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Rhodium-catalyzed arylative cyclization of alkynones induced by addition of arylboronic acids

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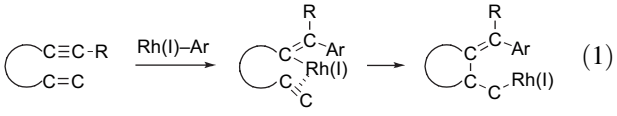
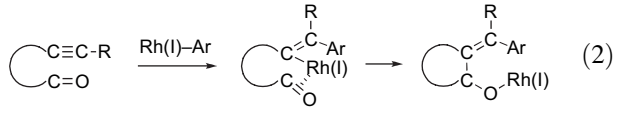
Abstract—Alkynones react with arylboronic acids in the presence of a rhodium(I) catalyst to afford four- and five-membered-ring cyclic alcohols equipped with a tetrasubstituted exocyclic olefin. The cyclic allylic alcohol skeleton is constructed by the carbon–carbon bond formation between the carbonyl group and an alkenylrhodium(I) intermediate formed by the regioselective addition of an arylrhodium(I) species across the carbon–carbon triple bond.

1. Introduction

Transition-metal-catalyzed cascade reactions involving multiple carbometallation steps serve as a powerful method for the preparation of complex cyclic molecules in an atom-economical manner.[1] A molecule containing two different unsaturated functionalities that can act as an acceptor of an organometallic species is particularly an attractive substrate for such cascade reactions. The initial intermolecular carbometallation onto the more reactive unsaturated functionality of the two results in the incorporation of a reactive carbon–metal linkage in the substrate molecule. The newly generated carbon–metal bond then adds to the secondary functionality in an intramolecular way to construct a carbocyclic skeleton. Recently, rhodium(I)-catalyzed cascade reactions[2] have emerged as a complement to the well-studied palladium-catalyzed cascade sequences.[3] High functional group compatibilities and stereoselectivities have been observed in a number of the rhodium-catalyzed reactions. For the rhodium(I)-catalyzed cascade reactions to start, an alkyne moiety can provide a convenient entry point for incorporation of an active Csp^2–Rh linkage by way of intermolecular carborhodation.[4] The resultant alkenylrhodium(I) species exhibits an enhanced reactivity to the second unsaturated functionality in the molecule than in an intermolecular case.[5] For example, when 1,6-enynes were treated with arylboronic acids in the presence of a rhodium(I) catalyst, an alkenylrhodium(I) intermediate formed by the regioselective addition of an arylrhodium(I) species across the carbon–carbon triple bond subsequently underwent an intramolecular carborhodation to the carbon–carbon double bond to give arylative cyclization product (Eq. 1).[5a] Like carbon–carbon double and triple bonds, the carbonyl groups of aldehydes and ketones can also accept an organorhodium(I) species to form a carbon–carbon bond.[6] We envisaged that an analogous sequential addition/cyclization reaction would be feasible with an alkynone, if a carbon–carbon triple bond and a carbonyl group are appropriately arranged in the molecule (Eq. 2). In this paper, we wish to describe our study on the rhodium-catalyzed reaction of alkynones with arylboronic acids, which has led to the development of a new acyl 1,3-migration reaction and a two-carbon-atom ring-expansion reaction.[7]



(1)



(2)

2. Results and discussion

2.1. Arylative cyclization of alkynones

We took 5-alkyn-1-ones **1** having a three-carbon tether between the carbon–carbon triple bond and the ketonic carbonyl group as the model substrate and examined the reaction with phenylboronic acid (**2a**). As for a rhodium catalyst,

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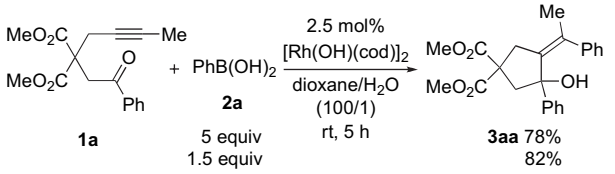
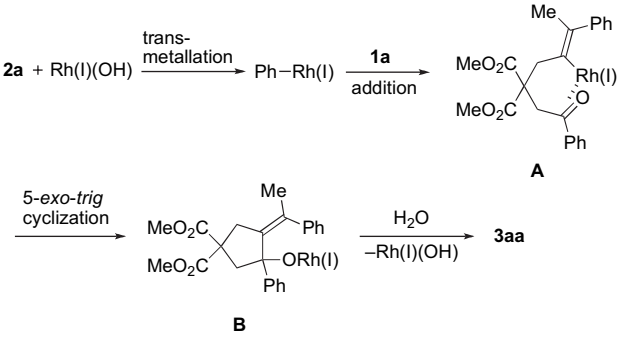
we employed hydroxo(diolefin)rhodium(I) complexes,[8] which successfully catalyzed the cascade reaction of 1,6-enynes with arylboronic acids.[5a] Thus, 5-alkyn-1-one **1a** was treated with **2a** (5.0 equiv) in the presence of [Rh(OH)(cod)]$_2$ (5 mol % of Rh, cod=cycloocta-1,5-diene) in dioxane/H_2O (100:1) at room temperature for 5 h under an argon atmosphere. Chromatographic isolation afforded cyclopentanol **3aa** equipped with a tetrasubstituted exocyclic olefin in 78% yield (Eq. 3). The *Z* configuration of the exocyclic double bond was corroborated by a difference NOE study. Interestingly, the use of 1.5 equiv of **2a** was sufficient to obtain a product yield of 82%. However, a lower catalyst loading (1–3 mol % of Rh) suffered from a poor reproducibility, probably due to deterioration of the catalyst.



(3)

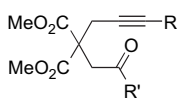
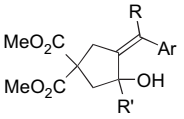
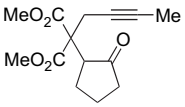
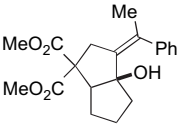
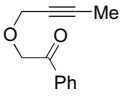
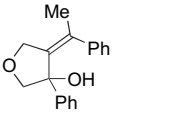
The proposed reaction pathway is depicted in Scheme 1. A phenylrhodium(I) species is initially generated by transmetallation of hydroxorhodium(I) with **2a**. The ketonic carbonyl group directs the regioselective *cis* carborhodation across the carbon–carbon triple bond.[9] The resulting alkenylrhodium(I) intermediate **A** undergoes intramolecular nucleophilic addition to the carbonyl group in a 5-*exo* mode, forming the rhodium(I) alkoxide **B**. Finally, the product **3aa** was released by protodemetalation with regeneration of the catalytically active hydroxorhodium(I) species. Of note is that carborhodation onto the carbon–carbon triple bond and the ketonic carbonyl group proceeds at room temperature.



Scheme 1.

The results obtained with a variety of 5-alkyn-1-ones **1** and arylboronic acids **2** are summarized in Table 1. The catalytic process worked well with a sterically and electronically diverse array of arylboronic acids **2b**–**2g** to give the corresponding products **3ab**–**3ag** in 69–82% yield (entries 1–6). 5-Alkyn-1-ones **1b** and **1c** also gave the corresponding products **3ba** and **3ca** in good yield (entries 7 and 8). In the case of 5-alkyn-1-al **1d**, a phenylrhodium(I) initially formed preferentially added to the carbon–carbon triple bond even in the presence of an aldehydic carbonyl group to give the secondary allylic alcohol **3da** in 62% yield (entry 9). The

Table 1. Rhodium(I)-catalyzed reaction of 5-alkyn-1-ones **1** and arylboronic acids **2**[a]

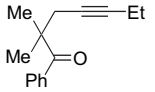
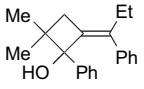
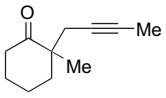
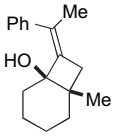
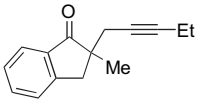
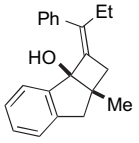
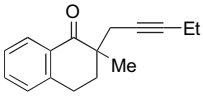
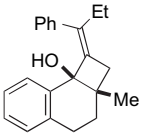
Entry	Substrate **1**	ArB(OH)$_2$ **2**	Product **3**	Yield (%)[b]
				
1	**1a** R=Me R′=Ph	**2b** 4-F–C_6H_4	**3ab**	76
2	**1a**	**2c** 4-NO_2–C_6H_4	**3ac**	78
3	**1a**	**2d** 4-Me–C_6H_4	**3ad**	69
4	**1a**	**2e** 3-MeO–C_6H_4	**3ae**	77
5	**1a**	**2f** 3-Cl–C_6H_4	**3af**	82
6	**1a**	**2g** 2-Me–C_6H_4	**3ag**	80[c]
7	**1b** R=*n*-Bu R′=Ph	**2a** Ph	**3ba**	82
8	**1c** R=Me R′=Me	**2a** Ph	**3ca**	72
9	**1d** R=Me R′=H	**2a** Ph	**3da**	62
10	 **1e**	**2a** Ph	 **3ea**	82
11	 **1f**	**2a** Ph	 **3fa**	21

[a] Reaction conditions: **1** (0.2 mmol), **2** (1.0 mmol), [Rh(OH)(cod)]$_2$ (5 mol % of Rh), dioxane/H_2O (2.0 mL/20 μL), room temperature, 2–5 h.
[b] Isolated yield.
[c] A mixture of atropisomers (56:44).

reaction of substrate **1f** with an ether tether gave the product **3fa** in only 21% yield due to the lower regioselectivity of the initial 1,2-addtion of a phenylrhodium(I) species (entry 11). We assume that the high regioselectivity of the initial 1,2-addition observed with **1a**–**1e** is to be ascribed not only to the carbonyl coordination but also to the steric effects of the two alkyl substituents flanking the carbon–carbon triple bond. The tether substituent connected to a carbonyl group through the malonate ester was considerably bulkier than the other with **1a**–**1e**.[10] The corresponding steric contrast of **1f** was not sufficient to cause a regioselective addition.

