

Elemental iodine catalyzed [4 + 2] cycloaddition reactions of *o*-quinomethanes: an efficient synthesis of *trans*-fused pyrano[3,2-*c*]benzopyrans

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Elemental iodine has been utilized as an efficient catalyst for the intramolecular[4 + 2]cycloaddition of *o*-quinomethanes generated *in situ* from *o*-hydroxybenzaldehydes and unsaturated alcohol in the presence of trimethyl orthoformate to afford the corresponding *trans*-annulated pyrano[3,2-*c*]benzopyrans in high yields with high diastereoselectivity

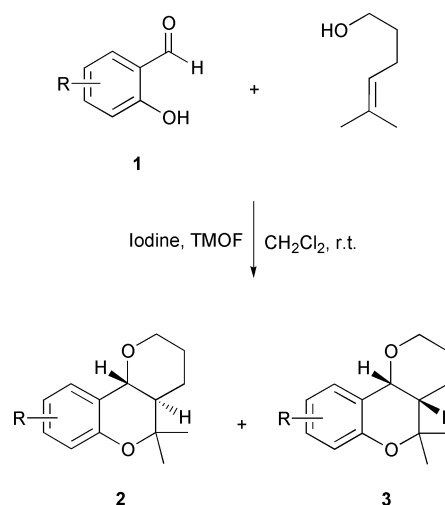
Introduction

The hetero-Diels–Alder reaction is one of the most powerful synthetic routes for the construction of a variety of heterocycles.¹ *o*-Quinomethanes are very useful intermediates in the synthesis of steroid and alkaloid skeletons having aromatic ring systems.² They are highly reactive and unstable intermediates in organic synthesis. This is because of the restoration of aromaticity after cycloaddition, which has been utilized for the construction of polycyclic ring systems that are otherwise difficult to synthesize.³ They are widely used as hetero dienes in the inter- and intramolecular Diels–Alder reactions to construct polycyclic oxygen heterocycles.⁴ *o*-Quinomethanes generated *in situ* from *o*-hydroxybenzaldehydes and unsaturated alcohol provide a useful entry to fused pyranobenzopyrans.⁵ However, there are no reports on the synthesis of *trans*-annulated pyrano[3,2-*c*]benzopyrans using elemental iodine as catalyst. Therefore, the development of new reagents that are efficient and lead to convenient procedures and better yields are well appreciated. The use of iodine as catalyst in promoting various transformations is well documented in the literature.⁶

Results and discussion

In continuation of our work on the synthesis of benzopyrans and its derivatives⁷ we herein describe a simple and efficient method for the synthesis of tetrahydropyrano[3,2-*c*]benzopyrans involving intramolecular(4 + 2)cycloaddition of *o*-quinomethanes. The treatment of *o*-hydroxybenzaldehyde with 5-methylhex-4-en-1-ol and trimethyl orthoformate in the presence of 5 mol% elemental iodine in dichloromethane at ambient temperature led to the formation of *trans*-fused pyrano[3,2-*c*]benzopyran **2** in 92% yield (Scheme 1).

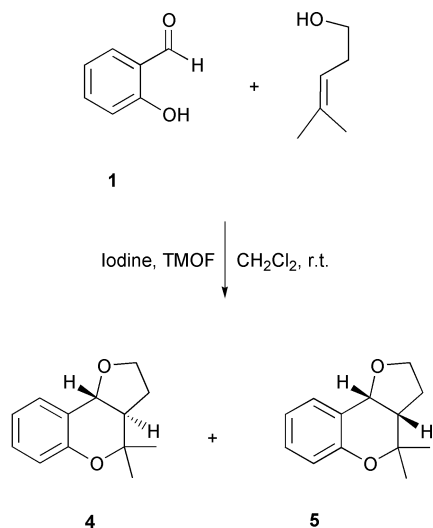
In a similar fashion, several substituted *o*-hydroxybenzaldehydes reacted smoothly with 5-methylhex-4-en-1-ol to afford the corresponding *trans*-fused pyranobenzopyrans in high yields. In all cases, the reactions proceeded efficiently at ambient temperature with high diastereoselectivity. Only a single diastereomer was obtained in each reaction, the structure of which was established by ¹H, ¹³C NMR and mass spectroscopy. The assigned structure was further confirmed by direct comparison with known compounds.⁵ The reactions were clean and completed within 1–2.0 h. This method is highly diastereoselective, affording high yields of products in a short reaction



