Selective Synthesis of (Z)-Chalcogenoynes and (Z,Z)-1,4-bis-Chalcogenbuta-1,3-dienes Using PEG-400

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We present here our results on the temperature controlled, selective hydrochalcogenation of 1,4-diorganyl-1,3-butadiynes with nucleophilic species of selenium, tellurium and sulfur generated in situ from the respective diaryl dichalcogenide and NaBH₄. Using polyethylene glycol (PEG)-400 at 30 °C the (Z)-chalcogenoynes are obtained and at 90 °C the (Z,Z)-bis-chalcogen-1,3-butadienes are produced in good to excellent yields. Alternatively to conventional oil bath heating, the use of microwave irradiation is also presented as an alternative energy source that provides the expected products in few minutes.

Keywords: organochalcogens, PEG-400, enyne, microwave irradiation, 1,3-butadienes

Introduction

Enynes, dienes and related unsaturated structures are key fragments found in a diverse array of natural products.¹ A widely studied example is the naturally occurring pheromone bombykol, isolated from the silkworm moth (Bombyx mori), which was firstly characterized by Butenandt et al.² over 40 years ago. Bombykol contains conjugated olefins of E,Z-configuration and represents a milestone on the structural elucidation of a natural compound important for chemical interactions between live organisms.³ Moreover, these unsaturated structures represent important moieties found in a diverse array of biologically active compounds, for example the drug lovastatin, an important 3-hydroxy-3-methylglutaryl-coenzyme A (HMG-CoA) reductase inhibitor and antihypercholesterolemic agent that has a diene portion in its structure.⁴

The broad scope of applications for conjugated enynes and dienes requires selective and efficient methods of synthesis commonly involving transition metal catalyzed cross-coupling reactions.⁶ Although these methods are undeniably efficient, protocols using stable and easily handled materials for rigorous regio- and stereochemical controlled synthesis remains a challenge.

In this way, vinyl chalcogenides have been found to be very useful tools in organic synthesis and materials science since they are versatile intermediates for the selective construction of isolated or conjugated olefins.⁷ One of the main advantages of using vinyl chalcogenides is the fact that these species can be transmetalated with many organometallic reagents to generate the corresponding vinyl organometallics with retention of the double-bond geometry.⁸ Still, among the broad scope of applications of vinyl chalcogenides, the importance for the synthesis of enediynes,⁹ enynols¹⁰ and chalcogenophenes¹⁰ is well documented in the literature.

On the other hand, the development of environmentally benign and clean synthetic methods, including those involving solvent-free or alternative solvents, such as water, ionic liquids (ILs) and glycerol, has increased in the last years and is the main topic of many books and reviews.¹¹ Alternatively, the use of polyethylene glycol (PEG) has been shown as promising medium for organic reactions that suppresses some drawbacks of conventional solvents,¹² and its application was previously described by our group¹² and others.¹³ Furthermore, compared to the use of other hydroxylated solvents, such as ethanol or glycerol, better results have been obtained in the synthesis of vinyl chalcogenides using PEG-400.¹⁴,¹⁵

In this sense, we describe herein our results on the hydrochalcogenation of 1,4-diorganyl-1,3-butadiynes 1 under mild reaction conditions using diaryl dichalcogenides 2 and PEG-400 as solvent (Scheme 1). The selective product formation 3 or 4 was obtained by a simple temperature
controlled reaction. When the reaction was carried out at 30 °C, using conventional heating or microwave (MW) irradiation as the heating source, the mono-hydrochalcogenated product 3 was obtained. In contrast, at 90 °C the uncommon 1,4-bis-chalcogenbutadiene 4 was isolated.

Results and Discussion

Initially, we chose 1,4-diphenyl-1,3-butadiyne 1a (0.4 mmol) and diphenyl diselenide 2a (0.2 mmol) as standard materials to optimize reaction conditions for the synthesis of (Z)-chalcogenoynes 3a using PEG-400 as solvent and NaBH₄ as reducing agent under N₂ atmosphere. The influence of solvent, temperature, stoichiometry and two different heating sources, the conventional oil bath and the focused microwave irradiation, were examined and the results are presented in Table 1.

