Supplementary Material for Organic & Biomolecular Chemistry

The Baylis-Hillman Approach to Quinoline Derivatives

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Electronic Supplementary Information (ESI).

4-Hydroxy-4-(5-hydroxy-2-nitrophenyl)-3-methylenebutan-2-one **3c** (0.25g, 33%), as brown crystals, m.p. 131 – 133°C (Found, $\mathbf{M}^+$-NO_2: 191.10242. $C_{11}H_{11}NO_5$ requires *M*-NO_2, 191.06925); ν_{max}(KBr)/cm^{-1} 3357 (OH) and 1675 (C=O); δ_H (DMSO-d_6) 2.34 (3H, s, CH_3), 3.33 (1H, br s, OH), 5.63 and 6.19 (2H, 2x s, C=CH_2), 6.22 (1H, overlapping s, C*H*OH), 6.84 (1H, d, *J* 8.4Hz, 3'-H), 7.17 (1H, s, 6'-H), 7.99 (1H, d, *J* 8.4Hz, 4'-H) and 10.85 (1H, br s, Ar-OH); δ_C (DMSO-d_6) 26.01 (C-1), 64.6 (C-4), 114.4, 114.9, 124.9, 127.7, 138.9, 142.3, 150.4 and 162.3 (C=CH_2 and Ar-C) and 198.0 (C=O); *m/z* 191 (M^+-NO_2, 100%).

4-Hydroxy-4-(3-methoxy-2-nitrophenyl)-3-methylenebutan-2-one **3d** *and 5-acetyl-6-hydroxy-6-(3-methoxy-2-nitrophenyl)-3-methylene-2-hexanone* **17**. – Workup and flash chromatography on silica [elution with EtOAc-hexane-$CHCl_3$ (1:1:3)] gave:

i) 4-hydroxy-4-(3-methoxy-2-nitrophenyl)-3-methylenebutan-2-one **3d**.[25] as a reddish-brown oil (0.48g, 24%); and

ii) *5-acetyl-6-hydroxy-6-(3-methoxy-2-nitrophenyl)-3-methylene-2-hexanone* **17** as a reddish-brown oil (1.21g, 60%) [Found (FAB): $\mathbf{M}H^+$, 322.2. $C_{16}H_{19}NO_6$ requires *MH*, 322.13]; δ_H 2.06 and 2.30 (6H, 2x s, 2x CH_3), 2.31 (1H, m, overlapping CH_3 singlet, 4-H_a), 2.50 (1H, m, 4-H_b), 3.09 (1H, m, 5-H), 3.84 (3H, s, OCH_3), 4.04 (1H, br s, OH), 4.66 (1H, br s, 6-H), 5.83 and 6.04 (2H, 2 x s, C=CH_2), 6.94 (1H, d, *J* 8Hz, 6'-H), 7.14 (1H, d, *J* 8Hz, 4'-H) and 7.41 (1H, t, *J* 8.2Hz, 5'-H); δ_C 25.6 (C-1), 30.9 (C-4), 31.9 (5-*C*H_3CO), 54.9 (C-6), 56.4 (OMe), 69.4 (C-5), 111.8, 118.9, 128.6, 131.1, 135.2, 140.0, 144.9 and 150.4 (C=*C*H_2 and Ar-C), 211.3 and 213.1 (2x C=O); *m/z* 321 (M^+, 0.68%) and 200 (100).

