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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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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

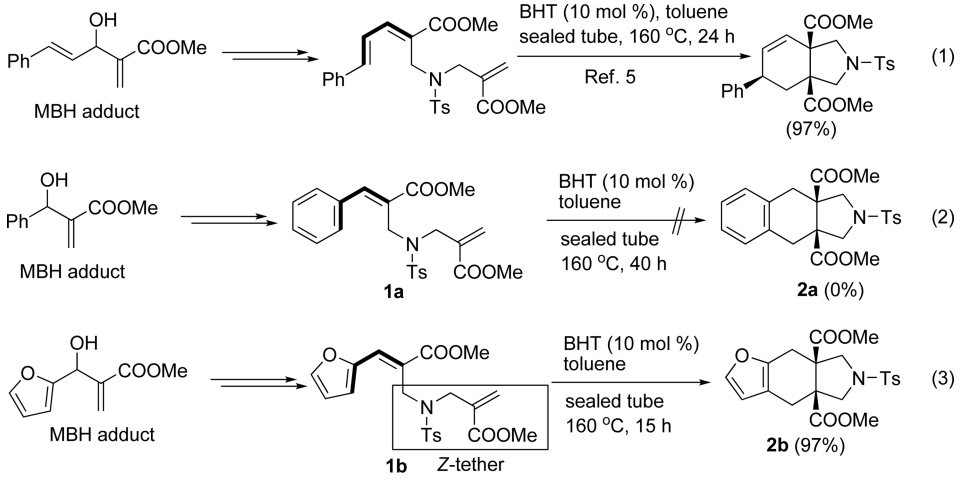
Introduction

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.[1-4] 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.[3,4] The intramolecular Diels-Alder (IMDA) reaction of *E*-vinylarenes has been studied extensively.[3,4] 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.[3c,g,4e]

Results and Discussion

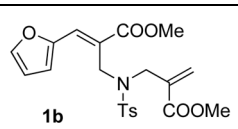
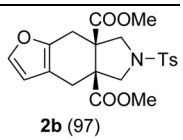
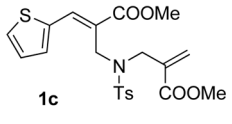
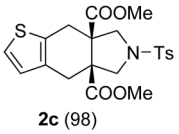
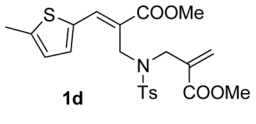
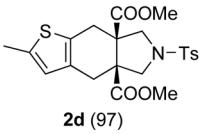
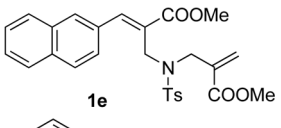
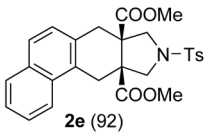
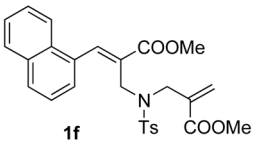
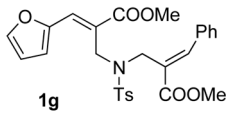
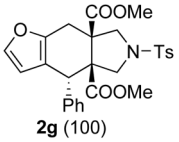
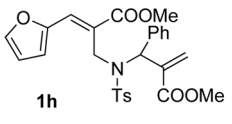
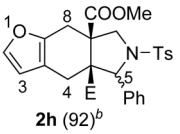
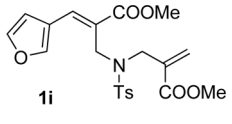
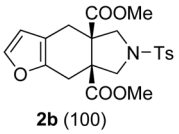
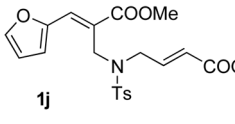
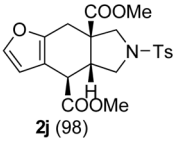
Very recently, we reported an efficient synthesis of hexahydroisoindole-3a-carboxylates by IMDA reaction of modified Morita-Baylis-Hillman (MBH) adducts, as shown in Scheme 1.[5] In the reaction, a typical 1,3-diene and a *Z*-alkenyl moiety have been involved as reaction partners (Eq. 1). As a continuous 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%)[6] 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**.[2a,4a-e]

