

## Supplementary Information

### **A generalized approach for iron catalyzed chemo- and regioselective formation of anti-Markovnikov acetals from styrene derivatives**

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## 1. General information

All the reactions were performed using standard Schlenk techniques in oven-dried glassware under an atmosphere of argon and air, unless otherwise specified. Solvents were dried by standard procedures [methanol was distilled from  $\text{Mg}(\text{OMe})_2$ , ethanol and ethylene glycol were distilled from  $\text{CaO}$ ] under argon and used immediately.<sup>S1</sup> Molecular sieves (3Å) were crushed and activated by putting it under vacuum in a flask and heated with a Bunsen burner prior to use. Solvents were purchased from Merck, India and all other reagents and chemicals were obtained from Aldrich, USA. Only styrene substrates were purified by passing through a plug of activated alumina before use and other reagents were used as received. Column chromatography was performed by using a silica gel column (60-120 mesh, Merck India). TLC experiments were carried out on Merck silica gel 60 F<sub>254</sub> pre-coated sheets and visualized by UV (254 nm) lamp.

NMR spectra were recorded by 300 MHz Bruker spectrometer in  $\text{CDCl}_3$ . Chemical shift data are quoted as  $\delta$  in ppm, coupling constants ( $J$ ) are reported in Hertz (Hz) and s, d, dd, t, q, m and br represent singlet, doublet, doublet of doublet, triplet, quartet, multiplet and broad respectively. HRMS spectra were recorded using micromass Q-TOF mass spectrometer. GC analysis was done by Shimadzu GC-2014 gas chromatograph with a FID detector using a capillary column (112-2562 CYCLODEXB, from J & W Scientific, length 60 m, inner diameter 0.25 mm, film 0.25  $\mu\text{m}$ ) and GC-MS analysis was performed on an Agilent Technologies 7890A GC system coupled with 5975C inert XL EI/CI Mass Selective Detector (GCMSD) with its triple axis detector. The products were either isolated or yield of the products were determined by  $^1\text{H}$  NMR with PhTMS as an internal standard.<sup>S2</sup>

## 2. General method for dimethyl acetal formation, 3a-u

In a 25 mL Schlenk tube,  $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$  (6.75 mg, 0.02 mmol), pyridine-2,6-dicarboxylic acid (3.5 mg, 0.02 mmol) and 200 mg of crushed 3Å molecular sieves were taken and stirred for 5 min in 3 mL methanol which resulted in a deep red solution. 1.5 equivalent of  $\text{PhI}(\text{OAc})_2$  was then added after evacuating and backfilling the flask three times with air and the resultant reaction mixture was then stirred under air at room

temperature for 1 min. The solution immediately turned yellowish. The corresponding styrene (2 mmol) was then added in additional 1 mL methanol and then stirred at room temperature for 20 h. The solvent was removed in *vacuo* and the resultant material was then passed through a silica gel column using hexane:ethyl acetate (20:1→10:1, v/v) as eluent to isolate the desired product. The product was confirmed by GC against authenticated samples and GCMSD. The isolated product was then characterized by NMR in CDCl<sub>3</sub> with TMS as an internal standard and HRMS (Table 1). Most of the acetal products reported in this work are previously reported in the literature.<sup>S3-S12</sup> All the reactions were performed thrice to establish the reproducibility and reliability.

### 3. Method for (2,2-diethoxyethyl)benzene formation, 4a

In a 25 mL Schlenk tube, Fe(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (6.75 mg, 0.02 mmol), pyridine-2,6-dicarboxylic acid (3.5 mg, 0.02 mmol) and 200 mg of crushed 3 Å molecular sieves were taken and stirred for 5 min in 3 mL ethanol which led to a deep red solution. 1.5 equivalent of PhI(OAc)<sub>2</sub> was then added after evacuating and backfilling the flask three times with air and the resultant reaction mixture was then stirred under air at room temperature for 1 min. The solution immediately turned yellowish. Styrene (2 mmol) was then added in additional 1 mL ethanol and then stirred at room temperature for 20 h. The solvent was removed in *vacuo* and it was then passed through a short silica gel column using hexane:ethyl acetate (10:1, v/v) as eluent to isolate the desired product. The product was confirmed by GC against authenticated samples and GCMSD. The isolated product was then characterized by NMR in CDCl<sub>3</sub> with TMS as an internal standard and HRMS. This acetal has been previously reported in the literature.<sup>S3,S5</sup> The said reaction was performed thrice to establish the reproducibility and reliability.

### 4. Method for (2,2-Dioxolaneethyl)benzene formation, 5a

In a 25 mL Schlenk tube, Fe(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (6.75 mg, 0.02 mmol), pyridine-2,6-dicarboxylic acid (3.5 mg, 0.02 mmol) and 200 mg of crushed 3 Å molecular sieves were taken and stirred for 5 min in 3 mL ethylene glycol leading to a deep red solution. 1.5 equivalent of PhI(OAc)<sub>2</sub> was then added after evacuating and backfilling the flask three

times with air and the resultant reaction mixture was then stirred under air at room temperature for 1 min. The solution immediately turned yellowish. Styrene (2 mmol) was then added in additional 1 mL ethylene glycol and then stirred at room temperature for 20 h. 10 mL of 1N NaOH was then added to the above reaction mixture and the aqueous layer extracted four times with diethylether. The combined organic layers were washed with distilled water, dried it using  $\text{Na}_2\text{SO}_4$  and the solvent removed in *vacuo*. The resultant material was then passed through a short silica gel column using hexane:ethyl acetate (10:1, v/v) as eluent which afforded the desired product. The product was confirmed by GCMSD. The yield was then determined by  $^1\text{H}$  NMR with PhTMS as an internal standard.<sup>S2</sup> The acetal has been previously reported in the literature.<sup>S13-S15</sup> The said reaction was performed thrice to establish the reproducibility and reliability.

#### **5. Method for (2,2-dimethoxyethyl)benzene (3a) formation from phenylacetaldehyde**

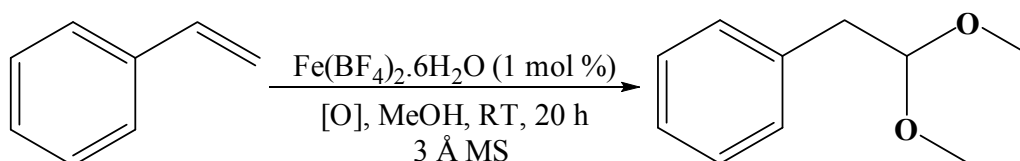
In a 25 mL Schlenk tube,  $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$  (6.75 mg, 0.02 mmol), pyridine-2,6-dicarboxylic acid (3.5 mg, 0.02 mmol) and 200 mg of crushed 3Å molecular sieves were taken and stirred for 5 min in 3 mL methanol which led to a deep red solution. 1.5 equivalent of  $\text{PhI}(\text{OAc})_2$  was then added after evacuating and backfilling the flask three times with air and the resultant reaction mixture was then stirred under air at room temperature for 1 min. The solution immediately turned yellowish. Phenylacetaldehyde (2 mmol) was then added in additional 1 mL methanol and then stirred at room temperature for 20 h. The solvent was removed in *vacuo* and it was then passed through a short silica gel column using hexane:ethyl acetate (10:1, v/v) as eluent to isolate the desired product. The product was confirmed by GC against authenticated sample and GCMSD. The isolated product was then characterized by NMR in  $\text{CDCl}_3$  with TMS as an internal standard and HRMS. The said reaction was performed thrice to establish the reproducibility and reliability.

#### **6. Method for (1,2-dimethoxyethyl)benzene (6a) formation from styrene oxide**

In a 25 mL Schlenk tube,  $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$  (6.75 mg, 0.02 mmol), pyridine-2,6-dicarboxylic acid (3.5 mg, 0.02 mmol) and 200 mg of crushed 3Å molecular sieves were

taken and stirred for 5 min in 3 mL dry methanol which gave a deep red solution. 1.5 equivalent of  $\text{PhI}(\text{OAc})_2$  was then added after evacuating and backfilling the flask three times with air and the resultant reaction mixture was then stirred under air at room temperature for 1 min. The solution immediately turned yellowish. Styrene oxide (2 mmol) was then added in additional 1 mL methanol and then stirred at room temperature for 20 h. The solvent was removed in *vacuo* and it was then passed through a short silica gel column using hexane:ethyl acetate (10:1, v/v) as eluent to afford the desired product. The product was confirmed by GCMSD.<sup>S16-S17</sup> The yield was then determined by  $^1\text{H}$  NMR with PhTMS as an internal standard.<sup>S2</sup>

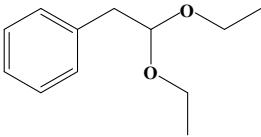
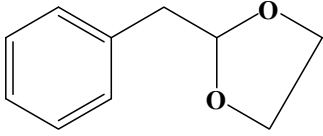
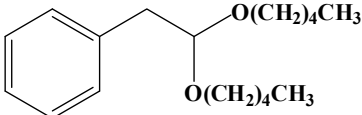
**Table S1** Influence of oxidant<sup>a</sup>



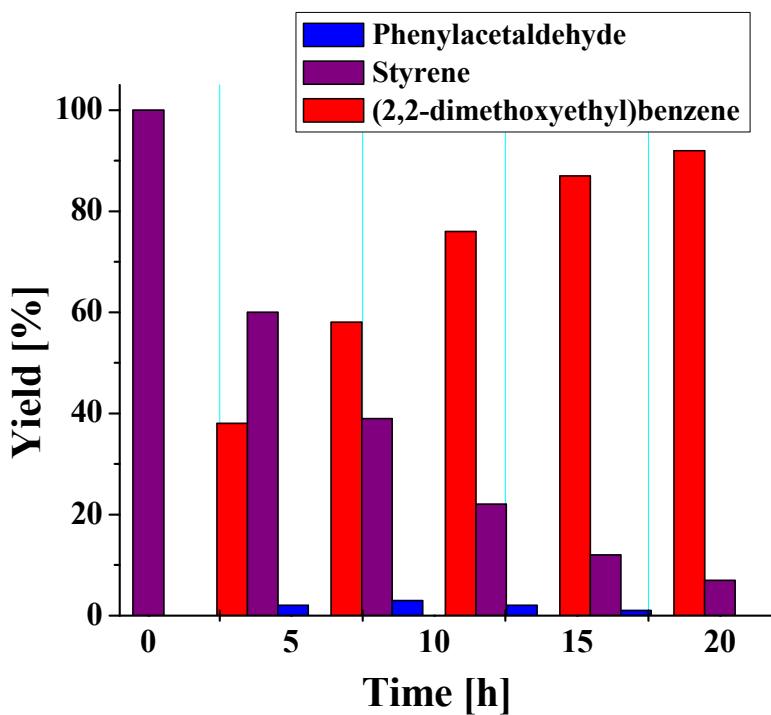
Entry	Oxidant	Conversion (%)	Yield (%) <sup>b</sup>
1	PhI(OAc) <sub>2</sub>	97	92(89) <sup>c</sup>
2	H <sub>2</sub> O <sub>2</sub>	>99 <sup>d</sup>	<1
3	<sup>t</sup> Butylhydroperoxide	70 <sup>d</sup>	0
4	m-Chloroperbenzoic acid	30	0
5	NaOCl	0	0
6	O <sub>2</sub> (1 atm)	0	0

<sup>a</sup> Reaction conditions: 1 mol%  $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ , 1 mol% dipic, styrene, 1.5 eqv. oxidant in 4 mL methanol, RT, 20 h. See the experimental part for the details. <sup>b</sup> Determined by GC using n-dodecane as an internal standard. <sup>c</sup> Determined by <sup>1</sup>H NMR with PhTMS as an internal standard. Isolated yield is given in parenthesis. <sup>d</sup> Mixture of phenylacetaldehyde, styreneoxide and one unknown product.

**Table S2** Influence of other solvents<sup>a</sup>

Entry	Solvent	Product	Yield
1	Ethanol		82 <sup>b</sup>
2	Ethylene glycol		59 <sup>c</sup>
3	1-pentanol		12 <sup>d</sup>

<sup>a</sup> Reaction conditions: 1 mol% Fe(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, 1 mol% dipic, styrene, 1.5 eqv. PhI(OAc)<sub>2</sub> in 4 mL solvent, RT, 20 h. See the experimental part for the details. <sup>b</sup> Isolated yield is given. <sup>c</sup> Determined by <sup>1</sup>H NMR with PhTMS as an internal standard. <sup>d</sup> Identified by GCMSD and yield is determined by GC using n-dodecane as an internal standard.



**Fig. S1** Yield *versus* time diagram for terminal acetalization of styrene. Maximum up to 3% of phenylacetaldehyde is observed during the course of reaction.



### Details of product characterization

#### **(2,2-dimethoxyethyl)benzene (3a)**<sup>S3-S5</sup>

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.40-7.18 (m, 5H), 4.55 (t, *J*=5.6, 1H), 3.32 (s, 6H), 2.92 (d, *J*=5.6 Hz, 2H); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>): δ 137.3, 129.7, 127.8, 126.2, 105.4, 53.4, 39.7; HRMS(ESI+): *m/z* 189.0891 (Calcd. for [M+Na<sup>+</sup>]: 189.0891).

#### **1-(2,2-dimethoxyethyl)-4-methylbenzene (3b)**<sup>S5-S6</sup>

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.18 (d, *J*=7.8, 2H), 7.11 (d, *J*=7.8, 2H), 4.52 (t, *J*=5.8, 1H), 3.33 (s, 6H), 2.87 (d, *J*=5.6 Hz, 2H), 2.17 (s, 3H); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>): δ 137.6, 130.4, 129.2, 127.6, 105.6, 53.6, 39.3, 21.2; HRMS(ESI+): *m/z* 203.1048 (Calcd. for [M+Na<sup>+</sup>]: 203.1048).

#### **1-(2,2-dimethoxyethyl)-3-methylbenzene (3c)**<sup>S5-S6</sup>

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.30-7.04 (m, 4H), 4.53 (t, *J* = 5.6, 1H), 3.30 (s, 6H), 2.86 (d, *J* = 5.6, 2H), 2.19 (s, 3H); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>): δ 137.4, 136.9, 128.2, 127.4, 127.1, 126.4, 105.2, 53.15, 39.5, 21.4; HRMS(ESI+): *m/z* 203.1048 (Calcd. for [M+Na<sup>+</sup>]: 203.1048).

#### **(1,1-dimethoxypropan-2-yl)benzene (3d)**<sup>S7</sup>

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.40-7.06 (m, 5H), 4.45 (d, *J* = 5.5, 1H), 3.31 (s, 3H), 3.15 (s, 3H), 2.93 (m, 1H), 1.28 (d, *J* = 5.5, 3H); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>): δ 143.4, 129.4, 128.7, 127.4, 112.4, 53.2, 52.9, 38.3, 17.5; HRMS(ESI+): *m/z* 203.1046 (Calcd. for [M+Na<sup>+</sup>]: 203.1048).

#### **(2,2-dimethoxypropyl)benzene (3e, 3f)**<sup>S8</sup>

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.26-7.16 (m, 5H), 3.25 (s, 6H), 2.90 (s, 2H), 1.12 (s, 3H); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>): δ 137.3, 130.0, 127.8, 126.1, 101.5, 48.9, 42.7, 21.0; HRMS(ESI+): *m/z* 203.1047 (Calcd. for [M+Na<sup>+</sup>]: 203.1048).

