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SYNTHESIS OF SPIROACETALS USING FUNCTIONALIZED TITANIUM CARBENOIDS

\[ \text{R}^1\begin{array}{c} \text{O} \\ \text{n} \end{array} \rightarrow \text{R}^1\begin{array}{c} \text{O} \\ \text{n} \end{array} \]

(i) \[ \text{TMSO} \quad \text{Cp}_2\text{Ti} \quad \text{Cl} \]

(ii) conc. HCl(aq)-MeOH (1:9)
Synthesis of Spiroacetals using Functionalized Titanium Carbenoids

Calver A. Main, a Shahzad S. Rahman b and Richard C. Hartley a

a WestChem, Department of Chemistry, The Joseph Black Building, University of Glasgow, Glasgow G12 8QQ, UK. b GlaxoSmithKline, New Frontiers Science Park, Third Avenue, Harlow, Essex, CM19 5AW, UK.

Abstract - Alkylidenation of lactones with functionalized titanium carbenoid reagents (Schrock carbenes) followed by acid-induced cyclization of the resulting enol ethers constitutes a new method for the preparation of [4,4], [4,5] and [5,5] spiroacetals (1,6-dioxaspiro[4.4]nonanes, 1,6-dioxaspiro[4.5]decanes and 1,7-dioxaspiro[5.5]undecanes, respectively, sometimes termed 5,5-, 5,6- and 6,6-spiroketalss). The titanium carbenoids are easily generated from readily available thioacetals.

Spiroacetals have attracted a great deal of interest as synthetic targets as they are found widely in Nature and have a range of biological activities.1,2 We envisaged synthesizing such compounds 4 by the alkylidenation of lactones 1 using titanium carbenoids 2 bearing a masked hydroxyl group, followed by cyclisation of the resulting exocyclic enol ethers 3 in acid (Scheme 1).

Scheme 1

Exocyclic enol ethers have been used to prepare spiroacetals by cycloadditions,3-8 or through acid-induced cyclisation of alcohols.9-13 Such enol ethers have been prepared by cyclisation of alcohols onto alkynes bearing an electron-withdrawing group,12 by E2 elimination of hemiacetal derivatives8,14 or β-alkoxyalkyl iodides,4 by

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Corresponding author. Tel: +44 141-330-4398; Fax: +44 141-330-4888; email: richh@chem.gla.ac.uk
Ramberg-Bäcklund rearrangement,\textsuperscript{9} by Wittig reaction between exocyclic \(\alpha\)-alkoxyphosphorus ylides and aldehydes,\textsuperscript{10-12} and by methylenation of lactones\textsuperscript{5-7} using the Tebbe reagent,\textsuperscript{15} Petasis methylation\textsuperscript{16} or Yan's CH\(_2\)Cl\(_2\)-Mg-TiCl\(_4\) reagent system.\textsuperscript{17} The last two methods are particularly relevant to our work as they use titanium carbenoids,\textsuperscript{18} but the titanium reagents employed only introduced a methylene unit. In their pioneering work, Mortimore and Kocienski used titanium carbenoids bearing THP-protected alcohols to alkylidenate acyclic esters and then induced cyclisation to spiroacetals in acid.\textsuperscript{19} However, the titanium carbenoids were prepared from 1,1-dibromoalkanes,\textsuperscript{20} which were at the time synthetically difficult to access,\textsuperscript{21} and alkylidation of lactones was reported to be slow and low yielding. Lactones are attractive starting materials, as they are straightforward to prepare by ring-closing metathesis,\textsuperscript{22} Baeyer-Villiger oxidation of cyclic ketones\textsuperscript{23} and by oxidation of sugars,\textsuperscript{24} as well as by methods which would be appropriate for preparation of acyclic esters.

We have previously shown that using Takeda's procedure,\textsuperscript{25} a range of functionalized titanium carbenoids\textsuperscript{18} can be generated from easily prepared thioacetals. We had used titanium carbenoids bearing masked oxygen nucleophiles,\textsuperscript{26,27} but exclusively for solid-phase synthesis and never to prepare spiroacetals. As in this earlier work,\textsuperscript{26} dithiane 6, was synthesized in two steps from 2-hydroxybenzaldehyde, and converted into a titanium carbenoid, presumably titanium benzylidene 7, using low valent titanium reagent 5 (Scheme 2). Similarly, new titanium alkylidenes 9 and 11 were prepared from dithiane 8 and thioacetal 10, respectively (Schemes 2 and 3). Titanium reagents 7, 9 and 11 (1.2 or 3 eq.) were then used to alkylidenate a range of lactones 12-19 (Figure 1) in dry THF overnight to give enol ethers, which were immediately treated with 10% HCl-MeOH for 1.5-2 h to form spiroacetals 20-31 (Figure 2).\textsuperscript{28,29} The results are summarised in Table 1.

