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# FAST, SOLVENT-FREE, MICROWAVE-PROMOTED FRIEDLÄNDER ANNULATION WITH A REUSABLE SOLID CATALYST

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A fast, solvent-free method is described for the synthesis of substituted quinoline derivatives via Friedländer cyclization, employing a reusable solid catalyst (silica-propylsulfonic acid). Although it worked best under microwave irradiation (with generally more than 90% isolated yields in 30 min), the reaction was also feasible under conventional heating (with fair to good yields in about 5 h).

Keywords: Friedländer synthesis; microwaves; quinoline; solid catalyst; solvent-free

## INTRODUCTION

In the Friedländer synthesis, a classic example of heterocyclic chemistry, o-aminoaryl aldehydes or ketones typically react with enolizable carbonyl compounds in the presence of a Brønsted or Lewis acid catalyst. After an initial amino-ketone condensation, the intermediate product undergoes a base- or acid-catalyzed cyclo-condensation to afford a quinoline derivative. Unfortunately, the yield can be lowered by self-condensation of o-aminoaryl carbonyl compounds.

Quinoline derivatives are widespread in natural products[1,2] and, owing to their wide range of biological activities, play pivotal roles in medicinal chemistry.[3–6] They have also found very interesting applications in polymer chemistry[7] and electronics.[8–10]

In the past decade, several improved versions of the Friedländer synthesis have appeared in the literature,[11–15] proof that interest in this old cyclization, dating from 1882,[16] is far from waning. Just in the past two years, more than one hundred peer-reviewed papers covered some useful application of it. The best protocols,

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benefiting from microwave (MW) irradiation, proved more efficient than those carried out under conventional heating.[17–19] A wide variety of newer catalysts have also been explored, including p-toluenesulfonic acid,[20] molecular iodine,[21] neodymium(III) nitrate hexahydrate,[22] and a group of amino compounds.[23] Of particular interest are recyclable catalysts such as silver phosphotungstate,[24] a Lewis acid–surfactant combined catalyst,[25] and an HCl-catalyzed Friedländer reaction carried out in plain water without any added metal catalyst and phase transfer catalyst (PCT).[26] Recently Das et al. described the use of solid acid catalysts such as $NaHSO_4$ $SiO_2$, $H_2SO_4$ $SiO_2$, Amberlyst-15, and $HClO_4$ $SiO_2$ working under reflux in ethanol.[27] The $HClO_4$ $SiO_2$-catalyzed Friedländer annulation had been previously introduced by Narasimhulu et al. working under reflux in acetonitrile.[28]

In the present communication, we report a new solvent-free protocol by which the Friedländer synthesis is promoted, either under conventional heating or under MW irradiation, by a solid catalyst, namely a derivatized silica bearing alkylsulfonic acid groups.

According to the guidelines of green chemistry, we aimed to achieve a fast, efficient, solventless procedure using a recyclable catalyst. It is well documented[29] that the use of solid acids as catalysts, besides simplifying the isolation of products, often allows reactions to be run under milder conditions and improves their selectivity.

## RESULTS AND DISCUSSION

The present preparation of quinoline derivatives by Friedländer annulation draws on our previous experience in developing more efficient and greener synthetic protocols exploiting solid reusable catalysts[30,31] and MW irradiation.[32] We started by preparing the solid catalyst, propylsulfonic silica (PSS) (Fig. 1), by the published procedure.[33,34]

Preliminary experiments showed that cyclization occurred under conventional heating conditions, but reactions were quite sluggish with prolonged reaction time. Although we monitored the temperature in the MW oven with an infrared (IR) pyrometer, under solvent-free conditions it is very likely that localized hot spots did reach somewhat greater temperatures, which can account for such a difference in the results. Whereas the (scientific) debate on the existence of nonthermal MW effects seems to be closed,[35] there are no doubts that dielectric heating does optimize heat transfer. Table 1 reports reaction times and yields under MW as well as conductive heating.