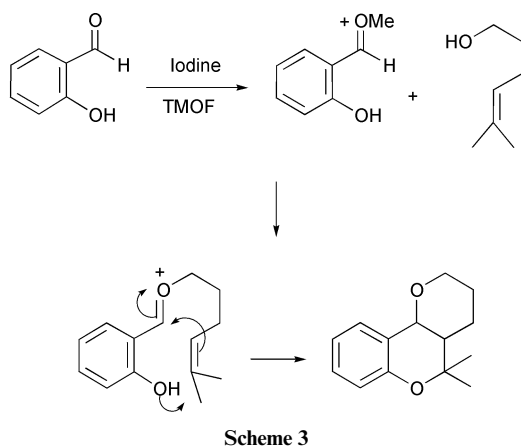
Scheme 1

time. However, in the absence of either iodine or trimethyl orthoformate, the reaction did not yield any product even under reflux conditions. The lowering of the reaction temperature was detrimental to the efficiency of this procedure. However, the treatment of *o*-hydroxybenzaldehyde with 4-methylpent-3-en-1-ol in the presence of trimethyl orthoformate under the influence of catalytic amount of iodine in dichloromethane for 3 h afforded the corresponding tetrahydrofuro[3,2-*c*]benzopyran in 75% yield. The product was obtained as a mixture of *trans*- and *cis*-isomers in a ratio of 80 : 20 respectively (Scheme 2).

Furthermore, the reaction did not proceed with but-3-en-1-ol under these reaction conditions. This method was successful only with 5-methylhex-4-en-1-ol and 4-methylpent-3-en-1-ol. There are many advantages in the use of elemental iodine as catalyst for this transformation, which include high yields of products, mild reaction conditions, greater diastereoselectivity, short reaction times and simplicity in operation. The catalyst is readily available at low cost and highly efficient in promoting intramolecular (4 + 2) cycloadditions. In addition, this method does not require any promoters or anhydrous conditions and no precautions need to be taken to exclude moisture from the reaction media. Furthermore, this method is equally effective with salicylaldehydes carrying electron deficient substituents in the aromatic ring. The reaction may proceed through an



intramolecular (4 + 2) cycloaddition of *o*-quinomethanes generated *in situ* from salicylaldehyde and unsaturated alcohol in the presence of trimethyl orthoformate as show in Scheme 3.



The scope and generality of this process is illustrated with respect to various substituted *o*-hydroxybenzaldehydes and 5-methylhex-4-en-1-ol and the results are presented in the Table 1.

In summary, we have developed a simple and efficient method for the synthesis of *trans*-fused pyranobenzopyrans from salicylaldehydes and unsaturated alcohol using cheap and readily available reagent *i.e.* elemental iodine as catalyst. In addition to its efficiency, simplicity and milder reaction conditions, this method provides high yields of products with high selectivity, which makes it a useful and attractive process for the synthesis of fused benzopyran derivatives.

Experimental

General procedure

A mixture of *o*-hydroxybenzaldehyde (5 mmol), 5-methylhex-4-en-1-ol (5 mmol), trimethyl orthoformate (7.5 mmol) and iodine (5 mol%) in dichloromethane (15 ml) was stirred at ambient temperature for a specified time (Table 1). After complete conversion as indicated by TLC, the reaction mixture was quenched with water (15 mL) and extracted with dichloromethane (2 × 15 mL). The combined extracts were washed with 15% solution of sodium thiosulfate, dried over anhydrous Na₂SO₄, and concentrated *in vacuo*. The resulting product was purified by column chromatography on silica gel (Merck, 100–200 mesh, ethyl acetate–hexane, 1 : 9) to afford pure product.

