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[4 + 2] Annulation of Donor–Acceptor Cyclopropanes with Acetylenes Using 1,2-Zwitterionic Reactivity

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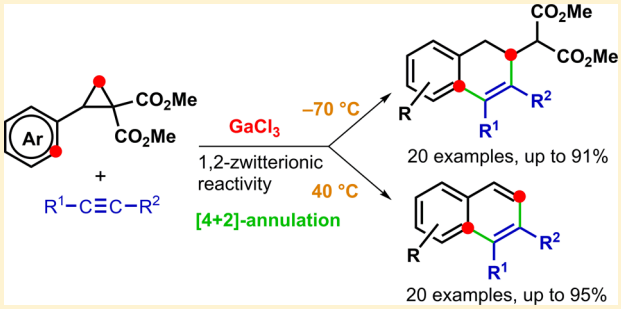
Supporting Information

ABSTRACT: A new process for the [4 + 2] annulation of donor–acceptor cyclopropanes with acetylenes under the effect of anhydrous $GaCl_3$ using 1,2-zwitterion reactivity was elaborated. The reaction opens access to substituted dihydronaphthalenes, naphthalenes, and other fused carbocycles. The direction of the reaction can be efficiently controlled by temperature.



INTRODUCTION

Cyclopropanes with donor and acceptor substituents in the vicinal position (donor–acceptor cyclopropanes, DACs) are remarkable building blocks widely used in contemporary organic synthesis to assemble diverse carbo- and heterocyclic systems.[1,2] DACs have a great synthetic potential that stimulates researchers to intensify studies on their chemistry.[3] Most commonly, DACs are used as sources of 1,3-zwitterion intermediates,[1,2] which are then used in reactions with a broad range of substrates. Reactions of this kind have been studied thoroughly. However, DACs are multifunctional substrates, and their application is not limited to 1,3-zwitterionic reactivity.

Use of DACs as sources for generation of 1,2-zwitterions[4] (Scheme 1, top) employs quite a different type of reactivity of DAC, 2-arylcyclopropane-1,1-dicarboxylates (ACDC) in particular. This type of reactivity was recently discovered by our team. Currently, it is under intense development and gaining popularity.[4−10] A distinctive feature of this approach is that gallium compounds are used for complexation and opening of the three-membered ring with displacement of the carbocationic center.[4,5a] To date, use of ACDC as 1,2-zwitterions has been studied for isomerization,[6] dimerization,[5] fragmentation,[7] reactions with alkenes (Scheme 1, a)[8] and aldehydes,[9] and addition of nucleophiles.[10]

In this work, we expanded the 1,2-zwitterionic type of reactivity to reactions with acetylenes. In total, reactions of DACs with acetylenes have been studied rather poorly in comparison with other substrates.[1,2,11] In fact, two pathways of reactions with acetylenes[11] are known for the most popular ACDC that are commonly used as model substrates, namely, formal [3 + 2] cycloaddition[12] and [3 + 2] annulation[13] to give cyclopentene and indene structures, respectively (Scheme 1, b). In this study, we succeeded in the development of new ACDC reactions with acetylenes that occur by [4 + 2] annulation type to give the dihydronaphthalene frame (Scheme 1, c) and performed some reactions involving these compounds.

Dihydronaphthalene derivatives belong to important classes of organic compounds. The dihydronaphthalene frame is part of various natural compounds (Figure 1).[14] Its derivatives, both natural and synthetic, show a very broad spectrum of biological activity such as cytotoxic, antimicrobial, antimalarial, antiestrogenic, anti-inflammatory activities, etc. as well as lipoxygenase enzyme inhibition and anti-HIV and anticancer properties.[14,15] They also serve as versatile building blocks in the construction of biologically important compounds.[16] Also, dihydronaphthalenes are used as compounds with luminescent, phosphorescent, and other properties.[17]

RESULTS AND DISCUSSION

The two-stage approach, which involved preliminary in situ generation of 1,2-zwitterionic gallium complex **1** immediately brought into a reaction with acetylene, was found to be the most efficient way to use ACDC in the function of 1,2-zwitterions. This approach was found to be quite efficient and allowed the pathway of reactions with acetylenes to be totally changed in the desired direction. However, a detailed optimization of the process conditions was required to obtain high product yields (Table 1); it was carried out using ACDC **2a** and phenylacetylene **3a** as the model compounds. During

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Scheme 1. Strategy of This Study

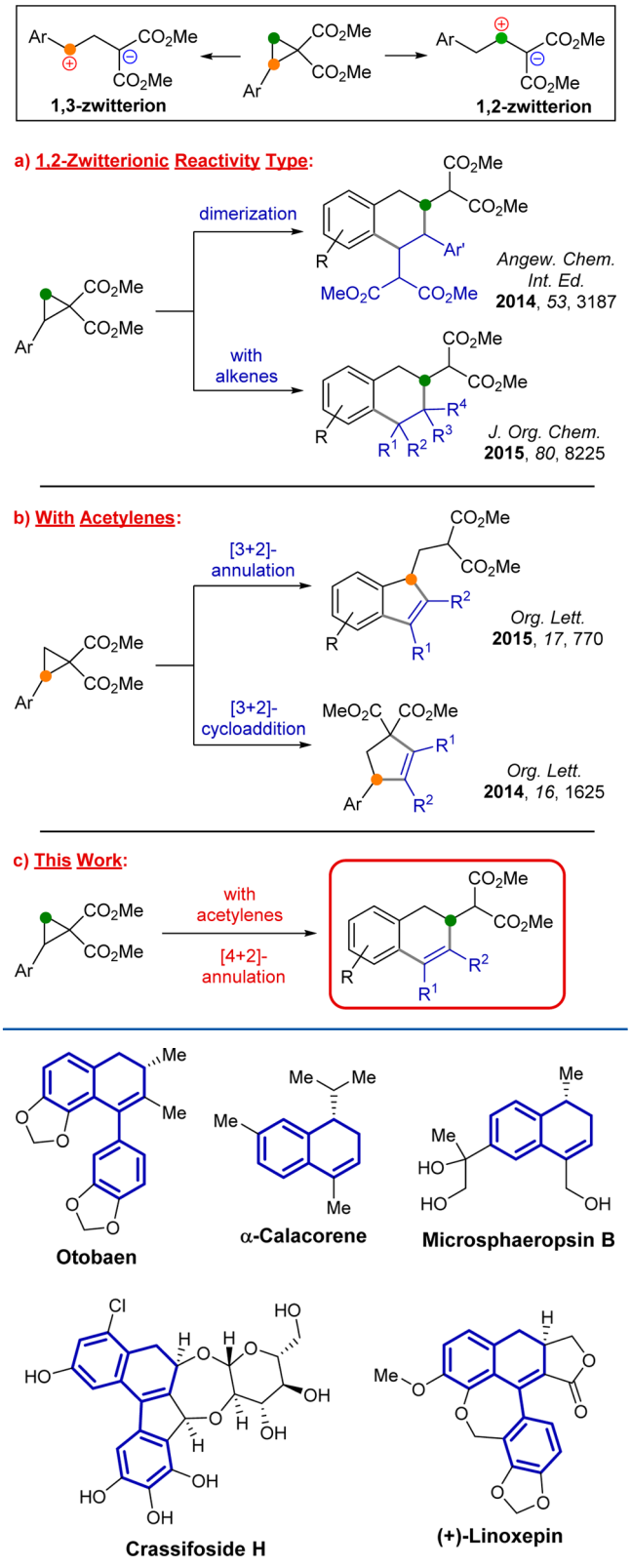
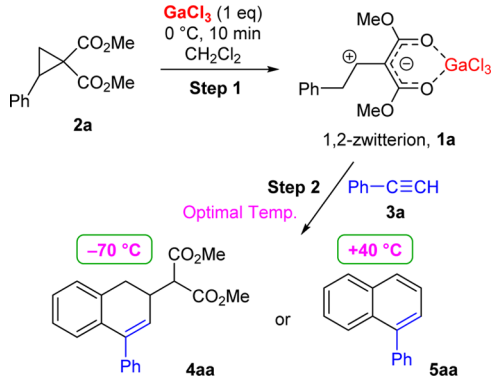


Figure 1. Dihydronaphthalene skeleton in nature.

the optimization, we found that the conditions of ACDC reactions with acetylenes differed principally from similar reactions of ACDC with alkenes or dimerization reactions studied previously. In fact, acetylenes turned out to be much more efficient than alkenes, and their reactions with ACDC occurred at lower temperatures. Furthermore, the [4 + 2] annulation product, i.e., dihydronaphthalenylmalonate **4aa**, readily eliminated a dimethylmalonate moiety in the presence of gallium trichloride even at reduced temperatures, which resulted in its aromatization to give naphthalene **5aa** (Table 1). All of this complicated the implementation of the target [4 + 2] annulation considerably. However, we managed to turn the drawbacks of the process into advantages and to develop, in addition to the target reaction, new pathways of the ACDC reaction with acetylenes that can be carried out with high selectivity. Temperature is the main condition for easy control of the process direction (apart from generation of 1,2-zwitterion **1a**). For example, selective synthesis of dihydronaphthalene **4aa** requires that the second reaction stage be carried out at temperatures not higher than −70 °C to prevent subsequent fragmentation of the product (Table 1, entries 10 and 11). Furthermore, ingress of moisture at reduced temperatures should be avoided as it can decrease the yield of the target product considerably (entry 9). Conversely, selective synthesis of naphthalene **5aa** requires that the temperature be increased to 40 °C (entry 3).

The conditions that we developed proved to be rather general and were perfectly reproduced for other substituted ACDC **2** and acetylenes **3**, both in [4 + 2] annulation to give dihydronaphthalenes **4** (Scheme 2) and in fragmentation reactions to give naphthalenes **5** (Scheme 3). The scope of both reactions was found to be similar and wide: ACDC with substituents at the *ortho*-, *meta*-, and *para*-positions of the

Table 1. Optimization of the Reaction Conditions



		step 2		yield, (%)[b,c]	
entry[a]	**3a** (equiv)	*T* (°C)	*t* (min)	**5aa**	**4aa**
1	3	40	30	70[b]	0
2	3	40	5	67[b]	0
3	6	40	30	85	0
4	3	0	30	71[b]	0
5	4	−30	30	62[b]	12[b]
6	2	−70	30	<5[b]	40[b,c]
7	4	−70	30	<5[b]	67[b]
8	4	−70	120	36[b]	29[b]
9[d]	4	−70	30	<5[b]	35[b]
10	6	−70	30	<5[b]	79
11[e]	5	−70	30	<5[b]	84

[a]A two-step method was used. Standard conditions: 0.35 mmol of **2a** in 5 mL of CH_2Cl_2. [b]NMR yields. [c]The dimers of starting cyclopropane **2a** were also formed (see refs 3h and g). [d]Water traces were introduced into the reaction mixture after the first step by a short contact with air. [e]About 8 g (34 mmol) of cyclopropane **2a** was used.

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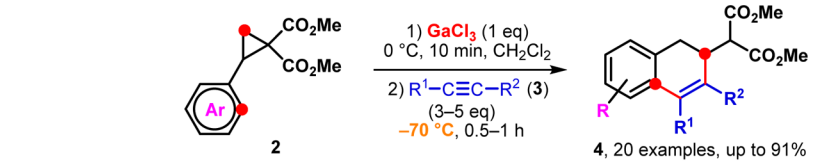
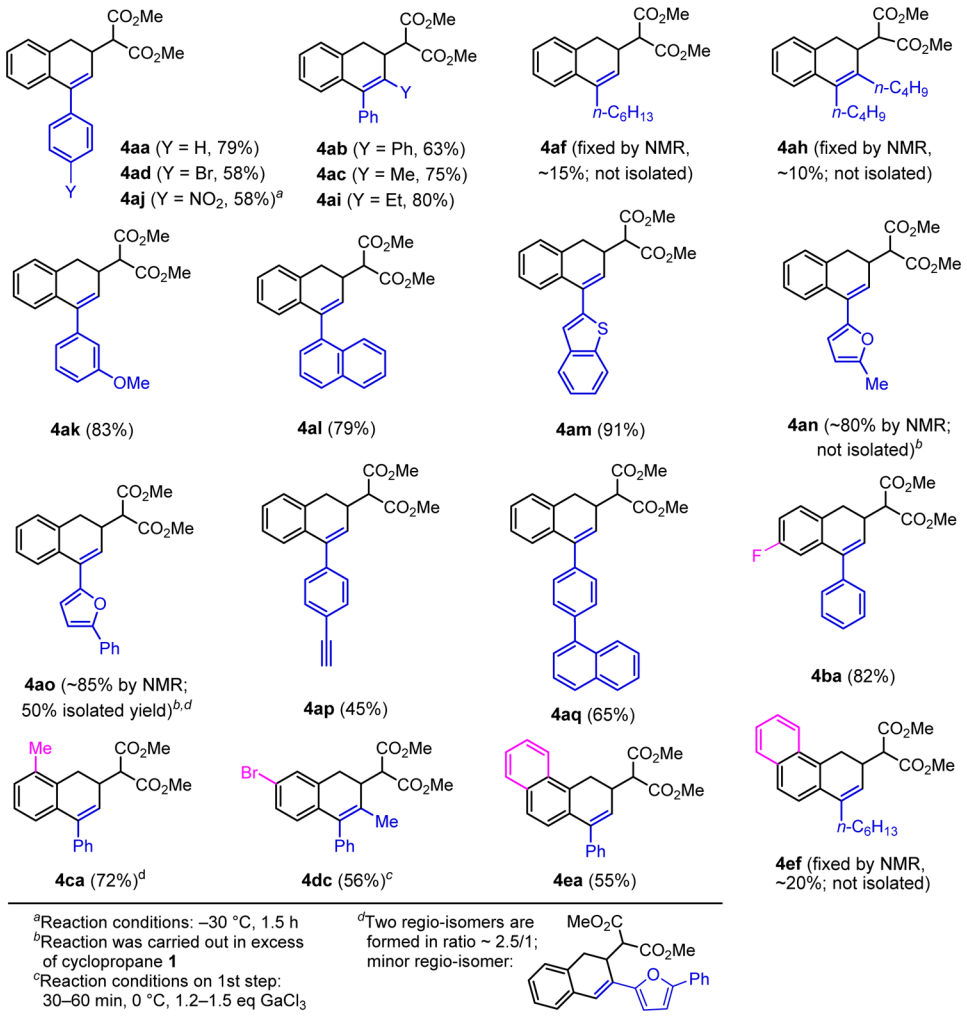
Scheme 2. Scope of the Reactions for Dihydronaphthylmalonates 4



Ar = Ph (**a**), 4-FC_6H_4 (**b**), 2-MeC_6H_4 (**c**), 3-BrC_6H_4 (**d**), 1-Naphthyl (**e**)
R^1,R^2 = Ph, H (**a**); Ph, Ph (**b**); Ph, Me (**c**); 4-BrC_6H_4, H (**d**); 4-MeC_6H_4, H (**e**); *n*-Hexyl, H (**f**); *n*-Pentyl, H (**g**); *n*-Butyl, *n*-Butyl (**h**); Ph, Et (**i**); 4-$NO_2C_6H_4$, H (**j**); 3-$MeOC_6H_4$, H (**k**); 1-Naphthyl, H (**l**); Benzo[*b*]thiophen-2-yl, H (**m**); 5-Me-furan-2-yl, H (**n**); 5-Ph-furan-2-yl, H (**o**); 4-Ethynyl-C_6H_4, H (**p**); 4-(1-Naphthyl)C_6H_4, H (**q**)



4aa (Y = H, 79%)
4ad (Y = Br, 58%)
4aj (Y = NO_2, 58%)[a]

4ab (Y = Ph, 63%)
4ac (Y = Me, 75%)
4ai (Y = Et, 80%)

4af (fixed by NMR, ~15%; not isolated)

4ah (fixed by NMR, ~10%; not isolated)

4ak (83%)

4al (79%)

4am (91%)

4an (~80% by NMR; not isolated)[b]

4ao (~85% by NMR; 50% isolated yield)[b,d]

4ap (45%)

4aq (65%)

4ba (82%)

4ca (72%)[d]

4dc (56%)[c]

4ea (55%)

4ef (fixed by NMR, ~20%; not isolated)

[a]Reaction conditions: –30 °C, 1.5 h
[b]Reaction was carried out in excess of cyclopropane **1**
[c]Reaction conditions on 1st step: 30–60 min, 0 °C, 1.2–1.5 eq $GaCl_3$
[d]Two regio-isomers are formed in ratio ~ 2.5/1; minor regio-isomer:

benzene ring as well as different aryl-, heteroaryl-, diaryl-, and arylalkylacetylenes readily underwent these reactions. Arylacetylenes with substituents at the *ortho*-, *meta*-, and *para*-positions as well as with electron-donor or electron-withdrawing groups in the aromatic ring can be used in these reactions. In the case of arylacetylenes containing electron-withdrawing groups, yields of the products obtained are lower. It should be noted that all tested compounds come into these reactions. The reaction regioselectivity proved to be very high in the case of *meta*-substituted ACDC or nonsymmetric acetylenes. Only one isomer was formed in both cases (for the explanations, see the mechanistic part below). ACDC with high electron-rich aryl substituents (e.g., *p*-methoxyphenyl substituted cyclopropane-1,1-dicarboxylate) cannot be efficiently introduced into these reactions. This is due to the bad generation of corresponding 1,2-zwitterions from the starting cyclopropanes, what has been described in our previous works.[5a,8]

Alkynes with aliphatic substituents also enter these reactions, though much worse. For example, naphthalenes **5af**, **5ef**, **5ag**, **5ah**, and **5ff** are formed, but their yields are low (Scheme 3). The corresponding dihydronaphthalenes **4** could not be isolated at all because their transformation occurs more rapidly than their formation. Nevertheless, corresponding dihydronaphthalenes were fixed by NMR spectroscopy at low temperatures. By changing the process conditions toward a higher ACDC excess at reduced temperatures, we managed to trap dihydronaphthalene, which is formed in the reaction of **2a** with 1-octyne, by entering it into formal [3 + 2] cycloaddition to the double bond with excess of cyclopropane **2a** (Scheme 4a). As a result, polycyclic compound **6** was obtained as a single diastereomer in 35% yield.

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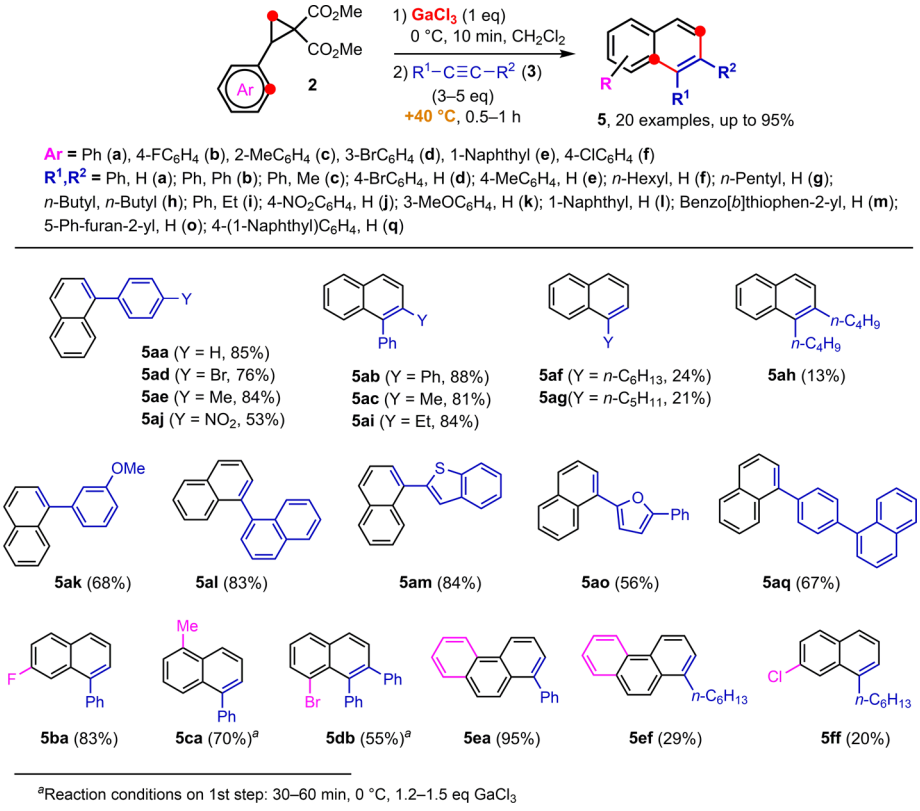
Scheme 3. Scope of the Reactions for Naphthalenes 5



In turn, for naphthylcyclopropanedicarboxylate **2e**, we selectively performed a coupling of two phenylacetylene **3a** molecules with one ACDC molecule (Scheme 4c). In this case, the main core of compound **8** is formed by [4 + 2] annulation/fragmentation type followed by alkylation of the aromatic ring by a second phenylacetylene molecule. A similar process for dihydronaphthalene occurs in the case of benzo[*b*]thiophen-2-yl substituent (**3m**) (Scheme 4d). In this case, the second molecule of acetylene is attached to the benzo[*b*]thiophene ring system from first acetylene with formation of complex compound **9**. A very interesting process is realized if *para*-nitrophenylacetylene **3j** is used in great excess (Scheme 4e). It is a rare example of [4 + 2 + 2] annulation with formation of an 8-member ring (cyclooctatriene) as a part of 5,6-dihydrobenzo[8]annulene cyclic system. Herewith, two molecules of acetylene incorporated into cyclic system and formed the product **10** with moderate yield.

