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Alumina-mediated dealkylative dimerization of 4-aminobenzyl esters

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Abstract—Treatment of 4-aminobenzyl esters with Al_2O_3 in DCM at rt afforded the dealkylative dimerized 4,4′-diamino-diphenylmethanes in satisfactory yield. The reaction may proceed via a quinone methide iminium ion intermediate, which may then undergo Michael type addition followed by retro-aldol extrusion of a formaldehyde species.

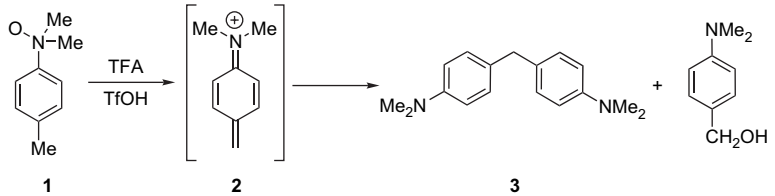
1. Introduction

Diarylmethane derivatives are useful building blocks for the design of supramolecular structures,[1] polymer synthesis,[2] as well as biologically active compounds.[3] The preparation of diarylmethanes can be achieved by numerous procedures such as Friedel–Crafts reaction,[4] cross coupling reactions,[5] reduction of the corresponding diaryl ketones[6] or alcohols,[7] or disproportionation reactions.[8] Reaction of *N*,*N*-dimethyl-4-toluidine-*N*-oxide **1** in trifluoroacetic acid–triflic acid gives diarylmethane **3** as the side product (Scheme 1).[9] A quinone methide iminium ion intermediate **2** was suggested.

We recently reported the first helical DNA-like double stranded polymer **5** by ring opening metathesis polymerization[10] of a bisnorbornene derivative **4**.[11] Because of the presence of the relatively labile aminobenzyl fragment in **5**, the corresponding single stranded polymer **6** is easily obtained by hydrolysis (Scheme 2).[11] As can be seen from Scheme 2, the methyl ether **6** is obtained exclusively. Presumably, an intermediate similar to **2** would be formed during the course of hydrolysis. The chemistry shown in Scheme 2 might be a unique process involving a quinone methide iminium ion intermediate, which would react with methoxide nucleophile in the medium. It is interesting to note that quinone methide derivatives are important intermediates in DNA alkylation and DNA cross-linking reactions.[12] In order to understand the generality of this novel polymeric system, we have synthesized various kinds of monomers having a range of different linkers to connect the two norbornene units.

During the course of this investigation, we have synthesized bisnorbornene **7** using a diester linkage to tether two aminobenzyl moieties. Attempts to purify **7** by column chromatography on neutral alumina or silica gel were unsuccessful. A new dimeric diarylmethane **8** was obtained. The structure of **8** was unambiguously proved by X-ray crystallography (Fig. 1 and Table 1).

The isolation of **8** was somewhat striking. Presumably, the benzylic C–O bond would be extremely labile and cleaved readily under chromatographic separation conditions to give quinone methide iminium ion intermediate **9**. In the absence of other nucleophiles, Michael type addition of another aminobenzyl moiety to **9** would yield **10**, which would



1 2 3

Scheme 1.