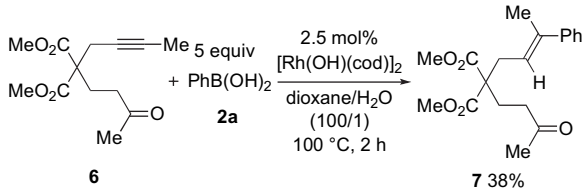
Next, we examined analogous cyclization in a 4-*exo-trig* mode (Table 2). Thus, 4-alkyn-1-one **4a** having a two-carbon tether was treated with phenylboronic acid (**2a**, 5.0 equiv) under conditions similar to those used for **1**. Chromatographic isolation afforded cyclobutanol **5aa** in 67% yield together with a small amount of 1,2-addition product (6%) (entry 1). It was noteworthy that an intermediate alkenylrhodium(I) species underwent intramolecular nucleophilic carbonyl addition in a 4-*exo-trig* mode, although such four-membered-ring formation would suffer from developing ring strain. The minor product was formed by the 1,2-addition of a phenylrhodium(I) species to the carbon–carbon triple bond with the opposite regiochemistry and subsequent protonolysis. Similar results were obtained with the reactions of 4-alkyn-1-ones **4b**–**4d** possessing cyclic structures, which afforded the corresponding bicyclic products **5ba**–**5da** in 58–61% yield (entries 2–4). The regioselectivities observed with 4-alkyn-1-ones were generally lower than those of 5-alkyn-1-ones.

Table 2. Rhodium(I)-catalyzed reaction of 4-alkyn-1-ones **4** and phenylboronic acid (**2a**)[a]

Entry	Substrate **4**	Product **5**	Yield (%)[b]
1	 **4a**	 **5aa**	67[c]
2	 **4b**	 **5ba**	58
3	 **4c**	 **5ca**	58
4	 **4d**	 **5da**	61

[a] Reaction conditions: **4** (0.25 mmol), **2a** (1.25 mmol), $[Rh(OH)(cod)]_2$ (5 mol % of Rh), dioxane/H_2O (2.5 mL/25 μL), room temperature, 6–25 h.
[b] Isolated yield.
[c] Obtained as a mixture with 1,2-adduct (6%).

In the case of 6-alkyn-1-ones **6** having a four-carbon tether, even the initial 1,2-addition of a phenylrhodium(I) species failed to occur at room temperature. When the reaction temperature was raised to 100 °C, 1,2-addition took place but the resultant alkenylrhodium(I) intermediate failed to add the carbonyl group, giving the hydrolyzed compound **7** as the major product (Eq. 4).

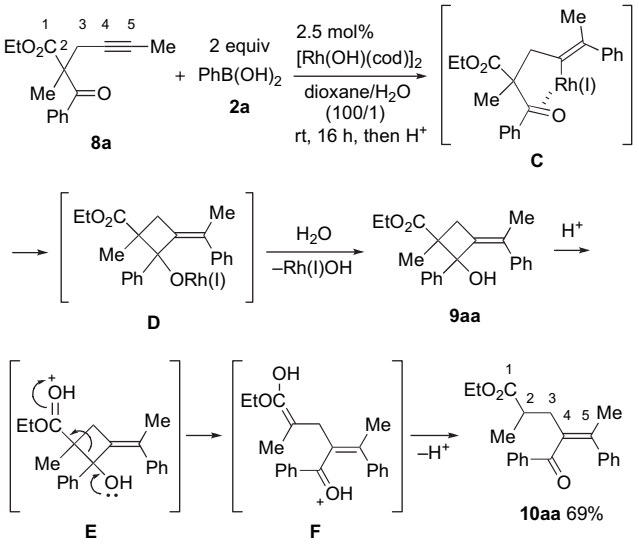


(4)

The contrasting results obtained with **1**, **4**, and **6** indicated that, with alkynones **1** and **4**, coordination of the carbonyl group to rhodium facilitates the 1,2-addition to the alkyne moiety and subsequent intramolecular nucleophilic addition to the carbonyl group and that the accelerating effect by coordination significantly depends on the tether length.[5e] Of note was that the four-membered ring formation was facile whereas the six-membered ring formation failed.

2.2. Arylative acyl 1,3-migration of acetylenic β-ketoesters

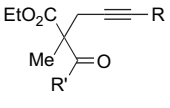
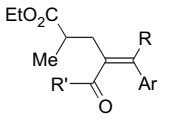
We next synthesized acetylenic β-ketoesters **8** as the substrate containing a 4-alkyn-1-one substructure by a simple alkylation reaction of a β-ketoester with 1-bromo-2-butyne. Compound **8a** was subjected to the standard reaction conditions for 4-alkyn-1-ones, and after 16 h, the ^1H NMR spectra of the crude reaction mixture was measured prior to chromatographic purification. It was suggested that, in addition to the expected cyclobutanol **9aa**, the mixture contained the ring-opened product **10aa** (**9aa/10aa**=ca.7:3). Subsequent purification by silica gel chromatography afforded only **10aa** in 69% isolated yield (Scheme 2). Therefore, the reaction is assumed to proceed in a similar manner to that of 4-alkyn-1-ones **4**, leading to the initial formation of cyclobutanol **9aa**. Then, opening of the cyclobutane ring through a retro-aldol reaction affords the product **10aa**. The retro-aldol reaction is promoted by the acidic nature of silica gel during purification.



Scheme 2.

During the transformation of **8a** to **10aa**, a phenyl group was introduced on the C(5) atom of **8a** and the benzoyl group bound to the C(2) atom of **8a** migrated to the C(4) atom of the product **10aa**.[11] This acyl 1,3-migration reaction was applied to a variety of combinations of acetylenic β-ketoesters **8** and arylboronic acids **2** (Table 3). Both electron-rich

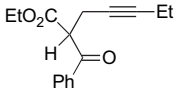
Table 3. Rhodium(I)-catalyzed acyl 1,3-migration in the reaction of acetylenic β-ketoesters **8** with arylboronic acids **2**[a]

Entry	Substrate **8**	$ArB(OH)_2$ **2**	Product **10**	Yield (%)[b]
				
1	**8a** R=Me R′=Ph	**2b** 4-F–C_6H_4	**10ab**	63
2	**8a**	**2d** 4-Me–C_6H_4	**10ad**	75
3	**8a**	**2e** 3-MeO–C_6H_4	**10ae**	77
4	**8a**	**2f** 3-Cl–C_6H_4	**10af**	66
5	**8b** R=Et R′=Ph	**2a** Ph	**10ba**	92
6	**8c** R=Et R′=Me	**2a** Ph	**10ca**	67
7	**8d** R=TMS R′=Ph	**2a** Ph	**10da**	25

[a] Reaction conditions: **8** (0.2 mmol), **2** (0.6–1.0 mmol), $[Rh(OH)(cod)]_2$ (5 mol % of Rh), dioxane/H_2O (2.0 mL/20 μL), room temperature, 5 h; then treatment with aq NH_4Cl.
[b] Isolated yield.

and -deficient arylboronic acids were suitably reactive (entries 1–4). In the case of *o*-tolylboronic acid (**2g**), however, the alkenylrhodium(I) intermediate was not reactive enough to add the benzoyl group probably due to steric reasons, affording a simple 1,2-adduct. Substituents at the alkyne termini were also examined. A better yield was obtained with ethyl-substituted **8b** than with methyl-substituted **8a** (entry 5). Methyl ketone **8c** also underwent the acyl 1,3-migration (entry 6). The reaction of trimethylsilyl-substituted alkyne **8d** suffered from lower regioselectivity of the initial 1,2-addition to give the product **10da** in only 25% yield (entry 7). We assume that the increased steric bulkiness of the trimethylsilyl group deteriorated the regioselectivity.

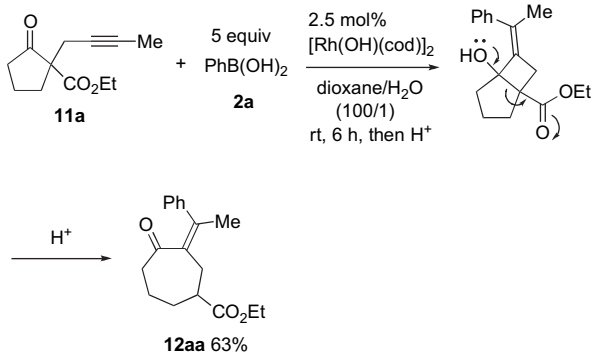
Acetylenic β-ketoesters **8e** having an active hydrogen failed to undergo the cyclization reaction, probably because of the predominance of a stable enol tautomer (Fig. 1).



8e

Figure 1.

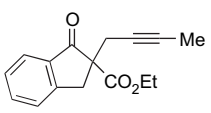
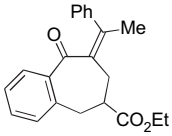
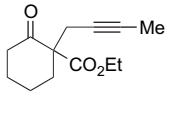
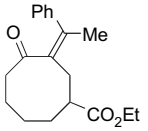
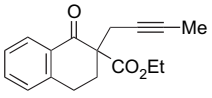
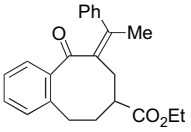
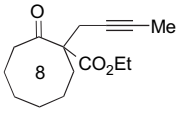
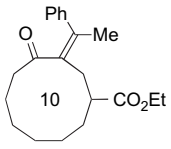
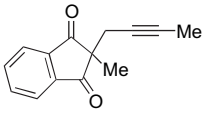
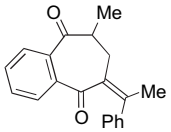
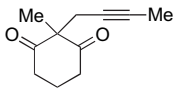
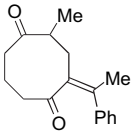
We next envisioned that, if the 4-alkyn-1-one substructure was installed in a cyclic skeleton, an analogous acyl 1,3-migration process would expand the ring by two carbons to serve as a synthetic method of medium-sized ring carbocyclic skeletons.[12,13] Thus, the cyclic substrate **11a** was reacted with phenylboronic acid (**2a**) under the similar reaction conditions. The resulting reaction mixture was successively treated with aq NH_4Cl for 24 h to promote a retro-aldol process. As expected, the cycloheptanone **12aa** was produced in 63% isolated yield through the arylative cyclization and the following ring expansion (Scheme 3).



Scheme 3.