4-(2-Chloro-6-nitrophenyl)-4-hydroxy-3-methylenebutan-2-one **3e** (0.36g, 85%), as a reddish-brown oil (Found, $\mathbf{M}^+$: 255.02984. $C_{11}H_{10}NO_4{}^{35}Cl$ requires *M*, 255.02984); ν_{max}(KBr)/cm^{-1} 3490 (OH) and 1687 (C=O); δ_H 2.33 (3H, s, CH_3), 3.68 (1H, s, OH), 5.92 and 6.17 (2H, 2x s, C=CH_2), 6.29 (1H, s, C*H*OH), 7.35 (1H, t, *J* 8.2Hz, 4'-H), 7.45 (1H, d, *J* 8Hz, 5'-H) and 7.55 (1H, d, *J* 8Hz, 3'-H); δ_C 26.0 (C-1), 68.5 (C-4), 122.6, 128.2, 129.2, 131.8, 133.1, 135.4, 146.1 and 151.4 (C=CH_2 and Ar-C) and 199.7(C=O); *m/z* 255 [M^+(^{35}Cl), 0.1%] and 43 (100).

4-Hydroxy-3-methylene-4-(4,5-methylenedioxy-2-nitrophenyl)butan-2-one **3g** (0.82g, 60%), as a reddish-yellow oil [also isolated as yellow crystals (33%); m.p. 100 – 103^{o}C] (Found, $\mathbf{M}^+$: 265.05794. $C_{12}H_{11}NO_6$ requires *M*, 265.05864); ν_{max} (nujol)/cm^{-1} 3463 (OH) and 1662 (C=O); δ_H 2.33 (3H, s, CH_3), 3.67 (1H, s, OH), 5.72 and 6.09 (5H, overlapping signals, C=CH_2, C*H*OH and OCH_2O), 7.16 (1H s, 6'-H) and 7.46 (1H s, 3'-H); δ_C 25.8 (C-1), 67.2 (C-4), 103.0 (OCH_2O), 105.4, 107.6, 125.8, 134.2, 141.7, 147.2, 149.2 and 152.2 (C=CH_2 and Ar-C) and 199.7 (C=O); *m/z* 265 (M^+, 0.9%) and 43 (100).

1-(2-Chloro-6-nitrophenyl)-1-hydroxy-2-methylenepentan-3-one **3i** as pale brown crystals (0.27 g, 25%), m.p. 77 – 79 ºC (Found $\mathbf{M}^+$- NO_2: 223.05111. $C_{12}H_{12}NO_4Cl$ requires *M*-NO_2, 223.05258); ν_{max} (nujol)/cm^{-1} 3389 (OH) and 1664 (C=O); δ_H 1.07 (3H, t, C*H*$_3$CH$_2$), 2.73 (2H, m,CH$_3$C*H*$_2$), 3.54 (1H, d, OH), 5.89 and 6.29 (2H, 2x s, C=CH_2), 6.22 (1H, d, C*H*OH), 7.36 (1H, t, Ar-H), 7.49 (1H, d, Ar-H) and 7.60 (1H, d, Ar-H); δ_C 8.0 (*C*H$_3$CH$_2$), 31.1 (CH$_3$*C*H$_2$), 68.8 (CHOH), 122.7, 126.7, 129.2, 131.9, 133.1, 135.5, 145.7 and 151.4 (C=*C*H$_2$ and Ar-C) and 202.4 (C=O); *m/z* 223 (M^+-NO_2, 3%) and 57 (100).

1-Hydroxy-1-(3-methoxy-2-nitrophenyl)-2-methylenepentan-3-one **3j**, as a brownish oil (2.63 g, 89.7%) (Found $\mathbf{M}^+$- NO_2: 219.10138. $C_{13}H_{15}NO_5$ requires *M*-NO_2, 219.10212); ν_{max}/cm^{-1} (nujol) 3410 (OH) and 1668 (C=O), δ_H 1.06 (3H, t, C*H*$_3$CH$_2$, 2.71 (2H, q, CH$_3$C*H*$_2$), 3.49 (1H, d, OH), 3.87 (3H, s, OCH_3), 5.65 (1H, d, C*H*OH), 5.89 and 6.20 (2H, 2x s, C=CH_2), 6.98 (1H, d, Ar-H), 7.14 (1H, d, Ar-H) and 7.43 (1H, t, Ar-H); δ_C 7.9 (*C*H$_3$CH$_2$), 31.0 (CH$_3$*C*H$_2$), 56.4 (CHOH), 69.4 (OCH_3), 112.0,

119.4, 127.4, 131.1, 135.5, 140.1, 146.9 and 150.8 (C=CH_2 and Ar-C) and 202.6 (C=O); *m/z* 219 (M^+-NO_2, 78%) and 57 (100).

