AMINE *N*-OXIDES DERIVED FROM ALKALOIDS AS CHIRAL PROMOTERS IN ENANTIOSELECTIVE PAUSON-KHAND REACTIONS

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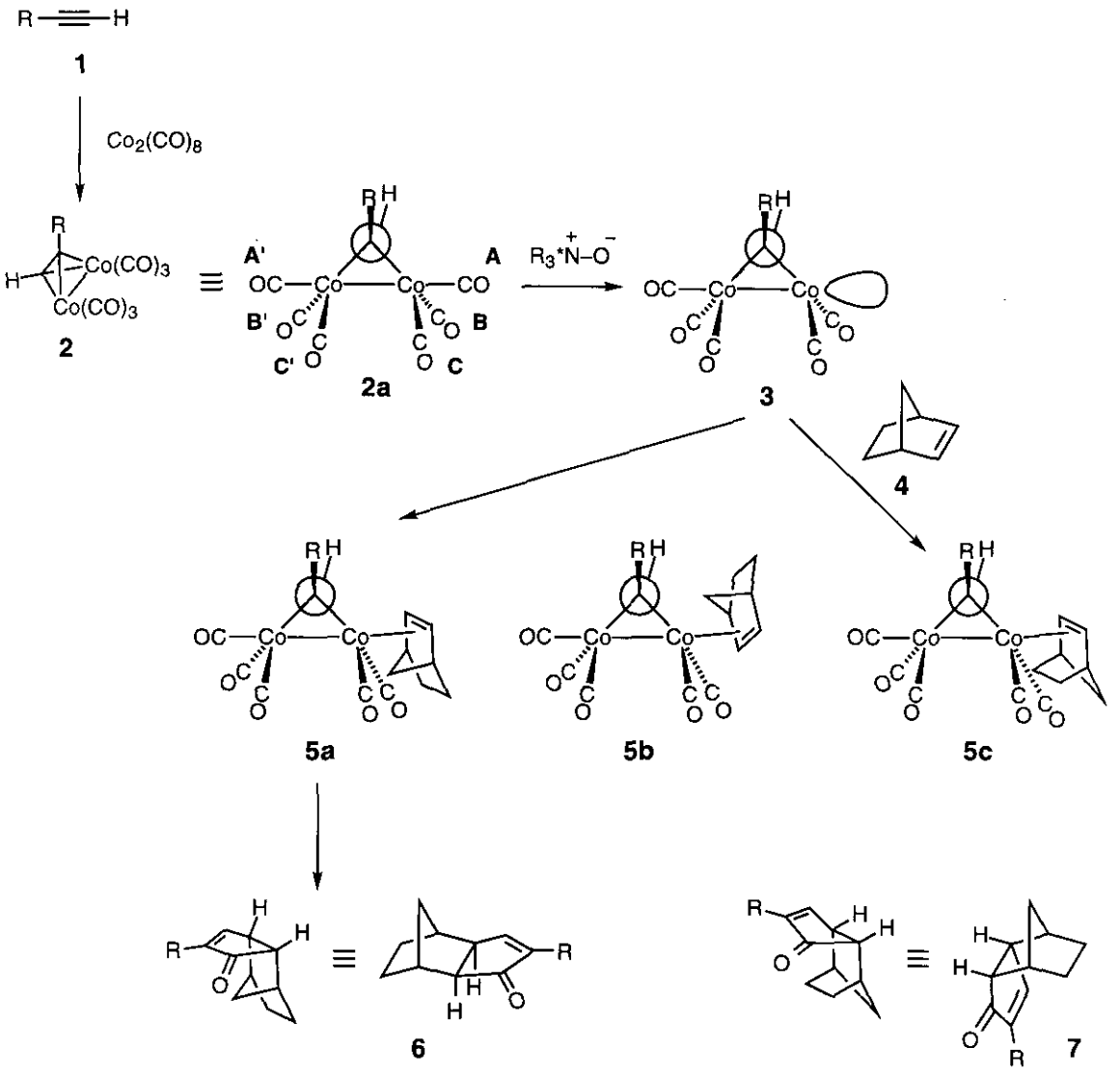
Abstract - The novel indolizino[3,4-*b*]quinoline *N*-oxide (**12**) was prepared and characterized by X-Ray crystal structure determination. Compound (**12**) and sparteine *N*-oxides (**8** - **10**) were employed as chiral promoters in the Pauson-Khand cocyclization of various alkynes (**1**) with norbornene (**4**) to the bicyclic cyclopentenones (**6**) with enantioselectivities up to 33 %ee.

