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SYNTHESIS OF A TYPE OF BRIDGED HETEROCYCLES VIA TETRAYNES

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Abstract – A simple method has been developed for the synthesis of a type of bridged heterocycles using tetraynes. The strategy uses 1,3-diphenylisobenzo-furan or 2,5-diphenylfuran and tetraynes as substrates and reactions proceed through an HDDA–[4+2] adduct. Products are obtained in moderate to good yield.

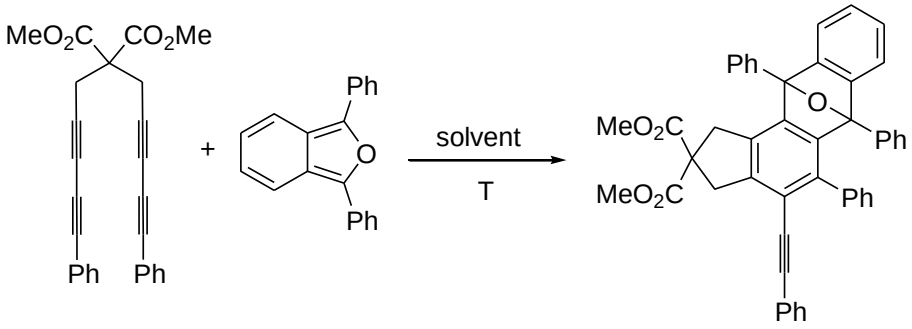
The hexadehydro–Diels–Alder (HDDA) reaction which capitalizes on the simple thermal cycloisomerization of a 1,3-diyne[1] with a diynophile to produce a benzyne intermediate[2,3] followed be captured, either intra- or intermolecular with a suitably reactive trapping agent to provide highly functionalized benzenoid products,[4,5] have played a very significant role in the field of organic synthesis.[6,7] Hoye described that three alkynyl substituted naphthalenes can be efficiently prepared by an HDDA-enabled strategy, the preparation just three chemical reactions from commercially available materials.[8] Aguilar presented a gold-catalyzed intermolecular HDDA reaction between captodative dienynes and nitriles for direct access to pyridines.[9] Lee and co-workers discovered an HDDA system based on the silver-catalyzed cycloaromatization of tetraynes.[10] Further, Lee have demonstrated that AgF, $AgCF_3$, and $AgSCF_3$ can all mediate HDDA reactions with incorporation of the respective fluorine-containing counterions to yield motifs that are valued in medicinal chemistry and agrochemistry.[11] Liu group observed benzyne intermediate can be captured by five-membered heterocyclic compounds, such as furans, pyrroles, thiophenes.[12]

Recently, the synthesis of yne-functionalized benzoisoindolines from triynes was described by our group.[13] Further, the reactions of diphenyl diselenide,[14] α,β-unsaturated aldehyde[15] with tetraynes have been reported by our group. We also reported the synthesis of fused salicylaldehydes and salicylketones[16]

from tetraynes. As part of a continuing effort, we report the reaction of tetraynes with isobenzofuran to produce bridged heterocycles in good to excellent yields in the absence of metals, catalysts, bases, or oxidants.

In our initial study, the reaction of dimethyl 2,2-bis(5-phenylpenta-2,4-diynyl)malonate **1a** with 1,3-diphenylisobenzofuran was used as a test experiment (Table 1). The **3a** was obtained in 16% yield when the reaction was carried out in toluene at 80 °C (Table 1 entry 1). The efficiency of the reaction could be greatly enhanced by increasing the reaction temperature to 100 °C (Table 1 entry 3). However, when the temperature was increased to 110 °C, **3a** was obtained in 75% yield (Table 1 entry 4), which indicates that further increasing the reaction temperature does not improve the efficiency. In entry 5, no reaction occurred at room temperature in toluene. Next, we sought to improve the efficiency of the reaction through solvent screening, and we observed that an nonpolar solvent is beneficial for the desired reaction, other polar solvent were unsuitable (Table 1 entries 5-7). The best results were obtained by using toluene as solvent (Table 1 entry 7). Thus, the following standard reaction conditions were used for subsequent experiments: 1 equivalent of **1** was reacted with 1.1 equivalents of 1,3-diphenylisobenzofuran in toluene at 100 °C.

Table 1. Optimization of reaction conditions[a]



1a **3a**

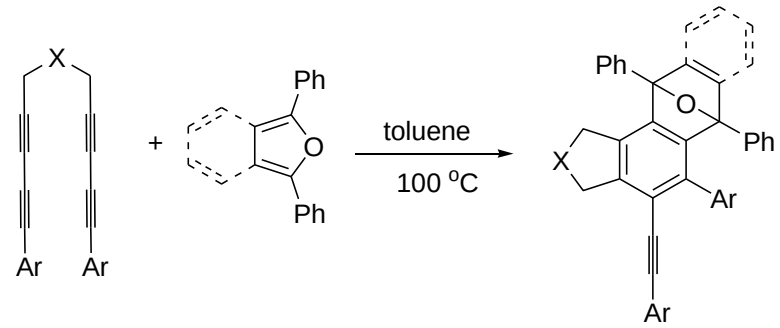
Entry	Solvent	t [h]	T [°C]	Yield (%)[b]
1	toluene	10	80	16
2	toluene	10	90	40
3	toluene	10	100	84
4	toluene	10	110	75
5	toluene	10	Rt	0
6	DMSO	10	100	trace
7	DMF	10	100	trace

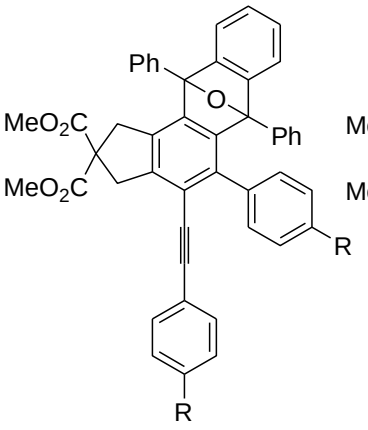
[a] **1a** (0.30 mmol), 1,3-diphenylisobenzofuran (0.33 mmol)
[b] Yield of the isolated product.

Having optimized reaction conditions in hands, the substrate scope of this reaction was studied. The scope of tetraynes was first examined and we found that various substituted tetraynes were compatible

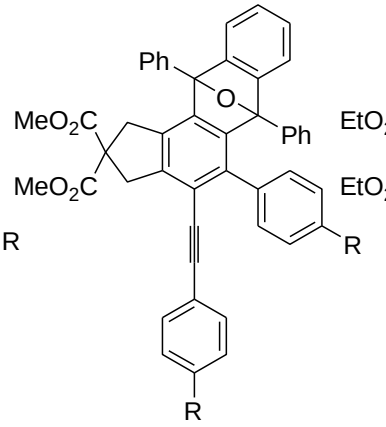
with this reaction. Compounds ranging from **3a** to **3m** (Table 2 **3a-3m**) were readily isolated with good to excellent yields from various differently substituted tetraynes. The substituted groups in the aryl ring of the tetraynes could be either electron-donating or electron-withdrawing; for instance, methyl, ethyl, fluoro, and chloro groups were all acceptable. Compound **3e** had the highest isolated yield (88%) among the examined products. When an alkylsubstituted *N*-tetrayne was used, the reaction afforded **3m** in 86%.

