Synthesis of Tricyclic Aromatic Compounds by the Intramolecular Pauson−Khand Reaction Promoted by Molecular Sieves[†,1]

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Pauson−Khand reactions are carried out with different substituted aromatic enynes, yielding tricyclic cyclopentenones related to natural products such as chromenes. Enynes are easily obtained in a two-step approximation from the corresponding salicylaldehydes. The reaction is promoted by dissolved TMANO (trimethylamine *N*-oxide) and/or 4 Å molecular sieves. This new way of induction for the Pauson−Khand reaction increases yields remarkably, allowing the reaction of some substituted alkenes which fail to react in the absence of the zeolite. Isomerization of the double bond of the cyclopentenone ring is observed except when nonterminal triple bonds are used. For trisubstituted alkenes, an interrupted Pauson−Khand process is observed with moderate yields.

The Pauson−Khand multicomponent cycloaddition reaction is now considered among the best approaches to the cyclopentenone ring system, and is probably the most useful reaction of cobalt hexacarbonyl−alkyne complexes.[2] Many research groups are using this reaction in synthetic applications, mainly in its intramolecular version.[3] This transformation implies the simultaneous formation of three carbon−carbon bonds and two cycles, leading to many frameworks present in natural products.[4]

Many efforts have been made to improve the reaction conditions, as conversions were normally moderate in the original thermally promoted version. The reaction begins with the facile obtention of the cobalt hexacarbonyl−alkyne complex, and then continues with the creation of free coordination sites to allow the alkene to be complexed. Several promoters such as DMSO,[5] ultraviolet radiation,[6] primary amines,[7] sulfides,[8] water,[9] and *N*-oxides[10] have been used to labilize the carbonyl ligands. Other methods such as the dry-state adsorption conditions (DSAC) induce the reaction by stabilization of a pretransition-state conformation of the enyne complex.[11] We have recently shown that molecular sieves can also induce the reaction, probably acting as the solid support in the DSAC method.[1b] There is little experimental evidence available on the reaction mechanism. Indeed, the generally accepted mechanism, first proposed by Magnus,[12] still lacks experimental evidence as no intermediates can be identified after the first hexacarbonyl−alkyne complex.

Although the use of stoichiometric amounts of metal is considered unacceptable for a potentially useful commercial synthesis, there are still no completely satisfactory catalytic versions. The catalytic Pauson−Khand reactions reported to date involve the use of high CO pressures,[13] modified cobalt complexes,[14] light induction,[15] or complexes of other metals such as titanium, ruthenium, or rhodium.[16]

Many functional groups are compatible with the Pauson−Khand reaction, but the carbon skeletons that undergo the cyclization are relatively few. Most intramo-

[†] Dedicated to Professor José Luis Soto Cámara on the occasion of his 70th birthday.

(1) For a preliminary communication of part of this work see: (a) Blanco-Urgoiti, J.; Casarrubios, L.; Pérez-Castells, J. *Tetrahedron Lett.* **1999**, *40*, 2817−2820. (b) Pérez-Serrano, L.; Casarrubios, L.; Domínguez, G.; Pérez-Castells, J. *Org. Lett.* **1999**, *1*, 1187.

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(4) For some recent examples of natural product syntheses using Pauson−Khand reactions, see: (a) Brummond, K. M.; Lu, J. *J. Am. Chem. Soc.* **1999**, *121*, 5087. (b) Kowalczyk, B. A.; Shmith, T. C.; Dauben, W. G. *J. Org. Chem.* **1998**, *63*, 1379. (b) Castro, J.; Moyano, A.; Pericàs, M. A.; Riera, A. *J. Org. Chem.* **1998**, *63*, 3346. (c) Jamison, T. F.; Shambayati, S.; Crowe, W. E.; Schreiber, S. L. *J. Am. Chem. Soc.* **1997**, *119*, 4353. (d) Tormo, J.; Moyano, A.; Pericàs, M. A.; Riera, A. *J. Org. Chem.* **1997**, *62*, 4851. (e) Bolton, G. L.; Hodges, J. C.; Rubin, J. R. *Tetrahedron* **1997**, *53*, 6611.

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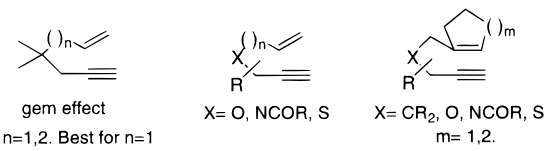


Figure 1.

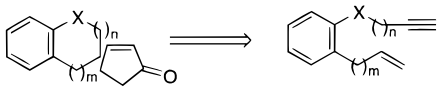


Figure 2.

lecular Pauson−Khand reactions described to date use systems derived from hept-1-en-6-yne or propargyl allyl ethers or amines. Good conversions are generally achieved when a *gem* effect is helping.[2e] These *gem* effects, widely studied for other cyclization processes,[17] are thought to enhance the rate of the reaction by selective destabilization of the ground-state conformation and increment of the population of the reactive conformation. This requirement seems important in the Pauson−Khand reaction as great yield reductions are observed when substituents are introduced into the alkene moiety, with the exception of strained cycles.[18] Worse conversions are also described with oct-1-en-7-yne systems (Figure 1).[19]

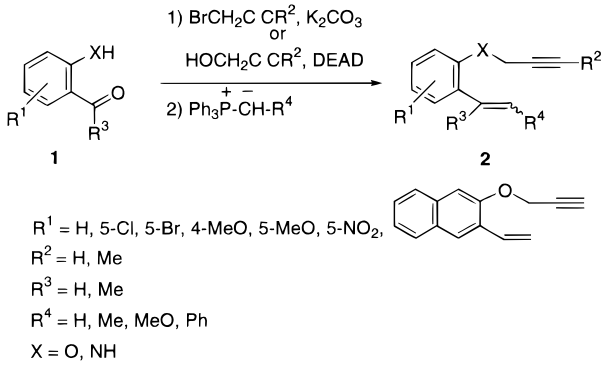
Moreover, aromatic rings have not yet been used as part of the skeleton of the enyne in intramolecular Pauson−Khand processes. These substrates probably have low populations in the reactive conformation due to the lack of *gem* effects, and they would lead to bicyclo-[4,3,0]-like systems. Nevertheless, a Pauson−Khand cyclization of these systems would lead to interesting tricyclic structures (Figure 2). Thus, a great number of natural products, such as metabolites of the shikimate pathway and some systems derived from the acetate pathway, include in their structure polycyclic systems with aromatic rings. Some tricothecanes and some polyketides have structures closely related to the structures of these compounds.

