

Rhodium(I)-Catalyzed Intramolecular Cyclohexadienyl Pauson–Khand Reaction: Facile Approach to Tricarbobicycles

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The rhodium-catalyzed Pauson–Khand reaction (PKR) of cyclohexa-1,3-dienes containing two methylene carbons and an alkyne in a chain produced regular PKR products. Cyclohexadienynes bearing three methylene units and an aromatic ring at the alkyne afforded regular PKR products and angularly fused tricyclic compounds, which were derived from diene migration followed by the PKR process.

Introduction

The cobalt-mediated formal $[2 + 2 + 1]$ cycloaddition reaction of an alkyne, an alkene, and carbon monoxide moieties, the Pauson–Khand reaction (PKR hereafter), is a powerful tool to construct cyclopentenone derivatives¹ and is being widely used in natural product synthesis.² Particularly, the possibility of achieving complex molecules containing a cyclopentenone moiety in a stereoselective fashion and in a single step has made this reaction especially attractive. Besides cobalt,³ other transition metals, such as rhodium,⁴ ruthenium,⁵ and iridium,⁶ have been shown to catalyze the reaction. Recently, allenes have been used in place of olefins in the Pauson–Khand-type $[2 + 2 + 1]$ cyclization.⁷ This allenic type PKR has enhanced the great synthetic

utility toward the synthesis of complex organic molecules.⁸ In the past few years, we have developed an easy synthetic route to cyclohexa-1,3-diene derivatives containing a functional group at the C-5 position. To continue our effort on these substrates, we have focused on the cyclohexadienyl version of the PKR in our laboratories.⁹ In this contribution, we report the PKR of cyclohexadienynes, which proceeds smoothly to afford tricarbobicycles. For cyclohexadienynes tethering three methylene units and an aromatic ring at the alkyne, the cycloadditions generate the regular PKR products and angularly fused tricyclic compounds, which are derived from diene migration followed by the PKR process.

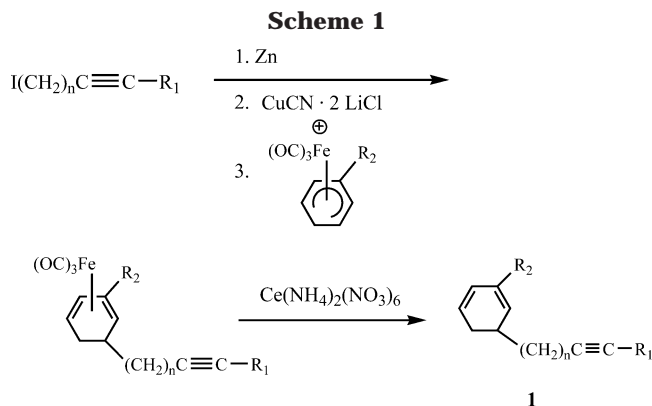
Results and Discussion

The starting alkynes **1a–i** were prepared from addition of the corresponding alkynylzinc–copper reagents to the (η^5 -cyclohexadienyl)tricarbonyliron cation salt in THF according to literature procedures.¹⁰ Decomplexation of the resulting complexes with cerium ammonium nitrate (CAN) in acetone at 0 °C afforded the starting substrates **1a–i** in good yields (Scheme 1).¹¹ Aromatic substrates **2a,b** were synthesized in a similar fashion starting from addition of the corresponding aromatic alkenyllithium–copper reagents to the (η^5 -cyclohexadienyl)tricarbonyliron cation salt in THF (Scheme 2).

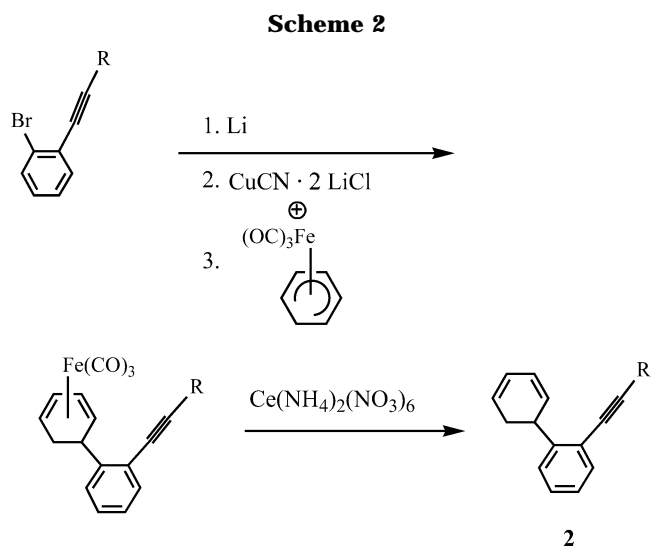
Under our optimized reaction conditions, intramolecular PKR of cyclohexadienyne derivatives **1a–i** and **2a,b** using $[\text{RhCl}(\text{CO})_2]_2$ (1.0 mol %) under an atmo-

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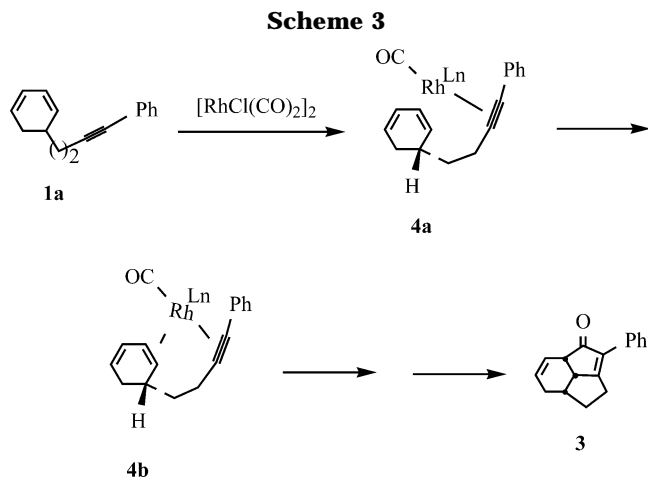


- a : R₁ = Ph, R₂ = H, n = 2
 b : R₁ = *p*-Tol, R₂ = H, n = 2
 c : R₁ = Ph, R₂ = SiMe₂Ph, n = 2
 d : R₁ = SiMe₃, R₂ = H, n = 2
 e : R₁ = SiMe₃, R₂ = H, n = 3
 f : R₁ = Ph, R₂ = SiMe₂Ph, n = 3
 g : R₁ = Ph, R₂ = H, n = 3
 h : R₁ = *p*-Tol, R₂ = H, n = 3
 i : R₁ = Np, R₂ = H, n = 3



- a : R = Ph
 b : R = SiMe₃

spheric pressure of CO in dibutyl ether with substrate concentrations at 0.1 M were investigated, and the results are listed in Table 1. Refluxing a dibutyl ether solution of cyclohexadienyne **1a** (entry 1, Table 1) and 1.0 mol % of [RhCl(CO)₂]₂ under 1.0 atm of CO for 6 h generated the tricyclo[5.3.1.0^{4,11}]undecadienone derivative **3** in 93% yield after flash column chromatography. NOE experiments provided the initial evidence for support of all syn relationships between hydrogen atoms at C(a), C(b), and C(c) of **3**. Further proof of the structure of **3** was accomplished by X-ray diffraction analysis. It is important to note that three new contiguous stereo-



