A Facile and Efficient Solid Supported, One-Pot Synthesis of Functionalized Piperidine Derivatives Catalyzed by Amberlite IRA400-Cl Resin/I_2/KI via Multicomponent Reaction

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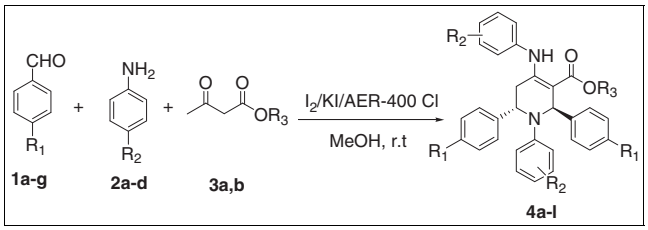

A facile and efficient one-pot, solid supported synthesis of functionalized piperidine derivatives catalyzed by Amberlite IRA400-Cl resin/I_2/KI via a multicomponent reaction of various aldehydes, aromatic amines, and 1,3-dicarbonyl compounds has been achieved. The reaction has been carried out in a one-pot reaction and Amberlite resin as a solid supported catalyst at room temperature. Shorter reaction time, easy workup, yield, and mild reaction condition make the novel synthetic strategy both practical and attractive.

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INTRODUCTION

Solid base heterogeneous catalysts such as quaternary ammonium halide type of anion exchange resin, Amberlite IRA400 (Cl^-), are an area of great interest from both environmental and economic points of view [1]. Anion exchange resins have been found as excellent catalysts and to provide solid support for various organic reactions [2]. Piperidines have been found as a core unit in alkaloids, fine chemicals [3], and pharmaceutical agents [4]. Recently, multicomponent reactions (MCRs) [5] have been paid much attention by synthetic chemists for the construction of complex molecules from readily available starting materials. Mostly a single product was obtained from three or more substrates by reacting in a well-defined manner through MCRs [6]. MCRs are considered as atom economic and cost-effective [7]. 1,3-Dicarbonyls represent important building blocks, incorporating as either nucleophilic or electrophilic species in a variety of synthetic transformations [8]. Thus, synthetic potential of these easily accessible reagents have been found for the synthesis of complex heterocycles [9]. Owing to numerous advantages associated with this eco-friendly element, iodine has been explored as a powerful catalyst for a number of organic reactions [10–12]. Structural motifs with piperidine exhibit a range of biological activities [13–16]. Hence, synthesis of highly functionalized piperidines has gained considerable attention [17], and a number of procedures have been developed [18–25], although the use of expensive and excess catalysts is disadvantages. Therefore, there is a need for efficient solid support and eco-friendly protocol to obtain these valuable compounds. Thus, we report herein a facile and efficient one-pot, solid support synthesis of functionalized piperidine derivatives catalyzed by Amberlite IRA400-Cl resin/I_2/KI via MCR.

Initially, a mixture of benzaldehyde **1a**, aniline **2a**, ethyl acetoacetate **3a**, and 0.5 equivalent of iodine in methanol was stirred at room temperature for 48 h, and the progress of the reaction was monitored by TLC. After the reaction, workup followed by purification of the crude compound by silica gel column chromatography afforded the piperidine derivative **4a** only in 10% yield. Repeating the above experiment with 0.5 equivalent of potassium iodide slightly increased the yield (13%). However, when Amberlite IRA400-Cl resin (0.5 g) was added to the above mixture, the yield of the product **4a** was substantially improved to 45%. A maximum yield of 76% was obtained when 1.2 equivalents of each of iodine and potassium iodide and 0.3 g of Amberlite IRA400-Cl resin were used, and this was found as the optimum condition. The optimized reaction condition afforded the desired compound **4a** with reduced reaction time (Table 1, Scheme 1).

