Supporting Information

Intramolecular Anionic Diels-Alder Reactions of 1-Aryl-4-oxahepta-1,6-diyne Systems in DMSO

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1. General Experimental Procedures

Instrumentation. IR spectra were recorded on a Fourier transform infrared spectrophotometer. ¹H-NMR and ¹³C-NMR spectra including COSY, delayed-COSY, HETECOR, or APT, if necessary, were recorded on a 300 MHz for proton and 75 MHz for carbon-13 instrument. The chemical shifts are given in δ units relative to internal CHCl₃ (7.26 ppm for ¹H) or CDCl₃ (77 ppm for ¹³C). All NMR experiments were performed using deuteriochloroform as a solvent unless otherwise indicated. Mass spectra and Elemental analyses data were obtained from the Instrumental Center of Okayama University on requests.

Analytical Procedure and Data Presentation. Analytical thin layer chromatography was performed on commercial 0.25 mm thickness precoated plates. ¹H-NMR spectral data were indicated in the form: δ -value of signal (peak multiplicity, integrated number of protons and coupling constant (if any)). Splitting patterns are abbreviated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; b, broad.

General Reaction Procedure. All reactions, unless otherwise noted, were conducted under a nitrogen or an argon atmosphere. Liquid reagents were transferred via a dry hypodermic syringe from sure seal bottles to a reaction flask through a rubber septa wired on to the reaction flask. The septa can also serve to permit evacuation to eliminate air and introduce the inert gas by means of a steady stream of inert gas flowing system. Organic extracts were concentrated by evaporation with a rotary evaporator evacuated at around 60 mmHg. Column chromatography was performed by

using a simple column packed with 70-230 mesh silica gel and ethyl acetate-hexane mixed solvent of an appropriate ratio as an eluent, and abbreviated as CC.

Materials. Unless otherwise noted, materials were obtained from commercial suppliers and reagent grade materials were used without further purification. Dimethylsulfoxide (DMSO), dimethylformamide (DMF), triethylamine (Et₃N), and dichloromethane (CH₂Cl₂) were freshly distilled from CaH₂ prior to use. Tetrahydrofuran was purchased from Kanto Chemical Co., Inc is dehydrated and stabilizer-free grade and was used as received.

2. Substrate Preparation.

Diversified 4-oxahepta-1,6-diyne compounds were synthesized as shown in Scheme 1.

Scheme 1. Substrate Preparation

Reagents and conditions: (a) *Sonogashira coupling*: 10 % Pd-C (2 mol %)/CuI (4 mol %)/PPh₃ (8 mol %)/K₂CO₃ (110 mol %)/DME-H₂O (1 : 1), 70 °C; (b) *Williamson ether synthesis*: alcohol + NaH/DMF, then 2-propynyl bromide or indicated halides, (c) 1. MsCl/Et₃N, 2. Bu₄NBr, (d) BuLi/THF, then aldehydes, (e) Routine THP protection.

(1) Synthesis of 3,3-dimethyl-4-oxahepta-1,6-diynes bearing aromatic substituents at both C(1) and C(7) (**1,10,12**) began with *Sonogashira Coupling* reaction between 2-methyl-3-butyn-2-ol and aromatic halide (Ar-I) to **A** followed by *Williamson ether synthesis* between **A** and 2-propynyl bromide to **B** and the second *Sonogashira coupling* with other aromatic halides (Ar'-I).

- Williamson ether synthesis between 2-methyl-3-butyn-2-ol and 3-phenyl-2-propynyl bromide provided **13**. **A** also led to **72** via Williamson ether synthesis with halide prepared from **C**.
- (2) Those bearing an aromatic group on one terminus of the 4-oxahepta-1,6-diyne backbone (**44-46**, **48-51**) were synthesized by Sonogashira reaction to 3-aryl-2-propyn-1-ol (**C**) and subsequent Williamson ether synthesis of **C** with 2-propynyl bromide. These compounds also served as starting materials for synthesizing those which bear desired substituents at both ends (**2**, **17 – 24**) through Sonogashira reaction. Enyne substrates such as **59** or **61** were synthesized from **C** via Williamson ether synthesis with cinnamyl chloride.
- (3) Acetylide anion prepared from 1-octyne was added to formaldehyde to give **D**, which led to **33** via Williamson ether synthesis and Sonogashira reaction.
- (4) For those (**34** or **47**) which have an isopropyl group at C(3), the synthesis was started by adding acetylide anion to 2-methylpropanal to give propynols (**E**) followed by Williamson ether synthesis with 3-phenyl-2-propynyl bromide.
- (5) For preparation of **35**, 2-butyne-1,4-diol was protected with a THP-group in a usual way to give **F**, which gave **35** via Williamson ether synthesis (**G**) and Sonogashira reaction.

3. General procedure for Sonogashira coupling

A mixture of iodobenzene (1.0 mL, 8.9 mmol), K₂CO₃ (3.0 g, 21.7 mmol), CuI (68 mg, 0.36 mmol), PPh₃ (188 mg, 0.72 mmol), and 10% Pd/C (180 mg) in 1,2-dimethoxyethane (10 mL) and water (10 mL) was stirred at room temperature for 30 min. To this mixture was added 2-methyl-3-butyn-2-ol (2.2 mL, 22.7 mmol) and the resulting solution was heated at 70 °C for 7 h, cooled to room temperature and filtered through a celite pad, which was rinsed with several portion of EtOAc (5 mL). The combined filtrates were concentrated by using a rotary evaporator and extracted with several portions of EtOAc. The combined organic solutions were dried (MgSO₄) and concentrated with a rotary evaporator. The crude residual material was purified by CC (hexane/EtOAc (10:1)) to afford 2-methyl-4-phenyl-3-butyn-2-ol [**A** (Ar = C₆H₅): 1.21 g, 85%] as an oil.

4. General procedure for Williamson etherification of alkynyl alcohols

To a solution of 2-methyl-4-phenyl-3-butyn 2-ol [**A** (Ar = C₆H₅): 1.2 g, 7.5 mmol] in DMF (40 mL) was added NaH (374 mg, 9.3 mmol) at 0 °C. The suspension was stirred at 0 °C for 1 h to effect the formation of an alkoxide, and to this mixture was added propargyl bromide (0.76 mL, 8.5 mmol). The mixture was stirred at room temperature for 14 h and quenched by the addition of sat NH₄Cl solution. The mixture was extracted with several portions of EtOAc, and the combined organic solutions were dried (MgSO₄) and concentrated by using a rotary evaporator. The residual mixture was purified by CC eluting with hexane/EtOAc (20:1) to afford a product [**B** (Ar = C₆H₅): 860 mg, 56%] as an oil.

5. General procedure for the addition of acetylide anions to aldehydes

To a solution of 3-[(2-tetrahydropyranyl)oxy]propyne (1.2 g, 8.4 mmol) in THF was added *n*-BuLi (6.0 mL, 1.56 mol/L in *n*-hexane) at –30 °C and the mixture was stirred at –30 °C for 30 min. To this mixture was added 2-methyl-2-propanal (1 mL, 11 mmol) at –30 °C, and the reaction was stirred at –30 °C for 1 h, quenched by the addition of sat NH₄Cl solution and extracted with EtOAc. The combined organic extracts were dried over MgSO₄, filtered, and concentrated to afford an adduct (**D**: 1.58 g, 89%), which was used for further organic transformations without purification.

6. General procedure for cycloaddition reactions of diyne compounds

To a solution of substrate in DMSO was added Triton B (40 wt % in MeOH: 120 mol %) or NaH (60% in oil: 120 mol %) at rt, and the mixture was stirred at rt until the disappearance of substrate by a TLC diagnosis. The reaction was quenched by the addition of saturated NH₄Cl solution and extracted with hexane/EtOAc (3:1). The combined organic layers were dried over

MgSO₄, filtered, and concentrated by a rotary evaporator to give a crude adduct, which was purified by CC to afford cycloaddition products.

7. Physical properties for 1–3 and NMR charts for 3.

7-(4-Methoxyphenyl)-3,3-dimethyl-1-phenyl-4-oxahepta-1,6-diyne (1): *R_f* 0.50 (3:1 hexane/EtOAc); ¹H-NMR δ 1.64 (s, 6H), 3.80 (s, 3H), 4.57 (s, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 7.3–7.5 (m, 7H); ¹³C-NMR δ 28.9, 53.4, 55.2, 71.5, 84.9, 85.0, 85.3, 90.5, 113.8, 115.0, 122.6, 128.2, 128.3, 131.7, 133.2, 159.6; IR (film) 2983, 2224, 1606, 1510 cm⁻¹.

1-(4-Methoxyphenyl)-7-phenyl-4-oxahepta-1,6-diyne (2): *R_f* 0.60 (3:1 hexane/EtOAc); ¹H-NMR δ 3.81 (s, 3H), 4.53 (s, 2H), 4.54 (s, 2H), 6.8–7.5 (m, 9H); ¹³C-NMR δ 55.2, 57.3, 57.5, 82.9, 84.4, 86.6, 86.7, 113.8, 114.5, 122.4, 128.2, 128.4, 131.7, 133.2, 159.7; IR (film) 2839, 1606, 1510, 1250, 1078 cm⁻¹.

