Versatile and Mild HCl-catalyzed Cationic Imino Diels-Alder Reaction for the synthesis of new tetrahydroquinoline derivatives.

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1. General Experimental Information

All reagents were purchased from Merck, J.T. Baker and Sigma and Aldrich Chemical Co. and used without further purification. The reaction progress was monitored using thin layer chromatography on PF254 TLC aluminum sheets from Merck. Column chromatography was performed using Silica gel (60-120 mesh). The melting points (uncorrected) were determined using a Fisher-Johns melting point apparatus. IR spectra were recorded on a FTIR Bruker Tensor 27 spectrophotometer coupled to a Bruker platinum ATR cell. Mass spectra were recorded on an ESI-IT Amazon X (Bruker Daltonics) with direct injection, operating in Full Scan mode at 300°C and 4500V in the capillary, using nitrogen as nebulizer gas with an influx of 8 L/min and 30 psi.

NMR spectra (^1H and ^{13}C) were measured on a Bruker Ultrashield-400 spectrometer (400 MHz ^1H NMR and 100 MHz ^{13}C NMR), using CDCl_3 as solvent and reference. J values are reported in Hz; chemical shifts are reported in ppm (δ) relative to the solvent peak (residual CHCl_3 in CDCl_3 at 7.26 ppm for protons). Signals were designated as follows: s, singlet; d, doublet; dd, doublet of doublets; ddd, doublet of doublets of doublets; t, triplet; td, triplet of doublets; q, quartet; m, multiplet; br., broad.

General procedure for the synthesis of *N*-benzyl-4-aryl tetrahydroquinolines: All the reactions were performed at room temperature unless otherwise stated. In a round bottom flask, a 5 mL solution in anhydrous acetonitrile of *N*-benzylaniline (1 mmol) and formaldehyde (37% in methanol) (1.1 mmol) was prepared and stirred for 10 minutes. A 5 mL solution of HCl 2N (1.1 mmol) in MeCN was then added and after stirring for 20 minutes, the dienophile (trans-anethole or isoeugenol) (1.1 mmol) was incorporated to the reaction mixture and was vigorously stirred. The reaction achieved completion within 2-21 hours (monitored by TLC). The mixture was poured into a saturated solution of NaHCO_3 (15 mL), extracted with ethyl acetate (3 x 15 mL) and dried over Na_2SO_4 . The crude product

was obtained by solvent removal under vacuum and then purified by column chromatography, eluted with the appropriate mixture of petroleum ether (b.p. 40-60°C) and ethyl acetate. The products were obtained as solids in all cases.

trans-N-benzyl-4-(4-methoxyphenyl)-3-methyl-1,2,3,4-tetrahydroquinoline (6a). White solid; m.p. 102-104 °C; IR (ATR): 3026, 2953, 1243, 1034, 732 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ (ppm): 0.89 (3H, d, J = 6.6 Hz, $-\text{CH}_3$), 2.15 (1H, m, 3-H), 3.02 (1H, dd, J = 11.3, 8.1 Hz, 2-Ha), 3.23 (1H, dd, J = 11.4, 3.6 Hz, 2-Hb), 3.43 (1H, d, J = 6.1 Hz, 5-H), 3.57 (1H, d, J = 7.7 Hz, 4-H), 3.78 (3H, s, $-\text{OCH}_3$), 4.45 (2H, s, $-\text{CH}_2\text{-Ph}$), 6.43 (2H, dd, J = 8.7 Hz, 2- H_{Ar} y 6- H_{Ar}), 6.65 (1H, d, J = 8.2, 1.3 Hz, 8-H), 6.80 (2H, d, J = 8.6 Hz, 3- H_{Ar} and 5- H_{Ar}), 6.98 (2H, dd, J = 8.7, 3.2 Hz, 6-H and 7-H), 7.21-7.32 (5H, m, all- H_{Ph}). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 18.2, 34.9, 50.6, 54.6, 55.2, 55.6, 110.9, 113.6 (2C), 127.3, 127.4, 128.5 (2C), 129.4, 129.9 (2C), 130.8, 130.9, 137.9, 139.3, 143.5, 157.9. MS (ESI-IT), m/z : $[\text{M}+\text{H}]^+$: 344.5 (70), $[\text{M}+\text{Na}]^+$: 366.5 (100). Anal. Calcd for $\text{C}_{24}\text{H}_{25}\text{NO}$: C, 83.93; H, 7.34; N, 4.08%. Found: C, 83.73; H, 7.28; N, 4.05%.

trans-N-benzyl-3,6-dimethyl-4-(4-methoxyphenyl)-1,2,3,4-tetrahydroquinoline (6b). White solid; m.p. 91-92 °C; IR (ATR): 3027, 2937, 1237, 1034, 728 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ (ppm): 0.97 (3H, d, J = 6.7 Hz, $-\text{CH}_3$), 2.12 (3H, s, 6- CH_3), 2.23 (1H, m, 3-H), 3.10 (1H, dd, J = 11.4, 8.0 Hz, 2-Ha), 3.32 (1H, dd, J = 11.4, 3.7 Hz, 2-Hb), 3.68 (1H, d, J = 7.9 Hz, 4-H), 3.85 (3H, s, $-\text{OCH}_3$), 4.54 (2H, s, $-\text{CH}_2\text{-Ph}$), 6.54 (2H, d, J = 8.4 Hz, 5-H and 8-H), 6.85 (1H, dd, J = 8.1, 1.9 Hz, 7-H), 6.89 (2H, d, J = 8.7 Hz, 2- H_{Ar} and 6- H_{Ar}), 7.08 (2H, d, J = 8.7 Hz, 3- H_{Ar} and 5- H_{Ar}), 7.28-7.37 (5H, m, all- H_{Ph}). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 18.5, 20.4, 34.9, 50.8, 54.6, 55.3, 55.7, 111.1, 113.7 (2C), 124.7, 125.2, 126.8 (2C), 126.9, 127.9, 128.7 (2C), 130.1 (2C), 131.2, 138.0, 139.4, 143.4, 158.0. MS (ESI-IT), m/z : $[\text{M}+\text{H}]^+$: 358.1 (100), $[\text{M}+\text{Na}]^+$: 380.1 (35). Anal. Calcd for $\text{C}_{25}\text{H}_{27}\text{NO}$: C, 83.99; H, 7.61; N, 3.92%. Found: C, 83.94; H, 7.54; N, 3.86%.

