Three-Step Synthesis of 2,4-Diaryl-5,6,7,8-tetrahydroquinoline Derivatives

Hayreddin Gezegen, Alparslan Dingil, and Mustafa Ceylan*

Department of Chemistry, Faculty of Arts and Sciences, Gaziosmanpasa University, Tokat 60250, Turkey
*E-mail: mceylan@gop.edu.tr
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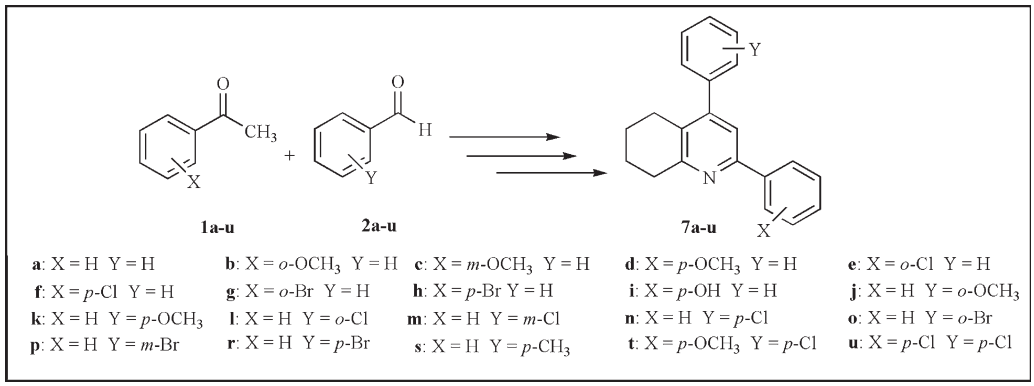

Addition of cylohexanone to chalcones, obtained from the appropriate acetophenone and benzaldehyde derivatives, under solvent-free conditions gave 1,5-diketones in good yields. Treatment of 1,5-diketones with ammonium acetate in acetic acid afforded directly 2,4-diaryl-5,6,7,8-tetrahydroquinoline derivatives **(7a–u)** in high yields. The structures of **7a–u** were elucidated by ^{1}H NMR, ^{13}C NMR, IR, and elemental analysis.

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INTRODUCTION

The synthesis of oxygen, nitrogen, or sulfur-containing heterocycles is of importance in the organic and medicinal chemistry [1]. Among these structures, quinolines [2], tetrahydroquinolines [3], and their derivatives are excellent precursor of potential drugs [4]. Quinoline and their derivatives, which usually possess diverse biological activities, play important roles as versatile building blocks for the synthesis of natural products and as therapeutic agents [5]. In particular, 2-arylquinolines are biologically active and occur in structures of a number of antimalarial compounds and antitumor agents [6]. The biological activity of quinoline compounds has been found to possess antiasthmatic, antibacterial, antianflammatory, and antihypertensive properties [7]. Therefore, the synthesis of quinolines has attracted much attention in organic synthesis. The classic methods for the synthesis of quinolines include Skraup [8], Doebner-Von Miller [9], Conrad and Limbach [10], Combes [11], and Pfizinger [12] quinoline syntheses. A number of general synthetic methods have also been reported [13]. However, some of these methods suffer from several disadvantages such as harsh reaction conditions, multi steps, a large amount of promoters, and long reaction time [14].

In this study, we report that the synthesis of novel 2,4-diaryl-5,6,7,8-tetrahydroquinoline derivatives **7a–u** via cyclization of 1,5-diketones **5a–u** with ammonium acetate in acetic acid.

RESULTS AND DISCUSSION

The general synthetic strategy used to prepare the chalcone derivatives (**3a–u**) was based on Claisen-Schmidt condensation, which was reported previously [15]. Chalcone derivatives (**3a–u**) were prepared by base-catalyzed condensation of appropriate substituted acetophenone with benzaldehyde in good yields (Scheme 1). All chalcone derivatives (**3a–u**) are well-known [16–26] according to our literature surveys. The structures of **3a–u** were characterized on the basis of spectral data (IR, ^{1}H NMR, and ^{13}C NMR) and comparison with authentic samples. After the structures of **3a–u** were determined, they were submitted to additional reaction of cyclohexanone (**4**). Addition of cyclohexanone to chalcones was performed according to our previously published method [27] in the presence of PTC (phase transfer catalyst = triethylammonium chloride) in solvent-free conditions. 1,5-Diketone derivatives **5a–u** were obtained in moderate to good yields (Scheme 1,

Scheme 1

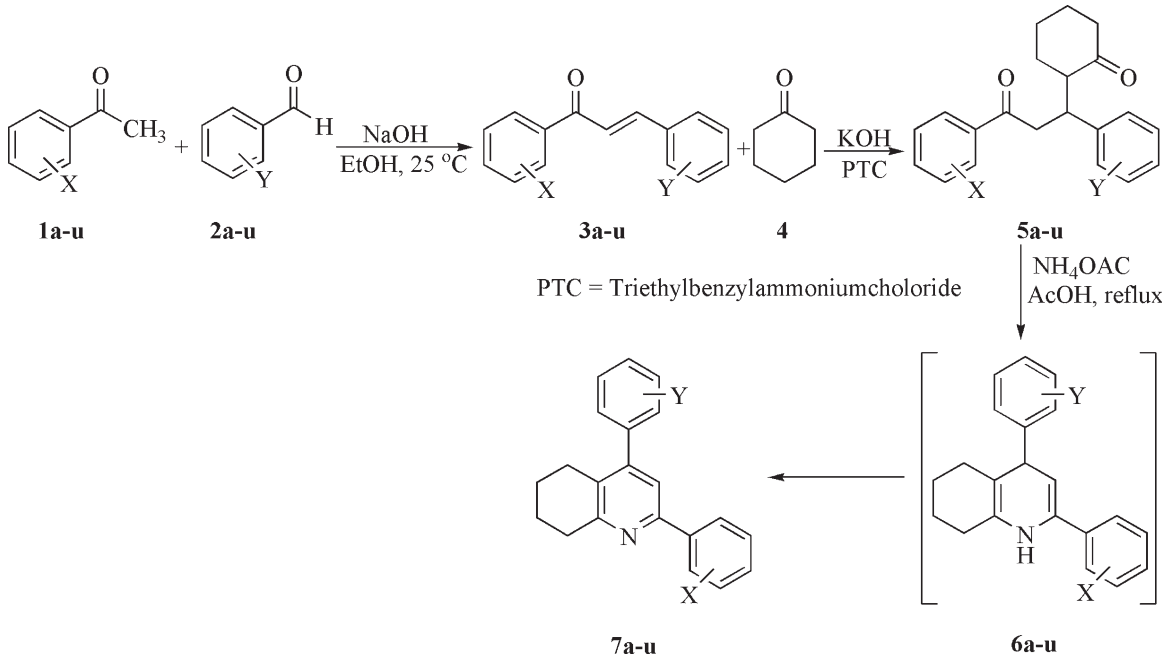

Table 1). In this series, the compounds **5a–g** are known in the literature [21,27–29]. The structures of other 1,5-diketones (**5h–u**) were determined by spectroscopic studies (^{1}H, ^{13}C NMR, IR, and elemental analysis). In the ^{1}H NMR spectrum of **5a–h**, the protons of $PhCOCH_2$ gave an AB system that is characteristic signals for these compounds. While part A of the AB system is shown as a doublet of doublet at $\delta = 3.50–3.42$ ($J = 15.7–16.7$ and 3.9–4.5 Hz) and that of part B is shown as a doublet of doublet at $\delta = 3.23–3.15$ ($J = 15.7–16.7$ and 9.5–9.6 Hz).

