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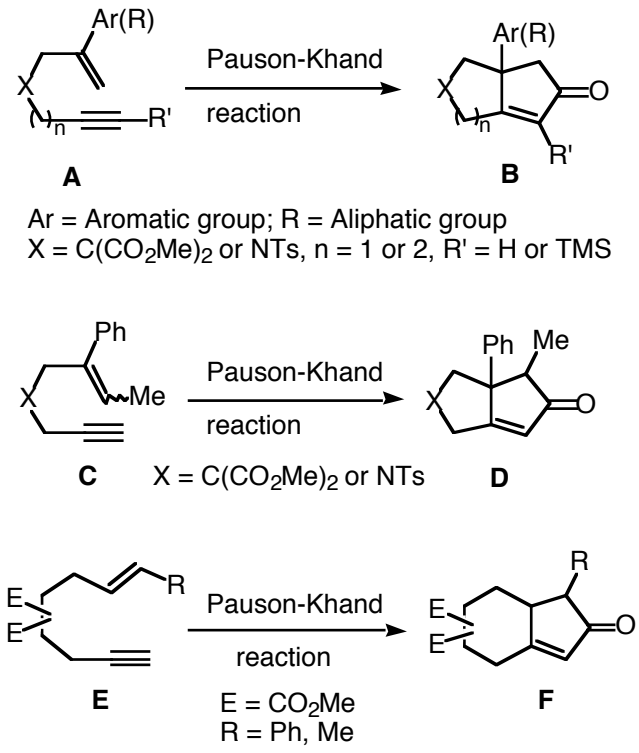
INVESTIGATION OF INTRAMOLECULAR PAUSON-KHAND REACTION OF 2-ARYL-1,6- AND 1-METHYL-1,7-ENYNES (*EXO*-OLEFINS) AND 1-PHENYL-1-OCTEN-7-YNE (*ENDO*-OLEFIN)

Miyuki Ishizaki,* Hiroshi Satoh, Osamu Hoshino, Kiyoshi Nishitani, and Hiroshi Hara*

Faculty of Pharmaceutical Sciences, Tokyo University of Science, 2641, Yamazaki, Noda-shi, Chiba 278-8510, Japan

Abstract – The intramolecular Pauson-Khand reaction of various 2-aryl-1-hepten-6-ynes and its aza-derivatives (*exo*-olefins) efficiently produced aryl-bicyclo[3.3.0]octenones and azaoctenone bearing quaternary carbon centers at angular positions in good yields. Although a similar reaction of 2-phenyl-1-octen-7-yne (*exo*-olefin), which is a homologue of 2-phenyl-1-hepten-6-yne, did not take place, the reaction of the methyl derivatives smoothly proceeded. However, the reaction of regioisomeric 1-phenyl-1-octen-7-yne (*endo*-olefin) afforded the desired product in moderate yields.

Since the first report on the Pauson-Khand reaction, the reaction has been widely used as one of the powerful methods for the construction of cyclopentenone derivatives.[1] The usefulness of the reaction has been recognized by a large number of applications to the total synthesis of natural products.[2] However, most of the substrates used were enynes containing *endo*-olefins, regardless of the cyclic or acyclic system. Recent studies[3] in our laboratory revealed a convenient synthesis of polycyclic compounds by the reaction of *exo*-cyclic olefins. One of the advantages in the reaction is the facile construction of a tricyclic skeleton containing quaternary carbon center(s), which could not be synthesized from *endo*-cyclic olefins.[3a,b] Some other features are easy access to spirobicyclic[3c,d] and tricyclic[3e-g] skeletons in natural products such as magellanine and cedranediol. Contrary to the cyclic enynes, although acyclic enynes having *exo*-olefin moiety have more flexible conformers, the reaction affords direct bicyclic compounds bearing quaternary carbon centers at angular positions. Furthermore, they can be useful intermediates for the total synthesis of natural products. However, as for the reaction of acyclic *exo*-olefins, the reaction of

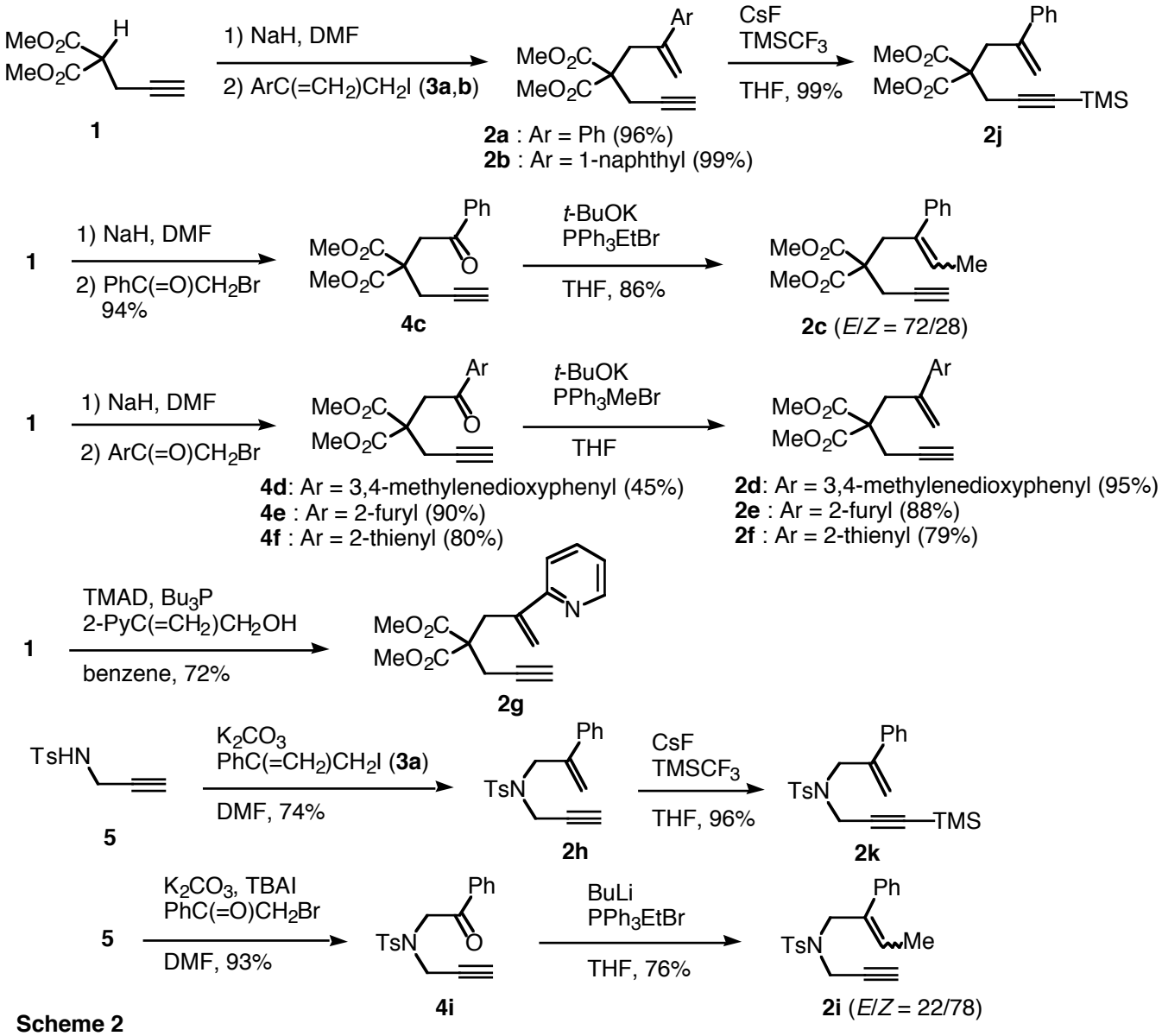


Scheme 1

enynes containing *aromatic* substituents has not been reported except for only a few works on derivatives bearing *aliphatic* substituents [**A** (n = 1); R = Me, R' = H, X = $C(CO_2Me)_2$[4a-g] or R = CH_2OBn, R' = H, X = $C(CO_2Et)_2$[4h,i] in Scheme 1]. In addition, no reports have appeared in regard to the reaction of 1,7-enynes (**A**; n = 2).[5] Thus, an examination of the Pauson-Khand reaction of acyclic 2-aryl-1-hepten-6-ynes and their homologues (**A**, **C**) seemed to be quite an interesting issue. Here, we wish to report fully on the intramolecular Pauson-Khand reaction of *acyclic exo*-olefins (**A**, **C**) having *aromatic* substituents to give the corresponding bicyclic compounds (**B**, **D**) bearing quaternary carbon centers and the reaction of regioisomeric *acyclic endo*-olefins (**E**) to give the cyclized products (**F**) (Scheme 1).[6]