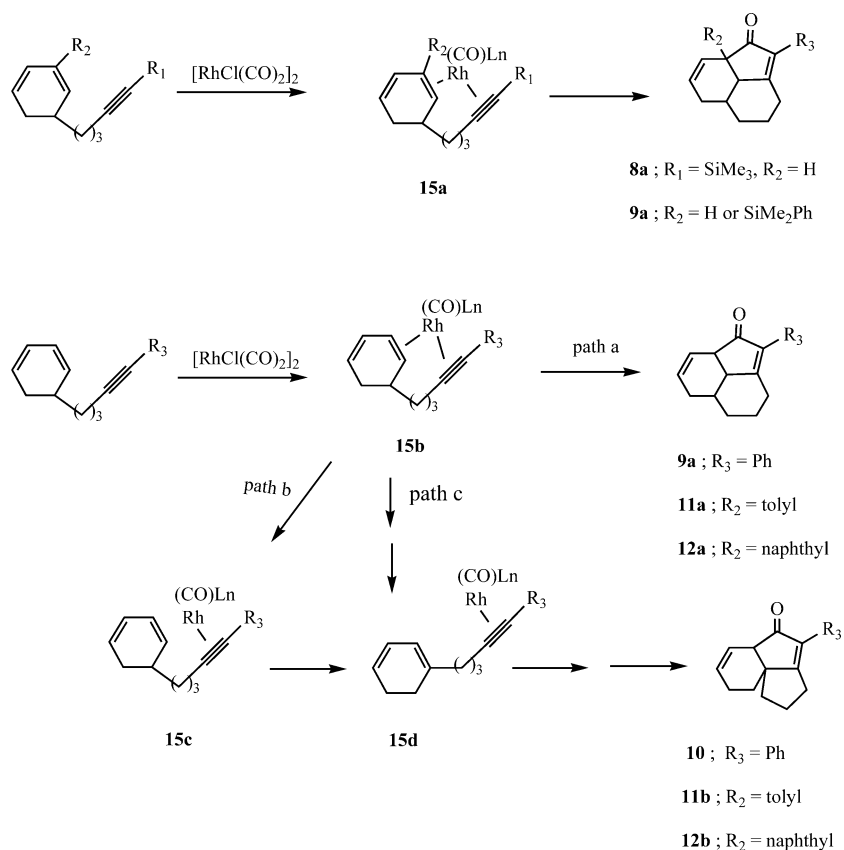
genic centers of tricyclic compound **3** are created with extreme diastereoselectivity; however, only the single diastereomer shown was isolated. This stereochemical outcome can be rationalized in the framework of the suggested rhodium–alkyne intermediate **4a** (Scheme 3), if one assumed that the intermediate **4b** arising from the attack of the rhodium–alkyne species at the β-face of the olefin would lead to **3**, which has all syn relationships among the three adjacent protons. However, treatment of substrate **1a** using the reported protocol⁹ for acyclic dieneynes ([RhCl(CO)(PPh₃)₂] (1.0 mol %), AgSbF₆ (1 mol %), CO (1.0 atm), 1,2-dichloroethane, room temperature, 3 days) produced **3** in 38% yield after separation of the crude mixture on silica gel. Substrates with two methylene units and a *p*-tolyl group at the alkyne, for example, compound **1b**, gave the PKR product **5**¹² (entry 2, Table 1) in 57% yield. Substrate **1c** with a phenyldimethylsilyl group at the 3-position of the cyclohexadiene ring afforded tricyclic compound **6** (77%, entry 3, Table 1) and a trace of the desilylation product, which is identical with compound **3**. With a trimethylsilyl group at the alkyne, substrate **1d** (entry 4, Table 1) also produced the regular PKR products **7a** (52%) and the desilylation product **7b** (13%). Similarly, cyclohexadienyne **1e** (entry 5, Table 1), with three methylene units and a silyl group at the terminal alkyne, gave tricyclo[6.3.1.0^{4,12}]dodecadienone derivative **8a** (63%) and the desilylation product **8b** (20%). Also, substrate **1f** (entry 6, Table 1) afforded the PKR product **9a** (48%) and the desilylation product **9b**¹² (23%). To understand the desilylation process, compound **7a** was treated with [RhCl(CO)₂]₂ (1.0 mol %) under an atmospheric pressure of CO in dibutyl ether. The reaction mixture was stirred at reflux for 24 h. TLC clearly showed that the crude mixture contained both **7a** and **7b**. Also, the ratio of **7a** and **7b** was determined to be 1:2 by ¹H NMR spectroscopy. Thus, it is reasonable to state that the desilylation may occur by attack of a chloride anion at the silicon atom under the harsh reaction conditions (145 °C, 24 h). Interestingly, cycloaddition of substrate **1g** (entry 7, Table 1), bearing three methylene units and a phenyl group at the alkyne, produced the usual PKR product **9b** (57%) and the angularly fused tricyclic compound **10** (34%), which contains a quaternary carbon center. Under the same

(12) The structure of this compound was further proved by X-ray diffraction analysis.

Table 1. Catalytic Intramolecular Pauson–Khand Reaction Cyclization of Cyclic Dienes Containing a Tethered Alkyne Using $[\text{RhCl}(\text{CO})_2]_2$ (1.0 mol %) and CO (1.0 atm) in Refluxing Dibutyl Ether

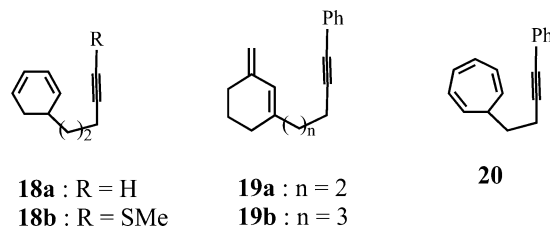
entry	Dienyne	time (h)	Products	Yield
1		6		93%
2		12		57%
3		12	 	77%
4		12	 4 : 1	65%
5		10	 3 : 1	83%
6		12	 2 : 1	71%
7		10	 3 : 2	91%
8		10	 1 : 1	57%
9		10	 1 : 2	70%
10		10		95%
11		10		35%
12		16		14%

Scheme 4



reaction conditions, substrates **1h** (entry 8, Table 1) and **1i** (entry 9, Table 1) produced both the regular cycloadducts **11a**¹² (29%, from **1h**) and **12a** (23%, from **1i**) and angularly fused tricyclic compounds **11b** (28%, from **1h**) and **12b** (47%, from **1i**), respectively. Cyclohexadienyne **2a** and **2b**, which contain a benzene tether, also gave the PKR products **13**¹² (93% from **2a**; entry 10, Table 1) and **14** (35% from **2b**; entry 11, Table 1). Several entries in Table 1 deserve special mention. Reactions of substrates **1a–d**, with a two-methylene tether, proceeded smoothly to give only the regular PKR products in each case. However, substrates containing three methylene units underwent different reaction paths, depending on the substituents at the dienyne. Substrates with a silyl group at the alkyne (for example, **1e**) or at the C-3 position of the cyclohexadiene ring (for example, **1f**) provided only PKR products. Substrates **1g–i**, bearing an aryl, tolyl, or naphthyl group at the alkyne, gave both regular PKR products and angularly fused tricyclics. The difference is explained in Scheme 4. The presence of the silyl group in the postulated intermediate **15a** may facilitate the cycloaddition to afford PKR products as the major products (path a). With an aromatic group at the alkyne, the postulated intermediate **15b** may require higher activation energy to give a seven-membered-ring transition state. Thus, detachment of the alkene ligand from the metal center occurred to give **15c** (path b). Intermediate **15c** could undergo double-bond migration to generate the C-1-substituted dienyne **15d**. Alternatively, intermediate **15b** could undergo β -hydride elimination/re-addition to give **15d** (path c). Intermediate **15d** led to the angularly fused tricyclic compounds **10b**, **11b**, and **11c** after the PKR process.

This chemistry can be extended to a seven-membered-ring substrate. Thus, cycloheptadienyne derivative **16** underwent PKR using the same reaction protocol to produce **17** in a 14% yield (entry 12, Table 1). However, it must be mentioned that terminal dienyne **18a**, (methylthio)alkyne **18b**,¹³ or alkylidene cyclohexene derivatives **19a,b** failed to produce any PKR product.



Moreover, cycloheptatrienyne substrate **20** gave no conversion on reflux in dibutyl ether for 96 h.

The reactions outlined herein demonstrate that $[\text{RhCl}(\text{CO})_2]_2$ is an effective catalyst for PKR of cyclic dienyne. The ability to achieve excellent stereocontrol of three stereogenic centers of fairly complex tricyclic skeletons in a simple reaction may have further applications.

