Supporting Information File 2

for

Addition of dithi(ol)anylium tetrafluoroborates to α,β-unsaturated ketones

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Collection of spectra and summary of IR data of starting materials

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Spectra of compounds type 4 and 5

[4a] 5-(1,3-dithiolan-2-ylidene)-5-phenylpentan-2-one
[5a] 5-(1,3-dithian-2-ylidene)-5-phenylpentan-2-one
[4b] 6-(1,3-dithiolan-2-ylidene)-6-phenylhexan-3-one
[5b] 6-(1,3-dithian-2-ylidene)-6-phenylhexan-3-one
[4c] 5-(1,3-dithiolan-2-ylidene)-4-methyl-5-phenylpentan-2-one
[5c] 5-(1,3-dithian-2-ylidene)-4-methyl-5-phenylpentan-2-one
[4d] 6-(1,3-dithiolan-2-ylidene)-5-methyl-6-phenylhexan-3-one
[5d] 6-(1,3-dithian-2-ylidene)-5-methyl-6-phenylhexan-3-one
[4e] 4-((1,3-Dithiolan-2-ylidene)(phenyl)methyl)-5-methylhexan-2-one
[4f] 4-((1,3-dithiolan-2-ylidene)(phenyl)methyl)octan-2-one
[5f] 4-((1,3-dithian-2-ylidene)(phenyl)methyl)octan-2-one
[4g] 5-(1,3-dithiolan-2-ylidene)-4,5-diphenylpentan-2-one
[5g] 5-(1,3-Dithian-2-ylidene)-4,5-diphenylpentan-2-one
[4h] 4-(1,3-Dithiolan-2-ylidene)-1,3,4-triphenylbutan-1-one
[5h] 4-(1,3-Dithian-2-ylidene)-1,3,4-triphenylbutan-1-one, impure (80%)
[4i] 6-(1,3-dithiolan-2-ylidene)-5-methylheptan-3-one (rac)
[5i] 6-(1,3-dithian-2-ylidene)-5-methylheptan-3-one
[4j] 4-(1-(1,3-dithiolan-2-ylidene)ethyl)-5-methylhexan-2-one
[4k] 4-((1,3-dithiolan-2-yl)idene)ethyl)octan-2-one
[4l] 5-(1,3-dithiolan-2-ylidene)-4-phenylhexan-2-one
[4m] 6-(1,3-dithiolan-2-ylidene)octan-3-one
[4n] 6-(1,3-dithiolan-2-ylidene)-5-methyloctan-3-one
[4o] 5-(1,3-dithiolan-2-ylidene)-4-isopropylheptan-2-one
[4p] 4-(1-(1,3-Dithiolan-2-ylidene)propyl)octan-2-one
[4q] 4-(1,3-dithiolan-2-ylidene)-1,3-diphenylhexan-1-one
[5r] Methyl 2-(1,3-dithian-2-ylidene)-3-methyl-5-oxoheptanoate
[4s] 6-(1,3-dithiolan-2-ylidene)-5-methylhexan-3-one
[4t] 4-((1,3-dithiolan-2-ylidene)methyl)octan-2-one
[4u] 3-((1,3-Dithiolan-2-ylidene)methyl)cyclopentan-1-one
[4v] 3-((1,3-dithiolan-2-ylidene)methyl)cyclohexan-1-one
Spectra of compounds type 9 and 10

[9a] 3-((1,3-dithiolan-2-ylidene)(phenyl)methyl)cyclopentan-1-one
[10a] 3-((1,3-dithian-2-ylidene)(phenyl)methyl)cyclopentan-1-one
[9b] 3-((1,3-dithiolan-2-ylidene)(phenyl)methyl)cyclohexan-1-one
[10b] 3-((1,3-dithian-2-ylidene)(phenyl)methyl)cyclohexan-1-one
[9c] 3-(1-(1,3-dithiolan-2-ylidene)ethyl)cyclopentan-1-one
[10c] 3-(1-(1,3-Dithian-2-ylidene)ethyl)cyclopentan-1-one
[9d] 3-(1,1-dithiolan-2-ylidene)ethyl)cyclohexan-1-one
[9e] 3-(1-(1,3-dithiolan-2-yliene)propyl)cyclopentan-1-one
[9f] 3-(1-(1,3-dithiolan-2-ylidene)propyl)cyclohexan-1-one
[10g] Methyl 2-(1,3-dithian-2-ylidene)-2-(3-oxocyclopentyl)acetate
[10h] Methyl 2-(1,3-dithian-2-ylidene)-2-(3-oxocyclohexyl)acetate
[9i] 3-(Chloro(1,3-dithiolan-2-ylidene)methyl)cyclohexan-1-one
[9j] 3-(3-Chloro-1-(1,3-dithiolan-2-ylidene)propyl)cyclohexan-1-one
Spectra of compounds type 11a and 11b

[11a] 6-(1,3-dithiolan-2-ylidene)-5,7-dimethylundecane-3,9-dione
[11b] 3,3'-(1,3-dithiolan-2-ylidene)methylene)bis(cyclopentan-1-one)
Spectra of compounds 13a, 13b, 15, 16a, 16b and 18a and 18b

[13a] Methyl 4-(1,3-dithiolan-2-ylidene)hexanoate
[13b] Dimethyl 2-(1-(1,3-dithiolan-2-ylidene)propyl)succinate
[15] 4-(1,3-dithiolan-2-ylidene)-1,3-diphenylhexan-1-one
[16a] 5-(1,3-Dithiolan-2-ylidene)-5-phenylpentan-2-ol
[16b] 5-(1,3-dithiolan-2-ylidene)-4-methyl-5-phenylpentan-2-ol, 2 diastereomers
[18a] (E)-5-(1,3-Dithiolan-2-ylidene)-5-phenylpent-3-en-2-one
[18b] (E)-5-(1,3-Dithiolan-2-ylidene)hex-3-en-2-one
Products of type 7: ring opening by hydrolysis

