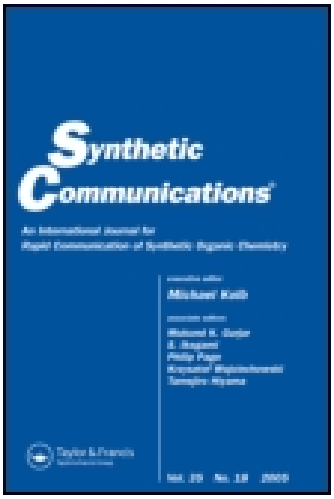

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# ONE-POT SYNTHESIS OF α-MONOSUBSTITUTED PYRIDINIUMS FROM CORRESPONDING PYRYLIUM SALTS

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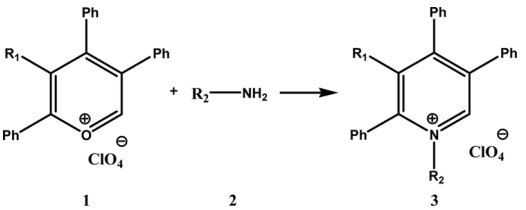
## GRAPHICAL ABSTRACT




**Abstract** α-*monosubstituted pyridiniums were readily prepared by the one-pot reaction of their corresponding pyrylium salts and primary amines. This result shows that such kind of pyridiniums can be prepared* via *this route. It was proved that the number of phenyl groups at the pyrylium ring had a crucial effect on this one-pot synthetic route.*

**Keywords** α-Monosubstituted pyridiniums; one-pot synthesis; primary amines; pyrylium salts



## INTRODUCTION

Pyridiniums have wide applications in many fields, including chemistry, biology, and materials science.[1] Accordingly, their synthesis is always the focus for many organic chemists. Until now, several synthetic routes to various pyridiniums have been developed, including the well-known Menschutkin reaction and Zincke reaction.[2] Additionally, the reaction of pyrylium salts with primary amines is an important and widely used synthetic method to corresponding pyridiniums, which allows a wide variation of pyrylium salts and primary amine structures.[3]

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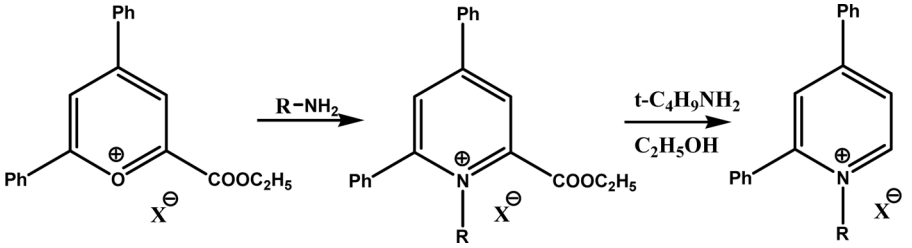
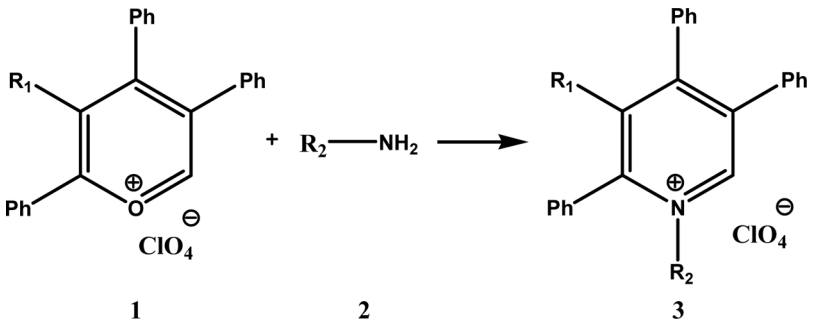



**Scheme 1.** Complex two-step synthetic route to α-monosubstituted pyridiniums.

In this field, Katritzky and coworkers did systematic studies of the factors affecting the conversion of pyrylium to pyridinium salts and the detailed mechanism kinetics.[4] However, when they tried the reaction of α-monosubstituted pyrylium salts (2,4-diphenylsubstituted pyrylium salt) with primary amines, only ring-opened products were formed and no expected α-monosubstituted pyridiniums were obtained.[5] Accordingly, they concluded that such kind of pyridiniums could not be prepared directly from their pyrylium precursors and successful conversion must require the presence of α,α′-substituents simultaneously.[6] As a result, to prepare α-monosubstituted pyridiniums, a more complex synthetic route will have to be utilized (Scheme 1).

