A Simple and Efficient Heterogeneous Procedure for Thioacetalization of Aldehydes and Ketones

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Abstract: A new procedure for the protection of aldehydes and ketones as thioacetals promoted by catalytic amount of p-toluene-sulfonic acid and silica gel has been developed. This procedure offers versatility, short reaction time, excellent yield, good selectivity, and flexibility in terms of choice of solvent that can be utilized in this reaction. The procedure is easy to carry out and does not require aqueous work-up. A simple filtration followed by removal of solvent in most cases produces pure product.

Key words: thioacetal, silica gel, heterogeneous, ketones, aldehydes

It is often necessary to protect carbonyl groups to avoid complications that may arise from involvement of a nucleophile targeted for another part of the molecule.1 Thioacetals are stable in both acidic and basic reaction media and a wide range of homogeneous and heterogeneous reagents are available to remove thioacetal protection from carbonyl groups.2 Therefore, conversion of a carbonyl group to a thioacetal is generally a preferred method of protection in organic syntheses. Thioacetalization of carbonyl groups using TiCl4,3 TeCl4,4 InCl3,5 Sc(OTf)3,6 zinc and magnesium triflates,7 BF3·OEt2,8 and Bi(NO3)39 in homogeneous reaction conditions have been reported. Heterogeneous reagents such as silica gel treated with thionyl chloride,10 Nafion-H,11 Zeolites,12 Amberlyst-15,13 Fe3+·Montmorillonite,14 ZrCl4,15 and CoBr2 on silica gel,16 Envirocatt EPZG,17 Cu(OTf)2·SiO2,18 and heteropolyacids19 are known to promote thioacetalization of carbonyl groups.

Heterogeneous reagents offer additional benefits that their homogeneous counterparts do not. In general, procedures involving heterogeneous reagents require minimum handling of the reagents, show higher product selectivity, produce enhanced reaction rates, generate smaller amounts of solid waste, and make product isolation easy. These advantages associated with heterogeneous reagents satisfy a number of important criteria for Green Chemistry.20

In continuation of our interest in the utilization of solid supports in organic reactions,21 we have investigated the title reaction using p-toluene-sulfonic acid and silica gel in dichloromethane and hexanes media.

\[ 	ext{[p-TsOH], silica gel} \]

\[ \begin{align*}
\text{R} & \quad \text{R} \\
\text{CH}_2\text{Cl}_2 & \quad \Delta \\
\text{HSCH}_2\text{CH}_2\text{SH} & \quad + \text{H}_2\text{O}
\end{align*} \]

1 R = Alkyl, 2 R' = H or Alkyl
3 R = Aryl, 4 R' = H
5 R = Aryl, 5 R' = Alkyl or Aryl

\[ \text{[p-TsOH], silica gel} \]

\[ \begin{align*}
\text{R} & \quad \text{R} \\
\text{CH}_2\text{Cl}_2 & \quad \Delta \\
\text{R} & \quad + \text{2R'SH} \\
\text{H} & \quad \text{+ H}_2\text{O}
\end{align*} \]

3c R = Aryl, 3c R' = Et
3c R = Aryl, 3c R' = Bu

Scheme 1

The most important advantages of this procedure are that an aqueous work-up is not necessary and a simple filtration allows isolation of products. The procedure for thioacetalization in the presence of silica gel reported here is very clean and produces excellent yields of the desired thioacetals. In most cases the isolated products required no further purification. Polar byproducts, if formed, remain absorbed on the silica gel and are removed during filtration. However, a limited number of products was found to be contaminated with a trace amount of p-toluenesulfonic acid. Products contaminated with p-toluenesulfonic acid were easily purified using the column or radial chromatography techniques.

