Supplementary Information for

The domino hexadehydro-Diels–Alder reaction transforms polyynes to benzyynes to naphthynes to anthracynes to tetracyanes (and beyond?)

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I. General Experimental Protocols

$^{13}$C and $^1$H NMR spectra were measured on Bruker Avance 500 (500 MHz) spectrometers. $^1$H NMR chemical shifts in CDCl$_3$ are referenced to CHCl$_3$ (δ = 7.26 ppm) or C$_6$H$_6$ (δ = 7.16 ppm). Non-first order multiplets are referred to by the acronym "nfom". Non-first order doublets, often seen for 1,4-disubstituted benzene derivatives, are identified as "nfot". Triplets and doublet of doublets having non-first order character are abbreviated as “nfot” and “nfodd”, respectively. $^{13}$C NMR chemical shifts for spectra collected in CDCl$_3$ are referenced to the carbon chemical shift in CDCl$_3$ (δ = 77.16 ppm) or C$_6$D$_6$ (δ = 128.06 ppm). The following format is used to report resonances in the $^1$H spectra: chemical shift in ppm [multiplicity, coupling constant(s) (J) in Hz, integration to the nearest whole number]. $^1$H NMR assignments are given by the substructure environment, e.g., OCH$_2$H$_6$. Complex structures are often numbered in the graphic in order to simplify the proton assignment identification. Coupling constant analysis was guided by methods we have described elsewhere.$^{1,2}$

Infrared spectra were measured on a Midac Corporation Prospect 4000 FT-IR spectrometer in the ATR mode (germanium window) as thin films. Only the most intense and/or diagnostic peaks are reported.

High-resolution mass spectrometry (HRMS) measurements were determined on a Bruker BioTOF II (ESI-TOF) instrument in the electrospray ionization (ESI) mode. PEG was used as an internal standard/calibrant. Samples were introduced as solutions in methanol or a methylene chloride and methanol solvent mixture.

Some polyaromatic compounds were not detected by ESI ionization. For these HRMS were collected on a Thermo Orbitrap Velos in the positive atmospheric pressure chemical ionization (APCI) mode using an external standard (Pierce™ LTQ) with mass accuracy < 3 ppm. Samples were injected directly as dilute solutions (concentration less than 10$^{-6}$ M) in methanol.

UV-Vis absorption spectra were recorded in DCM at a concentration of 10$^{-5}$ M on a Varian Cary 50 Bio UV-Visible Spectrophotometer. Fluorescence data were obtained in DCM at a concentration of 10$^{-7}$ M using a Varian Cary Eclipse Fluorescence Spectrophotometer.

MPLC refers to medium pressure liquid chromatography (ca. 50–100 psi) using columns packed with RediSep Rf Gold® Normal-Phase Silica (Teledyne/ISCO, 20–40 µm, 60 Å pore size). Eluent was delivered with a Waters HPLC pump; a differential refractive index detector (Waters R401) was used to detect the eluted solute. Flash chromatography was performed with columns packed with E. Merck silica gel (230-400 mesh). Thin layer chromatography was done on plastic-backed plates of silica gel; TLC visualization was done by ceric ammonium molybdate staining and/or UV detection.

Reactions performed under anhydrous conditions were done under an atmosphere of nitrogen in flame-dried glassware. Anhydrous toluene, tetrahydrofuran or methylene chloride was collected immediately prior to use after being freshly passed through a column containing activated alumina. The reaction temperatures reported are the temperature of an external heating bath or, for the photo-HDDA reaction, of the air surrounding the reaction tube. Reactions carried out at temperatures higher than the boiling point of the reaction solvent were performed in a screw-capped vial culture tube or vial, sealed with an inert, Teflon®-lined screw cap.
II. Preparation procedures and characterization data for all new compounds

General Procedures A–C.

A. General procedure for the Cadiot–Chodkiewicz cross-coupling reaction

\[
\begin{array}{c}
R^1\equiv \text{H} + R^2\equiv \text{Br} \xrightarrow{\text{CuCl, NH}_2\text{OH•HCl}} R^1\equiv \text{R}^2
\end{array}
\]

To a solution of CuCl (0.050–0.10 equiv with respect to the terminal alkyne substrate) in 30:70 (v:v) nBuNH$_2$·H$_2$O (5.0 mL/mmol with respect to the terminal alkyne substrate) was added an excess of NH$_2$OH•HCl (typically a few crystals) with stirring. The color of this mixture turned from deep blue to colorless immediately, indicating full conversion of Cu(II) to Cu(I). The headspace of the reaction flask was purged with N$_2$. The vessel was sealed with a septum, a nitrogen balloon was attached, and the vessel was cooled in an ice water bath. A solution of the terminal alkyne (1.0 equiv) in CH$_2$Cl$_2$ (ca. 2.5 mL/mmol) was added into the flask via syringe resulting in a yellow, orange, or red suspension, which is indicative for the formation of an alkynyl copper species. After stirring for ca. 5 min, the 1-bromoalkyne (0.90–1.5 equiv) in CH$_2$Cl$_2$ (ca. 2.5 mL/mmol) was added dropwise via syringe over ca. 15 min using a syringe pump. The mixture was then kept stirring at the indicated temperature (0 °C or rt). Typically, the suspension of the alkynyl copper turned clear over the course of 10–100 min, which indicated consumption of the alkynyl copper species. The mixture was quenched by the addition of saturated aqueous NH$_4$Cl and extracted with CH$_2$Cl$_2$. The extracts were dried and concentrated. The crude material was subsequently purified by flash chromatography on silica gel.

B. General procedure for bromination of terminal or TMS-alkyne

\[
\begin{array}{c}
R\equiv \text{H} \quad \text{or} \\
R\equiv \text{TMS} \xrightarrow{\text{NBS, AgNO}_3} \text{Acetone} \quad \text{r.t.} \quad R\equiv \text{Br}
\end{array}
\]

To a stirred solution of terminal alkyne or TMS-protected terminal alkyne (1.0 equiv) and N-bromosuccinimide (NBS, 1.1 equiv) in acetone (0.10 M), powdered AgNO$_3$ (0.10 equiv) was added. After being stirred at room temperature for 1–2 hours (TLC monitoring), an equal volume of hexanes was added to the suspension, and the solid succinimide was removed by filtration through Celite®. Following solvent removal from the filtrate, the crude material was purified by flash chromatography.

C. General procedure for the domino HDDA reaction

The poly-yne precursor (1.0 equiv) and the trapping reagent (typically 1.2–10 equiv) were added to an oven-dried glass vial. The indicated solvent (typically chloroform—the source was amylene-stabilized rather than ethanol-stabilized, since ethanol is known to react with HDDA-benzenes³) was then added to dissolve all the material and arrive at a concentration of the poly-ye of 0.005–0.040 M. The headspace of the reaction vial was purged with a gentle flow of N$_2$ gas and the vial was sealed with a Teflon-lined cap. The reaction mixture was stirred in a heated oil bath held at the indicated temperature. After the poly-ye had disappeared (TLC), the vial was cooled to ambient temperature, the solution was concentrated in vacuo, and the residue was directly subjected to flash column chromatography on silica gel or to MPLC for purification.
A. Procedures for syntheses of and characterization data for poly-yne substrates

Synthesis of 9

Following general procedure A, 1,5-hexadiyne (0.95 mL, 10 mmol), 3-bromoprop-2-yn-1-ol (1.35 g, 10 mmol), CuCl (50 mg, 0.5 mmol), n-butylamine/H$_2$O (v:v, 30:70, 50 mL), and DCM (50 mL) were used to prepare triyne S1. Purification of the crude material by flash chromatography (hexanes:EtOAc 4:1) provided triyne S1 (739 mg, 5.6 mmol, 56%) as a pinkish solid.

$^1$H NMR (500 MHz, CDCl$_3$): δ 4.32 (s, 2H, C$_2$H$_2$OH), 2.53 (nfot, J = 7.3 Hz, 2H, C≡CC≡CCH$_2$), 2.43 (nfd, J = 7.6, 2.6 Hz, 2H, HC≡C(CH)$_2$), 2.04 (t, J = 2.6 Hz, 1H, C≡CH), and 1.71 (br s, 1H, OH).

$^{13}$C NMR (126 MHz, CDCl$_3$): δ 82.0, 79.3, 74.6, 70.7, 70.0, 65.6, 51.6, 19.5, and 18.4.

IR (neat): 3305, 3269, 3175, 2921, 2252, 1490, 1434, 1353, 1229, 1029, 1008, and 927 cm$^{-1}$.

HRMS (ESI-TOF): Calcd for C$_9$H$_8$AgO$^+$ [M+Ag$^+$] requires 238.9621; found 238.9617.

Mp: 62–64 ºC.

Tetradeca-2,4,8,10-tetrayn-1-yl propiolate (9)
Following general procedure A, triyne S1 (185 mg, 1.4 mmol), 1-bromopentyno (309 mg, 2.1 mmol), CuCl (14 mg, 0.14 mmol), n-butylamine/H$_2$O (v:v, 30:70, 7.0 mL), and DCM (7.0 mL) were used to prepare tetranyne S2. Purification by flash chromatography (hexanes:EtOAc 4:1) afforded tetranyne S2 (263 mg, 1.3 mmol), as a white solid.

$^1$H NMR (500 MHz, CDCl$_3$): δ 4.32 (d, $J = 6.1$ Hz, 2H, CH$_2$OH), 2.54–2.47 (m, 4H, C≡CCH$_2$CH$_2$C≡C), 2.23 (t, $J = 6.9$ Hz, 2H, CH$_2$CH$_2$CH$_3$), 1.67 (t, $J = 6.1$ Hz, 1H, CH$_2$OH), 1.55 (sextet, $J = 7.0$ Hz, 2H, CH$_2$CH$_2$CH$_3$), and 0.98 (t, $J = 6.9$ Hz, 3H, CH$_2$CH$_2$CH$_3$).

$^{13}$C NMR (126 MHz, CDCl$_3$): δ 79.0, 78.8, 74.6, 74.4, 70.7, 67.0, 65.8, 65.2, 51.6, 21.9, 21.3, 19.5, 19.2, and 13.6.

IR (neat): 3327, 3207, 2961, 2934, 2872, 2254, 1459, 1431, 1353, 1263, 1228, 1027, and 908 cm$^{-1}$.

HRMS (ESI-TOF): Calcd for C$_{14}$H$_{14}$AgO$^+$ [M+Ag$^+$] requires 305.0090; found 305.0085.

Mp: 74–75 °C.

Tetranyne S2 (238 mg, 1.2 mmol), 4-dimethylaminopyridine (DMAP, 17 mg, 0.14 mmol), and propionic acid (124 μL, 2.0 mmol) were dissolved in anhydrous DCM (15 mL) and stirred at 0 °C. N,N'-Dicyclohexylcarbodiimide (DCC*, 402 mg, 1.95 mmol) was added to the solution, after which the headspace of the reaction flask was purged with N$_2$. The resulted brown suspension was warmed to room temperature and stirred for 16 h. The crude reaction mixture was filtered by passing through a short silica plug, concentrated, and purified by flash chromatography (hexanes:EtOAc 8:1) to give pentanyne 9 (217 mg, 0.87 mmol, 68% over two steps) as a colorless solid (pinkish solid when exposed to light).

*CAUTION: DCC is an irritant and can lead to sensitization. Avoid any direct contact with the skin and inhalation.

$^1$H NMR (500 MHz, CDCl$_3$): δ 4.83 (s, 2H, CH$_2$O), 2.95 (s, 1H, C=CH), 2.509 (nfot, $J = 5.0$ Hz, 2H, C≡CCH$_2$CH$_2$C≡C), 2.505 (nfot, $J = 5.2$ Hz, 2H, C≡CCH$_2$CH$_2$C≡C), 2.23 (t, $J = 7.0$ Hz, 2H, CH$_2$CH$_2$CH$_3$), 1.55 (sextet, $J = 7.2$ Hz, 2H, CH$_2$CH$_2$CH$_3$), and 0.98 (t, $J = 7.0$ Hz, 3H, CH$_2$CH$_2$CH$_3$).

$^{13}$C NMR (126 MHz, CDCl$_3$): δ 151.8, 80.0, 78.9, 76.2, 74.2, 73.9, 72.5, 68.8, 67.0, 65.6, 65.1, 54.1, 21.9, 21.3, 19.4, 19.1, and 13.6.

IR (neat): 3243, 2971, 2936, 2261, 2129, 2117, 1702, 1440, 1430, 1370, 1235, 982, 949, and 761 cm$^{-1}$.

HRMS (ESI-TOF): Calcd for C$_{17}$H$_{14}$NaO$_2$$^+$ [M+Na$^+$] requires 273.0886; found 273.0865.

Mp: 51–52 °C.
Synthesis of 13

To a stirred solution of triyne S1 (528 mg, 4.0 mmol) and imidazole (326 mg, 4.8 mmol) in DCM (10 mL) at 0 °C was added tert-butyldimethylsilyl chloride (TBSCl, 664 mg, 4.4 mmol). The solution was then warmed to room temperature. After being stirred for 16 hours, the reaction mixture was quenched by the addition of saturated aqueous ammonium chloride, and extracted with DCM. The combined organic solution was dried and concentrated, and the crude TBS-ether S3 was directly used in the following step without further purification.

Bromoalkyne S4 was prepared following general procedure B from the crude sample of S3, N-bromosuccinimide (NBS, 712 mg, 4.0 mmol), AgNO3 (68 mg, 0.40 mmol), and acetone (40 mL). Purification by flash chromatography (hexanes:EtOAc 9:1) afforded S4 (1.27 g, 3.9 mmol, 98%) as a white solid.

1H NMR (500 MHz, CDCl3): δ 4.36 (s, 2H, CH2O), 2.51 (br s, 4H, CH2CH2), 0.90 [s, 9H, Si(CH3)2C(CH3)3], and 0.12 [s, 6H, Si(CH3)2C(CH3)3].

13C NMR (126 MHz, CDCl3): δ 78.1, 75.7, 75.4, 69.7, 66.6, 66.2, 52.2, 25.9, 19.4, 19.3, 18.4, and -5.0.

IR (neat): 2955, 2930, 2859, 2255, 1462, 1375, 1259, 1234, 1092, 907, 840, and 781 cm⁻¹.

HRMS (ESI-TOF): Calcd for C15H21AgBrOSi⁺ [M+Ag⁺] requires 430.9590; found 430.9581.

Mp: 142–144 °C.
18-((tert-Butyldimethylsilyl)oxy)octadeca-2,4,8,10,14,16-hexyn-1-ol (S5)

Hexayne S5 was synthesized following general procedure A from triyne S1 (218 mg, 1.65 mmol), bromoalkyne S4 (643 mg, 1.98 mmol), CuCl (16 mg, 0.16 mmol), n-butylamine/H₂O (v:v, 30:70, 8.0 mL), and DCM (8.0 mL). Purification by flash chromatography (hexanes:EtOAc 2:1) provided hexayne S5 (556 mg, 1.48 mmol, 90%) as a white solid.

**¹H NMR** (500 MHz, CDCl₃): δ 4.36 (s, 2H, CH₂OTBS), 4.32 (br s, 2H, CH₂OH), 2.51 (br s, 8H, CH₂CH₂ and CH₂CH₂), 1.67 (br s, 1H, OH), 0.90 [s, 9H, Si(CH₃)₂C(CH₃)₃], and 0.12 [s, 6H, Si(CH₃)₂C(CH₃)₃].

**¹³C NMR** (126 MHz, CDCl₃): δ 78.9, 78.1, 75.8, 75.6, 74.7, 70.7, 69.7, 66.7, 66.6, 66.2, 65.9, 52.2, 51.7, 25.9, 19.39, 19.38, 19.3, 19.2, 18.4, and -5.0.

**IR** (neat): 3353, 2958, 2858, 1432, 1372, 1260, 1234, 1089, 1025, 840, and 780 cm⁻¹.

**HRMS** (ESI-TOF): Calcd for C₂₄H₂₈NaO₂Si⁺ [M+Na⁺] requires 399.1751; found 399.1754.

**Mp:** 119–120 °C.

18-((tert-Butyldimethylsilyl)oxy)octadeca-2,4,8,10,14,16-hexyn-1-yl propiolate (13)

Hexayne S5 (226 mg, 0.60 mmol), 4-dimethylaminopyridine (DMAP, 7.0 mg, 0.062 mmol), and propionic acid (56 µL, 0.90 mmol) were dissolved in anhydrous DCM (6.0 mL) and stirred at 0 °C. N,N'-Dicyclohexylcarbodiimide (DCC*, 161 mg, 0.78 mmol) was added to the solution, after
which the headspace of the reaction flask was purged with N₂. The resulting brown suspension was warmed to room temperature and stirred for 16 h. The crude reaction mixture was filtered by passing through a short silica plug, concentrated, and purified by flash chromatography (hexanes:EtOAc 2:1) to give heptayne 13 (218 mg, 0.51 mmol, 85%) as a white solid.

*CAUTION: DCC is an irritant and can lead to sensitization. Avoid any direct contact with the skin and inhalation.

**¹H NMR** (500 MHz, CDCl₃): δ 4.83 [s, 2H, CH₂O(C=O)], 4.36 (s, 2H, CH₂OTBS), 2.95 (s, 1H, C≡CH), 2.51 (br s, 8H, CH₂CH₂ and CH₂CH₂), 0.90 [s, 9H, Si(CH₃)₂C(CH₃)₃], and 0.12 [s, 6H, Si(CH₃)₂C(CH₃)₃].

**¹³C NMR** (126 MHz, CDCl₃): δ 151.8, 79.9, 78.1, 76.2 (x2), 75.8, 75.4, 74.0, 72.5, 69.6, 68.9, 66.7, 66.5, 66.2, 65.7, 54.1, 52.2, 25.9, 19.39, 19.36, 19.3, 19.1, 18.4, and -5.0.

**IR** (neat): 3278, 2954, 2930, 2857, 2260, 2123, 1715, 1432, 1374, 1232, 1092, 840, and 781 cm⁻¹.

**HRMS** (ESI-TOF): Calcd for C₂₇H₂₈NaO₃Si⁺ [M+Na⁺] requires 451.1700; found 451.1716.

**Mp:** 68–70 °C.

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**Synthesis of 17**

![Chemical diagram showing the synthetic route to 17](attachment:image.png)
1,4-bis(2-ethynylphenyl)buta-1,3-diyne (S6)

To a stirred solution of TMEDA (0.30 mL, 2.0 mmol) in DCM (25 mL) was added CuI (190 mg, 1.0 mmol) under air. The color of the clear solution quickly turned into deep blue, which indicated the generation of Cu(II) complexes. ((2-ethynylphenyl)ethynyl)trimethylsilane (2.0 g, 10 mmol) was added after the solution was exposed to air for ca. 10 min. The reaction was kept open to air and quenched after 16 hours by passing through a short silica plug (eluted with DCM). The DCM eluent was concentrated, and the crude tetryne S6-TMS (1.9 g) was used in the following step without further purification.

The crude tetryne S6-TMS (1.9 g) was then dissolved in THF (20 mL)/MeOH (80 mL) followed by addition of KF•2H2O (0.94 g, 10 mmol). After being stirred for 16 hours, the reaction was quenched by addition of deionized water and extracted with DCM. The combined organic phase was dried and concentrated. The residue was purified by flash chromatography (hexanes:EtOAc 12:1) to provide tetryne S6 (0.98 g, 3.9 mmol, 78% over two steps). The spectral data were consistent with reported values.

5-(2-((2-Ethynylphenyl)buta-1,3-diyn-1-yl)phenyl)penta-2,4-diy-1-ol (S7)

Pentayne S7 was synthesized following general procedure A from 1,4-bis(2-ethynylphenyl)buta-1,3-diyne (S6) (500 mg, 2.0 mmol), 3-bromoprop-2-yln-1-ol (405 mg, 3.0 mmol), CuCl (20 mg, 0.20 mmol), n-butylamine/H2O (v:v, 30:70, 10 mL), and DCM (10 mL). Purification by flash chromatography (hexanes:EtOAc 2:1) provided pentayne S7 (360 mg, 1.18 mmol, 59%) as an orange oil.

1H NMR (500 MHz, CDCl3): δ 7.58–7.48 (m, 4H, Ho), 7.36–7.29 (m, 4H, Hm), 4.44 (d, J = 6.1 Hz, 2H, CH2OH), 3.45 (s, 1H, C=CH), and 1.66 (t, J = 6.3 Hz, 1H, OH).
\textbf{13C NMR} (126 MHz, CDCl$_3$): $\delta$ 133.2, 133.1, 133.0, 132.7, 129.0 (x2), 128.9, 128.6, 125.7, 125.5, 125.0, 124.8, 82.1, 82.0, 81.6, 81.2, 80.5, 78.0, 77.6, 77.4, 76.4, 70.5, and 60.5.

\textbf{IR} (neat): 3340, 3289, 3059, 2860, 2249, 2213, 1474, 1356, 1190, 1084, 1013, 952, and 833 cm$^{-1}$.

\textbf{HRMS} (ESI-TOF): Calcd for C$_{23}$H$_{12}$NaO$^+$ [M+Na$^+$] requires 327.0780; found 327.0777.

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5-(2-((2-(Bromoethynyl)phenyl)buta-1,3-diyn-1-yl)phenyl)penta-2,4-diyn-1-ol (S8)

Bromoalkyne S8 was synthesized following general procedure B from pentayne S7 (164 mg, 0.54 mmol), N-bromosuccinimide (NBS, 107 mg, 0.60 mmol), AgNO$_3$ (9 mg, 0.054 mmol), and acetone (10 mL). Purification by flash chromatography (hexanes:EtOAc 3:1) afforded S8 (191 mg, 0.50 mmol, 92%) as a brownish oil.

\textbf{1H NMR} (500 MHz, CDCl$_3$): $\delta$ 7.56–7.52 (m, 2H, H$_o$), 7.50 (nfom, 1H, H$_2$ or H$_5$), 7.46 (nfom, 1H, H$_5$ or H$_2$), 7.35–7.30 (m, 4H, H$_m$), 4.44 (s, 2H, CH$_2$OH), and 1.72 (br s, 1H, OH).

\textbf{13C NMR} (126 MHz, CDCl$_3$): $\delta$ 133.42, 133.38, 133.2, 132.7, 129.11, 129.08, 129.0, 128.5, 126.4, 125.6, 125.1, 125.0, 82.1, 81.3, 80.6, 78.4, 78.2, 77.7, 77.5, 76.6, 70.7, 55.3, and 51.9.

\textbf{IR} (neat): 3376, 3062, 2962, 2862, 2290, 2196, 1714, 1702, 1588, 1473, 1427, 1160, 1160, 1018, 957, and 832 cm$^{-1}$.

\textbf{HRMS} (ESI-TOF): Calcd for C$_{23}$H$_{11}$BrNaO$^+$ [M+Na$^+$] requires 404.9885; found 404.9869.
5-(2-((2-(4-Methoxyphenyl)buta-1,3-diyne-1-yl)phenyl)buta-1,3-diyne-1-yl)phenyl)penta-2,4-diyne-1-ol (S9)

Hexayne S9 was synthesized following general procedure A from 1-ethynyl-4-methoxybenzene (132 mg, 1.0 mmol), bromoalkyne S8 (171 mg, 0.45 mmol), CuCl (5 mg, 0.050 mmol), n-butylamine/H$_2$O (v:v, 30:70, 5.0 mL), and DCM (5.0 mL). Purification by flash chromatography (hexanes:EtOAc 2:1) provided hexayne S9 (99 mg, 0.23 mmol, 51%) as a light brown oil.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.58–7.48 (m, 4H, $H_o$), 7.50 (nfod, $J = 8.9$ Hz, 2H, $H_o'$), 7.35–7.30 (m, 4H, $H_m$), 6.86 (nfod, $J = 8.9$ Hz, 2H, $H_m'$), 4.37 (d, $J = 6.4$ Hz, 2H, CH$_2$OH), 3.82 (s, 3H, OCH$_3$), and 1.62 (t, $J = 6.5$ Hz, 1H, OH).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 160.6, 134.4, 133.4, 133.34, 133.32, 133.28, 129.10, 129.07, 129.0, 128.8, 125.7, 125.6, 125.14, 125.13, 114.3, 113.6, 83.6, 82.3, 81.3, 80.9, 79.1, 78.7, 78.3, 78.1, 77.6, 76.5, 73.1, 70.6, 55.5, and 51.8.

IR (neat): 3351, 3059, 2933, 2838, 2209, 2140, 1699, 1602, 1509, 1474, 1440, 1292, 1027, and 826 cm$^{-1}$.

HRMS (ESI-TOF): Calcd for C$_{32}$H$_{18}$NaO$_2^+$ [M+Na$^+$] requires 457.1199; found 457.1192.
5-(2-(2-((4-Methoxyphenyl)buta-1,3-diyn-1-yl)phenyl)buta-1,3-diyn-1-yl)phenyl)penta-2,4-diyn-1-yl propiolate (17)

Hexayne S9 (87 mg, 0.20 mmol), 4-dimethylaminopyridine (DMAP, 2.4 mg, 0.021 mmol), and propiolic acid (19 μL, 0.31 mmol) were dissolved in anhydrous DCM (2.0 mL) and stirred at 0 °C. N,N'-Dicyclohexylcarbodiimide (DCC*, 49 mg, 0.24 mmol) was added to the solution, after which the headspace of the reaction flask was purged with N₂. The resulting brown suspension was warmed to room temperature and stirred for 16 h. The crude reaction mixture was filtered by passage through a short silica plug, the filtrate was concentrated, and the residue was purified by flash chromatography (hexanes:EtOAc 3:1) to give heptayne 17 (59 mg, 0.12 mmol, 60%) as a pale yellow solid.

*CAUTION: DCC is an irritant and can lead to sensitization. Avoid any direct contact with the skin and inhalation.

**H NMR** (500 MHz, CDCl₃): δ 7.59–7.49 (m, 4H, Hₒ), 7.50 (nfod, J = 8.9 Hz, 2H, Hₒ'), 7.37–7.31 (m, 4H, Hₘ), 6.86 (nfod, J = 8.9 Hz, 2H, Hₘ'), 4.88 [s, 2H, CH₂O(C=O)], 3.82 (s, 3H, OCH₃), and 2.94 (s, 1H, C≡CH).

**C NMR** (126 MHz, CDCl₃): δ 160.6, 151.8, 134.4, 133.4, 133.47, 133.4, 133.3, 129.4, 129.1, 129.0, 128.8, 125.8, 125.7, 125.1, 124.7, 114.3, 113.7, 83.6, 81.4, 80.7, 79.1, 78.7, 78.5, 78.0, 77.4, 77.1, 76.26⁺, 76.26⁻, 73.9, 73.1, 72.4, 55.5, and 54.2.

**IR** (neat): 3282, 3065, 2934, 2839, 2242, 2209, 2122, 1721, 1602, 1509, 1474, 1292, 1252, 1208, 1172, 1130, 964, and 873 cm⁻¹.

**HRMS** (ESI-TOF): Calcd for C₃₅H₁₈NaO₃⁺ [M+Na⁺] requires 509.1148; found 509.1145.

**Mₚ**: 124–128 °C (with decomposition occurring above ca. 120 °C).
N,N-Bis(12-((tert-butyldimethylsilyl)oxy)dodeca-2,4,8,10-tetrayn-1-yl)methanesulfonamide (20)

Octayne 20 was synthesized following general procedure A from N,N-di(prop-2-yn-1-yl)methanesulfonamide (171 mg, 1.0 mmol), bromoalkyne S4 (715 mg, 2.2 mmol), CuCl (20 mg, 0.20 mmol), n-butylamine/H2O (v:v, 30:70, 5.0 mL), and DCM (5.0 mL). Purification by flash chromatography (hexanes:EtOAc 5:1) provided octayne 20 (352 mg, 0.53 mmol, 53%) as a white solid.

1H NMR (500 MHz, CDCl3): δ 4.36 (s, 4H, CH2O), 4.24 (s, 4H, CH2N), 2.98 (s, 3H, CH3SO2), 2.53 (br s, 8H, CH2CH2), 0.91 [s, 18H, Si(CH3)2C(CH3)3], and 0.12 [s, 12H, Si(CH3)2C(CH3)3].

13C NMR (126 MHz, CDCl3): δ 78.6, 77.7, 75.6, 71.2, 69.6, 69.5, 66.4, 65.8, 52.2, 39.0, 37.6, 25.9, 19.3, 19.2, 18.4, and -5.1.

IR (neat): 2955, 2930, 2857, 2259, 1471, 1426, 1351, 1256, 1231, 1157, 1085, 1006, 964, 900, 838, 815 and 779 cm⁻¹.

HRMS (ESI-TOF): Calcd for C37H49NNaO4Si2⁺ [M+Na⁺] requires 682.2813; found 682.2789.

Mp: 87–88 °C.
**Synthesis of S11**

1-Ethynyl-2-(phenylbuta-1,3-diyne-1-yl)benzene (S10)

Triyne S10 was prepared following general procedure A from (bromoethynyl)benzene (754 mg, 4.2 mmol), 1,2-diethynylbenzene (580 mg, 5.0 mmol), CuCl (25 mg, 0.25 mmol), \(n\)-butylamine/H\(_2\)O (v:v, 30:70, 25 mL), and DCM (25 mL). Purification by MPLC (hexanes:EtOAc 25:1) provided triyne S10 (532 mg, 2.4 mmol, 56%) as a pale yellow solid. The spectral data of triyne S10 were consistent with reported values\(^5\).

Dimethyl 2,2-bis(5-(2-(phenylbuta-1,3-diyne-1-yl)phenyl)penta-2,4-diyne-1-yl)malonate (S11)

Octayne S11 was prepared following general procedure A from 1-ethynyl-2-(phenylbuta-1,3-diyne-1-yl)benzene (S10) (294 mg, 1.3 mmol), dimethyl 2,2-bis(3-bromoprop-2-yn-1-yl)malonate (220 mg, 0.60 mmol), CuCl (13 mg, 0.13 mmol), \(n\)-butylamine/H\(_2\)O (v:v, 30:70, 5.0 mL), and DCM (5.0 mL). Purification by flash chromatography (hexanes:EtOAc 5:1) provided octayne S11 (308 mg, 0.47 mmol, 78%) as a pale yellow solid.

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.55 (d, \(J = 7.3\) Hz, 4H, \(H2\')), 7.51 (d, \(J = 7.6\) Hz, 2H, \(H3\) or \(H6\)), 7.48 (d, \(J = 7.6\) Hz, 4H, \(H6\) or \(H3\)), 7.38–7.27 (m, 10H, \(H4\), \(H5\), \(H3\)' and \(H4\)'), 3.80 (s, 6H, \(CO_2CH_3\)), and 3.25 (s, 4H, \(\equiv CC\)H\(_2\)).

\(^13\)C NMR (126 MHz, CDCl\(_3\)): \(\delta\) 168.8, 133.4, 133.2, 132.7, 129.5, 128.90, 128.89, 128.6, 125.7, 125.3, 121.8, 83.2, 79.6, 79.5, 78.2, 78.1, 74.11, 74.10, 68.7, 57.0, 53.6, and 24.6.

IR (neat): 3061, 2955, 2926, 2855, 2244, 2215, 1742, 1478, 1442, 1335, 1304, 1289, 1210, 1068, 1052, 950, 858, and 755 cm\(^{-1}\).

HRMS (ESI-TOF): Calcd for C\(_{47}\)H\(_{28}\)NaO\(_4\)\(^{+}\) [M+Na\(^+\)] requires 679.1880; found 679.1844.

Mp: 80–83 °C.
Synthesis of S14

Following general procedure A, ((2-ethynylphenyl)ethynyl)trimethylsilane (240 mg, 1.2 mmol), 3-bromoprop-2-yn-1-ol (243 mg, 1.8 mmol), CuCl (12 mg, 0.12 mmol), n-butylamine/H$_2$O (v:v, 30:70, 6.0 mL), and DCM (6.0 mL) were used to prepare crude triyne S12-TMS (265 mg, ~1.0 mmol), which was used directly in the subsequent step without flash chromatography.

Bromoalkyne S12 was synthesized following general procedure B from crude S12-TMS (265 mg, ~1.0 mmol), N-bromosuccinimide (NBS, 205 mg, 1.2 mmol), AgNO$_3$ (17 mg, 0.10 mmol), and acetone (10 mL). Purification by flash chromatography (hexanes:EtOAc 4:1) afforded S12 (255 mg, 0.99 mmol, 82% over two steps, containing 3 wt% EtOAc based on integrations in $^1$H NMR spectrum, 80% corrected yield) as a light brown oil.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.48 (nfoddd, $J = 7.6, 1.7$ Hz, 1H, $H_o$ or $H_o'$), 7.44 (nfoddd, $J = 7.6, 1.5$ Hz, 1H, $H_o'$ or $H_o$), 7.30 (nfoddd, $J = 7.5, 7.5, 1.8$ Hz, 1H, $H_m$ or $H_m'$), 7.29 (nfoddd, $J = 7.8, 7.8, 1.7$ Hz, 1H, $H_m'$ or $H_m$), 4.45 (s, 2H, $CH_2$OH), and 1.75 (br s, 1H, OHO).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 133.2, 132.7, 129.1, 128.5, 126.5, 124.6, 81.8, 78.3, 76.9, 76.7, 70.6, 54.9, and 51.9.

IR (neat): 3343, 2925, 2855, 2239, 2196, 1478, 1443, 1356, 1275, 1260, 1182, 1083, 1016, and 757 cm$^{-1}$.

HRMS (ESI-TOF): Calcd for C$_{13}$H$_7^{79}$BrNaO$^+$ [M+Na$^+$] requires 280.9572; found 280.9567.
5-(2-((2-Methoxyphenyl)buta-1,3-diy-1-yl)phenyl)penta-2,4-diy-1-ol (S13)

Tetrayne S13 was prepared following general procedure A from bromoalkyne S12 (181 mg, 0.70 mmol), 1-ethynyl-2-methoxybenzene (111 mg, 0.84 mmol), CuCl (7 mg, 0.070 mmol), n-butylamine/H₂O (v:v, 30:70, 3.5 mL), and DCM (3.5 mL). Purification by flash chromatography (hexanes:EtOAc 2.5:1) provided tetrayne S13 (165 mg, 0.53 mmol, 76%) as a pale yellow oil.

¹H NMR (500 MHz, CDCl₃): δ 7.52 (d, J = 7.4 Hz, 1H, H₆), 7.52 (dd, J = 7.6, 1.9 Hz, 1H, H₉ or H₉’), 7.49 (dd, J = 7.6, 1.9 Hz, 1H, H₉’ or H₉), 7.35 (dd, J = 8.4, 7.6, 1.7 Hz, 1H, H₄), 7.32 (dd, J = 7.5, 7.5 1.7 Hz, 1H, H₆ or H₆’), 7.30 (dd, J = 7.7, 7.7, 1.7 Hz, 1H, H₆’ or H₆), 6.93 (dd, J = 7.6, 0.9 Hz, 1H, H₅), 6.90 (br d, J = 8.3 Hz, 1H, H₃), 4.45 (d, J = 3.7 Hz, 2H, CH₂OH), 3.92 (s, 3H, OCH₃), and 1.68 (t, J = 3.9 Hz, 1H, CH₂OH).

¹³C NMR (126 MHz, CDCl₃): δ 161.6, 134.7, 133.40, 133.39, 131.0, 129.1, 128.8, 125.9, 124.9, 120.7, 111.1, 110.9, 82.0, 80.0, 79.9, 78.6, 77.9, 77.3, 76.8, 70.8, 56.0, and 51.9.

IR (neat): 3355, 3006, 2931, 2837, 2211, 1594, 1573, 1492, 1478, 1463, 1434, 1277, 1258, 1250, 1162, 1117, 1084, 1020, and 754 cm⁻¹.

HRMS (ESI-TOF): Calcd for C₂₂H₁₄NaO₂⁺ [M+Na⁺] requires 333.0886; found 333.0889.

5-(2-((2-Methoxyphenyl)buta-1,3-diy-1-yl)phenyl)penta-2,4-diy-1-yl propiolate (S14)

Tetrayne S13 (124 mg, 0.40 mmol), 4-dimethylaminopyridine (DMAP, 5.0 mg, 0.045 mmol), and propionic acid (37 µL, 0.60 mmol) were dissolved in anhydrous DCM (5.0 mL) and stirred at 0 °C. N,N-Dicyclohexycarbodiimide (DCC*, 90 mg, 0.44 mmol) was added to the solution, after which the headspace of the reaction flask was purged with N₂. The resulting brown
suspension was warmed to room temperature and stirred for 16 h. The crude reaction mixture was filtered by passing through a short silica plug, concentrated, and purified by flash chromatography (hexanes:EtOAc 2:1) to give pentayne \textbf{S14} (135 mg, 0.37 mmol, 93\%) as a yellowish oil.

*CAUTION: DCC is an irritant and can lead to sensitization. Avoid any direct contact with the skin and inhalation.

\textbf{1H NMR} (500 MHz, CDCl$_3$): $\delta$ 7.52 (d, $J = 7.9$ Hz, 1H, H6), 7.52 (nfodd, $J = 7.5, 1.7$ Hz, 1H, $H_o$ or $H_o'$), 7.50 (nfodd, $J = 7.5, 1.7$ Hz, 1H, $H_o'$ or $H_o$), 7.35 (dd, $J = 8.0, 8.0$ Hz, 1H, H4), 7.33 (nfoddd, $J = 7.6, 7.6, 1.6$ Hz, 1H, $H_m$ or $H_m'$), 6.93 (dd, $J = 7.5, 7.5$ Hz, 1H, H5), 6.90 (d, $J = 8.4$ Hz, 1H, H3), 4.96 (s, 2H, CH$_2$O), 3.92 (s, 3H, OCH$_3$), and 2.95 (s, 1H, C≡CH).

\textbf{13C NMR} (126 MHz, CDCl$_3$): $\delta$ 161.6, 151.8, 134.7, 133.6, 133.4, 131.0, 129.3, 128.8, 126.0, 124.5, 120.7, 111.0, 110.8, 80.0, 79.8, 78.7, 77.8, 77.5, 76.3 (2x), 76.1, 73.9, 72.5, 56.0, and 54.2.

IR (neat): 3284, 3012, 2945, 2838, 2241, 2212, 2122, 1721, 1594, 1493, 1479, 1463, 1434, 1367, 1277, 1259, 1208, 1118, 1022, 961, and 754 cm$^{-1}$.

\textbf{HRMS} (ESI-TOF): Calcd for C$_{25}$H$_{14}$NaO$_3^+$ [M+Na$^+$] requires 385.0835; found 385.0843.

**Synthesis of S17**

\begin{center}
\includegraphics[width=\textwidth]{synthesis}\end{center}

\textbf{1-Ethynyl-4,5-dimethoxy-2-((4-methoxyphenyl)buta-1,3-diyn-1-yl)benzene (S15)}

Triyne \textbf{S15} was synthesized following general procedure A from 1,2-diethynyl-4,5-dimethoxybenzene (614 mg, 3.3 mmol), 1-(bromoethynyl)-4-methoxybenzene\textsuperscript{7} (633 mg, 3.0 mmol), CuCl (33 mg, 0.33 mmol), n-butylamine/H$_2$O (v:v, 30:70, 15 mL), and
DCM (15 mL). Purification by flash chromatography (hexanes:EtOAc 5:1) provided triyne **S15** (389 mg, 1.23 mmol, 41%) as a pale yellow solid.

**1H NMR** (500 MHz, CDCl₃): δ 7.47 (nfod, J = 8.7 Hz, 2H, H₀), 6.97 (s, 1H, H₂ or H₅), 6.95 (s, 1H, H₅ or H₂), 6.86 (nfod, J = 8.7 Hz, 2H, H₆), 3.89 (s, 3H, OCH₃), 3.88 (s, 3H, OCH₃), 3.82 (s, 3H, OCH₃), and 3.32 (s, 1H, C≡CH).

**13C NMR** (126 MHz, CDCl₃): δ 160.5, 149.7, 149.5, 134.3, 118.8, 118.2, 114.9, 114.9, 114.3, 113.9, 82.8, 82.0, 80.4, 79.5, 76.8, 73.0, 56.2⁺, 56.2⁻, and 55.5.

**IR** (neat): 3277, 2999, 2937, 2837, 2209, 2141, 1594, 1506, 1462, 1441, 1358, 1291, 1255, 1220, 1190, 1174, 1119, 1032, 851, and 828 cm⁻¹.

**HRMS** (ESI-TOF): Calcd for C₂₁H₁₆NaO₃⁺ [M+Na⁺] requires 339.0992; found 339.0980.

**Mp**: 132–135 °C.

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1-(Bromoethynyl)-4,5-dimethoxy-2-((4-methoxyphenyl)buta-1,3-diyln-1-yl)benzene (S16)

Bromoalkyne **S16** was synthesized following general procedure B from triyne **S15** (300 mg, 0.95 mmol), N-bromosuccinimide (NBS, 186 mg, 1.0 mmol), AgNO₃ (16 mg, 0.094 mmol), and acetone (10 mL). Purification by flash chromatography (hexanes:EtOAc 4:1) afforded **S16** (350 mg, 0.89 mmol, 93%) as a light orange solid.

**1H NMR** (500 MHz, CDCl₃): δ 7.49 (nfod, J = 8.8 Hz, 2H, H₀), 6.95 (s, 1H, H₂ or H₅), 6.91 (s, 1H, H₅ or H₂), 6.86 (nfod, J = 8.9 Hz, 2H, H₆), 3.883 (s, 3H, OCH₃), 3.877 (s, 3H, OCH₃), and 3.83 (s, 3H, OCH₃).

**13C NMR** (126 MHz, CDCl₃): δ 160.5, 149.7, 149.4, 134.3, 119.5, 118.1, 114.9, 114.8, 114.3, 113.9, 82.8, 79.5, 78.6, 76.8, 73.1, 56.2⁺, 56.2⁻, 55.5, and 53.0.

**IR** (neat): 3005, 2963, 2935, 2911, 2837, 2209, 2140, 1601, 1506, 1462, 1441, 1363, 1254, 1218, 1132, 1016, 860, and 833 cm⁻¹.

**HRMS** (ESI-TOF): Calcd for C₂₁H₁₅⁷⁹BrNaO₃⁺ [M+Na⁺] requires 417.0097; found 417.0102.

**Mp**: 117–119 °C.
N-((4,5-Dimethoxy-2-((4-methoxyphenyl)buta-1,3-diyn-1-yl)phenyl)buta-1,3-diyn-1-yl)-4-methyl-N-(2-((trimethylsilyl)ethynyl)phenyl)benzenesulfonamide (S17)

Pentayne S17 was synthesized following general procedure A from N-ethynyl-4-methyl-N-(2-((trimethylsilyl)ethynyl)phenyl)benzenesulfonamide\(^8\) (121 mg, 0.33 mmol), bromoalkyne S16 (120 mg, 0.30 mmol), CuCl (1.6 mg, 0.017 mmol), \(n\)-butylamine/H\(_2\)O (v:v, 30:70, 1.5 mL), and DCM (1.5 mL). Purification by flash chromatography (hexanes:EtOAc 3:1) provided triyne S17 (122 mg, 0.18 mmol, 60%) as a yellow solid.

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.70 (nfod, J = 8.3 Hz, 2H, \(H_o\)’), 7.455 (nfom, 1H, \(H_3\)’), 7.451 (nfod, J = 8.8, 2H, \(H_o\)), 7.33–7.27 (nfom, 3H, \(H_4\)’, \(H_5\)’ and \(H_6\)’), 6.92 (s, 1H, \(H_2\) or \(H_5\)), 6.88 (s, 1H, \(H_5\) or \(H_2\)), 6.84 (nfod, J = 8.9 Hz, 2H, \(H_m\)’), 3.86 (s, 3H, OC\(_3\)H\(_3\)), 3.84 (s, 3H, OC\(_3\)H\(_3\)), 3.80 (s, 3H, OC\(_3\)H\(_3\)), 2.39 (s, 3H, ArC\(_3\)H\(_3\)), and 0.20 [s, 9H, Si\((\text{CH}_3)_3\)].

\(^1^3\)C NMR (126 MHz, CDCl\(_3\)): \(\delta\) 160.4, 149.6, 149.5, 145.2, 138.3, 134.4, 134.2, 134.0, 129.9, 129.2, 129.1, 128.5, 122.6, 118.9, 118.4, 115.1, 115.0, 114.2, 113.8, 102.3, 99.4, 82.9, 80.3, 79.5, 77.1, 76.9, 74.7, 73.3, 59.1, 56.1, 56.1, 55.4, 21.8, and -0.2.

IR (neat): 3000, 2960, 2933, 2897, 2837, 2229, 2157, 1601, 1508, 1450, 1377, 1255, 1217, 1179, 1124, 1022, and 853 cm\(^{-1}\).

HRMS (ESI-TOF): Calcd for C\(_{41}\)H\(_{35}\)N\(_3\)O\(_2\)SSi\(^+\) [M+Na\(^+\)] requires 704.1897; found 704.1880.

\(\text{Mp: } 70–72 \, ^\circ\text{C}.

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**Synthesis of S20**

\(\text{S10} \xrightarrow{\text{NBS}} \text{S18} \xrightarrow{\text{CuCl}} \text{S19} \xrightarrow{\text{MnO}_2} \text{S20}\)
1-(Bromoethyl)-2-(phenylbuta-1,3-diyn-1-yl)benzene (S18)

Bromoalkyne S18 was synthesized following general procedure B from 1-ethyl-2-(phenylbuta-1,3-diyn-1-yl)benzene (S10) (339 mg, 1.5 mmol), N-bromosuccinimide (NBS, 294 mg, 1.6 mmol), AgNO₃ (26 mg, 0.15 mmol), and acetone (15 mL). Purification by flash chromatography (hexanes:EtOAc 20:1) afforded S18 (407 mg, 1.33 mmol, 89%) as a pale yellow solid.

\[^1\text{H}\ \text{NMR}\ (500\ \text{MHz, CDCl}_3): \delta\ 7.56\ (nfod, J = 8.0\ \text{Hz}, 2\ H, H_2), 7.52\ (nfodd, J = 7.5, 1.6\ \text{Hz}, 1\ H, H_6\text{ or }H_6^{\prime}), 7.47\ (nfodd, J = 7.5, 1.6\ \text{Hz}, 1\ H, H_6^{\prime}\text{ or }H_6), 7.41–7.33\ (m, 3\ H, H3\text{ and }H4),\text{ and }7.31\ (dd, J = 7.5, 7.5\ \text{Hz}, 1\ H, H_m\text{ or }H_m^{\prime}),\text{ and }7.30\ (dd, J = 7.5, 7.5\ \text{Hz}, 1\ H, H_m\text{ or }H_m^{\prime}).\]

\[^{13}\text{C}\ \text{NMR}\ (126\ \text{MHz, CDCl}_3): \delta\ 133.2, 132.8, 132.7, 129.5, 128.9, 128.6, 128.5, 126.3, 125.1, 121.9, 82.9, 79.7, 78.5, 77.8, 74.1,\text{ and }54.9.\]

IR (neat): 3060, 2215, 2196, 1594, 1491, 1476, 1442, 1176, 1098, 1027, 950, 915, and 754 cm⁻¹.

HRMS (ESI-TOF): Calcd for C₁₈H₇₉BrNa⁺ [M+Na⁺] requires 326.9780; found 326.9801.

Mp: 65–67 °C.

1-(2-((2-(Phenylbuta-1,3-diyn-1-yl)phenyl)buta-1,3-diyn-1-yl)phenyl)-3-(trimethylsilyl)prop-2-yn-1-ol (S19)

Pentayne S19 was prepared following general procedure A from bromoalkyne S18 (336 mg, 1.1 mmol), 1-(2-ethylphenyl)-3-(trimethylsilyl)prop-2-yn-1-ol⁹ (228 mg, 1.0 mmol), CuCl (5.0 mg, 0.050 mmol), n-butylamine/H₂O (v:v, 30:70, 5.0 mL), and DCM (5.0 mL). Purification by flash chromatography (hexanes:EtOAc 8:1) provided tetrayne S19 (404 mg, 0.90 mmol, 90%) as a light orange solid.

\[^1\text{H}\ \text{NMR}\ (500\ \text{MHz, CDCl}_3): \delta\ 7.74\ (dd, J = 7.9, 1.2\ \text{Hz}, 1\ H, H_o), 7.60–7.54\ (m, 5\ H,\text{ remaining ortho-ArH}), 7.43\ (ddd, J = 7.6, 7.6, 1.3\ \text{Hz}, 1\ H, H_m\text{ or }H_m^{\prime}),\text{ and }7.40–7.31\ (m, 6\ H,\text{ remaining meta and para-ArH}),\text{ and }5.89\ (s, 1\ H, \text{CHOH}), 2.69\ (br\ s, 1\ H, \text{OH})\text{, and }0.23\ [s, 9\ H, \text{Si(CH}_3)_3].\]
**13C NMR** (126 MHz, CDCl3): \( \delta \) 143.5, 133.8, 133.3, 132.6, 129.9, 129.4, 129.4, 129.1, 128.9, 128.5, 128.4, 127.0, 125.4, 125.2, 121.7, 120.3, 104.3, 91.9, 83.4, 81.0, 80.3, 79.5, 79.2, 78.4, 78.0, 74.1, 63.4, and -0.1.

**IR** (neat): 3405, 3060, 2961, 2213, 2174, 1475, 1442, 1275, 1250, 1037, 982, 846, and 755 cm\(^{-1}\).

**HRMS** (ESI-TOF): Calcd for C\(_{32}\)H\(_{24}\)NaOSi\(^+\) [M+Na\(^+\)] requires 475.1489; found 475.1464.

**Mp:** 97–100 °C.

1-(2-((2-(Phenylbuta-1,3-diyn-1-yl)phenyl)buta-1,3-diyn-1-yl)phenyl)-3-(trimethylsilyl)prop-2-yn-1-one (S20)

Activated manganese dioxide (1.1 g, ~15 equiv.) was added to a stirred solution of pentayne S19 (342 mg, 0.76 mmol) in DCM (8.0 mL). After being stirred for 2 hours, the reaction mixture was filtered by passing through a Celite\textsuperscript{®} plug, the filtrate was concentrated, and the residue was purified by flash chromatography (hexanes:EtOAc 10:1) to provide ketone S20 (331 mg, 0.74 mmol, 97%) as a pale yellow solid.

**1H NMR** (500 MHz, CDCl3): \( \delta \) 8.12 (dd, \( J = 7.8, 1.3 \) Hz, 1H, \( H_o \)), 7.70 (d, \( J = 7.7, 1.2 \) Hz, 1H, \( H_o' \)), 7.58–7.53 (m, 5H, remaining ortho-\( H \) and \( H_m' \)), 7.48 (ddd, \( J = 7.7, 7.7, 1.3 \) Hz, 1H, \( H_m \)), 7.37–7.31 (m, 5H, remaining meta-\( H \)), and 0.32 [s, 9H, Si(CH\(_3\))\(_3\)].

**13C NMR** (126 MHz, CDCl3): \( \delta \) 176.5, 139.0, 135.9, 133.43, 133.35, 132.72, 132.70, 131.9, 129.4, 129.1, 129.0, 128.9, 128.5, 125.4, 125.3, 121.8, 121.7, 101.8, 101.5, 83.3, 81.7, 81.3, 80.1, 79.6, 78.5, 78.4, 74.2, and -0.6.

**IR** (neat): 3061, 2962, 2153, 1649, 1588, 1561, 1475, 1442, 1296, 1251, 1236, 1015, 847, and 754 cm\(^{-1}\).

**HRMS** (ESI-TOF): Calcd for C\(_{32}\)H\(_{22}\)NaOSi\(^+\) [M+Na\(^+\)] requires 473.1332; found 473.1342.

**Mp:** 120–126 °C (with decomposition beginning at ca. 108 °C).
Synthesis of S22

1-(2-((4,5-Dimethoxy-2-((4-methoxyphenyl)buta-1,3-diyn-1-yl)phenyl)buta-1,3-diyn-1-yl)phenyl)-3-(trimethylsilyl)prop-2-yn-1-ol (S21)

Pentayne S21 was synthesized following general procedure A from 1-(2-ethynylphenyl)-3-(trimethylsilyl)prop-2-yn-1-ol\(^9\) (205 mg, 0.90 mmol), bromoalkyne S16 (316 mg, 0.80 mmol), CuCl (5.0 mg, 0.050 mmol), \(n\)-butylamine/H\(_2\)O (v:v, 30:70, 5.0 mL), and DCM (5.0 mL). Purification by flash chromatography (hexanes:EtOAc 4:1 to 2:1) provided pentayne S21 (298 mg, 0.55 mmol, 69\%) as an orange oil.

\(^{1}\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.73 (br d, \(J = 7.8\) Hz, 1H, \(H3'\)), 7.57 (dd, \(J = 7.5, 1.3\) Hz, 1H, \(H6'\)), 7.49 (nfod, \(J = 8.9\) Hz, 2H, \(H_o\)), 7.42 (ddd, \(J = 7.7, 7.7, 1.3\) Hz, 1H, \(H4'\) or \(H5'\)), 7.31 (ddd, \(J = 7.7, 7.7, 1.3\) Hz, 1H, \(H5'\) or \(H4'\)), 6.98 (s, 1H, \(H2\) or \(H5\)), 6.97 (s, 1H, \(H5\) or \(H2\)), 6.85 (nfod, \(J = 8.9\) Hz, 2H, \(H_m\)), 5.89 (br s, 1H, CHO\(_3\)), 3.901 (s, 3H, OCH\(_3\)), 3.895 (s, 3H, OCH\(_3\)), 3.82 (s, 3H, OCH\(_3\)), 2.54 (br s, 1H, CHO\(_3\)), and 0.20 [s, 9H, Si(CH\(_3\))\(_3\)].

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \(\delta\) 160.5, 150.0, 149.7, 143.5, 134.3, 133.8, 129.8, 128.5, 127.2, 120.6, 119.0, 118.2, 115.12, 115.10, 114.3, 113.9, 104.2, 92.0, 83.3, 81.5, 79.9, 79.5, 79.3, 77.5, 76.7, 73.1, 63.5, 56.2 (x2), 55.5, and -0.0.

IR (neat): 3495, 3005, 2961, 2837, 2209, 2172, 2144, 1602, 1506, 1463, 1442, 1378, 1290, 1252, 1218, 1140, 1031, 1052, 844, and 760 cm\(^{-1}\).

HRMS (ESI-TOF): Calcd for C\(_{39}\)H\(_{29}\)NaO\(_4\)Si\(^+\) [M+Na\(^+\)] requires 565.1806; found 565.1816.
1-(2-((4,5-Dimethoxy-2-((4-methoxyphenyl)buta-1,3-diyn-1-yl)phenyl)buta-1,3-diyn-1-yl)phenyl)-3-(trimethylsilyl)prop-2-yn-1-one (S22)

Activated manganese dioxide (0.5 g, ~10 equiv.) was added to a stirred solution of pentayne S21 (271 mg, 0.50 mmol) in DCM (5.0 mL). After stirring for 5 hours, the reaction mixture was filtered by passing through a Celite® plug. The filtrate was concentrated to provide ketone S22 (270 mg, 0.50 mmol, quantitative) as a yellow solid, sufficiently pure for characterization and further use.

**1H NMR** (500 MHz, CDCl₃): δ 8.11 (dd, J = 7.9, 1.1 Hz, 1H, H6'), 7.68 (dd, J = 7.8, 1.0 Hz, 1H, H3'), 7.52 (dd, J = 7.5, 7.5, 1.3 Hz, 1H, H4' or H5'), 7.48 (nfd, J = 8.8 Hz, 2H, H0), 7.46 (ddd, J = 7.7, 7.7, 1.2 Hz, 1H, H5' or H4'), 6.98 (s, 1H, H2 or H5), 6.96 (s, 1H, H5 or H2), 6.84 (nfd, J = 8.7 Hz, 2H, Hm), 3.89 (s, 3H, OCH₃), 3.89 (s, 3H, OCH₃), 3.81 (s, 3H, OCH₃), and 0.31 [s, 9H, Si(CH₃)₃].

**13C NMR** (126 MHz, CDCl₃): δ 176.5, 160.5, 150.0, 149.7, 139.0, 135.8, 134.3, 132.7, 131.9, 128.8, 121.9, 118.9, 118.4, 115.3, 115.1, 114.2, 113.9, 101.7, 101.5, 83.2, 82.2, 80.9, 80.4, 79.3, 77.5, 77.3, 73.2, 56.2 (x2), 55.4, and -0.6.

**IR** (neat): 3003, 2957, 2934, 2905, 2835, 2203, 2151, 1648, 1598, 1508, 1377, 1249, 1220, 1019, and 847 cm⁻¹.

**HRMS** (ESI-TOF): Calcd for C₃₅H₂₈NaO₄Si⁺ [M+Na⁺] requires 563.1649; found 563.1643.

**Mp:** 145–146 °C.
Synthesis of 29

Following general procedure A, (2-ethylphenyl)ethynyl)trimethylsilane (0.99 g, 5.0 mmol), 1-(bromoethyl)-4-chlorobenzene (1.10 g, 5.1 mmol), CuCl (25 mg, 0.25 mmol), n-butylamine/H$_2$O (v:v, 30:70, 25 mL), and DCM (25 mL) were used to prepare crude triyne S23-TMS (1.60 g, ~4.8 mmol), which was used directly in the subsequent step without purification due to solubility issues.

To a stirred solution of the crude S23-TMS (1.60 g, ~4.8 mmol) and N-bromosuccinimide (NBS, 1.78 g, 10 mmol) in acetone (50 mL) and DCM (50 mL), AgNO$_3$ (85 mg, 0.50 mmol) was added under N$_2$. After stirring for 24 h, the reaction mixture was filtered through a short silica plug, eluted with DCM, and concentrated. Purification by flash chromatography (hexanes:EtOAc 9:1) afforded S23 (1.30 g, 3.83 mmol, 77% over two steps), which contained a trace (less than 1%) of coeluting S23-TMS based on integrations in $^1$H NMR spectrum (76% corrected yield) as a pale yellow solid.
**1H NMR** (500 MHz, CDCl₃): δ 7.53–7.43 (m, 4H, Hₐ), and 7.34–7.28 (m, 4H, Hₖ).

**13C NMR** (126 MHz, CDCl₃): δ 135.6, 133.9, 133.2, 132.8, 129.1, 129.0, 128.5, 126.4, 124.9, 120.4, 81.7, 80.3, 78.4, 77.5, 75.1, and 55.0.

**IR** (neat): 3060, 2955, 2239, 1487, 1472, 1438, 1205, 1088, 1012, 949, 834, 822 and 809 cm⁻¹.

**HRMS** (ESI-TOF): Calcd for C₁₈H₂₀Br⁺ [M⁺] requires 444.8543; found 444.8554.

**Mp:** 88–90 °C.

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1-(4-Chlorophenyl)buta-1,3-diyn-1-yl)-2-((2-(2-ethynylphenyl)buta-1,3-diyn-1-yl)phenyl)buta-1,3-diyn-1-yl)benzene (S24)

Following general procedure A, 1,4-bis(2-ethynylphenyl)buta-1,3-diyne (S6) (875 mg, 3.5 mmol), bromoalkyne S23 (1.02 g, 3.0 mmol), CuCl (15 mg, 0.15 mmol), n-butylamine/H₂O (v:v, 30:70, 15 mL), and DCM (15 mL) were used. Purification by flash chromatography (hexanes:EtOAc 8:1) provided heptayne S24 (662 mg, 1.30 mmol, 43%) as a pale yellow solid.

**1H NMR** (500 MHz, CDCl₃): δ 7.59–7.52 (m, 5H, H₂ and H₃), 7.48 (dd, J = 2.0, 6.7 Hz, 1H, H₆), 7.44 (nfod, J = 8.6 Hz, 2H, H₀'), 7.37–7.31 (m, 4H, Hₘ), 7.29 (m, 2H, H₄ and H₅), 7.27 (nfod, J = 8.6 Hz, 2H, Hₘ'), and 3.39 (s, 1H, =CH).