6-Methoxy-3,3-dimethyl-4-phenyl-1,3-dihydronaphtho[2,3-*c*]furan (3): *R_f* 0.50 (3:1 hexane/EtOAc); ¹H-NMR δ 1.29 (s, 6H), 3.64 (s, 3H), 5.16 (d, *J* = 1.1 Hz, 2H), 6.60 (d, *J* = 2.5 Hz, 1H), 7.11 (dd, *J* = 2.5, 8.8 Hz, 1H), 7.27–7.37 (m, 2H), 7.43–7.51 (m, 3H), 7.60 (bs, 1H), 7.73 (d, *J* = 8.8 Hz, 1H): numerical values for signal integration, which were printed in NMR chart (Fig. 2, page S5), led to the accuracy of NMR experiments in terms of signal integration for one hydrogen as 1.02 ± 0.05. This value was used for deuterium-content determination experiments described just below: ¹³C-NMR δ (Fig. 3, page S6) 28.1, 55.0, 68.9, 86.0, 105.2, 117.6, 118.6, 127.3, 127.8, 128.4, 128.7, 130.5, 131.6, 134.1, 135.7, 137.2, 142.9, 157.0; IR (KBr) 3456, 1614, 1225 cm⁻¹; mp 155 °C; exact mass, *m/z* 304.14638 (calcd for C₂₁H₂₀O₂ *m/z* 304.14633). Anal. Calcd for C₂₁H₂₀O₂: C, 82.86; H, 6.62. Found: C, 82.95; H, 6.71.

The ¹H-NMR signal assignments are summarized below in which chemical shifts are indicated together with spin-spin coupling constants if any. These data were deduced on the basis of both normal and correlation spectra including COSY, delayed COSY, HETECOR, or APT and also decoupling experiments.

Figure 1. Chemical shifts and coupling constants for 3.

PULSE SEQUENCE
 Relax. delay 0.501 sec
 Pulse 45.0 degrees
 Acq. time 1.459 sec
 Width 18867.9 Hz
 10240 repetitions

OBSERVE C13, 75.4561109
 DECOUPLE H1, 300.0851348
 Power 42 dB
 continuously on
 WALTZ-16 modulated

DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65536
 Total time 5.7 hours

MS-IT-165-b
 Pulse sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
 Mercury-300 "varian"

Figure 3. ¹³C-NMR chart of 3.

Figure 4. Delayed COSY of **3**.

8. Deuterium content determination:

Cycloaddition reaction of **1** in DMSO- d_6 with NaH as a base: 6-methoxy-3,3-dimethyl-4-phenyl-1,3-dihydronaphtho[2,3-c]furan-1,9- d_2 (**3- d_2**). This compound **3- d_2** was obtained in 60% yield employing NaH as a base and DMSO- d_6 as a solvent. The reaction required 22 h at rt for disappearance of the substrate on TLC diagnosis and was quenched with H₂O: R_f 0.50 (3:1

hexane/EtOAc); ^1H -NMR data with numerical values for signal integration: δ 1.31 [s, 6H (5.97)], 3.65 [s, 3H (3.00)], 5.17 (s) accompanied by 5.15 (bs) [s, (1.58)], 6.62 [d, 1H (0.99), $J = 2.7$ Hz], 7.13 [dd, 1H (0.96), $J = 2.7, 8.9$ Hz], 7.27–7.35 [m, 2H (2.04)], 7.43–7.54 [m, 3H (2.96)], 7.61 [s, 1H (0.61)], 7.75 [d, 1H (0.98), $J = 8.9$ Hz].

The numerical values of integration for signals at 5.17 ppm (C1 hydrogen: 1.58) and 7.61 ppm (C9 hydrogen: 0.61) were definitely reduced beyond the experimental errors (± 0.05 /one hydrogen; *vide supra*) indicating that deuteriums were incorporated into these positions. Since the signal integrations for hydrogens other than both C1 and C9 positions provided us with signal integration per one hydrogen for this experiment as 1.02, the % deuterium content at both C1 and C9 positions can be calculated to be 40% (per one hydrogen) and 38%, respectively. Actual NMR charts used for this analysis are shown below (fig. 6, page S9).

Figure 5. Deuterium distribution of **3- d_2** .

The ^{13}C -NMR spectrum of **3- d_2** is shown below (fig. 7, page S10) in which both C(1) (68.9 ppm) and C(9) (118.6 ppm) signals are accompanied by a triplet [68.6 ppm ($J = 22.8$ Hz) and 118.3 ppm ($J = 24.5$ Hz)] due to a spin-spin coupling between the carbon and a deuterium incorporated. This is definitely consistent with the **3- d_2** structure indicated just above. Those J -values are quite reasonable judging from those reported for representative deuterated compounds (see Silverstein, R. M.; Webster, F. X., *Spectrometric Identification of Organic Compounds; Sixth Ed.*: John Wiley & Sons, New York, 1998, p. 245). A C(9a) signal [135.7 ppm (fig. 7, page S10)] was accompanied by three additional higher field signals due to deuterated isomers (135.61, 135.55, and 135.50 ppm; see the insetted spectrum of Fig. 7, page S10): two lower field signals among them probably stemmed from β -deuterium effect [C(1)- d or C(9)- d] and the higher field one can be explained by a β,β' -dideuterium effect [C(1,9)- d_2]. C(8a) and C(8) signals appeared respectively at 128.36 and 128.72 ppm were also accompanied by additional higher field signals (128.29 and 128.67 ppm; ; see the insetted spectrum of Fig. 7, page S10) probably due to the deuterated isomers mentioned above, whereas all the remaining carbon signals appeared as a singlet.

Figure 7. ^{13}C -NMR chart of **3-d₂**.

Cycloaddition reaction of **1** in DMSO with NaH as a base followed by D₂O quenching. The reaction required 2.5 h at rt for substrate disappearance on TLC diagnosis to give a cycloadduct which was identical in all respect with **3** provided under the conditions indicated above as "General

procedure for cycloaddition reactions of diyne compounds” and no deuterium was incorporated into the cycloadduct as far as the NMR diagnoses were concerned.

9. Physical properties for 4 – 6, 10 – 14, and 17 – 63

4-(4-Methoxyphenyl)-1,3-dihydronaphtho[2,3-c]furan (4): R_f 0.37 (3:1 hexane/EtOAc); ^1H -NMR δ 3.91 (s, 3H), 5.05 (s, 2H), 5.31 (s, 2H), 7.0–7.5 (m, 6H), 7.69 (bs, 1H), 7.75 (d, J = 8.5 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H); ^{13}C -NMR δ 55.3, 72.9, 73.3, 114.0, 118.5, 125.5, 125.6, 125.7, 128.0, 130.2, 130.5, 132.0, 132.2, 133.7, 137.0, 137.6, 159.0; IR(film) 2850, 1606, 1512, 1244 cm^{-1} ; mp 147–148 $^{\circ}\text{C}$; exact mass, m/z 276.11508 (calcd for $\text{C}_{19}\text{H}_{16}\text{O}_2$ m/z 276.11503). Anal. Calcd for $\text{C}_{19}\text{H}_{16}\text{O}_2$: C, 82.58; H, 5.84. Found: C, 82.79; H, 5.98.

6-Methoxy-4-phenyl-1,3-dihydronaphtho[2,3-c]furan (5): R_f 0.73 (3:1 hexane/EtOAc); ^1H -NMR δ 3.72 (s, 3H), 5.00 (s, 2H), 5.27 (d, J = 1.1 Hz, 2H), 6.99 (d, J = 2.7 Hz, 1H), 7.15 (dd, J = 2.7, 8.8 Hz, 1H), 7.3–7.5 (m, 5H), 7.63 (bs, 1H), 7.77 (d, J = 8.8 Hz, 1H); ^{13}C -NMR δ 55.1, 73.0, 73.3, 104.5, 117.9, 118.6, 127.6, 128.7, 129.1, 129.3, 129.4, 131.4, 132.9, 135.4, 137.4, 138.3, 157.6; IR (film) 2835, 1767, 1618, 1506, 1236 cm^{-1} ; exact mass, m/z 276.11499 (calcd for $\text{C}_{19}\text{H}_{16}\text{O}_2$ m/z 276.11503). Anal. Calcd for $\text{C}_{19}\text{H}_{16}\text{O}_2$: C, 82.58; H, 5.84. Found: C, 82.45; H, 5.72.

1-Phenyl-2-(tetrahydropyranyloxy)propyne (6): R_f 0.60 (3:1 hexane/EtOAc); ^1H -NMR δ 1.5–2.0 (m, 6H), 3.5–3.6 (m, 1H), 3.8–4.0 (m, 1H), 4.46 and 4.53 (ABq, J = 15.7 Hz, 2H), 4.91 (t, J = 3.3 Hz, 1H), 7.2–7.5 (m, 5H); ^{13}C -NMR δ 19.1, 25.4, 30.3, 54.8, 62.0, 85.1, 85.8, 96.8, 122.7, 128.2, 128.4, 131.8.

