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Enantioselective Michael addition of 2-nitropropane to chalcone analogues catalyzed by chiral azacrown ethers based on α-D-glucose and D-mannitol

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Abstract—The chiral monoaza-15-crown-5 type lariat ethers **1** and **2** derived from α-D-glucose and from D-mannitol, respectively, have been applied as phase transfer catalysts in the enantioselective Michael addition of 2-nitropropane to aromatic **3b–c** and heteroaromatic **3d–h** chalcone analogues. Among the catalysts, the glucose-based **1c** with a phosphinoxidobutyl side arm proved to be the most effective, it inducing 34% e.e. for **4b**, 59% e.e. for **4c**, 80% e.e. for **4d**, 64% e.e. for **4e**, 17% e.e. for **4f**. Catalyst **1a** having 3-hydroxypropyl substituent resulted in 81% e.e. for compound **4g**. The formation of the (+)-(*S*)-enantiomer of **4** was preferred using crown ethers **1a–c**, while the (−)-(*R*)-enantiomer was in excess with catalyst **2**. The absolute configuration of the Michael adduct **4d** was determined by single-crystal X-ray analysis.

1. Introduction

Due to its relevance in the synthesis of biologically active compounds, much effort has been directed into carrying out the Michael addition of carbon nucleophiles to conjugated enones stereoselectively. The stereoselective variants of the addition of enolates or their analogues to the carbon–carbon double bond of α,β-unsaturated ketones and aldehydes in the presence of chiral catalysts have been extensively investigated recently.[1] Serious efforts have been devoted to develop efficient catalysts for the enantioselective additions of nitroalkanes to enones. The reaction of nitroalkanes with chalcone catalyzed by chiral ammonium salts,[2a,b] quinine,[2c] L-proline,[2d–f] Ni(II) complexes,[3a] La-BINOL complexes[3b] and Al complexes of amino alcohols[3c] have been described. Recently, Corey et al. reported the enantioselective Michael addition of nitromethane to 4-chlorobenzylideneacetophenone catalyzed by a chiral cinchoninium salt as a phase transfer catalyst.[3d]

One of the most recent and interesting techniques in catalytic asymmetric synthesis is the phase transfer reaction in which the enantioselectivity is generated by a chiral crown ether catalyst.[1] A special group of optically active crown ethers contains carbohydrate moieties as the source of chirality. Although a number of chiral crown ethers have been prepared from monosaccharides,[4] only a few have been successfully used as catalysts in asymmetric reactions.[5] Recently, we have reported the asymmetric Michael addition of 2-nitropropane to chalcone **3a** catalyzed by glucose-based chiral lariat ethers of type **1** and crown ether **2** derived from D-mannitol (Scheme 1). It was observed that the substituents (alkyl-, arylalkyl-, alkoxy- and phosphonoalkyl groups) on the nitrogen atom in catalyst **1** and **2** had a significant effect on both the yield and the enantioselectivity of the 1,2-addition reaction.[6] The length of the chain connecting the nitrogen atom to the $P(O)Ph_2$ moiety had a major influence on the asymmetric induction.[6d,7a]

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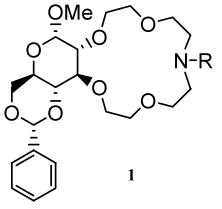
Herein, it is shown how the asymmetric induction in the reaction of chalcones and 2-nitropropane is affected by the β-aryl substituents. We wished to evaluate how the different aryl (e.g. naphthyl) and heteroaromatic (e.g. furyl and thiophenyl) substituents in **3a** influence the outcome of the addition.

