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Electronic effects of substituents on the stability of the iridanaphthalene compound $[IrCp*{=C(OMe)CH=C(o-C_6H_4)(Ph)}(PMe_3)]PF_6^{\dagger}$

M. Talavera,^a J. Bravo,^a J. Castro,^a S. García-Fontán,^a J. M. Hermida-Ramón^b and S. Bolaño*^a

Iridanaphthalene complexes are synthesized from the corresponding methoxy(alkenyl)carbeneiridium compounds. The electronic character of the substituents on the 6-position of the metallanaphthalene ring is crucial from the point of view of the stability of the iridanaphthalene, $[IrCp*{=C(OMe)CH=C(o-C_6H_4)-(Ph)}]PF_6$, vs. its transformation to the corresponding indanone derivatives. Stability studies of the iridanaphthalene compounds revealed that strong electron donor substituents (–OMe) stabilize the iridanaphthalene, while weak electron donor (–Me) and electron withdrawing (–NO₂) groups favor the formation of indanone derivatives. Two possible indanone isomers can be obtained in the conversion of the unstable iridanaphthalene complexes and a mechanism for the formation of these isomers is proposed.

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Introduction

Transition-metal cyclometalated complexes have increased their presence in organometallic chemistry. Much of the growing interest stems from a plethora of applications, for example, in organic transformations, catalysis, material science, and medicinal chemistry.¹ Within the large family of metallacycle compounds, the metallaaromatics have especially attracted attention since they can display both aromatic properties and organometallic reactivity.² The metal center, coligands, and substituents on the ring play an important role in the stabilization of these metallacycle compounds. Xia et al. have reported how phosphonium substituents on the aromatic ring are able to stabilize a great variety of osmaaromatic complexes.^{1b} Understanding how substituents on the ring with different electronic properties affect the stability of these derivatives is crucial to optimize their synthesis, reactivity and applications. Metallanaphthalenes or superior analogs are practically unknown and very few examples have been isolated,³ making their exploration of great interest in order to gain access to a promising rich chemistry.

We reported iridanaphthalene [IrCp*{ $=C(OMe)CH=C(o-C_6H_4)$ -(Ph)}(PMe₃)]PF₆, which is unstable in solution and evolves into 3-phenyl-1-indanone.^{3c} In order to exploit the full potential of iridanaphthalene complexes it is important to understand substituent effects on the metallanaphthalene ring. Herein, we report the synthesis of a series of new methoxy(alkenyl)carbeneiridium compounds bearing substituents of different electronic behavior and the corresponding iridanaphthalene complexes. In addition, we study how the substituents influence the conversion of the iridanaphthalene complexes to the corresponding indanone derivatives.

Results and discussion

Synthesis and characterization

The methoxy(alkenyl)carbeneiridium complexes 1–3 were prepared by a reaction of [IrCp*Cl(NCMe)(PMe₃)]PF₆ with the corresponding propargylic alcohol I–III (Scheme 1). The products 1–3 which contain a –NO₂, –OMe or –Me substituent, respectively, on one of the phenyl rings of the (alkenyl)carbene ligand were isolated as a mixture of *cis/trans* isomers with respect to the $C^{\beta}-C^{\gamma}$ double bond.

The corresponding mixture of two iridanaphthalene isomers 4(A,B)-6(A,B) were obtained using our synthetic route:^{3c} by treatment of 1–3 with AgPF₆ at room temperature, implying an intramolecular C–H bond activation of one phenyl ring of the (alkenyl)carbene ligand. It is a good general strategy for the preparation of a family of iridanaphthalene complexes

^aDepartamento de Química Inorgánica, Universidad de Vigo, Campus Universitario, E-36310 Vigo, Spain. E-mail: bgs@uvigo.es

^bDepartamento de Química Física, Universidad de Vigo, Campus Universitario, E-36310 Vigo, Spain

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from different aryl substituents of the (alkenyl)carbene ligand. Isomer **A** has a substituent on the 6-position of the iridanaphthalene skeleton, and the **B** isomer has a substituent on the *para*-position of the phenyl ring (Scheme 1).

Multidimensional and multinuclear NMR spectra, summarized in the Experimental section, supported the proposed structure for all complexes and, in particular, the NOESY spectra confirm the *cis/trans* isomerism.

When the mixture of 4(A,B) was treated with a solution of NaBPh₄ in methanol, brown monocrystals of [IrCp*{=C(OMe)CH=C(o-C₆H₄)(p-NO₂-C₆H₄)(PMe₃)]BPh₄ (4B) were obtained. The structure of 4B was confirmed by single-crystal X-ray diffraction analysis and the ORTEP representation of the complex cation 4B accompanied by a selection of distances and angles is given in Fig. 1. The asymmetric unit of complex 4B contains an iridium cation complex, a BPh₄⁻ anion and a CH₂Cl₂ solvent molecule.

The cation consists of a pentamethylcyclopentadienyl ligand (Cp*) η^5 -coordinated to an iridium atom. The metal becomes part of the naphthalene moiety and the coordination



Fig. 1 ORTEP view of the cation $[IrCp*{=C(OMe)CH=C(o-C_6H_4)-(p-NO_2-C_6H_4)(PMe_3)]^+ (4B)}$ drawn at a 50% probability level. Hydrogen atoms are not shown. Selected bond lengths (Å) and angles (deg): Ir–CT, 1.9167(3); Ir–C(11), 1.965(4); Ir–C(15), 2.037(4); Ir–P(1), 2.2754(11); C(11)–Ir–C(15), 89.47(16); CT–Ir–C(11), 125.49(11); CT–Ir–C(15), 123.26(12); C(15)–Ir–P(1), 89.46(12); C(11)–Ir–P(1), 87.43(12). CT refers to the centroid of the Cp* ligand.

sphere is completed by a phosphane ligand (PMe₃) with a "three-legged piano stool" structure in an octahedral arrangement. The iridanaphthalene shows Ir–C bond lengths of 1.965(4) and 2.037(4) Å. The distance between the iridium atom and the plane defined by the five carbon atoms of the ring is 0.425(5) Å, showing an envelope distortion. These data are similar to previously reported iridanaphthalene complexes.^{3,4}

How do the substituents influence the stability of the iridanaphthalene [IrCp*{=C(OMe)CH=C(o-C₆H₄)(Ph)}-(PMe₃)]PF₆?

We studied the influence of the electronic character of the substituent on the 6-position of the naphthalene ring on the stability of the iridanaphthalene complex $[IrCp^*{=C(OMe)CH=C(o-C_6H_4)-(Ph)}(PMe_3)]PF_6$, that is, the degree of conversion of the iridanaphthalene complex to the corresponding indanone derivatives, choosing –OMe, –Me, and –NO₂ as substituents due to their different electronic effects.

The nature of all the indanone derivatives⁵ (Chart 1) was confirmed by multidimensional and multinuclear NMR spectroscopy (Experimental section).

When a solution of the nitroiridanaphthalene isomeric mixture 4(A,B) (~57:43 mole ratio) in 1,2-dichloroethane was heated at 338 K for 24 hours, 7b was isolated in a 90% yield and 4A was recovered unaltered. In an attempt to obtain the indanone derivative 7a corresponding to 4A, a solution of 4A in 1,2-dichloroethane was heated at 368 K for 24 hours, resulting in a mixture of nitro-indanone derivatives 7a and 7b in a ~30:70 mole ratio (estimated by NMR, 91% yield of the isolated mixture), respectively. This suggests that:



Chart 1 Indanone derivatives.

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(1) nitro-iridanaphthalene isomer **4A** is more stable than **4B** and requires harsher reaction conditions to convert it into the indanone derivatives.

(2) nitro-iridanaphthalene isomer **4A** evolves into the nitroindanone derivatives **7a** and **7b**, with **7b** being the major product. This seems to indicate that during the conversion of **4A** in the corresponding indanone derivative **7a**, a transformation occurs giving **7b** as the major product (path "b" in Scheme 2). It has been tested that **7a** does not evolve to **7b** under the same conditions.

