

Regioselective Intramolecular Pauson–Khand Reactions of C₆₀: An Electrochemical Study and Theoretical Underpinning

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Dedicated to Professor José Elguero on the occasion of his 70th birthday

Abstract: Suitably functionalized fulleropyrrolidines endowed with one or two propargyl groups at the C-2 position of the pyrrolidine ring (1,6-enynes) react efficiently and regioselectively with [Co₂(CO)₈] to afford the respective Pauson–Khand products with an unprecedented three (**5a–d**, **7**, and **24**) or five (**25**) pentagonal rings, respectively, fused onto the fullerene sphere. Fulleropyrrolidines with 1,7-, 1,9-, 1,10-, or 1,11-enyne moieties do not undergo the PK reaction and, instead, the inter-

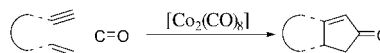
mediate dicobalt complexes formed with the alkynyl group are isolated in quantitative yields. These differences in reactivity have been studied by DFT calculations with a generalized gradient approximation (GGA) functional and several important energy and structural

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differences were found for the intermediates formed by the interaction between the coordinatively unsaturated Co atom and the π system of C₆₀ in 1,6- and 1,7-enynes. The different lengths of the alkyne chains are responsible for the observed reactivities. Cyclic voltammetry reveals that the presence of the cyclopentenone's carbonyl group connected directly to the C₆₀ core results in PK compounds with remarkable electron-accepting ability.

Introduction

The [2+2+1] cycloaddition of alkyne, alkene, and carbon monoxide mediated or catalyzed by a transition metal, also known as the Pauson–Khand (PK) reaction, has been widely used in organic synthesis for the construction of biologically active five-membered carbocycles in a convergent approach (Scheme 1).^[1] In contrast, the use of this successful reaction has almost been neglected in materials science despite the potential for the construction of complex modified molecules that exhibit nonconventional properties. With this in



Scheme 1. General scheme for the Pauson–Khand reaction.

mind, we recently reported in a preliminary communication the first example of a highly efficient and regioselective intramolecular PK reaction in which fullerene C₆₀ was used as the alkene component in the [2+2+1] cycloaddition reaction.^[2]

Fullerenes are a class of molecule made up of carbon atoms with an unusual hybridization (sp^{2.3})^[3] that exhibit a chemical reactivity similar to that of electron-deficient olefins.^[4] Although electron-poor alkenes are not suitable substrates for PK reactions as a result of their low reactivity and the competing elimination reaction that can take place to afford 1,3-dienes, a wide variety of inter- and intramolecular PK reactions involving alkenes with electron-withdrawing substituents have been reported in recent years.^[5] Therefore, fullerenes have emerged as suitable new substrates for the PK reaction provided that they have a spherical surface with multiple reactive double bonds and, in addition, the competing β -hydride elimination reaction has been over-

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come due to the absence of hydrogen atoms in their structure.

To carry out a systematic study of the PK reaction of the fullerene sphere we have synthesized a wide variety of novel suitably functionalized fulleropyrrolidines bearing one or two alkyne units on the pyrrolidine ring. Thus, suitably designed 1,6- and 1,7-enynes, as well as other enynes with a larger separation between the alkene and the alkyne groups, with one fullerene double bond as the alkene component, have been prepared (see Scheme 2, Scheme 3, and Scheme 4). Further, [2+2+1] cobalt-mediated carbonylative cycloaddition of the starting enynes should afford new fullerene *cis*-1 bisadducts endowed with unprecedented fused cyclopentenone structures. An electrochemical study of the novel modified fullerenes has been carried out by cyclic and square-wave voltammetry at room temperature in order to determine the redox behavior of the starting fulleropyrrolidines and the respective *cis*-1 bisadducts obtained in the PK reaction. Finally, to gain a better understanding of the effect of the curved fullerene surface as well as the length of the chain connecting the alkene and the alkyne functional groups on the PK reaction, theoretical calculations have been carried out on 1,6- and 1,7-enynes by using density functional theory (DFT) with a generalized gradient approximation (GGA) functional (see the Computational Details section).

Abstract in Spanish: *Fulleropyrrolidinas adecuadamente funcionalizadas con uno o dos grupos propargilo en el C-2 del anillo de pirrolidina (1,6-eninos), reaccionan con [Co₂(CO)₈] proporcionando de manera regioselectiva y con altos rendimientos los correspondientes productos Pauson-Khand (PK). Estos compuestos presentan una estructura sin precedentes con tres (5a–d, 7, 24) o cinco (25) anillos pentagonales fusionados sobre la esfera del C₆₀. Las fulleropyrrolidinas que contienen los grupos 1,7-, 1,9-, 1,10- o 1,11-enino no reaccionan en las condiciones de PK, aislándose únicamente los complejos de cobalto intermedios con rendimientos cuantitativos. Esta diferente reactividad ha sido estudiada mediante cálculos teóricos realizados a nivel DFT, utilizando el funcional de la aproximación del gradiente generalizado (GGA). Dichos cálculos muestran importantes diferencias energéticas y estructurales entre los intermedios formados por el cobalto coordinativamente insaturado y el sistema π del C₆₀ en los 1,6- y 1,7-eninos. La diferente longitud de la cadena hidrocarbonada que soporta el grupo alquino, es la responsable de la reactividad observada. El estudio de los productos de PK mediante voltamperometría cíclica (CV) muestra que la presencia del grupo CO del anillo de ciclopentenona unido directamente al C₆₀ es responsable de la notable capacidad aceptora de estos nuevos compuestos.*

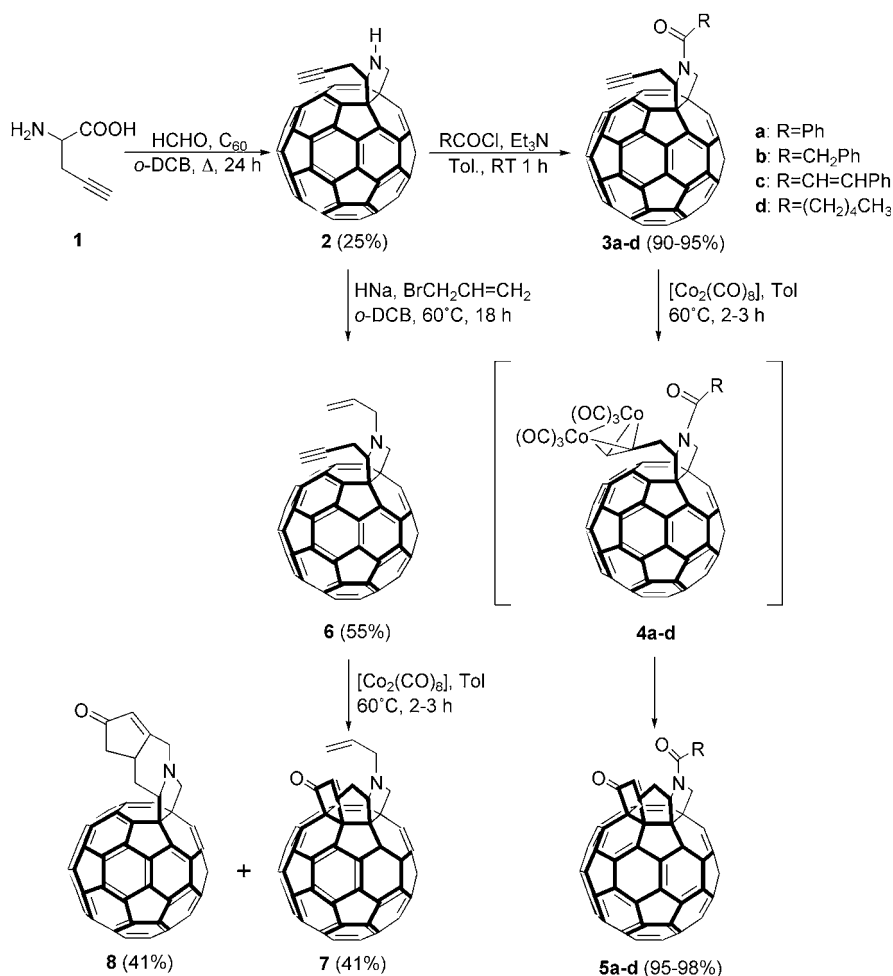
Results and Discussion

Synthesis: The Pauson–Khand reaction has a broad scope; it has proved successful with many functional groups (ethers, alcohols, tertiary amines, acetals, esters, amides, and heterocycles) as well as with different promoters, metal catalysts, and experimental conditions.^[1] An important disadvantage of the PK reaction is, however, that the intermolecular process is generally limited to strained olefins. Fullerenes are known to have a strained spherical geometry and, therefore, they appear to be suitable candidates for the PK reaction. However, all attempts to carry out the intermolecular PK reaction with C₆₀, alkynes, and [Co₂(CO)₈] were unsuccessful. Intramolecular PK reactions of fullerenes require the design of new fullerene derivatives suitably functionalized with an alkyne group. With this in mind, fulleropyrrolidines endowed with an alkyne group at the C-2 position of the pyrrolidine ring fulfil the requirements of appropriate geometry and variable length between the fullerene double bond and the alkyne.

Most of the intramolecular PK reactions reported have been carried out with systems derived from hept-1-en-6-yne or propargyl allyl ethers or amines which afford cyclopentenones fused to a carbo- or heterocyclic pentagonal ring. Enynes connected through aromatic rings have also been successfully used in the PK reaction which has allowed the synthesis of medium-sized rings (six- to eight-membered rings).^[6]

To carry out a thorough study of the scope of the PK reaction using C₆₀ as the alkene moiety, we synthesized a wide variety of suitably functionalized fulleropyrrolidines. Since hept-1-en-6-yne is the most widely used substrates in the PK reaction, we first prepared fulleropyrrolidine **2** which contains the required 1,6-enyne moiety. Compound **2** was synthesized by 1,3-cycloaddition of the azomethyne ylide generated in situ from DL-propargylglycine (**1**) and formaldehyde to C₆₀ in refluxing *o*-dichlorobenzene (*o*-DCB) following Prato's procedure (Scheme 2).^[7]

Fulleropyrrolidine **2** is suitably functionalized to undergo the PK reaction provided that it contains the required 1,6-enyne moiety. However, its reaction with [Co₂(CO)₈] in toluene at 60 °C (or in the presence of molecular sieves) did not afford the PK product owing to the ability of the lone-pair of the pyrrolidine's nitrogen atom to coordinate to the cobalt complex. Note that although secondary amines are not compatible with the PK reaction, fulleropyrrolidines are known to exhibit remarkably low basicity and nucleophilicity owing to the through-space interactions of the nitrogen's lone-pair and the fullerene π system. This results in a basicity six orders of magnitude lower than that of pyrrolidine.^[8] Therefore, we acylated fulleropyrrolidine **2** to prevent the negative effect of the nitrogen's lone-pair as well as to increase the solubility of the resulting compound for use in further chemical transformations. Thus, the reaction of **2** with different acyl chlorides afforded soluble *N*-acylfulleropyrrolidines (**3a–d**) in excellent yields (90–95 %). In contrast to fulleropyrrolidine **2**, whose ¹H NMR spectrum revealed a



Scheme 2.

well-resolved set of signals, the ¹H NMR spectra of compounds **3a–d** showed unresolved broad signals at room temperature due to the rotational barrier of the N–CO bond. This dynamic behavior has been found in related systems^[8] and, recently, it has been observed that the presence of the fullerene fragment close to the amide's nitrogen atom accelerates the rotation of the amide by a factor of 10³ at room temperature owing to the strong electron-withdrawing effect of the C₆₀ unit, thus lowering the N–CO rotational barrier ($\Delta H^{\ddagger}_{\text{N-CO}} = 16.0 \pm 0.1 \text{ kcal mol}^{-1}$).^[9] Figure 1 shows the variable-temperature high-resolution (500 MHz) ¹H NMR spectrum of compound **3a**. The signals were well resolved at 333 K; coalescence occurred at 295.12 K and therefore the energy barrier was $\Delta H^{\ddagger}_{\text{N-CO}} = 14.2 \pm 0.1 \text{ kcal mol}^{-1}$.

N-Acylfulleropyrrolidines (**3a–d**) were treated with stoichiometric amounts of [Co₂(CO)₈] in toluene at 60°C in the presence of previously activated molecular sieves (4 Å)^[10] to afford the respective PK products **5a–d** in almost quantitative yields (see the Experimental Section). Intermediate dicobalt carbonyl complexes (**4a–d**) can be isolated by carrying out the reaction at room temperature.^[11]

The PK products **5a–d** were unambiguously confirmed as the *cis*-1 biscycloadducts with an unprecedented structure that contains three pentagonal rings fused onto the fullerene surface. The structures of the novel compounds were established by spectroscopy (UV/Vis, FTIR, ¹H, and ¹³C NMR, and MS); the proton of the enone moiety at $\delta \sim 6.8 \text{ ppm}$ in the ¹H NMR spectra was used as a diagnostic signal. The structures of **5a–d** were further confirmed by HMQC and HMBC experiments, comparison with UV/Vis spectra,^[12] and by high-resolution MS (see the Experimental Section). Since the PK compounds exhibit C₁ symmetry, they were obtained as racemates.

The reaction of fulleropyrrolidine **2** with allyl bromide under basic conditions led to compound **6** which is endowed with a highly reactive allyl group able to compete with the fullerene double bond in the PK reaction. Further reaction of **6** with [Co₂(CO)₈] under the same experimental conditions (molecular sieves, toluene, 60°C) afforded the PK product **7** (41% yield), together with

compound **8** (41%), which results from the PK reaction of the allyl moiety. Compounds **7** and **8** are formed in the same

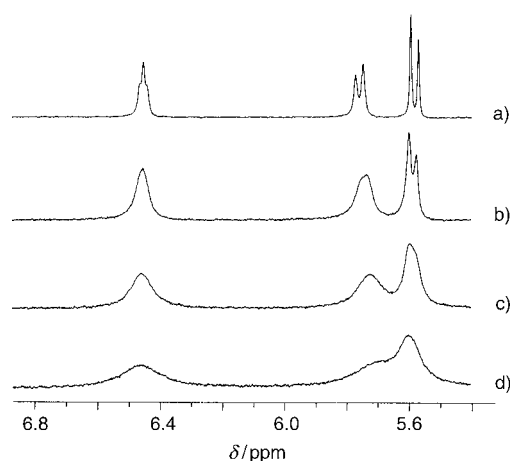


Figure 1. ¹H NMR spectra (500 MHz, CDCl₃/CS₂) of compound **3a** recorded at different temperatures: a) 333 K, b) 313 K, c) 303 K, d) 295.12 K.

yields, thus showing that fullerene double bonds are as reactive as those of the allyl moiety in the versatile PK reaction.

