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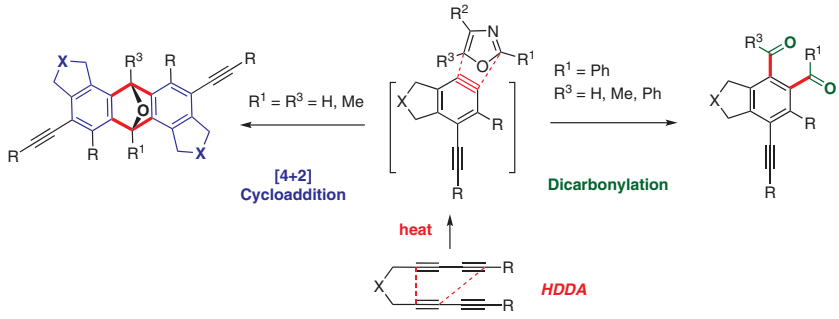
Epoxyanthracene Derivatives and Dicarbonylation on Benzene Ring via Hexadehydro-Diels–Alder (HDDA) Derived Benzynes with Oxazoles

Feihu Yang◊
Xiaojie Zheng◊
Yu Lei
Qiong Hu*
Wenjing Zhu
Yimin Hu*

Key Laboratory of Functional Molecular Solids, Ministry of Education; Anhui Laboratory of Molecule-Based Materials, State Laboratory Cultivation Base, College of Chemistry and Materials Science, Anhui Normal University, Wuhu, Anhui 241002, P. R. of China
huqiong@ahnu.edu.cn
yiminhu@ahnu.edu.cn

◊ These authors contributed equally



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Abstract A capture reaction of hexadehydro-Diels–Alder (HDDA) derived benzyne with various substituted oxazoles is reported. With methyl, hydrogen, or phenyl as the substituent at 2-position of oxazole, tetraynes afforded epoxyanthracene derivatives or underwent dicarbonylation on benzene ring. The reaction does not require any catalyst or additive. The mechanism behind the reaction was investigated. The obtained polycyclic product structure has potential application value in optoelectronic materials. The availability of dicarbonylated arene implies the uniqueness of HDDA benzyne reaction compared with traditional benzyne.

Key words HDDA, oxazole, epoxyanthracene, dicarbonylation, Diels–Alder reaction

Benzyne intermediates are one of the most common reaction intermediates.[1] Given their high reactivity and unique advantages in organic reactions, they are widely used in organic synthesis.[2] Hexadehydro-Diels–Alder (HDDA) reaction is a newly developed method to form benzyne in recent years.[3] Compared with the traditional method, HDDA reaction is performed by thermal cyclization of three alkyne bonds in the molecule to form a benzyne intermediate without using any catalyst or additive. HDDA-derived benzyne reaction tends to yield polycyclic compounds based on the particularity and diversity of the precursor's structure.[4] Importantly, considering the generation of its thermodynamics and the particularity of its substrate structure, the HDDA-derived benzyne tends to result in a different outcome compared with the traditional benzyne.[5]

Epoxyanthracene derivative can usually be obtained by reacting a benzyne intermediate with an isobenzofuran derivative,[6] or a naphthyne intermediate with a furan compound.[7] It is commonly used to obtain anthracene derivatives through subsequent deoxygenation.[8] Anthracene derivatives are widely used in optoelectronic materials such as blue organic light-emitting diodes (OLEDs) based on their polycyclic structure (Figure 1).[9–11]

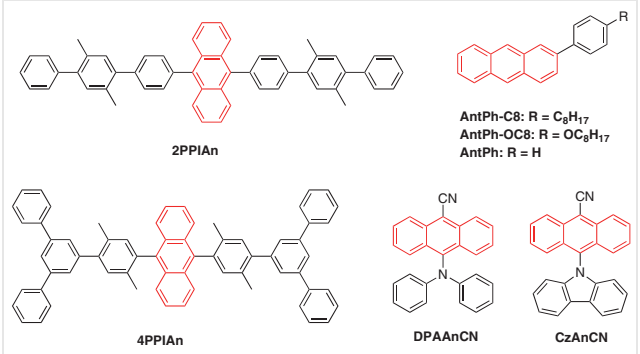


Figure 1 Application of anthracene derivatives in optoelectronic materials

The reaction between benzyne and oxazole has been studied early. Bhatt and Reddy first reported the cycloaddition reaction based on benzyne and oxazole.[12] Then Rickborn's group described the reaction in detail.[13–16] An epoxyanthracene derivative was obtained by cycloaddition of two molecules of benzyne at 101 °C by using benzyne precursor

anthranilic acid and substituted oxazole in 1,4-dioxane. In this process, a molecule of nitrile is removed. A 9,10-disubstituted anthracene derivative can be finally obtained through subsequent deoxygenation with Zn/AcOH.

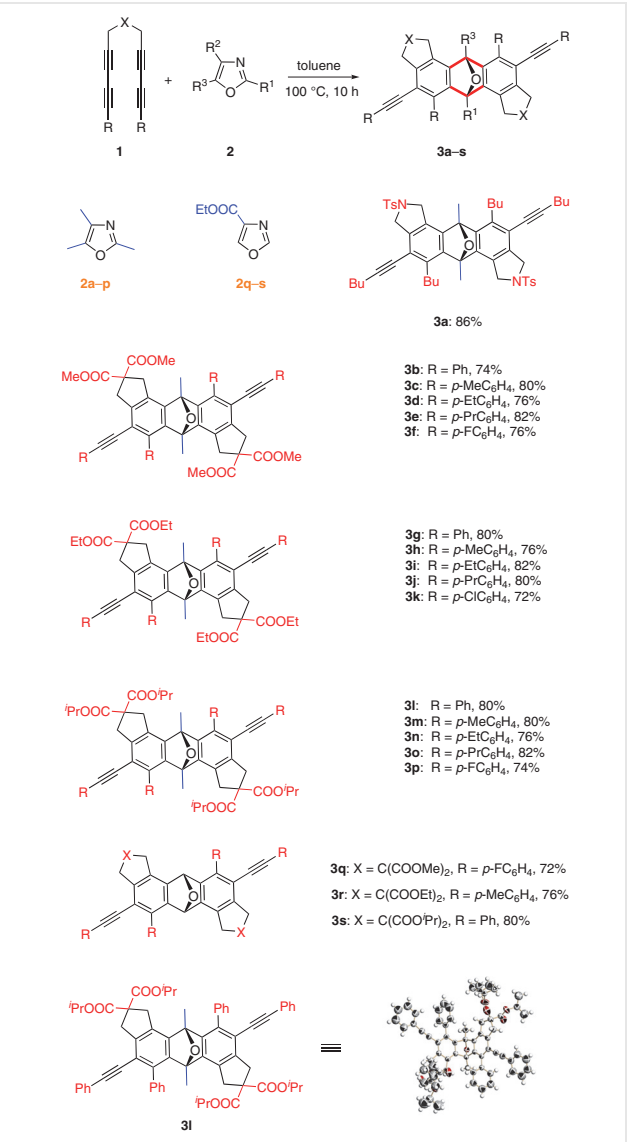
However, when using 1-aminobenzotriazole as benzyne precursor to react with oxazole at 0 °C under $Pd(OAc)_4$, only one molecule of benzyne intermediate is involved in the reaction. The low temperature is unfavorable to the occurrence of the retro-Diels–Alder reaction to make the elimination of nitrile compounds. Previously our group once reported the cycloaddition reaction between HDDA-derived benzyne[17–19] and imidazole, and accidentally obtained isoindole-1,3-dione compounds. Considering the different reactivity between HDDA-derived benzyne and traditional benzyne, we investigated the reaction results of HDDA-derived benzyne with oxazole compounds here.

In the beginning, we tried to react a tetrayne substrate **1** (R = Bu, X = NTs) with 2,4,5-trimethyloxazole (**2a**). The reaction was tracked by TLC, and a main product spot appeared. After separation by column chromatography and subjecting to NMR and X-ray diffraction,[20] the product structure was confirmed to be an epoxyanthracene derivative **3a** (Scheme 1).