The nitro group is an electron-withdrawing group through resonance and induction, and thus the *ortho-* and *para-*positions to the nitro group have a positive partial charge. We propose that the reaction follows a mechanism (Scheme 2) where the nitro group stabilizes the carbanion C and favors path "b" over path "a".⁶

Path "a": involves a carbene migratory insertion, leading to a η^1 -indenyl intermediate followed by switching from η^1 to η^3 hapticity to give the η^3 -indenyl complex, which detaches from the metallic center to form an indanone derivative.^{3c}

Path "b": involves the initial formation of carbanion C, followed by a rotation over the $C^{\gamma}-C^{1} \sigma$ bond and abstraction of a proton. Subsequent electronic rearrangements and rotations give an iridanaphthalene complex with the substituent in the *para*-position of the phenyl ring. This finally evolves into the corresponding indanone derivative.⁷

When a mixture of 5(A,B) (~33:66 mole ratio) in 1,2dichloroethane was heated at 338 K for 24 hours, methoxyindanone derivatives **8a** and **8b** were obtained in a ~13:87 mole ratio (estimated by NMR) (50% yield of the isolated mixture), respectively, and **5A** was recovered in a minor

proportion (80% regarding initial quantity). To confirm that 8a is formed only from 5A and 8b only from 5B, a solution of 5A in 1,2-dichloroethane was heated at 368 K for 24 hours. 8a together with 6-methoxy-3-phenylinden-1-one (~70:30 mole ratio estimated by NMR, respectively) were obtained and 5A was recovered at 78% regarding initial quantity. The formation of 8b was not observed. This suggests that the conversion of iridanaphthalene 5A to the respective methoxy-indanone derivative is less favored than that of 4A into the corresponding nitro-indanone derivatives 7(a,b). In this example, the methoxy group is an electron-withdrawing group and resonance donor but in alkoxy groups the resonance overrides induction. This means that ortho- and para-positions to the methoxy group have a negative partial charge. Thus, formation of carbanion C is not favored and path "b" is not followed. This significantly increases the stability of iridanaphthalene 5A with respect to the formation of the methoxy-indanone derivatives and it is only converted in 14% yield through path "a" (Scheme 2).

The mixture of methyl-iridanaphthalene isomers 6(A,B) (~50:50 mole ratio) in 1,2-dichloroethane at 338 K for 24 hours gave the methyl-indanone derivatives, **9a** and **9b**, with a ~45:55 mole ratio (estimated by NMR) in a 91% yield of the isolated mixture. In this case, isomer **6A** evolved to **9a** and **6B** to **9b**. Because the methyl group is a weak electron donor with no resonance effect, the carbanion is not favored and the stability of the iridanaphthalene decreases in favor of the methyl-indanone derivative formation following path "a" (Scheme 2).

Our results from solution stability studies of the iridanaphthalene compounds presented in this work demonstrate that donor substituents (–OMe) on the 6-position of the



Scheme 2 Proposed mechanism for the formation of the indanone derivatives from the iridanaphthalene complex substituted on 6-position of the naphthalene ring.

naphthalene skeleton stabilize the iridanaphthalene over the indanone derivative formation, whereas weak electron-donor (–Me) and electron-withdrawing (– NO_2) substituents on the 6-position favor the formation of indanone derivatives.

Conclusion

In conclusion, we presented the synthesis of new cis- and trans-isomers of methoxy(alkenyl)carbeneiridium complexes containing a nitro, methoxy or methyl substituent on one of the phenyl rings of the (alkenyl)carbene ligand. A mixture of two iridanaphthalene isomers was obtained from the methoxy(alkenyl)carbeneiridium complexes, one with the substituent on the 6-position of the iridanaphthalene skeleton and the other one with the substituent on the para-position of the phenyl ring. Given the broad range of properties, reactivity, and applications related to metallaaromatic compounds and that the metallanaphthalene compounds are practically unknown,³ it is important to understand how the substituents on the naphthalene skeleton affect their stability. Our studies indicate that the substituents have a significant effect on the stability of the iridanaphthalene complex $[IrCp*{=C(OMe)CH=C(o-C_6H_4)(Ph)}(PMe_3)]PF_6$ in the conversion to their corresponding indanone derivatives, with a π -donor substituent on the 6-position of the naphthalene skeleton stabilizing the iridanaphthalene. This information will be important for further exploration of different ways to create stable iridanaphthalene compounds to study their properties and future applications in material science.

Experimental section

Synthetic procedures, materials and methods

All experiments were carried out under an atmosphere of argon by Schlenk techniques. Solvents were dried by the usual procedures⁸ and, prior to use, distilled under argon. The starting material [IrCp*Cl(NCMe)(PMe₃)]PF₆^{3c} was prepared as described in the literature. All reagents were obtained from commercial sources except for the propargylic alcohols (I,II, III), which were synthesized following the method described by Mantovani et al.9 Unless stated, NMR spectra were recorded at room temperature on a Bruker ARX-400 instrument, with resonating frequencies of 400 MHz (¹H), 161 MHz (³¹P{¹H}), and 100 MHz $\binom{13}{14}$ using the solvent as the internal lock. ¹H and ¹³C{¹H} signals are referred to internal TMS and those of ${}^{31}P{}^{1}H$ to 85% H₃PO₄; downfield shifts (expressed in ppm) are considered positive. ¹H and ¹³C{1H} NMR (or JMOD) signal assignments were confirmed by {¹H, ¹H} COSY, {¹H, ¹H} NOESY, {¹H, ¹³C} HSQC, {¹H, ¹³C} HMBC and DEPT experiments. Coupling constants are given in hertz. The isomer ratios were determined using relaxation delays as long as 30 s in order to collect reliable integral data of the ¹H NMR resonances. Infrared spectra were run on a Jasco FT/IR-6100 spectrometer using KBr pellets. C, H, and N analyses were carried out with a Carlo Erba 1108 analyzer. Mass spectra are referred to the most abundant isotopes and they were acquired using an Apex-Qe spectrometer by a high resolution electrospray technique for the organometallic complexes and a high and low resolution electron impact technique for the organic compounds.

X-ray diffraction analysis

Crystallographic data were collected on a Bruker Smart 1000 CCD diffractometer at CACTI (Universidade de Vigo) using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å), and were corrected for Lorentz and polarisation effects. The software SMART¹⁰ was used for collecting frames of data, indexing reflections, and the determination of lattice parameters, SAINT¹¹ for the integration of the intensity of reflections and scaling, and SADABS¹² for empirical absorption correction.

The crystallographic treatment of the compound was performed with the Oscail program.¹³ The structure was solved by direct methods and refined by a full-matrix least-squares based on $F^{2,14}$ All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealized positions and refined with isotropic displacement parameters.

Crystal data and structural refinement details for complex **4B** are given in Table 1.

Preparation of *cis*- and *trans*-[IrCp*Cl{ \equiv C(OMe)-CH \equiv C(*p*-NO₂-C₆H₄)(Ph)}(PMe₃)]PF₆ (1). To a yellow solution of [IrCp*Cl(NCMe)(PMe₃)]PF₆ (300 mg, 0.48 mmol) in methanol (20 mL) 1-(4-nitrophenyl)-1-phenyl-2-propyn-1-ol (159 mg,

Table 1	Crystal data	and structure	refinement f	or 4B
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Empirical formula	C54H58BCl2NO3PIr	
Formula wt	1073.89	
Temp (K)	100(2)	
Wavelength (Å)	0.71073	
Cryst. syst.	Monoclinic	
Space group	$P2_1/n$	
a (Å)	18.696(2)	
$b(\mathbf{A})$	11.6073(14)	
c (Å)	24.032(3)	
$\alpha(\circ)$	90	
$\beta(\hat{\circ})$	112.526(2)	
γ (°)	90	
$V(A^3)$	4817.2(10)	
Z	4	
Density (Mg m^{-3})	1.481	
Abs. coeff. (mm^{-1})	2.960	
<i>F</i> (000)	2176	
Cryst. size (mm)	0.29 imes 0.24 imes 0.19	
θ range for data collection (°)	2.36-28.09	
Index ranges	$-24 \le h \le 24$	
C	$-15 \le k \le 15$	
	$-31 \le l \le 31$	
No. of rflns collected	82 883	
No. of indep. rflns	11700[R(int)=0.0593]	
No. of rflns obsd (> 2σ)	9026	
Data completeness	0.997	
Abs. cor.	Semi-empirical from equivalents	
Max. and min. transmission	0.4309 and 0.3395	
Refinement method	Full-matrix least-squares on F^2	
No. of data/restraints/params	11 700/0/577	
Goodness of fit on F^2	1.084	
<i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0347, wR_2 = 0.0668$	
<i>R</i> indices (all data)	$R_1 = 0.0599, wR_2 = 0.0784$	
Largest diff. peak and hole (e $Å^{-3}$)	5.259 and -3.510	