Table 2. Scope of the reaction

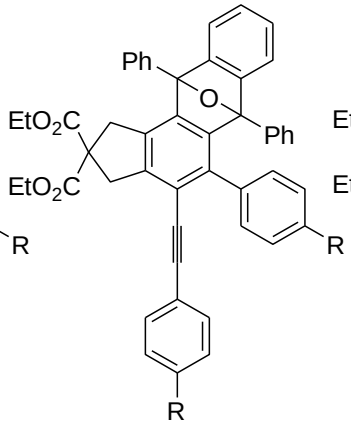




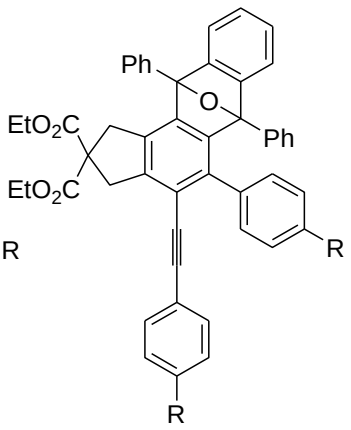
3a, R=H, 84%
3b, R=Me, 83%
3c, R=Et, 80%
3d, R=*n*-Pr, 80%



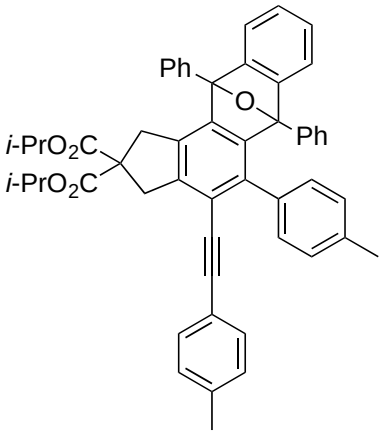
3e, R=F, 88%
3f, R=Cl, 86%



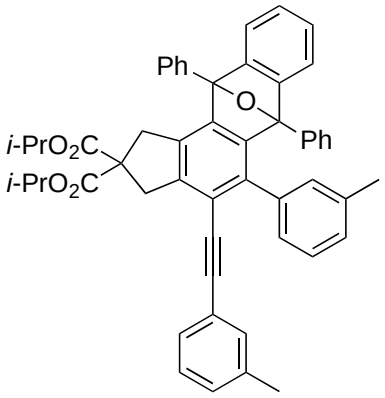
3g, R=H, 82%
3h, R=Et, 80%



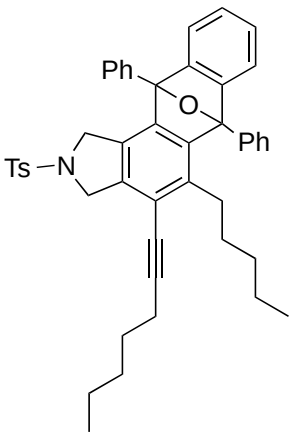
3i, R=F, 85%
3j, R=Cl, 84%



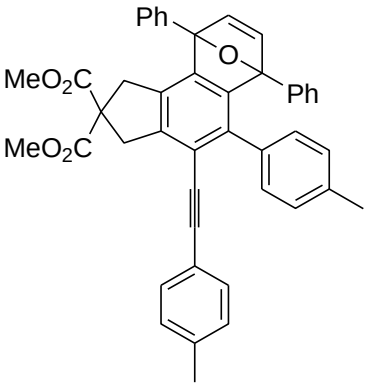
3k, 80%



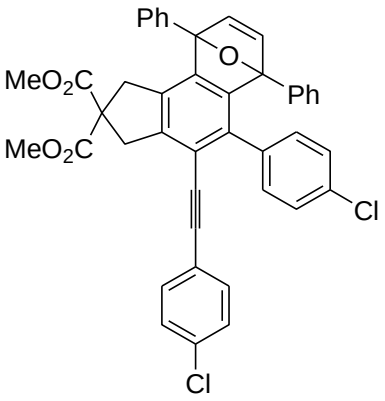
3l, 80%,



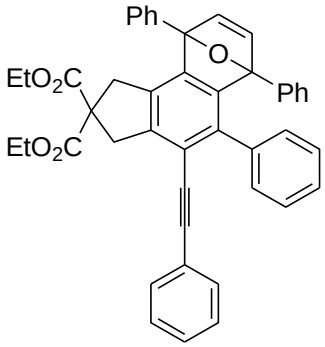
3m, 86%



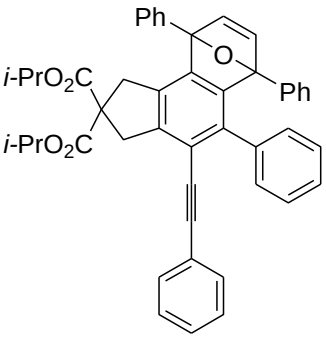
3n, 85%



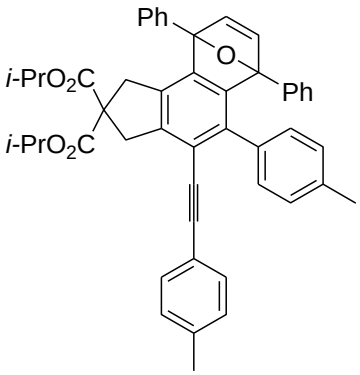
3o, 86%



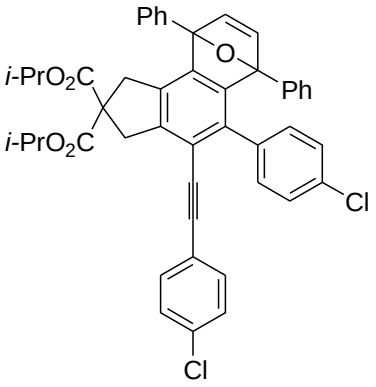
3p, 84%



3q, 82%



3r, 80%



3s, 84%

To further demonstrate the potential application of our methodology and extend the utility of this reaction, the reactivity of 2,5-diphenylfuran was also explored and the results are presented in Table 2 (**3n-3s**). Substituted groups in the aryl rings of tetraynes bearing *p*-methyl, or *p*-chlorine substituents reacted extremely well with 2,5-diphenylfuran, generating the corresponding products in high yields.

All of the bridged heterocycles compounds were verified via various spectroscopic techniques (^{1}H NMR, ^{13}C NMR, IR spectroscopy and/or HRMS). The molecular structures and relative configurations of **3j** and **3s** were confirmed unambiguously by X-ray diffraction (Figure 1). Further details are provided in the ESI.[17]

Scheme 1 indicates the sequence of steps involved in the synthesis of a bridged heterocycles by a cascade HDDA reaction. A HDDA reaction of tetrayne **1** produces an aryne as intermediate **I**, which subsequently reacts with diene (isobenzofuran, 2,5-diphenylfuran) components **2** with formal [4+2] cycloaddition to produce **3**.