Treatment of 1,5-diketones **5a–u** with NH_4OAc (ammonium acetate) in AcOH at reflux condition for 2.5–5 h afforded directly 2,4-diaryl-5,6,7,8-tetrahydroquinoline derivatives **7a–u** in excellent yields (Scheme 1, Table 2). The compounds **7a–u** were purified by column chromatography (on a silica gel) eluting $CHCl_3$/*n*-hexane (1:1).

Table 1

Synthesized 1,5-diketones (**5a–u**).

Entry	Products	X	Y	Yield (%)
1	**5a**	H	H	83
2	**5b**	2-OCH_3	H	40
3	**5c**	3-OCH_3	H	78
4	**5d**	4-OCH_3	H	78
5	**5e**	2-Cl	H	65
6	**5f**	4-Cl	H	72
7	**5g**	2-Br	H	63
8	**5h**	4-Br	H	56
9	**5i**	4-OH	H	66
10	**5j**	H	2-OCH_3	77
11	**5k**	H	4-OCH_3	50
12	**5l**	H	2-Cl	69
13	**5m**	H	3-Cl	60
14	**5n**	H	4-Cl	60
15	**5o**	H	2-Br	50
16	**5p**	H	3-Br	70
17	**5r**	H	4-Br	90
18	**5s**	H	4-CH_3	94
19	**5t**	4-OCH_3	4-Cl	97
20	**5u**	4-Cl	4-Cl	75

Table 2

Synthesized 2,4-diaryl-5,6,7,8-tetrahydroquinoline derivatives (**7a–u**).

Entry	Products	X	Y	Yield (%)
1	**7a**	H	H	82
2	**7b**	2-OCH_3	H	99
3	**7c**	3-OCH_3	H	83
4	**7d**	4-OCH_3	H	86
5	**7e**	2-Cl	H	94
6	**7f**	4-Cl	H	98
7	**7g**	2-Br	H	66
8	**7h**	4-Br	H	92
9	**7i**	4-OH	H	80
10	**7j**	H	2-OCH_3	88
11	**7k**	H	4-OCH_3	71
12	**7l**	H	2-Cl	87
13	**7m**	H	3-Cl	99
14	**7n**	H	4-Cl	90
15	**7o**	H	2-Br	82
16	**7p**	H	3-Br	98
17	**7r**	H	4-Br	94
18	**7s**	H	4-CH_3	81
19	**7t**	4-OCH_3	4-Cl	90
20	**7u**	4-Cl	4-Cl	97

Structures of **7a–u** were confirmed by their spectral (IR, NMR, and elemental analyses) data. In the ^{1}H NMR spectrum of **7a–u**, the H4 proton gave a singlet (between $\delta = 7.60$ and 7.30 ppm) that is characteristic signals for these compounds. All spectral data are consistent with the titled compounds.

In conclusion, we have described a mild, efficient, and convenient method for the synthesis of 2,4-diaryl-5,6,7,8-tetrahydroquinoline derivatives from cheap and easily available materials such as acetophenone and benzaldehyde derivatives, cyclohexanone and ammonium acetate.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were recorded with Bruker AC 400 instruments. As internal standards, we used TMS (δ 0.00) for ^{1}H NMR and $CDCl_3$ (δ 77.0) for ^{13}C NMR spectroscopy. *J* values are given in hertz. The multiplicities of the signals in the ^{1}H NMR spectra are abbreviated to s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad), and combinations thereof. IR spectra were recorded on a Jasco FT/IR-430 spectrometer. Elemental analyses were performed using a LECO CHNS 932 elemental analyzer. Melting points were measured on Electrothermal 9100 apparatus. All column chromatographies were performed on silica gel (60–230 mesh, Merck).

General procedure for the synthesis of chalcones 3a–u. To a solution of acetophenone derivative (1 mmol) in ethanol (20 mL) was added NaOH (8 mL, 2.5*M* NaOH) and benzaldehyde derivative (1 mmol) at room temperature. The mixture was stirred for 3 h. Then the mixture was washed with diluted HCl and extracted with $CHCl_3$. The organic layer was dried over Na_2SO_4 and the solvent was removed in vacuum. The residue was purified on a silica gel column eluting with $CHCl_3$/*n*-hexane (3:7) and/or crystallized from $CHCl_3$/*n*-hexane (3:7).

General procedure for the synthesis of 1,5-diketones 5a–u. To a mixture of chalcone (**1a**) (10 mmol) and cycylohexanone (**4**) (20 mmol) were added solid KOH (0.06% mol) with a few drop of water and PTC (benzyltrithylammonium chloride) (0.06% mol) and stirred for 3–4 h at room temperature. Then, the mixture was extracted with 20 mL of $CHCl_3$ and dried over Na_2SO_4. After the solvent was taken off in vacuum, the crude product was crystallized from CCl_4/hexane (3:1).

2-(3-Oxo-1,3-diphenlpropyl)cyclohexanone (5a). Yield 83%; colorless crystals; mp 146–148°C (CCl_4/*n*-hexane, 3:1). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.93–7.89 (m, 2H), 7.55–7.41 (m, 3H), 7.37–7.13 (m, 5H), 3.78–3.68 (m, 1H), 3.50 (dd, J = 16.2, 4.1 Hz, 1H), 3.23 (dd, J = 16.2, 9.5 Hz, 1H), 2.75–2.68 (m, 1H), 2.68–2.32 (m, 2H), 2.01–1.51 (m, 5H), 1.50–1.24 (m, 1H). ^{13}C NMR (50 MHz, $CDCl_3$) δ = 215.6, 200.8, 144.1, 139.1, 134.8, 130.5 (2C), 130.4 (2C), 130.3 (2C), 130.2 (2C), 57.8, 46.2, 44.3, 43.1, 34.5, 30.5, and 26.1. IR (KCl): 3056, 33025, 2939, 2918, 2854, 1708, 1683, 1596, 1446, 1340, 1216, 746, 696, and 567 cm^{-1}. *Anal*. *Calcd*. for: $C_{21}H_{22}O_2$: C, 82.32; H, 7.24. Found: C, 81.98; H, 7.22.

2-(3-(2-Methoxyphenyl)-3-oxo-1-phenylpropyl)cyclohexanone (5b). Yield 40%; colorless crystals; mp 108–111°C (CCl_4/*n*-hexane, 3:1). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.43–6.85 (m, 9H), 3.86 (s, 3H), 3.80–3.68 (m, 1H), 2.72–2.63 (m, 1H), 3.44–3.33 (m, 2H), 2.72–2.28 (m, 3H), 1.95–1.24 (m, 5H). ^{13}C NMR (50 MHz, $CDCl_3$) δ = 215.4, 203.2, 160.1, 144.5, 134.9, 132.1, 130.9, 130.6 (2C), 130.2 (2C), 128.3, 122.5, 113.3, 57.9, 57.5, 50.8, 43.8, 42.6, 33.8, 30.3, and 25.6. IR (KCl): 3058, 3026, 2925, 2854, 1703, 1666, 1483, 1433, 1284, 1242, 1022, 752, 698, and 567 cm^{-1}. *Anal*. *Calcd*. for: $C_{22}H_{24}O_3$: C, 78.54; H, 7.19. Found: C, 78.15; H, 7.48.

2-(3-(3-Methxyphenyl)-3-oxo-1-phenylpropyl)cylohexanone (5c). Yield 78%; colorless crystals; mp 89–92°C (CCl_4/*n*-hexane, 3:1). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.55–7.03 (m, 9H), 3.81 (s, 3H), 3.88–3.66 (m, 1H), 3.50 (dd, J = 16.1, 4.0 Hz, 1H), 3.20 (dd, J = 16.1, 9.6 Hz, 1H), 2.79–2.55 (m, 1H), 2.51–2.38 (m, 2H), 2.01–1.22 (m, 6H). ^{13}C NMR (50 MHz, $CDCl_3$) δ = 215.5, 200.6, 161.7, 143.9, 140.4, 131.4, 130.5 (2C), 130.4 (2C), 128.6, 122.8, 121.5, 114.5, 57.8, 57.4, 46.4, 44.4, 43.3, 34.5, 30.6, and 26.2. IR (KCl): 3058, 3028, 2931, 2912, 2852, 1709, 1678, 1581, 1431, 1259, 1049, 987, 700, and 573 cm^{-1}. *Anal*. *Calcd*. for: $C_{22}H_{24}O_3$: C, 78.54; H, 7.19. Found: C, 78.20; H, 7.42.

