Synthesis A. Cabré et al. Special Topic

Ethylene Glycol Assisted Intermolecular Pauson–Khand Reaction

Albert Cabré[a]
Xavier Verdaguer*[a,b]
Antoni Riera*[a,b]

[a] Institute for Research in Biomedicine (IRB Barcelona), The Barcelona Institute of Science and Technology, Baldiri Reixac 10, Barcelona 08028, Spain
antoni.riera@irbbarcelona.org
xavier.verdaguer@irbbarcelona.org
[b] Departament de Química Inorgànica i Orgànica, Secció Orgànica, Universitat de Barcelona, Martí i Franquès 1, Barcelona 08028, Spain

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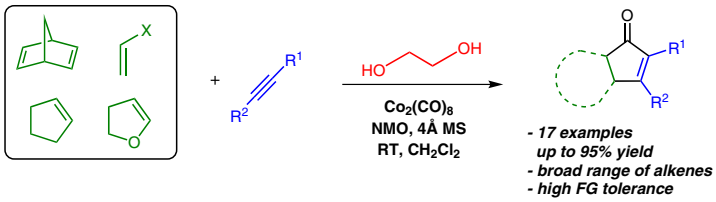

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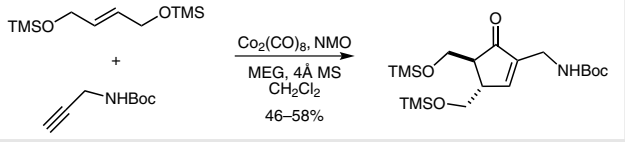
Abstract The use of ethylene glycol as additive in the *N*-oxide-promoted intermolecular Pauson–Khand reaction (PKR) has been studied. The addition of 15% ethylene glycol to the reaction mixture consistently increased (from 20% up to 2–4-fold) the reaction yields.

Key words Pauson–Khand reaction, cobalt, ethylene glycol, cyclopentenones, cycloaddition

The Pauson–Khand reaction (PKR)[1] is one of the few direct methods to synthesize five-membered ring carbocycles from acyclic precursors. When executed in an intramolecular fashion, this cobalt-mediated [2+2+1] cyclization is an extremely efficient way to build up complex cyclopentane polycycles.[1,2] The intermolecular PKR has found more limited use due to the narrow scope of the alkene. In fact, only strained olefins, such as norbornadiene or cyclopropene[3] or highly unhindered alkenes such as ethylene[4] gave high yields. However, the intermolecular version has a great potential since it allows cyclopentenones to be built up from very simple starting materials, namely an alkene, an alkyne, and carbon monoxide.[5]

During recent decades, much effort has been devoted to enhance the yields of this reaction using a variety of promoters or additives.[6] In 1990, Schreiber and co-workers discovered that the PKR, which was typically performed at high temperatures (60–110 °C), could also be promoted using *N*-oxides[7] such as *N*-methylmorpholine-*N*-oxide (NMO) in dichloromethane.[8] These conditions allowed the reaction to take place at room temperature and often gave better yields.[9]

In 2011, Baran and co-workers reported the total syntheses of (±)-axinellamines A and B.[10] The starting material of these synthesis was a cyclopentenone prepared by an intermolecular PKR using 1,4-bis[(trimethylsilyl)oxy]but-2-ene (Scheme 1). The success of the PKR with this unstrained olefin was possible only when using NMO as promoter and adding monoethylene glycol (MEG)[11] and 4 Å molecular sieves (MS) to the reaction. Under these conditions, a remarkable 46–58% yield was obtained (without MEG, yields dropped to 15–25%). Although Baran and co-workers stated that ethylene glycol was an essential additive, to the best of our knowledge, these conditions have not been used in any other PKR reported to date. We envisioned that, using this novel methodology, other olefins might give better yields and therefore a wider range of alkenes could be used.

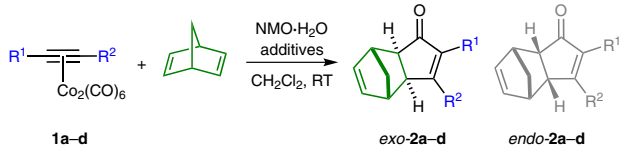


Scheme 1 Ethylene glycol assisted intermolecular PKR used in Baran's synthesis of axinellamines

Here, we studied the role that ethylene glycol displays in the stoichiometric *N*-oxide-promoted intermolecular PKR. The effect of Baran's conditions was tested when performing the reaction with strained alkenes such as norbornadiene, poorly reactive cyclopentenes,[12] and several ethylene synthetic equivalents.[13]

The new protocol was tested first with norbornadiene (NBD), which is the most relevant alkene substrate in intermolecular PKR. We observed that in all cases, the yields using ethylene glycol and molecular sieves as additives were substantially higher (Table 1, entries 2, 4, 6, and 8). The reaction is usually stereoselective affording the *exo*-adduct as the major stereoisomer. In the case of the reactions with ethylene glycol, the stereoselectivity towards the *exo* further increased slightly. The presence of ethylene glycol low-

