

## Synthesis of Arene-Fused Isoindoline Derivatives from Morita-Baylis-Hillman Adducts by IMDA Reaction Using *Z*-Vinylarenes as 1,3-Dienes

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Received July 1, 2014, Accepted July 21, 2014

Intramolecular Diels-Alder (IMDA) reaction of vinylarenes bearing a *Z*-alkenyl tether, prepared from Morita-Baylis-Hillman (MBH) adducts, afforded arene-fused isoindoline derivatives in good yields. Vinylfurans, vinylthiophenes, and vinylnaphthalenes could be used successfully as dienes, while vinylbenzene failed under the same reaction conditions.

**Key Words** : Intramolecular Diels-Alder reaction, Morita-Baylis-Hillman adducts, Vinylarenes, Isoindolines

### Introduction

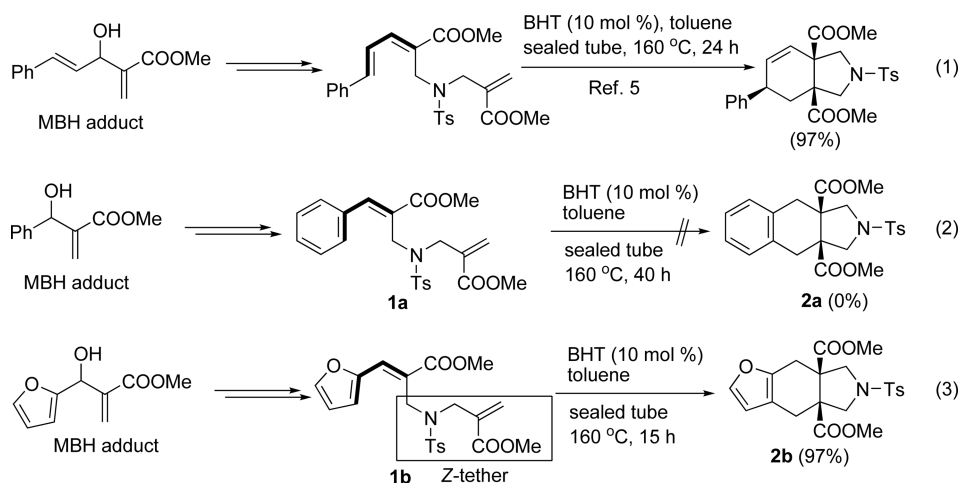
The construction of a cyclohexene ring by using vinylarene (such as styrenyl) as a 1,3-diene moiety in both inter- and intramolecular Diels-Alder reactions has been well documented.<sup>1-4</sup> However, vinylarenes (aromatic dienes) are usually poor dienes in Diels-Alder reaction because the initial step entails loss of aromaticity, thus the reaction is more efficient for the intramolecular version.<sup>3,4</sup> The intramolecular Diels-Alder (IMDA) reaction of *E*-vinylarenes has been studied extensively.<sup>3,4</sup> However, a limited number of papers examined the reaction of a substrate bearing *Z*-alkenyl tether because of its lower reactivity compared to *E*-vinylarenes.<sup>3c,g,4e</sup>

### Results and Discussion

Very recently, we reported an efficient synthesis of hexahydroisoindole-3a-carboxylates by IMDA reaction of modified Morita-Baylis-Hillman (MBH) adducts, as shown in Scheme 1.<sup>5</sup> In the reaction, a typical 1,3-diene and a *Z*-alkenyl moiety have been involved as reaction partners (Eq. 1).

As a continuous work, we were interested in the IMDA reactions of **1a** or **1b** bearing an aromatic diene, as shown in Scheme 1. At the outset of our experiment, the reaction of **1a** was examined in toluene in the presence of BHT (10 mol %) in a sealed tube (160 °C) for 40 h (Eq. 2). However, a desired product **2a** was not formed at all, and **1a** was recovered in high yield (81%). In contrast to the result of **1a**, the reaction of 2-furyl derivative **1b** produced a furan-fused isoindoline derivative **2b** in excellent yield (97%)<sup>6</sup> under the same reaction conditions (160 °C, 15 h) in short time (Eq. 3). The successful result must be due to small resonance energy of furan ring as compared to that of the benzene of **1a**.<sup>2a,4a-e</sup>

Encouraged by the results, we prepared starting materials **1c-j** from the corresponding MBH adducts according to the reported procedure,<sup>5,7</sup> and the IMDA reactions were examined. The results are summarized in Table 1. The reactions of **1c-e** (entries 2-4) afforded the IMDA products **2c-e** in high yields (92-98%). It is interesting to note that both 2-naphthyl derivative **1e** and 1-naphthyl derivative **1f** gave the same product **2e** in similar yields (entries 4 and 5). In the reaction of **1e**, the double bond at the 1,2-position of naphthalene ring was incorporated selectively in the IMDA reaction.<sup>1c</sup> The



Scheme 1

**Table 1.** IMDA reactions of modified MBH adducts

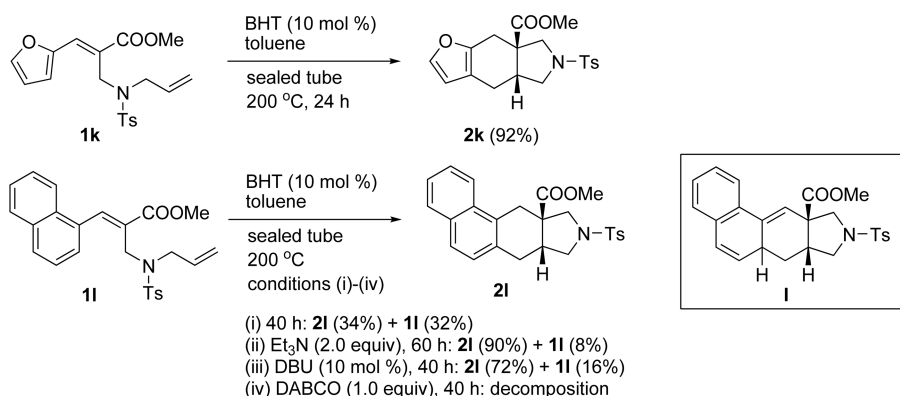
Entry	Substrate	Conditions <sup>a</sup>	Product (%)
1		160 °C, 15 h	 <b>2b</b> (97)
2		160 °C, 10 h	 <b>2c</b> (98)
3		160 °C, 10 h	 <b>2d</b> (97)
4		160 °C, 10 h	 <b>2e</b> (92)
5		160 °C, 10 h	<b>2e</b> (93)
6		190 °C, 20 h	 <b>2g</b> (100)
7		160 °C, 12 h	 <b>2h</b> (92) <sup>b</sup>
8		160 °C, 12 h	 <b>2b</b> (100)
9		160 °C, 12 h	 <b>2j</b> (98)

