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Synthesis of 2-amino-2,3-dihydrobenzofurans and fully substituted furans from modified Baylis–Hillman adducts

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Abstract—Syntheses of 2-amino-2,3-dihydrobenzofuran derivatives **3a–g** and fully substituted furans **5a–f** were achieved starting from the Baylis–Hillman adducts. We prepared 2-amino-2,3-dihydrobenzofurans from the Baylis–Hillman adducts of methyl and ethyl acrylates and fully substituted furans from the Baylis–Hillman adducts of alkyl vinyl ketones.

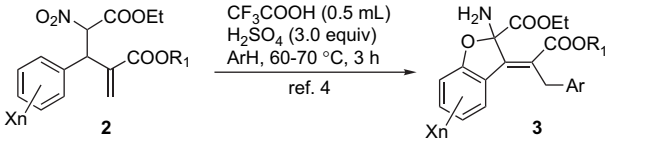
1. Introduction

The Baylis–Hillman reaction is a carbon–carbon bond-forming reaction between activated vinyls and electrophiles like aldehydes and imines with the aid of tertiary amine or phosphine.[1] The Baylis–Hillman adducts have versatile functionality and, as a result, the chemical transformations using the Baylis–Hillman adducts have been investigated extensively by us and other groups.[1–4]

Regioselective introduction of various nucleophiles either at the primary and secondary position of the Baylis–Hillman adducts can be carried out easily.[3] Recently, we introduced ethyl nitroacetate at the secondary position of Baylis–Hillman adduct of methyl and ethyl acrylates to prepare **2** (vide infra, Scheme 2).[3,4] We observed unusual formation of 2-amino-2,3-dihydrobenzofuran derivatives **3a–g** from **2** under the influence of H_2SO_4 and CF_3COOH (TFA) in arene solvent at elevated temperature as shown in Scheme 1.[4]

The structures of **3a** and **3e** were confirmed unequivocally by their X-ray crystal structures.[4] The mechanism for the formation of **3** was proposed as (i) protonation at the nitro group of **2**, (ii) intramolecular transfer of oxygen atom from nitrogen to carbon of benzene moiety, (iii) successive 1,3-H shift, (iv) intermolecular Friedel–Crafts type reaction with arene, and finally (v) formation of cyclic aminal derivative **3**.[4]

Cyclic α,α-disubstituted α-amino acids represent a unique class of sterically constrained amino acids, which have been used to modify the conformation and/or stability of a biologically active peptide.[5] In these respects, the synthesis of highly sterically constrained amino acids has been studied extensively.[5] However, there have been reported only a few examples of cyclic α-amino acid precursors having heteroatom-containing substituent as one of the α-substituents.[6]



3a: R_1 = Me, Xn = H, Ar = C_6H_5- (55%)
3b: R_1 = Me, Xn = H, Ar = 2,5-$Me_2C_6H_3$- (51%)
3c: R_1 = Me, Xn = H, Ar = 2,5-$(MeO)_2C_6H_3$- (38%)
3d: R_1 = Et, Xn = H, Ar = C_6H_5- (56%)
3e: R_1 = Et, Xn = H, Ar = 2,5-$Me_2C_6H_3$- (52%)
3f: R_1 = Me, Xn = *p*-Me, Ar = C_6H_5- (39%)
3g: R_1 = Me, Xn = *p*-Cl, Ar = C_6H_5- (36%)

Scheme 1.

2. Results and discussion

In these respects of the importance of cyclic α-amino acids and the unusual reaction mechanism for the formation of compounds **3a–g**, we examined the reaction with similar compounds, namely, ethyl 4-acetyl-2-nitro-3-phenylpent-4-enoic acid ethyl ester (**4a**) and 2-benzylidene-4-nitropentanedioic acid 5-ethyl ester 1-methyl ester (**6a**). We observed completely different products in these cases and wish to report herein the results.

The starting materials **2a–d**, **4a–d**, and **6a–c** were synthesized from the reaction of cinnamyl bromide derivative **1**, which was synthesized from Baylis–Hillman adduct and

