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Molybdenum-mediated cyclocarbonylation of 1-ethynyl-2-allenylbenzenes to 1*H*-cyclopenta[*a*]inden-2-ones

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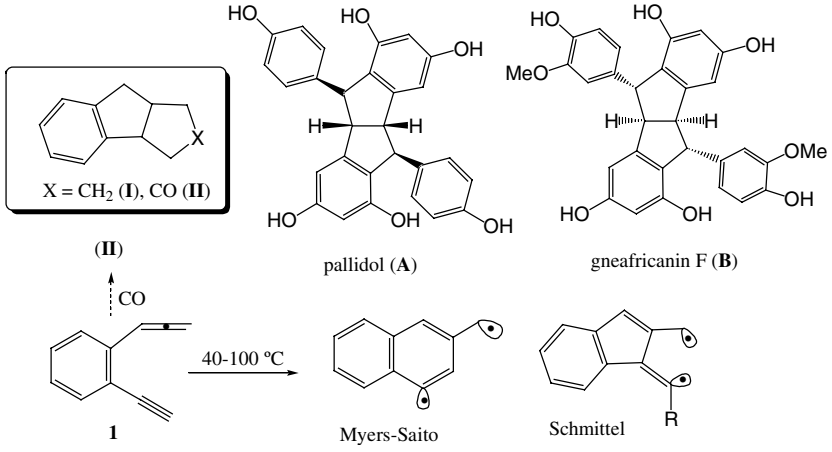
Abstract—Although 1-ethynyl-2-allenylbenzenes readily undergo Myers–Saito or Schmittel cyclization under mild conditions, cyclocarbonylation of these moieties to 1*H*-cyclopenta[*a*]inden-2-ones proceeds smoothly using suitable molybdenum carbonyl reagents, with $Mo(CO)_3(CH_3CN)_3$ being the most efficient. The yields of desired bicyclic ketones were up to 87–93%.

1,2,3,3a,8,8a-Hexahydrocyclopenta[*a*]indene with framework **I** (X = CH_2) is often encountered in naturally occurring polyphenol species.[1,2] Scheme 1 shows several representatives such as pallidol (**A**)[1a,d,2a,c] and gneafricanin F (**B**),[2b,c] which showed interesting biological activities. The more complex molecules comprising such a functionality include ampelopsin **H**,[1b] leachianol **A**, **C**, **D** and **E**.[1c,2d] A selective synthesis of this functionality from a simple precursor is a challenging synthetic issue. Scheme 1 shows a straightforward synthesis of this framework via metal-mediated Pauson–Khand cyclocarbonylation[3] of 1-ethynyl-2-allenylbenzene **1**. Although carbonylation of allene–yne functionalities has been implemented efficiently with $Co_2(CO)_8$,[4] $Mo(CO)_6$,[4] and $[Rh(CO)_2Cl]_2$,[5] similar reactions of compound **1** implemented with metal species are expected to be plagued with competitive Myers–Saito[6,7] or Schmittel cyclization,[8] which also occur under ambient conditions. The two radical pathways normally produce 2-methylnaphthalene or 2-methyl-1-alkylidene-1*H*-indene in suitable hydrogen-donor solvents. Here, we report a clean and efficient carbonylation of 1-ethynyl-2-allenylbenzene



Scheme 1.

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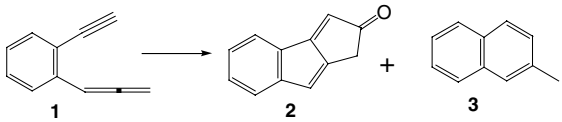
Table 1. Cyclocarbonylation of compound **1** with various metal species



Entry	Reagent[a]	Solvent[d]	Conditions	Yields[f,g]
1	$Co_2(CO)_8$	Benzene	80 °C, 8 h	**2** (47%)
2	$Mo(CO)_6$	Toluene[e]/DMSO	100 °C, 8 h	**2** (70%); **3** (10%)
3	$[RhCl(CO)_2(CO)_2]_2$[b]	Toluene	CO (1 atm) 90 °C, 8 h	**2** (62%); **3** (8%)
4	$Mo(CO)_5THF$	THF/DMSO	40 °C, 2 h	**2** (56%)
5	$Mo(CO)_4(CH_3CN)_2$	CH_3CN	40 °C, 2 h	**2** (61%)
6	$Mo(CO)_3(CH_3CN)_3$	CH_3CN	25 °C, 8 h	**2** (82%)
7	$Mo(CO)_3(CH_3CN)_3$[c]	CH_2Cl_2	CO (1 atm) 40 °C, 24 h	**1** (56%), **2** (12%), **3** (9%)
8	$Mo(CO)_6$[c]	Toluene[e]/DMSO	CO (1 atm) 55 °C, 24 h	**1** (75%), **2** (5%), **3** (10%)

