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Catalytic Pauson–Khand Reaction in Ethylene Glycol–Toluene: Activity, Selectivity, and Catalyst Recycling

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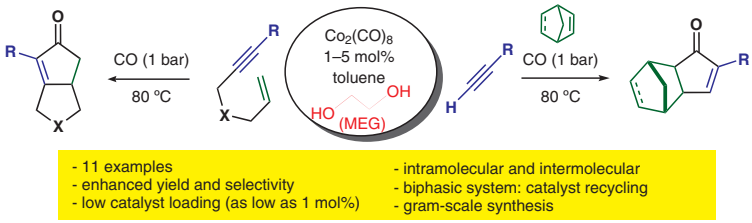

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Abstract The use of ethylene glycol (15% v/v in toluene) as additive in the catalytic Pauson–Khand reaction (PKR) is reported. In most cases both the yield and selectivity were enhanced compared to standard protocols. Moreover, the immiscibility of ethylene glycol in toluene allowed recycling of the catalyst (which remained mainly in the ethylene glycol). The recycling allowed catalyst loading to be reduced to only 3 mol%. A gram-scale reaction was also performed, allowing the use of only 1 mol% of $Co_2(CO)_8$, the lowest amount reported so far in intermolecular cobalt-catalyzed PKR.

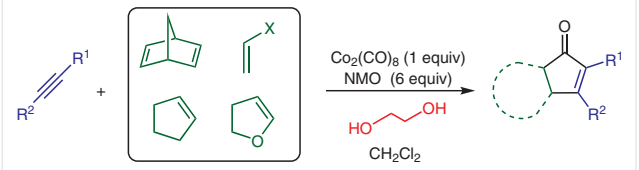
Key words Pauson–Khand Reaction, homogeneous catalysis, cyclization, cobalt, additives, cyclopentenones, cycloaddition, catalyst recycling

The Pauson–Khand reaction (PKR),[1,2] a metal-catalyzed [2+2+1] cycloaddition coupling of an alkyne, an alkene, and CO, is one of the most powerful synthetic tools with which to prepare cyclopentenones.[3,4] The stoichiometric version of the reaction uses large amounts of dicobalt octacarbonyl with the subsequent drawbacks of price, residue disposal, and difficult purification of the final product. In this regard, the development of catalytic methodologies to reduce the amount of metal are required for large-scale preparations. Several catalytic versions of the PKR involving the use of other metals, such as Ti,[5] Ru,[6] Rh,[7] Ni,[8] and Ir[9] or bimetallic species, have been described.[10] However, the use of cobalt complexes is probably the most practical and economical approach. Although the catalytic system can be prepared in situ by reducing $CoBr_2$ with Zn under CO pressure,[11] dicobalt octacarbonyl continues to be the most common catalyst.[12]

Many additives have been described to improve the yields in the cobalt-catalyzed PKR. Ureas such as tetramethylthiourea (TMTU),[13] phosphites,[14] triphenylphosphines,[15] hard Lewis bases,[16] and sulfides[17] are the most relevant. However, the use of large amounts of additives usually hinders the purification of the product.

Catalyst recycling is clearly desirable. Several heterogeneous catalytic systems such as colloidal cobalt nanoparticles (NPs),[18] cobalt on charcoal,[19] or cobalt Raney[20] have been described for the PKR.[21] However, to the best of our knowledge, there are no precedents of catalyst recycling in homogenous systems.

Based on a previous methodology developed by Baran and co-workers,[4a] our group recently reported that, ethylene glycol (ethane-1,2-diol, MEG) can enhance the alkene range in the stoichiometric *N*-oxide promoted intermolecular PKR (Scheme 1).[22] In the present study we report that this additive also has a positive effect on the cobalt-catalyzed PKR, allowing the reaction to be performed with very low catalyst loadings, reducing undesired byproducts, facilitating the purification of the final product, and permitting catalyst recycling by simple liquid–liquid separation.