In this paper, we report the results of the Pauson−Khand reaction of aromatic enynes to yield tricyclic cyclopentenones. We have developed a new experimental protocol based on the use of molecular sieves as the reaction promoters. This new method of promotion has allowed the reaction of substrates with different substituents, even in the less favorable cases such as enynes substituted in the alkene moiety or octenynes. These systems reacted with good yields as well as a disubstituted alkyne in the intermolecular version.[1b] The experimental conditions have a dramatic effect on the type of product obtained in the reaction. A novel isomerization of the emerging double bond will also be discussed.

Results and Discussion

The synthesis of the starting enynes was carried out in two steps from 2-hydroxy- or 2-aminobenzocarbonyl

Scheme 1



compounds, **1**. First, a propargylation reaction was done either under Mitsunobu conditions[20] or by using anhydrous potassium carbonate as base. The corresponding propargylated compounds were reacted with different phosphonium ylides to give enynes **2** with good yields. Scheme 1 summarizes the results obtained in the synthesis of compounds **2**. Compounds **2l, 2m**, and **2n** ($R^4 \neq$ H), were obtained as a mixture of *Z*/*E* isomers.[21] The alkyne-substituted compounds (**2i, 2j**) were obtained from **2a** and benzyl bromide or TMSCl, respectively.

To study the viability of the Pauson−Khand reaction of these aromatic enynes and to find the best reaction conditions, we submitted compounds **2** to the most common conditions used in Pauson−Khand reactions. After some disappointing results using conventional methods, we reported in the preliminary communication of this work[1a] that slow addition of a DCM solution of trimethylamine *N*-oxide at 0 °C followed by reaction at rt in the same solvent yielded the desired products in moderate to good yields. We observed though that the double bond of the new cyclopentenone ring had isomerized to conjugate with the aromatic ring and also detected a byproduct that turned out to be the depropargylated compound. In our attempt to improve yields, we found that molecular sieves (zeolites) promote the Pauson−Khand reaction.[1b] When using this method of promotion, variable mixtures of isomerized compounds **3** and **4,** and depropargylated compound **5**, were obtained depending on the reaction conditions. Table 1 shows a summary of the most relevant reaction conditions used with compound **2c**, which was taken as a model.

The first entries (1−5) show the influence of the solvent in the reaction. The more polar the solvent the more depropargylation is observed. Thus, with acetonitrile depropargylation was the major process observed.[22] With less polar solvents such as benzene or toluene no vinylphenols were detected, and the best conversions were achieved with the latter one (entry 5). This seems to show a competence between the Pauson−Khand process and a Nicholas-type reaction. Indeed, the propargyl moiety has been postulated as a hydroxy protecting group,[23] and similar reactions have been described with *N*-propargy-

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(21) Compounds **2l** and **2n** were separated by column chromatography (Biotage S40), and both isomers were assigned by the value of the coupling constants of the vinylic protons (**2l**, $_{cis} = 12.1$ *Hz*, $J_{trans} = 15.2$ *Hz;* ***2n***, $J_{cis} = 12.4$ *Hz*, $J_{trans} = 16.5$ *Hz).*

(22) This depropargylation reaction was also carried out with compounds **2a** and **2f**, obtaining in both cases compounds **5a** and **5f** (60−65%) as the only reaction products. See the Experimental Section.

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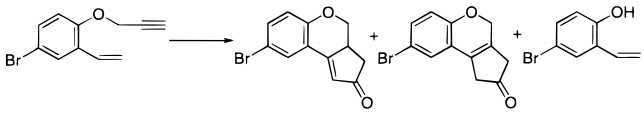
Table 1. Reaction Compound 2c in Different Conditions



2c 3c 4c 5c

				yield (%)[a]		
no.	solvent	promoter	*T* (°C)	**3c**	**4c**	**5c**
1	MeCN	TMANO	−10	7		60
2	MeCN	TMANO/MS 4 Å[b]	−10			65
3	DMC	TMANO	−10	45		20
4	benzene	TMANO	−10	30		
5	toluene	TMANO	−10	40		
6	toluene	TMANO/MS 4 Å[b]	−10	90	<5	
7	toluene	MS 4 Å[b]	112[c]	45	<5	
8	toluene		112[c]	15		
9	toluene	TMANO/MS 4 Å[d]	−10	15	75	

[a] Of pure material with correct spectroscopic data (^{1}H, ^{13}C NMR, IR). [b] Powdered molecular sieves preheated in an oven at 125 °C for 4 h and cooled under argon. Eight times the mass of the starting material. [c] No reaction was observed at lower temperatures. [d] Commercial powdered and activated 4 Å molecular sieves (8−12 mesh).

lated β-lactams.[24] The only promoter that yielded acceptable amounts of cyclization product was trimethylamine *N*-oxide (TMANO, entry 5). When cooperating with molecular sieves, this promoter led to high conversions (entry 6). In addition, raising the reaction temperature to refluxing toluene showed that molecular sieves are able to promote the reaction on their own although with lower yields (entry 7). In the absence of zeolite, the thermal promotion of the reaction only yielded 15% of compound **3c** (entry 8).

Molecular sieves are known to promote several organic transformations[25] such as Diels−Alder reactions,[26] epoxidation of allylic alcohols (Sharpless epoxidation),[27] asymmetric Heck reactions,[28] ene reactions,[29] or asymmetric sulfoxidations.[30] Some zeolites have been used for DSAC intermolecular Pauson−Khand cyclizations of methylene cyclopropane with alkynes, observing, in general, positive effects.[31] We have shown in the preliminary communication of this work the ability of these zeolites to promote Pauson-Khand reactions in different substrates selected among the less favorable cases described in the literature.[1b] In addition to favoring the reaction, molecular sieves also modify the double bond isomerization process. Different ratios of compounds **3** and **4** were obtained when using different types of molecular sieves. The results were somewhat erratic at the beginning, but afterward we realized that slight changes in the hydration of the sieves were responsible for these variations in the product ratio. Dramatic effects of molecular sieve hydration on the stereochemical outcome of asymmetric Diels−Alder reaction have been observed.[26] Entries 6 and 9 show that compound **4** is the major product when less water is present in the reaction. Thus, when using commercial activated molecular sieves (entry 9), compound **4** is the major product. Molecular sieves have a minimum water content of 3% in weight, so these conditions (entry 9) are not completely anhydrous. Compound **4** can be considered an intermediate in the formation of **3**, as it isomerizes quantitatively to **3** when stirred with acid traces, with bases, or simply in the presence of dicobalt octacarbonyl.