Methyl 3-(4,5-dimethoxy-2–nitrophenyl)-3-hydroxy-2-methylenepropanoate **3m** as a brown oil (0.58 g, 14 %), (Found **M**$^+$: 297.08578. $C_{13}H_{15}NO_7$ requires *M,* 297.08485); ν_{max} /cm^{-1} (nujol) 3489 (OH) and 1708 (C=O); δ_H 3.47 (1H, br s, OH), 3.76 (3H, s, OCH_3). 3.94 and 3.96 (6H, 2x overlapping s, 2x OCH_3), 5.55 and 6.1.7 (2H, 2x s, C=CH_2), 6.29 (1H, overlapping s, C*H*OH*),* 7.24 (1H, s, Ar-H) and 7.62 (1H, s, Ar-H); δ_C 52.3 (OCH_3), 56.7 (CHOH), 66.6 and 67.6 (2x OCH_3), 107.6, 110.0, 125.9, 131.4, 139.9, 141.4, 147.8 and 153.2 (C=CH_2 and Ar-C) and 166.6 (C=O); *m/z* 297 (M^+*,* 26 %) and 192 (100).

3-Hydroxy-2-methylene-3-(2-nitrophenyl)propanenitrile **3q**, as pale yellow crystals (5.2 g, 38 %), m.p. 41- 44 °C (Found **M**$^+$-H_2O: 186.04305. $C_{10}H_8N_2O_3$ requires *M*-H_2O*,* 186.04293); ν_{max} / cm-^{1} (nujol) 3396 (OH) and 2226 (CN); δ_H 3.32 (1H, br s, OH), 6.00 and 6.07 (2H, 2x s, C=CH_2), 6.09 (1H, s, C*H*OH), 7.51 (1H, t, *J* 7.8Hz, Ar-H), 7.70 (1H, t, *J* 7.6Hz, Ar-H), 7.84 (1H, d, *J* 7.4Hz, Ar-H) and 7.98 (1H, d, *J* 7.8Hz, Ar-H); δ_C 69.1 (CHOH), 116.5, 125.1, 124.2, 129.1, 129.7, 132.1, 134.3 and 134.4 (C=CH_2 and Ar-C) and 147.9 (CN); *m/z* 186 *(*M^+-H_2O, 11 %) and 77 (100).

1-(2-Nitrophenyl)-2-(phenylsulfonyl)-2-propenol **3r**, as pale yellow crystals (1.1 g, 32%), m.p. 85-88°C (Found M^+-NO_2: 273.05699. $C_{15}H_{13}NO_5S$ requires *M*-NO_2, 273.05854); ν_{max}/cm^{-1} (nujol) 3477 (OH); δ_H 3.99 (1H, s, OH), 5.68 and 6.48 (2H, 2x s, C=CH_2), 6.06 (1H, s, C*H*OH), 7.42 (1H, m, Ar-H), 7.48 (2H, t, *J* 7.8Hz, Ar-H), 7.61 (2H, m, Ar-H), 7.71 (2H, d, *J* 7.3Hz, Ar-H) and 7.84 (2H, m, Ar-H); δ_C 67.4 (CHOH), 124.6, 124.9, 128.1, 128.4, 129.2, 129.5, 129.7, 133.6, 133.9, 138.3, 147.4 and 151.0 (C=CH_2 and Ar-C); *m/z* 273 (M^+-NO_2, 4.8%) and 160 (100).