Encouraged by the results, we prepared starting materials **1c-j** from the corresponding MBH adducts according to the reported procedure,[5,7] 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.[1c] The



Scheme 1

Table 1. IMDA reactions of modified MBH adducts

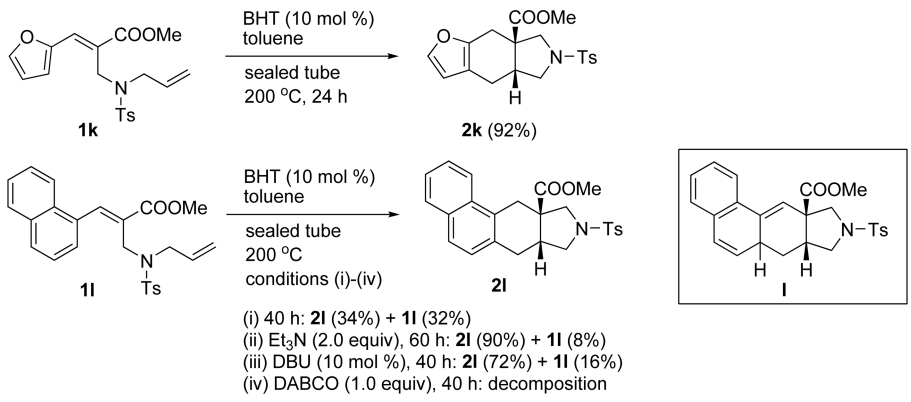
Entry	Substrate	Conditions[a]	Product (%)
1	 **1b**	160 °C, 15 h	 **2b** (97)
2	 **1c**	160 °C, 10 h	 **2c** (98)
3	 **1d**	160 °C, 10 h	 **2d** (97)
4	 **1e**	160 °C, 10 h	 **2e** (92)
5	 **1f**	160 °C, 10 h	**2e** (93)
6	 **1g**	190 °C, 20 h	 **2g** (100)
7	 **1h**	160 °C, 12 h	 **2h** (92)[b]
8	 **1i**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

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

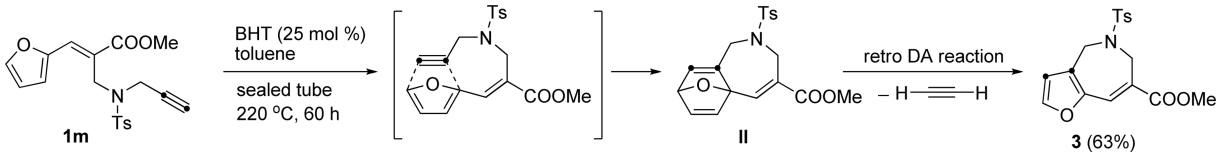
reactions of **1g** and **1h**, bearing phenyl-substituted dienophile moieties, afforded the corresponding products **2g** and **2h** in excellent yields (entries 6 and 7). Compound **2h** was obtained as a diastereomeric mixture (*syn*/*anti*, 1:1). The reaction of **1g** at 160 °C was somewhat slow, 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 ^{1}H NMR in a crude state, the structure could be assigned as an intermediate **I**.[2a,8] Thus we examined the reaction in the presence of Et_3N (2.0 equiv), and the yield of **2l** could be increased to 90%, to our delight. The use of Et_3N 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.

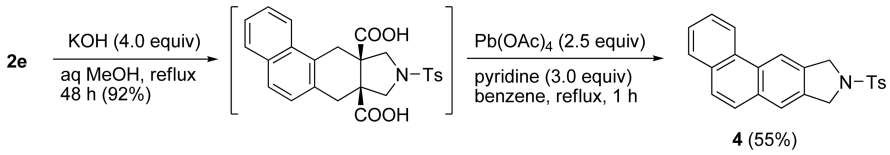
When the propargyl derivative **1m** was subjected under the same reaction conditions, the reaction was so sluggish (Scheme 3). To our surprise, however, a furo[3,2-*c*]azepine-7-carboxylate derivative **3**[9] was obtained in moderate yield (46%) under more vigorous conditions (220 °C, 36 h), and the starting material **1m** was recovered (36%). The reaction mechanism would be a sequential intramolecular furan Diels-Alder (IMDAF) reaction[10] to form the intermediate **II** and a retro-Diels-Alder reaction with liberation of acetylene.[11] 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