2. Results and discussion

The addition of 2-nitropropane to aromatic and heteroaromatic chalcone analogues was investigated under phase transfer catalytic conditions in the presence of azacrowns **1** and **2** (Scheme 1). In our experiments, lariat ethers **1a–c** containing a hydroxypropyl-, methoxypropyl- or a phosphinoxidobutyl-substituent[6b,7a] and **2** with a hydroxypropyl-group[7b] on the nitrogen atom, were assayed since they gave the best results in the earlier examinations. The α,β-unsaturated ketones **3b–f** and **3h–i** were prepared according to a procedure described in the literature[8–14] except in the case of **3g** with a pyridyl group where the original method had to be modified (see Section 3).[15] The Michael addition was carried out in a solid-liquid system; using toluene, 35 mol% of sodium *tert*-butoxide and 7 mol% of the chiral catalyst **1a–c** or **2** at 22°C. After obtaining the products by preparative TLC, the asymmetric inductions expressed in terms of enan-

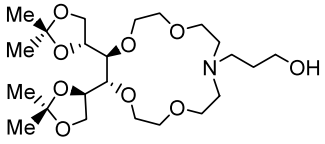


1

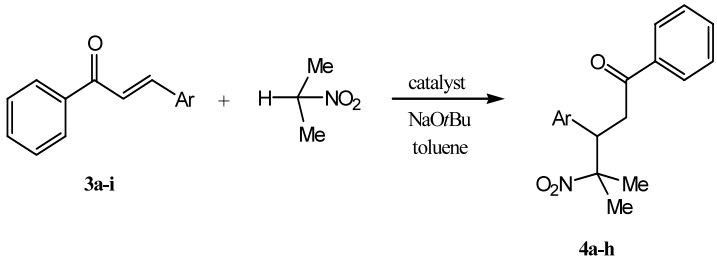
1a R = $(CH_2)_3OH$

1b R = $(CH_2)_3OMe$

1c R = $(CH_2)_4P(O)Ph_2$



2



3a-i

4a-h

Compound	Ar	Compound	Ar
a		**e**	
b		**f**	
c		**g**	
d		**h**	
		i	

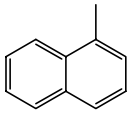
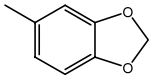
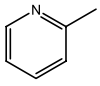
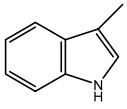
Scheme 1.

tiomeric excess (e.e.%) were determined by ^{1}H NMR spectroscopy in the presence of the chiral shift reagent (+)-Eu(hfc)$_3$.

The most important results are listed in Table 1. As a comparison, the earlier results obtained with chalcone **3a** (R = Ph) are also included: azacrown **1a**, **1b** and **1c** induced an e.e. of 85, 87 and 94%, respectively, in favor of the (+)-(*R*)-antipode of Michael adduct **4a**,[6b–e] while applying azacrown **2**, the (–)-(*S*) enantiomer was in an excess of 40%.[7b]

The change of the phenyl ring to a naphthyl group in chalcone **3** (**3a**→**3b**) resulted in a decreased asymmetric induction during the formation of **4b**. Using catalysts **1** and **2**, the e.e. was 23–34 and 14%, respectively. The best results were obtained applying lariat ether **1c** with a phosphinoxidobutyl side arm (34% e.e. in favor of the (+)-antipode). Product **4c** with pyperonyl substituent was obtained in somewhat better enantioselectivities, the use of crown ethers **1** and **2** led to e.e. values of 48–59 and 29%, respectively. Again catalyst **1c** gave the best results (59% e.e.). As the naphthyl- and pyperonyl groups are sterically demanding, the decrease in the enantioselectivity may be the consequence of steric effects. Comparing the results obtained with the chalcones containing heterocyclic substituents **3d**–**f**, it can be seen that the best enantioselectivities were obtained in the case of the furyl substituent **d**. During the formation of **4d**, catalysts **1** and **2** generated e.e. values

Table 1. Asymmetric Michael reaction of 2-nitropropane with aromatic and heteroaromatic chalcone analogues[a] mediated by chiral azacrown ethers **1** and **2**