As listed in Table 4, the catalytic ring-expansion process worked well with substrates of five-, six-, and eight-membered-ring structures **11b**–**11e** to give the corresponding seven-, eight-, and ten-membered ring products **12ba**–**12ea** in 49–58% yield (entries 1–4). In addition to the major products **12**, the simple 1,2-adducts to the carbon–carbon triple bond with both regiochemistries were obtained as by-products. Cyclic 1,3-diketones **11f** and **11g** also underwent the analogous ring-expansion reaction (entries 5 and 6). The

Table 4. Rhodium(I)-catalyzed two-carbon-atom ring expansion of acetylenic β-ketoesters **11** with phenylboronic acid (**2a**)[a]

Entry	Substrate **11**	Product **12**	Yield (%)[b]
1	 **11b**	 **12ba**	51
2	 **11c**	 **12ca**	49
3	 **11d**	 **12da**	58
4	 **11e**	 **12ea**	54[c]
5	 **11f**	 **12fa**	57
6	 **11g**	 **12ga**	66

[a] Reaction conditions: **11** (0.2 mmol), **2a** (1.0 mmol), $[Rh(OH)(cod)]_2$ (5 mol % of Rh), dioxane/H_2O (2.0 mL/20 μL), room temperature, 3–24 h; then treatment with aq NH_4Cl.
[b] Isolated yield.
[c] 100 °C.

ring-opening reaction of intermediate cyclobutanols formed from substrates **11c**, **11d**, and **11f** proceeded more slowly than that of **11a** under the weakly acidic conditions, and thus, required longer period of time for completion.

3. Conclusion

We have developed new cyclization reactions of alkynones induced by the rhodium-catalyzed regioselective addition of an arylrhodium(I) species across the carbon–carbon triple bond at room temperature. An alkenylrhodium(I) intermediate subsequently undergoes intramolecular carbonyl addition in 4-*exo* and 5-*exo-trig* modes to construct the carbocyclic alcohols under similar reaction conditions. An

addition reaction of ordinary alkynes with arylboronic acids requires heating over 80 °C.[4,9] The presence of the carbonyl group as the secondary acceptor functionality greatly contributes to the high reactivity. This method has been applied to a new acyl 1,3-migration reaction and a two-carbon-atom ring-expansion reaction, which gives a convenient access to medium-sized ring compounds.

4. Experimental

4.1. General

All manipulations were carried out with standard Schlenk technique under an argon atmosphere. Preparative thin layer chromatography was performed with silica gel 60 PF_{254} (Merck). ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 2000 (^1H at 300.07 MHz and ^{13}C at 75.46 MHz) spectrometer. NMR data were obtained in $CDCl_3$ otherwise noted. Proton chemical shifts were referenced to the residual proton signal of the solvent at 7.26 ppm. Carbon chemical shifts were referenced to the carbon signal of the solvent at 77.00 ppm. High resolution mass spectra were recorded on a JOEL JMS-SX102A spectrometer. IR spectra were recorded on a Shimadzu FTIR-8100 spectrometer. 1,4-Dioxane was distilled over sodium benzophenone ketyl prior to use. All other commercially available chemical resources were used without further purifications.

4.2. Starting materials

4.2.1. Dimethyl 2-(but-2-ynyl)-2-(2-oxo-2-phenylethyl)-malonate (1a). IR (neat) 2955, 1740, 1688, 1435, 1291, 1208 cm^{-1}; ^1H NMR δ 1.71 (t, J=2.4 Hz, 3H), 3.04 (q, J=2.5 Hz, 2H), 3.76 (s, 6H), 3.89 (s, 2H), 7.44–7.52 (m, 2H), 7.56–7.63 (m, 1H), 7.98–8.04 (m, 2H); ^{13}C NMR δ 3.5, 23.8, 41.1, 53.1, 54.9, 73.7, 79.4, 128.1, 128.6, 133.4, 136.4, 170.1, 196.8; HRMS (EI) calcd for $C_{17}H_{18}O_5$ (M^+) 302.1154, found 302.1155.

4.2.2. Dimethyl 2-(hept-2-ynyl)-2-(2-oxo-2-phenylethyl)-malonate (1b). IR (neat) 2955, 1743, 1688, 1435, 1291, 1207 cm^{-1}; ^1H NMR δ 0.84 (t, J=7.1 Hz, 3H), 1.22–1.45 (m, 4H), 2.02–2.13 (m, 2H), 3.05 (t, J=2.4 Hz, 2H), 3.76 (s, 6H), 3.90 (s, 2H), 7.43–7.53 (m, 2H), 7.55–7.63 (m, 1H), 7.98–8.06 (m, 2H); ^{13}C NMR δ 13.6, 18.3, 21.8, 23.8, 30.9, 41.1, 53.0, 55.0, 74.6, 84.1, 128.1, 128.6, 133.4, 136.4, 170.1, 196.8; HRMS (CI) calcd for $C_{20}H_{25}O_5$ ($M+H^+$) 345.1702, found 345.1706.

4.2.3. Dimethyl 2-(but-2-ynyl)-2-(2-oxo-propyl)malonate (1c). IR (Nujol) 2909, 1748, 1715, 1291, 1258, 1204 cm^{-1}; ^1H NMR δ 1.75 (t, J=2.7 Hz, 3H), 2.18 (s, 3H), 2.92 (q, J=2.5 Hz, 2H), 3.32 (s, 2H), 3.72 (s, 6H); ^{13}C NMR δ 3.5, 23.8, 30.2, 45.5, 53.0, 54.7, 73.6, 79.2, 169.9, 205.4; HRMS (CI) calcd for $C_{12}H_{17}O_5$ ($M+H^+$) 241.1076, found 241.1075.

4.2.4. Dimethyl 2-(but-2-ynyl)-2-(2-oxo-ethyl)malonate (1d). IR (Nujol) 2757, 1737, 1291, 1200, 1092, 1057 cm^{-1}; ^1H NMR δ 1.74 (t, J=2.6 Hz, 3H), 2.90 (q, J=2.5 Hz, 2H), 3.21 (d, J=1.2 Hz, 2H), 3.75 (s, 6H), 9.74 (t, J=1.1 Hz, 1H); ^{13}C NMR δ 3.5, 24.4, 46.2, 53.2, 54.3, 73.1, 79.9, 169.6, 198.7; HRMS (CI) calcd for $C_{11}H_{15}O_5$ ($M+H^+$) 227.0919, found 227.0915.

4.2.5. Dimethyl 2-(but-2-ynyl)-2-(2-oxo-cyclopentyl)malonate (1e). IR (neat) 2955, 1723, 1435, 1245, 1145, 1048 cm^{-1}; ^1H NMR δ 1.66–1.99 (m, 2H), 1.76 (t, J=2.7 Hz, 3H), 2.01–2.13 (m, 1H), 2.17–2.41 (m, 3H), 2.78 (dq, J=16.8, 2.6 Hz, 1H), 2.89 (dq, J=17.0, 2.6 Hz, 1H), 2.92–3.01 (m, 1H), 3.755 (s, 3H), 3.764 (s, 3H); ^{13}C NMR δ 3.6, 20.6, 24.4, 26.6, 37.9, 52.6, 52.7, 52.8, 58.5, 74.2, 78.9, 169.7, 170.3, 216.5; HRMS (CI) calcd for $C_{14}H_{19}O_5$ ($M+H^+$) 267.1232, found 267.1235.

4.2.6. But-2-ynyloxymethyl phenyl ketone (1f). IR (Nujol) 2923, 1701, 1449, 1229, 1157, 1121 cm^{-1}; ^1H NMR δ 1.86 (t, J=2.3 Hz, 3H), 4.32 (q, J=2.4 Hz, 2H), 4.85 (s, 2H), 7.43–7.52 (m, 2H), 7.55–7.63 (m, 1H), 7.91–7.98 (m, 2H); ^{13}C NMR δ 3.4, 58.8, 71.4, 74.1, 83.5, 127.6, 128.5, 133.3, 134.6, 195.6; HRMS (FAB) calcd for $C_{12}H_{13}O_2$ ($M+H^+$) 189.0916, found 189.0909.

4.2.7. 2,2-Dimethyl-1-phenylhept-4-yn-1-one (4a). IR (neat) 2975, 1678, 1468, 1320, 1215, 1159 cm^{-1}; ^1H NMR δ 1.09 (t, J=7.5 Hz, 3H), 1.39 (s, 6H), 2.14 (qt, J=7.6, 2.4 Hz, 2H), 2.52 (t, J=2.6 Hz, 2H), 7.35–7.49 (m, 3H), 7.60–7.67 (m, 2H); ^{13}C NMR δ 12.4, 14.2, 25.3, 30.4, 47.8, 76.1, 84.4, 127.3, 128.0, 130.6, 139.0, 208.3; HRMS (CI) calcd for $C_{15}H_{19}O$ ($M+H^+$) 215.1436, found 215.1438.

4.2.8. 2-(But-2-ynyl)-2-methylcyclohexanone (4b). IR (neat) 2936, 1709, 1453, 1375, 1127, 1073 cm^{-1}; ^1H NMR δ 1.18 (s, 3H), 1.67–1.96 (m, 9H), 2.25–2.50 (m, 4H); ^{13}C NMR δ 3.5, 21.2, 22.5, 27.4, 27.9, 38.0, 38.6, 48.2, 75.4, 78.0, 214.5; HRMS (CI) calcd for $C_{11}H_{17}O$ ($M+H^+$) 165.1279, found 165.1277.

4.2.9. 2-Methyl-2-(pent-2-ynyl)indan-1-one (4c). IR (neat) 2975, 1715, 1609, 1466, 1374, 1300 cm^{-1}; ^1H NMR δ 0.93 (t, J=7.5 Hz, 3H), 1.27 (s, 3H), 2.02 (qt, J=7.5, 2.4 Hz, 2H), 2.40 (t, J=2.6 Hz, 2H), 2.92 (d, J=17.1 Hz, 1H), 3.35 (d, J=17.1 Hz, 1H), 7.33–7.40 (m, 1H), 7.42–7.48 (m, 1H), 7.60 (td, J=7.2, 1.2 Hz, 1H), 7.73–7.78 (m, 1H); ^{13}C NMR δ 12.3, 14.1, 23.3, 28.0, 40.1, 48.8, 75.6, 83.6, 124.3, 126.5, 127.3, 134.9, 135.7, 152.8, 209.8; HRMS (EI) calcd for $C_{15}H_{16}O$ (M^+) 212.1201, found 212.1200.