7-(4-Cyanophenyl)-3,3-dimethyl-4-oxa-1-phenylhepta-1,6-diyne (10): R_f 0.70 (3:1 hexane/EtOAc); ^1H -NMR δ 1.63 (s, 6H), 4.59 (s, 2H), 7.3–7.5 (m, 5H), 7.51 (d, J = 8.5 Hz, 2H), 7.58 (d, J = 8.5 Hz, 2H); ^{13}C -NMR δ 28.9, 53.1, 71.9, 83.7, 85.3, 90.1, 91.0, 111.6, 118.4, 122.4, 127.8, 128.3, 128.4, 131.7, 131.9, 132.2; IR (film) 2983, 2227, 1605, 1500, 1379 cm^{-1} .

6-Cyano-3,3-dimethyl-4-phenyl-1,3-dihydronaphtho[2,3-c]furan (11): R_f 0.43 (3:1 hexane/EtOAc); ^1H -NMR δ 1.29 (s, 6H), 5.19 (d, J = 1.4 Hz, 2H), 7.2–7.3 (m, 2H), 7.50–7.55 (m, 3H), 7.57 (dd, J = 1.7, 8.2 Hz, 1H), 7.70–7.75 (m, 2H), 7.91 (d, J = 8.2 Hz, 1H); ^{13}C -NMR δ 27.8, 69.0, 86.2, 108.9, 119.2, 119.4, 126.1, 128.3, 128.4, 128.8, 130.45, 130.54, 132.47, 132.54, 132.8, 133.8, 134.5, 135.6, 142.0, 144.7; IR (KBr) 2966, 2224, 1345, 1043 cm^{-1} ; mp 221 $^{\circ}\text{C}$; exact mass, m/z 299.13105 (calcd for $\text{C}_{21}\text{H}_{17}\text{NO}$ m/z 299.13101). Anal. Calcd for $\text{C}_{21}\text{H}_{17}\text{NO}$: C, 84.25; H, 5.72. Found: C, 84.45; H, 5.89.

3,3-Dimethyl-7-(4-nitrophenyl)-4-oxa-1-phenylhepta-1,6-diyne (12): R_f 0.60 (3:1 hexane/EtOAc); ^1H -NMR δ 1.64 (s, 6H), 4.61 (s, 2H), 7.3–7.5 (m, 5H), 7.57 (d, J = 8.8 Hz, 2H), 8.16 (d, J = 8.8 Hz, 2H); ^{13}C -NMR δ 28.9, 53.1, 71.9, 83.5, 85.4, 90.0, 91.9, 122.4, 123.4, 128.2, 128.5, 129.7, 131.7, 132.4, 147.0; IR (film) 2983, 2362, 2226, 1593, 1518, 1342 cm^{-1} .

5,5-Dimethyl-4-oxa-1-phenylhepta-1,6-diyne (13): R_f 0.63 (3:1 hexane/EtOAc); ^1H -NMR δ 1.56 (s, 6H), 2.51 (s, 1H), 4.52 (s, 2H), 7.3–7.5 (m, 5H); ^{13}C -NMR δ 28.8, 53.3, 71.0, 73.0, 85.1, 85.3, 86.1, 122.8, 128.1, 128.2, 131.7, 131.8; IR (film) 3292, 2985, 2222, 2110 cm^{-1} .

1,3-Dihydro-1,1-dimethylnaphtho[2,3-c]furan (14): R_f 0.73 (3:1 hexane/EtOAc); ^1H -NMR δ 1.60 (s, 6H), 5.20 (s, 2H), 7.4–7.5 (m, 2H), 7.56 (s, 1H), 7.64 (bs, 1H), 7.8–7.9 (m, 2H); ^{13}C -NMR δ

28.4, 69.9, 84.9, 118.7, 119.2, 125.56, 125.59, 127.8, 127.9, 133.1, 133.2, 138.0, 146.3; IR (KBr) 3475, 1618 cm^{-1} ; mp 100 $^{\circ}\text{C}$; exact mass, m/z 198.10442 (calcd for $\text{C}_{14}\text{H}_{14}\text{O}$ m/z 198.10447). Anal. Calcd for $\text{C}_{14}\text{H}_{14}\text{O}$: C, 84.81; H, 7.12. Found: C, 84.65; H, 7.01.

1-(4-Dimethylaminophenyl)-4-oxa-7-phenylhepta-1,6-diyne (17): R_f 0.50 (3:1 hexane/EtOAc); $^1\text{H-NMR}$ δ 2.98 (s, 6H), 4.54 (s, 4H), 6.63 (d, J = 8.8 Hz, 2H), 7.3–7.5 (m, 7H); $^{13}\text{C-NMR}$ δ 40.1, 57.1, 57.7, 82.0, 84.7, 86.5, 87.9, 109.2, 111.7, 122.6, 128.2, 128.4, 131.7, 132.9, 150.2; IR (film) 2848, 2208, 1608, 1352 cm^{-1} .

1,7-Bis-(4-methoxyphenyl)-4-oxahepta-1,6-diyne (18): R_f 0.70 (3:1 hexane/EtOAc); $^1\text{H-NMR}$ δ 3.81 (s, 6H), 4.52 (s, 4H), 6.84 (d, J = 9.1 Hz, 4H), 7.40 (d, J = 9.1 Hz, 4H); $^{13}\text{C-NMR}$ δ 55.3, 57.5, 83.1, 86.6, 113.9, 114.6, 133.3, 159.8; IR (film) 1606, 1510, 1248 cm^{-1} .

1,7-Diphenyl-4-oxahepta-1,6-diyne (19): R_f 0.83 (3:1 hexane/EtOAc); $^1\text{H-NMR}$ δ 4.55 (s, 4H), 7.3–7.5 (m, 10H); $^{13}\text{C-NMR}$ δ 57.2, 84.2, 86.6, 122.2, 128.1, 128.3, 131.6; IR (film) 3059, 2237, 1489, 1078 cm^{-1} .

1-(4-Chlorophenyl)-4-oxa-7-phenylhepta-1,6-diyne (20): R_f 0.56 (3:1 hexane/EtOAc); $^1\text{H-NMR}$ δ 4.54 (s, 4H), 7.3–7.5 (m, 9H); $^{13}\text{C-NMR}$ δ 57.3, 57.5, 84.2, 85.4, 85.6, 86.9, 120.9, 122.4, 128.3, 128.5, 128.6, 131.8, 133.0, 134.6; IR (film) 2231, 1489, 1078 cm^{-1} .

1,7-Bis-(4-chlorophenyl)-4-oxahepta-1,6-diyne (21): R_f 0.90 (3:1 hexane/EtOAc); $^1\text{H-NMR}$ δ 4.52 (s, 4H), 7.29 (d, J = 8.5 Hz, 4H), 7.39 (d, J = 8.5 Hz, 4H); $^{13}\text{C-NMR}$ δ 57.5, 85.3, 85.8, 120.9, 128.6, 133.0, 134.7; IR (film) 2360, 1491, 1346 cm^{-1} .

1-(4-Cyanophenyl)-4-oxa-7-phenylhepta-1,6-diyne (22): R_f 0.53 (3:1 hexane/EtOAc); $^1\text{H-NMR}$ δ 4.54 (s, 2H), 4.56 (s, 2H), 7.3–7.5 (m, 5H), 7.53 (d, J = 8.5 Hz, 2H), 7.61 (d, J = 8.5 Hz, 2H); $^{13}\text{C-NMR}$ δ 57.2, 57.7, 84.0, 85.0, 87.1, 89.0, 111.9, 118.3, 122.3, 127.3, 128.3, 128.6, 131.7, 131.9, 132.2; IR (film) 2224, 1072 cm^{-1} .

1-(2-Fura)-4-oxa-7-phenylhepta-1,6-diyne (23): R_f 0.60 (3:1 hexane/EtOAc); $^1\text{H-NMR}$ δ 4.53 (s, 2H), 4.56 (s, 2H), 6.39 (dd, J = 1.9, 3.3 Hz, 1H), 6.62 (d, J = 3.3 Hz, 1H), 7.3–7.5 (m, 6H); $^{13}\text{C-NMR}$ δ 57.2, 57.5, 77.0, 84.1, 86.9, 89.0, 110.8, 115.9, 122.4, 128.2, 128.5, 131.8, 136.4, 143.7; IR (film) 2848, 2239, 1489, 1348 cm^{-1} .