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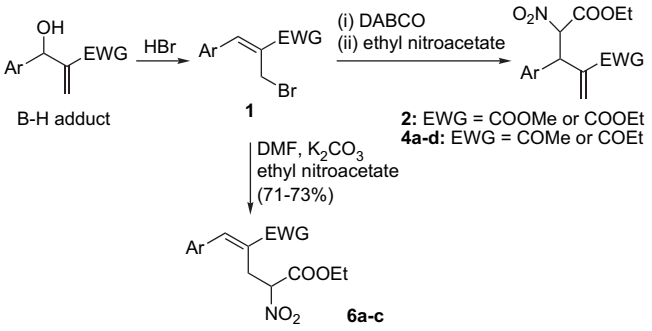
HBr, and ethyl nitroacetate as shown in Scheme 2 (see Section 3). With this compound **4a** (Ar=Ph, EWG=COMe) in our hands, we examined initially the reaction of **4a** in benzene under the influence of H_2SO_4 and CF_3COOH at 50–60 °C. We could not obtain the corresponding 2-amino-2,3-dihydrobenzofuran derivative. Instead, we could isolate fully substituted furan **5a** in 44% yield (Scheme 3 and entry 1 in Table 1).[7,8] The reaction of **4a** with *p*-xylene and mesitylene showed similar results (entries 2 and 3). In addition, the reaction of **4b–d** and benzene showed same pattern of reactivity (entries 4–6). In all cases, we could not obtain 2-amino-2,3-dihydrobenzofuran derivatives. The mechanism for the formation of **5a** could be postulated tentatively as shown in Scheme 3: (i) protonation at the nitro group, (ii) intramolecular attack of carbonyl group[2k,l] toward protonated nitro group to generate the allylic carbocation intermediate, (iii) intermolecular Friedel–Crafts reaction with benzene, and (iv) the final aromatization process by the elimination of *N*-hydroxy hydroxylamine species[9] gave the furan **5a**. As shown in the column of conditions in Table 1, we found that TFA was not critical in the reactions. However, somewhat elevated temperature was needed when we did not use TFA (entries 3–6) in order to obtain similar yields of products.



Scheme 2.

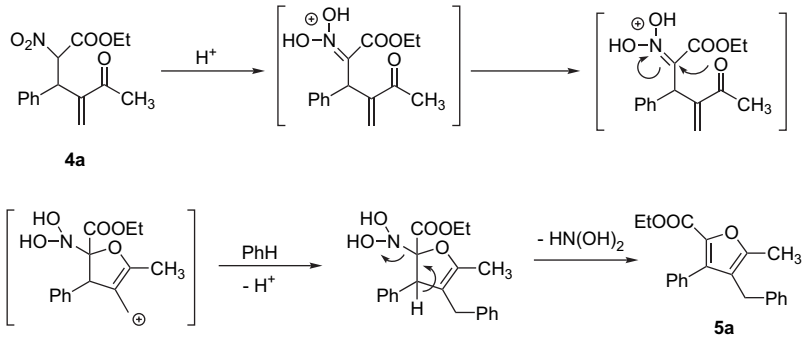
Table 1. Synthesis of tetrasubstituted furans

Entry	Substrate[a]	Conditions	Product (%)
1		Benzene, H_2SO_4 (3.0 equiv), TFA (0.5 mL), 50–60 °C, 2 h	**5a** (44)
2	**4a**	*p*-Xylene, H_2SO_4 (3.0 equiv), TFA (0.5 mL), 50–60 °C, 2 h	**5b** (45)
3		Mesitylene, H_2SO_4 (2.0 equiv), 70–80 °C, 4 h	**5c** (48)
4	**4b**	Benzene, H_2SO_4 (3.0 equiv), 70–80 °C, 5 h	**5d** (43)
5	**4c**	Benzene, H_2SO_4 (2.0 equiv), 70–80 °C, 4 h	**5e** (45)
6	**4d**	Benzene, H_2SO_4 (2.0 equiv), 70–80 °C, 4 h	**5f** (49)

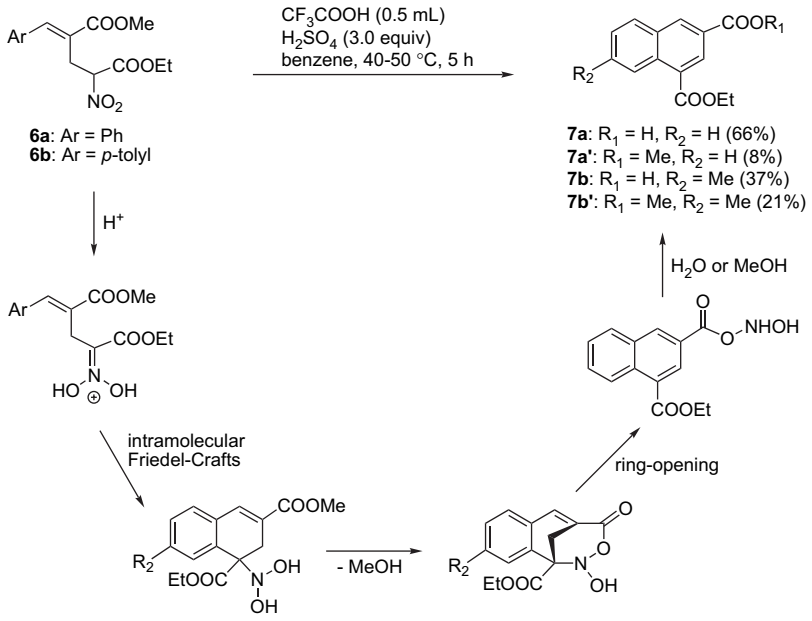
[a] Starting materials **4a–d** were obtained as a *syn*/*anti* mixtures (1:1 in all cases) and used without separation.

