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PHENOL NITRATION FROM A 2-(NITROOXY)ETHYL SIDE CHAIN

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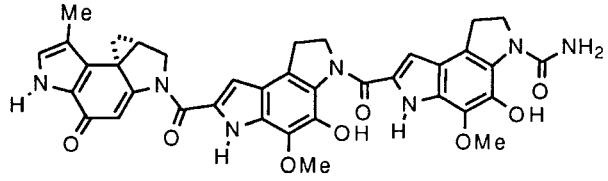
Abstract. A novel nitration of phenols is described on 2-(3-hydroxy-4-methoxyphenyl)ethyl nitrate (**2**), which is synthesized by three alternative routes.

As part of our research aimed at the synthesis of the antitumor agent CC-1065 (**1**),[1] we were interested in the development of a mild nitrating method for phenols, which could be used under non-oxidizing conditions.



1: CC-1065

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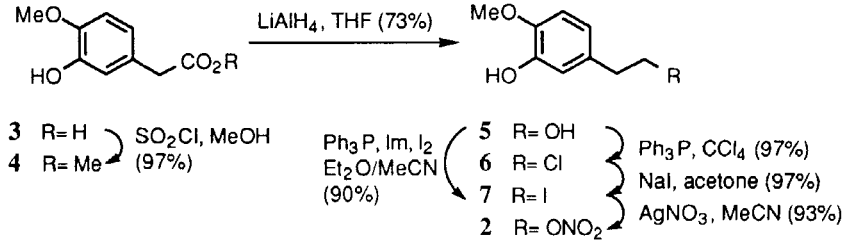
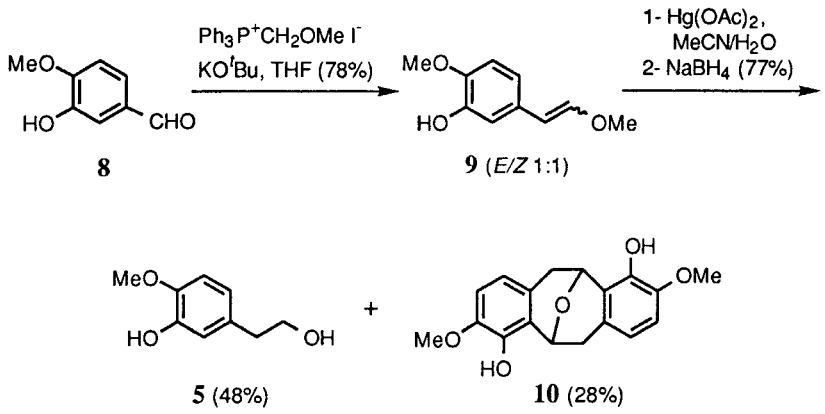
Alkyl nitrates are able to nitrate phenols in the presence of acids.[2] Nevertheless, although they nitrate many nucleophiles in the presence of base,[3] to the best of our knowledge no example of their nitration of phenolates has been published. In the anticipation that an intramolecular version of this reaction under basic conditions would succeed, providing a unique way to achieve a regioselective and mild procedure for the nitration of phenols, we chose the nitrate **2** as a model compound. Herein we wish to report several syntheses of nitrate **2** and the evidence that the treatment of this compound with base leads to a nitro transfer from the side chain to the aromatic ring.

We followed three different pathways for the synthesis of 2-methoxy-5-(2-nitratoethyl)phenol (**2**). In our first approach we started from 3-hydroxy-4-methoxyphenylacetic acid (**3**), which is easily prepared[4] from 4-methoxyphenylacetic acid by bromination with bromine followed by hydroxy-debromination with aqueous sodium hydroxide in the presence of catalytic Cu^{2+}. Sequential treatment of acid **3** with thionyl chloride in methanol and lithium aluminum hydride leads to the alcohol **5** in 71% overall yield, through methyl ester **4**. The iodide **7** may be obtained in two steps from alcohol **5** in 94% yield by reaction with Ph_3P and CCl_4, followed by NaI in refluxing acetone.[5] Alternatively, treatment of alcohol **5** with Ph_3P, imidazole and iodine[6] leads directly to iodide **7** in 90 % yield. Finally, the nitrate **2** was obtained in a 93% yield by treatment of the iodide **7** with silver nitrate in acetonitrile.[7]

