

Synthesis of New 4-Methyl-2-(4-pyridyl)-1,2,3,4-tetrahydroquinolines as Potent Antifungal Compounds

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Experimental

The melting points (uncorrected) were determined on a Fisher-Johns melting point apparatus. The IR spectra were recorded on a Lumex Infracum FT-02 spectrophotometer in KBr. ¹H NMR spectra were recorded on Bruker AM-400 spectrometer. Chemical shifts are reported in ppm (δ) relative to the solvent peak (CHCl₃ in CDCl₃ at 7.24 ppm for protons). Signals are designated as follows: s, singlet; d, doublet; dd, doublet of doublets; ddd, doublet of doublets of doublets; t, triplet; dt, doublet of triplets; td, triplet of doublets; q, quartet; quint., quintet; sext., sextet; m, multiplet; br, broad. On DEPT-135 spectra, the signals of CH₃, CH₂ and CH carbons are shown as positive (+) and negative (-), respectively. Quaternary carbons are not shown. A Hewlett Packard 5890a series II Gas Chromatograph interfaced to an HP 5972 Mass Selective Detector (MSD) with an hp ms Chemstation Data system was used for ms identification at 70 EV using a 60 m capillary column coated with HP-5 [5%-phenyl-poly(dimethyl-siloxane)]. Elemental analyses were performed on a Perkin Elmer 2400 Series II analyzer and were within ± 0.4 of theoretical values. The reaction progress was monitored using thin layer chromatography on a silufol UV254 TLC aluminum sheet.

General procedure for the preparation of 4-N-aryl-N-[1-(4-pyridyl)buten-3-yl]amines

Grignard protocol

To an Et₂O solution (200 mL) of allyl magnesium bromide, prepared from allyl bromide (36.3 g, 0.30 mol) and magnesium (12.15 g, 0.50 mol), were added slowly aldimines **1-5** (0.10 mol), dissolved in absolute THF

(15 mL). The mixture was kept during 4 h at room temperature, and then cooled to 0 °C to treat rapidly with water, and finally with saturated ammonium chloride solution. The organic layer was separated and the aqueous layer was extracted with ether (4x50 mL). The combined organic extracts were dried (Na₂SO₄) and concentrated. The residue was purified by Al₂O₃ column chromatography (eluent - hexanes/ethyl acetate) to give new homoallylamines **6-10**.

Barbier protocol

To a mixture of aldimines **1**, **4** and **5** (1 mmol) and powder indium (170 mg, 1.5 mmol) in methanol (10 mL) was added allyl bromide (365 mg, 3 mmol). The reaction mixture was stirred vigorously at room temperature until all the indium had dissolved (1 h to 4 h), at which time TLC indicated complete reaction. The reaction mixture was diluted with sat. NH₄Cl and extracted with ethyl acetate. The extract was washed with brine and dried (Na₂SO₄). The product was purified by flash column chromatography on alumina, using hexanes/ethyl acetate as eluent. Physicochemical characteristics of the obtained homoallylamines **6**, **9** and **10** were in agreement with those obtained by Grignard method.

4-N-Phenyl -N-[1-(4-pyridyl)buten-3-yl]amine **6**

Yellow viscous oil. Yield: 81%. Molecular formula: C₁₅H₁₆N₂. Molecular weight: 224.30 g mol⁻¹. Eluent: petroleum eter/AcOEt, 10:1. IR (KBr) ν_{\max} /cm⁻¹: 3287 (ν_{NH}), 1601 ($\nu_{\text{C=CH}}$). ¹H-NMR (CDCl₃, 400 MHz) δ (ppm): 2.43-2.66 (2H, m, -CH₂), 4.19 (1H, bs, N-H), 4.38 (1H, dd, *J* 7.9, 5.0 Hz, -CH), 5.18-5.24 (2H, m, =CH₂), 5.66-5.80 (1H, m, =CH), 6.45 (2H, d, *J* 8.5 Hz, 2(6)-H_{ph}), 6.69 (1H, tt, *J* 7.3 Hz, 4-H_{ph}), 7.10 (2H, td, *J* 7.7, 1.0 Hz, 3(5)-H_{ph}), 7.31 (2H, dd, *J* 4.4, 1.6 Hz, 3(5)-H_{py}), 8.56 (2H, dd, *J* 5.0, 1.6 Hz, 2(6)-H_{py}). ¹³C-NMR (100 MHz) δ (ppm): 42.4,

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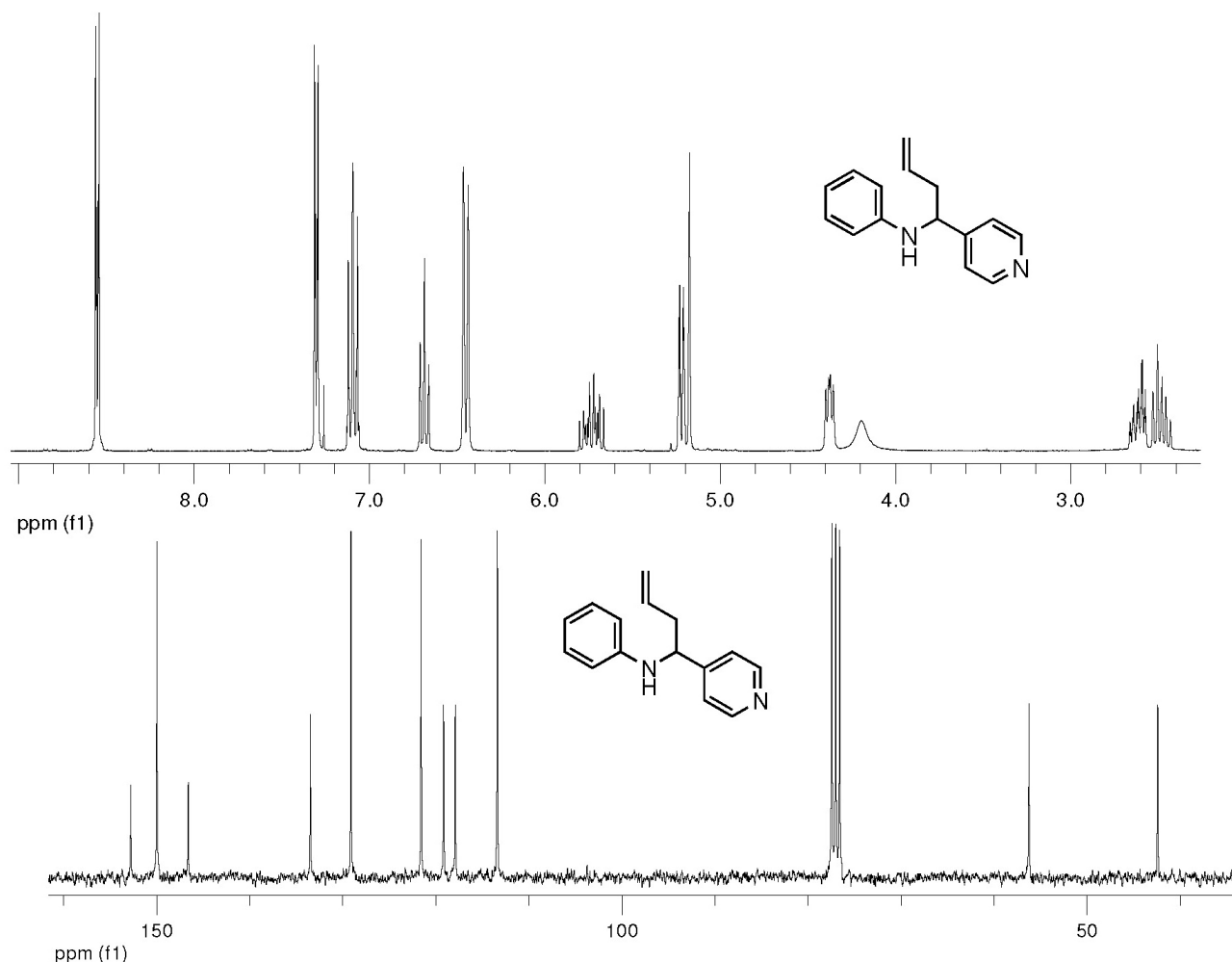