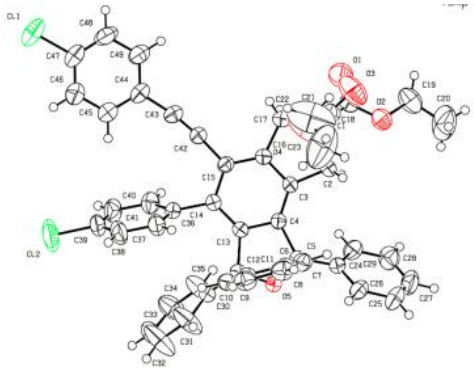
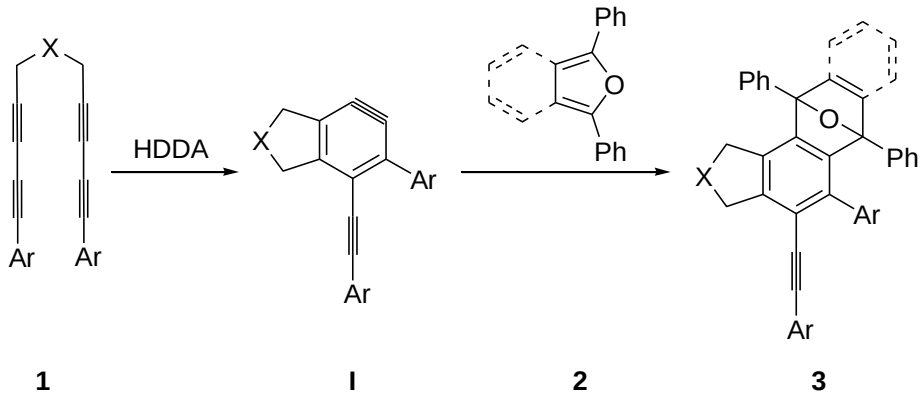


Figure 1. Molecular structure of **3j**



Scheme 1. Plausible mechanism

In summary, the [4+2] cyclization reaction offer an easy access to a type of bridged heterocycles. This approach requires no metals, catalysts, additives, or directing groups and can be used with a wide range of substrates. Given the generality of this process, the reaction is highly valuable due to the synthetic and medicinal importance of these unsaturated polycyclic compounds. This preliminary work has broad implications and may serve as a seminal study for the rapid synthesis of and direct access to a type of bridged heterocycles.

EXPERIMENTAL

All the catalytic reactions were performed under an argon atmosphere using the oven-dried Schlenk flask. The chemicals were purchased from Alfa Aesar and Acros Chemicals. All solvents and materials were pre-dried, redistilled or recrystallized before use. ^{1}H NMR (300 MHz) and ^{13}C NMR (125 MHz) spectra were recorded on a Bruker Avance 300 MHz spectrometer with C_6D_6 as the solvent. Chemical shifts are reported in ppm by assigning TMS resonance in the ^{1}H NMR spectra as 0.00 ppm and C_6D_6 resonance in the ^{13}C spectra as 124.0 ppm. All coupling constants (*J* values) were reported in Hertz (Hz). Column chromatography was performed on silica gel 300–400 mesh. Melting points were determined using a

Gallenkamp melting point apparatus and are uncorrected. The FT-IR spectra were recorded from KBr pellets or thin film from $CHCl_3$ on the NaCl window in the 4000-400 cm^{-1} ranges on a Nicolet 5DX spectrometer. All HRMS spectra were record using EI at 70 eV. X-Ray crystallography diffraction data of **3j, 3s** were collected at room temperature with a Bruker SMART Apex CCD diffractometer with Mo-Ka radiation (λ = 0.71073 Å) with a graphite monochromator using the ω-scan mode. Data reductions and absorption corrections were performed with SAINT and SADABS software, respectively. The structure was solved by direct methods and refined on F2 by full-matrix least squares using SHELXTL. All non-hydrogen atoms were treated anisotropically. The positions of hydrogen atoms were generated geometrically.

Typical procedure for the preparation of bridged heterocycles.

Tetraynes (1.0 equiv) and **2** (1.1 equiv) were added to toluene (2.0 mL), the mixture was stirred at room temperature then heated at 100 °C for 10 h in air. The reaction mixture was cooled to room temperature, and the solvent was evaporated in vacuo. The residue was purified by preparative thinlayer chromatography (TLC) on silica gel with the appropriate mixture of petroleum ether and EtOAc to give the desired product.

Dimethyl 5,6,11-triphenyl-4-(phenylethynyl)-6,11-dihydro-1*H*-6,11-epoxycyclopenta[*a*]anthracene-2,2(3*H*)-dicarboxylate (**3a**):

According to GP with **1a** (122.4 mg, 0.30 mmol, 1 equiv) and 1,3-diphenylisobenzofuran (89.1 mg, 0.33 mmol, 1.1 equiv); FC (silica gel, pentane/EtOAc 40:1) afforded **3a** (170.8 mg, 84%) as a white solid; mp 235-237 °C; FT-IR (KBr): 2980, 1743, 1722, 1491, 1464, 1258, 1065, 708, 617 cm^{-1}; ^{1}H NMR (C_6D_6, 300 MHz): δ = 8.16-8.13 (d, *J* = 7.5 Hz, 2H), 7.70-7.68 (d, *J* = 4.5Hz, 1H), 7.59-7.57 (m, 3H), 7.35-7.30 (m, 2H), 7.24-7.16 (m, 4H), 6.99-6.98 (m, 4H), 6.92-6.88 (m, 8H), 4.26-4.20 (d, *J* = 17.4 Hz, 1H), 3.79-3.78 (d, *J* = 3 Hz, 1H), 3.79-3.78 (d, *J* = 3.6 Hz, 1H), 3.47-3.42 (d, *J* = 17.5 Hz, 1H), 3.19 (s, 3H), 3.16 (s, 3H); ^{13}C NMR (C_6D_6, 125 MHz): δ = 171.9, 171.4, 151.5, 151.2, 149.6, 148.0, 143.9, 138.5, 137.5, 134.7, 134.6, 132.8, 131.8, 129.9, 129.7, 129.4, 128.9, 128.5, 128.4, 128.0, 127.8, 127.5, 127.3, 126.4, 126.3, 123.9, 122.9, 122.4, 118.2, 97.1, 93.0, 91.1, 88.1, 60.8, 52.6, 52.5, 41.1, 39.6; HRMS (APCI): *m/z* calcd for $C_{47}H_{35}O_5$ $[M+H]^+$ 679.2484; found 679.2479.

Dimethyl 6,11-diphenyl-5-(*p*-tolyl)-4-(*p*-tolylethynyl)-6,11-dihydro-1*H*-6,11-epoxycyclopenta[*a*]anthracene-2,2(3*H*)-dicarboxylate (**3b**):

According to GP with **1b** (130.8 mg, 0.30 mmol, 1 equiv) and 1,3-diphenylisobenzofuran (89.1 mg, 0.33 mmol, 1.1 equiv); FC (silica gel, pentane/EtOAc 40:1) afforded **3b** (175.8 mg, 83%) as a white solid; mp 231-233 °C; FT-IR (KBr): 3059, 2953, 1745, 1726, 1491, 1433, 1247, 1051, 694 cm^{-1}; ^{1}H NMR (C_6D_6, 300 MHz): δ = 8.16-8.14 (d, *J* = 7.5 Hz, 2H), 7.74-7.72 (d, *J* = 6.0 Hz, 1H), 7.60-7.55 (m, 3H), 7.35-7.30

(m, 2H), 7.24-7.16 (m, 5H), 7.00-6.96 (m, 2H), 6.92-6.90 (m, 3H), 6.82 (s, 2H), 6.74-6.71 (d, *J* = 7.2 Hz, 2H), 4.29-4.23 (d, *J* = 17.4 Hz, 1H), 3.80-3.73 (m, 2H), 3.49-3.44 (d, *J* = 16.2 Hz, 1H), 3.19 (s, 3H), 3.15 (s, 3H), 2.04 (s, 3H), 1.91 (s, 3H); ^{13}C NMR (C_6D_6, 125 MHz): δ = 171.9, 171.4, 151.6, 151.3, 149.6, 147.8, 143.9, 138.3, 137.5, 136.6, 135.6, 134.8, 134.7, 132.6, 131.8, 129.9, 129.9, 129.3, 128.9, 128.4, 127.7, 126.4, 126.2, 122.9, 122.4, 121.1, 118.4, 97.2, 93.1, 91.1, 87.7, 60.8, 52.6, 52.5, 41.1, 39.7, 21.3, 21.2; HRMS (APCI): *m/z* calcd for $C_{49}H_{39}O_5$ $[M+H]^+$ 706.2797; found 706.2792.