Entry	Michael adduct		Catalyst	Time (h)	Yield (%)[b]	$[\alpha]_D$[c]	E.e. (%)[d]
	Compd.	Ar					
1	**4b**		**1a**	89	51	+ 84.1	32
2	**4b**		**1b**	100	41	+ 61.3	23
3	**4b**		**1c**	144	46	+ 89.5	34
4	**4b**		**2**	110	35	- 36.9	14
5	**4c**		**1a**	72	57	+ 37.8	48
6	**4c**		**1b**	96	60	+ 40.3	52
7	**4c**		**1c**	96	62	+ 46.8	59
8	**4c**		**2**	96	52	- 22.5	29
9	**4d**		**1a**	72	57	+ 38.3	61 (S)
10	**4d**		**1b**	70	61	+ 40.8	65 (S)
11	**4d**		**1c**	70	56	+ 49.6	80 (S)
12	**4d**		**2**	70	34	- 14.0	22 (R)
13	**4e**		**1a**	144	72	+ 52.5	47
14	**4e**		**1b**	168	63	+ 41.2	38
15	**4e**		**1c**	144	52	+ 70.8	64
16	**4e**		**2**	120	43	- 21.0	19
17	**4f**		**1a**	168	21	+ 23.0	12
18	**4f**		**1c**	120	25	+ 32.5	17
19	**4g**		**1a**	3	90	+ 121.6	81
20	**4g**		**1b**	4	88	+ 105.3	70
21	**4g**		**1c**	4	85	+ 103.2	69
22	**4g**		**2**	8	75	- 36.4	24
23	**4h**		**1a**	240	15	+ 6.2	4

[a] Michael adduct **4a** (Ar = Ph) was obtained in following e.e. % values applying catalyst **1a-c** and **2**: 85 % (**1a**), 87 % (**1b**), 94 % (**1c**), 40 % (**2**) (lit. 6.); [b] Based on substrate isolated by preparative TLC; [c] In CH_2Cl_2 at 22°C; [d] Determined by ^{1}H NMR spectroscopy.

of 61–80 and 22%, respectively. With the thiophenyl substituent **e**, the e.e. values were significantly lower (38–64% with azacrowns **1** and 19% with species **2**), while the introduction of a pyrrole substituent **f** gave the worst results (12–17% e.e. with catalysts **1**). In the last three cases **4d–f**, the lariat ether with a phosphinoxidobutyl side arm **1c** induced the maximum e.e. values (80, 64 and 17%, respectively). It can be seen that in the case of the furyl-, thiophenyl- and the pyrrole substituted model compounds **3d–f**, the heteroatomic unit (O, S or NH) has a dramatic impact on the enantioselectivity. Obviously, electronic rather than steric factors seem to be responsible for the outcome of the Michael additions, although the effect of other characteristics, such as the lipophility and the solubility should also be considered.

As compared to the reaction of the pyrrole substituted chalcone **3f**, the e.e. values were significantly higher for the Michael addition of 2-nitropropane to the pyridylchalcone **3g**; applying azacrowns **1**, the e.e. value was 69–81%, while with crown **2**, the e.e. was 24% (entries 19–22). It is also noteworthy that the reaction time decreased to 3 and 8 h, respectively, and that the most efficient catalyst was lariat ether **1a** with a hydroxypropyl substituent (e.e. = 81%). Since the enantioselectivity is better with a pyridyl, than with a pyrrole substituent (**f** versus **g**), steric factors seem to be decisive in these cases (entries 17–18).

The reaction of the indolyl-chalcone **3h** was sluggish and the enantioselectivity was poor (entry 23). The morpholyl substituted model **3i** resisted reaction with 2-nitropropane and hence this case has not been listed in Table 1.

Comparing the catalytic effect of the glucose and the mannitol based lariat ethers, **1** and **2**, respectively, one can see that while compounds **1** induce the formation of the (+)-antipode, species **2** brings about excess of the (−)-antipode. The selectivity was markedly lower in the second case (entries 4, 8, 12, 16 and 22). This is presumably connected with the relative configuration of the monosaccharides in the crown ether, which is (2*R*,3*S*) in D-glucose and (3*S*,4*R*) in D-mannitol. While the azacrown moiety is identical in catalysts **1** and **2**, the sugar component is different. An important difference is that macrocycle **2** is more flexible than **1**, i.e. while **1** is rather rigid due to the anellation with the sugar ring, **2** is not blocked by an anellation. It is well-known that a rigid molecule is generally more suitable for enantiomeric discrimination than a flexible one. It can also be seen that the side arms of lariat ethers **1** and **2** have a significant impact on the asymmetric induction and on the yield. With one exception **4g**, the lariat ethers with a phosphinoxidobutyl substituent gave the best results, in the case of product **4g**, catalyst **1a** proved to be the best (e.e. = 81%). The results obtained for the reaction of unsubstituted chalcone **3a** could not be reproduced for the substituted derivatives **3b–h**.