Spectral data for products: 2a. Solid, mp 65–66 °C, ¹H NMR (CDCl₃) δ: 1.22 (s, 3H), 1.35–1.38 (m, 1H), 1.40 (s, 3H), 1.70–1.85 (m, 3H), 1.95–2.0 (m, 1H), 3.65 (dt, 1H, *J* = 3.5, 11.5 Hz), 4.18 (dd, 1H, *J* = 5.0, 11.5 Hz), 4.20 (d, 1H, *J* = 10.5 Hz), 6.78 (d, 1H, *J* = 8.0 Hz), 6.93 (t, 1H, *J* = 7.8 Hz), 7.18 (t, 1H, *J* = 8.0 Hz), 7.40 (d, 1H, *J* = 7.8 Hz). ¹³C NMR (Proton decoupled, CDCl₃) δ: 20.3, 24.9, 26.3, 27.5, 45.2, 68.2, 73.7, 78.2, 116.7, 119.9, 122.5, 126.0, 128.8, 152.6. EIMS: *m/z*: 218 M⁺, 200, 186, 163, 146, 96, 68, 55, 41. IR (KBr) ν: 3035, 2970, 1617, 1580, 1105, 1075 cm⁻¹. Anal. Calcd. for C₁₄H₁₈O₂ (218.294): C, 77.03; H, 8.31. Found: C, 77.05; H, 8.33%.

2b. Solid, mp 97–98 °C, ¹H NMR (CDCl₃) δ: 1.20 (s, 3H), 1.33–1.37 (m, 1H), 1.40 (s, 3H), 1.67–1.80 (m, 3H), 1.90–2.05 (m, 1H), 3.63 (dt, 1H, *J* = 3.8, 11.5 Hz), 3.85 (s, 3H), 4.15 (dd, 1H, *J* = 4.8, 11.6 Hz), 4.23 (d, 1H, *J* = 10.3 Hz), 6.70 (dd, 1H, *J* = 2.8, 8.2 Hz), 6.80 (t, 1H, *J* = 7.8 Hz), 7.05 (d, 1H, *J* = 8.2 Hz). ¹³C NMR (Proton decoupled, CDCl₃) δ: 20.1, 25.0, 26.4, 27.3, 29.8, 46.8, 56.3, 68.7, 73.5, 78.0, 103.1, 110.2, 129.4, 155.0, 160.2. EIMS: *m/z*: 248 M⁺, 234, 217, 166, 147, 138, 109, 96, 69, 55, 41. IR (KBr) ν: 3038, 2975, 1615, 1585, 1107, 1070 cm⁻¹. Anal. Calcd. for C₁₅H₂₀O₃ (248.32): C, 72.55; H, 8.12. Found: C, 72.57; H, 8.15%.