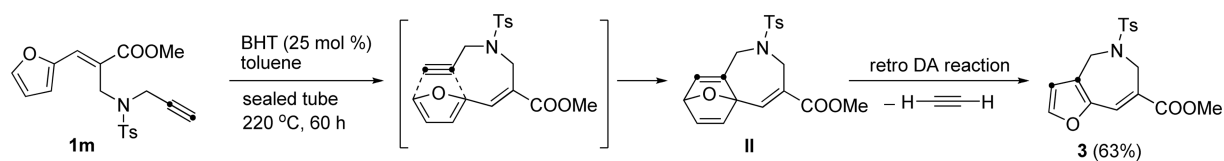
<sup>a</sup>Substrate (0.5 mmol), BHT (10 mol %), toluene (8 mL), sealed tube. <sup>b</sup>A mixture of *syn/anti* (1:1) and E is COOMe.

reactions of **1g** and **1h**, bearing phenyl-substituted dienophile moieties, afforded the corresponding products **2g** and **2h** in excellent yields (entries 6 and 7). Compound **2h** was obtained as a diastereomeric mixture (*syn/anti*, 1:1). The reaction of **1g** at 160 °C was somewhat slow, and the reaction was carried out at elevated temperature (190 °C). As expected, 3-furyl derivative **1i** (entry 8) and 2-furyl derivative **1b** (entry 1) afforded the same product **2b**. The crotonate derivative **1j** (entry 9) also gave **2j** in high yield (98%).

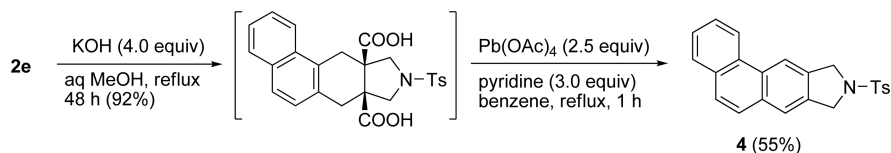
The reaction of *N*-allyl derivative **1k** afforded **2k** in good yield (92%), as shown in Scheme 2. However, the reaction required higher temperature than the reactions of **1b-j** bearing an ester group at the dienophile moiety. In addition, the reaction of naphthalene derivative **1l** produced **2l** in low yield (34%) even at 200 °C for 40 h. During the reaction of **1l**, we observed the presence of a small amount of unidentified compound near the product **2l** on TLC. When we checked this compound by <sup>1</sup>H NMR in a crude state, the structure could be assigned as an intermediate **I**.<sup>2a,8</sup> Thus we examined the reaction in the presence of Et<sub>3</sub>N (2.0 equiv), and the yield of **2l** could be increased to 90%, to our delight. The use of Et<sub>3</sub>N might be helpful for the double bond isomerization of the intermediate **I** to **2l**. The reaction with the aid of DBU or DABCO was less effective.

When the propargyl derivative **1m** was subjected under the same reaction conditions, the reaction was so sluggish (Scheme 3). To our surprise, however, a furo[3,2-*c*]azepine-7-carboxylate derivative **3**<sup>9</sup> was obtained in moderate yield (46%) under more vigorous conditions (220 °C, 36 h), and the starting material **1m** was recovered (36%). The reaction mechanism would be a sequential intramolecular furan Diels-Alder (IMDAF) reaction<sup>10</sup> to form the intermediate **II** and a retro-Diels-Alder reaction with liberation of acetylene.<sup>11</sup> As depicted in Scheme 3, two carbons of the furan ring were exchanged by the carbons of propargyl moiety with concomitant loss of acetylene. When we carried out the reaction for a longer time (60 h) in order to increase the yield of **3**, a severe decomposition was observed. Compound **3** could be obtained in an improved yield (63%) without much decomposition when we carried out the reaction in the presence of 25 mol % BHT. The different outcome of propargyl derivative **1m** might be ascribed to the linearity of the triple

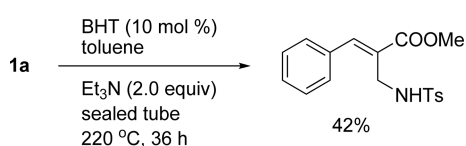
**Scheme 2**



Scheme 3



Scheme 4



Scheme 5

bond, which caused the approach toward vinylfuran moiety difficult.

As reported in a similar case,<sup>12</sup> the diester moiety of **2e** could be used for the introduction of double bonds, as shown in Scheme 4. Base-mediated hydrolysis of **2e** to diacid (92%) and a following treatment with  $\text{Pb}(\text{OAc})_4$  afforded known benzo[*f*]isoindoline derivative **4** in a reasonable yield (55%).<sup>3g,13</sup>

As noted in Scheme 1, the reaction of **1a** under the typical reaction condition at 160 °C did not produce **2a** in any trace amount. The reaction at elevated temperature (180–220 °C) caused a slow decomposition of **1a**. When we carried out the reaction in the presence of  $\text{Et}_3\text{N}$  as for the synthesis of **2l** (Scheme 2), deallylation occurred to produce a tosylamide derivative in moderate yield (42%), as shown in Scheme 5.

In summary, an intramolecular Diels-Alder reaction of modified Morita-Baylis-Hillman (MBH) adducts bearing a *Z*-alkenyl tether has been examined. Various aromatic diene and *Z*-alkenyl tether underwent a successful intramolecular Diels-Alder reaction in toluene in a sealed tube at 160 °C to produce arene-fused isoindoline derivatives in excellent yields.

## Experimental Section

**Typical Procedure for the Preparation of 1a.**<sup>5,7</sup> A mixture of (*E*)-3-phenyl-2-[(toluene-4-sulfonylamino)methyl]acrylic acid methyl ester (345 mg, 1.0 mmol), methyl 2-(bromomethyl)acrylate (269 mg, 1.5 mmol), and  $\text{K}_2\text{CO}_3$  (276 mg, 2.0 equiv) in DMF (3.0 mL) was stirred at room temperature for 5 h. After removal of the solvent and column chromatographic purification process (hexanes/ $\text{Et}_2\text{O}$ , 5:1) compound **1a** was obtained as a white solid, 401 mg (90%). Other compounds **1b–m** were prepared analogously, and the spectroscopic data of **1a–m** are as follows.

**Compound 1a:** 90%; white solid, mp 99–100 °C; IR (KBr)

1715, 1634, 1437, 1346  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  2.42 (s, 3H), 3.67 (s, 3H), 3.68 (s, 3H), 3.96 (s, 2H), 4.31 (s, 2H), 5.81 (d,  $J = 0.9$  Hz, 1H), 6.19 (d,  $J = 0.9$  Hz, 1H), 7.26 (d,  $J = 8.1$  Hz, 2H), 7.36–7.46 (m, 5H), 7.59 (d,  $J = 8.1$  Hz, 2H), 7.78 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  21.49, 44.95, 48.78, 51.77, 52.09, 126.81, 127.08, 127.45, 128.62, 129.27, 129.58, 129.69, 134.09, 135.64, 135.80, 143.40, 144.41, 166.10, 167.69; ESIMS  $m/z$  444  $[\text{M}+\text{H}]^+$ . Anal. Calcd for  $\text{C}_{23}\text{H}_{25}\text{NO}_6\text{S}$ : C, 62.29; H, 5.68; N, 3.16. Found: C, 62.51; H, 5.79; N, 3.11.