trans-N-benzyl-6-ethyl-3-methyl-4-(4-methoxyphenyl)-1,2,3,4-tetrahydroquinoline (6c). Red solid; m.p. 55-56 °C; IR (ATR): 3028, 2958, 1243, 1034, 732 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ (ppm): 0.95 (3H, d, $J = 6.7$ Hz, $-\text{CH}_3$), 1.09 (3H, t, $J = 7.6$ Hz, $-\text{CH}_2\text{CH}_3$), 2.23 (1H, m, 3-H), 2.41 (2H, q, $J = 7.6$ Hz, $-\text{CH}_2\text{CH}_3$), 3.10 (1H, dd, $J = 11.4$, 8.1 Hz, 2-H_a), 3.31 (1H, dd, $J = 11.4$, 3.8 Hz, 2-H_b), 3.68 (1H, d, $J = 8.1$ Hz, 4-H), 3.84 (3H, s, $-\text{OCH}_3$), 4.53 (2H, m, $-\text{CH}_2\text{-Ph}$), 6.55 (1H, s, 5-H), 6.55 (1H, d, $J = 8.3$ Hz, 8-H), 6.87 (1H, dd, $J = 8.0$, 2.0 Hz, 7-H), 6.88 (2H, d, $J = 8.7$ Hz, 2-H_{Ar} and 6-H_{Ar}), 7.08 (2H, d, $J = 8.7$ Hz, 3-H_{Ar} and 5-H_{Ar}), 7.28-7.36 (5H, m, all-H_{Ph}). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 15.9, 18.4, 27.9, 34.9, 50.9, 54.8, 55.3, 55.8, 111.0, 113.7 (2C), 124.7, 126.6, 126.8 (2C), 126.9, 128.7 (2C), 130.1, 130.1 (2C), 131.8, 137.9, 139.4, 143.6, 158.0. MS (ESI-IT), m/z : $[\text{M}+\text{H}]^+$: 372.1 (100), $[\text{M}+\text{Na}]^+$: 394.1 (73), $[\text{M}+\text{K}]^+$: 410.4 (44). Anal. Calcd for $\text{C}_{26}\text{H}_{29}\text{NO}$: C, 84.06; H, 7.87; N, 3.77%. Found: C, 83.94; H, 7.76; N, 3.69%.

trans-N-benzyl-6-methoxy-4-(4-methoxyphenyl)-3-methyl-1,2,3,4-tetrahydroquinoline (6d). White solid; m.p. 119-120 °C; IR (ATR): 3032, 2952, 1238, 1039, 701 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ (ppm): 0.95 (3H, d, $J = 6.7$ Hz, $-\text{CH}_3$), 2.24 (1H, m, 3-H), 3.08 (1H, dd, $J = 11.4$, 8.5 Hz, 2-H_a), 3.29 (1H, dd, $J = 11.4$, 3.7 Hz, 2-H_b), 3.61 (3H, s, $-\text{OCH}_3$), 3.65 (1H, d, $J = 8.3$ Hz, 4-H), 3.83 (3H, s, $-\text{OCH}_3$), 4.49 (2H, s, $-\text{CH}_2\text{Ph}$), 6.32 (1H, d, $J = 2.4$ Hz, 5-H), 6.55 (1H, d, $J = 8.9$ Hz, 8-H), 6.63 (1H, dd, $J = 8.8$, 3.0 Hz, 7-H), 6.87 (2H, d, $J = 8.7$ Hz, 2-H_{Ar} and 6-H_{Ar}), 7.07 (2H, d, $J = 8.6$ Hz, 3-H_{Ar} and 5-H_{Ar}), 7.36-7.28 (5-H, m, all-H_{Ph}). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 18.4, 35.1, 51.2, 55.1, 55.4, 55.7, 56.3, 112.1, 112.6, 113.8 (2C), 116.7, 126.5, 126.8, 126.9 (2C), 128.7 (2C), 130.1 (2C), 137.5, 139.5, 140.2, 151.0, 158.1. MS (ESI-IT) m/z : $[\text{M}+\text{H}]^+$: 374.1 (36), $[\text{M}+\text{Na}]^+$: 396.0 (100), $[\text{M}+\text{K}]^+$: 412.1 (3), $[2\text{M}+\text{Na}]^+$: 769.3 (38). Anal. Calcd for $\text{C}_{25}\text{H}_{27}\text{NO}_2$: C, 80.40; H, 7.29; N, 3.75%. Found: C, 80.25; H, 7.21; N, 3.70%.

trans-N-benzyl-6-chloro-4-(4-methoxyphenyl)-3-methyl-1,2,3,4-tetrahydroquinoline (6e). White solid; m.p. 90-92 °C; IR (ATR): 3031, 2955, 1245, 1025, 731 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ (ppm): 0.94 (3H, d, $J = 6.7$ Hz, - CH_3), 2.22 (1H, m, 3-H), 3.12 (1H, dd, $J = 11.6, 8.1$ Hz, 2-Ha), 3.33 (1H, dd, $J = 11.6, 3.9$ Hz, 2-Hb), 3.63 (1H, d, $J = 8.0$ Hz, 4-H), 3.83 (3H, s, $-\text{OCH}_3$), 4.52 (2H, s, $-\text{CH}_2\text{Ph}$), 6.48 (1H, d, $J = 8.8$ Hz, 8-H), 6.65 (1H, dd, $J = 2.6, 0.8$ Hz, 5-H), 6.88 (2H, d, $J = 8.7$ Hz, 2- H_{Ar} and 6- H_{Ar}), 6.94 (1H, dd, $J = 8.8, 2.6$ Hz, 7-H), 7.04 (2H, d, $J = 8.7$ Hz, 3- H_{Ar} and 5- H_{Ar}), 7.27-7.36 (5H, m, all- H_{Ph}), ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 18.3, 34.5, 50.7, 54.7, 55.4, 55.6, 112.1, 113.9 (2C), 120.7, 126.4, 126.6 (2C), 127.1, 127.2, 128.8 (2C), 130.0, 130.1, 136.8, 138.5, 144.0, 158.3. MS (ESI-IT), m/z : $[\text{M}+\text{H}]^+$: 379.0 (16), $[\text{M}+\text{Na}]^+$: 400.0 (14). Anal. Calcd for $\text{C}_{24}\text{H}_{24}\text{ClNO}$: C, 76.28; H, 6.40; Cl, 9.38; N, 3.71%. Found: C 76.13; H, 6.35; N, 3.64%.

trans-N-benzyl-6-fluor-4-(4-methoxyphenyl)-3-methyl-1,2,3,4-tetrahydroquinoline (6f). White solid; m.p. 94-95 °C; IR (ATR): 3024, 2955, 1236, 1030, 729 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ (ppm): 0.95 (3H, d, $J = 6.7$ Hz, - CH_3), 2.25 (1H, m, 3-H), 3.14 (1H, dd, $J = 11.5, 8.6$ Hz, 2-Ha), 3.33 (1H, dd, $J = 11.5, 3.8$ Hz, 2-Hb), 3.65 (1H, d, $J = 8.6$ Hz, 4-H), 3.84 (3H, s, $-\text{OCH}_3$), 4.52 (2H, s, $-\text{CH}_2\text{Ph}$), 6.43 (1H, ddd, $J = 9.7, 3.1, 0.8$ Hz, 5-H), 6.50 (1H, dd, $J = 8.5, 4.7$ Hz, 8-H), 6.72 (1H, td, $J = 8.5, 3.0$ Hz, 7-H), 6.90 (2H, d, $J = 8.7$ Hz, 2- H_{Ar} and 6- H_{Ar}), 7.07 (2H, d, $J = 8.7$ Hz, 3- H_{Ar} and 5- H_{Ar}), 7.41-7.26 (5H, m, all- H_{Ph}). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 18.2, 34.7, 51.1, 55.2, 55.4, 56.1, 111.8, 113.6 (1C, d, $J = 21.9$ Hz), 113.9 (2C), 116.8 (1C, d, $J = 22.4$ Hz), 126.4, 126.8 (2C), 127.1, 128.8 (2C), 130.1 (2C), 136.9, 138.9, 141.9, 155.1 (1C, d, $J = 238.9$ Hz), 158.3. MS (ESI-IT) m/z : $[\text{M}+\text{H}]^+$: 362.1 (100), $[\text{M}+\text{Na}]^+$: 384.0 (62), $[\text{M}+\text{K}]^+$: 400.0 (32). Anal. Calcd for $\text{C}_{24}\text{H}_{24}\text{FNO}$: C, 79.75; H, 6.69; F, 5.26; N, 3.88%. Found: C, 79.68; H, 6.61; N, 3.82%.