Figure S1. ^1H and ^{13}C NMR spectra of **6**.

56.2, 113.4 (2C), 117.9, 119.1, 121.6 (2C), 129.1 (2C), 146.6, 133.5, 150.0 (2C), 152.8. GC: t_{R} 17.27 min. MS: m/z (%): 224 (M^+ , 3), 183 (100), 77 (11), 51 (4). Anal. calc. for $\text{C}_{15}\text{H}_{16}\text{N}_2$: C, 80.32; H, 7.19; N, 12.49. Found: C, 80.54; H, 7.04; N, 12.40.

4-N-(4-Methylphenyl)-N-[1-(4-pyridyl)buten-3-yl]amine 7

White crystals. mp 95-96 °C. Yield: 73%. Molecular formula: $\text{C}_{16}\text{H}_{18}\text{N}_2$. Molecular weight: 238.33 g mol $^{-1}$. Eluent: petroleum eter/AcOEt, 20:1. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3273 (ν_{NH}), 1599 ($\nu_{\text{C=CH}}$). ^1H -NMR (CDCl_3 , 400 MHz) δ (ppm): 2.20 (3H, s, CH_3), 2.43-2.64 (2H, m, $-\text{CH}_2-$), 4.09 (1H, br. s, N-H), 4.34 (1H, dd, J 7.7, 5.0 Hz, $-\text{CH}$), 5.18 (1H, s, $\text{CH}_A=$), 5.21 (1H, d, J 7.8 Hz, $\text{CH}_B=$), 5.68-5.78 (1H, m, $=\text{CH}$), 6.38 (2H, d, J 8.4 Hz, 2(6)- H_{Ar}), 6.91 (2H, d, J 8.0 Hz, 3(5)- H_{Ar}), 7.31 (2H, dd, J 4.7, 1.1 Hz, 3(5)- H_{Py}), 8.55 (2H, dd, J 4.6, 1.4 Hz, 2(6)- H_{Py}). ^{13}C -NMR (100 MHz) δ (ppm): 20.3, 42.4 (-), 56.4 (+), 113.4 (2C, +), 119.0 (-), 121.6 (2C, +), 127.0, 129.6 (2C, +), 133.6 (+), 144.3, 150.0 (2C, +), 152.9. GC: t_{R} 19.27 min. MS: m/z (%): 238

(M^+ , 4), 197 (100), 91 (8), 65 (4). Anal. calc. for $\text{C}_{16}\text{H}_{16}\text{N}_2$: C, 80.63; H, 7.61; N, 11.75. Found: C, 80.51; H, 7.49; N, 12.05.

4-N-(4-Methoxyphenyl)-N-[1-(4-pyridyl)buten-3-yl]amine 8

Yellow viscous oil. Yield: 60%. Molecular formula: $\text{C}_{16}\text{H}_{18}\text{N}_2\text{O}$. Molecular weight: 254.33 g mol $^{-1}$. Eluent: petroleum eter/AcOEt, 20:1. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3294 (ν_{NH}), 1597 (δ_{NH}). ^1H -NMR (CDCl_3 , 400 MHz) δ (ppm): 2.41-2.61 (2H, m, $-\text{CH}_2-$), 3.68 (3H, s, OCH_3), 4.29 (1H, dd, J 8.0, 5.0 Hz, $-\text{CH}$), 5.16 (1H, s, $\text{CH}_A=$), 5.20 (1H, d, J 6.0 Hz, $\text{CH}_B=$), 5.67-5.77 (1H, m, $=\text{CH}$), 6.40 (2H, d, J 8.9 Hz, 2(6)- H_{Ar}), 6.68 (2H, d, J 8.9 Hz, 3(5)- H_{Ar}), 7.29 (2H, d, J 6.0 Hz, 3(5)- H_{Py}), 8.53 (2H, dd, J 4.5, 1.5 Hz, 2(6)- H_{Py}). ^{13}C -NMR (100 MHz) δ (ppm): 42.4, 55.6, 57.0, 114.5 (2C), 114.7 (2C), 119.0, 121.6 (2C), 133.6, 140.8, 149.8 (2C), 152.2, 153.1. GC: t_{R} 21.32 min. MS: m/z (%): 254 (M^+ , 5), 213 (100), 198 (4), 169 (7). Anal. calc. for $\text{C}_{16}\text{H}_{18}\text{N}_2\text{O}$: C, 75.56; H, 7.13; N, 11.01. Found: C, 75.29; H, 7.32; N, 11.12.

