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Co(porphyrin)-catalysed amination of 1,2-dihydronaphthalene derivatives by aryl azides

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ABSTRACT

Co(porphyrin) complexes promote an unusual reactivity of dihydronaphthalene towards several aryl azides. The reaction affords the benzylic amine of tetrahydronaphthalene instead yielding the amine of dihydronaphthalene as it normally happens in the presence of Ru(porphyrin)CO catalysts. The amination process occurs with the concomitant reduction of the dihydronaphthalene double bond probably due to the high reactivity of the endocyclic C=C bond coupled with the good hydrogen donor capability of dihydronaphthalene. Two mechanisms for this reaction are proposed.

1. Introduction

The development of efficient and clean procedures to synthesise nitrogen containing molecules in a few steps is a topic of high scientific interest due to their biological and pharmaceutical properties. The key points to perform sustainable amination reactions are i) the selection of a selective, active and stable catalytic system; and ii) the use of nitrogen sources presenting high reactivity and atom efficiency. These two characteristics are well exhibited by organic azides (RN_3) [1–3] which transfer a nitrene functionality to an organic skeleton by yielding eco-friendly N_2 as the only stoichiometric by-product. The reaction of RN_3 with organic compounds can be thermally or photochemically promoted [4] but, to improve the reaction selectivity, the presence of a metal catalyst is required. Amongst the catalysts used to achieve these chemical transformations [5,6], metallo-porphyrins show a good catalytic efficiency coupled with a very high chemical stability [7–9]. Organic azides react in the presence of iron [10,11], ruthenium [12–19] and cobalt porphyrins [18,20–30] with a variety of hydrocarbons.

In the last decade we have studied the efficiency of cobalt and ruthenium porphyrin complexes in catalysing the amination reaction of a wide class of substrates with aryl azides. Aryl azides are reactive towards olefins [15,16,19,26], dienes [17,31], benzylic [13,29,30] and allylic [12,14,26] hydrocarbons and the reaction chemoselectivity depends on the nature of the metal coordinated to the porphyrin skeleton. In fact, the amination of an identical substrate yields diverse aza-compounds by running the reaction in the presence of a cobalt [13] or a ruthenium [30] catalyst. This behaviour derives from the mechanisms of the nitrene transfer reaction that involves different intermediates depending on the transition metal nature. We have recently reported that the active species in ruthenium porphyrin catalysed C–H amination is a bis-imido complex, whose molecular structure and catalytic activity were provided [12,14] (Scheme 1). On the other hand, Zhang, De Bruin and co-authors proposed, on the basis of theoretical and EPR data, the formation of an active cobalt(III) nitrene radical intermediate during the cobalt(II) porphyrin catalysed amination of both saturated and unsaturated hydrocarbons [20,21] (Scheme 1). The formation of a similar intermediate was also suggested by Ghosh and co-authors based on DFT calculations [32].

As stated above, structurally different substrates can be aminated by organic azides and if an organic molecule contains more than one functional group reactive towards azides, the reaction chemoselectivity depends on the nature of the active catalytic species. Zhang and co-authors recently reported an excellent chemoselectivity of an intramolecular allylic C–H amination *versus* a C=C aziridination using a D_{2h}-symmetric cobalt porphyrin catalyst [22]. A similar trend was also observed by us [26] for the amination of cyclohexene catalysed by Co(TPP) (TPP = dianion of tetraphenyl porphyrin). The analysis of the reaction products revealed the presence of the allylic amine and the absence of the

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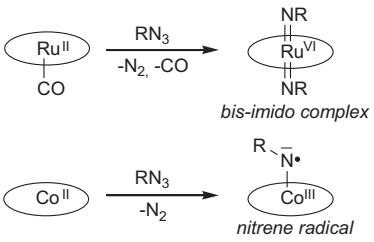


Scheme 1. Reaction between an organic azide and a ruthenium or cobalt porphyrin.

aziridine derived from the cyclohexene C=C bond amination. Nevertheless, it should be noted that DFT calculations indicated competitive energetic pathways for the aziridination and the C–H amination of olefins and allylic substrates respectively [32].

