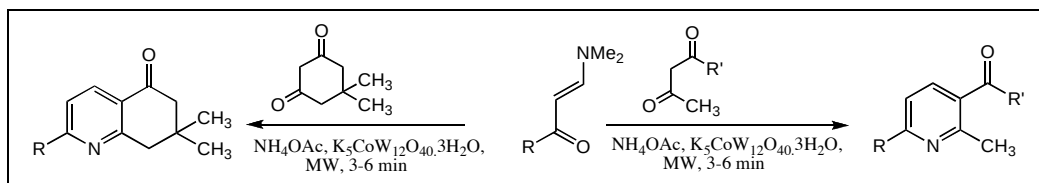


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A highly efficient, microwave-assisted, regioselective synthesis of 2,3-disubstituted-6-arylpyridines and new series of 7,7-dimethyl-2-aryl-5,6,7,8-tetrahydroquinoline-5-ones from enaminones in the presence of $K_5CoW_{12}O_{40} \cdot 3H_2O$ (1.0 mol %) as heterogeneous catalyst under solvent free conditions is reported.

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INTRODUCTION

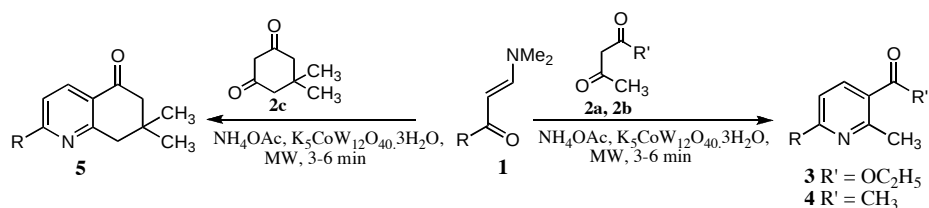
Synthesis of pyridine ring system and its derivatives [1] occupy an important place in the realm of natural and synthetic organic chemistry. Because of their therapeutic and pharmacological properties, they have emerged as integral backbones of over 7000 existing drugs [2] and are ideal scaffolds to make libraries of inhibitors of HIV-1 protease [3,4]. Enaminoketones are readily available versatile intermediates and play an important role in the synthesis of a number of heterocyclic compounds [5]. 6-Aryl-2-methylnicotinates are synthesized by the condensation of 3-amino-

temperatures, long reaction times; has difficulty in isolation and unsatisfactory yields.

RESULTS AND DISCUSSION

Microwave mediated [13] multicomponent reactions (MCRs) leading to heterocycles under solvent free [14] conditions are efficient, in terms of energy used, enhanced reaction rates and provides improved yields with often only water as waste. Over recent years potassium dodecatungstocobaltate trihydrate [15] ($K_5CoW_{12}O_{40} \cdot 3H_2O$) and heteropoly acid mediated reactions have attracted tremendous interest throughout the scientific communities due to their

Scheme 1.



crotonate with acetophenone Mannich base hydrochlorides in refluxing ethanol [6,7], with acetylenic ketones [8] at higher temperatures, from oxazolidines in refluxing acetonitrile in the presence of acetic acid [9] and its microwave modification [10] in DMSO. Recently these compounds are prepared by the condensation of enaminoketones, β -dicarbonyl compounds and ammonium acetate in refluxing acetic acid [11], and later by montmorillonite K10 in refluxing isopropanol [12]. However many of these methods involve the use of stoichiometric amounts of catalysts, more polar solvents like AcOH, DMSO, reflux

low toxicity, ease of handling, low cost, stability, reusability, water and organic solvent tolerant nature of the reagent. In continuation of our efforts towards the synthesis and development of new methodologies in organic synthesis [16], we herein describe a general and practical route for the synthesis of 2,3-disubstituted-6-aryl pyridines and 7,7-dimethyl-2-aryl-5,6,7,8-tetra-hydroquinoline-5-ones using $K_5CoW_{12}O_{40} \cdot 3H_2O$ (1.0 mol%) as the catalyst under solvent free microwave assisted reaction conditions (Scheme 1). To the best of our knowledge, the generality and applicability of $K_5CoW_{12}O_{40} \cdot 3H_2O$ in the preparation of substituted pyridines is not known.