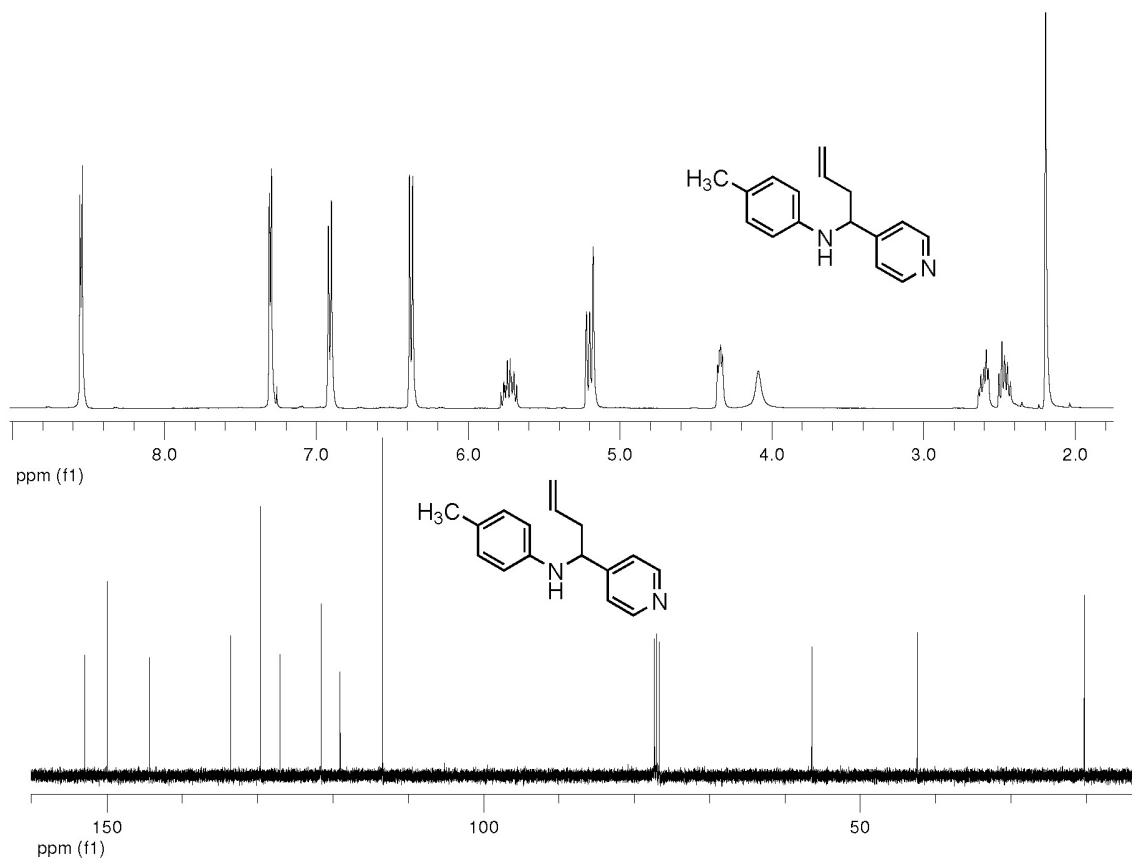


Figure S2. ^1H and ^{13}C NMR spectra of **7**.

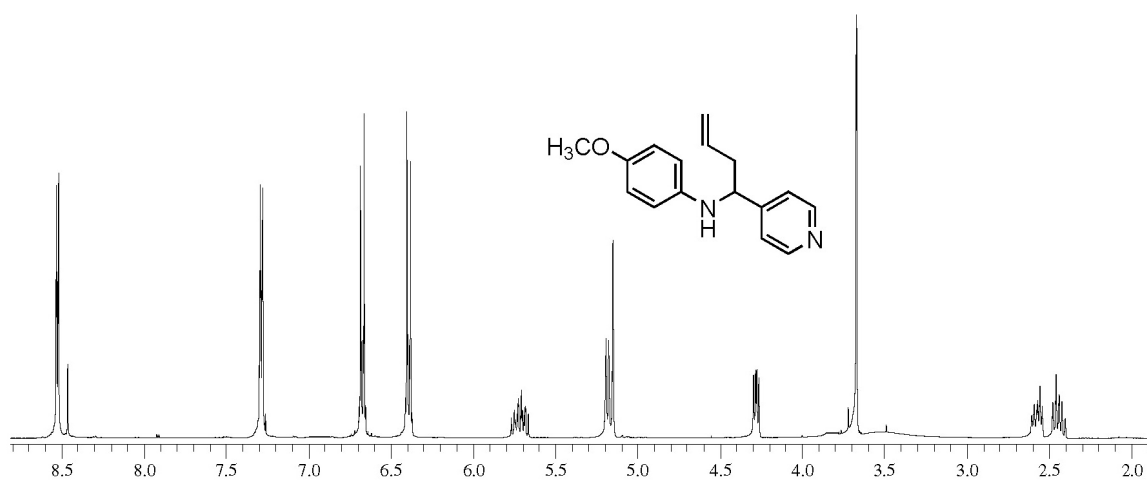


Figure S3. ^1H NMR spectrum of **8**.

4-*N*-(4-Bromophenyl)-*N*-[1-(4-pyridyl)buten-3-yl]amine **9**

Yellow crystals. mp 81-83 °C. Yield: 53%. Molecular formula: $\text{C}_{15}\text{H}_{15}\text{BrN}_2$. Molecular weight: 303.20 g mol^{-1} . Eluent: petroleum ether/AcOEt, 10:1. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3275 (ν_{NH}), 1594 ($\nu_{\text{C=CH}}$) cm^{-1} . ^1H -NMR (CDCl_3 , 300 MHz)

δ (ppm): 2.42-2.67 (2H, m, $-\text{CH}_2$), 4.19 (1H, bs, N-H), 4.34 (1H, m, $-\text{CH}$), 5.17-5.23 (2H, m, $\text{CH}_2=\text{CH}$), 5.63-5.78 (1H, m, $=\text{CH}$), 6.31 (2H, dd, J 8.8, 2.0 Hz, 2(6)- H_{Ar}), 7.16 (2H, dd, J 8.8, 2.0 Hz, 3(5)- H_{Ar}), 7.27 (2H, dd, J 3.9, 1.7 Hz, 3(5)- H_{Py}), 8.55 (2H, dd, J 4.4, 1.6 Hz, 2(6)- H_{Py}). ^{13}C -NMR

(75 MHz) δ (ppm): 42.3, 56.2, 109.7, 115.0 (2C), 119.5, 121.5 (2C), 128.1, 131.9 (2C), 133.2, 145.5, 150.0, 150.1. GC: t_R 22.15 min. MS: m/z (%): 302 (M^+ for ^{79}Br , 5), 261 [$(M-C_3H_5)^+$, 100]. Anal. calc. for $C_{15}H_{15}BrN_2$: C, 59.42; H, 4.99; N, 9.24. Found: C, 59.75; H, 5.21; N, 9.56.