4.2.10. 2-Methyl-2-(pent-2-ynyl)-3,4-dihydro-2*H*-naphthalen-1-one (4d). IR (neat) 2934, 1682, 1601, 1456, 1323, 1221 cm^{-1}; ^1H NMR δ 1.10 (t, J=7.5 Hz, 3H), 1.25 (s, 3H), 2.06 (dt, J=13.6, 5.6 Hz, 1H), 2.16 (qt, J=7.4, 2.4 Hz, 2H), 2.25 (ddd, J=13.5, 8.4, 6.0 Hz, 1H), 2.45 (dt, J=16.6, 2.4 Hz, 1H), 2.53 (dt, J=16.8, 2.4 Hz, 1H), 2.90–3.10 (m, 2H), 7.23 (d, J=7.8 Hz, 1H), 7.30 (t, J=7.7 Hz, 1H), 7.46 (td, J=7.5, 1.4 Hz, 1H), 8.04 (dd, J=7.5, 1.2 Hz, 1H); ^{13}C NMR δ 12.5, 14.3, 21.4, 25.5, 27.4, 33.1, 44.6, 75.6, 84.3, 126.6, 128.0, 128.7, 131.3, 133.1, 143.4, 201.4; HRMS (EI) calcd for $C_{16}H_{18}O$ (M^+) 226.1358, found 226.1358.

4.2.11. Ethyl 2-benzoyl-2-methylhex-4-ynoate (8a). IR (neat) 2984, 1738, 1686, 1449, 1244, 1100 cm^{-1}; ^1H NMR δ 1.09 (t, J=7.2 Hz, 3H), 1.64 (s, 3H), 1.74 (t, J=2.6 Hz, 3H), 2.77–2.93 (m, 2H), 4.06–4.23 (m, 2H), 7.36–7.46 (m,

2H), 7.48–7.56 (m, 1H), 7.79–7.86 (m, 2H); ^{13}C NMR δ 3.5, 13.8, 21.1, 27.3, 57.0, 61.6, 73.7, 79.2, 128.4, 132.7, 135.4, 172.9, 196.5; HRMS (CI) calcd for $C_{16}H_{19}O_3$ (M+H$^+$) 259.1334, found 259.1335.

4.2.12. Ethyl 2-benzoyl-2-methylhept-4-ynoate (8b). IR (neat) 2979, 1738, 1683, 1449, 1244, 1100 cm^{-1}; ^{1}H NMR δ 1.07 (t, J=7.5 Hz, 3H), 1.10 (t, J=7.2 Hz, 3H), 1.64 (s, 3H), 2.12 (qt, J=7.4, 2.4 Hz, 2H), 2.79–2.94 (m, 2H), 4.06–4.23 (m, 2H), 7.37–7.46 (m, 2H), 7.48–7.56 (m, 1H), 7.79–7.87 (m, 2H); ^{13}C NMR δ 12.3, 13.8, 14.1, 21.0, 27.2, 57.0, 61.5, 73.9, 85.3, 128.4, 132.7, 135.4, 172.8, 196.4; HRMS (CI) calcd for $C_{17}H_{21}O_3$ (M+H$^+$) 273.1491, found 273.1490.

4.2.13. Ethyl 2-acetyl-2-methylhept-4-ynoate (8c). IR (neat) 2983, 1742, 1717, 1237, 1192, 1107 cm^{-1}; ^{1}H NMR δ 1.08 (t, J=7.5 Hz, 3H), 1.26 (t, J=7.2 Hz, 3H), 1.45 (s, 3H), 2.12 (qt, J=7.5, 2.4 Hz, 2H), 2.18 (s, 3H), 2.61–2.76 (m, 2H), 4.12–4.29 (m, 2H); ^{13}C NMR δ 12.3, 14.0, 14.1, 19.1, 25.3, 26.1, 59.2, 61.5, 74.1, 84.9, 171.7, 204.1; HRMS (CI) calcd for $C_{12}H_{19}O_3$ (M+H$^+$) 211.1334, found 211.1337.

4.2.14. Ethyl 2-benzoyl-2-methyl-5-trimethylsilylpent-4-ynoate (8d). IR (neat) 2960, 1740, 1686, 1250, 1194, 1100 cm^{-1}; ^{1}H NMR δ 0.12 (s, 9H), 1.12 (t, J=7.2 Hz, 3H), 1.66 (s, 3H), 2.88 (d, J=17.4 Hz, 1H), 2.96 (d, J=17.1 Hz, 1H), 4.06–4.25 (m, 2H), 7.37–7.45 (m, 2H), 7.49–7.56 (m, 1H), 7.79–7.86 (m, 2H); ^{13}C NMR δ 0.0, 13.9, 21.1, 28.3, 57.0, 61.7, 88.5, 101.7, 128.4, 132.7, 135.4, 172.4, 196.2; HRMS (CI) calcd for $C_{18}H_{25}O_3Si$ (M+H$^+$) 317.1573, found 317.1573.

4.2.15. Ethyl 1-(but-2-ynyl)-2-oxocyclopentane-1-carboxylate (11a). IR (neat) 2980, 1751, 1727, 1229, 1157 cm^{-1}; ^{1}H NMR δ 1.24 (t, J=7.1 Hz, 3H), 1.74 (t, J=2.3 Hz, 3H), 1.94–2.13 (m, 2H), 2.19–2.35 (m, 2H), 2.39–2.53 (m, 2H), 2.65 (q, J=2.6 Hz, 2H), 4.15 (q, J=7.1 Hz, 2H); ^{13}C NMR δ 3.5, 14.1, 19.8, 23.6, 32.6, 38.4, 59.1, 61.6, 74.4, 78.0, 170.6, 214.2; HRMS (CI) calcd for $C_{12}H_{17}O_3$ (M+H$^+$) 209.1178, found 209.1175.

4.2.16. Ethyl 2-(but-2-ynyl)-1-oxoindane-2-carboxylate (11b). IR (Nujol) 1730, 1705, 1605, 1285, 1254, 1188 cm^{-1}; ^{1}H NMR δ 1.19 (t, J=7.1 Hz, 3H), 1.56 (t, J=2.6 Hz, 3H), 2.77 (dq, J=16.5, 2.5 Hz, 1H), 2.93 (dq, J=16.6, 2.5 Hz, 1H), 3.36 (d, J=17.4 Hz, 1H), 3.68 (d, J=17.4 Hz, 1H), 4.07–4.23 (m, 2H), 7.35–7.43 (m, 1H), 7.48–7.53 (m, 1H), 7.56–7.67 (m, 1H), 7.77 (d, J=7.8 Hz, 1H); ^{13}C NMR δ 3.3, 14.0, 24.5, 36.8, 59.6, 61.8, 73.9, 77.9, 124.7, 126.2, 127.6, 135.2, 135.3, 153.5, 170.2, 201.5; HRMS (CI) calcd for $C_{16}H_{17}O_3$ (M+H$^+$) 257.1178, found 257.1180.

4.2.17. Ethyl 1-(but-2-ynyl)-2-oxocyclohexane-1-carboxylate (11c). IR (neat) 2945, 1717, 1443, 1192, 1092, 1022 cm^{-1}; ^{1}H NMR δ 1.26 (t, J=7.2 Hz, 3H), 1.52–1.85 (m, 4H), 1.75 (t, J=2.7 Hz, 3H), 1.95–2.09 (m, 1H), 2.35–2.53 (m, 3H), 2.60–2.75 (m, 2H), 4.21 (q, J=7.1 Hz, 2H); ^{13}C NMR δ 3.6, 14.1, 22.4, 25.1, 27.4, 35.4, 40.9, 60.3, 61.5, 74.0, 78.7, 170.6, 206.4; HRMS (EI) calcd for $C_{13}H_{18}O_3$ (M$^+$) 222.1256, found 222.1257.

4.2.18. Ethyl 2-(but-2ynyl)-1-oxo-3,4-dihydro-2*H*-naphthalene-2-carboxylate (11d). IR (neat) 2980, 1732, 1690, 1601, 1455, 1238 cm^{-1}; ^{1}H NMR δ 1.16 (t, J=7.2 Hz, 3H), 1.73 (t, J=2.6 Hz, 3H), 2.43 (ddd, J=13.7, 10.7, 4.9 Hz, 1H), 2.62 (dt, J=13.7, 4.8 Hz, 1H), 2.84 (q, J=2.5 Hz, 2H), 2.96 (dt, J=17.4, 5.0 Hz, 1H), 3.15 (ddd, J=17.4, 10.8, 4.8 Hz, 1H), 4.15 (q, J=7.0 Hz, 2H), 7.19–7.26 (m, 1H), 7.27–7.35 (m, 1H), 7.48 (td, J=7.5, 1.5 Hz, 1H), 8.05 (dd, J=8.0, 1.4 Hz, 1H); ^{13}C NMR δ 3.6, 14.0, 24.6, 25.9, 30.6, 57.0, 61.5, 74.2, 78.6, 126.7, 128.1, 128.7, 131.8, 133.5, 143.3, 170.9, 194.1; HRMS (EI) calcd for $C_{17}H_{18}O_3$ (M$^+$) 270.1256, found 270.1255.

4.2.19. Ethyl 1-(but-2-ynyl)-2-oxocyclooctane-1-carboxylate (11e). IR (neat) 2930, 1736, 1707, 1466, 1204 cm^{-1}; ^{1}H NMR δ 0.82–0.99 (m, 1H), 1.23 (t, J=7.1 Hz, 3H), 1.27–1.93 (m, 7H), 1.75 (t, J=2.7 Hz, 3H), 2.16–2.29 (m, 2H), 2.42 (dq, J=17.2, 2.5 Hz, 1H), 2.49–2.63 (m, 1H), 2.78 (td, J=12.0, 3.7 Hz, 1H), 2.92–3.03 (m, 1H), 4.12–4.24 (m, 2H); ^{13}C NMR δ 3.5, 14.0, 21.3, 23.1, 24.3, 25.5, 27.8, 29.3, 38.3, 61.5, 62.5, 74.4, 78.2, 170.4, 211.1; HRMS (EI) calcd for $C_{15}H_{22}O_3$ (M$^+$) 250.1569, found 250.1569.