Table-1

$K_3CoW_{12}O_{40} \cdot 3H_2O$ Catalyzed synthesis of 2,3-disubstituted-6-aryl pyridines **3a–d**, **4a–d** and 7,7-dimethyl-2-aryl-5,6,7,8-tetrahydroquinoline-5-ones **5a–e**.

Entry	R	Product	Reaction time [a] (minutes)	Yield [b] (%)	Mp (°C)	Ref.
1	C ₆ H ₅	3a	5	90	45	[12]
2	<i>p</i> -NO ₂ C ₆ H ₄	3b	3	97	142	[12]
3	<i>p</i> -BrC ₆ H ₄	3c	4	95	75	[12]
4	1-Naphthyl	3d	5	92	oil	-
5	<i>p</i> -NO ₂ C ₆ H ₄	4a	4	95	131	-
6	<i>p</i> -BrC ₆ H ₄	4b	3	94	78	-
7	<i>p</i> -CH ₃ C ₆ H ₄	4c	6	91	84	-
8	C ₆ H ₅	4d	6	89	110	[12]
9	<i>p</i> -NO ₂ C ₆ H ₄	5a	3	98, 95, 90 [c]	182	-
10	C ₆ H ₅	5b	5	90	67	-
11	<i>p</i> -BrC ₆ H ₄	5c	4	93	132	-
12	<i>p</i> -OCH ₃ C ₆ H ₄	5d	6	83	125	-
13	1-Naphthyl	5e	6	90	oil	-

[a] All the reactions were carried out in a domestic microwave oven at 540W. [b] Yield of the corresponding isolated and purified product. All compounds were fully characterized by IR, NMR and mass spectroscopy. [c] The yields obtained after 1st, 3rd, and 5th successive reuse of catalyst.

In a typical general experimental procedure a mixture of enaminoketones **1**, β -dicarbonyl compounds (ethyl acetoacetate **2a**, acetylacetone **2b**, or dimedone **2c**) and ammonium acetate in the presence of catalytic amount of $K_3CoW_{12}O_{40} \cdot 3H_2O$ (1.0 mol %) were subjected to microwave irradiation under solvent free conditions to get substituted pyridines **3**, and **4** or substituted tetrahydroquinoline-5-ones **5** in excellent yields. In order to improve the yields we performed reactions using different quantities of reagents and varying microwave power settings and exposure times. The best results were obtained with 0.01:1:1:2.5 ratios of $K_3CoW_{12}O_{40} \cdot 3H_2O$, enaminoketone, 1,3-dicarbonyl compounds and ammonium acetate respectively in a domestic microwave oven at 540W for 3 to 6 min. After completion of reaction as indicated by TLC the reaction mixture was cooled to room temperature, methanol was added and catalyst was filtered off. The filtrate was quenched with crushed ice and precipitated solid was filtered to get substituted pyridines or substituted tetrahydroquinoline-5-one derivatives. To study the generality of this process several examples illustrating this novel and general method for the synthesis of 2,3-disubstituted-6-aryl pyridines and 7,7-dimethyl-2-aryl-5,6,7,8-tetrahydroquinoline-5-ones were studied and are summarized in Table 1. More over the catalyst could be quantitatively recovered from the reaction mixture and could be reused after thermal activation (80 °C, for 2h). For example the catalyst was reused in the preparation of 7,7-dimethyl-2-(4-nitrophenyl)-5,6,7,8-tetrahydroquinoline-5-one **5a** more than five times without loss of activity.