Experimental Section

General Considerations. All reactions were run under a nitrogen atmosphere in oven-dried glassware unless otherwise

(13) Although (methylthio)alkynes have been shown to be superb participants in the $\text{Co}_2(\text{CO})_8$ -catalyzed Pauson–Khand reaction, the $[\text{RhCl}(\text{CO})_2]_2$ complex is ineffective toward **18b**. Pagenkopf, B. L.; Belanger, D. B.; O'Mahony, D. J. R.; Livinghouse, T. *Synthesis* **2000**, 7, 1009.

indicated. Anhydrous solvents or reaction mixtures were transferred via an oven-dried syringe or cannula. Dibutyl ether was distilled under nitrogen over CaH₂. Flash column chromatography, following the method of Still, was carried out with E. Merck silica gel (Kieselgel 60, 230–400 mesh) using the indicated solvents.¹⁴ ¹H nuclear magnetic resonance (NMR) spectra were obtained with Bruker-AV 400 (400 MHz), Bruker-AV 500 (500 MHz), and Varian G-200 (200 MHz) spectrometers. Chemical shifts are reported in parts per million with either tetramethylsilane (0.00 ppm) or CHCl₃ (7.26 ppm) as internal standard. ¹³C NMR spectra were recorded with Bruker-AV 400 (100 MHz), Bruker-AV 500 (125 MHz), and Varian G-200 (50 MHz) spectrometers with CDCl₃ (77.0 ppm) as the internal standard. Infrared (IR) spectra were recorded with a JASCO IR-700 spectrometer. Mass spectra were acquired on a JEOL JMS-D 100 spectrometer at an ionization potential of 70 eV and are reported as mass/charge (*m/e*) with percent relative abundance. High-resolution mass spectra (HRMS) were obtained with an AEI MS-9 double-focusing mass spectrometer and a JEOL JMS-HX 110 spectrometer at the Department of Chemistry, Central Instrument Center, Taichung, Taiwan.

General Procedure for the Synthesis of Starting Cyclohexadienyne Derivatives 1a–i. Zinc particles (14–50 mesh, 9.6 g, 0.15 mol) were placed in a dried three-necked round-bottom flask equipped with a dropping funnel, a thermometer, and a nitrogen outlet. To the flask were added 15.0 mL of THF and 1.0 mL of 1,2-dibromoethane. The reaction mixture was heated with a heat gun for 30 s and cooled to room temperature. The process was repeated two times before 1.0 mL of chlorotrimethylsilane was added via syringe. The mixture was stirred for 30 min before a THF (20 mL) solution of I(CH₂)₂CCPh (6.5 g, 25.4 mmol) was added via the dropping funnel. Normally, the zinc reagent was formed after stirring at 40–50 °C for 6 h. Copper cyanide (6.7 g, 75 mmol) was added to dried LiCl (150 °C, 3 h under vacuum, 6.30 g, 0.150 mol) in a Schlenk flask under nitrogen. The reaction mixture was cooled to 0 °C before 50 mL of THF was added via syringe. The reaction mixture was stirred at 25 °C until the solid was dissolved. The above solution was cooled to –78 °C, and the freshly prepared IZn(CH₂)₂CCPh was added dropwise to the reaction mixture. The resulting light green solution was stirred at 0 °C for 30 min, and the zinc–copper reagent IZnCu(CH₂)₂CCPh was ready to use. A solution of the zinc–copper reagent was added via cannula to a stirred suspension of (η^5 -cyclohexadienyl)Fe(CO)₃ cation salt (5.2 g, 16.9 mmol) in 5 mL of THF at 5 °C under nitrogen. A homogeneous solution was obtained after the reaction mixture was stirred at 30 °C for 2 h. The reaction mixture was then quenched with saturated aqueous ammonium chloride solution at 0 °C and was diluted with 100 mL of 50% ethyl acetate/hexanes. The resultant solution was washed with water (100 mL \times 3) and brine (100 mL \times 3), dried over anhydrous magnesium sulfate (10 g), and concentrated to give the crude mixture. To the crude iron complex (3.8 g, 10.9 mmol) in 100 mL of acetone at 0 °C under nitrogen was added cerium ammonium nitrate (16.8 g, 30.6 mmol) in three portions. The reaction mixture was stirred at 30 °C for 1 h. The reaction mixture was then quenched with saturated aqueous sodium bicarbonate solution at 0 °C and was diluted with 100 mL of ether. The resultant solution was washed with water (100 mL \times 3) and brine (100 mL \times 3), dried over anhydrous magnesium sulfate (10 g), and concentrated to give the crude mixture.

General Procedure for [RhCl(CO)₂]₂-Catalyzed Intramolecular Cyclohexadienyl Pauson–Khand Reactions. To an oven-dried two-necked round-bottom flask equipped with a stirrer bar and a condenser and capped with rubber septa was added [RhCl(CO)₂]₂ (3.9 mg, 0.01 mmol) and 4 mL of dibutyl ether. The apparatus was evacuated (oil pump) and

filled with CO three times. To the reaction mixture was then added cyclohexadienyne **1a** (0.208 g, 1.0 mmol) in 6.0 mL of dibutyl ether. The resulting mixture was heated at reflux under a blanket of CO, vented through a bubbler. The reaction was monitored by TLC. The reaction mixture was cooled to room temperature after no **1a** was detected. The mixture was filtered through a bed of Celite and concentrated to give the crude mixture.

4-(Cyclohexa-1,3-dien-5-yl)-1-phenylbutyne (1a). The crude mixture obtained from oxidation (CAN in acetone) of the corresponding iron complex (3.8 g, 10.9 mmol) was purified by flash-column chromatography (silica gel, hexanes) to give **1a** (1.71 g, 8.22 mmol, 75%) as a colorless liquid: IR (CH₂Cl₂) 3503, 3044, 3060, 2301, 2122, 1598, 1518, 1419, 1258, 1252, 1017 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 7.38 (m, 2 H), 7.29 (m, 3 H), 5.88 (m, 2 H), 5.78 (m, 2 H), 2.46 (m, 4 H), 2.02 (m, 1 H), 1.71 (m, 2 H); ¹³C NMR (50 MHz, CDCl₃) δ 132.44, 131.77, 128.73, 128.23, 125.13, 123.58, 123.25, 121.81, 91.31, 81.23, 34.47, 34.19, 30.25, 17.31; MS (70 eV) *m/e* 208 (M⁺, 17), 180 (19), 129 (17), 128 (19), 117 (100), 115 (47), 91.0 (40), 79 (17), 77 (31); HRMS EI *m/e* calcd for C₁₆H₁₆ 208.1252, found 208.1250.

4-(Cyclohexa-1,3-dien-5-yl)-1-*p*-tolylbutyne (1b). The crude mixture obtained from oxidation (CAN in acetone) of the corresponding iron complex (3.74 g, 10.3 mmol) was purified by flash-column chromatography (silica gel, hexanes) to give **1b** (1.79 g, 8.06 mmol, 78%) as a colorless liquid: IR (CH₂Cl₂) 3601, 3063, 3044, 2309, 2302, 1606, 1510, 1449, 1437, 1374, 1267, 1265, 1022 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 7.30 (m, 2 H), 7.06 (m, 2 H), 5.87 (m, 2 H), 5.77 (m, 2 H), 2.44 (m, 4 H), 2.32 (s, 3 H), 2.01 (m, 1 H), 1.76 (m, 2 H); ¹³C NMR (50 MHz, CDCl₃) δ 137.48, 131.41, 131.37, 130.56, 128.93, 125.69, 124.05, 120.86, 89.02, 80.75, 33.12, 31.71, 28.07, 21.26, 16.77; MS (70 eV) *m/e* 222 (M⁺, 23), 207 (25), 194 (16), 179 (18), 131 (100), 129 (90), 128 (42), 115 (33), 91 (52); HRMS EI *m/e* calcd for C₁₇H₁₈ 222.1409, found 222.1412.