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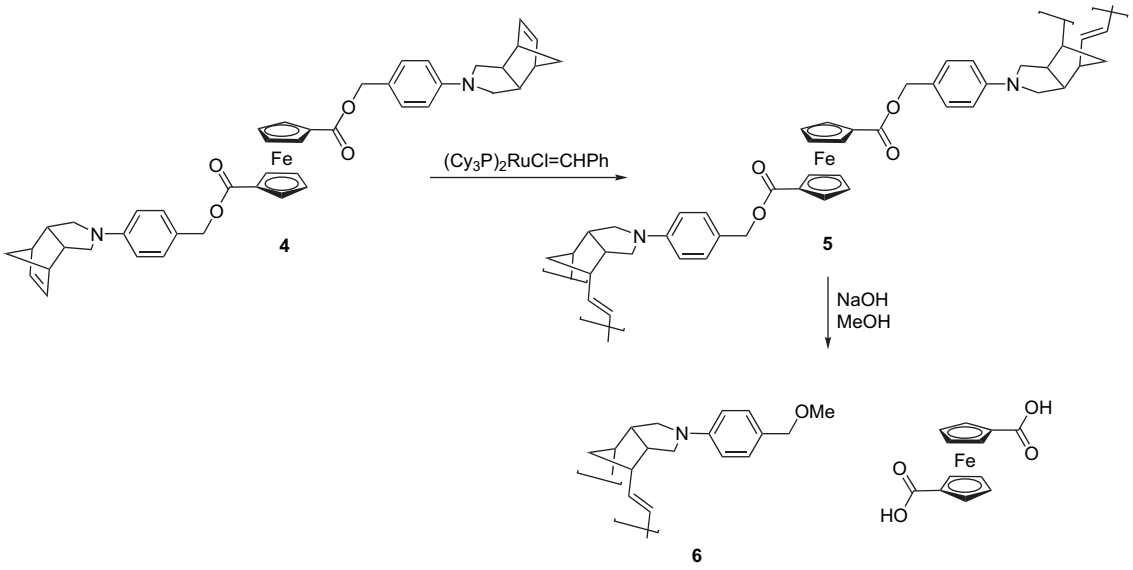


Scheme 2.

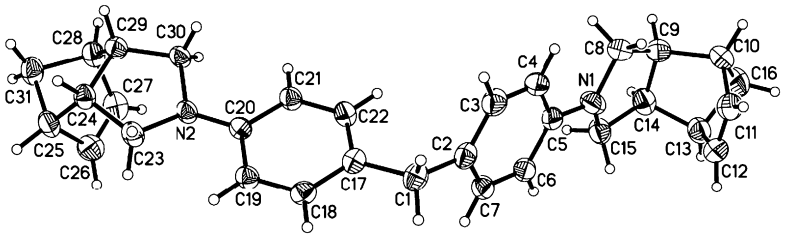
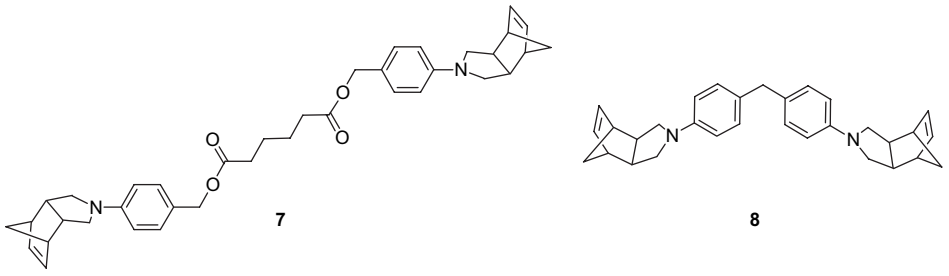
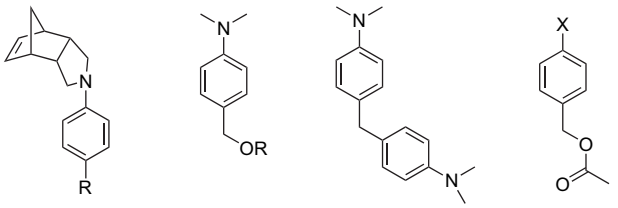


Figure 1. ORTEP structure of **8**.



then undergo a retro-aldol extrusion of the formaldehyde species to generate **8** (Scheme 3).

