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Flash vacuum pyrolysis (FVP) of aryl propargyl ethers, amines and acetylenic ester

Amal J. K. Alrajhei,[a] Asaad S. Mohamed,[a] Muna A. Mohammad,[b] Osama M. Habib,[b] and Nouria A. Al-Awadi[a]*

[a] *Chemistry Department, Faculty of Science, Kuwait University, P.O. Box 5969, Safat 13060, Kuwait*
[b] *Biochemistry Department, Faculty of Medicine, Kuwait University, Kuwait*
Email: na.nabaq.kw@gmail.com

Dedicated to our Dear Colleague Dr. Alan Aitken

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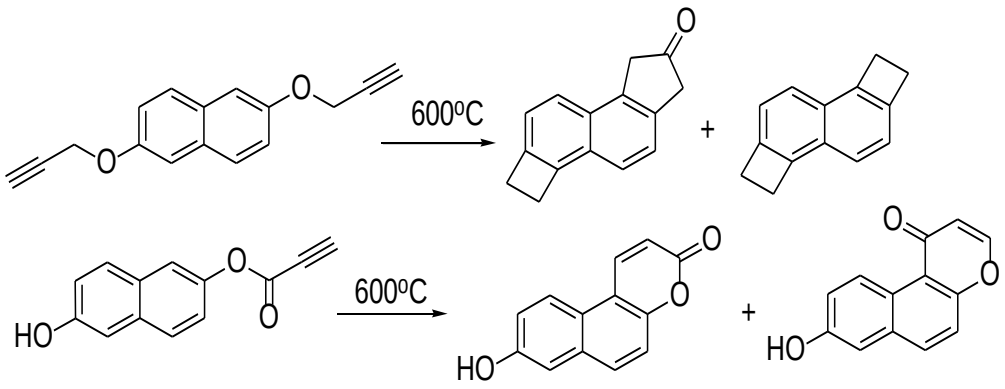
Abstract

The preparative utility of the pyrolysis of acetylenic compounds is demonstrated in the flash vacuum pyrolysis of some propargyl ethers, amines and an ester that has resulted in interesting furans, indanones, quinoline, and chromenones as major products. The products of the pyrolysis of each substrate were analyzed, identified, characterized, and compared.

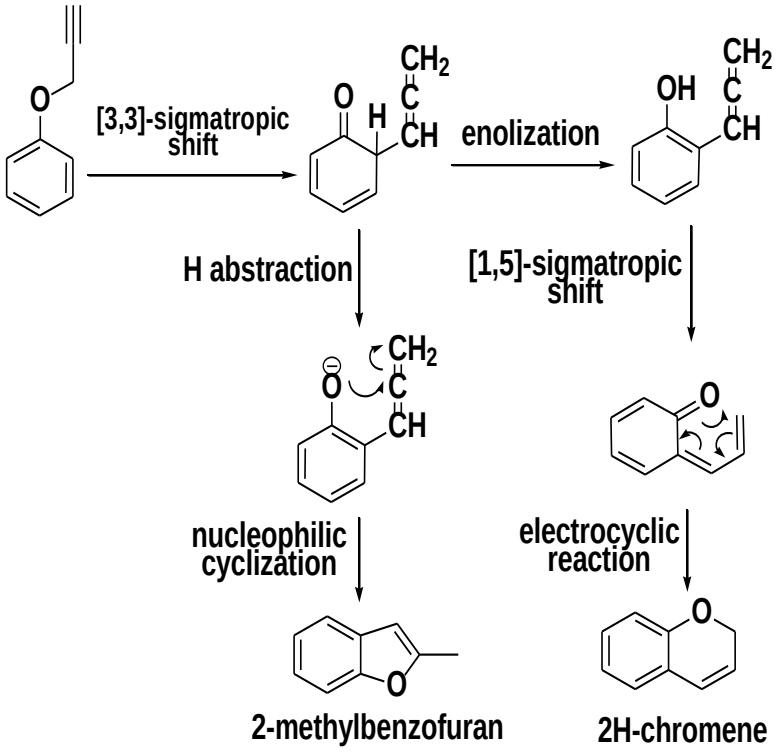


Keywords: FVP, furans, indanones, quinoline, chromenones

Introduction

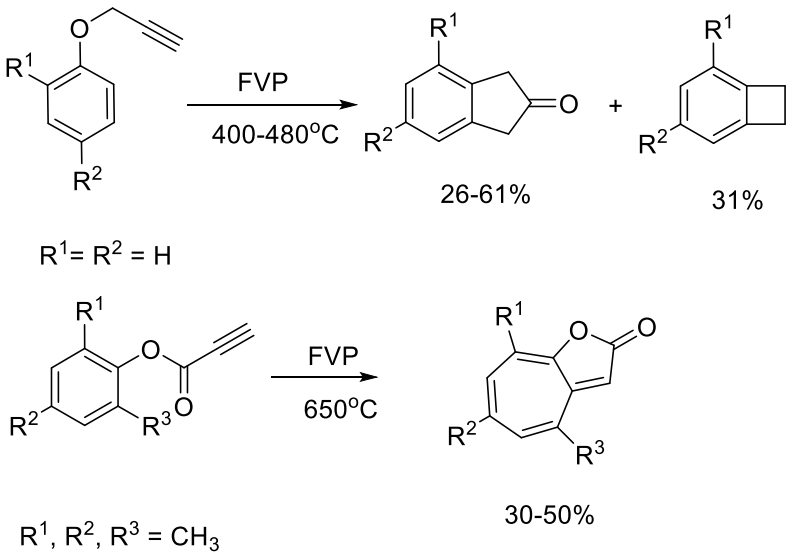
Naphthofurans have attracted significant attention in recent years, owing to their powerful paradigm in the development and design of potential anticancer drugs, [1-2] as well as other bioactivities. [3-4] Chromene is a privileged scaffold which appears as an important structural component in various bioactive natural products. The derivatives of chromene are able to interact with a variety of cellular targets which leads to their wide-ranging biological activities such as antitumor, antihepatotoxic, antioxidant, anti-inflammatory, antiviral, antifungal, and antimicrobial.[5-6]

Thermal rearrangement of aryl propynyl ethers to benzofuran and/or chromene derivatives is well documented.[7] Cyclization of propargyl ethers in the presence of CsF provides 2-methylbenzofurans[8], while the presence of catalytic amount of gold (I) complexes provides chromene derivatives (Scheme 1).[9]



Scheme 1. Formation of benzofuran and chromene via Claisen rearrangement.