Dimethyl 5-(4-ethylphenyl)-4-((4-ethylphenyl)ethynyl)-6,11-diphenyl-6,11-dihydro-1*H*-6,11-epoxycyclopenta[*a*]anthracene-2,2(3*H*)-dicarboxylate (**3c**):

According to GP with **1c** (139.2 mg, 0.30 mmol, 1 equiv) and 1,3-diphenylisobenzofuran (89.1 mg, 0.33 mmol, 1.1 equiv); FC (silica gel, pentane/EtOAc 40:1) afforded **3c** (176.2 mg, 80%) as a white solid; mp 223-225 °C; FT-IR (KBr): 3028, 2949, 1741, 1728, 1508, 1446, 1243, 1049, 619 cm^{-1}; ^{1}H NMR (C_6D_6, 300 MHz): δ = 8.17-8.14 (d, *J* = 7.5 Hz, 2H), 7.75-7.73 (d, *J* = 6.0 Hz, 1H), 7.60-7.56 (m, 3H), 7.35-7.31 (m, 2H), 7.24-7.16 (m, 5H), 7.00 (s, 2H), 6.91-6.76 (m, 7H), 4.29-4.23 (d, *J* = 17.1 Hz, 1H), 3.80-3.74 (d, *J* = 16.8 Hz, 2H), 3.49-3.43 (d, *J* = 16.5 Hz, 1H), 3.19 (s, 3H), 3.15 (s, 3H), 2.39-2.37 (m, 2H), 2.27-2.25 (m, 2H), 1.07-1.02 (t, *J* = 7.2 Hz, 3H), 0.96-0.91 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (C_6D_6, 125 MHz): δ = 171.9, 171.4, 151.6, 151.3, 149.6, 147.7, 144.6, 143.8, 143.1, 137.6, 135.9, 134.8, 134.7, 132.6, 131.9, 130.0, 129.8, 129.4, 128.9, 128.4, 127.7, 127.0, 126.4, 126.2, 122.9, 122.4, 121.3, 118.4, 97.3, 93.1, 91.1, 87.7, 60.8, 52.6, 52.5, 41.1, 39.7, 29.1, 29.1, 16.3, 15.6; HRMS (APCI): *m/z* calcd for $C_{51}H_{43}O_5$ $[M+H]^+$ 735.3110; found 735.3105.

Dimethyl 5-(4-isopropylphenyl)-4-((4-isopropylphenyl)ethynyl)-6,11-diphenyl-6,11-dihydro-1*H*-6,11-epoxycyclopenta[*a*]anthracene-2,2(3*H*)-dicarboxylate (**3d**):

According to GP with **1d** (147.6 mg, 0.30 mmol, 1 equiv) and 1,3-diphenylisobenzofuran (89.1 mg, 0.33mmol, 1.1 equiv); FC (silica gel, pentane/EtOAc 40:1) afforded **3d** (182.9 mg, 80%) as a white solid; mp 218-220 °C; FT-IR (KBr): 3068, 2954, 1743, 1603, 1450, 1435, 1249, 1068, 700 cm^{-1}; ^{1}H NMR (C_6D_6, 300 MHz): δ = 8.25-8.22 (d, *J* = 7.5 Hz, 2H), 7.83-7.81 (d, *J* = 5.4 Hz, 1H), 7.69-7.64 (m, 3H), 7.43-7.38 (m, 3H), 7.32-7.24 (m, 4H), 7.10 (s, 2H), 7.09-6.86 (m, 7H), 4.38-4.32 (d, *J* = 17.1 Hz, 1H), 3.88-3.82 (d, *J* = 16.8 Hz, 2H), 3.57-3.51 (d, *J* = 16.5 Hz, 1H), 3.27 (s, 3H), 3.23 (s, 3H), 2.46-2.41 (t, *J* = 7.2 Hz, 3H), 2.35-2.30 (t, *J* = 7.2 Hz, 3H). 1.59-1.51 (m, 2H), 1.48-1.41 (m, 2H), 0.92-0.87 (t, *J* = 7.2 Hz, 3H), 0.84-0.79 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (C_6D_6, 125 MHz): δ = 171.9, 171.4, 151.6, 151.3, 149.6, 147.8, 143.8, 143.0, 141.3, 137.6, 136.0, 134.8, 134.7, 132.7, 131.9, 129.9, 129.9, 129.3, 128.9, 128.7, 128.4, 127.7, 127.7, 126.3, 126.2, 123.0, 122.4, 121.4, 118.5, 97.3, 93.1, 91.1, 87.8, 60.8, 52.6, 52.5, 41.1, 39.7, 38.1, 38.1, 24.9, 24.6, 13.9, 13.8; HRMS (APCI): *m/z* calcd for $C_{53}H_{47}O_5$ $[M+H]^+$ 763.3423; found 763.3418.

Dimethyl 5-(4-fluorophenyl)-4-((4-fluorophenyl)ethynyl)-6,11-diphenyl-6,11-dihydro-1*H*-6,11-epoxycyclopenta[*a*]anthracene-2,2(3*H*)-dicarboxylate (**3e**):

According to GP with **1e** (133.2 mg, 0.30 mmol, 1 equiv) and 1,3-diphenylisobenzofuran (89.1 mg, 0.33 mmol, 1.1 equiv); FC (silica gel, pentane/EtOAc 40:1) afforded **3e** (188.5 mg, 88%) as a white solid; mp 221-223 °C; FT-IR (KBr): 3028, 2954, 2926, 1741, 1730, 1446, 1246, 1199, 750 cm^{-1}; ^1H NMR (C_6D_6, 300 MHz): δ = 8.22-8.19 (d, *J* = 7.21 Hz, 2H), 7.69-7.67 (d, *J* = 6.0 Hz, 1H), 7.63-7.58 (m, 3H), 7.43-7.38 (t, *J* = 15.0 Hz, 2H), 7.32-7.24 (m, 2H), 7.10-6.96 (m, 8H), 6.71 (s, 2H), 6.61-6.55 (t, *J* = 17.1 Hz, 2H), 4.31-4.26 (d, *J* = 17.1 Hz, 1H), 3.86-3.79 (m, 2H), 3.56-3.51 (d, *J* = 16.5 Hz, 1H), 3.29 (s, 3H), 3.25 (s, 3H); ^{13}C NMR (C_6D_6, 125 MHz): δ = 171.8, 171.3, 163.8 (J_{C-F} = 44.4 Hz), 163.4 (J_{C-F} = 41.4 Hz), 151.2, 151.1, 149.9, 148.0, 143.9, 136.2, 134.6 (J_{C-F} = 14.3 Hz), 134.4, 134.3, 133.6 (J_{C-F} = 8.3 Hz), 133.0, 129.8, 129.6, 129.5, 128.9, 128.4, 126.5, 126.4, 122.8, 122.5, 119.7 (J_{C-F} = 4.0 Hz), 118.0, 115.9 (J_{C-F} = 21.1 Hz), 114.4 (J_{C-F} = 21.8 Hz), 96.1, 92.8, 91.1, 87.4, 60.8, 52.7, 52.6, 41.0, 39.6; HRMS (APCI): *m/z* calcd for $C_{47}H_{33}F_2O_5$ $[M+H]^+$ 715.2296; found 715.2285.

