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TETRAHEDRON

Triphenyl phosphonium perchlorate—an efficient catalyst for the imino Diels–Alder reaction of imines with electron rich dienophiles. Synthesis of pyranoquinoline, furoquinoline and phenanthridine derivatives

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Abstract—Triphenyl phosphonium perchlorate (TPP) is found to be an efficient catalyst for the imino Diels–Alder reaction of aldimines with cyclopentadiene and 3,4-dihydro-2*H*-pyran is reported for the first time. One pot synthesis of furoquinoline, cyclopentaquinolines and phenanthridine catalysed by TPP is also reported in good yields. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

The pyranoquinoline moiety is present in many alkaloids such as flindersine, oricine and veprisine,[1] and derivatives of these alkaloids possess a wide range of biological activities such as psychotropic,[2] antiallergenic,[3] anti-inflammatory[4] and estronegic[5] activities. The furoquinoline skeleton is present in many alkaloids like skimmianine and balfouridine.[6] Naturally occuring derivatives include several Amaryllidaceae and Papaveraceae alkaloids, notably lycorine, haemanthamine and chelidonine, contain the phenanthridine framework and the chemistry of phenanthridine alkaloids has been reviewed.[7]

The imino Diels–Alder reaction of imines with electron rich dienophiles has been catalyzed by $BF_3{\cdot}Et_2O$,[8] lanthanide triflates,[9] $GdCl_3$,[10] and protic acids such as TFA[11] and *p*-TsOH.[12] However, to the best of our knowledge, there is no report of the use of triphenyl phosphonium perchlorate as a catalyst for the reaction of imines within electron rich alkenes. This prompted us to use TPP as a catalyst for such cycloadditions.

2. Results and discussion

In the presence of 40 mol% TPP, *N*-benzylidene aniline **1a** was treated with 3,4-dihydropyran **2** in acetonitrile at room temperature. After 30 min, pyranoquinolines **3a** and **4a** were obtained in a ratio of 73:27 and an overall yield of 91% (Scheme 1). The results with various substituents are given in Table 1. The isomeric ratio is based on isolation by column chromatography. The most diagnostic parameter for structural assignment is the scalar coupling constant between protons H-4a and H-5. In the isomer **3a**, the coupling constant J(4a–5)=4.5 Hz is significantly smaller and typical for a *gauche* conformation. This orientation is present in both conformers of the configuration having *cis* orientation of the pyran ring and phenyl group. In the isomer **4a**, the J(4a–5)=10.6 Hz is relevant and indicative of the *anti* reciprocal orientation of protons H-5 and H-4a. This orientation is only possible when the pyran ring and phenyl ring are on opposite sides of the quinoline ring of **4a**.

TPP also catalyses the reaction of cyclopentadiene with *N*-benzylidene aniline **1a** and resulted in the formation of cyclopentaquinoline **7a** in 68% yield (Scheme 2). Other examples are reported in Table 2. The stereochemistry of the product **7a** was assigned based on the low coupling constant J(4a–5)=2.9 Hz.

Generally, imines derived from phenylglyoxal are highly hygroscopic, unstable at high temperatures, difficult to purify by distillation or column chromatography and lack efficiency.[13] Moreover, the three component coupling reactions proceed smoothly at room temperature and the products are obtained in good yields. The reaction of phenyl glyoxal monohydrate, aniline and 2,3-dihydro-2*H*-furan was effectively catalysed by TPP in the presence of anhydrous Na_2SO_4 under mild conditions (Scheme 3). The reaction is instantaneous and produces the furoquinolines **11** and **12** in the ratio of 35:65 in an overall yield of 77%. The products were characterized by their coupling constant

Keywords: triphenyl phosphonium perchlorate; imines; Diels–Alder; pyranoquinolines; furoquinoline; phenanthridine.