**13C NMR** (126 MHz, CDCl₃): δ 135.6, 133.9, 133.54, 133.46, 133.4 (x2), 133.1, 132.7, 129.11 (x2), 129.08, 129.05, 129.01, 128.9, 128.6, 125.9, 125.51, 125.46, 125.44, 125.36, 125.0, 120.3, 82.1 (x2), 81.6, 81.5, 81.2, 81.1, 80.8, 80.1, 78.4, 78.3, 78.2, 77.8, 77.4, and 75.1.

**IR** (neat): 3288, 3056, 2925, 2855, 2212, 1505, 1488, 1472, 1438, 1205, 1088, 1012, 949, 834, 822 and 809 cm⁻¹.

**HRMS** (ESI-TOF): Calcd for C₃₈H₇ClNa⁺ [M⁺] requires 531.0911; found 531.0917.

**Mp:** 140–148 °C (with decomposition > 132 °C).
1-(Bromoethyl)-2-((2-((4-chlorophenyl)buta-1,3-diyn-1-yl)phenyl)buta-1,3-diyn-1-yl)phenyl)buta-1,3-diyn-1-yl)benzene (S25)

To a stirred solution of heptayne S24 (575 mg, 1.1 mmol) and N-bromosuccinimide (NBS, 402 mg, 2.3 mmol) in acetone (11 mL) and DCM (11 mL), AgNO₃ (19 mg, 0.11 mmol) was added under N₂. After stirring for 4 h, the reaction mixture was filtered by passing through a short silica plug, which was then washed with DCM. The filtrate was concentrated and the residue purified by flash chromatography (hexanes:EtOAc 10:1) to afford bromoalkyne S25 (544 mg, 0.93 mmol, 82%) as a yellowish oil.

**¹H NMR** (500 MHz, CDCl₃): δ 7.60–7.55 (m, 3H, Hₖ), 7.54 (m, 1H, Hₖ'), 7.51 (dd, J = 6.9, 2.1 Hz, 1H, H₃), 7.44 (m, J = 8.5 Hz, 2H, Hₖ), 7.42 (dd, J = 6.6, 2.2 Hz, 1H, H₆), 7.37–7.32 (m, 4H, Hₘ), 7.28 (m, 2H, H₄ and H₅), and 7.26 (m, J = 8.6 Hz, 2H, Hₘ').

**¹³C NMR** (126 MHz, CDCl₃): δ 135.6, 133.9, 133.53, 133.50, 133.46, 133.4, 133.2, 132.5, 129.11, 129.09, 129.07, 129.05, 129.0, 128.9, 128.4, 126.5, 125.47, 125.47, 125.4, 125.3, 125.0, 120.3, 82.1, 81.4, 81.2, 81.1, 80.8, 80.1, 78.43, 78.37, 78.36, 78.3, 78.2, 77.8, 75.1, and 55.4.

**IR** (neat): 3062, 2969, 2931, 2215, 2198, 1589, 1490, 1473, 1444, 1400, 1264, 1095, 1010, 950, 830, and 755 cm⁻¹.

**HRMS** (ESI-TOF): Calcd for C₃₈H₁₆⁷⁹Br³⁵ClNa⁺ [M+Na⁺] requires 609.0016; found 609.0021.
1-(2-((2-((2-((4-Chlorophenyl)b u-ta-1,3-diyn-1-yl)phenyl)b u-ta-1,3-diyn-1-yl)phenyl)b u-ta-1,3-diyn-1-yl)phenyl)b u-ta-1,3-diyn-1-yl)phenyl)-3-(trimethylsilyl)prop-2-yn-1-ol (S26)

Nonayne S26 was synthesized following general procedure A from 1-(2-ethynylphenyl)-3-(trimethylsilyl)prop-2-yn-1-ol (228 mg, 1.0 mmol), bromoalkyne S25 (470 mg, 0.80 mmol), CuCl (5 mg, 0.05 mmol), n-butylamine/H2O (v:v, 30:70, 5.0 mL), and DCM (5.0 mL). Purification by flash chromatography (hexanes:EtOAc 5:1) gave nonayne S26 (426 mg, 0.58 mmol, 73%) as a brown viscous oil.

1H NMR (500 MHz, CDCl3): δ 7.71 (d, J = 7.9 Hz, 1H, H3), 7.61–7.49 (m, 7H, Ho), 7.42 (nfod, J = 8.6 Hz, 2H, H_o'), 7.40 (t, J = 7.7 Hz, 1H, H_m), 7.36–7.26 (m, 7H, H_m), 7.25 (nfod, J = 8.4 Hz, 2H, H_m'), 5.87 (s, 1H, CHO), 2.49 (br s, 1H, OH), and 0.20 [s, 9H, Si(CH3)3].

13C NMR (126 MHz, CDCl3): δ 143.5, 135.5, 133.89, 133.86, 133.57, 133.54, 133.50, 133.4, 133.33, 133.27, 129.9, 129.11, 129.07, 129.03, 129.02, 129.01, 128.9, 128.5 (x2), 127.1, 125.5, 125.41 (x2), 125.35, 125.34, 125.31, 120.5, 120.3, 104.2, 92.1, 82.1, 81.20, 81.19, 81.18, 81.0, 80.4, 80.1, 79.3, 78.45, 78.41, 78.39, 78.35, 78.2, 78.1, 77.4, 75.2, 63.5, and -0.03.

IR (neat): 3483, 3067, 2966, 2212, 2174, 1650, 1560, 1541, 1476, 1252, 1095, 1039, 1016, 981, and 821 cm⁻¹.

HRMS (ESI-TOF): Calcd for C52H3135ClNaOSi⁺ [M+Na⁺] requires 757.1725; found 757.1705.
1-(2-((2-((4-Chlorophenyl)buta-1,3-diyn-1-yl)phenyl)buta-1,3-diyn-1-yl)phenyl)buta-1,3-diyn-1-yl)phenyl)-3-(trimethylsilyl)prop-2-yn-1-one (29)

To a stirred solution of nonayne S26 (351 mg, 0.48 mmol) in DCM (5.0 mL), activated manganese dioxide (1.0 g, ~20 equiv.) was added. After stirring for 4 hours, the reaction mixture was filtered by passing through a Celite® plug and concentrated. Purification of the residue by flash chromatography (hexanes:EtOAc 4:1) provided ketone 29 (279 mg, 0.38 mmol, 79%) as a green solid.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.07 (d, $J = 7.7$ Hz, 1H, $H_6$), 7.68 (d, $J = 7.7$ Hz, 1H, $H_3$), 7.60 (nfodd, $J = 6.6$, 2.6 Hz, 1H, $H_0$), 7.56 (nfodd, $J = 6.4$, 2.7 Hz, 1H, $H_0$), 7.54–7.47 (m, 5H, $H_o$ and $H_4$), 7.44 (dd, $J = 7.8$, 7.8 Hz, 1H, $H_5$), 7.42 (nfod, $J = 8.4$ Hz, 1H, $H_o'$), 7.37–7.27 (m, 6H, $H_m$), 7.25 (nfod, $J = 8.6$ Hz, 2H, $H_m'$), and 0.32 [s, 9H, Si(CH$_3$)$_3$].

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 176.4, 138.8, 136.0, 135.5, 133.8, 133.6, 133.5 (x2), 133.39, 133.38, 133.2, 132.7 (x2), 131.8, 129.1, 129.03, 129.02 (x2), 128.98, 128.90, 128.89, 125.5, 125.40, 125.36, 125.32, 125.31, 125.27, 121.7, 120.3, 101.8, 101.5, 82.0, 81.7, 81.4, 81.25, 81.20, 81.17, 81.15, 80.2, 80.1, 78.7, 78.40, 78.36, 78.35, 78.1, 77.4, 75.2, and -0.5.

IR (neat): 3065, 2963, 2855, 2212, 2151, 1653, 1639, 1560, 1476, 1240, 1095, 1016, 955, 827, and 798 cm$^{-1}$.

HRMS (ESI-TOF): Calcd for C$_{52}$H$_{29}$ClNaOSi$^+$ [M+Na$^+$] requires 755.1568; found 755.1577.

Mp: 76–82 ºC (with decomposition > 70 ºC).
B. Procedures for syntheses of and characterization data for domino-HDDA products.

\((\pm)-(1R,4S)-1,4\text{-dimethyl}-11\text{-propyl}-4,5,6,10\text{-tetrahydro}-1,4\text{-epoxyacetanthryleno}[4,5\text{-c}]\text{furan-8(1H)}\text{-one (12)}\)

\[
\begin{align*}
\text{11} & \quad \text{12} \\
\text{9} & \quad \text{12 equiv} \\
\text{Me} & \quad \text{Me} \\
\text{(12 equiv)} & \quad \text{CHCl}_3 \\
\text{130 °C} & \quad 40 \text{ h} \\
& \quad 85\% \\
\end{align*}
\]

Naphthalene 12 was obtained following general procedure C from pentayne 9 (17 mg, 0.068 mmol), 2,5-dimethylfuran (86 \(\mu\)L, 0.8 mmol), and CHCl\(_3\) (3.4 mL). Purification by MPLC (hexanes:EtOAc, 1.5:1) afforded naphthalene 12 (20 mg, 0.058 mmol, 85\%) as a pale yellow viscous oil that turned into an amorphous solid upon storage at ca. -20 °C.

\(^1\text{H} \text{NMR (500 MHz, CDCl}_3\text{): } \delta 7.80 \text{ (s, 1H, ArH)}, 6.78 \text{ (d, } J = 5.2 \text{ Hz, 1H, alkene } H-a\text{), 6.76 \text{ (d, } J = 5.3 \text{ Hz, 1H, alkene } H-b\text{), 5.68 \text{ [d, } J = 15.4 \text{ Hz, 1H, } CH_2\text{H}_5\text{O(C=O)]}, 5.60 \text{ [d, } J = 15.3 \text{ Hz, 1H, } CH_2\text{H}_5\text{O(C=O)]}, 3.54-3.28 \text{ (m, 4H, ArCH}_2\text{CH}_2\text{Ar]), 3.02 \text{ (very br s, 1H, } CH_2\text{H}_5\text{CH}_2\text{CH}_3\text{), 2.75 \text{ (very br s, 1H, } CH_2\text{H}_5\text{CH}_2\text{CH}_3\text{), 2.11 \text{ [s, 3H, bridgehead } CH_3-a\text{], 2.02 \text{ [s, 3H, bridgehead } CH_3-b\text{], 1.59 \text{ (very br s, 1H, } CH_2\text{CH}_2\text{H}_5\text{CH}_3\text{), 1.47 \text{ (very br s, 1H, } CH_2\text{CH}_2\text{H}_5\text{CH}_3\text{), and 1.09 \text{ (t, } J = 7.3 \text{ Hz, 3H, } CH_2\text{CH}_2\text{CH}_3\text{).}}
\]

\(^{13}\text{C} \text{NMR (126 MHz, CDCl}_3\text{): } \delta 172.0, 149.9, 147.9, 146.2, 145.8, 144.8, 143.5, 142.1, 133.7, 128.2, 125.8, 124.9, 115.4, 90.2, 87.7, 70.8, 31.1 \text{ (br), 30.3, 28.0, 26.9 \text{ (br), 18.6, 16.5, and 14.3.}}
\]

\(\text{IR (neat): } 3006, 2975, 2937, 2879, 1755, 1453, 1387, 1360, 1279, 1260, 1148, 1086, 1029, 862, \text{ and 752 cm}^{-1}\).

\(\text{HRMS (ESI-TOF): } \text{Calcd for } C_{23}\text{H}_{32}\text{NaO}_3^+ [M+Na^+] \text{ requires 369.1461; found 369.1454.} \)

\((\pm)-(8S,11R)-7-((tert-Butyldimethylsilyl)oxy)methyl)-5,6,8,11,12,13\text{-hexahydro-8,11-epoxydiencyclopenta}[4,5:11,12]tetraceno[1,2-c][furan-3(1H)]-one (15)\)

\[
\begin{align*}
\text{13} & \quad \text{15} \\
\text{OTBS} & \quad \text{OTBS} \\
\text{(5 equiv)} & \quad \text{HO}_{\text{DCB}} \text{(0.02 M)} \\
\text{130 °C, 24 h} & \quad 88\% \\
\end{align*}
\]

Anthracene 15 was obtained following general procedure C from heptyne 13 (21 mg, 0.049 mmol), furan (18 \(\mu\)L, 0.25 mmol), and ortho-dichlorobenzene (2.5 mL). Purification by MPLC
(hexanes:EtOAc, 1.5:1) afforded the anthracene derivative 15 (21 mg, 0.042 mmol, 86%) as a pale yellow solid.

**1H NMR** (500 MHz, CDCl₃): δ 7.38 (s, 1H, ArH), 6.96 (dd, J = 5.5, 1.6 Hz, 1H, AlkeneHₐ), 6.95 (dd, J = 5.5, 1.6 Hz, 1H, AlkeneHₖ), 6.18 (br s, 1H, bridgehead CHₖ), 5.83 (br s, 1H, bridgehead CHₖ), 5.521 (d, J = 16.6 Hz, 1H, (C=O)OCHₐHₖ), 5.518 (d, J = 16.6 Hz, 1H, (C=O)OCHₐHₖ), 5.25 (d, J = 12.6 Hz, 1H, TBSOCHₐHₖ), 5.18 (d, J = 12.6 Hz, 1H, TBSOCHₐHₖ), 3.86 (br t, J = 5.8 Hz, 2H, H₅), 3.50–3.40 (m, 5H, H₆, H₁₂, and H₁₃ₐ), 3.37–3.28 (nfom, 1H, H₁₃ₖ), 0.96 [s, 9H, Si(C₃H₇)₃], 0.21 [s, 3H, Si(CH₃)₃(CH₃)₃], and 0.17 [s, 3H, Si(CH₃)₃(CH₃)₃].

**13C NMR** (126 MHz, CDCl₃): δ 172.3, 149.5, 145.6, 143.7, 142.6, 141.0, 140.6, 140.1, 139.8, 138.6, 135.9, 135.0, 125.9 (x2), 124.0, 119.8, 111.4, 81.4, 80.0, 69.9, 61.9, 32.5, 30.8, 30.5, 28.4, 26.2, 18.6, -4.8, and -4.9.

**IR** (neat): 2952, 2928, 2855, 1754, 1455, 1392, 1337, 1280, 1258, 1110, 1083, 1015, 870, 832, and 776 cm⁻¹.

**HRMS** (ESI-TOF): Calcd for C₃₁H₃₂NaO₄Si⁺ [M+Na⁺] requires 519.1962; found 519.1969.

**Mp:** 260–268 °C (with decomposition > ca. 225 °C).

(±)-Diethyl (8R,11S)-7-(((tert-Butyldimethylsilyl)oxy)methyl)-3-oxo-1,3,5,6,8,11,12,13-octahydro-8,11-epoxydicyclopenta[4,5:11,12]tetraceno[1,2-c]furan-9,10-dicarboxylate (16)

[Diagram of the reaction]

Anthracene 16 was obtained following general procedure C from heptayne 13 (64 mg, 0.15 mmol), diethyl furan-3,4-dicarboxylate (139 uL, 0.75 mmol), and CHCl₃ (7.5 mL). Purification by MPLC (hexanes:EtOAc, 1.2:1) afforded the anthracene derivative 16 (59 mg, 0.092 mmol, 61%) as a yellow solid.

**1H NMR** (500 MHz, CDCl₃): δ 7.32 (br t, J = 1.5 Hz, 1H, ArH), 6.38 (br s, 1H, bridgehead CHₖ), 6.04 (br s, 1H, bridgehead CHₖ), 5.30 (d, J = 15.8 Hz, 1H, (C=O)OCHₐHₖ), 5.26 (d, J = 15.8 Hz, 1H, (C=O)OCHₐHₖ), 5.20 (d, J = 12.1 Hz, 1H, TBSOCHₐHₖ), 5.17 (d, J = 12.1 Hz, 1H, TBSOCHₐHₖ), 4.30 (q, J = 7.1 Hz, 2H, OCH₂CH₃), 4.29 (q, J = 7.0 Hz, 2H, OCH₂CH₃), 4.16–4.09 (nfom, 1H, H₁₃ₖ), 3.73–3.64 (nfom, 1H, H₁₃ₖ), 3.47–3.22 (m, 6H, H₅, H₆, and H₁₂), 1.36
The rubicene-lactone 19 was obtained following general procedure C from heptayne 17 (19 mg, 0.039 mmol), furan (58 μL, 0.80 mmol), and CHCl₃ (8.0 mL). Purification by flash chromatography (hexanes:EtOAc, 2:1 to 1:1) afforded the rubicene derivative 19 (11 mg, 0.020 mmol, 51%) as a red solid.

**1H NMR** (500 MHz, CDCl₃): δ 8.10 (s, 1H, H12), 7.96–7.94 (nfom, 1H, H5), 7.94–7.92 (nfom, 1H, H8), 7.78 (d, J = 7.4 Hz, 1H, H13), 7.52–7.47 (m, 2H, H6 and H7), 7.23 (dd, J = 8.4, 2.2 Hz, 1H, H2’α), 7.20 (dd, J = 8.5, 2.3 Hz, 1H, H2’β), 7.19 (dd, J = 7.2, 7.2 Hz, 1H, H14), 7.16 (dd, J = 5.5, 1.7 Hz, 1H, H3), 7.12 (dd, J = 5.5, 1.7 Hz, 1H, H2), 7.08 (dd, J = 8.4, 2.6 Hz, 1H, H3’β), 6.95 (dd, J = 8.4, 2.5 Hz, 1H, H3’α), 6.80 (ddd, J = 8.1, 8.1, 0.8 Hz, 1H, H15), 6.46 (d, J = 1.6 Hz, 1H, H4), 5.97 (d, J = 15.6 Hz, 1H, OCH₃H₀), 5.97 (d, J = 15.6 Hz, 1H, OCH₃H₀), 5.84 (d, J = 8.0 Hz, 1H, H16), 5.76 (d, J = 1.6 Hz, 1H, H1), and 3.92 (s, 3H, OCH₃).

**13C NMR** (126 MHz, CDCl₃): δ 171.7, 160.0, 154.7, 151.8, 148.7, 145.6, 141.9, 140.5, 140.4, 139.0, 138.5, 138.0, 137.5, 137.1, 132.3, 132.2, 130.8, 128.3, 128.0, 127.9, 127.4, 127.2, 126.5, 123.2, 122.7, 120.7, 120.0, 115.0, 114.8, 113.7, 113.2, 81.5, 80.5, 73.4, and 55.8. A high-quality 1D 13C NMR spectrum not attainable because of limited solubility. The listed values are from the
1D spectrum, supplemented by additional resonances discerned from the HSQC & HMBC 2D spectra.

**IR** (neat): 2955, 2922, 2852, 1753, 1645, 1605, 1510, 1468, 1440, 1249, 1175, 1032, 874, 768, and 756 cm$^{-1}$.

**HRMS** (APCI$^+$): Calcd for C$_{39}$H$_{25}$O$_4^+$ [M+H$^+$] requires 555.1591; found 555.1588.

**Mp**: 340–347 ºC (with decomposition > ca. 275 ºC).

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(±)-(6S,9R)-5-(7-((tert-Butyldimethylsilyl)oxy)hepta-3,5-diyne-1-yl)-4-(9-((tert-butyldimethylsil yl)oxy)nona-1,5,7-triyn-1-yl)-2-(methylsulfonyl)-2,3,6,9-tetrahydro-1H-6,9-epoxybenzo[e]is oindole (21)

Isoindoline 21 was synthesized following general procedure C by heating octayne 20 (53 mg, 0.080 mmol) in furan (2.0 mL). Purification by MPLC (hexanes:EtOAc, 2:1) afforded the isoindoline derivative 21 (46 mg, 0.063 mmol, 79%) as a white solid.

**$^1$H NMR** (500 MHz, CDCl$_3$): δ 7.18 (dd, $J = 5.6, 1.9$ Hz, 1H, alkeneH), 6.98 (dd, $J = 5.6, 1.9$ Hz, 1H, alkeneH'), 5.84 (dd, $J = 1.8, 0.5$ Hz, 1H, bridgehead-H), 5.67 (dd, $J = 1.8, 0.6$ Hz, 1H, bridgehead-H'), 4.74 (dt, $J = 13.3, 1.7$ Hz, 1H, $H_1$), 4.64 (br t, $J = 1.7$ Hz, 2H, $H_3$), 4.62 (dt, $J = 13.3, 1.7$ Hz, 1H, $H_1$), 4.36 (s, 2H, =CCH$_2$O), 4.34 (s, 2H, =C‘CH$_2$O), 3.09 (dt, $J = 13.0, 6.1$ Hz, 1H, ArCH$_2$H$_2$CH$_2$C=), 3.09 (ddd, $J = 13.3, 8.4, 6.2$ Hz, 1H, ArCH$_2$H$_2$CH$_2$C=), 2.88 (s, 3H, SO$_2$CH$_3$), 2.72–2.65 (m, 2H, ArCH$_2$CH$_2$C=), 2.67 (t, $J = 6.6$ Hz, 2H, =CCH$_2$CH$_2$C=), 2.57 (t, $J = 6.7$ Hz, 2H, =CCH$_2$CH$_2$C=), 0.90 [s, 9H, Si(CH$_3$)$_3$], 0.89 [s, 9H, Si(CH$_3$)$_3$], 0.11 [s, 6H, Si(CH$_3$)$_3$], and 0.10 [s, 6H, Si(CH$_3$)$_3$].

**$^{13}$C NMR** (126 MHz, CDCl$_3$): δ 148.6, 144.2, 143.0, 141.4, 138.0, 133.6, 127.0, 114.8, 96.2, 81.3, 81.1, 80.0, 78.4, 77.3, 75.4, 75.2, 69.8, 69.6, 66.2, 65.8, 54.0, 52.5, 52.20, 52.18, 35.1, 30.0, 25.89, 25.87, 20.1, 19.8, 19.5, 18.36, 18.36, and -5.1 (x2).

**IR** (neat): 3019, 2954, 2929, 2893, 2857, 2255, 1471, 1463, 1365, 1321, 1256, 1146, 1086, 964, 838, 778, and 758 cm$^{-1}$.

**HRMS** (ESI-TOF): Calcd for C$_{41}$H$_{53}$NNaO$_2$SSi$_2^+$ [M+Na$^+$] requires 750.3075; found 750.3085.

**Mp**: 105–110 ºC (with decomposition > ca. 100 ºC).
Naphthalene 22 was synthesized following general procedure C from octayne 20 (53 mg, 0.080 mmol), furan (17 μL, 0.24 mmol), and CHCl₃ (8.0 mL). Purification by MPLC (hexanes:EtOAc, 2:1) afforded the naphthalene derivative 22 (50 mg, 0.069 mmol, 86%) as a white solid.

**¹H NMR** (500 MHz, CDCl₃): δ 6.99 (dd, J = 5.6, 1.5 Hz, 1H, alkeneH), 6.98 (dd, J = 5.6, 1.5 Hz, 1H, alkeneH'), 6.02 (d, J = 1.3 Hz, 1H, bridgehead-H), 5.83 (d, J = 1.3 Hz, 1H, bridgehead-H'), 5.22 (br t, J = 2.5 Hz, 2H, MsNCH₂), 4.92 (d, J = 12.1 Hz, 1H, ArCH₃HbO), 4.89 (d, J = 12.1 Hz, 1H, ArCH₃HbO'), 4.39 (s, 2H, ≡CC₂CH₂O), 4.89 (d, J = 12.1 Hz, 1H, ArCH₃HbO'), 4.81 (br t, J = 2.6 Hz, 2H, MsNCH₂'), 4.39 (s, 2H, ≡CC₂CH₂O), 3.40 – 3.18 (m, 4H, ArCH₃HbO'), 2.87 (s, 3H, SO₂CH₃), 2.75 (t, J = 7.1 Hz, 2H, ≡CC₂CH₂C'-), 2.65 (t, J = 7.2 Hz, 2H, ≡CC₂CH₂C'-), 0.95 [s, 9H, SiC(CH₃)₃j], 0.92 [s, 9H, SiC(CH₃)₃j], 0.20 [s, 3H, Si(CH₃)a(CH₃)b], 0.16 [s, 3H, Si(CH₃)a(CH₃)b], and 0.14 [s, 6H, Si(CH₃)₂].

**¹³C NMR** (126 MHz, CDCl₃): δ 149.6, 148.0, 141.6, 141.5, 139.0, 138.1, 136.9, 136.6, 132.1, 124.7, 124.1, 110.9, 95.1, 81.2, 80.5, 78.6, 77.6, 75.2, 69.7, 66.1, 60.9, 55.3, 54.0, 52.2, 34.5, 30.5, 28.0, 26.1, 25.9, 20.0, 19.6, 18.43, 18.38, -4.9, -5.0, and -5.1 (x2).

**IR** (neat): 3015, 2953, 2929, 2886, 2856, 2259, 1471, 1463, 1361, 1339, 1255, 1155, 1081, 960, 874, 839, 779, and 757 cm⁻¹.

**HRMS** (ESI-TOF): Calcd for C₄₁H₅₃NNaO₂SSi₂⁺ [M+Na⁺] requires 750.3075; found 750.3093. **Mp:** 166–170 °C (with decomposition > ca. 160 °C).
Fluoranthene 25a was obtained following general procedure C from octayne S11 (26 mg, 0.040 mmol), furan (14 μL, 0.19 mmol), and CHCl₃ (2.0 mL). Purification by flash chromatography (hexanes:EtOAc, 2:1) afforded fluoranthene 25a (26 mg, 0.036 mmol, 90%) as a yellow solid. Alternatively, fluoranthene 25a was obtained by a photochemical HDDA procedure. Pentayne S11 (26 mg, 0.040 mmol), furan (14 μL, 0.19 mmol), and CHCl₃ (2.0 mL) was added to a quartz tube and irradiated at 300 nm for 1 h at room temperature. Purification by flash chromatography (hexanes:EtOAc, 2:1) afforded fluoranthene 25a (20 mg, 0.027 mmol, 67%) as a yellow solid.

**¹H NMR** (500 MHz, CDCl₃): δ 8.78 (br d, J = 7.6 Hz, 1H, H10), 7.86 (br d, J = 7.5 Hz, 1H, H13), 7.72 (dd, J = 7.8, 1.0 Hz, 1H, H2' or H5'), 7.64 (dd, J = 7.7, 1.0 Hz, 1H, H5' or H2'), 7.56–7.29 (m, 13H, ArH), 7.24–7.21 (nfom, 1H, H-Ph para), 7.06 (dd, J = 5.5, 1.8 Hz, 1H, H2), 6.99 (dd, J = 5.5, 1.9 Hz, 1H, H3), 6.36 (dd, J = 1.8, 0.7 Hz, 1H, H1), 5.48 (dd, J = 1.9, 0.7 Hz, 1H, H4), 3.93 (d, J = 17.0 Hz, 1H, H8a), 3.92 (d, J = 17.0 Hz, 1H, H8b), 3.64 (s, 3H, OCH₃), 3.60 (s, 3H, OCH₃), 3.21 (d, J = 17.3 Hz, 1H, H6a), and 3.04 (d, J = 17.2 Hz, 1H, H6b).

**¹³C NMR** (126 MHz, CDCl₃): δ 172.14, 172.08, 147.5, 143.2, 142.5, 141.1, 139.8, 139.6, 138.7, 137.5, 137.4, 136.2, 133.6, 132.9, 132.7, 131.9, 130.9, 130.0, 129.5, 129.4, 129.1, 128.64, 128.58, 128.55, 128.47, 128.46, 128.3, 127.8, 127.5, 126.6, 124.6, 124.2, 123.8, 122.4, 121.9, 113.3, 97.1, 90.9, 83.5, 81.1, 80.7, 80.3, 78.4, 74.3, 60.0, 52.99, 52.97, 41.6, and 40.4.

**IR** (neat): 3056, 3018, 2951, 2843, 2214, 1735, 1481, 1442, 1433, 1257, 1200, 1163, 1072, 872, 830, and 754 cm⁻¹.

**HRMS** (ESI-TOF): Calcd for C₅₁H₃₂NaO₅⁺ [M+Na⁺] requires 747.2142; found 747.2153.

**Mp:** 145–150 °C.
Fluoranthenes 25b and 25b’ were obtained following general procedure C from pentayne S14 (20 mg, 0.055 mmol), furan (20 μL, 0.28 mmol), and CHCl₃ (2.8 mL). Purification by flash column chromatography (hexanes:EtOAc:DCM, 3:1:1) afforded the fluoranthenes as a 1.2:1 coeluting mixture (21 mg, 0.050 mmol, 90%, a pale yellow solid containing 4wt% DCM based on the ¹H NMR spectrum, 86% corrected yield).

**Major isomer**

¹H NMR (500 MHz, CDCl₃): δ 8.22 (s, 1H, H9), 7.93 (d, J = 7.1 Hz, 1H, H10 or H13), 7.89 (d, J = 7.0 Hz, 1H, H13 or H10), 7.55 (dd, J = 8.2, 8.2 Hz, 1H, H4’), 7.47–7.43 (m, 2H, H11 and H12), 7.35 (d, J = 7.3 Hz, 1H, H6’), 7.17 (dd, J = 7.2, 7.2 Hz, 1H, H5’), 7.15–7.09 (m, 2H, H2 and H3’), 7.00 (d, J = 5.4 Hz, 1H, H3), 6.38 (s, 1H, H1), 5.54 (s, 1H, H4), 4.88 (d, J = 16.8 Hz, 1H, OCH₃H₆), 4.66 (d, J = 16.8 Hz, 1H, OCH₃H₆), and 3.74 (s, 3H, OCH₃).

**Minor isomer**

¹H NMR (500 MHz, CDCl₃): δ 8.22 (s, 1H, H9), 7.93 (d, J = 7.1 Hz, 1H, H10 or H13), 7.89 (d, J = 7.0 Hz, 1H, H13 or H10), 7.55 (dd, J = 8.2, 8.2 Hz, 1H, H4’), 7.47–7.43 (m, 2H, H11 and H12), 7.15–7.09 (m, 3H, H2, H5’, and H6’), 7.07 (d, J = 7.1 Hz, 1H, H3’), 7.04 (d, J = 5.5 Hz, 1H, H3), 6.38 (s, 1H, H1), 5.51 (s, 1H, H4), 4.86 (d, J = 16.8 Hz, 1H, OCH₃H₆), 4.69 (d, J = 16.8 Hz, 1H, OCH₃H₆), and 3.76 (s, 3H, OCH₃).

¹³C NMR (126 MHz, CDCl₃): δ 171.91, 171.86, 157.2, 157.0, 148.8, 148.4, 146.5, 146.4, 143.52, 143.50, 143.0, 142.8, 141.2, 140.9, 139.4, 139.3, 139.1, 139.0, 138.0, 137.9, 136.0, 135.8, 131.5, 131.05, 131.03, 130.96, 128.51, 128.50, 128.41, 128.39, 128.38, 128.2, 126.8, 126.5, 126.2, 126.1, 125.8, 125.2, 123.22, 123.16, 122.93, 122.92, 122.2 (x2), 121.3, 121.2, 115.42, 115.39, 111.6, 111.4, 81.0, 80.9, 80.7, 80.6, 70.0, 69.8, 55.8, and 55.6.

(signals from both diastereoisomers)

**IR (neat):** 3066, 3015, 2938, 2836, 1753, 1578, 1492, 1439, 1351, 1255, 1239, 1063, 1022, 1017, 871, and 753 cm⁻¹.
HRMS (ESI-TOF): Calcd for C_{29}H_{18}NaO_4^+ [M+Na^+] requires 453.1097; found 453.1106.

Mp: 263–282 °C (mixture of diastereoisomers, with decomposition > ca. 250 °C).

(±)-tert-Butyl
10-oxo-15-phenyl-9-(trimethylsilyl)-4,10-dihydro-1H,1,4-epiminobenzo[a]indeno[2,1-e]aceanthrylene-16-carboxylate (25c)

Fluoranthene 25c was obtained following general procedure C from pentayne S20 (23 mg, 0.051 mmol), N-Boc-pyrrole (42 mg, 0.25 mmol), and CHCl_3 (2.6 mL). Purification by MPLC (hexanes:EtOAc, 4:1) afforded fluoranthene 25c (31 mg, 0.050 mmol, 98%) as a bright orange solid.

^1H NMR (500 MHz, CDCl_3): δ 7.96 (d, J = 7.3 Hz, 1H, H5 or H8), 7.94 (d, J = 7.7 Hz, 1H, H8 or H5), 7.65 (very br s, 1H, H11), 7.56–7.45 (m, 4H, PhH_{ortho}, H6, and H7), 7.44–7.36 (m, 3H, PhH_{meta+para}), 7.08–6.99 (br m, 2H, H2 and H3), 6.98 (dd, J = 7.4, 7.4 Hz, 1H, H12), 6.75 (ddd, J = 7.6, 7.6, 1.1 Hz, 1H, H13), 6.19 (br s, 1H, H4), 5.72 (very br s, 1H, H1), 5.60 (d, J = 7.7 Hz, 1H, H14), 1.34 [br s, 9H, C(CH_3)_3], and 0.57 [s, 9H, Si(CH_3)_3].

^13C NMR (126 MHz, CDCl_3) δ 195.5, 155.1 (br), 148.0, 147.1, 144.2, 143.9 (br), 142.0, 141.9, 140.5, 139.8 (br), 138.4, 137.3, 136.0, 134.0, 133.6, 131.2, 130.1, 129.4 (br), 129.2, 128.3, 127.8, 127.7, 127.1, 126.4, 125.8 (br), 124.1, 122.9, 122.4 (br), 81.4, 65.1 (br), 64.3 (br), 28.2, and 2.0 (two resonances for sp^2-hybridized carbons not discernable, presumably due to Boc-rotation).

IR (neat): 3061, 2976, 2931, 2901, 1704, 1692, 1474, 1463, 1444, 1409, 1368, 1330, 1251, 1160, 1087, 929, 908, 846, and 758 cm\(^{-1}\).

HRMS (ESI-TOF): Calcd for C_{41}H_{35}NNaO_5Si^+ [M+Na^+] requires 640.2278; found 640.2270.

Mp: 125–128 °C.
(±)-(1R,4S,5R)-2,3-Dichloro-5-(2-methoxyphenyl)-4,6-dihydro-1,4-ethenobenzo[1,2]aceanthryleno[4,5-c]furan-8(1H)-one (25d) and
(±)-(1R,4S,5S)-2,3-Dichloro-5-(2-methoxyphenyl)-4,6-dihydro-1,4-ethenobenzo[1,2]aceanthryleno[4,5-c]furan-8(1H)-one (25d’)

Fluoranthenes 25d and 25d’ were obtained following general procedure C from pentayne S14 (36 mg, 0.10 mmol) and ortho-dichlorobenzene (5.0 mL). Purification by MPLC (hexanes:EtOAc, 2:1), in order of elution, the closely eluting minor and the major isomers, each containing a small amount of the other. Recrystallization of each from DCM/MeOH afforded the fluoranthenes, each as a pale yellow solid (12 mg, 0.024 mmol, 24%; and 15 mg, 0.029 mmol, 29%, both containing 2wt% DCM based on the 1H NMR spectra, 24% and 28% corrected yield, respectively).

**Major isomer (slower eluting)**

**1H NMR** (500 MHz, CDCl₃): δ 8.25 (s, 1H, H9), 8.19 (d, J = 7.6 Hz, 1H, H13), 7.97 (d, J = 7.6 Hz, 1H, H10), 7.60 (dd, J = 8.3, 8.3 Hz, 1H, H4’), 7.51 (dd, J = 7.6, 7.6 Hz, 1H, H11 or H12), 7.46 (dd, J = 7.6, 7.6 Hz, 1H, H12 or H11), 7.29 (d, J = 7.3 Hz, 1H, H6’), 7.21 (dd, J = 7.3, 7.3 Hz, 1H, H5’), 7.14 (d, J = 8.3 Hz, 1H, H3’), 7.07 (dd, J = 6.4, 6.4 Hz, 1H, H15), 6.92 (dd, J = 6.4, 6.4 Hz, 1H, H14), 5.77 (d, J = 6.2 Hz, 1H, H1), 4.69 (d, J = 17.0 Hz, 1H, OCH₃H₉), 4.68 (d, J = 17.0 Hz, 1H, OCH₃H₉), 4.67 (d, J = 6.2 Hz, 1H, H4), and 3.72 (s, 3H, OC₃H₃).

**13C NMR** (126 MHz, CDCl₃): δ 171.9, 157.3, 146.6, 144.8, 140.7, 139.0, 138.9, 138.7, 137.3, 136.0, 134.9, 134.8, 131.9, 131.1, 129.2, 128.69, 128.67, 128.3, 126.2, 125.6, 123.2, 122.6, 122.2, 121.5, 115.2, 111.5, 69.8, 55.7, 53.3, and 52.6 (one aromatic carbon resonance not discernable).

**IR** (neat): 3083, 3056, 2956, 2929, 2852, 1755, 1579, 1556, 1492, 1470, 1440, 1350, 1242, 1201, 1100, 1066, 892, 793, and 759 cm⁻¹.

**HRMS** (ESI-TOF): Calcd for C₃₄H₁₈³⁵Cl₅NaO₃³⁵Cl⁺ [M+Na⁺] requires 531.0525; found 531.0519.

**Mp:** decomposition > ca. 320 °C.

**Minor isomer (faster eluting)**

**1H NMR** (500 MHz, CDCl₃): δ 8.25 (s, 1H, H9), 8.20 (d, J = 7.6 Hz, 1H, H13), 7.98 (d, J = 7.6 Hz, 1H, H10), 7.62–7.58 (nfom, 1H, H4’), 7.51 (ddd, J = 7.5, 7.5, 1.1 Hz, 1H, H11 or H12), 7.47
(dd, $J = 7.6, 7.6, 1.1$ Hz, 1H, H12 or H11), 7.163 (dd, $J = 7.3, 7.3$ Hz, 1H, H5'), 7.156 (d, $J = 8.2$ Hz, 1H, H3'), 7.150 (d, $J = 7.8$ Hz, 1H, H6'), 7.07 (ddd, $J = 6.5, 6.5, 1.6$ Hz, 1H, H15), 6.91 (ddd, $J = 6.6, 6.6, 1.6$ Hz, 1H, H14), 5.77 (dd, $J = 6.0, 1.6$ Hz, 1H, H1), 4.72 (d, $J = 16.9$ Hz, 1H, OCH3H6), 4.64 (d, $J = 6.0, 1.6$ Hz, 1H, H4), 4.63 (d, $J = 17.1$ Hz, 1H, OCH2H6), and 3.72 (s, 3H, OCH3).

$^{13}$C NMR (126 MHz, CDCl3): $\delta$ 171.9, 157.5, 146.6, 144.9, 140.7, 139.0, 138.9, 138.83, 138.76, 137.6, 136.3, 134.8, 134.7, 131.2 (x2), 129.2, 128.7, 128.5, 128.3, 126.2, 125.6, 123.2, 122.5, 122.3, 121.2, 115.2, 111.4, 69.8, 55.7, 53.3, and 52.7.

IR (neat): 3083, 3053, 2927, 2855, 1748, 1728, 1653, 1543, 1477, 1417, 1378, 1350, 1256, 1241, 1176, 1149, 1103, 1067, 980, 870, and 763 cm$^{-1}$.

HRMS (ESI-TOF): Calcd for C31H18$^{35}$Cl$^{35}$ClNaO3$^+$ [M+Na$^+$] requires 531.0525; found 531.0515.

Mp: decomposition > ca. 280 °C.

13-(((tert-Butyldimethylsilyl)oxy)methyl)-4-((9-((tert-butyldimethylsilyl)oxy)nona-1,5,7-triyne-1-yl)-2-(methylsulfonyl)-2,3,5,6,7,12-hexahydro-1H-7,12-[1,2]benzenonaphtho[2',3';4,5]indeno[7,1-e]jisoindole (25e)

![Reaction Diagram]

Triptycene 25e was synthesized following general procedure C from octyne 20 (33 mg, 0.050 mmol), anthracene (45 mg, 0.25 mmol), and CHCl3 (2.5 mL). Purification by gradient flash chromatography (hexanes, removing excess anthracene, to DCM) followed by MPLC (hexanes:EtOAc, 3:1) afforded the triptycene derivative 25e (33 mg, 0.039 mmol, 78%) as a pale yellow solid.

$^1$H NMR (500 MHz, CDCl3): $\delta$ 7.45–7.41 (m, 4H, ArHortho), 7.07–7.02 (m, 4H, ArHmeta), 5.91 (s, 1H, bridgehead-H), 5.56 (s, 1H, bridgehead-H'), 5.25 (br t, $J = 2.4$ Hz, 2H, MsNCH2), 5.12 (s, 2H, ArCH2O), 4.79 (br t, $J = 2.5$ Hz, 2H, MsNCH2'), 4.38 (s, 2H, $=$CCH2O), 3.52–3.48 (m, 2H, ArCH2CH2Ar'), 3.40–3.36 (m, 2H, ArCH2CH2Ar'), 2.80 (s, 3H, SO2CH3), 2.71 (t, $J = 7.1$ Hz, 2H, $=$CCH2CH2C'=), 2.62 (t, $J = 7.0$ Hz, 2H, $=$CCH2CH2C'), 2.10 [s, 9H, SiC(CH3)3], 0.91 [s, 9H, SiC(CH3)3], 0.38 [s, 6H, Si(CH3)2], and 0.13 [s, 6H, Si(CH3)2].
$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 150.1, 146.1, 144.6, 144.3, 139.5, 138.0, 137.8, 135.9, 127.3, 125.8, 125.71, 125.69, 124.6, 124.2, 123.7, 110.0, 94.7, 78.6, 77.7, 75.2, 69.7, 66.1, 59.1, 55.7, 54.1, 52.3, 50.9, 50.8, 34.4, 30.1, 28.5, 26.2, 25.9, 20.0, 19.6, 18.5, 18.4, -4.8, and -5.0.

IR (neat): 3015, 2954, 2928, 2888, 2856, 2261, 1471, 1461, 1362, 1340, 1255, 1156, 1082, 839, 776, and 755 cm$^{-1}$.

HRMS (ESI-TOF): Calcd for C$_{51}$H$_{59}$NNaO$_4$S$_{2}$ $^+\left[\text{M+Na}^+\right]$ requires 860.3596; found 860.3613.

Mp: 124–128 °C.

Dimethyl
1,2,3,4,5-Pentaphenyl-9-((2-(phenylbuta-1,3-diyn-1-yl)phenyl)ethynyl)-6,8-dihydro-7H-benzo[a]cyclopenta[e]aceanthrylene-7,7-dicarboxylate (25f)

Fluoranthe 25f was obtained following general procedure C from octayne S11 (2 mg, 0.040 mmol), 2,3,4,5-tetraphenylecyclopenta-2,4-dien-1-one (46 mg, 0.12 mmol), and CHCl$_3$ (4.0 mL).

Purification by flash chromatography (hexanes:EtxOAc, 10:1, to hexanes:EtxOAc:DCM, 8:1:1) afforded fluoranthene 25f (37 mg, 0.037 mmol, 92%) as a bright red solid.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.71 (d, $J = 7.6$ Hz, 1H, $H10$), 7.73 (d, $J = 7.6$ Hz, 1H, $H2'$ or H5'), 7.65 (d, $J = 7.6$ Hz, 1H, $H5'$ or H2'), 7.46–7.28 (m, 7H, ArH), 7.23–7.15 (m, 3H, ArH), 7.08–6.87 (m, 11H, ArH), 6.83–6.66 (m, 7H, ArH), 6.64–6.55 (m, 5H, ArH), 6.36–6.32 (m, 2H, ArH), 3.92 (s, 2H, H8), 3.59 (s, 6H, OCH$_3$), and 2.77 (s, 2H, H6).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 172.2, 142.7, 141.7, 141.32, 141.29, 140.7, 140.4, 140.2, 140.1, 139.8, 139.5, 138.8, 138.7, 137.2, 135.7, 135.6, 135.2, 133.6, 133.3, 133.1, 133.0, 132.7, 132.6, 132.2, 131.60, 131.56, 131.2, 130.1, 129.3, 129.1, 128.7, 128.4, 127.3, 126.9, 126.84, 126.75, 126.64, 126.57, 126.39$, 126.39$, 126.3, 126.2, 126.0, 125.4, 125.1, 124.6, 124.3, 122.7, 121.9, 112.9, 97.9, 91.5, 83.5, 80.3, 78.4, 74.4, 59.5, 52.8, 41.9, and 40.5. (one aromatic signal was not discernible)

IR (neat): 3056, 3015, 2951, 2918, 2843, 2214, 1736, 1492, 1480, 1441, 1255, 1199, 1165, 1073, 1027, and 753 cm$^{-1}$.

HRMS (APCI$^+$): Calcd for C$_{75}$H$_{49}$O$_4$ $^+\left[\text{M+H}^+\right]$ requires 1013.3625; found 1013.3597.

Mp: 176–178 °C.
(±)-Dimethyl 3,18,20-Triphenyl-27-(2-(phenylbuta-1,3-diyin-1-yl)phenyl)ethynyl)-nonacyclo[19.13.1.0^{2,19}.0^{4,17}.0^{5,10}.0^{11,16}.0^{22,26}.0^{28,35}.0^{29,34}]pentatriaconta-1,3,5(10),6,8,11(16),12,14,17,19,21(35),22(26),27,29(34),30,32-hexadecaene-24,24-dicarboxylate (25g)

Fluoranthe-n-ketone 25g-CO was obtained following general procedure C from octayne S11 (26 mg, 0.040 mmol), 1,3-diphenyl-2H-cyclopenta[1]phenanthren-2-one\(^\text{12}\) (26) (76 mg, 0.20 mmol), and CHCl\(_3\) (4.0 mL). One deviation for this HDDA reaction was to keep the reaction vessel in the dark to avoid light-induced autoxidation of cyclopentadienone 26\(^\text{13}\). Purification by flash chromatography (hexanes:EtOAc, 10:1 to 4:1) afforded fluoranthe 25g-CO (31 mg, 0.030 mmol, 75%) as a yellow solid.

A stirred suspension of fluoranthe 25g-CO (20 mg, 0.019 mmol) in \(\text{o-DCB}\) (1.9 mL) in a glass vial sealed with Teflon-lined cap was placed in an oil bath held at 180 °C. The initial suspension quickly turned to a homogeneous solution and the vial was heated for 24 h. During the process, the color of the solution was changed from bright yellow to red. After being allowed to cool to room temperature, the solution was directly purified by flash chromatography (4:1 hexanes: EtOAc), which afforded the tetracene 25g (16 mg, 0.016 mmol, 81%) as a bright red solid.

Alternatively, tetracene 25g was obtained by directly heating a thin film of fluoranthe 25g-CO (5.0 mg, 0.0048 mmol) under a N\(_2\) atmosphere in a sand bath held at 250 °C for 1 h. After being allowed to cool to room temperature, the crude material was purified by flash chromatography (hexanes: EtOAc, 4:1) that afforded tetracene 25g (3.0 mg, 0.0030 mmol, 62%) as a bright red solid.

**Data for 25g-CO**

\(^1\text{H NMR}\) (500 MHz, CDCl\(_3\)): \(\delta\) 8.78 (d, \(J = 7.5\) Hz, 1H, \(H15\)), 8.75 (d, \(J = 8.1\) Hz, 1H, \(H4\) or H5), 8.74 (d, \(J = 8.0\) Hz, 1H, \(H5\) or H4), 8.52 (dd, \(J = 8.4, 0.8\) Hz, 1H, \(H1\) or H8), 8.20 (d, \(J = 8.4, 0.7\) Hz, 1H, \(H8\) or H1), 7.89 (br d, \(J = 7.7\) Hz, 1H, Ph\(_{\text{ortho}}\)), 7.78 (br d, \(J = 7.6\) Hz, 1H, Ph\(_{\text{ortho}}\)), 7.73 (nfod, \(J = 7.3\) Hz, 1H, Ph\(_{\text{ortho}}\)), 7.69–7.65 (m, 2H, Ph\(_{\text{ortho}}\) and \(H2\)), 7.63–7.59 (m, 2H, Ph\(_{\text{ortho}}\)), 7.52–7.27 (m, 18H, Ar\(_{\text{H}}\)), 7.17 (ddd, \(J = 7.6, 7.6, 0.8\) Hz, 1H, \(H3'\) or \(H4'\)), 7.15–7.11 (m, 3H, Ar\(_{\text{H}}\)), 7.11 (ddd, \(J = 7.7, 7.7, 1.0\) Hz, 1H, \(H17\)), 6.84 (br d, \(J = 7.6\) Hz, 1H,
$H18$, 3.86 (d, J = 17.3 Hz, 1H, $H13_a$), 3.79 (d, J = 17.3 Hz, 1H, $H13_b$), 3.63 (s, 3H, OCH$_3$), 3.40 (s, 3H, OCH$_3$), 3.26 (d, J = 17.7 Hz, 1H, $H11_a$), and 2.30 (d, J = 17.7 Hz, 1H, $H11_b$).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 171.9, 143.4, 141.1, 140.6, 139.5, 138.3, 137.2, 136.6, 135.5, 133.8, 133.3, 133.0, 132.7, 132.4, 132.2, 131.7, 131.3, 131.1, 130.9, 130.4, 130.0, 128.7, 128.6, 128.43, 128.38, 128.2, 128.0, 127.8, 127.2, 127.0, 126.83, 126.82, 126.7, 126.5, 125.9, 125.0, 124.2, 123.4, 122.9, 121.8, 113.7, 97.8, 83.3, 79.9, 69.0, 67.5, 60.0, 52.2, 52.0, 41.3, and 39.6. Quality 1D $^{13}$C NMR spectrum not attainable because of limited solubility. The listed values are from HSQC & HMBC 2D spectra, but many resonances are either not well resolved or absent because of being buried deeper in the core of the structure.

IR (neat): 3057, 3034, 2951, 2921, 2843, 2214, 1802, 1736, 1499, 1482, 1446, 1461, 1255, 1200, 1164, 1073, and 754 cm$^{-1}$.

HRMS (APCI$^+$): Calcd for C$_{76}$H$_{46}$O$_5$$^+$ [M$^+$] requires 1038.3340; found 1038.3331.

Mp: 300–308 ºC (color change from yellow to red observed > ca. 260 ºC).

Data for 25g

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.71 (d, J = 7.6 Hz, 1H, $H15$), 8.09 (d, J = 8.0 Hz, 2H, $H4$ and $H5$), 7.74 (br d, J = 7.5 Hz, 1H, PhH$_{ortho}$), 7.71 (br d, J = 7.6 Hz, 1H, PhH$_{ortho}$), 7.66 (br d, J = 7.6 Hz, 1H, PhH$_{ortho}$), 7.46–7.42 (m, 3H, ArH), 7.41–7.34 (m, 4H, ArH), 7.33–7.24 (m, 5H, ArH), 7.21 (dd, J = 7.5, 7.5 Hz, 1H, ArH), 7.16 (dd, J = 7.7, 7.7 Hz, 1H, ArH), 7.11–6.95 (m, 6H, ArH), 6.88 (dd, J = 7.7, 7.7 Hz, 1H, ArH), 6.86–6.80 (m, 3H, ArH), 6.76–6.71 (m, 2H, ArH), 6.68 (dd, J = 7.6, 7.6 Hz, 1H, ArH), 6.52 (br d, J = 8.3 Hz, 2H, $H1$ and $H8$), 6.31 (d, J = 7.8 Hz, 1H, $H18$), 3.98 (d, J = 17.1 Hz, 1H, $H13a$), 3.90 (d, J = 17.1 Hz, 1H, $H13b$), 3.65 (s, 3H, OCH$_3$), 3.51 (s, 3H, OCH$_3$), 3.34 (d, J = 17.7 Hz, 1H, $H11a$), and 2.44 (d, J = 17.6 Hz, 1H, $H11b$). The twist in the dibenzotetracene$^{14}$ renders the two pairs of methylene protons and the methyl groups inequivalent (diastereotopic).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 172.2, 142.5, 141.8, 141.6, 140.9, 140.4, 138.6, 138.5, 137.5, 136.6, 135.7, 135.5, 134.4, 134.0, 133.67, 133.65, 133.22, 133.20, 133.0, 132.9, 132.74, 132.66, 132.6, 132.2, 131.9, 131.8, 131.6, 131.4, 131.0, 130.4, 129.7, 129.6, 129.4, 129.2, 129.1, 128.98, 128.96, 128.92, 128.7, 128.5, 128.3, 128.0, 127.4, 127.2, 126.91 (br), 126.90, 126.87, 126.69, 126.68, 126.6, 126.42, 126.36, 126.1, 125.8, 124.3, 123.72, 123.67, 122.8, 121.9, 113.0, 97.9, 91.5, 83.5, 80.3, 78.4, 74.4, 59.6, 52.9, 42.4, and 40.6. The twist in the dibenzotetracene$^{14}$ renders all six of the carbons in each of the three non-terminal phenyl groups inequivalent.

IR (neat): 3059, 3025, 2952, 2927, 1736, 1599, 1492, 1480, 1443, 1253, 1200, 1168, 1074, 818, and 754 cm$^{-1}$.

HRMS (APCI$^+$): Calcd for C$_{75}$H$_{46}$O$_4$$^+$ [M$^+$] requires 1010.3391; found 1010.3394.

Mp: 306–310 ºC.
(±)-6,7-Dimethoxy-15-(4-methoxyphenyl)-14-tosyl-9-(trimethylsilyl)-14H-benzo[3,4]fluoren o[1,9-ab]carbazole (25h)

Carbazole 25h was synthesized following general procedure C from pentayne S17 (34 mg, 0.050 mmol), 2-pyrone (12 μL, 0.15 mmol), and CHCl₃ (5.0 mL). Purification by MPLC (hexanes:EtOAc, 2:1) afforded carbazole 25h (26 mg, 0.039 mmol, 78%) as a red solid.

**¹H NMR** (500 MHz, CDCl₃): δ 8.76 (br d, J = 8.6 Hz, 1H, H4), 8.42 (br d, J = 8.9 Hz, 1H, H1), 8.20 (s, 1H, H9), 8.17 (br s, 1H, SO₂-Ar ortho-a), 8.00 (s, 1H, H5), 7.90 (s, 1H, SO₂-Ar ortho-b and meta-b), 7.60 (s, 1H, H8), 7.48 (br dd, J = 8.4, 8.4 Hz, 1H, H2), 7.31 (br dd, J = 7.5, 7.5 Hz, 1H, H11 or H12), 7.29 (br s, 1H, SO₂-Ar meta-a), 7.26 (br dd, J = 7.6, 7.6 Hz, 1H, H12 or H11), 6.87 (br s, 2H, SO₂-Ar ortho-b and meta-b), 6.64 (br d, J = 7.9 Hz, 2H, MeO-Ar meta), 4.19 (s, 3H, OCH₃), 4.11(s, 3H, OCH₃), 3.99 (s, 3H, OCH₃), and 2.09 (s, 3H, SO₂-ArCH₃).

**¹³C NMR** (126 MHz, CDCl₃): δ 159.3, 149.6, 148.7, 143.7, 142.2, 139.2, 137.25, 137.22, 134.7, 133.8, 131.42, 131.40, 131.37, 131.33, 131.0, 130.9, 130.6, 129.4 (br), 129.3, 129.1, 128.22 (br), 128.20, 127.4, 127.1, 126.4, 125.7, 125.4, 124.0, 121.9, 119.62 (br), 119.38, 119.35, 111.8, 108.2, 105.4, 56.8, 56.5, 55.6, and 21.5 (one aromatic carbon resonance not discernable).

**IR** (neat): 3000, 2955, 2832, 1604, 1509, 1421, 1389, 1361, 1289, 1242, 1209, 1170, 1152, 1085, 1033, 908, and 763 cm⁻¹.

**HRMS** (APCI⁺): Calcd for C₄₂H₃₂N₀₅S⁺ [M+H⁺] requires 662.1996; found 662.1982.

**Mp**: 204–208 °C.
Methyl 10-Oxo-15-phenyl-9-(trimethylsilyl)-10H-benzo[a]indeno[2,1-e]aceanthrylene-3-carboxylate (25i) and

Methyl 10-Oxo-15-phenyl-9-(trimethylsilyl)-10H-benzo[a]indeno[2,1-e]aceanthrylene-2-carboxylate (25i’)

Anthracene 25i and 25i’ were obtained following general procedure C from pentayne S20 (45 mg, 0.10 mmol), methyl coumalate (46 mg, 0.30 mmol), and CHCl₃ (5 mL). Purification by MPLC (hexanes:EtOAc, 4:1) afforded, in order of elution, anthracenes 25i and 25i’ each as a dark red amorphous solid (35 mg, 0.062 mmol, 62%; and 18 mg, 0.032 mmol, 32%, respectively). Their ratio was 2.0:1 based on the ¹H NMR spectrum of the crude reaction mixture.

**Major isomer 25i (faster eluting)**

¹H NMR (500 MHz, CDCl₃): δ 9.36 (s, 1H, H4), 8.21 (d, J = 7.7 Hz, 1H, H5), 8.03 (d, J = 9.3 Hz, 1H, H2), 7.90 (d, J = 7.4 Hz, 1H, H8), 7.84 (d, J = 9.3 Hz, 1H, H1), 7.50 (dd, J = 7.4, 7.4 Hz, 1H, H6), 7.46–7.33 (m, 7H, PhH3, H11, and H7), 6.94 (dd, J = 7.3, 3.7 Hz, 1H, H12), 6.68 (dd, J = 7.6, 7.6 Hz, 1H, H13), 5.30 (d, J = 7.7 Hz, 1H, H14), 4.09 (s, 3H, OCH3), and 0.52 [s, 9H, Si(CH3)]₃.

¹³C NMR (126 MHz, CDCl₃): δ 195.8, 167.0, 148.8, 145.5, 144.2, 141.2, 140.5, 140.0, 139.2, 138.7, 135.0, 134.6, 134.3, 133.8, 133.6, 133.2, 132.9, 129.3, 128.8, 128.8, 128.7, 128.5, 128.4, 127.7, 127.6, 126.4, 126.4, 125.4, 124.9, 124.4, 124.1, 122.7, 52.7, and 2.0.

IR (neat): 3059, 2951, 2900, 1721, 1706, 1605, 1462, 1441, 1299, 1264, 1247, 1193, 1100, 909, 847, and 765 cm⁻¹.

HRMS (APCI⁺): Calcd for C₃₇H₂₅O₃Si⁺ [M-CH₃⁺] requires 545.1567; found 545.1573.

**Minor isomer 25i’ (slower eluting)**

¹H NMR (500 MHz, CDCl₃): δ 8.93 (d, J = 1.3 Hz, 1H, H1), 8.74 (d, J = 9.0 Hz, 1H, H4), 8.25 (d, J = 7.7 Hz, 1H, H5), 8.16 (dd, J = 8.9, 1.5 Hz, 1H, H3), 7.97 (d, J = 7.6 Hz, 1H, H8), 7.58–7.52 (m, 5H, PhH3), 7.44 (dd, J = 7.5, 7.5, 1.1 Hz, 1H, H6), 7.42 (dd, J = 7.4, 1.2 Hz, 1H, H11), 7.38 (dd, J = 7.5, 7.5, 0.8 Hz, 1H, H7), 6.97 (dd, J = 7.6, 7.6, 0.7 Hz, 1H, H12), 6.73 (dd, J = 7.6, 7.6, 1.3 Hz, 1H, H13), 5.44 (d, J = 7.7 Hz, 1H, H14), 3.96 (s, 3H, OCH3), and 0.55 [s, 9H, Si(CH3)]₃.
$^{13}$C NMR (126 MHz, CDCl$_3$): δ 195.8, 167.1, 148.5, 145.8, 144.4, 141.5, 140.9, 140.8, 139.8, 139.2, 136.0, 135.7, 133.8, 133.3, 133.04, 133.00, 132.4, 131.8, 131.1, 129.2, 129.0, 128.4, 127.8, 127.1, 126.9, 126.6, 126.4, 125.0, 124.8, 124.7, 123.9, 122.8, 52.5, and 2.0.

IR (neat): 3065, 2952, 2899, 1721, 1706, 1557, 1441, 1299, 1274, 1241, 1194, 1086, 862, 844, and 767 cm$^{-1}$.