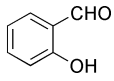
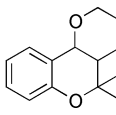
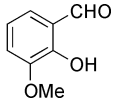
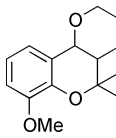
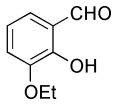
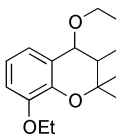
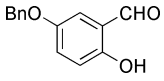
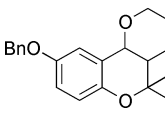
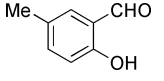
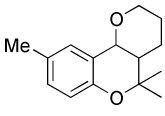
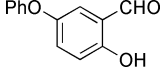
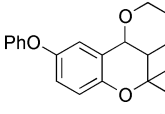
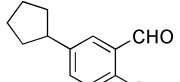
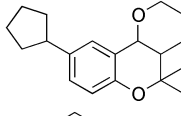
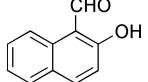
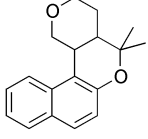
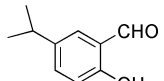
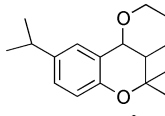
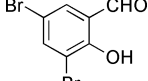
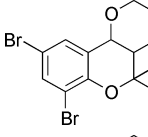
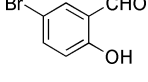
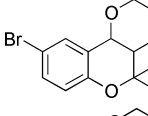
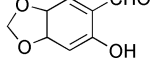
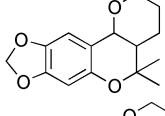
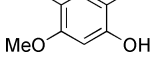
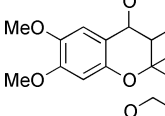
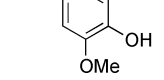
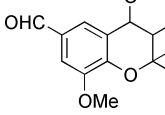
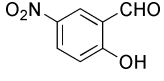
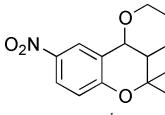
2c. Liquid, ¹H NMR (CDCl₃) δ: 1.28 (s, 3H), 1.38–1.14 (m, 1H), 1.45 (t, 3H, *J* = 6.8 Hz), 1.48 (s, 3H), 1.70–1.83 (m, 3H), 1.97–2.05 (m, 1H), 3.65 (dt, 1H, *J* = 3.7, 11.6 Hz), 4.15 (q, 2H, *J* = 6.8 Hz), 4.18 (dd, 1H, *J* = 5.0, 11.6 Hz), 4.25 (d, 1H, *J* = 10.5 Hz), 6.78 (dd, 1H, *J* = 2.7, 8.0 Hz), 6.80 (t, 1H, *J* = 7.8 Hz), 7.08 (d, 1H, *J* = 8.0 Hz). ¹³C NMR (Proton decoupled, CDCl₃) δ: 14.7, 20.2, 24.9, 26.1, 27.3, 44.9, 65.0, 68.1, 73.6, 78.3, 104.0, 118.3, 119.15, 123.3, 143.2, 147.3. EIMS: *m/z*: 262 M⁺, 248, 204, 166, 138, 109, 97, 81, 69, 55, 41. IR (KBr) ν: 3040, 2968, 1616, 1585, 1120, 1070 cm⁻¹. Anal. Calcd. for C₁₆H₂₂O₃ (262.347): C, 73.25; H, 8.45. Found: C, 73.29; H, 8.47%.

2d. Oil, ¹H NMR (CDCl₃) δ: 1.20 (s, 3H), 1.30–1.37 (m, 1H), 1.42 (s, 3H), 1.75–1.83 (m, 3H), 1.95–2.0 (m, 1H), 3.65 (dt, 1H, *J* = 3.5, 11.7 Hz), 4.18 (dd, 1H, *J* = 4.8, 11.7 Hz), 4.21 (d, 1H, *J* = 10.4 Hz), 5.05 (s, 2H), 6.70 (d, 1H, *J* = 8.2 Hz), 6.83 (dd, 1H, *J* = 2.7, 8.2 Hz), 7.09 (d, 1H, *J* = 2.7 Hz), 7.35–7.48 (m, 5H). ¹³C NMR (Proton decoupled, CDCl₃) δ: 20.2, 25.1, 26.3, 27.5, 45.2, 68.2, 70.7, 73.7, 77.9, 111.3, 116.6, 117.4, 122.8, 127.4, 127.6, 128.3, 137.5, 146.9, 152.6. EIMS: *m/z*: 324 M⁺, 234, 216, 187, 149, 91, 55, 43. IR (KBr) ν: 3037, 2960, 1610, 1580, 1115, 1083 cm⁻¹. Anal. Calcd. for C₂₁H₂₄O₃ (324.418): C, 77.75; H, 7.46. Found: C, 77.78; H, 7.47%.

