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$Co_2(CO)_8$-mediated cycloisomerization of arylene 1,7-enynes

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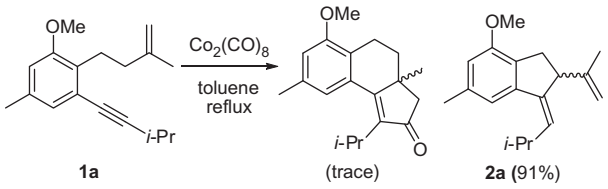
ABSTRACT

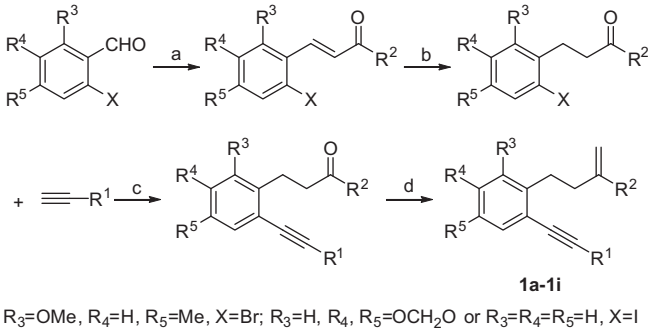
$Co_2(CO)_8$ was found to be effective for cycloisomerization reaction of arylene 1,7-enynes to form 2,3-dihydroindene derivatives, and a catalytic version assisted by different Lewis base ligands was also studied.

Cycloisomerization of various aliphatic or aromatic enynes has been regarded as an important synthetic method for functionalized cyclic structures. A number of transition metals have been used as effective mediators or catalysts in these transformations.[1] Among them, cobalt species have been well known for affecting [2+2+2] cyclotrimerizations,[2] Pauson–Khand reactions,[3] Diels–Alder reactions,[4] and ene type reactions.[5] In particular, Co(I) species were able to promote cycloisomerizations.[6] However, to the best of our knowledge, Co(0) species are rarely used for this purpose, and the only example we could find was the 5-endo-dig cycloisomerization of 1,6-enynes in the presence of $Co_2(CO)_8$.[7] During our studies using $Co_2(CO)_8$-mediated Pauson–Khand reactions for natural product synthesis,[8] we found that, rather than a conventional Pauson–Khand pathway[9–12] as designed for the synthesis of Hamigeran B,[13] a cycloisomerization of arylene-1,7-enyne occurred in the presence of $Co_2(CO)_8$ (Scheme 1).[14] Herein, we would like to report the expansion of this observation to a synthetic method for cycloisomerization reaction of arylene 1,7-enynes to form 2,3-dihydroindene derivatives.



Scheme 1. The cycloisomerization of **1a**.

The arylene 1,7-enyne substrates **1a–1i** were prepared as shown in Scheme 2. Then we studied a variety of substitution on the arylene 1,7-enynes for effects on the cycloisomerization reaction, and the results are summarized in Table 1.[15]



Scheme 2. Synthesis of arylene 1,7-enyne **1a–1i**.

In general, the cycloisomerization in the presence of 1.1 equiv of $Co_2(CO)_8$ in refluxing toluene for 5 h enjoyed excellent yields (>90%), and tolerated many alkynes with R^1 being alkyl (entries 1–3) or phenyl (entry 4). The results were also good for different aromatic skeletons (entries 1–8). The cycloisomerization proceeded in excellent yield with different substitutes on the alkenyl moiety (entries 6 and 9).[16]

On the basis of the reaction results from a cycloisomerization pathway (**A**–**P**) rather than the Pauson–Khand pathways (to **P1** and **P2**) as shown in Scheme 3, we reasoned that the steric