\textbf{Scheme 2}

\textbf{Scheme 3}

\(\gamma\)-Lactones 12-14 were converted effectively into [4,4] spiroacetals 20-23 using titanium benzylidenes 7 and 9 (entries 1-4). The transformation tolerates steric well,
with quaternary centres both $\alpha$ to the carbonyl group and $\alpha$ to the endocyclic oxygen atom presenting no difficulty (entries 1-3). The low diastereoselectivities observed in the formation of spiroacetals 22 and 23 under thermodynamic control are consistent with those reported for similar compounds in the literature.$^{1,30}$ [4.5] Spiroacetals 24 and 25 were also isolated with low diastereoselectivity when (+)-sclareolide 13 and $\gamma$-lactone 14 were treated with titanium alkylidene 11 followed by acid (entries 5 and 6). The transformation of sterically-hindered $\gamma$-lactone 12 into [4.5] spiroacetal 26 proceeded well (entry 7). Alternatively, [4.5] spiroacetals could be accessed from $\delta$-lactones (entries 8 and 9). Mixtures of anomeric spiroacetals were obtained from glucose-derived lactone 15 and from $\delta$-lactone 16: the structures 27 and 28 were presumably the major isomers as they are stabilized by the anomeric effect. The moderate diastereoselectivities agree with those in the literature for [4.5] spiroacetals, including glucose-derived [4.5] spiroacetals,$^{8,9}$ produced in acid.$^{31}$ [5.5] Spiroacetals 29 and 30 were prepared from dihydrocoumarin 17 and coumarin 18, respectively, by the same method (entries 10 and 11). Clearly an $\alpha,\beta$-unsaturated lactone presented no problem. However, $\varepsilon$-lactone 19 gave the benzofuran 31 rather than a [5.6] spiroacetal (entry 12).

The modest yields when using 1.2 eq. of the titanium alkylidenes 7, 9 and 11, were improved upon by using 3 eq., but the large quantity of triethylphosphite used under the latter conditions (12 eq.) hampered purification by chromatography. However, washing the crude spiroacetals with excess saturated aqueous iron(III) chloride prior to chromatography removed the triethylphosphite and expedited purification.

Figure 1
<table>
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<tr>
<th>Entry</th>
<th>Lactone</th>
<th>Titanium reagent</th>
<th>Spiroacetal</th>
<th>% Isolated yield using 1.2 eq. of titanium reagent</th>
<th>% Isolated yield using 3 eq. of titanium reagent</th>
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*Isolated yield of major diastereomer

Figure 2

In conclusion, we have developed a concise two-step method for the conversion of γ and δ-lactones into spiroacetals.
Acknowledgements
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References

28. General procedure: Cp₂TiCl₃ (1.84 g, 7.4 mmol, 4.1 eq.), Mg (210 mg, 4.9 eq., predried at 250 °C overnight) and freshly activated 4 Å molecular sieves (0.5 g) were heated, gently, under reduced pressure (0.3 mmHg) for about 1 min and then placed under argon. Dry THF (5 mL) was added followed by dry P(OEt)₃ (2.5 mL, 8.2 eq.). After stirring for 3 h at RT, a solution of thioacetal 7, 9 or 11 (2.2 mmol, 1.2 eq.) in dry THF (2 mL) was added and stirring continued for 15 min. A solution of one of the lactones 12-19 (1.8 mmol, 1 eq.) in dry THF (2 mL) was added, and the resulting mixture stirred overnight at RT. Aqueous NaOH (1 M, 40 mL) was added and the resulting suspension filtered through celite, washing through with diethyl ether. The mixture was extracted with ether, the combined organics were dried over K₂CO₃ and the solvent removed under reduced pressure to give the crude enol ether. 10% HCl-MeOH solution (1 mL concentrated aqueous HCl, 9 mL of MeOH) was added and the mixture stirred at RT for 1.5-2 h, before pouring into aqueous HCl (1 M) and extracting into dichloromethane. The combined organics were dried over MgSO₄ and the solvent removed under reduced pressure and the mixture separated by column chromatography on silica to give the corresponding spiroacetal 20-31. When 3 eq. of the titanium reagent was used, a dichloromethane solution of the crude spiroacetal was washed with 100 mL of saturated aqueous iron(III) chloride per gramme of crude material prior to column chromatography.