trans-N-benzyl-8-methoxy-4-(4-methoxyphenyl)-3-methyl-1,2,3,4-tetrahydroquinoline (6g). White solid; m.p. 115-116 °C; Yield: 12%; IR (ATR): 3024, 2958, 1238, 1026, 749 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ (ppm): 0.79 (3H, d, $J = 6.5$ Hz, $-\text{CH}_3$), 2.02 (1H, m, 3-H), 2.78 (1H, dd, $J = 13.2, 11.4$ Hz, 2-Ha), 3.06 (1H, dd, $J = 13.5, 3.2$ Hz, 2-Hb), 3.46 (1H, d, $J = 10.3$ Hz, 4-H), 3.82 (3H, s, $-\text{OCH}_3$), 3.91 (3H, s, $8-\text{OCH}_3$), 4.15 (1H, d, $J = 14.2$ Hz, $\text{CH}_{2(a)}\text{Ph}$), 4.56 (1H, d, $J = 14.1$ Hz, $\text{CH}_{2(b)}\text{Ph}$), 6.36 (1H, d, $J = 7.6$ Hz, 5-H), 6.73 (1H, d, $J = 8.0, 1.3$ Hz, 7-H), 6.78 (1H, dd, $J = 7.7, 8.2$ Hz, 6-H), 6.84 (2H, d, $J = 8.7$ Hz, 2- H_{Ar} and 6- H_{Ar}), 6.99-7.03 (2H, m, 3- H_{Ar} and 5- H_{Ar}), 7.28-7.33 (1H, m, 4- H_{ph}), 7.35-7.40 (2H, m, 3- H_{ph} and 5- H_{ph}), 7.52 (2H, d, $J = 7.1$ Hz, 2- H_{ph} and 6- H_{ph}), ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 17.7, 30.9, 52.3, 54.0, 55.3, 55.5, 58.2, 108.6, 113.7 (2C), 121.3, 122.9, 127.1, 128.4 (2C), 129.0 (2C), 130.2 (2C), 133.7, 137.5, 137.7, 140.3, 152.0, 158.1. MS (ESI-IT) m/z : $[\text{M}+\text{H}]^+$: 374.1 (100), $[\text{M}+\text{Na}]^+$: 396.1 (22), $[2\text{M}+\text{Na}]^+$: 769.2 (4). Anal. Calcd for $\text{C}_{25}\text{H}_{27}\text{NO}_2$: C, 80.40; H, 7.29; N, 3.75%. Found: C, 80.32; H, 7.22; N, 3.68%.

trans-N-benzyl-4-(4-hydroxy-3-methoxyphenyl)-3-methyl-1,2,3,4-tetrahydroquinoline (6j). White solid; m.p. 167-169 °C; IR (ATR): 3413, 3022, 2964, 1261, 1029, 725 cm^{-1} . ^1H -NMR (400 MHz, CDCl_3) δ (ppm): 0.89 (3H, d, $J = 6.4$ Hz, $-\text{CH}_3$), 2.16 (1H, m, 3-H), 3.04 (1H, dd, $J = 10.5, 9.0$ Hz, 2-Ha), 3.26 (1H, dd, $J = 11.2, 2.8$ Hz, 2-Hb), 3.44 (1H, s, 5-H), 3.54 (1H, d, $J = 8.1$ Hz, 4-H), 3.72 (3H, s, $-\text{OCH}_3$), 4.45 (2H, s, $-\text{CH}_2\text{-Ph}$), 5.52 (1H, s, $-\text{OH}$), 6.44 (2H, t, $J = 7.9$ Hz, 8-H and 6-H), 6.53 (1H, d, $J = 8.0$ Hz, 2- H_{Ar}), 6.58 (1H, d, $J = 7.9$ Hz, 6- H_{Ar}), 6.64 (1H, d, $J = 8.1$ Hz, 7-H), 6.82 (2H, d, $J = 8.0$ Hz, 5- H_{Ar}), 7.20-7.35 (5H, m, all- H_{ph}). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 18.2, 34.8, 51.3, 54.9, 55.7, 55.9, 110.8, 111.1, 113.9, 122.2, 124.4, 126.7 (2C), 126.7, 127.3, 128.5, 129.6, 130.7, 137.5, 139.3, 143.5, 143.8, 146.4. MS (ESI-IT), m/z : $[\text{M}+\text{H}]^+$: 360.5 (65), $[\text{M}+\text{Na}]^+$: 382.5 (100). Anal. Calcd for $\text{C}_{24}\text{H}_{25}\text{NO}_2$: C, 80.19; H, 7.01; N, 3.90%. Found: C, 80.09; H, 6.91; N, 3.84%.

trans-N-benzyl-3,6-dimethyl-4-(4-hydroxy-3-methoxyphenyl)-1,2,3,4-tetrahydroquinoline (6k). White solid; m.p. 127-129 °C; IR (ATR): 3541, 3024, 2947, 1258, 1020, 734 cm^{-1} . ^1H NMR (400 MHz, CDCl_3), δ (ppm): 0.99 (3H, d, $J = 6.7$ Hz, $-\text{CH}_3$), 2.15 (3H, s, 6- CH_3), 2.27 (1H, m, 3-H), 3.12 (1H, dd, $J = 11.3, 8.2$ Hz, 2-Ha), 3.36 (1H, dd, $J = 11.4, 3.8$ Hz, 2-Hb), 3.67 (1H, d, $J = 8.1$ Hz, 4-H), 3.87 (3H, s, $-\text{OCH}_3$), 4.55 (2H, d, $J = 7.2$ Hz, $-\text{CH}_2\text{-Ph}$), 5.58 (1H, s, $-\text{OH}$), 6.57 (1H, d, $J = 8.4$ Hz, 8-H), 6.59 (1H, s, 5-H), 6.69 (2H, d, $J = 8.3$ Hz, 2- H_{Ar} and 6- H_{Ar}), 6.86 (1H, dd, $J = 8.1, 1.4$ Hz, 7-H), 6.88 (1H, d, $J = 8.0$ Hz, 5- H_{Ar}), 7.26-7.40 (5H, m, all- H_{Ph}). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 18.2, 20.2, 34.7, 51.3, 54.7, 55.6, 55.9, 110.9, 111.1, 114.0, 122.2, 124.5, 125.1, 126.7 (2C), 126.7, 127.8, 128.5 (2C); 130.9, 137.6, 139.2, 143.2, 143.9, 146.5. MS (ESI-IT), m/z : $[\text{M}+\text{H}]^+$: 374.1 (100), $[\text{M}+\text{Na}]^+$: 396.1 (6). Anal. Calcd for $\text{C}_{24}\text{H}_{27}\text{NO}_2$: C, 80.40; H, 7.29; N, 3.75%. Found: C, 80.32; H, 7.21; N, 3.69.