Table 1 Intermolecular Pauson–Khand Reactions of Internal Alkynehexacarbonyldicobalt Complexes with Norbornadiene[a]



1a–d *exo*-**2a–d** *endo*-**2a–d**

Entry	R^1	R^2	Alkyne	Additives	Time (h)	Product	Yield (%)	*exo*/*endo*
1	CH_2SPh	H	**1a**	–	4	**2a**	8	>99
2	CH_2SPh	H	**1a**	MEG, 4 Å MS	17	**2a**	51	>99
3	CH_2NHBoc	H	**1b**	–	17	**2b**	65	91:9
4	CH_2NHBoc	H	**1b**	MEG, 4 Å MS	24	**2b**	85	93:7
5	TMS	H	**1c**	–	2	**2c**	72	96:4
6	TMS	H	**1c**	MEG, 4 Å MS	48–72	**2c**	89	98:2
7	*n*-Pr	CH_2OTBS	**1d**	–	24	**2d**	79	99:1
8	*n*-Pr	CH_2OTBS	**1d**	MEG, 4 Å MS	48–72	**2d**	95	99:1

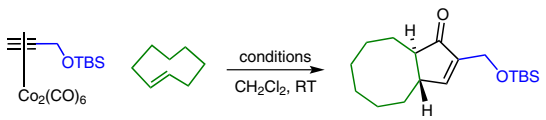
[a] The reactions were performed in CH_2Cl_2. NMO (6–10 equiv) was added in one portion.

ered the reaction rate and sometimes more than 6 equivalents of NMO were needed to complete the reaction. The reaction crudes using Baran's conditions were easier to workup because the ethylene glycol trapped the cobalt byproducts, thus affording a cleaner crude.

Another type of strained alkenes that showed satisfactory reactivity in the intermolecular PKR were medium-sized *trans*-cycloalkenes.[14] The PKR of these alkenes offered a modular, regioselective, and straightforward entry to *trans*-fused [n.3.0] bicyclic scaffolds.[15] In general, good to excellent yields were achieved using few equivalents of alkene and NMO as promoter. However, when using protected propargylic alcohols such as **1e**, the yield of the corresponding cyclopentenone dropped. We have found that under Baran's protocol the yield of **3e** increased from 38 to 60% as shown in Table 2.

Ethylene (**4**) is a useful alkene in intermolecular PKR. It has been used in the synthesis of taylorione[13] and phytoprostanes B1,[16] among others.[17] Its main drawbacks are the need of the equipment to manipulate a gas and its relatively low solubility. The latter issue can be improved by adding molecular sieves[18] and/or by slowly adding NMO. Thermal activation or other promoters usually worsened the reaction yields. Several alternatives to the use of ethylene gas have been described. For example, the use of supercritical ethylene was applied in the two-fold PKR of cyclic diynes[19] or in a catalytic version of the intermolecular PKR.[20] In 1999, Kerr and Pauson[13] reported the use of vinyl esters such as vinyl benzoate (**5**) as ethylene surrogates in the PKR. Therefore, we tested Baran's protocol on several ethylene equivalents as alkenes (Table 3).

Table 2 Comparative Study of the Intermolecular Pauson–Khand Reaction Using Terminal Alkyne **1e** with *trans*-Cyclooctene



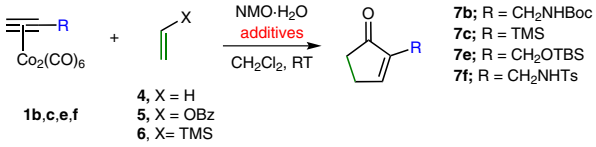
1e **3e**

Entry	Alkyne	Conditions	Product	Yield (%)
1	**1e**	NMO (6 equiv), 0 °C to r.t., 2 h	**3e**	38[14]
2	**1e**	NMO (10 equiv), MEG, 4 Å MS, 48 h	**3e**	60

Terminal alkynes **1b**,**c** were reacted with ethylene under the standard *N*-oxide-promoted PKR conditions (Table 3). For the sake of comparison, the standard protocol with vinyl benzoate by adding NMO in a single portion was used. Under these conditions the corresponding cyclopentenones **7b**,**c** were obtained in significantly lower yields than with ethylene. However, when using vinyl benzoate in the presence of ethylene glycol and 4 Å MS as additives, and also adding NMO in a single portion, the yields recovered or were higher than those achieved with ethylene. We also attempted, for the first time, the use of vinyltrimethylsilane (**6**) as ethylene surrogate (Table 3, entries 4 and 12). Olefin **6** showed good reactivity under these conditions, and the yields were comparable to those obtained with vinyl benzoate. However, a treatment with fluoride to cleave the silylated cyclopentenones was required.

