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$CoCl(PPh_3)_3$ as Cyclotrimerization Catalyst for Functionalized Triynes under Mild Conditions

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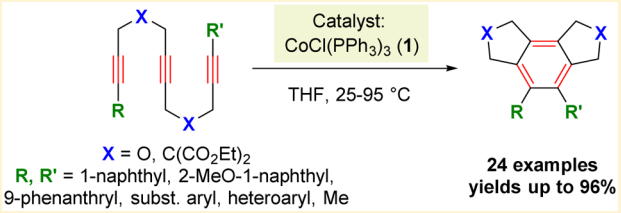
Supporting Information

ABSTRACT: The ubiquitary Co(I) complex $CoCl(PPh_3)_3$ was found to be a convenient catalyst for the [2 + 2 + 2] cycloaddition of functionalized triynes under mild reaction conditions and devoid of any additional additive, yielding the substituted arene compounds. Successful development of synthetic routes to various triynes and the subsequent cyclotrimerization key step gave systematic access to a variety of different bi- and triaryls with good to excellent yields for the cyclization.

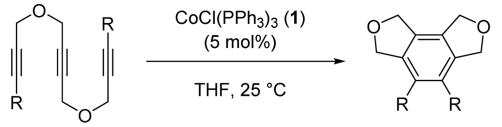


Cyclotrimerization reactions have flourished in an impressive manner,[1] especially as a synthetic tool for the assembly of carbo- and heterocyclic cores of complex organic molecules from structurally simple precursors.[2] However, the investigation of novel catalyst systems or reassessment of known precatalysts can still open the door for either novel synthetic applications and substrate classes or exceptionally mild reaction conditions. For the diverse cyclopentadienyl (Cp) cobalt complex chemistry, several recent examples exemplify the potential in the area of CpCo(I) (pre)catalyst development and uncovering of catalyst activation processes.[3] Recent examples of novel CpCo(I) precatalysts were reported by Gandon et al.[4] as well as by our group.[5] Further development led to the synthesis of air-stable and recyclable precatalysts like $[CpCo\{P(OR)_3\}(trans\text{-}MeO_2CHC{=}CHCO_2Me)]$.[6] Molecular defined phosphine complexes like $[Co(H)(PMe_3)_4]$ have been applied by Amatore, Aubert, and Petit et al. for the cycloaddition of enediynes, providing access to bicyclic trienes.[7]

Another approach is the *in situ* generation of the catalytically active Co(I) species. Okamoto et al. used Co(II) salts together with either bisphosphines, 2-iminomethylpyridines, or N-heterocyclic carbenes (NHC) in the presence of zinc as reductant for the synthesis of substituted benzenes and pyridines.[8] The group of Hilt introduced bisimines and substituted 1,2-dithioethanes as ligands for the *in situ* catalysis with Co(II) salts.[9] The addition of zinc(II) salts proved to be beneficial for the catalytic reaction, as recent mechanistic investigations corroborated for Diels–Alder-type reactions.[10] Cheng et al. applied $[CoI_2(dppe)]$ (dppe = 1,2-bis(diphenylphosphino)ethane) in the presence of zinc for the synthesis of pyridines, benzolactones, and benzolactames.[11]

Since we are interested in the synthesis of novel biaryl systems by [2 + 2 + 2] cycloadditions, we focus on the development of both novel cyclization substrates as well as catalysts. We have now investigated the catalytic activity of the molecular cobalt analogue $CoCl(PPh_3)_3$ (**1**) of the Wilkinson complex, $RhCl(PPh_3)_3$, toward its catalytic properties.[12] The latter has been identified as a suitable catalyst for cyclotrimerizations already by the work of Grigg et al. in the cyclization of acetylenes and diynes, and its application has prospered since.[13] Initial experiments with $CoCl(PPh_3)_3$ (**1**) as catalyst without any additive proved its high activity in intramolecular cyclization reactions from simple triynes **2** and **3** to yield **4** and **5** in high to excellent yields after a short reaction time at room temperature (Scheme 1). Complex **1** is

Scheme 1. Initial Triyne Cyclizations Using $CoCl(PPh_3)_3$ (1) as the Catalyst



commercially available or can be conveniently synthesized from $CoCl_2$ and PPh_3.[14] It is our intention to bring this easy to prepare and rather "cheap" $CoCl(PPh_3)_3$ (**1**) to the wider attention of the community involved in organic synthesis, especially as an alternative for the rather "expensive" Wilkinson catalyst in cyclotrimerizations.

To the best of our knowledge, only single reports for the application of **1** in cyclotrimerizations exist, as exemplified by a work by Butenschön et al., who transformed three molecules of tolane into hexaphenylbenzene in 97% yield.[16] The only more detailed investigations into the reactivity of **1** in cyclotrimerizations was performed by Chung et al. and Field et al., who found that monosubstituted alkynes possessing electron-deficient substituents can be reacted at ambient temperatures,

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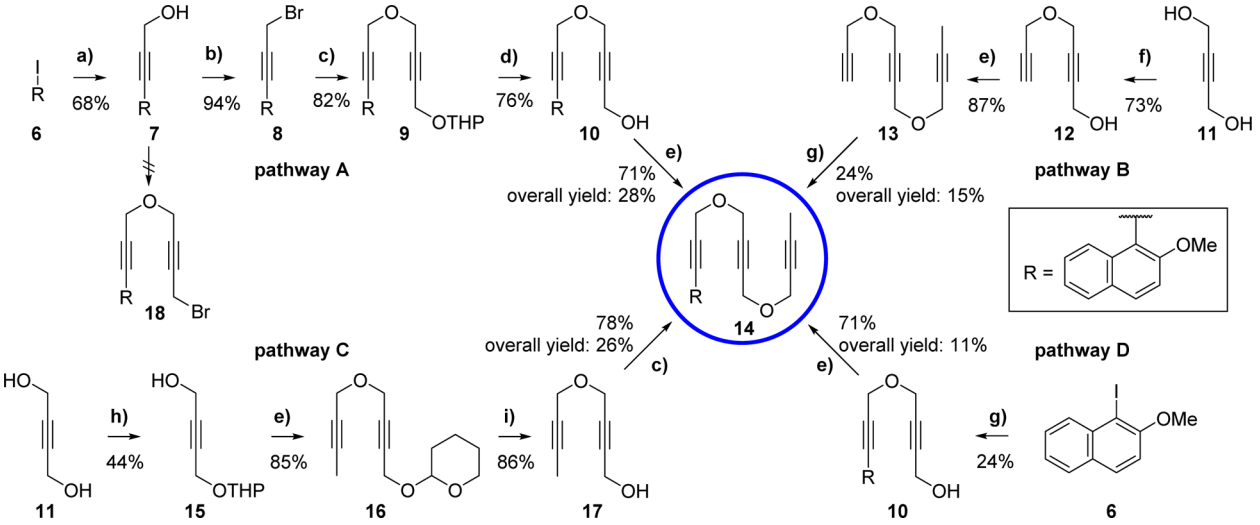
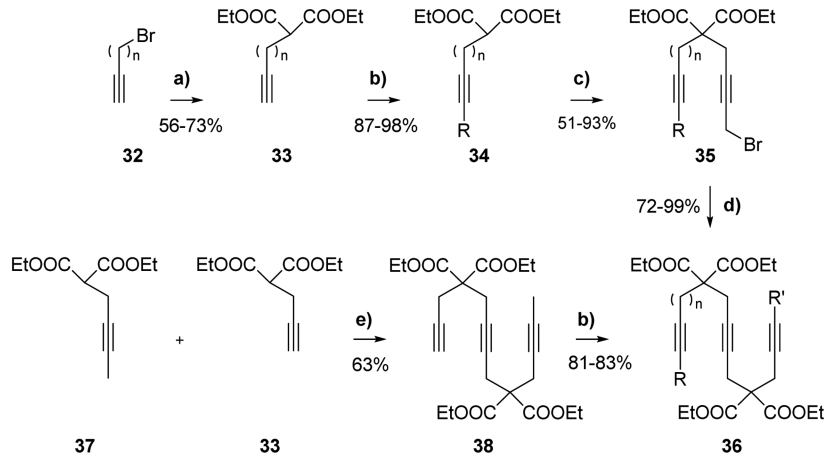
Scheme 2. Synthetic Studies toward Unsymmetrical Substituted Triynes, Exemplified for 14



Reaction conditions: (a) $Pd(PPh_3)_4$ (2 mol %), CuI (6 mol %), 1.3 equiv 2-propyn-1-ol, NEt_3, 50 °C, 15 h. (b) 1.5 equiv CBr_4, PPh_3, CH_2Cl_2, 0 °C, 1 h. (c) (1) 1.2 equiv NaH, **15** (pathway A) or **17** (pathway C), THF, 25 °C, 1 h; (2) **8**, 25 °C, 15 h. (d) *p*-TSA (2 mol %), MeOH, 0–25 °C, 68 h. (e) (1) 1.03 equiv NaH, THF, 0 °C, 1 h; (2) 1-bromo-2-butyne, 25 °C, 18 h. (f) 5 equiv KOH, 5 equiv **11**, 1-propyne, 0–25 °C, 20 h. (g) $Pd(PPh_3)_4$ (5 mol %), CuI (15 mol %), **6** (pathway B) or **12** (pathway D), NEt_3/THF, 25–100 °C, 22 h. (h) 1.09 equiv dihydropyrane, pyridine-*p*-TSA (11 mol %), 40 °C, 1 h, ref 15. (i) *p*-TSA 0.6 equiv, MeOH, 50 °C, 18 h.

Scheme 3. Synthetic Access to Malonate-Bridged Unsymmetrical Triynes Like 36 and Derivatives



Reaction conditions: (a) (1) 1.01 equiv NaH, THF, 0–25 °C, 1 h; (2) bromoalkyne, 0.5 equiv NaI, 65 °C, 15 h, ref 19. (b) $Pd(PPh_3)_4$ (5 mol %), CuI (15 mol %), R-I, NEt_3/THF, 50–60 °C, 18 h. (c) (1) 1.05 equiv NaH, THF, 25 °C, 1 h; (2) 2.5 equiv 1,4-dibromo-2-butyne, THF, 25 °C, 17 h. (d) (1) 1.05 equiv NaH, THF, malonylalkyne, 25 °C, 1 h, then **35**, 15 h. (e) (1) 1.03 equiv NaH, **33**, THF, 0 °C, 1 h; (2) 1,4-dibromo-2-butyne, 25 °C, 2 h; (3) 1.03 equiv NaH, **37**, THF, 0 °C, 1 h, then addition to reaction mixture, 25 °C, 15 h.

whereas disubstituted alkynes require the addition of $NaBPh_4$ for a successful transformation.[17] We report here the systematic preparation of novel triynes and their subsequent cyclotrimerization catalyzed by **1**, yielding highly substituted bi- and triaryls.

The study set out with the preparation of the triynes required for the reactivity study. We initially chose symmetrical triynes first synthesized by Otsuka et al. and adopted their synthetic procedures.[18] Furthermore, with the intention to identify the most efficient synthetic route, we investigated several pathways to construct unsymmetrical aryltriynes, as exemplified for compound **14** (Scheme 2). The potential cyclization products would thus obtain only one chiral biaryl axis. Scheme 2 represents four different approaches for the synthesis of triyne **14**. It is interesting to note that pathway **A** and **C** requiring more steps are more efficient than the conciser routes **B** and **D**. In the latter cases, this can be attributed to the low-yielding Sonogashira cross-coupling with the aryl iodide **6**. In pathway **B**, the synthesis of **12** is complicated by the concurrent formation of the not easily separable triyne byproduct. In addition, the final cross-coupling product still contains Pd residues even after column chromatography. In pathways **A** and **C**, the cross-coupling takes place in an early stage of the synthesis, followed by convenient operations like bromination or etherification during the later stages, which commonly occur in good to very good yields. Interestingly, the reaction of the deprotonated arylpropargylic alcohol **7** with 1,4-dibromobut-2-yne to **18** in pathway **A** did not work. A possible explanation

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would be that the aryl group on the propargylic alcohol is hampering the nucleophilic substitution by stabilizing the negative charge at the alcoholate through the aromatic ring. Circumventing this problem, we brominated the propargylic alcohol **7** to **8** and used the easily accessible partially THP-protected 2-butyn-1,4-diol (**15**) for the nucleophilic substitution. Deprotection of the THP group and one additional nucleophilic substitution furnished the unsymmetrical triyne **14** with the highest overall yield of all investigated routes (Scheme 2, pathway **A**).

Applying the developed optimized procedures, we were able to construct a significant library of symmetrical and unsymmetrical ether-bridged triynes **19**–**31** in mostly good overall yields. We furthermore adopted this procedure to construct a smaller library of unsymmetrical malonate-bridged triynes by using 1,4-dibromobut-2-yne as a key building block (Scheme 3).

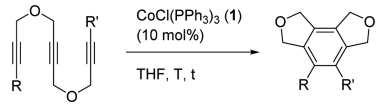
Starting from **33** and **37**, we were able to develop a basically one-pot procedure for the synthesis of triyne **38**. Interestingly, this is only possible starting from **33** and **37** for the malonate-bridged triynes, but not for the synthesis of ether-bridged triynes by using the related 2-butyn-1,4-diol (**11**).[20]

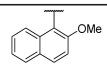
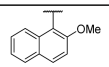
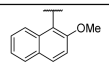
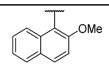
Having this substrate library in hand, we started investigating the catalytic potential of $CoCl(PPh_3)_3$ (**1**) in the cyclization reactions (Table 1). The screening of reaction conditions with the triynes **14** and **19**–**31** quickly showed that **1** is highly suited for the carbocyclization of these substrates in THF solution already at 25 °C and a catalyst loading of 4–10 mol %. For nearly all ether-bridged triynes, good to high yields of the corresponding products were obtained under rather mild conditions, including heteroaryl-substituted triynes like **26** and **27** (Table 1, entries 8 and 9). Only for substrate **20** with a methoxy substituent in the 2-position of the naphthalene (Table 1, entry 2), no conversion was observed, presumably result from steric hindrance, because the reactions performed with unsymmetrical triynes **14** and **30** with a smaller second terminal substituent were successful.

Experiments showed that, for the cyclization of the malonate-bridged triynes **36a**–**h**, higher temperatures (>65 °C) were required (Table 2). Only the triyne **36e** (entry 5) proved to be unreactive under any reaction condition tested. We have reproduced these experiments several times but cannot give an comprehensible explanation for this surprising observation of different reactivity of **36e** and **36f**. We also tested a catalyst system based on a cobalt(II) salt, after reducing with zinc and zinc(II) iodide (like in Table 2, entry 3 (**36c**); see footnote), but the product was not observed either.

We also synthesized and cyclized two examples of triynes exhibiting different bridging units between the alkyne moieties (**54** and **56**, Scheme 4). While **54** included silanol- as well as ether-bridged alkyne moieties, triyne **56** contained alkyl- as well as ether-linked alkyne units. The cyclization of triyne **54** to biaryl **55** worked in acceptable yields already at room temperature. The cyclization of **56** required a longer reaction time to observe the good yield of 74% of the interesting biaryl **57** with the newly formed saturated five- as well as six-membered backbone ring. An alternative reaction, the cyclization of a diyne and alkyne, is complicated by the fact that **1** can also catalyze the addition of terminal C–H bonds to unsaturated functions like other alkynes. The test reaction between internal diynes (like trideca-4,9-diyne) and an internal alkyne (3-hexyne) with **1** as catalyst gave only rather little amounts of the expected substituted arene as well as homocoupling byproducts.

Table 1. Cyclotrimerization of Ether-Bridged Triynes



#	Sm	R	R'	Pr	Yield	T	t
1	19			39	92%	25	36 h
2	20			40	--	25	--
3	21			41	86%	25	17 h
4	22			42	94%	25	24 h
5	23			43	78%[a]	25	36 h
6	24			44	72%[a]	25	36 h
7	25			45	51%[a]	25	36 h
8	26			46	94%	25	18 h
9	27			47	92%	25	18 h
10	28		Me	48	96%	25	36 h
11	14		Me	49	90%[b]	65	18 h
12	29		Ph	50	96%	25	17 h
13	30		Ph	51	85%	25	17 h
14	31			52	90%	25	24 h

[a]A catalyst loading of 4–5 mol % **1** was applied. [b]$CoBr_2$ (5 mol %), Zn, and ZnI_2 used as catalyst system, because **1** gave a very low yield.