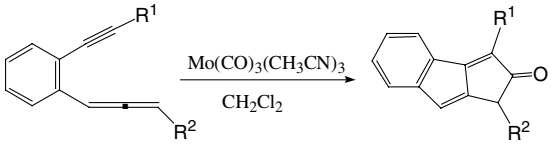
[a] One equivalent of metal reagent was used except for entries 3, 7 and 8.
[b] 5 mol % loading.
[c] 10 mol % loading.
[d] [substrate] = 0.15 M.
[e] Molar ratio: DMSO/Mo = 5.0.
[f] Yields are given after separation from a silica column.
[g] Starting substrate **1** was consumed completely in entries 1–6.

derivatives with suitable molybdenum-carbonyl species. These new reagents effectively eliminate by-products that arise from Myers–Saito[6,7] or Schmittel cyclization.[8]

Table 1 shows the results for cyclocarbonylation of 1-ethynyl-2-allenylbenzene (**1**) to 1*H*-cyclopenta[*a*]-inden-2-one (**2**) using various metal complexes. We first examined the cyclization with a traditional Pauson–Khand reagent $Co_2(CO)_8$[3] (1.0 equiv, entry 1) in hot benzene (80 °C, 8 h), which gave desired ketone **2** in 47% yield in addition to black tar material. Treatment of species **1** with $Mo(CO)_6$ (1.0 equiv) and DMSO promoter[4] (5.0 equiv) in hot toluene (100 °C, 8 h) gave an improved yield (70%, entry 2) of bicyclic ketone **2**, but the Myers–Saito cyclized product **3** was still present in 10% yield. We also attempted to perform this carbonylation with $[RhCl(CO)_2]_2$ (5 mol %) catalyst, operating under CO (1.0 atm) in hot toluene (90 °C, 8 h). But the corresponding efficiency is inferior to that observed for the $Mo(CO)_6$ species. We found that the use of $Mo(CO)_nL_{6-n}$[9,10] ($n = 5$–3, L = THF or CH_3CN, entries 4–6) species in equal proportion enable use of lower reaction temperatures (25–40 °C) to circumvent the Myers–Saito cyclization (entries 4–6), which normally proceeds in the range of 40–80 °C for 5-allenyl-3-en-1-yne derivatives. For these three metal carbonyl species, parent ligand L (L = THF or CH_3CN) serves as the reaction solvent to ensure the stability of their complexes. On the basis of those performances, $Mo(CO)_3(CH_3CN)_3$was found to be the most active for carbonylation reaction; it gave bicyclic ketone **2** in 82% yield at 25 °C. The high reactivity with $Mo(CO)_3(CH_3CN)_3$ is attributed to its highly coordinated unsaturation because of the three labile CH_3CN. A similar species $Mo(CO)_3(DMF)_3$ has been shown to be active in the Pauson–Khand-type reaction for acyclic enynes near room temperatures.[11] The cyclization efficiency of $Mo(CO)_3(CH_3CN)_3$ was maintained or even improved in various solvents at 25 °C (2–4 h) according to the following data: toluene (85%, 4 h), MeOH (85%, 3 h), THF (87%, 3 h), ethylacetate (90%), CH_2Cl_2 (92%, 2 h) and DMF (87%, 4 h). We made a final attempt to realize this cyclization with 10 mol % $Mo(CO)_3(CH_3CN)_3$under balloon CO, but the reaction became sluggish. The operating condition (CH_2Cl_2, 40 °C, 24 h) gave a mixture of ketone **2** and 2-methylnaphthalene **3** in 12% and 9% yields, respectively, in addition to a 56% recovery of unreacted **1** (entry 7). We employed a catalytic reaction[5c] on the basis of $Mo(CO)_6$ (10 mol %), which showed similarly disappointing result (entry 8).