In the light of these results, we decided to expand the scope of the PK reaction of the fullerenes to other derivatives with larger enyne moieties. Thus, in addition to the expected *cis*-1 biscycloadducts, other regioisomeric bisadducts may also be formed depending on the length of the chain connecting the fullerene double bond and the alkyne group. Thus, we have synthesized novel fulleropyrrolidines (**10** and **14**) with a 1,7-enyne moiety, which, under PK reaction conditions, should lead to cyclopentenones fused to six-membered carbocyclic rings. Thus, by following Prato's procedure^[7] we have synthesized fulleropyrrolidines **10a–g** from different 4,5-disubstituted 2-alkynylbenzaldehydes (**9a** and **9c**) by using glycine or sarcosine (*N*-methylglycine) and C₆₀ (see the Experimental Section). Similarly, fulleropyrrolidines **14a–c** were synthesized from 4-pentynal (**13**), which was generated in situ by oxidation of 4-pentynol (**12**) with pyridinium chlorochromate (PCC) (Scheme 3).

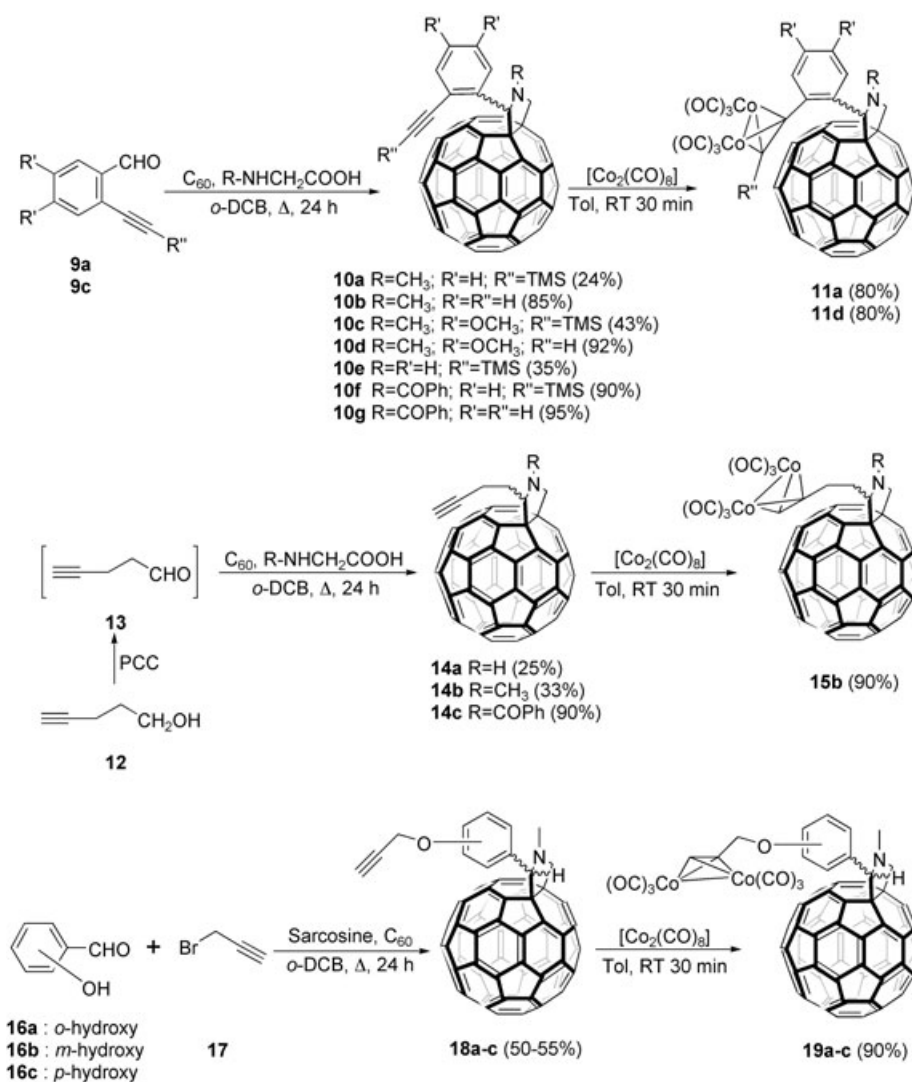
Compounds **10a–g** and **14a–c** were fully characterized by spectroscopic techniques. Further reaction with [Co₂(CO)₈] under the experimental conditions used for the preparation of **5a–d**, **7** and **8** did not afford, in any case, the corresponding PK products. Thus, the reactions carried out with *N*-substituted (N-CH₃, N-COPh) pyrrolidines or by activating the alkynyl group by introducing electron-releasing methoxy groups onto the benzene ring were futile. Instead, the intermediate dicobalt complexes **11** and **15** were obtained in almost quantitative yields. Further attempts to synthesize the PK products from the intermediate complexes by raising the temperature (RT → 60 °C) either in the presence or absence of molecular sieves also failed. Note that at temperatures higher than 60 °C, cobalt atoms were lost to give the precursor fulleropyrrolidines **10** and **14**, together with other uncharacterized products resulting from extensive decomposition.

Fulleropyrrolidines **18a–c** with 1,9-, 1,10-, and 1,11-enyne moieties, respectively, were prepared in two steps; the relevant propargyloxybenzaldehyde

was prepared from commercially available *o*-, *m*-, and *p*-hydroxybenzaldehyde and propargyl bromide under basic conditions and then treated with C₆₀ and sarcosine in *o*-DCB under standard conditions. Attempts to form the PK products by using the general conditions described above led only to the dicobalt complexes **19a–c** in quantitative yield, which behaved similarly to the cobalt complexes **11** and **15** under thermal treatment (Scheme 3).

All the dicobalt complexes studied were fully characterized by spectroscopic techniques. As a typical signature, three bands at 2000–2100 cm⁻¹, which correspond to the CO groups of the cobalt complex, were observed in the FTIR spectra, as well as a singlet at around δ = 6.2 ppm, which corresponds to the proton of the carbon atom linked to the cobalt atoms, in the ¹H NMR spectra of the complexes.

Note that there are remarkable differences in the reactivities of the fulleropyrrolidines endowed with a 1,6-enyne moiety, which led to PK products in almost quantitative yields, and those with longer-length enynes, which in any



Scheme 3.

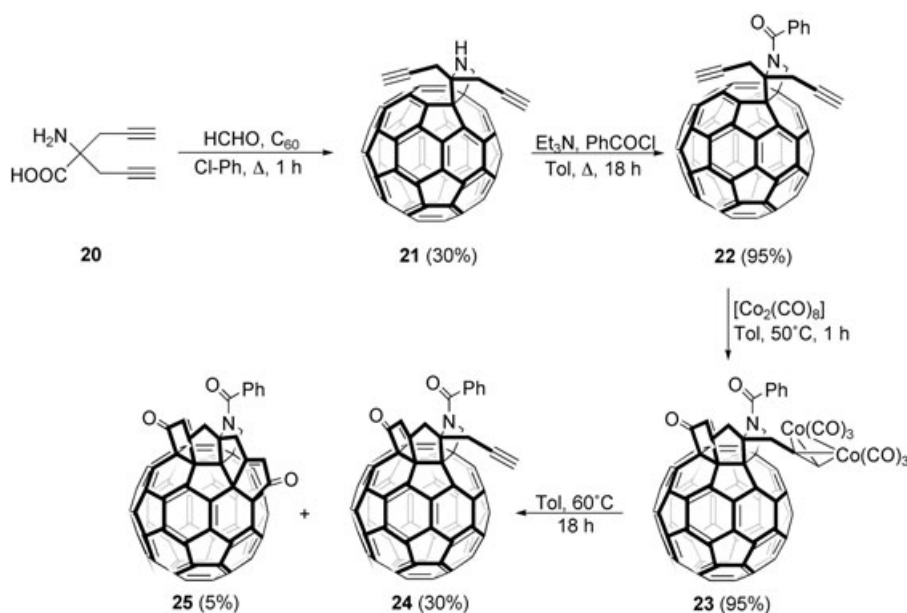
case underwent the [2+2+1] cyclization reaction. In particular, fulleropyrrolidines **10** and **14** with the 1,7-enyne moiety seemed to be suitably functionalized to undergo the PK reaction. Since these experimental findings cannot be rationalized in terms of electronic factors, the additional methylene group in the chain linking the olefin and the alkynyl groups must introduce important geometrical differences that are responsible for the observed reactivities.

In the light of the above results and as a result of the high efficiency of the PK reaction of the 1,6-enynes, we decided to explore the scope of the PK reaction of fulleropyrrolidines endowed with two propargyl groups at the same C-2 position of the pyrrolidine ring. According to the above results, the PK reaction of the fullerenes seems to be strongly influenced by their geometry and a twofold cyclization reaction should drastically increase the strain of the resulting triscycloadduct. Thus, we synthesized fulleropyrrolidine **21** from dipropargyl glycine,^[13] formaldehyde, and C₆₀ in refluxing chlorobenzene (Scheme 4).^[14] To facilitate the subse-

Intermediate dicobalt complex **23** could be isolated in 95% yield after 2 h reaction at 50°C. When **23** was heated at 60°C in toluene for 18 h, the mono-PK compound **24** was obtained in 30% yield together with the double-PK product **25** in 5% yield. Attempts to obtain compound **25** from **24** under the same PK experimental conditions afforded **25** in trace amounts (TLC) along with other unidentified decomposition compounds. The structures of compounds **21–25** were determined by means of a thorough spectroscopic study (see the Experimental Section). Thus, the ¹H NMR spectrum of fulleropyrrolidine **21** shows the hydrogen atoms of the alkyne at δ =2.28 ppm and of the pyrrolidine rings at δ =5.49 ppm. Compound **22** with a benzoyl moiety exhibited similar dynamic behavior to that of the related compounds **3a–d** due to the presence of the amido group. Intermediate dicobalt complex **23** shows, in addition to the features found for the cyclopentenone ring, a proton at δ =6.11 ppm corresponding to the CH group linked to the cobalt atoms. The structures of **24** and **25** were established by using the meth-

ods used to identify the other PK products (**5a–d**, **7**) and confirmed by HMQC and HMBC experiments. Note that the highly strained structure of **25**, in which the amido group should be located on one of the sides of the pyrrolidine ring, should be responsible for the C₁ symmetry observed in the NMR spectra.

In the light of the above findings, the Pauson–Khand reaction of C₆₀ emerges as a highly efficient regioselective procedure to obtain *cis*-1 biscycloadducts **5a–d**, **7**, and **24** as well as the rather unusual 1,2,3,4,11,12-triscycloadduct **25**, all of which are endowed with cyclopentenone moieties able to undergo further chemical transformations.



Scheme 4.

quent PK reaction, the amino pyrrolidine ring was acylated with benzoyl chloride in refluxing toluene and in the presence of triethylamine to form compound **22** in 95% yield. Compound **22** is suitably functionalized with two propargyl groups able to undergo the PK reaction on treatment with [Co₂(CO)₈] in the presence of activated molecular sieves in toluene at 50°C. Interestingly, *cis*-1 biscycloadduct **24**, the result of only one [2+2+1] cycloaddition reaction, was obtained in 30% yield as the main reaction product. 1,2,3,4,11,12-Triscycloadduct **25** formed from two PK reactions was also obtained, although in a very poor yield (5%), probably as a result of the high strain of the resulting molecule, an unprecedented structure with five pentagonal rings fused onto the fullerene surface.^[15]

Electrochemistry: The PK products as well as the precursor fulleropyrrolidines are electroactive molecules that, similarly to the pristine fullerene C₆₀, should behave as electron-accepting species. Therefore, we have studied the electrochemical properties of the novel compounds by cyclic voltammetry (CV) in *o*-DCB/MeCN (4:1) as solvent at room temperature and by using tetrabutylammonium perchlorate as the supporting electrolyte. The characteristic shapes of the redox waves and their unequivocal position on the potential scale virtually fingerprint the individual electrochemical properties of the different redox systems. For this reason, CV has been labeled as an electrochemical spectroscopy.^[18] In our case, the saturation of one olefinic double bond in the suitably functionalized precursor fulleropyrrolidines

should lead, in principle, to different electrochemical behavior to that shown by the related PK products in which two fullerene double bonds are saturated. This should raise the LUMO energy level and, therefore, the reduction waves should be shifted towards more negative potentials, thus slightly reducing their accepting ability.^[19] Therefore, a voltamperometric study of these compounds should allow us to determine the electronic effect of the substitution pattern on the electrochemical properties of the compounds obtained and, simultaneously, to use CV as a useful characterization technique.

The redox potentials of some representative novel compounds are collected in Table 1 together with those of C₆₀ as a reference. All the systems studied displayed electrochemically reversible behavior and, therefore, Table 1 gives the half-wave reduction potential values.

Table 1. Half-wave reduction potentials [V versus Ag/AgNO₃] of compounds **2**, **3**, **5**, **7**, **8**, **24**, **25**, and C₆₀.^[a]

Compound	$E_{1/2, \text{red}}^1$	$E_{1/2, \text{red}}^2$	$E_{1/2, \text{red}}^3$	$E_{1/2, \text{red}}^4$
C ₆₀	−0.800	−1.209	−1.673	−2.127
2	−0.894	−1.288	−1.818	−2.249
3a	−0.860	−1.253	−1.791	−2.205
3b	−0.852	−1.262	−1.784	−2.215
5a	−0.864	−1.256	−1.908	—
5b	−0.863	−1.265	−1.892	—
5c	−0.857	−1.255	−1.885	—
5d	−0.858	−1.252	−1.888	−2.232
7	−0.891	−1.289	−1.939	—
8	−0.875	−1.279	−1.818	−2.231
24	−0.838	−1.234	−1.865	—
25	−0.829	−1.222	−1.906	—

[a] Working electrode: GCE; reference electrode: Ag/Ag⁺; counter electrode: Pt; supporting electrolyte: 0.1 M Bu₄NClO₄; scan rate: 100 mV s^{−1}; sample concentrations: (0.5–2.0) × 10^{−3} M; solvent: *o*-DCB/MeCN (4:1 v/v).