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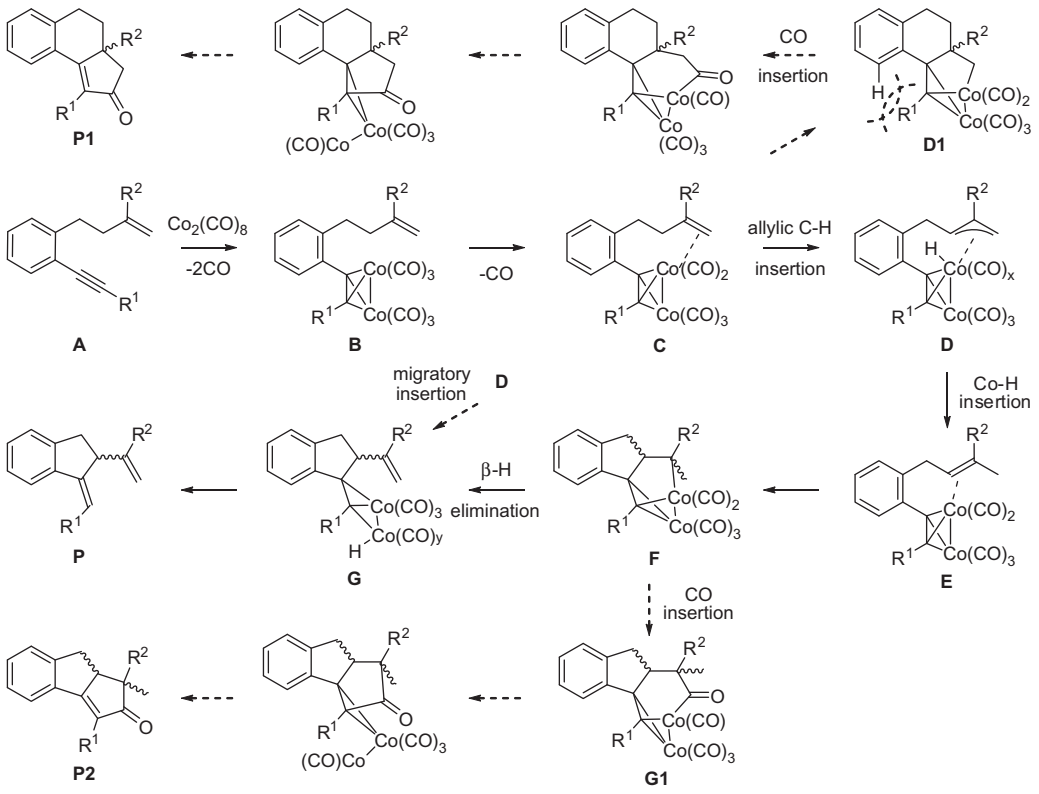
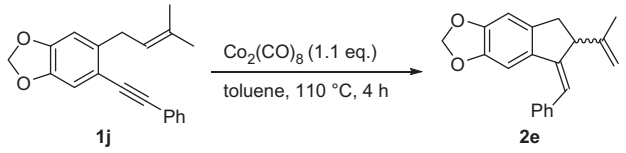


Scheme 3. Proposed mechanistic pathways.

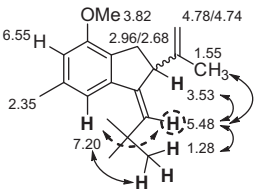


Scheme 4. Cycloisomerization of arylene-1,6-enyne **1j**.

hindrance between R^1 and the neighboring benzene ring or conformational issues might have restricted the conversion of **C**–**D1**,[17] and a beta-H elimination (**F** → **G**) might be favorable than a CO insertion (**F** → **G1**) with a tertiary carbon center,[18] or a direct migratory insertion (**D** → **G**) might have contributed to the cycloisomerization outcomes.[14]

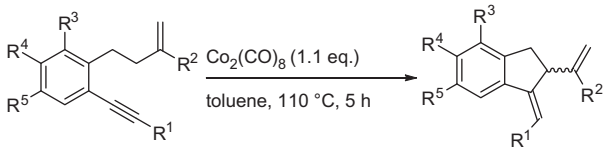
Since an alkene rearrangement sequence (**C** → **D** → **E**) might have been involved in the cycloisomerization pathway, we synthesized the arylene-1,6-enyne **1j**, and then tried the reaction under the same conditions and obtained **2e** in 80% yield (Scheme 4). This observation was in accordance with the major mechanistic pathways and diversions under Pauson–Khand reaction conditions as proposed in the literature for a plethora of unexpected results.[14]

The 1,1′-*exo*-double bond of the cycloisomerization product **2a–2i** could be expected as (*Z*)-configuration. As a representative



Scheme 5. The nOe study of **2c**.