**Compound 1b:** 92%; colorless oil; IR (film) 1714, 1635, 1436, 1346, 1158  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  2.44 (s, 3H), 3.64 (s, 3H), 3.66 (s, 3H), 3.98 (t,  $J = 1.8$  Hz, 2H), 4.52 (s, 2H), 5.88 (dd,  $J = 2.7$  and 1.8 Hz, 1H), 6.22 (dd,  $J = 2.7$  and 1.8 Hz, 1H), 6.50 (dd,  $J = 3.3$  and 1.8 Hz, 1H), 6.86 (d,  $J = 3.3$  Hz, 1H), 7.31 (d,  $J = 8.4$  Hz, 2H), 7.44 (s, 1H), 7.47 (d,  $J = 1.8$  Hz, 1H), 7.70 (d,  $J = 8.4$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  21.50, 45.55, 48.16, 51.71, 52.11, 112.51, 118.42, 121.53, 126.51, 127.45, 129.59, 130.19, 135.87, 136.30, 143.31, 145.41, 150.08, 166.15, 167.80; ESIMS  $m/z$  434  $[\text{M}+\text{H}]^+$ . Anal. Calcd for  $\text{C}_{21}\text{H}_{23}\text{NO}_7\text{S}$ : C, 58.19; H, 5.35; N, 3.23. Found: C, 58.30; H, 5.31; N, 3.42.

**Compound 1c:** 93%; white solid, mp 88–90 °C; IR (KBr) 1714, 1621, 1436, 1354, 1276, 1209, 1158  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  2.45 (s, 3H), 3.64 (s, 3H), 3.68 (s, 3H), 3.95 (s, 2H), 4.43 (s, 2H), 5.90 (d,  $J = 0.9$  Hz, 1H), 6.19 (d,  $J = 0.9$  Hz, 1H), 7.12 (dd,  $J = 5.1$  and 3.9 Hz, 1H), 7.32 (d,  $J = 8.1$  Hz, 2H), 7.49 (d,  $J = 3.9$  Hz, 1H), 7.52 (d,  $J = 5.1$  Hz, 1H), 7.71 (d,  $J = 8.1$  Hz, 2H), 7.84 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  21.52, 45.93, 48.19, 51.73, 52.15, 121.96, 126.72, 127.59, 128.07, 129.68, 130.84, 133.95, 135.17, 136.27, 136.71, 136.85, 143.54, 166.09, 167.73; ESIMS  $m/z$  450  $[\text{M}+\text{H}]^+$ .

**Compound 1d:** 94%; white solid, mp 85–87 °C; IR (KBr) 1732, 1598, 1435, 1346, 1162  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  2.46 (s, 3H), 2.50 (d,  $J = 0.6$  Hz, 3H), 3.65 (s, 3H), 3.66 (s, 3H), 3.95 (t,  $J = 1.5$  Hz, 2H), 4.40 (s, 2H), 5.94 (dd,  $J = 2.7$  and 1.5 Hz, 1H), 6.21 (dd,  $J = 2.7$  and 1.5 Hz, 1H), 6.77 (dq,  $J = 3.6$  and 0.6 Hz, 1H), 7.27 (d,  $J = 3.6$  Hz, 1H), 7.34 (d,  $J = 8.1$  Hz, 2H), 7.73 (d,  $J = 8.1$  Hz, 2H), 7.76 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  15.63, 21.52, 45.96, 47.91, 51.72, 52.03, 119.96, 126.55, 126.64, 127.66, 129.65,

134.71, 135.04, 135.27, 136.40, 137.51, 143.43, 146.66, 166.13, 167.89; ESIMS  $m/z$  486  $[M+Na]^+$ .

**Compound 1e:** 92%; white solid, mp 121-123 °C; IR (KBr) 1715, 1633, 1436, 1348, 1243, 1158  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ , 300 MHz)  $\delta$  2.42 (s, 3H), 3.66 (s, 3H), 3.74 (s, 3H), 4.02 (s, 2H), 4.43 (s, 2H), 5.89 (s, 1H), 6.19 (s, 1H), 7.24 (d,  $J = 8.1$  Hz, 2H), 7.51-7.60 (m, 3H), 7.63 (d,  $J = 8.1$  Hz, 2H), 7.85-7.97 (m, 3H), 7.98 (s, 1H), 8.10 (s, 1H);  $^{13}C$  NMR ( $CDCl_3$ , 75 MHz)  $\delta$  21.45, 45.32, 48.77, 51.73, 52.17, 126.62, 126.78, 126.82, 126.90, 127.26, 127.47, 127.57, 128.30, 128.75, 129.60, 130.10, 131.45, 133.04, 133.37, 135.30, 135.90, 143.47, 144.70, 166.08, 167.86; ESIMS  $m/z$  494  $[M+H]^+$ .

**Compound 1f:** 95%; white solid, mp 115-117 °C; IR (KBr) 1720, 1638, 1437, 1343, 1250, 1159  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ , 300 MHz)  $\delta$  2.38 (s, 3H), 3.59 (s, 3H), 3.77 (s, 3H), 3.83 (s, 2H), 4.27 (s, 2H), 5.73 (d,  $J = 1.2$  Hz, 1H), 6.16 (d,  $J = 1.2$  Hz, 1H), 7.16 (d,  $J = 8.4$  Hz, 2H), 7.33 (dt,  $J = 7.2$  and 0.9 Hz, 1H), 7.44-7.58 (m, 5H), 7.76-7.83 (m, 1H), 7.84-7.93 (m, 2H), 8.29 (s, 1H);  $^{13}C$  NMR ( $CDCl_3$ , 75 MHz)  $\delta$  21.42, 45.13, 48.99, 51.66, 52.15, 124.43, 125.08, 126.32, 126.53, 126.69, 126.93, 127.30, 128.56, 129.36, 129.43, 129.91, 131.18, 131.32, 133.32, 135.55, 135.93, 142.41, 143.20, 165.83, 167.22; ESIMS  $m/z$  494  $[M+H]^+$ .

**Compound 1g:** 75%; white solid, mp 130-131 °C; IR (KBr) 1714, 1633, 1435, 1350, 1253, 1164  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ , 300 MHz)  $\delta$  2.40 (s, 3H), 3.59 (s, 3H), 3.62 (s, 3H), 4.23 (s, 2H), 4.36 (s, 2H), 6.42-6.46 (m, 1H), 6.74 (d,  $J = 3.3$  Hz, 1H), 7.18 (d,  $J = 8.1$  Hz, 2H), 7.29-7.39 (m, 7H), 7.49 (d,  $J = 8.1$  Hz, 2H), 7.62 (s, 1H);  $^{13}C$  NMR ( $CDCl_3$ , 75 MHz)  $\delta$  21.48, 45.05, 46.31, 51.82, 51.89, 112.32, 117.68, 122.68, 127.99, 128.34, 128.79, 129.14, 129.17, 129.29, 129.88, 134.55, 134.59, 141.73, 143.10, 144.85, 150.27, 167.66, one carbon was overlapped; ESIMS  $m/z$  510  $[M+H]^+$ .

