

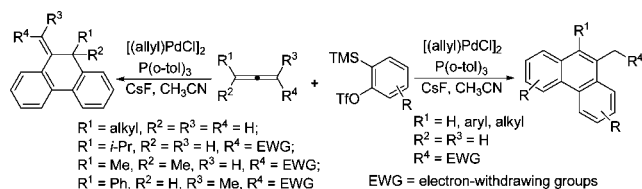
## Palladium-Catalyzed Cocyclootrimerization of Allenes with Arynes: Selective Synthesis of Phenanthrenes

Yi-Lin Liu,<sup>†</sup> Yun Liang,<sup>\*,†</sup> Shao-Feng Pi,<sup>†</sup>  
Xiao-Cheng Huang,<sup>†</sup> and Jin-Heng Li<sup>\*,†,‡</sup>

Key Laboratory of Chemical Biology & Traditional Chinese Medicine Research (Ministry of Education), Hunan Normal University, Changsha 410081, China, and State Key Laboratory of Chemo/Biosensing and Chemometrics, Hunan University, Changsha 410082, China

liangyun1972@126.com; jhli@hunnu.edu.cn

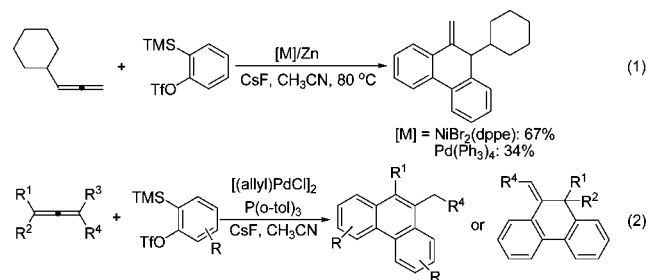
Received January 18, 2009



Palladium-catalyzed cocyclootrimerization of allenes with arynes has been developed for selectively synthesizing phenanthrenes. In the presence of  $[(\text{allyl})\text{PdCl}]_2$  and  $\text{P}(o\text{-tol})_3$ , a variety of allenes, including internal and terminal allenes, underwent the cocyclootrimerization with arynes to afford the corresponding phenanthrenes in moderate to good yields. The results showed the selectivity of the reaction based on allenes.

*o*-Silyl aryltriflates as benzyne precursors were first reported by Kobayashi in 1983.<sup>1</sup> Shortly after, many efficient methods were developed on the basis of *o*-silyl aryltriflates because *o*-silyl aryltriflates could be readily converted into benzynes in situ under mild conditions.<sup>1–4</sup> A representative example is cyclotrimerization of arynes with unsaturated compounds, such as alkynes, allenes, alkenes, or arynes, to construct the phenanthrene frameworks.<sup>3</sup> Both the Pérez group<sup>3a–h</sup> and the Yamamoto group,<sup>3i–k</sup> for example, have independently reported palladium-catalyzed cyclotrimerizations of benzynes with alkynes to afford the corresponding phenanthrenes. Subsequently, Larock and co-workers have described a novel route to prepare phenanthrene derivatives by palladium-catalyzed annulation of arynes with 2-halobiaryls.<sup>3l–n</sup> Cheng and co-workers have also developed a palladium-catalyzed [2+2+2] cocyclootrimerization

## SCHEME 1



of benzynes with bicyclic alkenes to give 9,10-dihydrophenanthrene derivatives.<sup>3o</sup> However, both regio- and chemoselectivities of these cycloaddition transformations are unsatisfactory. As an alternative to these methods, Cheng and co-workers recently demonstrated a highly chemoselective  $\text{NiBr}_2(\text{PPh}_3)_2$ -catalyzed cocyclootrimerization of benzynes with allenes to afford 10-methylene-9,10-dihydrophenanthrenes in moderate yields (eq 1, Scheme 1).<sup>3p</sup> However, an excess amount of Zn was necessary and only aliphatic terminal allenes were screened.  $\text{Pd}(\text{PPh}_3)_4$  was also investigated, and the results showed that it was less effective for the cocyclootrimerization of benzynes with (propa-1,2-dienyl)cyclohexane (eq 1, Scheme 1). Thus, the development of some general and selective routes involving new catalytic systems for the synthesis of phenanthrenes from the aryne