As a next trial, we examined the reaction of **6a** under the same reaction conditions. But, we obtained a mixture of **7a** (carboxylic acid form) and **7a′** (ester form) in 66% and 8%, respectively (Scheme 4). We were astonished by the formation of naphthalenic acid **7a** as the major product. The ester group at the 1-position of naphthalene ring was intact while that of the 3-position was hydrolyzed in part. The reaction with **6b** showed similar results although the ratio was different between the acid form **7b** (37%) and the ester form **7b′** (21%). Based on the experimental results, we could propose the reaction mechanism as in Scheme 4: (i) protonation at the nitro group, (ii) intramolecular Friedel–Crafts cyclization, (iii) formation of tricyclic oxazinone intermediate by loss of MeOH, (iv) ring-opening to naphthalene carboxylic acid derivative, (v) reaction with water or MeOH to produce **7a–b** and **7a′–b′** as a mixture. The reaction of **6c** and benzene under the similar conditions gave **7c** by following the similar mechanism (Scheme 5).

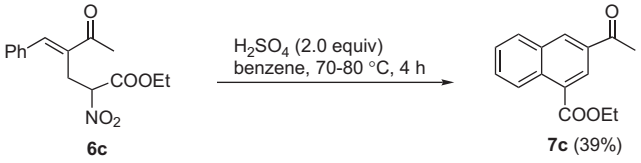
In summary, we disclosed the first synthesis of unusual 2-amino-2,3-dihydrobenzofurans[4] and fully substituted furans starting from the Baylis–Hillman adducts. Depending



Scheme 3.



Scheme 4.



Scheme 5.

upon the substituents on the modified Baylis–Hillman adducts, the major reaction pathway was changed to give different products although the yields were moderate. Further studies on the reaction mechanism and synthetic applications will be examined.

3. Experimental

3.1. General procedure

^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded in $CDCl_3$. The signal positions are reported in parts per million relative to TMS (δ scale) used as an internal standard. IR spectra are reported in cm^{-1}. Mass spectra were obtained from the Korea Basic Science Institute (Gwangju branch). Melting points are uncorrected. The elemental analyses were carried out at Korea Research Institute of Chemical Technology, Taejon, Korea. All reagents were purchased from commercial sources and used without further treatment. The separations were carried out by flash column chromatography over silica gel (230–400 mesh ASTM). Organic extracts were dried over anhydrous $MgSO_4$ and the solvents were evaporated on a rotary evaporator under water aspirator pressure.

3.2. Spectroscopic data of 2-amino-2,3-dihydrobenzofurans

The spectroscopic data of **3a** and **3e** were published in the previous paper.[4] The spectroscopic data of **3b–d**, **3f**, and **3g** are summarized as follows.

3.2.1. Compound 3b. Yield 51%; white solid, mp 177–178 °C; IR (film) 3410, 3336, 1751, 1720, 1200 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.28 (t, J=7.2 Hz, 3H), 2.21 (s, 3H), 2.34 (s, 3H), 2.87 (br s, 2H), 3.64 (s, 3H), 3.95 (d, J=16.8 Hz, 1H), 4.11 (d, J=16.8 Hz, 1H), 4.13–4.22 (m, 1H), 4.33–4.45 (m, 1H), 6.78–7.29 (m, 7H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.32, 19.47, 21.43, 33.85, 51.81, 62.14, 98.56, 110.99, 121.64, 124.23, 125.86, 126.46, 127.41 (2C), 130.35, 132.37, 133.53, 135.15, 135.68, 145.30, 161.26, 167.54, 169.54; ESIMS m/z 396 (M^++H). Anal. Calcd for $C_{23}H_{25}NO_5$: C, 69.86; H, 6.37; N, 3.54. Found: C, 69.97; H, 6.53; N, 3.45.

3.2.2. Compound 3c. Yield 38%; white solid, mp 126–127 °C; IR (film) 3417, 3332, 1747, 1720, 1281, 1219 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.26 (t, J=7.2 Hz, 3H), 2.26 (br s, 2H), 3.66 (s, 6H), 3.85 (s, 3H), 3.97 (d, J=17.1 Hz, 1H), 4.17 (d, J=17.1 Hz, 1H), 4.11–4.22 (m, 1H), 4.29–4.40 (m, 1H), 6.67–6.71 (m, 1H), 6.78–6.84 (m, 4H), 7.22–7.28 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.83, 30.28, 51.59, 55.50, 55.89, 62.03, 98.31, 110.54, 110.65, 110.71, 115.29, 121.38, 123.95, 125.81, 125.97, 126.74, 132.09, 145.38, 151.76, 153.75, 161.05, 167.36, 169.41; ESIMS m/z 428 (M^++H). Anal. Calcd for $C_{23}H_{25}NO_7$: C, 64.63; H, 5.90; N, 3.28. Found: C, 64.68; H, 6.02; N, 3.19.