Table 1
Cycloisomerization reaction of arylene-1,7-enyne[a]



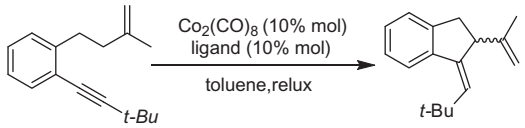
Entry	1	R^1	R^2	R^3	R^4	R^5	2	Yield[b] (%)
1	**1a**	*i*-Pr	Me	OMe	H	Me	**2a**	91
2	**1b**	*c*-Pr	Me	OMe	H	Me	**2b**	92
3	**1c**	*t*-Bu	Me	OMe	H	Me	**2c**	94
4	**1d**	Ph	Me	OMe	H	Me	**2d**	87
5	**1e**	Ph	Me	H	OCH_2O		**2e**	94
6	**1f**	*t*-Bu	Me	H	H	H	**2f**	92
7	**1g**	Ph	Me	H	H	H	**2g**	90
8	**1h**	*c*-Pr	Me	H	H	H	**2h**	91
9	**1i**	*t*-Bu	*c*-Pr	H	H	H	**2i**	99

[a] Reaction was carried out under argon atmosphere.
[b] Isolated yield.

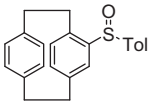
study, the nOe analysis of **2c** confirmed this geometry. The olefinic H1′ (δ 5.48 ppm) and H2 (δ 3.53 ppm) on the 2,3-dihydroindene ring showed remarkable nOe, while no clear nOe was observable between H1′ and H7 (δ 7.20 ppm) on the benzene ring (Scheme 5).

It has been well documented that Lewis bases or other ligands could serve as promoters in CO decoordination from the cobalt center, help to prevent the cobalt species from deactivations, and render the Pauson–Khand reaction catalytic.[19] Then catalytic conditions for the cycloisomerization were tried using some Lewis base ligands as usually used for the catalytic Pauson–Khand reactions,[20] and the results are shown in Table 2.[21] Without Lewis base ligands added, a catalytic amount of $Co_2(CO)_8$ was ineffective

Table 2
The catalytic cycloisomerization[a]



1f **2f**

Entry	Time (h)	Ligand	Yield[b] (%)
1	16	None	—
2	1.5	Ph_3P	89
3	1.5	*rac*-BINAP	>99
4	1.5		>99
5	1.5	BuSMe	90
6	1.5	$CyNH_2$	>99

[a] Reaction was carried out under argon atmosphere.
[b] Isolated yield.

(entry 1). When a ligand such as Ph_3P (entry 2), *rac*-Binap (entry 3), sulfone (entry 4), sulfide (entry 5), or amine (entry 6) was used, all the cycloisomerization with 10% mol of $Co_2(CO)_8$ completed in excellent yields (>90%) in only 1.5 h.

In conclusion, the cycloisomerization of various arylene 1,7-enynes mediated by $Co_2(CO)_8$ has been studied, and high yields of 2,3-dihydroindene have been achieved. We also demonstrated a catalytic version of this reaction with 10% mol of $Co_2(CO)_8$ and Lewis base ligands.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2012.12.016.

