further modifications to enhance triplex stability, for example replacing C by the 2-aminopyridine nucleoside **P** for recognition of guanine.[9, 10]

We can not definitely rule out the possibility of an energy-neutral contribution from the C–H···O arrangement in the corresponding base triples. Nevertheless, the experimental results described here are in good agreement with the general view that the energetic benefit of forming the C–H···O hydrogen bond is made up of a small, positive, direct electrostatic contribution[1] and a positive contribution due to the alleviation of a destabilizing interaction that arises if a hydrogen-bond acceptor (such as a carbonyl oxygen atom) is inactive or involved in secondary hydrogen bonding, for example, to solvent.[11] In any case, the final proof for the existence of a C–H···O hydrogen bond in the triplexes discussed here has to come from high-resolution structure analysis.

The efficient complexation of uracil by ^{7}H or T presented here is of direct relevance to the molecular recognition and folding of RNA. C–H···O hydrogen bonds in nucleic acids can compete with conventional hydrogen bonds under certain circumstances. This was shown by a recent X-ray structure analysis of an RNA duplex in which a U·U base pair built from one conventional and one C–H···O hydrogen bond was preferentially formed over an isomorphous base pair with two conventional hydrogen bonds.[12]

In applying this concept to triple-helical DNA recognition, the following restrictions have to be considered: 1. Uracil is not a DNA base, and there is no clear way to use the presented concept of C–H···O hydrogen bond assisted pyrimidine recognition for the complexation of the natural DNA base thymine. 2. Both thymidine and ^{7}H, as components of a third strand, have a primary binding preference for the purine bases adenine and guanine, respectively, which compromises the selectivity in the formation of DNA triple helices. This issue of selectivity, however, might be addressable by base design.

We have shown here that unconventional C–H···O hydrogen bonds may be advantageously used as a design element for enhancing the efficiency of weak base–base interactions in the complexation of nucleic acids. We are currently trying to expand this concept to triplex-mediated recognition of cytosine. Efficient and selective pyrimidine recognition definitely constitutes one way of extending the sequence range of triplex formation in nucleic acids, a widely sought but hitherto unsolved goal.[13]

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[1] G. R. Desiraju, *Acc. Chem. Res.* **1996,** *29*, 441–449.
[2] M. C. Wahl, M. Sundaralingam, *TIBS* **1997,** *22*, 97–102.
[3] G. R. Desiraju, *Angew. Chem.* **1995,** *107*, 2541–2558; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2311–2327.
[4] a) J. Marfurt, J. Hunziker, C. Leumann, *Bioorg. Med. Chem. Lett.* **1996**, *6*, 3021–3024; b) J. Marfurt, S. P. Parel, C. Leumann, *Nucleic Acids Res.* **1997,** *25*, 1875–1882.
[5] Melting curves were recorded with heating/cooling rates of 0.5 K min^{-1}. Under these conditions, melting and renaturation curves were superimposable in all cases and thus reflect equilibrium binding.
[6] The T_m data for third-strand binding in the triplexes **1·2** were independent of oligonucleotide concentration within the range 1–45 μM. The systems thus show pseudomonomolecular association, as reported previously for the parent canonical triplex.[7] Data for the Gibbs energy of formation for the triplexes (ΔG) were therefore calculated as described for a monomolecular two-state model from the experimentally determined association constant K_{ass} at 25 °C.[8]
[7] G. E. Plum, Y.-W. Park, S. F. Singleton, P. B. Dervan, K. J. Breslauer, *Proc. Natl. Acad. Sci. USA* **1990**, *87*, 9436–9440.
[8] L. A. Marky, K. J. Breslauer, *Biopolymers* **1987**, *26*, 1601–1620.
[9] S. Hildbrand, C. Leumann, *Angew. Chem.* **1996,** *108,* 2100–2102; *Angew. Chem. Int Ed. Engl.* **1996**, *35*, 1968–1970.
[10] S. Hildbrand, A. Blaser, S. P. Parel, C. Leumann, *J. Am. Chem. Soc.* **1997,** *119*, 5499–5511.
[11] G. A. Leonard, W. N. Hunter, *Acta Crystallogr. Sect. C* **1995,** *D51*, 136–139.
[12] M. C. Wahl, S. T. Rao, M. Sundaralingam, *Nature Struct. Biol.* **1996**, *3*, 24–31.
[13] J. Behr, S. O. Doronina, *Chem. Soc. Rev.* **1997,** 63–71.

