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# A Comparison of Two Effective Chiral Auxiliaries - (2*R*)-bornane-10,2-sultam and (2*R*)-bornane-10,2-cyclohydrazide - using the [4+2] Cycloaddition of Cyclopentadiene to their N,N'-fumaroyl derivatives

by **Christian Chapuis**[a])[1]*, **Anna Kucharska**[b]) and **Janusz Jurczak**[a])[b])*

a) Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, PL-01-224 Warsaw

b) Department of Chemistry, University of Warsaw, Pasteura 1, PL-02-093 Warsaw

E-mail: CHRISTIAN.CHAPUIS@firmenich.com

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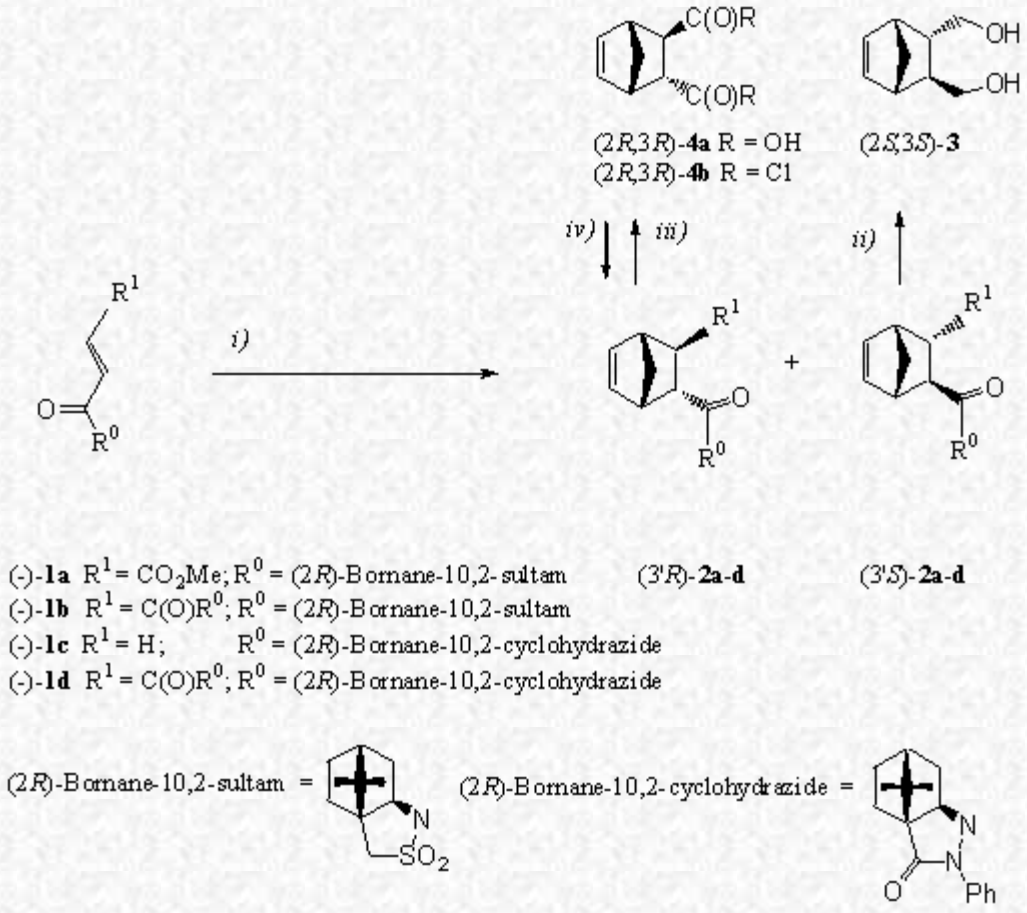
A correlation between the solvent polarity and the logarithm of the diastereoisomer ratio (dr) was found for the uncatalyzed [4+2] cycloaddition of cyclopentadiene to *N,N*'-fumaroyldi[(2*R*)-bornane-10,2-(2'phenyl-pyrazol-3'-one)]. Using the *Abboud-Abraham-Kamlet-Taft* parameters, predictive values for this method, allowed an optimum diastereoisomeric excess (de) of 94% in $CHCl_3$. Implications for the stereochemical course of the reaction as well as a comparison with the (2*R*)-bornane-10,2-sultam analogous auxiliary are discussed.

