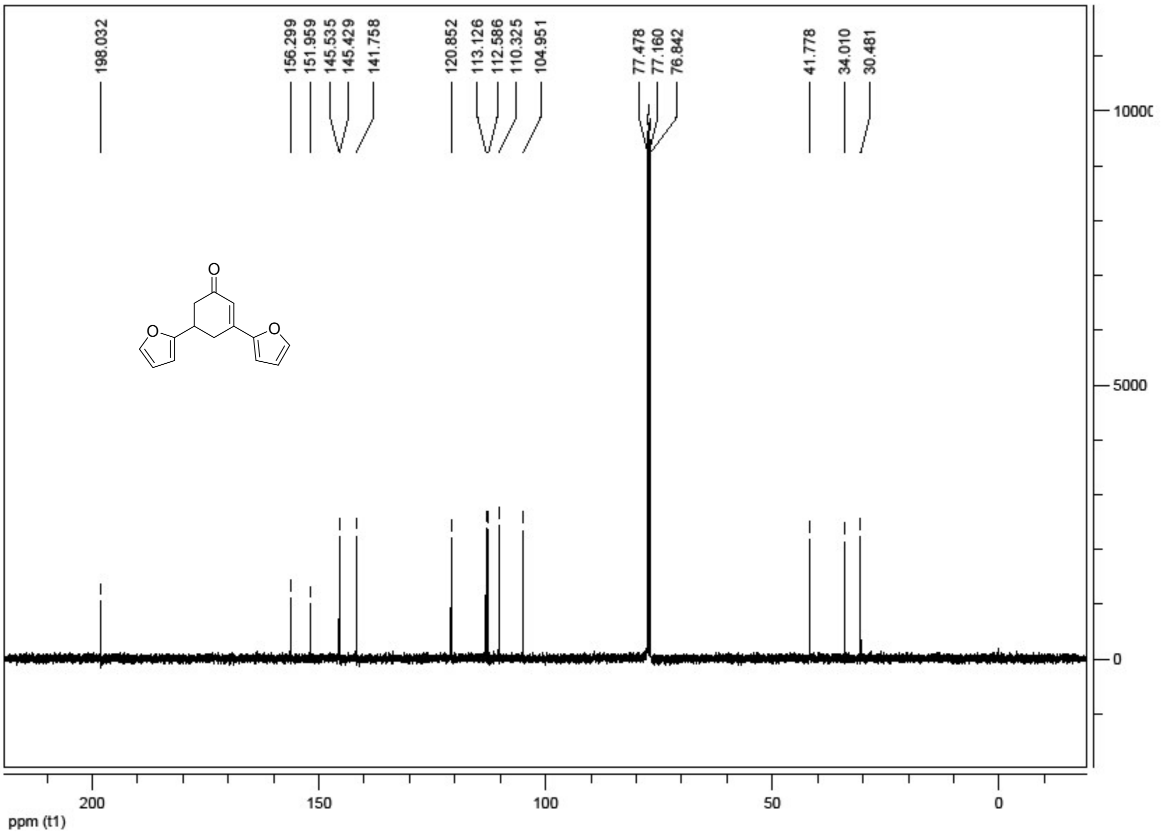


Figure 24. ^{1}H NMR spectrum of 1j in $CDCl_3$.

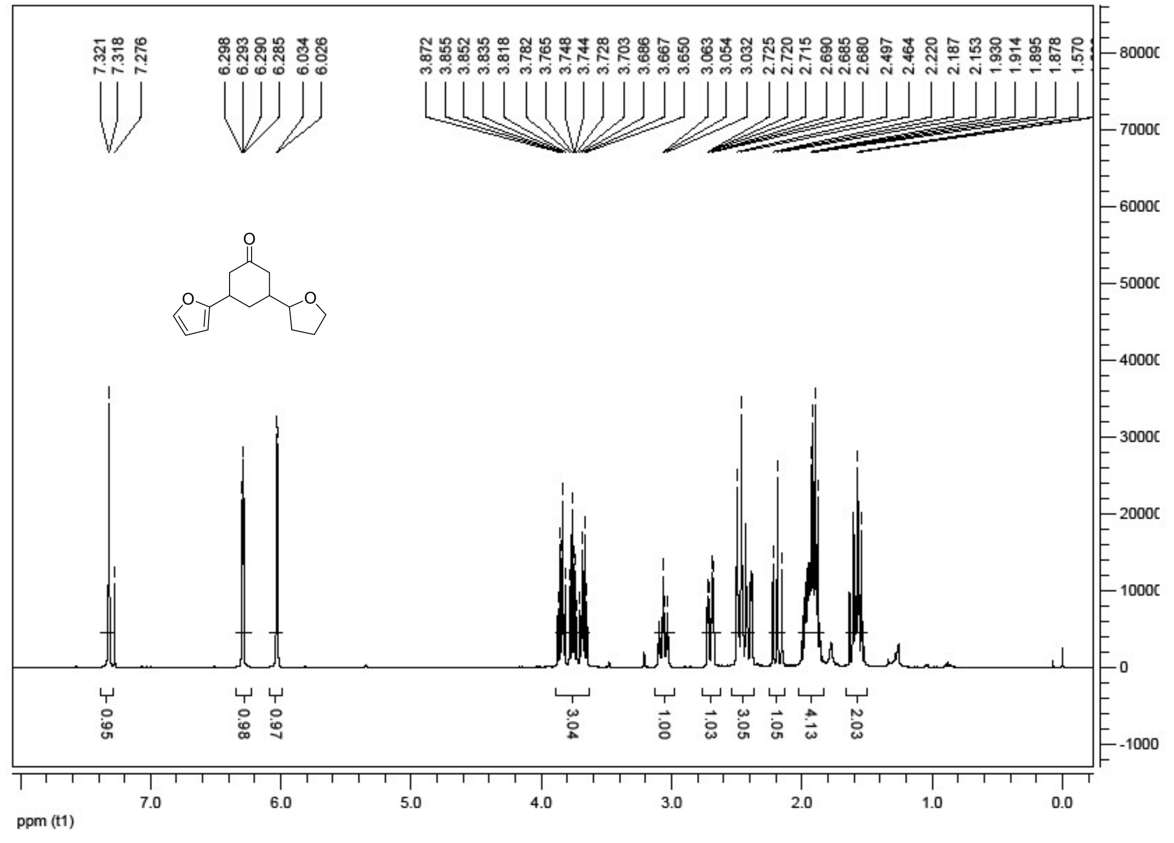


Figure 25. ^{13}C NMR spectrum of 1j in $CDCl_3$.

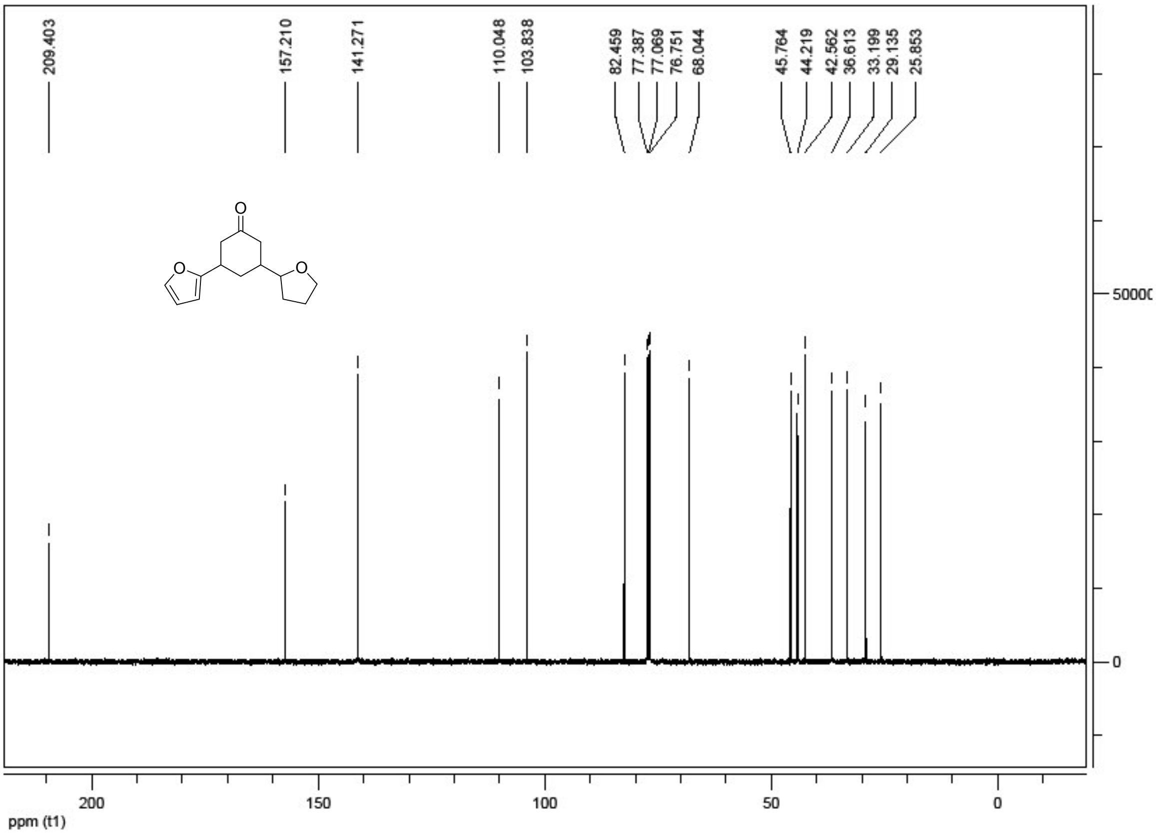


Figure 26. ^{1}H NMR spectrum of 1’v in $CDCl_3$.

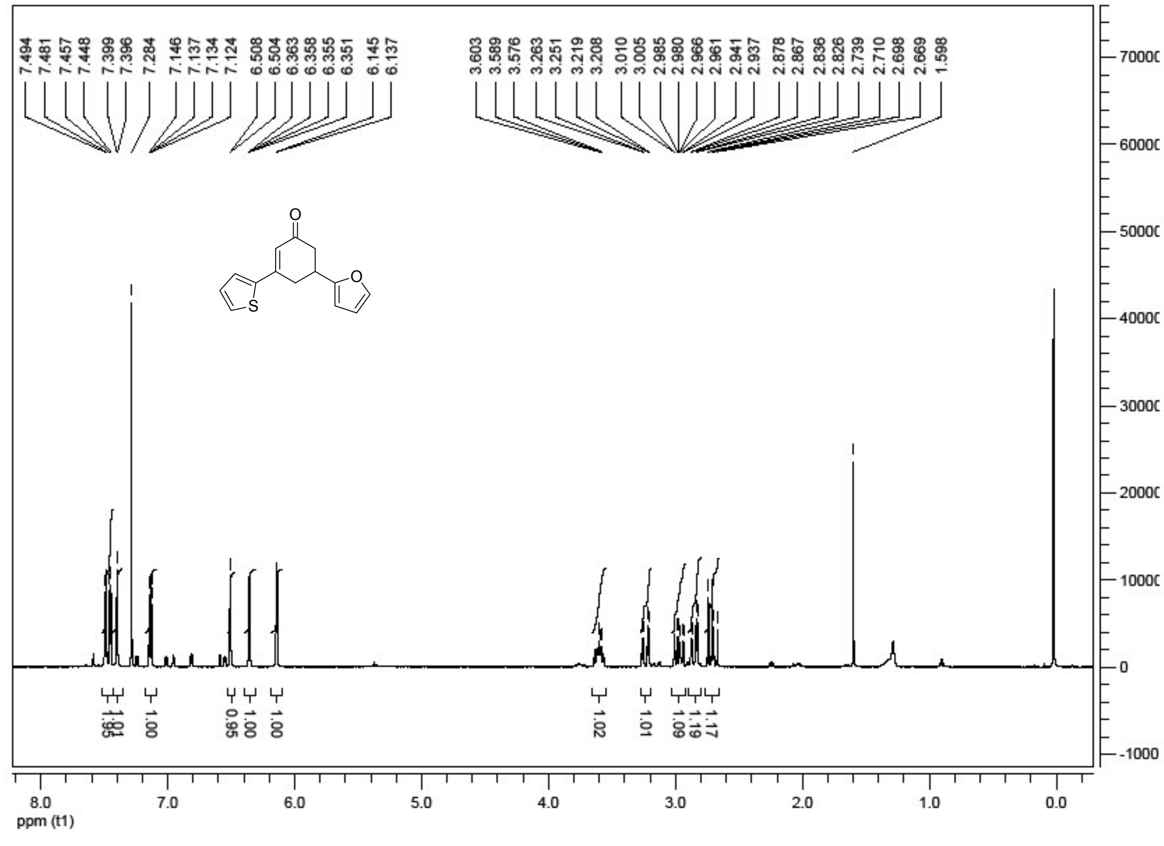


Figure 27. ^{1}H NMR spectrum of 2p in $CDCl_3$.

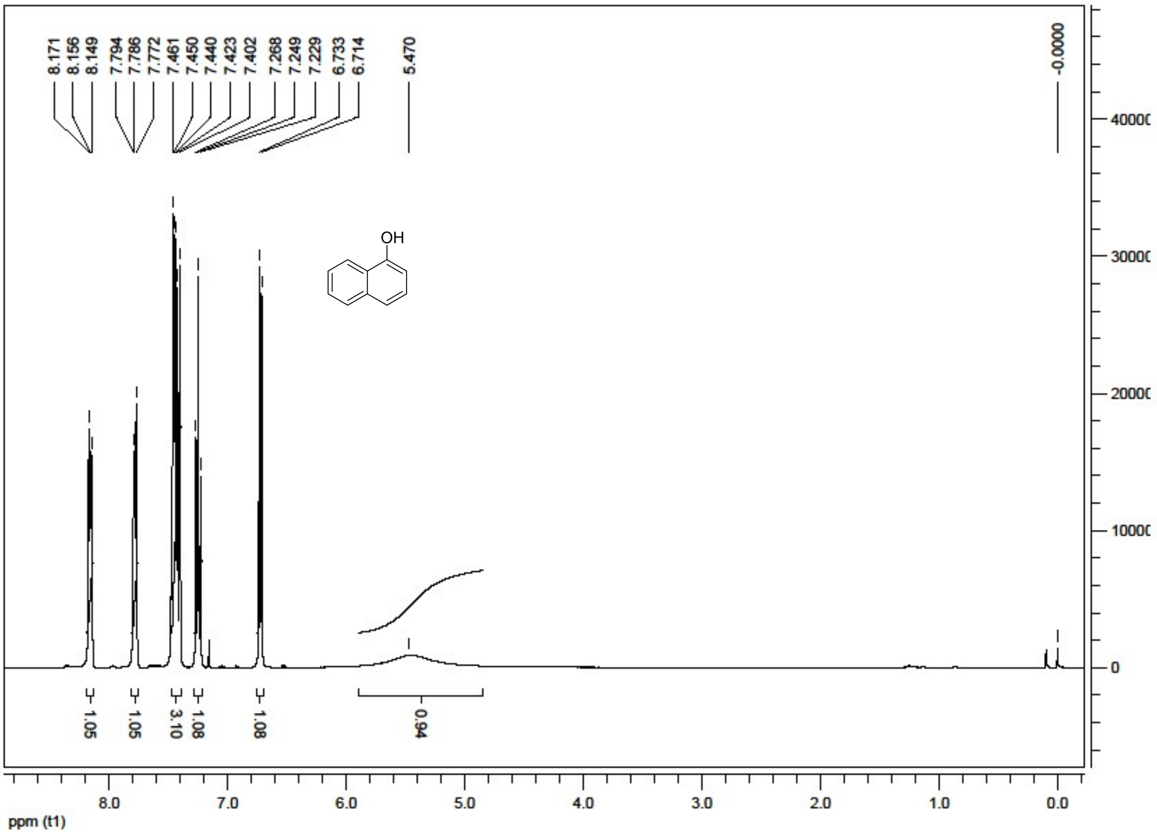


Figure 28. ^{13}C NMR spectrum of 2p in $CDCl_3$.