Dimethyl 5-(4-chlorophenyl)-4-((4-chlorophenyl)ethynyl)-6,11-diphenyl-6,11-dihydro-1*H*-6,11-epoxycyclopenta[*a*]anthracene-2,2(3*H*)-dicarboxylate (**3f**):

According to GP with **1f** (142.8 mg, 0.30 mmol, 1 equiv) and 1,3-diphenylisobenzofuran (89.1 mg, 0.33 mmol, 1.1 equiv); FC (silica gel, pentane/EtOAc 40:1) afforded **3f** (192.7 mg, 86%) as a white solid; mp 208-210 °C; FT-IR (KBr): 3026, 2963, 1735, 1508, 1450, 1247, 1201, 991, 702 cm^{-1}; ^1H NMR (C_6D_6, 300 MHz): δ = 8.21-8.18 (d, *J* = 6.9 Hz, 2H), 7.68-7.66 (d, *J* = 6.3 Hz, 1H), 7.62-7.56 (m, 3H), 7.43-7.38 (t, *J* = 15.0 Hz, 2H), 7.32-7.24 (t, *J* = 24.9 Hz, 2H), 7.06-6.98 (m, 8H), 6.89 (s, 4H), 4.29-4.23 (d, *J* = 16.8 Hz, 1H), 3.85-3.77 (m, 2H), 3.56-3.50 (d, *J* = 16.8 Hz, 1H), 3.29 (s, 3H), 3.26 (s, 3H); ^{13}C NMR (C_6D_6, 125 MHz): δ = 171.8, 171.3, 151.2, 151.0, 150.0, 148.2, 144.0, 136.8, 136.0, 134.5, 134.4, 133.4, 133.1, 132.8, 129.8, 129.5, 128.9, 128.4, 127.6, 126.5, 126.4, 122.8, 122.5, 121.9, 117.6, 96.1, 92.7, 91.1, 88.5, 60.8, 52.7, 52.6, 41.0, 39.6; HRMS (APCI): *m/z* calcd for $C_{47}H_{33}Cl_2O_5$ $[M+H]^+$ 747.1705; found 747.1700.

Diethyl 5,6,11-triphenyl-4-(phenylethynyl)-6,11-dihydro-1*H*-6,11-epoxycyclopenta[*a*]anthracene-2,2-(3*H*)-dicarboxylate (**3g**):

According to GP with **1g** (130.8 mg, 0.30 mmol, 1 equiv) and 1,3-diphenylisobenzofuran (89.1 mg, 0.33 mmol, 1.1 equiv); FC (silica gel, pentane/EtOAc 40:1) afforded **3g** (173.7 mg, 82%) as a white solid; mp 202-204 °C; FT-IR (KBr): 3057, 2980, 1735, 1490, 1450, 1246, 1072, 990, 754 cm^{-1}; ^1H NMR (C_6D_6, 300 MHz): δ = 8.24-8.21 (d, *J* = 7.5 Hz, 2H), 7.78-7.76 (d, *J* = 5.7 Hz, 1H), 7.67-7.62 (m, 3H), 7.43-7.38 (m, 2H), 7.32-7.24 (m, 5H), 7.06-6.96 (m, 11H), 4.40-4.35 (d, *J* = 17.4 Hz, 1H), 3.95-3.83 (m, 6H), 3.66-3.61 (d, *J* = 17.4 Hz, 1H), 0.92-0.84 (m, 6H); ^{13}C NMR (C_6D_6, 125 MHz): δ = 171.5, 171.0, 151.5,

151.3, 149.5, 148.0, 144.2, 138.5, 137.5, 134.9, 134.6, 132.9, 131.8, 129.8, 129.3, 128.9, 128.5, 128.4, 127.8, 127.7, 127.4, 127.3, 126.4, 126.2, 124.0, 122.9, 122.4, 118.2, 97.0, 93.0, 91.1, 88.2, 61.8, 61.7, 60.8, 41.0, 39.6, 14.0, 13.9; HRMS (APCI): *m/z* calcd for $C_{49}H_{39}O_5$ $[M+H]^+$ 707.2797; found 707.2785.

Diethyl 5-(4-ethylphenyl)-4-((4-ethylphenyl)ethynyl)-6,11-diphenyl-6,11-dihydro-1*H*-6,11-epoxycyclopenta[*a*]anthracene-2,2(3*H*)-dicarboxylate (**3h**):

According to GP with **1h** (147.6 mg, 0.30 mmol, 1 equiv) and 1,3-diphenylisobenzofuran (89.1 mg, 0.33 mmol, 1.1 equiv); FC (silica gel, pentane/EtOAc 40:1) afforded **3h** (182.9 mg, 80%) as a white solid; mp 184-186 °C; FT-IR (KBr): 3034, 2962, 1728, 1456, 1446, 1249, 1074, 835, 754 cm^{-1}; ^1H NMR (C_6D_6, 300 MHz): δ = 8.16-8.14 (d, *J* = 7.2 Hz, 2H), 7.74-7.72 (d, *J* = 6.6 Hz, 1H), 7.59-7.55 (m, 3H), 7.35-7.30 (m, 2H), 7.24-7.16 (m, 4H), 7.04-6.99 (m, 2H), 6.97-6.76 (m, 8H), 4.34-4.28 (d, *J* = 17.1 Hz, 1H), 3.87-3.75 (m, 6H), 3.59-3.53 (d, *J* = 17.5 Hz, 1H), 2.41-2.34 (q, *J* = 7.5 Hz, 2H), 2.30-2.22 (q, *J* = 7.5 Hz, 2H), 1.07-1.02 (t, *J* = 7.5 Hz, 3H), 0.96-0.91 (t, *J* = 7.5 Hz, 3H), 0.85-0.76 (m, 6H); ^{13}C NMR (C_6D_6, 125 MHz): δ = 171.5, 171.1, 151.6, 151.3, 149.5, 147.8, 144.5, 144.0, 143.0, 137.5, 135.9, 135.0, 134.8, 132.7, 131.9, 129.8, 129.2, 128.9, 128.4, 127.7, 127.0, 126.3, 126.2, 122.9, 122.3, 121.4, 118.5, 97.3, 93.0, 91.1, 87.8, 61.7, 61.6, 60.9, 41.1, 39.6, 29.1, 29.0, 16.2, 15.6, 14.0, 13.9; HRMS (APCI): *m/z* calcd for $C_{53}H_{47}O_5$ $[M+H]^+$ 763.3423; found 763.3418.