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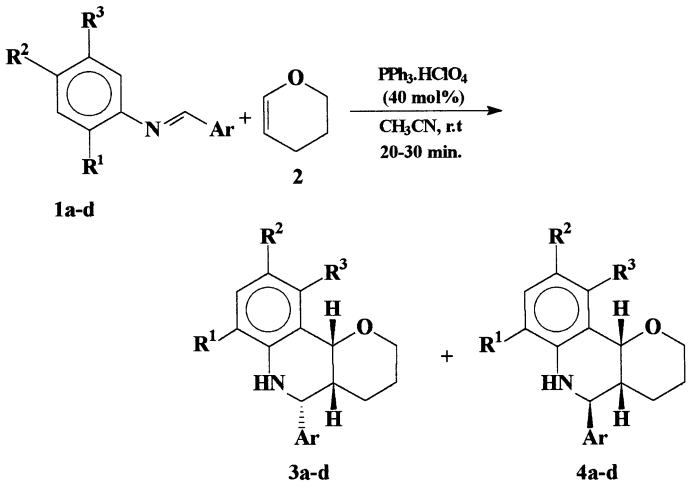
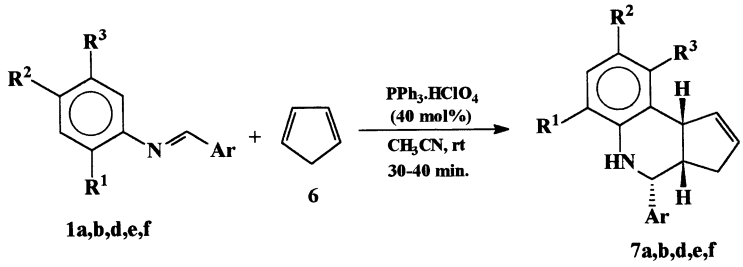


Scheme 1.

Table 1. Synthesis of pyranoquinolines employing 40 mol% $PPh_3 \cdot HClO_4$

Schiff base	Substituents			Ar	Product ratio[a] **3**:**4**	Time (min)	Overall yield (%)
	R^1	R^2	R^3				
1a	H	H	H	Ph	73:27	30 (720)[b]	91 (25)[b]
1b	H	Cl	H	Ph	45:55	25[b]	93 (75)[b]
1c	H	OCH_3	H	Ph	51:49	30	95 (81)[b]
1d	H	H	H	*p*-Cl–C_6H_5	66:34	20	80

[a] The isomeric ratio is based on isolation by column chromatography.
[b] Time and yield reported in the literature.[8,10]



Scheme 2.

Table 2. Synthesis of cyclopentaquinolines

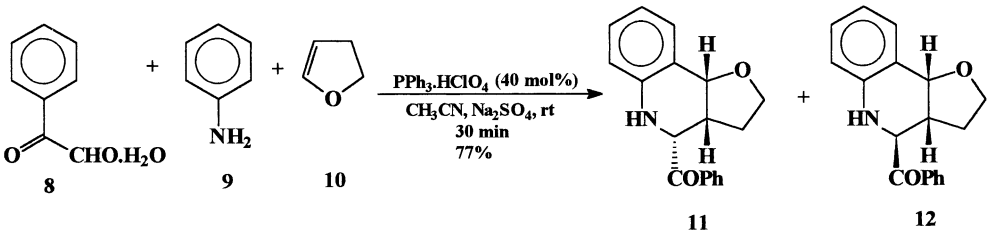
Schiff base	Substituents			Ar	Time (min)	Yield (%)
	R^1	R^2	R^3			
1a	H	H	H	Ph	30	68
1b	H	Cl	H	Ph	30	65
1d	H	H	H	*p*-Cl–C_6H_5	40	79
1e	H	COOH	H	Ph	35	83
1f	CH_3	H	CH_3	Ph	35	78

values J(4a–5)=3.1 Hz for **11** and 9.2 Hz for the compound **12**.