The Pauson−Khand reaction of compounds **2** allowed us to obtain the corresponding cyclopentenones **3** and **4**. Only compounds **2h**, **2i**, and **2k** led to Pauson−Khand products **6h**, **6i**, and **6k** (Table 2).

Yields are always good when the alkene moiety is unsubstituted (entries 1−7), although slightly worse when nonterminal alkynes are used (entries 8 and 9). Substituted alkenes fail to react under standard conditions (method A) but undergo the reaction with molecular sieves in refluxing toluene (method B). We had previously observed also that the DSAC procedure allows a small conversion of these substituted substrates.[1a] This points out the probable role of the sieves adsorbing the substrate and favoring the reactive conformation mentioned above. The only exception is compound **2m,** which reacted in standard conditions probably due to the effect of the oxygen as a soft ligand.[32] Due to isomerization of the double bond, both *Z* and *E* isomers of **2l** led to **3l**, and thus, mixtures of *Z*/*E* isomers were used in the other two cases (**2m**,**n**). Finally, the obtention of compound **3o** shows the possibility to extend this methodology to nitrogen-containing substrates.

As reported in previous examples, once again, substitutions in the double bond disfavor the reaction. The extension of this reaction to trisubstituted alkenes resulted in the failure to obtain Pauson−Khand products but led to an interesting interrupted-like process. Thus, we prepared compound **2t** ($R^3 = R^4 =$ Me). Besides, two cycloalkenyl compounds were prepared from 2-bromophenol and cycloalkanones, as shown Scheme 2.

These three substrates failed to react in our standard conditions with TMANO and molecular sieves, in these cases the depropargylation product being the only one identified in the reaction. When using molecular sieves as the only promoter in refluxing toluene, and after 48 h compound **2t** led to complex mixtures. Compounds **2p** and **2q**, however, yielded a new product, with moderate yields (20−30%), which turned out to be compound **7** (Scheme 3). This compound can be considered an interrupted Pauson−Khand product.[33] In these cases, after the formation of complex B, the combined steric demand of the substituents R^3 and R^4 seems to make impossible the subsequent CO insertion and lead directly to the

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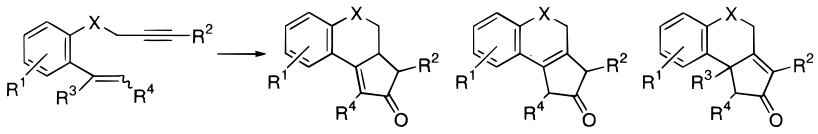
(31) Smit, W. A.; Kireev, S. L.; Nefedov, O. M.; Tarasov, V. A. *Tetrahedron Lett.* **1989**, *30*, 4021.

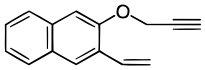
(32) Coordination of heteroatoms to cobalt is thought to enhance yields in these reactions. See: (a) Kraft, M. E.; Scott, I. L.; Romero, R. H.; Feibelmann, S.; Van Pelt, C. E. *J. Am. Chem. Soc.* **1993**, *115*, 7199. (b) Kraft, M. E.; Juliano, C. A.; Scott, I. L.; Wright, C.; McEaching, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 1693. Also intermolecular reactions with vinyl ethers and esters have recently been described: Kerr, W. J.; McLaughlin, M.; Pauson, P. L.; Robertson, S. M. *Chem. Commun.* **1999**, 2171.

(33) The interrupted Pauson−Khand reaction was first reported by Kraft involving the oxidation of the primary cyclization product. See: Kraft, M. E.; Wilson, A. M.; Dasse, O. A.; Shao, B.; Chung, Y. Y.; Fu, Z.; Bonaga, L. V. R.; Mollmann, M. K. *J. Am. Chem. Soc.* **1996**, *118*, 6080.

Table 2. Synthesis of Tricyclic Cyclopentenones 3, 4, and 6

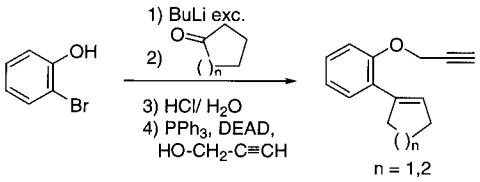


2 **3** **4** **6**

Entry	Substr	R^1	R^2	R^3	R^4	Method	Product[a]	Yield (%)	m.p.(°C)
1	**2a**	H	H	H	H	A	**3a**	60	100-102
							4a	10	127-128
2	**2b**	5-Cl	H	H	H	A	**3b**	45	169-170
							4b	27	
3	**2c**	5-Br	H	H	H	A	**3c**	90	178-179
4	**2d**	4-MeO	H	H	H	A	**3d**	37	123-125
							4d	35	130-131
5	**2e**	5-MeO	H	H	H	See ref 1a	**3e**	58	112-114
6	**2f**	5-NO_2	H	H	H	A	**3f**	70	190 dec.
7	**2g**					See ref 1a	**3g**	44	oil
8	**2h**	H	Me	H	H	A	**6h**	50	oil
9	**2i**	H	$PhCH_2$	H	H	A	**6i**	55	oil
10	**2j**	H	TMS	H	H	A	**3a**	55	100-102
11	**2j**	H	TMS	H	H	B	**3a**	50	100-102
12	**2k**	H	H	Me	H	B	**6k**	40	oil
13	**2l**[c]	H	H	H	Me	B	**3l**	40	109-111
14	**2m**[d]	H	H	H	OMe	A	**3m**	35	89-91
15	**2m**[d]	H	H	H	OMe	B	**3m**	25	89-91
16	**2n**[d]	H	H	H	Ph	B	**3n**	40	70-72
17	**2o**	H	H	H	H	A	**3o**	55	oil

[a] X = O for all products except for **2o**, and **3o**, where X = NH. [b] Of pure material with correct spectroscopic data (^1H, ^{13}C NMR, IR). [c] Both *Z* and *E* isomers were reacted separately to give **31**. [d] A mixture of *Z*/*E* isomers of **2** was used as starting material.

