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Photochemical Synthesis of Both Strained and Macrocyclic (1,7)Naphthalenophanes

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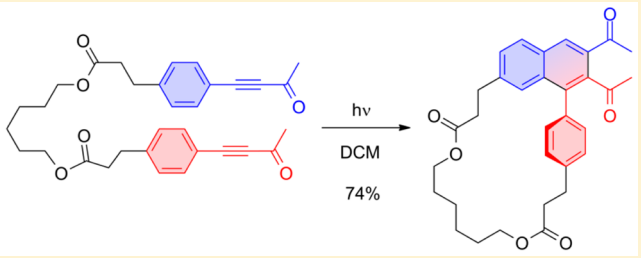
Supporting Information

ABSTRACT: Naphthalenophanes are a special type of cyclophanes. While in the past (1,5)-, (1,6)-, and (1,8)-naphthalenophanes were successfully prepared by using the photo-dehydro-Diels–Alder (DDA) reaction, access to (1,7)-naphthalenophanes by this method was hitherto unknown. After numerous unsuccessful attempts to prepare these compounds by thermal DDA, we found that the photoinitiated variant (PDDA) represents a very efficient method to [*k*](1,7)naphthalenophanes **13**. The scope ranged from highly strained (*k* = 11, 12) to macrocyclic products (*k* = 22, 24). The extraordinary reactivity could be explained by folded ground-state geometries of diketones **12** used as reactants of the PDDA. Furthermore, we calculated the ring-strain energies with the help of an isodesmic reaction and evaluated structural and spectroscopic (NMR) consequences of ring strain.



INTRODUCTION

Although the arsenal of synthetic methods is enormous today and seemingly every thinkable molecule can be prepared, there are still a number of challenging tasks. One of them is the synthesis of highly strained molecules due to their intrinsic reactivity and pronounced tendency to reduce the strain by rearrangement and decomposition reactions. Another challenge is the efficient synthesis of macrocyclic compounds, which are widely distributed in nature. Here, the difficulties arise mainly from entropically disfavored formation of large rings compared with the competing polymerization. Common strategies to overcome these problems are to use either large dilution (Ruggli–Ziegler dilution principle) or template effects.

The synthesis of cyclophanes, i.e., molecules consisting of an aromatic core and a chain forming a bridge between two nonadjacent atoms of this core, is often associated with one or both of the problems mentioned above.[1] If the aromatic core is a naphthalene scaffold, this type of cyclophanes is called naphthalenophane.[2] There are basically two strategies to synthesize naphthalenophanes: either the bridging chain is tethered at a naphthalene moiety already present or the naphthalene moiety is formed in the cyclization reaction. Pursuing the latter approach, we recently reported on the preparation of a series of naphthalenophanes[3] based on the application of the dehydro-Diels–Alder (DDA) reaction.[4] The DDA reaction differs from the classical Diels–Alder (DA) reaction in that at least one double bond of the diene moiety is replaced by a triple bond.

As a result, the DDA reaction proceeds in contrast to the DA reaction stepwise and diradicals and highly strained cycloallenes are assumed to be intermediates of the DDA reaction. Furthermore, the DDA reaction can be initiated both thermally and photochemically (with regard to the mechanistic details we refer to previous publications[4]).

The synthetic strategy toward naphthalenophanes **2** applied in our previous work is outlined in Figure 1. Thus, two 3-arylynones **1a** (R = alkyl),[3a−c] 3-arylpropiolic esters **1b** (R = alkoxy),[3c] or 3-arylpropiolic acids **1c** (R = hydroxy)[3c] are connected by a variable linker unit X. Whereas ketones **1a** and esters **1b** undergo the DDA reaction upon irradiation (photo-dehydro-Diels–Alder reaction, PDDA), the ring closure of carboxylic acids **1c** proceeds by first forming cyclic anhydrides **3** mediated by carbodiimides. In this way, we prepared (1,5)-, (1,6)-, and (1,8)naphthalenophanes **A**–**C** while (1,7)-naphthalenophanes **D** are still a "missing link" in this array (Figure 2).

Herein, we report on the efficient synthesis of (1,7)-naphthalenophanes as well as on their properties.

RESULTS AND DISCUSSION

1. Attempted Thermal Synthesis of (1,7)Naphthalenophanes. Based on the good results we previously achieved for the synthesis of other naphthalenophanes (cf. Figure 1), we first explored the thermal synthesis of (1,7)naphthalenophanes. The established method for mild DDA to arylnaphthalenes comprises the in situ preparation of 3-substituted propiolic anhydrides by treatment with reagents activating the carboxylic group. In most cases, carbodiimides were used for this task. In these anhydrides, the alkyne moieties are brought in spatial proximity by lowering the activation barrier of the DDA. To apply this approach to (1,7)naphthalenophanes we chose a

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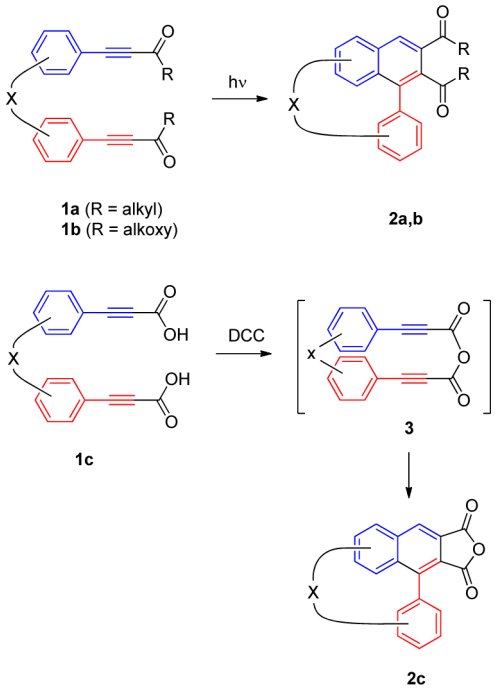


Figure 1. Formation of naphthalenophanes **2** from diynes **1**.

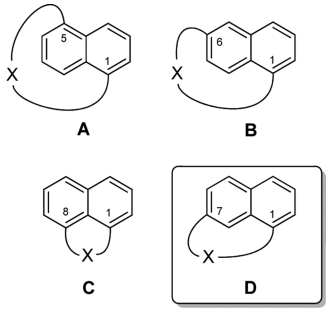


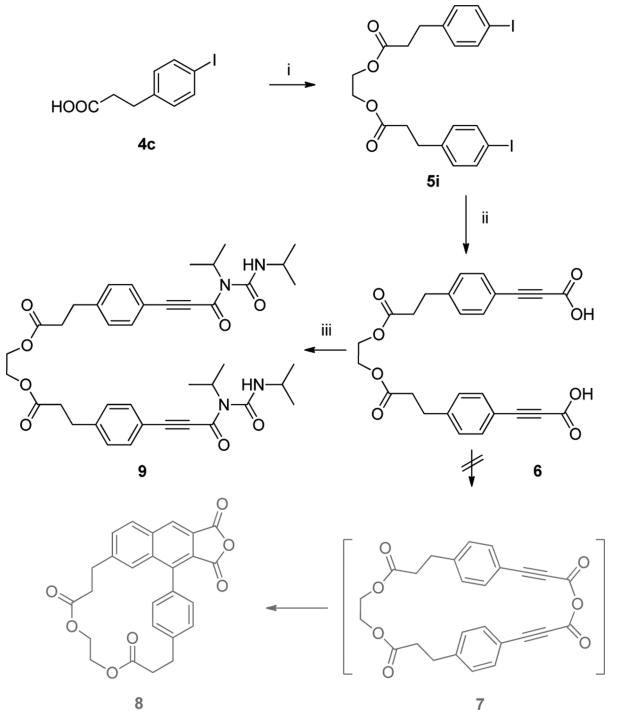
Figure 2. Structure of (1,5)-, (1,6)-, (1,8)-, and (1,7)-naphthalenophanes **A**–**D**.

medium linker length (10 atoms) to rule out the prevention of product formation by too small (ring strain) or too large (macrocycles) ring sizes. We started with 3-(4-iodophenyl)-propanoic acid **4c**,[5] which was converted into the diester **5i** by treatment with diisopropyl carbodiimide (DIC)/DMAP[6] in good yield. The subsequent Sonogashira coupling with propiolic acid furnished the dicarboxylic acid **6** in nearly quantitative yield.[7]

Surprisingly, all attempts using various reagents and conditions (for details, see the SI) failed to convert compound **6** into the desired naphthalenophane **8** via the cyclic anhydride **7** (Scheme 1).

In cases where DIC was used as activating agent, we always isolated the diureide **9** as the main product. The formation of ureides as byproducts upon activation of carboxylic acids with carbodiimides is a long-standing problem. It is the result of a 1,3-acyl migration in the primarily formed *O*-acyl isourea (the adduct of a carboxylic acid on the carbodimide) that occurs if this species does not react fast enough with the nucleophile (in our case the second carboxylate) or no nucleophile is available. From this outcome, we concluded that the conformational equilibrium of diacid **6** is dominated by straight conformation

Scheme 1. Attempted Thermal Synthesis of (1,7)Naphthalenophane 8[a]



[a]Key: (i) DIC, DMAP, DCM, 50 °C, 72 h, 70%; (ii) $PdCl_2(PPh_3)_2$, DMSO, DBU, dppb, propiolic acid, 50 °C, 5 h, 96%; (iii) various conditions (see the SI).

with a large distance between the carboxylic groups preventing any reaction to the anhydride **7** and subsequent DDA to **8**.

2. Photochemical Synthesis of (1,7)Naphthalenophanes. Assuming that the reaction centers point to diametrically oriented directions, we doubted whether a synthesis of (1,7)naphthalenophanes starting from *para*-substituted arylalkynes such as **6** is possible at all. Nevertheless, the significant mechanistic differences between the thermal and photochemical variant of the DDA[4a] gave rise to the assumption that (1,7)naphthalenophanes could be accessible by the PDDA reaction. To verify this, we prepared a library of 12 diketones **12** in a three-step sequence. For this purpose, we combined three ω-(4-iodophenyl)carboxylic acids **4a**–**c** with six diols **10a**–**f**. Steglich esterification[6] of **4** with **10** afforded diiodides **5**.

By subsequent Sonogashira coupling with but-3-yn-2-ol we obtained the diols **11**. In the third step, compounds **11** were converted into diketones **12** by an Albright–Goldman oxidation (Scheme 2).[8] The yields of **5**, **11**, and **12** are summarized in Table 1.

With diketones **12** in hand, we investigated the photochemical reactivity of these compounds. The UV spectra of all compounds **12** exhibit a broad structured absorption band with a maximum at 276 nm (log ε = 4.54–4.70; for details see the SI). Compared with the parent compound 4-phenylbut-3-yn-2-one **14**,[4a,9] the absorption maxima of diones **12** are slightly (3 nm) but significantly red-shifted. Furthermore, the molar extinction coefficients ε of **12f**–**l** (n > 0) are consistently higher by 16–30%, compared with **14**. (The ε values for **12a**–**e** are not directly comparable with **14** because the chromophore is extended by an ester group.) These findings strongly suggest

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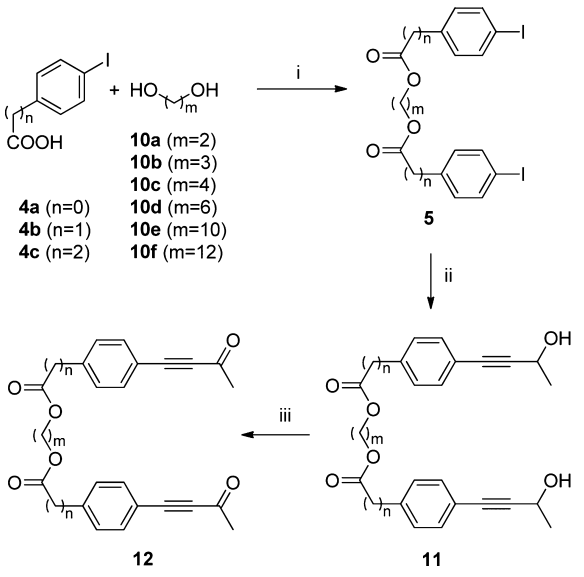
Scheme 2. Synthesis of Diketones 13[a]



[a]Key: (i) DIC, DMAP, DCM, 50 °C, 72 h; (ii) but-3-yn-2-ol, $PdCl_2(PPh_3)_2$, CuI, Et_3N, THF, rt, 24 h; (iii) DMSO, Ac_2O, rt, 24 h.

Table 1. Yields of Diiodides 5, Diols 11, and Diketones 12

	n	*m*	*N*[a]	5[b]	11[b]	12[b]
a	0	2	6	95	82	73
b	0	3	7	67	83	57
c	0	4	8	69	85	55
d	0	6	10	70	70	86
e	0	12	18	99	83	71
f	1	2	8	80	77	71
g	1	4	10	70	88	70
h	1	6	12	67	80	68
i	2	2	10	57	70	60
j	2	6	14	82	86	74
k	2	10	18	66	73	78
l	2	12	20	69	63	66

[a]$N = m + 2n + 4$. [b]Percent yields.

an interaction of the two chromophores in **12** in the ground state (see section 4).