Hydrogenation of 4-(5-chloro-2-nitrophenyl)-4-hydroxy-3-methylenebutan-2-one **3b**.– Work-up and flash chromatography on silica [elution with hexane-EtOAc (3:1)] gave:

i) 6-chloro-2,3-dimethylquinoline **8b**[31] as a brown oil (0.32g; 26%); and

ii) *6-chloro-2,3-dimethylquinoline-N-oxide* **9b** as a brown solid (0.30g; 23%) (Found **M**$^+$: 207.04608. $C_{11}H_{10}NO^{35}Cl$ requires *M*, 207.04509); δ_H 2.43 (3H, s, 3-CH_3), 2.64 (3H, s, 2-CH_3), 7.35 (1H, s, 4-H), 7.54 (1H, d, *J* 9.2Hz, 7-H), 7.66 (1H, s, 5-H) and 8.61 (1H, d, *J* 9.2Hz, 8-H); δ_C 13.7 (3-CH_3), 19.3 (2-CH_3), 120.6**,** 122.9, 124.8, 127.9, 128.9, 131.4, 132.8, 137.5 and 145.6 (Ar-C); *m/z* 207 [$M^+(^{35}Cl)$; 43.9%] and 190 (100).

Hydrogenation of 4-hydroxy-4-(5-hydroxy-2-nitrophenyl)-3-methylenebutan-2-one **3c**.– Work-up and flash chromatography on silica [elution with hexane-EtOAc (3:1)] gave:

i) *6-hydroxy-2,3-dimethylquinoline* **8c** as yellow crystals (0.165g, 15%), m.p. 260 – 262 ºC (Found M^+: 173.08338 $C_{11}H_{11}NO$ requires *M,* 173.08406); ν_{max}(KBr)/cm^{-1} 3412 (OH); δ_H 2.32 (3H, s, 3-CH_3), 2.46 (3H, s, 2-CH_3), 6.97 (1H, s, 4-H), 7.13 (1H, d, *J* 8.8Hz, 7-H), 7.69 (1H, d, *J* 8.8Hz, 8-H), 7.75 (1H, s, 5-H) and 9.71 (1H, s, Ar-OH); δ_C 22.7 and 30.6 (2x CH_3), 107.5, 120.4, 128.2, 129.2, 129.9, 133.2, 141.0, 154.6 and 154.9 (Ar-C); *m/z* 173 (M^+, 100%); and

ii) *6-hydroxy-2,3-dimethylquinoline*-N-*oxide* **9c** as cream crystals (0.22g, 20%), m.p. 266-268 ºC (Found, MH^+: 190.22136 requires $C_{11}H_{11}NO_2$, *MH*$^+$, 190.22084); ν_{max}(KBr)/cm^{-1} 3435 (OH) and 1230 (N-O); δ_H (DMSO-*d*$_6$) 2.39 (3H, s, 3-CH_3), 2.51 (3H, s, 2-CH_3), 7.10 (1H, s, 4-H), 7.23 (1H, m, 7-H), 7.52 (1H, d, *J* 2.4Hz, 5-H), 8.36 (1H, d, *J* 9.6Hz, 8-H) and 10.2 (1H, br s, Ar-OH); δ_C (DMSO-*d*$_6$) 14.8 and 20.5 (2x CH_3), 118.8, 121.7, 126.2, 127.9, 128.8, 131.1, 131.9, 141.1 and 147.0 (Ar-C); *m/z* 190 (MH^+, 100%).