We have prepared various 1-ethynyl-2-allenylbenzenes **4**–**11** to examine the generality of this carbonylation reaction; the results are shown in Table 2. In a typical operation, these substrates were treated with $Mo(CO)_3(CH_3CN)_3$ (1.1 equiv) in CH_2Cl_2 (25 °C, 4 h), and the resulting bicyclic ketones **12**–**19** were purified by elution on a short silica column. In all cases, we isolated no by-product corresponding to Myers–Saito[7] or Schmittel cyclization.[8] A lower reaction temperature

Table 2. Cyclocarbonylation of various 1-ethynyl-2-allylbenzenes



Entry	Allen–yne[a]	Ketones[b]
1	$R^1 = n\text{-}C_4H_9$, $R^2 = H$ (**4**)	**12** (91%)
2	$R^1 = Ph$, $R^2 = H$ (**5**)	**13** (90%)
3	$R^1 = TMS$, $R^2 = H$ (**6**)	**14** (91%)
4	$R^1 = (CH_2)_2CH{=}CH_2$, $R^2 = H$ (**7**)	**15** (87%)
5	$R^1 = H$, $R^2 = n\text{-}C_5H_{11}$ (**8**)	**16** (92%)
6	$R^1 = n\text{-}C_4H_9$, $R_2 = n\text{-}C_5H_{11}$ (**9**)	**17** (93%)
7	$R^1 = Ph$, $R^2 = n\text{-}C_5H_{11}$ (**10**)	**18** (91%)
8	$R^1 = TMS$, $R^2 = n\text{-}C_5H_{11}$ (**11**)	**19** (93%)

[a] Mo/substrate = 1.10, [substrate] = 0.15 M, 25 °C, 4 h.
[b] Yields are given after separation from a silica column.

efficiently avoids the thermal cyclization of these 5-allenyl-3-en-1-yne derivatives via diradical pathways. Entries 1–4 show various 1-ethynyl-2-allenylbenzenes **4**–**7** bearing various internal alkynes including *n*-butyl, phenyl, trimethylsilyl and 3-buten-1-yl groups, which gave desired ketones **12**–**15** in satisfactory yields (87–91%) using $Mo(CO)_3(CH_3CN)_3$ reagents. This cyclization also works well with substrates **8** bearing 1,3-disubstituted allene, and gave bicyclic ketone **16** in 92% yields. Entries 6–8 show the reliability of this synthetic approach, which can be extended efficiently to 1-ethynyl-2-allenylbenzenes **9**–**11** bearing both internal alkyne and 1,3-disubstituted allene functionalities.

In summary, we have realized a Pauson–Khand cyclocarbonylation[12] of 1-ethynyl-2-allenylbenzenes to 1*H*-cyclopenta[*a*]inden-2-ones efficiently with the use of $Mo(CO)_3(CH_3CN)_3$. The coordinated unsaturated nature of this molybdenum complex leads to lower reaction temperature (25 °C) and circumvent the thermally facile Myers–Saito cyclization of the substrate. This cyclization has been extended very successfully to various 1-ethynyl-2-allenylbenzene substrates bearing various alkynyl and allenyl substituents.