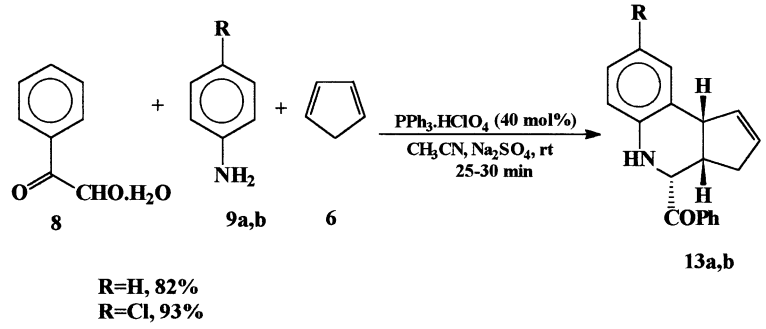
Similarly, the reaction of phenyl glyoxal and *para*-substituted anilines with cyclopentadiene catalysed by TPP in the presence of anhydrous Na_2SO_4 yielded the corresponding cyclopentaquinolines in good yields (Scheme 4). The *cis* orientation of the protons were conformed by their coupling constant values J(4a–5)= 3.1 Hz.

A phenanthridine derivative was prepared by the reaction of 4-nitro-1-naphthylamine and formaldehyde (37% aqueous) with cyclopentadiene catalysed by TPP in the presence of anhydrous Na_2SO_4 in 92% yield (Scheme 5).

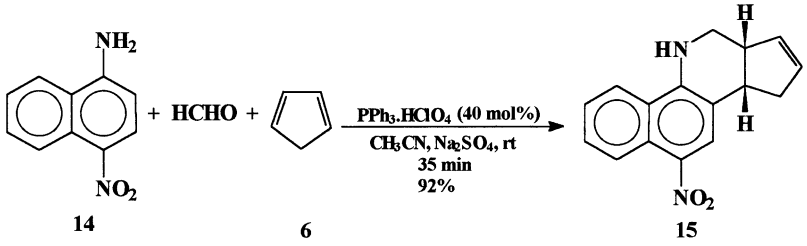
In conclusion, we have shown that TPP is an efficient catalyst for imino Diels–Alder reaction because it is mild and inexpensive, and only 40 mol% is required for the cycloaddition reactions. With the imino Diels–Alder reaction catalysed by perchloric acid, complete polymerization of imine was observed whereas the reaction catalysed by TPP yielded the product up to 95%, which shows TPP is effectively catalysing the cycloadditions.



Scheme 3.



Scheme 4.



Scheme 5.

3. Experimental

Mass spectra were recorded on a Varian VG 70–70H mass spectrometer. Melting points were measured in capillary tubes and are uncorrected. Analytical thin layer chromatography was performed on precoated sheets of silica gel G of 0.25 mm thickness containing PF 254 indicator (Merck, Darmstadt). Column chromatography was performed with silica gel (60–120 mesh; SD Fine, Boisar). IR spectra were recorded as solids in KBr pellets on a Nicolet Impact-400 spectrometer. NMR spectra were obtained on a Bruker spectrometer. ^{1}H NMR spectra were recorded at 300 MHz in $CDCl_3$ and the chemical shifts are given in δ relative to the internal standard TMS. ^{13}C NMR spectra were recorded at 75 MHz in $CDCl_3$ and the chemical shifts are given in δ relative to the solvent (77.0). Acetonitrile was distilled from calcium hydride and dried over 4 Å molecular sieves.

3.1. General procedure

To a mixture of imines **1a–d** (2.5 mmol) or a mixture of phenyl glyoxal monohydrate (2.5 mmol) and aromatic amines (2.5 mmol), dienophiles [cyclopentadiene (5 mmol) or 3,4-dihydropyran (5 mmol) or dihydrofuran (5 mmol)] in CH_3CN (10 mL), $PPh_3{\cdot}HClO_4$ (0.363 g, 40 mol%) was added and stirred at room temperature for appropriate times. To the reaction mixture water was added (25 mL) and extracted with $CHCl_3$ (3×10 mL), washed with brine and dried over anhydrous Na_2SO_4, filtered, and the solvent evaporated. The residue was purified by column chromatography with petroleum ether/ethyl acetate to afford the cycloadducts.