4-(2-(Dimethylphenylsilyl)cyclohexa-1,3-dien-5-yl)-1-phenylbutyne (1c). The crude mixture obtained from oxidation (CAN in acetone) of the corresponding iron complex (3.90 g, 1.87 mmol) was purified by flash-column chromatography (silica gel, hexanes) to give **1c** (0.44 g, 1.28 mmol, 68%) as a colorless liquid: IR (CH₂Cl₂) 3503, 3057, 2927, 2364, 1696, 1653, 1419 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.50 (m, 2 H), 7.37 (m, 5 H), 7.26 (m, 3 H), 6.06 (d, *J* = 3.5 Hz), 5.97 (d, *J* = 9.4 Hz, 1 H), 5.78 (m, 1 H), 2.45 (m, 3 H), 2.31 (m, 1 H), 1.97 (m, 1 H), 1.79 (m, 1 H), 1.68 (m, 1 H), 0.35 (s, 6 H); ¹³C NMR (100 MHz, CDCl₃) δ 141.05, 138.26, 134.01, 133.82, 131.54, 128.94, 128.17, 127.73, 127.53, 126.21, 124.69, 123.91, 89.91, 80.78, 33.07, 32.80, 27.78, 16.99, –3.28; MS (70 eV) *m/e* 342 (M⁺, 16), 225 (15), 206 (14), 167 (10), 149 (18), 136 (11), 135 (100), 117 (10); HRMS (EI) *m/e* calcd for C₂₄H₂₆Si 342.1804, found 342.1803.

4-(Cyclohexa-1,3-dien-5-yl)-1-trimethylbutyne (1d). The crude mixture obtained from oxidation (CAN in acetone) of the corresponding iron complex (1.10 g, 3.19 mmol) was purified by flash-column chromatography (silica gel, hexanes) to give **1d** (0.52 g, 2.55 mmol, 80%) as a colorless liquid: IR (CH₂Cl₂) 3425, 3356, 3045, 2309, 2170, 1415, 1272, 1016, 1004 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 5.84 (m, 2 H), 5.70 (m, 2 H), 2.40 (m, 1 H), 2.25 (m, 3 H), 1.96 (m, 1 H), 1.57 (m, 2 H), 0.13 (s, 9 H); ¹³C NMR (50 MHz, CDCl₃) δ 130.44, 125.61, 124.05, 124.02, 107.15, 84.48, 32.97, 31.73, 28.02, 17.25, 0.02.

5-(Cyclohexa-1,3-dien-5-yl)-1-trimethylpentyne (1e). The crude mixture obtained from oxidation (CAN in acetone) of the corresponding iron complex (1.73 g, 4.83 mmol) was purified by flash-column chromatography (silica gel, hexanes) to give **1e** (0.88 g, 4.04 mmol, 85%) as a colorless liquid: ¹H NMR (200 MHz, CDCl₃) δ 5.83 (m, 2 H), 5.68 (m, 2 H), 2.20 (m, 4 H), 1.94 (m, 1 H), 1.51 (m, 4 H), 0.13 (s, 9 H); ¹³C NMR (50 MHz, CDCl₃) δ 131.17, 125.79, 124.03, 123.78, 107.30, 84.43, 33.55, 32.30, 28.48, 25.90, 19.88, 0.02.

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5-(2-(Dimethylphenylsilyl)cyclohexa-1,3-dien-5-yl)-1-phenylpentene (1f). The crude mixture obtained from oxidation (CAN in acetone) of the corresponding iron complex (1.09 g, 2.20 mmol) was purified by flash-column chromatography (silica gel, hexanes) to give **1f** (0.61 g, 1.72 mmol, 78%) as a colorless liquid: IR (CH₂Cl₂) 3443, 3058, 2984, 2928, 1653, 1374, 1299 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.50 (m, 2 H), 7.39 (m, 2 H), 7.34 (m, 3 H), 7.27 (m, 3 H), 6.04 (d, *J* = 3.3 Hz, 1 H), 5.96 (d, *J* = 9.9 Hz, 1 H), 5.78 (m, 1 H), 2.41 (t, *J* = 6.8 Hz, 2 H), 2.27 (m, 2 H), 1.94 (m, 1 H), 1.65 (m, 3 H), 1.53 (m, 1 H), 0.35 (s, 6 H); ¹³C NMR (100 MHz, CDCl₃) δ 141.85, 138.37, 134.01, 133.44, 131.54, 128.90, 128.18, 127.71, 127.50, 126.21, 124.93, 123.99, 90.14, 80.77, 33.68, 33.46, 28.25, 26.26, 19.61, -3.28; MS (70 eV) *m/e* 356 (M⁺, 6), 339 (13), 261 (18), 165 (11), 136 (16), 135 (100), 121 (20), 105 (13), 91 (16), 71 (14); HRMS (EI) *m/e* calcd for C₂₅H₂₈Si 356.1960, found 356.1948.

5-(Cyclohexa-1,3-dien-5-yl)-1-phenylpentene (1g). The crude mixture obtained from oxidation (CAN in acetone) of the corresponding iron complex (2.5 g, 6.9 mmol) was purified by flash-column chromatography (silica gel, hexanes) to give **1g** (1.00 g, 4.50 mmol, 67%) as a colorless liquid: IR (CH₂Cl₂) 3506, 346, 3053, 3046, 2303, 2202, 1599, 1415, 1419, 1287, 1017, 1014 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 7.4 (m, 2 H), 7.29 (m, 3 H), 5.86 (m, 2 H), 5.73 (m, 2 H), 2.41 (m, 4 H), 2.08 (m, 2 H), 1.64 (m, 5 H); ¹³C NMR (50 MHz, CDCl₃) δ 131.59, 131.29, 128.24, 127.55, 125.96, 124.06, 123.82, 90.14, 80.76, 33.71, 32.44, 28.56, 26.05, 19.50; MS (70 eV) *m/e* 205 (14), 191 (11), 178 (18), 143 (45), 142 (28), 141 (20), 129 (34), 128 (58), 115 (100), 91 (18); HRMS (EI) *m/e* calcd for C₁₇H₁₈ 222.1409, found 222.1338.

5-(Cyclohexa-1,3-dien-5-yl)-1-*p*-tolylpentene (1h). The crude mixture obtained from oxidation (CAN in acetone) of the corresponding iron complex (1.34 g, 3.56 mmol) was purified by flash-column chromatography (silica gel, hexanes) to give **1h** (0.60 g, 2.54 mmol, 71%) as a colorless liquid: IR (CH₂Cl₂) 3497, 3066, 2936, 2322, 2312, 1509, 1434, 1427, 1277, 1262, 1246, 1014 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 7.30 (m, 2 H), 7.10 (m, 2 H), 5.86 (m, 2 H), 5.74 (m, 2 H), 2.40 (m, 4 H), 2.33 (s, 3 H), 2.21 (m, 1 H), 1.55 (m, 4 H); ¹³C NMR (50 MHz, CDCl₃) δ 137.52, 131.45, 131.33, 128.98, 125.98, 124.06, 123.81, 120.94, 89.29, 80.76, 33.73, 32.44, 28.56, 26.11, 21.32, 19.51; MS (70 eV) *m/e* 236 (M⁺, 21), 221 (20), 194 (49), 179 (36), 141 (32), 131 (66), 129 (100), 128 (74), 115 (43), 79 (47); HRMS (EI) *m/e* calcd for C₁₈H₂₀ 236.1565, found 236.1559.

5-(Cyclohexa-1,3-dien-5-yl)-1-naphthylpentene (1i). The crude mixture obtained from oxidation (CAN in acetone) of the corresponding iron complex (1.96 g, 4.76 mmol) was purified by flash-column chromatography (silica gel, hexanes) to give **1i** (0.97 g, 3.57 mmol, 75%) as a colorless liquid: IR (CH₂Cl₂) 3603, 3508, 3042, 2988, 2359, 2304, 1431, 1273, 1245, 1017 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 7.51 (m, 7 H), 5.86 (m, 2 H), 5.75 (m, 2 H), 2.55 (t, 2 H), 2.34 (m, 2 H), 2.2 (m, 1 H), 1.71 (m, 4 H); ¹³C NMR (50 MHz, CDCl₃) δ 133.52, 133.21, 131.21, 130.01, 128.21, 127.93, 126.48, 126.29, 126.22, 125.92, 125.23, 124.06, 123.84, 121.73, 95.19, 78.79, 33.76, 32.41, 28.54, 26.17, 19.80; MS (70 eV) *m/e* 228 (31), 193 (31), 178 (39), 166 (24), 165 (100), 164 (30), 163 (31), 152 (20), 139 (11); HRMS (EI) *m/e* calcd for C₂₁H₂₀ 272.1565, found 271.1443.

