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Expedient synthesis of highly substituted α-pyrones from Baylis–Hillman adducts and their conversion to poly-substituted aromatics

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Dedicated to the memory of the late Professor Eung Kul Ryu whose vision, passion in Organic, Medicinal Chemistry was an inspiration for all

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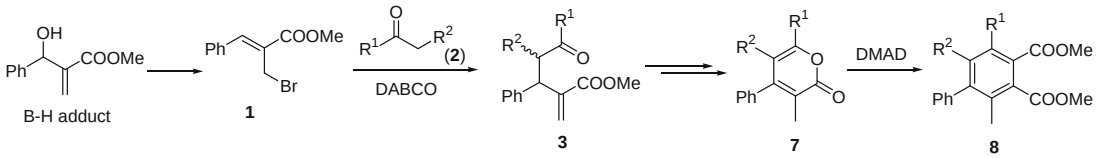
ABSTRACT

An efficient synthetic protocol of fully substituted α-pyrones has been developed starting from the Baylis–Hillman adducts. Subsequent Diels–Alder reaction of the α-pyrones and DMAD produced poly-substituted aromatic compounds in high yields.

Recently, syntheses of a variety of acyclic and cyclic compounds including various aromatic and heterocyclic compounds have been carried out starting from the Baylis–Hillman adducts.[1] Based on the importance of poly-substituted aromatic compounds, the synthesis of highly substituted benzenes and naphthalenes in a regioselective manner has been regarded as the most fruitful chemical transformation in Baylis–Hillman chemistry.[1]

α-Pyrones have been used as important synthetic intermediates[2–6] and are found in a wide variety of biologically interesting natural substances.[4] Thus, considerable efforts have been devoted to the synthesis of α-pyrones[2,5] and related compounds[3] by numerous approaches involving transition metal-catalyzed reactions.[2a,c,d,f] Among the synthetic usefulness of α-pyrones, Diels–Alder cycloaddition has been used as an efficient method to reach highly substituted aromatic compounds.[6]

In these contexts, we decided to develop an efficient synthetic method of highly substituted α-pyrones **7** and their chemical transformations including Diels–Alder reaction with DMAD (dimethylacetylene dicarboxylate) to benzene derivatives **8** and their oxidation with DDQ (1,2-dichloro-4,5-dicyanobenzoquinone) to naphthalene derivatives **9** when R^1-R^2 is a cyclohexane moiety (vide infra), as shown in Scheme 1. Our synthetic rationale of α-pyrone skeleton is a combination of the first introduction of a suitable ketone derivative **2** at the secondary position of the Bay-



Scheme 1.

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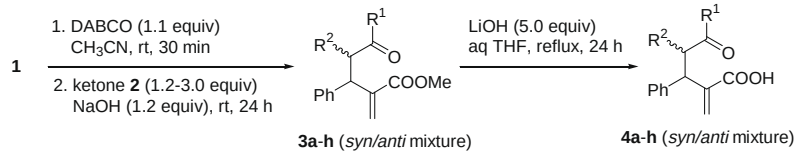
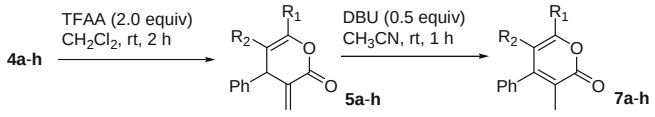
Table 1
Synthesis of starting materials **4a–h** from **1** and **2a–h**



Entry	Ketone **2**[a]	**3a–h**[b] (%)	**4a–h**[c] (%)
1	Deoxybenzoin (**2a**)	**3a** (78, 2:1)	**4a** (97)
2	Desoxyanisoin (**2b**)	**3b** (75, 2:1)	**4b** (95)
3	Propiophenone (**2c**)	**3c** (62, 2:1)	**4c** (90)
4	α-Tetralone (**2d**)	**3d** (62, 3:2)	**4d** (89)
5	Acetophenone (**2e**)	**3e** (60)	**4e** (93)
6	Cyclohexanone (**2f**)	**3f** (54, 9:1)	**4f** (92)
7	4-Methlcyclohexanone (**2g**)	**3g** (44, 2:1)	**4g** (92)
8	4-Phenylcyclohexanone (**2h**)	**3h** (45, 4:1)	**4h** (92)

[a] Ketone **2a–d** (1.2 equiv) and ketone **2e–h** (3.0 equiv) were used.
[b] The ratio of *syn*/*anti* is arbitrary and measured in ^{1}H NMR.
[c] Crude product (*syn*/*anti* mixture) and not characterized.