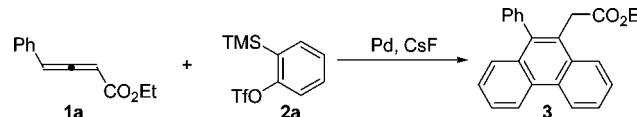
(3) For selected papers on the cyclotrimerization of arynes with unsaturated compounds, such as alkynes, allenes, alkenes, or arynes, to construct the phenanthrene frameworks, see: (a) Peña, D.; Escudero, S.; Pérez, D.; Guitián, E.; Castedo, L. *Angew. Chem., Int. Ed.* **1998**, *37*, 2659–2661. (b) Peña, D.; Pérez, D.; Guitián, E.; Castedo, L. *J. Am. Chem. Soc.* **1999**, *121*, 5827–5828. (c) Peña, D.; Pérez, D.; Guitián, E.; Castedo, L. *Org. Lett.* **1999**, *1*, 1555–1557. (d) Peña, D.; Cobas, A.; Pérez, D.; Guitián, E.; Castedo, L. *Org. Lett.* **2000**, *2*, 1629–1632. (e) Peña, D.; Pérez, D.; Guitián, E.; Castedo, L. *J. Org. Chem.* **2000**, *65*, 6944–6950. (f) Cairo, J.; Peña, D.; Cobas, A.; Pérez, D.; Guitián, E. *Adv. Synth. Catal.* **2006**, *348*, 2466–2474. (g) Quintana, I.; Boersma, A. J.; Peña, D.; Pérez, D.; Guitián, E. *Org. Lett.* **2006**, *8*, 3347–3349. (h) Romero, C.; Peña, D.; Pérez, D.; Guitián, E. *Chem. Eur. J.* **2006**, *12*, 5677–5684. (i) Radhakrishnan, K. V.; Yoshikawa, E.; Yamamoto, Y. *Tetrahedron Lett.* **1999**, *40*, 7533–7535. (j) Yoshikawa, E.; Yamamoto, Y. *Angew. Chem., Int. Ed.* **2000**, *39*, 173–175. (k) Yoshikawa, E.; Radhakrishnan, K. V.; Yamamoto, Y. *J. Am. Chem. Soc.* **2000**, *122*, 7280–7286. (l) Liu, Z.; Zhang, X.; Larock, R. C. *J. Am. Chem. Soc.* **2005**, *127*, 15716–15717. (m) Liu, Z.-J.; Larock, R. C. *J. Org. Chem.* **2007**, *72*, 223–232. (n) Liu, Z.-J.; Larock, R. C. *Angew. Chem., Int. Ed.* **2007**, *46*, 2535–2538. (o) Jayanth, T. T.; Jeganmohan, M.; Cheng, C.-H. *J. Org. Chem.* **2004**, *69*, 8445–8450. (p) Hsieh, J.-C.; Rayabarapu, D. K.; Cheng, C.-H. *Chem. Commun.* **2004**, 532–533. (q) Bhuvaneshwari, S.; Jeganmohan, M.; Cheng, C.-H. *Org. Lett.* **2006**, *8*, 5581–2284. (r) Jayanth, T.-T.; Cheng, C.-H. *Chem. Commun.* **2006**, 894–896. (s) Henderson, J. L.; Edwards, A. S.; Greaney, M. F. *J. Am. Chem. Soc.* **2006**, *128*, 7426–7427.