1-(Cyclohexa-1,3-dien-5-yl)-2-phenylethynylbenzene (2a). The crude mixture obtained from oxidation (CAN in acetone) of the corresponding iron complex (0.80 g, 2.00 mmol) was purified by flash-column chromatography (silica gel, hexanes) to give **2a** (0.41 g, 8.22 mmol, 75%) as a colorless liquid: IR (CH₂Cl₂) 3294, 3051, 2868, 2820, 2154, 2037, 1715, 1650, 1558, 1247, 1224, 1092 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 7.41 (m, 9 H), 5.94 (m, 4 H), 4.37 (tt, 1 H), 2.75 (m, 1 H), 2.51 (m, 1 H); ¹³C NMR (50 MHz, CDCl₃) δ 147.00, 132.33, 131.45, 129.48, 128.56, 128.32, 128.22, 127.51, 126.19, 125.49, 124.75, 123.85, 123.41, 122.08, 93.60, 87.92, 77.62, 76.99, 76.35, 37.52, 30.29.

1-(Cyclohexa-1,3-dien-5-yl)-2-(2-(trimethylsilyl)ethynyl)benzene (2b). The crude mixture obtained from oxidation (CAN in acetone) of the corresponding iron complex (3.8 g, 10.9 mmol) was purified by flash-column chromatography (silica gel, hexanes) to give **1a** (1.71 g, 8.22 mmol, 75%) as a colorless liquid: IR (CH₂Cl₂) 3294, 3051, 2961, 2356, 2153, 2037, 1558, 1247, 1224, 1092 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 7.32 (m, 4 H), 6.00 (m, 4 H), 4.25 (m, 1 H), 2.70 (m, 1 H), 2.40 (m, 1 H), 1.54 (m, 1 H), 0.33 (s, 9 H); ¹³C NMR (50 MHz, CDCl₃) δ 147.46, 132.55, 129.33, 128.75, 127.37, 126.04, 125.45, 124.82, 123.84, 122.02, 103.67, 98.65, 37.26, 30.09, -0.18; MS (70 eV) *m/e* 252 (M⁺, 10), 237 (9), 178 (100), 165 (13), 88 (19), 73 (44), 61 (53); HRMS (EI) *m/e* calcd for C₁₇H₂₀Si 252.1334, found 252.1342.

4-(Cyclohepta-1,3-dien-5-yl)-1-phenylbutyne (16). The crude mixture obtained from oxidation (CAN in acetone) of the corresponding iron complex (1.6 g, 4.4 mmol) was purified by flash-column chromatography (silica gel, hexanes) to give **16** (0.76 g, 3.42 mmol, 77%) as a colorless liquid: IR (CH₂Cl₂) 3521, 3047, 2987, 2396, 2305, 1598, 1518, 1490, 1275, 1263, 1069 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 7.38 (m, 2 H), 7.25 (m, 3 H), 5.77 (m, 4 H), 2.62 (m, 1 H), 2.49 (m, 2 H), 2.34 (m, 2 H), 1.80 (m, 4 H); ¹³C NMR (50 MHz, CDCl₃) δ 137.31, 134.21, 131.59, 128.24, 127.58, 124.84, 124.41, 123.99, 89.93, 80.85, 39.98, 34.31, 30.09, 28.92, 16.93.

(1S*,7R*,11R*)-2-Oxo-3-phenyltricyclo[5.3.1.0^{4,11}]undeca-3,9-diene (3). The crude mixture obtained from the intramolecular PKR reaction of **1a** (0.22 g, 1.0 mmol) was purified by flash-column chromatography (silica gel, gradient elution 3–30% ethyl acetate in hexanes) to give **3** (0.22 g, 0.93 mmol, 93%) as a white solid: mp 136–137 °C; IR (CH₂Cl₂) 3623, 3461, 3059, 2944, 2837, 2360, 2340, 1695, 1276, 1018 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.57 (m, 2 H), 7.35 (m, 2 H), 7.25 (m, 1 H), 5.77 (m, 1 H), 5.69 (m, 1 H), 3.33 (m, 1 H), 3.16 (t, *J* = 6.4 Hz, 1 H), 2.88 (dd, *J* = 19.2, 11.2 Hz, 1 H), 2.62 (m, 1 H), 2.21 (m, 1 H), 2.20 (m, 1 H), 1.94 (dt, *J* = 16.8, 6.4 Hz, 1 H), 1.75 (m, 1 H), 1.30 (m, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 206.76, 182.01, 133.96, 131.62, 128.05, 128.03, 127.49, 127.48, 123.01, 48.14, 48.07, 31.21, 31.06, 25.73, 25.11; MS (70 eV) *m/e* 236 (M⁺, 100), 207 (24), 179 (27), 165(25), 117 (55), 115 (53), 105 (70), 91 (57), 77 (46), 57 (27); HRMS (EI) *m/e* calcd for C₁₇H₁₆O (M⁺) 236.1201, found 236.1201. Anal. Calcd for C₁₇H₁₆O: C, 86.40; H, 6.82. Found: C, 86.13; H, 6.74. Crystals suitable for X-ray diffraction were grown from CH₂Cl₂ and hexanes.

(1S*,7R*,11R*)-2-Oxo-3-*p*-tolyltricyclo[5.3.1.0^{4,11}]undeca-3,9-diene (5). The crude mixture obtained from the intramolecular PKR reaction of **1b** (0.22 g, 1.0 mmol) was purified by flash-column chromatography (silica gel, gradient elution 3–30% ethyl acetate in hexanes) to give **5** (0.14 g, 0.57 mmol, 57%) as a white solid: mp 103–105 °C; IR (CH₂Cl₂) 3674, 3624, 3032, 2943, 2881, 2360, 2340, 1733, 1699, 1513, 1345, 1018 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.47 (d, *J* = 8.15 Hz, 2 H), 7.20 (d, *J* = 8.00 Hz, 2 H), 5.78 (m, 1 H), 5.71 (m, 1 H), 3.37 (t, *J* = 5.5 Hz, 1 H), 3.21 (t, *J* = 6.2 Hz, 1 H), 2.89 (dd, *J* = 8.25, 11.0 Hz, 1 H), 2.68 (m, 1 H), 2.35 (s, 3 H), 2.27 (m, 1 H), 2.23 (m, 1 H), 1.99 (dt, *J* = 16.9, 6.4 Hz, 1 H), 1.81 (m, 1 H), 1.37 (m, 1 H); ¹³C NMR (125 MHz, CDCl₃) δ 206.20, 180.25, 136.54, 133.15, 127.96, 127.89, 127.12, 126.61, 122.24, 47.30, 47.20, 30.41, 30.29, 24.88, 24.29, 20.27; MS (70 eV) *m/e* 250 (M⁺, 100), 207 (17), 165 (15), 131 (33), 129 (26), 119 (26), 115 (24), 91 (31), 77 (18); HRMS (EI) *m/e* calcd for C₁₈H₁₈O 250.1358, found 250.1358. Crystals suitable for X-ray diffraction were grown from CH₂Cl₂ and hexanes.