References and notes

1. For reviews see (a) Michelet, V.; Toullec, P. Y.; Genet, J.-P. *Angew. Chem., Int. Ed.* **2008**, *47*, 4268; (b) Zhang, L.-M.; Sun, J.-W.; Kozmin, S. A. *Adv. Synth. Catal.* **2006**, *348*, 2271; (c) Trost, B. M.; Frederiksen, M. U.; Rudd, M. T. *Angew. Chem., Int. Ed.* **2005**, *44*, 6630; (d) Solan, G. A. *Organomet. Chem.* **2005**, *32*, 314; (e) Aubert, C.; Buisine, O.; Malacria, M. *Chem. Rev.* **2002**, *102*, 813; (f) Trost, B. M.; Toste, F. D.; Pinkerton, A. B. *Chem. Rev.* **2001**, *101*, 2067; (g) Trost, B. M. *Chem. Eur. J.* **1998**, *4*, 2405; (h) Trost, B. M.; Krische, M. J. *Synlett* **1998**, 1; (i) Ojima, I.; Tzamarioudaki, M.; Li, Z. Y.; Donovan, R. J. *Chem. Rev.* **1996**, *96*, 635; For examples see (j) Gryparis, C.; Efe, C.; Raptis, C.; Lykakis, I. N.; Stratakis, M. *Org. Lett.* **2012**, *14*, 2956; (k) Ozawa, T.; Kurahashi, T.; Matsubara, S. *Org. Lett.* **2012**, *14*, 3008; (l) Wang, W.-F.; Yang, J.-M.; Wang, F.-J; Shi, M. *Organometallics* **2011**, *30*, 3859; (m) Corkum, E. G.; Hass, M. J.; Sullivan, A. D.; Bergens, S. H. *Org. Lett.* **2011**, *13*, 3522; (n) Nishimura, T.; Maeda, Y.; Hayashi, T. *Org. Lett.* **2011**, *13*, 3674; (o) Lopez-Carrillo, V.; Huguet, N.; Mosquera, A.; Echavarren, A. *Chem. Eur. J.* **2011**, *17*, 10972; (p) Kim, S.-Y.; Chung, Y.-K. *J. Org. Chem.* **2010**, *75*, 1281; (q) Trost, B. M.; Gutierrez, A. C.; Ferreira, E. M. *J. Am. Chem. Soc.* **2010**, *132*, 9206; (r) Fuerstner, A.; Majima, K.; Martin, R.; Krause, H.; Kattnig, E.; Goddard, R.; Lehmann, C. W. *J. Am. Chem. Soc.* **1992**, *2008*, 130; (s) Fuerstner, A.; Martin, R.; Majima, K. *J. Am. Chem. Soc.* **2005**, *127*, 12236; (t) Schmidt, B. *Eur. J. Org. Chem.* **2004**, *9*, 1865; (u) Lloyd-Jones, G. C. *Org. Biomol. Chem.* **2003**, *1*, 215.
2. For reviews see (a) Dominguez, G.; Perez-Castells, J. *Chem. Soc. Rev.* **2011**, *40*, 3430; For examples see (b) Weding, N.; Jackstell, R.; Jiao, H.; Spannenberg, A.; Hapke, M. *Adv. Synth. Catal.* **2011**, *353*, 3423; (c) Sugiyama, Y. K.; Kato, R.; Sakurada, T.; Okamoto, S. *J. Am. Chem. Soc.* **2011**, *133*, 9712; (d) Eichman, C. C.; Bragdon, J. P.; Stambuli, J. P. *Synlett* **2011**, 1109; (e) Turek, P.; Hocek, M.; Pohl, R.; Klepetarova, B.; Kotora, M. *Eur. J. Org. Chem.* **2008**, *19*, 3335; (f) Hilt, G.; Hengst, C.; Hess, W. *Eur. J. Org. Chem.* **2008**, *13*, 2293; (g) Agenet, N.; Gandon, V.; Vollhardt, K. P. C.; Malacria, M.; Aubert, C. *J. Am. Chem. Soc.* **2007**, *129*, 8860; (h) Chang, H.-T.; Jeganmohan, M.; Cheng, C.-H. *Org. Lett.* **2007**, *9*, 505; (i) Lombardo, M.; Pasi, F.; Trombini, C.; Seddon, K. R.; Pitner, W. R. *Green Chem.* **2007**, *9*, 321; (j) Hilt, G.; Vogler, T.; Hess, W.; Galbiati, F. *Chem. Commun.* **2005**, *11*, 1474; (k) Hilt, G.; Hess, W.; Vogler, T.; Hengst, C. *J. Organomet. Chem.* **2005**, *690*, 5170; (l) Petit, M.; Aubert, C.; Malacria, M. *Org. Lett.* **2004**, *6*, 3937.
