Research Article

A Facile Synthesis of New 2-Amino-4H-pyran-3-carbonitriles by a One-Pot Reaction of α, α' -Bis(arylidene) Cycloalkanones and Malononitrile in the Presence of K_2CO_3

Zahed Karimi-Jaberi and Baharak Pooladian

Department of Chemistry, Firoozabad Branch, Islamic Azad University, P.O. Box 74715-117 Firoozabad, Fars, Iran

Correspondence should be addressed to Zahed Karimi-Jaberi, zahed.karimi@yahoo.com

Received 6 October 2011; Accepted 24 October 2011

Academic Editor: Aurelio G. Csaky

Copyright © 2012 Z. Karimi-Jaberi and B. Pooladian. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

A rapid and environmentally friendly method is developed for the synthesis of a series of new substituted 2-amino-4H-pyran-3-carbonitriles through a one-pot condensation of malononitrile and α, α' -bis(arylidene) cycloalkanones in ethanol by using K_2CO_3 as a catalyst. Short experimental reaction times, excellent yields, no need to use cumbersome apparatus for purification of the products, and inexpensiveness and commercial availability of the catalyst are the advantages of this method.

1. Introduction

In the past few decades, the synthesis of new heterocyclic compounds has been a subject of great interest due to the wide applicability of them. Heterocyclic compounds occur very widely in nature and are essential to life. The importance of multicomponent reactions in organic synthesis has been recognized, and considerable efforts have been focused on the design and development of one-pot procedures for the generation of libraries of heterocyclic compounds [1, 2]. 4H-Pyrans and their derivatives are of considerable interest due to their pharmacological activities [3], such as spasmolytic, diuretic, anticoagulant, anticancer, and antianaphylactic activity [4–6]. Moreover, 4H-pyrans are useful intermediates for synthesis of various compounds, such as pyranopyridine derivatives [7], polyazanaphthalenes [8], pyranopyrimidines [9], and pyridin-2-ones [10].

Furthermore, 4H-pyrans represent building blocks of a series of natural products [11, 12]. A number of 2-amino-4H-pyrans are used as photoactive materials [13], pigments [14], and potential biodegradable agrochemicals [15], and consequently, numerous methods have been reported for the synthesis of these compounds. Thus,

the synthesis of 4H-pyran is of much importance to organic chemists. Several methods have been reported for the synthesis of pyran derivatives via a three-component condensation of β -dicarbonyl compounds with aldehydes and malononitrile [16]. From the literature, we observed that very few catalysts have been used for the synthesis of 2-amino-4H-pyran-3-carbonitriles based on the reactions of α, α' -bis(arylidene) cycloalkanones with malononitrile, for example, NaOH/piperidine [17], $KF \cdot Al_2O_3$ [18], and hexadecyltrimethyl ammonium bromide (HTMAB) [19]. However, these methods show varying degrees of success as well as limitations such as prolonged reaction times, low yields, and use of toxic solvents. Thus, the development of an alternate milder and clean procedure is highly demanding for the synthesis of 2-amino-4H-pyran-3-carbonitriles, which surpasses those limitations. Herein, we planned to synthesize these compounds using sequential reactions of α, α' -bis(arylidene) cycloalkanones and malononitrile in the presence of K_2CO_3 as a catalyst in ethanol under reflux conditions (Scheme 1).

Nowadays, organic reactions in ethanol without the use of harmful organic solvents have attracted much attention, because ethanol is a cheap, safe, and environmentally benign

SCHEME 1: Synthesis of 2-amino-4H-pyran-3-carbonitriles.

solvent [7]. In recent years, K₂CO₃ has been considered as an efficient, inexpensive, and readily available catalyst for several organic transformations [20, 21].

2. Results and Discussion

In continuation of our studies on the development of inexpensive and environmentally benign methodologies for organic reactions [22–24], herein we report a highly versatile and efficient synthesis of 2-amino-4H-pyran-3-carbonitriles **3a–q** (Scheme 1) from α, α' -bis(Arylidene) cycloalkanone **1**, malononitrile **2** and catalytic amounts of K₂CO₃. In a typical reaction, a mixture of **1** and **2** (1 : 1) equivalents, respectively, and K₂CO₃ (cat.) was refluxed in ethanol for 5–60 min. The results are summarized in (Table 1).