[7e] S-(3-((2-methyl-5-oxohexan-3-yl)thio)propyl) 2-phenylethanthioate
[7j] S-(3-((2-methyl-5-oxohexan-3-yl)thio)propyl) propanethioate
[7m] $S$-(3-((3-oxopentyl)thio)propyl) butanethioate
[7n] S-(3-((4-oxohexan-2-yl)thio)propyl) butanethioate

\[
\begin{align*}
\text{S} & - \text{S} - \left(3 - \left(\text{4-oxohexan-2-yl}\right)\text{thio}\right) - \text{propyl} - \text{butanethioate}
\end{align*}
\]
Properties and IR (Raman) spectra of compounds 1 and 2

Table S2: Properties and IR spectra of starting materials 1a-e and 2a-e.

<table>
<thead>
<tr>
<th>No</th>
<th>Structure</th>
<th>properties</th>
<th>IR</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td><img src="image" alt="Structure" /> Colorless solid</td>
<td>IR (ATR, $\tilde{\nu}$): 3025, 1493, 1456, 1420, 1397, 1286, 1122, 1095, 1024, 925, 809, 774, 701, 667, 632, 578, 520, 505, 445, 426 cm$^{-1}$.</td>
<td></td>
</tr>
<tr>
<td>2a</td>
<td><img src="image" alt="Structure" /> Colorless solid</td>
<td>IR (ATR, $\tilde{\nu}$): 2947, 1685, 1596, 1494, 1446, 1433, 1420, 1289, 1246, 1181, 1024, 928, 909, 878, 823, 768, 708, 672, 628, 571, 520, 467 cm$^{-1}$.</td>
<td></td>
</tr>
<tr>
<td>1b</td>
<td><img src="image" alt="Structure" /> Orange oil</td>
<td>IR (ATR, $\tilde{\nu}$): 2944, 1639, 1459, 1421, 1287, 1028, 945, 840, 763, 668, 519 cm$^{-1}$.</td>
<td></td>
</tr>
<tr>
<td>2b</td>
<td><img src="image" alt="Structure" /> Orange oil</td>
<td>IR (ATR, $\tilde{\nu}$): 2991, 1638, 1435, 1421, 1198, 1048, 977, 909, 763, 662, 578, 520 cm$^{-1}$.</td>
<td></td>
</tr>
<tr>
<td>1c</td>
<td><img src="image" alt="Structure" /> Yellow oil</td>
<td>IR (ATR, $\tilde{\nu}$): 3532, 2971, 1637, 1462, 1420, 1287, 1049, 970, 764, 668, 520 cm$^{-1}$.</td>
<td></td>
</tr>
<tr>
<td>2c</td>
<td><img src="image" alt="Structure" /> Yellow oil</td>
<td>IR (ATR, $\tilde{\nu}$): 3531, 2972, 1632, 1436, 1422, 1245, 1051, 992, 909, 764, 662, 578, 520 cm$^{-1}$.</td>
<td></td>
</tr>
<tr>
<td>1d</td>
<td><img src="image" alt="Structure" /> Orange oil</td>
<td>Raman (1064 nm, 150 mW, $\tilde{\nu}$) =3004, 2956, 2700, 2637, 1463, 1423, 1187, 1423, 1187, 1115, 1024, 997, 888, 766, 662, 501, 478, 364, 247, 81 cm$^{-1}$.</td>
<td></td>
</tr>
<tr>
<td>2d</td>
<td><img src="image" alt="Structure" /> Orange solid</td>
<td>IR (ATR, $\tilde{\nu}$): 2937, 1737, 1458, 1435, 1420, 1322, 1258, 1210, 1181, 1025, 980, 886, 730, 682, 661, 574, 521, 418 cm$^{-1}$.</td>
<td></td>
</tr>
<tr>
<td>1e</td>
<td><img src="image" alt="Structure" /> Yellow to red solid</td>
<td>IR (ATR, $\tilde{\nu}$): 3021, 1421, 1290, 1153, 1121, 1088, 1025, 874, 839, 668, 520, 446 cm$^{-1}$.</td>
<td></td>
</tr>
<tr>
<td>2e</td>
<td><img src="image" alt="Structure" /> Yellow solid</td>
<td>IR (ATR, $\tilde{\nu}$): 3000, 2926, 1688, 1427, 1361, 1287, 1239, 1209, 1155, 1118, 1094, 1021, 905, 880, 824, 765, 660, 566, 519, 448 cm$^{-1}$.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Colorless to violet solid</td>
<td>Raman (1064 nm, 150 mW, $\tilde{\nu}$) = 2984, 2968, 2937, 2922, 2905, 1418, 1283, 1250, 816, 742, 717, 689, 672, 534, 463, 421, 369, 331, 289, 204, 126, 84 cm$^{-1}$.</td>
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</tr>
<tr>
<td>If</td>
<td><img src="image1" alt="Chemical Structure" /></td>
<td><strong>Orange oil</strong></td>
<td>Raman (1064 nm, 150 mW, $\tilde{\nu}$) = 3017, 2956, 1436, 1185, 995, 766, 661, 541, 476, 70 cm$^{-1}$.</td>
</tr>
</tbody>
</table>