3.2.3. Compound 3d. Yield 56%; white solid, mp 124–125 °C; IR (film) 3417, 3340, 1751, 1716 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.18 (t, J=7.2 Hz, 3H), 1.24 (t, J=7.2 Hz, 3H), 2.88 (br s, 2H), 4.00–4.41 (m, 6H), 6.81–6.87 (m, 2H), 7.16–7.30 (m, 6H), 7.39 (d, J=8.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.95, 14.15, 35.82, 61.20, 61.98, 98.39, 111.09, 121.58, 124.25, 125.82, 126.55, 126.65, 128.12, 128.80, 132.38, 137.37, 144.96, 161.29, 167.70, 168.93; ESIMS m/z 382 (M^++H). Anal. Calcd for $C_{22}H_{23}NO_5$: C, 69.28; H, 6.08; N, 3.67. Found: C, 69.35; H, 6.00; N, 3.63.

3.2.4. Compound 3f. Yield 39%; white solid, mp 128–129 °C; IR (KBr) 3421, 3332, 1751, 1716, 1203 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.24 (t, J=6.9 Hz, 3H), 2.19 (s, 3H), 2.70 (br s, 2H), 3.62 (s, 3H), 4.14 (d, J=16.2 Hz, 1H), 4.08–4.15 (m, 1H), 4.21 (d, J=16.2 Hz, 1H), 4.31–4.42 (m, 1H), 6.75 (d, J=8.4 Hz, 1H), 7.09 (dd, J=8.4 and 1.2 Hz, 1H), 7.19–7.31 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.98, 21.02, 35.57, 51.54, 61.81, 98.29, 110.46, 123.81, 125.68, 125.93, 126.47, 127.95, 128.63, 130.61, 133.11, 137.26, 145.04, 159.22, 167.37, 169.37; ESIMS m/z 382 (M^++H). Anal. Calcd for $C_{22}H_{23}NO_5$: C, 69.28; H, 6.08; N, 3.67. Found: C, 69.22; H, 6.33; N, 3.55.

3.2.5. Compound 3g. Yield 36%; white solid, mp 139–141 °C; IR (KBr) 3421, 3336, 1751, 1720 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.24 (t, J=7.2 Hz, 3H), 2.84 (br s, 2H), 3.63 (s, 3H), 4.14 (s, 2H), 4.07–4.18 (m, 1H), 4.33–4.42 (m, 1H), 6.77 (d, J=8.1 Hz, 1H), 7.20–7.35 (m, 7H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.95, 35.60, 51.66, 62.01, 99.08, 111.77, 125.07, 125.38, 126.29, 126.73, 127.83, 128.01, 128.78, 131.92, 136.43, 143.07, 159.45, 166.83, 169.02; ESIMS m/z 402 (M^++H). Anal. Calcd for $C_{21}H_{20}ClNO_5$: C, 62.77; H, 5.02; N, 3.49. Found: C, 62.59; H, 5.28; N, 3.41.

3.3. Synthesis of starting materials 4a–d and 6a–c

Cinnamyl bromide derivatives **1** were prepared from the corresponding Baylis–Hillman adducts by the treatment with HBr as reported.[10] Synthesis of **4a–d** was carried out by using the DABCO salt concept as reported.[3,4] We obtained **4a–d** as *syn*/*anti* mixtures (almost 1:1). The *syn*/*anti* mixtures were used without separation. Synthesis of **6a–c** was carried out by the simple S_N2-type reaction of **1** with ethyl nitroacetate in the presence of K_2CO_3 in DMF as reported.[2b] The spectroscopic data of **6c** were published in the previous paper[2h] and the spectroscopic data of **2a–d**,[4] **4a–d** and **6a–c** are as follows.

3.3.1. Compound 2a (compound 3a in Ref. 4: X_n=H, R_1=Me in Scheme 1). Yield 75% (*syn*/*anti*=1:1); colorless oil; IR (film) 1751, 1724, 1562 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.97 (t, J=7.2 Hz, 3H), 1.27 (t, J=7.2 Hz, 3H), 3.70 (s, 3H), 3.72 (s, 3H), 3.93–4.04 (m, 2H), 4.25 (q, J=7.2 Hz, 2H), 4.89 (d, J=12.0 Hz, 1H), 4.95 (d, J=12.0 Hz, 1H), 5.81 (s, 1H), 5.86 (s, 1H), 5.87 (d, J=12.0 Hz, 1H), 6.06 (d, J=12.0 Hz, 1H), 6.34 (s, 1H), 6.37 (s, 1H), 7.21–7.34 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.42, 13.73, 48.16, 48.55, 52.23 (2C), 62.93, 63.21, 89.56, 90.13, 125.46, 127.31, 127.89, 128.06, 128.20, 128.70, 128.80, 128.87, 134.78, 136.08, 138.33, 138.41, 162.98, 163.18, 165.58, 165.65; ESIMS m/z 308 (M^++H).

