JOC The Journal of Organic Chemistry

University of Sunderland

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Note

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J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.8b02280 • Publication Date (Web): 24 Oct 2018

ACS Publications

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Functionalization of the "bay region" of perylene in reaction with 1-arylalk-2-yn-1-ones catalyzed by trifluoromethanesulfonic acid—one-step approach to 1-acyl-2-alkylbenzo[ghi]perylenes

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Dedication

This work is dedicated to Professor Janusz Zakrzewski of University of Łódź on the occasion of his 70th birthday

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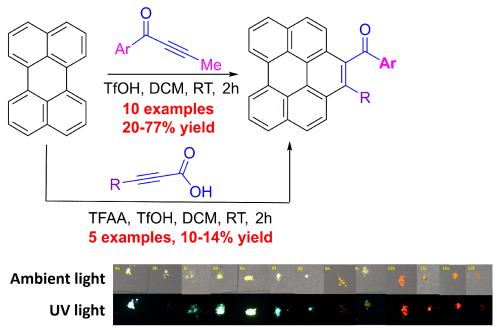


ABSTRACT

We describe a convenient method of the synthesis of 1-acyl-2-alkylbenzo[ghi]perylenes *via* functionalization of the "bay region" of perylene in the reaction with 1-arylalk-2-yn-1-ones catalyzed by trifluoromethanesulfonic acid. We showed that the formation of 1-acyl-2-alkylbenzo[ghi]perylenes from perylene and 1-arylalk-2-yn-1-ones might occur via spontaneously aromatization of 1-acyl-2-alkyl-2a,12a-dihydrogenbenzo[ghi]perylenes by oxidation with dioxygen or by the hydrogen transfer to 1-arylalk-2-yn-1-ones. These compounds are fluorescent in solution with a high Stokes shift and with a Φ_F value of up to 0.17 (and 0.36 in solid).

Functionalized polycyclic aromatic hydrocarbons (PAHs) are widely used in organic semiconductors and organic photovoltaics[1]. These compounds are often synthesized in the Scholl reaction[2-7] or by inter- and intramolecular Diels–Alder reactions;[8] however, some other methods including ring-closing metathesis and photocyclization are also applied.[2,9] Unfortunately, many of these reactions require multistep synthesis of starting reagents,[10] or extreme reaction conditions such as high temperature. Moreover, the Scholl reaction is difficult to control which often results in a low yield of the desired products.[7,10,11] Despite these disadvantages, the Scholl reaction is still commonly used for the synthesis of PAHs.[12-14] Recently, comprehensive reviews in this field have been published.[9,15-17]

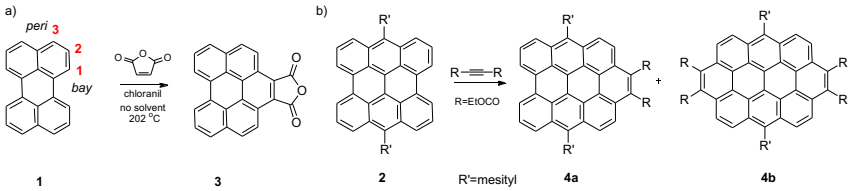
Perylene **1**, a simple example of a PAH containing "bay region", can be readily functionalized in an electrophilic substitution reaction leading to 3-substituted perylenes as the primary product. In some cases, for instance, formylation of **1**,[18] the formation of 1-formylperylene has also been observed with significantly lower yield than that of predominant 3-formylperylen.

Because the "bay region" of hydrocarbons are notoriously resistant to Diels–Alder reaction, they require harsh conditions such as very high temperature, prolonged reaction time, and highly oxidative conditions, and the availability of dienophiles that can withstand such reaction conditions limits its use. The functionalization of "bay regions" of hydrocarbons such as **1** and its homologs such as bisanthen **2** can be performed in the Diels–Alder cycloaddition with dienophiles such as maleic anhydride or diethyl acetylenedicarboxylate, leading to the formation of compounds **3-4** (Scheme 1a). For instance, **1** reacts with an excess of melted maleic anhydride and chloranil at 202°C to produce **3** with a yield of up to 100%[19] or with an excess of diethyl acetylenedicarboxylate at 150°C to produce 1,2-diethoxycarbonylbenzo[ghi]perylene with an

yield of 25% after 72 h. 7,14-bismesitylbisanthen **2** reacts smoothly with diethyl acetylenedicarboxylate in toluene solution at 120°C to form a mono- (compound **4a**) and di-addition (compound **4b**) products with a yield of 44 and 12%, respectively (Scheme 1b).[20]

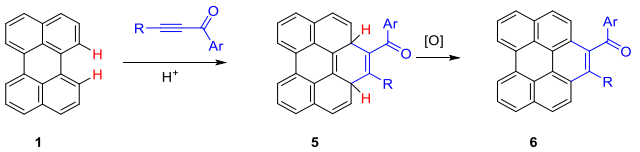
Alkenes bearing EWG groups are commonly used as dienophiles in Diels–Alder reaction,[21,22] however, acetylenic ketones have been reported only as dienophiles in reaction with simple dienes catalyzed by Lewis acids and chiral Lewis acids [23,24] leading to the formation of 1,4-cyclohexadiene derivatives.

Scheme 1. Diels-Alder Reaction of (a) 1 with Maleic Anhydride; and (b) 2 with Diethyl Acetylenedicarboxylate



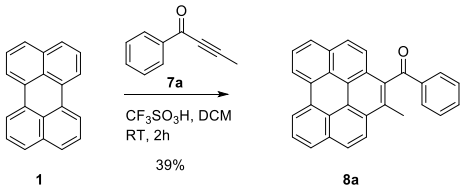
Continuing our study of straightforward functionalization of perylene,[25] we became interested in the reaction of 1-arylalk-2-yn-1-ones with **1** catalyzed by a strong protic acid, trifluoromethanesulfonic acid, which should allow to functionalize the "bay region" of **1** thereby producing benzo[ghi]perylenes (Scheme 2). Herein, we describe the synthesis, mechanistic investigation, and fluorescence properties of a new PAH derivative, 1-acyl-2-alkylbenzo[ghi]perylenes **6**.

Scheme 2. Reaction of 1 with 1-arylalk-2-yn-1-ones Studied Herein



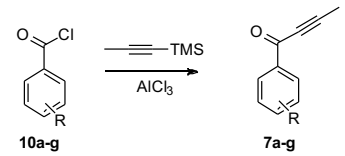
To realize our goal, first, we performed a preliminary experiment starting from **1** and 1-phenylbut-2-yn-1-one **7a**. Our study showed that the reaction of an equimolar amount of **1** with **7a** in DCM catalyzed by an equimolar amount of TfOH leads to the formation of **8a** with a yield of 39% (Scheme 3). 1D and 2D NMR spectra and MS analysis have confirmed the structure of the product. Unfortunately, further attempts to optimize the reaction by changing the reaction conditions or ratios of the modifying reagents failed.

Scheme 3. Reaction of 1 with 7a Catalyzed by Trifluoromethanesulfonic Acid



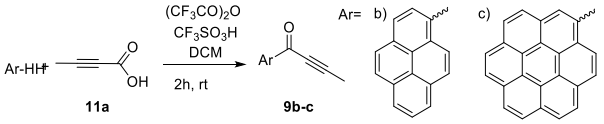
Next, we examined the scope of reaction of **1** with a series of 1-arylbut-2-yn-1-ones **7b-g** and **9a-c**. The required **7b-g** were synthesized with an yield of 45–78% in a reaction of acid chlorides **10b-g** with 1-trimethylsilylpropyne catalyzed by aluminum chloride (Scheme 4), whereas compounds **9a-c** were synthesized in Friedel–Crafts acylation of corresponding arenes with but-2-ynoic acid **11a**, TFAA, and TfOH (Schemes 5 and 6) by applying known procedure.[26]

Scheme 4. Synthesis of 1-arylbut-2-yn-1-ones **7a-g**



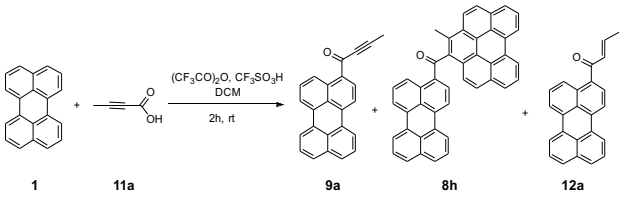
R= (**a**) H, (**b**) 4-CF_3, (**c**) 2-Cl, (**d**) 4-Me, (**e**) 4-OMe, (**f**) 3,4,5-$(OMe)_3$, (**g**) 2,4,6-F_3

Scheme 5. Synthesis of 1-(pyren-1-yl)but-2-yn-1-one **9b and** 1-(coronen-1-yl)but-2-yn-1-one **9c**



To our surprise, acylation of **1** with **11a** not only produced the expected product, 1-(perylen-3-yl)but-2-yn-1-one **9a** (56% yield) but also gave **8h** (10% yield) together with 1-(perylen-3-yl)but-2-en-1-one **12a** (11% yield) (Scheme 6). These results encored us to study the reaction of **1** with alk-2-ynoic acid, and the results have been discussed in the following sections.

Scheme 6. Reaction of 1 with 11a in the Presence of TfOH

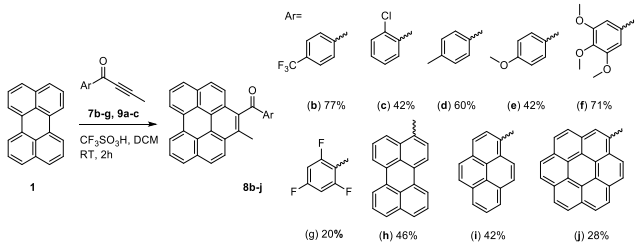


We found that **1** reacts with **7b-g** or **9a-c** and TfOH under optimized conditions to yield compounds **8b-g** and **8h-j**, respectively, in decent yields (Scheme 7). The structure of the products have been confirmed by using ^{1}H, ^{13}C, and 2D NMR spectra. The structures of two compounds, **8d** and **8h**, have also been confirmed by using X-ray crystallography (Figure S6-S7).

In general, in all cases, 1-acyl-1-alkylbenzo[ghi]perylenes **8a-j** have been isolated in similar yields, ca. 42%; however, in two instances, **8b** and **8f**, the yield of the products was found to be significantly higher, 77 and 71% yield, respectively.

We also found that **1** does not react with **7a** in refluxing xylene (24 h, with and without DDQ) or with dimethyl acetylenedicarboxylate in the presence of TfOH. Moreover, in the reaction of **8a** with an additional amount of **7a**, we did not observe the formation of any products, and only unreacted substrates were recovered. As could be expected, phenanthrene, which is significantly less active as dienes in Diels–Alder reaction,[20,27] does not react with **7a** and TfOH even after prolonged reaction times, and only starting hydrocarbon was recovered.