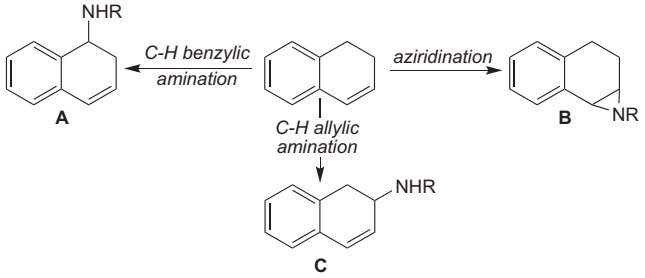
Our previous data on the amination of α-substituted cyclic styrenes, such as dihydronaphthalene derivatives, showed a low chemoselectivity for the ruthenium porphyrins catalysed reactions [12]. This is probably due to the simultaneous presence of an endocyclic olefin, an allylic and a benzylic C–H bond in the same molecule. A mixture of aziridine and allylic and benzylic amines was obtained with a product distribution that depends on the employed substrate.

In order to improve the chemoselectivity of the reaction, we studied the efficiency of cobalt porphyrins in the catalytic amination discussed above. Experimental data herein shows an unusual reactivity of the C–C double bond due to the peculiarity of dihydronaphthalene being a very active hydrogen donor.

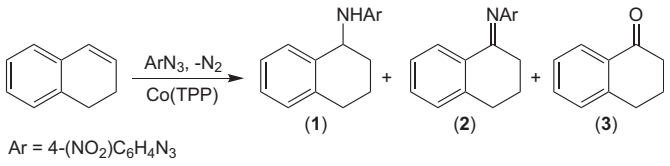
2. Results and discussion

The dihydronaphthalene molecule contains three functional groups that can be potentially aminated by a nitrene transfer reaction (Scheme 2). Published data reported different chemoselectivities depending on the employed catalyst.

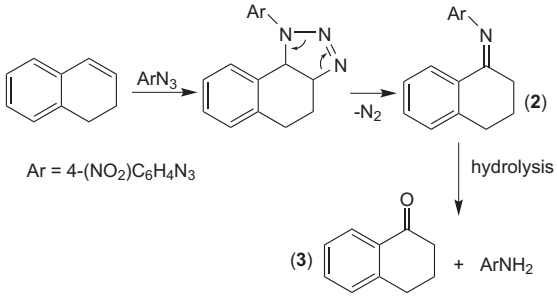
We have already published that benzylic and allylic amines **A** and **C** were obtained in the presence of ruthenium porphyrin catalysts [12], while the synthesis of aziridines **B** was promoted by dirhodium(II) complexes as reported by Hashimoto and co-authors [33]. We then performed the reaction between dihydronaphthalene and 4-nitrophenyl azide in benzene in the presence of Co(TPP), using a catalytic ratio Co(TPP)/azide = 4:50 and an excess of dihydronaphthalene (see experimental section). The chromatographic purification of the reaction crude yielded the benzylic amine of tetrahydronaphthalene (**1**) (34%) and a mixture (32% total yield) of *N*-(3,4-dihydro-1(2*H*)-naphthalenylidene)-4-nitrobenzenamine (**2**) and 1(2*H*)-naphthalenone-3,4-dihydro (**3**) (Scheme 3). The last compound is derived from the hydrolysis of **2** during the purification process. Compound **1** was unequivocally identified by comparing it to the product obtained by the



Scheme 2. Amination pathways of dihydronaphthalene.



Scheme 3. Amination of dihydronaphthalene by 4-nitrophenyl azide catalysed by Co(TPP).



Scheme 4. Blank reaction between 4-nitrophenyl azide and dihydronaphthalene.

tetrahydronaphthalene amination catalysed by ruthenium porphyrins [13].

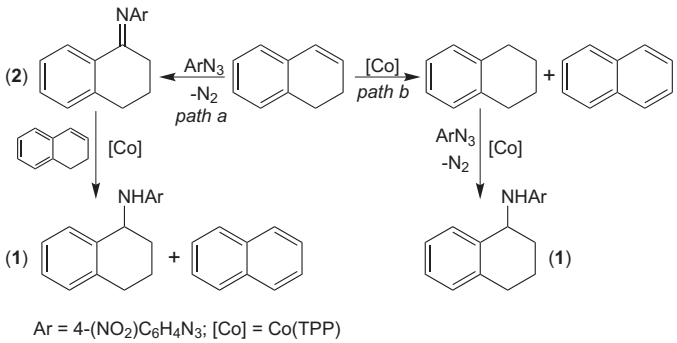
The rest of the material was 4-nitroaniline and none of the compounds reported in Scheme 2 have been isolated.