3. (a) Shore, N. E. In *Comprehensive Organic Synthesis*; Trost, B. M., Felming, I., Paquette, L. A., Eds.; Pergamon Press: Oxford, 1991; Vol. 5, pp 1037–1064; (b) Geis, O.; Schmalz, H.-G. *Angew. Chem., Int. Ed.* **1998**, *37*, 911; (c) Gibson, S. E.; Mainolfi, N. *Angew. Chem., Int. Ed.* **2005**, *44*, 3022; (d) Cambeiro, X. C.; Pericas, M. A. In *The Pauson–Khand Reaction: Scope, Variations and Applications*; Rios Torres, R., Ed.; John Wiley & Sons, 2012.
4. For reviews see (a) Hilt, G. *Synlett* **2011**, 1654; (b) Lautcns, M.; Tam, W.; CraigLautens, J.; Edwards, C. G.; Crudden, C. M.; Smith, C. *J. Am. Chem. Soc.* **1995**, *117*, 6863; For examples see (c) Arndt, M.; Hilt, G.; Khlebnikov, A. F.; Kozhushkov, S. I.; Meijere, A. *Eur. J. Org. Chem.* **2012**, *16*, 3112; (d) Erver, F.; Hilt, G. *Org. Lett.* **2012**, *14*, 1884; (e) Reus, C.; Liu, N.-W.; Bolte, M.; Lerner, H.-W.; Wagner, M. *J. Org. Chem.* **2012**, *77*, 3518; (f) Erver, F.; Hilt, G.; Harms, K. *Synthesis* **2011**, 972; (g) Hilt, G.; Arndt, M.; Weske, D. F. *Synthesis* **2010**, 1321; (h) Hilt, G.; Janikowski, J. *Org. Lett.* **2009**, *11*, 773; (i) Moerschel, P.; Janikowski, J.; Hilt, G.; Frenking, G. *J. Am. Chem. Soc.* **2008**, *130*, 8952; (j) Hilt, G.; Danz, M. *Synthesis* **2008**, 225; (k) Hilt, G.; Hess, W.; Harms, K. *Org. Lett.* **2006**, *8*, 3287; (l) Hilt, G.; Jaikowski, J.; Hess, W. *Angew. Chem., Int. Ed.* **2006**, *45*, 5204; (m) Hilt, G.; Luers, S.; Harms, K. *J. Org. Chem.* **2004**, *69*, 624.
5. (a) Hilt, G.; Erver, F.; Harms, K. *Org. Lett.* **2011**, *13*, 304; (b) Hilt, G.; Paul, A.; Treutwein, J. *Org. Lett.* **2010**, *12*, 1536; (c) Hilt, G.; Treutwein, J. *Angew. Chem., Int. Ed.* **2007**, *46*, 8500; (d) Hutson, G. E.; Dave, A. H.; Rawal, V. H. *Org. Lett.* **2007**, *9*, 3869; (e) Kezuka, S.; Ikeno, T.; Yamada, T. *Org. Lett.* **2001**, *3*, 1937; (f) Llerena, D.; Aubert, C.; Malacria, M. *Tetrahedron Lett.* **1996**, *37*, 7027.
6. (a) Buisine, O.; Aubert, C.; Malacria, M. *Chem. Eur. J.* **2001**, *7*, 3517; (b) Llerena, D.; Aubert, C.; Malacria, M. *Tetrahedron Lett.* **1996**, *37*, 7353.
7. (a) Ajamian, A.; Gleason, J. L. *Org. Lett.* **2003**, *5*, 2409; (b) Ajamian, A.; Gleason, J. L. *Org. Lett.* **2001**, *3*, 4161; (c) Dolaine, R.; Gleason, J. L. *Org. Lett.* **2000**, *2*, 1753.
8. (a) Jiang, B.; Xu, M. *Angew. Chem., Int. Ed.* **2004**, *43*, 2543; (b) Jiang, B.; Xu, M. *Org. Lett.* **2002**, *4*, 4077.
9. Khand, I. U.; Knox, G. R.; Pauson, P. L.; Watts, W. E. *J. Chem. Soc. Chem. Commun.* **1971**, *1*, 36.
10. Magnus, P.; Principe, L. M. *Tetrahedron Lett.* **1985**, *26*, 4851.
11. Magnus, P.; Exon, C.; Albaugh-Robertson, P. *Tetrahedron* **1985**, *41*, 5861.
12. Magnus, P.; Principe, L. M.; Slater, M. J. *J. Org. Chem.* **1987**, *52*, 1483.
13. (a) Wellington, K. D.; Cambie, R. C.; Rutledge, P. S.; Bergquist, P. R. *J. Nat. Prod.* **2000**, *63*, 79; (b) Madu, C. M.; Lovely, C. J. *Org. Lett.* **2007**, *9*, 4697; (c) Arnaiz, E.; Blanco-Urgoiti, J.; Abdi, D.; Dominguez, G.; Castells, J. P. *J. Organomet. Chem.* **2008**, *693*, 2431.