2-(3-(4-Methoxyphenyl)-3-oxo-1-phenylpropyl)cyclohexanone (5d). Yield 78%; colorless crystals; mp 128–130°C (CCl_4/*n*-hexane, 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.91–7.89 (m, 2H), 6.91–6.87 (m, 2H), 7.88–7.14 (m, 5H), 3.84 (s, 3H), 3.75–3.69 (m, 1H), 2.75–2.69 (m, 1H), 3.42 (dd, J = 15.7, 4.0 Hz, 1H), 3.17 (dd, J = 15.7, 9.5 Hz, 1H), 2.55–2.48 (m, 1H), 2.02–1.92 (m, 1H), 1.80–1.50 (m, 5H), 1.31–1.10 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 213.9, 197.5, 163.5, 142.3, 130.4, 130.7 (2C), 128.7 (2C), 128.6 (2C), 126.8 (1C), 113.8 (1C), 56.1, 55.6, 44.1, 42.5, 41.5, 32.6, 28.7, and 24.2. IR (KCl): 3057, 3026, 2933, 2852, 1707, 1672, 1603, 1420, 1255, 1167, 984, 816, 698, and 565 cm^{-1}. *Anal*. *Calcd*. for: $C_{22}H_{24}O_3$: C, 78.54; H, 7.19. Found: C, 78.30; H, 7.18.

2-(3-(2-Chlorophenyl)-3-oxo-1-phenylpropyl)cyclohexanone (5e). Yield 65%; colorless crystals; mp 120–124°C (CCl_4/*n*-hexane, 3:1). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.43–7.11 (m, 9H), 3.71–3.59 (m, 1H), 3.46 (dd, J = 16.6, 4.5 Hz, 1H), 3.23 (dd, J = 16.6, 9.5 Hz, 1H), 2.72–2.60 (m, 1H), 2.55–2.34 (m, 2H), 1.99–1.22 (m, 6H). ^{13}C NMR (50 MHz, $CDCl_3$) δ = 215.2, 203.8, 143.7, 141.5, 132.7, 133.3, 132.2, 130.9, 130.5 (2C), 128.7 (2C), 57.7, 50.2, 44.2, 43.0, 34.2, 30.4, and 26.0. IR (KCl): 3058, 3026, 2933, 2918, 2854, 1705, 1691, 1431, 1369, 1122, 1072, 983, 750, 721, and 567 cm^{-1}. *Anal*. *Calcd*. for: $C_{21}H_{21}ClO_2$: C, 74.00; H, 6.21. Found: C, 73.74; H, 6.23.

2-(3-(4-Chlorophenyl)-3-oxo-1-phenylpropyl)cyclohexanone (5f). Yield 72%; colorless crystals; mp 113–116°C (CCl_4/*n*-hexane, 3:1). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.94–7.83 (m, 2H), 7.42–7.29 (m, 2H), 7.27–7.12 (m, 5H), 3.68–3.61 (m, 1H), 3.54 (dd, J = 15.8, 4.0 Hz, 1H), 3.15, (dd, J = 15.8, 9.6 Hz, 1H), 2.74–2.66 (m, 1H), 2.51–2.35 (m, 2H), 2.02–1.21 (m, 6H). ^{13}C NMR (50 MHz, $CDCl_3$) δ = 215.7, 199.6, 143.7, 141.2, 137.4, 131.7 (2C), 130.7 (2C), 130.6 (2C), 130.3 (2C), 128.7, 57.8, 46.4, 44.5, 43.4, 34.7, 30.6, and 26.3. IR (KCl): 3057, 3024, 2939, 2918, 2852, 1707, 1685, 1589, 1446, 1398, 1215, 1095, 982, 816, 696, and 567 cm^{-1}. *Anal*. *Calcd*. for: $C_{21}H_{21}ClO_2$: C, 74.00; H, 6.21. Found: C, 73.68; H, 6.26.

2-(3-(2-Bromophenyl)-3-oxo-1-phenylpropyl)cyclohexanone (5g). Yield 63%; colorless crystals; mp 120–122°C (CCl_4/*n*-hexane, 3:1). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.53–7.49 (m, 1H), 7.31–7.09 (m, 8H), 3.46 (dd, J = 16.7, 4.4 Hz, 1H), 3.21

(dd, J = 16.7, 9.5 Hz, 1H), 3.72–3.62 (m, 1H), 2.73–2.61 (m, 1H), 2.55–2.32 (m, 2H), 1.99–1.22 (m, 6H). ^{13}C NMR (50 MHz, $CDCl_3$) δ = 215.2, 204.5, 143.6, 143.6, 135.5, 133.3, 130.5 (2C), 130.5 (2C), 130.3, 129.2, 128.7, 120.6, 57.6, 49.9, 44.2, 42.9, 34.2, 30.4, and 26.0. IR (KCl): 3055, 3026, 2933, 2918, 2854, 1705, 1693, 1404, 1369, 1122, 1030, 983, 750, 698, and 567 cm^{-1}. *Anal*. *Calcd*. for: $C_{21}H_{21}BrO_2$: C, 65.46; H, 5.49. Found: C, 65.08; H, 5.83.

2-(3-(4-Bromophenyl)-3-oxo-1-phenylpropyl)cyclohexanone (5h). Yield 56%; colorless crystals; mp 146–149°C (CCl_4/*n*-hexane, 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.79 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 8.4 Hz 2H), 7.26 (t, J = 7.2 Hz, 2H), 7.19–7.14 (m, 3H), 3.66 (td, J = 8.8, 3.6 Hz, 1H), 3.50 (dd, J = 15.6, 4.0 Hz, 1H), 3.15 (dd, J = 16.0, 9.6 Hz, 1H), 2.72 (td, J = 10.0, 4.2 Hz, 1H), 2.53–2.48 (m, 1H), 2.44–2.36 (m, 1H), 2.02–1.98 (m, 1H), 1.80–1.50 (m, 4H), 1.28–1.19 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 213.6, 197.89, 141.7, 135.7, 131.8 (2C), 129.8 (2C), 128.5 (2C), 128.3 (2C), 127.9, 126.7, 55.6, 44.4, 42.5, 41.4, 32.7, 28.6, and 24.3. IR (KCl): 3056, 3023, 2938, 2917, 2854, 1706, 1687, 1586, 1397, 1229, 1071, 982, 812, 698, and 569 cm^{-1}. *Anal*. *Calcd*. for: $C_{21}H_{21}BrO_2$: C, 65.46; H, 5.49. Found: C, 65.08; H, 5.87.

2-(3-(4-Hydroxyphenyl)-3-oxo-1-phenylpropyl)cyclohexanone (5i). Yield 66%; colorless crystals; mp 149–151°C (CCl_4/*n*-hexane, 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.80 (d, J = 8.6 Hz, 2H), 7.28–7.23 (m, 3H), 7.19 (d, J = 7.2 Hz, 2H), 6.81 (d, J = 8.6 Hz, 2H), 3.75 (dt, J = 9.6, 4.4 Hz, 1H), 3.42 (dd, J = 16.1, 4.2 Hz 1H), 3.16 (dd, J = 16.1, 9.2 Hz, 1H), 2.79–2.70 (m, 1H), 2.63–2.55 (m, 1H), 2.46–2.38 (m, 1H), 1.98–1.90 (m, 1H), 1.85–1.76 (m, 1H), 1.70–1.52 (m, 3H), 1.36–1.26 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 215.9, 197.6, 160.6, 141.9, 130.8 (2C), 129.6, 128.5 (2C), 128.4 (2C), 126.7, 115.3 (2C), 56.0, 43.9, 42.0, 41.2, 32.3, 28.5, and 23.6. IR (KCl): 3116, 3054, 3024, 2931, 2857, 1707, 1678, 1428, 1245, 1136, 984, 814, 699, and 567 cm^{-1}. *Anal*. *Calcd*. for: $C_{21}H_{22}O_3$: C, 78.23; H, 6.88. Found: C, 78.12; H, 6.87.