To rationalise this experimental result we repeated the reaction in absence of the catalyst and the azide completely converted into mixture **2** and **3**. Compound **1** was not detected. It is well known that the non-catalysed reaction between olefins and organic azides [19,34,35] affords imines by thermal decomposition of 1,2,3-triazolines, therefore we proposed a blank reaction mechanism illustrated in Scheme 4.

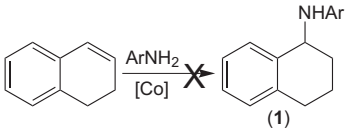
Considering that dihydronaphthalene can easily be involved in hydrogen transfer reaction [36,37], we then hypothesised that the formation of **1** could be due either to a hydrogenation process of **2**, in which an equimolar amount of dihydronaphthalene is converted in naphthalene (*path a*, Scheme 5), or to an amination of tetrahydronaphthalene formed by a cobalt-mediated disproportionation of dihydronaphthalene (*path b*, Scheme 5) [37–40].

The feasibility of this last reaction was confirmed by obtaining **1** (80%) from the Co(TPP) catalysed direct amination of tetrahydronaphthalene by 4-nitrophenyl azide.

Both proposals were not supported by experimental data. The reaction of imine (**2**) with a dihydronaphthalene excess, run in the presence of Co(TPP), did not afford **1** and a disproportionation to tetrahydronaphthalene and naphthalene was not observed after refluxing dihydronaphthalene for 2 h with Co(TPP). Thinking that



Scheme 5. Potential pathways for the synthesis of **1**.



Ar = 4-(NO_2)$C_6H_4N_3$; [Co] = Co(TPP)

Scheme 6. Failed hydroamination of dihydronaphthalene by 4-nitrophenyl aniline.

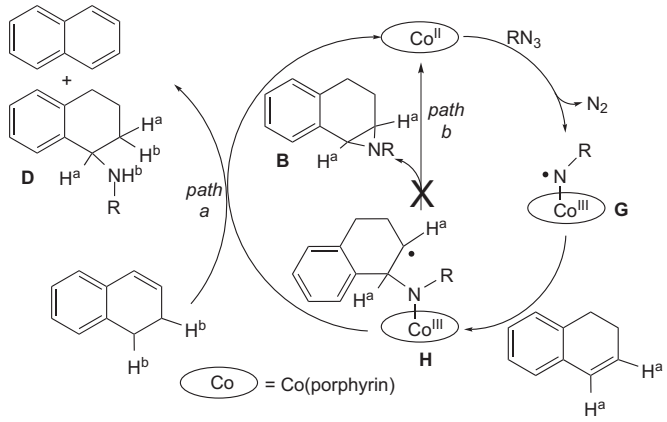
Table 1
Cobalt porphyrin catalysed amination of dihydronaphthalene by 4-nitrophenyl azide.[a]

Entry		Time (h)[b]	**1** (%)[c]	**2** + **3** (%)[c]
1[d]	Co(TPP); R = H; R′ = R″ = C_6H_5	10	23	22
2[e]	Co(TPP); R = H; R′ = R″ = C_6H_5	3	27	25
3[e]	Co(TMOP); R = H; R′ = R″ = 4-$CH_3OC_6H_4$	1.5	40	34
4[e]	Co(4-^{n}BuTPP); R = H; R′ = R″ = 4-^{n}BuC_6H_4	3	32	20
5[e]	Co(4-CF_3TPP); R = H; R′ = R″ = 4-$CF_3C_6H_4$	4.5	23	41
6[e]	Co(OEP); R = Et; R′ = R″ = H	1.5	22	21
7[e]	Co(4′MPyP); R = H; R′ = C_6H_5; R″ = Py	2.5	19	56