To our great surprise, most of the diketones **12** exhibit a remarkable photochemical reactivity (excitation wavelength >300 nm) and smoothly cyclize to the corresponding [*k*](1,7)naphthalenophanes **13** (Scheme 3; *k* is the total number of atoms in the linker connecting positions 1 and 7 of naphthalene). As already mentioned, the PDDA reaction proceeds stepwise via biradicals **BR** and cycloallenes **CA**, which are also depicted in Scheme 3 for the reaction from **12** to **13**.

For $k > 12$, we obtained the target compounds in almost all cases with yields >50% (except **13e**). With decreasing length of the linker (**13b**,**c**), the yields decreased and **13a** bearing the shortest linker was not accessible by PDDA of **12a** (Table 2).

The structure of (1,7)naphthalenophanes **13** was unambiguously proven with the X-ray structure of **13i** (Figure 3).[10]

3. Mechanism of the PDDA to (1,7)Naphthalenophanes. As mentioned previously, we felt that diketones **12** exhibit an unusually high photochemical reactivity. To substantiate this impression, we compared their photokinetics with previously investigated *ortho*- and *meta*-substituted

Scheme 3. PDDA Reaction to (1,7)Naphthalenophanes 13 and Dimerization of the Parent Compound 14 to 15

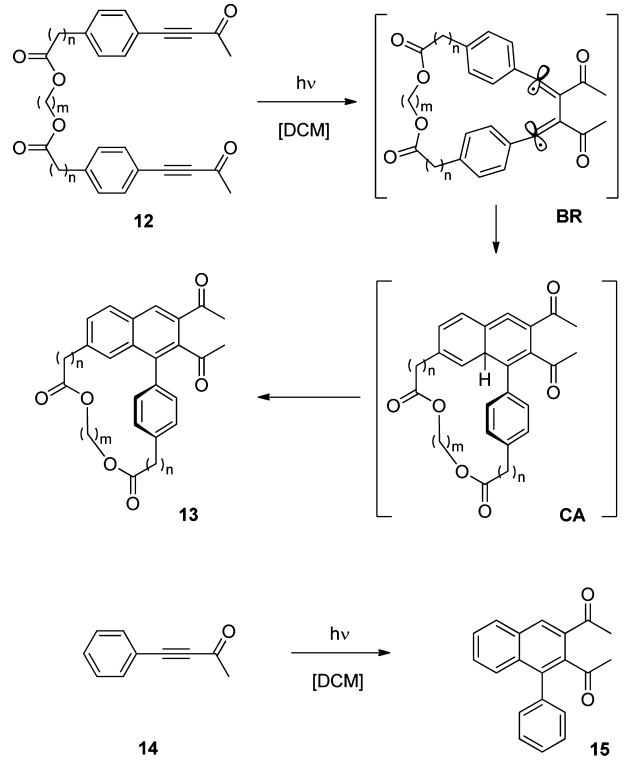


Table 2. Yields of [*k*](1,7)Naphthalenophanes 13a–l

	k[a]	yield[b] (%)		*k*[a]	yield[b] (%)
13a	10	0 (**12a**: 99)	**13g**	14	53
13b	11	33 (**12b**: 32)	**13h**	16	70
13c	12	47 (**12c**: 23)	**13i**	14	59
13d	14	70	**13j**	18	74
13e	22	39	**13k**	22	66
13f	12	52	**13l**	24	70

[a]$k = N + 4$. [b]Starting concentration for irradiation: 1.0 mM.

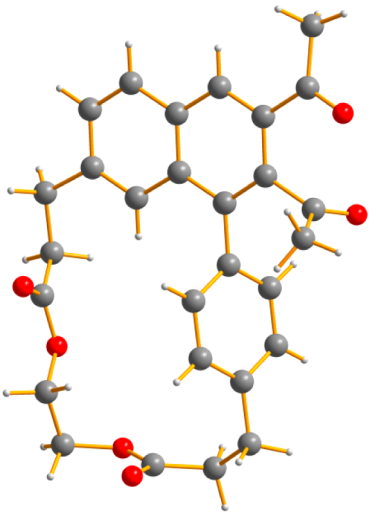


Figure 3. X-ray crystal structure of **13i**.

systems. For this purpose, we measured the decay rate of **12h** as well as of *ortho*-substituted precursor **16**[3a] and of *meta*-

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substituted precursor **17**.[3b] The degradation curves of these three compounds are depicted in Figure 4. It is clearly

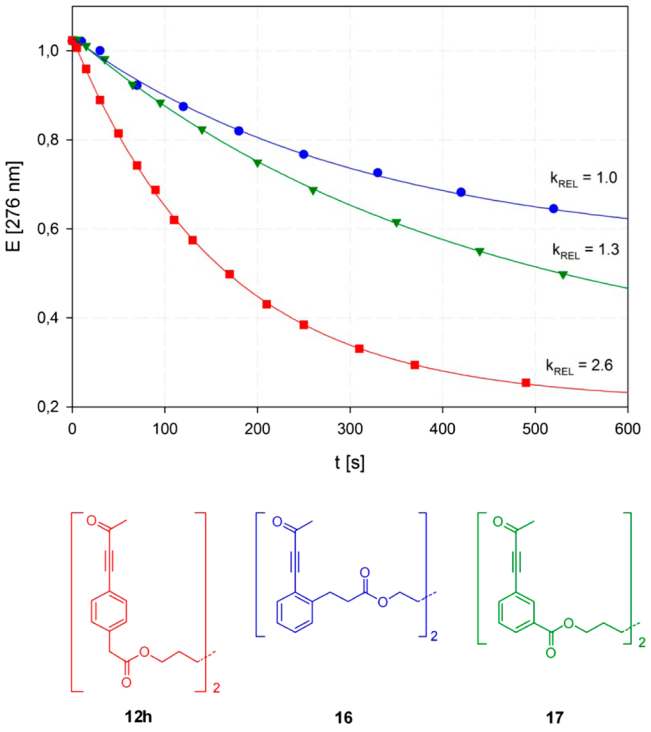


Figure 4. Degradation curves of the irradiation of **12h**, **16**, and **17**.

discernible that the decay rate of **12h** is more than twice the decay rates of **16** and **17** (for k_{REL} the decay rate of **16** was set to unity). Although the exact cause of the increased reactivity of ketones **12** is still unclear, we hypothesized that a "folded" ground-state conformation of **12**, which facilitates the PDDA, is responsible for this behavior. In the preceding section, we mentioned conspicuous changes in the UV spectra of **12** compared with the parent compound **14**. Indeed, a comparative conformational analysis of **12h**, **16**, and **17** (force field MMFF94x,[11] for details see the SI) revealed a folded conformation for **12h** as the global minimum but not for **16** and **17**. The stabilization of this conformation originates from head-to-tail dipole−dipole interactions between the ketocarbonyl groups resulting in a relatively short distance between the alkyne moieties. To verify these findings at a higher level of theory, we optimized both the folded and the stretched geometry using a DFT method (B3LYP[12]/6-31G*[13]). The geometry of the folded conformer is depicted in Figure 5. We

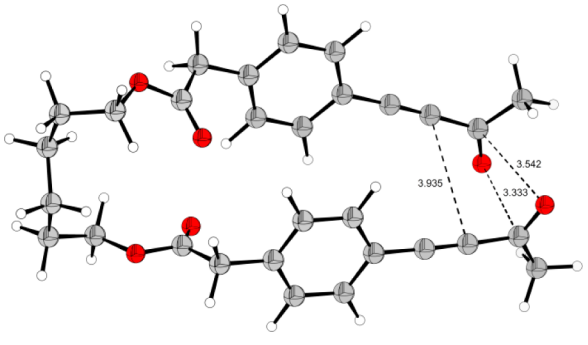


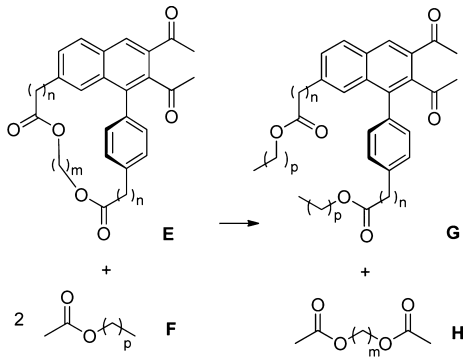
Figure 5. DFT-optimized ground-state geometry of **12h**.

found that this structure is more stable by about 3 kcal/mol compared with the stretched conformation. A similar result was obtained for **12i**. The close proximity of the photoreactive ynone moieties in these folded conformers could be the explanation for the high reactivity of compounds **12**.

4. Ring Strain and Structural Strain Indicators. Some of the (1,7)naphthalenophanes **13** should be considerably strained,[14] and we were interested in the corresponding ring-strain energies as well as possible structural and spectroscopic consequences of the strain.

For the determination of strain energy by means of quantum chemical calculations, the definition of an isodesmic reaction is the method of choice.[15] This is understood to be a hypothetic reaction in which the type and number of bonds cleaved in the reactants are the same as the type and number of bonds formed in the products. Recently, we successfully applied this approach for calculating the ring strain of (1,5)naphthalenophanes.[3a] In analogy to this work, we defined the isodesmic reaction shown in Scheme 4 for even values of m (this applies to all cases

Scheme 4. Isodesmic Reaction for the Calculation Ring Strain of (1,7)Naphthalenophanes 13



except **13b** where two different cuts from **E** to **G** are possible; for details see the SI). Starting from the naphthalenophane **E**, the central C−C bond of the diol linker is cleaved to the 1-arylnaphthalene **G**, releasing potential ring strain. The simultaneous cleavage of a C−C bond and the formation of two C−H bonds are compensated by the reaction between two alkyl acetates **F** to diol diacetate **H**. Here, the value of p is given in eq 1 and the strain energy E_{STR} is defined by eq 2 (Scheme 4).

$$p = \frac{m}{2} - 1 \tag{1}$$

$$E_{STR} = E(\mathbf{G}) + E(\mathbf{H}) - E(\mathbf{E}) - 2E(\mathbf{F}) \tag{2}$$

The resulting strain energies are summarized in Table 3 (third column). The highest value (25.4 kcal/mol) was obtained for the inaccessible compound **13a** (k = 10). Compound **13b** with the next larger linker (k = 11), which was obtained with 33% yield, exhibits a ring strain energy of 19.3 kcal/mol. Obviously, products with strain energies above about 20 kcal/mol cannot be obtained with this method. The strain energies of [12](1,7)naphthalenophanes **13c** and **13f** are quite different (13.2 kcal/mol vs 3.7 kcal/mol). This can be explained by the conjugation of the ester groups with the π-systems of the aromatic rings (n = 0) in the case of **13c**, resulting in conformational stiffening. Most of the other (1,7)-

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Table 3. Strain Energy E_{STR}, Deformation Angle γ_{Ph} (See Figure 6), and Selected ^{1}H NMR shifts of [k](1,7)Naphthalenophanes 13

13	k[a]	E_{STR}[b]	γ_{Ph}[c]	δ(H-8)[d]	δ(Ac-2)[e]
a	10	25.4	29.01		
b	11	19.3	25.63	6.34	2.60
c	12	13.2	19.16	6.74	2.55
d	14	6.0	10.03	7.46	2.41
e	22	3.5	1.74	*f*	2.08
f	12	3.7	9.46	6.83	2.37
g	14	1.0	3.75	*f*	2.14
h	16	1.1	1.23	*f*	2.09
i	14	3.0	4.76	7.04	2.11
j	18	2.7	1.71	*f*	2.08
k	22	3.9	1.36	*f*	2.09
l	24	3.7	1.78	*f*	2.08

[a] $k = N + 4 = m + 1n + 8$. [b] Strain energy (kcal/mol). [c] Deformation angle of the phenyl ring in degrees. [d] Chemical shift of H-8 in ppm. [e] Chemical shift of Ac-2. [f] Signal could not be unambiguously determined due to superposition of signals in NMR spectra.

naphthalenophanes are only moderately strained, and the strain energies range from 1 to 4 kcal/mol (Table 3).

In our previous work on (1,5)naphthalenophanes, we observed an increasing twist of naphthalene moiety with increasing ring strain.[3a]

In order to find out whether in the case of (1,7)-naphthalophanes **13** the naphthalene part is also the "weakest link", we carefully explored the optimized geometries. The first striking detail was the nearly perpendicular orientation of the phenyl ring relative to the naphthalene system in all cases (cf. Figure 3). In contrast to the previously investigated (1,5)-naphthalenophanes, the naphthalene moiety is virtually planar even for highly strained cases.

By contrast, the two C−C bonds connecting the phenyl ring with the rest of the naphthalenophane are considerably inclined from the π-plane in these cases. This effect can be expressed by a deformation angle γ_{Ph}, which is defined by the difference between 180 and the arithmetic average of two pseudovalence angles α and β (Figure 6a). The values for γ_{Ph}, which correlate well with E_{STR}, are listed in Table 3 (fourth column).

