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Intramolecular [2+2]-cycloaddition of propargylic 2,3-allenoates for the efficient synthesis of 3-oxabicyclo[4.2.0]octa-1(8),5-dien-4-ones: a dramatic substituent effect

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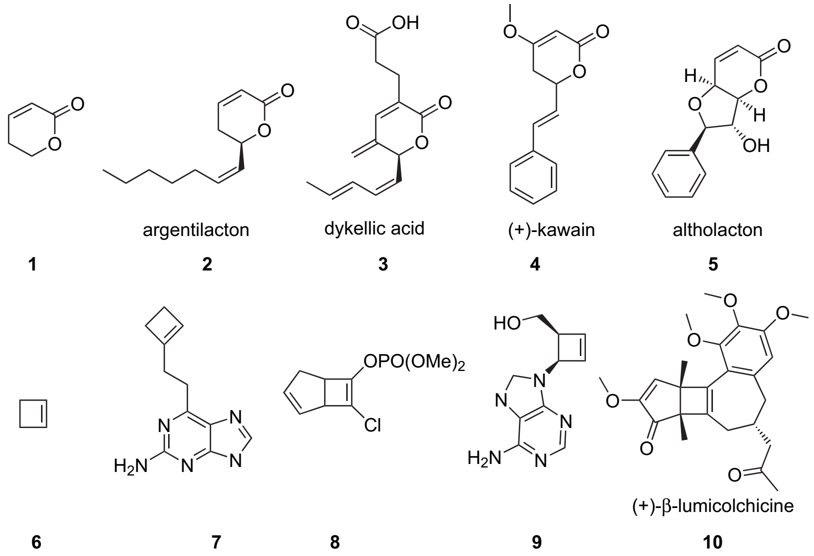
Abstract—[2+2]-Cycloaddition reactions of propargylic 2,3-allenoates under conventional heating conditions afforded 3-oxabicyclo-[4.2.0]octa-1(8),5-dien-4-ones, which contain both the biologically important 5,6-dihydropyran-2-one and cyclobutene units.

1. Introduction

5,6-Dihydropyran-2-one has greatly affected the pharmacological and ecological properties of natural products: the simplest compound **1** could both be antiulcer[1a] and cytotoxic;[1b] argentilacton **2** has antiproliferative[1c] and antiparasitic[1d] effects; dykellic acid **3** shows growth and apoptosis inhibition activity toward some cancer cells;[1e] (+)-kawain **4** is a vasodilator and muscle relaxant;[1f] altholacton **5** could induce apoptosis via oxidative stress in human HL-60 leukemia cells.[1g] Cyclobutenes are also key structural units frequently observed in biologically important compounds: 1-cyclobutenylmethylguanine **7** was proved to be excellent AGT inactivator, whose chemical reactivity may be further enhanced by ring strain arising from the 4-carbon ring,[2a] and **8** shows toxicity toward invertebrates;[2b] compound **9** has been tested to show anti-AIDS and anticancer activities;[2c] (+)-β-lumicolchicine **10** could be responsive to the a1-adrenoceptor (Scheme 1).[2d] Thus, we showed strong interest in the synthesis of 3-oxabicyclo[4.2.0]octa-1(8),5-



Scheme 1. Biologically active 5,6-dihydropyran-2-one and cyclobutene.

Keywords: [2+2]-Cycloaddition; Propargylic 2,3-allenoate; 5,6-Dihydropyran-2-one; Cyclobutene; Heat of formation.
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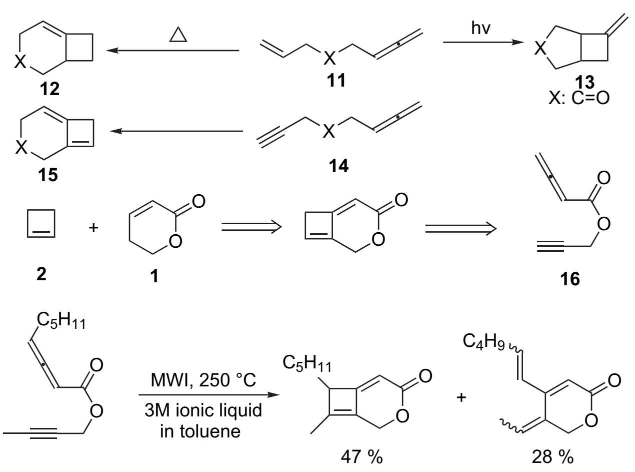
dien-4-ones, which contain both 5,6-dihydropyran-2-one and cyclobutene.

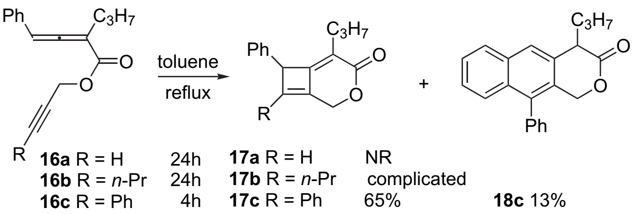
On the other hand, photochemical or heat initiated [2+2]-cycloaddition reactions of allenenes **11** are well documented[3] and constitute a powerful method for the synthesis of methylenecyclobutane derivatives **12** and **13**.[4] Shen and Hammond reported the $Mo(CO)_6$-mediated [2+2]-cycloaddition reactions of the electron-withdrawing *gem*-difluoro-substituted allenynes;[5] Oh et al. observed the Pd-catalyzed or microwave-mediated [2+2]-cycloaddition reactions of allenynes;[6] Brummond and Chen reported [2+2]-cycloaddition of but-2-ynyl nona-2,3-dienoate in ionic liquid/toluene to afford 7-methyl-8-pentyl-3-oxabicyclo[4.2.0]octa-1(8),5-dien-4-one in 47% yield together with 28% byproduct, i.e. 5-ethylidene-4-hex-1-enyl-5,6-dihydropyran-2-one under 250 °C microwave irradiation;[7] Ohno et al. observed thermal [2+2]-cycloaddition of allenynes to give azabicyclo[4.2.0] octadienes[8] (Scheme 2). In this paper we wish to report an efficient synthesis of 3-oxabicyclo[4.2.0]octa-1(8),5-dien-4-ones via the intramolecular [2+2]-cycloaddition of propargylic 2,3-allenoates under conventional heating conditions.