The energetically favorable azacrown-sodium ion complex accompanied by the anion formed from nitropropane is probably somehow stabilized by the bending, e.g. phosphinoxidoalkyl group. The oxygen and/or phosphorus heteroatoms may play an important role in stabilizing the transient species. The steric influence of the aryl and heteroaromatic groups may also have an impact on the complexation.

It can be seen that with the aryl and heteroaromatic substituted model compounds **3b–h**, the enantioselectivity is more or less decreased. It is not certain whether steric or electronic effects of the substituents are more important from the point of view asymmetric induction. The situation may be complicated by the possible retro-Michael addition reaction and by deracemization modifying the outcome of the asymmetric induction.

In some cases, pure enantiomers were obtained by fractional crystallization. The specific rotations obtained in dichloromethane at 22°C are as follows: $[\alpha]_D = +79.3$ for **4c**, $[\alpha]_D = +62.8$ for **4d**, $[\alpha]_D = +110.6$ for **4e**, $[\alpha]_D = +150.1$ for **4g**.

The structure of pure enantiomer (+)-**4d** was established by single-crystal X-ray diffraction which shows that the absolute configuration of the Michael adduct is (*S*)-**6d**. The racemic mixture crystallizes in the centrosymmetric space group $P2_1/c$ (see Figure 1).

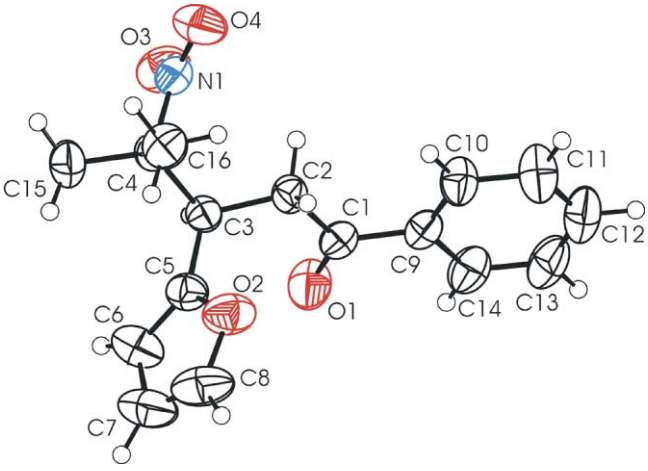


Figure 1. The ORTEP drawing of the structure of **4d**.

3. Experimental

3.1. General procedures

Melting points were determined using a Büchi 510 apparatus and are uncorrected. The specific rotation was measured on a Perkin–Elmer 241 polarimeter at 22°C, while the IR spectra were recorded on a Perkin–Elmer 237 spectrophotometer. NMR spectra were obtained on a Brucker DRX-500 instrument in $CDCl_3$. Mass spectra were obtained on a Varian MAT 312 instrument. Elemental analyses were determined on a Perkin–Elmer 240 automatic analyzer. Analytical and

preparative thin layer chromatography was performed on silica gel plates (60 GF-254, Merck), while column chromatography was carried out using 70–230 mesh silica gel (Merck). The shift reagent was $Eu(hfc)_3$ (Aldrich Chem. Co.).

3.1.1. Preparation of heteroaromatic chalcones. Compounds **3b**, **3c**, **3d**, **3e**, **3f**, **3h**, **3i** were prepared according to the literature procedures: 3-naphthalen-1-yl-1-phenyl-propenone,[8] 3-benzo[1,3]dioxol-5-yl-1-phenyl-propenone,[9] 3-furan-2-yl-1-phenyl-propenone,[10] 1-phenyl-3-thiophen-2-yl-propenone,[11] 1-phenyl-3-(1*H*-pyrrol-2-yl)-propenone,[12] 3-(1*H*-indol-3-yl)-1-phenyl-propenone,[13] 3-morpholin-4-yl-1-phenyl-propenone.[14]