**Introduction**. - We recently presented the complete p-facial selectivity observed in the $TiCl_4$-catalyzed [4+2] cycloadditions of cyclopentadiene to N-fumaroyl mono and *bis* [(2*R*)-bornane-10,2-sultam] ((-)-**1a,b**) [2][3]. Besides the influence of diverse *Lewis* acids, as well as applications using diverse dienes [4], we also reported in detail the influence of the solvent polarity, ranging from the apolar $CO_2$ supercritical fluid to ionic liquid salts [5]. We observed that, in contrast to other auxiliaries [6], a strong influence and a clear correlation between increasing solvent polarity and increasing p-facial selectivity was found during the uncatalyzed cycloaddition of (-)-**1b** to cyclopentadiene. This was rationalized by the stabilization in polar solvents of the thermodynamically less favored *syn-s-cis* conformers and thus a more effective reactivity due to the cooperation of both steric and stereoelectronic effects for this class of dienophiles [7]. This effect is also reinforced by the additional stabilization by polar solvents of the C(a)-*re* transition states, exhibiting larger dipole moments in *syn* and *anti* conformations, as compared to their C(a)-*si* attacks. We were thus particularly interested when *Chen et al.* recently reported the new *N*-acryloyl dipolarophile (-)-**1c**, which, according to these authors, is believed to react in the *syn-s-cis* conformation on the C(a)-*re* face [8]. Furthermore, these authors, depending on the solvent conditions used, also noticed an unexplained complete reversal of the inductive effect, during the *Baylis-Hillman* reaction on substrate (-)-**1c** [9]. This has thus prompted us to study in more detail the uncatalysed cycloaddition of cyclopentadiene to the new dienophile (-)-**1d**.

**Results and Discussion**. - The (+)-(2*R*)-bornane-10,2-cyclohydrazide chiral auxiliary was prepared from (+)-(1*S*)-ketopinic acid, according to the reported method [9]. The 2'-phenyl-pyrazol-3'-one was then deprotonated with NaH in toluene prior to addition of fumaroyl chloride to afford crystalline (-)-**1d** in 70% yield. It appears to be far less reactive than its camphorsultam analogue ((-)-**1b,** 0.02M, 20°, 4.0 mol equiv. of cyclopentadiene, 18h, full conversion [5]), since at higher concentration (0.05M) and in the presence of an excess of cyclopentadiene (10.0 mol equiv.), the reaction was incomplete at 20°, even after 24 h.




*i)* Solvent, 20°, 24 hours, 10.0 mol-equiv. 1,3-cyclopentadiene; *ii)* $NaBH_4$, $MeOH/H_2O$; *iii)* LiOH, $THF/H_2O$; iv) NaH, toluene, (2*R*)-Bornane-10,2-cyclohydrazide-H.

The p-facial selectivity was measured directly by integration, in the 500 MHz $^1$H-NMR spectrum, of the olefinic signals of the diastereoisomeric mixture of cycloadducts **2d**, with a precision of +/- 2%. Indeed, the main stereoisomer shows signals at 5.92 and 6.28 ppm, while the minor one resonates at 6.00 and 6.21 ppm. The absolute configuration was determined by reduction of the main stereoisomer to the known diol (-)-(2*S*,3*S*)-**3** [10] ($NaBH_4$, 2.0 mol equiv., $MeOH/H_2O$ 3:1, 20°, 1.5h, 85% yield, $SiO_2$ hexane/$Et_2O$ 7:3, $[a]_D^{20}$ = -15.9, c = 0.3, $CHCl_3$). Alternatively, the minor stereoisomer was prepared by acylation of the chiral cyclohydrazide with optically pure *bis*-acid chloride (2*R*,3*R*)-**4b** (NaH, toluene), readily obtained by saponification (LiOH.$7H_2O$, $THF/H_2O$ 4:1) of the analogous optically pure major cycloadduct (2*R*,3*R*)-**2b** [2].