Scheme 2. Intramolecular [2+2]-cycloadditions of allenenes and allenynes.

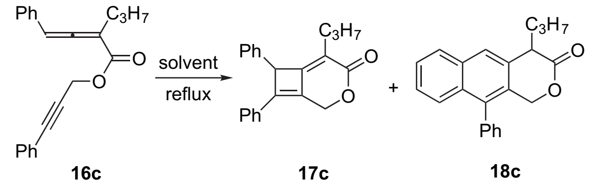
2. Results and discussions

At first we tried the [2+2]-cycloaddition reactions of propargylic 2,3-allenoate **16a**, but no reaction occurred in refluxing toluene. If R is *n*-propyl, then the reaction was complicated; however, when we introduced a phenyl group to the terminal position of the propargylic group, it successfully proceeded to afford **17c** in 65% yield (Scheme 3). In addition to **17c**, 13% of tricyclic lactone product **18c** was also formed.



Scheme 3.

Table 1. Solvent effect of the [2+2]-cycloaddition reaction of **16c**



Entry	Solvent	Time (h)	Isolated yield of **17c** (%)	Isolated yield of **18c** (%)
1	Toluene	4	65	13
2	Dioxane	9	41	9
3	Xylene	2	61	9
4	DMF	2	52	8

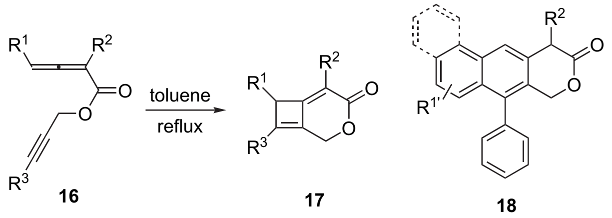
Then, we studied the solvent effect of the [2+2]-cycloaddition reaction of propargylic 2,3-allenoate **16c**, which led to the conclusion that toluene is the best solvent (Table 1).

With the standard reaction conditions in hand, we investigated the scope of [2+2]-cycloaddition reactions of propargylic 2,3-allenoates. Some of the typical results are summarized in Table 2. (1) When R^1 is an aryl group and R^3 is a phenyl group, Diels–Alder-aromatization reaction products **18** were formed as byproducts in the yields of 8–13% (entries 1–5, Table 2). With naphthyl-substituted substrate **16g**, **18g** was formed in 25% yield together with the normal [2+2]-cycloaddition product **17g** (53%) (entry 5, Table 2). The structure of byproducts **18** was confirmed by the X-ray diffraction study of **18g**[9] (Fig. 1). The structure of **17** was further confirmed by the NOE effect observed between the aromatic proton (H^2) and the proton at δ 4.64 ppm (H^1) (Fig. 2). It should be noted that the reaction proceeded smoothly when R^1 is p-BrC_6H_4, which makes possible for further derivatization (entries 4 and 12, Table 2). (2) When R^3 is TMS, the [2+2]-cycloaddition reactions could also proceed leading to the possibility of further elaboration. Furthermore, the reaction is highly selective, i.e. no **18**-type Diels–Alder-aromatization reaction products were formed, although the reaction time was longer (entries 7–13, Table 2). (3) When R^1 was alkyl group, the reactions take longer time with lower yields (entries 6 and 14, Table 2). (4) R^2 can be alkyl, benzyl, allyl group, and H.

3. Conclusion

In conclusion, we have performed [2+2]-cycloaddition reactions of propargylic 2,3-allenoates just under conventional heating conditions for the efficient formation of 3-oxabicyclo[4.2.0]octa-1(8),5-dien-4-ones, which contain both 5,6-dihydropyran-2-one and cyclobutene units. A dramatic alkynic substituent effect on the selectivity of the reaction was observed: when R^3 is Ph or TMS, the [2+2]-cycloaddition reaction of propargylic 2,3-allenoate could proceed smoothly probably due to their stabilization effect for the possible diradical intermediates involved in the reaction. When R^3 is TMS, no Diels–Alder-aromatization reaction products were formed because of the steric and electronic effects. Due to the biological importance of these products, these reactions may be useful tools in organic synthesis and medicinal chemistry. Further studies in this area are being conducted in our laboratory.

