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Synthesis of Poly-Substituted Benzene Derivatives *via* [3+3] Annulation Protocol from Morita-Baylis-Hillman Adducts and Glutaconates

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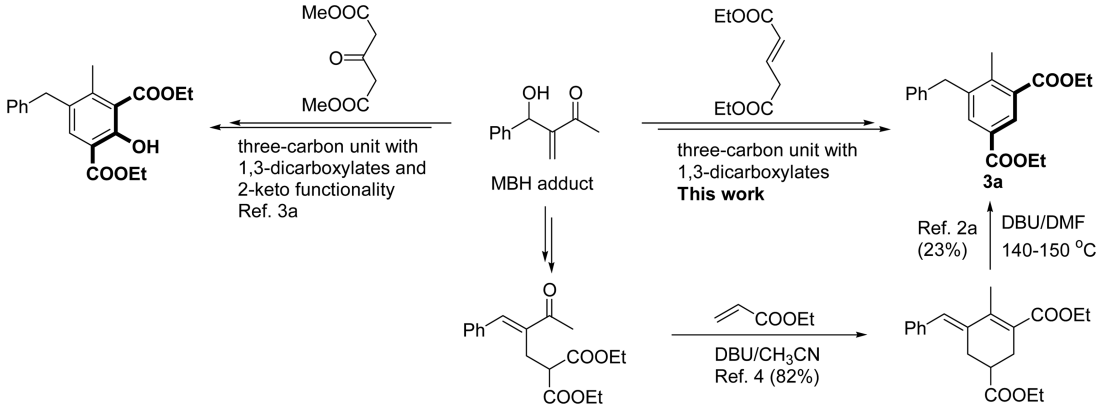
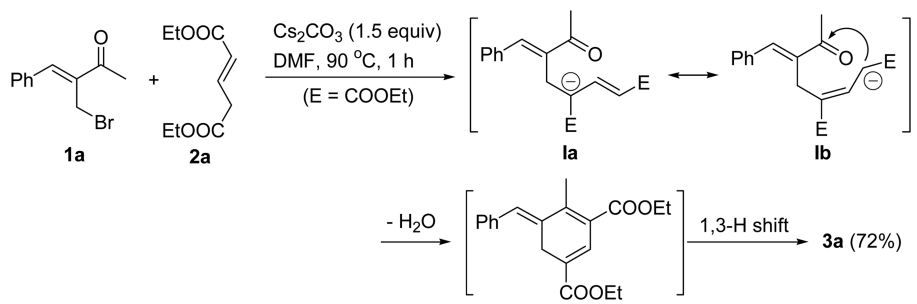
Morita-Baylis-Hillman (MBH) adducts[1] have been used for the synthesis of various aromatic compounds including poly-substituted benzenes[2] and phenols.[3] The reaction of MBH adduct and 1,3-dimethylacetone dicarboxylate has been used for the synthesis of poly-substituted phenols bearing 2,6-dicarboxylates *via* the [3+3] annulation protocol (*vide infra*, Scheme 1).[3a] 1,3-Dimethylacetone dicarboxylate served a three-carbon unit with 1,3-dicarboxylates and 2-keto functionality in the reaction. The corresponding poly-substituted benzene **3a** has been synthesized in low yield (23%)[2a] by DBU-mediated dehydrogenation of the cyclohexene intermediate which was prepared from MBH adduct and diethyl malonate (*vide infra*, Scheme 1).[4]

Glutaconates have been used in organic synthesis in order to introduce a three-carbon unit bearing two carboxylates at the 1,3-position.[5,6] In these respects, we presumed that the reaction of MBH adduct and diethyl glutaconate could be used for the preparation of poly-substituted benzene derivatives bearing 1,3-dicarboxylates such as **3a**, as shown in Scheme 1.