0.62 mmol) was added and the mixture was stirred for 20 min. The dark red solution obtained was concentrated under vacuum yielding a dark red solid that was washed with pentane $(3 \times 5 \text{ mL})$ and diethylether $(2 \times 5 \text{ mL})$. Finally, it was dried under a vacuum giving a mixture of *cis-*, *trans-***1** isomers in a ~50:50 mole ratio (estimated by NMR), respectively. Yield (isolated mixture): 400 mg (98%).

Anal. calcd for $C_{29}H_{37}O_3NClF_6IrP_2$ (851.23 g mol⁻¹): C 40.92, H 4.38, N 1.65; found: C 41.05, H 4.45, N 1.71. MS (m/z): 706.18114 $[M]^+$. IR (cm⁻¹): ν (NO₂) 1519 (m), 1346 (m); (PF₆) 840 (s). *cis*-1: ¹H NMR: δ 1.69 (d, 9H, ²J_{HP} = 11.0 Hz, $P(CH_3)_3$; 1.79 (d, 15H, ${}^{4}J_{HP}$ = 2.2 Hz, $C_5(CH_3)_5$); 4.20 (s, 3H, OCH₃); 7.34 (d, 2H, ${}^{3}J_{HH} = 8.9$ Hz, C²H); 7.37–7.39 (m, 2H, Ph); 7.40–7.60 (m, 3H, *Ph*); 7.64 (s br, 1H, $C_{B}H$); 8.30 (d, 2H, ${}^{3}J_{HH} =$ 8.9 Hz, $C^{3}H$ ppm. ${}^{31}P{}^{1}H$ NMR: δ -144.14 (sept, ${}^{1}J_{PF}$ = 710.9 Hz, PF₆); -30.93 (s, P(CH₃)₃) ppm. ${}^{13}C{}^{1}H$ NMR: δ 9.2 (s, $C_5(CH_3)_5$); 15.2 (d, ${}^{1}J_{CP} = 40.9$ Hz, $P(CH_3)_3$); 68.9 (s, OCH_3); 99.2 (d, ${}^{2}J_{CP} = 2.2$ Hz, $C_{5}(CH_{3})_{5}$); 124.0 (s, 2C C^{3}); 129.2 (s, 2C C²); 129.7 (s, 2C Ph); 129.8 (s, 2C Ph); 132.3 (s, 1C Ph); 138.9 (s, C_{ipso}); 139.5 (s, C_{β}); 146.1 (s, C^{1}); 148.2 (s, C^{4}); 150.7 (s br, C_{γ}); 264.0 (s br, C_{α}) ppm. *trans*-1: ¹H NMR: δ 1.70 (d, 9H, ${}^{2}J_{\text{HP}} = 11.0 \text{ Hz}, P(CH_{3})_{3}$; 1.74 (d, 15H, ${}^{4}J_{\text{HP}} = 2.1 \text{ Hz}, C_{5}(CH_{3})_{5}$); 4.17 (s, 3H, OC H_3); 6.97 (s br, 1H, C_{β}H); 7.12–7.15 (m, 2H, Ph); 7.40–7.60 (m, 3H, *Ph*); 7.59 (d, 2H, ${}^{3}J_{HH} = 8.9$ Hz, $C^{2}H$); 8.22 (d, 2H, ${}^{3}J_{HH} = 8.9$ Hz, $C^{3}H$) ppm. ${}^{31}P{}^{1}H$ NMR: δ -144.14 (sept, ${}^{1}J_{PF} = 710.9 \text{ Hz}, PF_{6}$); -29.41 (s, $P(CH_{3})_{3}$) ppm. ${}^{13}C{}^{1}H$ NMR: δ 9.2 (s, C₅(*C*H₃)₅); 15.2 (d, ¹*J*_{CP} = 40.9 Hz, P(*C*H₃)₃); 69.0 (s, OCH₃); 100.2 (s br, $C_5(CH_3)_5$); 124.3 (s, 2C C^3); 130.6 (s, 2C C²); 129.4 (s, 2C Ph); 129.7 (s, 2C Ph); 129.8 (s, 1C Ph); 137.9 (s, C_{ipso}); 139.8 (s, C_{β}); 146.8 (s, C^{1}); 149.0 (s, C^{4}); 150.7 $(s br, C_{\gamma}); 264.0 (s br, C_{\alpha}) ppm.$

Preparation of *cis-* **and** *trans-***[IrCp*Cl{=C(OMe)-CH=C(***p***-OCH₃-C₆H₄)(Ph)}(PMe₃)]PF₆ (2).** To a yellow solution of [IrCp*Cl(NCMe)(PMe₃)]PF₆ (150 mg, 0.24 mmol) in methanol (10 mL), 1-(4-methoxyphenyl)-1-phenyl-2-propyn-1-ol (74 mg, 0.31 mmol) was added and the mixture was stirred for 15 min. The dark solution obtained was vacuum-concentrated yielding a dark red solid that was washed with pentane (2 × 5 mL) and diethylether (2 × 5 mL). Finally, it was dried under a vacuum giving *cis-, trans-***2** isomers in a ~33 : 66 mole ratio (estimated by NMR), respectively. Yield (isolated mixture): 150 mg (75%).

Anal. calcd for C₃₀H₄₀O₂ClF₆IrP₂ (836.26 g mol⁻¹): C 43.09, H 4.82; found: C 43.36, H 4.77. MS (*m*/*z*): 691.20651 [M]⁺; 655.22979 [M - HCl]⁺. IR (cm⁻¹): ν (PF₆) 840 (s). *cis*-2: ¹H NMR: δ 1.70 (d, 9H, ²J_{HP} = 11.0 Hz, P(CH₃)₃); 1.77 (d, 15H, ⁴J_{HP} = 2.3 Hz, C₅(CH₃)₅); 3.87 (s, 3H, C⁴-OCH₃); 4.11 (s, 3H, C_α-OCH₃); 6.94 (d, 2H, ³J_{HH} = 9.0 Hz, C³H); 7.01 (s br, 1H, C_βH); 7.09 (d, 2H, ³J_{HH} = 9.0 Hz, C²H); 7.37-7.40 (m, 2H, *Ph*); 7.40-7.43 (m, 3H, *Ph*) ppm. ³¹P{¹H} NMR: δ -144.17 (sept, ¹J_{PF} = 710.5 Hz, *PF*₆); -29.59 (s, *P*(CH₃)₃) ppm. ¹³C{¹H} NMR: δ 9.3 (s, C₅(CH₃)₅); 15.0 (d, ¹J_{CP} = 40.5 Hz, P(CH₃)₃); 55.9 (s, C⁴-OCH₃); 68.4 (s, C_α-OCH₃); 99.4 (d, ²J_{CP} = 2.2 Hz, C₅(CH₃)₅); 114.4 (s, 2C C³); 129.5 (s, 3C *Ph*); 130.2 (s, 2C *Ph*); 131.2 (s, C¹); 131.7 (s, 2C C²); 137.4 (s br, C_β); 141.1 (s, C_{*ipso*}); 161.9 (s, C⁴); 154.1 (s br, C_γ); 260.6 (d, ²J_{CP} = 11.9 Hz, C_α) ppm. *trans*-2: ¹H NMR: δ 1.70 (d, 9H, ²J_{HP} = 10.8 Hz, P(CH₃)₃); 1.78 (d, 15H, ⁴*J*_{HP} = 2.2 Hz, C₅(*CH*₃)₅); 3.85 (s, 3H, C⁴–OC*H*₃); 4.05 (s, 3H, C_α–OC*H*₃); 6.93 (d, 2H, ³*J*_{HH} = 9.1 Hz, C³*H*); 7.09–7.12 (m, 2H, *Ph*); 7.37 (d, 2H, ³*J*_{HH} = 9.1 Hz, C²*H*); 7.43–7.47 (m, 3H, *Ph*); 7.49 (s br, 1H, C_β*H*) ppm. ³¹P{¹H} NMR: δ –144.17 (sept, ¹*J*_{PF} = 710.5 Hz, *PF*₆); -31.05 (s, *P*(CH₃)₃) ppm. ¹³C{¹H} NMR: δ 9.2 (s, C₅(*CH*₃)₅); 15.0 (d, ¹*J*_{CP} = 40.5 Hz, P(*CH*₃)₃); 56.1 (s, C⁴–OCH₃); 68.0 (s, C_α–OCH₃); 98.6 (d, ²*J*_{CP} = 2.6 Hz, *C*₅(CH₃)₅); 115.1 (s, 2C *C*³); 128.7 (s, 2C *Ph*); 128.7 (s, 2C *Ph*); 129.4 (s, 1C *Ph*); 132.1 (s, *C*¹); 132.3 (s, 2C *C*²); 136.7 (d, ³*J*_{CP} = 3.1 Hz, *C*_β); 139.7 (s, *C*_{*ipso*); 163.5 (s, *C*⁴); 155.6 (s br, *C*_γ); 259.4 (d, ²*J*_{CP} = 11.5 Hz, *C*_α) ppm.}

