Tetrahedron Letters 54 (2013) 387–391

Contents lists available at SciVerse ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

An efficient synthesis of poly-substituted benzene and tricyclo[3.2.1.0^{2,7}]oct-3-ene derivatives starting from Morita–Baylis–Hillman adducts

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ARTICLE INFO

Article history:
Received 24 September 2012
Revised 1 November 2012
Accepted 5 November 2012
Available online 15 November 2012

Keywords:
Poly-substituted benzenes
Tricyclo[3.2.1.0^{2,7}]oct-3-enes
Diels–Alder reaction
Aerobic oxidation
Morita–Baylis–Hillman adducts

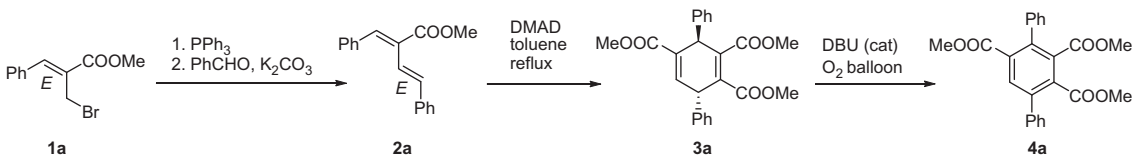
ABSTRACT

Various poly-substituted benzenes including terphenyl, quaterphenyl, and quinquephenyl were synthesized starting from the Morita–Baylis–Hillman bromides. The synthesis was carried out via a three-step protocol, namely, a sequential Wittig reaction, Diels–Alder reaction with DMAD, and an aerobic oxidation.

Various chemical transformations of the Morita–Baylis–Hillman (MBH) adducts have been studied extensively during the last two decades.[1,2] Among them the synthesis of aromatic compounds including poly-substituted benzenes has received a special attention.[2]

Due to our continuous interest for the synthesis of poly-substituted benzene derivatives,[2c–m] we presumed that a Diels–Alder reaction between a 1,3-diene derivative **2a**, prepared from the MBH bromide **1a** via a Wittig reaction,[3] and a suitable dienophile such as dimethyl acetylenedicarboxylate (DMAD)[4] could provide an efficient way to synthesize poly-substituted benzene **4a**, as shown in Scheme 1.

The preparation of (*E,E*)-1,3-diene derivative **2a** was carried out via a sequential bromination of a MBH adduct with HBr to form **1a**,[5] formation of a phosphonium salt with PPh_3, and a Wittig reaction with benzaldehyde in the presence of K_2CO_3 in CH_3CN.[3] A subsequent Diels–Alder reaction of **2a** with DMAD in toluene produced dihydrobenzene derivative **3a**.[6] At the outset of our experiment, we carried out an aerobic oxidation of crude **3a** in the presence of DBU (0.5 equiv) under O_2 balloon atmosphere.[2d,2f,4a] As expected, a terphenyl derivative **4a** was obtained in moderate yield (45%); however, an appreciable amount of unknown compound (vide infra, **5a**, 22%) was isolated. The unknown compound has five different ester groups and must be formed by the reaction of **3a** and DMAD that remained in the reaction mixture. The structure of this unknown compound was confirmed as a tricyclo[3.2.1.0^{2,7}]oct-3-ene[7] derivative **5a** by various spectroscopic data and unequivocally by its crystal structure.[8,9] The crystal structures of **3a** and **5a** are shown in Figure 1.[8] The tricyclo[3.2.1.0^{2,7}]oct-3-ene skeleton has been found in many biologically interesting substances such as Salvileucalin B[7a,7b] and various staphirine alkaloids.[7c,d] Thus, the synthesis of this interesting backbone has received much attention.[7h–n]



1a 2a 3a 4a

Scheme 1.