14. Bonaga, L. V. R.; Krafft, M. E. *Tetrahedron* **2004**, *60*, 9795.
15. *General procedure for the stoichiometric cycloisomerization of **1a**–**1i***: A mixture of 1,7-enyne **1** (0.1 mmol) and $Co_2(CO)_8$ (0.11 mmol) in PhMe (4 mL) was stirred at room temperature under argon atmosphere for 1 h. Then it was heated to reflux for 5 h. The resultant reaction mixture was concentrated, the residue was purified by flash chromatogra-phy on silica gel to provide 2,3-dihydroindene **2**.
16. *(Z)-4-Methoxy-6-methyl-1-(2-methylpropylidene)-2-(prop-1-en-2-yl)-2,3-dihydro-1H-indene (**2a**)*: ^{1}H NMR: δ 7.05 (s, 1H), 6.55 (s, 1H), 5.21 (dd, J = 9.4, 1.9 Hz, 1H), 4.82 (s, 1H), 4.77 (s, 1H), 3.83 (s, 3H), 3.62–3.54 (m, 1H), 3.24–3.08 (m, 1H), 2.99 (dd, J = 16.7, 9.1 Hz, 1H), 2.72 (dd, J = 16.7, 5.4 Hz, 1H), 2.38 (s, 3H), 1.59 (s, 3H), 1.08 (t, J = 6.1 Hz, 6H). ^{13}C NMR: δ 155.9, 147.9, 140.0, 137.7, 132.6, 130.8, 117.3, 112.0, 109.9, 55.2, 52.8, 32.0, 27.1, 23.1, 23.0, 22.0, 17.9. EI-MS m/z (%): 256 (M^+, 62.72), 213 (100). HRMS (EI) calcd for $C_{18}H_{24}O$: 256.1827; found: 256.1835. IR (KBr): 2959, 1586, 1465, 1287, 890, 830 cm^{-1}.
*(Z)-1-(Cyclopropylmethylene)-4-methoxy-6-methyl-2-(prop-1-en-2-yl)-2,3-dihydro-1H-indene (**2b**)*: ^{1}H NMR: δ 7.26 (s, 1H), 6.56 (s, 1H), 4.86 (d, J = 9.1 Hz, 1H), 4.77 (d, J = 13.1 Hz, 1H), 3.83 (s, 3H), 3.58 (t, J = 6.3 Hz), 3.00 (dd, J = 16.7, 9.0 Hz, 1H), 2.73 (dd, J = 16.6, 5.3 Hz, 1H), 2.38 (s, 3H), 2.10–1.94 (m, 1H), 1.58 (s, 3H), 0.92–0.83 (m, 2H), 0.48–0.37 (m, 2H). ^{13}C NMR: δ 155.8, 147.8, 142.4, 142.0, 137.6, 130.5, 128.1, 117.0, 112.0, 110.0, 55.1, 52.9, 32.0, 22.0, 17.9, 10.8, 7.9, 7.8. EI-MS m/z (%): 254 (M^+, 42.97), 199 (100). HRMS (EI) calcd for $C_{18}H_{22}O$: 254.1671; found: 254.1667. IR (KBr): 2926, 1716, 1595, 1464, 1314, 1139 cm^{-1}.
*(Z)-1-(2,2-Dimethylpropylidene)-4-methoxy-6-methyl-2-(prop-1-en-2-yl)-2,3-dihydro-1H-indene (**2c**)*: ^{1}H NMR: δ 7.20 (s, 1H), 6.55 (s, 1H), 5.48 (s, 1H), 4.78 (s, 1H), 4.74 (s, 1H), 3.82 (s, 3H), 3.53 (t, J = 6.6 Hz, 1H), 2.96 (dd, J = 16.6, 9.1 Hz, 1H), 2.68 (dd, J = 16.6, 4.5 Hz, 1H), 2.35 (s, 3H), 1.55 (s, 3H), 1.28 (s, 9H). ^{13}C NMR: δ 155.7, 148.5, 141.5, 140.5, 136.9, 135.9, 132.0, 120.1, 112.0, 109.8, 55.2, 55.1, 31.8, 31.6, 30.5, 22.1, 17.9. EI-MS m/z (%): 270 (M^+, 48.82), 213 (100). HRMS (EI) calcd for $C_{19}H_{26}O$: 270.1984; found: 270.1984. IR (KBr): 2961, 1646, 1585, 1296, 833 cm^{-1}.
*(Z)-1-Benzylidene-4-methoxy-6-methyl-2-(prop-1-en-2-yl)-2,3-dihydro-1H-indene (**2d**)*: ^{1}H NMR: δ 7.42–7.26 (m, 4H), 6.64 (s, 1H), 6.50 (s, 1H), 6.44 (s, 1H), 4.93 (s, 1H), 4.85 (s, 1H), 3.81 (s, 3H), 3.80–3.71 (m, 1H), 3.07 (dd, J = 16.7, 9.1 Hz, 1H), 2.80 (dd, J = 16.7, 5.4 Hz, 1H), 2.14 (s, 3H), 1.67 (s, 3H). ^{13}C NMR: δ 155.9, 147.5, 145.0, 141.1, 138.4, 137.2, 131.9, 128.6, 128.2, 126.7, 123.1, 117.2,