Scheme 2



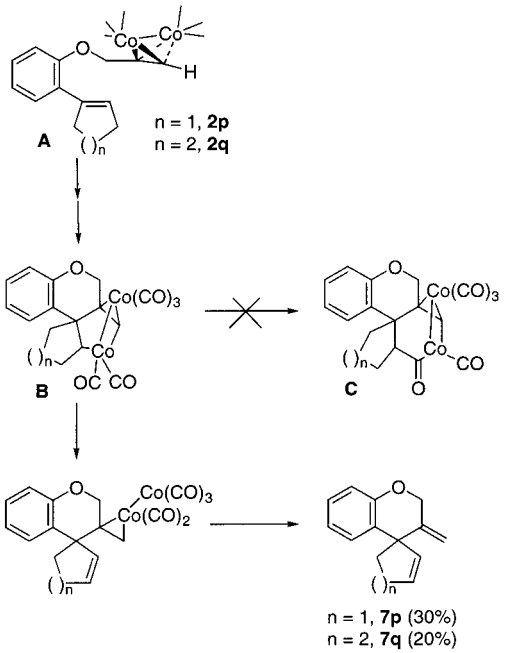
decomplexation of the cobalt (Scheme 3). We have not found any examples of an intramolecular Pauson−Khand reaction with trisubstituted alkenes.

The results obtained with the silylated compound **2j** which led to **3a** in both experimental conditions (entries 10 and 11, Table 2) show that complete desilylation has occurred. This process is previous to the isomerization as shown by the spectroscopic data of the cobalt hexacarbonyl complex of **2j**, where the TMS group is still present. In addition, the reaction in the absence of molecular sieves led to compound **3a**. Another interesting fact in the Pauson−Khand reaction of these substrates is the double bond shift we have observed in most cases. As shown in Table 2, the emerging double bond is shifted in most cases. Besides compound **2k**, in which isomerization is structurally impossible, this process was not observed in compounds **2h** and **2i**, probably due to the more stable trisubstituted double bond of the Pauson−Khand product. In all other cases, no traces of compounds **6** were observed. Some double bond shifts have been described with metal complexes in which a π-allyl complex mechanism is accepted. In Scheme 4, the commonly accepted mechanism for the Pauson−Khand reaction is depicted for our substrates. The probable course of the isomerization process, starting from complex E, would involve the formation of π-allyl cobalt carbonyl complexes F and H.[34]

The obtention of mixtures of compounds **3** and **4** may depend on the amount of water present in the reaction. During the reaction course, two carbonyls are lost by one

(34) These allyl complexes are known in the literature and have found synthetic applications: (a) Kraft, M. E.; Pankowski, J. *Tetrahedron Lett.* **1990**, *31*, 5139. (b) Barinelli, L. S.; Li, Z.; Nicholas, K. M. *Organometallics* **1989**, *8*, 2474. (c) Hegedus, L. S.; Perry, R. J. *J. Org. Chem.* **1984**, *49*, 2570.

Scheme 3



of the cobalts, and this vacant site is thought to be occupied by the solvent.[35] In our case, the water present in the sieves (at least 3% in weight) may coordinate to the cobalt and facilitate the isomerization. The observation that the more anhydrous the conditions the higher the quantity of compound **4** obtained may support this. Nevertheless, to obtain some more information on this reaction course, we prepared two deuterated substrates, **2r** and **2s**, and submitted them to the two reaction conditions described in Table 2. In both cases the hexacarbonyl−alkyne complexes were isolated and characterized, both of them showing the presence of the deuteriums.[36] Nevertheless, after the Pauson−Khand reaction both substrates led to compounds **3a** and **4a**, with good yields (65−67% overall yield) (Scheme 5). This points out the presence of protic sources in this reaction that interchange the deuterium.

In conclusion, the intramolecular Pauson−Khand reaction can be applied to aromatic substrates, leading to intermediates in the synthesis of several groups of natural products. To achieve good conversions, a new method of promotion of the reaction, based on molecular sieves, has been developed. The role of the zeolites in the reaction mechanism is currently being studied as it could interfere in the selectivity of the reaction. Finally the isomerization of the newly formed double bond and the loses of deuterium or TMS linked to the substrates gives new data on the course of this reaction.

Experimental Section

General Procedures.

Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were obtained at 300 and 75.43 MHz, respectively. NMR spectra were registered in $CDCl_3$, and chemical shifts are given in parts per million relative to TMS (^{1}H, 0.00 ppm) or $CDCl_3$ (^{13}C, 77.00 ppm). Elemental analyses were performed at the UCM Microanalysis Service (Facultad de Farmacia, Universidad Complutense de Madrid, Spain). For purification of crude reaction mixtures flash chromatography was applied in all cases. Silica gel (230−400 mesh) was used as the stationary phase. TMANO (trimethylamine *N*-oxide) was dehydrated by refluxing a toluene solution overnight using a Dean−Stark apparatus. Molecular sieves (4 Å) (beads, 8−12 mesh) were powdered by vigorous stirring in toluene overnight. After filtration, the powder was dried in an oven for 4 h at 120 °C.

General Procedure for the Synthesis of Enynes 2.

Method A. A mixture of substituted 2-hydroxybenzaldehydes (1.00 mmol), the corresponding bromide (1.10 mmol), and anhydrous potassium carbonate (1.10 mmol) in dry acetone (10 mL) was refluxed until total reaction (TLC). The solution was diluted with water and extracted with ether (3 × 20 mL). The solvent was evaporated under vacuum and the crude product purified by flash chromatography (hexane/EtOAc mixtures). This intermediate was dissolved in dry ether or THF and treated for 2 h with a freshly prepared solution of the corresponding phosphorus ylide[37] (1.50 mmol) at room temperature. The resulting suspension was poured into a 1:1 Et_2O/H_2O mixture. The organic layer was separated and the aqueous phase extracted with ether. The combination of the organic phases was evaporated and purified by flash chromatography (hexane/EtOAc mixtures) to obtain pure enynes **2**.

Method B. To a cooled solution (0 °C) of the substituted 2-hydroxybenzaldehydes or 2-hydroxyacetophenone (1.00 mmol) in 4 mL of anhydrous THF were added the corresponding alcohol (2.50 mmol), triphenylphosphine (1.00 mmol), and diethylazodicarboxylate (1.00 mmol) in 5 mL of THF. The reaction was stirred at room temperature for 24 h. The solvent was eliminated, and the crude product thus obtained was purified by chromatography (hexane/EtOAc mixtures). Treatment of this intermediate with the conditions described in method A yielded pure enynes **2**.