1-(2-Fura)-7-(4-methoxyphenyl)-4-oxahepta-1,6-diyne (24): R_f 0.40 (5:1 hexane/EtOAc); $^1\text{H-NMR}$ δ 3.81 (s, 3H), 4.51 (s, 2H), 4.55 (s, 2H), 6.39 (dd, J = 1.9, 3.3 Hz, 1H), 6.62 (dd, J = 0.8, 3.3 Hz, 1H), 6.84 (d, J = 9.1 Hz, 2H), 7.3–7.5 (m, 3H); $^{13}\text{C-NMR}$ δ 55.2, 57.1, 57.6, 77.0, 82.7, 86.9, 89.1, 110.8, 113.9, 114.5, 115.8, 133.3, 136.4, 143.7, 159.8; IR (film) 2839, 2237, 1606, 1510 cm^{-1} .

4-(4-Dimethylaminophenyl)-1,3-dihydronaphtho[2,3-c]furan (25): R_f 0.53 (3:1 hexane/EtOAc); $^1\text{H-NMR}$ δ 3.05 (s, 6H), 5.08 (s, 2H), 5.29 (d, J = 0.83 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H), 7.26 (d, J = 8.8 Hz, 2H), 7.37 (ddd, J = 1.4, 6.9, 8.2 Hz, 1H), 7.45 (ddd, J = 1.4, 6.9, 8.2 Hz, 1H), 7.65 (d, J = 0.83 Hz, 1H), 7.81 (dd, J = 1.4, 8.2 Hz, 1H), 7.85 (dd, J = 1.4, 8.2 Hz, 1H); $^{13}\text{C-NMR}$ δ 40.5, 73.1, 73.4, 112.2, 118.0, 125.4, 125.7, 126.0, 127.9, 130.2, 132.2, 132.9, 133.8, 136.9, 137.6, 149.7; IR (KBr) 3431, 1612, 1524 cm^{-1} ; mp 182 $^{\circ}\text{C}$; exact mass, m/z 289.14670 (calcd for $\text{C}_{20}\text{H}_{19}\text{NO}$ m/z 289.14666). Anal. Calcd for $\text{C}_{20}\text{H}_{19}\text{NO}$: C, 83.01; H, 6.62. Found: C, 83.23; H, 6.75.

1,3-Dihydro-6-methoxy-4-(4-methoxyphenyl)naphtho[2,3-c]furan (26): R_f 0.70 (3:1 hexane/EtOAc); $^1\text{H-NMR}$ δ 3.72 (s, 3H), 3.88 (s, 3H), 4.99 (s, 2H), 5.24 (d, J = 0.8 Hz, 2H), 7.0–7.1 (m,

3H), 7.12 (dd, $J = 2.5, 9.1$ Hz, 1H), 7.28 (d, $J = 8.8$ Hz, 2H), 7.59 (bs, 1H), 7.74 (d, $J = 9.1$ Hz, 1H); ^{13}C -NMR δ 55.1, 55.2, 73.0, 73.3, 104.4, 114.1, 117.9, 118.3, 129.1, 129.4, 130.42, 130.45, 131.1, 133.1, 135.3, 137.5, 157.5, 158.9; IR (KBr) 1616, 1506, 1244 cm^{-1} ; mp 55 $^{\circ}\text{C}$; exact mass, m/z 306.12554 (calcd for $\text{C}_{20}\text{H}_{18}\text{O}_3$ m/z 306.12559). Anal. Calcd for $\text{C}_{20}\text{H}_{18}\text{O}_3$: C, 78.41; H, 5.92. Found: C, 78.23; H, 5.78.

1,3-Dihydro-4-phenylnaphtho[2,3-*c*]furan (27): R_f 0.57 (3:1 hexane/EtOAc); ^1H -NMR δ 5.04 (s, 2H), 5.31 (d, $J = 0.9$ Hz, 2H), 7.3–7.8 (m, 9H), 7.89 (d, $J = 7.7$ Hz, 1H); ^{13}C -NMR δ 72.9, 73.3, 118.8, 125.6, 125.7, 127.6, 128.0, 128.6, 129.4, 131.7, 132.5, 133.6, 136.8, 137.6, 138.1; IR (KBr) 3435, 1495, 1049 cm^{-1} ; mp 128 $^{\circ}\text{C}$; exact mass, m/z 246.10442 (calcd for $\text{C}_{18}\text{H}_{14}\text{O}$ m/z 246.10447). Anal. Calcd for $\text{C}_{18}\text{H}_{14}\text{O}$: C, 87.78; H, 5.73. Found: C, 87.55; H, 5.61.

Figure 8. Chem-3D drawing of crystal structure of **27**.

For the supplementary crystallographic data of **27**, see Supporting Information (CIF format).

6-Chloro-4-phenyl-1,3-dihydronaphtho[2,3-*c*]furan (28): R_f 0.53 (3:1 hexane/EtOAc); ^1H -NMR δ 5.00 (s, 2H), 5.28 (d, $J = 1.2$ Hz, 2H), 7.3–7.6 (m, 6H), 7.64 (d, $J = 2.2$ Hz, 1H), 7.67 (s, 1H), 7.80 (d, $J = 8.8$ Hz, 1H); ^{13}C -NMR δ 72.8, 73.2, 118.7, 124.6, 126.5, 127.9, 128.8, 129.3, 129.5, 131.8, 131.9, 132.5, 137.3, 138.0; IR (KBr) 2846, 1601, 1489 cm^{-1} ; mp 117 $^{\circ}\text{C}$; exact mass, m/z 280.06553 (calcd for $\text{C}_{18}\text{H}_{13}\text{ClO}$ m/z 280.06549). Anal. Calcd for $\text{C}_{18}\text{H}_{13}\text{ClO}$: C, 77.01; H, 4.67. Found: C, 77.21; H, 4.75.

6-Chloro-4-(4-chlorophenyl)-1,3-dihydronaphtho[2,3-*c*]furan (29) R_f 0.67 (3:1 hexane/EtOAc); ^1H -NMR δ 4.99 (s, 2H), 5.27 (d, $J = 1.9$ Hz, 2H), 7.27 (d, $J = 8.4$ Hz, 2H), 7.42 (dd, $J = 1.9, 8.8$ Hz, 1H), 7.42 (dd, $J = 1.9, 8.8$ Hz, 1H), 7.50 (d, $J = 8.4$ Hz, 2H), 7.60 (bs, 1H), 7.67 (s, 1H), 7.79 (d, $J = 8.8$ Hz, 1H); ^{13}C -NMR δ 72.7, 73.2, 119.0, 124.2, 126.6, 129.1, 129.6, 130.5, 130.7, 131.9, 132.0, 132.3, 134.0, 135.7, 138.1, 138.2; IR (KBr) 2848, 1736, 1489 cm^{-1} ; mp 115 $^{\circ}\text{C}$; exact mass, m/z 314.02649 (calcd for $\text{C}_{18}\text{H}_{12}\text{Cl}_2\text{O}$ m/z 314.02652). Anal. Calcd for $\text{C}_{18}\text{H}_{12}\text{Cl}_2\text{O}$: C, 68.59; H, 3.84. Found: C, 68.35; H, 3.66.

6-Cyano-4-phenyl-1,3-dihydronaphtho[2,3-*c*]furan (30): R_f 0.30 (3:1 hexane/EtOAc); ^1H -NMR δ 5.03 (s, 2H), 5.31 (s, 2H), 7.3–7.6 (m, 6H), 7.75 (bs, 1H), 7.94 (d, $J = 8.5$ Hz, 1H), 8.06 (s, 1H); ^{13}C -NMR δ 72.6, 73.1, 109.0, 118.8, 119.3, 126.0, 128.3, 128.9, 129.1, 129.2, 130.8, 132.0, 133.2, 134.9, 136.4, 138.8, 141.2; IR (KBr) 3442, 2360 cm^{-1} ; mp 117 $^{\circ}\text{C}$; exact mass, m/z 271.09968 (calcd for $\text{C}_{19}\text{H}_{13}\text{NO}$ m/z 271.09971). Anal. Calcd for $\text{C}_{19}\text{H}_{13}\text{NO}$: C, 84.11; H, 4.83. Found: C, 83.97; H, 4.67.

4-Fura-2-yl-1,3-dihydronaphtho[2,3-c]furan (31): R_f 0.63 (3:1 hexane/EtOAc); $^1\text{H-NMR}$ δ 5.18 (d, $J = 1.6\text{ Hz}$, 2H), 5.24 (s, 2H), 6.76 (dd, $J = 0.82, 2.2\text{ Hz}$, 1H), 7.34 (s, 1H), 7.4–7.5 (m, 5H), 7.63 (d, $J = 2.2\text{ Hz}$, 1H); $^{13}\text{C-NMR}$ δ 72.7, 73.4, 103.0, 105.9, 126.2, 127.6, 128.3, 128.5, 128.6, 132.0, 136.9, 138.0, 145.5, 155.3; IR (film) 2843, 1736, 1597 cm^{-1} ; exact mass, m/z 236.08379 (calcd for $\text{C}_{16}\text{H}_{12}\text{O}_2$ m/z 236.08373). Anal. Calcd for $\text{C}_{16}\text{H}_{12}\text{O}_2$: C, 81.34; H, 5.12. Found: C, 81.56; H, 5.24.