2e. Liquid, ¹H NMR (CDCl₃) δ: 1.18 (s, 3H), 1.30–1.37 (m, 1H), 1.38 (s, 3H), 1.65–1.78 (m, 3H), 1.88–1.97 (m, 1H), 2.25 (s, 3H), 3.60 (dt, 1H, *J* = 3.7, 11.8 Hz), 4.10 (dd, 1H, *J* = 5.0, 11.8 Hz), 4.18 (d, 1H, *J* = 10.5 Hz), 6.60 (d, 1H, *J* = 8.2 Hz), 6.90 (dd, 1H, *J* = 2.8, 8.2 Hz), 7.18 (d, 1H, *J* = 2.7 Hz). ¹³C NMR (Proton decoupled, CDCl₃) δ: 20.0, 20.3, 24.9, 26.1, 27.3, 45.1, 68.0, 73.5, 77.7, 116.2, 121.9, 126.0, 128.6, 129.2, 150.3. EIMS: *m/z*: 232 M⁺, 217, 173, 159, 136, 121, 98, 69, 55, 41. IR (KBr) ν: 3038, 2965, 1615, 1578, 1128, 1080 cm⁻¹. Anal. Calcd. for C₁₅H₂₀O₂ (232.321): C, 77.55; H, 8.68. Found: C, 77.58; H, 8.70%.

2f. Oil, ¹H NMR (CDCl₃) δ: 1.20 (s, 3H), 1.35–1.38 (m, 1H), 1.40 (s, 3H), 1.65–1.80 (m, 3H), 1.90–1.98 (m, 1H), 3.60 (dt, 1H, *J* = 3.8, 11.8 Hz), 4.15 (dd, 1H, *J* = 5.0, 11.8 Hz), 4.20 (d, 1H, *J* = 10.5 Hz), 6.70 (d, 1H, *J* = 8.0 Hz), 6.80 (dd, 1H, *J* = 2.5, 8.0), 6.85–6.97 (m, 3H), 7.08 (d, 1H, *J* = 2.5 Hz), 7.18–7.20 (m, 2H). EIMS: *m/z*: 310 M⁺, 234, 217, 95, 81, 69, 55, 41. IR (KBr) ν: 3040, 2970, 1610, 1580, 1130, 1078 cm⁻¹. Anal. Calcd. for C₂₀H₂₂O₃ (310.39): C, 77.39; H, 7.14. Found: C, 77.40; H, 7.17%.

Table 1 Elemental iodine-catalyzed synthesis of pyrano[3,2-*c*]benzopyrans

Entry	<i>o</i> -Hydroxybenzaldehyde (1)	Product ^a (2)	Reaction time/h	Yield (%) ^b
a			1.5	92
b			1.0	90
c			1.5	88
d			1.0	90
e			1.5	87
f			2.0	85
g			1.0	82
h			2.0	85
i			1.0	90
j			2.5	80
k			2.0	83
l			1.0	92
m			1.5	85
n			3.5	80
o			5.0	71

^a All products were characterised by ¹H, ¹³C NMR, IR and mass spectroscopy. ^b Isolated and unoptimised yields.

2g. Liquid, ^1H NMR (CDCl_3) δ : 1.20 (s, 3H), 1.33 (m, 1H), 1.39 (s, 3H), 1.50–1.80 (m, 8H), 1.85–2.10 (m, 4H), 2.85–2.93 (m, 1H), 3.60 (dt, 1H, $J = 3.7, 11.5$ Hz), 4.12 (dd, 1H, $J = 11.5, 5.0$ Hz), 4.18 (d, 1H, $J = 10.6$ Hz), 6.65 (d, 1H, $J = 7.8$ Hz), 6.95 (dd, 1H, $J = 2.3, 7.8$ Hz), 7.20 (d, 1H, $J = 2.3$ Hz). EIMS: m/z : 286 M^+ , 217, 163, 146, 97, 84, 69, 55, 41. IR (KBr): 3043, 2963, 1620, 1570, 1128, 1075 cm^{-1} . Anal. Calcd. for $\text{C}_{19}\text{H}_{26}\text{O}_2$ (286.41): C, 79.68; H, 9.15. Found: C, 79.70; H, 9.18%.