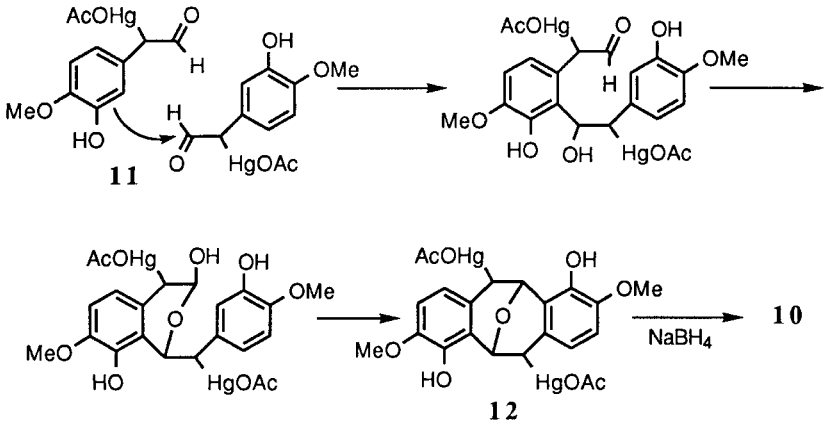


As an alternative to the above synthesis, which requires at least 6 steps from commercially available *p*-methoxyphenylacetic acid, we developed another preparation of the alcohol **5** starting from inexpensive isovanillin (**8**). Wittig reaction with the ylide generated from methoxymethyltriphenylphosphonium iodide and potassium *tert*-butoxide in dry THF yielded 78% of the methoxystyrene **9** as a

1:1 mixture of the *E* and *Z* isomers. Treatment of the methoxystyrene **9** with mercury diacetate in acetonitrile-water followed by reduction[8] of the resulting α-(acetoxymercurio)phenylacetaldehyde (**11**) with $NaBH_4$ leads to the expected alcohol **5** in 48% yield. The Kagan type[9] ether **10** was also isolated in 28% yield.

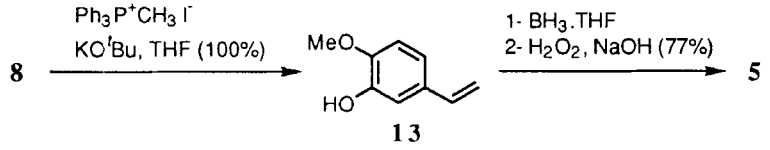


We propose that the intermediate α-(acetoximercurio)phenylacetaldehyde **11** is dimerized by the acidic Hg^{2+} to give the dimercurio compound **12**, which is reduced by $NaBH_4$ to the Kagan ether **10**.



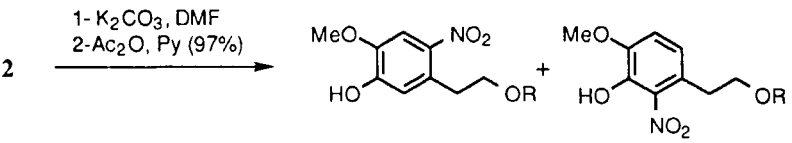
A more convenient way to prepare the alcohol **5** involves the quantitative Wittig reaction of isovanillin (**8**) with methylenetriphenylphosphorane followed by

hydroboration of the resulting styrene **13** to give the desired alcohol **5** in a 77% overall yield. Using this last method the nitrate **2** can be synthesized from isovanillin (**8**) in four steps and 67% overall yield.