It is envisaged that the reaction might be considered to be a general reaction for 4-aminobenzyl esters. Thus, upon treatment with Al_2O_3 in DCM at rt, the crude **12**, prepared from the reaction of **11** and Ac_2O, afforded **8** in 40% yield. When pure **12** was employed, **8** was isolated in 62% yield. Several different conditions have been tried and the results are outlined in Table 2. It is interesting to note that DCM at rt was the best condition for this transformation. At refluxing temperature, a significant amount of side products was observed and **8** was obtained in 50% yield. When the reaction was carried out in polar solvents such as THF or DMF, starting compound **12** was almost completely recovered (>90). It is noteworthy that **8** was obtained in 10% yield together with a mixture of unidentified products when EtOAc was used as the reaction medium. When the reaction was carried out in MeOH, the solvent may serve as the nucleophile to quench the quinone methide iminium ion intermediate leading to the corresponding methoxy ether **13** in 99% yield (Table 2).



11 R = CH_2OH
12 R = CH_2OAc
13 R = CH_2OMe
14 R = CHO

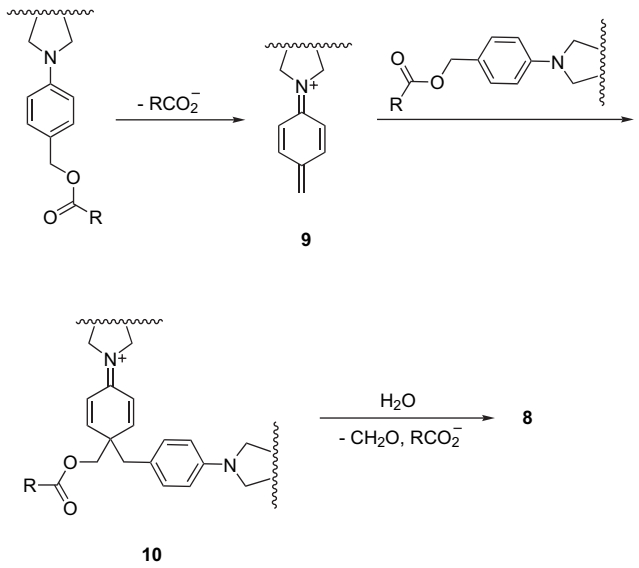
15 R = H
16 R = Ac

17

18 X = OH
19 X = OMe
20 X = Me

Table 1. Crystal data and structure refinement for **8**

Empirical formula	$C_{31}H_{34}N_2$
Formula weight	434.60
Temperature	295(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	*P*2(1)/*n*
Unit cell dimensions	*a*=19.0940(5) Å, α=90°
	b=6.19200(10) Å, β=94.9880(10)°
	c=19.9310(3) Å, γ=90°
Volume	2347.52 (8) Å^3
Z	4
Density (calculated)	1.230 Mg/m^3
Absorption coefficient	0.071 mm^{-1}
F(000)	936
Crystal size	0.30×0.25×0.15 mm^3
Theta range for data collection	2.05–27.47°
Index ranges	$-24\leq h\leq 24$, $-8\leq k\leq 8$, $-24\leq l\leq 25$
Reflections collected	16,793
Independent reflections	5337 [*R*(int)=0.0369]
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.990 and 0.974
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5288/0/299
Goodness-of-fit on F^2	0.876
Final *R* indices [*I*>2sigma(*I*)]	*R*1=0.0485, *wR*2=0.1403
R indices (all data)	*R*1=0.0926, *wR*2=0.1864
Extinction coefficient	0.0143 (33)
Largest diff. peak and hole	0.212 and −0.191 eÅ^{-3}



Scheme 3.

Table 2. Reaction of **12** with Al_2O_3

Solvent	Temperature	%Yield
THF	rt	0[a]
EtOAc	rt	10[b]
Toluene	rt	2[c]
DMF	rt	0[a]
DCM	rt	62
DCM	Reflux	50
MeOH	rt	0[d]

[a] Starting material was recovered in more than 90%.
[b] A mixture of unidentified products was obtained in addition to about 25% of unreacted **12**.
[c] A mixture of unidentified products was obtained including a significant amount of aldehyde **14**.
[d] Methoxymethyl derivative **13** was obtained in 99% yield.