Flash vacuum pyrolysis (FVP) of acetylenic compounds was shown to give direct and easy access to many interesting compounds, some of which are otherwise difficult to obtain. Trahanovsky et al., studied the FVP of phenyl propargyl ether derivatives and its Claisen rearrangement type reaction mechanism. The major pyrolysis products were 2-indanone and benzocyclobutene (Scheme 2),[10-11] while FVP of aryl propiolates at 650 °C and 10^{-2} Torr gave 30-50% yield of tropolone derivatives (cyclohepta[*b*]furan-2-ones) (Scheme 2).[12]



Scheme 2. FVP of aryl propargyl ethers.

We have recently reported on the FVP of acetylenic esters and thioesters that has resulted in the formation of cyclohepta[*b*]furan-2-ones and 2*H*-chromen-2-ones.[13] 2*H*-Chromen-2-ones (11-13%) were not reported under FVP condition in previous studies.[12] FVP of acetylenic amides has resulted in cyclohepta[*b*]pyrrol-2-ones**.**[14]. Furthermore**,** FVP of aryl propargyl ethers produced mixtures of benzofuran, 2*H*-chromene, 2-indanone, and benzocyclobutene derivatives.[15] We have postulated mechanisms for the conversion of the acetylenic compounds into various carbocyclic and heterocyclic compounds.[15]

The propensity of acetylenic compounds to cyclize/rearrange cleanly in FVP reactions makes them potentially powerful compounds for the synthesis of valuable medicinal and pharmaceutical products such as benzofurans and naphthofurans. We present in this work further interesting examples of some biologically important propargyl ethers **2**,**4**,[16-20] amines **6**,**7**,**9**,[21-23] and polycyclic aromatic acetylenic ester **11** that have been prepared and subjected to FVP conditions. The products of the pyrolysis were further analyzed.

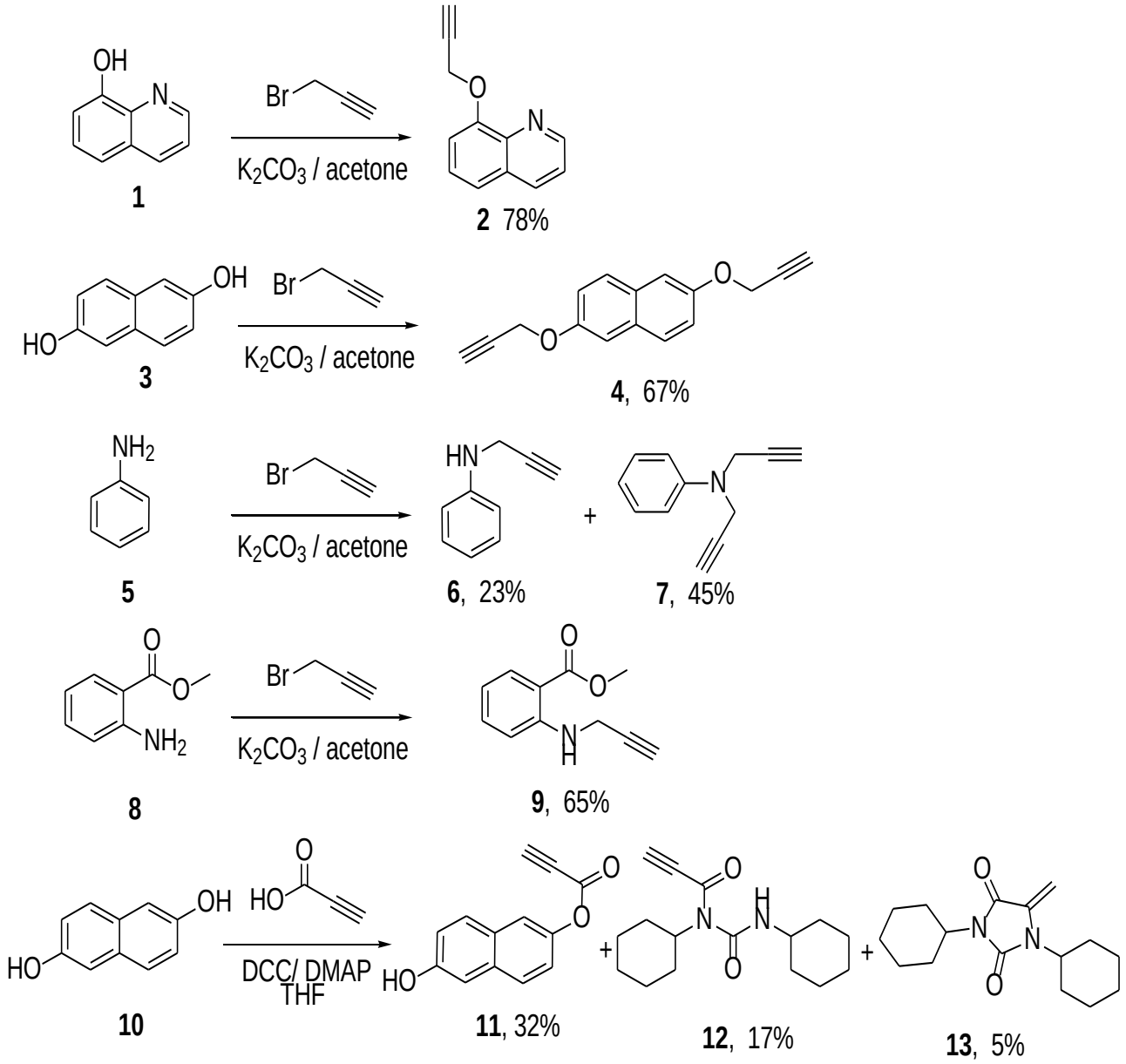
Results and Discussion

Synthesis:

Propargyl ethers **2**,**4** and amines **6**,**7**,**9** were prepared from the reaction of quinolin-8-ol, 2,6- naphthalene-2,6-diol, aniline, methyl anthranilate respectively, and (3.0 eq.) propargyl bromide in acetone with excess of K_2CO_3. The reaction mixture was heated at reflux until reaction completion based on TLC monitoring, then the crude product was purified by flash chromatography. The propargylation reaction gave the desired products in good yield (Scheme 3). The ^{1}H-NMR spectra showed the characteristic absorption signal of an acetylenic proton as a triplet peak at δ 2.24-2.56 ppm with coupling constant 2.4 Hz. and singlet signal for CH≡ proton of ester **11** at 4.86 ppm (Table 1). Furthermore, mass spectra showed the corresponding peaks of the molecular ions.