HRMS (APCI$^+$): Calcd for C$_{37}$H$_{25}$O$_2$ [M+H$^+$] requires 501.1849; found 501.1838.

$\text{M}p$: decomposes $> \text{ca. 240} \, ^\circ\text{C}$.

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9-Propyl-14,15-dihydrocyclopenta[4,5]dinaphtho[2′,1′,8′:6,7,8;1′′,2′′:9,10,11]tetraceno[1,2-c]furan-12(10H)-one (25j)

Anthracenoperylene 25j were obtained following general procedure C from pentayne 9 (25 mg, 0.10 mmol), perylene (76 mg, 0.30 mmol), and CHCl$_3$ (20 mL). Purification by flash column chromatography (hexanes:DCM, 1:1) followed by recrystallization DCM/MeOH afforded anthracenoperylene 25j (28 mg, 0.056 mmol, 56%, containing 4 wt% DCM, 54% corrected yield) as an orange solid, which slowly decomposed under air and ambient light. The sample was stored in the dark and kept at -20 °C.

$^1$H NMR (500 MHz, CDCl$_3$): δ 9.08 (d, $J = 9.2$ Hz, 1H, H8 or H16), 8.81 (d, $J = 7.7$ Hz, 1H, H3 or H4), 8.79 (d, $J = 7.7$ Hz, 1H, H4 or H3), 8.51 (d, $J = 9.0$ Hz, 1H, H16 or H8), 8.19 (d, $J = 8.8$ Hz, 1H, H7 or H17), 8.12 (d, $J = 7.6$ Hz, 1H, H1 or H6), 8.08 (d, $J = 7.5$ Hz, 1H, H6 or H1), 8.00 (d, $J = 8.7$ Hz, 1H, H17 or H7), 7.92 (dd, $J = 7.8$, 7.8 Hz, 1H, H2 or H5), 7.91 (dd, $J = 7.9$, 7.9 Hz, 1H, H5 or H2), 7.75 (s, 1H, H13) 5.99 (br s, 2H, OCH$_2$), 4.45 (br s, 2H, H15), 4.03 (very br s, 2H, CH$_2$CH$_2$CH$_3$), 3.71 (br s, 2H, CH$_2$), 1.22 (br m, 2H, CH$_2$CH$_2$CH$_3$), and 0.55 (t, $J = 7.3$ Hz, 3H, CH$_2$CH$_2$CH$_3$).

$^{13}$C NMR (126 MHz, CDCl$_3$): Limited solubility properties prevented the collection of a high enough quality 1-D or 2-D $^{13}$C spectral data set. The following are resonances that could be observed with confidence: δ 132.6, 132.1, 130.9, 129.8, 127.6, 127.1, 127.0 (x2 in HSQC), 126.2, 125.3, 125.2, 124.8, 120.9, 120.5, 112.5, 71.5, 37.5, 36.8, 31.0, 27.4, and 13.7. (15 aromatic C and 1 carbonyl were not observed).

IR (neat): 2969, 2928, 2873, 1755, 1654, 1581, 1563, 1461, 1441, 1359, 1266, 1176, 1100, 850, and 821 cm$^{-1}$.

HRMS (APCI$^+$): Calcd for C$_{37}$H$_{25}$O$_2$ $^+$ [M+H$^+$] requires 501.1849; found 501.1838.
(±)-(7R,18bR)-18-Phenyl-12-(trimethylsilyl)-7,18b-ethenodibenzo[ij,pq]diindeno[1,2-a:1',2', 3'-de]pentaphen-13(7H)-one (25k) and
(±)-(7S,18dS)-8-Phenyl-14-(trimethylsilyl)-7,18d-ethenodibenzo[ij,pq]diindeno[2,1-c:1',2',3' -uv]pentaphen-13(7H)-one (25k')

The fused fluorenone derivatives 25k and 25k' were obtained following general procedure C from pentayne S20 (22 mg, 0.049 mmol), perylene (38 mg, 0.15 mmol), and CHCl₃ (10 mL). Purification by flash column chromatography (hexanes:DCM, 2:1) afforded fluorenones 25k and 25k' as a 2.0:1 co-eluting mixture, containing minor impurities (21 mg, 0.030 mmol, ~61%), as judged from its ¹H NMR spectrum. A pristine sample of the mixture of 25k and 25k' was acquired by recrystallization from DCM/MeOH (15 mg, 0.021 mmol, 44%, as a red solid). A single crystal of the major isomer 25k suitable for X-ray diffraction analysis was grown by slow evaporation at ambient temperature of a toluene solution of the mixture (CCDC deposition number: 1818244).

Major isomer 25k

¹H NMR (500 MHz, CDCl₃): δ 8.47 (d, J = 7.5 Hz, 1H, H8), 8.19 (d, J = 7.0 Hz, 1H, H3), 7.98 (dd, J = 8.0, 0.8 Hz, 1H, H11), 7.96 (d, J = 7.8 Hz, 1H, H1), 7.78 (d, J = 7.8 Hz, 1H, H4), 7.60 (dd, J = 7.9, 7.4 Hz, 1H, H5), 7.508 (ddd, J = 7.6, 7.6, 0.9 Hz, 1H, H9 or H10), 7.507 (dd, J = 7.2, 0.6 Hz, 1H, H6), 7.43 (dd, J = 7.9, 1.1 Hz, 1H, H21), 7.41 (dd, J = 7.6, 7.6, 0.9 Hz, 1H, H10 or H9), 7.31 (dd, J = 7.0, 0.8 Hz, 1H, H14), 7.27 (dd, J = 7.8, 7.2 Hz, 1H, H2), 7.26 (dd, J = 6.8, 6.8 Hz, 1H, H23), 7.04 (br d, J = 7.2 Hz, 1H, PhH₉₀ᵗₐ₉), 6.95 (dd, J = 7.2, 1.3 Hz, 1H, H19), 6.91 (dd, J = 7.5, 7.5 Hz, 1H, H20), 6.85 (br dd, J = 7.3, 7.3 Hz, 1H, PhH₉₂₉), 6.82 (dd, J = 6.9, 1.5 Hz, 1H, H22), 6.81 (br t, J = 7.2, 1.3 Hz, 1H, PhH₉₂₉), 6.73 (dd, J = 7.7, 7.7, 0.7 Hz, 1H, H15), 6.48 (br d, J = 7.2 Hz, 1H, PhH₉₀ᵗₐ₉), 6.38 (dd, J = 6.6, 1.5 Hz, 1H, bridgehead-H), 6.36 (ddd, J = 7.7, 7.7, 1.3 Hz, 1H, H16), 6.10 (br dd, J = 7.3, 7.3 Hz, 1H, PhH₉₂₉), 4.78 (d, J = 7.8 Hz, 1H, H17), and 0.55 [s, 9H, Si(CH₃)₃]. The inequivalency of the protons on the phenyl substituent indicate that rotation about the Ph–Ar bond is slow on the NMR time-scale.

¹³C NMR (126 MHz, CDCl₃): δ 195.6, 150.8, 146.2, 145.8, 145.5, 145.1, 144.9, 143.5, 141.8, 140.4, 140.2, 139.6, 138.6, 137.1, 136.6, 135.9, 135.5, 134.8, 133.7, 133.3, 133.1, 132.3, 131.9, 130.8, 129.4, 129.2, 128.6, 128.5, 128.4, 127.8, 127.6, 127.2, 127.04, 126.98, 126.9, 126.8, 126.6, 126.4, 126.2, 125.8, 125.0, 123.4, 123.1, 122.4, 120.1, 119.4, 56.1, 47.1, and 2.0.
IR (neat): 3052, 3026, 2926, 2853, 1704, 1607, 1463, 1443, 1401, 1381, 1249, 1207, 843, and 764 cm⁻¹.

HRMS (APCI⁺): Calcd for C₅₁H₃₁OSi⁺ [M-CH₃⁺] requires 687.2139; found 687.2131.

Mp: 298–301 °C.

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**Minor isomer 25k’ (deduced from mixture)**

H NMR (500 MHz, CDCl₃): δ 8.18 (d, J = 7.2 Hz, 1H, H3), 8.03 (d, J = 8.2, 0.9 Hz, 1H, H21), 8.00 (d, J = 8.1 Hz, 1H, H1), 7.89 (dd, J = 8.0, 0.8 Hz, 1H, H4), 7.73 (dd, J = 7.4, 1.1 Hz, 1H, H19), 7.66 (dd, J = 8.0, 7.4 Hz, 1H, H2), 7.66–7.55 (m, 6H, PhH₅ and H15), 7.54 (dd, J = 8.0, 7.4 Hz, 1H, H20), 7.43 (dd, J = 7.7, 0.9 Hz, 1H, H12), 7.23 (dd, J = 7.2, 1.0 Hz, 1H, H6), 7.20 (dd, J = 7.3, 7.3 Hz, 1H, H5), 7.06 (dd, J = 6.8, 6.8 Hz, 1H, H23), 6.96 (ddd, J = 7.5, 7.5, 0.6 Hz, 1H, H11), 6.94 (ddd, J = 7.4, 7.4, 0.7 Hz, 1H, H16), 6.91 (dd, J = 6.9, 1.5 Hz, 1H, H22), 6.73 (ddd, J = 7.7, 7.7, 1.3 Hz, 1H, H10), 6.34 (ddd, J = 7.7, 7.7, 1.1 Hz, 1H, H17), 5.63 (dd, J = 6.6, 1.5 Hz, 1H, bridgehead-H7), 5.45 (d, J = 7.7 Hz, 1H, H9), 4.84 (d, J = 7.9 Hz, 1H, H18), and 0.49 [s, 9H, Si(CH₃)₃].

C NMR (126 MHz, CDCl₃): δ 195.8, 149.5, 147.5, 146.5, 146.0, 145.7, 144.9, 143.1, 142.2, 141.1, 140.0, 138.84, 138.76, 138.6, 136.9, 134.5, 133.9, 133.7, 133.4, 133.0, 132.5, 132.0, 129.8, 129.5, 129.4, 129.1, 129.0, 128.9, 128.6, 128.2, 128.1, 127.9, 127.4, 127.0, 126.8, 126.5, 126.3, 125.5, 125.3, 125.2, 124.4, 122.9, 122.8, 120.0, 119.6, 55.8, 48.7, and 2.1.

IR (neat): 3052, 2950, 2924, 2852, 1704, 1603, 1462, 1444, 1399, 1377, 1248, 1200, 1083, 844, and 765 cm⁻¹. (of the mixture)

HRMS (APCI⁺): Calcd for C₅₁H₃₁OSi⁺ [M-CH₃⁺] requires 687.2139; found 687.2131. (of the mixture)

Mp: 260–288 °C (of the mixture).
7-Oxo-1-propyl-4,5,7,9-tetrahydroacenaphtho[4,5-c]furan-3-yl acetate (25l) and 7-Oxo-1-propyl-4,5,7,9-tetrahydroacenaphtho[4,5-c]furan-2-yl acetate (25l’)

Naphthalenes 25l and 25l’ were obtained following general procedure C from pentayne 9 (25 mg, 0.10 mmol), acetic acid (300 μL, 5.0 mmol), and CHCl₃ (5.0 mL). Purification by MPLC (hexanes:EtOAc, 2:1) afforded naphthalene 25l and 25l’ (20 mg, 0.065 mmol, 65%, as a pale yellow solid) as a 1:1.3 coeluting mixture.

**25l (major)**

**¹H NMR** (500 MHz, CDCl₃): δ 7.60 (s, 1H, H6), 7.19 (s, 1H, H3), 5.67 [s, 2H, CH₂O(C=O)], 3.47–3.39 (m, 4H, ArCH₂CH₂Ar), 2.73 (t, J = 7.7 Hz, 2H, CH₂CH₂CH₃), 2.40 [s, 3H, O(C=O)CH₃], 1.57 (sextet, J = 7.7 Hz, 2H, CH₂CH₂CH₃), and 1.06 (t, J = 7.5 Hz, 3H, CH₂CH₂CH₃).

**25l’ (minor)**

**¹H NMR** (500 MHz, CDCl₃): δ 7.60 (s, 1H, H6), 7.13 (s, 1H, H2), 5.67 [s, 2H, CH₂O(C=O)], 3.47–3.39 (m, 2H, H5), 3.32–3.28 (m, 2H, H4), 2.86 (t, J = 7.7 Hz, 2H, CH₂CH₂CH₃), 2.38 [s, 3H, O(C=O)CH₃], 1.71 (sextet, J = 7.6 Hz, 2H, CH₂CH₂CH₃), and 1.07 (t, J = 7.4 Hz, 3H, CH₂CH₂CH₃).

**¹³C NMR** (126 MHz, CDCl₃): δ 171.9, 171.8, 170.0, 168.7, 149.7, 149.3, 148.9, 146.2, 145.1, 145.0, 142.7, 142.3, 141.4, 138.4, 134.4, 126.4, 126.3, 126.0, 125.4, 124.4, 123.7, 119.0, 114.7, 114.2, 70.7, 70.6, 35.8, 30.5, 30.11, 30.06, 30.01, 28.3, 24.9, 24.8, 21.1, 21.0, 14.4, and 14.0 (signals from both regioisomers)

**IR** (neat): 2961, 2932, 2874, 1755, 1611, 1450, 1422, 1364, 1345, 1203, 1182, 1106, 1071, 1040, 909, and 778 cm⁻¹.

**HRMS (ESI-TOF):** Calcd for C₁₀H₁₈NaO₄⁺ [M+Na⁺] requires 333.1097; found 333.1098.

**Mp:** 158–172 °C (mixture of regioisomers).
4-((9-Oxo-1-phenyl-8-(trimethylsilyl)-9H-indeno[2,1-b]fluoranthen-2-yl)thio)butyl acetate (25m) and
4-((9-Oxo-1-phenyl-8-(trimethylsilyl)-9H-indeno[2,1-b]fluoranthen-3-yl)thio)butyl acetate (25m’)

Fluoranthenes 25m and 25m’ were obtained following general procedure C from pentayne S20 (50 mg, 0.11 mmol) and tetrahydrothiophene (12 µL, 0.14 mmol), acetic acid (33 µL, 0.55 mmol), and benzene (11 mL). Purification by MPLC (hexanes:EtOAc, 5:1) afforded, in order of elution, fluoranthenes 25m and 25m’, each as an orange-red solid (21 mg, 0.035 mmol, 32%; and 39 mg, 0.065 mmol, 59%).

Minor isomer 25m (faster eluting)

\(^1\)H NMR (500 MHz, CDCl\textsubscript{3}): \(\delta\) 7.99 (s, 1H, \(H3\)), 7.90 (nfom, 1H, \(H4\)), 7.83 (nfom, 1H, \(H7\)), 7.52 (d, \(J = 7.0\) Hz, 2H, Ph\textsubscript{ortho}), 7.48–7.43 (m, 4H, Ph\textsubscript{meta+para} and \(H10\)), 7.38–7.35 (m, 2H, \(H5\) and \(H6\)), 6.97 (ddd, \(J = 7.4, 7.4, 0.6\) Hz, 1H, \(H11\)), 6.73 (ddd, \(J = 7.7, 7.7, 1.3\) Hz, 1H, \(H12\)), 5.47 (d, \(J = 7.8\) Hz, 1H, \(H13\)), 3.98 (t, \(J = 6.0\) Hz, 2H, \(CH_2\text{OAc}\)), 2.92 (t, \(J = 6.9\) Hz, 2H, \(SCH_2\)), 1.96 [s, 3H, O(C=O)\(CH_3\)], 1.66–1.57 (m, 4H, \(CCH_2\text{CH}_2\text{C}\)), and 0.56 [s, 9H, Si(\(CH_3\))\textsubscript{3}].

\(^1\)3C NMR (126 MHz, CDCl\textsubscript{3}): \(\delta\) 195.6, 171.2, 147.7, 144.4, 143.9, 142.4, 140.5, 139.8, 139.4, 138.6, 138.3, 137.1, 136.2, 135.4, 133.8, 133.5, 132.4, 128.6, 128.5, 127.8, 127.7, 127.5, 127.0, 126.4, 125.3, 122.9, 121.8, 120.9, 63.9, 34.4, 27.8, 25.5, 21.0, and 2.0.

IR (neat): 3059, 2951, 2902, 1737, 1706, 1604, 1462, 1445, 1381, 1239, 1088, 1042, 908, 843, and 765 cm\textsuperscript{-1}.

HRMS (ESI-TOF): Calcd for C\textsubscript{38}H\textsubscript{34}NaO\textsubscript{3}SSi\textsuperscript{+} [M+Na\textsuperscript{+}] requires 621.1890; found 621.1901.

Mp: 56–59 °C.

Major isomer 25m’ (slower eluting)

\(^1\)H NMR (500 MHz, CDCl\textsubscript{3}): \(\delta\) 8.38 (d, \(J = 7.6\) Hz, 1H, \(H4\)), 7.93 (d, \(J = 7.4\) Hz, 1H, \(H7\)), 7.56–7.53 (nfom, 2H, Ph\textsubscript{ortho}), 7.52 (s, 1H, \(H2\)), 7.46 (d, \(J = 7.4\) Hz, 1H, \(H10\)), 7.46–7.43 (m, 3H, Ph\textsubscript{meta+para}), 7.40 (ddd, \(J = 7.5, 7.5, 1.2\) Hz, 1H, \(H5\)), 7.35 (ddd, \(J = 7.5, 7.5, 1.2\) Hz, 1H, \(H6\)), 6.98 (ddd, \(J = 7.4, 7.4, 0.8\) Hz, 1H, \(H11\)), 6.74 (ddd, \(J = 7.6, 7.6, 1.3\) Hz, 1H, \(H12\)), 5.60 (d, \(J =
7.7 Hz, 1H, H13), 4.12 (t, J = 6.1 Hz, 2H, CH2OAc), 3.25 (t, J = 6.8 Hz, 2H, SCH2), 2.00 [s, 3H, O(C=O)CH3], 1.94–1.84 (m, 4H, CCH2CH2C), and 0.59 [s, 9H, Si(CH3)3].

13C NMR (126 MHz, CDCl3): δ 195.4, 171.2, 146.5, 143.8, 143.8, 142.3, 140.7, 140.3, 139.5, 139.4, 138.3, 136.4, 135.6, 133.9, 133.39, 133.36, 131.0, 130.2, 129.3, 128.4, 127.9 (x2), 126.5, 126.1, 125.9, 122.82, 122.80, 63.9, 32.5, 28.0, 26.0, 21.0, and 2.0.

IR (neat): 3063, 2954, 2899, 1737, 1704, 1561, 1445, 1403, 1234, 1199, 1076, 1043, 949, 914, 859, 842, and 765 cm⁻¹.

HRMS (ESI-TOF): Calcd for C38H34NaO3SSi+[M+Na+] requires 621.1890; found 621.1894.

Mp: 74–77 ºC.

Dimethyl
1-Morpholino-3-phenyl-7-((2-(phenylbuta-1,3-diyin-1-yl)phenyl)ethyl)-4,6-dihydro-5H-cyclopenda[b]fluoranthene-5,5-dicarboxylate (25n)

Dimethyl
2-Morpholino-3-phenyl-7-((2-(phenylbuta-1,3-diyin-1-yl)phenyl)ethyl)-4,6-dihydro-5H-cyclopenda[b]fluoranthene-5,5-dicarboxylate (25n′)

Fluoranthenes 25n and 25n’ were obtained following general procedure C from octayne S11 (33 mg, 0.050 mmol), morpholine (13 μL, 0.15 mmol), and CHCl3 (2.5 mL). Purification by MPLC (hexanes:EtOAc, 3:1) afforded fluoranthene 25n and 25n’ as a 4.5:1 coeluting mixture (36 mg, 0.048 mmol, 96%, as a yellow solid). A pure sample of just the major regioisomer 25n (24 mg, 0.032 mmol, 64%) was isolated by recrystallization from DCM/MeOH.

Data for the major isomer (25n)

1H NMR (500 MHz, CDCl3): δ 8.70 (d, J = 7.6 Hz, 1H, H8), 7.85 (br d, J = 7.4 Hz, 1H, H11), 7.81 (s, 1H, H1), 7.71 (dd, J = 7.8, 1.0 Hz, 1H, H2’ or H5’), 7.64 (dd, J = 7.7, 1.0 Hz, 1H, H5’ or H2’), 7.50 (ddd, J = 7.6, 7.6, 1.0 Hz, 1H, H9 or H10), 7.48–7.40 (m, 6H, ArH), 7.39–7.28 (m, 7H, ArH), 3.91 (s, 2H, H6), 3.61 (s, 6H, OCH3), 3.46 (br t, J = 4.3 Hz, 4H, OCH2), 3.03 (s, 2H, H4), and 2.93 (br t, J = 4.5 Hz, 4H, NCH2).
$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 172.2, 151.8, 142.7, 139.4, 139.0, 138.9, 137.7, 137.5, 135.8, 134.1, 133.6, 132.9, 132.7, 131.0, 130.0, 129.4, 129.1, 128.63, 128.62, 128.5, 127.9, 127.7, 127.53, 127.49, 126.7, 124.2, 123.8, 121.9, 120.9, 114.5, 112.5, 96.9, 91.0, 83.5, 80.4, 78.4, 74.4, 67.3, 59.7, 52.9, 52.8, 41.8, and 40.5.

IR (neat): 3058, 2952, 2851, 2813, 2214, 1736, 1609, 1480, 1442, 1370, 1260, 1199, 1166, 1113, 1069, and 755 cm$^{-1}$.

HRMS (ESI-TOF): Calcd for C$_{51}$H$_{37}$NNaO$_5^+$ [M+Na$^+$] requires 766.2564; found 766.2541.

Mp: 134–139 °C.

Data for the major isomer (25n’, extracted from mixture)

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.82 (d, $J = 7.6$ Hz, 1H, $H8$), 7.94 (d, $J = 7.5$ Hz, 1H, $H11$), 7.74 (dd, $J = 7.8$, 1.0 Hz, 1H, $H2’$ or $H5’$), 7.65 (dd, $J = 7.7$, 1.0 Hz, 1H, $H5’$ or $H2’$), 7.52–7.28 (m, 14H, Ar H), 7.23 (s, 1H, $H2$), 4.03 (br t, $J = 4.5$ Hz, 4H, OCH$_2$), 3.96 (s, 2H, $H6$), 3.62 (s, 6H, OCH$_3$), 3.29 (br t, $J = 4.4$ Hz, 4H, NCH$_2$), and 3.19 (s, 2H, $H4$).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 172.2, 147.5, 141.8, 141.7, 140.8, 138.0, 137.8, 136.7, 135.6, 134.6, 133.67, 133.64, 133.0, 132.7, 129.7, 129.1, 128.7, 128.5, 128.2, 128.0, 127.5, 127.3, 126.6, 125.4, 124.3, 123.7, 123.6, 123.2, 121.9, 117.2, 113.7, 100.1, 97.4, 91.2, 83.5, 80.3, 74.4, 67.4, 60.0, 53.0, 52.4, 47.4, and 42.0.

IR (neat): 3059, 2953, 2853, 2812, 2218, 1735, 1694, 1616, 1455, 1372, 1260, 1200, 1167, 1114, 1070, 838, and 757 cm$^{-1}$. (from the mixture of regioisomers)

HRMS (ESI-TOF): Calcd for C$_{51}$H$_{37}$NNaO$_5^+$ [M+Na$^+$] requires 766.2564; found 766.2552. (obtained from the mixture of regioisomers)

Mp: 117–128 °C (of the mixture of regioisomers).

(±)-(6cS,7R,10S,10aR)-11-Propyl-5,6,6c,7,8,9,10a-octahydro-7,10-methanobenzo[3′,4′]cyclobuta[1′,2′:7,8]acenaphtho[4,5-c]furan-3(1H)-one (25o)

Naphthalene 25o was obtained following general procedure C from pentayne 9 (25 mg, 0.10 mmol), norbornene (94 mg, 1.0 mmol), and CHCl$_3$ (5.0 mL). Purification by MPLC (hexanes:EtOAc, 2.5:1) afforded naphthalene 25o (22 mg, 0.064 mmol, 64%) as a white solid.
Ethyl 9-Oxo-14-phenyl-8-(trimethylsilyl)-3,9-dihydroindeno[1',2':2,3]fluoreno[1,9-fg]indazole-1-carboxylate (25p)

Fluoranthene 25p was obtained following general procedure C from pentayne S20 (22 mg, 0.049 mmol), ethyl 2-diazoacetate (18 µL, 90 wt%, 0.15 mmol), and CHCl₃ (2.4 mL). Purification by flash column chromatography (hexanes:EtOAc, 2:1 to 1:1) afforded fluoranthene 25p (24 mg, 0.042 mmol, 86%) as a red solid.

**1H NMR** (500 MHz, CDCl₃): δ 7.53 (s, 1H, Ar>H), 5.67 [s, 2H, CH₂O(C=O)], 3.41 (br t, J = 6.5 Hz, 2H, ArCH₂CH₂Ar), 3.37 (br d, J = 3.9 Hz, 1H, ArRCHCRAr), 3.28 (br d, J = 3.8 Hz, 1H, ArRCHCRAr), 3.26 (br t, J = 6.4 Hz, 2H, ArCH₂CH₂Ar), 2.75 (dt, J = 13.8, 7.7 Hz, 1H, CH₃H₃CH₂CH₃), 2.74 (dt, J = 13.9, 7.8 Hz, 1H, CH₃H₃CH₂CH₃), 2.42 [br s, 2H, bridgehead methines-a and b], 1.68–1.59 (m, 4H, CH₂H₃CH₂H₃ and CH₂H₃CH₂H₃), 1.30–1.25 (m, 2H, CH₃H₃CH₂H₃), 1.08 (t, J = 7.3 Hz, 3H, CH₃H₃CH₂CH₃), 1.04 (br d, J = 10.2 Hz, 1H, bridge CH₃H₃), and 0.92 (br d, J = 10.2 Hz, 1H, bridge CH₃H₃).

**13C NMR** (126 MHz, CDCl₃): δ 172.5, 148.4, 147.8, 144.7, 142.6, 141.6, 137.2, 128.3, 125.8, 124.0, 112.8, 70.8, 50.4, 48.8, 37.3, 36.6, 32.6, 31.8, 30.5, 28.0, 27.9, 27.8, 25.6, and 14.6.

**IR** (neat): 2952, 2871, 1756, 1649, 1449, 1424, 1395, 1355, 1293, 1220, 1178, 1162, 1100, 1019, 961, 911, 870, and 753 cm⁻¹.

**HRMS** (ESI-TOF): Calcd for C₂₄H₂₄NaO₂⁺ [M+Na⁺] requires 367.1669; found 367.1674.

**Mp:** 167–170 °C.
IR (neat): 3298, 3064, 2954, 2926, 2854, 1728, 1707, 1604, 1462, 1436, 1387, 1262, 1248, 1135, 1044, 959, 848, and 765 cm\(^{-1}\).

HRMS (ESI-TOF): Calcd for C\(_{36}\)H\(_{28}\)N\(_2\)O\(_3\)Si\(^+\) [M+Na\(^+\)] requires 587.1761; found 587.1770.

Mp: decomposition > ca. 160 \(^\circ\)C.

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(±)-2,3-Dichloro-5,6-dimethoxy-1-(4-methoxyphenyl)-13-tosyl-8-(trimethylsilyl)-13H-fluoreno[1,9-ab]carbazole (25q)

![Chemical Structure](image)

Carbazole 25q was synthesized following general procedure C from pentayne S17 (23 mg, 0.033 mmol), Li\(_2\)CuCl\(_4\) (0.1 mL, 1 M in THF, 0.10 mmol), and anhydrous THF (3.2 mL). Purification by MPLC (hexanes:EtOAc, 3:1) afforded the carbazole derivative 25q (17 mg, 0.023 mmol, 68%) as a red solid.

\(^1\)H NMR (500 MHz, CDCl\(_3\)): δ 8.11 (br dd, J = 8.5, 1.5 Hz, 1H, SO\(_2\)-Ar\(_{ortho}\)), 8.05 (s, 1H, H4), 7.82 (d, J = 8.0 Hz, 1H, H12), 7.60 (d, J = 7.8 Hz, 1H, H9), 7.53 (s, 1H, H7), 7.26 (ddd, J = 7.8, 7.8, 0.9 Hz, 1H, H10 or H11), 7.20 (br dd, J = 8.5, 2.2 Hz, 1H, SO\(_2\)-Ar\(_{meta}\)), 7.18 (ddd, J = 7.7, 7.7, 1.0 Hz, 1H, H11 or H10), 6.80 (br dd, J = 8.4, 2.3 Hz, 1H, SO\(_2\)-Ar\(_{ortho}\)), 6.69 (br dd, J = 8.4, 2.3 Hz, 1H, SO\(_2\)-Ar\(_{meta}\)), 6.65 (nfod, J = 8.2 Hz, 2H, MeO-ArH\(_{meta}\)), 6.50 (nfod, J = 8.3 Hz, 2H, MeO-ArH\(_{ortho}\)), 4.10 (s, 3H, OCH\(_3\)), 4.06 (s, 3H, OCH\(_3\)), 3.94 (s, 3H, OCH\(_3\)), 2.10 (s, 3H, SO\(_2\)-ArCH\(_3\)), and 0.47 [s, 9H, Si(\(\text{CH}_3\))\(_3\)].

\(^13\)C NMR (126 MHz, CDCl\(_3\)): δ 159.2, 149.1, 148.5, 145.2, 143.9, 141.8, 138.5, 137.5, 136.2 (br), 135.6, 134.0, 133.2, 132.74, 132.67 (br), 132.5, 131.6, 131.1, 130.6, 130.5, 128.2, 127.3, 127.2, 126.2, 124.3, 123.7, 122.6, 119.2, 112.4, 111.9, 110.0, 107.8, 56.3, 56.2, 55.3, 21.3, and 2.5 (one aromatic carbon resonance not discernable).

IR (neat): 2997, 2955, 2902, 2834, 1607, 1576, 1513, 1482, 1466, 1439, 1375, 1291, 1276, 1249, 1210, 1171, 1090, 1068, 1033, 838, 821, and 762 cm\(^{-1}\).

HRMS (APCI\(^+\)): Calcd for C\(_{41}\)H\(_{36}\)Cl\(_3\)NO\(_3\)SSi\(^+\) [M+H\(^+\)] requires 752.1455; found 752.1415.

Mp: 231–235 \(^\circ\)C.
Naphthalene 25r was synthesized following general procedure C from octayne 20 (33 mg, 0.050 mmol), (iodoethynyl)benzene\textsuperscript{15} (25 mg, 0.11 mmol), and anhydrous CH\(_3\)CN (2.5 mL). The reaction mixture was quenched with saturated ammonium chloride and extracted with DCM. The combined organic phase was concentrated, the residue was re-dissolved in DCM, and the product was precipitated by addition of MeOH. The diiodonaphthalene 25r (39 mg, 0.042 mmol, 85\%) was obtained as a white solid by filtration and washing with additional MeOH.

\( ^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 5.22 (br t, \(J = 2.5\) Hz, 2H, MsNCH\(_2\)), 5.20 (s, 2H, ArC\(_2\)H\(_2\)), 4.79 (br t, \(J = 2.6\) Hz, 2H, MsNCH\(_2\)^'), 4.37 (s, 2H, =CCH\(_2\)O), 3.32–3.27 (nfom, 2H, ArC\(_2\)H\(_2\)CH\(_2\)Ar'), 3.24–3.19 (nfom, 2H, ArCH\(_2\)C\(_2\)H\(_2\)Ar'), 2.86 (s, 3H, SO\(_2\)CH\(_3\)), 2.74 (t, \(J = 6.6\) Hz, 2H, =CCH\(_2\)CH\(_2\)C'^), 2.65 (t, \(J = 6.8\) Hz, 2H, =CCH\(_2\)CH\(_2\)C'^), 0.91 [s, 9H, SiC(CH\(_3\))\(_3\)], 0.89 [s, 9H, SiC(CH\(_3\))\(_3\)], 0.25 [s, 6H, Si(C(CH\(_3\)))\(_2\)], and 0.11 [s, 6H, Si(C(CH\(_3\)))\(_2\)].

\( ^{13}\)C NMR (126 MHz, CDCl\(_3\)): \(\delta\) 154.5, 151.5, 139.0, 139.0, 137.3, 127.3, 125.5, 118.4, 112.6, 103.8, 96.4, 78.5, 77.0, 75.4, 72.6, 69.7, 66.3, 55.8, 54.2, 52.2, 40.3, 35.0, 28.8, 26.1, 25.9, 19.9, 19.7, 18.41, 18.36, -4.6, and -5.0.

IR (neat): 2954, 2929, 2894, 2857, 2257, 1471, 1463, 1364, 1331, 1255, 1157, 1083, 1058, 953, 837, 776, and 752 cm\(^{-1}\).

HRMS (APCI\(^{+}\)): Caled for C\(_{37}\)H\(_{53}\)I\(_2\)N\(_2\)O\(_4\)Si\(_2\)\(^{+}\) [M+NH\(_4\)]\(^{+}\) requires 931.1348; found 931.1344.

Mp: 202–205 °C.
1-Phenyl-8-(trimethylsilyl)-9H-indeno[2,1-b]fluoranthen-9-one (25s)

Fluoranthene 25s was obtained following general procedure C from pentayne S20 (40 mg, 0.089 mmol), cyclooctane (2.2 mL), and CHCl₃ (2.2 mL). Purification by MPLC (hexanes:EtOAc, 9:1) afforded fluoranthene 25s (35 mg, 0.077 mmol, 87%) as an orange-red solid.

**¹H NMR** (500 MHz, CDCl₃): δ 7.913 (d, J = 7.3 Hz, 1H, H3), 7.93–7.89 (nfom, 1H, H4 or H7), 7.83–7.79 (nfom, 1H, H7 or H4), 7.64 (d, J = 7.3 Hz, 1H, H2), 7.55–7.51 (nfom, 2H, PhHortho), 7.47 (dd, J = 7.2, 0.8 Hz, 1H, H10), 7.45–7.41 (m, 3H, PhHortho+meta), 7.37–7.32 (m, 2H, H5 and H6), 6.99 (dd, J = 7.4, 7.4, 0.8 Hz, 1H, H11), 6.76 (dd, J = 7.6, 7.6, 1.3 Hz, 1H, H12), 5.64 (br d, J = 7.7 Hz, 1H, H13), and 0.60 [s, 9H, Si(CH₃)₃].

**¹³C NMR** (126 MHz, CDCl₃): δ 195.6, 147.6, 144.1, 144.0, 142.8, 141.0, 140.7, 139.9, 139.8, 137.9, 136.6, 135.9, 133.7, 133.5, 132.2, 130.2, 129.2, 128.0, 127.87, 127.85, 127.1, 126.3, 126.0, 124.8, 122.9, 121.3, 121.0, and 2.0.

**IR** (neat): 3054, 3027, 2951, 2897, 1706, 1603, 1463, 1413, 1393, 1263, 1248, 895, 841, and 763 cm⁻¹.

**HRMS** (APCI⁺): Calcd for C₃₁H₂₁OSi⁺ [M-CH₃⁺] requires 437.1356; found 437.1352.

**Mp**: 234–236 °C.

5,6-Dimethoxy-1-(4-methoxyphenyl)-8-(trimethylsilyl)-9H-indeno[2,1-b]fluoranthen-9-one (25t)

Fluoranthene 25t was obtained following general procedure C from pentayne S22 (81 mg, 0.15 mmol), cyclooctane (3.8 mL), and CHCl₃ (3.8 mL). Purification by MPLC (hexanes:EtOAc, 2:1) afforded fluoranthene 25t (64 mg, 0.12 mmol, 79%) as a red solid.
1H NMR (500 MHz, CDCl3): δ 7.75 (d, J = 7.2 Hz, 1H, H3), 7.53 (d, J = 7.2 Hz, 1H, H2), 7.46 (s, 1H, H4), 7.45 (d, J = 7.0 Hz, 1H, H10), 7.42 (nfod, J = 8.7 Hz, 2H, H_o), 7.30 (s, 1H, H7), 6.98 (dd, J = 7.2, 7.2 Hz, 1H, H11), 6.96 (nfod, J = 8.6 Hz, 2H, H_m), 6.81 (ddd, J = 7.6, 7.6, 1.2 Hz, 1H, H12), 5.74 (br d, J = 7.7 Hz, 1H, H13), 4.03 (s, 3H, OCH3), 4.02 (s, 3H, OCH3), 3.85 (s, 3H, OCH3), and 0.60 [s, 9H, Si(CH3)3].

13C NMR (126 MHz, CDCl3): δ 195.6, 159.9, 149.4, 148.3, 147.8, 144.1, 143.7, 140.8, 139.8, 137.8, 136.3, 135.5, 134.1, 133.7, 133.6, 133.4, 132.7, 131.7, 131.3, 127.7, 126.1, 124.8, 122.8, 120.6, 114.6, 110.2, 104.3, 56.30, 56.27, 55.6, and 2.0.

IR (neat): 3059, 3000, 2953, 2901, 2834, 1704, 1606, 1513, 1484, 1460, 1440, 1383, 1279, 1248, 1210, 1175, 1039, 893, 831, and 760 cm⁻¹.

HRMS (APCI⁺): Calcd for C34H27O4Si+ [M-CH3⁺] requires 527.1673; found 527.1671.

Mp: 260–262 °C.

5,6-Dimethoxy-1-(4-methoxyphenyl)-2,3-bis(phenylthio)-8-(trimethylsilyl)-9H-indeno[2,1-b]fluoranthen-9-one (25u)

Fluoranthenone 25u was obtained following general procedure C from pentayne S22 (40 mg, 0.075 mmol), diphenyl disulfide (82 mg, 0.38 mmol), and CHCl3 (3.8 mL). Purification by MPLC (hexanes:EtOAc, 4:1) afforded fluoranthenone 25u (53 mg, 0.070 mmol, 93%) as a red solid.

1H NMR (500 MHz, CDCl3): δ 8.02 (s, 1H, H4), 7.48 (d, J = 7.2 Hz, 1H, H10), 7.43 (s, 1H, H7), 7.41 (d, J = 8.0 Hz, 2H, H_o), 7.14 (t, J = 7.5 Hz, 2H, A-PhHmeta), 7.11–7.03 (m, 5H, A-PhHortho, H11, and B-PhHmeta), 7.00 (tt, J = 7.6, 2.3 Hz, 2H, PhHpara), 6.90 (d, J = 7.6 Hz, 2H, B-PhHortho), 6.86 (d, J = 8.1 Hz, 2H, H_m), 6.83 (dd, J = 7.6, 7.6 Hz, 1H, H12), 5.73 (d, J = 7.8 Hz, 1H, H13), 3.99 (s, 3H, OCH3), 3.81 (s, 3H, OCH3), 3.76 (s, 3H, OCH3), and 0.61 [s, 9H, Si(CH3)3].

13C NMR (126 MHz, CDCl3): δ 195.4, 160.3, 149.0, 148.6, 147.7, 145.6, 144.3, 144.0, 142.4, 141.9, 139.9, 139.6, 138.4, 137.7, 135.4, 134.3, 134.0, 133.9, 133.8, 133.3, 133.2, 132.4, 129.2, 128.9, 127.8, 127.4, 127.4, 126.8, 125.7, 125.6, 125.4, 123.0, 113.5, 109.5, 109.4, 56.2, 56.1, 55.6, and 2.1.

IR (neat): 3003, 2945, 2834, 1706, 1606, 1578, 1511, 1478, 1460, 1438, 1375, 1283, 1247, 1207, 1176, 1024, 846, and 764 cm⁻¹.

HRMS (APCI⁺): Calcd for C46H35O4S2Si+ [M-CH3⁺] requires 743.1741; found 743.1735.
**Mp:** 135–138 °C.

5,6-Dimethoxy-1-(4-methoxyphenyl)-2,3-bis(phenylselanyl)-8-(trimethylsilyl)-9H-indeno[2,1-b]fluoranthen-9-one (25v) and 7,8-Dimethoxy-16-(4-methoxyphenyl)-10-(trimethylsilyl)-11H-benzo[b]indeno[1',2':4,5]fluorantheno[2,1-d]selenophen-11-one (25v')

Fluoranthenes 25v and 25v' were obtained following general procedure C from pentayne S22 (54 mg, 0.10 mmol), diphenyl diselenide (47 mg, 0.15 mmol), and toluene (5.0 mL). The crude solid mixture was triturated with hexanes:DCM (2:1) three times (ca. 5 mL each). The remaining solid (25v') was collected and shown to be quite pure (1H NMR). The initial wash solutions were concentrated and the residue was purified by MPLC (hexanes:EtOAc:DCM, 6:1:1) to give fluoranthene 25v (30 mg, 0.035 mmol, 35%) as a dark red solid followed by additional 25v', which was combined with the initial portion to give 29 mg (0.042 mmol, 42%) as a bright red solid.

**Minor product 25v (faster eluting)**

1H NMR (500 MHz, CDCl3): δ 7.98 (s, 1H, H4), 7.47 (d, J = 7.1 Hz, 1H, H10), 7.41 (s, 1H, H7), 7.37 (d, J = 8.0 Hz, 2H, H6), 7.16 (d, J = 7.5 Hz, 2H, A-PhH_ortho), 7.10–7.02 (m, 8H, B-PhH_ortho, and PhH_meta_para), 6.99 (dd, J = 7.5, 7.5 Hz, 1H, H11), 6.85 (d, J = 8.2 Hz, 2H, Hm), 6.82 (dd, J = 7.6, 7.6 Hz, 1H, H12), 5.75 (d, J = 7.8 Hz, 1H, H13), 3.98 (s, 3H, OCH3), 3.83 (s, 3H, OCH3), 3.72 (s, 3H, OCH3), and 0.60 [s, 9H, Si(CH3)3].

13C NMR (126 MHz, CDCl3): δ 195.4, 160.3, 148.6, 148.4, 147.4, 144.4, 144.1, 144.0, 142.3, 142.2, 141.2, 138.6, 135.7, 135.4, 134.8, 134.3, 134.0, 133.8, 133.6, 133.4, 133.2, 132.7, 130.6, 129.5, 129.2, 128.7, 127.7, 126.9, 126.4, 125.5, 122.9, 113.6, 109.45, 109.40, 56.1, 56.0, 55.6, and 2.2. (one resonance for an sp^2-C not discernable)

IR (neat): 3062, 2996, 2951, 2902, 2832, 1706, 1605, 1578, 1511, 1475, 1461, 1438, 1372, 1282, 1249, 1206, 1176, 843, and 761 cm⁻¹.

HRMS (APCI): Calcd for C_{46}H_{35}O_{4}^{80}Se_{80}SeSi^{+} [M-CH_{3}] requires 839.0630; found 839.0627.

**Mp:** decomposition > ca. 130 °C.

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**Major product 25v' (slower eluting)**
The crude reaction mixture was directly subjected to flash chromatography (hexanes:EtOAc, 3:1), and the oxidized anthracene derivative 27 (6.9 mg, 11 μmol, 57%) was obtained as a brownish solid.

**1H NMR** (500 MHz, CDCl3): δ 7.90 (s, 1H, H4), 7.67 (d, J = 5.5 Hz, 1H, H6), 7.18 (d, J = 5.4 Hz, 1H, H13), 7.14 (d, J = 5.4 Hz, 1H, H12), 7.06 (d, J = 5.5 Hz, 1H, H5), 6.48 (d, J = 1.1 Hz, 1H, H11), 6.30 (d, J = 1.1 Hz, 1H, H8), 5.81 [d, J = 16.3 Hz, 1H, CH2H5O(C=O)], 5.76 [d, J = 16.3 Hz, 1H, CH2H5O(C=O)], 5.48 (d, J = 12.9 Hz, 1H, CH2H5OTBS), 5.34 (d, J = 12.9 Hz, 1H, CH2H5OTBS), 4.30 (q, J = 7.1 Hz, 2H, OCH2CH3), 4.28 (q, J = 7.2 Hz, 2H, OCH2CH3), 1.34 (t, J = 7.1 Hz, 3H, OCH2CH3), 1.33 (t, J = 7.0 Hz, 3H, OCH2CH3), 0.92 [s, 9H, Si(CH3)3], 0.27 [s, 3H, Si(CH3)2(CH3)3], and 0.07 [s, 3H, Si(CH3)2(CH3)3].
IR (neat): 2953, 2928, 2857, 1764, 1736, 1634, 1470, 1445, 1370, 1258, 1212, 1104, 1078, 1019, 853, 841, and 780 cm\(^{-1}\).

HRMS (APCI\(^{+}\)): Calcd for C\(_{37}H_{37}O_{8}Si\)^{+} [M+H\(^{+}\)] requires 637.2252; found 637.2242.

Mp: amorphous, decomposition > ca. 280 °C.

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**2-Phenylspiro[indenol[2,1-b]fluoranthene-9,9’-xanthene] (28)**

To a stirred solution of the fluoranthene-ketone 25s (32 mg, 0.071 mmol) in o-DCB (5.2 mL), methanesulfonic acid (1.8 mL) was added dropwise under a nitrogen atmosphere. This reaction mixture was heated at 80 °C for 30 min, at which time phenol (66 mg, 0.70 mmol) was added, again under nitrogen. The temperature was raised to 150 °C and kept for 24 hours. The reaction mixture was quenched by addition of deionized water, extracted with DCM (x3), dried, and concentrated. Purification by step-gradient flash chromatography [hexanes:EtOAc, 10:1] afforded the spirocyclic xanthene 28 (20 mg, 0.038 mmol, 54%) as a yellow solid. A single crystal suitable for X-ray diffraction analysis was obtained by slow evaporation of a solution of 28 in toluene (CCDC deposition number: 1818243).

\(^1H\) NMR (500 MHz, CDCl\(_3\)): \(\delta\) 8.79 (d, \(J = 0.9\) Hz, 1H, \(H1\)), 8.40 (d, \(J = 7.8\) Hz, 1H, \(H13\)), 8.21 (d, \(J = 0.9\) Hz, 1H, \(H3\)), 7.91 (d, \(J = 7.2\) Hz, 1H, \(H4\)), 7.88 (dd, \(J = 8.0, 1.0\) Hz, 2H, \(H_o\)), 7.714 (d, \(J = 7.4\) Hz, 1H, \(H7\)), 7.706 (s, 1H, \(H8\)), 7.61 (dd, \(J = 7.6, 7.6\) Hz, 2H, \(H_{m}\)), 7.50 (tt, \(J = 7.4, 1.1\) Hz, 1H, \(H_p\)), 7.49–7.45 (nfom, 1H, \(H12\)), 7.34 (ddd, \(J = 7.5, 7.5, 1.2\) Hz, 1H, \(H5\)), 7.300 (ddd, \(J = 7.3, 7.3, 1.1\) Hz, 1H, \(H6\)), 7.296 (dd, \(J = 8.3, 1.2\) Hz, 2H, \(H4^{'})\), 7.27–7.25 (m, 2H, \(H11\) and \(H10\)), 7.23 (ddd, \(J = 8.5, 7.1, 1.5\) Hz, 2H, \(H3^{'})\), 6.77 (ddd, \(J = 8.1, 7.2, 1.3\) Hz, 2H, \(H2^{'})\), and 6.51 (dd, \(J = 8.0, 1.5\) Hz, 2H, \(H1^{'})\).

\(^{13}C\) NMR (126 MHz, CDCl\(_3\)): \(\delta\) 157.4, 156.8, 151.8, 142.8, 142.4, 140.3, 139.8, 139.4, 138.4, 138.0, 135.7, 132.5, 129.2, 128.5, 128.23, 128.20, 128.12, 128.07, 128.0, 127.8, 127.77, 126.1, 125.9, 123.6, 123.0, 122.9, 121.9, 121.6, 120.4, 118.6, 117.1, 116.9, and 54.7.

IR (neat): 3085, 3065, 3054, 3038, 1601, 1572, 1479, 1458, 1443, 1312, 1287, 1245, 1152, 1125, 882, and 752 cm\(^{-1}\).

HRMS (APCI\(^{+}\)): Calcd for C\(_{41}H_{25}O^{-}\) [M+H\(^{-}\)] requires 533.1900; found 533.1908.

Mp: > 350 °C (sublimation > ca. 300 °C).
(±)-15-(4-Chlorophenyl)-16,21-dihydro-6H-16,21-[1,2]benzenoindenophthal[2,3-n]rubicen-6-one (31) via
(±)-15-(4-Chlorophenyl)-5-(trimethylsilyl)-16,21-dihydro-6H-16,21-[1,2]benzenoindenophthal[2,3-n]rubicen-6-one (30)

Tetracene 30 was obtained following general procedure C from nonayne 29 (73 mg, 0.10 mmol), anthracene (107 mg, 0.60 mmol), and CHCl₃ (10 mL). Purification by flash chromatography (hexanes to hexanes:EtOAc, 40:1) followed by washing of the solid with cold MeOH afforded tetracene 30 (80 mg, 0.088 mmol, 88%) as an amorphous dark green solid. Tetracene 30 exists as an interconverting diastereomeric mixture, and the ratio of the two isomers is determined by ¹H NMR analysis (1.8:1 in CDCl₃, and 1:1.3 in d⁶-benzene).

See computational analysis of ¹H NMR spectral data: “Calculated and experimental ¹H NMR analysis of tetracenes 30 and 31”, page 105

IR (neat): 3066, 2922, 2853, 1708, 1601, 1482, 1459, 1450, 1407, 1219, 1193, 1092, 1016, 938, and 770 cm⁻¹.

Because the complexity of the NMR spectra of 30 due to the presence of a mixture of topological isomers that interconverted rapidly on the laboratory time-scale, rendering them inseparable, and because it also ionized poorly by ESI or APCI, the compound was converted directly into the desilylated derivative 31, which was fully characterized.
To a stirred solution of tetracene 30 (80 mg, 0.088 mmol) in CHCl₃ (10 mL), methanesulfonic acid (28 μL, 0.43 mmol) was added and the solution was stirred for 3 hours. The reaction was quenched by the addition of deionized water, extracted with DCM (x3), and dried. The crude material was passed through a short silica plug (DCM), concentrated in vacuo, and rinsed with MeOH. Tetracene 31 (71 mg, 0.085 mmol, 96%) was obtained as an amorphous dark green solid by simple filtration to remove the MeOH without any further purification. Tetracene 31 exists also as a diastereomeric mixture, but the ratio of the two isomers in CDCl₃ is changed to 47:1. Multiple attempts to grow crystals from various solvents and solvent pairs failed to yield a single crystal, always resulting in amorphous solid.

¹H NMR (500 MHz, CDCl₃): δ 8.59 (d, J = 7.6 Hz, 1H, H22), 8.14 (s, 1H, H5), 8.06 (d, J = 7.7 Hz, 1H, H4), 7.85 (d, J = 7.4 Hz, 1H, H25), 7.82 (d, J = 6.9 Hz, 1H, H1), 7.80 (dd, J = 8.2, 2.2 Hz, 1H, Cl-ArH), 7.75 (d, J = 7.6 Hz, 1H, ArHₘ), 7.71 (dd, J = 8.0, 1.9 Hz, 1H, Cl-ArH), 7.68–7.63 (m, 3H, ArH), 7.62–7.58 (m, 2H, ArH), 7.53 (ddd, J = 7.6, 7.6, 0.7 Hz, 1H, ArHₘ), 7.40–7.37 (nfom, 1H, ArH), 7.35 (dd, J = 8.0, 1.9 Hz, 1H, Cl-ArH), 7.29 (ddd, J = 7.5, 7.5, 0.9 Hz, 1H, ArHₘ), 7.28 (ddd, J = 7.6, 7.6, 1.2 Hz, 1H, ArHₘ), 7.25 (dd, J = 7.7, 1.1 Hz, 1H, ArHₘ), 7.211 (ddd, J = 7.8, 7.8, 1.1 Hz, 1H, ArHₘ), 7.208 (ddd, J = 7.4, 7.4, 1.2 Hz, 1H, ArHₘ), 7.19–7.16 (m, 2H, ArH), 7.15 (ddd, J = 7.5, 7.5, 1.2 Hz, 1H, ArHₘ), 7.10 (ddd, J = 7.4, 7.4, 1.1 Hz, 1H, ArHₘ), 6.90 (ddd, J = 7.6, 7.6, 0.6 Hz, 1H, H12), 6.65 (ddd, J = 7.9, 7.9, 1.0 Hz, 1H, H13), 6.61 (s, 1H, bridgehead-Hₖ), 5.67 (d, J = 7.9 Hz, 1H, H14), and 5.66 (s, 1H, bridgehead-Hₐ).

¹³C NMR (126 MHz, CDCl₃): δ 194.3, 145.8, 145.6, 145.2, 143.5, 143.2, 143.0, 142.8, 140.7, 140.4, 139.9, 139.8, 139.6, 139.51, 139.46, 139.34, 139.27, 138.3, 138.0, 137.1, 136.9, 136.3, 136.1, 134.7, 134.2, 134.0, 133.9, 133.8, 133.6, 133.2, 133.1, 132.7, 132.1, 132.0, 130.9, 129.9, 129.6, 129.0, 128.8, 128.2, 127.9, 127.5, 127.43, 127.35, 127.24, 127.16, 126.9, 126.8, 126.6, 126.6, 126.4, 125.6, 124.5, 124.2, 123.6, 123.3, 121.4, 120.7, 119.8, 119.1, 114.6, 51.4, and 50.3.

IR (neat): 3066, 2924, 2852, 1708, 1603, 1482, 1459, 1450, 1407, 1264, 1193, 1092, 1016, and 938, and 759 cm⁻¹.

HRMS (APCI⁺): Calcd for C₆₃H₃₂³⁵ClO⁺ [M+H⁺] requires 839.2136; found 839.2140.
(±)-(16R,25S)-15-(4-Chlorophenyl)-16,25-diphenyl-5-(trimethylsilyl)-16,25-dihydro-6H-16,25-methanoindeno[1',2':2,3]fluoreno[9,1-ab]triphenyleno[2,3-n]rubicene-6,30-dione (32), (±)-(16R,25S)-15-(4-Chlorophenyl)-16,25-diphenyl-16,25-dihydro-6H-16,25-methanoindeno[1',2':2,3]fluoreno[9,1-ab]triphenyleno[2,3-n]rubicene-6,30-dione (32-H), and (±)-15-(4-Chlorophenyl)-16,25-diphenyl-6H-indeno[1',2':2,3]fluoreno[9,1-ab]triphenyleno[2,3-n]rubicen-6-one (33)

Tetracene 32 was obtained following general procedure C from nonayne 29 (73 mg, 0.10 mmol), 1,3-diphenyl-2H-cyclopenta[l]phenanthren-2-one12 (191 mg, 0.50 mmol), and CHCl₃ (10 mL). One deviation was that the reaction vessel was kept in the dark to avoid light-induced autoxidation of the trapping agent, 1,3-diphenyl-2H-cyclopenta[l]phenanthren-2-one.13 Purification by flash chromatography (hexanes:EtOAc:DCM, 40:1:1, to toluene:DCM, 10:1) followed by precipitation from DCM/MeOH afforded tetracene 32 (67 mg, 0.060 mmol, 60%) as an amorphous dark green solid. Tetracene 32 exists as an interconverting diastereomeric mixture, and the ratio of the two isomers was determined by NMR analysis (4:1 in CDCl₃, and 8:1 in d⁶-benzene).

¹H NMR (500 MHz, C₆D₆): δ 9.02 (d, J = 8.3 Hz, 0.9H, ArH₀), 8.98 (d, J = 8.4 Hz, 0.1H, ArH₀), 8.84 (d, J = 8.3 Hz, 0.9H, ArH₀), 8.78 (d, J = 8.4 Hz, 0.1H, ArH₀), 8.64 (d, J = 8.3 Hz, 0.9H, ArH₀), 8.61 (d, J = 8.3 Hz, 0.1H, ArH₀), 8.55 (d, J = 8.3 Hz, 0.9H, ArH₀), 8.52 (d, J = 8.3 Hz, 0.1H, ArH₀), 8.45 (d, J = 8.2 Hz, 0.1H, ArH₀), 8.39–8.34 (m, 1H, ArH), 8.30 (d, J = 7.5 Hz, 1H,
To a stirred solution of tetracene 32 (20 mg, 18 µmol) in CHCl₃ (2.0 mL), methanesulfonic acid (5.8 µL, 0.090 mmol) was added. The reaction flask was evacuated and back-filled with N₂ three times and then heated at 50 °C. After full consumption of the starting material (as indicated by TLC, 4 hours), the reaction was quenched by addition of deionized water and extracted with DCM (x3). The combined organic layer was dried and concentrated. The crude dark green solid 32-H was directly used in the following step without further purification. Tetracene 32-H exists as an interconverting diastereomeric mixture, and the ratio of the two isomers was determined by NMR analysis (5:1 in CDCl₃, and 3:1 in d₆-benzene). (See computational analysis of ⁱH NMR spectral data: “Possible topological isomers of tetracene 32-H,” page 106.)

A single crystal suitable for X-ray diffraction analysis was obtained by slow evaporation of the solution of crude 32-H in EtOAc/DCM. Only one topological isomer is present in the crystal (CCDC deposition number: 1818245).


**Supplementary Information**

\(^1\)H NMR (500 MHz, C\(_6\)D\(_6\)): \(\delta\) 9.02 (d, \(J = 8.2\) Hz, 0.3H, ArH\(_o\)), 8.96 (d, \(J = 8.5\) Hz, 1H, ArH\(_o\)), 8.83 (d, \(J = 8.4\) Hz, 0.3H, ArH\(_o\)), 8.68 (d, \(J = 8.4\) Hz, 1H, ArH\(_o\)), 8.64 (d, \(J = 8.3\) Hz, 0.3H, ArH\(_o\)), 8.59 (d, \(J = 8.2\) Hz, 1H, ArH\(_o\)), 8.55 (d, \(J = 8.3\) Hz, 0.3H, ArH\(_o\)), 8.51 (d, \(J = 8.2\) Hz, 1H, ArH\(_o\)), 8.30–8.24 (m, 2.3H, ArH), 8.22 (s, 0.3H, H5), 8.19 (d, \(J = 7.1\) Hz, 1H, ArH\(_o\)), 8.18 (s, 1H, H5), 8.05 (d, \(J = 7.5\) Hz, 0.3H, ArH\(_o\)), 7.97 (d, \(J = 7.2\) Hz, 0.3H, ArH\(_o\)), 7.96 (d, \(J = 7.2\) Hz, 0.3H, ArH\(_o\)), 7.92 (d, \(J = 7.5\) Hz, 1H, ArH\(_o\)), 7.74 (d, \(J = 7.4\) Hz, 1H, ArH\(_o\)), 7.79–7.71 (m, 2H, ArH), 7.63 (d, \(J = 7.0\) Hz, 0.3H, ArH\(_o\)), 7.58 (dd, \(J = 7.5\), 0.9 Hz, 1H, ArH\(_o\)), 7.57–7.32 (m, 11H, ArH), 7.25–7.20 (m, 3.3H, ArH), 7.11–7.01 (m, 7.3H, ArH), 6.99–6.89 (m, 4.3H, ArH), 6.85–6.73 (m, 3.3H, ArH), 6.72–6.67 (m, 3H, ArH), 6.65 (ddd, \(J = 7.5\), 7.5, 1.3 Hz, 1H, H13), 6.56 (dd, \(J = 7.8\), 7.8 Hz, 0.3H, H13), 5.81 (d, \(J = 8.1\) Hz, 0.3H, H14), and 5.77 (d, \(J = 7.9\) Hz, 1H, H14). The crystal contains EtOAc and DCM that are difficult to remove.