Many of the pharmacologically relevant substitution patterns on the aromatic ring of the enaminoketones could

be introduced with high efficiency and are produced with high yields of products in high purity (≥ 95 % by ¹H NMR). However the nature of the functional group on the aromatic ring of the enaminoketones exerted a strong influence on the reaction time. An increase of the reaction rate was observed with enaminoketones bearing an electron withdrawing group in the *p*-position **5a** in comparison to the unsubstituted **5b** enaminoketone. The presence of an electron donating methoxy group **5d** decreased both the rate of reaction and yield of product. Acid sensitive β -dicarbonyl compounds such as ethyl acetoacetate, acetylacetone and dimedone worked well without formation of any side products with variety of structurally and electronically divergent enaminoketones. Use of just 1 mol % of $K_3CoW_{12}O_{40} \cdot 3H_2O$ is sufficient to push the reaction forward. No additive or protic/Lewis acid is necessary in the procedure. Another important aspect of this procedure is survival of variety of functional groups, NO₂, Br, OCH₃ and various β -dicarbonyl compounds and the catalyst is reusable under the reaction condition employed.

In conclusion we described herein the regioselective one-pot three component synthesis of trisubstituted pyridines and 7,7-dimethyl-2-aryl-5,6,7,8-tetrahydroquinoline-5-ones by a reusable potassium dodecatungstocobaltate trihydrate under solvent free microwave irradiation conditions. Moreover this method offers several advantages including high yields, short reaction times, and a simple workup procedure and it also has the ability to tolerate a wide variety of substitution in the components and reaction conditions. Furthermore, the present procedure is readily amenable to parallel synthesis and generation of combinatorial 2,3,6-trisubstituted

pyridines and 7,7-dimethyl-2-aryl-5,6,7,8-tetrahydroquinoline-5-ones libraries.

EXPERIMENTAL

General procedure for the preparation of 2,3,6-trisubstituted pyridines (3a-d, 4a-d) and 7,7-dimethyl-2-aryl-5,6,7,8-tetrahydroquinoline-5-ones (5a-e). Enaminoketone **1** (2 mmol), β -dicarbonyl compound **2** (2 mmol) ammonium acetate (5 mmol) and $\text{K}_2\text{CoW}_{12}\text{O}_{40} \cdot 3\text{H}_2\text{O}$ (0.064 g, 0.02 mmol, 1 mol%) was charged into a 15 mL open glass vial with a 20 mm diameter. The mixture was stirred gently with a spatula for a few seconds and was subjected to microwave irradiation (Kenstar-3D Power OM-34ECR) at 540W for 3 to 6 min. After completion of reaction (monitored by TLC) the crude mixture was cooled to 30 °C, hot methanol (5 mL) was added and catalyst was filtered and cake was washed with hot MeOH (2x2 mL). Filtrate was cooled and triturated with crushed ice (1 g) and precipitated solid was filtered to get pure products (single spot on TLC). They were further purified by column chromatography on silica gel using petroleum ether/EtOAc, 9:1 as the eluent to give trisubstituted pyridines **3a-d**, **4a-d** and tetrahydroquinoline-5-ones **5a-e** in 83-98% yields. The filtered catalyst was reactivated by heating in oven at 80 °C for 2h and reused at least for five times without loss of activity.

Ethyl (2-methyl-6-phenyl)nicotinate (3a). Pale yellow solid (90 %), mp 43-45 °C (lit. [12] 43-45 °C); ir (KBr): 2991, 2928, 1715, 1581, 1451, 1269, 1088, 758, 691 cm^{-1} ; ^1H nmr (300MHz, CDCl_3 , TMS): δ 1.42 (t, $J=7.1$ Hz, 3H), 2.92 (s, 3H), 4.38 (q, $J=7.1$ Hz, 2H) 7.42 (m, 3H), 7.60 (d, $J=8.1$ Hz, 1H), 8.05 (m, 2H), 8.22 (d, $J=8.3$ Hz, 1H); ^{13}C nmr (50 MHz, CDCl_3): δ 14.1, 25.1, 60.9, 117.1, 123.5, 127.2, 128.6, 129.5, 138.4, 139.1, 158.9, 159.8, 166.5; ms: m/z 241 (M^+ , 100%), 213 (26), 196 (93), 169 (32), 155 (12), 141 (57), 128 (26), 115 (70), 98 (22), 84 (20), 77 (26), 57 (12), 51 (15). *Anal.* Calcd for $\text{C}_{15}\text{H}_{15}\text{NO}_2$: C, 74.67; H, 6.27; N, 5.81. Found: C, 74.59; H, 6.31; N, 5.93.