Table 2. [2+2]-Cycloaddition reactions of propargylic 2,3-allenoates[a]



Entry	R^1	R^2	R^3	**16**	Time (h)	Products	
						17 (%)	**18** (%)
1	Ph	*n*-Pr	Ph	**16c**	4	**17c** (65)	**18c** (13)
2	Ph	Me	Ph	**16d**	8	**17d** (82)	—[b]
3	Ph	Bn	Ph	**16e**	5	**17e** (66)	**18e** (5)
4	*p*-BrC_6H_4	*n*-Pr	Ph	**16f**	12	**17f** (61)	**18f** (5)
5	Naphthyl	*n*-Pr	Ph	**16g**	12	**17g** (53)	**18g** (25)
6	Cyclohexanyl	H	Ph	**16h**	72	**17h** (36)	—[c]
7	Ph	*n*-Bu	TMS	**16i**	9	**17i** (69)	—[d]
8	Ph	*n*-Pr	TMS	**16j**	8	**17j** (74)	—[d]
9	Ph	Et	TMS	**16k**	24	**17k** (75)	—[d]
10	Ph	Me	TMS	**16l**	48	**17l** (50)	—[d]
11	Ph	Bn	TMS	**16m**	28	**17m** (70)	—[d]
12	*p*-BrC_6H_4	*n*-Pr	TMS	**16n**	48	**17n** (71)	—[d]
13	Ph	Allyl	TMS	**16o**	44	**17o** (64)	—[d]
14	*n*-C_6H_{13}	Me	TMS	**16p**	72	**17p** (25)	—[d]

[a] Isolated yields.

[b] Not detected by chromatographic isolation.

[c] Other unidentified products were found.

[d] No Diels–Alder reaction products were found.

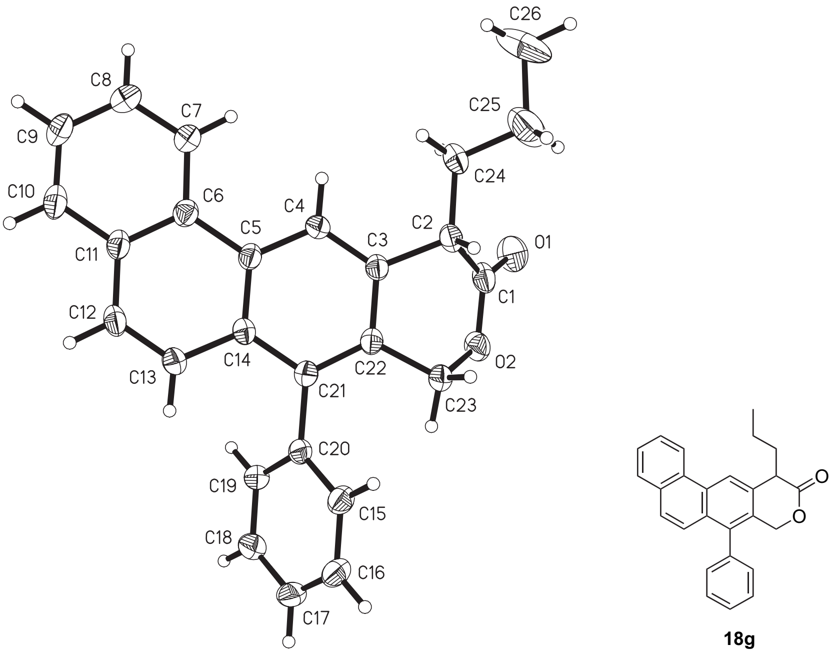


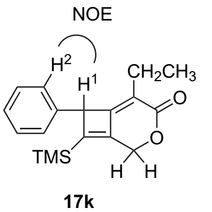
Figure 1. ORTEP representation of **18g**.

4. Experimental

4.1. General procedure

A solution of propargylic 2,3-allenoates **16** (0.25 mmol) in 6 mL of dry toluene was refluxed under Ar. After complete conversion as monitored by TLC (petroleum ether/ethyl acetate=5:1), the reaction was worked up by rotary evaporation and flash chromatography on silica gel (eluent: petroleum ether/ethyl ether=10:1) to afford the product **17** (and **18**).

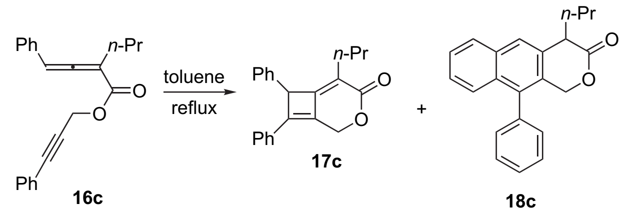
The following compounds were prepared according to the general procedure.



17k

Figure 2.

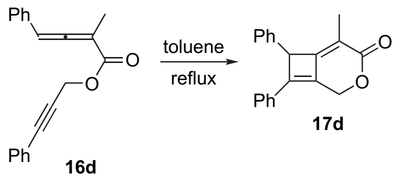
4.1.1. 7,8-Diphenyl-5-(*n*-propyl)-3-oxabicyclo[4.2.0]octa-1(8),5-dien-4-one (17c) and 10-phenyl-4-propyl-3,4-dihydro-1*H*-naphtho[2,3-*c*]pyrane-3-one (18c).



A solution of propargylic 2,3-allenoate **16c** (72 mg, 0.25 mmol) in 6 mL of dry toluene was refluxed under Ar for 4 h to afford 47 mg (65%) of **17c** and 9 mg (13%) of **18c**. Compound **17c**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40–7.22 (m, 8H), 7.18–7.08 (m, 2H), 5.63 (dd, J=18.0, 2.4 Hz, 1H), 5.53 (dd, J=18.0, 3.6 Hz, 1H), 4.93 (dd, J=3.6, 2.4 Hz, 1H), 2.28–2.12 (m, 1H), 2.10–1.95 (m, 1H), 1.40–1.20 (m, 2H), 0.73 (t, J=7.5 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 164.5, 153.8, 143.3, 136.9, 134.5, 131.7, 129.2, 128.9, 128.8, 127.7, 127.4, 127.2, 113.6, 67.1, 53.9, 27.8, 21.8, 13.7; MS (EI) *m/z* (%) 316 (M$^+$, 2.38), 84 (100); IR (neat) 3061, 3028, 2960, 2929, 2871, 1698, 1600, 1493, 1448, 1380, 1087 cm^{-1}; HRMS (MALDI/DHB) calcd for $C_{22}H_{21}O_2$ (M+H$^+$) 317.1536. Found 317.1540.