3.1.1. (4aα,5β,10bα)-3,4,4a,5,6,10b-Hexahydro-5-phenyl-2*H*-pyrano[3,2-c]quinoline (3a). 0.440 g (66%) of colourless solid, mp 123–124°C; IR (KBr) 3378, 3316, 2936, 1605, 1485, 1071 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41–7.24 (m, 6H), 7.13–7.06 (m, 1H), 6.83–6.76 (m, 1H), 6.62 (d, 1H, *J*=7.6 Hz), 5.34 (d, 1H, *J*=4.5 Hz), 4.68 (brs, 1H), 3.89 (brs, 1H, NH), 3.61 (d, 1H, *J*=11.2 Hz), 3.44–3.26 (m, 1H), 2.17–1.99 (m, 1H), 1.75–1.31 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.2, 141.1, 128.3, 128.0, 127.6, 127.5, 126.8, 119.8, 118.3, 114.4, 72.8, 60.6, 59.3, 38.9, 25.4, 18.0; MS *m*/*z* 265 (M^+); Anal. calcd for $C_{18}H_{19}NO$: C, 81.48; H, 7.22; N, 5.28. Found: C, 81.07; H, 7.25; N, 5.30.

3.1.2. (4aα,5α,10bα)-3,4,4a,5,6,10b-Hexahydro-5-phenyl-2*H*-pyrano[3,2-c]quinoline (4a). 0.250 g (25%) of colourless solid, mp 94–95°C; IR (KBr) 3374, 2928, 1610, 1489, 1077 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43–7.34 (m, 5H), 7.26 (d, 1H, *J*=7.0 Hz), 7.13–7.03 (m, 1H), 6.75–6.59 (m, 1H), 6.54 (d, 1H, *J*=7.8 Hz), 4.74 (d, 1H, *J*=10.6 Hz), 4.41 (brs, 1H), 4.10–4.02 (m, 2H), 3.78–3.69 (m, 1H),

2.08–2.02 (m, 1H), 1.89–1.31 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.1, 141.7, 130.2, 128.7, 128.0, 127.2, 127.1, 120.0, 116.8, 113.5, 73.9, 68.0, 54.1, 38.2, 23.5, 21.4; MS *m/z* 265 (M^+); Anal. calcd for $C_{18}H_{19}NO$: C, 81.48; H, 7.22; N, 5.28. Found: C, 81.09; H, 7.24; N, 5.25.

3.1.3. (4aα,5β,10bα)-9-Chloro-3,4,4a,5,6,10b-hexahydro-5-phenyl-2*H*-pyrano[3,2-c]quinoline (3b). 0.313 g (42%) of colourless solid, mp 154–155°C; IR (KBr) 3362, 3326, 2937, 1615, 1487, 1071 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37–7.28 (m, 6H), 7.03 (d, 1H, *J*=8.2 Hz), 6.53 (d, 1H, *J*=8.3 Hz), 5.24 (brs, 1H), 4.64 (brs, 1H) 3.89 (brs, 1H, NH), 3.61 (d, 1H, *J*=11.2 Hz), 3.43–3.31 (m, 1H), 2.13–2.07 (m, 1H), 1.78–1.31 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.6, 141.3, 128.1, 128.0, 127.3, 127.1, 126.8, 119.3, 118.0, 114.4, 72.7, 60.5, 59.0, 38.2, 25.4, 18.2; MS *m/z* 265 (M^+); Anal. calcd for $C_{18}H_{18}ClNO$: C, 72.11; H, 6.05; N, 4.67. Found: C, 72.34; H, 6.09; N, 4.73.