Global and Local Aromaticity in Porphyrins: An Analysis Based on Molecular Geometries and Nucleus-Independent Chemical Shifts**

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Dedicated to Professor Emanuel Vogel on the occasion of his 70th birthday

How and to what extent does aromaticity contribute to the geometric and electronic structure of porphyrins? Despite its widespread use for nearly two centuries, "aromaticity" is difficult to define.[1] Usually, this is done on the basis of energetic, geometric and magnetic criteria.[2] Molecular geometries are often the most accessible, and aromaticity indices have been derived from bond lengths.[3] Recently the nucleus-independent chemical shift (NICS) was proposed as a new magnetic criterion, based on MO calculations of the magnetic shieldings at the centers or other points of aromatic systems.[4] The aim of this paper is to deduce the electronic structure of porphyrins based both on a large number of geometries retrieved from the Cambridge Structural Database [5] and on computed NICS values.

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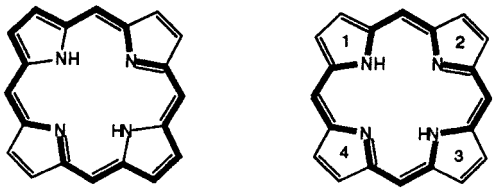
The present analysis of the molecular geometry does not use the popular depiction of the porphyrin skeleton as a bridged [18]annulene derivative.[6] Instead, we divide the porphyrin moiety into the macrocyclic "internal cross"—an 18 π-electron system of 16 atoms—and the four peripheral pyrrole rings, as shown in Scheme 1.



Scheme 1. Two models of the π-electron system of porphyrin. Left: as bridged [18]annulene derivative; right: as macrocyclic internal cross (in bold) and four pyrrole rings (1–4).

The CC and CN bond lengths in porphyrins can be perturbed by exocyclic substitution and by coordination with a metal cation. Bond lengths can be analyzed by the harmonic oscillator model of aromaticity (HOMA),[3c] which in turn may be dissected into two components, EN and GEO [Eq. (1)]. Here, n is the number of bonds taken into the

$$\mathrm{HOMA} = 1 - \alpha(R_{\mathrm{opt}} - R_{\mathrm{av}})^2 - \frac{\alpha}{n}\Sigma\,(R_{\mathrm{av}} - R_{\mathrm{i}})^2 = 1 - \mathrm{EN} - \mathrm{GEO} \qquad (1)$$

summation, and α is an empirical constant fixed to give HOMA = 0 for the hypothetical Kekule structures of aromatic systems and 1 for the system with all bonds equal to the optimal value R_{opt}.[3c, d] R_{av} stands for the average bond length, while the individual bond lengths R_{i} are obtained[7] from the Pauling definition of bond number.[8] The EN term describes changes in aromatic character due to deviation of the average bond length from the optimal value, while the GEO term reflects the consequences of bond length alternation.[7]

Of the 456 porphyrin derivatives with the highest measurement precision (i.e., with AS = 1, 2[9]) that we retrieved from the Cambridge Structural Database,[5] 32 are exocyclically substituted species, while 424 are metal complexes. In free base porphyrin, two of the four pyrrole rings (rings 1 and 3 in Scheme 1) are protonated. Since it is difficult to localize the inner hydrogen positions accurately by X-ray diffraction,[10] the harmonic oscillator stabilization energy (HOSE) model[11] was used to assign the hydrogen atoms to the pyrrole rings. Note that N-H tautomerization[12] will tend to reduce the difference between the pyrrole rings. For comparison, we calculated the optimized structures of porphyrin, its dianion, and the Mg(II)-porphyrin complex at the B3LYP/6-31G* DFT level and computed the nucleus independent chemical shift (NICS) at characteristic points at GIAO-RHF/6-31+G*. All computations were performed with the Gaussian 94 program package.[13] Figure 1 presents the calculated[12, 14] and mean experimental geometries, which are in good agreement; the HOMA, EN, GEO and NICS values are given in Table 1.