13

Nitrate **2** is recovered unchanged after refluxing for several hours in xylenes or after standing with $TiCl_4$ in CH_2Cl_2. Its treatment with *p*-toluenesulfonic acid in benzene leads to decomposition to a complex mixture. In variance with these results, reaction under basic conditions with either potassium carbonate or potassium *tert*-butoxide in DMF at room temperature leads cleanly to a mixture of **14a** and **14b**. As these compounds could not be efficiently isolated because of its high insolubility, we performed an *in situ* diacetylation that allowed the isolation of the nitrocompounds **15a** and **15b** as a 3:1 mixture in a 97% yield from the nitrate **2**.



14a R= H **14b** R= H
15a R= Ac **15b** R= Ac

We believe that this is the first reported case of a phenol nitration through an intramolecular nitro transfer from a side chain, and that this procedure can find preparative interest because of its mildness and selectivity.

EXPERIMENTAL

General. All the reactions were carried out under argon, which was previously dried and deoxygenated. The solvents were purified as recommended

by D. Perrin[10], and dried immediately before using by distillation under argon over an appropriate drying agent.

Melting points were measured using a Büchi apparatus, and are uncorrected.

Infrared spectra (IR) were carried out as KBr pellets or as liquid film, using Perkin-Elmer 1420 and 180 spectrometers. Ultraviolet spectra (UV) were carried out in ethanol solution using Kontron Uvikon 820 and 810 P and Hewlett Packard 8452 A spectrophotometers. Proton magnetic resonance spectra (^{1}H NMR) were carried out in $CDCl_3$ solutions (unless otherwise stated) with tetramethylsilane as standard using a Bruker WM-250 (250 MHz) instrument. Mass spectra (MS) were recorded in a Kratos MS-50 spectrometer and a Hewlett Packard HP 59970MS quadrupolar spectrometer, employing electron impact at 70 e.v.

Methyl 3-hydroxy-4-methoxyphenylacetate (4). $SOCl_2$ (0.5 mL, 6.89 mmol) was slowly added to a solution of **3** (1.00 g, 5.49 mmol) in dry methanol (5 mL). After stirring 18 h at room temperature, water was added, and the resulting mixture was extracted with EtOAc. The organic layer was washed with aqueous $NaHCO_3$ and brine, dried ($MgSO_4$) and concentrated in the rotary evaporator. The crude was purified by flash chromatography (CH_2Cl_2-EtOAc, 95:5) on silica gel, yielding 1.04 g (97%) of methyl ester **4** as a clear oil. IR ν_{max}: 3450, 2960, 1735 (C=O), 1590, 1510, 1440 cm^{-1}. UV λ_{max}: 216, 230 (sh) and 282 nm. ^{1}H NMR δ: 6.9-6.7 (m, 3H, ArH), 5.64 (s, 1H, ArOH), 3.87 (s, 3H, -$COOCH_3$), 3.69 (s, 3H, $ArOCH_3$) and 3.53 (s, Ar-CH_2-$COOCH_3$) ppm. MS m/z (%): 196 (M^+, 61), 137 (100), 122 (29), 94 (18), 77 (5), 66 (7). Acc. mass cltd. for $C_{10}H_{12}O_4$: 196.0735; found: 196.0745.

2-Methoxy-5-(2-methoxyethenyl)phenol (9). A suspension of methoxymethyltriphenylphosphonium iodide (28.82 g, 72.56 mmol) and freshly sublimed potassium *tert*-butoxide (18.13 g, 195.8 mmol) in dry THF (150 mL) was stirred 1 h under Ar. Isovanillin (5.10 g, 33.54 mmol) was added and the resulting mixture was stirred 72 h at room temperature. A saturated aqueous solution of NH_4Cl was added, most THF was removed in the rotary evaporator and the remaining mixture was extracted with diethyl ether. The organic layer was dried ($MgSO_4$) and the solvent was removed under vacuum. CH_2Cl_2 (20 mL) and methyl iodide (20 mL) were added and the resulting solution was stirred 4 h at room temperature to eliminate the triphenylphosphine formed in the hydrolisis of