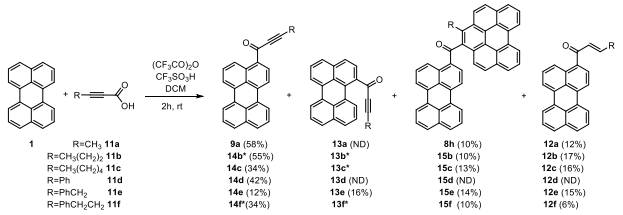
Scheme 7. Reaction of 1 with 7b-g and 9a-c Catalyzed by TfOH



Unexpected formation of **8h** in the reaction of **1** with **11a** and TFAA catalyzed by TfOH (Scheme 6) inspired us to study the reaction of **1** with various alk-2-ynoic acids **11a-f** in detail. We expected the formation of 1-(perylen-3-yl)alk-2-yn-1-ones (compounds **9a** and **14b-f**) as the primary products in addition to the formation of 1-acyl-2-alkylbenzo[ghi]perylenes (compounds **8h** and **15b-f**), 1-(perylen-1-yl)alk-2-yn-1-ones (compounds **13a-f**), and 1-(perylen-3-yl)alk-2-en-1-ones (compounds **12a-f**) as the minor products. Indeed, most of the investigated alk-2-ynoic acids produced a complex mixture of the expected compounds (Scheme 8). The reaction of **1** with phenylpropynoic acid **11d** gave **14d** with a yield of 42% as the sole isolable product. In this reaction, we did not observe the formation of benzo[ghi]perylenes or the formation of other products. All other alk-2-ynoic acids bearing alkyl substituent at C-3 position such as methyl

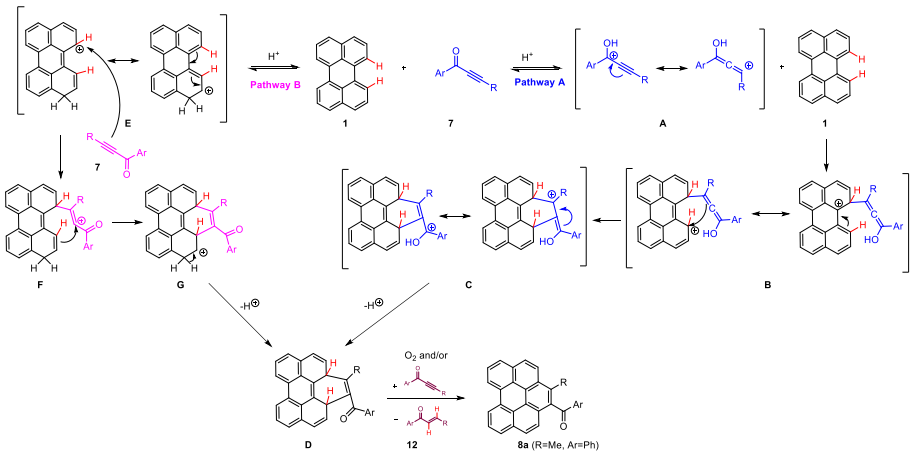
(but-2-ynoic acid, **11a**), *n*-propyl (hex-2-ynoic acid, **11b**), *n*-pentyl (oct-2-ynoic acid, **11c**), benzyl (4-phenylbut-2-ynoic acid, **11e**), and phenethyl group (5-phenylpent-2-ynoic acid, **11f**) gave a mixture of 1-(perylen-3-yl)alk-2-yn-1-ones (compounds **9a** and **14b-c,e-f**, respectively) as the primary products and 1-(perylen-1-yl)alk-2-yn-1-ones (compounds **13a-c,e-f**, respectively) as the minor products, in addition to small amounts (10–14% yield of the isolated products) of 1-(perylen-3-oyl)-2-alkylbenzo[ghi]perylenes (compounds **8h, 15b-c,e-f**, respectively) and 1-(perylen-3-yl)alk-2-en-1-ones (compounds **12a-c,e-f**, respectively). The structure of the products was confirmed by 1D and 2D NMR spectra and MS analysis. Moreover, structure of **9a** and **14d** were also confirmed by X-ray crystallography (Figures S8-S9).

Scheme 8. Reaction of 1 with 11a-f , TFAA and TfOH



*—inseparable mixture of 1- and 3-isomers; ND—not determined

Scheme 9. The Proposed Mechanism of the Reaction of 1 with 7 Catalyzed by TfOH



The formation of benzo[ghi]perylenes **8** and alkenes **12** in the reaction of **1** and **7** catalyzed by TfOH or in the reaction of **1** with but-2-ynoic acid **11a** and TFAA and TfOH (in this case **7** is formed in a reaction of **1** with **11a)** can occur in stepwise mechanism (Scheme 9) or according to Diels–Alder reaction. We hypothesized that two pathways may occurs. First, the protonation of **7** leads to the formation of allenium cation **A** (Pathway A) which reacts as an electrophile with **1** to yield 2a,12a-dihydrobenzo[ghi]perylene **D**. In the pathway B, **1** is protonated to cation **E** which reacts as an electrophile with **7** to yield **D.** Finally, **D** is aromatized in the reaction with dioxygen (from the air) or in a hydrogen transfer to **7**, which resulted in the formation of **8** and **12**. The NMR studies confirmed that **1** and **7** are protonated by TfOH and the resulted species **E** and **A**, respectively, afforded the same products in reaction with **7** or **1**, respectively. The hydrogen transfer from **D** to 1-arylalk-2-yn-1-ones is in contrast to the results reported in previous studies of Diels-Alder reaction of **1** or **2** with diethyl acetylenedicarboxylate where it was not observed.[20,28] Therefore, to prove the proposed mechanism, we performed additional experiments using perylene-d_{12} **16** instead of **1** and/or using TfOD instead of TfOH. We observed that reaction of **1** with **9b** catalyzed by TfOH or TfOD afforded **8i** and **17** lacking deuterium atoms. The reaction of **16** with **9b** catalyzed by TfOH in DCM led to the synthesis of two isolable products: deuterated-benzo[ghi]perylene **18** (42%) and deuterated-alkene **19** (37%) (Schemes S1-S2 and Figure S1-S3). When TfOH was replaced by TfOD, the same products were formed from **16** and **9b**. Moreover, we did not observe the exchange of proton in the solution of 1-(pyren-1-yl)but-2-en-1-one in DCM in the presence of 1 eq of TfOD. The reaction of **16** with **11a** catalyzed by TfOH led to a separable mixture of the deuterated products: **20** (38%), **21** (17%), and **22** (18%) and unreacted **16** (38%), which were isolated by column chromatography and identified by NMR and MS spectroscopy (Scheme S3 and Figures S4-S5). These results confirmed that the formation of benzo[ghi]perylenes in the reaction of **1** with 1-arylbut-2-yn-1-ones catalyzed by TfOH might

occur *via* aromatization of intermediate **D** by oxidation with dioxygen or by hydrogen transfer to 1-arylbut-2-yn-1-ones which are reduced to 1-arylbut-2-en-1-ones.

A comparison of electronic absorption spectra in DCM solution of **8a-i** and **15b,c,e,f** showed that benzo[ghi]perylenes bearing benzoyl moiety (compounds **8a-g**) possess very similar spectra with the absorption maximum in the range of 390-391 nm, whereas compounds bearing perylen-3-oyl moiety (compounds **8h** and **15b,c,e,f**) showed an additional broad absorption band with the absorption maximum in the range of 467–470 nm. However, pyren-1-oyl derivative **8i** exhibits the absorption maximum of 391 nm. All of the investigated compounds were fluorescent in dilute DCM solution and in solid state at room temperature. Benzo[ghi]perylenes bearing benzoyl moiety **8a-g** showed broad fluorescence band in the range of 400–700 nm with low fluorescence quantum yield (up to Φ_F=0.039 for **8d**). The fluorescence lifetimes were in the range of nanoseconds with one or two components. All of these compounds possess high Stokes shift in the range of 3002–7227 cm^{-1}. In comparison, benzo[ghi]perylenes bearing perylen-3-oyl, (compounds **8h** and **15b,c,e,f**) showed broad fluorescence band in the range of 500–700 nm, with significantly higher fluorescence quantum yields (Φ_F values in the range of 0.058–0.17) and significantly lower Stokes shift (in the range of 2229–2474 cm^{-1}). All of the synthesized compounds were fluorescent in solid state (Table S1, Figures S10–S23). The quantum yields of investigated compounds in the solid state were found to be significantly higher (up to Φ_F=0.36 for powdered and Φ_F=0.22 for crystals of **8d**) than that in the DCM solution, with a maximum emission wavelength in the range of 543–674 nm. In addition, compounds bearing benzoyl moiety (compounds **8a, c-g**) possess two emission bands at ca. 450–479 nm and 586–611 nm, whereas compounds bearing perylen-3-oyl (compounds **8h** and **15b,c,e,f**) or pyren-1-oyl moiety **8i** exhibit one, broad fluorescence band.

We developed a convenient method of the synthesis of 1-acyl-2-alkylbenzo[ghi]perylenes *via* functionalization of the "bay region" of perylene. We have found that perylene reacts smoothly with readily available 1-arylalk-2-yn-1-ones in the presence of TfOH. We showed that the formation of 1-acyl-2-alkylbenzo[ghi]perylenes from perylene and 1-arylalk-2-yn-1-ones might involve the hydrogen transfer from preliminarily formed 2a,12a-dihydrobenzo[ghi]perylenes to 1-arylalk-2-yn-1-ones. In addition, we showed that acylation of perylene with alk-2-ynoyl trifluoroacetates (generated in situ from alk-2-ynoic acids and trifluoroacetic anhydride) catalyzed by TfOH led to a mixture of 1-(perylen-3-yl)alk-2-yn-1-ones and 1-(perylen-1-yl)alk-2-yn-1-ones, 1-acyl-2-alkylbenzo[ghi]perylenes, and 1-(perylen-1-yl)alk-2-en-1-ones.

The new PAH derivatives are fluorescent in solution and in solid state with high Stokes shift and fluorescence quantum yield (up to 0.17 and 0.36 in DCM solution and solid state, respectively). In our opinion, the developed method of functionalization of the "bay region" of **1** might be useful in the functionalization of other PAHs containing "bay regions".

EXPERIMENTAL SECTION

General Experimental Methods. All reagents were purchased from Sigma-Aldrich of Fluorochem or TCI Chemicals and used as received. Solvents for column chromatography were of HPLC grade and used as received. DCM was dried by distillation from calcium hydride under argon atmosphere and stored over molecular sieves 4 A under argon atmosphere. Column chromatography was performed on silica gel 60 (0.040–0.063 mm). ^{1}H, $^{13}C\{^{1}H\}$ and 2D NMR (^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC, DEPT 135) spectra were recorded in $CDCl_3$ or CD_2Cl_2 on a Bruker Avance III 600 MHz (600.26 MHz for ^{1}H and 150.90 MHz for ^{13}C).

Chemical shifts were referenced to the residual solvent peak δ=7.26 ppm for $CDCl_3$ and 5.32 ppm for CD_2Cl_2 for ^1H and 77.0 ppm for $CDCl_3$ and 53.84 ppm for CD_2Cl_2 for ^{13}C. Spectra were recorded at 299 K, chemical shifts are in ppm, and coupling constants in Hz. IR spectra were recorded on FT-IR Nexus spectrometer in KBr pellets or in a neat film. HRMS spectra were recorder at Institute of Organic Chemistry Polish Academy of Science (Warsaw, Poland) on magnetic sector mass spectrometer AutoSpec Premier (Waters, USA), equipped with an electron impact (EI) ion source and the EBE double focusing geometry mass analyzer. The instrument was controlled and recorded data were processed using MassLynx 4.1 software package (Waters, USA). Thin layer chromatography (TLC) was performed on aluminum sheets precoated with Merck 5735 Kieselgel 60F254. Melting points were determined for all new compounds with at least 95% purity in capillaries with a DigiMelt MPA161 apparatus (SRS) and were uncorrected. UV-Vis spectra were recorded on Lambda 45 UV-VIS spectrometer (PerkinElmer) at 294 K, whereas emission spectra were recorded on Fluoromax-4 (Horiba) spectrofluorimeter equipped with long pass filter. The fluorescence lifetimes were measured on the same spectrofluorimeter equipped with the TCSPC accessory by using the time-domain technique. The quantum yields were measured on the same spectrofluorimeter equipped with integrating sphere Quanta.

General procedure A - synthesis of 1-arylbut-2-yn-1-ones 7a-g

1-phenylbut-2-yn-1-one (**7a**). Briefly, anhydrous aluminum chloride (300 mg, 2.25 mmol) was added in one portion to a stirred solution of benzoyl chloride (281 mg, 232 μL, 2 mmol) and 1-(trimethylsilyl)propyne (224.5 mg, 294 μL, 2.0 mmol) in 6 mL of anhydrous DCM. The resulting mixture was stirred at room temperature for 2 h, and the reaction was quenched by adding 10 mL of 1 M hydrochloric acid. The product was extracted with DCM, and the organic solution was washed with water and brine and then dried over sodium sulfate; finally, the solvent was

evaporated. Purified compound **7a** was obtained as a yellow oil with a yield of 66% (191 mg) *via* column chromatography on silica gel using DCM:cyclohexane 1:1 (v/v) as the eluent. Its NMR spectra (in CD_2Cl_2) were identical with those of an authentic sample.[29]

1-(4-trifluoromethylphenyl)but-2-yn-1-one (**7b**). This compound was synthesized according to the General Procedure A starting from 421 mg (300 μL, 2 mmol) of **10b**. Pure **7b** was obtained as a white solid with a yield of 72% (308 mg) *via* column chromatography on silica using DCM:cyclohexane 3:2 (v/v) as the eluent. Its NMR spectra were identical with those of an authentic sample.[30]

1-(2-chlorophenyl)but-2-yn-1-one (**7c**). This compound was synthesized as **2a** starting from 367.5 mg (266 μL, 2 mmol) of **10c**. Pure **7c** was obtained as an orange oil with a yield of 60% (225 mg) *via* column chromatography on silica using DCM:*n*-hexane 3:7 (v/v) as the eluent. ^{1}H NMR ($CDCl_3$, 600.29 MHz): δ = 8.01-7.99 (m, 1H, H_{ArH}), 7.45-7.41 (m, 2H, H_{ArH}), 7.35 (ddd, J=7.9, 5.7, 2.7 Hz, 1H, H_{ArH}), 2.19 (s, 3H, CH_3); $^{13}C\{^1H\}$- NMR ($CDCl_3$, 150.90 MHz): δ = 176.9 (C=O), 135.8 (C_{Ar}), 133.3 (C_{Ar}), 133.1 (CH_{ArH}), 132.6 (CH_{ArH}), 131.4 (CH_{ArH}), 126.6 (CH_{ArH}), 93.4 (C≡C), 80.3 (C≡C), 4.4 (CH_3); IR (neat film, cm^{-1}) 2234 (C≡C), 2212 (C≡C), 1656 (C=O); HRMS (EI-EBE) m/z: [M^+] Calcd for $C_{10}H_7ClO$ 178.0185; Found 178.0179.