With the exception of entry 7 (A and B), all the products listed in Table 1 are known, and spectroscopic data are available in the literature.[36–42] With solid carbonyl compounds such as dimedone and 4-hydroxycoumarin (entries 3/10 and 7, respectively), longer times were required even under MW. With 4-hydroxycoumarin,

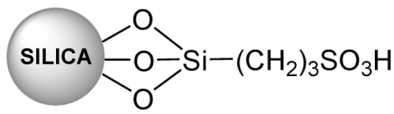
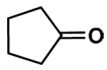
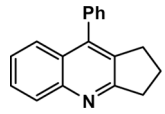
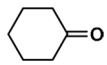
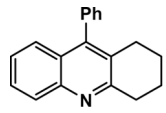
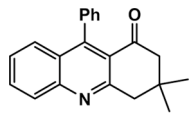
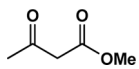
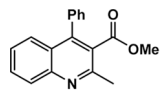
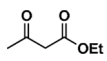
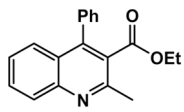
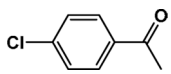
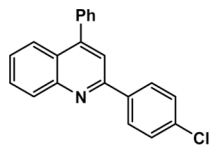
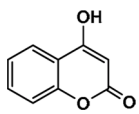
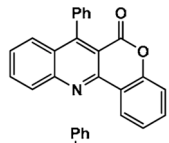
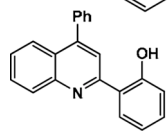
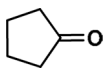
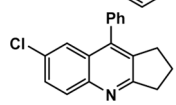
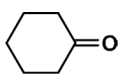
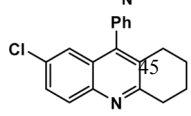


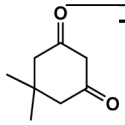
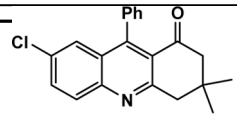
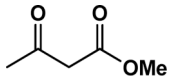
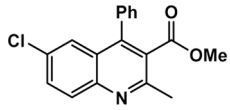
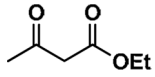
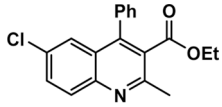
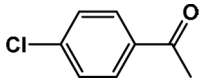
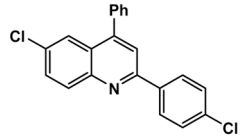

Figure 1. Structure of propylsulfonic silica (PSS).

Table 1. MW vs. conventional heating: reaction times and yields

| Entry | Reagent | Product | MW irradiation Time (min) | MW irradiation Yield (%) | Conventional heating Time (h) | Conventional heating Yield (%) |
|---|---|---|---|---|---|---|
| 1 |  |  [27] | 45 | 88 | 5 | 80 |
| 2 |  |  [37] | 30 | 61 | 5 | |
| 24 | | | | | | |
| 3 | |  [37] | 210 | 92 | 5 | 80 |
| 4 |  |  [27] | 30 | 90 | 5 | |
| 83 | | | | | | |
| 5 |  |  [37] | 30 | 91 | 5 | 84 |
| 6 |  |  [42] | 90 | 92 | 5 | 12 |
| 7 |  |  A | 60 | 22 | 5 | 13 |
| | |  B | 60 | 36 | 5 | 20 |
| 8 |  |  [39] | 45 | 89 | 5 | 81 |
| 9 |  |  [39] | 45 | 70 | 5 | 22 |

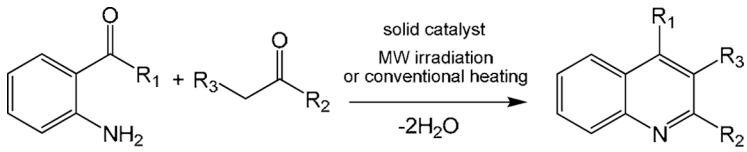
(Continued )

Table 1. Continued

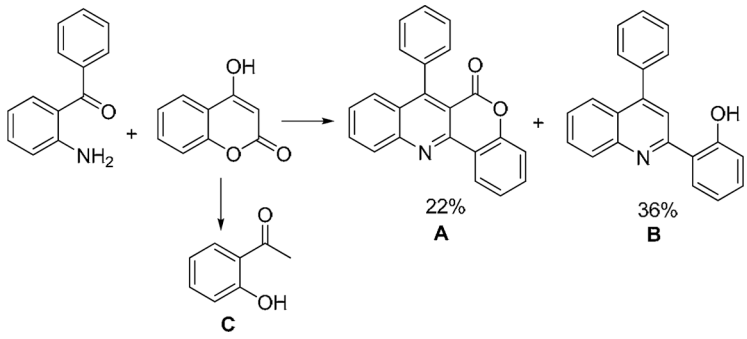
| Entry | Reagent | Product | MW irradiation Time (min) | MW irradiation Yield (%) | Conventional heating Time (h) | Conventional heating Yield (%) |
|---|---|---|---|---|---|---|
| 10 |  |  [38] | 210 | 89 | 5 | 75 |
| 11 81 |  |  [40] | 30 | 86 | 5 | |
| 12 85 |  |  [39] | 30 | 93 | 5 | |
| 13 13 |  |  [36] | 90 | 90 | 5 | |

