Electrochemical reduction of 4-benzoyl-N-(4-substituted benzyl)pyridinium cations: substitution effects and linear free energy relationships

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Abstract

In analogy to 4-(p-substituted benzoyl)-N-methylpyridinium cations (1-Xs), the title species (2-Xs, X = -OCH3, -CH3, -H, -Br, -COCH3, -NO2) undergo two reversible, well-separated (ΔE1/2 ≥ 650 mV) one-electron reductions. The effect of substitution on the E1/2sof 2-Xs is much weaker than the effect of the same substituents on 1-Xs: the Hammett r-values are 0.80 and 0.93 for the first- and second-electron reduction of 2-Xs vs. 2.3 and 3.3 for the same reductions of 1-Xs, respectively. The difference has been attributed to the different polarizability of p-v's, and to the fact that in 1-Xs the electronic properties of the substituents are transmitted through the p-system, while in 2-Xs there is a –CH2– spacer. From a practical standpoint, these results suggest that the 4-benzoylpyridinium system can be used as an almost continuously tunable redox couple, whose redox potential can be course-tuned via p-benzoyl substitution and fine-tuned via p-benzyl substitution. Importantly, the nitro group of 2-NO2 undergoes reduction before the second-electron reduction of the 4-benzoylpyridinium system. Introducing the recently derived substituent constant of the –NO2 + group (σp,NO2 = −0.97) yields an excellent correlation for the third-electron reduction of 2-NO2 (corresponding to the reduction of the carbonyl group) with the second-electron reduction of the other 2-Xs, and confirms the electron-donating properties of –NO2 +.

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1. Introduction

We reported recently that 4-benzoyl-N-methylpyridinium cations, 1-Xs, undergo two successive, well-separated (± 0.6 V) one-electron (1-e) reductions where the first electron neutralizes the pyridinium and the second one yields the enolate, [1-X]− (Eq. (1)) [1,2].

\[
\begin{align*}
\text{[1-X]} & \xrightarrow{-\epsilon} \text{[1-X]^+} \\
\text{[1-X]^+} & \xrightarrow{-\epsilon} \text{[1-X]^−} \quad \text{(1)}
\end{align*}
\]

The 1-e-reduced ketones [1-X]^+ are stable towards pinacolization [1], while the 2-e-reduced forms [1-X]^− (Eq. (1)) are chemically stable only in the absence of proton donors. In the presence of protic acids, [1-X]^−s develop hydrogen (H) bonding through the enolate-O, shifting the second cyclic voltammetric reduction wave to more positive potentials; the first reduction wave

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remains completely unaffected [1,2]. H-bonded adducts with stronger acids (e.g. CH₃CO₂H) undergo irreversible proton transfer to the corresponding quaternized carbinols within the time scale (20–30 s) of cyclic voltammetry at 0.1 V s⁻¹ [1]. H-bonded adducts with weak protic acids (e.g. water, alcohols) undergo proton transfer on longer time scales (~400 s) to the corresponding non-quaternized carbinols [1]. These findings suggest that this class of compounds could be used as main-stream redox catalysts or electron-transfer quenchers, while in aprotic environments they could be used as electrochromic materials (turning from colorless to red upon 1-e reduction), for which the basic requirement is chemical reversibility [2]. In view of those applications, the synthetic accessibility of the para-position of the benzoyl group provides an additional degree of freedom, by allowing tuning of the redox properties of the 4-benzoylpyridinium system (I-X) through the electronic properties of the substituent X (Eq. (1)). As expected, both reductions are facilitated by electron-withdrawing substituents and it was found experimentally that the redox potential of the carbonyl reduction of \( \text{I-NO}_2 \) undergoes reduction before the carbonyl. So, when the carbonyl group of \( \text{I-NO}_2 \) is reduced, \( \text{NO}_2^- \) has been already transformed into \( \text{NO}_2^-^* \). Reasoning that the redox potential of the carbonyl reduction of \( \text{I-NO}_2 \) (third wave) should correlate with the corresponding redox potentials of the other I-Xs (second waves) has allowed calculation of the substituent constant for \( \text{NO}_2^-^* \). It was found that \( \sigma_{p-\text{NO}_2^-} = -0.97 \), suggesting that \( \text{NO}_2^-^* \) is a strong electron donor [2].