29. Spectral data for spiroacetals: (a) 20: solid, mp: 142 °C (MeOH). ν_max (Golden gate)/cm⁻¹: 1480, 1461, 1598, 2899. δ_H (400 MHz, CDCl₃): 2.70 (1H, ddd, J 3.1 Hz, 7.8 Hz and 12.3 Hz), 3.17 (1H, d, J 17.4 Hz), 3.25 (1H, ddd, J 8.5 Hz, 9.9 Hz and 12.3 Hz), 3.57 (1H, d, J 17.4 Hz), 4.22 (1H, apparent q, J 8.2 Hz), 4.35 (1H, ddd, J 3.1 Hz, 8.6 Hz and 9.9 Hz), 6.61 (1H, d, J 8.0 Hz), 6.81 (1H, dt, J 0.7 and 7.5 Hz), 7.03 (1H, t, J 7.5 Hz), 7.10 (1H, d, J 7.3 Hz, H-7), 7.13-7.29 (10H, m, Ar-H). δ_C (100 MHz, CDCl₃): 37.32 (CH₂), 38.39 (CH₂), 61.36 (C), 65.42 (CH₂), 109.59 (CH), 119.99 (C), 120.48 (CH), 124.43 (CH), 125.38 (C), 126.37 (CH), 126.56 (CH), 127.91 (CH), 128.00 (CH), 128.32 (CH), 128.40 (CH), 143.25 (C), 145.47 (C), 157.52 (C). m/z, (El⁺): 328 (M⁺, 6 %), 194 (100). HRMS: 328.1463. C₂₃H₂₉O₂ requires 328.1465. (b) 21: solid, mp: 138 °C. R₆ [SiO₂, Pet.Ether-DCM (4:1)]: 0.19. ν_max (Golden gate)/cm⁻¹: 1445, 1596, 1609, 2889, 2985. δ_H (400 MHz, CDCl₃): 2.65 (1H, ddd, J 2.9 Hz, 7.6 Hz and 12.1 Hz), 3.16 (1H, d, J 17.7 Hz), 3.25 (1H, ddd, J 8.7 Hz, 9.9 Hz and 12.2 Hz), 3.55 (1H, d, J 17.7 Hz), 4.21 (1H, apparent q, J 8.3 Hz), 4.35 (1H, ddd, J 2.9 Hz, 8.6 Hz and 9.9 Hz), 6.59 (1H, d, J 2.1 Hz), 6.79 (1H, dd, J 2.1 and 8.0 Hz), 7.00 (1H, d, J 8.0 Hz), 7.10-7.14 (4H,
m), 7.18-7.27 (6H, m). δC (100 MHz, CDCl3): 36.59 (CH3), 37.97 (CH3), 61.39 (C), 65.54 (CH3), 110.16 (CH), 120.44 (CH), 120.98 (C), 124.01 (C), 124.80 (CH), 126.42 (CH), 126.53 (CH), 127.86 (CH), 127.94 (CH), 128.07 (CH), 128.21 (CH), 133.11 (C), 142.70 (C), 144.96 (C), 158.10 (C). m/z, (Cl+): 363 [(M+H)+ (35Cl), 97 %], 211 (100). HRMS: 363.1152 and 365.1132. C23H23O235Cl requires (M+H)+ 363.1151, and C23H23O237Cl requires (M+H)+ 365.1122. (c) 22 (mixture of epimers A and B), solid. vmax