Again, using Baran's conditions the workup was much cleaner and all cobalt residues were easily removed by a simple decantation. In terms of reactivity, vinyl benzoate proved to be the most useful ethylene equivalent. The yields were comparable to those achieved with ethylene, and in

Table 3 Intermolecular Pauson–Khand Reactions of Terminal Alkynehexacarbonyldicobalt Complexes with Ethylene and Ethylene Equivalents[a]



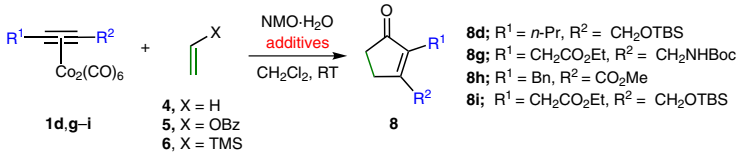
Entry	R	Alkyne	X	Alkene	Additives	Time (h)	Product	Yield (%)
1	CH_2NHBoc	**1b**	H	**4**	–	4	**7b**	63
2	CH_2NHBoc	**1b**	OBz	**5**	–	5	**7b**	36
3	CH_2NHBoc	**1b**	OBz	**5**	MEG, 4 Å MS	17	**7b**	67
4[b]	CH_2NHBoc	**1b**	TMS	**6**	MEG, 4 Å MS	17	**7b**	57
5	TMS	**1c**	H	**4**	–	4	**7c**	67
6	TMS	**1c**	OBz	**5**	–	5	**7c**	15
7	TMS	**1c**	OBz	**5**	MEG, 4 Å MS	24	**7c**	43
8	CH_2OTBS	**1e**	H	**4**	–	3	**7e**	20
9	CH_2OTBS	**1e**	OBz	**5**	MEG, 4 Å MS	17	**7e**	40
10	CH_2NHTs	**1f**	H	**4**	–	5	**7f**	54
11	CH_2NHTs	**1f**	OBz	**5**	MEG, 4 Å MS	17	**7f**	72
12[b]	CH_2NHTs	**1f**	TMS	**6**	MEG, 4 Å MS	17	**7f**	64

[a] The reactions were performed in CH_2Cl_2 with 6 equiv of NMO.
[b] Once complete, the reaction was quenched with a catalytic amount of HF·Pyr.

some cases even improved (Table 3, entries 3, 9 and 11). The presence of additives did not affect the C–O cleavage to take place, which still occurred spontaneously.

Ethylene glycol can help to extend the scope of alkynes available for this transformation. In this regard, when internal alkynes are used in the intermolecular PKR, the reactiv-

Table 4 Intermolecular Pauson–Khand Reaction of Internal Alkynehexacarbonyldicobalt Complexes with Ethylene and Ethylene Equivalents[a]



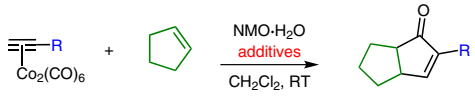
Entry	R^1	R^2	Alkyne	X	Alkene	Additives	Time (h)	Product	Yield (%)
1	*n*-Pr	CH_2OTBS	**1d**	H	**4**	–	5	**8d**	65
2	*n*-Pr	CH_2OTBS	**1d**	OBz	**5**	MEG, 4 Å MS	36	**8d**	12
3	CH_2CO_2Et	CH_2NHBoc	**1g**	H	**4**	–	4	**8g**	75
4	CH_2CO_2Et	CH_2NHBoc	**1g**	OBz	**5**	–	5	**8g**	20
5	CH_2CO_2Et	CH_2NHBoc	**1g**	OBz	**5**	MEG, 4 Å MS	17	**8g**	64
6[b]	CH_2CO_2Et	CH_2NHBoc	**1g**	TMS	**6**	MEG, 4 Å MS	17	**8g**	56
7	CH_2Ph	CO_2Me	**1h**	H	**4**	–	4	**8h**	57
8	CH_2Ph	CO_2Me	**1h**	OBz	**5**	–	5	**8h**	11
9	CH_2Ph	CO_2Me	**1h**	OBz	**5**	MEG, 4 Å MS	24	**8h**	46
10	CH_2CO_2Et	CH_2OTBS	**1i**	H	**4**	–	4	**8i**	53
11	CH_2CO_2Et	CH_2OTBS	**1i**	OBz	**5**	MEG, 4 Å MS	17	**8i**	49
12[b]	CH_2CO_2Et	CH_2OTBS	**1i**	TMS	**6**	MEG, 4 Å MS	17	**8i**	43

[a] The reactions were performed in CH_2Cl_2. NMO (6–10 equiv) was added.
[b] Once completed, the reaction was quenched with catalytic amount of HF·Pyr.

ity decreases. To the best of our knowledge, there is no precedent in which internal alkynes have been used to synthesize α,β-substituted cyclopentenones via regioselective[21] PKR with ethylene surrogates. We observed (Table 4) that when using ethylene equivalents with Baran's protocol, reaction yields were comparable to those obtained with ethylene in most cases (Table 4, entries 5, 9, and 11). Only for the one bearing an alkyl chain, the reactivity decreased considerably (entry 2).

