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Efficient synthesis of 9*H*-pyrrolo[1,2-*a*]indol-9-one derivatives based on active manganese dioxide promoted intramolecular cyclization

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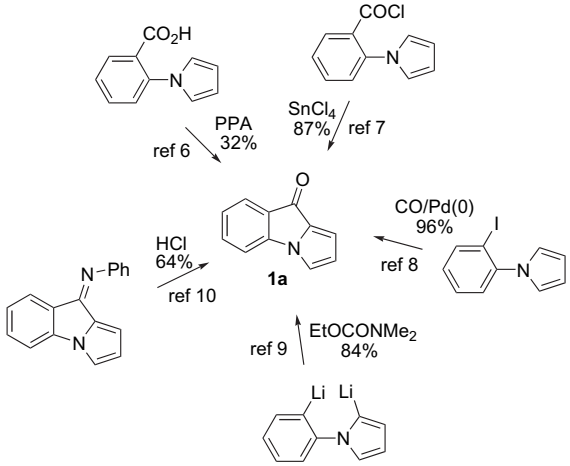
ABSTRACT

A series of 9*H*-pyrrolo[1,2-*a*]indol-9-ones have been prepared via in-situ sequential oxidation of [2-(1*H*-pyrrol-1-yl)phenyl]methanols promoted by active manganese dioxide. The procedure led to title compounds in good yields under mild conditions, without the need to isolate the intermediate aldehydes.

1. Introduction

In recent years, many investigations have focused on the chemistry and biological activities of 9*H*-pyrrolo[1,2-*a*]indol-9-one (fluorazone) (**1a**) and its derivatives. This considerable interest arises from the fact that fluorazone represents the direct chemical precursor of 9*H*-pyrrolo[1,2-*a*]indole (fluorazene), the basic framework of cytostatic mytomycine derivatives.[1] Moreover, psychostimulant activity,[2] cytotoxic[3] and photosensitizing properties[4] have been reported for some fluorazone derivatives. Very recently, we have found that some *N*′-heteroacyl-9*H*-pyrrolo[1,2-*a*]indol-9-hydrazones, directly obtained from 9*H*-pyrrolo[1,2-*a*]indol-9-one, demonstrate moderate activity against a colon cancer cell line.[5] Thus far, several methods are known for the synthesis of 9*H*-pyrrolo[1,2-*a*]indol-9-ones. The reference ketone was first prepared in a 25% yield from methyl 2-(1*H*-pyrrol-1-yl)benzoate via hydrolysis and subsequent cyclization of the corresponding acid promoted by polyphosphoric acid.[6] The original method was however greatly improved by use of classical Friedel–Crafts reactants in the cyclization step.[7] Unsubstituted fluorazone has also been prepared by palladium-catalyzed cyclocarbonylation of 1-(2-iodophenyl)-1*H*-pyrrole[8] or by direct double metallation of 1-phenyl-1*H*-pyrrole followed by treatment of the resulting dilithium salt with ethyl *N*,*N*-dimethylcarbamate as a carbonylating reagent.[9]

More recently, Kobayashi et al.[10] prepared fluorazone (**1a**), along with some benzo-substituted derivatives, by acidic hydrolysis of 9-phenylimino-9*H*-pyrrolo[1,2-*a*]indole, in turn obtained by reaction of 2-(1*H*-pyrrol-1-yl)benzaldehyde and aniline (Scheme 1). However, low yield, harsh reaction conditions or the use of harmful reactants prevented a general application of previous procedures. Thus, our continued interest in the synthesis of drug-like molecules, derived from nitrogen containing polycondensed heterocyclic systems, spurred us to investigate an alternative and efficient method for the production of fluorazone and its benzo-substituted derivatives.



Scheme 1. Known methods for the synthesis of **1a**.

