As a result of hydrolysis, dicarbonyl compounds (e.g., the behavior of cations
formed, which is opened as for azanaphthalenes and in the case of the reaction of
1,3,5-triazines with naphthalene-1,8-dicarbaldehyde (Scheme 1; Table 1, entry 1). A byproduct, isoquinolino[6',5',4':10,5,6]anthra[2,1,9-def]isoquinoline (10), is formed in ~6% yield. It is likely that compound 10 is formed by the mechanism shown in Scheme 3. Thus, sequential heating of naphthalene (1) with 1,3,5-triazine (3a) at 65–70 °C for 3 hours, then at 130–140 °C for 6 hours, leads to the formation of 10 in 27% yield (Table 1, entry 2).

In the case of the 2-naphthyl ethers 2a,b, reaction with an equimolar quantity of 1,3,5-triazine (3a) in polyphosphoric acid at 110–115 °C leads to the formation of 4H-benzo[de]isoquinolin-4-one (9a) in 36–64% yield.
In conclusion, the advantages of the described methods in polyphosphoric acid at 40–45 °C for one hour, then at 100–110 °C for three hours (Table 1, entries 3, 5 and 7).

Accordingly, we were able to increase the yield of the 4H-benzo[de]isoquinolin-4-ones 9 up to 67–89% by heating 2-naphthyl ethers 2 with a 1.1 molar excess of triazines 3 in polyphosphoric acid at 40–45 °C for one hour, then at 100–115 °C for three hours (Table 1, entries 3, 5 and 7). Compounds 11 were obtained in 68–91% yield by the reaction of compounds 2 with a 2.5 molar excess of triazines 3 at 75–80 °C for five hours (Table 1, entries 4, 6 and 8).

In conclusion, the advantages of the described methods for 1,6-diacylation (diformylation) and [cd]pyridine cycle peri-annelation include reagent availability, experimental simplicity and applicability to the synthesis of a broad range of naphthalene derivatives.

Preparative column chromatography was performed on SDS flash silica gel (35–70 mesh). Evaporation of solvent was carried out using a rotary evaporator under reduced pressure (2–400 mbar) with a bath temperature of up to 60 °C. Thin-layer chromatography (TLC) was performed on Silufol UV-254 silica gel plates. In general, the course of reactions was followed by TLC. NMR spectra were obtained on a Bruker AM-300 spectrometer at 300 MHz (1H) and 75 MHz (13C) using CD3OD, CDCl3 or DMSO-d6 as solvent. Chemical shifts are expressed in ppm downfield from TMS, which was used as an internal standard. IR spectra were recorded on a Perkin-Elmer FTIR spectrophotometer. Mass spectra were recorded on a Varian CH 7 spectrometer. Melting points of small samples were obtained after recrystallization; solvents are given in parentheses. Microanalyses were carried out on a CHN-1 Elemental Analyzer. 2,4,6-Trimethyl-1,3,5-triazine (3b) was obtained by a known procedure. Other chemicals used in this study were commercially available.

**Naphthalene-1,8-dicarbalddehyde (8)**

A mixture of naphthalene (1; 0.128 g, 1 mmol) and 1,3,5-triazine (3a; 0.12 g, 1.5 mmol) in PPA (3–4 g) was stirred at 65–70 °C for 3 h and then at 100–110 °C for 2 h. The reaction mixture was poured into cold H2O (30 mL) with intense stirring. The resulting mixture was extracted with EtOAc (3 × 50 mL). The solution was concentrated under reduced pressure; compound 8 was purified by flash chromatography on silica gel (EtOAc): yield: 0.057 g (31%); mp 139–141 °C (H2O) (Lit.5 140–141 °C). For spectroscopic data, see Ref.1d.

**4H-Benzof[cd]isoquinolin-4-ones 9a,b**

A mixture of the 2-naphthyl ether 2a or 2b (1 mmol) and the corresponding 1,3,5-triazine 3a,b (1.1 mmol) in PPA (3–4 g) was stirred at 40–45 °C for 1 h and then at 100–110 °C for 3 h. The reaction mixture was poured into cold H2O (30 mL) with intense stirring. The resulting mixture was extracted with EtOAc (3 × 50 mL); compounds 11 were extracted. The aqueous layer was basified with ammonia to pH 8–9 and, after cooling, the precipitated crystals or oil was extracted with EtOAc (3 × 50 mL). The solution was concent-

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**Table 1** Reaction Conditions

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>X</th>
<th>Ratio</th>
<th>Temp (°C), time (h)</th>
<th>Product: yield (%)</th>
<th>Product: yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>H</td>
<td>1:1.5</td>
<td>65–70, 3; then 100–110, 2</td>
<td>8: 31</td>
<td>10: 6</td>
</tr>
<tr>
<td>2</td>
<td>H</td>
<td>H</td>
<td>1:1.5</td>
<td>65–70, 3; then 130–140, 6</td>
<td>10: 27</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>OMe</td>
<td>1:1.1</td>
<td>40–45, 1; then 100–110, 3</td>
<td>9a: 87</td>
<td>11a: 9</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>OMe</td>
<td>1:2.5</td>
<td>75–80, 5</td>
<td>9a: 8</td>
<td>11a: 88</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>OEt</td>
<td>1:1.1</td>
<td>40–45, 1; then 100–110, 3</td>
<td>9a: 89</td>
<td>11b: 7</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>OEt</td>
<td>1:2.5</td>
<td>75–80, 5</td>
<td>9a: 7</td>
<td>11b: 91</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>OEt</td>
<td>1:1.1</td>
<td>40–45, 1; then 110–115, 3</td>
<td>9b: 67</td>
<td>11c: 11</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>OEt</td>
<td>1:2.5</td>
<td>75–80, 5</td>
<td>9b: 6</td>
<td>11c: 68</td>
<td></td>
</tr>
</tbody>
</table>
trated under reduced pressure, and the residue was purified by crystallization.