The reaction of [4 + 2] annulation of ACDC can proceed with diacetylenes. Thus, diacetylene **3p** reacts with ACDC **2a** to form 1,4-bis(dihydronaphthyl)benzene **11** at −60 °C or 1,4-dinaphthylbenzene **5aq** at 40 °C (Scheme 5). This process requires the use of excess of cyclopropane **2a** to reduce the formation of monoadduct **4ap** (Scheme 2). We showed that the compound **11** under the action of gallium trichloride at 40 °C easily transformed into the compound **5aq** in a high yield. At intermediate conditions (between −60 and 40 °C), the product of monocleavage **4aq** can be identified in low yield (~3%). Compounds **4aq** and **5aq** are also independently prepared starting from 1-(4-ethynylphenyl)naphthalene **3q** (Schemes 2 and 3).

In general, the mechanism of the discovered reactions of ACDC with acetylenes agrees with the concept of the mechanism reported previously.[4,5a,8] Generation of 1,2-zwitterion **1** under the effect of $GaCl_3$ is the key stage. The latter adds to the acetylene molecule at the triple bond to give a cation which subsequently undergoes cyclization at the aromatic ring (Scheme 6). Fragmentation of dihydronaphthalene **4** to naphthalene **5** under the effect of $GaCl_3$ apparently occurs by the mechanism considered previously.[7] It was confirmed by independent conversion of **4a** to **5a**. Only one regio-isomer was formed in both cases (**4** and **5**). This occurs due to the significantly higher stabilization of the carbonium ion by the aryl substituent in the corresponding acyclic intermediate (Scheme 6). The formation of a minor regioisomer was detected in only one case (**4ao**). The determination of the position of the aryl substituent in the final product is easy, routine, and based on analysis of H−H spin systems by conventional NMR spectra.

The dihydronaphthylmalonates obtained contain functional groups and multiple bonds that can be easily modified (Scheme 7). For example, the malonyl moiety in compound **4aa** can be reduced to a 1,3-diol **12** or subjected to monodecarboxylation **13**. The carboxy group can be hydrolyzed to an acid **14**. The dihydronaphthalene moiety is readily oxidized to a naphthalene one (**15**) or converted to **5aa** upon elimination of a malonyl moiety. The double bond in dihydronaphthalenes can enter cycloaddition, e.g., with a 1,3-zwitterion generated from ACDC to give compounds **16** or **17**, depending on the conditions.

The aromatization process with elimination of dimethylmalonate by the action of $GaCl_3$ is typical for other substituted dihydronaphthylmalonates **4**. Herewith, the yields of corresponding naphthalenes **5** come near to quantitative (Scheme 8).

The structure and configuration of the compounds obtained were uniquely determined by ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy. A full set of modern 2D NMR experiments

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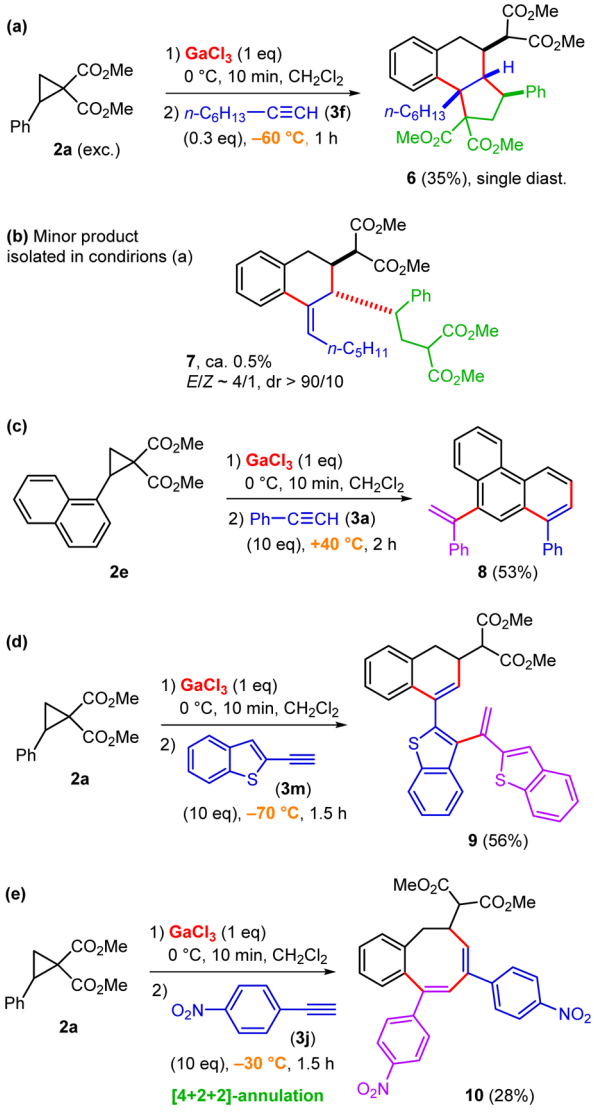
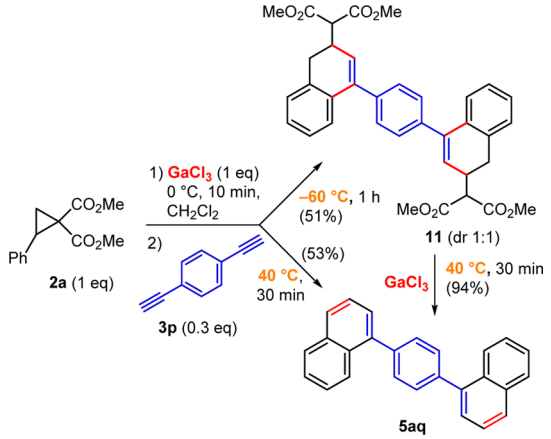
Scheme 4. Other Cascade Processes of ACDC with Acetylenes

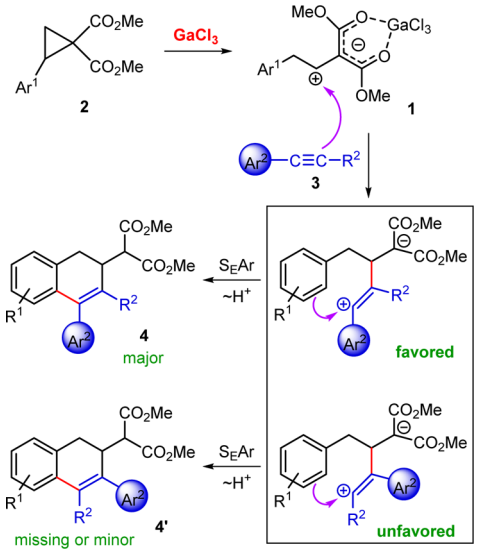


Scheme 5. Reaction of 2a with Diacetylene 3p

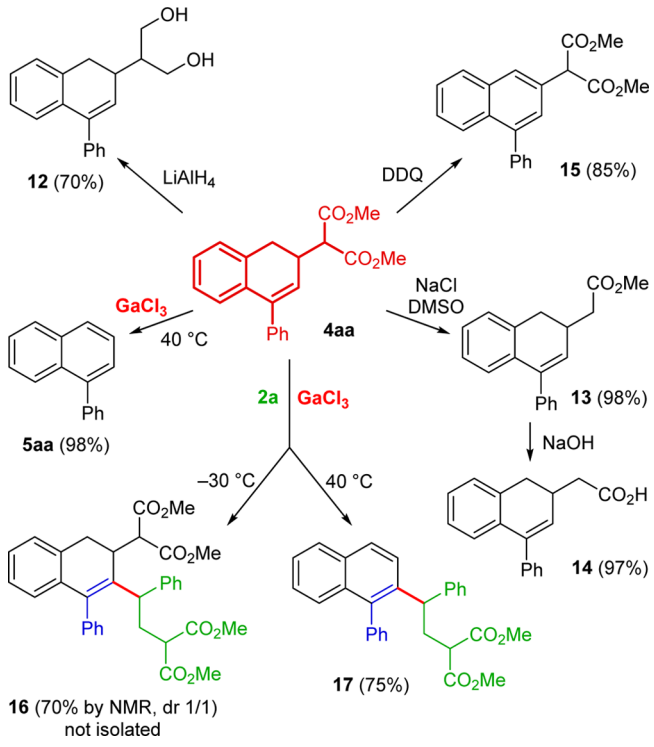


such as COSY, NOESY, HSQC, HSQC-COSY, HSQC-TOCSY, HMBC, H2BC, etc., was used. For compound **4ab**, X-ray analysis was carried out (Supporting Information).

Scheme 6. Proposed Mechanism



Scheme 7. Examples of Transformations of 4aa



CONCLUSION

We developed a new class of ACDC reactions with acetylenes based on [4 + 2] annulation to give a dihydronaphthalene core. A number of related processes based on this reaction were developed. They involve elimination of a malonyl moiety and addition of a second ACDC or acetylene molecule to give a naphthalene structure or more complex carbocyclic structures. The methodology that we developed has a powerful synthetic potential and allows one to assemble complex polyheterocyclic structures with high regio- and diastereoselectivity in one synthetic stage from simple starting compounds.

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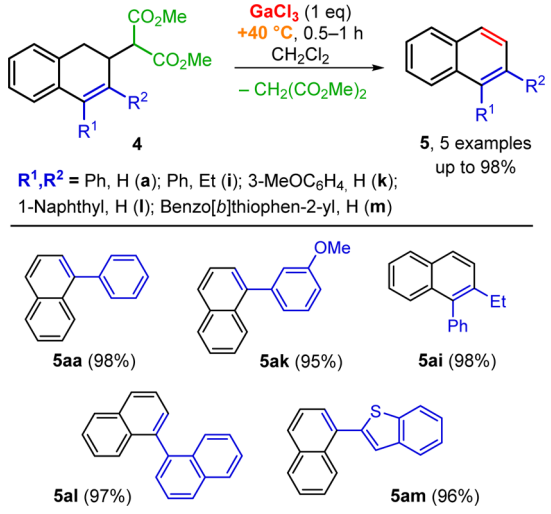
Scheme 8. Examples of Aromatization of Dihydronaphthalenes 4 in Naphthalenes 5



EXPERIMENTAL SECTION

General Experimental Details. All reagents and solvents used were commercial grade chemicals without additional purification. All operations with $GaCl_3$ were carried out under dry argon atmosphere. TLC analysis was performed on Silufol chromatographic plates. For preparative chromatography, silica gel 60 (0.040–0.063 mm) was used. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a 400 MHz (400.1 and 100.6 MHz, respectively) and 300 MHz (300.1 and 75.5 MHz, respectively) spectrometers in $CDCl_3$ containing 0.05% Me_4Si as the internal standard. Determinations of structures and stereochemistry of obtained compounds and assignments of ^1H and ^{13}C signals were made with the aid of 1D and 2D DEPT, JMOD, COSY, TOCSY, NOESY, XHCORR, HSQC, HSQC-COSY, HSQC-TOCSY, HMBC, CT-HMBC, and H2BC spectra. ^{19}F NMR spectra were recorded on a 300 MHz spectrometer (282.4 MHz) with the standard $CFCl_3$; determinations of structures and assignments of ^{19}F signals were made with the aid of 2D ^1H,^{19}F HMQC and HMBC spectra. IR spectra were obtained on an FT-IR spectrometer in $CHCl_3$ solution (1.5%). Mass spectra were recorded using electron impact ionization (EI, 70 eV, direct inlet probe). High resolution mass spectra were obtained using simultaneous electospray (ESI TOF). The elemental compositions were determined on a CHN analyzer instrument. The melting points were determined on Kofler hot-stage microscope.

X-ray Diffraction Experiments. XRD experiments were carried out with a SMART APEX II CCD diffractometer using graphite monochromatic Mo Kα radiation (l = 0.71073 Å, ω-scans) at 120 K. Single crystals of $C_{27}H_{24}O_4$ are triclinic, space group P-1: a = 9.1127(7) Å, b = 11.0557(9) Å, c = 12.2422(9) Å; α = 115.584(2)°, β = 100.509(2)°, γ = 94.304(2)°, V = 1077.20(14) Å^3, Z = 2, M = 412.46, d_{calc} = 1.272 g·cm^{-3}. The structures were solved by direct method and refined by the full-matrix least-squares method on F^2 in anisotropic approximation for nonhydrogen atoms. Hydrogen atom positions were calculated and included in the refinement within the riding model. The 5720 independent reflections (R_{int} = 0.0441) were used in the refinement procedure that was converged to wR_2 = 0.1318 calculated on F^2_{hkl} (GOF = 1.090, R_1 = 0.0589 calculated on F_{hkl} using 4244 reflections with $I > 2\sigma(I)$). Crystal data and structure refinement parameters for the structure **4ab** can be retrieved free of charge from www.ccdc.cam.ac.uk/conts/retrieving.html (CCDC 1490361). All calculations were performed using the SHELXTL software.[18a]

*Synthesis of Starting Cyclopropanes **2a–e**.* Starting cyclopropanes **2a–e** (ACDC) were synthesized from the corresponding aromatic aldehydes through a standard synthetic sequence of Knoevenagel/Corey–Chaykovsky reactions.

*Optimization of the Reaction of DAC **2a** with Alkyne **3a**.* All operations were performed under a dry argon atmosphere. A solution of ACDC **2a** (100 mg, 0.43 mmol) in dry CH_2Cl_2 (4 mL) was cooled at 0 °C; solid $GaCl_3$ (79 mg, 0.45 mmol) was added in one portion, and the reaction mixture was stirred at the same temperature for 10 min. Then, a solution of alkyne **3a** (219 mg, 2.15 mmol) in dry CH_2Cl_2 (1 mL) was added, and the reaction mixture was heated or cooled to the set temperature and stirred for the necessary time (Table 1). After that, an aqueous solution of HCl (5%) was added until pH 3 was achieved, and the reaction mixture was extracted with CH_2Cl_2 (3 × 10 mL). The organic layer was dried over $MgSO_4$, and the solvent was removed in vacuo. The NMR spectra were acquired from the residue for calculation of the product ratio. If it was necessary, the residue was purified by column chromatography on silica gel (benzene:EtOAc, 100:1 to 10:1) to afford title dihydronaphthalenes **4a** and **5a** as thick colorless oils.

*Synthetic Procedure and Spectroscopic Data for Dihydronaphthalenylmalonates **4**.* All operations were performed under a dry argon atmosphere. To a solution of ACDC **2** (1 equiv) in dry CH_2Cl_2 (3–5 mL), a solid $GaCl_3$ (1 equiv) was added in one portion at 0 °C, and the mixture was stirred at the same temperature until a generation of 1,2-zwitterion **1** was completed (optimal conditions: 1 equiv $GaCl_3$, 10–13 min for cyclopropanes **2a–c** and **e**; 1.1 equiv $GaCl_3$, 20–25 min for cyclopropane **2d**). Then, the reaction mixture was cooled to −70 °C, and a solution of alkyne **3** (5 equiv) in dry CH_2Cl_2 (1–2 mL) was added. The reaction mixture was stirred for 1 h; then, an aqueous solution of HCl (5%) was added until pH 3 was achieved, and the mixture was extracted with CH_2Cl_2 (3 × 10 mL). The organic layer was dried over $MgSO_4$, and the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel (benzene:EtOAc, 50:1 to 10:1) to afford dihydronaphthalenes **4** as thick colorless oils. If it is necessary, the resulting compounds can be additionally purified on a silufol chromatographic plate (20 × 20 cm) eluting with hexane:acetone 5:1 or benzene:EtOAc 10:1 to afford the pure products.

*2-(1,3-Dimethoxy-1,3-dioxopropan-2-yl)-4-phenyl-1,2-dihydronaphthalene (**4aa**).* The title compound was prepared according to the general procedure from ACDC **2a** (164 mg, 0.7 mmol), $GaCl_3$ (123 mg, 0.7 mmol), and alkyne **3a** (357 mg, 3.5 mmol) in 186 mg yield (79%). Colorless thick oil. IR ($CHCl_3$) $\tilde{\nu}$ 3037, 3011, 2955, 1733 br (C=O), 1600, 1493, 1436, 1355, 1236, 1157 cm^{-1}. MS (EI) (m/z, %) 336 (2, M$^+$), 276 (2), 244 (6), 215 (15), 205 (65), 204 (100), 202 (20), 190 (6), 189 (7), 178 (5), 165 (4), 127 (5). HRMS (ESI) calcd for $C_{21}H_{20}O_4$: M + Na, 359.1254. Found: m/z 359.1242. ^1H NMR ($CDCl_3$, 400.1 MHz) δ 2.80 (dd, 1H, *anti*-H(1), ^2J = 15.4 Hz, ^3J = 7.7 Hz), 3.04 (dd, 1H, *syn*-H(1), ^2J = 15.4 Hz, ^3J = 6.2 Hz), 3.31 (dddd, 1H, H(2), ^3J = 9.5, 7.6, 6.3, and 4.6 Hz), 3.47 (d, 1H, H(2″), ^3J = 9.6 Hz), 3.73 and 3.74 (both s, 2 × 3H, 2 OMe), 5.97 (d, 1H, H(3), ^3J = 4.7 Hz), 6.99 (br.d, 1H, H(5), ^3J = 7.5 Hz), 7.09–7.15 (m, 1H, H(6)), 7.16 (m, 1H, H(8)), 7.17 (m, 1H, H(7)), 7.28–7.32 (m, 2H, 2 *o*-H), 7.33 (m, 1H, *p*-H), 7.34–7.39 (m, 2H, 2 *m*-H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz) δ 32.3 (CH_2(1)), 33.9 (CH(2)), 52.54 and 52.56 (2 OMe), 54.2 (CH(2″)), 125.9 (CH(5)), 126.7 (CH(6)), 127.4(C(3)), 127.5 (*p*-CH), 127.6 (CH(7)),128.3 (3C, CH(8) and 2 *m*-CH), 128.8 (2 *o*-CH), 134.2 (C(4a)), 134.5 (C(8a)), 140.1 (*i*-C), 141.2 (C(4)), 168.74 and 168.78 (2 COO) ppm.

*2-(1,3-Dimethoxy-1,3-dioxopropan-2-yl)-3,4-diphenyl-1,2-dihydronaphthalene (**4ab**).* The title compound was prepared according to the general procedure from ACDC **2a** (234 mg, 1 mmol), $GaCl_3$ (176 mg, 1 mmol), and alkyne **3b** (891 mg, 5 mmol) in 260 mg yield (63%). Colorless powder, mp 110–111 °C. IR ($CHCl_3$) $\tilde{\nu}$ 3036, 3012, 2954, 1731 (C=O), 1600, 1488, 1450, 1437, 1277, 1234, 1198, 1163, 1030, 795, 715, 701, 667 cm^{-1}. MS (EI) (m/z, %) 412 (7, M$^+$), 352 (2), 294 (9), 291 (10), 281 (52), 280 (100), 265 (19), 252 (11), 215 (16), 203 (17), 202 (15), 149 (31), 132 (6), 112 (12), 97 (21), 85 (91), 77 (23), 69 (16), 55 (19). HRMS (ESI) calcd for $C_{27}H_{24}O_4$: M + Na, 435.1567; M + K, 451.1306. Found: m/z 435.1547, 451.1292. ^1H NMR ($CDCl_3$, 400.1 MHz) δ 3.26 (dd, 1H, *anti*-H(1), ^2J = 16.4 Hz, ^3J = 2.8 Hz), 3.3 and 3.4 (both s, 2 × 3H, 2 OMe), 3.45 (dd, 1H, *syn*-H(1), ^2J = 16.5 Hz, ^3J = 7.4 Hz), 3.54 (d, 1H, H(2″), ^3J = 7.2 Hz), 3.68 (ddd, 1H, H(2), ^3J = 7.3 and 2.9 Hz), 6.89 (br.d, 1H, H(5), ^3J = 7.5 Hz), 6.99–7.05 (m, 1H, H(6)), 7.05–7.07 (m, 1H, H(8)), 7.09

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(m, 5H), 7.11−7.17 (m, 3H), 7.17−7.22 (m, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz) δ 32.2 (CH_2(1)), 39.1 (CH(2)), 52.10 (2 OMe), 52.16 (CH(2″)), 126.3 (CH(5)), 126.5, 126.57, 126.6, 127.4, 127.8, and 128.2 (6 CH), 127.4 and 130.7 (2 × 3 CH), 132.9, 135.1, 136.7, 138.2, 138.7, and 140.7 (5 C), 168.6 and 168.7 (2 COO) ppm.