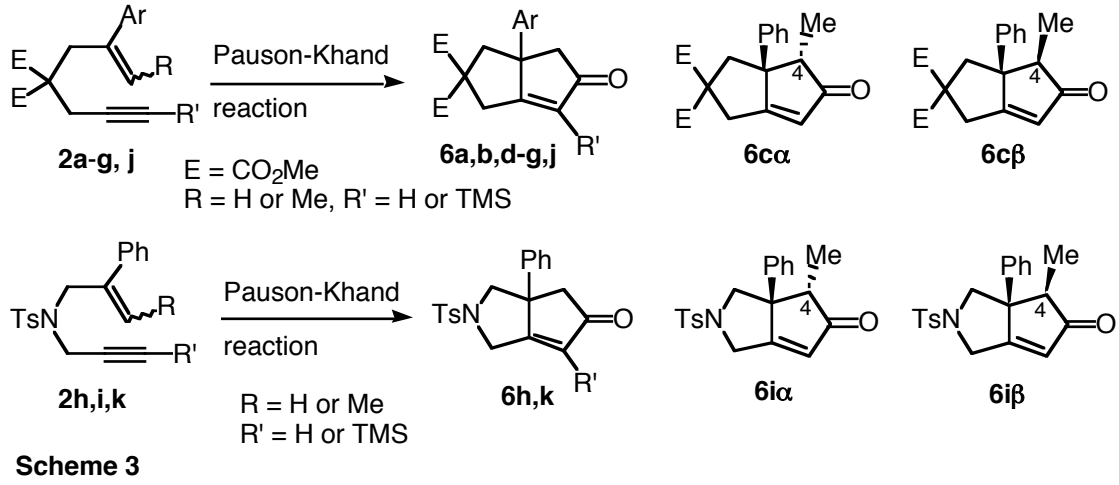
Various Pauson-Khand precursors (**2a**-**k**) bearing the alkylidene group were synthesized as follows (Scheme 2). The reaction of dimethyl propargylmalonate (**1**)[7] with 2-aryl-3-iodopropenes (**3a**,**b**), which were easily obtained from the corresponding alcohols,[8] afforded 2-aryl-1,6-enynes (**2a**,**b**) in high yield. A similar reaction of *N*-propargyltosylamide (**5**)[9] furnished **2h**. Enynes (**2c**-**f**,**i**) containing the phenyl, 3,4-methylenedioxyphenyl, furyl or thienyl group were attained by the coupling of **1** or **5** with aryl bromomethyl ketones,[10] followed by Wittig olefination. A pyridyl-substituted enyne (**2g**) was synthesized by the Mitsunobu reaction of **1** with 2-pyridyl-2-propenol[11] in the presence of *N,N,N',N'*-tetramethylazodicarboxamide (TMAD).[12] TMS-substituted alkynes (**2j**,**k**) were obtained by the reaction of **2a** and **2h** with $TMSCF_3$ in the presence of CsF.[13]

With enynes in hand, the intramolecular Pauson-Khand reaction of *exo*-enynes (**2a**-**j**) was examined by following three methods after treatment with $Co_2(CO)_8$; a reaction with 9-12 equivalents of NMO (*N*-methylmorpholine *N*-oxide)[14a] in CH_2Cl_2 at room temperature (Method A); refluxing in toluene (Method B); heating at 83°C with BuSMe[14b] in 1,2-dichloroethane (Method C). The results are shown in Table 1. The reaction of α-styryl-type enynes (**2a**,**d**,**h**) gave corresponding bicyclic cyclopentenones (**6a**,**d**,**h**) in moderate to good yields (40-73%) by Methods A-C. However, a similar reaction of a naphthyl derivative (**2b**) resulted in formation of the product (**6b**) in low to moderate yields (4-57%). The difference of the yields among **2a**,**b**,**d** by Method A can be explained by considering that the bulky naphthyl group in **2b** would interfere with the proximity of the alkyne-cobalt complex moiety and the olefinic part owing to a



Scheme 2

low reaction temperature. The reaction of other enynes (**2e-g**) containing heterocycles such as furan, thiophene and pyridine also smoothly proceeded to afford desired bicyclic compounds (**6e-g**) in moderate to good yields (45-79%). In the case of trisubstituted *exo*-olefins (**2c**,**i**), cyclized products (**6c**,**i**) were obtained as a mixture of stereoisomers in moderate yields by Method C. The stereochemistry of the products was determined by ^{1}H-NMR spectrometry. Thus, chemical shifts of the Me group at C4 (δ 1.24 for **6cβ**, δ 1.13 for **6iβ**) were observed at a lower field than those of their isomers (δ 0.64 for **6cα**, δ 0.65 for **6iα**) due to anisotropic effect caused by benzene rings. The ratio of stereoisomers was estimated by the integration of peaks due to the Me group at C4 in its ^{1}H NMR spectrum. Unfortunately, the reaction of TMS-substituted enynes (**2j**,**k**) failed to cyclize and only starting enynes, which were produced by decomplexation during the reaction, were recovered in quantitative yields. From the results mentioned above, it was found that thermal conditions (Methods B and C) were superior to an oxidative condition



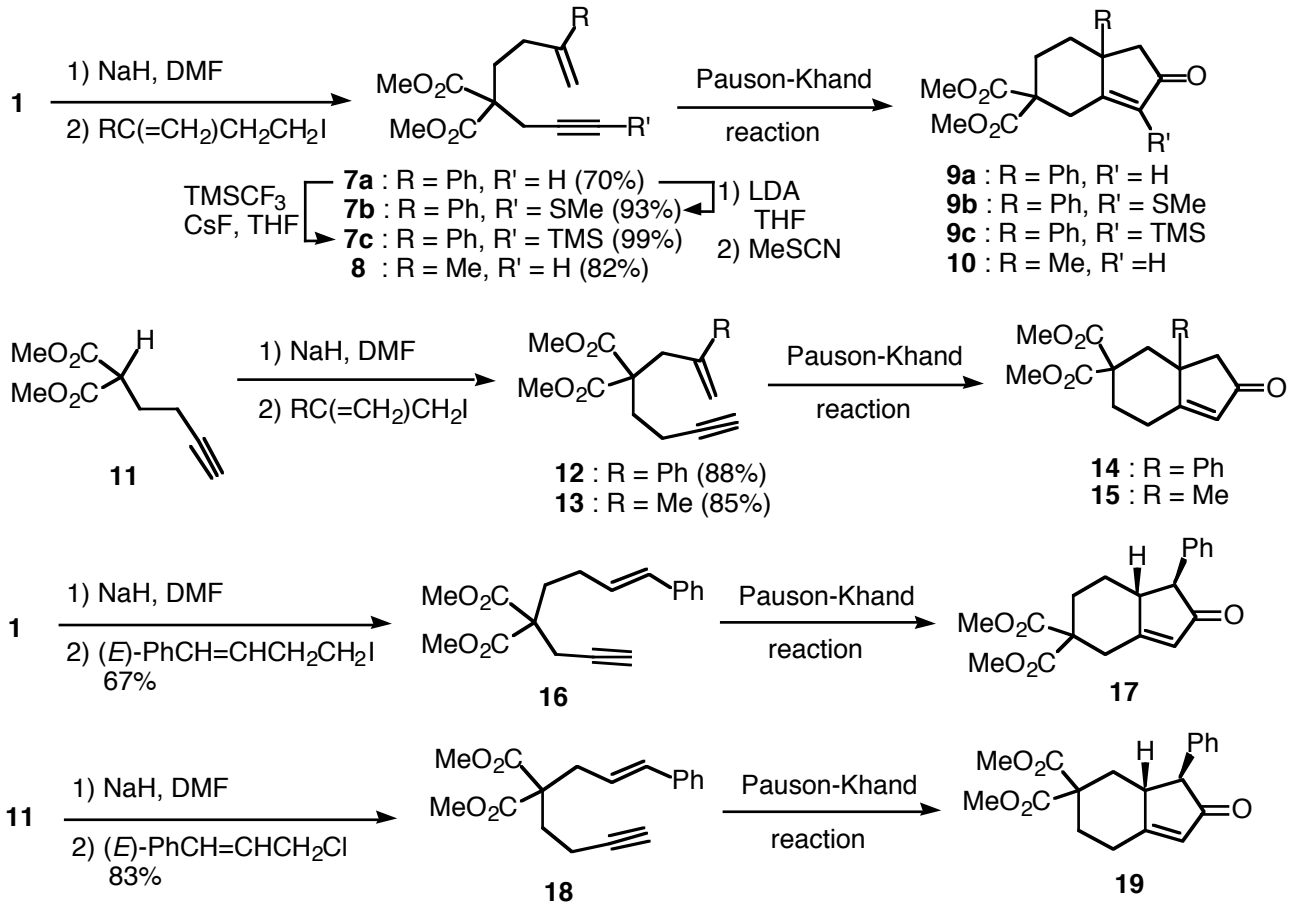
Scheme 3

Table 1. Pauson-Khand reaction of *exo*-enynes (2a-i)

Entry	Substrate	Method[a]	Time(h)	Product	Yield(%)
1	**2a**	A	2	**6a**	56
2	**2a**	B	8	**6a**	70
3	**2a**	C	10	**6a**	73
4	**2b**	A	2	**6b**	4
5	**2b**	B	8	**6b**	57
6	**2b**	C	8	**6b**	48
7	**2c**	A	2	**6c**	0[b]
8	**2c**	B	8	**6c**	18[c,d]
9	**2c**	C	13	**6c**	52[c,e]
10	**2d**	A	2	**6d**	40
11	**2d**	B	8	**6d**	62
12	**2d**	C	10	**6d**	66
13	**2e**	A	2.5	**6e**	66
14	**2e**	B	5	**6e**	70
15	**2e**	C	12	**6e**	79
16	**2f**	A	2	**6f**	49
17	**2f**	B	5	**6f**	62
18	**2f**	C	10	**6f**	66
19	**2g**	A	2	**6g**	45
20	**2g**	B	2	**6g**	46
21	**2g**	C	3	**6g**	51
22	**2h**	A	2	**6h**	61
23	**2h**	B	8	**6h**	60
24	**2h**	C	10	**6h**	64
25	**2i**	A	2	**6i**	0[b]
26	**2i**	B	8	**6i**	11[f,g]
27	**2i**	C	15	**6i**	56[f,h]

a) Method A; reaction with 9-12 eq. of NMO at rt in CH_2Cl_2. Method B; refluxing in toluene. Method C; heating at 83°C with BuSMe in 1,2-dichloroethane. b) Complex mixtures were formed. c) Combined yield of **6cα** and **6cβ**. d) **6cα**/**6cβ** = 54/46. e) **6cα**/**6cβ** = 58/42. f) Combined yield of **6iα** and **6iβ**. g) **6iα**/**6iβ** = 85/15. h) **6cα**/**6cβ** = 60/40.