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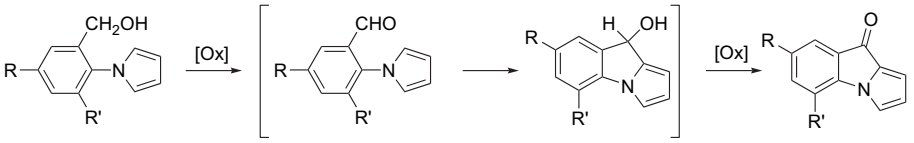
2. Results and discussion

Recently, we investigated the preparation of some pyrrolobenzazepines using 2-(1*H*-pyrrol-1-yl)benzaldehyde (**3a**) as starting material.[11a] The latter was obtained by oxidation of [2-(1*H*-pyrrol-1-yl)phenyl]methanol[11b] (**2a**) in benzene at reflux by the action of active MnO_2, an agent widely used for the conversion of benzylic alcohols to aldehydes by a free radical mechanism.[12] During the reaction, the unexpected formation of traces of fluorazone (**1a**) as a side-product was noticed, especially after prolonged reaction time (Scheme 2). This result prompted us to thoroughly re-examine the conditions with the aim of driving the reaction towards exclusive formation of the ketone **1a**. Even though it has been reported that aldehydes generated by MnO_2 oxidation may be in-situ trapped by nucleophilic species,[13] to the best of our knowledge, no examples have been yet reported about the use of MnO_2 as a promoter of cyclization reactions through carbon–carbon bond formation. Furthermore, it is known that the oxidant properties of manganese dioxide can be greatly enhanced by increasing temperature.[14] Several conditions were then attempted during the oxidation reaction by varying temperature, solvent, type of MnO_2 used and oxidant/alcohol ratio. As a result, it was concluded that the conversion of alcohol **2a** into fluorazone (**1a**), through 'intermediate' aldehyde **3a**, depends mainly on the boiling temperature of the solvent. Either commercial or freshly-prepared[15] active MnO_2 was used, but neither the type nor the amount of oxidant excess used seem to significantly affect the course of the reaction. Thus, the best results were obtained by using a fivefold excess of commercially available active MnO_2 in toluene at reflux for 72 h, under Dean–Stark conditions. In these neutral and essentially anhydrous conditions, fluorazone (**1a**) was obtained in 64% yield, after chromatographic purification. Attempts to shorten the reaction time, by running the reaction in a sealed tube, were unsuccessful. A parallel experiment conducted on aldehyde **3a**, under a stream of dry air, in the absence of MnO_2, did not lead to the reference ketone **1a**. The MnO_2 promoted procedure was then extended to analogous alcohols **2b–f** variously substituted on the phenyl ring, to give corresponding substituted-ketones **1b–f** in 60–72% yield. As an exception, [5-methoxy-2-(1*H*-pyrrol-1-yl) phenyl]methanol (**2d**) generated the corresponding 7-methoxyfluorazone (**1d**) in a 28% yield only, while unreacted aldehyde **3d** was isolated in a 30% yield. This behaviour could be due to a generally different absorption of methoxy derivatives on the solid MnO_2 surface.[12b] In all cases, GC monitoring confirmed that the reaction proceeds through the formation of intermediate aldehyde, the carbonyl group of which is in turn exposed to intramolecular nucleophilic attack from the pyrrole, promoted by the temperature increase and a likely coordinating action of superficial molecules of MnO_2 on the carbonyl. The putative fluorenol-like carbinol formed is then readily in-situ oxidized by a second equivalent of oxidant[12b] driving the reaction to the almost exclusive formation of cyclic ketone. On the other hand, the same reaction conditions applied to

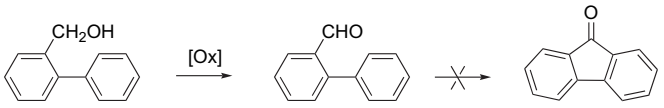


2a-f **3a-f** **1a-f** (28-72%)

a R=R'=H
b R=F, R'=H
c R=CH_3, R'=H
d R=OCH_3, R'=H
e R=NO_2, R'=H
f R=H, R'=CH_3

Scheme 2. Sequential oxidation process.