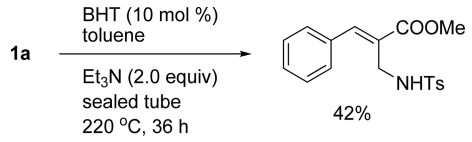
Scheme 2



Scheme 3



Scheme 4



Scheme 5

bond, which caused the approach toward vinylfuran moiety difficult.

As reported in a similar case,[12] 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 $Pb(OAc)_4$ afforded known benzo[*f*]isoindoline derivative **4** in a reasonable yield (55%).[3g,13]

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 Et_3N 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.[5,7] 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 K_2CO_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/Et_2O, 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 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 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}C NMR ($CDCl_3$, 125 MHz) δ 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 $[M+H]^+$. Anal. Calcd for $C_{23}H_{25}NO_6S$: 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 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 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}C NMR ($CDCl_3$, 75 MHz) δ 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 $[M+H]^+$. Anal. Calcd for $C_{21}H_{23}NO_7S$: 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 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 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}C NMR ($CDCl_3$, 75 MHz) δ 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 $[M+H]^+$.

Compound 1d: 94%; white solid, mp 85-87 °C; IR (KBr) 1732, 1598, 1435, 1346, 1162 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 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}C NMR ($CDCl_3$, 75 MHz) δ 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) δ 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) δ 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) δ 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) δ 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) δ 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) δ 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) δ 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) δ 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) δ 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) δ 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) δ 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) δ 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) δ 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) δ 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) δ 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) δ 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) δ 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) δ 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-l** and **3** were prepared analogously, and the spectroscopic data of **2b-l** 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) δ 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}C NMR ($CDCl_3$, 75 MHz) δ 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 $[M+H]^+$. Anal. Calcd for $C_{21}H_{23}NO_7S$: 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 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 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}C NMR ($CDCl_3$, 75 MHz) δ 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 $[M+H]^+$. Anal. Calcd for $C_{21}H_{23}NO_6S_2$: 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 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 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}C NMR ($CDCl_3$, 75 MHz) δ 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 $[M+H]^+$. Anal. Calcd for $C_{22}H_{25}NO_6S_2$: 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 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 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}C NMR ($CDCl_3$, 75 MHz) δ 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 $[M+H]^+$. Anal. Calcd for $C_{27}H_{27}NO_6S$: 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 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 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}C NMR ($CDCl_3$, 75 MHz) δ 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 $[M+H]^+$. Anal. Calcd for $C_{27}H_{27}NO_7S$: 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 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 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}C NMR ($CDCl_3$, 75 MHz) δ 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 $[M+H]^+$. Anal. Calcd for $C_{27}H_{27}NO_7S$: 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 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 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}C NMR ($CDCl_3$, 75 MHz) δ 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 $[M+H]^+$. The proton of furan (3-position of **2h**) of *anti*-form appeared upfield (δ = 5.77 ppm) relative to that of the *syn*-form (δ = 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 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 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}C NMR ($CDCl_3$, 75 MHz) δ 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 $[M+H]^+$. Anal. Calcd for $C_{21}H_{23}NO_7S$: 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 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 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}C NMR ($CDCl_3$, 75 MHz) δ 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 $[M+H]^+$. Anal. Calcd for $C_{19}H_{21}NO_5S$: 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 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 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}C NMR ($CDCl_3$, 75 MHz) δ 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 $[M+H]^+$. Anal. Calcd for $C_{25}H_{25}NO_4S$: 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 °C; IR (KBr) 1703, 1628, 1437, 1342, 1160 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 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}C NMR ($CDCl_3$, 75 MHz) δ 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 $[M+H]^+$. Anal. Calcd for $C_{17}H_{17}NO_5S$: C, 58.78; H, 4.93; N, 4.03. Found: C, 58.90; H, 5.05; N, 3.87.

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References and Notes

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