Table 2
Synthesis of α-pyrones **7a–h** from **4a–h**



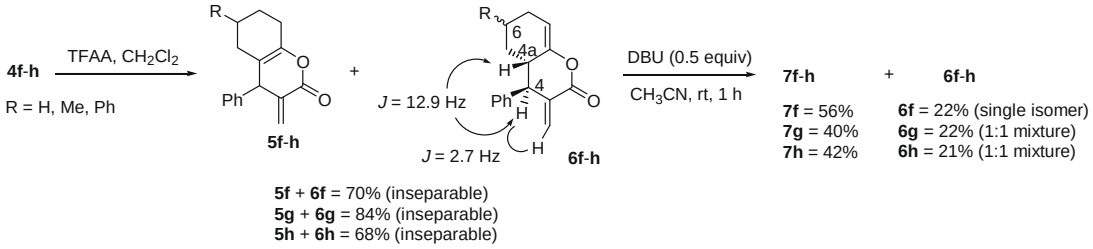
Entry	**5** (%)	**7** (%)
1	**5a** (91)	**7a** (87)
2	**5b** (88)	**7b** (74)
3	**5c** (83)	**7c** (78)
4	**5d** (90)	**7d** (74)
5	**5e** (85)	**7e** (85)
6	**5f** + **6f** (70)[a]	**7f** (56)[b] + **6f** (22)[b]
7	**5g** + **6g** (84)[a]	**7g** (40)[b] + **6g** (22)[b]
8	**5h** + **6h** (68)[a]	**7h** (42)[b] + **6h** (21)[b]

[a] Inseparable mixture of **5f–h** and **6f–h**.
[b] See Scheme 2.

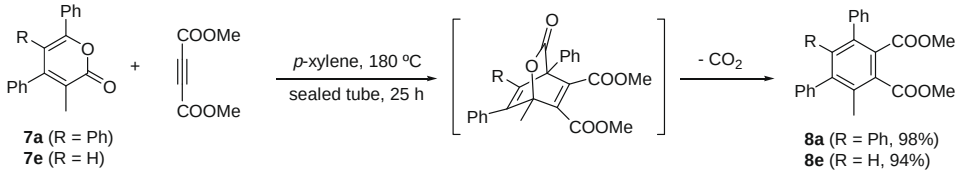
lis–Hilman adduct via the DABCO salt concept[7] and the following cyclization to α-pyrone as reported previously.[5]

As summarized in Table 1, synthesis of starting materials δ-keto acids **4a–h** was carried out by the following sequential processes: (i) synthesis of cinnamyl bromide **1** from Baylis–Hillman adduct as reported,[8] (ii) introduction of various ketone derivatives **2a–h** at the secondary position of the Baylis–Hillman adduct via the DABCO salt of **1** to form **3a–h**,[7,9] and (iii) hydrolysis of **3a–h** with LiOH in aqueous THF to make **4a–h**.[9] The δ-keto esters **3a–h** and δ-keto acids **4a–h** were obtained as an inseparable *syn/anti* mixture and we used them in the next cyclization without separation.

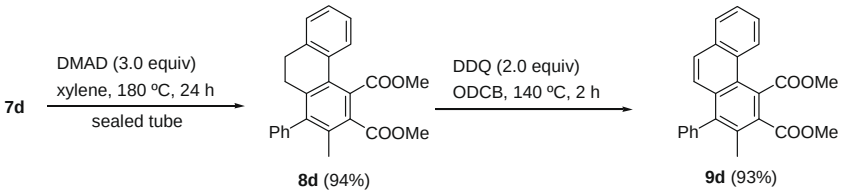
With δ-keto acids **4a–h**, we synthesized α-pyrones **7a–h** via the sequential lactonization of **4a–h** with TFAA to methylene lactones **5a–h** and the following DBU-catalyzed isomerization.[9,10] The results are summarized in Table 2. The yields of methylene lactones **5a–e** were good (83–91%) and the following DBU-catalyzed isomerization produced α-pyrones **7a–e** in good yields (74–87%) also. However, *exo*-methylene compounds **6f–h** were formed together in appreciable amounts during the synthesis of **5f–h** (entries 6–8) and the separation of **5f–h**/**6f–h** was very difficult. However,



