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Captodative olefins: methyl 2-aryloxy-3-dimethylaminopropenoates and their application in a new synthesis of benzofurans

María del Carmen Cruz and Joaquín Tamariz*

Departamento de Química Orgánica, Escuela Nacional de Ciencias Biológicas, Instituto Politécnico Nacional. Prol. Carpio y Plan de Ayala, 11340 México, DF, Mexico

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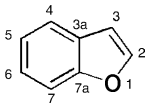
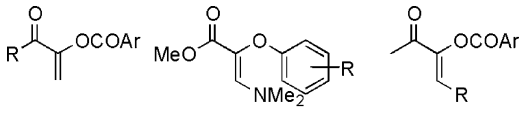
Abstract—The β-substituted captodative olefins methyl 2-aryloxy-3-dimethylaminopropenoates **4a**–**h** were synthesized, via aminomethylenation of the corresponding 2-phenoxyacetic esters **9a**–**h**. Lewis acid promoted intramolecular cyclization of alkenes **4** led to benzofurans **7a**–**h**, in an efficient synthetic approach to the benzofuran frame.

Benzofurans have attracted widespread interest in view of their biological activity,[1] their presence in a large number of natural products,[2] and their potential as pharmacological agents.[3] Consequently, diverse synthetic strategies have been developed to build their fused skeleton, commonly starting from a benzene ring with the appropriate substituents. A large number of syntheses of the heterocyclic moiety are based on the formation of the O–C_2[4] or the C_2–C_3 bonds,[5] as the ring closure step.[1] However, those strategies involving C_3–C_{3a} bond formation, by intramolecular cyclization of a properly functionalized precursor, have been particularly used as an attractive and versatile approach.[1,6]



Recently we reported the preparation of the new captodative olefins **1** and **2**, which bear the acrylic acid frame.[7] These alkenes were designed to mimic the structural features of the very reactive and selective captodative olefins **3**.[8] Thus, both kinds of compounds hold the same electron-donating group but a different electron-withdrawing group. It was found that derivatives **1** and **2** were less reactive and selective than alkenes **3** as dienophiles in Diels–Alder reactions. FMO calculations suggested that the electron-withdrawing group controls the reactivity, and that the higher reactivity of **3** is determined by its less energetic LUMO.[9]



1, R = OMe
2, R = OEt
3, R = Me

4

5, R = NMe_2
6, R = SR'

With the aim of evaluating the effect of the electron-donating group on the reactivity of the double bond, we carried out the synthesis of alkenes **4**. The acrylic skeleton in this case is analogous to that found in **1** and **2**, but with an aryloxy group attached to the double bond as the electron-releasing group. The dimethylamino group in the beta position is expected to decrease the reactivity of these dienophiles in Diels–Alder reactions, in agreement with the behavior of alkenes **5**,[10] which are enaminones with a high synthetic potential.[11] However, the dimethylamino group promotes conjugate addition of nucleophiles such as thiolates to alkenes **5**, leading to

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* Corresponding author. Fax: +52-55-53963503; e-mail: jtamariz@woodward.encb.ipn.mx

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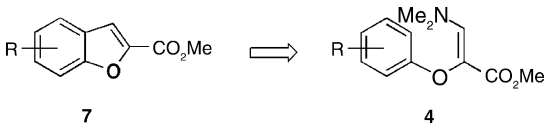
products **6**,[12] in which substitution of this group took place.

Since olefins **3** undergo fast Friedel–Crafts addition of activated benzene rings under Lewis acid catalysis,[13] alkenes **4** might be suitable substrates to provide benzofurans by intramolecular addition (Scheme 1). Hence, we hereby describe the synthesis of the series of alkenes **4a**–**g**, and their use in the preparation of substituted 2-methoxycarbonylbenzofurans **7**.