*2-(1,3-Dimethoxy-1,3-dioxopropan-2-yl)-6-fluoro-4-phenyl-1,2-dihydronaphthalene (**4ba**).* The title compound was prepared according to the general procedure from ACDC **2b** (252 mg, 1 mmol), $GaCl_3$ (176 mg, 1 mmol), and alkyne **3a** (511 mg, 5 mmol) in 290 mg yield (82%). Colorless thick oil. IR ($CHCl_3$) $\tilde{\nu}$ 3036, 3012, 2956, 1734 (C═O), 1609, 1579, 1490, 1436, 1235, 1196, 1159, 676 cm^{-1}. MS (EI) (*m*/*z*, %) 354 (1, M^+), 294 (2), 262 (7), 235 (16), 233 (23), 223 (58), 222 (100), 220 (23), 203 (23), 202 (19), 196 (5), 183 (5), 146 (2), 133 (6), 59 (7). HRMS (ESI) calcd for $C_{21}H_{19}FO_4$: M + Na, 377.1160. Found: *m*/*z* 377.1148. ^1H NMR ($CDCl_3$, 400.1 MHz) δ 2.76 (dd, 1H, *anti*-H(1), ^2J = 15.3 Hz, ^3J = 7.8 Hz), 2.99 (dd, 1H, *syn*-H(1), ^2J = 15.3 Hz, ^3J = 6.1 Hz), 3.31 (dddd, 1H, H(2), ^3J = 9.5, 7.8, 6.1, and 4.7 Hz), 3.45 (d, 1H, H(2″), ^3J = 9.5 Hz), 3.74 and 3.75 (both s, 2 × 3H, 2 OMe), 6.04 (d, 1H, H(3), ^3J = 4.7 Hz), 6.72 (dd, 1H, H(5), ^4J = 2.6 Hz, $^3J_{HF}$ = 10.2 Hz), 6.87 (dt, 1H, H(7), ^3J = 8.4 Hz, ^4J = 2.6 Hz, $^3J_{HF}$ = 8.4 Hz), 7.12 (dd, 1H, H(8), ^3J = 8.3 Hz, $^4J_{HF}$ = 5.7 Hz), 7.27−7.30 (m, 2H, 2 *o*-H), 7.33−7.41 (m, 3H, 2 *m*-H and *p*-H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz) δ 31.4 (CH_2(1)), 34.0 (CH(2)), 52.60 and 52.62 (2 OMe), 54.12 (CH(2″)), 112.9 (d, CH(7), $^2J_{CF}$ = 23.2 Hz), 114.0 (d, CH(5), $^2J_{CF}$ = 21.4 Hz), 127.8 (CH(3)), 128.5 (2 *m*-CH), 128.6 (*p*-CH), 128.7 (2 *o*-CH), 129.4 (d, CH(8), $^3J_{CF}$ = 7.9 Hz), 129.9 (d, C(4), $^4J_{CF}$ = 3.0 Hz), 136.0 (d, C(4a), $^3J_{CF}$ = 7.6 Hz), 139.4 (*i*-C), 140.6 (d, C(8a), $^4J_{CF}$ = 2.2 Hz), 161.8 (d, C(6), $^1J_{CF}$ = 243.1 Hz), 168.63 and 168.68 (2 COO) ppm. ^{19}F NMR ($CDCl_3$, 282.4 MHz) δ −116.4 (ddd, 1F, $^3J_{HF}$ = 10.2 and 8.4 Hz, $^4J_{HF}$ = 5.9 Hz) ppm.

*2-(1,3-Dimethoxy-1,3-dioxopropan-2-yl)-8-methyl-4-phenyl-1,2-dihydronaphthalene (**4ca**).* The title compound was prepared according to the general procedure (reaction time on first step 30−60 min) from ACDC **2c** (199 mg, 0.8 mmol), $GaCl_3$ (211 mg, 1.2 mmol), and alkyne **3a** (408 mg, 4 mmol) in 202 mg yield (72%). Colorless thick oil. IR ($CHCl_3$) $\tilde{\nu}$ 3034, 3013, 2955, 1733 br (C═O), 1493, 1436, 1335, 1275, 1235, 1197, 1159, 1088, 1027, 803, 784, 744, 669 cm^{-1}. MS (EI) (*m*/*z*, %) 350 (2, M^+), 290 (2), 258 (2), 219 (55), 218 (100), 204 (23), 203 (25), 202 (19), 189 (6), 178 (5), 165 (6), 115 (11), 105 (17), 91 (9), 77 (13), 69 (15), 59 (19). HRMS (ESI) calcd for $C_{22}H_{22}O_4$: M + Na, 373.1410. Found: *m*/*z* 373.1405. ^1H NMR ($CDCl_3$, 400.1 MHz) δ 2.30 (s, 3H, Me), 2.83 (dd, 1H, *anti*-H(1), ^2J = 15.8 Hz, ^3J = 6.8 Hz), 2.94 (dd, 1H, *syn*-H(1), ^2J = 15.9 Hz, ^3J = 6.3 Hz), 3.29 (dddd, 1H, H(2), ^3J = 9.5, 6.8, 6.3, and 5.0 Hz), 3.45 (d, 1H, H(2″), ^3J = 9.5 Hz), 3.72 and 3.73 (both s, 2 × 3H, 2 OMe), 5.99 (d, 1H, H(3) ^3J = 5.0 Hz), 6.84 (br.d, 1H, H(5), ^3J = 7.4 Hz), 7.01 (t, 1H, H(6), ^3J = 7.6 Hz), 7.06 (br.d, 1H, H(7), ^3J = 7.5 Hz), 7.26−7.30 (m, 2H, 2 *o*-H), 7.30−7.39 (m, 3H, *p*-H and 2 *m*-H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz) δ 19.6 (CH_3), 27.8 (CH_2(1)), 33.7 (CH(2)), 52.4 and 52.5 (2 OMe), 54.1 (CH(2″)), 124.0 (CH), 125.8 (CH), 126.9 (CH), 127.3(CH), 128.1 (2 *o*-CH), 128.9 (2 *m*-CH), 129.7 (CH), 132.6 (C(8)), 134.0 (C(4a)), 135.4 (C(8a)), 140.5 (*i*-C), 141.5 (C(4)), 168.7 and 168.9 (2 COO) ppm.

*2-(1,3-Dimethoxy-1,3-dioxopropan-2-yl)-3-methyl-4-phenyl-1,2-dihydronaphthalene (**4ac**).* The title compound was prepared according to the general procedure from ACDC **2a** (234 mg, 1 mmol), $GaCl_3$ (176 mg, 1 mmol), and alkyne **3c** (581 mg, 5 mmol) in 263 mg yield (75%). Colorless thick oil. IR ($CHCl_3$) $\tilde{\nu}$ 3034, 3012, 2954, 1732 (C═O), 1599, 1486, 1452, 1436, 1341, 1278, 1251, 1197 cm^{-1}. MS (EI) (*m*/*z*, %) 350 (4, M^+), 290 (1), 258 (2), 231 (3), 218 (100), 215 (20), 204 (25), 203 (27), 202 (22), 189 (4), 178 (3), 165 (2), 141 (4), 115 (6), 100 (5), 69 (5), 59 (8). HRMS (ESI) calcd for $C_{22}H_{22}O_4$: M + Na, 373.1410; M + K, 389.1150. Found: *m*/*z* 373.1395, 389.1148. ^1H NMR ($CDCl_3$, 400.1 MHz) δ 1.7 (s, 3H, Me), 2.9 (dd, 1H, *anti*-H(1), ^2J = 16.0 Hz, ^3J = 1.6 Hz), 3.13 (ddd, 1H, H(2), ^3J = 8.6, 6.3, and 1.7 Hz), 3.29 (dd, 1H, *syn*-H(1), ^2J = 15.9 Hz, ^3J = 6.3 Hz), 3.5 (d, 1H, H(2″), ^3J = 8.8 Hz), 3.5 and 3.7 (both s, 2 × 3H, 2 OMe), 5.97 (d, 1H, H(3) ^3J = 4.7 Hz), 6.6 (br.d, 1H, H(5), ^3J = 7.5 Hz), 6.99−7.09 (m, 1H, H(6)), 7.11 (dd, 2H, ^3J = 5.0 Hz, ^4J = 1.1 Hz), 7.31−7.39 (m, 1H), 7.39−7.47 (m, 2H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz) δ 20.9 (CH_3), 32.2 (CH_2(1)), 39.6 (CH(2)), 51.7 (CH(2″)), 52.2 and 52.3 (2 OMe), 125.7 (CH(5)), 126.5 (2C, CH(6) and CH(7)), 126.6 (*p*-CH), 126.8 (2 *m*-CH), 128.0 (CH(8)), 128.4 (2 *o*-CH), 132.35 (C(3)), 132.3 (C(8a)), 135.9 (C(4a)), 136.6 (C(4)), 139.6 (*i*-C), 168.8 and 169.24 (2 COO) ppm.

*2-(1,3-Dimethoxy-1,3-dioxopropan-2-yl)-4-(4-bromophenyl)-1,2-dihydronaphthalene (**4ad**).* The title compound was prepared according to the general procedure from ACDC **2a** (234 mg, 1 mmol), $GaCl_3$ (176 mg, 1 mmol), and alkyne **3d** (905 mg, 5 mmol) in 240 mg yield (58%). Colorless thick oil. IR ($CHCl_3$) $\tilde{\nu}$ 3031, 3015, 2955, 1733 br (C═O), 1487, 1436, 1334, 1291, 1235, 1196, 1157, 1012, 824, 802, 763, 669 cm^{-1}. MS (EI) (*m*/*z*, %) 416 and 414 (1, M^+), 356 and 354 (1), 284 and 282 (36), 215 (53), 204 and 202 (100), 189 (15), 178 and 176 (5), 165 (6), 115 (11), 107 (10), 100 (23), 69 (45), 59 (64). HRMS (ESI) calcd for $C_{21}H_{19}BrO_4$: M + Na, 437.0359. Found: *m*/*z* 437.0361. ^1H NMR ($CDCl_3$, 400.1 MHz) δ 2.79 (dd, 1H, *anti*-H(1), ^2J = 15.5 Hz, ^3J = 7.8 Hz), 3.02 (dd, 1H, *syn*-H(1), ^2J = 15.5 Hz, ^3J = 6.1 Hz), 3.30 (dddd, 1H, H(2), ^3J = 9.5, 7.9, 6.2, and 4.8 Hz), 3.46 (d, 1H, H(2″), ^3J = 9.4 Hz), 3.73 and 3.74 (both s, 2 × 3H, 2 OMe), 5.97 (d, 1H, H(3), ^3J = 4.7 Hz), 6.95 (br.d, 1H, H(5), ^3J = 7.5 Hz), 7.09−7.15 (m, 1H, H(6)), 7.16−7.22 (m, 4H, H(7)), H(8), and 2 *o*-H), 7.46−7.52 (m, 2H, 2 *m*-H,^3J = 8.4 Hz) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz) δ 32.2 (CH_2(1)), 33.9 (CH(2)), 52.5 and 52.6 (2 OMe), 54.1 (CH(2″)), 121.5 (*p*-C), 125.6 (CH(5)), 126.8 (CH(6)), 127.9 (C(3) and C(8)), 128.4 (CH(7)), 130.5 (2 *o*-CH), 131.5 (2 *m*-CH), 133.7 (C(4a)), 134.5 (C(8a)), 139.0 (*i*-C), 140.2 (C(4)), 168.6 and 168.7 (2 COO) ppm.

*2-(1,3-Dimethoxy-1,3-dioxopropan-2-yl)-7-bromo-3-methyl-4-phenyl-1,2-dihydronaphthalene (**4dc**).* The title compound was prepared according to the general procedure (reaction time on first step ∼30 min) from ACDC **2d** (313 mg, 1 mmol), $GaCl_3$ (220 mg, 1.25 mmol), and alkyne **3c** (581 mg, 5 mmol) in 241 mg yield (56%). Colorless thick oil. IR ($CHCl_3$) $\tilde{\nu}$ 3036, 3012, 2954, 1732 (C═O), 1589, 1478, 1436, 1340, 1280, 1248, 1235, 1196, 1165, 1027, 806, 736, 699, 679 cm^{-1}. MS (EI) (*m*/*z*, %) 430 and 428 (18, M^+), 370 and 368 (10), 298 and 296 (69), 281 (16), 218 (100), 202 and 204 (11), 189 (10), 115 (11), 83 (24), 59 (8). HRMS (ESI) calcd for $C_{22}H_{21}BrO_4$: M + Na, 451.0515 and 453.0496. Found: *m*/*z* 451.0515 and 453.0495. ^1H NMR ($CDCl_3$, 400.1 MHz) δ 1.68 (s, 3H, Me), 2.87 (dd, 1H, *anti*-H(1), ^2J = 16.1 Hz, ^3J = 1.5 Hz), 3.13 (ddd, 1H, H(2), ^3J = 8.5, 6.6, and 1.6 Hz), 3.23 (dd, 1H, *syn*-H(1), ^2J = 16.1 Hz, ^3J = 6.4 Hz), 3.47 (d, 1H, H(2″), ^3J = 8.6 Hz), 3.5 and 3.7 (both s, 2 × 3H, 2 OMe), 6.43 (d, 1H, H(5), ^3J = 8.3 Hz), 7.13 (dd, 1H, ^3J = 8.3 Hz, ^4J = 1.2 Hz), 7.21−7.24 (m, 2H), 7.29−7.36 (m, 2H), 7.36−7.45 (m, 2H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz) δ 21.0 (CH_3), 31.9 (CH_2(1)), 39.4 (CH(2)), 51.7 (CH(2″)), 52.4 and 52.5 (2 OMe), 120.3 (C(7)), 127.1, 129.6, and 130.8 (3 CH), 127.3 (2 CH), 128.6 (3 CH), 133.1, 134.7, 134.9, 135.9, and 139.1 (5 C), 168.6 and 169.0 (2 COO) ppm.

*2-(1,3-Dimethoxy-1,3-dioxopropan-2-yl)-4-phenyl-1,2-dihydrophenanthrene (**4ea**).* The title compound was prepared according to the general procedure from ACDC 2e (227 mg, 0.8 mmol), $GaCl_3$ (141 mg, 0.8 mmol), and alkyne **3a** (408 mg, 4 mmol) in 170 mg yield (55%). Colorless thick oil. IR ($CHCl_3$) $\tilde{\nu}$ 3035, 3011, 2956, 2256, 1733 br (C═O), 1600, 1511, 1436, 1338, 1235, 1196, 1159, 1028, 820, 701, 674 cm^{-1}. MS (EI) (*m*/*z*, %) 386 (5, M^+), 321 (1), 297 (3), 265 (10), 254 (100), 253 (24), 239 (18), 226 (2), 215 (1), 189 (3), 178 (4), 149 (6), 141 (12), 133 (6), 115 (3), 69 (3), 59 (8). HRMS (ESI) calcd for $C_{25}H_{22}O_4$: M + Na, 409.1410. Found: *m*/*z* 409.1399. ^1H NMR ($CDCl_3$, 400.1 MHz) δ 3.37 (m, 2H, H(1), ^3J = 5.5 Hz), 3.39−3.49 (m, 1H, H(2), ^3J = 8.9, 5.4, and 4.4 Hz), 3.51 (d, 1H, H(2″), ^3J = 8.9 Hz), 3.69 and 3.73 (both s, 2 × 3H, 2 OMe), 6.12 (d, 1H, H(3) ^3J = 4.4 Hz), 7.18 (br.d, 1H, H(5), ^3J = 8.6 Hz), 7.28−7.41 (m, 5H), 7.41−7.58 (m, 2H, H(8) and H(9), ^3J = 8.4, 7.9, and 1.1 Hz), 7.62 (d, 1H, H(6), ^3J = 8.6 Hz), 7.80 (d, 1H, H(7), ^3J = 7.9 Hz), 8.06 (d, 1H, H(10), ^3J = 8.4 Hz) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz) δ 27.1 (CH_2(1)), 33.7 (CH(2)), 52.50 and 52.55 (2 OMe), 53.9 (CH(2″)), 123.7 (CH(10)), 124.4 (CH(5)), 125.6 (CH(8)), 126.31 (CH(9)), 126.38 (CH(6)), 127.2 (CH(3)), 127.5 (*p*-CH), 128.3 (2C, 2 *m*-CH), 128.6 (CH(7)), 128.8 (2 *o*-CH), 130.1

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(C(10b)), 131.3 (C(4a)), 131.6 (C(10a)), 133.3 (C(6a)), 140.4 (*i*-C), 141.8 (C(4)), 168.80 and 168.87 (2 COO) ppm.

*2-(1,3-Dimethoxy-1,3-dioxopropan-2-yl)-3-ethyl-4-phenyl-1,2-dihydronaphthalene (**4ai**).* The title compound was prepared according to the general procedure (reaction time 1−1.5 h) from ACDC **2a** (234 mg, 1 mmol), $GaCl_3$ (176 mg, 1 mmol), and alkyne **3i** (650 mg, 5 mmol) in 291 mg yield (80%). Colorless thick oil. IR ($CHCl_3$) $\tilde{\nu}$ = 3061, 3036, 3011, 2969, 2955, 2935, 2874, 2846, 1749, 1732, 1599, 1493, 1486, 1452, 1436, 1342, 1282, 1250, 1235 cm^{-1}. MS (EI) (*m*/*z*, %) 232 (100), 217 (18), 205 (20), 84 (10). HRMS (ESI) calcd for $C_{23}H_{25}O_4$: M + H, 365.1747. Found: *m*/*z* 365.1739. ^1H NMR ($CDCl_3$, 300.1 MHz) δ 0.98 (t, 3H, Me, ^3J = 7.5 Hz), 1.71 (dq, 1H, CH_2(Et)-a, ^2J = 13.4 Hz, ^3J = 7.5 Hz), 2.24 (dq, 1H, CH_2(Et)-b, ^2J = 13.4 Hz, ^3J = 7.5 Hz), 2.97 (br. d, 1H, H(1)-a, ^2J = 15.5 Hz), 3.17−3.36 (m, 2H, H(1)-b and H(2)), 3.51 (d, 1H, H(2′), ^3J = 8.8 Hz), 3.60 and 3.74 (both s, 2 × 3H, 2 OMe), 6.58 (br. d, 1H, H(5), ^3J = 7.3 Hz), 6.99−7.10 (m, 1H, H(5)), 7.04−7.41 (br. m, 2H, 2 *o*-H), 7.09−7.15 (m, 2H, H(6) and H(7)), 7.32−7.55 (br.m, 2H, 2 *m*-H), 7.33−7.39 (m, 1H, *p*-H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz) δ 14.3 (Me), 26.5 (CH_2(Et)), 33.0 (CH_2(1)), 35.8 (CH(2)), 51.8 (CH(2′)), 52.3 and 52.4 (2 OMe), 125.9 (CH(5)), 126.6 (CH(6)), 126.7 (CH(7) or CH(8)), 126.8 (*i*-CH), 128.1 (CH(7) or CH(8)), 128.4 (br., 2 *m*-CH), 129.5 and 130.3 (both br., 2 *o*-CH), 132.4, 136.0, 136.1, 139.1, and 139.5 (5 C(Ar)), 168.9 and 169.3 (2 COO) ppm.

*2-(1,3-Dimethoxy-1,3-dioxopropan-2-yl)-4-(4-nitrophenyl)-1,2-dihydronaphthalene (**4aj**).* The title compound was prepared according to the general procedure (temperature −30 °C, reaction time 1.5 h) from ACDC **2a** (150 mg, 0.64 mmol), $GaCl_3$ (113 mg, 0.64 mmol), and alkyne **3j** (282 mg, 1.92 mmol, 3 equiv) in 100 mg yield with ∼85% purity (35%). Colorless thick oil. IR ($CHCl_3$) $\tilde{\nu}$ = 3686, 3533, 3203, 3167, 3084, 3037, 3010, 2941, 2627, 2451, 2420, 2293, 2255, 2206, 2065, 1616, 1485, 1439, 1373, 1238 cm^{-1}. MS (EI) (*m*/*z*, %) 249 (80), 232 (27), 215 (29), 202 (33), 189 (9), 165 (10), 155 (7), 145 (25), 132 (20), 59 (100). HRMS (ESI) calcd for $C_{21}H_{19}NNaO_6$: M + Na, 404.1105. Found: *m*/*z* 404.1098. ^1H NMR ($CDCl_3$, 400.1 MHz) δ 2.81 (dd, 1H, H(1)-a, ^2J = 15.5 Hz, ^3J = 8.0 Hz), 3.03 (dd, 1H, H(1)-b, ^2J = 15.5 Hz, ^3J = 6.2 Hz), 3.34 (dddd, 1H, H(2), ^3J = 9.2, 8.0, 6.2, and 4.6 Hz), 3.34 (d, 1H, H(2′), ^3J = 9.2 Hz), 3.73 and 3.75 (both s, 2 × 3H, 2 OMe), 6.10 (d, 1H, H(3), ^3J = 4.6 Hz), 6.80−7.01 and 7.10−7.26 (both m, 2 × 2H, H(5)−H(8)), 7.44−7.52 (m, 2H, 2 *o*-H), 8.19−8.27 (m, 2H, 2 *m*-H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz) δ 32.2 (CH_2(1)), 34.0 (CH(2)), 52.68 and 52.70 (2 OMe), 54.1 (CH(2′)), 123.7 (2 *o*-CH), 125.5, 127.0, 128.4, 128.6, and 129.9 (CH(3) and CH(5)−CH(8)), 129.7 (2 *m*-CH), 132.7, 133.2, 134.6, 139.6, and 147.0 (5 C(Ar)), 168.6 (2 COO) ppm.