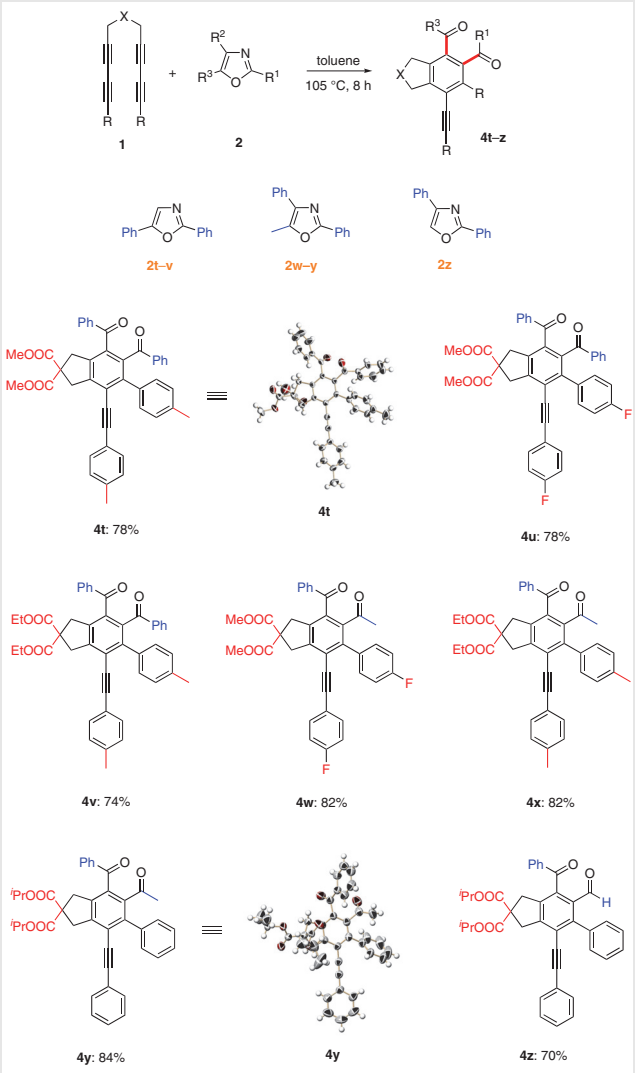
We then optimized the reaction conditions and obtained the best yield under conditions at 100 °C in toluene for 10 hours. In consideration of the universality of the reaction, we extended the tetrayne substrate. The overall yield did not change remarkably, and the substituent effect was not obvious. When the carbon tetrayne substrate was linked with dimethyl malonate and the R substituent was changed to phenyl, *p*-methylphenyl, *p*-ethylphenyl, *p*-propylphenyl, and *p*-fluorophenyl, we obtained compounds **3b–f** in yields of 74–82%. When the tetrayne substrate was linked with diethyl malonate, and the R substituent was phenyl, *p*-methylphenyl, *p*-ethylphenyl, *p*-propylphenyl, and *p*-chlorophenyl, we obtained compounds **3g–k** in yields of 72–82%. When the tetrayne substrate was linked with diisopropyl malonate, and the R substituents was phenyl, *p*-methylphenyl, *p*-ethylphenyl, *p*-propylphenyl, and *p*-fluorophenyl, we obtained compounds **3l–p** in yields of 74–82%. The nitrogen-based tetrayne was also compatible with the reaction, and the yield of compound **3a** was 86% higher than that of the carbon-based tetrayne. The formation of compounds **3a–p** indicated that the reaction is suitable for trisubstituted oxazoles. We also considered expanding the oxazole substrate. Compounds **3q–s** were obtained in yields of 72–80% by reacting different tetraynes with 4-ethoxycarbonyloxazole. The oxazole substrates with hydrogen at 2,5-positions and ester group at 4-positions were also suitable for this reaction.

Interestingly, when the oxazole substrates R^1 and R^3 were changed to phenyl groups, and 2,5-diphenyloxazole was used as the reaction substrate, we unexpectedly obtained the product **4t** (Scheme 2). By optimizing the reaction conditions, the best yield was obtained under the conditions of 105 °C in toluene for 8 hours. Different tetrayne substrates were used to obtain compounds **4t–v** in yields of 74–78%. To further explore the reaction principle, the oxazole substrate R^3 substituent was changed to hydrogen and methyl. When the R^3 substituent was hydrogen, the decarbonylated arene **4z** is also obtained despite a relatively low yield (70%). When the R^3 substituent is methyl, the yield of **4w–y** was generally higher (82–84%) than with hydrogen or phenyl as substituent.

Based on the above results and literature reports,[21,22] we speculated a possible reaction mechanism. For the synthesis of epoxyanthracene derivatives, we took the tetrayne



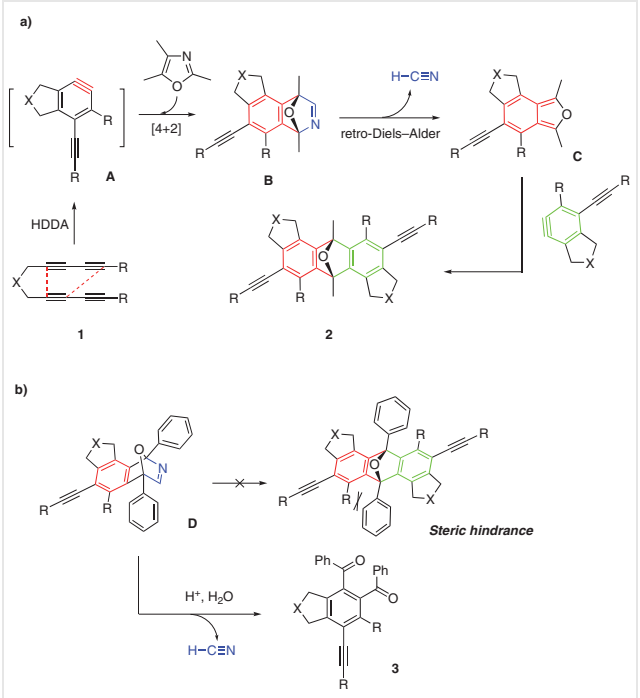
Scheme 1 Preparation of epoxyanthracene derivatives **3a–s**. *Reagents and conditions*: **1** (2.1 equiv, 2.1 mmol), oxazole **2** (1.0 equiv, 1.0 mmol), 100 °C, toluene (5 mL), 10 h. Isolated yields by column chromatography are shown.



Scheme 2 Preparation of dicarbonylated arene derivatives **4t–z**. *Reagents and conditions*: **1** (1.0 equiv, 1.0 mmol), oxazole **2** (1.2 equiv, 1.2 mmol), 105 °C, toluene (5 mL), 8 h. Isolated yields by column chromatography are shown.

substrate with 2,4,5-trimethyloxazole as an example (Scheme 3a). First, tetrayne substrate **1** formed the benzyne intermediate **A** through the HDDA reaction. Next, the benzyne intermediate **A** underwent an aza [4 + 2] cycloaddition reaction with oxazole substrate to form the intermediate **B**. Subsequently, a retro-Diels–Alder reaction occurred and a molecule of HCN was removed to form the isobenzofuran intermediate **C**. Then the intermediate **C** with a second molecule benzyne intermediate **A** was subjected to another [4+2] cycloaddition with isobenzofuran to finally obtain the epoxyanthracene derivative **2**.

When tetrayne substrates were tried with 2,4-diphenyloxazole in this reaction, the synthesized intermediate **A** formed intermediate **D** (Scheme 3) via an aza [4+2] cycloaddition reaction with 2,4-diphenyloxazole. However, the results showed that adduct **2** with two molecules of benzyne could not be obtained, and the derivative **3** can only be formed by the carbonylation on the benzene ring. This result might be due to steric hindrance enforced by the benzene ring on the 2,4-diphenyloxazole and thus it is unfavorable to form above epoxyanthracene derivative. Considering a previous report,[17] oxidation may be involved in the reaction, and product of dicarbonylation was finally achieved.



Scheme 3 Possible mechanism between HDDA-derived benzyne and oxazole

In summary, we have reported a capture reaction of HDDA-derived benzyne with various substituted oxazoles. When the substituent at 2-position of oxazole was methyl or hydrogen, we obtained epoxyanthracene derivatives. Different from the traditional benzyne reaction, we obtained the dicarbonylation arene when the substituent at 2-position of oxazole was changed to phenyl. This reaction does not require any catalyst or additive and provides a new method for the synthesis of polycyclic compounds and dicarbonylation on benzene ring. Our team will continue to explore its application potential in organic synthesis.

All the catalytic reactions were performed under an argon atmosphere using the oven-dried Schlenk flask. The chemicals were purchased from Alfa Aesar, TCI, and Acros Chemicals. All solvents and materials were pre-dried, redistilled, or recrystallized before use. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra were recorded on a Bruker Avance 400 spectrometer with $CDCl_3$ as the solvent. ^{1}H NMR (500 MHz) spectra were recorded on a Bruker Avance 500 spectrometer in $CDCl_3$. Chemical shifts are reported in ppm by assigning TMS resonance in the ^{1}H NMR spectra as 0.00 ppm, $CDCl_3$ resonance in the

^{13}C spectra as 77.0 ppm. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (standard abbreviations), coupling constant (Hz), and integration. Data for ^{13}C NMR are recorded with broad-band proton decoupling technique and are reported in terms of chemical shift. Column chromatography was performed on silica gel 300–400 mesh. TLC was performed on silica gel plates (HSGF 254). Melting points were determined using a Gallenkamp melting point apparatus and are uncorrected. IR spectra were recorded on a Jasco ATR MIRacle spectrophotometer. Samples were scanned in the 400–4000 cm^{-1} region with KBr pellet. All HRMS spectra were obtained on a Bruker Apex IV RTMS. X-ray Crystallography diffraction data of **3l**, **4t**, and **4y** were collected at rt with a Bruker SMART Apex CCD diffractometer with Mo-Kα 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 F^2 by full-matrix least squares using SHELXTL. All non-hydrogen atoms were treated anisotropically. The positions of hydrogen atoms were generated geometrically.