(1R*,7R*,11S*)-1-(Dimethylphenylsilyl)-2-oxo-3-phenyltricyclo[5.3.1.0^{4,11}]undeca-3,9-diene (6). The crude mixture obtained from the intramolecular PKR reaction of **1c** (0.437 g, 1.3 mmol) was purified by flash-column chromatography (silica gel, gradient elution 5–30% ethyl acetate in hexanes) to give **6** (0.373 g, 1.00 mmol, 77%) as a white solid and **3** (trace). Compound **6**: mp 95–96 °C; IR (CH₂Cl₂) 3624, 2927, 2853, 2041, 1967, 1699, 1674, 1465 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.57 (m, 4 H), 7.34 (m, 5 H), 7.27 (m, 1 H),

5.80 (d, $J = 9.8$ Hz, 1 H), 5.65 (m, 1 H), 2.98 (dd, $J = 6.8, 1.2$ Hz, 1 H), 2.84 (dd, $J = 19.2, 10.8$ Hz, 1 H), 2.58 (m, 1 H), 2.17 (m, 1 H), 1.91 (m, 1 H), 1.90 (m, 1 H), 1.74 (ddd, $J = 13.1, 8.5, 6.0$ Hz, 1 H), 1.34 (m, 1 H), 0.46 (d, $J = 9.6, 6$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 208.50, 181.24, 136.22, 134.46, 134.05, 132.14, 129.27, 128.25, 128.15, 127.63, 127.50, 126.26, 125.44, 51.47, 50.67, 31.95, 31.62, 25.54, 25.31, -4.94, -5.51; MS (70 eV) m/e 370 (M^+ , 100), 366 (19), 342 (27), 293 (14), 291 (20), 277 (13), 268 (11), 264 (19), 135 (41); HRMS (EI) m/e calcd for $\text{C}_{25}\text{H}_{26}\text{OSi}$ 370.1753, found 370.1754.

(1S*,7R*,11R*)-3-(Trimethylsilyl)-2-oxotricyclo[5.3.1.0^{4,11}]-undeca-3,9-diene (7a). The crude mixture obtained from the intramolecular PKR reaction of **1d** (0.36 g, 1.76 mmol) was purified by flash-column chromatography (silica gel, gradient elution 3–30% ethyl acetate in hexanes) to give **7a** (0.21 g, 0.91 mmol, 52%) and **7b** (0.05 g, 0.22 mmol, 13%), both as colorless liquids. Compound **7a**: IR (CH_2Cl_2) 3676, 3630, 3354, 2925, 2356, 2083, 1684, 1653, 1558, 1457, 1420, 1271, 1221 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 5.70 (m, 1 H), 5.68 (m, 1 H), 3.14 (m, 1 H), 3.12 (m, 1 H), 2.69 (dd, $J = 19.0, 18.8$ Hz, 1 H), 2.59 (m, 1 H), 2.21 (m, 1 H), 2.20 (m, 1 H), 1.99 (dt, $J = 16.8, 6.3$ Hz, 1 H), 1.79 (m, 1 H), 1.39 (m, 1 H), 0.18 (s, 9 H); ^{13}C NMR (125 MHz, CDCl_3) δ 212.91, 196.12, 135.45, 126.68, 123.64, 51.76, 48.70, 31.37, 31.27, 25.92, 25.14, -1.29; MS (70 eV) m/e 232 (M^+ , 100), 217 (56), 189 (20), 143 (12), 130 (13), 118 (15), 91 (21), 75 (25), 73 (66), 59 (13); HRMS (EI) m/e calcd for $\text{C}_{14}\text{H}_{20}\text{OSi}$ 232.1283, found 232.1288.

(1S*,7R*,11R*)-2-Oxotricyclo[5.3.1.0^{4,11}]-undeca-3,9-diene (7b): IR (CH_2Cl_2) 3676, 3381, 3057, 3053, 2924, 2038, 1696, 1653, 1160 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 5.84 (s, 1 H), 5.72 (m, 1 H), 5.71 (m, 1 H), 3.20 (m, 1 H), 3.19 (m, 1 H), 2.70 (dd, $J = 19.1, 19.2$ Hz, 1 H), 2.56 (m, 1 H), 2.24 (m, 1 H), 2.21 (m, 1 H), 2.03 (dt, $J = 17.8, 6.1$ Hz, 1 H), 1.79 (m, 1 H), 1.44 (m, 1 H); ^{13}C NMR (125 MHz, CDCl_3) δ 209.69, 188.73, 127.45, 124.64, 123.33, 50.19, 47.82, 31.60, 30.38, 25.27, 24.73; MS (70 eV) m/e 160 (M^+ , 100), 159 (25), 132 (19), 131 (34), 117 (52), 115 (17), 104 (27), 92 (14), 97 (49), 77 (19); HRMS (EI) m/e calcd for $\text{C}_{11}\text{H}_{12}\text{O}$ 160.0888, found 160.1143.

(1S*,8R*,12R*)-3-(Trimethylsilyl)-2-oxotricyclo[6.3.1.0^{4,12}]-dodeca-3,9-diene (8a). The crude mixture obtained from the intramolecular PKR reaction of **1e** (0.44 g, 2.0 mmol) was purified by flash-column chromatography (silica gel, gradient elution 3–30% ethyl acetate in hexanes) to give **8a** (0.31 g, 1.26 mmol, 63%) and **8b** (0.07 g, 0.4 mmol, 20%), both as colorless liquids. Compound **8a**: IR (CH_2Cl_2) 3676, 3355, 3058, 2370, 1679, 1558, 1437, 1317, 1235, 1125 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 5.80 (m, 1 H), 5.68 (m, 1 H), 3.07 (m, 1 H), 3.05 (m, 1 H), 3.00 (m, 1 H), 2.25 (m, 1 H), 2.20 (m, 1 H), 1.94 (m, 1 H), 1.90 (m, 1 H), 1.87 (m, 1 H), 1.74 (m, 1 H), 1.71 (m, 1 H), 1.70 (m, 1 H), 0.20 (s, 9 H); ^{13}C NMR (125 MHz, CDCl_3) δ 210.71, 188.32, 138.38, 128.09, 123.98, 48.33, 46.49, 33.82, 31.05, 29.40, 25.01, 21.75, -0.36; MS (70 eV) m/e 246 (M^+ , 85), 231 (100), 230 (32), 218 (26), 203 (30), 157 (16), 129 (23), 128 (17), 115 (18), 91 (28), 75 (40), 73 (85); HRMS (EI) m/e calcd for $\text{C}_{15}\text{H}_{22}\text{OSi}$ 246.1440, found 246.1446.

(1S*,8R*,12R*)-2-Oxotricyclo[6.3.1.0^{4,12}]-dodeca-3,10-diene (8b): IR (CH_2Cl_2) 3676, 3382, 3032, 2212, 1690, 1623, 1559, 1319, 1182, 1093 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 5.90 (s, 1 H), 5.84 (m, 1 H), 5.70 (m, 1 H), 3.15 (m, 1 H), 3.06 (m, 1 H), 2.82 (m, 1 H), 2.32 (m, 1 H), 2.20 (m, 1 H), 1.98 (m, 1 H), 1.86 (m, 1 H), 1.83 (m, 1 H), 1.79 (m, 1 H), 1.77 (m, 1 H), 1.72 (m, 1 H); ^{13}C NMR (125 MHz, CDCl_3) δ 207.25, 181.52, 128.61, 128.22, 123.52, 48.00, 44.69, 33.39, 30.42, 29.21, 24.82, 21.23; MS (70 eV) m/e 174 (M^+ , 100), 173 (43), 146 (17), 145 (20), 131 (46), 117 (32), 115 (15), 105 (12), 91 (31), 77 (16), 65 (8); HRMS (EI) m/e calcd for $\text{C}_{12}\text{H}_{14}\text{O}$ 174.1045, found 174.1047.

(1R*,8R*,12S*)-1-(Dimethylphenylsilyl)-2-oxo-3-phenyltricyclo[6.3.1.0^{4,12}]-dodeca-3,10-diene (9a). The crude mixture obtained from the intramolecular PKR reaction of **1f** (0.61 g, 1.70 mmol) was purified by flash-column chromatography (silica gel, gradient elution 3–30% ethyl acetate in hexanes)

to give **9a** (0.32 g, 0.83 mmol, 48%) and **9b** (0.10 g, 0.40 mmol, 23%), both as colorless liquids. Compound **9a**: mp 111–112 °C; IR (CH_2Cl_2) 3627, 2952, 2858, 2359, 1605, 1467, 1378 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.53 (d, $J = 6.5$ Hz, 2 H), 7.33 (m, 6 H), 7.16 (d, $J = 7.1$ Hz, 2 H), 5.80 (m, 1 H), 5.78 (m, 1 H), 2.87 (m, 1 H), 2.85 (m, 1 H), 2.10 (td, $J = 13.8, 5.7$ Hz, 1 H), 1.93 (m, 1 H), 1.90 (m, 1 H), 1.78 (tt, $J = 13.4, 3.7$ Hz, 1 H), 1.69 (m, 1 H), 1.68 (m, 1 H), 1.65 (m, 1 H), 1.55 (tt, $J = 13.5, 3.7$ Hz, 1 H), 0.45 (d, $J = 15.9, 6$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 206.19, 172.25, 138.72, 135.68, 134.32, 131.76, 129.36, 129.21, 128.05, 127.56, 127.41, 127.38, 125.64, 49.25, 46.80, 34.18, 29.75, 28.46, 25.08, 21.09, -5.44, -6.15; MS (70 eV) m/e 384 (M^+ , 39), 313 (21), 165 (19), 136 (15), 135 (100), 128 (17), 115 (23), 97 (29), 95 (28), 91 (31); HRMS (EI) m/e calcd for $\text{C}_{26}\text{H}_{28}\text{OSi}$ 384.1909, found 384.1907.