1-(4-methylphenyl)but-2-yn-1-one (**7d**). This compound was synthesized according to General Procedure A starting from 315 mg (270 μL, 2 mmol) of **10d**. Pure **7d** was obtained as a yellow oil with a yield of 60% (255 mg) *via* column chromatography on silica using DCM:*n*-hexane 7:3 (v/v) as the eluent. ^{1}H NMR ($CDCl_3$, 600.29 MHz): δ = 8.02 (d, J=8.2 Hz, 2H, H_{ArH}), 7.26 (d, J=7.9 Hz, 2H, H_{ArH}), 2.42 (s, 3H, CH_3), 2.14 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150.90 MHz):

δ = 177.9 (C=O), 144.9 (C_{Ar}), 134.6 (C_{Ar}), 129.7 (CH_{ArH}), 129.2 (CH_{ArH}), 91.8 (C≡C), 79.1 (C≡C), 21.7 (CH_3), 4.2 (CH_3); IR (neat film, cm^{-1}) 2243 (C≡C), 2202 (C≡C), 1636 (C=O); HRMS (EI-EBE) m/z: [M^+] Calcd for $C_{11}H_{10}O$ 158.0732; Found 158.0727.

1-(4-methoxyphenyl)but-2-yn-1-one (**7e**) This compound was synthesized according to General Procedure A starting from 340 mg (270 μL, 2.0 mmol) of **10e**. Pure compound **7e** was obtained as a white foam with a yield of 78% (275 mg) *via* column chromatography on silica using DCM:*n*-hexane 1:1 (v/v) as the eluent. Its NMR spectra were identical with those of an authentic sample.[30] ^{1}H NMR ($CDCl_3$, 600.29 MHz): δ = 8.10 (d, J=8.9 Hz, 2H, H_{ArH}), 6.93 (d, J=8.9 Hz, 2H, H_{ArH}), 3.87 (s, 3H, OCH_3), 2.13 (s, 3H, CH_3).

1-(3,4,5-trimethoxyphenyl)but-2-yn-1-one (**7f**). This compound was synthesized according to General Procedure A starting from 461.2 mg (2.0 mmol) of **10f**. Pure compound **7f** was obtained as a white foam with a yield of 45% (209 mg) *via* column chromatography on silica using DCM:*n*-hexane 1:1 (v/v) as the eluent. Its NMR spectra were identical with those of an authentic sample.[31] ^{1}H NMR ($CDCl_3$, 600.29 MHz): δ = 7.40 (s, 2H, H_{ArH}), 3.921 (s, 3H, OCH_3), 3.916 (s, 6H, OCH_3), 2.15 (s, 3H, CH_3).

1-(2,4,6-trifluorophenyl)but-2-yn-1-one (**7g**). This compound was synthesized according to the General Procedure A starting from 389 mg (262 μL, 2.0 mmol) of **10g**. Pure compound **2g** was obtained as a yellow oil with a yield of 56% (220 mg) *via* column chromatography on silica using DCM:*n*-hexane 1:1 (v/v) as the eluent. ^{1}H NMR ($CDCl_3$, 600.29 MHz): δ = 6.73-6.69 (m, 2H, H_{ArH}), 2.10 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150.90 MHz): δ = 170.3 (C=O), 164.5 (dt, $^1J_{C-F}$=257, $^3J_{C-F}$=15 Hz, C_{Ar}), 161.75 (dd, $^1J_{C-F}$=257, $^3J_{C-F}$=15 Hz, C_{Ar}) overlapped with 161.69 (dd, $^1J_{C-F}$=257, $^3J_{C-F}$=15 Hz, C_{Ar}), 101.4-101.0 (m, CH_{ArH}), 93.5 (C≡C), 81.2 (C≡C), 4.4 (CH_3); IR

(neat film, cm^{-1}) 2250 (C≡C), 2209 (C≡C), 1639 (C=O); HRMS (EI-EBE) m/z: [M^+] Calcd for $C_{10}H_5F_3O$ 198.0292; Found 198.0295.

1-(pyren-1-yl)but-2-yn-1-one (**9b**) This compound was synthesized as previously described.[26]

1-(coronen-1-yl)but-2-yn-1-one (**9c**) This compound was synthesized by adopting the known procedure[26] starting from 300 mg (1.0 mmol) of coronene, 102 mg (1.0 mmol) of but-2-ynoic acid, 210 mg (2.0 mmol) of TFAA, and 150 mg (1.0 mmol) of TfOH. Compound **9c** was obtained as a yellow solid with a yield of 28% (102 mg) *via* column chromatography on silica using DCM–cyclohexane as the eluent. Mp: 216-217; ^{1}H NMR ($CDCl_3$, 600.29 MHz): δ = 9.72 (d, J=8.6 Hz, 1H), 9.22 (s, 1H), 8.46-8.41 (m, 5H), 8.39 (d, J=8.2 Hz, 1H), 8.28 (d, J=8.2 Hz, 1H), 8.24 (d, J=8.2 Hz, 1H), 8.21 (d, J=8.2 Hz, 1H), 2.43 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 150.90 MHz): δ = 180.5 (C=O), 134.4 (CH_{ArH}), 129.5 (C_{Ar}), 129.4 (C_{Ar}), 128.3 (C_{Ar}), 127.8 (C_{Ar}), 127.7 (C_{Ar}), 127.2 (CH_{ArH}), 127.0 (CH_{ArH}), 126.2 (CH_{ArH}), 126.0 (CH_{ArH}), 125.8 (CH_{ArH}), 125.7 (C_{Ar}), 125.6 (CH_{ArH}), 125.5 (CH_{ArH}), 125.4 (C_{Ar}), 125.3 (C_{Ar}), 123.6 (CH_{ArH}), 121.8 (C_{Ar}), 121.1 (C_{Ar}), 120.9 (C_{Ar}), 120.8 (C_{Ar}), 120.6 (C_{Ar}), 91.2 (C≡C), 81.2 (C≡C), 4.7 (CH_3); IR (KBr, cm^{-1}) 2228 (C≡C), 2207 (C≡C), 1635 (C=O), HRMS (EI-EBE) m/z: [M^+] Calcd for $C_{28}H_{14}O$ 366.1045; Found 366.1045.

General procedure B—synthesis of 1-methyl-2-(aroyl)benzo[ghi]perylenes (compounds **8a-j**)

1-methyl-2-benzoylbenzo[ghi]perylene (**8a**). Briefly, 89 µl (1 mmol) of TfOH was added dropwise to a solution of 144 mg (1 mmol) of **7a** and 252.3 mg (1 mmol) of **1** in 35 mL of anhydrous DCM. A resulting solution was stirred at RT for 4 h and the reaction was quenched by addition of 100 mL of sodium bicarbonate. The product was extracted with DCM and organic solution was washed with brine, dried over sodium sulfate, and evaporated. Compound **8a** was obtained as a yellow solid with a yield of 39% (155 mg) *via* column chromatography on silica

using the mixture of DCM:cyclohexane 3:2 (v/v) as the eluent. Mp: >260 °C; ^{1}H NMR ($CDCl_3$, 600.29 MHz): δ = δ 9.03 (t, J=8.2 Hz, 2H, H_{ArH}), 8.36 (d, J=9.0 Hz, 1H, H_{ArH}), 8.22 (d, J=7.6 Hz, 1H, H_{ArH}), 8.19 (d, J=9.1 Hz, 1H, H_{ArH}), 8.15 (d, J=7.5 Hz, 1H, H_{ArH}), 8.05 (t, J=7.7 Hz, 1H, H_{ArH}), 8.01 (t, J= 7.7 Hz, 1H, H_{ArH}), 7.98 (d, J= 9.0 Hz, 1H, H_{ArH}), 7.90 (br s, 1H, Ph), 7.88 (br s, 1H, Ph), 7.80 (d, J = 8.9 Hz, 1H, H_{ArH}), 7.60 (dt, J=7.4, 1.3 Hz, 1H, Ph), 7.45 (d, J=7.4 Hz, 1H, Ph), 7.43 (d, J=7.5 Hz, 1H, Ph), 2.89 (s, 3 H, CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 150.90 MHz): δ = 200.9 (C=O); 138.1 (C_{Ar}), 135.1 (C_{Ar}), 133.9 (CH_{Ph}), 132.1 (C_{Ar}), 131.7 (C_{Ar}), 130.6 (C_{Ar}), 130.2 (C_{Ar}), 130.0 (CH_{Ph}), 128.9 (CH_{Ph}), 128.6 (C_{Ar}), 128.1 (2xC, CH_{ArH} and C_{Ar}), 128.0 (CH_{ArH}), 126.8 (2xCH_{ArH}), 126.6 (CH_{ArH}), 126.4 (CH_{ArH}), 126.1 (C_{Ar}), 125.7 (C_{Ar}), 125.6 (C_{Ar}), 124.4 (CH_{ArH} and C_{Ar}), 123.3 (CH_{ArH}), 122.9 (C_{Ar}), 121.0 (2xCH_{ArH}), 17.2 (CH_3); IR (KBr, cm^{-1}) 1664 (C=O), HRMS (EI-EBE) m/z: [M^+] Calcd for $C_{30}H_{18}O$ 394.1358; Found 394.1352.

1-methyl-2-(4-trifluoromethylbenzoyl)benzo[ghi]perylene (**8b**). This compound was synthesized according to the General Procedure B starting from 53.4 mg (0.25 mmol) of **7b**, 63.1 mg (0.25 mmol) of **1**, 22 μL (0.25 mmol) of TfOH and 25 mL of DCM. Chromatography on silica using DCM:cyclohexane 3:2 (v/v) as the eluent produced 20 mg of unreacted **1** followed by 89 mg (77% yield) of pure **8b** as a yellow solid. Mp: 218-220 °C; ^{1}H NMR ($CDCl_3$, 600.29 MHz): δ = 9.04 (t, J=7.3 Hz, 2H, H_{ArH}), 8.36 (d, J=9.0 Hz, 1H, H_{ArH}), 8.24 (d, J=7.6 Hz, 1H, H_{ArH}), 8.20 (d, J=9.1 Hz, 1H, H_{ArH}), 8.16 (d, J=7.6 Hz, 1H, H_{ArH}), 8.07 (t, J=7.7 Hz, 1H, H_{ArH}), 8.03 (t, J=7.7 Hz, 1H, H_{ArH}), 7.99-7.98 (m, 3H, H_{Ph} and H_{ArH}), 7.72 (d, J=9.0 Hz, 1H, H_{ArH}), 7.71 (br s, 1H, H_{Ph}), 7.70 (br s, 1H, H_{Ph}),2.87 (s, 3H, CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 150.90 MHz): δ = 199.9 (C=O), 140.6 (C_{Ar}), 135.6 (d, $^{2}J_{C-F}$=32.6 Hz, C_{Ar}), 134.1 (C_{Ar}), 132.2 (C_{Ar}), 131.7 (C_{Ar}), 130.7 (C_{Ar}), 130.3 (C_{Ar}), 130.2 (CH_{ArH}), 128.7 (C_{Ar}), 128.4 (CH_{ArH}), 128.3 (CH_{ArH}), 128.0 (C_{Ar}), 126.9 (2xCH_{ArH}), 126.8 (CH_{ArH}), 126.5 (CH_{ArH}), 126.1 (q, $^{3}J_{C-F}$=3.9 Hz, CH_{ArH}), 125.9 (C_{Ar}),

125.6 (2xC_{Ar}), 124.7 (C_{Ar}), 124.0 (CH_{ArH}), 123.2 (CH_{ArH}), 123.0 (C_{Ar}), 121.2 (2xCH_{ArH}), 17.3 (CH_3); IR (KBr, cm^{-1}) 1672 (C=O); HRMS (EI-EBE) m/z: [M^+] Calcd for $C_{31}H_{17}F_3O$ 462.1232; Found 462.1242.