Cycloadditon Reactions of HDDA-Derived Benzynes with Oxazoles; General Procedure

Tetrayne **1** (2.1 and 1.0 equiv), substituted oxazole **2** (1.0 and 1.2 equiv), and toluene (5 mL) were mixed in an oven-dried Schlenk tube (50 mL) equipped with a magnetic stir bar and heated in an oil bath at 100–105 °C for 8–10 h under air. The reaction mixture was cooled to rt, and the solvent was evaporated in vacuo. After preparative TLC on silica gel with an appropriate mixture of PE and EtOAc, epoxyanthracene derivatives and dicarbonyl arene were separated and purified by column chromatography on silica gel with EtOAc/PE (1:60–20) as eluent.

(6*S*,12*S*)-5,11-Dibutyl-4,10-di(hex-1-yn-1-yl)-6,12-dimethyl-2,8-ditosyl-1,2,3,6,7,8,9,12-octahydro-6,12-epoxybenzo[1,2-*e*:4,5-*e*′]diisoindole (3a)

White solid; yield: 761.1 mg (86%); mp 196.3–198.3 °C; R_f = 0.18 (PE/EtOAc 8:1).

FT-IR (KBr): 3447, 2956, 2928, 2872, 2861, 2354, 2225, 1600, 1465, 1334, 1162, 674 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 8.0 Hz, 4 H), 7.27 (d, *J* = 8.0 Hz, 4 H), 4.77 (d, *J* = 12.0 Hz, 2 H), 4.58 (d, *J* = 12.0 Hz, 2 H), 4.47 (t, *J* = 16.0 Hz, 4 H), 2.83–2.75 (m, 2 H), 2.70–2.62 (m, 2 H), 2.43 (t, *J* = 6.0 Hz, 4 H), 2.38 (s, 6 H), 2.07 (s, 6 H), 1.60–1.53 (m, 4 H), 1.51–1.42 (m, 12 H), 1.01–0.94 (m, 12 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 147.6, 144.7, 143.8, 138.8, 137.3, 133.6, 129.8, 127.4, 124.9, 117.4, 98.7, 87.3, 77.2, 75.9, 53.6, 52.3, 33.8, 30.8, 30.1, 23.2, 21.9, 21.5, 19.3, 17.5, 13.9, 13.6.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{54}H_{64}N_2O_5S_2$: 885.4329; found: 885.4334.

Tetramethyl (6*R*,12*R*)-6,12-Dimethyl-5,11-diphenyl-4,10-bis(phenylethynyl)-1,3,6,7,9,12-hexahydro-6,12-epoxydicyclopenta[*a*,*h*]anthracene-2,2,8,8-tetracarboxylate (3b)

White solid; yield: 655.8 mg (74%); mp 263.7–265.7 °C; R_f = 0.10 (PE/EtOAc 8:1).

FT-IR (KBr): 2358, 2333, 1738, 1248, 1196, 1061, 752, 689 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60–7.57 (m, 2 H, ArH), 7.56–7.53 (m, 2 H, ArH), 7.51–7.48 (m, 4 H, ArH), 7.23–7.21 (m, 6 H, ArH), 7.18 (d, *J* = 8.0 Hz, 2 H, ArH), 7.13–7.11 (m, 4 H, ArH), 3.87 [d, *J* = 12.0 Hz, 2 H, $C(CO_2Me)_2CH_2$], 3.83 [s, 6 H, $C(CO_2CH_3)_2$], 3.82 [s, 6 H, $C(CO_2CH_3)_2$], 3.75 [d, *J* = 4.0 Hz, 4 H, 2 × $C(CO_2Me)_2CH_2$], 3.54 [d, *J* = 16.0 Hz, 2 H, $C(CO_2Me)_2CH_2$], 1.43 (s, 6 H, 2 × $OCCH_3$).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.9, 171.8, 148.3, 145.7, 142.4, 138.2, 136.5, 131.4, 130.4, 130.3, 129.8, 128.1, 128.0, 127.9, 127.8, 127.7, 123.3, 117.1, 96.2, 87.5, 86.9, 77.2, 60.1, 53.2, 53.2, 40.4, 38.7, 16.8.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{58}H_{46}O_9$: 887.3215; found: 887.3219.

Tetramethyl (6*R*,12*R*)-6,12-Dimethyl-5,11-di-*p*-tolyl-4,10-bis(*p*-tolylethynyl)-1,3,6,7,9,12-hexahydro-6,12-epoxydicyclopenta[*a*,*h*]anthracene-2,2,8,8-tetracarboxylate (3c)

White solid; yield: 753.4 mg (80%); mp 279.6–281.6 °C; R_f = 0.13 (PE/EtOAc 8:1).

FT-IR (KBr): 2949, 2361, 2339, 1733, 1508, 1439, 1248, 1207, 1160, 816 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.41 (m, 2 H, ArH), 7.35 (d, *J* = 8.0 Hz, 2 H, ArH), 7.29 (d, *J* = 8.0 Hz, 2 H, ArH), 7.04 (s, 8 H, ArH), 7.02–7.03 (m, 2 H, ArH), 3.88 [d, *J* = 16.0 Hz, 2 H, $C(CO_2Me)_2CH_2$], 3.83 [s, 6 H, $C(CO_2CH_3)_2$], 3.82 [s, 6 H, $C(CO_2CH_3)_2$], 3.73 [dd, *J* = 28.0, 20.0 Hz, 4 H, 2 × $C(CO_2Me)_2CH_2$], 3.57 [d, *J* = 16.0 Hz, 2 H, $C(CO_2Me)_2CH_2$], 2.49 (s, 6 H, 2 × $ArCH_3$), 2.31 (s, 6 H, 2 × $ArCH_3$), 1.45 (s, 6 H, 2 × $OCCH_3$).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.6, 171.5, 148.3, 145.6, 142.4, 138.1, 137.2, 136.4, 135.3, 131.3, 130.4, 130.2, 129.9, 128.9, 128.5, 128.3, 120.5, 117.4, 96.2, 87.5, 86.9, 77.3, 61.9, 60.2, 40.4, 38.7, 21.5, 16.9, 14.2, 14.1.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{62}H_{54}O_9$: 943.3841; found: 943.3848.

Tetramethyl (6*R*,12*R*)-5,11-Bis(4-ethylphenyl)-4,10-bis[(4-ethylphenyl)ethynyl]-6,12-dimethyl-1,3,6,7,9,12-hexahydro-6,12-epoxydicyclopenta[*a*,*h*]anthracene-2,2,8,8-tetracarboxylate (3d)

White solid; yield: 758.4 mg (76%); mp 254.5–256.5 °C; R_f = 0.19 (PE/EtOAc 8:1).

FT-IR (KBr): 2968, 2358, 2333, 1733, 1516, 1426, 1246, 1196, 1168, 831 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 (dd, *J* = 8.0, 4.0 Hz, 2 H, ArH), 7.34 (q, *J* = 8.0 Hz, 4 H, ArH), 7.08–7.01 (m, 10 H, ArH), 3.88–3.82 [d, *J* = 24.0 Hz, 2 H, $C(CO_2Me)_2CH_2$], 3.83 [s, 6 H, $C(CO_2CH_3)_2$], 3.82 (s, 6 H, $C(CO_2CH_3)_2$], 3.73 [dd, *J* = 28.0, 16.0 Hz, 4 H, 2 × $C(CO_2Me)_2CH_2$], 3.57 [d, *J* = 16.0 Hz, 2 H, $C(CO_2Me)_2CH_2$], 2.80 (q, *J* = 8.0 Hz, 4 H, 2 × $ArCH_2$), 2.60 (q, *J* = 6.7 Hz, 4 H, 2 × $ArCH_2$), 1.45 (s, 6 H, 2 × $OCCH_3$), 1.36 (t, *J* = 8.0 Hz, 6 H, 2 × CH_3), 0.75 (t, *J* = 8.0 Hz, 6 H, 2 × CH_3).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.9, 148.3, 145.5, 144.4, 143.8, 141.9, 136.6, 135.5, 131.4, 130.3, 130.2, 129.7, 127.7, 127.2, 127.1, 120.6, 117.5, 96.4, 87.5, 86.7, 77.2, 60.1, 53.2, 53.2, 40.5, 38.7, 28.9, 28.8, 16.9, 16.0, 15.4.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{66}H_{62}O_9$: 999.4467; found: 999.4462.