In a similar manner, the reaction of **16** under similar conditions in DCM gave dealkylative dimer **17** in 70% yield. Attempts to use other substrates having *para*-hydroxy-, methoxy- or alkyl-substituted benzyl esters **18**–**20** under similar conditions were unsuccessful. Even in the presence of a base (e.g., DBN), **18** gave a mixture of unidentified products, no desired diarylmethane being detected. Presumably, the reaction may require a strong electron donating substituent to facilitate the leaving of the carboxylate group leading to quinone methide imminium ion intermediate. In addition, the aromatic ring may not be nucleophilic enough to proceed the Michael type addition reaction giving the corresponding diarylmethane derivative.

In summary, we have uncovered an unprecedented dealkylative dimerization of 4-aminobenzyl esters promoted by Al_2O_3. The absence of other nucleophiles would be the prerequisite for this reaction. The reaction furnishes a convenient route for the synthesis of dianilinomethane derivatives. Further applications of this protocol are in progress in our laboratory.

2. Experimental section

2.1. Bis-[4-(4-aza-tricyclo[5.2.1.0^{2,6}]dec-8-en-4-yl)]-benzyl hexandioate (7)

To a DCM solution (60 mL) of **11**[13] (2.0 g, 8.3 mmol) and dimethylaminopyridine (DMAP, 1.0 g, 8.3 mmol) was added slowly adipoyl dichloride (0.75 g, 4.14 mmol) in DCM (20 mL) and the mixture was stirred at rt for 24 h. Water (100 mL) was added and the organic layer was separated and washed with brine (50 mL), dried ($MgSO_4$), and filtered. The filtrate was evaporated in vacuo and the oily residue was taken up in DCM/hexane and cooled to −78 °C. Yellowish solid was precipitated. After filtration, the solid was collected and recrystallized from DCM/hexane to give **7**; mp 113–114 °C (dec); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.50 (d, *J*=8.2 Hz, 2H), 1.60 (d, *J*=8.2 Hz, 2H), 1.62–1.64 (m, 4H), 2.29 (br s, 4H), 2.88–2.91 (m, 4H), 2.97 (br s, 4H), 3.06–3.07 (m, 4H), 3.18–3.24 (m, 4H), 4.97 (s, 4H), 6.13 (s, 4H), 6.40 (d, *J*=8.5 Hz, 4H), 7.18 (d, *J*=8.5 Hz, 4H); ^{13}C NMR (100 MHz) δ 24.5, 34.1, 45.6, 46.7, 50.7, 52.3, 66.9, 111.8, 122.5, 130.2, 135.9, 147.8, 173.5; IR (KBr) ν 2965, 2935, 2848, 1720, 1613, 1526, 1480, 1375, 1260, 1184, 1155, 915, 800, 731; MS (70 eV, EI) *m*/*z* (%) 592 (10) [M$^+$], 526 (8), 434 (10), 369 (25), 367 (8), 301 (5), 224 (45), 159 (24), 158 (100), 118 (16); HRMS (EI) ($C_{38}H_{44}O_4N_2$) calcd: 592.3301; found: 592.3315.

2.2. 4-(4-Aza-tricyclo[5.2.1.0^{2,6}]dec-8-en-4-yl)benzyl acetate (12)

To a solution of **11** (2.0 g, 8.3 mmol) and triethylamine (3.5 mL, 25 mmol) in DCM (15 mL) was added dropwise acetyl chloride (1.2 mL, 9.1 mmol) at 0 °C. The mixture was stirred at rt for 2 h, poured into water (100 mL), and extracted with DCM (50 mL). The organic layer was separated, dried ($MgSO_4$), filtered, and evaporated in vacuo. The residue was chromatographed on silica gel (hexane/EtOAc 4:1) to afford **12** as a white solid (2.1 g, 92%); mp 85–87 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.51 (d, *J*=8.2 Hz, 1H), 1.61

(d, J=8.2 Hz, 1H), 2.04 (s, 3H), 2.84–2.87 (m, 2H), 2.88–3.00 (m, 2H), 3.01–3.11 (m, 2H), 3.19–3.24 (m, 2H), 4.98 (s, 2H), 6.13 (s, 2H), 6.41 (d, J=8.6 Hz, 2H), 7.20 (d, J=8.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 45.5, 46.6, 50.5, 52.1, 66.9, 111.6, 122.0, 130.1, 135.6, 147.4, 170.9.