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9. $Mo(CO)_5THF$ was prepared by irradiation of pre-evacuated $Mo(CO)_6$ in THF with mercury lamp at 30 °C for 12 h. See Maeyama, K.; Iwasawa, N. *J. Org. Chem.* **1999**, *64*, 1344.
10. The preparation of $Mo(CO)_4(CH_3CN)_2$ and $Mo(CO)_3(CH_3CN)_3$ was obtained by heating $Mo(CO)_6$ with CH_3CN at 80 °C for 10 h and 24 h, respectively. See Al-Kathumi, K. M.; Kane-Maguire, A. P. *J. Inorg. Nucl. Chem.* **1972**, *34*, 3759.
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12. Cyclization operations and spectral data: To a dichloromethane (4.75 ml) solution of 1-ethynyl-2-allylbenzene **1** (100 mg, 0.713 mmol) was added $Mo(CO)_3(CH_3CN)_3$ (238 mg, 0.784 mmol) under N_2 atmosphere and the mixture was stirred at 25 °C for 2 h. The solution was filtered over a short silica bed and the filtrate was concentrated in vacuo. The residue was chromatographed over a short silica column to afford bicyclic ketone **2** (110.3 mg, 0.655 mmol, 92%). Spectral data of 1*H*-cyclopenta[*a*]inden-2-one (**2**): IR (neat, cm^{-1}): 2962(w), 1706(s), 1603(m); ^1H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, 1H, $J = 7.6$ Hz), 7.30 (t, 1H, $J = 7.6$ Hz), 7.16 (d, 1H, $J = 7.6$ Hz), 7.10 (t, 1H, $J = 7.6$ Hz), 6.53 (s, 1H), 6.43 (s, 1H), 3.18 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.2, 171.5, 148.1, 142.2, 132.1, 130.1, 125.4, 125.2, 125.1, 123.1, 121.5, 35.5; HRMS calcd for $C_{12}H_8O$: 168.0575. Found 168.0575. 3-Butyl-1*H*-cyclopenta[*a*]inden-2-one (**12**): IR (neat, cm^{-1}): 2964(w), 1708(s), 1601(m); ^1H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, 1H, $J = 7.6$ Hz), 7.29 (t, 1H, $J = 7.6$ Hz), 7.19 (d, 1H, $J = 7.6$ Hz), 7.11 (t, 1H, $J = 7.6$ Hz), 6.39 (s, 1H), 3.21 (s, 2H), 2.67 (t, 2H, $J = 7.2$ Hz), 1.62–1.55 (m, 2H), 1.42–1.36 (m, 2H), 0.92 (t, 3H, $J = 7.2$ Hz); ^{13}C NMR (150 MHz, $CDCl_3$): δ 206.8, 164.9, 148.2, 142.2, 141.0, 131.0, 130.6, 124.9, 124.8, 121.4, 120.7, 35.2, 30.7, 24.2, 22.9, 13.8; HRMS calcd for $C_{16}H_{16}O$: 224.1201. Found 224.1202. 3-Phenyl-1*H*-cyclopenta[*a*]inden-2-one (**13**): IR (neat, cm^{-1}): 2971(w), 1710(s), 1609(m); ^1H NMR (400 MHz, $CDCl_3$): δ 7.75–7.69 (m, 3H), 7.49 (t, 2H, $J = 7.6$ Hz), 7.43 (t, 1H, $J = 7.6$ Hz), 7.28 (t, 1H, $J = 7.2$ Hz), 7.19 (d, 1H, $J = 7.2$ Hz), 7.02 (t, 1H, $J = 7.2$ Hz), 6.49 (s, 1H), 3.37 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.0, 164.4, 148.2, 140.7, 138.2, 131.7, 130.6, 130.4, 129.6, 129.3, 128.4, 125.2, 124.7, 122.1, 121.6, 35.6; HRMS calcd for $C_{18}H_{12}O$: 244.0888. Found 244.0887. 3-Trimethylsilanyl-1*H*-cyclopenta[*a*]inden-2-one (**14**): IR (neat, cm^{-1}): 2960(w), 1705(s), 1604(m), 1600(m); ^1H NMR (600 MHz, $CDCl_3$): δ 7.68 (d, 1H, $J = 7.2$ Hz), 7.27 (t, 1H, $J = 7.2$ Hz), 7.14 (d, 1H, $J = 7.2$ Hz), 7.09 (t, 1H, $J = 7.2$ Hz), 6.41 (s, 1H),3.12 (s, 2H), 0.40 (s, 9 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 211.2, 177.8, 148.3, 142.8, 142.7, 131.5, 131.4, 126.2, 125.0, 121.7, 121.4, 35.9, −0.5; HRMS calcd for $C_{15}H_{16}OSi$: 240.0970. Found 240.0971. 3-But-3-enyl-1*H*-cyclopenta[*a*]inden-2-one (**15**): IR (neat, cm^{-1}): 2962(w), 1706(s), 1651(m), 1603(m); ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, 1H, $J = 7.2$ Hz), 7.28 (t, 1H, $J = 7.2$ Hz), 7.18 (d, 1H, $J = 7.2$ Hz), 7.11 (t, 1H, $J = 7.6$ Hz), 6.38 (s, 1H), 5.84–5.80 (m, 1H), 5.04 (dd, 1H, $J = 17.6$, 1.6 Hz), 4.96 (dd, 1H, $J = 10.4$, 1.6 Hz), 3.19 (s, 2H), 2.77 (t, 2H, $J = 7.6$ Hz), 2.39–2.35 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 206.7, 165.3, 148.2, 141.0, 140.8, 137.2, 131.1, 130.5, 124.9, 124.8, 121.5, 121.0, 115.6, 35.2, 32.4, 24.0; HRMS calcd for

