Ring Selectivity in the Na/EtOH Reduction of 1-Aryl-7-methoxynaphthalenes

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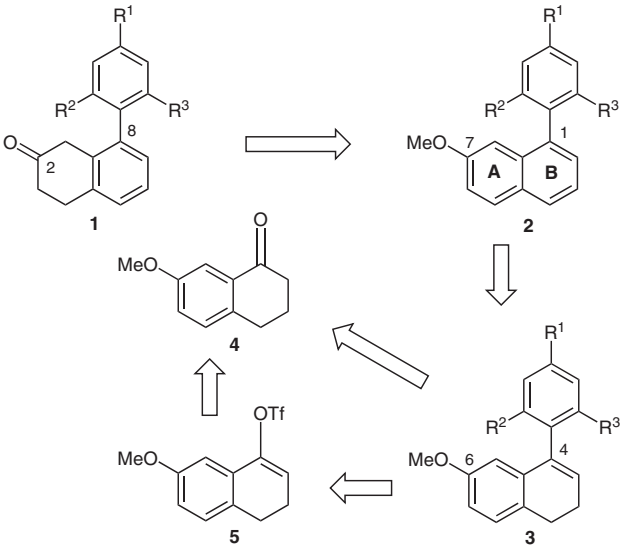
Abstract: Na/EtOH reduction of 1-aryl-7-methoxynaphthalenes occurred preferentially at the A-ring when no substituents were present at the *ortho*-positions of the aryl group (up to 100% selectivity), to afford 1-aryl-7-methoxy-1,2,3,4-tetrahydronaphthalenes. *Ortho*-substitution of the 1-aryl moiety favored B-ring reduction (up to 85:15 selectivity) giving rise, after acidic hydrolysis of the vinyl ether intermediate, to the corresponding 8-aryl-2-tetralones.

Key words: biaryls, chemoselectivity, steric hindrance, reductions, sodium

Selective reduction of polyaromatic compounds has received little attention despite the fact there is much interest in a controlled access to differently substituted hydroaromatic derivatives. The few studies published so far deal with metal/ammonia reduction of terphenyls[1] and naphthyl or dinaphthylbenzenes.[2] These studies revealed that the ratio of central to outer ring reduction products depended on the particular metal used in the case of *p*-terphenyls, whereas *m*- and *o*-terphenyls gave only central ring reduction. Moreover, reduction of 1- and 2-phenylnaphthalene never occurred at the phenyl ring.[2a] The controlled reduction of substituted 2-methoxy naphthalene derivatives is of great interest since the resulting vinyl ether can be easily hydrolyzed to 2-tetralones. Such compounds have been frequently used in organic synthesis due to their high versatility and suitability as precursors of a wide range of synthetic and natural products and their derivatives,[3] heterocycles,[4] and pharmaceuticals[5] showing biological activities and other useful properties. However, unlike their congeners the 1-tetralones, which are inexpensive, easily prepared, and commercially available substances, 2-tetralones are often very expensive and much more difficult to synthesize.

The most common methods for the preparation of 2-tetralones[6] involves 1,2-transposition of the carbonyl group of 1-tetralones,[7] reduction of substituted 2-methoxy-naphthalenes followed by hydrolysis,[8] cyclization of diazoketones,[9] and the Friedel–Crafts reaction of aromatic acyl chlorides with olefins.[10]

In connection with a program devoted to the synthesis of polyaromatic compounds such as helicenes,[11] we required several 8-aryl-2-tetralones (**1**; Scheme 1) bearing different substituents at the aryl moiety. To the best of our knowledge, the synthesis of 8-aryl-2-tetralones has been addressed only using the carbanion-induced condensation of differently substituted 2*H*-pyran-2-ones with a 1,4-cyclohexanedione monoketal,[12] however, the synthesis of these starting materials is not easy.



Scheme 1 Retrosynthesis to 8-aryl-2-tetralones **1**.