Ethyl (2-methyl-6-*p*-nitrophenyl)nicotinate (3b). Pale yellow solid (97 %), mp 142 °C (lit. [12] 142-143 °C); ir (KBr): 3094, 2974, 2928, 2849, 1719, 1580, 1517, 1436, 1371, 1340, 1260, 1160, 1087, 847, 791, 746 cm^{-1} ; ^1H nmr (300MHz, CDCl_3 , TMS): δ 1.45 (t, $J=7.5$ Hz, 3H), 2.92 (s, 3H), 4.42 (q, $J=7.5$ Hz, 2H) 7.70 (d, $J=8.3$ Hz, 1H), 8.22 to 8.37 (m, 5H); ^{13}C nmr (50 MHz, CDCl_3): δ 14.2, 25.0, 61.3, 117.9, 123.8, 125.0, 127.9, 139.5, 144.1, 148.4, 156.0, 160.2, 166.1; ms: m/z 286 (M^+ , 100%), 242 (88), 207 (55), 178 (27), 150 (91), 140 (26), 104 (32), 75 (28), 43 (60). *Anal.* Calcd for $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_4$: C, 62.93; H, 4.93; N, 9.79. Found: C, 63.08; H, 4.86; N, 9.88.

Ethyl (2-methyl-6-*p*-bromophenyl)nicotinate (3c). (95 %), mp 75 °C (lit. [12] 72-74 °C); ir (KBr): 2978, 2929, 1721, 1582, 1451, 1369, 1267, 1089, 1009, 826, 779 cm^{-1} ; ^1H nmr (300MHz, CDCl_3 , TMS): δ 1.44 (t, $J=6.8$ Hz, 3H), 2.89 (s, 3H), 4.36 (q, $J=6.8$ Hz, 2H) 7.55 (m, 3H), 7.93 (d, $J=7.5$ Hz, 2H), 8.20 (d, $J=8.3$ Hz, 1H); ms: m/z 319 (M^+ , 96%), 317 (100), 275 (16), 275 (64), 274 (66), 249 (47), 247 (54), 182 (25), 167 (77), 155 (21), 141 (41), 126 (11), 115 (9), 83 (13), 75 (15), 63 (11), 39 (14). *Anal.* Calcd for $\text{C}_{15}\text{H}_{14}\text{BrNO}_2$: C, 56.27; H, 4.41; N, 4.37. Found: C, 56.31; H, 4.30; N, 4.31.

Ethyl (2-methyl-6-1-naphthyl)nicotinate (3d). Pale yellow oil (92%); ir (film): 3052, 2979, 2931, 1721, 1584, 1556, 1508, 1445, 1390, 1269, 1148, 1081, 858, 782, 740 cm^{-1} ; ^1H nmr

(300MHz, CDCl_3 , TMS): δ 1.45 (t, $J=7.0$ Hz, 3H), 2.98 (s, 3H), 3.82 (s, 3H), 4.35 (q, $J=7.0$ Hz, 2H), 7.42 to 7.65 (m, 5H), 7.82 to 8.15 (m, 3H), 8.32 (d, $J=8.5$ Hz, 1H); ms: m/z 291 (M^+ , 11%), 263 (43), 219 (20), 128 (40), 113 (13), 105 (80), 86 (11), 77 (65), 58 (222), 44 (100); (Found: C, 78.32; H, 5.88; N, 4.80). *Anal.* Calcd for $\text{C}_{19}\text{H}_{17}\text{NO}_2$: C, 78.32; H, 5.88; N, 4.80) (Found: MH^+ , 291.3479; $\text{C}_{19}\text{H}_{17}\text{NO}_2$ requires MH , 291.3483).