Hydrogenation of 4-hydroxy-4-(3-methoxy-2-nitrophenyl)-3-methylenebutan-2-one **3d**.– Work-up and flash chromatography on silica [elution with hexane-EtOAc (1:1)] gave:

i) 8-methoxy-2,3-dimethylquinoline **8d**[32] as yellow crystals (0.09g, 26%); and

ii) *4-hydroxy-3-methyl-4-(2-nitro-3-methoxyphenyl)butan-2-one* **10d** as yellow crystals (0.15g, 38%), m.p. 154 – 156°C [Found, **M**H$^+$(FAB): 254.2**.** $C_{12}H_{15}NO_5$ requires *MH*, 254.1); ν_{max}(KBr)/cm^{-1} 3449 (OH) and 1712 (C=O); δ_H 1.01 (3H, d, *J* 7.2Hz, C*H*$_3$CH), 2.18 (3H, s, CH_3CO), 3.02 (1H, m, 3-H), 3.26 (1H, br s, 4-H), 3.90 (3H, s, OMe), 4.78 (1H, br s, OH), 6.97 (1H, d, *J* 8.4Hz, 6'-H), 7.05 (1H, d, *J* 8Hz, 4'-

H) and 7.42 (1H, t, *J* 7Hz, 5'-H); δ_C (100MHz; $CDCl_3$) 14.1 (*C*H_3CH), 29.9 (C-3), 52.3 (*C*H_3CO), 56.5 (OCH_3), 71.9 (C-4), 111.9, 119.3, 131.1, 134.8 (2x overlapping signals) and 150.6 (Ar-C) and 212.7 (C=O).

Hydrogenation of 4-(6-chloro-2-nitrophenyl)-4-hydroxy-3-methylenebutan-2-one **3e**.– Work-up and flash chromatography on silica [elution with hexane-EtOAc (1:1)] gave:
i) *5-chloro-2,3-dimethylquinoline* **8e** as a brown oil (0.087g, 29%), (Found $\mathbf{M}^+$: 191.04614. $C_{11}H_{10}N^{35}Cl$, requires *M*, 191.05018); ν_{max}(KBr)/cm^{-1} 799 (C-Cl); δ_H 1.89 (3H, s, 3-CH_3), 2.46 (3H, s, 2-CH_3), 7.03 (1H, overlapping t, 7-H), 7.04 (1H, overlapping s, 4-H), 7.23 and 7.24 (2H, 2 x overlapping d, 6-H and 8-H); δ_C 9.54 and 32.7 (2x CH_3), 107.4, 110.5, 113.7, 118.4, 122.8, 124.7, 134.4 and 138.5 (Ar-C) and 201.2 (C=O); *m/z* 191 [M^+(^{35}Cl), 19.8%] and 43 (100); and
ii) *5-chloro-2,3-dimethylquinoline*-N-*oxide* **9e** as a brown oil (0.04g, 13%) (Found M^+: 207.04475. $C_{11}H_{10}NO^{35}Cl$, requires *M*, 207.04509); δ_H 2.49 (3H, s, 3-CH_3), 2.68 (3H, s, 2-CH_3), 7.55 (1H, t, *J* 8Hz, 7-H), 7.61 (1H, d, *J* 7.2Hz, 6-H), 7.84 (1H, s, 4-H) and 8.63 (1H, d, *J* 8.8Hz, 8-H); δ_C 14.8 and 20.5 (2x CH_3), 118.8, 121.7, 126.2, 127.9, 128.8, 131.1, 131.9, 141.1 and 147.0 (Ar-C); *m/z* 207 [M^+(^{35}Cl), 71.6%] and 190 (100).

Hydrogenation of 4-hydroxy-3-methylene-4-(4,5-methylenedioxy-2-nitrophenyl)butan-2-one **3g**.– Work-up and flash chromatography on silica [elution with hexane-EtOAc-$CHCl_3$ (1:1:3)] afforded. as yellow crystals, 2,3-dimethyl-6,7-methylenedioxy-quinoline **8g**[33] (0.22g, 26%).