Tetramethyl (6*R*,12*R*)-6,12-Dimethyl-5,11-bis(4-propylphenyl)-4,10-bis[(4-propylphenyl)ethynyl]-1,3,6,7,9,12-hexahydro-6,12-epoxydicyclopenta[*a*,*h*]anthracene-2,2,8,8-tetracarboxylate (3e)

White solid; yield: 864.0 mg (82%); mp 239.3–241.3 °C; R_f = 0.24 (PE/EtOAc 8:1).

FT-IR (KBr): 2949, 2923, 2863, 2371, 2335, 1723, 1506, 1437, 1252, 1201, 1166 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (dd, *J* = 8.0, 4.0 Hz, 2 H, ArH), 7.34 (d, *J* = 8.0 Hz, 2 H, ArH), 7.30 (d, *J* = 8.0 Hz, 2 H, ArH), 7.06 (d, *J* = 8.0 Hz, 2 H, ArH), 7.02 (s, 8 H, ArH), 3.84 [d, *J* = 24.0 Hz, 2 H, $C(CO_2Me)_2CH_2$], 3.83 [s, 6 H, $C(CO_2CH_3)_2$], 3.81 [s, 6 H, $C(CO_2CH_3)_2$], 3.73 [dd, *J* = 24.0, 16.0 Hz, 4 H, 2 × $C(CO_2Me)_2CH_2$], 3.55 (d, *J* = 16.0 Hz, 2 H, CH_2), 2.76–2.71 (m, 4 H, 2 × CH_2), 2.53 (m, 4 H, 2 × CH_2), 1.81–1.72 (m, 4 H, 2 × CH_2), 1.61–1.58 (m, 4 H, 2 × CH_2), 1.44 (s, 6 H, 2 × $OCCH_3$), 1.02 (t, *J* = 8.0 Hz, 6 H, 2 × CH_3), 0.90 (t, *J* = 8.0 Hz, 6 H, 2 × CH_3).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.9, 148.3, 145.5, 142.9, 142.1, 141.9, 136.6, 135.6, 131.3, 130.2, 129.6, 128.3, 127.9, 127.8, 120.6, 117.5, 96.4, 87.5, 86.7, 77.2, 60.1, 53.2, 53.2, 40.5, 38.7, 37.9, 24.7, 24.4, 16.8, 13.8, 13.7.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{70}H_{70}O_9$: 1055.5093; found: 1055.5084.

Tetramethyl (6*R*,12*R*)-5,11-Bis(4-fluorophenyl)-4,10-bis[(4-fluorophenyl)ethynyl]-6,12-dimethyl-1,3,6,7,9,12-hexahydro-6,12-epoxydicyclopenta[*a*,*h*]anthracene-2,2,8,8-tetracarboxylate (3f)

White solid; yield: 728.1 mg (76%); mp 270.5–272.5 °C; R_f = 0.14 (PE/EtOAc 8:1).

FT-IR (KBr): 2951, 2365, 2341, 1740, 1510, 1435, 1216, 1156, 1095, 836, 730 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52–7.48 (m, 2 H, ArH), 7.35–7.30 (m, 2 H, ArH), 7.23–7.18 (m, 4 H, ArH), 7.14–7.11 (m, 4 H, ArH), 6.97–6.93 (m, 4 H, ArH), 3.84 [d, *J* = 8.0 Hz, 2 H, $C(CO_2Me)_2CH_2$], 3.83 [s, 6 H, $C(CO_2CH_3)_2$], 3.81 [s, 6 H, $C(CO_2CH_3)_2$], 3.73 [dd, *J* = 36.0, 20 Hz, 4 H, $C(CO_2Me)_2CH_2$], 3.47 [d, *J* = 16.0 Hz, 2 H, $C(CO_2Me)_2CH_2$], 1.44 (s, 6 H, 2 × $OCCH_3$).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.9, 171.6, 163.9, 163.7, 161.4, 161.2, 148.6, 145.6, 142.4, 135.4, 134.1 (d, *J* = 4.0 Hz), 133.2 (d, *J* = 8.1 Hz), 131.9 (d, *J* = 8.1 Hz), 131.6 (d, *J* = 8.1 Hz), 131.6, 130.6, 119.2, 119.2, 117.2, 115.6, 115.4, 115.1, 114.9 (d, *J* = 3.0 Hz), 114.6, 95.4, 87.4, 86.3, 77.2, 60.0, 53.3, 40.4, 38.7, 16.8.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{58}H_{42}F_4O_9$: 959.2838; found: 959.2844.

Tetraethyl (6*R*,12*R*)-6,12-Dimethyl-5,11-diphenyl-4,10-bis(phenylethynyl)-1,3,6,7,9,12-hexahydro-6,12-epoxydicyclopenta[*a*,*h*]-anthracene-2,2,8,8-tetracarboxylate (3g)

White solid; yield: 753.4 mg (80%); mp 241.2–243.2 °C; R_f = 0.15 (PE/EtOAc 8:1).

FT-IR (KBr): 2984, 2938, 2348, 2341, 1736, 1252, 1181, 1151, 1098, 758 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59–7.53 (m, 4 H, ArH), 7.50–7.48 (m, 4 H, ArH), 7.23–7.21 (m, 8 H, ArH), 7.13–7.11 (m, 4 H, ArH), 4.31–4.24 [m, 8 H, 2 × $C(CO_2CH_2CH_3)_2$], 3.83 [d, *J* = 16.0 Hz, 2 H, $C(CO_2Et)_2CH_2$], 3.73 [d, *J* = 4.0 Hz, 4 H, 2 × $C(CO_2Et)_2CH_2$], 3.54 [d, *J* = 16.0 Hz, 2 H, $C(CO_2Et)_2CH_2$], 1.44 (s, 6 H, 2 × $OCCH_3$), 1.34–1.29 [m, 12 H, 2 × $C(CO_2CH_2CH_3)_2$].

^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.5, 171.4, 148.2, 145.7, 142.5, 138.2, 136.5, 131.3, 130.6, 130.3, 129.9, 128.1, 127.9, 127.7, 127.6, 123.4, 117.1, 96.1, 87.5, 87.1, 77.2, 61.9, 61.9, 60.1, 40.3, 38.6, 16.8, 14.1, 14.1.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{62}H_{54}O_9$: 943.3841; found: 943.3842.

Tetraethyl (6*R*,12*R*)-6,12-Dimethyl-5,11-di-*p*-tolyl-4,10-bis(*p*-tolylethynyl)-1,3,6,7,9,12-hexahydro-6,12-epoxydicyclopenta[*a*,*h*]-anthracene-2,2,8,8-tetracarboxylate (3h)

White solid; yield: 758.2 mg (76%); mp 236.1–238.1 °C; R_f = 0.11 (PE/EtOAc 8:1).

FT-IR (KBr): 2953, 2926, 2361, 1757, 1527, 1435, 1246, 1220, 1160, 812 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (dd, *J* = 8.0, 4.0 Hz, 2 H, ArH), 7.33 (d, *J* = 8.0 Hz, 2 H, ArH), 7.29 (d, *J* = 8.0 Hz, 2 H, ArH), 7.06 (dd, *J* = 8.0, 4.0 Hz, 2 H, ArH), 7.04 (s, 8 H, ArH), 4.31–4.24 [m, 8 H, 2 × $C(CO_2CH_2CH_3)_2$], 3.82 [d, *J* = 16.0 Hz, 2 H, $C(CO_2Et)_2CH_2$], 3.71 [d, *J* = 4.0 Hz, 4 H, $C(CO_2Et)_2CH_2$], 3.58 [d, *J* = 16.0 Hz, 2 H, $C(CO_2Et)_2CH_2$], 2.48 (s, 6 H, 2 × $ArCH_3$), 2.31 (s, 6 H, 2 × $ArCH_3$), 1.45 (s, 6 H, 2 × $OCCH_3$), 1.34–1.29 [m, 12 H, 2 × $C(CO_2CH_2CH_3)_2$].

^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.0, 148.4, 145.5, 142.2, 138.1, 137.3, 136.4, 135.2, 131.3, 130.2, 129.7, 128.9, 128.4, 120.4, 117.5, 96.3, 87.5, 86.6, 77.2, 60.4, 60.1, 53.2, 53.2, 40.5, 38.8, 21.5, 16.8, 14.2.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{66}H_{62}O_9$: 999.4467; found: 999.4462.

Tetraethyl (6*R*,12*R*)-5,11-Bis(4-ethylphenyl)-4,10-bis[(4-ethylphenyl)ethynyl]-6,12-dimethyl-1,3,6,7,9,12-hexahydro-6,12-epoxydicyclopenta[*a*,*h*]anthracene-2,2,8,8-tetracarboxylate (3i)

White solid; yield: 864.2 mg (82%); mp 223.5–225.5 °C; R_f = 0.23 (PE/EtOAc 8:1).