2h. Solid, mp 113–114 $^\circ\text{C}$, ^1H NMR (CDCl_3) δ : 1.18 (s, 3H), 1.38–1.43 (m, 1H), 1.45 (s, 3H), 1.70–1.85 (m, 3H), 1.97–2.05 (m, 1H), 3.80 (dt, 1H, $J = 3.7, 11.56$ Hz), 4.18 (dd, 1H, $J = 5.0, 11.6$ Hz), 4.58 (d, 1H, $J = 9.8$ Hz), 6.97 (d, 1H, $J = 8.7$ Hz), 7.30 (t, 1H, $J = 7.8$ Hz), 7.38 (t, 1H, $J = 7.8$ Hz), 7.65 (d, 1H, $J = 8.7$ Hz), 7.70 (d, 1H, $J = 7.8$ Hz), 8.20 (d, 1H, $J = 8.7$ Hz). ^{13}C NMR (Proton decoupled, CDCl_3) δ : 19.0, 25.6, 26.6, 27.2, 46.9, 68.2, 74.6, 78.1, 113.3, 119.3, 122.9, 125.1, 125.9, 128.0, 129.3, 130.0, 132.5, 151.6. EIMS: m/z : 270 M^+ , 254, 196, 173, 145, 115, 84, 41. IR (KBr) ν : 3040, 2967, 1618, 1580, 1125, 1075 cm^{-1} . Anal. Calcd. for $\text{C}_{18}\text{H}_{20}\text{O}_2$ (268.35): C, 80.56; H, 7.51. Found: C, 79.98; H, 7.60%.

2i. Liquid, ^1H NMR (CDCl_3) δ : 1.80 (d, 6H, $J = 7.0$ Hz), 1.23 (s, 3H), 1.32–1.37 (m, 1H), 1.39 (s, 3H), 1.65–1.77 (m, 3H), 1.90–1.97 (m, 1H), 2.80 (m, 1H), 3.60 (dt, 1H, $J = 3.5, 11.5$ Hz), 4.17 (dd, 1H, $J = 4.9, 11.5$ Hz), 4.19 (d, 1H, $J = 10.0$ Hz), 6.60 (d, 1H, $J = 8.2$ Hz), 6.98 (dd, 1H, $J = 2.7, 8.2$ Hz), 7.20 (d, 1H, $J = 2.7$ Hz). ^{13}C NMR (Proton decoupled, CDCl_3) δ : 20.4, 24.0, 24.3, 25.1, 26.2, 27.6, 33.4, 45.2, 68.2, 73.8, 77.9, 116.4, 121.9, 123.5, 126.7, 140.1, 150.6. EIMS: m/z : 260 M^+ , 246, 218, 149, 98, 71, 55. IR (KBr) ν : 3045, 2961, 1617, 1583, 1117, 1080 cm^{-1} . Anal. Calcd. for $\text{C}_{17}\text{H}_{24}\text{O}_2$ (260.375): C, 78.42; H, 9.29. Found: C, 78.45; H, 9.30%.