As illustrated in Scheme 2, the phenoxyacetic compounds **9a**–**h** reacted with *N*,*N*-dimethylformamide dimethyl acetal (DMFDMA) at 90 °C for 24 h to provide the corresponding 2-aryloxy-3-dimethylaminopropenoates **4a**–**h** (Table 1).[14,15] The yields were not significantly modified by the position of the substituents in the benzene ring. In all cases, the propenoates were obtained as a single stereoisomer, as shown by NMR analysis of the crude mixture. The *Z* configuration of the double bond was established by NOE experiments, which showed an enhancement of the signal of the aromatic protons when the signal attributed to the dimethylamino protons was irradiated. This effect was not observed by irradiation of the vinylic proton. The preference for the configuration of the *Z* stereoisomer parallels that observed in the preparation of olefins **5**,[10] and analogous compounds.[16] This is probably due to the higher stability gained by the planar π-conjugated acrylate system when the bulky dimethylamino group is located at the opposite side of the double bond.[10]

The phenoxyacetic methyl esters **9a**–**h** were prepared by a two-step procedure, starting from the corresponding phenols **8a**–**h**. Thus, by treatment of these phenols with the sodium salt of chloroacetic acid in aqueous NaOH, and heating to 60 °C for 8 h, the phenoxyacetic acids were prepared in good yields (75–82%).[17] Esterification of the latter in the presence of methanol and *p*-TsOH furnished the methyl esters **9a**–**h** in high yields (80–95%).[18]

Compounds **4a**–**d** and **4g** were heated in acetonitrile (100 °C) for 24 h in order to promote the cyclization to the heterocycle. While derivatives **4b**, **d**, and **4g** bearing benzene rings activated with electron-donating groups such as methoxy or alkoxy substituents, provided the corresponding benzofurans **7a**–**b** (Table 2, entries 1–3), aminopropenoates **4a**, and **4c** failed to undergo cyclization to the heterocycle. In these cases, the starting material was recovered unchanged.



7 4

Scheme 1.

Table 1. Preparation of the methyl 2-aryloxy-3-dimethylaminopropenoates **4a**–**h**[a]

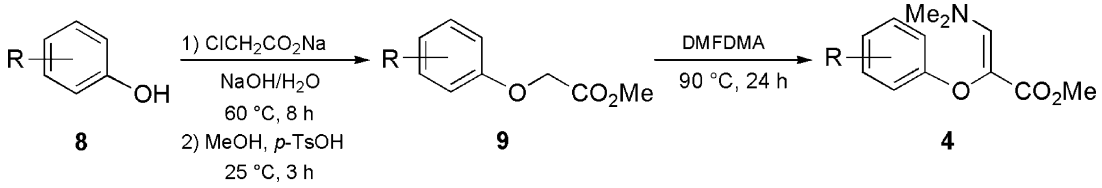
Entry	**9** (R)	**4**	Mp (°C)	Yield (%)[b]
1	**9a** (3-Me)	**4a**	53–54	64
2	**9b** (3-OMe)	**4b**	Oil	61
3	**9c** (2,5-$(Me)_2$)	**4c**	93–94	65
4	**9d** (3,4-$(OMe)_2$)	**4d**	81–82	68
5	**9e** (3-OMe,4-OEt)	**4e**	80–82	74
6	**9f** (3-OMe,4-OBn)	**4f**	73–74	63
7	**9g** (3,4-OCH_2O)	**4g**	99–100	60
8	**9h** (2,3,4-$(OMe)_3$)	**4h**	72–73	76

[a] Under N_2 atmosphere, with 3.0 mol equiv of DMFDMA at 90 °C for 24 h.
[b] After column chromatography and recrystallization.

We also investigated the one-step tandem reaction leading to the benzofurans **7a**–**c** from the phenoxyacetic methyl esters **9b**, **9d**, and **9g** (Table 2). Thus, when the latter were treated with DMFDMA (2 mol equiv) in acetonitrile at 100 °C for 48 h, the desired benzofurans were obtained (Table 2, entries 4–6). The yields were slightly lower than the overall yields for the two steps starting from the dimethylaminopropenoates **4**.

Mechanistically, the cyclization reaction might proceed via a nucleophilic Michael addition of the substituted benzene ring to the dimethylaminopropenoate moiety, followed by aromatization through elimination of the dimethylamino group. Therefore, the cyclization process could be facilitated by complexation of the carbonyl with a Lewis acid, like a typical Friedel–Crafts alkylation.[19] Consequently, we also investigated the effect of a Lewis acid on the chemical yield for the transformation of compounds **4** to benzofurans **7** (Table 2). Catalysts such as $AlCl_3$ and $BF_3{\cdot}OEt_2$ were unable to carry out the reaction, giving either recovered starting materials or a complex mixture of products. However, zinc chloride was efficient in providing the desired benzofurans **7a**–**f** in moderate to good yields (Table 2, entries 7–12).[20]

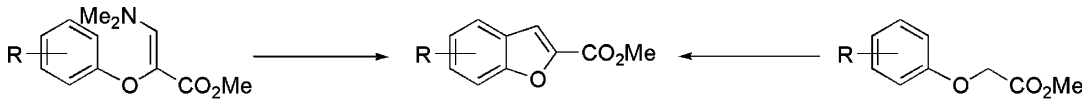
In summary, we have described a novel synthesis of benzofurans via intramolecular cyclization of the captodative alkenes **4**. It was established that this reaction needs that the benzene ring be substituted by elec-



8 9 4

Scheme 2.