(Method A) in the reaction of malonates (**2a-g**). On the other hand, in the reaction of tosylamide (**2h**), the cyclized product (**6h**) was formed in similar yields (60-64%) without regard to Methods A-C. Because there was only one report[15] on the reaction of *acyclic* 1,7-enynes bearing the *exo*-methylene group, we next investigated the reaction of the homologues of **2a** (Scheme 4). Thus, the reaction of α-



Scheme 4

Table 2. Pauson-Khand reaction of *exo*- and *endo*-enynes (8, 13, 16, 18)

Entry	Substrate	Method[a]	Time(h)	Product	Yield(%)
1	**8**	A	3	**10**	0[b]
2	**8**	B	2	**10**	28
3	**8**	C	13	**10**	5
4	**13**	A	2	**15**	0[b]
5	**13**	B	7	**15**	18
6	**13**	C	13	**15**	0[b]
7	**16**	A	2	**17**	41
8	**16**	B	8	**17**	16
9	**16**	C	10	**17**	65
10	**18**	A	1	**19**	62
11	**18**	B	3	**19**	48
12	**18**	C	5	**19**	63

a) See foot note in Table 1. b) Complex mixtures were formed.

styryl-type enynes (**7a**, **12**) was examined. The substrates were synthesized in the usual manner from **1** and **11**.[16] Unfortunately, the reaction of **7a** and **12** by Methods A-C resulted in the formation of complex mixtures and failed to give the desired cyclopentenones (**9a**, **14**). Livinghouse[17a] and Magnus[17b] reported that the reaction of enynes bearing the methylthio or trimethylsilyl group on terminal alkyne moiety improved the yields and stereoselectivity compared with those of enynes having no substituted terminal alkyne. Thus, we carried out the reaction of such substrates (**7b**,**c**), which were prepared according to the reported procedure.[13,17b] However, the reaction of **7b** and **7c** did not give cyclized products (**9b**,**c**) at all. To investigate the effect of substituents on alkenyl moiety, a similar reaction of methyl derivatives (**8**, **13**), which were prepared in a manner similar to that noted for **7a**, was performed (Table 2). As shown in Table 2, the reaction of **8** furnished **10** in 5-28% yields under thermal conditions (Entries 2 and 3), although the reaction with NMO failed (Entry 1). A similar reaction of **13** proceeded to give **15** in 18% yield only by Method B (Entry 5).

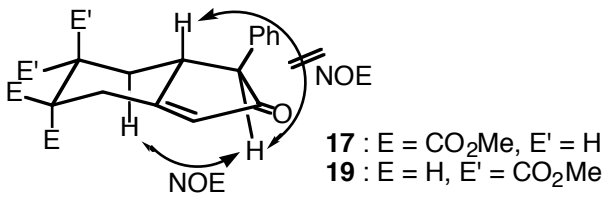
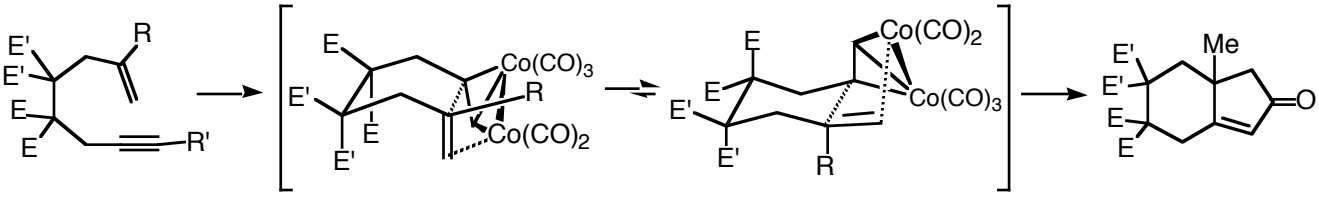
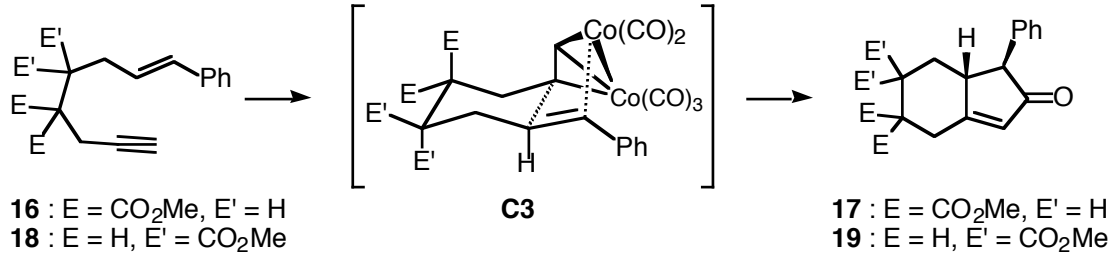


Figure 1

These findings promted us to examine the reaction of *endo*-type 1,7-enynes (**16**, **18**), which were regioisomers of **7a** and **12**, to compare the reactivity in the reaction, because there were very few reports[15,18] on the Pauson-Khand reaction of acyclic styryl *endo*-type 1,7-enynes. Interestingly, in the reaction of **16**, a cyclized product (**17**) was obtained in 16-65% yields under both oxidative and thermal conditions (Table 2, Entries 7-9). In addition, the reaction of **18** furnished **19** in 48-63% yields (Entries 10-12). The stereochemistry of the products (**17**, **19**) was determined by NOE experiments (Figure 1). These results suggested that the steric factor around the olefinic moiety should be crucial. As depicted in Scheme 5, the reaction of *exo*-enynes (**7a**, **8**, **12**, **13**) could occur *via* the boat (**C1**) or chair (**C2**)





Scheme 5

conformational transition state. The former conformation (**C1**) would be excluded by high steric repulsion. When the reaction proceeds *via* the chair conformer (**C2**), the bulky phenyl group has to set in an undesired axial position. Thus, the cyclization of enynes (**7a**, **12**) would not occur. Contrary to phenyl derivatives, the reaction of enynes (**8**, **13**) with a smaller methyl group could proceed *via* **C2** to afford cyclized products (**10**, **15**), although in low yield. In the case of *endo*-enynes (**16**, **18**), the reaction proceeded *via* **C3** to give adducts (**17**, **19**) in moderate yields.

In conclusion, we have investigated the intramolecular Pauson-Khand reaction of various *acyclic exo*-olefins bearing an aromatic substituent (**2a**-**k**) to give bicyclic cyclopentenones (**6a-i**) except for **6j** and **6k**. In a similar reaction of 2-subsituted 1,7-enynes (*exo*-olefins) (**7a-c**, **8**, **12**, **13**), phenyl derivatives (**7a-c**, **8**) failed to cyclize. However, methyl derivatives (**8**, **13**) proceeded to afford adducts (**10, 15**). Contrary to 2-phenyl-1,7-enynes (*exo*-olefins), the reaction of 1-phenyl-1,7-enynes (*endo*-olefins) (**16, 18**) yielded cyclized products (**17, 19**). The present study revealed the nature of the reaction of acyclic *exo*- and *endo*-enynes, and provides a convenient approach to bicyclic cyclopentenones (**6a-g**) having aromatic substituents at their quaternary carbon center.

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EXPERIMENTAL

General. All melting points were measured on a Yanagimoto melting point apparatus and are uncorrected. IR spectra were obtained with a JASCO FT/IR-400. ^{1}H and ^{13}C NMR spectra were taken with a JEOL EX-270 (270 MHz for ^{1}H NMR and 67.5 MHz for ^{13}C NMR) spectrometer in a $CDCl_3$ solution with tetramethylsilane as an internal standard. MS spectra were measured on a Hitachi M-80 or a JEOL JMS D-300 spectrometer. Column chromatography was performed over silica gel (Merck Kiegelsel 60). Preparative TLCs were run on a Merck 5744 plate. Organic extracts were dried over $MgSO_4$.

General Procedure for Synthesis of Iodides (3a,b).

To a stirred mixture of 2-phenyl-2-propenol[8a] or 2-(α-naphthyl)-2-propenol[8b] (1 eq.), PPh_3 (1.5 eq.) and pyridine (2.5 eq.) in CH_2Cl_2 (10 mL per 1 mmol of the alcohol) at 0°C was added I_2 (1.5 eq.) in one portion. After the mixture was stirred for 2 h, the reaction was quenched with a 10% aqueous $Na_2S_2O_3$ solution. The organic layer was washed with 1M HCl, water and brine, respectively, and dried. Evaporation of the solvent *in vacuo* gave a residue, which was purified by column chromatography (hexane) to give the corresponding iodides (**3a,b**).

3-Iodo-2-phenylpropene (3a); from 2-phenyl-2-propenol (0.375 g, 2.80 mmol), **3a** (0.552 g, 80.0%) was

obtained as a pale yellow oil; ^{1}H NMR δ 7.29-7.47 (5H, m), 5.52, 5.47 (each 1H, s), 4.31 (2H, s); IR (neat) 3081, 2961, 1493 cm^{-1}; MS *m/z* 244 (M^+); HRMS *m/z* calcd for C_9H_9I (M^+) 243.9749, found: 243.9740.

3-Iodo-2-(α-naphthyl)propene (3b); from 2-(α-naphthyl)-2-propenol (0.920 g, 5.0 mmol), **3b** (1.040 g, 70.7%) was obtained as a pale yellow oil; ^{1}H NMR δ 7.81-7.97 (3H, m), 7.37-7.52 (4H, m), 5.85, 5.25 (each 1H, s), 4.37 (2H, s); IR (neat) 3290, 2960, 1490 cm^{-1}; MS *m/z* 294 (M^+); HRMS *m/z* calcd for $C_{13}H_{11}I$ (M^+) 293.9905, found: 293.9912.

General Procedure for Synthesis of Enynes (2a,b, 7a, 8, 12, 13, 16, 18). To a stirred mixture of NaH (1.5 eq.) and **1** (1 eq.) or **11** (1 eq.) in DMF (10 mL per 1 mmol of **1** or **11**) at 0°C was added a solution of allyl iodide (1.2 eq.) or homoallyl iodide (1.2 eq.) in DMF (4.5 mL per 1 mmol of the iodide). Then, the mixture was allowed to warm to rt and stirred overnight. After cooling at 0°C, the reaction was quenched with water. The mixture was extracted with ether. The organic extracts were washed with water and brine, respectively, and dried. Evaporation of the solvent *in vacuo* gave a residue, which was purified by column chromatography (hexane/AcOEt = 20 : 1 ~ 5 : 1) to furnish the corresponding enynes (**2a,b, 7a, 8, 12, 13, 16, 18**).