At the outset of our experiment, the reaction of MBH bromide **1a** and diethyl glutaconate (**2a**) was examined in CH_3CN in the presence of Cs_2CO_3 at 50 °C for 2 h. To our delight, desired product **3a** was obtained in moderate yield (61%).[7] The nucleophilic substitution of **1a** with the anion of **2a** would produce a resonance-stabilized carbanion intermediate **I**,[8] and the following cyclization, dehydration and a base-catalyzed 1,3-H shift produced **3a** *via* an overall [3+3] annulation approach, as shown in Scheme 2. The reaction in refluxing CH_3CN gave a similar yield of **3a** (60%). After some trials, we found that the reaction in DMF at 90 °C produced **3a** in good yield (72%) in short time (1 h), and we

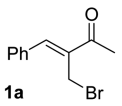
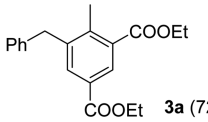
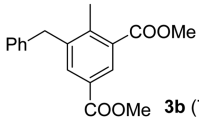
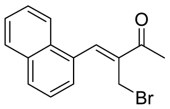
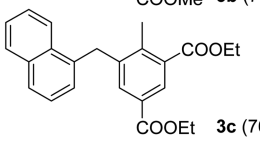
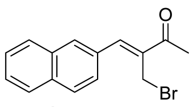
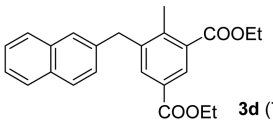
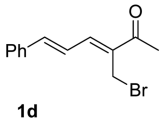
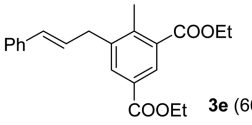
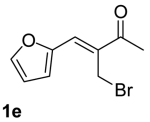
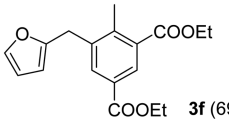
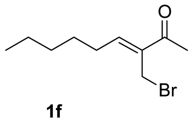
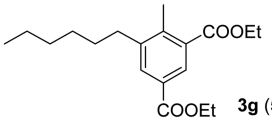
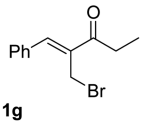
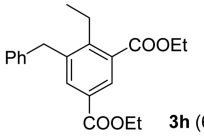
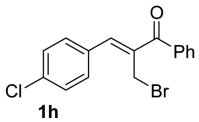
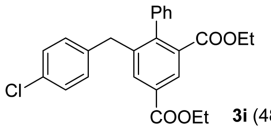


Scheme 1



Scheme 2

Table 1. Synthesis of poly-substituted benzene derivatives

Entry	MBH bromide	Product (%)[a]
1	 **1a**	 **3a** (72)
2	**1a**	 **3b** (70)[b]
3	 **1b**	 **3c** (76)
4	 **1c**	 **3d** (71)
5	 **1d**	 **3e** (66)
6	 **1e**	 **3f** (69)
7	 **1f**	 **3g** (53)
8	 **1g**	 **3h** (69)
9	 **1h**	 **3i** (48)[c]

[a]Conditions: MBH bromide **1** (1.0 mmol), diethyl glutaconate (**2a**, 1.1 equiv), Cs_2CO_3 (1.5 equiv), DMF, 90 °C, 1 h. [b]Dimethyl glutaconate (**2b**) was used. [c]Reaction time was 48 h.

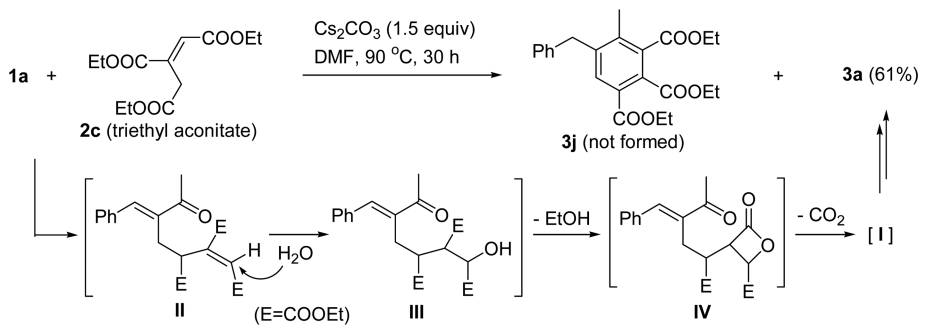
selected this condition as an optimum one.