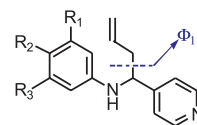
4-N-(3,5-Dimethylphenyl)-N-[1-(4-pyridyl)buten-3-yl] amine 10

White crystals. Mp 91-92 °C. Yield: 74%. Molecular formula: $C_{17}H_{20}N_2$. Molecular weight: 252.35 g mol⁻¹. Eluent: petroleum eter/AcOEt, 10:1. IR (KBr) ν_{\max} /cm⁻¹: 3293 (ν_{NH}), 1603 ($\nu_{\text{C=CH}}$). ¹H-NMR (CDCl_3 , 400 MHz) δ (ppm): 2.15 (6H, s, 3(5)- CH_3), 2.41-2.62 (2H, m, - CH_2), 4.07 (1H, bs, N-H), 4.35 (1H, dd, J 7.7, 5.0 Hz, -CH), 5.20-5.15 (2H, m, $\text{CH}_2=\text{}$), 5.65-5.76 (1H, m, =CH), 6.08 (2H, s, 2(6)- H_{Ar}), 6.34 (1H, s, 4- H_{Ar}), 7.29 (2H, dd, J 4.7, 1.3 Hz, 3(5)- H_{py}), 8.54 (2H, dd, J 4.5, 1.5 Hz, 2(6)- H_{py}). ¹³C-NMR (100 MHz) δ (ppm): 21.4 (2C), 42.4, 56.2, 111.3 (2C), 119.0, 119.9, 121.5 (2C), 133.6, 138.8 (2C), 146.8, 150.0 (2C), 152.9. GC: t_R 19.99 min. MS: m/z (%): 252 (M^+ , 3), 211 (100), 105 (5), 77 (7). Anal. calc. for $C_{17}H_{20}N_2$: C, 80.91; H, 7.99; N, 11.10. Found: C, 81.14; H, 7.70; N, 11.21.

General procedure for the preparation of 4-methyl-2-(4-pyridyl)-1,2,3,4-tetrahydro-quinolines

85% (v/v) sulfuric acid (4.0 mL) was added dropwise at 0 °C to the homoallylamines **6-10** (2.0 g) in minimal CH_2Cl_2 amount, and the resulting mixture was heated at 80-90 °C for 3 h while stirring vigorously. The reaction progress was monitored *via* TLC. At the end of the reaction the mixture

Table S1. Possible fragmentation and principal ions in the MS of homoallylamines **6-10**



Compound	m/z (I%)	
	M^+	Φ_1 [$M-C_3H_5$] ⁺
6	224 (3)	183 (100)
7	238 (4)	197 (100)
8	254 (5)	213 (100)
9	302 (5)	261 (100)
10	252 (3)	211 (100)

was cooled down to room temperature and concentrated ammonium hydroxide solution was added to pH 10. Four 25 mL extractions with dichloromethane were performed. The organic layers were combined, dried (Na_2SO_4) and concentrated. The oily residue was purified by column chromatography over alumina to give new THQ **11-14** and quinoline sulfonic acid **15**. The synthesis of THQ **13** was realized using PPA.

4-Methyl-2-(4-pyridyl)-1,2,3,4-tetrahydroquinoline 11

White crystals. mp 88-90 °C. Yield: 84%. Molecular formula: $C_{15}H_{16}N_2$. Molecular weight: 224.30 g mol⁻¹. Eluent: petroleum eter/AcOEt, 5:1. IR (KBr) ν_{\max} /cm⁻¹: 3266 (ν_{NH}). ¹H-NMR (CDCl_3 , 400 MHz) δ (ppm): *cis* Isomer: 1.34 (3H, d, J 6.8 Hz, 4- CH_3), 1.70 (1H, c, J 12.7 Hz, 3-Ha), 2.11 (1H, ddd, J 12.9, 4.3, 3.0 Hz, 3-He), 3.13 (1H, sp, J 6.0 Hz, 4-H), 4.00 (1H, s, NH), 4.47 (1H,