**Compound 1h:** 90%; white solid, mp 141-143 °C; IR (KBr) 1719, 1637, 1436, 1340, 1249, 1157  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ , 300 MHz)  $\delta$  2.37 (s, 3H), 3.50 (s, 3H), 3.61 (s, 3H), 4.63 (d,  $J = 13.8$  Hz, 1H), 4.76 (d,  $J = 13.8$  Hz, 1H), 5.86 (s, 1H), 6.15 (s, 1H), 6.43 (dd,  $J = 3.3$  and 1.8 Hz, 1H), 6.56 (s, 1H), 6.66 (d,  $J = 3.3$  Hz, 1H), 7.06-7.22 (m, 7H), 7.31-7.40 (m, 4H);  $^{13}C$  NMR ( $CDCl_3$ , 75 MHz)  $\delta$  21.39, 45.60, 51.69, 51.90, 62.70, 112.07, 118.01, 122.98, 127.46, 127.49, 127.93, 128.85, 129.30, 129.37, 129.78, 136.96, 138.36, 138.80, 142.36, 144.96, 150.16, 166.39, 167.79; ESIMS  $m/z$  510  $[M+H]^+$ .

**Compound 1i:** 90%; white solid, mp 96-98 °C; IR (KBr) 1737, 1436, 1349, 1265, 1163  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ , 300 MHz)  $\delta$  2.45 (s, 3H), 3.65 (s, 3H), 3.67 (s, 3H), 3.94 (s, 2H), 4.28 (s, 2H), 5.84 (d,  $J = 1.2$  Hz, 1H), 6.16 (d,  $J = 1.2$  Hz, 1H), 6.95 (s,  $J = 1.5$  Hz, 1H), 7.33 (d,  $J = 8.1$  Hz, 2H), 7.49 (dd,  $J = 1.5$  and 0.6 Hz, 1H), 7.60 (s, 1H), 7.70 (d,  $J = 8.1$  Hz, 2H), 7.91 (d,  $J = 0.6$  Hz, 1H);  $^{13}C$  NMR ( $CDCl_3$ , 75 MHz)  $\delta$  21.53, 45.82, 48.11, 51.76, 52.12, 110.70, 120.77, 122.89, 126.69, 127.62, 129.78, 134.66, 135.83, 136.29, 143.76, 144.49, 146.65, 166.14, 167.93; ESIMS  $m/z$  434  $[M+H]^+$ .

**Compound 1j:** 74%; white solid, mp 110-112 °C; IR (KBr) 1721, 1634, 1435, 1349, 1278, 1162  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ ,

300 MHz)  $\delta$  2.44 (s, 3H), 3.68 (s, 3H), 3.69 (s, 3H), 3.90 (dd,  $J = 5.4$  and 1.5 Hz, 2H), 4.52 (s, 2H), 5.78 (dt,  $J = 15.9$  and 1.5 Hz, 1H), 6.52 (dd,  $J = 3.3$  and 1.8 Hz, 1H), 6.71 (dt,  $J = 15.9$  and 5.4 Hz, 1H), 6.88 (d,  $J = 3.3$  Hz, 1H), 7.32 (d,  $J = 8.1$  Hz, 2H), 7.49 (s, 1H), 7.52 (d,  $J = 1.8$  Hz, 1H), 7.70 (d,  $J = 8.1$  Hz, 2H);  $^{13}C$  NMR ( $CDCl_3$ , 75 MHz)  $\delta$  21.49, 44.81, 48.61, 51.48, 52.15, 112.58, 118.64, 121.52, 122.24, 127.54, 129.61, 130.14, 135.82, 143.49, 144.07, 145.52, 149.98, 166.15, 167.79; ESIMS  $m/z$  434  $[M+H]^+$ .

**Compound 1k:** 95%; white solid, mp 124-126 °C; IR (KBr) 1738, 1598, 1435, 1351, 1212, 1162  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ , 300 MHz)  $\delta$  2.36 (s, 3H), 3.62 (s, 3H), 3.71 (d,  $J = 6.0$  Hz, 2H), 4.42 (s, 2H), 4.86-4.95 (m, 2H), 5.48-5.61 (m, 1H), 6.44 (dd,  $J = 3.3$  and 1.8 Hz, 1H), 6.82 (d,  $J = 3.3$  Hz, 1H), 7.22 (d,  $J = 8.1$  Hz, 2H), 7.40 (s, 1H), 7.44 (d,  $J = 1.8$  Hz, 1H), 7.62 (d,  $J = 8.1$  Hz, 2H);  $^{13}C$  NMR ( $CDCl_3$ , 75 MHz)  $\delta$  21.46, 44.38, 50.38, 52.05, 112.51, 117.38, 118.01, 122.46, 127.51, 129.45, 129.58, 133.98, 136.32, 143.09, 145.13, 150.20, 167.94; ESIMS  $m/z$  376  $[M+H]^+$ .

**Compound 1l:** 98%; colorless oil; IR (film) 1721, 1597, 1436, 1346, 1249, 1160  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ , 300 MHz)  $\delta$  2.35 (s, 3H), 3.63 (dt,  $J = 6.3$  and 1.5 Hz, 2H), 3.81 (s, 3H), 4.15 (s, 2H), 4.68-4.81 (m, 2H), 5.29-5.43 (m, 1H), 7.11 (d,  $J = 8.1$  Hz, 2H), 7.36 (dt,  $J = 7.2$  and 1.2 Hz, 1H), 7.40 (d,  $J = 8.1$  Hz, 2H), 7.47 (d,  $J = 8.1$  Hz, 1H), 7.50-7.58 (m, 2H), 7.85-7.93 (m, 3H), 8.28 (s, 1H);  $^{13}C$  NMR ( $CDCl_3$ , 75 MHz)  $\delta$  21.42, 43.48, 51.19, 52.15, 118.35, 124.65, 125.11, 126.34, 126.68, 127.17, 127.37, 128.52, 129.20, 129.34, 130.84, 131.40, 131.55, 132.91, 133.34, 136.24, 141.40, 143.00, 167.55; ESIMS  $m/z$  436  $[M+H]^+$ .

**Compound 1m:** 96%; white solid, mp 137-139 °C; IR (KBr) 3276, 2119, 1712, 1637, 1435, 1349, 1246, 1162  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ , 300 MHz)  $\delta$  1.94 (t,  $J = 2.4$  Hz, 1H), 2.43 (s, 3H), 3.74 (s, 3H), 4.10 (d,  $J = 2.4$  Hz, 2H), 4.56 (s, 2H), 6.51 (dd,  $J = 3.6$  and 1.8 Hz, 1H), 6.83 (d,  $J = 3.6$  Hz, 1H), 7.29 (d,  $J = 8.4$  Hz, 2H), 7.51 (d,  $J = 1.8$  Hz, 1H), 7.52 (s, 1H), 7.76 (d,  $J = 8.4$  Hz, 2H);  $^{13}C$  NMR ( $CDCl_3$ , 75 MHz)  $\delta$  21.55, 37.29, 43.61, 52.15, 73.14, 77.60, 112.48, 118.10, 122.44, 128.13, 129.28, 129.36, 135.79, 143.43, 145.06, 150.19, 167.92; ESIMS  $m/z$  374  $[M+H]^+$ . Anal. Calcd for  $C_{19}H_{19}NO_5S$ : C, 61.11; H, 5.13; N, 3.75. Found: C, 61.23; H, 5.38; N, 3.61.