Encouraged by the successful result, we examined the reactions of various MBH bromides **1b-h** under the optimized conditions (DMF, 90 °C, 1 h), and the results are summarized in Table 1. The reaction of **1a** and dimethyl glutaconate (**2b**) afforded **3b** in a similar yield (70%, entry 2). The reactions of MBH bromides **1b-f** (entries 3-7) afforded the corresponding poly-substituted benzenes **3c-g** in good to moderate yields (53-76%). The MBH bromide **1g**, derived from ethyl vinyl ketone, gave **3h** in a similar yield (69%, entry 8). The benzoyl derivative **1h**, derived from phenyl vinyl ketone, gave the biphenyl derivative **3i** in moderate yield (48%); however a long reaction time (48 h) was required (entry 9) presumably due to the steric hindrance during the cyclization.

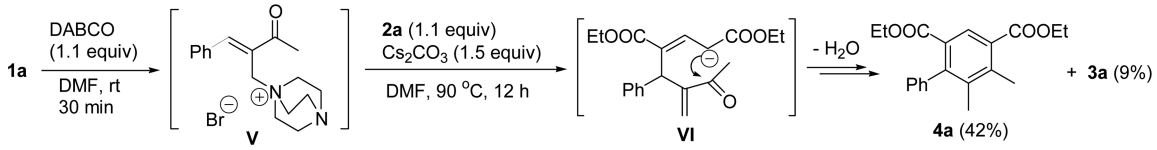
The reaction of **1a** and triethyl aconitate (**2c**), bearing an ester moiety at the 3-position, afforded **3a** (61%) unexpectedly instead of a desired product **3j**, as shown in Scheme 3. When we monitored the reaction of **1a** and **2c** on TLC both components disappeared rapidly to form somewhat polar compounds, presumably a stereo- and/or regioisomeric mixture of **II**. The polar components slowly converted to **3a**. In order to check the possibility for the conversion of **2c** into **2a** by a selective removal of the ester moiety at the 3-position, we examined the reaction of **2c**. However, **2c** was not converted to **2a** under the same reaction conditions. Thus, the mechanism for the formation of **3a** could be tentatively proposed as follows: (i) conjugate addition of water in the reaction mixture to **II** to form a β-hydroxy ester **III**,[9a-c] formation of b-lactone **IV**, decarboxylation to form **I**,[9d,e] and the final cyclization to **3a**. However, further studies are required in order to understand the mechanism more precisely.

As a last examination, the reaction of **2a** and the DABCO salt of **1a** was examined, as shown in Scheme 4. The corresponding DABCO salt **V** was formed quantitatively in DMF at room temperature;[10] however, the reaction with **2a** afforded benzene derivative **4a** in moderate yield (42%) *via* the S_N2' type reaction of **2a** to form an intermediate **VI** and a following cyclization process. In the reaction, compound **3a** (9%) was also formed *via* the competitive S_N2 reaction of **2a** to form an intermediate **I** and a following cyclization process.

In summary, various poly-substituted benzene derivatives bearing 1,3-dicarboxylates have been synthesized *via* an efficient [3+3] annulation protocol from Morita-Baylis-Hillman bromides and glutaconate derivatives.



Scheme 3



Scheme 4

Experimental Section

The starting materials MBH bromides were prepared according to the reported method from MBH adducts with aqueous HBr or PBr_3.[11] Glutaconate derivatives **2a** (*E*) and **2b** (*E*) were prepared by esterification of commercial *trans*-glutaconic acid. Triethyl aconitate (**2c**, *E*) was prepared by esterification of commercial *trans*-aconitic acid.[12]

Typical Synthetic Procedure of 3a. A stirred solution of **1a** (239 mg, 1.0 mmol), **2a** (205 mg, 1.1 mmol), Cs_2CO_3 (489 mg, 1.5 mmol) in DMF (3.0 mL) was heated to 90 °C for 1 h. After the usual aqueous extractive workup and column chromatographic purification process (hexane/ether, 10:1), compound **3a**[2a] was obtained as colorless oil, 235 mg (72%). Other compounds were synthesized similarly, and the spectroscopic data of **3b-i** and **4a** are as follows.

Compound 3b: 70%; white solid, mp 52-54 °C; IR (KBr) 1719, 1434, 1322, 1233 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.39 (s, 3H), 3.82 (s, 3H), 3.83 (s, 3H), 4.02 (s, 2H), 6.98-7.02 (m, 2H), 7.08-7.23 (m, 3H), 7.90 (d, *J* = 1.8 Hz, 1H), 8.28 (d, *J* = 1.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 16.98, 39.78, 52.16, 52.18, 126.27, 127.43, 128.41, 128.54, 129.62, 131.87, 134.11, 139.14, 140.77, 143.37, 166.37, 168.09; ESIMS *m/z* 299 $[M+H]^+$. Anal. Calcd for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08. Found: C, 72.69; H, 6.31.