1-methyl-2-(2-chlorobenzoyl)benzo[ghi]perylene (**8c**). This compound was synthesized according to the General Procedure B starting from 44.2 mg (0.25 mmol) of **7c**, 63 mg (0.25 mmol) of **1**, 22 μL (0.25 mmol) of TfOH and 25 mL of DCM. Chromatography on silica using DCM:*n*-hexane 1:1 (v/v) as the eluent produced 20 mg of unreacted **1** followed by 45 mg (42% yield) of pure **8c** as a yellow solid. Mp: 214-215 °C; ^{1}H NMR ($CDCl_3$, 600.29 MHz): δ = 8.96 (d, J=7.8 Hz, 2H, H_{ArH}), 8.29 (d, J=9.0 Hz, 1H, H_{ArH}), 8.15 (d, J=7.6 Hz, 1H, H_{ArH}), 8.12 (d, J=7.2 Hz, 1H, H_{ArH}), 8.11 (d, J=8.9 Hz, 1H, H_{ArH}), 8.01-7.96 (m, 3H, H_{ArH}), 7.89 (d, J=8.9 Hz, 1H, H_{ArH}), 7.57 (d, J=8.0 Hz, 1H, H_{Ph}), 7.50 (d, J=7.1 Hz, 1H, H_{Ph}), 7.43 (td, J=8.1, 1.1 Hz, 1H, H_{Ph}), 7.16 (t, J=7.6 Hz, 1H, H_{Ph}), 2.90 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150.90 MHz): δ = 199.3 (C=O), 137.2 (C_{Ar}), 135.7 (C_{Ar}), 133.9 (C_{Ar}), 133.3 (CH_{Ph}), 133.1 (CH_{Ph}), 132.1 (C_{Ar}), 132.0 (CH_{Ph}), 131.6 (C_{Ar}), 130.6 (C_{Ar}), 130.1 (C_{Ar}), 128.9 (C_{Ar}), 128.3 (CH_{ArH}), 128.0 (CH_{ArH} and C_{Ar}), 126.9 (CH_{ArH}), 126.8 (CH_{Ph}), 126.7 (CH_{ArH}), 126.6 (CH_{ArH}), 126.3 (CH_{ArH}), 126.1 (C_{Ar}), 125.5 (C_{Ar}), 124.6 (C_{Ar}), 124.0 (CH_{ArH}), 123.2 (CH_{ArH}), 122.9 (C_{Ar}), 121.0 (2xCH_{ArH}), 17.0 (CH_3); IR (KBr, cm^{-1}) 1680 (C=O); HRMS (EI-EBE) m/z: [M^+] Calcd for $C_{30}H_{17}ClO$ 428.0968; Found 428.0971.

1-methyl-2-(4-methylbenzoyl)benzo[ghi]perylene (**8d**). This compound was synthesized according to the General Procedure B starting from 42.2 mg (0.267 mmol) of **7d**, 67.3 mg (0.267 mmol) of **1**, 23.5 μL (0.267 mmol) of TfOH and 25 mL of DCM. Chromatography on silica using DCM:*n*-hexane 3:2 (v/v) as the eluent produced 28 mg of unreacted **1** followed by 65 mg (60% yield) of pure **8d**. Crystallization from DCM:*n*-hexane yielded **8d** as green crystals. Mp: 237-238

°C; ^{1}H NMR ($CDCl_3$, 600.29 MHz): δ = 9.04 (t, J=8.9 Hz, 2H, H_{ArH}), 8.37 (d, J=9.1 Hz, 1H, H_{ArH}), 8.23 (d, J=7.6 Hz, 1H, H_{ArH}), 8.19 (d, J=9.0 Hz, 1H, H_{ArH}), 8.15 (d, J=7.6 Hz, 1H, H_{ArH}), 8.05 (t, J=7.7 Hz, 1H, H_{ArH}), 8.01 (t, J=7.7 Hz, 1H, H_{ArH}), 7.97 (d, J=8.9 Hz, 1H, H_{ArH}), 7.80 (d, J=8.9 Hz, 1H, H_{ArH}), 7.78 (d, J=7.7 Hz, 2H, H_{Ph}), 7.23 (d, J=8.2 Hz, 2H, H_{Ph}), 2.88 (s, 3H, CH_3), 2.41 (s, 3H, CH_3); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 150.90 MHz): δ = 200.5 (C=O), 145.0 (C_{Ar}), 135.8 (C_{Ar}), 135.4 (C_{Ar}), 132.1 (C_{Ar}), 131.7 (C_{Ar}), 130.7 (C_{Ar}), 130.3 (C_{Ar}), 130.2 (CH_{ArH}), 129.6 (CH_{ArH}), 128.5 (C_{Ar}), 128.1 (C_{Ar}), 128.0 (2xCH_{ArH}), 126.8 (CH_{ArH}), 126.7 (CH_{ArH}), 126.6 (CH_{ArH}), 126.3 (CH_{ArH}), 126.1 (C_{ArH}), 125.7 (2xC_{Ar}), 124.5 (CH_{ArH}), 124.4 (C_{Ar}), 123.4 (CH_{ArH}), 122.9 (C_{Ar}), 121.0 (2xCH_{ArH}), 21.8 (CH_3), 17.2 (CH_3); IR (KBr, cm^{-1}) 1662 (C=O); HRMS (EI-EBE) m/z: [M^+] Calcd for $C_{31}H_{20}O$ 408.1514; Found 408.1505.

1-methyl-2-(4-methoxybenzoyl)benzo[ghi]perylene (**8e**). This compound was synthesized according to the General Procedure B starting from 43.6 mg (0.25 mmol) of **7e**, 63.1 mg (0.25 mmol) of **1**, 22 μL (0.25 mmol) of TfOH, and 25 mL of DCM. Chromatography on silica using DCM:cyclohexane 3:2 (v/v) as the eluent produced 47 mg of unreacted **1** followed by 45 mg (42% yield) of pure **8e** as a yellow solid. Mp: 241-242 °C; ^{1}H NMR ($CDCl_3$, 600.29 MHz): δ = 9.02 (t, J=8.4 Hz, 2H, H_{ArH}), 8.36 (d, J=9.1 Hz, 1H, H_{ArH}), 8.21 (d, J=7.7 Hz, 1H, H_{ArH}), 8.18 (d, J=9.1 Hz, 1H, H_{ArH}), 8.14 (d, J=7.6 Hz, 1H, H_{ArH}), 8.04 (t, J=7.7 Hz, 1H, H_{ArH}), 8.00 (t, J=7.7 Hz, 1H, H_{ArH}), 7.97 (d, J=9.0 Hz, 1H, H_{ArH}), 7.85 (br s, 2H, H_{ArH}), 7.82 (d, J=8.9 Hz, 1H, H_{ArH}), 6.90 (d, J=8.9 Hz, 2H, H_{ArH}), 3.84 (s, 3H, CH_3), 2.89 (s, 3H, CH_3); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 150.90 MHz): δ = 199.3 (C=O), 164.3 (C_{Ar}), 135.4 (C_{Ar}), 132.4 (C_{Ar}), 132.1 (C_{Ar}), 131.7 (C_{Ar}), 131.5 (C_{Ar}), 130.6 (C_{Ar}), 130.2 (C_{Ar}), 128.5 (C_{Ar}), 128.1 (C_{Ar}), 128.0 (2xCH_{ArH}), 126.8 (CH_{ArH}), 126.7 (CH_{ArH}), 126.5 (CH_{ArH}), 126.3 (CH_{ArH}), 126.2 (C_{ArH}), 125.7 (2xC_{Ar}), 124.6 (CH_{ArH}), 124.4 (C_{Ar}),

123.4 (CH_{ArH}), 122.9 (C_{Ar}), 121.0 (2xCH_{ArH}), 114.2 (CH_{ArH}), 55.5 (OCH_3), 17.2 (CH_3); IR (KBr, cm^{-1}) 1655 (C=O); HRMS (EI-EBE) m/z: [M^+] Calcd for $C_{31}H_{20}O_2$ 424.1463; Found 424.1470.

1-methyl-2-(3,4,5-trimethoxybenzoyl)benzo[ghi]perylene (**8f**). This compound was synthesized according to the General Procedure B starting from 58.6 mg (0.25 mmol) of **7f**, 63.1 mg (0.25 mmol) of **1**, 22 μL (0.25 mmol) of TfOH and 25 mL of DCM. Chromatography on silica using gradient of DCM:cyclohexane as the eluent starting from 1:1 to 7:3 (v/v) produced 32 mg of unreacted **1** followed by 86 mg (71% yield) of pure **8f** as a yellow solid. Mp: >260 °C; ^{1}H NMR ($CDCl_3$, 600.29 MHz): δ = 9.05 (t, J=9.4 Hz, 2H, H_{ArH}), 8.38 (d, J=9.0 Hz, 1H, H_{ArH}), 8.24 (d, J=7.6 Hz, 1H, H_{ArH}), 8.20 (d, J=9.1 Hz, 1H, H_{ArH}), 8.17 (d, J=7.6 Hz, 1H, H_{ArH}), 8.06 (t, J=7.7 Hz, 1H, H_{ArH}), 8.03 (t, J=7.7 Hz, 1H, H_{ArH}), 8.00 (d, J=8.9 Hz, 1H, H_{ArH}), 7.82 (d, J=8.9 Hz, 1H, H_{ArH}), 7.17 (br s, 2H, H_{ArH}), 3.94 (s, 3H, OCH_3), 3.69 (br s, 6H, OCH_3), 2.91 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150.90 MHz): δ = 199.7 (C=O), 153.4 (C_{Ar}), 143.6 (C_{Ar}), 134.9 (C_{Ar}), 133.3 (C_{Ar}), 132.1 (C_{Ar}), 131.7 (C_{Ar}), 130.7 (C_{Ar}), 130.3 (C_{Ar}), 128.7 (C_{Ar}), 128.1 (CH_{ArH}), 128.0 (CH_{ArH}), 126.8 (2xCH_{ArH}), 126.7 (CH_{ArH}), 126.4 (CH_{ArH}), 126.2 (C_{Ar}), 125.7 (C_{Ar}), 125.6 (C_{Ar}), 124.5 (CH_{ArH}), 123.4 (CH_{ArH}), 122.9 (C_{Ar}), 121.1 (2xCH_{ArH}), 107.5 (C_{Ar}), 60.9 (OCH_3), 56.3 (OCH_3), 17.3 (CH_3); IR (KBr, cm^{-1}) 1664 (C=O); HRMS (EI-EBE) m/z: [M^+] Calcd for $C_{33}H_{24}O_4$ 484.1675; Found 484.1683.

1-methyl-2-(2,4,6-trifluorobenzoyl)benzo[ghi]perylene (**8g**). This compound was synthesized according to the General Procedure B starting from 49.5 mg (0.25 mmol) of **7g**, 63.1 mg (0.25 mmol) of **1**, 22 μL (0.25 mmol) of TfOH and 25 mL of DCM. Chromatography on silica using gradient starting from 3:2 to 1:1 (v/v) of DCM:*n*-hexane as the eluent produced 15 mg of unreacted **1** followed by 23 mg (20% yield) of pure **8g** as a yellow solid. Mp: 226-228 °C; ^{1}H NMR ($CDCl_3$, 600.29 MHz): δ = 9.02 (d, J=7.7 Hz, 1H, H_{ArH}), 9.01 (d, J=7.7 Hz, 1H, H_{ArH}),

8.35 (d, J=9.1 Hz, 1H, H_{ArH}), 8.20 (d, J=7.7 Hz, 1H, H_{ArH}), 8.16 (d, J=8.7 Hz, 2H, H_{ArH}), 8.04 (t, J=7.7 Hz, 1H, H_{ArH}), 8.04 (d, J=9.1 Hz, 1H, H_{ArH}), 8.01 (t, J=7.7 Hz, 1H, H_{ArH}), 7.95 (d, J=9.0 Hz, 1H, H_{ArH}), 6.71 (t, J=8.6 Hz, 2H, H_{ArH}), 2.97 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150.90 MHz): δ = 193.7 (C=O), 165.0 (dt, $^1J_{C-F}$=257.1, $^3J_{C-F}$=15.7 Hz, C_{Ar}), 162.24 (dd, $^1J_{C-F}$=259.7, $^3J_{C-F}$=15.0 Hz, C_{Ar}) overlapped with 162.18 (dd, $^1J_{C-F}$=261.1, $^3J_{C-F}$=15.0 Hz, C_{Ar}), 136.7 (C_{Ar}), 132.2 (C_{Ar}), 131.6 (C_{Ar}), 130.7 (C_{Ar}), 130.2 (C_{Ar}), 128.6 (C_{Ar}), 128.3 (CH_{ArH}), 128.1 (CH_{ArH}), 126.9 (CH_{ArH}), 126.8 (2xCH_{ArH}), 126.4 (CH_{ArH}), 125.7 (C_{Ar}), 125.6 (C_{Ar}), 125.4 (C_{Ar}), 124.8 (C_{Ar}), 123.4 (2xCH_{ArH}), 123.0 (C_{Ar}), 121.1 (CH_{ArH}), 121.0 (CH_{ArH}), 116.2 (brs, C_{Ar}), 101.6 (td, J=26.1, 4.6 Hz, CH_{ArH}), 16.9 (CH_3); IR (KBr, cm^{-1}) 1677 (C=O); HRMS (EI-EBE) m/z: [M^+] Calcd for $C_{30}H_{15}F_3O$ 448.1075; Found 448.1074.