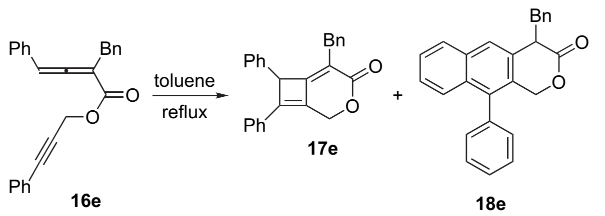
Compound **18c**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, J=7.8 Hz, 1H), 7.71 (s, 1H), 7.60–7.45 (m, 5H), 7.45–7.35 (m, 1H), 7.35–7.20 (m, 2H), 5.33 (d, J=14.4 Hz, 1H), 5.14 (d, J=14.4 Hz, 1H), 3.83 (t, J=6.9 Hz, 1H), 2.20–2.05 (m, 1H), 2.05–1.90 (m, 1H), 1.75–1.50 (m, 2H), 0.89 (t, J=6.9 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 173.2, 136.7, 133.1, 132.4, 130.0, 129.9, 128.7, 128.6, 128.1, 127.7, 127.2, 126.51, 126.49, 126.4, 125.0, 67.8, 46.4, 32.1, 20.7, 13.9; MS (EI) *m/z* (%) 316 (M$^+$, 5.63), 57 (100); IR (neat) 2955, 2923, 1750, 1367, 1248, 1037 cm^{-1}; HRMS (EI) calcd for $C_{22}H_{20}O_2$ (M$^+$) 316.1463. Found 316.1465.

4.1.2. 5-Methyl-7,8-diphenyl-3-oxabicyclo[4.2.0]octa-1(8),5-dien-4-one (17d).



A solution of propargylic 2,3-allenoate **16d** (71 mg, 0.25 mmol) in 6 mL of dry toluene was refluxed under Ar for 8 h to afford 58 mg (82%) of **17d**. Liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40–7.22 (m, 8H), 7.18–7.08 (m, 2H), 5.63 (d, J=17.5, 3.3 Hz, 1H), 5.53 (dd, J=17.5, 3.3 Hz, 1H), 4.96–4.92 (m, 1H), 1.72 (s, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 165.0, 153.6, 143.1, 136.7, 134.4, 131.7, 129.2, 128.9, 127.7, 127.4, 127.2, 109.2, 67.2, 53.6, 10.7; MS (EI) *m/z* (%) 288 (M$^+$, 8.24), 84 (100); IR (neat) 3060, 3027, 2921, 1698, 1601, 1493, 1447, 1374, 1281, 1240, 1086, 1074 cm^{-1}; HRMS (MALDI/DHB) calcd for $C_{20}H_{16}O_2Na$ (M+Na$^+$) 311.1043. Found 311.1046.

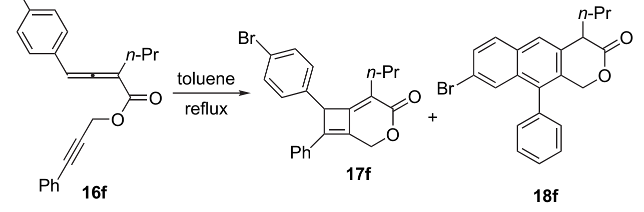
4.1.3. 5-Benzyl-7,8-diphenyl-3-oxabicyclo[4.2.0]octa-1(8),5-dien-4-one (17e) and 10-phenyl-4-benzyl-3,4-dihydro-1*H*-naphtho[2,3-*c*]pyrane-3-one (18e).



A solution of propargylic 2,3-allenoate **16e** (108 mg, 0.29 mmol) in 7 mL of dry toluene was refluxed under Ar for 5 h to afford 71 mg (66%) of **17e** and 5 mg (5%) of **18e**. Compound **17e**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40–7.22 (m, 8H), 7.20–7.08 (m, 5H), 7.05–6.90 (m, 2H), 5.62 (dd, J=17.8, 2.4 Hz, 1H), 5.51 (dd, J=17.8, 3.9 Hz, 1H), 4.87–4.80 (m, 1H), 3.64 (d, J=15.0 Hz, 1H), 3.33 (d, J=15.0 Hz, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 164.1, 154.1, 144.2, 139.0, 136.6, 134.5, 131.5, 129.4, 128.9, 128.8, 128.1, 127.7, 127.5, 127.2, 126.0, 112.7, 67.0, 53.9, 31.7; MS (EI) *m/z* (%) 364 (M$^+$, 11.71), 91 (100); IR (neat) 3061, 3027, 2921, 1701, 1601, 1493, 1452, 1380, 1076 cm^{-1}; HRMS (EI) calcd for $C_{26}H_{20}O_2$ (M$^+$) 364.1463. Found 364.1456.