**1-(2,2-dimethoxyethyl)-4-fluorobenzene (3g)**<sup>S6,S9</sup>

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.28 (d, *J*=7.8, 2H), 7.18 (d, *J*=6.8, 2H), 4.48 (t, *J*=5.6, 1H), 3.32 (s, 6H), 2.87 (d, *J*=5.6 Hz, 2H); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>): δ 160.5, 132.7, 130.9, 115.2, 105.3, 53.5, 38.9; <sup>19</sup>F NMR (300 MHz, CDCl<sub>3</sub>): δ -116.84; HRMS(ESI+): *m/z* 207.0795 (Calcd. for [M+Na<sup>+</sup>]: 207.0797).

**1-bromo-2-(2,2-dimethoxyethyl)benzene (3h)**<sup>S10</sup>

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.59-7.19 (m, 5H), 4.61 (t, *J*=5.6, 1H), 3.33 (s, 6H), 3.05 (d, *J*=5.6 Hz, 2H); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>): δ 139.5, 132.6, 130.3, 128.2, 127.5, 124.8, 103.9, 53.9, 39.9; HRMS(ESI+): *m/z* 245.0175 (Calcd. for [M+H<sup>+</sup>]: 245.0177).

**1-chloro-4-(2,2-dimethoxyethyl)benzene (3i)**<sup>S11</sup>

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.38-7.20 (m, 4H), 4.47 (t, *J*=5.6, 1H), 3.31 (s, 6H), 2.85 (d, *J*=5.6 Hz, 2H); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>): δ 135.2, 131.8, 128.8, 127.5, 105.0, 49.7, 38.9; HRMS(ESI+): *m/z* 223.0502 (Calcd. for [M+Na<sup>+</sup>]: 223.0501).

**1-(2,2-dimethoxyethyl)-3-nitrobenzene (3j)**<sup>S11</sup>

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 8.13-8.07 (m, 2H), 7.58-7.46 (m, 2H), 4.55 (t, 1H, *J*=5.5), 3.37 (s, 6H), 3.01 (d, 2H, *J*=5.5); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>): δ 139.3, 136.1, 129.3, 124.6, 121.9, 101.5, 52.8, 29.8; HRMS(ESI+): *m/z* 212.0923 (Calcd. for [M+H<sup>+</sup>]: 212.0922).

**1-(2,2-dimethoxyethyl)-2-methoxybenzene (3k)**<sup>S6,S9</sup>

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.20-6.93 (m, 4H), 4.62 (t, *J*=5.6, 1H), 3.80 (s, 3H), 3.31 (s, 6H), 2.93 (d, *J*=5.6 Hz, 2H); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>): δ 158.4, 130.9, 126.8, 126.6, 114.6, 105.9, 56.3, 55.4, 38.8; HRMS(ESI+): *m/z* 219.0995 (Calcd. for [M+Na<sup>+</sup>]: 219.0997).

**1-(2,2-dimethoxyethyl)-4-methoxybenzene (3l)**<sup>S6,S9</sup>

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.15-7.00 (m, 4H), 4.48 (t, *J*=5.7, 1H), 3.75 (s, 3H), 3.30 (s, 6H), 2.85 (d, *J*=5.6 Hz, 2H); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>): δ 158.2, 130.4, 130.3, 127.5, 114.5, 113.8, 105.4, 55.3, 53.4, 38.8; HRMS(ESI+): *m/z* 219.0998 (Calcd. for [M+Na<sup>+</sup>]: 219.0997).

**(2,2-dimethoxycyclohexyl)benzene (3m)**<sup>S12</sup>

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.48-7.20 (m, 5H), 3.41 (t, *J*=5.9, 1H), 3.28 (s, 3H), 3.03 (s, 3H), 1.85-1.30 (br, m, 8H); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>): δ 143.8, 128.7, 126.8, 126.2, 104.4, 52.7, 49.5, 43.7, 32.4, 28.8, 23.6, 20.7; HRMS(ESI+): *m/z* 243.1360 (Calcd. for [M+Na<sup>+</sup>]: 243.1361).

**1-(chloromethyl)-4-(2,2-dimethoxyethyl)benzene (3n)**

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.30-7.10 (m, 4H), 4.61 (s, 2H), 4.45 (t, *J*=5.4, 1H), 3.32 (s, 6H), 2.90 (d, *J*=5.8 Hz, 2H); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>): δ 138.8, 137.4, 128.9, 128.3, 105.3, 57.3, 45.9, 39.2; HRMS(ESI+): *m/z* 237.0659 (Calcd. for [M+Na<sup>+</sup>]: 237.0658).

**3-(2,2-dimethoxyethyl)benzaldehyde (3o)**<sup>S9</sup>

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 10.0 (s, 1H), 7.5-7.3 (m, 4H), 4.55 (t, *J*= 5.5, 1H), 3.31 (s, 6H), 2.91 (d, *J*= 5.5, 2H); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>): δ 194.4, 138.4, 137.6, 133.5, 129.3, 129.1, 127.2, 103.1, 52.79, 39.7; HRMS(ESI+): *m/z* 195.1021 (Calcd. for [M+H<sup>+</sup>]: 195.1021).

**2,2-dimethoxy-3-phenylpropanal (3p)**

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 9.88 (s, 1H), 7.40-7.28 (m, 5H), 3.30 (s, 6H), 3.26 (s, 1H); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>): δ 199.7, 133.9, 129.1, 128.9, 127.8, 127.4, 117.7, 55.1, 31.6; HRMS(ESI+): *m/z* 195.1021 (Calcd. for [M+H<sup>+</sup>]: 195.1021).

**3-(2,2-dimethoxyethyl)aniline (3q)**<sup>S9</sup>

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.2-6.7 (m, 4H), 5.50 (m, 2H), 4.58 (t, *J*= 5.5, 1H), 3.45 (s, 6H), 2.90 (d, *J*= 5.5, 2H); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>): δ 149.2, 139.1, 129.3, 117.7, 114.5, 104.3, 54.8, 40.6; HRMS(ESI+): *m/z* 182.1181 (Calcd. for [M+H<sup>+</sup>]: 182.1181).

**2-(2,2-dimethoxyethyl)naphthalene (3r)**<sup>S9</sup>

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.80-7.11 (m, 7H), 4.61 (t, *J*=5.6, 1H), 3.32 (s, 6H), 3.05 (d, *J*=5.6, 2H); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>): δ 137.1, 133.6, 1332.3, 128.3, 128.2, 127.8, 127.5, 126.9, 126.1, 125.4, 105.4, 53.5, 39.9; HRMS(ESI+): *m/z* 239.1048 (Calcd. for [M+Na<sup>+</sup>]: 239.1048).

**2-(3,3-dimethoxypropyl)phenol (3s)**

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.18-6.82 (m, 4H), 4.17 (t, *J*= 5.5, 1H), 3.48 (s, 6H), 2.90 (t, *J*= 5.5, 2H), 1.80 (q, *J*=5.6, 2H); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>): δ 154.2, 130.5, 127.9, 127.5, 121.3, 115.8, 104.5, 55.94, 40.01, 22.8; HRMS(ESI+): *m/z* 219.0999 (Calcd. for [M+Na<sup>+</sup>]: 219.0997).

**4-(3,3-dimethoxypropyl)-2-methoxyphenol (3t)**

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 6.85-6.66 (m, 3H), 5.45 (s, 1H), 4.17 (t, *J*= 5.5, 1H), 3.87 (s, 3H), 3.48 (s, 6H), 2.92 (t, *J*= 5.5, 2H), 1.85 (q, *J*=5.6, 2H); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>): δ 147.6, 146.2, 137.5, 121.32, 115.7, 114.3, 104.4, 56.7, 56.0, 40.0, 31.1; HRMS(ESI+): *m/z* 249.1102 (Calcd. for [M+Na<sup>+</sup>]: 249.1103).

**4,4'-bis(2,2-dimethoxyethyl)biphenyl (3u)**

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.69 (dd, *J*=6.9, 8H), 4.58 (t, *J*= 5.5, 2H), 3.33 (s, 12H), 2.92 (d, *J*= 5.5, 4H); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>): δ 139.2, 137.6, 130.4, 127.6, 105.4, 53.5, 39.4; HRMS(ESI+): *m/z* 353.1728 (Calcd. for [M+Na<sup>+</sup>]: 353.1728).

**(2,2-diethoxyethyl)benzene (4a)<sup>S3-S5</sup>**

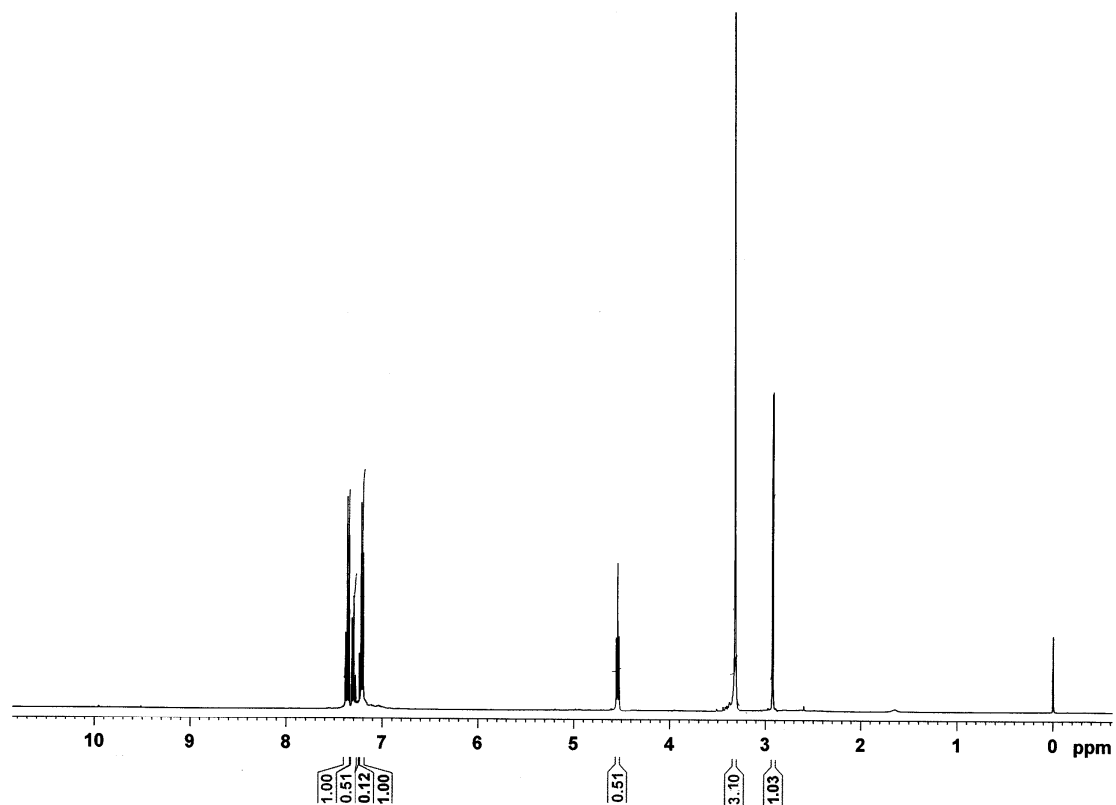
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.43-7.22 (m, 5H), 4.63 (t, *J*=5.7, 1H), 3.45 (q, *J*=5.9, 4H), 2.92 (d, *J*=5.7 Hz, 2H), 1.16(t, *J*=5.4, 6H) ; <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>): δ 137.6, 130.4, 127.6, 126.4, 104.1, 62.0, 41.0, 15.4; HRMS(ESI+): *m/z* 217.1204 (Calcd. for [M+Na<sup>+</sup>]: 217.1204).

**(2,2-Dioxolaneethyl)benzene (5a)<sup>S13-S15</sup>**

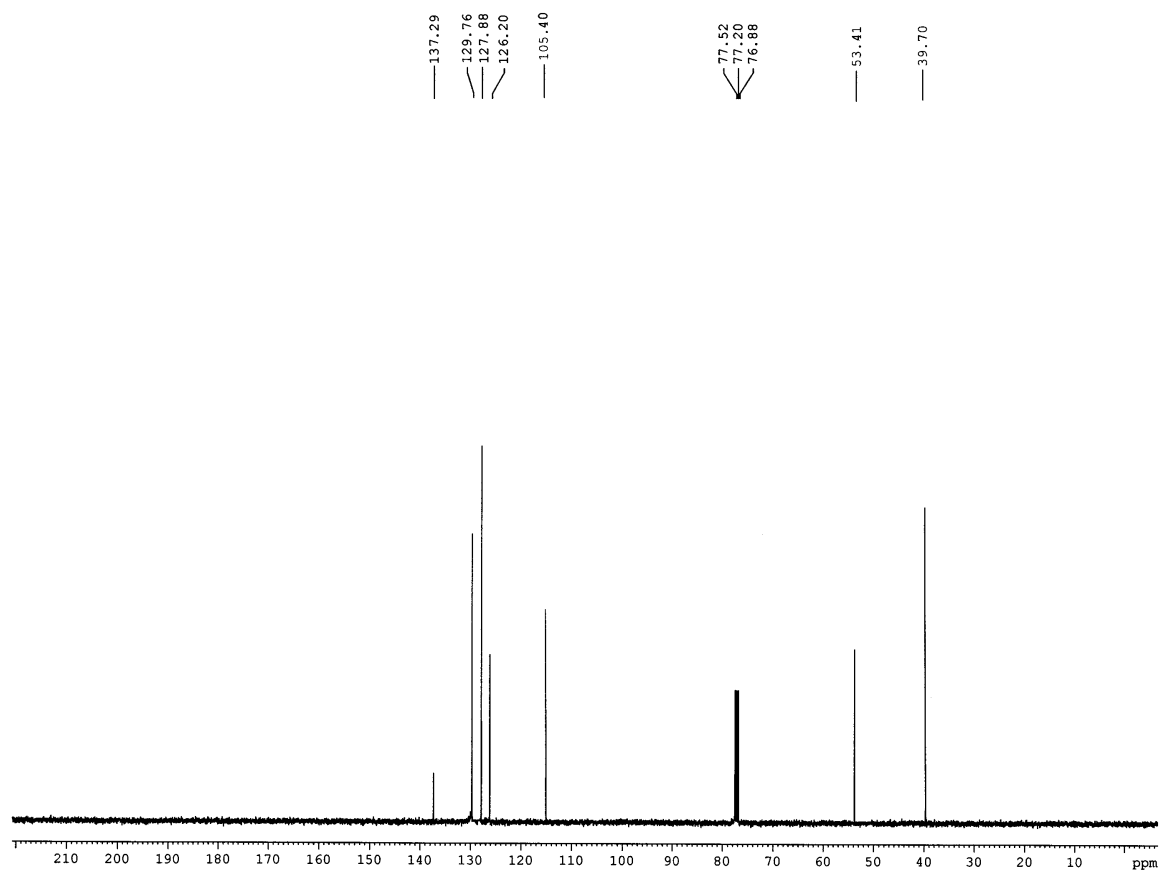
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.40-7.28 (m, 5H), 5.42 (t, *J*=5.7, 1H), 3.99-3.87 (m, 4H), 2.94 (d, *J*=5.7 Hz, 2H), 1.16(t, *J*=5.4, 6H); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>) δ 137.3, 129.1, 127.6, 125.9, 102.5, 64.5, 40.3; HRMS(ESI+): *m/z* 187.0735 (Calcd. for [M+Na<sup>+</sup>]: 187.0735).