Hammett linear free energy correlations are used generally in order to quantify experimental observations and deduce stereoelectronic communication effects (e.g. resonance vs. inductive) between substituents and reaction sites. By the same token, Hammett correlation studies with compounds undergoing successive e-transfer reactions are rather uncommon [3]. So, motivated by the results summarized above, we decided to explore how reduction of the two redox centers would be affected by placing the substituents closer to the pyridinium rather than to the carbonyl, and thus perhaps get a glimpse of how the redox properties of the 4-benzoylpyridinium system could be adjusted by varying the two sets of substituents independently. These issues were investigated with compounds \( 2-X \), where \( X = -\text{OCH}_3, -\text{CH}_3, -\text{H}, -\text{Br}, -\text{COCH}_3, \) and \( -\text{NO}_2 \).

2. Experimental

2.1. Methods

All electrochemical experiments were carried out with a Au disk working electrode (1.6 mm in diameter, from Bioanalytical Systems, Inc., West Lafayette, IN), an aqueous Ag/AgCl reference electrode (also from BAS), and a Au foil (2.5 cm²) as a counter electrode, in Ar-degassed anhydrous CH₃CN/0.1 M tetrabutylammonium perchlorate (TBAP) solutions at room temperature (23±1 °C). All voltammograms have been 80% compensated for solution resistance. All reactions were carried out under N₂. Melting points are uncorrected. Elemental analyses were performed by Prevalere Life Sciences, Inc. (Former Oneida Research Services, Inc.), Whiteboro, NY.

2.2. Materials

All starting materials, reagents, and solvents were commercially available and were used as received. Ferrocene and 4-benzoylpyridine were sublimed. TBAP was prepared as described before [1,2]. All 2-Xs were prepared by quaternization of 4-benzoylpyridine according to the following general procedure: 4-benzoylpyridine (1 equiv.) and the corresponding p-substituted benzyl halide (2–3 equiv. bromide or chloride) were dissolved in CH₃CN and refluxed for 24 h. At the end of the period, the solvent was removed and the residue was dissolved in water. An aqueous solution of ammonium tetrafluoroborate (10 equiv.) was added and the mixture was refluxed until all solids were dissolved. The solution was cooled to ~5 °C, and the precipitate was collected, dissolved in CH₃CN, and precipitated with diethylether. The precipitate was collected and recrystallized once again from water. All 2-Xs of this study are white solids.

2.3. 4-Benzoyl-N-benzylpyridinium tetrafluoroborate

\( 2\text{-H} \) was prepared from 4-benzoylpyridine (5 g, 0.027 mol) and benzyl bromide (14 g, 0.081 mol). Yield: 5.2 g (53%); m.p.: 151–153 °C; \( ^1\text{H} \) NMR (DMSO-\( d_6 \), 400 MHz): \( \delta \) 5.93 (2H, s, \(-\text{CH}_2\text{N}^+\)), 7.45–7.50 (3H, m, H-...
1,2,6), 7.58–7.63 (4H, m, H-3,5,17,19), 7.77–7.81 (1H, m, H-18), 7.83–7.86 (2H, m, H-16,20), 8.38 (2H, d, \( J_{9,10} = J_{12,13} = 6.6 \) Hz, H-9,13), 9.36 (2H, d, \( J_{9,10} = J_{12,13} = 6.8 \) Hz, H-10,12); \(^{13}\)C NMR (DMSO-\(d_6\), 100 MHz): \( \delta \) 63.5 (–CH\(_2\)N\(^+\)), 127.5, 129.2, 129.4, 129.6, 130.4, 133.9, 134.2, 134.9, 145.8, 151.9, 192.1 (C=O). Anal. Calc. for \( \text{C}_{19}\text{H}_{16}\text{NO}_2\text{BF}_4\): C, 61.41; H, 4.64; N, 3.58. Found: C, 61.10; H, 3.94; N, 3.68%.