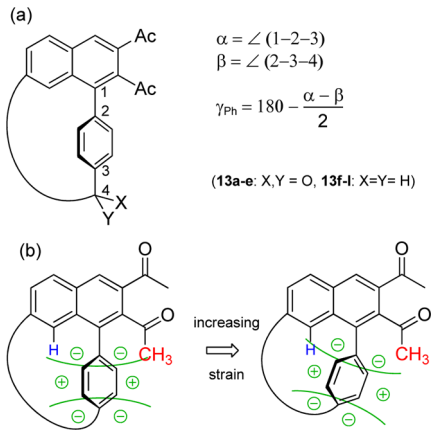

Figure 6. (a) Definition of the deformation angle γ_{Ph}. (b) Effects of increasing ring strain on the chemical shifts of H-8 (blue) and the methyl group of Ac-2 (red).

The bending of the phenyl ring should significantly influence the ^{1}H NMR spectra of compounds **13**. Caused by the aromatic ring current in a static magnetic field, each phenyl ring exhibits an anisotropy cone. The chemical shift values of all protons inside this cone are decreased (upfield), whereas signals of protons outside the cone are shifted downfield.[16] Looking at the geometries of naphthalenophanes **13**, the positions both of H-8 (blue) and of the methyl group of Ac-2 (red) regarding the anisotropy cone (green) are altered upon bending of the phenyl ring (Figure 6). Whereas H-8 is moved toward the interior of the cone, the aforementioned methyl group is moved out of the cone. The measured ^{1}H NMR shift values of H-8 and Ac-2, which are also summarized in Table 3, excellently reflect the forecasted trend. Comparing highly strained **13b** and moderately strained **13i**, the signal of H-8 is downfield-shifted by 0.70 ppm and the signal of Ac-2 is upfield-shifted by 0.49 ppm.

CONCLUSION

Based on our previous successful synthesis of naphthalenophanes[3c] by thermal DDA reaction, we first examined whether this approach is also an appropriate path to (1,7)naphthalenophanes. Unfortunately, all attempts in this direction failed. On the other hand, the photochemical variant (PDDA reaction) using diketones **12** smoothly provided the [k](1,7)-naphthalenophanes **13** even in highly strained (k = 11, 12) and macrocyclic (k up to 24) cases. The photochemical reactivity of compounds **12** is unusually high, compared with previously investigated systems, and could be explained by folded ground-state geometries of the reactants bringing the ynone moieties in close proximity. The ring strain energies E_{STR} of naphthalenophanes **13** were determined with the help of an isodesmic reaction. The most strained product **13b** (k = 11) exhibits a strain energy of about 19 kcal/mol, whereas **13a** (k = 10, E_{STR} = 25.4 kcal/mol) was not accessible. The most conspicuous change in the geometry of highly strained (1,7)naphthalenophanes is a bending of the phenyl ring, expressed by the deformation angle γ_{Ph}. This bending causes distinct changes of the NMR signals of protons, which are located near the anisotropy cone of the phenyl ring. Finally, it should be noted that, according to our experience, the cyclization of diketones **12** to (1,7)naphthalenophanes **13** is one of the most efficient PDDA systems known to date. Currently, we are investigating applications as peptide mimetics and in supramolecular assemblies.

EXPERIMENTAL SECTION

General Information. All reactions were conducted in heat-gun-dried and nitrogen-flushed glassware using Schlenk techniques. Solvents and reagents were purchased in the highest available purity and used without additional purification unless stated otherwise. Solvents were dried and distilled prior to use. Reaction monitoring was performed by thin-layer chromatography (TLC) until the starting material was completely consumed as indicated. Crude mixtures were purified by flash column chromatography (FSC). For the visualization of the products UV and/or dark light (254/366 nm) was used. The individual solvent mixtures for the elution of the product and the corresponding retardation factors (R_f) were noted in the appropriate sections. Melting points of solids were recorded and not corrected. NMR spectra were recorded on a 300 MHz spectrometer with appropriate deuterated solvents and used as internal standard: $CDCl_3$ (^{1}H: δ = 7.26 ppm, ^{13}C: δ = 77.2 ppm); CD_3OD (^{1}H: δ = 3.31 ppm, 13C: δ = 49.0 ppm). Coupling constants (J) are given in hertz (Hz). Fine structure analysis was performed, and multiplicities are

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abbreviated as follows: broad singlet (br s), doublet (d), triplet (t), quartet (q), multiplet (m). FT-IR measurements were performed on ATR crystals, and the characteristic intensities of absorption bands ($\overline{\nu}$, cm^{-1}) are abbreviated as follows: weak (w), medium (m), strong (s), very strong (vs). High-resolution mass spectrometry (HRMS) was performed with impact ionization (EI) and recorded on a mass spectrometer equipped with a quadrupol. UV−vis spectra were recorded in a two-cuvette spectrometer in the range of 200−500 nm. Phosphorescence spectra were recorded in an EPA (diethyl ether, isopentane, ethanol, 5:5:2, v/v/v) matrix at 77 K. Photochemical reactions were performed in a standard (semi)preparative batch apparatus equipped with an internal cooling jacket (quartz) and external Pyrex vessel water-cooling system. For efficient stirring of the reaction medium a gentle stream of nitrogen was needed and bubbled 15 min before the reaction was initiated with a high-pressure mercury arc lamp (150 W; excitation λ > 300 nm). 2-(4-Iodophenyl)acetic acid[17] and 3-(4-iodophenyl)propionic[5] acid were synthesized according to the literature.

General Procedures. *General Procedure 1 (GP1) for the Synthesis of Diiodides **5**.* To a suspension containing the diol **10** (1.0 equiv) and the carboxylic acid **4** (2.67 equiv) in dry DCM (10 mL/mmol) were added *N*,*N*′-diisopropylcarbodiimide (DIC, 2.5 equiv) and DMAP (20 mol %). Stirring at 50 °C was continued until TLC indicated the complete consumption of the starting material. The heterogeneous reaction mixture was washed three times with brine, and the combined organic phases were dried with magnesium sulfate. Before solvent removal under reduced pressure the suspension was filtered over Celite. The purification of compounds **5** was accomplished by FSC.

*General Procedure 2 (GP2) for the Synthesis of Diols **11**.* The diiodide **5** (1.0 equiv) was dissolved in a mixture of triethylamine (Et_3N) and THF (10 mL/mmol, 3:1, v/v). The solution was degassed three times and flushed with nitrogen. Bis(triphenylphosphine) palladium(II)dichloride ($Pd(PPh_3)_2Cl_2$, 10 mol %) and copper iodide (CuI, 5 mol %) were added, and the mixture was stirred for 5 min. 3-Butyn-2-ol (97%, 4.0 equiv) was added, and the reaction mixture was stirred until TLC indicated complete consumption of the starting material. The heterogeneous mixture was poured into diethyl ether and washed subsequently (each two times) with water, aqueous tartaric acid (20%), sodium bicarbonate, and brine. The combined organic phases were dried with magnesium sulfate and filtered over Celite. After the solvent was removed under reduced pressure, the crude product **11** was purified by FSC.

*General Procedure 3 (GP3) for the Synthesis of Diketones **12**.* The diol **11** (1.0 equiv) was dissolved in anhyd DMSO (10 mL/mmol). Acetic anhydride (10.0 equiv) was added, and stirring was continued until TLC indicated the complete consumption of the starting material. The solvent was removed in vacuo. The pure product **12** was isolated after FSC.

*General Procedure 4 (GP4) for the PDDA Reaction to (1,7)-Naphthalenophanes **13**.* The diketone **12** was dissolved in DCM (380 mL) using a standard photochemical batch apparatus for (semi)preparative-scale reactions. The solution was purged 15 min with nitrogen and irradiated with a high-pressure mercury arc lamp until TLC indicated the complete consumption of the starting material. The solvent was removed under reduced pressure. The crude material **13** was purified by FSC.

*3,3′-[Ethane-1,2-diylbis[oxy(3-oxopropane-3,1-diyl)benzene-4,1-diyl]]bisprop-2-ynoic Acid **6**.* Bis(3-(4-iodophenyl)propionic acid)-ethane-1,2-diyl ester (0.60 g, 1.04 mmol) (**5i**) was dissolved in dry DMSO (40 mL) and DBU (1.60 mL, 10.38 mmol), and 1,4-bis(diphenylphosphino)butane (dppb, 0.089 g, 0.21 mmol) and bis(triphenylphosphine)palladium(II) dichloride ($Pd(PPh_3)_2Cl_2$, 0.057 g, 0.10 mmol) were added subsequently. Before dropwise addition of propiolic acid (0.13 mL, 2.08 mmol), the heterogeneous reaction mixture was degassed three times and flushed with nitrogen. Stirring at 50 °C was continued until TLC indicated the complete consumption of the starting material (5 h). The dark mixture was diluted with ethyl acetate (100 mL) and extracted three times (3 × 80) with saturated aq $NaHCO_3$ solution. The combined aqueous phases were acidified with ice-cold HCl (aq, 6 M, 50 mL) up to pH 2. The resulting precipitate was extracted five times (5 × 50 mL) with DCM. The combined phases were dried over magnesium sulfate, and the solvent was removed under reduced pressure. After FSC, compound **6** was isolated as light yellowish solid (0.46 g, 96%): R_f 0.48 (EtOAc + 1% formic acid); mp 159−160 °C; ^{1}H NMR (300 MHz, CD_3OD) δ 7.48 (d, J = 8.2 Hz, 4H), 7.27 (d, J = 8.2 Hz, 4H), 4.20 (s, 4H), 2.92 (t, J = 7.4 Hz, 4H, 2.61 (t, J = 7.4 Hz, 4H; ^{13}C NMR (75 MHz, MeOD) δ 173.9, 156.7, 145.3, 134.0, 130.0, 118.8, 86.7, 63.5, 35.9, 31.7; IR: 3436 (w), 2972 (m), 2569 (m), 2201 (s), 1681 (vs), 1606 (m), 1367 (m), 1282 (m), 1216 (s), 1173 (s), 830 (m) cm^{-1}; HRMS (m/z) [M^+] calcd for $C_{26}H_{22}O_8$ 462.1315, found 462.1320.

*Ethane-1,2-diyl Bis[3-(4-[3-oxo-3-[propan-2-yl(propan-2-ylcarbamoyl)amino]prop-1-yn-1-yl]phenyl)propanoate] (**9**).* According to Table SI-1 (see conditions), the diureide **9** was isolated as a vitreous oil: R_f 0.60 (PE/EtOAc 1:1); ^{1}H NMR 300 MHz, $CDCl_3$) δ 8.48 (br s, 2H), 7.53 (d, J = 8.1 Hz, 4H), 7.32−7.25 (m, 4H), 4.98 (dt, J = 13.7, 6.8 Hz, 2H), 4.29 (s, 4H), 4.03 (dq, J = 13.3, 6.6 Hz, 2H), 3.02 (t, J = 7.5 Hz, 4H), 2.69 (t, J = 7.6 Hz, 4H), 1.59 (d, J = 6.8 Hz, 12H, 1.24 (d, J = 6.5 Hz, 12H; ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.2, 156.9, 152.9, 143.7, 132.9, 128.9, 118.0, 93.8, 82.3, 62.4, 51.9, 42.7, 35.2, 30.9, 22.8, 21.2. HRMS (m/z) [M^+] calcd for $C_{40}H_{50}N_4O_8$ 714.3629, found 714.3634.

*Bis(4-iodobenzoic acid)ethane-1,2-diyl Ester (**5a**).* 1,2-Ethanediol (0.77 mL, 13.69 mmol) and 4-iodobenzoic acid (9.07 g, 36.56 mmol) were subjected to the reaction conditions described in GP1. The reaction was complete after 43 h, yielding the title compound as a colorless solid (6.79 g, 95%). R_f = 0.38 (PE/EtOAc 1:1); mp 142−143 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81−7.72 (m 8H), 4.64 (s, 4H; ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.0, 137.9, 131.2, 129.3, 101.3, 63.0; IR ($\overline{\nu}$) 3077 (w), 2857 (w), 1713 (vs), 1581 (s), 1454 (m), 1393 (m), 1291 (m), 1255 (s), 1176 (m), 1101 (s), 1009 (s), 837 (m), 751 (s), 680 (m) cm^{-1}; HRMS (m/z) [M^+] calcd for $C_{16}H_{12}I_2O_4$ 521.8820, found 521.8821.

*Bis(4-iodobenzoic acid)propane-1,3-diyl Ester (**5b**).* 1,3-Propanediol (0.67 mL, 9.25 mmol) and 4-Iodobenzoic acid (6.12 g, 24.68 mmol) were subjected to the reaction conditions described in GP1. The reaction was complete after 38 h, yielding the title compound as a colorless solid (3.31 g, 67%): R_f 0.58 (PE/EtOAc 3:1); mp 116−117 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79−7.69 (m, 8H), 4.48 (t, J = 6.2 Hz, 4H), 2.24 (p, J = 6.1 Hz, 2H; ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.1, 137.9, 131.1, 129.6, 101.0, 62.1, 28.3; IR ($\overline{\nu}$) 2980 (m), 1709 (vs), 1586 (s), 1393 (s), 1272 (vs), 1122 (vs), 1008 (s), 840 (m), 748 (s)cm^{-1}; HRMS (m/z) [M^+] calcd for $C_{17}H_{14}I_2O_4$ 535.8982, found 535. 8985.