trans-N-benzyl-6-ethyl-3-methyl-4-(4-hydroxy-3-methoxyphenyl)-1,2,3,4-tetrahydroquinoline (6l). Red solid; m.p. 57-59 °C; IR (ATR): 3520, 3025, 2959, 1231, 1034, 732 cm^{-1} . ^1H NMR (400 MHz, CDCl_3), δ (ppm): 0.96 (3H, d, $J = 6.7$ Hz, $-\text{CH}_3$), 1.11 (3H, t, $J = 7.6$ Hz, $-\text{CH}_2\text{CH}_3$), 2.26 (1H, m, 3-H), 2.43 (2H, q, $J = 7.6$ Hz, $-\text{CH}_2\text{CH}_3$), 3.13 (1H, dd, $J = 11.4, 8.4$ Hz, 2-Ha), 3.35 (1H, dd, $J = 11.4, 3.8$ Hz, 2-Hb), 3.66 (1H, d, $J = 8.4$ Hz, 4-H), 3.86 (3H, s, $-\text{OCH}_3$), 4.54 (2H, m, $-\text{CH}_2\text{-Ph}$), 5.63 (1H, s, $-\text{OH}$), 6.55-6.59 (2H, m, 5-H and 8-H), 6.66-6.70 (2H, m, 2- H_{Ar} and 6- H_{Ar}), 6.88 (1H, d, $J = 8.0$ Hz, 7-H), 6.91 (1H, s, 5- H_{Ar}), 7.27-7.40 (5H, m, all- H_{Ph}). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 16.0, 18.3, 27.8, 34.8, 51.5, 55.0, 55.7, 56.0, 110.9, 111.1, 114.0, 122.4, 124.8, 126.6, 126.7 (2C), 126.8, 128.6 (2C), 129.9, 131.8, 137.5, 139.3, 143.5, 143.9, 146.6. MS (ESI-IT), m/z : $[\text{M}+\text{H}]^+$: 388.1 (11), $[\text{M}+\text{Na}]^+$: 410.2 (21), $[2\text{M}+\text{Na}]^+$: 796.4 (4). Anal. Calcd for $\text{C}_{26}\text{H}_{29}\text{NO}_2$: C, 80.59; H, 7.54; N, 3.61%. Found: C, 80.47; H, 7.46; N, 3.55%.

trans-N-benzyl-6-methoxy-3-methyl-4-(4-hydroxy-3-methoxyphenyl)-1,2,3,4-tetrahydroquinoline (6m). Beige solid; m.p. 114-115 °C; Yield: 83 %; IR (ATR): 3542, 3023, 2945, 1234, 1021, 728 cm⁻¹. ¹H NMR (400 MHz, CDCl₃), δ (ppm): 0.92 (3H, d, *J* = 6.6 Hz, -CH₃), 2.22 (1H, m, 3-H), 3.04 (1H, dd, *J* = 11.2, 8.7 Hz, 2-Ha), 3.27 (1H, dd, *J* = 11.4, 3.7 Hz, 2-Hb), 3.58 (3H, s, 6-OCH₃), 3.59 (1H, d, *J* = 8.5 Hz, 4-H), 3.80 (3H, s, -OCH₃), 4.46 (2H, d, *J* = 2.6 Hz, -CH₂-Ph), 5.55 (1H, s, -OH), 6.32 (1H, d, *J* = 2.6 Hz, 5-H), 6.53 (1H, d, *J* = 8.9 Hz, 8-H), 6.59 (2H, m, 2-H_{Ar} and 6-H_{Ar}), 6.63 (1H, dd, *J* = 8.2, 1.3 Hz, 7-H), 6.84 (1H, d, *J* = 8.0 Hz, 5-H_{Ar}), 7.23-7.32 (5H, m, all-H_{Ph}). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 18.2, 34.8, 51.7, 55.1, 55.6, 55.9, 56.1, 111.1, 111.9, 112.6, 114.0, 116.6, 122.2, 126.3, 126.7 (2C), 126.8, 128.5 (2C), 137.1, 139.3, 140.1, 144.0, 146.5, 150.9. MS (ESI-IT), *m/z*: [M+H]⁺: 390.1 (100), [M+Na]⁺: 412.1 (15), [2M+Na]⁺: 801.0 (14). Anal. Calcd for C₂₅H₂₇NO₃: C, 77.09; H, 6.99; N, 3.60%. Found: C, 77.01; H, 6.93; N, 3.55%.

trans-N-benzyl-6-chloro-3-methyl-4-(4-hydroxy-3-methoxyphenyl)-1,2,3,4-tetrahydroquinoline (6n). White solid; m.p. 136-138 °C; Yield: 93 %; IR (ATR): 3536, 3029, 2947, 1232, 1016, 730 cm⁻¹. ¹H NMR (400 MHz, CDCl₃), δ (ppm): 0.91 (3H, d, *J* = 6.6 Hz, -CH₃), 2.20 (1H, m, 3-H), 3.10 (1H, dd, *J* = 11.5, 8.3 Hz, 2-Ha), 3.32 (1H, dd, *J* = 11.6, 3.8 Hz, 2-Hb), 3.57 (1H, d, *J* = 8.2 Hz, 4-H), 3.82 (3H, s, -OCH₃), 4.50 (2H, s, -CH₂-Ph), 5.57 (1H, s, -OH), 6.47 (1H, d, *J* = 8.8 Hz, 8-H), 6.58 (1H, s, 5-H), 6.59 (1H, d, *J* = 8.2, 2.4 Hz, 6-H_{Ar}), 6.65 (1H, d, *J* = 2.2 Hz, 2-H_{Ar}), 6.86 (1H, d, *J* = 7.9 Hz, 5-H_{Ar}), 6.91 (1H, dd, *J* = 8.2, 1.5 Hz, 7-H), 7.22-7.34 (5H, m, all-H_{Ph}). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 18.1, 34.2, 51.1, 54.7, 55.4, 55.9, 110.9, 111.9, 114.2, 120.5, 122.1, 126.2, 126.5 (2C), 127.0, 127.1, 128.6 (2C), 129.8, 136.4, 138.3, 143.8, 144.2, 146.6. MS (ESI-IT), *m/z*: [M+Na]⁺: 416.2 (85), [2M+Na]⁺: 809.1 (8). Anal. Calcd for C₂₄H₂₄ClNO₃: C, 73.18; H, 6.14; Cl, 9.00; N, 3.56%. Found: C, 73.04; H, 6.06; N, 3.51%.