4-(4-Methoxyphenyl)-5,7-dihydro-1,6-dioxo-s-indacene (32): R_f 0.50 (5:1 hexane/EtOAc); $^1\text{H-NMR}$ δ 3.88 (s, 3H), 5.18 (d, $J = 1.1\text{ Hz}$, 2H), 5.23 (s, 2H), 6.76 (dd, $J = 1.1, 2.2\text{ Hz}$, 1H), 7.02 (d, $J = 8.8\text{ Hz}$, 2H), 7.31 (bs, 1H), 7.40 (d, $J = 8.8\text{ Hz}$, 2H), 7.62 (dd, $J = 2.2\text{ Hz}$, 1H); $^{13}\text{C-NMR}$ δ 55.3, 72.8, 73.4, 102.6, 106.0, 114.1, 126.2, 128.1, 129.6, 130.4, 131.9, 136.8, 145.3, 155.4, 159.1; IR (KBr) 2837, 1734, 1610, 1518 cm^{-1} ; mp 97 $^\circ\text{C}$; exact mass, m/z 266.09424 (calcd for $\text{C}_{17}\text{H}_{14}\text{O}_3$ m/z 266.09429). Anal. Calcd for $\text{C}_{17}\text{H}_{14}\text{O}_3$: C, 76.68; H, 5.30. Found: C, 76.88; H, 5.41.

1-Phenyl-4-oxatrideca-1,6-diyne (33): R_f 0.9 (3:1 hexane/EtOAc); $^1\text{H-NMR}$ δ 0.89 (t, $J = 6.9\text{ Hz}$, 3H), 1.2–1.6 (m, 8H), 2.23 (m, 2H), 4.30 (t, $J = 2.2\text{ Hz}$, 2H), 4.47 (s, 2H), 7.3–7.5 (m, 5H); $^{13}\text{C-NMR}$ δ 14.0, 18.8, 22.5, 28.5, 31.3, 57.1, 57.3, 75.1, 84.6, 86.5, 87.8, 122.6, 128.2, 128.4, 131.8; IR (film) 2931, 2281, 2224, 1348, 1076 cm^{-1} .

4-Isopropyl-8-phenyl-1-[(2-tetrahydropyranyl)oxy]-5-oxaocta-2,7-diyne (34): R_f 0.60 (5:1 hexane/EtOAc); $^1\text{H-NMR}$ δ 1.02 (d, $J = 6.6\text{ Hz}$, 3H), 1.03 (d, $J = 6.6\text{ Hz}$, 3H), 1.4–1.9 (m, 6H), 1.99 (m, 1H), 3.5–3.6 (m, 1H), 3.8–3.9 (m, 1H), 4.20 (m, 1H), 4.35 (d, $J = 1.7\text{ Hz}$, 2H), 4.46 and 4.56 (ABq, $J = 15.9\text{ Hz}$, 2H), 4.85 (m, 1H), 7.3–7.5 (m, 5H).

1-Phenyl-8-[(2-tetrahydropyranyl)oxy]-5-oxaocta-2,7-diyne (35): R_f 0.63 (3:1 hexane/EtOAc); $^1\text{H-NMR}$ δ 1.4–2.0 (m, 6H), 3.5–3.6 (m, 1H), 3.7–3.9 (m, 1H), 4.2–4.4 (m, 4H), 4.47 (s, 2H), 4.81 (t, $J = 3.3\text{ Hz}$, 1H), 7.2–7.5 (m, 5H); $^{13}\text{C-NMR}$ δ 19.0, 25.3, 30.2, 54.2, 56.9, 57.3, 62.0, 81.2, 83.0, 84.2, 86.7, 96.9, 122.4, 128.2, 128.5, 131.7; IR (film) 2239, 1749, 1599, 1491 cm^{-1} .

4-Hexyl-1,3-dihydronaphtho[2,3-c]furan (36): R_f 0.77 (3:1 hexane/EtOAc); $^1\text{H-NMR}$ δ 0.90 (distorted t, $J = 7.1\text{ Hz}$, 3H), 1.2–1.8 (m, 8H), 2.93 (t, $J = 8.2\text{ Hz}$, 2H), 5.25 (s, 4H), 7.4–7.6 (m, 2H), 7.55 (bs, 1H), 7.83 (distorted d, 1H), 8.02 (distorted d, 1H); $^{13}\text{C-NMR}$ δ 14.1, 22.6, 29.7, 30.18, 30.22, 31.7, 72.6, 73.4, 117.4, 123.5, 125.2, 125.4, 128.7, 131.38, 131.43, 133.9, 136.3, 137.5; IR (film) 2929, 2856, 1466, 1057 cm^{-1} ; exact mass, m/z 254.16701 (calcd for $\text{C}_{18}\text{H}_{22}\text{O}$ m/z 254.16706). Anal. Calcd for $\text{C}_{18}\text{H}_{22}\text{O}$: C, 84.99; H, 8.72. Found: C, 85.20; H, 8.94.

1-Isopropyl-9-[(2-tetrahydropyranyl)oxy]methyl-1,3-dihydronaphtho[2,3-c]furan (37): R_f 0.53 (3:1 hexane/EtOAc); $^{13}\text{C-NMR}$ δ 15.1, 19.4, 19.5, 20.7, 25.4, 30.6, 30.7, 34.8, 35.2, 59.0, 62.5, 62.6, 63.3, 63.9, 71.8, 73.3, 88.1, 97.9, 98.9, 119.7, 124.3, 124.4, 125.5, 125.8, 125.9, 126.1, 126.5, 128.2, 128.3, 132.3, 133.8, 138.3, 138.4, 140.2, 140.6; IR (film) 2953, 1738 cm^{-1} ; exact mass, m/z 326.18823 (calcd for $\text{C}_{21}\text{H}_{26}\text{O}_3$ m/z 326.18819). Anal. Calcd for $\text{C}_{21}\text{H}_{26}\text{O}_3$: C, 77.27; H, 8.03. Found: C, 77.02; H, 7.92.

4-[(2-Tetrahydropyranyl)oxy]methyl-1,3-dihydronaphtho[2,3-c]furan (38): R_f 0.50 (3:1 hexane/EtOAc); $^1\text{H-NMR}$ δ 1.4–1.9 (m, THP-ring $-(\text{CH}_2)_3-$, 6H), 3.5–3.6 (m, THP-ring $-\text{O}-\text{CHH}-$, 1H), 3.9–4.0 (m, THP-ring $-\text{O}-\text{CHH}-$, 1H), 4.71 (t, $J = 3.3\text{ Hz}$, THP-ring $\text{O}-\text{CH}-\text{O}$, 1H), 4.90 and 5.20 (ABq, $J = 12.1\text{ Hz}$, $\text{Ar}-\text{CH}_2-\text{OTHP}$, 2H), 5.23 (d, $J = 0.8\text{ Hz}$, $\text{O}-\text{C}(1)\text{H}_2$, 2H), 5.36 and 5.38

(ABq, $J = 14.0$ Hz, O-C(3) H_2 , 2H), 7.47 (td, $J = 6.9$, 1.4 Hz, C(6) or C(7)-H, 1H), 7.52 (td, $J = 6.9$, 1.6 Hz, C(6) or C(7)-H, 1H), 7.65 (bs, C(9)-H, 1H), 7.80–7.86 (distorted d, C(5) or C(8)-H, 1H), 8.11–8.17 (distorted d, C(5) or C(8)-H, 1H); ^{13}C -NMR δ 19.3, 25.4, 30.5, 62.3, 64.1, 72.7, 72.9, 97.8, 119.5, 123.8, 125.5, 125.9, 126.0, 128.4, 131.5, 133.6, 137.7, 138.1; IR (film) 2943, 1510, 1456, 1340 cm^{-1} ; exact mass, m/z 284.14127 (calcd for $\text{C}_{18}\text{H}_{20}\text{O}_3$ m/z 284.14124). Anal. Calcd for $\text{C}_{18}\text{H}_{20}\text{O}_3$: C, 76.03; H, 8.03. Found: C, 76.18; H, 8.17.

3-Benzyl-4-[(*E*)-1-heptenyl]furan (39): R_f 0.87 (3:1 hexane/EtOAc); ^1H -NMR δ 0.8–1.0 (m, 3H), 1.2–1.5 (m, 6H), 2.0–2.2 (m, 2H), 3.75 (s, 2H), 5.5–6.1 (m, 2H), 7.0–7.4 (m, 7H).