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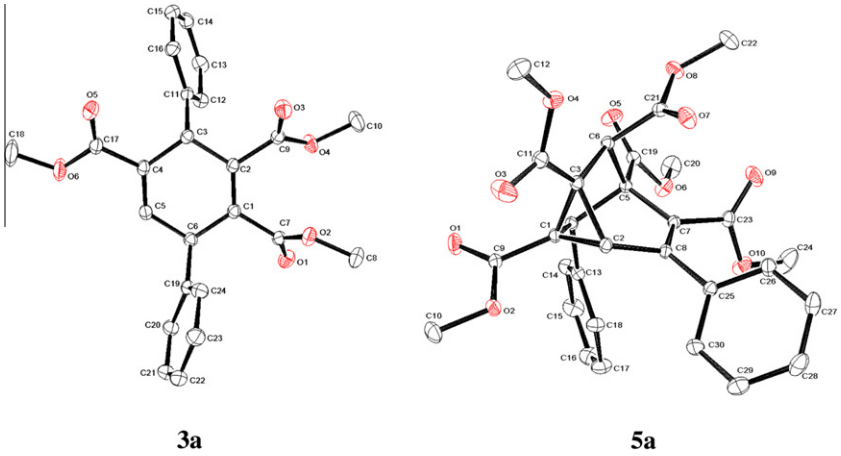
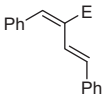
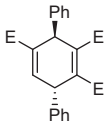
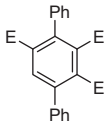
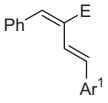
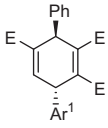
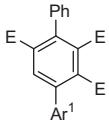
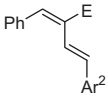
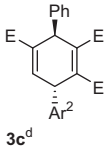
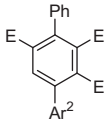
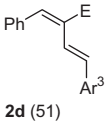
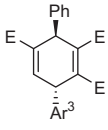
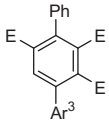
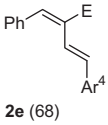
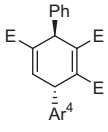
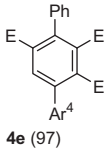
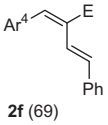
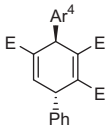
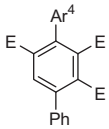
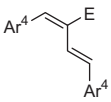
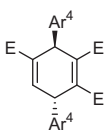
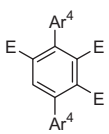
http://dx.doi.org/10.1016/j.tetlet.2012.11.020



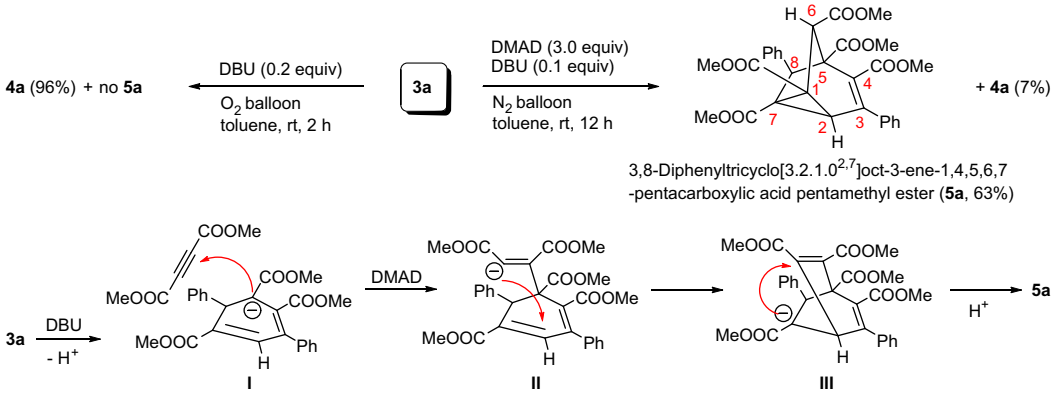
3a **5a**

Figure 1. ORTEP drawings of compounds **3a** and **5a**.