3.1.4. (4aα,5α,10bα)-9-Chloro-3,4,4a,5,6,10b-hexahydro-5-phenyl-2*H*-pyrano[3,2-c]quinoline (4b). 0.382 g (51%) of colourless solid, mp 122–123°C; IR (KBr) 3348, 2934, 1494, 1265 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (m, 5H), 7.19 (s, 1H), 7.03 (d, 1H, *J*=8.3 Hz), 6.45 (d, 1H, *J*=8.3 Hz), 4.67 (d, 1H, *J*=10.5 Hz), 4.33 (s, 1H), 4.08 (m, 2H), 3.73 (m, 1H), 2.05 (m, 1H), 1.83–1.31 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.2, 141.8, 130.3, 129.1, 128.6, 127.6, 121.8, 121.7, 115.2, 73.8, 68.4, 54.8, 38.6, 23.9, 22.0; MS *m/z* 299 (M^+), 301 (M+2); Anal. calcd for $C_{18}H_{18}ClNO$: C, 72.11; H, 6.05; N, 4.67. Found: C, 71.78; H, 6.02; N, 4.65.

3.1.5. (4aα,5β,10bα)-3,4,4a,5,6,10b-Hexahydro-9-methoxy-5-phenyl-2*H*-pyrano[3,2-c]quinoline (3c). 0.357 g (48%) of colourless solid, mp 146–147°C; IR (KBr) 3295, 2942, 1502, 1262, 1065 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40–7.29 (m, 5H), 7.03 (s, 1H), 6.73 (d, 1H, *J*=8.2 Hz), 6.57 (d, 1H, *J*=8.2 Hz), 5.31 (d, 1H, *J*=5.4 Hz), 4.61 (s, 1H), 3.73 (s, 3H), 3.67 (brs, 1H), 3.61–3.36 (m, 2H), 2.15 (m, 1H), 1.54–1.26 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.8, 141.3, 139.1, 128.3, 127.4, 126.8, 121.1, 115.7, 115.0, 111.8, 72.9, 60.8, 59.5, 55.8, 39.1, 25.3, 17.9; MS *m/z* 295 (M^+); Anal. calcd for $C_{19}H_{21}NO_2$: C, 77.26; H, 7.17; N, 4.74. Found: C, 77.65; H, 7.20; N, 4.77.

3.1.6. (4aα,5α,10bα)-3,4,4a,5,6,10b-Hexahydro-9-methoxy-5-phenyl-2*H*-pyrano[3,2-c]quinoline (4c). 0.343 g (47%), dense liquid; IR (neat) 3361, 2938, 1504, 1255, 1032 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43–7.27 (m, 5H), 6.82 (s, 1H), 6.75 (d, 1H, *J*=9.1 Hz), 6.49 (d, 1H, *J*=8.5 Hz), 4.62 (d, 1H, *J*=10.5 Hz), 4.38 (s, 1H), 4.10 (m, 1H), 3.75 (m, 5H), 2.10 (m, 1H), 1.84–1.30 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.9, 142.2, 138.7, 128.1, 127.7, 121.3, 116.7, 115.5, 114.7, 74.5, 68.3, 55.7, 55.1, 38.8, 24.0, 21.9; MS *m/z* 295 (M^+).

3.1.7. (4aα,5β,10bα)-3,4,4a,5,6,10b-Hexahydro-5-(4-chlorophenyl)-2*H*-pyrano[3,2-c]quinoline (3d). 0.395 g (53%) of colourless solid, mp 168.4–169°C; IR (KBr) 3379, 2928, 1492, 1261 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35–7.26 (m, 5H), 7.21 (s, 1H), 6.76–6.62 (m, 1H), 6.54 (d, 1H, *J*=8.1 Hz), 5.23 (d, 1H, *J*=5.4 Hz), 4.84 (s, 1H), 3.91 (brs, 1H), 3.71 (d, 1H, *J*=11.3 Hz), 3.64–3.43 (m, 1H), 1.98–1.81 (m, 1H), 1.79–1.54 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.1, 140.6, 133.0, 130.4, 129.1, 128.8, 128.5, 120.6, 117.4, 113.9, 74.5, 68.6, 53.9, 38.8, 24.0, 21.9; MS *m/z* 299 (M^+), 301 (M+2); Anal. calcd for $C_{18}H_{18}ClNO$: C, 72.11; H, 6.05; N, 4.67. Found: C, 72.38; H, 5.98; N, 4.65.