In our studies on pyrylium salts, we have successfully prepared two novel α-monosubstituted pyrylium salts, namely 2,4,5-triphenyl pyrylium salts and 2,3,4,5-tetraphenyl pyrylium salts, from aerobic oxidation of multiphenyl substituted cyclopentadienes.[7] To test the possibility of converting them to their corresponding α-unsubstituted pyridiniums, we tried to react them with various primary amines (Scheme 2). Surprisingly, in our case, α-monosubstituted pyridiniums were obtained smoothly in excellent yields, which is in contrast to Katritzky's conclusion.[5] The biggest difference between our case and Katritzky's case is the number of phenyl groups on the pyrylium ring, indicating some positively steric and electronic effects for the transformation we reported here. Detailed studies of this issue are ongoing in our laboratory. Anyway, the realization of this transformation provided an efficient one-pot synthetic route to α-monosubstituted pyridiniums.

All results, including primary amines selected, reaction times, and the yields of pyridiniums, are summarized in Table 1.




**Scheme 2.** One-pot synthetic route to α-monosubstituted pyridiniums from pyrylium precursors.

**Table 1.** One-pot synthesis of α-monosubstituted pyridiniums from pyrylium precursors and various primary amines

| Entry | $R_1$ | $R_2$ | Time (h) | Product | Yield (%) |
|---|---|---|---|---|---|
| 1 | H | p-$(NH_2)C_6H_4$ | 6 | 3a | 89 |
| 2 | H | p-[4-$(NH_2)C_6H_4$]$C_6H_4$ | 18 | 3b | 87 |
| 3 | H | p-$(Cl)C_6H_4$ | 4 | 3c | 74 |
| 4 | H | p-$(Br)C_6H_4$ | 5 | 3d | 70 |
| 5 | H | p-$C_5H_3N$ | 4.5 | 3e | 88 |
| 6 | $C_6H_5$ | p-$(NH_2)C_6H_4$ | 8 | 3f | 86 |
| 7 | $C_6H_5$ | p-[4-$(NH_2)C_6H_4$]$C_6H_4$ | 24 | 3g | 81 |
| 8 | $C_6H_5$ | p-$(Cl)C_6H_4$ | 6 | 3h | 70 |
| 9 | $C_6H_5$ | p-$(Br)C_6H_4$ | 9 | 3i | 68 |
| 10 | $C_6H_5$ | p-$C_5H_3N$ | 7.5 | 3j | 84 |



We should mention that this synthetic route shows a wide variation of primary amine structures from electron-withdrawing halogen substituents to electron-donating pyridinyl and aminophenyl substituents. Most of investigated primary amines gave rather satisfactory yields just as shown in Table 1. More important, all of the selected primary amines have been modified with various functional groups to be readily transferred into other functional compounds. We can do coupling reaction with halogen substituents,[8] condensation with amino moiety,[9] and coordination with metal using pyridine fragment.[10]

In summary, 10 α-monosubstituted pyridiniums modified with reactive amino-, pyridinyl-, and halogen functional groups were prepared by one-pot reactions of pyrylium precursors with primary amines. This route was thought to be impossible and our result proved otherwise. In fact, the number of phenyl groups on the pyrylium ring played a crucial role in this one-pot transformation. Undoubtedly, the realization of this one-pot transformation provided a more efficient and mild synthetic route to α-monosubstituted pyridiniums.

## EXPERIMENTAL

Infrared (IR) spectra were recorded on a Jasco Fourier transform (FT)–IR-460 Plus spectrometer. $^1H$ and $^{13}C$ NMR spectra were performed on a Varian Inova 400 spectrometer using tetramethylsilane (TMS) as internal standard. API mass spectra were recorded on HP1100 high performance liquid chromatography/mass selective detector (HPLC/MSD) spectrometer. High-resolution mass spectra (HRMS) electrospray ionization (ESI) was carried out on a UPLC-Q-ToF MS spectrometer. Elemental analyses were meaured on a Vario EL III elemental analyzer.

2,4,5-Triphenylpyrylium and 2,3,4,5-tetraphenylpyrylium perchlorate were synthesized according to our previously reported paper.[7b] Other chemical reagents were used as received without further purification.