2-(2-Propynyloxy)styrene, 2a. Following method A, from 10.00 g (81.90 mmol) of salicylaldehyde, 10.0 mL (90.10 mmol) of propargyl bromide, and 12.40 g (90.10 mmol) of potassium carbonate, and after purification by chromatography, 10.50 g (80%) of the corresponding propargylated intermediate was obtained. A 2.50 g (15.60 mmol) sample of this intermediate was treated with 8.40 g (23.40 mmol) of methyltriphenylphosphonium bromide and 40.6 mL of KHMDS to obtain, after purification, 2.45 g (quantitative) of **2a** as a colorless oil: ^{1}H NMR δ 2.51 (t, 1H, J = 2.2 Hz), 4.72 (d, 2H, J = 2.2 Hz), 5.27 (dd, 1H, J_1 = 11.0 Hz, J_2 = 1.6 Hz), 5.74 (dd, 1H, J_1 = 17.6 Hz, J_2 = 1.6 Hz), 6.96−7.01 (m, 1H), 7.06 (dd, 1H, J_1 = 17.6 Hz, J_2 = 11.0 Hz), 7.21−7.27 (m, 1H), 7.30−7.35 (m, 1H), 7.50 (dd, 1H, J_1 = 7.7 Hz, J_2 = 1.6 Hz); ^{13}C NMR δ 154.6, 131.3, 128.6, 127.3, 126.5, 121.6, 114.7, 112.6, 78.6, 75.5, 56.1; IR (neat) ν 3280, 2110, 1620, 1590, 1570 cm^{-1}. Anal. Calcd for $C_{11}H_{10}O$: C, 83.51; H, 6.37. Found: C, 83.65; H, 6.44.

General Procedure for the Pauson−Khand Reaction.

Method A. A 1.00 mmol sample of the enyne **2** was dissolved in dry toluene (40 mL) at room temperature under argon, in a flask containing 8 times the mass of the enyne of powdered 4 Å molecular sieves. To this solution was added 1.20 mmol of $Co_2(CO)_8$, and the resulting mixture was stirred for 2 h until total complexation of the enyne (TLC). The reaction was then cooled to −10 °C with an ice/salt bath, and a suspension of Me_3NO (9.00 mmol) in toluene at 0 °C was added dropwise. After 18 h of stirring, the mixture was filtrated, the solvent was evaporated under vacuum and the crude product was purified and/or separated by flash chromatography (hexane/EtOAc mixtures).

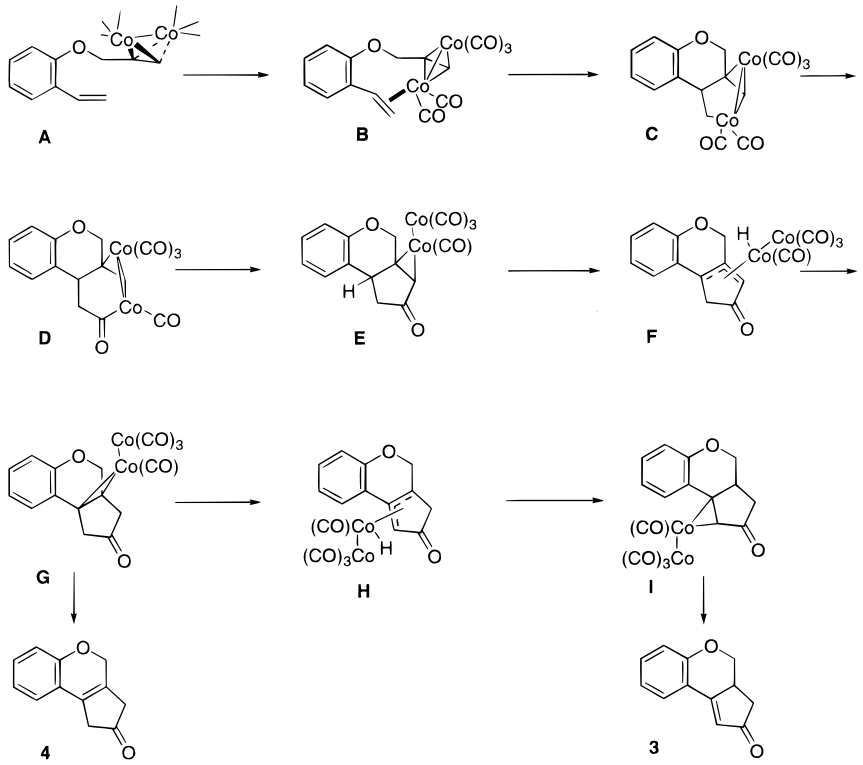
Method B. A 1.00 mmol sample of the enyne **2** was dissolved in dry toluene (40 mL) at room temperature under argon, in a flask containing 8 times the mass of the enyne of powdered 4 Å molecular sieves. To this solution was added

(35) Castro, J.; Moyano, A.; Pericàs, M.; Riera, A. *Tetrahedron* **1995**, *51*, 6541.

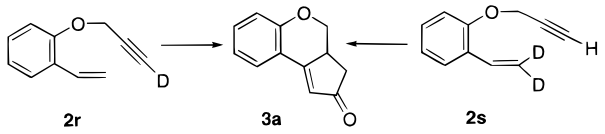
(36) The ^{1}H NMR spectra of these two cobalt complexes were compared with that of the cobalt hexacarbonyl complex of **2a**. See Experimental Section.

(37) Phosphorus ylide was generated by stirring the corresponding (1.50 mmol) phosphonium salt with (1.30 mmol) BuLi (1.6 M in hexane), KHMDS (0.5 M in toluene), or NaOH (phase-transfer conditions) for 30 min.

Scheme 4



Scheme 5



1.20 mmol of $Co_2(CO)_8$, and the resulting mixture was stirred for 2 h until total complexation of the enyne (TLC). The reaction was refluxed for 18 h. After filtration and solvent elimination the crude was purified and/or separated by flash chromatography (hexane/EtOAc mixtures).

Preparation of 3a and 4a. Following method A, from 0.15 g (0.95 mmol) of **2a**, 0.39 g (1.15 mmol) of $Co_2(CO)_8$, 1.20 g of molecular sieves, and 0.64 g (8.55 mmol) of TMANO, 0.11 g (60%) of **3a** as a white solid (mp 100−102 °C (hexane/EtOAc)) and 0.02 g (10%) of **4a** as a white solid (mp 127−128 °C (hexane/EtOAc)) were obtained.

3a,4-Dihydro-*3H*-cyclopenta[*c*]chromen-2-one, 3a: ^{1}H NMR δ 2.07 (dd, 1H, J_1 = 18.1 Hz, J_2 = 4.4 Hz), 2.72 (dd, 1H, J_1 = 18.1 Hz, J_2 = 6.6 Hz), 3.25−3.37 (m, 1H), 3.88 (dd, 1H, J_1 = 13.2 Hz, J_2 = 10.4 Hz), 4.61 (dd, 1H, J_1 = 10.4 Hz, J_2 = 5.5 Hz), 6.35 (d, 1H, J = 1.6 Hz), 6.96−7.04 (m, 2H), 7.37 (t, 1H, J = 8.2 Hz), 7.56 (dd, 1H, J_1 = 8.2 Hz, J_2 = 1.6 Hz); ^{13}C NMR δ 206.1, 168.6, 156.0, 133.3, 127.2, 121.7, 121.3, 117.9, 117.4, 70.1, 37.8, 36.3; IR (KBr) ν 1695, 1605, 1475 cm^{-1}. Anal. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.39; H, 5.72.