2.7. 4-Benzoyl-N-(4-bromobenzyl)pyridinium tetrafluoroborate

2-Br was prepared from 4-benzoylpyridine (5 g, 0.027 mol) and 4-bromobenzylbromide (10 g, 0.049 mol). Yield: 5.9 g (51%); m.p.: 188–190 °C; \(^1\)H NMR (DMSO-\(d_6\), 400 MHz): \( \delta \) 5.90 (2H, s, –CH\(_2\)N\(^+\)), 7.58 (2H, d, \( J_{2,3} = J_{5,6} = 8.6 \) Hz, H-3,4), 7.59–7.65 (2H, m, H-16,20), 7.70 (2H, d, \( J_{2,3} = J_{5,6} = 8.6 \) Hz, H-2,6), 7.77–7.82 (1H, m, H-18), 7.83–7.86 (2H, m, H-16,20), 8.37 (2H, d, \( J_{9,10} = J_{12,13} = 6.8 \) Hz, H-9,13), 9.34 (2H, d, \( J_{9,10} = J_{12,13} = 6.8 \) Hz, H-10,12); \(^{13}\)C NMR (DMSO-\(d_6\), 100 MHz): \( \delta \) 20.8 (–CH\(_3\)), 63.5 (–CH\(_2\)N\(^+\)), 127.5, 129.0, 129.2, 129.7, 130.0, 130.4, 130.9, 131.4, 139.3, 145.6, 151.8, 192.1 (C=O). Anal. Calc. for \( \text{C}_{29}\text{H}_{18}\text{NOBF}_4\): C, 51.86; H, 3.44; N, 3.18. Found: C, 51.80; H, 2.55; N, 3.18%.

2.8. 4-Benzoyl-N-(4-acetylbenzyl)pyridinium tetrafluoroborate

2-COCH\(_3\) was prepared from 4-benzoylpyridine (5 g, 0.027 mol) and 4-bromomethylacetophenone. The latter was prepared from 4-methylacetophenone (10 g, 0.075 mol), N-bromosuccinimide (15 g, 0.084 mol) and 1,1-azobisiso(cyclohexanecarbonitrile) (3.6 g, 0.015 mol) in 150 ml CCl\(_4\) (reflux, 24 h) and was used as received (light yellow solid) without further purification. Yield: 7.6 g (70%); m.p.: 175–177 °C; \(^1\)H NMR (DMSO-\(d_6\), 400 MHz): \( \delta \) 2.59 (3H, s, –COCH\(_3\)), 6.02 (2H, s, –CH\(_3\)N\(^+\)), 6.70–6.75 (2H, m, H-17,19), 7.72 (2H, d, \( J_{2,3} = J_{5,6} = 8.6 \) Hz, H-3,5), 7.77–7.83 (1H, m, H-18), 7.84–7.88 (2H, m, H-16,20), 8.04 (2H, d, \( J_{2,3} = J_{5,6} = 8.6 \) Hz, H-2,6), 8.41 (2H, d, \( J_{9,10} = J_{12,13} = 6.8 \) Hz, H-9,13), 9.39 (2H, d, \( J_{9,10} = J_{12,13} = 7.0 \) Hz, H-10,12); \(^{13}\)C NMR (DMSO-\(d_6\), 100 MHz): \( \delta \) 26.9 (–CH\(_3\)), 63.0 (–CH\(_2\)N\(^+\)), 127.5, 129.0, 129.3, 129.3, 130.4, 134.1, 134.9, 137.4, 138.6, 146.0, 152.0, 192.1 (C=O). Anal. Calc. for \( \text{C}_{21}\text{H}_{16}\text{NO}_3\text{BF}_4\): C, 62.56; H, 4.50; N, 3.47. Found: C, 62.47; H, 3.78; N, 3.50%.