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Silica gel facilitates the reaction by removing water as soon as it is produced in the reaction mixture. We have carried out our thioacetalization reaction on a number of aldehydes and ketones, some containing additional functionalities. These results are presented in the tables below. Thioacetalization of aliphatic aldehydes and ketones are presented in Table 1. Aliphatic aldehydes and ketones produced excellent yields of the protected thioacetals. As expected, sterically hindered ketones reacted sluggishly compared to unhindered ketones thereby requiring longer reaction times. For example, cyclohexanone (1a) produced a near quantitative yield of the corresponding cyclic thioacetal 2a in 6 hours compared to 25 hours required for cyclododecanone (1b) to produce the corresponding thioacetals 2b in dichloromethane reaction media (Table 1). Also, we observed that the thioacetalization of aldehydes is faster than those for ketones. The \( \alpha,\beta \)-unsaturated aldehyde 1h produced excellent yields of the aldehyde protected product 2h. We conclude that this rate difference is due to greater steric hindrance posed by the ketones compared to the aldehydes. Under similar reaction conditions, aromatic aldehydes and ketones also produced excellent yields of cyclic thioacetals. Results of acetalization of aromatic aldehydes 3a–j and ketones 5a–g are presented in the Tables 2 and 3 respectively.

Thioacetalization of aromatic aldehydes 3a–j are significantly faster than those for the ketones 5a–g. Presence of an electron-donating group on the benzene ring help the thioacetalization reaction proceeds faster. On the other hand, an electron-withdrawing group on the benzene ring slows the rate of the reaction. Also, comparison of the data clearly indicates that the aromatic aldehydes are more reactive towards the thioacetalization reaction than their aliphatic counterparts. Significant rate differences between the thioacetalization of aldehydes and ketones under heterogeneous reaction conditions encouraged us to investigate the possibility for the selective protection of aldehydes in the presence of ketones. Such selective protection has been previously reported in homogeneous reaction media.5,13

We carried out a number of competitive thioacetalization reactions using equimolar mixture of various aldehydes and ketones with 1,2-ethanediithiol (Scheme 2). These reactions produced thioacetals of the aldehydes and the ketones remained unchanged. Thioacetalization of compound 7 possessing an aldehyde and a ketone functional group produced compound 8. The results of this study are presented in Table 4. These results clearly demonstrate that selective protection of aldehyde in the presence of ketone is possible using the procedure reported in this communication.

Acyclic thioacetals are produced in excellent yields when 1,2-ethanediithiol is replaced with alkanethiols in our procedure. Reactions of vanillin (3c) with two equivalents of ethanethiol and butanethiol produced thioacetals 9 and 10, respectively, in excellent yields (Table 5).

### Table 1: Thioacetalization of Aliphatic Aldehydes and Ketones

<table>
<thead>
<tr>
<th>Entry</th>
<th>Aldehyde/Ketone 1</th>
<th>Reaction time (h)</th>
<th>Yield (%) of thioacetal 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>1a</td>
<td>6</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>93&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15</td>
<td>77&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>b</td>
<td>1b</td>
<td>25</td>
<td>94</td>
</tr>
<tr>
<td>c</td>
<td>1c</td>
<td>7.5</td>
<td>78</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8</td>
<td>75&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>d</td>
<td>1d</td>
<td>3.5</td>
<td>77</td>
</tr>
<tr>
<td>e</td>
<td>1e</td>
<td>3.5</td>
<td>88</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8</td>
<td>71&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>f</td>
<td>1f</td>
<td>24</td>
<td>86</td>
</tr>
<tr>
<td>g</td>
<td>1g</td>
<td>27</td>
<td>94</td>
</tr>
<tr>
<td>h</td>
<td>1h</td>
<td>4</td>
<td>97</td>
</tr>
<tr>
<td>i</td>
<td>1i</td>
<td>12</td>
<td>91</td>
</tr>
<tr>
<td>j</td>
<td>1j</td>
<td>6</td>
<td>87</td>
</tr>
<tr>
<td>k</td>
<td>1k</td>
<td>6</td>
<td>81</td>
</tr>
</tbody>
</table>

<sup>a</sup> Chromatographically isolated product.

<sup>b</sup> Hexanes used as the reaction media.

<sup>c</sup> Reaction carried out in the absence of silica gel.