Among the known synthetic approaches to 2-tetralones, we decided to use the Na/EtOH reduction of 2-methoxy-naphthalenes,[13] initially described by Cornforth et al.,[14] which had been successfully applied by us for the synthesis of differently substituted 8-alkyl-2-tetralones.[15] Birch reductions[16] of naphthalenes bearing electron-releasing substituents at the C-1 are known to occur at the unsubstituted aromatic ring, whereas electron-withdrawing groups at C-1 direct the reduction to the same ring.[17] On the other hand, reduction of 1-phenylnaphthalene afforded exclusively the product resulting from reaction of the naphthalene ring bearing the phenyl substituent, but the effect of the presence of an alkyl- or alkoxy-substituted phenyl ring on the reduction of 1-arylnaphthalenes is unknown. In the present paper we report a study on the ring selectivity of the Na/EtOH reduction of differently substituted 1-aryl-7-methoxynaphthalenes **2** (Scheme 1) and show that the relative ratio of reduction of the A or B rings of the naphthalene unit is dependent on the substitution pattern at the aryl moiety.

In order to describe a general synthesis of 1-aryl-7-methoxynaphthalenes **2** we decided to apply the retrosynthesis shown in Scheme 1. Thus, compounds **2** could be formed by aromatization of the corresponding 4-aryl-6-methoxy-

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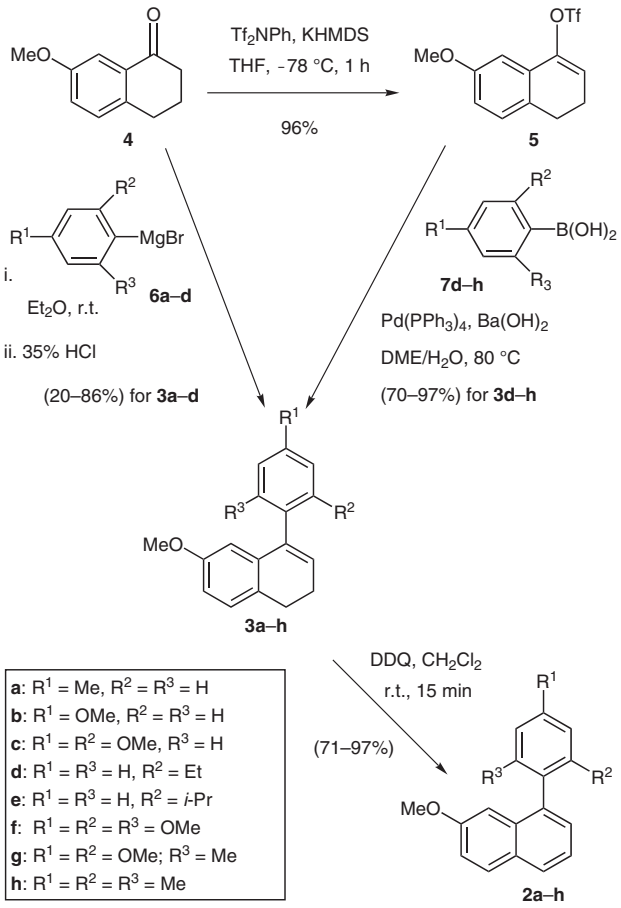
1,2-dihydronaphthalene derivatives **3**. The introduction of the aryl substituent at the required position was envisaged by two alternative routes: addition of the corresponding aryl Grignard to the α-tetralone **4**, followed by dehydration of the resulting carbinol, or metal-catalyzed cross-coupling reaction of the corresponding aryl organometallic species with the enol triflate **5**, also accessible from **4**.

For the synthesis of compounds **3** (Scheme 2), we initially chose the route based on the addition of differently substituted aryl Grignard reagents **6** to α-tetralone **4**.[18]



Scheme 2 Synthesis of 1-aryl-7-methoxynaphthalenes **2a**–**h**.

Thus, the reaction of *p*-tolylmagnesium bromide **6a** with commercially available 7-methoxy-1-tetralone (**4**) afforded the corresponding carbinol which, after treatment with 35% HCl, gave 4-(*p*-tolyl)-6-methoxy-1,2-dihydronaphthalene (**3a**), in 73% yield (Scheme 2). Under the same conditions, 4-methoxyphenyl magnesium bromide (**6b**) and the 2,4-dimethoxyphenyl derivative **6c** furnished dihydronaphthalenes **3b** (86%) and **3c** (72%), respectively. Nevertheless, when the reaction was carried out with 2-ethylphenyl magnesium bromide (**6d**), bearing a bulky ethyl substituent at the *ortho*-position, compound **3d** was formed in a poor 20% yield.