FT-IR (KBr): 2973, 2926, 2870, 2363, 2341, 1736, 1512, 1252, 1190, 1061, 829 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 (dd, *J* = 8.0, 4.0 Hz, 2 H, ArH), 7.33 (q, *J* = 6.7 Hz, 4 H, ArH), 7.09 (dd, *J* = 8.0, 4.0 Hz, 2 H, ArH), 7.04 (dd, *J* = 12.0, 8.0 Hz, 8 H, ArH), 4.31–4.23 [m, 8 H, 2 × $C(CO_2CH_2CH_3)_2$], 3.80 [d, *J* = 20.0 Hz, 2 H, $C(CO_2Et)_2CH_2$], 3.71 [d, *J* = 4.0 Hz, 4 H, 2 × $C(CO_2Et)_2CH_2$], 3.57 [d, 2 H, *J* = 16 Hz, $C(CO_2Et)_2CH_2$], 2.79 (q, *J* = 8.0 Hz, 4 H, 2 × $ArCH_2$), 2.59 (q, *J* = 8.0 Hz, 4 H, 2 × $ArCH_2$), 1.46 (s, 6 H, 2 × $OCCH_3$), 1.37–1.29 [m, 18 H, 2 × $C(CO_2CH_2CH_3)_2$ + 2 × $ArCH_2CH_3$], 1.19 (d, *J* = 8.0 Hz, 6 H, 2 × $ArCH_2CH_3$).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.6, 171.5, 148.2, 145.6, 144.4, 143.7, 142.2, 136.5, 135.6, 131.4, 130.4, 130.3, 129.9, 127.6, 127.3, 127.1, 120.7, 117.5, 96.3, 87.5, 86.7, 77.2, 61.9, 60.2, 40.3, 38.6, 28.9, 28.8, 16.9, 15.9, 15.4, 14.2, 14.1.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{70}H_{70}O_9$: 1055.5093; found: 1055.5090.

Tetraethyl (6*R*,12*R*)-6,12-Dimethyl-5,11-bis(4-propylphenyl)-4,10-bis[(4-propylphenyl)ethynyl]-1,3,6,7,9,12-hexahydro-6,12-epoxydicyclopenta[*a*,*h*]anthracene-2,2,8,8-tetracarboxylate (3j)

White solid; yield: 887.6 mg (80%); mp 178.9–180.9 °C; R_f = 0.30 (PE/EtOAc 8:1).

FT-IR (KBr): 2964, 2932, 2880, 1736, 1514, 1252, 1190, 1194, 1063, 857 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (dd, *J* = 8.0, 4.0 Hz, 2 H, ArH), 7.33 (d, *J* = 8.0 Hz, 2 H, ArH), 7.29 (d, *J* = 8.0 Hz, 2 H, ArH), 7.09 (dd, *J* = 4.0, 4.0 Hz, 2 H, ArH), 7.02 (s, 8 H, ArH), 4.31–4.23 [m, 8 H, $C(CO_2CH_2CH_3)_2$], 3.80 [d, *J* = 20.0 Hz, 2 H, $C(CO_2Et)_2CH_2$], 3.72 [s, 4 H, 2 × $C(CO_2Et)_2CH_2$], 3.55 [d, *J* = 16.0 Hz, 2 H, $C(CO_2Et)_2CH_2$], 2.73 (t, *J* = 8.0 Hz, 4 H, $ArCH_2$), 2.53 (t, *J* = 8.0 Hz, 4 H, $ArCH_2$), 1.80–1.71 (m, 4 H, CH_2), 1.63–1.56 (m, 4 H, CH_2), 1.44 (s, 6 H, 2 × $OCCH_3$), 1.31 [q, *J* = 8.0 Hz, 12 H, 2 × $C(CO_2CH_2CH_3)_2$], 1.01 (t, *J* = 6.0 Hz, 6 H, 2 × CH_2CH_3), 0.90 (t, *J* = 8.0 Hz, 6 H, 2 × CH_2CH_3).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.5, 171.5, 148.2, 145.5, 142.8, 142.2, 141.9, 136.6, 135.6, 131.3, 130.4, 130.2, 129.8, 128.3, 127.9, 127.7, 120.7, 117.4, 96.3, 87.5, 86.7, 77.2, 61.9, 61.9, 60.2, 40.3, 38.6, 37.9, 24.7, 24.4, 16.8, 14.1, 14.1, 13.7.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{74}H_{78}O_9$: 1111.5719; found: 1111.5711.

Tetraethyl (6*R*,12*R*)-5,11-Bis(4-chlorophenyl)-4,10-bis[(4-chlorophenyl)ethynyl]-6,12-dimethyl-1,3,6,7,9,12-hexahydro-6,12-epoxydicyclopenta[*a*,*h*]anthracene-2,2,8,8-tetracarboxylate (3k)

White solid; yield: 775.2 mg (72%); mp 109.6–111.6 °C; R_f = 0.27 (PE/EtOAc 8:1).

FT-IR (KBr): 2960, 2932, 2872, 1738, 1514, 1489, 1452, 1364, 1248, 1186, 1251, 1186 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (dd, *J* = 8.0 Hz, 2 H, ArH), 7.50–7.44 (m, 4 H, ArH), 7.23 (d, *J* = 8.0 Hz, 4 H, ArH), 7.20 (dd, *J* = 8.0, 4.0 Hz, 2 H, ArH), 7.05 (d, *J* = 12 Hz, 4 H, ArH), 4.33–4.21 [m, 8 H, 2 × $C(CO_2CH_2CH_3)_2$], 3.78 [dd, *J* = 16.0, 4.0 Hz, 4 H, 2 × $C(CO_2Et)_2CH_2$], 3.65 [d, *J* = 16.0 Hz, 2 H, $C(CO_2Et)_2CH_2$], 3.48 [d, *J* = 16.0 Hz, 2 H, $C(CO_2Et)_2CH_2$], 1.47 (s, 6 H, 2 × $OCCH_3$), 1.34–1.30 [m, 12 H, 2 × $C(CO_2CH_2CH_3)_2$].

^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.4, 171.2, 148.4, 145.8, 142.9, 136.6, 135.2, 134.3, 133.9, 132.5, 131.6, 131.5, 130.9, 128.6, 128.3, 127.9, 121.6, 116.9, 95.4, 87.6, 87.4, 77.2, 62.1, 60.1, 40.3, 38.6, 16.9, 14.1, 14.1.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{62}H_{50}Cl_4O_9$: 1079.2282; found: 1079.2291.

Tetraisopropyl (6*R*,12*R*)-6,12-Dimethyl-5,11-diphenyl-4,10-bis(phenylethynyl)-1,3,6,7,9,12-hexahydro-6,12-epoxydicyclopenta[*a*,*h*]anthracene-2,2,8,8-tetracarboxylate (3l)

White solid; yield: 798.2 mg (80%); mp 253.7–255.7 °C; R_f = 0.23 (PE/EtOAc 8:1).

FT-IR (KBr): 2966, 2917, 2865, 1740, 1495, 1267, 1181, 1085, 964, 803 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.59–7.54 (m, 4 H, ArH), 7.52–7.48 (m, 4 H, ArH), 7.24–7.22 (m, 8 H, ArH), 7.12–7.10 (m, 4 H, ArH), 5.13–5.06 {m, 4 H, 2 × $C[CO_2CH(CH_3)_2]_2$}, 3.77 [dd, *J* = 10.0, 5.0 Hz, 4 H, 2 × $C(CO_2{}^i Pr)_2CH_2$], 3.64 [d, *J* = 15.0 Hz, 2 H, $C(CO_2{}^i Pr)_2CH_2$], 3.51 [d, *J* = 20.0 Hz, 2 H, $C(CO_2{}^i Pr)_2CH_2$], 1.45 (s, 6 H, 2 × $OCCH_3$), 1.33–1.27 {m, 24 H, 2 × $C[CO_2CH(CH_3)_2]_2$}.

^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.9, 148.1, 145.7, 142.6, 138.3, 136.4, 131.3, 130.7, 130.3, 130.1, 128.1, 127.9, 127.7, 127.5, 123.4, 117.1, 96.0, 87.5, 87.1, 69.4, 60.2, 40.2, 38.4, 21.6, 21.6, 21.5, 16.8.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{66}H_{62}O_9$: 999.4467; found: 999.4460.

Tetraisopropyl (6*R*,12*R*)-6,12-Dimethyl-5,11-di-*p*-tolyl-4,10-bis-(*p*-tolylethynyl)-1,3,6,7,9,12-hexahydro-6,12-epoxydicyclopenta-[*a*,*h*]anthracene-2,2,8,8-tetracarboxylate (3m)

White solid; yield: 842.4 mg (80%); mp 251.6–253.6 °C; R_f = 0.24 (PE/EtOAc 8:1).