The differences between the global HOMA values for the free base porphyrins and the metal complexes are insignificant. Decrease in aromaticity due to the bond length alternation (GEO term) is about twice as large as that due to the nonoptimal average bond length (EN term). Interestingly, both terms are somewhat smaller for the complexes containing trivalent metals (M = Mn^{III}, Fe^{III}, Tl^{III}) than for the divalent metal complexes (M = Mg^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}). Hence, the HOMA values for the complexes with trivalent metals are slightly higher.

Table 1. HOMA, EN, GEO, and NICS values for porphyrins and their metal complexes.

	HOMA[a]	HOMA[b]	EN[a]	GEO[a]	NICS [ppm][b]
Porphyrin	0.652	0.666	0.107	0.240	−16.5[c]
ring (1,3)	0.666	0.702	0.132	0.202	−15.2
ring (2,4)	0.452	0.381	0.175	0.373	−4.5
internal cross	0.880	0.932	0.075	0.045	−21.7
Porphyrin metal complex	0.656	0.671	0.094	0.249	
ring (1,3)	0.566	0.556	0.158	0.276	−10.0
;ring (2,4)	0.524	0.556	0.153	0.323	−10.0
internal cross	0.872	0.906	0.071	0.057	−21.0
Porphyrin dianion		0.448			−14.9[c]
ring (1,2,3,4)		0.287			−4.0
internal cross		0.908			−17.5
Porphyrin M^{II} complex	0.638		0.102	0.259	
Porphyrin M^{III} complex	0.682		0.084	0.233	

[a] Mean experimental geometries. [b] Calculated geometries. [c] Value at ring center, see Figure 2.

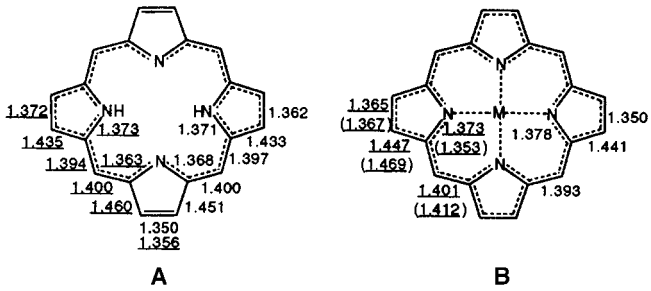


Figure 1. Mean experimental and calculated (underscored) bond lengths for porphyrin (**A**) and its metal complexes (**B**, calculated for M = Mg; values for the free anion in parentheses).

The pyrrole rings with NH groups (1 and 3) are clearly more aromatic[2d] than the other five-membered rings (2 and 4). The mean HOMA values are 0.666 and 0.452, respectively. The NICS values computed in the ring centers (Figure 2) show the difference more explicitly: the −15.2 NICS for rings 1 and 3 is identical with the pyrrole value (−15.1).[4] Thus, the NH groups are not inert bridging groups, as is suggested by the [18]annulene model, but instead are an integral part of the aromatic system. However, rings 2 and 4 have much lower NICS values (−4.5), implying that the C_2H_2 groups function as exocyclic "bridges".

Metal complexation strongly reduces the difference between the two types of pyrrole rings, but does not lead fully to D_{4h} symmetry for the porphyrin skeleton. Application of the HOSE model[11] reveals small residual differences. The HOMA values, as well as the contributing EN and GEO terms, approach the mean of the corresponding data for the free base porphyrin. This is reflected by the results of the DFT computations: The structure of the magnesium complex optimized to D_{4h} symmetry (Figure 1); the NICS at the centers of all the pyrrole rings is −10.0, the mean of the values

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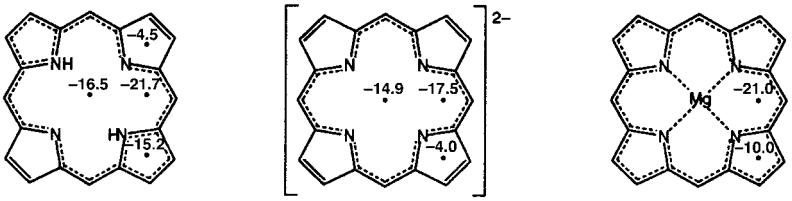


Figure 2. Computed NICS values for free porphyrin base, its dianion, and the Mg complex. The dashed lines indicate the delocalized π systems deduced from the NICS and HOMA analyses.