The cobalt-mediated cocylization of an alkyne, an alkene and CO, commonly known as the Pauson-Khand reaction, has developed into a useful method for the construction of cyclopentenones.[1] Up to now stereoselective versions of this cocyclization rely mainly on the use of chiral auxiliaries that are bound either to the alkene[2] or alkyne[3] moiety.[4] If the chiral auxiliary possesses an additional donor substituent, e.g. a thiomethyl group, which might be able to stabilize the coordinatively unsaturated cobalt complex during the reaction, enhanced diastereoselectivities were observed.[5] In an alternative approach enantiomerically pure cobalt alkyne complexes prepared *via* ligand exchange reactions from the prochiral $Co_2(CO)_6$(alkyne) and a chiral phosphine ligand were used in the cocyclization.[6] However, the latter method requires chromatographic separation of the cobalt alkyne complexes.[7] It has been found by several groups that the rate of the Pauson-Khand reaction is significantly increased by the addition of tertiary amine *N*-oxides.[8] This rate enhancement is probably due to the fact that CO ligands from the initially formed cobalt alkyne complex are removed more easily in the presence of amine *N*-oxide

Scheme 1

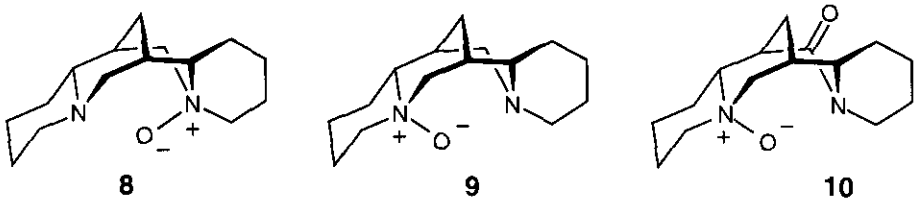


because CO is oxidized to CO_2.[9] A Newman projection (**2a**) of the cobalt alkyne complex viewed along the C-C bond of the alkyne shows that the sterically least hindered CO at position **A** will be removed first (Scheme 1). Thus the question arose whether chiral amine *N*-oxides might be able to differentiate between the two enantiotopic CO ligands at positions **A**, **A'**. The resulting coordinatively unsaturated chiral complex **3** can attack norbornene (**4**) either from the *exo* face (**5a**) or from the *endo* face (**5c**). *Exo* attack would lead to the enantiomerically pure *exo* product **6**, whereas *endo* attack should give the enantiomerically pure *endo* product **7**.[10] However, *endo* attack should be disfavored due to steric interactions between the methylene bridge of **4** and the remaining CO ligands. In addition, other possible

exo conformers like **5b** should be disfavored due to the steric bias caused by the alkyne substituent.[11] Thus we decided to investigate various alkaloid-derived *N*-oxides as chiral promoters in the Pauson-Khand reaction. The results are reported in this manuscript.

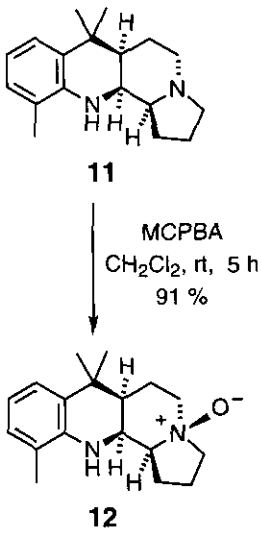
The following enantiomerically pure *N*-oxides were used: (-)-sparteine *N*16-oxide (**8**), (+)-sparteine *N*1-oxide (**9**) and (-)-17-oxosparteine *N*-oxide (**10**), because they were easily available from the naturally occurring lupine alkaloid (-)-sparteine (Scheme 2).[12,13] In addition the *cis*-configurated decahydro-