(4) For selected recent papers on the use of *o*-silyl aryltriflates as the benzyne precursors, see: (a) Huang, X.-C.; Liu, Y.-L.; Liang, Y.; Pi, S.-F.; Wang, F.; Li, J.-H. *Org. Lett.* **2008**, *10*, 1525–1528. (b) Shi, F.; Waldo, J. P.; Chen, Y.; Larock, R. C. *Org. Lett.* **2008**, *10*, 2409–2412. (c) Liu, Z.; Shi, F.; Martinez, P. D. G.; Raminelli, C.; Larock, R. C. *J. Org. Chem.* **2008**, *73*, 219–226. (d) Waldo, J. P.; Zhang, X.; Shi, F.; Larock, R. C. *J. Org. Chem.* **2008**, *73*, 6679–6685. (e) Xie, C.; Liu, L.; Zhang, Y.; Xu, P. *Org. Lett.* **2008**, *10*, 2393–2396. (f) Yoshida, H.; Morishita, T.; Ohshita, J. *Org. Lett.* **2008**, *10*, 3845–3847. (g) Ganta, A.; Snowden, T. S. *Org. Lett.* **2008**, *10*, 5103–5106. (h) Bhuvaneshwari, S.; Jeganmohan, M.; Yang, M.-C.; Cheng, C.-H. *Chem. Commun.* **2008**, 2158–2160. (i) Bhuvaneshwari, S.; Jeganmohan, M.; Cheng, C.-H. *Chem. Commun.* **2008**, 5013–5015. (j) Morishita, T.; Fukushima, H.; Yoshida, H.; Ohshita, J.; Kunai, A. *J. Org. Chem.* **2008**, *73*, 5452–5457. (k) Allan, K. M.; Stoltz, B. M. *J. Am. Chem. Soc.* **2008**, *130*, 17270–17271. (l) Gilmore, C. D.; Allan, K. M.; Stoltz, B. M. *J. Am. Chem. Soc.* **2008**, *130*, 1558–1559. (m) Gerfaut, T.; Neuville, L.; Zhu, J. *Angew. Chem., Int. Ed.* **2009**, *48*, 572–577. (n) Jeganmohan, M.; Bhuvaneshwari, S.; Cheng, C.-H. *Angew. Chem., Int. Ed.* **2009**, *48*, 391–394. (o) Tambar, U. K.; Stoltz, B. M. *J. Am. Chem. Soc.* **2005**, *127*, 5340–5341.

<sup>†</sup> Hunan Normal University.

<sup>‡</sup> Hunan University.

(1) Himeshima, Y.; Sonoda, T.; Kobayashi, H. *Chem. Lett.* **1983**, 1211–1214.  
(2) For reviews, see: (a) Pellissier, H.; Santelli, M. *Tetrahedron* **2003**, *59*, 701–730. (b) Wenk, H. H.; Winkler, M.; Sander, W. *Angew. Chem., Int. Ed.* **2003**, *42*, 502–528. (c) Guitián, E.; Pérez, D.; Peña, D. *Top. Organomet. Chem.* **2005**, *14*, 109–146.

**TABLE 1.** Palladium-Catalyzed Cocyclootrimerization of Ethyl 4-Phenylbuta-2,3-dienoate (**1a**) with 2-(Trimethylsilyl)phenyl Triflate (**2a**)<sup>a</sup>


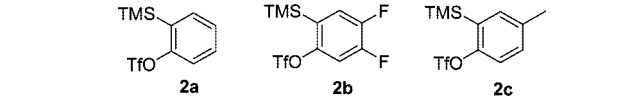
entry	[Pd]	<i>t</i> (°C)	time (h)	yield (%) <sup>b</sup>
1 <sup>c</sup>	Pd(dba) <sub>2</sub>	80	20	30
2	Pd(dba) <sub>2</sub>	80	20	39
3	PdCl <sub>2</sub>	80	10	8
4	Pd(PPh <sub>3</sub> ) <sub>4</sub>	80	10	23
5	Pd(OAc) <sub>2</sub>	80	6	38
6	[(allyl)PdCl] <sub>2</sub>	80	6	40
7	[(allyl)PdCl] <sub>2</sub>	60	24	54
8	[(allyl)PdCl] <sub>2</sub>	0	24	12
9 <sup>d</sup>	[(allyl)PdCl] <sub>2</sub>	0 to 60	3	71
10 <sup>d</sup>	Pd(OAc) <sub>2</sub>	0 to 60	12	49
11		0 to 60	20	0
12 <sup>e</sup>	[(allyl)PdCl] <sub>2</sub>	0 to 60	20	17