All the compounds studied showed three or four reversible reduction waves that correspond to the reduction steps of the fullerene moiety (Figure 2). A remarkable negative shift in the redox potentials relative to the values for pristine C₆₀ was observed in all cases which can be attributed to the saturation of one (**2**, **3a**, **3b**, and **8**) or two (**5a–d** and **7**) fullerene double bonds, which slightly reduces the electron-accepting ability of the fullerene. Fulleropyrrolidine **2** with a free secondary amino group showed the highest cathodic shift relative to C₆₀. Fulleropyrrolidines **3a,b** with an acyl group linked to the pyrrolidine's nitrogen atom showed a significant anodic shift in comparison with **2** ($\Delta E_{\text{red}}^{1/2} \sim 40$ mV) due to the presence of the carbonyl group and the subsequent delocalization of the nitrogen atom's lone-pair (Figure 2 and Table 1).

cis-1 Biscycloadducts **5a–d** and **7** resulting from the PK reaction exhibit half-wave reduction potentials similar to those observed for their precursor fulleropyrrolidines **3** (Figure 2). Although it is known that the reduction potentials of biscycloadducts have a significant cathodic shift rela-

tive to related monocycloadducts,^[19,20] in our case the values observed are a result of the electron-withdrawing effect of the carbonyl group of the cyclopentenone ring fused to the fullerene cage. These experimental data are supported by the BP86 LUMO energy levels calculated for **3** (−5.795 eV, R = CH₃) and the related PK product **5** (−5.791 eV, R = CH₃) which have almost identical energy values and similar shapes (Figure 3). This finding is in full agreement with previous electrochemical studies carried out on the parent fullerocyclopentenone which exhibited the same reduction potential as pristine C₆₀ despite the saturation of one of the double bonds of the fullerene core.^[21]

Figure 2 shows that the cyclic voltammograms of biscycloadducts **5a,b** have three reversible reduction waves that correspond to those of the C₆₀ moiety. However, in addition

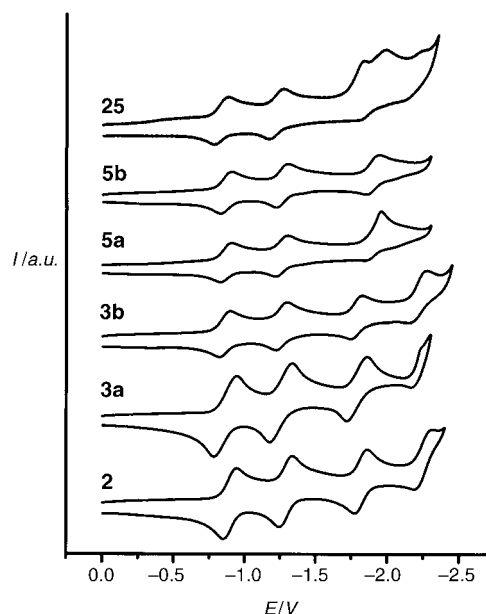


Figure 2. Cyclic voltammograms of compounds **2**, **3a,b**, **5a,b**, and **25** measured in *o*-DCB/MeCN (4:1) at 100 mV s^{−1}.

to these waves, another two very weak waves can also be observed at around 1.50 and 2.00 V. These waves were better observed in the square-wave voltammograms (Figure 4) and have been assigned to the reduction of the ketone and amido groups, respectively, present in the molecules. These assignments were confirmed by CV of the used solvent mixture (in order to discard the presence of impurities), as well as by the presence of a weak wave found at about 1.50 V in the voltammograms of compounds **7** and **8** which only have the cyclopentenone moiety. The amido group could also be observed as a very weak wave at about 2.00 V in the square-wave voltammograms of the precursor fulleropyrrolidines (see the Supporting Information).

The above electrochemical data reveal that despite the saturation of two of the double bonds of the fullerene cage in biscycloadducts **5a–d** and **7**, these adducts are remarkable electron acceptors, like their fulleropyrrolidine precursors,

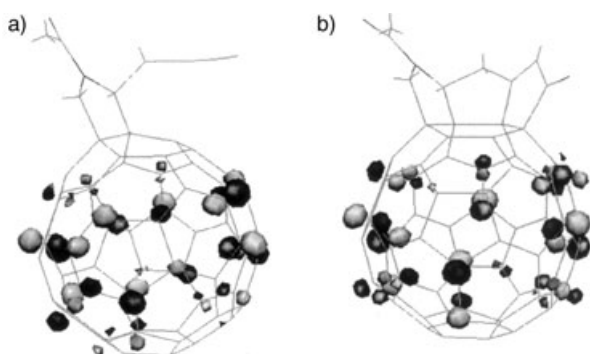


Figure 3. Three-dimensional representation of the LUMO of a) reactant **3** and b) product **5** with $R=CH_3$ computed at the BP86 level. Isosurface values are -0.05 and 0.05 a.u.

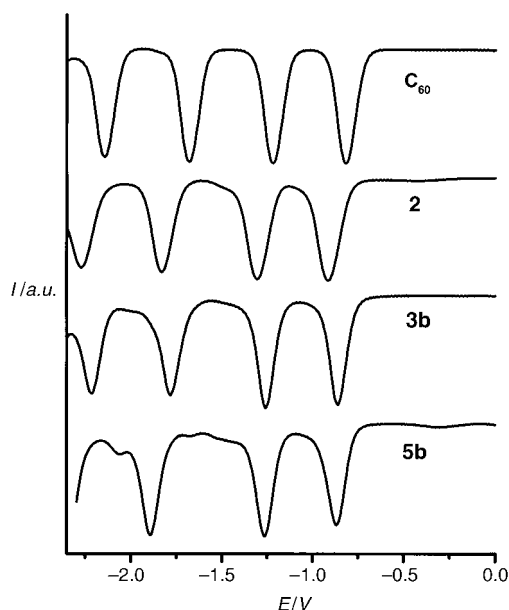


Figure 4. Square-wave voltammograms of compounds C_{60} , **2**, **3b**, and **5b** measured in o -DCB/MeCN (4:1).

as a result of the fused cyclopentenone ring and the electron-withdrawing effect of the carbonyl group directly linked to the C_{60} sphere.

The half-wave reduction potentials of PK products **24** and **25** are also given in Table 1. The first reduction potential of **24** is quite similar to those observed for related PK products. However, compound **25** with two cyclopentenone rings had the strongest electron-accepting ability of the PK products, slightly more negative than pristine C_{60} , owing to the electron-withdrawing effect of the two carbonyl groups directly attached to the C_{60} cage. Note that the cyclic voltammogram of **25** clearly shows the presence of reduction waves arising from the carbonyl and amido groups (Figure 2).

Theoretical calculations: Calculations at the BP86 level (see the Computational Details section) were performed on the PK-reactive complex **3e** (complex **3** in Scheme 2 with $R=$

CH_3) and the PK-unreactive species **14b** (Scheme 3). From a thermodynamic viewpoint, the reaction $3e+CO \rightarrow 5e$ and the equivalent PK reaction for **14b** are exothermic by 73.9 and 64.0 kcal mol $^{-1}$, respectively. Apparently, the final product formed from **14b** is more strained than **5e** as indicated by the fact that the fullerene C–C bond length of the centrally formed ring is 1.643 Å in the final product formed from **14b** compared with 1.618 Å in **5e**. However, although the thermodynamics of the PK reaction is about 10 kcal mol $^{-1}$ more favorable starting from **3e** than from **14b**, the reason for the lack of reactivity in **14b** should not be ascribed to the thermodynamics of the process and must have a kinetic basis.

Previous theoretical studies^[22,23] have shown that the most probable rate-determining step in PK reactions is the loss of CO from intermediate dicobalt carbonyl complexes such as complex **4**. This finding is supported by the fact that these are the only intermediates that can be experimentally observed. For this reason we have analyzed the energies and the molecular structures of species **4e** and **15b** obtained from the reaction of **3e** and **14b** with $[Co_2(CO)_8]$ and the complexes formed when these intermediates lose a CO ligand, hereafter labeled complexes **4e–CO** and **15b–CO**, in which the coordinatively unsaturated Co atom interacts with the π system of the fullerene. Unfortunately, the sizes of these systems prevented the calculation of the full energy profile.

Figure 5a and 5b show the geometries of complexes **4e** and **15b**, respectively. The differences between the two species are not significant. The shortest distance between a Co atom and the C=C bond on the fullerene to be attacked is about 4.5–5 Å. The lengths of the C=C double bonds being attacked are almost the same as those of **3e** and **14b** (1.390 and 1.386 Å, respectively, by calculation at the BP86 level of theory). The molecular structures of complexes **4e–CO** and **15b–CO** depicted in Figures 6a and 6b, respectively, are more informative; a clear difference is observed. The distances between the coordinatively unsaturated Co atoms and the C=C bond being attacked are 2.131 and 2.108 Å for complex **4e–CO**, about 0.1–0.2 Å shorter than those found for complex **15b–CO**. This is likely to be due to the fact that the donation and back-donation interactions between the coordinatively unsaturated Co atoms and the π system of the fullerene are stronger in complex **4e–CO** than in **15b–CO**. The stronger π interaction in **4e–CO** is also reflected by the length of the C=C double bond attacked, which increases by 0.064 Å in the conversion of **4e** into **4e–CO** and by no more than 0.050 Å in the conversion of **15b** into **15b–CO**. Therefore the C=C double bond that interacts with the Co atom is sufficiently well activated in **4e** to continue the PK process. Thus, the differences observed in the two complexes can be attributed to the different lengths of the organic chain containing the alkyne and alkene functional groups. The alkynyl chain in **4e–CO** is of an appropriate length to favor the metal– π interaction.

Interestingly, this has a relevant effect on the thermodynamics of the formation of **4e–CO** and **15b–CO** by loss of

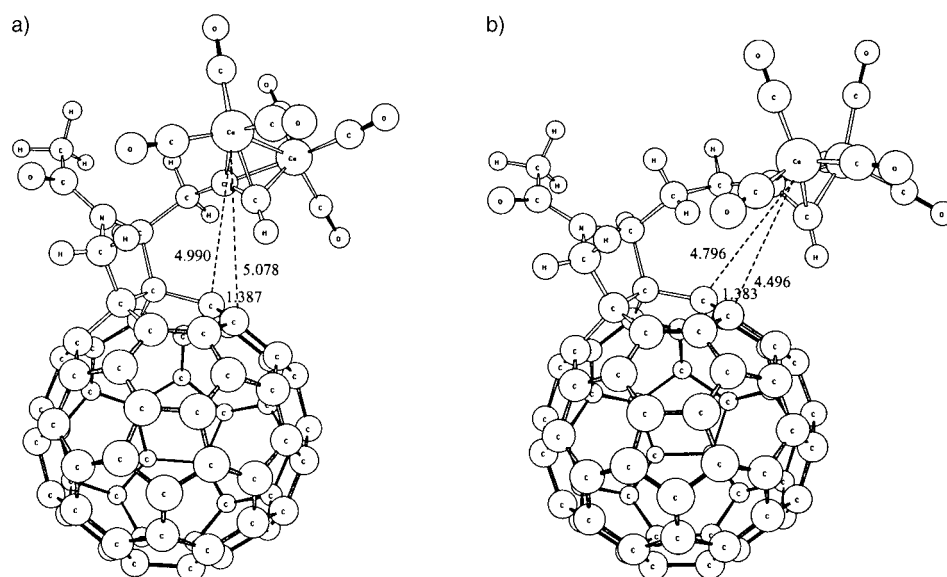


Figure 5. BP86-optimized geometry of complexes a) **4e** and b) **15b** with the most relevant distances given in Å.

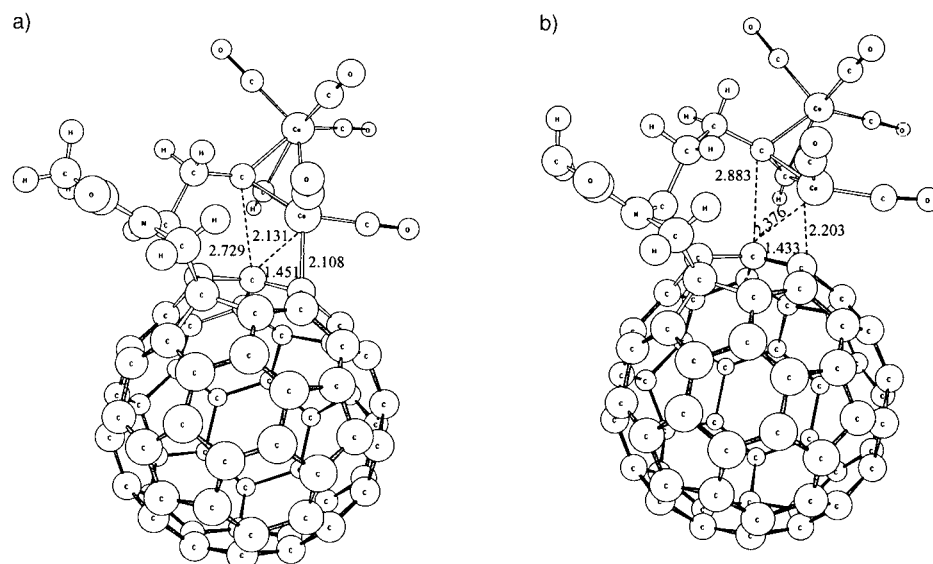


Figure 6. BP86-optimized geometry of complexes a) **4e-CO** and b) **15b-CO** with the most relevant distances given in Å.

a CO molecule from **4e** and **15b**. While the loss of CO from **15b** (**15b** → **15b-CO** + CO) requires 25.3 kcal mol⁻¹, the same process starting from **4e** involves only 15.2 kcal mol⁻¹. Although the transition states of these processes have not been identified owing to high computational costs, it is clear that the loss of CO from **15b** needs more than 25.3 kcal mol⁻¹ and for this reason **15b** does not react further when the temperature is less than 60 °C. As explained before, an increase in the reaction temperature leads to the decomposition of **15b** and so the reaction does not take place at higher temperatures. On the other hand, the loss of CO from **4e** is much more facile. In general terms, the differen-

ces in the strength of the interactions between the coordinatively unsaturated Co atom and the π system of the fullerene in the **4e-CO** and **15b-CO** species explain the different reactivities of complexes **3e** and **14b**.