To further investigate the role of the anionic ligand at the cobalt center, we used chiral anions usually applied in asymmetric counteranion-directed catalysis (ACDC) to evaluate a potential application for asymmetric [2 + 2 + 2] cycloadditions (Scheme 5).[21] As a screening substrate, we used

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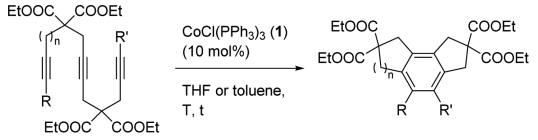
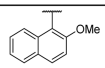
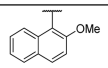
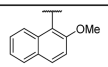
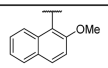
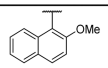
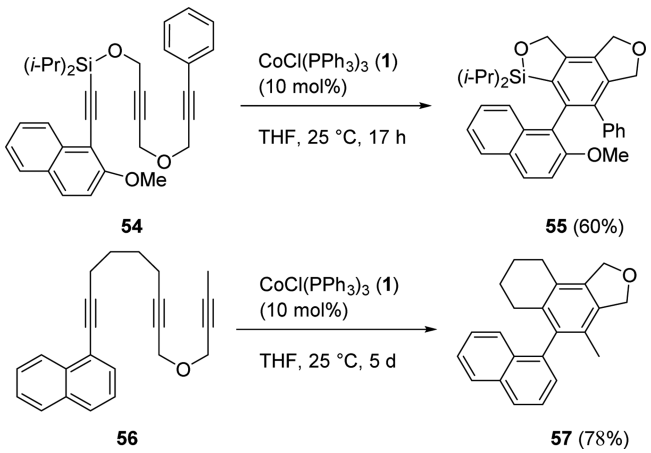
Table 2. Cyclotrimerization of Malonate-Bridged Triynes



#	Sm	n	R	R'	Pr	Yield	T	t
1	36a	1			53a	81%	80	18 h
2	36b	1			53b	96%	80	20 h
3	36c	1		Me	53c	95%[a]	65	21 h
4	36d	1		Me	53d	82%	60 80	18 h 17 h
5	36e	1		Ph	53e	--	95	--
6	36f	1		Ph	53f	46%	80 95	22 h 2 h
7	36g	2		Me	53g	20%	80	20 h
8	36h	2		Ph	53h	92%	80 95	22 h 2 h

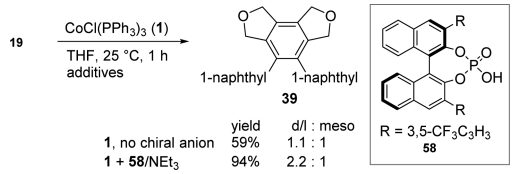
[a]At first $CoBr_2$, Zn, and ZnI_2 were used with basically no conversion; then $CoCl(PPh_3)_3$ (**1**, 5 mol %) was added as catalyst.

Scheme 4. Cyclotrimerization of Triynes 54 and 56



triyne **19** in combination with a chiral anionic ligand salt in the presence of NEt_3. Compound **19** was used before in asymmetric iridium-catalyzed [2 + 2 + 2] cycloadditions by the group of Shibata,[18] and we, therefore, used it as reference for the attempted asymmetric induction experiments. The biaryl has a sufficiently large activation barrier for racemization,

Scheme 5. Screening of Catalytic Activity for 1 in Combination with Selected Chiral Anion



making it a suitable model compound for such experiments being configurationally stable even at higher temperatures.[22] Although we did not observe any enantioselectivity, the application of the TRIP anions **58** and **59** improved the overall yield significantly from 59% using **1** without additives to up to 94% yield using TRIP derivative **58** in just 1 h reaction time (Scheme 5).[23] This phenomenon has been observed and reported earlier applying $NaBPh_4$ as additive in cyclizations with **1**.[17] The possible explanation of raising available coordination space around the Co center by the abstraction of Cl from the metal center can be transferred to the present case. However, we think that the proximity of the tested chiral anion to the metal center is not close enough for providing enantioselectivity beside the observed higher reactivity.

In summary, we presented a study of the systematic access to ether- and malonate-bridged triynes and their conversion under mild conditions to the corresponding biaryl and triaryl products in mostly good to excellent yields. While different possibilities for the preparation of the triynes were investigated, the synthetic differences with respect to the bridging of the alkyne moieties (ether vs malonate) were identified. Furthermore, the commercially available and well-known, albeit for cyclotrimerizations rarely investigated, Co(I) complex $CoCl(PPh_3)_3$ (**1**) has been identified as an excellent catalyst without the requirement of preactivation or the necessity of additional additives. The use of chiral counterions as additives did not induce chirality but showed to improve the reaction rate and yield.

EXPERIMENTAL SECTION

General Experimental Details. All reactions were carried out under an inert gas atmosphere (argon) in flame-dried Schlenk tubes or flasks if not mentioned otherwise. The used chemicals were stored under argon and used as received from the suppliers without further purification. The anhydrous solvents (tetrahydrofuran, toluene, dichloromethane) for the reactions were filtered through 2 columns filled with activated alumina D-201 5 × 8 in a Solvent Purification System. Triethylamine and diisopropylamine were dried over P_2O_5 and distilled under inert conditions and stored under argon. Column chromatography was performed on silica gel with eluent mixtures of cyclohexane (*c*-hex), ethyl acetate (EE), petrol ether (PE), tetrahydrofuran (THF), *n*-hexane (*n*-hex), diethyl ether (DE), and acetone. Compounds first appearing in the Supporting Information or not numbered in the paper are enumerated with **SI**. High-resolution mass spectroscopy (HRMS) analyses were performed using an electron spray ionization time-of-flight (ESI-TOF) method or an electron ionization (EI) with a sector field analyzer.

Syntheses of Building Blocks for Ether-Bridged Triynes. *1-(3-Bromoprop-1-yn-1-yl)-2-methoxynaphthalene (**8**).* Under an argon atmosphere, **7** (2.12 g, 10 mmol, 1.0 equiv) was dissolved in 30 mL of CH_2Cl_2 and cooled to 0 °C. Then, solid PPh_3 (3.93 g, 15 mmol, 1.5 equiv) and CBr_4 (4.97 g, 15 mmol, 1.5 equiv) were added, and the mixture was stirred at 0 °C for 1 h. The solvent was removed under reduced pressure, and the crude product was purified by column chromatography with *c*-hex/EE (10:1). Alkyne **8** (2.58 g, 94%) was received as a colorless solid.

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^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.03 (s, 3H), 4.40 (s, 2H), 7.24 (d, J = 9.1 Hz, 1H), 7.39 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H), 7.56 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.78 (dt, J = 8.1, 0.8 Hz, 1H), 7.84 (d, J = 8.7 Hz, 1H), 8.22 (dq, J = 8.4, 0.8 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 16.1, 56.7, 81.7, 93.6, 105.1, 112.5, 124.4, 125.0, 127.7, 128.2, 128.5, 130.9, 134.8, 159.5 ppm.

HRMS-EI ($C_{14}H_{11}BrO$): calcd: 273.9987; found: 273.9984.

EA: calcd: C 61.11, H 4.03, Br 29.04; found: C 61.09, H 3.87, Br 30.49.

Mp. 76−77 °C.

*2-((4-((3-(2-Methoxynaphthalen-1-yl)prop-2-yn-1-yl)oxy)but-2-yn-1-yl)oxy)tetrahydro-2H-pyran (**9**).* To a cooled solution of sodium hydride (0.17 g, 4.4 mmol, 1.2 equiv, 60 wt % in oil) in 5 mL of THF was slowly added compound **15** (0.61 g, 3.6 mmol, 1.0 equiv) dissolved in 5 mL of THF using a dropping funnel. The solution was stirred for 1 h until the hydrogen evolution ceased. Then, a solution of compound **8** (1.0 g, 3.6 mmol, 1.0 equiv) in 5 mL of THF was slowly added, and the resulting mixture was stirred at 25 °C for 15 h. The reaction was monitored by TLC. After no more observable changes, the reaction was quenched with water and extracted with ethyl acetate. The organic phases were washed with brine and dried over sodium sulfate, and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography with *c*-hex/EE (20:1), and the starting material **8** (0.24 g, 24%) was reisolated and product **9** (0.78 g, 82%) was obtained as a yellow oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.48−1.88 (m, 6H), 3.54 (dtd, J = 11.2, 4.2, 1.8 Hz, 1H), 3.85 (ddd, J = 11.2, 8.4, 3.3 Hz, 1H), 4.02 (s, 3H), 4.26−4.43 (m, 2H), 4.48 (t, J = 1.8 Hz, 2H), 4.69 (s, 2H), 4.83 (dd, J = 3.8, 2.8 Hz, 1H), 7.25 (d, J = 8.7 Hz, 1H), 7.38 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H), 7.54 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.78 (dd, J = 8.1, 0.7 Hz, 1H), 7.83 (d, J = 8.9 Hz, 1H), 8.23 (dd, J = 8.4, 1.0 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 19.1, 25.3, 30.2, 54.3, 56.6, 56.8, 57.8, 62.0, 81.3, 81.5, 82.9, 93.8, 96.9, 105.4, 112.5, 124.2, 125.2, 127.5, 128.1, 128.5, 130.4, 134.6, 159.2 ppm.

HRMS-ESI (TOF) ($C_{23}H_{24}O_4$): calcd: 387.1567 $[M + Na]^+$; found: 387.1568 $[M + Na]^+$.

*4-((3-(2-Methoxynaphthalen-1-yl)prop-2-yn-1-yl)oxy)but-2-yn-1-ol (**10**). Pathway A.* Compound **9** (0.76 g, 2.18 mmol, 1.0 equiv) was dissolved in 15 mL of methanol and cooled to 0 °C, and *para*-toluenesulfonic acid monohydrate (*p*-TSA, 17 mg, 0.08 mmol, 4 mol %) was added. The reaction mixture stirred at 25 °C for 3 days. The reaction was stopped with 3 mL of sat. aqueous $NaHCO_3$ sol., and the solvent was evaporated. The aqueous phase was extracted with ethyl acetate, and the combined organic phases were washed with brine and dried over sodium sulfate. Purification by column chromatography with *c*-hex/EE (2:1) as eluent gave product **10** (0.47 g, 76%) as a colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.64 (s_{br}, 1H), 4.03 (s, 3H), 4.34 (s_{br}, 2H), 4.48 (t, J = 1.8 Hz, 2H), 4.69 (s, 2H), 7.25 (d, J = 9.1 Hz, 1H), 7.38 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H), 7.54 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.78 (d, J = 8.3 Hz, 1H), 7.84 (d, J = 9.1 Hz, 1H), 8.23 (dd, J = 8.5, 1.0 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 51.2, 56.6, 56.8, 58.0, 81.5 (2×), 85.1, 93.7, 105.5, 112.6, 124.3, 125.2, 127.5, 128.1, 128.5, 130.5, 134.6, 159.3 ppm.

HRMS-EI ($C_{18}H_{16}O_3$): calcd: 280.1094, found: 280.1091.

EA: calcd: C 77.12, H 5.75; found: C 77.02, H 5.85.

Pathway D. Following the procedure for **34a**, complex $Pd(PPh_3)_4$ (0.23 g, 0.20 mmol, 5 mol %), CuI (0.12 g, 0.60 mmol, 15 mol %), and **6** (1.14 g, 4.02 mmol, 1.0 equiv) as solution in 23 mL of NEt_3 and **12** (0.50 g, 4.02 mmol, 1.0 equiv) dissolved in 4 mL of THF were mixed and stirred at 50 °C for 19 h. After flash chromatography with *n*-hex/EE (4:1, 2:1, 1:1), product **10** (0.27 g, 24%) was obtained as a colorless oil.

*2-((4-((3-(Naphthalen-1-yl)prop-2-yn-1-yl)oxy)but-2-yn-1-yl)oxy)-tetrahydro-2H-pyran (**SI-VI**).* Following the above synthetic procedure for compound **9**, a mixture of sodium hydride (0.27 g, 6.6 mmol, 1.2 equiv, 60 wt % in oil), compound **15** (0.90 g, 5.3 mmol, 1.0 equiv), and **SI-V** (1.3 g, 5.3 mmol, 1.0 equiv) in 25 mL of THF was stirred at 25 °C for 17 h. After flash chromatography with cyclohexane, the product **SI-VI** (1.43 g, 81%) was obtained as a slightly yellow oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.48−1.68 (m, 4H), 1.69−1.89 (m, 2H), 3.54 (dddd, J = 11.2, 5.8, 3.6, 2.0 Hz, 1H), 3.85 (ddd, J = 11.5, 8.7, 3.3 Hz, 1H), 4.31 (dt, J = 15.7, 1.8 Hz, 1H), 4.39 (dt, J = 15.7, 1.8 Hz, 1H), 4.46 (t, J = 1.8 Hz, 2H), 4.64 (s, 2H), 4.84 (t, J = 3.3 Hz, 1H), 7.42 (dd, J = 8.3, 7.1 Hz, 1H), 7.48−7.62 (m, 2H), 7.69 (dd, J = 7.2, 1.2 Hz, 1H), 7.81−7.88 (m, 2H), 8.32 (dd, J = 8.1, 1.0 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 19.1, 25.4, 30.3, 54.3, 57.0, 57.6, 62.1, 81.3, 83.2, 84.9, 89.1, 96.9, 120.1, 125.2, 126.1, 126.5, 126.9, 128.3, 129.1, 130.8, 133.1, 133.3 ppm.

HRMS-EI ($C_{22}H_{22}O_3$): calcd: 334.1564, found: 334.1558.

*4-((3-(Naphthalene-1-yl)prop-2-yn-1-yl)oxy)but-2-yn-1-ol (**SI-VII**).* Following the above procedure for **10** (pathway A), compound **SI-VI** (1.38 g, 4.13 mmol, 1.0 equiv) and *p*-TSA (15 mg, 0.08 mmol, 2 mol %) in 30 mL of methanol were stirred at 25 °C for 3 days. After workup and flash chromatography with *c*-hex/EE (10:1), the product **SI-VII** (0.92 g, 89%) was obtained as a slightly yellow oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.69 (s, 1H), 4.35 (t, J = 1.8 Hz, 2H), 4.45 (t, J = 1.8 Hz, 2H), 4.64 (s, 2H), 7.43 (dd, J = 8.3, 7.2 Hz, 1H), 7.49−7.62 (m, 2H), 7.69 (dd, J = 7.2, 1.2 Hz, 1H), 7.81−7.88 (m, 2H), 8.30−8.34 (m, 1H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 51.2, 57.0, 57.7, 81.2, 85.0, 85.3, 89.0, 120.1, 125.2, 126.1, 126.5, 126.9, 128.4, 129.2, 130.9, 133.1, 133.3 ppm.

HRMS-ESI (TOF) ($C_{17}H_{14}O_2$): calcd: 251.1067 $[M + H]^+$, 273.0886 $[M + Na]^+$; found: 251.1067 $[M + H]^+$, 273.0888 $[M + Na]^+$.

*4-((3-Phenylprop-2-yn-1-yl)oxy)but-2-yn-1-ol (**SI-VIII**).* Following the procedures for the nucleophilic substitution and the deprotection of the crude product, sodium hydride (1.35 g, 33.8 mmol, 1.1 equiv, 60 wt % in oil), compound **15** (5.24 g, 30.8 mmol, 1.0 equiv), and **SI-III** (6.0 g, 30.8 mmol, 1.0 equiv) suspended in 120 mL of THF were stirred at 25 °C for 17 h. The crude product and *p*-TSA (0.25 g, 1.33 mmol, 4 mol %) were stirred in 130 mL of methanol at 40 °C for 16 h. Workup and flash chromatography with *c*-hex/EE (3:1) delivered the product **SI-VIII** (4.32 g, 65% over two steps) as a colorless oil.