\(^1\)C NMR (126 MHz, C\(_6\)D\(_6\)): \(\delta\) 193.9, 193.2,145.8, 145.5, 145.1, 141.2, 140.9, 140.4, 140.2, 140.0, 139.8, 139.1, 138.7, 137.9, 137.6, 137.1, 136.5, 136.1, 135.3, 134.2, 133.8, 133.3, 132.8, 132.7, 131.6, 131.4, 131.1, 130.8, 130.7, 130.5, 129.7, 129.5, 129.3, 128.7, 128.6 (x2), 128.4 (x2), 128.3, 128.2, 128.1 (x2), 128.0 (x2), 127.7, 127.6 (x2), 127.5 (x2), 127.4, 127.2, 127.0 (x2), 126.9 (x2), 126.8 (x2), 126.7, 126.6 (x2), 126.5, 126.4, 126.1, 125.7, 125.3, 124.0, 123.9 (x2), 123.6, 123.3, 123.1, 121.7, 115.3, 115.0, and 68.1. The crystal contains EtOAc and DCM that are difficult to remove. Data are from HSQC (non-highlighted) & HMBC (highlighted) data sets due to limited solubility. The structure of 32-H is further supported by its single crystal X-ray diffraction analysis (see page 150).

IR (neat): 3052, 3013, 2925, 2855, 1793, 1713, 1601, 1460, 1450, 1409, 1264, 1124, 1092, 845, and 759 cm\(^{-1}\).

HRMS (APCI\(^+\)): Calcd for C\(_{78}\)H\(_{40}\)ClO\(_2\)\(^+\) [M+H\(^+\)] requires 1043.2711; found 1043.2713.

Mp: > 350 °C (color change > ca. 270 °C).

The crude material was suspended in anhydrous o-DCB (2.0 mL). The reaction vessel was evacuated and back-flushed with N\(_2\) three times and then heated at 180 °C (became a homogeneous solution) for 24 hours. Purification by directly subjecting to flash chromatography (hexanes:EtOAc, 50:1 to 20:1) followed by precipitation from DCM/MeOH afforded dibenzohexacene 33 (13 mg, 13 \(\mu\)mol, 73%) as a cherry-red amorphous solid. Dibenzohexacene 33 exists also as a diastereomeric mixture, the ratio of the two isomers is 1:1.1 in CDCl\(_3\), and 1:1.4 in d\(^6\)-benzene. (See computational analysis of \(^1\)H NMR spectral data.: “Possible topological isomers of hexacene 33”, page 117)

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 8.20 (s, 0.5H, H5), 8.18 (s, 0.5H, H5), 8.14–8.02 (m, 3H, ArH), 7.99 (dd, \(J = 7.1\), 7.1 Hz, 1H, ArH\(_m\)), 7.91 (dd, \(J = 7.8\), 7.8 Hz, 1H, ArH\(_m\)), 7.84 (d, \(J = 7.8\) Hz, 0.5H, ArH\(_m\)), 7.84 (d, \(J = 7.5\) Hz, 0.5H, ArH\(_m\)), 7.71 (d, \(J = 7.2\) Hz, 1H, ArH\(_m\)), 7.67 (dd, \(J = 8.1\), 8.1 Hz, 1H, ArH\(_m\)), 7.55 (d, \(J = 8.3\) Hz, 0.5H, ArH\(_o\)), 7.49–7.28 (m, 9H, ArH), 7.25–7.19 (m, 2H, ArH), 7.12 (d, \(J = 8.3\) Hz, 0.5H, ArH\(_o\)), 7.08 (d, \(J = 8.0\) Hz, 0.5H, ArH\(_o\)), 7.06–6.83 (m, 6.5H, ArH), 6.83–6.72 (m, 3.5H, ArH), 6.72–6.64 (m, 2H, ArH), 6.63–6.57 (m, 1H, ArH), 6.54 (dd, \(J = 7.8\), 7.8 Hz, 0.5H, H13), 6.48 (dd, \(J = 7.7\), 7.7 Hz, 0.5H, H13), 6.45 (d, \(J = 8.1\) Hz, 0.5H, H17),...
6.392 (d, $J = 7.6$ Hz, 0.5H, $H26$), 6.388 (d, $J = 7.9$ Hz, 0.5H, $H26$), 5.52 (d, $J = 7.8$ Hz, 0.5H, $H14$), and 5.41 (d, $J = 7.9$ Hz, 0.5H, $H14$).

**1H NMR** (500 MHz, C$_6$D$_6$): $\delta$ 8.323 (d, $J = 7.7$ Hz, 0.4H, Ar$H_o$), 8.318 (d, $J = 7.4$ Hz, 0.6H, Ar$H_o$), 8.21 (d, $J = 7.7$ Hz, 0.6H, Ar$H_o$), 8.18 (s, 0.6H, $H5$), 8.13 (s, 0.4H, $H5$), 8.06 (d, $J = 7.5$ Hz, 0.4H, Ar$H_o$), 8.00 (d, $J = 7.3$ Hz, 0.6H, Ar$H_o$), 7.95–7.89 (m, 2.4H, Ar$H$), 7.78 (d, $J = 7.2$ Hz, 0.6H, Ar$H_o$), 7.75 (d, $J = 7.8$ Hz, 0.6H, Ar$H_o$), 7.62 (dd, $J = 7.2$, 7.2 Hz, 1H, Ar$H_m$), 7.57–7.48 (m, 2.6H, Ar$H$), 7.45 (d, $J = 8.1$ Hz, 0.6H, Ar$H_o$), 7.37 (d, $J = 7.4$ Hz, 0.4H, Ar$H_o$), 7.26 (d, $J = 8.1$ Hz, 0.9H, Ar$H_o$, overlapped with solvent), 7.10–7.01 (m, 5.8H, Ar$H$), 6.98 (dd, $J = 7.3$, 7.3 Hz, 1H, Ar$H_m$), 6.95–6.81 (m, 4H, Ar$H$), 6.80–6.45 (m, 14.4H, Ar$H$), 6.37 (d, $J = 7.8$ Hz, 0.4H, $H26$), 5.82 (d, $J = 7.9$ Hz, 0.4H, $H14$), and 5.72 (d, $J = 7.9$ Hz, 0.6H, $H14$).

**13C NMR** (126 MHz, CDC$_3$): $\delta$ 194.4, 145.7, 145.5, 145.1, 144.9, 141.6, 141.1, 141.0, 140.8, 140.3, 140.1, 139.8, 139.5, 139.3, 138.9, 138.7, 138.5, 138.3, 138.1, 138.0, 137.7, 137.4, 136.8, 134.6, 134.2, 134.0, 133.6 (x2), 133.4, 133.1, 132.9, 132.5, 132.3, 131.9, 131.0, 130.8, 130.1, 129.9, 129.4, 129.0 (x2), 128.8, 128.6, 128.3 (x2), 128.2, 128.0 (x2), 127.8, 127.6 (x2), 127.3 (x2), 127.2, 127.1, 127.0 (x2), 126.8, 126.5, 126.4, 126.3, 126.2, 126.0 (x2), 125.5, 125.4, 125.0, 124.8, 123.9, 123.6, 121.3, 121.0, and 114.6 (x2). Data are from HSQC (non-highlighted) & HMBC (highlighted) data sets.

**IR** (neat): 2956, 2923, 2852, 1712, 1668, 1646, 1598, 1465, 1405, 1259, 1087, 1015, 801, and 760 cm$^{-1}$.

**HRMS** (APCI$^+$): Calcd for C$_{77}$H$_{39}$ClO$^+$ [M$^+$] requires 1014.2684; found 1014.2688.
III. Computational methods

The DFT calculations were performed using Gaussian 09\textsuperscript{16}. The geometry of each structure (including the transition states) was optimized at the B3LYP\textsuperscript{17}/6-31G(d) level of theory in the gas phase. The nature of the optimized structure was verified by frequency calculation (298K, at the same level of theory). For complex tetracene and hexacene derivatives, single point calculations were done at the B3LYP-D3BJ\textsuperscript{18,19}/6-31G(d,p) level of theory with SMD\textsuperscript{20} (chloroform) solvation model to obtain more accurate results. NMR calculations were done at the WP04\textsuperscript{21}/cc-pvdz level of theory with SMD(chloroform) for the already optimized structures from the above methods. Listed on the following pages are the zero-point correction, thermal correction to Gibbs free energy, the sum of the electronic and thermal free energies, and the Cartesian coordinates at B3LYP/6-31G(d), for each structure. For the tetracene and hexacene derivatives, electronic energy at SMD(chloroform)/B3LYP-D3BJ/6-31G(d,p) is also included. The three dimensional views of all the transition states and several global minimum structures were visualized using CYLview\textsuperscript{22}.

**Supplementary Figure 1. Distortion of HDDA-benzynes vs -naphthynes.**

**benz-1**

Zero-point correction = 0.274922 (Hartree/Particle)

Thermal correction to Gibbs Free Energy = 0.231147

Sum of electronic and thermal Free Energies = -1021.848746

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
|               | 1             | 6           | 0.000000                |
|               | 2             | 6           | 0.000000                |
|               | 3             | 6           | 0.000000                |
|               | 4             | 6           | 0.000000                |
|               | 5             | 6           | 0.000000                |
|               | 6             | 6           | 0.000000                |
|               | 7             | 6           | 0.000000                |
|               | 8             | 6           | 0.000000                |
|               | 9             | 6           | 0.000000                |
|               | 10            | 8           | 0.000000                |
|               | 11            | 6           | 0.000000                |
|               | 12            | 14          | 0.000000                |
|               | 13            | 6           | 0.000000                |
|               | 14            | 6           | 0.000000                |
|               | 15            | 6           | 0.000000                |
|               | 16            | 6           | 0.000000                |
| Number | Atomic Type | X     | Y     | Z     |
|--------|-------------|-------|-------|-------|
| 0.433990 (Hartree/Particle) | 3.292666 | -1.538641 |
| 0.376156 | 1.951693 | -1.560628 |
| -1596.931775 | 0.927302 | -1.157358 |
| -2.049415 | 1.266205 | -0.708355 |
| -1.664072 | 2.620913 | -0.733937 |
| -2.515023 | 3.636276 | -1.136128 |
| -0.216839 | 2.712574 | -0.404146 |
| 0.239713 | 1.310183 | -0.128791 |
| -0.864629 | 0.452589 | -0.290211 |
| -0.675546 | 0.962578 | -0.172379 |
| 0.696560 | -1.338628 | -0.271695 |
| 1.813470 | -0.449096 | -0.167122 |
| 1.595363 | 0.910127 | 0.083373 |
| 0.470237 | 3.721277 | -0.460815 |
| 2.876035 | 2.104555 | 0.903426 |
| 3.959982 | 1.098888 | 2.097782 |
| 3.909208 | 3.018480 | -0.390755 |
| 2.018718 | 3.324428 | 2.074206 |
| -1.688882 | -2.015697 | -0.008430 |
| -1.089372 | -3.238596 | -0.207361 |
| 0.118220 | -3.565342 | -0.343369 |
| 1.176058 | -2.692680 | -0.370729 |
| -3.073695 | -1.853039 | 0.469408 |
| -3.399786 | -0.917932 | 1.466757 |
| -4.700827 | -0.832098 | 1.958398 |
| -5.698083 | -1.676002 | 1.465353 |
| -5.382807 | -2.618640 | 0.483069 |
| -4.081566 | -2.711902 | -0.004533 |
### Supplementary Information

**benz-2**

Zero-point correction = 0.199110 (Hartree/Particle)

Thermal correction to Gibbs Free Energy = 0.158427

Sum of electronic and thermal Free Energies = -866.104187

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
|               |               |             | X           | Y           | Z           |
| 1             | 6             | 0           | 2.040976    | 0.997750    | 0.000000    |
| 2             | 6             | 0           | 1.570692    | -0.167037   | 0.000000    |
| 3             | 6             | 0           | 0.336507    | -0.784862   | 0.000000    |
| 4             | 6             | 0           | -0.625870   | 0.270983    | 0.000000    |
| 5             | 6             | 0           | -0.235104   | 1.617183    | 0.000000    |
| 6             | 6             | 0           | 1.107423    | 2.032514    | 0.000000    |
| 7             | 6             | 0           | 1.140281    | 3.534267    | 0.000000    |
| 8             | 8             | 0           | -0.245434   | 3.927223    | 0.000000    |
| 9             | 6             | 0           | -1.083976   | 2.832026    | 0.000000    |
| 10            | 8             | 0           | -2.284164   | 2.939766    | 0.000000    |
| 11            | 14            | 0           | -0.077242   | -2.639802   | 0.000000    |
| 12            | 6             | 0           | -1.083976   | -3.029040   | 1.551308    |
| 13            | 6             | 0           | -1.083976   | -3.029040   | -1.551308   |
| 14            | 6             | 0           | 1.556163    | -3.585870   | 0.000000    |
| 15            | 1             | 0           | -1.687004   | 0.032068    | 0.000000    |
| 16            | 1             | 0           | 1.624146    | 3.954988    | -0.889250   |
| 17            | 1             | 0           | 1.624146    | 3.954988    | 0.889250    |
| 18            | 1             | 0           | -1.355345   | -4.091436   | 1.581968    |
| 19            | 1             | 0           | -0.517814   | -2.802874   | 2.462085    |
naph-2

| Center Number | Atomic Number | Atomic Type | Coordinates (Å) |
|---------------|---------------|-------------|-----------------|
| 1             | 6             | 0           | -0.225558 -0.236264 0.000403 |
| 2             | 6             | 0           | 0.713491 -1.321656 0.000508 |
| 3             | 6             | 0           | 2.127798 -1.72122 0.000391 |
| 4             | 6             | 0           | 2.678468 0.086147 -0.00053 |
| 5             | 6             | 0           | 1.772079 1.72839 0.00053 |
| 6             | 6             | 0           | 0.395513 1.047585 0.000388 |
| 7             | 6             | 0           | -0.183583 2.44302 0.000606 |
| 8             | 1             | 0           | -0.788572 2.663231 -0.886677 |
| 9             | 1             | 0           | -0.787683 2.663245 0.888494 |
| 10            | 6             | 0           | 2.122552 2.690673 -0.000240 |
| 11            | 8             | 0           | 0.946646 3.326405 0.000113 |
| 12            | 8             | 0           | 3.206043 3.139068 -0.000669 |
| 13            | 6             | 0           | 2.779114 2.546902 0.000671 |
| 14            | 6             | 0           | 1.595265 3.573286 -0.000906 |
| 15            | 1             | 0           | 1.625116 -4.230097 0.876464 |
| 16            | 1             | 0           | 1.625223 -4.227423 -0.880289 |
| 17            | 1             | 0           | 3.748040 0.274458 -0.000461 |
| 18            | 1             | 0           | 3.423065 2.679471 -0.876322 |
| 19            | 1             | 0           | 3.420554 2.679878 0.879473 |
| 20            | 6             | 0           | 0.359207 2.707333 0.00004 |
| 21            | 6             | 0           | -1.003052 2.839116 -0.000532 |
| 22            | 6             | 0           | -1.824701 1.882483 -0.000270 |
| 23            | 6             | 0           | -1.654712 0.521664 -0.000135 |
| 24            | 6             | 0           | -2.745540 0.520415 -0.001026 |
| 25            | 6             | 0           | -4.156345 -0.082891 0.00025 |
| 26            | 6             | 0           | -5.258836 0.978732 -0.000963 |
| 27            | 1             | 0           | -4.264815 -0.736516 -0.873390 |
| 28            | 1             | 0           | -5.192497 1.626419 0.881884 |
| 29            | 1             | 0           | -2.632216 1.176659 0.874199 |
| 30            | 1             | 0           | -2.634312 1.172556 -0.879653 |
| 31            | 1             | 0           | -4.263651 -0.730378 0.882172 |
| 32            | 1             | 0           | -5.193777 1.619953 -0.888606 |
| 33            | 1             | 0           | -6.251332 0.515289 0.001463 |
Supplementary Figure 2. Diels–Alder reactions of the HDDA-naphthyne (leading to 25k) and perylene.

**perylene**

Zero-point correction = 0.254519 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.214999
Sum of electronic and thermal Free Energies = -769.191121

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
|               |               | X           | Y           | Z             |
| 1              | 6             | 0           | -1.479583   | -2.427562    | 0.000440     |
| 2              | 6             | 0           | -0.738292   | -1.249871    | 0.000132     |
| 3              | 6             | 0           | 0.738275    | -1.249871    | 0.000132     |
| 4              | 6             | 0           | 1.479622    | -2.427542    | -0.000119    |
| 5              | 6             | 0           | -1.439419   | 0.000015     | -0.000047    |
| 6              | 6             | 0           | -0.738308   | 1.249961     | 0.000065     |
| 7              | 6             | 0           | 0.738300    | 1.249976     | 0.000167     |
| 8              | 6             | 0           | 1.439407    | 0.000010     | -0.000001    |
| 9              | 6             | 0           | -2.874689   | -0.000017    | -0.000202    |
| 10             | 6             | 0           | -3.575683   | 1.232509     | -0.000336    |
| 11             | 6             | 0           | -2.886193   | 2.422691     | -0.000197    |
| 12             | 6             | 0           | -1.479681   | 2.427567     | 0.000033     |
| 13             | 6             | 0           | 1.479658    | 2.427575     | 0.000331     |
| 14             | 6             | 0           | 2.886187    | 2.422696     | 0.000221     |
| 15             | 6             | 0           | 3.575676    | 1.232534     | -0.000075    |
| 16             | 6             | 0           | 2.874695    | -0.000025    | -0.000151    |
| 17             | 6             | 0           | 3.575633    | -1.232541    | -0.000262    |
TS1

One imaginary frequency:  
-275.43 cm⁻¹

Zero-point correction= 0.689638 (Hartree/Particle)

Thermal correction to Gibbs Free Energy= 0.614663

Sum of electronic and thermal Free Energies= -2366.088604

| Center Number | Atomic Number | Atomic Type | X       | Y       | Z       |
|---------------|---------------|-------------|---------|---------|---------|
| 1             | 6             | 0           | -4.595185 | 4.644160 | 1.950915 |
| 2             | 6             | 0           | -3.207658 | 4.672330 | 1.818652 |
| 3             | 6             | 0           | -2.491160 | 3.585474 | 1.289862 |
| 4             | 6             | 0           | -3.184791 | 2.453163 | 0.868584 |
| 5             | 6             | 0           | -4.582163 | 2.427833 | 1.054672 |
| 6             | 6             | 0           | -5.297305 | 3.490401 | 1.579504 |
| 7             | 6             | 0           | -5.082898 | 1.069310 | 0.731266 |
| 8             | 6             | 0           | -3.890158 | 0.277365 | 0.294825 |
| 9             | 6             | 0           | -2.757087 | 1.112544 | 0.340555 |
| 10            | 6             | 0           | -1.474115 | 0.556949 | -0.004077 |
| 11            | 6             | 0           | -1.465779 | -0.864594 | 0.026655 |
| 12            | 6             | 0           | -2.625518 | -1.698796 | 0.106214 |
| 13            | 6             | 0           | -3.898908 | -1.129114 | 0.046618 |
| 14            | 8             | 0           | -6.225972 | 0.666319 | 0.893558 |
| 15            | 14            | 0           | -5.483828 | -2.031330 | -0.589231 |
TS2

One imaginary frequency: \(-282.18\) cm\(^{-1}\)

Zero-point correction= 0.689133 (Hartree/Particle)

Sum of electronic and zero-point Energies= -2366.015353

Sum of electronic and thermal Free Energies= -2366.091213

| Center Number | Atomic Number | Atomic Type | X   | Y   | Z   |
|---------------|---------------|-------------|-----|-----|-----|
| 1             | 6             | 0           | 6.577811 | -1.427856 | 1.470849 |
| 2             | 8             | 0           | 5.483183 | -2.518983 | -1.089846 |
| 3             | 6             | 0           | 7.188111 | 0.371184  | -0.844221 |
| 4             | 6             | 0           | 6.142765 | 1.441684  | 1.989757  |
| 5             | 6             | 0           | 4.184350 | 0.042841  | 0.017611  |
| 6             | 6             | 0           | 3.581696 | -1.219738 | -0.270263 |
| 7             | 6             | 0           | 4.295147 | -2.416924 | -0.818970 |
| 8             | 6             | 0           | 3.244707 | -3.430536 | -1.107129 |
| 9             | 6             | 0           | 3.396321 | -4.679990 | -1.684301 |
| 10            | 6             | 0           | 2.242325 | -5.417615 | -1.979944 |
| 11            | 6             | 0           | 0.986337 | -4.867818 | -1.721282 |
| 12            | 6             | 0           | 0.841842 | -3.596131 | -1.142470 |
| 13            | 6             | 0           | 1.985588 | -2.876217 | -0.804857 |
| 14            | 6             | 0           | 2.200995 | -1.500051 | -0.256325 |
|    |     |    |            |            |            |
|----|-----|----|------------|------------|------------|
| 15 | 6   | 0  | 1.278968   | -0.474708  | 0.120704   |
| 16 | 6   | 0  | 1.862536   | 0.821950   | 0.107490   |
| 17 | 6   | 0  | 3.263980   | 1.097704   | 0.045821   |
| 18 | 6   | 0  | 3.388035   | 2.574061   | 0.051959   |
| 19 | 6   | 0  | 4.480553   | 3.413270   | -0.162809  |
| 20 | 6   | 0  | 4.305551   | 4.801466   | -0.136962  |
| 21 | 6   | 0  | 3.044730   | 5.355702   | 0.094083   |
| 22 | 6   | 0  | 1.928678   | 4.529483   | 0.259635   |
| 23 | 6   | 0  | 2.088552   | 3.145057   | 0.211913   |
| 24 | 6   | 0  | 1.122996   | 2.043045   | 0.246394   |
| 25 | 6   | 0  | -0.231272  | 1.813392   | 0.341894   |
| 26 | 6   | 0  | -0.785509  | 0.647166   | 0.480599   |
| 27 | 6   | 0  | -1.37286   | -0.572348  | 0.476247   |
| 28 | 6   | 0  | -1.546235  | 3.458125   | 0.000680   |
| 29 | 6   | 0  | -2.354144  | 2.869368   | -1.039027  |
| 30 | 6   | 0  | -3.391423  | 1.971710   | -0.659337  |
| 31 | 6   | 0  | -3.639347  | 1.753045   | 0.741435   |
| 32 | 6   | 0  | -2.062728  | 3.511062   | 1.311717   |
| 33 | 6   | 0  | -3.069945  | 2.638360   | 1.678258   |
| 34 | 6   | 0  | -2.094388  | 3.108981   | -2.400388  |
| 35 | 6   | 0  | -2.862730  | 2.487705   | -3.367935  |
| 36 | 6   | 0  | -3.890654  | 1.608132   | -3.001575  |
| 37 | 6   | 0  | -4.176513  | 1.328972   | -1.664635  |
| 38 | 6   | 0  | -5.253180  | 0.406815   | -1.257749  |
| 39 | 6   | 0  | -6.092199  | -0.213558  | -2.179048  |
| 40 | 6   | 0  | -7.094821  | -1.116702  | -1.781797  |
| 41 | 6   | 0  | -7.268341  | -1.421972  | -0.451075  |
| 42 | 6   | 0  | -6.445068  | -0.818549  | 0.533289   |
| 43 | 6   | 0  | -6.603137  | -1.129837  | 1.908295   |
| 44 | 6   | 0  | -5.790509  | -0.548671  | 2.856039   |
| 45 | 6   | 0  | -4.809080  | 0.380821   | 2.470769   |
| 46 | 6   | 0  | -4.630449  | 0.746185   | 1.138883   |
| 47 | 6   | 0  | -5.436020  | 0.118804   | 0.133435   |
| 48 | 6   | 0  | -0.791686  | -1.801700  | 0.976388   |
| 49 | 6   | 0  | -2.142751  | -2.051755  | 0.678832   |
| 50 | 6   | 0  | -2.790522  | -3.174857  | 1.188254   |
| 51 | 6   | 0  | -2.104675  | -4.065280  | 2.018969   |
| 52 | 6   | 0  | -0.767728  | -3.818977  | 2.337527   |
| 53 | 6   | 0  | -0.116732  | -2.699104  | 1.822375   |
| 54 | 14  | 0  | 6.024526   | 0.157989   | 0.589973   |
| 55 | 1   | 0  | 4.390436   | -5.056451  | -1.908720  |
| 56 | 1   | 0  | 2.323006   | -6.404762  | -2.426445  |
| 57 | 1   | 0  | 0.092082   | -5.430389  | -1.976634  |
| 58 | 1   | 0  | -0.150547  | -3.199385  | -0.975444  |
| 59 | 1   | 0  | 5.463086   | 3.003818   | -0.366985  |
| 60 | 1   | 0  | 5.160880   | 5.451555   | -0.299489  |
| 61 | 1   | 0  | 2.924897   | 6.435136   | 0.129564   |
| 62 | 1   | 0  | 0.953281   | 4.974993   | 0.428698   |
| 63 | 1   | 0  | 5.792970   | -1.806859  | 2.137200   |
| 64 | 1   | 0  | -0.805178  | 4.186650   | -0.309720  |
| 65 | 1   | 0  | 7.445993   | -1.190434  | 2.099218   |
| 66 | 1   | 0  | 6.853125   | -2.227495  | 0.782590   |
| 67 | 1   | 0  | -1.589865  | 4.146013   | 2.055278   |
| 68 | 1   | 0  | -3.406004  | 2.619929   | 2.708641   |
| 69 | 1   | 0  | -1.288992  | 3.783364   | -2.678572  |
| 70 | 1   | 0  | -2.672547  | 2.676374   | -4.420712  |
| 71 | 1   | 0  | -4.464708  | 1.137745   | -3.791935  |
TS3

One imaginary frequency:
-266.65 cm⁻¹

Zero-point correction = 0.689343 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.614117
Sum of electronic and thermal Free Energies = -2366.089891

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
| 1             | 6             | 0           | 3.980204 5.197103 -0.060134 |
| 2             | 8             | 0           | 5.767175 2.215483 -0.081867 |
| 3             | 6             | 0           | 4.614632 3.392850 2.411290 |
| 4             | 6             | 0           | 1.893369 4.505066 2.174854 |
| 5             | 6             | 0           | 2.715558 2.295777 0.137239 |
| 6             | 6             | 0           | 3.564256 1.161339 -0.046151 |
| 7             | 6             | 0           | 5.055168 1.223673 -0.152459 |
| 8             | 6             | 0           | 5.505259 -0.148664 -0.498594 |
| 9             | 6             | 0           | 6.793854 -0.576557 -0.766924 |
| 10            | 6             | 0           | 6.977755 -1.893191 -1.208903 |
| 11            | 6             | 0           | 5.866271 -2.712984 -1.399867 |
| 12            | 6             | 0           | 4.561531 -2.265733 -1.131840 |
| 13            | 6             | 0           | 4.372125 -0.974173 -0.644826 |
|   |   |   |   |   |   |
|---|---|---|---|---|---|
| 14 | 6 | 0 | 3.152988 | -0.158189 | -0.324952 |
| 15 | 6 | 0 | 1.748499 | -0.453541 | -0.362681 |
| 16 | 6 | 0 | 0.945282 | 0.716053 | -0.454672 |
| 17 | 6 | 0 | 1.394879 | 2.059444 | -0.255282 |
| 18 | 6 | 0 | 0.218746 | 2.927136 | -0.507876 |
| 19 | 6 | 0 | 0.093486 | 4.308192 | -0.658888 |
| 20 | 6 | 0 | -1.156482 | 4.856244 | -0.970376 |
| 21 | 6 | 0 | -2.274224 | 4.036457 | -1.150417 |
| 22 | 6 | 0 | -2.156473 | 2.646449 | -1.051911 |
| 23 | 6 | 0 | -0.914995 | 2.097900 | -0.744293 |
| 24 | 6 | 0 | -0.471837 | 0.704277 | -0.674470 |
| 25 | 6 | 0 | -1.019811 | -0.552211 | -0.742073 |
| 26 | 6 | 0 | -0.298596 | -1.619466 | -0.562102 |
| 27 | 6 | 0 | 1.060879 | -1.746879 | -0.345722 |
| 28 | 6 | 0 | -3.591843 | -1.559049 | -0.864941 |
| 29 | 6 | 0 | -3.368074 | -1.875450 | 0.524838 |
| 30 | 6 | 0 | -2.370749 | -2.835745 | 0.846446 |
| 31 | 6 | 0 | -1.604234 | -3.405384 | -0.231968 |
| 32 | 6 | 0 | -3.110251 | -2.453388 | -1.846523 |
| 33 | 6 | 0 | -4.116712 | -1.249395 | 1.563061 |
| 34 | 6 | 0 | -3.837716 | -1.610719 | 2.882590 |
| 35 | 6 | 0 | -2.848189 | -2.552314 | 3.195416 |
| 36 | 6 | 0 | -2.112590 | -3.156699 | 2.191602 |
| 37 | 6 | 0 | 1.709890 | -3.025196 | 0.035256 |
| 38 | 6 | 0 | 2.430370 | -3.126334 | 1.236476 |
| 39 | 6 | 0 | 3.008148 | -4.335842 | 1.621690 |
| 40 | 6 | 0 | 2.878487 | -5.467379 | 0.814311 |
| 41 | 6 | 0 | 2.161906 | -5.382348 | -0.382082 |
| 42 | 6 | 0 | 1.580281 | -4.173756 | -0.765460 |
| 43 | 14 | 0 | 3.322519 | 3.855193 | 1.100442 |
| 44 | 6 | 0 | -4.543134 | -0.489640 | -1.204060 |
| 45 | 6 | 0 | -5.321575 | 0.113216 | -0.163551 |
| 46 | 6 | 0 | -5.151637 | -0.259255 | 1.209639 |
| 47 | 6 | 0 | -6.290743 | 1.112004 | -0.509404 |
| 48 | 6 | 0 | -7.086594 | 1.690656 | 0.508856 |
| 49 | 6 | 0 | -6.925470 | 1.311443 | 1.819870 |
| 50 | 6 | 0 | -5.963051 | 0.344328 | 2.164621 |
| 51 | 6 | 0 | -4.708222 | 0.048958 | -2.513833 |
| 52 | 6 | 0 | -5.651444 | 0.940230 | -2.845960 |
| 53 | 6 | 0 | -6.436700 | 1.503676 | -1.865025 |
| 54 | 1 | 0 | 4.281821 | 6.084527 | 0.510226 |
| 55 | 1 | 0 | 4.858443 | 4.821517 | -0.594658 |
| 56 | 1 | 0 | 3.240033 | 5.513989 | -0.803901 |
| 57 | 1 | 0 | 4.642823 | 4.187986 | 3.167472 |
| 58 | 1 | 0 | 4.338576 | 2.466168 | 2.929865 |
| 59 | 1 | 0 | 5.616642 | 3.266272 | 2.000191 |
| 60 | 1 | 0 | 0.991755 | 4.821169 | 1.649045 |
| 61 | 1 | 0 | 1.598913 | 3.736546 | 2.900576 |
| 62 | 1 | 0 | 2.264113 | 5.363452 | 2.750732 |
| 63 | 1 | 0 | 7.626777 | 0.110739 | -0.647737 |
| 64 | 1 | 0 | 7.975300 | -2.266535 | -1.422716 |
| 65 | 1 | 0 | 6.003481 | -3.724999 | -1.772136 |
| 66 | 1 | 0 | 3.731983 | -2.931737 | -1.319433 |
| 67 | 1 | 0 | 0.953412 | 4.961527 | -0.561158 |
| 68 | 1 | 0 | -1.253108 | 5.932854 | -1.083150 |
| 69 | 1 | 0 | -3.237293 | 4.479510 | -1.389676 |
| 70 | 1 | 0 | -3.012676 | 2.003154 | -1.228701 |
### 25k-bay

![25k-bay diagram](image)

Zero-point correction: 0.693890 (Hartree/Particle)
Thermal correction to Gibbs Free Energy: 0.622353
Sum of electronic and thermal Free Energies: -2366.160079

| Center Number | Atomic Number | Atomic Type | X        | Y        | Z        |
|---------------|---------------|-------------|----------|----------|----------|
| 1             | 6             | 0           | -0.854167| -4.15971 | 0.022842 |
| 2             | 1             | 0           | -3.468946| -2.375119| -2.866674|
| 3             | 1             | 0           | -4.386007| -1.156004| 3.700015 |
| 4             | 1             | 0           | -2.661244| -2.802768| 4.235938 |
| 5             | 1             | 0           | -1.335863| -3.879227| 2.427561 |
| 6             | 1             | 0           | 2.530370 | -2.250057| 1.870120 |
| 7             | 1             | 0           | 3.561263 | -4.393789| 2.555336 |
| 8             | 1             | 0           | 3.332250 | -6.408187| 1.113693 |
| 9             | 1             | 0           | 2.059949 | -6.256453| -1.020119|
| 10            | 1             | 0           | -7.821422| 2.448737 | -3.01585 |
| 11            | 1             | 0           | -7.536279| 1.755183 | 2.601129 |
| 12            | 1             | 0           | -5.864889| 0.075790 | 3.210427 |
| 13            | 1             | 0           | -4.082015| -0.453530| -3.30185 |
| 14            | 1             | 0           | -5.751472| -0.453530| -3.30185 |
| 15            | 1             | 0           | -7.172577| 2.264548 | -2.112856|
| 16            | 6             | 0           | -2.143318| -3.387266| -1.532327|
| 17            | 6             | 0           | -0.993428| -0.872737| -0.228801|
| 22 | 6   | 0   | 0.207020 | -1.557496 | -0.384257 |
| 23 | 6   | 0   | -2.271652 | 1.339074  | 0.050901  |
| 24 | 6   | 0   | -3.542720 | 0.512977  | 0.076076  |
| 25 | 6   | 0   | -3.559741 | -0.833246 | -0.089282 |
| 26 | 6   | 0   | -2.306631 | -1.641425 | -0.316480 |
| 27 | 6   | 0   | -4.789373 | 1.232223  | 0.205738  |
| 28 | 6   | 0   | -6.023374 | 0.600196  | -0.096865 |
| 29 | 6   | 0   | -6.037108 | -0.849034 | -0.255653 |
| 30 | 6   | 0   | -4.812250 | -1.548086 | -0.113258 |
| 31 | 6   | 0   | -4.775269 | 2.565144  | 0.711101  |
| 32 | 6   | 0   | -5.955820 | 3.298939  | 0.733747  |
| 33 | 6   | 0   | -7.153915 | 2.725107  | 0.279838  |
| 34 | 6   | 0   | -7.194151 | 1.394003  | -0.100494 |
| 35 | 6   | 0   | -7.219880 | -1.608421 | -0.415081 |
| 36 | 6   | 0   | -7.195004 | -2.990991 | -0.332203 |
| 37 | 6   | 0   | -6.000849 | -3.756845 | -0.32005  |
| 38 | 6   | 0   | -4.809247 | -2.959875 | 0.087247  |
| 39 | 6   | 0   | -3.572991 | -3.557104 | 0.598718  |
| 40 | 6   | 0   | -2.399151 | -2.912156 | 0.521547  |
| 41 | 6   | 0   | -2.374848 | 2.384736  | 1.158846  |
| 42 | 6   | 0   | -3.542132 | 3.012939  | 1.359826  |
| 43 | 6   | 0   | 0.292968  | 2.750260  | 0.031249  |
| 44 | 6   | 0   | 0.924309  | 3.348972  | 1.133154  |
| 45 | 6   | 0   | 0.929534  | 4.734786  | 1.289041  |
| 46 | 6   | 0   | 0.311368  | 5.550703  | 0.339669  |
| 47 | 6   | 0   | -0.307605 | 4.969977  | -0.769238 |
| 48 | 6   | 0   | -0.315537 | 3.583256  | -0.921290 |
| 49 | 6   | 0   | 1.981660  | -3.094284 | -0.491240 |
| 50 | 6   | 0   | 0.573775  | -2.967691 | -0.672321 |
| 51 | 6   | 0   | -0.150612 | -4.042744 | -1.191674 |
| 52 | 6   | 0   | 0.509085  | -5.238055 | -1.498669 |
| 53 | 6   | 0   | 1.887465  | -5.358606 | -1.317778 |
| 54 | 6   | 0   | 2.631230  | -4.280644 | -0.829056 |
| 55 | 1   | 0   | 6.010662  | 5.188179  | -1.655535 |
| 56 | 1   | 0   | 3.574211  | 5.416612  | -2.055479 |
| 57 | 1   | 0   | 2.013469  | 3.631403  | -1.476961 |
| 58 | 1   | 0   | 6.897768  | 3.021095  | -0.707331 |
| 59 | 1   | 0   | 5.011081  | -4.269970 | 2.688687  |
| 60 | 1   | 0   | 3.520966  | -3.329729 | 2.780148  |
| 61 | 1   | 0   | 3.743911  | -4.500390 | 1.478999  |
| 62 | 1   | 0   | 7.146286  | -3.680927 | 0.504057  |
| 63 | 1   | 0   | 5.990312  | -3.682801 | -0.836443 |
| 64 | 1   | 0   | 6.982596  | -2.245668 | -0.526083 |
| 65 | 1   | 0   | 6.443423  | -2.029266 | 3.203370  |
| 66 | 1   | 0   | 6.638360  | -0.605159 | 2.158946  |
| 67 | 1   | 0   | 5.159289  | -0.821937 | 3.114978  |
| 68 | 1   | 0   | -5.952404 | 4.311801  | 1.129439  |
| 69 | 1   | 0   | -8.067521 | 3.313437  | 0.278405  |
| 70 | 1   | 0   | -8.147125 | 0.953228  | -0.373426 |
| 71 | 1   | 0   | -8.170038 | -1.108208 | -0.570458 |
| 72 | 1   | 0   | -8.117549 | -3.553544 | -0.446911 |
| 73 | 1   | 0   | -6.009476 | -4.740577 | 0.133297  |
| 74 | 1   | 0   | -3.650567 | -4.507910 | 1.122024  |
| 75 | 1   | 0   | -1.506147 | -3.307299 | 0.990355  |
| 76 | 1   | 0   | -1.498512 | 2.655121  | 1.730467  |
| 77 | 1   | 0   | -3.617683 | 3.820758  | 2.084653  |
| 78 | 1   | 0   | 1.404351  | 2.718590  | 1.876455  |
Zero-point correction=  0.693374 (Hartree/Particle)
Thermal correction to Gibbs Free Energy=   0.621572
Sum of electronic and thermal Free Energies= -2366.161343

| Center Number | Atomic Number | Atomic Type | X     | Y     | Z     |
|---------------|---------------|-------------|-------|-------|-------|
| 1             | 6             | 0           | 5.940188 | -1.580716 | 1.976591 |
| 2             | 8             | 0           | 5.160606 | -2.749488 | -0.679824 |
| 3             | 6             | 0           | 7.070367 | 0.074257  | -0.430319 |
| 4             | 6             | 0           | 5.801065 | 1.363558  | 2.124098  |
| 5             | 6             | 0           | 3.937932 | -0.064779 | 0.076728  |
| 6             | 6             | 0           | 3.262535 | -1.277414 | -0.243692 |
| 7             | 6             | 0           | 3.955595 | -2.543775 | -0.636769 |
| 8             | 6             | 0           | 2.894226 | -3.470534 | -1.093795 |
| 9             | 6             | 0           | 3.055467 | -4.727765 | -1.651422 |
| 10            | 6             | 0           | 1.927705 | -5.372001 | -2.174163 |
| 11            | 6             | 0           | 0.697206 | -4.716426 | -2.153937 |
| 12            | 6             | 0           | 0.547321 | -3.439110 | -1.589847 |
| 13            | 6             | 0           | 1.650061 | -2.811585 | -1.015826 |
| 14            | 6             | 0           | 1.871027 | -1.448637 | -0.417935 |
| 15            | 6             | 0           | 1.003153 | -0.339348 | -0.117337 |
| 16            | 6             | 0           | 1.696551 | 0.889835  | -0.081311 |
| 17            | 6             | 0           | 3.111823 | 1.056057  | -0.049278 |
| 18            | 6             | 0           | 3.356633 | 2.507715  | -0.152191 |
| 19            | 6             | 0           | 4.533825 | 3.223643  | -0.368610 |
| 20            | 6             | 0           | 4.480738 | 4.612312  | -0.517066 |
| 21            | 6             | 0           | 3.256456 | 5.281146  | -0.468198 |
| 22            | 6             | 0           | 2.063717 | 4.570695  | -0.298347 |
| 23            | 6             | 0           | 2.101044 | 3.183517  | -0.152369 |
| 24            | 6             | 0           | 1.044637 | 2.154752  | -0.043177 |
| 25            | 6             | 0           | -0.318523 | 2.172151  | 0.122054  |
| 26            | 6             | 0           | -1.047098 | 0.945183  | 0.336435  |
| 27            | 6             | 0           | -0.430177 | -0.297743 | 0.160123  |
| 28            | 6             | 0           | -1.173108 | 3.433516  | 0.197512  |
| 29            | 6             | 0           | -2.341220 | 3.199802  | -0.749585 |
|   |   |   |   |   |
|---|---|---|---|---|
| 30 | 6 | 0 | -3.086534 | 2.063972 |
| 31 | 6 | 0 | -2.537598 | 1.291276 |
| 32 | 6 | 0 | -1.721664 | 3.441296 |
| 33 | 6 | 0 | -2.396311 | 2.336852 |
| 34 | 6 | 0 | -2.687348 | 3.982408 |
| 35 | 6 | 0 | -3.812512 | 3.621400 |
| 36 | 6 | 0 | -4.572452 | 2.512087 |
| 37 | 6 | 0 | -4.228827 | 1.704571 |
| 38 | 6 | 0 | -5.049551 | 0.568072 |
| 39 | 6 | 0 | -6.194717 | 0.165022 |
| 40 | 6 | 0 | -5.049551 | 0.568072 |
| 41 | 6 | 0 | -6.729098 | -1.472777 |
| 42 | 6 | 0 | -5.557969 | -1.117720 |
| 43 | 6 | 0 | -4.090481 | -1.432227 |
| 44 | 6 | 0 | -3.221195 | -0.452563 |
| 45 | 6 | 0 | -3.483638 | 0.199037 |
| 46 | 6 | 0 | -4.685140 | 0.061129 |
| 47 | 6 | 0 | -5.043959 | -5.176780 |
| 48 | 6 | 0 | -2.013733 | -3.631631 |
| 49 | 6 | 0 | -1.149454 | -1.591796 |
| 50 | 6 | 0 | -2.242526 | -0.081200 |
| 51 | 6 | 0 | -2.427693 | -0.408146 |
| 52 | 6 | 0 | -1.343330 | -3.747848 |
| 53 | 6 | 0 | -0.709328 | -2.515199 |
| 54 | 14 | 0 | 5.700033 | -0.061129 |
| 55 | 1 | 0 | 4.043959 | -5.176780 |
| 56 | 1 | 0 | 2.013733 | -3.631631 |
| 57 | 1 | 0 | 0.901257 | -1.591796 |
| 58 | 1 | 0 | -0.422443 | -2.966615 |
| 59 | 1 | 0 | 5.486392 | 2.712210 |
| 60 | 1 | 0 | 5.397947 | 5.170665 |
| 61 | 1 | 0 | 3.223160 | -6.360915 |
| 62 | 1 | 0 | 1.127565 | 5.117417 |
| 63 | 1 | 0 | 5.050602 | -1.762618 |
| 64 | 1 | 0 | -0.617671 | 4.333074 |
| 65 | 1 | 0 | 6.772629 | -1.383423 |
| 66 | 1 | 0 | 6.159028 | -2.490141 |
| 67 | 1 | 0 | -1.538177 | 4.269672 |
| 68 | 1 | 0 | -2.870719 | 2.141854 |
| 69 | 1 | 0 | -2.103183 | 4.860773 |
| 70 | 1 | 0 | -4.105669 | -2.221119 |
| 71 | 1 | 0 | 5.108422 | 2.284193 |
| 72 | 1 | 0 | 6.962274 | 0.958934 |
| 73 | 1 | 0 | 7.057014 | -0.811349 |
| 74 | 1 | 0 | 8.053308 | 0.130933 |
| 75 | 1 | 0 | 5.711807 | 2.374352 |
| 76 | 1 | 0 | 6.769059 | 1.292662 |
| 77 | 1 | 0 | 5.023781 | 1.242736 |
| 78 | 1 | 0 | -6.477579 | 0.647526 |
| 79 | 1 | 0 | -7.920180 | -1.135321 |
| 80 | 1 | 0 | -7.377450 | -2.245749 |
| 81 | 1 | 0 | -5.911464 | -2.524608 |
| 82 | 1 | 0 | -3.843363 | -1.927748 |
| 83 | 1 | 0 | -2.308297 | -0.218739 |
| 84 | 1 | 0 | -2.584112 | -1.241793 |
| 85 | 1 | 0 | -3.723965 | -3.418111 |
| 86 | 1 | 0 | -2.920718 | -5.043271 |
Zero-point correction=                           0.693648 (Hartree/Particle)
Thermal correction to Gibbs Free Energy=         0.621484  
Sum of electronic and thermal Free Energies=  -2366.165926  

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
| 1             | 6             | 0           | 3.678339                |
| 2             | 6             | 0           | 5.544538                |
| 3             | 6             | 0           | 6.470407                |
| 4             | 6             | 0           | 4.906723                |
| 5             | 6             | 0           | 2.536214                |
| 6             | 6             | 0           | 3.396243                |
| 7             | 6             | 0           | 4.862861                |
| 8             | 6             | 0           | 5.308896                |
| 9             | 6             | 0           | 6.59632                |
| 10            | 6             | 0           | 7.40373                |
| 11            | 6             | 0           | 5.639436                |
| 12            | 6             | 0           | 4.362616                |
| 13            | 6             | 0           | 4.191717                |
| 14            | 6             | 0           | 2.993873                |
| 15            | 6             | 0           | 1.607214                |
| 16            | 6             | 0           | 0.744172                |
| 17            | 6             | 0           | 1.186685                |
| 18            | 6             | 0           | -0.015557               |
| 19            | 6             | 0           | -0.142452               |
| 20            | 6             | 0           | -1.413498               |
| 21            | 6             | 0           | -2.544791               |
| 22            | 6             | 0           | -2.424369               |
| 23            | 6             | 0           | -1.161266               |
| 24            | 6             | 0           | -0.691291               |
| 25            | 6             | 0           | -1.255249               |
| 26            | 6             | 0           | -0.408354               |
| 27            | 6             | 0           | 0.973851                |
| 28            | 6             | 0           | -2.736012               |
| 29            | 6             | 0           | -3.170340               |
| 30            | 6             | 0           | -2.333044               |
| 31            | 6             | 0           | -1.221921               |
| 32            | 6             | 0           | -2.628703               |
| 33            | 6             | 0           | -4.296983               |
| 34            | 6             | 0           | -4.528727               |
| 35            | 6             | 0           | -3.678415               |
| 36            | 6             | 0           | -2.573008               |
| 37            | 6             | 0           | 1.755113                |

25k
|   |   |   |   |   |
|---|---|---|---|---|
| 38 | 6 | 0 | 2.556615 | 2.974271 | -1.400826 |
| 39 | 6 | 0 | 3.277581 | 4.103960 | -1.787598 |
| 40 | 6 | 0 | 3.213484 | 5.273918 | -1.029369 |
| 41 | 6 | 0 | 2.421896 | 5.305621 | 0.120674 |
| 42 | 6 | 0 | 1.701010 | 4.175285 | 0.506143 |
| 43 | 14 | 0 | 3.205116 | -3.789335 | -1.400826 |
| 44 | 6 | 0 | -3.721386 | 0.106654 | 1.283434 |
| 45 | 6 | 0 | -4.906629 | -0.206143 | 0.547959 |
| 46 | 6 | 0 | -5.202625 | 0.384548 | -0.731450 |
| 47 | 6 | 0 | -5.821274 | -1.166438 | 1.011109 |
| 48 | 6 | 0 | -6.990401 | -1.519548 | 0.376481 |
| 49 | 6 | 0 | -7.242688 | -0.955447 | -0.850379 |
| 50 | 6 | 0 | -6.353696 | -0.008375 | -1.396714 |
| 51 | 6 | 0 | -3.759720 | -0.490354 | 2.511170 |
| 52 | 6 | 0 | -4.399911 | -1.425546 | 3.053729 |
| 53 | 6 | 0 | -5.539655 | -1.758559 | 2.359531 |
| 54 | 1 | 0 | 4.017707 | -6.085922 | -0.682641 |
| 55 | 1 | 0 | 4.501425 | -4.919678 | 0.563563 |
| 56 | 1 | 0 | 2.852014 | -5.567270 | 0.545385 |
| 57 | 1 | 0 | 4.749964 | -4.027206 | -3.142618 |
| 58 | 1 | 0 | 4.511918 | -2.315454 | -2.787405 |
| 59 | 1 | 0 | 5.619337 | -3.270396 | -1.789407 |
| 60 | 1 | 0 | 2.326462 | -5.131064 | -3.106912 |
| 61 | 1 | 0 | 0.937532 | -4.628899 | -2.133852 |
| 62 | 1 | 0 | 1.727803 | -3.475071 | -3.209566 |
| 63 | 1 | 0 | 7.389807 | -0.282482 | 1.185983 |
| 64 | 1 | 0 | 7.716842 | 2.061875 | 2.062322 |
| 65 | 1 | 0 | 5.762981 | 3.577518 | 2.217409 |
| 66 | 1 | 0 | 3.537667 | 2.870923 | 1.480057 |
| 67 | 1 | 0 | 0.736064 | -4.845697 | 0.084691 |
| 68 | 1 | 0 | -1.516520 | -5.869872 | 0.157347 |
| 69 | 1 | 0 | -3.536758 | -4.416747 | 0.165870 |
| 70 | 1 | 0 | -3.322210 | -1.986256 | 0.225751 |
| 71 | 1 | 0 | -0.609626 | 3.964493 | -0.247919 |
| 72 | 1 | 0 | -3.178813 | 2.217284 | 2.728638 |
| 73 | 1 | 0 | -5.388367 | 1.869484 | -3.095353 |
| 74 | 1 | 0 | -3.884379 | 3.644368 | -3.836407 |
| 75 | 1 | 0 | -1.922811 | 4.318091 | -2.447932 |
| 76 | 1 | 0 | 2.607559 | 2.069250 | -1.998925 |
| 77 | 1 | 0 | 3.890124 | 4.068856 | -2.684540 |
| 78 | 1 | 0 | 3.776564 | 6.153129 | -1.330307 |
| 79 | 1 | 0 | 2.369863 | 6.208905 | 0.723037 |
| 80 | 1 | 0 | 1.108042 | 4.199494 | 1.416865 |
| 81 | 1 | 0 | -7.674614 | -2.245691 | 0.808165 |
| 82 | 1 | 0 | -8.135480 | -1.230719 | -1.407668 |
| 83 | 1 | 0 | -6.593991 | 0.420458 | -2.363371 |
| 84 | 1 | 0 | -2.589331 | -0.247432 | 3.059637 |
| 85 | 1 | 0 | -4.186165 | -1.884560 | 4.014820 |
| 86 | 1 | 0 | -6.242751 | -2.483085 | 2.762993 |
| 87 | 6 | 0 | -1.876287 | 3.320602 | 1.423706 |
| 88 | 1 | 0 | -1.700517 | 4.212371 | 2.017540 |
Supplementary Figure 3. Possible isomers of tetracenes 30 and 31.
### Zero-point correction
0.837102 (Hartree/Particle)

### Thermal correction to Gibbs Free Energy
0.752119

### Sum of electronic and thermal Free Energies
-3362.773751

### E[SMD(chloroform)/B3LYP-D3BJ/6-31G**//B3LYP/6-31G*] = -3363.99058853

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
| 1             | 6             | 0           | 3.177308 0.593641 0.346652 |
| 2             | 6             | 0           | 3.241594 -0.799123 0.026771 |
| 3             | 6             | 0           | 4.452330 -1.469086 -0.380755 |
| 4             | 6             | 0           | 5.654842 -0.770911 -0.455052 |
| 5             | 6             | 0           | 5.615692 0.492584 0.236846 |
| 6             | 6             | 0           | 4.462426 1.159189 0.652819 |
| 7             | 6             | 0           | 1.886690 1.157866 0.294107 |
| 8             | 6             | 0           | 0.755082 0.295969 0.258676 |
| 9             | 6             | 0           | 0.845866 -1.139598 0.271206 |
| 10            | 6             | 0           | 2.132694 -1.662249 -0.039817 |
| 11            | 6             | 0           | -0.462041 1.050646 0.208005 |
| 12            | 6             | 0           | -1.690445 0.338926 0.161566 |
| 13            | 6             | 0           | -1.571878 -1.055372 0.474501 |
| 14            | 6             | 0           | -0.376603 -1.790715 0.578376 |
| 15            | 6             | 0           | -3.044366 0.807095 -0.124142 |
| 16            | 6             | 0           | -4.107223 -0.060730 0.065357 |
| 17            | 6             | 0           | -3.954876 -1.409360 0.559362 |
| 18            | 6             | 0           | -2.695969 -1.909539 0.752253 |
| 19            | 6             | 0           | 4.843768 2.289003 1.549683 |
| 20            | 6             | 0           | 6.249477 2.345882 1.610058 |
| 21            | 6             | 0           | 6.801483 1.210338 0.817355 |
| 22            | 6             | 0           | 6.924656 3.248050 2.412758 |
| 23            | 6             | 0           | 6.168305 4.131249 3.198143 |
| 24            | 6             | 0           | 4.775728 4.054005 3.184294 |
| 25            | 6             | 0           | 4.098021 3.127810 2.372359 |
| 26            | 8             | 0           | 7.975174 0.877844 0.760407 |
| 27            | 14            | 0           | 7.166824 -1.235141 -1.562464 |
| 28            | 6             | 0           | 8.388540 -2.356818 -0.651692 |
| 29            | 6             | 0           | 6.529922 -2.026861 -3.169282 |
| 30            | 6             | 0           | 8.034628 0.323693 -2.203549 |
| 31            | 6             | 0           | 4.046387 -2.852969 -0.701052 |
| 32            | 6             | 0           | 2.632250 -2.956589 -0.536829 |
|   | 6  | 0  | 1.975402 | -4.132644 | -0.898951 |
|---|----|----|----------|-----------|------------|
| 34| 6  | 0  | 2.726085 | -5.237020 | -1.318417  |
| 35| 6  | 0  | 4.119217 | -5.172480 | -1.364581  |
| 36| 6  | 0  | 4.784239 | -3.978744 | -1.058364  |
| 37| 6  | 0  | 1.376505 |  2.528192 |  0.207589  |
| 38| 6  | 0  | -0.051646|  2.478414 |  0.217899  |
| 39| 6  | 0  | 2.045701 |  3.742163 |  0.065889  |
| 40| 6  | 0  | 1.312935 |  4.933516 |  0.049681  |
| 41| 6  | 0  | -0.073589|  4.899319 |  0.184742  |
| 42| 6  | 0  | -0.758686|  3.679727 |  0.261899  |
| 43| 6  | 0  | -0.727090| -3.120451 |  1.100923  |
| 44| 6  | 0  | -2.147976| -3.204380 |  1.192539  |
| 45| 6  | 0  | -2.744242| -4.349353 |  1.717721  |
| 46| 6  | 0  | -1.937854| -5.398090 |  2.174034  |
| 47| 6  | 0  | -0.546213| -5.293696 |  2.130261  |
| 48| 6  | 0  |  0.066700| -4.153097 |  1.602530  |
| 49| 6  | 0  | -5.580582|  0.237416 | -0.269928  |
| 50| 6  | 0  | -5.288104| -2.149852 |  0.691072  |
| 51| 6  | 0  | -6.031199| -0.855298 | -1.237453  |
| 52| 6  | 0  | -5.880680| -2.149220 | -0.717364  |
| 53| 6  | 0  | -6.349776|  0.022814 |  1.031632  |
| 54| 6  | 0  | -6.185494| -1.269100 |  1.556328  |
| 55| 6  | 0  | -6.544559| -0.667648 | -2.515989  |
| 56| 6  | 0  | -6.911753| -1.784731 | -3.276699  |
| 57| 6  | 0  | -6.760543| -3.071594 | -2.758583  |
| 58| 6  | 0  | -6.239350| -3.259943 | -1.472423  |
| 59| 6  | 0  | -6.810026| -1.630937 |  2.744529  |
| 60| 6  | 0  | -7.609751| -0.694167 |  3.410974  |
| 61| 6  | 0  | -7.775808|  0.589048 |  2.888812  |
| 62| 6  | 0  | -7.142790|  0.953879 |  1.693958  |
| 63| 1  | 0  |  8.010715|  3.247059 |  2.439117  |
| 64| 1  | 0  |  6.665466|  4.857106 |  3.835245  |
| 65| 1  | 0  |  4.195845|  4.716020 |  3.821940  |
| 66| 1  | 0  |  3.016767|  3.073601 |  2.405163  |
| 67| 1  | 0  |  7.933227| -3.288107 | -0.296025  |
| 68| 1  | 0  |  9.226822| -2.623396 | -1.307268  |
| 69| 1  | 0  |  8.792995| -1.825892 |  0.216292  |
| 70| 1  | 0  |  7.395008| -2.242772 | -3.810210  |
| 71| 1  | 0  |  5.953776| -2.947295 | -3.067386  |
| 72| 1  | 0  |  5.904482| -1.305042 | -3.709254  |
| 73| 1  | 0  |  7.309068|  1.075978 | -2.537302  |
| 74| 1  | 0  |  8.636714|  0.048810 | -3.079188  |
| 75| 1  | 0  |  8.688911|  0.786648 | -1.464005  |
| 76| 1  | 0  |  0.895284| -4.209028 | -0.856656  |
| 77| 1  | 0  |  2.215744| -6.155472 | -1.595222  |
| 78| 1  | 0  |  4.694784| -6.047822 | -1.652726  |
| 79| 1  | 0  |  5.866614| -3.944512 | -1.100109  |
| 80| 1  | 0  |  3.125043|  3.770169 | -0.026745  |
| 81| 1  | 0  |  1.830096|  5.883160 | -0.055700  |
| 82| 1  | 0  | -0.640974|  5.825619 |  0.209485  |
| 83| 1  | 0  | -1.833619|  3.693760 |  0.353806  |
| 84| 1  | 0  | -3.821641| -4.436295 |  1.806084  |
| 85| 1  | 0  | -2.402052| -6.289552 |  2.586837  |
| 86| 1  | 0  |  0.069733| -6.099750 |  2.519410  |
| 87| 1  | 0  |  1.147275| -4.072813 |  1.600081  |
| 88| 1  | 0  | -5.731096|  1.232125 | -0.683976  |
| 89| 1  | 0  | -5.179529| -3.155773 |  1.092565  |
**Supplementary Information**

| Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|--------|---------------|-------------|------------------------|
| 90     | 1             | 0           | -6.659455 0.335067 -2.920616 |
| 91     | 1             | 0           | -7.315754 -1.646777 -4.275947 |
| 92     | 1             | 0           | -7.047024 -3.933530 -3.355033 |
| 93     | 1             | 0           | -6.117645 -4.262817 -1.070123 |
| 94     | 1             | 0           | -6.681238 -2.630937 3.151921 |
| 95     | 1             | 0           | -8.103684 -0.970341 4.338563 |
| 96     | 1             | 0           | -8.400459 1.309660 3.409701 |
| 97     | 1             | 0           | -7.276288 1.952793 1.285016 |
| 98     | 6             | 0           | -3.303190 2.127926 -0.765146 |
| 99     | 6             | 0           | -2.741007 2.424374 -2.015865 |
| 100    | 6             | 0           | -4.148112 3.082299 -0.174565 |
| 101    | 6             | 0           | -3.005256 3.632311 -2.659185 |
| 102    | 1             | 0           | -2.088253 1.699768 -2.493050 |
| 103    | 6             | 0           | -4.421021 4.296759 -0.804014 |
| 104    | 1             | 0           | -4.581916 2.879612 0.800839 |
| 105    | 6             | 0           | -3.844604 4.561274 -2.045993 |
| 106    | 1             | 0           | -2.565279 3.851589 -3.626169 |
| 107    | 1             | 0           | -5.068165 5.031092 -0.335877 |
| 108    | 17            | 0           | -4.183522 6.088095 -2.849721 |

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**30b**

Zero-point correction= 0.836831 (Hartree/Particle)
Thermal correction to Gibbs Free Energy= 0.751684
Sum of electronic and thermal Free Energies= -3362.774470
E[SMD(chloroform)/B3LYP-D3BJ/6-31G***/B3LYP/6-31G*]= -3363.99043582