Table 1
Synthesis of poly-substituted benzene derivatives[a]

Entry	1,3-Diene	Dihyddrobenzene[b] (%)	Product[c] (%)
1	 **2a** (68)	 **3a** (74)	 **4a** (96)
2	 **2b** (71)	 **3b** (72)	 **4b** (97)
3	 **2c** (82)	 **3c**[d]	 **4c** (64)
4	 **2d** (51)	 **3d** (77)	 **4d** (94)
5	 **2e** (68)	 **3e** (64)	 **4e** (97)
6	 **2f** (69)	 **3f** (63)	 **4f** (95)
7	 **2g** (65)	 **3g** (68)	 **4g** (95)

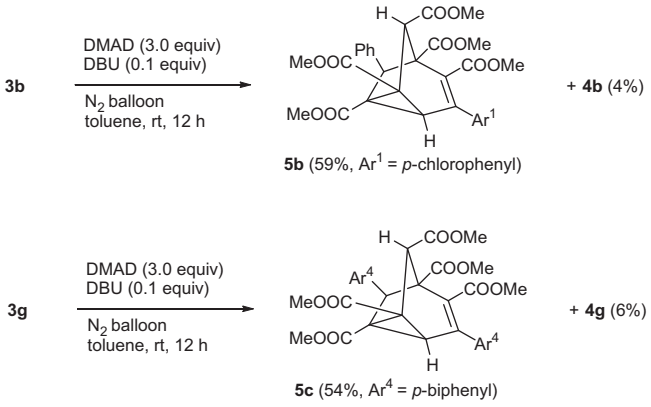
[a] *E* = COOMe, Ar^1 = *p*-chlorophenyl, Ar^2 = *p*-nitrophenyl, Ar^3 = *p*-methoxyphenyl, Ar^4 = *p*-biphenyl.
[b] Conditions: diene **2** (1.0 mmol), DMAD (3.0 equiv), toluene, reflux, 40 h.
[c] Conditions: dihydrobenzene **3** (0.5 mmol), DBU (0.2 equiv), toluene, rt, 2 h.
[d] 1,2-Dichlorobenzene, 160 °C, 20 h, and **3c** was not isolated (see text).



Scheme 2.

When we subjected pure dihydrobenzene **3a** (74%, entry 1 in Table 1) in an aerobic oxidation condition a terphenyl **4a** was isolated in high yield (96%),[6] whereas the reaction of **3a** and DMAD in the presence of a catalytic amount of DBU (0.1 equiv) produced **5a** in good yield (63%),[9] as shown in Scheme 2. Although the reaction was performed under N_2 balloon atmosphere, the oxidation product **4a** was also formed in small amount (7%).[10] The mechanism for the formation of **5a** could be proposed, as shown in Scheme 2. DBU-catalyzed isomerization of the double bond of **3a** and a subsequent deprotonation generated a carbanion intermediate **I**. An intermolecular conjugate addition of **I** to DMAD and following successive intramolecular conjugate additions afforded **5a**.[11]