2j. Solid, mp 93–94 $^\circ\text{C}$, ^1H NMR (CDCl_3) δ : 1.20 (s, 3H), 1.32–1.35 (m, 1H), 1.42 (s, 3H), 1.63–1.80 (m, 3H), 1.90–2.0 (m, 1H), 3.60 (dt, 1H, $J = 3.8, 11.5$ Hz), 4.10 (dd, 1H, $J = 5.0, 11.5$ Hz), 4.17 (d, 1H, $J = 10.2$ Hz), 7.60 (d, 1H, $J = 2.8$ Hz), 7.90 (d, 1H, $J = 2.8$ Hz). EIMS: m/z : 378, 376 M^+ , 190, 162, 131, 105, 71, 59. IR (KBr) ν : 3398, 2938, 1595, 1133, 1095 cm^{-1} . Anal. Calcd. for $\text{C}_{14}\text{H}_{16}\text{Br}_2\text{O}_2$ (376.08): C, 44.71; H, 4.29; Br, 42.49. Found: C, 44.75; H, 4.30; Br, 42.50%.

2k. Oil, ^1H NMR (CDCl_3) δ : 1.18 (s, 3H), 1.35–1.39 (m, 1H), 1.40 (s, 3H), 1.65–1.80 (m, 3H), 1.90–2.0 (m, 1H), 3.60–3.63 (m, 1H), 4.18 (m, 1H), 4.20 (d, 1H, $J = 10.5$ Hz), 6.60 (d, 1H, $J = 8.3$ Hz), 7.21 (dd, 1H, $J = 2.7, 8.3$ Hz), 7.50 (d, 1H, $J = 2.7$ Hz). EIMS: m/z : 299, 297 M^+ , 217, 149, 98, 69, 55, 41. IR (KBr) ν : 3040, 2968, 1585, 1508, 1133, 1089 cm^{-1} . Anal. Calcd. for $\text{C}_{14}\text{H}_{17}\text{BrO}_2$ (297.19): C, 56.58; H, 5.77; Br, 26.89. Found: C, 56.60; H, 5.78; Br, 26.90%.

2l. Oil, ^1H NMR (CDCl_3) δ : 1.18 (s, 3H), 1.30–1.35 (m, 1H), 1.37 (s, 3H), 1.60–1.78 (m, 3H), 1.85–1.93 (m, 1H), 3.58 (dt, 1H, $J = 3.5, 11.5$ Hz), 4.05 (dd, 1H, $J = 5.0, 11.5$ Hz), 4.18 (d, 1H, $J = 10.2$ Hz), 5.82 (s, 2H), 6.25 (s, 1H), 6.80 (s, 1H). ^{13}C NMR (Proton decoupled, CDCl_3) δ : 20.0, 25.0, 26.4, 27.5, 45.2, 68.2, 74.0, 78.3, 98.4, 100.8, 105.1, 147.7. EIMS: m/z : 262 M^+ , 243, 200, 186, 163, 146, 96, 68, 55, 41. IR (KBr) ν : 3025, 2968, 1580, 1510, 1138, 1090 cm^{-1} . Anal. Calcd. for $\text{C}_{15}\text{H}_{18}\text{O}_4$ (262.303): C, 68.69; H, 6.92. Found: C, 68.70; H, 6.94%.

2m. Solid, mp 53–55 $^\circ\text{C}$, ^1H NMR (CDCl_3) δ : 1.20 (s, 3H), 1.32–1.37 (m, 1H), 1.42 (s, 3H), 1.76–1.84 (m, 3H), 1.89–1.97 (m, 1H), 3.61 (dt, 1H, $J = 3.7, 11.5$ Hz), 3.80 (s, 6H), 4.05 (dd, 1H, $J = 5.0, 11.5$ Hz), 4.18 (d, 1H, $J = 10.2$ Hz), 6.30 (s, 1H), 6.85 (s, 1H). EIMS: m/z : 278 M^+ , 264, 247, 234, 189, 138, 109,

97, 69, 55, 41. IR (KBr) ν : 3038, 2975, 1616, 1587, 1107, 1070 cm^{-1} . Anal. Calcd. for $\text{C}_{16}\text{H}_{22}\text{O}_4$ (278.34): C, 69.04; H, 7.97. Found: C, 69.07; H, 7.99%.