Finally, we sought to explore the effect of Baran's conditions when using other alkenes such as cyclopentene (**9**) or 2,3-dihydrofuran (**10**), which are poorly reactive and less common in PKR. *N*-Boc propargylamine and trimethylsilylacetylene complexes **1b** and **1c** were selected due to their synthetic importance.[22] Using ethylene glycol as additive, the yields of *N*-oxide-promoted cyclizations of cyclopentene, doubled those achieved when using the standard protocol or when 4 Å MS was the only additive (Table 5). The reaction using of 2,3-dihydrofuran afforded the products with the biggest yield increase and with complete regioselectivity (Table 6).

Table 5 Comparative Study of the Intermolecular Pauson–Khand Reaction Using Terminal Alkynes and Cyclopentene[a]



1b, R = CH_2NHBoc **1c**, R = TMS — **9** — **11b** R = CH_2NHBoc **11c** R = TMS

Entry	Alkyne	Additives	Time (h)	Product	Yield (%)
1	**1b**	–	3	**11b**	35
2	**1b**	4 Å MS	3	**11b**	37
3	**1b**	MEG, 4 Å MS	5	**11b**	60
4	**1c**	–	4	**11c**	16
5	**1c**	4 Å MS	4	**11c**	14
6	**1c**	MEG, 4 Å MS	48–72	**11c**	31

[a] The reactions were performed in CH_2Cl_2. NMO (6 equiv) was added in one portion.

In conclusion, we have shown that the use of ethylene glycol as additive consistently improves the *N*-oxide-promoted intermolecular PKR in terms of yield, stereoselectivity, and practicality. When using norbornadiene as alkene, which is the most reactive alkene in the intermolecular PKR, a slight increase in both yield and stereoselectivity was observed. Using ethylene surrogates such as vinyl benzoate and vinyltrimethylsilane, the yields of the corresponding cyclopentenones were similar to those achieved with ethylene gas. The greatest advantage was found when using less activated alkenes such as cyclopentene or 2,3-dihydrofuran. This methodology greatly facilitates the workup of

Table 6 Comparative Study of the Intermolecular Pauson–Khand Reaction Using Terminal Alkynes and 2,3-Dihydrofuran[a]

1b, R = CH_2NHBoc **1c**, R = TMS — **10** — **12b** R = CH_2NHBoc **12c** R = TMS

Entry	Alkyne	Additives	Time (h)	Product	Yield (%)
1	**1b**	–	17	**12b**	40
2	**1b**	MEG, 4 Å MS	36	**12b**	57
3	**1c**	–	4	**12c**	21
4	**1c**	MEG, 4 Å MS	24	**12c**	82

[a] The reactions were performed in CH_2Cl_2. NMO (6 equiv) was added in one portion.

the reactions because the ethylene glycol absorbs the cobalt by-products. Moreover, since the reaction rate decreases, the addition of the *N*-oxide promoter can be done in a single portion. We believe that the main effect of ethylene glycol is to stabilize the unsaturated cobalt complexes that are the key intermediates of the PKR. This new protocol may help to address one of the most important drawbacks of the intermolecular PKR, namely the limited range of reactive alkenes.

Reactions were carried out under N_2 in previously oven-dried vials or round-bottomed flasks. CH_2Cl_2 was degassed and dried with a solvent purification system (SPS PS-MD-3). Reactions were monitored by TLC analysis using Merck silica gel 60 F-254 thin layer plates. Solvents were removed under reduced pressure with a rotary evaporator. Silica gel chromatography was performed using an automated chromatography system (PuriFlash® 430, Interchim). NMR spectra were recorded at 400 MHz for ^1H and at 101 MHz for ^{13}C. Chemical shifts (δ) are given in ppm and referenced to internal solvent resonances and reported relative to TMS. The coupling constants (*J*) are reported in hertz (Hz). High-resolution mass spectra (ESI) were recorded on a LC/MSD-TOF G1969A spectrometer (Agilent Technologies).

The synthesis of alkynes and their hexacarbonyldicobalt complexes are described in detail in the Supporting Information.

Intermolecular Pauson–Khand Reaction Using the Standard Protocol; General Procedure

Method A: The corresponding hexacarbonyldicobalt complex (1.0 equiv) was dissolved in anhyd CH_2Cl_2 (11 mL/mmol complex) and charged to a vial, which was previously purged with N_2. The respective alkene (5.0 equiv, unless otherwise indicated) was then added. The reaction mixture was stirred for 10 min. A solution of NMO (6 equiv, unless otherwise indicated) in anhyd CH_2Cl_2 was added in a single portion. The reaction was monitored by TLC until no cobalt complex was observed. Then, the crude was filtered through a plug of SiO_2 and washed with CH_2Cl_2 (3 ×). The solvent was concentrated under vacuum and the crude was purified by column chromatography on SiO_2 using mixtures of hexanes/EtOAc of increasing polarities.