(Golden Gate)cm⁻¹: 1479, 1610, 2866, 2925. δH (400 MHz, CDCl3): 0.84 (3H, d, s), 0.88 (6H, s, s), 0.91 (3H, s), 1.20 (3H, s), 1.35 (3H, s), 0.99-2.12 (13H, m), 2.21 (1H, dd, J 3.4 and 10.1 Hz), 2.45 (1H, d, J 12.8 and 14.1 Hz), 3.20 (2H, s), 3.23 (2H, s), 6.76-6.82 (2H, m), 7.00-7.05 (1H, m). δC (100 MHz, CDCl3): δ 12.81 (CH3), 13.13 (CH3), 15.95 (CH3), 15.98 (CH3), 18.13 (CH3), 18.49 (CH3), 18.64 (CH3), 18.69 (CH3), 20.29 (CH3), 20.59 (CH3), 27.35 (CH3), 31.11 (CH3), 33.43 (CH3), 33.98 (CH3), 37.44 (CH3), 37.59 (CH3), 37.73 (CH3), 39.10 (CH2), 40.02 (CH2), 40.05 (CH2), 40.39 (CH2), 54.40 (CH), 54.70 (CH), 56.35 (CH), 58.77 (CH), 81.91 (C), 82.33 (C), 107.73 (CH), 107.77 (CH), 115.70 (C), 116.73 (C), 118.08 (CH), 122.07 (C), 122.26 (C), 122.63 (CH), 122.68 (CH), 130.75 (C), 130.79 (C), 155.97 (C), 156.49 (C). m/z (EI+): 374 [M+ (35Cl), 78%], 191 (100). HRMS: 374.2013 and 376.1993. C23H31O235Cl requires 374.2018, and C23H31O237Cl requires 376.1899. (d) 23 (50:50 mixture of diastereomers A and B), oil. Rf [SiO2, Pet.Ether-DCM (1:1)]: 0.76. vmax