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|------------------------|
| 1             | 6             | 0           | -5.818728 5.226099 1.135360 |
| 2             | 6             | 0           | -4.433806 5.064827 1.110592 |
| 3             | 6             | 0           | -3.840182 3.848780 0.729186 |
| 4             | 6             | 0           | -4.661149 2.791766 0.346456 |
| 5             | 6             | 0           | -6.057903 2.953459 0.432002 |
| 6             | 6             | 0           | -6.651224 4.144629 0.810837 |
| 7             | 6             | 0           | -6.700055 1.627156 0.218134 |
| 8             | 6             | 0           | -5.578225 0.655631 -0.019015 |
| 9             | 6             | 0           | -4.377400 1.371281 -0.018118 |
| 10            | 6             | 0           | -3.137650 0.661035 -0.184794 |
| 11            | 6             | 0           | -3.250195 -0.738798 0.091521 |
| 12 | 6 | 0 | -4.50484 | -1.428274 | 0.247763 |
| 13 | 6 | 0 | -5.705270 | -0.777160 | -0.021799 |
| 14 | 8 | 0 | -7.892484 | 1.381733 | 0.316944 |
| 15 | 6 | 0 | -1.837896 | 1.116078 | -0.488415 |
| 16 | 6 | 0 | -0.736783 | 0.222091 | -0.349473 |
| 17 | 6 | 0 | -0.859600 | -1.191078 | -0.098142 |
| 18 | 6 | 0 | -2.170826 | -1.641735 | 0.211796 |
| 19 | 6 | 0 | 0.496198 | 0.925466 | -0.534652 |
| 20 | 6 | 0 | 1.705644 | 0.231849 | -0.294723 |
| 21 | 6 | 0 | 1.564201 | -1.191915 | -0.277688 |
| 22 | 6 | 0 | 0.336115 | -1.913990 | -0.271272 |
| 23 | 6 | 0 | 3.054504 | 0.750821 | -0.100277 |
| 24 | 6 | 0 | 4.106899 | -0.146913 | -0.035027 |
| 25 | 6 | 0 | 3.942689 | -1.572898 | -0.205902 |
| 26 | 6 | 0 | 2.682969 | -2.093997 | -0.331968 |
| 27 | 6 | 0 | -4.160483 | -2.782138 | 0.720573 |
| 28 | 6 | 0 | -2.738647 | -2.895865 | 0.740888 |
| 29 | 6 | 0 | -2.138874 | -3.978972 | 1.384722 |
| 30 | 6 | 0 | -2.943043 | -4.978865 | 1.943224 |
| 31 | 6 | 0 | -4.334504 | -4.881097 | 1.898600 |
| 32 | 6 | 0 | -4.947696 | -3.769669 | 1.308909 |
| 33 | 6 | 0 | -1.291966 | 2.363010 | -1.040045 |
| 34 | 6 | 0 | 0.132609 | 2.266799 | -1.039285 |
| 35 | 6 | 0 | -1.925863 | 3.424801 | -1.684102 |
| 36 | 6 | 0 | -1.155214 | 4.435932 | -2.267920 |
| 37 | 6 | 0 | 0.236800 | 4.362815 | -2.239131 |
| 38 | 6 | 0 | 0.884274 | 3.273558 | -1.643862 |
| 39 | 6 | 0 | 0.702819 | -3.322724 | -0.530494 |
| 40 | 6 | 0 | 2.125749 | -3.442222 | -0.531677 |
| 41 | 6 | 0 | 2.722831 | 4.670882 | -0.806950 |
| 42 | 6 | 0 | 1.919296 | -5.774878 | -1.112451 |
| 43 | 6 | 0 | 0.531055 | -5.643300 | -1.172855 |
| 44 | 6 | 0 | -0.082876 | -4.418654 | -0.892026 |
| 45 | 1 | 0 | -6.250146 | 6.177738 | 1.432270 |
| 46 | 1 | 0 | -3.792263 | 5.892644 | 1.400942 |
| 47 | 1 | 0 | -2.762279 | 3.750747 | 0.748107 |
| 48 | 1 | 0 | -7.733887 | 4.217273 | 0.873110 |
| 49 | 1 | 0 | -1.061644 | -4.041565 | 1.478756 |
| 50 | 1 | 0 | -2.474849 | -5.824601 | 2.439428 |
| 51 | 1 | 0 | -4.947843 | -5.651766 | 2.357357 |
| 52 | 1 | 0 | -6.025815 | -3.664787 | 1.357936 |
| 53 | 1 | 0 | -3.006295 | 3.462370 | -1.757117 |
| 54 | 1 | 0 | -1.647980 | 5.267241 | -2.764471 |
| 55 | 1 | 0 | 0.831359 | 5.141558 | -2.708932 |
| 56 | 1 | 0 | 1.962182 | 3.211831 | -1.690851 |
| 57 | 1 | 0 | 3.801363 | -4.784378 | -0.819592 |
| 58 | 1 | 0 | 2.384347 | -6.732241 | -1.330996 |
| 59 | 1 | 0 | -0.082374 | -6.495642 | -1.451809 |
| 60 | 1 | 0 | -1.158571 | -4.326388 | -0.974396 |
| 61 | 14 | 0 | -7.331458 | -1.651454 | -0.580829 |
| 62 | 6 | 0 | -8.530975 | -1.927913 | 0.859905 |
| 63 | 1 | 0 | -8.851653 | -0.965273 | 1.265329 |
| 64 | 1 | 0 | -9.421938 | -2.466011 | 0.508828 |
| 65 | 1 | 0 | -8.085802 | -2.512602 | 1.669357 |
| 66 | 6 | 0 | -6.892702 | -3.296941 | -1.424832 |
| 67 | 1 | 0 | -6.186904 | -3.126596 | -2.247005 |
| 68 | 1 | 0 | -6.465260 | -4.066384 | -0.779682 |
|   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|
| 69 | 1 | 0 | -7.810056 | -3.706285 | -1.868203 |
| 70 | 6 | 0 | -8.139197 | -0.657939 | -1.977224 |
| 71 | 1 | 0 | -8.599838 | 0.267218 | -1.628463 |
| 72 | 1 | 0 | -7.409883 | -0.409807 | -2.758349 |
| 73 | 1 | 0 | -8.915708 | -1.276286 | -2.445689 |
| 74 | 6 | 0 | 5.573938 | 0.205563 | 0.271147 |
| 75 | 6 | 0 | 5.268514 | -2.337596 | -0.114931 |
| 76 | 6 | 0 | 6.380074 | -0.317324 | -0.915990 |
| 77 | 6 | 0 | 5.972317 | -0.635027 | 1.482587 |
| 78 | 6 | 0 | 6.207310 | -1.694239 | -1.129639 |
| 79 | 6 | 0 | 5.813006 | -2.013031 | 1.274292 |
| 80 | 6 | 0 | 6.863058 | -2.331299 | -2.177033 |
| 81 | 6 | 0 | 7.213507 | 0.423217 | -1.747439 |
| 82 | 6 | 0 | 6.125652 | -2.920064 | 2.280342 |
| 83 | 6 | 0 | 6.448176 | -0.159104 | 2.699325 |
| 84 | 6 | 0 | 6.769166 | -1.071137 | 3.712431 |
| 85 | 6 | 0 | 6.609180 | -2.441742 | 3.504474 |
| 86 | 6 | 0 | 7.702848 | -1.586124 | -3.014216 |
| 87 | 6 | 0 | 7.877849 | -0.218533 | -2.800290 |
| 88 | 1 | 0 | 8.533737 | 0.352641 | -3.451714 |
| 89 | 1 | 0 | 8.221146 | -2.077660 | -3.833008 |
| 90 | 1 | 0 | 7.354580 | 1.488208 | -1.577625 |
| 91 | 1 | 0 | 6.727961 | -3.397284 | -2.344267 |
| 92 | 1 | 0 | 5.997467 | -3.987813 | 2.119481 |
| 93 | 1 | 0 | 6.569320 | 0.909106 | 2.862530 |
| 94 | 1 | 0 | 7.143906 | -0.707702 | 4.665451 |
| 95 | 1 | 0 | 6.859801 | -3.143166 | 4.295633 |
| 96 | 1 | 0 | 5.730342 | 1.268317 | 0.445778 |
| 97 | 1 | 0 | 5.150328 | -3.408551 | -0.272068 |
| 98 | 6 | 0 | 3.295321 | 2.196648 | 0.169377 |
| 99 | 6 | 0 | 2.636516 | 2.839848 | 1.228547 |
| 100 | 6 | 0 | 4.203956 | 2.946554 | -0.596649 |
| 101 | 6 | 0 | 2.871537 | 4.182660 | 1.518371 |
| 102 | 1 | 0 | 1.933005 | 2.280517 | 1.837511 |
| 103 | 6 | 0 | 4.448919 | 4.291386 | -0.321191 |
| 104 | 1 | 0 | 4.709895 | 2.475723 | -1.435125 |
| 105 | 6 | 0 | 3.777968 | 4.899674 | 0.738916 |
| 106 | 1 | 0 | 2.358670 | 4.668305 | 2.341755 |
| 107 | 1 | 0 | 5.145960 | 4.862985 | -0.924994 |
| 108 | 17 | 0 | 4.079616 | 6.594617 | 1.096169 |
31a

Zero-point correction = 0.734710 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.658095
Sum of electronic and thermal Free Energies = -2954.205557

E[SMD(chloroform)/B3LYP-D3BJ/6-31G**/B3LYP/6-31G*] = -2955.28315654

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
|               | Atomic Number |             | X          | Y          | Z          |
| 1             | 6             | 0           | 3.915321 | 0.074451 | -0.029364 |
| 2             | 6             | 0           | 3.803720 | -1.299300 | -0.427259 |
| 3             | 6             | 0           | 4.910032 | -2.092439 | -0.877858 |
| 4             | 6             | 0           | 6.177411 | -1.561818 | -0.854546 |
| 5             | 6             | 0           | 6.323410 | -0.278553 | -0.281197 |
| 6             | 6             | 0           | 5.270151 | 0.514482  | 0.182583  |
| 7             | 6             | 0           | 2.678054 | 0.759672  | 0.031236  |
| 8             | 6             | 0           | 1.468362 | 0.009657  | 0.042072  |
| 9             | 6             | 0           | 2.911899 | -2.049447 | -0.42076  |
| 10            | 6             | 0           | 0.327159 | 0.875828  | 0.126310  |
| 11            | 6             | 0           | -0.965780| 0.287709  | 0.134681  |
| 12            | 6             | 0           | -0.965436| -1.131539 | 0.345822  |
| 13            | 6             | 0           | 0.154114 | -1.980603 | 0.306588  |
| 14            | 6             | 0           | -2.285852| 0.898779  | -0.011891 |
| 15            | 6             | 0           | -3.412500| 0.123164  | 0.205686  |
| 16            | 6             | 0           | -3.359593| -1.268274 | 0.591001  |
| 17            | 6             | 0           | -2.146308| -1.897208 | 0.646952  |
| 18            | 6             | 0           | 5.860590 | 1.640133  | 0.967824  |
| 19            | 6             | 0           | 7.264832 | 1.601913  | 0.820390  |
| 20            | 6             | 0           | 7.623741 | 0.401938  | 0.008152  |
| 21            | 6             | 0           | 8.104083 | 2.489761  | 1.470083  |
| 22            | 6             | 0           | 7.530415 | -1.268274 | 0.591001  |
| 23            | 6             | 0           | 6.150229 | 3.453768  | 2.525917  |
| 24            | 6             | 0           | 5.303074 | 2.551205  | 1.860360  |
| 25            | 6             | 0           | 8.735218 | 0.028827  | -0.326073 |
| 26            | 8             | 0           | 4.357349 | -3.375111 | -1.320978 |
| 27            | 6             | 0           | 2.949070 | -3.348292 | -1.095662 |
| 28            | 6             | 0           | 2.162285 | -4.01262  | -1.564127 |
| 29            | 6             | 0           | 2.780269 | -5.491077 | -2.190345 |
| 30            | 6             | 0           | 4.165910 | -5.532227 | -2.363579 |
| 31            | 6             | 0           | 4.963647 | -4.463393 | -1.938053 |
| 32            | 6             | 0           | 2.294104 | 2.173882  | 0.033016  |
| 33            | 6             | 0           | 0.873652 | 2.256202  | 0.168389  |
| 34            | 6             | 0           | 3.057077 | 3.327074  | -0.140563 |
| 35            | 6             | 0           | 2.442696 | 4.580576  | -0.049882 |
| 36            | 6             | 0           | 1.079123 | 4.668524  | 0.221532  |
| 37            | 6             | 0           | 0.291732 | 3.514069  | 0.322290  |
| 38            | 6             | 0           | -0.288662| -3.312223 | 0.745664  |
| 39            | 6             | 0           | -1.700765| -3.270457 | 0.941540  |
| 40            | 6             | 0           | -2.369676| -4.398004 | 1.414406  |
| 41            | 6             | 0           | -1.641857| -5.555093 | 1.714300  |
| 42            | 6             | 0           | -0.253668| -5.578893 | 1.566568  |
| 43            | 6             | 0           | 0.431445 | 4.457021  | 1.089948  |
| 44            | 6             | 0           | -4.870158| 0.582160  | 0.012057  |
| 45            | 6             | 0           | -4.746004| -1.889183 | 0.777479  |
| 46            | 6             | 0           | -5.496244| -0.385823 | -0.990000 |
| 47            | 6             | 0           | -5.436824| -1.724540 | -0.575348 |
|   |   |   |         |         |         |
|---|---|---|---------|---------|---------|
| 49 | 6 | 0 | -5.558618 | 0.340170 | 1.353366 |
| 50 | 6 | 0 | -5.485676 | -0.997932 | 1.771596 |
| 51 | 6 | 0 | -6.080671 | -0.053009 | -2.207098 |
| 52 | 6 | 0 | -6.610659 | -1.069049 | -3.012090 |
| 53 | 6 | 0 | -6.549766 | -2.400589 | -2.599066 |
| 54 | 6 | 0 | -5.957457 | -2.735485 | -1.375030 |
| 55 | 6 | 0 | -6.055207 | -1.390478 | 2.977613  |
| 56 | 6 | 0 | -6.708079 | -0.437346 | 3.769131  |
| 57 | 6 | 0 | -6.610671 | -0.997932 | 1.771596  |
| 58 | 6 | 0 | -6.205888 | 1.287369  | 2.139526  |
| 59 | 1 | 0 | 9.179398  | 2.422166  | 1.330593  |
| 60 | 1 | 0 | 8.161167  | 4.154596  | 2.849975  |
| 61 | 1 | 0 | 5.714601  | 4.169236  | 3.218301  |
| 62 | 1 | 0 | 4.237597  | 2.570881  | 2.054546  |
| 63 | 1 | 0 | 1.083748  | -4.381059 | -1.461583 |
| 64 | 1 | 0 | 2.167562  | -6.311830 | -2.532038 |
| 65 | 1 | 0 | 4.625911  | -6.388559 | -2.849133 |
| 66 | 1 | 0 | 6.037590  | -4.478812 | -2.105669 |
| 67 | 1 | 0 | 4.118804  | 3.261642  | -0.343784 |
| 68 | 1 | 0 | 3.035668  | 5.481685  | -0.179305 |
| 69 | 1 | 0 | 0.606786  | 5.640745  | 0.332137  |
| 70 | 1 | 0 | -0.763855 | 3.622487  | 0.515921  |
| 71 | 1 | 0 | -3.441498 | -4.392872 | 1.579649  |
| 72 | 1 | 0 | -2.162661 | -6.433324 | 2.085876  |
| 73 | 1 | 0 | 0.304057  | -6.472314 | 1.833518  |
| 74 | 1 | 0 | 1.511386  | -4.479105 | 1.004768  |
| 75 | 1 | 0 | -4.952273 | 1.615636  | -0.317588 |
| 76 | 1 | 0 | -4.707506 | -2.928471 | 1.098596  |
| 77 | 1 | 0 | -6.125609 | 0.984257  | -2.30253  |
| 78 | 1 | 0 | -7.070899 | -0.817332 | -3.963707 |
| 79 | 1 | 0 | -6.962816 | -3.183308 | -3.229523 |
| 80 | 1 | 0 | -5.906625 | -3.773405 | -1.054833 |
| 81 | 1 | 0 | -5.997426 | -2.426657 | 3.302465  |
| 82 | 1 | 0 | -7.158681 | -0.736964 | 4.711381  |
| 83 | 1 | 0 | -7.295109 | 1.625584  | 3.970289  |
| 84 | 1 | 0 | -6.269280 | 2.322760  | 1.812858  |
| 85 | 6 | 0 | -2.464404 | 2.279544  | -0.545243 |
| 86 | 6 | 0 | -1.982329 | 2.607838  | -1.821016 |
| 87 | 6 | 0 | -3.159065 | 3.264858  | 0.175802  |
| 88 | 6 | 0 | -2.177727 | 3.877075  | -2.363036 |
| 89 | 1 | 0 | -1.445657 | 1.860359  | -2.397324 |
| 90 | 6 | 0 | -3.361709 | 4.540175  | -0.351405 |
| 91 | 1 | 0 | -3.529376 | 3.035322  | 1.171256  |
| 92 | 6 | 0 | -2.866589 | 4.835590  | -1.621314 |
| 93 | 1 | 0 | -1.799714 | 4.120863  | -3.350128 |
| 94 | 1 | 0 | -3.892377 | 5.297345  | 0.216335  |
| 95 | 17| 0 | -3.116784 | 6.440054  | -2.295770 |
| 96 | 1 | 0 | 7.060180  | -2.098053 | -1.191531 |
31b
Zero-point correction=                           0.734795 (Hartree/Particle)
Thermal correction to Gibbs Free Energy=         0.658549
Sum of electronic and thermal Free Energies     -2954.202263
E[SMD(chloroform)/B3LYP-D3BJ/6-31G**//B3LYP/6-31G*]  = -2955.27993275

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
|               |               |             | X          | Y          | Z          |
| 1             | 6             | 0           | -7.332946  | 4.038733  | 0.695137   |
| 2             | 6             | 0           | -5.941462  | 4.108454  | 0.752706   |
| 3             | 6             | 0           | -5.135813  | 2.990329  | 0.476143   |
| 4             | 6             | 0           | -5.745768  | 1.791055  | 0.117763   |
| 5             | 6             | 0           | -7.157230  | 1.720320  | 0.131189   |
| 6             | 6             | 0           | -7.956420  | 2.817869  | 0.398269   |
| 7             | 6             | 0           | -7.561687  | 0.292199  | -0.012761  |
| 8             | 6             | 0           | -6.277907  | -0.471659 | -0.082392  |
| 9             | 6             | 0           | -5.203819  | 0.420461  | -0.143900  |
| 10            | 6             | 0           | -3.867772  | -0.102615 | -0.288719  |
| 11            | 6             | 0           | -3.757006  | -1.514108 | -0.045436  |
| 12            | 6             | 0           | -4.884035  | -2.378962 | 0.147867   |
| 13            | 6             | 0           | -6.156721  | -1.872448 | 0.039376   |
| 14            | 8             | 0           | -2.644665  | 0.544899  | -0.576008  |
| 15            | 6             | 0           | -1.422596  | -0.173727 | -0.426741  |
| 16            | 6             | 0           | -1.326353  | -1.596822 | -0.215559  |
| 17            | 6             | 0           | -2.555730  | -2.254300 | 0.056438   |
| 18            | 6             | 0           | -0.309246  | 0.216540  | -0.300883  |
| 19            | 6             | 0           | 1.070681   | -1.211450 | -0.328128  |
| 20            | 6             | 0           | -0.007757  | -2.113116 | -0.383346  |
| 21            | 6             | 0           | 2.230723   | 0.935434  | -0.053205  |
| 22            | 6             | 0           | 3.409524   | 0.212609  | 0.018312   |
| 23            | 6             | 0           | 3.476861   | -1.215438 | -0.198970  |
| 24            | 6             | 0           | 2.319322   | -1.923652 | -0.379042  |
| 25            | 6             | 0           | -4.358130  | -3.697090 | 0.501442   |
| 26            | 6             | 0           | -2.935424  | -3.609047 | 0.515559   |
| 27            | 6             | 0           | -2.198824  | -4.665210 | 1.054946   |
| 28            | 6             | 0           | -2.864503  | -5.825282 | 1.470247   |
| 29            | 6             | 0           | -4.254007  | -5.933653 | 1.373468   |
| 30            | 6             | 0           | -5.012868  | -4.856541 | 0.902575   |
| 31            | 6             | 0           | -2.282889  | 1.865901  | -1.108568  |
| 32            | 6             | 0           | -0.861786  | 1.994660  | -1.060251  |
| 33            | 6             | 0           | -3.050909  | 2.812890  | -1.784551  |
| 34            | 6             | 0           | -2.429191  | 3.936020  | -2.341374  |
| 35            | 6             | 0           | -1.046326  | 4.088103  | -2.254543  |
| 36            | 6             | 0           | -0.257000  | 3.112069  | -1.634125  |
| 37            | 6             | 0           | 0.563459   | -3.436557 | -0.689840  |
| 38            | 6             | 0           | 1.987068   | -3.332673 | -0.646969  |
| 39            | 6             | 0           | 2.777611   | -4.438359 | -0.953994  |
| 40            | 6             | 0           | 2.166678   | -5.637180 | -1.337997  |
| 41            | 6             | 0           | 0.777552   | -5.718879 | -1.447004  |
| 42            | 6             | 0           | -0.028998  | -4.620017 | -1.134285  |
| 43            | 6             | 0           | -7.930959  | 4.919785  | 0.909712   |
| 44            | 6             | 0           | -5.461968  | 5.045017  | 1.024841   |
| 45            | 6             | 0           | -4.059662  | 3.075071  | 0.555378   |
| 46            | 6             | 0           | -9.037807  | 2.713362  | 0.401114   |
|   |   |   |   |   |   |
|---|---|---|---|---|---|
|   |   |   |   |   |   |
| 49 | 1 | 0 | -1.124186 | -4.596302 | 1.168216 |
| 50 | 1 | 0 | -2.287101 | -6.648955 | 1.881294 |
| 51 | 1 | 0 | -4.750826 | -6.844491 | 1.695948 |
| 52 | 1 | 0 | -6.098048 | -4.915956 | 0.880959 |
| 53 | 1 | 0 | -4.118557 | 2.675707 | -1.905249 |
| 54 | 1 | 0 | -3.028403 | 4.677516 | -2.862476 |
| 55 | 1 | 0 | -0.565828 | 4.954317 | -2.701109 |
| 56 | 1 | 0 | 0.818071 | 3.222736 | -1.640248 |
| 57 | 1 | 0 | 3.028403 | 4.677516 | -2.862476 |
| 58 | 1 | 0 | 0.565828 | 4.954317 | -2.701109 |
| 59 | 1 | 0 | 0.818071 | 3.222736 | -1.640248 |
| 60 | 1 | 0 | -1.102556 | -4.689486 | -1.257659 |
| 61 | 6 | 0 | 4.794818 | 0.781887 | 0.373922 |
| 62 | 6 | 0 | 4.902244 | -1.763866 | -0.095592 |
| 63 | 6 | 0 | 5.697878 | 0.433148 | -0.807436 |
| 64 | 6 | 0 | 5.296454 | -0.025509 | 1.569493 |
| 65 | 6 | 0 | 5.749624 | -0.945864 | -1.066672 |
| 66 | 6 | 0 | 5.361840 | -1.403606 | 1.316317 |
| 67 | 6 | 0 | 6.515135 | -1.435795 | -2.118730 |
| 68 | 6 | 0 | 6.417084 | 1.323617 | -1.597579 |
| 69 | 6 | 0 | 5.793894 | -2.283140 | 2.302448 |
| 70 | 6 | 0 | 5.666663 | 0.478693 | 2.811410 |
| 71 | 6 | 0 | 6.107790 | -0.404650 | 3.804528 |
| 72 | 6 | 0 | 6.171067 | -1.775632 | 3.551977 |
| 73 | 6 | 0 | 7.239582 | -0.539521 | -2.914429 |
| 74 | 6 | 0 | 7.192095 | 0.830503 | -2.654828 |
| 75 | 1 | 0 | 7.759830 | 1.519630 | -3.274144 |
| 76 | 1 | 0 | 7.842355 | -0.915021 | -3.736801 |
| 77 | 1 | 0 | 6.384148 | 2.391265 | -1.392706 |
| 78 | 1 | 0 | 6.552801 | -2.503433 | -2.321812 |
| 79 | 1 | 0 | 5.839344 | -3.351757 | 2.106552 |
| 80 | 1 | 0 | 5.614808 | 1.546681 | 3.009105 |
| 81 | 1 | 0 | 6.401305 | -0.018659 | 4.776955 |
| 82 | 1 | 0 | 6.513648 | -2.454724 | 4.327991 |
| 83 | 1 | 0 | 4.775743 | 1.849345 | 0.584621 |
| 84 | 1 | 0 | 4.962325 | -2.833817 | -0.287283 |
| 85 | 1 | 0 | 2.231070 | 2.392140 | 0.260690 |
| 86 | 1 | 0 | 1.450269 | 2.890585 | 1.315117 |
| 87 | 1 | 0 | 3.028172 | 3.299298 | -0.458060 |
| 88 | 1 | 0 | 1.461296 | 4.244265 | 1.646517 |
| 89 | 1 | 0 | 0.829371 | 2.208750 | 1.888036 |
| 90 | 1 | 0 | 3.048366 | 4.656998 | -0.141036 |
| 91 | 1 | 0 | 3.624315 | 2.939730 | -1.292363 |
| 92 | 1 | 0 | 2.261981 | 5.118923 | 0.913613 |
| 93 | 1 | 0 | 0.856556 | 4.617570 | 2.466137 |
| 94 | 1 | 0 | 3.660866 | 5.349855 | -0.708403 |
| 95 | 17 | 0 | 2.281189 | 6.828561 | 1.323285 |
| 96 | 1 | 0 | -7.054250 | -2.478659 | 0.125416 |
Supplementary Figure 4. Model studies for the kinetic barrier between two isomers of tetracene 30.

**model-1**

Zero-point correction = 0.322761 (Hartree/Particle)  
Thermal correction to Gibbs Free Energy = 0.277117  
Sum of electronic and thermal Free Energies = -1112.280718  

\[
E[\text{SMD(chloroform/3LYP-D3BJ/6-31G**/B3LYP/6-31G*)]}] = -1112.72710428
\]

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) | X      | Y      | Z      |
|---------------|---------------|-------------|-------------------------|--------|--------|--------|
|               | 6             | 0           |                         | 3.993096 | -2.337936 | 0.633102 |
| 2             | 6             | 0           |                         | 2.622390 | -2.022436 | 0.343135 |
| 3             | 6             | 0           |                         | 2.312106 | -0.655583 | 0.174217 |
| 4             | 6             | 0           |                         | 3.297307 | 0.374455  | 0.212051 |
| 5             | 6             | 0           |                         | 4.598700 | 0.040111  | 0.501270 |
| 6             | 6             | 0           |                         | 4.931079 | -1.333496 | 0.720887 |
| 7             | 6             | 0           |                         | 1.580635 | -2.926594 | 0.125740 |
| 8             | 6             | 0           |                         | 0.271841 | -2.477982 | -0.129613|
| 9             | 6             | 0           |                         | -0.062896| -1.046685 | -0.114470|
| 10            | 6             | 0           |                         | 1.029691 | -0.142935 | -0.099922|
| 11            | 6             | 0           |                         | -0.740667| -3.446765 | -0.424226|
| 12            | 6             | 0           |                         | -2.040933| -3.078175 | -0.650839|
| 13            | 6             | 0           |                         | -2.386172| -1.728250 | -0.444385|
| 14            | 6             | 0           |                         | -1.464579| -0.740906 | -0.110745|
| 15            | 6             | 0           |                         | -3.767912| -1.155136 | -0.433202|
| 16            | 6             | 0           |                         | 2.604800 | 1.613845  | -0.160927|
| 17            | 6             | 0           |                         | 1.231003 | 1.297453  | -0.398514|
| 18            | 6             | 0           |                         | -2.233946| 0.463965  | 0.335436 |
### TS-model-1

**One imaginary frequency=** -162.97 cm\(^{-1}\)

**Zero-point correction=** 0.321896 (Hartree/Particle)

**Thermal correction to Gibbs Free Energy=** 0.276632

**Sum of electronic and thermal Free Energies=** -1112.246318

**E[SMD(chloroform)/B3LYP-D3BJ/6-31G**/**B3LYP/6-31G**]** = -1112.69169415

| Center | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|--------|---------------|-------------|-------------------------|
|        |               |             | X          | Y          | Z          |
| 1      | 6             | 0           | -3.06084   | 0.232396  | 0.091075  |
| 2      | 6             | 0           | 0.401799   | 2.268473  | -0.961926 |
| 3      | 6             | 0           | 0.907138   | 2.894080  | -0.391452 |
| 4      | 6             | 0           | -4.588455  | 1.139567  | 0.448822  |
| 5      | 6             | 0           | -4.199659  | 2.318582  | 1.102187  |
| 6      | 6             | 0           | -2.855391  | 2.531670  | 1.404872  |
| 7      | 6             | 0           | -1.861870  | 1.60792   | 1.035451  |
| 8      | 6             | 0           | 4.284169   | -3.375517 | 0.775185  |
| 9      | 6             | 0           | 5.382555   | 0.791456  | 0.553483  |
| 10     | 6             | 0           | 5.963721   | -1.586827 | 0.944931  |
| 11     | 6             | 0           | 1.771734   | -3.997311 | 0.132575  |
| 12     | 6             | 0           | -0.444989  | -4.491691 | -0.470196 |
| 13     | 6             | 0           | -0.622784  | 2.040900  | -1.22937  |
| 14     | 6             | 0           | 0.255694   | 4.306854  | -1.632958 |
| 15     | 6             | 0           | 2.605330   | 4.875363  | -1.088176 |
| 16     | 6             | 0           | 4.140618   | 3.127732  | -0.204368 |
| 17     | 6             | 0           | -5.632377  | 0.917427  | 0.245547  |
| 18     | 6             | 0           | -4.945800  | 3.050765  | 1.397424  |
| 19     | 6             | 0           | -2.562860  | 3.427634  | 1.946031  |
| 20     | 6             | 0           | -0.830325  | 1.793229  | 1.307583  |
| 21     | 6             | 0           | -2.813506  | -3.797884 | -0.903559 |
| 22     | 6             | 0           | -4.798849  | -1.721393 | -0.752992 |

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![Diagram of TS-model-1](image-url)
### Supplementary Information

#### model-2

Zero-point correction= 0.359606 (Hartree/Particle)
Thermal correction to Gibbs Free Energy= 0.313340
Sum of electronic and thermal Free Energies= -1152.552823

\[
E_{\text{SMD(chloroform)}/B3LYP-3D3J/6-31G**}/B3LYP/6-31G*] = -1153.05407134
\]

| Center | Atomic Number | Atomic Number | Type | Coordinates (Angstroms) |
|--------|---------------|---------------|------|-------------------------|
|        |               |               |      | X           | Y           | Z           |
| 1      | 6             | 6             | 0    | 3.685721    | -2.974324  | 0.654251    |
| 2      | 6             | 6             | 0    | 2.416684    | -2.357789  | 0.398021    |
| 3      | 6             | 6             | 0    | 2.414811    | -0.954005  | 0.205215    |
| 4      | 6             | 6             | 0    | 3.615696    | -0.179884  | 0.182540    |
| 5      | 6             | 6             | 0    | 4.812786    | -0.801307  | 0.440095    |
| 6      | 6             | 6             | 0    | 4.829995    | -2.212462  | 0.687175    |
| 7      | 6             | 6             | 0    | 1.191766    | -2.999689  | 0.229236    |
| 8      | 6             | 6             | 0    | 0.000036    | -2.268583  | -0.000006   |
| 9      | 6             | 6             | 0    | 0.000024    | -0.785747  | 0.000066    |
|   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|
| 10| 6 |  0|  1.281336| -0.166384| -0.047633|   |
| 11| 6 |  0| -1.191699| -2.999698| -0.229308|   |
| 12| 6 |  0| -2.416606| -2.357812| -0.398087|   |
| 13| 6 |  0| -2.414748| -0.954014| -0.205303|   |
| 14| 6 |  0| -1.281324| -0.166394|  0.047667|   |
| 15| 6 |  0| -3.685650| -2.974381| -0.654267|   |
| 16| 6 |  0| -4.829947| -2.212567| -0.687088|   |
| 17| 6 |  0| -4.812768| -0.801407| -0.439964|   |
| 18| 6 |  0| -3.615681| -0.179936| -0.182551|   |
| 19| 6 |  0|  3.216527|  1.176028| -0.208274|   |
| 20| 6 |  0|  1.798994|  1.178985| -0.398467|   |
| 21| 6 |  0| -1.799014|  1.178971|  0.398498|   |
| 22| 6 |  0| -3.216552|  1.175968|  0.208311|   |
| 23| 6 |  0|  1.199246|  2.299000| -0.977242|   |
| 24| 6 |  0|  1.979845|  3.423843| -1.271993|   |
| 25| 6 |  0|  3.352637|  3.437735| -1.014720|   |
| 26| 6 |  0|  3.981661|  2.301316| -0.494512|   |
| 27| 6 |  0| -3.981723|  2.301249|  0.494474|   |
| 28| 6 |  0| -3.352747|  3.437701|  1.014667|   |
| 29| 6 |  0| -1.979962|  3.423847|  1.271968|   |
| 30| 6 |  0| -1.199315|  2.299032|  0.977229|   |
| 31| 1 |  0|  3.734961| -4.048498|  0.813886|   |
| 32| 1 |  0|  5.750304| -0.250869|  0.446064|   |
| 33| 1 |  0|  5.785046| -2.691268|  0.885623|   |
| 34| 1 |  0|  1.133672| -4.085641|  0.255018|   |
| 35| 1 |  0| -1.133576| -4.085647| -0.255157|   |
| 36| 1 |  0| -3.734849| -4.048548| -0.813957|   |
| 37| 1 |  0| -5.789996| -2.691392| -0.885498|   |
| 38| 1 |  0| -5.750315| -0.251016| -0.445805|   |
| 39| 1 |  0|  0.142415|  2.305158| -1.213559|   |
| 40| 1 |  0|  1.506137|  4.295254| -1.716192|   |
| 41| 1 |  0|  3.939326|  4.322670| -1.245723|   |
| 42| 1 |  0|  5.058183|  2.291515| -0.341954|   |
| 43| 1 |  0| -5.058239|  2.291412|  0.341877|   |
| 44| 1 |  0| -3.939465|  4.322626|  1.245637|   |
| 45| 1 |  0| -1.506282|  4.295279|  1.716158|   |
| 46| 1 |  0| -0.142496|  2.305237|  1.213591|   |
TS-model-2

One imaginary frequency = -207.41 cm⁻¹
Zero-point correction = 0.358628 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.312569
Sum of electronic and thermal Free Energies = -1152.520596

E[SMD(chloroform)/B3LYP-D3BJ/6-31G***/B3LYP/6-31G***] = -1153.02046026

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|------------------------|
|               | 1             | 6           | -3.614552 -3.107381 -0.033625 |
|               | 2             | 6           | -2.402021 -2.377319 0.188172 |
|               | 3             | 6           | -2.417942 -0.969467 0.052988 |
|               | 4             | 6           | -3.624874 -0.309765 -0.328411 |
|               | 5             | 6           | -4.768268 -1.029639 -0.574249 |
|               | 6             | 6           | -4.756559 -2.448691 -0.413986 |
|               | 7             | 6           | -1.173253 -2.927315 0.494285 |
|               | 8             | 6           | 0.000158 2.139973 0.503908 |
|               | 9             | 6           | 0.000038 0.644200 0.379597 |
|               | 10            | 6           | -1.335029 -0.073322 0.255821 |
|               | 11            | 6           | 1.173743 -2.927080 0.495082 |
|               | 12            | 6           | 2.402513 -2.376964 0.189215 |
|               | 13            | 6           | 2.418123 -0.969187 0.053205 |
|               | 14            | 6           | 1.335051 -0.073172 0.255683 |
|               | 15            | 6           | 3.615282 -3.106854 -0.031858 |
|               | 16            | 6           | 4.757212 -2.448097 -0.412331 |
|               | 17            | 6           | 4.768583 -1.029143 -0.573528 |
|               | 18            | 6           | 3.624962 -0.309402 -0.328366 |
|               | 19            | 6           | -3.339431 1.112843 -0.298004 |
|               | 20            | 6           | -1.992768 1.284833 0.154125 |
|               | 21            | 6           | 1.992561 1.285047 0.153523 |
|               | 22            | 6           | 3.339157 1.113154 -0.298834 |
|               | 23            | 6           | -1.650112 2.580153 0.539105 |
|               | 24            | 6           | -2.515936 3.660064 0.332282 |
|               | 25            | 6           | -3.776403 3.477293 -0.233214 |
|               | 26            | 6           | -4.203087 2.180363 -0.519685 |
|               | 27            | 6           | 4.202484 2.180819 -0.521108 |
|               | 28            | 6           | 3.775490 3.477752 -0.235091 |
|               | 29            | 6           | 2.515181 3.660430 0.330793 |
|               | 30            | 6           | 1.649699 2.580374 0.538265 |
|               | 31            | 1           | -3.608754 -4.187662 0.086911 |
### 30b-model

Zero-point correction=                           0.618060 (Hartree/Particle)
Thermal correction to Gibbs Free Energy=          0.551298
Sum of electronic and thermal Free Energies=      -2173.320153

E[SMD(chloroform)/B3LYP-D3BJ/6-31G***/B3LYP/6-31G*]= -2174.19761186

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
|               |               |             | X          | Y          | Z          |
| 1             | 6             | 0           | 4.999423   | 4.247700  | -1.413477  |
| 2             | 6             | 0           | 3.627150   | 4.481962  | -1.494018  |
| 3             | 6             | 0           | 2.689641   | 3.520734  | -1.076944  |
| 4             | 6             | 0           | 3.151027   | 2.317268  | -0.551289  |
| 5             | 6             | 0           | 4.538428   | 2.074074  | -0.530566  |
| 6             | 6             | 0           | 5.468244   | 3.011914  | -0.943014  |
| 7             | 6             | 0           | 4.761059   | 0.646851  | -0.168602  |
| 8             | 6             | 0           | 3.396072   | 0.054174  | 0.043634   |
| 9             | 6             | 0           | 2.452790   | 1.073124  | -0.109526  |
| 10            | 6             | 0           | 1.053598   | 0.756747  | 0.005024   |
| 11            | 6             | 0           | 0.777725   | -0.638191 | -0.163390  |
| 12            | 6             | 0           | 1.791387   | -1.662196 | -0.162566  |
| 13            | 6             | 0           | 3.108302   | -1.350832 | 0.161920   |
| 14            | 6             | 0           | 5.836759   | 0.068924  | -0.149132  |
| 15            | 6             | 0           | -0.075529  | 1.581951  | 0.173511   |
| 16            | 6             | 0           | -1.378089  | 1.021575  | 0.012583   |
| 17            | 6             | 0           | -1.651486  | -0.388320 | -0.137733  |
| 18            | 6             | 0           | -0.504020  | -1.210949 | -0.311870  |
| 19            | 6             | 0           | -2.363578  | 2.054215  | 0.062865   |
| 20            | 6             | 0           | -3.709606  | 1.716231  | -0.211602  |
| 21            | 6             | 0           | -3.976805  | 0.311751  | -0.144789  |
| 22            | 6             | 0           | -3.029593  | -0.727700 | -0.020985  |
| 23            | 6             | 0           | -4.839954  | 2.564639  | -0.530730  |
| 24            | 6             | 0           | -6.098818  | 1.996039  | -0.594061  |
| 25            | 6             | 0           | -6.362190  | 0.617175  | -0.359116  |
| 26            | 6             | 0           | -5.302836  | -0.224270 | 0.144086   |
| 27            | 6             | 0           | 1.105268   | -2.903172 | -0.567441  |
| 28            | 6             | 0           | -0.285099  | -2.615650 | -0.705392  |
| 29            | 6             | 0           | -1.124605  | -3.538791 | -1.329932  |
| 30            | 6             | 0           | -0.605039  | -4.769747 | 1.746901   |
| 31            | 6             | 0           | 0.749176   | -5.063312 | -1.582466  |
|   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|
| 32 | 6 | 0 | 1.614063 | -4.120138 | -1.015143 |
| 33 | 6 | 0 | -0.271351 | 2.976494 | 0.594272 |
| 34 | 6 | 0 | -1.665135 | 3.276080 | 0.504404 |
| 35 | 6 | 0 | 0.601499 | 3.876532 | 1.203948 |
| 36 | 6 | 0 | 0.115744 | 5.105207 | 1.665549 |
| 37 | 6 | 0 | -1.240384 | 5.410894 | 1.558469 |
| 38 | 6 | 0 | -2.136598 | 4.491845 | 0.999337 |
| 39 | 6 | 0 | -3.794967 | -1.962021 | 0.261054 |
| 40 | 6 | 0 | -5.183062 | -1.656804 | 0.139308 |
| 41 | 6 | 0 | -6.154773 | -2.620061 | 0.384033 |
| 42 | 6 | 0 | -5.755536 | -3.897554 | 0.794022 |
| 43 | 6 | 0 | -4.401671 | -4.184313 | 0.983289 |
| 44 | 6 | 0 | -3.416645 | -3.222689 | 0.727640 |
| 45 | 1 | 0 | 5.701204 | 5.009403 | -1.740856 |
| 46 | 1 | 0 | 3.266961 | 5.424835 | -1.897024 |
| 47 | 1 | 0 | 1.631490 | 3.725014 | -1.179920 |
| 48 | 1 | 0 | 6.527896 | 2.773991 | -0.919336 |
| 49 | 1 | 0 | -6.937516 | 2.638005 | -0.854558 |
| 50 | 1 | 0 | -7.386474 | 0.254683 | -0.390554 |
| 51 | 1 | 0 | -2.164962 | -3.304319 | -1.518492 |
| 52 | 1 | 0 | -1.261355 | -5.489924 | -2.227750 |
| 53 | 1 | 0 | 1.145374 | -6.012846 | -1.931669 |
| 54 | 1 | 0 | 2.677742 | -4.326558 | -0.974189 |
| 55 | 1 | 0 | 1.645584 | 3.625254 | 1.347436 |
| 56 | 1 | 0 | 0.797577 | 5.808679 | 2.135188 |
| 57 | 1 | 0 | -1.616498 | 6.354459 | 1.944375 |
| 58 | 1 | 0 | -3.193565 | 4.720037 | 1.005333 |
| 59 | 1 | 0 | -7.210633 | -2.380499 | 0.284984 |
| 60 | 1 | 0 | -6.504119 | -4.696662 | 0.992518 |
| 61 | 1 | 0 | -4.103614 | -5.165277 | 1.343307 |
| 62 | 1 | 0 | -2.376058 | -3.460816 | 0.909335 |
| 63 | 14 | 0 | 4.377165 | -2.586865 | 0.926651 |
| 64 | 6 | 0 | 5.539020 | -3.322785 | -0.372594 |
| 65 | 1 | 0 | 6.148018 | -2.529823 | -0.816870 |
| 66 | 1 | 0 | 6.214018 | -4.054015 | 0.089496 |
| 67 | 1 | 0 | 5.000451 | -3.831968 | -1.180326 |
| 68 | 6 | 0 | 3.429976 | -3.953162 | 1.846431 |
| 69 | 1 | 0 | 2.755820 | -3.513471 | 2.591591 |
| 70 | 1 | 0 | 2.836943 | -4.625046 | 1.223717 |
| 71 | 1 | 0 | 4.160200 | -4.563837 | 2.393502 |
| 72 | 6 | 0 | 5.342930 | -1.724016 | 2.309944 |
| 73 | 1 | 0 | 6.080383 | -1.014726 | 1.931647 |
| 74 | 1 | 0 | 4.666174 | -1.192142 | 2.990068 |
| 75 | 1 | 0 | 5.865557 | -2.484513 | 2.904235 |
| 76 | 6 | 0 | -4.702110 | 4.023389 | -0.908116 |
| 77 | 1 | 0 | -4.944033 | 4.695714 | -0.075391 |
| 78 | 1 | 0 | -3.694892 | 4.266821 | -1.252224 |
| 79 | 1 | 0 | -5.400400 | 4.263381 | -1.716973 |

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**Supplementary Information**

### 30a-model

Zero-point correction= 0.618220 (Hartree/Particle)
Thermal correction to Gibbs Free Energy= 0.551080
Sum of electronic and thermal Free Energies= -2173.320167

\[ \text{E[SMD(chloroform)/B3LYP-D3BJ/6-31G**/B3LYP/6-31G*]} = -2174.19753741 \]

| Center Number | Atomic Number | Atomic Type | Coordinates (Ångstroms) |
|---------------|---------------|-------------|-------------------------|
|               |               |             | X           | Y           | Z           |
| 1              | 6             | 0           | -4.539457   | 4.043840   | 2.534923   |
| 2              | 6             | 0           | -3.170244   | 4.262984   | 2.384767   |
| 3              | 6             | 0           | -2.354299   | 3.363141   | 1.676979   |
| 4              | 6             | 0           | -2.941635   | 2.243399   | 1.095952   |
| 5              | 6             | 0           | -4.315765   | 2.010491   | 1.297133   |
| 6              | 6             | 0           | -5.124184   | 2.885590   | 2.000524   |
| 7              | 6             | 0           | -4.643902   | 0.652514   | 0.776604   |
| 8              | 6             | 0           | -3.367380   | 0.107691   | 0.199591   |
| 9              | 6             | 0           | -2.373026   | 1.071064   | 0.369259   |
| 10             | 6             | 0           | -1.015050   | 0.744364   | 0.029306   |
| 11             | 6             | 0           | -0.779777   | -0.665533  | -0.041511  |
| 12             | 6             | 0           | -1.830348   | -1.642082  | -0.202050  |
| 13             | 6             | 0           | -3.162875   | -1.242759  | -0.261196  |
| 14             | 8             | 0           | -5.708770   | 0.070271   | 0.909454   |
| 15             | 6             | 0           | 0.104924    | 1.550245   | -0.252012  |
| 16             | 6             | 0           | 1.401451    | 0.960177   | -0.255506  |
| 17             | 6             | 0           | 1.642896    | -0.436612  | 0.006258   |
| 18             | 6             | 0           | 0.489271    | -1.269086  | -0.079776  |
| 19             | 6             | 0           | 2.403994    | 1.937848   | -0.547958  |
| 20             | 6             | 0           | 3.761598    | 1.517973   | -0.590980  |
| 21             | 6             | 0           | 3.981201    | 0.204169   | -0.057863  |
| 22             | 6             | 0           | 2.996915    | -0.748333  | 0.283961   |
| 23             | 6             | 0           | 4.953164    | 2.194905   | -1.073654  |
| 24             | 6             | 0           | 6.190137    | 1.620786   | -0.840622  |
| 25             | 6             | 0           | 6.386832    | 0.386352   | -0.164116  |
| 26             | 6             | 0           | 5.282064    | -0.329643  | 0.210125   |
| 27             | 6             | 0           | -1.139948   | -2.942181  | -0.333396  |
| 28             | 6             | 0           | 0.267798    | -2.708554  | -0.304557  |
| 29             | 6             | 0           | 1.151599    | -3.760963  | -0.543554  |
| 30             | 6             | 0           | 0.648760    | -5.057438  | -0.701255  |
| 31             | 6             | 0           | -0.721606   | -5.303293  | -0.610930  |
| 32             | 6             | 0           | -1.621397   | -4.245329  | -0.430412  |
| 33             | 6             | 0           | 0.279699    | 2.957022   | -0.621131  |
| 34             | 6             | 0           | 1.680145    | 3.218827   | -0.737738  |
| 35             | 6             | 0           | -0.655728   | 3.949747   | -0.905869  |
| 36             | 6             | 0           | -0.217510   | 5.246273   | -1.195843  |
| 37             | 6             | 0           | 1.144871    | 5.539385   | -1.184350  |
| 38             | 6             | 0           | 2.093265    | 4.532919   | -0.960070  |
| 39             | 6             | 0           | 3.690747    | -1.869686  | 0.947344   |
| 40             | 6             | 0           | 5.091582    | -1.621177  | 0.876473   |
| 41             | 6             | 0           | 6.003390    | -2.493119  | 1.460552   |
| 42             | 6             | 0           | 5.523316    | -3.610848  | 2.153342   |
| 43             | 6             | 0           | 4.148546    | -3.829598  | 2.275541   |
| 44             | 6             | 0           | 3.224629    | -2.960807  | 1.682340   |
| 45             | 1             | 0           | -5.145987   | 4.756101   | 3.086938   |
| 46             | 1             | 0           | -2.715909   | 5.142904   | 2.832455   |
| 47             | 1             | 0           | -1.289283   | 3.546255   | 1.603617   |
| 48             | 1             | 0           | -6.176823   | 2.658759   | 2.144468   |
|   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|
| 49 | 1 | 0 | 7.068814 | 2.136441 | -1.221264 |
| 50 | 1 | 0 | 7.396063 | 0.017378 | -0.006502 |
| 51 | 1 | 0 | 2.218402 | -3.586016 | -0.607392 |
| 52 | 1 | 0 | 1.337009 | -5.878611 | -0.881687 |
| 53 | 1 | 0 | -1.098763 | -6.318656 | -0.696108 |
| 54 | 1 | 0 | -2.683192 | -4.452371 | -0.369014 |
| 55 | 1 | 0 | -1.716303 | 3.727060 | -0.899466 |
| 56 | 1 | 0 | -0.943513 | 6.024704 | -1.412970 |
| 57 | 1 | 0 | 1.483979 | 6.555797 | -1.365102 |
| 58 | 1 | 0 | 3.138222 | 4.801072 | -0.955435 |
| 59 | 1 | 0 | 7.071966 | -2.301491 | 1.402090 |
| 60 | 1 | 0 | 6.224094 | -4.298970 | 2.618115 |
| 61 | 1 | 0 | 3.787094 | -4.680860 | 2.845953 |
| 62 | 1 | 0 | 2.162545 | -3.135643 | 1.808694 |
| 63 | 14 | 0 | -4.599111 | -2.228520 | -1.095791 |
| 64 | 6 | 0 | -3.904143 | -3.119265 | -2.624765 |
| 65 | 1 | 0 | -3.566876 | -2.372606 | -3.354677 |
| 66 | 1 | 0 | -3.076006 | -3.808421 | -2.454798 |
| 67 | 1 | 0 | -4.718491 | -3.683681 | -3.098113 |
| 68 | 6 | 0 | -5.429484 | -3.418964 | 0.118157 |
| 69 | 1 | 0 | -5.904568 | -2.846986 | 0.922327 |
| 70 | 1 | 0 | -6.209323 | -4.001855 | -0.387658 |
| 71 | 1 | 0 | -4.728713 | -4.125246 | 0.577154 |
| 72 | 6 | 0 | -5.879417 | -1.057283 | -1.858980 |
| 73 | 1 | 0 | -6.595142 | -0.674682 | -1.130296 |
| 74 | 1 | 0 | -5.398324 | -0.200253 | -2.346355 |
| 75 | 1 | 0 | -6.428016 | -1.602737 | -2.637569 |
| 76 | 6 | 0 | 4.932954 | 3.448684 | -1.918688 |
| 77 | 1 | 0 | 4.025156 | 3.526760 | -2.520480 |
| 78 | 1 | 0 | 5.020881 | 4.361491 | -1.316320 |
| 79 | 1 | 0 | 5.787276 | 3.442826 | -2.603139 |
### TS-model

![TS-model Diagram]

One imaginary frequency = \(-194.99 \text{ cm}^{-1}\)

Zero-point correction = 0.616806 (Hartree/Particle)

Thermal correction to Gibbs Free Energy = 0.549784

Sum of electronic and thermal Free Energies = -2173.290468

E[SMD(chloroform)/B3LYP-D3BJ/6-31G**/*B3LYP/6-31G*] = -2174.16667084

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
| 1             | 6             | 0           | -4.148789, -4.88194, -2.061165 |
| 2             | 6             | 0           | -2.799776, -4.623894, -1.735535 |
| 3             | 6             | 0           | -2.081762, -3.584332, -1.118400 |
| 4             | 6             | 0           | -2.746776, -2.401575, -0.809027 |
| 5             | 6             | 0           | -4.098282, -2.264853, -1.183335 |
| 6             | 6             | 0           | -4.809933, -3.278979, -1.799002 |
| 7             | 6             | 0           | -4.519931, -0.858567, -0.930078 |
| 8             | 6             | 0           | -3.327637, -0.171650, -0.327161 |
| 9             | 6             | 0           | -2.292150, -1.097138, -0.239836 |
| 10            | 6             | 0           | -0.994964, -0.654558, 0.188411 |
| 11            | 6             | 0           | -0.775862, 0.755200, 0.124114 |
| 12            | 6             | 0           | -1.881055, 1.672043, -0.017685 |
| 13            | 6             | 0           | -3.202870, 1.235194, -0.061824 |
| 14            | 8             | 0           | -5.585217, -0.357506, -1.254560 |
| 15            | 6             | 0           | 0.106673, -1.392369, 0.620270 |
| 16            | 6             | 0           | 1.401060, -0.796224, 0.545424 |
| 17            | 6             | 0           | 1.681153, 0.615907, 0.321794 |
| 18            | 6             | 0           | 0.468038, 1.426589, 0.287529 |
| 19            | 6             | 0           | 2.352043, -1.866786, 0.619212 |
| 20            | 6             | 0           | 3.618236, -1.651655, 0.052823 |
| 21            | 6             | 0           | 3.914584, -0.269626, -0.175659 |
| 22            | 6             | 0           | 3.091988, 0.869589, 0.088104 |
| 23            | 6             | 0           | 4.583895, -2.632772, -0.409942 |
| 24            | 6             | 0           | 5.757743, -2.189260, -0.984350 |
| 25            | 6             | 0           | 6.077339, -0.817270, -1.141581 |
| 26            | 6             | 0           | 5.165034, 0.121862, -0.742071 |
| 27            | 6             | 0           | -1.286785, 3.005124, -0.000219 |
| 28            | 6             | 0           | 0.104782, 2.878451, 0.289889 |
| 29            | 6             | 0           | 0.789776, 4.054208, 0.581952 |
| 30            | 6             | 0           | 0.192457, 5.307187, 0.407084 |
| 31            | 6             | 0           | -1.114164, 5.411037, -0.062527 |
|   |   |   | 32  | 6   | 0  | -1.864604 | 4.247184 | -0.247980 |
|---|---|---|-----|-----|----|-----------|----------|-----------|
| 33 | 6 | 0 | 0.259228 | -2.750019 | 1.142097 |
| 34 | 6 | 0 | 1.649428 | -3.040471 | 1.170628 |
| 35 | 6 | 0 | -0.665458 | -3.610648 | 1.730940 |
| 36 | 6 | 0 | -0.206717 | -4.780869 | 2.345043 |
| 37 | 6 | 0 | 1.160479 | -5.059782 | 2.399420 |
| 38 | 6 | 0 | 2.094869 | -4.187345 | 1.827838 |
| 39 | 6 | 0 | 4.006316 | -0.133323 | 
| 40 | 6 | 0 | 5.210546 | -0.733489 | 
| 41 | 6 | 0 | 6.254963 | -1.099601 | 
| 42 | 6 | 0 | 6.164348 | -0.816033 | 
| 43 | 6 | 0 | 1.649428 | -3.040471 | 1.170628 |
| 44 | 6 | 0 | 5.210546 | 1.571618 | -0.733489 |
| 45 | 1 | 0 | -4.678549 | -5.308386 | -2.537121 |
| 46 | 1 | 0 | -2.282402 | -5.550408 | -1.970245 |
| 47 | 1 | 0 | -1.029209 | -3.716373 | -0.904535 |
| 48 | 1 | 0 | -5.846912 | -3.121292 | -2.081921 |
| 49 | 1 | 0 | 6.462501 | -2.928972 | -1.356205 |
| 50 | 1 | 0 | 7.021958 | -0.532664 | -1.597477 |
| 51 | 1 | 0 | 1.775612 | 4.020521 | 0.995748 |
| 52 | 1 | 0 | 0.767036 | 6.201801 | 0.631043 |
| 53 | 1 | 0 | -1.559390 | 6.389317 | -0.250159 |
| 54 | 1 | 0 | -2.893703 | 4.314790 | -0.580986 |
| 55 | 1 | 0 | -1.723083 | -3.369486 | 1.737518 |
| 56 | 1 | 0 | -0.917634 | -5.458297 | 2.809658 |
| 57 | 1 | 0 | 1.509979 | -5.951450 | 2.912615 |
| 58 | 1 | 0 | 3.151292 | -4.393795 | 1.941213 |
| 59 | 1 | 0 | 7.145342 | 2.005128 | -1.571510 |
| 60 | 1 | 0 | 6.968231 | 4.451692 | -1.095189 |
| 61 | 1 | 0 | 5.007268 | 5.287999 | 0.190937 |
| 62 | 1 | 0 | 3.242314 | 3.794793 | 0.873583 |
| 63 | 14 | 0 | -4.759003 | 2.253471 | 0.471563 |
| 64 | 6 | 0 | -4.279589 | 3.469944 | 1.851379 |
| 65 | 1 | 0 | -3.844509 | 2.921412 | 2.696027 |
| 66 | 1 | 0 | -3.582299 | 4.263461 | 1.580830 |
| 67 | 1 | 0 | -5.200777 | 3.942848 | 2.216873 |
| 68 | 6 | 0 | -5.584193 | 3.130565 | -0.987691 |
| 69 | 1 | 0 | -5.935401 | 2.386189 | -1.709456 |
| 70 | 1 | 0 | -6.452600 | 3.706182 | -0.643616 |
| 71 | 1 | 0 | -4.914063 | 3.821067 | -1.512124 |
| 72 | 6 | 0 | -5.996334 | 1.117729 | 1.353345 |
| 73 | 1 | 0 | -6.595563 | 0.521200 | 0.664534 |
| 74 | 1 | 0 | -5.489611 | 0.435213 | 2.046918 |
| 75 | 1 | 0 | -6.672190 | 1.740930 | 1.952732 |
| 76 | 6 | 0 | 4.342411 | -4.124544 | -0.394174 |
| 77 | 1 | 0 | 4.644729 | -4.586558 | 0.553318 |
| 78 | 1 | 0 | 3.293696 | -4.378768 | -0.562272 |
| 79 | 1 | 0 | 4.935656 | -4.601198 | -1.180724 |
Supplementary Figure 5. Calculated vs experimental $^1$H NMR chemical shift of selected, unambiguously assigned resonances in tetracenes 30a, 30b and 31.
Supplementary Figure 6. Possible topological isomers of tetracene 32-H.