Then, we turned our attention to the alternative route depicted in Scheme 1, the metal-catalyzed cross-coupling reaction between enol triflate **5** and an organometallic species. Among the different organometallic reagents available, we decided to use boronic acids,[19] due to the excellent results achieved in their cross-coupling reactions with sterically hindered derivatives.[20] Thus, the reaction of enol triflate **5**,[21] prepared in 96% yield from α-tetralone **4**, with commercially available 2-ethylphenyl boronic acid (**7d**) [$Pd(PPh_3)_4$, $Ba(OH)_2 \cdot 8H_2O$, DME–H_2O, 80 °C, 40 min],[20] furnished dihydronaphthalene **3d** in, an excellent, 94% yield. Under the same experimental conditions, the cross-coupling reactions between enol triflate **5** and differently substituted aryl boronic acids **7e**–**h**,[22] bearing one or two substituents at the *ortho*-positions, afforded the corresponding dihydronaphthalenes **3e**–**h** with good to excellent yields (70–97%, Scheme 2).

The full aromatization of dihydroaromatic derivatives **3a**–**h** was achieved using DDQ in dichloromethane at room temperature for 15 minutes giving rise to the corresponding 1-aryl-7-methoxynaphthalenes **2a**–**h** with excellent yields ranging from 71–97% (Scheme 2).

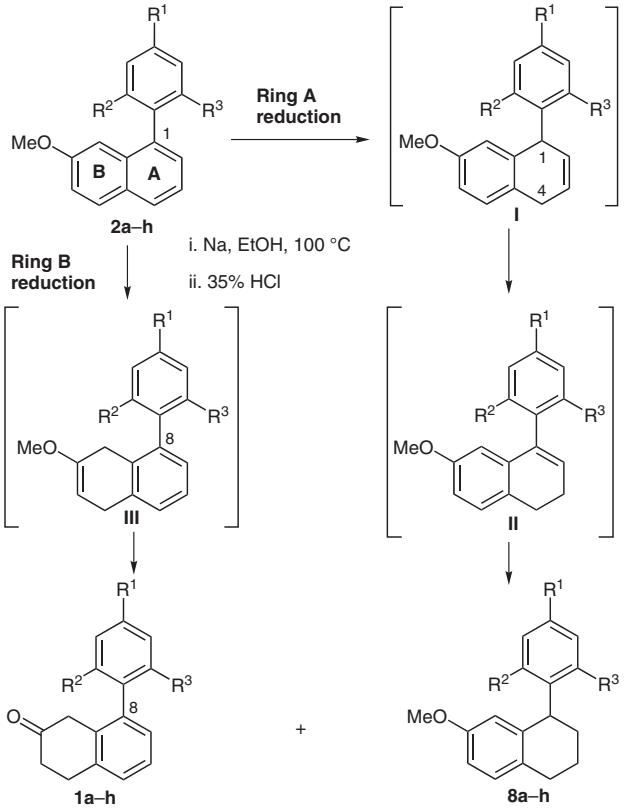
With 1-aryl-7-methoxynaphthalenes **2a**–**h** in hand, we carried out metal-mediated reductions (Scheme 3). All reactions were performed with an excess of sodium in ethanol at 100 °C until all of the starting material had been consumed by TLC, this was followed by treatment with 35% hydrochloric acid to hydrolyze the vinyl methyl ether initially formed from the reduction of the B-ring of compounds **2a**–**h**.