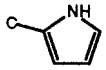
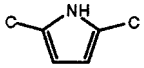
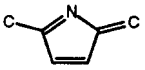
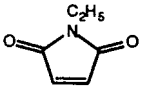
computed for uncomplexed porphyrin (Figure 2). Thus all four pyrrole rings are incorporated into the aromatic system. Interestingly, much lower NICS (only −4.0) are computed for all the pyrrole rings in the uncomplexed porphyrin dianion (Figure 2). Hence, the aromatic system of the dianion consists primarily of the *internal cross*, which must be considered to be an 18 π-electron species.

The mean HOMA values of the *internal cross* (Scheme 1) are significantly higher than those of the pyrrole rings for both the metallic and nonmetallic derivatives. The dearomatization contributions from the GEO and EN terms are comparable. The NICS values corroborate this finding. However, since computation of NICS in the center of the internal cross is impossible for the magnesium complex, we chose an additional point at the geometric mean of two adjacent C–N bonds (see Figure 2). NICS computed at this point for porphyrin is −21.7, slightly higher than the value of −21.0 computed for the Mg complex. The value for the porphyrin dianion is lower (−17.5) implying that the uncomplexed dianion is less aromatic than the Mg complex.

What is responsible for the decrease in aromaticity of the pyrrole rings, in particular rings 2 and 4, in the porphyrin macrocycle? Doubly bonded substituents are known to lead to strongly localized, quinonoid-like structures and hence to decrease the aromatic character of rings. For example, negative HOMA values and positive NICS are obtained for *para*-benzoquinone. Similar structural effects are observed for 2- and/or 5-substituted pyrroles (Table 2). The typical HOMA value for pyrroles of about 0.92 decreases substantially to 0.27, when a doubly bonded substituent is present. Similarly, the NICS value of −15.1 for pyrrole is reduced to −1.8 for 2-azafulvene. Maleimide has a negative HOMA and a positive NICS value (Table 2).

In conclusion, both the NICS values and the HOMA analyses (albeit attenuated due to the uncertainty in the hydrogen positions) agree: rings 1 and 3 in the porphyrin system can be considered to be true pyrrole rings. The π system consists of these rings and the internal cross. Rings 2 and 4 behave almost like pyrroles with doubly bonded substituents and have short, localized CC double bonds. While the dianion has four essentially localized double bonds, the corresponding metal derivatives involve all the π electrons in the aromatic system.

Table 2. HOMA, EN, GEO, and NICS values for four kinds of 2- and 5-substituted pyrrole derivatives and for *para*-benzoquinone.

Compound	HOMA	EN	GEO	NICS [ppm]
	0.907[a]	0.002	0.091	−15.1[d]
	0.932[b]	0.015	0.052	−15.1[d]
	0.274[c]	0.217	0.509	−1.8[e]
	−0.443	0.380	1.060	+0.9[f]
	−0.508	0.392	1.116	+7.9

[a] Mean of 15 geometries. [b] Mean of 6 geometries. [c] Mean of 5 geometries. [d] Computed for unsubstituted pyrrole. [e] Computed for 2-azafulvene. [f] Computed for maleimide.

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[1] a) V. I. Minkin, M. N. Glukhovtsev, B. Ya. Simkin, *Aromaticity and Antiaromaticity—Electronic and Structural Aspects*, Wiley, New York, **1994**; b) P. von R. Schleyer, H. Jiao, *Pure Appl. Chem.* **1996**, *28*, 209–218.