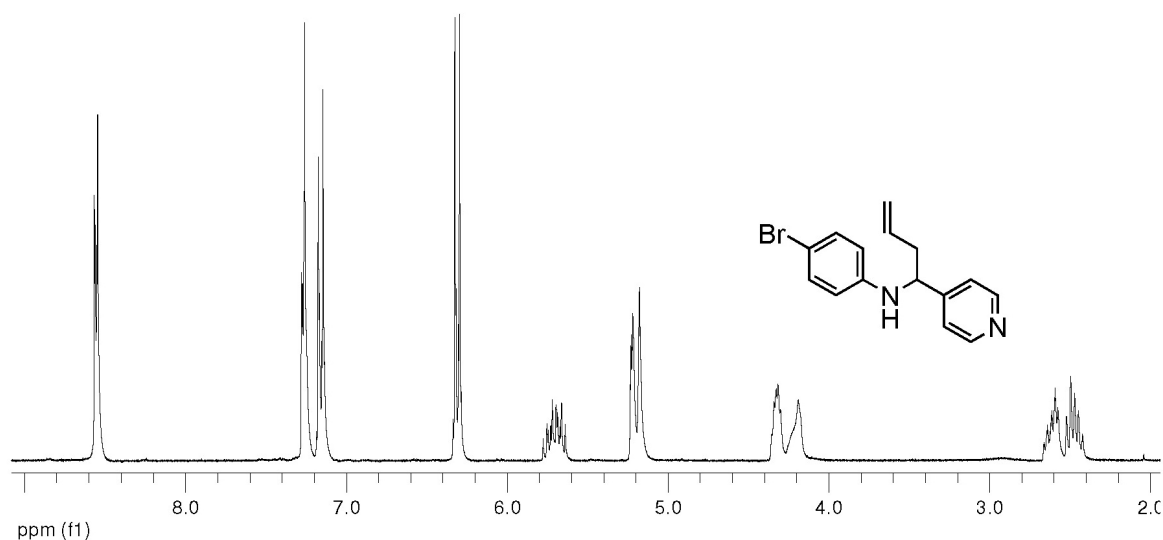
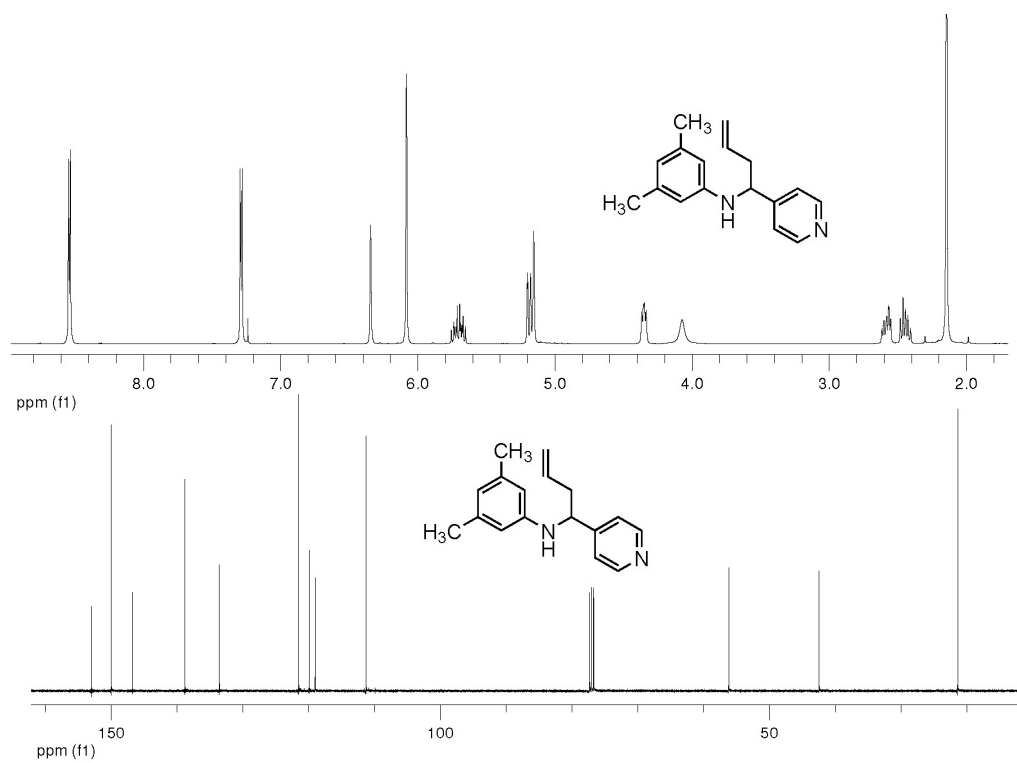
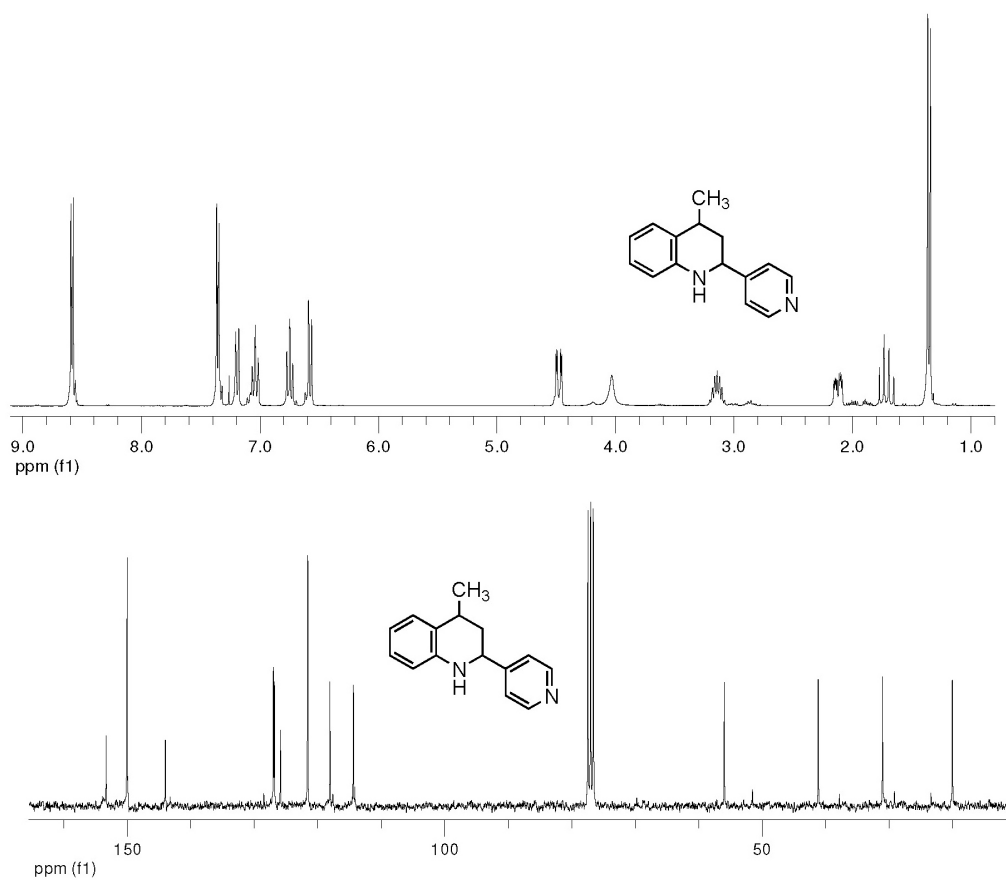


Figure S4. ¹H NMR spectrum of **9**.

**Figure S5.** ^1H and ^{13}C NMR spectra of **10**.**Figure S6.** ^1H and ^{13}C NMR spectra of **11**.

dd, J 11.3, 2.8 Hz, 2-H), 6.56 (1H, dd, J 7.9, 0.9 Hz, 8-H), 6.74 (1H, td, J 7.4, 0.9 Hz, 6-H), 7.03 (1H, t, J 7.6 Hz, 7-H), 7.18 (1H, d, J 7.7 Hz, 5-H), 7.35 (2H, dd, J 4.7, 1.3 Hz, 3(5)-H_{py}), 8.58 (2H, dd, J 4.5, 1.5 Hz, 2(6)-H_{py}). ¹³C-NMR (100 MHz) δ (ppm): 20.1, 31.1, 41.2, 56.0, 114.4, 118.2, 121.6 (2C), 126.0, 126.9, 127.1, 144.1, 150.2 (2C), 153.4. GC: t_R 20.06 min. MS: m/z (%): 224 (M⁺, 9), 132 (100), 117 (28), 93 (29), 77 (5). t_R 20.29 min. 224 (M⁺, 91), 209 (46), 146 (100), 130 (24), 117 (15), 104 (7), 91 (11), 77 (14), 51 (8). Anal. calc. for C₁₅H₁₆N₂: C, 80.32; H, 7.19; N, 12.49. Found: C, 80.34; H, 7.23; N, 12.51.