trans-N-benzyl-6-fluor-3-methyl-4-(4-hydroxy-3-methoxyphenyl)-1,2,3,4-tetrahydroquinoline (6o). Beige solid; m.p. 91-92 °C; Yield: 58 % (recrystallized); IR (ATR): 3550, 3029, 2947, 1259, 1020, 734 cm⁻¹. ¹H NMR (400 MHz, CDCl₃), δ (ppm): 0.92 (3H, d, *J* = 6.6 Hz, -CH₃), 2.23 (1H, m, 3-H), 3.12 (1H, dd, *J* = 11.4, 8.9 Hz, 2-Ha), 3.32 (1H, dd, *J* = 11.5, 3.8 Hz, 2-Hb), 3.59 (1H, d, *J* = 8.9 Hz, 4-H), 3.84 (3H, s, -OCH₃), 4.50 (2H, s, -CH₂-Ph), 5.57 (1H, s, -OH), 6.42 (1H, d, *J* = 9.8 Hz, 5-H), 6.47 (1H, dd, *J* = 8.9, 4.8 Hz, 8-H), 6.59 (1H, d, *J* = 1.9 Hz, 2-H_{Ar}), 6.63 (1H, dd, *J* = 8.1, 1.9 Hz, 6-H_{Ar}), 6.69 (1H, td, *J* = 8.5, 3.0 Hz, 7-H), 6.88 (1H, d, *J* = 8.0 Hz, 5-H_{Ar}), 7.24-7.38 (5H, m, all-H_{Ph}). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 18.1, 34.5, 51.6, 55.3, 55.9, 56.0, 110.9, 111.6 (1C, d, *J* = 10.1 Hz), 113.6 (1C, d, *J* = 21.9 Hz), 114.1, 116.7 (1C, d, *J* = 22.4 Hz), 122.2, 126.7 (2C), 126.9, 128.7 (2C), 132.7, 136.5, 138.8, 141.8, 144.2, 146.7, 154.9 (1C, d, *J* = 232.8 Hz). MS (ESI-IT), *m/z*: [M+H]⁺: 378.1 (87), [M+Na]⁺: 400.1 (86), [2M+Na]⁺: 776.4 (8). Anal. Calcd for C₂₄H₂₄FN₃O₃: C, 76.37; H, 6.41; F, 5.03; N, 3.71%. Found: C, 76.29; H, 6.34; N, 3.66%.

trans-N-benzyl-8-methoxy-3-methyl-4-(4-hydroxy-3-methoxyphenyl)-1,2,3,4-tetrahydroquinoline (6p). White solid; m.p. 119-120 °C; Yield: 45 %; IR (ATR): 3275, 3060, 2952, 1244, 1040, 744 cm⁻¹. ¹H NMR (400 MHz, CDCl₃), δ (ppm): 0.78 (3H, d, *J* = 6.5 Hz, -CH₃), 2.00 (1H, m, 3-H), 2.78 (1H, t, *J* = 12.1 Hz, 2-Ha), 3.06 (1H, dd, *J* = 13.5, 3.0 Hz, 2-Hb), 3.42 (1H, d, *J* = 10.4 Hz, 4-H), 3.83 (3H, s, -OCH₃), 3.90 (3H, s, 8-OCH₃), 4.18 (1H, d, *J* = 14.1 Hz, CH_{2(a)}Ph), 4.54 (1H, d, *J* = 14.2 Hz, CH_{2(b)}Ph), 5.54 (1H, s, -OH), 6.37 (1H, m, 5-H), 6.54 (1H, d, *J* = 1.9 Hz, 2-H_{Ar}), 6.61 (1H, dd, *J* = 8.1, 1.9 Hz, 6-H_{Ar}), 6.71-6.80 (2H, m, 6-H and 7-H), 6.84 (1H, d, *J* = 8.0 Hz, 5-H_{Ar}), 7.29-7.37 (5H, m, all-H_{Ph}). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 17.6, 30.6, 52.8, 54.1, 55.4, 55.9, 58.2, 108.6, 112.0, 113.9, 121.0, 122.2, 122.7, 126.9, 128.2 (2C), 128.5 (2C), 133.3, 137.1, 137.2, 140.2, 143.9, 146.4, 151.8. MS (ESI-IT), *m/z*: [M+H]⁺: 390.1 (100), [M+Na]⁺: 412.1 (37), [2M+Na]⁺: 801.1 (19). Anal. Calcd for C₂₅H₂₇N₃O₃: C, 77.09; H, 6.99; N, 3.60%. Found: C, 77.00; H, 6.89; N, 3.54%.

General procedure for the synthesis of 4-aryl tetrahydroquinolines: Palladium/charcoal activated (10% Pd) was added in a 10% weight ratio to a solution of 1.0 mmol of the corresponding *N*-benzyl-4-aryl tetrahydroquinoline in 4 mL of a methanol-dichloromethane 3:1 mixture as solvent. The suspension was vigorously stirred at room temperature under hydrogen atmosphere (1 atm) achieving full conversion at 4-6 hours as monitored by TLC. The mixture was filtered over SiO₂, poured into a saturated NaHCO₃ solution (15 mL), extracted with ethyl acetate (3x 15 mL) and dried over Na₂SO₄. The crude product was obtained by solvent removal under vacuum and then purified by flash chromatography, eluted with the appropriate mixture of petroleum ether (b.p. 40-60°C) and ethyl acetate.

***trans*-4-(4-methoxyphenyl)-3-methyl-1,2,3,4-tetrahydroquinoline (7a).** Green solid; m.p. 72-74°C; IR (ATR): 3410, 3024, 2954, 1612, 1242, 1034 cm⁻¹; ¹H NMR (400 MHz, CDCl₃), δ (ppm): 0.89 (3H, d, *J* = 6.6 Hz, -CH₃), 2.04 (1H, m, 3-H), 2.95 (1H, dd, *J* = 11.1, 8.6 Hz, 2-Ha), 3.21 (1H, dd, *J* = 11.2, 3.5 Hz, 2-Hb), 3.45 (1H, dd, *J* = 6.1, 2.0 Hz, 5-H), 3.51 (1H, d, *J* = 8.1 Hz, 4-H), 3.80 (3H, s, -OCH₃), 6.46 (2H, dd, *J* = 8.6, 6.5 Hz, 2-H_{Ar} and 6-H_{Ar}), 6.64 (1H, dd, *J* = 8.2, 1.8 Hz, 8-H), 6.81 (2H, d, *J* = 8.6 Hz, 3-H_{Ar} and 5-H_{Ar}), 6.98 (2H, dd, *J* = 8.7, 3.1 Hz, 6-H and 7-H). ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 18.0, 35.3, 47.2, 50.3, 55.1, 113.5 (2C), 114.1, 124.0, 127.1, 127.1, 130.0 (2C), 130.7, 130.9, 138.0, 142.5, 158.0. MS (ESI-IT) *m/z*: [M+H]⁺: 254.2 (45), [M+Na]⁺: 276.2 (100), [2M+Na]⁺: 529.3(75). Anal. Calcd for C₁₇H₁₉NO: C, 80.60; H, 7.56; N, 5.53%. Found: C, 80.52; H, 7.51; N, 5.47%.

***trans*-3,6-dimethyl-4-(4-methoxyphenyl)-1,2,3,4-tetrahydroquinoline (7b).** Green solid; m.p. 77-79 °C; Yield: 92%; IR (ATR): 3409, 3010, 2949, 1611, 1242, 1031 cm⁻¹; ¹H NMR (400 MHz, CDCl₃), δ (ppm): 0.91 (3H, d, *J* = 6.7 Hz, -CH₃), 2.08 (4H, m, 6-CH₃ and 3-H), 2.98 (1H, dd, *J* = 11.1, 8.5 Hz, 2-Ha), 3.24 (1H, dd, *J* = 11.2, 3.5 Hz, 2-Hb), 3.56 (1H, d, *J* = 8.2 Hz, 4-H), 3.80 (3H, s, -OCH₃), 6.46 (2H, d, *J* = 8.1 Hz, 5-H and 8-H), 6.79 (1H, dd, *J* = 8.1, 1.4 Hz, 7-H), 6.83 (2H, d, *J* = 8.6 Hz, 2-H_{Ar} and 6-H_{Ar}), 7.03 (2H, d, *J* = 8.6 Hz, 3-H_{Ar} and 5-H_{Ar}). ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 18.0, 20.4, 35.3, 47.2, 50.4, 55.2, 113.6 (2C), 114.1, 124.3, 126.3, 127.6, 130.0 (2C), 131.0, 138.0, 142.3, 157.9. MS (ESI-IT) *m/z*: [M+H]⁺: 268.1 (45), [M+Na]⁺: 290.2 (100). Anal. Calcd for C₁₈H₂₁NO: C, 80.86; H, 7.92; N, 5.24%. Found: C, 80.76; H, 7.84; N, 5.18%.