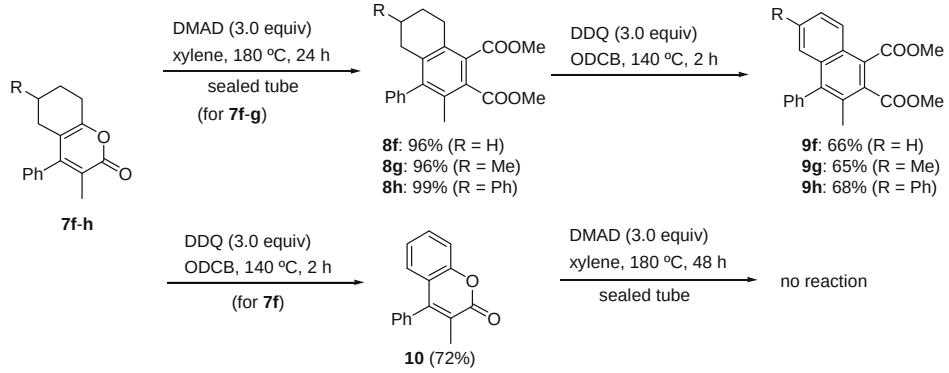
Scheme 2.



Scheme 3.



Scheme 4.



Scheme 5.

treatment of the mixture **5f**/**6f** with DBU produced desired α-pyrone **7f** (56%). During the isomerization process, **6f** (22%) was recovered without change very fortunately as schematically explained in Scheme 2. The situation was same for the mixtures **5g**/**6g** and **5h**/**6h**. Compound **6f** was obtained as a single isomer while **6g** and **6h** were a diastereomeric mixture (1:1) due to the presence of the substituent -R at 6-position.[11] In ^{1}H NMR spectrum of compound **6f**, as an example, the proton at 4-position (δ = 3.36 ppm) coupled with the proton at 4a-position with a large coupling constant (J = 12.9 Hz), which stated that the two protons are in *trans*-relationships, as shown in Scheme 2.

As a next trial, we examined the synthesis of fully substituted aromatic compounds with the synthesized α-pyrone derivatives (Schemes 3–5). The reaction of **7a** and DMAD in *p*-xylene in a sealed tube afforded a fully substituted benzene **8a** in 98% via the [4+2] cycloaddition and concomitant decarboxylation process (Scheme 3).[6] Compound **8e** was synthesized from **7e** in 94% similarly. Diels–Alder reaction of **7d** and DMAD also produced **8d** (94%), which was converted into phenanthrene derivative **9d** via oxidation with DDQ in *o*-dichlorobenzene (ODCB) in 93% (Scheme 4). Cyclohexane-fused compounds **7f**–**h** were also converted into naphthalene derivatives **9f**–**h**, via the sequential Diels–Alder reaction with DMAD to **8f**–**h** (96–99%) and the following oxidation with DDQ (Scheme 5). It is interesting to note that oxidation of **7f** with DDQ produced compound **10**, however, Diels–Alder reaction of **10** and DMAD did not produce compound **9f** at all, as depicted also in Scheme 5.

In summary, we developed an efficient synthetic protocol of poly-substituted α-pyrones including chromen-2-one. In addition, we prepared various aromatic compounds including poly-substi-

tuted benzenes, naphthalene, and phenanthrene from the prepared α-pyrones by using DDQ oxidation and/or Diels–Alder reaction with DMAD.