*2-(1,3-Dimethoxy-1,3-dioxopropan-2-yl)-4-(3-methoxyphenyl)-1,2-dihydronaphthalene (**4ak**).* The title compound was prepared according to the general procedure from ACDC **2a** (234 mg, 1.0 mmol), $GaCl_3$ (176 mg, 1.0 mmol), and alkyne **3k** (660 mg, 5.0 mmol) in 304 mg yield (83%). Neutral Al_2O_3 was used as a sorbent for column chromatography for isolation of the product. Colorless thick oil. IR ($CHCl_3$) $\tilde{\nu}$ = 3687, 3672, 3534, 3203, 3167, 3082, 3037, 3011, 2941, 2839, 2627, 2451, 2420, 2293, 2255, 2206, 2065, 1828, 1751, 1733, 1485, 1437, 1373, 1239 cm^{-1}. MS (EI) (*m*/*z*, %) 366 (7, M^+), 234 (100), 203 (11). HRMS (ESI) calcd for $C_{22}H_{23}O_5$: M + H, 367.1572. Found: *m*/*z* 367.1572. ^1H NMR ($CDCl_3$, 400.1 MHz) δ 2.82 (dd, 1H, H(1)-a, ^2J = 15.4 Hz, ^3J = 7.7 Hz), 3.06 (dd, 1H, H(1)-b, ^2J = 15.4 Hz, ^3J = 6.1 Hz), 3.34 (dddd, 1H, H(2), ^3J = 9.6, 7.7, 6.1, and 4.7 Hz), 3.49 (d, 1H, H(2′), ^3J = 9.6 Hz), 3.76 and 3.77 (both s, 2 × 3H, 2 CO_2Me), 3.83 (s, 2H, OMe), 6.00 (d, 1H, H(3), ^3J = 4.7 Hz), 6.85−6.96 (m, 3H, H(3″), H(4″) and H(6″)), 7.05 (br. d, 1H, H(5), ^3J = 7.3 Hz), 7.11−7.25 (m, 3H, H(6)−H(8)), 7.21 (t, 1H, H(5″), ^3J = 7.8 Hz) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz) δ 32.2 (CH_2(1)), 33.9 (CH(2)), 52.5 (2 CO_2Me), 54.1 (CH(2′)), 55.3 (OMe), 113.0 (CH(4″)), 114.4 (CH(2″)), 121.3 CH(6″)), 125.9 (CH(5)), 126.7 (CH(6)), 127.4 (CH(4)), 127.6 and 128.2 (CH(7) and CH(8)), 129.3 (CH(5″)), 134.1, 134.4, 141.0, and 141.5 (C(4), C(4a), C(8a) and C(1″)), 159.5 (C(3″)), 168.64 and 168.69 (2 COO) ppm.

*2-(1,3-Dimethoxy-1,3-dioxopropan-2-yl)-4-(1-naphthyl)-1,2-dihydronaphthalene (**4al**).* The title compound was prepared according to the general procedure from ACDC **2a** (200 mg, 0.85 mmol), $GaCl_3$ (150 mg, 0.85 mmol), and alkyne **3l** (646 mg, 4.25 mmol) in 258 mg yield (79%). Compound **4al** exists in $CDCl_3$ solution as a mixture of 2 rotamers in ∼1/1 ratio in equilibrium with each other (naphthyl substituent is directed up and down to malonyl fragment due to the hindered rotation around the C−C bond). Colorless thick oil. IR ($CHCl_3$) $\tilde{\nu}$ = 3061, 3031, 3021, 2955, 2891, 2847, 1752, 1733, 1592, 1507, 1486, 1451, 1436, 1397, 1338, 1280, 1234 cm^{-1}. MS (EI) (*m*/*z*, %) 386 (9, M^+), 265 (17), 254 (100), 239 (21). HRMS (ESI) calcd for $C_{25}H_{22}NaO_4$: M + Na, 409.1410. Found: *m*/*z* 409.1419. ^1H NMR ($CDCl_3$, 300.1 MHz) (2 rotamers) δ 2.91−3.06 (m, 2H, 2 H(1)), 3.16 (dd, 1H, H(1), ^2J = 15.5 Hz, ^3J = 6.3 Hz), 3.33 (dd, 1H, H(1), ^2J = 15.7 Hz, ^3J = 6.4 Hz), 3.39−3.53 (m, 2H, 2 H(2)), 3.56 (d, 1H, H(2″), ^3J = 9.5 Hz), 3.69 (d, 1H, H(2″), ^3J = 9.3 Hz), 3.73, 3.75, 3.77, and 3.80 (all s, 4 × 3H, 4 OMe), 6.00 (d, 1H, H(3), ^3J = 4.1 Hz), 6.09 (d, 1H, H(3), ^3J = 5.0 Hz), 6.52−6.61 (m, 2H, Ar), 6.94−7.03 (m, 2H, Ar), 7.12−7.20 (m, 2H, Ar), 7.20−7.26 (m, 2H, Ar), 7.31−7.42 (m, 4H, Ar), 7.42−7.57 (m, 4H, Ar), 7.64 (br. d, 1H, Ar, ^3J = 8.3 Hz), 7.76 (br. d, 1H, Ar, ^3J = 8.5 Hz), 7.84−7.94 (m, 4H, Ar) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz) (2 rotamers) δ 32.1 and 32.2 (2 CH_2(1)), 33.4 and 34.4 (2 CH(2)), 52.47, 52.50, 52.53, and 52.56 (4 OMe), 53.9 and 54.5 (2 CH(2″)), 125.5, 125.6, 125.76 (2C), 125.86 (3C), 125.92, 126.1, 126.3, 126.8 (2C), 127.0, 127.3, 127.6, 127.7, 127.8, 128.0, 128.1, 128.2 (2C), 128.3 (22 CH(Ar)), 128.7 and 129.1 (2 CH(3)), 132.0, 132.3, 133.0, 133.53, 133.58, 133.60, 134.7, 135.0, 137.85, 137.92, 139.6, and 140.2 (12 C(Ar)), 168.7 and 169.0 (both 2C, 4 COO) ppm.

*2-(1,3-Dimethoxy-1,3-dioxopropan-2-yl)-4-(benzo[b]thiophen-2-yl)-1,2-dihydronaphthalene (**4am**).* The title compound was prepared according to the general procedure from ACDC **2a** (200 mg, 0.85 mmol), $GaCl_3$ (150 mg, 0.85 mmol), and alkyne **3m** (537 mg, 3.4 mmol) in 303 mg yield (91%). Colorless thick oil. IR ($CHCl_3$) $\tilde{\nu}$ = 3060, 3028, 3014, 2955, 2891, 2846, 1751, 1734, 1486, 1452, 1436, 1333, 1303, 1290, 1279, 1249, 1235 cm^{-1}. MS (EI) (*m*/*z*, %) 392 (18, M^+), 271 (15), 261 (100), 228 (9). HRMS (ESI) calcd for $C_{23}H_{20}NaO_4S$: M + Na, 415.0975. Found: *m*/*z* 415.0961. ^1H NMR ($CDCl_3$, 300.1 MHz) δ 2.84 (dd, 1H, H(1)-a, ^2J = 15.4 Hz, ^3J = 7.9 Hz), 3.07 (dd, 1H, H(1)-a, ^2J = 15.4 Hz, ^3J = 6.0 Hz), 3.37 (dddd, 1H, H(2), ^3J = 9.5, 7.9, 6.0, and 4.7 Hz), 3.52 (d, 1H, H(2″), ^3J = 9.5 Hz), 3.794 and 3.797 (both s, 2 × 3H, 2 OMe), 6.34 (d, 1H, H(3), ^3J = 4.7 Hz), 7.19−7.32 (m, 3H, H(6)−H(8)), 7.33 (s, 1H, H(3′)), 7.32−7.43 (m, 2H, H(5′) and H(6′)), 7.44−7.53 (m, 1H, H(5)), 7.74−7.81 (m, 1H, H(4′)), 7.81−7.88 (m, 1H, H(7′)) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz) δ 32.0 (CH_2(1)), 34.0 (CH(2)), 52.6 (2 OMe), 53.8 (CH(2″)), 122.1 (CH(7′)), 122.8 (CH(3′)), 123.5 (CH(4′)), 124.36 (CH(6′)), 124.39 (CH(5′)), 125.8 (CH(5)), 126.9 and 128.1 (CH(6) and CH(7)), 128.4 (CH(8)), 130.1 (CH(3)), 133.1 (C(4a)), 134.40 and 134.43 (C(4) and C(8a)), 139.4 (C(7a′)), 140.0 (C(3a′)), 142.1 (C(2′)), 168.6 (2 COO) ppm.

*2-(1,3-Dimethoxy-1,3-dioxopropan-2-yl)-4-(5-methylfuran-2-yl)-1,2-dihydronaphthalene (**4an**).* The reaction was carried out in excess of cyclopropane. The title compound was prepared according to the general procedure from ACDC **2a** (150 mg, 0.64 mmol), $GaCl_3$ (113 mg, 0.64 mmol), and alkyne **3n** (34 mg, 0.32 mmol, 0.5 equiv) addition to the reaction mixture (∼80% yield of **3n** by ^1H NMR and 2D TOCSY spectra). The attempts of isolation of target product failed because compound **4an** fully decomposes during chromatography on SiO_2 and Al_2O_3 (neutral). ^1H NMR ($CDCl_3$, 300.1 MHz) (key signals) δ 2.36 (br. s, 3H, Me), 2.73 (dd, 1H, H(1)-a, ^2J = 15.5 Hz, ^3J = 7.1 Hz), 2.96 (dd, 1H, H(1)-b, ^2J = 15.5 Hz, ^3J = 4.4 Hz), 3.30 (dddd, 1H, H(2), ^3J = 9.6, 7.1, 4.5, and 4.4 Hz), 3.45 (d, 1H, H(2″), ^3J = 9.6 Hz), 6.03−6.07 and 6.36−6.40 (both m, 2H, H(3′) and H(4′)), 6.38 (d, 1H, H(3), ^3J = 4.5 Hz) ppm. Other signals are overlapped.

*2-(1,3-Dimethoxy-1,3-dioxopropan-2-yl)-4-(5-phenylfuran-2-yl)-1,2-dihydronaphthalene (**4ao**).* The reaction was carried out in excess of cyclopropane. The title compound was prepared according to the general procedure from ACDC **2a** (150 mg, 0.64 mmol), $GaCl_3$ (113 mg, 0.64 mmol), and alkyne **3o** (54 mg, 0.32 mmol, 0.5 equiv) in 64 mg yield (50%) (yield by ^1H NMR in reaction mixture is ∼85% on 3o). Neutral Al_2O_3 was used as a sorbent for column chromatography

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for isolation. Product partially decomposes during chromatography. Compound **4ao** was isolated as a mixture of two regioisomers (on acetylene fragment) in the ratio ~2.5:1. Colorless thick oil. IR ($CHCl_3$) $\tilde{\nu}$ = 3066, 3038, 3010, 2955, 2848, 1951, 1733, 1606, 1485, 1449, 1437, 1376, 1336, 1283, 1241 cm^{-1}. MS (EI) (*m*/*z*, %) 436 (11, M^+), 402 (65), 304 (11), 271 (100), 170(23). HRMS (ESI) calcd for $C_{25}H_{22}NaO_5$: M + Na, 425.1359. Found: *m*/*z* 425.1371. Major isomer. ^1H NMR ($CDCl_3$, 400.1 MHz) δ 2.78 (dd, 1H, H(1)-a, ^2J = 15.3 Hz, ^3J = 8.0 Hz), 3.01 (dd, 1H, H(1)-b, ^2J = 15.3 Hz, ^3J = 5.8 Hz), 3.36 (dddd, 1H, H(2), ^3J = 9.7, 8.0, 5.8, and 4.9 Hz), 3.49 (d, 1H, H(2″), ^3J = 9.7 Hz), 3.788 and 3.790 (both s, 2 × 3H, 2 OMe), 6.51 (d, 1H, H(3), ^3J = 4.9 Hz), 6.59 (br. d, 1H, H(3′) or H(4′), ^3J = 3.4 Hz), 6.74 (br. d, 1H, H(3′) or H(4′), ^3J = 3.4 Hz), 7.19−7.33 (m, 4H, H(5)−H(8)), 7.37−7.46 (m, 2H, 2 *m*-H (Ph)), 7.56−7.64 (m, 1H, *p*-H (Ph)), 7.69−7.75 (m, 2H, 2 *o*-H (Ph)) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz) δ 32.2 (CH_2(1)), 33.8 (CH(2)), 52.6 (2 OMe), 54.0 (CH(2″)), 106.6 and 110.6 (CH(3′) and CH(4′)), 123.9 (2 *o*-CH), 125.5, 126.8, 126.9, 127.5, 127.9, and 128.5 (CH(3), CH(5)−CH(8) and *p*-CH), 128.8 (2 *m*-CH), 130.5, 130.8, 131.9, and 134.9 (C(4), C(4a), C(8a) and *i*-C), 151.9 and 153.3 (C(1′) and C(5′)), 168.7 (2 COO) ppm. Minor isomer (2-(1,3-Dimethoxy-1,3-dioxopropan-2-yl)-3-(5-phenylfuran-2-yl)-1,2-dihydronaphthalene). ^1H NMR ($CDCl_3$, 400.1 MHz) δ 3.08 (dd, 1H, *anti*-H(1), ^2J = 15.7 Hz, ^3J = 1.6 Hz), 3.42−3.60 (m, 2H, H(1)-b and H(2)), 3.63 (d, 1H, H(2″), ^3J = 7.6 Hz), 3.51 and 3.81 (both s, 2 × 3H, 2 OMe), 6.74 (br. d, 1H, H(3′) or H(4′), ^3J = 3.4 Hz), 6.81 (br. d, 1H, H(3′) or H(4′), ^3J = 3.4 Hz), 7.07−7.33 (m, 5H, H(4) and H(5)−H(8)), 7.35−7.43 (m, 2H, 2 *m*-H (Ph)), 7.56−7.64 (m, 1H, *p*-H (Ph)), 7.67−7.72 (m, 2H, 2 *o*-H (Ph)) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz) δ 32.4 (CH_2(1)), 42.6 (CH(2)), 51.2 (CH(2″)), 52.8 (2 OMe), 106.2 and 115.2 (CH(3′) and CH(4′)), 124.0 (2 *o*-CH), 126.5, 127.1, 127.6, 128.2, 128.5, and 128.8 (CH(4), CH(5)−CH(8) and *p*-CH), 128.8 (2 *m*-CH), 130.7, 132.0, 132.4, and 134.9 (C(3), C(4a), C(8a) and *i*-C), 148.1 and 157.1 (C(1′) and C(5′)), 168.7 (2 COO) ppm.

*2-(1,3-Dimethoxy-1,3-dioxopropan-2-yl)-4-(4-ethynylphenyl)-1,2-dihydronaphthalene (**4ap**).* The title compound was prepared according to the general procedure from ACDC **2a** (100 mg, 0.43 mmol), $GaCl_3$ (76 mg, 0.43 mmol), and alkyne **3p** (271 mg, 2.15 mmol) in 87 mg yield with ~80% purity (45%). Colorless thick oil. IR ($CHCl_3$) $\tilde{\nu}$ = 3303, 3033, 3012, 2956, 2848, 2108, 1732, 1684, 1604, 1505, 1437, 1402, 1233 cm^{-1}. MS (EI) (*m*/*z*, %) 256 (30), 239 and 229 (100), 215 (58), 188 (15). HRMS (ESI) calcd for $C_{23}H_{20}NaO_4$: M + Na, 383.1254. Found: *m*/*z* 383.1262. ^1H NMR ($CDCl_3$, 300.1 MHz) δ 2.81 (dd, 1H, H(1)-a, ^2J = 15.4 Hz, ^3J = 7.7 Hz), 3.05 (dd, 1H, H(1)-b, ^2J = 15.4 Hz, ^3J = 6.2 Hz), 3.13 (s, 1H, ≡CH), 3.33 (dddd, 1H, H(2), ^3J = 9.4, 7.7, 6.2, and 4.7 Hz), 3.49 (d, 1H, H(2″), ^3J = 9.4 Hz), 3.76 and 3.77 (both s, 2 × 3H, 2 OMe), 6.02 (d, 1H, H(3), ^3J = 4.7 Hz), 6.99 (br.d, 1H, H(5), ^3J = 7.4 Hz), 7.08−7.62 (m, 7H, Ar) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz) δ 32.2 (CH_2(1)), 33.8 (CH(2)), 52.51 and 52.53 (2 OMe), 54.1 (CH(2″)), 78.1 (≡CH), 79.6 (≡C), 125.7, 126.7, 127.8, 128.0, and 128.3 (CH(3) and CH(5)−CH(8)), 128.7 and 132.0 (2 *o*-CH and 2 *m*-CH), 133.7, 134.5, 140.5, 140.6, and 149.0 (5 C(Ar)), 168.60 and 168.63 (2 COO) ppm.

*2-(1,3-Dimethoxy-1,3-dioxopropan-2-yl)-4-(4-(1-naphthyl)-phenyl)-1,2-dihydronaphthalene (**4aq**).* The title compound was prepared according to the general procedure from ACDC **2a** (100 mg, 0.43 mmol), $GaCl_3$ (76 mg, 0.43 mmol), and alkyne **3q** (195 mg, 0.86 mmol) in 128 mg yield (65%). Colorless thick oil. IR ($CHCl_3$) $\tilde{\nu}$ 3032, 3011, 2956, 1734 (C═O), 1599, 1509, 1436, 1335 cm^{-1}. HRMS (ESI) calcd for $C_{31}H_{26}NaO_4$: M + Na, 485.1723. Found: *m*/*z* 485.1730. ^1H NMR ($CDCl_3$, 300.1 MHz) δ 2.87 (dd, 1H, H(1)-a, ^2J = 15.4 Hz, ^3J = 7.7 Hz), 3.11 (dd, 1H, H(1)-b, ^2J = 15.4 Hz, ^3J = 6.1 Hz), 3.39 (dddd, 1H, H(2), ^3J = 9.6, 7.7, 6.1, and 4.6 Hz), 3.54 (d, 1H, H(2″), ^3J = 9.6 Hz), 3.79 and 3.80 (both s, 2 × 3H, 2 OMe), 6.13 (d, 1H, H(3), ^3J = 4.6 Hz), 7.18−7.27 (m, 4H, H(5)−H(8)), 7.43−7.61 (m, 8H, 2 *o*-H, 2 *m*-H, H(2′), H(3′), H(6′) and H(7′)), 7.87−7.93, 7.93−7.98 and 7.98−8.05 (all m, 3 × 1H, H(4′), H(5′) and H(8′)) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz) δ 32.4 (CH_2(1)), 34.1 (CH(2)), 52.6 (2 OMe), 54.3 (CH(2″)), 125.5, 125.9, and 126.1 (CH(3′), CH(6′) and CH(7′)), 126.0, 126.8, 127.8, and 128.4 (CH(5)−CH(8)), 126.1, 127.8, and 128.4 (CH(4′), CH(5′) and CH(8′)), 127.0 (CH(2′)), 127.7 (CH(3)), 128.8 and 130.1 (2 *o*-CH and 2 *m*-CH), 131.7, 134.0, 134.2, 134.7, 139.0, 140.1 (2C) and 141.0 (8 C(Ar)), 168.78 and 168.82 (2 COO) ppm.