***trans*-6-ethyl-4-(4-methoxyphenyl)-3-methyl-1,2,3,4-tetrahydroquinoline (7c).** Yellow solid; m.p. 49-50 °C; Yield: 95%; IR (ATR): 3406, 2997, 2957, 1612, 1242, 1034 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3), δ (ppm): 0.92 (3H, d, J = 6.7 Hz, $-\text{CH}_3$), 1.07 (3H, t, J = 7.6 Hz, $-\text{CH}_2\text{CH}_3$), 2.10 (1H, m, 3-H), 2.39 (2H, q, J = 7.6 Hz, $-\text{CH}_2\text{CH}_3$), 3.01 (1H, dd, J = 11.1, 8.7 Hz, 2-Ha), 3.27 (1H, dd, J = 11.2, 3.5 Hz, 2-Hb), 3.59 (1H, d, J = 8.4 Hz, 4-H), 3.82 (3H, s, $-\text{OCH}_3$), 6.48 (1H, d, J = 1.4 Hz, 5-H), 6.52 (1H, d, J = 8.1 Hz, 8-H), 6.85 (3H, m, 7-H, 2- H_{Ar} and 6- H_{Ar}), 7.05 (2H, d, J = 8.6 Hz, 3- H_{Ar} and 5- H_{Ar}). ^{13}C NMR (100 MHz, CDCl_3), δ (ppm): 16.1, 18.2, 28.1, 35.5, 47.5, 50.6, 55.3, 113.7 (2C), 114.4, 124.6, 126.4, 130.1, 130.2 (2C), 133.3, 138.1, 142.5, 158.0. MS (ESI-IT) m/z : $[\text{M}+\text{H}]^+$: 282.3 (52), $[\text{M}+\text{Na}]^+$: 304.2 (84), $[\text{2M}+\text{Na}]^+$: 585.3(70). Anal. Calcd for $\text{C}_{19}\text{H}_{23}\text{NO}$: C, 81.10; H, 8.24; N, 4.98%. Found: C, 81.00; H, 8.15; N, 4.91%.

***trans*-6-methoxy-4-(4-methoxyphenyl)-3-methyl-1,2,3,4-tetrahydroquinoline (7d).** Yellow solid; m.p. 70-72 °C; Yield: 91%; IR (ATR): 3409, 3006, 2934, 1609, 1248, 1029 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3), δ (ppm): 0.91 (3H, d, J = 6.7 Hz, $-\text{CH}_3$), 2.07 (1H, s, N-H), 2.10 (1H, m, 3-H), 2.98 (1H, dd, J = 11.1, 8.9 Hz, 2-Ha), 3.25 (1H, dd, J = 11.2, 3.4 Hz, 2-Hb), 3.57 (1H, d, J = 9.0 Hz, 4-H), 3.59 (3H, s, 6- OCH_3), 3.78 (3H, s, $-\text{OCH}_3$), 6.24 (1H, d, J = 2.7 Hz, 5-H), 6.51 (1H, d, J = 8.6 Hz, 8-H), 6.61 (1H, dd, J = 8.6, 2.8 Hz, 7-H), 6.83 (2H, dd, J = 8.6 Hz, 2- H_{Ar} and 6- H_{Ar}), 7.04 (2H, d, J = 8.6 Hz, 3- H_{Ar} and 5- H_{Ar}). ^{13}C NMR (100 MHz, CDCl_3), δ (ppm): 17.9, 35.4, 47.6, 50.7, 55.2, 55.6, 113.1, 113.6 (2C), 115.2, 116.0, 125.9, 130.0 (2C), 137.6, 138.8, 151.9, 158.0. EM (ESI-IT) m/z : $[\text{M}+\text{H}]^+$: 284.1 (40), $[\text{M}+\text{Na}]^+$: 306.0 (100), $[\text{2M}+\text{Na}]^+$: 589.4 (61). Anal. Calcd for $\text{C}_{18}\text{H}_{21}\text{NO}_2$: C, 76.29; H, 7.47; N, 4.94%. Found: C, 76.18; H, 7.40; N, 4.88%.

trans-6-chloro-4-(4-methoxyphenyl)-3-methyl-1,2,3,4-tetrahydroquinoline (7e). Green solid; m.p. 108-110°C; Yield: 93%; IR (ATR): 3392, 3001, 2918, 1604, 1241, 1029 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3), δ (ppm): 0.93 (3H, d, $J = 6.7$ Hz, $-\text{CH}_3$), 2.12 (1H, m, 3-H), 3.03 (1H, d, $J = 11.2, 8.7$ Hz, 2-Ha), 3.29 (1H, dd, $J = 11.2, 3.6$ Hz, 2-Hb), 3.61 (1H, d, $J = 8.5$ Hz, 4-H), 3.81 (1H, s, $-\text{OCH}_3$), 6.54 (2H, m, 5-H and N-H), 6.65 (1H, m, 8-H), 6.85 (2H, d, $J = 8.7$ Hz, 2- H_{Ar} and 6- H_{Ar}), 6.99 (1H, m, 7-H), 7.05 (2H, d, $J = 8.6$ Hz, 3- H_{Ar} and 5- H_{Ar}). ^{13}C NMR (100 MHz, CDCl_3), δ (ppm): 17.1, 33.5, 47.9, 49.9, 55.2, 114.1 (2C), 123.1, 127.6, 128.7, 130.2 (2C), 130.4, 131.2, 134.2, 134.7, 158.0. MS (ESI-IT) m/z : $[\text{M}+\text{H}]^+$: 288.4 (35), $[\text{M}+\text{Na}]^+$: 310.2 (100), $[2\text{M}+\text{Na}]^+$: 597.4 (73). Anal. Calcd for $\text{C}_{17}\text{H}_{18}\text{ClNO}$: C, 70.95; H, 6.30; Cl, 12.32; N, 4.87%. Found: C, 70.86; H, 6.24; N, 4.81%.