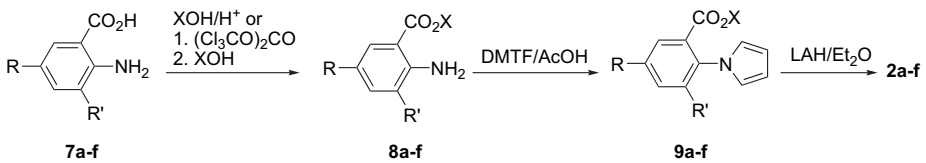
2-biphenylmethanol (**4**), a commercially available analogue, which bears an inert phenyl ring instead of the reactive electron-richer pyrrole, did not promote any conversion to 9*H*-fluoren-9-one (**6**), making the 2-biphenylcarboxaldehyde (**5**) as the sole product recovered (Scheme 3).



4 **5** **6**

Scheme 3. Oxidation of 2-biphenylmethanol.

The starting [2-(1*H*-pyrrol-1-yl)phenyl]methanols **2a–f** were obtained in a three-step procedure from (un)substituted anthranilic acids **7a–f**, which were first transformed to esters **8a–f** directly or via isatoic anhydrides. Clauson–Kaas pyrrolation of esters **8a–f** with dimethoxytetrahydrofuran (DMTF) gave pyrrole derivatives **9a–f**, which in turn were subjected to lithium aluminium hydride (LAH) reduction to give alcohols **2a–f** in generally good yield (Scheme 4).[16,17]



7a-f **8a-f** **9a-f**

a R=R'=H, X=Me
b R=F, R'=H, X=Me
c R=CH_3, R'=H, X=Me
d R=OCH_3, R'=H, X=Et
e R=NO_2, R'=H, X=Et
f R=H, R'=CH_3, X=Me

Scheme 4. Synthesis of [2-(1*H*-pyrrol-1-yl)phenyl]methanols **2a–f**.

3. Conclusion

The reaction sequence outlined in Scheme 2 provides an alternative and simple route to various (un)substituted-fluorazones via intramolecular oxidative-cyclization, starting from either [2-(1*H*-pyrrol-1-yl)phenyl]methanols or 2-(1*H*-pyrrol-1-yl)benzaldehydes. The reaction represents the first example of an intramolecular cyclization promoted by active MnO_2 through bond formation between a pyrrole α-carbon and an aldehyde carbonyl. Studies are in progress with the aim of finding the most suitable conditions to extend the method to a wider range of substrates.

4. Experimental

4.1. General

Progress of the reaction was monitored by TLC on silica gel plates (Riedel-de Haën, Art. 37341) or GC by a Hewlett–Packard 6890 apparatus. Organic solutions were dried over $MgSO_4$ and evaporated on a rotary evaporator under reduced pressure. Melting points were measured using an Electrothermal 8103 apparatus and are uncorrected. IR spectra were recorded as KBr discs on a Jasco FT/IR-4200 spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Brüker 300 MHz spectrometer with TMS as an internal standard: chemical shifts are expressed in δ values (ppm) and coupling constants (J) in Hz. Mass spectral data were determined after electron impact ionisation at 70 eV with a HP 5973 MS spectrometer. Merck silica gel (Kieselgel 60/230–400 mesh) was used for flash chromatography columns. Elemental analyses were performed on a Perkin–Elmer 240C elemental analyzer, and the results are within ±0.4% of the theoretical values. All reactions were carried out under a nitrogen atmosphere. Yields refer to purified products and are not optimized.