a masked b-ketoester (Scheme 2), the reaction afforded, alongside the expected tetracyclic derivative (A), the product of lactone hydrolysis–decarboxylation (B). The addition of activated 4-Å-molecular-sieved powder to the reacting mixture increased the yield of A (40%) while dramatically reducing the yield of B (11%). o-Hydroxyacetophenone (C) was the main product (about 50%) generated by the partial degradation of excess 4-hydroxycoumarin.

Results reported in Table 2 indicate that the reaction with cyclopentanone, cyclohexanone and methyl acetoacetate occurred even in the absence of catalyst. A study carried out with the last-mentioned substrate demonstrated that the catalyst could be filtered off and reused to afford comparable product yields (90% ! 87% ! 85%).




Scheme 1. General synthetic scheme.




Scheme 2. Reaction of o-aminobenzophenone with 4-hydroxycoumarin.

## EXPERIMENTAL

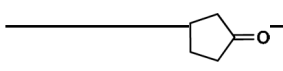
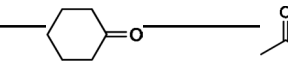
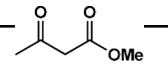
### Preparation of 3-Mercaptopropyl Silica (MPS)

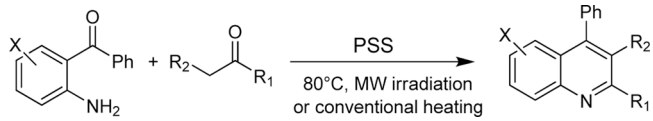
Silica gel (average pore diameter 60 Å) was activated by refluxing in concentrated hydrochloric acid (6 M) for 24 h, then thoroughly washed with distilled water and dried under vacuum before undergoing chemical surface modification. This was carried out by refluxing the activated silica gel (10 g) with 3-mercaptopropyltrimethoxysilane (MPTMS, 5 mmol) in dry toluene for 18 h. The solid product was isolated by centrifugation (2000 rpm), washed with hot toluene (three times), and oven-dried at 110 C overnight.

### Preparation of Propylsulfonic Silica (PSS)

The thiol groups of the modified silica (MPS, 5 g) were oxidized with 30% $H_2O_2$ (50 ml), to which two drops of concentrated $H_2SO_4$ in 15 ml methanol were added. After the mixture had stood 12 h at room temperature, the solid was isolated by centrifugation (2000 rpm) and washed three times with 50-ml portions of distilled water. To ensure that the sulfonic acid groups were fully protonated, the solid was suspended for 4 h in 10 wt% aqueous $H_2SO_4$ (30 ml), centrifuged off, thoroughly

Table 2. Reaction times and yields in the absence of catalyst or using recycled catalyst

| | |  | |  | |  | |
|---|---|---|---|---|---|---|---|
| Conditions | Catalyst | Time (h) | Yield (%) | Time (h) | Yield (%) | Time (h) | Yield (%) |
| MW | None | 2 | 69 | 2 | 26 | 0.5 | 63 |
| Conventional heating | None | 5 | 48 | 5 | 7 | 5 | 17 |
| MW | Sandard | — | — | — | — | 0.5 | 90 |
| MW | 1st recycle | — | — | — | — | 0.5 | 87 |
| MW | 2nd recycle | — | — | — | — | 0.5 | 85 |




Scheme 3. Operative conditions.

washed with distilled water (until the pH of washing was close to neutrality), and dried at 60–70 C overnight. About 5 g of a buff-colored solid was recovered, to be directly used as catalyst in the reactions described next. Its full characterization followed methods reported in the literature.[33,34]

## General Reaction Conditions

Under Conventional Heating. A well-blended mixture of o-aminobenzophenone (0.5 mmol), the ketone (1.5 mmol), and PSS catalyst (100 mg) was poured into a Pyrex tube that was stoppered and heated at 80 C in an electric oven. After o-aminobenzophenone was shown by thin-layer chromatography (TLC) to have disappeared, the reacted mixture was cooled and purified by column chromatography on silica gel (Merck, 100–200 mesh, petroleum ether–EtOAc, 9:1) to afford the pure quinoline derivative.