**(1,2-dimethoxyethyl)benzene (6a)<sup>S16</sup>**

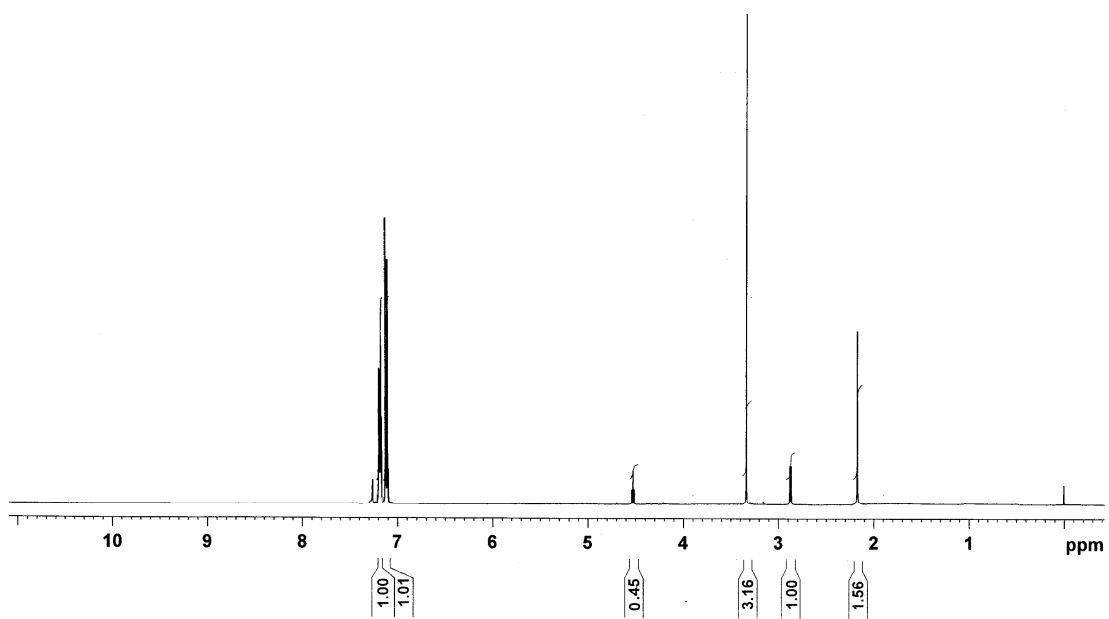
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.37-7.28 (m, 5H), 4.55 (t, *J*=5.7, 1H), 3.90-3.75 (m, 2H), 3.33 (s, 3H), 3.18 (s, 3H); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>): δ 137.9, 129.1, 128.5, 127.6, 86.1, 77.5, 60.2, 56.3; HRMS(ESI+): *m/z* 189.0891 (Calcd. for [M+Na<sup>+</sup>]: 189.0891).



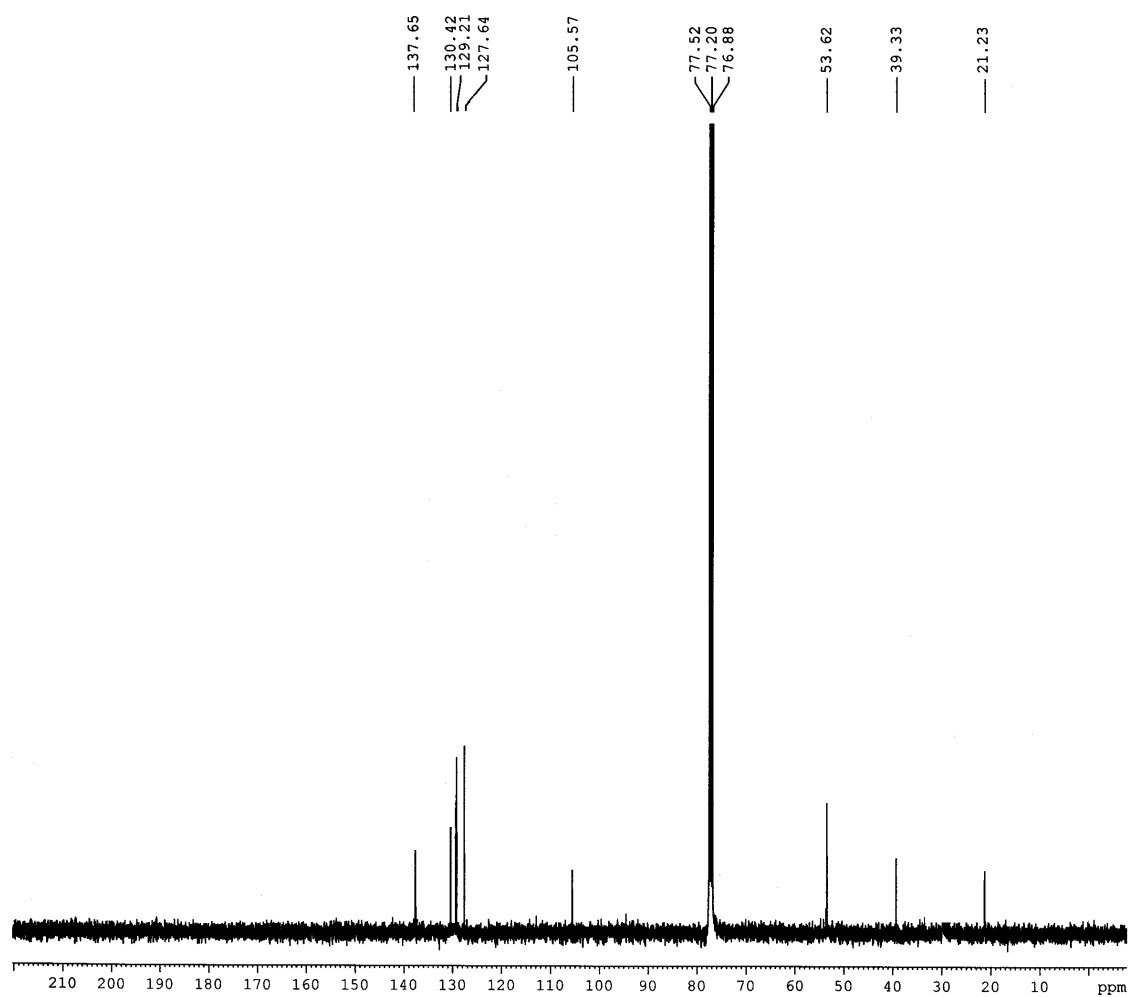
**Fig. S2**  $^1\text{H}$  NMR spectrum of (2,2-dimethoxyethyl)benzene (**3a**) in  $\text{CDCl}_3$ .



**Fig. S3**  $^{13}\text{C}$  NMR spectrum of (2,2-dimethoxyethyl)benzene (**3a**) in  $\text{CDCl}_3$ .

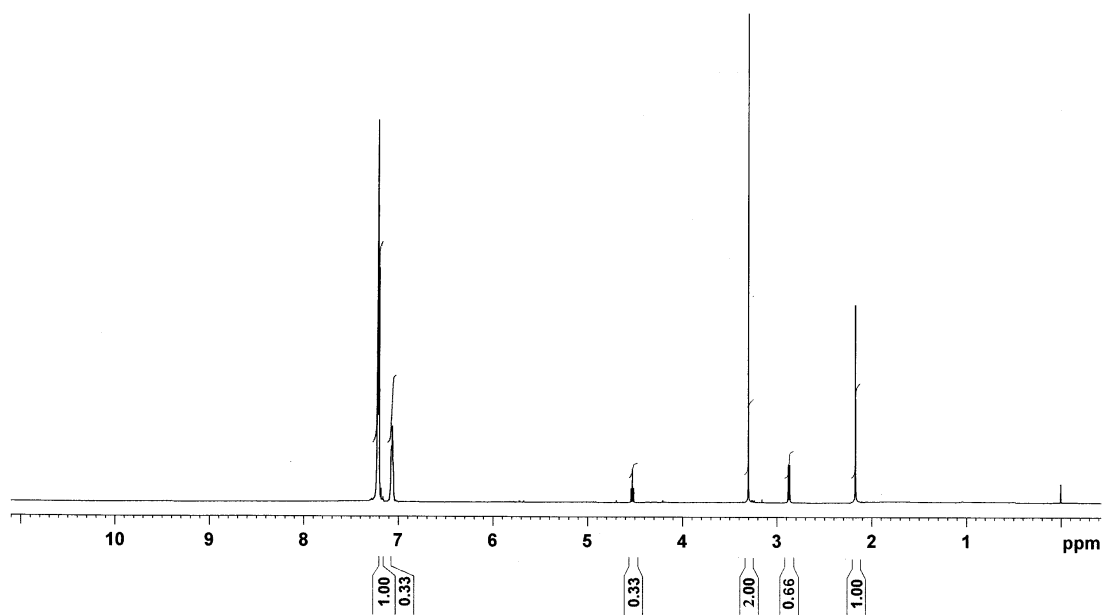


**Fig. S4**  $^1\text{H}$  NMR spectrum of 1-(2,2-dimethoxyethyl)-4-methylbenzene (**3b**) in  $\text{CDCl}_3$ .

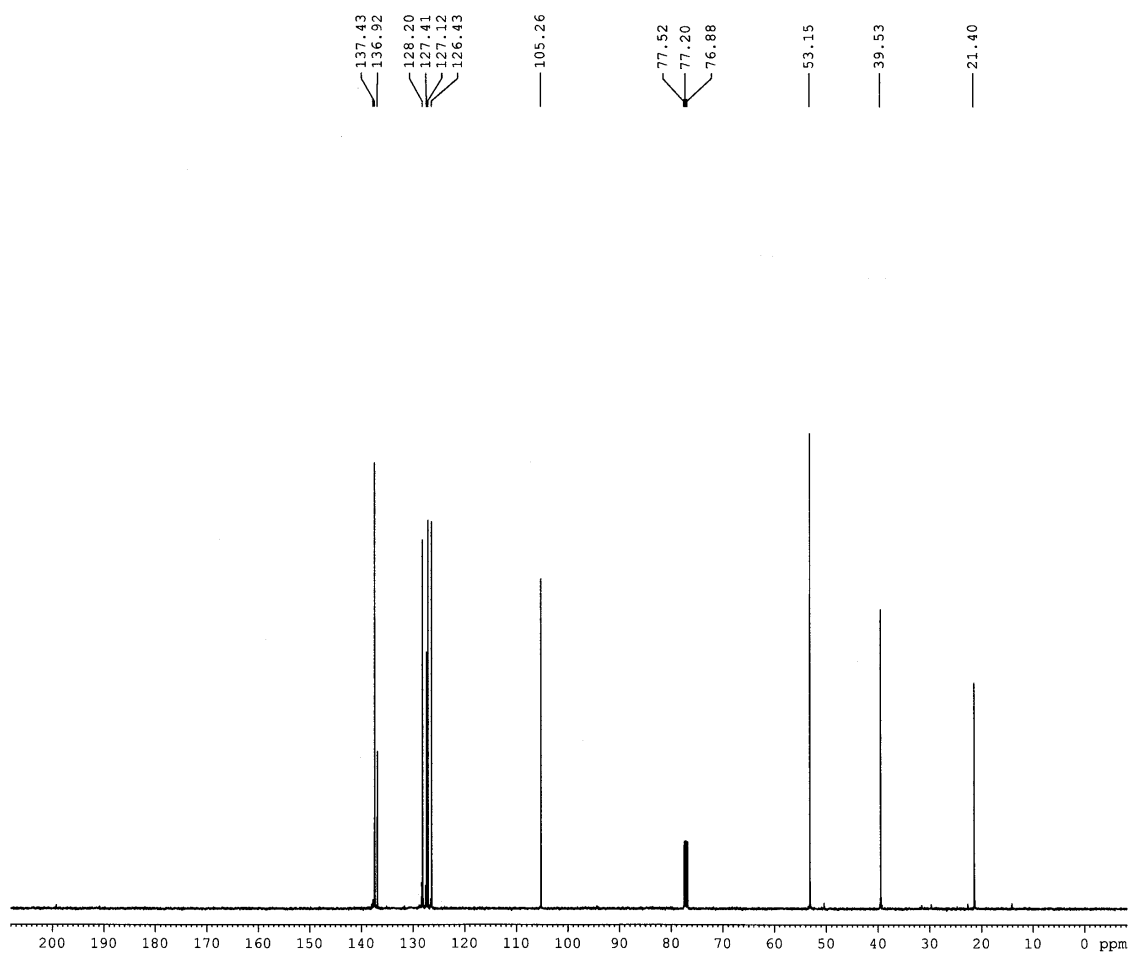


**Fig. S5**  $^{13}\text{C}$  NMR spectrum of 1-(2,2-dimethoxyethyl)-4-methylbenzene (**3b**) in  $\text{CDCl}_3$ .

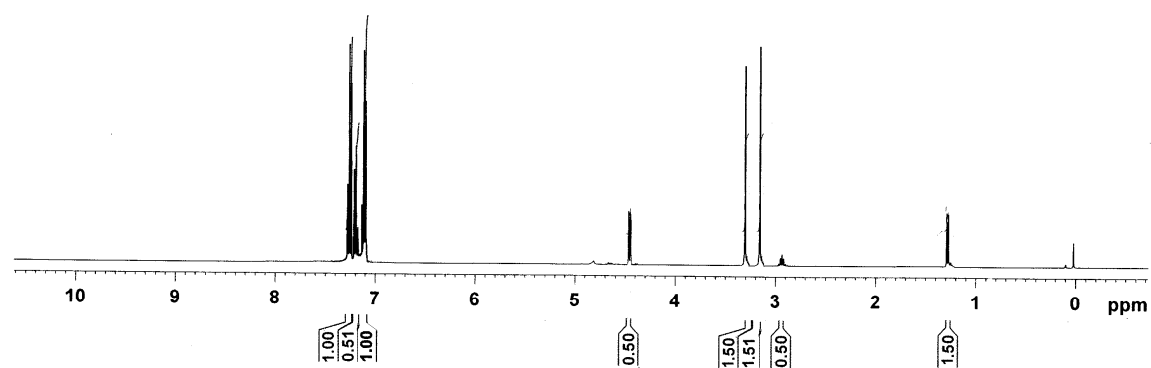




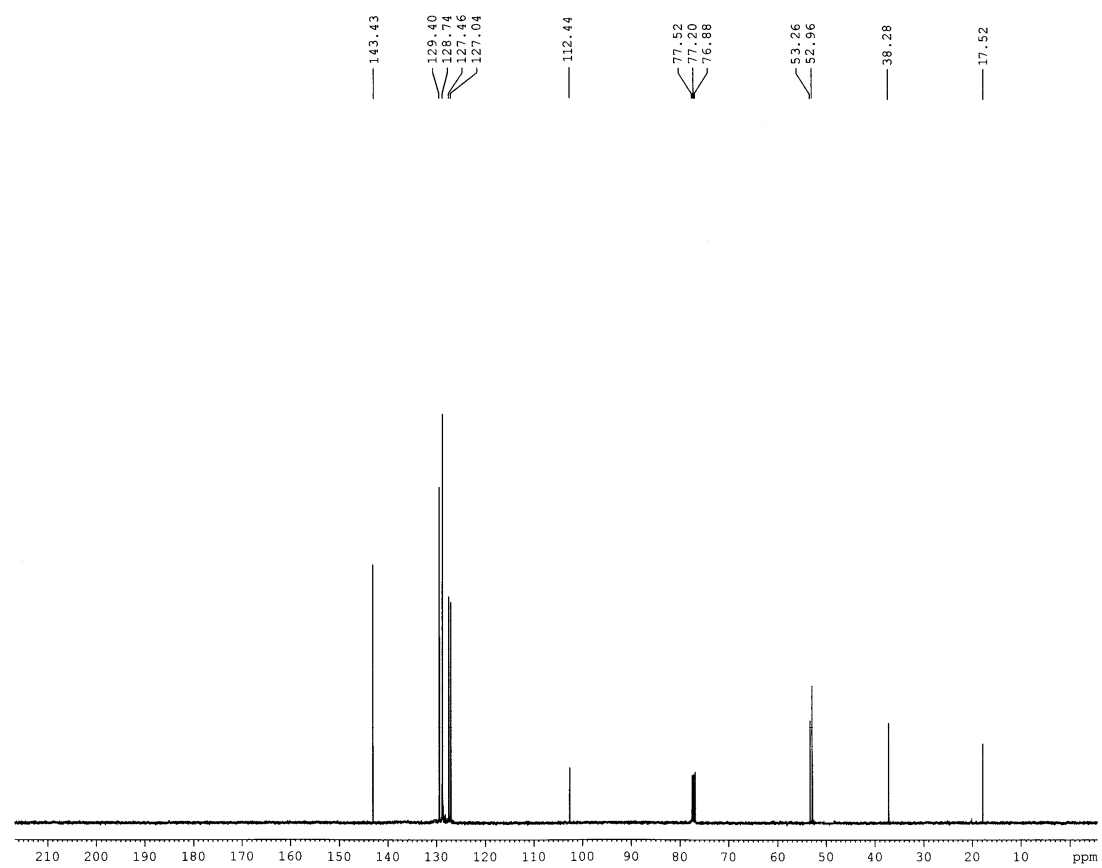
**Fig. S6** <sup>1</sup>H NMR spectrum of 1-(2,2-dimethoxyethyl)-3-methylbenzene (**3c**) in CDCl<sub>3</sub>.