2.3. Bis-{4-(4-aza-tricyclo[5.2.1.0^{2,6}]dec-8-en-4-yl)-phenyl}methane (8)

To a DCM solution (60 mL) of **11**[13] (2 g, 8.3 mmol) and DMAP (1.0 g, 8.3 mmol) was added slowly acetyl chloride (0.65 g, 8.3 mmol) in DCM (20 mL) and the mixture was stirred at rt for 24 h. Water (100 mL) was added and the organic layer was separated and washed with brine, dried ($MgSO_4$), and filtered. The solvent was evaporated in vacuo and the oily residue was dissolved in DCM (40 mL). Neutral alumina (45 g) was added and the mixture was stirred at rt for 8 h. After filtration, solvent was removed in vacuo and the residue was recrystallized from DCM/hexane to give **8** (0.72 g, 40%); mp 188–189 °C (dec); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.50 (d, J=8.2 Hz, 2H), 1.59 (d, J=8.2 Hz, 2H), 2.85–2.88 (m, 4H), 2.95 (br s, 4H), 3.03–3.05 (m, 4H), 3.17–3.22 (m, 4H), 3.75 (s, 2H), 6.13 (m, 4H), 6.37 (d, J=8.5 Hz, 4H), 6.99 (d, J=8.5 Hz, 4H); ^{13}C NMR (100 MHz) 40.0, 45.5, 46.5, 50.7, 52.2, 111.9, 129.1, 129.3, 135.8, 146.0; IR (KBr) ν 2964, 2942, 2864, 2833, 1688, 1615, 1518, 1473, 1432, 1369, 1341, 1201, 1186, 1134, 971, 904, 797, 776, 739, 717; MS (70 eV, EI) m/z (%) 434 (100) [M$^+$], 393 (18), 367 (82), 372 (13), 301 (52); HRMS (FAB$^+$) ($C_{31}H_{34}N_2$) calcd: 434.2722; found: 434.2725.

From pure **12**. Under N_2, to a solution of **12** (500 mg, 1.8 mmol) in DCM (7 mL) was added Al_2O_3 (neutral, 8 g) at rt. The mixture was stirred for 20 h at rt and then filtered. The Al_2O_3 was washed with DCM/NEt_3 (10:1) (10 mL×2) and the filtrate was concentrated in vacuo. The residue was chromatographed on silica gel (hexane/EtOAc 7:1) to afford **8** as a white solid (230 mg, 62%); mp 188–189 °C (dec).

2.4. 4-(4-Aza-tricyclo[5.2.1.0^{2,6}]dec-8-en-4-yl)benzyl methyl ether (13)

Under N_2, to a solution of **12** (50 mg, 0.2 mmol) in MeOH (5 mL) was added Al_2O_3 (neutral, 1 g) at rt. The mixture was stirred for 20 h at rt and then filtered. The Al_2O_3 was washed with DCM/NEt_3 (10:1) (10 mL×2) and the filtrate was concentrated in vacuo. The residue was passed through a silica gel bed (thickness=5 cm) and washed with (hexane/EtOAc (7:1, 20 mL). Evaporation of the solvent afforded **13** as a white solid (44 mg, 99%); mp 64–65 °C (lit.[11a] 64–65 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.47 (dt, J=1.6, 8.0 Hz, 2H), 1.58 (dt, J=1.6, 8.0 Hz, 2H), 2.81–2.84 (m, 2H), 2.90–2.96 (m, 2H), 2.98–3.06 (m, 2H), 3.15–3.22 (m, 2H), 3.21 (s, 3H), 4.30 (s, 2H), 6.10 (s, 2H), 6.38 (d, J=8.6 Hz, 2H), 7.12 (d, J=8.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 45.4, 46.4, 50.5, 52.0, 57.2, 74.6, 111.4, 124.3, 129.1, 135.5, 147.0.