Diethyl 5-(4-fluorophenyl)-4-((4-fluorophenyl)ethynyl)-6,11-diphenyl-6,11-dihydro-1*H*-6,11-epoxycyclopenta[*a*]anthracene-2,2(3*H*)-dicarboxylate (**3i**):

According to GP with **1i** (141.6 mg, 0.30 mmol, 1 equiv) and 1,3-diphenylisobenzofuran (89.1 mg, 0.33 mmol, 1.1 equiv); FC (silica gel, pentane/EtOAc 40:1) afforded **3i** (189.2 mg, 85%) as a white solid; mp 220-222 °C; IR (KBr): 3057, 2978, 1739, 1722, 1508, 1367, 1228, 1182, 837, 700 cm^{-1}; ^1H NMR (C_6D_6, 300 MHz): δ = 8.13-8.10 (d, *J* = 7.2 Hz, 2H), 7.61-7.59 (d, *J* = 6.3 Hz, 1H), 7.52-7.50 (m, 3H), 7.34-7.30 (m, 2H), 7.24-7.16 (m, 2H), 7.02-6.92 (m, 8H), 6.63 (s, 2H), 6.53-6.47 (t, *J* = 16.8 Hz, 2H), 4.30-4.24 (d, *J* = 17.4 Hz, 1H), 3.89-3.73 (m, 6H), 3.59-3.53 (d, *J* = 17.1 Hz, 1H), 0.85-0.77 (m, 6H); ^{13}C NMR (C_6D_6, 125 MHz): δ = 171.4, 171.0, 163.8 ($J_{C\text{-}F}$ = 43.4 Hz), 161.8 ($J_{C\text{-}F}$ = 39.9 Hz), 151.2, 149.8, 148.1, 144.2, 136.1, 134.7, 134.5, 134.4, 134.4, 133.6 ($J_{C\text{-}F}$ = 8.3 Hz), 133.0, 129.7 ($J_{C\text{-}F}$ = 7.8 Hz), 129.3, 128.9, 128.4, 128.0, 127.6, 126.4, 126.4, 122.7, 122.4, 119.8, 119.7 ($J_{C\text{-}F}$ = 2.9 Hz), 118.0, 115.9 ($J_{C\text{-}F}$ = 21.5 Hz), 114.4($J_{C\text{-}F}$ = 21.9 Hz), 96.0, 92.8, 91.1, 87.4, 61.9, 61.8, 60.9, 41.0, 39.6, 14.0, 13.9; HRMS (APCI): *m/z* calcd for $C_{49}H_{37}F_2O_5$ $[M+H]^+$ 743.2609; found 743.2609.

Diethyl 5-(4-chlorophenyl)-4-((4-chlorophenyl)ethynyl)-6,11-diphenyl-6,11-dihydro-1*H*-6,11-epoxycyclopenta[*a*]anthracene-2,2(3*H*)-dicarboxylate (**3j**):

According to GP with **1j** (151.2 mg, 0.30 mmol, 1 equiv) and 1,3-diphenylisobenzofuran (89.1 mg, 0.33 mmol, 1.1 equiv); FC (silica gel, pentane/EtOAc 40:1) afforded **3j** (195.0 mg, 84%) as a white solid; mp

214-216 °C; FT-IR (KBr): 3059, 2976, 1739, 1724, 1487, 1303, 1251, 1087, 829, 754 cm^{-1}; ^1H NMR (C_6D_6, 300 MHz): δ= 8.20-8.18 (d, *J* = 7.8 Hz, 2H), 7.68-7.66 (d, *J* = 6.3 Hz, 1H), 7.62-7.55 (m, 3H), 7.42-7.37 (m, 2H), 7.32-7.24 (m, 2H), 7.08-6.98 (m, 8H), 6.88 (s, 4H), 4.35-4.29 (d, *J* = 17.1 Hz, 1H), 3.97-3.90 (m, 4H), 3.86-3.79 (m, 2H), 3.67-3.61 (d, *J* = 17.1 Hz, 1H), 0.93-0.85 (m, 6H); ^{13}C NMR (C_6D_6, 125 MHz): δ= 171.4, 171.0, 151.1, 151.0, 149.9, 148.2, 144.3, 136.8, 136.0, 134.7, 134.5, 134.4, 133.4, 133.2, 133.8, 129.7, 129.5, 129.4, 128.9, 128.4, 127.6, 126.5, 126.4, 122.7, 122.4, 122.0, 117.6, 96.0, 92.6, 91.1, 88.6, 61.9, 61.8, 60.8, 41.0, 39.6, 14.0, 13.9; HRMS (APCI): *m/z* calcd for $C_{49}H_{37}Cl_2O_5$ $[M+H]^+$ 775.2018; found 775.2010.

Diisopropyl 6,11-diphenyl-5-(*p*-tolyl)-4-(*p*-tolylethynyl)-6,11-dihydro-1*H*-6,11-epoxycyclopenta[*a*]anthracene-2,2(3*H*)-dicarboxylate (**3k**):

According to GP with **1k** (147.6 mg, 0.30 mmol, 1 equiv) and 1,3-diphenylisobenzofuran (89.1 mg, 0.33 mmol, 1.1 equiv); FC (silica gel, pentane/EtOAc 40:1) afforded **3k**(182.9 mg, 80%) as a white solid; mp 217-219 °C; FT-IR (KBr): 3034, 2980, 1751, 1726, 1508, 1450, 1253, 1182, 815, 700 cm^{-1}; ^1H NMR (C_6D_6, 300 MHz): δ= 8.23-8.20 (d, *J* = 7.5 Hz, 2H), 7.82-7.80 (d, *J* = 6.3 Hz, 1H), 7.68-7.63 (m, 3H), 7.42-7.37 (m, 2H), 7.34-7.23 (m, 4H), 7.11-6.99 (m, 6H), 6.90-6.79 (m, 4H), 5.05-4.95(m, 2H), 4.47-4.41(d, *J* = 17.1 Hz, 1H), 3.85-3.75 (m, 3H), 2.12 (s, 3H), 1.99 (s, 3H), 1.04-0.95 (m, 12H); ^{13}C NMR (C_6D_6, 125 MHz): δ= 171.0, 170.7, 151.5, 151.4, 149.3, 147.8, 144.3, 138.1, 137.4, 136.5, 135.7, 135.1, 134.8, 132.7, 131.8, 129.9, 129.7, 129.3, 129.1, 128.8, 128.4, 127.7, 126.3, 126.2, 122.9, 122.3, 121.2, 118.4, 97.1, 93.1, 91.0, 87.8, 69.1, 60.9, 41.0, 39.7, 24.5, 21.4, 21.4, 21.3, 21.2; HRMS (APCI): *m/z* calcd for $C_{53}H_{47}O_5$ $[M+H]^+$ 763.3423; found 763.3413.

Diisopropyl 6,11-diphenyl-5-(*m*-tolyl)-4-(*m*-tolylethynyl)-6,11-dihydro-1*H*-6,11-epoxycyclopenta[*a*]-anthracene-2,2(3*H*)-dicarboxylate (**3l**):

According to GP with **1l** (147.6 mg, 0.30 mmol, 1 equiv) and 1,3-diphenylisobenzofuran (89.1 mg, 0.33 mmol, 1.1 equiv); FC (silica gel, pentane/EtOAc 40:1) afforded **3l** (182.9 mg, 80%) as a white solid; mp 164-166 °C; FT-IR (KBr): 3035, 2980, 1726, 1600, 1454, 1247, 1192, 1101, 815, 752 cm^{-1}; ^1H NMR (C_6D_6, 300 MHz): δ= 8.23-8.20 (d, *J* = 6.9 Hz, 2H), 7.80 (s, 1H), 7.65 (s, 3H), 7.42-7.37 (m, 2H), 7.32-7.24 (m, 2H), 7.14-6.81 (m, 12H), 5.05-4.95 (m, 2H), 4.47-4.41 (d, *J* = 17.1 Hz, 1H), 3.86-3.69 (m, 3H), 2.11 (s, 3H), 1.97 (s, 3H), 1.04-0.95 (m, 12H). ^{13}C NMR (125 MHz, C_6D_6): δ = 171.0, 170.7, 151.4, 149.3, 138.0, 136.6, 135.1, 132.7, 132.5, 129.7, 129.6, 129.1, 129.0, 128.8, 128.4, 127.6, 127.4, 126.3, 126.2, 124.0, 122.3, 97.2, 91.0, 88.0, 69.1, 60.9, 41.0, 39.7, 21.5, 21.4, 21.4, 21.3, 21.1; HRMS (APCI): *m/z* calcd for $C_{53}H_{47}O_5$ $[M+H]^+$ 763.3423; found 763.3414.