Conclusions

In summary, we have synthesized a wide variety of novel fulleropyrrolidines endowed with one or two propargyl groups which efficiently and regioselectively undergo the PK reaction with [Co₂(CO)₈] to afford the unprecedented *cis*-1 biscycloadduct and 1,2,3,4,11,12-triscycloadduct fullerene structures with three (**5a-d**, **7**, and **24**) or five (**25**) pentagonal rings, respectively, fused onto the fullerene surface. Cyclic voltammetry reveals that the novel biscycloadducts that result from the PK reaction have the same electron-accepting ability as the precursor fulleropyrrolidines owing to the electron-withdrawing effect of the cyclopentenone moiety directly linked to the fullerene sphere. Remarkably, triscycloadduct **25** with two cyclopentenone rings has a better electron-accepting ability with a first reduction potential value close to that of pristine C₆₀.

In an attempt to expand the scope of the PK reaction to other fullerene derivatives, novel fulleropyrrolidines endowed with 1,7- to 1,11-enynes were synthesized. However, no PK products were obtained and, instead, the intermediate dicobalt complexes were isolated in almost quantitative yields. The remarkably different reactivities exhibited by the fulleropyrrolidines endowed with the 1,6-enyne moiety and those with the 1,7-enyne fragment have been rationalized by means of DFT theoretical calculations. The energies and the molecular structures of the intermediates formed through the interaction between the coordinatively unsaturated Co atom and the π system of the fullerene (**4e-CO** versus **15b-CO**) reveal important differences between the two systems and clearly confirm

that the interaction in the 1,6-enyne (**4e**–CO) is stronger as a consequence of the different length of the organic chain linking the alkyne and alkene functional groups.

These results show that the highly versatile PK reaction can be applied to the spherical molecular surfaces of C₆₀ and other fullerenes, and that CO loss in longer 1,7-enynes may be facilitated by photoirradiation. These possibilities are currently being explored as is the chemical modification of the reactive cyclopentenone ring formed in the PK reactions of these systems.

Experimental Section

Computational details: The calculations were carried out by using the 2002.03 release of the Amsterdam density functional (ADF)^[24] package developed by Baerends and co-workers.^[25,26] The numerical integration scheme of te Velde and Baerends was employed.^[27] Both geometry optimizations and energy evaluations of the neutral closed-shell singlet ground-state structures were performed by using a generalized gradient approximation (GGA) which includes Becke's GGA exchange correction^[28] and Perdew's GGA correlation correction,^[29] the so-called BP86 functional. For geometry optimizations we used an uncontracted double- ζ basis set augmented by an extra polarization function to describe the 3s, 3p, 3d, and 4s orbitals of cobalt, while for the carbon (2s, 2p), nitrogen (2s, 2p), oxygen (2s, 2p), and hydrogen (1s) atoms, double- ζ basis sets were employed.^[30,31] Electrons in lower orbital shells were treated within the frozen core approximation.^[25] A set of auxiliary s, p, d, f, and g functions, centered in all nuclei, was introduced in order to fit the molecular density and Coulomb potential accurately in each SCF cycle.^[32]

General: All reactions were carried out in dry, freshly distilled solvent under anhydrous conditions: toluene and Et₂O were distilled from sodium benzophenone and *o*-dichlorobenzene (*o*-DCB) was used without further purification. All reagents purchased were of the highest commercial quality available and used without further purification.

NMR spectra were recorded with Bruker AC-200, Bruker Avance DPX-300, and Bruker Avance AV-500 spectrometers. Chemical shifts are reported in ppm downfield from tetramethylsilane (TMS). FTIR spectra were recorded as KBr pellets with a Nicolet-Magna-IR 5550 spectrometer. Electrospray ionization (ESI) mass spectra were recorded with a HP1100MSD spectrometer.

Cyclic voltammograms were recorded with a potentiostat/galvanostat AUTOLAB with PGSTAT30 equipped with GPES software for Windows version 4.8 in a conventional three-compartment cell by using a GCE (glassy carbon electrode) as the working electrode, Ag/AgNO₃ as the reference electrode, Bu₄NClO₄ as the supporting electrolyte, *o*-dichlorobenzene/acetonitrile as the solvent (4:1 v/v), and a scan rate of 100 mV s⁻¹.

General procedure for the synthesis of fulleropyrrolidines 2, 10e, and 14a: The corresponding aldehyde (0.694 mmol) and DL-propargylglycine (0.694 mmol for compound **2**) or glycine (0.694 mmol for compounds **10e** and **14a**) were added to a solution of C₆₀ (250 mg, 0.347 mmol) in *o*-DCB (80 mL). The mixture was refluxed for 24 h and after cooling it was concentrated under reduce pressure. Flash chromatography over silica gel eluting initially with CS₂ (for the separation of C₆₀) and then with CS₂/toluene gave the final product in 25–35% yield (56–65% based on consumed C₆₀).

Compound 2: Yield 25% (56%). ¹H NMR (CDCl₃/CS₂, 298 K, 500 MHz): δ = 2.22 (t, J = 2.7 Hz, 1H; CH), 3.24 (ddd, J = 16.7, 4.8, 2.7 Hz, 1H; CH₂), 3.49 (ddd, J = 16.7, 7.8, 2.7 Hz, 1H; CH₂), 4.77 (d, J = 11.3 Hz, 1H; CH₂N), 4.87 (dd, J = 7.8, 4.8 Hz, 1H; CHN), 4.99 ppm (d, J = 11.3 Hz, 1H; CH₂N); ¹³C NMR (CDCl₃/CS₂, 298 K, 75 MHz): δ = 30.58, 62.6, 72.0, 72.7, 75.1, 77.0, 81.4, 136.11, 136.16, 136.4, 137.7, 140.4, 140.5, 140.7, 140.8, 142.2, 142.3, 142.4, 142.5, 142.53, 142.64, 142.67, 142.7, 142.9, 143.0, 143.14, 143.15, 143.2, 143.5, 143.7, 143.79, 144.8, 144.9, 145.1, 145.66, 145.69, 145.7, 145.72, 145.78, 145.8, 145.82, 145.86, 145.9, 145.96,

145.97, 146.0, 146.4, 146.5, 146.54, 146.57, 146.6, 146.7, 146.71, 146.76, 146.8, 146.9, 147.1, 147.53, 147.54, 147.56, 147.6, 151.9, 154.0, 154.5, 156.0 ppm; FTIR (KBr): $\tilde{\nu}$ = 1508, 1461, 1425, 526 cm⁻¹; MS (ESI): m/z : 802.1 [M+H]⁺.

Compound 10e: Yield 35% (65%). ¹H NMR (CDCl₃/CS₂, 298 K, 300 MHz): δ = 0.28 (s, 9H; (CH₃)₃Si), 4.94 (d, J = 10.3 Hz, 1H; CH₂N), 5.15 (d, J = 10.3, 1H; CH₂N), 6.43 (s, 1H; CHN), 7.28–7.33 (m, 1H; H–Ar), 7.42–7.47 (m, 1H; H–Ar), 7.51–7.54 (m, 1H; H–Ar), 8.03–8.06 ppm (m, 1H; H–Ar); ¹³C NMR (CDCl₃/CS₂, 298 K, 75 MHz): δ = 0.57, 61.9, 73.0, 74.6, 76.5, 101.4, 104.2, 123.7, 128.5, 128.9, 129.5, 134.0, 135.4, 136.4, 136.7, 137.1, 139.6, 140.1, 140.3, 140.6, 142.1, 142.2, 142.3, 142.4, 142.5, 142.6, 142.64, 142.7, 142.8, 142.9, 143.0, 143.1, 143.4, 143.5, 144.7, 144.8, 144.9, 145.5, 145.65, 145.67, 145.7, 145.75, 145.8, 145.9, 146.1, 146.37, 146.39, 146.4, 146.5, 146.6, 146.66, 146.7, 146.9, 147.3, 147.5, 147.6, 153.1, 154.0, 154.9, 156.5 ppm; FTIR (KBr): $\tilde{\nu}$ = 2850, 2343, 526 cm⁻¹; MS (ESI): m/z : 936 [M+H]⁺.

Compound 14a: Yield 25% (60%). ¹H NMR (CDCl₃/CS₂, 298 K, 200 MHz): δ = 2.12 (t, J = 2.4 Hz, 1H; CH), 2.80–2.96 (m, 4H; 2CH₂), 4.76 (d, J = 11.9 Hz, 1H; CH₂N), 4.87 (dd, J = 1.2, 2.7 Hz, 1H; CHN), 4.99 ppm (d, J = 11.9 Hz, 1H; CH₂N); ¹³C NMR (CDCl₃/CS₂, 50 MHz): δ = 17.5, 32.4, 62.4, 69.8, 72.9, 74.9, 83.1, 135.3, 135.5, 135.6, 136.5, 139.7, 140.0, 141.1, 141.58, 141.6, 141.7, 141.8, 141.9, 141.98, 142.1, 142.3, 142.4, 142.43, 142.48, 142.5, 142.8, 143.0, 144.1, 144.2, 144.3, 144.9, 144.99, 145.0, 145.08, 145.1, 145.13, 145.18, 145.2, 145.21, 145.4, 145.43, 145.7, 145.75, 145.8, 145.83, 145.9, 145.94, 145.98, 146.0, 146.1, 146.8, 151.9, 153.5, 154.0, 155.2 ppm; FTIR (KBr): $\tilde{\nu}$ = 526.5, 632.6, 1423 cm⁻¹; MS (ESI): m/z : 815.9 [M+H]⁺.

General procedure for the synthesis of *N*-acylfulleropyrrolidines 3a–d, 10f, and 14c: NEt₃ (0.30 mmol) was added to a solution of fulleropyrrolidines **2**, **10e** or **14a** (0.15 mmol) in toluene (50 mL). After 5 minutes, the corresponding acyl chloride (0.30 mmol) was added and the mixture stirred at room temperature for 1 h (for compound **14c** heating was necessary). When the reaction was complete, the solvent was removed in vacuo. The crude product was purified by flash chromatography over neutral alumina (eluent: toluene/ethyl acetate 4:1) to afford the final product (90–95% yield).

Compound 3a: Yield 95%. ¹H NMR (CDCl₃, 333 K, 500 MHz): δ = 2.32 (t, J = 2.6 Hz, 1H; CH), 3.58 (dd, J = 6.4, 2.6 Hz, 2H; CH₂), 5.54 (d, J = 12 Hz, 1H; CH₂N), 5.71 (d, J = 12 Hz, 1H; CH₂N), 6.41 (brt, 1H; CHN), 7.57–7.56 (m, 3H; Ar–H), 7.91–7.89 ppm (m, 2H; Ar–H); ¹³C NMR (CDCl₃, 298 K, 75 MHz): δ = 29.9, 65.4, 70.6, 73.5, 80.2, 125.3, 128.2, 128.3, 128.8, 129.0, 130.9, 135.3, 136.9, 138.1, 139.9, 140.3, 140.33, 141.7, 141.8, 141.9, 142.1, 142.12, 142.17, 142.2, 142.3, 142.4, 142.7, 142.77, 142.8, 143.1, 143.2, 144.4, 144.44, 144.5, 144.6, 144.65, 145.3, 145.4, 145.44, 145.5, 145.6, 145.68, 145.7, 145.76, 146.1, 146.2, 146.38, 146.39, 146.4, 147.4, 147.42, 150.1, 152.4, 154.2, 154.7, 170.1 ppm; FTIR (KBr): $\tilde{\nu}$ = 1641, 1400, 526 cm⁻¹; MS (ESI): m/z : 906 [M+H]⁺.

Compound 3b: Yield 95%. ¹H NMR (CDCl₃, 298 K, 500 MHz, mixture of rotamers, 1:1): δ = 2.44, 2.25 (brs, brs, 1H), 3.54, 3.37 (brm, brm, 2H), 4.17, 3.93 (brs, brm, 1H), 4.43, 4.21 (d, d, J = 14.6 Hz, 1H), 5.49 (brs, 2H), 6.27, 4.93 (d, d, J = 12.4 Hz, 1H), 6.39, 5.98 ppm (brt, brm, 1H); ¹³C NMR (CDCl₃, 298 K, 125 MHz, mixture of rotamers, 1:1): δ = 25.7, 29.7, 42.4, 42.8, 58.3, 64.4, 66.4, 69.5, 70.3, 72.6, 73.0, 73.7, 74.2, 96.1, 127.5, 127.7, 129.1, 134.9, 135.1, 139.8, 140.2, 141.7, 141.8, 142.0, 142.1, 142.2, 142.7, 143.0, 143.1, 144.4, 144.5, 144.6, 145.2, 145.3, 145.37, 145.4, 145.6, 145.66, 146.0, 146.1, 146.2, 146.3, 146.36, 147.4, 149.5, 169.6, 170.2 ppm; FTIR (KBr): $\tilde{\nu}$ = 1641, 1400, 526 cm⁻¹; MS (ESI): m/z : 920 [M+H]⁺.