4-Benzyl-2-isopropyl-3-[(*E*)-2-(2-tetrahydropyranyl)oxyethenyl]furan (40): R_f 0.67 (3:1 hexane/EtOAc); ^1H -NMR δ 1.23 (d, $J = 7.1$ Hz, 6H), 1.5–1.9 (m, 6H), 2.9–3.1 (m, 1H), 3.5–3.6 (m, 1H), 3.74 (s, 2H), 3.7–3.9 (m, 1H), 4.89 (t, $J = 3.3$ Hz, 1H), 5.81 (d, $J = 12.9$ Hz, 1H), 6.52 (d, $J = 12.9$ Hz, 1H), 6.87 (s, 1H), 7.1–7.4 (m, 5H); ^{13}C -NMR δ 18.7, 21.3, 21.4, 25.1, 26.5, 29.7, 31.1, 61.9, 98.3, 100.0, 113.1, 123.5, 126.0, 128.3, 128.7, 139.9, 141.9, 156.6; IR (film) 2943, 1732, 1668 cm^{-1} ; exact mass, m/z 326.18813 (calcd for $\text{C}_{21}\text{H}_{26}\text{O}_3$ m/z 326.18819). Anal. Calcd for $\text{C}_{21}\text{H}_{26}\text{O}_3$: C, 77.27; H, 8.03. Found: C, 77.01; H, 7.87.

3-Benzyl-4-[(*E*)-2-[(2-tetrahydropyranyl)oxy]ethenyl]furan (41): R_f 0.77 (3:1 hexane/EtOAc); ^1H -NMR δ 1.5–1.9 (m, 6H), 3.5–3.6 (m, 1H), 3.77 (s, 2H), 3.8–3.9 (m, 1H), 4.92 (t, $J = 3.3$ Hz, 1H), 5.75 (d, $J = 12.6$ Hz, 1H), 6.70 (d, $J = 12.6$ Hz, 1H), 7.06 (m, 1H), 7.2–7.3 (m, 5H), 7.36 (bs, 1H); ^{13}C -NMR δ 18.6, 25.0, 29.6, 30.3, 62.0, 98.3, 98.7, 121.0, 123.1, 126.1, 128.4, 128.5, 138.3, 139.6, 141.0, 144.4; IR (film) 2945, 1948, 1759, 1660 cm^{-1} ; exact mass, m/z 284.14128 (calcd for $\text{C}_{18}\text{H}_{20}\text{O}_3$ m/z 284.14124). Anal. Calcd for $\text{C}_{18}\text{H}_{20}\text{O}_3$: C, 76.03; H, 7.09. Found: C, 75.92; H, 6.99.

8-[(2-Tetrahydropyranyl)oxy]-4-oxahepta-1,6-diyne (42): R_f 0.57 (3:1 hexane/EtOAc); ^1H -NMR δ 1.5–1.8 (m, 6H), 2.44 (t, $J = 2.5$ Hz, 1H), 3.4–3.6 (m, 1H), 3.8–3.9 (m, 1H), 4.24 (d, $J = 2.5$ Hz, 2H), 4.25–4.35 (m, 4H), 4.79 (t, $J = 3.0$ Hz, 1H); ^{13}C -NMR δ 18.9, 25.2, 30.1, 54.0, 56.3, 56.6, 61.8, 74.8, 78.8, 80.8, 82.9, 96.7; IR (film) 3288, 2945, 2116, 1442, 1344 cm^{-1} .

3-Methyl-4-[(*E*)-2-[(2-tetrahydropyranyl)oxy]ethenyl]furan (43): R_f 0.73 (3:1 hexane/EtOAc); ^1H -NMR δ 1.5–1.9 (m, 6H), 2.02 (d, $J = 0.9$ Hz, 3H), 3.5–3.7 (m, 1H), 3.8–4.0 (m, 1H), 5.01 (t, $J = 3.3$ Hz, 1H), 5.85 (d, $J = 12.6$ Hz, 1H), 6.78 (d, $J = 12.6$ Hz, 1H), 7.14 (m, 1H), 7.30 (m, 1H); ^{13}C -NMR δ 9.10, 18.6, 25.1, 29.7, 62.0, 98.4, 99.3, 119.0, 121.4, 138.1, 140.0, 144.1; IR (film) 2945, 1957, 1732, 1662 cm^{-1} ; exact mass, m/z 208.10990 (calcd for $\text{C}_{12}\text{H}_{16}\text{O}_3$ m/z 208.10995). Anal. Calcd for $\text{C}_{12}\text{H}_{16}\text{O}_3$: C, 69.21; H, 7.74. Found: C, 69.01; H, 7.62.

1-Phenyl-4-oxahepta-1,6-diyne (44): R_f 0.73 (3:1 hexane/EtOAc); ^1H -NMR δ 2.48 (t, $J = 2.4$ Hz, 1H), 4.33 (d, $J = 2.4$ Hz, 2H), 4.50 (s, 2H), 7.3–7.5 (m, 5H).

1-(4-Methoxyphenyl)-4-oxahepta-1,6-diyne (45): R_f 0.47 (3:1 hexane/EtOAc); ^1H -NMR δ 2.47 (t, $J = 2.5$ Hz, 1H), 3.81 (s, 3H), 4.32 (d, $J = 2.5$ Hz, 2H), 4.48 (s, 2H), 6.8–7.4 (m, 4H); ^{13}C -NMR δ 55.2, 56.4, 57.4, 74.8, 79.1, 82.6, 86.7, 113.9, 114.4, 133.2, 159.8; IR (film) 3290, 2237, 1606, 1510 cm^{-1} .

1-(4-Chlorophenyl)-4-oxahepta-1,6-diyne (46): R_f 0.87 (3:1 hexane/EtOAc); ^1H -NMR δ 2.48 (t, $J = 2.5$ Hz, 1H), 4.31 (d, $J = 2.5$ Hz, 2H), 4.48 (s, 2H), 7.29 (d, $J = 8.5$ Hz, 2H), 7.38 (d, $J = 8.5$

Hz, 2H); ^{13}C -NMR δ 56.6, 57.3, 75.1, 78.9, 85.2, 85.7, 120.9, 128.7, 133.0, 134.7; IR (film) 3298, 2854, 2243, 2118, 1489 cm^{-1} .

5-Isopropyl-1-phenyl-4-oxahepta-1,6-diyne (47): R_f 0.73 (3:1 hexane/EtOAc); ^1H -NMR δ 1.04 (d, J = 6.9 Hz, 3H), 1.06 (d, J = 6.6 Hz, 3H), 1.9–2.1 (m, 1H), 2.46 (d, J = 1.9 Hz, 1H), 4.17 (dd, J = 2.2, 5.8 Hz, 1H), 4.49 and 4.59 (ABq, J = 15.9 Hz, 2H), 7.3–7.5 (m, 5H); ^{13}C -NMR δ 17.7, 18.4, 32.8, 56.8, 73.6, 74.8, 81.0, 84.9, 86.2, 122.7, 128.2, 128.4, 131.8; IR (film) 3294, 2964, 2239 cm^{-1} .

1-(1-Naphtyl)-4-oxahepta-1,6-diyne (48): R_f 0.53 (3:1 hexane/EtOAc); ^1H -NMR δ 2.51 (t, J = 2.5 Hz, 1H), 4.42 (d, J = 2.5 Hz, 2H), 4.66 (s, 2H), 7.43 (dd, J = 7.1, 8.2 Hz, 1H), 7.50–7.65 (m, 2H), 7.70 (dd, J = 1.1, 7.1 Hz, 1H), 7.86 (m, 2H), 8.3–8.4 (m, 1H); ^{13}C -NMR δ 56.6, 57.5, 75.1, 79.0, 85.0, 88.9, 120.0, 125.1, 126.0, 126.4, 126.8, 128.2, 129.0, 130.8, 133.1, 133.3; IR (film) 3294, 2227, 2118 cm^{-1} .

1-(2-Naphtyl)-4-oxahepta-1,6-diyne (49): R_f 0.87 (3:1 hexane/EtOAc); ^1H -NMR δ 2.50 (t, J = 2.5 Hz, 1H), 4.37 (d, J = 2.5 Hz, 2H), 4.55 (s, 2H), 7.4–8.0 (m, 7H); ^{13}C -NMR δ 56.6, 57.4, 75.0, 79.0, 84.3, 87.2, 119.6, 126.5, 126.8, 127.7, 128.0, 128.3, 131.8, 132.8; IR (film) 3292, 2227, 1348, 1082 cm^{-1} .

1-(2-Furyl)-4-oxahepta-1,6-diyne (50): R_f 0.76 (3:1 hexane/EtOAc); ^1H -NMR δ 2.47 (t, J = 2.5 Hz, 1H), 4.3 (d, J = 2.5 Hz, 2H), 4.50 (s, 2H), 6.39 (dd, J = 1.9, 3.3 Hz, 1H), 6.62 (dd, J = 0.8, 3.3 Hz, 1H), 7.39 (dd, J = 0.8, 1.9 Hz, 1H); ^{13}C -NMR δ 56.5, 57.0, 75.1, 77.1, 78.8, 88.7, 110.8, 115.9, 136.3, 143.8; IR (film) 3300, 2241, 1082 cm^{-1} .