FT-IR (KBr): 2981, 2936, 2878, 1903, 1731, 1516, 1383, 1259, 1108, 814, 672 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 8.0 Hz, 2 H, ArH), 7.33 (d, *J* = 8.0 Hz, 2 H, ArH), 7.28 (d, *J* = 8.0 Hz, 2 H, ArH), 7.10 (d, *J* = 8.0 Hz, 2 H, ArH), 7.03 (s, 8 H, ArH), 5.14–5.04 {m, 4 H, 2 × $C[CO_2CH(CH_3)_2]_2$}, 3.77–3.53 [m, 8 H, 4 × $C(CO_2{}^i Pr)_2CH_2$], 2.47 (s, 6 H, 2 × $ArCH_3$), 2.31 (s, 6 H, 2 × $ArCH_3$), 1.45 (s, 6 H, 2 × $OCCH_3$), 1.33–1.26 {m, 24 H, 2 × $C[CO_2CH(CH_3)_2]_2$}.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.1, 171.0, 148.2, 145.6, 142.5, 137.9, 137.1, 136.3, 135.3, 131.2, 130.5, 130.2, 130.0, 128.8, 128.4, 128.2, 120.5, 117.3, 96.0, 87.5, 86.7, 77.2, 69.4, 69.3, 60.2, 40.2, 38.5, 21.6, 21.6, 21.6, 21.5, 21.5, 16.9.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{70}H_{70}O_9$: 1055.5093; found: 1055.5091.

Tetraisopropyl (6*R*,12*R*)-5,11-Bis(4-ethylphenyl)-4,10-bis[(4-ethylphenyl)ethynyl]-6,12-dimethyl-1,3,6,7,9,12-hexahydro-6,12-epoxydicyclopenta[*a*,*h*]anthracene-2,2,8,8-tetracarboxylate (3n)

White solid; yield: 843.0 mg (76%); mp 262.4–264.4 °C; R_f = 0.30 (PE/EtOAc 8:1).

FT-IR (KBr): 2975, 2932, 2872, 1733, 1512, 1278, 1246, 1192, 1100, 829 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 (d, *J* = 8.0 Hz, 2 H, ArH), 7.36 (d, *J* = 8.0 Hz, 2 H, ArH), 7.31 (d, *J* = 8.0 Hz, 2 H, ArH), 7.15 (d, *J* = 8.0 Hz, 2 H, ArH), 7.04 (dd, *J* = 12.0, 8.0 Hz, 8 H, ArH), 5.14–5.05 {m, 4 H, 2 × $C[CO_2CH(CH_3)_2]_2$}, 3.76–3.51 [m, 8 H, 4 × $C(CO_2{}^i Pr)_2CH_2$], 2.78 (q, *J* = 8.0 Hz, 4 H, 2 × $ArCH_2$), 2.60 (q, *J* = 6.7 Hz, 4 H, 2 × $ArCH_2$), 1.46 (s, 6 H, 2 × $OCCH_3$), 1.37–1.26 {m, 30 H, 2 × $C[CO_2CH(CH_3)_2]_2$ + 2 × CH_3}, 1.19 (t, *J* = 8.0 Hz, 6 H, 2 × CH_3).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.0, 171.0, 148.1, 145.6, 144.3, 143.6, 142.2, 136.5, 135.6, 131.3, 130.5, 130.3, 130.1, 127.6, 127.2, 127.0, 120.8, 117.4, 96.1, 87.5, 86.8, 77.2, 69.3, 69.3, 60.2, 40.2, 38.4, 28.9, 28.8, 21.6, 21.6, 16.9, 15.9, 15.4.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{74}H_{78}O_9$: 1111.5719; found: 1111.5715.

Tetraisopropyl (6*R*,12*R*)-6,12-Dimethyl-5,11-bis(4-propylphenyl)-4,10-bis[(4-propylphenyl)ethynyl]-1,3,6,7,9,12-hexahydro-6,12-epoxydicyclopenta[*a*,*h*]anthracene-2,2,8,8-tetracarboxylate (3o)

White solid; yield: 956.9 mg (82%); mp 185.8–187.8 °C; R_f = 0.38 (PE/EtOAc 8:1).

FT-IR (KBr): 2981, 2943, 2874, 1731, 1508, 1373, 1257, 1186, 1113, 1063, 823 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (dd, *J* = 8.0, 4.0 Hz, 2 H, ArH), 7.34 (d, *J* = 8.0 Hz, 2 H, ArH), 7.29 (d, *J* = 8.0 Hz, 2 H, ArH), 7.15 (dd, *J* = 8.0, 4.0 Hz, 2 H, ArH), 7.02 (s, 8 H, ArH), 5.14–5.05 {m, 4 H, 2 × $C[CO_2CH(CH_3)_2]_2$}, 3.75 [dd, *J* = 16.0, 4.0 Hz, 4 H, 2 × $C(CO_2{}^i Pr)_2CH_2$], 3.64 [d, *J* = 20.0 Hz, 2 H, $C(CO_2{}^i Pr)_2CH_2$], 3.50 [d, *J* = 16.0 Hz, 2 H, $C(CO_2{}^i Pr)_2CH_2$], 2.72 (t, *J* = 8.0 Hz, 4 H, 2 × $ArCH_2$), 2.53 (t, *J* = 8.0 Hz, 4 H, 2 × $ArCH_2$), 1.80–1.71 (m, 4 H, 2 × CH_2), 1.61–1.56 (m, 4 H, 2 × CH_2), 1.44 (s, 6 H, 2 × $OCCH_3$), 1.33–1.26 {m, 24 H, 2 × $C[CO_2CH(CH_3)_2]_2$}, 1.01 (t, *J* = 6.0 Hz, 6 H, 2 × CH_2CH_3), 0.90 (t, *J* = 8.0 Hz, 6 H, 2 × CH_2CH_3).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.0, 170.9, 148.1, 145.5, 142.8, 142.2, 141.9, 136.5, 135.6, 131.2, 130.5, 130.1, 129.9, 128.2, 127.9, 127.7, 120.8, 117.4, 96.1, 87.5, 86.8, 77.2, 69.3, 60.2, 40.1, 38.4, 37.9, 37.9, 24.7, 24.4, 21.6, 21.6, 16.8, 13.7, 13.7.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{78}H_{86}O_9$: 1167.6345; found: 1167.6352.

Tetraisopropyl (6*R*,12*R*)-5,11-Bis(4-fluorophenyl)-4,10-bis[(4-fluorophenyl)ethynyl]-6,12-dimethyl-1,3,6,7,9,12-hexahydro-6,12-epoxydicyclopenta[*a*,*h*]anthracene-2,2,8,8-tetracarboxylate (3p)

White solid; yield: 790.4 mg (74%); mp 95.8–97.8 °C; R_f = 0.25 (PE/EtOAc 8:1).

FT-IR (KBr): 3426, 2975, 2926, 2848, 1787, 1727, 1504, 1251, 1261, 1072, 962 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.52–7.48 (m, 2 H, ArH), 7.32–7.26 (m, 4 H, ArH), 7.22–7.18 (m, 2 H, ArH), 7.13–7.09 (m, 4 H, ArH), 6.96–6.92 (m, 4 H, ArH), 5.12–5.05 {m, 4 H, 2 × C[$CO_2CH(CH_3)_2]_2$}, 3.77 [q, *J* = 8.0 Hz, 4 H, 2 × C($CO_2^iPr)_2CH_2$], 3.57 [d, *J* = 16.0 Hz, 2 H, C($CO_2^iPr)_2CH_2$], 3.43 [d, *J* = 16.0 Hz, 2 H, C($CO_2^iPr)_2CH_2$], 1.45 (s, 6 H, 2 × $OCCH_3$), 1.32–1.25 {m, 24 H, 2 × C[$CO_2CH(CH_3)_2]_2$}.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.9, 170.8, 148.5, 145.6, 142.8, 135.3, 134.2 (d, *J* = 3.0 Hz), 133.2, 133.1, 131.9 (dd, *J* = 8.1, 6.1 Hz), 130.9, 119.3, 117.2, 115.7, 115.4, 115.1, 114.8 (d, *J* = 8.1 Hz), 114.6, 95.2, 87.4, 86.5, 77.2, 69.6 (d, *J* = 7.1 Hz), 60.2, 40.2, 38.5, 21.6 (q, *J* = 2.0 Hz), 16.9, 14.1.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{66}H_{58}F_4O_9$: 1071.4090; found: 1071.4088.

Tetramethyl (6*R*,12*R*)-5,11-Bis(4-fluorophenyl)-4,10-bis[(4-fluorophenyl)ethynyl]-1,3,6,7,9,12-hexahydro-6,12-epoxydicyclopenta-[*a*,*h*]anthracene-2,2,8,8-tetracarboxylate (3q)

White solid; yield: 669.1 mg (72%); mp 162.2–164.2 °C; R_f = 0.06 (PE/EtOAc 8:1).