2.5. Bis-[4-(*N*,*N*-dimethylamino)phenyl]methane (17)

Under N_2, to a solution of **16** (500 mg, 1.8 mmol) in DCM (12 mL) was added Al_2O_3 (neutral, 14 g) at rt. The mixture was stirred for 20 h at rt and then filtered. The Al_2O_3 was washed with DCM/NEt_3 (10:1, 10 mL×2) and the filtrate was concentrated in vacuo to give the residue, which was chromatographed on silica gel (hexane/EtOAc 7:1) to afford **17** as a white solid (220 mg, 70%); mp 82–83 °C (lit.[14] 86.5–87 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.87 (s, 12H), 3.79 (s, 2H), 6.66 (d, J=8.8 Hz, 2H), 7.03 (d, J=8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.9, 40.9, 112.8, 129.2, 130.1, 148.8. HRMS (FAB$^+$) ($C_{17}H_{22}N_2$) calcd: 254.1783; found: 254.1780.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.02.094.

References and notes

1. (a) Ma, J. C.; Dougherty, D. A. *Chem. Rev.* **1997**, *97*, 1303; (b) Jäfer, R.; Vögtle, F. *Angew. Chem., Int. Ed.* **1997**, *36*, 930.
2. (a) Bruno, J. G.; Chang, M. N.; Choi-Sledeski, Y. M.; Green, D. M.; MaGarry, D. G.; Regan, J. R.; Volz, F. A. *J. Org. Chem.* **1997**, *62*, 5174; (b) Wllkinson, J. A.; Rossington, S. B.; Leonard, J.; Hussain, N. *Tetrahedron Lett.* **2004**, *45*, 5481; (c) Maciejewska, M.; Gawdzik, B. *J. Appl. Polym. Sci.* **2005**, *95*, 863.
3. (a) Stanchev, S.; Rakovska, R.; Berova, N.; Snatzke, G. *Tetrahedron: Asymmetry* **1995**, *6*, 183; (b) Ku, Y.-Y.; Patel, R. P.; Sawick, D. P. *Tetrahedron Lett.* **1996**, *37*, 1949; (c) de Lang, R.-J.; van Hooijdonk, M. J. C. M.; Brandsma, L.; Kramer, H.; Seinen, W. *Tetrahedron* **1998**, *54*, 2953; (d) Prat, L.; Mojovic, L.; Levacher, V.; Dupas, G.; Quéguiner, G.; Bourguignon, J. *Tetrahedron: Asymmetry* **1998**, *9*, 2509; (e) Rische, T.; Eilbracht, P. *Tetrahedron* **1999**, *55*, 1915.
4. For examples: (a) Coq, B.; Gourves, V.; Figueras, F. *Appl. Catal., A* **1993**, *100*, 69; (b) Yadav, G. D.; Thorat, T. S.; Khumbar, P. S. *Tetrahedron Lett.* **1993**, *34*, 529; (c) Cseri, T.; Bekassy, S.; Figueras, F.; Rizner, S. *J. Mol. Catal. A* **1995**, *98*, 101; (d) Tanabe, K.; Holderich, W. F. *Appl. Catal., A* **1999**, *181*, 339; (e) de la Cruz, M. H. C.; da Silva, J. F. C.; Lachter, E. R. *Appl. Catal., A: Gen.* **2003**, *245*, 377; (f) Sun, H.-B.; Hua, R.; Yin, Y. *Tetrahedron Lett.* **2006**, *47*, 2291.
5. For examples, see: (a) Hossain, K. M.; Takagi, K. *Chem. Lett.* **1999**, 1241; (b) García Martínez, A.; Osío Barcina, J.; Colorado Heras, M.; de Fresno Cerazo, A. *Org. Lett.* **2000**, *2*, 1377; (c) Itami, K.; Mineno, M.; Kamei, T.; Yoshida, J.-I. *Org. Lett.* **2002**, *4*, 3635; Park, C.-M.; Sun, C.; Olejniczak, E. T.; Wilson, A. E.; Meadows, R. P.; Betz, S. F.; Elmore, S. W.; Fesik, S. W. *Bioorg. Med. Chem. Lett.* **2005**, *15*, 771; (d) Frisch, A. C.; Shaikh, N.; Zapf, A.; Beller, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 4056; (e) Pirrung, M. C.; Wedel, M.; Zhao, Y. *Synlett* **2002**, 143; (f) Langle, S.; Abarbri, M.; Duchêne, A. *Tetrahedron Lett.* **2003**, *44*, 9255; (g) Nobre, S. M.; Monteiro, A. L. *Tetrahedron Lett.* **2004**, *45*, 8225; (h) Park, S. Y.; Kang, M.; Yie, J. E.; Kim, J. M.; Lee, I.-M. *Tetrahedron Lett.* **2005**, *46*, 2849.