Table 1. Investigation of the best conditions for synthesis of 3a

<table>
<thead>
<tr>
<th>entry</th>
<th>2a / eq</th>
<th>Solvent</th>
<th>Temperature / °C</th>
<th>time / h</th>
<th>Yield / %</th>
<th>3a:4a ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>PEG-400</td>
<td>r.t.</td>
<td>96</td>
<td>44</td>
<td>100:0</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>PEG-400</td>
<td>30</td>
<td>24</td>
<td>72</td>
<td>100:0</td>
</tr>
<tr>
<td>3</td>
<td>1.0</td>
<td>PEG-400</td>
<td>30</td>
<td>24</td>
<td>81</td>
<td>100:0</td>
</tr>
<tr>
<td>4</td>
<td>1.0</td>
<td>PEG-400</td>
<td>60</td>
<td>24</td>
<td>78 c</td>
<td>56:44</td>
</tr>
<tr>
<td>5</td>
<td>1.0</td>
<td>PEG-400</td>
<td>90</td>
<td>6</td>
<td>51 c</td>
<td>7:93</td>
</tr>
<tr>
<td>6</td>
<td>1.0</td>
<td>glycerol</td>
<td>90</td>
<td>12</td>
<td>n.r.</td>
<td>–</td>
</tr>
<tr>
<td>7</td>
<td>1.0</td>
<td>PEG-400</td>
<td>30 (MW)</td>
<td>1.25</td>
<td>95</td>
<td>100:0</td>
</tr>
<tr>
<td>8</td>
<td>1.0</td>
<td>PEG-400</td>
<td>90 (MW)</td>
<td>0.5</td>
<td>69</td>
<td>0:100</td>
</tr>
</tbody>
</table>

a The reactions were performed using 1a (0.4 mmol), NaBH₄ (2 eq to 2a) and solvent (3.0 mL) under N₂ atmosphere; b determined by ¹H nuclear magnetic resonance (NMR); c yield is given for the mixture 3a + 4a. PEG: polyethylene glycol; r.t.: room temperature; n.r.: no reaction; MW: microwave.
Relying on this result, we performed the reaction at a higher temperature expecting to increase the formation of the product 4a (Table 1, entry 5). Thus, the reaction was carried out at 90 °C using 1.0 eq of the dichalcogenide 2a in PEG-400 as solvent and the compound 4a was obtained preferentially in 51% yield after 6 h.

Ethanol is the traditional solvent employed in hydrochalcogenation reactions, however, our recent findings have demonstrated the satisfactory use of glycerol as an alternative. Based on this, glycerol was also tested as solvent, but no products were detected (Table 1, entry 6).

In order to obtain an efficient protocol in terms of energy economy, we chose to perform the reaction under microwave irradiation. Thus, reacting the buta-1,3-diyne 1a with the diphenyl diselenide 2a at 30 °C for 75 min, resulted in all starting materials being completely consumed and the desired product 3a was obtained in excellent yield and selectivity (Table 1, entry 7). When the reaction was performed at 90 °C under microwave irradiation, the product 4a was detected after only 0.5 h in 69% yield without the formation of 3a as byproduct (Table 1, entry 8).

With the optimized reaction conditions for the synthesis of the organochalcogenenoyn 3 in hand, using conventional heating (method A) (Table 1, entry 3) or microwave irradiation (method B) (Table 1, entry 7), we envisioned extending these protocols to different diaryl dichalcogenides 2a-e and diynes 1a-b at 30 °C (Table 2). In regards to product stereochemistry, the formation of (Z)-enyne was preferential for all the tested examples, which complies with the literature. Thus, (Z)-3a was obtained exclusively for the reaction of 1,4-diphenyl-1,3-butadiyne 1a with diphenyl diselenide 2a and in excellent yields (Table 2, entry 1). When diphenyl disulfide 2b was tested, a similar stereoselectivity was observed and the (Z)-thioyn 3b was obtained in 82% yield after 24 h (Table 2, entry 2). The alternative MW irradiation also gave the corresponding product 3b in 96% after 75 min. Diphenyl ditelluride 2c was also used as the starting material to react with the 1,3-butadiyne 1a and furnished the corresponding 1-phenyltelluro-1-en-3-yne 3c preferentially in (Z)-configuration (Table 2, entry 3). In order to increase the screening of (Z)-enyn compounds, we next turned our attention to reactions of 2,7-dimethylocta-3,5-diyne-2,7-diol 1b with the diaryl dichalcogenides 2a-c (Table 2, entries 4-6). A closer inspection shows that the (Z)-configuration was obtained for all formed products 3d-f rather than (E). Furthermore, the products were obtained in good to excellent yields for both methods A and B, while the reaction times required for method B, MW irradiation, were much shorter. Interestingly, when 1b was reacted with dibutyl diselenide 2d, the expected (Z)-butylselenenoyn 3g was obtained in 97% yield after 6 h (Table 2, entry 7). Under microwave irradiation, the reaction time reduced to 10 min and 3g was isolated in 98% yield.