4,6-Dimethyl-2-(4-pyridyl)-1,2,3,4-tetrahydroquinoline **12**

White crystals. mp 138-139 °C. Yield: 72%. Molecular formula: C₁₆H₁₈N₂. Molecular weight: 238.33 g mol⁻¹. Eluent: petroleum eter/AcOEt, 5:1. IR (KBr) ν_{\max} /cm⁻¹: 3273 (ν_{NH}) cm⁻¹. ¹H-NMR (CDCl₃, 400 MHz) δ (ppm): *cis* Isomer: 1.34 (3H, d, J 6.8 Hz, 4-CH₃), 1.69 (1H, c, J 11.6 Hz, 3-Ha), 2.10 (1H, ddd, J 12.9, 5.3, 2.1 Hz, 3-He), 2.26 (3H, s, 6-CH₃), 3.12 (1H, sp, J 6.6 Hz, 4-H), 3.86 (1H, bs, NH), 4.43 (1H, dd, J 11.3, 2.6 Hz, 2-H), 6.50 (1H, d, J 8.0 Hz, 8-H), 6.86 (1H, d, J 8.0 Hz, 7-H), 7.00 (1H, s, 5-H), 7.35 (2H, dd, J 4.5, 1.4 Hz, 3(5)-H_{py}), 8.58 (2H, dd, J 4.4, 1.6 Hz,

2(6)-H_{py}). ¹³C-NMR (100 MHz) δ (ppm): 20.2, 20.6, 31.1, 41.4, 56.1, 114.6, 121.6 (2C), 126.0, 127.3, 127.5, 127.6, 141.7, 150.1 (2C), 153.5. GC: t_R 20.78 min. MS: m/z (%): 238 (M⁺, 10), 146 (100), 131 (26), 93 (25). t_R 21.84 min. 238 (M⁺, 100), 223 (44), 160 (83), 144 (20), 130 (12), 115 (8), 91 (8), 51 (6). Anal. calc. for C₁₆H₁₈N₂: C, 80.63; H, 7.61; N, 11.75. Found: C, 80.33; H, 7.57; N, 12.02.

4-Methyl-6-methoxy-2-(4-pyridyl)-1,2,3,4-tetrahydroquinoline **13**

Yellow crystals. mp 113-115 °C. Yield: 54%. Molecular formula: C₁₆H₁₈N₂O. Molecular weight: 254.33 g mol⁻¹. Eluent: petroleum eter/AcOEt, 1:1. IR (KBr) ν_{\max} /cm⁻¹: 3267 (ν_{NH}). ¹H-NMR (CDCl₃, 300 MHz) δ (ppm): *cis* Isomer: 1.33 (3H, d, J 6.8 Hz, 4-CH₃), 1.69 (1H, c, J 11.6 Hz, 3-Ha), 2.11 (1H, ddd, J 13.0, 5.5, 2.7 Hz, 3-He), 3.13 (1H, sp, J 6.3 Hz, 4-H), 3.76 (3H, s OCH₃), 4.40 (1H, dd, J 11.2, 2.3 Hz, 2-H), 6.56 (1H, d, J 8.6 Hz, 8-H), 6.65 (1H, dd, J 8.6, 2.8 Hz, 7-H), 6.79 (1H, d, J 2.7 Hz, 5-H), 7.36 (2H, dd, J 4.6, 1.6 Hz, 3(5)-H_{py}), 8.58 (2H, dd, J 4.6, 1.6 Hz, 2(6)-H_{py}). ¹³C-NMR (75 MHz) δ (ppm): 20.3, 31.3, 41.3, 55.8, 56.2, 112.6, 113.1, 115.4, 121.7 (2C), 127.4, 138.2, 150.0 (2C), 152.5, 153.5. GC: t_R 22.74 min. MS:

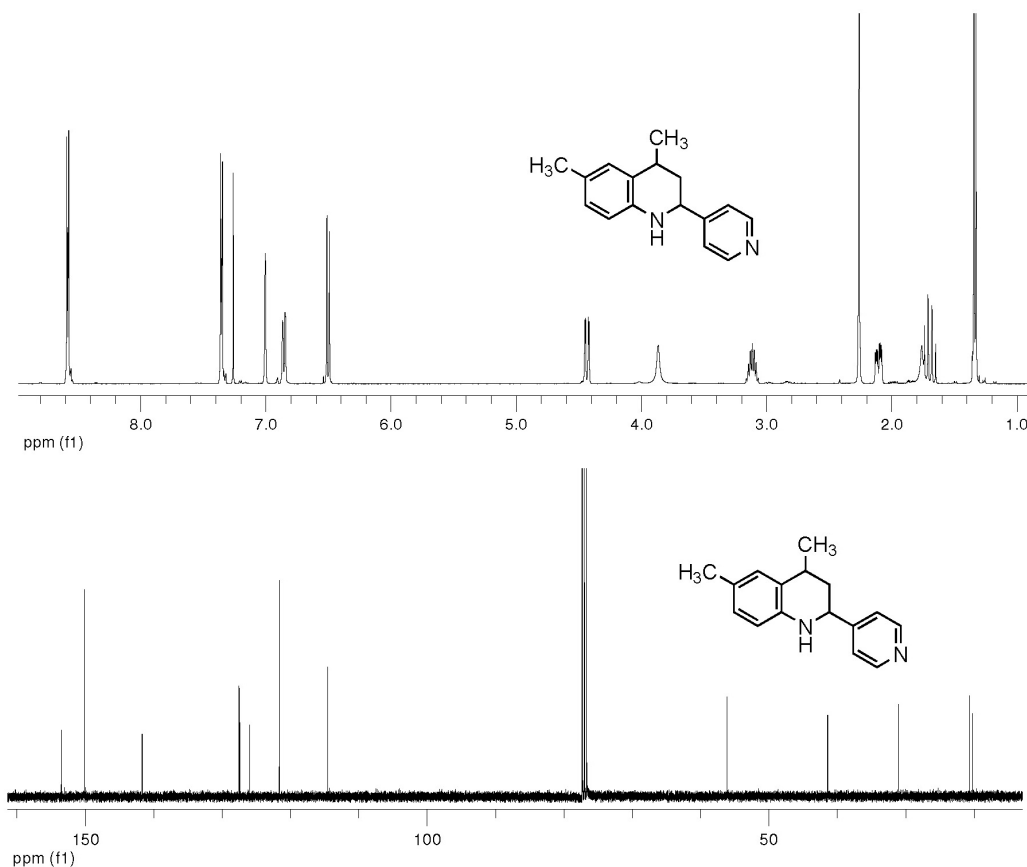


Figure S7. ¹H and ¹³C NMR spectra of **12**.