*Synthetic Procedure and Spectroscopic Data for Naphthalenes **5**.* All operations were performed under a dry argon atmosphere. To a solution of ACDC **2** (1 equiv) in dry CH_2Cl_2 (3−5 mL) was added solid $GaCl_3$ (1 equiv) in one portion at 0 °C, and the mixture was stirred at the same temperature for 10−30 min until a generation of 1,2-zwitterion **1** was completed (optimal conditions: 1 equiv $GaCl_3$, 10−13 min for cyclopropanes **2a−c** and **e**; 1.1 equiv $GaCl_3$, 20−25 min for cyclopropane **2d**). Then, the solution of alkyne **3** (5 equiv) in dry CH_2Cl_2 (1−2 mL) was added at 0 °C, and the reaction mixture was immediately heated to 40 °C and refluxed for 1 h. An aqueous solution of HCl (5%) was added at room temperature until pH 3 was achieved, and the reaction mixture was extracted with CH_2Cl_2 (3 × 10 mL). The organic layer was dried over $MgSO_4$, and the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel (hexane, hexane:acetone, 50:1 to 10:1) to afford naphthalenes **5** as a thick colorless oils. If necessary, the resulting compounds can be additionally purified on a silufol chromatographic plate (20 × 20 cm) eluting with hexane:acetone 5:1 to afford the pure products.

*1-Phenylnaphthalene (**5aa**).* The title compound was prepared according to the general procedure from ACDC **2a** (117 mg, 0.5 mmol), $GaCl_3$ (88 mg, 0.5 mmol), and alkyne **3a** (255 mg, 2.5 mmol) in 87 mg yield (85%). Yellow thick oil. IR ($CHCl_3$) $\tilde{\nu}$ 3062, 3012, 2927, 1592, 1508, 1495, 1447, 1396, 1020, 806, 769, 747, 701, 675, 570 cm^{-1}. MS (EI) (*m*/*z*, %) 204 (100, M^+), 189 (2), 176 (3), 150 (4), 101 (34), 94 (3), 89 (10), 76 (6), 69 (3), 63 (7), 57 (3), 51 (8), 39 (8). ^1H NMR ($CDCl_3$, 400.1 MHz) δ 7.37−7.43 (m, 3H), 7.43−7.52 (m, 6H), 7.83 (d, 1H,^3J = 8.2 Hz), 7.87 (d, 1H, ^3J = 4.7 Hz), 7.89 (dd, 1H, ^3J = 4.7 Hz, ^4J = 0.8 Hz,) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz) δ 125.4, 125.8, 126.0, 126.1, 126.9, 127.3, and 127.7 (7 CH), 128.3 and 130.1 (2 × 2 CH), 131.7, 133.9, 140.3, and 140.8 (4 C). NMR data were consistent with those reported in the literature.[18b]

*1,2-Diphenylnaphthalene (**5ab**).* The title compound was prepared according to the general procedure from ACDC **2a** (200 mg, 0.85 mmol), $GaCl_3$ (150 mg, 0.85 mmol), and alkyne **3b** (761 mg, 4.27 mmol) in 209 mg yield (88%). Colorless powder, mp 110−111 °C. IR ($CHCl_3$) $\tilde{\nu}$ 3060, 3011, 1731, 1601, 1495, 1445, 1380, 1250, 1029, 825, 715, 699, 590 cm^{-1}. MS (EI) (*m*/*z*, %) 280 (100, M^+), 265 (13), 252 (12), 239 (7), 226 (6), 214 (6), 202 (9), 190 (2), 177 (2), 164 (2), 150 (2), 138 (3), 126 (3), 113 (3). Calcd for $C_{22}H_{16}$: C 94.25; H 5.75. Found: C 94.14; H 5.76. ^1H NMR ($CDCl_3$, 400.1 MHz) δ 7.08−7.20 (m, 7H), 7.21−7.30(m, 3H), 7.37 (ddd, 1H, H(7), ^3J = 8.2 and 6.9 Hz, ^4J = 1.3 Hz), 7.45 (ddd, 1H, H(6), ^3J = 8.0 and 6.8, ^4J = 1.2 Hz), 7.55 (d, 1H, H(3), ^3J = 8.5 Hz), 7.66 (d, 1H, H(8), ^3J = 8.3 Hz), 7.88 (d, 1H, H(5), ^3J = 8.1 Hz), 7.89 (d, 1H, H(4), ^3J = 8.4 Hz) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz) δ 125.7 (CH(6)), 126.26 (*p*-CH), 126.29 (CH(7)), 126.7 (*p*-CH), 126.9 (CH(8)), 127.6 (3C, CH(4) and 2 *o*-CH), 127.8 (2 *o*-CH), 127.9 (CH(5)), 128.3 (CH(3)), 130.2 (2 *m*-CH), 131.5 (2 *m*-CH), 132.7 (C(8a)), 132.8 (C(4a)), 137.7 (C(1)), 138.4 (C(2)), 139.1 (*i*-C) and 142.1 (*i*′-C) ppm. NMR data were consistent with those reported in the literature.[18c]

*7-Fluoro-1-phenylnaphthalene (**5ba**).* The title compound was prepared according to the general procedure from ACDC **2b** (164 mg, 0.65 mmol), $GaCl_3$ (114 mg, 0.65 mmol), and alkyne **3a** (332 mg, 3.25 mmol) in 120 mg yield (83%). Colorless oil. IR ($CHCl_3$) $\tilde{\nu}$ 3060, 3012, 1738, 1631, 1596, 1514, 1496, 1457, 1367, 1246, 1198, 1162, 979, 907, 876, 832, 804, 766, 677, 616, 567, 437 cm^{-1}. MS (EI) (*m*/*z*, %) 222 (100), 207 (2), 202 (10), 110 (8), 18 (7). Calcd for $C_{16}H_{11}F$: C 86.46; H 4.99. Found: C 86.41; H 4.98. ^1H NMR ($CDCl_3$, 400.1 MHz) δ 7.26 (ddd, 1H, H(6), ^3J = 8.4 Hz, ^4J = 2.6 Hz, $^3J_{HF}$ = 8.2 Hz), 7.40−7.51 (m, 7H), 7.51 (dd, 1H, H(8), ^4J = 2.6 Hz, $^3J_{HF}$ = 11.3 Hz), 7.83 (br.d, 1H, ^3J = 7.8 Hz), 7.87 (dd, 1H, H(5), ^3J = 8.4 Hz, $^4J_{HF}$ = 6.0 Hz) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz) δ 109.5 (d, HC(8), $^2J_{CF}$ = 21.9 Hz), 116.2 (d, HC(6), $^2J_{CF}$ = 25.2 Hz), 124.7 (d, HC(2),

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$^5J_{CF}$ = 2.3 Hz), 127.5 (HC(3) and HC(4)), 127.8 (*p*-CH), 128.5 (2 *o*-CH), 129.9 (2 *m*-CH), 130.7 (d, HC(5), $^3J_{CF}$ = 9.0 Hz), 130.9 (C(8a)), 132.6 (d, C(4a), $^3J_{CF}$ = 8.8 Hz), 139.9 (d, C(1), $^3J_{CF}$ = 5.5 Hz), 140.3 (*i*-C), 161.0 (CF, $^1J_{CF}$ = 244 Hz) ppm. ^{19}F NMR ($CDCl_3$, 282.4 MHz): δ −114.5 (ddd, 1F, CF, $^3J_{HF}$= 8.2 and 11.3 Hz, $^4J_{HF}$= 6.0 Hz) ppm.

*5-Methyl-1-phenylnaphthalene (**5ca**).* The title compound was prepared according to the general procedure (reaction time on first step 30−60 min) from ACDC **2c** (174 mg, 0.7 mmol), $GaCl_3$ (184 mg, 1.05 mmol), and alkyne **3a** (357 mg, 3.5 mmol) in 106 mg yield (70%). Colorless oil. IR ($CHCl_3$) $\tilde{\nu}$ 3063, 3036, 3011, 2949, 1594, 1511, 1493, 1444, 1411, 1073, 1024, 770, 733, 699, 581 cm^{-1}. MS (EI) (*m*/*z*, %) 218 (100, M$^+$), 203 (88), 189 (19), 165 (12), 152 (9), 139 (14), 115 (19), 108 (56), 101 (84), 95 (55), 88 (23), 81 (13), 75 (18), 63 (36), 51 (39), 39 (40), 32 (17), 27 (30), 18 (19). Calcd for $C_{17}H_{14}$: C 93.54; H 6.46. Found: C 93.30; H 6.41. ^{1}H NMR ($CDCl_3$, 400.1 MHz) δ 2.73 (s, 3H, Me), 7.27−7.36 (m, 2H), 7.37−7.44 (m, 2H), 7.44−7.49 (m, 4H), 7.55 (dd, 1H, ^3J = 8.5 and 7.0 Hz), 7.74 (dd, 1H, ^3J = 7.1 Hz, ^4J = 1.6 Hz,), 8.01 (dt, 1H, ^3J = 8.4 Hz) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz) δ 19.9 (CH_3), 123.7, 124.6, 125.2, 125.6, 126.6, 126.7, and 127.2 (7 CH), 128.2 and 130.2 (2 × 2 CH), 131.8, 133.0, 134.5, 140.9, and 141.3 (5 C) ppm.

*2-Methyl-1-phenylnaphthalene (**5ac**).* The title compound was prepared according to the general procedure from ACDC **2a** (187 mg, 0.8 mmol), $GaCl_3$ (141 mg, 0.8 mmol), and alkyne **3c** (465 mg, 4 mmol) in 141 mg yield (81%). Colorless oil. IR ($CHCl_3$) $\tilde{\nu}$ 3058, 3016, 2924, 1600, 1509, 1494, 1442, 1381, 1231, 1200, 1086, 909, 814, 712, 672 cm^{-1}. MS (EI) (*m*/*z*, %) 218 (100, M$^+$), 203 (86), 189 (26), 176(7), 165 (13), 152 (9), 139 (23), 126 (7), 115 (48), 108 (48), 101 (67), 94 (40), 88 (18), 77 (17), 63 (26), 51 (25), 39 (18). ^{1}H NMR ($CDCl_3$, 400.1 MHz) δ 7.23−7.28 (m, 2H), 7.28−7.32 (m, 1H), 7.34−7.43 (m, 4H), 7.47 (ddd, 2H, ^3J = 7.5 and 4.5 Hz, ^4J = 1.3 Hz), 7.75 (d, 1H, ^3J = 8.4 Hz), 7.81 (d, 1H, ^3J = 8.0 Hz) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz) δ 20.8 (CH_3), 124.8, 125.8, 126.2, 127.0, 127.3, 127.8, and 128.6 (7 CH), 128.4 and 130.2 (2 × 2 CH), 132.0, 133.0, 133.1, 138.2, and 139.9 (5 C) ppm. NMR data were consistent with those reported in the literature.[18d]

*8-Bromo-1,2-diphenylnaphthalene (**5db**).* The title compound was prepared according to the general procedure (reaction time on first step ∼30 min) from ACDC **2d** (203 mg, 0.65 mmol), $GaCl_3$ (142 mg, 0.81 mmol), and alkyne **3b** (579 mg, 3.25 mmol) in 128 mg yield (55%). Colorless powder, mp 146−148 °C. IR ($CHCl_3$) $\tilde{\nu}$ 3059, 3011, 2929, 1735, 1600, 1491, 1444, 1351, 1185, 1128, 1074, 832, 763, 700, 638, 593 cm^{-1}. MS (EI) (*m*/*z*, %) 358 and 360 (14, M$^+$), 278 and 280 (100), 252 (6), 202 (14), 138 (19), 125 (6), 77 (10), 70 (17), 51 (6), 39 (5). Calcd for $C_{22}H_{15}Br$: C 73.55; H 4.21. Found: C 73.28; H 4.27. ^{1}H NMR ($CDCl_3$, 400.1 MHz) δ 6.98−7.03 (m, 2H), 7.06−7.09 (m, 2H), 7.1−7.19 (m, 6H), 7.28 (t, 1H, ^3J = 7.7 Hz), 7.51 (d, 1H, ^3J = 8.4 Hz), 7.81 (dd, 1H, ^3J = 7.5 Hz, ^4J = 1.2 Hz), 7.89 (d, 1H, ^3J = 7.5 Hz, ^4J = 1.2 Hz), 7.9 (d, 1H, ^3J = 8.3 Hz) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz) δ 126.0, 126.1, 126.7, 128.4, 128.7, 128.9, and 134.7 (7 CH), 126.9, 127.3, 139.9, and 132.4 (4 × 2 CH), 120.6, 135.3, 137.5, 139.7, 141.9, and 142.3 (6 C) ppm.

*1-(4-Methylphenyl)-naphthalene (**5ae**).* The title compound was prepared according to the general procedure from ACDC **2a** (234 mg, 1.0 mmol), $GaCl_3$ (176 mg, 1.0 mmol), and alkyne **3e** (581 mg, 5.0 mmol) in 183 mg yield (84%). Colorless powder, mp 51−52 °C. IR ($CHCl_3$) $\tilde{\nu}$ 3049, 3011, 2925, 1515, 1506, 1454, 1396, 1111, 1022, 823, 764, 670, 571 cm^{-1}. MS (EI) (*m*/*z*, %) 218 (100, M$^+$), 202 (73), 189 (13), 165 (7), 152 (7), 115 (11), 108 (29), 101 (33), 95 (29), 88 (9), 81 (5), 75 (9), 69 (6), 63 (18), 57 (16), 51 (16), 43 (17), 39 (29). ^{1}H NMR ($CDCl_3$, 400.1 MHz) δ 2.43 (s, 3H, Me), 7.27 (d, 2H, ^3J = 7.8 Hz), 7.35−7.42 (m, 4H), 7.42−7.52 (m, 2H), 7.81 (d, 1H, ^3J = 8.3 Hz), 7.87 (d, 1H, ^3J = 7.8 Hz), 7.91 (d, 1H, ^3J = 8.4 Hz) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz) δ 21.2 (CH_3), 125.4, 125.7, 125.9, 126.1, 126.9, 127.5, and 128.3 (7 CH), 129.0 and 130.0 (2 × 2 CH), 131.8, 133.9, 136.9, 137.9, and 140.3 (5 C) ppm. NMR data were consistent with those reported in the literature.[18b]

*1-(4-Bromophenyl)naphthalene (**5ad**).* The title compound was prepared according to the general procedure from ACDC **2a** (117 mg, 0.5 mmol), $GaCl_3$ (88 mg, 0.5 mmol), and alkyne **3d** (452 mg, 2.5 mmol) in 108 mg yield (76%). Yellow thick oil. IR ($CHCl_3$) $\tilde{\nu}$ 3063, 3016, 1594, 1509, 1488, 1396, 1336, 1073, 1012, 962, 836, 824, 802, 762, 748, 734, 675, 568, 557, 498 cm^{-1}. MS (EI) (*m*/*z*, %) 284 and 282 (39, M$^+$), 202 and 200 (100), 176 and 174 (11), 163 (7), 152 and 150 (17), 126 (11), 101 and 99 (100), 88 (36), 75 (18), 63 (11), 50 (15), 39 (7). Calcd for $C_{16}H_{11}Br$: C 67.87; H 3.92. Found: C 68.01; H 3.86. ^{1}H NMR ($CDCl_3$, 400.1 MHz) δ 7.31−7.38 (m, 3H), 7.38−7.52 (m, 3H), 7.63 (d, 2H, ^3J = 8.2 Hz), 7.79−7.92 (m, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz) δ 125.4, 125.7, 125.9, 126.3, 126.9, 128.1, and 128.4 (7 CH), 121.5, 131.4, 133.8, 139.0, and 139.7 (5 C), 131.5 and 131.7 (2 × 2 CH) ppm. NMR data were consistent with those reported in the literature.[18e]

*1-Phenylphenanthrene (**5ea**).* The title compound was prepared according to the general procedure from ACDC **2e** (284 mg, 1 mmol), $GaCl_3$ (176 mg, 1 mmol), and alkyne **3a** (511 mg, 5 mmol) in 241 mg yield (95%). Colorless oil. IR ($CHCl_3$) $\tilde{\nu}$ 3061, 3011, 2929, 1593, 1503, 1456, 1230, 1198, 1031, 868, 897 cm^{-1}. MS (EI) (*m*/*z*, %) 254 (100, M$^+$), 126 (31), 112 (14), 39 (3). ^{1}H NMR ($CDCl_3$, 400.1 MHz) δ 7.39−7.45 (m, 1H, *p*-CH), 7.46−7.5 (m, 4H, 2 *o*-CH and 2 *m*-CH), 7.52 (dd, 1H, CH(2), ^3J = 7.2 Hz, ^4J = 1.1 Hz), 7.54−7.6 (ddd, 1H, CH(7), ^3J = 7.8 and 7.0 Hz, ^4J = 1.2 Hz), 7.6−7.69 (m, 3H, CH(3), CH(6) and CH(9)), 7.79 (d, 1H, CH(10), ^3J = 9.2 Hz), 7.85 (dd, 1H, CH(8), ^3J = 7.8 Hz, ^4J = 1.3 Hz), 8.71 (d, 1H, CH(4), ^3J = 8.4 Hz), 8.72 (d, 1H, CH(5), ^3J = 8.2 Hz) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz) δ 122.1 (HC(4)), 123.0 (HC(5)), 124.6 (HC(10)), 126.0 (HC(3)), 126.69 (HC(6)), 126.73 (HC(7)), 126.9 (HC(9)), 127.2 (*p*-CH), 127.9 (HC(2)), 128.3 (2 *m*-CH), 128.5 (HC(8)), 130.2 (2 *o*-CH), 129.9, 130.4, 130.7, 131.7, 141.0, and 141.1 (6 C) ppm. NMR data were consistent with those reported in the literature.[18f]

*1-Hexylnaphthalene (**5af**).* The title compound was prepared according to the general procedure from ACDC **2a** (213 mg, 0.75 mmol), $GaCl_3$ (132 mg, 0.75 mmol), and alkyne **3f** (413 mg, 3.75 mmol) in 36 mg yield (24%). Colorless oil. IR ($CHCl_3$) $\tilde{\nu}$ 3065, 3010, 2958, 2930, 2858, 1596, 1510, 1467, 1395, 1379, 795, 757, 668 cm^{-1}. MS (EI) (*m*/*z*, %) 212 (21, M$^+$), 141 (100), 128 (6), 115 (26), 43 (5). ^{1}H NMR ($CDCl_3$, 400.1 MHz) δ 0.84−0.94 (m, 3H, CH_3(6′), ^3J = 7.5 Hz), 1.24−1.32 (m, 2H, CH_2(5′)), 1.32−1.38 (m, 2H, CH_2(4′)), 1.39−1.53 (m, 2H, CH_2(3′)), 1.69−1.79 (m, 2H, CH_2(2′), ^2J = 15.1 Hz, ^3J = 7.8, 6.9, and 6.0 Hz, ^4J = 1.8 Hz), 3.06 (m, 2H, CH_2(1′), ^3J = 7.8 Hz), 7.31 (br.d, 1H, CH(2), ^3J = 6.9 Hz), 7.38 (dd, 1H, CH(3), ^3J = 8.0 and 7.0 Hz), 7.42−7.52 (m, 2H, CH(6) and CH(7), ^3J = 8.3, 7.5, and 6.8 Hz, ^4J = 1.6 Hz), 7.69 (d, 1H, CH(4), ^3J = 8.1 Hz), 7.83 (dd, 1H, CH(5), ^3J = 7.7 Hz, ^4J = 1.7 Hz), 8.04 (d, 1H, CH(8), ^3J = 8.2 Hz) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz) δ 14.1 (CH_3(6′)), 22.7 (CH_2(5′)), 29.6 (CH_2(3′)), 30.9 (CH_2(2′)), 31.8 (CH_2(4′)), 33.2 (CH_2(1′)), 123.9 (CH(8)), 125.4 (CH(3)), 125.61 and 125.68 (CH(6) and CH(7)), 125.9 (CH(2)), 126.4 (CH(4)), 128.8 (CH(5)), 132.0, 134.0, and 139.1 (C(1), C(4a) and C(8a)) ppm. NMR data were consistent with those reported in the literature.[18g]

*1-Hexylphenanthrene (**5ef**).* The title compound was prepared according to the general procedure from ACDC **2e** (284 mg, 1 mmol), $GaCl_3$ (176 mg, 1 mmol), and alkyne **3f** (551 mg, 5 mmol) in 73 mg yield (29%). Colorless powder, mp 41−42 °C. IR ($CHCl_3$) $\tilde{\nu}$ 3061, 3049, 3012, 2958, 2931, 2872, 2858, 1599, 1458, 1135, 1114, 1086, 866, 807, 775, 666 cm^{-1}. MS (EI) (*m*/*z*, %) 262 (38, M$^+$), 214 (5), 203 (14), 191 (100), 178 (10), 165 (24), 152 (8), 41 (5). Calcd for $C_{20}H_{22}$: C 91.55; H 8.45. Found: C 91.46; H 8.43. ^{1}H NMR ($CDCl_3$, 400.1 MHz) δ 0.85−0.94 (m, 3H, CH_3(6′), ^3J = 7.1 Hz), 1.25−1.40 (m, 6H, CH_2(3′), CH_2(4′) and CH_2(5′)), 1.69−1.83 (m, 2H, CH_2(2′), ^2J = 15.2 Hz, ^3J = 7.7, 6.8, and 6.0 Hz, ^4J = 1.7 Hz), 3.1 (m, 2H, CH_2(1′), ^3J = 7.8 Hz), 7.43 (d, 1H, CH(2), ^3J = 6.9 Hz), 7.52−7.56 (m, 1H, CH(3), ^3J = 8.4 and 7.0 Hz), 7.57−7.59 (m, 1H, CH(7), ^3J = 7.8 and 7.0 Hz), 7.59−7.64 (m, 1H, CH(6), ^3J = 8.2 and 7.0 Hz, ^4J = 1.5 Hz), 7.75 (d, 1H, CH(9), ^3J = 9.2 Hz), 7.87 (dd, 1H, CH(8), ^3J = 7.8 Hz, ^4J = 1.5 Hz), 7.98 (d, 1H, CH(10), ^3J = 9.2 Hz), 8.57 (d, 1H, CH(4), ^3J = 8.4 Hz), 8.68 (d, 1H, CH(5), ^3J = 8.1 Hz) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz) δ 14.1 (CH_3(6′)), 22.7 (CH_2(5′)), 29.5

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(CH_2(3′)), 31.3 (CH_2(2′)), 31.8 (CH_2(4′)), 33.6 (CH_2(1′)), 120.9 (CH(4)), 122.7 (CH(10)), 123.0 (CH(5)), 126.2 (CH(3)), 126.4 (CH(7)), 126.5 (CH(6)), 126.6 (CH(9)), 127.1 (CH(2)), 128.4 (CH(8)), 130.2, 130.7, 130.9, 131.6, and 139.8 (5 C) ppm.