4.2.20. 2-(But-2-ynyl)-2-methylindane-1,3-dione (11f). IR (Nujol) 1744, 1713, 1597, 1455, 1264, 1184 cm^{-1}; ^{1}H NMR δ 1.26 (s, 3H), 1.41 (t, J=2.4 Hz, 3H), 2.60 (q, J=2.5 Hz, 2H), 7.82–7.89 (m, 2H), 7.96–8.04 (m, 2H); ^{13}C NMR δ 3.1, 18.7, 24.8, 53.3, 73.5, 79.0, 123.3, 135.7, 141.5, 203.1; HRMS (EI) calcd for $C_{14}H_{12}O_2$ (M$^+$) 212.0837, found 212.0842.

4.2.21. 2-(But-2-ynyl)-2-methyl-cyclohexane-1,3-dione (11g). IR (Nujol) 1725, 1700, 1325, 1208, 1100, 1028 cm^{-1}; ^{1}H NMR δ 1.26 (s, 3H), 1.69–1.73 (m, 3H), 1.87–2.08 (m, 2H), 2.55–2.60 (m, 2H), 2.65–2.73 (m, 4H); ^{13}C NMR δ 3.4, 17.2, 21.3, 26.0, 38.3, 64.1, 74.6, 78.3, 209.4; HRMS (EI) calcd for $C_{11}H_{14}O_2$ (M$^+$) 178.0994, found 178.0990.

4.3. General procedure for arylative cyclization of 5-alkyn-1-ones 1

To an oven-dried, Ar-purged flask were added [Rh(OH)(cod)]$_2$ (2.28 mg, 5 μmol, 5 mol % of Rh), arylboronic acid **2** (1.0 mmol, 5.0 equiv), and 1,4-dioxane (1 mL). A solution of substrate **1** (0.2 mmol, 1.0 equiv) in 1,4-dioxane (1.0 mL) and H_2O (20 μL) was added to the reaction mixture at room temperature. After complete consumption of substrate was observed, water was added. The aqueous layer was extracted with ethyl acetate three times. The combined extracts were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by preparative thin layer chromatography (hexane/ethyl acetate) to give the product **3**.

4.3.1. 1,1-Dimethoxycarbonyl-3-hydroxy-3-phenyl-4-[(*Z*)-1-phenylethylidene]cyclopentane (3aa). IR (Nujol) 3546, 2920, 1732, 1444, 1240, 1202 cm^{-1}; ^{1}H NMR δ 2.00 (br s, 3H), 2.45 (s, 1H), 2.70 (d, J=14.1 Hz, 1H), 2.76 (dd, J=14.1, 1.5 Hz, 1H), 3.13 (dq, J=17.0, 1.9 Hz, 1H), 3.63 (d, J=16.5 Hz, 1H), 3.70 (s, 3H), 3.82 (s, 3H), 6.63–6.71 (m, 2H), 6.87–7.03 (m, 8H); ^{13}C NMR δ 23.9,

40.5, 52.9, 53.0, 53.2, 57.5, 82.0, 125.2, 125.9, 126.0, 127.2, 127.5, 127.7, 134.9, 141.5, 141.9, 146.1, 171.8, 172.7; HRMS (FAB) calcd for $C_{23}H_{24}O_5$ (M^+) 380.1624, found 380.1624.

4.3.2. 1,1-Dimethoxycarbonyl-3-hydroxy-3-phenyl-4-[(*Z*)-1-(4-fluorophenyl)ethylidene]cyclopentane (3ab). IR (Nujol) 3555, 1732, 1509, 1260, 1254, 1213 cm^{-1}; ^1H NMR δ 1.96 (br s, 3H), 2.64–2.72 (m, 2H), 2.75 (dd, J=14.4, 1.8 Hz, 1H), 3.15 (dq, J=17.3, 2.0 Hz, 1H), 3.59 (d, J=17.1 Hz, 1H), 3.72 (s, 3H), 3.83 (s, 3H), 6.54–6.68 (m, 4H), 6.94–7.05 (m, 5H); ^{13}C NMR δ 23.9, 40.5, 52.9, 53.1, 53.5, 57.5, 82.0, 114.2 (d, J=20.9 Hz), 125.2, 126.0, 127.2, 129.5 (d, J=8.1 Hz), 134.1, 137.7 (d, J=3.5 Hz), 142.0, 145.8, 161.0 (d, J=244.7 Hz), 171.7, 173.2; HRMS (FAB) calcd for $C_{23}H_{23}FO_5$ (M^+) 398.1530, found 398.1531.

4.3.3. 1,1-Dimethoxycarbonyl-3-hydroxy-3-phenyl-4-[(*Z*)-1-(4-nitrophenyl)ethylidene]cyclopentane (3ac). IR (Nujol) 3528, 1732, 1597, 1518, 1347, 1256 cm^{-1}; ^1H NMR (C_6D_6) δ 1.60 (br s, 3H), 2.74 (d, J=14.4 Hz, 1H), 2.88 (dd, J=14.3, 2.3 Hz, 1H), 3.18–3.29 (m, 2H), 3.32 (s, 3H), 3.39 (s, 3H), 3.63 (d, J=17.7 Hz, 1H), 6.45–6.52 (m, 2H), 6.68–6.75 (m, 3H), 6.83–6.90 (m, 2H), 7.53–7.59 (m, 2H); ^{13}C NMR (C_6D_6) δ 23.0, 40.9, 52.6, 52.9, 54.4, 58.0, 82.1, 122.3, 125.7, 126.3, 127.5, 129.3, 133.2, 143.9, 145.4, 146.3, 148.7, 171.4, 173.9; HRMS (FAB) calcd for $C_{23}H_{23}NO_7$ (M^+) 425.1475, found 425.1472.

4.3.4. 1,1-Dimethoxycarbonyl-3-hydroxy-3-phenyl-4-[(*Z*)-1-(4-methylphenyl)ethylidene]cyclopentane (3ad). IR (Nujol) 3546, 1733, 1514, 1247, 1200, 1092 cm^{-1}; ^1H NMR δ 1.98 (br s, 3H), 2.16 (s, 3H), 2.40 (s, 1H), 2.71 (d, J=14.1 Hz, 1H), 2.76 (dd, J=14.1, 1.2 Hz, 1H), 3.13 (dq, J=16.8, 1.8 Hz, 1H), 3.61 (d, J=16.8 Hz, 1H), 3.67 (s, 3H), 3.82 (s, 3H), 6.55 (d, J=7.8 Hz, 2H), 6.73 (d, J=7.8 Hz, 2H), 6.97–7.05 (m, 5H); ^{13}C NMR δ 21.0, 23.9, 40.4, 52.8, 53.0, 57.4, 82.1, 125.3, 125.9, 127.2, 127.5, 128.2, 134.7, 135.6, 138.9, 141.2, 146.4, 171.8, 172.6; HRMS (FAB) calcd for $C_{24}H_{26}O_5$ (M^+) 394.1780, found 394.1778.

4.3.5. 1,1-Dimethoxycarbonyl-3-hydroxy-3-phenyl-4-[(*Z*)-1-(3-methoxyphenyl)ethylidene]cyclopentane (3ae). IR (neat) 3563, 2955, 1733, 1597, 1457, 1067 cm^{-1}; ^1H NMR δ 1.99 (br s, 3H), 2.48 (s, 1H), 2.71 (dd, J=14.3, 0.8 Hz, 1H), 2.77 (dd, J=14.1, 1.5 Hz, 1H), 3.13 (dq, J=17.1, 2.1 Hz, 1H), 3.50 (s, 3H), 3.61 (d, J=17.1 Hz, 1H), 3.68 (s, 3H), 3.82 (s, 3H), 6.12 (dd, J=2.4, 1.5 Hz, 1H), 6.33–6.39 (m, 1H), 6.47–6.55 (m, 1H), 6.86–6.95 (m, 1H), 6.96–7.09 (m, 5H); ^{13}C NMR δ 23.7, 40.4, 52.8, 52.9, 53.0, 54.8, 57.4, 82.0, 112.66, 112.71, 119.8, 125.3, 125.9, 127.2, 128.7, 134.5, 141.4, 143.2, 146.4, 158.7, 171.7, 172.6; HRMS (FAB) calcd for $C_{24}H_{26}O_6$ (M^+) 410.1729, found 410.1728.

4.3.6. 1,1-Dimethoxycarbonyl-3-hydroxy-3-phenyl-4-[(*Z*)-1-(3-chlorophenyl)ethylidene]cyclopentane (3af). IR (neat) 3505, 2958, 1735, 1593, 1436, 1068 cm^{-1}; ^1H NMR δ 1.96 (br s, 3H), 2.69 (s, 1H), 2.70 (d, J=14.1 Hz, 1H), 2.77 (dd, J=14.6, 1.7 Hz, 1H), 3.14 (dq, J=17.3, 2.0 Hz, 1H), 3.60 (d, J=17.4 Hz, 1H), 3.74 (s, 3H), 3.84 (s, 3H), 6.59–6.64 (m, 2H), 6.81–6.92 (m, 2H), 6.95–7.06 (m, 5H); ^{13}C NMR δ 23.5, 40.4, 53.0, 53.1, 53.4, 57.5, 81.9, 125.1, 125.9, 126.1, 127.2, 128.2, 128.5, 133.1, 133.7, 142.4, 143.5, 145.3, 171.7, 173.1; HRMS (FAB) calcd for $C_{23}H_{23}ClO_5$ (M^+) 414.1234, found 414.1234.