Compound 3c: Yield 90%. ¹H NMR (CDCl₃, 323 K, 500 MHz): δ = 2.34 (t, J = 2.5 Hz, 1H; CH=C), 3.67–3.35 (brm, 2H; CH₂), 5.46 (brm, 1H), 6.05 (brm, 1H), 6.34 (brm, 1H), 7.32 (d, J = 15.4 Hz, 1H; CH=CH), 7.48–7.42 (m, 3H; Ar–H), 7.72–7.69 (m, 2H; Ar–H), 8.04 ppm (d, J = 15.4 Hz, 1H; CH=CH); ¹³C NMR (CDCl₃, 298 K, 50 MHz): δ = 29.9, 65.8, 69.7, 73.6, 77.2, 80.1, 117.1, 128.1, 128.9, 130.1, 134.9, 139.7, 140.1, 140.2, 141.6, 141.7, 141.97, 142.0, 142.02, 142.03, 142.05, 142.1, 142.14, 142.3, 142.6, 142.7, 143.0, 143.1, 144.2, 144.3, 144.4, 144.5, 144.6, 145.2, 145.25, 145.3, 145.35, 145.4, 145.5, 145.6, 146.0, 146.08, 146.1, 146.2, 146.27, 146.3, 147.2, 147.3, 149.8, 152.5, 154.2, 165.0 ppm; FTIR (KBr): $\tilde{\nu}$ = 1652, 1400, 526 cm⁻¹; MS (ESI): m/z : 932 [M+H]⁺.

Compound 3d: Yield 95%. ¹H NMR (CDCl₃, 298 K, 500 MHz, mixture of rotamers): δ = 2.79 (m, 1H), 2.95 (m, 1H), 3.42, 3.35 (brd, brd, 1H), 3.89, 3.61 (m, brm, 1H), 5.69, 5.49 (d, d, J = 11.5 Hz, 1H), 6.19, 4.96 (d, d, J = 12.6 Hz, 1H), 6.37, 5.94 ppm (brt, brm, 1H); ¹³C NMR (CDCl₃, 298 K, 125 MHz, mixture of rotamers): δ = 14.0, 22.6, 29.6, 31.6, 66.4, 70.3, 72.5, 72.7, 72.9, 73.1, 73.5, 74.4, 96.1, 139.8, 140.3, 141.7, 141.9, 142.1, 142.7, 142.77, 143.1, 143.2, 144.4, 144.48, 144.5, 144.57, 144.6, 144.7, 144.73, 145.3, 145.37, 145.4, 145.44, 145.5, 144.53, 145.6, 145.66, 145.7, 146.1, 146.2, 146.3, 146.35, 146.4, 146.45, 146.6, 147.39, 147.4, 147.44, 149.5, 150.3, 152.3, 164.2 ppm; FTIR (KBr): $\tilde{\nu}$ = 1655, 1410, 526 cm⁻¹; MS (ESI): m/z : 900 [M+H]⁺.

Compound 10f: Yield 90%. ¹H NMR (CDCl₃/CS₂, 298 K, 300 MHz): δ = 0.03 (s, 9H; (CH₃)₃Si), 5.83 (d, J = 12.7 Hz, 1H; CH₂N), 6.36 (brd, 1H; CH₂N), 7.32–7.37 (m, 1H; H–Ar), 7.45–7.54 (m, 5H; H–Ar), 7.60 (s, 1H; CHN), 7.62–7.68 (m, 2H; H–Ar), 8.12–8.14 ppm (m, 1H; H–Ar); ¹³C NMR (CDCl₃/CS₂, 298 K, 75 MHz): δ = -0.2, 62.0, 66.3, 69.5, 71.5, 76.4, 101.8, 103.7, 123.4, 125.5, 127.9, 128.6, 129.2, 130.3, 131.0, 133.8, 134.9, 135.4, 136.0, 136.4, 136.6, 139.64, 139.7, 140.5, 140.8, 142.05, 142.06, 142.1, 142.3, 142.7, 142.9, 142.44, 142.46, 142.5, 142.7, 143.0, 143.07, 143.1, 143.13, 143.45, 144.7, 144.8, 144.9, 145.0, 145.5, 145.6, 145.7, 145.75, 145.8, 145.9, 146.0, 146.06, 146.2, 146.4, 146.5, 146.6, 146.66, 146.7, 146.76, 146.8, 146.82, 146.84, 147.7, 147.9, 151.9, 154.0, 154.7, 155.8, 171.7 ppm; FTIR (KBr): $\tilde{\nu}$ = 526, 840, 866, 1388, 1654 cm⁻¹; MS (ESI): m/z : 1063.0 [M+Na]⁺, 1077.9 [M+K]⁺.

Compound 14c: Yield 90%. ¹H NMR (CDCl₃/CS₂, 298 K, 500 MHz): δ = 2.07 (s, 1H; CH), 2.76–2.83 (m, 3H; CH₂), 2.93–3.06 (m, 1H; CH₂), 5.31 (d, J = 11.8 Hz, 1H; CH₂N), 5.64 (brs, 1H; CH₂N), 6.46 (brs, 1H; CHN), 7.52–7.56 (m, 3H; H–Ar), 7.82–7.86 ppm (m, 2H; H–Ar); ¹³C NMR (CDCl₃/CS₂, 298 K, 125 MHz): δ = 17.2, 35.0, 58.7, 66.2, 70.3, 71.5, 74.6, 83.7, 128.7, 129.3, 131.3, 135.3, 135.5, 135.8, 137.2, 137.7, 140.5, 140.6, 140.7, 140.8, 142.1, 142.12, 142.4, 142.47, 142.5, 142.57, 142.6, 142.64, 142.7, 142.8, 142.9, 143.1, 143.16, 143.19, 143.2, 143.6, 143.7, 144.7, 144.8, 144.9, 145.0, 145.1, 145.3, 145.7, 145.8, 145.82, 145.85, 145.9, 146.0, 146.02, 146.1, 146.2, 146.4, 146.6, 146.7, 146.8, 147.8, 151.2, 152.8, 154.4, 155.3, 170.7 ppm; FTIR (KBr): $\tilde{\nu}$ = 526.5, 1637 cm⁻¹; MS (ESI): m/z : 919.8 [M+1].

Synthesis of N-allylfulleropyrrolidine 6: NaH (0.625 mmol) was added to a solution of fulleropyrrolidine **2** (100 mg; 0.125 mmol) in *o*-DCB (40 mL). After 5 min allyl bromide was added (0.375 mmol). The solution was stirred for 18 h at 60 °C. The reaction was quenched with water (20 mL). The organic layer was dried (MgSO₄) and, after solvent removal, the crude product was purified by flash chromatography over silica gel (eluent: toluene/CS₂ 8:2) to give pure **6** in 55% yield. ¹H NMR (CDCl₃/CS₂, 298 K, 200 MHz): δ = 2.19 (t, J = 2.7 Hz, 1H; CH), 3.24 (ddd, J = 17.3, 6.1, 2.7 Hz, 1H; CH₂), 3.51 (ddd, J = 17.3, 5.3, 2.7 Hz, 1H; CH₂), 3.56 (brdd, 1H; N–CH₂–C=), 4.14 (d, J = 9.7 Hz, 1H; CH₂N), 4.30 (brt, 1H; CHN), 4.36 (ddt, J = 13.7, 5.1, 1.6 Hz, 1H; N–CH₂–C=), 4.86 (d, J = 9.7 Hz, 1H; CH₂N), 5.43 (brd, 1H; C=CH₂), 5.59 (ddd, J = 17.09, 2.9, 1.6 Hz, 1H; CH=CH₂), 6.35 ppm (m, 1H; CH=CH₂); ¹³C NMR (CDCl₃/CS₂, 298 K, 50 MHz): δ = 29.9, 66.5, 69.1, 72.6, 73.5, 75.0, 81.7, 118.8, 135.5, 135.6, 135.9, 136.2, 137.2, 137.7, 139.6, 140.1, 140.2, 140.9, 141.6, 141.8, 141.9, 142.07, 142.1, 142.5, 142.57, 142.6, 142.9, 143.9, 144.0, 144.3, 144.33, 144.5, 144.7, 145.1, 145.28, 145.2, 145.3, 145.4, 145.46, 145.5, 145.6, 145.8, 145.88, 145.9, 145.96, 146.0, 146.06, 146.1, 146.16, 146.2, 146.26, 146.3, 146.5, 146.9, 147.1, 147.2, 151.7, 153.8, 154.1, 155.9 ppm; FTIR (KBr): $\tilde{\nu}$ = 1558, 1508, 1458, 1419, 526 cm⁻¹; MS (ESI): m/z : 842.3 [M+H]⁺.

General procedure for the synthesis of N-methylfulleropyrrolidines 10a, 10c, 14b and 18a–c: A mixture of the corresponding aldehyde (0.694 mmol), C₆₀ (250 mg, 0.347 mmol), and sarcosine (0.694 mmol) in *o*-DCB (80 mL) was refluxed for 24 h. After cooling to room temperature, the solvent was removed in vacuo and the crude product was purified by flash chromatography over silica gel initially with CS₂ as eluent (to separate the unreacted fullerene) and then with toluene/CS₂ (4:1) [for compound **10a** cyclohexane/CH₂Cl₂ (4:1) was used] to yield the corresponding products.

Compound 10a: Yield 24% (35%). ¹H NMR (CDCl₃/CS₂, 298 K, 200 MHz): δ = 0.25 (2, 9H; (CH₃)₃Si), 2.81 (s, 3H; CH₃), 4.35 (d, J =

9.5 Hz, 1H; CH₂N), 5.01 (d, J = 9.5 Hz, 1H; CH₂N), 5.37 (s, 1H; CHN), 7.23–7.31 (m, 1H; Ar–H), 7.42–7.54 (m, 2H; Ar–H), 8.09 ppm (m, 1H; Ar–H); ¹³C NMR (CDCl₃/CS₂, 298 K, 50 MHz): δ = 0.05, 39.8, 69.2, 69.7, 79.6, 100.8, 103.4, 124.0, 127.8, 129.0, 120.3, 132.3, 133.1, 134.8, 135.7, 136.5, 139.4, 139.7, 140.06, 140.1, 141.6, 141.63, 141.64, 141.87, 141.9, 142.0, 142.06, 142.07, 142.12, 142.15, 142.2, 142.4, 142.45, 142.5, 142.9, 143.0, 144.2, 144.4, 144.49, 144.5, 145.0, 145.1, 145.13, 145.16, 145.2, 145.3, 145.35, 145.4, 145.5, 145.6, 145.8, 145.85, 145.9, 145.97, 146.0, 146.1, 146.15, 146.2, 146.4, 146.8, 147.2, 153.3, 153.7, 154.5, 156.3 ppm; FTIR (KBr): $\tilde{\nu}$ = 526, 760, 842, 866, 1230, 1247, 1463, 1506 cm⁻¹; MS (ESI): m/z : 950.3 [M+H]⁺.

Compound 10c: Yield 43% (55%). ¹H NMR (CDCl₃/CS₂, 298 K, 300 MHz): δ = 0.25 (s, 9H; (CH₃)₃Si), 2.80 (s, 3H; CH₃), 3.88 (s, 3H; OCH₃), 3.96 (s, 3H; OCH₃), 4.33 (d, J = 9.5 Hz, 1H; CH₂N), 4.99 (d, J = 9.5 Hz, 1H; CH₂N), 5.63 (s, 1H; CHN), 6.99 (s, 1H; Ar–H), 7.60 ppm (s, 1H; Ar–H); ¹³C NMR (CDCl₃/CS₂, 298 K, 75 MHz): δ = 0.5, 40.5, 56.3, 56.7, 69.7, 70.2, 80.1, 99.5, 103.9, 112.0, 113.1, 116.6, 125.7, 128.6, 132.7, 133.0, 135.3, 136.3, 136.6, 136.8, 140.1, 140.3, 140.5, 140.6, 142.0, 142.1, 142.13, 142.2, 142.4, 142.5, 142.53, 142.55, 142.6, 142.66, 142.7, 143.0, 143.1, 143.4, 143.5, 144.8, 144.9, 145.0, 145.05, 145.5, 145.6, 145.7, 145.72, 145.8, 145.9, 145.96, 146.1, 146.4, 146.5, 146.51, 146.6, 146.7, 146.9, 147.4, 147.7, 147.72, 148.6, 150.5, 154.3, 155.1, 156.8 ppm; FTIR (KBr): $\tilde{\nu}$ = 526, 840, 1247, 1267, 1460, 1508 cm⁻¹; MS (ESI): m/z : 1009.9 [M+1]⁺.

Compound 14b: Yield 33% (56%). ¹H NMR (CDCl₃/CS₂, 298 K, 200 MHz): δ = 2.05 (t, J = 2.4 Hz, 1H; CH), 2.64–2.82 (m, 4H; 2CH₂), 3.44 (s, 3H; CH₃), 4.14 (brt, J = 4.8 Hz, 1H; CHN), 4.24 (d, J = 9.8 Hz, 1H; CH₂N), 4.83 ppm (d, J = 9.8 Hz, 1H; CH₂N); ¹³C NMR (CDCl₃/CS₂, 298 K, 50 MHz): δ = 16.5, 29.9, 39.7, 69.7, 69.8, 70.0, 70.9, 75.7, 83.4, 135.3, 135.7, 136.0, 136.1, 137.1, 139.6, 139.8, 140.0, 140.05, 140.1, 141.6, 141.7, 141.8, 141.9, 141.96, 141.99, 142.0, 142.45, 142.47, 142.5, 142.51, 142.8, 142.9, 143.0, 144.1, 144.2, 144.3, 144.5, 145.0, 145.03, 145.09, 145.1, 145.2, 145.23, 145.26, 145.3, 145.5, 145.7, 145.8, 145.86, 145.9, 145.96, 145.99, 146.0, 146.06, 146.1, 146.14, 146.9, 147.0, 152.5, 153.8, 154.1, 154.5, 156.0 ppm; FTIR (KBr): $\tilde{\nu}$ = 526.5, 1508.2, 2360 cm⁻¹; MS (ESI): m/z : 830.0 [M+1]⁺.

Compound 18a: Yield 55% (70%). ¹H NMR (CDCl₃/CS₂, 298 K, 200 MHz): δ = 2.42 (t, J = 2.38 Hz, 1H; CH), 2.86 (s, 3H; CH₃N), 4.34 (d, J = 9.33 Hz, 1H; CH₂N), 4.58 (AB syst., 2H; CH₂O), 4.99 (d, J = 9.33 Hz, 1H; CH₂N), 5.61 (s, 1H; CHN), 6.87–7.33 (m, 3H; Ar–H), 8.04 ppm (m, 1H; Ar–H); ¹³C NMR (CDCl₃/CS₂, 298 K, 50 MHz): δ = 40.1, 56.1, 69.2, 69.7, 75.3, 75.6, 76.3, 78.1, 112.2, 122.2, 125.3, 128.2, 129.1, 130.1, 134.8, 136.1, 136.6, 139.5, 139.6, 140.1, 140.2, 141.5, 141.7, 141.8, 142.0, 142.1, 142.21, 142.26, 142.3, 142.35, 142.57, 142.58, 142.65, 142.68, 143.0, 143.07, 144.3, 144.4, 144.6, 145.1, 145.24, 145.27, 145.32, 145.35, 145.4, 145.6, 145.7, 145.95, 145.97, 146.0, 146.13, 146.17, 146.21, 146.26, 146.27, 146.6, 146.7, 147.2, 147.3, 156.3 ppm.