### Scheme 2

**Synthesis 2005, No. 8, 1326–1332 © Thieme Stuttgart · New York**
Since the silica gel used in this procedure is slightly acid-ic, we wanted to examine the role silica gel play promot-ing this reaction. We carried out thioacetalizations of piperonal (3h) with 1,2-ethanedithiol in the presence and in the absence of p-toluenesulfonic acid. Silica gel was present in both of these reactions.

Data presented in Scheme 3 indicate that both silica gel and p-toluenesulfonic acids are capable of promoting thioacetalization reactions. However, the role p-toluenesulfonic acid play in promoting this reaction is far greater than that of silica gel. In the presence of p-toluenesulfonic

**Table 2** Thioacetalization of Aromatic Aldehydes

<table>
<thead>
<tr>
<th>Entry</th>
<th>Aldehyde 3</th>
<th>Reaction time (h)</th>
<th>Yield (%) of thioacetal 4a</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>3</td>
<td>93b</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>76c</td>
</tr>
<tr>
<td>b</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>4.5</td>
<td>98</td>
</tr>
<tr>
<td>c</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>1.5</td>
<td>ca. 100</td>
</tr>
<tr>
<td>d</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>1.5</td>
<td>ca. 100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.5</td>
<td>91b</td>
</tr>
<tr>
<td>e</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>1.5</td>
<td>90</td>
</tr>
<tr>
<td>f</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>3</td>
<td>97</td>
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<tr>
<td>g</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>3</td>
<td>85</td>
</tr>
<tr>
<td>h</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>0.75</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.5</td>
<td>88b</td>
</tr>
<tr>
<td>i</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>6</td>
<td>97</td>
</tr>
<tr>
<td>j</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>0.25</td>
<td>71</td>
</tr>
</tbody>
</table>

a Chromatographically isolated product.
b Hexanes used as the reaction media.
c Reaction carried out in the absence of silica gel.

**Table 3** Thioacetalization of Aromatic Ketones

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ketone 5</th>
<th>Reaction time (h)</th>
<th>Yield (%) of thioacetal 6a</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>26</td>
<td>97</td>
</tr>
<tr>
<td>b</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>27</td>
<td>96</td>
</tr>
<tr>
<td>c</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>72</td>
<td>98 (71% conversion)b</td>
</tr>
<tr>
<td>d</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>12.5</td>
<td>81b</td>
</tr>
<tr>
<td>e</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>22</td>
<td>80b</td>
</tr>
<tr>
<td>f</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>27</td>
<td>95</td>
</tr>
<tr>
<td>g</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>22</td>
<td>91</td>
</tr>
</tbody>
</table>

a Chromatographically isolated product.
b Remaining unreacted ketones recovered.

**Table 4** Competitive Thioacetalization of Aromatic Aldehydes/Ketones with 1,2-Ethanedithiol

<table>
<thead>
<tr>
<th>Entry</th>
<th>Aldehyde + Ketone</th>
<th>Product</th>
<th>Reaction-time (h)</th>
<th>Yield (%)a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3a + 5a</td>
<td>4a</td>
<td>3</td>
<td>ca. 100</td>
</tr>
<tr>
<td>2</td>
<td>3i + p-nitroacetophenone</td>
<td>4i</td>
<td>4</td>
<td>98</td>
</tr>
<tr>
<td>3</td>
<td>3b + 5f</td>
<td>4b</td>
<td>2</td>
<td>96</td>
</tr>
<tr>
<td>4</td>
<td>3d + 5b</td>
<td>4d</td>
<td>1.5</td>
<td>ca. 100</td>
</tr>
<tr>
<td>5</td>
<td>3e + 5d</td>
<td>4e</td>
<td>1</td>
<td>95</td>
</tr>
<tr>
<td>6</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>4f</td>
<td>3</td>
<td>97</td>
</tr>
</tbody>
</table>

a Chromatographically isolated product.
acid thioacetalization reaction of piperonal (3h) took 45 minutes to complete. In the absence of p-toluene sulfonic acid no significant amount of thioacetal 4h was detected during the same reaction period. However, when the later reaction was allowed to continue for 24 hours, 35% of the piperonal (3h) was converted to the corresponding thioacetal 4h and the remaining piperonal (3h) was recovered unchanged.