4.2. Typical procedure for sequential MnO_2 oxidation of [2-(1*H*-pyrrol-1-yl)phenyl]methanols

*4.2.1. 9H-Pyrrolo[1,2-a]indol-9-one (**1a**)*[9]. A suspension of activated manganese dioxide (Merck art. 805958) (4.14 g, 47.62 mmol) in toluene (200 mL) was heated at reflux for 1 h under a Dean–Stark trap. A solution of [2-(1*H*-pyrrol-1-yl)phenyl]methanol **2a** (1.65 g, 9.53 mmol) in toluene (10 mL) was then added dropwise under stirring. The heating was continued for 72 h. Removal of the solid by filtration on Celite gave a clear solution which was concentrated under vacuum. The residue obtained was purified by silica gel column chromatography (AcOEt/hexanes, 1/6 as eluent) to give pure compound **1a** as a yellow solid. The yield, after recrystallization from $CHCl_3$/cyclohexane, was 1.03 g (64% yield). ^{1}H NMR ($CDCl_3$, 25 °C), δ: 7.59 (d, 1H, J=7.7 Hz), 7.40 (dt, 1H, J=7.7, 1.2 Hz), 7.13–7.06 (m, 3H), 6.76 (d, 1H, J=3.7 Hz), 6.29 (dd, 1H, J=3.7, 2.6 Hz). ^{13}C NMR ($CDCl_3$, 25 °C) δ: 178.6, 142.7, 133.9, 130.9, 129.2, 124.4, 123.4, 118.4, 114.9, 112.9, 109.3. IR (KBr discs) 1680, 1617 cm^{-1}. MS (EI, 70 eV): m/z 169 (M^+, 100), 140 (25), 114 (17). Anal. Calcd for $C_{11}H_7NO$ (%): 78.09 C; 4.17 H; 8.28 N. Found (%): 77.88 C; 4.05 H; 8.39 N. Mp: 121–123 °C (lit.[9] Mp: 121–122 °C).

*4.2.2. 7-Fluoro-9H-pyrrolo[1,2-a]indol-9-one (**1b**).* Following the identical procedure as described for compound **1a**, starting from [5-fluoro-2-(1*H*-pyrrol-1-yl)phenyl]methanol (**2b**), compound **1b** was obtained after silica gel column chromatography (AcOEt/hexanes, 3/7 as eluent). The yield, after recrystallization from Et_2O/hexanes, was 60%. ^{1}H NMR ($CDCl_3$, 25 °C), δ: 7.22 (dm, 1H, J=7.1 Hz), 7.10–6.95 (m, 3H), 6.76 (d, 1H, J=3.8 Hz), 6.29 (m, 1H). ^{13}C NMR ($CDCl_3$, 25 °C) δ: 162.3, 159.0, 120.2, 119.9, 119.8, 116.1, 114.9, 112.4, 112.1, 111.2, 111.1. IR (KBr discs) 1690, 1610 cm^{-1}. MS (EI, 70 eV): m/z 187 (M^+, 100), 158 (32), 132 (22). Anal. Calcd for $C_{11}H_6FNO$ (%): 70.59 C; 3.23 H; 7.48 N. Found (%): 70.30 C; 3.09 H; 7.70 N. Mp: 124 °C.

*4.2.3. 7-Methyl-9H-pyrrolo[1,2-a]indol-9-one (**1c**)*[1b]. Following the identical procedure as described for compound **1a**, starting from [5-methyl-2-(1*H*-pyrrol-1-yl)phenyl]methanol (**2c**), compound **1c** was obtained after silica gel column chromatography (Me_2CO/hexanes, 1/9 as eluent). The yield, after recrystallization from $CHCl_3$/cyclohexane, was 66%. ^{1}H NMR ($CDCl_3$, 25 °C), δ: 7.37 (s, 1H), 7.20 (d, 1H, J=7.9 Hz), 7.02 (d, 1H, J=2.5 Hz), 6.98 (d, 1H, J=7.8 Hz), 6.74 (d, 1H, J=3.8 Hz), 6.27 (t, 1H, J=3.5 Hz), 2.30 (s, 3H). ^{13}C NMR ($CDCl_3$, 25 °C) δ: 177.3, 138.4, 135.9, 134.2, 133.6, 125.1, 124.2, 119.3, 115.5, 113.7, 109.9, 29.7. IR (KBr discs) 1686, 1619 cm^{-1}. MS (EI, 70 eV): m/z 183 (M^+, 100), 154 (54), 128 (15), 77 (11). Anal. Calcd for $C_{12}H_9NO$ (%): 78.67 C; 4.95 H; 7.65 N. Found (%): 78.38 C; 5.01 H; 7.88 N. Mp: 110–111 °C (lit.[1b] Mp: 110–111 °C).