FT-IR (KBr): 3432, 2745, 1733, 1605, 1510, 1435, 1284, 1222, 829, 526 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.46 (dd, *J* = 4.0, 4.0 Hz, 4 H, ArH), 7.29–7.20 (m, 8 H, ArH), 6.97 (t, *J* = 8.0 Hz, 4 H, ArH), 5.83 (s, 2 H, 2 × OCH), 3.82 [d, *J* = 8.0 Hz, 2 H, C($CO_2Me)_2CH_2$], 3.81 [s, 6 H, 2 × C($CO_2CH_3)_2$], 3.79 [s, 6 H, 2 × C($CO_2CH_3)_2$], 3.67 [dd, *J* = 20.0, 16.0 Hz, 4 H, C($CO_2Me)_2CH_2$], 3.49 [d, *J* = 16.0 Hz, 2 H, C($CO_2Me)_2CH_2$].

^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.7, 171.5, 163.9, 163.8, 161.4, 161.3, 145.9, 142.7, 142.4, 133.3 (d, *J* = 8.1 Hz), 131.5 (d, *J* = 8.1 Hz), 131.3, 116.2, 115.7, 115.5, 115.3, 115.0, 95.1, 81.1, 77.2, 60.1, 53.3 (d, *J* = 1.0 Hz), 40.8, 38.9.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{56}H_{38}F_4O_9$: 931.2525; found: 931.2533.

Tetraethyl (6*R*,12*R*)-5,11-Di-*p*-tolyl-4,10-bis(*p*-tolylethynyl)-1,3,6,7,9,12-hexahydro-6,12-epoxydicyclopenta[*a*,*h*]anthracene-2,2,8,8-tetracarboxylate (3r)

White solid; yield: 736.9 mg (76%); mp 125.1–127.1 °C; R_f = 0.11 (PE/EtOAc 8:1).

FT-IR (KBr): 2981, 2365, 2341, 1738, 1514, 1248, 1186, 1070, 863, 821 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.37 (dd, *J* = 20.0, 8.0 Hz, 8 H, ArH), 7.17 (d, *J* = 8.0 Hz, 4 H, ArH), 7.07 (d, *J* = 8.0 Hz, 4 H, ArH), 5.85 (s, 2 H, 2 × OCH), 4.26 [q, *J* = 8.0 Hz, 8 H, 4 × C($CO_2CH_2CH_3)_2$], 3.75 [dd, *J* = 28.0, 20.0 Hz, 4 H, 2 × C($CO_2Et)_2CH_2$], 3.64 [dd, *J* = 36.0, 12.0 Hz, 4 H, 2 × C($CO_2Et)_2CH_2$], 2.48 (s, 6 H, 2 × ArCH_3), 2.33 (s, 6 H, 2 × ArCH_3), 1.30 [t, *J* = 8.0 Hz, 12 H, 4 × C($CO_2CH_2CH_3)_2$].

^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.4, 171.3, 145.7, 142.7, 142.4, 138.2, 137.4, 136.0, 135.0, 131.3, 131.0, 129.7, 128.9, 128.7, 120.4, 116.2, 95.8, 86.6, 81.3, 77.2, 61.9, 61.9, 60.3, 40.7, 38.9, 21.5, 21.4, 14.1, 14.1.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{64}H_{58}O_9$: 971.4154; found: 971.4146.

Tetraisopropyl (6*R*,12*R*)-5,11-Diphenyl-4,10-bis(phenylethynyl)-1,3,6,7,9,12-hexahydro-6,12-epoxydicyclopenta[*a*,*h*]anthracene-2,2,8,8-tetracarboxylate (3s)

White solid; yield: 776.1 mg (80%); mp 221.2–223.2 °C; R_f = 0.17 (PE/EtOAc 8:1).

FT-IR (KBr): 2979, 1733, 1497, 1377, 1280, 1254, 1184, 1104, 921, 758 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.57–7.47 (m, 10 H, ArH), 7.25 (s, 10 H, ArH), 5.88 (s, 2 H, 2 × OCH), 5.12–5.04 {m, 4 H, 2 × C[$CO_2CH(CH_3)_2]_2$}, 3.73 [dd, *J* = 40.0, 16.0 Hz, 4 H, 2 × C($CO_2^iPr)_2CH_2$], 3.55 [dd, *J* = 24.0, 16.0 Hz, 4 H, 2 × C($CO_2^iPr)_2CH_2$], 1.30–1.26 {m, 24 H, 2 × C[$CO_2CH(CH_3)_2]_2$}.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.8, 170.8, 145.7, 142.9, 142.6, 138.0, 136.1, 131.5, 131.4, 129.9, 128.2, 128.1, 128.0, 127.7, 123.4, 115.9, 95.7, 87.1, 81.2, 77.2, 69.5, 69.4, 60.2, 40.6, 38.7, 21.6, 21.6, 21.6.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{64}H_{58}O_9$: 971.4154; found: 971.4145.

Dimethyl 4,5-Dibenzoyl-6-(*p*-tolyl)-7-(*p*-tolylethynyl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate (4t)

White solid; yield: 503.7 mg (78%); mp 174.8–176.8 °C; R_f = 0.09 (PE/EtOAc 8:1).

FT-IR (KBr): 2960, 2365, 2337, 2212, 1744, 1658, 1596, 1450, 1287, 1239 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.79–7.77 (m, 2 H, ArH), 7.55 (t, *J* = 8.0 Hz, 1 H, ArH), 7.44–7.40 (m, 4 H, ArH), 7.29 (t, *J* = 8.0 Hz, 1 H, ArH), 7.16–7.13 (m, 5 H, ArH), 7.09 (t, *J* = 8.0 Hz, 3 H, ArH), 6.93 (d, *J* = 8.0 Hz, 2 H, ArH), 3.89 [s, 2 H, C($CO_2Me)_2CH_2$], 3.76 [s, 6 H, C($CO_2CH_3)_2$], 3.43 [s, 2 H, C($CO_2Me)_2CH_2$], 2.33 (s, 3 H, ArCH_3), 2.21 (s, 3 H, ArCH_3).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 197.8, 196.7, 171.5, 144.6, 141.7, 139.1, 138.9, 137.9, 137.3, 136.9, 136.8, 135.3, 134.4, 133.7, 132.5, 131.5, 130.3, 129.9, 129.5, 129.1, 128.6, 128.2, 127.7, 121.6, 119.7, 98.6, 85.5, 77.2, 59.5, 53.2, 40.9, 40.3, 21.5, 21.1.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{43}H_{34}O_6$: 647.2428; found: 647.2427.

Dimethyl 4,5-Dibenzoyl-6-(4-fluorophenyl)-7-[(4-fluorophenyl)ethynyl]-1,3-dihydro-2*H*-indene-2,2-dicarboxylate (4u)

White solid; yield: 509.5 mg (78%); mp 295.3–297.3 °C; R_f = 0.08 (PE/EtOAc 8:1).

FT-IR (KBr): 3411, 2361, 1736, 1508, 1287, 1229, 1076, 990, 844, 765 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.80–7.78 (m, 2 H, ArH), 7.57 (t, *J* = 8.0 Hz, 1 H, ArH), 7.46–7.42 (m, 4 H, ArH), 7.32 (t, *J* = 8.0 Hz, 1 H, ArH), 7.24–7.20 (m, 4 H, ArH), 7.16 (t, *J* = 8.0 Hz, 2 H, ArH), 6.99 (t, *J* = 8.0 Hz, 2 H, ArH), 6.84 (t, *J* = 8.0 Hz, 2 H, ArH), 3.87 [s, 2 H, C($CO_2Me)_2CH_2$], 3.77 [s, 6 H, 2 × C($CO_2CH_3)_2$], 3.44 [s, 2 H, C($CO_2Me)_2CH_2$].

^{13}C NMR (101 MHz, $CDCl_3$): δ = 197.5, 196.5, 171.4, 171.2, 164.1, 163.5, 161.6, 160.9, 144.7, 140.5, 139.3, 137.8, 137.4, 136.8, 135.6, 133.8, 133.5 (d, *J* = 9.1 Hz), 133.3 (d, *J* = 3.0 Hz), 132.8, 132.2 (d, *J* = 8.1 Hz), 129.9, 129.4, 128.7, 127.9, 121.3, 118.6, 118.5, 115.9, 115.7, 114.6, 114.4, 97.5, 85.4, 77.2, 60.4, 59.5, 53.3, 40.8, 40.3, 21.1, 14.2.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{41}H_{28}F_2O_6$: 655.1927; found: 655.1931.

Diethyl 4,5-Dibenzoyl-6-(*p*-tolyl)-7-(*p*-tolylethynyl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate (4v)

White solid; yield: 498.2 mg (74%); mp 161.9–163.9 °C; R_f = 0.13 (PE/EtOAc 8:1).