Scheme 2



8 **9** **10**

Scheme 3



11 **12**

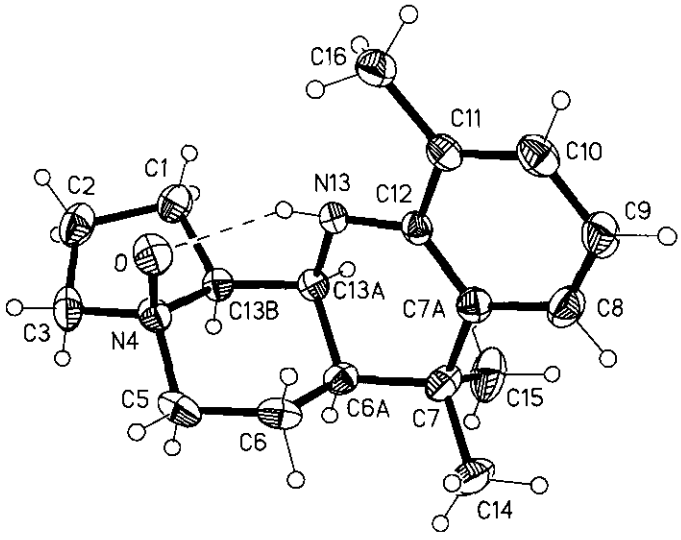


Figure 1 X-Ray crystal structure of (±)-**12**. Only the (+)-isomer is shown here. Bond lengths [Å] and angles [°] of the intramolecular hydrogen bond: O–H13 2.00(2), H–N13 0.87(2)Å, O–H–N13 145(2)°.

7,7,11-trimethylindolizino[3,4-*b*]quinoline (**11**) was employed for amine oxidation (Scheme 3). As previously reported, this concave molecule is easily available by a highly diastereoselective Lewis acid-catalyzed cyclization of prolinal-derived *N*-tolylimine.[14] Treatment of **11** with MCPBA gave the corresponding *N*-oxide (**12**) in high yield. In order to establish the enantiomeric purity of **12** the racemic mixture was prepared for comparison.[15] It was found that (±)-**12** crystallized more easily. Fortunately, an X-Ray crystal structure of (±)-**12** could be obtained.[16] As shown in Figure 1 the *N*-oxide is stabilized by an intramolecular hydrogen bond.

Amine *N*-oxides (**8** - **10**, **12**) were employed as chiral promoters in the Pauson-Khand reaction of norbornene (**4**) with various monosubstituted alkynes (**1**) to give *exo*-4-tricyclo[5.2.1.$0^{2,6}$]dec-2-en-1-ones (**6**). In a typical cyclization experiment a solution of the cobalt-alkyne complex (**2**), which was formed *in situ* from **1** and $Co_2(CO)_8$ at room temperature, was treated at - 78°C with **4** and 6 equiv. of the amine *N*-oxide for 8 h. After warming up to room temperature and workup the crude cyclopentenones (**6**) were submitted to GC analysis.[15] The results are summarized in Table 1. Sparteine *N*-oxides (**8**, **9**) gave enantioselectivities ≤ 13 %. A moderate increase of the ee-values was observed with oxosparteine *N*-oxide (**10**). This outcome was unexpected, because Eilbracht and Petrowitsch found a dramatic

Table 1 Enantioselectivities in the Pauson-Khand reaction of norbornene (**4**) with various alkynes (**1**) in the presence of chiral amine *N*-oxides (**8** - **10** and **12**) [a,b]

Alkyne	R	**8**		**9**		**10**		**12**	
		%ee	Yield [%]	%ee	Yield [%]	%ee	Yield [%]	%ee	Yield [%]
1a	Pr	13	46	9	74	10	33	12	42
1b	*t*-Bu	8	62	12	58	4	22	33	37
1c	Ph	5	46	4	22	16	73	4	60
1d	Me_2COH	6	40	8	72	14	71	18	57
1e	CH_2CH_2OH	2	33	5	80	10	60	10	53
1f	CH_2OBn	3	28	4	35	10	43	8	47

a Reaction conditions: 6 equiv. of amine *N*-oxide, THF, 8 h, -78°C. Reactions in the presence of **12** were run in CH_2Cl_2 instead of THF because of the low solubility of **12** in THF; however, the enantioselectivities were similar in both solvents. No other byproducts were found. In all cases (-)-**6** was the major product.