The formation of the compounds **3** was assumed to proceed via formation of a Michael adduct intermediate followed by cyclization according to Scheme 2. A α, α' -bis(arylidene) cycloalkanones **1** was firstly condensed with malononitrile **2** to afford the intermediate **4**, this step can be regarded as a Michael addition. Then, the intermediate **5** cyclized by nucleophilic attack of the OH group on the cyano (CN) moiety and gave the intermediate **6**. Finally, the expected products **3** were afforded (Scheme 2) [17–19].

To test the catalysts, the reaction of α, α' -bis(arylidene) cyclohexanone and malononitrile in ethanol was selected as a model reaction. The scope and the generality of the present method were then further demonstrated by the reaction of various α, α' -bis(arylidene) cycloalkanones with malononitrile and K₂CO₃. In all cases, good yields with good selectivity were obtained. The catalyst plays a crucial role in the success of the reaction in terms of the rate and the yields. The present methodology afforded high yields of the products within short times (5–60 min). The results (Table 1, entries 1–17) indicated that substrates **1** bearing both electron-donating groups (such as alkoxy and methyl) and electron-withdrawing groups (such as halide) can be involved in this one-pot synthesis to afford desired products **3** with high yields. Thus, it should be concluded that the electronic nature of the substituents has no significant effect on this reaction.

In order to show the merits of K₂CO₃ over other catalysts reported in the literature, results for the synthesis of 2-amino-4H-pyran-3-carbonitriles obtained using K₂CO₃ as the catalyst were compared with those obtained using other catalysts. Table 2 clearly shows that K₂CO₃ appears to

promote the reaction more effectively than a number of other catalysts, particularly in terms of the time and yield required to complete the reaction.

3. Conclusion

In conclusion, the present method is a simple and environmentally friendly procedure for the synthesis of a series of new 2-amino-4H-pyran-3-carbonitriles using catalytic amount of K₂CO₃. The simple experimental procedure, short reaction times, excellent yields of products, mild reaction condition, easy purification, economic availability of the catalyst, and green standard are the advantages of this method.

4. Method

α, α' -Bis(arylidene)cycloalkanones have been synthesized through cross-aldol condensation of cycloalkanones and aldehydes using our reported method [25].

4.1. General Procedure for Synthesis of 2-Amino-4H-pyran-3-carbonitrile Derivatives 3a–q. A mixture of appropriate α, α' -bis(arylidene)cycloalkanone **1** (1 mmol), malononitrile **2** (1 mmol) and 5% mol K₂CO₃ (0.05 mmol, 0.006 g) in ethanol 96% (10 mL) was refluxed for the appropriate time indicated in Table 1 (5–60 min). The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was cooled to room temperature, and the resulting cream precipitate was filtered and washed with *n*-hexane (10 mL) to furnish the corresponding 2-amino-4H-pyran-3-carbonitriles.

The structure of the products was deduced from their IR, ¹H NMR, ¹³C NMR, and elemental analysis. The spectral (IR, ¹H NMR, ¹³C NMR) and analytical data of unknown compounds are given below.

4.1.1. 8-(4-fluorobenzylidene)-2-amino-4-(4-fluorophenyl)-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (Entry 7, **3g).** Cream powder, IR(KBr): 3465, 3342, 2945, 2196, 1671, 1643, 1599, 1503, 1414, 1221, 1134, 1029, 834, 803 cm⁻¹; ¹H NMR (250 MHz, CDCl₃): δ = 1.59–1.63 (m, 2H, CH₂), 1.85–2.04 (m, 2H, CH₂), 2.50–2.71 (m, 2H, CH₂), 3.95 (s, 1H, CH), 4.55 (s, 2H, NH₂), 6.82 (s, 1H, =CH), 6.99–7.07 (m, 4H, ArH), 7.18–7.28 (m, 4H, ArH); ¹³C NMR (62.9 MHz, CDCl₃): δ = 22.17, 26.96, 27.37, 42.88, 60.44, 115.03, 115.36,

TABLE 1: Synthesis of 2-amino-4*H*-pyran-3-carbonitriles 3a–q^a.