3-Acetyl-2-methyl-6-(*p*-nitrophenyl)pyridine (4a). Pale yellow solid (95 %), mp 131 °C; ir (KBr): 2925, 2851, 1719, 1682, 1581, 1517, 1428, 1341, 1261, 830, 739 cm^{-1} ; ^1H nmr (300MHz, CDCl_3 , TMS): δ 2.62 (s, 3H), 2.82 (s, 3H), 7.72 (d, $J=7.5$ Hz, 1H), 8.08 (d, $J=7.5$ Hz, 1H), 8.25 (d, $J=9.0$ Hz, 2H), 8.30 (d, $J=9.0$ Hz, 2H); ^{13}C nmr (200 MHz, CDCl_3): δ 199.7, 158.7, 155.6, 148.4, 144.0, 137.9, 131.9, 128.0, 123.9, 117.9, 29.3, 25.0; ms: m/z 256 (M^+ , 7%), 241 (25), 167 (8), 148(9), 115 (8), 105 (100), 91 (32), 77 (80), 51 (44), 43 (54); (Found: C, 65.61; H, 4.71; N, 10.92. *Anal.* Calcd for $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_3$: C, 65.61; H, 4.71; N, 10.93) (Found: MH^+ , 256.2589; $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_3$ requires MH , 256.2598).

3-Acetyl-2-methyl-6-(*p*-bromophenyl)pyridine (4b). Pale yellow solid (94 %), mp 76-78 °C; ir (KBr): 2925, 1678, 1576, 1485, 1430, 1352, 1256, 1005, 952, 816, 762 cm^{-1} ; ^1H NMR (300MHz, CDCl_3 , TMS): δ 2.62 (s, 3H), 2.86 (s, 3H), 7.62 (m, 3H), 7.96 to 8.10 (m, 3H); ^{13}C NMR (200 MHz, CDCl_3): δ 199.6, 158.4, 157.1, 137.8, 137.0, 131.8, 130.8, 128.6, 124.2, 116.8, 29.1, 25.1; ms: m/z 289 (M^+ , 20%), 273 (35), 247 (100), 221 (17), 182 (15), 167 (57), 141 (37), 101 (61), 75 (88), 43 (83); (Found: C, 57.95; H, 4.16; N, 4.82. *Anal.* Calcd for $\text{C}_{14}\text{H}_{12}\text{BrNO}$: C, 57.95; H, 4.16; N, 4.82) (Found: MH^+ , 290.1379; $\text{C}_{14}\text{H}_{12}\text{BrNO}$ requires MH , 290.1588).

3-Acetyl-2-methyl-6-(*p*-methylphenyl)pyridine (4c). Pale yellow solid (91 %), mp 82-84 °C; ir (KBr): 2921, 1681, 1578, 1451, 1260, 1184, 818, 788, 763 cm^{-1} ; ^1H nmr (300MHz, CDCl_3 , TMS): δ 2.45 (s, 3H), 2.60 (s, 3H), 2.85, (s, 3H), 7.28 (d, $J=7.8$ Hz, 2H), 7.60 (d, $J=7.8$ Hz, 1H), 7.95 to 8.05 (m, 3H); ^{13}C nmr (200 MHz, CDCl_3): δ 199.773, 158.54, 138.01, 137.84, 129.46, 128.30, 127.10, 126.76, 117.45, 116.74, 29.13, 25.28, 21.24; ms: m/z 225 (M^+ , 8%), 210 (7), 197 (46), 183 (100), 167 (19), 115 (13), 91 (33), 39 (42); (Found: C, 79.949; H, 6.70; N, 6.21. *Anal.* Calcd for $\text{C}_{15}\text{H}_{15}\text{NO}$: C, 79.95; H, 6.71; N, 6.22) (Found: MH^+ , 225.1389; $\text{C}_{15}\text{H}_{15}\text{NO}$ requires MH , 255.1395).