the excess of phosphonium iodide. The crude obtained after removal of the CH_2Cl_2 and the excess of methyl iodide was purified by flash chromatography (hexanes-CH_2Cl_2, 75:25) on silica gel, yielding 4.72 g (78%) of a 1:1 mixture of the *Z* and *E* isomers of enol ether **9**. IR ν_{max}: 3430, 2940, 1720, 1590, 1510, 1440 cm^{-1}. UV λ_{max}: 226, 264, 282 and 320 (sh) nm. ^1H NMR(*E* isomer) δ: 6.84 (d, J= 2.0 Hz, 1H, **H**6), 6.92 (d, J= 13.0 Hz, 1H, **H**β), 6.75 (d, J= 8.3 Hz, 1H, **H**4), 6.69 (dd, J= 8.3 and 2.0 Hz, 1H, **H**3), 5.73 (d, J= 13.0 Hz, 1H, **H**α), 5.57 (s, 1H, Ar**OH**), 3.86 (s, 3H, Ar**OCH**$_3$) and 3.65 (s, 3H, -CH=CH-**OCH**$_3$) ppm; ^1H NMR(*Z* isomer) δ: 7.30 (d, J= 2.0 Hz, 1H, **H**6), 7.02 (dd, J= 8.4 and 2.0 Hz, 1H, **H**3), 6.77 (d, J= 8.4 Hz, 1H, **H**4), 6.05 (d, J= 7.0 Hz, 1H, **H**β), 5.54 (s, 1H, Ar**OH**), 5.12 (d, J= 7.0 Hz, 1H, **H**α), 3.86 (s, 3H, Ar**OCH**$_3$) and 3.75 (s, 3H, -CH=CH-**OCH**$_3$) ppm. MS m/z (%): 180 (M^+, 100), 165 (95), 151 (7), 137 (58), 133 (51), 105 (19), 94 (26), 77 (24), 65 (25), 51 (23). Acc. mass cltd for $C_{10}H_{12}O_3$: 180.0786; found: 180.0773.

3-Hydroxy-4-methoxystyrene (13). A suspension of methyltriphenylphosphonium iodide (1.50 g, 3.71 mmol) and freshly sublimed potassium *tert*-butoxide (455 mg, 4.95 mmol) in dry THF (6 mL) was stirred 1 h under Ar. Isovanillin (206 mg, 1.33 mmol) was added, and the mixture was stirred 24 h under Ar at room temperature. A saturated aqueous NH_4Cl solution was added, most THF was removed in the rotary evaporator, and the residue was extracted with CH_2Cl_2. The organic layer was dried ($MgSO_4$) and the solvent was removed under vacuum. The crude was purified by flash chromatography (CH_2Cl_2-hexanes, 75:25) on silica gel, yielding 203 mg (100%) of the styrene **10**; mp: 55-56 °C. IR ν_{max}: 1570, 1510, 1440, 1340, 1270, 1230, 1150 cm^{-1}. UV λ_{max}: 216, 260 and 300 nm. ^1H NMR δ: 7.04 (d, J= 2.0 Hz, 1H, **H**2), 6.87 (dd, J= 8.2 and 2.0 Hz, 1H, **H**5), 6.80 (d, J= 8.2 Hz, 1H, **H**6), 6.61 (dd, J= 17.5 and 10.8 Hz, 1H, **H**α), 5.60 (d, J= 17.5 Hz, 1H, **H**β), 5.59 (s, 1H, Ar**OH**), 5.13 (d, J= 10.8 Hz, 1H, **H**β) and 3.89 (s, 3H, Ar**OCH**$_3$) ppm. MS m/z (%): 150 (M^+, 88), 135 (100), 107 (61), 81 (14), 77 (80). Acc. mass cltd. for $C_9H_{10}O_2$: 150.0681; found: 150.0675.