Compound 18b: Yield 50% (65%). ¹H NMR (CDCl₃/CS₂, 298 K, 200 MHz): δ = 2.38 (t, J = 2.3 Hz, 1H; CH), 2.78 (s, 3H; CH₃N), 4.22 (d, J = 9.3 Hz, 1H; CH₂N), 4.64 (d, J = 2.3 Hz, 2H; CH₂O), 4.86 (s, 1H; CHN), 4.92 (d, J = 9.3 Hz, 1H; CH₂N), 6.82–6.88 (m, 1H; Ar–H), 7.20–7.36 ppm (m, 3H; Ar–H); ¹³C NMR (CDCl₃/CS₂, 298 K, 50 MHz): δ = 40.1, 55.8, 69.0, 70.1, 75.7, 76.6, 78.8, 83.4, 115.5, 122.1, 125.0, 128.2, 128.6, 129.8, 135.0, 135.9, 136.6, 138.6, 139.6, 140.0, 141.6, 141.7, 141.8, 142.10, 142.11, 142.16, 142.3, 142.6, 143.7, 144.43, 144.69, 145.0, 145.2, 145.3, 145.4, 145.56, 145.59, 145.65, 146.0, 146.1, 146.2, 146.3, 146.4, 146.45, 146.6, 146.9, 147.3, 147.4, 147.63, 147.65, 147.7, 147.75, 147.8, 147.9, 148.1, 148.15, 153.3 ppm.

Compound 18c: Yield 55% (70%). ¹H NMR (CDCl₃/CS₂, 298 K, 200 MHz): δ = 2.49 (t, J = 2.3 Hz, 1H; CH), 2.79 (s, 3H; CH₃N), 4.25 (d, J = 9.2 Hz, 1H; CH₂N), 4.67 (d, J = 2.3 Hz, 2H; CH₂O), 4.89 (s, 1H; CHN), 4.97 (d, J = 9.2 Hz, 1H; CH₂N), 7.00 (d, J = 8.4 Hz, 2H; Ar–H), 7.71 ppm (brs, 2H; Ar–H); ¹³C NMR (CDCl₃/CS₂, 298 K, 50 MHz): δ = 40.5, 56.3, 69.2, 70.1, 76.1, 79.0, 83.5, 115.5, 125.8, 127.8, 129.7, 136.2, 136.7, 137.0, 142.0, 142.1, 142.3, 142.4, 142.5, 142.52, 142.55, 142.58, 142.6, 142.7, 142.74, 143.0, 143.01, 143.04, 143.1, 143.4, 143.6, 144.8, 145.1, 145.2, 145.6, 145.7, 145.74, 145.8, 145.87, 145.9, 145.99, 146.0, 146.1, 146.2, 146.4, 146.42, 146.5, 146.62, 146.66, 146.7, 146.78, 146.8, 146.9, 147.1, 147.7, 157.8 ppm.

Synthesis of fulleropyrrolidines 10b, 10d, and 10g: Anhydrous $n\text{Bu}_4\text{NF}$ (0.099 mmol) dissolved in dry CH_2Cl_2 (10 mL) was added to a solution of fulleropyrrolidines **10a**, **10c**, or **10f** (0.099 mmol) in dry CH_2Cl_2 under argon at 0°C . After 10 minutes, the reaction mixture was allowed to warm to room temperature and stirred for 2 h. The solution was washed with water. The organic layer was dried (MgSO_4) and the solvent was removed in vacuo. The crude reaction was purified by flash chromatography over silica gel with toluene/ethyl acetate (9:1) as eluent for compounds **10d** and **10g** and cyclohexane/ CH_2Cl_2 (9:1) as eluent for compound **10b** (85–95% yield).

Compound 10b: Yield 85%. ^1H NMR ($\text{CDCl}_3/\text{CS}_2$, 298 K, 300 MHz): δ = 2.81 (s, 3H; CH_3), 3.32 (s, 1H; CH), 4.37 (d, J = 9.4 Hz, 1H; CH_2N), 5.00 (d, J = 9.4 Hz, 1H; CH_2N), 5.73 (s, 1H; CHN), 7.26–7.33 (m, 1H; Ar–H), 7.47–7.57 (m, 2H; Ar–H), 8.11–8.13 ppm (m, 1H; Ar–H); ^{13}C NMR ($\text{CDCl}_3/\text{CS}_2$, 298 K, 75 MHz): δ = 40.3, 66.4, 69.6, 70.0, 75.9, 79.9, 84.2, 123.5, 128.5, 129.9, 130.0, 133.9, 135.3, 136.5, 140.0, 140.2, 140.6, 142.2, 142.36, 142.38, 142.4, 142.6, 143.0, 143.1, 143.5, 143.52, 144.8, 144.9, 145.0, 145.6, 145.7, 145.8, 145.9, 146.15, 146.17, 146.4, 146.5, 146.67, 146.7, 146.9, 147.7 ppm; FTIR (KBr): $\tilde{\nu}$ = 526, 759, 1508 cm^{-1} ; MS (ESI): m/z : 878.1 $[M+1]^+$.

Compound 10d: Yield 92%. ^1H NMR ($\text{CDCl}_3/\text{CS}_2$, 298 K, 300 MHz): δ = 2.79 (s, 3H; CH_3), 3.26 (s, 1H; CH), 3.89 (s, 3H; OCH_3), 3.96 (s, 3H; OCH_3), 4.36 (d, J = 9.4 Hz, 1H; CH_2N), 4.98 (d, J = 9.4 Hz, 1H; CH_2N), 5.64 (s, 1H; CHN), 6.99 (s, 1H; Ar–H), 7.69 ppm (s, 1H; Ar–H); ^{13}C NMR ($\text{CDCl}_3/\text{CS}_2$, 298 K, 75 MHz): δ = 40.3, 56.2, 56.3, 68.9, 76.6, 79.2, 80.0, 82.7, 113.0, 115.4, 115.8, 144.72, 144.78, 144.8, 144.9, 145.0, 145.07, 145.1, 145.15, 145.2, 145.4, 145.5, 145.6, 145.65, 145.68, 145.7, 145.8, 145.9, 146.0, 146.2, 146.4, 146.5, 146.53, 146.6, 146.7, 146.75, 146.8, 147.7, 147.8, 147.9, 151.1 ppm; FTIR (KBr): $\tilde{\nu}$ = 526, 1267, 1458, 1508, 1650 cm^{-1} ; MS (ESI): m/z : 938.1 $[M+1]^+$.

Compound 10g: Yield 95%. ^1H NMR ($\text{CDCl}_3/\text{CS}_2$, 298 K, 300 MHz): δ = 3.15 (br, 1H; CH), 5.89 (d, J = 12.6 Hz, 1H; CH_2N), 6.13 (br, 1H; CH_2N), 7.34–7.38 (m, 1H; Ar–H), 7.50–7.55 (m, 4H; Ar–H, CHN), 7.61–7.70 (m, 4H; Ar–H), 8.13–8.15 ppm (m, 1H; H–Ar); ^{13}C NMR ($\text{CDCl}_3/\text{CS}_2$, 298 K, 75 MHz): δ = 69.0, 75.0, 75.4, 75.9, 82.2, 84.2, 121.9, 125.4, 127.5, 128.1, 128.6, 130.0, 130.7, 133.8, 135.4, 139.18, 139.2, 140.0, 140.2, 140.6, 141.5, 141.6, 141.7, 141.8, 141.9, 141.94, 142.0, 142.03, 142.1, 142.15, 142.2, 142.3, 142.5, 142.6, 142.8, 142.9, 142.95, 143.1, 143.12, 143.3, 143.4, 143.6, 143.7, 143.77, 143.8, 143.9, 144.2, 144.3, 144.4, 144.5, 144.7, 144.9, 145.1, 145.17, 145.2, 145.3, 145.45, 145.5, 145.53, 145.6, 145.9, 146.0, 146.06, 146.1, 146.2, 146.3, 146.32, 146.4, 147.3, 147.35, 151.4, 153.4, 153.9, 155.0, 170.8 ppm; FTIR (KBr): $\tilde{\nu}$ = 526, 1541, 1560, 1654 cm^{-1} ; MS (ESI): m/z : 967.7 $[M]^+$.

General procedure for the synthesis of metal complexes: The respective enyne (0.055 mmol) was dissolved in toluene (25 mL) at room temperature under argon in a flask containing powdered molecular sieves (eight times the mass of the enyne, oven-dried for 4 h at 120°C in a vacuum). $[\text{Co}_2(\text{CO})_8]$ (0.055 mmol) was added to this solution and the resulting mixture was stirred for 30 min until total complexation of the enyne (TLC). The reaction was then filtered over Celite and purified by flash chromatography over silica gel using cyclohexane/toluene (1:1) as eluent (80–90% yield).

Compound 11a: Yield 80%. ^1H NMR ($\text{CDCl}_3/\text{CS}_2$, 298 K, 300 MHz): δ = 0.51 (s, 9H; $(\text{CH}_3)_3\text{Si}$), 2.84 (s, 3H; CH_3), 4.55 (d, J = 9.3 Hz, 1H; CH_2N), 4.93 (d, J = 9.3 Hz, 1H; CH_2N), 7.34–7.48 (m, 2H; H–Ar), 7.65–7.68 (m, 1H; Ar–H), 8.27–8.29 ppm (m, 1H; Ar–H); ^{13}C NMR ($\text{CDCl}_3/\text{CS}_2$, 298 K, 75 MHz): δ = 0.0, 36.6, 67.2, 68.1, 73.2, 84.8, 99.2, 123.8, 126.5, 126.7, 126.8, 127.5, 131.2, 132.3, 134.7, 135.9, 136.9, 137.8, 138.6, 138.7, 140.0, 140.1, 140.2, 140.5, 140.6, 140.8, 141.0, 141.1, 141.4, 141.7, 142.7, 142.9, 143.0, 143.2, 143.6, 143.7, 143.8, 143.85, 143.9, 144.2, 144.3, 144.4, 144.5, 144.6, 144.7, 144.75, 144.8, 144.9, 145.1, 145.7, 151.0, 152.3, 152.6, 155.5, 198.2, 198.7 ppm; MS (ESI): m/z : 950 $[M - [\text{Co}_2(\text{CO})_8]]$.

Compound 11d: Yield 80%. ^1H NMR ($\text{CDCl}_3/\text{CS}_2$, 298 K, 200 MHz): δ = 2.64 (s, 3H; CH_3), 3.84 (s, 3H; OCH_3), 3.88 (s, 3H; OCH_3), 4.24 (d, J = 9.3 Hz, 1H; CH_2N), 4.92 (d, J = 9.3 Hz, 1H; CH_2N), 5.51 (s, 1H; CHN), 6.54 (s, 1H; CH–Cobalt), 7.16 (s, 1H; Ar–H), 7.63 ppm (s, 1H; Ar–H); FTIR (KBr): $\tilde{\nu}$ = 526.5, 2017.4, 2048.3, 2086.8 cm^{-1} ; MS (ESI): m/z : 1223.5 $[M]^+$, 1139.7 $[M - 3\text{CO}]$, 721.4 $[M+1]_{\text{C}_{60}}$, 285.2 $[M - 2\text{Co}(\text{CO})_3]$.

Compound 15b: Yield 90%. ^1H NMR ($\text{CDCl}_3/\text{CS}_2$, 298 K, 500 MHz): δ = 2.76–2.84 (m, 2H; CH_2), 3.00 (s, 3H CH_3), 3.39–3.63 (m, 2H CH_2), 4.05 (brt, 1H; CHN), 4.19 (d, J = 9.5 Hz, 1H; CH_2N), 4.86 (d, J = 9.5 Hz, 1H; CH_2N), 6.06 ppm (s, 1H; CH); ^{13}C NMR ($\text{CDCl}_3/\text{CS}_2$, 298 K, 125 MHz): δ = 30.4, 33.3, 40.4, 70.3, 70.8, 73.7, 76.3, 97.0, 125.3, 134.9, 135.9, 136.4, 136.7, 137.6, 137.7, 138.5, 140.3, 140.4, 140.7, 140.8, 141.1, 142.2, 142.3, 142.4, 142.6, 142.62, 142.64, 142.9, 143.1, 143.2, 143.3, 143.5, 143.7, 144.2, 144.8, 144.9, 145.0, 145.2, 145.7, 145.74, 145.8, 145.87, 145.9, 145.93, 146.0, 146.2, 146.3, 146.4, 146.5, 146.54, 146.6, 146.63, 146.66, 146.7, 146.75, 146.8, 147.7, 147.72, 153.1, 154.4, 154.7, 156.5, 200.1, 200.2 ppm; FTIR (KBr): $\tilde{\nu}$ = 526.5, 2013.5, 2046.3, 2090.7 cm^{-1} ; MS (ESI): m/z : 1114.4 $[M+1]^+$.