Preparation of *cis*- and *trans*-[IrCp*Cl{ \equiv C(OMe)-CH \equiv C(*p*-CH₃-C₆H₄)(Ph)}(PMe₃)]PF₆ (3). To a yellow solution of [IrCp*Cl(NCMe)(PMe₃)]PF₆ (150 mg, 0.24 mmol) in methanol (10 mL), 1-(4-methylphenyl)-1-phenyl-2-propyn-1-ol (70 mg, 0.31 mmol) was added and the mixture was stirred for 15 min. The dark solution obtained was vacuum-concentrated yielding a dark green solid that was washed with pentane (2 × 5 mL) and diethylether (2 × 5 mL). Finally, it was dried under a vacuum giving a mixture of *cis*-, *trans*-3 isomers in a ~50:50 mole ratio (estimated by NMR), respectively. Yield (isolated mixture): 153 mg (78%).

Anal. calcd for $C_{30}H_{40}OClF_6IrP_2$ (820.26 g mol⁻¹): C 43.93, H 4.92; found: C 44.06, H 4.96. MS (m/z): 675.21166 $[M]^+$. IR (cm⁻¹): ν (PF₆) 839 (s). *cis*-3: ¹H NMR: δ 1.70 (d, 9H, ²J_{HP} = 11.0 Hz, $P(CH_3)_3$; 1.77 (d, 15H, ${}^4J_{HP}$ = 2.2 Hz, $C_5(CH_3)_5$); 2.42 (s, 3H, CH_3); 4.10 (s, 3H, OCH_3); 7.01 (d, 2H, ${}^{3}J_{HH} = 8.1$ Hz, $C^{3}H$; 7.13 (s br, 1H, $C_{\beta}H$); 7.18–7.33 (m, 2H, $C^{2}H$); 7.36–7.55 (m, 5H, Ph) ppm. ${}^{31}P{}^{1}H$ NMR: δ -144.17 (sept, ${}^{1}J_{PF}$ = 710.6 Hz, PF_6 ; -29.80 (s, $P(CH_3)_3$) ppm. ¹³C{¹H} NMR: δ 9.3 (s, $C_5(CH_3)_5$); 15.1 (d, ${}^{1}J_{CP} = 40.4$ Hz, $P(CH_3)_3$); 21.5 (s, CH_3); 68.5 (s, OCH₃); 99.4 (d, ${}^{2}J_{CP}$ = 2.17 Hz, $C_{5}(CH_{3})_{5}$); 128.7–130.3 (all s, 5C Ph + 4C $C_6H_4CH_3$); 137.9 (s br, C_β); 139.5 (s, C_{ipso}); 140.7 (s, C^1); 140.8 (s, C^4); 154.3 (s br, C_{γ}); 261.6 (d, ${}^2J_{CP}$ = 11.1 Hz, C_{α}) ppm. trans-3: ¹H NMR: δ 1.70 (d, 9H, ² J_{HP} = 10.9 Hz, $P(CH_3)_3$; 1.78 (d, 15H, ${}^4J_{HP}$ = 2.3 Hz, $C_5(CH_3)_5$); 2.37 (s, 3H, CH₃); 4.08 (s, 3H, OCH₃); 7.08-7.12 (m, 2H, Ph); 7.18–7.33 (m, 4H, $C^{3}H + C^{2}H$); 7.36–7.55 (m, 4H, $C_{\beta}H + Ph$) ppm. ³¹P{¹H} NMR: δ -144.17 (sept, ¹J_{PF} = 710.6 Hz, *P*F₆); -30.56 (s, $P(CH_3)_3$) ppm. ¹³C{¹H} NMR: δ 9.2 (s, C₅($CH_3)_5$); 15.0 $(d, {}^{1}J_{CP} = 40.6 \text{ Hz}, P(CH_3)_3); 21.7 (s, CH_3); 68.3 (s, OCH_3); 98.9 (d, CH_3); 98.9 (d, CH_3);$ ${}^{2}J_{CP} = 2.3 \text{ Hz}, C_{5}(CH_{3})_{5}; 128.7-130.3 \text{ (all s, 5C } Ph + 4C C_{6}H_{4}CH_{3});$ 136.2 (s, C^1); 137.3 (s, C_{ipso}); 137.7 (d, ${}^{3}J_{CP} = 2.3$ Hz, C_{β}); 143.2 (s, C^4); 154.7 (s br, C_{γ}); 261.2 (d, ${}^2J_{CP}$ = 10.3 Hz, C_{α}) ppm.

The synthesis of complexes **1–3** was done with different experimental conditions trying to direct the synthesis towards one isomer but a mixture of *cis/trans* isomers was always obtained. Different attempts to separate them by a silica column were unsuccessful. Using this mixture did not have any influence on the cyclometallation reaction since each isomer gives the corresponding isomer of iridanaphthalene as it is observed in the isomers ratio.

Preparation of $[IrCp^*{=C(OMe)-CH=C(o-C_6H_3-p-NO_2)-(Ph)}(PMe_3)]PF_6$ (4A) and $[IrCp^*{=C(OMe)-CH=C(o-C_6H_4)-(p-NO_2-C_6H_4)}(PMe_3)]PF_6$ (4B). A dark red solution of the mixture *cis*-, *trans*-1 (~50:50 mole ratio, 350 mg, 0.41 mmol) in

30 mL of dichloromethane was treated with AgPF₆ (117 mg, 0.45 mmol). The brown solution was stirred for 5 min at room temperature, and then filtered obtaining a brown oil that was treated with pentane obtaining a brown solid that was washed with pentane (3×5 mL). Finally, the solid was dried under a vacuum obtaining a mixture of isomers **4**(**A**,**B**) (~57:43 mole ratio estimated by NMR, respectively). Yield (mixture isolated): 240 mg (72%). This solid was dissolved in dichloromethane and a solution of NaBPh₄ in methanol was added dropwise yielding brown monocrystals of complex **4B** adequate for X-ray diffraction analysis.

Anal. calcd for $C_{29}H_{36}O_3NF_6IrP_2$ (814.77 g mol⁻¹): C 42.75, H 4.45, N 1.72; found: C 42.88, H 4.48, N 1.76. MS (*m/z*): 670.20487 [M]⁺. IR (cm⁻¹): ν (NO₂) 1519 (m) and 1345 (m); (PF₆) 839 (s).