*2-Ethyl-1-phenylnaphthalene (**5ai**).* The title compound was prepared according to the general procedure from ACDC **2a** (234 mg, 1.00 mmol), $GaCl_3$ (176 mg, 1.00 mmol), and alkyne **3i** (520 mg, 4.00 mmol, 4 equiv) in 195 mg yield (84%). Colorless oil. ^{1}H NMR ($CDCl_3$, 300.1 MHz) δ 1.17 (t, 3H, Me, ^3J = 7.6 Hz), 2.59 (q, 2H, CH_2, ^3J = 7.6 Hz), 7.30−7.58 (m, 9H, 9 H(Ar)), 7.83−7.92 (m, 2H, 2 H(Ar)) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz) δ 16.0 (Me), 27.0 (CH_2), 124.8, 125.7, 126.4, 127.0, 127.2, 127.6, and 127.7 (7 CH(Ar)), 128.2 (2 *m*-CH), 130.3 (2 *o*-CH), 131.9, 133.1, 137.6, 139.4, and 139.6 (5 C(Ar)) ppm. NMR data were consistent with those reported in the literature.[19a]

*1-(4-Nitrophenyl)naphthalene (**5aj**).* The title compound was prepared according to the general procedure from ACDC **2a** (100 mg, 0.43 mmol), $GaCl_3$ (76 mg, 0.43 mmol), and alkyne **3j** (253 mg, 1.72 mmol, 4 equiv) in 56 mg yield (53%). Colorless oil. IR ($CHCl_3$) $\tilde{\nu}$ = 3299, 3064, 3048, 3023, 3016, 3010, 2928, 2856, 2456, 2286, 2116, 1931, 1820, 1734, 1691, 1599, 1521, 1493, 1458, 1397, 1349, 1310, 1286 cm^{-1}. MS (EI) (*m*/*z*, %) 249 (100, M$^+$), 202 (86), 189 (10), 101 (9). HRMS (ESI) calcd for $C_{16}H_{11}NNaO_2$: M + Na, 250.0863. Found: *m*/*z* 250.0867. ^{1}H NMR ($CDCl_3$, 400.1 MHz) δ 7.42 (dd, 1H, H(Ar), ^3J = 7.1 ^4J = 1.1 7.47 (ddd, 1H, H(Ar), ^3J = 8.2 and 6.8 ^4J = 1.4 7.77 (br. d, 1H, H(Ar), ^3J = 8.4 7.93 (br. d, 1H, H(Ar), ^3J = 8.2 7.94 (br. d, 1H, H(Ar), ^3J = 7.6 ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz) δ 123.7 and 131.0 (2 *o*-CH and 2 *m*-CH), 125.2, 125.4, 126.3, 126.8, 127.2, 128.7, and 129.1 (7 CH(Ar)), 133.1, 133.9, 137.9, 147.3, and 147.8 (5 C(Ar)) ppm. NMR data were consistent with those reported in the literature.[19b]

*1-(3-Methoxyphenyl)naphthalene (**5ak**).* The title compound was prepared according to the general procedure from ACDC **2a** (150 mg, 0.64 mmol), $GaCl_3$ (113 mg, 0.64 mmol), and alkyne **3k** (422 mg, 3.20 mmol, 5 equiv) in 102 mg yield (68%). Colorless oil. ^{1}H NMR ($CDCl_3$, 300.1 MHz) δ 3.89 (s, 3H, OMe), 7.01 (ddd, 1H, H(4′) or H(6′), ^3J = 8.2 Hz, ^4J = 2.5 and 1.0 Hz), 7.08 (dd, 1H, H(2′), ^4J = 2.5 and 1.4 Hz), 7.12 (ddd, 1H, H(4′) or H(6′), ^3J = 7.5 Hz, ^4J = 1.4 and 1.0 Hz), 7.39−7.56 (m, 3H, H(2), H(6) and H(7)), 7.43 (dd, 1H, H(5′), ^3J = 8.2 and 7.5 Hz), 7.55 (dd, 1H, H(3), ^3J = 8.0 and 7.1 Hz), 7.89 (br. d, 1H, H(4), ^3J = 8.0 Hz), 7.91−7.99 (m, 2H, H(5) and H(8)) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz) δ 55.3 (OMe), 112.9 (CH(4′) or CH(6′)), 115.6 (CH(2′)), 122.6 (CH(4′) or CH(6′)), 125.3 (CH(3)), 125.8, 126.02, 126.06, and 128.2 (CH(5)−CH(8)), 126.8 (CH(2)), 127.7 (CH(4)), 129.2 (CH(5′)), 131.6, 133.8, 140.1, and 142.2 (4 C(Ar)), 159.5 (C(3′)) ppm. NMR data were consistent with those reported in the literature.[19c]

*1,1′-Binaphthalene (**5al**).* The title compound was prepared according to the general procedure from ACDC **2a** (100 mg, 0.43 mmol), $GaCl_3$ (76 mg, 0.43 mmol), and alkyne **3l** (327 mg, 2.15 mmol, 5 equiv) in 90 mg yield (83%). Colorless oil. ^{1}H NMR ($CDCl_3$, 400.1 MHz) δ 7.28 (ddd, 2H, H(7), ^3J = 8.5 and 6.7 Hz, ^4J = 1.3 Hz), 7.39 (br. d, 2H, H(8), ^3J = 8.5 Hz), 7.46 (ddd, 2H, H(6), ^3J = 8.1 and 6.7 Hz, ^4J = 1.3 Hz), 7.49 (dd, 2H, H(2), ^3J = 7.0 Hz, ^4J = 1.2 Hz), 7.58 (dd, 2H, H(3), ^3J = 8.2 and 7.0 Hz), 7.90−7.98 (m, 4H, H(4) and H(5)) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz) δ 125.5, 125.9, 126.1, 126.7, 127.9, 128.0, and 128.2 (7 CH(Ar)), 132.97, 133.6, and 138.6 (3 C(Ar)) ppm. NMR data were consistent with those reported in the literature.[19d]

*1-(Benzo[b]thiophen-2-yl)naphthalene (**5am**).* The title compound was prepared according to the general procedure from ACDC **2a** (100 mg, 0.43 mmol), $GaCl_3$ (76 mg, 0.43 mmol), and alkyne **3m** (340 mg, 2.15 mmol, 5 equiv) in 94 mg yield (84%). Colorless oil. IR ($CHCl_3$) $\tilde{\nu}$ = 3036, 3034, 3023, 3012, 2961, 2929, 2857, 1940, 1719, 1593, 1507, 1457, 1436, 1392, 1325, 1304 1250, 1235, 1227, 1206 cm^{-1}. MS (EI) (*m*/*z*, %) 260 (100, M$^+$), 226 and 213 (8), 129 (15). HRMS (ESI) calcd for $C_{18}H_{13}S$: M + H, 261.0732. Found: *m*/*z* 261.0727. ^{1}H NMR ($CDCl_3$, 300.1 MHz) δ 7.37−7.48 (m, 2H, H(6) and H(7)), 7.49 (s, 1H, H(3′)), 7.50−7.60 (m, 3H, H(3), H(5′) and H(6′)), 7.69 (dd, 1H, H(2), ^3J = 7.1 Hz, ^4J = 1.1 Hz), 7.85−7.98 (m, 4H, H(5), H(8), H(4) and H(7′)), 8.28−8.36 (m, 1H, H(4′)) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz) δ 122.1 and 123.6 (CH(5) and CH(8)), 124.1 (CH(3′)), 124.3 and 124.5 (CH(6) and CH(7)), 125.2 (CH(3)), 125.8 (CH(4′)), 126.1 and 126.6 (CH(5′) and CH(6′)), 128.4 (CH(7′)), 128.5 (CH(2)), 128.9 (CH(4)), 131.8, 132.4, 133.8, 140.2, 140.3, and 142.2 (6 C(Ar)) ppm. NMR data were consistent with those reported in the literature.[19e]

*1-(5-Phenylfuran-2-yl)naphthalene (**5ao**).* The title compound was prepared according to the general procedure from ACDC **2a** (50 mg, 0.21 mmol), $GaCl_3$ (42 mg, 0.24 mmol), and alkyne **3o** (70 mg, 0.42 mmol) in 35 mg yield with ∼90% purity (56%). Colorless oil. IR ($CHCl_3$) $\tilde{\nu}$ = 3059, 3030, 3012, 2955, 2927, 2855, 1725, 1654, 1598, 1579, 1509, 1462, 1377, 1326, 1295, 1269, 1249, 1212, 1200 cm^{-1}. MS (EI) (*m*/*z*, %) 286 (43, M$^+$), 181 (92), 155 (68), 127 (100), 105 (65). HRMS (ESI) calcd for $C_{20}H_{15}O$: M + H, 287.1067. Found: *m*/*z* 287.1063. ^{1}H NMR ($CDCl_3$, 300.1 MHz) δ 6.85 (d, 1H, H(3′) or H(4′), ^3J = 3.4 Hz), 6.89 (d, 1H, H(3′) or H(4′), ^3J = 3.4 Hz), 7.27−7.36 (m, 1H, *p*-H), 7.41−7.50 (m, 2H, *m*-H), 7.51−7.65 (m, 3H, 3 H(Ar)), 7.78−7.97 (m, 5H, 5 H(Ar)), 8.51−8.59 (m, 1H, H(Ar)) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz) δ 106.9 and 111.4 (CH(3′) and CH(4′)), 123.8 (2 *o*-CH), 125.3, 125.6, 125.9, 126.0, and 126.6 (5 CH(Ar)), 127.4 (*p*-CH), 128.55 and 128.58 (2 CH(Ar)), 128.8 (2 *m*-CH), 129.6, 130.8, 134.1, and 138.9 (4 C(Ar)), 153.0 and 153.9 (C(2′) and C(5′)) ppm. NMR data were consistent with those reported in the literature.[19f]

*1,4-Di(naphthalen-1-yl)benzene (**5aq**).* The title compound was prepared according to the general procedure from ACDC **2a** (50 mg, 0.21 mmol), $GaCl_3$ (42 mg, 0.24 mmol), and alkyne **3q** (96 mg, 0.42 mmol) in 46 mg yield (67%). Colorless oil. ^{1}H NMR ($CDCl_3$, 300.1 MHz) δ 7.48−7.64 (m, 8H, 8 H(naphthyl)), 7.66 (s, 4H, central benzene ring), 7.88−8.01 (m, 4H, 4 H(naphthyl)), 8.06−8.15 (m, 2H, 2 H(naphthyl)) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz) δ 125.5, 125.9, 126.19, 126.20, 127.2, 127.8, and 128.4 (14 CH(naphthyl)), 130.1 (4 CH, central benzene ring), 131.8, 134.0, 139.8, and 140.1 (8 C(Ar)) ppm. NMR data were consistent with those reported in the literature.[19g]

*1-(n-Pentyl)naphthalene (**5ag**).* The title compound was prepared according to the general procedure from ACDC **2a** (100 mg, 0.43 mmol), $GaCl_3$ (76 mg, 0.43 mmol), and alkyne **3g** (206 mg, 2.15 mmol) in 18 mg yield (21%). Colorless oil. IR ($CHCl_3$) $\tilde{\nu}$ 3064, 3011, 2959, 2932, 2872, 2860, 1781, 1738, 1597, 1510, 1467, 1459, 1396, 1379, 1262 cm^{-1}. MS (EI) (*m*/*z*, %) 198 (15, M$^+$), 179 (23), 141 (100), 115 (53), 91 (20), 71 (38), 57 (41), 43 (62). ^{1}H NMR ($CDCl_3$, 400.1 MHz) δ 0.89 (t, 3H, Me, ^3J = 7.1 Hz), 1.31−1.49 (m, 4H, 2 CH_2), 1.68−1.79 (m, 2H, CH_2), 2.99−3.09 (m, 2H, CH_2(1′)), 7.29 (br. d, 1H, H(Ar), ^3J = 6.8 Hz), 7.36 (dd, 1H, H(3), ^3J = 8.1 and 7.0 Hz), 7.40−7.51 (m, 2H, 2 H(Ar)), 7.67 (br. d, 1H, H(Ar), ^3J = 8.1 Hz), 7.80−7.84 (m, 1H, H(Ar)), 8.02 (br. d, 1H, H(Ar), ^3J = 8.3 Hz) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz) δ 14.2 (Me), 22.8, 30.7, 32.2, and 33.2 (4 CH_2), 124.1, 125.5, 125.7, 125.8, 126.0, 126.5, and 128.9 (7 CH(Ar)), 132.1, 134.1, and 139.2 (3 C(Ar)) ppm. NMR data were consistent with those reported in the literature.[19h]

*1,2-Di(n-butyl)naphthalene (**5ah**).* The title compound was prepared according to the general procedure from ACDC **2a** (100 mg, 0.43 mmol), $GaCl_3$ (76 mg, 0.43 mmol), and alkyne **3h** (297 mg, 2.15 mmol) in 13 mg yield (13%). Colorless oil. IR ($CHCl_3$) $\tilde{\nu}$ 3051, 3031, 3011, 2959, 2932, 2873, 2862, 1726, 1599, 1511, 1466, 1380, 1264 cm^{-1}. MS (EI) (*m*/*z*, %) 240 (41, M$^+$), 197 (5), 165 (7), 155 (100), 141 (19), 128 (5), 115 (6), 41 (7). ^{1}H NMR ($CDCl_3$, 300.1 MHz) δ 1.00 (t, 3H, Me, ^3J = 7.3 Hz), 1.04 (t, 3H, Me, ^3J = 7.2 Hz), 1.39−1.77 (m, 8H, 4 CH_2), 2.75−2.88 and 3.04−3.15 (both m, 2 × 2H, CH_2(1′) and CH_2(1″)), 7.32 (d, 1H, H(3), ^3J = 8.4 Hz), 7.42 (ddd, 1H, H(6), ^3J = 7.9 and 6.8 Hz, ^4J = 1.2 Hz), 7.50 (ddd, 1H, H(7), ^3J = 8.5 and 6.8 Hz, ^4J = 1.5 Hz), 7.65 (br. d, 1H, H(4), ^3J = 8.4 Hz), 7.81 (br. dd, 1H, H(5), ^3J = 7.9 Hz, ^4J = 1.5 Hz), 8.05 (br. d, 1H, H(8), ^3J = 8.5 Hz) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz) δ 14.00 and 14.02 (2 Me), 22.9 and 23.4 (2 CH_2), 28.0 (CH_2(1′)), 33.3 (CH_2), 33.4 (CH_2(1″)), 33.9 (CH_2), 124.0 (CH(8)), 124.4 (CH(6)), 125.6 (CH(7)), 126.0 (CH(4)), 128.4 (CH(3)), 128.5 (CH(5)),

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132.3, 132.5, 135.5, and 137.6 (4 C(Ar)) ppm. Data for the compound were consistent with those reported in the literature.[19i]

*7-Chloro-1-(n-hexyl)naphthalene (**5ff**).* The title compound was prepared according to the general procedure from ACDC **2f** (100 mg, 0.37 mmol), $GaCl_3$ (65 mg, 0.37 mmol), and alkyne **3f** (204 mg, 1.85 mmol) in 18 mg yield (20%). Colorless oil. HRMS (ESI) calcd for $C_{16}H_{20}{}^{35}Cl$: M + H, 247.1248. Found: *m/z* 247.1239. IR ($CHCl_3$) $\tilde{\nu}$ 3053, 2958, 2931, 2859, 1731, 1593, 1500, 1467, 1379, 1364 cm^{-1}. MS (EI) (*m/z*, %) 246 (29, M^+), 175 (100), 153 (27), 139 (55), 126 (8), 115 (8), 41 (13). ^1H NMR ($CDCl_3$, 400.1 MHz) δ 0.85−0.96 (m, 3H, Me), 1.21−1.52 (m, 6H, 3 CH_2), 1.67−1.80 (m, 2H, CH_2), 2.95−3.06 (m, 2H, $CH_2(1')$), 7.31−7.43 (m, 3H, H(2), H(3) and H(6)), 7.66 (br. d, 1H, H(4), ^3J = 8.0 Hz), 7.77 (d, 1H, H(5), ^3J = 8.7 Hz), 8.00 (br. d, 1H, H(8), ^4J = 1.9 Hz) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz) δ 14.2 (Me), 22.8, 29.6, 30.8, 31.9, and 33.1 (5 CH_2), 123.2, 126.0, 126.3, 126.4, 126.9, and 130.5 (6 CH(Ar)), 131.7, 132.3, 132.8, and 138.5 (4 C(Ar)) ppm.

Other Cascade Processes of DACs with Acetylenes. *Dimethyl 4-(1,3-dimethoxy-1,3-dioxopropan-2-yl)-9b-hexyl-3-phenyl-3,3a,4,5-tetrahydro-1H-cyclopenta[a]naphthalene-1,1(2H,9bH)-dicarboxylate (**6**).* All operations were performed under a dry argon atmosphere. To a solution of ACDC **2a** (234 mg, 1 mmol, 1 equiv) in dry CH_2Cl_2 (4 mL) was added solid $GaCl_3$ (176 mg, 1 mmol, 1 equiv) in one portion at 0 °C, and the mixture was stirred at the same temperature for 10 min. Then, the reaction mixture was cooled to −70 °C; the solution of alkyne **3f** (36 mg, 0.33 mmol, 0.33 equiv) in dry CH_2Cl_2 (1 mL) was added, and the mixture was stirred for 1 h. An aqueous solution of HCl (5%) was added until pH 3 was achieved, and the reaction mixture was extracted with CH_2Cl_2 (3 × 10 mL). The organic layer was dried over $MgSO_4$, and the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel (hexane) and then on a silufol chromatographic plate (20 × 20 cm, hexane:acetone, 5:1) to yield the title compound **6** as a thick colorless oil with ∼90% purity (73 mg, 35%). IR ($CHCl_3$) $\tilde{\nu}$ 3038, 3011, 2954, 2931, 2858, 1729 (C═O), 1602, 1494, 1455, 1436, 1235, 1197, 1161, 1030, 789, 749, 706, 666 cm^{-1}. MS (EI) (*m/z*, %) 578 (7, M^+), 547 (12), 446 (100, $M^+-C_5H_8O_4$), 301 (26), 283 (19), 235 (40), 212 (81), 171 (21), 145 (14), 132 (9), 115 (14), 91 (7). HRMS (ESI) calcd for $C_{34}H_{42}O_8$: M + Na, 601.2772; M + K, 617.2511. Found: *m/z* 601.2774, 617.2518. ^1H NMR ($CDCl_3$, 400.1 MHz) δ 0.81−0.88 (m, 3H, $CH_2(6')$), 0.89−0.96 (m, 1H, $CH_2(2')$), 1.17−1.29 (m, 6H, $CH_2(3')$, $CH_2(4')$ and $CH_2(5')$), 1.29−1.39 (m, 1H, $CH_2(2')$), 1.90−2.08 (m, 2H, $CH_2(1')$, ^2J = 12.2 Hz, ^3J = 8.2 and 4.4 Hz), 2.54−2.61 (m, 3H, $CH_2(2)$ and CH(4), ^2J = 15.7 Hz, ^3J = 11.3 Hz), 2.72−2.81 (m, 2H, $CH_2(5)$ and CH(3a)), 2.86−2.95 (dd, 1H, $CH_2(5)$, ^2J = 15.4 Hz, ^3J = 9.7 Hz), 3.43 (d, 1H, CH(3), ^3J = 11.5 Hz), 3.47 (d, 1H, CH(2″), ^3J = 6.3 Hz), 3.34, 3.38, 3.58, and 3.80 (all s, 4 × 3H, 4 OMe), 6.98 (br.d, 1H, H(8), ^3J = 7.9 Hz), 7.08 (t, 1H, H(7), ^3J = 7.2 Hz), 7.16−7.18 (m, 1H, H(8)), 7.19−7.27 (m, 1H, *p*-CH), 7.27−7.37 (m, 4H, 2 *o*-CH and 2 *m*-CH), 8.01 (d, 1H, ^3J = 8.0 Hz) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz) δ 14.1 ($CH_3(6')$), 22.6 ($CH_2(5')$), 24.4 ($CH_2(2')$), 29.8 ($CH_2(3')$), 31.5 ($CH_2(5)$), 31.7 ($CH_2(4')$), 39.3 (CH(4)), 43.0 ($CH_2(1')$), 44.8 ($CH_2(2)$), 49.4 (CH(3)), 51.8, 52.2, 52.4, and 52.5 (4 OMe), 53.1 (CH(2″)), 56.1 (C(9b)), 70.2 (C(1)), 125.9 (CH(7)), 126.4 (CH(8)), 126.7 (*p*-CH), 127.8 (CH(9)), 128.0 (2 *o*-CH), 128.1 (CH(6)), 128.8 (2 *m*-CH), 137.0 (C(5a)), 140.6 (C(9a)), 144.2 (*i*-C), 168.4, 169.5, 171.1, and 171.8 (4 COO) ppm.