**Typical Procedure for the Synthesis of Compound 2b.** A mixture of **1b** (222 mg, 0.5 mmol) and BHT (11 mg, 10 mol %) in toluene (8.0 mL) was heated to 160 °C for 15 h in a sealed tube. After removal of the solvent and column chromatographic purification process (hexanes/ $Et_2O$ , 5:1) compound **2b** was obtained as a white solid, 215 mg (97%). Other compounds **2c-1** and **3** were prepared analogously, and the spectroscopic data of **2b-1** and **3** are as follows.

**Compound 2b:** 97%; white solid, mp 148-150 °C; IR (KBr) 1737, 1598, 1435, 1350, 1162  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ , 300 MHz)  $\delta$  2.43 (s, 3H), 2.61 (d,  $J = 17.1$  Hz, 1H), 2.74 (d,  $J = 17.4$  Hz, 1H), 2.88 (d,  $J = 17.1$  Hz, 1H), 3.01 (d,  $J = 17.4$  Hz, 1H), 3.45 (d,  $J = 9.9$  Hz, 2H), 3.52 (s, 3H+3H), 3.84 (d,  $J = 9.9$  Hz, 1H), 3.85 (d,  $J = 9.9$  Hz, 1H), 6.13 (d,  $J = 1.8$  Hz, 1H), 7.25 (d,  $J = 1.8$  Hz, 1H), 7.33 (d,  $J = 8.4$  Hz, 2H), 7.70

(d,  $J = 8.4$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  21.49, 27.80, 28.06, 51.91, 52.38, 52.47, 52.51, 54.62, 54.78, 109.69, 112.19, 127.40, 129.72, 133.90, 141.88, 143.66, 145.27, 172.90, 173.13; ESIMS  $m/z$  434  $[\text{M}+\text{H}]^+$ . Anal. Calcd for  $\text{C}_{21}\text{H}_{23}\text{NO}_7\text{S}$ : C, 58.19; H, 5.35; N, 3.23. Found: C, 58.42; H, 5.56; N, 3.07.

**Compound 2c:** 98%; white solid, mp 148-150 °C; IR (KBr) 1736, 1620, 1435, 1350, 1162  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  2.43 (s, 3H), 2.77 (d,  $J = 17.4$  Hz, 1H), 2.86 (d,  $J = 17.7$  Hz, 1H), 3.06 (d,  $J = 17.4$  Hz, 1H), 3.18 (d,  $J = 17.7$  Hz, 1H), 3.44 (d,  $J = 10.2$  Hz, 1H), 3.46 (d,  $J = 10.2$  Hz, 1H), 3.52 (s, 3H), 3.53 (s, 3H), 3.86 (d,  $J = 10.2$  Hz, 2H), 6.66 (d,  $J = 5.4$  Hz, 1H), 7.09 (d,  $J = 5.4$  Hz, 1H), 7.32 (d,  $J = 8.1$  Hz, 2H), 7.69 (d,  $J = 8.1$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  21.49, 29.57, 30.49, 51.55, 52.07, 52.40, 52.42, 54.63, 54.75, 123.44, 126.58, 127.40, 129.73, 130.04, 130.06, 133.94, 143.65, 172.91, 173.20; ESIMS  $m/z$  450  $[\text{M}+\text{H}]^+$ . Anal. Calcd for  $\text{C}_{21}\text{H}_{23}\text{NO}_6\text{S}_2$ : C, 56.11; H, 5.16; N, 3.12. Found: C, 56.37; H, 5.14; N, 3.03.

**Compound 2d:** 97%; white solid, mp 118-120 °C; IR (KBr) 1736, 1597, 1435, 1349, 1162  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  2.37 (s, 3H), 2.43 (s, 3H), 2.68 (d,  $J = 17.4$  Hz, 1H), 2.77 (d,  $J = 17.4$  Hz, 1H), 2.96 (d,  $J = 17.4$  Hz, 1H), 3.09 (d,  $J = 17.4$  Hz, 1H), 3.43 (d,  $J = 10.2$  Hz, 1H), 3.45 (d,  $J = 10.2$  Hz, 1H), 3.51 (s, 3H), 3.52 (s, 3H), 3.85 (d,  $J = 10.2$  Hz, 2H), 6.31 (s, 1H), 7.32 (d,  $J = 8.1$  Hz, 2H), 7.69 (d,  $J = 8.1$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  15.20, 21.47, 29.47, 30.40, 51.44, 51.93, 52.35 (2C), 54.61, 54.75, 124.63, 127.37, 127.54, 129.67, 129.70, 133.96, 137.87, 143.60, 172.96, 173.25; ESIMS  $m/z$  464  $[\text{M}+\text{H}]^+$ . Anal. Calcd for  $\text{C}_{22}\text{H}_{25}\text{NO}_6\text{S}_2$ : C, 57.00; H, 5.44; N, 3.02. Found: C, 56.88; H, 5.67; N, 3.19.

**Compound 2e:** 93%; white solid, mp 190-192 °C; IR (KBr) 1736, 1598, 1435, 1349, 1164  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  2.40 (s, 3H), 2.99 (d,  $J = 17.7$  Hz, 1H), 3.11 (d,  $J = 17.7$  Hz, 1H), 3.32 (d,  $J = 17.7$  Hz, 1H), 3.44 (t,  $J = 9.9$  Hz, 2H), 3.46 (d,  $J = 17.7$  Hz, 1H), 3.55 (s, 3H+3H), 3.94 (t,  $J = 9.9$  Hz, 2H), 7.09 (d,  $J = 8.4$  Hz, 1H), 7.26 (d,  $J = 8.1$  Hz, 2H), 7.42-7.55 (m, 2H), 7.60-7.70 (m, 3H), 7.71-7.84 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  21.49, 30.56, 34.50, 51.35, 51.73, 52.41, 52.45, 55.02, 55.44, 122.29, 125.32, 126.14, 126.35, 126.66, 127.00, 127.40, 128.64, 128.72, 129.68, 131.40, 132.41, 133.59, 143.66, 173.33, 173.45; ESIMS  $m/z$  494  $[\text{M}+\text{H}]^+$ . Anal. Calcd for  $\text{C}_{27}\text{H}_{27}\text{NO}_6\text{S}$ : C, 65.70; H, 5.51; N, 2.84. Found: C, 65.83; H, 5.34; N, 2.79.