4A: ¹H NMR: δ 1.30 (d, 9H, ² J_{HP} = 10.9 Hz, P(CH₃)₃); 1.84 (d, 15H, ${}^{4}J_{HP}$ = 1.7 Hz, C₅(CH₃)₅); 4.50 (d, 3H, ${}^{5}J_{HP}$ = 0.8 Hz, OCH₃); 6.80 (d, 1H, ${}^{4}J_{HP}$ = 1.0 Hz, C²H); 7.42–7.47 (m, 2H, Ph); 7.56-7.60 (m, 3H, Ph); 7.79-7.83 (m, 1H, C⁴H); 7.85-7.90 (m, 1H,C⁵*H*); 8.63 (d, 1H, ${}^{4}J_{HP}$ = 2.4 Hz, C⁷*H*) ppm. ${}^{31}P{}^{1}H$ NMR: δ -144.14 (sept, ¹*J*_{PF} = 711.3 Hz, *P*F₆); -34.43 (s, *P*(CH₃)₃) ppm. ¹³C{¹H} NMR: δ 9.6 (s, C₅(*C*H₃)₅); 14.2 (d, ¹*J*_{CP} = 41.1 Hz, $P(CH_3)_3$; 64.9 (s, OCH₃); 100.9 (d, ² J_{CP} = 1.8 Hz, $C_5(CH_3)_5$); 118.0 (s, C^5); 121.8 (d, ${}^{3}J_{CP}$ = 1.9 Hz, C^2); 129.0 (s, 1C Ph); 129.1 (s, 2C *Ph*); 129.3 (s, 2C *Ph*); 136.2 (d, ${}^{3}J_{CP} = 4.7$ Hz, C^{7}); 137.2 (s, C^4); 140.6 (s, C^9); 140.9 (s, C_{ipso}); 146.8 (s, C^6); 154.2 (d, ${}^{2}J_{CP}$ = 10.3 Hz, C^{8}); 175.1 (s, C^{3}); 251.2 (d, ${}^{2}J_{CP}$ = 9.7 Hz, C^{1}) ppm. **4B**: ¹H NMR: δ 1.27 (d, 9H, ²*J*_{HP} = 11.0 Hz, P(C*H*₃)₃); 1.81 (d, 15H, ${}^{4}J_{HP} = 1.7$ Hz, C₅(CH₃)₅); 4.43 (d, 3H, ${}^{5}J_{HP} = 0.7$ Hz, OCH₃); 6.59 (d, 1H, ${}^{4}J_{HP}$ = 1.0 Hz, C²H); 7.14–7.17 (m, 2H, $C^{4}H + C^{5}H$; 7.48–7.51 (m, 1H, $C^{6}H$); 7.61–7.64 (m, 2H, $C^{2'}H +$ $C^{6'}H$; 7.87–7.88 (m, 1H, $C^{7}H$); 8.33–8.37 (m, 2H, $C^{3'}H + C^{5'}H$) ppm. ${}^{31}P{}^{1}H$ NMR: δ -144.14 (sept, ${}^{1}J_{PF}$ = 710.7 Hz, PF_{6}); -34.80 (s, $P(CH_3)_3$) ppm. ¹³C{¹H} NMR: δ 9.7 (s, C₅(CH_3)₅); 14.1 (d, ${}^{1}J_{CP}$ = 41.0 Hz, P(CH₃)₃); 64.1 (s, OCH₃); 100.5 (d, ${}^{2}J_{CP}$ = 1.9 Hz, $C_5(CH_3)_5$; 118.5 (d, ${}^{3}J_{CP} = 2.1$ Hz, C^2); 123.8 (s, C^5); 124.0 (s, $C^{3'} + C^{5'}$); 130.6 (s, $C^{2'} + C^{6'}$); 132.1 (s, C^4); 133.1 (s, C^9); 137.2 (s, C^{6}); 143.2 (d, ${}^{3}J_{CP} = 4.7$ Hz, C^{7}); 148.1 (s, $C^{4'} + C^{1'}$); 156.5 (d, ${}^{2}J_{CP} = 10.3 \text{ Hz}, C^{8}$; 175.1 (s, C^{3}); 249.5 (d, ${}^{2}J_{CP} = 9.9 \text{ Hz}, C^{1}$) ppm.

Note: During NMR characterization the formation of **7b** was observed.

Preparation of $[IrCp^*{\eta^3-(C_9H_5)(OMe)(p-NO_2-C_6H_4)}(PMe_3)]$ -PF₆ (D). In a NMR tube, a mixture of 4(A,B) (57 : 43 mole ratio, 10 mg, 0.012 mmol) was dissolved in 500 µL of dichloromethane- d^2 and heated at 308 K for 7 days. After that, complex 4A remained unaltered and 4B had almost completely evolved to a new complex $[IrCp^*{\eta^3-(C_9H_5)(OMe)-(p-NO_2-C_6H_4)}(PMe_3)]$ -PF₆ (~10 : 90 mole ratio estimated by NMR, respectively).



¹H NMR: δ 1.31 (d, 9H, ²*J*_{HP} = 9.8 Hz, P(*CH*₃)₃); 1.45 (d, 15H, ⁴*J*_{HP} = 2.0 Hz, C₅(*CH*₃)₅); 3.86 (s, 3H, OC*H*₃); 5.98 (d, 1H, ³*J*_{HP} = 10.6 Hz, C²*H*); 6.57 (d, 1H, ³*J*_{HH} = 7.6 Hz, C₆*H*₄); 6.84 (d, 1H, ³*J*_{HH} = 7.6 Hz, C₆*H*₄); 7.41–7.46 (m, 3H, C₆*H*₄ + C²*'H* + C⁶*'H*); 7.79–7.84 (m, 1H, C₆*H*₄); 8.17–8.22 (m, 2H, C³*'H* + C⁵*'H*) ppm. ³¹P{¹H} NMR: δ –144.16 (sept, ¹*J*_{PF} = 710.6 Hz, *P*F₆); –38.92 (s, *P*(CH₃)₃)ppm. ¹³C{¹H} NMR: δ 8.9 (s, C₅(CH₃)₅); 18.2 (d, ¹*J*_{CP} = 38.5 Hz, P(*C*H₃)₃); 62.0 (s, OCH₃); 96.4 (d, ²*J*_{CP} = 2.6 Hz, C₅(CH₃)₅); 187.0 (*C*¹, observed by {¹H, ¹³C} HMBC correlations) ppm.

Preparation of $[IrCp^*{=C(OMe)-CH=C(o-C_6H_3-p-OCH_3)-(Ph)}(PMe_3)]PF_6$ (5A) and $[IrCp^*{=C(OMe)-CH=C(o-C_6H_4)-(p-OCH_3-C_6H_4)}(PMe_3)]PF_6$ (5B). A dark red solution of the mixture *cis-*, *trans-*2 (~33:66 mole ratio, 150 mg, 0.18 mmol) in 10 mL of dichloromethane was treated with AgPF_6 (50 mg, 0.20 mmol). The brown solution was stirred for 5 min at room temperature, and then filtered and vacuum-concentrated giving a dark green oil that was treated with pentane (3 × 5 mL). Finally, the solid was dried under a vacuum obtaining a mixture of isomers **5(A,B)** (~33:66 mole ratio estimated by NMR, respectively). Yield (isolated mixture): 110 mg (76%).

Anal. calcd for $C_{30}H_{39}O_2F_6IrP_2$ (799.80 g mol⁻¹): C 45.05, H 4.91; found: C 45.23, H 4.96. MS (*m*/*z*): 655.23038 [M]⁺. IR (cm⁻¹): ν (PF₆) 839 (s).