1-methyl-2-(perylen-3-oyl)benzo[ghi]perylene (**8h**). This compound was synthesized as **8a** starting from 15.9 mg (0.05 mmol) of **9a**, 12.6 mg (0.05 mmol) of **1**, 4.4 μL (0.05 mmol) of TfOH, and 7.5 mL of DCM. Chromatography on silica using DCM:cyclohexane 3:2 (v/v) as the eluent produced 8 mg (28% yield) of pure **8h** as an orange solid. Due to the very low solubility of this compound in the available solvents, we were not able to obtain $^{13}C\{^1H\}$ NMR spectra. Mp: >260°C; ^1H NMR ($CDCl_3$, 600.29 MHz): δ = 9.65 (d, J=7.7 Hz, 1H, CH_{ArH}), 9.10 (d, J=7.6 Hz, 1H, CH_{ArH}), 9.07 (d, J=8.0 Hz, 1H, CH_{ArH}), 8.46 (d, J=7.7 Hz, 1H, CH_{ArH}), 8.42 (d, J=9.0 Hz, 1H, CH_{ArH}), 8.37 (d, J=7.6 Hz, 1H, CH_{ArH}), 8.27 (d, J=8.0 Hz, 1H, CH_{ArH}), 8.23 (J=9.1 Hz, 1H, CH_{ArH}), 8.17 (d, J=7.7 Hz, 1H, CH_{ArH}), 8.13 (d, J=7.5 Hz, 1H, CH_{ArH}), 8.09 (t, J=7.8 Hz, 1H, CH_{ArH}), 8.04 (t, J=7.7 Hz, 1H, CH_{ArH}), 8.00 (s, 2H, CH_{ArH}), 7.93 (d, J=8.2 Hz, 1H, CH_{ArH}), 7.89 (t. J=8.0 Hz, 1H, CH_{ArH}), 7.78 (d, J=7.9 Hz, 1H, CH_{ArH}), 7.76 (d, J=8.0 Hz, 1H, CH_{ArH}), 7.58 (t, J=7.8 Hz, 2H, CH_{ArH}), 7.46 (t, J=7.8 Hz, 1H, CH_{ArH}), 2.98 (s, 3H, CH_3); IR (KBr, cm^{-1}) 1646

(C=O); Anal. Calcd for $C_{44}H_{24}O$: 92.93; H 4.25; Found: C 93.19; H 4.25; HRMS (EI-EBE) m/z: [M^+] Calcd for $C_{44}H_{24}O$ 568.1827; Found 568.1822.

1-methyl-2-(pyren-1-oyl)benzo[ghi]perylene (**8i**). This compound was synthesized according to the General Procedure B starting from 67 mg (0.25 mmol) of **7i**, 63.1 mg (0.25 mmol) of **1**, and 22 μL (0.25 mmol) of TfOH. Chromatography on silica using DCM:cyclohexane 3:2 (v/v) as the eluent produced 54 mg (42% yield) of pure **8i** as a yellow solid. Due to the very low solubility of this compound in the available solvents, we were not able to obtain $^{13}C\{^1H\}$ NMR spectra of **8i**.; Mp: >260°C; ^1H NMR ($CDCl_3$, 600.29 MHz): δ = 9.97 (brs, 1H, H_{ArH}), 9.10 (d, J=7.7 Hz, 1H, H_{ArH}), 9.07 (d, J=7.7 Hz, 1H, H_{ArH}), 8.50 (d, J=9.2 Hz, 1H, H_{ArH}), 8.42 (d, J=9.0 Hz, 1H, H_{ArH}), 8.41 (d, J=7.6 Hz, 1H, H_{ArH}), 8.33 (d, J=7.6 Hz, 1H, H_{ArH}), 8.27 (d, J=7.7 Hz, 1H, H_{ArH}), 8.23 (d, J=9.0 Hz, 1H, H_{ArH}) overlapped with 8.23 (d, J=8.8 Hz, 1H, H_{ArH}), 8.15 (t, J=7.7 Hz, 1H, H_{ArH}) overlapped with 8.15 (d, J=7.6 Hz, 1H, H_{ArH}), 8.09 (t, J=7.8 Hz, 1H, H_{ArH}), 8.04-7.99 (m, 4H, H_{ArH}), 7.95 (d, J=9.1 Hz, 1H, H_{ArH}), 7.90 (d, J=8.2 Hz, 1H, H_{ArH}), 2.98 (s, 3H, CH_3); IR (KBr, cm^{-1}) 1648 (C=O); HRMS (EI-EBE) m/z: [M^+] Calcd for $C_{40}H_{22}O$ 518.1671; Found 518.1675.

The reaction of 25.2 mg (0.1 mmol) of **1**, 53.7 mg (0.2 mmol) of **7i**, and 8.8 μL (0.1 mmol) of TfOH afforded 13 mg of unreacted **1** followed by 24 mg of **8i**, 23 mg of unreacted **7i**, and 10 mg of **17**—in this case, chromatography was performed on silica using DCM:*n*-hexane 1:1 (v/v) as the eluent.

1-(pyren-1-yl)but-2-en-1-one (**17**). Mp: 91-93°C; ^1H NMR ($CDCl_3$, 600.29 MHz): δ = 8.54 (d, J=9.2 Hz, 1H, H_{ArH}), 8.23 (d, J=7.6 Hz, 1H, H_{ArH}), 8.17 (d, J=8.0 Hz, 1H, H_{ArH}), 8.15 (t, J=8.2 Hz, 1H, H_{ArH}), 8.07 (d, J=8.8 Hz, 1H, H_{ArH}), 8.04 (t, J=7.6 Hz, 1H, H_{ArH}), 6.92-6.83 (m, 2H, CH_{vinyl}), 2.01 (d, J=6.2 Hz, 3H, CH_3); $^{13}C\{^1H\}$ ($CDCl_3$, 150.90 MHz): δ = 196.3 (C=O), 146.9 (CH_{vinyl}), 133.7 (C_{Ar}), 133.1 (CH_{vinyl}), 133.0 (C_{Ar}), 131.2 (C_{Ar}), 130.7 (C_{Ar}), 129.7 (C_{Ar}), 129.3

(C_{Ar}), 129.0 (CH_{ArH}), 128.9 (CH_{ArH}), 127.2 (CH_{ArH}), 126.3 (CH_{ArH}), 126.1 (CH_{ArH}), 126.0 (CH_{ArH}), 125.8 (CH_{ArH}), 124.9, 124.7 (CH_{ArH}), 124.5 (C_{Ar}), 123.9 (CH_{ArH}), 18.6 (CH_3); IR (KBr, cm^{-1}) 1630 (C=O); HRMS (EI-EBE) m/z: [M^+] Calcd for $C_{20}H_{14}O$ 270.1045; Found 270.1042.

1-methyl-2-(coronen-1-oyl)benzo[ghi]perylene (**8j**). This compound was synthesized according to the General Procedure B starting from 36.6 mg (0.1 mmol) of **7j**, 25.2 mg (0.1 mmol) of **1**, 9 μL (0.1 mmol) of TfOH, and 15 mL of DCM. Chromatography on silica using DCM:*n*-hexane 3:2 (v/v) as the eluent produced 17 mg (28% yield) of pure **8j** as a yellow powder.

Due to the very low solubility of this compound in available solvents we were not able to obtain NMR spectra. HRMS (EI-EBE) Calcd for $C_{48}H_{24}O$: 616.1827; Found 616.1830.

General procedure C—reaction of 1 with 2-alkynoic acids

Briefly, 71 μL (0.51 mmol) of TFAA was added to a solution of 0.51 mmol of 2-alkynoic acid **11a-f** in 11 mL of anhydrous DCM. To the resulting solution, 126 mg (0.5 mmol) of **1** followed by 45 μL (0.51 mmol) of TfOH were added. After 2 h of stirring at room temperature, 50 mL of sodium bicarbonate was added and the products were extracted with DCM (5 × 30 mL). The organic solution was washed with sodium bicarbonate, water, and brine and then dried over sodium sulfate and evaporated. Chromatography on silica allows separating products.

Reaction with but-2-ynoic acid 11a. This reaction was performed according to the General procedure C starting from 43.1 mg (0.51 mmol) of **11a**. Chromatography on silica using DCM:cyclohexane 3:2 (v/v) as the eluent gave 8 mg of recovered **1** followed by 30 mg (10%) of **8h**, 89 mg (56%) of **9a**, and 20 mg (11%) of **12a**.

1-(perylen-3-yl)but-2-yn-1-one (**9a**): Mp: >260°C; ^{1}H NMR ($CDCl_3$, 600.29 MHz): δ = 9.18 (d, J=8.6 Hz, 1H, H_{ArH}), 8.56 (d, J=8.0 Hz, 1H, H_{ArH}), 8.32 (d, J=7.4 Hz, 1H, H_{ArH}) overlapped with 8.32 (d, J=7.6 Hz, 1H, H_{ArH}), 8.29 (d, J=7.4 Hz, 1H, H_{ArH}), 8.26 (d, J=8.0 Hz, 1H, H_{ArH}),

7.82 (d, J=8.0 Hz, 1H, H_{ArH}), 7.75 (d, J=8.0 Hz, 1H, H_{ArH}), 7.68 (t, J=8.0 Hz, 1H, H_{ArH}), 7.57 (d, J=7.4 Hz, 1H, H_{ArH}), 7.54 (d, J=7.6 Hz, 1H, H_{ArH}), 2.19 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 150.90 MHz): δ = 179.1 (C=O), 137.2 (C_{Ar}), 135.4 (CH_{ArH}), 134.4 (C_{Ar}), 132.6 (C_{Ar}), 131.6 (C_{Ar}), 131.2 (C_{Ar}), 130.9 (C_{Ar}), 130.1 (C_{Ar}), 129.8 (CH_{ArH}), 129.1 (CH_{ArH}), 128.3 (CH_{ArH}), 128.2 (C_{Ar}), 127.0 (CH_{ArH}), 126.7 (CH_{ArH}), 126.0 (CH_{ArH}), 122.6 (CH_{ArH}), 121.5 (CH_{ArH}), 121.1 (CH_{ArH}), 118.8 (CH_{ArH}), 90.8 (C≡C), 80.7 (C≡C), 4.4 (CH_3); IR (KBr, cm^{-1}) 1615 (C=O); HRMS (EI-EBE) m/z: [M^+] Calcd for $C_{24}H_{14}O$ 318.1045; Found 318.1044.

1-(perylen-3-yl)but-2-en-1-one (**12a**). The NMR spectra were identical with those of authentic sample.[26]

Reaction with hex-2-ynoic acid 11b. This reaction was performed according to the General procedure C starting from 57 mg (58 μL, 0.51 mmol) of **11b**. Chromatography on silica using DCM:cyclohexane 1:1 (v/v) as the eluent produced 27 mg of recovered **1** followed by 43 mg (10%) of **15b**, 95 mg (55%) of a mixture of **14b** and **13b**, and 30 mg (17%) of **12b**.