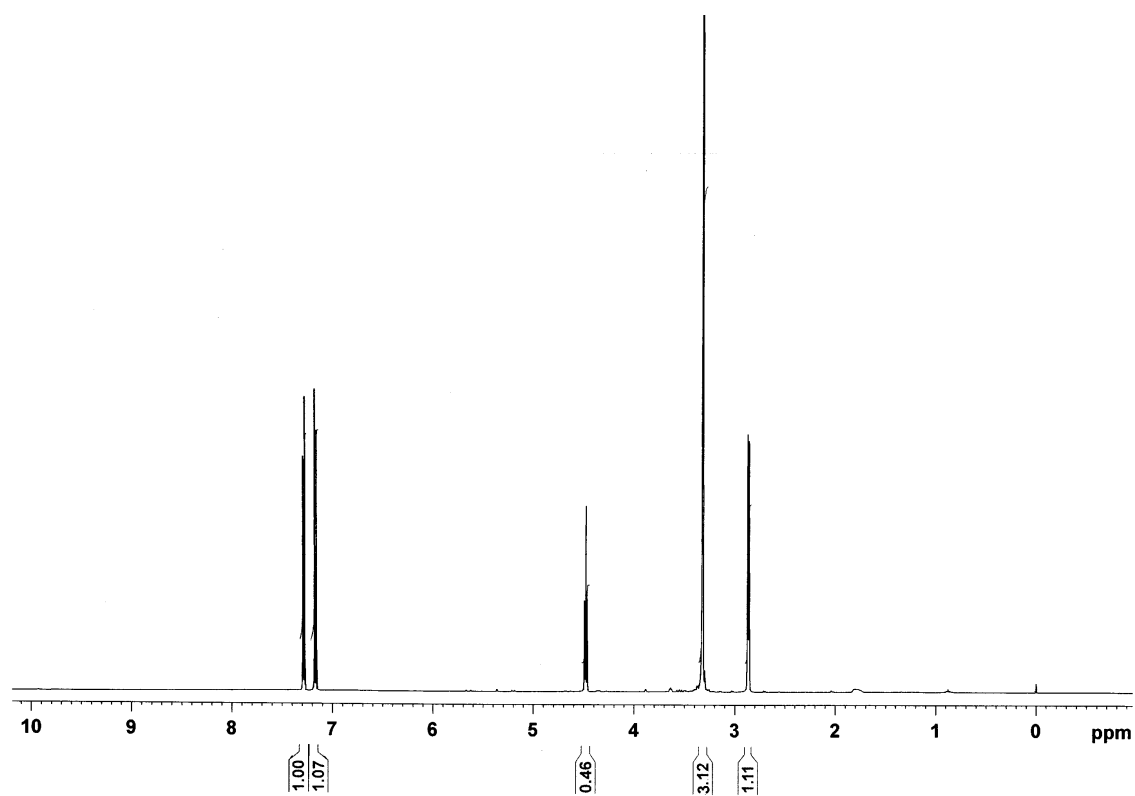
**Fig. S7**  $^{13}\text{C}$  NMR spectrum of 1-(2,2-dimethoxyethyl)-3-methylbenzene (**3c**) in  $\text{CDCl}_3$ .



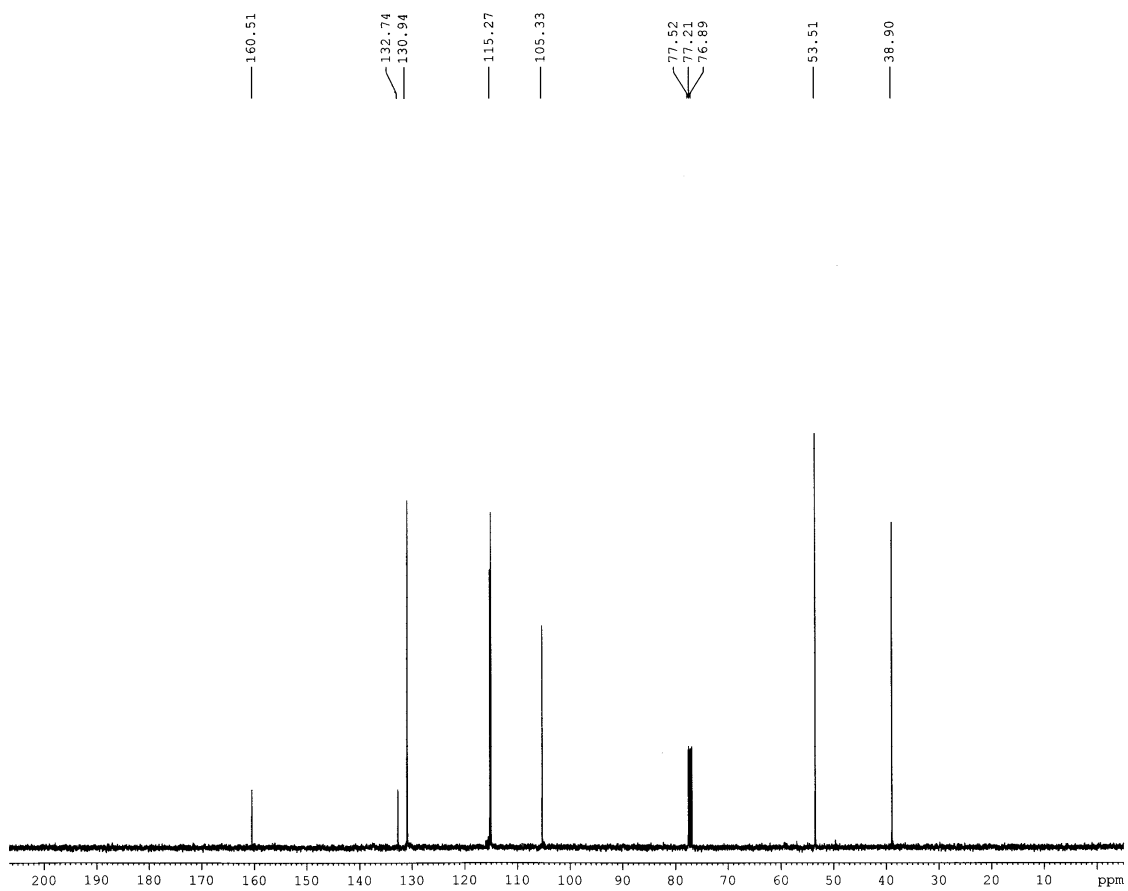
**Fig. S8**  $^1\text{H}$  NMR spectrum of (1,1-dimethoxypropan-2-yl)benzene (**3d**) in  $\text{CDCl}_3$ .



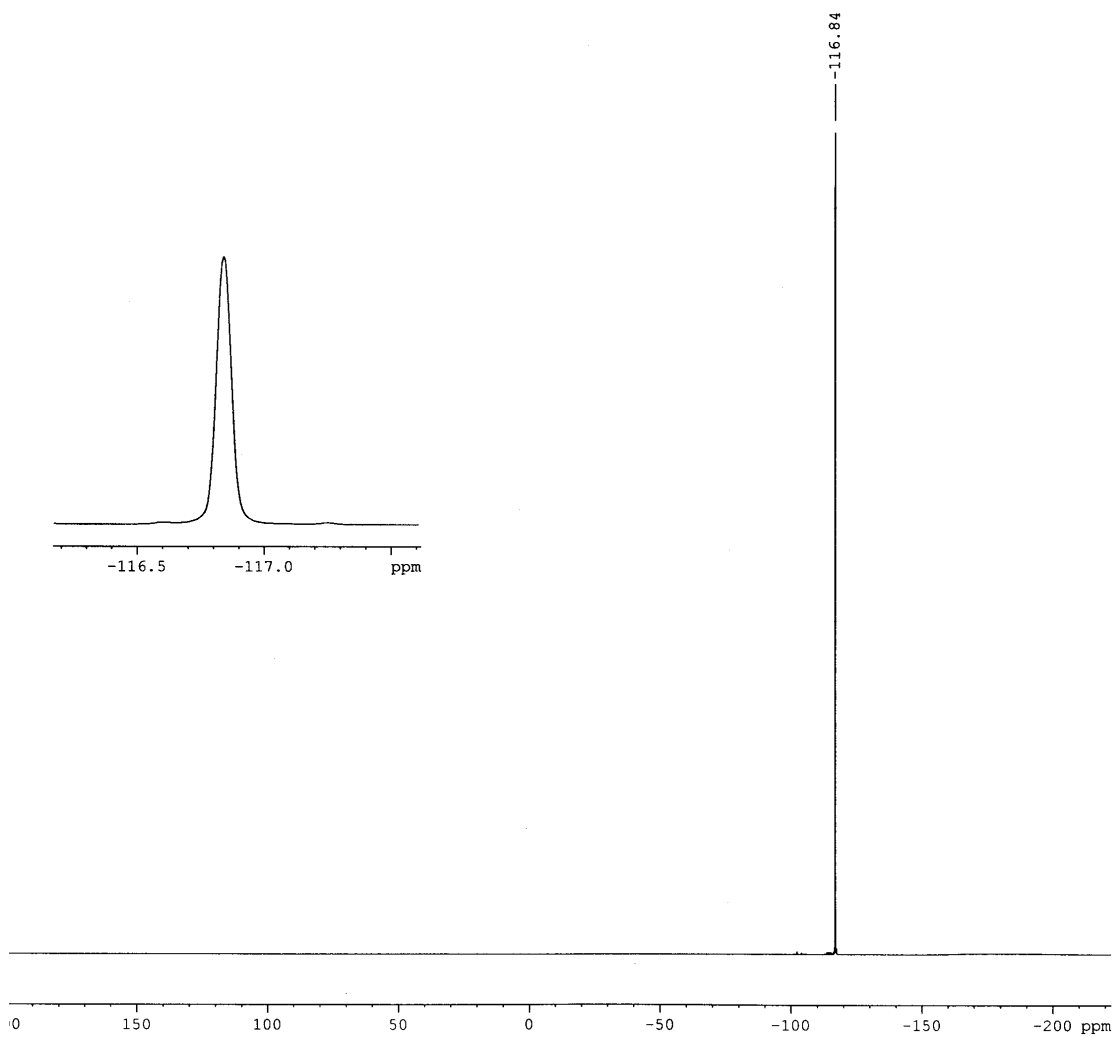
**Fig. S9**  $^{13}\text{C}$  NMR spectrum of (1,1-dimethoxypropan-2-yl)benzene (**3d**) in  $\text{CDCl}_3$ .



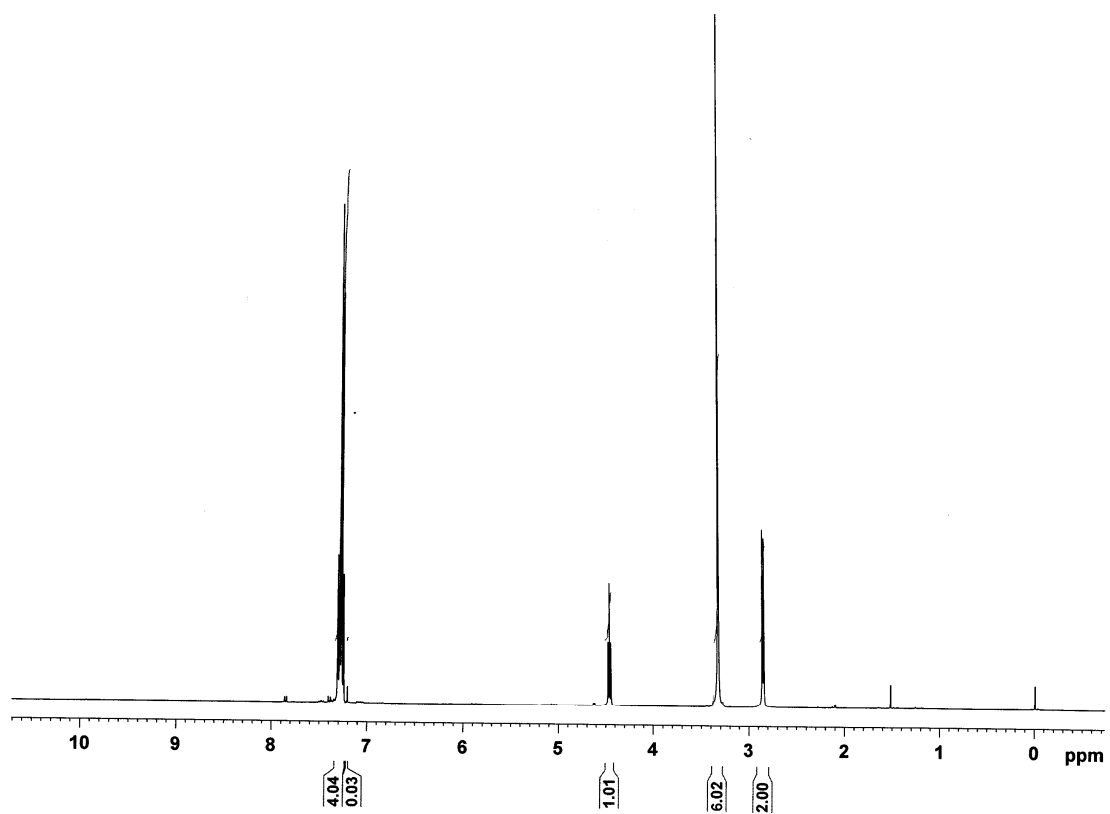
**Fig. S10**  $^1\text{H}$  NMR spectrum of 1-(2,2-dimethoxyethyl)-4-fluorobenzene (**3g**) in  $\text{CDCl}_3$ .