5A: ¹H NMR: δ 1.27 (d, 9H, ² J_{HP} = 10.8 Hz, P(CH₃)₃); 1.80 (d, 15H, ${}^{4}J_{HP}$ = 1.6 Hz, C₅(CH₃)₅); 3.91 (s, 3H, C⁶-OCH₃); 4.31 (s, 3H, C¹-OCH₃); 6.54 (s, 1H, C²H); 6.74 (dd, 1H, ${}^{3}J_{HH} =$ 9.2 Hz, ${}^{4}J_{HH} = 2.7$ Hz, $C^{5}H$; 7.37–7.40 (m, 3H, Ph + $C^{7}H$); 7.50–7.54 (m, 3H, Ph); 7.62 (d, 1H, ${}^{3}J_{HH} = 8.9$ Hz, C⁴H) ppm. ³¹P{¹H} NMR: δ -144.17 (sept, ¹J_{PF} = 710.4 Hz, *P*F₆); -34.99 (s, $P(CH_3)_3$) ppm. ¹³C{¹H} NMR: δ 9.7 (s, $C_5(CH_3)_5$); 14.1 (d, ${}^{1}J_{CP} = 40.9 \text{ Hz}, P(CH_3)_3$; 55.8 (s, C⁶-OCH₃); 63.0 (s, C¹-OCH₃); 100.0 (d, ${}^{2}J_{CP}$ = 2.0 Hz, $C_{5}(CH_{3})_{5}$); 110.4 (s, C^{5}); 116.1 (d, ${}^{3}J_{CP}$ = 2.0 Hz, C^2 ; 126.9 (s, C_{ipso}); 127.9 (d, ${}^{3}J_{CP} = 5.2$ Hz, C^7); 128.8-129.7 (all s, Ph); 140.5 (s, C⁴); 142.4 (s, C⁹); 160.1 (d, ${}^{2}J_{CP}$ = 10.1 Hz, C^{8}); 162.0 (s, C^{6}); 178.7 (s, C^{3}); 241.7 (d, ${}^{2}J_{CP}$ = 10.6 Hz, C^1) ppm. 5B: ¹H NMR: δ 1.24 (d, 9H, ² J_{HP} = 10.8 Hz, $P(CH_3)_3$; 1.77 (d, 15H, ${}^4J_{HP}$ = 1.6 Hz, $C_5(CH_3)_5$); 3.90 (s, 3H, C^{6} -OCH₃); 4.38 (s, 3H, C^{1} -OCH₃); 6.64 (s, 1H, $C^{2}H$); 7.05 (d, 2H, ${}^{3}J_{\text{HH}} = 8.8$ Hz, $C^{3'}H + C^{5'}H$; 7.09–7.14 (m, 1H, $C^{6}H$); 7.14–7.19 (m, 1H, C^5H); 7.41 (d, 2H, ${}^{3}J_{HH}$ = 7.13 Hz, $C^{2'}H$ + $C^{6'}H$; 7.71 (dd, 1H, ${}^{3}J_{HH} =$ 7.8 Hz, ${}^{4}J_{HH} =$ 1.7 Hz, $C^{4}H$); 7.80–7.84 (m, 1H, C^7H) ppm. ³¹P{¹H} NMR: δ –144.17 (sept, ${}^{1}J_{PF} = 710.4 \text{ Hz}, PF_{6}$; -34.83 (s, $P(CH_{3})_{3}$) ppm. ${}^{13}C{}^{1}H$ NMR: δ 9.7 (s, C₅(CH₃)₅); 14.3 (d, ¹J_{CP} = 40.8 Hz, P(CH₃)₃); 56.0 (s, $C^{6}-OCH_{3}$; 63.6 (s, $C^{1}-OCH_{3}$); 99.8 (d, ${}^{2}J_{CP} = 2.0$ Hz, $C_{5}(CH_{3})_{5}$); 114.4 (s, $C^{3'} + C^{5'}$); 118.7 (d, ${}^{3}J_{CP} = 2.0$ Hz, C^{2}); 123.6 (s, C^{5}); 131.2 (s, $C^{2'} + C^{6'}$); 131.6 (s, C^{6}); 134.2 (s, $C^{1'}$); 134.5 (s, C^{9}); 137.7 (s, C^4); 143.1 (d, ${}^{3}J_{CP} = 5.1 \text{ Hz}, C^7$); 156.0 (d, ${}^{2}J_{CP} = 9.9 \text{ Hz},$ C^{8}); 161.8 (s, C^{4}); 178.9 (s, C^{3}); 246.7 (d, ${}^{2}J_{CP} = 10.4 \text{ Hz}, C^{1}$) ppm. Preparation of $[IrCp*{=C(OMe)-CH=C(o-C_6H_3-p-CH_3)-}$ (Ph){ (PMe_3)] PF_6 (6A) and $[IrCp*{=C(OMe)-CH=C(o-C_6H_4)-CH=C(O-C_6H_4)-C$ $(p-CH_3-C_6H_4)$ (PMe₃)]PF₆ (6B). A green solution of the mixture cis-, trans-3 (~50:50 mole ratio, 130 mg, 0.16 mmol) in 10 mL of dichloromethane was treated with $AgPF_6$ (45 mg,

0.17 mmol). The brown solution was stirred for 5 min at room temperature, and then filtered and vacuum-concentrated giving a dark green oil that was treated with pentane obtaining a dark green solid that was washed with pentane $(3 \times 5 \text{ mL})$. The solid obtained was dried under a vacuum yielding a mixture of the isomers **6(A,B)** (~50 : 50 mole ratio estimated by NMR, respectively). Yield (isolated mixture): 105 mg (84%).

Anal. calcd for $C_{30}H_{39}OF_6IrP_2$ (783.80 g mol⁻¹): C 45.97, H 5.02; found: C 45.19, H 5.07. MS (*m*/*z*): 639.22447 [M]⁺. IR (cm⁻¹): ν (PF₆) 840 (s).

6A: ¹H NMR: δ 1.25 (d, 9H, ² J_{HP} = 10.9 Hz, P(CH₃)₃); 1.78 (d, 15H, ${}^{4}J_{HP}$ = 1.6 Hz, C₅(CH₃)₅); 2.41 (s, 3H, CH₃); 4.35 (s, 3H, OCH₃); 6.58 (s, 1H, $C^{2}H$); 6.94–7.00 (m, 1H, $C^{5}H$); 7.39–7.42 (m, 2H, Ph); 7.51-7.56 (m, 4H, $H^4 + Ph$); 7.66-7.68 (m, 1H, $C^{7}H$) ppm. ³¹P{¹H} NMR: δ –144.17 (sept, ¹*J*_{PF} = 710.4 Hz, *P*F₆); -34.87 (s, *P*(CH₃)₃) ppm. ¹³C{¹H} NMR: δ 9.7 (s, C₅(CH₃)₅); 14.2 (d, ${}^{1}J_{CP} = 40.7$ Hz, P(CH₃)₃); 21.3 (s, CH₃); 63.4 (s, OCH₃); 99.9 (d, ${}^{2}J_{CP} = 1.8$ Hz, $C_{5}(CH_{3})_{5}$); 117.7 (d, ${}^{3}J_{CP} = 2.0$ Hz, C^{2}); 124.8 (s, C⁵); 128.6–129.9 (all s, Ph); 131.4 (s, C⁹); 137.8 (s, C⁴); 142.1 (s, C_{ipso}); 142.9 (s, C^{6}); 143.9 (d, ${}^{3}J_{CP} = 4.9$ Hz, C^{7}); 157.0 (d, ${}^{2}J_{CP} = 10.2 \text{ Hz}, C^{8}$; 179.3 (s, C^{3}); 245.7 (d, ${}^{2}J_{CP} = 10.3 \text{ Hz}, C^{1}$) ppm. 6B: ¹H NMR: δ 1.25 (d, 9H, ² J_{HP} = 10.9 Hz, P(C H_3)₃); 1.78 (d, 15H, ${}^{4}J_{HP}$ = 1.6 Hz, C₅(CH₃)₅); 2.47 (s, 3H, CH₃); 4.37 (s, 3H, OCH₃); 6.63 (s, 1H, $C^{2}H$); 7.10–7.14 (m, 2H, $C^{5}H + C^{6}H$); 7.32-7.35 (m, 4H, C₆H₄CH₃); 7.66-7.70 (m, 1H, C⁴H); 7.81-7.84 (m, 1H, C^7H) ppm. ³¹P{¹H} NMR: δ -144.17 (sept, ¹J_{PF} = 710.4 Hz, PF_6 ; -35.05 (s, $P(CH_3)_3$) ppm. ¹³C{¹H} NMR: δ 9.7 (s, $C_5(CH_3)_5$); 14.1 (d, ${}^{1}J_{CP} = 40.8$ Hz, $P(CH_3)_3$); 21.5 (s, CH_3); 63.6 (s, OCH₃); 100.0 (d, ${}^{2}J_{CP} = 1.9$ Hz, $C_{5}(CH_{3})_{5}$); 118.7 (d, ${}^{3}J_{CP} = 2.1 \text{ Hz}, C^{2}$; 123.6 (s, C^{5}); 128.6–129.9 (all s, $C_{6}H_{4}CH_{3}$); 131.7 (s, C^6); 134.4 (s, C^9); 137.9 (s, C^4); 139.1 (s, $C^{1'}$); 140.7 (s, $C^{4'}$); 143.0 (d, ${}^{3}J_{CP} = 5.0 \text{ Hz}, C^{7}$); 156.1 (d, ${}^{2}J_{CP} = 10.1 \text{ Hz}, C^{8}$); 179.0 (s, C^3); 247.6 (d, ${}^2J_{CP} = 10.4 \text{ Hz}, C^1$) ppm.