Table 2. Preparation of benzofurans **7a**–**f** by cyclization of 3-dimethylaminopropenoates **4**, or by reaction of phenoxyacetates **9** with DMFDMA[a]



4 **7a-7f** **9**

Entry	Substrate	Solvent	Reagent	Temperature (°C)	Time (h)	Product	Yield (%)[b]
1	**4b** (3-OMe)	CH_3CN	—	100	24	**7a**	40
2	**4d** (3,4-$(OMe)_2$)	CH_3CN	—	100	24	**7b**	42
3	**4g** (3,4-OCH_2O)	CH_3CN	—	100	24	**7c**	45
4	**9b** (3-OMe)	CH_3CN	DMFDMA	100	48	**7a**	20
5	**9d** (3,4-$(OMe)_2$)	CH_3CN	DMFDMA	100	48	**7b**	22
6	**9g** (3,4-OCH_2O)	CH_3CN	DMFDMA	100	48	**7c**	25
7	**4b** (3-OMe)	CH_2Cl_2	$ZnCl_2$	20	72	**7a**	62
8	**4d** (3,4-$(OMe)_2$)	CH_2Cl_2	$ZnCl_2$	20	72	**7b**	68
9	**4e** (3-OMe,4-OEt)	CH_2Cl_2	$ZnCl_2$	20	72	**7c**	65
10	**4f** (3-OMe,4-OBn)	CH_2Cl_2	$ZnCl_2$	20	72	**7d**	70
11	**4g** ((3,4-OCH_2O)	CH_2Cl_2	$ZnCl_2$	20	72	**7e**	68
12	**4h** (2,3,4-$(OMe)_3$)	CH_2Cl_2	$ZnCl_2$	20	72	**7f**	72

[a] Under N_2 atmosphere, with 2.0 mol equiv of DMFDMA or 3.0 mol equiv of $ZnCl_2$.
[b] After column chromatography and recrystallization.

tron-releasing groups. A shorter pathway to attain the desired heterocycles was also reported by a tandem thermal condensation–cyclization process between the phenoxyacetates **9** and DMFDMA. Application of this methodology to the synthesis of natural occurring benzofurans is currently in progress.