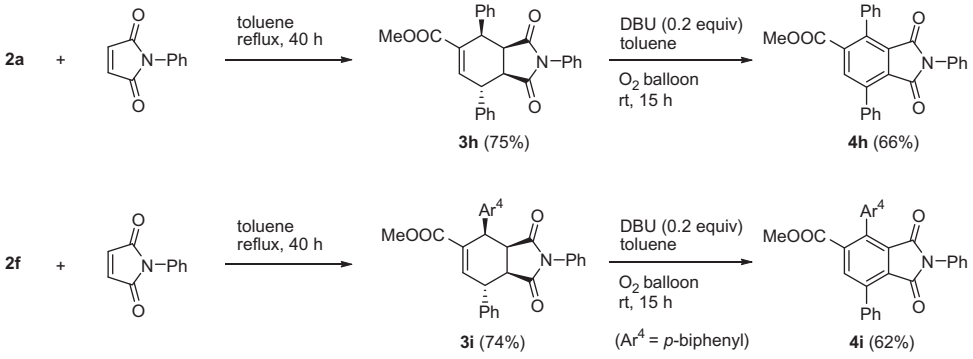
Encouraged by the results, various 1,3-diene derivatives **2b–g** were prepared from the corresponding MBH bromides,[5] and the syntheses of poly-substituted benzenes **4b–g** were carried out. The results are summarized in Table 1. The syntheses of dihydrobenzenes **3b** and **3d–g** were carried out by the Diels–Alder reaction of **2b** and **2d–g** with DMAD in refluxing toluene for 40 h. During the preparation of dihydrobenzenes **3b** and **3d–g**, the corresponding aromatized compounds **4b** and **4d–g** were observed in trace amount (<5%). The Diels–Alder reaction of *p*-nitro derivative **2c** and DMAD was sluggish in refluxing toluene, thus we carried out the reaction at 160 °C in *o*-dichlorobenzene for 20 h (entry 3). It is interesting to note that an appreciable amount of *p*-nitro derivative **4c** was formed during the preparation of **3c** along with some intractable side products even under N_2 balloon atmosphere. Thus we separated **3c** and **4c** together using a short-path column chromatography and the mixture was treated with DBU to obtain **4c**. However, the yield of **4c** was moderate (64%). For the other entries (entries 2 and 4–7), a subsequent aerobic oxidation of dihydrobenzenes was carried out under the same conditions for the preparation of **4a**. In this way, various terphenyls **4b–d**,[4b,4c,4e] quaterphenyls **4e** and **4f**,[12] and quinquephenyl **4g**[4c,12a,12b] were synthesized in high yields.



Scheme 3.

As shown in Scheme 3, the reactions of **3b** and **3g** with DMAD in the presence of a catalytic amount of DBU (0.1 equiv) afforded the corresponding tricyclic compounds **5b** and **5c**, respectively, in moderate yields. As in the previous synthesis of **5a**, trace amounts of the aromatized compounds **4b** and **4g** were formed via an aerobic oxidation even under N_2 balloon atmosphere.

As a next entry, we examined a Diels–Alder reaction between **2a** and *N*-phenylmaleimide,[13,14] as shown in Scheme 4. In the reaction, the corresponding Diels–Alder adduct **3h** was isolated in 75% as a single diastereomer; however, the stereochemistry was not confirmed decisively.[14] Compound **3h** was converted into a polyarylphthalimide **4h** by DBU-catalyzed aerobic oxidation in



Scheme 4.

moderate yield (66%). Similarly, the reaction of **2f** and *N*-phenylmaleimide afforded **3i** in 74%. DBU treatment of **3i** afforded polyarylphthalimide **4i** in moderate yield (62%).[15] The oxidation of tetrahydrobenzenes **3h** and **3i** required somewhat a longer reaction time (15 h) than the previous dihydrobenzene derivatives **3a**–**g** (2 h).

In summary, we disclosed an efficient synthesis of poly-substituted aromatic compounds from MBH bromides via a sequential Wittig reaction, Diels–Alder reaction with DMAD or *N*-phenylmaleimide, and an aerobic oxidation process. In addition, an interesting consecutive conjugate addition pathway to form a novel tricyclo[3.2.1.0^{2,7}]oct-3-ene scaffold has been found serendipitously.

Acknowledgments

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2012R1A1B3000541). Spectroscopic data were obtained from the Korea Basic Science Institute, Gwangju branch.