Acknowledgments

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9. Typical procedure for the synthesis of **3a**, **4a**, **7a,** and **8a**: A mixture of cinnamyl bromide **1** (765 mg, 3.0 mmol) and DABCO (370 mg, 3.3 mmol) in CH_3CN (5 mL) was stirred for 30 min at room temperature (20–25 °C). To the reaction mixture deoxybenzoin (**2a**, 706 mg, 3.6 mmol) and NaOH (144 mg, 3.6 mmol) were added and stirred further for 24 h at room temperature (20–25 °C). After the usual aqueous extractive workup and column chromatographic purification process (hexanes/CH_2Cl_2/ether, 15:1:1) compound **3a** was isolated as a white solid, 866 mg (78%, *syn/anti* mixture). *Compound* **3a** (740 mg, 2.0 mmol) was dissolved in aqueous THF (H_2O/THF, 1:1, 5 mL) and LiOH (420 mg, 10 mmol) was added and the reaction mixture was heated to reflux for 24 h. After cooling to room temperature, the reaction mixture was acidified with dilute HCl solution and extracted with CH_2Cl_2 (50 mL). Drying with $MgSO_4$ and removal of solvent provided compound **4a** as a white solid in a crude state, 691 mg (97%). To the crude **4a** (534 mg, 1.5 mmol) in CH_2Cl_2 (4 mL) was added TFAA (630 mg, 3.0 mmol) and stirred at room temperature (20–25 °C) for 2 h. After the usual aqueous extractive workup and column chromatographic purification process (hexanes/ether, 10:1) compound **5a** was isolated as a white solid, 461 mg (91%). *Compound* **5a** (338 mg, 1.0 mmol) in CH_3CN (3 mL) was treated with DBU (76 mg, 0.5 mmol) and stirred at room temperature (20–25 °C) for 1 h. After the usual aqueous extractive workup and column chromatographic purification process (hexanes/CH_2Cl_2/ether, 15:1:1) compound **7a** was isolated as a white solid, 294 mg (87%). A mixture of **7a** (169 mg, 0.5 mmol) and DMAD (213 mg, 1.5 mmol) in *p*-xylene (1 mL) was heated to 180 °C in a sealed tube for 25 h. After removal of solvent and column chromatographic purification process (hexanes/CH_2Cl_2/ether, 15:1:1) compound **8a was isolated** as a white solid, 214 mg (98%). Other compounds were synthesized analogously and representative spectroscopic data of **7a**, **7b**, **7d**, **7f**, **6f**, **8a**, **8d**, **9d**, and **9h** are as follows. Known compounds, **7c**,[2a] **7e**,[2a] **8f**,[6a] and **10**[3a] were identified by comparison with the reported data.
Compound **7a**: 87%; white solid, mp 176–178 °C; IR (KBr) 1712, 1540, 1489 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.98 (s, 3H), 6.81–6.92 (m, 4H), 6.98–7.08 (m, 3H), 7.12–7.29 (m, 8H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.63, 119.37, 121.13, 127.05, 127.53, 127.81, 127.91, 128.00, 128.27, 129.14 (2C), 131.19, 132.73, 135.15, 136.57, 154.59, 154.61, 163.46; ESIMS *m/z* 339 (M^++1). Anal. Calcd for $C_{24}H_{18}O_2$: C, 85.18; H, 5.36. Found: C, 85.01; H, 5.49.
Compound **7b**: 74%; pale yellow solid, mp 202–204 °C; IR (KBr) 1705, 1606, 1504 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.95 (s, 3H), 3.69 (s, 3H), 3.75 (s, 3H), 6.55–6.60 (m, 2H), 6.67–6.75 (m, 4H), 6.87–6.91 (m, 2H), 7.14–7.26 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.57, 55.00, 55.17, 113.28, 113.56, 117.96, 120.13, 125.29, 127.41, 127.61, 127.93, 128.25, 130.62, 132.26, 136.89, 154.62, 155.19, 158.38, 160.02, 163.66; ESIMS *m/z* 399 (M^++1). Anal. Calcd for $C_{26}H_{22}O_4$: C, 78.37; H, 5.57. Found: C, 78.62; H, 5.44.
Compound **7d**: 74%; yellow solid, mp 172–174 °C; IR (KBr) 1697, 1629, 1530 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.92 (s, 3H), 2.31 (t, *J* = 7.8 Hz, 2H), 2.78 (t, *J* = 7.8 Hz, 2H), 7.12–7.18 (m, 3H), 7.25–7.34 (m, 2H), 7.39–7.51 (m, 3H), 7.88–7.91 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.50, 23.39, 27.49, 112.64, 120.98, 123.04, 127.04, 127.47, 127.56, 128.24, 128.37, 128.77, 129.65, 136.14, 136.69, 151.64, 153.90, 163.40; ESIMS *m/z* 289 (M^++1). Anal. Calcd for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 83.24; H, 5.76.