**Compound 2g:** 100%; white solid, mp 128-130 °C; IR (KBr) 1737, 1599, 1347, 1168  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  2.40 (s, 3H), 2.90 (d,  $J = 17.4$  Hz, 1H), 3.06 (d,  $J = 17.4$  Hz, 1H), 3.23 (s, 3H), 3.44 (d,  $J = 10.5$  Hz, 1H), 3.51 (d,  $J = 10.5$  Hz, 1H), 3.58 (d,  $J = 9.9$  Hz, 2H), 3.72 (s, 3H), 4.62 (s, 1H), 5.95 (d,  $J = 1.8$  Hz, 1H), 6.99-7.03 (m, 2H), 7.24-7.31 (m, 6H), 7.64 (d,  $J = 8.4$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  21.47, 29.51, 43.29, 49.78, 52.25, 52.55, 53.03, 54.54, 60.22, 109.97, 116.13, 127.26, 127.78, 128.53, 128.81, 129.56, 134.98, 138.25, 141.48, 143.33, 146.24, 171.74, 172.36; ESIMS  $m/z$  510  $[\text{M}+\text{H}]^+$ . Anal. Calcd for  $\text{C}_{27}\text{H}_{27}\text{NO}_7\text{S}$ : C, 63.64; H, 5.34; N, 2.75. Found: C, 63.87;

H, 5.41; N, 2.76.

**Compound 2h:** 47% (*syn*-form); white solid, mp 123-125 °C; IR (KBr) 1736, 1598, 1435, 1343, 1245, 1165  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  2.26 (d,  $J = 14.1$  Hz, 1H), 2.35 (s, 3H), 2.56 (d,  $J = 17.4$  Hz, 1H), 2.72 (d,  $J = 14.1$  Hz, 1H), 3.06 (d,  $J = 17.4$  Hz, 1H), 3.57 (s, 3H), 3.60 (d,  $J = 13.8$  Hz, 1H), 3.78 (s, 3H), 3.83 (d,  $J = 13.8$  Hz, 1H), 5.28 (s, 1H), 6.58 (d,  $J = 1.8$  Hz, 1H), 7.06 (d,  $J = 8.1$  Hz, 2H), 7.18 (d,  $J = 8.1$  Hz, 2H), 7.23-7.31 (m, 4H), 7.34-7.38 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  21.42, 29.65, 31.51, 42.27, 47.50, 49.01, 51.99, 52.72, 61.82, 108.66, 118.36, 126.95, 128.03, 128.43, 128.75, 129.16, 136.48, 137.51, 141.09, 142.92, 149.59, 171.85, 174.30; ESIMS  $m/z$  510  $[\text{M}+\text{H}]^+$ . Anal. Calcd for  $\text{C}_{27}\text{H}_{27}\text{NO}_7\text{S}$ : C, 63.64; H, 5.34; N, 2.75. Found: C, 63.56; H, 5.65; N, 2.90. **Compound 2h:** 45% (*anti*-form); white solid, mp 115-117 °C; IR (KBr) 1736, 1598, 1435, 1354, 1213, 1164  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  2.41 (s, 3H), 2.43 (d,  $J = 17.1$  Hz, 1H), 2.83 (d,  $J = 17.1$  Hz, 1H), 3.06 (s, 2H), 3.47 (s, 3H), 3.58 (s, 3H), 3.73 (d,  $J = 10.5$  Hz, 1H), 4.12 (d,  $J = 10.5$  Hz, 1H), 5.28 (s, 1H), 5.77 (d,  $J = 2.1$  Hz, 1H), 7.06 (d,  $J = 2.1$  Hz, 1H), 7.15-7.23 (m, 3H), 7.28 (d,  $J = 8.1$  Hz, 2H), 7.38-7.42 (m, 2H), 7.60 (d,  $J = 8.1$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  21.49, 26.39, 29.26, 52.32, 52.61, 53.19, 55.55, 56.50, 68.31, 109.26, 112.93, 127.22, 127.67, 127.93, 128.17, 129.47, 134.07, 136.96, 141.36, 143.60, 145.47, 173.37, 173.51; ESIMS  $m/z$  510  $[\text{M}+\text{H}]^+$ . The proton of furan (3-position of **2h**) of *anti*-form appeared upfield ( $\delta = 5.77$  ppm) relative to that of the *syn*-form ( $\delta = 6.58$  ppm) due to the anisotropy of the phenyl group at the 5-position of **2h**.

**Compound 2j:** 98%; white solid, mp 137-140 °C; IR (KBr) 1738, 1597, 1435, 1347  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  2.46 (s, 3H), 2.49 (d,  $J = 17.0$  Hz, 1H), 3.14 (d,  $J = 17.0$  Hz, 1H), 3.16 (t,  $J = 9.5$  Hz, 1H), 3.22-3.26 (m, 1H), 3.38 (d,  $J = 2.5$  Hz, 1H), 3.44 (d,  $J = 10.0$  Hz, 1H), 3.57 (s, 3H), 3.60 (t,  $J = 9.5$  Hz, 1H), 3.69 (s, 3H), 3.71 (d,  $J = 10.0$  Hz, 1H), 6.29 (d,  $J = 2.0$  Hz, 1H), 7.28 (d,  $J = 2.0$  Hz, 1H), 7.34 (d,  $J = 8.0$  Hz, 2H), 7.71 (d,  $J = 8.0$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  21.54, 25.83, 39.15, 41.52, 50.20, 50.96, 52.38, 52.65, 56.22, 110.53, 110.88, 127.30, 129.83, 133.96, 141.80, 143.85, 147.18, 172.09, 172.65; ESIMS  $m/z$  434  $[\text{M}+\text{H}]^+$ . Anal. Calcd for  $\text{C}_{21}\text{H}_{23}\text{NO}_7\text{S}$ : C, 58.19; H, 5.35; N, 3.23. Found: C, 58.41; H, 5.53; N, 3.11.

**Compound 2k:** 92%; white solid, mp 125-127 °C; IR (KBr) 1733, 1598, 1436, 1345, 1163  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  2.24 (d,  $J = 16.2$  Hz, 1H), 2.33 (d,  $J = 17.1$  Hz, 1H), 2.37 (s, 3H), 2.61-2.78 (m, 2H), 3.00 (t,  $J = 9.6$  Hz, 1H), 3.02 (d,  $J = 17.1$  Hz, 1H), 3.39 (d,  $J = 9.6$  Hz, 1H), 3.46 (dd,  $J = 9.6$  and 7.5 Hz, 1H), 3.49 (d,  $J = 9.6$  Hz, 1H), 3.54 (s, 3H), 6.06 (d,  $J = 1.8$  Hz, 1H), 7.16 (d,  $J = 1.8$  Hz, 1H), 7.26 (d,  $J = 8.4$  Hz, 2H), 7.64 (d,  $J = 8.4$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  20.59, 21.52, 26.14, 38.91, 50.64, 50.69, 52.60, 56.37, 110.10, 112.87, 127.24, 129.78, 134.17, 141.51, 143.68, 145.76, 173.08; ESIMS  $m/z$  376  $[\text{M}+\text{H}]^+$ . Anal. Calcd for  $\text{C}_{19}\text{H}_{21}\text{NO}_5\text{S}$ : C, 60.78; H, 5.64; N, 3.73. Found: C, 60.59; H, 5.62; N, 3.58.