On the other hand, The acetylenic ester required for this study was synthesized by base-catalysed esterification of propiolic acid (2 moles) with naphthalene-2,6-diol using dichloromethane (DCM) in the presence of *N,N*′-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) as a dehydrating reagent mixture. 6-Hydroxynaphthalen-2-yl propiolate **11** (32%) was obtained as the major product. The

reaction of propiolic acid with *N,N'*-dicyclohexylcarbodiimide (DCC) resulted in a amide **12** (17%) as by-product which was cyclized to 1,3-dicyclohexyl-5-methyleneimidazolidine-2,4-dione **13** (5%).



Scheme 3. Synthesis of propargyl ethers **2**,**4**, amines **6**,**7**,**9,** and ester **11**.

Table 1. Yield and **H**, **C** chemical shifts of three characteristic signals of products **2**,**4**,**6**,**7**,**9**,**11** and **12**

Comp.	Yield (%)	δC**H**≡ (ppm)	δC**H$_2$** (ppm)	δ**C**≡**C**H (ppm)
2	78	2.55 (t, *J* 2.4)	5.06 (d, *J* 2.4)	78.4, 76.3
4	67	2.56 (t, *J* 2.4)	4.81 (d, *J* 2.4)	78.7, 75.8
6	23	2.27 (t, *J* 2.4)	3.97 (d, *J* 2.4)	81.1, 71.5
7	45	2.29 (t, 2H, *J* 1.8)	4.16 (s, 4H)	79.3, 72.9
9	65	2.24 (t, *J* 2.4)	4.05 (d, *J* 2.4)	80.3, 71.5
11	32	4.86 (s)	-	81.5, 74.3
12	17	3.37 (s)	-	82.0, 76.2

FVP and product analysis

8-(Prop-2-ynyloxy)quinoline **2**: FVP and product analysis at 600 °C and 10^{-2} Torr gave a mixture of two new furo[3,2-*h*]quinolines **14-15** and **1** (44%) (Scheme 4). The pyrolytic reaction mixture was carefully analyzed and fully characterized by their ^{1}H and ^{13}C NMR spectra (Table 2), the major product was 2-methylfuro[3,2-*h*]quinoline **14** (23%), which might be formed via either Claisen rearrangement (Scheme 1), while furo[3,2-*h*]quinoline **15** (11%) can be formed by reductive elimination of methyl group of **14**. Reductive elimination of propargyl group of the substrate **2** led to formation of quinolin-8-ol **1** (7%).

Table 2. Yield and **H**, **C** chemical shifts of four characteristic signals of **14** and **15**

Comp.	Yield (%)	δ**H**-3 (ppm)	δ**H**-2 (ppm)	δC**H$_3$**, δ**C**H$_3$ (ppm)	δ**H**-8 (ppm)
14	23	6.58 (d, *J* 1.2)	-	2.63 (d, *J* 0.8), 14.4	8.95 (dd, *J* 4.0, 1.6)
15	11	6.99 (d, *J* 2.0)	7.91 (d, *J* 2.4)	-	9.00 (dd, *J* 4.4, 1.6)

FVP of 2,6-bis(prop-2-ynyloxy)naphthalene **4** at 600 °C and 10^{-2} Torr resulted in a mixture of three compounds **16-17** and quinolin-8-ol **3** (41%). The major products were 1,2,5,7-tetrahydro-6*H*-cyclobuta[*a*]cyclopenta[*f*]naphthalen-6-one **16** and 1,2,5,6-tetrahydrodicyclobuta[*a,f*]naphthalene **17**, might be formed via a similar mechanism to that reported by Trahanovsky and our group (Scheme 2,4).[10-15] The ^{1}H NMR spectrum of compound **17** shows two triplet signals at δ 3.40 and 3.30 ppm for unsymmetrical methylene groups of cyclobutene ring, and four doublet signals of aromatic protons, revealing that cyclization takes place at positions 1 and 5 of naphthalene to give non-linear compound **17**. The ^{1}H NMR spectrum of compound **16** shows two triplet signals at δ 3.44 and 3.33 ppm for unsymmetrical methylene groups of cyclobutene ring, and two singlet signals at lower field δ 3.84 and 3.75 ppm for cyclopent-3-enone ring (Table 3).

Table 3. Yield and **H**, **C** chemical shifts of four characteristic signals of **16** and **17**

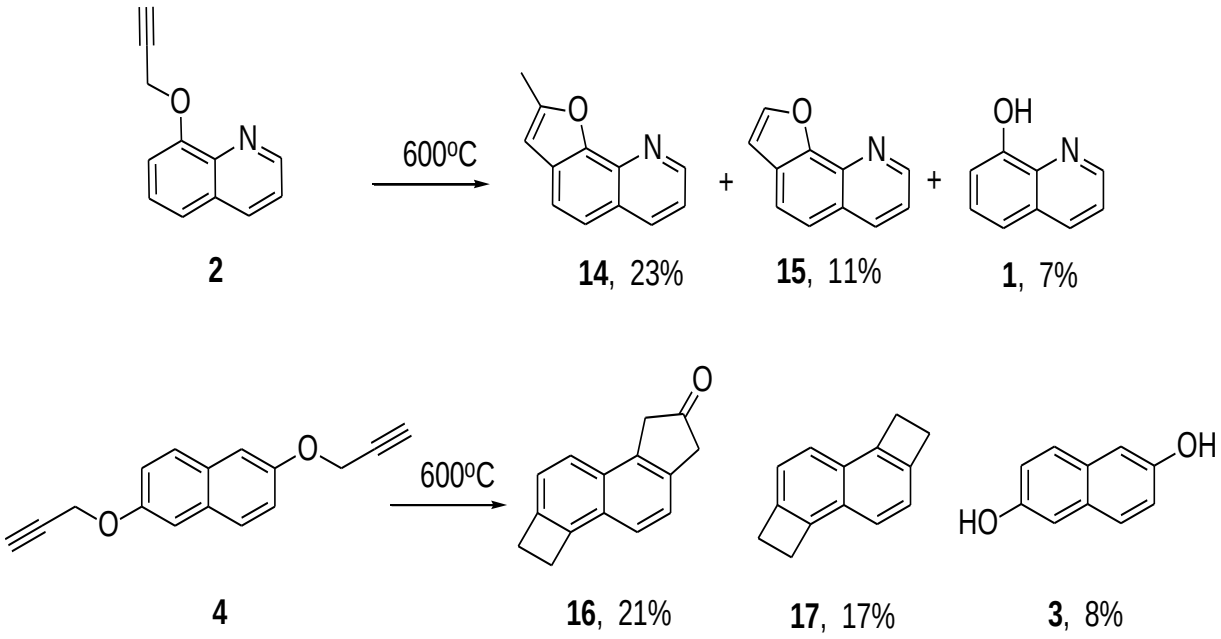
Comp.	Yield (%)	δC**H$_2$**C**H$_2$** (ppm)	δ**C**H$_2$**C**H$_2$** (ppm)	δC**H$_2$**COC**H$_2$** (ppm)	δ**C**H$_2$**C**O**C**H$_2$** (ppm)
16	21	3.44 (t, *J* 4.0), 3.33 (t, *J* 4.0)	29.5, 28.7	3.84 (s), 3.75 (s)	45.3, 215.2, 42.9
17	17	3.40 (t, J 4.0), 3.30 (t, *J* 4.0)	29.4, 28.7	-	-