When 1-*p*-tolyl-7-methoxynaphthalene **2a** was submitted to typical reduction conditions and treated with 35% hydrochloric acid, we obtained 1-(*p*-tolyl)-7-methoxy-1,2,3,4-tetrahydronaphthalene (**8a**), resulting from reduction of ring-A of the naphthalene unit, as the exclusive product, in 62% yield (Scheme 3). Compound **8a** was probably formed from reduction of **2a** to the corresponding 1,4-dihydroaromatic intermediate **I** (Scheme 3), isomerization of the double bond to derivative **II** and further reduction under the experimental conditions to give the 1,2,3,4-tetrahydronaphthalene **8a**. This result was not unexpected since Rabideau et al.[2a] had shown that the Birch reduction of 1-phenylnaphthalene afforded exclusively the product resulting from the reduction of the naphthalene ring bearing the phenyl substituent.

The reduction of derivative **2b**, bearing a *p*-methoxyphenyl substituent at C-1 afforded 1-(*p*-methoxyphenyl)-7-methoxy-1,2,3,4-tetrahydronaphthalene (**8b**) again as the exclusive product, in 71% yield, showing that the presence of a more electron-donating substituent on the phenyl unit has no influence on the ring-selectivity of the reduction process.

Reduction of compound **2c**, with a 2,4-dimethoxyphenyl substituent, gave a 30:70 mixture of β-tetralone **1c** and tetrahydronaphthalene **8c**. Compound **1c** was formed from reduction of the B-ring of **2c** followed by acidic hydrolysis of the vinyl ether intermediate **III** (Scheme 3).

With the aim of evaluating if this result was due to the presence of two electron-donor groups or the existence of a methoxy substituent at the *ortho*-position of the 1-aryl group in **2c**, we performed the reduction of naphthalene **2d**, bearing a 2-ethylphenyl group at C-1. In this case, a 50:50 mixture of compounds **1d** and **8d** was obtained, showing that the presence of a bulky substituent at the *ortho*-position enhanced the B-ring reduction of the naphthalene derivative. This assumption was confirmed after reduction of compound **2e**, with a 2-isopropylphenyl group at C-1, which gave a 60:40 mixture of compounds **1e** and **8e**, with reduction of the B-ring of **2e** the major process. An identical result was obtained from reduction of derivative **2f**, with two methoxy groups at the *ortho*-positions, affording a 60:40 mixture of compounds **1f** and **8f**.



0	**a**: R^1 = Me, R^2 = R^3 = H	**100** (62)[a]
0	**b**: R^1 = OMe, R^2 = R^3 = H	**100** (71)
30 (29)[a]	**c**: R^1 = R^2 = OMe, R^3 = H	**70** (50)
50 (36)	**d**: R^1 = R^3 = H, R^2 = Et	**50** (36)
60 (45)	**e**: R^1 = R^3 = H, R^2 = *i*-Pr	**40** (20)
60 (32)	**f**: R^1 = R^2 = R^3 = OMe	**40** (28)
75 (60)	**g**: R^1 = R^2 = OMe; R^3 = Me	**25** (22)
85 (54)	**h**: R^1 = R^2 = R^3 = Me	**15** (8)

[a] In brackets, isolated yields of compounds **1** and **8** after flash chromatography

Scheme 3 Na/EtOH reduction of 1-aryl-7-methoxynaphthalenes **2a**–**h**.

To further increase the ratio of B-ring reduction, and as a consequence the yield of the 8-aryl-2-tetralones, we carried out the reaction with 1-arylnaphthalene **2g**, with a methoxy and a methyl group at the *ortho*-positions. In this case, a 75:25 mixture of derivatives **1g** (60% isolated yield) and **8g**[23] resulted.

Finally, the best B-ring selectivity in the reduction process (85:15) was achieved using compound **2h**, bearing two methyl groups at the *ortho*-positions, as starting material. Under the reduction conditions followed by acidic hydrolysis, 8-aryl-2-tetralone **1h** could be isolated pure after flash chromatography in 54% yield.