2n. Solid, mp 122 $^\circ\text{C}$, ^1H NMR (CDCl_3) δ : 1.21 (s, 3H), 1.32–1.37 (m, 1H), 1.45 (s, 3H), 1.75–1.85 (m, 3H), 1.90–2.05 (m, 1H), 3.65 (dt, 1H, $J = 3.7, 11.5$ Hz), 3.85 (s, 3H), 4.10 (dd, 1H, $J = 5.0, 11.3$ Hz), 4.20 (d, 1H, $J = 10.2$ Hz), 7.25 (br s, 1H), 7.58 (br s, 1H), 9.80 (s, 1H). EIMS: m/z : 276 M^+ , 263, 245, 189, 135, 107, 97, 69, 55, 41. IR (KBr) ν : 3035, 2971, 1619, 1578, 1101, 1075 cm^{-1} . Anal. Calcd. for $\text{C}_{16}\text{H}_{20}\text{O}_4$ (276.33): C, 69.55; H, 7.29. Found: C, 69.59; H, 7.31%.

2o. Solid, mp 113–114 $^\circ\text{C}$, ^1H NMR (CDCl_3) δ : 1.23 (s, 3H), 1.35–1.41 (m, 1H), 1.45 (s, 3H), 1.65–1.80 (m, 3H), 1.97–2.0 (m, 1H), 3.63–3.66 (m, 1H), 4.18 (m, 1H), 4.20 (d, $J = 10.7$ Hz), 6.80 (d, 1H, $J = 8.8$ Hz), 8.08 (dd, 1H, $J = 2.8, 8.8$ Hz), 8.38 (d, 1H, $J = 2.8$ Hz). ^{13}C NMR (Proton decoupled, CDCl_3) δ : 20.7, 25.0, 25.8, 27.4, 44.6, 68.1, 72.3, 80.8, 117.1, 123.0, 124.7, 141.0, 158.4. EIMS: m/z : 263 M^+ , 248, 149, 98, 69, 63. IR (KBr) ν : 3040, 2968, 1585, 1508, 1133, 1089 cm^{-1} . Anal. Calcd. for $\text{C}_{14}\text{H}_{17}\text{NO}_4$ (263.291): C, 63.87; H, 6.51; N, 5.32. Found: C, 63.88; H, 6.53; N, 5.34%.

4 and 5 (diastereomeric mixture). Solid, mp 84–86 $^\circ\text{C}$, ^1H NMR (CDCl_3 , *trans*-isomer 4) δ : 1.30 (s, 3H), 1.45 (s, 3H), 1.80–2.10 (m, 3H), 4.10–4.25 (m, 2H), 4.40 (d, 1H, $J = 10.7$ Hz), 6.78 (d, 1H, $J = 8.0$ Hz), 6.93 (t, 1H, $J = 7.5$ Hz), 7.18 (t, 1H, $J = 8.0$ Hz), 7.40 (d, 1H, $J = 7.5$ Hz). ^1H NMR (CDCl_3 , *cis*-isomer 4) δ : 1.30 (s, 3H), 1.40 (s, 3H), 1.80–2.20 (m, 2H), 2.40 (dd, 1H, $J = 7.5, 8.5$ Hz), 3.75–3.90 (m, 2H), 5.0 (d, 1H, $J = 7.5$ Hz), 6.78 (d, 1H, $J = 8.0$ Hz), 6.93 (t, 1H, $J = 7.5$ Hz), 7.18 (t, 1H, $J = 8.0$ Hz), 7.40 (d, 1H, $J = 7.5$ Hz). EIMS: m/z : 204, 185, 137, 107, 67, 55, 43. IR (KBr) ν : 3035, 2970, 1615, 1583, 1127, 1081 cm^{-1} . Anal. Calcd. for $\text{C}_{13}\text{H}_{16}\text{O}_2$ (204.42): C, 76.44; H, 7.89. Found: C, 76.51; H, 7.78%.

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