Attracted by promising results in our recent studies regarding of glycerol derivatives, we investigated the possibility of using the diselenium glycerol derivative 2e in the presence of diyne 1a (Table 2, entry 8). The reaction proceeds smoothly, furnishing the unprecedented product 3h in 77% yield after 24 h. The use of microwave irradiation was also satisfactorily employed to generate the product 3h, which was obtained in an almost quantitative yield after 10 min.

The use of chalcogen-substituted dienes as reagents for the construction of more complex structures is well documented in literature. On this basis of this and the results shown in entries 5 and 8 in Table 1, we undertook a systematic study to generate a series of (Z,Z)-1,4-bis-chalcogenbuta-1,3-dienes 4 employing 1,4-diphenyl-1,3-butadiyne 1a or 2,7-dimethylocta-3,5-diyne-2,7-diol 1b and different diorganyl dichalcogenides 2a-d (Table 3). When the 1,3-butadiyne 1a was reacted with the diphenyl diselenide 2a at 90 °C, the 1,4-bis-phenylseleno-1,3-diene 4a was obtained in 51% yield under conventional heating after 24 h. However, using MW irradiation allowed a yield increase to 69% and a reaction time decrease to 30 min. It is important to mention that the (Z,Z)-configuration was obtained for both heating methods (Table 3, entry 1). Similarly, the synthesis of (Z,Z)-1,4-bis-phenyltellurobuta-1,3-diene 4b is also demonstrated in entry 2. In this case, the diphenyl disulfide 2b was employed, giving the corresponding diene 4b in 65 and 69% yield for methods A and B, respectively, at 90 °C. Using the dibutyl diselenide 2d in the presence of 1a, the desired product 4e was obtained in 71% yield using conventional oil bath and 64% yield by microwave irradiation even at 30 °C (Table 3, entry 3). We believe that the more pronounced nucleophilicity of the dibutyl diselenide 2d relative to diphenyl diselenide 2a contributed to the good yield of 4e, which was also observed for 3g. When the 2,7-dimethylocta-3,5-diyne-2,7-diol 1b was reacted with diphenyl diselenide 2a, the product 4d was isolated in 69 and 73% yield by the method A and B, respectively (Table 3, entry 4). Finally, the diyne 1a and the diphenyl ditelluride 2c were employed to react under the same reaction conditions (Table 3, entry 5). However, the product (Z,Z)-1,4-bis-phenyltellurobuta-1,3-diene 4e was not observed. Instead, a complex mixture of compounds was obtained.

At the same time we were preparing our manuscript, Venkateswarlu and Chandrasekaran reported the mono- or bis-chalcogenation of buta-1,3-diynes using rongalite and potassium carbonate in N,N-dimethylformamide (DMF):H2O as solvent. Despite a satisfactory procedure to produce (Z)-
Table 2. Synthesis of chalcogenoynes 3a-h using NaBH₄ and PEG-400 at 30 °C