3-Acetyl-2-methyl-6-phenylpyridine (4d). Pale yellow solid (89 %), mp 110 °C (lit. [12] 110 °C); ir (KBr): 2930, 1679, 1575, 1422, 1351, 1254, 742, 689 cm^{-1} ; ^1H nmr (300MHz, CDCl_3 , TMS): δ 2.58 (s, 3H), 2.82 (s, 3H) 7.36 to 7.50 (m, 3H), 7.62 (d, $J=8.3$ Hz, 1H), 8.01 to 8.10 (m, 3H); ^{13}C nmr (50 MHz, CDCl_3): δ 25.2, 29.1, 117.1, 127.2, 128.7, 129.6, 137.8, 138.3, 158.4, 158.5, 199.8; ms: m/z 211 (M^+ , 60%), 196 (100), 168 (40), 153 (10), 141 (57), 115 (15), 77 (11), 43 (20). *Anal.* Calcd for $\text{C}_{14}\text{H}_{13}\text{NO}$: C, 79.59; H, 6.20; N, 6.63. Found: 79.48; H, 6.19; N, 6.71.

7,7-Dimethyl-5-oxo-2-(4-nitrophenyl)-5,6,7,8-tetrahydroquinoline (5a): Yellow solid (98 %), mp 182 °C; ir (KBr): 3076, 2928, 2870, 1688, 1575, 1515, 1419, 1344, 835, 732 cm^{-1} ; ^1H nmr (300MHz, CDCl_3 , TMS): δ 1.18 (s, 6H), 2.59 (s, 2H), 3.12 (s, 2H), 7.80 (d, $J=8.3$ Hz, 1H), 8.22 to 8.40 (m, 5H); ^{13}C NMR (200 MHz, CDCl_3): δ 197.3, 162.5, 158.0, 148.5, 144.0, 135.6, 129.1, 128.1, 126.4, 123.8, 119.3, 51.9, 46.5, 32.8, 28.1; ms: m/z 296 (M^+ , 2%), 240 (3), 150 (100), 141 (20), 104 (73), 76 (31), 43 (100); (Found: C, 68.90; H, 5.44; N, 9.45. *Anal.* Calcd for $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_3$: C, 68.90; H, 5.44; N, 9.45) (Found: MH^+ , 296.3239; $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_3$ requires MH , 296.3244).

7,7-Dimethyl-5-oxo-2-(phenyl)-5,6,7,8-tetrahydroquinoline (5b). Pale yellow solid (90 %), mp 65-67 °C; ir (KBr): 3059, 2950, 2867, 1678, 1581, 1446, 1395, 1304, 1186, 1122, 837, 778 cm^{-1} ; ^1H nmr (300MHz, CDCl_3 , TMS): δ 1.15 (s, 6H), 2.02 (s, 2H), 3.08 (s, 2H), 7.49 (m, 3H), 7.70 (d, J = 7.5 Hz, 1H), 8.05 (m, 2H), 8.26 (d, J = 8.3 Hz, 1H); ^{13}C nmr (200 MHz, CDCl_3): δ 197.3, 162.0, 160.6, 138.1, 136.7, 129.6, 128.5, 127.1, 125.2, 118.4, 51.7, 46.4, 32.6, 28.0, 25.2; ms: m/z 251 (M^+ , 76%), 236 (12), 223 (23), 208 (7), 195 (100), 167 (28), 141 (23), 77 (10); (Found: C, 81.24; H, 6.81; N, 5.57. *Anal.* Calcd for $\text{C}_{17}\text{H}_{17}\text{NO}$: C, 81.24; H, 6.81; N, 5.57) (Found: MH^+ , 251.3269; $\text{C}_{17}\text{H}_{17}\text{NO}$ requires *MH*, 251.3273).