trans-6-fluor-4-(4-methoxyphenyl)-3-methyl-1,2,3,4-tetrahydroquinoline (7f). Green solid; m.p. 114-115 °C; Yield: 93%; IR (ATR): 3418, 2999, 2952, 1610, 1243, 1031 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3), δ (ppm): 0.91 (3H, d, $J = 6.7$ Hz, $-\text{CH}_3$), 2.10 (1H, m, 3-H), 3.00 (1H, dd, $J = 11.2, 9.0$ Hz, 2-Ha), 3.28 (1H, dd, $J = 11.3, 3.5$ Hz, 2-Hb), 3.55 (1H, d, $J = 8.7$ Hz, 4-H), 3.81 (3H, s, $-\text{OCH}_3$), 6.36 (1H, ddd, $J = 9.9, 2.9, 0.9$ Hz, 5-H), 6.49 (1H, dd, $J = 8.7, 4.9$ Hz, 8-H), 6.70 (1H, tdd, $J = 8.2, 3.0, 0.8$ Hz, 7-H), 6.85 (2H, dd, $J = 8.8$ Hz, 2- H_{Ar} and 6- H_{Ar}), 7.03 (2H, d, $J = 8.6$ Hz, 3- H_{Ar} and 5- H_{Ar}). ^{13}C NMR (100 MHz, CDCl_3), δ (ppm): 17.9, 34.9, 47.6, 50.6, 55.3, 113.7 (1C, d, $J = 22.7$ Hz), 113.8 (2C), 114.9 (1C, d, $J = 7.6$ Hz), 116.7 (1C, d, $J = 22.2$ Hz), 126.1 (1C, d, $J = 6.4$ Hz), 130.0 (2C), 136.9, 140.6 (1C, d, $J = 1.7$ Hz), 155.7 (1C, d, $J = 234.6$ Hz), 158.2. MS (ESI-IT) m/z : $[\text{M}+\text{H}]^+$: 272.2 (42), $[\text{M}+\text{Na}]^+$: 294.2 (100), $[2\text{M}+\text{Na}]^+$: 565.2 (64). Anal. Calcd for $\text{C}_{17}\text{H}_{18}\text{FNO}$: C, 75.25; H, 6.69; F, 7.00; N, 5.16%. Found: C, 75.18; H, 6.61; N, 5.08%.

trans-4-(4-hydroxy-3-methoxyphenyl)-3-methyl-1,2,3,4-tetrahydroquinoline (7g). Green solid; m.p. 118-120 °C; Yield: 96 %; IR (ATR): 3341, 3015, 2919, 1607, 1265, 1031 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3), δ (ppm): 0.89 (3H, d, $J = 6.4$ Hz, $-\text{CH}_3$), 2.12 (1H, m, 3-H), 3.00 (1H, dd, $J = 10.5, 9.0$ Hz, 2-Ha), 3.30 (1H, dd, $J = 11.1, 2.7$ Hz, 2-Hb), 3.45 (2H, br. s, 4-H and 5-H), 3.73 (3H, s, $-\text{OCH}_3$), 5.18 (1H, s, $-\text{OH}$), 6.41-6.53 (3H, m, 8-H, 6-H and 2- H_{Ar}), 6.59 (1H, d, $J = 7.8$ Hz, 6- H_{Ar}), 6.67 (1H, dd, $J = 8.0$ Hz, 7-H), 6.81 (1H, d, $J = 7.7$ Hz, 5- H_{Ar}). ^{13}C NMR (100 MHz, CDCl_3), δ (ppm): 17.8, 35.0, 47.7, 50.9, 111.1, 113.9, 115.3, 122.4, 125.7, 127.2, 130.9 (2C), 132.4, 137.1, 140.5, 144.0, 146.6. MS (ESI-IT) m/z : $[\text{M}+\text{H}]^+$: 270.3 (58), $[\text{M}+\text{Na}]^+$: 292.2 (100), $[2\text{M}+\text{Na}]^+$: 561.1 (42). Anal. Calcd for $\text{C}_{17}\text{H}_{19}\text{NO}_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.72; H, 7.04; N, 5.12%.

trans-3,6-dimethyl-4-(4-hydroxy-3-methoxyphenyl)-1,2,3,4-tetrahydroquinoline (7h). Yellow solid; m.p. 140-141 °C; Yield: 92%; IR (ATR): 3307, 3014, 2959, 1601, 1225, 1029 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3), δ (ppm): 0.93 (3H, d, $J = 6.6$ Hz, $-\text{CH}_3$), 2.12 (4H, m, 6- CH_3 and 3-H), 3.02 (1H, dd, $J = 10.7, 9.2$ Hz, 2-Ha), 3.29 (1H, dd, $J = 11.1, 3.1$ Hz, 2-Hb), 3.56 (1H, d, $J = 8.5$ Hz, 4-H), 3.82 (3H, s, $-\text{OCH}_3$), 4.64 (1H, s, $-\text{OH}$), 6.49 (2H, d, $J = 8.0$ Hz, 5-H and 8-H), 6.63 (1H, s, 2- H_{Ar}), 6.66 (1H, d, $J = 8.8$ Hz, 6- H_{Ar}), 6.82 (1H, d, $J = 7.7$ Hz, 7-H), 6.86 (1H, d, $J = 7.9$ Hz, 5- H_{Ar}). ^{13}C NMR (100 MHz, CDCl_3), δ (ppm): 18.0, 20.4, 35.3, 47.5, 51.1, 55.9, 111.1, 113.9, 114.2, 122.3, 124.4, 126.4, 127.5, 130.9, 137.6, 142.2, 144.0, 146.5. MS (ESI-IT), m/z : $[\text{M}+\text{H}]^+$: 384.3 (22), $[\text{M}+\text{Na}]^+$: 306.3 (12), $[2\text{M}+\text{Na}]^+$: 589.1 (66). Anal. Calcd for $\text{C}_{18}\text{H}_{21}\text{NO}_2$: C, 76.29; H, 7.47; N, 4.94%. Found: C, 76.21; H, 7.39; N, 4.86%.

trans-6-ethyl-4-(4-hydroxy-3-methoxyphenyl)-3-methyl-1,2,3,4-tetrahydroquinoline (7i). Beige solid; m.p. 50-52 °C; Yield: 85%; IR (ATR): 3406, 3017, 2959, 1611, 1231, 1033 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3), δ (ppm): 0.91 (3H, d, $J = 6.6$ Hz, $-\text{CH}_3$), 1.06 (3H, t, $J = 7.6$ Hz, $-\text{CH}_2\text{CH}_3$), 2.11 (1H, m, 3-H), 2.38 (2H, q, $J = 7.6$ Hz, $-\text{CH}_2\text{CH}_3$), 3.02 (1H, dd, $J = 11.1, 9.1$ Hz, 2-Ha), 3.28 (1H, dd, $J = 11.1, 3.5$ Hz, 2-Hb), 3.55 (1H, d, $J = 8.8$ Hz, 4-H), 3.81 (3H, s, $-\text{OCH}_3$), 6.49 (1H, s, 5-H), 6.51 (1H, d, $J = 8.1$ Hz, 6- H_{Ar}), 6.60 (1H, d, $J = 1.9$ Hz, 2- H_{Ar}), 6.65 (1H, dd, $J = 8.0, 2.0$ Hz, 8-H), 6.84 (2H, m, 7-H and 5- H_{Ar}). ^{13}C NMR (100 MHz, CDCl_3), δ (ppm): 16.2, 18.2, 28.1, 35.5, 47.9, 51.3, 56.1, 111.2, 113.9, 114.4, 122.6, 124.7, 126.5, 130.1, 133.5, 137.7, 142.5, 144.0, 146.6. MS (ESI-IT), m/z : $[\text{M}+\text{H}]^+$: 298.3 (22), $[\text{M}+\text{Na}]^+$: 320.2 (36), $[\text{2M}+\text{Na}]^+$: 617.1 (52). Anal. Calcd for $\text{C}_{19}\text{H}_{23}\text{NO}_2$: C, 76.73; H, 7.80; N, 4.71%. Found: C, 76.65; H, 7.72; N, 4.65%.