| entry | Diyne 1 | Diaryl dichalcogenide 2 | Product 3 | Yield / % (method)  
<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1a</td>
<td>(C₆H₅Se)₂</td>
<td>3a</td>
<td>81 (A) 95 (B)</td>
</tr>
<tr>
<td>2</td>
<td>1a</td>
<td>(C₆H₅S)₂</td>
<td>3b</td>
<td>82 (A) 96 (B)</td>
</tr>
<tr>
<td>3</td>
<td>1a</td>
<td>(C₆H₅Te)₂</td>
<td>3c</td>
<td>61 (A) 77 (B)</td>
</tr>
<tr>
<td>4</td>
<td>1b</td>
<td>2a</td>
<td>3d</td>
<td>70 (A) 69 (B)</td>
</tr>
<tr>
<td>5</td>
<td>1b</td>
<td>2b</td>
<td>3e</td>
<td>99 (A) 81 (B)</td>
</tr>
<tr>
<td>6</td>
<td>1b</td>
<td>2c</td>
<td>3f</td>
<td>97 (A) 98 (B)</td>
</tr>
<tr>
<td>7</td>
<td>1b</td>
<td>(C₄H₉Se)₂</td>
<td>3g</td>
<td>97 (A) 98 (B)</td>
</tr>
<tr>
<td>8</td>
<td>1a</td>
<td>(C₄H₉Se)₂</td>
<td>3h</td>
<td>77 (A) 98 (B)</td>
</tr>
</tbody>
</table>

The reactions were performed using diyne 1 (0.4 mmol), diaryl dichalcogenide 2 (0.4 mmol), NaBH₄ (0.8 mmol) and PEG-400 (3.0 mL) under N₂; method A: conventional heating at 30 °C during 24 h; method B: MW irradiation at 30 °C during 1.25 h; ratio of Z:E isomers determined by gas chromatography-mass spectrometry (GC-MS): 93:7; reaction time: 2 h; reaction time: 6 h; reaction time: 10 min.
Selective Synthesis of \((Z)\)-Chalcogenoenynes and \((Z,Z)\)-1,4-bis-Chalcogenbuta-1,3-dienes


Chalcogenenynes, lower reaction yields and poor selectivity were observed when buta-1,3-dienes were synthesized. In contrast, we developed an efficient and selective method to synthesize \((Z,Z)\)-1,4-bis-organylchalcogen-1,3-dienes 4 in good yields using conventional heating or microwave irradiation to promote the reaction in an environmentally benign solvent.

**Conclusions**

We developed an alternative and stereoselective method for the hydrochalcogenation of conjugated 1,3-butadiynes under mild reaction conditions using PEG-400 as solvent. This study is relevant because under similar reaction conditions, by choosing the temperature, a selective product formation can be controlled. At 30 °C the \((Z)\)-chalcogenenynes are obtained and increasing the temperature to 90 °C the \((Z,Z)\)-1,4-bis-chalcogen-1,3-butadienes are produced in good to excellent yields. Alternatively to the conventional method using oil bath heating, the results for the use of microwave irradiation under the same reaction conditions are also presented as an alternative heating source that provide the expected products in few minutes. In general, aliphatic dichalcogenides

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Table 3. Synthesis of bis-chalcogen-1,3-butadienes 4a-d using NaBH₄ and PEG-400

<table>
<thead>
<tr>
<th>entry</th>
<th>((ArY)), 2</th>
<th>Temperature / °C</th>
<th>Products 4</th>
<th>Yield / % (method)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>((C₆H₅Se)₂) 2a</td>
<td>90</td>
<td>4a</td>
<td>51 (A) 69 (B)</td>
</tr>
<tr>
<td>2</td>
<td>((C₆H₅S)₂) 2b</td>
<td>90</td>
<td>4b</td>
<td>65 (A) 69 (B)</td>
</tr>
<tr>
<td>3</td>
<td>((C₄H₉Se)₂) 2d</td>
<td>30</td>
<td>4c</td>
<td>71 (A) 64 (B)</td>
</tr>
<tr>
<td>4</td>
<td>2a</td>
<td>90</td>
<td>4d</td>
<td>69 (A) 73 (B)</td>
</tr>
<tr>
<td>5</td>
<td>2c</td>
<td>90</td>
<td>4e</td>
<td>–</td>
</tr>
</tbody>
</table>

*The reactions were performed using the diyne 1a (0.4 mmol), diaryl dichalcogenide 2 (0.4 mmol), NaBH₄ (0.8 mmol) and PEG-400 (3.0 mL) under N₂; method A: conventional heating during 6 h; method B: MW irradiation during 30 min; \(^3\)\(^-\)\(^5\)% of the corresponding \((Z)\)-enyne was isolated; \(^4\)the reaction was performed using the 2,7-dimethyl-octa-3,5-diyne-2,7-diol 1b.*
were more reactive than acrylic chalcogenides, specially dibutyl diselenide due to high nucleophilicity, and the corresponding enynes and dienes were obtained in higher yields. The use of PEG as a non-toxic solvent opens new possibilities for future applications of this in green and sustainable chemistry.