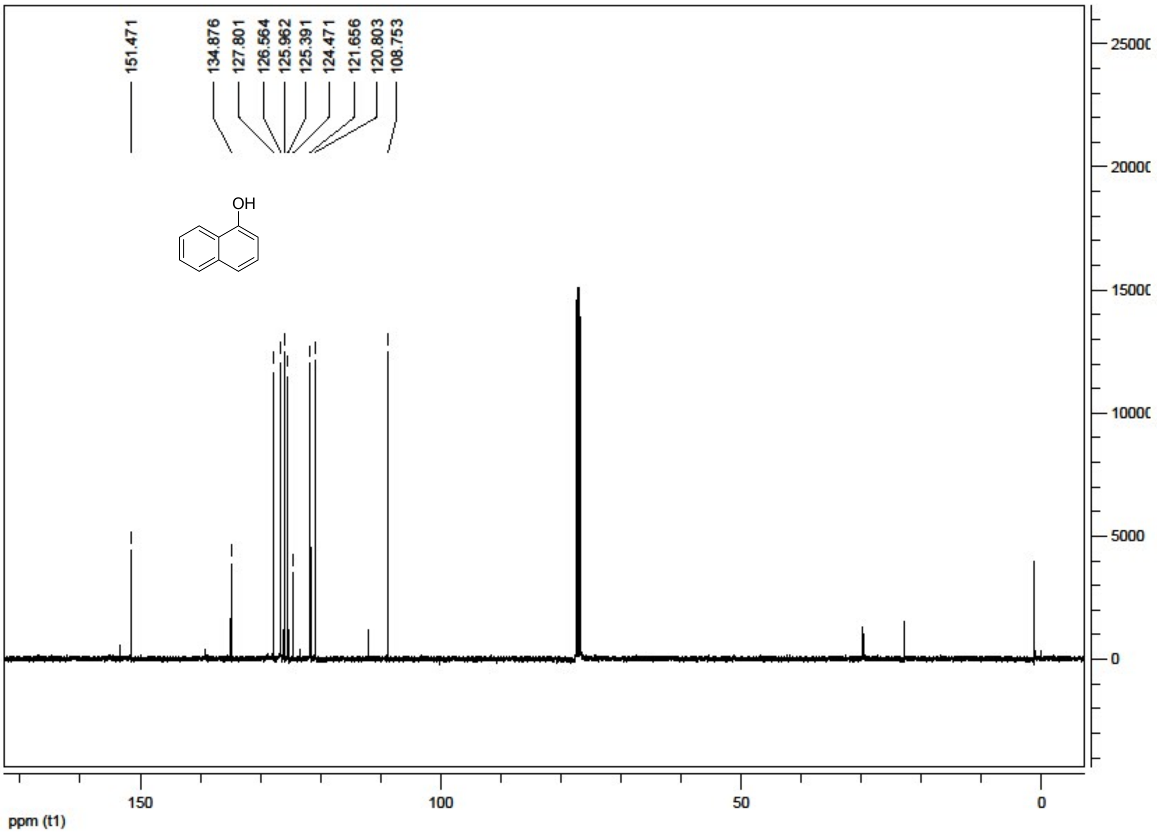


Figure 29. ^{1}H NMR spectrum of 2g in CDCl$_3$

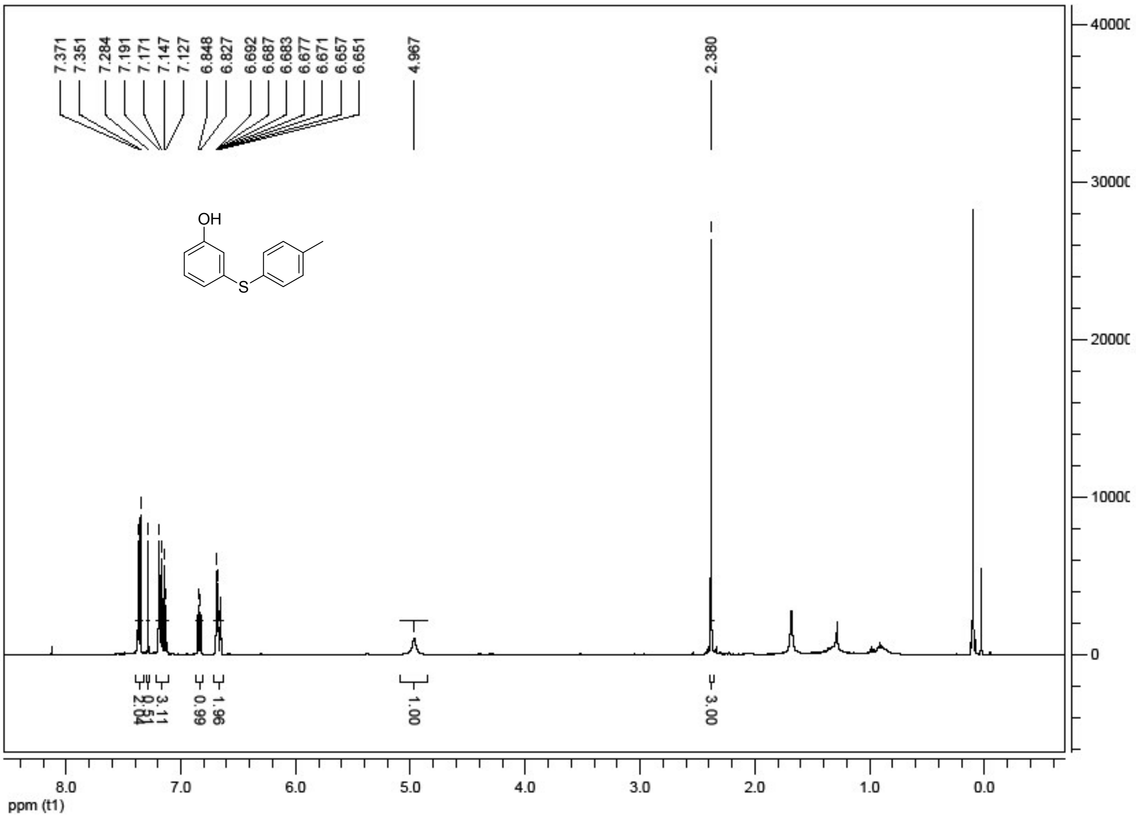


Figure 30. ^{13}C NMR spectrum of 2g in CDCl$_3$.

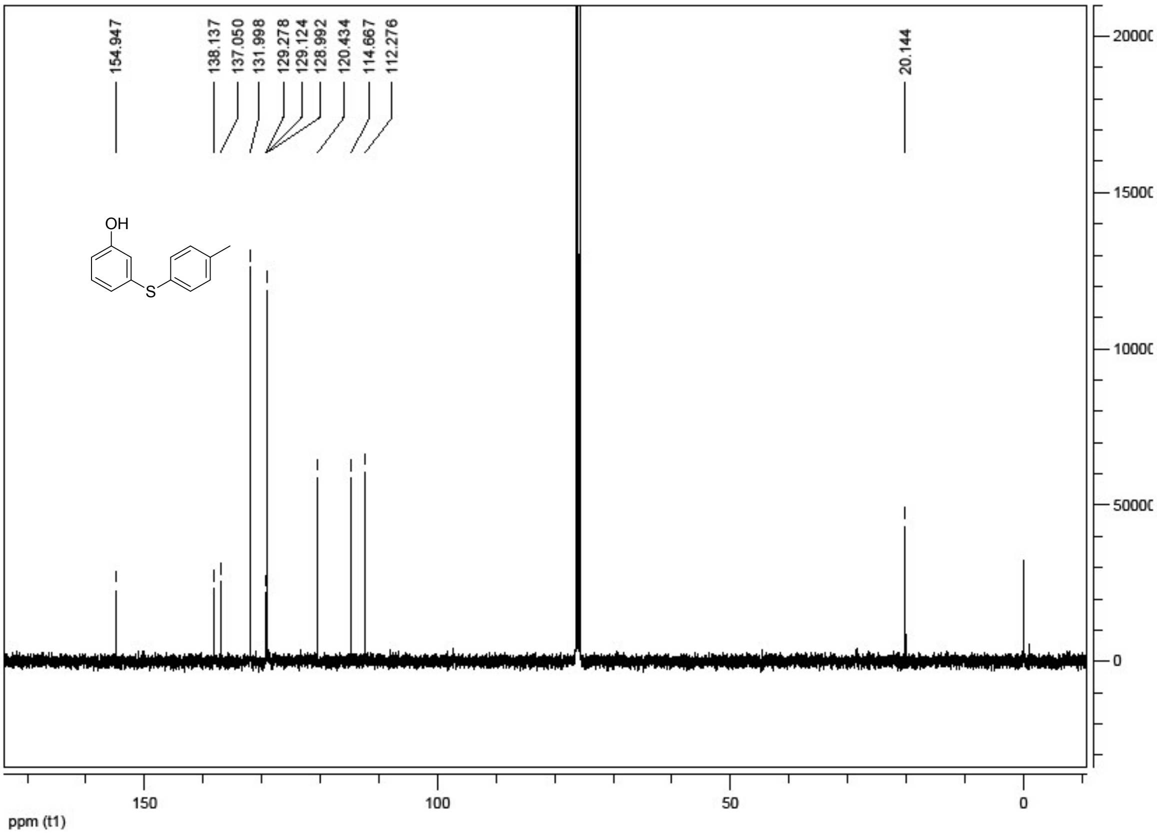


Figure 31. ^{1}H NMR spectrum of 2q in CDCl$_3$.

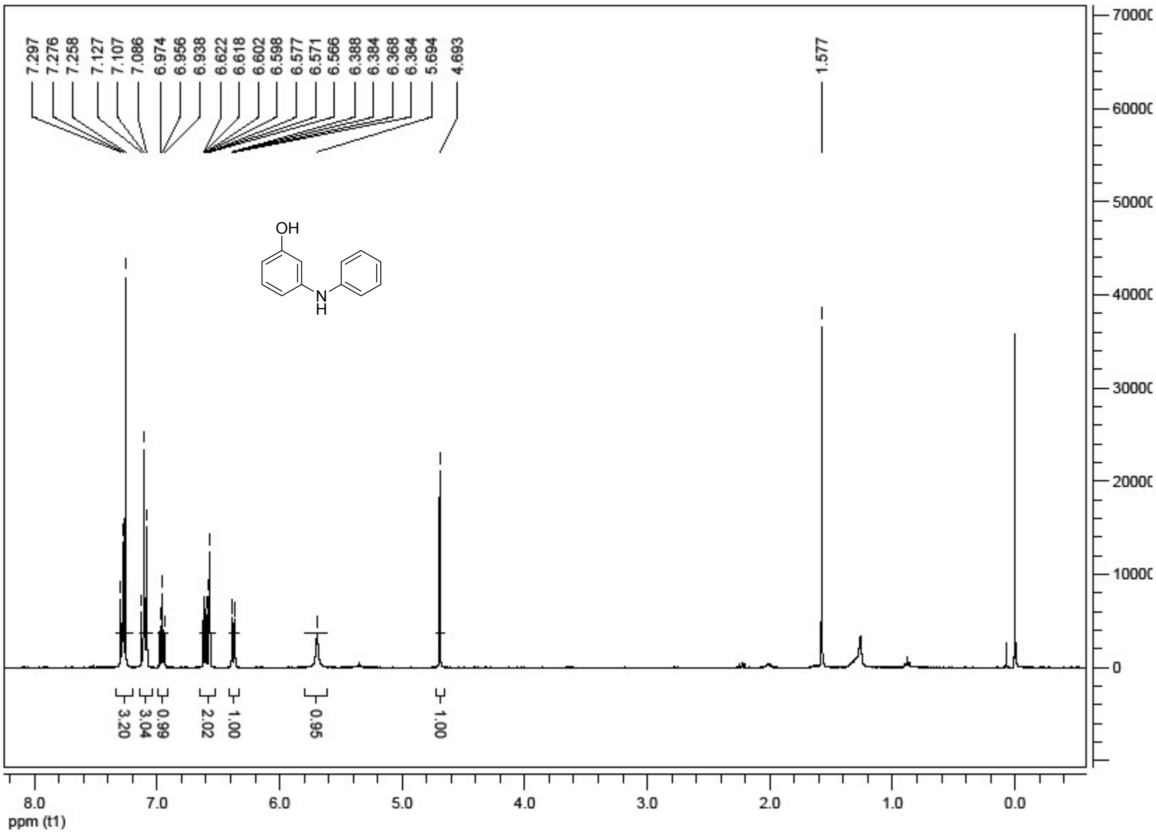


Figure 32. ^{13}C NMR spectrum of 2q in CDCl$_3$.

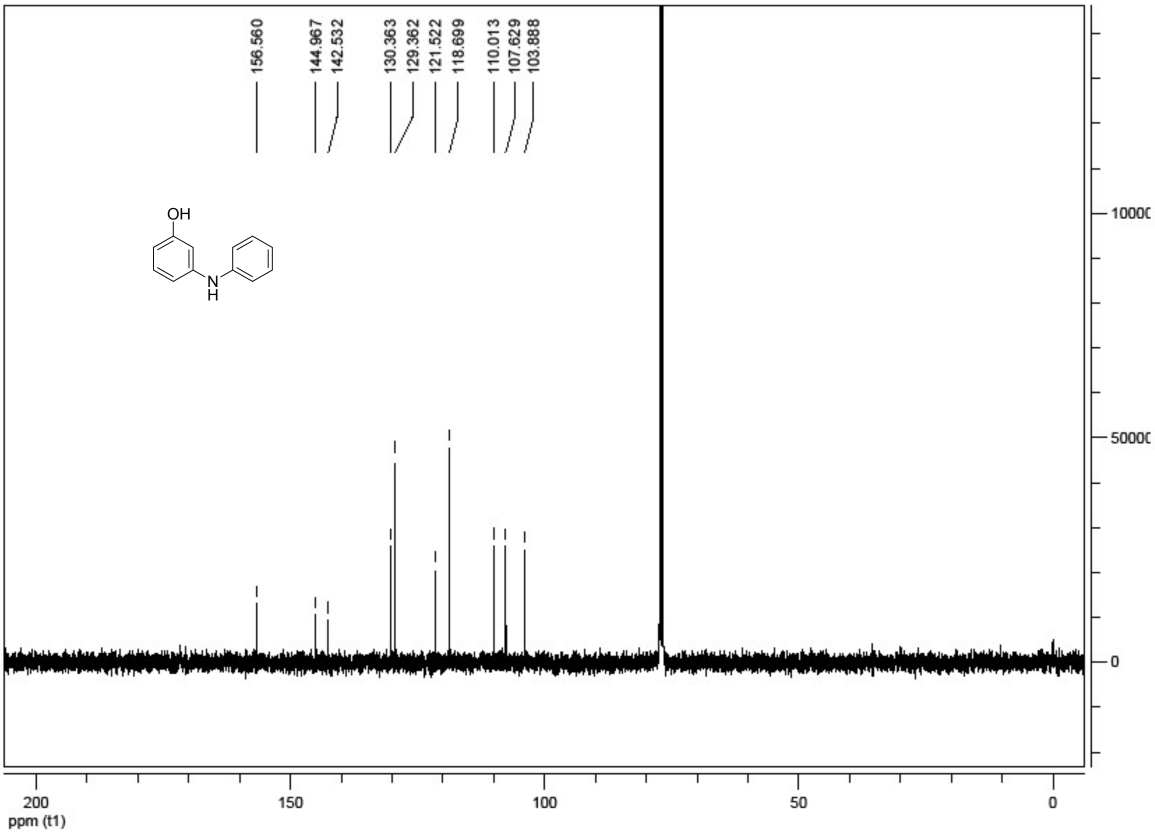


Figure 33. ^{1}H NMR spectrum of 2t in $CDCl_3$.