Encouraged by the preliminary results and in order to demonstrate that the method is general, we have used a number of aryl aldehydes, aryl amines, and 1,3-dicarbonyl compounds for the reactions. Under optimized condition, all the reactions underwent smoothly and provided the desired compounds **4b–l** in very good yield. From the experimental results, it has been observed that both electron

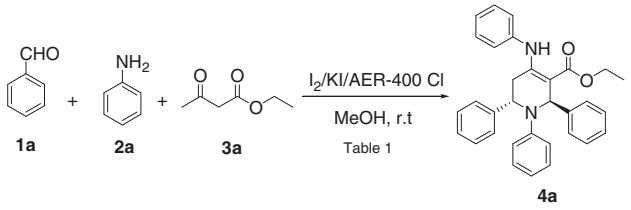
Table 1

Optimization of reaction conditions using compound **4a**.[a]

Entry	Catalyst[a]	Time (h)	Yield %
1	I_2 (0.5 mmol)	48	10
2	I_2/KI (0.5 mmol)	48	13
3	I_2/KI/AER-400Cl (0.5 mmol)	36	45
4	I_2/KI/AER-400Cl (1.2 mmol)	24	76

[a]All the reactions were carried out in methanol.

Scheme 1



donating and withdrawing substitutions in both aldehydes and amines did not alter the yields of the products significantly. All the compounds **4b–l** were obtained in the range of 62–85% yield (Table 2, entries 1–10). Interestingly, heteroaryl aldehyde such as 2-thiophene carboxaldehyde also took part in the reaction and provided the piperidine product **4l** in 62% yield (Table 2, entries 11, Scheme 2).

All the compounds were characterized by spectroscopic data (IR, ^{1}H NMR, ^{13}C NMR, and MS). Final structure proof of compounds **4c** and **4i** was obtained from single crystal X-ray studies [26,27] (Figs 1 and 2). The results are shown in Table 2.

A plausible mechanism for the formation of piperidine product is shown in Scheme 3. Generally, the formation of piperidine derivative **4** via a Knoevenagel-type intermediate followed by [4 + 2]-aza-Diels–Alder reaction has been proposed by various groups [11,18,19]. However, in the present reaction, it is assumed that the interaction of β-ketoester with resin and iodide ion facilitates the formation of enolate anion that subsequently reacts with aldehyde to form α-substituted β-ketoester **5**. Intermediate **5** subsequently reacts with aniline to provide the Mannich-type intermediate **6**, which finally undergoes the [4 + 2]-aza-Diels–Alder reaction with imine **7** to form the compound **4**.

CONCLUSION

In conclusion, we have demonstrated a facile, efficient, one-pot solid supported synthesis of functionalized piperidine derivatives catalyzed by Amberlite IRA400-Cl resin/I_2/KI via an MCR of various aldehydes, aromatic amines, and 1,3-dicarbonyl compounds. The reaction has been carried out in a one-pot reaction and Amberlite resin as solid supported catalyst at room temperature. Shorter reaction time, easy workup, yield, and mild reaction condition make the novel synthetic strategy both practical and attractive.

EXPERIMENTAL

All the chemicals were purchased from Fluka (Buchs, Switzerland) and Aldrich (St. Louis, MO), Chemical Companies. Fourier Transform–IR spectra of the compounds were recorded on a Thermo Mattson Satellite Fourier Transform-IR 3000 spectrophotometer (Madison) by KBr pellet method, and ^{1}H and ^{13}C NMR (JEOL-DELTA2_NMR 500MHz spectrometer, Tokyo, Japan) spectra were recorded on a JEOL spectrometer in $CDCl_3$ as solvent using TMS as internal standard. Melting points of all synthesized compounds were determined in open capillaries and are uncorrected. Mass spectra were recorded on Micromass Q-TOF spectrometer (Waters Q-TOF *Micro*™ spectrometer Milford, MA). Chromatography purification was conducted by column chromatography. Solvents used for purification are of commercial grade and purified before used.

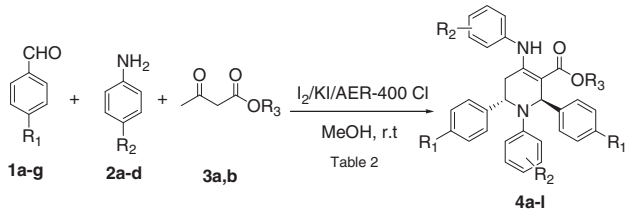
General experimental procedure. To a mixture of aniline **1a** (2.0 mmol), aryl aldehyde **2a** (2.0 mmol), and ethyl acetoacetate **3a** (1.0 mmol) in methanol (10 mL), iodine (1.2 mmol), potassium iodide (1.2 mmol), and 0.3 g of anion exchange Amberlite resin (Cl in form) were sequentially added. The mixture was stirred at room temperature and continued till the disappearance of

Table 2

Synthesis of functionalized piperidine derivatives catalyzed by Amberlite IRA400-Cl resin/I_2/KI.