4.3.7. 1,1-Dimethoxycarbonyl-3-hydroxy-3-phenyl-4-[(*Z*)-1-(2-methylphenyl)ethylidene]cyclopentane (3ag). A mixture of atropisomers (56:44). IR (Nujol) 3530, 1736, 1458, 1238, 1203, 1063 cm^{-1}; ^1H NMR δ 1.59 (s, 1.680H), 1.90 (br s, 1.680H), 1.94 (br s, 1.320H), 2.19 (s, 0.440H), 2.24 (s, 1.320H), 2.52 (s, 0.560H), 2.68–2.86 (m, 2H), 3.03 (dq, J=16.8, 2.1 Hz, 0.560H), 3.12 (dq, J=16.4, 2.0 Hz, 0.440H), 3.57–3.74 (m, 1H), 3.66 (s, 1.320H), 3.78 (s, 1.680H), 3.80 (s, 1.320H), 3.84 (s, 1.680H), 6.01 (dd, J=7.5, 1.2 Hz, 0.440H), 6.51 (t, J=7.7 Hz, 0.440H), 6.55–6.62 (m, 0.560H), 6.83–7.16 (m, 7.560H); ^{13}C NMR δ 19.2, 19.4, 22.4, 22.9, 40.2, 40.6, 52.6, 52.8, 52.9, 53.0, 57.4, 57.6, 81.5, 81.8, 124.6, 124.7, 124.99, 125.05, 125.6, 126.2, 126.4, 126.8, 127.0, 127.5, 128.2, 128.3, 129.5, 129.8, 133.7, 134.4, 134.8, 135.0, 140.5, 140.8, 140.9, 141.8, 144.5, 147.7, 171.5, 172.0, 172.3, 172.7; HRMS (FAB) calcd for $C_{24}H_{25}O_5$ ($M-H^+$) 393.1702, found 393.1701.

4.3.8. 1,1-Dimethoxycarbonyl-3-hydroxy-3-phenyl-4-[(*Z*)-1-phenylpentylidene]cyclopentane (3ba). IR (neat) 3570, 2955, 1732, 1447, 1255, 1067 cm^{-1}; ^1H NMR δ 0.87 (t, J=6.8 Hz, 3H), 1.18–1.44 (m, 4H), 2.14–2.41 (m, 3H), 2.69 (d, J=14.1 Hz, 1H), 2.75 (d, J=14.4 Hz, 1H), 3.08 (d, J=16.5 Hz, 1H), 3.63–3.73 (m, 4H), 3.82 (s, 3H), 6.53–6.61 (m, 2H), 6.86–7.07 (m, 8H); ^{13}C NMR δ 14.0, 22.6, 29.3, 37.1, 40.1, 52.85, 52.90, 57.6, 81.9, 125.0, 125.8, 125.9, 127.2, 127.4, 128.3, 139.7, 140.4, 142.0, 146.6, 171.8, 172.4; HRMS (FAB) calcd for $C_{26}H_{30}O_5$ (M^+) 422.2093, found 422.2092.

4.3.9. 1,1-Dimethoxycarbonyl-3-hydroxy-3-methyl-4-[(*Z*)-1-phenylethylidene]cyclopentane (3ca). IR (neat) 3520, 2955, 1732, 1435, 1258, 1071 cm^{-1}; ^1H NMR δ 0.88 (s, 3H), 1.95 (t, J=1.5 Hz, 3H), 2.16 (br s, 1H), 2.33 (d, J=13.8 Hz, 1H), 2.54 (dd, J=14.0, 2.0 Hz, 1H), 2.95 (dq, J=17.4, 1.7 Hz, 1H), 4.40 (d, J=17.3 Hz, 1H), 3.76 (s, 3H), 3.79 (s, 3H), 7.15–7.35 (m, 5H); ^{13}C NMR δ 24.1, 27.3, 39.7, 50.5, 52.8, 52.9, 56.5, 78.1, 126.7, 128.0, 128.2, 133.2, 139.0, 142.9, 172.1, 173.1; HRMS (FAB) calcd for $C_{18}H_{21}O_4$ ($M-OH^+$) 301.1440, found 301.1440.

4.3.10. 1,1-Dimethoxycarbonyl-3-hydroxy-4-[(*Z*)-1-phenylethylidene]cyclopentane (3da). IR (neat) 3526, 2953, 1732, 1435, 1257, 1082 cm^{-1}; ^1H NMR δ 1.96 (d, J=4.2 Hz, 1H), 2.02 (br s, 3H), 2.37 (dd, J=14.1, 5.1 Hz, 1H), 2.47 (d, J=14.1 Hz, 1H), 2.92 (dq, J=17.7, 1.5 Hz, 1H), 3.39 (d, J=17.7 Hz, 1H), 3.76 (s, 3H), 3.79 (s, 3H), 4.45–4.53 (m, 1H), 7.21–7.37 (m, 5H); ^{13}C NMR δ 21.6, 37.5, 43.0, 52.9, 53.0, 58.3, 72.2, 126.9, 127.5, 128.2, 134.1, 138.0, 142.5, 172.2, 173.3; HRMS (FAB) calcd for $C_{17}H_{20}O_5$ (M^+) 304.1311, found 304.1304.

4.3.11. (1*S,5*R**)-4,4-Dimethoxycarbonyl-1-hydroxy-2-[(*Z*)-1-phenylethylidene]bicyclo[3.3.0]octane (3ea).** IR (Nujol) 3544, 1755, 1728, 1458, 1281, 1071 cm^{-1}; ^1H NMR δ 1.07–1.25 (m, 1H), 1.46–1.67 (m, 4H), 1.73–1.87

(m, 1H), 1.96 (br s, 3H), 2.83–2.93 (m, 1H), 3.05 (d, J=17.4 Hz, 1H), 3.23 (s, 1H), 3.25 (dq, J=17.3, 2.0 Hz, 1H), 3.74 (s, 3H), 3.80 (s, 3H), 7.16–7.39 (m, 5H); ^{13}C NMR δ 23.7, 25.4, 29.4, 38.3, 41.9, 52.4, 53.1, 59.2, 59.6, 88.8, 126.4, 127.6, 128.2, 133.3, 139.8, 143.2, 170.6, 174.3; HRMS (FAB) calcd for $C_{20}H_{24}O_5$ (M^+) 344.1624, found 344.1621.

4.3.12. 3-Phenyl-4-[(*Z*)-1-phenylethylidene]tetrahydrofuran-3-ol (3fa). IR (Nujol) 3436, 1493, 1204, 1100, 1038 cm^{-1}; ^{1}H NMR δ 1.97 (br s, 3H), 2.36 (br s, 1H), 3.85 (d, J=9.0 Hz, 1H), 4.00 (d, J=9.3 Hz, 1H), 4.74 (d, J=13.5 Hz, 1H), 4.89 (d, J=13.5 Hz, 1H), 6.79–6.87 (m, 2H), 6.96–7.22 (m, 8H); ^{13}C NMR δ 22.7, 72.5, 81.1, 83.7, 125.2, 126.4, 126.7, 127.55, 127.60, 127.8, 131.5, 140.7, 141.0, 144.0; HRMS (FAB) calcd for $C_{18}H_{18}O_2$ (M^+) 266.1307, found 266.1307.

4.4. General procedure for arylative cyclization of 4-alkyn-1-ones 4

To an oven-dried, Ar-purged flask were added [Rh(OH)(cod)]$_2$ (2.58 mg, 6.25 μmol, 5 mol % of Rh), arylboronic acid **2** (1.25 mmol, 5.0 equiv), and 1,4-dioxane (1.25 mL). A solution of substrate **4** (0.25 mmol, 1.0 equiv) in 1,4-dioxane (1.25 mL) and H_2O (25 μL) was added to the reaction mixture at room temperature. After complete consumption of substrate was observed, water was added. The aqueous layer was extracted with ethyl acetate three times. The combined extracts were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by preparative thin layer chromatography (hexane/ethyl acetate) to give the product **5**.

4.4.1. 2,2-Dimethyl-1-phenyl-4-[(*Z*)-1-phenylpropylidene]cyclobutan-1-ol (5aa). IR (neat) 3580, 2964, 1599, 1493, 1447, 1071 cm^{-1}; ^{1}H NMR δ 0.59 (s, 3H), 1.04 (t, J=7.5 Hz, 3H), 1.23 (s, 3H), 1.85 (s, 1H), 2.31–2.55 (m, 4H), 7.06–7.17 (m, 5H), 7.22–7.29 (m, 1H), 7.30–7.38 (m, 2H), 7.40–7.46 (m, 2H); ^{13}C NMR δ 13.4, 24.1, 25.4, 26.4, 39.4, 41.5, 83.7, 126.6, 126.7, 127.6, 127.9, 128.1, 137.1, 139.2, 139.9, 144.7; HRMS (EI) calcd for $C_{21}H_{24}O$ (M^+) 292.1827, found 292.1833.

4.4.2. (1*R,6*S**)-1-Hydroxy-6-methyl-8-[(*Z*)-1-phenylethylidene]bicyclo[4.2.0]octane (5ba).** IR (Nujol) 3561, 3474, 2926, 1069 cm^{-1}; ^{1}H NMR δ 1.04 (s, 3H), 1.20–1.66 (m, 7H), 1.81–1.88 (m, 2H), 1.91 (br s, 3H), 2.07 (d, J=14.1 Hz, 1H), 2.40 (d, J=14.4 Hz, 1H), 7.18–7.25 (m, 1H), 7.26–7.36 (m, 4H); ^{13}C NMR δ 19.3, 21.0, 21.7, 23.4, 33.0, 35.5, 36.3, 39.1, 77.7, 126.6, 127.5, 127.8, 127.9, 141.5, 142.0; HRMS (EI) calcd for $C_{17}H_{22}O$ (M^+) 242.1671, found 242.1670.

4.4.3. (2a*R,7a*S**)-7a-Methyl-2-[(*Z*)-1-phenylpropylidene]-1,2,7,7a-tetrahydrocyclobuta[*a*]inden-2a-ol (5ca).** IR (Nujol) 3467, 2961, 1601, 1456, 1144, 1069 cm^{-1}; ^{1}H NMR δ 0.86 (t, J=7.5 Hz, 3H), 1.31 (s, 3H), 2.02 (s, 1H), 2.14–2.24 (m, 3H), 2.48 (d, J=15.3 Hz, 1H), 2.92 (d, J=16.5 Hz, 1H), 2.99 (d, J=16.5 Hz, 1H), 6.95 (d, J=7.5 Hz, 1H), 7.10–7.25 (m, 3H), 7.30–7.46 (m, 5H); ^{13}C NMR δ 12.6, 19.3, 27.3, 38.1, 45.0, 45.3, 89.0, 125.2, 125.3, 126.9, 127.0, 128.0, 128.2, 128.7, 136.5, 139.0, 140.5, 142.8, 145.5; HRMS (EI) calcd for $C_{21}H_{22}O$ (M^+) 290.1671, found 290.1670.