The relative ratio of A-ring/B-ring reduction products achieved from 1-arylnaphthalenes **2** is not easy to rationalize from the mechanistic point of view. Taking into account that the structure of the metal-mediated reduction product is determined by the site of protonation of the radical anion formed after the first electron transfer,[24] this favored formation of the radical anion of the initial intermediate **I**, (Scheme 3) which could explain the preferred ring-A reduction. Two resonance forms with the radical at C-1 of **I** and the anion at C-4, or the reverse, can be considered. In the former, an *ortho*-unsubstituted aryl group could result in delocalization of the electrons, thus favoring the reduction of the A-ring. The existence of *ortho*-substituents on the aryl group could distort the planarity of the system causing the destabilization of the radical intermediate and increasing the ratio of the product resulting from B-ring reduction. If the negative charge on the radical anion is situated at C-1 of **I**, the non-planar geometry caused by *ortho*-substitution at the aryl group could inhibit protonation of this intermediate due to steric influences, thus B-ring reduction would be favored.

In summary, we have shown that the ring-selectivity of the reduction of 1-aryl-7-methoxynaphthalenes can be modulated by the substitution pattern at the 1-aryl fragment. The existence of small substituents (H or OMe) at the *ortho*-positions gives rise mainly to the formation of the products resulting from reduction of the aryl substituted A-ring of the naphthalene unit affording 1-aryl-7-methoxy-1,2,3,4-tetrahydronaphthalenes. With one or two alkyl groups at the *ortho*-positions of the 1-aryl moiety, reduction of the B-ring is preferred, giving rise to the corresponding 8-aryl-2-tetralones, after acidic work-up. The ring-selectivity of the process seems to be governed by the ease of protonation and/or stabilization of the initially formed radical anion at C-1, both disfavored when the co-planarity between the 1-aryl group and the dihydronaphthalene ring is lost due to the presence of different bulky substituents at the *ortho*-positions of the 1-aryl moiety.

Na/EtOH Reduction; Typical Procedure

To a solution of the corresponding 1-aryl-7-methoxynaphthalene **2** (0.7 mmol) in EtOH (35 mL) heated at 100 °C, under argon, 6 or 7 pieces of Na of ca. 0.5 cm were added, and during the reaction time the same amount of Na was maintained in the reaction media. The mixture was vigorously stirred at 100 °C until all the starting material had been consumed by TLC. The reaction was quenched with EtOH and cooled to room temperature. When all the Na had completely disappeared, H_2O was slowly added, the mixture was cooled to 0 °C and 35% HCl was added dropwise until acid pH (1–2). After

extraction with CH_2Cl_2, washing with sodium bicarbonate, and usual workup, the corresponding mixture of 1-aryl-7-methoxy-1,2,3,4-tetrahydronaphthalenes **8** and 8-aryl-2-tetralones **1** was obtained and separated by flash chromatography.

Spectral Data for 8-Aryl-2-tetralones 1c–h

Compound **1c**: ^{1}H NMR: δ = 2.49 (m, 2 H), 3.12 (m, 2 H), 3.28 and 3.48 (AB system, 2 H, *J* = 19.6 Hz), 3.72 (s, 3 H), 3.84 (s, 3 H), 6.52 (t, 1 H, *J* = 2.3 Hz), 6.55 (d, 1 H, *J* = 2.5 Hz), 7.04 (d, 1 H, *J* = 8.0 Hz), 7.13 (dd, 1 H, *J* = 2.3 and 6.8 Hz), 7.24 (m, 2 H). ^{13}C NMR: δ = 28.4, 38.1, 43.0, 55.3, 55.4, 98.5, 104.5, 121.9, 126.3, 126.6, 128.9, 131.4, 132.4, 136.5, 138.0, 157.4, 160.7, 211.6.

Compound **1d**: ^{1}H NMR: δ = 1.02 (t, 3 H, *J* = 7.6 Hz), 2.35 (ddd, 2 H, *J* = 7.4, 7.6 and 10.2 Hz), 2.57 (t, 2 H, *J* = 6.7 Hz), 3.15 (t, 2 H, *J* = 6.7 Hz), 3.19 and 3.33 (AB system, 2 H, *J* = 19.0 Hz), 7.01–7.32 (m, 7 H). ^{13}C NMR: δ = 16.1, 27.1, 29.9, 39.1, 43.7, 126.7, 127.2, 127.6, 128.8, 129.3, 129.4, 130.4, 132.3, 137.8, 140.3, 142.0, 142.7, 211.7.