### General Procedure

A solution of pyrylium perchlorate **1** (0.49 mmol), primary amine **2** (0.59 mmol), and triethylamine (50 mg, 0.49 mmol) in 15 mL dichloromethane was

stirred at room temperature. After 20 min, acetic acid (59 mg, 0.98 mmol) was added into this solution. When thin-layer chromatography (TLC) showed the complete conversion of **1**, dichloromethane was concentrated under reduced pressure to 2–3 mL. To this solution, 30 mL diethyl ether was poured and the precipitate was formed. The filtered precipitate was washed by diethyl ether ($3 \times 10$ mL) and dried to give pure target α-monosubstituted pyridiniums.

### Spectral Data

**1-(4-Aminophenyl)-2,4,5-triphenylpyridinium perchlorate (3a).** IR (KBr) *v*: 3468, 3377 ($NH_2$), 1623 (C=N), 1092, 621 ($ClO_4^-$) $cm^{-1}$; $^1H$ NMR (400 MHz, $CD_3CN$): δ = 8.72 (s, 1H, PyH), 8.09 (s, 1H, PyH), 7.31–7.56 (m, 15H, ArH), 7.11 (d, 2H, $J = 8.8$ Hz, ArH), 6.59 (d, 2H, $J = 8.8$ Hz, ArH), 4.64 (s, 2H, $NH_2$); $^{13}C$ NMR (100 MHz, $CD_3CN$): δ = 157.9, 154.9, 151.1, 147.8, 139.6, 136.45, 134.8, 133.2, 131.9, 131.8, 131.6, 131.2, 130.8, 130.5, 130.2, 129.8, 129.7, 129.6, 128.4, 114.5; MS (API-ES) *m/z*: 399.1 ($M^+$); HRMS (ESI) calcd. for $C_{29}H_{23}N_2$ ($M^+$) 399.1816; found 399.1876.; Anal. calcd. for $C_{29}H_{23}N_2O_4Cl$: C, 69.81; H, 4.65; N, 5.61. Found: C, 69.71; H, 4.53; N, 5.78.

**1-(4′-Amino-4-biphenylyl)-2,4,5-triphenylpyridinium perchlorate (3b).** IR (KBr) *v*: 3464, 3368 ($NH_2$), 1623 (C=N), 1095, 623 ($ClO_4^-$) $cm^{-1}$; $^1H$ NMR (400 MHz, $CD_3CN$): δ = 8.83 (s, 1H, PyH), 8.18 (s, 1H, PyH), 7.63 (d, 2H, $J = 8.4$ Hz, ArH), 7.30–7.54 (m, 19H, ArH), 6.70 (d, 2H, $J = 8.4$ Hz, ArH), 4.38 (s, 2H, $NH_2$); $^{13}C$ NMR (100 MHz, $CD_3CN$): δ = 158.7, 154.9, 149.9, 147.6, 144.4, 140.3, 139.8, 136.4, 134.7, 132.8, 132.0, 131.9, 131.6, 131.4, 130.9, 130.8, 130.7, 130.6, 130.3, 129.9, 129.8, 129.5, 129.2, 129.1, 128.8, 128.5, 127.9, 127.7, 127.4, 127.1, 116.1, 115.7; MS (API-ES) *m/z*: 475.1 ($M^+$); HRMS (ESI) calcd. for $C_{35}H_{27}N_2$ ($M^+$) 475.2174; found 475.2182. Anal. calcd. for $C_{35}H_{27}N_2O_4Cl$: C, 73.10; H, 4.73; N, 4.87. Found: C, 72.92; H, 4.88; N, 4.72.

**1-(4-Chlorophenyl)-2,4,5-triphenylpyridinium perchlorate (3c).** IR (KBr) *v*: 1621 (C=N), 1016 (Ar-Cl), 1095, 620 ($ClO_4^-$) $cm^{-1}$; $^1H$ NMR (400 MHz, $CD_3CN$): δ = 8.78 (s, 1H, PyH), 8.17 (s, 1H, PyH), 7.30–7.56 (m, 19H, ArH); $^{13}C$ NMR (100 MHz, $CD_3CN$): δ = 159.4, 155.0, 147.5, 141.2, 140.0, 137.5, 136.4, 134.8, 132.5, 132.1, 132.0, 131.5, 131.1, 131.0, 130.9, 130.7, 130.5, 130.0, 129.9, 129.6; MS (API-ES) *m/z*: 418.0 ($M^+$); HRMS (ESI) calcd. for $C_{29}H_{21}NCl$ ($M^+$) 418.1363; found 418.1372. Anal. calcd. for $C_{29}H_{21}NO_4Cl_2$: C, 67.19; H, 4.08; N, 2.70. Found: C, 67.42; H, 3.92; N, 2.84.