3.1.2. Synthesis of 1-phenyl-3-pyridin-2-yl-propenone 3g by a modified literature method.[15] 40 mL of 10% aqueous sodium hydroxide solution and 3 mL of methanol were added to a flask and the mixture was cooled to 0–10°C with stirring. 12.4 mL (0.13 mol) of pyridine-2-carboxaldehyde was added in one portion. 7.6 mL (0.065 mol) of acetophenone was then added in small portions over a period of an hour maintaining the temperature at around 10°C. The contents of the flask were stirred for 5 h and the reaction mixture was poured onto 50 mL of water. The resulting solid was filtrated and washed with 20 mL of water. The solid was then dried and recrystallized three times from ethanol to give 10.6 g (78%) of product **3g**; mp 60–61°C; ^{1}H NMR ($CDCl_3$) δ: 7.30 (t, 1H, CHPhH-*m*), 7.50 (m, 3H, COPhH-*m* and CHPhH-*m*), 7.60 (t, 1H, COPhH-*p*), 7.75 (m, 2H, CHPhH-*o*,*p*), 8.11 (m, 3H, COPhH-*o* and CH), 8.69 (dd, J=4.2 Hz, 1H); MS(FAB) m/z 210 ($M+H^+$). Anal. calcd for $C_{14}H_{11}NO$: C, 80.38; H, 5.26. Found: C, 80.60; H, 5.22%.

3.2. General procedure for the Michael addition of 2-nitropropane to aryl and heteroaromatic chalcones in the presence of glucose-based azacrown ethers

The corresponding azacrown ether (0.1 mmol) and sodium *tert*-butoxide (0.05 g, 0.5 mmol) was added to a solution of chalcone (1.44 mmol) and 2-nitropropane (0.3 mL, 3.36 mmol) in dry toluene (3 mL). The mixture was stirred under argon at rt. After a reaction time of 3–168 h, a new portion of toluene (7 mL) was added and the mixture stirred with water (10 mL). The organic phase was washed with water and dried (Na_2SO_4). The crude product obtained after evaporating the solvent was purified by preparative TLC (silica gel, hexane:ethyl acetate, 10:1, eluent) to give pure adducts **4b**–**h**.

3.2.1. 4-Methyl-3-naphthalen-2-yl-4-nitro-1-phenyl-pentan-1-one, 4b. Yield: 51%; $[\alpha]_{22}^{D}$ +84.1 (*c* 1, CH_2Cl_2), 32% e.e.; IR (KBr), *v* 3000, 1689, 1590, 1531, 1454, 1341, 1238, 765, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.47 (s, 3H), 1.66 (s, 3H), 3.45 (dd, J_{gem}=17.4, 3.2 Hz, 1H), 3.86 (dd, J_{gem}=17.4, 10.2 Hz, 1H), 5.28 (dd, 1H), 7.33–7.38 (m, 5H, naphthalene-CH), 7.50 (t, 2H, COPhH-*m*), 7.61 (t, 1H, COPhH-*p*), 7.76 (d, 1H, naphthalene-CH), 7.82 (d, 2H, COPhH-*o*), 8.47 (d, 1H, naphthalene-CH); MS(FAB) m/z 350 ($M+H^+$). Anal. calcd for $C_{22}H_{23}NO_3$: C, 75.65; H, 6.59. Found: C, 75.38; H, 6.64%.

3.2.2. 3-Benzo[1,3]dioxol-5-yl-4-methyl-4-nitro-1-phenyl-pentan-1-one, 4c. Yield: 62%; mp 92°C; $[\alpha]_{22}^{D}$ +46.8 (*c* 1, CH_2Cl_2), 59% e.e.; IR (KBr), *v* 3441, 1687, 1597, 1580, 1534, 1489, 1448, 1345, 1253, 1039, 748, 689 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.47 (s, 3H), 1.55 (s, 3H), 3.14 (dd, J_{gem}=17.1, 3.2 Hz, 1H), 3.53 (dd, J_{gem}=17.1, 10.6 Hz, 1H), 3.98 (dd, 1H), 5.83 (s, 2H), 6.58–6.63 (m, 3H, CHPhH), 7.35 (t, 2H, COPhH-*m*), 7.47 (t, 1H, COPhH-*p*), 7.79 (d, 2H, COPhH-*o*); MS(FAB) m/z 342 ($M+H^+$). Anal. calcd for $C_{19}H_{19}NO_5$: C, 66.86; H, 5.57. Found: C, 66.51; H, 5.63%.