4.4.4. (2a*S,8b*R**)-2a-Methyl-1-[(*Z*)-1-phenylpropylidene]-2,2a,3,4-tetrahydro-1*H*-cyclobuta[*a*]naphthalen-8b-ol (5da).** IR (neat) 3443, 2963, 1601, 1456, 1175, 1107 cm^{-1}; ^{1}H NMR δ 0.84 (t, J=7.7 Hz, 3H), 1.30 (s, 3H), 1.36 (td, J=13.3, 4.6 Hz, 1H), 1.80 (ddd, J=13.2, 4.4, 2.9 Hz, 1H), 2.02–2.26 (m, 3H), 2.43 (d, J=15.6 Hz, 1H), 2.54 (d, J=15.6 Hz, 1H), 2.70 (ddd, J=15.6, 4.5, 2.7 Hz, 1H), 2.82 (ddd, J=15.5, 13.1, 4.4 Hz, 1H), 6.67 (d, J=7.5 Hz, 1H), 6.77–6.86 (m, 1H), 6.90–6.98 (m, 2H), 6.98–7.03 (m, 2H), 7.15–7.22 (m, 3H); ^{13}C NMR δ 12.4, 23.4, 27.4, 27.5, 32.1, 35.0, 40.7, 77.8, 125.5, 125.9, 126.4, 126.5, 127.2, 127.5, 128.7, 137.0, 138.6, 139.1, 139.7, 139.8; HRMS (EI) calcd for $C_{22}H_{24}O$ (M^+) 304.1827, found 304.1828.

4.5. General procedure for the rhodium-catalyzed acyl 1,3-migration reaction

To an oven-dried, Ar-purged flask were added [Rh(OH)(cod)]$_2$ (2.28 mg, 5 μmol, 5 mol % of Rh), arylboronic acid **2** (2.0–5.0 equiv), and 1,4-dioxane (1 mL). A solution of substrate **8** or **11** (0.20 mmol, 1.0 equiv) in 1,4-dioxane (1.0 mL) and H_2O (20 μL) was added to the reaction mixture at room temperature. After complete consumption of the substrate was observed, the reaction was quenched with aq NH_4Cl. Then, the resulting solution was stirred at room temperature overnight. The aqueous layer was extracted with ethyl acetate three times. The combined organic extracts were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by preparative thin layer chromatography (hexane/ethyl acetate) to give the product **10** or **12**. The ring-opening of **11c**, **11d**, and **11f** required three weeks for completion.

4.5.1. Ethyl 2-hydroxy-1-methyl-2-phenyl-3-[(*Z*)-1-phenylethylidene]cyclobutane-1-carboxylate (9aa). This compound is unstable. Only ^{1}H NMR data are shown here: ^{1}H NMR δ 0.89 (t, J=7.1 Hz, 3H), 1.48 (s, 3H), 2.09 (br s, 3H), 2.19 (s, 1H), 2.42 (dq, J=15.8, 1.1 Hz, 1H), 3.36 (dq, J=15.6, 1.5 Hz, 1H), 3.49–3.70 (m, 2H), 7.12–7.63 (m, 10H).

4.5.2. Ethyl (*Z*)-4-benzoyl-2-methyl-5-phenylhex-4-enoate (10aa). IR (neat) 2980, 1732, 1651, 1449, 1246, 1183 cm^{-1}; ^{1}H NMR δ 1.21 (t, J=7.1 Hz, 3H), 1.25 (d, J=6.6 Hz, 3H), 2.26 (s, 3H), 2.59–2.77 (m, 2H), 2.92–3.05 (m, 1H), 4.06 (q, J=7.1 Hz, 2H), 6.91–7.06 (m, 5H), 7.10–7.18 (m, 2H), 7.22–7.29 (m, 1H), 7.57–7.63 (m, 2H); ^{13}C NMR δ 14.2, 17.7, 20.9, 35.6, 38.9, 60.4, 127.3, 127.7, 127.8, 128.2, 129.2, 132.1, 135.2, 137.5, 141.3, 142.6, 176.1, 200.6; HRMS (CI) calcd for $C_{22}H_{25}O_3$ (M+H$^+$) 337.1804, found 337.1804.

4.5.3. Ethyl (*Z*)-4-benzoyl-2-methyl-5-(4-fluorophenyl)-hex-4-enoate (10ab). IR (neat) 2980, 1732, 1651, 1509, 1227, 1183 cm^{-1}; ^{1}H NMR δ 1.20 (t, J=7.2 Hz, 3H), 1.24 (d, J=6.6 Hz, 3H), 2.23 (s, 3H), 2.57–2.75 (m, 2H), 2.90–3.03 (m, 1H), 4.06 (q, J=7.1 Hz, 2H), 6.65–6.74 (m, 2H), 6.95–7.03 (m, 2H), 7.13–7.21 (m, 2H), 7.26–7.34 (m, 1H), 7.56–7.62 (m, 2H); ^{13}C NMR δ 14.1, 17.7, 20.9, 35.5, 38.8, 60.4, 114.7 (d, J=20.9 Hz), 127.8, 129.1, 129.9

(d, J=8.1 Hz), 132.3, 135.6, 137.2, 138.5 (d, J=3.5 Hz), 140.0, 161.7 (d, J=247.1 Hz), 176.0, 200.5; HRMS (CI) calcd for $C_{22}H_{24}FO_3$ (M+H$^+$) 355.1709, found 355.1708.

4.5.4. Ethyl (*Z*)-4-benzoyl-2-methyl-5-(4-methylphenyl)-hex-4-enoate (10ad). IR (neat) 2980, 1732, 1653, 1449, 1248, 1183 cm^{-1}; ^{1}H NMR δ 1.20 (t, J=7.1 Hz, 3H), 1.24 (d, J=6.9 Hz, 3H), 2.12 (s, 3H), 2.23 (s, 3H), 2.57–2.75 (m, 2H), 2.91–3.03 (m, 1H), 4.05 (q, J=7.0 Hz, 2H), 6.81 (d, J=7.8 Hz, 2H), 6.88–6.96 (m, 2H), 7.12–7.20 (m, 2H), 7.23–7.32 (m, 1H), 7.58–7.64 (m, 2H); ^{13}C NMR δ 14.1, 17.6, 20.9, 21.0, 35.6, 38.8, 60.4, 127.6, 128.1, 128.5, 129.2, 132.0, 134.7, 137.0, 137.4, 139.6, 141.3, 176.1, 200.8; HRMS (CI) calcd for $C_{23}H_{27}O_3$ (M+H$^+$) 351.1960, found 351.1959.

4.5.5. Ethyl (*Z*)-4-benzoyl-2-methyl-5-(3-methoxyphenyl)hex-4-enoate (10ae). IR (neat) 2980, 1730, 1656, 1578, 1221, 1179 cm^{-1}; ^{1}H NMR δ 1.21 (t, J=7.2 Hz, 3H), 1.25 (d, J=6.6 Hz, 3H), 2.24 (s, 3H), 2.58–2.71 (m, 2H), 2.92–3.03 (m, 1H), 3.63 (s, 3H), 4.06 (q, J=7.1 Hz, 2H), 6.50 (ddd, J=8.2, 2.8, 1.0 Hz, 1H), 6.54–6.58 (m, 1H), 6.63 (ddd, J=7.8, 1.5, 0.9 Hz, 1H), 6.92 (t, J=7.8 Hz, 1H), 7.13–7.21 (m, 2H), 7.24–7.32 (m, 1H), 7.58–7.64 (m, 2H); ^{13}C NMR δ 14.1, 17.6, 20.7, 35.5, 38.8, 55.1, 60.4, 113.2, 113.6, 120.8, 127.6, 128.9, 129.0, 132.1, 135.2, 137.3, 141.0, 143.8, 158.8, 176.0, 200.6; HRMS (CI) calcd for $C_{23}H_{27}O_4$ (M+H$^+$) 367.1909, found 367.1910.

4.5.6. Ethyl (*Z*)-4-benzoyl-2-methyl-5-(3-chlorophenyl)-hex-4-enoate (10af). IR (neat) 2980, 1732, 1653, 1449, 1242, 1183 cm^{-1}; ^{1}H NMR δ 1.18–1.27 (m, 6H), 2.23 (s, 3H), 2.58–2.76 (m, 2H), 2.92–3.03 (m, 1H), 4.07 (q, J=7.1 Hz, 2H), 6.86–6.94 (m, 3H), 6.99–7.03 (m, 1H), 7.14–7.22 (m, 2H), 7.25–7.34 (m, 1H), 7.54–7.62 (m, 2H); ^{13}C NMR δ 14.1, 17.7, 20.7, 35.5, 38.7, 60.5, 126.4, 127.3, 127.8, 128.2, 129.0, 129.1, 132.3, 133.6, 136.3, 137.2, 139.7, 144.2, 175.9, 200.2; HRMS (CI) calcd for $C_{22}H_{24}ClO_3$ (M+H$^+$) 371.1414, found 371.1412.

4.5.7. Ethyl (*Z*)-4-benzoyl-2-methyl-5-phenylhept-4-enoate (10ba). IR (neat) 2977, 1732, 1651, 1449, 1238, 1183 cm^{-1}; ^{1}H NMR δ 0.94 (t, J=7.5 Hz, 3H), 1.22 (t, J=7.1 Hz, 3H), 1.25 (d, J=6.6 Hz, 3H), 2.49–2.66 (m, 2H), 2.67–2.82 (m, 2H), 3.00 (dd, J=14.1, 7.8 Hz, 1H), 4.07 (q, J=7.1 Hz, 2H), 6.90–7.04 (m, 5H), 7.10–7.19 (m, 2H), 7.21–7.30 (m, 1H), 7.56–7.63 (m, 2H); ^{13}C NMR δ 12.7, 14.1, 17.7, 27.2, 34.7, 38.8, 60.4, 127.2, 127.6, 127.7, 128.9, 129.1, 132.0, 134.5, 137.6, 140.8, 147.3, 176.0, 200.6; HRMS (CI) calcd for $C_{23}H_{27}O_3$ (M+H$^+$) 351.1960, found 351.1959.