![Scheme 3](image)

In the presence of silica gel thioacetalization reactions proceed faster and produce higher yield of the products compared to the reactions carried out in the absence of silica gel (Table 1, entries a and e and Table 2, entries a and h). Various amounts of the starting materials were isolated along with the products in the silica gel free reactions. We believe that the observed rate enhancement is due to the spreading of the acid catalysts over a large surface area provided by the silica gel. However other factor(s) may also be responsible for the observed rate enhancement.

We then examined hexanes as the reaction media in thioacetalization of cyclohexanone (1a), heptan-4-one (1c), benzaldehyde (3a), and p-tolualdehyde (3d) with 1,2-ethanethiol. These reactions proceeded smoothly to produce excellent yields of the corresponding thioacetals (Tables 1 and 2). Efficiency (product yield and reaction time) of these reactions in hexanes and in dichloromethane is very similar. It is clearly evident that hexanes can be utilized as a reaction media in this heterogeneous thioacetalization procedure. Replacing a halogenated solvent with a non-halogenated solvent is a big plus for this procedure. Poor solubility of some carbonyl compounds and/or products in hexanes are the only disadvantages we anticipate in using hexanes as the reaction media. Currently we are investigating thioacetalization of various carbonyl compounds in several non-halogenated solvents including hexanes. These results will be published in due course.

In summary, we have developed a simple and highly efficient heterogeneous procedure for thioacetalization of aldehydes and ketones. Other notable advantages of the procedure presented here include selective protection of an aldehyde in the presence of a ketone, high product yield, clean reaction, easy workup and smaller amounts of waste. This procedure is equally efficient for generating cyclic as well as acyclic thioacetals. In addition, this procedure holds promise in replacing dichloromethane with non-halogenated solvents without sacrificing the efficiency.

All reaction mixtures were stirred using Teflon coated magnetic stirring bars. All reagents and solvents were used as they were received from the suppliers without further purification. All products were identified by NMR and IR data. The silica gel, used as solid support, was MN-Kieselgel 60 (0.04–0.063 mm mesh size) supplied by Fisher Scientific. 1H NMR spectra were recorded on a Bruker DPX-300 NMR instrument. Samples for NMR were dissolved in CDCl3. Proton chemical shifts are expressed in ppm relative to tetramethylsilane. IR spectra were recorded on a Perkin-Elmer Spectrum 1000 FT-IR instrument and are reported in wave numbers (cm⁻¹). Chromatographic separations were carried out by preparative centrifugal TLC with silica gel (Merck #5715) and developed in EtOAc–hexanes mixed solvent systems. Compounds were visualized by a UV lamp and/or by staining either with p-anisidinediethyl/H2SO4 or phosphomolybdic acid.

### Thioacetalization of Aldehydes and Ketones; General Procedure

A 100 mL round-bottom flask fitted with a condenser was charged with silica gel (4 g), CH2Cl2 or hexane (20 mL), an aldehyde or a ketone (2.5 mmol), 1,2-ethanethiol (2.75 mmol or 5.50 mmol of an alkythiol), and p-toluene sulfonic acid (10–15 mg). The heterogeneous mixture was refluxed under stirring with a magnetic stirrer. Progress of the reaction was monitored either by TLC analysis or IR spectroscopy. After complete disappearance of the starting carbonyl compound, the reaction mixture was filtered through a sintered-glass funnel. The solid residue was washed with CH2Cl2 (ca. 75 mL), or with EtOAc (ca. 75 mL) when hexane was used as the reaction media. The solvent was evaporated under vacuum to isolate the product. In most of the cases the isolated crude product was found to be pure as indicated by NMR and IR spectra. However, the impure products were purified utilizing flash column or radial chromatography using a mixture of EtOAc and hexane. Several thioacetalization reactions were scaled up to 100 mmol of carbonyl compounds. Yields of these large scale reactions were comparable to the yields reported in Tables 1–5.
**1** IR (neat): 732, 908, 963, 1014, 1275, 1455, 2853, 2925 cm\(^{-1}\).
\[ ^{1}H\text{ NMR: } \delta = 1.60 \text{ (m, 8 H), 2.20 (m, 4 H), 3.28 (m, 4 H).} \]
\[ ^{13}C\text{ NMR: } \delta = 25.60, 28.60, 38.90, 46.10, 71.90. \]