FVP of mono- and dipropargyl aniline **6** and **7** at 600 °C and 10^{-2} Torr resulted in quinoline **18** as a major product (26-33%). The reaction starts with insertion of carbene intermediate at *ortho* C-H bond followed by oxidation to give quinoline **18** (Scheme 5). Furthermore, pyrolysis of propargyl methyl anthranilate **9** at 600 °C and 10^{-2} Torr produced the unexpected product 7-aminoisobenzofuran-1(3*H*)-one **19** (34%), which might be formed by cyclization of the methyl ester group at *ortho* position with elimination of the propargyl group (Scheme 5).

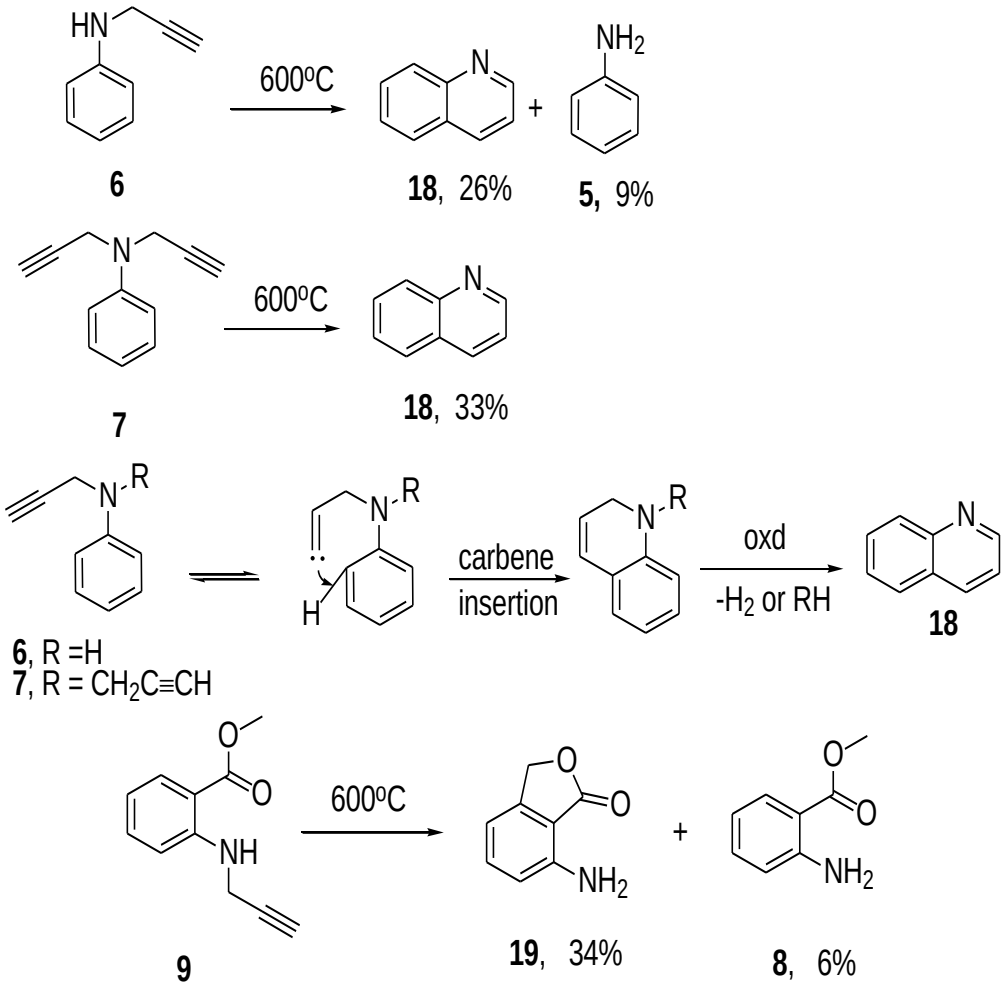
The result of the FVP of 6-Hydroxynaphthalen-2-yl propiolate **11** at 600 °C and 10^{-2} Torr was surprising by the fact that we found no indication for the presence of tropolone derivative as reported in previous studies.[12-13]. Instead, we isolated by chromatography two new compounds **20** (18%) and **21** (27%) in addition to naphthalene-2,6-diol **10** (4%) (Scheme 6). First, we thought that the two inseparable isomers could be 8-hydroxy-3*H*-benzo[*f*]chromen-3-one **20** and 7-hydroxy-2*H*-benzo[*g*]chromen-2-one **22**, which formed via intramolecular carbene insertion at C-H bonds at C(1) and C(3) respectively. An in-depth analysis of the ^{1}H, ^{13}C, and 2D-NMR spectra suggested the structure of 8-hydroxy-3*H*-benzo[*f*]chromen-3-one **20** with the unexpected product 8-hydroxy-1*H*-benzo[*f*]chromen-1-one **21**. The ^{1}H-NMR spectrum provided evidence that the inseparable coumarin **20** and chromone **21** exist in ratio (1.5:1.0) respectively. All aromatic proton signals are doublets with ortho coupling constant 8.8-5.6 except one signal for each compound. A marked downfield shift in the H-10 resonance δ 9.75 ppm in the chromone **21** indicated the magnetic anisotropy effect of the carbonyl group (Table 4). The IR spectrum confirmed coumarin and chromone formulas, by carbonyl bands at 1688 and 1636 cm^{-1} respectively.[24]Furthermore, mass spectrum characterized coumarin by the ion peak (M^+, *m/z*=212, 100%) and by intense loss of CO (M-CO, m/z = 184, 89%) followed by further loss of CHO (M-CO-CHO, *m/z*=155, 15%), while chromone **21** showed ion peak (M^+, *m/z*=212, 100%) and loss of CO (M-CO, m/z = 184, 34%). Compounds **21** and **20** were identified by comparison with reported spectral data of 8-hydroxy-3-methyl-1*H*-benzo[*f*]chromen-1-one,[24] 1*H*-benzo[*f*]chromen-1-one,[25] and 9-hydroxy-3*H*-benzo[*f*]chromen-3-one.[26] Unfortunately, we did not obtain suitable crystals for X-ray crystal-structure analysis or have an explanation for formation of **21**.