Entry	Aldehyde	Amine	β-Diketone	Time (h)	Product	mp (°C)	Yield %
1	Benzaldehyde **1a**	4-Bromoaniline **2b**	Ethyl acetoacetate **3a**	18	**4b**	200–202	72
2	4-Methylbenzaldehyde **1b**	Aniline **2a**	Ethyl acetoacetate **3a**	18	**4c**	226–228	70
3	4-Methylbenzaldehyde **1b**	4-Chloroaniline **2c**	Ethyl acetoacetate **3a**	18	**4d**	180–182	72
4	4-Methylbenzaldehyde **1b**	4-Bromoaniline **2b**	Ethyl acetoacetate **3a**	20	**4e**	162–164	85
5	4-Methoxybenzaldehyde **1c**	4-Methylaniline **2d**	Ethyl acetoacetate **3a**	16	**4f**	150–152	70
6	4-Methoxybenzaldehyde **1c**	4-Bromoaniline **2b**	Ethyl acetoacetate **3a**	18	**4g**	216–218	81
7	4-Methoxybenzaldehyde **1c**	4-Chloroaniline **2c**	Methyl acetoacetate **3b**	17	**4h**	192–194	82
8	4-Cholorobenzaldehyde **1d**	4-Methylaniline **2d**	Ethyl acetoacetate **3a**	11	**4i**	186–188	74
9	4-Fluorobenzaldehyde **1e**	4-Methylaniline **2d**	Ethyl acetoacetate **3a**	12	**4j**	162–164	68
10	4-Fluorobenzaldehyde **1f**	4-Bromoaniline **2b**	Ethyl acetoacetate **3a**	16	**4k**	174–176	70
11	2-Thiophenecarboxaldehyde **1g**	4-Methylaniline **2d**	Ethyl acetoacetate **3a**	16	**4l**	176–178	62

Scheme 2



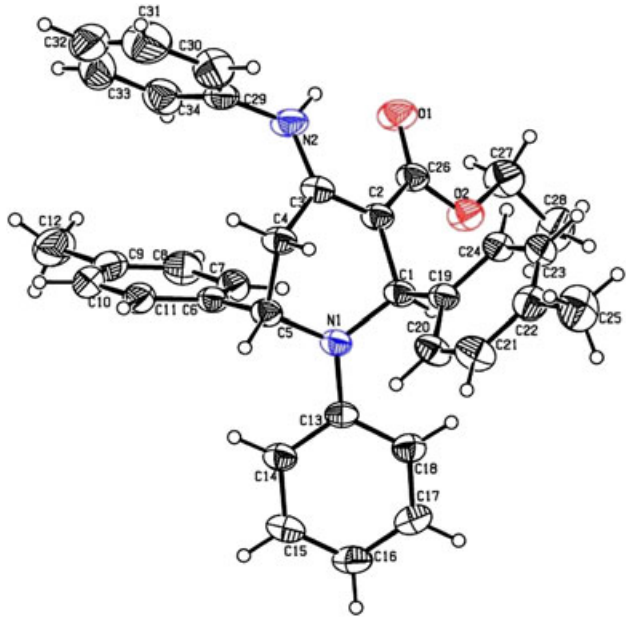


Figure 1. ORTEP diagram of compound **4c**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

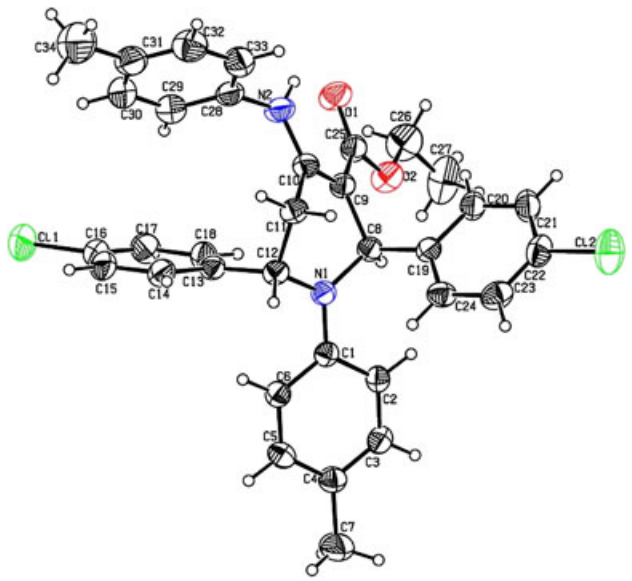


Figure 2. ORTEP diagram of compound **4i**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