3,4-Dihydro-*1H*-cyclopenta[*c*]chromen-2-one, 4a: ^{1}H NMR δ 3.01 (s, 2H), 3.18 (t, 2H, J = 3.3 Hz), 5.01 (m, 2H), 6.81 (d, 1H, J = 8.2 Hz), 6.85−6.90 (m, 2H), 7.11−7.17 (m, 1H); ^{13}C NMR δ 212.1, 153.0, 129.3, 129.2, 128.7, 123.5, 121.3, 119.8, 115.7, 66.2, 43.7, 40.9; IR (KBr) ν 1740, 1695, 1600, 1570, 1490 cm^{-1}. Anal. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41, Found: C, 77.50; H, 5.54.

Preparation of 3c and 4c. Following method B, from 0.10 g (0.42 mmol) of **2c**, 0.17 g (0.50 mmol) of $Co_2(CO)_8$, 0.80 g of molecular sieves, and 0.28 g (3.78 mmol) of TMANO, 0.06 g (55%) (method A, 90%) of **3c** as an orange solid (mp 178−179 °C (hexane/EtOAc)) and 0.04 g (35%) (only traces when method A is used) of **4c** as a pale yellow solid (mp 162−163 °C (hexane/EtOAc)) were obtained.

8-Bromo-3a,4-dihydro-*3H*-cyclopenta[*c*]chromen-2-one, 3c: ^{1}H NMR δ 2.08 (dd, 1H, J_1 = 18.1 Hz, J_2 = 4.4 Hz), 2.73 (dd, 1H, J_1 = 18.1 Hz, J_2 = 6.6 Hz), 3.23−3.34 (m, 1H), 3.86 (dd, 1H, J_1 = 13.2 Hz, J_2 = 10.4 Hz), 4.62 (dd, 1H, J_1 = 10.4 Hz, J_2 = 5.5 Hz), 6.35 (d, 1H, J = 1.6 Hz), 6.87 (d, 1H, J = 9.0 Hz), 7.44 (dd, 1H, J_1 = 9.0 Hz, J_2 = 2.2 Hz), 7.66 (d, 1H, J = 2.2 Hz); ^{13}C NMR δ 205.6, 166.8, 154.9, 135.8, 129.4, 122.6, 119.7, 118.9, 113.4, 70.1, 37.7, 36.0; IR (KBr) ν 1695, 1605, 1470 cm^{-1}. Anal. Calcd for $C_{12}H_9BrO_2$: C, 54.37; H, 3.42. Found: C, 54.23; H, 3.46.

8-Bromo-3,4-dihydro-*1H*-cyclopenta[*c*]chromen-2-one, 4c: ^{1}H NMR δ 3.03 (s, 2H), 3.15 (t, 2H, J = 3.3 Hz), 5.01 (m, 2H), 6.69 (d, 1H, J = 8.2 Hz), 6.96 (d, 1H, J = 2.2 Hz), 7.22 (dd, 1H, J_1 = 8.2 Hz, J_2 = 2.2 Hz); ^{13}C NMR δ 211.5, 152.0, 131.7, 130.1, 128.3, 126.1, 121.6, 117.4, 113.2, 66.3, 43.6, 40.7; IR (KBr) ν 1750, 1485 cm^{-1}. Anal. Calcd for $C_{12}H_9BrO_2$: C, 54.37; H, 3.42. Found: C, 54.19; H, 3.41.

Preparation of 3d and 4d. Following method A, from 0.15 g (0.80 mmol) of **2d**, 0.33 g (0.96 mmol) of $Co_2(CO)_8$, 1.20 g of molecular sieves, and 0.54 g (7.20 mmol) of TMANO, 0.06 g (37%) of **3d** as a yellow solid (mp 123−125 °C (hexane/EtOAc)) and 0.06 g (35%) of **4d** as a yellow solid (mp 130−131 °C (hexane/EtOAc)) were obtained.

7-Methoxy-3a,4-dihydro-*3H*-cyclopenta[*c*]chromen-2-one, 3d: ^{1}H NMR δ 2.06 (dd, 1H, J_1 = 18.1 Hz, J_2 = 4.4 Hz), 2.68 (dd, 1H, J_1 = 18.1 Hz, J_2 = 6.6 Hz), 3.21−3.32 (m, 1H), 3.83 (s, 3H), 3.86 (dd, 1H, J_1 = 13.2 Hz, J_2 = 10.4 Hz), 4.59 (dd, 1H, J_1 = 10.4 Hz, J_2 = 5.5 Hz), 6.21 (d, 1H, J = 1.6 Hz), 6.45 (d, 1H, J = 2.5 Hz), 6.59 (dd, 1H, J_1 = 8.5 Hz, J_2 = 2.5 Hz), 7.46 (d, 1H, J = 8.5 Hz); ^{13}C NMR δ 205.9, 168.6, 163.9, 157.8, 128.5, 119.4, 110.7, 109.7, 101.3, 70.2, 55.5, 37.6, 36.4; IR (KBr) ν 1680, 1590, 1490 cm^{-1}. Anal. Calcd for $C_{13}H_{12}O_3$: C, 72.21; H, 5.59. Found: C, 72.45; H, 5.70.

7-Methoxy-3,4-dihydro-*1H*-cyclopenta[*c*]chromen-2-one, 4d: ^{1}H NMR δ 3.00 (s, 2H), 3.16 (t, 2H, J = 3.3 Hz), 3.79 (s, 3H), 4.99 (m, 2H), 6.42−6.46 (m, 2H), 6.79 (d, 1H, J = 7.7 Hz); ^{13}C NMR δ 211.8, 160.7, 154.3, 128.9, 125.5, 124.2, 113.1, 106.5, 101.9, 66.4, 55.3, 43.5, 40.9; IR (KBr) ν 1740, 1700, 1660, 1605 cm^{-1}. Anal. Calcd for $C_{13}H_{12}O_3$: C, 72.21; H, 5.59. Found: C, 72.44; H, 5.68.