b Enantioselectivities were determined by capillary GC using a ß-cyclodextrine column. See ref.[15]

increase of the enantioselectivity in the kinetic resolution of eucarvone tricarbonyl iron complexes when using oxosparteine *N*-oxide (**10**) instead of sparteine *N*-oxides (**8, 9**).[17] Surprisingly, the indolizino[3,4-*b*]quinoline *N*-oxide (**12**) performed much better as a chiral promoter in the Pauson-Khand reaction than the alkaloid-derived *N*-oxides (**8** - **10**). The best enantioselectivity was observed for *tert*-butyl-substituted alkyne (**1b**) (33 %ee). *N*-Oxides (**8** - **10** and **12**) yielded the (-)-enantiomer of **6** as the major product of the cocyclization.[6]

In conclusion alkaloid *N*-oxides (**8** - **10** and **12**) can be used as chiral promoters for the Pauson-Khand reaction. However, a more detailed investigation of the enantioselectivity determining step, i.e. insertion of the alkene and in particular the role of the *N*-oxide, is required in order to obtain increased enantioselectivities. Studies towards this end are currently in progress.

EXPERIMENTAL

All reactions were carried out under nitrogen by using standard Schlenk technique unless otherwise mentioned. Solvents were dried and deoxygenated by standard procedures. Analytical TLC was performed on precoated Merck Si 254 F plates (0.25 mm thickness) and visualized with UV light. Flash chromatography was carried out with Merck silica gel 60 (230 - 400 mesh). NMR spectra: Bruker AC 200 (200 MHz ^{1}H, 50 MHz ^{13}C), Bruker AM 400 (400 MHz ^{1}H, 100 MHz ^{13}C). IR spectra: Nicolet 320 FT-IR. Optical rotations (1 dm cells, 1 ml capacity, room temperature): Perkin-Elmer Model 241 polarimeter. MS: Finnigan MAT 8430 (EI). GC analysis: Hewlett Packard GC with a HP5 fused silica capillary column (ID 0.32 mm, length 25 m). Determination of enantiomeric purity by GC: Dani GC with a heptakis(2,3-di-*O*-methyl-6-*O*-dimethylthexylsilyl)-β-cyclodextrine column (ID 0.32 mm, length 17 m).[14] Pentyne (**1a**), 3,3-dimethylbutyne (**1b**), phenylacetylene (**1c**), 2-methyl-but-3-ynol (**1d**) and 3-butynol (**1e**) were purchased from Aldrich. 1-Benzyloxy-2-butyne (**1f**) was prepared according to ref.[18] Analytical and spectroscopic data for cyclopentenones (**6c,d**) were described in ref.[6]

(6aS,12aS,12bS)-1,2,3,5,6,6a,7,12,12a,12b-Decahydro-7,7,11-trimethylindolizino[3,4-b]quinoline N-oxide **(12).** To an ice-cooled solution of amine (**11**) (405 mg, 1.50 mmol) in (10 mL) was added dropwise *m*-chloroperbenzoic acid (468 mg, 1.80 mmol, 80% purity) in CH_2Cl_2 (5 mL) and the resulting solution was stirred for 5 h at rt. The solvent was removed *in vacuo* and 2 N HCl (1 mL) was added to the residue. The aqueous layer was washed with Et_2O (5 x 15 mL) and then adjusted to pH 8 - 9 by addition of KOH (50 wt % in H_2O) under ice-cooling. The aqueous alkaline layer was extracted with CH_2Cl_2 (5 x 30

