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FLASH VACUUM PYROLYSIS OF NAPHTHALEN-1-YL AND -2-YL PROP-2-YNOATE

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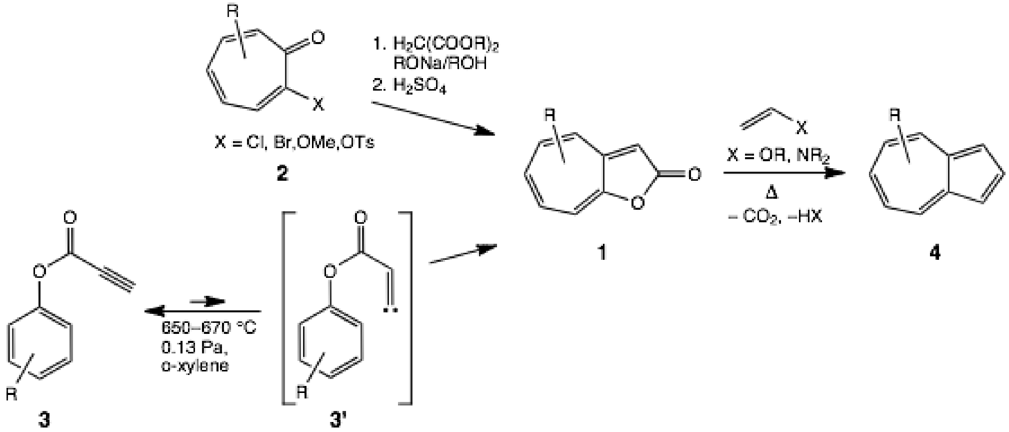
Dedicated to Albert Padwa on the occasion of his 75th birthday

Abstract – In contrast to phenyl prop-2-ynoates, which give on flash vacuum pyrolysis (FVP, 650 °C, 0.13 Pa, *o*-xylene) the corresponding 2*H*-cyclohepta[*b*]-furan-2-ones in acceptable yields, leads the FVP of naphthalen-1-yl prop-2-ynoate (**5a**) to the formation of benzo[1,2-*b*]furan (**6**, 17%) and naphthalen-1-ol (25%). A blue component (1.8%), which is found in the product mixture, turned out to be (*E*)-2-(4-metyl-2*H*-benzo[*h*]chromen-2-ylidene)naphthalen-1(2*H*)-one ((*E*)-**7**). On the other hand, naphthalene-2-yl prop-2-ynoate (**5b**) behave on FVP “normal” in that a cycloaddition dimer **11** (15%) of the primarily formed benzo[4,5]cyclohepta[1,2-*b*]furan-2(2*H*)-one (**10**) was isolated from the pyrolysate.

INTRODUCTION

2*H*-Cyclohepta[*b*]furan-2-ones **1** are excellent starting materials for the synthesis of azulenes by thermal [8 + 2] addition with enol ethers or enamines under loss of carbon dioxide and HX (X = OR and NR_2, respectively).[1] There are two main accesses to **1**, namely, following the Nozoe way, by base-catalyzed condensation reaction of tropolone derivatives **2** with C–H acidic compounds[2,3] or by flash vacuum pyrolysis (FVP) of phenyl prop-2-ynoates **3** according to original experiments of Trahanovsky *et al.*,[4,5] whereby the last procedure permits a broader variation and higher number of substituents at the seven-membered ring (Scheme 1).[6,7] The onset of the alkyne-ethenylidene equilibrium **3** ⇆ **3’**, which is necessary for the formation of **1** by intramolecular carbene addition to the benzene ring of **3’** followed by ring enlargement, lies at temperatures >600 °C. Ideal conditions for the FVP of **1** are therefore 650 °C at a pressure of 0.13 to 0.013 Pa with xylene as carrier of **3**. However, substituents at C(3) of the prop-2-ynoates such as Ph or Me hinder markedly the establishment of the discussed equilibrium at 650–670 °C, so that the yields of 3-substituted cyclohepta[1,2-*b*]furan-2-ones **1** are low or the furanones are not formed at all (see[8] and literature cited there). In the following part, we report on the FVP of a highly substituted phenyl prop-2-ynoate, and naphthalen-1-yl and 2-yl prop-2-ynoate where the alkyne-ethenylidene equilibrium should work, but which offer in part other problems as we found.