Compound 3c: 76%; colorless oil, IR (film) 1720, 1318, 1228 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.25 (t, *J* = 7.2 Hz, 3H), 1.34 (t, *J* = 7.2 Hz, 3H), 2.41 (s, 3H), 4.24 (q, *J* = 7.2 Hz, 2H), 4.32 (q, *J* = 7.2 Hz, 2H), 4.42 (s, 2H) 6.77 (d, *J* = 6.6 Hz, 1H), 7.25 (t, *J* = 7.8 Hz, 1H), 7.38-7.50 (m, 2H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.76-7.86 (m, 1H), 7.79 (d, *J* = 1.8 Hz, 1H), 7.90-7.96 (m, 1H), 8.29 (d, *J* = 1.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.21, 14.28, 16.89, 36.42, 61.04, 61.27, 123.23, 125.53, 125.72, 125.79, 126.19, 127.19, 128.00, 128.82, 129.43, 131.81, 132.32, 133.72, 133.97, 134.96, 140.11, 143.02, 165.92, 167.96; ESIMS *m/z* 377 $[M+H]^+$. Anal. Calcd for $C_{24}H_{24}O_4$: C, 76.57; H, 6.43. Found: C, 76.45; H, 6.68.

Compound 3d: 71%; colorless oil, IR (film) 1720, 1368, 1228 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.39 (t, *J* = 7.2 Hz, 3H), 1.41 (t, *J* = 7.2 Hz, 3H), 2.48 (s, 3H), 4.26 (s, 2H), 4.37 (q, *J* = 7.2 Hz, 2H), 4.38 (q, *J* = 7.2 Hz, 2H), 7.26 (dd, *J* = 8.4 and 1.8 Hz, 1H), 7.38-7.47 (m, 3H), 7.68-7.73 (m, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.76-7.81 (m, 1H), 8.04 (d, *J* = 1.8 Hz, 1H), 8.36 (d, *J* = 1.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.26, 14.30, 17.04, 40.01, 61.13, 61.23, 125.48, 126.07, 126.63, 126.95, 127.52, 127.57, 127.91, 128.19, 129.48, 132.09, 132.53, 133.49, 134.08, 136.80, 140.41, 143.02, 165.99, 167.91; ESIMS *m/z* 377 $[M+H]^+$.

Compound 3e: 66%; colorless oil, IR (film) 1720, 1316, 1228 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.33 (t, *J* = 7.2 Hz, 3H), 1.34 (t, *J* = 7.2 Hz, 3H), 2.49 (s, 3H), 3.50-3.63 (m, 2H), 4.31 (q, *J* = 7.2 Hz, 2H), 4.32 (q, *J* = 7.2 Hz, 2H), 6.21 (dd, *J* = 15.9 and 4.2 Hz, 1H), 6.28 (dd, *J* = 15.9 and 2.4 Hz, 1H), 7.09-7.27 (m, 5H), 7.92 (d, *J* = 1.8 Hz, 1H), 8.24 (d, *J* = 1.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.28, 14.32, 16.75, 37.20, 61.12, 61.23, 126.10, 127.27, 127.32, 127.91, 128.49, 129.27, 131.53, 132.30, 133.26, 137.11, 140.09, 142.54, 166.01, 167.95; ESIMS *m/z* 353 $[M+H]^+$. Anal. Calcd for $C_{22}H_{24}O_4$: C, 74.98; H, 6.86. Found: C, 75.12; H, 6.93.

Compound 3f: 69%; colorless oil, IR (film) 1721, 1303, 1229, 1177 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.39 (t, *J* = 7.2 Hz, 3H), 1.41 (t, *J* = 7.2 Hz, 3H), 2.53 (s, 3H), 4.06 (s, 2H), 4.37 (q, *J* = 7.2 Hz, 2H), 4.38 (q, *J* = 7.2 Hz, 2H), 5.89 (dd, *J* = 3.3 and 0.9 Hz, 1H), 6.27 (dd, *J* = 3.3 and 1.8 Hz, 1H), 7.32 (dd, *J* = 1.8 and 0.9 Hz, 1H), 7.97 (d, *J* = 1.8 Hz, 1H), 8.33 (d, *J* = 1.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.25, 14.27, 16.69, 32.70, 61.11, 61.23, 106.56, 110.30, 127.91, 129.64, 132.34, 133.58, 138.16, 141.58, 142.68, 152.90, 165.84, 167.79; ESIMS *m/z* 317 $[M+H]^+$.