Compound 19a: Yield 90%. ^1H NMR ($\text{CDCl}_3/\text{CS}_2$, 298 K, 500 MHz): δ = 2.78 (s, 3H; CH_3), 4.25 (d, J = 9.03 Hz, 1H; CH_2N), 4.96 (d, J = 9.03 Hz, 1H; CH_2N), 4.97 (d, J = 12.9 Hz, 1H; CH_2O), 5.33 (d, J = 12.9 Hz, 1H; CH_2O), 5.67 (s, 1H; CHN), 6.03 (s, 1H; CH–Cobalt), 7.03 (d, J = 7.8 Hz, 1H; Ar–H), 7.15–7.21 (m, 2H; Ar–H), 8.09 ppm (d, J = 7.8 Hz, 1H; Ar–H); ^{13}C NMR ($\text{CDCl}_3/\text{CS}_2$, 298 K, 125 MHz): δ = 40.2, 68.9, 69.8, 70.2, 73.6, 75.2, 77.0, 88.7, 112.1, 122.2, 125.7, 126.2, 128.6, 129.4, 131.0, 135.6, 136.5, 136.7, 137.0, 139.9, 139.94, 140.5, 140.6, 142.0, 142.1, 142.16, 142.2, 142.44, 142.45, 142.52, 142.54, 142.57, 142.6, 142.7, 142.98, 143.0, 143.02, 143.07, 143.4, 143.5, 144.8, 144.86, 145.0, 145.02, 145.5, 145.56, 145.6, 145.7, 145.8, 145.94, 145.98, 146.0, 146.1, 146.3, 146.37, 146.47, 146.5, 146.51, 146.54, 146.6, 146.65, 146.67, 147.12, 146.15, 147.7, 147.73, 154.4, 154.6, 155.4, 157.2, 199.54 ppm.

Compound 19b: Yield 90%. ^1H NMR ($\text{CDCl}_3/\text{CS}_2$, 298 K, 300 MHz): δ = 2.85 (s, 3H; CH_3), 4.28 (d, J = 9.3 Hz, 1H; CH_2N), 4.93 (s, 1H; CHN), 4.99 (d, J = 9.3 Hz, 1H; CH_2N), 5.18–5.28 (AB syst., 2H; CH_2O), 5.99 (s, 1H; CH–Cobalt), 6.89–6.93 (m, 1H; Ar–H), 7.33–7.51 ppm (m, 3H; Ar–H); ^{13}C NMR ($\text{CDCl}_3/\text{CS}_2$, 298 K, 75 MHz): δ = 39.8, 68.1, 68.7, 69.8, 71.9, 76.5, 83.2, 89.0, 114.7, 122.2, 129.6, 135.5, 135.6, 136.3, 136.4, 138.6, 139.3, 139.6, 139.9, 140.0, 141.3, 141.4, 141.61, 141.69, 141.7, 141.83, 141.89, 141.93, 141.95, 142.0, 142.3, 142.4, 142.48, 142.8, 142.9, 144.16, 144.17, 144.41, 144.49, 144.9, 144.99, 145.0, 145.04, 145.08, 145.1, 145.19, 145.2, 145.3, 145.4, 145.5, 145.7, 145.8, 145.88, 145.9, 145.96, 146.0, 146.05, 146.1, 146.18, 146.5, 147.0, 153.0, 153.06, 154.6, 155.8, 157.1, 198.2 ppm.

Compound 19c: Yield 90%. ^1H NMR ($\text{CDCl}_3/\text{CS}_2$, 298 K, 300 MHz): δ = 2.81 (s, 3H; CH_3), 4.26 (d, J = 9.5 Hz, 1H; CH_2N), 4.91 (s, 1H; CHN), 4.99 (d, J = 9.5 Hz, 1H; CH_2N), 5.22 (s, 2H; CH_2O), 5.98 (s, 1H; CH–cobalt), 7.02 (d, J = 8.5 Hz, 2H; Ar–H), 7.75 ppm (brs, 2H; Ar–H); ^{13}C NMR ($\text{CDCl}_3/\text{CS}_2$, 298 K, 75 MHz): δ = 40.4, 68.5, 69.3, 70.4, 72.4, 77.7, 83.5, 89.6, 115.3, 130.0, 130.9, 136.22, 136.29, 137.0, 137.3, 140.0, 140.4, 140.61, 140.65, 142.0, 142.1, 142.2, 142.45, 142.48, 142.5, 142.6, 142.7, 143.0, 143.1, 143.4, 143.6, 144.8, 145.0, 145.1, 145.5, 145.6, 145.7, 145.74, 145.82, 145.88, 145.9, 146.0, 146.2, 146.3, 146.5, 146.6, 146.65, 146.7, 146.9, 147.1, 147.7, 153.8, 153.9, 154.4, 156.7, 158.5, 199.6 ppm.

General procedure for the PK reaction—the formation of compounds 5a–d, 7, and 8: Powdered 4 Å molecular sieves (7 g per mmol of propargylglycine, oven dried for 4 h at 120°C) were added to a solution of **3a–d** or **6** (0.05 mmol) in dry toluene (45 mL) at room temperature and the mixture was stirred for 15 min under argon. Then $[\text{Co}_2(\text{CO})_8]$ (0.05 mmol) was added in one portion and the mixture was stirred at 60°C . After 2–3 h, the reaction mixture was filtered through Celite and the solvent was evaporated under vacuum. Flash chromatography over neutral silica gel (eluent: $\text{CH}_2\text{Cl}_2/\text{cyclohexane}$ 1:1) afforded the pure product (**5a–d** in 95–98% yield; **7** and **8** in 41% yield).

Compound 5a: Yield 98%. ^1H NMR (CDCl_3 , 298 K, 500 MHz): δ = 3.76 (dd, J = 14.6, 5.6 Hz, 1H; CH_2), 4.64 (d, J = 14.6 Hz, 1H; CH_2), 4.87 (d, J = 11.5 Hz, 1H; CH_2N), 5.28 (d, J = 11.5 Hz, 1H; CH_2N), 5.34 (d, J = 5.6 Hz, 1H; CHN), 6.92 (s, 1H; CH=C), 7.59–7.55 (m, 3H; Ar–H), 7.75–7.74 ppm (m, 2H; Ar–H); ^{13}C NMR (CDCl_3 , 298 K, 125 MHz): δ = 33.68 (CH_2), 62.99 (CH_2N), 64.26 ($\text{C}_{\text{sp}^3}\text{C}_{60}$), 70.10 ($\text{C}_{\text{sp}^3}\text{C}_{60}$), 72.08 (CH–N), 73.56 ($\text{C}_{\text{sp}^3}\text{C}_{60}$), 73.95 ($\text{C}_{\text{sp}^3}\text{C}_{60}$), 126.05 (C=CH), 127.91 (2C, Ar–C), 129.17 (2C, Ar–C), 131.65 (Ar–C), 135.0, 135.3, 135.6, 135.7, 138.5, 138.7, 140.7, 141.1, 141.6, 141.7, 141.9, 142.4, 142.5, 142.6, 142.8, 143.0, 143.63, 143.65, 143.67, 143.7, 143.76, 143.8, 144.1, 144.3 (2C), 144.33, 144.4, 144.5 (2C), 144.6, 144.7, 144.84, 144.85, 145.03, 145.05, 145.3, 145.4, 145.5, 145.7, 146.0, 146.3, 146.5, 146.6, 146.7, 146.9, 147.4, 147.5, 147.62, 147.63,

148.33, 148.34, 148.4, 149.08, 149.09, 149.13, 149.15, 150.6, 173.7 (CO–N), 184.5 (C=CH), 202.2 ppm (CO); FTIR (KBr): $\bar{\nu}$ = 1718, 1637, 526 cm^{−1}; UV/Vis (CH₂Cl₂): λ (ϵ) = 692 (176), 425 (3932), 322 (22810), 252 nm (76727 dm³ mol^{−1} cm^{−1}); HRMS (MALDI-TOF): calcd. for [C₇₃H₁₁NO₂]⁺: 933.07892; found: 933.07811.

Compound 5b: Yield 95%. ¹H NMR (CDCl₃, 298 K, 500 MHz): δ = 3.67 (ddd, J = 14.9, 6.3, 1.5 Hz, 1H; CH₂), 3.99 (AB syst., 2H; CH₂–CO), 4.82 (d, J = 14.9 Hz, 1H; CH₂), 5.02 (d, J = 11.0 Hz, 1H; CH₂N), 5.25 (d, J = 6.3 Hz, 1H; CHN), 5.28 (d, J = 11.0 Hz, 1H; CH₂N), 6.81 (d, J = 1.5 Hz, 1H; CH=C), 7.37–7.34 (m, 1H; Ar–H), 7.47–7.41 ppm (m, 4H; Ar–H); ¹³C NMR (CDCl₃, 298 K, 125 MHz): δ = 33.8 (CH₂), 43.7 (CH₂–CO), 60.6 (CH₂–N), 63.9 (C_{sp3}–C₆₀), 69.8 (C_{sp3}–C₆₀), 73.0 (CH–N), 73.7 (C_{sp3}–C₆₀), 74.0 (C_{sp3}–C₆₀), 126.1 (C=CH), 127.5 (Ar–C), 128.2, 128.96 (2C, Ar–C), 129.0, 129.1 (2C, Ar–C), 133.6, 134.9, 135.2, 135.3, 138.5, 138.6, 140.8, 140.9, 141.7, 141.9, 142.4, 142.6, 142.7, 142.8, 143.1, 143.6, 143.61, 143.65, 143.67, 143.7, 143.8, 144.2, 144.25, 144.3, 144.34, 144.5, 144.6, 144.63, 144.7, 144.8, 144.84, 145.0, 145.06, 145.3, 145.4, 145.45, 145.9, 146.1, 146.4, 146.5, 146.7, 146.9, 147.1, 147.44, 147.46, 148.3, 148.37, 148.4, 149.1, 149.14, 149.15, 149.2, 150.5, 172.9 (CO–N), 184.2 (C=CH), 201.9 ppm (CO); FTIR (KBr): $\bar{\nu}$ = 1718, 1637, 524 cm^{−1}; UV/Vis (CH₂Cl₂): λ (ϵ) = 632 (183), 425 (3553), 323 (20230), 252 nm (66941 dm³ mol^{−1} cm^{−1}); MS (FAB): m/z : 947 [M]⁺.

Compound 5c: Yield 95%. ¹H NMR (CDCl₃, 298 K, 500 MHz): δ = 3.77 (ddd, J = 15.1, 6.5, 1.5 Hz, 1H; CH₂), 4.67 (d, J = 15.1 Hz, 1H; CH₂), 5.20 (d, J = 10.9 Hz, 1H; CH₂N), 5.42 (d, J = 6.5 Hz, 1H; CHN), 5.50 (d, J = 10.9 Hz, 1H; CH₂N), 6.87 (d, J = 1.5 Hz, 1H; CH=C), 7.02 (d, J = 15.4 Hz, 1H; CH=CH), 7.46–7.44 (m 3H; Ar–H), 7.67–7.65 (m, 2H; Ar–H), 7.93 ppm (d, J = 15.4 Hz, 1H; CH=CH); ¹³C NMR (CDCl₃, 298 K, 125 MHz): δ = 34.5 (CH₂), 60.8 (CH₂–N), 63.8 (C_{sp3}–C₆₀), 69.5 (C_{sp3}–C₆₀), 73.3 (CH–N), 74.0 (C_{sp3}–C₆₀), 74.2 (C_{sp3}–C₆₀), 118.3 (CH=CH), 126.3 (C=CH), 128.3, 129.0, 130.5, 134.5, 134.8, 134.9, 135.4, 138.7, 140.8, 140.9, 141.6, 141.8, 141.9, 142.4, 142.6, 142.7, 142.8, 143.1, 143.6, 143.67, 143.7, 143.9, 144.2, 144.24, 144.3, 144.35, 144.4, 144.5, 144.6, 144.7, 144.8, 144.83, 144.9, 145.0, 145.1, 145.4, 145.45, 145.5, 146.2, 146.3, 146.4, 146.5, 146.6, 146.7, 146.9, 147.3, 147.5, 147.7, 148.37, 148.4, 148.42, 149.1, 149.13, 149.2, 149.23, 150.7, 168.4 (CO–N), 184.4 (C=CH), 202.0 ppm (CO); FTIR (KBr): $\bar{\nu}$ = 1716, 1654, 1375, 524 cm^{−1}; UV/Vis (CH₂Cl₂): λ (ϵ) = 693 (408), 631 (605), 422 (4066), 323 (23560), 253 nm (78290 dm³ mol^{−1} cm^{−1}); MS (FAB): m/z : 960 [M+1]⁺, 959 [M]⁺.

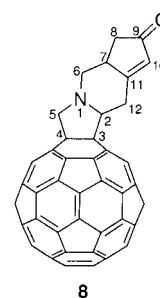
Compound 5d: Yield 98%. ¹H NMR (CDCl₃, 298 K, 500 MHz): δ = 1.01–0.97 (m, 3H; CH₃), 1.51–1.45 (m, 4H; 2CH₂), 1.86–1.81 (m, 2H; CH₂), 2.74–2.49 (m, 2H; CH₂–CO), 3.68 (ddd, J = 14.8, 6.3, 1.5 Hz, 1H; CH₂), 4.72 (d, J = 14.8 Hz, 1H; CH₂), 5.06 (d, J = 11.1 Hz, 1H; CH₂N), 5.23 (d, J = 6.3 Hz, 1H; CHN), 5.24 (d, J = 11.1 Hz, 1H; CH₂N), 6.84 ppm (d, J = 1.5 Hz, 1H; CH=C); ¹³C NMR (CDCl₃, 298 K, 125 MHz): δ = 14.02 (CH₃), 22.55 (CH₂), 24.51 (CH₂), 31.55 (CH₂), 34.24 (CH₂), 36.34 (CH₂–CO), 60.64 (CH₂–N), 63.88 (C_{sp3}–C₆₀), 69.71 (C_{sp3}–C₆₀), 72.96 (CH–N), 73.87 (C_{sp3}–C₆₀), 74.1 (C_{sp3}–C₆₀), 126.1 (C=CH), 134.9, 135.0, 135.3, 138.6, 138.7, 140.8, 141.0, 141.6, 141.8, 141.9, 142.4, 142.6, 142.7, 142.8, 143.1, 143.58, 143.6, 143.65, 143.7, 143.73, 144.0, 144.2, 144.26, 144.3, 144.34, 144.4, 144.5, 144.6, 144.7, 144.8, 144.84, 144.85, 145.0, 145.1, 145.3, 145.5 (2C), 146.1, 146.2, 146.4, 146.5, 146.6, 146.7, 146.9, 147.0, 147.4, 147.5, 147.7, 148.3, 148.4, 148.5, 149.1, 149.14, 149.17, 149.2, 150.7, 175.4 (CO–N), 184.4 (C=CH), 202.0 ppm (CO); FTIR (KBr): $\bar{\nu}$ = 1718, 1637, 524 cm^{−1}; UV/Vis (CH₂Cl₂): λ (ϵ) = 425 (9152), 292 (103491), 259 nm (164778 dm³ mol^{−1} cm^{−1}); MS (FAB): m/z : 927 [M]⁺.