2-(1-(2-Methoxyphenyl)-3-oxo-3-phenylpropyl)cyclohexanone (5j). Yield 77%; viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.00–7.91 (m, 2H), 7.54–7.47 (m, 1H), 7.43–7.38 (m, 2H), 7.23–7.05 (m, 2H), 6.88–6.80 (m, 2H), 3.74 (s, 3H), 3.50–3.30 (m, 2H), 2.99–2.97 (m, 1H), 2.55–2.26 (m, 2H), 1.99 (br s, 1H), 1.92–1.53 (m, 5H), 1.28–1.23 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 214.3, 199.5, 157.7, 137.2, 132.7, 130.2, 128.7, 128.4, 128.3 (2C), 128.2 (2C), 127.7, 127.3, 55.3, 42.9, 39.1, 32.8, 28.7, 27.7, and 24.4. IR (KCl): 3055, 2956, 2926, 2855, 1699, 1682, 1517, 1443, 1297, 1245, 1174, 987, 824, 725, and 566 cm^{-1}. *Anal*. *Calcd*. for: $C_{22}H_{24}O_3$: C, 78.54; H, 7.19. Found: C, 78.32; H, 7.28.

2-(1-(4-Methoxyphenyl)-3-oxo-3-phenylpropyl)cyclohexanone (5k). Yield 50%; colorless crystals; mp 136–139°C (CCl_4/*n*-hexane, 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.92 (d, J = 7.2 Hz, 2H), 7.51 (t, J = 7.2 Hz, 1H), 7.41 (t, J = 7.2 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 6.79 (d, J = 8.4 Hz, 2H), 3.75 (s, 3H), 3.68 (m, 1H), 3.47 (dd, J = 16.0, 4.0 Hz, 1H), 3.18 (dd, J = 16.0, 9.6 Hz, 1H), 2,68 (m, 1H), 2.52–2.48 (m, 1H), 2.41–2.37 (m, 1H), 1.98–1.95 (m, 1H), 1.80–1.66 (m, 3H), 1.57–1.53 (m, 1H),1.28–1.24 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 213.8, 198.9, 158.1, 113.8 (2C), 128.4 (2C), 128.2 (2C), 56.0, 55.1, 44.4, 42.3, 40.4, 32.4, 28.6, and 24.1. IR (KCl): 3035, 2965, 2943, 2920, 2852, 1699, 1679, 1610, 1514, 1445, 1294, 1247, 1177, 1027, 987, 821, 723, and 563 cm^{-1}. *Anal*. *Calcd*. for: $C_{22}H_{24}O_3$: C, 78.54; H, 7.19. Found: C, 78.20; H, 7.42.

2-(1-(2-Chlorophenyl)-3-oxo-3-phenylpropyl)cyclohexanone (5l). Yield 66%; colorless crystals; mp 126–128°C (CCl_4/*n*-hexane, 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.94 (dd, J = 14.6 Hz, J = 7.2 Hz, 2H), 7.48 (dd, J = 14.6 Hz, J = 7.2 Hz, 1H), 7.40 (t, J = 7.6 Hz, 2H), 7.33–7.23 (m, 2H), 7.15 (t, J = 7.2 Hz, 1H), 7.12–7.04 (m, 1H), 3.55 (dt, J = 16.8, 3.6 Hz, 1H), 3.40 (dd, J = 10, 3.6 Hz, 1H), 2.86–2.42 (m, 1H), 2.54–2.26 (m, 2H), 1.99 (br s, 1H), 1.85–1.50 (m, 5H), 1.48–1.59 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 213.0, 198.5, 139.8, 136.9, 134.0, 132.8, 129.8, 128.4 (2C), 128.1 (2C), 127.6, 127.0, 126.5, 53.4, 42.9, 42.7, 38.7, 32.6, 28.6, and 24.8. IR (KCl): 3085, 3061, 2936, 2928, 2859, 1698, 1680, 1592, 1574, 1447, 1223, 1119, 981, 748, and 687 cm^{-1}. *Anal*. *Calcd*. for: $C_{21}H_{21}ClO_2$: C, 74.00; H, 6.21. Found: C, 73.89; H, 6.25.

2-(1-(3-chlorophenyl)-3-oxo-3-phenylpropyl)cyclohexanone (5m). Yield 60%; colorless crystals; mp 124–127°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.91 (d, J = 7.6 Hz, 2H), 7.52 (t, J = 7.2 Hz, 1H), 7.42 (t, J = 7,6 Hz, 2H), 7.21–7.10 (m, 4H), 3.73 (m, 1H), 3.51 (dd, J = 16.8, 4.0 Hz, 1H), 3.23 (dd, J = 16.4, 9.6 Hz, 1H), 2.71 (m, 1H), 2.52–2.38 (m, 2H), 2.02–1.99 (m, 1H), 1.80–1.55 (m, 4H), 1.27–1.23 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 213.0, 189.3, 144.4, 128.5 (2C), 128.1 (2C), 134.2, 132.9, 129.7, 128.4, 126.9, 126.8, 55.5, 43.8, 42.8, 40.7, 32.6, 28.5, and 24.4. IR (KCl): 3083, 3059, 2932, 2924, 2858, 1698, 1681, 1593, 1571, 1449, 1360, 1232, 1127, 983, 748, and 685 cm^{-1}. *Anal*. *Calcd*. for: $C_{21}H_{21}ClO_2$: C, 74.00; H, 6.21. Found: C, 73.77; H, 6.22.

2-(1-(4-Chlorophenyl)-3-oxo-3-phenylpropyl)cyclohexanone (5n). Yield 60%; colorless crystals; mp 122–125°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.91 (d, J = 7.2 Hz, 2H), 7.52 (t, J = 7.2 Hz, 1H), 7.42 (t, J = 7.6 Hz, 2H), 7.23 (d, J = 6.4 Hz, 2H), 7.13 (d, J = 6.4 Hz, 2H), 3.72 (m, 1H), 3.51 (dd, J = 16.4, 4.0 Hz, 1H), 3.21 (dd, J = 16.4, 10.0 Hz, 1H), 2,71 (m, 1H), 2.51–2.47 (m, 1H), 2.42–2.37 (m, 1H), 2.03–1.99 (m, 1H), 1.80–1.53 (m, 4H), 1.26–1.20 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 213.1, 198.5, 129.8 (2C), 128.6 (2C) 128.5 (2C), 128.1 (2C), 140.6, 136.5, 132.9, 128.4, 132.2, 55.6, 43.9, 42.5, 40.5, 32.5, 28.5, and 24.4. IR (KCl): 3085, 3060, 2940, 2921, 2856, 1698, 1682, 1594, 1491, 1446, 1217, 1096, 984, 826, 750, and 688 cm^{-1}. *Anal*. *Calcd*. for: $C_{21}H_{21}ClO_2$: C, 74.00; H, 6.21. Found: C, 73.84; H, 6.23.