[a] Experimental conditions: 4-nitrophenyl azide (1.34×10^{-4} mol) was added to a solution of catalyst (1.07×10^{-5} mol) and dihydronaphthalene (2.5 ml) in the appropriate solvent (2.5 mL). The mixture was heated at 75 °C until complete azide conversion.
[b] Time required to reach complete aryl azide conversion.
[c] Isolated yield calculated with respect to the initial amount of the azide.
[d] Reaction run in benzene.
[e] Reaction run in 1,2-dichloroethane.

amine **1** could also be formed by a less probable but still possible intermolecular hydroamination reaction, we reacted dihydronapthalene with 4-nitrophenyl aniline in the presence of Co(TPP). No reaction was observed after refluxing the reaction mixture for 5 h (Scheme 6).

In order to assess the generality of the process we repeated the reaction of dihydronaphthalene with 4-nitrophenyl azide in the presence of several cobalt complexes; results are listed in Table 1. For all reported reactions the balance of the material was 4-nitrophenyl aniline.



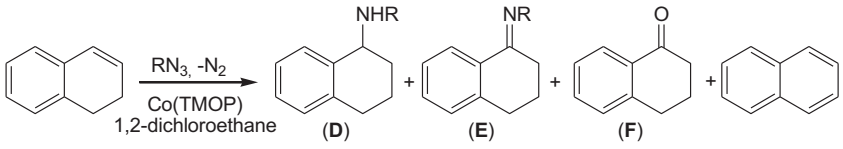
Scheme 7. Mechanistic proposal for the dihydronapthalene amination.

As reported in Table 1, the electronic behaviour of the catalyst has little influence on reaction yields. The best catalyst/solvent combination seems to be Co(TMOP)/1,2-dichloroethane (entry 3, Table 1), therefore it was employed to test the reactivity of several azides towards dihydronaphthalene. Experimental data are reported in Table 2.

Experimental results indicated long reaction times when using azides bearing electron donating substituents (entries 2 and 4, Table 2) and comparable compound **D** yields for all the reactions. In particular, best yields were achieved for the amination of dihydronaphthalene by NsN_3 (entry 6, Table 2) and TsN_3 (entry 7, Table 2). The purification procedure on silica provoked the partial hydrolysis of imines **E** into 3,4-dihydronaphthalen-1(2*H*)-one (**F**) and the corresponding aryl amine therefore in Table 2 overall **E** + **F** isolated yields are reported. In the particular case of the reaction between 4-*tert*butylphenyl azide with dihydronaphthalene, the chromatographic purification afforded only **D** and **F** because the imine **E**, detected in the crude by GC–MS, was completely hydrolysed to **F** during the purification procedure. It is worth noting that the GC–MS analysis of the crude revealed, in all the reported runs, the presence of naphthalene.

Data collected up to now indicate that the formation of the benzylic amine of tetrahydronaphthalene (**D**) by dihydronaphthalene amination is a general reaction. On the basis of recent studies on

Table 2
Co(TMOP) catalysed amination of dihydronaphthalene by organic azides.[a]



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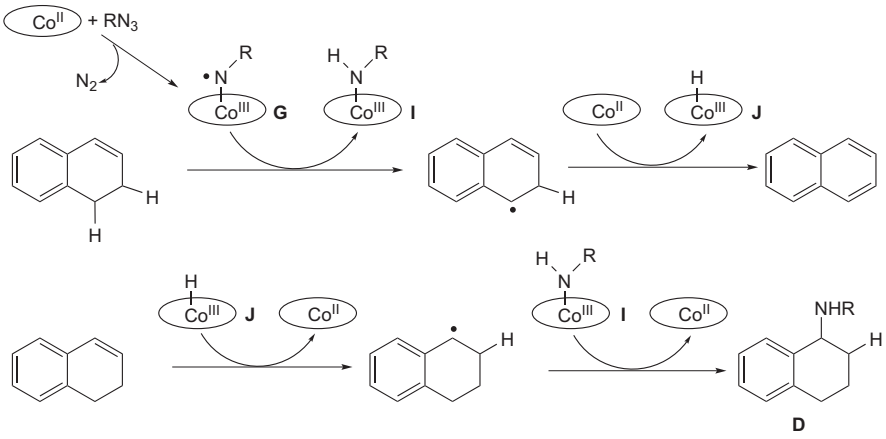
Entry	Azide	Time (h)[b]	**D** (%)[c]	**E** + **F** (%)[c]
1	4-(NO_2)$C_4H_3N_3$	1.5	**1** (40)	**2** + **3** (34)
2	4-(CH_3O)$C_4H_3N_3$	11	**4** (32)	**5** + **3** (29)
3	4-(CN)$C_6H_4N_3$	3.5	**6** (34)	**7** + **3** (36)
4	4-(^{t}Bu)$C_6H_4N_3$	18	**8** (37)	**9**[d] +**3** (19)
5	3,5-(CF_3)$_2C_6H_3N_3$	1.5	**10** (21)	**11** + **3** (20)
6	4-(NO_2)$C_6H_4SO_2N_3$	2	**12** (41)	**13** + **3** (18)
7	4-(CH_3)$C_6H_4SO_2N_3$	5	**14** (44)	**15** + **3** (11)