Compound **1e**: ^{1}H NMR: δ = 1.11 (d, 3 H, *J* = 6.8 Hz), 1.17 (d, 3 H, *J* = 6.8 Hz), 2.61 (t, 2 H, *J* = 6.8 Hz), 2.65 (sept, 1 H, *J* = 6.8 Hz), 3.18 (t, 2 H, *J* = 6.8 Hz), 3.23 and 3.37 (AB system, 2 H, *J* = 19.6 Hz), 7.02–7.46 (m, 7 H). ^{13}C NMR: δ = 23.1, 24.6, 28.8, 29.9, 38.1, 42.9, 125.5, 125.6, 126.1, 126.6, 128.0, 128.3, 129.3, 131.4, 136.8, 138.6, 141.1, 146.5, 210.6.

Compound **1f**: ^{1}H NMR: δ = 2.56 (t, 2 H, *J* = 6.6 Hz), 3.11 (t, 2 H, *J* = 6.6 Hz), 3.32 (s, 2 H), 3.68 (s, 6 H), 3.86 (s, 3 H), 6.21 (s, 2 H), 7.11–7.30 (m, 3 H). ^{13}C NMR: δ = 28.9, 38.2, 42.7, 55.4, 55.7, 90.7, 109.9, 125.8, 126.5, 130.0, 133.1, 133.6, 136.2, 158.2, 161.0, 211.8.

Compound **1g**: ^{1}H NMR: δ = 1.96 (s, 3 H), 2.60 (m, 2 H), 3.15 (t, 2 H, *J* = 6.4 Hz), 3.20 and 3.33 (AB system, 2 H, *J* = 19.9 Hz), 3.68 (s, 3 H), 3.86 (s, 3 H), 6.40 (d, 1 H, *J* = 2.1 Hz), 6.45 (d, 1 H, *J* = 2.1 Hz), 7.05 (dd, 1 H, *J* = 2.1 and 6.4 Hz), 7.25 (m, 2 H). ^{13}C NMR: δ = 20.5, 28.9, 38.3, 42.3, 55.3, 55.5, 96.0, 106.4, 121.0, 126.3, 126.5, 129.0, 132.5, 136.5, 136.8, 138.1, 157.6, 159.8, 211.7.

Compound **1h**: ^{1}H NMR: δ = 1.87 (s, 6 H), 2.32 (s, 3 H), 2.56 (t, 2H, *J* = 6.6 Hz), 3.10–3.15 (m, 4 H), 6.92 (s, 2 H), 6.99 (d, 1 H, *J* = 2.0 Hz), 7.25 (m, 2 H). ^{13}C NMR: δ = 20.2, 21.0, 28.9, 38.3, 42.1, 126.4, 126.8, 127.9, 128.2, 131.3, 135.6, 136.5, 136.9, 137.0, 140.2, 210.9.