7,7-Dimethyl-5-oxo-2-(4-bromophenyl)-5,6,7,8-tetrahydroquinoline (5c). Pale yellow solid (93 %), mp 132 °C; ir (KBr): 2953, 2928, 2867, 1678, 1574, 1413, 1378, 1299, 1070, 1008, 828, 806, 743 cm^{-1} ; ^1H nmr (300MHz, CDCl_3 , TMS): δ 1.16 (s, 6H), 2.52 (s, 2H), 3.08 (s, 2H), 7.59 (d, J = 9.0 Hz, 2H), 7.66 (d, J = 8.3 Hz, 1H), 7.95 (d, J = 8.3 Hz, 2H), 8.28 (d, J = 8.3 Hz, 1H); ^{13}C nmr (200 MHz, CDCl_3): δ 197.5, 162.3, 159.5, 137.1, 135.3, 131.8, 129.6, 128.8, 125.6, 124.5, 118.3, 51.9, 46.5, 32.8, 28.1; ms: m/z 329 (M^+ , 96%), 300 (18), 273 (93), 191 (8), 166 (100), 139 (32), 102 (26), 75 (28) 39 (95); (Found: C, 61.83; H, 4.88; N, 4.24. *Anal.* Calcd for $\text{C}_{17}\text{H}_{16}\text{BrNO}$: C, 61.83; H, 4.88; N, 4.24) (Found: MH^+ , 330.2230; $\text{C}_{17}\text{H}_{16}\text{BrNO}$ requires *MH*, 330.2234).

7,7-Dimethyl-5-oxo-2-(4-methoxyphenyl)-5,6,7,8-tetrahydroquinoline (5d). Light yellow solid (83 %), mp 125 °C; ir (KBr): 3071, 2959, 2932, 2840, 1676, 1580, 1510, 1447, 1307, 1254, 1173, 1028, 830, 809, 759 cm^{-1} ; ^1H nmr (300MHz, CDCl_3 , TMS): δ 1.15 (s, 6H), 2.52 (s, 2H), 3.05 (s, 2H), 3.90 (s, 3H), 6.95 (d, J = 8.7 Hz, 2H), 7.65 (d, J = 8.0 Hz, 1H), 8.05 (d, J = 8.7 Hz, 2H), 8.25 (d, J = 8.0 Hz, 1H); ^{13}C nmr (200 MHz, CDCl_3): δ 197.6, 162.2, 161.2, 135.0, 130.8, 130.4, 128.7, 124.8, 117.7, 114.1, 113.5, 55.2, 51.9, 46.6, 32.8, 28.2; ms: m/z 281 (M^+ , 100%), 267 (6), 254 (8), 239 (8), 226 (61), 183 (11), 151 (28), 136 (95), 128 (22), 109 (10), 105 (10), 89 (35), 77 (44), 52 (35), 42 (55); (Found: C, 76.84; H, 6.80; N, 4.98. *Anal.* Calcd for $\text{C}_{18}\text{H}_{19}\text{NO}_2$: C, 76.84; H, 6.80; N, 4.97) (Found: MH^+ , 281.3528; $\text{C}_{18}\text{H}_{19}\text{NO}_2$ requires *MH*, 281.3531).

7,7-Dimethyl-5-oxo-2-(1-naphthyl)-5,6,7,8-tetrahydroquinoline (5e). Pale yellow oil (90%); ir (film): 3053, 2956, 2870, 1729, 1686, 1581, 1560, 1508, 1396, 1305, 1115, 848, 801, 778, 741, 663 cm^{-1} ; ^1H nmr (300MHz, CDCl_3 , TMS): δ 1.20 (s, 6H), 2.60 (s, 2H), 3.15 (s, 2H), 3.15 (s, 2H), 7.45 to 7.65 (m, 5H) 7.85 to 7.95 (m, 2H), 8.10 (m, 1H), 8.35 (d, J = 8.3 Hz, 1H); ^{13}C nmr (200 MHz, CDCl_3): δ 197.8, 163.3, 162.1, 137.5, 134.8, 133.9, 130.7, 129.5, 128.4, 127.7, 126.6, 125.9, 125.4, 125.2, 125.1, 123.5, 52.0, 46.5, 32.9, 28.2; ms: m/z 301 (M^+ , 38%), 217 (11), 171 (16), 156 (50), 138 (11), 128 (71), 118 (57), 106 (46), 89 (27), 66 (51), 64 (93), 42 (100); (Found: C, 83.68; H, 6.35; N, 4.64. *Anal.* Calcd for $\text{C}_{21}\text{H}_{19}\text{NO}$: C, 83.69; H, 6.35; N, 4.64) (Found: MH^+ , 301.3869; $\text{C}_{21}\text{H}_{19}\text{NO}$ requires *MH*, 301.3871).

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