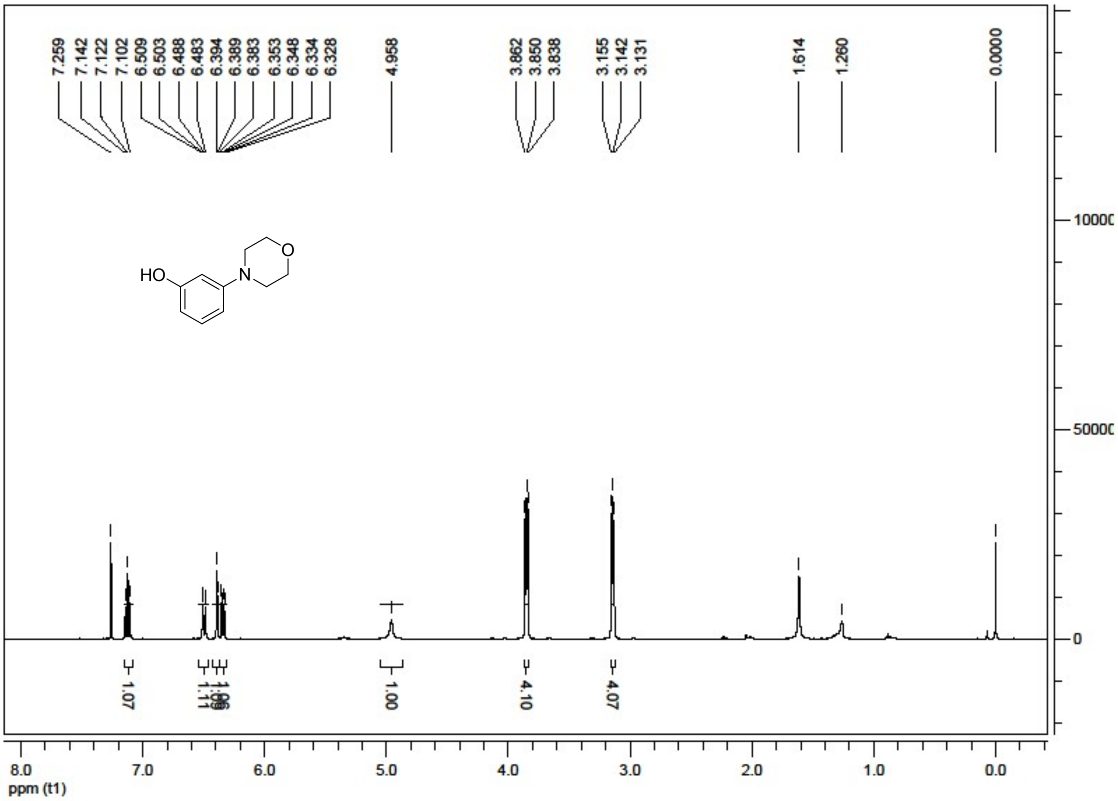


Figure 34. ^{13}C NMR spectrum of 2t in $CDCl_3$.

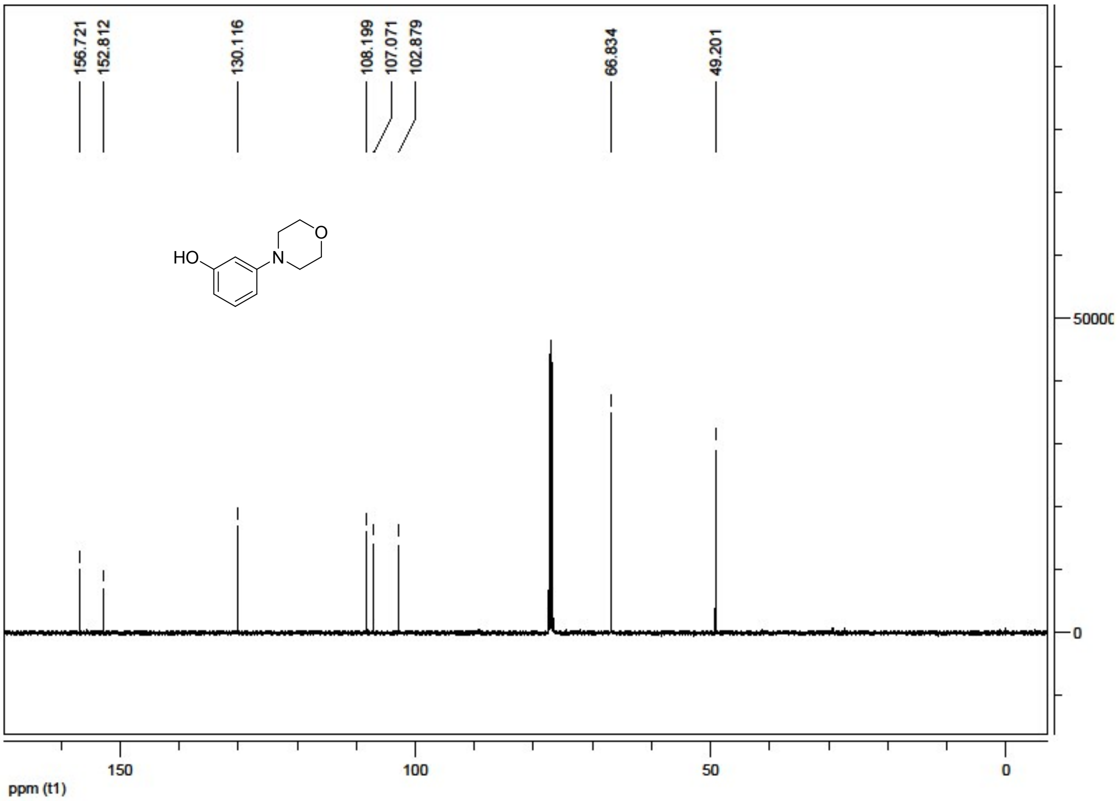


Figure 35. ^{1}H NMR spectrum of 2r in $CDCl_3$.

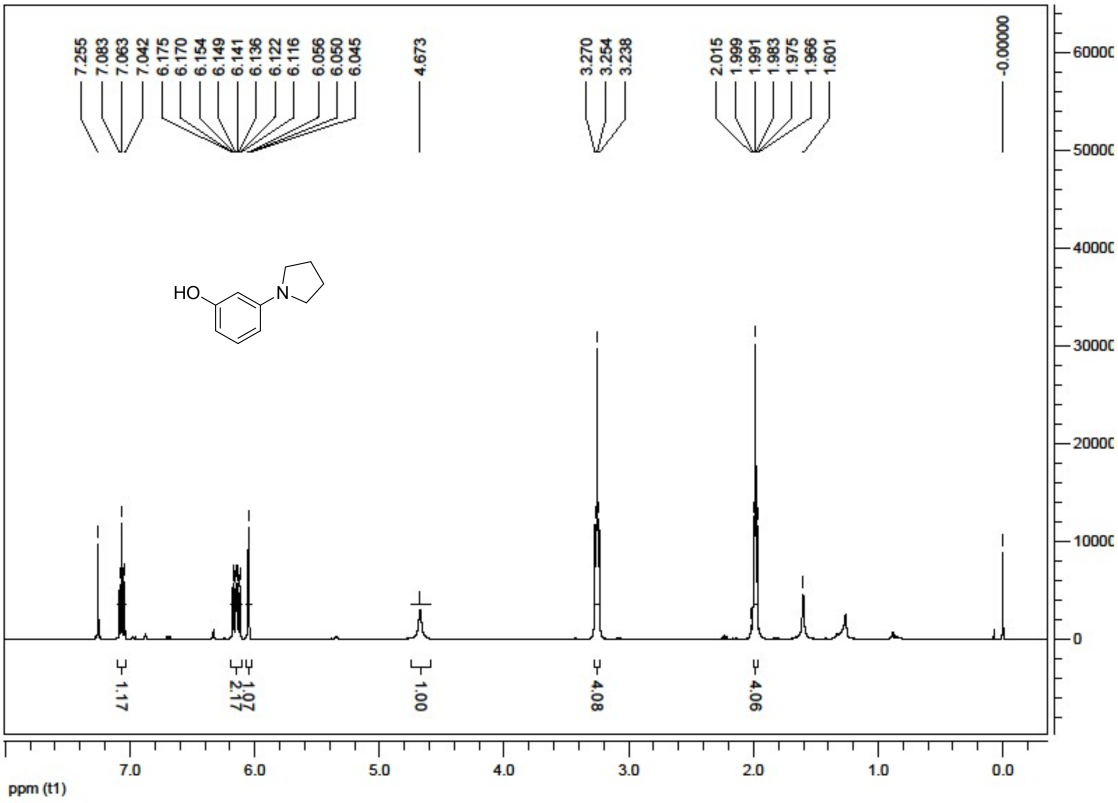


Figure 36. ^{13}C NMR spectrum of 2r in $CDCl_3$.

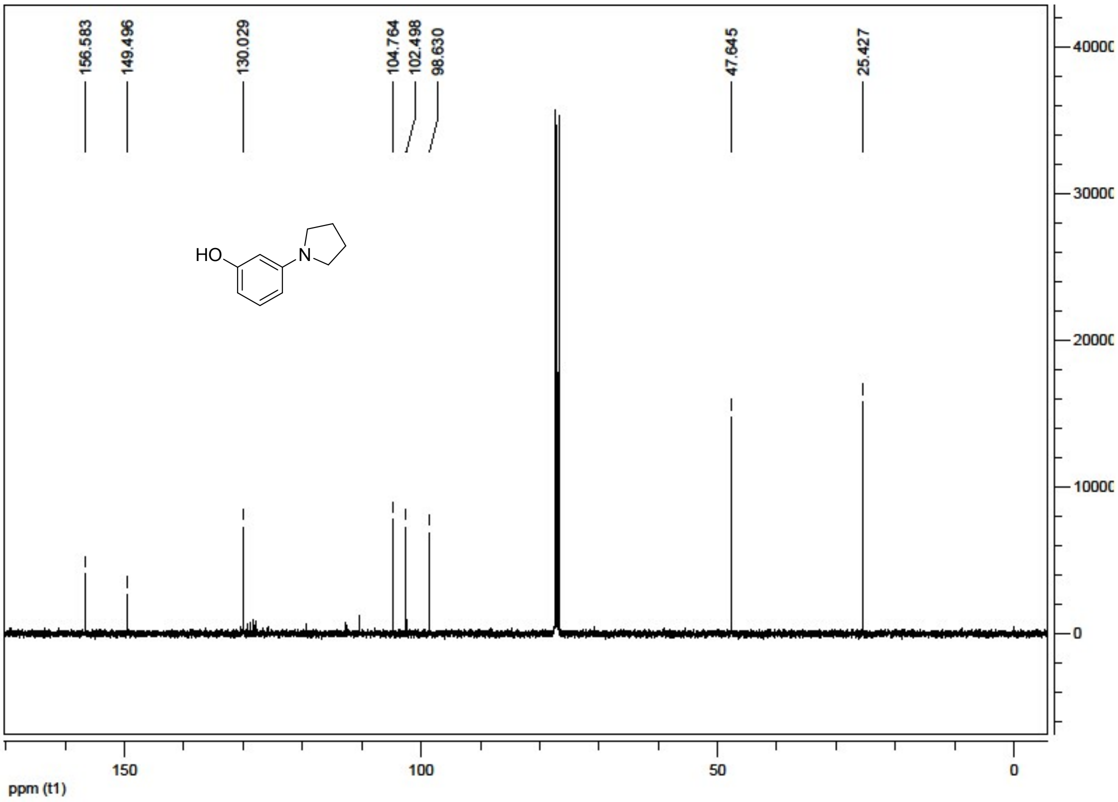


Figure 37. ^{1}H NMR spectrum of 2s in $CDCl_3$.

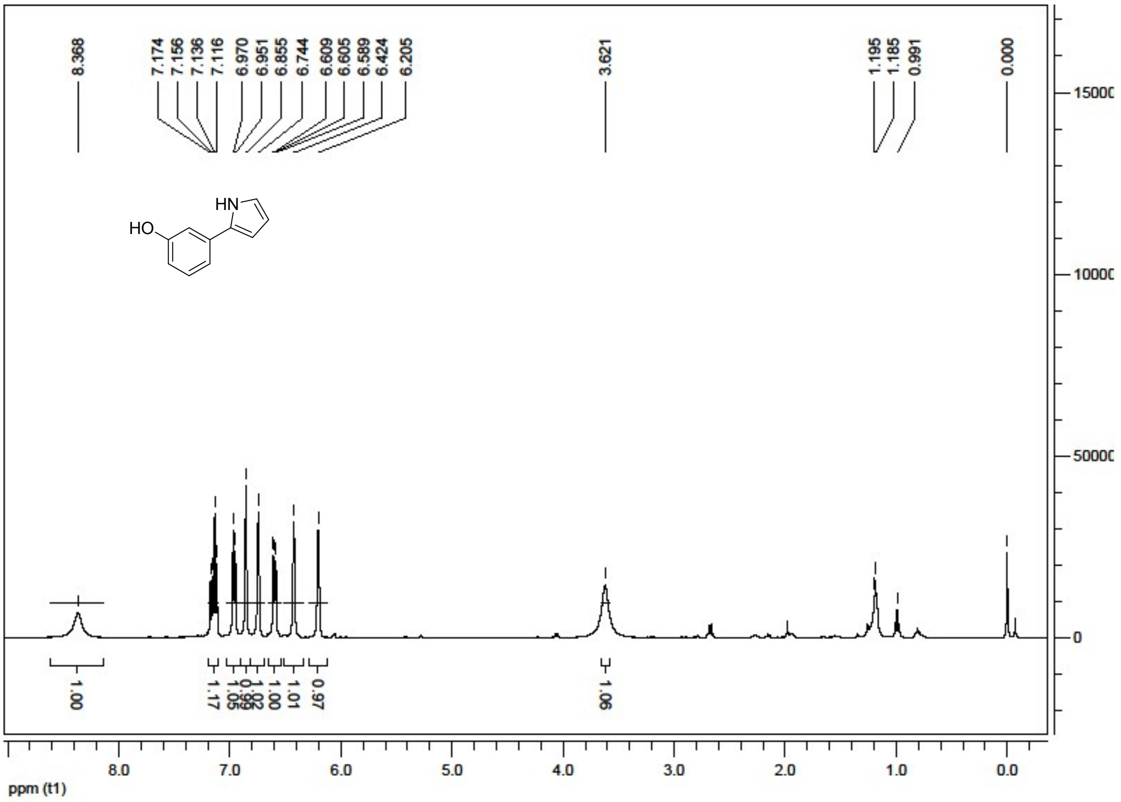


Figure 38. ^{13}C NMR spectrum of 2s in $CDCl_3$.