112.7, 110.7, 55.2, 53.6, 32.0, 29.7, 21.8, 17.9. EI-MS *m*/*z* (%): 290 (M^+, 100). HRMS (EI) calcd for $C_{21}H_{22}O$: 290.1671; found: 290.1664.

(Z)-5-Benzylidene-6-(prop-1-en-2-yl)-6,7-dihydro-5H-indeno[5,6-d][1,3]dioxole (**2e**): ^{1}H NMR (acetone-d_6: δ 7.49–7.23 (m, 5H), 6.76 (s, 1H), 6.51 (s, 1H), 6.32 (s, 1H), 5.92 (s, 2H), 4.93 (s, 1H), 4.85 (s, 1H), 3.81–3.73 (m, 1H), 3.08 (dd, *J* = 16.4, 8.8 Hz, 1H), 2.84 (dd, *J* = 16.5, 5.1 Hz, 1H), 1.66 (s, 3H). ^{13}C NMR (acetone-d_6): δ 149.4, 148.1, 147.1, 145.3, 142.1, 139.1, 133.4, 128.3, 129.1, 127.5, 121.1, 113.1, 105.8, 104.3, 102.1, 54.6, 36.0, 17.9. EI-MS *m*/*z* (%): 290 (M^+, 100). HRMS (EI) calcd for $C_{20}H_{18}O_2$: 290.1307; found: 290.1312. IR (KBr): 2919, 1473, 1249, 1041 cm^{-1}.

(Z)-1-(2,2-Dimethylpropylidene)-2-(prop-1-en-2-yl)-2,3-dihydro-1H-indene (**2f**): ^{1}H NMR: δ 7.78 (d, *J* = 6.7 Hz, 1H), 7.30–7.15 (m, 3H), 5.55 (d, *J* = 1.9 Hz, 1H), 4.83 (s, 1H), 4.79 (s, 1H), 3.62–3.54 (m, 1H), 3.10 (dd, *J* = 16.3, 8.8 Hz, 1H), 2.85 (dd, *J* = 16.3, 5.4 Hz, 1H), 1.59 (s, 3H), 1.31 (s, 9H). ^{13}C NMR: δ 148.1, 147.0, 141.1, 138.8, 136.0, 127.2, 127.1, 125.8, 125.1, 112.3, 55.1, 35.6, 31.9, 30.3, 18.0. EI-MS *m*/*z* (%): 226 (M^+, 30.98), 155 (100). HRMS (EI) calcd for $C_{17}H_{22}$: 226.1722; found: 226.1718. IR (KBr): 2956, 1471, 1363, 891, 739 cm^{-1}.

(Z)-1-Benzylidene-2-(prop-1-en-2-yl)-2,3-dihydro-1H-indene (**2g**): ^{1}H NMR: δ 7.46–7.22 (m, 7H), 7.18 (t, *J* = 7.5 Hz, 1H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.50 (d, *J* = 1.6 Hz, 1H), 4.98 (s, 1H), 4.92 (s, 1H), 3.81 (ddd, *J* = 8.4, 5.9, 2.1 Hz, 1H), 3.19 (dd, *J* = 16.5, 8.9 Hz, 1H), 2.99 (dd, *J* = 16.5, 5.8 Hz, 1H), 1.72 (s, 3H). ^{13}C NMR: δ 147.1, 146.6, 144.5, 139.4, 138.3, 128.4, 128.3, 126.7, 125.9, 125.1, 124.2, 123.1, 113.1, 53.5, 35.7, 18.0. EI-MS *m*/*z* (%): 246 (M^+, 79.35), 142 (100). HRMS (EI) calcd for $C_{19}H_{18}$: 246.1409; found: 246.1411. IR (KBr): 3066, 2922, 1715, 1448, 1027, 699 cm^{-1}.