4.5.8. Ethyl (*Z*)-4-acetyl-2-methyl-5-phenylhept-4-enoate (10ca). IR (neat) 2979, 1732, 1676, 1352, 1177, 1121 cm^{-1}; ^{1}H NMR δ 0.87 (t, J=7.7 Hz, 3H), 1.19 (d, J=6.6 Hz, 3H), 1.27 (t, J=7.1 Hz, 3H), 1.58 (s, 3H), 2.36–2.69 (m, 4H), 2.78 (dd, J=13.7, 8.6 Hz, 1H), 4.08–4.19 (m, 2H), 7.09–7.15 (m, 2H), 7.28–7.34 (m, 3H); ^{13}C NMR δ 12.5, 14.3, 17.2, 27.9, 31.3, 34.2, 38.8, 60.4, 128.0, 128.4, 128.5, 138.0, 141.4, 148.0, 176.0, 207.3; HRMS (EI) calcd for $C_{18}H_{24}O_3$ (M$^+$) 288.1725, found 288.1723.

4.5.9. Ethyl (*E*)-4-benzoyl-2-methyl-5-phenyl-5-trimethylsilylpent-4-enoate (10da). IR (neat) 2980, 1732, 1664, 1449, 1250, 1183 cm^{-1}; ^{1}H NMR δ 0.20 (s, 9H), 1.17 (t, J=7.1 Hz, 3H), 1.26 (d, J=6.9 Hz, 3H), 2.49–2.63 (m, 1H), 2.79 (dd, J=14.1, 7.5 Hz, 1H), 3.07 (dd, J=14.4, 6.9 Hz, 1H), 3.97–4.08 (m, 2H), 6.72–6.79 (m, 2H), 6.84–7.00 (m, 3H), 7.19–7.28 (m, 2H), 7.32–7.39 (m, 1H), 7.61–7.67 (m, 2H); ^{13}C NMR δ 0.7, 14.1, 17.7, 37.4, 38.3, 60.4, 125.6, 127.4, 127.9, 128.2, 129.1, 132.5, 136.6, 142.1, 145.6, 149.6, 175.7, 200.0; HRMS (CI) calcd for $C_{24}H_{31}O_3Si$ (M+H$^+$) 395.2042, found 395.2044.

4.5.10. Ethyl 4-oxo-3-[(*Z*)-1-phenylethylidene]cycloheptane-1-carboxylate (12aa). IR (Nujol) 1725, 1648, 1289, 1161, 1102, 1028 cm^{-1}; ^{1}H NMR δ 1.29 (t, J=7.1 Hz, 3H), 1.63–1.86 (m, 2H), 1.92–2.09 (m, 1H), 2.10 (s, 3H), 2.16–2.52 (m, 4H), 2.54–2.67 (m, 1H), 2.97 (d, J=14.7 Hz, 1H), 4.18 (q, J=6.9 Hz, 2H), 7.05–7.12 (m, 2H), 7.18–7.33 (m, 3H); ^{13}C NMR δ 14.2, 20.8, 22.5, 31.5, 32.6, 42.8, 45.3, 60.7, 126.97, 127.03, 128.1, 137.2, 140.0, 142.9, 174.8, 208.6; HRMS (EI) calcd for $C_{18}H_{22}O_3$ (M$^+$) 286.1569, found 286.1569.

4.5.11. Ethyl 9-oxo-8-[(*Z*)-1-phenylethylidene]-6,7,8,9-tetrahydro-5*H*-benzo[7]annulene-6-carboxylate (12ba). IR (Nujol) 1732, 1663, 1595, 1186, 1159 cm^{-1}; ^{1}H NMR δ 1.30 (t, J=7.2 Hz, 3H), 2.22 (s, 3H), 2.65 (dd, J=14.7, 8.4 Hz, 1H), 2.95 (dd, J=14.6, 7.4 Hz, 1H), 3.08–3.19 (m, 1H), 3.27–3.42 (m, 2H), 4.10–4.27 (m, 2H), 7.10–7.17 (m, 2H), 7.23–7.35 (m, 5H), 7.45 (td, J=7.5, 1.5 Hz, 1H), 7.81 (dd, J=7.8, 1.5 Hz, 1H); ^{13}C NMR δ 14.3, 22.5, 28.6, 33.9, 41.9, 60.9, 127.1, 127.4, 128.2, 129.7, 130.7, 132.7, 134.5, 137.4, 137.8, 143.7, 147.2, 173.8, 195.7; HRMS (EI) calcd for $C_{22}H_{22}O_3$ (M$^+$) 334.1569, found 334.1567.

4.5.12. Ethyl 4-oxo-3-[(*Z*)-1-phenylethylidene]cyclooctane-1-carboxylate (12ca). IR (neat) 2938, 1732, 1684, 1443, 1179, 1028 cm^{-1}; ^{1}H NMR δ 1.27 (t, J=7.2 Hz, 3H), 1.35–1.89 (m, 7H), 1.92–2.06 (m, 1H), 2.15 (s, 3H), 2.34–2.48 (m, 1H), 2.53–2.67 (m, 1H), 2.93 (dd, J=13.8, 3.3 Hz, 1H), 4.14 (q, J=7.1 Hz, 2H), 7.11–7.19 (m, 2H), 7.21–7.33 (m, 3H); ^{13}C NMR δ 14.3, 19.9, 24.4, 27.2, 29.7, 35.1, 43.1, 43.3, 60.6, 127.6, 127.7, 128.4, 135.8, 137.6, 142.5, 175.5, 215.4; HRMS (EI) calcd for $C_{19}H_{24}O_3$ (M$^+$) 300.1725, found 300.1723.

4.5.13. Ethyl 5,6,7,8,9,10-hexahydro-10-oxo-9-[(*Z*)-1-phenylethylidene]benzo[8]annulene-7-carboxylate (12da). IR (neat) 2936, 1732, 1653, 1445, 1240, 1184 cm^{-1}; ^{1}H NMR δ 1.22 (t, J=7.2 Hz, 3H), 2.00 (ddt, J=13.7, 11.9, 4.6 Hz, 1H), 2.09–2.18 (m, 1H), 2.18–2.23 (m, 3H), 2.66 (tdd, J=12.0, 4.1, 2.9 Hz, 1H), 2.80 (dd, J=14.9, 12.2 Hz, 1H), 2.89–2.99 (m, 1H), 3.02 (dt, J=14.4, 4.4 Hz, 1H), 3.65 (ddd, J=14.3, 11.9, 4.0 Hz, 1H), 4.11 (q, J=7.2 Hz, 2H), 6.96–7.05 (m, 2H), 7.08–7.23 (m, 5H), 7.40 (td, J=7.4, 1.5 Hz, 1H), 7.69 (dd, J=7.7, 1.4 Hz, 1H); ^{13}C NMR δ 14.2, 21.0, 31.8, 32.0, 32.1, 40.8, 60.7, 126.8, 126.9, 127.2, 128.0, 129.3, 131.3, 133.1, 136.2, 138.0, 138.9, 140.9, 142.7, 175.0, 199.8; HRMS (EI) calcd for $C_{23}H_{24}O_3$ (M$^+$) 348.1725, found 348.1725.

4.5.14. Ethyl 4-oxo-3-[(*Z*)-1-phenylethylidene]cyclodecane-1-carboxylate (12ea). IR (neat) 2934, 1732, 1667, 1445, 1177, 1034 cm^{-1}; ^{1}H NMR δ 1.15–1.85 (m, 12H), 1.28 (t, J=7.2 Hz, 3H), 2.16 (s, 3H), 2.60–2.78 (m, 2H),

2.82–2.96 (m, 1H), 4.17 (q, J=7.2 Hz, 2H), 7.11–7.20 (m, 2H), 7.26–7.35 (m, 3H); ^{13}C NMR δ 14.3, 21.7, 22.6, 24.5, 26.6, 30.1, 31.9, 42.4, 43.4, 60.5, 128.1, 128.4, 140.8, 142.2, 143.2, 176.1, 212.6; HRMS (EI) calcd for $C_{21}H_{28}O_3$ (M^+) 328.2038, found 328.2039.

4.5.15. 5,9-Dioxo-6-methyl-8-[(*Z*)-1-phenylethylidene]-6,7,8,9-tetrahydro-5*H*-benzo[7]annulene (12fa). IR (neat) 2975, 1682, 1592, 1443, 1375, 1240 cm^{-1}; ^{1}H NMR δ 1.31 (d, J=6.6 Hz, 3H), 2.11 (s, 3H), 2.48 (dd, J=14.9, 11.6 Hz, 1H), 2.88 (ddq, J=15.3, 5.4, 0.9 Hz, 1H), 3.15–3.30 (m, 1H), 6.91–6.98 (m, 2H), 7.17–7.25 (m, 3H), 7.51–7.66 (m, 3H), 7.68–7.72 (m, 1H); ^{13}C NMR δ 17.2, 21.5, 32.1, 45.8, 127.2, 128.1, 128.3, 128.4, 131.9, 132.3, 136.0, 137.8, 138.2, 142.4, 143.4, 197.0, 205.3; HRMS (EI) calcd for $C_{20}H_{18}O_2$ (M^+) 290.1307, found 290.1306.

4.5.16. 2-Methyl-4-[(*Z*)-1-phenylethylidene]cyclooctane-1,5-dione (12ga). IR (Nujol) 1700, 1671, 1306, 1125, 1073 cm^{-1}; ^{1}H NMR δ 1.12 (d, J=6.3 Hz, 3H), 1.84–2.01 (m, 4H), 2.16 (s, 3H), 2.22–2.35 (m, 1H), 2.41–2.58 (m, 2H), 2.71 (dd, J=13.4, 4.7 Hz, 1H), 2.93–3.07 (m, 1H), 7.12–7.19 (m, 2H), 7.25–7.33 (m, 3H); ^{13}C NMR δ 16.8, 19.8, 22.7, 38.4, 43.46, 43.51, 44.7, 127.7, 128.0, 128.5, 137.3, 138.1, 142.0, 213.0, 216.3; HRMS (EI) calcd for $C_{17}H_{20}O_2$ (M^+) 256.1463, found 256.1464.

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