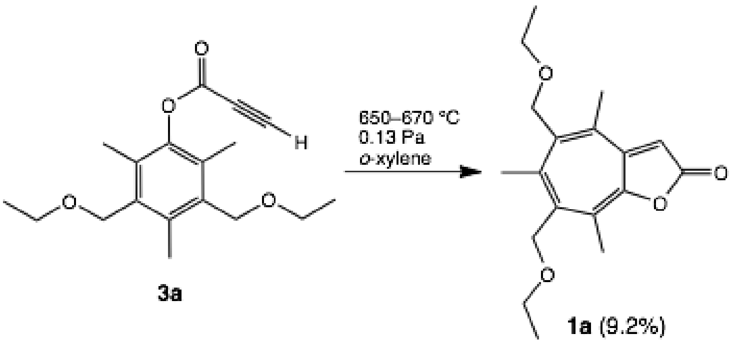


Scheme 1. Ways to cyclohepta[1,2-*b*]furan-2(2*H*)-ones

RESULTS AND DISCUSSION

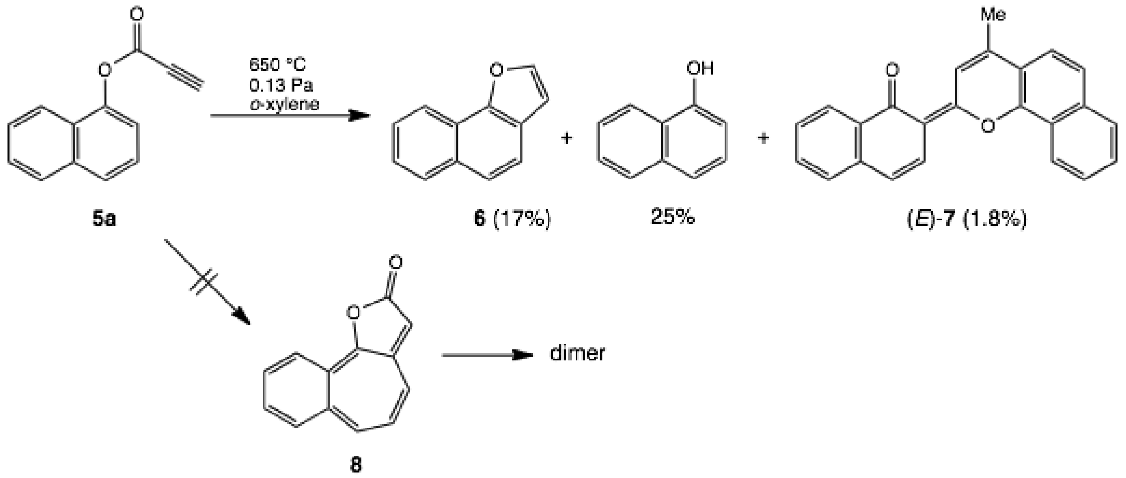
Naphthalen-1-yl prop-2-ynoate and naphthalene-2-yl prop-2-ynoate (**5a** and **5b**, respectively) as well as 3,5-bis(ethoxymethyl)-2,4,6-trimethylphenyl prop-2-ynoate (**3a**) were prepared from the corresponding naphthols and 4,6-bis(ethoxymethyl)-mesitol according to our earlier described procedure in excellent yield.[6]

The result of the FVP of **3a** was not surprising since we found the expected cyclohepta[*b*]furan-2-one **1a** in the pyrolysate, collected in the cooling trap (Scheme 2), albeit in a yield distinctly lower than in the comparable case of the FVP of 2,3,4,5,6-pentamethylphenyl prop-2-ynoate, where yields in the range of 15 – 40% of the corresponding pentamethylcyclohepta[*b*]furan-2-one **1** are realizable.[6] Nevertheless, the FVP of **3a** indicates that C–O bonds in benzylic position do survive the FVP at 650 – 670 °C (Scheme 2).



Scheme 2. FVP of 3,5-bis(ethoxymethyl)-2,4,6-trimethylphenyl prop-2-ynoate (**3a**)

The result of the FVP of **5a** was surprising by the fact that we found no indication for the presence of 2*H*-benzo[6,7]cyclohepta[1,2-*b*]furan-2-one (**8**) or a dimer of it (see later) in the cooling trap after warming (Scheme 3). Instead, we isolated by chromatography naphtho[1,2-*b*]furan (**6**) and 1-naphthol in moderate yields. Both compounds were identified by comparison with authentic samples spectroscopically.



Scheme 3. FVP of Naphthalen-1-yl propynoate (**5a**)

Most interesting was the isolation of a third blue component, the color of which developed just on warming of the yellow colored pyrolysate. It was characterized spectroscopically as (*E*)-2-(4-methyl-2*H*-benzo[*h*]chromen-2-ylidene)naphthalene-1(2*H*)-one ((*E*)-**7**). Most informative was its UV/VIS spectrum in $CHCl_3$ (Figure 1), since it showed in the long-wavelength region around 560 nm an intense almost symmetric band with clear recognizable vibrational splitting of $\Delta\nu$ = ca. 1200 cm^{-1} (IR (KBr): 1227 cm^{-1}), which spoke for the presence of an almost rigid structure. In the presence of 1% (v/v) TFA, the solution