*Bis(4-iodobenzoic acid)butane-1,4-diyl Ester (**5c**).* 1,4-Butanediol (1.0 g, 11.1 mmol) and 4-iodobenzoic acid (7.35 g, 29.63 mmol) were subjected to the reaction conditions described in GP1. The reaction was complete after 47 h, yielding the title compound as a colorless solid (4.2 g, 69%): R_f 0.25 (PE/EtOAc 10:1); mp 134−135 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80−7.71 (m, 8H), 4.38 (s, 4H), 1.92 (s, 4H, CH_2);^{13}C NMR (75 MHz, $CDCl_3$) δ 166.2, 137.9, 131.1, 129.8, 100.9, 64.8, 25.6; IR ($\overline{\nu}$) 1703 (vs), 1585 (m), 1267 (vs), 1102 (s), 915 (m), 757 (m), 745 (m) cm^{-1}; HRMS (m/z) [M^+] calcd for $C_{18}H_{16}I_2O_4$ 549.9138, found 549.9150.

*Bis(4-iodobenzoic acid)hexane-1,6-diyl Ester (**5d**).* 1,6-Hexanediol (0.71 g, 6.0 mmol) and 4-iodobenzoic acid (3.97 g, 16.02 mmol) were subjected to the reaction conditions described in GP1. The reaction was complete after 44 h, yielding the title compound as a colorless solid (2.41 g, 70%): R_f 0.61 (PE/EtOAc 1:1); mp 85−86 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83−7.67 (m, 8H), 4.31 (t, J = 6.6 Hz, 4H), 1.88−1.68 (m, 4H), 1.56−1.44 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.2, 137.8, 131.1, 130.0, 100.8, 65.3, 28.7, 25.9; IR ($\overline{\nu}$) 2941 (m), 1710 (s), 1584 (s), 1264 (vs), 1103 (s), 1004 (s), 753 (w) cm^{-1}; HRMS (m/z) [M^+] calcd for $C_{20}H_{20}I_2O_4$ 577.9446, found 577.9436.

*Bis(4-iodobenzoic acid)dodecane-1,12-diyl Ester (**5e**).* 1,12-Dodecanediol (1.00 g, 4.94 mmol) and 4-Iodobenzoic acid (3.27 g, 13.20 mmol) were subjected to the reaction conditions described in GP1. The reaction was complete after 65 h, yielding the title compound as a colorless solid (3.27 g, 99%): R_f 0.51 (PE/EtOAc

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10:1); mp 55−57 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (q, J = 8.5 Hz, 8H), 4.30 (t, J = 6.7 Hz, 4H), 1.89−1.60 (m, 4H, H-7), 1.51−1.10 (m, 16H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.3, 137.8, 131.1, 130.1, 100.7, 65.5, 29.6,29.4, 28.8, 26.1; IR ($\bar{\nu}$) 2916 (s), 2849 (s), 1716 (vs), 1584 (m), 1392 (m), 1314 (m), 1272 (m), 1181 (m), 1104 (m), 1007 (m), 845 (m), 750 (m) cm^{-1}; HRMS (m/z) [M$^+$] calcd for $C_{26}H_{32}I_2O_4$ 662.0385, found 662.0395.

*Bis(2-(4-iodophenyl)acetic acid)ethane-1,2-diyl Ester (**5f**).* 1,2-Ethanediol (0.46 mL, 8.22 mmol) and 2-(4-iodophenyl)acetic acid (5.76 g, 21.96 mmol) were subjected to the reaction conditions described in GP1. The reaction was complete after 48 h, yielding the title compound as a colorless solid (3.62 g, 80%): R_f 0.47 (PE/EtOAc 1:1); mp 60−61 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, J = 8.3 Hz, 4H), 7.01 (d, J = 8.2 Hz, 4H), 4.29 (s, 4H), 3.54 (s, 4H; ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.8, 137.8, 133.4, 131.4, 92.9, 62.6, 40.7; IR ($\bar{\nu}$) 2982 (w), 2921 (w), 1729 (vs), 1483 (s), 1338 (m), 1251 (s), 1159 (s), 1136 (vs), 1043 (s), 1007 (s), 976 (s),737(s), 485 (s) cm^{-1}; HRMS (m/z) [M$^+$] calcd for $C_{18}H_{16}I_2O_4$ 549.9138, found 549.9136.

*Bis(2-(4-iodophenyl)acetic acid)-butane-1,4-diyl Ester (**5g**).* 1,4-Butanediol (0.99 mL, 11.15 mmol) and 2-(4-iodophenyl)acetic acid (7.8 g, 29.77 mmol) were subjected to the reaction conditions described in GP1. The reaction was complete after 63 h, yielding the title compound as a colorless solid (4.53 g, 70%): R_f 0.35 (PE/EtOAc 1:1); mp 71−72 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, J = 8.4 Hz, 4H), 7.02 (d, J = 8.4 Hz, 4H), 4.08 (t, J = 5.6 Hz, 4H), 3.55 (s, 4H), 1.69−1.59 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.0, 137.8, 133.7, 131.4, 92.7, 64.5, 41.0, 25.3; IR ($\bar{\nu}$) 2956 (w), 1722 (vs), 1485 (m), 1348 (m), 1216 (m), 1164 (m), 800 (m) cm^{-1}; HRMS (m/z) [M$^+$] calcd for $C_{20}H_{20}I_2O_4$ 577.9451, found 577.9442.

*Bis(2-(4-iodophenyl)acetic acid)hexane-1,6-diyl Ester (**5h**).* 1,6-Hexanediol (0.86 g, 8.46 mmol) and 2-(4-iodophenyl)acetic acid (5.0 g, 19.08 mmol) were subjected to the reaction conditions described in GP1. The reaction was complete after 71 h, yielding the title compound as a colorless solid (2.94 g, 67%): R_f 0.52 (PE/EtOAc 3:1); mp 97−98 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (d, J = 8.2 Hz, 4H), 7.03 (d, J = 8.2 Hz, 4H), 4.06 (t, J = 6.6 Hz, 4H), 3.55 (s, 4H, 4H), 1.57 (d, J = 6.5 Hz, 4H), 1.35−1.21 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2, 137.8, 133.9, 131.4, 92.7, 65.0, 41.1, 28.5, 25.5; IR ($\bar{\nu}$) 2935 (w), 2886 (w), 1723 (vs), 1484 (m), 1218 (m), 1170 (s), 981 (m), 800 (m), 733 (m) cm^{-1}; HRMS (m/z) [M$^+$] calcd for $C_{22}H_{24}I_2O_4$ 605.9764, found 605.9745.

*Bis(3-(4-iodophenyl)propionic acid)ethane-1,2-diyl Ester (**5i**).* Ethylene glycol (0.31 mL, 5.55 mmol) and 3-(4-Iodophenyl)propionic acid (4.0 g, 14.49 mmol) were subjected to the reaction conditions described in GP1. The reaction was complete after 46 h, yielding the title compound as a colorless solid (1.84 g, 57%): R_f 0.38 (PE/EtOAc 1:1); mp 55−56 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, J = 8.3 Hz, 4H), 6.95 (d, J = 8.4 Hz, 4H), 4.24 (s, 4H), 2.88 (t, J = 7.6 Hz, 4H), 2.61 (t, J = 7.7 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.3, 140.1, 137.6, 130.5, 91.6, 62.3, 35.4, 30.4; IR ($\bar{\nu}$) 2932 (w), 1745 (m), 1726 (vs), 1484 (m), 1152 (s), 1006 (m), 805 (m) cm^{-1}; HRMS (m/z) [M$^+$] calcd for $C_{20}H_{20}I_2O_4$ 577.9451, found 577.9446.

*Bis(3-(4-iodophenyl)propionic acid)hexane-1,6-diyl Ester (**5j**).* 1,6-Hexanediol (1.00 g, 8.46 mmol) and 3-(4-Iodophenyl)propionic acid (6.24 g, 22.59 mmol) were subjected to the reaction conditions described in GP1. The reaction was complete after 48 h, yielding the title compound as a colorless solid (4.41 g, 82%): R_f 0.50 (PE/EtOAc 3:1); mp 77−78 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, J = 8.3 Hz, 4H), 6.95 (d, J = 8.3 Hz, 4H), 4.04 (t, J = 6.6 Hz, 4H), 2.88 (t, J = 7.6 Hz, 4H), 2.59 (t, J = 7.6 Hz, 4H), 1.58 (dd, J = 11.6, 4.9 Hz, 4H), 1.30 (d, J = 7.0 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.8, 140.3, 137.6, 130.6, 91.5, 64.6, 35.7, 30.6, 28.6, 25.7; IR ($\bar{\nu}$) 2935 (m), 2854 (w), 1721 (vs), 1484 (m), 1288 (m), 1172 (s), 981 (m), 834 (m), 801 (m) cm^{-1}; HRMS (m/z) [M$^+$] calcd for $C_{24}H_{28}I_2O_4$ 634.0077, found 634.0089.

*Bis(3-(4-iodophenyl)propionic acid)decane-1,10-diyl Ester (**5k**).* 1,10-Decanediol (0.50 g, 2.87 mmol) and 3-(4-iodophenyl)propionic acid (11.64 g, 7.66 mmol) were subjected to the reaction conditions described in GP1. The reaction was complete after 66 h, yielding the title compound as a colorless solid (1.32 g, 66%): R_f 0.35 (PE/EtOAc 5:1); mp 56−57 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, J = 8.1 Hz, 4H), 6.95 (d, J = 8.0 Hz, 4H), 4.04 (t, J = 6.7 Hz, 4H), 2.89 (t, J = 7.6 Hz, 4H), 2.59 (t, J = 7.6 Hz, 4H), 1.72−1.43 (m, 4H), 1.23 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.8, 140.3, 137.6, 130.6, 91.5, 64.8, 35.7, 30.6, 29.5, 28.7, 26.0; IR ($\bar{\nu}$) $\bar{\nu}$ 2958 (m), 2928 (m), 2852(m), 1731 (vs), 1480 (m), 1356 (m), 1203 (m), 1193 (s), 1176 (m), 1040 (w), 1007 (m), 947 (w), 806 (m) cm^{-1}; HRMS (m/z) [M$^+$] calcd for $C_{28}H_{36}I_2O_4$ 690. 0703, found 690.0708.

*Bis(3-(4-iodophenyl)propionic acid)dodecane-1,12-diyl Ester (**5l**).* 1,12-Dodecanediol (1.00 g, 4.94 mmol) and 3-(4-iodophenyl)-propionic acid (3.64 g, 13.20 mmol) were subjected to the reaction conditions described in GP1. The reaction was complete after 72 h, yielding the title compound as a colorless solid (3.52 g, 99%): R_f 0.63 (PE/EtOAc 3:1); mp 59−61 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, J = 8.2 Hz, 4H), 6.95 (d, J = 8.2 Hz, 4H), 4.04 (t, J = 6.7 Hz, 4H), 2.89 (t, J = 7.6 Hz, 4H), 2.59 (t, J = 7.6 Hz, 4H), 1.58 (dd, J = 12.2, 6.0 Hz, 4H), 1.22 (m, 16H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.8, 140.3, 137.6, 130.6, 91.5, 64.9, 35.7, 30.6, 29.7, 29.4, 28.7, 26.0; IR ($\bar{\nu}$) 2958 (w), 2919 (m), 2850 (m), 1731 (vs), 1480 (m), 1358 (m), 1204 (m), 1193 (m), 1149 (s), 1007 (m), 806 (m) cm^{-1}; HRMS (m/z) [M$^+$] calcd for $C_{30}H_{40}I_2O_4$ 718.1016, found 718.0992.

*Bis(4-(2-(3-hydroxybut-1-ynyl)benzoic acid))ethane-1,2-diyl Ester (**11a**).* Bis(4-iodobenzoic acid)ethane-1,2-diyl ester (**5a**) (2.46 g, 4.71 mmol) was subjected to the reaction conditions described in GP2. The reaction was complete after 24 hm yielding the title compound as a light brown solid (1.58 g, 82%): R_f 0.5 (PE/EtOAc 1:1); mp 136−138 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, J = 8.2 Hz, 4H), 7.45 (d, J = 8.2 Hz, 4H), 4.76 (q, J = 6.6 Hz, 2H), 4.64 (s, 4H), 2.28 (br s, 2H), 1.55 (d, J = 6.6 Hz, 6H; ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.9, 131.7, 129.7, 129.3, 127.8, 94.3, 83.3, 63.0, 58.9, 24.3; IR ($\bar{\nu}$) 3296 (m), 2977 (w), 1714 (vs), 1605 (m), 1466 (w), 1407 (w), 1343 (m), 1271 (s), 1176 (m), 1097 (m), 1077 (m), 1033 (m), 1018 (m), 935 (w), 859 (m), 767 (m), 696 (m) cm^{-1}; HRMS (m/z) [M$^+$] calcd for $C_{24}H_{22}O_6$ 406.1411, found 406.1421.