Compound **18e**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, J=8.1 Hz, 1H), 7.58 (s, 1H), 7.56–7.44 (m, 5H), 7.44–7.35 (m, 1H), 7.30–7.20 (m, 4H), 7.16–7.05 (m, 3H), 4.96 (d, J=15.0 Hz, 1H), 4.64 (d, J=15.0 Hz, 1H), 4.22 (t, J=6.0 Hz, 1H), 3.46 (d, J=6.0 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 172.8, 137.4, 136.6, 136.2, 133.0, 131.5, 131.2, 129.9, 129.8, 129.3, 128.7, 128.5, 128.1, 127.8, 127.3, 127.0, 126.5, 126.4, 125.6, 68.1, 47.7, 37.9; MS (ESI) *m/z* (%) 365 (M+H$^+$, 100), 382 (M+NH$_4^+$, 60); IR (KBr) 3062, 2828, 1749, 1603, 1494, 1455, 1370, 1251, 1220, 1054 cm^{-1}; HRMS (EI) calcd for $C_{26}H_{20}O_2$ (M$^+$) 364.1463. Found 364.1470.

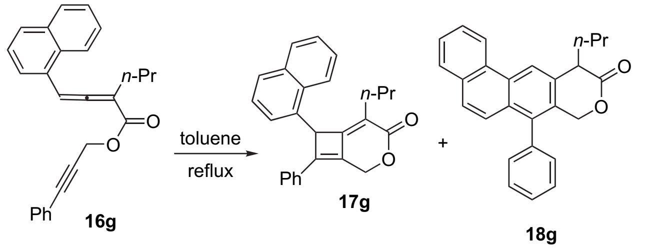
4.1.4. 7-(4-Bromophenyl)-8-phenyl-5-propyl-3-oxabicyclo[4.2.0]octa-1(8),5-dien-4-one (17f) and 10-phenyl-8-bromo-4-propyl-3,4-dihydro-1*H*-naphtho[2,3-*c*]pyrane-3-one (18f).



A solution of propargylic 2,3-allenoate **16f** (96 mg, 0.25 mmol) in 6 mL of dry toluene was refluxed under Ar for 12 h to afford 59 mg (61%) of **17f** and 5 mg (5%) of **18f**. Compound **17f**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, *J*=7.8 Hz, 2H), 7.38–7.26 (m, 3H), 7.23 (d, *J*=7.8 Hz, 2H), 7.12–7.04 (m, 2H), 5.60 (dd, *J*=18.0, 2.4 Hz, 1H), 5.51 (dd, *J*=18.0, 3.9 Hz, 1H), 4.93–4.85 (m, 1H), 2.28–2.12 (m, 1H), 2.08–1.90 (m, 1H), 1.40–1.20 (m, 2H), 0.74 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 164.3, 153.1, 143.0, 136.1, 134.9, 132.0, 131.5, 129.4, 129.2, 129.0, 127.1, 121.6, 114.0, 67.1, 53.3, 27.9, 21.8, 13.8; MS (EI) *m*/*z* (%) 395 ($M^+(^{81}Br)$, 2.55), 393 ($M^+(^{79}Br)$, 2.23), 105 (100); IR (neat) 2960, 2929, 2870, 1700, 1606, 1488, 1448, 1379, 1080, 1011 cm^{-1}; HRMS (EI) calcd for $C_{22}H_{19}O_2Br$ ($M+H^+$) 394.0568. Found 394.0568.

Compound **18f**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (d, *J*=9.0 Hz, 1H), 7.60–7.55 (m, 2H), 7.55–7.40 (m, 4H), 7.22–7.10 (m, 2H), 5.23 (d, *J*=14.4 Hz, 1H), 5.03 (d, *J*=14.4 Hz, 1H), 3.72 (t, *J*=7.2 Hz, 1H), 2.15–1.95 (m, 1H), 1.95–1.80 (m, 1H), 1.68–1.42 (m, 2H), 0.97 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 172.8, 136.0, 135.9, 133.0, 132.6, 131.5, 130.0, 129.8, 129.4, 128.93, 128.88, 128.6, 128.5, 128.4, 124.8, 120.8, 67.7, 46.3, 31.9, 20.7, 13.9; MS (EI) *m*/*z* (%) 395 ($M-H^+(^{81}Br)$, 78.43), 393 ($M-H^+(^{79}Br)$, 79.05), 215 (100); IR (neat) 2960, 2932, 2872, 1750, 1591, 1487, 1372, 1247, 1041 cm^{-1}; HRMS (EI) calcd for $C_{22}H_{19}O_2Br$ (M^+) 394.0568. Found 394.0570.

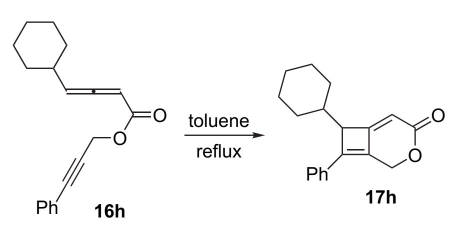
4.1.5. 7-Naphthalen-1-yl-8-phenyl-5-propyl-3-oxabicyclo[4.2.0]octa-1(8),5-dien-4-one (17g) and 7-phenyl-11-propyl-8,11-dihydro-9-oxabenzo[*a*]anthracen-10-one (18g).