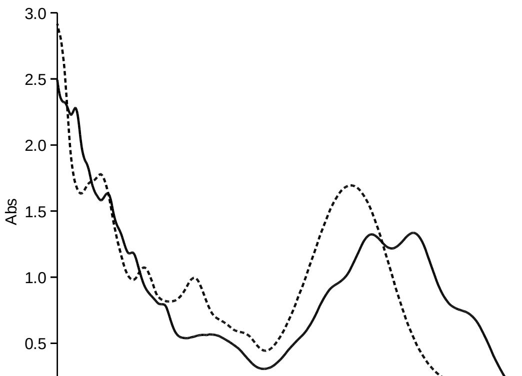
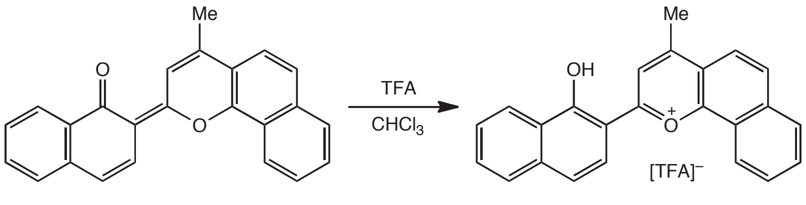


Figure 1. UV/VIS spectrum of (*E*)-**7** in $CHCl_3$ (–) and in $CHCl_3$/1% TFA (- -)

took a red-violet color and the structured band had vanished and a new unstructured broad band appeared hypsochromically shifted to 523 nm (Figure 1), a fact, which spoke for the protonation of the C=O group and formation of 2-(1-hydroxynaphthalen-2-yl)-4-methylbenzo[*h*]chromenium trifluoroacetate (**9**) (Scheme 4). The structure of (*E*)-**7** was finally solved by NMR spectroscopy with full assignment of all H- and C-atom positions, of which the ^{13}C-NMR shifts were compared with those obtained by DFT calculation for (*E*)-**7** (for the used program, see[9]). The agreement was excellent (Figure 2). The structure of (*E*)-**7** was also supported by the spectroscopic data of a dimethoxy derivative of it, which has been prepared together with its (*Z*)-analogue by oxidation of correspondingly substituted naphthopyranes with AgO or chloranil.[10]



(*E*)-**7** **9**

Scheme 4. Protonation of (*E*)-**7** in $CHCl_3$/1% TFA (v/v)

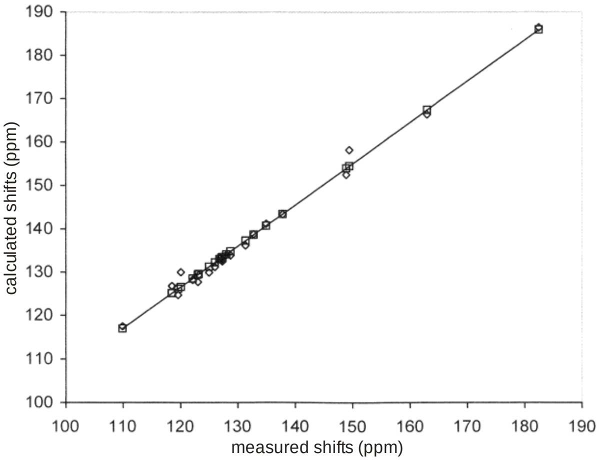
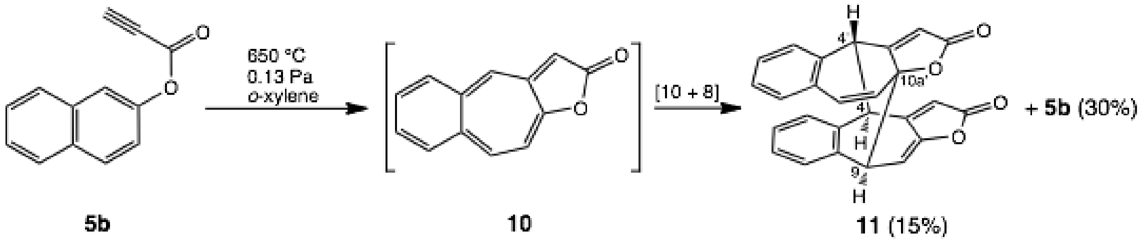


Figure 2. Correlation of measured (◇) versus calculated (□) ^{13}C-NMR shifts for (*E*)-**7** ($r^2 = 0.991$)

The pyrolysate of the FVP of **5b** exhibited in the cooling trap an intense yellow color, which changed to almost colorless on warming to ambient temperature. Chromatography gave beside 30% starting material **5b** as colorless solid, which showed the $[M + NH_4]^+$ ion with twice the mass of **10** in the CI-MS, however, with the basis peak at m/z = 197 in correspondence with a [**10** + 1]$^+$ ion (Scheme 5). Therefore, there was



Scheme 5. FVP of Naphthalen-2-yl propynoate (**5b**)

little doubt that the new product, formed in 15% chemical yield, represented a dimer of the preliminary formed benzo[4,5]cyclohepta[1,2-b]furan-2(2*H*)-one (**10**). An in depth analysis of the ^{1}H- and ^{13}C-NMR spectra suggested the structure of a cycloaddition dimer **11** of **10** with the suspension of the 1,2-quinodimethane partial structure of both molecules of **10** (cf. Scheme 5). Dimer **11** crystallized from CH_2Cl_2 in colorless prisms, and one of them was well suited for an X-ray crystal-structure analysis, which fully supported the structure of **11** (Figure 3). The asymmetric unit contained one molecule of **11** plus two molecules of CH_2Cl_2 without disorder.