Entry	Z	R	Product	Time (min)	Yield (%) ^b	mp (°C)	Ref
1	CH ₂	H	3a	45	87	227–228	[19]
2	CH ₂	2-Cl	3b	5	90	213–214	[19]
3	CH ₂	2,4-Cl ₂	3c	15	93	238–239	[18]
4	CH ₂ -CH ₂	H	3d	10	95	228–230	[17]
5	CH ₂ -CH ₂	2-Cl	3e	10	85	237–238	[19]
6	CH ₂ -CH ₂	4-Cl	3f	15	85	215–216	[19]
7	CH ₂ -CH ₂	4-F	3g	10	90	222–224	—
8	CH ₂ -CH ₂	4-Br	3h	15	88	214–217	—
9	CH ₂ -CH ₂	4-Me	3i	60	90	161–162	[19]
10	CH ₂ -CH ₂	4-OMe	3j	10	80	220–222	—
11	CH ₂ -CH ₂	2,4-Cl ₂	3k	15	87	195–196	[18]
12	CH ₂ -CH ₂	2-Cl, 6-F	3l	10	85	233–236	—
13	CH(CH ₃)CH ₂	H	3m	20	90	199–202	—
14	CH(CH ₃)CH ₂	2-Cl	3n	25	87	198–201	—
15	CH(CH ₃)CH ₂	4-Cl	3o	15	85	208–209	—
16	CH(CH ₃)CH ₂	4-Me	3p	60	75	214–218	—
17	CH(CH ₃)CH ₂	4-OMe	3q	20	80	199–202	—

^aReaction conditions: α, α' -bis(arylidene) cycloalkanones **1** (1 mmol), malononitrile **2** (1 mmol), K₂CO₃ (0.05 mmol, 5 mol%), EtOH (10 mL), reflux.

^bIsolated yields.

SCHEME 2: Proposed mechanism.

115.50, 115.84, 119.77, 121.37, 129.35, 129.48, 130.75, 130.88, 138.61, 141.40, 158.08, 151.80. Anal. Calcd For C₂₃H₁₈F₂N₂O: C, 73.39; H, 4.82; N, 7.44; Found: C, 73.25; H, 4.79; N, 7.40.

4.1.2. 8-(4-bromobenzylidene)-2-amino-4-(4-bromophenyl)-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (Entry 8, **3h).** Cream powder, IR(KBr): 3443, 3318, 3212, 2194, 1665, 1635, 1416, 1126, 1007, 821 cm⁻¹; ¹HNMR (250 MHz, CDCl₃): δ = 1.61–1.79 (m, 2H, CH₂), 1.84–2.16 (m, 2H, CH₂), 2.49–2.94 (m, 2H, CH₂), 3.93 (s, 1H, CH), 4.56 (s, 2H, NH₂), 6.79 (s, 1H, =CH), 7.16–7.23 (m, 4H, ArH), 7.45–7.48 (m, 4H, ArH); ¹³CNMR (62.9 MHz, CDCl₃): δ = 22.11, 27.0, 27.37, 43.14,

60.03, 115.14, 120.82, 121.36, 121.80, 121.85, 129.62, 129.86, 130.80, 131.36, 131.95, 135.78, 141.51, 141.80, 158.86. Anal. Calcd For C₂₃H₁₈Br₂N₂O: C, 55.45; H, 3.64; N, 5.62; Found: C, 55.34; H, 3.60; N, 5.59.

4.1.3. 8-(4-methoxybenzylidene)-2-amino-4-(4-methoxyphenyl)-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (Entry 10, **3j).** Cream powder, IR(KBr): 3446, 3335, 2925, 2836, 2188, 1667, 1630, 1603, 1508, 1404, 1249, 1127, 1029, 831 cm⁻¹; ¹HNMR (250 MHz, CDCl₃): δ = 1.34–1.62 (m, 2H, CH₂), 1.94–1.96 (m, 2H, CH₂), 2.53–2.91 (m, 2H, CH₂), 3.79 (s, 3H, OCH₃), 3.82 (s, 3H, OCH₃), 3.91 (s, 1H, CH), 4.51 (s, 2H, NH₂), 6.81 (s, 1H, =CH), 6.85–6.91 (m, 4H,

TABLE 2: Comparison of results using K_2CO_3 with other catalyst for synthesis of 2-amino-4H-pyran-3-carbonitriles.