Ethylene Glycol-Assisted Intermolecular Pauson–Khand Reaction; General Procedures

Method B: The corresponding hexacarbonyldicobalt complex (1.0 equiv) was dissolved in anhyd CH_2Cl_2 (11 mL/mmol complex) and charged to a vial containing 4 Å MS (317 mg/mmol complex), which was previously purged with N_2. The respective alkene (5.0 equiv, unless otherwise indicated) and ethylene glycol (1.7 mL/mmol complex) were then added. The reaction mixture was stirred for 10 min. A solution of NMO (6 equiv, unless otherwise indicated) in anhyd CH_2Cl_2 was added in a single portion. The reaction was monitored by TLC until no cobalt complex was observed. Then, the crude was filtered through a plug of neutral Al_2O_3 and washed with CH_2Cl_2 (3 ×). The solvent was concentrated under vacuum and the crude was purified by column chromatography on SiO_2 using mixtures of hexanes/EtOAc of increasing polarities.

Method C: The corresponding hexacarbonyldicobalt complex (1.0 equiv) was dissolved in anhyd CH_2Cl_2 (11 mL/mmol complex) and charged to a vial containing 4 Å MS (317 mg/mmol complex), which was previously purged with N_2. Vinyltrimethylsilane (5.0 equiv) and ethylene glycol (1.7 mL/mmol complex) were then added. The reaction mixture was stirred for 10 min. A solution of NMO (6 equiv, unless otherwise indicated) in anhyd CH_2Cl_2 was added in a single portion. The reaction was monitored by TLC until no cobalt complex was observed. Once completed, the reaction was quenched with a catalytic amount of HF·Pyr and stirred for 10 min. Afterwards, the mixture was quickly filtered through a short plug of neutral Al_2O_3. The solvent was concentrated under vacuum and the crude was purified by column chromatography on SiO_2 using mixtures of hexanes/EtOAc of increasing polarities.

(3a*R*,4*S*,7*R*,7a*R*)-2-[(Phenylthio)methyl]-3a,4,7,7a-tetrahydro-1*H*-4,7-methanoinden-1-one (2a)

Starting from 0.33 mmol of Co complex **1a**; isolated yield; Method A: 7 mg (8%); Method B: 46 mg (51%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33–7.21 (m, 5 H), 7.20–7.14 (m, 1 H), 6.24 (dd, *J* = 5.6, 3.1 Hz, 1 H), 6.18 (dd, *J* = 5.6, 3.0 Hz, 1 H), 3.74–3.58 (m, 2 H), 2.91 (p, *J* = 1.4 Hz, 1 H), 2.68 (dhept, *J* = 5.4, 1.3 Hz, 1 H), 2.57 (dt, *J* = 2.9, 1.5 Hz, 1 H), 2.31 (dt, *J* = 5.0, 1.4 Hz, 1 H), 1.30 (dp, *J* = 9.4, 1.6 Hz, 1 H), 1.07 (dd, *J* = 9.4, 1.6 Hz, 1 H).

The analytical and spectral data for this compound were in excellent agreement with the reported data.[22a]

***tert*-Butyl {[(3a*R*,4*S*,7*R*,7a*R*)-1-Oxo-3a,4,7,7a-tetrahydro-1*H*-4,7-methanoinden-2-yl]methyl}carbamate (2b)**

Starting from 0.30 mmol of Co complex **1b**; isolated yield; Method A: 54 mg (65%); Method B: 70 mg (85%); off-white solid; mp 161–163 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 (d, *J* = 2.6 Hz, 1 H), 6.27 (dd, *J* = 5.6, 3.1 Hz, 1 H), 6.18 (dd, *J* = 5.6, 3.0 Hz, 1 H), 5.04 (br s, 1 H), 3.85 (t, *J* = 6.5 Hz, 2 H), 2.89 (t, *J* = 1.8 Hz, 1 H), 2.74 (ddp, *J* = 5.3, 2.6, 1.3 Hz, 1 H), 2.70–2.65 (m, 1 H), 2.29 (dt, *J* = 5.1, 1.4 Hz, 1 H), 1.41 (s, 9 H), 1.38–1.33 (m, 1 H), 1.21–1.16 (m, 1 H).