Under MW. A well-blended mixture of o-aminobenzophenone (0.5 mmol), the ketone (1.5 mmol), and PSS catalyst (100 mg) was poured into a stoppered Pyrex tube and irradiated with MW (80 C, 200 W) for the appropriate time (see Table 1). After o-aminobenzophenone was shown by TLC to have disappeared, the reacted mixture was cooled and purified by column chromatography on silica gel (Merck, 100–200 mesh, petroleum ether–EtOAc, 9:1) to afford the pure quinoline derivative.

In either version, when catalyst recovery was desired, the reacted mixture was treated with EtOAc (15 ml), run through a 10-mm sintered glass filter, and washed with EtOAc (5 ml 3 times) to recover the clean catalyst. This was activated at 60 C prior to reuse.

Reaction times and results are listed in Tables 1 and 2.

## Data

7-Phenyl-6H-chromen[4,3-*b*]quinolin-6-one (7a). Yellow powder; $R_f$ ¼ 0.6 (PE=EtOAc 6:4). $^1$H NMR (300 MHz, $CDCl_3$): d ¼ 8.15–8.10 (overlap, 2H, H-4,11), 7.86 (t, J ¼ 6.9 Hz, 1H, H-10), 7.75 (t, J ¼ 6.9 Hz, 1H, H-3), 7.61–7.55 (overlap, 5H, H-1,8, Ph), 7.46 (t, J ¼ 6.6, 1H, H-9), 7.36–7.29 (overlap, 3H, H-2, Ph). $^{13}$C NMR (75 MHz, $CDCl_3$): d ¼ 178.2, 157.97, 155.75, 155.48, 148.75, 137.16, 135.85, 133.31, 128.42, 128.27, 128.14, 128.03, 127.28, 127.16, 126.27, 124.36, 121.99, 118.03, 113.52. FT-IR (KBr): t ¼ 1670, 1612, 1576, 1556, 1466, 1375, 1358, 1330, 1325, 1246, 1115, 837, 752, 719, 108. MS (ESI) m=z (%) ¼ 324 (M þ 1).

2-(4-Phenylquinolin-2-yl)phenol (7b). Pale yellow powder. $R_f$ ¼ 0.4 (PE=EtOAc 9:1). $^1$H NMR (300 MHz, $CDCl_3$): d ¼ 8.11 (d, J ¼ 8.4 Hz, 1 H, H-8), 8.0–7.95 (overlap, 2H, 3,6$^0$), 7. 90 (d, J ¼ 8.4 Hz, 1H, H-5), 7.75 (t, J ¼ 8.1 Hz, 1H,

H-7), 7.60–7.55 (overlap, 5H, Ph), 7.52 (t, J ¼ 7.2 Hz, 1H, H-6), 7.37 (t, J ¼ 7.2 Hz, 1H, H-5′), 7.10 (d, J ¼ 8.1 Hz, 1H, H-4′), 6.94 (t, J ¼ 7.2 Hz, 1H, H-3′). $^{13}$C NMR (75 MHz, $CDCl_3$): d ¼ 161.24, 157.57, 150.34, 145.4, 138.06, 132.19, 130.47, 129.60, 128.89, 128.85, 128.11, 127.10, 126.82, 125.99, 125.48, 119.11, 118.87, 118.78, 117.71. FT-IR (KBr): t ¼ 3485.2, 1605.0, 1589.5, 1549.0, 1508.5, 1493.1, 1466.1, 1213.4, 1122.7, 1074.5, 873.9, 765.8, 704.1 cm $^{-1}$. MS (CI) m=z (%) ¼ 298 (M þ 1).

## CONCLUSION

Our solvent-free protocol for Friedländer's annulation is simple, fast, and efficient. It employs a catalyst that is easily recovered by filtration and can be reused without appreciable loss of activity. When carried out under MW, the reaction was faster and gave somewhat better yields.

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