Entry	Catalyst	Solvent	T	Time	Yield (%)	Ref
1	NaOH/Piperidine	EtOH	MW	5–9 h	70–71	[17]
2	KF- Al_2O_3	DMF	R·T	10–14 h	68–90	[18]
3	HTMAB	H ₂ O	110°C	8 h	76–93	[19]
4	K_2CO_3	EtOH	Reflux	5–60 min	75–95	This work

ArH), 7.14–7.26 (m, 4H, ArH); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 22.29, 27.12, 27.35, 27.40, 42.76, 55.27, 60.81, 113.66, 114.10, 114.74, 122.02, 127.95, 128.92, 129.60, 129.70, 130.54, 135.10, 135.15, 141.42, 158.41, 158.81. Anal. Calcd For $C_{25}H_{24}N_2O_3$: C, 74.98; H, 6.04; N, 7.0; Found: C, 75.01; H, 6.07; N, 7.04.

4.1.4. 8-(2-chloro-6-fluorobenzylidene)-2-amino-4-(2-chloro-6-fluorophenyl)-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (Entry 12, **3l**). Cream powder, IR(KBr): 3456, 3339, 2944, 2913, 2188, 1672, 1637, 1597, 1443, 1413, 1240, 1130, 897, 780, 756 cm^{-1} ; 1H NMR (250 MHz, $CDCl_3$): δ = 1.59–1.65 (m, 2H, CH_2), 1.93–2.11 (m, 2H, CH_2), 2.25–2.86 (m, 2H, CH_2), 4.60 (s, 1H, CH), 4.89 (s, 2H, NH_2), 6.56 (s, 1H, =CH), 6.84–7.03 (m, 2H, ArH), 7.14–7.25 (m, 4H, ArH); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.80, 27.15, 27.56, 43.10, 58.01, 113.26, 113.89, 114.27, 119.60, 124.11, 124.39, 124.76, 125.10, 128.76, 128.91, 129.17, 129.33, 132.56, 133.53, 134.72, 135.05, 158.41, 160.13. Anal. Calcd For $C_{23}H_{16}Cl_2F_2N_2O$: C, 62.04; H, 3.62; N, 6.29; Found: C, 62.08; H, 3.64; N, 2.23.

4.1.5. 2-amino-8-benzylidene-6-methyl-4-phenyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (Entry 13, **3m**). Cream powder, IR(KBr): 3433, 3329, 2925, 2910, 2190, 1670, 1632, 1594, 1485, 1409, 1009 cm^{-1} ; 1H NMR (250 MHz, $CDCl_3$): δ = 0.90 (d, 3H, J = 6.2 Hz, CH_3), 1.60–2.27 (m, 4H, $2CH_2$), 2.81–2.87 (m, 1H, CH), 3.94 (s, 1H, CH), 4.49 (s, 2H, NH_2), 6.88 (s, 1H, =CH), 7.22–7.37 (m, 10H, ArH); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.0, 28.55, 34.76, 35.09, 43.09, 61.01, 114.62, 119.20, 120.0, 122.86, 126.82, 127.36, 127.90, 128.22, 128.82, 129.27, 137.01, 142.13, 143.01, 158.93. Anal. Calcd For $C_{24}H_{22}N_2O$: C, 81.33; H, 6.26; N, 7.90; Found: C, 81.40; H, 6.23; N, 7.95.