[a] Experimental conditions: azide (1.34×10^{-4} mol) was added to a solution of catalyst (1.07×10^{-5} mol) and dihydronaphthalene (2.5 ml) in 1,2-dichloroethane (2.5 mL). The mixture was heated at 75 °C until complete azide conversion.
[b] Time required to reach complete aryl azide conversion.
[c] Isolated yield calculated with respect to the initial amount of the azide.
[d] Detected by GC–MS in the reaction mixture.



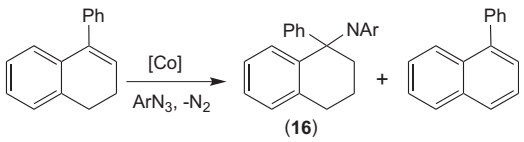
Scheme 8. Alternative mechanistic proposal for the dihydronapthalene amination.

cobalt porphyrin catalysed aminations [20,21], we propose the mechanism shown in Scheme 7.

Taking into account the aziridination mechanism proposed by Zhang and De Bruin [20,21], we first suggest the formation of the nitrene radical **G** that reacts with dihydronaphthalene to form the carboradical **H** which could evolve through different pathways. We propose that the good hydrogen donor capacity of dihydronaphthalene favoured a hydrogen transfer reaction (*path a*) forming benzylic amine **D** and avoiding the olefin aziridination to **B** (*path b*). The absence of compounds deriving from benzylic or allylic amination of dihydronaphthalene (**A** and **C**, Scheme 2) are probably due to high reactivity of an endocyclic C—C double bond that can be easily activated towards a H-atom abstraction homolytic process.

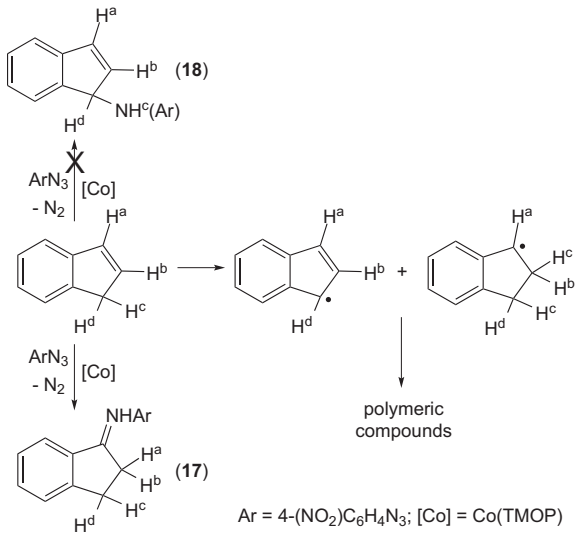
Alternatively, [41] complex **G** may abstract a hydrogen atom from dihydronaphthalene forming cobalt(III) amido species (**I**) (Scheme 8). The obtained benzylic radical could be responsible for a hydrogen transfer reaction to cobalt(II) porphyrin yielding cobalt(III) hydride (**J**) and a naphthalene molecule. Then, the transfer of a hydrogen atom from complex **J** to the substrate forms another benzylic radical which, by reacting with complex **I**, affords the benzylic amine **D**. This mechanistic proposal is in accord with that already described [42] for the transfer of hydrogen atoms in the reactions of organic radicals with Co(II) porphyrin complexes.