Dimethyl 2-(2-phenyl-2-propenyl)-2-(2-propynyl)malonate (2a); from **1** (0.310 g, 1.82 mmol), **2a** (0.502 g, 95.9%) was obtained as colorless crystals; mp 73°C (hexane); ^{1}H NMR δ 7.18-7.34 (5H, m), 5.31, 5.30 (each 1H, d, *J* = 1.7 Hz), 3.42 (6H, s), 3.33 (2H, s), 2.76 (2H, d, *J* = 2.6 Hz), 2.05 (1H, t, *J* = 2.6 Hz); ^{13}C NMR δ 170.0, 143.8, 140.9, 128.1, 127.6, 126.9, 119.0, 79.2, 71.8, 56.4, 52.5, 36.9, 22.3; IR (KBr) 3273, 2949, 2123, 1734 cm^{-1}; MS *m/z* 286 (M^+); HRMS *m/z* calcd for $C_{17}H_{18}O_4$ (M^+) 286.1203, found: 286.1193.

Dimethyl 2-[2-(1-naphthyl-2-propenyl)]-2-(2-propynyl)malonate (**2b**); from **1** (0.425 g, 2.50 mmol), **2b** (0.835 g, 99.4%) was obtained as colorless crystals; mp 85°C (hexane); ^{1}H NMR δ 8.01-8.04 (1H, m), 7.80-7.83 (1H, m), 7.73 (1H, d, *J*= 8.3 Hz), 7.45-7.52 (2H, m), 7.39 (1H, dd, *J* = 6.9, 8.3 Hz), 7.24 (1H, dd, *J* = 1, 6.9 Hz), 5.63 (1H, d, *J* = 1 Hz), 5.34 (1H, d, *J* = 2 Hz), 3.48 (2H, d, *J* = 1 Hz), 3.25 (6H, s), 2.88 (2H, d, *J* = 2.6 Hz), 2.02 (1H, t, *J* = 2.6 Hz); ^{13}C NMR δ 169.8, 143.0, 139.3, 133.6, 130.9, 128.3, 127.8, 126.1, 126.0, 125.7, 125.0, 122.0, 79.1, 71.8, 56.4, 52.3, 39.4, 22.4; IR (KBr) 3291, 2957, 2120, 1735 cm^{-1}; MS *m/z* 336 (M^+); HRMS *m/z* calcd for $C_{21}H_{20}O_4$ (M^+) 336.1362, found: 336.1370.

Dimethyl 2-(3-phenyl-3-butenyl)-2-(2-propynyl)malonate (7a); from **1** (0.500 g, 2.94 mmol), **7** (0.590 g, 70.4%) was obtained as colorless crystals; mp 44-45°C; ^{1}H NMR δ 7.51-7.54 (2H, m), 7.38-7.47 (3H, m), 5.45, 5.24 (each 1H, s), 3.86 (6H, s), 3.02 (2H, d, *J* = 2.6 Hz), 2.52-2.59 (2H, m), 2.32-2.39 (2H, m), 2.13 (1H, t, *J* = 2.6 Hz); ^{13}C NMR δ 170.6, 147.1, 140.5, 128.3, 127.5, 126.0, 122.9, 78.6, 71.6, 56.8, 52.8, 31.2, 29.8, 23.0; IR (KBr) 3282, 2952, 2121, 1753, 1733 cm^{-1}; MS *m/z* 300 (M^+); HRMS *m/z* calcd for $C_{18}H_{20}O_4$(M^+) 300.1362, found: 300.1358.

Dimethyl 2-(3-methyl-3-butenyl)-2-(2-propynyl)malonate (8); from **1** (1.00 g, 5.88 mmol), **8** (1.16 g, 82.3%) was obtained as a colorless oil; ^{1}H NMR δ 4.67, 4.66 (each 1H, s), 3.69 (6H, s), 2.79 (2H, d, *J* = 2.6 Hz), 2.12-2.18 (2H, m), 1.98 (1H, t, *J* = 2.6 Hz), 1.80-1.87 (2H, m), 1.68 (3H, s); ^{13}C NMR δ 170.6, 144.5, 120.6, 78.7, 71.1, 67.0, 52.8, 32.1, 30.2, 22.9, 22.4; IR (neat) 3289, 2954, 2120, 1735, 1437 cm^{-1}; MS *m/z* 238 (M^+); HRMS *m/z* calcd for $C_{13}H_{18}O_4$ (M^+) 238.1206, found: 238.1207.

Dimethyl 2-(3-butynyl)-2-(2-phenyl-2-propenyl)malonate (12); from **11** (0.184 g, 1.00 mmol), **12** (0.265 g, 88.3%) was obtained as a colorless oil; ^{1}H NMR δ 7.26-7.29 (5H, m), 5.26, 5.14 (each 1H, s), 3.45 (6H, s), 3.18 (2H, s), 2.09 (4H, s), 1.91 (1H, br s); ^{13}C NMR δ 170.6, 147.1, 140.5, 128.3, 127.5, 126.0, 112.9, 78.7, 71.6, 56.8, 52.8, 31.3, 29.8, 23.0; IR (neat) 3291, 2952, 2129, 1732 cm^{-1}; MS *m/z* 300 (M^+); HRMS *m/z* calcd for $C_{18}H_{20}O_4$ (M^+) 300.1362, found: 300.1369.

Dimethyl 2-(3-butynyl)-2-(2-methyl-2-propenyl)malonate (13); from **11** (0.920 g, 5.00 mmol), **13** (1.02 g, 85.4%) was obtained as colorless crystals; mp 41°C; ^{1}H NMR δ 4.89, 4.75 (each 1H, s), 3.73 (6H, s), 2.73 (2H, s), 2.17 (4H, s), 1.95 (1H, br s), 1.65 (3H, s); ^{13}C NMR δ 171.5, 140.1, 116.0, 83.2, 68.7, 56.4, 52.5, 40.7, 31.6, 23.0, 14.1; IR (KBr) 3309, 2957, 2122, 1731 cm^{-1}; MS *m/z* 238 (M^+); HRMS *m/z* calcd for $C_{13}H_{18}O_4$ (M^+) 238.1206, found: 238.1194.

Dimethyl 2-(4-phenyl-3-butenyl)-2-(2-propynyl)malonate (16); from **1** (0.187 g, 1.10 mmol), **16** (0.222 g, 67.1%) was obtained as colorless crystals; mp 67-68°C (hexane); ^{1}H NMR δ 7.17-7.35 (5H, m), 6.41 (1H, d, *J* = 15.8 Hz), 6.17 (1H, dt, *J* = 15.8, 6.4 Hz), 3.74 (6H, s), 2.89 (2H, d, *J* = 2.6 Hz), 2.23-2.27 (2H, m), 2.16-2.20 (2H, m), 2.03 (1H, t, *J* = 2.6 Hz); ^{13}C NMR δ 170.6, 137.4, 130.7, 128.9, 128.5, 127.1, 126.0, 78.7, 71.5, 56.6, 52.8, 31.6, 27.6, 23.0; IR (KBr) 3275, 2955, 1734 cm^{-1}; MS *m/z* 300 (M^+); HRMS *m/z* calcd for $C_{18}H_{20}O_4$ (M^+) 300.1362, found: 300.1346.

Dimethyl 2-(3-butynyl)-2-(3-phenyl-2-propenyl)malonate (18); from **11** (0.368 g, 2.0 mmol), **18** (0.500 g, 83.3%) was obtained as a colorless oil; ^{1}H NMR δ 7.19-7.34 (5H, m), 6.45 (1H, d, *J* = 15.6 Hz), 6.01 (1H, dd, *J* = 7.5, 15.6 Hz), 3.73 (6H, s), 2.08 (2H, dd, *J* = 7.5, 12.8 Hz), 2.20-2.25 (4H, m), 1.97 (1H, t, *J* = 2.1 Hz); ^{13}C NMR δ 171.1, 136.9, 134.2, 128.5, 127.5, 126.2, 123.4, 83.0, 78.8, 57.3, 52.5, 36.7, 31.7, 13.9; IR (neat) 3292, 2952, 2119, 1731 cm^{-1}; MS *m/z* 300 (M^+); HRMS *m/z* calcd for $C_{18}H_{20}O_4$ (M^+) 300.1362, found: 300.1366.

Dimethyl 2-(3-methylthio-2-propynyl)-2-(3-phenyl-3-butenyl)malonate (7b). To a solution of diisopropylamine (130 μL, 0.916 mmol) in THF (6 mL) at –78°C was added 1.59 M BuLi in hexane (0.58 mL, 0.92 mmol). After being stirred for 30 min, a solution of **7a** (0.250 g, 0.83 mmol) in THF (4 mL) was added over a period of 10 min and stirring was continued for an additional 30 min. Then, MeSCN (70 μL, 1.00 mmol) was added. The mixture was allowed to warm up to rt for 17 h. The reaction was quenched with saturated aqueous $NaHCO_3$ solution and the mixture was extracted with ether. The organic extracts were washed with water and brine, respectively, and dried. Evaporation of the solvent *in vacuo* gave a

residue, which was purified by column chromatography (hexane/AcOEt = 5 : 1) to give **7b** (0.270 g, 93.4%) as a pale yellow oil; ^{1}H NMR δ 7.22-7.45 (5H, m), 5.33, 5.11 (each 1H, d, *J* = 1 Hz), 3.74 (6H, s), 3.00 (2H, s), 2.39-2.46 (2H, m), 2.27 (3H, s), 2.17-2.23 (2H, m); ^{13}C NMR δ 170.6, 147.2, 140.5, 128.4, 127.5, 126.0, 112.9, 87.2, 74.2, 57.1, 52.7, 31.4, 29.9, 24.6, 19.2; IR 2952, 2193, 1734 cm^{-1}; MS *m/z* 346 (M^+); HRMS *m/z* calcd for $C_{19}H_{22}O_4S$ (M^+) 346.1238, found: 346.1241.