4.1.6. 8-(2-chlorobenzylidene)-2-amino-4-(2-chlorophenyl)-6-methyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (Entry 14, **3n**). Cream powder, IR(KBr): 3472, 3330, 2945, 2924, 2192, 1674, 1635, 1594, 1411, 1130, 1036, 738 cm^{-1} ; 1H NMR (250 MHz, $CDCl_3$): δ = 0.85 (d, 3H, J = 6.2 Hz, CH_3), 1.53–1.87 (m, 2H, CH_2), 1.96–2.17 (m, 2H, CH_2), 2.59–2.65 (m, 1H, CH), 4.62 (s, 1H, CH), 4.69 (s, 2H, NH_2), 6.92 (s, 1H, =CH), 7.25–7.43 (m, 8H, ArH); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 20.90, 28.81, 35.10, 35.55, 39.69, 59.24, 119.63, 120.19, 126.27, 127.61, 128.30, 128.59, 129.49, 129.77, 130.46, 130.68, 133.48, 134.08, 135.24, 135.55, 139.84, 140.89, 141.31, 159.36. Anal. Calcd For $C_{24}H_{20}Cl_2N_2O$: C, 68.09; H, 4.76; N, 6.62; Found: C, 68.0; H, 4.78; N, 6.58.

4.1.7. 8-(4-chlorobenzylidene)-2-amino-4-(4-chlorophenyl)-6-methyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (Entry 15, **3o**). Cream powder, IR(KBr): 3423, 3329, 2925, 2190, 1672, 1636, 1590, 1483, 1409, 1126, 1010, 823 cm^{-1} ; 1H NMR (250 MHz, $CDCl_3$): δ = 0.88 (d, 3H, J = 6.0 Hz, CH_3), 1.55–2.45 (m, 4H, $2CH_2$), 2.75–2.80 (m, 1H, CH), 3.93 (s, 1H, CH), 4.62 (s, 2H, NH_2), 6.82 (s, 1H, =CH), 7.14–7.34 (m, 8H, ArH); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 20.97, 28.86, 34.64, 35.07, 43.39, 60.05, 114.36, 114.48, 119.76, 121.85, 128.43, 128.98, 129.29, 130.52, 132.64, 135.34, 141.16, 141.56, 158.90, 158.99. Anal. Calcd For $C_{24}H_{20}Cl_2N_2O$: C, 68.09; H, 4.76; N, 6.62; Found: C, 68.07; H, 4.78; N, 6.64.

4.1.8. 8-(4-methylbenzylidene)-2-amino-4-(4-methoxyphenyl)-6-methyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (Entry 16, **3p**). Cream powder, IR(KBr): 3441, 3350, 2960, 2944, 2194, 1675, 1639, 1598, 1411, 1131, 809 cm^{-1} ; 1H NMR (250 MHz, $CDCl_3$): δ = 0.91 (d, 3H, J = 6.7 Hz, CH_3), 1.64–2.08 (m, 4H, $2CH_2$), 2.34 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 2.81–2.87 (m, 1H, CH), 3.91 (s, 1H, CH), 4.50 (s, 2H, NH_2), 6.83 (s, 1H, =CH), 7.12–7.32 (m, 8H, ArH); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.06, 21.14, 21.24, 29.01, 35.24, 36.11, 43.51, 60.68, 114.28, 114.37, 122.49, 127.83, 128.95, 129.22, 129.45, 134.13, 136.63, 136.97, 139.73, 140.13, 141.19, 158.79. Anal. Calcd For $C_{26}H_{26}N_2O$: C, 81.64; H, 6.85; N, 7.32; Found: C, 81.57; H, 6.86; N, 7.34.

4.1.9. 8-(4-methoxybenzylidene)-2-amino-4-(4-methoxyphenyl)-6-methyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (Entry 17, **3q**). Cream powder, IR(KBr): 3461, 3323, 2924, 2846, 2194, 1671, 1635, 1593, 1417, 1124, 845 cm^{-1} ; 1H NMR (250 MHz, $CDCl_3$): δ = 0.88 (d, 3H, J = 5.7 Hz, CH_3), 1.60–2.17 (m, 4H, $2CH_2$), 2.81–2.87 (m, 1H, CH), 3.80 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 3.90 (s, 1H, CH), 4.51 (s, 2H, NH_2), 6.81 (s, 1H, =CH), 6.85–6.92 (m, 4H, ArH), 7.13–7.26 (m, 4H, ArH); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.08, 28.50, 28.97, 35.25, 36.06, 43.09, 55.28, 60.83, 113.68, 114.09, 120, 122.10, 127.31, 128.40, 128.95, 129.56, 130.56, 135.10, 141.10, 158.42, 159.24, 159.83. Anal. Calcd For $C_{26}H_{26}N_2O_3$: C, 75.34; H, 6.32; N, 6.76; Found: C, 75.37; H, 6.28; N, 6.73.