To confirm the direct amination of the double bond and to rule out a C—H benzylic amination we studied the reactivity of 4-nitrophenyl azide towards 1-phenyl-1,2-dihydronapthalene, where a phenyl group is present on the C-C double bond. The formation of 1,2,3,4-tetrahydro-*N*-(4-nitrophenyl)-1-phenylnaphthalen-1-amine (**16**) in 54% yield (Scheme 9) definitely pointed out the amination of the unsaturated position to sustain mechanisms illustrated in Schemes 7 and 8. The GC—MS analysis of the crude disclosed the presence of 1-phenylnaphthalene.



Ar = 4-$(NO_2)C_6H_4N_3$; [Co] = Co(TPP)

Scheme 9. Synthesis of compound **16**.



Ar = 4-$(NO_2)C_6H_4N_3$; [Co] = Co(TMOP)

Scheme 10. Reaction between 4-nitrophenyl azide and indene.

Considering that the reaction between 1-phenyl-1,2-dihydronapthalene and an azide molecule cannot yield the corresponding imine, this last experiment definitely excludes the involvement of imine compounds (**E**) in the formation of benzylic amines (**D**).

It is worth noting that the ruthenium porphyrin catalysed amination of 1-phenyl-1,2-dihydronapthalene by 3,5-bis-trifluoromethylphenyl azide [12] afforded the type **C** allylic amine and a minor amount of the type **B** aziridine (Scheme 2).

In order to clarify the role of the hydrocarbon in the hydrogen transfer process (Scheme 7, *path a*) we investigated the reaction between 4-nitrophenyl azide and indene, an olefin that, not being convertible into the corresponding aromatic compound, cannot be involved in *path a* (Scheme 7). The reaction was run at 75 °C with and without Co(TMOP) in a solvent mixture indene/benzene = 1:1. In both cases no azide conversion was observed after 6 h at 75 °C. When the two reactions were repeated by using indene as the reaction solvent, the imine *N*-(1,2-dihydroinden-3-ylidene)-4-nitrobenzenamine (**17**) [43] was the only isolated aminated compound in approximately 30% yield in both cases. Large amounts of polymeric material was observed due to the well known tendency of indene to polymerise by radical coupling reactions [36] (Scheme 10).

The lack of formation of 2,3-dihydro-*N*-(4-nitrophenyl)-1*H*-inden-1-amine (**18**) confirmed that cobalt porphyrins are not competent catalysts for the direct C–H amination of α-substituted cyclic styrenes. Thus, when a hydrogen atom abstraction is impossible the uncatalysed reaction is the only achievable process [34]. It should be noted that the ruthenium porphyrin mediated C–H amination of indene yielded **18** in moderate yields [12].

In our belief, the dissimilar catalytic performance of ruthenium and cobalt complexes in the amination of 1-phenyl-1,2-dihydronapthalene (Scheme 8) and indene (Scheme 9) strongly agrees with different mechanisms for the two catalytic reactions.

3. Conclusions

In summary, data reported herein indicate that the mechanism of amination reactions catalysed by cobalt (II) porphyrins should be determined well through the substrate behaviour. The high reactivity of an endocyclic C–C double bond coupled with the good hydrogen donor capability of dihydronaphthalene establishes a mechanism in which hydrogen atom abstractions are the key-steps in C–H amination.