4-(Hept-1-yn-1-yl)-5-pentyl-6,11-diphenyl-2-tosyl-2,3,6,11-tetrahydro-1*H*-6,11-epoxynaphtho[2,3-*e*]isoindole (**3m**):

According to GP with **1m** (134.1 mg, 0.30 mmol, 1 equiv) and 1,3-diphenylisobenzofuran (89.1 mg, 0.33 mmol, 1.1 equiv); FC (silica gel, pentane/EtOAc 40:1) afforded **3m** (185.0 mg, 80%) as a white solid; mp 160-161 °C; FT-IR (KBr): 3059, 2954, 2927, 1597, 1496, 1454, 1207, 1155, 914, 750 cm^{-1}; ^1H NMR (C_6D_6, 300 MHz): δ = 8.05-8.03 (d, *J* = 6.6 Hz, 2H), 7.90-7.87 (m, 2H), 7.76-7.69 (m, 3H), 7.42-7.24 (m, 7H), 7.03-6.90 (m, 2H), 6.75-6.73 (d, *J* = 8.4 Hz, 2H), 4.81 (s, 2H), 4.58-4.44 (m, 2H), 2.85-2.83 (m, 1H), 2.65-2.64 (m, 1H), 2.24-2.20 (m, 2H), 1.88 (s, 3H), 1.47-1.11 (m, 12H), 0.97-0.89 (m, 6H); ^{13}C NMR (125 MHz, C_6D_6): δ = 151.1, 150.2, 150.1, 146.1, 143.0, 140.1, 138.2, 136.5, 135.2, 134.7, 129.8, 129.6, 129.3, 129.2, 128.8, 128.7, 128.6, 128.4, 127.2, 126.2, 122.7, 122.0, 118.0, 98.5, 92.5, 90.2, 77.3, 54.1, 53.2, 32.5, 31.3, 30.5, 29.7, 28.8, 22.8, 22.6, 21.1, 19.8, 14.3, 14.2; HRMS (APCI): *m/z* calcd for $C_{47}H_{48}NO_3S$ $[M+H]^+$ 706.3355; found 706.3350.

Dimethyl 6,9-diphenyl-5-(*p*-tolyl)-4-(*p*-tolylethynyl)-6,9-dihydro-1*H*-6,9-epoxycyclopenta[*a*]naphthalene-2,2(3*H*)-dicarboxylate (**3n**):

According to GP with **1n** (130.8 mg, 0.30 mmol, 1 equiv) and 2,5-diphenylfuran (72.6 mg, 0.33 mmol, 1.1 equiv); FC (silica gel, pentane/EtOAc 40:1) afforded **3n** (157.4 mg, 80%) as a white solid; mp 190-192 °C; FT-IR (KBr): 3032, 2954, 1734, 1593, 1490, 1450, 1249, 1014, 829, 698 cm^{-1}; ^1H NMR (C_6D_6, 300 MHz): δ = 7.89-7.87 (d, *J* = 7.2 Hz, 2H), 7.38-7.32 (m, 6H), 7.24-7.21 (m, 4H), 6.97-6.95 (m, 4H), 6.82-6.77 (m, 4H), 4.35-3.30 (m, 4H), 3.24 (s, 3H), 3.23 (s, 3H), 2.16 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (125 MHz, C_6D_6): δ = 171.8, 171.7, 150.5, 148.8, 145.0, 144.5, 142.6, 138.1, 137.3, 136.6, 136.2, 136.1, 134.9, 132.1, 131.8, 130.4, 129.3, 129.0, 128.9, 128.6, 128.4, 127.7, 127.5, 121.1, 117.4, 97.0, 95.4, 93.4, 87.7, 60.7, 52.5, 52.5, 41.2, 38.6, 21.3, 21.2; HRMS (APCI): *m/z* calcd for $C_{45}H_{37}O_5$ $[M+H]^+$ 657.2641; found 657.2637.

Dimethyl 5-(4-chlorophenyl)-4-((4-chlorophenyl)ethynyl)-6,9-diphenyl-6,9-dihydro-1*H*-6,9-epoxycyclopenta[*a*]naphthalene-2,2(3*H*)-dicarboxylate (**3o**):

According to GP with **1o** (142.8 mg, 0.30 mmol, 1 equiv) and 2,5-diphenylfuran (72.6 mg, 0.33 mmol, 1.1 equiv); FC (silica gel, pentane/EtOAc 40:1) afforded **3o** (179.6 mg, 86%) as a white solid; mp 185-187 °C; FT-IR (KBr): 3034, 2981, 1728, 1600, 1490, 1440, 1244, 1049, 758 cm^{-1}; ^1H NMR (C_6D_6, 300 MHz): δ = 7.86-7.84 (d, *J* = 7.2 Hz, 2H), 7.37-7.32 (m, 3H), 7.28-7.24 (m, 5H), 6.97-6.93 (m, 5H), 6.86 (s, 5H), 4.25-4.19 (d, *J* = 7.1 Hz, 1H), 4.07-4.02 (d, *J* = 7.1 Hz, 1H), 3.53-3.48 (d, *J* = 6.9 Hz, 1H), 3.26 (s, 3H), 3.24 (s, 3H), 3.22 (s, 1H); ^{13}C NMR (125 MHz, C_6D_6): δ = 171.7, 171.6, 150.8, 149.2, 144.8, 144.4, 142.9, 136.2, 136.1, 135.9, 135.8, 134.4, 133.1, 132.8, 132.6, 131.7, 129.1, 129.0, 128.9, 128.4, 128.0, 127.5, 122.0, 116.6, 95.9, 95.0, 93.4, 88.5, 60.6, 52.6, 52.6, 41.0, 38.5; HRMS (APCI): *m/z* calcd for $C_{43}H_{31}Cl_2O_5$ $[M+H]^+$ 697.1549; found 697.1537.