3.3.2. Compound 2b (compound 3b in Ref. 4: X_n=H, R_1=Et in Scheme 1). Yield 80% (*syn*/*anti*=1:1); colorless oil; IR (film) 1751, 1716, 1562 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.96 (t, J=7.2 Hz, 3H), 1.22 (t, J=7.2 Hz, 3H), 1.25 (t, J=7.2 Hz, 3H), 1.27 (t, J=7.2 Hz, 3H), 3.91–4.07 (m, 2H), 4.09–4.20 (m, 4H), 4.26 (q, J=7.2 Hz, 2H), 4.89 (d, J=12.0 Hz, 1H), 4.94 (d, J=12.0 Hz, 1H), 5.79 (s, 1H), 5.83 (s, 1H), 5.87 (d, J=12.0 Hz, 1H), 6.06 (d, J=12.0 Hz, 1H), 6.34 (s, 1H), 6.38 (s, 1H), 7.22–7.33 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.42, 13.74, 13.93, 13.97, 48.16, 48.56, 61.28 (2C), 62.91, 63.18, 89.60, 90.18, 125.15, 127.02, 127.92, 128.01, 128.15, 128.74 (2C), 128.83, 134.89, 136.15, 138.59, 138.65, 163.04, 163.21, 165.11, 165.17; ESIMS m/z 322 (M^++H).

3.3.3. Compound 2c (compound 3c in Ref. 4: X_n=*p*-Me, R_1=Me in Scheme 1). Yield 84% (*syn*/*anti*=1:1); colorless oil; IR (film) 1751, 1724, 1562 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.99 (t, J=7.2 Hz, 3H), 1.26 (t, J=7.2 Hz, 3H), 2.29 (s, 3H), 2.30 (s, 3H), 3.70 (s, 3H), 3.72 (s, 3H), 3.96–4.04 (m, 2H), 4.25 (q, J=7.2 Hz, 2H), 4.85 (d, J=12.0 Hz, 1H), 4.91 (d, J=12.0 Hz, 1H), 5.79 (s, 1H), 5.83 (s, 1H), 5.85 (d, J=12.0 Hz, 1H), 6.03 (d, J=12.0 Hz, 1H), 6.32 (s, 1H), 6.35 (s, 1H), 7.08–7.21 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.43, 13.72, 20.99 (2C), 47.77, 48.20, 51.18 (2C), 62.89, 63.14, 89.64, 90.24, 125.20, 127.01, 127.74, 128.52, 129.47, 129.56, 131.69, 133.03, 137.83, 137.99, 138.49, 138.57, 162.98, 163.22, 165.63, 165.69; ESIMS m/z 322 (M^++H).

3.3.4. Compound 2d (compound 3d in Ref. 4: X_n=*p*-Cl, R_1=Me in Scheme 1). Yield 83% (*syn*/*anti*=1:1); colorless oil; IR (film) 1751, 1724, 1566 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.03 (t, J=7.2 Hz, 3H), 1.27 (t, J=7.2 Hz, 3H), 3.71 (s, 3H), 3.73 (s, 3H), 3.99–4.07 (m, 2H), 4.26 (q, J=7.2 Hz, 2H), 4.85 (d, J=12.0 Hz, 1H), 4.92 (d, J=12.0 Hz, 1H), 5.82 (s, 1H), 5.86 (s, 1H), 5.87 (d, J=12.0 Hz, 1H), 6.03 (d, J=12.0 Hz, 1H), 6.35 (s, 1H), 6.38 (s, 1H), 7.22–7.31 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.46, 13.70, 47.64, 48.10, 52.28 (2C), 63.11, 63.30, 89.20, 89.82, 125.95, 127.55, 128.96, 129.04, 129.32, 130.07, 133.44, 134.04, 134.18, 134.61, 137.93, 138.00, 162.75, 162.93, 165.39, 165.44; ESIMS m/z 342 (M^++H).

3.3.5. Compound 4a. Yield 62% (*syn*/*anti*=1:1); colorless oil; IR (film) 1751, 1682, 1562 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.97 (t, J=7.2 Hz, 3H), 1.25 (t, J=7.2 Hz, 3H), 2.28 (s, 3H), 2.29 (s, 3H), 3.94–4.05 (m, 2H), 4.22 (q, J=7.2 Hz, 2H), 4.95 (d, J=12.0 Hz, 1H), 5.01 (d, J=12.0 Hz, 1H), 5.89 (d, J=12.0 Hz, 1H), 5.99 (s, 1H), 6.06 (s, 1H), 6.07 (d, J=12.0 Hz, 1H), 6.19 (s, 1H), 6.21 (s, 1H), 7.19–7.34 (m, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.41, 13.74, 26.10 (2C), 47.05, 47.46, 62.87, 63.10, 89.61, 90.24, 125.53, 127.60, 127.88 (2C), 128.00, 128.66, 128.74, 128.86, 135.22, 136.63, 146.36, 146.59, 163.08, 163.24, 197.58, 197.83; ESIMS m/z 292 (M^++H).