Note: During NMR characterization the formation of **9b** (\sim 5%) was observed.

Preparation of 6-nitro-3-phenylindan-1-one (7a) and 3-(4nitrophenyl)indan-1-one (7b). A dark brown solution of a 4(A,B) mixture (~57:43 mole ratio, 106 mg, 0.13 mmol) in 10 mL of 1,2-dichloroethane was stirred and heated at 338 K for 24 hours. The brown solution obtained was vacuum-concentrated yielding a brown oil from which the indanone 7b was extracted with diethylether. The solid that remained after the extraction was washed with pentane $(3 \times 4 \text{ mL})$ and it was identified as the complex 4A without alteration (60.4 mg, 0.074 mmol). The indanone 7b was purified through a silica column using hexane-AcOEt (7:4) as the eluent. 7b: yield (calculated on the complex 4B): 12.8 mg (90%). Anal. calcd for C₁₅H₁₁O₃N (253.26 g mol⁻¹): C 71.14, H 4.38, N 5.53; found: C 71.21, H 4.40, N 5.57. MS (m/z): 254.0769 $[M + 1]^+$; 253.0736 [M]; 207.08 [M - NO₂]⁺. IR (cm⁻¹): ν (CO) 1712 (s); (NO₂) 1518 (s) and 1348 (s). ¹H NMR: δ 2.64 (dd, 1H, ² J_{HH} = 19.2 Hz, ${}^{3}J_{\text{HH}}$ = 3.9 Hz, C²H₂); 3.26 (dd, 1H, ${}^{2}J_{\text{HH}}$ = 19.2 Hz, ${}^{3}J_{\text{HH}}$ = 8.2 Hz, $C^{2}H_{2}$; 4.74 (dd, 1H, ${}^{3}J_{HH}$ = 8.2 Hz, ${}^{3}J_{HH}$ = 3.7 Hz, $C^{3}H$); 7.24–7.28 (m, 1H, C^4H); 7.30–7.34 (m, 2H, $C^{2'}H + C^{6'}H$); 7.45-7.51 (m, 1H, C⁶H); 7.60-7.65 (m, 1H, C⁵H); 7.79-7.83 (m, 1H, C^7H); 8.14–8.19 (m, 2H, $C^{3'}H + C^{5'}H$) ppm. ¹³C{¹H} NMR:

$$\begin{split} &\delta \, 44.5 \; ({\rm s}, \, C^3); \, 46.7 \; ({\rm s}, \, C^2); \, 123.9 \; ({\rm s}, \, C^7); \, 124.5 \; ({\rm s}, \, C^{3'} + C^{5'}); \, 127.2 \\ &({\rm s}, \, \, C^4); \; 128.8 \; ({\rm s}, \, \, C^6); \; 129.0 \; ({\rm s}, \, \, C^{2'} + \, C^{6'}); \; 135.7 \; ({\rm s}, \, C^5); \; 137.3 \\ &({\rm s}, \, C^8); \, 147.4 \; ({\rm s}, \, C^{4'}); \; 151.8 \; ({\rm s}, \, C^1); \; 156.7 \; ({\rm s}, \, C^9); \; 204.6 \; ({\rm s}, \, CO) \; {\rm ppm}. \end{split}$$

A dark brown solution of the complex 4A previously isolated (60.4 mg, 0.074 mmol) in 10 mL of 1,2-dichloroethane was stirred and heated at 368 K for 24 hours. The brown solution obtained was vacuum-concentrated yielding a brown oil. The mixture of 7(a,b) (~30:70 mole ratio estimated by NMR, respectively) was extracted with diethylether and purified through a silica column using hexane-AcOEt (7:4) as the eluent. Yield (isolated mixture): 17 mg (91%) (~27% for 7a, ~64% for 7b). 7a: ¹H NMR: δ 2.81 (dd, 1H, ²J_{HH} = 19.5 Hz, ${}^{3}J_{\rm HH}$ = 4.1 Hz, C²H₂); 3.35 (dd, 1H, ${}^{2}J_{\rm HH}$ = 19.4 Hz, ${}^{3}J_{\rm HH}$ = 8.2 Hz, $C^{2}H_{2}$; 4.69 (dd, 1H, ${}^{3}J_{HH} = 8.3$ Hz, ${}^{3}J_{HH} = 4.0$ Hz, $C^{3}H$); 7.12–7.38 (*Ph*, overlapped with isomer 7b); 7.45 (d, 1H, ${}^{3}J_{HH} =$ 8.4 Hz, C^4H ; 8.40 (dd, 1H, ${}^{3}J_{HH}$ = 8.4 Hz, ${}^{4}J_{HH}$ = 2.2 Hz, $C^{5}H$); 8.56 (d, 1H, ${}^{4}J_{HH}$ = 2.1 Hz, $C^{7}H$) ppm. ${}^{13}C{}^{1}H$ NMR: δ 45.0 (s, C^3); 47.5 (s, C^2); 119.0 (s, C^7); 126.7–130.4 (*Ph* + C^4 , overlapped with isomer 7b); 129.5 (s, C^5); 138.1 (s, C^8); 142.6 (s, C^{6}) ; 136.4 $(s, C^{1'})$; 163.8 (s, C^{9}) ; 203.8 (s, CO) ppm.