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4. For the selected Diels–Alder reaction between 1,3-dienes and various dienophiles including DMAD, see: (a) Horie, H.; Kurahashi, T.; Matsubara, S. *Chem. Commun.* **2012**, *48*, 3866–3868; (b) Thirion, D.; Poriel, C.; Rault-Berthelot, J.; Barriere, F.; Jeannin, O. *Chem. Eur. J.* **2010**, *16*, 13646–13658; (c) Davis, M. C.; Groshens, T. J. *Synth. Commun.* **2011**, *41*, 206–218; (d) Muraoka, O.; Tanabe, G.; Yamamoto, E.; Ono, M.; Minematsu, T.; Kimura, T. *J. Chem. Soc. Perkin Trans. 1* **1997**, 2879–2890; (e) Fieser, L. F.; Haddadin, M. J. *J. Am. Chem. Soc.* **1964**, *86*, 2392–2395.
5. For the preparation of MBH bromides, see: (a) Das, B.; Damodar, K.; Bhunia, N.; Shashikanth, B. *Tetrahedron Lett.* **2009**, *50*, 2072–2074; (b) Basavaiah, D.; Reddy, K. R.; Kumaragurubaran, N. *Nat. Protoc.* **2007**, *2*, 2665–2676; (c) Das, B.; Banerjee, J.; Ravindranath, N. *Tetrahedron* **2004**, *60*, 8357–8361; (d) Gowrisankar, S.; Kim, S. H.; Kim, J. N. *Bull. Korean Chem. Soc.* **2009**, *30*, 726–728. and further references cited therein.
6. *Typical procedure for the synthesis of* ***3a*** *and* ***4a***: A stirred mixture of **2a** (264 mg, 1.0 mmol) and DMAD (426 mg, 3.0 mmol) in toluene (2.5 mL) was heated to reflux for 40 h under N_2 atmosphere. After aqueous extractive workup and column chromatographic purification process (hexanes/CH_2Cl_2/Et_2O, 15:5:1), compound **3a** was obtained as a white solid, 301 mg (74%). To a stirred solution of **3a** (203 mg, 0.5 mmol) in toluene (2.0 mL) was added DBU (15 mg, 0.1 mmol), and the reaction mixture was stirred at room temperature for 2 h under O_2 balloon atmosphere. After aqueous extractive workup and column chromatographic purification process (hexanes/CH_2Cl_2/Et_2O, 4:1:1), compound **4a** was obtained as a white solid, 194 mg (96%). Other compounds were synthesized similarly, and the selected spectroscopic data of **3a**, **3d**, **3h**, **4a**, **4f**, and **4h** are as follows.
Compound ***3a***: 74%; white solid, mp 134–136 °C; IR (KBr) 2952, 1735, 1521 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.46 (s, 3H), 3.53 (s, 3H), 3.59 (s, 3H), 4.78 (dd, J = 6.9 and 3.0 Hz, 1H), 4.99 (dd, J = 6.9 and 1.2 Hz, 1H), 6.97 (dd, J = 3.0 and 1.2 Hz, 1H), 7.18–7.37 (m, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 42.87, 44.77, 51.78, 51.98, 52.11, 127.40, 127.77, 128.55, 128.64, 128.76, 128.92, 129.04, 133.17, 135.71, 136.84, 139.34, 139.70, 165.79, 167.07, 167.36; ESIMS m/z 429 [M$^+$+Na]. Anal. Calcd for $C_{24}H_{22}O_6$: C, 70.92; H, 5.46. Found: C, 71.08; H, 5.33.