2-(1-(2-Bromophenyl)-3-oxo-3-phenylpropyl)cyclohexanone (5o). Yield 50%; colorless crystals; mp 92–95°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 (d, J = 8.2 Hz, 2H), 7.55–7.50 (m, 2H), 7.44 (t, J = 7.2 Hz, 2H), 7.27–7.19 (m, 2H), 7.04 (t, J = 7.6 Hz, 1H), 3.55 (dd, J = 16.4, 4.4 Hz, 1H), 3.38 (dd, J = 16.4, 9.6 Hz, 1H), 2.78–2.75 (m, 1H), 2.54–2.30 (m, 2H), 2.01–1.59 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 211.4, 198.6, 128.5 (2C), 128.2 (2C) 141.3, 136.8, 133.3, 132.9, 128.8, 127.8, 127.1, 125.2, 53.5, 42.3, 38.8, 38.3, 28.6, 27.6, and 25.0. IR (KCl): 3054, 3025, 2933, 2917, 2854, 1704, 1693, 1583, 1403, 1369, 1230, 1122, 983, 750, 698, and 566 cm^{-1}. *Anal*. *Calcd*. for: $C_{21}H_{21}BrO_2$: C, 65.46; H, 5.49. Found: C, 65.26; H, 5.64.

2-(1-(3-Bromophenyl)-3-oxo-3-phenylpropyl)cyclohexanone (5p). Yield 70%; colorless crystals; mp 113–116°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.91 (d, J = 7.2 Hz, 2H), 7.52 (t, J = 7.6 Hz, 1H), 7.42 (t, J = 7.6 Hz, 2H), 7.34 (s, 1H), 7.30 (d, J

= 7.2 Hz, 1H), 7.17–6.96 (m, 2H), 3.71 (m, 1H), 3.50 (dd, *J* = 16.8, 4.0 Hz, 1H), 3.22 (dd, *J* = 16.4, 9.6 Hz, 1H), 2.72–2.69 (m, 1H), 2.51–2.47 (m, 1H), 2.42–2.37 (m, 1H), 2.02–1.99 (m, 1H), 1.78–1.55 (m, 4H), 1.27–1.22 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 212.9, 198.3, 128.5 (2C), 128.1 (2C), 144.7, 122.6, 144.7, 136.8, 132.9, 131.2, 129.8, 27.3, 55.5, 43.8, 42.5, 40.7, 32.6, 28.5, and 24.4. IR (KCl): 3057, 2940, 2927, 2847, 1697, 1681, 1565, 1446, 1233, 1128, 979, 749, 687, and 590 cm^{-1}. *Anal*. *Calcd*. for: $C_{21}H_{21}BrO_2$: C, 65.46; H, 5.49. Found: C, 65.31; H, 5.73.

2-(1-(4-Bromopheyl)-3-oxo-3-phenylpropyl)cyclohexanone (5r). Yield 90%; colorless crystals; mp 122–125°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.91 (d, *J* = 7.6 Hz, 2H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.41 (t, *J* = 6.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 3.71 (m, 1H), 3.51 (dd, *J* = 16.4, 3.6 Hz, 1H), 3.20 (dd, *J* = 16.4, 9.6 Hz, 1H), 2.71–2.67 (m, 1H), 2.51–2.47 (m, 1H), 2.42–2.38 (m, 1H), 2.02–1.99 (m, 1H), 1.81–1.51 (m, 4H), 1.26–1.21 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 213.1, 198.5, 131.6 (2C), 130.2 (2C) 128.5 (2C), 128.1 (2C), 141.1, 136.8, 132.9, 120.4, 55.5, 43.9, 42.5, 40.5, 32.5, 28.5, and 24.4. IR (KCl): 3061, 2935, 2911, 2853, 1697, 1682, 1593, 1487, 1446, 1217, 1128, 1009, 824, 749, and 688 cm^{-1}. *Anal*. *Calcd*. for: $C_{21}H_{21}BrO_2$: C, 65.46; H, 5.49. Found: C, 65.19; H, 5.56.

2-(1-(4-Methylphenyl)-3-oxo-3-phenylpropyl)cyclohexanone (5s). Yield 94%; colorless crystals; mp 130–133°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.93 (d, *J* = 7.6 Hz, 2H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.41 (t, *J* = 7.2 Hz, 2H), 7.08–7.05 (m, 4H), 3.71 (m, 1H), 3.50 (dd, *J* = 16.0, 4.0 Hz, 1H), 3.21 (dd, *J* = 16.4, 9.6 Hz, 1H), 2.70 (m, 1H), 2.28 (s, 3H), 2.54–2.49 (m, 1H), 2.42–2.38 (m, 1H), 2.01–1.97 (m, 1H), 1.80–1.65 (m, 3H), 1.57–1.54 (m, 1H), 1.28–1.24 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 213.8, 198.9, 129.2 (2C), 128.4 (2C) 128.2 (2C), 128.2 (2C), 138.9, 137.0, 136.1, 132.8, 55.9, 44.3, 42.3, 40.7, 32.5, 28.6, 24.1, and 21.0. IR (KCl): 3033, 2942, 2923, 2857, 1698, 1671, 1596, 1449, 1249, 1125, 819, 760, 694, and 558 cm^{-1}. *Anal*. *Calcd*. for: $C_{22}H_{24}O_2$: C, 82.46; H, 7.55. Found: C, 82.19; H, 7.56.

2-(1-(4-Cholorophenyl)-3-(4-methokxyphenyl)-3-oxopropyl) cyclohexanone (5t). Yield 97%; colorless crystals; mp 131–134°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.92 (d, *J* = 8.7 Hz, 2H), 7.22 (d, *J* = 7.8 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 3.83 (s, 3H), 3.71 (dt, *J* = 9.6, 3.9 Hz, 1H), 3.46 (dt, *J* = 15.9, 4.8 Hz, 1H), 3.12 (dd, *J* = 15.9, 9.9 Hz, 1H), 2.69 (dt, *J* = 9.9, 5.1 Hz, 1H), 2.54–2.23 (m, 2H), 2.05–1.45 (m, 5H), 1.29–1.15 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 213.2, 197.0, 163.4, 140.6, 132.2, 130.5 (2C), 129.9, 129.8 (2C), 128.6 (2C), 113.6 (2C), 55.6, 55.4, 43.6, 42.5, 40.7, 32.5, 28.5, and 24.3. IR (KCl): 3048, 3016, 2933, 2852, 1704, 1670, 1575, 1421, 1257, 1174, 981, 815, and 570 cm^{-1}. *Anal*. *Calcd*. for: $C_{22}H_{23}ClO_3$: C, 71.25; H, 6.25. Found: C, 71.04; H, 6.21.

2-(1,3-Bis-(4-chlorophenyl)-3-oxopropyl)cyclohexanone (5u). Yield 75%; colorless crystals; mp 101–104°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.86 (d, *J* = 8.50 Hz, 2H), 7.38 (d, *J* = 7.9 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 7.09 (d, *J* = 7.9 Hz, 2H), 3.69–3.61 (m, 1H), 3.55–3.43 (m, 1H), 3.16–3.06 (m, 1H), 2.72–2.63 (m, 1H), 2.51–2.33 (m, 2H), 2.01 (br s, 1H), 1.81–1.49 (m, 4H), 1.27–1.15 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 213.1, 197.3, 140.3, 139.4, 135.1, 132.3, 129.7 (2C), 129.6 (2C), 128.8 (2C), 128.7 (2C), 55.5, 44.1, 42.6, 40.7, 32.7, 28.6, and 24.5. IR (KCl): 3024, 2938, 2862, 1704, 1685, 1589, 1490, 1092, 1012, 984, 827, 756, and 530 cm^{-1}. *Anal*. *Calcd*. for: $C_{21}H_{20}Cl_2O_2$: C, 67.21; H, 5.37. Found: C, 67.14; H, 5.32.