aldehyde (monitored by TLC). After the completion of the reaction, the mixture was filtered to remove the resin. The solvent was evaporated *in vacuo*. The crude product was dissolved in EtOAc and washed with aqueous $Na_2S_2O_3$ to remove excess iodine and dried over (anhydrous Na_2SO_4). Removal of solvent was followed by purification by silica gel column chromatography (60–120, 5–10% EtOAc in hexane) to afford **4a**.

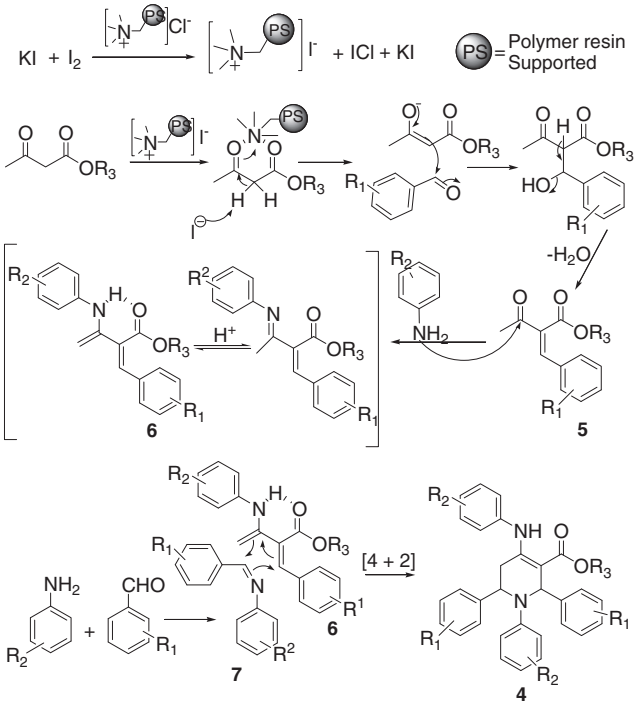
Ethyl 2,6-bis(phenyl)-1-(4-bromophenyl)-4-(4-bromophenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate (4b). White solid, mp 200–202°C; IR (KBr): 3459, 3247, 3059, 2974, 2367, 2346, 1647, 1603, 1492, 1347, 1319, 1255, 1068, 1012, 941, 699 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 10.23 (s, 1H, NH), 7.12–7.29 (m, 14H, Ar–H), 6.38–6.40 (m, 3H, Ar–H), 6.11 (d, 2H, *J* = 9.2 Hz, Ar–H), 5.11 (br, s, 1H, H-6), 4.46–4.48 (m, 1H, OCH_2), 4.32–4.36 (m, 1H, OCH_2), 2.84–2.88 (m, 1H, H-5b), 2.69–2.73 (m, 1H, H-5a), 1.48 (t, 3H, *J* = 7.3 Hz, $COOCH_2CH_3$); ^{13}C NMR (125.1 MHz, $CDCl_3$): δ = 168.2, 155.4, 145.9, 143.2, 142.2, 137.0, 132.1, 131.7, 128.9, 128.5, 127.6, 126.7, 126.6, 127.4, 126.4, 114.7, 108.5, 98.9, 60.1, 58.4, 55.3, 33.5, 14.9; HRMS (EI) Calcd for $C_{32}H_{29}Br_2N_2O_2$ (M^+): 631.0596; found: 631.0584.