Compound 3g: 53%; colorless oil, IR (film) 2957, 2930, 1722, 1315, 1226 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.90 (t, *J* = 7.2 Hz, 3H), 1.25-1.38 (m, 6H), 1.40 (t, *J* = 7.2 Hz, 3H), 1.41 (t, *J* = 7.2 Hz, 3H), 1.54-1.65 (m, 2H), 2.53 (s, 3H), 2.69 (t, *J* = 7.8 Hz, 2H), 4.38 (q, *J* = 7.2 Hz, 2x2H), 7.92 (d, *J* = 1.8 Hz, 1H), 8.24 (d, *J* = 1.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.04, 14.27, 14.32, 16.50, 22.57, 29.25, 30.20, 31.63, 33.79, 61.02, 61.13, 127.56, 128.55, 132.08, 132.73, 141.85, 142.90, 166.18, 168.15; ESIMS *m/z* 321 $[M+H]^+$. Anal. Calcd for $C_{19}H_{28}O_4$: C, 71.22; H, 8.81. Found: C, 71.47; H, 8.79.

Compound 3h: 69%; colorless oil, IR (film) 1721, 1317, 1228 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.04 (t, *J* = 7.5 Hz, 3H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.33 (t, *J* = 7.2 Hz, 3H), 2.86 (q, *J* = 7.5 Hz, 2H), 4.06 (s, 2H), 4.29 (q, *J* = 7.2 Hz, 2H), 4.31 (q, *J* = 7.2 Hz, 2H), 6.97-7.04 (m, 2H), 7.08-7.23 (m, 3H), 7.88 (d, *J* = 1.8 Hz, 1H), 8.23 (d, *J* = 1.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.24, 14.30, 15.01, 23.37, 38.77, 61.09, 61.24, 126.28, 127.98, 128.47, 128.52, 129.67, 132.10, 134.57, 139.90, 139.91, 148.50, 165.95, 167.91; ESIMS *m/z* 341 $[M+H]^+$.

Compound 3i: 48%; pale yellow oil, IR (film) 1722, 1368, 1245 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.92, (t, *J* = 7.2 Hz, 3H), 1.41 (t, *J* = 7.2 Hz, 3H), 3.82 (s, 2H), 3.99 (q, *J* = 7.2 Hz, 2H), 4.40 (q, *J* = 7.2 Hz, 2H), 6.75 (d, *J* = 8.4 Hz, 2H), 7.00-7.07 (m, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 7.29-7.36 (m, 3H), 8.04 (d, *J* = 1.8 Hz, 1H), 8.35 (d, *J* = 1.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.59, 14.31, 38.60, 61.08, 61.35, 127.48, 127.91, 128.34, 128.57, 128.65, 129.75, 129.95, 131.86, 133.32, 133.60, 138.54, 138.63, 140.04,

145.83, 165.66, 167.74; ESIMS *m/z* 423 $[M+H]^+$, 425 $[M+H+2]^+$. Anal. Calcd for $C_{25}H_{23}ClO_4$: C, 71.00; H, 5.48. Found: C, 71.13; H, 5.71.

Compound 4a: 42%; colorless oil, IR (film) 1721, 1310, 1233, 1176 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.92 (t, J = 7.2 Hz, 3H), 1.41 (t, J = 7.2 Hz, 3H), 2.04 (s, 3H), 2.54 (s, 3H), 3.96 (q, J = 7.2 Hz, 2H), 4.39 (q, J = 7.2 Hz, 2H), 7.09-7.15 (m, 2H), 7.31-7.43 (m, 3H), 8.09 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.59, 14.29, 17.64, 17.67, 60.75, 61.15, 127.01, 127.89, 128.15, 128.59, 129.54, 130.63, 137.38, 140.56, 141.13, 144.33, 167.96, 168.02; ESIMS *m/z* 327 $[M+H]^+$. Anal. Calcd for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.75; H, 6.92.

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References and Notes

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