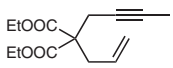
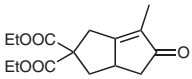
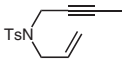
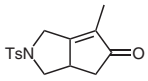
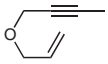
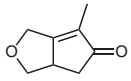


Scheme 1 Previous work of MEG-assisted intermolecular PKR

We chose three standard enynes **1a–c** to test the intramolecular catalytic PKR (Table 1). As expected the reaction proceeded smoothly in toluene using 5 mol% of $Co_2(CO)_6$ to afford the corresponding bicyclic cyclopentenones **2a–c** in moderate to good yields. The yield of **2c** from the oxygen-containing enyne **1c** was slightly lower than those of **2a** and **2b** from all-carbon **1a** and nitrogen-containing **1b**, respectively. Under the same conditions but using 15% MEG/tolu-

ene instead of pure toluene (Table 1, entries 1–3) the yields consistently increased by approximately 10% points. Although the increase in yield was moderate, the reaction crudes were much cleaner in MEG/toluene, thus allowing easier workup and purification.

Table 1 Catalytic Intramolecular Pauson–Khand Reaction[a]

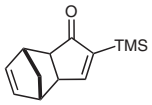
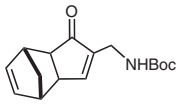
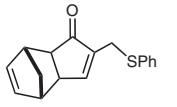
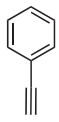
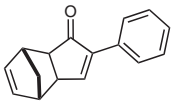
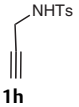
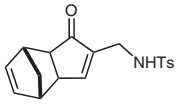
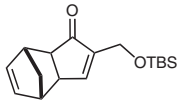
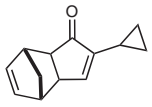
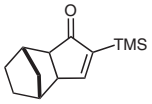
Entry	Enyne	Cyclopentenone	Yield[b] (%)
1	 **1a**	 **2a**	A: 81 B: 90
2	 **1b**	 **2b**	A: 83 B: 91
3	 **1c**	 **2c**	A: 47 B: 60

[a] Reaction conditions A: enyne (100 mg, 1.0 equiv), $Co_2(CO)_8$ (0.05 equiv, 5 mol%), toluene, 80 °C, under CO (1 bar), overnight. Reaction conditions B: as A but 15% MEG/toluene was used as the solvent system.
[b] Isolated yields.

We then, turned our attention to the intermolecular version. Terminal alkynes **1d–j** were reacted with norbornadiene (NBD) or norbornene (Table 2, entries 1–7 and 8, respectively) under CO pressure using dicobalt octacarbonyl as catalyst affording cyclopentenones **2d–j** in good to excellent yields. Except in one case (entry 7) the yields clearly improved when using the MEG/toluene mixture. Moreover, a significant improvement in terms *exo*/*endo* selectivity was also achieved in all cases. In entry 4, for instance, only traces of trimerization of phenylacetylene, a common byproduct in catalytic PKR that is usually avoided by adding triphenylphosphine, was detected. In addition, no *endo* adduct was observed. It is worth noting that **2d** and **2e** are the most interesting substrates from the synthetic point of view since they have been used in the synthesis of several biologically active compounds.[4b–d]

Apart from the effect of MEG on the yield and *exo*/*endo* selectivity, the addition of this compound to the reaction mixture also gave a much cleaner crude product. In fact, after completion of the reaction, two phases were clearly observed: a slightly colored upper toluene layer and a dark red lower MEG layer (Figure 1). Therefore, when the reaction finished, toluene and MEG formed two immiscible liquid layers. We assumed that most of the product remained in the organic phase, whereas most of the cobalt species were trapped in the MEG layer.