Dimethyl 2-(3-trimethylsilyl-2-propynyl)-2-(3-phenyl-3-butenyl)malonate (7c). To a suspension of **7a** (0.250 g, 0.83 mmol) and CsF (0.003 g , 0.02 mmol) in THF (6 mL) at rt $TMSCF_3$ (160 μL, 1.08 mmol) was added. After being stirred for 30 min, the mixture was filtered and the filtrate was evaporated *in vacuo* to give a residue, which was purified by column chromatography (hexane/AcOEt = 5 : 1) to afford **7c** (0.307 g, 99.2%) as a colorless oil; ^{1}H NMR δ 7.26-7.32, (2H, m), 7.13-7.25 (3H, m), 5.22 (1H, s), 5.00 (1H, d, *J* = 1 Hz), 3.63 (6H, s), 2.81 (2H, s), 2.29-2.36 (2H, m), 2.06-2.16 (2H, m), 0.00 (9H, s); ^{13}C NMR δ 170.7, 147.3, 140.6, 138.4, 137.6, 136.1, 122.9, 101.1, 88.4, 57.1, 52.8, 40.6, 30.0, 24.4, 0.1; IR (neat) 2954, 2179, 1738, 1436 cm^{-1}; MS *m/z* 372 (M^+); HRMS *m/z* calcd for $C_{21}H_{28}O_4Si$ (M^+) 372.1755, found: 372.1762.

General Procedure for Synthesis of Ketones (4c-f). To a stirred mixture of NaH (1.5 eq.) and **1** (1 eq.) in DMF (10 mL per 1 mmol of **1**) at 0°C was added a solution of aryl bromomethyl ketone (1.2 eq.) in DMF (3.0-5.5 mL per 1 mmol of the ketone). Then, the mixture was allowed to warm to rt and stirred overnight. After cooling at 0˚C, the reaction was quenched with water. The mixture was extracted with ether. A similar work-up, as noted above, gave a residue, which was purified by column chromatography (hexane/AcOEt = 10 : 1 ~ 2 : 1) to give the corresponding ketones (**4c**-**f**).

Dimethyl 2-[2-phenyl-2-oxoethyl]-2-(2-propynyl)malonate (4c); from **1** (0.855 g, 5.0 mmol), **4c** (1.369 g, 94.4%) was obtained as a colorless oil; ^{1}H NMR δ 7.97-8.03 (2H, m), 7.56-7.63 (1H, m), 7.44-7.52 (2H, m), 3.93 (2H, s), 3.77 (6H, s), 3.16 (2H, d, *J* = 2.7 Hz), 2.02 (1H, t, *J* = 2.7 Hz); ^{13}C NMR δ 196.6, 169.7, 136.2, 133.5, 128.6, 128.1, 79.2, 71.8, 54.5, 53.1, 40.9, 23.3; IR (neat) 3282, 2954, 1746, 1684 cm^{-1}; MS *m/z* 288 (M^+); HRMS *m/z* calcd for $C_{16}H_{16}O_5$ (M^+) 288.0998, found: 288.1011.

Dimethyl 2-[2-(3,4-methylenedioxyphenyl)-2-oxoethyl]-2-(2-propynyl)malonate (4d); from **1** (1.26 g, 7.41 mmol), **4d** (1.10 g, 44.7%) was obtained as colorless crystals; mp 97-98˚C (AcOEt-hexane); ^{1}H NMR δ 7.63 (1H, dd, *J* = 1.7, 8.3 Hz), 7.44 (1H, d, *J* = 1.7 Hz), 6.86 (1H, d, *J* = 8.3 Hz), 6.05 (2H, s), 3.84 (2H, s), 3.77 (6H, s), 3.11 (2H, d, *J* = 2.6 Hz), 2.01 (1H, t, *J* = 2.6 Hz); ^{13}C NMR δ 194.6, 169.8, 152.1, 148.2, 131.1, 124.6, 107.9, 107.8, 101.9, 79.3, 71.8, 54.6, 53.1, 40.7, 23.3 ; IR (KBr) 3258, 1754, 1742 cm^{-1}; MS *m/z* 332 (M^+); HRMS *m/z* calcd for $C_{17}H_{16}O_7$ (M^+) 332.0895, found: 332.0901.

Dimethyl 2-[2-(2-furyl-2-oxoethyl)]-2-(2-propynyl)malonate (4e); from **1** (0.043 g, 0.25 mmol), **4e** (0.063 g, 90.0%) was obtained as colorless crystals; mp 81-82˚C (AcOEt-hexane); ^{1}H NMR δ 7.61 (1H, d, *J* = 1.7 Hz), 7.26 (1H, d, *J* = 3.6 Hz), 6.56 (1H, dd, *J* = 1.7, 3.6 Hz), 3.77 (8H, s), 3.09 (2H, d, *J* = 2.6 Hz),

2.03 (1H, t, J = 2.6 Hz); ^{13}C NMR δ 185.5, 169.5, 152.1, 146.8, 117.8, 112.4, 79.1, 71.9, 54.4, 53.2, 40.5, 23.5; IR (KBr) 3282, 2955, 1742 cm^{-1}; MS *m/z* 278 (M^+); HRMS *m/z* calcd for $C_{14}H_{14}O_6$ (M^+) 278.0789, found: 278.0803.

Dimethyl 2-(2-propynyl)-2-[2-(2-thienyl-2-oxoethyl)]malonate (4f); from **1** (0.219 g, 1.29 mmol), **4f** (0.303 g, 79.9%) was obtained as colorless crystals; mp 78°C (AcOEt-hexane); ^{1}H NMR δ 7.83 (1H, dd, J = 1, 3.8 Hz), 7.67 (1H, dd, J = 1, 5 Hz), 7.15 (1H, dd, J = 3.8, 5 Hz), 3.86 (2H, s), 3.77 (6H, s), 3.10 (2H, d, J = 2.6 Hz), 2.04 (1H, t, J = 2.6 Hz); ^{13}C NMR δ 189.5, 169.5, 143.4, 134.3, 132.6, 128.2, 79.1, 72.0, 54.6, 53.2, 41.3, 23.4; IR (KBr) 3263, 2958, 1741 cm^{-1}; MS *m/z* 294 (M^+); HRMS *m/z* calcd for $C_{14}H_{14}O_5S$ (M^+) 294.0561, found: 294.0553.

***N*-(2-Phenyl-2-oxoethyl)-*N*-2-propynyltosylamide (4i).** To a mixture of **5** (0.816 g, 3.9 mmol), TBAI (0.100 g, 0.27 mmol), and K_2CO_3 (0.663 g, 4.8 mmol) in DMF (30 mL) at rt was added a solution of 2-bromoacetophenone 0.956 g, 4.8 mmol) in DMF (10 mL). After being stirred for 24 h, the reaction was quenched with water. The mixture was extracted with ether. The organic extracts were washed with water and brine, respectively, and dried. Evaporation of the solvent *in vacuo* gave a residue, which was purified by column chromatography (hexane/AcOEt = 3 : 1) to furnish **4i** (1.198 g, 93.8%) as pale yellow crystals; mp 93-94°C (AcOEt-hexane); ^{1}H NMR δ 7.94 (2H, d, J = 7.3 Hz), 7.76, 7.31 (each 2H, d, J = 8.2 Hz), 7.60 (1H, t, J = 7.3 Hz), 7.47 (2H, t, J = 7.3 Hz), 4.81 (2H, s), 4.29 (2H, d, J = 2.4 Hz), 2.43 (3H, s), 2.12 (1H, t, J = 2.4 Hz); ^{13}C NMR δ 193.2, 143.8, 136.0, 134.7, 133.8, 129.6, 128.8, 127.9, 127.5, 74.4, 51.4, 37.3, 21.5**;** IR (KBr) 3264, 2121, 1697 cm^{-1}; MS *m/z* 327 (M^+); HRMS *m/z* calcd for $C_{18}H_{17}NO_3S$ (M^+) 327.0929, found: 327.0930.

Dimethyl 2-(2-phenyl-2-butenyl)-2-(2-propynyl)malonate (2c). A suspension of PPh_3•EtBr (2.32 g, 6.3 mmol), and *t*-BuOK(0.673 g, 6.0 mmol) in THF (30 mL) was stirred at rt for 10 min. To this mixture was added a solution of **4c** (0.720 g, 2.5 mmol) in THF (10 mL). After being stirred for 1 h, the reaction was quenched with water. The mixture was extracted with $CHCl_3$. The usual work-up gave a residue, which was purified by column chromatography (hexane/AcOEt = 10 : 1) to give **2c** (0.643 g, 85.7%) as a pale yellow oil; ^{1}H NMR δ 7.10-7.33 (5H, m), 5.81 (0.72H, q, J = 6.9 Hz), 5.76 (0.28H, q, J = 7 Hz), 3.38 (0.56H, s), 3.52 (1.44H, s), 3.63 (4.32H, s), 3.21 (1.68H, s), 2.77 (1.44H, d, J = 2.6 Hz), 2.67 (0.56H, d, J = 2.6 Hz), 2.03 (1H, t, J = 2.6 Hz), 1.88 (0.84H, d, J = 7 Hz), 1.88 (2.16H, d, J = 6.9 Hz); ^{13}C NMR δ 170.0, 169.9, 143.2, 138.8, 135.2, 130.4, 129.2, 127.9, 127.8, 127.6, 127.2, 126.7, 126.6, 79.8, 79.3, 71.5, 71.4, 56.8, 56.2, 52.3, 52.2, 30.9, 22.3, 22.1, 14.8, 14.7; IR (neat) 3273, 2955, 1733 cm^{-1}; MS *m/z* 300 (M^+); HRMS *m/z* calcd for $C_{18}H_{20}O_4$ (M^+) 300.1362, found: 300.1354.