trans-6-methoxy-4-(4-hydroxy-3-methoxyphenyl)-3-methyl-1,2,3,4-tetrahydroquinoline (7j). Beige solid; m.p. 118-120 °C; Yield: 83%; IR (ATR): 3301, 3023, 2951, 1599, 1275, 1022 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3), δ (ppm): 0.91 (3H, d, $J = 6.6$ Hz, $-\text{CH}_3$), 2.10 (1H, m, 3-H), 3.04 (1H, dd, $J = 10.9, 9.4$ Hz, 2-Ha), 3.27 (1H, dd, $J = 11.1, 3.3$ Hz, 2-Hb), 3.54 (1H, d, $J = 9.0$ Hz, 4-H), 3.59 (3H, s, 6- OCH_3), 3.81 (3H, s, $-\text{OCH}_3$), 6.26 (1H, d, $J = 2.4$ Hz, 5-H), 6.53 (1H, d, $J = 8.9$ Hz, 8-H), 6.59 (1H, s, 2- H_{Ar}), 6.61 (1H, dd, $J = 8.8, 2.7$ Hz, 6- H_{Ar}), 6.63 (1H, dd, $J = 8.2, 1.3$ Hz, 7-H), 6.84 (1H, d, $J = 8.6$ Hz, 5- H_{Ar}). ^{13}C NMR (100 MHz, CDCl_3), δ (ppm): 18.0, 35.4, 48.0, 51.5, 55.7, 55.9, 111.0, 113.3, 113.8, 115.3, 116.0, 122.4, 126.1, 137.2, 138.6, 144.1, 146.6, 152.0. MS (ESI-IT), m/z : $[\text{M}+\text{H}]^+$: 300.4 (17), $[\text{M}+\text{Na}]^+$: 322.1 (53), $[\text{2M}+\text{Na}]^+$: 621.1 (100). Anal. Calcd for $\text{C}_{18}\text{H}_{21}\text{NO}_3$: C, 72.22; H, 7.07; N, 4.68%. Found: C, 72.15; H, 7.01; N, 4.59%.

***trans*-6-chloro-4-(4-hydroxy-3-methoxyphenyl)-3-methyl-1,2,3,4-tetrahydroquinoline (7k).** Beige solid; m.p. 112-114°C; Yield: 64%; IR (ATR): 3314, 3006, 2964, 1589, 1216, 1034 cm⁻¹; ¹H NMR (400 MHz, CDCl₃), δ (ppm): 0.93 (3H, d, *J* = 6.6 Hz, -CH₃), 2.14 (1H, m, 3-H), 3.05 (1H, dd, *J* = 11.0, 9.2 Hz, 2-Ha), 3.30 (1H, dd, *J* = 11.2, 3.5 Hz, 2-Hb), 3.58 (1H, d, *J* = 8.8 Hz, 4-H), 3.81 (3H, s, -OCH₃), 4.73 (1H, s, -OH), 6.56 (2H, br. dd, *J* = 7.8, 6.1 Hz, 5-H and 8-H), 6.62 (1H, s, N-H), 6.67 (2H, m, 2-H_{Ar} and 6-H_{Ar}), 6.86 (1H, d, *J* = 8.0 Hz, 5-H_{Ar}), 6.99 (1H, t, *J* = 7.4 Hz, 7-H). ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 18.0, 34.9, 47.4, 51.1, 55.9, 111.1, 113.9 (2C), 117.2, 122.3, 124.3, 126.9, 130.6, 137.4, 144.0, 144.5, 146.5. MS (ESI-IT), *m/z*: [M+H]⁺: 304.4 (26), [M+Na]⁺: 326.3 (18), [2M+Na]⁺: 629.2 (68). Anal. Calcd for C₁₇H₁₈ClNO₂: C, 67.21; H, 5.97; Cl, 11.67; N, 4.61%. Found: C, 67.09; H, 5.91; N, 4.54%.

***trans*-6-fluor-4-(4-hydroxy-3-methoxyphenyl)-3-methyl-1,2,3,4-tetrahydroquinoline (7l).** Yellow oil; Yield: 79%; IR (ATR): 3322, 3025, 2964, 1600, 1218, 1026 cm⁻¹; ¹H NMR (400 MHz, CDCl₃), δ (ppm): 0.90 (3H, d, *J* = 6.6 Hz, -CH₃), 2.11 (1H, m, 3-H), 3.01 (1H, dd, *J* = 11.2, 9.3 Hz, 2-Ha), 3.28 (1H, dd, *J* = 11.2, 3.5 Hz, 2-Hb), 3.52 (1H, d, *J* = 9.0 Hz, 4-H), 3.81 (3H, s, -OCH₃), 6.37 (1H, ddd, *J* = 9.9, 2.9, 0.9 Hz, 5-H), 6.48 (1H, dd, *J* = 8.7, 4.9 Hz, 8-H), 6.57 (1H, d, *J* = 1.9 Hz, 2-H_{Ar}), 6.64 (1H, dd, *J* = 8.1, 1.9 Hz, 6-H_{Ar}), 6.70 (1H, m, 7-H), 6.85 (1H, d, *J* = 8.0 Hz, 5-H_{Ar}). ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 18.0, 35.0, 48.0, 51.4, 56.0, 111.0, 113.9 (1C, d, *J* = 22.8 Hz), 114.1, 115.0 (1C, d, *J* = 7.6 Hz), 116.7 (1C, d, *J* = 22.3 Hz), 122.5, 126.3 (1C, d, *J* = 6.2 Hz), 136.7, 140.7, 144.3, 146.8, 155.8 (1C, d, *J* = 234.6 Hz). MS (ESI-IT), *m/z*: [M+H]⁺: 288.3 (82), [M+Na]⁺: 310.2 (99), [2M+Na]⁺: 597.1 (69). Anal. Calcd for C₁₇H₁₈FNO: C, 71.06; H, 6.31; F, 6.61; N, 4.87%. Found: C, 70.99; H, 6.24; N, 4.79%.

2. ^1H NMR and ^{13}C NMR spectra of *N*-benzyl-4-aryl tetrahydroquinolines 6a-6p.

3. ^1H NMR and ^{13}C NMR spectra of 4-aryl tetrahydroquinolines 7a-7l.

4- Single crystal X-Ray diffraction data for *N*-benzyl-4-aryl-3-methyl tetrahydroquinoline **6d**

Crystal data and refinement ^a	<i>N</i> -benzyl THQ
<i>Data crystal</i>	
Empirical Formula	C ₂₄ H ₂₄ ClNO
Formula weight	377.89
Temperature (°C)	25
Wavelength (Å)	0.71073 Å
Crystal system	Orthorhombic
Space group	<i>Fdd2</i> (N° 43)
<i>Unit cell dimensions</i>	
<i>a</i> (Å)	33.100 (2) Å
<i>b</i> (Å)	41.628 (3) Å
<i>c</i> (Å)	5.8511 (4) Å
$\alpha = \beta = \gamma$ (°)	90°
Volume (Å ³)	8062.2 (9) Å ³
<i>Z</i>	16
Density (calculated) (Mg/m ³)	1.245
Reflections collected	18042
Independent reflections	2006 [<i>R</i> _{int} = 0.023]
Refinement methods	Full-matrix least-squares on <i>F</i> ²
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>) = 1914 data]	<i>R</i> _I = 0.027, <i>wR</i> ₂ = 0.069

^a The data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/products/csd/request/> (or from the CCDC, 12 Union Road, Cambridge CB2, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).