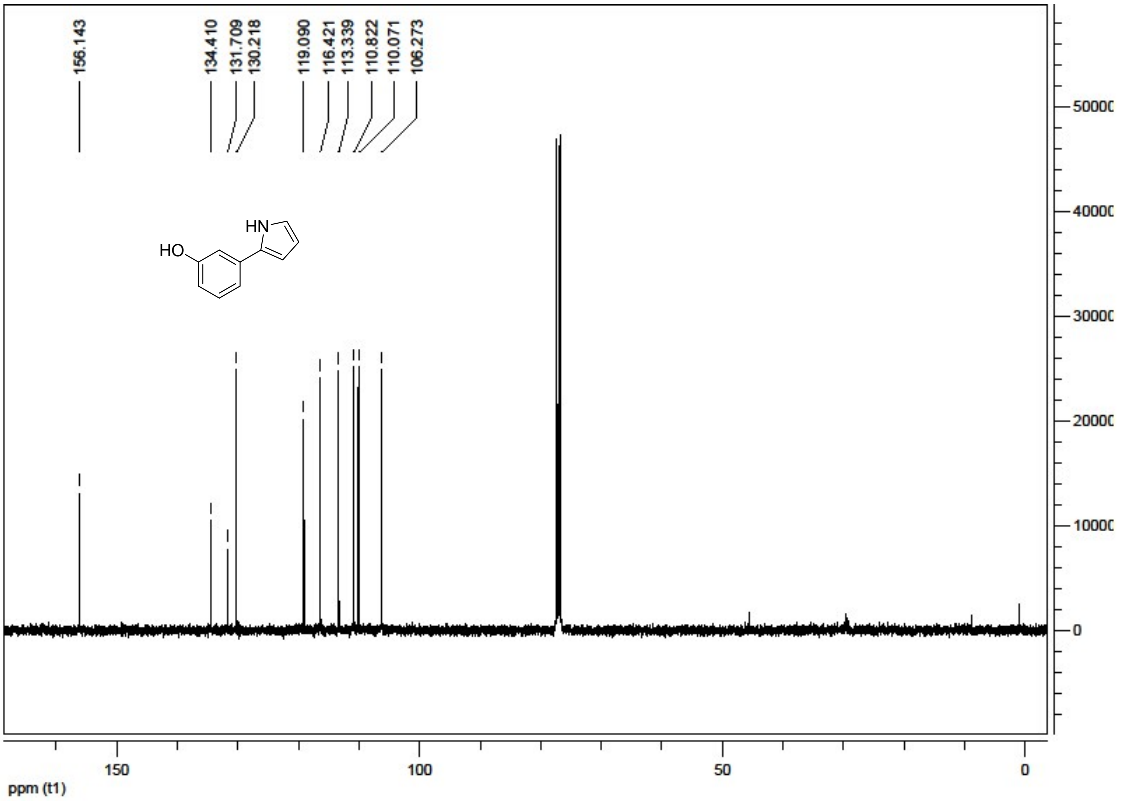


Figure 39. ^{1}H NMR spectrum of 2k in $CDCl_3$.

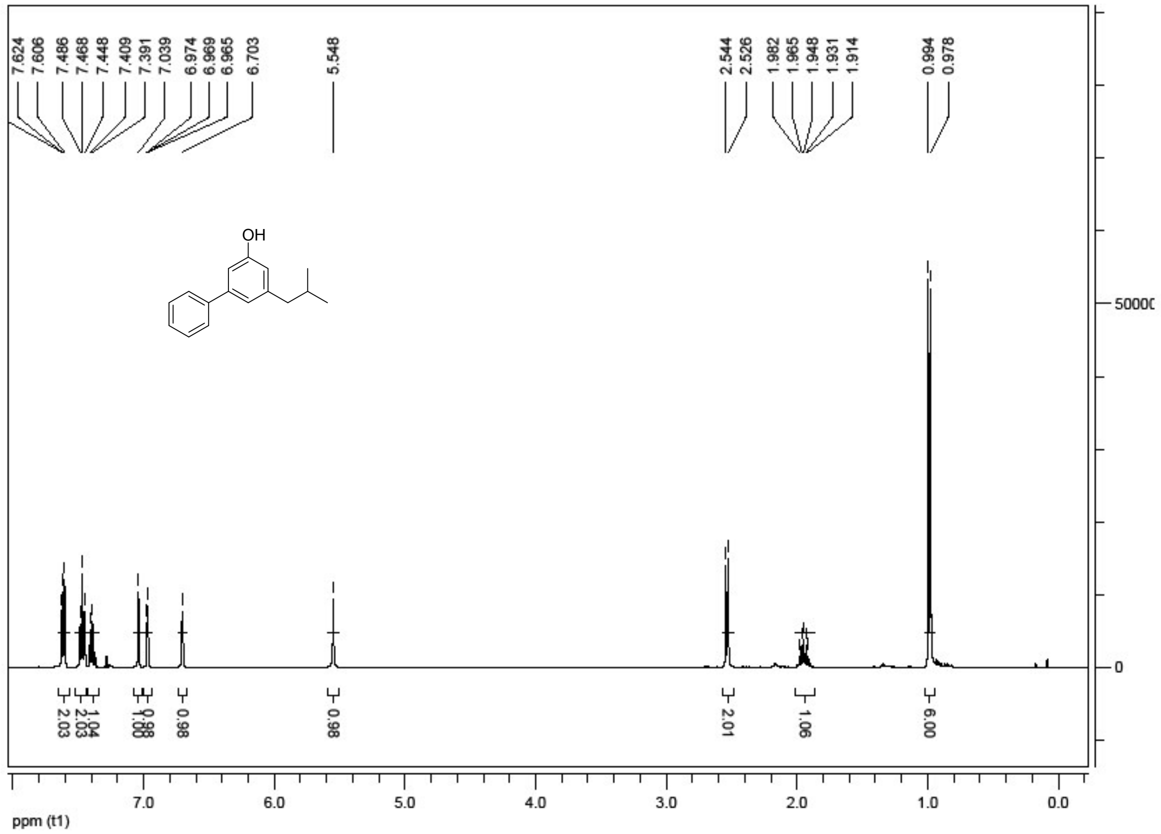


Figure 40. ^{13}C NMR spectrum of 2k in $CDCl_3$.

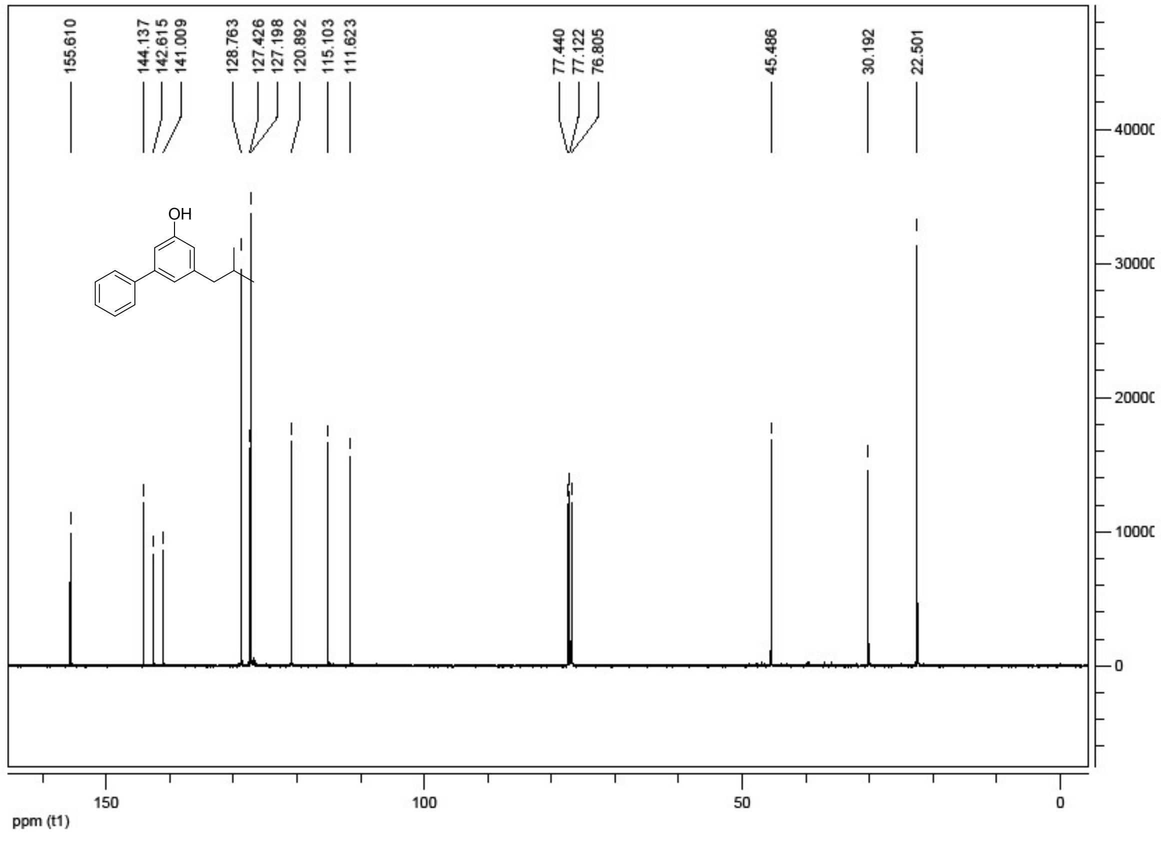


Figure 41. ^{1}H NMR spectrum of 2h in $CDCl_3$

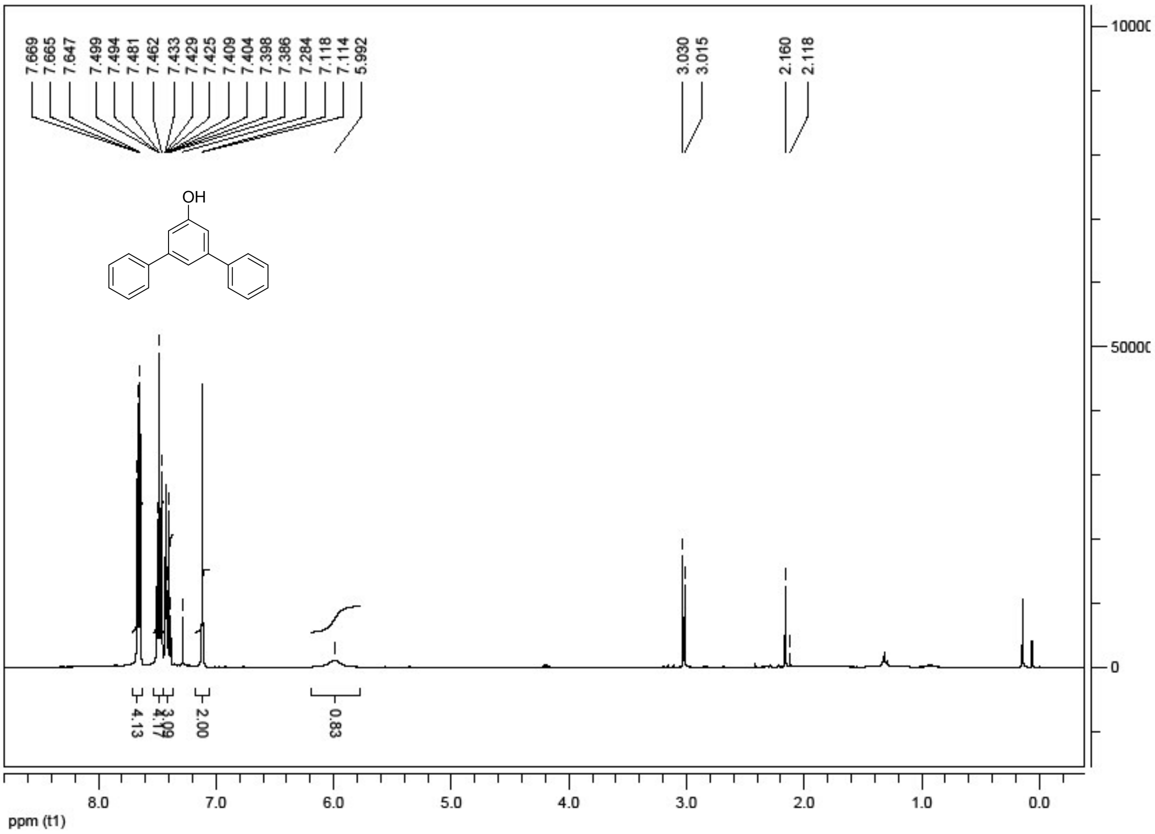


Figure 42. ^{13}C NMR spectrum of 2h in $CDCl_3$.

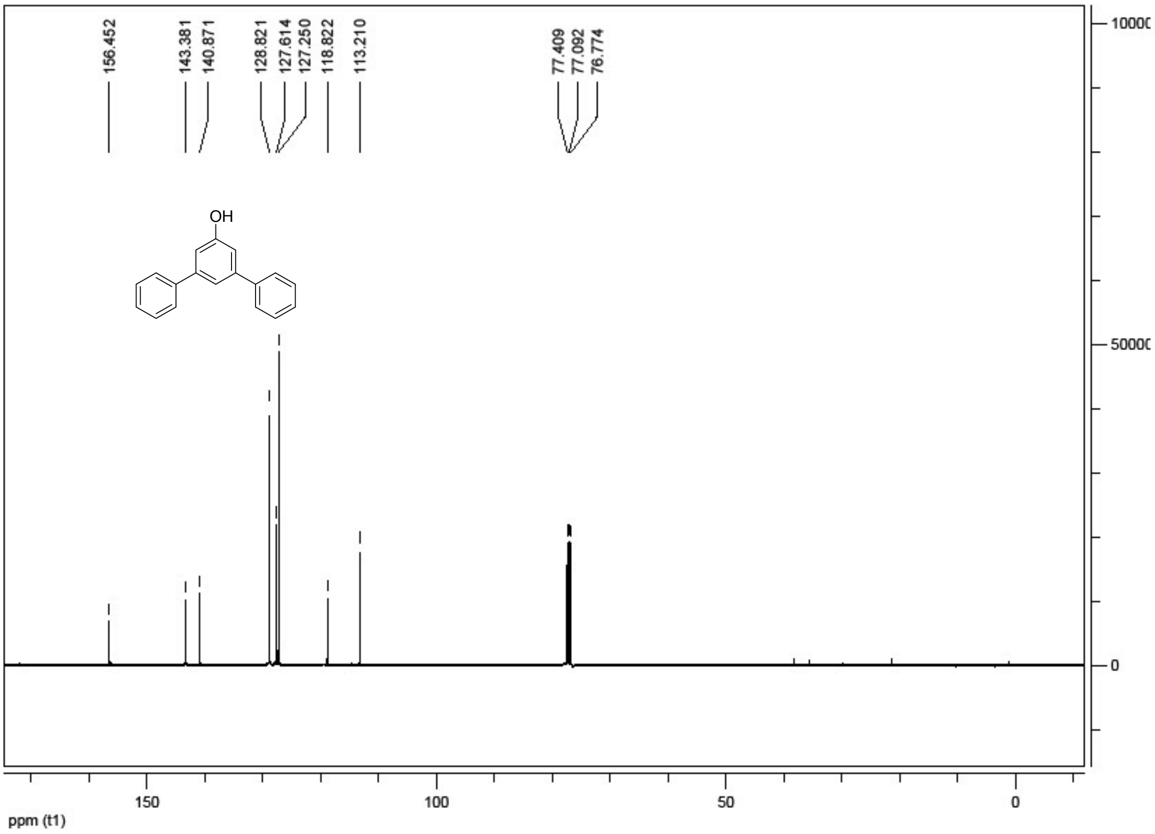


Figure 43. ^{1}H NMR spectrum of 2w in $CDCl_3$.