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References and notes

1. (a) Cagniant, P.; Cagniant, D. Recent Advances in the Chemistry of Benzo[*b*]furan and Its Derivatives. Part I: Occurrence and Synthesis. *Adv. Heterocycl. Chem.* **1975**, *18*, 337–482; (b) Bird, C. W.; Cheeseman, G. W. H. Synthesis of Five-membered Rings with One Heteroatom. In *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Ed.; Pergamon: New York, 1984; Vol. 4, pp 89–153; (c) Donelly, D. M. X.; Meegan, M. J. Furans and Their Benzo Derivatives: (iii) Synthesis and Applications. In *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Ed.; Pergamon: New York, 1984; Vol. 4, pp 657–712.
2. For recent examples, see: (a) Stevenson, P. C.; Simmonds, M. S. J.; Yule, M. A.; Veitch, N. C.; Kite, G. C.; Irwin, D.; Legg, M. *Phytochemistry* **2003**, *63*, 41–46; (b) Tanaka, H.; Oh-Uchi, T.; Etoh, H.; Sako, M.; Sato, M.; Fukai, T.; Teteishi, Y. *Phytochemistry* **2003**, *63*, 597–602; (c) Ali, Z.; Tanaka, T.; Iliya, I.; Iinuma, M.; Furusawa, M.; Ito, T.; Nakaya, K.-I.; Murata, J.; Darnaedi, D. *J. Nat. Prod.* **2003**, *66*, 558–560.
3. (a) Wyatt, P. G.; Allen, M. J.; Chilcott, J.; Gardner, C. J.; Livermore, D. G.; Mordaunt, J. E.; Nerozzi, F.; Patel, M.; Perren, M. J.; Weingarten, G. G.; Shabbir, S.; Woollard, P. M.; Zhou, P. *Bioorg. Med. Chem. Lett.* **2002**, *12*, 1405–1411; (b) Malamas, M. S.; Sredy, J.; Moxham, C.; Katz, A.; Xu, W.; McDevitt, R.; Adebayo, F. O.; Sawicki, D. R.; Seestaller, L.; Sullivan, D.; Taylor, J. R. *J. Med. Chem.* **2000**, *43*, 1293–1310; (c) Huang, H.-C.; Chamberlain, T. S.; Seibert, K.; Koboldt, C. M.; Isakson, P. C.; Reitz, D. B. *Bioorg. Med. Chem. Lett.* **1995**, *5*, 2377–2380; (d) Gubin, J.; de Vogelaer, H.; Inion, H.; Houben, C.; Lucchetti, J.; Mahaux, J.; Rosseels, G.; Peiren, M.; Clinet, M.; Polster, P.; Chatelain, P. *J. Med. Chem.* **1993**, *36*, 1425–1433.
4. (a) Novák, Z.; Timári, G.; Kotschy, A. *Tetrahedron* **2003**, *59*, 7509–7513; (b) Bishop, B. C.; Cottrell, I. F.; Hands, D. *Synthesis* **1997**, 1315–1320; (c) Larock, R. C.; Yum, E. K.; Doty, M. J.; Sham, K. K. C. *J. Org. Chem.* **1995**, *60*, 3270–3271; (d) Hiroya, K.; Hashimura, K.; Ogasawara, K. *Heterocycles* **1994**, *38*, 2463–2472; (e) Satoh, M.; Miyaura, N.; Suzuki, A. *Synthesis* **1987**, 373–377; (f) de Souza, N. J.; Nayak, P. V.; Secco, E. *J. Heterocycl. Chem.* **1966**, *3*, 42–45.
5. (a) Bosch, J.; Roca, T.; Catena, J.-L.; Farrerons, C.; Miquel, I. *Synthesis* **2000**, 721–725; (b) Hellwinkel, D.; Göke, K. *Synthesis* **1995**, 1135–1141; (c) Fürstner, A.; Jumbam, D. N. *Tetrahedron* **1992**, *48*, 5991–6010; (d) Burke, J. M.; Stevenson, R. *J. Chem. Res. (S)* **1985**, 34; (e) Elliott, E. D. *J. Am. Chem. Soc.* **1951**, *73*, 754.
6. (a) Gardiner, M.; Grigg, R.; Sriharan, V.; Vicker, N. *Tetrahedron Lett.* **1998**, *39*, 435–438; (b) Beckwith, A. L. J.; Meijs, G. F. *J. Chem. Soc., Chem. Commun.* **1981**, 136–137; (c) Spagnolo, P.; Tiecco, M.; Tundo, A.; Martelli, G. *J. Chem. Soc., Perkin Trans. 1* **1972**, 556–559; (d) MacLeod, J. K.; Worth, B. R. *Tetrahedron Lett.* **1972**, 237–240; (e) Royer, R.; René, L. *Bull. Soc. Chim. Fr.* **1970**, 1037–1040; (f) Elvidge, J. A.; Foster, R. G. *J. Chem. Soc.* **1964**, 981–991.