The analytical and spectral data for this compound were in excellent agreement with the reported data.[22a]

(3a*S*,4*S*,7*R*,7a*R*)-2-(Trimethylsilyl)-3a,4,7,7a-tetrahydro-1*H*-4,7-methanoinden-1-one (2c)

Starting from 0.36 mmol of Co complex **1c**; isolated yield; Method A: 69 mg (72%); Method B: 53 mg (89%); white solid; mp 94–95 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59 (d, *J* = 2.5 Hz, 1 H), 6.27 (dd, *J* = 5.7, 3.1 Hz, 1 H), 6.20 (dd, *J* = 5.6, 3.0 Hz, 1 H), 2.91 (d, *J* = 2.8 Hz, 1 H), 2.83 (s, 1 H), 2.69 (s, 1 H), 2.28 (d, *J* = 5.2 Hz, 1 H), 1.37 (d, *J* = 9.3 Hz, 1 H), 1.19 (d, *J* = 9.3 Hz, 1 H), 0.17 (s, 9 H).

The analytical and spectral data for this compound were in excellent agreement with the reported data.[23]

(3a*S*,4*S*,7*R*,7a*R*)-3-{[(*tert*-Butyldimethylsilyl)oxy]methyl}-2-propyl-3a,4,7,7a-tetrahydro-1*H*-4,7-methanoinden-1-one (2d)

Starting from 0.27 mmol of Co complex **1d**; isolated yield; Method A: 69 mg (79%); Method B: 84 mg (95%); colorless oil. 10 equiv of NMO were used in both cases.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.19 (dd, *J* = 5.6, 3.1 Hz, 1 H), 6.12 (dd, *J* = 5.6, 2.9 Hz, 1 H), 4.51 (d, *J* = 15.1 Hz, 1 H), 4.41 (dd, *J* = 15.1, 1.0 Hz, 1 H), 2.83 (dd, *J* = 3.0, 1.6 Hz, 1 H), 2.81–2.75 (m, 2 H), 2.19 (dd, *J* = 5.2, 1.5 Hz, 1 H), 2.13–2.08 (m, 1 H), 2.02 (dt, *J* = 7.5, 6.2 Hz, 1 H), 1.37–1.26 (m, 3 H), 1.10 (dtd, *J* = 9.2, 1.4, 0.7 Hz, 1 H), 0.87 (s, 9 H), 0.80 (d, *J* = 7.3 Hz, 3 H), 0.04 (s, 6 H).

The analytical and spectral data for this compound were in excellent agreement with the reported.[21]

(3a*S*,9a*R*)-2-{[(*tert*-Butyldimethylsilyl)oxy]methyl}-3a,4,5,6,7,8,9,9a-octahydro-1*H*-cyclopenta[8]annulen-1-one (3e)

Starting from 0.22 mmol of Co complex **1e**; isolated yield; Method A: 19 mg (38%);[14] Method B (using 10 equiv of NMO): 31 mg (60%); colorless oil. In both cases, 3 equiv of alkene were used.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 (q, *J* = 2.0 Hz, 1 H), 4.34 (dd, *J* = 2.9, 1.9 Hz, 2 H), 2.68 (dq, *J* = 12.3, 3.0 Hz, 1 H), 2.20–1.20 (m, 13 H), 0.91 (s, 9 H), 0.07 (s, 6 H).

The analytical and spectral data for this compound were in excellent agreement with the reported data.[14]

***tert*-Butyl [(5-Oxocyclopent-1-en-1-yl)methyl]carbamate (7b)**

Starting from 0.23 mmol of Co complex **1b**; isolated yield; Method A: 17 mg (36%); Method B: 32 mg (67%); Method C: 28 mg (57%); pale orange oil.

IR (ATR-FTIR): 3368, 2981, 2928, 1735, 1698 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 (s, 1 H), 5.02 (br s, 1 H), 3.91 (d, *J* = 6.7 Hz, 2 H), 2.69–2.55 (m, 2 H), 2.47–2.38 (m, 2 H), 1.44 (s, 9 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 209.22, 159.29, 155.81, 143.05, 79.43, 36.09, 34.81, 28.33, 26.61.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{11}H_{17}NO_3Na$: 234.1101; found: 234.1099.

2-(Trimethylsilyl)cyclopent-2-en-1-one (7c)

Starting from 0.22 mmol of Co complex **1c**; isolated yield; Method A: 6 mg (15%); Method B: 16 mg (43%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (t, *J* = 2.6 Hz, 1 H), 2.66 (dt, *J* = 7.5, 2.5 Hz, 2 H), 2.37–2.30 (m, 2 H), 0.18 (s, 9 H).

The analytical and spectral data for this compound were in excellent agreement with the reported data.[22c]

2-{[(*tert*-Butyldimethylsilyl)oxy]methyl}cyclopent-2-en-1-one (7e)

Starting from 0.41 mmol of Co complex **1e**; isolated yield; Method B: 36 mg (40%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53 (ddd, *J* = 4.6, 2.7, 1.9 Hz, 1 H), 4.37 (td, *J* = 2.8, 1.8 Hz, 2 H), 2.66–2.57 (m, 2 H), 2.54–2.42 (m, 2 H), 0.92 (s, 9 H), 0.08 (s, 6 H).