Compound ***3d***: 77%; white solid, mp 118–120 °C; IR (KBr) 3028, 1717, 1600 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.41 (s, 3H), 3.46 (s, 3H), 3.52 (s, 3H), 3.72 (s, 3H), 4.66 (dd, J = 6.9 and 3.0 Hz, 1H), 4.90 (dd, J = 6.9 and 0.9 Hz, 1H), 6.79 (d, J = 8.4 Hz, 2H), 6.88 (dd, J = 3.0 and 0.9 Hz, 1H), 7.05 (d, J = 8.4 Hz, 2H), 7.10–7.23 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 42.74, 43.94, 51.76, 52.02, 52.09, 55.24, 114.25, 127.34, 128.51, 128.75, 128.78, 129.74, 131.26, 133.65, 135.07, 137.09, 139.77, 159.08, 165.84, 167.06, 167.52; ESIMS m/z 459 [M$^+$+Na]. Anal. Calcd for $C_{25}H_{24}O_7$: C, 68.80; H, 5.54. Found: C, 68.95; H, 5.27.
Compound ***3h***: 75%; white solid, mp 150–152 °C; IR (KBr) 2953, 1738, 1596 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.48–3.54 (m, 2H), 3.63 (s, 3H), 4.05–4.10 (m, 1H), 4.94 (s, 1H), 6.66–6.70 (m, 2H), 7.09–7.12 (m, 2H), 7.16–7.33 (m, 11H), 7.38 (d, J = 4.2 and 3.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 37.43, 41.04, 43.40, 47.52, 52.15, 125.91, 126.93, 127.16, 127.87, 128.35, 128.71, 128.85, 129.14, 129.30, 131.34, 132.90, 137.63, 140.19, 141.48, 166.02, 174.88, 176.37; ESIMS m/z 438 [M+H]$^+$. Anal. Calcd for $C_{28}H_{23}NO_4$: C, 76.87; H, 5.30; N, 3.20. Found: C, 77.03; H, 5.52; N, 3.09.
Compound ***4a***: 96%; white solid, mp 196–198 °C; IR (KBr) 2949, 1740, 1720, 1609 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.50 (s, 3H), 3.59 (s, 3H), 3.60 (s, 3H), 7.24–7.26 (m, 2H), 7.37–7.46 (m, 8H), 7.92 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 52.28, 52.34, 52.53, 127.79, 127.84, 128.16, 128.17, 128.46, 128.52, 132.26, 133.55, 133.61, 134.66, 137.65, 138.86, 139.24, 140.19, 167.20, 167.79, 168.01; ESIMS m/z 427 [M$^+$+Na]. Anal. Calcd for $C_{24}H_{20}O_6$: C, 71.28; H, 4.98. Found: C, 71.01; H, 5.14.
Compound ***4f***: 95%; white solid, mp 158–160 °C; IR (KBr) 2925, 1726, 1608 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.45 (s, 3H), 3.53 (s, 3H), 3.54 (s, 3H), 7.23–7.41 (m, 10H), 7.55–7.61 (m, 4H), 7.86 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 52.35, 52.46, 52.55, 126.41, 127.01, 127.46, 128.17, 128.18, 128.55, 128.80, 128.97, 132.32, 133.58, 133.65, 134.72, 136.64, 138.84, 138.89, 140.25, 140.39, 140.42, 167.25, 167.85, 168.01; ESIMS m/z 503 [M$^+$+Na], 449 [M$^+$-OMe]. Anal. Calcd for $C_{30}H_{24}O_6$: C, 74.99; H, 5.03. Found: C, 75.30; H, 5.15.
Compound ***4h***: 66%; white solid, mp 174–176 °C; IR (KBr) 2988, 1726, 1435 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.55 (s, 3H), 7.21–7.33 (m, 7H), 7.35–7.44 (m, 6H), 7.53–7.57 (m, 2H), 8.03 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 52.54, 126.64, 127.77, 128.06, 128.17, 128.39, 128.61, 128.81, 129.04, 129.40, 129.47, 129.67, 131.24, 134.74, 135.26, 137.18, 138.23, 139.42, 140.51, 165.40, 165.58, 167.05; ESIMS m/z 434 [M$^+$+H]. Anal. Calcd for $C_{28}H_{19}NO_4$: C, 77.59; H, 4.42; N, 3.23. Found: C, 77.67; H, 4.61; N, 3.12.