After a rapid survey of common solvents such as toluene, THF, AcOEt, DMSO and MeCN, we rapidly concluded that the diastereoselectivity slightly diminished from 92 % to 81 % de on increasing the solvent polarity according to the *Reichardt* scale [11]. We then studied more systematically the complete range of solvent polarity from $Et_3N$ (90 % de) to $CF_3CH_2OH$ (56 % de) (see *Table 1*). As illustrated in *Fig. 1*, in contrast to the camphorsultam analogue, the logarithm of the diastereoisomer ratio (dr) decreased with increasing polarity. The optimum conversions (96-98%) and selectivities (94 % de) were obtained in chlorinated solvents such as $CHCl_3$ or $CCl_4$.

**Table 1.** *Dependence of the Diastereoselectivity of the Cycloaddition* (-)-**1d** *to* **2d** *on the Polarity and Solvatochromic Indexes.*

| solvent | conv [%] | de [%] | $E_T(30)$ [kcal/mol] | log(dr) | p* | a | b | d | *Calculated log(dr)* | *Residuals log(dr)* |
|---|---|---|---|---|---|---|---|---|---|---|
| $CF_3CH_2OH$ | 85 | 56 | 59.8 | 0.550 | 0.73 | 1.51 | 0.00 | 0.0 | 0.586 | -0.036 |
| MeOH | 85 | 66 | 55.4 | 0.689 | 0.60 | 0.98 | 0.66 | 0.0 | 0.693 | -0.004 |
| $MeNO_2$ | 94 | 88 | 46.3 | 1.195 | 0.85 | 0.22 | 0.06 | 0.0 | 1.138 | 0.057 |
| $CH_3CN$ | 92 | 81 | 45.6 | 0.979 | 0.76 | 0.00 | 0.29 | 0.0 | 1.205 | -0.226 |
| DMSO | 92 | 84 | 45.1 | 1.061 | 1.00 | 0.00 | 0.76 | 0.0 | 1.008 | 0.052 |
| DMF | 94 | 84 | 43.2 | 1.061 | 0.88 | 0.00 | 0.69 | 0.0 | 1.062 | -0.002 |
| $CH_2Cl_2$ | 91 | 91 | 40.7 | 1.327 | 0.82 | 0.13 | 0.10 | 0.5 | 1.276 | 0.051 |
| $CHCl_3$ | 98 | 94 | 39.1 | 1.510 | 0.58 | 0.20 | 0.10 | 0.5 | 1.313 | 0.197 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| AcOEt | 82 | 89 | 38.1 | 1.235 | 0.55 | 0.00 | 0.45 | 0.0 | 1.223 | 0.012 |
| THF | 86 | 88 | 37.4 | 1.195 | 0.58 | 0.00 | 0.55 | 0.0 | 1.187 | 0.008 |
| Toluene | 89 | 92 | 33.9 | 1.380 | 0.54 | 0.00 | 0.11 | 1.0 | 1.512 | -0.132 |
| $CCl_4$ | 96 | 94 | 32.4 | 1.510 | 0.28 | 0.00 | 0.10 | 0.5 | 1.493 | 0.016 |
| $Et_3N$ | 96 | 90 | 32.1 | 1.279 | 0.14 | 0.00 | 0.71 | 0.0 | 1.272 | 0.007 |