Table 4. Yield and **H**, **C** chemical shifts of five characteristic signals of **20** and **21**

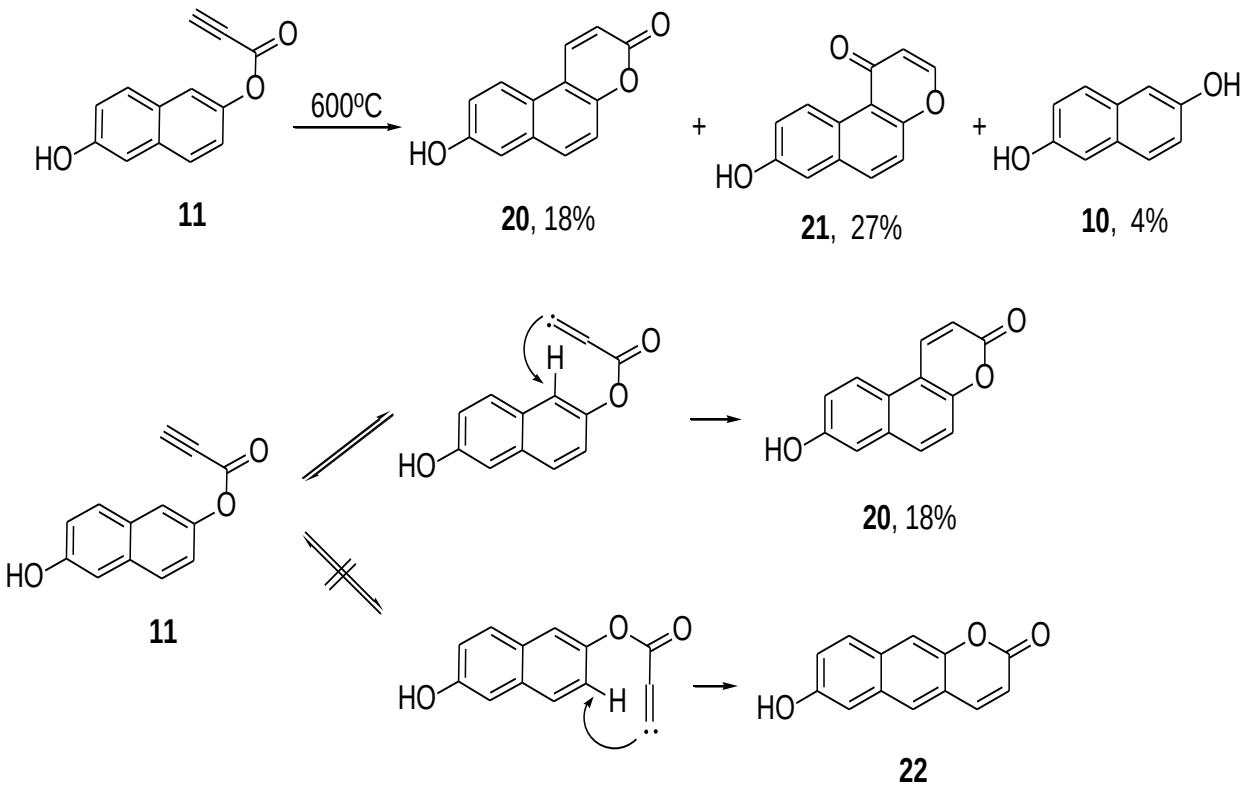
Comp.	Yield (%)	δCOC**H**=C**H** (ppm)	δCO**C**H=**C**H (ppm)	δ**C**O (ppm)
20	18	8.82 (d, *J* 10.0), 6.58 (d, *J* 10.0)	140.5, 115.2	160.2
21	27	8.31 (d, *J* 6.0), 6.46 (d, *J* 5.6)	154.3, 114.9	178.3



Scheme 4. FVP of propargyl ethers **2** and **4**.



Scheme 5. FVP of propargyl amines **6-7** and **9**.



Scheme 6. FVP of acetylenic ester **11**.

Conclusions

Naphthofurans **14** and **15** are the major products from FVP of **2**.
2-Indolinone- and cyclobutenenaphthalene derivatives **16** and **17** are the major products from FVP of **4**.
Quinoline **18** is the major product from FVP of **6** and **7**.
Chromenones **20** and **21** are the major products from FVP of **11**.
This study has resulted in synthesis of seven new compounds, substrate **11** and six FVP products **14-17**, **20** & **21** of potential medicinal and pharmaceutical applications.

Experimental Section

General. All reactions were carried out in oven-dried glassware under nitrogen atmosphere, using commercially supplied solvents and reagents. *N,N'*-Dicyclohexylcarbodiimide(DCC), 4-dimethylaminopyridine (DMAP), quinolin-8-ol, 2,6- naphthalene-2,6-diol, aniline, propargyl bromide, propiolic acid and methyl anthranilate were purchased from Sigma Aldrich. Column chromatography was carried out on silica gel using flash techniques (eluents are given in parentheses). Analytical thin-layer chromatography was performed on precoated silica gel F254 aluminum plates with visualization under UV light.

All analyses were determined in the Research Sector Projects Unit (RSPU) at Kuwait university. Melting points were determined on a Gallenkamp apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on

a Bruker DPX 400, 600 MHz super-conducting NMR spectrometer. GCMS were measured using Agilent 1100 series LC/MSD with an API-ES/APCI ionization mode. Mass spectra were recorded with a Thermo Fisher DFS Magnetic Sector GC-HRMS spectrometer. Infrared were recorded with Perkin Elmer FT-IR / IR Spectrometer.