5-(2-Hydroxyethyl)-2-methoxyphenol (5). *Method A*: $LiAlH_4$ (1.07 g, 28.03 mmol) was added in small portions to a solution of the ester **4** (2.34g, 11.92 mmol) in dry THF (52 mL). The mixture was refluxed 12 h under

Ar. Water (1 mL), 15% aqueous NaOH (1 mL) and water (2 mL) were secuentially added dropwise. The aluminum salts were filtered and subjected to continuous extraction with EtOAc for 24 h. The combined organic layers were dried ($MgSO_4$) and the solvent was removed under vacuum. The crude was purified by flash chromatography (CH_2Cl_2-EtOAc, 9:1) on silica gel, yielding 1.46 g (73%) of the alcohol **5**; mp: 72-73 °C. IR ν_{max}: 3450, 2950, 1580, 1530, 1430, 1250, 1160, 1130 cm^{-1}. UV λ_{max}: 206, 224 (sh), 280 and 288 (sh) nm. ^1H NMR δ: 6.8-6.6 (m, 3H, Ar**H**), 5.64 (br s, 1H, Ar**OH**), 3.87 (s, 3H, ArO**CH**$_3$), 3.82 (t, J= 6.5 Hz, 2H, Ar-CH_2-**CH**$_2$OH) and 2.77 (t, J= 6.5 Hz, 2H, Ar-**CH**$_2$-CH_2OH) ppm. MS m/z (%): 168 (M^+, 43), 154 (5), 137 (100), 122 (24), 94 (16), 77 (9), 65 (9). Acc. mass cltd. for $C_9H_{12}O_3$: 168.0786; found: 168.0783.

Method B: A mixture of the enol ether **9** (799 mg, 4.44 mmol), $Hg(OAc)_2$ (1.71 g, 5.35 mmol), CH_3CN (16 mL) and water (16 mL) was stirred 3 h at room temperature. The solvents were removed by freeze drying and the resulting solid organomercuric was suspended in EtOH (3 mL). $NaBH_4$ (420 mg, 11.05 mmol) was added in small portions, and the mixture was stirred 2 h at room temperature. Silica gel (2 g) was added, the solvent was removed in the rotary evaporator, and the resulting solid was loaded on a flash chromatography column. After elution (CH_2Cl_2-EtOAc, 85:15) 358 mg (48% yield) of the alcohol **5** and 198 mg (28% yield) of the ether **10** were obtained. The data for this later product are: IR ν_{max}: 3375, 2940, 1595, 1510, 1440, 1275 cm^{-1}. UV λ_{max}: 218 (sh), 240 and 280 nm. ^1H NMR (Py-d_5) δ: 7.23 (dd, J= 8.2 and 2.0 Hz, 2H, **H**4), 6.99 (d, J= 8.2 Hz, 2H, **H**5), 5.26 (t, J= 6.0 Hz, 2H, ArCH$_2$**CH**(Ar)-O-), 4.19 (d, J= 6.0 Hz, 4H, Ar**CH**$_2$CH(Ar)-O-) and 3.74 (s, 6H, ArO**CH**$_3$) ppm. MS m/z (%): 314 (M^+, 23), 283 (18), 271 (8), 211 (6), 177 (39), 167 (100), 150 (39), 137 (62), 107 (34), 79 (30). Acc. mass cltd. for $C_{18}H_{18}O_5$: 314.1154; found: 314.1166.

Method C: A 0.36 M solution of BH_3·THF in THF (58 mL, 20.88 mmol) was added dropwise during 45 min to a stirred cooled (ice-water bath) solution of the styrene **13** (3.14 g, 20.92 mmol) in dry THF (5 mL). After 3 h of stirring at room temperature under Ar, the mixture was cooled (ice-water bath) and water (1 mL) was added. After 10 min 10% aqueous NaOH (8.5 mL) was added and the mixture was allowed to reach room temperature. 8.5 mL of 30% H_2O_2 (8.5 mL) was added and the resulting mixture was stirred 0.5 h at room temperature and 1 h

at 50-60 °C. Aqueous NH_4Cl was added and the mixture was extracted with Et_2O. The organic layer was dried ($MgSO_4$) and the solvent was removed under vacuum. Flash chromatography (CH_2Cl_2-EtOAc, 75:25) on silica gel yielded the alcohol **5** (2.72 g, 77% yield).