The spectral data are in accordance with the literature.[24]

Syntheses of Ether-Bridged Triynes. *1-(3-((4-(But-2-yn-1-yloxy)but-2-yn-1-yl)oxy)prop-1-yn-1-yl)-2-methoxynaphthalene (**14**). Pathway A or D.* Following the above procedure for compound **9**, sodium hydride (0.04 g, 1.0 mmol, 1.2 equiv, 60 wt % in oil), compound **10** (0.237 g, 0.85 mmol, 1.0 equiv), and 1-bromo-2-butyne (0.07 mL, 0.85 mmol, 1.0 equiv) were reacted in 5 mL of THF under stirring at 25 °C for 17 h. The product **14** (0.20 g, 71%) was obtained as a yellow oil after flash chromatography with *c*-hex/EE (4:1).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.86 (t, J = 2.3 Hz, 3H), 4.02 (s, 3H), 4.22 (q, J = 2.3 Hz, 2H), 4.31 (t, J = 1.8 Hz, 2H), 4.48 (t, J = 1.8 Hz, 2H), 4.69 (s, 2H), 7.25 (d, J = 9.1 Hz, 1H), 7.38 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H), 7.54 (ddd, J = 8.3, 6.8, 1.2 Hz, 1H), 7.78 (dt, J = 8.2, 0.8 Hz, 1H), 7.83 (d, J = 9.1 Hz, 1H), 8.23 (dd, J = 8.4, 1.0 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 3.6, 56.5, 56.6, 56.7, 57.2, 57.8, 74.3, 81.4, 82.2, 82.3, 83.2, 93.7, 105.4, 112.5, 124.2, 125.1, 127.5, 128.1, 128.4, 130.5, 134.6, 159.3 ppm.

HRMS-ESI (TOF) ($C_{22}H_{20}O_3$): calcd: 333.1485 $[M + H]^+$, 355.1305 $[M + Na]^+$; found: 333.1490 $[M + H]^+$, 355.1309 $[M + Na]^+$.

Pathway C. Following the above procedure for **9**, sodium hydride (0.14 g, 3.5 mmol, 1.07 equiv, 60 wt % in oil), compounds **17** (0.45 g, 3.26 mmol, 1.0 equiv) and **8** (0.90 g, 3.26 mmol, 1.0 equiv) dissolved in 5 mL of THF were stirred at 25 °C for 19 h. After flash chromatography with *c*-hex/EE (6:1), the starting material **8** (0.10 g, 12%) was reisolated as well as product **14** (0.71 g, 78%) was obtained as a yellow oil.

Pathway B. Following the procedure for **34a**, catalyst $Pd(PPh_3)_4$ (46 mg, 0.04 mmol, 2 mol %), CuI (23 mg, 0.12 mmol, 6 mol %), and compound **6** (0.65 g, 2.2 mmol, 1.1 equiv) as reaction mixture in 7 mL of NEt_3 and **13** (0.35 g, 2.0 mmol, 1.0 equiv) dissolved in 3 mL of THF were mixed and stirred at 25 °C for 18 h and finally at 100 °C for

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4 h. After flash chromatography with *n*-hex/EE (4:1), product **14** (0.19 g, 24%) was obtained as a yellow oil.

*1,4-Bis((3-(2-methoxynaphthalen-1-yl)prop-2-yn-1-yl)oxy)but-2-yne (**20**).* Following the procedure for compound **23**, catalyst $Pd(PPh_3)_4$ (0.36 g, 0.31 mmol, 10 mol %), CuI (0.12 g, 0.62 mmol, 20 mol %), and compound **6** (1.76 g, 6.2 mmol, 2.0 equiv) as solution in 40 mL of toluene beside added **2** (0.5 g, 3.10 mmol, 1.0 equiv) and *N*,*N*-diisopropylamine (2.20 mL, 15.5 mmol, 5.0 equiv) were stirred at 25 °C for 18 h. After workup and flash chromatography with *c*-hex/EE (1:1), triyne **20** (0.41 g, 50%) was obtained as a yellow oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.01 (s, 6H), 4.54 (s, 4H), 4.74 (s, 4H), 7.22 (d, J = 9.5 Hz, 2H), 7.37 (ddd, J = 8.1, 6.8, 1.2 Hz, 2H), 7.55 (ddd, J = 8.4, 6.8, 1.2 Hz, 2H), 7.77 (d, J = 8.0 Hz, 2H), 7.81 (d, J = 9.0 Hz, 2H), 8.26 (d, J = 9.0 Hz, 2H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 56.6, 56.8, 57.9, 81.5, 82.5, 93.8, 105.4, 112.5, 124.3, 125.2, 127.6, 128.1, 128.5, 130.5, 134.7, 159.3 ppm.

HRMS-EI ($C_{32}H_{26}O_4$): calcd: 474.1826; found: 474.1823.

*1,4-Bis((3-(phenanthren-9-yl)prop-2-yn-1-yl)oxy)but-2-yne (**21**).* Following the procedure for **23**, catalyst $Pd(PPh_3)_4$ (0.81 g, 0.70 mmol, 10 mol %), CuI (0.27 g, 1.40 mmol, 20 mol %), and **2** (1.14 g, 7.0 mmol, 1.0 equiv) as solution in 50 mL of NEt_3 and a solution of 9-bromophenanthrene (3.84 g, 14.4 mmol, 2.05 equiv) in 20 mL of THF were combined and stirred at 50 °C for 2 h and an additional 47 h at 25 °C. After flash chromatography with toluene/CH_2Cl_2 (1:1), 9-bromophenanthrene (1.35 g) was reisolated and triyne **21** (1.58 g, 67%) was obtained as a brown solid.

The spectral data are in accordance with the literature.[18]

HRMS-EI ($C_{38}H_{26}O_2$): calcd: 514.1927; found: 514.1918.

EA: calcd: C 88.69, H 5.09; found: C 88.52, H 5.03.

Mp. 93.5−94.5 °C.

*1,4-Bis((3-(4-methylnaphthalen-1-yl)prop-2-yn-1-yl)oxy)but-2-yne (**22**).* In a flame-dried Schlenk flask, $Pd(PPh_3)_4$ (0.76 g, 0.66 mmol, 5 mol %) and CuI (0.38 g, 1.97 mmol, 15 mol %) were suspended in 40 mL of NEt_3. Then, compound **2** (1.06 g, 6.56 mmol, 1.0 equiv) and 1-bromo-4-methylnaphthalene (2.9 g, 13.1 mmol, 2.0 equiv) dissolved in 5 mL of THF were added. The solution was stirred at 25 °C for 18 h and monitored by TLC. After completion, the reaction mixture was quenched with aqueous sat. NH_4Cl sol., and the aqueous phase was extracted several times with ethyl acetate. The organic phase was washed with brine, dried over Na_2SO_4, evaporated, and purified by column chromatography with *n*-hex/EE (4:1). 1-Bromo-4-methylnaphthalene (1.51 g) was reisolated, and triyne **22** (0.65 g, 46%) was obtained as a yellow oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.70 (s, 6H), 4.49 (s, 4H), 4.66 (s, 4H), 7.26 (dd, J = 7.3, 1.1 Hz, 2H), 7.51−7.63 (m, 6H), 7.96−8.04 (m, 2H), 8.33−8.39 (m, 2H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 19.7, 56.9, 57.7, 82.4, 85.3, 88.4, 118.3, 124.4, 126.1, 126.3, 126.5, 126.7, 130.7, 132.3, 133.3, 135.9 ppm.

HRMS-ESI (TOF) ($C_{32}H_{26}O_2$): calcd: 443.2006 [M + H]$^+$, 465.1825 [M + Na]$^+$; found: 443.2005 [M + H]$^+$, 465.1826 [M + Na]$^+$.

*1,4-Bis((3-(o-tolyl)prop-2-yn-1-yl)oxy)but-2-yne (**23**).* In a flame-dried Schlenk flask, $Pd(PPh_3)_4$ (0.36 g, 0.31 mmol, 10 mol %) and CuI (0.12 g, 0.62 mmol, 20 mol %) were suspended in 9 mL of toluene. Then, 1-iodo-2-methylbenzene (0.89 mL, 6.82 mmol, 2.20 equiv), compound **2** (0.5 g, 3.10 mmol, 1.0 equiv) dissolved in 9 mL of toluene, and *N*,*N*-diisopropylamine (2.20 mL, 15.5 mmol, 5.0 equiv) were added, and the solution was stirred at 25 °C for 17 h. The reaction was monitored by TLC, and after completion, the reaction mixture was quenched with aqueous sat. NH_4Cl sol. and filtered through a pad of Celite. The aqueous phase was extracted several times with ethyl acetate, and the combined organic phase was washed with brine, dried over Na_2SO_4, evaporated, and purified by column chromatography with *c*-hex/EE (10:1). Triyne **23** (0.79 g, 74%) was obtained as a yellow oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.49 (s, 6H), 4.46 (s, 4H), 4.59 (s, 4H), 7.18 (td, J = 7.2, 2.2 Hz, 2H), 7.20−7.34 (m, 4H), 7.47 (dd, J = 7.4, 1.5 Hz, 2H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 20.7, 56.7, 57.5, 82.3, 85.8, 87.9, 122.2, 125.5, 128.6, 129.4, 132.2, 140.3 ppm.

HRMS-ESI (TOF) ($C_{24}H_{22}O_2$): calcd: 343.1693 [M + H]$^+$, 365.1512 [M + Na]$^+$; found: 343.1694 [M + H]$^+$, 365.1512 [M + Na]$^+$.

*1,4-Bis((3-(2-isopropylphenyl)prop-2-yn-1-yl)oxy)but-2-yne (**24**).* Following the above procedure for **23**, catalyst $Pd(PPh_3)_4$ (0.36 g, 0.31 mmol, 10 mol %), CuI (0.12 g, 0.62 mmol, 20 mol %), and 1-iodo-2-isopropylbenzene (1.15 mL, 6.82 mmol, 2.2 equiv) dissolved in 20 mL of toluene as well as added **2** (0.5 g, 3.10 mmol, 1.0 equiv) and *N*,*N*-diisopropylamine (2.20 mL, 15.5 mmol, 5.0 equiv) were stirred at 25 °C for 17 h. After flash chromatography with *c*-hex/EE (20:1), triyne **24** (1.03 g, 83%) was obtained as a yellow oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.24 (d, J = 6.9 Hz, 12H), 3.42 (sept, J = 6.9 Hz, 2H), 4.39 (s, 4H), 4.52 (s, 4H), 7.10 (ddd, J = 7.6, 6.5, 2.2 Hz, 2H), 7.23−7.28 (m, 4H), 7.40 (dt, J = 7.6, 1.0 Hz, 2H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 23.2, 31.5, 56.7, 57.5, 82.2, 85.7, 87.6, 121.2, 124.9, 125.5, 128.9, 132.7, 150.7 ppm.

HRMS-ESI (TOF) ($C_{28}H_{30}O_2$): calcd: 399.2319 [M + H]$^+$, 421.2138 [M + Na]$^+$; found: 399.2321 [M + H]$^+$, 421.2136 [M + Na]$^+$.

*Dimethyl-2,2′-((but-2-yne-1,4-diylbis(oxy))bis(prop-1-yne-3,1-diyl))dibenzoate (**25**).* Following the above procedure for **23** $Pd(PPh_3)_4$ (0.36 g, 0.31 mmol, 10 mol %), CuI (0.12 g, 0.62 mmol, 20 mol %), methyl 2-iodobenzoate (1.15 mL, 6.82 mmol, 2.2 equiv) in 20 mL of toluene, **2** (0.5 g, 3.10 mmol, 1.0 equiv), and *N*,*N*-diisopropylamine (2.20 mL, 15.5 mmol, 5.0 equiv) were stirred at 25 °C for 24 h. After flash chromatography with *c*-hex/EE (4:1, 2:1), triyne **25** (1.30 g, 97%) was obtained as a yellow oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.92 (s, 6H), 4.45 (s, 4H), 4.55 (s, 4H), 7.37 (td, J = 7.3, 1.1 Hz, 2H), 7.46 (td, J = 7.6, 1.1 Hz, 2H), 7.56 (d, J = 7.6 Hz, 2H), 7.93 (d, J = 7.8 Hz, 2H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 52.2, 56.8, 57.4, 82.4, 85.5, 89.5, 122.9, 128.2, 130.4, 131.7, 131.9, 134.3, 166.4 ppm.

HRMS-ESI (TOF) ($C_{26}H_{22}O_6$): calcd: 431.1489 [M + H]$^+$, 453.1309 [M + Na]$^+$; found: 431.1491 [M + H]$^+$, 453.1306 [M + Na]$^+$.

*1,4-Bis((3-(quinolin-4-yl)prop-2-yn-1-yl)oxy)but-2-yne (**26**).* Following the above procedure for **23**, $Pd(PPh_3)_4$ (0.53 g, 0.46 mmol, 10 mol %), CuI (0.17 g, 0.92 mmol, 20 mol %), **SI−I** (2.0 g, 9.6 mmol, 2.1 equiv) in 40 mL of toluene, **2** (0.74 g, 4.6 mmol, 1.0 equiv), and *N*,*N*-diisopropylamine (3.2 mL, 22.9 mmol, 5.0 equiv) were stirred at 50 °C for 23 h. After workup and flash chromatography with *n*-hex/THF (1:1, 0.5% NEt_3) and recrystallization from acetone, triyne **26** (1.36 g, 71%) was obtained as a yellow solid.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.48 (s, 4H), 4.66 (s, 4H), 7.50 (d, J = 4.5 Hz, 2H), 7.62 (ddd, J = 8.2, 6.9, 1.3 Hz, 2H), 7.75 (ddd, J = 8.4, 6.9, 1.5 Hz, 2H), 8.12 (d, J = 8.2 Hz, 2H), 8.24 (ddd, J = 8.4, 1.5, 0.7 Hz, 2H), 8.87 (d, J = 4.5 Hz, 2H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 57.3, 57.5, 82.4, 82.7, 93.6, 124.0, 125.8, 127.4, 127.6, 128.8, 129.9, 130.0, 148.1, 149.8 ppm.

HRMS-EI ($C_{28}H_{20}N_2O_2$): calcd: 416.1519; found: 416.1516.

EA: calcd: C 80.75, H 4.84, N 6.73; found: C 80.74, H 4.86, N 6.46.

Mp. 146.5−147.5 °C.

*1,4-Bis((3-(isoquinolin-4-yl)prop-2-yn-1-yl)oxy)but-2-yne (**27**).* Following the above procedure for **23**, catalyst $Pd(PPh_3)_4$ (0.53 g, 0.46 mmol, 10 mol %), CuI (0.17 g, 0.92 mmol, 20 mol %), and 4-bromoisoquinoline (2.0 g, 9.6 mmol, 2.1 equiv) suspended in 40 mL of toluene as well as added **2** (0.74 g, 4.6 mmol, 1.0 equiv) and *N*,*N*-diisopropylamine (3.2 mL, 22.9 mmol, 5.0 equiv) were stirred at 75 °C for 38 h. After workup and flash chromatography with *n*-hex/THF (1:1, 0.5% NEt_3) and recrystallization from acetone triyne, **27** (0.41 g, 22%) was obtained as a yellow solid.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.48 (s, 4H), 4.66 (s, 4H), 7.64 (ddd, J = 8.2, 6.8, 1.2 Hz, 2H), 7.78 (ddd, J = 8.4, 6.8, 1.2 Hz, 2H), 7.97 (dt, J = 8.2, 1.0 Hz, 2H), 8.21 (dq, J = 8.4, 1.0 Hz, 2H), 8.69 (s, 2H), 9.19 (s, 2H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 57.1, 57.6, 82.1, 82.4, 91.6, 115.1, 124.9, 127.7, 127.9, 128.6, 131.3, 132.0, 146.9, 152.4 ppm.