Table 2 Catalytic Intermolecular Pauson–Khand Reaction[a]

Entry	Alkyne	Cyclopentenone	Ratio *exo*/*endo*	Yield[b] (%)
1	 **1d**	 **2d**	A: 93:7 B: 93:7	A: 75 B: 99
2	 **1e**	 **2e**	A: 83:17 B: 93:7	A: 60 B: 93
3	 **1f**	 **2f**	A: 93:7 B: 96:4	A: 79 B: 93
4	 **1g**	 **2g**	A: 98:2 B: >99	A: 89 B: 91
5	 **1h**	 **2h**	A: 93:7 B: 95:5	A: 80 B: 85
6	 **1l**	 **2i**	A: 93:7 B: 95:5	A: 56 B: 70
7	 **1j**	 **2j**	A: 93:7 B: >99	A: 75 B: 72
8[c]	 **1d**	 **3**	A: 86:14 B: >99	A: 94 B: 98

[a] Reaction conditions A: norbornadiene (5.0 equiv), alkyne (100 mg, 1.0 equiv), $Co_2(CO)_8$ (0.05 equiv, 5 mol%), toluene, 80 °C under CO (1 bar), overnight. B: as A but 15% MEG/toluene was used as the solvent system.
[b] Isolated yields.
[c] Norbornene was used as alkene.

To test this assumption, the upper layer was separated and a solution of alkyne and alkene in toluene was added to the MEG phase. Heating at 80 °C under CO (1 bar), the PKR proceeded again thereby proving that the cobalt species that remain in the MEG phase were catalytically active. This observation prompted us to use the novel methodology to test the recycling of $Co_2(CO)_8$. For this purpose, **1d** and

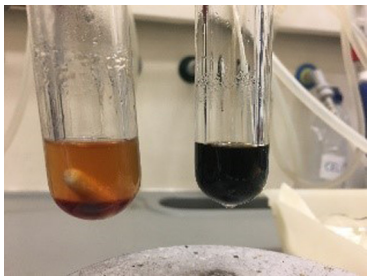
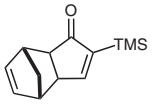
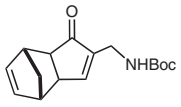
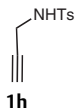
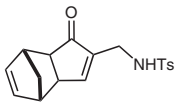


Figure 1 Reaction crude of **3** after 17 h of heating (Table 2, entry 8); with MEG as additive (left) and without MEG (right)

N-protected propargylamine acetylenes **1e** and **1h** were selected as alkynes and norbornadiene as alkene. The reaction was performed using an initial loading of 10 mol% of $Co_2(CO)_8$ in 15% MEG/toluene. The reaction mixture was stirred at 80 °C overnight under CO (1 bar). Then, the reactor was depressurized and the supernatant organic layer was separated. A fresh toluene solution of alkyne and NBD was added to the MEG layer containing the cobalt complexes. The second catalytic cycle finished after 36 hours (monitored by TLC) and the operation was repeated. Finally, the third catalytic cycle lasted 72 hours. Each of the toluene layers was collected, evaporated, and chromatographed affording the corresponding PK-adducts (Table 3). The overall yields were excellent and less than 10% of the product was found in the final MEG layer. Therefore, it was possible to perform up to three catalytic cycles (Table 3). In this case, the *exo*/*endo* selectivities were similar to those obtained with the previous methodology.

Table 3 Catalytic Recyclability[a]

Entry	Alkyne	Cyclopentenone	Yield[b] (%) (cycle)	Overall yield[c] (%) (ratio *exo*/*endo*)
1	 **1d**	 **2d**	95 (1st) 90 (2nd) 71 (3rd)	85 (90:10)
2	 **1e**	 **2e**	99 (1st) 93 (2nd) 85 (3rd)	92 (92:8)
3	 **1h**	 **2h**	99 (1st) 92 (2nd) 85 (3rd)	92 (95:5)

[a] Reaction conditions C. Three cycles of alkyne (200 mg, 1.0 equiv) and norbornadiene (5.0 equiv), were run with $Co_2(CO)_8$ (10 mol%), 15% MEG/toluene, 80 °C under CO (1 bar);
[b] Yield after each catalytic cycle.
[c] Isolated overall yield. In parentheses, overall *exo*/*endo* ratio.