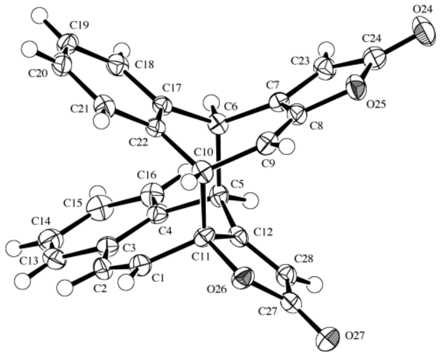
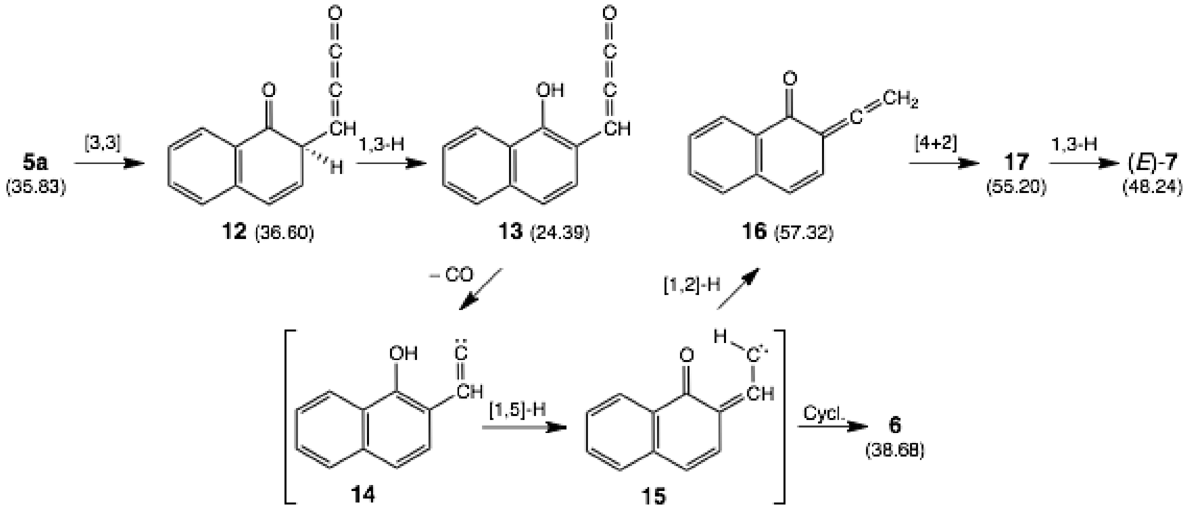


Figure 3. X-Ray crystal structure of the [10 + 8]-dimer **11** of benzo[4,5]cyclohepta[1,2-*b*]furan-2(2*H*)-one (**10**) (50% probability ellipsoids)

Finally, it can be said that the phenyl propynoate **3a** and the naphthyl propynoate **5b** behave normal on FVP at 650 °C by undergoing the alkyne-ethenylidene equilibrium with the result of the formation of cyclohepta[1,2-*c*]furans **1a** and **10**, respectively. On the other hand, the pyrolysis of naphthyl propynoate **5a** at 650 °C does not lead to products derived from benzocyclohepta[1,2-*b*]furan-2-one **8** as primary intermediate, despite the fact that the AM1 calculated $\Delta H_f°$ values of **8** (28.70 Kcal·mol^{-1}) and **10** (28.84 Kcal·mol^{-1}) are quite similar. Also a possible dimer of **8**, built by [10 + 8] cycloaddition with bond formation between C(4)/C(10b') and C(10b)/C(6'), shows $\Delta H_f° = 20.72$ Kcal·mol^{-1} close to that of **10** (AM1: $\Delta H_f° = 18.33$ Kcal·mol^{-1}). Therefore, it can be concluded that the isolated products of the FVP of **5a** result from a thermal process, which takes place before the alkyne-ethenylidene equilibrium of **5a** (cf.