General Procedure for Synthesis of Enynes (2d-f) from Ketones (4d-f). A suspension of PPh_3•MeBr (2.6 eq.), and *t*-BuOK (2.5 eq.) in THF (6 mL per 1 mmol of the ketone) was stirred at rt for 30 min. To this mixture was added a solution of the ketone (1 eq.) in THF (5 mL per 1 mmol of the ketone). After

being stirred for 1 h, the reaction was quenched with water. The mixture was extracted with $CHCl_3$. The usual work-up gave a residue, which was purified by column chromatography (hexane/AcOEt = 10 : 1 ~ 4 : 1) to give the corresponding *exo*-olefins (**2c-f**, **i**).

Dimethyl 2-[2-(3,4-methylenedioxyphenyl)-2-propenyl]-2-(2-propynyl)malonate (**2d**); from **4d** (0.837 g, 2.52 mmol), **2d** (0.788 g, 94.7%) was obtained as pale yellow crystals; mp 66-67°C (hexane); ^{1}H NMR δ 6.78-6.83 (2H, m), 6.72 (1H, d, *J* = 8.6 Hz), 5.93 (2H, s), 5.24, 5.20 (each 1H, d, *J* = 1 Hz), 3.52 (6H, s), 3.27 (2H, s), 2.74 (2H, d, *J* = 2.6 Hz), 2.04 (1H, t, *J* = 2.6 Hz); ^{13}C NMR δ 170.0, 147.5, 146.2, 143.3, 135.0, 120.3, 118.1, 107.8, 107.5, 101.1, 79.2, 71.8, 56.6, 52.5, 37.0, 22.4; IR (KBr) 3286, 2957, 1729 cm^{-1}; MS *m/z* 330 (M^+); HRMS *m/z* calcd for $C_{18}H_{18}O_6$ (M^+) 330.1101, found: 330.1093

Dimethyl 2-[2-(2-furyl-2-propenyl)]-2-(2-propynyl)malonate (2e); from **4e** (0.743 g, 2.67 mmol), **2e** (0.648 g, 87.9%) was obtained as pale yellow crystals; mp 81-82°C (hexane); ^{1}H NMR δ 7.32 (1H, d, *J* = 1.5 Hz), 6.38 (1H, d, *J* = 3.3 Hz), 6.34 (1H, dd, *J* = 1.5, 3.3 Hz), 5.66 (1H, d, *J* = 1 Hz), 5.14 (1H, s), 3.66 (6H, s), 3.18 (2H, d, *J* = 1 Hz), 2.84 (2H, d, *J* = 2.6 Hz), 2.09 (1H, t, *J* = 2.6 Hz); ^{13}C NMR δ 170.1, 154.0, 142.1, 131.9, 114.7, 111.1, 106.8, 79.4, 72.0, 57.1, 53.2, 34.6, 22.7; IR 3289, 2952, 1759, 1738 cm^{-1}; MS *m/z* 276 (M^+); HRMS *m/z* calcd for $C_{15}H_{16}O_5$ (M^+) 276.0997, found: 276.0998.

Dimethyl 2-(2-propynyl)-2-[2-(2-thienyl-2-propenyl)]malonate (2f); from **4f** (0.431 g, 1.47 mmol), **2f** (0.339 g, 78.9%) was obtained as pale yellow crystals; mp 73-74°C (hexane); ^{1}H NMR δ 7.14 (1H, dd, *J* = 1, 5.2 Hz), 7.01 (1H, dd, *J* = 1, 3.6 Hz), 6.93 (1H, dd, *J* = 3.6, 5.2 Hz), 5.48, 5.17 (each 1H, s), 3.57 (6H, s), 3.29 (2H, s), 2.83 (2H, d, *J* = 2.6 Hz), 2.08 (1H, t, *J* = 2.6 Hz); ^{13}C NMR δ 170.0, 144.3, 136.5, 127.0, 124.8, 124.3, 117.1, 79.2, 71.9, 56.8, 52.6, 37.0, 22.6; IR (KBr) 3289, 3103, 2950, 1734 cm^{-1}; MS *m/z* 292 (M^+); HRMS *m/z* calcd for $C_{15}H_{16}O_4S$ (M^+) 292.0768, found: 292.0759.

Dimethyl 2-(2-propynyl)-2-[2-(2-pyridyl-2-propenyl)]malonate (2g). To a stirred mixture of **1** (0.038 g, 0.23 mmol), 2-(2-pyridyl)propen-1-ol (0.021 g, 0.15 mmol) and Bu_3P (0.051 g, 0.23 mmol) in benzene (1 mL) at 0°C was added *N*, *N*, *N*', *N*'-tetramethylazodicarboxamide (TMAD) (0.039 g, 0.23 mmol) in one portion. After being stirred for 10 min, the reaction mixture was stirred at rt for 7 h. The precipitate was filtered off and the filtrate was evaporated under reduced pressure to give a residue, which was purified by column chromatography (Et_2O/hexane = 8 : 1) to afford **2g** (0.031 g, 72.2%) as colorless crystals; mp 47-48°C (hexane); ^{1}H NMR δ 8.53 (1H, d, *J* = 4.6 Hz), 7.63 (1H, dt, *J* = 1.7, 7.8 Hz), 7.44 (1H, d, *J* = 7.8 Hz), 7.11-7.18 (1H, m), 5.74 (1H, d, *J* = 1 Hz), 5.54 (1H, s), 3.54 (2H, s), 3.53 (6H, s), 2.78 (2H, d, *J* = 2.6 Hz), 2.06 (1H, t, *J* = 2.6 Hz); ^{13}C NMR δ 170.2, 158.2, 148.4, 143.5, 136.4, 122.2, 121.0, 79.3, 71.7, 56.6, 52.4, 34.9, 22.7; IR (KBr) 3277, 2958, 1752, 1733 cm^{-1}; MS *m/z* 286 (M^+-1); HRMS *m/z* calcd for $C_{16}H_{16}NO_4$ (M^+-1) 286.1077, found: 286.1066.

***N*-(2-Phenyl-2-propenyl)-*N*-2-propynyltosylamide (2h).** To a mixture of **5** (0.326 g, 1.56 mmol) and K_2CO_3 (0.261 g, 1.89 mmol) in DMF (18 mL) at 0°C was added a solution of 3-iodo-2-phenylpropene

(0.460 g, 1.89 mmol) in DMF (5 mL). Then, the mixture was allowed to warm to rt and stirred for 2 h. After cooling at 0°C, the reaction was quenched with water. The mixture was extracted with ether. The organic extracts were washed with water and brine, respectively, and dried. Evaporation of the solvent *in vacuo* gave a residue, which was purified by column chromatography (hexane/AcOEt = 10 : 1) to furnish **2h** (0.375 g, 74.0%) as pale yellow crystals; mp 60-61°C (hexane); ^{1}H NMR δ 7.74, 7.51 (each 2H, d, *J* = 8 Hz), 7.25-7.38 (5H, m), 5.57, 5.35 (each 1H, s), 4.27 (2H, s), 3.99 (2H, d, *J* = 2.3 Hz), 2.43 (3H, s), 1.97 (1H, t, *J* = 2.3 Hz); ^{13}C NMR δ 143.7, 141.3, 137.6, 135.5, 129.4, 128.5, 128.2, 128.0, 126.4, 117.3, 74.1, 49.9, 35.5, 21.6; IR (KBr) 3270, 2119, 1596 cm^{-1}; MS *m/z* 325 (M^+); HRMS *m/z* calcd for $C_{19}H_{19}NO_2S$ (M^+) 325.1134, found: 325.1133.

***N*-(2-Phenyl-2-butenyl)-*N*-2-propynyltosylamide (2i).** To a suspension of PPh_3•EtBr (1.866 g, 5.0 mmol) in THF (25 mL) was added 1.58 M BuLi in THF (3.0 mL, 4.74 mmol) and the mixture was stirred at rt for 10 min. To this mixture was added a solution of **4i** (0.654 g, 2.0 mmol) in THF (5 mL). After being stirred for 10 min, the reaction was quenched with water. The mixture was extracted with $CHCl_3$. The usual work-up gave a residue, which was purified by column chromatography (hexane/AcOEt = 10 : 1) to give **2i** (0.513 g, 75.7%) as pale yellow crystals; mp 80-83°C; ^{1}H NMR δ 7.15-7.71 (9H, m), 6.04 (0.22H, q, *J* = 7.1 Hz), 5.76 (0.78H, q, *J* = 6.9 Hz), 4.35 (0.44H, s), 4.11 (1.56H, s), 4.00 (1.56H, s), 3.83 (0.44H, s), 2.38 (0.68H, s), 2.36 (2.32H, s), 2.01 (0.22H, t, *J* = 2 Hz), 1,86 (0.78H, d, *J* = 1.7 Hz), 1.85 (0.68H, d, *J* = 7.1 Hz), 1.63 (2.32H, d, *J* = 6.9 Hz); ^{13}C NMR δ 143.3, 143.1, 139.8, 137.2, 135.7, 135.3, 134.6, 133.8, 129.7, 129.1, 128.4, 128.0, 127.9, 127.8, 127.5, 126.9, 126.3, 77.2, 76.7, 76.4, 73.7, 52.5, 43.2, 35.1, 34.8, 21.3, 21.2, 14.6, 14.1; IR (KBr) 3297, 2118, 1598 cm^{-1}; MS *m/z* 339 (M^+); HRMS *m/z* calcd for $C_{20}H_{21}NO_2S$ (M^+) 339.1291, found: 339.1285.