*(2RS,3RS,E)-3-(1,3-Dimethoxy-1,3-dioxopropan-2-yl)-2-(2-(1,3-dimethoxy-1,3-dioxopropan-2-yl)-1-phenylehtyl)-1-hexylidene-1,2,3,4-tetrahydronaphthalene (**7**).* The title compound was isolated as a trace product during separation of the reaction mixture from the synthesis of compound **6**. Three consecutive chromatography runs were used for isolation and purification of the title product. The yield of compound **7** was 1.5 mg with ∼70% purity (ca. 0.5%). Ratio of isomers for **7** is *E*/*Z* ∼ 4/1 and dr >90/10. Colorless oil. IR ($CHCl_3$) $\tilde{\nu}$ 3035, 3011, 2954, 2932, 1730 (C═O), 1601, 1493, 1457, 1436 cm^{-1}. HRMS (ESI) calcd for $C_{34}H_{42}O_8$: M + Na, 601.2772. Found: *m/z* 601.2779. *E*-isomer (major): ^1H NMR ($CDCl_3$, 400.1 MHz) δ 0.94 (t, 3H, Me, ^3J = 7.4 Hz), 1.27−1.52 (m, 6H, 3 CH_2), 1.87−1.97 (m, 1H, H(2″)-a), 2.17−2.26 (m, 2H, $CH_2(2')$), 2.26−2.48 (m, 3H, H(2″)-b and $CH_2(4)$), 2.85−3.07 (m, 3H, H(3), H(1″) and H(3″)), 3.27−3.39 (m, 2H, H(2) and H(2‴)), 3.30, 3.49, 3.58, and 3.70 (all s, 4 × 3H, 4 OMe), 6.20 (t, 1H, ═CH (1′), ^3J = 7.2 Hz), 6.96−7.02 (m, 1H, H(Ar)), 7.05−7.42 (m, 7H, 7 H(Ar)), 7.50−7.56 (m, 1H, H(Ar)) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz) δ 14.2 (Me), 22.8, 27.7, 29.0, 29.6, 32.1, 34.1, and 34.7 (CH and 6 CH_2), 41.8, 44.6, and 50.2 (2 CH), 52.1, 52.3, 52.4, and 52.5 (4 OMe), 54.5 (CH), 125.1, 126.4, 127.2, 127.3, and 128.1 (5 CH(Ar)), 128.8 and 129.2 (2 *o*-CH and 2 *m*-CH), 131.4 (CH(Ar)), 132.6, 133.2, 134.7, and 141.2 (4 C(Ar)), 168.9, 169.3, 169.4, and 169.7 (4 COO) ppm. *Z*-isomer (minor), key signal: ^1H NMR ($CDCl_3$, 400.1 MHz) δ 5.48 (dd, 1H, ═CH (1′), ^3J = 8.5 and 5.7 Hz), other signals are overlapped.

*1-Phenyl-9-(1-phenylvinyl)phenanthrene (**8**).* All operations were performed under a dry argon atmosphere. To a solution of ACDC **2e** (117 mg, 0.5 mmol) in dry CH_2Cl_2 (3 mL) was added solid $GaCl_3$ (88 mg, 0.5 mmol) in one portion at 0 °C, and the mixture was stirred at the same temperature for 10 min to form 1,2-zwitterion **1e**. Then, the solution of alkyne **3a** (510 mg, 5 mmol, 10 equiv) in dry CH_2Cl_2 (2 mL) was added at 0 °C, and the reaction mixture was immediately heated to 40 °C and refluxed for 2 h. An aqueous solution of HCl (5%) was added until pH 3 was achieved, and the reaction mixture was extracted with CH_2Cl_2 (3 × 10 mL). The organic layer was dried over $MgSO_4$, and the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel (hexane, hexane:acetone, 50:1 to 10:1) and then on a silufol chromatographic plate (20 × 20 cm, hexane:acetone, 10:1) to yield the title compound **8** as a thick colorless oil (94 mg, 53%). Colorless oil. IR ($CHCl_3$) $\tilde{\nu}$ 3035, 3012, 2941, 2293, 2256, 1601, 1442, 1411, 1373, 1230, 1036, 920, 803, 754 cm^{-1}. MS (EI) (*m/z*, %) 356 (100, M^+), 276 (33), 252 (14), 178 (8), 138 (8), 77 (17), 51 (6), 39 (3). HRMS (ESI) calcd for $C_{28}H_{20}$: M + H, 357.1638. Found: *m/z* 357.1632. ^1H NMR ($CDCl_3$, 400.1 MHz) δ 5.40 (d, 1H, H(2′), ^2J = 1.4 Hz), 5.92 (d, 1H, H(2′), ^2J = 1.4 Hz), 7.20−7.24 (m, 3H, 2 *m*′-CH and *p*′-CH), 7.30−7.34 (m, 2H, 2 *o*′-CH), 7.39−7.41 (m, 1H, *p*-CH), 7.41−7.43 (m, 1H, CH(7)), 7.43−7.49 (m, 2H, 2 *m*-CH), 7.50−7.54 (m, 2H, 2 *o*-CH), 7.57 (dd, 1H, CH(2), ^3J = 7.2 Hz, ^4J = 1.1 Hz), 7.61 (ddd, 1H, CH(6), ^3J = 8.4 and 7.3 Hz, ^4J = 1.3 Hz), 7.71 (dd, 1H, CH(3), ^3J = 8.4 and 7.3 Hz), 7.75 (dd, 1H, CH(8), ^3J = 8.2, ^4J = 1.1 Hz), 7.83 (s, 1H, CH(10)), 8.74 (d, 1H, CH(4), ^3J = 7.5 Hz), 8.75 (d, 1H, CH(5), ^3J = 7.6 Hz) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz) δ 116.2 ($CH_2(2')$, 122.1 (CH(4)), 123.1 (CH(5)), 125.5 (CH(10)), 126.1 (CH(3)), 126.54 (CH(6)), 126.56 (2 *o*′-CH), 126.67 (CH(7)), 127.3 (*p*-CH), 127.4 (CH(8)), 127.8 (*p*′-CH), 128.3 (CH(2)), 128.42 (2 *m*-CH), 128.48 (2 *m*′-CH), 130.2 (2 *o*-CH), 129.5, 130.7, 130.80, and 130.82 (4C), 138.4 (C(9)), 140.5 (*i*′-C), 141.0 (C(1)), 141.1 (*i*-C), 148.7 (C(1′)) ppm.

*2-(1,3-Dimethoxy-1,3-dioxopropan-2-yl)-4-(3-(1-(benzo[b]thiophen-2-yl)vinyl)benzo[b]thiophen-2-yl)-1,2-dihydronaphthalene (**9**).* All operations were performed under a dry argon atmosphere. To a solution of ACDC **2a** (100 mg, 0.43 mmol) in dry CH_2Cl_2 (4 mL) was added solid $GaCl_3$ (76 mg, 0.43 mmol) in one portion at 0 °C, and the mixture was stirred at the same temperature for 10 min to form 1,2-zwitterion **1a**. Then, the reaction mixture was cooled to −70 °C, and the solution of alkyne **3m** (680 mg, 4.3 mmol) in dry CH_2Cl_2 (2 mL) was added. The reaction mixture was stirred at the same temperature for 1.5 h. An aqueous solution of HCl (5%) was added until pH 3 was achieved (without heating to room temperature), and the reaction mixture was extracted with CH_2Cl_2 (3 × 10 mL). The organic layer was dried over $MgSO_4$, and the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel (hexane, hexane:acetone, 50:1 to 10:1) and then on a silufol chromatographic plate (20 × 20 cm, hexane:acetone, 10:1, or benzene:ethyl acetate, 10:1) to yield the title compound **9** as a thick colorless oil (132 mg, 56%). IR ($CHCl_3$) $\tilde{\nu}$ = 3060, 3043, 2955, 2849, 1751, 1733, 1608, 1559, 1488, 1457, 1436, 1328, 1328, 1235 cm^{-1}. MS (EI) (*m/z*, %) 550 (17, M^+), 418 (45), 285 (82), 271 (40), 134 (94), 59 (100). HRMS (ESI) calcd for $C_{33}H_{26}NaO_4S_2$: M + Na, 573.1165. Found: *m/z* 573.1149. ^1H NMR ($CDCl_3$, 300.1 MHz) δ 2.60 (dd, 1H, H(1)-a, ^2J = 15.5 Hz, ^3J = 7.6 Hz), 2.87 (dd, 1H, H(1)-a, ^2J = 15.5 Hz,

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^3J = 6.1 Hz), 3.23 (dddd, 1H, H(2), ^3J = 9.8, 7.6, 6.1, and 4.7 Hz), 3.35 (d, 1H, H(2′), ^3J = 9.8 Hz), 3.50 and 3.68 (both s, 2 × 3H, 2 OMe), 5.30 and 5.82 (both s, 2 × 1H, =CH_2), 6.22 (d, 1H, H(3), ^3J = 4.7 Hz), 6.90 (s, 1H, H(3‴)), 7.04−7.22 (m, 4H, H(5)−H(8)), 7.22−7.43 (m, 4H, H(5″), H(6″), H(5‴) and H(6‴)), 7.51−7.58 (m, 1H, H(4‴)), 7.58−7.64 (m, 1H, H(4″)), 7.68−7.79 (m, 1H, H(7‴)), 7.85−7.91 (m, 1H, H(7″)) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz) δ 31.6 (CH_2(1)), 33.8 (CH(2)), 52.3 and 52.4 (2 OMe), 54.0 (CH(2′)), 118.4 (=CH_2), 122.0 (CH(7‴)), 122.1 (CH(7″)), 123.2 (CH(3‴)), 123.6 (CH(4″)), 123.7 (CH(4‴)), 124.3 (CH(5‴) or CH(6‴)), 124.4 (CH(5″)), 124.6 (CH(6″)), 124.7 (CH(5‴) or CH(6‴)), 125.7 (CH(5)), 126.7, 127.9, and 128.0 (CH(6)−CH(8)), 131.8 (CH(3)), 133.4, 133.55, 133.57, and 133.59 (C(4), C(4a), C(8a) and C(3″)), 136.8 (=C), 139.0, 139.1, 139.3, 139.4, and 140.1 (C(2″), C(3a″), C(7a″), C(3a‴) and C(7a‴)), 144.1 (C(2‴)), 168.2 and 168.5 (2 COO) ppm.

*(7E,9Z)-6-(1,3-Dimethoxy-1,3-dioxopropan-2-yl)-8,10-bis(4-nitrophenyl)-5,6-dihydrobenzo[8]annulene (**10**).* All operations were performed under a dry argon atmosphere. To a solution of ACDC **2a** (70 mg, 0.30 mmol) in dry CH_2Cl_2 (3 mL) was added solid $GaCl_3$ (58 mg, 0.33 mmol) in one portion at 0 °C and the mixture was stirred at the same temperature for 10 min to form 1,2-zwitterion **1a**. Then, the reaction mixture was cooled to −30 °C, and the solution of alkyne **3j** (441 mg, 3.0 mmol, 10 equiv) in dry CH_2Cl_2 (3 mL) was added. The reaction mixture was stirred at the same temperature for 1.5 h. An aqueous solution of HCl (5%) was added until pH 3 was achieved (without heating to room temperature), and the reaction mixture was extracted with CH_2Cl_2 (3 × 10 mL). The organic layer was dried over $MgSO_4$, and the solvent was removed in vacuo. Excess of acetylene **3j** can be separated by crystallization. The residue was purified by column chromatography on silica gel (hexane, hexane:acetone, 50:1 to 10:1). Crude target product **10** was prepared as a mixture with dihydronaphthalene **4aj**. Then, it was additionally separated on a silufol chromatographic plate (20 × 20 cm, hexane:acetone, 10:1, or benzene:ethyl acetate, 10:1) to yield the title compound **10** as a thick colorless oil with ∼70% purity in 62 mg yield (∼28%). Compound **10** is partially decomposed during chromatography. IR ($CHCl_3$) $\tilde{\nu}$ = 3075, 3004, 2927, 2852, 2256, 1733, 1601, 1459, 1404, 1244, 1230 cm^{-1}. HRMS (ESI) calcd for $C_{29}H_{24}N_2NaO_8$: M + Na, 551.1425. Found: m/z 551.1431. ^1H NMR ($CDCl_3$, 300.1 MHz) δ 2.84 (dd, 1H, H(5)-a, ^2J = 15.5 Hz, ^3J = 7.7 Hz), 3.07 (dd, 1H, H(5)-a, ^2J = 15.5 Hz, ^3J = 6.1 Hz), 3.37 (dddd, 1H, H(6), ^3J = 9.5, 7.7, 6.1, and 4.8 Hz), 3.51 (d, 1H, H(2′), ^3J = 9.5 Hz), 3.78 and 3.79 (both s, 2 × 3H, 2 OMe), 6.11 (d, 1H, H(7), ^3J = 4.8 Hz), 7.07 (br. d, 1H, H(1), ^3J = 7.3 Hz), 7.12−7.33 (m, 3H, H(2)−H(4)), 7.22 (s, 1H, H(9)), 7.43−7.51 and 7.63−7.70 (both m, 2 × 2H, 2 × 2 *o*-H), 8.21−8.29 and 8.29−8.37 (both m, 2 × 2H, 2 × 2 *m*-H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz) δ 32.2 (CH_2(5)), 33.9 (CH(6)), 52.5 (2 OMe), 54.1 (CH(2′)), 122.4 and 125.7 (2 × 2 *m*-CH), 125.8 (CH(1)), 126.8, 127.9, and 128.3 (3C) (CH(2)−CH(4), CH(7) and CH(9)), 129.1 and 132.6 (2 × 2 *o*-CH), 133.7, 134.5 (2C), 135.1, 139.5, 140.5, 141.8, and 143.2 (8C(Ar)), 168.6 (2 COO) ppm.

*1,4-Bis(2-(1,3-dimethoxy-1,3-dioxopropan-2-yl)-1,2-dihydronaphthalen-4-yl)benzene (**11**).* All operations were performed under a dry argon atmosphere. To a solution of ACDC **2a** (234 mg, 1.00 mmol) in dry CH_2Cl_2 (4 mL) was added solid $GaCl_3$ (176 mg, 1.00 mmol) in one portion at 0 °C, and the mixture was stirred at the same temperature for 10 min to form 1,2-zwitterion **1a**. Then, the reaction mixture was cooled to −60 °C, and the solution of alkyne **3p** (38 mg, 0.3 mmol, 0.3 equiv) in dry CH_2Cl_2 (1 mL) was added. The reaction mixture was stirred at the same temperature for 1 h. An aqueous solution of HCl (5%) was added until pH 3 was achieved (without heating to room temperature), and the reaction mixture was extracted with CH_2Cl_2 (3 × 10 mL). The organic layer was dried over $MgSO_4$, and the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel (hexane, hexane:acetone, 50:1 to 10:1). Then, it was additionally separated on a silufol chromatographic plate (20 × 20 cm, hexane:acetone, 10:1, or benzene:ethyl acetate, 10:1) to yield the title compound **11** as a thick colorless oil with ∼90% purity in 100 mg yield (51%). IR ($CHCl_3$) $\tilde{\nu}$ = 3032, 3014, 2955, 2890, 2846, 1922, 1751, 1733, 1604, 1507, 1486, 1451, 1436, 1403, 1334, 1291, 1235 cm^{-1}. MS (EI) (m/z, %) 595 (100, M^+), 463 (86), 330 (80). HRMS (ESI) calcd for $C_{36}H_{34}NaO_8$: M + Na, 617.2146. Found: m/z 617.2145. ^1H NMR ($CDCl_3$, 300.1 MHz) δ 2.84 (dd, 2H, 2 H(1)-a, ^2J = 15.4 Hz, ^3J = 7.8 Hz), 3.08 (dd, 2H, 2 H(1)-a, ^2J = 15.4 Hz, ^3J = 6.0 Hz), 3.36 (dddd, 2H, 2 H(2), ^3J = 9.6, 7.8, 6.0, and 4.6 Hz), 3.51 (d, 2H, 2 H(2′), ^3J = 9.6 Hz), 3.77 and 3.78 (both s, 2 × 6H, 4 OMe), 6.05 (d, 2H, 2 H(3), ^3J = 4.6 Hz), 7.11 (br. s, 2H, 2 H(5)), 7.13−7.22 (m, 6H, 2 × H(6)−H(8)), 7.34 (s, 4H, central benzene ring) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz) δ 32.3 (2 CH_2(1)), 33.9 (2 CH(2)), 52.5 (4 OMe), 54.1 (2 CH(2′)), 125.9 (2 CH(5)), 126.7, 127.7, and 128.3 (2 × CH(6)−CH(8)), 127.4 (2 CH(3)), 128.6 (4 CH, central benzene ring), 134.1, 134.5, 139.2, and 140.8 (2 × 4 C(Ar)), 168.67 and 168.70 (2 × 2 COO) ppm.

Modifications of Dihydronaphthalenylmalonates. *1-Phenylnaphthalene **5a**.* All operations were performed under dry argon atmosphere. To a solution of dihydronaphthalene **5a** (299 mg, 0.89 mmol) in dry CH_2Cl_2 (4 mL) was added solid $GaCl_3$ (206 mg, 1.17 mmol) in one portion, and the reaction mixture was immediately heated to 40 °C and refluxed for 30 min. An aqueous solution of HCl (5%) was added at room temperature until pH 3 was achieved, and the reaction mixture was extracted with CH_2Cl_2 (3 × 10 mL). The organic layer was dried over $MgSO_4$, and the solvent was removed in vacuo to yield the compound **5a** (178 mg, 98%), which was the same as that prepared above.

*2-(1,3-Dimethoxy-1,3-dioxopropan-2-yl)-4-phenylnaphthalene (**15**).* A mixture of dihydronaphthalene **4a** (100 mg, 0.3 mmol) and DDQ (67.4 mg, 0.3 mmol) in benzene (6 mL) was stirred at room temperature for about 1 h. The mixture was diluted with ether, washed with aqueous NH_4Cl and then with brine, dried over $MgSO_4$, and evaporated. The residue was purified by column chromatography on silica gel (benzene) to afford compound **15** as an oil (84 mg, 85%). IR ($CHCl_3$) $\tilde{\nu}$ 3037, 3011, 2956, 1737 br (C=O), 1600, 1494, 1436, 1394, 1315, 1291, 1235, 1196, 1152, 1032, 909 cm^{-1}. MS (EI) (m/z, %) 334 (100, M^+), 275 (17), 247 (24), 231 (15), 215 (100), 202 (28), 189 (13), 108 (14), 94 (13), 59 (28). HRMS (ESI) calcd for $C_{21}H_{18}O_4$: *M* + *H*, 335.1278; M + Na, 357.1097; M + K, 373.0837. Found: m/z 335.1281, 357.1093, 373.0833. ^1H NMR ($CDCl_3$, 400.1 MHz) δ 3.77 (s, 2 × 3H, 2 OMe), 4.85 (s, 1H, H(2″)), 7.39−7.45 (m, 2H), 7.45−7.52 (m, 6H), 7.86−7.91 (m, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz) δ 52.9 (2 OMe), 57.7 (CH(2″)), 125.9, 126.3, 126.6, 127.5, 127.8, 128.2, and 128.5 (7 CH), 128.3 and 130.1 (2 × 2 CH, 2 *m*-CH and 2 *o*-CH), 129.6, 131.4, 133.8, 140.2, and 140.9 (5 C), 168.6 (2 COO) ppm.