<sup>a</sup> Reaction conditions: **1a** (0.2 mmol), **2a** (2 equiv), [Pd] (5 mol %), P(*o*-tol)<sub>3</sub> (10 mol %), and CsF (3 equiv) in MeCN (2 mL). <sup>b</sup> Isolated yield. The benzyne cyclotrimerization product was observed by GC-MS analysis. <sup>c</sup> Without P(*o*-tol)<sub>3</sub>. <sup>d</sup> At 0 °C for 2 h, then at 60 °C for 1 h. <sup>e</sup> In THF (2 mL) instead of MeCN.

partners is still a challenging area. Here, we report a selective cocyclootrimerization of benzynes with allenes to synthesize phenanthrenes in moderate yields using [(allyl)PdCl]<sub>2</sub> and P(*o*-tol)<sub>3</sub> catalytic systems (eq 2, Scheme 1).

The reaction between ethyl 4-phenylbuta-2,3-dienoate (**1a**) and 2-(trimethylsilyl)phenyl triflate (**2a**) was conducted to optimize the reaction conditions, and the results are summarized in Table 1. Initially, a set of the Pd catalytic systems were investigated (entries 1–6). Without ligands, treatment of allene **1a** with triflate **2a** and Pd(dba)<sub>2</sub> at 80 °C afforded the corresponding product **3** in a 30% yield (entry 1). The yield of **3** was enhanced to 39% in the presence of P(*o*-tol)<sub>3</sub> (entry 2). Identical results were obtained with either Pd(OAc)<sub>2</sub> or [(allyl)PdCl]<sub>2</sub> (entries 5 and 6). However, both PdCl<sub>2</sub> and Pd(PPh<sub>3</sub>)<sub>4</sub> were less effective (entries 3 and 4). The reaction temperature was subsequently examined in the presence of [(allyl)PdCl]<sub>2</sub> and P(*o*-tol)<sub>3</sub>. The screening results demonstrated that the reaction temperature affected the reaction (entries 6–9). The yield of the target product **3** was enhanced to 54% at 60 °C (entry 7), and 12% yield was still isolated at 0 °C (entry 8). Interestingly, the yield of **3** was increased to 71% when the reaction was conducted at 0 °C for 2 h, then at 60 °C for 1 h (entry 9). However, Pd(OAc)<sub>2</sub> displayed less activity under the same conditions (entry 10). It is worthy noting that no desired product is observed by GC-MS analysis without Pd catalysts (entry 11).<sup>3</sup> Another solvent, THF, was also tested, and the results showed that it was inferior to MeCN (entry 12).

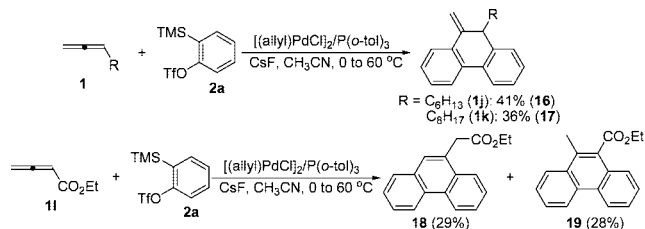
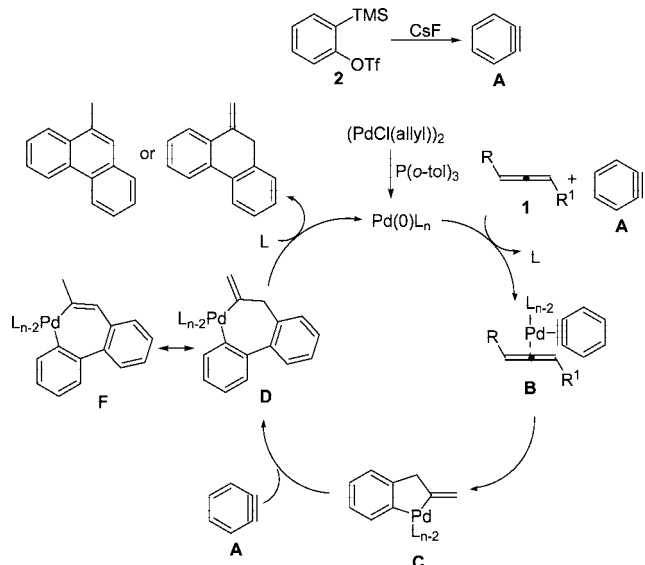
With the optimal reaction conditions in hand, the scope of the cocyclootrimerization reaction was screened (Table 2 and Scheme 2). As shown in Table 2, a variety of internal allenes **1b–i** were first evaluated by reacting with triflate **2a**, [(allyl)PdCl]<sub>2</sub>, and P(*o*-tol)<sub>3</sub> (entries 1–8). The results demonstrated that the structures of the allenes affected the yield and selectivity to some extent. While ethyl 4-(4-methoxyphenyl)buta-2,3-dienoate **1b**, for instance, was treated with triflate **2a**, [(allyl)PdCl]<sub>2</sub>, and P(*o*-tol)<sub>3</sub> to afford the desired product **4** in a 77% yield (entry 1), substrate **1d** with an *o*-methoxyphenyl group reduced the yield of the corresponding product **6** to 53% under the same