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References

(1) Harvey, R. G.; Lindow, D. F.; Rabideau, P. W. *J. Am. Chem. Soc.* **1972**, *94*, 5412.
(2) (a) Rabideau, P. W.; Marcinow, Z. *J. Org. Chem.* **1990**, *55*, 3812. (b) Eisenbraun, E. J.; Melton, R. G.; Flanagan, P. W.; Hamming, M. C.; Keen, G. W. *Prepr.–Am. Chem. Soc., Div. Pet. Chem.* **1971**, *16*, B43.
(3) Recent examples: (a) Tririya, G.; Zanger, M. *Synth. Commun.* **2004**, *34*, 3047. (b) Silveira, C. C.; Machado, A.; Braga, A. L.; Lenardao, E. J. *Tetrahedron Lett.* **2004**, *45*, 4077. (c) Barolo, S. M.; Lukach, A. E.; Rossi, R. A. *J. Org. Chem.* **2003**, *68*, 2807. (d) Renaud, J. L.; Dupau, P.; Hay, A.-E.; Guingouain, M.; Dixneuf, P. H.; Bruneau, C. *Adv. Synth. Catal.* **2003**, *345*, 230.
(4) Recent examples: (a) Jha, A.; Beal, J. *Tetrahedron Lett.* **2004**, *45*, 8999. (b) Li, D.; Zhao, B.; Sim, S.-P.; Li, T.-K.; Liu, A.; Liu, L. F.; LaVoie, E. J. *Bioorg. Med. Chem.* **2003**, *11*, 521. (c) Wang, X.-Z.; Yao, Z.-J.; Liu, H.; Zhang, M.; Yang, D.; George, C.; Burke, T. R. *Tetrahedron* **2003**, *59*, 6087.
(5) Recent examples: (a) Youngman, M. A.; Willard, N. M.; Dax, S. L.; McNally, J. J. *Synth. Commun.* **2003**, *33*, 2215. (b) Gemma, S.; Butini, S.; Fattorusso, C.; Fiorini, I.; Nacci, V.; Bellebaum, K.; McKissic, D.; Saxenac, A.; Campiani, G. *Tetrahedron* **2003**, *59*, 87.
(6) Reviews: (a) Silveira, C. C.; Braga, A. L.; Kaufman, T. S.; Lenardao, E. J. *Tetrahedron* **2004**, *60*, 8295. (b) Schner, V. F.; Przhiyaglovskaya, N. M. *Russ. Chem. Rev.* **1966**, *35*, 523.
(7) (a) Chen, F.; Feng, X.; Qin, B.; Zhang, G.; Jiang, Y. *Synlett* **2003**, 558. (b) Alcock, L. J.; Mann, I.; Peach, P.; Wills, M. *Tetrahedron: Asymmetry* **2002**, *13*, 2485. (c) Parker, M. H.; Chen, R.; Conway, K. A.; Lee, D. H. S.; Luo, C.; Boyd, R. E.; Nortey, S. O.; Ross, T. M.; Scorr, M. K.; Reitz, A. B. *Bioorg. Med. Chem.* **2002**, *10*, 3565.
(8) (a) Hirayama, Y.; Ikunaka, M.; Matsumoto, J. *Org. Process Res. Dev.* **2005**, 30. (b) Banerjee, A. K.; Vera, W. J. *J. Chem. Res., Synop.* **2004**, 135. (c) Cheung, A. W.-H.; Danho, W.; Swistok, J.; Qi, L.; Kurylko, G.; Rowan, K.; Yeon, M.; Franco, L.; Chu, X.-J.; Chen, L.; Yagaloff, K. *Bioorg. Med. Chem. Lett.* **2003**, *13*, 133. (d) Jha, A.; Dimmock, J. R. *Can. J. Chem.* **2003**, *81*, 293. (e) Taber, D. F.; Neubert, T. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **2002**, *124*, 12416.
(9) (a) Li, D.; Zhao, B.; Sim, S.-P.; Li, T.-K.; Liu, A.; Liu, L. F.; LaVoie, E. J. *Bioorg. Med. Chem.* **2003**, *11*, 3795. (b) Makhey, D.; Li, D.; Zhao, B.; Sim, S.-P.; Li, T. K.; Liu, A.; Liu, L. F.; LaVoie, E. J. *Bioorg. Med. Chem.* **2003**, *11*, 1809. (c) Maguire, A. R.; O'Leary, P.; Harrington, F.; Lawrence, S. E.; Blake, A. J. *J. Org. Chem.* **2001**, *66*, 7166.
(10) (a) Oishi, S.; Kang, S. U.; Liu, H.; Zhang, M.; Yang, D.; Deschamps, J. R.; Burke, T. R. Jr. *Tetrahedron* **2004**, *60*, 2971. (b) Gray, A. D.; Smith, T. P. *J. Org. Chem.* **2001**, *66*, 7113.
(11) (a) Carreño, M. C.; González-López, M.; Urbano, A. *Chem. Commun.* **2005**, 611. (b) Carreño, M. C.; García-Cerrada, S.; Urbano, A. *Chem.–Eur. J.* **2003**, *9*, 4118–4131. (c) Carreño, M. C.; García-Cerrada, S.; Urbano, A. *Chem. Commun.* **2002**, 1412. (d) Carreño, M. C.; García-Cerrada, S.; Urbano, A. *J. Am. Chem. Soc.* **2001**, *123*, 7929.
(12) (a) Ram, V. J.; Agarwal, N.; Saxena, A. S.; Farhanullah, ; Sharon, A.; Maulik, P. R. *J. Chem. Soc., Perkin Trans. 1* **2002**, 1426. (b) Ram, V. J.; Agarwal, N.; Farhanullah, *Tetrahedron Lett.* **2002**, *43*, 3281.
(13) Soffer, M. D.; Bellis, M. P.; Gellerson, H. E.; Stewart, R. A. *Org. Synth.* **1952**, *32*, 97.
(14) Cornforth, J. W.; Cornforth, R. H.; Robinson, R. *J. Chem. Soc.* **1942**, 689.
(15) (a) Carreño, M. C.; García-Cerrada, S.; Sanz-Cuesta, M. J.; Urbano, A. *Chem. Commun.* **2001**, 1452–1453. (b) Carreño, M. C.; Enríquez, A.; García-Cerrada, S.; Sanz-Cuesta, M. J.; Urbano, A. unpublished results.
(16) Birch, A. J. *J. Chem. Soc.* **1944**, 430.
(17) (a) Harvey, R. G. *Synthesis* **1970**, 161. (b) Rabideau, P. W. *Tetrahedron* **1989**, *45*, 1579. (c) Rabideau, P. W.; Marcinow, Z. *Org. React.* **1992**, *42*, 1.
(18) For examples on the additions of aryl Grignard reagents to α-tetralones see: (a) Alcock, N. J.; Mann, I.; Peach, P.; Wills, M. *Tetrahedron: Asymmetry* **2002**, *13*, 2485. (b) Schneider, M. R.; Schiller, C. D. *Arch. Pharm.* **1990**, *323*, 17. (c) Laus, G.; Tourwe, D.; Van Binst, G. *Heterocycles* **1984**, *22*, 311. (d) Adam, G.; Andrieux, J.; Plat, M. *Tetrahedron* **1982**, *38*, 2403. (e) Bindal, R. D.; Durani, S.; Kapil, R. S.; Anand, N. *Synthesis* **1982**, 405.