2-Methoxy-5-(2-chloroethyl)phenol (**6**). A solution of the alcohol **5** (524 mg, 3.12 mmol) and triphenylphosphine (1.04 g, 4.10 mmol) in CCl_4 (2 mL, 20.63 mmol) was refluxed 4 h under Ar. Water was added and the resulting mixture was extracted with CH_2Cl_2. The organic layer was dried ($MgSO_4$) and concentrated. The crude was purified by flash chromatography (CH_2Cl_2) on silica gel, yielding 565 mg (97%) of the chloride **6**; mp: 51-52 °C. IR ν_{max}: 3390 (OH), 1590, 1515, 1455, 1445 cm^{-1}. UV λ_{max}: 209, 230 and 282 nm. ^1H NMR δ: 6.82-6.79 (m, 2H, **H**3 and **H**4), 6.71 (dd, J= 8.3 and 2.0 Hz, 1H, **H**6), 5.66 (br s, 1H, ArO**H**), 3.88 (s, 3H, Ar-OC**H**$_3$), 3.68 (t, J= 7.5 Hz, 2H, Ar-CH_2-C**H**$_2$Cl) and 2.98 (t, J= 7.5 Hz, 2H, Ar-C**H**$_2$-CH_2Cl) ppm. MS m/z (%): 188 (M^+, 7.5), 186 (M^+, 23), 149 (8), 137 (100), 122 (7.5), 111 (5), 97 (8), 91 (5), 81 (6), 79 (4), 69 (17). Acc. Mass cltd. for $C_9H_{11}{}^{35}ClO_2$: 186.0447; found: 186.0448.

2-Methoxy-5-(2-iodoethyl)phenol (**7**). *Method A:* NaI (1.44 g, 9.63 mmol) was added to a solution of the chloride **6** (565 mg, 3.03 mmol) in dry acetone (10 mL). The resulting suspension was refluxed 24 h. Most of the acetone was removed under vacuum, CH_2Cl_2 was added and the resulting suspension was filtered. The filtrate was dried ($MgSO_4$) and concentrated, yielding 821 mg (97%) of the iodide **7**; mp: 93-95 °C. IR ν_{max}: 3370 (OH), 1590, 1515, 1445, 1275, 1170 cm^{-1}. UV λ_{max}: 213, 234 (sh) and 282 nm. ^1H NMR δ: 6.81-6.76 (m, 2H, **H**3 and **H**4), 6.66 (dd, J= 8.2 and 2.1 Hz, 1H, **H**6), 5.59 (br s, 1H, ArO**H**), 3.87 (s, 3H, Ar-OC**H**$_3$), 3.31 (t, J= 7.7 Hz, 2H, Ar-CH_2-C**H**$_2$I) and 3.07 (t, J= 7.7 Hz, 2H, Ar-C**H**$_2$-CH_2I) ppm. MS m/z (%): 278 (M^+), 151 (100), 137, 119, 107, 91, 77. Acc. mass cltd. for $C_9H_{11}IO_2$: 278.9806; found: 278.9803.

Method B: Iodine (116 mg, 0.46 mmol) was added to a cooled (ice-water) solution of alcohol **5** (54 mg, 0.32 mmol), triphenylphosphine (109 mg, 0.42 mmol) and imidazole (32 mg, 0.47 mmol) in dry CH_3CN (0.3 mL) and Et_2O (0.5 mL). After stirring at 0 °C for 3 h, c.a. 6 mL of Et_2O was added and the

resulting solution was washed with saturated aqueous solutions of $Na_2S_2O_3$, $CuSO_4$ and NaCl, dried ($MgSO_4$) and concentrated. The crude was purified by flash chromatography (CH_2Cl_2-hexanes, 75:25) on silica gel, giving 80 mg (90% yield) of the iodide **7**.