32-Ha
|    |    |    |          |          |          |
|----|----|----|----------|----------|----------|
|  3 |  6 |  0 | 5.974179 | -2.447835 | 0.548520 |
|  4 |  6 |  0 | 7.259583 | -1.965050 | 0.485878 |
|  5 |  6 |  0 | 7.421068 | -0.603257 | 0.142590 |
|  6 |  6 |  0 | 6.371183 |  0.297279 | -0.050291|
|  7 |  6 |  0 | 6.941921 |  1.564926 | -0.592391|
|  8 |  6 |  0 | 8.349609 |  1.452632 | -0.601591|
|  9 |  6 |  0 | 8.721323 |  0.087705 | -0.120758|
| 10 |  6 |  0 | 9.169354 |  2.454275 | -1.090683|
| 11 |  6 |  0 | 8.568308 |  3.610670 | -1.610617|
| 12 |  6 |  0 | 7.177844 |  3.715876 | -1.647090|
| 13 |  6 |  0 | 6.350247 |  2.696093 | -1.146667|
| 14 |  8 |  0 | 9.839505 | -0.380222 |  0.009197|
| 15 |  6 |  0 | 3.817861 |  0.577384 |  0.332335|
| 16 |  6 |  0 | 2.578213 | -0.110780 |  0.218015|
| 17 |  6 |  0 | 2.456249 | -1.537281 |  0.076623|
| 18 |  6 |  0 | 3.650525 | -2.263183 |  0.365893|
| 19 |  6 |  0 | 1.480342 |  0.809084 |  0.322712|
| 20 |  6 |  0 | 0.181271 |  0.350683 | -0.034713|
| 21 |  6 |  0 | 0.090151 | -1.057035 | -0.302683|
| 22 |  6 |  0 | 1.156268 | -1.980995 | -0.213221|
| 23 |  6 |  0 | -1.050930 |  1.124442 |  0.213221|
| 24 |  6 |  0 | -2.222761 |  0.460586 | -0.545072|
| 25 |  6 |  0 | -2.280417 | -0.986268 | -0.755901|
| 26 |  6 |  0 | -1.138986 | -1.740311 | -0.637589|
| 27 |  6 |  0 | -3.697109 |  0.988371 | -0.697366|
| 28 |  6 |  0 | -4.418231 |  0.333874 |  0.515931|
| 29 |  6 |  0 | -4.414494 | -1.038724 |  0.335169|
| 30 |  6 |  0 | -3.752176 | -1.368341 | -1.020776|
| 31 |  6 |  0 | -4.900431 |  0.918839 |  1.743867|
| 32 |  6 |  0 | -5.424327 |  0.046333 |  2.752686|
| 33 |  6 |  0 | -5.338339 | -1.399285 |  2.587410|
| 34 |  6 |  0 | -4.785582 | -1.945090 |  1.388275|
| 35 |  6 |  0 |  5.398171 | -3.752290 |  0.881325|
| 36 |  6 |  0 |  3.977403 | -3.635283 |  0.815501|
| 37 |  6 |  0 |  3.189807 | -4.684775 |  1.292192|
| 38 |  6 |  0 |  3.807356 | -5.859155 |  1.740323|
| 39 |  6 |  0 |  5.198007 | -5.990549 |  1.734142|
| 40 |  6 |  0 |  6.004233 | -4.925014 |  1.317716|
| 41 |  6 |  0 |  3.508387 |  1.933518 |  0.783251|
| 42 |  6 |  0 |  2.087300 |  2.072988 |  0.832918|
| 43 |  6 |  0 |  4.347211 |  2.899102 |  1.337920|
| 44 |  6 |  0 |  3.790469 |  4.030280 |  1.942101|
| 45 |  6 |  0 |  2.406577 |  4.157559 |  2.029767|
| 46 |  6 |  0 |  1.557491 |  3.178694 |  1.497013|
| 47 |  6 |  0 |  0.623485 | -3.276198 | -0.710429|
| 48 |  6 |  0 | -0.791514 | -3.164322 | -0.831064|
| 49 |  6 |  0 | -1.543547 | -4.302390 | -1.122629|
| 50 |  6 |  0 | -0.893106 | -5.077786 | -1.408496|
| 51 |  6 |  0 |  0.499993 | -5.574631 | -1.430695|
| 52 |  6 |  0 |  1.265309 | -4.458655 | -1.081831|
| 53 |  6 |  0 | -0.078824 |  2.346572 |  1.257174|
| 54 |  6 |  0 | -4.178473 | -2.516315 | -1.909501|
| 55 |  6 |  0 | -4.884795 |  2.313486 |  2.001610|
| 56 |  6 |  0 | -5.397183 |  2.842680 |  3.170011|
| 57 |  6 |  0 | -5.957618 |  1.991897 |  4.135808|
| 58 |  6 |  0 | -5.963684 |  0.626880 |  3.925183|
| 59 |  6 |  0 | -5.723046 | -2.297701 |  3.611217|
|   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|
| 60 | 6 | 0 | -5.538391 | -3.661486 | 3.489853 |
| 61 | 6 | 0 | -4.938316 | -4.188532 | 2.334028 |
| 62 | 6 | 0 | -4.571739 | -3.343317 | 1.306290 |
| 63 | 6 | 0 | -5.418710 | -3.148599 | -1.750021 |
| 64 | 6 | 0 | -5.873441 | -4.078262 | -2.687181 |
| 65 | 6 | 0 | -5.110166 | -4.371044 | -3.816642 |
| 66 | 6 | 0 | -3.893248 | -3.714506 | -4.008925 |
| 67 | 6 | 0 | -3.439531 | -2.790008 | -3.071029 |
| 68 | 6 | 0 | -3.284083 | 2.951045 | -2.240418 |
| 69 | 6 | 0 | -3.705785 | 4.101689 | -2.903407 |
| 70 | 6 | 0 | -4.954718 | 4.657141 | -2.624679 |
| 71 | 6 | 0 | -5.786116 | 4.027980 | -1.699503 |
| 72 | 6 | 0 | -5.358896 | 2.876421 | -1.037390 |
| 73 | 6 | 0 | -1.024839 | 2.612106 | -0.125135 |
| 74 | 6 | 0 | -1.759878 | 3.298627 | 0.848794 |
| 75 | 6 | 0 | -0.270233 | 3.360378 | -1.040700 |
| 76 | 6 | 0 | -1.762632 | 4.692479 | 0.904468 |
| 77 | 6 | 0 | -0.264105 | 4.752565 | -1.002536 |
| 78 | 6 | 0 | -1.016391 | 5.409144 | -0.029046 |
| 79 | 17 | 0 | -1.012915 | 7.166415 | 0.028845 |
| 80 | 6 | 0 | -4.158044 | -0.058448 | -1.743540 |
| 81 | 8 | 0 | -4.671798 | 0.097616 | -2.811200 |
| 82 | 1 | 0 | 8.139516 | -2.582081 | 0.645548 |
| 83 | 1 | 0 | 10.248230 | 2.326805 | -1.082349 |
| 84 | 1 | 0 | 9.183535 | 4.415522 | -2.002571 |
| 85 | 1 | 0 | 6.718611 | 4.602473 | -2.076140 |
| 86 | 1 | 0 | 5.273118 | 2.801127 | -1.201116 |
| 87 | 1 | 0 | 2.110958 | -4.597820 | 1.333730 |
| 88 | 1 | 0 | 3.190622 | -6.675151 | 2.107153 |
| 89 | 1 | 0 | 5.657401 | -6.912231 | 2.080351 |
| 90 | 1 | 0 | 7.087420 | -5.005960 | 1.360192 |
| 91 | 1 | 0 | 5.421536 | 2.759469 | 1.342551 |
| 92 | 1 | 0 | 4.439893 | 4.784840 | 2.377065 |
| 93 | 1 | 0 | 1.969328 | 5.014156 | 2.535234 |
| 94 | 1 | 0 | 0.494794 | 3.285695 | 1.643656 |
| 95 | 1 | 0 | -2.621773 | -4.267277 | -1.164456 |
| 96 | 1 | 0 | -1.485058 | -6.387073 | -1.646886 |
| 97 | 1 | 0 | 0.997715 | -6.499265 | -1.709882 |
| 98 | 1 | 0 | 2.345524 | -4.518996 | -1.103175 |
| 99 | 1 | 0 | -4.480803 | 2.983055 | 1.256450 |
| 100 | 1 | 0 | -5.375227 | 3.916845 | 3.331937 |
| 101 | 1 | 0 | -6.379645 | 2.401000 | 5.049464 |
| 102 | 1 | 0 | -6.393635 | -0.008235 | 4.690496 |
| 103 | 1 | 0 | -6.153235 | -1.918299 | 4.530419 |
| 104 | 1 | 0 | -5.838478 | -4.321142 | 4.299274 |
| 105 | 1 | 0 | -4.756929 | -5.256159 | 2.248615 |
| 106 | 1 | 0 | -4.099371 | -3.754740 | 0.424877 |
| 107 | 1 | 0 | -6.041605 | -2.913953 | -0.893845 |
| 108 | 1 | 0 | -6.833736 | -4.563613 | -2.534683 |
| 109 | 1 | 0 | -5.465373 | -5.092850 | -4.547108 |
| 110 | 1 | 0 | -3.295987 | -3.916516 | -4.893815 |
| 111 | 1 | 0 | -2.496051 | -2.793331 | -3.237777 |
| 112 | 1 | 0 | -2.329591 | 2.510631 | -2.502261 |
| 113 | 1 | 0 | -3.059070 | 4.556281 | -3.648977 |
| 114 | 1 | 0 | -5.284127 | 5.555732 | -3.139076 |
| 115 | 1 | 0 | -6.778362 | 4.422405 | -1.497169 |
| 116 | 1 | 0 | -6.039727 | 2.381719 | -0.353591 |
Xiao and Hoye: Domino-HDDA

Supplementary Information

Zero-point correction= 0.917888 (Hartree/Particle)
Thermal correction to Gibbs Free Energy= 0.827844
Sum of electronic and thermal Free Energies= -3605.640953
E[SMD(chloroform)/B3LYP-D3BJ/6-31G**//B3LYP/6-31G*] = -3607.00767700

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
|               | X             | Y           | Z                       |
| 1             | -5.030370     | -0.087140   | 0.070329                |
| 2             | -4.961611     | 1.251713    | -0.440688               |
| 3             | -6.108050     | 2.021543    | -0.827324               |
| 4             | -7.365995     | 1.504168    | -0.632085               |
| 5             | -7.450983     | 0.269579    | 0.050818                |
| 6             | -6.355771     | -0.494384   | 0.462808                |
| 7             | -6.860720     | -1.541619   | 1.401717                |
| 8             | -8.272655     | -1.501459   | 1.401620                |
| 9             | -8.714355     | -0.370769   | 0.532950                |
| 10            | -9.038833     | -2.318467   | 2.214436                |
| 11            | -8.378292     | -3.197111   | 3.086070                |
| 12            | -6.984590     | -3.203411   | 3.140680                |
| 13            | -6.212351     | -2.373515   | 2.309945                |
| 14            | -9.854299     | -0.014326   | 0.288942                |
| 15            | -3.794455     | -0.776960   | 0.052585                |
| 16            | -2.588609     | -0.042230   | -0.132177               |
| 17            | -2.543575     | 1.381181    | -0.327241               |
| 18            | -3.781549     | 1.986904    | -0.664763               |
| 19            | -1.443153     | -0.905830   | 0.099264                |
| 20            | -0.158477     | -0.325662   | -0.312720               |
| 21            | -0.134864     | 1.103261    | -0.203101               |
| 22            | -1.256790     | 1.946800    | -0.152497               |
| 23            | 1.130068      | -0.966013   | -0.585950               |
| 24            | 2.278523      | -0.184947   | -0.591359               |
| 25            | 2.265978      | 1.245863    | -0.279704               |
| 26            | 1.071321      | 1.886658    | -0.069783               |
| 27            | 3.783895      | -0.573294   | -0.815949               |
| 28            | 4.403787      | -0.398959   | 0.599073                |
|   |   |   |   |   |
|---|---|---|---|---|
| 29 | 6 | 0 | 4.322339 | 0.939168 | 0.945217 |
| 30 | 6 | 0 | 3.725494 | 1.735727 | -0.238491 |
| 31 | 6 | 0 | 4.877025 | -1.383760 | 1.542513 |
| 32 | 6 | 0 | 5.286764 | -0.938534 | 2.841316 |
| 33 | 6 | 0 | -5.602992 | 3.270169 | -1.405202 |
| 34 | 6 | 0 | -4.179390 | 3.249843 | -1.319485 |
| 35 | 6 | 0 | -3.442697 | 4.276407 | -1.911050 |
| 36 | 6 | 0 | -4.120146 | 5.334110 | -2.530588 |
| 37 | 6 | 0 | -5.516181 | 5.368500 | -2.574168 |
| 38 | 6 | 0 | -6.267658 | 4.326419 | -2.018020 |
| 39 | 6 | 0 | -3.411854 | -2.186603 | 0.150343 |
| 40 | 6 | 0 | -1.984762 | -2.268940 | 0.153623 |
| 41 | 6 | 0 | -4.190061 | -3.342224 | 0.176267 |
| 42 | 6 | 0 | -3.573335 | -4.584775 | 0.355385 |
| 43 | 6 | 0 | -2.192093 | -4.654975 | 0.520528 |
| 44 | 6 | 0 | -0.787005 | 5.542879 | 1.057518 |
| 45 | 6 | 0 | -1.492661 | -4.418253 | 0.620632 |
| 46 | 6 | 0 | -0.786351 | 3.286738 | 0.210974 |
| 47 | 6 | 0 | -1.323662 | 4.386147 | 0.725358 |
| 48 | 6 | 0 | -0.607411 | 5.527911 | 1.103147 |
| 49 | 6 | 0 | -0.787005 | 5.542879 | 1.057518 |
| 50 | 6 | 0 | -1.105774 | 3.506666 | 0.210974 |
| 51 | 6 | 0 | -1.492661 | -4.418253 | 0.620632 |
| 52 | 6 | 0 | -1.323662 | 4.386147 | 0.725358 |
| 53 | 6 | 0 | -0.607411 | 5.527911 | 1.103147 |
| 54 | 6 | 0 | -0.787005 | 5.542879 | 1.057518 |
| 55 | 6 | 0 | -1.105774 | 3.506666 | 0.210974 |
| 56 | 6 | 0 | -0.607411 | 5.527911 | 1.103147 |
| 57 | 6 | 0 | -0.787005 | 5.542879 | 1.057518 |
| 58 | 6 | 0 | -1.105774 | 3.506666 | 0.210974 |
| 59 | 6 | 0 | -0.607411 | 5.527911 | 1.103147 |
| 60 | 6 | 0 | -0.787005 | 5.542879 | 1.057518 |
| 61 | 6 | 0 | -1.105774 | 3.506666 | 0.210974 |
| 62 | 6 | 0 | -0.607411 | 5.527911 | 1.103147 |
| 63 | 6 | 0 | -0.787005 | 5.542879 | 1.057518 |
| 64 | 6 | 0 | -1.105774 | 3.506666 | 0.210974 |
| 65 | 6 | 0 | -0.607411 | 5.527911 | 1.103147 |
| 66 | 6 | 0 | -0.787005 | 5.542879 | 1.057518 |
| 67 | 1 | 0 | -10.122786 | -2.251574 | 2.184948 |
| 68 | 1 | 0 | -8.950101 | -3.851617 | 3.737683 |
| 69 | 1 | 0 | -6.478383 | -3.857632 | 3.845008 |
| 70 | 1 | 0 | -5.132532 | -2.385946 | 2.392534 |
| 71 | 1 | 0 | -2.359047 | 4.260506 | -1.905105 |
| 72 | 1 | 0 | -3.547233 | 6.135151 | -2.989742 |
| 73 | 1 | 0 | -6.022366 | 6.199833 | -3.056951 |
| 74 | 1 | 0 | -7.352880 | 4.338330 | -2.079861 |
| 75 | 1 | 0 | -5.265624 | -3.285677 | 0.063760 |
| 76 | 1 | 0 | -4.176787 | -5.487787 | 0.382286 |
| 77 | 1 | 0 | -1.712806 | -6.111893 | 0.707550 |
| 78 | 1 | 0 | -3.293882 | -3.605038 | 0.527729 |
| 79 | 1 | 0 | 2.402298 | 4.395750 | 0.789407 |
| 80 | 1 | 0 | 1.148709 | 6.403062 | 1.451752 |
| 81 | 1 | 0 | -1.332109 | 6.426236 | 1.378675 |
| 82 | 1 | 0 | -2.576172 | 4.423496 | 0.622337 |
| 83 | 1 | 0 | 4.651562 | -3.121182 | 0.274867 |
| 84 | 1 | 0 | 5.529002 | -4.728371 | 1.894711 |
| 85 | 1 | 0 | 6.321047 | -3.938048 | 4.131882 |
|   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
| 86 | 1 | 0 | 6.158814 | -1.579564 | 4.719241 |
| 87 | 1 | 0 | 2.522583 | 3.432604 | -1.984951 |
| 88 | 1 | 0 | 3.320341 | 5.613844 | -2.798911 |
| 89 | 1 | 0 | 5.424815 | 6.596236 | -1.896660 |
| 90 | 1 | 0 | 6.732140 | 5.330797 | -0.195883 |
| 91 | 1 | 0 | 5.939274 | 3.146781 | 0.605755 |
| 92 | 1 | 0 | 2.518905 | -1.444263 | -3.077767 |
| 93 | 1 | 0 | 3.390679 | -2.901389 | -4.853545 |
| 94 | 1 | 0 | 5.677706 | -3.873093 | -4.670013 |
| 95 | 1 | 0 | 7.086268 | -3.304523 | -2.693882 |
| 96 | 1 | 0 | 6.206651 | -1.850062 | -0.923135 |
| 97 | 6 | 0 | 1.178288 | -2.407771 | -0.954488 |
| 98 | 6 | 0 | 1.932554 | -3.327300 | -0.215280 |
| 99 | 6 | 0 | 0.467097 | -2.875145 | -2.070398 |
|100 | 6 | 0 | 1.995979 | -4.671784 | -0.580623 |
|101 | 6 | 0 | 2.453039 | -2.995887 | 0.675733 |
|102 | 6 | 0 | 0.523580 | -4.212961 | -2.453151 |
|103 | 1 | 0 | -0.134434 | -2.182302 | -2.651437 |
|104 | 6 | 0 | 1.293316 | -5.102669 | -1.704280 |
|105 | 1 | 0 | 2.578528 | -5.376921 | 0.002926 |
|106 | 1 | 0 | -0.026261 | -4.564488 | -3.319601 |
|107 | 17 | 0 | 1.367939 | -6.794417 | -2.176831 |
|108 | 1 | 0 | -8.279448 | 2.021639 | -0.911772 |
|109 | 6 | 0 | 4.253541 | 0.803913 | -1.361702 |
|110 | 8 | 0 | 4.846436 | 1.072972 | -2.363409 |
|111 | 6 | 0 | 5.107825 | 0.455171 | 3.227779 |
|112 | 6 | 0 | 5.377238 | 0.911250 | 4.540349 |
|113 | 6 | 0 | 4.587620 | 1.393409 | 2.284069 |
|114 | 6 | 0 | 5.119188 | 2.212403 | 4.926310 |
|115 | 1 | 0 | 5.775624 | 0.226676 | 5.279575 |
|116 | 6 | 0 | 4.301523 | 2.717182 | 2.716292 |
|117 | 6 | 0 | 4.559621 | 3.118085 | 4.009767 |
|118 | 1 | 0 | 5.331714 | 2.526064 | 5.944550 |
|119 | 1 | 0 | 3.860942 | 3.410408 | -2.019227 |
|120 | 1 | 0 | 4.323809 | 4.133169 | 4.316407 |

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**32-Hc**

Zero-point correction= 0.917716 (Hartree/Particle)
Thermal correction to Gibbs Free Energy= 0.827487
Sum of electronic and thermal Free Energies= -3605.640491
E[SMD(chloroform)/B3LYP-D3BJ/6-31G***/B3LYP/6-31G*]= -3607.00581805

---
### Atomic Coordinates (Angstroms)

| Center Number | Atomic Number | Atomic Type | X           | Y           | Z           |
|---------------|---------------|-------------|-------------|-------------|-------------|
| 1             | 6             | 0           | -5.014190   | 0.195510    | 0.419211    |
| 2             | 6             | 0           | -4.895314   | 1.597163    | 0.126490    |
| 3             | 6             | 0           | -6.017129   | 2.478693    | -0.015360   |
| 4             | 6             | 0           | -7.288652   | 1.998678    | 0.186296    |
| 5             | 6             | 0           | -7.425750   | 0.604383    | 0.358557    |
| 6             | 6             | 0           | -6.365700   | -0.305777   | 0.382805    |
| 7             | 6             | 0           | -6.946004   | -1.674587   | 0.209807    |
| 8             | 6             | 0           | -8.354142   | -1.576529   | 0.279120    |
| 9             | 6             | 0           | -8.724359   | -0.136603   | 0.394821    |
| 10            | 6             | 0           | -9.187006   | -2.667741   | 0.105290    |
| 11            | 6             | 0           | -8.603959   | -3.911594   | -0.313988   |
| 12            | 6             | 0           | -7.219781   | -4.011657   | 0.372913    |
| 13            | 6             | 0           | -2.459580   | 1.628363    | 0.112710    |
| 14            | 8             | 0           | -9.840873   | 0.347786    | 0.464625    |
| 15            | 6             | 0           | -3.786697   | -0.467799   | 0.642907    |
| 16            | 6             | 0           | -2.565471   | 0.216309    | 0.394821    |
| 17            | 6             | 0           | -2.459580   | 1.628363    | 0.112710    |
| 18            | 6             | 0           | -3.691027   | 2.309963    | -0.075421   |
| 19            | 6             | 0           | -1.461509   | -0.692559   | 0.453597    |
| 20            | 6             | 0           | -0.188249   | -0.231362   | 0.032007    |
| 21            | 6             | 0           | -0.071061   | 1.192958    | 0.007149    |
| 22            | 6             | 0           | -1.122177   | 2.114641    | 0.158366    |
| 23            | 6             | 0           | 1.000131    | -0.997833   | -0.331662   |
| 24            | 6             | 0           | 2.175557    | -0.306970   | -0.593924   |
| 25            | 6             | 0           | 2.296435    | 1.141405    | -0.411336   |
| 26            | 6             | 0           | 1.192493    | 1.885022    | -0.073779   |
| 27            | 6             | 0           | 3.589576    | -0.818999   | -1.031066   |
| 28            | 6             | 0           | 4.467006    | -0.585114   | 0.230545    |
| 29            | 6             | 0           | 4.524624    | 0.776980    | 0.471171    |
| 30            | 6             | 0           | 3.767709    | 1.525702    | -0.651714   |
| 31            | 6             | 0           | 5.721250    | 0.407260    | 2.591430    |
| 32            | 6             | 0           | 5.072668    | 1.307858    | 1.690929    |
| 33            | 6             | 0           | -5.491162   | 3.779457    | -0.429067   |
| 34            | 6             | 0           | -4.073795   | 3.665140    | -0.529641   |
| 35            | 6             | 0           | -3.351208   | 4.704355    | -1.118566   |
| 36            | 6             | 0           | -4.020473   | 5.871441    | -1.507214   |
| 37            | 6             | 0           | -5.400392   | 6.003882    | -1.333149   |
| 38            | 6             | 0           | -6.148443   | 4.945846    | -0.805217   |
| 39            | 6             | 0           | -3.409783   | -1.768003   | 1.211919    |
| 40            | 6             | 0           | -1.997463   | -1.926293   | 1.072183    |
| 41            | 6             | 0           | -4.145200   | -2.658849   | 1.992395    |
| 42            | 6             | 0           | -3.503518   | -3.754897   | 2.579231    |
| 43            | 6             | 0           | -2.130345   | -3.931034   | 2.418362    |
| 44            | 6             | 0           | -1.371547   | -3.011330   | 1.684263    |
| 45            | 6             | 0           | -0.505788   | 3.419455    | 0.431865    |
| 46            | 6             | 0           | 0.906706    | 3.294303    | 0.269817    |
| 47            | 6             | 0           | 1.733330    | 4.374940    | 0.572007    |
| 48            | 6             | 0           | 1.171384    | 5.564038    | 1.050321    |
| 49            | 6             | 0           | -0.204629   | 5.666715    | 1.256170    |
| 50            | 6             | 0           | -1.048606   | 4.592981    | 0.957545    |
| 51            | 6             | 0           | 3.801838    | -1.969494   | -1.996449   |
| 52            | 6             | 0           | 4.190631    | 2.881891    | -1.174908   |
| 53            | 6             | 0           | 6.273527    | 0.938786    | 3.781405    |
| 54            | 6             | 0           | 6.168704    | 2.279443    | 4.097778    |
|   |   |   | 5.485267 | 3.152088 | 3.234810 |
|---|---|---|---------|---------|---------|
| 56 | 6 | 0 | 4.950893 | 2.670855 | 2.056936 |
| 57 | 6 | 0 | 5.498354 | 3.354104 | -0.992385 |
| 58 | 6 | 0 | 5.932858 | 4.521842 | -1.620490 |
| 59 | 6 | 0 | 5.076563 | 5.227156 | -2.465705 |
| 60 | 6 | 0 | 3.786843 | 4.743998 | -2.689270 |
| 61 | 6 | 0 | 3.353494 | 3.578776 | -2.059126 |
| 62 | 6 | 0 | 2.820343 | -2.303990 | -2.938106 |
| 63 | 6 | 0 | 3.074816 | -3.830955 | -4.051923 |
| 64 | 6 | 0 | 5.076563 | -5.227156 | -3.159027 |
| 65 | 6 | 0 | 3.786843 | -4.743998 | -2.689270 |
| 66 | 6 | 0 | 3.353494 | -3.578776 | -2.059126 |
| 67 | 1 | 0 | -10.264576 | -2.542106 | 0.163296 |
| 68 | 1 | 0 | -9.229153 | -4.788339 | -0.320527 |
| 69 | 1 | 0 | -6.773981 | -4.968067 | -0.574043 |
| 70 | 1 | 0 | -5.311504 | -3.009592 | -0.269778 |
| 71 | 1 | 0 | -2.285203 | 4.617938 | 1.285768 |
| 72 | 1 | 0 | -3.454015 | -6.919759 | -1.636723 |
| 73 | 1 | 0 | -7.229047 | 5.025824 | -0.718635 |
| 74 | 1 | 0 | -5.200785 | -2.495223 | 2.172312 |
| 75 | 1 | 0 | -4.077222 | -4.452858 | 3.182587 |
| 76 | 1 | 0 | -1.630868 | -4.771845 | 2.891707 |
| 77 | 1 | 0 | -0.299893 | -3.138484 | 1.630941 |
| 78 | 1 | 0 | 2.804926 | 4.308278 | 0.447044 |
| 79 | 1 | 0 | 1.820531 | 6.402885 | 1.285768 |
| 80 | 1 | 0 | -0.626507 | 6.580508 | 1.665616 |
| 81 | 1 | 0 | -2.110511 | 4.669602 | 1.156435 |
| 82 | 1 | 0 | 6.776612 | 0.284542 | 4.483406 |
| 83 | 1 | 0 | 6.598776 | 2.651194 | 5.023617 |
| 84 | 1 | 0 | 5.370992 | 4.201007 | 3.493107 |
| 85 | 1 | 0 | 4.419029 | 3.346248 | 1.402180 |
| 86 | 1 | 0 | 6.188428 | 2.806388 | -0.359828 |
| 87 | 1 | 0 | 6.948171 | 4.871632 | -1.453883 |
| 88 | 1 | 0 | 5.414884 | 6.135923 | -2.956032 |
| 89 | 1 | 0 | 3.114493 | 5.269818 | -3.361680 |
| 90 | 1 | 0 | 2.353269 | 3.208333 | -2.257131 |
| 91 | 1 | 0 | 1.850237 | -1.824202 | -2.895714 |
| 92 | 1 | 0 | 2.287921 | -3.485446 | -4.651244 |
| 93 | 1 | 0 | 4.529028 | -4.558206 | -4.834448 |
| 94 | 1 | 0 | 6.332028 | -3.889460 | -3.24869 |
| 95 | 1 | 0 | 5.884543 | -2.232601 | -1.492062 |
| 96 | 1 | 0 | 0.889819 | -2.474226 | -0.489867 |
| 97 | 6 | 0 | 1.719195 | -3.346935 | 0.226180 |
| 98 | 6 | 0 | -0.064891 | -3.028333 | -1.357403 |
| 99 | 6 | 0 | 1.618808 | -4.729497 | 0.076015 |
| 100 | 6 | 0 | 2.433534 | -2.942386 | 0.933762 |
| 101 | 6 | 0 | -0.725023 | -2.372332 | -1.916829 |
| 102 | 6 | 0 | -0.74964 | -4.406433 | -1.524441 |
| 103 | 1 | 0 | -2.262478 | -5.395122 | 0.641442 |
| 104 | 6 | 0 | -0.910804 | -4.824806 | -2.202833 |
| 105 | 1 | 0 | 0.537594 | -6.989947 | -1.005696 |
| 106 | 6 | 0 | 5.745799 | -1.019917 | 2.297370 |
| 107 | 6 | 0 | 6.391692 | -1.942320 | 3.154651 |
| 108 | 6 | 0 | 5.063963 | -1.529223 | 1.144936 |
Zero-point correction=                      0.917576 (Hartree/Particle)
Thermal correction to Gibbs Free Energy=       0.826715 
Sum of electronic and thermal Free Energies=   -3605.635070 
E[SMD(chloroform)/B3LYP-D3BJ/6-31G**//B3LYP/6-31G*] =  -3606.99749159

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
|               |               |             | X           | Y          | Z          |
| 1             | 6             | 0           | 4.918286    | 0.407813  | -0.333788  |
| 2             | 6             | 0           | 4.660961    | 1.772565  | 0.038704   |
| 3             | 6             | 0           | 5.689502    | 2.700392  | 0.409556   |
| 4             | 6             | 0           | 7.007443    | 2.316903  | 0.348528   |
| 5             | 6             | 0           | 7.264253    | 0.952102  | 0.097274   |
| 6             | 6             | 0           | 6.282621    | -0.014839 | -0.133120  |
| 7             | 6             | 0           | 6.926570    | -1.354972 | 0.038125   |
| 8             | 6             | 0           | 8.322143    | -1.169372 | 0.163907   |
| 9             | 6             | 0           | 8.604704    | 0.294650  | 0.189860   |
| 10            | 6             | 0           | 9.196424    | -2.218455 | 0.386930   |
| 11            | 6             | 0           | 8.665725    | -3.509873 | 0.522057   |
| 12            | 6             | 0           | 7.285246    | -3.699257 | 0.470506   |
| 13            | 6             | 0           | 8.403230    | -2.629385 | 0.239474   |
| 14            | 8             | 0           | 9.684194    | 0.849452  | 0.303292   |
| 15            | 6             | 0           | 3.783868    | -0.305743 | -0.779772  |
| 16            | 6             | 0           | 2.498193    | 0.302004  | -0.670200  |
| 17            | 6             | 0           | 2.251009    | 1.679867  | -0.328005  |
| 18            | 6             | 0           | 3.392992    | 2.397673  | 0.122546   |
| 19            | 6             | 0           | 1.482406    | -0.655435 | -0.968440  |
| 20            | 6             | 0           | 0.133092    | -0.290484 | -0.800752  |
| 21            | 6             | 0           | -0.089369   | 1.115522  | -0.729223  |
| 22            | 6             | 0           | 0.906069    | 2.097841  | -0.568020  |
| 23            | 6             | 0           | -1.027848   | -1.167631 | -0.690152  |
|   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 24| 6 | 0 | -2.274772 | -0.587619 | -0.842801|
| 25| 6 | 0 | -2.473585 | 0.865935  | -0.939895|
| 26| 6 | 0 | -1.397613 | 1.715984  | -0.825364|
| 27| 6 | 0 | -3.688439 | -1.217033 | -0.706041|
| 28| 6 | 0 | -4.176332 | -0.674744 | 0.658117 |
| 29| 6 | 0 | -4.367475 | 0.692086  | 0.550762 |
| 30| 6 | 0 | -3.995784 | 1.133071  | -0.890540|
| 31| 6 | 0 | -4.947044 | 0.832626  | 2.939539 |
| 32| 6 | 0 | -4.688092 | 1.497403  | 1.698380 |
| 33| 6 | 0 | 5.024403  | 3.919918  | 0.866464 |
| 34| 6 | 0 | 3.618003  | 3.712521  | 0.764945 |
| 35| 6 | 0 | 2.736407  | 4.622912  | 1.379909 |
| 36| 6 | 0 | 3.285497  | 5.771866  | 1.980856 |
| 37| 6 | 0 | 4.661971  | 6.010077  | 1.994672 |
| 38| 6 | 0 | 5.544039  | 5.069768  | 1.451052 |
| 39| 6 | 0 | 3.571310  | -1.601962 | -1.445423|
| 40| 6 | 0 | 2.165699  | -1.837188 | -1.517481|
| 41| 6 | 0 | 4.450650  | -2.434209 | -2.136498|
| 42| 6 | 0 | 3.950180  | -3.543739 | -2.828841|
| 43| 6 | 0 | 2.579129  | -3.794814 | -2.866388|
| 44| 6 | 0 | 1.680065  | -2.929442 | -2.231257|
| 45| 6 | 0 | 0.236393  | 3.397313  | -0.729369|
| 46| 6 | 0 | -1.173864 | 3.178595  | -0.802980|
| 47| 6 | 0 | -2.032965 | 4.271672  | -0.901748|
| 48| 6 | 0 | -1.502629 | 5.562160  | -1.018103|
| 49| 6 | 0 | -0.123352 | 5.760062  | -1.065949|
| 50| 6 | 0 | 0.752165  | 4.678867  | -0.923669|
| 51| 6 | 0 | -4.043032 | -2.581669 | -1.262667|
| 52| 6 | 0 | -4.643440 | 2.284747  | -1.626140|
| 53| 6 | 0 | -5.339397 | 1.622362  | 4.046335 |
| 54| 6 | 0 | -5.420717 | 2.999373  | 3.966658 |
| 55| 6 | 0 | -5.090832 | 3.653241  | 2.767765 |
| 56| 6 | 0 | -4.733869 | 2.912831  | 1.658677 |
| 57| 6 | 0 | -5.929960 | 2.728439  | -1.289585|
| 58| 6 | 0 | -6.592723 | 3.666020  | -2.082463|
| 59| 6 | 0 | -5.992976 | 4.157603  | -3.242036|
| 60| 6 | 0 | -4.729581 | 3.692364  | -3.609212|
| 61| 6 | 0 | -4.067559 | 2.757954  | -2.814351|
| 62| 6 | 0 | -3.528103 | -2.941666 | -2.519338|
| 63| 6 | 0 | -3.956231 | -4.094071 | -3.173725|
| 64| 6 | 0 | -4.933620 | -4.906643 | -2.594513|
| 65| 6 | 0 | -5.491735 | -4.533412 | -1.373707|
| 66| 6 | 0 | -5.063987 | -3.373124 | -0.723397|
| 67| 1 | 0 | 10.261549 | -2.026205 | 0.481135 |
| 68| 1 | 0 | 9.324356  | -4.355478 | 0.698267 |
| 69| 1 | 0 | 6.873936  | -4.693959 | 0.620312 |
| 70| 1 | 0 | 5.335922  | -2.809356 | 0.233567 |
| 71| 1 | 0 | 1.688418  | 4.447994  | 1.411106 |
| 72| 1 | 0 | 2.610707  | 6.482574  | 2.450221 |
| 73| 1 | 0 | 5.052110  | 6.910753  | 2.460494 |
| 74| 1 | 0 | 6.618413  | 5.221646  | 1.516036 |
| 75| 1 | 0 | 5.511738  | -2.218790 | -2.166831|
| 76| 1 | 0 | 4.637201  | -4.195722 | -3.361108|
| 77| 1 | 0 | 2.198527  | -4.646622 | -3.423299|
| 78| 1 | 0 | 0.615998  | -3.093327 | -2.335240|
| 79| 1 | 0 | -3.104724 | 4.138782  | -0.925152|
| 80| 1 | 0 | -2.177956 | 6.408914  | -1.103798|
81 1 0 0.279446 6.758489 -1.212822
82 1 0 1.821172 4.841563 -0.974859
83 1 0 -5.569307 1.147768 2.710065
84 1 0 -5.720200 3.574234 4.838605
85 1 0 -5.115743 4.737768 2.710065
86 1 0 -4.480581 3.423534 0.739911
87 1 0 -6.422965 2.336613 -0.406109
88 1 0 -7.585449 4.002218 -1.795421
89 1 0 -6.510090 4.886345 -3.860295
90 1 0 -4.256914 4.051717 -4.519218
91 1 0 -3.088774 2.397148 -3.115371
92 1 0 -2.785387 -2.304565 -2.992562
93 1 0 -3.536247 -4.349042 -4.143202
94 1 0 -5.270325 -5.807005 -3.101033
95 1 0 -6.25099 -5.137267 -0.923546
96 1 0 -5.542040 -3.085830 0.205646
97 6 0 -0.801714 -2.515135 -0.058513
98 6 0 -0.236783 -2.499203 1.231500
99 6 0 -1.10745 -3.764465 -0.614005
100 6 0 -0.004231 -3.671401 1.946017
101 1 0 0.013865 -1.548044 1.690502
102 6 0 -0.87955 -4.949931 0.086768
103 1 0 -1.524244 -3.832361 -1.608889
104 6 0 -0.332751 -4.894828 1.365306
105 1 0 0.421798 -3.634404 2.942927
106 1 0 -1.122742 -5.906376 -0.363733
107 17 0 -0.049736 -6.385162 2.256497
108 1 0 7.837690 2.983127 0.565842
109 6 0 -4.451265 -0.176438 -1.575363
110 8 0 -5.182308 -0.341115 -2.506459
111 6 0 -4.719667 -0.602953 3.057588
112 6 0 -4.859236 -1.286560 4.289106
113 6 0 -4.255338 -1.346709 1.927036
114 6 0 -4.506161 -2.615231 4.427621
115 1 0 -5.231251 -0.759899 5.160092
116 6 0 -3.850613 -2.692863 2.109742
117 6 0 -3.971577 -3.318290 3.334539
118 1 0 -4.620038 -3.106396 5.390081
119 1 0 -3.425719 -3.236176 1.275863
120 1 0 -3.648481 -4.348886 3.449823

---------------------------------------------------------------------
Supplementary Figure 7. Possible topological isomers of tetracene 33.
**Zero-point correction=** 0.906440 (Hartree/Particle)
**Thermal correction to Gibbs Free Energy=** 0.817421
**Sum of electronic and thermal Free Energies=** -3492.340244

E[SMD(chloroform)/B3LYP-D3BJ/6-31G**/*B3LYP/6-31G*] = -3493.68486378

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|--------------|-------------|-------------------------|
|               |              |             | X          | Y          | Z          |
| 1             | 6            | 0           | -5.048154  | 0.020552   | -0.025014  |
| 2             | 6            | 0           | -4.918194  | -1.149077  | 0.798889   |
| 3             | 6            | 0           | -6.022837  | -1.792643  | 1.450161   |
| 4             | 6            | 0           | -7.300279  | -1.343215  | 1.219336   |
| 5             | 6            | 0           | -7.455123  | -0.321120  | 0.254896   |
| 6             | 6            | 0           | -6.404826  | 0.315967   | -0.410584  |
| 7             | 6            | 0           | -6.991115  | 1.100476   | -1.538764  |
| 8             | 6            | 0           | -8.398786  | 1.061348   | -1.428480  |
| 9             | 6            | 0           | -8.759500  | 0.179841   | -0.278855  |
| 10            | 6            | 0           | -9.233269  | 1.655063   | -2.358893  |
| 11            | 6            | 0           | -8.649718  | 2.295046   | -3.462735  |
| 12            | 6            | 0           | -7.263413  | 2.288780   | -3.615847  |
| 13            | 6            | 0           | -6.421215  | 1.686490   | -2.665313  |
| 14            | 6            | 0           | -9.873700  | -0.104516  | 0.126211   |
| 15            | 6            | 0           | -3.829702  | 0.699011   | -0.259769  |
| 16            | 6            | 0           | -2.60090   | 0.033781   | 0.023805   |
| 17            | 6            | 0           | -2.508229  | -1.303424  | 0.558036   |
| 18            | 6            | 0           | -3.713160  | -1.800995  | 1.123753   |
| 19            | 6            | 0           | -1.483931  | 0.871788   | -0.282538  |
| 20            | 6            | 0           | -0.176388  | 0.365755   | -0.031206  |
| 21            | 6            | 0           | -0.124424  | -1.057414  | 0.164413   |
| 22            | 6            | 0           | -1.227836  | -1.895163  | 0.426146   |
| 23            | 6            | 0           | 1.092732   | 1.039245   | 0.100136   |
| 24            | 6            | 0           | 2.271705   | 0.268347   | 0.166762   |
| 25            | 6            | 0           | 2.268834   | -1.142255  | -0.225881  |
| 26            | 6            | 0           | 1.067600   | -1.826737  | -0.003825  |
| 27            | 6            | 0           | 3.544879   | 0.749143   | 0.712781   |
| 28            | 6            | 0           | 4.707778   | 0.098082   | 0.345876   |
| 29            | 6            | 0           | 4.637132   | -0.878558  | -0.742134  |
| 30            | 6            | 0           | 3.476870   | -1.627827  | -0.873704  |
| 31            | 6            | 0           | 6.034501   | 0.206555   | 0.999959   |
| 32            | 6            | 0           | 7.197951   | -0.106796  | 0.250408   |
| 33 | 6   | 0          |    7.061462 | -0.460055 | -1.171264 |
| 34 | 6   | 0          |    5.804449 | -0.910868 | -1.647530 |
| 35 | 6   | 0          | -5.457797  | -2.844240 |  2.299784 |
| 36 | 6   | 0          | -4.043233  | -2.842756 |  2.117858 |
| 37 | 6   | 0          | -3.249344  | -3.661844 |  2.921686 |
| 38 | 6   | 0          | -3.864457  | -4.513424 |  3.848021 |
| 39 | 6   | 0          | -5.254388  | -4.544177 |  3.986642 |
| 40 | 6   | 0          | -6.060874  | -3.696918 |  3.217357 |
| 41 | 6   | 0          | -3.477995  |  2.047973 | -0.716627 |
| 42 | 6   | 0          | -2.054170  |  2.134323 | -0.807074 |
| 43 | 6   | 0          | -4.268178  |  3.164652 | -0.982969 |
| 44 | 6   | 0          | -3.669882  |  4.331401 | -1.472575 |
| 45 | 6   | 0          | -2.295416  |  4.369677 | -1.699155 |
| 46 | 6   | 0          | -1.483043  |  3.280117 | -1.359160 |
| 47 | 6   | 0          | -0.735719  | -3.277055 |  0.387965 |
| 48 | 6   | 0          |  0.671018  | -3.241585 |  0.141269 |
| 49 | 6   | 0          |  1.395751  | -4.432050 |  0.128421 |
| 50 | 6   | 0          |  0.721987  | -5.651107 |  0.266640 |
| 51 | 6   | 0          | -0.666044  | -5.686915 |  0.406717 |
| 52 | 6   | 0          | -1.402579  | -4.499353 |  0.470187 |
| 53 | 6   | 0          |  3.530604  |  1.796712 |  1.779596 |
| 54 | 6   | 0          |  3.424628  | -2.831704 | -1.750137 |
| 55 | 6   | 0          |  6.180500  |  0.477299 |  2.374798 |
| 56 | 6   | 0          |  7.429339  |  0.484965 |  2.984447 |
| 57 | 6   | 0          |  8.575228  |  0.208346 |  2.235311 |
| 58 | 6   | 0          |  8.451369  | -0.094816 |  0.885466 |
| 59 | 6   | 0          |  8.139563  | -0.361844 | -2.067214 |
| 60 | 6   | 0          |  7.997564  | -0.696872 | -3.407913 |
| 61 | 6   | 0          |  6.754927  | -1.123859 | -3.884895 |
| 62 | 6   | 0          |  5.675787  | -1.221337 | -3.016266 |
| 63 | 6   | 0          |  4.399128  | -3.838222 | -1.627850 |
| 64 | 6   | 0          |  4.373722  | -4.961976 | -2.451059 |
| 65 | 6   | 0          |  3.374818  | -5.101503 | -3.417733 |
| 66 | 6   | 0          |  2.400960  | -4.110312 | -3.549815 |
| 67 | 6   | 0          |  2.423023  | -2.987976 | -2.721974 |
| 68 | 6   | 0          |  4.290638  |  2.970719 |  1.673333 |
| 69 | 6   | 0          |  4.313534  |  3.901296 |  2.710675 |
| 70 | 6   | 0          |  3.584118  |  3.670966 |  3.879306 |
| 71 | 6   | 0          |  2.823430  |  2.506202 |  3.998253 |
| 72 | 6   | 0          |  2.792087  |  1.580808 |  2.955168 |
| 73 | 1   | 0          | -10.311291 |  1.597462 | -2.236926 |
| 74 | 1   | 0          | -9.276439  |  2.770926 | -4.211544 |
| 75 | 1   | 0          | -6.818560  |  2.752283 | -4.492393 |
| 76 | 1   | 0          | -5.349742  |  1.679255 | -2.824103 |
| 77 | 1   | 0          | -2.168408  | -3.639010 |  2.845882 |
| 78 | 1   | 0          | -3.246707  | -5.153226 |  4.472384 |
| 79 | 1   | 0          | -5.711898  | -5.214864 |  4.708670 |
| 80 | 1   | 0          | -7.139733  | -3.695338 |  3.350764 |
| 81 | 1   | 0          | -5.338129  |  3.138523 | -0.817632 |
| 82 | 1   | 0          | -4.284615  |  5.201232 | -1.686894 |
| 83 | 1   | 0          | -1.836802  |  5.261404 | -2.117344 |
| 84 | 1   | 0          | -0.417780  |  3.348737 | -1.524675 |
| 85 | 1   | 0          |  2.469054  | -4.429857 | -0.006020 |
| 86 | 1   | 0          |  1.289425  | -6.577457 |  0.242745 |
| 87 | 1   | 0          | -1.181875  | -6.640851 |  0.475174 |
| 88 | 1   | 0          | -2.479339  | -4.536831 |  0.583210 |
| 89 | 1   | 0          |  5.303808  |  0.657744 |  2.981206 |
Zero-point correction = 0.906522 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.817867
Sum of electronic and thermal Free Energies = -3492.339623

E[SMD(chloroform)/B3LYP-D3BJ/6-31G**]/B3LYP/6-31G* = -3493.68475591

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
| 1             | 6             | 0           | X: -5.042808 Y: 0.118327 Z: -0.094384 |
|   |   |   |   |   |
|---|---|---|---|---|
| 2 | 6 | 0 | -4.927263 | 1.539767 0.066999 |
| 3 | 6 | 0 | -6.058866 | 2.421703 0.110901 |
| 4 | 6 | 0 | -7.329159 | 1.898643 0.124383 |
| 5 | 6 | 0 | -7.446489 | 0.489608 0.156966 |
| 6 | 6 | 0 | -6.371686 | -0.399006 0.090978 |
| 7 | 6 | 0 | -6.888200 | -1.770793 0.373004 |
| 8 | 6 | 0 | -8.295278 | -2.812734 0.475005 |
| 9 | 6 | 0 | -8.717427 | -0.280456 0.324912 |
| 10 | 6 | 0 | -9.068587 | -2.812734 0.775842 |
| 11 | 6 | 0 | -8.418948 | -4.035077 1.005500 |
| 12 | 6 | 0 | -7.026765 | -4.103256 0.953073 |
| 13 | 6 | 0 | -6.246635 | -2.975565 0.644509 |
| 14 | 8 | 0 | -9.849557 | 0.170962 0.356283 |
| 15 | 6 | 0 | -3.840908 | -0.514574 -0.475019 |
| 16 | 6 | 0 | -2.606067 | 0.171832 -0.282289 |
| 17 | 6 | 0 | -2.498770 | 1.545069 0.154880 |
| 18 | 6 | 0 | -3.726677 | 2.273862 0.115972 |
| 19 | 6 | 0 | -1.509022 | -0.683151 -0.619471 |
| 20 | 6 | 0 | -0.193532 | -0.263818 -0.271905 |
| 21 | 6 | 0 | -0.104186 | 1.087403 0.211926 |
| 22 | 6 | 0 | -1.187087 | 1.962226 0.478435 |
| 23 | 6 | 0 | 1.035756 | -1.021851 -0.199353 |
| 24 | 6 | 0 | 2.241860 | -0.363352 0.120385 |
| 25 | 6 | 0 | 2.321904 | 1.094655 0.119829 |
| 26 | 6 | 0 | 1.131664 | 1.766023 0.417501 |
| 27 | 6 | 0 | 3.461387 | -1.036473 0.584070 |
| 28 | 6 | 0 | 4.670234 | -0.374477 0.465480 |
| 29 | 6 | 0 | 4.708897 | 0.871534 -0.301826 |
| 30 | 6 | 0 | 3.586051 | 1.686567 -0.274221 |
| 31 | 6 | 0 | 5.951394 | -0.735154 1.120486 |
| 32 | 6 | 0 | 7.170087 | -0.291354 0.547544 |
| 33 | 6 | 0 | 7.136296 | 0.462112 -0.715328 |
| 34 | 6 | 0 | 5.931693 | 1.105201 -1.095677 |
| 35 | 6 | 0 | -5.528410 | 3.785692 0.070127 |
| 36 | 6 | 0 | -4.104214 | 3.702434 0.032001 |
| 37 | 6 | 0 | -3.365165 | 4.863187 -0.203179 |
| 38 | 6 | 0 | -4.030202 | 6.090895 -0.313910 |
| 39 | 6 | 0 | -5.420681 | 6.170589 -0.208936 |
| 40 | 6 | 0 | -6.181072 | 5.009027 -0.310140 |
| 41 | 6 | 0 | -3.529597 | -1.750726 -1.195573 |
| 42 | 6 | 0 | -2.109632 | -1.849151 -1.314756 |
| 43 | 6 | 0 | -4.366716 | -2.618412 -1.895712 |
| 44 | 6 | 0 | -3.806108 | -3.613054 -2.703584 |
| 45 | 6 | 0 | -2.422210 | -3.702039 -2.840945 |
| 46 | 6 | 0 | -1.573495 | -2.815127 -2.166159 |
| 47 | 6 | 0 | -0.613069 | 3.155587 1.115514 |
| 48 | 6 | 0 | 0.807940 | 3.070896 1.015630 |
| 49 | 6 | 0 | 1.609551 | 4.028526 1.635259 |
| 50 | 6 | 0 | 1.007240 | 5.062891 2.358963 |
| 51 | 6 | 0 | -0.380886 | 5.117907 2.499783 |
| 52 | 6 | 0 | -1.196385 | 4.156780 1.893475 |
| 53 | 6 | 0 | 3.344107 | -2.323335 1.337426 |
| 54 | 6 | 0 | 3.630972 | 3.102568 -0.737811 |
| 55 | 6 | 0 | 6.006068 | -1.384112 2.373623 |
| 56 | 6 | 0 | 7.215198 | -1.631938 3.012352 |
| 57 | 6 | 0 | 8.414197 | -1.225614 2.422980 |
| 58 | 6 | 0 | 8.382389 | -0.552221 1.208757 |
| 59 | 6 | 0 | 8.263312 | 0.567914 -1.548020 |
| 60 | 6 | 0 | 8.220249 | 1.291964 -2.732770 |
| 61 | 6 | 0 | 7.030170 | 1.916429 -3.117674 |
|   |   |   |                  |                  |                  |
|---|---|---|-----------------|-----------------|-----------------|
| 62| 6 | 0 | 5.903397        | 1.816290        | -2.312375       |
| 63| 6 | 0 | 4.619950        | 3.974503        | -0.249291       |
| 64| 6 | 0 | 4.682258        | 5.298404        | -0.678940       |
| 65| 6 | 0 | 3.759660        | 5.778088        | -1.611604       |
| 66| 6 | 0 | 2.773412        | 4.923261        | -2.106543       |
| 67| 6 | 0 | 2.706488        | 3.599980        | -1.671063       |
| 68| 6 | 0 | 2.576126        | -2.367785       | 2.513149        |
| 69| 6 | 0 | 2.517755        | -3.528608       | 3.284238        |
| 70| 6 | 0 | 3.215682        | -4.670345       | 2.885539        |
| 71| 6 | 0 | 3.972524        | -4.641020       | 1.712124        |
| 72| 6 | 0 | 4.040124        | -3.476300       | 0.948578        |
| 73| 1 | 0 | -10.148552      | -2.718564       | 0.847650        |
| 74| 1 | 0 | -8.997018       | -4.923300       | 1.243941        |
| 75| 1 | 0 | -6.528130       | -5.046447       | 1.160051        |
| 76| 1 | 0 | -5.166405       | -3.056565       | 0.625505        |
| 77| 1 | 0 | -2.887009       | 4.826061        | -0.314636       |
| 78| 1 | 0 | -3.450799       | 6.992636        | -0.492804       |
| 79| 1 | 0 | -5.916923       | 7.133587        | -0.291608       |
| 80| 1 | 0 | -7.266282       | 5.062557        | 0.003569        |
| 81| 1 | 0 | -5.443369       | -2.505858       | 1.848853        |
| 82| 1 | 0 | -4.455026       | -4.291459       | -3.250440       |
| 83| 1 | 0 | -1.988043       | -4.453178       | -3.495010       |
| 84| 1 | 0 | -0.509548       | -2.879621       | -2.341781       |
| 85| 1 | 0 | 2.689342        | 3.967992        | 1.581570        |
| 86| 1 | 0 | 1.631070        | 5.810957        | 2.840633        |
| 87| 1 | 0 | -0.834955       | 5.901324        | 3.100482        |
| 88| 1 | 0 | -2.267854       | 4.183227        | 2.050127        |
| 89| 1 | 0 | 5.089847        | -1.674193       | 2.867869        |
| 90| 1 | 0 | 7.217591        | -2.125511       | 3.980273        |
| 91| 1 | 0 | 9.363504        | -1.407249       | 2.919484        |
| 92| 1 | 0 | 9.311287        | -0.186863       | 0.783212        |
| 93| 1 | 0 | 9.177793        | 0.049360        | -1.279049       |
| 94| 1 | 0 | 9.102782        | 1.352724        | -3.363758       |
| 95| 1 | 0 | 6.974671        | 2.463354        | -4.054786       |
| 96| 1 | 0 | 4.979340        | 2.274114        | -2.641223       |
| 97| 1 | 0 | 5.339571        | 3.604751        | 0.475412        |
| 98| 1 | 0 | 5.451237        | 5.956869        | -0.283628       |
| 99| 1 | 0 | 3.807765        | 6.810329        | -1.947649       |
| 100|1 | 0 | 5.251907        | 5.286245        | -2.833672       |
| 101|1 | 0 | 1.937243        | 2.942059        | -2.063775       |
| 102|1 | 0 | 2.037107        | -1.478977       | 2.829564        |
| 103|1 | 0 | 1.928355        | -3.539892       | 4.197569        |
| 104|1 | 0 | 3.168765        | -5.576906       | 3.482899        |
| 105|1 | 0 | 4.513349        | -5.527050       | 1.390636        |
| 106|1 | 0 | 4.637590        | -3.455759       | 0.042331        |
| 107|1 | 0 | 1.065820        | -2.484344       | -0.474523       |
| 108|1 | 0 | 0.321422        | -3.404889       | 0.276500        |
| 109|1 | 0 | 1.852010        | -2.969389       | -1.532658       |
| 110|1 | 0 | 0.361303        | -4.766932       | -0.009778       |
| 111|1 | 0 | -0.287087       | -3.053555       | 1.103402        |
| 112|1 | 0 | 1.889493        | -4.327714       | -1.844186       |
| 113|1 | 0 | 2.431980        | -2.269988       | -2.127653       |
| 114|1 | 0 | 1.142192        | -5.217075       | -1.073804       |
| 115|1 | 0 | -0.209819       | -5.473676       | 0.582458        |
| 116|1 | 0 | 2.489100        | -4.692170       | -2.670358       |
| 117|1 | 0 | 1.186681        | -6.935704       | -1.448065       |
| 118|1 | 0 | -8.227901       | 2.508332        | 0.155544        |
Zero-point correction=                           0.906539 (Hartree/Particle)
Thermal correction to Gibbs Free Energy=         0.817806
Sum of electronic and thermal Free Energies=      -3492.323772