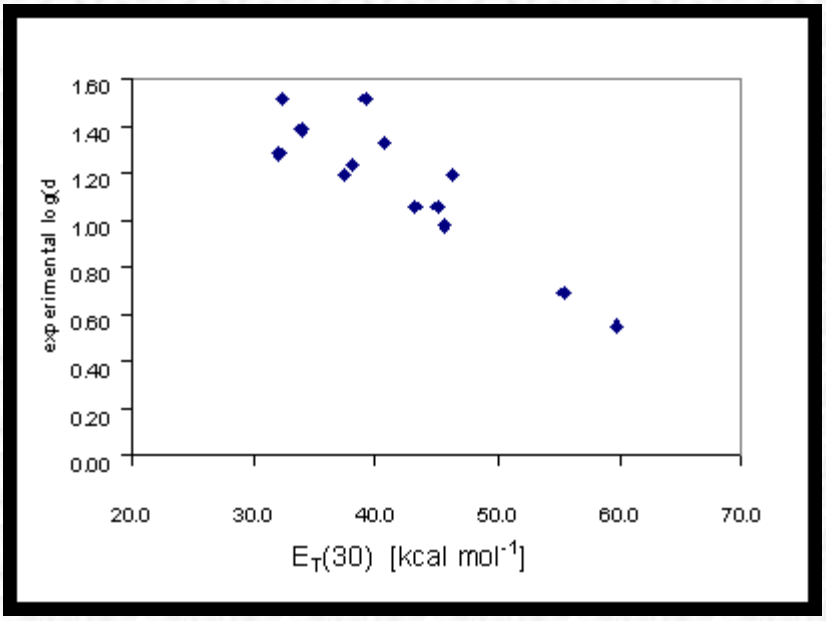



Fig 1. *Diastereoselectivity of the uncatalyzed cycloaddition of* (-)-**1d** *to cyclopentadiene as a function of the solvent polarity as defined by the* $E_T(30)$ *values of* Reichardt *(dr = diastereoisomer ratio)*

In hexane, the dienophile was practically insoluble and the conversion only reached 23% (82% de, reflecting here the solid/liquid interface interactions, rather than those of homogeneous conditions), while in refluxing toluene (83 % conversion) the selectivity dropped to 61 % de. Since hydroxylic or some chlorinated solvents may activate the dienophile by forming a hydrogen bond, we then turned our attention towards a more generalized definition of the polarity as expressed by the multi-parameter *Abboud-Abraham-Kamlet-Taft* model [12], where the log (dr) may be expressed as a linear correlation of diverse solvatochromic parameters as defined earlier [5]. The p*, a, b, d and square of *Hildebrand* indexes are characteristic of the solvent and have been recently compiled by *Marcus et al.* [13] and *Chastrette et al.* [14].

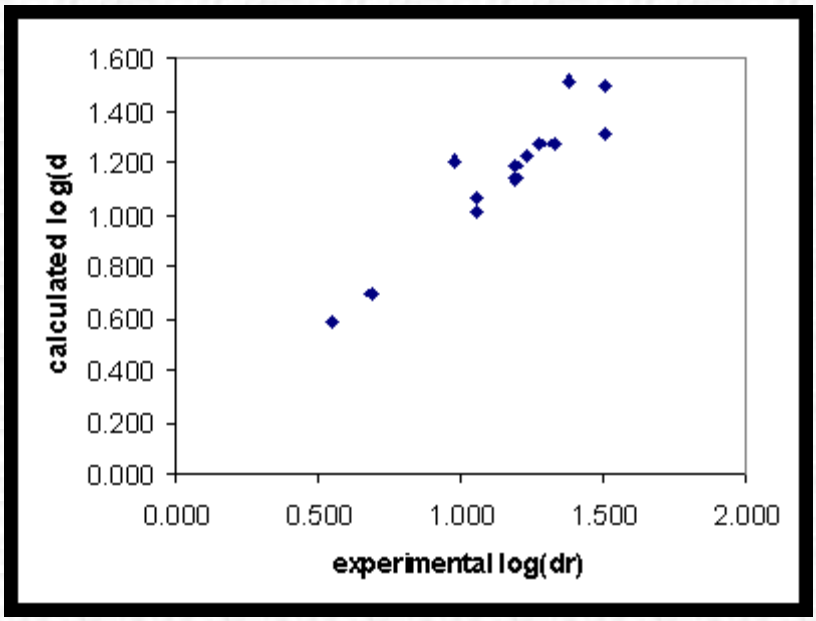



Fig 2. *Experimental* vs. *predicted diastereoselectivity of* (-)-**1d** *based on the* Abboud-Abraham-Kamlet-Taft *model (dr = diastereoisomer ratio)*