(Z)-1-(Cyclopropylmethylene)-2-(prop-1-en-2-yl)-2,3-dihydro-1H-indene (**2h**): ^{1}H NMR: δ 7.84 (d, *J* = 7.1 Hz, 1H), 7.32–7.15 (m, 3H), 4.95 (d, *J* = 8.8 Hz, 1H), 4.83 (s, 1H), 4.79 (s, 1H), 3.63 (t, *J* = 7.3 Hz, 1H), 3.11 (dd, *J* = 16.4, 8.9 Hz, 1H), 2.90 (dd, *J* = 16.4, 5.8 Hz, 1H), 2.08–1.92 (m, 1H), 1.61 (s, 3H), 0.96–0.78 (m, 2H), 0.49–0.41 (m, 2H). ^{13}C NMR: δ 147.5, 145.7, 141.8, 140.8, 128.1, 127.3, 126.3, 125.0, 124.1, 112.3, 52.9, 35.9, 18.0, 10.9, 8.0, 7.8. EI-MS *m*/*z* (%): 210 (M^+, 7.14), 173 (59.34). HRMS (EI) calcd for $C_{16}H_{18}$: 210.1409; found: 210.1377. IR (KBr): 2927, 1714, 1461, 1380, 1027, 761 cm^{-1}.

(Z)-2-(1-Cyclopropylvinyl)-1-(2,2-dimethylpropylidene)-2,3-dihydro-1H-indene (**2i**): ^{1}H NMR: δ 7.77 (d, *J* = 6.5 Hz, 1H), 7.29–7.14 (m, 3H), 5.59 (d, *J* = 1.9 Hz, 1H), 4.68 (s, 1H), 4.54 (s, 1H), 3.69–3.62 (m, 1H), 3.19–3.01 (m, 2H), 1.30 (s, 9H), 1.17–1.05 (m, 1H), 0.64–0.35 (m, 4H). ^{13}C NMR: δ 154.2, 147.2, 141.5, 139.0, 136.4, 127.2, 127.1, 125.8, 125.1, 106.4, 55.6, 36.3, 31.9, 30.3, 12.6, 7.79, 6.99. EI-MS *m*/*z* (%): 252 (M^+, 12.24), 195 (100). HRMS (EI) calcd for $C_{19}H_{24}$: 252.1878; found: 252.1883. IR (KBr): 2956, 1638, 1471, 1363 cm^{-1}.

17. For a less sterically hindered example: Blanco-Urgoiti, J.; Abdi, D.; Dominguez, G.; Perez-Castells, J. *Tetrahedron* **2008**, *64*, 67.
18. For less sterically hindered examples (a) Morimoto, T.; Fuji, K.; Tsutsumi, K.; Kakiuchi, K. *J. Am. Chem. Soc.* **2002**, *124*, 3806; (b) Fuji, K.; Morimoto, T.; Tsutsumi, K.; Kakiuchi, K. *Angew. Chem., Int. Ed.* **2003**, *42*, 2409; (c) Ikeda, K.; Morimoto, T.; Tsumagari, T.; Tanimoto, H.; Nishiyama, Y.; Kakiuchi, K. *Synlett* **2012**, 393.
19. (a) Kerr, W. J. In *The Pauson–Khand Reaction: Scope, Variations and Applications*; Rios Torres, R., Ed.; John Wiley & Sons, 2012; (b) Shibata, T. In *The Pauson–Khand Reaction: Scope, Variations and Applications*; Rios Torres, R., Ed.; John Wiley & Sons, 2012; (c) Gibson, S. E.; Stevenazzi, A. *Angew. Chem., Int. Ed.* **1800**, *2003*, 42; (d) Sugihara, T.; Yamaguchi, M.; Nishizawa, M. *Chem. Eur. J.* **2001**, *7*, 1589.
20. Catalytic Pauson–Khand reaction using Lewis base as ligand. See (a) Tang, Y.-F.; Deng, L.-J.; Zhang, Y.-D.; Dong, G.-B.; Chen, J.-H.; Yang, Z. *Org. Lett.* **2005**, *7*, 593; (b) Krafft, M. E.; Bonaga, L. V. R.; Hirosawa, C. *J. Org. Chem.* **2001**, *66*, 3004; (c) Hayashi, M.; Hashimoto, Y.; Yamamoto, Y.; Usuki, J.; Saigo, K. *Angew. Chem., Int. Ed.* **2000**, *39*, 631; (d) Jeong, N.; Hwang, S. H.; Lee, Y.; Chung, Y. K. *J. Am. Chem. Soc.* **1994**, *116*, 3159.
21. *General procedure for the catalytic cycloisomerization of* **1f**: A mixture of 1,7-enyne **1f** (0.1 mmol), $Co_2(CO)_8$ (0.01 mmol), and ligand (0.01 mmol) in PhMe (4 mL) was stirred at room temperature under argon atmosphere for a while. Then it was heated to reflux for 1.5 h. The resultant reaction mixture was concentrated, and the residue was purified by flash chromatography on silica gel to provide 2,3-dihydroindene **2f**.