7. Herrera, R.; Jiménez-Vázquez, H. A.; Modelli, A.; Jones, D.; Söderberg, B. C.; Tamariz, J. *Eur. J. Org. Chem.* **2001**, 4657–4669.
8. Reyes, A.; Aguilar, R.; Muñoz, A. H.; Zwick, J.-C.; Rubio, M.; Escobar, J.-L.; Soriano, M.; Toscano, R.; Tamariz, J. *J. Org. Chem.* **1990**, *55*, 1024–1034, and references included therein.
9. Jiménez-Vázquez, H. A.; Ochoa, M. E.; Zepeda, G.; Modelli, A.; Jones, D.; Mendoza, J. A.; Tamariz, J. *J. Phys. Chem. A* **1997**, *101*, 10082–10089.
10. Peralta, J.; Bullock, J. P.; Bates, R. W.; Bott, S.; Zepeda, G.; Tamariz, J. *Tetrahedron* **1995**, *51*, 3979–3996.
11. In particular, enaminones have proved to be privileged Michael acceptors: (a) Lue, P.; Greenhill, J. V. Enaminones in Heterocyclic Synthesis. *Adv. Heterocycl. Chem.* **1997**, *67*, 207–343; (b) Elassar, A.-Z. A.; El-Khair, A. A. *Tetrahedron* **2003**, *59*, 8463–8480; (c) Stanovnik, B.; Svete, J. *Synlett* **2000**, 1077–1091; (d) Greenhill, J. V. *Chem. Soc. Rev.* **1977**, *6*, 277–294.
12. Mendoza, J. A.; Jiménez-Vázquez, H. A.; Herrera, R.; Liu, J.; Tamariz, J. *Rev. Soc. Quím. Méx* **2003**, *47*, 116–208.
13. Aguilar, J. R. M.Sc. Thesis, Escuela Nacional de Ciencias Biológicas, Instituto Politécnico Nacional, 2000.
14. Typical procedure for preparation of **4d**: A mixture of **9d** (0.50 g, 2.21 mmol) and DMFDMA (0.79 g, 6.63 mmol) was heated to 90 °C for 24 h. The crude mixture was diluted with CH_2Cl_2 (20 mL), and the solvent was removed. The residue was purified by column chromatography on silica gel (20 g, hexane/EtOAc, 8:2), to give 0.42 g (68%) of **4d** as a white solid (hexane/EtOAc, 1:1): R_f 0.20 (hexane/EtOAc, 6:4); mp 81–82 °C; IR (KBr) 1695, 1633, 1508, 1438, 1299, 1224, 1188, 1120, 1086, 1026 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 2.93 (s, 6H, $N(CH_3)_2$), 3.59 (s, 3H, CO_2Me), 3.78 (s, 3H, OMe), 3.81 (s, 3H, OMe), 6.38 (dd, $J = 8.7$, 2.7 Hz, 1H, ArH), 6.55 (d, $J = 2.7$ Hz, 1H, ArH), 6.71 (d, $J = 8.7$ Hz, 1H, ArH), 7.10 (s, 1H, HC=); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 42.0 ($N(CH_3)_2$), 51.1 (CO_2CH_3), 55.7 (MeO), 56.2 (MeO), 100.1 (ArH), 104.3 (ArH), 111.6 (ArH), 115.0 (OC=), 139.6 (HC=), 143.6 (Ar), 149.7 (Ar), 153.6 (Ar), 166.6 (CO_2CH_3). Anal. calcd for $C_{14}H_{19}NO_5$: C, 59.91; H, 6.81. Found: C, 60.02; H, 6.95.
15. For a related synthesis of 3-dimethylaminopropenoates, see: (a) Smodis, J.; Stanovnik, B. *Tetrahedron* **1998**, *54*, 9799–9810; (b) Selic, L.; Grdadolnik, S. G.; Stanovnik, B. *Helv. Chim. Acta.* **1997**, *80*, 2418–2425.
16. Grdadolnik, S. G.; Stanovnik, B. *Magn. Reson. Chem.* **1997**, *35*, 482–486.
17. Labarrios, F.; Garduño, L.; Vidal, M. R.; García, R.; Salazar, M.; Martínez, E.; Díaz, F.; Chamorro, G.; Tamariz, J. *J. Pharm. Pharmacol.* **1999**, *51*, 1–7.
18. Typical procedure for preparation of **9d**: An aqueous solution (10 mL) of NaOH (3.1 g, 77.5 mmol) and chloroacetic acid (4.1 g, 43.4 mmol) in water (10 mL) were successively added dropwise to phenol **8d** (6.0 g, 38.9 mmol) at room temperature. The mixture was stirred at 60 °C for 7 h. A concentrated aqueous solution of HCl (36%) was added until pH 2, and the precipitate was filtered. The solid was recrystallized from hexane/EtOAc (6:4), giving 6.6 g (80%) of the corresponding phenoxyacetic acid as a pale brown solid: R_f 0.38 (hexane/EtOAc/AcOH, 2:3:0.1); mp 114–115 °C; IR (CH_2Cl_2) 3502–2340, 1734, 1599, 1509, 1458, 1436, 1281, 1261, 1225, 1203, 1164, 1082, 1024, 930, 826, 767 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 3.81 (s, 3H, CO_2Me), 3.82 (s, 3H, OMe), 4.62 (s, 3H, CH_2O), 6.33 (dd, $J = 8.5$, 2.7 Hz, 1H, ArH), 6.58 (d, $J = 2.7$ Hz, 1H, ArH), 6.74 (d, $J = 8.5$ Hz, 1H, ArH), 10.30 (br s, 1H, CO_2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 55.8 (MeO), 56.2 (MeO), 65.3 (CH_2O), 101.2 (ArH), 103.5 (ArH), 111.3 (ArH), 144.3 (Ar), 149.9 (Ar), 151.9 (Ar), 174.6 (CO_2H). Anal. calcd for $C_{10}H_{12}O_5$: C, 56.60; H, 5.70. Found: C, 56.64; H, 5.65. A mixture of the phenoxyacetic acid (1.0 g, 4.7 mmol) and *p*-toluenesulfonic acid (0.1 g, 0.53 mmol) in dry methanol (5 mL) was stirred at room temperature for 2 h. The solvent was removed under vacuum. The residue was dissolved in EtOAc (5 mL) and washed with saturated solution of $NaHCO_3$ until neutral. The organic layer was dried (Na_2SO_4) and the solvent was removed. The residue was purified by column chromatography on silica gel (15 g, hexane/EtOAc, 9:1), to give 0.9 g (84%) of **9d** as a white solid (hexane/EtOAc, 6:4): R_f 0.72 (hexane/EtOAc, 6:4); mp 43–44 °C; IR (CH_2Cl_2) 2947, 1753, 1601, 1509, 1444, 1259, 1222, 1192, 1157, 1080, 1023, 838, 769 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 3.77 (s, 3H, CO_2Me), 3.79 (s, 3H, OMe), 3.82 (s, 3H, OMe), 4.56 (s, 3H, CH_2O), 6.30 (dd, $J = 8.7$, 2.7 Hz, 1H, ArH), 6.58 (d, $J = 2.7$ Hz, 1H, ArH), 6.72 (d, $J = 8.7$ Hz, 1H, ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 52.1 (CO_2CH_3), 55.7 (MeO), 56.2 (MeO), 65.8 (CH_2O), 101.2 (ArH), 103.4 (ArH), 111.3 (C-2), 144.1 (Ar), 149.8 (Ar), 152.2 (Ar), 169.4 (CO_2CH_3); MS (70 eV) m/z 226 (M^+, 100), 211 (55), 183 (16), 153 (64), 137 (10), 125 (47), 110 (21), 95 (16), 79 (30). Anal. calcd for $C_{11}H_{14}O_5$: C, 58.40; H, 6.24. Found: C, 58.48; H, 6.14.
19. (a) Olah, G. A.; Krishnamurti, R.; Prakash, G. K. S. Friedel–Crafts Alkylations. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 3, pp 293–339; (b) Mahindaratne, M. P. D.; Wimalasena, K. *J. Org. Chem.* **1998**, *63*, 2858–2866.
20. Typical procedure for preparation of **7b**: To a solution of **4d** (0.05 g, 0.18 mmol) in dry CH_2Cl_2 (100 mL) at room temperature, anhydrous $ZnCl_2$ (0.072 g, 0.53 mmol) was added. The mixture was stirred at room temperature for 72 h, filtered, and the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel (5 g, hexane/EtOAc, 8:2), to give 0.028 g (68%) of **7b** as a white solid: R_f 0.44 (hexane/EtOAc, 7:3); mp 133–134 °C (hexane/EtOAc, 7:3); IR (KBr) 2951, 2833, 2358, 1723, 1621, 1561, 1489, 1436, 1299, 1221, 1137, 1004, 854, 762 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 3.92 (s, 3H, CO_2Me), 3.94 (s, 3H, OMe), 3.95 (s, 3H, OMe), 7.03 (s, 1H, H-7), 7.07 (s, 1H, H-4), 7.44 (s, 1H, H-3); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 52.2 (CO_2CH_3), 56.23 (MeO), 56.28 (MeO), 95.1 (C-7), 102.5 (C-4), 114.4 (C-3), 118.8 (Ar), 144.4 (Ar), 147.5 (Ar), 151.0 (Ar), 151.2 (Ar), 159.9 (CO_2CH_3); MS (70 eV) m/z 236 (M^+, 100), 221 (30), 205 (16), 193 (34), 178 (9), 161 (13), 137 (34), 119 (72), 105 (19), 88 (9), 63 (46). Anal. calcd for $C_{12}H_{12}O_5$: C, 61.02; H, 5.12. Found: C, 61.07; H, 5.39.