Based on 13 solvents, we found that the *Hildebrand* index was statistically not relevant and could be omitted without further alteration of the linear correlation (r = 0.940 with this supplementary index, standard error = 0.127). Thus, a good correlation was found between the experimental and calculated diastereoselectivity (log(dr)), for the cycloaddition of (-)-**1d** to cyclopentadiene as shown in *Fig. 2*. A correlation coefficient of 0.939 was found with a standard deviation of 0.121 when the equation was

fitted with the following parameters.

$$Log(dr) = 1.504 – 0.291p^* + 0.195d - 0.468a - 0.270b$$

In summary, for the uncatalysed cycloaddition to cyclopentadiene, dienophile (-)-**1d** exhibits opposite directing effects and relationships as compared to dienophile (-)-**1b**, as regards the diastereoselectivity obtained with respect to the solvent polarity.

Based on the X-ray analysis of (-)-**1c**, *Chen et al.* concluded that the C(a)-*re* sense of induction observed in their [3+2] cycloadditions resulted from the steric shielding of the top face by the C(8) Me group of the NPh/C=O *syn* C=O/C=C s-*cis* conformer [8]. This rationalization, initially suggested by *Oppolzer* in the case of the sultam auxiliary [15], was later abandoned and replaced by a pure sterically masked *C*2 symmetric concept described by *Kim* and *Curran* [16], where the sense of induction is directed on the C(a)-*re* face by the C(2)-C(3) and *pseudo* axial S=O substituents in the *syn*- and *anti*-s-*cis* conformations, respectively. Although originally proposed [17][18] but later rescinded [19] by *Oppolzer* and *Curran*, the stereoelectronic influence of the nitrogen lone pair was only recently demonstrated by PM3 calculations, thus allowing us to tune the simple steric model by a supplementary matching or mismatching electronic factor in the *syn*- and *anti*-s-*cis* conformation, respectively [7]. By comparison of the X-ray analysis of (-)-**1c** [8] and the corresponding sultam analogue [18], three main features appears to be worthy of comment. First of all, similarly to the sultam auxiliary, the cyclohydrazide moiety possesses a pyramidalized N atom. This probably results from the anomeric influence of the neighboring N lone pair, this atom preferring a *pseudo* equatorial orientation of the Ph substituent. Also stabilized by the *anti*-periplanar most polarized C(2)-H bond, the N lone pair favors electronic attack on the *syn*-s-*cis* C(a)-*re* and *anti*-s-*cis* C(a)-*si* faces [7]. Secondly, in agreement with the generalized anomeric effect [20], the most polarized N-C(2) bond is stabilized by the *anti*-periplanar C=O bond, thus thermodynamically favoring the *syn*-s-*cis* conformer, in direct contrast to the sultam analogue which prefers to align the C=O moiety *anti*-periplanar to the most polarized $O_2S$-N bond. Finally, the aromatic ring is not parallel to the C(1)-C(7)-C(4) plane, but is tilted and mobile, and thus may protect either of the two faces, depending on the steric nature and trajectory of the incoming reagent. This is the main stereo-difference with the fixed $SO_2$ moiety of the sultam analogue. In consequence, the attack on (-)-**1c** should be sterically and electronically favored on the C(a)-*re* face of the *syn*-s-*cis* conformer, whilst, in the absence of a rigid steric influence, electronically directed onto the C(a)-*si* face of the *anti*-s-*cis* conformer, in contrast to the *C*2 symmetrical concept of the sultam analogue. The same reasoning may also be applied to the thermodynamically less favored *syn*- and *anti*-s-*trans* conformers.