3.1.8. (4aα,5α,10bα)-3,4,4a,5,6,10b-Hexahydro-5-(4-chlorophenyl)-2*H*-pyrano[3,2-c]quinoline (4d). 0.203 g (27%) of colourless solid, mp 139.2–140.1°C; IR (KBr) 3345, 2931, 1492, 1265 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34–7.06 (m, 6H), 6.73–6.68 (m, 1H), 6.53 (d, 1H, *J*=8.0 Hz), 4.70 (d, 1H, *J*=10.8 Hz), 4.37 (d, 1H, *J*=2.5 Hz), 4.11–4.06 (m, 1H), 4.02 (brs, 1H), 3.75–3.67 (m, 1H), 2.05–2.00 (m, 1H), 1.83–1.60 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.5, 140.8, 133.5, 130.9, 129.4, 129.1, 128.8, 120.6, 117.7, 114.2, 74.3, 68.6, 54.2, 38.9, 24.0, 22.0; MS *m/z* 299 (M^+), 301 (M+2); Anal. calcd for $C_{18}H_{18}ClNO$: C, 72.11; H, 6.05; N, 4.67. Found: C, 72.01; H, 5.98; N, 4.75.

3.1.9. 4-Phenyl-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[c]-quinoline (7a). 0.420 g (68%) of colourless solid, mp 120–121°C; IR (KBr) 3353, 1478 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (m, 5H), 7.06 (m, 2H), 6.78 (m, 1H), 6.64 (d, 1H, *J*=7.9 Hz), 5.90 (m, 1H), 5.71 (m, 1H), 4.67 (d, 1H, *J*=2.9 Hz), 4.15 (d, 1H, *J*=8.6 Hz), 3.78 (brs, 1H), 3.05 (m, 1H), 2.71 (m, 1H), 1.85 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.6, 142.8, 134.0, 130.3, 129.0, 128.4, 127.2, 126.4, 126.3, 126.0, 119.1, 115.9, 58.0, 46.4, 46.0, 31.5; MS *m/z* 247 (M^+); Anal. calcd for $C_{18}H_{17}N$: C, 87.41; H, 6.93; N, 5.66. Found: C, 86.88; H, 6.95; N, 5.68.

3.1.10. 8-Chloro-4-phenyl-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[c]quinoline (7b). 0.457 g (65%) of white solid, mp 150–151°C; IR (KBr) 3363, 1469 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44–7.31 (m, 5H), 7.04 (d, 1H, *J*=2.1 Hz), 6.96 (dd, 1H, *J*=2.2, 8.4 Hz), 6.56 (d, 1H, *J*=8.5 Hz), 5.81 (d, 1H, *J*=2.6 Hz), 5.69 (s, 1H), 4.61 (d, 1H, *J*=3.0 Hz), 4.08 (d, 1H, *J*=8.6 Hz), 3.76 (brs, 1H), 3.05–2.96 (m, 1H), 2.67–2.58 (m, 1H), 1.87–1.78 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.1, 142.3, 133.4, 130.8, 128.6, 128.5, 127.6, 127.3, 126.5, 123.4, 116.9, 58.0, 46.2, 45.7, 31.4; MS *m/z* 281 (M^+); 283 (M+2); Anal. calcd for $C_{18}H_{16}ClN$: C, 76.72; H, 5.72; N, 4.97. Found: C, 76.40; H, 5.74; N, 4.98.

3.1.11. 4-(4-Chlorophenyl)-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[c]quinoline (7d). 0.555 g (79%) of colourless solid, mp 141–142°C; IR (KBr) 3363, 1478 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (m, 4H), 7.36–6.98 (m, 2H), 6.80–6.75 (m, 1H), 6.65 (d, 1H, *J*=7.7 Hz), 5.87–5.85 (m, 1H), 5.66 (s, 1H), 4.62 (d, 1H, *J*=3.0 Hz), 4.13 (d, 1H, *J*=8.5 Hz), 3.69 (brs, 1H), 3.03–2.93 (m, 1H), 2.65–2.56 (m, 1H), 1.85–1.76 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.2, 141.3, 133.9, 132.8, 130.2, 128.9, 127.9, 126.3, 125.9, 119.4, 115.9, 57.4, 46.2, 45.9, 31.3; MS *m/z* 281 (M^+), 283 (M+2); Anal. calcd for $C_{18}H_{16}ClN$: C, 76.72; H, 5.72; N, 4.97. Found: C, 76.56; H, 5.53; N, 4.91.