A solution of propargylic 2,3-allenoate **16g** (92 mg, 0.25 mmol) in 6 mL of dry toluene was refluxed under Ar for 12 h to afford 49 mg (53%) of **17g** and 23 mg (25%) of **18g**. Compound **17g**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.36 (d, *J*=8.7 Hz, 1H), 7.94 (d, *J*=8.7 Hz, 1H), 7.81 (d, *J*=8.1 Hz, 1H), 7.70–7.50 (m, 2H), 7.45–7.32 (m, 2H), 7.32–7.25 (m, 3H), 7.18–7.05 (m, 2H), 5.81–5.78 (m, 1H), 5.68 (dd, *J*=17.7, 2.4 Hz, 1H), 5.59 (dd, *J*=17.7, 3.8 Hz, 1H), 2.10–1.85 (m, 2H), 1.40–1.15 (m, 1H), 1.15–0.80 (m, 1H), 0.46 (t, *J*=7.5 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 164.4, 154.3, 142.7, 134.6, 134.0, 132.5, 131.7, 131.5, 129.3, 129.2, 128.9, 128.2, 127.3, 126.4, 125.8, 125.7, 124.8, 122.6, 114.0, 67.2, 49.1, 28.0, 22.2, 13.4; MS (EI) *m*/*z* (%) 366 (M^+, 3.07), 105 (100); IR (neat) 3060, 2960, 2928, 2870, 1698, 1597, 1448, 1378, 1087 cm^{-1}; HRMS (MALDI/DHB) calcd for $C_{26}H_{22}O_2Na$ ($M+Na^+$) 389.1512. Found 389.1515.

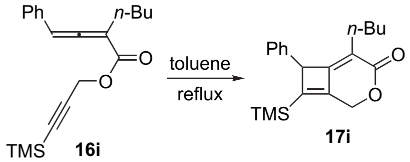
Compound **18g**: solid; mp 153–154 °C (petroleum ether/ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.73 (d, *J*=8.1 Hz, 1H), 8.54 (s, 1H), 7.87 (d, *J*=4.5 Hz, 1H), 7.75–7.40 (m, 7H), 7.40–7.22 (m, 2H), 5.39 (d, *J*=14.7 Hz, 1H), 5.15 (d, *J*=14.7 Hz, 1H), 3.95 (t, *J*=7.5 Hz, 1H), 2.25–2.08 (m, 1H), 2.08–1.95 (m, 1H), 1.75–1.50 (m, 2H), 1.08 (t, *J*=7.5 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 173.1, 137.0, 133.0, 131.7, 130.1, 129.9, 129.7, 129.6, 128.74, 128.68, 128.56, 128.1, 127.7, 127.3, 127.1, 126.9, 124.5, 122.7, 120.1, 68.0, 46.8, 32.8, 20.7, 13.9; MS (EI) *m*/*z* (%) 366 (M^+, 29.12), 365 (100); IR (neat) 2958, 2871, 1743, 1598, 1379, 1210, 1133, 1041, 1016 cm^{-1}; Anal. Calcd for $C_{26}H_{22}O_2$: C, 85.22; H, 6.05. Found: C, 85.02; H, 5.99.

4.1.6. 7-Cyclohexyl-8-phenyl-3-oxabicyclo[4.2.0]octa-1(8),5-dien-4-one (17h).



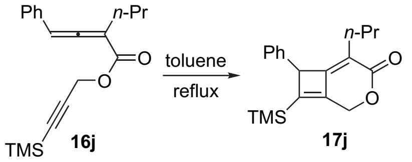
A solution of propargylic 2,3-allenoate **16h** (70 mg, 0.25 mmol) in 5 mL of dry toluene was refluxed under Ar for 72 h to afford 25 mg (36%) of the product **17h**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50–7.30 (m, 3H), 7.30–7.20 (m, 2H), 5.56 (s, 1H), 5.51 (dd, *J*=17.7, 2.1 Hz, 1H), 5.39 (dd, *J*=17.7, 3.9 Hz, 1H), 3.95–3.89 (m, 1H), 2.05–0.80 (m, 11H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 163.2, 159.0, 146.8, 132.5, 132.4, 129.7, 129.0, 127.2, 101.6, 66.8, 56.0, 37.9, 32.4, 28.3, 26.4, 26.1, 25.9; MS (EI) *m*/*z* (%) 280 (M^+, 7.94), 105 (100); IR (neat) 2923, 2851, 1708, 1600, 1447, 1372, 1033 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{20}O_2$ (M^+) 280.1463. Found 280.1464.

4.1.7. 5-Butyl-7-phenyl-8-(trimethylsilyl)-3-oxabicyclo[4.2.0]octa-1(8),5-dien-4-one (17i).



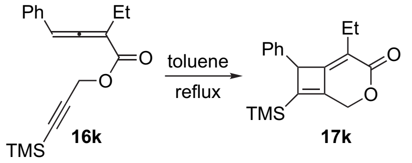
A solution of propargylic 2,3-allenoate **16i** (80 mg, 0.25 mmol) in 6 mL of dry toluene was refluxed under Ar for 9 h to afford 55 mg (69%) of the product **17i**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38–7.18 (m, 5H), 5.38–5.20 (m, 2H), 4.57 (t, *J*=3.0 Hz, 1H), 2.25–2.10 (m, 1H), 2.00–1.83 (m, 1H), 1.35–1.20 (m, 2H), 1.20–1.03 (m, 2H), 0.72 (t, *J*=3.9 Hz, 3H), −0.03 (s, 9H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 164.6, 154.8, 154.1, 151.5, 138.7, 128.5, 127.4, 127.3, 113.3, 67.6, 55.7, 30.3, 25.4, 22.3, 13.6, −2.0; MS (EI) *m*/*z* (%) 326 (M^+, 0.63), 73 (100); IR (neat) 3028, 2956, 2929, 2871, 1704, 1602, 1494, 1453, 1368, 1250, 1096 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{26}O_2Si$ (M^+) 326.1702. Found 326.1706.