General procedure for synthesis of 2,4-diaryl-5,6,7,8-tetrahydroquinoline derivatives (7a-5u). The 1,5-diketone (**5**) (1.5 mmol) and ammonium acetate (NH_4OAc) (4.5 mmol) were dissolved in acetic acid (10 mL) and refluxed for 2–5 h. After the removal of acetic acid in vacuum, the residue was added with $CHCl_3$ (30 mL) and washed with diluted $NaHCO_3$. Organic layer was dried over Na_2SO_4. Removal of the solvent in vacuum gave the 2,4-diaryl-5,6,7,8-tetrahydroqinoline derivative (**7**). The crude product was purified by column chromatography (on a silica gel) eluting with hexane/$CHCl_3$ (1:1).

2,4-Diphenyl-5,6,7,8-tetrahydroquinoline (7a). Yield 82%; yellowish viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 8.5 Hz, 2H), 7.44–7.36 (m, 9H), 3.01 (t, *J* = 6.5 Hz, 2H), 2.69 (t, *J* = 6.2 Hz, 2H), 2.07–1.93 (m, 2H), 1.82–1.75 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.6, 154.3, 150.3, 139.7, 128.7, 128.6, 128.5, 128.4, 128.3, 127.7, 127.1, 126.9, 119.5, 33.4, 27.3, 23.1, and 23.0. IR (KCl): 3060, 3027, 2977, 1582, 1494, 1446, 1236, 1018, 982, 846, 752, 700, and 665 cm^{-1}. *Anal*. *Calcd*. for: $C_{21}H_{19}N$: C, 88.38; H, 6.71; N, 4.91. Found: C, 88.23; H, 6.79; N, 4.98.

2-(2-Methoxyphenyl)-4-phenyl-5,6,7,8-tetrahydroquinoline (7b). Yield 99%; yellowish crystals, mp 90–93°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.50 (s, 1H), 7.46 (d, *J* = 7.2 Hz, 2H), 7.43–7.34 (m, 4H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 3.83 (s, 3H), 3.13 (t, *J* = 6.4 Hz, 2H), 2.70 (t, *J* = 6.0, 2H), 1.99–1.93 (m, 2H), 1.80–1.74 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.2, 156.9, 152.9, 149.2, 139.8, 131.2, 129.6, 129.4, 128.8 (2C), 128.3 (2C) 128.1, 127.7, 123.4, 120.8, 111.3, 55.6, 33.1, 27.4, 23.2, and 23.1. IR (KCl): 3058, 3008, 2936, 1600, 1585, 1493, 1436, 1381, 1243, 1026, 890, 753, 701, and 665 cm^{-1}. *Anal*. *Calcd*. for: $C_{22}H_{21}NO$: C, 83.78; H, 6.71; N, 4.44. Found: C, 83.69; H, 6.67; N, 4.24.

2-(3-Methoxyphenyl)-4-phenyl-5,6,7,8-tetrahydroquinoline (7c). Yield 93%; yellowish crystals, mp 99–102°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (m, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.50–7.41 (m, 4H), 7.40–7.35 (m, 3H), 6.96 (dd, *J* = 8.4, 2.4 Hz, 1H), 3.89 (s, 3H), 3.15 (t, *J* = 7.2 Hz, 2H), 2.70 (t, *J* = 6.4 Hz, 2H), 2.00–1.94 (m, 2H), 1.81–1.75 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.01, 157.6, 154.1, 150.4, 139.6, 141.1, 129.7, 128.8, 128.6 (2C), 128.4 (2C), 127.9, 119.4 (2C), 112.2, 111.6, 55.4, 33.2, 27.4, 23.1, and 23.1. IR (KCl): 3057, 3007, 2936, 2860, 1583, 1541, 1494, 1455, 1262, 1215, 1161, 1044, 872, 755, 701, and 599 cm^{-1}. *Anal*. *Calcd*. for: $C_{22}H_{21}NO$: C, 83.78; H, 6.71; N, 4.44. Found: C, 83.71; H, 6.45; N, 4.14.

2-(4-Methoxyphenyl)-4-phenyl-5,6,7,8-tetrahydroquinoline (7d). Yield 86%; yellowish viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 8.8 Hz, 2H), 7.47 (d, *J* = 7.2 Hz, 2H), 7.37–7.35 (m, 3H), 7.23 (t, *J* = 8.0 Hz, 1H), 7,00 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H), 3.11 (t, *J* = 6.5 Hz, 2H), 2.66 (t, *J* = 6.2 Hz, 2H), 1.99–1.93 (m, 2H), 1.80–1.74 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.1, 157.5, 153.9, 150.2, 139.9, 132.5, 128.6 (2C), 128.3 (2C), 128.1 (2C), 127.7 (2C), 118.4, 111.0 (2C), 55.3, 33.4, 27.3, 23.2, and 23.1. IR (KCl): 3058, 3007, 2935, 2859, 1608, 1587, 1513, 1450, 1248, 1172,

1032, 834, 754, 702, 666, and 570 cm^{-1}. *Anal*. *Calcd*. for: $C_{22}H_{21}NO$: C, 83.78; H, 6.71; N, 4.44. Found: C, 83.63; H, 6.61; N, 4.28.

2-(2-Chlorophenyl)-4-phenyl-5,6,7,8-tetrahydroquinoline (7e). Yield 94%; yellowish viscous oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.65 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.47–7.41 (m, 3H), 7.40–7.34 (m, 5H), 7.32–7.30 (m, 1H), 3.13 (t, *J* = 6.4 Hz, 2H), 2.73 (t, *J* = 6.4 Hz, 2H), 2.00–1.94 (m, 2H), 1.81–1.76 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.6, 153.6, 149.4, 139.4, 139.3, 132.3, 131.6, 130.0, 129.3, 128.8, 128.7 (2C), 128.4 (2C), 127.9, 127.0, 123.1, 33.2, 27.4, 23.1, and 23.0. IR (KCl): 3058, 3010, 2945, 2868, 1584, 1542, 1497, 1371, 1094, 995, 832, 750, 702, and 668 cm^{-1}. *Anal*. *Calcd*. for: $C_{21}H_{18}ClN$: C, 78.86; H, 5.67; N, 4.38. Found: C, 78.76; H, 5.53; N, 4.21.

2-(4-Chlorophenyl)-4-phenyl-5,6,7,8-tetrahydroquinoline (7f). Yield 98%; yellowish crystals, mp 130–133°C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 8.8 Hz, 2H), 7.46 (d, *J* = 7.6 Hz, 2H), 7.43 (d, *J* = 8.8 Hz, 2H), 7.39 (s, 1H), 7.36 (t, *J* = 6.4 Hz, 2H), 7.29 (t, *J* = 6.4 Hz, 1H), 3.09 (t, *J* = 6.4 Hz, 2H), 2.67 (t, *J* = 6.3 Hz, 2H), 1.98–1.92 (m, 2H), 1.80–1.71 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.8, 152.9, 150.5, 139.5, 138.1, 134.5, 128.9, 128.8 (2C), 128.5 (2C), 128.4 (2C), 128.2 (2C), 127.9, 118.9, 33.3, 27.3, 23.1, and 23.0. IR (KCl): 3059, 3025, 2937, 2861, 1586, 1540, 1492, 1448, 1215, 1091, 1013, 835, 755, 701, and 666 cm^{-1}. *Anal*. *Calcd*. for: $C_{21}H_{18}ClN$: C, 78.86; H, 5.67; N, 4.38. Found: C, 78.73; H, 5.58; N, 4.34.