(Golden Gate)cm⁻¹: 1451, 1594, 1609, 2915, 2950. δH (400 MHz, CDCl3): 2.01 (1H, d, dd, J 4.4 and 5.8 Hz, 9.7 and 12.4 Hz), 2.21-2.29 (3H, s), 2.44-2.53 (3H, s, s), 2.66 (1H, dd, J 8.3 and 12.4 Hz), 3.29 (1H, d, J 16.7 Hz), 3.34 (1H, d, J 16.7 Hz), 3.36 (1H, d, J 16.6 Hz), 3.45 (1H, d, J 16.6 Hz), 5.16-5.22 (1H, s, s), 5.34 (1H, d, J 5.9 and 7.8 Hz), 6.80-6.86 (2H, m), 7.05-7.09 (1H, m), 7.24-7.44 (5H, m, ArH). δC (100 MHz, CDCl3): 32.28 (CH2), 33.75 (CH2), 35.60 (CH2), 37.62 (CH2), 37.77 (CH2), 37.88 (CH2), 80.61 (CH), 83.07 (CH), 109.58 (CH), 109.72 (CH), 118.73 (C), 119.93 (C), 120.04 (CH), 123.94 (C), 123.96 (C), 124.51 (CH), 125.05 (CH), 125.36 (CH), 125.57 (CH), 126.97 (CH), 127.13 (CH), 127.83 (2CH), 132.68 (C), 141.41 (C), 141.79 (C), 157.97 (C), 158.06 (C). m/z (Cl+): 287 [(M+H)+ (35Cl), 100%]. HRMS: 287.0839 and 289.0815. C17H16O235Cl requires (M+H)+ 287.0838, and C17H16O237Cl requires (M+H)+ 289.0816. (e) 24 (major diastereomer), solid. mp: 116 °C (MeOH). [α]D2 + 49.1 (c = 0.1 M, DCM). vmax (Golden Gate)cm⁻¹: 2931. δH (400 MHz, CDCl3): 0.78 (3H, s), 0.84 (3H, s), 0.86 (3H, s), 0.89-0.95 (2H, m), 1.05-1.12 (1H, m), 1.21 (3H, s), 1.21-1.77 (16H, m), 1.87(1H, td, J 3.2 Hz and 11.3
Hz), 3.56 (1H, broad d, J 11.6 Hz), 3.89 (1H, dt, J 3.1 Hz and 11.3 Hz). δc (100 MHz, CDCl₃): 15.18 (CH₃), 18.37 (CH₃), 19.62 (CH₃), 20.53 (CH₃), 21.08 (CH₃), 23.07 (CH₃), 25.30 (CH₃), 33.11 (C), 33.53 (CH₃), 36.02 (C), 36.89 (CH₃), 37.05 (CH₃), 39.75 (CH₃), 40.40 (CH₃), 42.50 (CH₃), 57.10 (CH), 60.24 (CH), 62.74 (CH₂), 82.31 (C), 106.04 (C). m/z (EI⁺): 306 (M⁺, 13%), 291 (M⁺ – CH₃, 37), 111 (100). HRMS: 306.2559. C₂₀H₂₄O₂ requires 306.2562. (f) 25 (63:37 mixture of diastereomers A and B), oil. Rᵣ [SiO₂, 100% DCM]: 0.26. νmax (Golden Gate)/cm⁻¹: 1461, 2894. δh (400 MHz, CDCl₃): 1.42-2.09 (9Hₐ₋ₖ, m), 2.10-2.18 (1H, m), 2.33-2.42 (1H, m), 3.55-3.60 (1H, m), 3.60-3.65 (1H, m), 3.81 (1H, dt, J 2.9 Hz and 11.3 Hz), 3.89 (1H, dt, J 2.9 Hz and 11.5 Hz), 4.88 (1H, dd, J 6.6 Hz and 9.6 Hz), 5.10 (1H, t, J 7.1 Hz), 7.15-7.36 (5Hₐ₋ₖ, m, Ph). δc (100 MHz, CDCl₃): 20.23 (CH₂), 20.27 (CH₂), 25.30 (CH₂), 25.37 (CH₂), 33.17 (CH₂), 33.86 (CH₂), 33.96 (CH₂), 34.40 (CH₂), 37.89 (CH₂), 39.59 (CH₂), 61.89 (CH₂), 61.99 (CH₂), 79.47 (CH), 83.18 (CH), 105.94 (C), 106.29 (C), 125.84 (CH), 126.74 (CH), 127.43 (CH), 127.56 (CH), 128.44 (CH), 128.50 (CH), 143.29 (C), 143.44 (C). m/z (CI⁺): 219 [(M+H)⁺, 100%]. HRMS: 219.1385. C₁₄H₁₀O₂ requires (M+H)⁺ 219.1384. (g) 26: solid. mp: 85 °C. Rᵣ [SiO₂, hexane-DCM (1:1)]: 0.14. νmax (Golden Gate)/cm⁻¹: 1442, 1490, 2941. δh (400 MHz, CDCl₃): 1.02 (1H, broad d, J 13.1 Hz), 1.50-1.92 (5H, m), 2.80-2.95 (2H, m), 3.72 (1H, broad dd, J 4.1 and 11.0 Hz), 3.88 (1H, dt, J 2.6 and 11.1 Hz), 4.09 (1H, ddd, J 4.9, 8.6 and 10.0 Hz), 4.22 (1H, dt, J 6.6 and 8.7 Hz), 6.97-6.99 (2H, m), 7.12-7.36 (6H, m), 7.44-7.46 (2H, m). δc (100 MHz, CDCl₃): 19.14 (CH₃), 23.88 (CH₂), 29.61 (CH₂), 39.11 (CH₂), 60.15 (CH₂), 60.67 (C), 62.56 (CH₂), 105.68 (C), 124.58 (CH), 124.80 (CH), 126.26 (CH), 126.45 (CH), 127.61 (CH), 128.32 (CH), 144.22 (C), 145.38 (C). m/z (Cl⁺): 295 (M+H⁺, 100%). HRMS: 