3-Methyl-4,9b-dihydro-*1H*-cyclopenta[*c*]chromen-2-one, 6h. Following method A, from 0.15 g (0.87 mmol) of **2h**,

0.36 g (1.04 mmol) of $Co_2(CO)_8$, 1.20 g of molecular sieves and 0.59 g (7.83 mmol) of TMANO, 0.09 g (50%) of **6h** was obtained as a colorless oil: ^{1}H NMR δ 1.75 (s, 3H), 2.51 (dd, 1H, J_1 = 18.1 Hz, J_2 = 2.7 Hz), 2.98 (dd, 1H, J_1 = 18.1 Hz, J_2 = 6.6 Hz), 3.92−4.03 (m, 1H), 4.94 (d, 1H, J = 14.8 Hz), 5.06 (d, 1H, J = 14.8 Hz), 6.89 (d, 1H, J = 7.8 Hz), 6.96 (t, 1H, J = 7.8 Hz), 7.07 (d, 1H, J = 7.7 Hz), 7.16 (t, 1H, J = 7.7 Hz); ^{13}C NMR δ 206.9, 163.9, 153.6, 134.5, 128.1, 126.8, 125.8, 121.8, 116.9, 64.7, 40.0, 37.1, 7.9; IR (neat) ν 1710, 1660, 1600, 1580, 1480 cm^{-1}. Anal. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04. Found: C, 77.69; H, 5.98.

9b-Methyl-4,9b-dihydro-*1H*-cyclopenta[*c*]chromen-2-one, 6k. Following method B, from 0.15 g (0.87 mmol) of **2k**, 0.36 g (1.05 mmol) of $Co_2(CO)_8$, and 1.20 g of molecular sieves, 0.07 g (40%) of **6k** was obtained as a colorless oil: ^{1}H NMR δ 1.58 (s, 3H), 2.75 (d, 1H, J = 18.1 Hz), 2.86 (d, 1H, J = 18.1 Hz), 5.05 (d, 1H, J = 14.8 Hz), 5.13 (d, 1H, J = 14.8 Hz), 6.04 (s, 1H), 6.88 (d, 1H, J = 8.8 Hz), 6.98 (t, 1H, J = 7.1 Hz), 7.12−7.19 (m, 2H); ^{13}C NMR δ 207.0, 171.4, 146.2, 132.7, 127.7, 120.4, 117.8, 115.4, 115.1, 46.7, 39.9, 36.7, 29.7; IR (neat) ν 1710, 1640, 1575 cm^{-1}. Anal. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04, Found: C, 77.87; H, 5.96.

1-Methyl-3a,4-dihydro-*3H*-cyclopenta[*c*]chromen-2-one, 3l: Following method B, from 0.10 g (0.58 mmol) of **2l**, 0.24 g (0.70 mmol) of $Co_2(CO)_8$, and 0.80 g of molecular sieves, 0.05 g (40%) of **3l** was obtained as a yellow solid: mp 109−111 °C (hexane/EtOAc); ^{1}H NMR δ 1.97 (dd, 1H, J_1 = 18.1 Hz, J_2 = 3.8 Hz), 2.09 (d, 3H, J = 1.6 Hz), 2.72 (dd, 1H, J_1 = 18.1 Hz, J_2 = 6.6 Hz), 3.16−3.22 (m, 1H), 3.82 (dd, 1H, J_1 = 13.2 Hz, J_2 = 10.4 Hz), 4.61 (dd, 1H, J_1 = 10.4 Hz, J_2 = 5.5 Hz), 6.97−7.06 (m, 2H), 7.34 (t, 1H, J = 8.8 Hz), 7.68 (d, 1H, J = 8.2 Hz); ^{13}C NMR δ 206,6, 159.5, 155.8, 132.0, 131.7, 128.2, 120.9, 119.0, 117.7, 70.5, 36.0, 34.7, 9.5; IR (KBr) ν 1685, 1615, 1600 cm^{-1}. Anal. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04. Found: C, 78.12; H, 6.33.

3,3a,4,5-Tetrahydrocyclopenta[*c*]quinolin-2-one, 3o. Following method A, from 0.06 g (0.38 mmol) of **2o**, 0.16 g (0.46 mmol) of $Co_2(CO)_8$, 0.48 g of molecular sieves and 0.26 g (3.42 mmol) of TMANO, 0.04 g (55%) of **3o** was obtained as a yellow oil: ^{1}H NMR δ 2.07 (dd, 1H, J_1 = 18.1 Hz, J_2 = 3.9 Hz), 2.71−2.79 (m, 1H), 3.11−3.15 (m, 2H), 3.58−3.69 (m, 1H), 4.48 (brs, 1H), 6.30 (d, 1H, J = 1.7 Hz), 6.63 (d, 1H, J = 8.3 Hz), 6.74 (t, 1H, J = 8.3 Hz), 7.21 (t, 1H, J = 8.3 Hz), 7.50 (dd, 1H, J_1= 8.3 Hz); ^{13}C NMR δ 207.0, 171.4, 146.2, 132.8, 127.7, 120.4, 117.8, 115.4, 115.1, 46.7, 39.9, 36.7; IR (neat) ν 3300, 1650, 1610, 1575 cm^{-1}: Anal. Calcd for $C_{12}H_{11}NO$: C, 77.81; H, 5.99, N 7.56. Found: C, 77.61; H, 5.90, N 7.53.

3-Methylencyclopentene-3′-spyro-4-chromane, 7p. Following method B, from 0.10 g (0.50 mmol) of **2p**, 0.21 g (0.61 mmol) of $Co_2(CO)_8$, and 0.80 g of molecular sieves, 0.03 g (30%) of **7p** was obtained as a colorless oil: ^{1}H NMR δ 2.09−2.27 (m, 2H), 2.36−2.57 (m, 2H), 4.59 (d, 1H, J = 11.8 Hz), 4.65 (d, 1H, J = 11.8 Hz), 4.99 (s, 1H), 5.05 (s, 1H), 5.53 (m, 1H), 6.13 (m, 1H), 6.83 (d, 1H, J = 8.2 Hz), 6.90 (t, 1H, J = 7.2 Hz), 7.06−7.15 (m, 2H); ^{13}C NMR δ 153.8, 144.8, 136.0, 133.3, 130.2, 128.4, 127.4, 121.1, 116.5, 110.8, 69.4, 55.0, 43.9, 31.2; IR (neat) ν 1650, 1600, 1480 cm^{-1}. Anal. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 85.00; H, 7.21.