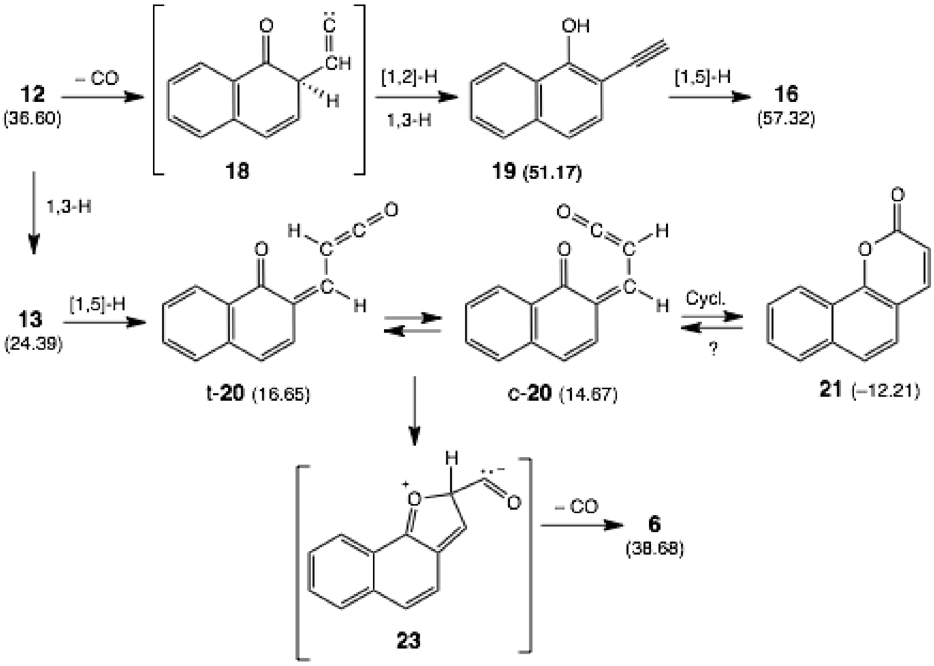
Scheme 1) starts to become product determining. The relatively high amount of naphthalen-1-ol that is formed speaks for a sigmatropic process accompanied by cleavage of the migrating σ-bond. It seems therefore that the original idea of Trahanovsky *et al.*[4] is realized in the case of **5a**, namely that the first step of the FVP of phenyl propynoates represents a "Claisen type rearrangement" (Scheme 6), which leads in the present case to the formation of 2-(3-oxapropa-1,2-dienyl)naphthalen-1(2*H*)-one (**12**). Propa-1,2-dien-1-ones are known to undergo decarbonylation under FVP conditions to corresponding ethenylidene intermediates.[11] However, **12** may undergo wall-catalyzed enolization (prototropic shift) to naphthol **13** before decarbonylation to **14** takes place. The latter, on [1,5]-H shift to prop-2-enylidene **15**, opens by cyclization the way to naphthofurane **6** and by [1,2]-H shift to 2-vinylidenenaphthalen-1(2*H*)-one (**16**), which then is engaged in the trap in a [4+2] dimerization to (*E*)-2-(4-methylene-3,4-dihydro-2*H*-benzo[*h*]chromen-2-ylidene)naphthalen-1(2*H*)-one (**17**). A 1,3-prototropic shift in **17** concludes finally the formation (*E*)-**7**. On the other hand, it could also be that intermediate **16** results by [1,5]-H shift of 2-ethynylnaphthalen-1-ol (**19**), which itself is an outcome of the decarbonylation of **12** accompanied by [1,2]-H shift and enolization (Scheme 7).[12]



Scheme 6. Formation of **6** and (*E*)-**7** by FVP of **5a** *via* 3-(1-hydroxynaphthalen-2-yl)propa-1,2-dien-1-one (**13**) as decisive intermediate (in parentheses AM1 calculated $\Delta H_f°$ values in Kcal·mol^{-1})

The postulated appearance of **13** in the FVP of **5a** leads necessarily to the question whether it also opens a further reaction channel, which will lead by [1,5]-H shift to (*Z*)-2-(3-oxaallylidene)naphthalen-1(2*H*)-one (**20**) in an s-*trans* (t-**20**, Θ (H–C(1)–C(2)–H) = 179.8°) and s-cis (c-**20**, Θ (H–C(1)–C(2)–H) = 0.1°) conformation, which differ distinctly in their heat of formation (Scheme 7). The latter may cyclize to 2*H*-benzo[*h*]chromen-2-one (**21**). However, this compound was not present in isolable amounts in the mixture of products (Scheme 3), and it seems that the FVP of coumarines and their benzo forms has not been investigated so far. Nevertheless, the rotation of the 3-oxaallylidene group of **20** around the C(1)–C(2) bond shows local minima at an H–C(1)–C(2)–H torsion angle of about 45°, ideal for binding interaction of the n-electron pair of the naphthalen-1-one O-atom with C(2) and thereby entering the hypersurface of thermal gas-phase decarbonylation reactions of aromatic and α,β-unsaturated aldehydes at temperatures >400 °C (see[16] and literature cited there). The result in the present case would be the formation of **6** by loss of CO from **23** formulated as zwitterion.

In summary, we can say that the important steps of the pyrolysis of **5a** are the cleavage and [3,3]-migration of the C(1)–O bond leading to the formation of naphthalene-1-ol and 2-(3-oxapropa-1,2-dienyl)naphthalen-1(2*H*)-one (**12**), respectively. The next steps towards **6** and **16**, the precursor of (*E*)-**7**, depend on the interplay of decarbonylation reactions and H-shifts, and it would need further FVP experiments to elucidate the sequence of these steps.