In a later experiment, hydrogenation of 4-hydroxy-3-methylene-4-(4,5-methylene-dioxy-2-nitrophenyl)butan-2-one **3g** afforded, after work-up and chromatography, *4-(2-nitro-4,5-methylenedioxyphenyl)-4-hydroxy-3-methylbutan-2-one* **10g** (0.23g, 30%); δ_H 1.16 (3H, d, *J* 7.2Hz, C*H*$_3$CH), 2.12 (3H, s, CH_3CO), 2.98 (1H, m, 3-H), 3.93 (1H, br s, OH), 5.42 (1H, d, *J* 6.0Hz, 4-H), 6.09 (2H, s, CH_2), 7.08 (1H, s, 3'-H) and 7.43 (1H, s, 6'-H); δ_C 13.5 (*C*H_3CH), 30.1 (*C*H_3CO), 52.3 (C-3), 70.3 (C-4), 102.3, 104.5, 134.4, 141.1, 106.8, 147.4 and 151.2 (Ar-C) and 212.7 (C=O).

Hydrogenation of 1-hydroxy-2-methylene-5-(2-nitrophenyl)pentan-3-one **3h**. - Work-up and flash chromatography on silica [elution with hexane-EtOAc (1:2)] gave:
i) 2-ethyl-3-methylquinoline-N-oxide **9h**[36] as brown crystals (0.31 g, 39%); and
ii) 2-ethyl-3-methylquinoline **8h**[34] as a brown oil (0.25 g, 34%).

Hydrogenation of methyl 3-hydroxy-2-methylene-3-(2-nitrophenyl)propanoate **3l**. - Work-up and flash chromatography on silica [elution with hexane-EtOAc (3:2)] gave:
i) 3-methyl-2-quinolone **12l**[37] as a brown oil (0.10 g, 15%);
ii) 3-Methyl-2-oxo-1,2,3,4-tetrahydroquinoline **13l**[39] as a brown oil (0.31 g, 41%); and
iii) *4-Hydroxy-3-methyl-2-oxo-1,2,3,4-tetrahydroquinoline* **11l** as a brown oil (0.12 g, 18%), (Found **M**H^+: 178.086922. $C_{10}H_{11}NO_2$ requires MH^+ 178.086804); ν_{max}/cm^{-1} (nujol) 3423 (OH) and 1649 (C = O); δ_H 1.67 (3H, d, CH_3), 2.79 (1H, m, CH_3CH), 4.58 (1H, s, OH), 4.74 (1H, d, C*H*OH), 6.97 (1H, d, Ar-H), 7.17 (1H, d, Ar-H), 7.19 (1H, t, Ar-H), 7.28 (1H, t, Ar-H) and 10.47 (1H, br s, NH); δ_C (100 MHz; $CDCl_3$) 10.4 (CH_3), 41.4 (CH_3CH), 70.8 (CHOH), 115.4, 123.5, 128.0, 129.7, 133.3 and 133.9 (Ar-C) and 167.5 (C=O); *m/z* 178 (MH^+, 38%) and 154 (100).

Hydrogenation of methyl 3-(5-chloro-2-nitrophenyl)-3-hydroxy-2-methylenepropanoate **3n**. - Work-up and flash chromatography on silica [elution with hexane-EtOAc (1:2)] gave:
i) 6-chloro-3-methyl-2-quinolone **12n**[38] as brown crystals (0.08g, 11%); and
ii) 6-chloro-3-methyl-2-oxo-1,2,3,4-tetrahydroquinoline **13n**[40] as yellow crystals (0.17 g, 24%).

Hydrogenation of 5-acetyl-6-hydroxy-6-(3-methoxy-2-nitrophenyl)-3-methylene-2-hexanone **17**.– Work-up and flash chromatography on silica [elution with hexane-EtOAc (1:3)] gave:
i) *8-methoxy-2-methyl-3-(2-methyl-3-oxobutyl)quinoline* **19** as a yellow oil (0.025g, 7%), (Found **M**$^+$: 257.14224. $C_{16}H_{19}NO_2$ requires *M*, 257.14158); δ_H 1.16 (3H, d, *J* 6.8Hz, CH_3CH), 2.09 (3H, s, CH_3CO), 2.71 and 3.19 (2H, 2 x m, CH_2), 2.79 (3H, s, 2-CH_3), 2.91 (1H, m, 2'-H), 4.06 (3H, s, OCH_3), 6.98 (1H, d, *J* 7.6Hz, 5-H), 7.28 (1H, d, *J* 8Hz, 7-H), 7.39 (1H, t, *J* 8Hz, 6-H) and 7.78 (1H, s, 4-H); δ_C 16.6 ($CHCH_3$), 23.6