Earlier calculations showed that, as a result of its convexity, the thermodynamically most stable *bis*(*anti*-s-*cis*) conformer of (-)-**1b** possesses the smallest dipole moment, while the highly reactive *bis*(*syn*-s-*cis*) conformer, due to the vectorial addition of the $SO_2$ and C=O intrinsic dipoles, shows a more important global dipole moment [5]. The situation seems to be much more complicated with the auxiliary developed by *Chen et al.*. Indeed, for this dienophile, we found four more stable co-planar conformers below the energy of the *bis*(*syn*-s-*cis*) conformer (-)-**1d** (see *Table 2* [21]). The thermodynamically more stable *anti*-s-*cis*-s-*trans*-*syn* conformer thus possesses a higher dipole moment as compared to the *bis* NPh/C=O *anti* C=O/C=C s-*cis* conformer. In the *anti*-s-*cis* conformation, in addition to the electronic effect, the cumulative steric congestion of the aromatic ring and the C(8) Me group may also hypothetically explain a more efficient directing effect on the bottom face, leading in our case to the (2*S*,3*S*)-cycloadduct **2d**. We thus suggest that the C(a)-*si* directing *bis*(*anti*-s-*cis*) conformer, possessing a small dipole moment (see *Table 2*) may be more relevant in apolar solvents than the thermodynamically more stable *syn*-s-*cis*-s-*trans*-*syn* conformer. This latter conformer may be favored in polar solvents and thus, due to the C(a)-*re* directing effect of one of the C(2) atom, contributes to the erosion of the observed C(a)-*si* selectivity, imparted by the most stable and polar *anti*-s-*cis*-s-*trans*-*syn* conformer.

## **Table 2.** PM3-Calculated Conformational Energies, LUMO and Dipole Moments of (-)-**2d**.

| | DE [kcal/mol] | LUMO [eV] | Dipole [Debye] | Preferred attack for each auxiliary |
|---|---|---|---|---|
| *anti*-s-*trans*-s-*cis*-*syn* | -20.8 | -0.95 | 4.7 | C(a)-*re* + C(a)-*re* |
| *bis(syn*-s-*trans)* | -21.2 | -1.19 | 2.6 | C(a)-*si* + C(a)-*si* |
| *bis(syn*-s-*cis)* | -21.6 | -1.05 | 0.3 | C(a)-*re* + C(a)-*re* |
| *anti*-s-*cis*-s-*cis*-*syn* | -21.9 | -0.99 | 4.4 | C(a)-*si* + C(a)-*re* |
| *bis(anti*-s-*cis)* | -22.2 | -0.83 | 1.8 | C(a)-*si* + C(a)-*si* |
| *syn*-s-*cis*-s-*trans*-*syn* | -23.5 | -1.14 | 3.3 | C(a)-*re* + C(a)-*si* |
| *anti*-s-*cis*-s-*trans*-*syn* | -23.6 | -1.04 | 4.5 | C(a)-*si* + C(a)-*si* |

Although all the possible co-planar conformers were calculated, only those within 3.0 kcal/mol of the ground state conformation (-23.9 kcal/mol) are presented and only the three most stable are taken in consideration for the discussion (less than 2.0 kcal/mol; > 96% of the populated conformers).

**Conclusion**. - As a result of the cooperation of both prosthetic groups [22], very high diastereoselectivity (94% de, 92 % yield) was obtained for the uncatalyzed [4+2] cycloaddition of (-)-**1d** to cyclopentadiene. A good linear correlation between the diastereoselectivity and the solvatochromic properties of the solvent was found, but, in contrast to the sultam analog (-)-**1b**, dienophile (-)-**1d** exhibits opposite and decreasing selectivity in polar solvents. This is rationalized by the absence of a masked $C_2$ symmetry and stabilization of the *syn*-s-*cis*-s-*trans*-*syn* conformer, which partially favours attack on the C(a)-*re* face. In contrast, in apolar solvents, the small dipole moment of the *bis*(*anti*-s-*cis*) conformer accentuates the C(a)-*si* directing effect of the thermodynamically most favored conformer. The stereoelectronic influence of the nitrogen atom, with a pyramidalization similar to the sultam analogue, as well as the energies and dipole moments of the different transition states, shall be soon calculated and discussed.