The MEG-phase containing the cobalt residues degraded during each catalytic cycle, until it became inactive (Figure 2). As far as we know, this is the first example of catalyst recycling performed homogeneously by simple liquid–liquid separation. In this regard, the amount of cobalt catalyst was reduced to 3 mol%.

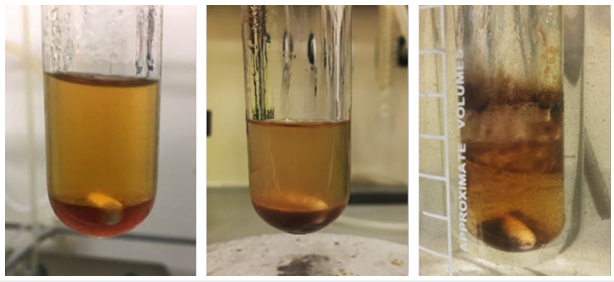
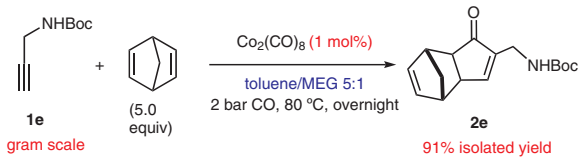


Figure 2 Catalytic intermolecular PK reaction of **1e** with NBD recycling the catalyst that remains in the MEG phase; after the 1st cycle (left), after the 2nd cycle (center), and after the 3rd cycle (right)

The process was scaled up to gram scale, and catalyst loading was reduced to 1 mol% without the need for catalyst recycling (Scheme 2). To the best of our knowledge, this is the lowest catalyst loading successfully used in the intermolecular PKR.



Scheme 2 Gram-scale intermolecular PKR using MEG/toluene as solvent with alkyne **1e** (1 g), norbornadiene (5.0 equiv), and $Co_2(CO)_8$ (1 mol%)

In summary, we have demonstrated that the mixture of 15% MEG/toluene enhances the PKR allowing the use 1 mol% of $Co_2(CO)_8$ as catalyst under low CO pressure (1 bar). When the reactions were finished, the toluene and MEG formed immiscible layers thus facilitating the workup because the toluene layer contained most of the product. Since the MEG layer contains most of the cobalt species it can be reused by adding a fresh solution of alkyne and alkyne. This new synthetic protocol for catalytic PKR is efficient and practical and has the lowest catalyst loading reported to date in cobalt-catalyzed PKR.

Reactions were carried out under CO in an oven-dried pressure tube. Anhyd toluene was obtained from commercial suppliers. 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 at 400 MHz for ^1H and at 101 MHz for ^{13}C. Chemical shifts were

referenced to internal solvent resonances and reported relative to TMS. HRMS (ESI) were recorded on a LC/MSD-TOF G1969A (Agilent Technologies). Enynes **1a**,[7c] **1b**,[7c] and **1c**[23] were prepared following the literature. Terminal alkynes **1h** and **1e** were prepared by following our previously reported procedure.[19]

Catalytic Pauson–Khand Reaction; General Procedure A (GPA)

In a flame-dried pressure tube containing a magnetic stirrer, the 1,6-enyne (100 mg, 1.0 equiv) or alkyne (100 mg, 1 equiv) was dissolved in anhyd toluene (0.3 M). $Co_2(CO)_8$ (5 mol% or 1 mol% as indicated) was added. In the case of intermolecular reactions, norbornadiene or norbornene (5.0 equiv) was also added. The pressure vessel was first purged with N_2 and then with CO (3 ×). Finally, it was charged with CO (1–2 bar) and heated to 80 °C; the mixture was stirred overnight. The CO was removed using a vacuum line and the biphasic solution was concentrated under reduced pressure. The crude was purified by column chromatography (hexanes/EtOAc mixtures of increasing polarity).