[2] J. L. Eldridge, L. M. Jackman, *J. Chem. Soc.* **1961**, 859–866; b) H. J. Dauben, Jr., J. D. Wilson, J. L. Laity in *Non-benzenoid Aromatics, Vol. 2* (Ed.: J. Snyder), Academic Press, New York, **1971**, and references therein; c) A. R. Katritzky, P. Barczyñski, G. Musumarra, D. Pisano, M. Szafran, *J. Am. Chem. Soc.* **1989**, *111*, 7–15; K. Jug, A. Köster, *J. Phys. Org. Chem.* **1991**, *4*, 163–169; d) however, see P. von R. Schleyer, P. K. Freeman, H. Jiao, B. Goldfuss, *Angew. Chem.* **1995**, *107*, 332–335; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 337–340, and ref. [1b]; e) U. Fleischer, W. Kutzelnigg, P. Lazzeretti, V. Müllenkamp, *J. Am. Chem. Soc.* **1994**, *116*, 5298–5306; f) H. Jiao, P. von R. Schleyer, M. N. Glukhovtsev, *J. Phys. Chem.* **1996**, *110*, 12299–12304.

[3] a) A. Julg, P. François, *Theor. Chim. Acta* **1967**, *8*, 249–259; b) C. W. Bird, *Tetrahedron* **1985**, *41*, 1409–1414; c) J. Kruszewski, T. M. Krygowski, *Tetrahedron Lett.* **1972**, 3839–3842; d) T. M. Krygowski, *J. Chem. Inf. Comput. Sci.* **1993**, *33*, 70–78; e) T. M. Krygowski, A. Ciesielski, C. W. Bird, A. Kotschy, *ibid.* **1995**, *35*, 203–210.

[4] a) P. von R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. R. van Eikema Hommes, *J. Am. Chem. Soc.* **1996**, *118*, 6317–6318; b) G. Subramanian, P. von R. Schleyer, H. Jiao, *Angew. Chem.* **1996**, *108*, 2824–2827; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2638–2641.

[5] Cambridge Structural Database, release October 1996; see: F. H. Allen, J. E. Davies, J. J. Galloy, O. Johnson, O. Kennard, C. F. MacRae, E. M. Mitchell, G. F. Mitchell, J. M. Smith, D. G. Watson, *J. Chem. Inf. Comput. Sci.* **1991**, *31*, 187–204.

[6] See, for example, E. Vogel, *J. Heterocycl. Chem.* **1996**, *33*, 1461–1487 and references therein.

[7] a) T. M. Krygowski, M. Cyrañski, *Tetrahedron* **1996**, *52*, 1713–1722; b) *ibid.* **1996**, *52*, 10255–10264.

[8] L. Pauling, *J.Am. Chem. Soc.* **1947**, *69*, 542–553.

[9] In the Cambridge Structural Database, AS refers to the precision of the crystal structure determination. For example, "AS = 1, 2" means that the mean estimated standard deviation for the bond lengths does not exceed 0.01 Å.

[10] See, for example, J. D. Dunitz, *X-Ray Analysis and the Structure of Organic Molecules*, Cornell University Press, Ithaca, **1979**.

[11] a) T. M. Krygowski, R. Anulewicz, J. Kruszewski, *Acta Crystallogr. Sect. B* **1983**, *39*, 732–739; b) T. M. Krygowski, R. Anulewicz, M. Wisiorowski, *Pol. J. Chem.* **1995**, *69*, 1579–1584. The HOSE model permits the estimation of the canonical structure weights directly from

  1433-7851/98/3701-0179 $ 17.50+.50/0

the bond lengths of the molecule containing π electrons or its fragment.
[12] See M. Boronat, E. Ortí, P. M. Viruela, F. Tomás, *J. Mol. Struct. Theochem* **1997**, *390*, 149–156.
[13] Gaussian 94: M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, Gaussian, Pittsburgh, PA, **1995**.
[14] For further calculations on the porphyrin system, see a) D. Lamoen, M. Parinello, *Chem. Phys. Lett.* **1996**, *248*, 309–315 and references therein; b) P. M. Kozlowski, A. A. Jarzecki, P. Pulay, *J. Phys. Chem.* **1996**, *100*, 7007–7013 and references therein.