4. Experimental

4.1. Materials and methods

Unless otherwise specified all reactions were carried out in nitrogen atmosphere employing standard Schlenk techniques and magnetic stirring. Benzene was dried by M. Braun SPS-800 solvent purification system. 1,2-Dichloroethane was distilled over anhydrous calcium chloride and kept under nitrogen. All the other starting materials were commercial products used as received. Aryl azides [1,16,44], tetraphenylporphyrin [45,46] and Co(TPP) [47] were synthesised by methods as reported in the literature or with minor modifications. The purity of olefins and aryl azides employed was confirmed by GC–MS or ^{1}H NMR spectroscopy. NMR spectra were recorded at room temperature on a Bruker AC-300, operating at 300 MHz for ^{1}H, at 75 MHz for ^{13}C and at 282 MHz for ^{19}F or on a Bruker Avance 400-DRX spectrometers, operating at 400 MHz for ^{1}H and at 100 MHz for ^{13}C. Chemical shifts (ppm) are reported relative to TMS. The ^{1}H NMR signals of the compounds described in the following have been attributed by COSY and NOESY techniques. Assignments of the resonance in ^{13}C NMR were made using the APT pulse sequence and HSQC and HMBC techniques. GC–MS analyses were performed on Shimadzu QP5050A instrument. Infrared spectra were recorded on a Varian Scimitar FTS 1000 spectrophotometer. Elemental analyses were recorded in the analytical laboratories of Milan University. All the reagents employed for the preparation of the ligands and their complexes were of the highest grade available and used without further purification. Unless otherwise stated, all catalytic tests were carried out under an atmosphere of purified dinitrogen using modified Schlenk techniques.

Analytic data for compounds **1** [13], **2** [48], **4** [49], **5** [50], **10** [13], **12** [23], **14** [23], **15** [51], **17** [43] and **18** [13] are in agreement with those reported in the literature. Compound **3** was spectroscopically identical with an authentic sample. All reaction yields are reported in Table 2.

4.2. General procedure for catalytic reactions

In a typical run, the azide (1.34×10^{-4} mol) was added to a solution of catalyst (1.07×10^{-5} mol) and dihydronaphthalene (2.5 ml) in 1,2-dichloroethane (2.5 mL). The resulting solution was heated at 75 °C using a preheated oil bath. The consumption of the aryl azide was monitored by TLC up to the point that its spot was no longer observable, and then by IR spectroscopy, which measured the characteristic N_3 absorbance in the range 2095–2130 cm^{-1}. The reaction was considered to be finished when the absorbance of the azide measured was below 0.03 (by using a 0.5 mm thick cell). The solution was then evaporated to dryness and the residue purified by flash chromatography using a mixture ethyl acetate/*n*-hexane = 1:50 as the eluent.

6: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ, ppm: 7.46 (d, 2H, J = 8.7 Hz), 7.33 (d, 1H, J = 7.6 Hz), 7.27–7.17 (m, 3H), 6.66 (d, 2H, J = 8.7 Hz), 4.73–4.68 (m, 1H), 4.66 (d, 1H, J = 6.4 Hz, N*H*), 2.93–2.77 (m, 2H), 2.07–1.96 (m, 2H), 1.94–1.85 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ, ppm: 150.4 (CN), 137.7 (C), 136.6 (C), 133.9 (2 CH), 129.3 (CH), 129.0 (CH), 127.7 (CH), 126.3 (CH), 120.4 (C), 112.3 (2 CH), 98.6 (C), 50.7 (CH), 29.1 (CH_2), 28.6 (CH_2), 19.4 (CH_2). Anal. Calcd for $C_{17}H_{16}N_2$ C, 82.22; H, 6.49; N, 11.28. Found C, 82.30; H, 6.54; N, 10.97.

7: ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ, ppm: 8.28 (d, 1H, J = 7.6 Hz), 7.64 (d, 2H, J = 8.6 Hz), 7.45–7.40 (m, 1H), 7.34 (d, 1H, J = 7.6 Hz), 7.26–7.23 (m, 1H), 6.88 (d, 2H, J = 8.6 Hz), 2.94 (pst, 2H, J = 6.1 Hz), 2.49 (pst, 2H, J = 6.1 Hz), 2.01–1.93 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K) δ, ppm: 166.7 (C), 156.4 (CN), 142.1 (C), 133.7 (2 CH), 133.4 (C), 131.7 (CH), 129.3 (CH), 127.0 (CH), 126.9 (CH), 120.5 (2 CH), 119.8 (C), 106.6 (C), 30.7 (CH_2), 30.2 (CH_2), 23.6 (CH_2). Anal. Calcd for $C_{17}H_{14}N_2$ C, 82.90; H, 5.73; N, 11.37. Found C, 83.15; H, 5.85; N, 10.95.