**Fig. S11**  $^{13}\text{C}$  NMR spectrum of 1-(2,2-dimethoxyethyl)-4-fluorobenzene (**3g**) in  $\text{CDCl}_3$ .

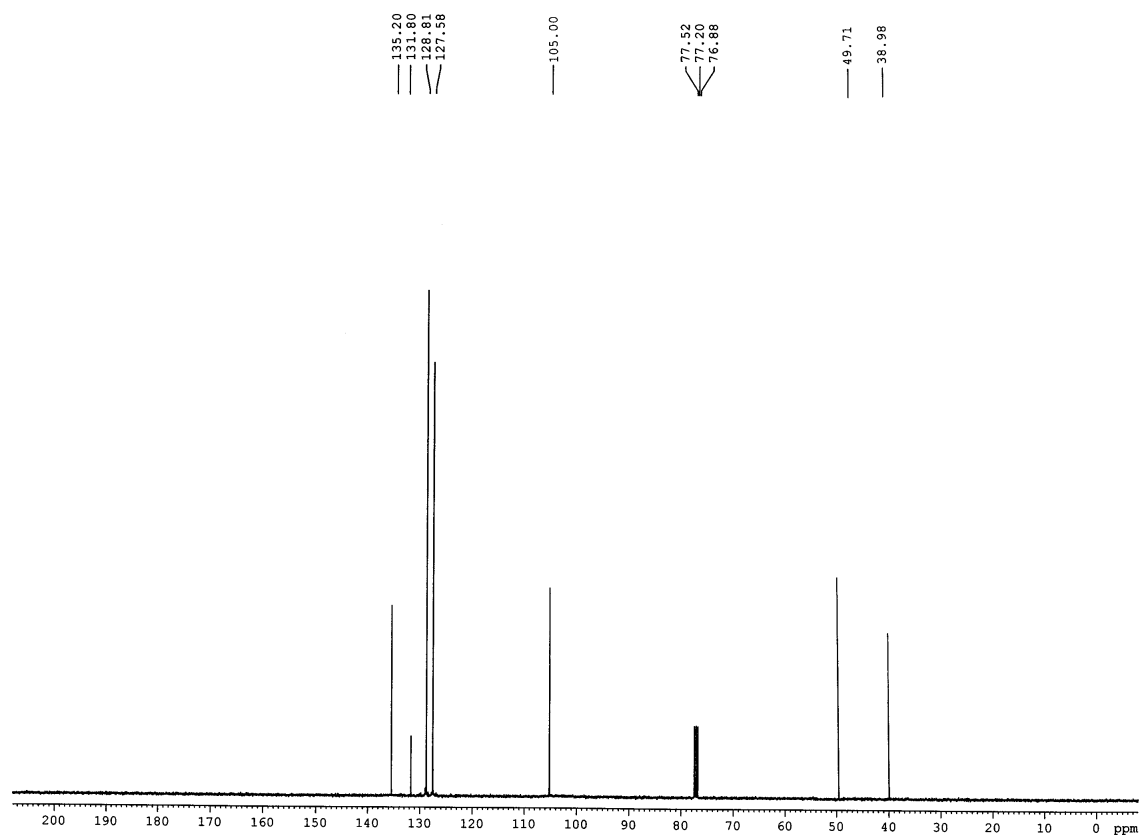


**Fig. S12**  $^{19}\text{F}$  NMR spectrum of 1-(2,2-dimethoxyethyl)-4-fluorobenzene (**3g**) in  $\text{CDCl}_3$ .

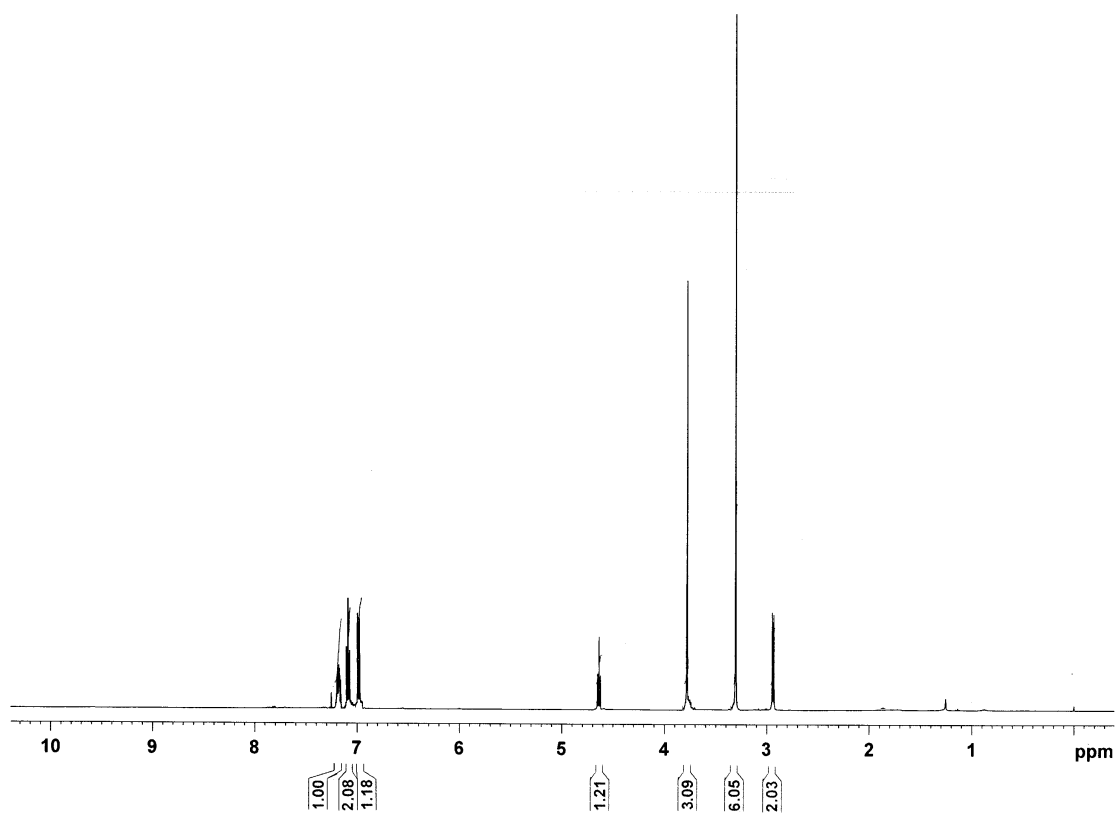


**Fig. S13**  $^1\text{H}$  NMR spectrum of 1-chloro-4-(2,2-dimethoxyethyl)benzene (**3i**) in  $\text{CDCl}_3$ .

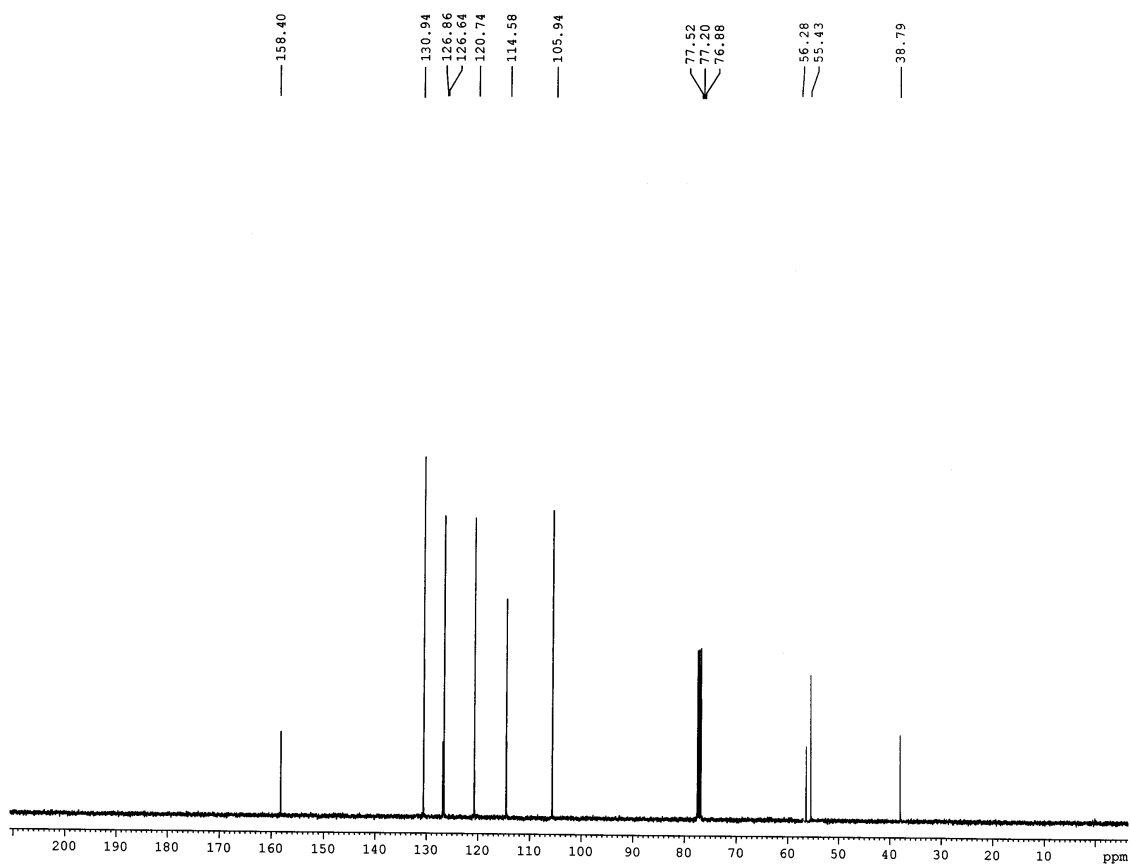




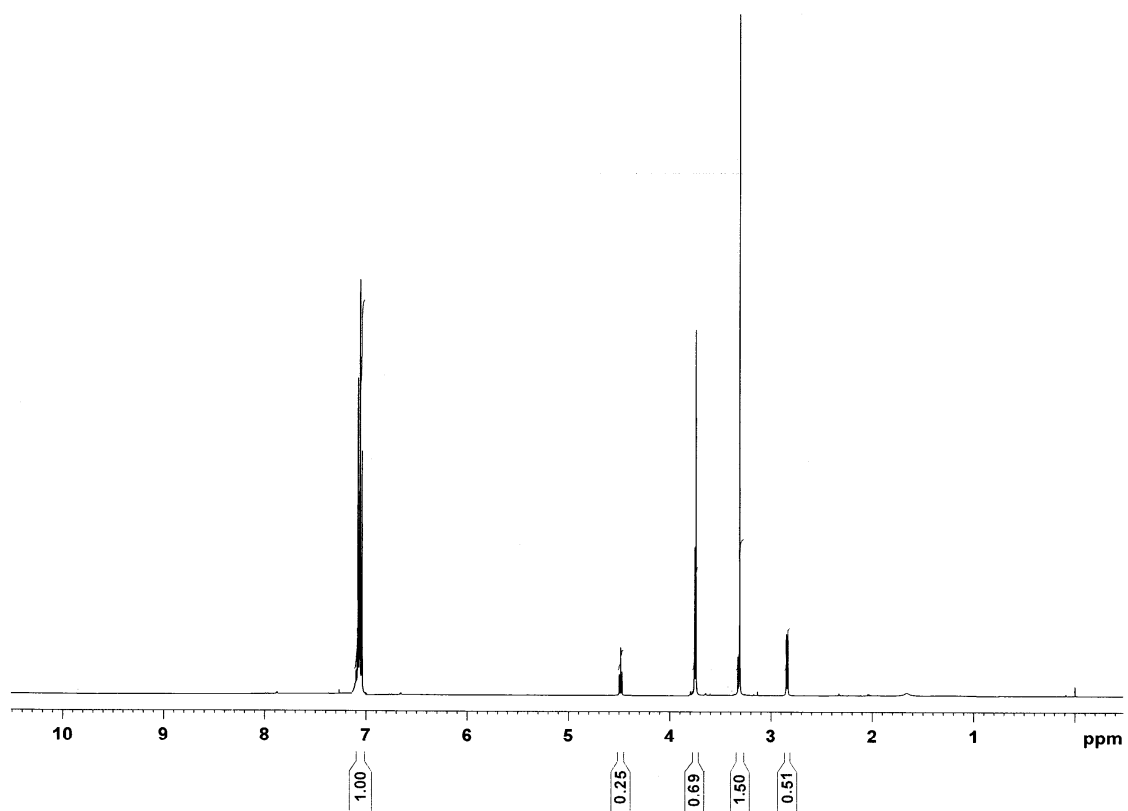
**Fig. S14**  $^{13}\text{C}$  NMR spectrum of 1-chloro-4-(2,2-dimethoxyethyl)benzene (**3i**) in  $\text{CDCl}_3$ .



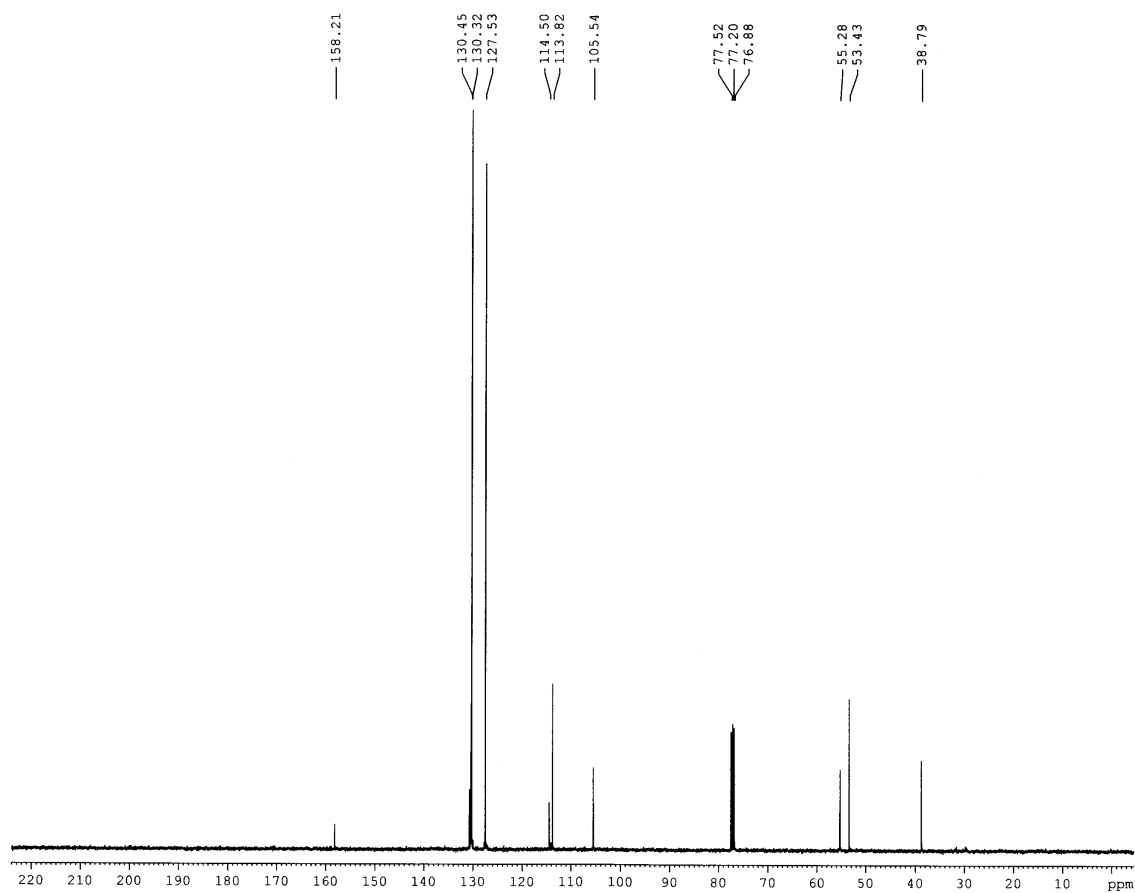
**Fig. S15** <sup>1</sup>H NMR spectrum of 1-(2,2-dimethoxyethyl)-2-methoxybenzene (**3k**) in CDCl<sub>3</sub>.