**TABLE 2.** Selective Cocyclootrimerization of Allene **1** with Triflate **2** in the Presence of [(allyl)PdCl]<sub>2</sub> and P(*o*-tol)<sub>3</sub><sup>a</sup>


Entry	Allene <b>1</b>	<b>2</b>	Product	Yield (%) <sup>b</sup>
1	<b>1b</b>	<b>2a</b>	<b>4</b>	77
2	<b>1c</b>	<b>2a</b>	<b>5</b>	69
3	<b>1d</b>	<b>2a</b>	<b>6</b>	53
4	<b>1e</b>	<b>2a</b>	<b>7</b>	70
5	<b>1f</b>	<b>2a</b>	<b>8</b>	66
6	<b>1g</b>	<b>2a</b>	<b>9</b>	51
7 <sup>c</sup>	<b>1h</b>	<b>2a</b>	<b>10</b>	60
8	<b>1i</b>	<b>2a</b>	<b>11</b>	29
9	<b>1a</b>	<b>2b</b>	<b>12</b>	63
10	<b>1b</b>	<b>2b</b>	<b>13</b>	50
11	<b>1e</b>	<b>2b</b>	<b>14</b>	47
12	<b>1a</b>	<b>2c</b>	<b>15</b>	mixture

<sup>a</sup> Reaction conditions: **1** (0.2 mmol), **2** (2 equiv), [(allyl)PdCl]<sub>2</sub> (5 mol %), P(*o*-tol)<sub>3</sub> (10 mol %), and CsF (3 equiv) in MeCN (2 mL) at 0 °C for 2 h, then at 60 °C for 1 h. <sup>b</sup> Isolated yield. <sup>c</sup> (Z)/(E) isomers = 2:1 determined by <sup>1</sup>H NMR spectra.

conditions (entry 3). In the presence of [(allyl)PdCl]<sub>2</sub> and P(*o*-tol)<sub>3</sub>, the other disubstituted allenes **1c**, **1e**, and **1g** also provided the target phenanthrene products in satisfactory yields (entries 2 and 4–6). Surprisingly, 9,10-dihydro-9-methylenephenan-

**SCHEME 2. Cocyclotrimerization of Terminal Allenes **1j–l** with Triflate **2a****

**SCHEME 3. A Possible Mechanism**


threne **8** was obtained from the reaction of allene **1f** (entry 5). We were interested to find that the chemoselectivities of trisubstituted allenes were shifted toward 9,10-dihydro-9-methylenephenanthrenes (entries 7 and 8). In the presence of [(allyl)PdCl]<sub>2</sub> and P(*o*-tol)<sub>3</sub>, the reaction of 2-methyl-1,4-diphenylbuta-2,3-dien-1-one (**1h**) with triflate **2a** was conducted smoothly to afford a mixture of (*Z*)- and (*E*)-9,10-dihydro-9-methylenephenanthrene **10** in a 60% total yield (*Z/E* = 2:1; entry 7). It was found that a 29% yield was still achieved from the reaction between ethyl 4-methylpenta-2,3-dienoate (**1i**) and triflate **2a** under the standard conditions (entry 8). Another triflate **2b** was investigated by the reaction with allenes **1a**, **1b**, or **1e** in the presence of [(allyl)PdCl]<sub>2</sub> and P(*o*-tol)<sub>3</sub>, and the results indicated that these reactions were carried out selectively in moderate yields (entries 9–11). However, triflate **2c** reacted with allene **2a** provided a mixture of products (entry 12).