(1S*,8R*,12R*)-2-Oxo-3-phenyltricyclo[6.3.1.0^{4,12}]-dodeca-3,10-diene (9b): mp 121–122 °C; IR (CH_2Cl_2) 3623, 2944, 2359, 1733, 1692, 1605, 1339 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.38 (m, 2 H), 7.29 (m, 3 H), 5.86 (m, 1 H), 5.76 (m, 1 H), 3.27 (m, 1 H), 3.14 (t, $J = 6.2$ Hz, 1 H), 3.03 (dt, $J = 14.2$ Hz, 1 H), 2.29 (m, 1 H), 2.27 (m, 1 H), 1.99 (m, 1 H), 1.97 (m, 1 H), 1.80 (m, 1 H), 1.79 (m, 1 H), 1.78 (m, 1 H), 1.68 (m, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 204.69, 174.18, 138.47, 131.48, 129.19, 128.69, 128.17, 127.55, 123.51, 47.47, 43.33, 33.40, 29.46, 28.60, 24.93, 21.19; MS (70 eV) m/e 250 (M^+ , 100), 249 (22), 207 (25), 178 (35), 165 (36), 131 (25), 128 (23), 115 (46), 91 (40), 77 (20); HRMS (EI) m/e calcd for $\text{C}_{18}\text{H}_{18}\text{O}$ 250.1358, found 250.1355. Crystals suitable for X-ray diffraction were grown from CH_2Cl_2 and hexanes.

(1S*,8S*)-2-Oxo-3-phenyltricyclo[6.4.0.0^{4,11}]-dodeca-3,10-diene (10). The crude mixture obtained from the intramolecular PKR reaction of **1g** (0.22 g, 1.00 mmol) was purified by flash-column chromatography (silica gel, gradient elution 3–30% ethyl acetate in hexanes) to give **9b** (0.14 g, 0.57 mmol, 57%) and **10** (0.085 g, 0.34 mmol, 34%), both as colorless liquids. Compound **10**: IR (CH_2Cl_2) 3623, 3447, 3057, 2944, 2837, 2360, 2340, 1606, 1339, 1075 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.58 (m, 2 H), 7.37 (m, 2 H), 7.33 (m, 1 H), 6.14 (m, 1 H), 5.96 (m, 1 H), 2.95 (m, 1 H), 2.76 (m, 1 H), 2.71 (s, 1 H), 2.28 (m, 1 H), 2.11 (m, 2 H), 2.09 (m, 1 H), 2.07 (m, 1 H), 1.88 (d, $J = 13.0$ Hz, 1 H), 1.33 (m, 1 H), 1.05 (m, 1 H); ^{13}C NMR (125 MHz, CDCl_3) δ 207.10, 186.69, 132.10, 131.79, 128.63, 128.29, 128.22, 127.66, 124.17, 57.13, 51.35, 33.06, 31.74, 26.32, 23.69, 22.77; MS (70 eV) m/e 250 (M^+ , 41), 195 (18), 194 (100), 193 (22), 179 (20), 178 (21), 129 (19), 128 (21), 115 (26), 91 (17); HRMS (EI) m/e calcd for $\text{C}_{18}\text{H}_{18}\text{O}$ 250.1358, found 250.1360.

(1S*,8R*,12R*)-2-Oxo-3-*p*-tolyltricyclo[6.3.1.0^{4,12}]-dodeca-3,10-diene (11a). The crude mixture obtained from the intramolecular PKR reaction of **1h** (0.47 g, 2.0 mmol) was purified by flash-column chromatography (silica gel, gradient elution 3–30% ethyl acetate in hexanes) to give **11a** (0.16 g, 0.58 mmol, 29%) as a white solid and **11b** (0.18 g, 0.55 mmol, 28%) as a colorless oil. Compound **11a**: mp 103–105 °C; IR (CH_2Cl_2) 3676, 3368, 3032, 3057, 2928, 2057, 2039, 1733, 1690, 1654, 1636, 1374, 1244, 1132, 1046 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.9 (dt, $J = 8.05, 10.55$ Hz, 4 H), 5.85 (m, 1 H), 5.75 (m, 1 H), 3.25 (dd, $J = 5.1$ Hz, 1 H), 3.12 (t, $J = 6.3$ Hz, 1 H), 3.04 (tt, $J = 4.1$ Hz, 1 H), 2.35 (s, 3 H), 2.28 (m, 1 H), 2.27 (m, 1 H), 1.95 (m, 1 H), 1.93 (m, 1 H), 1.81 (m, 1 H), 1.78 (m, 1 H), 1.76 (m, 1 H), 1.69 (m, 1 H); ^{13}C NMR (125 MHz, CDCl_3) δ 204.91, 173.74, 138.30, 137.28, 129.02, 128.85, 128.62, 128.42, 123.48, 47.40, 43.23, 33.34, 29.41, 28.55, 24.87, 21.19, 21.12; MS (70 eV) m/e 264 (M^+ , 100), 235 (11), 221 (10), 210 (6), 179 (7), 178 (6), 165 (6), 129 (5); HRMS (EI) m/e calcd for $\text{C}_{19}\text{H}_{20}\text{O}$ 264.1514, found 264.1506. Crystals suitable for X-ray diffraction were grown from CH_2Cl_2 and hexanes.

(1S*,8S*)-2-Oxo-3-*p*-tolyltricyclo[6.4.0.0^{4,11}]-dodeca-3,10-diene (11b): IR (CH_2Cl_2) 3677, 3630, 3382, 2925, 2357, 2036, 1968, 1734, 1559, 1457, 1374, 1092 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.48 (d, $J = 8.1$ Hz, 2 H), 7.19 (t, $J = 8.1$ Hz, 2 H),

6.14 (m, 1 H), 5.94 (m, 1 H), 2.72 (m, 1 H), 2.72 (m, 1 H), 2.66 (s, 1 H), 2.34 (s, 3 H), 2.09 (m, 1 H), 2.07 (m, 2 H), 2.05 (m, 1 H), 2.03 (m, 1 H), 1.87 (tt, $J = 6.6, 6.5$ Hz, 1 H), 1.32 (m, 1 H), 1.02 (m, 1 H); ^{13}C NMR (125 MHz, CDCl_3) δ 206.94, 185.57, 137.30, 131.81, 128.85, 128.80, 128.43, 128.06, 124.18, 56.99, 51.13, 32.96, 31.64, 26.21, 23.61, 22.68, 21.13; MS (70 eV) m/e 264 (M^+ , 65), 208 (100), 193.1 (28), 179.1 (22), 136.0 (29), 119.0 (67), 115.0 (22), 91.0 (49), 70.0 (24); HRMS EI m/e calcd for $\text{C}_{19}\text{H}_{20}\text{O}$ 264.1514, found 264.1501.