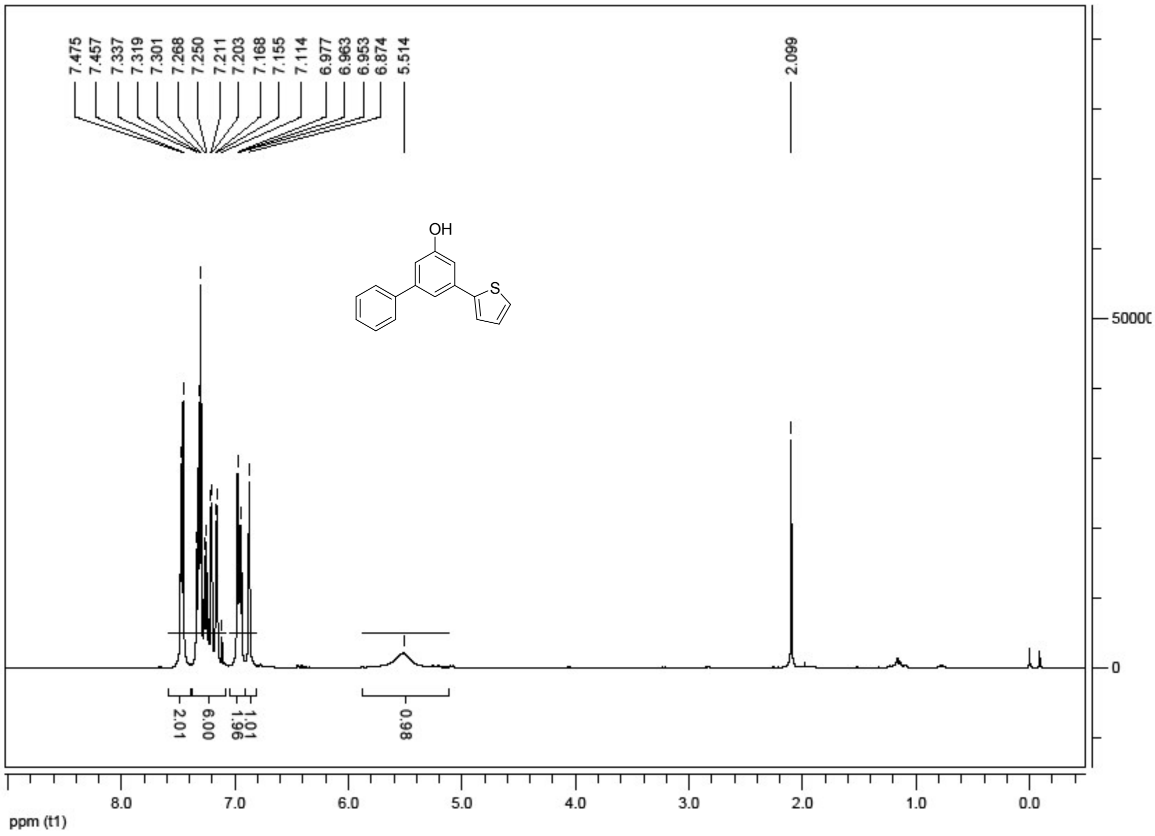


Figure 44. ^{13}C NMR spectrum of 2w in $CDCl_3$.

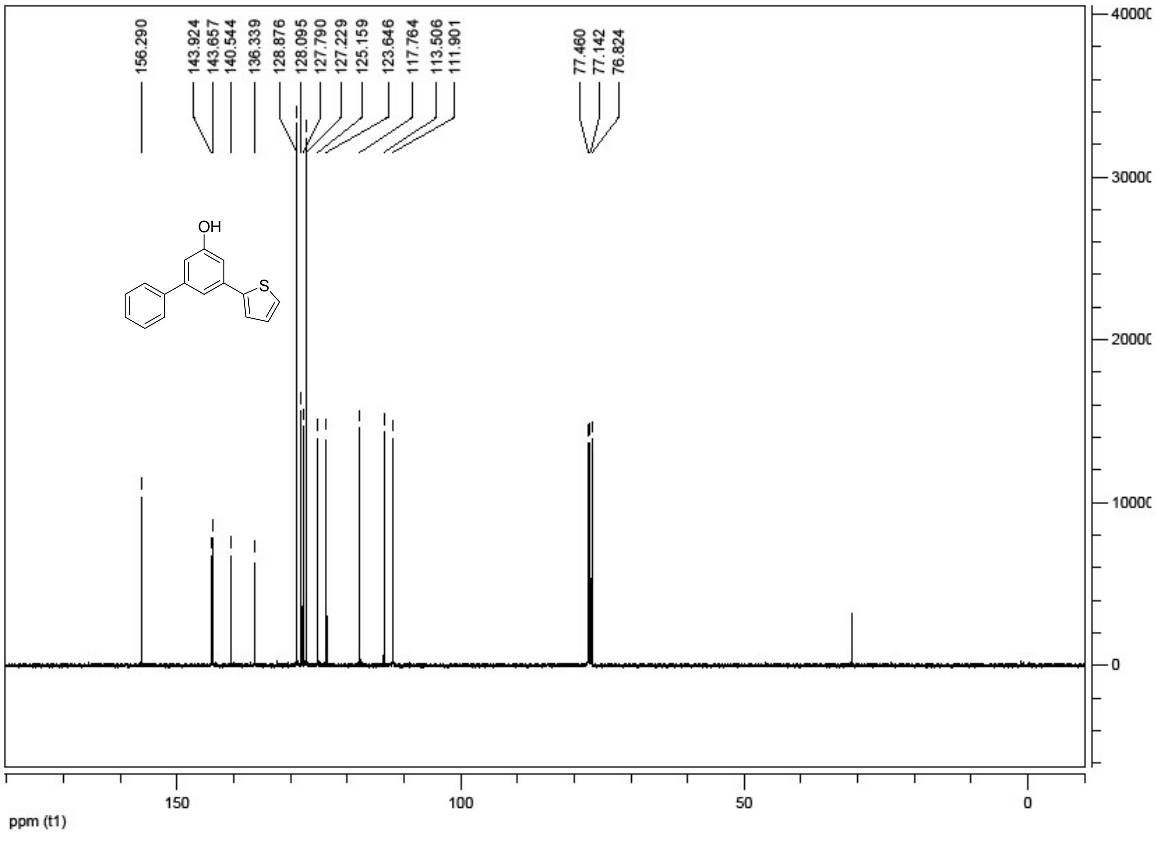


Figure 45. ^{1}H NMR spectrum of 2o in CDCl$_3$.

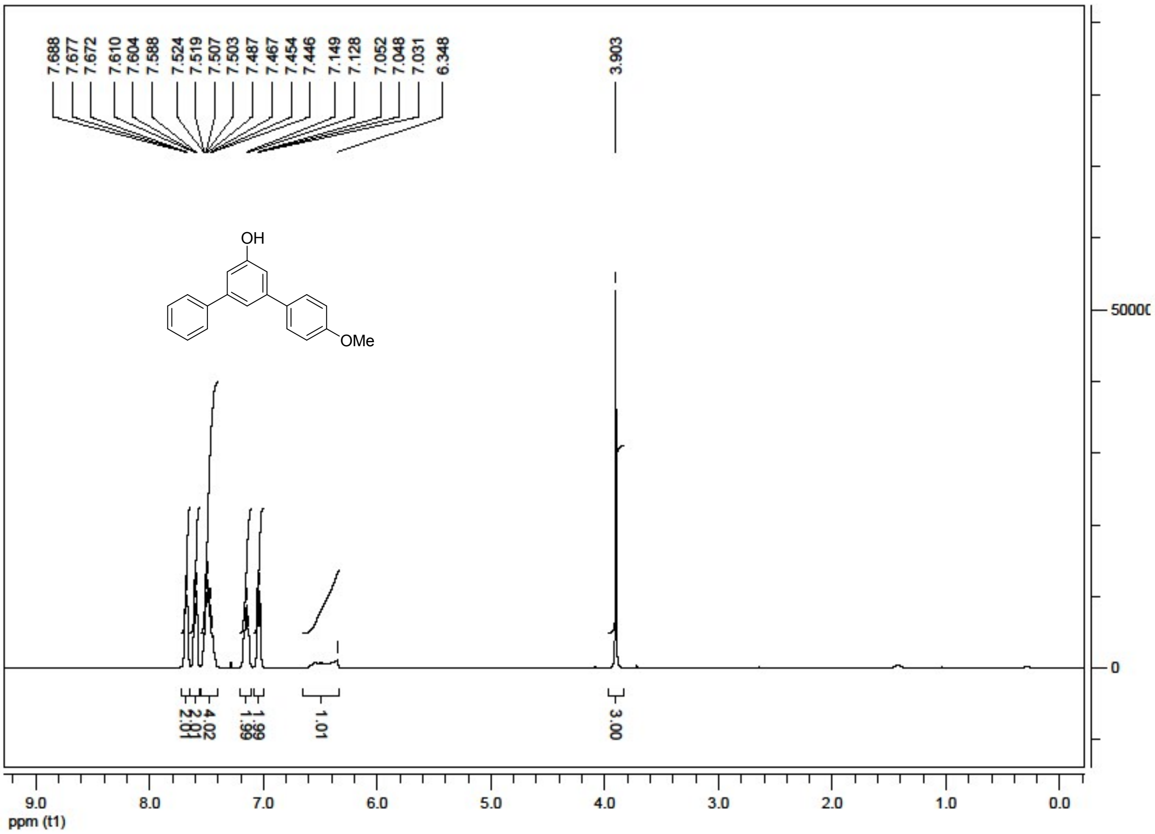


Figure 46. ^{13}C NMR spectrum of 2o in CDCl$_3$.

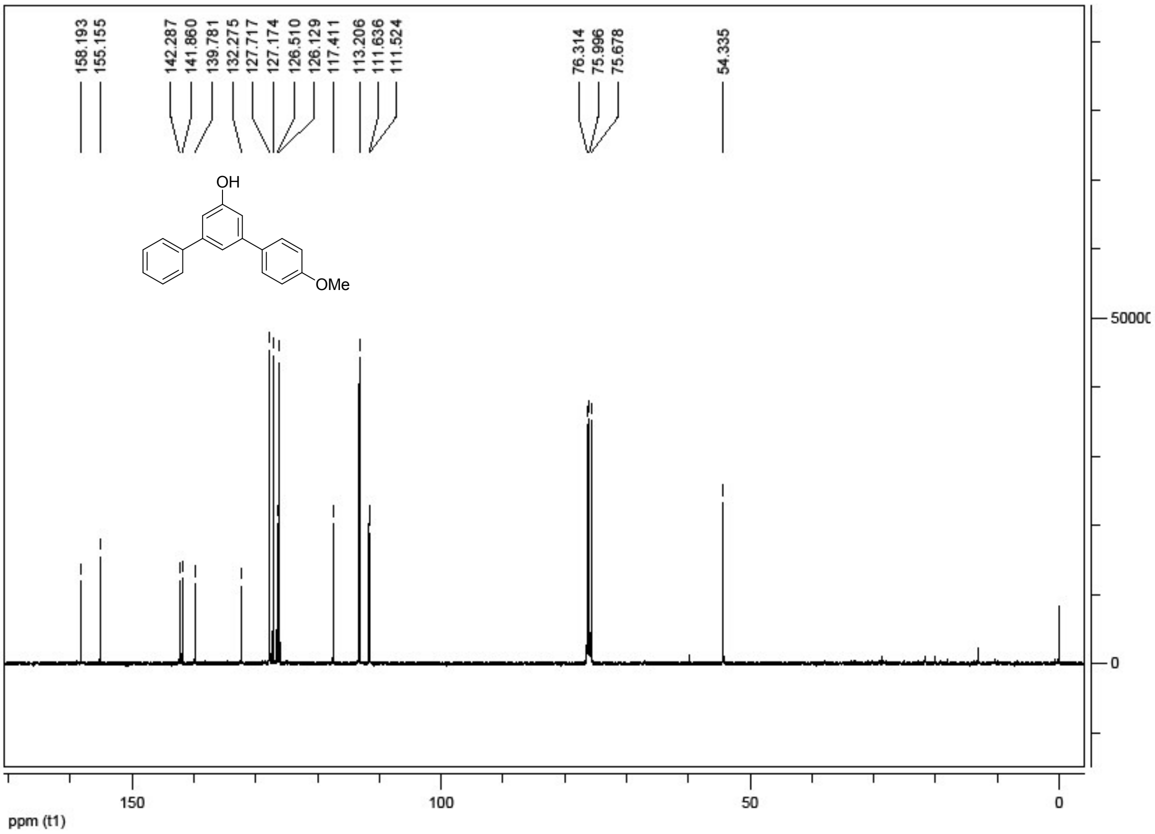


Figure 47. ^{1}H NMR spectrum of 2n in $CDCl_3$.