3.3.6. Compound 4b. Yield 71% (*syn*/*anti*=1:1); colorless oil; IR (film) 1751, 1682, 1562 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.97 (t, J=7.2 Hz, 3H), 1.01 (t, J=7.2 Hz, 3H), 1.03 (t, J=7.2 Hz, 3H), 1.25 (t, J=7.2 Hz, 3H), 2.64 (qd, J=7.2 and 1.2 Hz, 2H), 2.65 (q, J=7.2 Hz, 2H), 3.95–4.04 (m, 2H), 4.22 (qd, J=7.2 and 1.2 Hz, 2H), 4.94 (d, J=12.0 Hz, 1H), 5.00 (d, J=12.0 Hz, 1H), 5.89 (d, J=12.0 Hz, 1H), 5.94 (s, 1H), 6.01 (s, 1H), 6.08 (d, J=12.0 Hz, 1H), 6.17 (s, 1H), 6.19 (s, 1H), 7.22–7.30 (m, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 7.94, 8.00, 13.43, 13.76, 31.21 (2C), 47.45, 47.87, 62.87, 63.07, 89.65, 90.30, 124.11, 126.12, 127.86, 127.90, 127.98, 128.66, 128.74, 128.86, 135.30, 136.66, 145.92, 146.17, 163.12, 163.27, 200.41, 200.63; ESIMS m/z 306 (M^++H).

3.3.7. Compound 4c. Yield 60% (*syn*/*anti*=1:1); colorless oil; IR (film) 1751, 1682, 1562 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.04 (t, J=7.2 Hz, 3H), 1.26 (t, J=7.2 Hz, 3H), 2.29 (s, 3H), 2.30 (s, 3H), 3.99–4.10 (m, 2H), 4.23 (qd, J=7.2 and 0.9 Hz, 2H), 4.89 (d, J=12.0 Hz, 1H), 4.96 (d, J=12.0 Hz, 1H), 5.87 (d, J=12.0 Hz, 1H), 5.99 (s, 1H), 6.04 (d, J=12.0 Hz, 1H), 6.06 (s, 1H), 6.19 (s, 1H), 6.21 (s, 1H), 7.18–7.29 (m, 8H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.54, 13.78, 26.14 (2C), 46.73, 47.22, 63.12, 63.24, 89.28, 89.95, 126.12, 127.83, 128.94, 129.08, 129.37, 130.07, 133.90, 133.92, 134.04, 135.12, 146.06, 146.31, 162.86, 163.03, 197.54, 197.78; ESIMS *m*/*z* 326 (M^++H).

3.3.8. Compound 4d. Yield 69% (*syn*/*anti*=1:1); colorless oil; IR (film) 1751, 1682, 1562 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.01 (t, J=7.2 Hz, 3H), 1.26 (t, J=7.2 Hz, 3H), 2.28 (s, 6H), 2.29 (s, 6H), 3.97–4.06 (m, 2H), 4.22 (qd, J=7.2 and 1.2 Hz, 2H), 4.90 (d, J=12.0 Hz, 1H), 4.97 (d, J=12.0 Hz, 1H), 5.86 (d, J=12.0 Hz, 1H), 5.97 (s, 1H), 6.03 (s, 1H), 6.04 (d, J=12.0 Hz, 1H), 6.17 (s, 1H), 6.18 (s, 1H), 7.07–7.19 (m, 8H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.48, 13.78, 20.99 (2C), 26.18 (2C), 46.74, 47.20, 62.88, 63.07, 89.71, 90.37, 125.34, 127.34, 127.77, 128.51, 129.45, 129.59, 132.16, 133.60, 137.70, 137.83, 146.56, 146.81, 163.09, 163.31, 197.64, 197.91; ESIMS *m*/*z* 306 (M^++H).

3.3.9. Compound 6a. Yield 71%; colorless oil; IR (film) 1753, 1709, 1566, 1371, 1265, 1219 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.21 (t, J=7.2 Hz, 3H), 3.41 (dd, J=14.4 and 6.6 Hz, 1H), 3.55 (dd, J=14.4 and 8.7 Hz, 1H), 3.84 (s, 3H), 4.14–4.22 (m, 2H), 5.59 (dd, J=8.7 and 6.6 Hz, 1H), 7.28–7.42 (m, 5H), 7.92 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.61, 28.15, 52.27, 62.94, 85.81, 125.19, 128.67, 128.73, 129.03, 134.14, 144.33, 163.96, 167.18; ESIMS *m*/*z* 308 (M^++H).

3.3.10. Compound 6b. Yield 71%; colorless oil; IR (film) 1753, 1707, 1562, 1373, 1263, 1219 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.22 (t, J=7.2 Hz, 3H), 2.37 (s, 3H), 3.42 (dd, J=14.7 and 6.6 Hz, 1H), 3.57 (dd, J=14.7 and 8.7 Hz, 1H), 3.83 (s, 3H), 4.13–4.24 (m, 2H), 5.58 (dd, J=8.7 and 6.6 Hz, 1H), 7.18–7.26 (m, 4H), 7.88 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.61, 21.19, 28.19, 52.19, 62.90, 85.82, 124.24, 128.89, 129.40, 131.22, 139.38, 144.30, 164.02, 167.34; ESIMS *m*/*z* 322 (M^++H).