Catalytic Pauson–Khand Reaction; General Procedure B (GPB)

As for GPA but MEG (15% v/v) was added to the mixture.

Catalyst Recycling in the Catalytic Ethylene Glycol Assisted Pauson–Khand Reaction; General Procedure C (GPC)

In a flame-dried pressure tube containing a magnetic stirrer, the alkyne (200 mg, 1.0 equiv) and alkene (5.0 equiv) were dissolved in anhyd toluene (0.3 M). Then, MEG (15% v/v) and $Co_2(CO)_8$ (10 mol%) were added. The pressure vessel was first purged with N_2 and then with CO (3 ×). Finally, it was charged with 1–2 bar of CO and heated to 80 °C; the mixture was stirred overnight. The CO was removed in the vacuum line. The biphasic solution was separated and the supernatant phase was collected. The MEG-containing phase was kept in the pressure tube and alkyne (200 mg, 1.0 equiv), alkene (5.0 equiv), and freshly anhyd toluene were added. The same procedure as above was carried out and the mixture was stirred for 36 h (second cycle). For the third cycle, the methodology was repeated again and the mixture was stirred for 48–72 h. Finally, each organic phase was concentrated under reduced pressure and purified by column chromatography (hexane/EtOAc mixtures of increasing polarity).

Diethyl 6-Methyl-5-oxo-3,3a,4,5-tetrahydropentalene-2,2(1*H*)-dicarboxylate (2a)

Starting from alkyne **1a** (0.40 mmol) gave **2a** as a colorless oil; isolated yield: 91 mg (81%, GPA); 101 mg (90%, GPB).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.23 (dq, *J* = 15.8, 7.1 Hz, 4 H), 3.28–3.13 (m, 2 H), 2.97 (s, 1 H), 2.78 (dd, *J* = 12.7, 7.4 Hz, 1 H), 2.65 (ddd, *J* = 17.9, 6.3, 0.8 Hz, 1 H), 2.08 (dd, *J* = 17.9, 3.1 Hz, 1 H), 1.72 (ddd, *J* = 2.5, 1.7, 1.0 Hz, 3 H), 1.65 (t, *J* = 12.6 Hz, 1 H), 1.27 (dt, *J* = 9.8, 7.1 Hz, 6 H).

The analytical data for this compound were in excellent agreement with the reported data.[7c]

6-Methyl-2-tosyl-2,3,3a,4-tetrahydrocyclopenta[*c*]pyrrol-5(1*H*)-one (2b)

Starting from alkyne **1b** (0.38 mmol) gave **2b** as an off-white solid; isolated yield: 92 mg (83%, GPA); 101 mg (91%, GPB).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78–7.69 (m, 2 H), 7.40–7.33 (m, 2 H), 4.24 (d, *J* = 16.1 Hz, 1 H), 4.00 (dd, *J* = 6.8, 2.5 Hz, 1 H), 3.97 (d, *J* = 2.7 Hz, 1 H), 3.01 (s, 1 H), 2.65–2.54 (m, 2 H), 2.44 (s, 3 H), 2.07–1.98 (m, 1 H), 1.68 (ddd, *J* = 2.5, 1.7, 0.9 Hz, 3 H).

The analytical data for this compound were in excellent agreement with the reported data.[7c]

6-Methyl-3a,4-dihydro-1*H*-cyclopenta[*c*]furan-5(3*H*)-one (2c)

Starting from alkyne **1c** (0.91 mmol) gave **2c** as a pale orange oil; isolated yield: 59 mg (47%, GPA); 75 mg (60%, GPB).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.63–4.44 (m, 2 H), 4.31 (d, *J* = 5.0 Hz, 1 H), 3.18 (d, *J* = 3.8 Hz, 2 H), 2.71–2.62 (m, 1 H), 2.12 (dd, *J* = 18.0, 2.6 Hz, 1 H), 1.76 (s, 3 H).