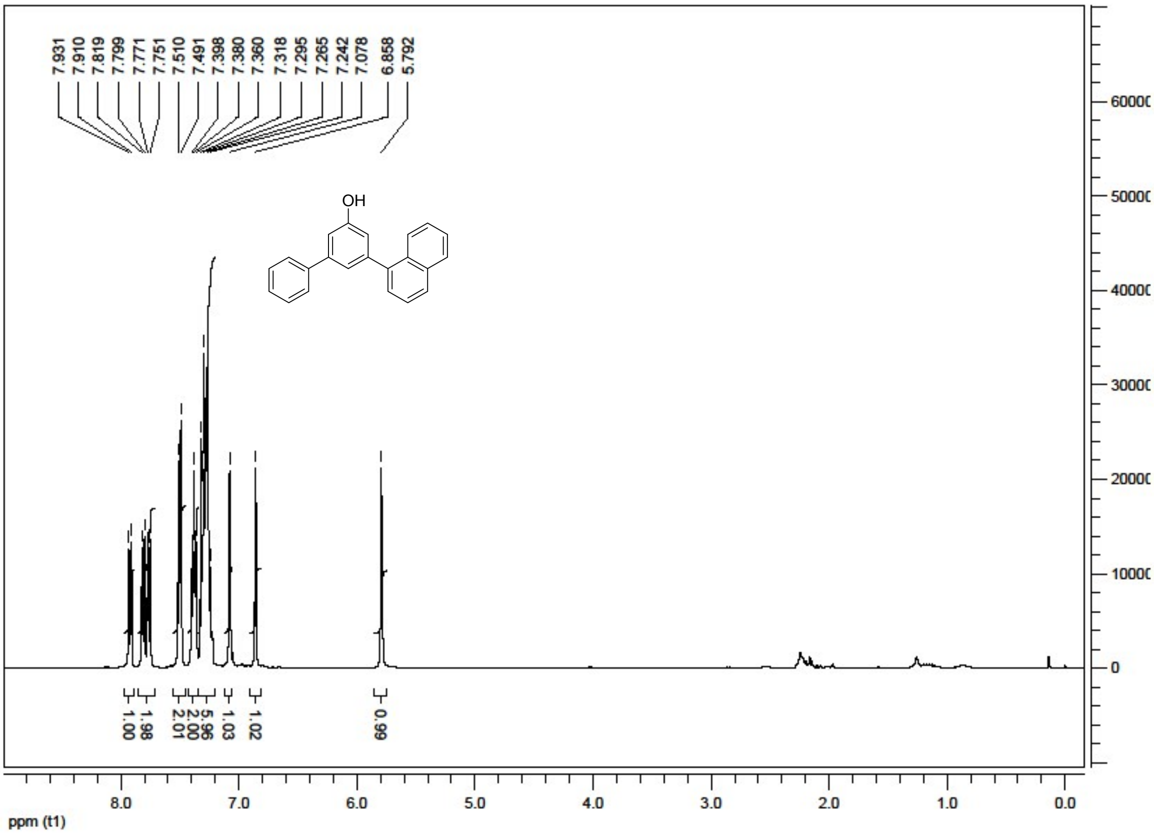


Figure 48. ^{13}C NMR spectrum of 2n in $CDCl_3$.

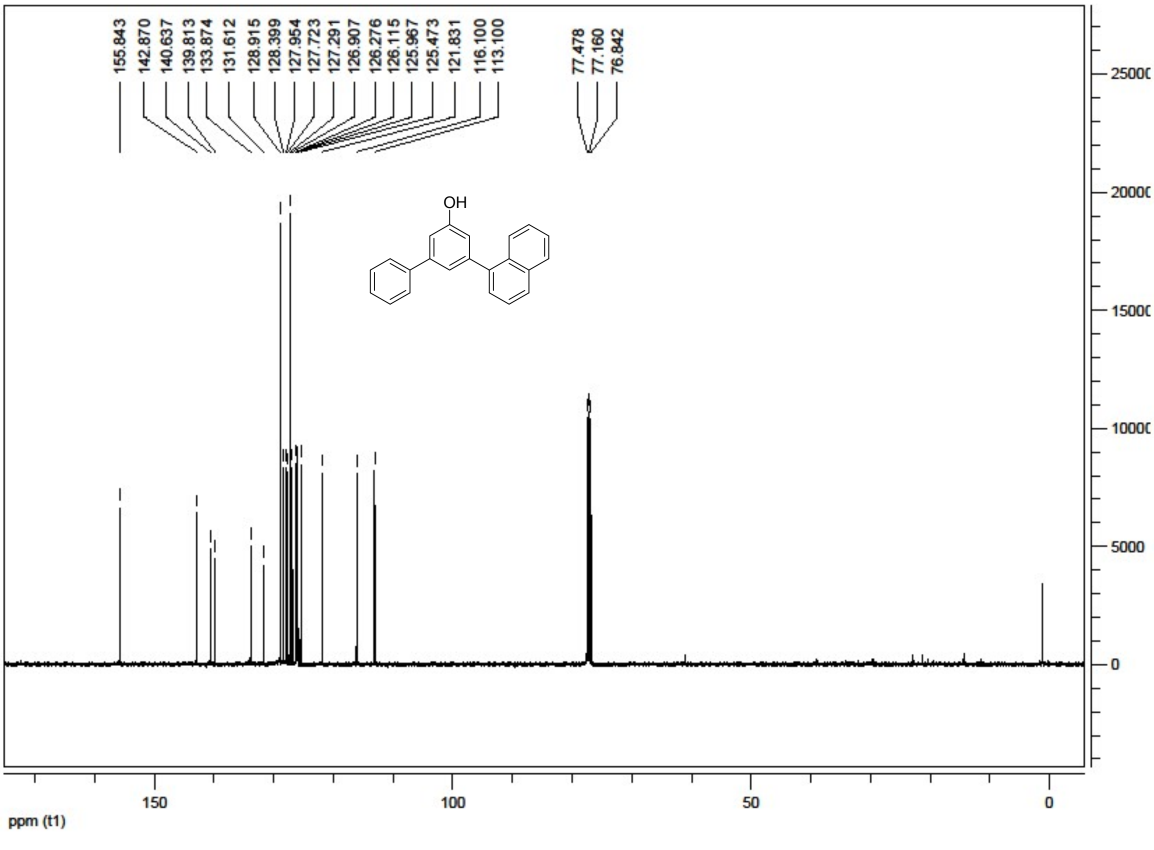


Figure 49. ^1H NMR spectrum of 2i in $CDCl_3$.

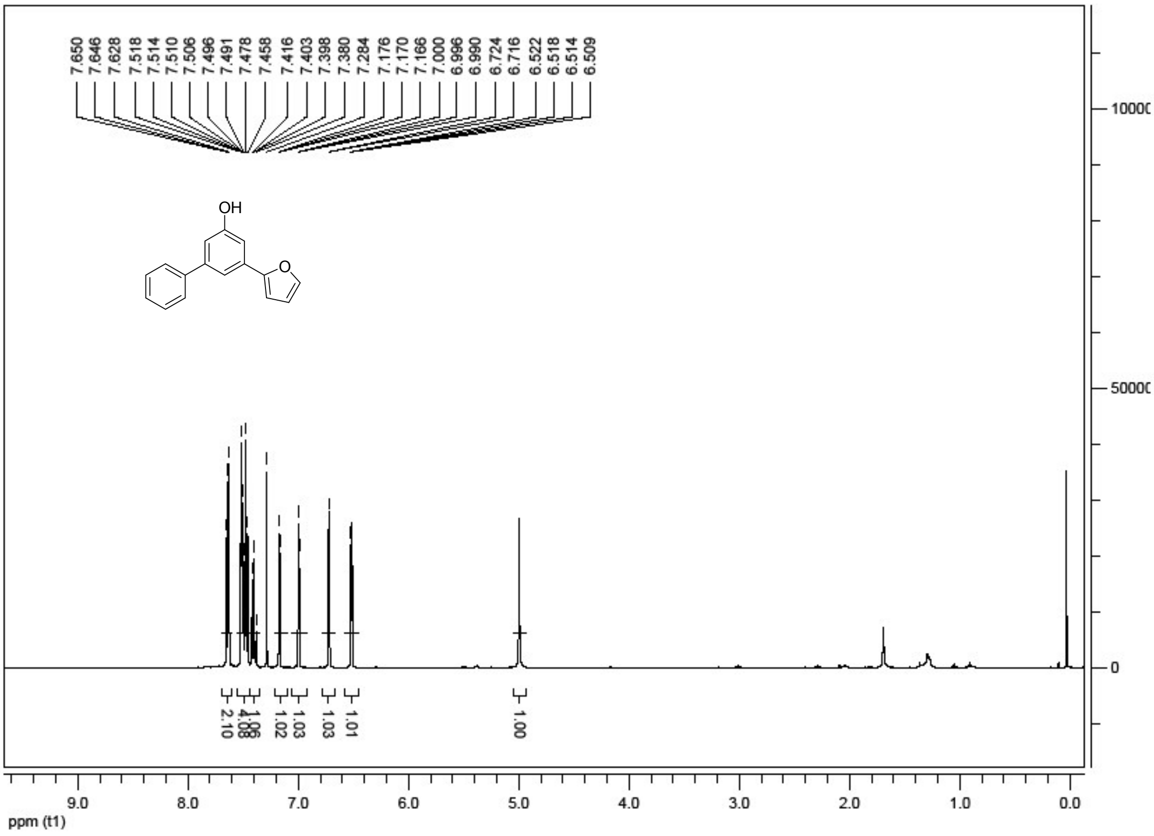


Figure 50. ^{13}C NMR spectrum of 2i in $CDCl_3$.

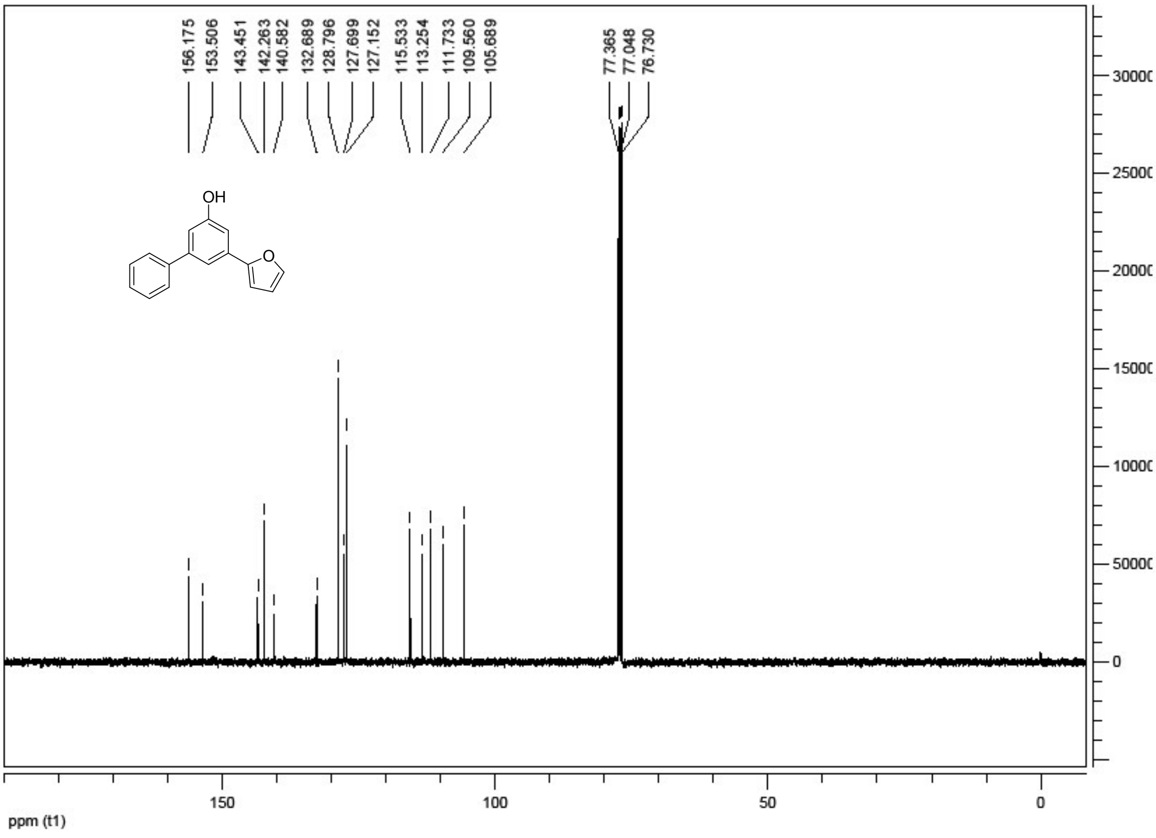


Figure 51. ^{1}H NMR spectrum of 2m in $CDCl_3$.

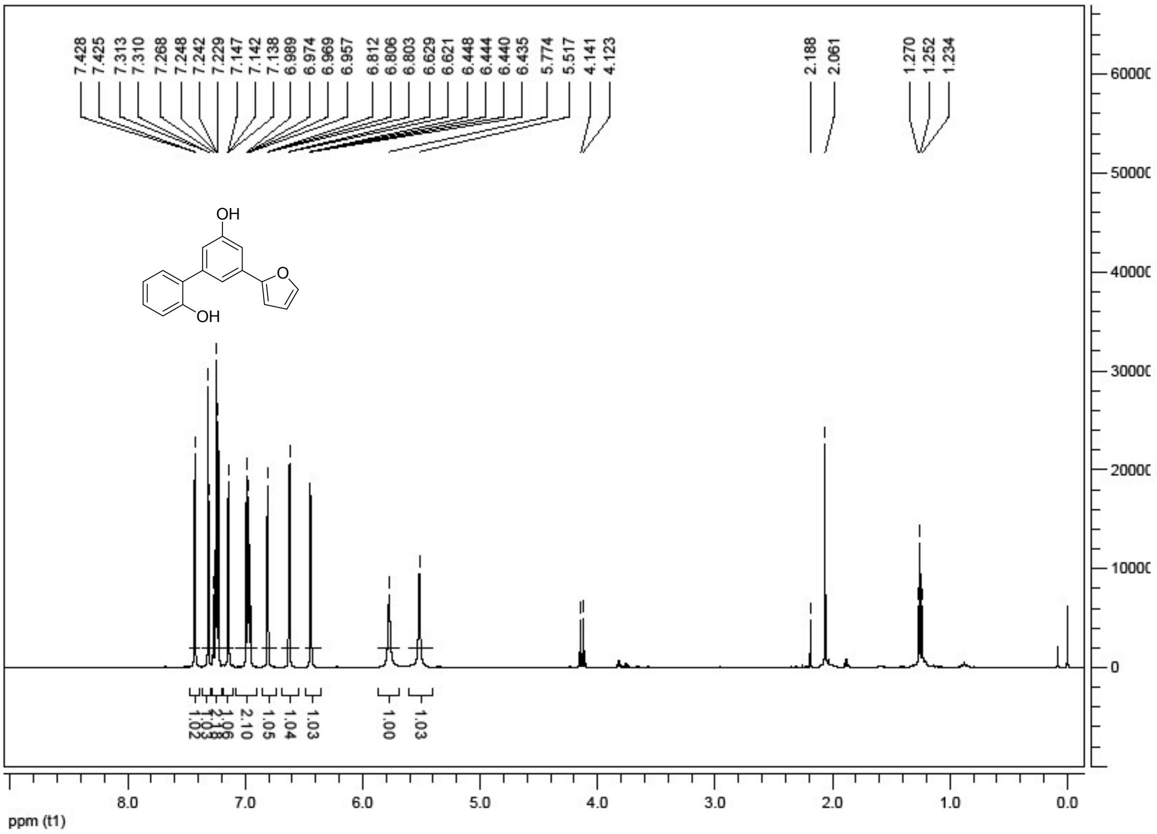


Figure 52. ^{13}C NMR spectrum of 2m in $CDCl_3$.