6. (a) Popielarz, R.; Arnold, D. R. *J. Am. Chem. Soc.* **1990**, *112*, 3068; (b) Lee, W. Y.; Park, W. Y.; Kim, Y. D. *J. Org. Chem.* **1992**, *57*, 4074; (c) Lee, W. Y.; Park, C. H.; Kim, H. J.; Kim, S. J. *J. Org. Chem.* **1994**, *59*, 878; (d) Gadhwal, S.; Baruah, M.; Sandhu, J. S. *Synlett* **1999**, 1573; (e) Hicks, L. D.; Han, J. K.; Fry, A. J. *Tetrahedron Lett.* **2000**, *41*, 7817; (f) Studer, M.; Burkhardt, S.; Indolese, A. F.; Blaser, H.-U. *Chem. Commun.* **2000**, 1327; (g) Chandrasekhar, S.; Reddy, C. R.; Babu, B. N. *J. Org. Chem.* **2002**, *67*, 9080; (h) Toyota, S.; Nakagawa, T.; Kotani, M.; Oki, M.; Uekusa, H.; Ohashi, Y. *Tetrahedron* **2002**, *58*, 10345; (i) Mahmoodi, N. O.; Salehpour, M. *J. Heterocycl. Chem.* **2003**, *40*, 875; (j) Hatano, B.; Tagaya, H. *Tetrahedron Lett.* **2003**, *44*, 6331; (k) Tremont, S. J.; Lee, L. F.; Huang, H.-C.; Keller, B. T.; Banerjee, S. C.; Both, S. R.; Carpenter, A. J.; Wang, C.-C.; Garland, D. J.; Huang, W.; Jones, C.; Koeller, K. J.; Kolodziej, S. A.; Li, J.; Manning, R. E.; Mahoney, M. W.; Miller, R. E.; Mischke, D. A.; Rath, N. P.; Fletcher, T.; Reinhard, E. J.; Tollefson, M. B.; Vernier, W. F.; Wagner, G. M.; Rapp, S. R.; Beaudry, J.; Glenn, K.; Regina, K.; Schuh, J. R.; Smith, M. E.; Trivedi, J. S.; Reitz, D. B. *J. Med. Chem.* **2005**, *48*, 5837; (l) Zaccheria, F.; Ravasio, N.; Ercoli, M.; Allegrini, P. *Tetrahedron Lett.* **2005**, *46*, 7743.
7. (a) Miyai, T.; Onishi, Y.; Baba, A. *Tetrahedron Lett.* **1998**, *39*, 6291; (b) Bringmann, G.; Pabst, T.; Henschel, P.; Michel, M. *Tetrahedron* **2001**, *57*, 1269; (c) Waterlot, C.; Hasiak, B.; Couturier, D.; Rigo, B. *Tetrahedron* **2001**, *57*, 4889; (d) Brousmiche, D. W.; Xu, M.; Lukeman, M.; Wan, P. *J. Am. Chem. Soc.* **2003**, *125*, 12961; (e) Barda, D. A.; Wang, Z.-Q.; Britton, T. C.; Henry, S. S.; Jagdmann, G. E.; Coleman, D. S.; Johnson, M. P.; Andis, S. L.; Schoepp, D. D. *Bioorg. Med. Chem. Lett.* **2004**, *14*, 3099; (f) Okimoto, M.; Takahashi, Y.; Nagata, Y.; Satoh, M.; Sueda, S.; Yamashina, T. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 1405; (g) Long, Y.