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HRMS-ESI (TOF) ($C_{28}H_{20}N_2O_2$): calcd: 417.1598 [M + H]$^+$, 439.1417 [M + Na]$^+$; found: 417.1600 [M + H]$^+$, 439.1420 [M + Na]$^+$.

EA: calcd: C 80.75, H 4.84, N 6.73; found: C 80.68, H 4.82, N 6.30.

Mp. 116−117 °C.

*1-(3-((4-(But-2-yn-1-yloxy)but-2-yn-1-yl)oxy)prop-1-yn-1-yl)-naphthalene (**28**).* Following the above procedure for **9**, sodium hydride (0.08 g, 1.98 mmol, 1.1 equiv, 60 wt % in oil), **SI-VII** (0.45 g, 1.79 mmol, 1.0 equiv), and 1-bromo-2-butyne (0.24 g, 0.85 mmol, 1.0 equiv) suspended in 10 mL of THF were stirred at 25 °C for 12 h. After flash chromatography with *c*-hex/EE (20:1), product **28** (0.46 g, 85%) was obtained as a slightly yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.86 (t, J = 2.3 Hz, 3H), 4.23 (q, J = 2.3 Hz, 2H), 4.32 (t, J = 1.8 Hz, 2H), 4.46 (t, J = 1.8 Hz, 2H), 4.64 (s, 2H), 7.42 (dd, J = 8.3, 7.1 Hz, 1H), 7.52 (ddd, J = 8.1, 6.8, 1.4 Hz, 1H), 7.58 (ddd, J = 8.3, 6.8, 1.4 Hz, 1H), 7.69 (dd, J = 7.1, 1.1 Hz, 1H), 7.85 (ddd, J = 7.4, 3.3, 2.3 Hz, 2H), 8.32 (dd, J = 8.3, 1.1 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 3.6, 56.6, 56.9, 57.2, 57.5, 74.3, 81.9, 82.5, 83.2, 84.9, 89.0, 120.0, 125.1, 126.0, 126.4, 126.9, 128.3, 129.1, 130.8, 133.1, 133.3 ppm.

HRMS-ESI (TOF) ($C_{21}H_{18}O_2$): calcd: 303.1380 [M + H]$^+$, 325.1199 [M + Na]$^+$; found: 303.1397 [M + H]$^+$, 325.1201 [M + Na]$^+$.

*1-(3-((4-((3-Phenylprop-2-yn-1-yl)oxy)but-2-yn-1-yl)oxy)prop-1-yn-1-yl)naphthalene (**29**).* Following the above procedure for **9**, sodium hydride (0.29 g, 7.3 mmol, 1.1 equiv, 60 wt % in oil), **SI-VIII** (1.32 g, 6.6 mmol, 1.0 equiv), and **8** (1.62 g, 6.6 mmol, 1.0 equiv) as reaction mixture in 40 mL of THF were stirred at 25 °C for 20 h. After workup and flash chromatography with *c*-hex/EE (6:1), triyne **29** (1.80 g, 75%) was obtained as a yellow oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.44 (dt, J = 20.4, 1.8 Hz, 4H), 4.50 (s, 2H), 4.65 (s, 2H), 7.28−7.34 (m, 3H), 7.39−7.48 (m, 3H), 7.52 (ddd, J = 8.2, 6.8, 1.5 Hz, 1H), 7.58 (ddd, J = 8.4, 6.8, 1.5 Hz, 1H), 7.70 (dd, J = 7.2, 1.2 Hz, 1H), 7.85 (ddd, J = 7.5, 3.0, 1.6 Hz, 2H), 8.30−8.34 (m, 1H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 56.9, 57.0, 57.5, 57.6, 82.3, 82.4, 84.2, 85.0, 86.9, 89.1, 120.1, 122.5, 125.2, 126.1, 126.5, 126.9, 128.3, 128.4, 128.6, 129.1, 130.9, 131.9, 133.1, 133.3 ppm.

HRMS-EI ($C_{26}H_{20}O_2$): calcd: 364.1458; found: 364.1451.

*2-Methoxy-1-(3-((4-((3-phenylprop-2-yn-1-yl)oxy)but-2-yn-1-yl)-oxy)prop-1-yn-1-yl)naphthalene (**30**).* Following the above procedure for **9**, sodium hydride (0.29 g, 7.3 mmol, 1.1 equiv, 60 wt % in oil), **SI-VIII** (1.32 g, 6.6 mmol, 1.0 equiv), and **8** (1.82 g, 6.6 mmol, 1.0 equiv) were suspended in 40 mL of THF, and the mixture was stirred at 25 °C for 17 h. After workup and flash chromatography with *c*-hex/EE (4:1), triyne **30** (2.49 g, 96%) was obtained as a yellow oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.02 (s, 3H), 4.40 (t, J = 1.8 Hz, 2H), 4.49−4.52 (m, 4H), 4.71 (s, 2H), 7.25 (d, J = 8.9 Hz, 1H), 7.31 (dd, J = 5.1, 2.0 Hz, 3H), 7.37 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H), 7.42−7.47 (m, 2H), 7.54 (ddd, J = 8.4, 6.8, 1.3 Hz, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.83 (d, J = 9.1 Hz, 1H), 8.23 (dd, J = 8.4, 0.9 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 56.6, 56.8, 56.9, 57.4, 57.9, 81.5, 82.2, 82.6, 84.3, 86.9, 93.7, 105.4, 112.5, 122.4, 124.3, 125.2, 127.5, 128.1, 128.3, 128.5, 128.6, 130.5, 131.9, 134.6, 159.3 ppm.

HRMS-EI ($C_{27}H_{22}O_3$): calcd: 394.1564; found: 394.1560.

*2-Methoxy-1-(3-((4-((3-(naphthalen-1-yl)prop-2-yn-1-yl)oxy)but-2-yn-1-yl)oxy)prop-1-yn-1-yl)naphthalene (**31**).* Following the above procedure for **9**, sodium hydride (0.07 g, 1.65 mmol, 1.1 equiv, 60 wt % in oil), compound **10** (0.42 g, 1.51 mmol, 1.0 equiv), and **SI-V** (0.37 g, 1.51 mmol, 1.0 equiv) as reaction mixture in 15 mL of THF were stirred at 25 °C for 18 h. After workup and flash chromatography with *c*-hex/EE (6:1, 1:1), the triyne product **31** (0.51 g, 76%) was obtained as a yellow oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.02 (s, 3H), 4.51 (dt, J = 10.6, 1.8 Hz, 4H), 4.66 (s, 2H), 4.72 (s, 2H), 7.25 (d, J = 9.1 Hz, 1H) 7.31−7.48 (m, 2H), 7.45−7.63 (m, 3H), 7.69 (d, J = 7.2, 1.2 Hz, 1H), 7.75−7.80 (m, 1H), 7.81−7.87 (m, 3H), 8.24 (dq, J = 8.4, 0.9 Hz, 1H), 8.32 (ddt, J = 8.4, 1.4, 0.8 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 56.6, 56.8, 57.0, 57.6, 57.9, 81.5, 82.2, 82.7, 85.0, 89.1, 93.7, 105.4, 112.5, 120.1, 124.2, 125.1, 125.2, 126.1, 126.5, 126.9, 127.5, 128.1, 128.3, 128.4, 129.1, 130.5, 130.8, 133.1, 133.3, 134.6, 159.3 ppm.

HRMS-EI ($C_{31}H_{24}O_3$): calcd: 444.1720; found: 444.1712.

Syntheses of Building Blocks for Malonate-Bridged Triynes.

*Diethyl-2-(3-(naphthalen-1-yl)prop-2-yn-1-yl)malonate (**34a**).* In a flame-dried Schlenk flask, $Pd(PPh_3)_4$ (0.58 g, 0.50 mmol, 5 mol %) and CuI (0.28 g, 1.5 mmol, 15 mol %) were suspended in 50 of mL NEt_3. 1-Iodonaphthalene (1.46 mL, 10 mmol, 1.0 equiv) was added via syringe, followed by the addition of compound **33a** (1.98 g, 10 mmol, 1.0 equiv) dissolved in 20 mL of THF. The solution was heated to 50 °C for 15 h. The reaction was monitored by TLC, and after completion, aqueous sat. NH_4Cl sol. was used to quench the reaction. The aqueous phase was extracted several times with ethyl acetate, washed with brine, dried over Na_2SO_4, and purified by column chromatography with *n*-hex/EE (10:1). Alkyne **34a** (3.17 g, 98%) was obtained as a slightly yellow oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.29 (t, J = 7.1 Hz, 6H), 3.17 (d, J = 7.7 Hz, 2H), 3.77 (t, J = 7.7 Hz, 1H), 4.27 (qd, J = 7.1, 1.5 Hz, 4H), 7.39 (dd, J = 8.3, 7.2 Hz, 1H), 7.44−7.61 (m, 2H), 7.60 (d, J = 7.2 Hz, 1H), 7.76−7.86 (m, 2H), 8.27 (d, J = 8.6 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.1, 19.8, 51.6, 61.8, 80.6, 90.4, 120.9, 125.2, 126.2, 126.3, 126.6, 128.2, 128.5, 130.3, 133.1, 133.5, 168.1 ppm.

HRMS-EI ($C_{20}H_{20}O_4$): calcd: 324.1356; found: 324.1361.

*Diethyl-2-(3-(2-methoxynaphthalen-1-yl)prop-2-yn-1-yl)-malonate (**34b**).* Following the above procedure for **34a**, catalyst $Pd(PPh_3)_4$ (1.16 g, 1.0 mmol, 1 mol %), CuI (0.40 g, 2.04 mmol, 2 mol %), and compound **6** (2.85 g, 10 mmol, 1.0 equiv) dissolved in 50 mL of NEt_3 as well as a solution of **33a** (2.0 g, 10 mmol, 1.0 equiv) in 10 mL of THF were combined and stirred at 50 °C for 15 h. After workup and flash chromatography with *n*-hex/EE (10:1), the alkyne product **34b** (3.05 g, 87%) was obtained as a slightly yellow oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.29 (t, J = 7.1 Hz, 6H), 3.24 (d, J = 7.8 Hz, 2H), 3.81 (t, J = 7.8 Hz, 1H), 4.00 (s, 3H), 4.27 (qd, J = 7.1, 2.4 Hz, 4H), 7.22 (d, J = 9.1 Hz, 1H), 7.36 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H), 7.51 (ddd, J = 8.5, 6.8, 1.2 Hz, 1H), 7.77 (t, J = 8.1 Hz, 2H), 8.18 (dd, J = 8.4, 1.0 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.1, 20.2, 51.8, 56.6, 61.8, 76.8, 95.2, 106.3, 112.7, 124.1, 125.3, 127.2, 128.0, 128.5, 129.8, 134.8, 158.9, 168.2 ppm.

HRMS-ESI (TOF) ($C_{21}H_{22}O_5$): calcd: 355.1540 [M + H]$^+$, 377.1359 [M + Na]$^+$; found: 355.1546 [M + H]$^+$, 377.1362 [M + Na]$^+$.

*Diethyl-2-(4-(2-methoxynaphthalen-1-yl)but-3-yn-1-yl)malonate (**34c**).* Following the above procedure for **34a**, catalyst $Pd(PPh_3)_4$ (0.27 g, 0.24 mmol, 10 mol %), CuI (0.09 g, 0.47 mmol, 20 mol %), and compound **6** (0.67 g, 10 mmol, 1.0 equiv) dissolved in 15 mL of NEt_3 and a solution of **33b** (0.50 g, 2.4 mmol, 1.0 equiv) in 2 mL of THF were mixed and stirred at 50 °C for 17 h. After workup and flash chromatography with *n*-hex/EE (10:1), alkyne **34c** (0.85 g, 98%) was obtained as a slightly yellow oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.28 (t, J = 7.1 Hz, 6H), 2.33 (q, J = 7.2 Hz, 2H), 2.75 (t, J = 7.0 Hz, 2H), 3.83 (t, J = 7.4 Hz, 1H), 4.02 (s, 3H), 4.23 (qd, J = 7.1, 1.3 Hz, 4H), 7.24 (d, J = 9.1 Hz, 1H), 7.37 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H), 7.52 (ddd, J = 8.3, 6.8, 1.2 Hz, 1H), 7.77 (d, J = 8.3 Hz, 1H), 7.79 (d, J = 9.0 Hz, 1H), 8.24 (dd, J = 8.5, 1.0 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.1, 18.2, 28.1, 50.8, 56.6, 61.5, 76.2, 97.8, 112.7, 124.1, 125.3, 127.2, 128.0, 128.5, 129.5, 134.7, 144.0, 158.8, 169.3 ppm.

HRMS-EI ($C_{22}H_{24}O_5$): calcd: 368.1618; found: 368.1616.

*Diethyl-2-(3-phenylprop-2-yn-1-yl)malonate (**SI-IX**).* Following the above procedure for **34a**, catalyst $Pd(PPh_3)_4$ (0.57 g, 0.49 mmol, 5 mol %), CuI (0.28 g, 1.5 mmol, 15 mol %), and 1-iodobenzene (1.1 mL, 9.8 mmol, 1.0 equiv) dissolved in 60 mL of NEt_3 as well as a solution of **33a** (1.93 g, 9.75 mmol, 1.0 equiv) in 5 mL of THF were combined and stirred at 50 °C for 17 h. After

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workup and flash chromatography with *n*-hex/EE (10:1), product **SI-IX** (2.59 g, 97%) was obtained as a slightly yellow oil.

The spectral data are according to those reported in the literature.[25]

*Diethyl-2-(4-bromobut-2-yn-1-yl)-2-(3-(naphthalen-1-yl)prop-2-yn-1-yl)malonate (**35a**).* Following the procedure for **35b**, sodium ethanolate (0.34 g, 5.0 mmol, 1.04 equiv), **34a** (1.55 g, 4.79 mmol, 1.0 equiv), and **SI−II** (1.06 g, 5.0 mmol, 1.04 equiv) suspended in 50 mL of THF were stirred at 25 °C for 16 h. After workup and flash chromatography with *c*-hex/EE (10:1), diyne **35a** (1.10 g, 51%) was obtained as a yellow oil and triyne **36a** (0.69 g, 21%) was isolated as a yellow oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.29 (t, J = 7.1 Hz, 6H), 3.19 (t, J = 2.4 Hz, 2H), 3.36 (s, 2H), 3.90 (t, J = 2.4 Hz, 2H), 4.28 (q, J = 7.1 Hz, 4H), 7.39 (dd, J = 8.3, 7.2 Hz, 1H), 7.50 (ddd, J = 8.1, 6.8, 1.5 Hz, 1H), 7.53−7.63 (m, 2H), 7.82 (ddd, J = 9.3, 8.2, 1.1 Hz, 2H), 8.26 (dd, J = 8.2, 0.8 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.1, 14.7, 23.5, 24.1, 56.8, 62.2, 78.6, 81.9, 82.1, 88.8, 120.7, 125.2, 126.1, 126.3, 126.7, 128.2, 128.6, 130.5, 133.1, 133.4, 168.8 ppm.

HRMS-ESI (TOF) ($C_{24}H_{23}BrO_4$): calcd: 455.0853 $[M + H]^+$, 477.0672 $[M + Na]^+$; found: 455.0851 $[M + H]^+$, 477.0670 $[M + Na]^+$.

*Diethyl-2-(4-bromobut-2-yn-1-yl)-2-(3-(2-methoxynaphthalen-1-yl)prop-2-yn-1-yl)malonate (**35b**).* A solution of **34b** (1.0 g, 2.82 mmol, 1.0 equiv) in 5 mL of THF was added dropwise to a cooled solution of sodium hydride (0.12 g, 2.96 mmol, 1.05 equiv, 60 wt % in oil) in 20 mL of THF at 0 °C. The solution was allowed to warm to 25 °C and stirred for 1 h, until the hydrogen evolution ceased. The resulting mixture was slowly added to a solution of **SI-II** (1.6 g, 7.05 mmol, 2.5 equiv) in 5 mL of THF and stirred at 25 °C for 18 h. The reaction was monitored by TLC, and after completion, the reaction was quenched with water and extracted with ethyl acetate. The organic phases were washed with brine and dried over Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography with *c*-hex/EE (4:1), and product **35b** (1.07 g, 79%) was obtained as a yellow oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.28 (t, J = 7.1 Hz, 6H), 3.24 (t, J = 2.4 Hz, 2H), 3.41 (s, 2H), 3.90 (t, J = 2.3 Hz, 2H), 4.00 (s, 3H), 4.27 (q, J = 7.1 Hz, 4H), 7.22 (d, J = 9.1 Hz, 1H), 7.36 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H), 7.53 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.73−7.81 (m, 2H), 8.17 (dd, J = 8.4, 1.0 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.1, 14.9, 23.4, 23.5, 56.6, 56.9, 62.1, 78.1, 78.5, 82.4, 93.4, 106.3, 112.8, 124.1, 125.3, 127.3, 128.0, 128.5, 129.8, 134.7, 159.2, 168.9 ppm.