*4.2.4. 7-Methoxy-9H-pyrrolo[1,2-a]indol-9-one (**1d**).* Following the identical procedure as described for compound **1a**, starting from [5-methoxy-2-(1*H*-pyrrol-1-yl)phenyl]methanol (**2d**), compound **1d** was obtained after silica gel column chromatography (CH_2Cl_2 as eluent). The yield, after recrystallization from CH_2Cl_2/cyclohexane, was 28%. ^{1}H NMR ($CDCl_3$, 25 °C), δ: 7.13 (d, 1H, J=2.5 Hz), 7.01 (m, 2H), 6.93 (d, 1H, J=2.5 Hz), 6.75 (d, 1H, J=3.8 Hz), 6.25 (m, 1H), 3.80 (s, 3H). ^{13}C NMR ($CDCl_3$, 25 °C) δ: 179.5, 157.8, 137.4, 132.2, 131.5, 119.6, 119.2, 115.3, 114.2, 111.0, 109.7, 55.9. IR (KBr discs) 1692, 1630, 1607 cm^{-1}. MS (EI, 70 eV): m/z 199 (M^+, 86), 184 (100), 156 (31), 128 (23), 63 (15). Anal. Calcd for $C_{12}H_9NO_2$ (%): 72.35 C; 4.55 H; 7.03 N. Found (%): 72.50 C; 4.84 H; 7.26 N. Mp: 124–125 °C.

*4.2.5. 5-Methoxy-2-(1H-pyrrol-1-yl)benzaldehyde (**3d**).* This compound was isolated as a brown oil in 30% yield during chromatographic purification of compound **1d**. ^{1}H NMR ($CDCl_3$, 25 °C), δ: 9.70 (s, 1H), 7.47 (d, 1H, J=3.0 Hz), 7.34 (d, 1H, J=8.7 Hz), 7.19 (dd, 1H, J=8.7, 3.0 Hz), 6.87 (t, 2H, J=2.0 Hz), 6.35 (t, 2H, J=2.0 Hz), 3.89 (s, 3H). IR (KBr discs) 1695 cm^{-1}. Anal. Calcd for $C_{12}H_{11}NO_2$ (%): 71.63 C; 5.51 H; 6.96 N. Found (%): 71.41 C; 5.76 H; 7.15 N.

*4.2.6. 7-Nitro-9H-pyrrolo[1,2-a]indol-9-one (**1e**)*[1c]. Following the identical procedure as described for compound **1a**, starting from [5-nitro-2-(1*H*-pyrrol-1-yl)phenyl]methanol (**2e**), compound **1e** was obtained after silica gel column chromatography (CH_2Cl_2 as eluent). The yield, after recrystallization from $CHCl_3$/cyclohexane, was 68%. ^{1}H NMR ($CDCl_3$, 25 °C), δ: 8.42 (m, 1H), 7.24 (t, 2H, J=3.4 Hz), 7.18 (d, 1H, J=2.1 Hz), 6.91 (d, 1H, J=3.1 Hz), 6.43 (t, 1H, J=3.1 Hz). ^{13}C NMR ($CDCl_3$, 25 °C) δ: 178.5, 150.5, 139.8, 133.5, 130.3, 126.0, 121.1, 120.4, 116.1, 116.3, 110.4. IR (KBr discs) 1696, 1635 cm^{-1}. MS (EI, 70 eV): m/z 214 (M^+, 100), 184 (21), 168 (18), 140 (47), 113 (15). Anal. Calcd for $C_{11}H_6N_2O_3$ (%): 61.69 C; 2.82 H; 13.08 N. Found (%): 61.44 C; 2.71 H; 13.31 N. Mp: 200–201 °C (lit.[1c] Mp: 202–204 °C).