(2-CH_3), 28.9 (CH_3CO), 35.5 (C-1'), 46.8 (C-2'), 55.9 (OCH_3), 107.1, 118.9, 126.0, 128.2, 132.2, 136.1, 138.2, 154.6 and 157.3 (Ar-C) and 211.2 (C=O); and

ii) *5-acetyl-6-hydroxy-3-methyl-6-(2-nitro-3-methoxyphenyl)-2-hexanone* **18** as a red oil (0.18g, 43%); ν_{max}(KBr)/cm^{-1} 1687 (C=O); δ_H 1.07 (3H, d, *J* 7.2Hz, CHC*H*$_3$), 1.71 (1H, m, 3-H), 2.09 and 2.14 (6H, 2x s, 2x CH_3CO), 3.02 (1H, m, 5-H), 3.15 and 3.89 (2H, 2x s, 4-CH_2), 3.25 (1H, br s, OH), 3.90 (3H, s, OCH_3), 4.74 (1H, br t, *J* 5.4Hz, 6-H), 6.98 (1H, t, *J* 9.8Hz, 5'-H), 7.10 (1H, d, *J* 8.0Hz, 6'-H) and 7.48 (1H, d, *J* 8.0Hz, 4'-H); δ_C 17.2 (CH*C*H$_3$), 27.8 and 31.7 (2 x *C*H$_3$CO), 44.5 (C-4), 54.8 (C-5), 56.5 (OCH_3), 70.7 (C-3), 112.1, 118.9, 131.4, 134.9, 140.4, 140.5 and 150.6 (Ar-C), 211.5 and 212.5 (2x C=O).

3-Acetyl-1-hydroxy-1,2-dihydroquinoline **14a**, as a yellow powder (0.07 g, 21 %), m.p. 77-80 °C (Found **M**$^+$: 189.07992. $C_{11}H_{11}NO_2$ requires *M,* 189.07698); δ_H 2.45 (3H, s, CH_3), 5.01 (2H, s, CH_2), 6.81 (1H, d, *J* 11.4Hz, Ar-H), 7.13 (1H, t, *J* 11.4Hz, Ar-H), 7.29 (1H, m, Ar-H), 7.33 (1H, s, OH), 7.43 (1H, d, *J* 11.4Hz, Ar-H) and 7.48 (1H, s 4-H); δ_C 25.8 (CH_3), 77.2 (C-2), 116.5, 124.3, 125.6, 130.0, 134.4, 138.3, 142.5 and 150.3 (Ar-C) and 198.5 (C=O); *m/z* 190 *(*M$^+$*,* 87 %) and 189 (100).

1-Hydroxy-3-propanoyl-l,2-dihydroquinoline **14h**, as yellow crystals (0.04 g, 10 %), m.p. 85-89°C (Found **M**H$^+$: 204.102416. $C_{12}H_{13}NO_2$ requires *MH,* 204.102454); δ_H 1.16 (3H, t, CH_3), 2.84 (2H, q, CH_3CH_2*),* 4.98 (2H, s, CH_2), 6.81 (1H, d, Ar-H), 7.11 (1H, t, Ar-H), 7.27 7(1H, t, Ar-H), 7.34 (1H, s, OH), 7.42 (1H, d, Ar-H) and 7.49 (1H, s, 4-H); δ_C 8.5 (CH_3), 30.6 (CH_3CH_2), 77.1 (C-2), 116.5, 124.3, 125.3, 129.8, 134.3, 136.8, 142.0 and 150.2 (Ar-C) and 201.1 (C=O); *m/z* 204 (MH$^+$*,* 83 %) and 203 (100).