Dimethyl 2-(2-phenyl-2-propenyl)-2-(3-trimethylsilyl-2-propynyl)malonate (2j). To a suspension of **2a** (0.069 g, 0.24 mmol) and CsF (0.001 g , 0.007 mmol) in THF (2 mL) at rt $TMSCF_3$ (46 μL, 0.31 mmol) was added. After being stirred for 30 min, the mixture was filtered and the filtrate was evaporated *in vacuo* to give a residue, which was purified by preparative TLC (hexane/AcOEt = 10 : 1) to afford **2i** (0.085 g, 98.6%) as a colorless oil; ^{1}H NMR δ 6.93-7.05 (5H, m), 5.01 (1H, d, *J* = 1.7 Hz), 4.95 (1H, d, *J* = 1.2 Hz), 3.13 (6H, s), 3.04 (2H, s), 2.48 (2H, s), -0.12 (9H, s); ^{13}C NMR δ 169.9, 143.9, 140.9, 128.0, 127.5, 126.8, 118.8, 101.7, 88.5, 56.7, 52.3, 36.8, 23.5, -0.1; IR (neat) 2954, 2179, 1738, 1436 cm^{-1}; MS *m/z* 358 (M^+); HRMS *m/z* calcd for $C_{20}H_{26}O_4Si$ (M^+) 358.1600, found: 358.1661.

***N*-(2-Phenyl-2-propenyl)-*N*-(3-trimethylsilyl-2-propynyl)tosylamide (2k).** To a suspension of **2h** (0.093 g, 0.29 mmol) and CsF (0.001 g , 0.007 mmol) in THF (6 mL) at rt $TMSCF_3$ (55 μL, 0.37 mmol) was added. After being stirred for 30 min, the mixture was filtered and the filtrate was evaporated *in vacuo* to give a residue, which was purified by column chromatography (hexane/AcOEt = 10 : 1) to afford **2k** (0.109 g, 95.6%) as colorless crystals; mp 108-109°C (hexane); ^{1}H NMR δ 7.69, 7.49 (each 2H,

d, *J* = 8 Hz), 7.20-7.32 (5H, m), 5.52, 5.27 (each 1H, s), 4.20, 3.93 (each 2H, s), 2.36 (3H, s), -0.08 (9H, s); ^{13}C NMR δ 143.4, 141.1, 137.6, 135.5, 129.4, 129.3, 128.0, 127.8, 126.3, 117.2, 97.4, 91.3, 49.8, 36.4, 21.6, -0.5; IR (KBr) 3270, 2119, 1596 cm^{-1}; MS *m/z* 397 (M^+); HRMS *m/z* calcd for $C_{22}H_{27}NO_2SSi$ (M^+) 397.1532, found: 397.1528.

General Procedures for Pauson-Khand Reaction of Enynes. A mixture of enyne (1 eq.) and $Co_2(CO)_8$ (1.2 eq.) in CH_2Cl_2 or toluene or 1,2-dichloroethane was stirred at rt for 1 h. Method A: NMO (3 eq.) was added to the mixture three or four times at intervals of 15 min. Method B: The mixture in toluene was refluxed. Method C: BuSMe (3.5 eq.) was added to the mixture and the resulting mixture was heated at 83°C. The reaction mixture was diluted with ether and the precipitate was removed by suction filtration through a Celite 545 short pad. After the solvent was removed *in vacuo*, purification of the residue obtained by Methods A-C was carried out on preparative TLC (hexane/AcOEt = 8 : 5 ~ 3 : 2).

2,2-Dimethoxycarbonyl-5-oxo-3a-phenyl-3,3a,4,5-tetrahydro-1*H*-pentalene (6a); mp 137-138°C (AcOEt-hexane); ^{1}H NMR δ 7.18-7.31 (3H, m), 7.09-7.16 (2H, m), 6.19 (d, 1H, *J* = 2 Hz), 3.73 (3H, s), 3.67 (1H, dd, *J* = 2, 18.1 Hz), 3.48 (1H, d, *J* = 13.7 Hz), 3.26 (3H, s), 3.15, 2.71 (each 1H, d, *J* = 18.1 Hz), 2.52 (1H, d, *J* = 18.1 Hz), 2.46 (1H, d, *J* = 13.7 Hz); ^{13}C NMR δ 204.9, 181.3, 167.9, 166.8, 139.0, 125.0, 123.8, 123.6, 122.4, 56.5, 54.4, 49.8, 49.7, 49.2, 41.1, 31.2; IR (KBr) 2953, 1758, 1729, 1706, 1638 cm^{-1}; MS *m/z* 314 (M^+); HRMS *m/z* calcd for $C_{18}H_{18}O_5$ (M^+) 314.1153, found: 314.1168.

2,2-Dimethoxycarbonyl-5-oxo-3a-(1-naphthyl)-3,3a,4,5-tetrahydro-1*H*-pentalene (6b); mp 125-126°C (AcOEt-hexane); ^{1}H NMR δ 7.93 (1H, d, *J* = 8.3 Hz), 7.84-7.87 (1H, m), 7.71 (1H, d, *J* = 8.3 Hz), 7.48-7.60 (2H, m), 7.27 (1H, t, *J* = 8.3 Hz), 6.93 (1H, d, *J* = 6.9 Hz), 6.3 (1H, d, *J* = 1.8 Hz), 3.94 (1H, dd, *J* = 1.8, 18.2 Hz), 3.70 (3H, s), 3.59 (1H, d, *J* = 13.2 Hz), 3.37 (1H, d, *J* = 18.2 Hz), 3.06 (1H, d, *J* = 17.2 Hz), 2.92 (3H, s), 2.92 (1H, d, *J* = 17.2 Hz), 2.66 (1H, d, *J* = 13.2 Hz); ^{13}C NMR δ 207.7, 185.7, 171.4, 170.2, 139.7, 134.6, 130.2, 129.4, 128.4, 128.3, 126.1, 125.6, 125.0, 124.6, 124.5, 60.6, 57.6, 53.3, 53.2, 52.3, 45.9, 35.7; IR (KBr) 2650, 1732, 1704, 1638 cm^{-1}; MS *m/z* 364 (M^+); HRMS *m/z* calcd for $C_{22}H_{20}O_5$ (M^+) 364.1293, found: 364.1321.

2,2-Dimethoxycarbonyl-4-methyl-5-oxo-3a-phenyl-3,3a,4,5-tetrahydro-1*H*-pentalene (6c); mp 94-101°C; ^{1}H NMR δ 7.04-7.30 (5H, m), 6.24 (0.58H, s), 6.15 (0.42H, s), 3.74 (1.62H, s), 3.73 (1.38H, s), 3.51-3.77 (1.58H, m), 3.38 (1.62H, s), 3.31 (1.38H, s), 3.04-3.19 (1.42H, m), 2.39-2.86 (2H, m), 1.24 (1.38H, d, *J* = 7.9 Hz), 0.64 (1.62H, d, *J* = 7.3 Hz); ^{13}C NMR δ 211.8, 210.7, 183.6, 182.9, 171.6, 170.5, 144.1, 138.4, 128.7, 128.3, 127.4, 127.2, 127.1, 126.3, 125.8, 125.7, 62.0, 61.6, 60.1, 59.6, 55.9, 55.1, 53.2, 52.8, 52.7, 44.5, 43.4, 39.3, 34.8, 34.4, 13.8, 11.7; IR (KBr) 2949, 1739, 1704, 1638 cm^{-1}; MS *m/z* 328 (M^+); HRMS *m/z* calcd for $C_{19}H_{20}O_5$ (M^+) 328.1311, found: 328.1319.

2,2-Dimethoxycarbonyl-5-oxo-3a-(3,4-methylenedioxyphenyl)-3,3a,4,5-tetrahydro-1*H*-pentalene (6d); mp 145-147°C (AcOEt-hexane); ^{1}H NMR δ 6.68 (1H, d, *J* = 7.9 Hz), 6.64 (1H, d, *J* = 2 Hz), 6.55

(1H, dd, *J* = 2, 7.9 Hz), 6.16 (1H, d, *J* = 2 Hz), 5.93 (2H, s), 3.73 (3H, s), 3.65 (1H, dd, *J* = 2, 18.3 Hz), 3.48 (3H, s), 3.39 (1H, d, *J* = 13.5 Hz), 3.11 (1H, d, *J* = 18.3 Hz), 2.66, 2.47 (each 1H, d, *J* = 17.7 Hz), 2.43 (1H, d, *J* = 13.5 Hz); ^{13}C NMR δ 208.5, 184.7, 171.4, 170.4, 148.1, 146.6, 136.3, 127.3, 119.5, 108.1, 106.6, 101.1, 60.0, 57.6, 53.4, 53.3, 52.9, 44.6, 34.7; IR (KBr) 2952, 1751, 1729, 1704, 1638 cm^{-1}; MS *m/z* 358 (M^+); HRMS *m/z* calcd for $C_{19}H_{18}O_7$ (M^+) 358.1051, found: 358.1052.

2,2-Dimethoxycarbonyl-5-oxo-3a-(2-furyl)-3,3a,4,5-tetrahydro-1*H*-pentalene (6e); mp 115°C (AcOEt-hexane); ^{1}H NMR δ 7.31 (1H, dd, *J* = 0.7, 2 Hz), 6.24 (1H, dd, *J* = 2, 3.3 Hz), 6.06 (1H, d, *J* = 2 Hz), 5.97 (1H, dd, *J* = 0.7, 3.3 Hz), 3.75, 3.66 (each 3H, s), 3.56 (1H, dd, *J* = 2, 17.8 Hz), 3.36 (1H, d, *J* = 13.7 Hz), 3.19 (1H, d, *J* = 17.8 Hz), 2.63, 2.57 (each 1H, d, *J* = 17.5 Hz), 2.41 (1H, d, *J* = 13.7 Hz); ^{13}C NMR δ 208.0, 182.5, 171.5, 170.6, 154.6, 142.4, 126.4, 110.3, 105.9, 60.3, 53.7, 53.3, 53.2, 50.1, 42.7, 34.8; IR (KBr) 2957, 1730, 1706, 1642 cm^{-1}; MS *m/z* 304 (M^+); HRMS *m/z* calcd for $C_{16}H_{16}O_6$ (M^+) 304.0946, found: 304.0954.