*4.2.7. 5-Methyl-9H-pyrrolo[1,2-a]indol-9-one (**1f**)*[1b]. Following the identical procedure as described for compound **1a**, starting from [3-methyl-2-(1*H*-pyrrol-1-yl)phenyl]methanol (**2f**), compound **1f** was obtained after silica gel column chromatography (AcOEt/hexanes, 3/7 as eluent). The yield, after recrystallization from $CHCl_3$/cyclohexane, was 72%. ^{1}H NMR ($CDCl_3$, 25 °C), δ: 7.49 (d, 1H, J=7.3 Hz), 7.23 (d, 1H, J=7.7 Hz), 7.20 (dd, 1H, J=2.6, 0.8 Hz), 7.05 (t, 1H, J=7.4 Hz), 6.82 (dd, 1H, J=2.9, 0.8 Hz), 6.30 (dd, 1H, J=2.6, 1.2 Hz), 2.50 (s, 3H). ^{13}C NMR ($CDCl_3$, 25 °C) δ: 179.9, 142.1, 136.8, 133.0, 126.3, 125.3, 122.3, 122.2, 121.1, 115.7, 113.5, 17.7. IR (KBr discs) 1687, 1675, 1620, 1599 cm^{-1}. MS (EI, 70 eV): m/z 183 (M^+, 83), 154 (100), 127 (13). Anal. Calcd for $C_{12}H_9NO$ (%): 78.67 C; 4.95 H; 7.65 N.

Found (%): 78.85 C; 4.71 H; 7.97 N. Mp: 137–139 °C (lit.[1b] Mp: 139–140 °C).

4.3. Typical procedure for the reduction of 2-(1*H*-pyrrol-1-yl)benzoates

*4.3.1. [2-(1H-Pyrrol-1-yl)phenyl]methanol (**2a**)[11b].* This compound was prepared by LAH reduction of ester **9a** following the method described in Ref. 11b. The oil obtained was purified by column chromatography on silica gel (AcOEt/hexanes, 3/7 as eluent).

*4.3.2. [5-Fluoro-2-(1H-pyrrol-1-yl)phenyl]methanol (**2b**).* Following the identical procedure as described for compound **2a**, starting from ester **9b**, compound **2b** was obtained as a brown oil in 72% yield after column chromatography purification on silica gel (AcOEt/hexanes, 3/7 as eluent). ^{1}H NMR ($CDCl_3$, 25 °C), δ: 7.30 (m, 2H), 7.05 (td, 1H, J=8.0, 3.0 Hz), 6.78 (t, 2H, J=2.1 Hz), 6.34 (t, 2H, J=2.0 Hz), 4.60 (s, 2H), 2.18 (br s, 1H). ^{13}C NMR ($CDCl_3$, 25 °C) δ: 160.5, 128.4, 128.2, 122.5, 115.4, 115.1, 114.8, 109.4, 60.7. Anal. Calcd for $C_{11}H_{10}FNO$ (%): 69.10 C; 5.27 H; 7.33 N. Found (%): 68.91 C; 5.45 H; 7.03 N.

*4.3.3. [5-Methyl-2-(1H-pyrrol-1-yl)phenyl]methanol (**2c**).* Following the identical procedure as described for compound **2a**, starting from ester **9c**, compound **2c** was obtained as an oil in 87% yield after column chromatography purification on silica gel (AcOEt/hexanes, 1/2 as eluent). ^{1}H NMR ($CDCl_3$, 25 °C), δ: 7.35 (m, 3H), 6.93 (t, 2H, J=2.0 Hz), 6.43 (t, 2H, J=2.0 Hz), 4.60 (s, 2H), 2.50 (s, 3H), 2.25 (br s, 1H). ^{13}C NMR ($CDCl_3$, 25 °C) δ: 135.9, 135.7, 130.9, 130.5, 128.4, 123.6, 119.9, 109.8, 60.8, 24.4. Anal. Calcd for $C_{12}H_{13}NO$ (%): 76.98 C; 7.00 H; 7.48 N. Found (%): 77.13 C; 7.18 H; 7.36 N.