Ethyl 1,2-dihydroquinoline-3-carboxylate **15p**, as an off-white powder (0.15 g, 15 %), m.p. 170-172°C (Found **M**$^+$: 203.09556. $C_{12}H_{13}NO_2$ requires *M,* 203.09463); ν_{max} (nujol)/cm^{-1} 1662 (C=O); δ_H 1.26 (3H, t, CH_3), 3.69 (2H, q, CH_2CH_3*),* 4.56 (2H, s, CH_2), 7.22 (1H, t, Ar-H), 7.32 (1H, d, Ar-H), 7.47 (1H, t, Ar-H), 7.59 (1H, d, Ar-H), 7.91 (1H, s, Ar-H) and 9.95 (1H, br s, NH); δ_C 15.3 (CH_3), 66.7 (OCH_2, 67.2 (C-2), 115.3, 120.1, 122.7, 127.8, 129.9, 130.7, 136.0 and 137.3 (Ar-C) and 162.5 (C=O); *m/z* 204 *(*MH$^+$*,* 1 %) and 159 (100).

3-(2-aminophenyl)-3-hydroxy-2-methylpropanenitrile **20q** as a brown oil (0.43 g, 50%), (Found **M**H$^+$: 177.102697. $C_{10}H_{13}N_2O$ requires *MH*$^+$, 177.102788); ν_{max}(nujol)/cm^{-1} 3371 (OH) and 2244 (CN); δ_H 1.08/1.35 (3H, d, CH_3), 3.24/3.39 (1H, m CHCN), 3.93 (1H, br s, OH), 4.57/4.72 (1H, d, C*H*OH), 6.64 (1H, d, Ar-H), 6.70 (1H, m, Ar-H), 6.76 (1H, d, Ar-H), 7.11 (1H, m, Ar-H) and 7.12 (2H, br s, NH_2); δ_C 14.2/15.3 (CH_3), 30.26/30.9 (CH_3*C*H), 75.0 (CHOH), 117.7/117.5, 118.3/118.3, 121.2/122.0, 122.7/124.0, 128.5/129.3 and 129.6/129.8 (Ar-C) and 144.5/145.0 (CN); *m/z* 177 *(MH*$^+$, 68%) and 122 (100).

1-(2-aminophenyl)-2-phenylsulfonylpropanol **20r** as yellow crystals (0.39 g, 43%), m.p. 63-66 °C (Found **M**H$^+$: 292.100812. $C_{15}H_{17}NO_3S$ requires *MH*, 292.100740); ν_{max}/cm^{-1}(nujol) 3366 (OH) and 3162 (NH_2); δ_H 0.81/1.24 (3H, d, CH_3), 3.41/4.09 (1H, m, SO_2CH), 5.02 (1H, d, CHOH), 4.41 (2H, br s, NH_2), 4.55 (1H, br s, OH), 6.62 (1H, m, Ar-H), 6.75 (1H, t, Ar-H), 6.85 (1H, d, Ar-H), 7.07 (1H, m, Ar-H), 7.21 (1H, t, Ar-H), 7.60 (1H, m, Ar-H), 7.70 (1H, m, Ar-H), 7.82 (1H, t, Ar-H) and 7.94 (1H, d, Ar-H); δc 6.73/12.93 (CH_3); 62.3/62.6 ($CHCH_3$), 66.3/75.2 (CHOH), 116.3/117.1, 117.9/118.4, 122.6/124.0, 126.3/128.4, 128.8/129.1, 129.3/129.7, 133.9/137.0, 142.2, 144.3 and 145.6; *m/z* 292 (MH$^+$, 34%) and 122 (100).