Scheme 7. Alternative reaction paths for the formation of **6** and (*E*)-**7** in the FVP of **5a** (in parentheses AM1 calculated $\Delta H_f°$ values in Kcal·mol^{-1})

EXPERIMENTAL

General: Melting points (mp) were measured on a Büchi FP5 apparatus. They are not corrected. TLC on aluminum sheets coated with silica gel 60 F_{254} (Merck). Column chromatography (CC) was performed on silica gel 60 (40-63 µm; Chemie Uetikon AG*)*. IR spectra were recorded on a Perkin Elmer 1600 FT-IR spectrometer. Band positions are given in wave-numbers (cm^{-1}). Transmissions are classified as vs = very strong (< 10%), s = strong (10-30%), m = middle (30-50%), and w = weak (> 60%). ^{1}H-NMR and ^{13}C-NMR spectra ($CDCl_3$) were measured at 300 K on Bruker instruments at 600, 500 or 300 MHz; δ in ppm related to internal TMS (= 0 ppm) and adjusted to the solvent signals 7.26 ppm and 77.00 ppm, respectively, *J* in Hz. Assignments of the signals are based on additional DEPT 90, DEPT 135, COSY, NOSEY, NOE, HSQC, HMBC, and TOCSY measurements. Mass spectra (MS) were measured on a Finnigan MAT 95 instrument; chemical ionisation (CI) with NH_3, 70 eV, at a temp. of 250 °C.

Synthesis of the Prop-2-ynoates. – The prop-2-ynoates were prepared according to our described procedure [6] from the corresponding phenols *via* their arylcarbonochloridates and reaction of them with sodium prop-2-ynoate in overall yields of >80%.

3,5-Bis(ethoxymethyl)-2,4,6-trimethylphenyl prop-2-ynoate (3a). Crystallized from hexane/Et_2O, mp 108.7–109.3 °C. 3,5-Bis(ethoxymethyl)-2,4,6-trimethylphenol (mp 85.5–88.1 °C (hexane/Et_2O)) was prepared by bisbromomethylation of mesitol with 1,3,5-trioxane/HBr in AcOH,[17] followed by heating of the resultant 3,5-bis(bromomethyl)mesitol with EtONa in EtOH/MeCN (1:1).

Naphthalen-1-yl prop-2-ynoate (5a). Crystallized from hexane/*t*-BuOMe, mp 56.0–57.8 °C.

Naphthalen-2-yl prop-2-ynoate (5b). Crystallized from hexane/*t*-BuOMe, mp 73.5–75.0 °C (mp 74°).[18]

Flash Vacuum Pyrolysis (FVP) of the Prop-2-ynoates. – The pyrolysis experiments were performed as described in detail in ref.[6] However, the heating device (oven for combustion analyses in[6]) was exchanged by a Thermolyne® 21100 tube furnace of Sigma-Aldrich, which formed with the quartz tube inside an angle of inclination of 45° (vertical in[6]). The solution of the prop-2-ynoates (in each case 2.0 g) in *o*-xylene (2.0 mL) was passed through the quartz tube at 650 – 670 °C with a residual stream of nitrogen. After warming of the cooling trap to rt, the *o*-xylene in the resulting pyrolysate was evaporated, and the residue was subjected to chromatography on silica gel with hexane/Et_2O mixtures.

FVP of 3,5-Bis(ethoxymethyl)-2,4,6-trimethylphenyl prop-2-ynoate (1a). – 5,7-Bis(ethoxymethyl)-4,6,8-trimethyl-2*H*-cyclohepta[*b*]furan-2-one (3a). CC of the pyrolysate gave 0.184 g (9.2%) **3a** as yellow solid.

Data of 3a: Lemon yellow crystals, mp 136.8–140.4 °C (toluene). UV/VIS (MeCN): λ_{max} 403 (4.10), 265 (4.28), 249 (4.28); λ_{min} 318 (3.32), 256 (4.27). IR ($CHCl_3$): 3027w, 3022w, 3012m, 2980w, 2930w, 2877w, 1721vs, 1609w, 1575w, 1480m, 1445w, 1412w, 1375w, 1351w, 1286w, 1253w, 1235w, 1198w, 1171w, 1125w, 1095m. ^{1}H-NMR: δ 5.76 (s, H–C(3)); 4.44 (s, CH_2–C(7)); 4.27 (s, CH_2–C(5)); 3.63 (m, $MeCH_2OCH_2$–C(5)); 3.60 (m, $MeCH_2OCH_2$–C(7)); 2.55 (s, Me–C(8)); 2.52 (s, Me–C(6)); 2.39 (s, Me–C(4)); 1.31 (t, $MeCH_2OCH_2$–C(7)); 1.28 (t, $MeCH_2OCH_2$–C(5)). ^{13}C-NMR: δ 168.88 (C(2)); 151.79 (C(3a,8a)); 142.37 (C(5)); 141.80 (C(7)); 137.90 (C(6)); 137.19 (C(4)); 127.50 (C(8)); 98.20 (c(3)); 70.70

(EtO*C*H$_2$–C(5)); 69.30 (EtO*C*H$_2$–C(7)); 66.18 (Me*C*H$_2$O*C*H$_2$–C(5,7)); 21.15 (Me–C(8)); 20.59 (Me–C(6)); 16.31 (Me–C(8)); 14.94 (*Me*CH$_2$OCH$_2$–C(5,7)). EI-MS: 304 (9, [*M*]$^+$), 258 (17, [*M* – EtOH]$^+$), 212 (100, [*M* – 2 EtOH]$^+$).