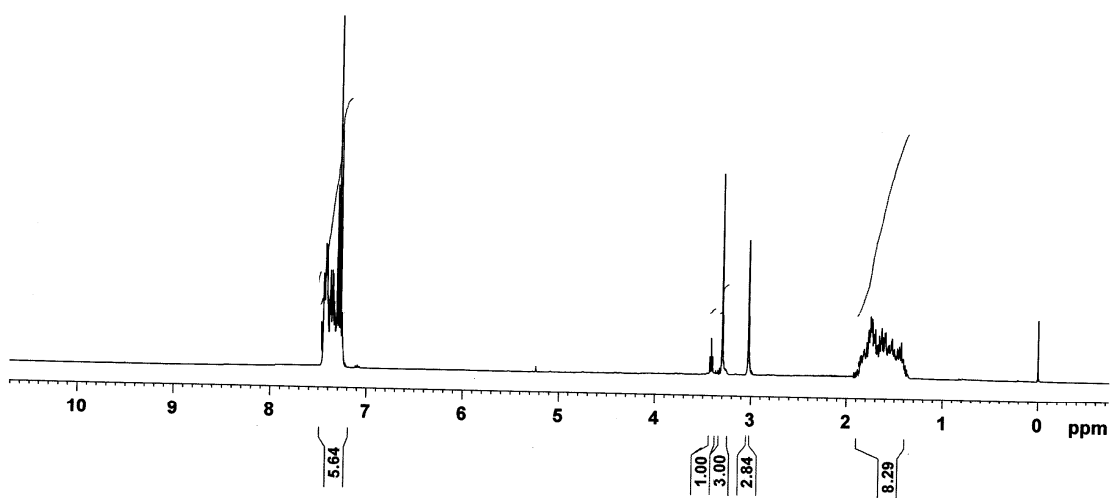
**Fig. S16**  $^{13}\text{C}$  NMR spectrum of 1-(2,2-dimethoxyethyl)-2-methoxybenzene (**3k**) in  $\text{CDCl}_3$ .



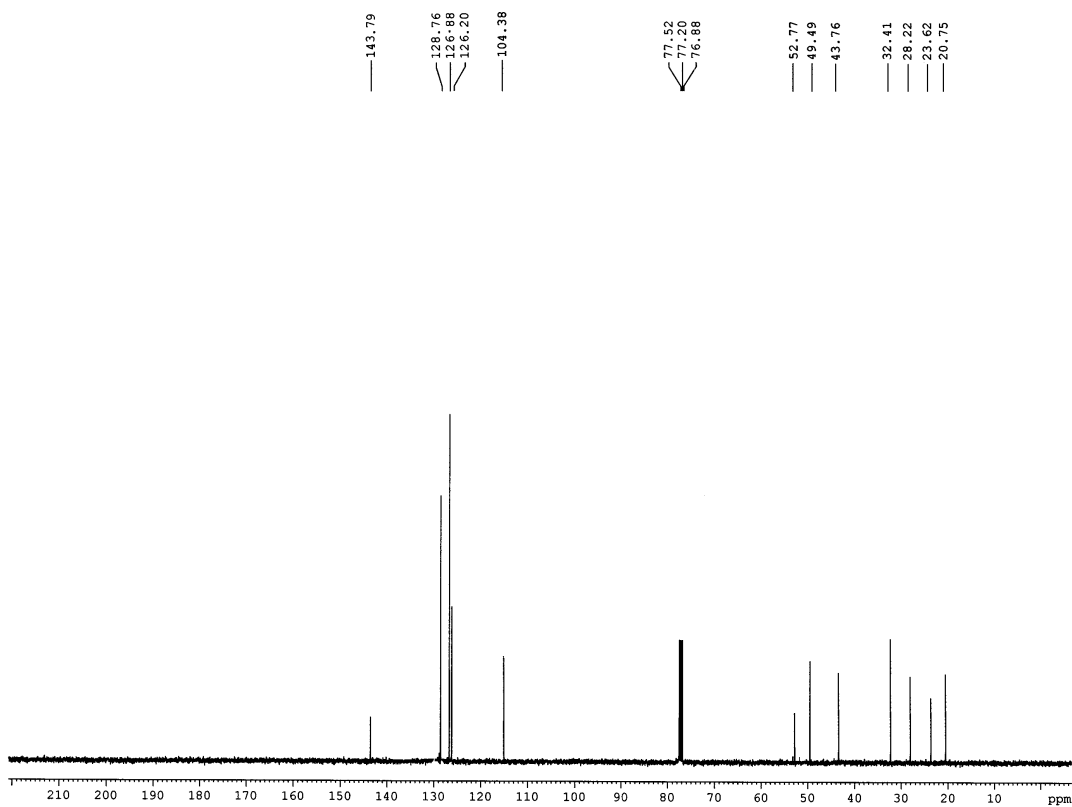
**Fig. S17** <sup>1</sup>H NMR spectrum of 1-(2,2-dimethoxyethyl)-4-methoxybenzene (**3I**) in CDCl<sub>3</sub>.



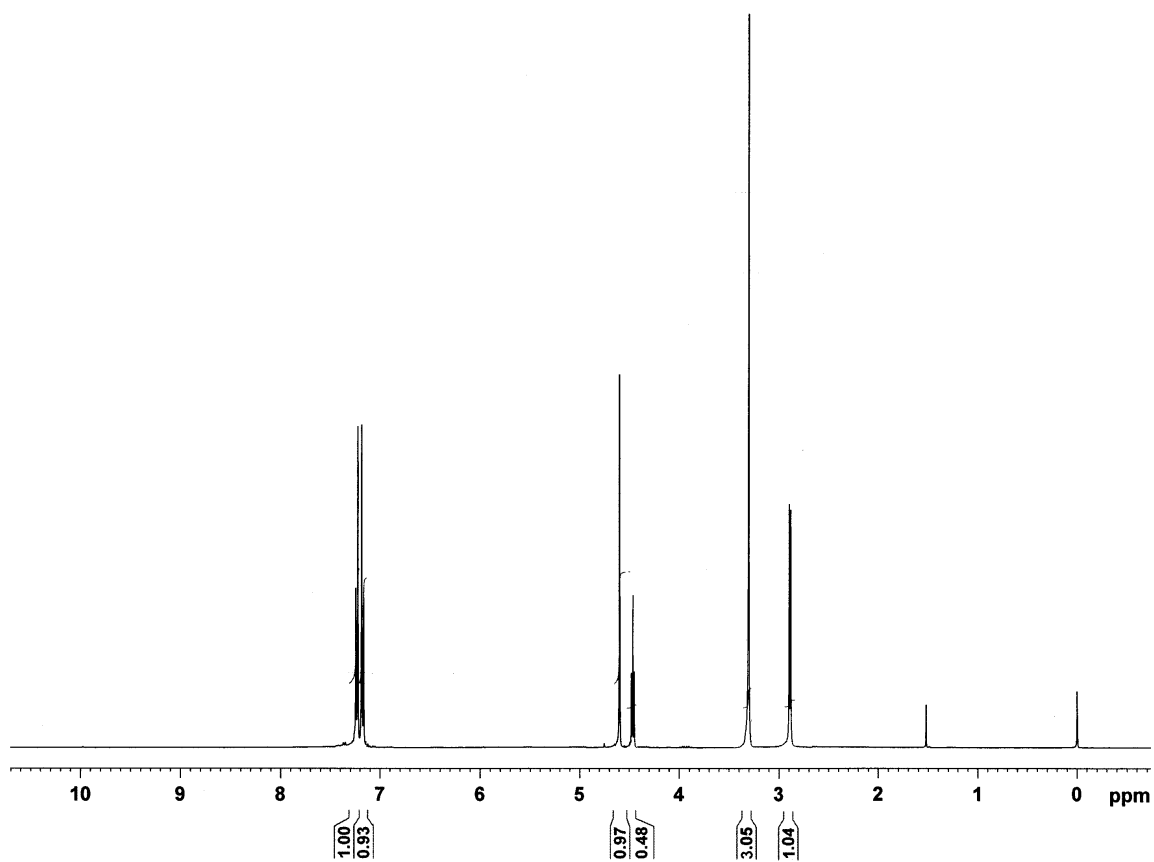
**Fig. S18**  $^{13}\text{C}$  NMR spectrum of 1-(2,2-dimethoxyethyl)-4-methoxybenzene (**31**) in  $\text{CDCl}_3$ .



**Fig. S19** <sup>1</sup>H NMR spectrum of (2,2-dimethoxycyclohexyl)benzene (**3m**) in CDCl<sub>3</sub>.

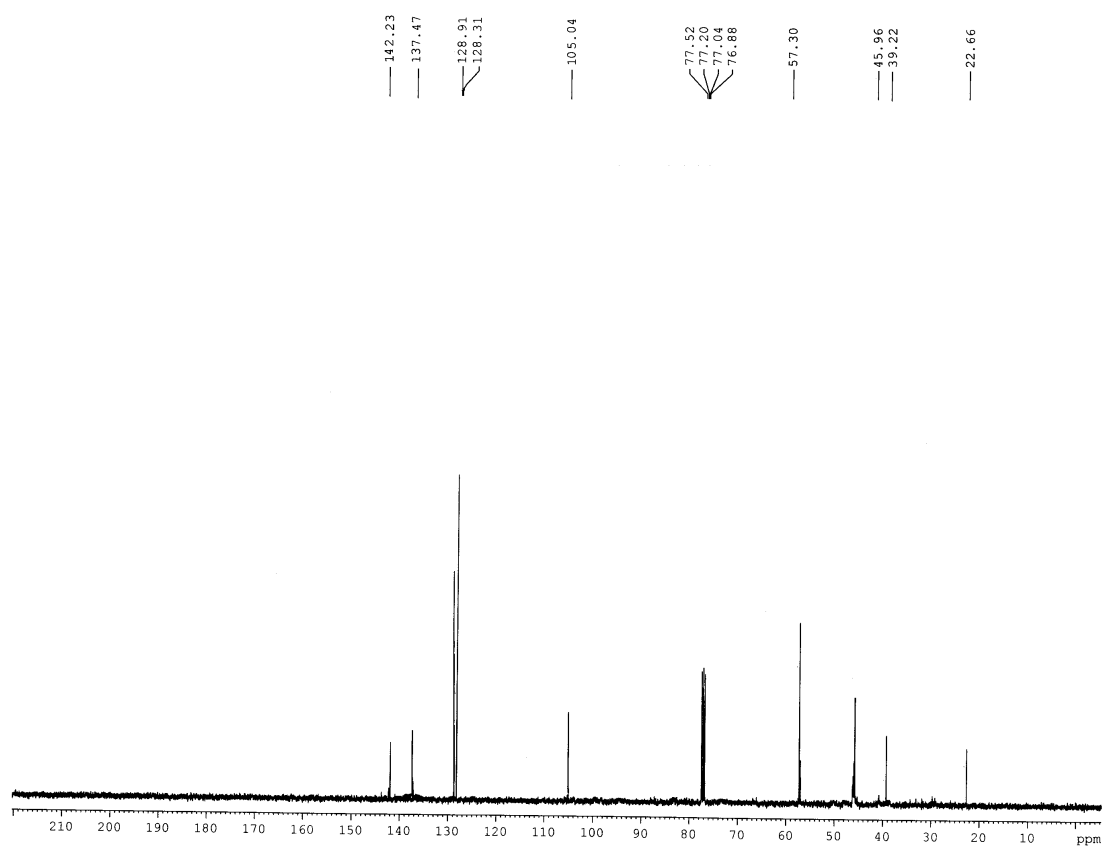


**Fig. S20**  $^{13}\text{C}$  NMR spectrum of (2,2-dimethoxycyclohexyl)benzene (**3m**) in  $\text{CDCl}_3$ .

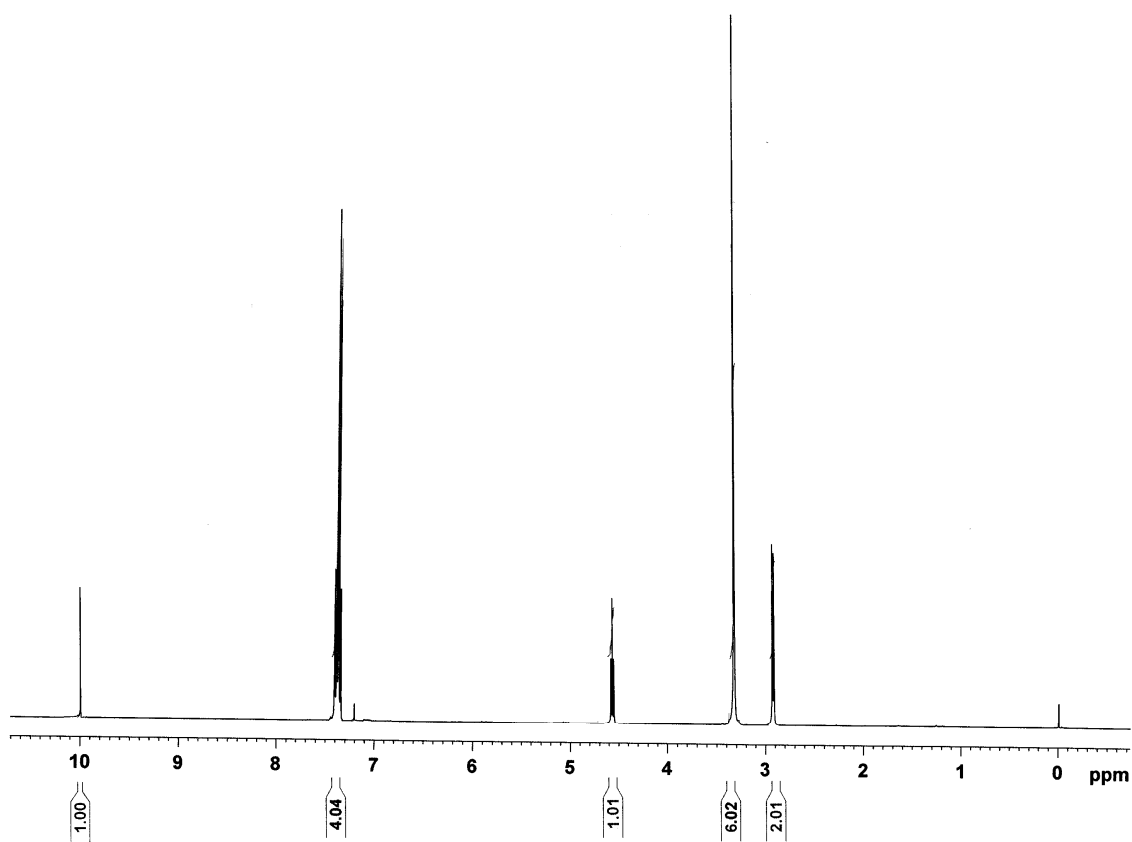


**Fig. S21**  $^1\text{H}$  NMR spectrum of 1-(chloromethyl)-4-(2,2-dimethoxyethyl)benzene (**3n**) in  $\text{CDCl}_3$ .