**Compound 2l:** 90%; white solid, mp 168-170 °C; IR

(KBr) 1732, 1598, 1346, 1162  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  2.28 (s, 3H), 2.59-2.67 (m, 1H), 2.70-2.82 (m, 2H), 2.94-3.08 (m, 2H), 3.13 (d,  $J = 10.2$  Hz, 1H), 3.34 (d,  $J = 16.5$  Hz, 1H), 3.44-3.51 (m, 1H), 3.52 (s, 3H), 3.64 (d,  $J = 10.2$  Hz, 1H), 7.03-7.13 (m, 3H), 7.32-7.45 (m, 2H), 7.46-7.56 (m, 3H), 7.70 (d,  $J = 7.8$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  21.49, 29.16, 30.09, 39.01, 51.30, 52.29, 52.58, 56.82, 122.21, 124.99, 126.14, 126.63, 127.01, 127.44, 128.20, 128.56, 129.48, 131.41, 131.48, 132.39, 132.62, 143.60, 174.43; ESIMS  $m/z$  436  $[\text{M}+\text{H}]^+$ . Anal. Calcd for  $\text{C}_{25}\text{H}_{25}\text{NO}_4\text{S}$ : C, 68.94; H, 5.79; N, 3.22. Found: C, 69.06; H, 5.94; N, 3.40.

**Compound 3:** 63%; white solid, mp 136-138  $^\circ\text{C}$ ; IR (KBr) 1703, 1628, 1437, 1342, 1160  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  2.37 (s, 3H), 3.79 (s, 3H), 4.42 (s, 2H), 4.63 (s, 2H), 6.35 (d,  $J = 1.5$  Hz, 1H), 7.16 (d,  $J = 8.4$  Hz, 2H), 7.28 (s, 1H), 7.41 (d,  $J = 1.5$  Hz, 1H), 7.54 (d,  $J = 8.4$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  21.45, 46.89, 47.58, 52.18, 111.89, 124.48, 127.14, 127.72, 128.46, 129.12, 136.47, 143.48, 144.78, 147.07, 166.20; ESIMS  $m/z$  348  $[\text{M}+\text{H}]^+$ . Anal. Calcd for  $\text{C}_{17}\text{H}_{17}\text{NO}_5\text{S}$ : C, 58.78; H, 4.93; N, 4.03. Found: C, 58.90; H, 5.05; N, 3.87.

**Acknowledgments.** This study was financially supported by Chonnam National University, 2013. Spectroscopic data were obtained from the Korea Basic Science Institute, Gwangju branch.