Compound 7: Yield 41%. ¹H NMR (CDCl₃, 298 K, 500 MHz): δ = 3.29 (brdd, J = 13.9, 7.4 Hz, 1H; CH₂–CH=), 3.54 (ddd, J = 13.9, 4.6, 1.6 Hz, 1H; CH₂), 3.72 (d, J = 13.9 Hz, 1H; CH₂), 3.86 (ddt, J = 13.9, 5.0, 1.6 Hz, 1H; CH₂–CH=), 3.89 (d, J = 9.6 Hz, 1H; CH₂N), 4.06 (d, J = 4.6 Hz, 1H; CHN), 4.58 (d, J = 9.6 Hz, 1H; CH₂N), 5.36 (ddd, J = 10.0, 2.6, 1.6 Hz, 1H; CH=CH₂), 5.48 (ddd, J = 17.1, 2.6, 1.7 Hz, 1H; CH=CH₂), 6.15 (m, 1H; CH=CH₂), 6.81 ppm (d, J = 1.6 Hz, 1H; CO–CH=); ¹³C NMR (CDCl₃/CS₂, 298 K, 125 MHz): δ = 33.4 (CH₂), 55.0 (CH₂–CH=), 64.9 (C_{sp3}–C₆₀), 66.5 (CH₂–N), 71.1 (C_{sp3}–C₆₀), 73.0 (C_{sp3}–C₆₀), 73.9 (CH–N), 77.3 (C_{sp3}–C₆₀), 118.5 (CH=CH₂), 125.3, 126.5 (C=CH), 128.2, 129.0, 130.8, 134.2, 134.5, 134.7, 135.5, 136.3, 137.7, 138.2, 138.5, 140.9, 141.7, 141.8, 141.9, 142.3, 142.6, 142.7, 142.8, 143.0, 143.5, 143.6, 143.65, 144.1,

144.16, 144.2, 144.3, 144.4, 144.5, 144.6, 144.7, 144.8, 144.85, 144.9, 145.0, 145.1, 145.3, 145.4, 145.9, 146.2, 146.4, 146.45, 146.6, 146.9, 147.3, 147.9, 148.1, 148.3, 148.34, 148.6, 149.0, 149.1, 149.2, 149.6, 150.3, 152.6, 184.1 (C=CH), 202.2 ppm (CO); FTIR (KBr): $\bar{\nu}$ = 1712, 524 cm^{−1}; UV/Vis (CH₂Cl₂): λ (ϵ) = 555 (1113), 424 (3686), 323 (20294), 253 nm (66769 dm³ mol^{−1} cm^{−1}); HRMS (MALDI-TOF): calcd. for [C₆₉H₁₂NO]⁺ ([M+1]⁺): 870.09134; found: 870.09094.

Compound 8: Aleatory numbering is used for the spectroscopic assignment of compound 8.

Yield 41%. ¹H NMR (CDCl₃/CS₂, 298 K, 500 MHz): δ = 2.27 (dd, J = 18.5, 2.5 Hz, 1H; 8-H), 2.47 (brt, 1H; 6-H), 2.78 (dd, J = 18.5, 6.6 Hz, 1H; 8-H), 3.25 (brt, 1H; 12-H), 3.47 (m, 1H; 7-H), 3.81 (dd, J = 13.0, 3.1 Hz, 1H; 12-H), 3.89 (dd, J = 11.5, 3.1 Hz, 1H; 2-H), 4.04 (dd, J = 10.5, 6.0 Hz, 1H; 6-H), 4.12 (d, J = 9.1 Hz, 1H; 5-H), 4.86 (d, J = 9.1 Hz, 1H; 5-H), 6.19 ppm (s, 1H; 10-H); ¹³C NMR (CDCl₃/CS₂, 298 K, 125 MHz): δ = 35.6 (CH₂), 39.8 (C-8), 40.9 (C-7), 59.1 (C-6), 67.8 (C-5), 70.3 (C_{sp3}–C₆₀), 74.7 (C_{sp3}–C₆₀), 75.4 (C-2), 128.7, 129.7 (2C), 136.2, 136.6, 136.8, 138.1, 140.4, 140.7, 140.74, 140.8, 142.2, 142.24, 142.4, 142.44, 142.48, 142.5, 142.54, 142.6 (2C), 142.64, 143.1, 143.14, 143.2, 143.22, 143.5, 143.6,



144.8, 144.85, 145.0, 145.2, 145.7, 145.73, 145.8, 145.82 (2C), 145.85, 145.9, 146.0, 146.03, 146.1, 146.14, 146.5 (2C), 146.52, 146.6, 146.61, 146.68, 146.7, 146.75, 146.77, 146.83, 146.86, 147.7, 147.8, 152.2, 153.1, 153.7, 156.0, 179.1 (C=CH), 207.7 ppm (CO); IR (KBr): $\bar{\nu}$ = 1706, 1624, 526 cm^{−1}; UV/Vis (CH₂Cl₂): λ (ϵ) = 696 (1215), 428 (4219), 307 (29631), 252 nm (86782 dm³ mol^{−1} cm^{−1}); HRMS (MALDI-TOF): calcd. for [C₆₉H₁₂NO]⁺ ([M+1]⁺): 870.09134; found: 870.09117.

Synthesis of fulleropyrrolidine 21: Compound 20^[13] (2 mmol) and formaldehyde (1 mmol) were added to a solution of C₆₀ (720 mg, 1 mmol) in chlorobenzene (200 mL) under argon. The mixture was refluxed for 1 h and, after cooling, it was concentrated under reduced pressure. The crude product was purified by flash chromatography over silica gel eluting initially with CS₂ (to separate C₆₀) and then with toluene to yield the final product in 30% yield. ¹H NMR (CDCl₃/CS₂, 298 K, 500 MHz): δ = 2.29 (t, J = 2.6 Hz, 2H; CH), 3.64 (dq, J = 17.1, 2.6 Hz, 4H; CH₂), 4.90 ppm (s, 2H; CH₂N); MS (ESI): m/z : 840 [M+1]⁺.

Synthesis of N-acylfulleropyrrolidine 22: NEt₃ (0.15 mmol) was added to a solution of fulleropyrrolidine 21 (840 mg, 0.1 mmol) in toluene (100 mL). After 5 min, benzoyl chloride (0.15 mmol) was added and the mixture refluxed for 18 h. When the reaction was complete, the solvent was removed in vacuo. The crude product was purified by flash chromatography over neutral alumina, with toluene as the eluent, to afford the final product in 95% yield. ¹H NMR (CDCl₃, 298 K, 500 MHz): δ = 2.28 (t, J = 2.5 Hz, 2H; CH), 4.18 (t, J = 2.5 Hz, 4H; CH₂), 5.49 (s, 2H; CH₂N), 7.60 (m, 3H; Ar–H), 7.93 ppm (m, 2H; Ar–H); ¹³C NMR (CDCl₃, 298 K, 125 MHz): δ = 28.6, 62.4, 68.4, 73.4, 74.5, 79.1, 81.0, 115.5, 127.9, 129.4, 131.2, 136.4, 137.7, 137.8, 139.5, 140.7, 141.8, 142.2, 142.3, 142.5, 142.8, 143.2, 143.6, 144.9, 145.0, 145.6, 145.7, 145.8, 145.9, 146.0, 146.2, 146.5, 146.8, 146.9, 147.2, 147.8, 147.9, 151.7, 154.5, 173.0 ppm; FTIR (KBr): $\bar{\nu}$ = 526, 1961, 2119, 2350, 1922 cm^{−1}; MS (ESI): m/z : 944 [M+H]⁺.

Synthesis of metal complex 23: [Co₂(CO)₈] (0.3 mmol) was added to a solution of N-acylfulleropyrrolidine 22 (94 mg, 0.1 mmol) in toluene

(100 mL) at room temperature under argon and the resulting mixture was stirred at 50 °C for 1 h until total complexation of the enyne (TLC). The reaction was then purified by flash chromatography over silica gel using toluene as eluent (95% yield). ¹H NMR (CDCl₃, 298 K, 300 MHz): δ = 3.58 (d, *J* = 13.5, 1H; CH₂), 4.11 (d, *J* = 17.13 Hz, 1H; CH₂), 4.57 (d, *J* = 17.3 Hz, 1H; CH₂), 4.97 (d, *J* = 12.5 Hz, 1H; CH₂N), 5.27 (d, *J* = 12.5 Hz, 1H; CH₂N), 5.50 (d, *J* = 13.5 Hz, 1H; CH₂), 6.11 (s, 1H; CH-cobalt), 6.92 (s, 1H; CH=C), 7.60 ppm (m, 5H; Ar-H); ¹³C NMR (CDCl₃, 298 K, 125 MHz): δ = 37.0, 42.0, 60.9, 65.1, 69.6, 73.9, 74.2, 75.4, 77.9, 79.8, 87.7, 126.4, 127.2, 129.7, 131.3, 135.3, 136.6, 137.0, 137.9, 138.9, 141.0, 141.3, 142.0, 142.3, 142.4, 142.9, 143.0, 143.1, 143.5, 143.6, 143.7, 143.9, 144.0, 144.1, 144.2, 144.6, 144.7, 144.78, 144.8, 144.9, 145.0, 145.07, 145.1, 145.2, 145.5, 145.9, 146.9, 147.2, 147.3, 147.4, 148.2, 148.3, 148.8, 149.5, 149.6, 150.8, 171.4, 183.9, 199.9, 202.3 ppm; FTIR (KBr): $\tilde{\nu}$ = 1641, 1718, 2017, 2350, 2922 cm⁻¹.

Synthesis of compounds 24 and 25: A solution of compound 23 (60 mg, 0.047 mmol) in toluene (80 mL) was stirred at 60 °C for 18 h under argon. The solvent was evaporated under reduced pressure and the crude product was purified by flash chromatography over silica gel eluting with toluene/ethyl acetate (9:1) to yield compounds 24 (30% yield) and 25 (5% yield).

Compound 24: ¹H NMR (CDCl₃, 298 K, 500 MHz): δ = 2.22 (t, *J* = 2.6 Hz, 1H; CH), 3.47 (dd, *J* = 17.3, 2.6 Hz, 1H; CH₂), 3.87 (dd, *J* = 14.5, 1.3 Hz, 1H; CH₂-C=C), 3.88 (dd, *J* = 17.3, 2.6 Hz, 1H; CH₂), 5.14 (d, *J* = 11.9 Hz, 1H; CH₂N), 5.24 (d, *J* = 14.5 Hz, 1H; CH₂-C=C), 5.28 (d, *J* = 11.9 Hz, 1H; CH₂N), 6.97 (d, *J* = 1.3 Hz, 1H; CH-CO), 7.57–7.67 ppm (m, 5H; Ar-H); ¹³C NMR (CDCl₃, 298 K, 125 MHz): δ = 24.7 (CH₂), 36.7 (CH₂-C=C), 62.0 (CH₂N), 64.1, 74.1, 74.4, 74.6, 75.0, 78.8, 80.0, 125.7, 127.0, 129.2, 130.9, 134.9, 136.7, 137.1, 137.5, 138.2, 138.4, 140.6, 140.7, 141.5, 141.8, 142.0, 142.4, 142.6, 142.7, 142.75, 143.1, 143.3, 143.4, 143.5, 143.69, 143.7, 143.73, 144.2, 144.3, 144.37, 144.4, 144.5, 144.58, 144.6, 144.8, 144.9, 145.0, 145.1, 145.3, 145.4, 145.5, 146.2, 146.3, 146.4, 146.5, 146.7, 146.8, 146.9, 147.4, 148.0, 148.02, 148.3, 148.35, 148.4, 149.0, 149.1, 150.6, 172.0, 183.8, 202.0 ppm; FTIR (KBr): $\tilde{\nu}$ = 526, 1365, 1647, 1718 cm⁻¹; MS (ESI): *m/z*: 972 [M+H]⁺; UV/Vis (CH₂Cl₂): λ (ε) = 551 (693), 429 (3048), 325 (17976), 254 nm (70866 dm³ mol⁻¹ cm⁻¹).

Compound 25: ¹H NMR (CDCl₃, 298 K, 500 MHz): δ = 3.45 (d, *J* = 8.5 Hz, 1H; CH₂), 3.75 (d, *J* = 8.5 Hz, 1H; CH₂), 3.96 (d, *J* = 8.4 Hz, 1H; CH₂), 5.09 (d, *J* = 7.1 Hz, 1H; CH₂N), 5.20 (d, *J* = 7.1 Hz, 1H; CH₂N), 5.55 (d, *J* = 8.4 Hz, 1H; CH₂), 6.92 (s, 1H), 6.98 (s, 1H), 7.53–7.57 ppm (m, 5H; Ar-H); ¹³C NMR (CDCl₃, 298 K, 125 MHz): δ = 32.4 (CH₂), 37.3 (CH₂), 47.9 (CH₂N), 60.8, 64.4, 73.8, 76.3, 125.6, 126.7, 129.2, 130.7, 134.9, 136.1, 136.6, 137.2, 137.4, 137.7, 137.8, 138.0, 138.4, 138.5, 139.1, 139.5, 139.8, 140.6, 140.9, 141.5, 141.6, 141.9, 141.92, 142.0, 142.5, 142.6, 142.7, 142.8, 143.0, 143.1, 143.2, 143.4, 143.5, 143.6, 143.64, 143.7, 143.71, 143.8, 144.3, 144.36, 144.4, 144.5, 144.56, 144.6, 144.7, 144.8, 145.1, 145.4, 145.5, 146.2, 146.46, 146.5, 146.55, 146.8, 146.9, 147.4, 147.8, 148.0, 148.4, 148.5, 148.6, 149.1, 149.2, 150.5, 171.9, 183.5, 201.9, 105.4 ppm; UV/Vis (CH₂Cl₂): λ (ε) = 428 (2838), 338 (15165), 323 (19017), 256 nm (93789 dm³ mol⁻¹ cm⁻¹); MS (ESI): *m/z*: 1022 [M+Na]⁺.

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