Synthesis of propargyl ethers 2,4, and amines 6,7,9. Phenol/amine (3 mmol) derivatives were added to (1-3 eq.) propargyl bromide and (2-4 eq.) K_2CO_3 in acetone. The reaction mixture was heated at reflux until reaction completion based on TLC monitoring. On completion, the reaction mixture was cooled up to room temperature and the solvent was removed under reduced pressure. The residue was dissolved in distilled water, then the extraction was done by dichloromethane (DCM). Organic layer was separated and dried by anhydrous magnesium sulfate. The solvent was removed under reduced pressure. Then the crude product was purified by flash chromatography. 60/40 mixture of hexane and ethyl acetate.

8-(Prop-2-yn-1-yloxy)quinoline (2).[16] Brown solid, mp 67-68°C, 0.429 g, yield (78%); δH(400 MHz, CDCl3) 8.98-8.96 (dd, 1H, *J* 4.0, 1.6), 8.18-8.16 (dd, 1H, *J* 8.4, 1.6), 7.53-7.44 (m, 3H), 7.31-7.28 (dd, 1H, *J* 7.2, 1.6), 5.06 (d, 1H, *J* 2.4), 2.55 (t, 1H, *J* 2.4); δ_c(100 MHz, $CDCl_3$) 153.1, 149.5, 140.2, 136.4, 129.7, 126.7, 121.9, 120.8, 110.3, 78.4, 76.3, 56.7; IR (KBr): v 3274 (s), 3068 (w),2976 (w), 2119 (m), 1607 (vs), 1502 (vs), 1106 (vs), 791 (s) cm^{-1}; EIMS *m/z* (%) 183 (M^+, 52), 154 (61), 129 (100), 116 (38), 101 (6), 89 (19), 63 (4); Anal. Calcd for $C_{12}H_9NO$ (183.07): C, 78.67; H, 4.95; N, 7.65; found: C, 78.73; H, 4.91; N, 7.60.

2,6-Bis(prop-2-yn-1-yloxy)naphthalene (4).[20] White solid, mp 134-136°C, 0.475 g, yield (67%); δ_H(400 MHz, $CDCl_3$) 7.71 (d, 2H, *J* 8.8), 7.24-7.19 (m, 4H), 4.81 (d, 4H, *J* 2.4), 2.56 (t, 2H, *J* 2.4); δ_c(100 MHz, $CDCl_3$) 154.5, 130.1, 128.7, 119.3, 108.0, 78.7, 75.8, 56.1; IR (KBr): v 3274 (s), 3067 (w), 2904 (w), 2130 (m), 1601 (vs), 1508 (s), 1224 (vs), 840 (vs) cm^{-1}; EIMS *m/z* (%) 236 (M^+, 48), 197 (100), 169 (8), 141 (14), 115 (6); Anal. Calcd for $C_{16}H_{12}O_2$ (236.08): C, 81.34; H, 5.12; found: C, 81.36; H, 5.08.

***N*-(Prop-2-yn-1-yl)aniline 6**:[21] yellow oil, 0.092 g, yield (23%); δ_H(600 MHz, $CDCl_3$) 7.26 (t, 2H, *J* 7.2), 6.85 (t, 1H, *J* 7.3), 6.75 (d, 1H, *J* 7.8), 3.97 (d, 2H, *J* 2.4), 2.27 (t, 1H, *J* 2.4); δ_c(150 MHz, $CDCl_3$) 146.8, 129.4, 118.8, 113.7, 81.1, 71.5, 33.8; EIMS *m/z* (%) 131 (M^+, 100), 103 (10), 65 (20); HR-MS (EI) *m/z* 131.0731 (M^+, C_9H_9N requires 131.0730).

***N,N*-Di(prop-2-yn-1-yl)aniline 7**:[22] yellow oil, 0.229 g, yield (45%); δ_H(600 MHz, $CDCl_3$) 7.35-7.32 (m, 2H), 7.02 (d, 2H, *J* 7.8), 6.94 (t, 1H, *J* 7.2), 4.16 (s, 4H), 2.29 (t, 2H, *J* 1.8); δ_c(150 MHz, $CDCl_3$) 147.9, 129.3, 120.1, 116.0, 79.3, 72.9, 40.6; EIMS *m/z* (%) 169 (M^+, 100), 154 (6), 130 (64), 115 (13); HR-MS (EI) *m/z* 169.0887 (M^+, $C_{12}H_{11}N$ requires 169.0886).

Methyl 2-(prop-2-ynylamino)benzoate 9:[23] mp 80-81°C, 0.369 g, yield (65%); δ_H(600 MHz, $CDCl_3$) 7.94 (d, 1H, *J* 8.4), 7.45-7.42 (m, 1H), 6.86-6.82 (q, 1H, *J* 8.4), 6.73-6.69 (q, 1H, *J* 8.4), 4.05 (d, 2H, *J* 2.4), 3.88 (s, 3H), 2.24 (d, 1H, *J* 2.4); δ_C(150 MHz, $CDCl_3$)169.0, 134.7, 131.8, 116.3, 112.1, 80.3, 71.5, 51.8, 32.9; EIMS *m/z* (%) 189 (M^+, 19), 156 (59), 130 (46), 102 (67), 77 (100), 63 (46); HR-MS (EI) *m/z* 189.0784 (M^+, $C_{11}H_{11}O_2N$ requires 189.079).

A solution of DCC (9.29 g, 45 mmol) and DMAP (0.366 g, 3 mmol) in 150 ml DCM was added dropwise to a mixture of propiolic acid (3.08 g, 44 mmol) and naphthalene-2,6-diol **3** (6.4 g, 40 mmol) in dry dichloromethane (DCM) at 0 °C under nitrogen gas. The reaction mixture was stirred for 1−12 h. The reaction mixture was filtered then washed with 0.1 N HCl (2×50 ml) and a saturated solution of sodium chloride (2×50 ml). The evaporation of the dried solution gave crude products which were purified by silica gel chromatography (95/5 hexane /ethyl acetate).