4H-Benzof[de]isoquinolin-4-one (9a)
Yield: 0.158 g (87%) from 2a with 3a; yield: 0.161 g (89%) from 2b with 3a; yellow crystals; mp 169–171 °C (EtOAc; with sublimation).

IR (KBr): 1654 (C=O) cm–1.

1H NMR (300 MHz, DMSO-d6): δ = 6.71 (d, J = 9.9 Hz, 1 H, H-5), 7.87 (dd, J = 7.3, 8.0 Hz, 1 H, H-6), 8.07 (d, J = 9.9 Hz, 1 H, H-6), 8.22 (dd, J = 7.3, 0.8 Hz, 1 H, H-7), 8.40 (dd, J = 8.0, 0.8 Hz, 1 H, H-9), 9.31 (s, 1 H, H-1), 9.71 (s, 1 H, H-3).

13C NMR (75 MHz, CF3CO2D): δ = 147.30, 147.41, 130.38, 124.89, 126.12, 127.00, 132.12, 133.91, 134.14, 139.11, 165.01, 190.93, 191.61.

MS (EI): m/z (%) = 328 (100) [M+], 240 (98), 191 (80), 153 (32), 131 (22).


2-Methoxynaphthalene-1,6-dicarbaldehyde (11a)
Yield: 0.188 g (88%) from 2a with 3a; light yellow crystals; mp 158–159 °C (EtOH).

IR (KBr): 1691, 1682 (C=O) cm–1.

1H NMR (300 MHz, CDCl3): δ = 4.07 (s, 3 H, Me), 7.36 (d, J = 9.1 Hz, 1 H, H-3), 8.01 (dd, J = 9.1, 1.8 Hz, 1 H, H-7), 8.16 (d, J = 9.1 Hz, 1 H, H-4), 8.20 (d, J = 1.8 Hz, 1 H, H-5), 9.31 (d, J = 9.1 Hz, 1 H, H-6), 10.07 (s, 1 H, 1-CHO), 10.81 (s, 1 H, 1-CHO).

13C NMR (75 MHz, DMSO-d6): δ = 56.57, 113.53, 116.65, 125.72, 127.03, 127.49, 132.60, 133.49, 134.98, 137.81, 165.13, 191.45, 191.61.

Anal. Calcd for C13H10O3: C, 73.70; H, 4.64.

2-Ethynaphthalene-1,6-dicarbaldehyde (11b)
Yield: 0.207 g (91%) from 2b with 3a; light yellow crystals; mp 147–148 °C (EtOH).

IR (KBr): 1690, 1681 (C=O) cm–1.

1H NMR (300 MHz, CDCl3): δ = 1.54 (t, J = 6.9 Hz, 3 H, MeCH2), 4.34 (q, J = 6.9 Hz, 2 H, MeCH2), 7.36 (d, J = 9.1 Hz, 1 H, H-3), 8.05 (dd, J = 9.1, 1.8 Hz, 1 H, H-7), 8.19 (d, J = 9.1 Hz, 1 H, H-4), 8.25 (d, J = 1.8 Hz, 1 H, H-5), 9.37 (d, J = 9.1 Hz, 1 H, H-6), 10.11 (s, 1 H, 1-CHO), 10.90 (s, 1 H, 1-CHO).

13C NMR (75 MHz, DMSO-d6): δ = 14.42, 65.32, 115.44, 124.46, 124.89, 126.12, 127.00, 132.12, 133.91, 134.14, 139.11, 165.01, 190.93, 191.67.

MS (EI): m/z (%) = 228 (54) [M+], 199 (87), 171 (43), 144 (36), 115 (100).


1,6-Diacetyl-2-ethynaphthalene (11c)
Yield: 0.173 g (68%) from 2b with 3b; light yellow crystals; mp 172–173 °C (EtOH).

IR (KBr): 1736, 1678 (C=O) cm–1.

1H NMR (300 MHz, CDCl3): δ = 1.52 (t, J = 6.9 Hz, 3 H, MeCH2), 2.69 (s, 3 H, 6-COMe), 3.07 (s, 3 H, 1-COMe), 4.18 (q, J = 6.9 Hz, 2 H, MeCH2), 7.09 (d, J = 9.1 Hz, 1 H, H-3), 7.73 (d, J = 8.8 Hz, 1 H, H-8), 7.86 (d, J = 9.1 Hz, 1 H, H-4), 7.99 (dd, J = 8.8, 1.8 Hz, 1 H, H-7), 8.38 (d, J = 1.8 Hz, 1 H, H-5).


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References


(4) Polyphosphoric acid containing 86% P₂O₅ was used; preparation according to: Uhlig, F. Angew. Chem. 1954, 66, 435.