1-(2-Pyridyl)-4-oxahepta-1,6-diyne (51): R_f 0.40 (1:1 hexane/EtOAc); ^1H -NMR δ 2.45 (t, J = 2.5 Hz, 1H), 4.30 (d, J = 2.5 Hz, 2H), 4.48 (s, 2H), 7.21 (ddd, J = 1.4, 4.9, 6.3 Hz, 1H), 7.41 (ddd, J = 1.1, 6.3, 7.7 Hz, 1H), 7.63 (ddd, J = 1.4, 1.9, 7.7 Hz, 1H), 8.54 (ddd, J = 1.1, 1.9, 4.9 Hz, 1H); ^{13}C -NMR δ 56.6, 56.9, 75.1, 78.7, 84.1, 85.9, 123.0, 127.0, 136.0, 142.4, 149.8; IR (film) 3292, 2854, 2116 cm^{-1} .

1,3-Dihydronaphtho[2,3-c]furan (52): R_f 0.40 (3:1 hexane/EtOAc); ^1H -NMR δ 5.23 (d, J = 0.6 Hz, 4H), 7.46 (dd, J = 3.3, 6.3 Hz), 2H, 7.68 (bs, 2H), 7.83 (dd, J = 3.3, 6.3 Hz, 2H); ^{13}C -NMR δ 72.7, 119.1, 125.6, 127.8, 133.0, 138.1; IR (KBr) 2845, 1045, 872 cm^{-1} ; mp 155 $^{\circ}\text{C}$; exact mass, m/z 170.07313 (calcd for $\text{C}_{12}\text{H}_{10}\text{O}$ m/z 170.07316). Anal. Calcd for $\text{C}_{12}\text{H}_{10}\text{O}$: C, 84.68; H, 5.92. Found: C, 84.89; H, 6.03.

6-Methoxy-1,3-dihydronaphtho[2,3-c]furan (53): R_f 0.37 (3:1 hexane/EtOAc); ^1H -NMR δ 3.92 (s, 3H), 5.21 (s, 4H), 7.1–7.2 (m, 2H), 7.56 (bs, 1H), 7.59 (bs, 1H), 7.71 (d, J = 8.5 Hz, 2H); ^{13}C -NMR δ 55.2, 72.7, 72.8, 105.8, 117.9, 118.4, 119.0, 128.5, 129.1, 134.2, 135.8, 138.7, 157.5; IR (KBr) 2854, 1616, 1502, 1246, 1207, 1028 cm^{-1} ; mp 107 $^{\circ}\text{C}$; exact mass, m/z 200.08379 (calcd for $\text{C}_{13}\text{H}_{12}\text{O}_2$ m/z 200.08373). Anal. Calcd for $\text{C}_{13}\text{H}_{12}\text{O}_2$: C, 77.98; H, 6.04. Found: C, 78.11; H, 6.16.

6-Chloro-1,3-dihydronaphtho[2,3-c]furan (54): R_f 0.76 (3:1 hexane/EtOAc); ^1H -NMR δ 5.22 (s, 4H), 7.40 (dd, J = 2.2, 8.8 Hz, 1H), 7.60 (bs, 1H), 7.66 (bs, 1H), 7.76 (d, J = 8.8 Hz, 1H), 7.80 (d, J = 2.2 Hz, 1H); ^{13}C -NMR δ 72.66, 72.69, 118.4, 119.2, 126.5, 126.6, 129.3, 131.3, 131.4, 133.7, 138.6, 139.4; IR (KBr) 3435, 1045 cm^{-1} ; mp 103 $^{\circ}\text{C}$; exact mass, m/z 204.03413 (calcd for $\text{C}_{12}\text{H}_9\text{ClO}$ m/z 204.03419). Anal. Calcd for $\text{C}_{12}\text{H}_9\text{ClO}$: C, 70.43; H, 4.43. Found: C, 70.29; H, 4.31.

1-Isopropyl-1,3-dihydronaphtho[2,3-*c*]furan (55): R_f 0.86 (3:1 hexane/EtOAc); $^1\text{H-NMR}$ δ 0.87 (d, J = 6.6 Hz, 3H), 1.12 (d, J = 6.9 Hz, 3H), 2.1–2.3 (m, 1H), 5.1–5.3 (m, 3H), 7.4–7.5 (m, 2H), 7.62 (bs, 1H), 7.65 (bs, 1H), 7.8–7.9 (m, 2H); $^{13}\text{C-NMR}$ δ 16.3, 19.1, 34.0, 72.3, 88.0, 119.0, 119.9, 125.5, 125.6, 127.7, 127.9, 133.1, 133.2, 139.1, 140.2; IR (KBr) 2966, 1036 cm^{-1} ; mp 35 $^{\circ}\text{C}$; exact mass, m/z 212.12010 (calcd for $\text{C}_{15}\text{H}_{16}\text{O}$ m/z 212.12012). Anal. Calcd for $\text{C}_{15}\text{H}_{16}\text{O}$: C, 84.87; H, 7.60. Found: C, 85.06; H, 7.82.

1,3-Dihydrophenanthro[2,3-*c*]furan (56): R_f 0.60 (3:1 hexane/EtOAc); $^1\text{H-NMR}$ δ 5.28 (s, 2H), 5.33 (s, 2H), 7.5–7.8 (m, 5H), 7.9–8.0 (m, 1H), 8.50 (bs, 1H), 8.63 (d, J = 7.7 Hz, 1H); $^{13}\text{C-NMR}$ δ 73.0, 73.3, 114.4, 120.1, 122.4, 126.4, 126.5, 126.6, 126.8, 128.5, 129.9, 130.2, 131.6, 131.9, 138.3, 138.5; IR (KBr) 2833, 1456, 1248, 1045, 816, 754 cm^{-1} ; mp 102 $^{\circ}\text{C}$; exact mass, m/z 220.08886 (calcd for $\text{C}_{16}\text{H}_{12}\text{O}$ m/z 220.08881). Anal. Calcd for $\text{C}_{16}\text{H}_{12}\text{O}$: C, 87.25; H, 5.49. Found: C, 87.37; H, 5.56.

Figure 9. Chem-3D drawing of crystal structure of **56**.

For the supplementary crystallographic data of **56**, see Supporting Information (CIF format).

5,7-Dihydrofuro[3,4-*f*]benzo[*b*]furan (57): R_f 0.50 (5:1 hexane/EtOAc); $^1\text{H-NMR}$ δ 5.2–5.3 (m, 4H), 6.74 (d, J = 2.2 Hz, 1H), 7.34 (bs, 1H), 7.39 (bs, 1H), 7.62 (d, J = 2.2 Hz, 1H); $^{13}\text{C-NMR}$ δ 73.0, 73.2, 103.9, 106.4, 112.8, 127.2, 134.0, 136.3, 145.4, 154.9; IR (KBr) 3475, 2858, 1296, 1041 cm^{-1} ; mp 75 $^{\circ}\text{C}$; exact mass, m/z 160.05240 (calcd for $\text{C}_{10}\text{H}_8\text{O}_2$ m/z 160.05243). Anal. Calcd for $\text{C}_{10}\text{H}_8\text{O}_2$: C, 74.99; H, 5.03. Found: C, 75.21; H, 5.17.

6,8-Dihydrofuro[3,4-*g*]quinolines (58): R_f 0.23 (1:1 hexane/EtOAc); $^1\text{H-NMR}$ δ 5.23 (s, 2H), 5.26 (s, 2H), 7.37 (dd, J = 4.1, 8.2 Hz, 1H), 7.63 (bs, 1H), 7.93 (bs, 1H), 8.13 (dd, J = 1.1, 8.2 Hz, 1H), 8.88 (dd, J = 1.1, 4.1 Hz, 1H); $^{13}\text{C-NMR}$ δ 72.6, 72.8, 119.0, 120.79, 120.82, 127.8, 136.1, 139.0, 142.4, 148.0, 150.0; IR (KBr) 2852, 1491, 1045 cm^{-1} ; mp 117 $^{\circ}\text{C}$; exact mass, m/z 171.06845 (calcd for $\text{C}_{11}\text{H}_9\text{NO}$ m/z 171.06841). Anal. Calcd for $\text{C}_{11}\text{H}_9\text{NO}$: C, 77.17; H, 5.30. Found: C, 77.02; H, 5.19.

1,7-Diphenyl-4-oxa-1-hepten-6-yne (59): R_f 0.60 (3:1 hexane/EtOAc); $^1\text{H-NMR}$ δ 4.32 (dd, 2H, J = 1.4, 6.3 Hz), 4.44 (s, 2H), 6.34 (dt, J = 6.3, 15.9 Hz, 1H), 6.69 (dd, J = 1.4, 15.9 Hz, 1H), 7.2–7.6 (m, 10H).