4.1.8. 7-Phenyl-5-propyl-8-(trimethylsilyl)-3-oxabicyclo[4.2.0]octa-1(8),5-dien-4-one (17j).



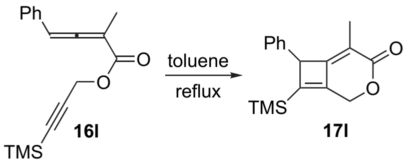
A solution of propargylic 2,3-allenoate **16j** (74 mg, 0.24 mmol) in 6 mL of dry toluene was refluxed under Ar for 8 h to afford 55 mg (74%) of the product **17j**: liquid; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.35–7.18 (m, 5H), 5.40–5.20 (m, 2H), 4.57 (t, J=3.3 Hz, 1H), 2.25–2.10 (m, 1H), 2.00–1.83 (m, 1H), 1.40–1.20 (m, 2H), 0.72 (t, J=7.5 Hz, 3H), −0.03 (s, 9H); ^{13}C NMR (75.4 MHz, CDCl$_3$) δ 164.4, 154.8, 154.2, 151.5, 138.7, 128.6, 127.4, 127.3, 113.2, 67.6, 55.7, 27.7, 21.5, 13.8, −1.9; MS (EI) *m/z* (%) 312 (M$^+$, 0.94), 73 (100); IR (neat) 3028, 2958, 2930, 2871, 1704, 1494, 1453, 1366, 1250, 1117, 1099 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{24}O_2Si$ (M$^+$) 312.1546. Found 312.1552.

4.1.9. 5-Ethyl-7-phenyl-8-(trimethylsilyl)-3-oxabicyclo[4.2.0]octa-1(8),5-dien-4-one (17k).



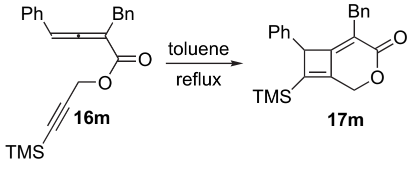
A solution of propargylic 2,3-allenoate **16k** (97 mg, 0.33 mmol) in 8 mL of dry toluene was refluxed under Ar for 24 h to afford 73 mg (75%) of the product **17k**: liquid; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.40–7.20 (m, 5H), 5.40–5.22 (m, 2H), 4.64 (t, J=3.3 Hz, 1H), 2.30–2.15 (m, 1H), 2.15–2.02 (m, 1H), 0.88 (t, J=7.8 Hz, 3H), 0.004 (s, 9H); ^{13}C NMR (75.4 MHz, CDCl$_3$) δ 164.3, 154.4, 154.1, 151.4, 138.9, 128.5, 127.3, 127.2, 114.6, 67.5, 55.7, 19.4, 12.7, −2.0; MS (EI) *m/z* (%) 298 (M$^+$, 0.67), 73 (100); IR (neat) 3062, 3028, 2959, 1704, 1494, 1452, 1372, 1250, 1118 cm^{-1}; HRMS (MALDI/DHB) calcd for $C_{18}H_{22}O_2SiNa$ (M+Na$^+$) 321.1281. Found 321.1278.

4.1.10. 5-Methyl-7-phenyl-8-(trimethylsilyl)-3-oxabicyclo[4.2.0]octa-1(8),5-dien-4-one (17l).



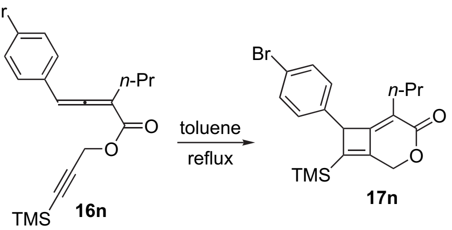
A solution of propargylic 2,3-allenoate **16l** (94 mg, 0.33 mmol) in 8 mL of dry toluene was refluxed under Ar for 48 h to afford 47 mg (50%) of the product **17l**: liquid; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.40–7.20 (m, 5H), 5.40–5.22 (m, 2H), 4.61 (t, J=3.0 Hz, 1H), 1.67 (s, 3H), 0.00 (s, 9H); ^{13}C NMR (75.4 MHz, CDCl$_3$) δ 164.8, 154.7, 153.9, 151.3, 138.4, 128.6, 127.3, 127.2, 108.8, 67.7, 55.2, 10.5, −2.0; MS (EI) *m/z* (%) 284 (M$^+$, 2.56), 73 (100); IR (neat) 2954, 2920, 1705, 1452, 1368, 1249, 1111 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{20}O_2Si$ (M$^+$) 284.1233. Found 284.1242.

4.1.11. 5-Benzyl-7-phenyl-8-(trimethylsilyl)-3-oxabicyclo[4.2.0]octa-1(8),5-dien-4-one (17m).