*Bis(4-(3-hydroxybut-1-ynyl)benzoic acid)propane-1,3-diyl Ester (**11b**).* Bis(4-iodobenzoic acid)propane-1,3-diyl ester (**5b**) (2.27 g, 4.24 mmol) was subjected to the reaction conditions described in GP2. The reaction was complete after 23 h, yielding the title compound as a light brown solid (1.48 g, 83%): R_f 0.43 (PE/EtOAc 1:2); mp 140−141 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (d, J = 8.3 Hz, 4H), 7.43 (d, J = 8.3 Hz, 4H), 4.78 (q, J = 6.6 Hz, 2H), 4.50 (t, J = 6.1 Hz, 4H), 2.34−2.15 (m, 2H), 1.94 (br s, 2H), 1.57 (d, J = 6.6 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.9, 131.5, 129.5, 129.4, 127.6, 94.0, 83.2, 62.2, 58.8, 28.2, 24.2; IR ($\bar{\nu}$) 3324 (m), 2979 (m), 1706 (vs), 1607 (m), 1470 (m), 1407 (m), 1275 (vs), 1094 (s) cm^{-1}; HRMS (m/z) [M$^+$] calcd for $C_{25}H_{24}O_6$ 420.1573, found 420.1565.

*Bis(4-(3-hydroxybut-1-ynyl)benzoic acid)butane-1,4-diyl Ester (**11c**).* Bis(4-iodobenzoic acid)butane-1,4-diyl ester (**5c**) (2.73 g, 4.96 mmol) was subjected to the reaction conditions described in GP2. The reaction was complete after 23 h, yielding the title compound as a light brown solid (1.83 g, 85%): R_f 0.35 (PE/EtOAc 1:1); mp 119−120 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, J = 8.4 Hz, 4H), 7.45 (d, J = 8.4 Hz, 4H), 4.77 (q, J = 6.6 Hz, 2H), 4.38 (s, 4H), 2.18 (br s, 2H), 1.93 (s, 4H), 1.56 (d, J = 6.6 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.1, 131.7, 129.8, 129.5, 127.5, 94.1, 64.8, 58.9, 25.6, 24.4; IR ($\bar{\nu}$) 3353 (w), 2977 (w), 1713 (vs), 1606 (m), 1266 (s), 1255 (s), 1099 (m) cm^{-1}; HRMS (m/z) [M$^+$] calcd for $C_{26}H_{26}O_6$ 434.1729, found 434.1745.

*Bis(4-(3-hydroxybut-1-ynyl)benzoic acid)hexane-1,6-diyl Ester (**11d**).* Bis(4-iodobenzoic acid)hexane-1,6-diyl ester (**5d**) (1.88 g, 3.25 mmol) was subjected to the reaction conditions described in GP2. The reaction was complete after 24 h, yielding the title compound as a light yellowish solid (1.41 g, 88%): R_f 0.5 (PE/EtOAc 1:1); mp 80−82 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, J = 8.6 Hz, 4H), 7.44 (d, J = 8.6 Hz, 4H), 4.77 (q, J = 6.6 Hz, 2H), 4.32 (t, J = 6.5 Hz, 4H), 2.14 (br s, 2H), 1.89−1.68 (m, 4H), 1.56 (d, J = 6.6 Hz, 6H), 1.53−1.44 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.2, 131.7, 130.0, 129.5, 127.4, 94.0, 83.4, 65.3, 58.9, 28.7, 26.0, 24.4; IR ($\bar{\nu}$) 3327 (m), 2950 (m), 2906 (m), 2852 (m), 1707 (vs), 1606 (m), 1271 (s), 1096 (s)

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cm^{-1}; HRMS (m/z) [M^+] calcd for $C_{28}H_{30}O_6$ 462.2042, found 462.2044.

*Bis(4-(3-hydroxybut-1-ynyl)benzoic acid)dodecane-1,12-diyl Ester (**11e**).* Bis(4-iodobenzoic acid)dodecane-1,12-diyl ester (**5e**) (2.00 g, 3.02 mmol) was subjected to the reaction conditions described in GP2. The reaction was complete after 24 h, yielding the title compound as a light brown solid (1.37 g, 83%): R_f 0.47 (PE/EtOAc 1:1); mp 94−96 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, J = 8.3 Hz, 4H), 7.45 (d, J = 8.2 Hz, 4H), 4.76 (q, J = 9.9 Hz, 2H), 4.30 (t, J = 6.6 Hz, 4H), 2.21 (bs, 2H), 1.83−1.66 (m, 4H), 1.54 (t, J = 10.7 Hz, 6H), 1.44−1.19 (m, 16H_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.3, 131.7, 130.1, 129.5, 127.3, 94.0, 83.4, 65.5, 58.8, 29.5, 28.8, 26.1, 24.4; IR ($\bar{\nu}$) 3332 (m), 2913 (vs), 2848 (s), 1706 (vs), 1605 (m), 1470 (m), 1407 (m), 1316 (m), 1273 (s), 1175 (m), 1097 (s), 1019 (m), 933 (w), 862 (m), 769 (m), 697 (m) cm^{-1}; HRMS (m/z) [M^+] calcd for $C_{34}H_{42}O_6$ 546.2976, found 546.2978.

*Bis(2-(4-(3-hydroxybut-1-ynyl)phenyl)acetic acid)ethane-1,2-diyl Ester (**11f**).* Bis(2-(4-iodophenyl)acetic acid)ethane-1,2-diyl ester (**5f**) (2.50 g, 4.55 mmol) was subjected to the reaction conditions described in GP2. The reaction was complete after 19 h, yielding the title compound as a light brown solid (1.52 g, 77%): R_f 0.53 (PE/EtOAc 1:2); mp 71−73 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 (d, J = 8.0 Hz, 4H), 7.17 (d, J = 8.0 Hz, 4H), 4.74 (q, J = 6.5 Hz, 2H), 4.27 (s, 4H), 3.57 (s, 4H), 2.33 (br s, 2H), 1.54 (d, J = 6.6 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.0, 134.0, 132.0, 129.3, 121.7, 91.4, 83.7, 62.6, 58.9, 41.1, 24.5; IR ($\bar{\nu}$) 3391 (m), 2984 (w), 1730 (vs), 1511 (w), 1353 (m), 1215 (m), 1158 (m), 1102 (m), 1035 (m) cm^{-1}; HRMS (m/z) [M^+] calcd for $C_{34}H_{42}O_6$ 546.2976, found 546.2978.

*Bis(2-(4-(3-hydroxybut-1-ynyl)phenyl)acetic acid)butane-1,4-diyl Ester (**11g**).* Bis(2-(4-iodophenyl)acetic acid)butane-1,4-diyl ester (**5g**) (2.00 g, 3.46 mmol) was subjected to the reaction conditions described in GP2. The reaction was complete after 26 h, yielding the title compound as a light brown solid (1.41 g, 88%): R_f 0.28 (PE/EtOAc 1:1); mp 75−76 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (d, J = 8.2 Hz, 4H), 7.20 (d, J = 8.2 Hz, 4H), 4.74 (q, J = 6.6 Hz, 2H), 4.14−3.99 (m, 4H), 3.59 (s, 4H), 2.20 (br s, 2H), 1.65−1.58 (m, 4H), 1.54 (d, J = 6.6 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2, 134.4, 132.0, 129.3, 121.6, 91.3, 83.8, 64.5, 58.9, 41.4, 25.2, 24.5; IR ($\bar{\nu}$) 3322 (m), 2981 (m), 1726 (vs), 1510 (m), 1318 (m), 1296 (m), 1239 (m), 1098 (m), 1039 (m) cm^{-1}; HRMS (m/z) [M^+] calcd for $C_{28}H_{30}O_6$ 462.2042, found 462.2026.

*Bis(2-(4-(3-hydroxybut-1-ynyl)phenyl)acetic acid)hexane-1,6-diyl Ester (**11h**).* Bis(2-(4-iodophenyl)acetic acid)hexane-1,6-diyl ester (**5h**) (2.00 g, 3.30 mmol) was subjected to the reaction conditions described in GP2. The reaction was complete after 23 h, yielding the title compound as highly viscous oil (1.28 g, 80%): R_f 0.48 (PE/EtOAc 1:2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (d, J = 8.1 Hz, 4H), 7.21 (d, J = 8.0 Hz, 4H), 4.74 (q, J = 6.5 Hz, 2H), 4.05 (t, J = 6.5 Hz, 4H), 3.59 (s, 4H), 2.14 (br s, 2H), 1.55 (s, 6H, H-1), 1.53 (s, 4H), 1.24 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2, 124.4, 131.8, 129.2, 121.4, 91.2, 83.7, 64.9, 58.8, 41.4, 28.4, 25.4, 24.4; IR ($\bar{\nu}$) 3416 (m), 2934 (m), 1729 (vs), 1510 (m), 1250 (m), 1157 (s), 1103 (m), 1034 (m) cm^{-1}; HRMS (m/z) [M^+] calcd for $C_{30}H_{34}O_6$ 490.2355, found 490.2366.

*Bis(3-(4-(3-hydroxybut-1-ynyl)phenyl)propionic acid)ethane-1,2-diyl Ester (**11i**).* Bis(3-(4-iodophenyl)propionic acid)ethane-1,2-diyl ester (**5i**) (0.70 g, 1.21 mmol) was subjected to the reaction conditions described in GP2. The reaction was complete after 23 h, yielding the title compound as a light brown solid (0.39 g, 70%): R_f 0.23 (PE/EtOAc 1:1); mp 48−49 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (d, J = 8.0 Hz, 4H), 7.10 (d, J = 8.0 Hz, 4H), 4.72 (q, J = 6.5 Hz, 2H), 4.21 (s, 4H), 2.90 (t, J = 7.6 Hz, 4H), 2.60 (t, J = 7.6 Hz, 4H), 2.50 (br s, 2H), 1.52 (d, J = 6.6 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.5, 140.9, 131.9, 128.4, 120.7, 91.0, 83.9, 62.3, 58.9, 35.4, 30.7, 24.5; IR ($\bar{\nu}$) 3414 (m), 2980 (m), 1733 (vs), 1509 (m), 1371 (m), 1254 (m), 1147 (s), 1104 (s), 1034 (m) cm^{-1}; HRMS (m/z) [M^+] calcd for $C_{28}H_{30}O_6$ 462.2042, found 462.2063.

*Bis(3-(4-(3-hydroxybut-1-ynyl)phenyl)propionic acid)hexane-1,6-diyl Ester (**11j**).* Bis(3-(4-iodophenyl)propionic acid)hexane-1,6-diyl ester (**5j**) (2.05 g, 3.23 mmol) was subjected to the reaction conditions described in GP2. The reaction was complete after 24 h, yielding the title compound as a light brown solid (1.44 g, 86%): R_f 0.6 (PE/EtOAc 1:2); mp 32−33 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (d, J = 8.1 Hz, 4H), 7.13 (d, J = 8.0 Hz, 4H), 4.73 (q, J = 6.5 Hz, 2H), 4.04 (t, J = 6.5 Hz, 4H), 2.93 (t, J = 7.5 Hz, 4H), 2.6 (t, J = 7.5 Hz, 4H), 2.27 (br s, 2H), 1.54 (s, 4H, H-14), 1.52 (s, 6H), 1.23 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.0, 141.0, 131.9, 128.4, 120.7, 90.9, 83.9, 64.7, 58.9, 35.7, 31.0, 28.6, 25.7, 24.5; IR ($\bar{\nu}$) 3423 (m), 2933 (m), 1729 (vs), 1509 (m), 1180 (m), 1155 (m), 1104 (s), 1034 (m) cm^{-1}; HRMS (m/z) [M^+] calcd for $C_{32}H_{38}O_6$ 518.2668, found 518.2685.

*Bis(3-(4-(3-hydroxybut-1-ynyl)phenyl)propionic acid)decane-1,10-diyl Ester (**11k**).* Bis(3-(4-iodophenyl)propionic acid)decane-1,10-diyl ester (**5k**) (0.388 g, 0.562 mmol) was subjected to the reaction conditions described in GP2. The reaction was complete after 23 h, yielding the title compound as a light brown solid (0.234 g, 73%): R_f 0.5 (PE/EtOAc 1:1); mp 48−50 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (d, J = 8.0 Hz, 4H), 7.13 (d, J = 8.0 Hz, 4H), 4.74 (q, J = 6.6 Hz, 2H), 4.04 (t, J = 6.7 Hz, 4H), 2.93 (t, J = 7.7 Hz, 4H), 2.60 (t, J = 7.7 Hz, 4H), 2.04 (br s, 2H), 1.57−1.45 (m, 10H), 1.26 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.0, 141.2, 131.9, 128.4, 120.6, 90.8, 84.0, 64.9, 58.9, 35.7, 31.0, 29.4, 28.7, 26.0, 24.6, 24.0; IR ($\bar{\nu}$) 3326 (m), 2959 (m), 2922 (s), 2855 (m), 1726 (vs), 1510 (w), 1478 (w), 1446 (w), 1428 (w), 1369 (m), 1323 (m), 1296 (m), 1169 (m), 1152 (m), 1106 (m), 1078 (m), 1037 (m), 931 (w), 832 (m) cm^{-1}; HRMS (m/z) [M^+] calcd for $C_{36}H_{46}O_6$ 574.3294, found 574.3300.