## References and Notes

- For the intermolecular Diels-Alder reaction involving a styrene moiety, see: (a) Kolis, S. P.; Chordia, M. D.; Liu, R.; Kopach, M. E.; Harman, W. D. *J. Am. Chem. Soc.* **1998**, *120*, 2218-2226. (b) Stranix, B. R.; Darling, G. D. *J. Org. Chem.* **1997**, *62*, 9001-9004. (c) Carreno, M. C.; Mahugo, J.; Urbano, A. *Tetrahedron Lett.* **1997**, *38*, 3047-3050. (d) Willmore, N. D.; Hoic, D. A.; Katz, T. J. *J. Org. Chem.* **1994**, *59*, 1889-1891.
- For the intermolecular Diels-Alder reaction of vinylfurans or vinylnaphthalenes, see: (a) Drew, M. G. B.; Jahans, A.; Harwood, L. M.; Apoux, S. A. B. H. *Eur. J. Org. Chem.* **2002**, 3589-3594. (b) Kotsuki, H.; Kondo, A.; Nishizawa, H.; Ochi, M.; Matsuoka, K. *J. Org. Chem.* **1981**, *46*, 5454-5455. (c) Marrocchi, A.; Minuti, L.; Taticchi, A.; Scheeren, H. W. *Tetrahedron* **2001**, *57*, 4959-4965. (d) Bodalski, R.; Koszuk, J.; Krawczyk, H.; Pietrusiewicz, K. M. *J. Org. Chem.* **1982**, *47*, 2219-2220.
- For the intramolecular Diels-Alder reaction involving a styrene moiety, see: (a) Pedrosa, R.; Andres, C.; Nieto, J. *J. Org. Chem.* **2002**, *67*, 782-789. (b) Sun, S.; Turchi, I. J.; Xu, D.; Murray, W. V. *J. Org. Chem.* **2000**, *65*, 2555-2559. (c) Klemm, L. H.; McGuire, T. M.; Gopinath, K. W. *J. Org. Chem.* **1976**, *41*, 2571-2579. (d) Dawson, J. R.; Mellor, J. M. *Tetrahedron Lett.* **1995**, *36*, 9043-9046. (e) Chackalamannil, S.; Doller, D.; Clasby, M.; Xia, Y.; Eagen, K.; Lin, Y.; Tsai, H.-A.; McPhail, A. T. *Tetrahedron Lett.* **2000**, *41*, 4043-4047. (f) Kocsis, L. S.; Benedetti, E.; Brummond, K. M. *Org. Lett.* **2012**, *14*, 4430-4433. (g) Ozawa, T.; Kurahashi, T.; Matsubara, S. *Org. Lett.* **2011**, *13*, 5390-5393. (h) Park, J.-E.; Lee, J.; Seo, S.-Y.; Shin, D. *Tetrahedron Lett.* **2014**, *55*, 818-820. (i) Parvatkar, P. T.; Kadam, H. K.; Tilve, S. G. *Tetrahedron* **2014**, *70*, 2857-2888 and further references cited therein.
- For the intramolecular Diels-Alder reaction involving a hetero-aromatic diene moiety, (a) Uchida, T.; Rodriguez, M.; Schreiber, S. L. *Org. Lett.* **2009**, *11*, 1559-1562. (b) Patre, R. E.; Gawas, S.; Sen, S.; Parameswaran, P. S.; Tilve, S. G. *Tetrahedron Lett.* **2007**, *48*, 3517-3520. (c) Sun, S.; Murray, W. V. *J. Org. Chem.* **1999**, *64*, 5941-5945. (d) Kotsuki, H.; Kawamura, A.; Ochi, M.; Tokoroyama, T. *Chem. Lett.* **1981**, 917-920. (e) Cooper, J. A.; Cornwall, P.; Dell, C. P.; Knight, D. W. *Tetrahedron Lett.* **1988**, *29*, 2107-2110. (f) Kim, P.; Tsuruda, J. M.; Olmstead, M. M.; Eisenberg, S.; Kurth, M. J. *Tetrahedron Lett.* **2002**, *43*, 3963-3966. (g) Madalengoitia, J. S.; Macdonald, T. L. *Tetrahedron Lett.* **1993**, *34*, 6237-6240. (h) Torney, P.; Patre, R.; Tilve, S. *Synlett* **2011**, 639-642. (i) He, Y.; Krishnamoorthy, P.; Lima, H. M.; Chen, Y.; Wu, H.; Sivappa, R.; Dias, H. V. R.; Lovely, C. J. *Org. Biomol. Chem.* **2011**, *9*, 2685-2701. (j) He, Y.; Chen, Y.; Wu, H.; Lovely, C. J. *Org. Lett.* **2003**, *5*, 3623-3626. (k) Hayakawa, K.; Nagatsugi, F.; Kanematsu, K. *J. Org. Chem.* **1988**, *53*, 860-863.
- Kim, K. H.; Lee, S.; Go, M. J.; Kim, J. N. *Tetrahedron Lett.* **2013**, *54*, 5739-5743 and further references cited therein.
- For the synthesis and their applications of arene-fused isoindoline derivatives, see: (a) Hu, Y.; Song, F.; Wu, F.; Cheng, D.; Wang, S. *Chem. Eur. J.* **2008**, *14*, 3110-3117. (b) Hu, Y.; Ouyang, Y.; Qu, Y.; Hu, Q.; Yao, H. *Chem. Commun.* **2009**, 4575-4577. (c) Hu, Y.; Qu, Y.; Wu, F.; Gui, J.; Wei, Y.; Hu, Q.; Wang, S. *Chem. Asian J.* **2010**, *5*, 309-314. (d) Ohno, H.; Miyamura, K.; Mizutani, T.; Kadoh, Y.; Takeoka, Y.; Hamaguchi, H.; Tanaka, T. *Chem. Eur. J.* **2005**, *11*, 3728-3741. (e) Ohno, H.; Miyamura, K.; Takeoka, Y.; Tanaka, T. *Angew. Chem. Int. Ed.* **2003**, *42*, 2647-2650.
- For the general review on Morita-Baylis-Hillman reaction, see: (a) Basavaiah, D.; Rao, A. J.; Satyanarayana, T. *Chem. Rev.* **2003**, *103*, 811-891. (b) Basavaiah, D.; Reddy, B. S.; Badsara, S. S. *Chem. Rev.* **2010**, *110*, 5447-5674. (c) Singh, V.; Batra, S. *Tetrahedron* **2008**, *64*, 4511-4574. (d) Declerck, V.; Martinez, J.; Lamaty, F. *Chem. Rev.* **2009**, *109*, 1-48. (e) Ciganek, E. In *Organic Reactions*; Paquette, L. A., Ed.; John Wiley & Sons: New York, 1997; Vol. 51, pp 201-350. (f) Kim, J. N.; Lee, K. Y. *Curr. Org. Chem.* **2002**, *6*, 627-645. (g) Lee, K. Y.; Gowrisankar, S.; Kim, J. N. *Bull. Korean Chem. Soc.* **2005**, *26*, 1481-1490. (h) Gowrisankar, S.; Lee, H. S.; Kim, S. H.; Lee, K. Y.; Kim, J. N. *Tetrahedron* **2009**, *65*, 8769-8780. (i) Shi, M.; Wang, F.-J.; Zhao, M.-X.; Wei, Y. *The Chemistry of the Morita-Baylis-Hillman Reaction*; RSC Publishing: Cambridge, UK, 2011.
- For the isolation of the initial Diels-Alder adducts without double bond migration, see: Howell, B. A.; Powers, J. J.; Priddy, D. B. *Polym. Prepr.* **2002**, *43*, 386-387. The  $^1\text{H}$  NMR data of **I** is as follows:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  1.83-1.88 (m, 2H), 2.29 (s, 3H), 2.80-2.92 (m, 1H), 3.05 (t,  $J = 9.8$  Hz, 1H), 3.04-3.15 (m, 1H), 3.39 (d,  $J = 10.5$  Hz, 1H), 3.44 (t,  $J = 9.6$  Hz, 1H), 3.50 (d,  $J = 10.5$  Hz, 1H), 3.58 (s, 3H), 5.58 (d,  $J = 3.6$  Hz, 1H), 5.64 (dd,  $J = 9.6$  and 2.1 Hz, 1H), 6.29 (dd,  $J = 9.6$  and 3.3 Hz, 1H), 6.93 (dd,  $J = 7.5$  and 1.5 Hz, 1H), 7.00 (dd,  $J = 7.5$  and 1.5 Hz, 1H), 7.07 (ddd,  $J = 7.5$ , 7.5 and 1.5 Hz, 1H), 7.14 (ddd,  $J = 7.5$ , 7.5 and 1.5 Hz, 1H), 7.21 (d,  $J = 8.4$  Hz, 2H), 7.62 (d,  $J = 8.4$  Hz, 2H).
- For the synthesis of furo[3,2-*c*]azepine derivatives, see: (a) Ding, M.; He, F.; Hudyma, T. W.; Zheng, X.; Poss, M. A.; Kadov, J. F.; Beno, B. R.; Rigat, K. L.; Wang, Y.-K.; Fridell, R. A.; Lemm, J. A.; Qiu, D.; Liu, M.; Voss, S.; Pelosi, L. A.; Roberts, S. B.; Gao, M.; Knipe, J.; Gentles, R. G. *Bioorg. Med. Chem. Lett.* **2012**, *22*, 2866-2871. (b) Fishwick, C. W. G.; Grigg, R.; Sridharan, V.; Virica, J. *Tetrahedron* **2003**, *59*, 4451-4468.
- For the intramolecular furan Diels-Alder (IMDAF) reaction, see: (a) Kappe, C. O.; Murphree, S. S.; Padwa, A. *Tetrahedron* **1997**, *53*, 14179-14233 and further references cited therein. (b) Nieto-Garcia, O.; Alonso, R. *J. Org. Chem.* **2013**, *78*, 2564-2570. (c) Chen, Y.; Wang, L.; Liu, Y.; Li, Y. *Chem. Eur. J.* **2011**, *17*, 12582-12586. (d) Liu, L.; Gao, Y.; Che, C.; Wu, N.; Wang, D. Z.; Li, C.-C.; Yang, Z. *Chem. Commun.* **2009**, 662-664. (e) Li, C.-C.; Liang, S.; Zhang, X.-H.; Xie, Z.-X.; Chen, J.-H.; Wu, Y.-D.; Yang, Z. *Org. Lett.* **2005**, *7*, 3709-3712.
- For the retro-Diels-Alder elimination of acetylene, see: Anderson, M. R.; Brown, R. F. C.; Coulston, K. J.; Eastwood, F. W.; Ward,

- A. *Aus. J. Chem.* **1990**, *43*, 1137-1150.
12. For the Pb(OAc)<sub>4</sub>-mediated didecarboxylation, see: (a) Matsumoto, K.; Goto, S.; Hayashi, N.; Iida, H.; Uchida, T.; Kakehi, A. *Eur. J. Org. Chem.* **2004**, 4667-4671. (b) Doecke, C. W.; Garratt, P. J. *J. Chem. Soc., Chem. Commun.* **1981**, 873-874. (c) Thummel, R. P. *J. Chem. Soc., Chem. Commun.* **1974**, 899-900.
13. For the synthesis of benzo[*f*]isoindoline and its tetrahydro derivatives, see: (a) Hu, Y.-M.; Lim, X.-G.; Zhu, T.; Wan, J.; Sun, Y.-J.; Zhao, Q.-S.; Yu, T. *Synthesis* **2010**, 3467-3473. (b) Shibata, T.; Fujiwara, R.; Takano, D. *Synlett* **2005**, 2062-2066. (c) Rodriguez, D.; Navarro-Vazquez, A.; Castedo, L.; Dominguez, D.; Saa, C. *J. Am. Chem. Soc.* **2001**, *123*, 9178-9179.
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