3.4. Synthesis of furan derivatives 5a–f

A mixture of **4a** (291 mg, 1.0 mmol), H_2SO_4 (295 mg, 3.0 mmol), and TFA (0.5 mL) in benzene (3 mL) was heated to 50–60 °C for 2 h. After cooling to room temperature, the reaction mixture was poured into cold water and extracted with ether. After removal of the solvent and column chromatographic purification process (hexanes/ether, 98:2) we obtained **5a** as a colorless oil, 141 mg (44%). The other compounds were synthesized analogously and the spectroscopic data of **5a–f** are as follows.

3.4.1. Compound 5a. Yield 44%; colorless oil; IR (film) 1713, 1315, 1176 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.15 (t, J=7.2 Hz, 3H), 2.31 (s, 3H), 3.64 (s, 2H), 4.19 (q, J=7.2 Hz, 2H), 6.91–6.95 (m, 2H), 7.11–7.33 (m, 8H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.51, 14.02, 29.02, 60.35, 120.98, 125.99, 127.68, 127.70, 128.00, 128.31, 129.61, 132.00, 136.17, 137.88, 139.73, 153.02, 159.08; ESIMS *m*/*z* 321 (M^++H). Anal. Calcd for $C_{21}H_{20}O_3$: C, 78.73; H, 6.29. Found: C, 78.61; H, 6.37.

3.4.2. Compound 5b. Yield 45%; colorless oil; IR (film) 1716, 1308, 1176 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.16 (t, J=7.2 Hz, 3H), 2.07 (s, 3H), 2.20 (s, 3H), 2.23 (s, 3H), 3.52 (s, 2H), 4.20 (q, J=7.2 Hz, 2H), 6.93 (s, 1H), 6.87–6.98 (m, 2H), 7.13–7.17 (m, 2H), 7.25–7.30 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.52, 14.04, 19.05, 21.03, 26.69, 60.40, 120.30, 126.72, 127.64, 127.66, 128.79, 129.50, 129.81, 132.02, 132.78, 135.27, 136.47, 137.22, 137.87, 153.14, 159.16; ESIMS *m*/*z* 349 (M^++H). Anal. Calcd for $C_{23}H_{24}O_3$: C, 79.28; H, 6.94. Found: C, 79.44; H, 6.91.

3.4.3. Compound 5c. Yield 48%; colorless oil; IR (film) 1716, 1261, 1180 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.12 (t, J=7.2 Hz, 3H), 1.73 (s, 3H), 2.10 (s, 6H), 2.24 (s, 3H), 3.53 (s, 2H), 4.17 (q, J=7.2 Hz, 2H), 6.78 (s, 2H), 7.24–7.42 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.06, 14.00, 20.06, 20.81, 24.69, 60.28, 119.34, 127.64, 127.79, 128.78, 129.52, 132.20, 132.38, 135.73, 136.44, 136.69, 137.46, 151.86, 159.10; ESIMS *m*/*z* 363 (M^++H). Anal. Calcd for $C_{24}H_{26}O_3$: C, 79.53; H, 7.23. Found: C, 79.78; H, 7.49.

3.4.4. Compound 5d. Yield 43%; colorless oil; IR (film) 1713, 1315, 1176 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.13 (t, J=7.2 Hz, 3H), 1.22 (t, J=7.5 Hz, 3H), 2.66 (q, J=7.5 Hz, 2H), 3.65 (s, 2H), 4.18 (q, J=7.2 Hz, 2H), 6.93–6.95 (m, 2H), 7.10–7.33 (m, 8H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.45, 14.03, 20.25, 28.89, 60.32, 120.10, 125.97, 127.62, 127.70, 128.02, 128.28, 129.63, 132.15, 136.10, 137.95, 140.00, 157.88, 159.18; ESIMS *m*/*z* 335 (M^++H). Anal. Calcd for $C_{22}H_{22}O_3$: C, 79.02; H, 6.63. Found: C, 79.11; H, 6.77.

3.4.5. Compound 5e. Yield 45%; colorless oil; IR (film) 1713, 1319, 1176 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.18 (t, J=7.2 Hz, 3H), 2.23 (s, 3H), 3.62 (s, 2H), 4.21 (q, J=7.2 Hz, 2H), 6.91–6.94 (m, 2H), 7.06–7.30 (m, 7H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.48, 14.10, 29.01, 60.52, 120.83, 126.16, 127.95, 127.99, 128.42, 130.49, 131.02, 133.77, 134.93, 138.00, 139.48, 153.21, 158.92; ESIMS *m*/*z* 355 (M^++H). Anal. Calcd for $C_{21}H_{19}ClO_3$: C, 71.08; H, 5.40. Found: C, 70.94; H, 5.53.

3.4.6. Compound 5f. Yield 49%; colorless oil; IR (film) 1713, 1315, 1176 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.19 (t, J=7.2 Hz, 3H), 2.29 (s, 3H), 2.35 (s, 3H), 3.64 (s, 2H), 4.21 (q, J=7.2 Hz, 2H), 6.94–6.97 (m, 2H), 7.06–7.25 (m, 7H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.53, 14.12, 21.26, 28.98, 60.32, 120.95, 125.97, 127.99, 128.32, 128.46, 128.84, 129.51, 136.35, 137.41, 137.79, 139.83, 152.98, 159.08; ESIMS *m*/*z* 335 (M^++H). Anal. Calcd for $C_{22}H_{22}O_3$: C, 79.02; H, 6.63. Found: C, 79.10; H, 6.87.