We are indebted to Prof H.-J. Schneider for stimulating discussions, as well as to the University of Warsaw for financial support.

## Experimental Part

*General*. See [23].

*Dienophile (-)-**1d.***

A soln. of the chiral auxiliary [9] (2.3g, 9.0 mmol; $[a]_D^{20}$ = +56.5, c = 1.0 $CHCl_3$) in dry toluene (40 ml) was added dropwise to a suspension of NaH (0.9g, 22.5 mmol, 60% in min oil). After 30 min at rt, a soln. of fumaroyl chloride (0.49 ml, 4.5 mmol) in toluene (2 ml) was added dropwise and the mixture was stirred for 3 days. The excess of NaH was quenched with $H_2O$. The mixture was extracted with $CH_2Cl_2$, the org. phases were dried ($MgSO_4$) and the solvent was evaporated. The residue was chromatographed on $SiO_2$ ($CHCl_3$/hexane 1:1 to 7:3) to afford crystalline (-)-**1d** in 70% yield. $R_f$ = 0.24 (hexane/AcOEt 3:2); Mp: 150-153° (AcOEt/hexane). $[a]_D^{20}$ = -23.3, c=1.0, $CHCl_3$. IR(KBr): 2959, 2881, 1725, 1653, 1594, 1491, 1300, 1212, 1133, 755. $^1$H-NMR: 1.12 (*s*, 12H); 1.26-1.51 (*m*, 4H); 2.01 (*dd*, J=13, 8, 2H); 2.05-2.40 (*m*, 6H); 2.54 (*brm*, 2H); 4.16 (*dd*, J=8, 5, 2H); 7.04 (*brs*, 2H); 7.2-7.4 (*m*, 10H). $^{13}$C-NMR: 20.0(2*q*), 20.2(2*q*), 26.7(2*t*), 28.3(2*t*), 38.8(2*t*), 46.6(2*d*), 53.0(2*s*), 59.2(2*s*), 66.8(2*d*), 121.5(4*d*), 126.1(2*d*), 128.6(4*d*), 131.5(2*d*), 138.0(2*s*), 161.0(2*s*), 170.0(2*s*). HRMS: $C_{36}H_{40}O_4N_4$ 592.30734, calcd 592.30496. LRMS: 592 (6, M+.), 337 (19), 255 (100), 246 (7), 185 (6), 149 (9), 121 (11), 93 (12), 77 (17), 55 (8), 41 (11).