3. Results and discussion

All six 2-Xs were prepared by straightforward quaternization of 4-benzoylpyridine with the corresponding \( p \)-substituted benzyl halides. With the exception of the chloride salt of 2-H, which was first reported in 1959 in conjunction with its potential properties as a local anesthetic [4], all other 2-Xs are new compounds.
Generally, the redox properties of 2-Xs were determined with 3 mM solutions by cyclic voltammetry at 0.1 V s\(^{-1}\) in anhydrous CH\(_3\)CN/0.1 M TBAP using ferrocene as internal standard. All electrochemical data are summarized in Table 1 and representative voltammograms are shown in Fig. 1. With the exception of 2-NO\(_2\), all other 2-Xs show two chemically reversible redox waves (cathodic-to-anodic peak current ratios, \(i_\text{p,c}/i_\text{p,a} \approx 1\)). By analogy to 1-Xs (Eq. (1)), all first reduction waves correspond to the reduction of the pyridinium moiety, and with the exception of 2-NO\(_2\), all second reduction waves correspond to the reduction of the carbonyl. In most cases, the cathodic to anodic peak-to-peak potential separations, \(\Delta E_{p-p}\), are comparable to the values given by the ferrocenium/ferrocene (Fc\(^+\)/Fc) couple (73±2 mV) [6], and are close to the theoretical value of 60 mV for 1-e kinetically reversible systems. As expected, Fig. 1A shows that electron-withdrawing substituents facilitate both reductions, as both waves move to less negative potentials. However, the effect of substitution does not appear to be strong. Meanwhile, the behavior of the nitro-derivative, 2-NO\(_2\), is remarkably different: at 0.1 V s\(^{-1}\) 2-NO\(_2\) shows four irreversible waves (Fig. 1B, dotted line). A potential sweep at the same sweep rate through the first wave only shows that the first-electron reduction of 2-NO\(_2\) is chemically reversible (Table 1). On the other hand, successive potential sweeps through the second- and third-electron reduction waves of 2-NO\(_2\) produce irreversible behavior. By decreasing the concentration of 2-NO\(_2\) to \(\sim 0.3\) mM and by increasing simultaneously the sweep rate to \(\geq 5\) V s\(^{-1}\), 2-NO\(_2\) yields three apparently reversible voltammetric waves (Fig. 1B, solid line). The first wave correlates with the first reduction wave of all other 2-Xs (vide infra) and corresponds to the reduction of the pyridinium ring (in analogy to Eq. (1)); as expected, it is positively shifted in comparison to the first waves of the other 2-Xs (Table 1), reflecting the strong electron-withdrawing properties of -NO\(_2\). The second (middle) wave of 2-NO\(_2\) is close to the reduction of nitrobenzene (see Fig. 1B, inset) and is associated with the reduction of the \(p\)-nitrobenzyl substituent (Eq. (2)). The third wave is due to the reduction of the carbonyl and it has been shifted to more negative potentials in contrast to the second waves of all other 2-Xs, which move in the positive direction as the electron-withdrawing ability of the substituents increases (Table 1). As it will be discussed below, this is attributed to the electron-donating properties of –NO\(_2\)\(^-\). Meanwhile, the fact that the three expected reversible waves are observed only by simultaneously decreasing the concentration of 2-NO\(_2\) and increasing the potential sweep rate indicates that the 2-e-reduced form, [2-NO\(_2\)\(^-\)], participates in irreversible bimolecular reactions. This deduction, taken together with the fact that the 1-e-reduced form of nitrobenzene does not seem

<table>
<thead>
<tr>
<th>X</th>
<th>(E_{1/2}(1)(\text{V}))</th>
<th>(\Delta E_{p-p}(1)(\text{mV}))</th>
<th>(E_{1/2}(2)(\text{V}))</th>
<th>(\Delta E_{p-p}(2)(\text{mV}))</th>
<th>(E_{1/2}(3)(\text{V}))</th>
<th>(\Delta E_{p-p}(3)(\text{mV}))</th>
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</thead>
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<tr>
<td>2-CH(_3)</td>
<td>0.00</td>
<td>1.00</td>
<td>0.14</td>
<td>1.04</td>
<td>0.98</td>
<td>1.04</td>
</tr>
<tr>
<td>2-CH(_2)OH</td>
<td>0.34</td>
<td>1.01</td>
<td>0.12</td>
<td>1.04</td>
<td>0.98</td>
<td>1.04</td>
</tr>
<tr>
<td>2-COCH(_3)</td>
<td>0.63</td>
<td>1.01</td>
<td>0.26</td>
<td>1.04</td>
<td>0.98</td>
<td>1.04</td>
</tr>
<tr>
<td>2-Br</td>
<td>0.26</td>
<td>1.00</td>
<td>0.33</td>
<td>1.01</td>
<td>0.98</td>
<td>1.04</td>
</tr>
<tr>
<td>2-NO(_2)</td>
<td>0.90</td>
<td>1.01</td>
<td>0.33</td>
<td>1.01</td>
<td>0.98</td>
<td>1.04</td>
</tr>
<tr>
<td>Ph-NO(_2)</td>
<td>0.78</td>
<td>1.01</td>
<td>0.33</td>
<td>1.01</td>
<td>0.98</td>
<td>1.04</td>
</tr>
</tbody>
</table>