mL) and the combined organic layers were dried over $MgSO_4$ and evaporated. 390 mg (1.37 mmol, 91 %) of a colorless, hygroscopic solid; mp 180°C (decomp); $[\alpha]_D^{20}$ = + 165.3° (c = 0.99; $CHCl_3$); IR (film) $\tilde{\nu}$ 3400 - 3100, 1637, 1632, 1471, 1385, 1299, 747 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.09 (d, *J* = 7.8 Hz, 1H, 8-H), 6.91 (d, *J* = 6.8 Hz, 1H, 10-H), 6.69 (dd, *J* = 7.8/6.8 Hz, 1H, 9-H), 3.93 (s, 1H, 13a-H), 3.69 (ddd, *J* = 2.4/3.8/9.0 Hz, 1H, 5-H), 3.47 (ddd, *J* = 5.8/5.8/14.5 Hz, 1H, 3-H), 3.23 (ddd, *J* = 9.3/9.3/14.5 Hz, 1H, 3-H), 3.15 - 3.12 (m, 1H, 13b-H), 3.06 (ddd, *J* = 3.0/3.0/9.0 Hz, 1H, 5-H), 2.97 - 2.86 (m, 1H, 1-H), 2.53 - 2.43 (m, 1H, 1-H), 2.16 (s, 3H, 16-H), 2.13 - 1.80 (m, 4H, 6-H, 1-H, 2-H, NH), 1.61 - 1.57 (m, 1H, 6-H), 1.36 (s, 3H, 14-H), 1.31 (s, 3H, 15-H), 1.30 - 1.25 (m, 1H, 6-H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.9, 129.4, 127.5, 126.4, 123.7, 118.1, 72.5, 69.3, 64.7, 48.4, 44.4, 35.4, 33.9, 26.9, 22.8, 19.7, 18.9, 17.9; MS (EI) *m/z* (%): 286 (M, 32), 270 (M - O, 31), 255 (8), 241 (4), 200 (16), 186 (20), 171 (8), 158 (21), 152 (26), 144 (12), 120 (8), 96 (23), 91 (4), 84 (100), 77 (3), 69 (14), 55 (8), 42 (5); HRMS (EI) calcd for $C_{18}H_{26}N_2O$ 286.2045, found 286.2040.

***General procedure for the Pauson-Khand reaction in the presence of chiral amine N-oxides* (5) - (7), (9).** To a solution of alkyne **1** (0.13 mmol) in THF (10 mL) was added $Co_2(CO)_8$ (48.0 mg, 0.13 mmol) and the resulting mixture was stirred for 1 h at rt. The solution was cooled to -78°C and then were added norbornene (**4**) (14.0 mg, 0.15 mmol) and amine *N*-oxide (0.75 mmol). After stirring for 8 h at -78°C the mixture was warmed to room temperature overnight. To the blue solution was added SiO_2 (1 g) and the solvent was removed in vacuo. The crude product was purified by flash chromatography on SiO_2 (eluent: hexanes/ethyl acetate 25 : 1).

***exo-4-Propyltricyclo[5.2.1.0^{2,6}]dec-4-en-3-one* (6a).** 239 mg (1.26 mmol, 63 %) of a colorless oil; IR (film) $\tilde{\nu}$ 1698, 1455, 1249, 1186, 1129, 1055 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.03 (dd, *J* = 1.3/1.3 Hz, 1H), 2.49 (s, 1H), 2.31 (d, *J* = 4.0 Hz, 1H), 2.13-2.00 (m, 4H), 1.63-1.35 (m, 4H), 1.23-1.16 (m, 2H), 0.99 - 0.86 (m, 2H) 0.84 (t, 3H, *J* = 7.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 211.2, 158.7, 149.2, 53.8, 48.1, 38.9, 38.0, 30.9, 29.0, 28.4, 26.7, 21.0, 13.8; MS (EI) *m/z* (%): 190 (M, 100), 175 (30), 161 (55), 147 (22), 133 (18), 122 (22), 107 (24), 91 (30), 79 (26), 67 (32), 55 (9); HRMS (EI) calcd for $C_{13}H_{18}O$ 190.1357, found 190.1354.

***exo-4-t-Butyltricyclo[5.2.1.0^{2,6}]dec-4-en-3-one* (6b).** 45 mg (0.22 mmol, 11 %) of a colorless oil; IR (film) $\tilde{\nu}$ 1692, 1456, 1250, 1198, 1059, 853 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.05 (s, 1H, 5-H), 2.49 (s, 1H, 6-H), 2.33 (s, 1H, 7-H), 2.12 - 2.10 (m, 2H, 1-H, 2-H), 1.69 - 1.51 (m, 2H, 8a-H, 9a-H), 1.31 - 1.21 (m, 2H, 8b-H, 9b-H), 1.16 (s, 9H, 2'-H, 3'-H, 4'-H), 0.98 - 0.88 (m, 2H, 10-H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 210.2, 157.0, 156.7, 54.8, 47.0, 39.2, 38.2, 31.8, 30.8, 29.2, 28.4, 27.9; MS (EI) *m/z* (%): 204 (M, 100), 189 (38), 162 (11), 149 (8), 119 (4), 105 (6), 95 (22), 91 (38), 77 (8), 67 (5), 53 (5); HRMS (EI) calcd for $C_{14}H_{20}O$ 204.1514, found 204.1510. Anal. calcd for $C_{14}H_{20}O$: C 82.30, H 9.87. Found: C 81.77, H 9.86