*Bis(3-(4-(3-hydroxybut-1-ynyl)phenyl)propionic acid)dodecane-1,12-diyl Ester (**11l**).* Bis(3-(4-iodophenyl)propionic acid)dodecane-1,12-diyl ester (2.5 g, 3.48 mmol) was subjected to the reaction conditions described in GP2. The reaction was complete after 20 h, yielding the title compound as a light brown solid (1.32 g, 63%): R_f 0.48 (PE/EtOAc 1:1); mp 59−61 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (d, J = 8.1 Hz, 4H), 7.12 (d, J = 8.0 Hz, 4H), 4.73 (q, J = 6.6 Hz, 2H), 4.04 (t, J = 6.7 Hz, 4H), 2.92 (t, J = 7.7 Hz, 4H), 2.59 (t, J = 7.7 Hz, 4H), 2.27 (br s, 2H), 1.62−1.46 (m, 10H), 1.25 (s, 16H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.0, 141.1, 131.9, 128.4, 120.6, 90.8, 84.0, 64.9, 58.8, 35.7, 30.9, 29.6, 29.3, 28.7, 26.0, 24.5, 24.0; IR ($\bar{\nu}$) 3340 (m), 2916 (vs), 2851 (s), 1725 (vs), 1510 (w), 1472 (w), 1445 (w), 1419 (w), 1396 (w), 1320 (m), 1296 (m), 1266 (m), 1178 (m), 1169 (m), 1106 (m), 1077 (m), 1037 (m), 933 (w), 833 (m) cm^{-1}; HRMS (m/z) [M^+] calcd for $C_{38}H_{50}O_6$ 602.3602, found 602.3600.

*Bis(4-(3-oxobut-1-ynyl)benzoic acid)ethane-1,2-diyl Ester (**12a**).* Bis(4-(3-hydroxybut-1-ynyl)benzoic acid)ethane-1,2-diyl ester (**11a**) (1.00 g, 2.46 mmol) was subjected to the reaction conditions described in GP3. The reaction was complete after 23 h, yielding the title compound as a light yellowish solid (0.72 g, 73%): R_f 0.6 (PE/EtOAc 1:1); mp 160−162 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (d, J = 8.2 Hz, 4H), 7.62 (d, J = 8.2 Hz, 4H), 4.68 (s, 4H), 2.46 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.3, 165.4, 133.0, 131.3, 129.9, 124.9, 90.1, 88.3, 63.1, 32.9; IR ($\bar{\nu}$) 2962 (w), 2200 (s), 1711 (vs), 1664 (s), 1604 (m), 1403 (m), 1366 (m), 1258 (vs), 1178 (m), 1118 (s), 1106 (s), 1010 (m) cm^{-1}; HRMS (m/z) [M^+] calcd for $C_{24}H_{18}O_6$ 402.1103, found 402.1100; UV−vis (ACN) λ_{max} (nm) = 276 (ε = 42506 $M^{-1}\cdot cm^{-1}$).

*Bis(4-(3-oxobut-1-ynyl)benzoic acid)propane-1,3-diyl Ester (**12b**).* Bis(4-(3-hydroxybut-1-ynyl)benzoic acid)propane-1,3-diyl ester (**11b**) (1.00 g, 2.38 mmol) was subjected to the reaction conditions described in GP3. The reaction was complete after 24 h, yielding the title compound as a light yellowish solid (0.72 g, 73%): R_f 0.32 (PE/EtOAc 3:1); mp 118−119 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (d, J = 8.2 Hz, 4H), 7.59 (d, J = 8.2 Hz, 4H), 4.51 (t, J = 6.1 Hz, 4H), 2.46 (s, 6H), 2.27 (d, J = 5.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.4, 165.5, 132.9, 131.6, 129.7, 124.7, 90.0, 88.4, 62.3, 32.9, 28.2; IR ($\bar{\nu}$) 2914 (w), 2205 (s), 1710 (s), 1668 (vs), 1405 (w), 1361 (s), 1269 (vs), 1178 (s), 1123 (s), 1108 (s) cm^{-1}; HRMS (m/z) [M^+] calcd for $C_{25}H_{20}O_6$ 416.1260, found 416.1266; UV−vis (ACN) λ_{max} (nm) = 276 (ε = 48978 $M^{-1}\cdot cm^{-1}$),

*Bis(4-(3-oxobut-1-ynyl)benzoic acid)-butan-1,4-diyl Ester (**12c**).* Bis(4-(3-hydroxybut-1-ynyl)benzoic acid)-butane-1,4-diyl ester (**11c**) (1.5 g, 3.45 mmol) was subjected to the reaction conditions described in GP3. The reaction was complete after 23 h, yielding the title

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compound as a light yellowish solid (0.82 g, 55%). R_f 0.15 (PE/EtOAc 3:1); mp 127.128 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (d, J = 8.4 Hz, 4H), 7.61 (d, J = 8.4 Hz, 4H), 4.41 (s, 4H), 2.46 (s, 6H), 1.95 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.4, 165.6, 132.9, 131.9, 129.7, 124.6, 90.0, 88.5, 65.0, 32.9, 25.6; IR ($\bar{\nu}$) 2959 (w), 2198 (s), 1714 (s), 1667 (s), 1266 (vs), 1239 (s), 1108 (s) cm^{-1}; HRMS (m/z) [M$^+$] calcd for $C_{26}H_{22}O_6$ 430.1416, found 430.1408; UV−vis (ACN) λ_{max} (nm) = 276 (ε = 47245 M^{-1}·cm^{-1}).

*Bis(4-(3-oxobut-1-ynyl)benzoic acid)hexane-1,6-diyl Ester (**12d**).* Bis(4-(3-hydroxybut-1-ynyl)benzoic acid)hexane-1,6-diyl ester (**11d**) (0.935 g, 2.02 mmol) was subjected to the reaction conditions described in GP3. The reaction was complete after 20 h, yielding the title compound as a light yellowish solid (0.78 g, 86%): R_f 0.43 (PE/EtOAc 3:1); mp 101−102 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (d, J = 8.7 Hz, 4H), 7.60 (d, J = 8.7 Hz, 4H), 4.33 (t, J = 6.6 Hz, 4H), 2.45 (s, 6H), 1.92−1.69 (m, 4H), 1.58−1.45 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.3, 165.7, 132.9, 132.1, 129.7, 124.4, 89.9, 88.6, 65.4, 32.8, 28.7, 25.8; IR ($\bar{\nu}$) 2945 (w), 2205 (m), 1707 (s), 1668 (s), 1269 (vs), 1105 (s), 771 (s), 697 (s) cm^{-1}; HRMS (m/z) [M$^+$] calcd for $C_{28}H_{26}O_6$ 458.1729, found 458.1725; UV−vis (ACN) λ_{max} (nm) = 276 (ε = 47904 M^{-1}·cm^{-1}).

*Bis(4-(3-oxobut-1-ynyl)benzoic acid)dodecane-1,12-diyl Ester (**12e**).* Bis(4-(3-hydroxybut-1-ynyl)benzoic acid)dodecane-1,12-diyl ester (**11e**) (1.10 g, 2.01 mmol) was subjected to the reaction conditions described in GP3. The reaction was complete after 22 h, yielding the title compound as an orange solid (0.77 g, 71%): R_f 0.5 (PE/EtOAc 3:1); mp 78−79 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (d, J = 8.3 Hz, 4H, H−Ar), 7.61 (d, J = 8.3 Hz, 4H, H-Ar), 4.31 (t, J = 6.7 Hz, 4H, CH_2), 2.46 (s, 6H, CH_3), 1.87−1.64 (m, 4H, CH_2), 1.53−1.16 (m, 16H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.4, 165.7, 132.9, 132.2, 129.7, 124.4, 89.9, 88.6, 65.7, 32.9, 29.9−29.2, 28.8, 26.1; IR ($\bar{\nu}$) 2918 (s), 2850 (m), 2208 (m), 1709 (vs), 1670 (s), 1604 (w), 1408 (w), 1359 (w), 1271 (s), 1181 (m), 1122 (m), 1015 (w) cm^{-1}; HRMS (m/z) [M$^+$] calcd for $C_{34}H_{38}O_6$ 542.2668, found 542.2641; UV−vis (ACN) λ_{max} (nm) = 276 (ε = 50282 M^{-1}·cm^{-1}).

*Bis(4-(2-(3-oxobut-1-ynyl)phenyl)acetic acid)-ethane-1,2-diyl Ester (**12f**).* Bis(2-(4-(3-hydroxybut-1-ynyl)phenyl)acetic acid)-ethane-1,2-diyl ester (**11f**) (1.00 g, 2.3 mmol) was subjected to the reaction conditions described in GP3. The reaction was complete after 24 h, yielding the title compound as a light yellowish solid (0.7 g, 71%). R_f 0.55 (PE/EtOAc 1:1); mp 79−80 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (d, J = 8.1 Hz, 4H), 7.27 (d, J = 8.2 Hz, 4H), 4.30 (s, 4H), 3.62 (s, 4H), 2.44 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.6, 170.5, 136.7, 133.4, 129.8, 119.0, 90.0, 88.6, 62.7, 41.1, 32.8; IR ($\bar{\nu}$) 2986 (w), 200 (vs), 1738 (vs), 1664 (vs), 1362 (m), 1149 (s) cm^{-1}; HRMS (m/z) [M$^+$] calcd for $C_{26}H_{22}O_6$ 430.1416, found 430.1424; UV−vis (ACN): λ_{max} (nm) = 276 (ε = 37840 M^{-1}·cm^{-1}).

*Bis(4-(2-(3-oxobut-1-ynyl)phenyl)acetic acid)-butane-1,4-diyl Ester (**12g**).* Bis(2-(4-(3-hydroxybut-1-ynyl)phenyl)acetic acid)-butane-1,4-diyl ester (**11g**) (0.20 g, 0.432 mmol) was subjected to the reaction conditions described in GP3. The reaction was complete after 23 h, yielding the title compound as a light yellowish solid (0.14 g, 70%). R_f 0.67 (PE/EtOAc 1:1); mp 62−63 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, J = 8.3 Hz, 4H), 7.30 (d, J = 8.4 Hz, 4H), 4.09 (t, J = 5.0 Hz, 4H), 3.64 (s, 4H), 2.44 (s, 6H), 1.67−1.61 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.7, 170.8, 137.1, 133.5, 129.8, 118.9, 90.1, 88.6, 64.6, 41.4, 32.9, 25.3; IR ($\bar{\nu}$) 2962 (w), 2201 (vs), 1721 (vs), 1670 (vs), 1224 (s), 1146 (s), 970 (m) cm^{-1}; HRMS (m/z) [M$^+$] calcd for $C_{28}H_{26}O_6$ 458.1729, found 413.1726 ; UV−vis (ACN): λ_{max} (nm) = 276 (ε = 35073 M^{-1}·cm^{-1}).

*Bis(4-(2-(3-oxobut-1-ynyl)phenyl)acetic acid)hexane-1,6-diyl Ester (**12h**).* Bis(2-(4-(3-hydroxybut-1-ynyl)phenyl)acetic acid)-hexane-1,6-diyl ester (**11h**) (1.14 g, 2.32 mmol) was subjected to the reaction conditions described in GP3. The reaction was complete after 24 h, yielding the title compound as a light yellowish solid (0.77 g, 68%). R_f 0.35 (PE/EtOAc 3:1); mp 52−53 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, J = 8.2 Hz, 4H), 7.30 (d, J = 8.1 Hz, 4H), 4.07 (t, J = 6.6 Hz, 4H), 3.63 (s, 4H), 2.44 (s, 6H), 1.67−1.49 (m, 4H), 1.29 (t, J = 10.1 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.7, 170.9, 137.2, 133.4, 129.8, 118.8, 90.2, 88.6, 65.1, 41.5, 32.9, 28.5, 25.5; IR ($\bar{\nu}$) 2958 (w), 2199 (s), 1730 (vs), 1668 (vs), 1215 (m), 1153 (s), 986 (m) cm^{-1}; HRMS (m/z) [M$^+$] calcd for $C_{30}H_{30}O_6$ 486.2042, found 486.2044; UV−vis (ACN): λ_{max} (nm) = 276 (ε = 37412 M^{-1}·cm^{-1}).

*Bis(3-(4-(3-oxobut-1-ynyl)phenyl)propionic acid)-ethane-1,2-diyl Ester (**12i**).* Bis(3-(4-(3-hydroxybut-1-ynyl)phenyl)propionic acid)-ethane-1,2-diyl ester (**11i**) (1.00 g, 2.16 mmol) was subjected to the reaction conditions described in GP3. The reaction was complete after 22 h, yielding the title compound as a light yellowish solid (0.6 g, 60%). R_f 0.4 (PE/EtOAc 3:1); mp 54−55 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (d, J = 8.2 Hz, 4H), 7.21 (d, J = 8.1 Hz, 4H), 4.24 (s, 4H), 2.96 (t, J = 7.6 Hz, 4H), 2.63 (t, J = 7.6 Hz, 4H), 2.43 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.7, 172.3, 143.7, 133.4, 128.8, 118.0, 90.5, 88.4, 62.4, 35.1, 32.9, 30.9; IR ($\bar{\nu}$) 2919 (w), 2197 (vs), 1733 (s), 1657 (vs), 1605 (w), 1356 (m), 1282 (m), 1150 (s), 978 (m), 836 (m) cm^{-1}; HRMS (m/z) [M$^+$] calcd for $C_{28}H_{26}O_6$ 458.1729, found 458.1714; UV−vis (ACN): λ_{max} (nm) = 276 (ε = 36700 M^{-1}·cm^{-1}).