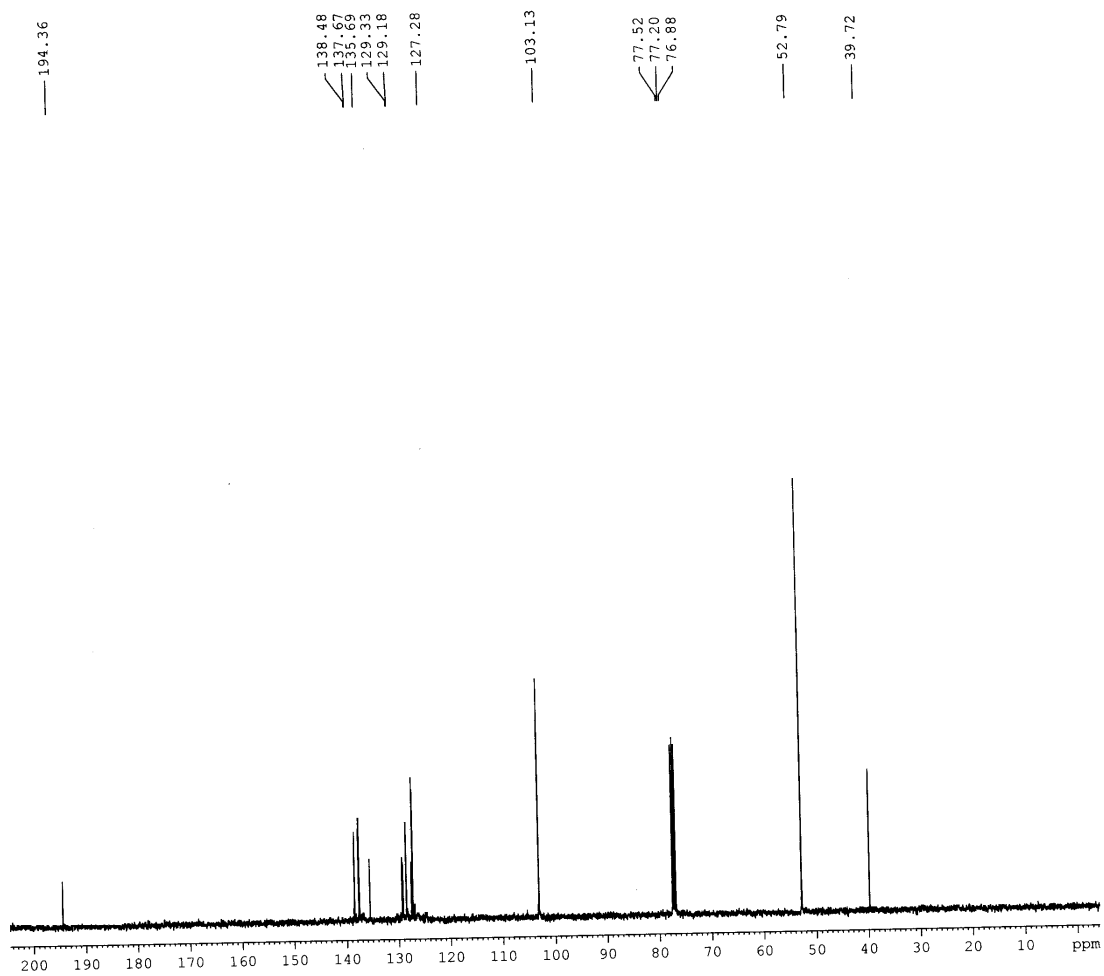




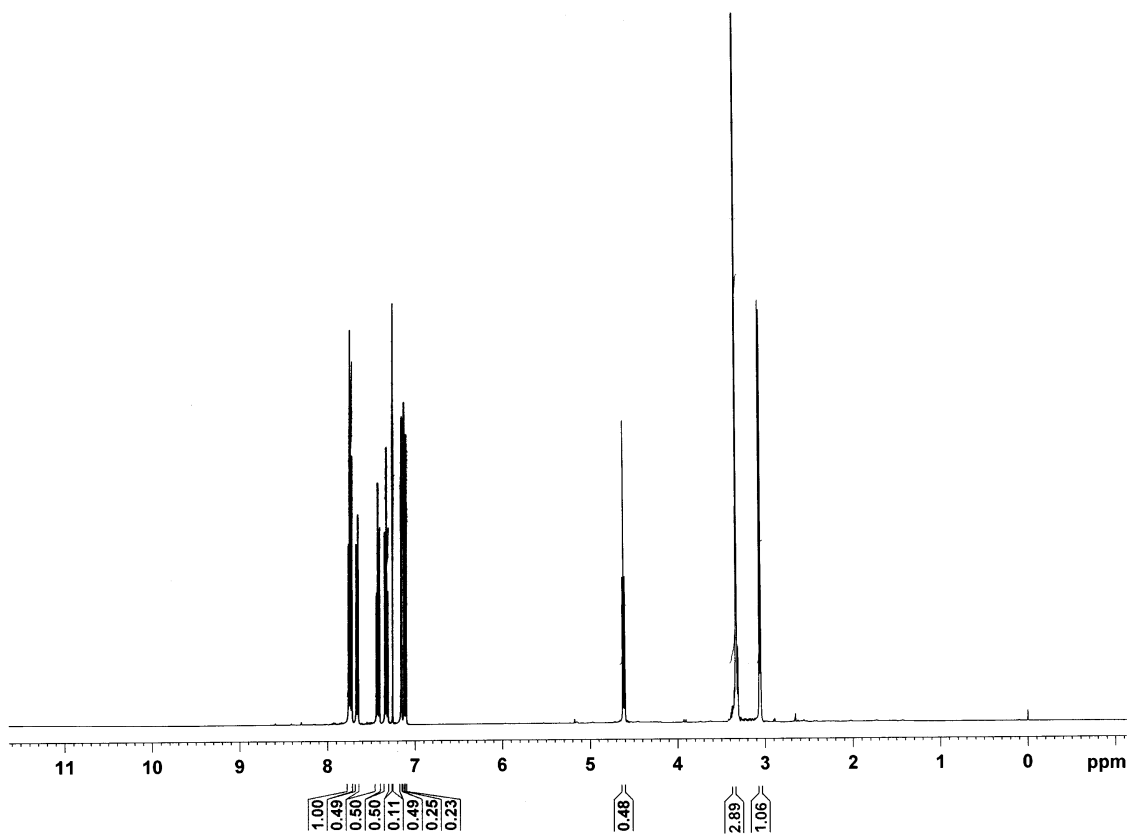
**Fig. S22**  $^{13}\text{C}$  NMR spectrum of 1-(chloromethyl)-4-(2,2-dimethoxyethyl)benzene (**3n**) in  $\text{CDCl}_3$ .



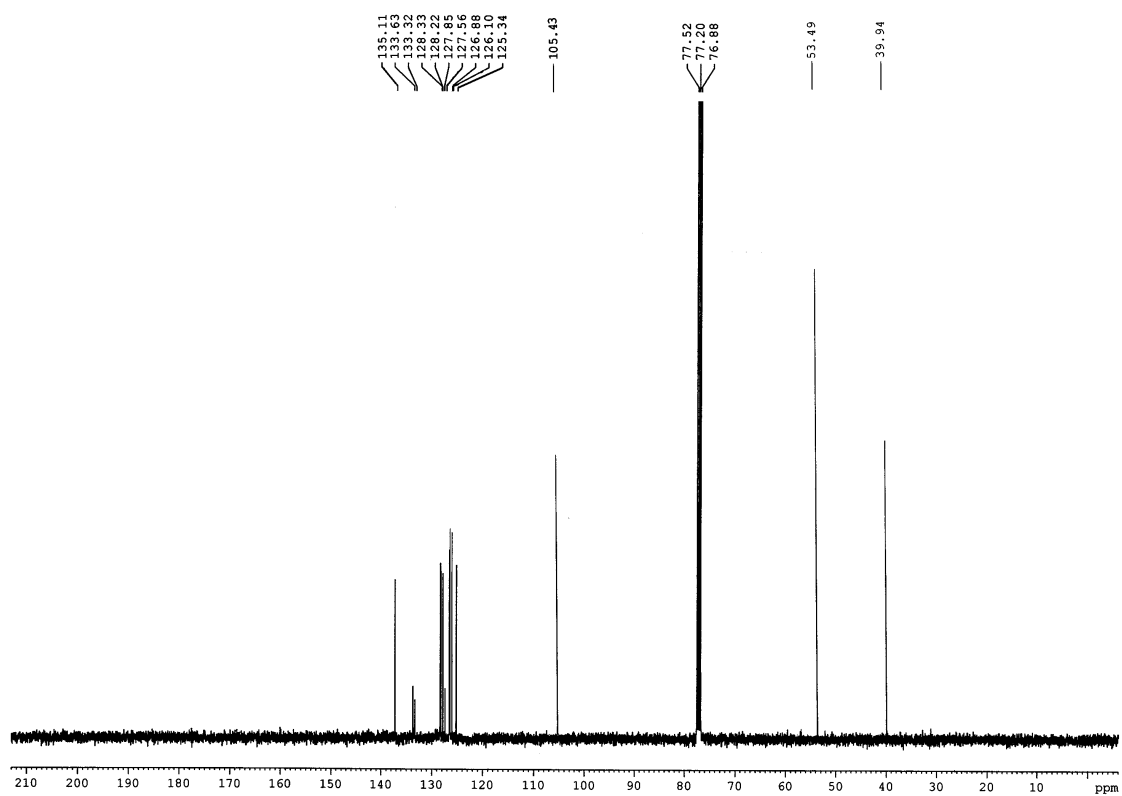
**Fig. S23**  $^1\text{H}$  NMR spectrum of 3-(2,2-dimethoxyethyl)benzaldehyde (**3o**) in  $\text{CDCl}_3$ .