**1-(4-Bromophenyl)-2,4,5-triphenylpyridinium perchlorate (3d).** IR (KBr) *v*: 1623 (C=N), 1013 (Ar-Br), 1096, 621 ($ClO_4^-$) $cm^{-1}$; $^1H$ NMR (400 MHz, $CD_3CN$): δ = 8.781 (s, 1H, PyH), 8.164 (s, 1H, PyH), 7.24–7.70 (m, 19H, ArH); $^{13}C$ NMR (100 MHz, $CD_3CN$): δ = 159.0, 154.8, 147.3, 141.5, 139.7, 136.2, 134.5, 133.8, 132.3, 132.0, 131.5, 131.0, 130.8, 130.6, 130.4, 130.0, 129.9, 129.8, 129.6, 125.5; MS (API-ES) *m/z*: 464.0 ($M^+$); HRMS (ESI) calcd. for $C_{29}H_{21}NBr$ ($M^+$) 462.0857; found 462.0873. Anal. calcd. for $C_{29}H_{21}NO_4ClBr$: C, 61.88; H, 3.76; N, 2.49. Found: C,62.05; H, 3.62; N, 2.35.

**1-(4-Pyridyl)-2,4,5-triphenylpyridinium perchlorate (3e).** IR (KBr) *v*: 1626 (C=N), 1578, 1521, 1483, 1454 ($C_5H_4N$), 1096, 621 ($ClO_4^-$) $cm^{-1}$; $^1H$ NMR (400 MHz, $CD_3CN$): $\delta = 8.79$ (s, 1H, PyH), 8.71 (d, 2H, $J = 6.0$ Hz, PyH), 8.22 (s, 1H, PyH), 7.38–7.58 (m, 17H, ArH & PyH); $^{13}C$ NMR (100 MHz, $CD_3CN$): $\delta = 159.8$, 154.6, 152.7, 149.3, 147.0, 140.2, 136.4, 134.7, 132.3, 132.2, 132.1, 131.6, 131.2, 131.0, 130.7, 130.5, 130.0, 129.9, 122.5; MS (API-ES) *m/z*: 385.1 ($M^+$); HRMS (ESI) calcd. for $C_{28}H_{21}N_2$ ($M^+$) 385.1705; found 385.1722. Anal. calcd. for $C_{28}H_{21}N_2O_4Cl$: C, 69.35; H, 4.36; N, 5.78. Found: C, 69.12; H, 4.48; N, 5.92.

**1-(4-Aminophenyl)-2,3,4,5-tetraphenylpyridinium perchlorate (3f).** IR (KBr) *v*: 3463, 3370 ($NH_2$), 1628 (C=N), 1089, 622 ($ClO_4^-$) $cm^{-1}$; $^1H$ NMR (400 MHz, $CD_3CN$): $\delta = 8.82$ (s, 1H, PyH), 6.78–7.45 (m, 22H, ArH), 6.52 (d, 2H, $J = 8.8$ Hz, ArH), 4.55 (s, 2H, $NH_2$); $^{13}C$ NMR (100 MHz, $CD_3CN$): $\delta = 158.6$, 155.2, 150.8, 145.9, 143.3, 141.1, 136.3, 135.9, 135.3, 132.8, 131.5, 131.4, 130.9, 130.5, 130.3, 129.9, 129.5, 129.3, 129.1, 128.7, 128.5, 128.4, 117.9, 114.5; MS (API-ES) *m/z*: 475.2 ($M^+$); HRMS (ESI) calcd. for $C_{35}H_{27}N_2$ ($M^+$) 475.2174; found 475.2155. Anal. calcd. for $C_{35}H_{27}N_2O_4Cl$: C,73.10; H, 4.73; N, 4.87. Found: C,72.92; H, 4.86; N, 4.70.