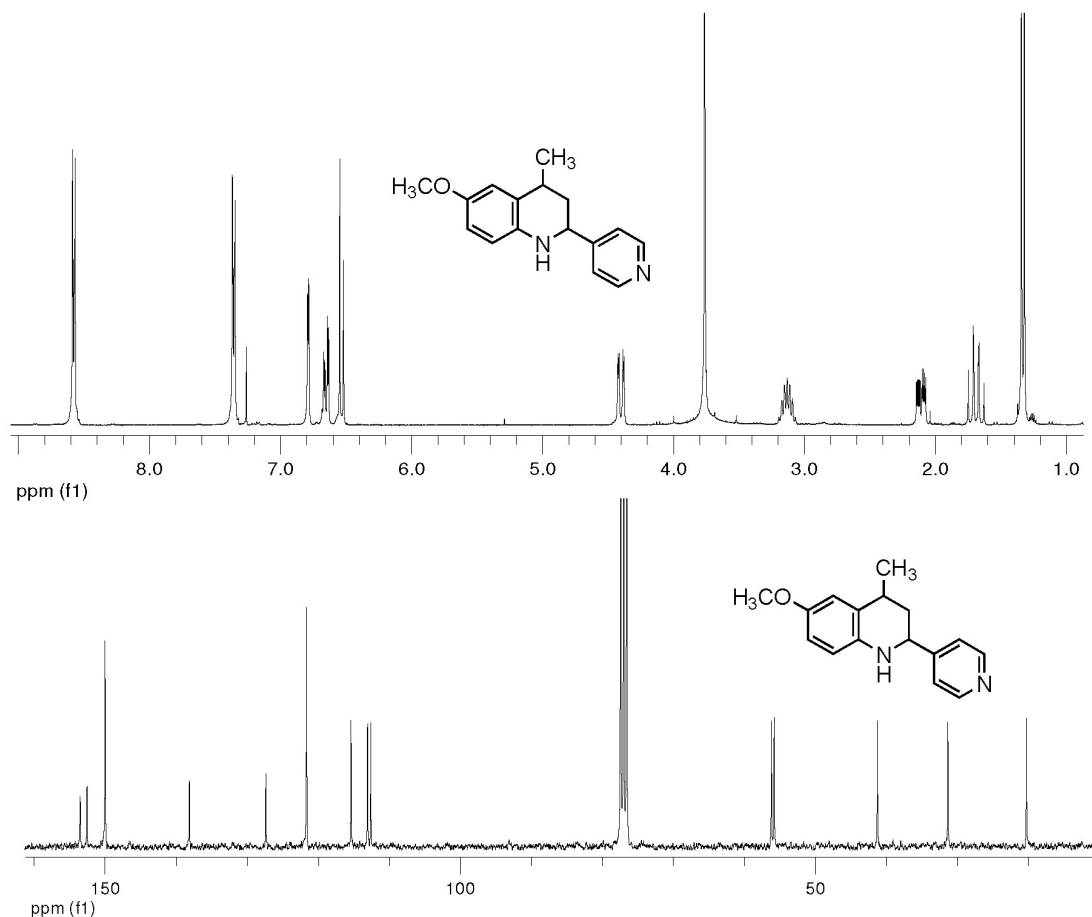


Figure S8. ^1H and ^{13}C NMR spectra of **13**.

m/z (%): 254 (M^+ , 100), 239 (60), 176 (61), 93 (5). Anal. calc. for $\text{C}_{16}\text{H}_{18}\text{N}_2\text{O}$: C, 75.56; H, 7.13; N, 11.01. Found: C, 75.44; H, 7.08; N, 11.15.