As shown in Scheme 2, three terminal allenes **1j–l** were also examined under the standard conditions. Treatment of aliphatic allenes **1j** or **1k** with triflate **2a**, [(allyl)PdCl]<sub>2</sub>, and P(*o*-tol)<sub>3</sub> afforded the corresponding 9,10-dihydro-9-methylenephenanthrenes **16** and **17**, respectively, in moderate yields, whose selectivity is identical to Cheng's Pd results.<sup>3p</sup> We were pleased to find that the reaction of the electron-deficient terminal allene **1l** with triflate **2a** was also conducted smoothly in a 57% total yield under the same conditions. However, the regioselectivity was not satisfactory, and a mixture of **18** and **19** was obtained in a 1:1 ratio.

A possible mechanism as outlined in Scheme 3 for the palladium-catalyzed cocyclotrimerization reaction is proposed on the basis of the present results and the previously reported mechanisms.<sup>1–4</sup> Initially, complexation of the active Pd(0)L<sub>n</sub>

species with allene **1** and benzyne **A**, which is generated from the reaction of **2** with CsF, occurs readily to afford intermediate **B**. Subsequently, intermediate **B** undergoes cis-addition to give intermediate **C**, followed by insertion with another benzyne **A** to yield intermediate **D**. Finally, reductive elimination of intermediate **D** takes place to provide the target 9,10-dihydro-9-methylenephenanthrene product and regenerate the active Pd(0) species. Intermediate **D** to intermediate **D** readily occurs by isomerization to give the phenanthrene product due to the electronic effect of allenes. However, the formation of 9,10-dihydro-9-methylenephenanthrenes from allenes **1f**, **1h**, and **1i** may be because the steric hindrance effect preponderates over the electronic effect. The identical effects are presented among the reactions of the electron-neutral and electron-deficient terminal allenes.

In summary, we have developed a selective protocol for the synthesis of phenanthrenes by palladium-catalyzed cocyclotrimerization of allenes with benzynes. This method allows for a wide range of various allenes, including internal and terminal allenes, to proceed the cocyclotrimerization with arynes. It is noteworthy that the products, phenanthrenes, are the common structural motifs in both naturally occurring biological compounds with antimalarial, anticancer and emetic activities,<sup>5</sup> and materials with photoconducting, photochemical, and electroluminescent properties.

**Experimental Section**

**Typical Experimental Procedure for the Palladium-Catalyzed Cocyclotrimerization of Allenes with Benzynes.** A mixture of allene **1** (0.2 mmol), 2-(trimethylsilyl)phenyl triflate **2** (2 equiv), [(allyl)PdCl]<sub>2</sub> (5 mol %), P(*o*-tol)<sub>3</sub> (10 mol %), and CsF (3 equiv) was stirred in MeCN (2 mL) at 0 °C for 2 h, then at 60 °C for 1 h until complete consumption of starting material as monitored by TLC and GC-MS analysis. Then the mixture was filtered by crude flash column chromatography with diethyl ether, and evaporated under vacuum. The residue was purified by flash column chromatography to afford the pure product (hexane/ethyl acetate).

**Ethyl 2-(10-phenylphenanthren-9-yl)acetate (3):** pale yellow solid, mp 105.8 °C (uncorrected); <sup>1</sup>H NMR (500 MHz) δ 8.76 (d, *J* = 9.5 Hz, 1H), 8.72 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 9.0 Hz, 1H), 7.67–7.63 (m, 2H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.51–7.43 (m, 3H), 7.42–7.40 (m, 1H), 7.38–7.35 (m, 3H), 4.11–4.06 (m, 2H), 3.90 (s, 2H), 1.15 (t, *J* = 7.5 Hz, 3H); <sup>13</sup>C NMR (125 MHz) δ 171.7, 139.7, 139.1, 132.1, 131.1, 130.2, 130.0, 128.4, 128.2, 128.0, 127.7, 127.4, 127.1, 127.0, 126.4, 126.3, 124.7, 123.0, 122.4, 60.7,