exo-4-(2'-Hydroxyethyl)-tricyclo[5.2.1.0^{2,6}]dec-4-en-3-one **(6c).** 319 mg (1.66 mmol, 83 %) of a colorless oil; IR (film) $\tilde{\nu}$ 1686, 1456, 1348, 1248, 1186, 1128, 1054 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.25 (d, *J* = 1.3 Hz, 1H, 5-H), 3.77-3.68 (m, 2H, 2'-H), 2.61 (s,1H, 6-H), 2.51 - 2.47 (m, 3H, 7-H, 1'-H), 2.40 (d, *J* = 3.8 Hz, 1H, 2-H), 2.22 (dd, 2H, *J* = 5.0/5.0 Hz, 1H, OH), 2.19 (d, *J* = 4.1 Hz, 1H, 1-H) 1.72 - 1.55 (m, 2H, 8a-H, 9a-H), 1.35 - 1.24 (m, 2H, 8b-H, 9b-H), 1.03 - 0.94 (m, 2H, 10-H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 212.3, 161.7, 146.7, 61.2, 53.8, 48.5, 39.0, 37.9, 31.0, 29.1, 29.0, 28.3; MS (EI) *m/z* (%): 192 (M, 32), 174 (6), 163 (100), 145 (10), 125 (8), 117 (7), 105 (6), 95 (24), 79 (9), 67 (10), 53 (4); HRMS (EI) calcd for $C_{12}H_{16}O$ 192.1150, found 192.1150.

exo-4-Benzyloxymethyltricyclo[5.2.1.0^{2,6}]dec-4-en-3-one **(6d).** 139 mg (0.52 mmol, 26 %) of a colorless oil; IR (film) $\tilde{\nu}$ 1699, 1455, 1249, 1186, 1128, 1053 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.42 - 7.27 (m, 6H, 5-H, 4'-H, 5'-H, 6'-H), 4.57 (s, 2H, 2'-H), 4.20 (s, 2H, 1'-H), 2.64 (s, 1H, 6-H), 2.41 (s, 1H, 7-H), 2.22 - 2.20 (m, 2H, 1-H, 2-H), 1.71 - 1.54 (m, 2H, 8a-H, 9a-H), 1.43 -1.21 (m, 2H, 8b-H, 9b-H), 1.01 (d, *J* = 9.4 Hz, 1H, 10a-H), 0.96 (d, *J* = 9.4 Hz, 1H, 10b-H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 209.8, 160.5, 146.3, 137.9, 128.4, 127.8, 127.7, 73.1, 64,1, 54.3, 48.6, 38.9, 37.9, 31.1, 29.0, 28.3; MS (CI) *m/z* (%): 286 (M + NH_4^+, 100), 269 (M + H, 42), 226 (20), 210 (8), 196 (33), 186 (5), 179 (21), 108 (2).

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16. X-Ray structure analysis of racemic **12**. *Crystal data*: orthorhombic, *Pbca*, a = 16.410(2), b = 9.3760(12), c = 20.292(2)Å, U = 3122Å^3, Z = 8, D_x = 1.219 Mg m^{-3}, μ = 0.08 mm^{-1}, $F(000)$ = 1248, T = 173K. *Data collection*: Siemens P4 diffractometer with LT-2 low temperature attachment; 4987 reflections to 2θ 55°, 3584 unique (R_{int} 0.036). *Structure solution*: direct methods. *Structure refinement*: on F^2 (program: SHELXL-93, G.M. Sheldrick, Univ. of Göttingen, Germany); H atoms as rigid methyls or riding (exception: NH free); $wR(F^2)$ 0.102, $R(F)$ 0.044 for 198 parameters, S = 0.84, max. Δρ 0.22 eÅ^{-3}. Full details have been deposited at the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, and can be obtained from there on quoting a full literature citation and the reference number CSD 408123.

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