Design and Evaluation of a Practical Camphor-Based Methyl Ketone Enolate for Highly Stereoselective "Acetate" Aldol Reactions**

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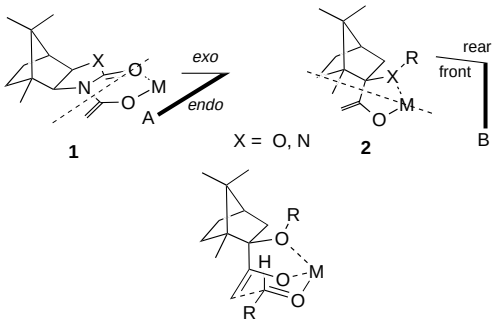
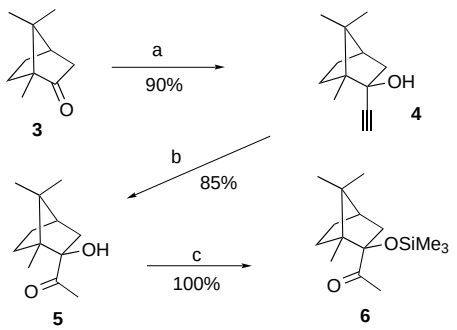
Control of the configuration of newly forming stereogenic carbon atoms in aldol condensation processes has focused enormous efforts over the last two decades.[1] Special attention has been given to the use of chiral enolates derived from carboxylic acids[2] because of the easy final removal of the auxiliary to obtain either β-hydroxy carbonyl or 1,3-dihydroxylic compounds, which are frequently present in natural products.[3] A conceptually different, but in practice equivalent, strategy to access to these fragments lies in the use of enolates derived from chiral α-hydroxy ketones.[4] In this instance, the aldol products, upon oxidative cleavage of the α-ketol moiety, give the desired β-hydroxy carbonyl system.[5] The major drawbacks associated with this strategy are the destruction of the covalently bounded chiral adjuvant at the final stage, and the insufficient stereoselectivity generally attained with α-unsubstituted enolates.[6] Although considerable advances have been made in recent years to overcome this latter limitation by carrying out acetate aldol reactions mediated by both metal enolates bearing chiral ligands and external chiral catalysts,[7] the problem associated with enolates of chiral acetates still remains not well resolved;[8] in all but one case,[4j] the lack of stereoselection in aldol reactions with methyl ketone enolates is specially dramatic.[4b,g,h,i]

We have recently reported on the reaction of *N*-acetyl imide enolates **1** with aldehydes to give the corresponding adducts with modest levels of diastereoselectivity (Scheme 1).[9] In an attempt to take advantage of the stereodifferentiating power of the camphor skeleton more effectively, we designed the new camphor-derived enolate **2**. The conception of **2** has been guided by two major goals: a) to provoke the electrophilic aldehyde to follow a trajectory of approach closer to the camphor skeleton, and b) to force a facial discrimination between the rear side and the sterically more demanding front side of the camphor skeleton, depicted as the half-spaces defined by plane B in Scheme 1,[10] instead of the more commonly used *endo/exo* discrimination across opposite sides of plane A.[11] Accordingly, if one assumes that a chelating metal ion like lithium engages in three-point coordination, a very high diastereoselectivity should be expected through a Zimmerman–Traxler six-membered transition state.[12] From this design the methyl ketone **5**[13] (Scheme 2) is a primary candidate to evaluate the above



Scheme 1. Design of the new chiral methyl ketone enolate **2** by moving the acetyl moiety of **1** nearer to the camphor skeleton. Also shown is the transition state accounting for the aldol reaction of **2**.



Scheme 2. Synthesis of the chiral methyl ketone reagents **5** and **6**: a) HC≡CLi, THF, −78 →room temperature (RT) (*endo:exo* 97:3); b) HgO, H_2SO_4, Me_2CO, reflux; c) TMSO, TfOH cat., RT.

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[+] X-ray structure analysis.

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