*2-(4-Phenyl-1,2-dihydronaphthalen-2-yl)propane-1,3-diol (**12**).* To a stirred suspension of $LiAlH_4$ (65 mg, 1.6 mmol) in 10.0 mL of THF dihydronaphthalene **4a** (100 mg, 0.3 mmol) in 5.0 mL THF was added via syringe. After 2 h, the mixture was quenched with 20 mL of H_2O, followed by 35 mL of aq. 10% NaOH solution and 2 × 15 mLof brine. The organic layer was dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography on silica gel (hexane:acetone, 3:1) to afford the expected product **12** as an oil (59 mg, 70%). Colorless thick oil. IR ($CHCl_3$) $\tilde{\nu}$ 3038, 3009, 2954, 1600, 1491, 1438 cm^{-1}. HRMS (ESI) calcd for $C_{19}H_{20}O_2$: M + Na, 280.1463. Found: m/z 280.1475. ^1H NMR ($CDCl_3$, 300.1 MHz) δ 1.82−1.95 (m, 1H, H(2″)), 2.70−2.85 (m, 1H, H(2)), 2.72 (br.s, 2H, 2 OH), 2.84 (dd, 1H, *syn*-H(1), ^2J = 14.3 Hz, ^3J = 9.2 Hz), 2.99 (dd, 1H, *anti*-H(1), ^2J = 14.3 Hz, ^3J = 5.7 Hz), 3.80−4.03 (m, 4H, 2 CH_2OH), 6.06 (d, 1H, H(3), ^3J = 4.3 Hz), 7.03 (br.d, 1H, H(5), ^3J = 7.1 Hz), 7.09−7.25 (m, 3H), 7.31−7.45 (m, 5H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz) δ 31.8 (CH_2(1)), 32.3 (CH(2)), 44.5 (CH(2″)), 64.3 and 64.6 (2 CH_2OH), 125.6 (CH(5)), 126.4 (CH(6)), 127.32 and 127.35 (*p*-CH and CH(7)), 128.0 (CH(8)), 128.3 and 128.7 (2 *o*-CH and 2 *m*-CH), 130.1 (CH(3)), 134.6 (C(4a)), 135.7 (C(8a)), 140.3 (C(4)), 140.4 (*i*-C).

*Methyl 2-(4-phenyl-1,2-dihydronaphthalen-2-yl)acetate (**13**).* A solution of dihydronaphthalene **4a** (300 mg, 0.89 mmol), NaCl (26 mg, 0.44 mmol), and water (0.2 mL) in DMSO (10 mL) was refluxed for 4 h. Then, the mixture was cooled to room temperature, diluted a 10 mL of brine, and extracted with CH_2Cl_2 (3 × 10 mL). The organic

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layer was washed with a brine and dried over $MgSO_4$, and the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel (benzene) to afford the title compound **13** in yield 238 mg (95%). Colorless thick oil. IR ($CHCl_3$) $\tilde{\nu}$ 3035, 3012, 2954, 1732 br (C=O), 1600, 1493, 1438, 1363, 1235, 1163 cm^{-1}. MS (EI) (*m*/*z*, %) 278 (17, M^+), 217 (18), 204 (100), 189 (11), 178 (7), 165 (7), 141 (7), 127 (8), 115 (8), 101 (6), 91 (10), 74 (10), 59 (8), 42 (18), 28 (12), 18 (31). HRMS (ESI) calcd for $C_{19}H_{18}O_2$: M + H, 279.1380. Found: *m*/*z* 279.1390. ^1H NMR ($CDCl_3$, 400.1 MHz) δ 2.46 and 2.50 (both dd, AB-part, CH_2, ^2J = 15.3 Hz, ^3J = 7.6 and 7.0 Hz), 2.71 (dd, 1H, *syn*-H(1), ^2J = 14.4 Hz, ^3J = 9.4 Hz), 2.99 (dd, 1H, *anti*-H(1), ^2J = 14.3 Hz, ^3J = 6.1 Hz), 3.02−3.09 (m, 1H, H(2)), 3.7 (s, 3H, OMe), 5.94 (d, 1H, H(3), ^3J = 4.0 Hz), 7.0 (br.d, 1H, H(5), ^3J = 7.4 Hz), 7.07−7.21 (m, 3H), 7.28−7.42 (m, 5H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz) δ 31.3 (CH(2)), 34.3 (CH_2(1)), 38.4 (CH_2), 51.6 (OMe), 125.7 (CH(5)), 126.5 (CH(6)), 127.4 (*p*-CH and CH(7)), 128.1 (CH(8)), 128.3 and 128.8 (2 *o*-CH and 2 *m*-CH), 130.4 (CH(3)), 134.5 (C(4a)), 135.3 (C(8a)), 140.2 (C(4)), 140.3 (*i*-C), 172.8 (COO).

*2-(4-Phenyl-1,2-dihydronaphthalen-2-yl)acetic acid (**14**).* A solution of NaOH (72 mg, 1.8 mmol) in 1 mL of H_2O was added to dihydronaphthalene **9** (100 mg, 0.36 mmol) in EtOH (2 mL), and the solution was stirred at room temperature for 1 h. Then, an aqueous solution of HCl (5%) was added at room temperature, and the reaction mixture was extracted with CH_2Cl_2 (3 × 10 mL). The organic layer was dried over $MgSO_4$, and the solvent was removed in vacuo to yield the compound **14** as a thick colorless oil in a yield of 92 mg (97%). The resulting compounds can be additionally purified on a silufol chromatographic plate (20 × 20 cm) eluting with hexane:acetone, 3:1 to afford the pure products. Colorless thick oil. IR ($CHCl_3$) $\tilde{\nu}$ 3044 br (OH), 3006, 2964, 1719 br (C=O), 1500, 1438, 1361 cm^{-1}. HRMS (ESI) calcd for $C_{18}H_{16}O_2$: M + Na, 287.1043. Found: *m*/*z* 287.1040. ^1H NMR ($CDCl_3$, 300.1 MHz) δ 2.54 and 2.60 (both dd, AB-part, CH_2, ^2J = 15.3 Hz, ^3J = 7.4 and 6.7 Hz), 2.79 (dd, 1H, *syn*-H(1), ^2J = 16.7 Hz, ^3J = 11.4 Hz), 3.00−3.16 (m, 2H, *anti*-H(1) and H(2)), 6.01 (d, 1H, H(3), ^3J = 3.8 Hz), 7.05 (br.d, 1H, H(5), ^3J = 7.1 Hz), 7.11−7.31 (m, 3H), 7.31−7.46 (m, 5H), 10.6 (br.d, 1H, COOH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz) δ 31.0 (CH(2)), 34.2 (CH_2(1)), 38.2 (CH_2), 125.7 (CH(5)), 126.5 (CH(6)), 127.36 and 127.40 (*p*-CH and CH(7)), 128.1 (CH(8)), 128.2 and 128.8 (2 *o*-CH and 2 *m*-CH), 130.0 (CH(3)), 134.4 (C(4a)), 135.1 (C(8a)), 140.2 (C(4)), 140.3 (*i*-C), 178.3 (COO).

*Dimethyl 2-(2-phenyl-2-(1-phenylnaphthalen-2-yl)ethyl)-malonate (**17**).* All operations were performed under a dry argon atmosphere. To a solution of dihydronaphthalene **4a** (101 mg, 0.29 mmol) and ACDC **2a** (102 mg, 0.43 mmol) in dry CH_2Cl_2 (4.5 mL) was added solid $GaCl_3$ (53 mg, 0.29 mmol) in one portion, and the reaction mixture was immediately heated to 40 °C and refluxed for 30 min. Then, an aqueous solution of HCl (5%) was added at room temperature until pH 3 was achieved, and the reaction mixture was extracted with CH_2Cl_2 (3 × 10 mL). The organic layer was dried over $MgSO_4$, and the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel (benzene; benzene:EtOAc, 50:1 to 10:1) to afford compound **17** as a thick colorless oil to yield 95 mg (75%). The resulting compound can be additionally purified on a silufol chromatographic plate (20 × 20 cm) eluting with hexane:acetone, 5:1 to afford the pure product, if it is necessary. IR ($CHCl_3$) $\tilde{\nu}$ 3012, 2953, 1733 br (C=O), 1600, 1439, 1365 cm^{-1}. HRMS (ESI) calcd for $C_{29}H_{26}O_4$: M + Na, 461.1723. Found: *m*/*z* 461.1718. ^1H NMR ($CDCl_3$, 400.1 MHz) δ 2.62 and 2.73 (both dt, 2 × 1H, CH_2), ^2J = 15.1 Hz, ^3J = 8.1 and 7.5 Hz), 3.26 (t, 1H, H(3″), ^3J = 7.5 Hz), 3.54 and 3.63 (both s, 2 × 3H, 2 OMe), 4.02 (t, 1H, H(1″), ^3J = 8.0 Hz), 7.02 (dd, 1H, H(8), ^3J = 7.5 Hz, ^4J = 1.9 Hz), 7.07−7.12 (m, 2H, 2 *o*-C′H), 7.13−7.19 (m, 1H, *p*-C′H), 7.20−7.27 (m, 2H, 2 *m*-C′H), 7.29−7.36 (m, 3H, H(7), 2 *m*-H), 7.40−7.51 (m, 3H, H(6), 2 *o*-H), 7.52−7.58 (m, 1H, *p*-H), 7.67 (d, 1H, H(3), ^3J = 8.7 Hz), 7.86 (br.d, 1H, H(5), ^3J = 8.1 Hz), 7.91 (d, 1H, H(4), ^3J = 8.7 Hz) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz) δ 35.0 (CH_2), 44.9 (HC(1″)), 50.0 (HC(3″)), 52.40 and 52.44 (2 OMe), 124.6 (HC(3)), 126.3 (*p*′-C), 127.95 (2 *o*′-C), 128.39 (2 *m*′-C), 125.5, 125.9, 126.9, 127.3, 128.17, and 128.3 (6 CH), 127.6 (C(5)), 128.1 (C(4)), 130.3 (C(7)), 130.7 (C(8)), 132.18 (C(4a)), 133.22 (C(8a)), 137.5 (C(2)), 138.7 (*i*-C), 138.9 (C(1)), 143.4 (*i*′-C), 169.4 and 169.6 (2 COO) ppm.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.7b00209.

Crystal structure of **4ab** (CIF)

Copies of NMR spectra for all new compounds (PDF)

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The authors declare no competing financial interest.

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■ REFERENCES

(1) Reissig, H. U.; Zimmer, R. *Chem. Rev.* **2003**, *103*, 1151.

(2) (a) Schneider, T. F.; Kaschel, J.; Werz, D. B. *Angew. Chem., Int. Ed.* **2014**, *53*, 5504. (b) De Nanteuil, F.; De Simone, F.; Frei, R.; Benfatti, F.; Serrano, E.; Waser, J. *Chem. Commun.* **2014**, *50*, 10912. (c) Novikov, R. A.; Tomilov, Y. V. *Mendeleev Commun.* **2015**, *25*, 1. (d) Grover, H. K.; Emmett, M. R.; Kerr, M. A. *Org. Biomol. Chem.* **2015**, *13*, 655. (e) Reissig, H.-U.; Werz, D. B. (Guest Editorial), Special Issue: Chemistry of Donor-Acceptor Cyclopropanes and Cyclobutanes. *Israel J. Chem.* **2016**, *56*, 365−577.

(3) (a) Chidley, T.; Vemula, N.; Carson, C. A.; Kerr, M. A.; Pagenkopf, B. L. *Org. Lett.* **2016**, *18*, 2922. (b) Das, S.; Chakrabarty, S.; Daniliuc, C. G.; Studer, A. *Org. Lett.* **2016**, *18*, 2784. (c) Garve, L. K. B.; Petzold, M.; Jones, P. G.; Werz, D. B. *Org. Lett.* **2016**, *18*, 564. (d) Tejeda, J. E. C.; Landschoot, B. K.; Kerr, M. A. *Org. Lett.* **2016**, *18*, 2142. (e) Garve, L. K. B.; Pawliczek, M.; Wallbaum, J.; Jones, P. G.; Werz, D. B. *Chem. - Eur. J.* **2016**, *22*, 521.

(4) Novikov, R. A.; Balakirev, D. O.; Timofeev, V. P.; Tomilov, Y. V. *Organometallics* **2012**, *31*, 8627.

(5) (a) Novikov, R. A.; Tarasova, A. V.; Korolev, V. A.; Timofeev, V. P.; Tomilov, Y. V. *Angew. Chem., Int. Ed.* **2014**, *53*, 3187. (b) Novikov, R. A.; Tarasova, A. V.; Tomilov, Y. V. *Mendeleev Commun.* **2015**, *25*, 341.

(6) Novikov, R. A.; Tarasova, A. V.; Tomilov, Y. V. *Synlett* **2016**, *27*, 1367.

(7) (a) Novikov, R. A.; Tarasova, A. V.; Suponitsky, K. Y.; Tomilov, Y. V. *Mendeleev Commun.* **2014**, *24*, 346. (b) Novikov, R. A.; Tarasova, A. V.; Tomilov, Y. V. *Russ. Chem. Bull.* **2014**, *63*, 2737.

(8) Novikov, R. A.; Tarasova, A. V.; Korolev, V. A.; Shulishov, E. V.; Timofeev, V. P.; Tomilov, Y. V. *J. Org. Chem.* **2015**, *80*, 8225.

(9) Borisov, D. D.; Novikov, R. A.; Tomilov, Y. V. *Angew. Chem., Int. Ed.* **2016**, *55*, 12233.

(10) Budynina, E. M.; Ivanov, K. L.; Chagarovskiy, A. O.; Rybakov, V. B.; Trushkov, I. V.; Melnikov, M. Y. *Chem. - Eur. J.* **2016**, *22*, 3692.

(11) (a) Graziano, L.; Iesce, R.; Cermola, F.; Cimminello, G. *J. Chem. Res.* **1992**, 4. (b) Yadav, V.; Sriramurthy, V. *Angew. Chem., Int. Ed.* **2004**, *43*, 2669. (c) Qi, X.; Ready, J. M. *Angew. Chem., Int. Ed.* **2008**, *47*, 7068. (d) Yadav, V.; Kumar, N.; Parvez, M. *Chem. Commun.* **2007**,

DOI: 10.1021/acs.joc.7b00209
J. Org. Chem. 2017, 82, 2724−2738

2281. (e) Grover, H. K.; Lebold, T. P.; Kerr, M. A. *Org. Lett.* **2011**, *13*, 220.
(12) Mackay, W. D.; Fistikci, M.; Carris, R. M.; Johnson, J. S. *Org. Lett.* **2014**, *16*, 1626.
(13) Rakhmankulov, E. R.; Ivanov, K. L.; Budynina, E. M.; Ivanova, O. A.; Chagarovskiy, A. O.; Skvortsov, D. A.; Latyshev, G. V.; Trushkov, I. V.; Melnikov, M. Y. *Org. Lett.* **2015**, *17*, 770.
(14) (a) Letcher, R. M.; Shirley, I. M. *Phytochemistry* **1992**, *31*, 4171. (b) Zhu, C.-C.; Wang, T.-M.; Wang, K.-J.; Li, N. *Z. Naturforsch., B: J. Chem. Sci.* **2009**, *64*, 1077. (c) Schmidt, T. J.; Voessing, S.; Klaes; Grimme, S. *Planta Med.* **2007**, *73*, 1574. (d) Li, Y.; Wu, L.; Ouyang, D.; Yu, P.; Xia, J.; Pan, Y.; Yang, X.; Zeng, H.; Cheng, X.; Jin, H.; Zhang, W. *Chem. Biodiversity* **2011**, *8*, 2299. (e) Rehman, A.; Malik, A.; Riaz, N.; Ahmad, H.; Nawaz, S.; Iqbal, M. *Chem. Pharm. Bull.* **2005**, *53*, 263.
(15) (a) Almansa, C.; Gomez, L. A.; Cavalcanti, F. L.; Rodriguez, R.; Carceller, E.; Bartroli, J.; Garcia-Rafanell, J.; Forn, J. *J. Med. Chem.* **1993**, *36*, 2121. (b) Delgado, G.; del Socorro Olivares, M.; Chávez, M. I.; Ramírez-Apan, T.; Linares, E.; Bye, R.; Espinosa-García, F. J. *J. Nat. Prod.* **2001**, *64*, 861. (c) Krueger, A. C.; Madigan, D. L.; Green, B. E.; Hutchinson, D. K.; Jiang, W. W.; Kati, W. M.; Liu, Y.; Maring, C. J.; Masse, S. V.; McDaniel, K. F.; Middleton, T. R.; Mo, H.; Molla, A.; Montgomery, D. A.; Ng, T. I.; Kempf, D. J. *Bioorg. Med. Chem. Lett.* **2007**, *17*, 2289. (d) Andrews, R. C.; Teague, S. J.; Meyers, A. I. *J. Am. Chem. Soc.* **1988**, *110*, 7854. (e) Voets, M.; Antes, I.; Scherer, C.; Muller-Vieira, U.; Biemel, K.; Marchais-Oberwinkler, S.; Hartmann, R. W. *J. Med. Chem.* **2006**, *49*, 2222.
(16) (a) Pape, A. R.; Kaliappan, K. P.; Kundig, E. P. *Chem. Rev.* **2000**, *100*, 2917. (b) Wu, Y. J. In *Heterocyclic scaffolds II: Topics in heterocyclic chemistry*; Gribble, G. W., Ed.; Springer: New York, 2011; Vol. *26*, pp 1−29.
(17) (a) Freudenberg, J.; Uptmoor, A. C.; Rominger, F.; Bunz, U. H. F. *J. Org. Chem.* **2014**, *79*, 11787. (b) Aldred, M. P.; Li, C.; Zhu, M.-Q. *Chem. - Eur. J.* **2012**, *18*, 16037. (c) Zeng, X.; Ilies, L.; Nakamura, E. *J. Am. Chem. Soc.* **2011**, *133*, 17638. (d) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253.
(18) (a) Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *A64*, 112. (b) Umeda, R.; Nishi, S.; Kojima, A.; Kaiba, K.; Nishiyama, Y. *Tetrahedron Lett.* **2013**, *54*, 179. (c) Balamurugan, R.; Gudla, V. *Org. Lett.* **2009**, *11*, 3116. (d) Castro, S.; Fernandez, J. J.; Vicente, R.; Fananas, F. J.; Rodriguez, F. *Chem. Commun.* **2012**, *48*, 9089. (e) Luo, S.; Yu, D.-G.; Zhu, R.-Y.; Wang, X.; Wang, L.; Shi, Z.-J. *Chem. Commun.* **2013**, *49*, 7794. (f) Xiang, S.; Hu, H.; Ma, J.; Li, Y.; Wang, B.; Feng, C.; Zhao, K.; Hu, P.; Chen, X. *Sci. China: Chem.* **2013**, *56*, 945. (g) Guignard, R. F.; Zard, S. Z. *Chem. Commun.* **2011**, *47*, 12185.
(19) (a) Umeda, R.; Nishi, S.; Kojima, A.; Kaiba, K.; Nishiyama, Y. *Tetrahedron Lett.* **2013**, *54*, 179. (b) Stibingerova, I.; Voltrova, S.; Kocova, S.; Lindale, M.; Srogl, J. *Org. Lett.* **2016**, *18*, 312. (c) Ines, B.; Sanmartin, R.; Moure, M. J.; Dominguez, E. *Adv. Synth. Catal.* **2009**, *351*, 2124. (d) Buter, J.; Heijnen, D.; Vila, C.; Hornillos, V.; Otten, E.; Giannerini, M.; Minnaard, A. J.; Feringa, B. L. *Angew. Chem., Int. Ed.* **2016**, *55*, 3620. (e) Baghbanzadeh, M.; Pilger, C.; Kappe, C. O. *J. Org. Chem.* **2011**, *76*, 8138. (f) Yang, Y.; Yao, J.; Zhang, Y. *Org. Lett.* **2013**, *15*, 3206. (g) Bright, S. T.; Coxon, J. M.; Steel, P. J. *J. Org. Chem.* **1990**, *55*, 1338. (h) Tobisu, M.; Takahira, T.; Morioka, T.; Chatani, N. *J. Am. Chem. Soc.* **2016**, *138*, 6711. (i) Huisgen, R.; Zirngibl, L. *Chem. Ber.* **1958**, *91*, 1438.

DOI: 10.1021/acs.joc.7b00209
J. Org. Chem. 2017, 82, 2724−2738