*Bis(3-(4-(3-oxobut-1-ynyl)phenyl)propionic acid)hexane-1,6-diyl Ester (**12j**).* Bis(3-(4-(3-hydroxybut-1-ynyl)phenyl)propionic acid)-hexane-1,6-diyl ester (**11j**) (1.00 g, 2.62 mmol) was subjected to the reaction conditions described in GP3. The reaction was complete after 23 h, yielding the title compound as an orange solid (1.0 g, 74%): R_f 0.45 (PE/EtOAc 3:1); mp 62−63 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 (d, J = 8.1 Hz, 4H), 7.22 (d, J = 8.1 Hz, 4H), 4.04 (t, J = 6.6 Hz, 4H), 2.95 (d, J = 7.6 Hz, 4H), 2.62 (t, J = 7.6 Hz, 4H), 2.43 (s, 6H), 1.57 (m, 4H,), 1.28 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.7, 172.6, 144.0, 133.4, 128.8, 117.9, 90.6, 88.4, 64.6, 35.4, 32.8, 31.0, 28.6, 25.6; IR ($\bar{\nu}$) 2929 (w), 2197 (vs), 1718 (s), 1670 (vs), 1355 (m), 1278 (m), 1151 (s) cm^{-1}; HRMS (m/z) [M$^+$] calcd for $C_{32}H_{34}O_6$ 514.2355, found 514.2363; UV−vis (ACN): λ_{max} (nm) = 276 (ε = 36707 M^{-1}·cm^{-1}).

*Bis(3-(4-(3-oxobut-1-ynyl)phenyl)propionic acid)decane-1,10-diyl Ester (**12k**).* Bis(3-(4-(3-hydroxybut-1-ynyl)phenyl)propionic acid)-decane-1,10-diyl ester (**11k**) (0.211 g, 0.367 mmol) was subjected to the reaction conditions described in GP3. The reaction was complete after 25 h, yielding the title compound as a light yellowish solid (0.163 g, 78%): R_f 0.25 (PE/EtOAc 3:1); mp 38−40 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (d, J = 8.0 Hz, 4H), 7.22 (d, J = 8.0 Hz, 4H), 4.04 (t, J = 6.7 Hz, 4H), 2.97 (t, J = 7.6 Hz, 4H), 2.62 (t, J = 7.6 Hz, 4H), 2.43 (s, 6H), 1.63−1.49 (m, 4H), 1.26 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.7, 172.6, 144.0, 133.4, 128.8, 117.9, 90.6, 88.3, 64.9, 35.4, 32.8, 31.1, 29.4, 28.7, 26.0; IR ($\bar{\nu}$) 2958(m), 2920 (m), 2850 (m), 2202 (s), 1725 (vs), 1668 (vs), 1509 (w), 1413 (w), 1360 (m), 1281 (m), 1180 (m), 1152 (s), 983 (w), 834 (w), 641 (w) cm^{-1}; HRMS (m/z) [M$^+$] calcd for $C_{36}H_{42}O_6$ 570.2981, found 570.2983; UV−vis (ACN) λ_{max} (nm) = 276 (ε = 37243 M^{-1}·cm^{-1}).

*Bis(3-(4-(3-oxobut-1-ynyl)phenyl)propionic acid)dodecane-1,12-diyl Ester (**12l**).* Bis(3-(4-(3-hydroxybut-1-ynyl)phenyl)propionic acid)dodecane-1,12-diyl ester (**11l**) (1.08 g, 1.79 mmol) was subjected to the reaction conditions described in GP3. The reaction was complete after 23 h, yielding the title compound as a light yellowish solid (0.71 g, 66%): R_f 0.32 (PE/EtOAc 3:1); mp 51−53 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (d, J = 8.1 Hz, 4H), 7.22 (d, J = 8.1 Hz, 4H), 4.04 (t, J = 6.7 Hz, 4H), 2.97 (t, J = 7.6 Hz, 4H), 2.62 (t, J = 7.6 Hz, 4H), 2.43 (s, 6H), 1.67−1.46 (m, 4H), 1.25 (s, 16H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.7, 172.6, 144.0, 133.4, 128.8, 117.9, 90.6, 88.4, 64.9, 35.4, 32.8, 31.1, 29.6, 29.3, 28.7, 26.0; IR ($\bar{\nu}$) 2960 (m), 2921 (m), 2851 (m), 2203 (vs), 1725 (vs), 1668 (s), 1510 (w), 1426 (w), 1360 (m), 1282 (m), 1185 (s), 1151 (s), 1051 (w) cm^{-1}; HRMS (m/z) [M$^+$] calcd for $C_{38}H_{46}O_6$ 598.3294, found 598.3307; UV−vis (ACN) λ_{max} (nm) = 276 (ε = 39223 M^{-1}·cm^{-1}).

Bis(4-(3-oxobut-1-ynyl)benzoic acid)ethane-1,2-diyl ester (**12a**) (0.132 g, 0.32 mmol) was subjected to the reaction conditions described in GP4. The starting material was recovered completely (0.131 g, 99%).

*14,15-Diacetyl-6,7-dihydro-5H,9H-2,17-(ethanediylidene)-10,13-etheno-4,8-benzodioxacyclopentadecine-3,9-dione (**13b**).* Bis(4-(3-oxobut-1-ynyl)benzoic acid)propane-1,3-diyl ester (**12b**) (0.141 g, 0.34 mmol) was subjected to the reaction conditions described in GP4. The reaction was complete after 70 min, yielding the title compound

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as a yellowish solid (0.047 mg, 33%). The starting material **12b** was recovered (45 mg, 32%): R_f 0.39 (PE/EtOAc 1:1); mp 200−201 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.41 (s, 1H), 8.04−7.91 (m, 2H), 7.74 (d, J = 8.2 Hz, 2H), 7.45 (d, J = 8.2 Hz, 2H), 6.34 (s, 1H), 4.38 (t, J = 7.0 Hz, 2H), 4.28−4.16 (m), 2.79 (s, 3H), 2.60 (s, 3H), 2.11−1.97 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.1, 198.3, 169.6, 164.9, 141.0, 136.8, 136.5, 136.0, 135.1, 133.8, 132.5, 131.0, 130.1, 129.1, 127.7, 126.5, 66.9, 62.9, 32.5, 29.5, 27.1; IR ($\bar{\nu}$) 2925 (w), 1720 (vs), 1703 (vs), 1677 (s), 1383 (m), 1259 (s), 1237 (s), 1125 (m), 1100 (m), 1076 (m) cm^{-1}; HRMS (m/z) [M$^+$] calcd for $C_{25}H_{20}O_6$ 416.1260, found 416.1279.

*15,16-Diacetyl-5,6,7,8-tetrahydro-10H-2,18-(ethanediylidene)-11,14-etheno-4,9-benzodioxacyclohexadecine-3,10-dione (**13c**).* Bis(4-(3-oxobut-1-ynyl)benzoic acid)butane-1,4-diyl ester (**12c**) (0.124 g, 0.27 mmol) was subjected to the reaction conditions described in GP4. The reaction was complete after 60 min, yielding the title compound as a yellowish solid (0.058 g, 47%). The starting material **12c** was recovered (0.029 g, 23%): R_f 0.43 (PE/EtOAc 1:1); mp 216−217 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.07 (dd, J = 10.8, 4.6 Hz, 3H), 7.98 (d, J = 8.5 Hz, 1H), 7.41 (d, J = 8.2 Hz, 2H), 6.74 (s, 1H), 4.56−4.34 (m, 2H), 4.17−4.06 (m, 2H), 2.79 (s, 3H), 2.55 (s, 3H), 1.87−1.76 (m, 2H), 1.70−1.57 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.6, 198.5, 179.7, 168.7, 166.0, 141.4, 137.5, 136.9, 135.6, 134.2, 133.2, 132.2, 131.4, 130.7, 129.9, 129.7, 129.5, 127.2, 66.6, 66.0, 32.8, 29.5, 27.4, 26.3; IR ($\bar{\nu}$) 2965 (w), 1709 (vs), 1673 (s), 1382 (m), 1262 (s), 1239 (s), 1111 (m), 1092 (s),1016 (m) cm^{-1}; HRMS (m/z) [M$^+$] calcd for $C_{26}H_{22}O_6$ 430.1416, found 430.1424.

*17,18-Diacetyl-5,6,7,8,9,10-hexahydro-12H-2,20-(ethanediylidene)-13,16-etheno-4,11 benzodioxacyclo-octadecine-3,12-dione (**13d**).* Bis(4-(3-oxobut-1-ynyl)benzoic acid)hexane-1,6-diyl ester (**12d**) (0.106 g, 0.23 mmol) was subjected to the reaction conditions described in GP4. The reaction was complete after 50 min, yielding the title compound as a yellowish solid (0.074 g, 70%): R_f 0.50 (PE/EtOAc 1:1); mp 169−170 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.44 (s, 1H), 8.21−8.10 (m, 3H), 8.02 (d, J = 8.5 Hz, 1H), 7.46 (s, 1H), 7.40 (d, J = 8.1 Hz, 2H), 4.53 (t, J = 5.2 Hz, 2H), 4.24−4.11 (m, 2H), 2.79 (s, 3H), 2.41 (s, 3H), 1.87−1.76 (m, 2H), 1.59−1.46 (m, 4H), 1.40−1.29 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.7, 198.3, 166.5, 166.0, 140.7, 136.7, 134.7, 134.4, 134.0, 131.3, 131.1, 130.7, 129.6, 129.5, 129.0, 127.2, 66.7, 32.4, 30.4, 29.5, 29.1, 28.2, 27.2; IR ($\bar{\nu}$) 2930 (m), 2857 (w), 1715 (vs), 1681 (s), 1383 (m), 1266 (vs), 1101 (s), 1018 (m), 761 (m) cm^{-1}; HRMS (m/z) [M$^+$] calcd for $C_{28}H_{26}O_6$ 458.1729, found 458.1734.

*23,24-Diacetyl-5,6,7,8,9,10,11,12,13,14,15,16-dodecahydro-18H-2,26-(ethanediylidene)-19,22-etheno-4,17-benzodioxacyclotetracosine-3,18-dione (**13e**).* Bis(4-(3-oxobut-1-ynyl)benzoic acid)-dodecane-1,12-diyl ester (0.130 g, 0.24 mmol) was subjected to the reaction conditions described in GP4. The reaction was complete after 60 min, yielding the title compound as a yellowish solid (0.051 g, 39%): R_f 0.52 (PE/EtOAc 1:1); mp 95−97 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.44 (s, 1H), 8.21 (dd, J = 12.6, 8.4 Hz, 4H), 8.08 (d, J = 8.4 Hz, 1H), 7.42 (d, J = 8.0 Hz, 2H), 4.51−4.39 (m, 2H), 4.24 (t, J = 6.2 Hz, 2H), 2.76 (s, 3H), 2.08 (s, 3H), 1.56 (ddd, J = 20.9, 12.9, 6.7 Hz, 4H), 1.38−1.15 (m, 16H); ^{13}C NMR (75 MHz, $CDCl_3$) δ ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.2, 198.5, 166.4, 166.1, 140.4, 140.0, 136.8, 135.2, 134.3, 133.1, 131.2, 131.1, 129.8, 129.6, 128.4, 127.5, 65.5, 65.5, 64.9, 31.9, 28.7, 28.6, 28.4, 28.1, 27.8, 27.5, 27.3, 27.0, 25.6, 24.9; IR ($\bar{\nu}$) 2926 (s), 2855 (m), 1716 (vs), 1684 (s), 1383 (m), 1266 (vs), 1177 (m), 1106 (m), 1019 (w) cm^{-1}; HRMS (m/z) [M$^+$] calcd for $C_{34}H_{38}O_6$ 542.2668, found 542.2640.

*15,16-Diacetyl-6,7-dihydro-2,18-(ethanediylidene)-11,14-etheno-5,8-benzodioxacyclohexadecine-4,9(3H,10H)-dione (**13f**).* Bis(2-(4-(3-oxobut-1-ynyl)phenyl)acetic acid)ethane-1,2-diyl ester (**12f**) (0.121 g, 0.28 mmol) was subjected to the reaction conditions described in GP4. The reaction was complete after 50 min, yielding the title compound as a yellowish solid (0.063 g, 52%): R_f 0.24 (PE/EtOAc 1:1); mp 219−220 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.92 (d, J = 8.3 Hz, 1H), 7.43−7.30 (m, 3H), 7.20 (d, J = 8.0 Hz, 2H), 6.83 (s, 1H), 4.41−4.24 (m, 2H), 4.16−4.01 (m, 2H), 3.80 (s, 2H), 3.66 (s, 2H), 2.75 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.4, 198.2, 170.8, 170.7, 138.1, 135.9, 135.6, 134.4, 132.6, 131.3, 131.1, 130.8, 129.6, 126.5, 129.4, 125.3, 64.3, 62.2, 42.0, 41.7, 32.5, 26.9; IR ($\bar{\nu}$) 2924 (w), 1728 (vs), 1699 (s), 1675 (s), 1427 (m), 1309 (m), 1260(m), 1232 (s), 1134 (m) cm^{-1}; HRMS (m/z) [M$^+$] calcd for $C_{26}H_{22}O_6$ 430.1416, found 430.1411.