Compound **7f**: 56%; colorless oil; IR (film) 1712, 1642, 1558 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.56–1.64 (m, 2H), 1.66–1.80 (m, 2H), 1.82 (s, 3H), 1.93–1.97 (m, 2H), 2.55–2.59 (m, 2H), 7.06–7.10 (m, 2H), 7.35–7.47 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.95, 21.68, 22.29, 25.18, 27.47, 112.50, 119.58, 127.29, 127.96, 128.60, 136.37, 154.50, 156.07, 164.19; ESIMS *m/z* 241 (M^++1).
Compound **6f**: 22%; colorless oil; IR (film) 1739, 1680, 1237, 1166 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.10–1.26 (m, 1H), 1.34–1.49 (m, 1H), 1.53–1.71 (m, 2H), 2.03–2.16 (m, 2H), 2.67–2.77 (m, 1H), 3.36 (dt, *J* = 12.9 and 2.7 Hz, 1H), 5.13 (dd, *J* = 2.7 and 1.2 Hz, 1H), 5.49–5.52 (m, 1H), 6.56 (dd, *J* = 2.7 and 1.2 Hz, 1H), 7.13–7.17 (m, 2H), 7.28–7.41 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.96, 23.41, 28.31, 37.79, 50.22, 107.33, 127.53, 128.76, 128.94, 130.19, 138.74, 138.78, 150.03, 162.73; ESIMS *m/z* 241 (M^++1).
Compound **8a**: 98%; white solid, mp 159–162 °C; IR (KBr) 1736, 1219 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.18 (s, 3H), 3.46 (s, 3H), 3.91 (s, 3H), 6.65–6.71 (m, 2H), 6.79–6.87 (m, 3H), 6.92–7.19 (m, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.28, 52.09, 52.56, 125.83, 126.58, 126.62, 126.69, 127.17, 127.71, 129.69, 129.84, 130.57, 131.41, 132.03, 133.94, 137.77, 138.63, 138.71, 139.38, 143.33, 144.46, 168.82, 168.97; ESIMS *m/z* 437 (M^++1). Anal. Calcd for $C_{29}H_{24}O_4$: C, 79.80; H, 5.54. Found: C, 79.97; H, 5.78.
Compound **8d**: 94%; white solid, mp 174–175 °C; IR (KBr) 1736, 1221 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.07 (s, 3H), 2.38–2.42 (m, 2H), 2.64–2.69 (m, 2H), 3.76 (s, 3H), 3.91 (s, 3H), 7.07–7.14 (m, 2H), 7.17–7.25 (m, 3H), 7.33–7.49 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.90, 27.71, 28.85, 52.46, 52.53, 126.38, 126.63, 127.37, 127.50, 127.83, 128.53, 128.76, 128.79, 131.71, 131.87, 132.98, 133.15, 138.48, 139.64, 140.23, 143.12, 169.34, 170.53; ESIMS *m/z* 387 (M^++1). Anal. Calcd for $C_{25}H_{22}O_4$: C, 77.70; H, 5.74. Found: C, 77.89; H, 5.48.
Compound **9d**: 93%; white solid, mp 67–69 °C; IR (KBr) 1736, 1282 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.21 (s, 3H), 3.97 (s, 3H), 3.98 (s, 3H), 7.20–7.25 (m, 3H), 7.43–7.61 (m, 6H), 7.80–7.84 (m, 1H), 8.19–8.23 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.06, 52.73, 52.92, 124.64, 125.58, 125.77, 126.27, 127.06, 127.60, 128.45, 128.57, 128.68, 128.72, 128.92, 129.74, 130.74, 132.27, 132.43, 132.70, 139.05, 142.27, 169.58, 171.47; ESIMS *m/z* 385 (M^++1). Anal. Calcd for $C_{25}H_{20}O_4$: C, 78.11; H, 5.24. Found: C, 78.05; H, 5.49.
Compound **9h**: 68%; colorless oil; IR (film) 1732, 1212 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.22 (s, 3H), 3.96 (s, 3H), 4.04 (s, 3H), 7.24–7.56 (m, 11H), 7.77 (dd, *J* = 8.7 and 1.8 Hz, 1H), 8.27 (d, *J* = 8.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.39, 52.58, 52.76, 124.58, 126.23, 126.49, 127.30, 127.35, 127.64, 127.71, 128.71, 128.81 (2C), 129.74, 130.16, 132.22, 133.83, 138.70, 139.88, 140.45, 142.87, 168.22, 169.25; ESIMS *m/z* 411 (M^++1). Anal. Calcd for $C_{27}H_{22}O_4$: C, 79.01; H, 5.40. Found: C, 79.33; H, 5.74.
10. For DBU-mediated isomerization, see: (a) Kim, K. H.; Lee, H. S.; Kim, J. N. *Tetrahedron Lett.* **2009**, *50*, 1249–1251; (b) Kim, S. C.; Lee, H. S.; Lee, Y. J.; Kim, J. N. *Tetrahedron Lett.* **2006**, *47*, 5681–5685; (c) Lee, M. J.; Lee, K. Y.; Gowrisankar, S.; Kim, J. N. *Tetrahedron Lett.* **2006**, *47*, 1355–1358.
11. It is interesting to note that the phenyl group at 4-position of **7g** and **7h** showed the presence of six carbon peaks in their ^{13}C NMR spectrum, presumably due to an asymmetry effect provided by the substituent at 6-position (–CH_3 or phenyl). The situation is same for the phenyl group of compounds **8g** and **8h**.