4-Phenyl-1,3,9,9a-tetrahydronaphtho[2,3-*c*]furan (60): R_f 0.63 (3:1 hexane/EtOAc); $^1\text{H-NMR}$ δ 2.76 (dd, J = 14.6, 15.1 Hz, 1H), 2.96 (dd, J = 6.3, 14.6 Hz, 1H), 3.1–3.3 (m, 1H), 3.59 (dd, J = 8.5, 9.3 Hz, 1H), 4.24 (dd, J = 2.8, 14.8 Hz, 1H), 4.42 (t, J = 8.5 Hz, 1H), 4.74 (dd, J = 1.9, 14.8 Hz, 1H), 6.8–7.5 Hz (m, 9H); $^{13}\text{C-NMR}$ δ 31.9, 40.3, 69.4, 74.5, 125.4, 126.5, 126.7, 127.3, 127.7,

128.3, 129.1, 129.8, 134.7, 136.4, 138.2, 141.4; IR (KBr) 3437, 1481, 1443, 1043 cm^{-1} ; exact mass, m/z 248.12018 (calcd for $\text{C}_{18}\text{H}_{16}\text{O}$ m/z 248.12012). Anal. Calcd for $\text{C}_{18}\text{H}_{16}\text{O}$: C, 87.06; H, 6.49. Found: C, 87.27; H, 6.65.

7-(4-Methoxyphenyl)-1-phenyl-4-oxahepten-6-yne (61): R_f 0.63 (3:1 hexane/EtOAc); ^1H -NMR δ 3.81 (s, 3H), 4.30 (dd, $J = 1.4, 6.0$ Hz, 1H), 4.42 (s, 2H), 6.33 (dt, $J = 6.0, 15.9$ Hz, 1H), 6.68 (dd, $J = 1.4, 15.9$ Hz, 1H), 6.85 (d, $J = 8.8$ Hz, 2H), 7.2–7.5 (m, 7H).

7-Methoxy-9-phenyl-1,3,3a,4-tetrahydronaphtho[2,3-c]furan (62): R_f 0.60 (3:1 hexane/EtOAc); ^1H -NMR δ 2.66 (dd, $J = 14.6, 15.1$ Hz, 1H), 2.90 (dd, $J = 6.6, 14.6$ Hz, 1H), 3.1–3.3 (m, 1H), 3.57 (dd, $J = 8.5, 9.6$ Hz, 1H), 3.67 (s, 3H), 4.21 (dd, $J = 2.8, 14.8$ Hz, 1H), 4.40 (dd, $J = 8.0, 8.5$ Hz, 1H), 4.71 (dd, $J = 1.9, 14.8$ Hz, 1H), 6.45 (d, $J = 2.5$ Hz, 1H), 6.69 (dd, $J = 2.5, 8.3$ Hz, 1H), 7.1–7.5 (m, 6H); ^{13}C -NMR δ 31.2, 40.8, 55.2, 69.5, 74.5, 111.1, 112.3, 126.9, 127.4, 128.2, 128.4, 129.1, 129.9, 137.7, 138.1, 142.1, 158.5; IR (KBr) 2835, 1738, 1605, 1574, 1489 cm^{-1} ; exact mass, m/z 278.13061 (calcd for $\text{C}_{19}\text{H}_{18}\text{O}_2$ m/z 278.13068). Anal. Calcd for $\text{C}_{19}\text{H}_{18}\text{O}_2$: C, 81.99; H, 6.52. Found: C, 82.24; H, 6.68.

4-(4-Methoxyphenyl)-1,3,9,9a-tetrahydronaphtho[2,3-c]furan (63): R_f 0.53 (3:1 hexane/EtOAc); ^1H -NMR δ 2.73 (dd, $J = 14.8, 15.1$ Hz, 1H), 2.93 (dd, $J = 6.3, 14.8$ Hz, 1H), 3.1–3.3 (m, 1H), 3.57 (dd, $J = 8.5, 9.3$ Hz, 1H), 3.85 (s, 3H), 4.23 (dd, $J = 2.5, 14.6$ Hz, 1H), 4.40 (dd, $J = 8.0, 8.5$ Hz, 1H), 4.72 (dd, $J = 1.7, 14.6$ Hz, 1H), 6.9–7.3 (m, 8H); ^{13}C -NMR δ 32.1, 40.3, 55.2, 69.5, 74.6, 113.8, 125.5, 126.6, 126.7, 127.7, 130.3, 130.5, 134.9, 136.7, 141.0, 158.8; IR (KBr) 2835, 2359, 1734, 1608, 1510 cm^{-1} ; exact mass, m/z 278.13062 (calcd for $\text{C}_{19}\text{H}_{18}\text{O}_2$ m/z 278.1306). Anal. Calcd for $\text{C}_{19}\text{H}_{18}\text{O}_2$: C, 81.99; H, 6.52. Found: C, 81.84; H, 6.39.

10. DFT studies:

Cartesian coordinates of B3LYP/6-31+G(d,p) structures of Y and Z

DFT-Y

Standard orientation:						
Center	Atomic	Atomic	Coordinates (Angstroms)			
Number	Number	Type	X	Y	Z	
1	8	0	-3.355846	-0.489342	0.559763	
2	6	0	-2.246750	-1.227608	0.907254	
3	6	0	-1.113185	-1.333002	0.254045	
4	6	0	0.053946	-1.487710	-0.340725	
5	6	0	-3.284028	0.241665	-0.669231	
6	6	0	-2.468411	1.456224	-0.585073	
7	6	0	-1.821653	2.477373	-0.543400	
8	6	0	1.271100	-0.683096	-0.116489	
9	6	0	1.313982	0.370843	0.814628	
10	6	0	2.485564	1.100038	1.004782	
11	6	0	3.637191	0.795459	0.268326	
12	6	0	3.606248	-0.247527	-0.660347	

13	6	0	2.432692	-0.979952	-0.849679
14	1	0	-2.430754	-1.756537	1.838704
15	1	0	0.157310	-2.286166	-1.079443
16	1	0	-4.320689	0.503847	-0.897554
17	1	0	-2.904442	-0.411375	-1.466655
18	1	0	-1.235774	3.367421	-0.502040
19	1	0	0.420890	0.610700	1.383532
20	1	0	2.503575	1.909307	1.729515
21	1	0	4.548911	1.366134	0.419347
22	1	0	4.494261	-0.492322	-1.236137
23	1	0	2.413307	-1.792506	-1.571925

DFT-Z

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	8	0	2.653481	0.317510	-0.684161
2	6	0	1.853039	0.489450	0.476063
3	6	0	0.521221	0.573223	0.359729
4	6	0	-0.692278	0.982885	0.151464
5	6	0	3.322127	-0.942752	-0.774236
6	6	0	4.420795	-1.096794	0.189760
7	6	0	5.332152	-1.230621	0.974994
8	6	0	-1.934924	0.207344	0.105734
9	6	0	-1.978178	-1.120007	-0.373849
10	6	0	-3.178800	-1.827110	-0.436014
11	6	0	-4.371280	-1.234920	-0.005071
12	6	0	-4.348247	0.077386	0.477056
13	6	0	-3.149497	0.791711	0.516183
14	11	0	0.644935	2.808339	-0.478879
15	1	0	2.401573	0.508492	1.414312
16	1	0	3.720632	-0.998029	-1.793265
17	1	0	2.596697	-1.757948	-0.642054
18	1	0	6.131043	-1.349024	1.671178
19	1	0	-1.054042	-1.587801	-0.701695
20	1	0	-3.184432	-2.846331	-0.814335
21	1	0	-5.305653	-1.787408	-0.049300
22	1	0	-5.268190	0.549330	0.812534
23	1	0	-3.136561	1.818144	0.872695

11. NMR Charts for representative products

Proton and carbon (with insetted APT) NMR spectral charts for representative cycloadducts or byproducts such as **4**, **5**, **11**, **14**, **25**, **31**, **36**, **38**, **41**, **43**, **56**, **57**, **58**, and **60** are listed below.

Figure 10. ^1H -NMR chart of **4**.

Figure 11. ^{13}C -NMR chart of **4**.

Figure 12. ^1H -NMR chart of **5**.

Figure 13. ¹³C-NMR chart of 5.

Figure 14. ^1H -NMR chart of 11.

Figure 15. ^{13}C -NMR chart of 11.

14

Figure 16. ^1H -NMR chart of **14**.

Figure 17. ^{13}C -NMR chart of **14**.

25

Figure 18. ¹H-NMR chart of **25**.

Figure 19. ¹³C-NMR chart of **25**.

Figure 20. ^1H -NMR chart of **31**.

Figure 21. ¹³C-NMR chart of **31**.

Figure 22. ¹H-NMR chart of **36**.

Figure 23. ¹³C-NMR chart of **36**.

Figure 24. ^1H -NMR chart of **38**.

Figure 25. ¹³C-NMR chart of **38**.

41

Figure 25. ¹H-NMR chart of 41.

Figure 26. ¹³C-NMR chart of 41.

43

Figure 27. ¹H-NMR chart of **43**.

Figure 28. ¹³C-NMR chart of 43.

56

Figure 29. ^1H -NMR chart of **56**.

Figure 30. ¹³C-NMR chart of **56**.

57

Figure 31. ^1H -NMR chart of **57**.

Figure 32. ¹³C-NMR chart of **57**.

58

Figure 33. ¹H-NMR chart of **58**.

Figure 34. ¹³C-NMR chart of **58**.

Figure 35. ^1H -NMR chart of **60**.

Figure 36. ¹³C-NMR chart of **60**.