(1S*,8R*,12R*)-2-Oxo-3-naphthyltricyclo[6.3.1.0^{4,12}]dodeca-3,10-diene (12a). The crude mixture obtained from intramolecular PKR reaction of **1i** (0.27 g, 1.0 mmol) was purified by flash-column chromatography (silica gel, gradient elution 3–30% ethyl acetate in hexanes) to give **12a** (0.07 g, 0.23 mmol, 23%) and **12b** (0.14 g, 0.47 mmol, 47%), both as colorless liquids. Compound **12a**: IR (CH_2Cl_2) 3368, 3062, 2928, 2365, 1733, 1374, 1245, 1046 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.84 (m, 2 H), 7.47 (m, 4 H), 7.20 (m, 1 H), 6.03 (m, 1 H), 5.85 (m, 1 H), 3.40 (m, 1 H), 3.26 (m, 1 H), 2.54 (m, 1 H), 2.34 (m, 1 H), 2.21 (m, 1 H), 2.19 (m, 1 H), 1.96 (m, 1 H), 1.94 (m, 1 H), 1.80 (m, 1 H), 1.64 (m, 2 H); ^{13}C NMR (125 MHz, CDCl_3) δ 204.84, 176.34, 138.82, 133.71, 131.90, 129.69, 128.86, 128.64, 128.40, 127.43, 126.12, 125.80, 125.27, 125.06, 123.88, 47.93, 43.86, 33.46, 29.71, 28.74, 25.23, 21.01; MS (70 eV) m/e 300 (M^+ , 100), 229 (20), 215 (20), 202 (17), 167 (15), 165 (36), 152 (19), 91 (19); HRMS EI m/e calcd for $\text{C}_{22}\text{H}_{20}\text{O}$ 300.1514, found 300.1522.

(1S*,8S*)-2-Oxo-3-naphthyltricyclo[6.4.0.0^{4,11}]dodeca-3,10-diene (12b): IR (CH_2Cl_2) 3624, 3054, 2944, 2834, 2359, 2342, 1700, 1606, 1338, 1075 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.83 (m, 2 H), 7.62 (m, 1 H), 7.45 (m, 3 H), 7.34 (m, 1 H), 6.19 (m, 1 H), 6.00 (m, 1 H), 2.85 (m, 1 H), 2.63 (m, 1 H), 2.39 (m, 1 H), 2.23 (m, 1 H), 2.15 (m, 2 H), 2.12 (m, 1 H), 2.00 (m, 1 H), 1.98 (m, 1 H), 1.47 (m, 1 H), 1.26 (m, 1 H); ^{13}C NMR (125 MHz, CDCl_3) δ 206.85, 189.22, 135.06, 133.66, 131.36, 129.61, 128.68, 128.41, 128.27, 127.41, 125.76, 125.58, 125.17, 124.94, 124.27, 56.87, 51.43, 33.66, 32.28, 25.67, 23.12, 22.75; MS (70 eV) m/e 300.2 (M^+ , 100), 244.1 (93), 243.1 (39), 229.1 (35), 228.1 (25), 215.0 (43), 202.0 (26), 165.0 (43), 91.0 (25); HRMS EI m/e calcd for $\text{C}_{22}\text{H}_{20}\text{O}$ 300.1514, found 300.1518.

1-Phenyl-2a,5,5a,9c-tetrahydrocyclopenta[*jk*]fluoren-2-one (13). The crude mixture obtained from the intramolecular PKR reaction of **2a** (0.26 g, 1.0 mmol) was purified by flash-column chromatography (silica gel, gradient elution 3–30% ethyl acetate in hexanes) to give **13** (0.27 g, 0.95 mmol, 95%) as a white solid: mp 139–140 °C; IR (CH_2Cl_2) 3453, 3384, 3062, 2305, 1701, 1692, 1419, 1270, 1017 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.78 (m, 1 H), 7.42 (m, 7 H), 7.21 (m, 1 H), 5.98 (m, 1 H), 5.82 (m, 1 H), 3.62 (t, $J = 6.9$ Hz, 1 H), 3.48 (m, 1 H), 3.25 (q, $J = 7.9$ Hz, 1 H), 2.51 (dt, $J = 17.5, 6.7$ Hz, 1 H), 1.49 (m, 1 H); ^{13}C NMR (125 MHz, CDCl_3) δ 205.73, 175.01, 155.45, 134.82, 134.56, 131.74, 131.40, 129.04, 128.12, 128.04,

127.04, 126.21, 125.02, 124.95, 123.08, 48.35, 46.92, 37.24, 29.65; MS (70 eV) m/e 284 (M^+ , 100), 256 (28), 255 (41), 252 (29), 241 (36), 239 (42), 178 (45), 167 (27), 165 (46); HRMS EI m/e calcd for $\text{C}_{21}\text{H}_{16}\text{O}$ 284.1201, found 284.1197. Crystals suitable for X-ray diffraction were grown from CH_2Cl_2 and hexanes.

1-(Trimethylsilyl)-2a,5,5a,9c-tetrahydrocyclopenta[*jk*]fluoren-2-one (14). The crude mixture obtained from the intramolecular PKR reaction of **2b** (0.25 g, 1.0 mmol) was purified by flash-column chromatography (silica gel, gradient elution 3–30% ethyl acetate in hexanes) to give **14** (0.094 g, 0.35 mmol, 35%) as a colorless oil: IR (CH_2Cl_2) 3533, 3384, 3059, 2302, 1702, 1681, 1418, 1162, 1021 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.76 (m, 1 H), 7.42 (m, 2 H), 7.33 (m, 1 H), 5.89 (m, 1 H), 5.76 (m, 1 H), 3.54 (t, $J = 7.2$ Hz, 1 H), 3.28 (m, 1 H), 3.16 (dt, $J = 9.6, 7.6$ Hz, 1 H), 2.48 (dt, $J = 17.2, 7.2$ Hz, 1 H), 1.48 (m, 1 H), 0.29 (s, 9 H); ^{13}C NMR (125 MHz, CDCl_3) δ 211.87, 188.44, 155.40, 136.09, 135.78, 131.13, 126.95, 126.21, 125.79, 125.07, 123.48, 52.61, 48.05, 37.23, 29.42, -0.38; MS (70 eV) m/e 280.0 (M^+ , 100), 265 (37), 191 (24), 189 (17), 179 (27), 178 (51), 167 (40), 166 (83); HRMS EI m/e calcd for $\text{C}_{18}\text{H}_{20}\text{OSi}$ 280.1283, found 280.1288.

(1S*,7R*,12R*)-2-Oxo-3-phenyltricyclo[5.4.1.0^{4,12}]dodeca-3,10-diene (17). The crude mixture obtained from the intramolecular PKR reaction of **16** (0.22 g, 1.0 mmol) was purified by flash-column chromatography (silica gel, gradient elution 3–30% ethyl acetate in hexanes) to give **17** (0.034 g, 0.14 mmol, 14%) as a colorless oil: IR (CH_2Cl_2) 3520, 3393, 2954, 2309, 1732, 1681, 1421, 1258, 1022 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.64 (d, $J = 7.4$ Hz, 2 H), 7.40 (t, $J = 7.6$ Hz, 2 H), 7.31 (dd, $J = 7.4$ Hz, 1 H), 5.71 (m, 1 H), 5.63 (m, 1 H), 3.43 (d, $J = 6.2$ Hz, 1 H), 3.38 (t, $J = 6.8$ Hz, 1 H), 2.87 (dd, $J = 10.8$ Hz, 1 H), 2.69 (tt, $J = 10.4$ Hz, 1 H), 2.43 (m, 1 H), 2.34 (m, 1 H), 2.20 (m, 2 H), 1.82 (m, 1 H), 1.80 (m, 2 H); ^{13}C NMR (125 MHz, CDCl_3) δ 208.38, 183.65, 133.03, 131.92, 129.83, 128.21, 128.12, 127.59, 124.73, 53.23, 51.28, 41.14, 34.89, 30.83, 30.58, 25.95; MS (70 eV) m/e 250 (M^+ , 4), 220 (19), 178 (9), 150 (11), 149 (100), 147 (4), 135 (2), 108 (9), 107 (97), 77 (4); HRMS EI m/e calcd for $\text{C}_{18}\text{H}_{18}\text{O}$ 250.1358, found 250.1363.

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Supporting Information Available: Tables of atomic coordinates, bond lengths, bond angles and anisotropic thermal parameters for compounds **3**, **5**, **9b**, **11a**, and **13**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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