3.1.12. 4-Phenyl-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[c]-quinoline-4-carboxylic acid (7e). 0.604 g (83%) of colourless solid, mp 206–207°C; IR (KBr) 3349, 1608,

1491 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, 1H, J=8.0 Hz), 7.38 (m, 5H), 6.64 (m, 2H), 5.81 (m, 1H), 5.65 (m, 1H), 4.75 (d, 1H, J=2.7 Hz), 4.48 (s, 1H), 4.13 (d, 1H, J=8.4 Hz), 3.02 (m, 1H), 2.58 (m, 1H), 1.82 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.3, 150.2, 142.1, 135.5, 134.9, 130.6, 130.0, 128.6, 128.2, 127.1, 127.0, 126.8, 126.1, 116.2, 111.8, 56.4, 45.8, 45.3, 31.7; MS *m/z* 291 (M^+); Anal. calcd for $C_{19}H_{17}NO_2$: C, 78.33; H, 5.88; N, 4.81. Found: C, 77.99; H, 5.86; N, 4.82.

3.1.13. 6,7-Dimethyl-4-phenyl-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[c]quinoline (7f). 0.536 g (78%) of pale yellow solid, mp 114.5–114.6°C; IR (KBr) 3384, 1469 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.62–7.40 (m, 5H), 6.97(d, 1H, J=7.5 Hz), 6.71 (d, 1H, J=7.5 Hz), 5.98 (m, 1H), 5.79 (s, 1H), 4.65 (d, 1H, J=2.7 Hz), 4.42 (d, 1H, J=8.1 Hz), 3.80 (brs, 1H), 3.33–3.25 (m, 1H), 2.96–2.87 (m, 1H), 2.48 (s, 3H), 2.26 (s, 3H), 2.04–1.96 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.8, 142.9, 134.2, 130.6, 128.4, 127.6, 126.4, 124.4, 120.5, 119.7, 58.5, 46.1, 45.6, 32.0, 19.5, 17.0; MS *m/z* 275; Anal. calcd for $C_{20}H_{21}N$: C, 87.23; H, 7.69; N, 5.09. Found: C, 87.36; H, 7.01; N, 4.99.

3.1.14. (3aα,4β,9bα)-2,3,3a,4,5,9b-Tetrahydro-4-benzyloxy-2*H*-furo[3,2-c]quinoline (11). 0.188 g (27%), dense liquid; IR (neat) 3380, 1679 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, 1H, J=7.5 Hz), 7.61–7.03 (m, 6H), 6.80–6.64 (m, 2H), 5.19 (d, 1H, J=3.1 Hz), 5.12 (m, 1H), 3.94 (brs, 1H), 3.87–3.81 (m, 2H), 3.72–3.64 (m, 1H), 2.98 (m, 1H), 2.66–2.61 (m, 1H), 1.98–1.80 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.7, 143.2, 134.0, 133.6, 133.4, 130.7, 128.9, 128.8, 128.6, 126.2, 120.4, 119.0, 115.5, 75.1, 65.5, 57.6, 38.7, 29.2; MS *m/z* 279 (M^+).