2-(2-Bromophenyl)-4-phenyl-5,6,7,8-tetrahydroquinoline (7g). Yield 66%; yellowish viscous oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.66 (d, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.32 (s, 1H), 7.22 (t, *J* = 8.0 Hz, 1H), 7.47–7.37 (m, 6H), 3.12 (t, *J* = 6.4 Hz, 2H), 2.73 (t, *J* = 6.0 Hz, 2H), 2.00–1.94 (m, 2H), 1.85–1.77 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.4, 154.9, 149.4, 141.3, 139.3, 133.2, 131.6, 129.5, 128.8, 128.4 (2C), 128.7 (2C), 127.9, 127.6, 122.0, 123.0, 33.3, 27.3, 23.1, and 23.0. IR (KCl): 3057, 3027, 2935, 2859, 1583, 1540, 1494, 1447, 1381, 1217, 1025, 762, 701, 668, and 599 cm^{-1}. *Anal*. *Calcd*. for: $C_{21}H_{18}BrN$: C, 69.24; H, 4.98; N, 3.85. Found: C, 68.98; H, 4.93; N, 3.78.

2-(4-Bromophenyl)-4-phenyl-5,6,7,8-tetrahydroquinoline (7h). Yield 92%; yellowish viscous oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.46 (m, 2H), 7.39 (s, 1H), 7.36–7.34 (m, 2H), 7.27 (t, *J* = 8.0 Hz, 1H), 3.01 (t, *J* = 6.4 Hz, 2H), 2.67 (t, *J* = 6,4 Hz, 2H), 1.98–1.92 (m, 2H), 1.80–1.74 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.8, 152.9, 150.5, 139.5, 138.5, 131.7 (2C), 128.9, 128.6 (2C), 128.5 (2C), 128.4 (2C), 127.9, 122.9, 118.9, 33.3, 27.4, 23.1, and 23.0. IR (KCl): 3059, 3026, 2936, 2860, 1587, 1540, 1490, 1449, 1402, 1215, 1072, 1009, 832, 756, and 701 cm^{-1}. *Anal*. *Calcd*. for: $C_{21}H_{18}BrN$: C, 69.24; H, 4.98; N, 3.85. Found: C, 69.03; H, 4.94; N, 3.73.

4-(4-Phenyl-5,6,7,8-tetrahydroquinolin-2-yl)phenol (7i). Yield 80%; yellowish viscous oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.94 (br s, 1H—OH), 7.68 (d, *J* = 8.0 Hz, 2H), 7.47–7.39 (m, 3H), 7.33–7.27 (m, 3H), 6.80 (br d, *J* = 7.6 Hz, 2H), 3.14 (t, *J* = 6.0 Hz, 2H), 2.64 (t, *J* = 6.0 Hz, 2H), 1.99–1.88 (m, 2H), 1.75–1.71 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.3, 157.5, 156.7, 154.4, 151.7, 139.2, 129.5, 128.9, 128.7, 128.5, 128.4, 128.3, 128.0, 127.3, 119.8, 116.1, 31.9, 27.2, 22.8, and 22.7. IR (KCl): 3112, 3058, 2936, 2855, 1589, 1515, 1445, 1296, 1242, 1175, 1033, 832, 755, and 687 cm^{-1}. *Anal*. *Calcd*. for: $C_{21}H_{19}NO$: C, 83.69; H, 6.35; N, 4.65. Found: C, 83.44; H, 6.29; N, 4.62.

4-(2-Methoxyphenyl)-2-phenyl-5,6,7,8-tetrahydroquinoline (7j). Yield 88%; yellowish viscous oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.06 (d, *J* = 7.2 Hz, 2H), 7.48–7.37 (m, 5H), 7.18 (dd, *J* = 7.2 Hz, 1.4 Hz, 1H), 7.07 (t, *J* = 7.2 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 3.81 (s, 3H), 3.16–3.11 (m, 4H), 2.00–1.94 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.1, 156.3, 154.1, 147.6, 140.0, 130.3, 129.9, 129.4, 128.6, 128.3, 126.9, 120.6, 119.7, 110.8, 55.5, 33.4, 26.4, 23.2, and 22.8. IR (KCl): 3059, 2937, 2856, 2838, 1584, 1514, 1445, 1292, 1243, 1175, 1030, 835, 752, and 695 cm^{-1}. *Anal*. *Calcd*. for: $C_{22}H_{21}NO$: C, 83.78; H, 6.71; N, 4.44. Found: C, 83.71; H, 6.69; N, 4.35.

4-(4-Methoxyphenyl)-2-phenyl-5,6,7,8-tetrahydroquinoline (7k). Yield 71%; yellowish viscous oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 7.6 Hz, 2H), 7.48–7.37 (m, 3H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 3.87 (s, 3H), 3.12 (t, *J* = 6.4 Hz, 2H), 2.71 (t, *J* = 4 Hz, 2H), 1.99–1.93 (m, 2H), 1.81–1.75 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.3, 157.6, 154.3, 150.1, 139.7, 131.9, 128.9 (2C), 128.8, 128.7 (2C), 128.5, 126.9 (2C), 119.5, 113.8 (2C), 55.3, 33.2, 27.5, 23.2, and 23.1. IR (KCl): 3059, 2934, 2859, 2835, 1609, 1588, 1511, 1442, 1290, 1247, 1177, 1032, 833, 754, and 696 cm^{-1}. *Anal*. *Calcd*. for: $C_{22}H_{21}NO$: C, 83.78; H, 6.71; N, 4.44. Found: C, 83.68; H, 6.70; N, 4.39.

4-(2-Chlorophenyl)-2-phenyl-5,6,7,8-tetrahydroquinoline (7l). Yield 87%; yellowish viscous oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.99 (br d, *J* = 8.0 Hz, 2H), 7.47–7.23 (m, 8H), 2.55 (t, *J* = 6.4 Hz, 2H), 2.46 (t, *J* = 6.0 Hz, 2H), 1.99–1.93 (m, 2H), 1.83–1.73 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.6, 154.2, 147.9, 139.6, 138.4, 132.6, 130.2, 129.6, 129.4, 129.3, 129.2, 128.6, 128.5, 126.9, 126.8, 118.9, 33.2, 26.4, 23.1, and 22.7. IR (KCl): 3061, 3028, 2937, 2859, 1592, 1537, 1444, 1267, 1084, 1004, 854, 756, 697, and 663 cm^{-1}. *Anal*. *Calcd*. for: $C_{21}H_{18}ClN$: C, 78.86; H, 5.67; N, 4.38. Found: C, 78.81; H, 5.64; N, 4.30.

4-(3-Chlorophenyl)-2-phenyl-5,6,7,8-tetrahydroquinoline (7m). Yield 99%; yellowish viscous oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 8.0 Hz, 2H), 7.46 (t, *J* = 6.8 Hz, 2H), 7.40–7.36 (m, 5H), 7.25–7.22 (m, 1H), 3.12 (t, *J* = 6.4 Hz, 2H), 2.65 (t, *J* = 6.4 Hz, 2H), 1.99–1.88 (m, 2H), 1.81–1.73 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.8, 154.4, 148.9, 118.9, 141.4, 139.4, 134.3, 129.7, 128.7 (2C), 128.6 (2C), 128.3, 127.9, 126.9 (2C), 126.8, 33.2, 27.2, 23.0, and 22.9. IR (KCl): 3061, 3030, 2937, 2860, 1586, 1541, 1443, 1380, 1216, 1078, 878, 755, and 697 cm^{-1}. *Anal*. *Calcd*. for: $C_{21}H_{18}ClN$: C, 78.86; H, 5.67; N, 4.38. Found: C, 78.74; H, 5.62; N, 4.33.