E[SMD(chloroform)/B3LYP-D3BJ/6-31G***/B3LYP/6-31G*] = -3493.67071520

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
|               |               |             | X           | Y           | Z             |
| 1             | 6             | 0           | -5.082874    | 0.093378    | -0.142181     |
| 2             | 6             | 0           | -4.975969    | -1.293110   | -0.501977     |
| 3             | 6             | 0           | -6.104762    | -2.134696   | -0.780729     |
| 4             | 6             | 0           | -7.365740    | -1.593471   | -0.803277     |
| 5             | 6             | 0           | -7.496197    | -0.272176   | -0.321339     |
| 6             | 6             | 0           | -6.438087    | 0.524857    | 0.121734      |
| 7             | 6             | 0           | -7.032699    | 1.614677    | 0.961444      |
| 8             | 6             | 0           | -8.437244    | 1.588544    | 0.805319      |
| 9             | 6             | 0           | -8.796389    | 0.407852    | -0.030130     |
| 10            | 6             | 0           | -9.281626    | 2.438125    | 1.498431      |
| 11            | 6             | 0           | -8.716533    | 3.334859    | 2.416967      |
| 12            | 6             | 0           | -7.340490    | 3.316890    | 2.641598      |
| 13            | 6             | 0           | -6.488871    | 2.454596    | 1.929672      |
| 14            | 6             | 0           | -9.906465    | 0.035900    | -0.370113     |
| 15            | 6             | 0           | -3.850337    | 0.776966    | -0.053280     |
| 16            | 6             | 0           | -2.619076    | 0.058420    | -0.176858     |
| 17            | 6             | 0           | -2.536753    | -1.343236   | -0.527494     |
| 18            | 6             | 0           | -3.781244    | -2.038825   | -0.589599     |
| 19            | 6             | 0           | -1.504254    | 0.928911    | 0.073901      |
| 20            | 6             | 0           | -0.182009    | 0.415983    | -0.092938     |
| 21            | 6             | 0           | -0.127768    | -0.979496   | -0.439140     |
| 22            | 6             | 0           | -1.223431    | -1.815192   | -0.769277     |
| 23            | 6             | 0           | 1.107884     | 1.082093    | -0.103973     |
| 24            | 6             | 0           | 2.292016     | 0.318940    | -0.182091     |
| 25            | 6             | 0           | 2.260301     | -1.132361   | -0.041229     |
| 26            | 6             | 0           | 1.075144     | -1.742916   | -0.452807     |
| 27            | 6             | 0           | 3.621162     | 0.852687    | -0.518925     |
| 28            | 6             | 0           | 4.739423     | 0.131804    | -0.140550     |
| 29            | 6             | 0           | 4.561845     | -1.032882   | 0.730049      |
| 30            | 6             | 0           | 3.398999     | -1.774483   | 0.583354      |
| 31            | 6             | 0           | 6.135762     | 0.342870    | -0.604103     |
| 32            | 6             | 0           | 7.206014     | -0.100219   | 0.216605      |
| 33 | 6 | 0 | 6.909102 | -0.721187 | 1.516749 |
| 34 | 6 | 0 | 5.617772 | -1.263203 | 1.734522 |
| 35 | 6 | 0 | -5.600161 | -3.500070 | -0.903622 |
| 36 | 6 | 0 | -4.190526 | -3.461157 | -0.692428 |
| 37 | 6 | 0 | -3.518016 | -4.662024 | -0.457053 |
| 38 | 6 | 0 | -4.211953 | -5.874050 | -0.563287 |
| 39 | 6 | 0 | -5.573017 | -5.902345 | -0.875244 |
| 40 | 6 | 0 | -6.282245 | -4.705813 | -1.025550 |
| 41 | 6 | 0 | -3.497516 | 2.178123 | 0.164688 |
| 42 | 6 | 0 | -2.092028 | 2.252530 | 0.404440 |
| 43 | 6 | 0 | -4.268573 | 3.338092 | 0.113439 |
| 44 | 6 | 0 | -3.702459 | 4.557342 | 0.499031 |
| 45 | 6 | 0 | -2.385586 | 4.594040 | 0.952264 |
| 46 | 6 | 0 | -1.576326 | 3.451606 | 0.898815 |
| 47 | 6 | 0 | -0.645254 | -3.051420 | -1.323962 |
| 48 | 6 | 0 | 0.751075 | -3.051793 | -1.034476 |
| 49 | 6 | 0 | 1.572553 | -4.066295 | -1.523163 |
| 50 | 6 | 0 | 1.017347 | -5.066486 | -2.327978 |
| 51 | 6 | 0 | -0.332945 | -5.023971 | -2.680243 |
| 52 | 6 | 0 | -1.165717 | -4.009464 | -2.195013 |
| 53 | 6 | 0 | 3.732141 | 2.037844 | -1.425331 |
| 54 | 6 | 0 | 3.261335 | -3.149239 | 1.142834 |
| 55 | 6 | 0 | 6.446446 | 0.845292 | -1.883377 |
| 56 | 6 | 0 | 7.760541 | 0.958985 | -2.321658 |
| 57 | 6 | 0 | 8.116388 | 0.560959 | -1.493209 |
| 58 | 6 | 0 | 8.527830 | 0.025519 | -0.243691 |
| 59 | 6 | 0 | 7.869846 | -0.805283 | 2.538588 |
| 60 | 6 | 0 | 7.581278 | -1.416174 | 3.752483 |
| 61 | 6 | 0 | 6.306490 | -1.945766 | 3.973405 |
| 62 | 6 | 0 | 5.339835 | -1.861670 | 2.980060 |
| 63 | 6 | 0 | 4.244252 | -4.118786 | 0.877306 |
| 64 | 6 | 0 | 4.138337 | -5.406635 | 1.398698 |
| 65 | 6 | 0 | 3.048987 | -5.751450 | 2.202000 |
| 66 | 6 | 0 | 2.065840 | -4.798823 | 2.474812 |
| 67 | 6 | 0 | 2.168017 | -3.511882 | 1.947252 |
| 68 | 6 | 0 | 3.181467 | 1.968879 | -2.716275 |
| 69 | 6 | 0 | 3.354112 | 3.014583 | -3.623034 |
| 70 | 6 | 0 | 4.069296 | 4.154315 | -3.249691 |
| 71 | 6 | 0 | 4.611010 | 4.238174 | -1.965095 |
| 72 | 6 | 0 | 4.448632 | 3.187235 | -1.063581 |
| 73 | 1 | 0 | -10.355733 | 2.376455 | 1.347314 |
| 74 | 1 | 0 | -9.350843 | 4.015290 | 2.977848 |
| 75 | 1 | 0 | -6.909868 | 3.976883 | 3.389985 |
| 76 | 1 | 0 | -5.429538 | 2.448629 | 2.150676 |
| 77 | 1 | 0 | -2.472141 | -4.671482 | -0.180627 |
| 78 | 1 | 0 | -3.678694 | -6.805023 | -0.390747 |
| 79 | 1 | 0 | -6.091391 | -6.853319 | -0.961247 |
| 80 | 1 | 0 | -7.355612 | -4.719701 | -1.196682 |
| 81 | 1 | 0 | -5.302302 | 3.300106 | -0.206079 |
| 82 | 1 | 0 | -4.301480 | 5.463353 | 0.473094 |
| 83 | 1 | 0 | -1.959176 | 5.239282 | 1.318114 |
| 84 | 1 | 0 | -0.558236 | 3.524210 | 1.245055 |
| 85 | 1 | 0 | 2.634921 | -4.070359 | -1.311020 |
| 86 | 1 | 0 | 1.653700 | -5.858994 | -2.712334 |
| 87 | 1 | 0 | -0.742491 | -5.773496 | -3.351974 |
| 88 | 1 | 0 | -2.198429 | -3.963779 | -2.516685 |
| 89 | 1 | 0 | 5.650259 | 1.125015 | -2.558208 |
|   |   |   |          |          |          |
|---|---|---|----------|----------|----------|
| 90| 1 | 0 | 7.960318 | 1.341666 | -3.318714 |
| 91| 1 | 0 | 9.841641 | 0.639414 | -1.830288 |
| 92| 1 | 0 | 9.343711 | -0.339307 | 0.371629  |
| 93| 1 | 0 | 8.847985 | -0.359285 | 2.391254  |
| 94| 1 | 0 | 8.338845 | -1.462196 | 4.530080  |
| 95| 1 | 0 | 6.059385 | -2.403829 | 4.927085  |
| 96| 1 | 0 | 4.345740 | -2.240632 | 3.179678  |
| 97| 1 | 0 | 5.093517 | -3.853527 | 0.254238  |
| 98| 1 | 0 | 4.906604 | -6.142319 | 1.175813  |
| 99| 1 | 0 | 2.965944 | -6.755319 | 2.609594  |
|100| 1 | 0 | 1.215442 | -5.056578 | 3.100463  |
|101| 1 | 0 | 1.400408 | -2.776699 | 2.168787  |
|102| 1 | 0 | 2.630826 | 1.079844 | -3.012124 |
|103| 1 | 0 | 2.931257 | 2.937631 | -4.621511 |
|104| 1 | 0 | 4.202827 | 4.971642 | -3.953285 |
|105| 1 | 0 | 5.163742 | 5.124094 | -1.664248 |
|106| 1 | 0 | 4.881813 | 3.252342 | -0.070276 |
|107| 6 | 0 | 1.241517 | 2.563525 | -0.024087 |
|108| 6 | 0 | 1.868886 | 3.140061 | 1.091002  |
|109| 6 | 0 | 0.771804 | 3.410415 | -1.037562 |
|110| 6 | 0 | 2.014869 | 4.522532 | 1.204288  |
|111| 6 | 0 | 2.236487 | 2.497674 | 1.885830  |
|112| 6 | 0 | 0.928395 | 4.791289 | -0.950852 |
|113| 6 | 0 | 0.286784 | 2.983945 | -1.909455 |
|114| 6 | 0 | 1.544813 | 5.336539 | 0.175116  |
|115| 6 | 0 | 2.490567 | 4.961989 | 2.074769  |
|116| 6 | 0 | 0.571570 | 5.439656 | -1.743653 |
|117| 17| 0  | 1.734440 | 7.082093 | 0.298126  |
|118| 1 | 0 | -8.258152 | -2.154388 | -1.066403 |

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### Zero-point correction

Zero-point correction = 0.906469 (Hartree/Particle)

### Thermal correction to Gibbs Free Energy

Thermal correction to Gibbs Free Energy = 0.817405

### Sum of electronic and thermal Free Energies

Sum of electronic and thermal Free Energies = -3492.337656

### E[SMD(chloroform)/B3LYP-D3BJ/6-31G**//B3LYP/6-31G*] = -3493.6815442

| Center Number | Atomic Number | Atomic Type | X        | Y        | Z        |
|---------------|---------------|-------------|----------|----------|----------|
| 1             | 6             | 0           | 5.011439 | 0.269724 | -0.276037|
| 2             | 6             | 0           | 4.866903 | 1.567162 | 0.328231 |
| 3             | 6             | 0           | 5.974543 | 2.389392 | 0.722067 |
| 4             | 6             | 0           | 7.257081 | 1.973142 | 0.460115 |
| 5             | 6             | 0           | 7.415010 | 0.657827 | -0.028302|
| 6             | 6             | 0           | 6.366457 | -0.224617| -0.300356|
| 7             | 6             | 0           | 6.955604 | -1.595530| -0.419309|
| 8             | 6             | 0           | 8.364220 | -1.480430| -0.416280|
| 9             | 6             | 0           | 8.722090 | -0.051015| -0.186667|
| 10            | 6             | 0           | 9.202481 | -2.580233| -0.463652|
| 11            | 6             | 0           | 8.623704 | -3.857829| -0.486198|
| 12            | 6             | 0           | 7.237229 | -3.989846| -0.420576|
| 13            | 6             | 0           | 6.391659 | -2.867815| -0.376584|
| 14            | 8             | 0           | 9.834926 | 0.439993 | -0.103314|
| 15            | 6             | 0           | 3.800221 | -0.326200| -0.690743|
| 16            | 6             | 0           | 2.562032 | 0.287644 | -0.329521|
| 17            | 6             | 0           | 2.429714 | 1.612319 | 0.230881 |
| 18            | 6             | 0           | 3.649975 | 2.215812 | 0.639982 |
| 19            | 6             | 0           | 1.475328 | -0.578485| -0.652057|
| 20            | 6             | 0           | 0.172423 | -0.195837| -0.242707|
| 21            | 6             | 0           | 0.037665 | 1.204456 | 0.037104 |
| 22            | 6             | 0           | 1.099413 | 2.120299 | 0.194097 |
| 23            | 6             | 0           | -1.012068| -0.989371| -0.048944|
| 24            | 6             | 0           | -2.235357| -0.330063| 0.187621 |
| 25            | 6             | 0           | -2.384091| 1.095340 | -0.121758|
| 26            | 6             | 0           | -1.225714| 1.873780 | 0.007225 |
| 27            | 6             | 0           | -3.396196| -0.950910| 0.828144 |
| 28            | 6             | 0           | -4.639447| -0.377293| 0.636719 |
| 29            | 6             | 0           | -4.769558| 0.652287 | -0.394889|
| 30            | 6             | 0           | -3.692823| 1.498086 | -0.617719|
| 31            | 6             | 0           | -5.865624| -0.626417| 1.430984 |
| 32            | 6             | 0           | -7.130241| -0.367834| 0.842267 |
| Row | Num | Cycles | Data  | Data  | Data  |
|-----|-----|--------|-------|-------|-------|
| 33  | 6   | 0      | -7.190677 | 0.060848 | -0.563849 |
| 34  | 6   | 0      | -6.035369  | 0.628219 | -1.158953 |
| 35  | 6   | 0      | 5.421582   | 3.548869 | 1.421648  |
| 36  | 6   | 0      | 4.003088   | 3.412003 | 1.435166  |
| 37  | 6   | 0      | 3.248943   | 4.258329 | 2.249942  |
| 38  | 6   | 0      | 3.890746   | 5.286931 | 2.950649  |
| 39  | 6   | 0      | 5.273869   | 5.463444 | 2.863461  |
| 40  | 6   | 0      | 4.052117   | 4.580956 | 2.108398  |
| 41  | 6   | 0      | 3.453425   | -1.482658| -1.529879 |
| 42  | 6   | 0      | 2.039222   | -1.670555| -1.467979 |
| 43  | 6   | 0      | 4.213933   | -2.200628| -2.451982 |
| 44  | 6   | 0      | 3.951118   | -3.166780| -3.253836 |
| 45  | 6   | 0      | 2.221313   | -3.385446| -3.159154 |
| 46  | 6   | 0      | 1.435769   | -2.628040| -2.281819 |
| 47  | 6   | 0      | 0.496951   | 3.461093 | 0.183468  |
| 48  | 6   | 0      | -0.923858  | 3.314097 | 0.118166  |
| 49  | 6   | 0      | -1.735682  | 4.444872 | 0.189997  |
| 50  | 6   | 0      | -1.150780  | 5.715965 | 0.209035  |
| 51  | 6   | 0      | 0.234891   | 5.860416 | 0.127067  |
| 52  | 6   | 0      | 1.064833   | 4.734514 | 0.127067  |
| 53  | 6   | 0      | -3.183152  | -2.070315| 1.795371  |
| 54  | 6   | 0      | -3.323546  | 2.726054 | -1.450297 |
| 55  | 6   | 0      | -5.823334  | -0.976781| 2.794804  |
| 56  | 6   | 0      | -6.985138  | -1.112522| 3.545045  |
| 57  | 6   | 0      | -8.230224  | -0.887818| 2.952856  |
| 58  | 6   | 0      | -8.293355  | -0.508627| 1.618065  |
| 59  | 6   | 0      | -8.358881  | -0.081911| -1.331732 |
| 60  | 6   | 0      | -8.403436  | 0.318970 | -2.661015 |
| 61  | 6   | 0      | -7.260021  | 0.858273 | -3.257351 |
| 62  | 6   | 0      | -6.094334  | 1.002879 | -2.516348 |
| 63  | 6   | 0      | -4.856998  | 3.651988 | -1.185111 |
| 64  | 6   | 0      | -5.007456  | 4.794575 | -1.968118 |
| 65  | 6   | 0      | -4.140145  | 5.032183 | -3.037387 |
| 66  | 6   | 0      | -3.120104  | 4.120118 | -3.313005 |
| 67  | 6   | 0      | -2.964806  | 2.980128 | -2.524677 |
| 68  | 6   | 0      | -3.884629  | -3.280265| 1.685442  |
| 69  | 6   | 0      | -3.719534  | -4.288990| 2.632882  |
| 70  | 6   | 0      | -2.856075  | -4.103632| 3.714921  |
| 71  | 6   | 0      | -2.151591  | -2.904419| 3.836470  |
| 72  | 6   | 0      | -2.309004  | -1.899791| 2.881804  |
| 73  | 1   | 0      | 10.279979  | -2.441496| -0.454833 |
| 74  | 1   | 0      | 9.253189   | -4.742307| -0.523295 |
| 75  | 1   | 0      | 6.793263   | -4.981490| -0.394851 |
| 76  | 1   | 0      | 5.321236   | -3.008900| -0.300580 |
| 77  | 1   | 0      | 2.179232   | 4.124629 | 2.354850  |
| 78  | 1   | 0      | 3.300248   | 5.950308 | 3.576759  |
| 79  | 1   | 0      | 5.751790   | 6.273464 | 3.410278  |
| 80  | 1   | 0      | 7.134228   | 4.681995 | 2.086323  |
| 81  | 1   | 0      | 5.271989   | -2.001599| -2.572432 |
| 82  | 1   | 0      | 4.189294   | -3.731112| -3.967214 |
| 83  | 1   | 0      | 1.744535   | -4.128208| -3.792808 |
| 84  | 1   | 0      | 0.363838   | -2.772764| -2.269247 |
| 85  | 1   | 0      | -2.813399  | 4.356340 | 0.206203  |
| 86  | 1   | 0      | -1.788676  | 6.594628 | 0.249652  |
| 87  | 1   | 0      | 0.678604   | 6.851614 | 0.099968  |
| 88  | 1   | 0      | 2.138497   | 4.860175 | 0.071261  |
| 89  | 1   | 0      | -4.868265  | -1.117959| 3.281851  |
|    |     | 0  | -6.916044 | -1.374671 | 4.597162 |
|---|-----|----|-----------|-----------|----------|
| 91| 1   | 0  | -9.143050 | -0.981761 | 3.534756 |
| 92| 1   | 0  | -9.259192 | -0.282092 | 1.178166 |
| 93| 1   | 0  | -9.235191 | -0.545165 | -0.890145|
| 94| 1   | 0  | -9.316216 | 0.190649  | -3.236247|
| 95| 1   | 0  | -7.270593 | 1.147710  | -4.304499|
| 96| 1   | 0  | -5.207753 | 1.389386  | -3.002073|
| 97| 1   | 0  | -5.532088 | 3.470318  | -0.354000|
| 98| 1   | 0  | -5.801977 | 5.501035  | -1.742575|
| 99| 1   | 0  | -4.257026 | 5.922870  | -3.648786|
|100|1   | 0  | -2.440005 | 4.296750  | -4.141937|
|101|1   | 0  | -2.167685 | 2.276495  | -2.744599|
|102|1   | 0  | -4.562866 | -3.425842 | 0.850093 |
|103|1   | 0  | -4.266423 | -5.221967 | 2.526110 |
|104|1   | 0  | -2.731573 | -4.889031 | 4.455524 |
|105|1   | 0  | -1.479352 | -2.748753 | 4.676341 |
|106|1   | 0  | -1.763206 | -0.965803 | 2.983554 |
|107|6   | 0  | -0.948031 | -2.472894 | -0.102159|
|108|6   | 0  | -1.810551 | -3.180231 | -0.957376|
|109|6   | 0  | -0.010451 | -3.203599 | 0.643985 |
|110|6   | 0  | -1.738256 | -4.566500 | -1.075855|
|111|1   | 0  | -2.537550 | -2.632788 | -1.549966|
|112|6   | 0  | 0.065984  | -4.590434 | 0.547157 |
|113|1   | 0  | 0.660847  | -2.681626 | 1.318160 |
|114|6   | 0  | -0.797287 | -5.261895 | -0.317810|
|115|1   | 0  | -2.401290 | -5.101373 | -1.747709|
|116|1   | 0  | 0.788259  | -5.146767 | 1.134851 |
|117|17  | 0   | -0.698224 | -7.012534 | -0.454223|
|118|1   | 0  | 8.139359  | 2.565605  | 0.685922 |
IV. UV & FL data

Supplementary Figure 8. UV-Vis absorption of tetracenes 31, 32, and hexacene 33.

Supplementary Figure 9. UV-Vis absorption of spiroxanthene 28.
Supplementary Figure 10. Fluorescence spectra of spiroxanthene 28.
V. X-ray data for 25k, 28, and 32-H.

Data for 25k (CCDC deposition number: 1818244)

Structure description

The structure with the molecular formula is the one suggested. Solvent of crystallization is found in two different locations, as shown in a figure below. Toluene is found disordered on an inversion center for the first and disordered on a general position near an inversion center for the second. Therefore, there are 1.5 molecules of toluene per asymmetric unit. Reasonable restraints and necessary constraints were included to refine the toluene portion.

Crystal data and structure refinement for 25k.

| Property                        | Value                  |
|---------------------------------|------------------------|
| Empirical formula               | C_{62.50}H_{46}OSi     |
| Formula weight                  | 841.08                 |
| Temperature                     | 100(2) K               |
| Wavelength                      | 0.71073 Å              |
| Crystal system                  | Triclinic              |
| Space group                     | P-1                    |
| Unit cell dimensions            |                        |
| a                               | 12.4695(8) Å           |
| b                               | 14.0287(11) Å          |
| c                               | 14.0414(10) Å          |
| Volume                          | 2157.3(3) Å³           |
| Z                               | 2                      |
| Density (calculated)            | 1.295 Mg/m³            |
| Absorption coefficient          | 0.101 mm⁻¹             |
| F(000)                          | 886                    |
| Crystal color, morphology       | Orange, Block          |
| Crystal size                    | 0.190 x 0.100 x 0.050 mm³ |
| Theta range for data collection | 2.228 to 28.328°       |
| Index ranges                    | -15 ≤ h ≤ 16, -18 ≤ k ≤ 18, -18 ≤ l ≤ 18 |
| Reflections collected           | 41477                  |
| Independent reflections         | 10719 [R(int) = 0.0314] |
| Observed reflections            | 8864                   |
| Completeness to theta = 25.242° | 99.9%                  |
Absorption correction                        Multi-scan
Max. and min. transmission                  0.8621 and 0.8270
Refinement method                           Full-matrix least-squares on $F^2$
Data / restraints / parameters              10719 / 234 / 671
Goodness-of-fit on $F^2$                     1.036
Final $R$ indices [$I>2\sigma(I)$]           $R_1 = 0.0437$, $wR_2 = 0.1098$
$R$ indices (all data)                      $R_1 = 0.0559$, $wR_2 = 0.1193$
Largest diff. peak and hole                  0.593 and -0.359 eÅ$^{-3}$

Atomic coordinates (x $10^4$) and equivalent isotropic displacement parameters (Å$^2x 10^3$) for 25k. $U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

|     | x      | y      | z      | $U_{eq}$ |
|-----|--------|--------|--------|----------|
| Si1 | 5694(1)| 9835(1)| 7713(1)| 17(1)    |
| O1  | 7634(1)| 7732(1)| 7959(1)| 21(1)    |
| C1  | 6104(2)| 9177(1)| 9065(1)| 36(1)    |
| C2  | 6829(1)|10414(1)| 6831(1)| 26(1)    |
| C3  | 4394(1)|10904(1)| 7864(1)| 28(1)    |
| C4  | 5280(1)| 8888(1)| 7252(1)| 15(1)    |
| C5  | 5796(1)| 7772(1)| 7576(1)| 14(1)    |
| C6  | 6997(1)| 7288(1)| 7843(1)| 15(1)    |
| C7  | 7283(1)| 6176(1)| 7858(1)| 15(1)    |
| C8  | 8336(1)| 5455(1)| 7915(1)| 19(1)    |
| C9  | 8439(1)| 4481(1)| 7811(1)| 22(1)    |
| C10 | 7492(1)| 4270(1)| 7638(1)| 21(1)    |
| C11 | 6428(1)| 5010(1)| 7563(1)| 17(1)    |
| C12 | 6316(1)| 5974(1)| 7684(1)| 14(1)    |
| C13 | 5363(1)| 6976(1)| 7531(1)| 13(1)    |
| C14 | 4232(1)| 7273(1)| 7240(1)| 14(1)    |
| C15 | 3841(1)| 8376(1)| 6738(1)| 15(1)    |
| C16 | 4363(1)| 9168(1)| 6683(1)| 15(1)    |
| C17 | 3700(1)|10184(1)| 6001(1)| 16(1)    |
| C18 | 3928(1)|11172(1)| 5538(1)| 18(1)    |
| C19 | 3171(1)|12001(1)| 4883(1)| 21(1)    |
| C20 | 2206(1)|11842(1)| 4683(1)| 21(1)    |
| C21 | 2002(1)|10839(1)| 5094(1)| 20(1)    |
| C22 | 2755(1)|10002(1)| 5743(1)| 16(1)    |
| C23 | 2822(1)| 8853(1)| 6238(1)| 15(1)    |
| C24 | 2130(1)| 8225(1)| 6345(1)| 16(1)    |
| C25 | 2409(1)| 7122(1)| 6981(1)| 15(1)    |
| C26 | 3458(1)| 6628(1)| 7384(1)| 14(1)    |
| C27 | 997(1) | 8612(1)| 5892(1)| 19(1)    |
| C28 | 1016(1)| 7835(1)| 5369(1)| 18(1)    |
| C29 | 1194(1)| 6785(1)| 6039(1)| 16(1)    |
| C30 | 1371(1)| 6642(1)| 7135(1)| 16(1)    |
| C31 | 141(1) | 8438(1)| 6832(1)| 21(1)    |
| C32 | 344(1) | 7445(1)| 7466(1)| 20(1)    |
| C33 | 856(1) | 8089(1)| 4347(1)| 22(1)    |
| C34 | 846(1) | 7274(1)| 4007(1)| 24(1)    |
| C35 | 998(1) | 6237(1)| 4676(1)| 21(1)    |
| C36 | 1191(1)| 5964(1)| 5713(1)| 17(1)    |
| C37 | 1352(1)| 4871(1)| 6456(1)| 17(1)    |
| C38 | 1434(1)| 4010(1)| 6162(1)| 21(1)    |
| C39 | 1540(1)| 2980(1)| 6884(1)| 23(1)    |
| C40 | 1542(1)| 2806(1)| 7909(1)| 22(1)    |
| C41 | 1469(1) | 3655(1) | 8255(1) | 19(1) |
| C42 | 1485(1) | 3480(1) | 9312(1) | 23(1) |
| C43 | 1438(1) | 4296(1) | 9636(1) | 23(1) |
| C44 | 1394(1) | 5320(1) | 8918(1) | 20(1) |
| C45 | 1402(1) | 5531(1) | 7877(1) | 17(1) |
| C46 | 1402(1) | 4698(1) | 7523(1) | 16(1) |
| C47 | 3806(1) | 5471(1) | 7969(1) | 14(1) |
| C48 | 3891(1) | 4739(1) | 7488(1) | 17(1) |
| C49 | 4290(1) | 3655(1) | 7996(1) | 23(1) |
| C50 | 4607(1) | 3292(1) | 8991(1) | 28(1) |
| C51 | 4495(1) | 4009(1) | 9489(1) | 25(1) |
| C52 | 4100(1) | 5097(1) | 8981(1) | 19(1) |
| C53 | 1521(3) | 8629(3) | 9246(2) | 33(1) |
| C54 | 461(4) | 8498(4) | 9698(4) | 30(1) |
| C55 | -508(4) | 9261(3) | 9340(3) | 37(1) |
| C56 | -437(3) | 10177(3) | 8487(3) | 36(1) |
| C57 | -562(4) | 10307(3) | 8033(3) | 37(1) |
| C58 | 1571(4) | 9545(4) | 8408(3) | 30(1) |
| C59 | 2582(4) | 7802(4) | 9678(4) | 53(1) |
| C59' | 205(4) | 9212(5) | 9109(4) | 50(1) |
| C54' | 765(6) | 8221(7) | 9737(8) | 63(2) |
| C55' | 1952(5) | 7898(5) | 9712(4) | 51(1) |
| C56' | 2568(4) | 8579(4) | 9056(3) | 43(1) |
| C57' | 2006(5) | 9546(6) | 8437(5) | 43(1) |
| C58' | 832(5) | 9891(6) | 8448(5) | 51(1) |
| C59' | -1086(5) | 9575(5) | 9113(5) | 61(2) |
| C60 | 5044(3) | 4335(2) | 5125(2) | 24(1) |
| C61 | 5908(7) | 4663(5) | 5288(9) | 24(1) |
| C62 | 5779(3) | 5740(3) | 5079(3) | 37(1) |
| C63 | 4793(6) | 6471(4) | 4724(6) | 43(1) |
| C64 | 3931(3) | 6169(3) | 4558(3) | 33(1) |
| C65 | 4052(7) | 5070(5) | 4767(9) | 24(1) |
| C66 | 5164(6) | 3188(4) | 5338(6) | 43(1) |
Bond lengths [Å] and angles [°] for 25k.

| Bond        | Length(Å) | Bond        | Length(Å) | Angle(°) |
|-------------|-----------|-------------|-----------|----------|
| Si1-C2      | 1.8650(15)| C27-H27     | 1.0000    |
| Si1-C1      | 1.8680(16)| C28-C33     | 1.3823(19)|
| Si1-C3      | 1.8744(15)| C28-C29     | 1.3949(19)|
| Si1-C4      | 1.9105(13)| C29-C36     | 1.3916(18)|
| O1-C6       | 1.2170(16)| C29-C30     | 1.5262(18)|
| C1-H1A      | 0.9800    | C30-C45     | 1.5108(19)|
| C1-H1B      | 0.9800    | C30-C32     | 1.5455(18)|
| C1-H1C      | 0.9800    | C31-C32     | 1.318(2)  |
| C2-H2A      | 0.9800    | C31-H31     | 0.9500    |
| C2-H2B      | 0.9800    | C32-H32     | 0.9500    |
| C2-H2C      | 0.9800    | C33-C34     | 1.398(2)  |
| C3-H3A      | 0.9800    | C33-H33     | 0.9500    |
| C3-H3B      | 0.9800    | C34-C35     | 1.382(2)  |
| C3-H3C      | 0.9800    | C34-H34     | 0.9500    |
| C4-C16      | 1.3922(18)| C35-C36     | 1.4092(19)|
| C4-C5       | 1.4244(17)| C35-H35     | 0.9500    |
| C5-C13      | 1.4072(17)| C36-C37     | 1.4736(19)|
| C5-C6       | 1.4960(17)| C37-C38     | 1.3838(19)|
| C6-C7       | 1.4820(18)| C37-C46     | 1.4372(18)|
| C7-C8       | 1.3818(18)| C38-C39     | 1.405(2)  |
| C7-C12      | 1.4038(17)| C38-H38A    | 0.9500    |
| C8-C9       | 1.3932(2) | C39-C40     | 1.367(2)  |
| C8-H8       | 0.9500    | C39-H39A    | 0.9500    |
| C9-C10      | 1.3861(19)| C40-C41     | 1.418(2)  |
| C9-H9       | 0.9500    | C40-H40A    | 0.9500    |
| C10-C11     | 1.4020(18)| C41-C42     | 1.414(2)  |
| C10-H10     | 0.9500    | C41-C46     | 1.4266(19)|
| C11-C12     | 1.3862(18)| C42-C43     | 1.365(2)  |
| C11-H11     | 0.9500    | C42-H42A    | 0.9500    |
| C12-C13     | 1.5069(17)| C43-C44     | 1.404(2)  |
| C13-C14     | 1.4357(17)| C43-H43A    | 0.9500    |
| C14-C15     | 1.4059(17)| C44-C45     | 1.3776(19)|
| C14-C26     | 1.4560(17)| C44-H44A    | 0.9500    |
| C15-C23     | 1.4216(17)| C45-C46     | 1.4301(18)|
| C15-C16     | 1.4261(17)| C47-C48     | 1.3943(18)|
| C16-C17     | 1.4784(17)| C47-C52     | 1.3975(18)|
| C17-C18     | 1.3876(18)| C48-C49     | 1.3879(19)|
| C17-C22     | 1.4166(18)| C48-H48A    | 0.9500    |
| C18-C19     | 1.3933(19)| C49-C50     | 1.387(2)  |
| C18-H18     | 0.9500    | C49-H49A    | 0.9500    |
| C19-C20     | 1.387(2)  | C50-C51     | 1.387(2)  |
| C19-H19     | 0.9500    | C50-H50A    | 0.9500    |
| C20-C21     | 1.391(2)  | C51-C52     | 1.391(2)  |
| C20-H20     | 0.9500    | C51-H51A    | 0.9500    |
| C21-C22     | 1.3913(18)| C52-H52A    | 0.9500    |
| C21-H21     | 0.9500    | C53-C54     | 1.387(6)  |
| C22-C23     | 1.4792(18)| C53-C58     | 1.390(5)  |
| C23-C24     | 1.3658(18)| C53-C59     | 1.515(5)  |
| C24-C25     | 1.4374(18)| C54-C55     | 1.374(6)  |
| C24-C27     | 1.5193(17)| C54-H54A    | 0.9500    |
| C25-C26     | 1.3930(17)| C55-C56     | 1.404(5)  |
| C25-C30     | 1.5812(17)| C55-H55A    | 0.9500    |
| C26-C47     | 1.4843(17)| C56-C57     | 1.319(5)  |
| C27-C28     | 1.5183(19)| C56-H56A    | 0.9500    |
| C27-C31     | 1.522(2)  | C57-C58     | 1.415(5)  |
|                  | Value 1  | Value 2  | Value 3  |
|------------------|---------|---------|---------|
| C57-H57A        | 0.9500  | C59'-H59E | 0.9800  |
| C58-H58A        | 0.9500  | C59'-H59F | 0.9800  |
| C59-H59A        | 0.9800  | C60-C61  | 1.380(7) |
| C59-H59B        | 0.9800  | C60-C65  | 1.380(8) |
| C59-H59C        | 0.9800  | C60-C66  | 1.486(5) |
| C53'-C58'       | 1.379(8) | C61-C62  | 1.390(6) |
| C53'-C54'       | 1.384(8) | C61-H61A | 0.9500  |
| C53'-C59'       | 1.530(7) | C62-C63  | 1.372(7) |
| C54'-C55'       | 1.405(9) | C62-H62A | 0.9500  |
| C54'-H54B       | 0.9500  | C63-C64  | 1.358(7) |
| C55'-C56'       | 1.370(6) | C63-H63A | 0.9500  |
| C55'-H55B       | 0.9500  | C64-C65  | 1.421(6) |
| C56-C57''       | 1.361(8) | C64-H64A | 0.9500  |
| C56'-H56B       | 0.9500  | C65-H65A | 0.9500  |
| C57'-C58'       | 1.390(6) | C66-H66A | 0.9800  |
| C57'-H57B       | 0.9500  | C66-H66B | 0.9800  |
| C58'-H58B       | 0.9500  | C66-H66C | 0.9800  |
| C59'-H59D       | 0.9800  | C7-C8-H8  | 120.7  |
| C2-Si1-C1       | 111.06(8) | C9-C10-C11 | 121.96(13) |
| C2-Si1-C3       | 111.36(7) | C9-C10-H10 | 119.0  |
| C1-Si1-C3       | 101.40(8) | C10-C9-C8  | 119.35(12) |
| C2-Si1-C4       | 112.36(6) | C10-C9-H9  | 120.3  |
| C1-Si1-C4       | 111.40(7) | C8-C9-H9   | 120.3  |
| C3-Si1-C4       | 108.73(6) | C9-C10-C11 | 121.96(13) |
| Si1-C1-H1A      | 109.5   | C9-C10-H10 | 119.0  |
| Si1-C1-H1B      | 109.5   | C11-C10-H10 | 119.0  |
| H1A-C1-H1B      | 109.5   | C12-C11-C10 | 119.01(12) |
| Si1-C1-H1C      | 109.5   | C12-C11-H11 | 120.5  |
| H1A-C1-H1C      | 109.5   | C10-C11-H11 | 120.5  |
| H1B-C1-H1C      | 109.5   | C11-C12-C7  | 118.32(11) |
| Si1-C2-H2A      | 109.5   | C11-C12-C13 | 132.82(11) |
| Si1-C2-H2B      | 109.5   | C7-C12-C13  | 108.33(11) |
| H2A-C2-H2B      | 109.5   | C5-C13-C14  | 118.47(11) |
| Si1-C2-H2C      | 109.5   | C5-C13-C12  | 107.70(10) |
| H2A-C2-H2C      | 109.5   | C14-C13-C12 | 133.27(11) |
| H2B-C2-H2C      | 109.5   | C15-C14-C13 | 112.24(11) |
| Si1-C3-H3A      | 109.5   | C15-C14-C26 | 117.01(11) |
| Si1-C3-H3B      | 109.5   | C13-C14-C26 | 130.75(11) |
| H3A-C3-H3B      | 109.5   | C14-C15-C23 | 123.26(11) |
| Si1-C3-H3C      | 109.5   | C14-C15-C16 | 126.13(11) |
| H3A-C3-H3C      | 109.5   | C23-C15-C16 | 110.57(11) |
| H3B-C3-H3C      | 109.5   | C4-C16-C15  | 119.86(12) |
| C16-C4-C5       | 112.11(11) | C4-C16-C17 | 134.27(12) |
| C16-C4-Si1      | 124.79(10) | C15-C16-C17 | 105.82(11) |
| C5-C4-Si1       | 122.60(9)  | C18-C17-C22 | 119.93(12) |
| C13-C5-C4       | 126.86(11) | C18-C17-C16 | 130.84(12) |
| C13-C5-C6       | 108.79(11) | C22-C17-C16 | 108.84(11) |
| C4-C5-C6        | 123.50(11) | C17-C18-C19 | 119.33(13) |
| O1-C6-C7        | 126.70(12) | C17-C18-H18 | 120.3  |
| O1-C6-C5        | 127.24(12) | C19-C18-H18 | 120.3  |
| C7-C6-C5        | 105.91(10) | C20-C19-C18 | 120.65(13) |
| C8-C7-C12       | 122.82(12) | C20-C19-H19 | 119.7  |
| C8-C7-C6        | 127.79(12) | C18-C19-H19 | 119.7  |
| C12-C7-C6       | 109.02(11) | C19-C20-C21 | 120.53(12) |
| C7-C8-C9        | 118.53(12) | C19-C20-H20 | 119.7  |
|       |       |       |       |       |
|-------|-------|-------|-------|-------|
| C21-C20-H20 | 119.7 | C38-C37-C36 | 122.24(12) |
| C20-C21-C22 | 119.40(13) | C46-C37-C36 | 118.79(12) |
| C20-C21-H21 | 120.3 | C37-C38-C39 | 121.70(13) |
| C22-C21-H21 | 120.3 | C37-C38-H38A | 119.1 |
| C21-C22-C17 | 119.88(12) | C39-C38-H38A | 119.1 |
| C21-C22-C23 | 132.50(12) | C40-C39-C38 | 120.22(13) |
| C17-C22-C23 | 107.57(11) | C40-C39-H39A | 119.9 |
| C24-C23-C15 | 118.18(12) | C38-C39-H39A | 119.9 |
| C24-C23-C22 | 134.98(12) | C39-C40-C41 | 120.61(13) |
| C15-C23-C22 | 106.74(11) | C39-C40-H40A | 119.7 |
| C23-C24-C25 | 120.52(11) | C41-C40-H40A | 119.7 |
| C23-C24-C27 | 125.02(12) | C42-C41-C40 | 120.95(13) |
| C25-C24-C27 | 114.34(11) | C42-C41-C46 | 119.48(13) |
| C26-C25-C24 | 121.11(11) | C40-C41-C46 | 119.56(13) |
| C26-C25-C30 | 128.96(11) | C43-C42-C41 | 120.61(13) |
| C24-C25-C30 | 109.91(10) | C43-C42-H42A | 119.7 |
| C25-C26-C14 | 118.85(11) | C41-C42-H42A | 119.7 |
| C25-C26-C47 | 122.27(11) | C42-C43-C44 | 120.19(13) |
| C14-C26-C47 | 118.87(11) | C42-C43-H43A | 119.9 |
| C28-C27-C24 | 105.90(10) | C44-C43-H43A | 119.9 |
| C28-C27-C31 | 107.01(11) | C45-C44-C43 | 121.61(13) |
| C24-C27-C31 | 104.01(11) | C45-C44-H44A | 119.2 |
| C28-C27-H27 | 113.0 | C43-C44-H44A | 119.2 |
| C24-C27-H27 | 113.0 | C44-C45-C46 | 119.18(12) |
| C31-C27-H27 | 113.0 | C44-C45-C30 | 119.53(12) |
| C33-C28-C29 | 120.78(13) | C46-C45-C30 | 121.26(12) |
| C33-C28-C27 | 126.21(13) | C41-C46-C45 | 118.82(12) |
| C29-C28-C27 | 112.99(12) | C41-C46-C37 | 118.83(12) |
| C36-C29-C28 | 121.49(12) | C45-C46-C37 | 122.35(12) |
| C36-C29-C30 | 124.51(12) | C48-C47-C52 | 119.12(12) |
| C28-C29-C30 | 113.99(11) | C48-C47-C26 | 119.56(11) |
| C45-C30-C29 | 112.85(11) | C52-C47-C26 | 121.26(12) |
| C45-C30-C32 | 109.36(11) | C49-C48-C47 | 120.56(13) |
| C29-C30-C32 | 105.16(10) | C49-C48-H48A | 119.7 |
| C45-C30-C25 | 120.04(10) | C47-C48-H48A | 119.7 |
| C29-C30-C25 | 103.49(10) | C50-C49-C48 | 119.94(14) |
| C32-C30-C25 | 104.69(10) | C50-C49-H49A | 120.0 |
| C32-C31-C27 | 126.50(12) | C48-C49-H49A | 120.0 |
| C32-C31-H31 | 123.2 | C51-C50-C49 | 120.03(13) |
| C27-C31-H31 | 123.2 | C51-C50-H50A | 120.0 |
| C31-C32-C30 | 116.24(12) | C49-C50-H50A | 120.0 |
| C31-C32-H32 | 121.9 | C50-C51-C52 | 120.17(13) |
| C30-C32-H32 | 121.9 | C50-C51-H51A | 119.9 |
| C28-C33-C34 | 118.47(13) | C52-C51-H51A | 119.9 |
| C28-C33-H33 | 120.8 | C51-C52-C47 | 120.12(13) |
| C34-C33-H33 | 120.8 | C51-C52-H52A | 119.9 |
| C35-C34-C33 | 120.75(13) | C47-C52-H52A | 119.9 |
| C35-C34-H34 | 119.6 | C54-C53-C58 | 117.9(3) |
| C33-C34-H34 | 119.6 | C54-C53-C59 | 120.3(4) |
| C34-C35-C36 | 121.32(13) | C58-C53-C59 | 121.8(4) |
| C34-C35-H35 | 119.3 | C55-C54-C53 | 121.0(4) |
| C36-C35-H35 | 119.3 | C55-C54-H54A | 119.5 |
| C29-C36-C35 | 117.15(13) | C53-C54-H54A | 119.5 |
| C29-C36-C37 | 119.59(12) | C54-C55-C56 | 120.1(4) |
| C35-C36-C37 | 123.24(12) | C54-C55-H55A | 119.9 |
| C38-C37-C46 | 118.96(13) | C56-C55-H55A | 119.9 |
Symmetry transformations used to generate equivalent atoms:

Anisotropic displacement parameters (Å² x 10^3) for 25k.
The anisotropic displacement factor exponent takes the form: \(-2\pi^2 [h^2 a^*2 U_{11} + ... + 2 \ h \ k \ a^* \ b^* \ U_{12}]\)

|          | U_{11}  | U_{22}  | U_{33}  | U_{23}  | U_{13}  | U_{12}  |
|----------|---------|---------|---------|---------|---------|---------|
| Si1      | 20(1)   | 16(1)   | 19(1)   | -7(1)   | -4(1)   | -7(1)   |
| O1       | 16(1)   | 23(1)   | 28(1)   | -10(1)  | -4(1)   | -8(1)   |
| C1       | 62(1)   | 26(1)   | 26(1)   | -7(1)   | -16(1)  | -13(1)  |
| C2       | 24(1)   | 24(1)   | 33(1)   | -11(1)  | -1(1)   | -12(1)  |
| C3       | 29(1)   | 27(1)   | 34(1)   | -20(1)  | -2(1)   | -6(1)   |
| C4       | 14(1)   | 15(1)   | 17(1)   | -7(1)   | 0(1)    | 5(1)    |
| C5       | 13(1)   | 18(1)   | 15(1)   | -6(1)   | -2(1)   | -6(1)   |
| C6       | 14(1)   | 18(1)   | 15(1)   | -5(1)   | -1(1)   | -5(1)   |
| C7       | 14(1)   | 18(1)   | 15(1)   | -6(1)   | -1(1)   | -5(1)   |
| C8       | 13(1)   | 24(1)   | 23(1)   | -11(1)  | -4(1)   | -3(1)   |
| C9       | 14(1)   | 25(1)   | 30(1)   | -14(1)  | -4(1)   | 1(1)    |
| C10      | 17(1)   | 19(1)   | 29(1)   | -13(1)  | -3(1)   | -2(1)   |
| C11      | 13(1)   | 18(1)   | 22(1)   | -9(1)   | -2(1)   | -4(1)   |
| C12      | 12(1)   | 16(1)   | 13(1)   | -5(1)   | -1(1)   | -3(1)   |
| Index | Value |
|-------|-------|
| C13   | 12(1) |
| C14   | 15(1) |
| C15   | 15(1) |
| C16   | 13(1) |
| C17   | 17(1) |
| C18   | 18(1) |
| C19   | 21(1) |
| C20   | 24(1) |
| C21   | 18(1) |
| C22   | 17(1) |
| C23   | 14(1) |
| C24   | 12(1) |
| C25   | 12(1) |
| C26   | 12(1) |
| C27   | 13(1) |
| C28   | 11(1) |
| C29   | 10(1) |
| C30   | 12(1) |
| C31   | 11(1) |
| C32   | 10(1) |
| C33   | 17(1) |
| C34   | 20(1) |
| C35   | 18(1) |
| C36   | 11(1) |
| C37   | 11(1) |
| C38   | 18(1) |
| C39   | 19(1) |
| C40   | 15(1) |
| C41   | 12(1) |
| C42   | 20(1) |
| C43   | 21(1) |
| C44   | 16(1) |
| C45   | 10(1) |
| C46   | 9(1)  |
| C47   | 10(1) |
| C48   | 13(1) |
| C49   | 18(1) |
| C50   | 24(1) |
| C51   | 23(1) |
| C52   | 16(1) |
| C53   | 34(2) |
| C54   | 37(2) |
| C55   | 30(2) |
| C56   | 34(2) |
| C57   | 53(2) |
| C58   | 31(3) |
| C59   | 36(2) |
| C59'  | 41(3) |
| C60   | 33(2) |
| C61   | 21(1) |
|   | x     | y     | z     | U(eq) |
|---|-------|-------|-------|-------|
| C62 | 36(2) | 48(2) | 42(2) | -24(2) | 5(1) | -26(2) |
| C63 | 64(2) | 28(3) | 40(1) | -14(2) | 5(1) | -18(2) |
| C64 | 32(2) | 29(2) | 26(2) | -3(1)  | 1(1) | -2(1)  |
| C65 | 21(1) | 34(3) | 21(1) | -11(3) | -1(1) | -12(2) |
| C66 | 64(2) | 28(3) | 40(1) | -14(2) | 5(1) | -18(2) |

Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for 25k.
Torsion angles [°] for 25k.

|          | C16-C4-C5-C13 | C26-C14-C15-C16 | C5-C4-C16-C15 | C13-C5-C6-O1 | C4-C5-C6-O1 | C13-C5-C6-C7 | C5-C6-C7-C8 | C6-C7-C8-C9 | C7-C8-C9-C10 | C8-C9-C10-C11 | C9-C10-C11-C12 | C10-C11-C12-C7 | C10-C11-C12-C13 | C8-C7-C12-C11 | C6-C7-C12-C11 | C8-C7-C12-C13 | C6-C7-C12-C13 | C4-C5-C13-C14 | C6-C5-C13-C14 | C4-C5-C13-C12 | C6-C5-C13-C12 | C11-C12-C13-C5 | C7-C12-C13-C5 | C11-C12-C13-C14 | C7-C12-C13-C14 | C5-C13-C14-C15 | C12-C13-C14-C15 | C5-C13-C14-C26 | C12-C13-C14-C26 | C13-C14-C15-C23 | C26-C14-C15-C23 | C13-C14-C15-C16 |
|----------|----------------|------------------|----------------|---------------|--------------|--------------|-------------|-------------|--------------|----------------|----------------|----------------|----------------|----------------|--------------|----------------|--------------|----------------|----------------|----------------|----------------|---------------|----------------|---------------|
|          | -11.56(19)     | 167.74(12)       | 18.16(17)      | -179.11(13)   | 10.8(2)      | 5.07(14)     | -165.01(12) | -179.39(13) | 1.1(2)       | -1.1(2)        | 1.10(19)       | 171.61(13)     | 174.62(14)     | -0.01(19)      | 173.51(11)    | -172.69(12)   | 0.84(14)      | -7.54(19)     | 177.20(11)    | 165.05(12)    | -4.61(14)     | 168.81(14)    | 2.40(14)      | 2.2(2)        | 173.44(13)    | 18.31(16)      | -151.97(13)   | -161.38(13)   | 28.3(2)       |
|          |                |                  |                |               |              |              |             |             |              |                |                |                |                |                |               |              |              |                |                |                | 170.32(12)    | -9.95(18)     | -12.00(18)    |              |
| Compound | Chemical Shifts |
|----------|----------------|
| C23-C24-C25-C30 | 169.61(11) | 1.3(2) |
| C27-C24-C25-C30 | -6.44(15) | -1.8(2) |
| C24-C25-C26-C14 | 6.20(18) | -179.22(13) |
| C30-C25-C26-C14 | -172.30(11) | -0.45(19) |
| C24-C25-C26-C47 | -174.75(11) | 178.68(13) |
| C30-C25-C26-C47 | 6.8(2) | -0.1(2) |
| C15-C14-C26-C25 | 2.99(17) | -1.2(2) |
| C13-C14-C26-C25 | -177.34(12) | -0.2(2) |
| C15-C14-C26-C47 | -176.10(11) | 2.85(19) |
| C13-C14-C26-C47 | 3.6(2) | -179.15(12) |
| C23-C24-C27-C28 | 131.96(14) | -170.86(11) |
| C25-C24-C27-C28 | -52.20(15) | -54.19(15) |
| C23-C24-C27-C31 | -115.25(14) | 66.72(16) |
| C25-C24-C27-C31 | 60.59(14) | 7.10(16) |
| C24-C27-C28-C33 | -123.48(14) | 123.77(12) |
| C31-C27-C28-C33 | 125.95(14) | -115.32(13) |
| C24-C27-C28-C29 | 57.84(14) | 2.71(18) |
| C31-C27-C28-C29 | -52.73(14) | -176.08(11) |
| C33-C28-C29-C36 | -1.6(2) | -178.10(12) |
| C27-C28-C29-C36 | 177.20(11) | 3.10(18) |
| C33-C28-C29-C30 | 179.24(11) | -4.05(18) |
| C27-C28-C29-C30 | -1.99(15) | 177.99(11) |
| C36-C29-C30-C45 | -7.03(17) | 176.79(12) |
| C28-C29-C30-C45 | 172.15(11) | -1.17(18) |
| C36-C29-C30-C32 | -126.16(13) | -3.55(18) |
| C28-C29-C30-C32 | 53.01(14) | 175.16(11) |
| C36-C29-C30-C25 | 124.25(13) | 175.61(12) |
| C28-C29-C30-C25 | -56.58(13) | -5.68(18) |
| C26-C25-C30-C45 | 5.86(19) | 61.37(17) |
| C24-C25-C30-C45 | -172.77(11) | -119.58(13) |
| C26-C25-C30-C29 | -121.01(14) | -121.49(14) |
| C24-C25-C30-C29 | 45.30(13) | 57.56(16) |
| C26-C25-C30-C32 | 129.05(14) | -1.67(19) |
| C24-C25-C30-C32 | -49.58(13) | 175.53(12) |
| C28-C27-C31-C32 | 55.32(15) | 0.1(2) |
| C24-C27-C31-C32 | -56.56(15) | 1.8(2) |
| C27-C31-C32-C30 | -1.80(17) | -2.0(2) |
| C45-C30-C32-C31 | -173.49(12) | 0.4(2) |
| C29-C30-C32-C31 | -52.05(15) | 1.42(19) |
| C25-C30-C32-C31 | 56.67(15) | -175.73(12) |
| C29-C28-C33-C34 | 1.7(2) | 177.5(5) |
| C27-C28-C33-C34 | -176.86(12) | 1.8(2) |
| C28-C33-C34-C35 | -0.4(2) | 1.9(8) |
| C33-C34-C35-C36 | -1.2(2) | -0.46(6) |
| C28-C29-C36-C35 | -0.03(18) | -1.46(6) |
| C30-C29-C36-C35 | 179.08(11) | -0.3(7) |
| C28-C29-C36-C37 | -178.35(11) | -179.2(4) |
| C30-C29-C36-C37 | 0.76(19) | 1.8(7) |
| C34-C35-C36-C29 | 1.41(19) | 0.0(12) |
| C34-C35-C36-C37 | 179.66(12) | 179.2(7) |
| C29-C36-C37-C38 | -175.48(12) | 0.3(12) |
| C35-C36-C37-C38 | 6.3(2) | -0.89(9) |
| C29-C36-C37-C46 | 5.85(18) | 1.3(9) |
| C35-C36-C37-C46 | -172.37(12) | 0.4(9) |
| C46-C37-C38-C39 | 1.39(19) | -178.85(5) |
| C36-C37-C38-C39 | -177.27(12) | -1.1(9) |
| Bond                  | Energy (deg) |
|----------------------|--------------|
| C65-C60-C61-C62      | -0.8(18)     |
| C66-C60-C61-C62      | 179.7(7)     |
| C60-C61-C62-C63      | 0.8(14)      |
| C61-C62-C63-C64      | -0.8(11)     |
| C62-C63-C64-C65      | 0.8(11)      |
| C61-C60-C65-C64      | 0.7(18)      |
| C66-C60-C65-C64      | -179.8(7)    |
| C63-C64-C65-C60      | -0.7(13)     |
Data for 28 (CCDC deposition number: 1818243)

The structure is the one suggested.

Crystal data and structure refinement for 28.

| Property                        | Value                        |
|--------------------------------|-----------------------------|
| Empirical formula              | C_{41}H_{24}O                |
| Formula weight                 | 532.60                      |
| Temperature                    | 100(2) K                    |
| Wavelength                     | 0.71073 Å                   |
| Crystal system                 | Triclinic                   |
| Space group                    | P-1                         |
| Unit cell dimensions           | a = 9.7588(7) Å, b = 10.4470(8) Å, c = 14.3087(12) Å |
|                               | α = 93.472(3)°, β = 109.324(3)°, γ = 105.408(3)° |
| Volume                         | 1309.32(18) Å³              |
| Z                              | 2                           |
| Density (calculated)           | 1.351 Mg/m³                 |
| Absorption coefficient         | 0.079 mm⁻¹                  |
| F(000)                         | 556                         |
| Crystal color, morphology      | Yellow, Block               |
| Crystal size                   | 0.240 x 0.130 x 0.110 mm³   |
| Theta range for data collection| 2.273 to 28.350°            |
| Index ranges                   | -13 ≤ h ≤ 13, -13 ≤ k ≤ 13, -18 ≤ l ≤ 19 |
| Reflections collected          | 24904                       |
| Independent reflections        | 6492 [R(int) = 0.0333]       |
| Observed reflections           | 5246                        |
| Completeness to theta = 25.242°| 99.9%                       |
| Absorption correction          | Multi-scan                  |
| Max. and min. transmission     | 0.7457 and 0.6940            |
| Refinement method              | Full-matrix least-squares on F² |
| Data / restraints / parameters | 6492 / 0 / 379              |
| Goodness-of-fit on F²          | 1.036                       |
| Final R indices [I>2sigma(I)]  | R1 = 0.0450, wR2 = 0.1069   |
|                               | R1 = 0.0612, wR2 = 0.1224   |
| Largest diff. peak and hole    | 0.330 and -0.245 e.Å⁻³      |

Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å² x 10³) for 28.
$U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

|   | x     | y     | z     | $U_{eq}$ |
|---|-------|-------|-------|----------|
| O1 | 5332(1) | -274(1) | 1077(1) | 25(1)   |
| C1 | 3806(2) | -535(1) | 928(1)  | 19(1)   |
| C2 | 2916(2) | -1856(1) | 509(1)  | 24(1)   |
| C3 | 1386(2) | -2238(1) | 360(1)  | 24(1)   |
| C4 | 744(2)  | -1311(1) | 635(1)  | 24(1)   |
| C5 | 1643(2) | 3(1)    | 1045(1) | 23(1)   |
| C6 | 3197(1) | 424(1)  | 1192(1) | 17(1)   |
| C7 | 4154   | 1885(1) | 1602(1) | 16(1)   |
| C8 | 3806(2) | 2819(1) | 872(1)  | 17(1)   |
| C9 | 2916(2) | 3727(1) | -654(1) | 20(1)   |
| C10| 1386(2)| 360(1)  | 24(1)   |
| C11| 744(2) | 635(1)  | 24(1)   |
| C12| 3197(1)| 1080(2) | 1860(1) | 28(1)   |
| C13| 6318(2)| 960(1)  | 1599(1) | 20(1)   |
| C14| 3630(2)| 2819(1) | 872(1)  | 17(1)   |
| C15| 3579(2)| 2791(1) | -107(1) | 18(1)   |
| C16| 3032(2)| 3727(1) | -654(1) | 20(1)   |
| C17| 2536(2)| 4657(1) | -223(1) | 21(1)   |
| C18| 2590(2)| 4686(1) | 763(1)  | 20(1)   |
| C19| 3141(1)| 3758(1) | 1319(1) | 17(1)   |
| C20| 3314(1)| 3520(1) | 2349(1) | 17(1)   |
| C21| 3892(1)| 2434(1) | 2520(1) | 17(1)   |
| C22| 4217(2)| 1924(1) | 3435(1) | 19(1)   |
| C23| 3903(1)| 2525(1) | 4188(1) | 18(1)   |
| C24| 4064(2)| 2322(1) | 5224(1) | 20(1)   |
| C25| 4743(2)| 1501(1) | 5820(1) | 23(1)   |
| C26| 4757(2)| 1538(2) | 6796(1) | 28(1)   |
| C27| 4082(2)| 2363(2) | 7164(1) | 30(1)   |
| C28| 3416(2)| 3209(2) | 6576(1) | 25(1)   |
| C29| 3433(2)| 3209(1) | 5611(1) | 20(1)   |
| C30| 2942(1)| 4042(1) | 4844(1) | 18(1)   |
| C31| 2338(2)| 5092(1) | 4806(1) | 20(1)   |
| C32| 2094(1)| 5741(1) | 3942(1) | 18(1)   |
| C33| 2411(1)| 5281(1) | 3124(1) | 18(1)   |
| C34| 2978(1)| 4161(1) | 3126(1) | 17(1)   |
| C35| 3261(1)| 3597(1) | 4008(1) | 17(1)   |
| C36| 1523(2)| 6927(1) | 3925(1) | 20(1)   |
| C37| 1835(2)| 7770(2) | 4818(1) | 26(1)   |
| C38| 1375(2)| 8920(2) | 4805(1) | 29(1)   |
| C39| 579(2) | 9247(2) | 3902(1) | 32(1)   |
| C40| 236(2) | 8413(2) | 3016(1) | 33(1)   |
| C41| 694(2) | 7265(2) | 3026(1) | 27(1)   |

Bond lengths [Å] and angles [°] for 28.
| Bond         | Length (Å)     | Bond         | Length (Å)     |
|--------------|----------------|--------------|----------------|
| C5-C6        | 1.3995(18)     | C23-C24      | 1.4716(18)     |
| C5-H5        | 0.9500         | C24-C25      | 1.3858(19)     |
| C6-C7        | 1.5222(17)     | C24-C29      | 1.4185(19)     |
| C7-C8        | 1.5230(17)     | C25-C26      | 1.3901(19)     |
| C7-C21       | 1.5263(17)     | C25-H25      | 0.9500         |
| C7-C14       | 1.5308(17)     | C26-C27      | 1.3902(2)      |
| C8-C13       | 1.3812(19)     | C26-H26      | 0.9500         |
| C8-C9        | 1.3985(18)     | C27-C28      | 1.3942(2)      |
| C9-C10       | 1.380(2)       | C27-H27      | 0.9500         |
| C9-H9        | 0.9500         | C28-C29      | 1.3866(19)     |
| C10-C11      | 1.390(2)       | C28-H28      | 0.9500         |
| C10-H10      | 0.9500         | C29-C30      | 1.4765(19)     |
| C11-C12      | 1.374(2)       | C30-C31      | 1.3725(19)     |
| C11-H11      | 0.9500         | C30-C35      | 1.4151(18)     |
| C12-C13      | 1.3958(19)     | C31-C32      | 1.4272(19)     |
| C12-H12      | 0.9500         | C31-H31      | 0.9500         |
| C14-C15      | 1.3831(18)     | C32-C33      | 1.3949(18)     |
| C14-C19      | 1.4047(18)     | C32-C36      | 1.4865(18)     |
| C15-C16      | 1.3956(18)     | C33-C34      | 1.4208(18)     |
| C15-H15      | 0.9500         | C33-H33      | 0.9500         |
| C16-C17      | 1.3899(19)     | C34-C35      | 1.4006(18)     |
| C16-H16      | 0.9500         | C36-C41      | 1.3972(2)      |
| C17-C18      | 1.3940(18)     | C36-C37      | 1.4013(19)     |
| C17-H17      | 0.9500         | C37-C38      | 1.3902(2)      |
| C18-C19      | 1.3958(18)     | C37-H37      | 0.9500         |
| C18-H18      | 0.9500         | C38-C39      | 1.3862(2)      |
| C19-C20      | 1.4715(17)     | C38-H38      | 0.9500         |
| C20-C21      | 1.3952(18)     | C39-C40      | 1.3822(2)      |
| C20-C34      | 1.4359(17)     | C39-H39      | 0.9500         |
| C21-C22      | 1.4130(18)     | C40-C41      | 1.3872(2)      |
| C22-C23      | 1.3735(18)     | C40-H40      | 0.9500         |
| C22-H22      | 0.9500         | C41-H41      | 0.9500         |
| C23-C35      | 1.4190(18)     |              |                |
| Bond | Distance (Å) |
|------|--------------|
| C15-C14-C7 | 127.75(11) |
| C19-C14-C7 | 110.61(11) |
| C14-C15-C16 | 118.60(12) |
| C14-C15-H15 | 120.7 |
| C16-C15-H15 | 120.7 |
| C17-C16-C15 | 120.39(12) |
| C17-C16-H16 | 119.8 |
| C15-C16-H16 | 119.8 |
| C16-C17-C18 | 120.98(13) |
| C16-C17-H17 | 119.5 |
| C18-C17-H17 | 119.5 |
| C17-C18-C19 | 119.08(12) |
| C17-C18-H18 | 120.5 |
| C19-C18-H18 | 120.5 |
| C18-C19-C14 | 119.31(12) |
| C18-C19-C20 | 132.01(12) |
| C14-C19-C20 | 108.68(11) |
| C21-C20-C34 | 119.51(12) |
| C21-C20-C19 | 108.28(11) |
| C34-C20-C19 | 132.20(12) |
| C20-C21-C22 | 124.13(12) |
| C20-C21-C7 | 111.44(11) |
| C22-C21-C7 | 124.42(11) |
| C23-C22-C21 | 117.23(12) |
| C23-C22-H22 | 121.4 |
| C21-C22-H22 | 121.4 |
| C22-C23-C35 | 119.02(12) |
| C22-C23-C24 | 134.75(12) |
| C35-C23-C24 | 106.22(11) |
| C25-C24-C29 | 120.54(12) |
| C25-C24-C23 | 131.18(12) |
| C29-C24-C23 | 108.22(12) |
| C24-C25-C26 | 118.72(13) |
| C24-C25-H25 | 120.6 |
| C26-C25-H25 | 120.6 |
| C27-C26-C25 | 120.85(14) |
| C27-C26-H26 | 119.6 |
| C25-C26-H26 | 119.6 |
| C26-C27-C28 | 120.95(13) |
| C26-C27-H27 | 119.5 |
| C28-C27-H27 | 119.5 |
| C29-C28-C27 | 118.70(13) |