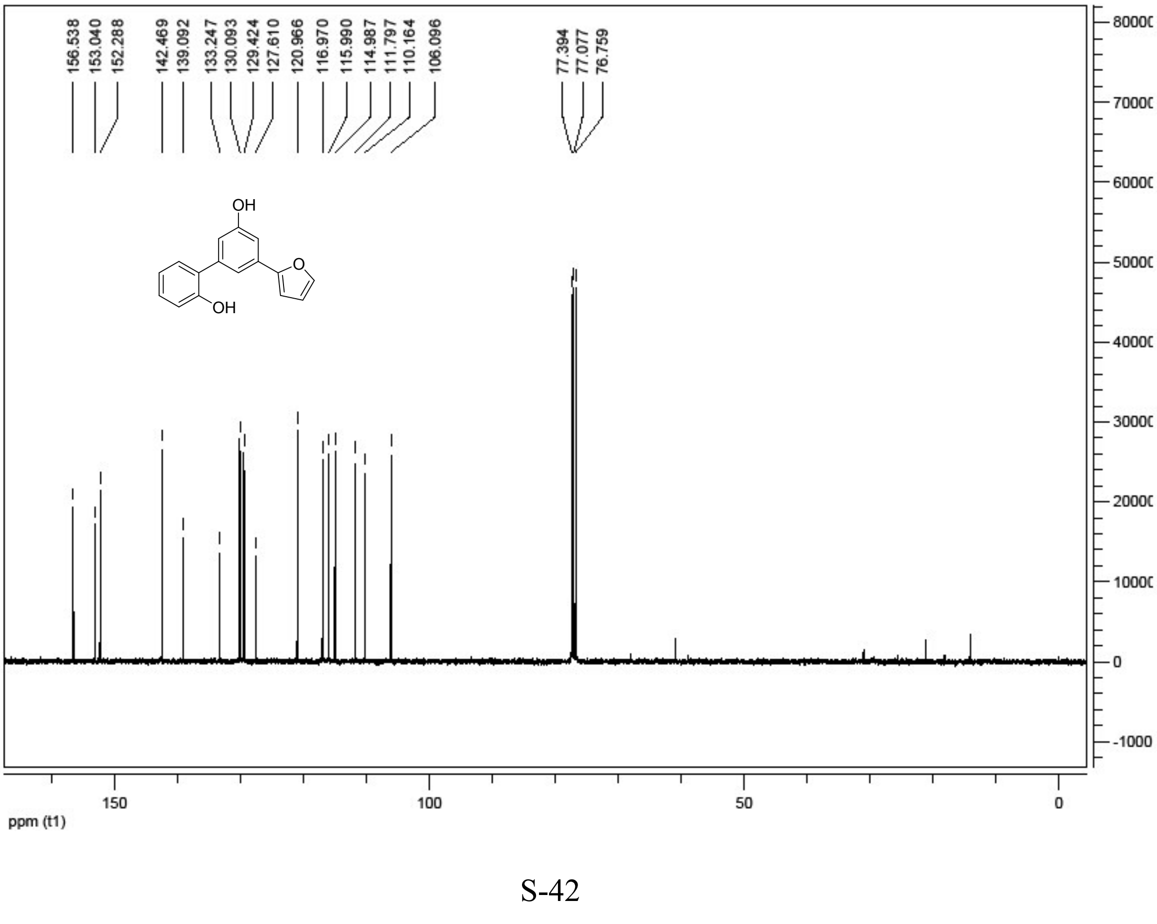


Figure 53. ^{1}H NMR spectrum of 2l in $CDCl_3$.

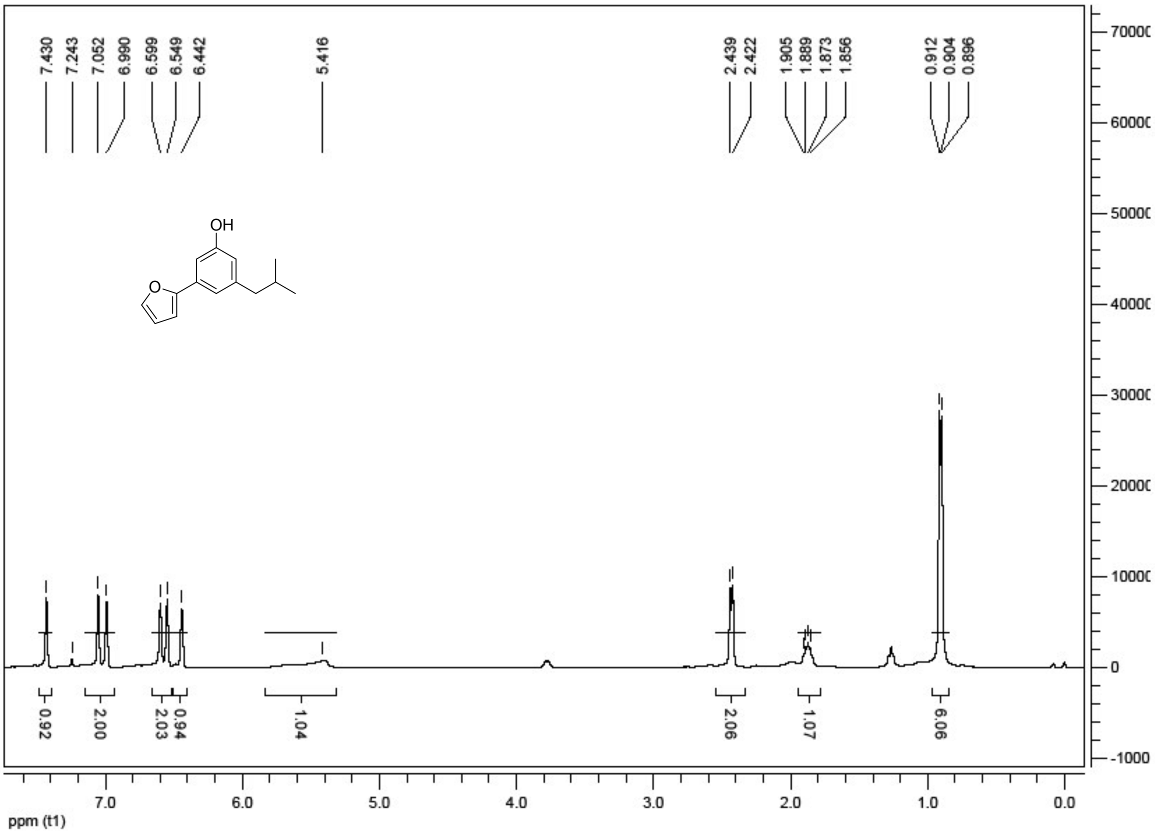


Figure 54. ^{13}C NMR spectrum of 2l in $CDCl_3$

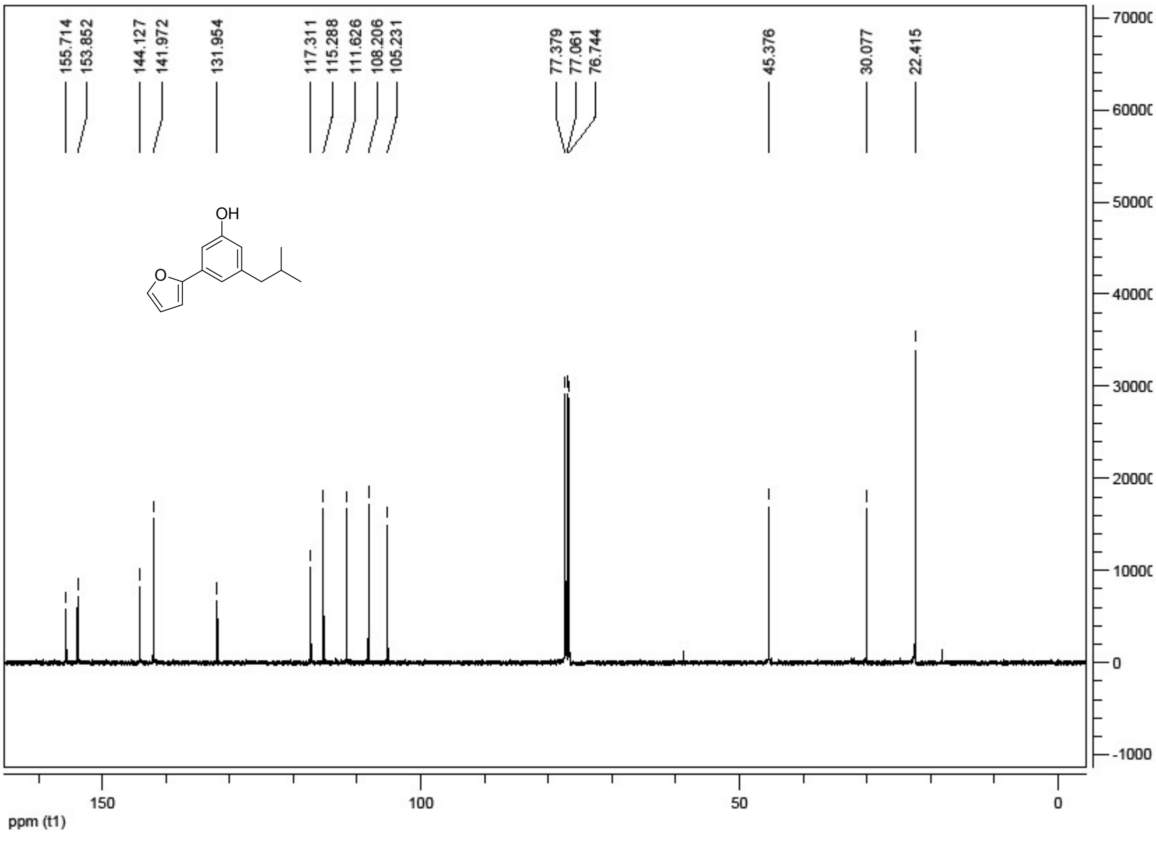


Figure 55. ^{1}H NMR spectrum of 2j in $CDCl_3$.

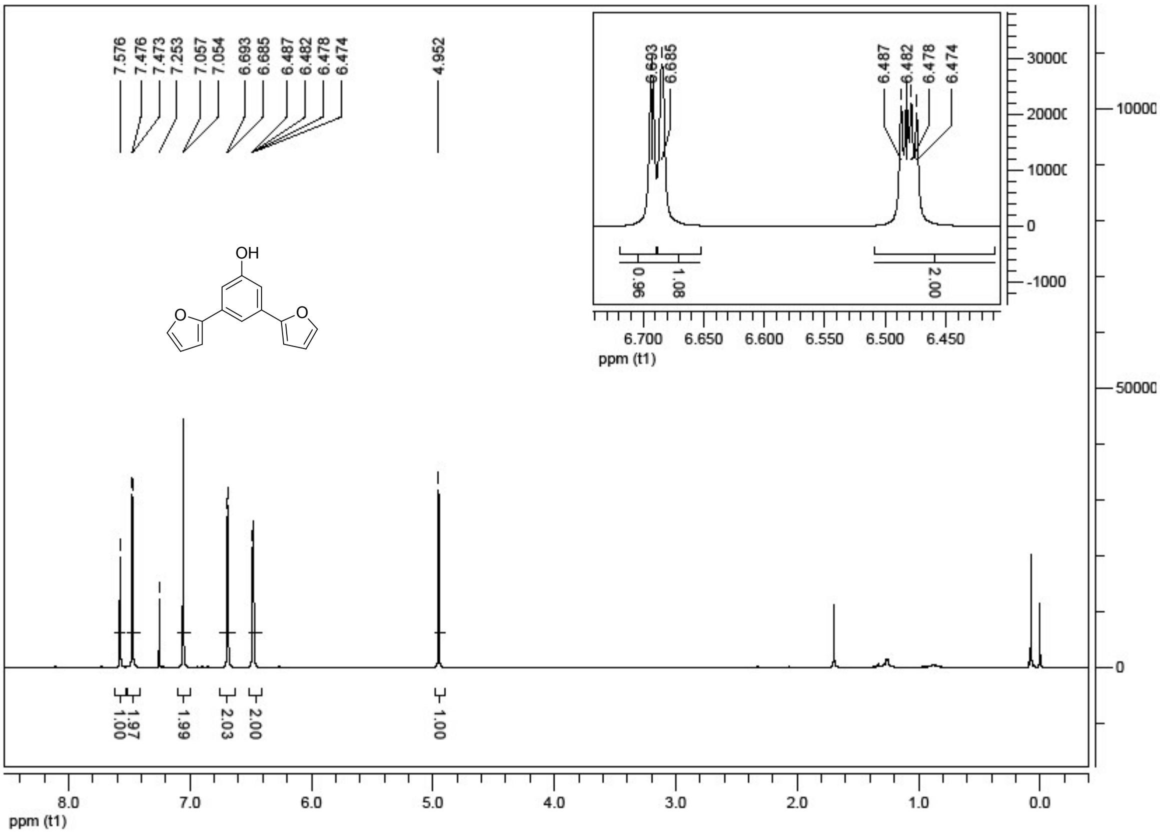


Figure 56. ^{13}C NMR spectrum of 2j in $CDCl_3$.

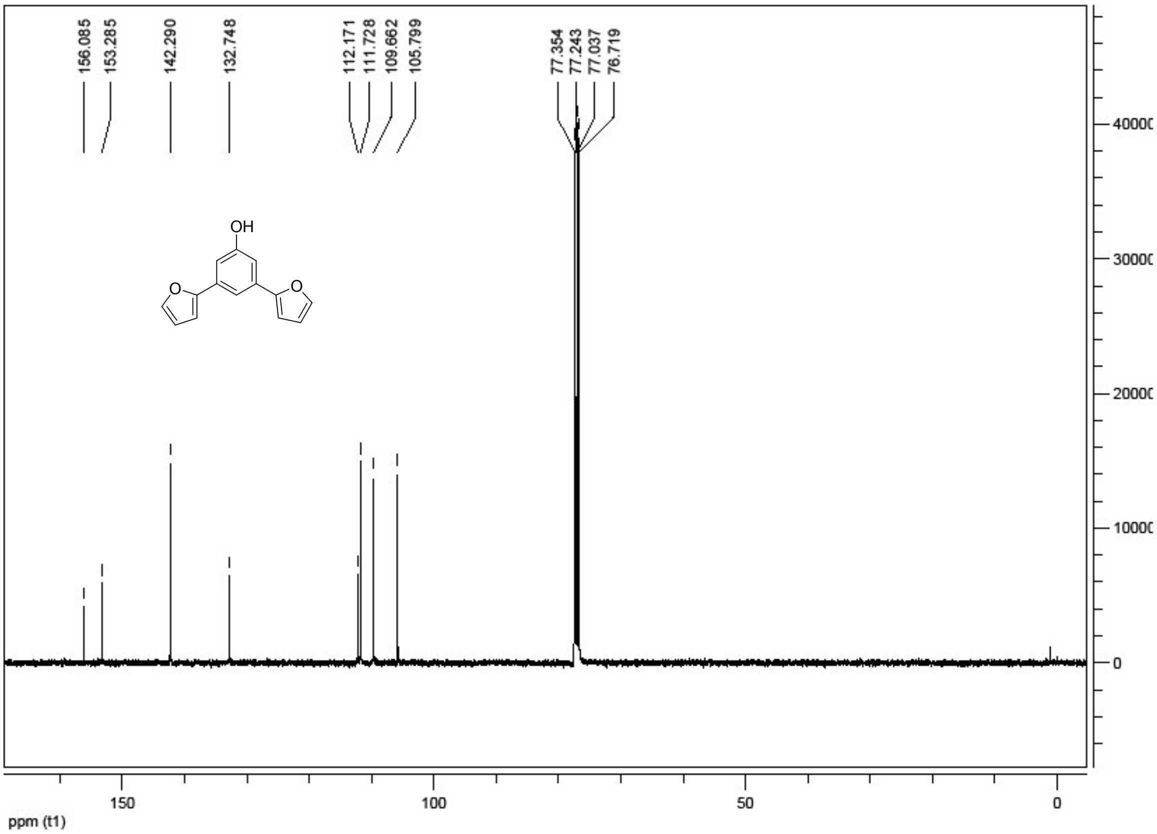


Figure 57. ^{1}H NMR spectrum of 2v in CDCl$_3$.