The analytical and spectral data for this compound were in excellent agreement with the reported data.[24]

4-Methyl-*N*-[(5-oxocyclopent-1-en-1-yl)methyl]benzenesulfonamide (7f)

Starting from 0.22 mmol of Co complex **1f**; isolated yield; Method B: 43 mg (72%); Method C: 38 mg (64%); colorless oil.

IR (ATR-FTIR): 3270, 3017, 1689 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73–7.68 (m, 2 H), 7.41 (tt, *J* = 2.7, 1.3 Hz, 1 H), 7.32–7.27 (m, 2 H), 5.14 (t, *J* = 6.4 Hz, 1 H), 3.80 (dtd, *J* = 6.6, 1.8, 1.2 Hz, 2 H), 2.51–2.45 (m, 2 H), 2.42 (s, 3 H), 2.28–2.24 (m, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 208.98, 160.31, 143.48, 140.71, 136.93, 129.60, 127.24, 39.18, 34.53, 26.87, 21.49.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{16}NO_3S$: 266.0845; found 266.0844.

3-{[(*tert*-Butyldimethylsilyl)oxy]methyl}-2-propylcyclopent-2-en-1-one (8d)

Starting from 0.18 mmol of Co complex **1d**; isolated yield; Method B (using 10 equiv of NMO): 6 mg (12%); colorless oil.

IR (ATR-FTIR): 2950, 1770, 1464, 840 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.54 (s, 2 H), 2.59 (dtd, *J* = 7.1, 2.3, 1.2 Hz, 2 H), 2.41–2.33 (m, 2 H), 2.21–2.10 (m, 2 H), 1.39 (dq, *J* = 14.8, 7.4 Hz, 2 H), 0.92 (s, 9 H), 0.87 (t, *J* = 7.4 Hz, 3 H), 0.10 (s, 6 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 210.07, 171.72, 139.49, 61.36, 34.19, 27.09, 25.96, 25.20, 21.91, 18.47, 14.20, –5.29.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{29}O_2Si$: 269.1931; found: 269.193.

Ethyl 2-(2-{[(*tert*-Butoxycarbonyl)amino]methyl}-5-oxocyclopent-1-en-1-yl)acetate (8g)

Starting from 0.23 mmol of Co complex **1g**; isolated yield; Method A: 14 mg (20%); Method B: 43 mg (64%); Method C: 37 mg (56%); colorless oil.

IR (ATR-FTIR): 3359, 2972, 1701, 1693, 1650 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.05 (br s, 1 H), 4.17–4.10 (m, 2 H), 4.12 (s, 2 H), 3.30 (s, 2 H), 2.69–2.58 (m, 2 H), 2.48–2.40 (m, 2 H), 1.46 (s, 9 H), 1.25–1.28 (m, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 208.04, 172.77, 171.21, 170.73, 156.13, 134.01, 80.01, 61.29, 60.46, 40.85, 33.90, 28.42, 21.11, 14.27.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{24}NO_5$: 298.1649; found: 298.1650.

Methyl 2-Benzyl-3-oxocyclopent-1-ene-1-carboxylate (8h)

Starting from 0.36 mmol of Co complex **1h**; isolated yield; Method A: 9 mg (11%); Method B: 36 mg (46%); colorless oil.

IR (ATR-FTIR): 2976, 2954, 1715, 1709 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30 (ddt, *J* = 7.6, 1.5, 0.7 Hz, 2 H), 7.27–7.21 (m, 2 H), 7.20–7.14 (m, 1 H), 3.91 (s, 2 H), 3.87 (s, 3 H), 2.81–2.75 (m, 2 H), 2.50–2.44 (m, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 209.03, 165.57, 154.54, 149.60, 138.28, 129.00, 128.36, 126.32, 52.14, 33.97, 29.65, 26.65.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{15}O_3$: 231.1016; found: 231.1022.

Ethyl 2-(2-{[(*tert*-Butyldimethylsilyl)oxy]methyl}-5-oxocyclopent-1-en-1-yl)acetate (8i)

Starting from 0.22 mmol scale of Co complex **1i**; isolated yield; Method B: 34 mg (49%); Method C: 29 mg (43%); colorless oil.

IR (ATR-FTIR): 2958, 2923, 2856, 1734, 1702 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.58 (s, 2 H), 4.12 (q, *J* = 7.1 Hz, 2 H), 3.32 (s, 2 H), 2.64 (dtd, *J* = 7.1, 2.3, 1.2 Hz, 2 H), 2.44–2.39 (m, 2 H), 1.25 (t, *J* = 7.1 Hz, 3 H), 0.92 (s, 9 H), 0.10 (s, 6 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 208.41, 174.71, 170.44, 132.66, 62.44, 61.04, 33.80, 28.67, 27.55, 25.95, 18.46, 14.30, –5.40.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{29}O_4Si$: 313.1830; found: 313.1834.