8: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ, ppm: 7.47 (d, 1H, J = 6.8 Hz), 7.30 (d, 2H, J = 8.7 Hz), 7.25–7.22 (m, 2H), 7.20–7.18 (m, 1H), 6.70 (d, 2H, J = 8.7 Hz), 4.67 (m, 1H), 3.85 (bs, 1H, N*H*), 2.94–2.78 (m, 2H), 2.05-1.82 (m, 4H), 1.37 (s, 9H, ^{t}Bu). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ, ppm: 145.1 (C), 139.9 (C), 138.4 (C), 137.7 (C), 129.4 (CH), 129.0 (CH), 127.1 (CH), 126.2 (2 CH), 126.1 (CH), 112.5 (2 CH), 51.2 (CH), 31.6 (CH_3), 29.4 (CH_2), 28.8 (CH_2), 19.4 (CH_2). Anal. Calcd for $C_{20}H_{25}N$ C, 85.97; H, 9.02; N, 5.01. Found C, 86.21; H, 9.17; N, 5.31.

11: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ, ppm: 8.29 (d, 1H, J = 7.9 Hz), 7.60 (s, 1H), 7.46–7.42 (m, 1H), 7.36–7.32 (m, 1H), 7.26–7.25 (m, 3H), 2.96 (pst, 2H, J = 6.1 Hz), 2.52 (pst, 2H, J = 6.1 Hz), 2.03–1.96 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ, ppm: 167.8 (C), 152.9 (C), 141.8 (C), 132.9 (C), 132.4 (q, J = 131 Hz, 2 *C*CF_3), 131.5 (CH), 128.9 (CH), 126.7 (CH), 126.6 (CH), 123.5 (J = 270 Hz, q, 2 CF_3), 119.9 (2 CH), 116.5 (CH), 30.3 (CH_2), 29.8 (CH_2), 22.8 (CH_2). ^{19}F NMR (282 MHz, $CDCl_3$, 298 K) δ, ppm: −63.2. Anal. Calcd for $C_{18}H_{13}F_6N$ C, 60.51; H, 3.67; N, 3.92. Found C, 60.87; H, 3.91; N, 3.78.

13: ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ, ppm: 8.42 (d, 2H, J = 8.9 Hz), 8.26 (d, 2H, J = 8.9 Hz), 8.04 (d, 1H, J = 7.3 Hz), 7.51 (pst, 1H, J = 7.3 Hz), 7.28-7.24 (m, 2H), 3.46 (pst, 2H, J = 6.1 Hz), 2.95 (pst, 2H, J = 6.1 Hz), 2.19-2.06 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K) δ, ppm: 134.8 (CH), 129.6 (CH), 128.6 (2 CH), 128.1 (CH), 127.3 (CH), 124.5 (2 CH), 34.1 (CH_2), 29.7 (CH_2), 22.8 (CH_2), (quaternary carbons were not detected). Anal. Calcd for $C_{16}H_{14}N_2O_4S$ C, 58.17; H, 4.27; N, 8.48. Found C, 58.44; H, 4.42; N, 8.22.

16: ^{1}H NMR (300 MHz, C_6D_6, 298 K) δ, ppm: 7.88 (d, 2H, J = 9.0 Hz), 7.16-7.00 (m, 9H), 5.83 (d, 2H, J = 9.0 Hz), 4.56 (s, 1H, N*H*), 2.70-2.64 (m, 2H), 2.03–1.97 (m, 2H), 1.47-1.34 (m, 2H). ^{13}C NMR (75 MHz, C_6D_6, 298 K) δ, ppm: 150.7 (C), 146.9 (C), 139.1 (C), 139.0 (C), 137.9 (C), 63.3 (C), 129.8 (CH), 129.5 (CH), 129.1 (CH), 128.9 (CH), 128.1 (CH), 127.7 (CH), 127.1 (CH), 126.9 (CH), 126.8 (CH), 125.7 (2 CH), 114.4 (2 CH), 42.1 (CH_2), 30.3 (CH_2), 20.0 (CH_2). Anal. Calcd for $C_{22}H_{20}N_2O_2$ C, 76.72; H, 5.85; N, 8.13. Found C, 76.98; H, 6.03; N, 7.94.

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