HRMS-ESI (TOF) ($C_{25}H_{25}BrO_5$): calcd: 485.0958 $[M + H]^+$, 507.0778 $[M + Na]^+$; found: 485.0964 $[M + H]^+$, 507.0775 $[M + Na]^+$.

*Diethyl-2-(4-bromobut-2-yn-1-yl)-2-(4-(2-methoxynaphthalen-1-yl)but-3-yn-1-yl)malonate (**35c**).* Following the procedure for **35b**, sodium hydride (0.14 g, 3.4 mmol, 1.05 equiv, 60 wt % in oil), **34c** (1.2 g, 3.26 mmol, 1.0 equiv), and **SI-II** (1.73 g, 8.2 mmol, 2.5 equiv) dissolved in 50 mL of THF were stirred at 25 °C for 18 h. After workup and flash chromatography with *c*-hex/EE (4:1), product **35c** (1.48 g, 79%) was obtained as a yellow oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.27 (t, J = 7.1 Hz, 6H), 2.47−2.60 (m, 2H), 2.59−2.72 (m, 2H), 3.01 (t, J = 2.4 Hz, 2H), 3.87 (t, J = 2.4 Hz, 2H), 4.02 (s, 3H), 4.22 (qd, J = 7.1, 4.5 Hz, 4H), 7.23 (d, J = 9.1 Hz, 1H), 7.37 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H), 7.53 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.76 (dd, J = 7.3, 0.9 Hz, 1H), 7.78 (d, J = 9.1 Hz, 1H), 8.25 (dd, J = 8.5, 0.9, 1H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.0, 14.8, 15.7, 23.6, 31.7, 56.6, 61.9, 75.3, 78.5, 82.2, 98.2, 106.6, 106.8, 112.6, 124.1, 125.4, 127.2, 128.0, 128.5, 129.5, 134.8, 158.6, 169.8 ppm.

HRMS-ESI (TOF) ($C_{26}H_{27}BrO_5$): calcd: 499.1115 $[M + H]^+$, 521.0934 $[M + Na]^+$; found: 499.1118 $[M + H]^+$, 521.0934 $[M + Na]^+$.

Syntheses of Malonate-Bridged Triynes. *Tetraethyl-1,12-di(naphthalen-1-yl)dodeca-1,6,11-triyne-4,4,9,9-tetracarboxylate (**36a**).* Following the above procedure for **35b**, sodium hydride (0.20 g, 5.0 mmol, 2.0 equiv, 60 wt % in oil), **34a** (1.62 g, 5.0 mmol, 2.0 equiv), and **SI-II** (0.53 g, 2.5 mmol, 1.0 equiv) as reaction mixture in 30 mL of THF were stirred at 25 °C for 21 h. After workup and purification by flash chromatography with *c*-hex/EE (10:1), triyne **36a** (1.54 g, 88%) was obtained as a yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.26 (t, J = 7.1 Hz, 12H), 3.13 (s, 4H), 3.38 (s, 4H), 4.27 (q, J = 7.1 Hz, 8H), 7.37 (dd, J = 8.3, 7.2 Hz, 2H), 7.48 (ddd, J = 8.0, 6.8, 1.3 Hz, 2H), 7.55 (ddd, J = 8.3, 6.8, 1.3 Hz, 2H), 7.60 (dd, J = 7.2, 1.1 Hz, 2H), 7.78 (dt, J = 8.4, 1.1 Hz, 2H), 7.82 (d, J = 8.0 Hz, 2H), 8.27 (d, J = 8.4 Hz, 2H) ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 14.1, 23.3, 23.9, 56.9, 62.1, 78.0, 81.6, 89.2, 120.9, 125.2, 126.2, 126.3, 126.7, 128.2, 128.4, 130.5, 133.1, 133.4, 169.0 ppm.

HRMS-EI ($C_{44}H_{42}O_8$): calcd: 698.2874; found: 698.2872.

*Tetraethyl-1,12-bis(2-methoxynaphthalen-1-yl)dodeca-1,6,11-triyne-4,4,9,9-tetracarboxylate (**36b**).* Following the above procedure for **35b**, a mixture consisting of sodium hydride (0.18 g, 4.44 mmol, 2.1 equiv, 60 wt % in oil), **34b** (1.5 g, 4.23 mmol, 2.0 equiv), and **SI-II** (0.45 g, 2.1 mmol, 1.0 equiv) dissolved in 60 mL of THF was stirred at 25 °C for 18 h. After flash chromatography with *c*-hex/EE (4:1), triyne **36b** (0.71 g, 45%) was obtained as a yellow oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.25 (t, J = 7.1 Hz, 12H), 3.16 (s, 4H), 3.42 (s, 4H), 3.97 (s, 6H), 4.26 (q, J = 7.1 Hz, 8H), 7.20 (d, J = 9.1 Hz, 2H), 7.33 (ddd, J = 8.1, 6.8, 1.2 Hz, 2H), 7.51 (ddd, J = 8.5, 6.8, 1.2 Hz, 2H), 7.70−7.81 (m, 4H), 8.19 (dd, J = 8.5, 1.0 Hz, 2H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.1, 23.2, 24.2, 56.6, 57.0, 61.9, 77.8, 78.0, 93.8, 106.5, 112.8, 124.0, 125.4, 127.2, 127.9, 128.4, 129.6, 134.7, 159.1, 169.1 ppm.

HRMS-EI ($C_{46}H_{46}O_{10}$): calcd: 758.3086; found: 758.3074.

*Tetraethyl-1-(naphthalen-1-yl)trideca-1,6,11-triyne-4,4,9,9-tetracarboxylate (**36c**).* Following the above procedure for **34a**, catalyst $Pd(PPh_3)_4$ (58 mg, 0.05 mmol, 5 mol %), CuI (29 mg, 0.15 mmol, 15 mol %), and 1-iodonaphthalene (0.18 mL, 1.2 mmol, 1.2 equiv) dissolved in 5 mL of NEt_3 and a solution of compound **38** (0.46 g, 1.0 mmol, 1.0 equiv) in 1 mL of THF were combined and stirred at 25 °C for 15 h. After flash chromatography with *n*-hex/acetone (10:1), the triyne product **36c** (0.48 g, 81%) was obtained as a colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.23 (t, J = 7.1 Hz, 6H), 1.28 (t, J = 7.1 Hz, 6H), 1.74 (t, J = 2.5 Hz, 3H), 2.91 (q, J = 2.4 Hz, 2H), 2.95 (t, J = 2.3 Hz, 2H), 3.08 (t, J = 2.3 Hz, 2H), 3.33 (s, 2H), 4.21 (q, J = 7.1 Hz, 4H), 4.27 (q, J = 7.1 Hz, 4H), 7.38 (dd, J = 8.2, 7.2 Hz, 1H), 7.49 (ddd, J = 8.2, 6.8, 1.3 Hz, 1H), 7.56 (ddd, J = 8.3, 6.8, 1.3 Hz, 1H), 7.60 (dd, J = 7.2, 1.2 Hz, 1H), 7.78 (d, J = 8.3 Hz, 1H), 7.82 (dd, J = 8.1, 0.6 Hz, 1H), 8.24-.8.28 (m, 1H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 3.5, 14.0 (2×), 22.8, 23.2, 23.8, 56.8, 56.9, 61.8, 62.0, 73.2, 77.2, 77.6, 78.1, 78.8, 81.5, 89.2, 120.9, 125.1, 126.2, 126.3, 126.6, 128.1, 128.4, 130.4, 133.1, 133.4, 168.9, 169.0 ppm.

Because of signal overlaps, not all expected carbon atoms could be assigned.

HRMS-ESI (TOF) ($C_{35}H_{38}O_8$): calcd: 587.2639 $[M + H]^+$, 609.2459 $[M + Na]^+$; found: 587.2640 $[M + H]^+$, 609.2463 $[M + Na]^+$.

*Tetraethyl-1-(2-methoxynaphthalen-1-yl)trideca-1,6,11-triyne-4,4,9,9-tetracarboxylate (**36d**).* Following the above procedure for **34a**, $Pd(PPh_3)_4$ (57 mg, 0.05 mmol, 5 mol %), CuI (28 mg, 0.15 mmol, 15 mol %), and **6** (0.31 g, 1.07 mmol, 1.1 equiv) in 11 mL of NEt_3 and compound **38** (0.45 g, 0.98 mmol, 1.0 equiv) in 3 mL of THF were stirred at 50 °C for 18 h. After flash chromatography with *n*-hex/EE (4:1), triyne **36d** (0.50 g, 83%) was obtained as a colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.24 (dt, J = 12.9, 7.1 Hz, 12H), 1.73 (t, J = 2.5 Hz, 3H), 2.90 (q, J = 2.3 Hz, 2H), 2.94 (t, J = 2.3 Hz, 2H), 3.11 (t, J = 2.3 Hz, 2H), 3.38 (s, 2H), 3.98 (s, 3H), 4.13−4.32 (m, 8H), 7.21 (d, J = 9.1 Hz, 1H), 7.35 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H), 7.52 (ddd, J = 8.5, 6.8, 1.2 Hz, 1H), 7.76 (dd, J = 8.5, 6.6 Hz, 2H), 8.15−8.20 (m, 1H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 3.5, 14.1, 22.8, 23.2, 24.2, 56.6, 56.8, 57.0, 61.8, 61.9, 73.3, 77.8, 78.0, 78.9, 93.8, 106.5, 112.9, 124.1, 125.4, 127.2, 127.9, 128.5, 129.6, 134.7, 159.1, 169.0, 169.1 ppm.

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Because of signal overlaps, not all expected carbon atoms could be assigned.

HRMS-ESI (TOF) ($C_{36}H_{40}O_9$): calcd: 617.2745 $[M + H]^+$, 639.2565 $[M + Na]^+$; found: 617.2758 $[M + H]^+$, 639.2571 $[M + Na]^+$.

*Tetraethyl-1-(naphthalen-1-yl)-12-phenyldodeca-1,6,11-triyne-4,4,9,9-tetracarboxylate (**36e**).* Following the above procedure for **35b**, sodium hydride (93 mg, 2.3 mmol, 1.05 equiv, 60 wt % in oil), **SI-IX** (0.60 g, 2.2 mmol, 1.0 equiv), and compound **35a** (1.0 g, 2.2 mmol, 1.0 equiv) as reaction mixture in 20 mL of THF were stirred at 25 °C for 18 h. After workup and flash chromatography with *c*-hex/EE (4:1), triyne **36e** (1.33 g, 94%) was obtained as a yellow oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.26 (q, J = 7.0 Hz, 12H), 3.03 (t, J = 2.2 Hz, 2H), 3.10 (t, J = 2.3 Hz, 2H), 3.20 (s, 2H), 3.35 (s, 2H), 4.25 (dq, J = 8.3, 7.1 Hz, 8H), 7.24−7.28 (m, 3H), 7.34−7.41 (m, 3H), 7.45−7.63 (m, 3H), 7.77−7.84 (m, 2H), 8.17−8.31 (m, 1H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.1, 23.1, 23.2, 23.5, 23.8, 56.9 (2×), 62.0 (2×), 77.9, 78.0, 81.6, 84.2, 89.2, 120.9, 124.9, 125.2, 126.2, 126.3, 126.7, 128.0, 128.2, 128.4, 130.5, 131.7, 133.1, 133.4, 168.9, 169.0 ppm. Because of signal overlaps, not all expected carbon atoms could be assigned.

HRMS-EI ($C_{40}H_{40}O_8$): calcd: 648.2718; found: 648.2708.

*Tetraethyl-1-(2-methoxynaphthalen-1-yl)-12-phenyldodeca-1,6,11-triyne-4,4,9,9-tetracarboxylate (**36f**).* Following the above procedure for **35b**, sodium hydride (30 mg; 0.74 mmol, 1.05 equiv, 60 wt % in oil), **SI-IX** (0.19 g, 0.7 mmol, 1.0 equiv), and compound **35b** (0.34 g, 0.7 mmol, 1.0 equiv) as reaction solution in 10 mL of THF were stirred at 25 °C for 18 h. After workup and flash chromatography with *c*-hex/EE (4:1), the triyne product **36f** (0.30 g, 99%) was obtained as a yellow oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.25 (tdd, J = 7.1, 6.1, 0.5 Hz, 12H), 3.03 (t, J = 2.3 Hz, 2H), 3.14 (t, J = 2.4 Hz, 2H), 3.20 (s, 2H), 3.40 (s, 2H), 3.98 (d, J = 0.4, 3H), 4.18−4.31 (m, 8H), 7.21 (d, J = 9.1 Hz, 1H), 7.23−7.29 (m, 3H), 7.30−7.39 (m, 3H), 7.52 (ddd, J = 8.3, 6.8, 1.3 Hz, 1H), 7.72−7.80 (m, 2H), 8.18 (dd, J = 8.6, 0.7 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.1, 23.1, 23.2, 23.5, 24.3, 56.6, 56.9, 57.0, 62.0, 77.8, 78.0, 83.5, 84.3, 93.8, 106.5, 112.9, 122.2, 123.3, 124.1, 125.4, 127.2, 127.9, 128.2, 128.5, 129.6, 131.7, 134.7, 159.1, 168.9, 169.1 ppm. Because of signal overlaps, not all expected carbon atoms could be assigned.

HRMS-EI ($C_{41}H_{42}O_9$): calcd: 678.2823; found: 678.2813.

*Tetraethyl-1-(2-methoxynaphthalen-1-yl)tetradeca-1,7,12-triyne-5,5,10,10-tetracarboxylate (**36g**).* Following the above procedure for **35b**, sodium hydride (45 mg, 1.11 mmol, 1.01 equiv, 60 wt % in oil), **37** (0.23 g, 1.1 mmol, 1.0 equiv), and compound **35c** (0.55 g, 1.1 mmol, 1.0 equiv) dissolved in 15 mL of THF were stirred at 25 °C for 18 h. After workup and flash chromatography with *c*-hex/EE (4:1), triyne **36g** (0.54 g, 79%) was obtained as a yellow oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.23 (dt, J = 9.2, 7.1 Hz, 12H), 1.70 (t, J = 2.5 Hz, 3H) 2.47−2.68 (m, 4H), 2.89 (t, J = 2.4 Hz, 4H), 2.93 (t, J = 2.1 Hz, 2H), 4.00 (s, 3H), 4.13−4.29 (m, 8H), 7.20−7.25 (m, 1H), 7.31−7.38 (m, 1H), 7.52 (ddd, J = 8.4, 6.8, 1.3 Hz, 1H), 7.75 (d, J = 8.2 Hz, 1H), 7.79 (d, J = 9.0 Hz, 1H), 8.27 (dd, J = 8.6, 1.0 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 3.5, 14.0, 15.6, 22.8, 22.9, 23.3, 31.5, 56.6, 56.8, 61.7, 61.8, 73.2, 75.1, 77.6, 78.1, 78.9, 98.4, 106.8, 112.7, 124.1, 125.5, 127.2, 127.9, 128.5, 129.4, 134.8, 158.7, 169.1, 169.9 ppm. Because of signal overlaps, not all expected carbon atoms could be assigned.

HRMS-EI ($C_{37}H_{42}O_9$): calcd: 630.2823; found: 630.2815.