**Experimental**

**Materials and methods**

Proton nuclear magnetic resonance (\(^1\)H NMR) spectra were obtained at 300 MHz on Varian Inova 300 and at 400 MHz on Bruker DPX spectrometers. Spectra were recorded in CDCl\(_3\) solutions. Chemical shifts are reported in ppm, referenced to tetramethylsilane (TMS) as the external reference. Data are reported as follows: chemical shift (\(\delta\)), multiplicity, integrated intensity and coupling constant (\(J\)) in Hz. \(^{13}\)C NMR spectra were obtained at 75 MHz on Varian Inova 300 and at 100 MHz on Bruker DPX spectrometers. Spectra were recorded in CDCl\(_3\) solutions. Chemical shifts are reported in ppm, referenced to the solvent peak of CDCl\(_3\). Low-resolution mass spectra (MS) were obtained with a Shimadzu gas chromatograph-mass spectrometer (GC-MS)-QP2010. High-resolution MS (HRMS) were obtained on an LTQ Orbitrap Discovery mass spectrometer (Thermo Fisher Scientific). This hybrid system has a LTQ XL linear ion trap mass spectrometer and an Orbitrap mass analyzer. The experiments were performed via direct infusion (DI) of sample (flow: 10 \(\mu\)L min\(^{-1}\)) in the positive-ion mode using electrospray ionization (ESI). Elemental composition calculations for comparison were executed using the specific tool included in the Qual Browser module of Xcalibur (Thermo Fisher Scientific, release 2.0.7) software. Column chromatography was performed using Merck silica gel (230-400 mesh). Thin layer chromatography (TLC) was performed using DC-Fertigfolien ALUGRAM\textsuperscript{Xtra} SIL G/UV\(_{254}\), 0.20 mm thickness. For visualization, TLC plates were immersed in a solution of 25% \(\text{H}_{2}\text{SO}_{4}\) in 95% ethanol, followed by heating for 10 min at 100 °C. The plates were then visualized under UV light (254 nm).

**General procedure for the synthesis of (Z)-chalcogenoeynes 3a-h**

Method A: to a mixture of diyne 1 (0.4 mmol) and diphenyl dichalcogenide 2 (0.4 mmol) in PEG-400 (3.0 mL) under \(N\)\(_2\) atmosphere, NaBH\(_4\) (0.8 mmol) was added at room temperature under stirring. Then, the mixture was heated slowly to 30 °C and the reaction progress was followed by TLC. After 24 h, water (3.0 mL) was added and the mixture was extracted with ethyl acetate (3 × 5.0 mL). The organic layers were combined, washed with brine solution (3.0 mL) and dried with MgSO\(_4\). The solvent was removed under vacuum and the product was isolated by column chromatography using hexane/ethyl acetate as eluent.

Method B: in a 10 mL glass vial equipped with a small magnetic stirring bar, containing a solution of diyne 1 (0.4 mmol) and diphenyl dichalcogenide 2 (0.4 mmol) in PEG-400 (2.0 mL) under \(N\)\(_2\) atmosphere, NaBH\(_4\) (0.8 mmol) was added at room temperature. The mixture was then irradiated in a focused microwaves reactor (CEM) at 30 °C, using an irradiation maximum power of 50 W. After stirring for 10-120 min the products were isolated as described above for method A. All the compounds were characterized and spectral data are listed below.