Preparation of 6-methoxy-3-phenylindan-1-one (8a) and 3-(4-methoxyphenyl)indan-1-one (8b). A dark brown solution of a 5(A,B) mixture (~33:66 mole ratio, 100 mg, 0.125 mmol) in 10 mL of 1,2-dichloroethane was stirred and heated at 338 K for 24 hours. The brown solution obtained was vacuum-concentrated yielding a brown oil from which 8(a,b) were extracted with diethylether. The solid that remained after the extraction was washed with pentane $(3 \times 4 \text{ mL})$ and it was identified as the complex 5A (80% recovered regarding the initial quantity, 26.4 mg, 0.033 mmol). The mixture 8(a,b) (~13:87 mole ratio estimated by NMR, respectively) was purified through a silica column using hexane-AcOEt (7:4) as the eluent. Yield (isolated mixture): 15 mg (50%) (~19% for 8a calculated on complex 5A, ~65% for 8b calculated on complex 5B). Anal. calcd for $C_{16}H_{14}O_2$ (238.29 g mol⁻¹): C 80.65, H 5.92; found: C 80.92, H 6.01. MS (m/z): 239.1024 $[M + 1]^+$; 238.0992 [M]; 223.08 $[M - CH_3]^+$. IR (cm⁻¹): ν (CO) 1710 (s). 8b: ¹H NMR: δ 2.60 (dd, 1H, ²*J*_{HH} = 19.1 Hz, ³*J*_{HH} = 3.9 Hz, C²*H*₂); 3.18 (dd, 1H, ${}^{2}J_{HH}$ = 19.2 Hz, ${}^{3}J_{HH}$ = 8.0 Hz, $C^{2}H_{2}$); 3.77 (s, 3H, OCH₃); 4.55 (dd, 1H, ${}^{3}J_{HH}$ = 7.9 Hz, ${}^{3}J_{HH}$ = 3.9 Hz, $C^{3}H$); 6.84 (d, 2H, ${}^{3}J_{\rm HH}$ = 8.7 Hz, $C^{3'}H + C^{5'}H$); 7.05 (d, 2H, ${}^{3}J_{\rm HH}$ = 8.7 Hz, $C^{2'}H +$ $C^{6'}H$; 7.26 (d, 1H, ${}^{3}J_{HH}$ = 7.7 Hz, $C^{4}H$); 7.41 (t, 1H, ${}^{3}J_{HH}$ = 7.4 Hz, $C^{6}H$; 7.55–7.61 (m, 1H, $C^{5}H$); 7.75 (d, 1H, ${}^{3}J_{HH}$ = 7.6 Hz, $C^{7}H$) ppm. ¹³C{¹H} NMR: δ 44.0 (s, C^3); 47.3 (s, C^2); 55.6 (s, OCH₃); 114.5 (s, $C^{3'} + C^{5'}$); 123.4 (s, C^7); 127.2 (s, C^4); 128.1 (s, C^6); 129.0 (s, $C^{2'} + C^{6'}$); 135.3 (s, C^5); 136.3 (s, $C^{1'}$); 137.1 (s, C^8); 158.7 (s, C⁹); 159.0 (s, C^{4'}); 206.0 (s, CO) ppm.

A dark brown solution of the complex 5A previously isolated (26.4 mg, 0.033 mmol) in 10 mL of 1,2-dichloroethane was stirred and heated at 368 K for 24 hours. The brown solution obtained was vacuum-concentrated yielding a brown oil. A mixture of 8a and 6-methoxy-3-phenylinden-1-one (\sim 70:30 mole ratio, respectively) was extracted with diethylether and purified through a silica column using hexane–AcOEt (7:4) as the eluent. Yield (isolated mixture): 1.6 mg (\sim 14% for 8a). The solid that remained after the extraction was washed with

pentane (3 × 4 mL) and it was identified as the complex **5A** (78% recovered regarding the initial quantity, 16.4 mg, 0.033 mmol). **8a**: ¹H NMR: δ 2.64 (dd, 1H, ²*J*_{HH} = 19.2 Hz, ³*J*_{HH} = 3.6 Hz, C²*H*₂); 3.22 (dd, 1H, ²*J*_{HH} = 19.1 Hz, ³*J*_{HH} = 7.9 Hz, C²*H*₂); 3.86 (s, 3H, OC*H*₃); 4.53 (dd, 1H, ³*J*_{HH} = 7.8 Hz, ³*J*_{HH} = 3.7 Hz, C³*H*); 7.10–7.14 (m, 2H, *Ph*); 7.15–7.17 (m, 2H, C⁴*H* + C⁵*H*); 7.20–7.25 (m, 2H, C⁷*H* + *Ph*); 7.28–7.33 (m, 2H, *Ph*) ppm. ¹³C{¹H} NMR: δ 44.1 (s, *C*³); 47.9 (s, *C*²); 56.1 (s, OC*H*₃); 104.8 (s, *C*⁷); 124.4 (s, *C*⁵); 127.2 (s, 2C *Ph*); 127.8 (s, 1C *Ph*); 127.9 (s, 2C *Ph*); 128.0 (s, *C*⁴); 160.2 (*C*⁶, observed by {¹H, ¹³C} HMBC correlations) ppm. Due to the final product mixture, the rest of the signals could not be assigned.

Preparation of 6-methyl-3-phenylindan-1-one (9a) and 3-(4-methylphenyl)indan-1-one (9b). A dark green suspension of 6(A,B) (~50:50 mole ratio, 80 mg, 0.10 mmol) in 10 mL of 1,2-dichloroethane was stirred and heated at 338 K for 24 hours. The brown solution obtained was filtered and vacuum-concentrated giving a brown oil. The mixture of 9(a,b) (~45:55 mole ratio, respectively) was purified through a silica column using hexane–AcOEt (95:5) as the eluent. Yield (isolated mixture): 20.2 mg (91%) (~41% for 9a calculated on complex 6A, ~50% for 9b calculated on complex 6B).

Anal. calcd for C₁₆H₁₄O (222.29 g mol⁻¹): C 86.45, H 6.35; found: C 86.62, H 6.39. MS (m/z): 223.1079 $[M + 1]^+$; 222.1040 [M]; 207.08 $[M - CH_3]^+$; 145.06 $[M - Ph]^+$; 130.04 $[M - C_6H_4]$ $- CH_3^{+}$. IR (cm⁻¹): ν (CO) 1713 (s). 9a: ¹H NMR: δ 2.42 (s, 3H, CH_3 ; 2.64 (dd, 1H, ${}^{2}J_{HH}$ = 19.1 Hz, ${}^{3}J_{HH}$ = 3.6 Hz, $C^{2}H_2$); 3.20 (dd, 1H, ${}^{2}J_{HH}$ = 19.1 Hz, ${}^{3}J_{HH}$ = 8.0 Hz, $C^{2}H_{2}$); 4.55 (dd, 1H, ${}^{3}J_{HH} = 7.8$ Hz, ${}^{3}J_{HH} = 3.9$ Hz, $C^{3}H$; 7.13–7.18 (m, 4H, $C^{4}H +$ *Ph*); 7.28–7.33 (m, 2H, *Ph*); 7.39–7.44 (m, 1H, C⁵*H*); 7.55–7.60 (m, 1H, C^7H) ppm. ¹³C{¹H} NMR: δ 21.2 (s, CH_3); 44.4 (s, C^3); 47.5 (s, C^2); 123.3 (s, C^7); 126.8 (s, C^4); 127.2 (s, 1C Ph); 128.0 (s, 2C Ph); 129.2 (s, 2C Ph); 135.6 (s, C^5); 137.1 (s, C^8); 138.4 (s, C^{6}); 144.6 (s, $C^{1'}$); 155.8 (s, C^{9}); 205.9 (s, CO) ppm. **9b**: ¹H NMR: δ 2.32 (s, 3H, CH₃); 2.63 (dd, 1H, ²J_{HH} = 19.1 Hz, ${}^{3}J_{\rm HH}$ = 3.8 Hz, C²H₂); 3.18 (dd, 1H, ${}^{2}J_{\rm HH}$ = 19.1 Hz, ${}^{3}J_{\rm HH}$ = 8.0 Hz, C^2H_2 ; 4.56 (dd, 1H, ${}^{3}J_{HH} = 7.8$ Hz, ${}^{3}J_{HH} = 3.9$ Hz, $C^{3}H$); 7.02 (d, 2H, ${}^{3}J_{HH}$ = 8.1 Hz, $C^{2'}H + C^{6'}H$); 7.13 (d, 2H, ${}^{3}J_{HH}$ = 7.7 Hz, $C^{3'}H + C^{5'}H$; 7.22–7.29 (m, 1H, $C^{4}H$); 7.39–7.44 (m, 1H, $C^{6}H$; 7.55–7.60 (m, 1H, $C^{5}H$); 7.76 (d, 1H, ${}^{3}J_{HH} = 7.7$ Hz, $C^{7}H$) ppm. ¹³C{¹H} NMR: δ 21.1 (s, CH₃); 44.4 (s, C³); 47.1 (s, C²); 123.4 (s, C^7); 127.1 (s, C^4); 127.8 (s, $C^{2'} + C^{6'}$); 128.0 (s, C^6); 129.8 (s, $C^{3'} + C^{5'}$); 135.3 (s, C^{5}); 137.0 (s, $C^{4'}$); 137.1 (s, C^{8}); 141.3 (s, C^{1'}); 158.6 (s, C⁹); 206.0 (s, CO) ppm.

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