Diethyl 5,6,9-triphenyl-4-(phenylethynyl)-6,9-dihydro-1*H*-6,9-epoxycyclopenta[*a*]naphthalene-2,2(3*H*)-

dicarboxylate (**3p**):

According to GP with **1p** (130.8 mg, 0.30 mmol, 1 equiv) and 2,5-diphenylfuran (72.6 mg, 0.33 mmol, 1.1 equiv); FC (silica gel, pentane/EtOAc 40:1) afforded **3p** (165.3 mg, 84%) as a white solid; mp 195-197 °C; FT-IR (KBr): 3034, 2976, 1726, 1718, 1598, 1493, 1246, 974, 698 cm^{-1}; ^1H NMR (C_6D_6, 300 MHz): δ = 7.88-7.86 (d, *J* = 7.5 Hz, 2H), 7.37-7.31 (m, 6H), 7.24-7.19 (m, 4H), 6.98-6.94 (m, 10H), 4.39-4.33 (d, *J* = 17.4 Hz, 1H), 4.12-4.06 (d, *J* = 17.4 Hz, 1H), 3.95-3.86 (m, 4H), 3.63-3.58 (d, *J* = 17.8 Hz, 1H), 3.30-3.24 (d, *J* = 17.5 Hz, 1H), 0.90-0.86 (t, *J* = 6.3 Hz, 6H). ^{13}C NMR (125 MHz, C_6D_6): δ = 171.4, 171.3, 150.3, 149.0, 145.0, 144.5, 142.9, 137.8, 137.4, 136.6, 136.1, 132.4, 131.8, 130.5, 128.9, 128.5, 128.4, 128.3, 128.1, 127.9, 127.8, 127.3, 126.9, 124.0, 117.2, 96.8, 95.3, 93.4, 88.2, 61.7, 61.6, 60.7, 41.1, 38.6, 14.0, 13.9; HRMS (APCI): *m/z* calcd for $C_{45}H_{37}O_5$ $[M+H]^+$ 657.2641; found 657.2636.

Diisopropyl 5,6,9-triphenyl-4-(phenylethynyl)-6,9-dihydro-1*H*-6,9-epoxycyclopenta[*a*]naphthalene-2,2-(3*H*)-dicarboxylate (**3q**):

According to GP with **1q** (139.2 mg, 0.30 mmol, 1 equiv) and 2,5-diphenylfuran (72.6 mg, 0.33 mmol, 1.1 equiv); FC (silica gel, pentane/EtOAc 40:1) afforded **3q** (168.3 mg, 82%) as a white solid; mp 202-204 °C; FT-IR (KBr): 3034, 2980, 1724, 1508, 1450, 1253, 1103, 813, 758 cm^{-1}; ^1H NMR (C_6D_6, 300 MHz): δ = 7.79-7.76 (d, *J* = 6.9 Hz, 2H), 7.27-7.22 (m, 6H), 7.16-7.10 (m, 4H), 6.90-6.86 (m, 10H), 4.94-4.89 (m, 2H), 4.37-4.31 (d, *J* = 17.1 Hz, 1H), 3.96-3.90 (d, *J* = 17.7 Hz, 1H), 3.61-3.55 (d, *J* = 17.1 Hz, 1H), 3.14-3.08 (d, *J* = 16.8 Hz, 1H), 0.95-0.89 (m, 12H); ^{13}C NMR (125 MHz, C_6D_6): δ = 171.1, 170.8, 150.2, 148.9, 144.9, 144.6, 143.1, 137.8, 137.4, 136.7, 136.1, 132.4, 131.8, 130.5, 128.9, 128.8, 128.6, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.3, 126.8, 124.1, 117.1, 96.7, 95.3, 93.3, 88.2, 69.2, 69.0, 60.7, 41.0, 38.6, 21.5, 21.4; HRMS (APCI): *m/z* calcd for $C_{47}H_{41}O_5$ $[M+H]^+$ 685.2954; found 685.2946.

Diisopropyl 6,9-diphenyl-5-(*p*-tolyl)-4-(*p*-tolylethynyl)-6,9-dihydro-1*H*-6,9-epoxycyclopenta[*a*]naphthalene-2,2(3*H*)-dicarboxylate (**3r**):

According to GP with **1r** (147.6 mg, 0.30 mmol, 1 equiv) and 2,5-diphenylfuran (72.6 mg, 0.33 mmol, 1.1 equiv); FC (silica gel, pentane/EtOAc 40:1) afforded **3r** (170.9 mg, 80%) as a white solid; mp 158-160 °C; FT-IR (KBr): 3039, 2980, 1722, 1489, 1375, 1267, 1101, 819, 731 cm^{-1}; ^1H NMR (C_6D_6, 300 MHz): δ = 7.87-7.85 (d, *J* = 6.9 Hz, 2H), 7.37-7.30 (m, 6H), 7.24-7.19 (m, 4H), 6.98-6.96 (m, 4H), 6.82-6.77 (m, 4H), 5.03-4.97 (m, 2H), 4.47-4.42 (d, *J* = 17.1 Hz, 1H), 4.07-4.01 (d, *J* = 17.4 Hz, 1H), 3.71-3.65 (d, *J* = 17.1 Hz, 1H), 3.23-3,17 (d, *J* = 17.5 Hz, 1H), 2.16 (s, 3H), 1.98 (s, 3H), 1.03-0.97 (m, 12H); ^{13}C NMR (125 MHz, C_6D_6): δ = 171.1, 170.8, 150.3, 148.8, 144.9, 144.6, 143.0, 138.0, 137.3, 136.8, 136.3, 136.0, 135.0, 132.2, 131.8, 130.4, 129.2, 128.9, 128.7, 128.0, 127.7, 127.5, 121.2, 117.3, 96.9, 95.3, 93.4, 87.8, 69.1, 69.0, 60.7, 41.1, 38.6, 21.5, 21.4, 21.3, 21.2; HRMS (APCI): *m/z* calcd for

$C_{49}H_{45}O_5$ $[M+H]^+$ 713.3267; found 713.3263.

Diisopropyl 5-(4-chlorophenyl)-4-((4-chlorophenyl)ethynyl)-6,9-diphenyl-6,9-dihydro-1*H*-6,9-epoxy-cyclopenta[*a*]naphthalene-2,2(3*H*)-dicarboxylate (**3s**):

According to GP with **1s** (159.6 mg, 0.30 mmol, 1 equiv) and 2,5-diphenylfuran (72.6 mg, 0.33 mmol, 1.1 equiv); FC (silica gel, pentane/EtOAc 40:1) afforded **3s** (189.5 mg, 80%) as a white solid; mp 205-207 °C; FT-IR (KBr): 3082, 2978, 1732, 1654, 1490, 1244, 852, 756 cm^{-1}; ^1H NMR (C_6D_6, 300 MHz): δ = 7.84-7.82 (d, *J* = 6.6 Hz, 2H), 7.35-7.24 (m, 8H), 7.02-6.85 (m, 10H), 5.04-4.97 (m, 2H), 4.40-4.34 (m, 1H), 3.97-3.92 (d, *J* = 17.1 Hz, 1H), 3.69-3,63 (d, *J* = 17.1 Hz, 1H), 3.20-3.14 (d, *J* = 17.1 Hz, 1H), 1.05-0.96 (m, 12H); ^{13}C NMR (125 MHz, C_6D_6): δ = 171.0, 170.7, 150.6, 149.2, 144.7, 144.6, 143.3, 136.4, 136.2, 135.8, 134.3, 133.0, 132.8, 132.7, 129.0, 128.8, 128.4, 127.4, 122.1, 116.5, 95.7, 95.0, 93.4, 88.6, 69.3, 69.1, 60.7, 53.4, 40.9, 38.5, 21.5, 21.4; HRMS (APCI): *m/z* calcd for $C_{47}H_{39}Cl_2O_5$ $[M+H]^+$ 753.2175; found 753.2164.

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17. CCDC 1554529 (**3j**), 1554535 (**3s**) contain the supplementary crystallographic data for this paper. These data can be obtained free charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.