*4.3.4. [5-Methoxy-2-(1H-pyrrol-1-yl)phenyl]methanol (**2d**).* Following the identical procedure as described for compound **2a**, starting from ester **9d**, compound **2d** was obtained as a yellow solid in 80% yield after column chromatography purification on silica gel (AcOEt/hexanes, 1/2 as eluent). Mp: 83–85 °C ($CHCl_3$/hexanes). ^{1}H NMR ($CDCl_3$, 25 °C), δ: 7.16 (m, 2H), 6.85 (dd, 1H, J=8.6, 2.8 Hz), 6.75 (t, 2H, J=2.0 Hz), 6.27 (t, 2H, J=2.0 Hz), 4.50 (s, 2H), 3.82 (s, 3H), 2.00 (br s, 1H). ^{13}C NMR ($CDCl_3$, 25 °C) δ: 159.8, 129.7, 129.2, 123.0, 119.9, 113.9, 111.6, 109.5, 60.1, 56.5. Anal. Calcd for $C_{12}H_{13}NO_2$ (%): 70.92 C; 6.45 H; 6.89 N. Found (%): 70.71 C; 6.09 H; 7.11 N.

*4.3.5. [5-Nitro-2-(1H-pyrrol-1-yl)phenyl]methanol (**2e**).* Following the identical procedure as described for compound **2a**, but operating at a temperature of −20 °C, starting from ester **9e**, compound **2e** was obtained as a waxy solid in 64% yield after column chromatography purification on silica gel (AcOEt/hexanes, 1/2 as eluent). ^{1}H NMR ($CDCl_3$, 25 °C), δ: 8.60 (d, 1H, J=2.4 Hz), 8.28 (dd, 1H, J=8.6, 2.5 Hz), 7.50 (dd, 1H, J=8.6, 2.6 Hz), 6.95 (t, 2H, J=2.1 Hz), 6.43 (t, 2H, J=2.1 Hz), 4.75 (s, 2H); 1.90 (br s, 1H). ^{13}C NMR ($CDCl_3$, 25 °C) δ: 147.5, 144.3, 131.0, 123.9, 123.1, 122.9, 121.1, 109.5, 56.9. Anal. Calcd for $C_{11}H_{10}N_2O_3$ (%): 60.55 C; 4.62 H; 12.84 N. Found (%): 60.78 C; 4.29 H; 13.14 N.

*4.3.6. [3-Methyl-2-(1H-pyrrol-1-yl)phenyl]methanol (**2f**).* Following the identical procedure as described for compound **2a**, starting from ester **9f**, compound **2f** was obtained as a yellow solid in 93% yield after column chromatography purification on silica gel (AcOEt/hexanes, 1/2 as eluent). Mp: 56–58 °C (AcOEt/hexanes). ^{1}H NMR ($CDCl_3$, 25 °C), δ: 7.34–7.13 (m, 3H), 6.58 (t, 2H, J=2.0 Hz), 6.27 (t, 2H, J=2.0 Hz), 4.30 (s, 2H), 2.00 (s, 3H), 1.80 (br s, 1H). ^{13}C NMR ($CDCl_3$, 25 °C) δ: 136.6, 130.4, 128.7, 123.4, 123.2, 122.3, 122.1, 109.3, 60.7, 18.4. Anal. Calcd for $C_{12}H_{13}NO$ (%): 76.98 C; 7.00 H; 7.48 N. Found (%): 76.71 C; 7.21 H; 7.65 N.

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Supplementary data

Synthesis and analytical data of compounds **9a**–**f**, copies of ^{1}H NMR spectra of **1a**–**f**, **2f**, **3d** and **9f**, ^{13}C NMR spectra of **1a**,**b** and **d** and IR spectra of **1a**,**b** and **d**. Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2009.10.111.

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