Ethyl 2,6-bis(4-methylphenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate (4c). White solid, mp 226–228°C; IR (KBr): 3427, 3227, 3057, 2982, 2870, 2358, 1651, 1592, 1501, 1445, 1372, 1328, 1256, 1071, 952, 861, 750, 692 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 10.30 (br, s, 1H, NH), 7.06–7.10 (m, 13H, Ar–H), 6.59–6.62 (m, 1H, Ar–H), 6.54 (d, 2H, *J* = 8.4 Hz, Ar–H), 6.42 (s, 1H, H-2), 6.31 (d, 2H, *J* = 6.1 Hz, Ar–H), 5.12 (br, s, 1H, H-6), 4.43–4.38 (m, 1H, OCH_2), 4.30–4.36 (m, 1H, OCH_2), 2.79–2.86 (m, 2H, H-5a, H-5b), 2.34 (d, 6H, *J* = 7.65 Hz, Ar–CH_3), 1.46 (t, 3H, *J* = 7.3 Hz, $COOCH_2CH_3$); ^{13}C NMR (125.1 MHz, $CDCl_3$): δ = 168.4, 163.6, 156.2, 147.2, 141.1, 139.8, 138.1, 136.7, 135.9, 129.4, 129.0, 128.9, 126.7, 126.4, 125.8, 116.0, 115.4, 112.8, 98.4, 59.7, 58.0, 54.9, 33.8, 21.2, 21.1, 14.9; HRMS (EI) Calcd for $C_{34}H_{35}N_2O_2$ (M^+): 503.2699; found: 503.2701.

Ethyl 2,6-bis(4-methylphenyl)-1-(4-chlorophenyl)-4-(4-chlorophenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate (4d). White solid, mp 180–182°C; IR (KBr): 3772, 3452, 3247, 2982, 2367, 2346, 1618, 1494, 1320, 1256, 1184, 1073, 940 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 10.23 (br, s, 1H, NH), 7.16 (d, 2H, *J* = 8.4 Hz, Ar–H), 7.01–7.10 (m, 8H, Ar–H), 6.98 (d, 2H, *J* = 9.2 Hz, Ar–H), 6.42 (d, 2H, *J* = 9.2 Hz, Ar–H), 6.32 (s, 1H, H-2), 6.18 (d, 2H, *J* = 8.4 Hz, Ar–H), 5.07 (br, s, 1H, H-6), 4.29–4.46 (m, 2H, OCH_2), 2.84 (m, 1H, H-5b), 2.69 (m, 1H, H-5a), 2.34 (s, 3H, Ar–CH_3), 2.32 (s, 3H, Ar–CH_3), 1.46 (t,3H, *J* = 7.3 Hz, $COOCH_2CH_3$); ^{13}C NMR (125.1 MHz, $CDCl_3$): δ = 168.2, 155.5, 145.7, 140.4, 139.3, 137.1, 136.6, 136.2, 129.5, 129.0, 128.8, 127.1, 126.3, 121.1, 114.1, 98.9, 59.9, 58.1, 55.1, 33.6, 21.2, 21.1, 14.9; HRMS (EI) Calcd for $C_{34}H_{33}Cl_2N_2O_2$ (M^+): 571.1919; found: 571.1918.

Ethyl (4-methylphenyl)-4-(4-methylphenylamino)-2, 6-di-(4-fluorophenyl)-1,2,5,6-tetrahydropyridine-3-carboxylate (4j). White solid, mp 162–164°C; IR (KBr): 3754, 3458, 3239, 2988, 2366, 1648, 1508, 1312, 1223, 1096, 1072, 947, 823, 796 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 10.22 (br, s, 1H, NH), 6.87–7.25 (m, 12H, Ar–H), 6.38 (d, 2H, *J* = 9.2 Hz, Ar–H), 6.33 (s, 1H, H-2), 6.26 (d, 2H, *J* = 8.4 Hz, Ar–H), 5.06 (br, s, 1H, H-6), 4.31–4.42 (m, 2H, OCH_2), 2.69–2.79 (m, 2H, m, 2H, H-5a, H-5b), 2.27 (s, 3H, CH_3), 2.16 (s, 3H, CH_3), 1.43 (t, 3H, *J* = 6.9 Hz, $COOCH_2CH_3$); ^{13}C NMR (125.1 MHz, $CDCl_3$): δ = 168.2, 144.6, 129.6, 128.2, 128.1, 128.0, 125.9, 115.6, 115.4, 113.1, 97.6, 59.8, 57.4, 54.8, 33.8, 20.9, 20.2, 14.9; HRMS (EI) Calcd for $C_{34}H_{33}F_2N_2O_2$ (M^+): 569.2510; found: 539.2501.

Scheme 3



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[26] CCDC 781128 [**4c**] contains the supplementary crystallographic data.

[27] CCDC 781129 [**4i**] contains the supplementary crystallographic data.