References

- [1] R. V. A. Orru and M. Greef, "Recent advances in solution-phase multicomponent methodology for the synthesis of heterocyclic compounds," *Synthesis*, no. 10, pp. 1471–1499, 2003.

- [2] A. Domling, "Recent developments in isocyanide based multi-component reactions in applied chemistry," *Chemical Reviews*, vol. 106, no. 1, pp. 17–89, 2006.
- [3] G. R. Green, J. M. Evans, and A. K. Vong, "Pyrans and their benzo derivatives synthesis," in *Comprehensive Heterocyclic Chemistry II*, A. R. Katritzky, C. W. Rees, and E. F. V. Scriven, Eds., vol. 5, p. 469, Pergamon Press, Oxford, UK, 1995.
- [4] F. M. Abdelrazek, P. Metz, O. Kataeva, A. Jager, and S. F. El-Mahrouky, "Synthesis and molluscicidal activity of new chromene and pyrano[2,3-*c*]pyrazole derivatives," *Archiv der Pharmazie*, vol. 340, no. 10, pp. 543–548, 2007.
- [5] L. Bonsignore, G. Loy, D. Secci, and A. Calignano, "Synthesis and pharmacological activity of 2-oxo-(2*H*) 1-benzopyran-3-carboxamide derivatives," *European Journal of Medicinal Chemistry*, vol. 28, no. 6, pp. 517–520, 1993.
- [6] E. C. Witte, P. Neubert, and A. Roesch, "7-(Piperazinyl-propoxy)-2*H*-1-benzo-pyran-2-ones. Ger Offen DE 3427985," *Chemical Abstracts*, vol. 104, no. 224915f, 1986.
- [7] M. Lei, L. Ma, and L. Hu, "A green, efficient, and rapid procedure for the synthesis of 2-amino-3-cyano-1,4,5,6-tetrahydropyrano[3,2-*c*]quinolin-5-one derivatives catalyzed by ammonium acetate," *Tetrahedron Letters*, vol. 52, no. 20, pp. 2597–2600, 2011.
- [8] A. H. Abdel-Fattah, A. M. Hesien, S. A. Metwally, and M. H. Elnagdi, "The Reaction of Ethyl 6-Amino-5-Cyano-4-aryl-2-methyl-4*H*-pyran-3-Carboxylate with Nucleophilic Reagents," *Liebigs Annalen der Chemie*, pp. 585–588, 1989.
- [9] J. M. Quintela, C. Peinador, and M. J. Moreira, "A novel synthesis of pyrano[2,3-*d*]pyrimidine derivatives," *Tetrahedron*, vol. 51, no. 20, pp. 5901–5912, 1995.
- [10] S. Srivastava, S. Batra, and A. P. Bhaduri, "A facile acid catalysed ring transformation of 4*H*-pyrans to 1,2,3,4-tetrahydropyridin-2-ones and 3,4-dihydronaphtho[1, 2-*b*]-pyran-2(*H*)-ones," *Indian Journal of Chemistry*, vol. 35, no. 6, pp. 602–604, 1996.
- [11] S. Hatakeyama, N. Ochi, H. Numata, and S. A. Takano, "new route to substituted 3-methoxycarbonyldihydropyrans; enantioselective synthesis of (–)-methyl elenolate," *Journal of the Chemical Society, Chemical Communications*, no. 17, pp. 1202–1204, 1988.
- [12] K. Singh, J. Singh, and H. Singh, "A synthetic entry into fused pyran derivatives through carbon transfer reactions of 1,3-oxazinanes and oxazolidines with carbon nucleophiles," *Tetrahedron*, vol. 52, no. 45, pp. 14273–14280, 1996.
- [13] D. Armesto, W. M. Horspool, N. Martin, A. Ramos, and C. Seoane, "Synthesis of cyclobutenes by the novel photochemical ring contraction of 4-substituted 2-amino-3,5-dicyano-6-phenyl-4*H*-pyrans," *Journal of Organic Chemistry*, vol. 54, no. 13, pp. 3069–3072, 1989.