***tert*-Butyl [(1-Oxo-1,3a,4,5,6,6a-hexahydropentalen-2-yl)methyl]carbamate (11b)**

Starting from 0.23 mmol of Co complex **1b**; isolated yield; Method A: 20 mg (35%); Method B: 35 mg (60%); colorless oil.

IR (ATR-FTIR): 2937, 2869, 1724, 1525, 758 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.26 (m, 1 H), 5.02 (br s, 1 H), 3.86 (d, *J* = 6.2 Hz, 2 H), 3.33–3.18 (m, 1 H), 2.74 (ddd, *J* = 10.1, 5.6, 1.8 Hz, 1 H), 1.91–1.83 (m, 1 H), 1.75–1.65 (m, 2 H), 1.63–1.54 (m, 2 H), 1.42 (s, 9 H), 1.19 (qt, *J* = 12.4, 6.5 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 212.36, 162.22, 155.79, 143.11, 79.44, 50.51, 44.25, 36.04, 30.07, 29.35, 28.33, 23.55.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{22}NO_3$: 252.1594; found: 252.1591.

2-(Trimethylsilyl)-4,5,6,6a-tetrahydropentalen-1(3a*H*)-one (11c)

Starting from 0.23 mmol of Co complex **1c**; isolated yield; Method A: 7 mg (16%); Method B: 14 mg (31%); colorless oil.

IR (ATR-FTIR): 2918, 2850, 1734, 1215, 758 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 2.6 Hz, 1 H), 3.30 (ddt, *J* = 8.5, 5.4, 2.5 Hz, 1 H), 2.71–2.62 (m, 1 H), 1.89 (dd, *J* = 12.7, 6.3 Hz, 1 H), 1.75–1.61 (m, 2 H), 1.56 (dt, *J* = 12.5, 6.0 Hz, 2 H), 1.13 (ddq, *J* = 18.8, 12.5, 6.4 Hz, 1 H), 0.16 (s, 9 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 216.84, 174.91, 147.66, 50.81, 47.85, 30.60, 29.75, 23.50, –1.64.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{11}H_{19}OSi$: 195.1200; found: 195.1197.

***tert*-Butyl [(6-Oxo-3,3a,6,6a-tetrahydro-2*H*-cyclopenta[*b*]furan-5-yl)methyl]carbamate (12b)**

Starting from 0.23 mmol of Co complex **1b**; isolated yield; Method A: 23 mg (40%); Method B: 33 mg (57%); colorless oil.

IR (ATR-FTIR): 2955, 2917, 2850, 1715, 1168, 758 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 (d, *J* = 2.7 Hz, 1 H), 5.02 (br s, 1 H), 4.33 (d, *J* = 5.6 Hz, 1 H), 3.96 (ddd, *J* = 9.3, 7.4, 2.0 Hz, 1 H), 3.88 (d, *J* = 6.9 Hz, 2 H), 3.56–3.48 (m, 1 H), 3.46–3.38 (m, 1 H), 2.07 (dddd, *J* = 10.9, 7.5, 3.4, 2.2 Hz, 1 H), 1.79 (ddt, *J* = 12.6, 5.4, 2.1 Hz, 1 H), 1.41 (s, 9 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 206.00, 159.05, 155.76, 143.56, 80.48, 67.48, 42.88, 35.96, 30.06, 28.31.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{20}NO_4$: 254.1387; found: 254.1382.

5-(Trimethylsilyl)-2,3,3a,6a-tetrahydro-6*H*-cyclopenta[*b*]furan-6-one (12c)

Starting from 0.23 mmol of Co complex **1c**; isolated yield; Method A: 9 mg (21%); Method B: 35 mg (82%); colorless oil.

IR (ATR-FTIR): 2955, 2859, 1706, 1248, 841 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.62 (d, *J* = 2.7 Hz, 1 H), 4.28 (d, *J* = 5.7 Hz, 1 H), 3.95 (ddd, *J* = 9.3, 7.4, 2.0 Hz, 1 H), 3.52–3.41 (m, 2 H), 2.08 (dddd, *J* = 12.5, 10.9, 9.8, 7.4 Hz, 1 H), 1.79 (ddt, *J* = 12.5, 5.5, 2.0 Hz, 1 H), 0.18 (s, 9 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 210.18, 171.32, 148.39, 80.92, 67.25, 46.04, 30.41, –1.80.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{10}H_{17}O_2Si$: 197.0992; found: 197.0996.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0036-1588813. Included are experimental procedures for the preparation of alkynes and alkynehexacarbonyldicobalt complexes, as well as ^1H and ^{13}C spectra of the new PK adducts synthesized in this work.

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