Symmetry transformations used to generate equivalent atoms:
Anisotropic displacement parameters (Å² x 10³) for 28.
The anisotropic displacement factor exponent takes the form: \(-2\pi²[ h^2 a^{*2} U_{11} + ... + 2 h k a^{*} b^{*} U_{12} ]\)

|       | U_{11}  | U_{22}  | U_{33}  | U_{23}  | U_{13}  | U_{12}  |
|-------|---------|---------|---------|---------|---------|---------|
| O1    | 20(1)   | 19(1)   | 36(1)   | -1(1)   | 10(1)   | 7(1)    |
| C1    | 18(1)   | 19(1)   | 20(1)   | 5(1)    | 7(1)    | 7(1)    |
| C2    | 27(1)   | 17(1)   | 28(1)   | 3(1)    | 9(1)    | 7(1)    |
| C3    | 25(1)   | 17(1)   | 25(1)   | 4(1)    | 5(1)    | 2(1)    |
| C4    | 19(1)   | 24(1)   | 27(1)   | 6(1)    | 7(1)    | 3(1)    |
| C5    | 21(1)   | 22(1)   | 26(1)   | 4(1)    | 10(1)   | 7(1)    |
| C6    | 20(1)   | 16(1)   | 14(1)   | 4(1)    | 6(1)    | 6(1)    |
| C7    | 19(1)   | 15(1)   | 15(1)   | 3(1)    | 7(1)    | 6(1)    |
| C8    | 20(1)   | 18(1)   | 15(1)   | 5(1)    | 7(1)    | 6(1)    |
| C9    | 25(1)   | 23(1)   | 26(1)   | -1(1)   | 8(1)    | 3(1)    |
| C10   | 23(1)   | 33(1)   | 29(1)   | 1(1)    | 4(1)    | -2(1)   |
| C11   | 17(1)   | 40(1)   | 34(1)   | 11(1)   | 5(1)    | 5(1)    |
| C12   | 22(1)   | 31(1)   | 35(1)   | 9(1)    | 10(1)   | 12(1)   |
| C13   | 20(1)   | 19(1)   | 21(1)   | 5(1)    | 6(1)    | 6(1)    |
| C14   | 18(1)   | 15(1)   | 17(1)   | 3(1)    | 6(1)    | 4(1)    |
| C15   | 21(1)   | 17(1)   | 19(1)   | 2(1)    | 8(1)    | 6(1)    |
| C16   | 25(1)   | 21(1)   | 16(1)   | 4(1)    | 9(1)    | 6(1)    |
| C17   | 27(1)   | 18(1)   | 19(1)   | 5(1)    | 8(1)    | 7(1)    |
| C18   | 25(1)   | 17(1)   | 19(1)   | 3(1)    | 8(1)    | 7(1)    |
| C19   | 19(1)   | 15(1)   | 16(1)   | 2(1)    | 7(1)    | 4(1)    |
| C20   | 18(1)   | 16(1)   | 16(1)   | 2(1)    | 6(1)    | 5(1)    |
| C21   | 20(1)   | 16(1)   | 16(1)   | 2(1)    | 7(1)    | 5(1)    |
| C22   | 23(1)   | 17(1)   | 18(1)   | 4(1)    | 7(1)    | 7(1)    |
| C23   | 20(1)   | 17(1)   | 16(1)   | 3(1)    | 6(1)    | 4(1)    |
| C24   | 23(1)   | 19(1)   | 18(1)   | 2(1)    | 9(1)    | 4(1)    |
| C25   | 30(1)   | 20(1)   | 20(1)   | 4(1)    | 10(1)   | 8(1)    |
| C26   | 41(1)   | 25(1)   | 21(1)   | 8(1)    | 12(1)   | 14(1)   |
| C27   | 48(1)   | 29(1)   | 20(1)   | 8(1)    | 18(1)   | 16(1)   |
| C28   | 36(1)   | 24(1)   | 20(1)   | 5(1)    | 14(1)   | 12(1)   |
| C29   | 23(1)   | 19(1)   | 18(1)   | 3(1)    | 8(1)    | 5(1)    |
| C30   | 19(1)   | 20(1)   | 16(1)   | 2(1)    | 7(1)    | 4(1)    |
| C31   | 22(1)   | 21(1)   | 18(1)   | 2(1)    | 8(1)    | 7(1)    |
| C32   | 17(1)   | 18(1)   | 19(1)   | 1(1)    | 5(1)    | 5(1)    |
| C33   | 18(1)   | 18(1)   | 18(1)   | 3(1)    | 6(1)    | 5(1)    |
| C34   | 17(1)   | 16(1)   | 16(1)   | 1(1)    | 6(1)    | 4(1)    |
| C35   | 18(1)   | 16(1)   | 16(1)   | 2(1)    | 6(1)    | 4(1)    |
| C36   | 20(1)   | 19(1)   | 23(1)   | 2(1)    | 10(1)   | 6(1)    |
| C37   | 25(1)   | 27(1)   | 26(1)   | -1(1)   | 9(1)    | 10(1)   |
| C38   | 29(1)   | 26(1)   | 35(1)   | -3(1)   | 16(1)   | 10(1)   |
| C39   | 39(1)   | 25(1)   | 44(1)   | 8(1)    | 23(1)   | 18(1)   |
| C40   | 45(1)   | 34(1)   | 33(1)   | 13(1)   | 18(1)   | 24(1)   |
| C41   | 34(1)   | 27(1)   | 25(1)   | 4(1)    | 13(1)   | 15(1)   |

Hydrogen coordinates (x 10⁴) and isotropic displacement parameters (Å² x 10³) for 28.

|       | x      | y      | z      | U(eq) |
|-------|--------|--------|--------|-------|
| H2    | 3361   | -2490  | 327    | 29    |
Torsion angles [°] for 28.

|        |        |        |        |        |        |
|--------|--------|--------|--------|--------|--------|
| C13-O1-C1-C6 | 6.31(19) | C10-C11-C12-C13 | -0.5(2) |
| C13-O1-C1-C2 | -172.20(12) | C1-O1-C13-C8 | -9.75(19) |
| O1-C1-C2-C3 | 177.73(13) | C1-O1-C13-C12 | 170.35(12) |
| C6-C1-C2-C3 | -0.8(2) | C9-C8-C13-O1 | -178.47(13) |
| C1-C2-C3-C4 | -0.5(2) | C7-C8-C13-O1 | 2.1(2) |
| C2-C3-C4-C5 | 0.9(2) | C9-C8-C13-C12 | 1.4(2) |
| C3-C4-C5-C6 | -0.1(2) | C7-C8-C13-C12 | -177.96(13) |
| O1-C1-C6-C5 | -176.80(12) | C11-C12-C13-O1 | 179.13(14) |
| C2-C1-C6-C5 | 1.6(2) | C11-C12-C13-C8 | -0.8(2) |
| O1-C1-C6-C7 | 4.7(2) | C6-C7-C14-C15 | -59.72(16) |
| C2-C1-C6-C7 | -176.93(12) | C8-C7-C14-C15 | 63.48(16) |
| C4-C5-C6-C1 | -1.2(2) | C21-C7-C14-C15 | -178.75(12) |
| C4-C5-C6-C7 | 177.40(13) | C6-C7-C14-C19 | 118.96(12) |
| C1-C6-C7-C8 | -10.96(17) | C8-C7-C14-C19 | -117.83(12) |
| C5-C6-C7-C8 | 170.55(12) | C21-C7-C14-C19 | -0.06(13) |
| C1-C6-C7-C21 | -134.26(13) | C19-C14-C15-C16 | 0.30(19) |
| C5-C6-C7-C21 | 47.26(16) | C7-C14-C15-C16 | 178.86(12) |
| C1-C6-C7-C14 | 113.51(13) | C14-C15-C16-C17 | -0.66(19) |
| C5-C6-C7-C14 | -64.98(15) | C15-C16-C17-C18 | 0.7(2) |
| C6-C7-C8-C13 | 7.77(17) | C16-C17-C18-C19 | -0.5(2) |
| C21-C7-C8-C13 | 131.83(13) | C17-C18-C19-C14 | 0.09(19) |
| C14-C7-C8-C13 | -116.35(13) | C17-C18-C19-C20 | -178.87(13) |
| C6-C7-C8-C9 | -171.61(12) | C15-C14-C19-C18 | -0.02(19) |
| C21-C7-C8-C9 | -47.54(16) | C7-C14-C19-C18 | -178.80(11) |
| C14-C7-C8-C9 | 64.28(16) | C15-C14-C19-C20 | 179.17(11) |
| C13-C8-C9-C10 | -0.9(2) | C7-C14-C19-C20 | 0.39(14) |
| C7-C8-C9-C10 | 178.54(13) | C18-C19-C20-C21 | 178.46(13) |
| C8-C9-C10-C11 | -0.3(2) | C14-C19-C20-C21 | -0.58(14) |
| C9-C10-C11-C12 | 1.0(2) | C18-C19-C20-C34 | -0.1(2) |
| Bond                | Distance (Å) |
|---------------------|--------------|
| C14-C19-C20-C34     | -179.14(13)  |
| C34-C20-C21-C22     | -1.77(19)    |
| C19-C20-C21-C22     | 179.46(12)   |
| C34-C20-C21-C7      | 179.32(11)   |
| C19-C20-C21-C7      | 0.55(14)     |
| C6-C7-C21-C20       | -118.86(12)  |
| C8-C7-C21-C20       | 118.38(12)   |
| C14-C7-C21-C20      | -0.31(13)    |
| C6-C7-C21-C22       | 62.23(16)    |
| C8-C7-C21-C22       | -60.52(16)   |
| C14-C7-C21-C22      | -179.21(12)  |
| C20-C21-C22-C23     | 1.74(19)     |
| C7-C21-C22-C23      | -179.50(12)  |
| C21-C22-C23-C35     | 0.75(18)     |
| C21-C22-C23-C45     | -179.74(13)  |
| C22-C23-C24-C25     | 7.0(3)       |
| C35-C23-C24-C25     | -173.48(14)  |
| C22-C23-C24-C29     | -175.90(15)  |
| C35-C23-C24-C29     | 3.65(14)     |
| C29-C24-C25-C26     | 1.7(2)       |
| C23-C24-C25-C26     | 178.54(14)   |
| C24-C25-C26-C27     | 1.1(2)       |
| C25-C26-C27-C28     | -2.1(2)      |
| C26-C27-C28-C29     | 0.3(2)       |
| C27-C28-C29-C24     | 2.4(2)       |
| C27-C28-C29-C30     | -174.68(14)  |
| C25-C24-C29-C28     | -3.5(2)      |
| C23-C24-C29-C28     | 179.01(12)   |
| C25-C24-C29-C30     | 174.26(12)   |
| C23-C24-C29-C30     | -3.24(15)    |
| C28-C29-C30-C31     | 1.2(3)       |
| C24-C29-C30-C31     | -176.16(15)  |
| C28-C29-C30-C35     | 178.97(15)   |
| C24-C29-C30-C35     | 1.59(14)     |
| C35-C30-C31-C32     | -2.15(19)    |
| C29-C30-C31-C32     | 175.38(13)   |
| C30-C31-C32-C33     | 2.45(19)     |
| C30-C31-C32-C36     | -176.52(12)  |
| C31-C32-C33-C34     | 0.13(19)     |
| C36-C32-C33-C34     | 179.09(11)   |
| C32-C33-C34-C35     | -2.82(18)    |
| C32-C33-C34-C20     | 177.50(12)   |
| C21-C20-C34-C35     | -0.69(17)    |
| C19-C20-C34-C35     | 177.73(12)   |
| C21-C20-C34-C33     | 178.99(12)   |
| C19-C20-C34-C33     | -2.6(2)      |
| C33-C34-C35-C30     | 3.17(19)     |
| C20-C34-C35-C30     | -177.10(12)  |
| C33-C34-C35-C23     | -176.43(12)  |
| C20-C34-C35-C23     | 3.30(19)     |
| C31-C30-C35-C34     | -0.7(2)      |
| C29-C30-C35-C34     | -178.90(12)  |
| C31-C30-C35-C23     | 178.93(12)   |
| C29-C30-C35-C23     | 0.76(14)     |
| C22-C23-C35-C34     | -3.4(2)      |
| C24-C23-C35-C34     | 176.94(12)   |
Data for 32-H (CCDC deposition number: 1818245)

Structure description
The structure is the one suggested as a partial ethyl acetate solvate. Very long exposures were used to collect requisite data to qualify as publishable by IUCr standards. PLATON/SQUEEZE was used to remove the effects of poorly resolved solvent. The three-dimensional structure appears to have void spaces that zig-zag through channels to allow solvent to evaporate from the lattice. Please see the CIF for additional details.
Table 1. Crystal data and structure refinement for 32-H.

| Property                  | Value                                      |
|---------------------------|--------------------------------------------|
| Empirical formula         | C_{78}H_{39}ClO_{2}                        |
| Formula weight            | 1043.54                                    |
| Temperature               | 100(2) K                                   |
| Wavelength                | 0.71073 Å                                  |
| Crystal system            | Triclinic                                  |
| Space group               | P-1                                        |
| Unit cell dimensions      | a = 12.2130(17) Å                         |
|                           | b = 15.407(2) Å                           |
|                           | c = 17.340(3) Å                           |
|                           | α = 64.126(6)°                             |
|                           | β = 75.588(6)°                             |
|                           | γ = 74.110(5)°                             |
| Volume                    | 2791.7(8) Å³                              |
| Z                         | 2                                          |
Density (calculated) 1.241 Mg/m$^3$
Absorption coefficient 0.119 mm$^{-1}$
$F(000)$ 1080
Crystal color, morphology Brown, Plate
Crystal size 0.200 x 0.080 x 0.005 mm$^3$
Theta range for data collection 2.347 to 25.427°
Index ranges $-14 \leq h \leq 14, -18 \leq k \leq 18, -20 \leq l \leq 20$
Reflections collected 50768
Independent reflections 10284 [R(int) = 0.0774]
Observed reflections 6730
Completeness to theta = 25.242° 99.9%
Absorption correction Multi-scan
Max. and min. transmission 0.8620 and 0.7798
Refinement method Full-matrix least-squares on $F^2$
Data / restraints / parameters 10284 / 0 / 730
Goodness-of-fit on $F^2$ 1.042
Final $R$ indices [$I>2\sigma(I)$] $R1 = 0.0629$, $wR2 = 0.1435$
$R$ indices (all data) $R1 = 0.1025$, $wR2 = 0.1571$
Largest diff. peak and hole 0.474 and -0.355 e.Å$^{-3}$

Table 2. Atomic coordinates (x 10$^4$) and equivalent isotropic displacement parameters (Å$^2$x 10$^3$) for 32-H. $U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

|      | x      | y      | z      | $U_{eq}$ |
|------|--------|--------|--------|----------|
| Cl1  | 8456(1) | 6282(1)| 3576(1)| 41(1)    |
| O1   | 3272(2) | -1322(2)| 8029(2)| 61(1)    |
| O2   | 2590(2) | 8828(2)| 1029(1)| 36(1)    |
| C1   | 3876(2) | 722(2) | 6129(2)| 29(1)    |
| C2   | 4996(2) | 13(2)  | 6152(2)| 32(1)    |
| C3   | 5988(2) | 40(2)  | 5554(2)| 32(1)    |
| C4   | 6892(3) | -770(2)| 5750(2)| 39(1)    |
| C5   | 6803(3) | -1598(2)| 6515(2)| 44(1)    |
| C6   | 5776(3) | -1640(2)| 7090(2)| 47(1)    |
| C7   | 4893(3) | -850(2)| 6900(2)| 37(1)    |
| C8   | 3695(3) | -740(2)| 7354(2)| 44(1)    |
| C9   | 3077(2) | 243(2) | 6807(2)| 34(1)    |
| C10  | 1884(3) | 630(2) | 6917(2)| 36(1)    |
| C11  | 1490(2) | 1488(2)| 6287(2)| 29(1)    |
| C12  | 344(2)  | 2122(2)| 6149(2)| 30(1)    |
| C13  | -703(2) | 2068(2)| 6689(2)| 35(1)    |
| C14  | -1606(2)| 2851(2)| 6446(2)| 37(1)    |
| C15  | -1473(2)| 3673(2)| 5692(2)| 35(1)    |
| C16  | -431(2) | 3738(2)| 5133(2)| 30(1)    |
| C17  | 480(2)  | 2948(2)| 5359(2)| 27(1)    |
| C18  | 1710(2) | 2843(2)| 4980(2)| 26(1)    |
| C19  | 2290(2) | 1995(2)| 5573(2)| 26(1)    |
| C20  | 3509(2) | 1702(2)| 5532(2)| 26(1)    |
| C21  | 4125(2) | 2448(2)| 4954(2)| 24(1)    |
| C22  | 5296(2) | 2600(2)| 4848(2)| 24(1)    |
| C23  | 6156(2) | 2059(2)| 5359(2)| 26(1)    |
| C24  | 7217(2) | 2346(2)| 5107(2)| 29(1)    |
| C25  | 7401(2) | 3158(2)| 4353(2)| 29(1)    |
| C26  | 6530(2) | 3734(2)| 3864(2)| 25(1)    |
| C27 | 5440(2) | 3491(2) | 4127(2) | 23(1) |
|-----|---------|---------|---------|-------|
| C28 | 4306(2) | 3979(2) | 3806(2) | 23(1) |
| C29 | 3556(2) | 3296(2) | 4334(2) | 23(1) |
| C30 | 2363(2) | 3465(2) | 4264(2) | 22(1) |
| C31 | 2036(2) | 3900(2) | 3130(2) | 26(1) |
| C32 | 1099(2) | 4240(2) | 3489(2) | 23(1) |
| C33 | -392(2) | 4198(2) | 2496(2) | 31(1) |
| C34 | -270(2) | 5036(2) | 1745(2) | 31(1) |
| C35 | 543(2)  | 5588(2) | 1608(2) | 29(1) |
| C36 | 1236(2) | 5302(2) | 2232(2) | 26(1) |
| C37 | 2246(2) | 4912(2) | 2996(2) | 22(1) |
| C38 | 2751(2) | 4880(2) | 3705(2) | 26(1) |
| C39 | 2363(2) | 3465(2) | 4264(2) | 22(1) |
| C40 | 3844(2) | 4880(2) | 3705(2) | 26(1) |
| C41 | 4357(2) | 5752(2) | 2647(2) | 23(1) |
| C42 | 5342(2) | 5837(2) | 3705(2) | 26(1) |
| C43 | 6280(2) | 5966(2) | 3926(2) | 29(1) |
| C44 | 7252(2) | 6140(2) | 3315(2) | 30(1) |
| C45 | 7300(2) | 6196(2) | 2489(2) | 30(1) |
| C46 | 6364(2) | 6044(2) | 2285(2) | 27(1) |
| C47 | 3837(2) | 6477(2) | 1957(2) | 24(1) |
| C48 | 2789(2) | 6418(2) | 1734(2) | 24(1) |
| C49 | 2543(2) | 7306(2) | 895(2) | 30(1) |
| C50 | 1348(2) | 7780(2) | 673(2) | 34(1) |
| C51 | 414(3)  | 7768(2) | 1328(2) | 37(1) |
| C52 | -658(3) | 8306(2) | 1138(2) | 46(1) |
| C53 | -801(3) | 8884(3) | 275(3) | 68(1) |
| C54 | 124(3)  | 8912(3) | -373(3) | 69(1) |
| C55 | 1190(3) | 8384(3) | -186(2) | 51(1) |
| C56 | 3030(2) | 8029(2) | 1047(2) | 24(1) |
| C57 | 4235(2) | 7429(2) | 1236(2) | 27(1) |
| C58 | 4882(2) | 8044(2) | 1367(2) | 28(1) |
| C59 | 4804(2) | 8080(2) | 2165(2) | 33(1) |
| C60 | 5360(2) | 8680(2) | 2265(2) | 39(1) |
| C61 | 5990(3) | 9299(2) | 1548(2) | 45(1) |
| C62 | 6007(2) | 9325(2) | 748(2) | 43(1) |
| C63 | 5458(2) | 8717(2) | 646(2) | 36(1) |
| C64 | 3582(3) | 7074(2) | 249(2) | 32(1) |
| C65 | 3626(3) | 6625(2) | -337(2) | 41(1) |
| C66 | 2650(3) | 6435(3) | -458(2) | 51(1) |
| C67 | 2732(4) | 6009(3) | -1041(2) | 63(1) |
| C68 | 3802(4) | 5788(3) | -1488(2) | 58(1) |
| C69 | 4773(4) | 5919(3) | -1350(2) | 56(1) |
| C70 | 4741(3) | 6352(2) | -776(2) | 44(1) |
| C71 | 5751(3) | 6494(2) | -619(2) | 44(1) |
| C72 | 6868(3) | 6238(3) | -1065(2) | 57(1) |
| C73 | 7832(3) | 6387(3) | -919(3) | 64(1) |
| C74 | 7791(3) | 6760(3) | -320(2) | 56(1) |
| C75 | 6729(3) | 7005(2) | 135(2) | 44(1) |
| C76 | 5708(3) | 6893(2) | -142(2) | 40(1) |
| C77 | 4559(3) | 7169(2) | 430(2) | 31(1) |
Table 3. Bond lengths [Å] and angles [°] for 32-H.

| Bond          | Length [Å] | Angle [°] |
|---------------|------------|-----------|
| C11-C45       | 1.735(3)   |           |
| C1-O8         | 1.216(4)   |           |
| C2-C57        | 1.190(3)   |           |
| C1-C9         | 1.395(4)   |           |
| C1-C20        | 1.430(4)   |           |
| C1-C2         | 1.495(4)   |           |
| C2-C3         | 1.382(4)   |           |
| C2-C7         | 1.404(4)   |           |
| C3-C4         | 1.397(4)   |           |
| C3-H3A        | 0.9500     |           |
| C4-C5         | 1.389(4)   |           |
| C4-H4A        | 0.9500     |           |
| C5-C6         | 1.391(5)   |           |
| C5-H5A        | 0.9500     |           |
| C6-C7         | 1.364(4)   |           |
| C6-H6A        | 0.9500     |           |
| C7-C8         | 1.483(4)   |           |
| C8-C9         | 1.497(4)   |           |
| C9-C10        | 1.414(4)   |           |
| C10-C11       | 1.351(4)   |           |
| C10-H10A      | 0.9500     |           |
| C11-C19       | 1.438(4)   |           |
| C11-C12       | 1.478(4)   |           |
| C12-C13       | 1.383(4)   |           |
| C12-C17       | 1.416(4)   |           |
| C13-C14       | 1.382(4)   |           |
| C13-H13A      | 0.9500     |           |
| C14-C15       | 1.379(4)   |           |
| C14-H14A      | 0.9500     |           |
| C15-C16       | 1.393(4)   |           |
| C15-H15A      | 0.9500     |           |
| C16-C17       | 1.390(4)   |           |
| C16-H16A      | 0.9500     |           |
| C17-C18       | 1.477(3)   |           |
| C18-C19       | 1.397(4)   |           |
| C18-C30       | 1.408(4)   |           |
| C19-C20       | 1.426(4)   |           |
| C20-C21       | 1.409(4)   |           |
| C21-C29       | 1.412(4)   |           |
| C21-C22       | 1.466(4)   |           |
| C22-C23       | 1.387(4)   |           |
| C22-C27       | 1.415(4)   |           |
| C23-C24       | 1.388(4)   |           |
| C23-H23A      | 0.9500     |           |
| C24-C25       | 1.380(4)   |           |
| C24-H24A      | 0.9500     |           |
| C25-C26       | 1.384(4)   |           |
| C25-H25A      | 0.9500     |           |
| C26-C27       | 1.394(4)   |           |
| C26-H26A      | 0.9500     |           |
| C27-C28       | 1.497(4)   |           |
| C28-C40       | 1.414(4)   |           |
| C28-C29       | 1.434(4)   |           |
| C29-C30       | 1.435(3)   |           |
| Bond Lengths (Å) | Bond Angles (°) |
|-----------------|-----------------|
|                 |                 |
| 1.393(4)        | C69-H69A        |
| 0.9500          | C70-C71         |
| 1.365(5)        | C70-H70A        |
| 0.9500          | C71-C72         |
| 1.382(4)        | C72-C77         |
| 0.9500          | C72-C73         |
| 1.365(4)        | C73-C74         |
| 1.443(4)        | C73-H73A        |
| 1.385(5)        | C74-C75         |
| 1.435(4)        | C75-C76         |
| 1.400(5)        | C75-H75A        |
| 0.9500          | C76-C77         |
| 1.380(5)        | C76-H76A        |
| 0.9500          | C77-C78         |
| 1.349(5)        |                 |
|                 |                 |
| C9-C1-C20       | 119.3(2)        |
| C15-C14-C13     | 121.3(3)        |
| C9-C1-C2        | 108.1(2)        |
| C15-C14-H14A    | 119.3           |
| C20-C1-C2      | 132.4(3)        |
| C13-C14-H14A    | 119.3           |
| C3-C2-C7       | 119.1(3)        |
| C14-C15-C16     | 121.4(3)        |
| C3-C2-C1       | 131.8(3)        |
| C14-C15-H15A    | 119.3           |
| C7-C2-C1       | 108.7(3)        |
| C16-C15-H15A    | 119.3           |
| C2-C3-C4       | 118.5(3)        |
| C17-C16-C15     | 118.0(3)        |
| C2-C3-H3A      | 120.7           |
| C17-C16-H16A    | 121.0           |
| C4-C3-H3A      | 120.7           |
| C15-C16-H16A    | 121.0           |
| C5-C4-C3       | 121.6(3)        |
| C16-C17-C12     | 120.1(2)        |
| C5-C4-H4A      | 119.2           |
| C16-C17-C18     | 131.0(3)        |
| C3-C4-H4A      | 119.2           |
| C12-C17-C18     | 108.2(2)        |
| C4-C5-C6       | 119.4(3)        |
| C19-C18-C30     | 118.5(2)        |
| C4-C5-H5A      | 120.3           |
| C19-C18-C17     | 107.0(2)        |
| C6-C5-H5A      | 120.3           |
| C30-C18-C17     | 133.7(2)        |
| C7-C6-C5       | 119.0(3)        |
| C18-C19-C20     | 125.6(2)        |
| C7-C6-H6A      | 120.5           |
| C18-C19-C11     | 110.7(2)        |
| C5-C6-H6A      | 120.5           |
| C20-C19-C11     | 123.4(2)        |
| C6-C7-C2       | 122.1(3)        |
| C21-C20-C19     | 114.2(2)        |
| C6-C7-C8       | 129.6(3)        |
| C21-C20-C1     | 131.8(2)        |
| C2-C7-C8       | 108.1(3)        |
| C19-C20-C1     | 113.8(2)        |
| O1-C8-C7       | 128.1(3)        |
| C20-C21-C29    | 119.1(2)        |
| O1-C8-C9       | 125.7(3)        |
| C20-C21-C22    | 134.3(2)        |
| C7-C8-C9       | 106.2(3)        |
| C29-C21-C22    | 106.5(2)        |
| C1-C9-C10      | 124.4(3)        |
| C23-C22-C27    | 121.1(2)        |
| C1-C9-C8       | 108.3(3)        |
| C23-C22-C21    | 130.1(2)        |
| C10-C9-C8      | 127.3(3)        |
| C27-C22-C21    | 108.6(2)        |
| C11-C10-C9     | 117.2(3)        |
| C22-C23-C24    | 119.2(3)        |
| C11-C10-H10A   | 121.4           |
| C22-C23-H23A   | 120.4           |
| C9-C10-H10A    | 121.4           |
| C24-C23-H23A   | 120.4           |
| C10-C11-C19    | 119.7(3)        |
| C25-C24-C23    | 119.7(3)        |
| C10-C11-C12    | 134.3(3)        |
| C25-C24-H24A   | 120.1           |
| C19-C11-C12    | 105.9(2)        |
| C23-C24-H24A   | 120.1           |
| C13-C12-C17    | 120.9(3)        |
| C24-C25-C26    | 121.6(2)        |
| C13-C12-C11    | 130.7(3)        |
| C24-C25-H25A   | 119.2           |
| C17-C12-C11    | 108.0(2)        |
| C26-C25-H25A   | 119.2           |
| C14-C13-C12    | 118.2(3)        |
| C25-C26-C27    | 119.8(3)        |
| C14-C13-H13A   | 120.9           |
| C25-C26-H26A   | 120.1           |
| C12-C13-H13A   | 120.9           |
|                 | C27-C26-H26A    | 120.1           |
| Bond Lengths (Å) | C26-C27-C22 | 118.0(2) | C26-C27-C28 | 120.0(3) | C26-C27-C28 | 117.3(3) | C26-C27-C28 | 119.9(2) |
|------------------|-------------|----------|-------------|----------|-------------|----------|-------------|----------|
|                  | C26-C27-C28 | 133.8(2) | C27-C46-C51 | 123.9(2) | C27-C46-C51 | 119.1(2) |
|                  | C27-C46-C51 | 107.9(2) | C27-C46-C51 | 109.7(2) | C27-C46-C51 | 117.8(2) | C27-C46-C51 | 116.0(2) |
|                  | C27-C46-C51 | 109.7(2) | C27-C46-C51 | 130.2(2) | C27-C46-C51 | 109.7(2) | C27-C46-C51 | 109.7(2) |
|                  | C27-C46-C51 | 117.8(2) | C27-C46-C51 | 107.9(2) | C27-C46-C51 | 117.8(2) | C27-C46-C51 | 107.9(2) |
|                  | C27-C46-C51 | 116.0(2) | C27-C46-C51 | 130.2(2) | C27-C46-C51 | 116.0(2) | C27-C46-C51 | 130.2(2) |
|                  | C27-C46-C51 | 109.7(2) | C27-C46-C51 | 109.7(2) | C27-C46-C51 | 109.7(2) | C27-C46-C51 | 109.7(2) |
|                  | C27-C46-C51 | 119.1(2) | C27-C46-C51 | 123.9(2) | C27-C46-C51 | 119.1(2) | C27-C46-C51 | 123.9(2) |
|                  | C27-C46-C51 | 123.0(2) | C27-C46-C51 | 123.0(2) | C27-C46-C51 | 123.0(2) | C27-C46-C51 | 123.0(2) |
|                  | C27-C46-C51 | 123.0(2) | C27-C46-C51 | 123.0(2) | C27-C46-C51 | 123.0(2) | C27-C46-C51 | 123.0(2) |
|                  | C27-C46-C51 | 123.0(2) | C27-C46-C51 | 123.0(2) | C27-C46-C51 | 123.0(2) | C27-C46-C51 | 123.0(2) |
|                  | C27-C46-C51 | 123.0(2) | C27-C46-C51 | 123.0(2) | C27-C46-C51 | 123.0(2) | C27-C46-C51 | 123.0(2) |
|                  | C27-C46-C51 | 123.0(2) | C27-C46-C51 | 123.0(2) | C27-C46-C51 | 123.0(2) | C27-C46-C51 | 123.0(2) |

**Notes:**
1. All bond lengths are given in Ångströms (Å).
2. Values in parentheses indicate the standard deviation.
Table 4. Anisotropic displacement parameters (Å² x 10²) for 32-H. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [ h^2 a^* U_{11} + \ldots + 2 h k a^* b^* U_{12} ]$

|      | U_{11}  | U_{22}  | U_{33}  | U_{23}  | U_{13}  | U_{12}  |
|------|---------|---------|---------|---------|---------|---------|
| C63-C62-H62A | 120.5   | 58(1)   | -26(1)  | -10(1)  | -6(1)   |
| C61-C62-H62A | 120.5   | 44(1)   | 12(1)   | 0(1)    | -12(1)  |
| C62-C63-C64  | 121.2(3)| 58(1)   | -26(1)  | -10(1)  | -6(1)   |
| C62-C63-H63A | 119.4   | 12(1)   | -6(1)   | -12(1)  | -5(1)   |
| C64-C63-H63A | 119.4   | 12(1)   | -6(1)   | -12(1)  | -5(1)   |
| C63-C64-C59  | 120.5(3)| 58(1)   | -26(1)  | -10(1)  | -6(1)   |
| C63-C64-H64A | 119.8   | 12(1)   | -6(1)   | -12(1)  | -5(1)   |
| C59-C64-H64A | 119.8   | 12(1)   | -6(1)   | -12(1)  | -5(1)   |
| C78-C65-C66  | 121.7(3)| 58(1)   | -26(1)  | -10(1)  | -6(1)   |
| C78-C65-C50  | 121.4(3)| 58(1)   | -26(1)  | -10(1)  | -6(1)   |
| C66-C65-C50  | 121.4(3)| 58(1)   | -26(1)  | -10(1)  | -6(1)   |
| C67-C66-C71  | 121.0(3)| 58(1)   | -26(1)  | -10(1)  | -6(1)   |
| C67-C66-C65  | 122.2(3)| 58(1)   | -26(1)  | -10(1)  | -6(1)   |
| C71-C66-C65  | 116.8(3)| 58(1)   | -26(1)  | -10(1)  | -6(1)   |
| C66-C67-C68  | 120.2(4)| 58(1)   | -26(1)  | -10(1)  | -6(1)   |
| C66-C67-H67A | 119.9   | 58(1)   | -26(1)  | -10(1)  | -6(1)   |
| C68-C67-H67A | 119.9   | 58(1)   | -26(1)  | -10(1)  | -6(1)   |
| C69-C68-C67  | 118.4(4)| 58(1)   | -26(1)  | -10(1)  | -6(1)   |
| C69-C68-H68A | 120.8   | 58(1)   | -26(1)  | -10(1)  | -6(1)   |
| C67-C68-H68A | 120.8   | 58(1)   | -26(1)  | -10(1)  | -6(1)   |
| C70-C69-C68  | 122.6(4)| 58(1)   | -26(1)  | -10(1)  | -6(1)   |
| C70-C69-H69A | 118.7   | 58(1)   | -26(1)  | -10(1)  | -6(1)   |
| C68-C69-H69A | 118.7   | 58(1)   | -26(1)  | -10(1)  | -6(1)   |
| C69-C70-C71  | 121.4(4)| 58(1)   | -26(1)  | -10(1)  | -6(1)   |
| C69-C70-H70A | 119.3   | 58(1)   | -26(1)  | -10(1)  | -6(1)   |

Symmetry transformations used to generate equivalent atoms:
| C20 | 27(1) | 24(2) | 25(2) | -5(1) | -2(1) | -8(1) |
| C21 | 24(1) | 24(2) | 23(2) | -8(1) | -2(1) | -5(1) |
| C22 | 24(1) | 26(2) | 23(2) | -10(1) | -2(1) | -5(1) |
| C23 | 27(1) | 22(2) | 25(2) | -6(1) | -2(1) | -4(1) |
| C24 | 27(2) | 30(2) | 28(2) | -10(1) | -8(1) | -1(1) |
| C25 | 20(1) | 36(2) | 31(2) | -14(1) | 1(1) | -9(1) |
| C26 | 22(1) | 23(2) | 25(2) | -8(1) | -1(1) | -5(1) |
| C27 | 24(1) | 23(1) | 20(1) | -9(1) | 1(1) | -3(1) |
| C28 | 20(1) | 25(2) | 24(2) | -12(1) | 0(1) | -4(1) |
| C29 | 22(1) | 21(1) | 23(2) | -7(1) | -1(1) | -4(1) |
| C30 | 21(1) | 20(1) | 24(2) | -10(1) | 0(1) | -4(1) |
| C31 | 21(1) | 23(1) | 24(2) | -11(1) | 1(1) | -2(1) |
| C32 | 20(1) | 28(2) | 24(2) | -13(1) | -1(1) | 2(1) |
| C33 | 22(1) | 27(2) | 28(2) | -13(1) | 3(1) | -3(1) |
| C34 | 23(1) | 36(2) | 36(2) | -21(2) | -2(1) | -3(1) |
| C35 | 24(1) | 39(2) | 34(2) | -19(2) | -8(1) | -1(1) |
| C36 | 29(2) | 28(2) | 30(2) | -13(1) | -8(1) | 2(1) |
| C37 | 24(1) | 24(2) | 28(2) | -13(1) | -3(1) | 0(1) |
| C38 | 28(1) | 21(1) | 20(1) | -9(1) | -1(1) | -2(1) |
| C39 | 22(1) | 21(1) | 22(2) | -12(1) | 0(1) | -2(1) |
| C40 | 21(1) | 22(1) | 16(1) | -6(1) | 2(1) | -5(1) |
| C41 | 22(1) | 20(1) | 22(2) | -9(1) | 4(1) | -4(1) |
| C42 | 23(1) | 15(1) | 26(2) | -5(1) | -2(1) | -2(1) |
| C43 | 22(1) | 23(2) | 31(2) | -10(1) | 1(1) | -4(1) |
| C44 | 30(2) | 23(2) | 32(2) | -10(1) | -5(1) | -2(1) |
| C45 | 23(1) | 24(2) | 44(2) | -17(1) | -5(1) | -1(1) |
| C46 | 24(1) | 23(2) | 36(2) | -10(1) | 3(1) | -4(1) |
| C47 | 28(2) | 21(1) | 24(2) | -4(1) | -4(1) | -4(1) |
| C48 | 29(1) | 21(1) | 19(2) | -9(1) | 4(1) | -6(1) |
| C49 | 27(1) | 22(1) | 23(2) | -11(1) | -2(1) | -1(1) |
| C50 | 39(2) | 25(2) | 21(2) | -4(1) | -7(1) | -7(1) |
| C51 | 37(2) | 30(2) | 34(2) | -8(1) | -13(1) | -8(1) |
| C52 | 41(2) | 31(2) | 41(2) | -14(2) | -18(2) | 1(1) |
| C53 | 38(2) | 44(2) | 52(2) | -15(2) | -13(2) | -2(2) |
| C54 | 47(2) | 69(3) | 67(3) | -6(2) | -32(2) | 4(2) |
| C55 | 55(2) | 74(3) | 48(2) | 9(2) | -21(2) | 9(2) |
| C56 | 46(2) | 61(2) | 35(2) | -3(2) | -14(2) | -12(2) |
| C57 | 24(1) | 21(2) | 17(1) | -3(1) | 1(1) | -3(1) |
| C58 | 28(1) | 24(2) | 21(2) | -6(1) | 2(1) | -3(1) |
| C59 | 20(1) | 23(2) | 32(2) | -6(1) | -1(1) | 0(1) |
| C60 | 27(2) | 23(2) | 41(2) | -9(1) | 2(1) | -6(1) |
| C61 | 35(2) | 34(2) | 48(2) | -14(2) | -5(2) | -9(1) |
| C62 | 36(2) | 42(2) | 58(2) | -16(2) | -9(2) | -14(2) |
| C63 | 28(2) | 36(2) | 51(2) | -2(2) | -1(1) | -15(1) |
| C64 | 28(2) | 34(2) | 33(2) | -2(2) | -5(1) | -4(1) |
| C65 | 50(2) | 21(2) | 17(2) | -3(1) | -2(1) | -3(1) |
| C66 | 66(2) | 26(2) | 24(2) | -5(1) | -6(2) | -6(2) |
| C67 | 81(3) | 45(2) | 28(2) | -8(2) | -2(2) | -27(2) |
| C68 | 99(3) | 50(2) | 47(2) | -19(2) | 1(2) | -36(2) |
| C69 | 100(3) | 47(2) | 30(2) | -17(2) | 5(2) | -27(2) |
| C70 | 86(3) | 40(2) | 35(2) | -18(2) | 0(2) | -3(2) |
| C71 | 73(2) | 22(2) | 21(2) | -8(1) | 4(2) | 2(2) |
| C72 | 56(2) | 30(2) | 28(2) | -5(2) | -2(2) | 8(2) |
| C73 | 66(3) | 51(2) | 29(2) | -13(2) | 4(2) | 13(2) |
| C74 | 51(2) | 60(3) | 47(2) | -11(2) | 3(2) | 17(2) |
| C75 | 44(2) | 56(2) | 36(2) | -5(2) | 3(2) | 8(2) |
|      | C76 | 34(2) | 37(2) | 31(2) | l(2) | 5(1) | 3(1) |
|------|-----|--------|--------|--------|------|------|------|
| C77  | 54(2) | 25(2)  | 20(2)  | -1(1)  | 5(1) | 3(1) |
| C78  | 43(2) | 20(2)  | 19(2)  | -4(1)  | 1(1) | 1(1) |

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for 32-H.

|      | x    | y    | z    | U(eq) |
|------|------|------|------|-------|
| H3A  | 6054 | 596  | 5023 | 38    |
| H4A  | 7585 | -753 | 5349 | 47    |
| H5A  | 7437 | -2132| 6645 | 53    |
| H6A  | 5692 | -2209| 7608 | 57    |
| H10A | 1380 | 301  | 7413 | 44    |
| H13A | -798 | 1507 | 7213 | 42    |
| H14A | -2334| 2823 | 6806 | 44    |
| H15A | -2104| 4207 | 5552 | 42    |
| H16A | -346 | 4304 | 4612 | 36    |
| H23A | 6021 | 1500 | 5876 | 31    |
| H24A | 7814 | 1984 | 5452 | 35    |
| H25A | 8144 | 3325 | 4166 | 35    |
| H26A | 6675 | 4293 | 3350 | 30    |
| H33A | 231  | 3323 | 3643 | 32    |
| H34A | -949 | 3827 | 2579 | 37    |
| H35A | -749 | 5236 | 1318 | 37    |
| H36A | 623  | 6157 | 1090 | 35    |
| H43A | 4667 | 5725 | 4120 | 32    |
| H44A | 6256 | 5935 | 4489 | 35    |
| H46A | 7965 | 6338 | 2069 | 36    |
| H47A | 6400 | 6059 | 1726 | 32    |
| H52A | 519  | 7382 | 1916 | 45    |
| H53A | -1293| 8284 | 1589 | 56    |
| H54A | -1537| 9258 | 135  | 81    |
| H55A | 20   | 9306 | -959 | 83    |
| H56A | 1826 | 8427 | -639 | 61    |
| H60A | 4353 | 7679 | 2656 | 39    |
| H61A | 5315 | 8672 | 2823 | 47    |
| H62A | 6402 | 9698 | 1614 | 54    |
| H63A | 6404 | 9770 | 253  | 51    |
| H64A | 5471 | 8755 | 82   | 44    |
| H67A | 1923 | 6596 | -144 | 62    |
| H68A | 2068 | 5874 | -1128| 76    |
| H69A | 3856 | 5534 | -1910| 70    |
| H70A | 5494 | 5714 | -1646| 68    |
| H73A | 6936 | 5959 | -1471| 68    |
| H74A | 8554 | 6230 | -1240| 77    |
| H75A | 8475 | 6849 | -220 | 67    |
| H76A | 6694 | 7253 | 557  | 52    |
### Supplementary Information

**Table 6.** Torsion angles [°] for 32-H.

|          | C9-C1-C2-C3 | C10-C11-C19-C18 | C177(3) |
|----------|--------------|-----------------|----------|
| C20-C1-C2-C3 | -8.4(5)     | C12-C11-C19-C18 | -4.7(3)  |
| C9-C1-C2-C7  | -6.4(3)      | C10-C11-C19-C20 | -7.3(4)  |
| C20-C1-C2-C7  | 178.9(3)    | C12-C11-C19-C20 | 170.1(3) |
| C7-C2-C3-C4  | -5.0(4)      | C18-C19-C20-C21 | 14.3(4)  |
| C1-C2-C3-C4  | -177.0(3)    | C11-C19-C20-C21 | -159.6(3)|
| C2-C3-C4-C5  | 1.4(4)       | C18-C19-C20-C21 | -169.5(3)|
| C3-C4-C5-C6  | 2.2(5)       | C11-C19-C20-C21 | 16.5(4)  |
| C4-C5-C6-C7  | -2.0(5)      | C9-C1-C20-C21   | 160.4(3) |
| C5-C6-C7-C2  | -1.7(5)      | C2-C1-C20-C21   | -25.4(5) |
| C5-C6-C7-C8  | 173.9(3)     | C9-C1-C20-C19   | -14.9(4) |
| C3-C2-C7-C6  | 5.3(5)       | C2-C1-C20-C19   | 159.3(3) |
| C1-C2-C7-C6  | 179.0(3)     | C19-C20-C21-C29 | -15.2(4) |
| C3-C2-C7-C8  | -171.1(3)    | C1-C20-C21-C29  | 169.5(3) |
| C1-C2-C7-C8  | 2.6(3)       | C19-C20-C21-C22 | 161.2(3) |
| C6-C7-C8-O1  | 4.9(6)       | C1-C20-C21-C22  | -14.1(5) |
| C2-C7-C8-O1  | -179.0(3)    | C20-C21-C22-C23 | -6.1(5)  |
| C6-C7-C8-C9  | -174.3(3)    | C29-C21-C22-C23 | 170.6(3) |
| C2-C7-C8-C9  | 1.8(3)       | C20-C21-C22-C27 | 178.5(3) |
| C20-C1-C9-C10 | 5.0(5)      | C29-C21-C22-C27 | -4.8(3)  |
| C2-C1-C9-C10 | -170.5(3)    | C27-C22-C23-C24 | -6.6(4)  |
| C20-C1-C9-C8  | -177.1(3)    | C21-C22-C23-C24 | 178.5(3) |
| C2-C1-C9-C8  | 7.4(3)       | C22-C23-C24-C25 | -0.2(4)  |
| O1-C8-C9-C1  | 175.0(3)     | C23-C24-C25-C26 | 3.9(4)   |
| C7-C8-C9-C1  | -5.8(3)      | C24-C25-C26-C27 | -0.6(4)  |
| O1-C8-C9-C10 | -7.2(6)      | C25-C26-C27-C22 | -6.1(4)  |
| C7-C8-C9-C10 | 171.9(3)     | C25-C26-C27-C28 | 174.2(3) |
| C1-C9-C10-C11 | 5.0(5)      | C23-C22-C27-C26 | 9.7(4)   |
| C8-C9-C10-C11 | -172.4(3)   | C21-C22-C27-C26 | -174.4(2)|
| C9-C10-C11-C19 | -3.9(4)     | C23-C22-C27-C28 | -170.5(2)|
| C9-C10-C11-C12 | 179.6(3)    | C21-C22-C27-C28 | 5.4(3)   |
| C10-C11-C12-C13 | 7.1(6)     | C26-C27-C28-C40 | -5.6(5)  |
| C19-C11-C12-C13 | -169.7(3)  | C22-C27-C28-C40 | 174.6(3) |
| C10-C11-C12-C17 | 179.1(3)    | C26-C27-C28-C29 | 175.8(3) |
| C19-C11-C12-C17 | 2.3(3)      | C22-C27-C28-C29 | -3.9(3)  |
| C17-C12-C13-C14 | -1.4(4)     | C20-C21-C29-C28 | 179.6(2) |
| C11-C12-C13-C14 | 169.8(3)    | C22-C21-C29-C28 | 2.3(3)   |
| C12-C13-C14-C15 | -0.8(4)     | C20-C21-C29-C30 | 1.5(4)   |
| C13-C14-C15-C16 | 1.8(4)      | C22-C21-C29-C30 | -175.7(2)|
| C14-C15-C16-C17 | -0.5(4)     | C40-C28-C29-C21 | -178.0(2)|
| C15-C16-C17-C12 | -1.7(4)     | C27-C28-C29-C21 | 0.9(3)   |
| C15-C16-C17-C18 | -170.4(3)   | C40-C28-C29-C30 | 0.0(4)   |
| C13-C12-C17-C16 | 2.6(4)      | C27-C28-C29-C30 | 178.9(2) |
| C11-C12-C17-C16 | -170.3(3)   | C19-C18-C30-C31 | 165.6(3) |
| C13-C12-C17-C18 | 173.7(3)    | C17-C18-C30-C31 | -26.4(5) |
| C11-C12-C17-C18 | 0.7(3)      | C19-C18-C30-C29 | -15.4(4) |
| C16-C17-C18-C19 | 166.2(3)    | C17-C18-C30-C29 | 152.7(3) |
| C12-C17-C18-C19 | -3.6(3)     | C21-C29-C30-C18 | 14.4(4)  |
| C16-C17-C18-C30 | -2.9(5)     | C28-C29-C30-C18 | -163.4(2)|
| C12-C17-C18-C30 | -172.6(3)   | C21-C29-C30-C31 | -166.4(3)|
| C30-C18-C19-C20 | 1.5(4)      | C28-C29-C30-C31 | 15.8(4)  |
| C17-C18-C19-C20 | -169.5(3)   | C18-C30-C31-C39 | 162.2(3) |
| C30-C18-C19-C11 | 176.2(2)    | C29-C30-C31-C39 | -16.8(3) |
| C17-C18-C19-C11 | 5.2(3)      | C18-C30-C31-C32 | -26.1(5) |
| Bond                  | Distance (Å) |
|-----------------------|--------------|
| C59-C60-C61-C62       | 2.3(4)       |
| C60-C61-C62-C63       | 2.4(5)       |
| C61-C62-C63-C64       | -3.1(5)      |
| C62-C63-C64-C59       | -1.0(5)      |
| C60-C59-C64-C63       | 5.6(4)       |
| C58-C59-C64-C63       | 176.6(3)     |
| C51-C50-C65-C78       | 147.2(3)     |
| C49-C50-C65-C78       | -69.7(3)     |
| C57-C50-C65-C78       | 29.3(3)      |
| C51-C50-C65-C66       | -45.6(4)     |
| C49-C50-C65-C66       | 97.6(3)      |
| C57-C50-C65-C66       | -163.4(3)    |
| C78-C65-C66-C67       | 173.3(3)     |
| C50-C65-C66-C67       | 7.5(5)       |
| C78-C65-C66-C71       | -4.8(4)      |
| C50-C65-C66-C71       | -170.7(3)    |
| C71-C66-C67-C68       | -2.7(5)      |
| C65-C66-C67-C68       | 179.2(3)     |
| C66-C67-C68-C69       | -0.2(5)      |
| C67-C68-C69-C70       | 3.7(6)       |
| C68-C69-C70-C71       | -4.2(6)      |
| C69-C70-C71-C72       | 179.9(3)     |
| C69-C70-C71-C66       | 1.2(5)       |
| C67-C66-C71-C70       | 2.2(4)       |
| C65-C66-C71-C70       | -179.6(3)    |
| C67-C66-C71-C72       | -176.5(3)    |
| C65-C66-C71-C72       | 1.7(4)       |
| C70-C71-C72-C77       | -177.4(3)    |
| C66-C71-C72-C77       | 1.1(5)       |
| C70-C71-C72-C73       | 2.5(5)       |
| C66-C71-C72-C73       | -178.9(3)    |
| C77-C72-C73-C74       | 0.9(5)       |
| C71-C72-C73-C74       | 179.2(3)     |
| C72-C73-C74-C75       | 2.0(6)       |
| C73-C74-C75-C76       | -1.1(6)      |
| C74-C75-C76-C77       | -1.0(5)      |
| C75-C76-C77-C72       | 2.1(5)       |
| C75-C76-C77-C78       | -178.1(3)    |
| C71-C72-C77-C76       | 178.8(3)     |
| C73-C72-C77-C76       | -1.2(4)      |
| C71-C72-C77-C78       | -1.0(4)      |
| C73-C72-C77-C78       | 179.0(3)     |
| C66-C65-C78-C77       | 5.1(4)       |
| C50-C65-C78-C77       | 173.3(2)     |
| C66-C65-C78-C58       | -165.9(2)    |
| C50-C65-C78-C58       | 2.3(3)       |
| C76-C77-C78-C65       | 178.1(3)     |
| C72-C77-C78-C65       | -2.1(4)      |
| C76-C77-C78-C58       | -12.8(5)     |
| C72-C77-C78-C58       | 167.0(3)     |
| C59-C58-C78-C65       | -149.5(3)    |
| C57-C58-C78-C65       | -32.9(3)     |
| C48-C58-C78-C65       | 65.4(3)      |
| C59-C58-C78-C77       | 40.3(4)      |
| C57-C58-C78-C77       | 156.8(3)     |
| C48-C58-C78-C77       | -104.8(3)    |
VI. References for Supporting Information

1. Hoye, T. R., Hanson, P. R. & Vyvyan, J. R. A practical guide to first-order multiplet analysis in $^1$H NMR spectroscopy. *J. Org. Chem.* 59, 4096–4103 (1994).

2. Hoye, T. R. & Zhao, H. A method for easily determining coupling constant (J) values: An addendum to "A practical guide to first-order multiplet analysis in $^1$H NMR spectroscopy." *J. Org. Chem.* 67, 4014–4016 (2002).

3. Willoughby, P. H. *et al.* Mechanism of the reactions of alcohols with o-benzynes. *J. Am. Chem. Soc.* 136, 13657–13665 (2014).

4. Guo, L., Hrabusa, J. M., Tessier, C. A., Youngs, W. J. & Lattimer, R. Syntheses and crystal structures of strained planar silacyclynes containing a diacetylene unit. *J. Organomet. Chem.* 578, 43–54 (1999).

5. Spence, J. D. *et al.* Syntheses, structure, and reactivity of acyclic enetriyne and enetetrayne derivatives. *Tetrahedron Lett.* 55, 1569–1572 (2014).

6. Nobusue, S. *et al.* Molecular propellers that consist of dehydrobenzo[14]annulene blades. *Chem. Eur. J.* 18, 12814–12824 (2012).

7. Dateer, R. B., Shaibu, B. S. & Liu, R. S. Gold-catalyzed intermolecular [4+2] and [2+2+2] cycloadditions of ynamides with alkenes. *Angew. Chem. Int. Ed.* 51, 113 (2012).

8. Laroche, C., Li, J., Freyer, M. W. & Kerwin, S. M. Coupling reactions of bromoalkynes with imidazoles mediated by copper salts: Synthesis of novel N-alkynylimidazoles. *J. Org. Chem.* 73, 6462–6465 (2008).

9. Suffert, J., Abraham, E., Raeppel, S. & Brückner, R. Synthesis of 5-/10-membered ring analogues of the dienediyne core of neocarzinostatine chromophore by palladium(0)-mediated ring-closure reaction. *Liebigs Ann.* 1996, 447–456 (1996).

10. Lehnherr, D., Alzola, J. M., Lobkovsky, E. B. & Dichtel, W. R. Regioselective synthesis of polyheterohalogenated naphthalenes via the benzannulation of haloalkynes. *Chem. Eur. J.* 21, 18122–18127 (2015).

11. Xu, F., Xiao, X. & Hoye, T. R. Photochemical hexadehydro-Diels–Alder reaction. *J. Am. Chem. Soc.* 139, 8400–8403 (2017).

12. Wooi, G. Y. & White, J. M. Structural manifestations of the cheletropic reaction. *Org. Biomol. Chem.* 3, 972–974 (2005).

13. Dennis, G. D. *et al.* Fused supracyclopentadienyl ligand precursors. Synthesis, structure, and some reactions of 1,3-diphenylcyclopenta[l]phenanthrene-2-one, 1,2,3-triphenylcyclopenta[l]phenanthrene-2-ol, 1-chloro-1,2,3-triphenylcyclopenta[l]phenanthrene,
1-bromo-1,2,3-triphenylcyclopenta[l]phenanthrene, and 1,2,3-triphenyl-1h-cyclopenta[l]phenanthrene. *Aust. J. Chem.* 59, 135–146 (2006).

14 Pascal, R. A. Twisted acenes. *Chem. Rev.* 106, 4809–4819 (2006).

15 Hashmi, A. S. K. *et al.* Scope and limitations of palladium-catalyzed cross-coupling reactions with organogold compounds. *Adv. Synth. Catal.* 352, 1307–1314 (2010).

16 Frisch, M. J. *et al.* *Gaussian 09*, revision C.01; Gaussian Inc.: Wallingford, CT (2010).

17 Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *Ab initio* calculation of vibrational absorption and circular dichroism spectra using density functional force fields. *J. Phys. Chem.* 98, 11623–11627 (1994).

18 Grimme, S., Antony, J., Ehrlich, S. & Krieg, H. A consistent and accurate *ab initio* parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* 132, 154104 (2010).

19 Johnson, E. R. & Becke, A. D. A post-Hartree-Fock model of intermolecular interactions: Inclusion of higher-order corrections. *J. Chem. Phys.* 124, 174104 (2006).

20 Marenich, A. V.; Cramer, C. J.; and Truhlar, D. G. Universal solvation model based on solute electron density and on a continuum model of the solvent defined by the bulk dielectric constant and atomic surface tensions. *J. Phys. Chem. B*, 113, 6378–6396 (2009).

21 Wiitala, K. W., Hoye, T. R. & Cramer, C. J. Hybrid density functional methods empirically optimized for the computation of $^{13}$C and $^1$H chemical shifts in chloroform solution. *J. Chem. Theory Comput.* 2, 1085–1092 (2006).

22 CYLview, 1.0b; Legault, C. Y., Université de Sherbrooke, 2009 (*http://www.cylview.org*).

**VII. Copies of $^1$H, and $^{13}$C NMR spectra**
Supplementary Information

S1
$^1$H NMR
500 MHz
CDCl$_3$
Supplementary Information

13C NMR
126 MHz
CDCl₃

δ (ppm)

85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5
**S7**

$^1$H NMR  
500 MHz  
CDCl$_3$  

- 4.45
- 4.44
- 3.45
- 1.67
- 1.64
- 1.26
$^{13}$C NMR
126 MHz
CDCl$_3$
$^{13}$C NMR
126 MHz
CDCl$_3$
$^{13}$C NMR
126 MHz
CDCl$_3$
$^{13}$C NMR
126 MHz
CDCl$_3$

**S17**

- Ts
- TMS
- MeO
- OMe

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)
$^{1}H$ NMR
500 MHz
CDCl$_3$

13

OTBS

-7.26 CDCl$_3$
-4.83
-4.36
2.95
2.51
2.52
1.54 HDO
9.00
0.12

f1 (ppm)

7.5  8.0  8.5  9.0  9.5 10.0 10.5 11.0 11.5 12.0 12.5 13.0 13.5 14.0 14.5 15.0 15.5 16.0

2.00 2.18 2.92 3.00 8.37 9.65 6.39

0.00
$^{13}$C NMR
126 MHz
CDCl$_3$
$^{1}$H NMR
500 MHz
CDCl$_3$
$^{1}$H NMR
500 MHz
CDCl$_3$

![NMR Spectrum of Compound 20](image)
Supplementary Information

$^{13}$C NMR
126 MHz
CDCl$_3$

Diagram of chemical structure with spectral data.
**Supplementary Information**

**13C NMR**

126 MHz

**CDCl₃**

**Chemical Shifts:**

- 25.0
- 30.0
- 40.0
- 50.0
- 60.0
- 70.0
- 80.0
- 90.0
- 100.0
- 110.0
- 120.0
- 130.0
- 140.0
- 150.0
- 160.0
- 170.0
- 180.0

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Supplementary Information

\[ 25f \]

\[^{13}\text{C}\] NMR
126 MHz
CDCl\(_3\)

\[ \text{MeO}_2\text{C} \]

\[ \text{MeO}_2\text{C} \]

\[ \text{Ph} \]

\[ \text{Ph} \]

\[ \text{Ph} \]

\[ \text{Ph} \]
1H NMR
500 MHz
CDCl₃

25i
CO₂Me

TMS
$^{13}$C NMR
126 MHz
CDCl$_3$
Supplementary Information

1H NMR
500 MHz
CDCl₃
Supplementary Information

$^1$H NMR
500 MHz
CDCl$_3$
$^{13}$C NMR
126 MHz
CDCl$_3$

25m
Supplementary Information

25m′

$^1$H NMR
500 MHz
CDCl$_3$
Supplementary Information

1H NMR
500 MHz
CDCl₃

25n' +25n

Ph

MeO₂C

N
\(\text{13C NMR} \quad 126 \text{ MHz} \quad \text{CDCl}_3\)
250

$^{13}$C NMR
126 MHz
CDCl$_3$
$^1$H NMR 
500 MHz
CDCl$_3$
$^1$H NMR
500 MHz
CDCl$_3$
30
$^1$H NMR
500 MHz
CDCl$_3$
Supplementary Information

1H NMR
C₆D₆
500 MHz

32-H Cl