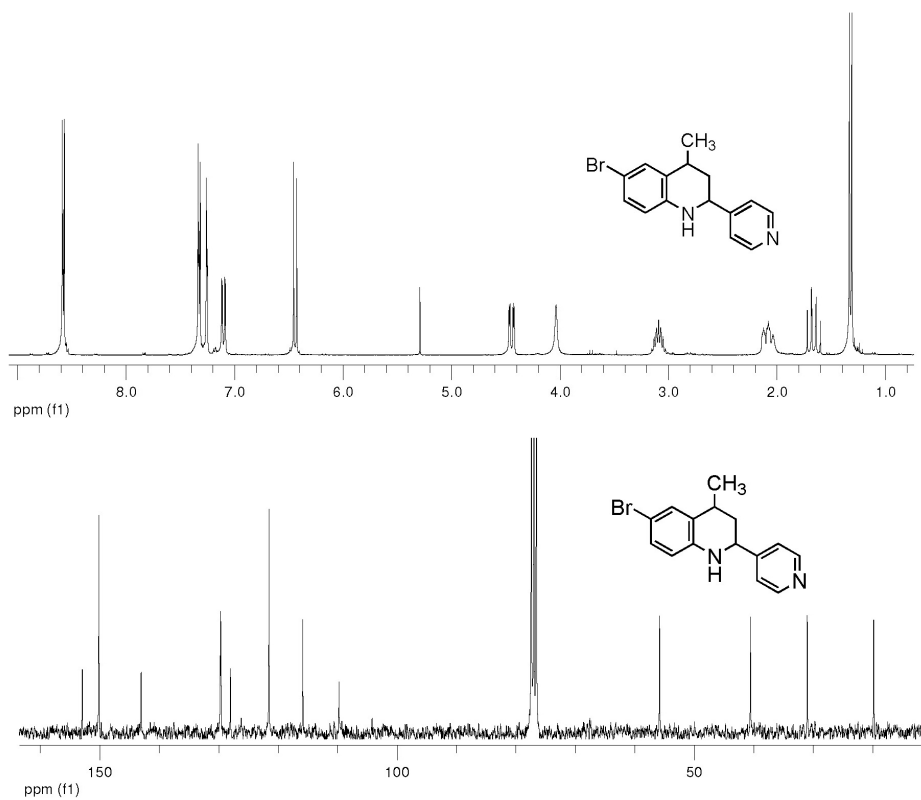
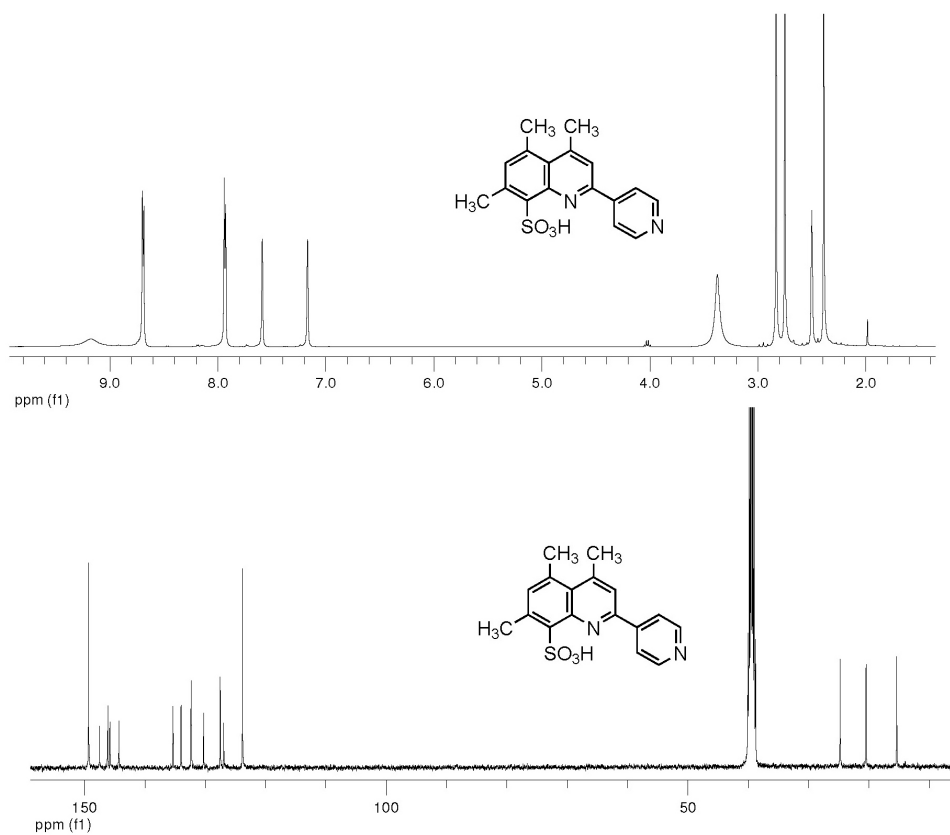
6-Bromo-4-methyl-(4-pyridyl)-1,2,3,4-tetrahydroquinoline **14**

Yellow crystals. mp 104-106 °C. Yield: 68%. Molecular formula: $\text{C}_{15}\text{H}_{15}\text{BrN}_2$. Molecular weight: 303.20 g mol^{-1} . Eluent: AcOEt. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3256 (ν_{NH}). $^1\text{H-NMR}$ (CDCl_3 , 300 MHz) δ (ppm): *cis* Isomer: 1.33 (3H, d, J 6.8 Hz, 4- CH_3), 1.67 (1H, c, J 11.5 Hz, 3-Ha), 2.09 (1H, bt, J 13.1 Hz, 3-He), 3.10 (1H, sp, J 6.4 Hz, 4-H), 4.05 (1H, bs, N-H), 4.46 (1H, dd, J 11.2, 2.9 Hz, 2-H), 6.45 (1H, d, J 8.5 Hz, 8-H), 7.11 (1H, dd, J 8.5, 2.3 Hz, 7-H), 7.27 (1H, d, J 2.2 Hz, 5-H), 7.34 (2H, dd, J 4.4, 1.6 Hz, 3(5)- H_{py}), 8.59 (2H, dd, J 4.5, 1.6 Hz, 2(6)- H_{py}). $^{13}\text{C-NMR}$ (75 MHz) δ (ppm): 19.8, 31.0, 40.6, 55.9, 109.8, 115.9, 121.5 (2C), 128.0, 129.6, 129.7, 143.1, 150.1 (2C), 152.9. GC: t_{R} 23.30 min. MS: m/z (%): 302 (M^+ for ^{79}Br , 100), 287 (19), 224 (80), 208 (48), 145 (39), 130 (87). t_{R} 24.05 min. 302 (M^+

for ^{79}Br , 100), 287 (13), 224 (74), 208 (47), 145 (24), 130 (68). Anal. calc. for $\text{C}_{15}\text{H}_{15}\text{BrN}_2$: C, 59.42; H, 4.99; N, 9.24. Found: C, 59.23; H, 5.16; N, 9.33.

Acid 4,5,7-trimethyl-2-(4-pyridyl)quinoline-8-sulfonic **15**

Green crystals. mp 239-240 °C. Yield: 56%. Molecular formula: $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_3\text{S}$. Molecular weight: 328.39 g mol^{-1} . Eluent: AcOEt/MeOH, 20:1. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 1265, 1180 ($\nu_{\text{S=O}}$), 710 ($\nu_{\text{S-O}}$). $^1\text{H-NMR}$ (DMSO-d_6 , 400 MHz) δ (ppm): 2.39 (3H, s, 5- CH_3), 2.75 (3H, s, 4- CH_3), 2.83 (3H, s, 7- CH_3), 7.17 (1H, s, 5-H), 7.59 (1H, s, 3-H), 7.93 (2H, dd, J 5.2, 1.2 Hz, 3(5)- H_{py}), 8.69 (2H, dd, J 6.0, 1.0 Hz, 2(6)- H_{py}), 9.17 (1H, bs, O-H). $^{13}\text{C-NMR}$ (100 MHz) δ (ppm): 15.4, 20.5, 24.8, 123.8 (2C), 126.9, 127.5, 130.3, 132.3, 134.0, 135.3, 144.3, 145.7, 146.1, 147.5, 149.3 (2C). GC: t_{R} 26.06 min. MS: m/z (%): 328 (M^+ , 100), 235 (52), 221 (12), 158 (15), 128 (7), 115 (13). Anal. calc. for $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_3\text{S}$: C, 62.18; H, 4.91; N, 8.53. Found: C, 62.25; H, 4.77; N, 8.37.

Figure S9. ^1H and ^{13}C NMR spectra of **14**.Figure S10. ^1H and ^{13}C NMR spectra of **15**.