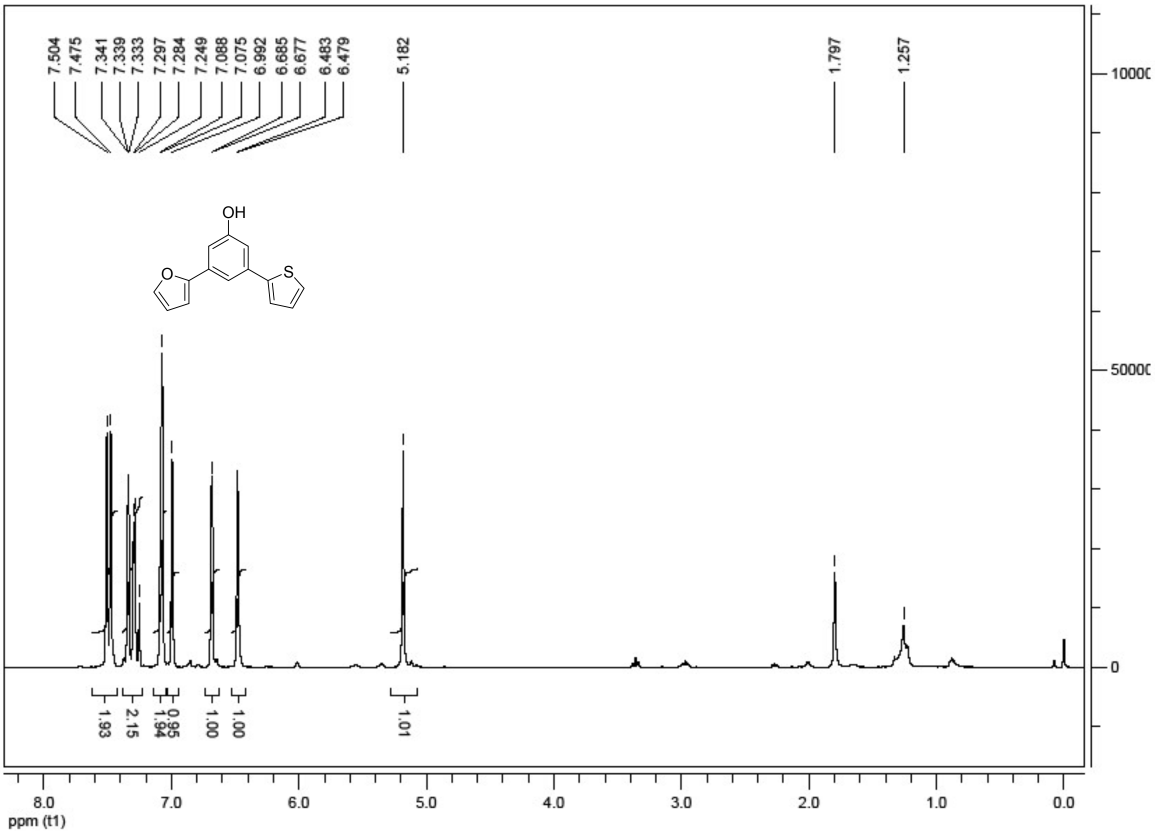


Figure 58. ^{13}C NMR spectrum of 2v in CDCl$_3$.

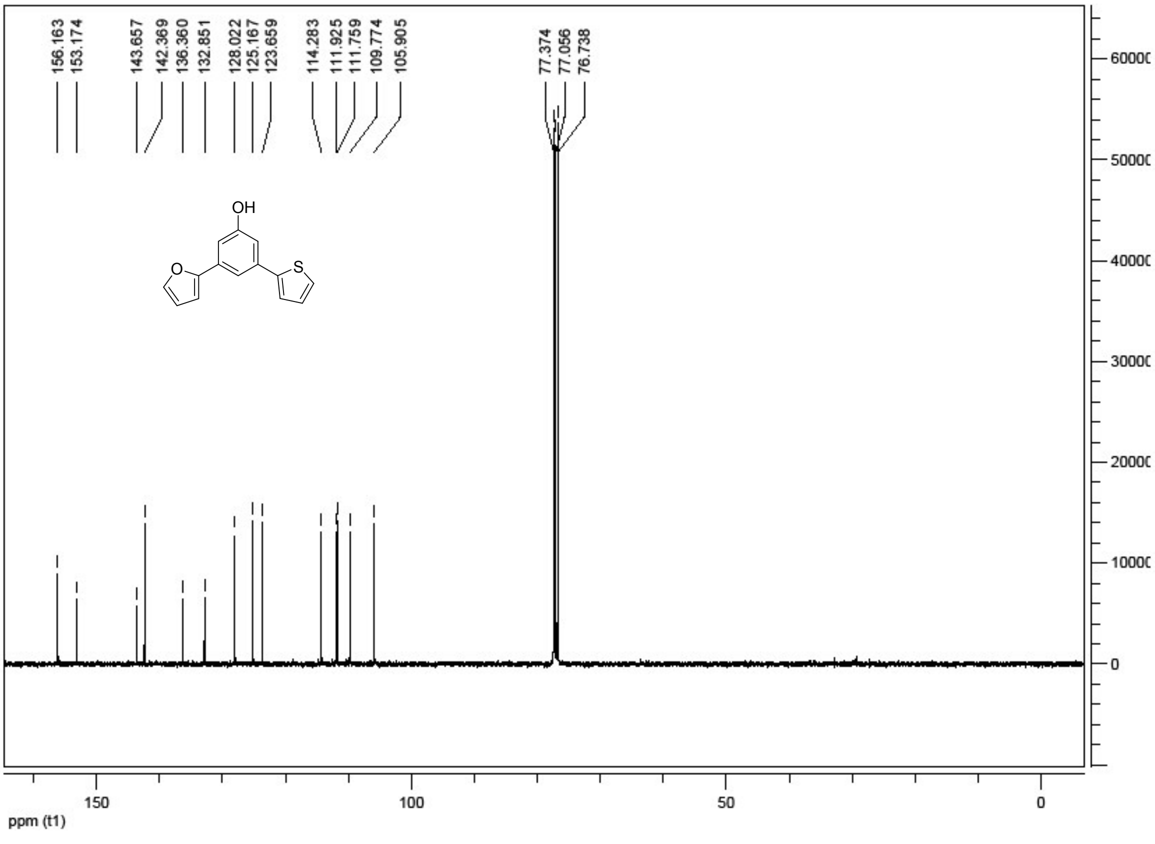


Figure 59. ^{1}H NMR spectrum of 2u in CDCl$_3$.

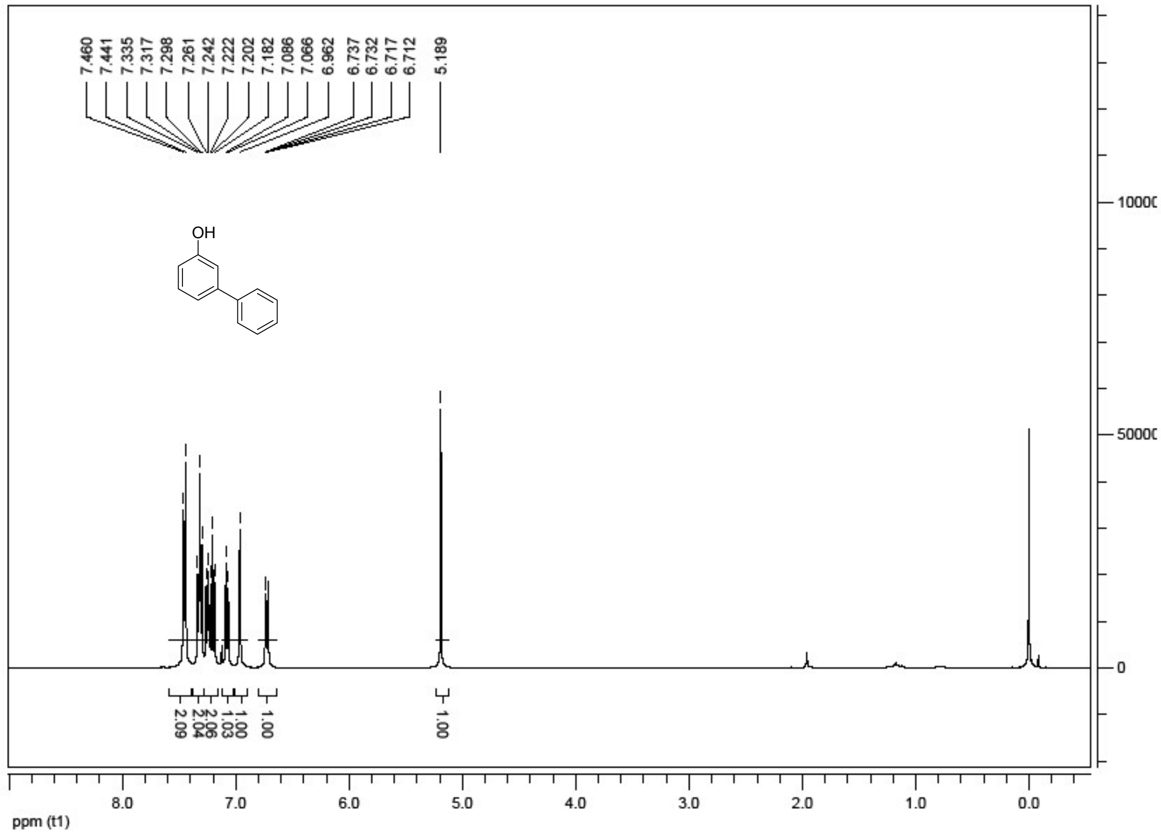


Figure 60. ^{13}C NMR spectrum of 2u in CDCl3.

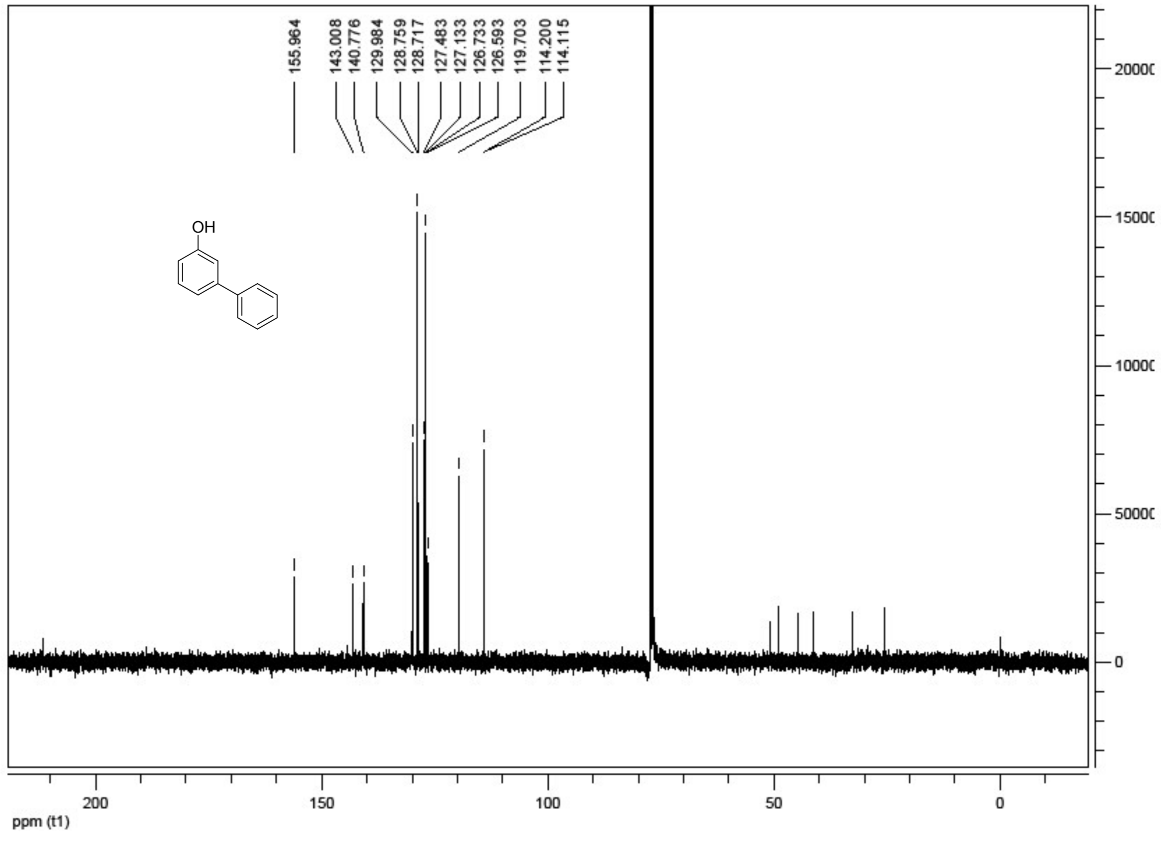
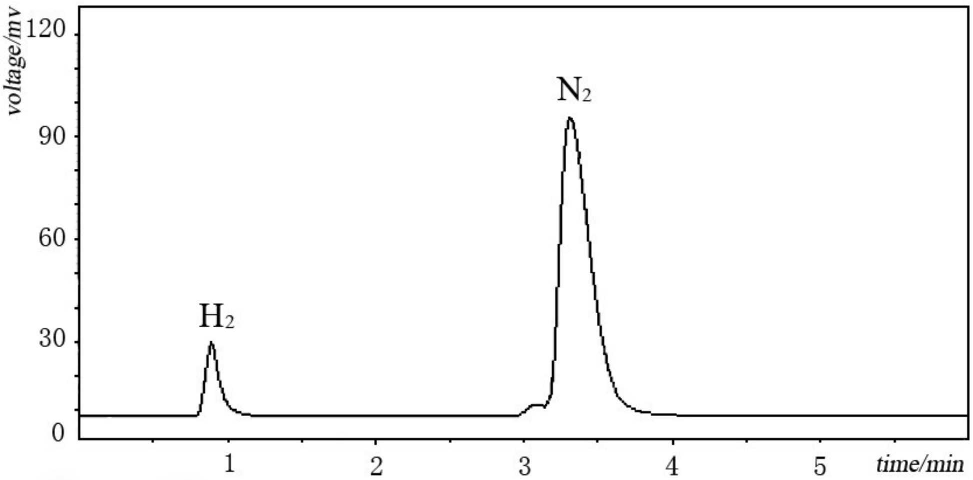


Figure 61. GC H_2 detection for the dehydrogenation of cyclohexanone.



The gas sample was sampled from the reaction gas atmosphere (reaction conditions: 1 mmol cyclohexanone, 5% mol Pd/C, 150 °C, 1.5 h, 2 ml DMA under 1 atm N_2 atmosphere). The H_2 and N_2 were confirmed by comparing with standard H_2 and N_2 GC spectra.