-Q.; Jiang, X.-H.; Dayam, R.; Sanchez, T.; Shoemaker, R.; Sei, S.; Neamati, N. *J. Med. Chem.* **2004**, *47*, 2561; (h) Wu, X.; Mahalingam, A. K.; Alterman, M. *Tetrahedron Lett.* **2005**, *46*, 1501; (i) Ihmels, H.; Meiswinkel, A.; Mohrschladt, C. J.; Otto, D.; Waidelich, M.; Towler, M.; White, R.; Albrecht, M.; Schnurpfeil, A. *J. Org. Chem.* **2005**, *70*, 3929.
8. (a) Bartlett, P. D.; McCollum, J. D. *J. Am. Chem. Soc.* **1956**, *78*, 1441; (b) Climent, M. J.; Corma, A.; Garcia, S.; Iborra, S.; Primo, J. *Recl. Trav. Chim. Pays-Bas* **1991**, *110*, 275; (c) Zhu, Z.; Espenson, J. H. *J. Org. Chem.* **1996**, *61*, 324; (d) Gautret, P.; El-Ghammarti, S.; Legrand, A.; Couturier, D.; Rigo, B. *Synth. Commun.* **1996**, *26*, 707; (e) Waterlot, C.; Couturier, D.; Backer, M. D.; Rigo, B. *Can. J. Chem.* **2000**, *78*, 1242; (f) Hatano, B.; Kadokawa, J.-I.; Tagaya, H. *Tetrahedron Lett.* **2002**, *43*, 5859; (g) Harig, M.; Neumann, B.; Stammler, H.-G.; Kuck, D. *Eur. J. Org. Chem.* **2004**, *69*, 2381; (h) L'Hermite, N.; Giraud, A.; Provot, O.; Peyrat, J.-F.; Alami, M.; Brion, J.-D. *Tetrahedron* **2006**, *62*, 11994.
9. Lindsay Smith, J. R.; Linford, J. M.; McKeer, L. C.; Morris, P. M. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1099.
10. Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100.
11. (a) Yang, H.-C.; Lin, S.-Y.; Yang, H.-c.; Lin, C.-L.; Tsai, L.; Huang, S.-L.; Chen, I.-W. P.; Chen, C.-h.; Jin, B.-Y.; Luh, T.-Y. *Angew. Chem., Int. Ed.* **2006**, *45*, 726; (b) Yang, H.-C.; Lin, S.-M.; Liu, Y.-H.; Wang, Y.; Chen, M.-M.; Sheu, H.-S.; Tsou, D.-L.; Lin, C.-H.; Luh, T.-Y. *J. Organomet. Chem.* **2006**, *691*, 3196.
12. For a recent review, see: Wang, P.; Song, Y.; Zhang, L.; He, H.; Zhou, X. *Curr. Med. Chem.* **2005**, *12*, 2893.
13. Lin, W.-Y.; Murugesh, M. G.; Sudhakar, S.; Yang, H.-C.; Tai, H.-C.; Chang, C.-S.; Liu, Y.-H.; Wang, Y.; Chen, I.-W. P.; Chen, C.-h.; Luh, T.-Y. *Chem.—Eur. J.* **2006**, *12*, 324.
14. Sakakibara, T.; Dogomori, Y.; Tsuzuki, Y. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 3592.