3.2.3. 3-Furan-2-yl-4-methyl-4-nitro-1-phenyl-pentan-1-one, 4d. Yield: 83%; mp 79–80°C; $[\alpha]_{22}^{D}$ +49.6 (*c* 1, CH_2Cl_2), 80% e.e.; IR (KBr), *v* 3447, 1681, 1596, 1539, 1450, 1397, 1380, 1346, 1231, 1149, 1016, 766, 750, 691 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.57 (s, 3H), 1.67 (s, 3H), 3.05 (dd, J_{gem}=17.0, 2.9 Hz, 1H), 3.69 (dd, J_{gem}=17.0, 10.8 Hz, 1H), 4.34 (dd, 1H), 6.19 (d, 1H, furane-CH), 6.27 (t, 1H, furane-CH), 7.29 (d, 1H, furane-CH), 7.44 (t, 2H, COPhH-*m*), 7.55 (t, 1H, COPhH-*p*), 7.89 (d, 2H, COPhH-*o*); MS(FAB) m/z 288 ($M+H^+$). Anal. calcd for $C_{16}H_{17}NO_4$: C, 66.90; H, 5.92. Found: C, 66.76; H, 5.97%.

3.2.4. 4-Methyl-4-nitro-1-phenyl-3-thiophen-2-yl-pentan-1-one, 4e. Yield: 81%; mp 107°C; $[\alpha]_{22}^{D}$ +70.8 (*c* 1, CH_2Cl_2), 64% e.e.; IR (KBr), *v* 3447, 1680, 1596, 1528, 1447, 1399, 1380, 1348, 1233, 848, 743, 710, 684 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.60 (s, 3H), 1.71 (s, 3H), 3.18 (dd, J_{gem}=17.1, 2.8 Hz, 1H), 3.63 (dd, J_{gem}=17.1, 10.6 Hz, 1H), 4.54 (dd, 1H), 6.92 (m, 2H, thiophene-CH), 7.16 (d, 1H, thiophene-CH), 7.44 (t, 2H, COPhH-*m*), 7.55 (t, 1H, COPhH-*p*), 7.87 (d, 2H, COPhH-*o*); MS(FAB) m/z 304 ($M+H^+$). Anal. calcd for $C_{16}H_{17}NO_3S$: C, 63.37; H, 5.61. Found: C, 63.11; H, 5.66%.

3.2.5. 4-Methyl-4-nitro-1-phenyl-3-(1*H*-pyrrol-2-yl)-pentan-1-one, 4f. Yield: 21%; $[\alpha]_{22}^{D}$ +23.0 (*c* 1, CH_2Cl_2), 12% e.e.; IR (KBr), *v* 3408, 1683, 1596, 1533, 1457, 1343, 1217, 1010, 847, 744, 689 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.58 (s, 3H), 1.69 (s, 3H), 3.12 (dd, J_{gem}=17.1, 2.7 Hz, 1H), 3.59 (dd, J_{gem}=17.1, 10.5 Hz, 1H), 4.26 (dd, 1H), 5.97 (s, 1H, pyrrole-CH), 6.07 (m, 1H, pyrrole-CH), 6.65 (d, 1H, pyrrole-CH), 7.44 (t, 2H, COPhH-*m*), 7.56 (t, 1H, COPhH-*p*), 7.88 (d, 2H, COPhH-*o*); MS(FAB) m/z 287 ($M+H^+$). Anal. calcd for $C_{16}H_{18}N_2O_3$: C, 67.13; H, 6.29. Found: C, 67.38; H, 6.23%.