**1-(4′-Amino-4-biphenylyl)-2,3,4,5-tetraphenylpyridinium perchlorate (3g).** IR (KBr) *v*: 3470, 3371($NH_2$), 1623 (C=N), 1093, 621 ($ClO_4^-$) $cm^{-1}$; $^1H$ NMR(400 MHz, $CD_3CN$): $\delta = 8.89$ (s, 1H, PyH), 6.90–7.66 (m, H, ArH), 6.68 (d, 2H, $J = 8.4$ Hz, ArH), 4.36 (s, 2H, $NH_2$); $^{13}C$ NMR (100 MHz, $CD_3CN$): $\delta = 159.6$, 154.8, 149.8, 145.5, 145.3, 144.1, 143.5, 141.3, 141.0, 136.2, 135.7, 135.3, 132.4, 131.7, 131.5, 131.2, 131.0, 130.8, 130.7, 130.6, 130.4, 130.0, 129.8, 129.5, 129.4, 128.8, 128.7, 128.5, 128.0, 127.7, 127.1, 126.2, 115.7, 115.6; MS (API-ES) *m/z*: 551.2 ($M^+$); HRMS (ESI) calcd. for $C_{41}H_{31}N_2$ ($M^+$) 551.2487; found 551.2470. Anal. calcd. for $C_{41}H_{31}N_2O_4Cl$: C, 75.63; H, 4.80; N, 4.30. Found: C, 75.89; H, 4.67; N, 4.12.

**1-(4-Chlorophenyl)-2,3,4,5-tetraphenylpyridinium perchlorate (3h).** IR (KBr) *v*: 1610 (C=N), 1022 (Ar-Cl), 1090, 622 ($ClO_4^-$) $cm^{-1}$; $^1H$ NMR (400 MHz, $CD_3CN$): $\delta = 8.85$ (s, 1H, PyH), 6.86–7.62 (m, 24H, ArH); $^{13}C$ NMR(100 MHz, $CD_3CN$): $\delta = 159.5$, 154.5, 145.3, 143.3, 141.7, 141.2, 136.9, 136.2, 135.6, 135.2, 132.1, 131.4, 130.9, 130.5, 130.4, 130.3, 129.8, 129.5, 129.4, 129.3, 128.8, 128.7, 128.6, 128.5; MS (API-ES) *m/z*: 494.2 ($M^+$); HRMS (ESI) calcd. for $C_{35}H_{25}NCl$ ($M^+$) 494.1676; found 494.1659. Anal. calcd. for $C_{35}H_{25}NO_4Cl$: C, 70.71; H, 4.24; N, 2.36. Found: C, 70.42; H, 4.41; N, 2.24.

**1-(4-Bromophenyl)-2,3,4,5-tetraphenylpyridinium perchlorate (3i).** IR (KBr) *v*: 1608 (C=N), 1018 (Ar-Br), 1086, 622 ($ClO_4^-$) $cm^{-1}$; $^1H$ NMR (400 MHz, $CD_3CN$): $\delta = 8.85$ (s, 1H, PyH), 6.80–7.63 (m, 24H, ArH); $^{13}C$ NMR (100 MHz, $CD_3CN$): $\delta = 159.7$, 154.6, 145.3, 143.5, 142.3, 141.3, 136.2, 135.7, 135.3, 133.5, 132.2, 131.5, 131.0, 130.6, 130.0, 129.8, 129.4, 129.3, 128.9, 128.8, 128.7, 128.5, 125.1,; MS (API-ES) *m/z*: 538.0 ($M^+$); HRMS (ESI) calcd for $C_{35}H_{25}NBr$ ($M^+$) 538.1170; found 538.1149. Anal. calcd. for $C_{35}H_{25}NO_4ClBr$: C, 65.79; H, 3.94; N, 2.19. Found: C, 66.01; H, 3.78; N, 2.36.

**1-(4-Pyridyl)-2,3,4,5-tetraphenylpyridinium perchlorate (3j).** IR (KBr) *v*: 1607 (C=N), 1577, 1533, 1492, 1457 ($C_5H_4N$), 1094, 620 ($ClO_4^-$) $cm^{-1}$; $^1H$ NMR (400 MHz, $CD_3CN$): $\delta = 8.86$ (s, 1H, PyH), 8.65 (d, 2H, $J = 6.0$ Hz, PyH), 7.52 (d, 2H, $J = 6.0$ Hz, PyH), 6.96–7.40 (m, 20H, ArH); $^{13}C$ NMR (100 MHz, $CD_3CN$): $\delta = 160.0$, 154.0, 152.3, 149.7, 144.7, 143.5, 141.5, 136.0, 135.4, 135.0, 131.6, 131.5, 131.4, 130.9, 130.4, 129.9, 129.4, 128.9, 128.8, 128.7, 128.5, 122.4; MS (API-ES) *m/z*: 461.1 ($M^+$); HRMS (ESI) calcd. for $C_{34}H_{25}N_2$ ($M^+$) 461.2018; found 461.2032. Anal. calcd. for $C_{34}H_{25}N_2O_4Cl$: C, 72.79; H, 4.49; N, 4.99. Found: C, 72.58; H, 4.62; N, 4.85.

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