1-(perylen-3-yl)hex-2-en-1-one (**12b**). Mp: 170-171 °C; ^{1}H NMR ($CDCl_3$, 600.29 MHz): δ = 8.24 (d, J=6.8 Hz, 1H, H_{ArH}), 8.23 (d, J=6.7 Hz, 1H, H_{ArH}), 8.22 (d, J=7.1 Hz, 1H, H_{ArH}), 8.18 (d, J=7.8 Hz, 1H, H_{ArH}), 8.17 (dd, J=8.4, 0.6 Hz, 1H, H_{ArH}), 7.74 (d, J=8.0 Hz, 1H, H_{ArH}), 7.71 (d, J=8.0 Hz, 1H, H_{ArH}), 7.67 (d, J=7.8 Hz, 1H, H_{ArH}), 7.55 (dd, J=8.4, 7.6 Hz, 1H, H_{ArH}), 7.509 (t, J=7.8 Hz, 1H, H_{ArH}), 7.508 (t, J=7.8 Hz, 1H, H_{ArH}), 6.9d (dt, J=15.7, J=6.9 Hz, 1H, COC<u>H</u>=CH), 6.67 (dt, J=15.7, 1.4 Hz, 1H, COCH=C<u>H</u>), 2.32-2.28 (m, 2H, CH_2), 1.58-1.52 (m, 2H), 0.98 (t, J=7.4 Hz, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 150.90 MHz): δ = 195.6 (C=O), 151.2 (CH_{vinyl}), 136.1 (C_{Ar}), 134.6 (C_{Ar}), 134.2 (C_{Ar}), 132.2 (C_{Ar}), 131.3 (C_{Ar}), 131.0 (CH_{vinyl} and C_{Ar}), 130.5 (C_{Ar}), 129.1 (C_{Ar}), 128.9 (CH_{ArH}), 128.4 (C_{Ar}), 128.1 (CH_{ArH}), 128.0 (CH_{ArH}), 127.7 (CH_{ArH}), 126.8 (CH_{ArH}), 126.6 (CH_{ArH}), 125.7 (CH_{ArH}), 121.4 (CH_{ArH}), 120.9 (CH_{ArH}), 120.7 (CH_{ArH}), 118.8

(CH_{ArH}), 34.8 (CH_2), 21.4 (CH_2), 13.8 (CH_3); IR (KBr, cm^{-1}) 1662 (C=O); HRMS (EI-EBE) m/z: [M^+] Calcd for $C_{26}H_{20}O$ 348.1514; Found 348.1510.

1-(perylen-3-yl)hex-2-yn-1-one (**14b**). Mp: 164-165 °C; ^1H NMR ($CDCl_3$, 600.29 MHz): δ = 9.14 (d, J=8.5 Hz, 1H, H_{ArH}), 8.49 (d, J=8.0 Hz, 1H, H_{ArH}), 8.23 (d, J=7.5 Hz, 2H, H_{ArH}), 8.20 (d, J=7.4 Hz, 1H, H_{ArH}), 8.16 (d, J=8.0 Hz, 1H, H_{ArH}), 7.77 (d, J=8.0 Hz, 1H, H_{ArH}), 7.70 (d, J=8.0 Hz, 1H, H_{ArH}), 7.62 (dd, J=8.4, 7.7 Hz, 1H, H_{ArH}), 7.50 (t, J=7.8 Hz, 1H, H_{ArH}), 7.50 (t, J=7.7 Hz, 1H, H_{ArH}), 2.53 (t, J=7.1 Hz, 2H, CH_2), 1.78-1.73 (m, 2H, CH_2), 1.14 (t, J=7.4 Hz, 3H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150.90 MHz): δ = 179.1 (C=O), 137.0 (C_{Ar}), 135.2 (CH_{ArH}), 134.3 (C_{Ar}), 132.5 (C_{Ar}), 131.6 (C_{Ar}), 131.1 (C_{Ar}), 130.8 (C_{Ar}), 130.0 (C_{Ar}), 129.7 (CH_{ArH}), 129.0 (CH_{ArH} and C_{Ar}), 128.2 (CH_{ArH}), 128.1 (C_{Ar}), 126.9 (CH_{ArH}), 126.6 (CH_{ArH}), 126.0 (CH_{ArH}), 122.5 (CH_{ArH}), 121.3 (CH_{ArH}), 120.9 (CH_{ArH}), 118.7 (CH_{ArH}), 94.9 (C≡C), 81.6 (C≡C), 21.5 (CH_2), 21.3 (CH_2), 13.7 (CH_3); IR (KBr, cm^{-1}) 2209 (C≡C), 1625 (C=O); HRMS (EI-EBE) m/z: [M^+] Calcd for $C_{26}H_{18}O$ 346.1358; Found 346.1352.

1-propyl-2-(perylen-3-oyl)benzo[ghi]perylene (**15b**). Mp: 224-225 °C; ^1H NMR ($CDCl_3$, 600.29 MHz): δ = 9.58 (brs, 1H, H_{ArH}), 9.08 (d, J=8.1 Hz, 1H, H_{ArH}), 9.07 (d, J=8.1 Hz, 1H, H_{ArH}), 8.45 (d, J=7.6 Hz, 1H, H_{ArH}), 8.39 (d, J=9.1 Hz, 1H, H_{ArH}), 8.36 (d, J=7.6 Hz, 1H, H_{ArH}), 8.25 (d, J=7.6 Hz, 1H, H_{ArH}), 8.21 (d, J=9.0 Hz, 1H, H_{ArH}), 8.16 (d, J=7.6 Hz, 1H, H_{ArH}), 8.11 (d, J=7.6 Hz, 1H, H_{ArH}), 8.08 (t, J=7.8 Hz, 1H, H_{ArH}), 8.03 (t, J=7.7 Hz, 1H, H_{ArH}), 8.00 (s, 2H, H_{ArH}), 7.90 (d, J=8.1 Hz, 1H, H_{ArH}), 7.89 (t, J=8.04, 1H, H_{ArH}), 7.77 (d, J=8.0 Hz, 1H, H_{ArH}), 7.75 (d, J=8.2 Hz, 1H, H_{ArH}), 7.57 (t, J=7.9 Hz, 1H, H_{ArH}), 7.56 (d, J=8.0 Hz, 1H, H_{ArH}), 7.45 (t, J=7.8 Hz, 1H, H_{ArH}), 3.42 (br s, 1H, H_{ArH}), 3.23 (br s, 1H, CH_2), 1.93 (br s, 1H, CH_2), 1.82 (brs, 1H, CH_2), 1.00 (t, J=7.3 Hz, 3H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150.90 MHz): δ = 202.1 (C=O), 137.1 (C_{Ar}), 136.7 (C_{Ar}), 135.1 (CH_{ArH}), 134.4 (C_{Ar}), 133.9 (C_{Ar}), 133.3 (C_{Ar}), 132.7 (C_{Ar}), 132.1 (C_{Ar}),

131.7 (C_{Ar}), 131.5 (C_{Ar}), 131.0 (C_{Ar}), 130.7 (C_{Ar}), 130.3 (C_{Ar}), 130.0 (C_{Ar}), 129.8 (CH_{ArH}), 129.5 (C_{Ar}), 129.4 (CH_{ArH}), 128.4 (CH_{ArH}), 128.2 (CH_{ArH} and C_{Ar}), 128.0 (CH_{ArH}), 127.7 (C_{Ar}), 127.0 (CH_{ArH}), 126.8 (C_{Ar}), 126.7 (2xCH_{ArH}), 126.6 (2xCH_{ArH}), 126.4 (2xCH_{ArH}), 125.9 (C_{Ar}), 125.7 (C_{Ar}), 124.9 (C_{Ar}), 124.8 (CH_{ArH}), 123.6 (CH_{ArH}), 123.0 (C_{Ar}), 122.5 (CH_{ArH}), 121.5 (CH_{ArH}), 121.2 (CH_{ArH}), 121.0 (2xCH_{ArH}), 118.9 (CH_{ArH}), 33.5 (CH_2), 25.1 (CH_2), 14.8 (CH_3); IR (KBr, cm^{-1}) 1648 (C=O); HRMS (EI-EBE) m/z: [M^+] Calcd for $C_{46}H_{28}O$ 596.2140; Found 596.2150.

Reaction with oct-2-ynoic acid 11c. This reaction was performed according to the General procedure C starting from 71.5 mg (74 μL, 0.51 mmol) of **11c**. Chromatography on silica using DCM:cyclohexane 3:2 (v/v) as the eluent produced 28 mg of recovered **1** followed by 41 mg (13%) of **15c**, 63 mg of **14c**, 11 mg of a mixture of **13c** and **12c**, and 30 mg of pure **12c**.

1-(perylen-3-yl)oct-2-en-1-one (**12c**). Mp: 148-149 °C; ^{1}H NMR ($CDCl_3$, 600.29 MHz): δ = 8.26-8.23 (m, 3H, H_{ArH}), 8.19 (d, J=7.8 Hz, 1H, H_{ArH}), 8.17 (d, J=8.4 Hz, 1H, H_{ArH}), 7.75 (d, J=8.0 Hz, 1H, H_{ArH}), 7.72 (d, J=8.1 Hz, 1H, H_{ArH}), 7.67 (d, J=7.7 Hz, 1H, H_{ArH}), 7.55 (t, J=8.0 Hz, 1H, H_{ArH}), 7.52 (t, J=7.7 Hz, 1H, H_{ArH}), 7.51 (t, J=7.8 Hz, 1H, H_{ArH}), 6.92 (dt, J=15.8, 6.9 Hz, 1H, H_{vinyl}), 6.67 (dt, J=15.6, 1.2 Hz, 1H, H_{vinyl}), 2.33-2.30 (m, 2H, CH_2), 1.52-1.51 (m, 2H, CH_2), 1.35-1.34 (m, 4H, CH_2), 0.92-0.90 (m, 3H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150.90 MHz): δ = 195.7 (C=O), 151.5 (CH_{vinyl}), 136.2 (C_{Ar}), 134.6 (C_{Ar}), 134.2 (C_{Ar}), 132.2 (C_{Ar}), 131.4 (C_{Ar}), 131.0 (C_{Ar}), 130.9 (CH_{vinyl}), 130.5 (C_{Ar}), 129.2 (C_{Ar}), 128.9 (CH_{ArH}), 128.5 (C_{Ar}), 128.1 (CH_{ArH}), 128.0 (CH_{ArH}), 127.7 (CH_{ArH}), 126.8 (CH_{ArH}), 126.6 (CH_{ArH}), 125.7 (CH_{ArH}), 121.4 (CH_{ArH}), 120.9 (CH_{ArH}), 120.7 (CH_{ArH}), 118.8 (CH_{ArH}), 32.8 (CH_2), 31.4 (CH_2), 27.8 (CH_2), 22.4 (CH_2), 13.9 (CH_3); IR (KBr, cm^{-1}) 1661 (C=O); HRMS (EI-EBE) m/z: [M^+] Calcd for $C_{28}H_{24}O$ 376.1827; Found 376.1824.

1-(perylen-3-yl)oct-2-yn-1-one (**14c**). Mp: 138-141 °C; ^{1}H NMR ($CDCl_3$, 600.29 MHz): δ = 9.14 (d, J=8.5 Hz, 1H, H_{ArH}), 8.49 (d, J=8.0 Hz, 1H, H_{ArH}), 8.23 (d, J=7.5 Hz, 2H, H_{ArH}), 8.21 (d, J=7.4 Hz, 1H, H_{ArH}), 8.17 (d, J=8.0 Hz, 1H, H_{ArH}), 7.77 (d, J=8.0 Hz, 1H, H_{ArH}), 7.71 (d, J=8.0 Hz, 1H, H_{ArH}), 7.62 (dd, J=8.4, 7.7 Hz, 1H, H_{ArH}), 7.51 (t, J=7.8 Hz, 1H, H_{ArH}), 7.50 (t, J=7.8 Hz, 1H, H_{ArH}), 2.54 (t, J=7.2 Hz, 2H, CH_2), 1.75-1.70 (m, 2H, CH_2), 1.53-1.48 (m, 2H, CH_2), 1.43-1.39 (m, 2H, CH_2), 0.97 (t, J=7.3 Hz, 3H, CH_3); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 150.90 MHz): δ = 179.2 (C=O), 137.0 (C_{Ar}), 135.2 (CH_{ArH}), 134.3 (C_{Ar}), 132.5 (C_{Ar}), 131.7 (C_{Ar}), 131.1 (C_{Ar}), 130.9 (C_{Ar}), 130.0 (C_{Ar}), 129.7 (CH_{ArH}), 129.0 (CH_{ArH} and C_{Ar}), 128.2 (CH_{ArH}), 128.1 (C_{Ar}), 126.9 (CH_{ArH}), 126.6 (CH_{ArH}), 126.0 (CH_{ArH}), 122.5 (CH_{ArH}), 121.3 (CH_{ArH}), 120.9 (CH_{ArH}), 118.7 (CH_{ArH}), 95.2 (C≡C), 81.4 (C≡C), 31.2 (CH_2), 27.6 (CH_2), 22.2 (CH_2), 19.3 (CH_2), 13.9 (CH_3); IR (KBr, cm^{-1}) 2211 (C≡C), 1626 (C=O); HRMS (EI-EBE) m/z: [M^+] Calcd for $C_{28}H_{22}O$ 374.1671; Found 374.1664.