*Tetraethyl-13-(2-methoxynaphthalen-1-yl)-1-phenyltrideca-1,6,12-triyne-4,4,9,9-tetracarboxylate (**36h**).* Following the above procedure for **35b**, sodium hydride (90 mg, 2.2 mmol, 1.05 equiv, 60 wt % in oil), **SI-IX** (0.59 g, 2.1 mmol, 1.0 equiv), and compound **35c** (1.0 g, 2.1 mmol, 1.0 equiv) as reaction mixture in 20 mL of THF were stirred for 22 h at 25 °C. After workup and flash chromatography with *c*-hex/EE (4:1), triyne **36h** (1.05 g, 72%) was obtained as a yellow oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.23 (dt, J = 9.2, 7.1 Hz, 12H), 2.47−2.68 (m, 4H), 2.96 (dt, J = 30.1, 2.4 Hz, 4H), 3.17 (s, 2H), 4.00 (s, 3H), 4.13−4.29 (m, 8H), 7.20−7.25 (m, 4H), 7.31−7.38 (m, 3H), 7.52 (ddd, J = 8.4, 6.8, 1.3 Hz, 1H), 7.75 (d, J = 8.2 Hz, 1H), 7.79 (d, J = 9.0 Hz, 1H), 8.27 (dd, J = 8.4 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.1 (2×), 15.7, 23.0, 23.3, 23.5, 31.5, 56.6, 61.8, 61.9, 75.2, 77.8, 77.9, 83.5, 84.2, 98.4, 106.8, 112.7, 123.2, 124.1, 125.5, 127.2, 127.9, 128.1, 128.4, 129.4, 131.7, 134.8, 158.6, 168.9, 170.0 ppm. Because of signal overlaps, not all expected carbon atoms could be assigned.

HRMS-EI ($C_{42}H_{44}O_9$): calcd: 692.2980; found: 692.2985.

*Tetraethyl-trideca-1,6,11-triyne-4,4,9,9-tetracarboxylate (**38**).* To a suspension of sodium hydride (0.20 g, 5.1 mmol, 1.04 equiv, 60 wt % in oil) in 10 mL of THF was slowly added compound **33a** (1.0 g, 5.04 mmol, 1.0 equiv) dissolved in 10 mL of THF via a dropping funnel, and the mixture was stirred at 25 °C for 40 min, until the hydrogen evolution had ceased. This solution was added dropwise over a period of 1 h to a solution of 1,4-dibromobut-2-yne (1.07 g, 5.04 mmol, 1.0 equiv) in 10 mL of THF and stirred for an additional 2 h. Meanwhile, to a suspension of sodium hydride (0.20 g, 5.1 mmol, 1.04 equiv, 60 wt % in oil) in 10 mL of THF was slowly added a solution of compound **33b** (1.1 g, 5.04 mmol, 1.0 equiv) in 10 mL of THF, and the mixture was stirred for 40 min, until the hydrogen evolution had ceased. The latter solution was then slowly added to the first solution, and the mixture was stirred at 25 °C for an additional 15 h. The reaction was monitored by TLC, quenched with water, and extracted with ethyl acetate. The organic phases were washed with brine and dried over sodium sulfate, and the solvent was removed under reduced pressure. The crude product was purified by bulb-to-bulb distillation, and triyne **38** (1.46 g, 63%) was obtained as a colorless oil.

The spectral data are in accordance with the literature.[26]

Syntheses of the Two Different Triynes. *Diisopropyl((2-methoxynaphthalen-1-yl)ethynyl)silane (**SI-X**).* To a cooled solution of 1-ethynyl-2-methoxynaphthalene (1.37 g, 7.5 mmol, 1.0 equiv) in 25 mL of THF was slowly added *n*-butyllithium (4.92 mL, 7.88 mmol, 1.05 equiv), and the mixture was stirred at −78 °C for 2 h. Then, chlorodiisopropylsilane (1.56 mL, 9.0 mmol, 1.2 equiv) was added at −78 °C, and the reaction mixture warmed to 25 °C and stirred for an additional 2 h. The reaction was monitored by TLC and stopped by the addition of diethyl ether. The organic phase was washed twice with aqueous sat. NH_4Cl sol. and subsequently with brine, dried with $MgSO_4$, filtered, and evaporated. The crude product was purified by flash chromatography with PE/EE 50:1, and product **SI-X** (1.98 g, 89%) was obtained as a colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.14−1.27 (m, 14H), 3.99 (s_{br}, 1H), 4.02 (s, 3H), 7.23 (d, J = 9.1 Hz, 1H), 7.38 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H), 7.55 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.77 (dt, J = 8.1, 0.9 Hz, 1H), 7.82 (d, J = 9.1 Hz, 1H), 8.29 (dd, J = 8.4, 0.9 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 11.1, 18.5, 18.7, 56.8, 98.1, 101.9, 106.4, 112.9, 124.2, 125.3, 127.5, 128.1, 128.5, 130.5, 134.8, 160.0 ppm.

^{29}Si NMR ($CDCl_3$, 79 MHz): δ = −15.4 ppm.

HRMS-EI ($C_{19}H_{24}OSi$): calcd: 296.1593; found: 296.1591.

*Diisopropyl((2-methoxynaphthalen-1-yl)ethynyl)((4-((3-phenyl-prop-2-yn-1-yl)oxy)but-2-yn-1-yl)oxy)silane (**54**).* In a flame-dried Schlenk flask, **SI-X** (1.49 g, 5.0 mmol, 1.0 equiv) was dissolved in 25 mL of CH_2Cl_2, *N*-bromosuccinimide (1.38 g, 7.76 mmol, 1.5 equiv) was added as solid, and the solution was stirred at 60 °C for 6 h. The resulting solution was then added to a solution of **SI-VIII** (0.90 g, 4.5 mmol, 0.9 equiv), *N*,*N*-dimethylaminopyridine (DMAP, 0.06 g, 0.50 mmol, 0.1 equiv), and NEt_3 (0.7 mL, 5.0 mmol, 1.0 equiv) in 23 mL of CH_2Cl_2, and the mixture was stirred at 25 °C for 16 h. After that time, the mixture was in addition heated to 40 °C for 4 h. Additional DMAP (0.06 g, 0.5 mmol, 0.1 equiv) and NEt_3 (0.7 mL, 5.0 mmol, 1.0 equiv) were added, and the solution was stirred at 25 °C for 3 days and finally followed by heating to 40 °C for 8 h. The solvent was removed under reduced pressure, and the crude product was purified with PE/EE 25:1. The expected triyne **54** was obtained as a yellow oil in 35% yield (0.79 g).

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^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.20 (d, J = 1.8 Hz, 14H), 4.02 (s, 3H), 4.37 (t, J = 1.8 Hz, 2H), 4.46 (s, 2H), 4.68 (t, J = 1.8 Hz, 2H), 7.24 (d, J = 9.1 Hz, 1H), 7.28−7.33 (m, 3H), 7.37 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H), 7.41−7.44 (m, 2H), 7.56 (ddd, J = 8.2, 6.8, 1.2 Hz, 1H), 7.78 (d, J = 8.2 Hz, 1H), 7.83 (d, J = 8.9 Hz, 1H), 8.28 (dq, J = 8.5, 0.9 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 13.3, 17.2, 17.3, 53.2, 56.7, 56.9, 57.2, 77.3, 80.2, 84.4, 85.7, 86.6, 97.7, 102.2, 112.8, 122.6, 124.3, 125.2, 127.7, 128.2, 128.3, 128.4, 128.5, 130.8, 131.8, 134.7, 160.4 ppm.

^{29}Si NMR ($CDCl_3$, 79 MHz): δ = 0.91 ppm.

HRMS-EI ($C_{32}H_{34}O_3Si$): calcd: 494.2272; found: 494.2263.

*9-(Naphthalen-1-yl)nona-2,8-diyn-1-ol (**SI-XI**).* In a flame-dried Schlenk flask, a suspension of $PdCl_2(PPh_3)_2$ (0.11 g, 0.16 mmol, 2.5 mol %) and CuI (0.09 g, 0.48 mmol, 7.5 mol %) in 16 mL of *N*,*N*-diisopropylethylamine was prepared, and a solution of 2,8-nonadiyn-1-ol (0.96 g, 7.06 mmol, 1.1 equiv) in 5 mL of NEt_3 was added dropwise, followed by the addition of 1-iodonaphthalene (0.94 mL, 6.4 mmol, 0.9 equiv) via syringe. The solution was stirred at 25 °C for 17 h and then heated for 30 min to 40 °C. The reaction mixture was quenched with aqueous sat. NH_4Cl sol., and the aqueous phase was extracted with ethyl acetate. The combined organic phases were washed with brine, dried over sodium sulfate, and evaporated. After flash chromatography with PE/DE (1:1), the product **SI-XI** (1.47 g, 87%) was obtained as a slightly yellow oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.57 (s, 1H), 1.70−1.90 (m, 4H), 2.34 (tt, J = 6.7, 2.2 Hz, 2H), 2.55−2.67 (m, 2H), 4.27 (t, J = 2.2 Hz, 2H), 7.40 (dd, J = 8.3, 7.1 Hz, 1H), 7.50 (ddd, J = 8.3, 6.8, 1.6 Hz, 1H), 7.56 (ddd, J = 8.3, 6.8, 1.6 Hz, 1H), 7.62 (dd, J = 7.1, 1.2 Hz, 1H), 7.78 (dt, J = 8.3, 1.1 Hz, 1H), 7.81−7.86 (m, 1H), 8.33 (ddt, J = 8.3, 1.4, 0.8 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 18.4, 19.3, 27.8, 28.0, 51.5, 78.8, 79.0, 86.1, 94.8, 121.6, 125.0, 125.3, 126.3, 126.6, 128.0, 128.3, 130.1, 133.2, 133.5 ppm.

HRMS-EI ($C_{19}H_{18}O$): calcd: 262.1352; found: 262.1347.

*1-(9-(But-2-yn-1-yloxy)nona-1,7-diyn-1-yl)naphthalene (**56**).* Following the above procedure for **9**, a mixture of sodium hydride (0.15 g, 3.85 mmol, 1.1 equiv, 60 wt % in oil), **SI-XI** (0.92 g, 3.50 mmol, 1.0 equiv), and 1-bromo-2-butyne (0.51 g, 3.85 mmol, 1.0 equiv) in 20 mL of THF was stirred at 25 °C for 16 h. After workup and flash chromatography with PE/DE (3:1), **56** (0.83 g, 75%) was obtained as a slightly yellow oily product.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.72−1.84 (m, 4H), 1.85 (t, J = 2.3 Hz, 3H), 2.34 (tt, J = 6.6, 2.1 Hz, 2H), 2.57−2.65 (m, 2H), 4.20 (q, J = 2.3 Hz, 2H), 4.23 (t, J = 2.1 Hz, 2H), 7.40 (dd, J = 8.3, 7.1 Hz, 1H), 7.50 (ddd, J = 8.1, 6.8, 1.5 Hz, 1H), 7.56 (ddd, J = 8.3, 6.8, 1.6 Hz, 1H), 7.62 (dd, J = 7.2, 1.2 Hz, 1H), 7.78 (dt, J = 8.3, 1.1 Hz, 1H), 7.81−7.86 (m, 1H), 8.33 (ddt, J = 8.3, 1.5, 0.8 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 3.7, 18.5, 19.3, 27.8, 28.0, 57.0, 57.1, 74.6, 75.8, 78.9, 82.9, 86.9, 94.8, 121.6, 125.3, 126.3, 126.6, 126.6, 128.0, 128.2, 130.1, 133.2, 133.5 ppm.

HRMS-ESI (TOF) ($C_{23}H_{22}O$): calcd: 315.1743 $[M + H]^+$, 337.1563 $[M + Na]^+$; found: 315.1737 $[M + H]^+$, 337.1569 $[M + Na]^+$.

Cyclization Products. *1,3,6,8-Tetrahydrobenzo[1,2-c:3,4-c′]difuran (**4**) and 4,5-Diphenyl-1,3,6,8-tetrahydrobenzo[1,2-c:3,4-c′]difuran (**5**).* Procedure for the cyclotrimerization of either **2** or **3** with catalytic amounts of $CoCl(PPh_3)_3$ (**1**, 5 mol %):

In a flame-dried Schlenk tube, $CoCl(PPh_3)_3$ (**1**, 5 mol %) was suspended in THF (6 mL/mmol triyne). The triyne (**2**, 1.23 mmol, or **3**, 0.58 mmol) was added as a solution in THF, and the resulting mixture was stirred at 25 °C. The TLC showed complete reaction within 3 h. The solvent was removed, and the crude product was purified by flash chromatography with *n*-hex/EE (1:1). The cyclotrimerization products were obtained as colorless (**4**, 195 mg, 98%) to light yellow (**5**, 156 mg, 85%) solids.

The spectral data are according to the literature.[8b]

*General Procedure for the Cyclotrimerization with Catalytic Amounts of $CoCl(PPh_3)_3$ (**1**).* In a flame-dried Schlenk tube, $CoCl(PPh_3)_3$ (**1**, 10 mol %) was suspended in THF (1 mL). The triyne (0.125−0.25 mmol) was added as solid or as a solution in THF, and the resulting mixture was stirred overnight at 25 °C or heated to temperatures up to 95 °C (see below at the individual products for the reaction temperature). The reaction was monitored by TLC, and after completion, the solvent was removed and the crude product was purified by flash chromatography with *c*-hex/EE. The cyclotrimerization products were obtained as colorless to yellow solids.

For every compound in parentheses: (amount of substrate, catalyst loading, solvent if not THF, reaction temperature, time, eluent for column chromatography, yield, d/l:meso ratio, aggregation state).

*4,5-Di(naphthalen-1-yl)-1,3,6,8-tetrahydrobenzo[1,2-c:3,4-c′]difuran (**39**).* (0.15 mmol, 10 mol % $CoCl(PPh_3)_3$, 25 °C, 36 h, *c*-hex/EE (4:1); 57 mg (92%), 1:1.1 (d/l:meso ratio), colorless solid).

The spectral data are according to the literature.[18]

*4,5-Bis(2-methoxynaphthalen-1-yl)-1,3,6,8-tetrahydrobenzo[1,2-c:3,4-c′]difuran (**40**).* (0.1 mmol, 10 mol % $CoCl(PPh_3)_3$, 25 °C, 24 h, no product isolated).

*4,5-Di(phenanthren-9-yl)-1,3,6,8-tetrahydrobenzo[1,2-c:3,4-c′]difuran (**41**).* (0.14 mmol, 10 mol % $CoCl(PPh_3)_3$, 25 °C, 17 h, *c*-hex/EE (4:1); 60 mg (86%), (d/l:meso ratio could not be assigned), colorless solid).

The spectral data are according to the literature.[18]

*4,5-Bis(4-methylnaphthalen-1-yl)-1,3,6,8-tetrahydrobenzo[1,2-c:3,4-c′]difuran (**42**).* (0.10 mmol, 10 mol % $CoCl(PPh_3)_3$, 25 °C, 24 h, *c*-hex/EE (4:1); 45 mg (94%), 1.1:1 (d/l:meso ratio, GC area) colorless solid).

Meso and d/l forms are not separable by column chromatography.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.51 (dd, J = 3.9, 0.8 Hz, 12H), 4.69 (ddt, J = 12.0, 3.5, 2.0 Hz, 8H), 5.15−5.31 (m, 8H), 6.73−6.86 (m, 4H), 7.06−7.32 (m, 8H), 7.41−7.55 (m, 4H), 7.60−7.67 (m, 2H), 7.68−7.79 (m, 4H), 7.88−7.97 (m, 2H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 19.4 (2×), 73.0 (2×), 73.8 (2×), 124.2, 124.5, 125.0, 125.2, 125.3, 125.4, 125.5, 125.7, 125.8, 126.0, 126.2, 126.4, 127.8, 130.9, 131.0, 131.1, 131.6, 132.4 (2×), 133.6, 133.7, 133.8, 134.3, 135.8, 140.0, 140.1 ppm.

HRMS-EI ($C_{32}H_{26}O_2$): calcd: 442.1927; found: 442.1924.