**Fig. S24**  $^{13}\text{C}$  NMR spectrum of 3-(2,2-dimethoxyethyl)benzaldehyde (**3o**) in  $\text{CDCl}_3$ .



**Fig. S25**  $^1\text{H}$  NMR spectrum of 2-(2,2-dimethoxyethyl)naphthalene (**3r**) in  $\text{CDCl}_3$ .



**Fig. S26**  $^{13}\text{C}$  NMR spectrum of 2-(2,2-dimethoxyethyl)naphthalene (**3r**) in  $\text{CDCl}_3$ .

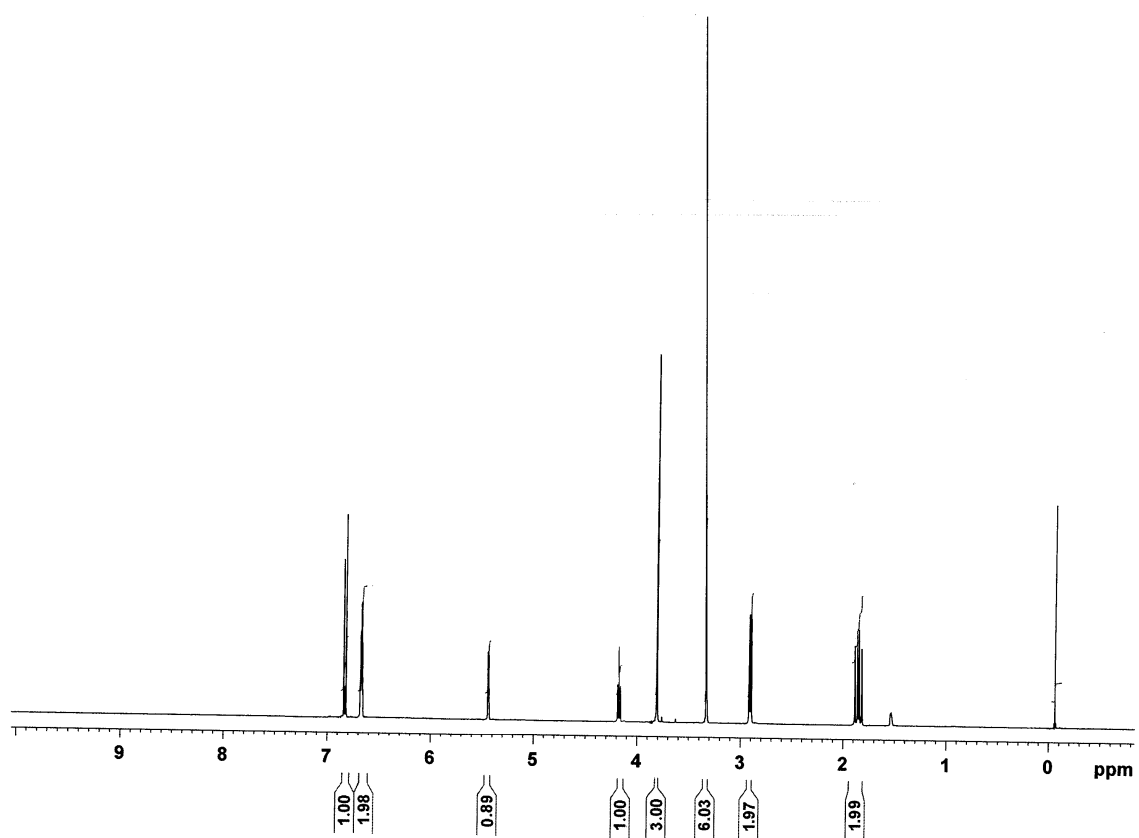
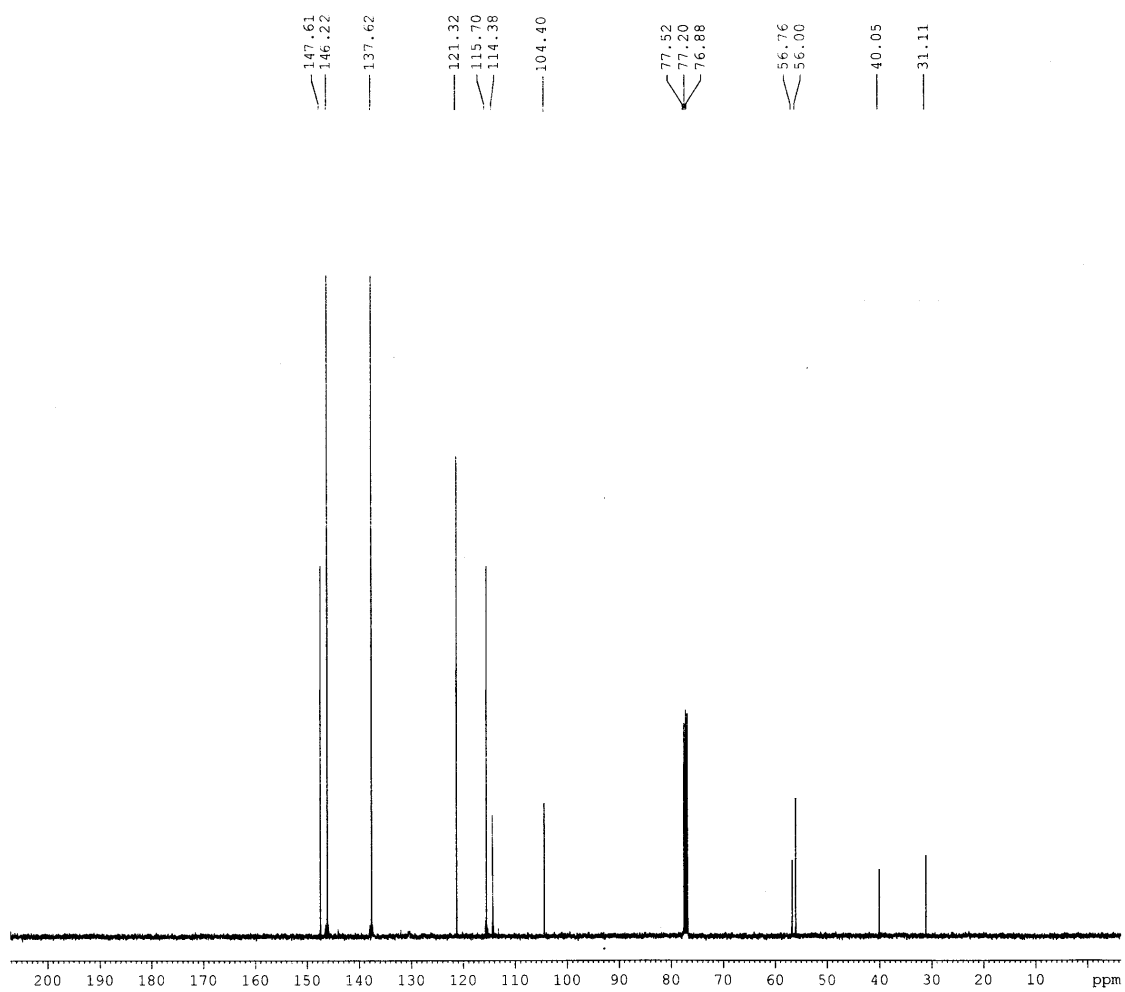
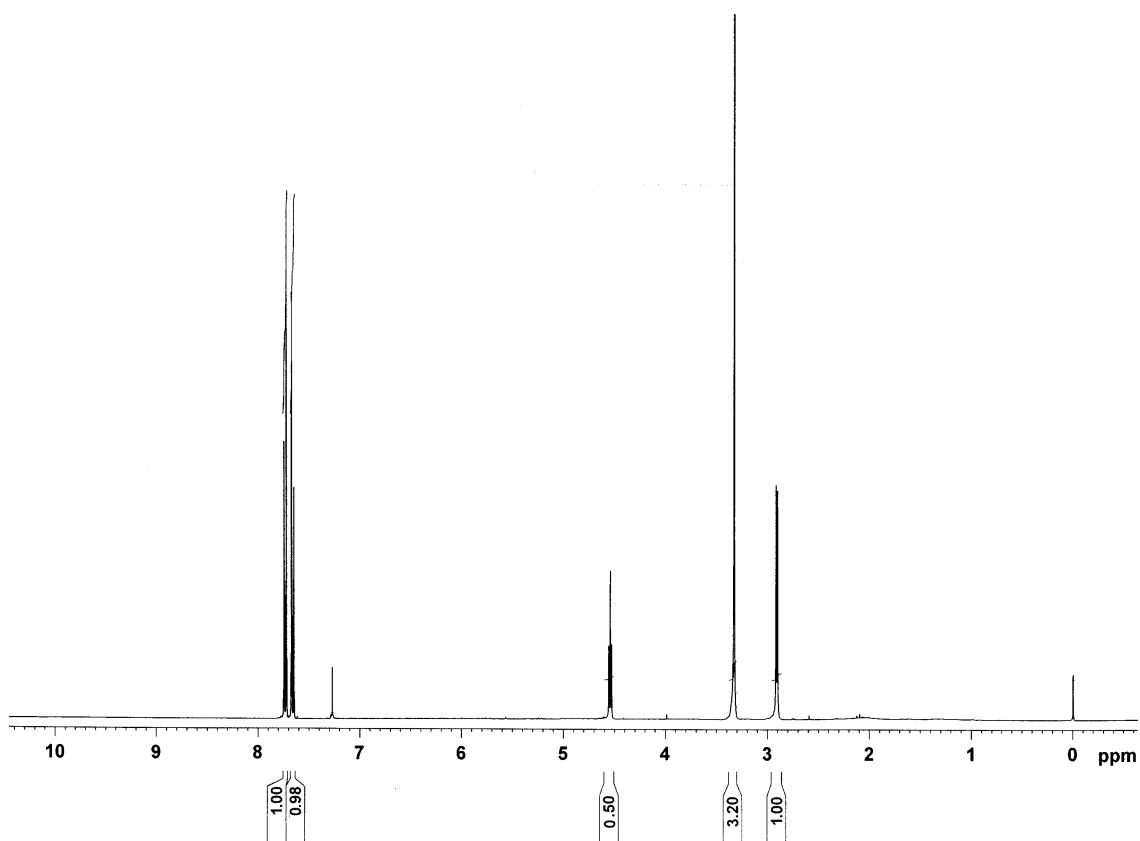


Fig. S27 <sup>1</sup>H NMR spectrum of 4-(3,3-dimethoxypropyl)-2-methoxyphenol (**3t**) in CDCl<sub>3</sub>.

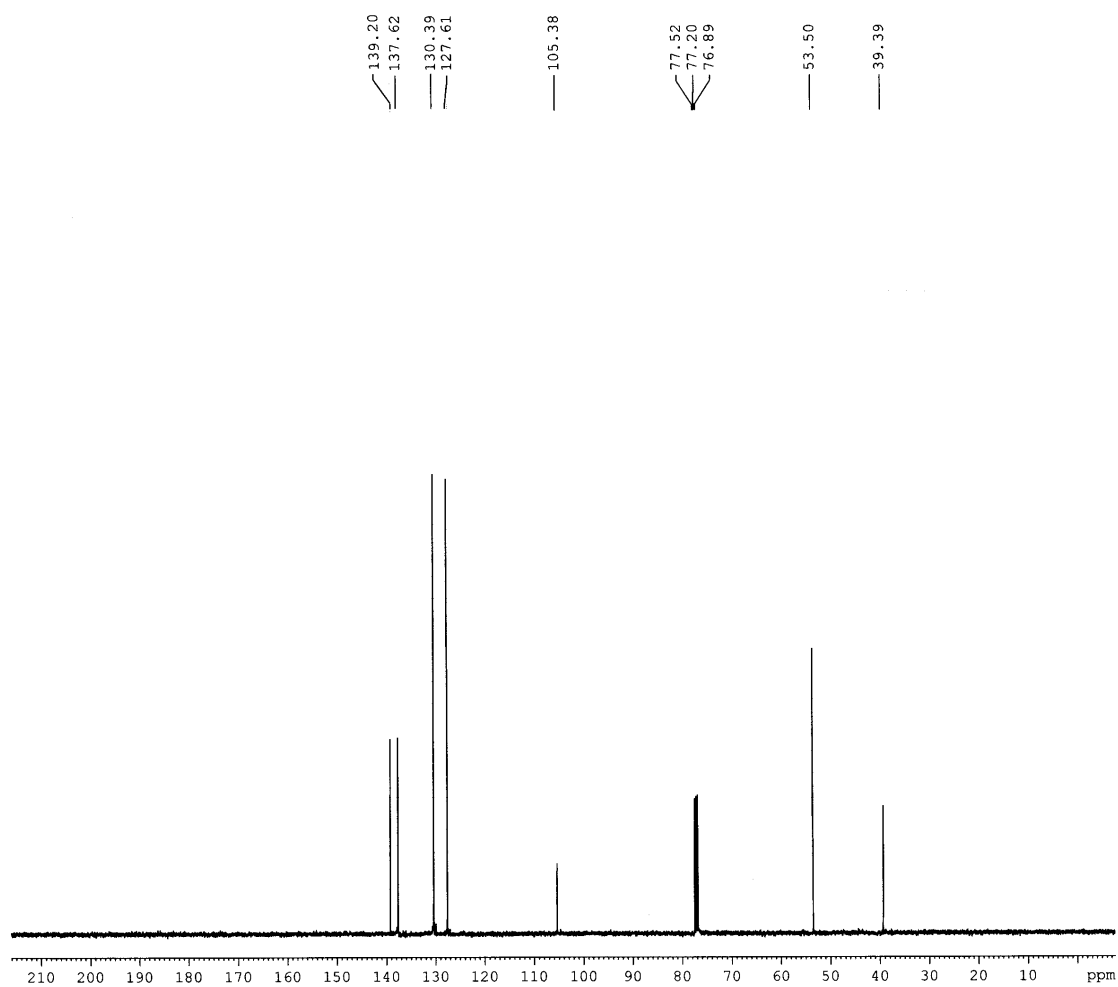


**Fig. S28**  $^{13}\text{C}$  NMR spectrum of 4-(3,3-dimethoxypropyl)-2-methoxyphenol (**3t**) in  $\text{CDCl}_3$ .

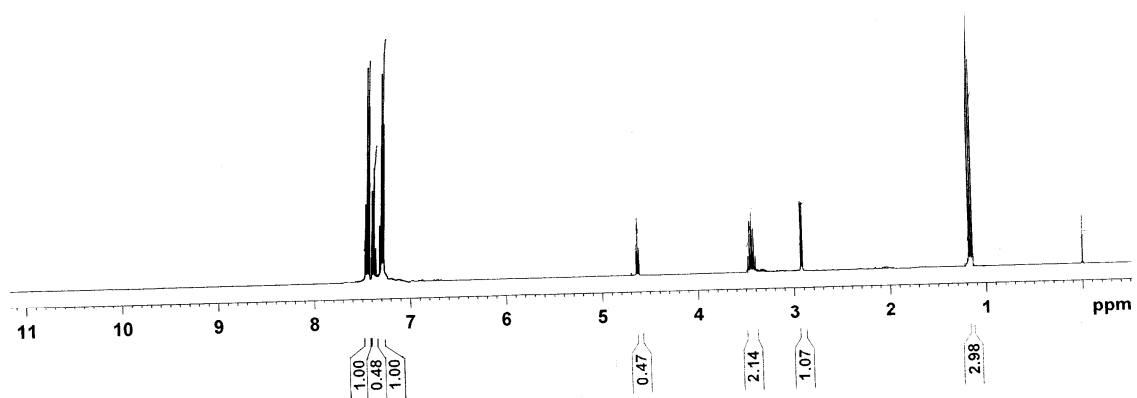


**Fig. S29**  $^1\text{H}$  NMR spectrum of 4,4'-bis(2,2-dimethoxyethyl)biphenyl (**3u**) in  $\text{CDCl}_3$ .

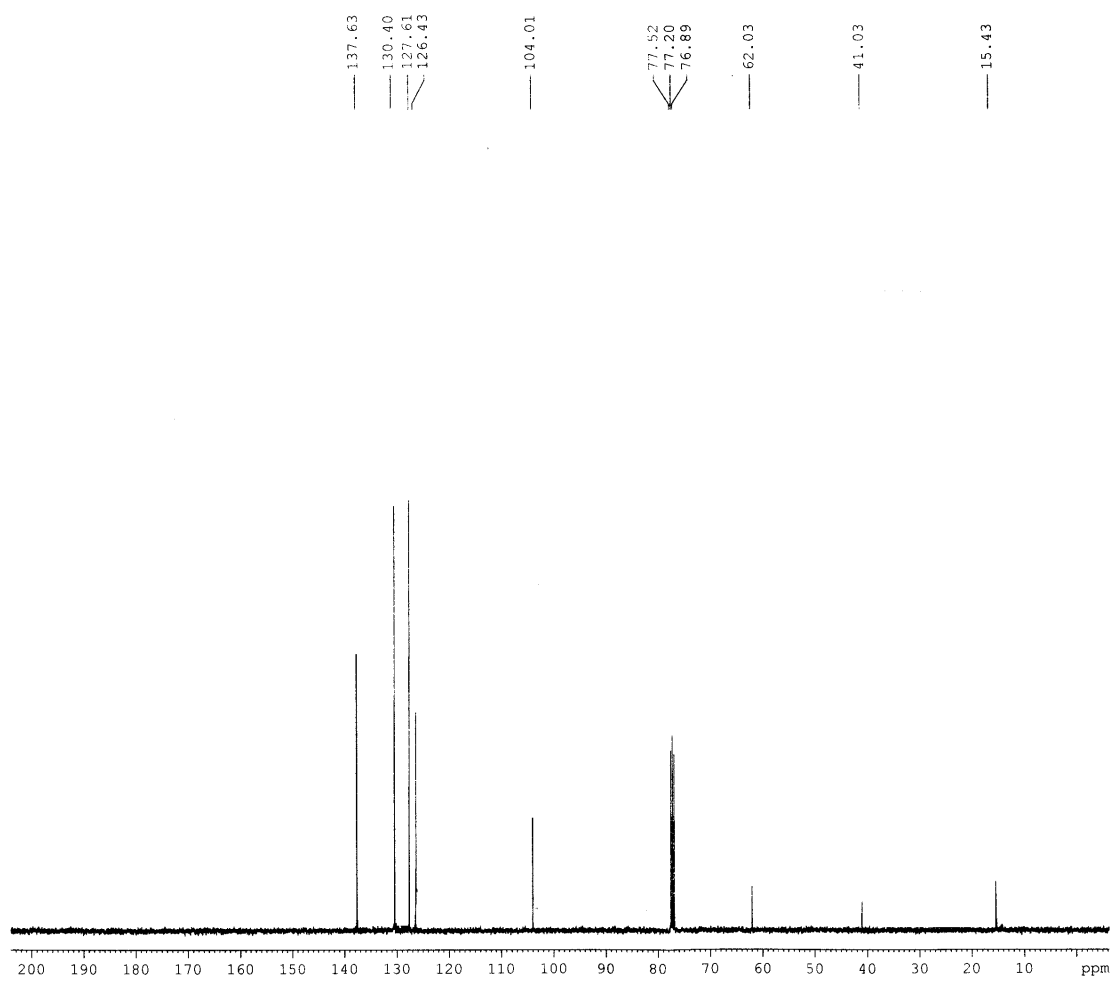




**Fig. S30**  $^{13}\text{C}$  NMR spectrum of 4,4'-bis(2,2-dimethoxyethyl)biphenyl (**3u**) in  $\text{CDCl}_3$ .



**Fig. S31**  $^1\text{H}$  NMR spectrum of (2,2-diethoxyethyl)benzene (**4a**) in  $\text{CDCl}_3$ .



**Fig. S32**  $^{13}\text{C}$  NMR spectrum of (2,2-diethoxyethyl)benzene (**4a**) in  $\text{CDCl}_3$ .

## Notes and references

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