FT-IR (KBr): 3432, 2358, 2341, 1727, 1658, 1446, 1276, 1235, 823, 743 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 8.0 Hz, 2 H, ArH), 7.54 (t, *J* = 8.0 Hz, 1 H, ArH), 7.44–7.39 (m, 4 H, ArH), 7.29 (t, *J* = 8.0 Hz, 1 H, ArH), 7.16–7.13 (m, 6 H, ArH), 7.09 (t, *J* = 8.0 Hz, 2 H, ArH), 6.93 (d, *J* = 8.0 Hz, 2 H, ArH), 4.22 [q, *J* = 6.7 Hz, 4 H, 2 × $C(CO_2CH_2CH_3)_2$], 3.87 [s, 2 H, $C(CO_2Et)_2CH_2$], 3.43 [s, 2 H, $C(CO_2Et)_2CH_2$], 2.33 (s, 3 H, $ArCH_3$), 2.21 (s, 3 H, $ArCH_3$), 1.24 [t, *J* = 8.0 Hz, 6 H, 2 × $C(CO_2CH_2CH_3)_2$].

^{13}C NMR (101 MHz, $CDCl_3$): δ = 197.8, 196.8, 171.1, 144.8, 138.9, 137.9, 137.2, 136.9, 136.9, 135.2, 134.4, 133.6, 132.5, 131.5, 130.3, 129.9, 129.4, 129.0, 128.6, 128.1, 127.7, 121.6, 119.8, 98.5, 85.5, 77.2, 62.0, 59.6, 40.8, 40.2, 21.6, 21.2, 14.0.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{45}H_{38}O_6$: 675.2741; found: 675.2748.

Dimethyl 5-Acetyl-4-benzoyl-6-(4-fluorophenyl)-7-[(4-fluorophenyl)ethynyl]-1,3-dihydro-2*H*-indene-2,2-dicarboxylate (4w)

White solid; yield: 484.4 mg (82%); mp 160.6–162.6 °C; R_f = 0.07 (PE/EtOAc 8:1).

FT-IR (KBr): 3428, 2958, 2361, 2341, 2221, 1751, 1729, 1699, 1654, 1506, 1229, 1158 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.84–7.82 (m, 2 H, ArH), 7.62 (t, *J* = 8.0 Hz, 1 H, ArH), 7.50 (t, *J* = 8.0 Hz, 2 H, ArH), 7.43–7.40 (m, 2 H, ArH), 7.27–7.23 (m, 2 H, ArH), 7.16 (t, *J* = 6.0 Hz, 2 H, ArH), 7.01 (t, *J* = 8.0 Hz, 2 H, ArH), 3.82 [s, 2 H, $C(CO_2Me)_2CH_2$], 3.74 [s, 6 H, $C(CO_2CH_3)_2$], 3.36 [s, 2 H, $C(CO_2Me)_2CH_2$], 1.80 (s, 3 H, $COCH_3$).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 204.5, 196.9, 171.3, 164.0 (d, *J* = 2.0 Hz), 161.6, 144.7, 141.5, 139.1, 137.3, 136.8, 134.8, 133.8, 133.4 (d, *J* = 8.1 Hz), 131.9, 131.9, 129.6, 128.8, 120.9, 118.5, 118.5, 115.9, 115.7, 115.4, 115.2, 97.4, 85.2, 77.2, 59.5, 53.2, 40.6, 39.9, 31.5.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{36}H_{26}F_2O_6$: 593.1770; found: 593.1765.

Diethyl 5-Acetyl-4-benzoyl-6-(*p*-tolyl)-7-(*p*-tolylethynyl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate (4x)

White solid; yield: 501.9 mg (82%); mp 177.0–179.0 °C; R_f = 0.14 (PE/EtOAc 8:1).

FT-IR (KBr): 3428, 2986, 2363, 2335, 1740, 1695, 1663, 1450, 1276, 1239, 823 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.83 (d, *J* = 8.0 Hz, 2 H, ArH), 7.59 (t, *J* = 8.0 Hz, 1 H, ArH), 7.48 (t, *J* = 8.0 Hz, 2 H, ArH), 7.33(d, *J* = 8.0 Hz, 2 H, ArH), 7.26–7.23 (m, 2 H, ArH), 7.18 (d, *J* = 8.0 Hz, 2 H, ArH), 7.11 (d, *J* = 8.0 Hz, 2 H, ArH), 4.19 [q, *J* = 6.7 Hz, 4 H, $C(CO_2CH_2CH_3)_2$], 3.82 [s, 2 H, $C(CO_2Et)_2CH_2$], 3.36 [s, 2 H, $C(CO_2Et)_2CH_2$], 2.42 (s, 3 H, $ArCH_2$), 2.35 (s, 3 H, $ArCH_2$), 1.75 (s, 3 H, $COCH_3$), 1.22 [t, *J* = 8.0 Hz, 6 H, $C(CO_2CH_2CH_3)_2$].

^{13}C NMR (101 MHz, $CDCl_3$): δ = 204.9, 197.3, 171.0, 144.8, 141.3, 140.4, 138.9, 138.2, 137.0, 136.9, 134.7, 134.6, 133.6, 131.5, 130.1, 129.7, 129.1, 128.9, 128.7, 121.3, 119.7, 98.4, 85.4, 77.2, 61.9, 59.6, 40.7, 39.9, 31.4, 21.6, 21.4, 13.9.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{40}H_{36}O_6$: 613.2585; found: 613.2593.

Diisopropyl 5-Acetyl-4-benzoyl-6-phenyl-7-(phenylethynyl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate (4y)

White solid; yield: 514.1 mg (84%); mp 170.2–172.2 °C; R_f = 0.15 (PE/EtOAc 8:1).

FT-IR (KBr): 3415, 2981, 2361, 2333, 1723, 1693, 1656, 1276, 1250, 1108, 758 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.83 (d, *J* = 6.0 Hz, 2 H, ArH), 7.59 (t, *J* = 8.0 Hz, 1 H, ArH), 7.48 (t, *J* = 8.0 Hz, 3 H, ArH), 7.44 (s, 5 H, ArH), 7.30–7.24 (m, 4 H, ArH), 5.06–5.00 {m, 2 H, $C[CO_2CH(CH_3)_2]_2$}, 3.80 [s, 2 H, $C(CO_2{}^i Pr)_2CH_2$], 3.36 [s, 2 H, $C(CO_2{}^i Pr)_2CH_2$], 1.74 (s, 3 H, $COCH_3$), 1.23 {d, *J* = 8.0 Hz, 6 H, $C[CO_2CH(CH_3)_2]$}, 1.18 {d, *J* = 8.0 Hz, 6 H, $C[CO_2CH(CH_3)_2]$}.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 204.6, 197.3, 170.6, 145.1, 141.2, 140.5, 137.8, 137.3, 137.1, 134.9, 133.6, 131.6, 130.3, 129.6, 128.8, 128.7, 128.4, 128.3, 128.2, 122.8, 121.0, 98.2, 85.9, 77.2, 69.6, 59.6, 40.6, 39.9, 31.4, 21.5.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{40}H_{36}O_6$: 613.2585; found: 613.2587.

Diisopropyl 4-Benzoyl-5-formyl-6-phenyl-7-(phenylethynyl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate (4z)

White solid; yield: 418.5 mg (70%); mp 171.6–173.6 °C; R_f = 0.15 (PE/EtOAc 8:1).

FT-IR (KBr): 3415, 2981, 2361, 2337, 1740, 1695, 1450, 1282, 1248, 1102, 769, 694 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 9.63 (s, 1 H, COH), 7.83–7.81 (m, 2 H, ArH), 7.56 (d, *J* = 8.0 Hz, 1 H, ArH), 7.51–7.43 (m, 7 H, ArH), 7.31–7.27 (m, 3 H, ArH), 7.22–7.19 (m, 2 H, ArH), 5.07–5.00 {m, 2 H, $C[CO_2CH(CH_3)_2]_2$}, 3.83 [s, 2 H, $C(CO_2{}^i Pr)_2CH_2$], 3.44 [s, 2 H, $C(CO_2{}^i Pr)_2CH_2$], 1.21 {d, *J* = 8.0 Hz, 6 H, $C[CO_2CH(CH_3)_2]$}, 1.18 {d, *J* = 8.0 Hz, 6 H, $C[CO_2CH(CH_3)_2]$}.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 197.3, 190.9, 170.4, 149.3, 147.9, 138.0, 136.5, 136.3, 135.8, 133.4, 132.1, 131.6, 130.7, 128.8, 128.7, 128.5, 128.3, 128.1, 122.6, 121.6, 98.7, 85.1, 77.2, 69.7, 59.6, 40.9, 38.8, 21.5.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{39}H_{34}O_6$: 599.2428; found: 599.2425.

Conflict of Interest

The authors declare no conflict of interest.

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Supporting Information

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