2,2-Dimethoxycarbonyl-5-oxo-3a-(2-thienyl)-3,3a,4,5-tetrahydro-1*H*-pentalene (6f); mp 125°C (AcOEt-hexane); ^{1}H NMR δ 7.18 (1H, d, *J* = 4.8 Hz), 6.86 (1H, dd, *J* = 3.6, 4.8 Hz), 6.72 (1H, d, *J* = 3.6 Hz), 6.11 (1H, d, *J* = 2 Hz), 3.74 (3H, s), 3.72 (1H, dd, *J* = 2, 18.1 Hz), 3.56 (3H, s), 3.39 (1H, d, *J* = 13.7 Hz), 3.12 (1H, d, *J* = 18.1 Hz), 2.72, 2.63 (each 1H, d, *J* = 17.5 Hz), 2.58 (1H, d, *J* = 13.7 Hz); ^{13}C NMR δ 207.9, 184.0, 171.4, 170.5, 147.1, 126.8, 126.3, 125.0, 124.2, 60.3, 55.2, 53.6, 53.3, 53.1, 45.5, 34.5; IR (KBr) 2954, 1730, 1708, 1637 cm^{-1}; MS *m/z* 320 (M^+); HRMS *m/z* calcd for $C_{16}H_{16}O_5S$ (M^+) 320.0708, found: 320.0707.

2,2-Dimethoxycarbonyl-5-oxo-3a-(2-pyridyl)-3,3a,4,5-tetrahydro-1*H*-pentalene (6g); mp 114-115°C (AcOEt-hexane); ^{1}H NMR δ 8.47 (1H, d, *J* = 4 Hz), 7.62 (1H, dt, *J* = 2, 7.8 Hz), 7.11-7.17 (2H, m), 6.14 (1H, d, *J* = 2 Hz), 3.75 (3H, s), 3.72 (1H, d, *J* = 13.2 Hz), 3.59 (1H, dd, *J* = 2, 17.8 Hz), 3.57 (3H, s), 3.11 (1H, d, *J* = 17.8 Hz), 2.75, 2.67 (each 1H, d, *J* = 18 Hz), 2.51 (1H, d, *J* = 13.2 Hz); ^{13}C NMR δ 208.7, 185.1, 171.8, 171.0, 161.5, 148.8, 137.1, 126.9, 122.2, 120.2, 60.2, 60.1, 53.3, 53.0, 52.1, 43.2, 35.1; IR (KBr) 2950, 1752, 1727, 1705, 1636 cm^{-1}; MS *m/z* 315 (M^+); HRMS *m/z* calcd for $C_{17}H_{17}NO_5$ (M^+) 315.0114, found: 315.0115.

3a-Phenyl-2-tosyl-2,3,3a,4-tetrahydro-1*H*-cyclopenta[*c*]pyrrol-5-one (6h); mp 171-172°C (AcOEt-hexane); ^{1}H NMR δ 7.57 (2H, d, *J* = 8.3 Hz), 7.19-7.27 (5H, m), 7.07-7.11 (2H, m), 6.17 (1H, s), 4.44 (1H, d, *J* = 9.7 Hz), 4.21, 4.14 (each 1H, d, *J* = 16.5 Hz), 3.13 (1H, d, *J* = 9.7 Hz), 2.58 (2H, s), 2.40 (3H, s); ^{13}C NMR δ 207.0, 178.9, 143.8, 141.2, 133.5, 129.8, 129.0, 127.4, 127.2, 127.1, 125.4, 57.8, 56.5, 50.4, 46.8, 21.5; IR (KBr) 1711, 1650 cm^{-1}; EI MS *m/z* 353 (M^+); HRMS *m/z* calcd for $C_{20}H_{19}NO_3S$ (M^+) 353.1085, found: 353.1085.

4-Methyl-3a-phenyl-2-(toluene-4-sulfonyl)-2,3,3a,4-tetrahydro-1*H*-cyclopenta[*c*]pyrrol-5-one (6i); mp 54-66°C; ^{1}H NMR δ 7.50-7.57 (2H, m), 7.15-7.27 (5H, m), 7.00-7.06 (2H, m), 6.27 (0.60H, s), 6.15

(0.40H, s), 4.55 (0.60H, d, *J* = 9.8 Hz), 4.19 (0.40H, d, *J* = 10.1 Hz), 4.18 (0.80H, s), 4.13 (1.20H, s), 3.17 (0.40H, d, *J* = 10.1 Hz), 3.09 (0.60H, d, *J* = 9.8 Hz), 2.83 (3H, s), 2.33 (1H, m), 1.13 (1.20H, d, *J* = 7.7 Hz), 0.65 (1.80H, d, *J* = 7.3 Hz); ^{13}C NMR δ 210.5, 209.0, 177.4, 176.7, 143.7, 143.2, 133.6, 129.7, 129.0, 128.8, 127.5, 127.2, 127.1, 126.6, 126.5, 125.7, 125.1, 61.0, 60.2, 57.6, 53.6, 53.2, 53.0, 47.2, 46.7, 21.5, 13.9, 11.3; IR (KBr) 2921, 1717, 1655 cm^{-1}; EI MS *m/z* 367 (M^+); HRMS *m/z* calcd for $C_{21}H_{21}NO_3S$ (M^+) 367.1240, found: 367.1242.

5,5-Dimethoxycarbonyl-7a-methyl-1,4,5,6,7,7a-hexahydroinden-2-one (10); mp 75-76°C (AcOEt-hexane); ^{1}H NMR δ 5.89 (1H, d, *J* = 2 Hz), 3.77, 3.72 (each 3H, s), 3.35 (1H, dd, *J* = 2.3 Hz, 13.9 Hz), 2.86 (1H, dd, *J* = 1.7, 13.9 Hz), 2.36-2.43 (1H, m), 2.31, 2.20 (each 1H, d, *J* = 18.8 Hz), 2.08 (1H, dt, *J* = 4 , 14 Hz), 1.88-1.96 (1H, m), 1.58 (1H, dt, *J* = 4, 14 Hz), 1.29 (3H, s); ^{13}C NMR δ 182.0, 171.7, 170.7, 129.2, 57.1, 53.1, 52.8, 51.6, 42.1, 36.6, 32.1, 27.5, 24.0; IR (KBr) 2962, 1737, 1698 cm^{-1}; MS *m/z* 266 (M^+); HRMS *m/z* calcd for $C_{14}H_{18}O_5$ (M^+) 266.1154, found: 266.1153.

6,6-Dimethoxycarbonyl-7a-methyl-1,4,5,6,7,7a-hexahydroinden-2-one (15); mp 68-70°C (AcOEt-hexane); ^{1}H NMR δ 5.84 (1H, d, *J* = 1.7 Hz), 3.80, 3.72 (each 3H, s), 2.66-2.88 (3H, m), 2.81 (1H, d, *J* = 13.9 Hz), 2.29 (2H, s), 2.09 (1H, d, *J* = 13.9 Hz), 1.56-1.68 (1H, m), 1.11 (3H, s); ^{13}C NMR δ 183.0, 171.2, 170.0, 127.1, 53.1, 52.9, 52.7, 43.5, 42.3, 32.3, 25.0, 24.6; IR (KBr) 2954, 1730, 1711, 1686, 1625 cm^{-1}; MS *m/z* 266 (M^+); HRMS *m/z* calcd for $C_{14}H_{18}O_5$ (M^+) 266.1154, found: 266.1158.

5,5-Dimethoxycarbonyl-1-phenyl-1,4,5,6,7,7a-hexahydroinden-2-one (**17**); mp 85-86°C (AcOEt-hexane); ^{1}H NMR δ 7.21-7.33 (3H, m), 7.08-7.11 (2H, m), 6.07 (1H, s), 3.75, 3.74 (each 3H, s), 3.56 (1H, dd, *J* = 2.2, 14.3 Hz), 3.12 (1H, d, *J* = 2.9 Hz), 2.73 (1H, d, *J* = 14.3 Hz), 2.67-2.78 (1H, m), 2.53 (1H, dq, *J* = 2.6, 13.8 Hz), 2.22-2.32 (1H, m), 1.91 (1H, dt, *J* = 13.8, 3.7 Hz) 1.43 (1H, dq, *J* = 13.1, 3 Hz); ^{13}C NMR δ 207.2, 177.0, 171.2, 170.0, 138.7, 128.9, 128.8, 127.9, 127.0, 59.6, 56.4, 53.1, 52.8, 50.5, 35.4, 30.6, 29.8; IR (KBr) 3275, 2955, 1734 cm^{-1}; MS *m/z* 328 (M^+); HRMS *m/z* calcd for $C_{19}H_{20}O_5$ (M^+) 328.1309, found: 328.1319.

6,6-Dimethoxycarbonyl-1-phenyl-1,4,5,6,7,7a-hexahydroinden-2-one (**19**); oil; ^{1}H NMR δ 7.21-7.36 (3H, m), 7.09-7.15 (2H, m), 5.99 (1H, s), 3.73, 3.72 (each 3H, s), 3.16 (1H, d, *J* = 2.6 Hz), 2.84-2.97 (3H, m), 2.62-2.72 (1H, m), 2.55 (1H, dd, *J* = 5, 14.1 Hz), 1.89 (1H, dt, *J* = 4.7, 13 Hz), 1.74 (1H, t, *J* = 9.7 Hz); ^{13}C NMR δ 207.0, 179.3, 171.3, 170.5, 138.3, 128.8, 128.0, 127.1, 126.9, 59.8, 54.7, 53.0, 52.9, 47.3, 37.9, 31.2, 27.1; IR (neat) 2954, 1732, 1705, 1629 cm^{-1}; MS *m/z* 328 (M^+); HRMS *m/z* calcd for $C_{19}H_{20}O_5$ (M^+) 328.1309, found: 328.1310.

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