EA: calcd: C 86.85, H 5.92; found: C 86.59, H 5.84.

Mp. 229.5−230.5 °C.

*4,5-Di-o-tolyl-1,3,6,8-tetrahydrobenzo[1,2-c:3,4-c′]difuran (**43**).* (0.26 mmol, 5 mol % $CoCl(PPh_3)_3$, THF, 25 °C, 36 h, *c*-hex/EE (4:1); 69 mg (78%), 1:1.1 (d/l:meso ratio, GC area), colorless solid).

The meso and d/l forms are not separable by column chromatography.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.06 (s, 8H), 2.09 (s, 4H), 4.70−4.83 (m, 8H), 5.11−5.21 (m, 8H), 6.90−6.95 (m, 2H), 6.96−7.02 (m, 6H), 7.03−7.07 (m, 8H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 19.5, 19.9, 72.8, 72.9, 73.7, 73.8, 125.0, 125.3, 127.3, 127.3, 127.5, 128.1, 129.8, 129.9, 130.6, 130.8, 133.9, 134.0, 135.1, 135.3, 137.2, 137.9, 138.8, 139.1 ppm.

HRMS-EI ($C_{24}H_{22}O_2$): calcd: 342.1614; found: 342.1611.

EA: calcd: C 84.18, H 6.48; found: C 84.03, H 6.00.

Mp. 154.5−155.5 °C.

*4,5-Bis(2-isopropylphenyl)-1,3,6,8-tetrahydrobenzo[1,2-c:3,4-c′]difuran (**44**).* (0.35 mmol, 4 mol % $CoCl(PPh_3)_3$, THF, 25 °C, 36 h, *c*-hex/EE (4:1); 99 mg (72%), 1.3:1 (d/l:meso ratio, GC area), colorless solid).

Meso and d/l forms are not separable by column chromatography.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.87 (d, J = 6.8 Hz, 4H), 0.94 (d, J = 6.8 Hz, 12H), 1.16 (d, J = 6.8 Hz, 8H), 2.70 (sept, J = 6.9 Hz, 2H), 2.81 (sept, J = 6.9 Hz, 2H), 4.67 (d, J = 12.5 Hz, 2H), 4.74 (d, J = 11.7 Hz, 2H), 4.89−4.97 (m, 4H), 5.11−5.21 (m, 8H), 6.90 (dd, J = 8.0, 7.7, 1.6 Hz, 2H), 6.95−7.00 (m, 2H), 7.05−7.12 (m, 5H), 7.15−7.23 (m, 7H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 22.5, 24.1, 25.4, 25.8, 29.6, 30.0, 72.8, 73.0, 73.9, 74.1, 124.9, 125.2, 125.3, 125.8, 127.8, 128.1, 129.7, 131.0, 131.1, 131.6, 133.8, 134.1, 135.9, 136.1, 139.1, 139.9, 146.0, 146.6 ppm.

HRMS-EI ($C_{28}H_{30}O_2$): calcd: 398.2240; found: 398.2239.

Mp. 159−160 °C.

*Dimethyl-2,2′-(1,3,6,8-tetrahydrobenzo[1,2-c:3,4-c′]difuran-4,5-diyl)dibenzoate (**45**).* (0.33 mmol, 5 mol % $CoCl(PPh_3)_3$, THF, 25

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°C, 36 h, *c*-hex/EE (4:1); 72 mg (51%), 2:1 (d/l:meso ratio), colorless solid).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.75 (d, J = 2.6 Hz, 6H), 4.76 (s, 4H), 5.14 (s, 4H), 7.12−7.16 (m, 2H), 7.17−7.23 (m, 2H), 7.25−7.32 (m, 2H), 7.76 (ddd, J = 7.7, 2.9, 1.6 Hz, 2H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 52.1, 73.0, 73.5, 127.4, 129.5, 129.9, 130.6, 130.9, 131.7, 132.7, 137.7, 139.9, 167.1 ppm.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.71 (d, J = 2.2 Hz, 6H), 4.75 (dd, J = 11.3, 1.3 Hz, 2H), 4.91 (dd, J = 11.3, 2.2 Hz, 2H), 5.17 (q, J = 11.4 Hz, 4H), 7.02 (dt, J = 7.7, 1.8 Hz, 2H), 7.19 (tdd, J = 7.5, 2.3, 1.3 Hz, 2H), 7.26−7.32 (m, 2H), 7.73 (ddd, J = 7.9, 2.2, 1.2 Hz, 2H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 51.9, 72.9, 73.8, 127.4, 129.9, 130.2, 130.3, 131.0, 131.8, 132.8, 138.5, 138.9, 166.6 ppm.

HRMS-ESI (TOF) ($C_{26}H_{22}O_6$): calcd: 431.1489 $[M + H]^+$, 453.1309 $[M + Na]^+$; found: 431.1495 $[M + H]^+$, 453.1317 $[M + Na]^+$.

Mp. 162.5−163.5 °C.

*4,5-Di(quinolin-4-yl)-1,3,6,8-tetrahydrobenzo[1,2-c:3,4-c′]difuran (**46**).* (0.125 mmol, 10 mol % $CoCl(PPh_3)_3$, THF, 25 °C, 18 h, *n*-hex/THF (1:1, 0.5% NEt_3); 48 mg (94%), 1.9:1 (d/l:meso ratio), yellow solid).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.69 (dt, J = 3.5, 1.9 Hz, 4H), 5.17−5.29 (m, 4H), 6.76 (d, J = 4.4 Hz, 2H), 7.57 (ddd, J = 8.3, 6.7, 1.2 Hz, 2H), 7.66−7.76 (m, 4H), 8.06 (dt, J = 8.3, 1.2 Hz, 2H), 8.45 (d, J = 4.4 Hz, 2H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 72.8, 73.3, 120.6, 120.9, 125.1, 126.5, 127.3, 129.7, 130.2, 132.8, 139.6, 144.1, 148.1, 149.7 ppm.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.66−4.84 (m, 4H), 5.17−5.30 (m, 4H), 7.16 (d, J = 4.4 Hz, 2H), 7.24 (ddd, J = 8.3, 6.9, 1.3 Hz, 2H), 7.51 (ddd, J = 8.4, 6.9, 1.3 Hz, 2H), 7.55−7.60 (m, 2H), 7.90 (dt, J = 8.4, 0.9 Hz, 2H), 8.72 (d, J = 4.4 Hz, 2H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 72.8, 73.3, 122.4, 125.2, 125.7, 126.6, 129.5, 129.9, 130.2, 132.9, 139.6, 143.8, 148.2, 149.3 ppm.

HRMS-EI ($C_{28}H_{20}N_2O_2$): calcd: 416.1519; found: 416.1511.

Mp. 126−127 °C.

*4,5-Di(isoquinolin-4-yl)-1,3,6,8-tetrahydrobenzo[1,2-c:3,4-c′]-difuran (**47**).* (0.125 mmol, 10 mol % $CoCl(PPh_3)_3$, THF, 25 °C, 18 h, *n*-hex/THF (1:1, 0.5% NEt_3); 48 mg (92%), 1.1:1 (d/l:meso ratio), yellow solid).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.65−4.81 (m, 4H), 5.17−5.33 (m, 4H), 7.53−7.67 (m, 2H), 7.64−7.76 (m, 4H), 7.90 (dt, J = 8.2, 1.0 Hz, 2H), 7.93 (s, 2H), 8.95 (s, 2H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 72.9, 73.4, 124.2, 127.5, 128.0, 128.2, 129.0, 130.1, 131.2, 132.5, 134.1, 140.5, 142.0, 152.4 ppm.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.67−4.88 (m, 4H), 5.19−5.32 (m, 4H), 7.33−7.44 (m, 4H), 7.50−7.59 (m, 2H), 7.69−7.82 (m, 2H), 8.34 (s, 2H), 8.96 (s, 2H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 72.9, 73.5, 124.3, 127.1, 127.9, 128.6, 130.1, 130.2, 132.6, 133.4, 140.6, 143.9 144.0, 152.2 ppm.

HRMS-EI ($C_{28}H_{20}N_2O_2$): calcd: 416.1519; found: 416.1519.

EA: calcd: C 80.75, H 4.84, N 6.73; found: C 80.80, H 5.03, N 6.08.

Mp. decomp. > 190.5 °C.

*4-Methyl-5-(naphthalen-1-yl)-1,3,6,8-tetrahydrobenzo[1,2-c:3,4-c′]difuran (**48**).* (0.15 mmol, 10 mol % $CoCl(PPh_3)_3$, THF, 25 °C, 36 h, *c*-hex/EE (4:1); 44 mg (96%), colorless solid).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.87 (s, 3H), 4.55 (dd, J = 12.5, 2.2 Hz, 1H), 4.78 (dd, J = 12.5, 2.2 Hz, 1H), 5.11 (s, 2H), 5.18 (s, 4H), 7.29 (dd, J = 7.0, 1.2 Hz, 1H), 7.37−7.43 (m, 2H), 7.46−7.57 (m, 2H), 7.84−7.97 (m, 2H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 16.1, 72.8, 73.1, 73.4, 73.5, 125.3, 125.6, 126.0, 126.3, 126.4, 127.9, 128.5, 129.3, 129.4, 130.9, 131.3, 132.9, 133.7, 136.3, 138.5, 139.3 ppm.

HRMS-ESI (TOF) ($C_{21}H_{18}O_2$): calcd: 303.1380 $[M + H]^+$, 325.1199 $[M + Na]^+$; found: 303.1374 $[M + H]^+$, 325.1202 $[M + Na]^+$.

Mp. 153.5−154.5 °C.

*4-(2-Methoxynaphthalen-1-yl)-5-methyl-1,3,6,8-tetrahydrobenzo[1,2-c:3,4-c′]difuran (**49**).* (0.25 mmol, 5 mol % $CoBr_2$,10 mol % Zn, ZnI_2, THF, 65 °C, 18 h, *c*-hex/EE (4:1); 75 mg (90%), colorless solid).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.85 (s, 3H), 3.87 (s, 3H), 4.54 (d, J = 12.3 Hz, 1H), 4.71 (d, J = 12.3 Hz, 1H), 5.12 (s, 2H), 5.18 (dd, J = 7.2, 2.4 Hz, 4H), 7.19−7.23 (m, 1H), 7.31−7.36 (m, 2H), 7.38 (d, J = 9.1 Hz, 1H), 7.82−7.87 (m, 1H), 7.92 (d, J = 9.1 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 15.9, 56.4, 72.9, 73.2, 73.5, 73.6, 113.2, 120.5, 123.7, 124.2, 126.9, 128.2, 128.8, 129.0, 129.3, 129.7, 129.9, 130.9, 132.5, 138.4, 139.7, 153.7 ppm.

HRMS-ESI (TOF) ($C_{22}H_{20}O_3$): calcd: 333.1485 $[M + H]^+$, 355.1305 $[M + Na]^+$; found: 333.1472 $[M + H]^+$, 355.1304 $[M + Na]^+$.

EA: calcd: C 79.50, H 6.06; found: C 79.40, H 6.12.

Mp. 214−215 °C.

*4-(Naphthalen-1-yl)-5-phenyl-1,3,6,8-tetrahydrobenzo[1,2-c:3,4-c′]difuran (**50**).* (0.14 mmol, 10 mol % $CoCl(PPh_3)_3$, THF, 25 °C, 17 h, *c*-hex/EE (4:1); 50 mg (96%), colorless solid).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.62−4.76 (m, 2H), 4.97 (d, J = 12.6 Hz, 1H), 5.11 (d, J = 13.6 Hz, 1H), 5.20 (dt, J = 7.3, 1.7 Hz, 4H), 6.93−7.04 (m, 5H), 7.10 (dd, J = 7.1, 1.3 Hz, 1H), 7.27−7.32 (m, 1H), 7.35−7.47 (m, 2H), 7.54−7.59 (m, 1H), 7.70 (dt, J = 8.3, 1.1 Hz, 1H), 7.80 (dd, J = 7.4, 2.2 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 72.8, 72.9, 73.6, 73.8, 124.9 (2×), 125.1, 125.5, 125.8, 126.3, 126.9, 127.6, 127.7, 127.8, 128.4, 128.6, 131.0, 131.6, 132.3, 135.4, 136.0, 138.8, 139.8, 139.9 ppm.

HRMS-EI ($C_{26}H_{20}O_2$): calcd: 364.1458; found: 364.1452.

Mp. 163.5−164.5 °C.

*4-(2-Methoxynaphthalen-1-yl)-5-phenyl-1,3,6,8-tetrahydrobenzo[1,2-c:3,4-c′]difuran (**51**).* (0.13 mmol, 10 mol % $CoCl(PPh_3)_3$, THF, 25 °C, 17 h, *c*-hex/EE (4:1); 44 mg (85%), colorless solid).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.68 (s, 3H), 4.67 (qt, J = 12.3, 2.1 Hz, 2H), 5.05 (q, J = 12.6 Hz, 2H), 5.20 (d, J = 2.1 Hz, 4H), 6.94−7.02 (m, 5H), 7.11 (d, J = 9.1 Hz, 1H), 7.29 (dt, J = 7.8, 1.9 Hz, 1H), 7.33−7.39 (m, 2H), 7.70−7.76 (m, 2H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 56.1, 72.9, 73.0, 73.7, 73.8, 112.6, 120.6, 123.5, 124.4, 124.9, 126.7, 126.8, 127.5, 128.1, 128.2, 128.3, 129.6, 131.2, 131.8, 132.7, 136.0, 138.5, 138.7, 140.2, 153.6 ppm.

HRMS-EI ($C_{27}H_{22}O_3$): calcd: 394.1564; found: 394.1566.

Mp. 170−171 °C.

*4-(2-Methoxynaphthalen-1-yl)-5-(naphthalen-1-yl)-1,3,6,8-tetrahydrobenzo[1,2-c:3,4-c′]difuran (**52**).* (0.1 mmol, 10 mol % $CoCl(PPh_3)_3$, THF, 25 °C, 24 h, *c*-hex/EE (6:1); 40 mg (90%), colorless solid).

Two diastereomers were isolated, which account together for the total yield.

First Fraction. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 3.09 (s, 3H), 4.63−4.85 (m, 4H), 5.18−5.31 (m, 4H), 6.78−6.86 (m, 2H), 6.92 (dd, J = 8.2, 7.1 Hz, 1H), 7.31 (ddd, J = 8.1, 6.8, 1.3 Hz, 1H), 7.37−7.47 (m, 3H), 7.52 (dd, J = 8.4, 1.0 Hz, 2H), 7.59 (d, J = 8.9 Hz, 1H), 7.68−7.75 (m, 2H), 7.77−7.81 (m, 1H) ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 55.1, 72.9, 73.1, 73.8, 73.9, 112.2, 120.3, 123.3, 124.6, 124.7, 125.4, 125.5, 126.1, 126.5, 126.8, 127.4, 128.1, 128.2, 128.4, 129.3, 131.0, 131.2, 131.4, 132.2, 133.1, 133.3, 134.3, 136.0, 139.7, 140.5, 153.3 ppm.

Second Fraction. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 3.89 (s, 3H), 4.61−4.83 (m, 4H), 5.17−5.31 (m, 4H), 7.07 (dt, J = 6.4, 3.4 Hz, 2H), 7.12 (d, J = 9.1 Hz, 1H), 7.16−7.23 (m, 2H), 7.24−7.28 (m, 1H), 7.31 (dd, J = 7.1, 1.3 Hz, 1H), 7.35−7.41 (m, 1H), 7.47−7.55 (m, 2H), 7.57−7.62 (m, 2H), 7.66 (dt, J = 8.2, 0.9 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 55.9, 73.0, 73.1, 73.8, 73.8, 112.1, 120.5, 123.3, 124.6, 124.7, 125.4, 125.5, 125.7, 126.1, 126.4, 127.6 (2×), 128.0, 128.5, 129.5, 129.6, 130.7, 131.4 (2×), 132.2, 133.2, 134.2, 135.8, 139.9, 140.5, 153.6 ppm.