**2** IR (neat): 806, 852, 971, 1026, 1083, 1135, 1234, 1276, 1376, 1427, 1440, 1455, 2848, 2918 cm\(^{-1}\).
\[ ^{1}H\text{ NMR: } \delta = 0.90 \text{ (d, } J = 6.5 \text{ Hz, 3 H), 1.2–1.40 (m, 3 H), 1.67–1.72 (m, 2 H), 1.85–1.96 (m, 2 H), 2.07–2.12 (m, 2 H), 3.22–3.29 (m, 4 H).} \]
\[ ^{13}C\text{ NMR: } \delta = 21.90, 31.10, 34.50 (2 \text{ CH}_2), 37.90, 38.70, 42.30 (2 \text{ CH}_2), 68.30. \]

**3** IR (neat): 2958, 2931, 2871, 1731, 1437, 1377, 1276, 1139, 853, 767 cm\(^{-1}\).
\[ ^{1}H\text{ NMR: } \delta = 0.85–1.00 \text{ (t, } J = 7.3 \text{ Hz, 6 H), 1.4–1.55 \text{ (m, 4 H), 1.8–1.93 \text{ (t, } J = 6.8 \text{ Hz, 4 H), 3.25 (s, 4 H).} \]
\[ ^{13}C\text{ NMR: } \delta = 14.25, 20.18, 28.73, 39.40 (2 \text{ CH}_2), 45.75. \]

**4** IR (thin film): 3429, 3060, 2926, 1922, 1690, 1661, 1600, 1494, 1451, 1442, 1276 cm\(^{-1}\).
\[ ^{1}H\text{ NMR: } \delta = 3.23–3.46 (m, 4 \text{ H), 5.61 (s, 1 \text{ H), 7.19–7.30 (m, 3 \text{ H), 7.49 (d, } J = 7.10 \text{ Hz, 2 \text{ H).} \]
\[ ^{13}C\text{ NMR: } \delta = 40.81 (2 \text{ CH}_2), 56.82, 128.52, 128.56, 129.02, 140.94. \]

**5** IR (thin film): 3434 (br), 2996, 2918, 1607, 1596, 1509, 1464, 1449, 1427, 1266, 1227, 1145, 1118, 1026 cm\(^{-1}\).
\[ ^{1}H\text{ NMR: } \delta = 3.29–3.53 (m, 4 \text{ H), 3.88 (s, 3 \text{ H), 5.69 (s, 1 \text{ H), 6.81 (d, } J = 8.11 \text{ Hz, 1 \text{ H), 7.09 (s, 1 \text{ H).} \]
\[ ^{13}C\text{ NMR: } \delta = 40.14 (2 \text{ CH}_2), 55.91, 56.69, 110.26, 113.97, 121.07, 131.22, 145.54, 146.47. \]

**6** IR (neat): 3004, 1510, 1437, 1411, 1277, 1177, 1165, 830, 777 cm\(^{-1}\).
\[ ^{1}H\text{ NMR: } \delta = 2.32 (s, 3 \text{ H), 3.29–3.52 (m, 4 \text{ H), 5.62 (s, 1 \text{ H), 7.10 (d, } J = 6.5 \text{ Hz, 2 \text{ H), 7.40 (d, } J = 6.5 \text{ Hz, 2 \text{ H).} \]
\[ ^{13}C\text{ NMR: } \delta = 21.11, 40.20 (2 \text{ CH}_2), 56.12, 127.80, 129.15, 137.10, 137.84. \]