6-Hydroxynaphthalen-2-yl propiolate (11). White solid, mp 144-146°C, 2.72 g, yield (32%); δ_H(400 MHz, DMSO) 9.85 (s, 1H), 7.77-7.74 (m, 2H), 7.65 (d, 1H, *J* 2.4), 7.28-7.25 (dd, 1H, *J* 8.8, 2.4), 7.17 (d, 1H, *J* 2.0), 7.15-7.12 (dd, 1H, J 8.8, 2.0), 4.86 (s, 1H); δ_c(100 MHz, DMSO) 155.5, 151.2, 144.7, 132.9, 129.1, 127.6, 127.5, 120.9, 119.6, 118.3, 108.7, 81.5, 74.3; IR (KBr): v 3444 (m), 3318 (m), 3232 (s), 2115 (s), 1713 (vs), 1699 (vs), 1608

(s),1210 (vs), 885 (s) cm^{-1}; EIMS *m/z* (%) 212 (M^+, 100), 184 (22), 160 (84), 131 (35), 103 (7), 77 (4); Anal. Calcd for $C_{13}H_8O_3$ (212.05): C, 73.58; H, 3.80; found: C, 73.31; H, 3.78.

***N*-Cyclohexyl-*N*-(cyclohexylcarbamoyl)propiolamide (12)**. White solid, mp 168-170°C, 2.11 g, yield (17%); δ_H(400 MHz, $CDCl_3$) 8.12 (s, 1H), 4.43-4.37 (m, 1H), 3.72-3.67 (m, 1H), 3.37 (s, 1H), 2.33-1.57 (m, 12H), 1.43-1.17 (m, 8H); δ_c(100 MHz, $CDCl_3$) 152.5, 82.0, 76.2, 60.5, 49.7, 32.8, 30.7, 26.7, 25.7, 25.3, 24.8; IR (KBr): v 3281 (m), 3202 (s), 3057 (w), 2932 (s), 2015 (s), 1704 (vs), 1622 (vs), 1540 (vs), 1238 (s), 771 (s) cm^{-1}; Anal. Calcd for $C_{16}H_{24}N_2O_2$ (276.18): C, 69.53; H, 8.75; N, 10.14; found: C, 69.30; H, 8.67; N, 10.11.

(Z)-3-Cyclohexyl-2-(cyclohexylimino)-4-methyleneoxazolidin-5-one (13). White solid, mp 62-64°C, 0.62 g, yield (5%); δ_H(400 MHz, $CDCl_3$) 5.26 (d, 1H, *J* 2.8), 4.99 (d, 1H, *J* 2.4), 4.05-4.03 (m, 1H), 3.69-3.64 (m, 1H), 2.30-2.20 (m, 2H), 1.85-1.60 (m, 10H), 1.44-1.17 (m, 8H); δ_c(100 MHz, $CDCl_3$) 161.2, 147.1, 91.7, 54.3, 53.2, 34.4, 28.6, 25.98, 25.94, 25.2, 24.7; IR (KBr): v 2928 (s), 2854 (m), 1710 (vs), 1667 (vs), 1390 (vs), 1283 (m), 955 (s), 691 (s) cm^{-1}; Anal. Calcd for $C_{16}H_{24}N_2O_2$ (276.18): C, 69.53; H, 8.75; N, 10.14; found: C, 69.48; H, 8.73; N, 10.12.

Flash vacuum pyrolysis. 0.20 g of each substrate was introduced into a sample tube and then volatilized in a Büchi sublimation oven. The gaseous molecules were passed through a 30 × 2.5 cm horizontal fused quartz tube housed in a Büchi Kugelrohr oven. The oven was heated externally by a Carbolite Eurotherm tube furnace MTF-12/38A up to 1000 °C, the temperature was monitored by a Pt/Pt-13%Rh thermocouple situated at the center of the furnace. The products were collected in a U-shaped trap cooled in liquid nitrogen. The whole system was maintained at a pressure of ca 10^{-2} Torr by an Ed-wards Model E2M5 high capacity rotary oil pump; the pressure being measured by a Pirani gauge situated between the cold trap and the pump. Under these conditions, the contact time in the hot zone was estimated to be ca10 ms. The different fractions of the product collected in the U-shaped trap were analyzed by ^1H, ^{13}C NMR, and GC-MS. Relative and percent yields were determined from NMR analysis.

Pyrolysis products of **2**.

2-Methylfuro[3,2-*h*]quinoline (14). Brown oil, yield (23%); δ_H(400 MHz, $CDCl_3$) 8.96-8.95 (dd, 1H, *J* 4.0, 1.6), 8.25-8.23 (dd, 1H, *J* 8.4, 1.6), 7.66 (d, 1H, *J* 8.4), 7.60 (d, 1H, *J* 8.4), 7.42-7.39 (m, 1H), 6.58 (d, 1H, *J* 1.2), 2.63 (d, 3H, *J* 0.8); δ_c(100 MHz, $CDCl_3$) 156.9, 150.0, 148.9, 136.6, 128.8, 125.7, 122.7, 120.6, 120.4, 120.0, 103.9, 14.4; IR (KBr): v 3063 (w), 3029 (w), 2920 (w), 2852 (w), 1718 (m), 1593 (s), 1368 (vs), 1058 (vs), 937 (s), 829 (vs) cm^{-1};EIMS *m/z* (%) 183 (M^+, 100), 154 (12), 127 (4); Anal. Calcd for $C_{12}H_9NO$ (183.07): C, 78.67; H, 4.95; N, 7.65; found: C, 78.72; H, 4.90; N, 7.61.

Furo[3,2-*h*]quinoline (15). Brown oil, yield (11%); δ_H(400 MHz, $CDCl_3$) 9.01-8.99 (dd, 1H, *J* 4.4, 1.6), 8.30-8.27 (dd, 1H, *J* 8.4, 1.6), 7.92 (d, 1H, *J* 2.4), 7.79 (d, 1H, *J* 8.4), 7.67 (d, 1H, *J* 8.4), 7.48-7.45 (m, 1H), 6.99 (d, 1H, *J* 2.0); δ_c(100 MHz, $CDCl_3$) 150.1, 149.6, 146.0, 137.0, 136.7, 127.2, 126.4, 123.1, 120.9, 120.6, 107.8; IR (KBr): v 3061 (w), 3029 (w), 2925 (w), 2852 (w), 1622 (m), 1510 (s), 1379 (vs), 1074 (s), 830 (vs), 697 (vs) cm^{-1};EIMS *m/z* (%) 169 (M^+, 100), 140 (15), 114 (9), 97 (3); Anal. Calcd for $C_{11}H_7NO$ (169.05): C, 78.09; H, 4.17; N,8.28; found: C, 77.83; H, 4.10; N, 8.19.