*17,18-Diacetyl-6,7,8,9-tetrahydro-2,20-(ethanediylidene)-13,16-etheno-5,10-benzodioxacyclooctadecine-4,11(3H,12H)-dione (**13g**).* Bis(2-(4-(3-oxobut-1-ynyl)phenyl)acetic acid)butane-1,4-diyl ester (**12g**) (0.137 g, 0.29 mmol) was subjected to the reaction conditions described in GP4. The reaction was complete after 40 min, yielding the title compound as a yellowish solid (0.072 g, 53%): R_f 0.54 (PE/EtOAc 1:1); mp 186−187 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.97 (d, J = 8.2 Hz, 1H), 7.45 (dd, J = 12.4, 5.8 Hz, 4H), 7.26 (d, J = 8.1 Hz, 2H), 4.22 (t, J = 5.4 Hz, 2H), 3.95 (t, J = 7.0 Hz, 2H), 3.72 (s, 4H), 2.76 (s, 3H), 2.16 (s, 3H), 1.60 (dt, J = 10.0, 5.7 Hz, 2H), 1.51−1.37 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.8, 198.5, 171.1, 170.6, 139.5, 135.8, 135.1, 134.6, 133.0, 131.1, 129.8, 129.5, 129.4, 125.5, 65.0, 63.9, 42.4, 41.9, 32.1, 27.1, 25.5, 25.4; IR ($\bar{\nu}$) 2959 (w), 1728 (vs), 1699 (s), 1678 (s), 1426 (m), 1246 (s), 1155 (m), 1140 (m), 1020 (w) cm^{-1}; HRMS (m/z) [M$^+$] calcd for $C_{28}H_{26}O_6$ 458.1729, found 458.1732.

*19,20-Diacetyl-6,7,8,9,10,11-hexahydro-2,22-(ethanediylidene)-15,18-etheno-5,12-benzodioxacycloicosine-4,13(3H,14H)-dione (**13h**).* Bis(2-(4-(3-oxobut-1-ynyl)phenyl)acetic acid)hexane-1,6-diyl ester (**12h**) (0.119 g, 0.24 mmol) was subjected to the reaction conditions described in GP4. The reaction was complete after 40 min, yielding the title compound as a yellowish solid (0.084 g, 70%): R_f 0.54 (PE/EtOAc 1:1); mp 149−150 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.96 (d, J = 8.3 Hz, 1H), 7.50 (d, J = 8.4 Hz, 1H), 7.47−7.41 (m, 3H), 7.25 (d, J = 7.6 Hz, 2H), 4.18 (t, J = 5.4 Hz, 2H), 3.97 (t, J = 5.5 Hz, 2H), 3.67 (d, J = 7.3 Hz, 4H), 2.73 (s, 3H), 2.09 (s, 3H), 1.62 (dd, J = 11.7, 5.8 Hz, 2H), 1.52−1.42 (m, 2H), 1.41−1.33 (m, 2H), 1.31−1.22 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.9, 198.5, 171.4, 170.9, 139.6, 135.9, 135.8, 135.0, 134.6, 134.5, 133.1, 131.2, 131.1, 129.8, 129.5, 129.3, 127.1, 65.2, 64.2, 42.4, 32.0, 28.6, 28.3, 27.1, 25.6, 25.3; IR ($\bar{\nu}$) 2926 (m), 2858 (m), 1733 (s), 1715 (vs), 1698 (vs), 1682 (vs), 1431 (m), 1381 (m), 1301 (m), 1247 (s), 1133 (m), 983 (m) cm^{-1}; HRMS (m/z) [M$^+$] calcd for $C_{30}H_{30}O_6$ 486.2042, found 486.2059.

*17,18-Diacetyl-3,4,7,8,11,12-hexahydro-5H,10H-2,20-(ethanediylidene)-13,16-etheno-6,9-benzodioxacyclooctadecine-5,10-dione (**13i**).* Bis(3-(4-(3-oxobut-1-ynyl)phenyl)propionic acid)ethane-1,2-diyl ester (**12i**) (0.115 g, 0.25 mmol) was subjected to the reaction conditions described in GP4. The reaction was complete after 55 min, yielding the title compound as a yellowish solid (0.068 g, 59%): R_f 0.40 (PE/EtOAc 1:1); mp 186−187 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.90 (d, J = 8.4 Hz, 1H), 7.42 (d, J = 8.3 Hz, 1H), 7.30 (d, J = 7.9 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 7.04 (s, 1H), 4.32 (dd, J = 5.1, 2.7 Hz, 2H), 4.05−3.96 (m, 2H), 3.19−3.10 (m, 2H), 3.05 (dd, J = 7.6, 4.4 Hz, 2H), 2.81−2.75 (m, 2H), 2.73 (s, 3H), 2.70−2.64 (m, 2H), 2.11 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.1, 198.6, 172.9, 172.3, 141.5, 140.3, 139.4, 136.0, 134.9, 134.5, 132.6, 131.0, 130.9, 130.6, 129.4, 129.2, 128.8, 122.9, 63.8, 62.1, 36.4, 32.0, 31.6, 29.9, 29.5, 27.1; IR ($\bar{\nu}$) 2921 (w), 1727 (vs), 1676 (s), 1434 (w), 1345 (w), 1294 (m), 1243 (m), 1196 (m), 1148 (m) cm^{-1}; HRMS (m/z) [M$^+$] calcd for $C_{28}H_{26}O_6$ 458.1729, found 458.1711.

*21,22-Diacetyl-3,4,7,8,9,10,11,12,15,16-decahydro-5H,14H-2,24-(ethanediylidene)-17,20-etheno-6,13-benzodioxacyclododecosine-5,14-dione (**13j**).* Bis(3-(4-(3-oxobut-1-ynyl)phenyl)propionic acid)-hexane-1,6-diyl ester (**12j**) (0.114 g, 0.22 mmol) was subjected to the reaction conditions described in GP4. The reaction was complete after 45 min, yielding the title compound as a yellowish solid (0.084 g, 74%): R_f 0.38 (PE/EtOAc 1:1); mp 146−147 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.45 (d, J = 8.3 Hz, 1H), 7.34 (d, J = 7.8 Hz, 2H), 7.26 (s, 1H), 7.19 (d, J = 7.9 Hz, 2H), 4.08 (t, J = 6.4 Hz, 2H), 4.01 (t, J = 5.5 Hz, 2H), 3.11−2.94 (m, 4H), 2.81−2.74 (m, 2H), 2.72 (s, 3H), 2.66−2.55 (m, 2H), 2.08 (s, 3H), 1.68−1.49 (m, 4H), 1.37 (d, J = 3.3 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.3, 198.6, 173.0, 172.3, 141.7, 140.8, 139.5, 136.0,

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134.7, 134.1, 132.8, 131.0, 130.9, 130.8, 129.7, 128.7, 128.2, 125.4, 64.7, 64.0, 35.4, 35.4, 31.9, 30.4, 28.2, 28.0, 27.1, 25.6, 25.0; IR ($\bar{\nu}$) 2923 (m), 2855 (m), 1717 (vs), 1698 (s), 1678 (vs), 1432 (m), 1388 (m), 1353 (m), 1289 (m), 1248 (s), 1150 (s), 1105 (m) cm^{-1}; HRMS (m/z) [M^+] calcd for $C_{32}H_{34}O_6$ 514.2355, found 514.2365.

25,26-Diacetyl-3,4,7,8,9,10,11,12,13,14,15,16,19,20-tetradecahydro-5H,18H-2,28-(ethanediylidene)-21,24-etheno-6,17-benzodioxacyclohexacosine-5,18-dione (**13k**). Bis(3-(4-(3-oxobut-1-ynyl)-phenyl)propionic acid)decane-1,10-diyl ester (**12k**) (0.093 g, 0.16 mmol) was subjected to the reaction conditions described in GP4. The reaction was complete after 30 min, yielding the title compound as a yellowish solid (0.061 g, 66%): R_f 0.6 (PE/EtOAc 1:1); mp 126−128 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.92 (d, J = 8.3 Hz, 1H), 7.44 (d, J = 8.3 Hz, 1H), 7.34−7.27 (m, 3H), 7.20 (d, J = 7.9 Hz, 2H), 4.15 (t, J = 5.6 Hz, 2H), 4.01 (t, J = 6.2 Hz, 2H), 3.04 (dt, J = 11.1, 8.3 Hz, 4H), 2.74 (d, J = 11.5 Hz, 5H), 2.61−2.54 (m, 2H), 2.09 (s, 3H), 1.66−1.51 (m, 4H), 1.37−1.19 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.2, 198.6, 173.0, 172.6, 142.0, 140.8, 139.5, 135.8, 134.7, 134.1, 132.8, 131.1, 130.8, 129.7, 128.7, 128.4, 125.0, 65.0, 64.9, 36.2, 35.5, 31.9, 31.6, 30.9, 29.2, 28.8, 28.7, 28.5, 28.2, 27.12, 26.3, 25.8; IR ($\bar{\nu}$) 2924 (s), 2851 (m), 1731 (vs), 1699 (s), 1670 (s), 1621 (w), 1435 (m), 1350 (m), 1256 (m), 1229 (m), 1135 (m), 1104 (m), 1048 (w), 1022 (m), 965 (w), 929 (w), 836 (w) cm^{-1}; HRMS (m/z) [M^+] calcd for $C_{36}H_{42}O_6$ 570.2981, found 570.2968.

27,28-Diacetyl-3,4,7,8,9,10,11,12,13,14,15,16,17,18,21,22-hexadecahydro-5H,20H-2,30-(ethanediylidene)-23,26-etheno-6,19-benzodioxacyclooctacosine-5,20-dione (**13l**). Bis(3-(4-(3-oxobut-1-ynyl)phenyl)propionic acid)dodecane-1,12-diyl ester (**12l**) (0.127 g, 0.21 mmol) was subjected to the reaction conditions described in GP4. The reaction was complete after 60 min, yielding the title compound as a yellowish solid (0.089 g, 70%): R_f 0.55 (PE/EtOAc 1:1); mp 108−110 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.93 (d, J = 8.3 Hz, 1H), 7.45 (d, J = 8.3 Hz, 1H), 7.32 (d, J = 6.2 Hz, 3H), 7.21 (d, J = 7.9 Hz, 2H), 4.16 (t, J = 5.6 Hz, 2H), 4.02 (t, J = 6.5 Hz, 2H), 3.16−2.90 (m, 4H), 2.85−2.66 (m, 5H, CH_2), 2.64−2.53 (m, 2H), 2.08 (s, 3H,), 1.63 (dd, J = 12.4, 6.2 Hz), 1.58−1.48 (m, 2H), 1.27 (s, 16H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.3, 198.6, 173.0, 172.6, 142.1, 140.7, 139.6, 135.8, 134.6, 134.1, 132.9, 131.1, 131.0, 130.8, 129.8, 128.6, 128.4, 125.3, 64.9, 64.8, 36.1, 35.9, 31.9, 31.8, 31.0, 29.1, 29.0, 28.8, 28.6, 27.2, 25.9; IR ($\bar{\nu}$) 2924 (s), 2852 (m), 1728 (vs), 1671 (s), 1622 (w), 1435 (m), 1350 (m), 1299 (m), 1255 (s), 1140 (m), 1104 (w), 1022 (w) cm^{-1}; HRMS (m/z) [M^+] calcd for $C_{38}H_{46}O_6$ 598.3294, found 598.3288.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01707.

X-ray data for compound **13i** (CIF)

^{1}H and ^{13}C NMR spectra; details of quantum chemical calculations; X-ray structure analysis of **13i** (PDF)

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Notes

The authors declare no competing financial interest.

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(10) Single-crystal X-ray diffraction analysis details of **13i** were deposited with the Cambridge Crystallographic Database (CCDC no. 1491636). Crystal data for **13i**: $C_{28}H_{26}O_6 \cdot C_2H_4O$, M_r = 502.54 g·mol^{-1}, crystal dimensions 0.34 × 0.42 × 0.54 mm, monoclinic, space group $P2_1/c$ (No. 14), a = 14.0313(8) Å, b = 8.1798(3) Å, c = 24.2030(13) Å; β = 104.913(4)°, V = 2684.3(2) Å^3, Z = 4, ρ_{calcd} = 1.24 g·cm^{-1}; μ(Mo Kα) = 0.09 mm^{-1} (λ = 0.71073 Å), T = 210 K; $2\Theta_{max}$ = 50.00°, 24331 reflections measured, 4706 unique (R_{int} = 0.0312), R_1 = 0.0381, w_R = 0.1027 ($I > 2\sigma(I)$).

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