(19) (a) Suzuki, A. *Modern Arene Chemistry*; Wiley-VCH: New York, **2002**, 53. (b) Miyaura, N.; Suzuki, A. *Chem. Rev.*; **1995**, 95, 2457. For examples of cross-coupling reactions between enol triflates and boronic acids and derivatives see: (c) Miyashita, K.; Sakai, T.; Imanishi, T. *Org. Lett.* **2003**, *5*, 2683. (d) Basil, L. F.; Nakano, H.; Frutos, R.; Kopach, M.; Meyers, A. I. *Synthesis* **2002**, 2064. (e) Pal, K. *Synthesis* **1995**, 1485.

(20) Watanabe, T.; Miyaura, N.; Suzuki, A. *Synlett* **1992**, 207.

(21) Scheiper, B.; Bonnekessel, M.; Krause, H.; Fürstner, A. *J. Org. Chem.* **2004**, *69*, 3943.

(22) Boronic acids **7d**–**h** were commercially available (**7d**–**f** and **7h**) or previously described: **7g**: Bringmann, G.; Goetz, R.; Keller, P. A.; Walter, R.; Boyd, M. R.; Lang, F.; Garcia, A.; Walsh, J. J.; Tellitu, I.; Bhaskar, K. V.; Kelly, T. R. *J. Org. Chem.* **1998**, *63*, 1090.

(23) The ^{1}H NMR spectrum ($CDCl_3$) of compound **8g** showed several broad non-well resolved signals probably due to the presence of atropisomers caused by a hindered rotation about the aryl(sp^2)-C_1(sp^3) single bond: Eliel, E. L.; Wilen, S. H.; Doyle, M. P. In *Basic Organic Stereochemistry*; Wiley: New York, **2001**, 629; when **8g** was heated in $C_2D_2Cl_4$ at 390 K the broad signals coalesced.

(24) Carey, F. A.; Sundberg, R. J. In *Advanced Organic Chemistry. Part B: Reactions and Synthesis*, 4th ed.; Kluwer: Norwell, **2000**.