3-Methylencyclohexene-3′-spyro-4-chromane, 7q. Following method B, from 0.15 g (0.71 mmol) of **2q**, 0.29 g (0.85 mmol) of $Co_2(CO)_8$, and 1.20 g of molecular sieves, 0.03 g (20%) of **7q** was obtained as a purple oil unpurified with a small amount of an unidentified cobalt complex: ^{1}H NMR δ 1.55−1.80 (m, 4H), 1.81−2.00 (m, 2H), 2.04−2.40 (m, 2H), 4.50 (d, 1H, J = 12.1 Hz), 4.70 (d, 1H, J = 12.1 Hz), 5.08 (s, 1H), 5.26 (s, 1H), 5.39 (m, 1H), 6.07 (m, 1H), 6.80 (d, 1H, J = 8.2 Hz), 6.91 (t, 1H, J = 8.2 Hz), 7.10 (d, 1H, J = 8.2 Hz), 7.19 (d, 1H, J = 8.2 Hz).

General Method for the Obtention of 5a, 5c, and 5f. A 1.00 mmol sample of the enyne **2** was dissolved in dry MeCN (40 mL) at room temperature under argon, in a flask containing 8 times the mass of the enyne of powdered 4 Å molecular sieves. To this solution was added 1.20 mmol of $Co_2(CO)_8$, and the resulting mixture was stirred for 2 h until total complexation of the enyne (TLC). The reaction was then cooled to −10 °C with an ice/salt bath, and a suspension of Me_3NO (9.00 mmol) in MeCN at 0 °C was added dropwise. After 18 h of stirring, the mixture was filtrated, the solvent was evaporated under vacuum, and the crude product was purified by flash chromatography (hexane/EtOAc mixtures).

4-Bromo-2-vinylphenol, 5c. Following the general method, from 0.10 g (0.42 mmol) of **2c**, 0.17 g (0.50 mmol) of $Co_2(CO)_8$, 0.80 g of molecular sieves, and 0.28 g (3.78 mmol) of TMANO, 0.04 g (65%) of **5c** was obtained as a pale yellow oil: ^{1}H NMR δ 5.37 (d, 1H, J = 11.3 Hz), 5.74 (d, 1H, J = 17.6 Hz), 5.83 (bs, 1H), 6.69 (d, 1H, J = 8.8 Hz), 6.88 (dd, 1H, J_1 = 17.6 Hz, J_2 = 11.3 Hz), 7.21 (dd, 1H, J_1 = 8.8 Hz, J_2 = 2.2 Hz), 7.50 (d, 1H, J = 2.2 Hz); ^{13}C NMR δ 152.1, 149.1, 131.3, 130.3, 129.6, 117.5, 116.6, 112.8; IR (neat) ν 3400, 1630, 1480, 1405 cm^{-1}.

General Method for the Obtention of Cobalt Hexacarbonyl−Alkyne Complexes of Enynes 2. A 1.00 mmol sample of the enyne **2** was dissolved in dry toluene (40 mL) at room temperature under argon. To this solution was added 1.20 mmol of $Co_2(CO)_8$, and the resulting mixture was stirred for 2 h until total complexation of the enyne (TLC). The mixture was filtrated through Celite and the solvent evaporated under vacuum to obtain pure cobalt hexacarbonylalkyne complexes.

[2-(2-Propynyloxy)styrene]dicobalt Hexacarbonyl. From 0.05 g (0.32 mmol) of **2a**, 0.13 g (0.38 mmol) of $Co_2(CO)_8$, and 0.40 g of molecular sieves, 0.14 g (quantitative) of the complex was obtained as a red oil: ^{1}H NMR δ 5.21 (s, 2H), 5.22 (dd, 1H, J_1 = 11.0 Hz, J_2 = 1.1 Hz), 5.69 (dd, 1H, J_1 = 17.6 Hz, J_2 = 1.1 Hz), 6.11 (s, 1H), 6.91 (d, 1H, J = 8.2 Hz), 6.98 (t, 1H, J = 7.7 Hz), 7.16 (dd, 1H, J_1 = 17.6 Hz, J_2 = 11.0 Hz), 7.24 (m, 1H), 7.54 (d, 1H, J = 7.7 Hz).

[2-(3-Deuterio-2-Propynyloxy)styrene]dicobalt hexacarbonyl: From 0.03 g (0.19 mmol) of **2r**, 0.08 g (0.23 mmol) of $Co_2(CO)_8$, and 0.24 g of molecular sieves, 0.08 g (quantitative) of the complex was obtained as a red oil. ^{1}H NMR δ 5.21 (s, 2H), 5.22 (d, 1H, J = 11.5 Hz), 5.69 (d, 1H, J = 17.6 Hz), 6.91 (d, 1H, J = 8.2 Hz), 7.00 (t, 1H, J = 7.7 Hz), 7.18 (dd, 1H, J_1 = 17.6 Hz, J_2 = 11.5 Hz), 7.25 (m, 1H), 7.55 (d, 1H, J = 7.7 Hz).

[2-(2-Propynyloxy)-β,β-dideuteriostyrene]dicobalt Hexacarbonyl. From 0.15 g (0.95 mmol) of **2s**, 0.39 g (1.14 mmol) of $Co_2(CO)_8$, and 1.20 g of molecular sieves, 0.42 g (quantitative) of the complex was obtained as a red solid: mp 55−56 °C; ^{1}H NMR δ 5.20 (s, 2H), 6.10 (s, 1H), 6.90 (d, 1H, J = 8.2 Hz), 6.98 (t, 1H, J = 7.1 Hz), 7.16 (d, 1H, J = 7.1 Hz), 7.23 (m, 1H), 7.53 (d, 1H, J = 7.7 Hz).

[2-(3-Trimethylsilyl-2-Propynyloxy)styrene]dicobalt Hexacarbonyl. From 0.02 g (0.09 mmol) of **2j**, 0.04 g (0.10 mmol) of $Co_2(CO)_8$, and 0.16 g of molecular sieves, 0.05 g (quantitative) of the complex was obtained as a red oil: ^{1}H NMR δ 0.06 (s, 3H), 0.30 (s, 6H), 5.21 (dd, 1H, J_1 = 11.0 Hz, J_2 = 1.6 Hz), 5.22 (s, 2H), 5.67 (dd, 1H, J_1 = 18.1 Hz, J_2 = 1.6 Hz), 6.94 (d, 1H, J = 8.2 Hz), 6.98 (t, 1H, J = 7.7 Hz), 7.17 (dd, 1H, J_1 = 18.1 Hz, J_2 = 11.0 Hz), 7.25 (m, 1H), 7.54 (d, 1H, J = 7.7 Hz).

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Supporting Information Available: Spectroscopic and analytical characterization of compounds **2b**−**t**, **3b**, **3e**−**g**, **3m**,**n**, **4b**,**f**, **5a**,**f**, and **6i**. This material is available free of charge via the Internet at http://pubs.acs.org.

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