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

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

Starting from alkyne **1d** (1.02 mmol) gave **2d** as an off-white solid; isolated yield: 167 mg (75%, GPA); 220 mg (99%, GPB). GPC: 1st cycle: 421 mg (95%); 2nd cycle: 400 mg (90%); 3rd cycle: 315 mg (71%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59 (dd, *J* = 2.5, 0.5 Hz, 1 H), 6.28–6.23 (m, 1 H), 6.22–6.16 (m, 1 H), 2.91 (d, *J* = 2.1 Hz, 1 H), 2.84 (ddt, *J* = 5.2, 2.3, 1.1 Hz, 1 H), 2.69 (dtt, *J* = 3.1, 1.6, 0.8 Hz, 1 H), 2.28 (ddd, *J* = 5.2, 1.6, 1.1 Hz, 1 H), 1.39–1.36 (m, 1 H), 1.20–1.16 (m, 1 H), 0.17 (s, 9 H).

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

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

Starting from alkyne **1e** (0.64 mmol) gave **2e** as a pale orange oil; isolated yield: 106 mg (60%, GPA); 164 mg (93%, GPB). GPC: 1st cycle: 349 mg (99%); 2nd cycle: 318 mg (93%); 3rd cycle: 300 mg (85%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 (s, 1 H), 6.29 (dd, *J* = 5.6, 3.1 Hz, 1 H), 6.20 (dd, *J* = 5.7, 3.0 Hz, 1 H), 5.01 (s, 1 H), 3.87 (d, *J* = 6.0 Hz, 2 H), 2.91 (s, 1 H), 2.78–2.72 (m, 1 H), 2.72–2.66 (m, 1 H), 2.31 (dt, *J* = 5.0, 1.4 Hz, 1 H), 1.43 (s, 9 H), 1.30–1.18 (m, 2 H).

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

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

Starting from alkyne **1f** (0.67 mmol) gave **2f** as a pale orange oil; isolated yield: 142 mg (79%, GPA); 167 mg (93%, GPB).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.21 (m, 5 H), 7.20–7.16 (m, 1 H), 6.25 (dd, *J* = 5.6, 3.1 Hz, 1 H), 6.18 (dd, *J* = 5.6, 3.0 Hz, 1 H), 3.73–3.56 (m, 2 H), 2.91 (d, *J* = 2.9 Hz, 1 H), 2.70–2.65 (m, 1 H), 2.58 (d, *J* = 2.9 Hz, 1 H), 2.31 (dq, *J* = 5.0, 1.2 Hz, 1 H), 1.31 (dd, *J* = 9.5, 2.1 Hz, 1 H), 1.08 (d, *J* = 9.4 Hz, 1 H).

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

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

Starting from alkyne **1g** (0.98 mmol) gave **2g** as an off-white solid; isolated yield: 194 mg (89%, GPA); 198 mg (91%, GPB).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73–7.67 (m, 3 H), 7.41–7.32 (m, 3 H), 6.34 (dd, *J* = 5.6, 3.1 Hz, 1 H), 6.26 (dd, *J* = 5.6, 2.9 Hz, 1 H), 3.03 (s, 1 H), 2.87–2.82 (m, 1 H), 2.79 (s, 1 H), 2.48 (dt, *J* = 5.1, 1.4 Hz, 1 H), 1.43 (dt, *J* = 9.4, 1.6 Hz, 1 H), 1.35 (d, *J* = 9.7 Hz, 1 H).

The analytical data for this compound were in excellent agreement with the reported data.[25]

4-Methyl-*N*-{[(4*S*,7*R*)-1-oxo-3a,4,7,7a-tetrahydro-1*H*-4,7-methanoinden-2-yl]methyl}benzenesulfonamide (2h)

Starting from alkyne **1h** (0.48 mmol) gave **2h** as a pale orange oil; isolated yield: 126 mg (80%, GPA); 134 mg (85%, GPB). GPC: 1st cycle: 312 mg (99%); 2nd cycle: 291 mg (92%); 3rd cycle: 268 mg (85%).