2-Methoxy-5-(2-nitratoethyl)phenol (2). $AgNO_3$ (1.30 g, 7.62 mmol) was added to a solution of the iodide **7** (821 mg, 2.95 mmol) in dry CH_3CN (15 mL). The reaction mixture was protected from light and stirred under Ar at room temperature for 48 h. The resulting precipitate was filtered off, water was added, and the mixture was extracted with CH_2Cl_2. The organic layer was dried ($MgSO_4$) and concentrated. Flash chromatography of the crude (silica gel, CH_2Cl_2-hexanes, 75:25) yielded 583 mg (93%) of the nitrate ester **2** as a colorless oil. IR ν_{max}: 3530 (OH), 1630, 1595, 1515, 1445, 1280 cm^{-1}. UV λ_{max}: 208, 224 (sh) and 280 nm. ^1H NMR δ: 6.82-6.79 (m, 2H, **H**3 and **H**4), 6.70 (dd, J= 8.2 and 2.1 Hz, 1H, **H**6), 5.64 (br s, 1H, ArO**H**), 4.60 (t, J= 7.1 Hz, 2H, Ar-CH_2-CH_2ONO_2), 3.88 (s, 3H, Ar-OCH_3) and 2.93 (t, J= 7.1 Hz, 2H, Ar-CH_2-CH_2ONO_2) ppm. MS m/z (%): 213 (M^+), 152, 137 (100), 122, 107, 94, 91, 77. Acc. mass cltd. for $C_9H_{11}NO_5$: 213.0637; found: 213.0634.

2-(5-Acetyl-4-methoxy-2-nitrophenyl)ethyl acetate (15a) and **2-(3-acetyl-4-methoxy-2-nitrophenyl)ethyl acetate (15b).** Potassium *tert*-butoxide (24 mg, 0.26 mmol) was added to a solution of alkyl nitrate **2** (34 mg, 0.16 mmol) in dry DMF (2 mL) . The resulting suspension was stirred 24 h at room temperature; pyridine (1 mL) and acetic anhydride (1 mL) were added, and the reaction mixture was stirred again for 24 h at room temperature. Water was added, and the mixture was extracted with CH_2Cl_2. The organic layer was washed with saturated aqueous solutions of $CuSO_4$ and NaCl; dried (Na_2SO_4) and concentrated. The crude was purified by preparative thin layer chromatography (CH_2Cl_2-EtOAc, 95:5) on silica gel, giving 46 mg (97% yield) of a 3:1 mixture of the nitrocompounds **15a** and **15b** as a liquid. IR ν_{max}: 2950, 1775, 1740, 1530, 1365, 1280 cm^{-1}. UV λ_{max}: 216, 236 (sh), 274 and 326 nm. ^1H NMR (**15a**) δ: 7.61 (s, 1H, **H**3), 7.04 (s, 1H, **H**6), 4.34 (t, J= 6.5 Hz, 2H, Ar-CH_2-CH_2OAc), 3.90 (s, 3H, Ar-OCH_3), 3.20 (t, J= 6.5 Hz, 2H, Ar-CH_2-CH_2OAc), 2.34 (s, 3H, Ar-$COCH_3$) and 2.01 (s, 3H, -CH_2-$COCH_3$) ppm. ^1H NMR (**15b**) δ:

7.18 (d, J = 8.7 Hz, 1H, **H** 3), 7.06 (d, J= 7.7 Hz, 1H, **H** 6), 4.25 (t, J= 6.6 Hz, 2H, Ar-CH_2-CH_2OAc), 3.87 (s, 3H, Ar-OCH_3), 2.92 (t, J= 6.6 Hz, 2H, Ar-CH_2-CH_2OAc), 2.29 (s, 3H, Ar-$COCH_3$) and 2.02 (s, 3H, -CH_2-$COCH_3$) ppm. MS m/z (%): 297 (M^+, 5), 255 (6), 237 (57), 195 (92), 178 (77), 166 (56), 152 (100), 138 (23), 124 (45), 96 (26), 77 (11). Acc. mass clcd. for $C_{13}H_{15}NO_7$: 297.0848; found: 297.0874.

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