\(a\) With the exception of 2-NO\(_2\) (see footnote d), all \(E_{1/2}\)s were determined by cyclic voltammetry at 0.1 V s\(^{-1}\) with \(\sim 3\) mM solutions of the 2-Xs and are reported vs. the ferrocenium/ferrocene couple used as internal standard.

\(b\) From Ref. [5].

\(c\) Determined with a 1 mM solution and a 0.1 V s\(^{-1}\) sweep rate.

\(d\) Merging waves; baseline current could not be established (see Fig. 1B).
to interfere with the redox processes of 1-H (Fig. 1B, inset), suggests that the reduced nitrobenzyl group is not involved, at least initially, in any bimolecular reaction. Therefore, it is suggested that the bimolecular reaction responsible for the irreversibility introduced as early as during 0.1 V s⁻¹ sweep through the second reduction wave of 2-NO₂ should be related to the electrostatic perturbation imposed by −NO₂⁻ upon the reduced pyridinium group of the same [2-NO₂⁻•] species [7].

The relative efficiency by which substituents X influence the reduction of the two redox centers of the 2-Xs is expressed via Hammett linear free energy relationships. Fig. 2 shows good correlations (see Fig. 2) between substituent constants σ_p,X and E_{1/2} of both waves of 2-Xs. The slopes are 0.047 and 0.055 V for the reduction of the pyridinium and the carbonyl, corresponding to reaction constants ρ_{1-e} = 0.80 and ρ_{2-e} = 0.93, respectively. It should be noted here that by using

\[
\begin{align*}
\text{[2-NO}_2\text{]} & \quad \text{(eq 2)} \\
\begin{array}{c}
\text{[2-NO}_2\text{]} \\
\end{array} & \quad \begin{array}{c}
\text{[2-NO}_2\text{]}^\text{−} \\
\end{array}
\end{align*}
\]

Fig. 1. (A) Cyclic voltammetry of 2-OCH₃ (; 3.04 mM), 2-H (−; 3.32 mM), and 2-COCH₃ (; 3.27 mM) in CH₃CN/0.1 M TBAP with a Au disk electrode (0.0201 cm²) at 0.1 V s⁻¹. Current bar: 10 μA. (B) Cyclic Voltammetry of 2-NO₂ 0.33 mM at 0.1 V s⁻¹ (; current bar: 2.7 μA) and at 5 V s⁻¹ (−; current bar: 16 μA). Inset: voltammetry in the same electrolytic solution at 0.1 V s⁻¹ of a mixture containing 1-H (3.08 mM) and nitrobenzene (PhNO₂, 1.90 mM). The middle wave is produced by the reduction of PhNO₂. Similar results have been obtained with 2-H and PhNO₂.
the $\sigma_{p-NO_2}$ value (0.78), neither the second nor the third wave of 2-NO$_2$ correlates with the second waves (reduction of the carbonyl) of the other 2-Xs. However, using the $\sigma_{p-NO_2}\cdot \kappa_{v=2}$ value ($-0.97$) [2], the reduction of the carbonyl group of 2-NO$_2$ (third voltammetric wave; Fig. 1B, solid line), correlates well with the reduction of the same group in all other 2-Xs (see Fig. 2). That finding confirms both the stereoelectronic communication between the para-benzyl substituents and the reduction sites, and the predictive power of the $\sigma_{p-NO_2}\cdot \kappa_{v=2}$ constant. Now, the good correlation of all $E_{1/2}$s with the $\sigma_{p-X}$ values indicates purely inductive interactions. The fact that both $\rho$-values for $p$-benzoyl substitution are significantly larger than the $\rho$-values for $p$-benzyl substitution simply reflects that $\pi$-electrons are more polarizable than $\sigma$-electrons, and therefore transmit the electrostatic properties of the substituents more effectively, over longer distances, even when the substituents are not in direct conjugation with the reaction site. In the case of 2-Xs, the electronic properties of the substituents are necessarily transmitted through $\sigma$-bonds ($-\text{CH}_2-$), and in such cases $\rho$-values lower than unity are expected. (For example, $\rho$-values less than “one” are well established with thermodynamic parameters—equilibrium constants—in systems containing methylene spacers [9].)