7. For the biologically interesting substances bearing a tricyclo[3.2.1.0^{2,7}]oct-3-ene skeleton and their synthesis, see: (a) Levin, S.; Nani, R. R.; Reisman, S. E. *J. Am. Chem. Soc.* **2011**, *133*, 774–776; (b) Tseng, C.-C.; Ding, H.; Li, A.; Guan, Y.; Chen, D. Y.-K. *Org. Lett.* **2011**, *13*, 4410–4413; (c) Pelletier, S. W.; Mody, N. V.; Djarmati, Z.; Lajsic, S. D. *J. Org. Chem.* **1976**, *41*, 3042–3044; (d) Ng, S. M.; Beaudry, C. M.; Trauner, D. *Org. Lett.* **2003**, *5*, 1701–1704; (e) Leverrier, A.; Martin, M.-T.; Servy, C.; Ouazzani, J.; Retailleau, P.; Awang, K.; Mukhtar, M. R.; Gueritte, F.; Litaudon, M. *J. Nat. Prod.* **2010**, *73*, 1121–1125; (f) Hong, Y. J.; Tantillo, D. J. *J. Am. Chem. Soc.* **2010**, *132*, 5375–5386; (g) Corey, E. J.; Wess, G.; Xiang, Y. B.; Singh, A. K. *J. Am. Chem. Soc.* **1987**, *109*, 4717–4718; (h) Zhu, S.; Wu, L.; Huang, X. *RSC Adv.* **2012**, *2*, 132–134; (i) Barluenga, J.; Tudela, E.; Vicente, R.; Ballesterous, A.; Tomas, M. *Angew. Chem., Int. Ed.* **2011**, *50*, 2107–2110; (j) Wu, T.-C.; Chen, J.-J.; Wu, Y.-T. *Org. Lett.* **2011**, *13*, 4794–4797; (k) Yamaguchi, K.; Eto, M.; Yoshitake, Y.; Harano, K. *Chem. Pharm. Bull.* **2009**, *57*, 749–751; (l) Skropeta, D.; Rickards, R. W. *Tetrahedron Lett.* **2007**, *48*, 3281–3284; (m) Mehta, G.; Ravikrishna, C. *Tetrahedron Lett.* **1996**, *37*, 2655–2658; (n) Brand, R. A.; Mulvaney, J. E. *J. Org. Chem.* **1980**, *45*, 633–636.
8. *Crystal data of compound* ***3a***: solvent of crystal growth (MeOH); empirical formula $C_{24}H_{22}O_6$, Fw = 406.42, crystal dimensions 0.20 × 0.15 × 0.12 mm^3, triclinic, space group P-1, a = 9.6339(2) Å, b = 10.8386(2) Å, c = 11.0779(2) Å, α = 91.7120(10)°, β = 100.6100(10)°, γ = 112.3090(10)°, V = 1045.50(3) Å^3, Z = 2, D_{calcd} = 1.291 mg/m^3, F_{000} = 428, MoKα (λ = 0.71073 Å), R_1 = 0.0495, wR_2 = 0.1246, GOF = 1.038 (I >2 (I)). We omitted hydrogen atoms for clarity (Fig. 1). The X-ray data have been deposited in CCDC with number 882797.
Crystal data of compound ***5a***: solvent of crystal growth (MeOH); empirical formula $C_{30}H_{28}O_{10}$, Fw = 548.52, crystal dimensions 0.30 × 0.15 × 0.12 mm^3, monoclinic, space group P2(1)/c, a = 8.99910(10) Å, b = 16.2594(3) Å, c = 18.6196(3) Å, α = 90.00°, β = 100.6950(10)°, γ = 90.00°, V = 2677.09(7) Å^3, Z = 4, D_{calcd} = 1.361 mg/m^3, F_{000} = 1152, MoKα (λ = 0.71073 Å), R_1 = 0.0539,