*General Procedure for the Uncatalyzed Cycloaddition*. To a soln of (-)-(2*R*)-**1d** (50 mg, 0.1 mmol) in the appropriate solvent (2 ml), cyclopentadiene (82 ml, 1.0 mmol) was added dropwise. After 24 h at rt, the solvent and the excess of cyclopentadiene were evaporated under medium, then high vacuum. The crude cycloadduct **2d,** obtained after filtration through a short plug of $SiO_2$ (hexane/AcOEt 3:1) (99% yield), was submitted to $^1$H-NMR analysis for conversion and de determination. Pure samples for analysis were obtained after chromatography. Major diastereoisomer ((+)-(2*S*,3*S*)-**2d**): $R_f$ = 0.37 (toluene/AcOEt 7:3); 0.40 (hexane/AcOEt 3:2); Mp: 153-156° (AcOEt/hexane); $[a]_D^{20}$ = +124.3 c = 1.0 $CHCl_3$; IR(KBr): 3009, 2962, 2881, 1726, 1689, 1596, 1492, 1377, 1300, 1271, 1204, 1134, 749. $^1$H-NMR: 0.99 (*s*, 6H); 1.05 (*s*, 6H); 1.20-1.35 (*m*, 5H); 1.6-2.2 (*m*, 9H); 2.63 (*brm*, 2H); 2.88 (*m*, 1H); 3.08 (*brs*, 1H); 3.22 (*brs*, 1H); 3.65 (*brs*, 1H); 3.88 (*dd*, J=13, 8, 2H); 5.98 (*m*, 1H); 6.34 (*m*, 1H); 7.06-7.14 (*m*, 2H); 7.20-7.33 (*m*, 8H). $^{13}$C-NMR: 19.8(2*q*), 20.4(2*q*), 26.6(2*t*), 27.9(2*t*), 39.4(2*t*), 44.9(*d*), 45.4(*d*), 45.7(2*d*), 47.3(*t*), 49.0(*d*), 50.5(*d*), 54.8(2*s*), 59.1(2*s*), 65.6(2*d*), 120.1(4*d*), 125.2(2*d*), 128.3(4*d*), 133.6(*d*), 137.3(*d*), 138.8(2*s*), 174.9(2*s*), 175.7(2*s*). HRMS: $C_{41}H_{46}O_4N_4$ 658.34924, calcd 658.35191. LRMS: 658 (4, M+.), 592 (6), 403 (77), 337 (100), 255 (85), 149 (31), 121 (34), 91 (45), 77 (39), 66 (44), 39 (35). Minor diastereoisomer ((-)-(2*R*,3*R*)-**2d**: $R_f$ = 0.39 (toluene/AcOEt 7:3); 0.31 (hexane/AcOEt 3:2). Mp: 204-207° (AcOEt/hexane); $[a]_D^{20}$ = -61.5 c = 1.0 $CHCl_3$; IR(KBr): 3010, 2960, 2880, 1725, 1690, 1595, 1490, 1375, 1300, 1270, 1205, 1135, 750; $^1$H-NMR: 0.85 (*m*, 2H); 1.10 (*s*, 3H); 1.13 (*s*, 3H); 1.15 (*s*, 3H); 1.19 (*s*, 3H); 1.26 (*m*, 1H); 1.40 (*m*, 5H); 1.60 (*m*, 1H); 2.0 (*m*, 4H); 2.28 (*m*, 1H); 2.40 (*m*, 1H); 2.50 (*m*, 1H); 2.60 (*m*, 1H); 3.00 (brs, 1H); 3.20 (brs, 1H); 3.35 (*dd*, J= 13, 8, 1H); 4.05 (*dd*, J = 19, 13, 1H); 4.15 (*dd*, J= 19, 13, 1H); 6.0 (*dd*, J = 14, 8, 1H); 6.21 (m, 1H); 7.26 (m, 10H); $^{13}$C-NMR: 20.1(*q*), 20.2(2*q*), 20.3(*q*), 26.8(2*t*), 28.4(2*t*), 40.1(*t*), 40.4(*t*), 45.8(*d*), 46.1(2*d*), 46.4(*d*), 47.2(*d*), 47.3(*t*), 47.9(*d*), 53.7(*s*), 54.1(*s*), 58.2(2*s*), 66.1(2*d*), 121.0(2*d*), 121.1(2*d*), 125.7(2*d*), 128.4(4*d*), 134.6(*d*), 136.8(*d*), 138.7(2*s*), 158.0(2*s*), 170.0(*s*), 172.0(*s*). HRMS: $C_{41}H_{16}O_4N_4$ 658.35181, calcd 658.35191. LRMS: 658 (5, M+.), 592 (5), 403 (75), 337 (100), 255 (85), 149 (30), 121 (35), 91 (45), 77 (40), 66 (45), 39 (35).

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[1] Present address: *Firmenich* SA, Corporate R & D Division, P.O. Box 239, CH-1211 Geneva 8.

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