3.2.6. 4-Methyl-4-nitro-1-phenyl-3-pyridin-2-yl-pentan-1-one, 4g. Yield: 90%; $[\alpha]_{22}^{D}$ +121.6 (*c* 1, CH_2Cl_2), 81% e.e.; IR (KBr), *v* 3448, 1680, 1594, 1535, 1447, 1400, 1374, 1341, 1238, 1001, 846, 760, 694 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.55 (s, 3H), 1.77 (s, 3H), 3.11 (dd, J_{gem}=17.3, 2.0 Hz, 1H), 4.24 (dd, J_{gem}=17.3, 10.7 Hz, 1H), 4.35 (dd, 1H), 7.15 (t, 1H, pyridine-CH), 7.38 (d, 1H, pyridine-CH), 7.44 (t, 2H, COPhH-*m*), 7.55 (t, 1H, pyridine-CH), 7.64 (t, 1H, COPhH-*p*), 7.91 (d, 2H,

COPhH-*o*), 8.48 (d, 1H, pyridine-CH); MS(FAB) *m*/*z* 299 ($M+H^+$). Anal. calcd for $C_{17}H_{18}N_2O_3$: C, 68.46; H, 6.04. Found: C, 68.71; H, 5.99%.

3.2.7. 3-(1*H*-Indol-5-yl)-4-methyl-4-nitro-1-phenyl-pentan-1-one, 4h. Yield: 31%; $[\alpha]_{22}^{D}$ +6.2 (*c* 1, CH_2Cl_2), 3% e.e.; IR (KBr), *v* 3409, 1683, 1596, 1533, 1457, 1344, 1217, 1011, 847, 744, 689 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 1.57 (s, 3H), 1.66 (s, 3H), 3.11 (dd, J_{gem}= 17.0, 2.7 Hz, 1H), 3.60 (dd, J_{gem}=17.0, 10.6 Hz, 1H), 4.26 (dd, 1H), 6.66 (s, 1H, indole-CH), 7.14 (t, 2H, indole-CH), 7.23 (d, 2H, indole-CH), 7.43 (t, 2H, COPhH-*m*), 7.56 (t, 1H, COPhH-*p*), 7.89 (d, 2H, COPhH-*o*); MS(FAB) *m*/*z* 337 ($M+H^+$). Anal. calcd for $C_{20}H_{20}N_2O_3$: C, 71.43; H, 5.95. Found: C, 71.59; H, 5.91%.

3.2.8. X-Ray structure analysis of 4d. Single-crystal X-ray diffraction data of **4d** (mounted on a glass fiber): $C_{16}H_{17}NO_4$, Fwt.: 287.31, colorless needle, size: 0.07× 0.1×0.4 mm, monoclinic, space group $P2_1/c$ (no. 14.), a=10.850(1) Å, b=12.760(1) Å, c=11.238(1)Å, β= 105.37(1)°, V=1500.13 $Å^3$, from least-squares fit of the setting angles of 25 ($24.98 \le \theta \le 46.61°$) reflections, T=293(2) K, Z=4, $F(000)$=608, D_x=1.272 Mg/m^3, μ=0.757 mm^{-1}, intensity data were collected on an Enraf–Nonius CAD4 diffractometer (graphite monochromator) using $\omega/2\theta$ scans (Cu-$K\alpha$ radiation, λ=1.54180 Å) at 293(2) K, total of 3422 reflections ($4.23 \le \theta \le 75.94°$), of which 3101 unique [$R_{(int)}$= 0.0091]; 2179 reflections $I>2\sigma(I)$. Empirical absorption correction was applied, initial structure model by direct methods. Anisotropic full-matrix least-squares refinement on F^2 for all non-hydrogen atoms yielded R_1=0.0381 and wR_2=0.1154 for 2197 [$I>2\sigma(I)$] and R_1=0.0629 and wR_2=0.1231 for all (3101) intensity data. (Goodness-of-fit=1.084, max./min. residual electron density in the final d.e.d. map was 0.17 and −0.20 e $Å^{-3}$. Hydrogen atoms were included in structure factor calculations but they were not refined. The isotropic displacement parameters of the hydrogen atoms were approximated from the U(eq) value of the atom they were bonded to. Programs used in the crystallographic analysis were: XCAD4,[16] SHELXS-97,[17] SHELXL-97,[18] PLATON,[19] PXX.[20] CCDC number is 155923.

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