The weak electronic communication of the substituents even with the point of the second-electron reduction (where the $\rho$-value is somewhat higher) is further reflected upon the lack of any significant ability of the $p$-benzyl substituents to affect H bond developing between the enolate oxygen and methanol in solution. In analogy to 1-Xs, such H bonding shifts the wave of the second-electron reduction to more positive potentials leaving the first wave unaffected (Fig. 3). The slope of the potential separation between the two waves vs. log([MeOH]) (Fig. 3, inset) yields the average (apparent) number of methanol molecules, $\langle m \rangle$, participating in the H-bonded adducts, $[2-X]^{-}\cdot m(\text{CH}_3\text{OH})$ (see Table 2) [2]. The intercepts of the same curves are related to the equilibrium constants ($K_{H})$ and therefore the free energy ($\Delta G^0$) of the H-bonded adduct formation [1,2]. While in the case of 1-Xs substitution played a significant role both on the strength of H bonding and
the number of MeOH molecules associating with the enolate-O, in the case of 2-Xs there is little variation in either one of those two properties as a function of substitution.

4. Conclusions

The effect of para-benzyl substituents on the reduction of the quaternized 4-benzoylpyridinium system is significantly weaker than the effect of para-benzoyl substitution. The practical significance of this finding is that the redox potential of the 4-benzoylpyridinium system can be tuned first via para-benzoyl substitution and then fine-tuned via para-benzyl substitution. For example, based on our previous results with 1-Xs [2], it is expected that a change of the para-benzyl substituent from --OCH$_3$ to --CH$_3$ ($\Delta \sigma_{p-X} = 0.3$) will change the redox potential of the first-electron reduction of the 4-benzoyl-N-benzylpyridinium system by ~40 mV. Then, a change of the para-benzyl substituent from --OCH$_3$ to --NO$_2$ ($\Delta \sigma_{p-X} = 1.05$) is expected to change the redox potential of the same reduction by ~50 mV. Therefore, by a judicious choice of the para-benzyl substituents the potential range between the first-electron reductions of 4-(p-CH$_3$O-benzoyl)- and 4-(p-CH$_3$-benzoyl)-N-benzylpyridinium cations can be covered almost continuously. A similar argument can be made for any other pair of substituents with sequential $\sigma_{p-X}$ values. Thus, 4-benzoylpyridinium cations can comprise the basis for a continuously tunable redox couple for redox mediation, catalysis, and electrochromics.

Acknowledgements

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References

[7] Once the --NO$_2$ group is reduced to the strongly electron-donating --NO$_2$* group, the reduced pyridinium group of the same species becomes a reducing agent for the pyridinium of 2-NO$_2$. So, [2-NO$_2$*]$_2$ diffusing away from the electrode can react in a comproportionation fashion with 2-NO$_2$ diffusing towards the electrode and yield not only 2 mol of [2-NO$_2$]$_2$, but also [2-NO$_2$*]$_2$ [8]. The latter is a new species that is generated only transiently because, upon reduction, the --NO$_2$ group changes from an electron acceptor into an electron donor, [2-NO$_2$*]$_2$ finds itself in two concentration gradients, one towards the electrode and one towards the bulk solution. [2-NO$_2$*]$_2$ diffusing towards the
electrode is reduced into $[\text{2-NO}_2^- \text{C}_2\text{8}]$ lost by diffusion towards the bulk becomes responsible for the chemical irreversibility observed past the second wave.


[9] For example, the $\rho$-values for the ionization (in water) of $\text{ArCO}_2\text{H}$, $\text{ArCH}_2\text{CO}_2\text{H}$, and $\text{ArCH}_2\text{CH}_2\text{CO}_2\text{H}$ are 1.00, 0.56, and 0.24, respectively (Ar, substituted phenyl group) [10].