(5) (a) Majumder, P. L.; Banerjee, S.; Sen, S. *Phytochemistry* **1996**, *42*, 847–852. (b) Leong, Y. W.; Kang, C. C.; Harrison, L. J.; Powell, A. D. *Phytochemistry* **1997**, *44*, 157–165. (c) Kumar, S. *J. Org. Chem.* **1997**, *62*, 8535–8539. (d) Hudson, B. P.; Barton, J. K. *J. Am. Chem. Soc.* **1998**, *120*, 6877–6888. (e) Banik, B. K.; Becker, F.; Banik, I. *Bioorg. Med. Chem.* **2004**, *12*, 2523–2528. (f) Schmidt, J. M.; Mercure, J.; Tremblay, G. B.; Page, M.; Kalbakji, A.; Feher, M.; Dunn-Dufault, R.; Peter, M. G.; Redden, P. R. *J. Med. Chem.* **2003**, *46*, 1408–1418. (g) McCurdy, C. R.; Le Bourdonnec, B.; Metzger, T. G.; Kouhen, R. E.; Zhang, Y.; Law, P. Y.; Portoghese, P. S. *J. Med. Chem.* **2002**, *45*, 2887–2890. (h) Cragg, G. M.; Newman, D. J. *J. Nat. Prod.* **2004**, *67*, 232–244. (i) Li, Z.; Jin, Z.; Huang, R. *Synthesis* **2001**, 2365–2378. (j) Banwell, M. G.; Bezos, A.; Burns, C.; Kruszelnicki, I.; Parish, C. R.; Su, S.; Sydnese, M. O. *Bioorg. Med. Chem. Lett.* **2006**, *16*, 181–185. (k) Wei, L.; Brossi, A.; Kendall, R.; Bastow, K. F.; Morris-Natschke, S. L.; Shi, Q.; Lee, K.-H. *Bioorg. Med. Chem.* **2006**, *14*, 6560–6569.

(6) (a) Lewis, F. D.; Baranczyk, S. V.; Burch, E. L. *J. Am. Chem. Soc.* **1992**, *114*, 3866–3870. (b) Lewis, F. D.; Burch, E. L. *J. Phys. Chem.* **1996**, *100*, 4055–4063. (c) Novak, B. H.; Lash, T. D. *J. Org. Chem.* **1998**, *63*, 3998–4010. (d) Liu, R.; Farinha, J. P. S.; Winnik, M. A. *Macromolecules* **1999**, *32*, 3957–3963. (e) Tanaka, F.; Mase, N.; Barbas, C. F., III. *J. Am. Chem. Soc.* **2004**, *126*, 3692–3693. (f) Watson, M. D.; Fechtenkötter, A.; Mullen, K. *Chem. Rev.* **2001**, *101*, 1267–1300. (g) Machado, A. M.; Munaro, M.; Martins, T. D.; Da'vila, L. Y. A.; Giro, R.; Caldas, M. J.; Atvars, T. D. Z.; Akcelrud, L. C. *Macromolecules* **2006**, *39*, 3398–3407.

37.0, 14.1; IR (KBr,  $\text{cm}^{-1}$ ) 1727; LRMS (EI, 70 eV)  $m/z$  (%) 340 ( $\text{M}^+$ , 55), 294 (29), 267 (100), 252 (28); HRMS (EI) for  $\text{C}_{24}\text{H}_{20}\text{O}_2$  ( $\text{M}^+$ ) calcd. 340.1463, found 340.1461.

**Acknowledgment.** We thank the Opening Fund of the State Key Laboratory of Chemo/Biosensing and Chemometrics (No. 2006016), New Century Excellent Talents in University (No. NCET-06-0711), Scientific Research Fund of Hunan Provincial Education Department (Nos. 08B053 and 08A037), Opening Fund of Key Laboratory of Chemical Biology and Traditional

Chinese Medicine Research (Ministry of Education of China) (No. KLCBTCMR2008-11), and Hunan Normal University (No. 080605) for financial support.

**Supporting Information Available:** General experimental procedures, characterization data for **3–19**, and copies of spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JO900117C