(Z)-1-Phenylselanyl-1,4-diphenylbut-1-en-3-yne (3a)

\begin{align*}
\text{Yield: } &0.117 \text{ g (81%, method A), 0.136 \text{ g (95%, method B); yellow solid; m.p.} \\
&67-70 ^\circ\text{C; } ^1\text{H NMR} \ (400 \text{ MHz, CDCl}_3) \ \delta \ 7.41-7.46 \ (m, 4H), 7.31-7.34 \ (m, 2H), \\
&7.27-7.29 \ (m, 3H), 7.15-7.16 \ (m, 3H), 7.05-7.06 \ (m, 3H), \\
&6.40 \ (s, 1H); ^{13}\text{C NMR} \ (100 \text{ MHz, CDCl}_3) \ \delta \ 147.1, 139.5, \\
&133.1, 131.5, 130.0, 128.7, 123.8, 123.3, 128.2, 128.1, 126.9, 123.3, 112.7, 97.7, 88.3; \text{MS 360 ([M]+, 18.9),} \\
&279 (23.0), 202 (100.0), 77 (12.6).}
\end{align*}

(Z)-1-Phenythio-1,4-diphenylbut-1-en-3-yne (3b)

\begin{align*}
\text{Yield: } &0.102 \text{ g (82%, method A), 0.120 \text{ g (96%, method B); yellow solid; m.p.} \\
&94-95 ^\circ\text{C; } ^1\text{H NMR} \ (400 \text{ MHz, CDCl}_3) \ \delta \ 7.50-7.53 \ (m, 2H), 7.43-7.46 \ (m, 2H), \\
&7.27-7.29 \ (m, 3H), 7.19-7.24 \ (m, 4H), 7.03-7.15 \ (m, 4H), \\
&6.32 \ (s, 1H); ^{13}\text{C NMR} \ (100 \text{ MHz, CDCl}_3) \ \delta \ 147.1, 138.2, \\
&134.4, 131.5, 130.3, 128.6, 128.3, 128.2, 127.9, 126.3, 123.2, 112.2, 98.3, 87.6; \text{MS 312 ([M]+, 93.7),} \\
&279 (12.1), 202 (100.0), 77 (13.7); \text{ESI-HRMS calcd. for C}_{22}\text{H}_{16}\text{S [M+H]}^+: 313.1051; \text{found: 313.1025.}
\end{align*}

(Z)-1-Phenyttellanyl-1,4-diphenylbut-1-en-3-yne (3c)

\begin{align*}
\text{Yield: } &0.100 \text{ g (61%, method A), 0.126 \text{ g (77%, method B); dark yellow solid; m.p.} \\
&62-66 ^\circ\text{C; } ^1\text{H NMR} \ (400 \text{ MHz, CDCl}_3) \ \delta \ 7.50-7.52 \ (m, 4H), 7.26-7.33 \ (m, 5H), \\
&7.09-7.13 \ (m, 4H), 6.97-7.01 \ (m, 2H), 6.46 \ (s, 1H); ^{13}\text{C NMR} \ (100 \text{ MHz, CDCl}_3) \ \delta \ 141.3, 139.3, 139.0, 131.4, \\
&128.9, 128.6, 128.4, 128.3, 127.8, 127.0, 123.1, 116.1, 114.7, 97.3, 90.1; \text{MS 410 ([M]+, 15.4),} \\
&279 (17.6), 202 (100.0), 77 (13.7); \text{ESI-HRMS calcd. for C}_{22}\text{H}_{16}\text{Te [M+H]}^+: 411.0392; \text{found: 411.0369.}
\end{align*}
Selectivc Synthesis of (Z)-Chalcogenoynes and (ZZ)-1,4-bis-Chalcogenbuta-1,3-dienes


Selective Synthesis of (Z)-Chalcogenoynes and (ZZ)-1,4-bis-Chalcogenbuta-1,3-dienes


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(3Z,5Z)-2,7-Dimethyl-3,6-bis(phenylselanyl)-octa-3,5-diene-2,7-diol (4d) \(^{17}\)

Yield: 0.133 g (69%, method A), 0.141 g (73%, method B); yellow solid; m.p. 147-150 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\) \(\delta\) 7.28-7.30 (m, 4H), 7.18-7.25 (m, 6H), 7.02 (s, 2H), 2.12 (br s, 2H), 1.29 (s, 12H); \(^13\)C NMR (100 MHz, CDCl\(_3\) \(\delta\) 147.6, 132.4, 131.8, 130.5, 129.1, 126.4, 74.6, 29.1; MS 464 ([M – 18]\(^+\), 1.1), 325 (21.7), 249 (34.1), 59 (100.0), 43 (77.7).

**Supplementary Information**

Supplementary data are available free of charge at http://jbcs.sbq.org.br as PDF file.

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**References**

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2054


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