295.1698. C₂₀H₂₄O₂ requires M+H⁺, 295.1699. (h) 27: oil. Rᵣ [SiO₂, hexane-ethyl acetate (4:1)]: 0.51. νmax (Golden Gate)/cm⁻¹: 1454, 1496, 1598, 2856, 2925. δh (400 MHz, CDCl₃): 2.99 (1H, d, J 16.3 Hz), 3.13 (1H, d, J 16.4 Hz), 3.17 (1H, d, J 16.3 Hz), 3.57 (1H, d, J 16.1 Hz), 3.57-4.26 (6Hₐ₋ₖ, m), 4.41-5.50 (8Hₐ₋ₖ, m), 6.71-7.40 (24Hₐ₋ₖ, m, ArH). m/z, (FAB⁺): 629 [(M+H)⁺, 100 %]. HRMS: 629.2824. C₄₅H₅₀O₆ requires 629.2821. (i) 28 (major diastereomer), oil. Rᵣ [SiO₂, Pet.Ether-DCM (4:1)]: 0.36. νmax (Golden Gate)/cm⁻¹: 1480, 1591, 1610, 2858, 2951. δh (400 MHz, CDCl₃): 0.86 (3H, t, J 6.8 Hz), 1.20-1.41 (8H, m), 1.42-1.49 (1H, m), 1.65-1.80 (3H, m), 1.92-2.03 (2H, m), 2.98 (1H, d, J 16.3 Hz), 3.06 (1H, d, J 16.3 Hz), 3.91-3.99 (1H, m), 6.77-6.82 (2H, m), 7.02 (1H, d, J 7.7 Hz). δc (100 MHz, CDCl₃): 13.07 (CH₃), 18.76 (CH₂), 21.60 (CH₂), 23.84 (CH₂), 29.07 (CH₂), 30.81 (CH₂), 33.00 (CH₂), 35.02 (CH₂), 41.44 (CH₂), 71.17
(CH), 109.41 (CH), 110.47 (C), 119.35 (CH), 124.00 (C), 124.40 (CH), 131.98 (C), 158.17 (C). m/z, (CI): 295 [(M+H)+ (35Cl), 100%]. HRMS: 295.1465 and 297.1441. C₁₇H₂₂O₅³Cl requires M+H+ 295.1461, and C₁₇H₂₂O₅³Cl requires M+H+ 297.1438. (j) 29: oil. Rr [SiO₂, PetEther-DCM (4:1)]: 0.22. v_max(Golden Gate)/cm⁻¹: 1456, 1491, 2845, 2874. δ_H (400 MHz, CDCl₃): 1.49–1.65 (4H, m), 1.72 (1H, dt, J 6.1 and 13.2 Hz), 1.77–1.83 (1H, m), 1.89 (1H, ddd, J 2.1, 6.4 and 13.4 Hz), 1.93–2.09 (1H, m), 2.53 (1H, ddd, J 1.9, 6.1 and 16.3 Hz), 2.93 (1H, ddd, J 6.4, 13.1, 16.3 Hz), 3.48–3.55 (1H, m), 3.73 (1H, dt, J 3.3 Hz and 11.5 Hz), 6.72–6.81 (2H, m), 6.95–7.06 (2H, m). δ_C (100 MHz, CDCl₃): 26.75 (CH₃), 31.94 (CH₂), 34.83 (CH₂), 61.84 (CH₂), 95.89 (C), 116.99 (CH), 120.56 (CH), 122.75 (C), 127.08 (CH), 129.25 (CH), 152.26 (C). m/z, (EI⁺): 204 (M⁺, 89%), 131 (100). HRMS: 204.1150. C₁₇H₁₆O₂ requires 204.1151. (k) 30: oil. Rr [SiO₂, PetEther-DCM (4:1)]: 0.24. v_max(Golden Gate)/cm⁻¹: 1458, 1488, 1638, 2851, 2923. δ_H (400 MHz, CDCl₃): 1.50–1.73 (4H, m), 2.00–2.18 (2H, m), 3.55 (1H, dd, J 4.6 Hz and 11.0 Hz), 3.93 (1H, dt, J 3.2 and 11.6 Hz), 5.67 (1H, d, J 9.6 Hz), 6.57 (1H, d, J 9.6 Hz), 6.83 (1H, t, J 7.4 Hz), 6.94 (1H, d, J 7.9 Hz), 7.06 (1H, dd, J 1.5 Hz and 7.5 Hz), 7.14 (1H, dt, J 1.6 Hz and 7.7 Hz). δ_C (100 MHz, CDCl₃): 18.55 (CH₂), 24.77 (CH₂), 35.07 (CH₂), 61.79 (CH₂), 95.38 (C), 116.53 (CH), 121.23 (C), 121.45 (CH), 125.47 (CH), 126.04 (CH), 127.02 (CH), 129.19 (CH), 151.45 (C). m/z, (FAB⁺): 203 [(M+H)⁺, 100%]. HRMS: 203.1072. C₁₃H₁₅O₂ requires M+H⁺ 203.1071. (l) 31: oil. Rr [SiO₂, hexane-DCM (4:1)]: 0.21. v_max(Golden Gate)/cm⁻¹: 1432, 1587, 2859, 2937, 3387. δ_H (400 MHz, CDCl₃): 1.33 (1H, s), 1.33–1.38 (2H, m), 1.46–1.53 (2H, m), 1.68 (2H, quin, J 7.6 Hz), 2.76 (2H, t, J 7.6 Hz), 3.51 (2H, t, J 6.6 Hz), 6.37 (1H, s), 7.30–7.13 (2H, m), 7.31 (1H, d, J 7.4 Hz), 7.38 (1H, dd, J 1.9 Hz and 7.8 Hz). δ_C (100 MHz, CDCl₃): 25.31 (CH₃), 27.47 (CH₂), 28.38 (CH₂), 32.42 (CH₂), 62.78 (CH₂), 101.92 (CH), 110.69 (CH), 120.17 (CH), 122.38 (CH), 123.07 (CH), 128.93 (C), 154.58 (C), 159.32 (C). m/z, (CI⁺): 205 [(M+H)⁺, 100%]. HRMS: 205.1229. C₁₃H₁₃O₂ requires M+H⁺ 205.1225.