3.1.15. (3aα,4α,9bα)-2,3,3a,4,5,9b-Tetrahydro-4-benzyloxy-2*H*-furo[3,2-c]quinoline (12). 0.349 g (50%) of colourless solid, mp 149–150°C; IR (KBr) 3359, 1680 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.09–7.98 (m, 2H), 7.61–7.07 (m, 5H), 6.82–6.77 (m, 1H), 6.64 (d, 1H, J=8.1 Hz), 4.67 (d, 1H, J=5.5 Hz), 4.50 (d, 1H, J=9.2 Hz), 4.24 (brs, 1H), 4.00–3.93 (m, 1H), 3.86–3.78 (m, 1H), 2.76–2.67 (m, 1H), 2.27–2.15 (m, 1H), 1.86–1.76 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.9, 143.4, 135.9, 133.8, 133.4, 130.8, 129.0, 128.9, 128.7, 126.1, 120.3, 119.0, 115.3, 75.1, 65.4, 57.4, 38.8, 29.3; MS *m/z* 255 (M^+); Anal. calcd for $C_{18}H_{17}NO_2$: C, 77.40; H, 6.14; N, 5.02. Found: C, 77.28; H, 6.22; N, 5.16.

3.1.16. 4-Benzyloxy-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[c]quinoline (13a). 0.564 g (82%) of colourless solid, mp 157–158°C; IR (KBr) 3384, 1681 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.93–7.85 (m, 2H), 7.60–7.47 (m, 3H), 7.06–6.98 (m, 2H), 6.76–6.67 (m, 2H), 5.73 (t, 1H), 5.56 (s, 1H), 5.05 (d, 1H, J=3.1 Hz), 4.42 (brs, 1H), 4.21 (d, 1H, J=8.9 Hz), 3.37–3.27 (m, 1H), 2.47–2.38 (m, 1H), 1.94–1.86 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.1, 143.9, 135.5, 133.9, 133.2, 129.5, 128.7, 128.0, 126.5, 125.8, 118.9, 115.8, 59.7, 46.9, 42.5, 31.4; MS *m/z* 309 (M^+), 311 (M+2); Anal. calcd for $C_{19}H_{17}NO$: C, 82.88; H, 6.22; N, 5.08. Found: C, 83.69; H, 6.19; N, 5.16.

3.1.17. 8-Chloro-4-benzyloxy-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[c]quinoline (13b). 0.718 g (93%) of colourless solid, mp 175–176°C; IR (KBr) 3386, 1679 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.93–7.88 (m, 2H), 7.59–7.24 (m, 3H), 6.98–6.91 (m, 2H), 6.60 (d, 1H, J=8.5 Hz), 5.68 (d, 1H, J=2.6 Hz), 5.56 (s, 1H), 5.01 (d, 1H, J=3.1 Hz), 4.46 (brs, 1H), 4.13 (d, 1H, J=8.8 Hz), 3.34–3.23 (m, 1H), 2.40–2.31 (m, 1H), 1.92–1.83 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.8, 142.4, 135.3, 133.4, 130.1, 128.8, 128.4, 128.0, 127.4, 126.5, 123.2, 116.9, 59.5, 46.8, 42.3, 31.4; MS *m/z* 309 (M^+), 311 (M+2); Anal. calcd for $C_{19}H_{16}ClNO$: C, 73.69; H, 5.22; N, 4.46. Found: C, 83.09; H, 6.19; N, 5.16.

3.1.18. 11-Nitro-6-phenyl-6,6a,7,9b-tetrahydro-5*H*-benzo-[h]cyclopenta[c]quinoline (15). 0.612 g (92%) of brown solid, mp 198.9°C (d); IR (KBr) 3398, 1495 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.99 (d, 1H, J=8.8 Hz), 8.41 (s, 1H), 7.72–7.60 (m, 2H), 7.49–7.44 (m, 1H), 5.90 (m, 1H), 5.74–5.72 (m, 1H), 5.54 (brs, 1H), 3.99 (s, 1H), 3.43–3.37 (m, 1H), 3.06 (t, 1H), 2.77–2.73 (m, 2H), 2.20–2.15 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.5, 135.5, 130.1, 129.1, 126.3, 121.9, 119.8, 115.6, 46.2, 43.5, 37.0, 34.7; MS *m/z* 266 (M^+); Anal. calcd for $C_{16}H_{14}N_2O_2$: C, 72.17; H, 5.30; N, 10.52. Found: C, 71.32; H, 5.49; N, 9.88.

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