Pyrolysis products of 4

1,2,5,7-Tetrahydro-6*H*-cyclobuta[*a*]cyclopenta[*f*]naphthalen-6-one (16). White solid, mp 145-147°C, yield (21%); δ_H(400 MHz, $CDCl_3$) 7.70 (d, 1H, *J* 8.4), 7.58 (d, 1H, *J* 8.4), 7.45 (d, 1H, *J* 8.4), 7.33 (d, 1H, *J* 8.4), 3.84 (s, 2H), 3.75 (s, 2H), 3.44 (t, 2H, *J* 4.0), 3.33 (t, 2H, *J* 4.0); δ_c(100 MHz, $CDCl_3$) 215.2, 142.9, 142.8, 135.4, 134.0, 129.5, 128.8, 123.8, 123.2, 122.5, 122.1, 45.3, 42.9, 29.5, 28.7; IR (KBr): v 3051 (w), 3022 (w), 2960 (w), 2922 (m), 2888 (w), 2829 (w), 1742 (vs), 1379 (s), 1224 (s), 1140 (s), 966 (s), 804 (vs) cm^{-1};EIMS m/z (%) 208 (M^+, 74), 180 (100), 165 (26), 152 (18), 139 (4); Anal. Calcd for $C_{15}H_{12}O$ (208.09): C, 86.51; H, 5.81; found: C, 86.24; H, 5.72.

1,2,5,6-Tetrahydrodicyclobuta[a,*f*]naphthalene (17). White solid, mp 136-138°C, yield (17%); δ_H(400 MHz, $CDCl_3$) 7.62 (d, 2H, *J* 7.6), 7.26 (d, 2H, *J* 8.0), 3.40 (t, 4H, *J* 4.0), 3.30 (t, 4H, *J* 4.0); δ_c(100 MHz, $CDCl_3$) 143.1, 141.6, 129.0 (2C), 121.8, 121.5, 29.4, 28.7; IR (KBr): v 3049 (w), 2958 (w), 2920 (s), 2827 (m), 1578 (w), 1345 (m), 1189 (m), 813 (vs) cm^{-1};EIMS m/z (%) 180 (M^+, 100), 135 (12), 97 (17), 69 (10); Anal. Calcd for $C_{14}H_{12}$ (180.09): C, 93.29; H, 6.71; found: C, 93.03; H, 6.61.

Naphthalene-2,6-diol (3). Pale brown solid, mp 223-225°C, yield (8%); δ_H(400 MHz, DMSO) 9.32 (s, 2H), 7.53 (d, 2H, *J* 8.8), 7.01-6.96 (m, 4H); δ_c(100 MHz, DMSO) 152.8, 128.9, 127.3, 118.7, 108.8; EIMS *m/z* (%) 160 (M^+, 100), 131 (26), 102 (7), 77 (2).

Pyrolysis products of **6** and **7**.

Quinoline (18). Yellow oil, yield (26-33%); δ_H(600 MHz, $CDCl_3$) 8.92 (d, 1H, *J* 2.4), 8.13 (t, 2H, *J* 7.2), 7.81 (d, 1H, *J* 8.4), 7.71 (t, 1H, *J* 7.2), 7.53 (t, 1H, *J* 7.2), 7.32-7.27 (m, 1H); δ_c(150 MHz, $CDCl_3$) 150.5, 148.4, 136.1, 129.5, 128.4, 127.9, 126.6, 121.2, 118.2

Pyrolysis products of **9**.

7-Aminoisobenzofuran-1(3*H*)-one (**19).**[27] White solid, mp 122-123°C, yield (34%); δ_H(400 MHz, $CDCl_3$) 7.38 (t, 1H, *J* 8.0), 6.69 (d, 1H, *J* 7.6), 6.63 (d, 1H, *J* 8.4), 5.23 (s, 3H); δ_C(100 MHz, $CDCl_3$) 172.6, 147.7, 147.3, 135.9, 113.7, 109.7, 108.5, 69.8; Anal. Calcd for $C_8H_7NO_2$ (149.05): C, 64.42; H, 4.73; N, 9.39; found: C, 64.10; H, 4.65; N, 9.30.

Pyrolysis products of **11**.

8-Hydroxy-3*H*-benzo[*f*]chromen-3-one (20). Yellow solid, yield (27%); δ_H(400 MHz, $CDCl_3$) 9.99 (s, 1H), 8.84 (d, 1H, *J* 10.0), 8.39 (d, 1H, *J* 10.0), 7.98 (d, 1H, *J* 8.8), 7.47 (d, 1H, *J* 9.2), 7.31-7.26 (m, 2H), 6.59 (d, 1H, *J* 10.0); δ_c(100 MHz, $CDCl_3$) 160.2, 155.4, 151.4, 140.5, 132.3, 131.6, 123.8, 122.6, 120.2, 116.8, 115.2, 113.0, 110.3; IR (KBr): v 3223 (br), 3092 (w), 3047 (w), 2918 (w), 2850 (w), 1688 (vs), 1565 (s), 1341 (s), 1121 (m), 800 (s)cm^{-1};EIMS *m/z* (%) 212 (M^+, 100), 184 (89), 155 (15), 92 (4), 91 (9).

8-Hydroxy-1*H*-benzo[*f*]chromen-1-one (**21).** Yellow solid, yield (18%); δ_H(400 MHz, $CDCl_3$) 9.99 (s, 1H), 9.77 (d, 1H, *J* 8.8), 8.31 (d, 1H, *J* 6.0), 8.13 (d, 1H, *J* 9.2), 7.62 (d, 1H, *J* 8.8), 7.31-7.26 (m, 2H), 6.47 (d, 1H, *J* 5.6); δ_c(100 MHz, $CDCl_3$) 178.3, 155.8, 155.6, 154.3, 134.3, 131.6, 127.1, 123.1, 120.3, 118.1, 117.4, 114.9, 110.6; IR (KBr): v 3223 (br), 3092 (w), 3047 (w), 2918 (w), 2850 (w), 1636 (s), 1565 (s), 1341 (s), 1121 (m), 800 (s)cm^{-1};EIMS *m/z* (%) 212 (M^+, 100), 184 (34), 130 (5).

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Supplementary Material

^1H and ^{13}C NMR spectra of all compounds are given in the supplementary material file associated with this manuscript.

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