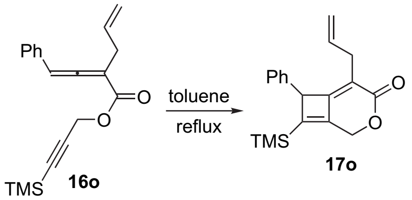
A solution of propargylic 2,3-allenoate **16m** (92 mg, 0.25 mmol) in 6 mL of dry toluene was refluxed under Ar for 28 h to afford 64 mg (70%) of the product **17m**: liquid; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.28–7.15 (m, 3H), 7.10–7.00 (m, 5H), 6.92–6.82 (m, 2H), 5.30–5.12 (m, 2H), 4.35 (t, J=3.0 Hz, 1H), 3.52 (d, J=15.0 Hz, 1H), 3.14 (d, J=15.0 Hz, 1H), −0.11 (s, 9H); ^{13}C NMR (75.4 MHz, CDCl$_3$) δ 164.1, 155.3, 155.2, 151.5, 138.8, 138.3, 129.0, 128.5, 128.1, 127.41, 127.36, 126.0, 112.2, 67.6, 55.6, 31.6, −2.0; MS (EI) *m/z* (%) 360 (M$^+$, 1.05), 73 (100); IR (neat) 3061, 3028, 2953, 1704, 1602, 1494, 1453, 1367, 1249, 1101 cm^{-1}; HRMS (EI) calcd for $C_{23}H_{24}O_2Si$ (M$^+$) 360.1546. Found 360.1545.

4.1.12. 7-(4-Bromophenyl)-5-propyl-8-(trimethylsilyl)-3-oxabicyclo[4.2.0]octa-1(8),5-dien-4-one (17n).



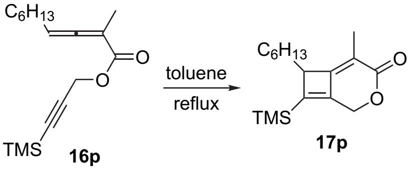
A solution of propargylic 2,3-allenoate **16n** (95 mg, 0.25 mmol) in 6 mL of dry toluene was refluxed under Ar for 48 h to afford 67 mg (71%) of the product **17n**: liquid; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.42 (d, J=9.0 Hz, 2H), 7.10 (d, J=9.0 Hz, 2H), 5.35–5.18 (m, 2H), 4.52 (t, J=3.6 Hz, 1H), 2.25–2.10 (m, 1H), 1.95–1.80 (m, 1H), 1.40–1.20 (m, 2H), 0.72 (t, J=7.2 Hz, 3H), −0.04 (s, 9H); ^{13}C NMR (75.4 MHz, CDCl$_3$) δ 164.1, 154.1, 153.8, 151.9, 137.9, 131.7, 129.0, 121.1, 113.5, 67.5, 55.0, 27.7, 21.4, 13.8, −1.9; MS (EI) *m/z* (%) 391 (M$^+$(^{81}Br), 0.36), 389 (M$^+$(^{79}Br), 0.31), 73 (100); IR (neat) 2958, 2931, 2871, 1705, 1487, 1451, 1404, 1366, 1250, 1116, 1101, 1072, 1011 cm^{-1}; HRMS (MALDI/DHB) calcd for $C_{19}H_{23}O_2SiBrNa$ (M+Na$^+$) 413.0543. Found 413.0534.

4.1.13. 5-Allyl-7-phenyl-8-(trimethylsilyl)-3-oxabicyclo[4.2.0]octa-1(8),5-dien-4-one (17o).



A solution of propargylic 2,3-allenoate **16o** (70 mg, 0.24 mmol) in 6 mL of dry toluene was refluxed under Ar for 44 h to afford 45 mg (64%) of the product **17o**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28–7.08 (m, 5H), 5.62–5.45 (m, 1H), 5.30–5.12 (m, 2H), 4.80–4.65 (m, 2H), 4.50 (t, J=3.0 Hz, 1H), 2.85 (dd, J=15.6, 6.6 Hz, 1H), 2.64 (dd, J=15.6, 6.6 Hz, 1H), −0.12 (s, 9H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 163.9, 155.1, 151.3, 138.6, 134.4, 128.5, 127.4, 116.2, 111.0, 67.6, 55.6, 30.1, −2.0; MS (EI) m/z (%) 310 (M^+, 1.55), 73 (100); IR (neat) 2954, 1705, 1638, 1602, 1494, 1452, 1367, 1249, 1100 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{22}O_2Si$ (M^+) 310.1389. Found 310.1382.

4.1.14. 7-Hexyl-5-methyl-8-(trimethylsilyl)-3-oxabicyclo[4.2.0]octa-1(8),5-dien-4-one (17p).



A solution of propargylic 2,3-allenoate **16p** (69 mg, 0.24 mmol) in 6 mL of dry toluene was refluxed under Ar for 72 h to afford 17 mg (25%) of the product **17p**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.09 (d, J=2.7 Hz, 2H), 3.55–3.45 (m, 1H), 1.76 (s, 3H), 1.70–1.50 (m, 2H), 1.35–1.10 (m, 8H), 0.81 (t, J=6.9 Hz, 3H), 0.08 (s, 9H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 164.9, 156.0, 152.9, 149.4, 109.0, 67.8, 51.9, 31.9, 31.7, 29.5, 27.1, 22.6, 14.1, 11.7, −1.6; MS (EI) m/z (%) 292 (M^+, 0.47), 43 (100); IR (neat) 2956, 2926, 2856, 1708, 1454, 1366, 1249, 1109 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{28}O_2Si$ (M^+) 292.1859. Found 292.1854.

Acknowledgements

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.05.040.

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9. Crystal data for compound **18g**: $C_{26}H_{22}O_2$, MW=366.44, orthorhombic, space group *Pbca*, final R indices [$I>2\sigma(I)$], $R1=0.0700$, $wR2=0.1788$, $a=12.5143(17)$ Å, $b=7.7229(11)$ Å, $c=39.906(5)$ Å, $\alpha=90°$, $\beta=90°$, $\gamma=90°$, $V=3856.8(9)$ Å^3, $T=293(2)$ K, $Z=8$, reflections collected/unique: 19,656/3792 (R(int)=0.1149). CCDC: 613373.