3.5. Synthesis of naphthalene derivatives

A mixture of **6a** (307 mg, 1.0 mmol), H_2SO_4 (295 mg, 3.0 mmol), and TFA (0.5 mL) in benzene (3 mL) was heated to 40–50 °C for 5 h. After cooling to room temperature, the reaction mixture was poured into cold water and extracted

with ether. After removal of the solvent and column chromatographic purification process (hexanes/ether, 10:1 for **7a′** and hexanes/EA, 4:1 for **7a**) we obtained **7a** (162 mg, 66%) and **7a′** (21 mg, 8%). The other compounds were synthesized analogously and the spectroscopic data of **7a–c**, **7a′**, and **7b′** are as follows.

3.5.1. Compound 7a. Yield 66%; white solid, mp 153–154 °C; IR (KBr) 3412, 1715, 1690 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.50 (t, J=7.2 Hz, 3H), 4.52 (q, J=7.2 Hz, 2H), 7.60–7.78 (m, 2H), 8.04 (d, J=8.7 Hz, 1H), 8.80 (d, J=1.8 Hz, 1H), 8.85 (s, 1H), 8.97 (d, J=8.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.60, 61.68, 126.26, 127.37, 128.46, 129.66, 130.42 (2C), 130.69, 133.37, 133.94, 136.80, 167.10, 171.22; ESIMS m/z 245 (M^++H). Anal. Calcd for $C_{14}H_{12}O_4$: C, 68.85; H, 4.95. Found: C, 68.94; H, 5.03.

3.5.2. Compound 7a′. Yield 8%; white solid, mp 49–50 °C; IR (KBr) 1723, 1306, 1233 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.48 (t, J=7.2 Hz, 3H), 4.01 (s, 3H), 4.50 (q, J=7.2 Hz, 2H), 7.56–7.75 (m, 2H), 7.99 (d, J=8.4 Hz, 1H), 8.73 (d, J=1.5 Hz, 1H), 8.74 (d, J=1.5 Hz, 1H), 8.94 (d, J=8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.36, 52.42, 61.35, 125.92, 126.23, 126.96, 128.00, 129.24, 129.97, 129.98, 133.15, 133.25, 135.56, 166.42, 166.96; ESIMS m/z 259 (M^++H).

3.5.3. Compound 7b. Yield 37%; white solid, mp 185–186 °C; IR (KBr) 3394, 1714, 1692 cm^{-1}; ^1H NMR ($CDCl_3$+CD_3OD, 300 MHz) δ 1.48 (t, J=7.2 Hz, 3H), 2.59 (s, 3H), 4.49 (q, J=7.2 Hz, 2H), 7.44 (dd, J=8.4 and 1.5 Hz, 1H), 7.90 (d, J=8.4 Hz, 1H), 8.70–8.72 (m, 3H); ^{13}C NMR ($CDCl_3$+CD_3OD, 75 MHz) δ 14.10, 22.23, 61.19, 124.69, 125.48, 126.89, 129.01, 129.57, 129.69, 131.33, 133.36, 135.57, 140.42, 167.32, 168.12; ESIMS m/z 259 (M^++H). Anal. Calcd for $C_{15}H_{14}O_4$: C, 69.76; H, 5.46. Found: C, 69.66; H, 5.74.

3.5.4. Compound 7b′. Yield 21%; white solid, mp 54–55 °C; IR (KBr) 1719, 1627, 1307, 1234 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.48 (t, J=7.2 Hz, 3H), 2.58 (s, 3H), 3.99 (s, 3H), 4.49 (q, J=7.2 Hz, 2H), 7.42 (dd, J=8.4 and 1.5 Hz, 1H), 7.87 (d, J=8.4 Hz, 1H), 8.68–8.73 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.36, 22.45, 52.32, 61.22, 124.94, 125.28, 127.13, 129.17, 129.35, 129.75, 131.40, 133.50, 135.30, 140.53, 166.52, 167.07; ESIMS m/z 273 (M^++H).

3.5.5. Compound 7c. Yield 39%; colorless oil; IR (KBr) 1715, 1684 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.48 (t, J=7.2 Hz, 3H), 2.76 (s, 3H), 4.51 (q, J=7.2 Hz, 2H), 7.58–7.76 (m, 2H), 8.02 (d, J=8.4 Hz, 1H), 8.61 (d, J=1.8 Hz, 1H), 8.70 (d, J=1.8 Hz, 1H), 8.93 (d, J=8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.38, 26.65, 61.41, 125.99, 127.10, 127.94, 128.31, 130.18, 130.19, 133.14, 133.19, 133.26, 134.43, 167.06, 197.13; ESIMS m/z 243 (M^++H). Anal. Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82. Found: C, 74.59; H, 5.93.

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