1-pentyl-2-(perylen-3-oyl)benzo[ghi]perylene (**15c**). Mp: 182-183 °C; ^{1}H NMR ($CDCl_3$, 600.29 MHz): δ = 9.58 (brs, 1H, H_{ArH}), 9.08-9.05 (m, 2H, H_{ArH}), 8.44 (d, J=7.6 Hz, 1H, H_{ArH}), 8.39 (d, J=9.1 Hz, 1H, H_{ArH}), 8.35 (d, J=7.2 Hz, 1H, H_{ArH}), 8.25 (d, J=7.6 Hz, 1H, H_{ArH}), 8.21 (d, J=9.1 Hz, 1H, H_{ArH}), 8.15 (dd, J=7.6, 0.8 Hz, 1H, H_{ArH}), 8.10 (d, J=7.4 Hz, 1H, H_{ArH}), 8.08 (t, J=7.8 Hz, 1H, H_{ArH}), 8.02 (t, J=7.7 Hz, 1H, H_{ArH}), 8.00 (s, 2H, H_{ArH}), 7.89 (d, J=8.2 Hz, 1H, H_{ArH}), 7.88 (t, J=7.9 Hz, 1H, H_{ArH}), 7.77 (d, J=7.9 Hz, 1H, H_{ArH}), 7.74 (d, J=8.2 Hz, 1H, H_{ArH}), 7.57 (t, J=7.9 Hz, 1H, H_{ArH}), 7.56 (d, J=8.1 Hz, 1H, H_{ArH}), 7.45 (t, J=7.8 Hz, 1H, H_{ArH}), 3.41 (brs, 1H, CH_2), 3.24 (brs, 1H, CH_2), 1.91 (brs, 1H, CH_2), 1.75 (brs, 1H, CH_2), 1.37 (brs, 2H, CH_2), 1.28-1.25 (m, 2H, CH_2), 0.79 (t, J=7.3 Hz, 3H, CH_3); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 150.90 MHz): δ = 202.1 (C=O), 137.1 (C_{Ar}), 136.6 (C_{Ar}), 135.1 (CH_{ArH}), 134.4 (C_{Ar}), 134.1 (C_{Ar}), 133.2 (C_{Ar}), 132.7 (C_{Ar}), 132.1 (C_{Ar}), 131.7 (C_{Ar}), 131.4 (C_{Ar}), 131.0 (C_{Ar}), 130.7 (C_{Ar}), 130.3 (C_{Ar}), 130.0

(C_{Ar}), 129.7 (CH_{ArH}), 129.5 (CH_{ArH}), 129.4 (CH_{ArH}), 128.3 (CH_{ArH}), 128.2 (CH_{ArH} and C_{Ar}), 128.0 (CH_{ArH}), 127.6 (C_{ArH}), 127.0 (CH_{ArH}), 126.8 (CH_{ArH}), 126.7 (CH_{ArH}), 126.6 (2xCH_{ArH} and C_{Ar}), 126.4 (CH_{ArH}), 125.9 (C_{Ar}), 125.7 (C_{Ar}), 124.9 (C_{Ar}), 124.8 (CH_{ArH}), 123.6 (CH_{ArH}), 123.0 (C_{Ar}), 122.5 (CH_{ArH}), 121.5 (CH_{ArH}), 121.2 (CH_{ArH}), 121.0 (2xCH_{ArH}), 118.9 (CH_{ArH}), 32.5 (CH_2), 31.4 (2xCH_2), 22.3 (CH_2), 13.9 (CH_3); IR (KBr, cm^{-1}) 1648 (C=O); HRMS (EI-EBE) m/z: [M^+] Calcd for $C_{48}H_{32}O$ 624.2453; Found 624.2458.

Reaction with phenylpropynoic acid 11d. This reaction was performed according to the General procedure C starting from 146 mg of phenylpropynoic acid. Chromatography on silica using DCM as the eluent produced 20 mg of recovered **1** followed by158 mg (42%) of **14d**.

3-(phenylpropynoyl)perylene (**14d**). Mp: 248-249 °C; ^{1}H NMR ($CDCl_3$, 600.29 MHz): δ = 9.23 (d, J=8.5 Hz, 1H, H_{ArH}), 8.65 (d, J=8.0 Hz, 1H, H_{ArH}), 8.32 (d, J=7.4 Hz, 1H, H_{ArH}), 8.29 (d, J=7.4 Hz, 1H, H_{ArH}), 8.28 (d, J=8.0 Hz, 1H, H_{ArH}), 7.75 (d, J=8.0 Hz, 1H, H_{ArH}), 7.73-7.69 (m, 3H, H_{ArH}), 7.57-7.54 (m, 2H, H_{ArH}), 7.51-7.48 (m, 1H, H_{ArH}), 7.46-7.43 (m, 2H, H_{ArH}); $^{13}C\{^1H\}$NMR ($CDCl_3$, 150.90 MHz): δ = 178.8 (C=O), 137.5 (C_{Ar}), 135.4 (CH_{ArH}), 134.4 (C_{Ar}), 132.9 (CH_{ArH}), 132.6 (C_{Ar}), 131.7 (C_{Ar}), 131.2 (C_{Ar}), 130.9 (C_{Ar}), 130.5 (CH_{ArH}), 130.0 (CH_{ArH} and C_{Ar}), 129.2 (CH_{ArH}), 129.1 (C_{Ar}), 128.7 (CH_{ArH}), 128.4 (CH_{ArH}), 128.2 (C_{Ar}), 127.0 (CH_{ArH}), 126.7 (CH_{ArH}), 126.0 (CH_{ArH}), 122.7 (CH_{ArH}), 121.5 (CH_{ArH}), 121.1 (CH_{ArH}), 120.6 (C_{Ar}), 118.9 (CH_{ArH}), 91.6 (C≡C), 88.7 (C≡C); IR (KBr, cm^{-1}) 2198 (C≡C) 1613 (C=O); HRMS (EI-EBE) m/z: [M^+] Calcd for $C_{29}H_{16}O$ 380.1201; found 380.1198.

Reaction with 4-phenylbut-2-ynoic acid 11e. This reaction was performed according to the General procedure C starting from 81.7 mg (0.51 mmol) of **11e**. Chromatography on silica using DCM:cyclohexane 1:1 (v/v) as the eluent produced 35 mg of recovered **1** followed by 46 mg (14%) of **15e**, 24 mg of **14e**, 33 mg of **13e**, and 30 mg of **12e**.

Due to the very low solubility of **15e** in available solvents, we were not able to obtain ^{13}C NMR spectra of **15e**.

1-(perylen-3-yl)-4-phenylbut-2-en-1-one (**12e**). Due to the very low solubility of this compound in available solvents, we were not able to obtain NMR spectra of **12e**. Mp. 151-154 °C; HRMS (EI-EBE) m/z: [M^+] Calcd for $C_{30}H_{20}O$ 396. 1514; Found 396.1512.

1-(perylen-1-yl)-4-phenylbut-2-yn-1-one (**13e**). Mp: 147-148 °C; ^1H NMR ($CDCl_3$, 600.29 MHz): δ = 8.36 (d, J=7.4 Hz, 1H, H_{ArH}), 8.32 (d, J=7.4 Hz, 1H, H_{ArH}), 7.85 (d, J=8.0 Hz, 1H, H_{ArH}), 7.79 (t, J=7.9 Hz, 2H, H_{ArH}), 7.76 (d, J=8.5 Hz, 1H, H_{ArH}) overlapped with 7.76 (d, J=7.3 Hz, 1H, H_{ArH}), 7.71 (d, J=8.4 Hz, 1H, H_{ArH}), 7.65 (t, J=7.7 Hz, 1H, H_{ArH}), 7.65 (t, J=7.7 Hz, 1H, H_{ArH}), 7.49 (t, J=7.7 Hz, 1H, H_{ArH}), 7.05 (t, J=7.4 Hz, 1H, H_{ArH}), 6.91 (t, J=7.7 Hz, 2H, H_{ArH}), 6.70 (d, J=7.5 Hz, 2H, H_{ArH}), 3.45 (s, 2H, CH_2); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150.90 MHz): δ = 183.1 (C=O), 136.4 (C_{Ar}), 135.1 (C_{Ar}), 134.0 (C_{Ar}), 133.9 (C_{Ar}), 133.0 (C_{Ar}), 132.1 (CH_{ArH}), 131.7 (C_{Ar}), 130.5 (C_{Ar}), 129.8 (CH_{ArH}), 129.2 (C_{Ar}), 128.9 (C_{Ar}), 128.6 (C_{Ar}), 128.3 (CH_{ArH}), 128.2 (CH_{ArH}), 128.0 (CH_{ArH}), 127.6 (CH_{ArH}), 127.2 (2x CH_{ArH}), 127.1 (CH_{ArH}), 126.7 (2x CH_{ArH}), 126.1 (CH_{ArH}), 121.3 (CH_{ArH}), 121.2 (CH_{ArH}), 88.0 (C≡C), 83.5 (C≡C), 25.1 (CH_2); IR (KBr, cm^{-1}) 2212 (C≡C), 1625 (C=O); HRMS (EI-EBE) m/z: [M^+] Calcd for $C_{30}H_{18}O$ 394.1358; Found 394.1371.

1-(perylen-3-yl)-4-phenylbut-2-yn-1-one (**14e**). Mp: 174-178 °C; ^1H NMR ($CDCl_3$, 600.29 MHz): δ = 9.16 (d, J=8.5 Hz, 1H, H_{ArH}), 8.51 (d, J=8.0 Hz, 1H, H_{ArH}), 8.26-8.22 (m, 2H, H_{ArH}), 8.15 (d, J=8.1 Hz, 1H, H_{ArH}), 7.77 (d, J=8.0 Hz, 1H, H_{ArH}), 7.71 (d, J=8.0 Hz, 1H, H_{ArH}), 7.63 (dd, J=8.5, 7.6 Hz, 1H, H_{ArH}), 7.51 (t, J=7.8 Hz, 2H, H_{ArH}), 7.45 (d, J=7.2 Hz, 2H, H_{ArH}), 7.40 (t, J=7.7 Hz, 2H, H_{ArH}), 7.32 (t, J=7.3 Hz, 1H, H_{ArH}), 3.96 (s, 2H, CH_2); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150.90 MHz): δ = 178.8 (C=O), 137.3 (C_{Ar}), 135.5 (, CH_{ArH}), 134.8 (C_{Ar}), 134.3 (C_{Ar}), 132.5

(C_{Ar}), 131.4 (C_{Ar}), 131.1 (C_{Ar}), 130.8 (C_{Ar}), 129.9 (C_{Ar}), 129.8 (CH_{ArH}), 129.1 (CH_{ArH}), 129.0 (C_{Ar}), 128.9 (CH_{ArH}), 128.3 (CH_{ArH}), 128.1 (CH_{ArH} and C_{Ar}), 127.2 (CH_{ArH}), 126.9 (CH_{ArH}), 126.6 (CH_{ArH}), 125.9 (CH_{ArH}), 122.6 (CH_{ArH}), 121.4 (CH_{ArH}), 121.0 (CH_{ArH}), 118.8 (CH_{ArH}), 91.7 (C≡C), 82.9 (C≡C), 25.7 (CH_2); IR (KBr, cm^{-1}) 2213 (C≡C), 1625 (C=O); HRMS (EI-EBE) m/z: [M^+] Calcd for $C_{30}H_{18}O$ 394.1358; Found 394.1367.