IR (ATR-FTIR): 3270, 2977, 2371, 2256, 1692, 1325, 1160 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.71 (dd, *J* = 8.3, 2.0 Hz, 2 H), 7.31 (d, *J* = 8.8 Hz, 1 H), 7.29–7.27 (m, 2 H), 6.26 (dd, *J* = 5.6, 3.0 Hz, 1 H), 6.17 (dd, *J* = 5.6, 3.0 Hz, 1 H), 5.10–5.02 (m, 1 H), 3.76 (d, *J* = 5.9 Hz, 2 H), 2.85–2.80 (m, 1 H), 2.65–2.62 (m, 2 H), 2.41 (s, 3 H), 2.18 (dt, *J* = 4.9, 1.4 Hz, 1 H), 1.32 (dt, *J* = 9.6, 1.5 Hz, 1 H), 1.06–0.99 (m, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 209.07, 161.35, 144.81, 143.55, 138.43, 136.99, 136.78, 129.70, 127.19, 52.83, 48.16, 43.55, 42.76, 41.13, 39.16, 21.49.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{20}NO_3S$: 330.1158; found: 330.1165.

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

Starting from alkyne **1i** (0.59 mmol) gave **2i** as a colorless oil; isolated yield: 96 mg (56%, GPA); 120 mg (70%, GPB).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.38 (q, *J* = 2.2 Hz, 1 H), 6.29 (dd, *J* = 5.6, 3.1 Hz, 1 H), 6.20 (dd, *J* = 5.6, 3.0 Hz, 1 H), 4.35 (td, *J* = 2.1, 0.9 Hz, 2 H), 2.91 (s, 1 H), 2.77 (s, 1 H), 2.71 (s, 1 H), 2.35–2.30 (m, 1 H), 1.40 (d, *J* = 9.3 Hz, 1 H), 1.27–1.24 (m, 1 H), 0.92 (s, 9 H), 0.08 (s, 6 H).

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

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

Starting from alkyne **1j** (1.51 mmol) gave **2j** as a colorless oil; isolated yield: 211 mg (75%, GPA); 203 mg (72%, GPB).

^1H NMR (400 MHz, $CDCl_3$): δ = 6.85 (d, *J* = 2.8 Hz, 1 H), 6.26 (dd, *J* = 5.6, 3.0 Hz, 1 H), 6.19 (dd, *J* = 5.6, 3.0 Hz, 1 H), 2.90 (p, *J* = 1.5 Hz, 1 H), 2.69–2.57 (m, 2 H), 2.29 (dt, *J* = 5.0, 1.4 Hz, 1 H), 1.56 (dddt, *J* = 9.4, 8.5, 5.2, 1.0 Hz, 1 H), 1.35 (dp, *J* = 9.2, 1.6 Hz, 1 H), 1.19 (dt, *J* = 9.3, 1.6 Hz, 1 H), 0.86–0.77 (m, 2 H), 0.60 (ddt, *J* = 6.6, 3.8, 1.3 Hz, 2 H).

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

(4*R*,7*S*)-2-(Trimethylsilyl)-3a,4,5,6,7,7a-hexahydro-1*H*-4,7-methanoinden-1-one (3)

Starting from alkyne **1d** (1.02 mmol) gave **3** as a colorless oil; isolated yield: 211 mg (94%, GPA); 220 mg (98%, GPB).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.56 (d, *J* = 2.6 Hz, 1 H), 2.65 (dd, *J* = 5.4, 2.5 Hz, 1 H), 2.38 (s, 1 H), 2.17 (d, *J* = 4.2 Hz, 1 H), 2.12 (d, *J* = 5.3 Hz, 1 H), 1.70–1.54 (m, 2 H), 1.32–1.20 (m, 2 H), 0.93–0.91 (m, 2 H), 0.17 (s, 9 H).

The analytical data for this compound were in excellent agreement with the reported data.[26]

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