wR_2 = 0.1396, GOF = 1.034 (I >2 (I)). We omitted hydrogen atoms for clarity (Fig. 1). The X-ray data have been deposited in CCDC with number 882798.

9. *Typical procedure for the synthesis of* ***5a***: To a stirred solution of **3a** (203 mg, 0.5 mmol) and DMAD (213 mg, 1.5 mmol) in toluene (2.0 mL) was added DBU (8 mg, 0.05 mmol), and the reaction mixture was stirred at room temperature for 12 h under N_2 atmosphere. After aqueous extractive workup and column chromatographic purification process (hexanes/CH_2Cl_2/Et_2O, 4:3:1), compound **5a** was obtained as a white solid, 173 mg (63%) along with **4a** (14 mg, 7%). Other compounds were synthesized similarly, and the selected spectroscopic data of **5a** and **5c** are as follows.
Compound ***5a***: 63%; white solid, mp 172–174 °C; IR (KBr) 2951, 1725, 1602, 1520, 1434 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.29 (s, 3H), 3.62 (s, 3H), 3.67 (s, 3H), 3.76 (s, 3H), 3.79 (s, 1H), 3.84 (s, 3H), 4.24 (s, 1H), 4.34 (s, 1H), 7.02–7.05 (m, 2H), 7.24–7.26 (m, 3H), 7.32–7.38 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 31.79, 39.27, 42.67, 49.39, 49.70, 51.51, 52.33, 52.67, 52.83 (2C), 58.13, 123.02, 127.77, 128.05, 128.11, 128.15, 128.31, 128.43, 133.23, 137.52, 139.23, 166.92, 167.28, 167.89, 168.47, 169.19; ESIMS m/z 571 [M^++Na]. Anal. Calcd for $C_{30}H_{28}O_{10}$: C, 65.69; H, 5.15. Found: C, 65.45; H, 5.30.
Compound ***5c***: 54%; white solid, mp 186–188 °C; IR (KBr) 2950, 1739, 1721, 1609, 1435 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.26 (s, 3H), 3.58 (s, 3H), 3.63 (s, 3H), 3.71 (s, 3H), 3.78 (s, 1H), 3.81 (s, 3H), 4.21 (s, 1H), 4.32 (s, 1H), 7.05 (d, J = 8.1 Hz, 2H), 7.22–7.45 (m, 10H), 7.48–7.56 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 31.83, 39.39, 42.78, 49.36, 49.62, 51.62, 52.40, 52.74, 52.89, 52.92, 58.22, 123.07, 126.79, 126.98, 127.10, 127.24, 127.30, 127.51, 128.27, 128.64, 128.70, 128.82, 132.31, 136.42, 139.11, 140.53, 140.55, 140.68, 141.25, 167.02, 167.31, 167.89, 168.50, 169.25; ESIMS m/z 669 [M^+−OMe]. Anal. Calcd for $C_{42}H_{36}O_{10}$: C, 71.99; H, 5.18. Found: C, 71.67; H, 5.42.
10. When we added an equivalent amount of DBU in order to shorten the reaction time, the amount of oxidation product **4a** increased. The mechanism for the aromatization of **3**–**4** is not clear at this stage. DBU-mediated dehydrogenation[2d] could be one of the possible mechanisms, while a sequential deprotonation, hydroperoxide formation, and a following dehydration process cannot be ruled out. [2f,4a] For some additional references on the base-mediated aerobic oxidations, see: (a) Ikeda, S.-i.; Mori, N.; Sato, Y. *J. Am. Chem. Soc.* **1997**, *119*, 4779–4780; (b) Gil, M. V.; Roman, E.; Serrano, J. A. *Tetrahedron Lett.* **2001**, *42*, 4625–4628; (c) Kim, S. H.; Lee, H. S.; Park, B. R.; Kim, J. N. *Bull. Korean Chem. Soc.* **2011**, *32*, 1725–1728.
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13. The Diels–Alder reaction between **2a** and other alkynes such as diphenylacetylene or ethyl propiolate was examined; however, no reaction was observed even under refluxing ODCB conditions.
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