1-benzyl-2-(perylen-3-oyl)benzo[ghi]perylene (**15e**). Mp: 245-246 °C; ^{1}H NMR ($CDCl_3$, 600.29 MHz): δ = 9.54 (brs, 1H, H_{ArH}), 9.10 (d, J=7.6 Hz, 1H, H_{ArH}), 9.09 (d, J=7.9 Hz, 1H, H_{ArH}), 8.42 (d, J=7.8 Hz, 1H, H_{ArH}), 8.34 (d, J=7.7 Hz, 1H, H_{ArH}), 8.30 (d, J=9.0 Hz, 1H, H_{ArH}), 8.21 (d, J=7.6 Hz, 1H, H_{ArH}), 8.19 (d, J=7.7 Hz, 1H, H_{ArH}), 8.10-8.02 (m, 6H, H_{ArH}), 7.82 (t, J=8.1 Hz, 1H, H_{ArH}), 7.79 (d, J=8.3 Hz, 1H, H_{ArH}), 7.78 (d, J=8.0 Hz, 1H, H_{ArH}), 7.75 (d, J=8.2 Hz, 1H, H_{ArH}), 7.57 (t, J=7.9 Hz, 1H, H_{ArH}), 7.52 (d, J=8.0 Hz, 1H, H_{ArH}), 7.46 (d, J=7.8 Hz, 1H, H_{ArH}), 7.13-7.08 (m, 4H, H_{ArH}), 7.04 (t, J=6.7 Hz, 1H, H_{ArH}), 4.80 (s, 2H, CH_2); IR (KBr, cm^{-1}) 1648 (C=O); HRMS (EI-EBE) m/z: [M^+] Calcd for $C_{50}H_{28}O$ 644.2140; Found 644.2147.

Reaction with 4-phenylpent-2-ynoic acid 11f. This reaction was performed according to the General procedure C starting from 88.8 mg (0.51 mmol) of **11f**. Chromatography on silica using DCM:cyclohexane 1:1 (v/v) as the eluent produced 13 mg of recovered **1** followed by 32 mg (10%) of **15f** and 70 mg of a mixture of **13f** and **14f** and 12 mg of **12f**. Small amounts of analytically pure samples of **14f** were obtained by repeated column chromatography of a mixture of **13f** and **14f** on silica.

1-(perylen-3-yl)-5-phenylpent-2-en-1-one (**12f**). Mp: 187-188 °C; ^{1}H NMR ($CDCl_3$, 600.29 MHz): δ = 8.25-8.22 (m, 3H, H_{ArH}), 8.16 (d, J=7.8 Hz, 1H, H_{ArH}), 8.14 (dd, J=8.5, 0.7 Hz, 1H, H_{ArH}), 7.75 (d, J=8.0 Hz, 1H, H_{ArH}), 7.72 (d, J=8.0 Hz, 1H, H_{ArH}), 7.60 (d, J=7.7 Hz, 1H, H_{ArH}), 7.54 (dd, J=8.3, 7.6 Hz, 1H, H_{ArH}), 7.52 (t, J=7.8 Hz, 1H, H_{ArH}), 7.51 (t, J=7.7 Hz, 1H, H_{ArH}),

7.32-7.30 (m, 2H, H_{ArH}), 7.23-7.21 (m, 1H, H_{ArH}), 7.20-7.19 (m, 2H, H_{ArH}), 6.94 (dt, J=15.7, 6.9 Hz, 1H, H_{vinyl}), 6.66 (dt, J=15.7, 1.4 Hz, 1H, H_{vinyl}), 2.85 (t, J=7.6 Hz, 2H, -C$\underline{H}_2$-CH_2Ph), 2.67-2.63 (m, 2H, -CH_2-C$\underline{H}_2$Ph); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150.90 MHz): δ = 195.4 (C=O), 149.7 (CH_{vinyl}), 140.7 (C_{Ar}), 135.9 (C_{Ar}), 134.6 (C_{Ar}), 134.4 (C_{Ar}), 132.2 (C_{Ar}), 131.5 (CH_{vinyl}), 131.3 (C_{Ar}), 131.0 (C_{Ar}), 130.5 (C_{Ar}), 129.1 (C_{Ar}), 128.9 (CH_{ArH}), 128.5 (CH_{ArH}), 128.4 (CH_{ArH} and C_{Ar}), 128.1 (CH_{ArH}), 127.7 (CH_{ArH}), 126.8 (CH_{ArH}), 126.6 (CH_{ArH}), 126.2 (CH_{ArH}), 125.6 (CH_{ArH}), 121.4 (CH_{ArH}), 120.9 (CH_{ArH}), 120.7 (CH_{ArH}), 118.8 (CH_{ArH}), 34.4 (2xCH_2); IR (KBr, cm^{-1}) 1662 (C=O); HRMS (EI-EBE) m/z: [M^+] Calcd for $C_{31}H_{22}O$ 410.1671; Found 410.1672.

1-(perylen-3-yl)-5-phenylpent-2-yn-1-one (**14f**). Mp: 168-169 °C; ^1H NMR ($CDCl_3$, 600.29 MHz): δ = 9.15 (d, J = 8.5 Hz, 1H, H_{ArH}), 8.29 (d, J = 8.0 Hz, 1H, H_{ArH}), 8.26 (d, J = 7.4 Hz, 2H, H_{ArH}), 8.24 (d, J = 7.4 Hz, 1H, H_{ArH}), 8.11 (d, J= 8.0 Hz, 1H, H_{ArH}), 7.80 (d, J= 8.0 Hz, 1H, H_{ArH}), 7.72 (d, J= 8.0 Hz, 1H, H_{ArH}), 7.64 (t, J= 8.0 Hz, 1H, H_{ArH}), 7.54 (t, J= 7.8 Hz, 1H, H_{ArH}), 7.52 (t, J= 7.8 Hz, 1H, H_{ArH}), 7.39 – 7.36 (m, 2H, H_{ArH}), 7.33 – 7.30 (m, 3H, H_{ArH}), 3.03 (t, J= 7.4 Hz, 2H, CH_2), 2.86 (t, J= 7.4 Hz, 2H, CH_2); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150.90 MHz): δ = 179.0 (C=O); 139.9 (C_{Ar}); 137.1 (C_{Ar}); 135.6 (CH_{ArH}); 134.4 (C_{Ar}); 132.5 (C_{Ar}); 131.4 (C_{Ar}); 131.1 (C_{Ar}); 130.9 (C_{Ar}); 130.0 (C_{Ar}); 129.8 (CH_{ArH}); 129.1 (CH_{ArH}); 129.0 (C_{Ar}); 128.7 (CH_{ArH}); 128.6 (CH_{ArH}), 128.3 (CH_{ArH}); 128.1 (C_{Ar}); 126.9 (CH_{ArH}); 126.7 (CH_{ArH}); 126.6 (CH_{ArH}); 126.0 (CH_{ArH}); 122.5 (CH_{ArH}); 121.4 (CH_{ArH}); 121.0 (CH_{ArH}); 118.8 (CH_{ArH}); 93.7 (C≡C); 82.0 (C≡C); 34.1 (CH_2); 21.4 (CH_2); IR (KBr, cm^{-1}) 2211 (C≡C), 1625 (C=O); HRMS (EI-EBE) m/z: [M^+] Calcd for $C_{31}H_{20}O$ 408.1514; Found 408.1507.

1-phenethyl-2-(perylen-3-oyl)benzo[ghi]perylene (**15f**). Due to the very low solubility of this compounds in available solvents we were not able to obtain ^{13}C NMR spectra. Mp: 205-206 °C; ^1H NMR ($CDCl_3$, 600.29 MHz): δ = 9.61 (brs, 1H, H_{ArH}), 9.09 (d, J=7.7 Hz, 1H, H_{ArH}), 9.08 (d,

J=7.7 Hz, 1H, H_{ArH}), 8.48 (d, J=9.1 Hz, 1H, H_{ArH}), 8.45 (d, J=7.6 Hz, 1H, H_{ArH}), 8.36 (d, J=7.4 Hz, 1H, H_{ArH}), 8.27 (d, J=7.6 Hz, 1H, H_{ArH}), 8.25 (d, J=9.1 Hz, 1H, H_{ArH}), 8.17 (d, J=7.5 Hz, 1H, H_{ArH}), 8.10 (t, J=7.7 Hz, 1H, H_{ArH}), 8.09 (d, J=7.4 Hz, 1H, H_{ArH}), 8.06-8.01 (m, 3H, H_{ArH}), 7.91-7.88 (m, 1H, H_{ArH}) overlapped with 7.89 (d, J=8.2 Hz, 1H, H_{ArH}), 7.76 (d, J=7.9 Hz, 1H, H_{ArH}), 7.74 (d, J=8.2 Hz, 1H, H_{ArH}), 7.59 (d, J=9.8 Hz, 1H, H_{ArH}), 7.57 (t, J=8.0 Hz, 1H, H_{ArH}), 7.44 (t, J=7.8 Hz, 1H, H_{ArH}), 7.20-7.18 (m, 2H, H_{ArH}), 7.13-7.11 (m, 3H, H_{ArH}), 3.69 (brs, 1H, CH_2), 3.58 (brs, 1H, CH_3), 3.22 (brs, 1H, CH_2), 2.99 (brs, 1H, CH_2); IR (KBr, cm^{-1}) 1648 (C=O); HRMS (EI-EBE) m/z: [M^+] Calcd for $C_{51}H_{30}O$ 658.2297; Found 658.2293.

Reactions with perylene-d_{12} 16

Reaction of 16 with 9b. This reaction was performed as described above starting with 26.4 mg (0.10 mmol) of **16**, 26.8 mg (0.10 mmol) of **9b**, 8.8 μL (0.10 mmol) of TfOH, and 10 mL of DCM. Chromatography on silica using DCM:cyclohexane 3:2 (v/v) as the eluent produced 14 mg (53%) of unreacted **16** followed by 22 mg (42% yield) of pure **18** as an orange solid, 8 mg (30%) of recovered **9b,** and 10 mg (37%) of **19**.

1-methyl-2-(pyren-1-oyl)benzo[ghi]perylene-3,4,5,6,7,8,9,10,11,12-d_{10} (18). ^{1}H NMR ($CDCl_3$, 600.29 MHz): δ = 9.96 (brs, 1H, H_{ArH}), 8.50 (d, J=9.2 Hz, 1H, H_{ArH}), 8.41 (d, J=7.7 Hz, 1H, H_{ArH}), 8.33 (d, J=7.6 Hz, 1H, H_{ArH}), 8.23 (d, J=8.9 Hz, 1H, H_{ArH}), 8.15 (t, J=7.7 Hz, 1H, H_{ArH}), 8.02 (d, J=8.8 Hz, 1H, H_{ArH}), 8.00 (d, J=8.1 Hz, 1H, H_{ArH}), 7.9 (d, J=8.2 Hz, 1H, H_{ArH}), 2.98 (s, 3H, CH_3); HRMS (EI-EBE) m/z: [M^+] Calcd for $C_{40}H_{12}D_{10}O$ 528.2298; Found 528.2296.

1-(pyren-1-yl)but-2-en-1-one-2,3-d_2 (19). HRMS (EI-EBE) Calcd for $C_{20}H_{12}D_2O$ 272.1170; Found 272.1163.

Reaction of 16 with 11a. This reaction was performed as mention above starting with **16** instead of **1**.

1-(perylen-3-yl-d_{11})but-2-yn-1-one (**20**). Yield 12 mg (36%). ^{1}H NMR ($CDCl_3$, 600.29 MHz): δ = 2.19 (s, 3H, CH_3); HRMS (EI-EBE) m/z: [M^+] Calcd for $C_{24}H_3D_{11}O$ 329.1735; Found 329.1734.

1-methyl-2-(perylen-3-oyl-d_{11})benzo[ghi]perylene-d_{10} (21). Yield 10 mg (34%). ^{1}H NMR ($CDCl_3$, 600.29 MHz): δ = 2.98 (s, 3H, CH_3); HRMS (EI-EBE) m/z: [M^+] Calcd for $C_{44}H_3D_{21}O$ 589.3145; Found 589.3148.

1-(perylen-3-yl-d_{11})but-2-en-1-one-2,3-d_2 (22). Yield 6 mg (18%). HRMS (EI-EBE) m/z: [M^+] Calcd for $C_{24}H_3D_{13}O$ 333.2017; Found 333.2003.

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NOTES

The authors declare no competing financial interest.

SUPPORTING INFORMATION

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Figures S1-S15, ^{1}H, ^{13}C{^{1}H}, ^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC, X-ray data (cif) for compounds **8a**, **8h**, **9a**, and **14d**.

ACKNOWLEDGMENTS

This work was supported by the National Science Centre of Poland, grant number UMO-2013/11/B/ST5/01077.

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