- [14] G. P. Ellis, "Chemistry of heterocyclic compounds: chromenes, chromanones, and chromones," in *The Chemistry of Heterocyclic Compounds*, A. Weissberger and E. C. Taylor, Eds., vol. 31, p. 13, Wiley, New York, NY, USA, 1977.
- [15] D. Kumar, V. B. Reddy, S. Sharad, U. Dube, and K. A. Suman, "A facile one-pot green synthesis and antibacterial activity of 2-amino-4*H*-pyrans and 2-amino-5-oxo-5,6,7,8-tetrahydro-4*H*-chromenes," *European Journal of Medicinal Chemistry*, vol. 44, no. 9, pp. 3805–3809, 2009.
- [16] N. S. Babu, N. Pasha, K. T. V. Rao, P. S. S. Prasad, and N. A. Lingaiah, "A heterogeneous strong basic Mg/La mixed oxide catalyst for efficient synthesis of polyfunctionalized pyrans," *Tetrahedron Letters*, vol. 49, no. 17, pp. 2730–2733, 2008.
- [17] J. F. Zhou, "One-step synthesis of pyridine and 4*H*-pyran derivatives from bisarylidencyclohexanone and malononitrile under microwave irradiation," *Synthetic Communications*, vol. 33, no. 1, pp. 99–103, 2003.
- [18] X. S. Wang, D. Q. Shi, Y. Du, Y. Zhou, and S. J. Tu, "Synthesis of 2-aminopyran derivatives and 3-arylpropionitrile derivatives catalyzed by $\text{KF/Al}_2\text{O}_3$," *Synthetic Communications*, vol. 34, no. 8, pp. 1425–1432, 2004.
- [19] T. S. Jin, L. B. Liu, Y. Zhao, and T. S. Li, "Clean, one-pot synthesis of 4*H*-pyran derivatives catalyzed by hexadecyltrimethyl ammonium bromide in aqueous media," *Synthetic Communications*, vol. 35, no. 14, pp. 1859–1863, 2005.
- [20] M. Misra, R. Sharma, R. Kant, P. R. Maulik, and R. P. Tripathi, "One pot protecting group free synthesis of multifunctional biphenyl methyl- $\text{C}-\beta$ -*D*-glycosides in aqueous medium," *Tetrahedron Letters*, vol. 67, no. 4, pp. 740–748, 2011.
- [21] L. Shen, S. Cao, J. Wu et al., " K_2CO_3 -assisted one-pot sequential synthesis of 2-trifluoromethyl-6-difluoromethylpyridine-3,5-dicarboxylates under solvent-free conditions," *Tetrahedron Letters*, vol. 51, no. 37, pp. 4866–4869, 2010.
- [22] Z. Karimi-Jaberi, S. Z. Abbasi, B. Pooladian, and M. Jokar, "Efficient, one-pot synthesis of tetrahydrobenzo[*a*]xanthene-11-ones and dibenzo[*a, j*]xanthenes using trichloroacetic acid as a solid heterogeneous catalyst under solvent-free conditions," *E-Journal of Chemistry*, vol. 8, no. 4, pp. 1895–1899, 2011.
- [23] Z. Karimi-Jaberi and M. Amiri, "One-pot synthesis of α -Aminophosphonates catalyzed by boric acid at room temperature," *Heteroatom Chemistry*, vol. 21, no. 2, pp. 96–98, 2010.
- [24] Z. Karimi-Jaberi, M. Amiri, and N. Sadeghi, "Sodium dihydrogen phosphate as an efficient catalyst for one-pot, three-component synthesis of α -aminophosphonates under solvent-free conditions at room temperature," *Synthetic Communications*, vol. 40, no. 19, pp. 2948–2953, 2010.
- [25] Z. Karimi-Jaberi and B. Pooladian, "A facile synthesis of α, α' -bis(substituted benzylidene)cycloalkanones catalyzed by p-TSA under solvent-free conditions," *Green Chemistry Letters and Reviews*. In press.