$C_{16}H_{14}O$: 222.1045. Found 222.104. 1-Pentyl-1*H*-cyclopenta[*a*]inden-2-one (**16**): IR (neat, cm^{-1}): 2960(w), 1702(s), 1600(m); ^1H NMR (500 MHz, $CDCl_3$): δ 7.56 (d, 1H, $J = 7.5$ Hz), 7.30 (t, 1H, $J = 7.5$ Hz), 7.17 (t, 1H, $J = 7.5$ Hz), 7.11 (t, 1H, $J = 7.5$ Hz), 6.49 (s, 1H), 6.45 (s, 1H), 3.15–3.13 (m, 1H), 1.89–1.86 (m, 1H), 1.63–1.55 (m, 1H), 1.45–1.39 (m, 2H), 1.29–1.23 (m, 4H), 0.86 (t, 3H, $J = 7.0$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.2, 170.3, 148.3, 147.4, 132.0, 130.1, 125.4, 125.1, 124.3, 122.8, 121.6, 45.8, 31.7, 30.3, 26.6, 22.4, 14.0; HRMS calcd for $C_{17}H_{18}O$: 238.1358, Found 238.1358. 3-Butyl-1-pentyl-1*H*-cyclopenta[*a*]inden-2-one (**17**): IR (neat, cm^{-1}): 2956(w), 1709(s), 1603(m); ^1H NMR (600 MHz, $CDCl_3$): δ 7.61 (d, 1H, $J = 7.4$ Hz), 7.29 (dt, 1H, $J = 7.4$, 1.0 Hz), 7.20 (d, 1H, $J = 7.4$ Hz), 7.11 (dt, 1H, $J = 7.4$, 1.0 Hz), 6.40 (s, 1H), 3.17–3.14 (m, 1H), 2.66 (t, 2 H, $J = 7.6$ Hz), 1.95–1.83 (m, 1H), 1.61–1.57 (m, 3H), 1.41–1.36 (m, 4H), 1.30–1.28 (m, 4H), 0.92 (t, 3 H, $J = 7.2$ Hz), 0.86 (t, 3H, $J = 7.2$ Hz); ^{13}C NMR (150 MHz, $CDCl_3$): δ 209.7, 163.8, 148.4, 146.4, 141.4, 130.9, 130.5, 124.9, 121.5, 120.4, 45.4, 31.7, 30.7, 30.6, 26.6, 24.2, 22.8, 22.4, 14.0, 13.9; HRMS calcd for $C_{21}H_{26}O$: 294.1984. Found 294.1985. 1-Pentyl-3-phenyl-1*H*-cyclopenta[*a*]inden-2-one (**18**): IR (neat, cm^{-1}): 2960(w), 1701(s), 1605(m); ^1H NMR (600 MHz, $CDCl_3$): δ 7.75 (d, 1H, $J = 7.4$ Hz), 7.71 (d, 2H, $J = 7.8$ Hz), 7.49 (t, 2H, $J = 7.8$ Hz), 7.44 (t, 1H, $J = 7.8$ Hz), 7.28 (t, 1H, $J = 7.4$ Hz), 7.21 (t, 1H, $J = 7.4$ Hz), 7.02 (t, 1H, $J = 7.4$ Hz), 6.51 (s, 1H), 3.32–3.29 (m, 1H), 2.00–1.95 (m, 1H), 1.73–1.66 (m, 1H), 1.55–1.40 (m, 2H), 1.33–1.24 (m, 4H), 0.88 (t, 3H, $J = 7.2$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.9, 163.4, 148.5, 146.2, 137.2, 131.7, 130.8, 130.3, 129.7, 128.5, 125.2, 124.8, 121.8, 121.6, 45.7, 31.8, 30.9, 29.7, 26.6, 22.5, 14.0 HRMS calcd for $C_{23}H_{22}O$: 314.1671. Found 314.1671. 1-Pentyl-3-trimethylsilanyl-1*H*-cyclopenta[*a*]inden-2-one (**19**): IR (neat, cm^{-1}): 2961(w), 1708(s), 1602(m); ^1H NMR (500 MHz, $CDCl_3$): δ 7.68 (d, 1H, $J = 7.4$ Hz), 7.27 (t, 1H, $J = 7.4$ Hz), 7.16 (d, 1H, $J = 7.4$ Hz), 7.08 (t, 1H, $J = 7.4$ Hz), 6.42 (s, 1H), 3.06–3.03 (m, 1H), 1.88–1.84 (m, 1H), 1.58–1.53 (m, 1H), 1.42–1.39 (m, 2H), 1.31–1.26 (m, 4H), 0.86 (t, 3 H, $J = 7.2$ Hz), 0.39 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 213.8, 176.5, 148.6, 141.6, 131.5, 131.4, 126.2, 125.0, 121.4, 45.8, 31.7, 30.6, 26.6, 22.4, 14.0, −0.5; HRMS calcd for $C_{20}H_{26}OSi$: 310.1753. Found 310.1753.