FVP of Naphthalen-1-yl prop-2-ynoate (5a). – Naphtho[1,2-*b*]furan (6), Naphthalen-1-ol, and (*E*)-2-(4-methyl-2*H*-benzo[*h*]chromen-2-ylidene)naphthalen-1-(2*H*)-one ((*E*)-7). CC of the pyrolysate gave 0.291 g **6** (17%), 0.367 g (25%) naphthalen-1-ol, and 0.0031 g (1.8%) (*E*)-**7**. 1% of **5a** was recovered.

Data of 6 (see[19,20]): Colorless oil. IR (CHCl$_3$): 3305m, 3064vs, 3013vs, 1593m, 1513vs, 1456m, 1439m, 1411m, 1393vs, 1323vs, 1296vs, 1223m, 1208m, 1170vs, 1129vs, 1069vs, 1040s, 1022vs. ^{1}H-NMR: δ 8.35 (br. d, ^3J(9,8) = 8.3, H–(9)); 7.96 (*dt*-like, ^3J(6.7) = 8.2, H–C(6)); 7.79 (*d*, ^3J(2,3) = 2.05, H–(2)); 7.69 (*s*, H–C(4,5)); 7.62 (td, ^3J(8,7) = ^3J(8,9) = 8.2, ^4J(8,6) = 1.20, H–C(8)); 7.52 (td, ^3J(7,8) = ^3J(7,6) = 8.2 ^4J(7,9) = 1.25, H–C(7)); 6.93 (d, ^3J(3,2) = 2.05, H–C(3)).

Data of (*E*)-7: Dark blue solid, mp >165 °C (decomp.). UV/VIS (CHCl$_3$; Figure 1): λ_{max} 256 (4.33), 267 (4.34), 277sh (4.25), 297 (4.21), 307sh (4.13), 320 (4.08), 347 (3.89), 394 (3.75), 474sh (3.74), 508sh (4.00), 540 (4.15), 579 (4.15), 623sh (3.89); λ_{min} 262 (4.33), 317 (4.08), 368 (3.71), 441 (3.46), 560 (4.11). UV/VIS (CHCl$_3$ + 1% (v/v) TFA): λ_{max} 253sh (4.43), 282sh (4.22), 291 (4.25), 331 (4.02), 377 (4.01), 400sh (3.84), 419sh (3.78), 523 (4.26); λ_{min} 271 (4.18), 321 (3.98), 351 (3.91), 443 (3.63). IR (KBr): 3053w, 2956w, 2922w, 2852w, 1715m, 1639s, 1604s, 1592s, 1575s, 1543vs, 1514vs, 1498s, 1479s, 1459vs, 1447vs, 1406m, 1385m, 1366vs, 1314s, 1258m, 1227s, 1150m, 1138m, 1093s, 1023m, 933s, 886m, 862m, 812s, 787s, 745s, 714m. ^{1}H-NMR: δ 9.07 (br. s, ^4J with Me–C(4'), H–C(3')); 8.38 (2 superimp. d with ^3J ca. 7.9); 8.383: H–C(10') and 8.381: H–C(8)); 7.80 (dd, ^3J(7',8') = 7.4, ^4J(7',9') = 1.4, H–C(7')); 7.63 (d, ^3J(3,4) = 9.4, H–C(3)); 7.62 (td, ^3J(9',10') = ^3J(9',8') = 7.8, ^4J(9',7') = 1.4, H–C(9')); 7.60 (d, ^3J(6',5') = 7.3, H–C(6')); 7.59 (td, ^3J(8',7') = ^3J(8',9') = 7.3, ^4J(8',10') = 1.4, H–C(8')); 7.49 (td, ^3J(6,7) = ^3J(6,5) = 7.8, ^4J(6,8) = 1.4, H–C(6)); 7.44 (d, ^3J(5',6') = 7.3, H–C(5')); 7.39 (dd, ^3J(5,6) = 7.7, ^4J(5,7) ~ 2 × ^5J(5,8) = 1.2, H–C(5)); 7.34 ((td, ^3J(7,8) = ^3J(7,6) = 1.3, H–C(7)); 6.69 (d, ^3J(4,5) = 9.5, H–C(4)); 2.49 (d, ^4J(Me–C(4'),3') ~ 1, Me–C(4')). ^{13}C-NMR (Figure 2): δ 182.49 (C(1)); 162.98 (C(2')); 149.44 (C(10b')); 148.90 (C(4')); 137.79 (C(4a)); 134.92 (C(6a')); 132.76 (C(8a)); 131.36 (C(6)); 128.72 (C(8')); 128.00 (C(7')); 127.32 (C(9')); 127.14 (C(5)); 126.82 (C(8)); 126.01 (C(7)); 124.97 (C(6')); 123.15 (C(10a')); 123.02 ((C(3)); 122.07 (C(10')); 120.02 (C(3')); 119.56 (C(5')); 118.50 (C(4a')); 118.47 (C(4)); 109.91 (C(2)); 19.70 (*Me*–C(4')). EI-MS: 336 (76, [*M*]$^+$), 321 (44, [*M* – Me]$^+$), 265 (39, [(*M* – Me) – 2 CO]$^+$), 171 (60), 168 (39), 115 (100), 91 (99, [C$_7$H$_7$]$^+$). CI-MS: 337 (100, [*M* + 1]$^+$).