HRMS-EI ($C_{31}H_{24}O_3$): calcd: 444.1720; found: 444.1719.

Mp. 234.5−235.5 °C.

*Tetraethyl-4,5-di(naphthalen-1-yl)-1,3,6,8-tetrahydro-as-indacene-2,2,7,7-tetracarboxylate (**53a**).* (0.125 mmol, 10 mol % $CoCl(PPh_3)_3$, toluene, 80 °C, 18 h, *c*-hex/EE (4:1); 70 mg (81%), 2.6:1 (d/l:meso ratio, GC area), colorless solid).

Meso and d/l forms are not separable by column chromatography.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.15−1.24 (m, 24H), 3.03−3.20 (m, 8H), 3.58−3.82 (m, 8H), 4.06−4.26 (m, 16H), 6.75−6.97 (m,

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6H), 7.07−7.25 (m, 4H), 7.40−7.47 (m, 6H), 7.50 (dt, J = 8.2, 1.0 Hz, 4H), 7.52−7.58 (m, 2H), 7.64−7.77 (m, 6H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.0, 22.7, 29.4, 29.7 (2×), 31.9, 39.3, 39.4, 40.2, 40.3, 60.1, 61.7, 124.6, 125.0, 125.2, 125.3, 125.4, 125.8, 126.0, 126.1, 126.2, 127.0, 127.8, 128.1, 131.2, 131.9, 133.1, 133.2, 134.6, 134.7, 135.3, 135.4, 136.6, 137.1, 139.6, 139.7, 171.6, 171.7, 171.8 ppm. Because of signal overlaps, not all expected carbon atoms could be assigned.

HRMS-EI ($C_{44}H_{42}O_8$): calcd: 698.2874; found: 698.2856.

Mp. 149.5−150.5 °C.

*Tetraethyl-4,5-bis(2-methoxynaphthalen-1-yl)-1,3,6,8-tetrahydro-as-indacene-2,2,7,7-tetracarboxylate (**53b**).* (0.1 mmol, 10 mol % $CoCl(PPh_3)_3$, toluene, 80 °C, 20 h, c-hex/EE (4:1); 73 mg (96%), (no meso form detectable), colorless solid).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.19 (dt, J = 12.4, 7.1 Hz, 12H), 3.16 (d, J = 16.2 Hz, 2H), 3.39 (d, J = 16.2 Hz, 2H), 3.61−3.82 (m, 10H), 4.09−4.23 (m, 8H), 6.93 (ddd, J = 8.3, 6.7, 1.5 Hz, 2H), 6.97−7.04 (m, 4H), 7.39 (d, J = 8.3 Hz, 2H), 7.41−7.45 (m, 2H), 7.48 (d, J = 9.0 Hz, 2H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.0, 14.1, 39.6, 40.5, 55.9, 59.9, 61.5, 61.6, 112.0, 121.6, 122.8, 125.2, 125.8, 127.2, 128.2, 128.6, 132.0, 132.2, 134.9, 140.5, 153.8, 171.7, 172.2 ppm. Because of signal overlaps, not all expected carbon atoms could be assigned.

HRMS-EI ($C_{46}H_{46}O_{10}$): calcd: 758.3086; found: 758.3068.

EA: calcd: C 72.81, H 6.11; found: C 72.76, H 6.17.

Mp. 196−197 °C.

*Tetraethyl-4-methyl-5-(naphthalen-1-yl)-1,3,6,8-tetrahydro-as-indacene-2,2,7,7-tetracarboxylate (**53c**).* (0.25 mmol, 10 mol % $CoCl(PPh_3)_3$, THF, 65 °C, 21 h, c-hex/EE (10:1); 140 mg (95%), yellow oil).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.12 (t, J = 7.1 Hz, 3H), 1.19 (t, J = 7.1 Hz, 3H), 1.30 (td, J = 7.1, 4.5 Hz, 6H), 1.83 (s, 3H), 2.90 (d, J = 16.7 Hz, 1H), 3.18 (d, J = 16.7 Hz, 1H), 3.48−3.62 (m, 4H), 3.64 (s, 2H), 4.02−4.17 (m, 4H), 4.26 (p, J = 7.2 Hz, 4H), 7.22−7.29 (m, 1H), 7.34−7.39 (m, 2H), 7.46 (ddd, J = 8.2, 5.3, 2.7 Hz, 1H), 7.52 (dd, J = 8.2, 7.0 Hz, 1H), 7.85 (d, J = 7.2 Hz, 1H), 7.89 (d, J = 8.3 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 13.9, 14.0, 14.1 (2×), 16.4, 39.1, 39.4, 39.9, 40.1, 59.9, 60.2, 61.5, 61.6, 61.8 (2×), 125.6, 125.7, 125.8, 126.0, 126.6, 127.4, 128.2, 131.2, 131.7, 132.4, 133.7, 134.4, 134.9, 137.7, 138.4, 139.0, 171.6, 171.7, 171.9, 188.9 ppm.

HRMS-ESI (TOF) ($C_{35}H_{38}O_8$): calcd: 587.2639 $[M + H]^+$, 609.2459 $[M + Na]^+$; found: 587.2628 $[M + H]^+$, 609.2450 $[M + Na]^+$.

*Tetraethyl-4-(2-methoxynaphthalen-1-yl)-5-methyl-1,3,6,8-tetrahydro-as-indacene-2,2,7,7-tetracarboxylate (**53d**).* (0.25 mmol, 10 mol % $CoCl(PPh_3)_3$, toluene, 60 °C, 18 h, 80 °C, 17 h, c-hex/EE (4:1); 126 mg (82%), yellow oil).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.10 (td, J = 7.1, 1.2 Hz, 3H), 1.19 (td, J = 7.1, 1.2 Hz, 3H), 1.30 (tt, J = 7.1, 1.2 Hz, 6H), 1.82 (s, 3H), 2.89 (d, J = 16.7 Hz, 1H), 3.17 (d, J = 16.7 Hz, 1H), 3.50−3.60 (m, 2H), 3.63 (d, J = 13.6 Hz, 4H), 3.85 (d, J = 0.9 Hz, 3H), 3.99−4.18 (m, 4H), 4.26 (dddq, J = 7.2, 4.5, 3.1, 1.6 Hz, 4H), 7.17 (dd, J = 6.8, 2.9 Hz, 1H), 7.25−7.33 (m, 2H) 7.37 (dd, J = 9.1, 1.3 Hz, 1H), 7.78−7.84 (m, 1H), 7.88 (d, J = 0.9 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 13.9, 14.0, 14.1, 16.3, 39.2, 39.5, 40.0, 40.2, 56.5, 59.9, 60.2, 61.5, 61.7, 61.8, 113.6, 122.1, 123.5, 124.8, 126.5, 127.9, 129.1, 130.8, 131.7, 132.5, 132.9, 134.4, 138.4, 139.4, 153.8, 171.7, 171.9, 172.0, 172.2 ppm. Because of signal overlaps, not all expected carbon atoms could be assigned.

HRMS-ESI (TOF) ($C_{36}H_{40}O_9$): calcd: 617.2745 $[M + H]^+$, 639.2565 $[M + Na]^+$; found: 617.2747 $[M + H]^+$, 639.2569 $[M + Na]^+$.

*Tetraethyl-4-(2-methoxynaphthalen-1-yl)-5-phenyl-1,3,6,8-tetrahydro-as-indacene-2,2,7,7-tetracarboxylate (**53f**).* (0.1 mmol, 10 mol % $CoCl(PPh_3)_3$, toluene, 80 °C, 22 h, 95 °C, 2 h, c-hex/EE (4:1); 31 mg (46%), colorless oil).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.13 (t, J = 7.1 Hz, 3H), 1.19 (t, J = 7.1 Hz, 3H), 1.25 (td, J = 7.1, 3.1 Hz, 6H), 2.97 (d, J = 16.9 Hz, 1H), 3.17 (d, J = 16.9 Hz, 1H), 3.45 (q, J = 16.9 Hz, 2H), 3.59−3.75 (m, 7H), 4.04−4.27 (m, 8H), 6.95 (s, 4H), 7.08 (d, J = 9.1 Hz, 1H), 7.21−7.34 (m, 4H), 7.68 (d, J = 8.6 Hz, 2H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 13.9, 14.0, 14.1, 39.4, 39.5, 40.1, 40.6, 56.0, 60.1, 60.2, 61.6, 61.8, 62.0, 112.8, 121.9, 123.2, 125.0, 126.2, 126.3, 127.1, 127.8, 127.9, 128.6, 128.7, 129.0, 130.2, 131.7, 133.1, 134.5, 134.9, 138.0, 138.2, 139.7, 139.8, 153.6, 171.6, 171.8 (2×), 171.9 ppm.

HRMS-EI ($C_{41}H_{42}O_9$): calcd: 678.2823; found: 678.2812.

*Tetraethyl-5-(2-methoxynaphthalen-1-yl)-4-methyl-1,6,7,9-tetrahydro-2H-cyclopenta[a]naphthalene-2,2,8,8(3H)-tetracarboxylate (**53g**).* (0.11 mmol, 10 mol % $CoCl(PPh_3)_3$, toluene, 80 °C, 20 h, c-hex/EE (4:1); 14 mg (20%), colorless solid).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.15 (t, J = 7.1 Hz, 3H), 1.22 (t, J = 7.1 Hz, 3H), 1.30 (td, J = 7.1, 2.1 Hz, 6H), 1.73 (s, 3H), 1.95−2.06 (m, 1H), 2.05−2.14 (m, 2H), 2.20−2.33 (m, 1H), 3.12 (d, J = 16.4 Hz, 1H), 3.25 (d, J = 16.4 Hz, 1H), 3.62 (s, 2H), 3.68 (s, 2H), 3.82 (s, 3H), 4.07−4.16 (m, 2H), 4.12−4.22 (m, 2H), 4.26 (qd, J = 7.1, 4.6 Hz, 4H), 7.05 (dt, J = 8.3, 0.7 Hz, 1H), 7.25 (ddd, J = 8.3, 6.8, 1.6 Hz, 1H), 7.30 (ddd, J = 8.1, 6.7, 1.4 Hz, 1H), 7.36 (d, J = 9.1 Hz, 1H), 7.81 (dd, J = 8.3, 1.2 Hz, 1H), 7.87 (d, J = 8.9 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 14.0, 14.1, 16.4, 24.2, 28.1, 32.6, 39.8, 40.2, 53.4, 56.3, 59.5, 61.3 (2×), 61.8 (2×), 113.4, 122.8, 123.5, 124.5, 126.5, 126.9, 127.9, 128.9, 129.1, 130.5, 132.7, 133.1, 134.0, 136.6, 137.4, 153.5, 171.4, 171.7, 172.1, 172.2 ppm. Because of signal overlaps, not all expected carbon atoms could be assigned.

HRMS-EI ($C_{37}H_{42}O_9$): calcd: 630.2823; found: 630.2810.

Mp. 56−57 °C

*Tetraethyl-5-(2-methoxynaphthalen-1-yl)-4-phenyl-1,6,7,9-tetrahydro-2H-cyclopenta[a]naphthalene-2,2,8,8(3H)-tetracarboxylate (**53h**).* (0.1 mmol, 10 mol % $CoCl(PPh_3)_3$, toluene, 80 °C, 22 h, 95 °C, 2 h, c-hex/EE (4:1); 63 mg (92%), colorless syrup).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.18 (t, J = 7.1 Hz, 3H), 1.20−1.32 (m, 9H), 2.06−2.33 (m, 4H), 3.15 (d, J = 16.7 Hz, 1H), 3.35−3.54 (m, 3H), 3.65 (s, 3H), 3.70−3.82 (m, 2H), 4.09−4.29 (m, 8H), 6.53−6.97 (m, 3H), 7.06 (d, J = 9.1, 2H), 7.14−7.33 (m, 4H), 7.67 (ddt, J = 8.9, 2.6, 1.1 Hz, 2H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.1, 24.4, 28.1, 32.8, 39.7, 40.5, 53.4, 55.8, 59.7, 61.4, 61.5, 61.7, 100.0, 112.6, 122.4, 123.2, 124.8, 126.1, 126.3, 127.0, 127.8, 128.5 (2×), 128.9, 129.1, 133.1, 133.5 (2×), 136.4, 136.9, 137.9, 139.9, 153.4, 171.2, 171.8, 171.9, 172.0 ppm. Because of signal overlaps, not all expected carbon atoms could be assigned.

HRMS-EI ($C_{42}H_{44}O_9$): calcd: 692.2980; found: 692.2967.

*3,3-Diisopropyl-4-(2-methoxynaphthalen-1-yl)-5-phenyl-1,3,6,8-tetrahydro[1,2]oxasilolo[4,3-e]isobenzofuran (**55**).* (0.125 mmol, 10 mol % $CoCl(PPh_3)_3$, THF, 25 °C, 17 h, PE/EE (6:1); 37 mg (60%), yellow oil).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.30 (d, J = 6.6 Hz, 3H), 0.32−0.41 (m, 1H), 0.55 (d, J = 7.0 Hz, 3H), 0.62 (d, J = 7.0 Hz, 3H), 0.73−0.85 (m, 1H), 0.86 (d, J = 6.5 Hz, 3H), 3.76 (s, 3H), 5.01 (ddt, J = 17.8, 12.9, 2.2 Hz, 2H), 5.12 (d, J = 2.0 Hz, 2H), 5.19 (s, 2H), 6.93−6.97 (m, 3H), 7.00−7.04 (m, 2H), 7.22 (ddd, J = 8.0, 6.4, 1.8 Hz, 1H), 7.24−7.29 (m, 1H), 7.29−7.32 (m, 1H), 7.65 (dd, J = 7.5, 1.4 Hz, 1H), 7.69 (d, J = 9.1 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 12.9, 13.1, 15.8, 16.2, 16.5, 16.7, 55.1, 70.6, 72.9, 73.9, 111.6, 123.2, 124.5, 125.8, 125.9, 126.7, 127.3, 127.6, 128.0, 128.3, 129.2, 131.6, 133.8, 135.2, 135.7, 138.9, 139.2, 140.9, 143.3, 153.8 ppm. Because of signal overlaps, not all expected carbon atoms could be assigned.

^{29}Si NMR ($CDCl_3$, 79 MHz): δ = 32.2 ppm.

HRMS-EI ($C_{32}H_{34}O_3Si$): calcd: 494.2272, found: 494.2267.

*4-Methyl-5-(naphthalen-1-yl)-1,3,6,7,8,9-hexahydronaphtho[1,2-c]furan (**57**).* (0.15 mmol, 10 mol % $CoCl(PPh_3)_3$, THF, 25 °C, 5 d, c-hex/EE (4:1); 37 mg (78%), colorless solid).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.39−1.56 (m, 2H), 1.58−1.72 (m, 5H), 1.86 1. 98 (m, 1H), 2.16−2.29 (m, 1H), 2.54 (t, J = 6.4 Hz, 2H), 5.08 (s, 4H), 7.11−7.16 (m, 1H), 7.23−7.27 (m, 2H), 7.29−7.43 (m, 2H), 7.44 (dd, J = 8.2, 7.0 Hz, 1H), 7.80 (dt, J = 8.2, 1.0 Hz, 1H) ppm.

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^{13}C NMR ($CDCl_3$, 75 MHz): δ = 16.7, 22.6, 23.3, 27.1, 27.9, 73.9, 74.1, 125.4, 125.8, 125.9, 126.1, 126.9, 127.3, 128.1, 128.4, 132.0, 133.8, 135.2, 135.3, 136.8, 138.4, 138.9 ppm. Because of signal overlaps, not all expected carbon atoms could be assigned.

HRMS-EI ($C_{23}H_{22}O$): calcd: 314.1671; found: 314.1665.

Mp. 78−79 °C.

■ ASSOCIATED CONTENT

Supporting Information

Schemes of all molecules synthesized, references for literature-known products, further results for cyclizations with chiral anions, and ^{1}H and ^{13}C NMR spectra for all new synthesized compounds. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01623 (PDF)

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

This work is dedicated to Prof. Dr. Rüdiger Beckhaus on the occasion of his 60th birthday.

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