4-(4-Chlorophenyl)-2-phenyl-5,6,7,8-tetrahydroquinoline (7n). Yield 90%; yellowish viscous oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 7.2 Hz, 2H), 7.47–7.40 (m, 4H), 7.32 (t, *J* = 4.4 Hz, 1H), 7.28 (d, *J* = 8.4 Hz, 2H), 3.63 (s, 1H), 3.11 (t, *J* = 6.4 Hz, 2H), 2.64 (t, *J* = 6.4 Hz, 2H), 2.00–1.93 (m, 2H), 1.80–1.74 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.8, 154.4, 149.2, 139.4, 138.0, 133.9, 129.9 (2C), 128.8 (2C), 128.7, 128.6 (2C), 128.5, 126.9 (2C), 119.0, 33.2, 27.3, 23.0, and 23.0. IR (KCl): 3061, 3029, 2937, 2861, 1599, 1491, 1444, 1215, 1091, 1015, 832, 759, 697, and 666

cm^{-1}. *Anal*. *Calcd*. for: $C_{21}H_{18}ClN$: C, 78.86; H, 5.67; N, 4.38. Found: C, 78.85; H, 5.63; N, 4.31.

4-(2-Bromophenyl)-2-phenyl-5,6,7,8-tetrahydroquinoline (7o). Yield 82%; yellowish viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): 8.05 (d, J = 7.6 Hz, 2H), 7.71 (d, J = 7.6 Hz, 1H), 7.48 (t, J = 7.2 Hz, 2H), 7.42–7.39 (m, 3H), 7.30–7.23 (m, 2H), 3.20–3.11 (m, 2H), 2.62–2.55 (m, 1H), 2.48–2.39 (m, 1H), 2.00–1.94 (m, 2H), 1.84–1.78 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.8, 154.2, 149.5, 140.6, 139.6, 132.9, 130.1, 129.5, 128.9, 128.7 (2C), 128.6, 127.5, 126.9 (2C), 118.7, 122.6, 33.4, 26.6, 23.2, and 22.8. IR (KCl): 3060, 3031, 2936, 2859, 1596, 1543, 1442, 1382, 1216, 1025, 881, 758, and 695 cm^{-1}. *Anal*. *Calcd*. for: $C_{21}H_{18}BrN$: C, 69.24; H, 4.98; N, 3.85. Found: C, 69.20; H, 4.96; N, 3.81.

4-(3-Bromophenyl)-2-phenyl-5,6,7,8-tetrahydroquinoline (7p). Yield 98%; yellowish viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 (d, J = 7.4 Hz, 2H), 7.56–7.52 (m, 2H), 7.46 (t, J = 7.7 Hz, 2H), 7.38 (s, 1H), 7.36–7.27 (m, 3H), 3.11 (t, J = 6.5 Hz, 2H), 2.65 (t, J = 6.2 Hz, 2H), 2.01–1.92 (m, 2H), 1.81–1.76 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.9, 154.4, 148.7, 141.8, 139.5, 131.5, 130.8, 129.9, 128.7 (2C), 128.6, 128.2, 127.3, 126.9 (2C), 122.5, 118.8, 33.4, 27.2, 23.1, and 23.0. IR (KCl): 3061, 3011, 2937, 2860, 1586, 1541, 1475, 1444, 1215, 1072, 997, 879, 759, 698, and 666 cm^{-1}. *Anal*. *Calcd*. for: $C_{21}H_{18}BrN$: C, 69.24; H, 4.98; N, 3.85. Found: C, 69.12; H, 4.88; N, 3.79.

4-(4-Bromophenyl)-2-phenyl-5,6,7,8-tetrahydroquinoline (7r). Yield 94%; yellowish viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, J = 7.2 Hz, 2H), 7.60 (d, J = 8.8 Hz, 2H), 7.46 (t, J = 8.0 Hz, 2H), 7.39 (t, J = 8.0 Hz, 1H), 7.38 (s, 1H), 7.23 (d, J = 8.8 Hz, 2H), 3.11 (t, J = 6.5 Hz, 2H), 2.64 (d, J = 6.3 Hz, 2H) 1.81–1.73 (m, 2H), 1.99–1.92 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.9, 154.5, 149.1, 139.5, 138.6, 131.6 (2C), 130.3 (2C), 128.9 (2C), 128.7 (2C), 128.6, 128.3, 122.1, 118.9, 33.2, 27.3, 23.1, and 23.0. IR (KCl): 3060, 3029, 2936, 2860, 1594, 1488, 1443, 1216, 1070, 1011, 827, 755, and 696 cm^{-1}. *Anal*. *Calcd*. for: $C_{21}H_{18}BrN$: C, 69.24; H, 4.98; N, 3.85. Found: C, 69.19; H, 4.92; N, 3.78.

2-Phenyl-4-p-tolyl-5,6,7,8-tetrahydroquinoline (7s). Yield 81%; yellowish viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (d, J = 8.8 Hz, 2H), 7.48 (t, J = 7.8 Hz, 2H), 7.44 (s, 1H), 7.40 (t, J = 7.2 Hz, 1H), 7.31–7.27 (m, 4H), 3.14 (t, J = 6.6 Hz, 2H), 2.71 (t, J = 6.3 Hz, 2H), 2.02–1.94 (m, 2H), 1.81–1.76 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.6, 154.3, 150.4, 139.7, 137.6, 136.8, 129.1 (2C), 128.7 (3C), 128.5 (2C), 128.4, 126.9 (2C), 119.4, 33.3, 27.4, 23.1, 23.1, and 21.3. IR (KCl): 3058, 3027, 2935, 2860, 1589, 1541, 1513, 1443, 1380, 1216, 1024, 820, 755, and 696 cm^{-1}. *Anal*. *Calcd*. for: $C_{22}H_{21}N$: C, 88.25; H, 7.07; N, 4.68. Found: C, 88.19; H, 6.98; N, 4.65.

4-(4-Chlorophenyl)-2-(4-methoxyphenyl)-5,6,7,8-tetrahydroquinoline (7t). Yield 90%; yellowish viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 (br d, J = 6.4 Hz, 2H), 7.43 (br d, J = 7.2 Hz, 2H), 7.31 (s, 1H), 7.26 (br d, J = 6.4 Hz, 2H), 6.98 (br d, J = 7.2 Hz, 2H), 3.85 (s, 3H), 3.08 (t, J = 6.4 Hz, 2H), 2.62 (t, J = 6.0 Hz, 2H), 1.96–1.90 (m, 2H), 1.79–1.74 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.2, 157.6, 154.1, 149.1, 138.2, 133.8, 132.0, 129.9, 128.6, 128.1, 127.6, 118.3, 114.1, 55.3, 33.2, 27.2, 23.1, and 23.0. IR (KCl): 3065, 3008, 2936, 2860, 2835, 1607, 1514, 1491, 1448, 1251, 1172, 1090, 1031, 832, 755, and 666 cm^{-1}. *Anal*. *Calcd*. for: $C_{22}H_{20}ClNO$: C, 75.53; H, 5.76; N, 4.00. Found: C, 75.49; H, 5.70; N, 3.96.

2,4-Bis(4-chlorophenyl)-5,6,7,8-tetrahydroquinoline (7u). Yield 97%; yellowish viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (d, J = 8.0 Hz, 2H), 7.41 (br d, J = 7.6 Hz, 2H), 7.39 (br d, J = 7.32 Hz, 2H), 7.33 (s, 1H), 7.26 (d, J = 8 Hz, 2H), 3.07 (t, J = 6.8 Hz, 2H), 2.63 (t, J = 6.4 Hz, 2H), 1.99–1.91 (m, 2H), 1.79–1.73 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.9, 153.0, 149.3, 137.8, 137.7, 134.7, 134.0, 130.3, 128.8, 128.6, 128.2, 118.7, 33.1, 27.3, 23.0, and 22.9. IR (KCl): 3015, 2938, 2862, 1597, 1539, 1491, 1446, 1215, 1090, 1014, 830, 755, and 665 cm^{-1}. *Anal*. *Calcd*. for: $C_{21}H_{17}Cl_2N$: C, 71.20; H, 4.84; N, 3.95 Found: C, 71.14; H, 4.79; N, 3.96.

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