FVP of Naphthalen-2-yl prop-2-ynoate (5b). – (4*R,4'*S**,9*R**,10a'*R**)-4,9-dihydro-4,9-(4',10a'-dihydro-2’-oxo-2*H*-benzo[4,5]cyclohepta[1,2-*c*]furan-4',10a'-diyl)-2*H*-benzo[4,5]cyclohepta[1,2-*c*]-furan-2-one (11**; systematic name: (1*R**,2*R**,11*S**,12*R**)-16,28-dioxaheptacyclo[10.6.6.$4^{2,11}$.$0^{2,25}$.$0^{5,10}$.$0^{13,17}$.$0^{19,24}$]octacosa-3,5,7,9,13,17,19,21,23,25-decaene-15,27-dione**)**. CC of the pyrolysate gave 0.210 g (10.5%) **11** as colorless solid and 0.601 g (30%) non-reacted **5b**.

Data of 11: Colorless prisms from CH_2Cl_2. IR ($CHCl_3$): 3029w, 1766s, 1664w, 1600w, 1494w, 1228w, 1200w, 1090w, 1004w. ^{1}H-NMR: δ 7.44 (d, ^3J(5’,6’) = 7.5, H–C(5’)); 7.37 (td, ^3J(6’,5’) = ^3J(6’,7’) = 7.5, H–C(6’)); 7.20 (td, ^3J(7’,6’) = ^3J(7’,8’) = 7.5, ^4J(7’,5’) = 1.4, H–C(7’)); 6.93 – 6.88 (m, H–C(6,8’)); 7.15 – 7.11 (m, H–C(7,8)); 6.57 (d, ^3J(5,6) = 7.4, H–C(5)); 6.28 – 6.22 (m, H–C(10,3)); 6.02 (d, ^3J(9’,10’) = 12.2, H–C(9’)); 5.98 (s, H–C(3’)); 5.78 (d, ^3J(10’,9’)) = 12.2, H–C(10’)); 4.67 (d, ^3J(4’4) = 5.0, H–C(4’)); 4.47 (d, ^3J(4,4’) = 5.0, H–C(4)); 4.35 (d, ^3J(9,10) = 9.5, H–C(9)). ^{13}C-NMR: δ 169.62 (C(2’)); 167.75 (C(2)); 164.32 (C(3a’)); 155.32 (C(3a)); 152.88 (C(10a)); 137.68 (C(8a)); 134.72 (C(8’)); 134.19 (C(4a’)); 133.86 (C(4a)); 132.62 (C(8a’)); 131.77 (C(9’)); 130.97 (C(8)); 130.91 (C(5)); 129.80 (C(5’)); 129.41 (C(6’)); 128.23 (C(7)); 128.10 (C(7’)); 127.77 (C(6)); 126.14 (C(10’)); 121.37 (C(3’)); 116.58 (C(3)); 109.77 (C(10)); 89.83 (C(10’)); 53.95 (C(4)); 52.82 (C(4’)); 50.64 (C(9)). CI-MS: 410 (47, [M + NH_4]$^+$), 393 (3.6, [M + 1]$^+$), 214 (4.7, [**10** + NH_4]$^+$), 197 (100, [**10** + 1]$^+$).

2. X-Ray crystal structure determination of 11·2CH$_2$Cl$_2$. Crystal data: Crystals obtained from CH_2Cl_2, $C_{26}H_{16}O_4\cdot 2CH_2Cl_2$, M = 562.27, monoclinic, space group: $P2_1/n$, a = 8.073(2) Å, b = 14.822 (3) Å, c = 20.402 (2) Å, β = 97.35(1)°, V = 2420.9(6) Å^3, Z = 4, D_X = 1.543 g cm^3, $\theta_{(\max)}$ = 55°, T = –83 °C, crystal dimensions: 0.18 × 0.35 × 0.45 mm, Rigaku AFC5R diffractometer, Mo Kα□radiation, λ = 0.71069 Å, μ(Mo*K*α) = 0.524 mm^{-1}, 6183 measured reflections, 5558 independent reflections, 3705 reflections with $I > 2\sigma(I)$, refinement on F with *teXsan*,[21] 405 parameters, $R(F)$ [$I > 2\sigma(I)$] = 0.0422, $wR(F^2)$ [$I > 2\sigma(I)$ reflections] = 0.0369, goodness of fit = 1.449, $\Delta\rho_{\max}$ = 0.33 e Å^{-3}. The asymmetric unit contains one molecule of **11** plus two molecules of dichloromethane. There is no disorder. The non-hydrogen atoms were refined anisotropically. All of the H-atoms were placed in geometrically calculated positions.
CCDC-829303 contains the supplementary crystallographic data for this compound. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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