**7** IR (neat): 3188 (br), 2919, 1595, 1509, 1448, 1237, 1173, 838 cm\(^{-1}\).
\[ ^{1}H\text{ NMR: } \delta = 3.30–3.51 (m, 4 \text{ H), 5.00 (s, 1 \text{ H), 5.62 (s, 1 \text{ H), 6.73–6.79 (m, 2 \text{ H), 7.37–7.43 (m, 2 \text{ H).} \]
\[ ^{13}C\text{ NMR: } \delta = 40.20 (2 \text{ CH}_2), 56.01, 115.31, 129.41, 131.99, 155.31. \]
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1H NMR: δ = 2.31 (s, 3 H), 3.39 (m, 4 H), 7.08 (d, J = 8.1 Hz, 2 H), 7.23–7.27 (m, 3 H), 7.48 (d, J = 8 Hz, 2 H), 7.60 (m, 2 H).

13C NMR: δ = 20.96, 40.12 (2 CH2), 127.10, 127.73, 127.97, 128.17, 128.64, 136.95, 141.47, 144.77.

6d

IR (neat): 687, 738, 831, 844, 1074, 1180, 1230, 1273, 1375, 1442, 1508, 1596, 1608, 2876, 2929, 2969, 3225 (br) cm⁻¹.

1H NMR: δ = 2.13 (s, 3 H), 3.35–3.51 (m, 4 H), 5.60 (br s, 1 H), 6.75 (d, J = 7.7 Hz, 2 H), 7.63 (d, J = 7.7 Hz, 2 H).

13C NMR: δ = 33.91, 40.35 (2 CH2), 68.22, 114.71, 128.33, 137.73, 154.64.

6e

IR (thin film): 3061, 3015, 2924, 2960, 1580, 1474, 1447, 1418, 1277, 741 cm⁻¹.

1H NMR: δ = 3.73 (br s, 4 H), 7.28–7.34 (m, 4 H), 7.58–7.69 (m, 4 H).

13C NMR: δ = 28.65, 42.24 (2 CH2), 119.76, 125.09, 128.25, 128.51, 138.35, 150.36.

6f

IR (neat): 734, 830, 1011, 1069, 1093, 1275, 1372, 1396, 1422, 1444, 1489, 1570, 1591, 2860, 2922, 2966, 3059 cm⁻¹.

1H NMR: δ = 2.1 (s, 3 H), 3.30–3.45 (m, 4 H), 7.26 (d, J = 6.4 Hz, 2 H), 7.68 (d, J = 6.4 Hz, 2 H).

13C NMR: δ = 33.46, 40.31 (2 CH2), 67.82, 127.87, 128.24, 132.70, 144.55.

6g

IR (neat): 731, 827, 1007, 1077, 1275, 1391, 1486, 1583, 2858, 2922, 2965, 3061 cm⁻¹.

1H NMR: δ = 2.07 (s, 3 H), 3.30–3.45 (m, 4 H), 7.38 (d, J = 6.8 Hz, 2 H), 7.60 (d, J = 6.8 Hz, 2 H).

13C NMR: δ = 34.10, 41.01 (2 CH2), 68.50, 114.03, 129.60, 131.50, 145.76.

8f

IR (neat): 760, 861, 960, 1017, 1111, 1271, 1355, 1414, 1574, 1605, 1677, 2876, 2918, 2952, 3086 cm⁻¹.

1H NMR: δ = 2.59 (s, 3 H), 3.36–3.53 (m, 4 H), 5.65 (s, 1 H), 7.60 (d, J = 8 Hz, 2 H), 7.91 (d, J = 8 Hz, 2 H).

13C NMR: δ = 26.64, 40.33 (2 CH2), 55.41, 128.08, 128.54, 136.57, 146.19, 197.45.
$^{13}$C NMR: $\delta = 13.66$ (2 CH$_3$), 21.77 (2 CH$_2$), 31.27 (2 CH$_2$), 32.06 (2 CH$_2$), 53.07, 55.92, 110.01, 113.86, 120.78, 132.43, 145.29, 147.77.

References