

# Stable iridium(IV) complexes supported by tetradentate salen ligands. Synthesis, structures and reactivity

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A series of *trans*-dichloroiridium(IV)-salen complexes were synthesized and structurally characterized by spectroscopic means and X-ray crystal structures. These Ir(IV) complexes are able to catalyze intramolecular C–H amination of aryl azides. The catalytic amination was drastically accelerated under microwave-assisted conditions, and possibly involves Ir–imido intermediates as supported by high-resolution ESI-MS analysis.

Iridium-catalyzed organic transformations have been receiving a great deal of attention.<sup>1</sup> Among the important intermediates proposed to be involved in these processes are Ir(IV) species.<sup>1c,2</sup> Ir(IV) species represent one class of the key intermediates proposed in iridium-catalyzed water oxidation.<sup>3</sup> Nonetheless, isolated Ir(IV) complexes are relatively sparse, all of which are supported by monodentate ligands only,<sup>4</sup> or bidentate S<sup>^</sup>S,<sup>5</sup> N<sup>^</sup>N,<sup>5,6</sup> B<sup>^</sup>C,<sup>7</sup> N<sup>^</sup>O,<sup>8</sup> O<sup>^</sup>O ligands,<sup>9</sup> or tridentate O<sup>^</sup>N<sup>^</sup>O,<sup>10</sup> O<sup>^</sup>O<sup>^</sup>O,<sup>11</sup> P<sup>^</sup>N<sup>^</sup>P,<sup>12</sup> N<sup>^</sup>N<sup>^</sup>O<sup>13</sup> ligands, or polyoxometalates.<sup>14</sup> Indeed, the chemistry and catalytic activity of Ir(IV) complexes in organic transformations remain underdeveloped. We are interested to explore the chemistry and catalytic properties of mononuclear iridium complexes in high oxidation states, which are supported by tetradentate O<sup>^</sup>N<sup>^</sup>O Schiff base ligands, namely, *N,N'*-bis(salicylidene)-ethylenediamine derivatives (salens). This type of ligands has been employed to support efficient Ir(III) catalysts for carbene transfer/insertion with diazo compounds<sup>15a,b</sup> and nitrene C–H insertion with sulfonyl azides.<sup>15c</sup> However, mononuclear Ir(IV)-salen complexes, to the best of our knowledge, are unprecedented. The catalytic reaction examined in this work is nitrene C–H insertion,<sup>15d,16</sup> a catalytic reaction previously not documented for Ir(IV) chemistry.<sup>1,2,15d,16</sup> Herein we describe the isolation, characterization, and catalytic behavior of several stable mononuclear Ir(IV)-salen complexes [Ir<sup>IV</sup>(salen)Cl<sub>2</sub>] (salen = L<sup>1</sup>: **1**, L<sup>2</sup>: **2**, L<sup>3</sup>: **3**; Fig. 1). These Ir(IV)-salen complexes were found to catalyze intramolecular amination of C(sp<sup>3</sup>)–H bonds of aryl azides, possibly via reactive Ir–imido species,<sup>12,17</sup> with up to 96% product yields obtained under

microwave-assisted conditions.

Complexes **1** and **2** were prepared by reactions of [Ir<sup>I</sup>(Cl)(COD)]<sub>2</sub> (COD = 1,5-cyclooctadiene) with H<sub>2</sub>L<sup>1</sup> and H<sub>2</sub>L<sup>2</sup>, respectively, in 1,2,4-trichlorobenzene in open atmosphere at 185 °C for 40 min (**1**: red solid, 28% yield; **2**: orange solid, 20% yield). However, similar reaction of [Ir<sup>I</sup>(Cl)(COD)]<sub>2</sub> with H<sub>2</sub>L<sup>3</sup> gave [Ir<sup>III</sup>(L<sup>3</sup>)(Cl)(CO)]. Treatment of [Ir<sup>III</sup>(L<sup>3</sup>)(Cl)(CO)] in refluxing CCl<sub>4</sub> under argon atmosphere led to the isolation of complex **3** (brown solid, 46% yield).

Complexes **1–3** are paramagnetic, with magnetic moment ( $\mu_{\text{eff}}$ ) of 1.82  $\mu_{\text{B}}$  for **1**, 1.63  $\mu_{\text{B}}$  for **2**, and 1.73  $\mu_{\text{B}}$  for **3** (determined by the Evans method in solution at room temperature), corresponding to the presence of one unpaired electron in each molecule and indicating an  $S = 1/2$  spin state.<sup>11</sup> DFT calculations using **1** as example (details in the ESI<sup>†</sup>) revealed a spin density distribution of 56% on Ir and 43% on phenoxide O atoms, comparable to that reported for the Ir(IV)-N<sup>^</sup>O complexes (48–57% on Ir<sup>8</sup> and 47–48% on alkoxide O atoms,<sup>8a</sup> which indicate high covalency and delocalization in the coordination bonds<sup>8</sup>). We measured the X-band EPR spectra of **1–3** in CH<sub>2</sub>Cl<sub>2</sub> at 10 K (Fig. 1); all the spectra are anisotropic and are assigned with the help of the empirical simulations, each being simulated as an  $S = 1/2$  system with significant  $g$  anisotropy. The EPR spectra of **1** and **2** both show a rhombic signal with simulated  $g$  values of  $g_x = 2.11$ ,  $g_y = 2.10$ ,  $g_z = 1.55$  for **1** (Fig. S5, ESI<sup>†</sup>) and  $g_x =$

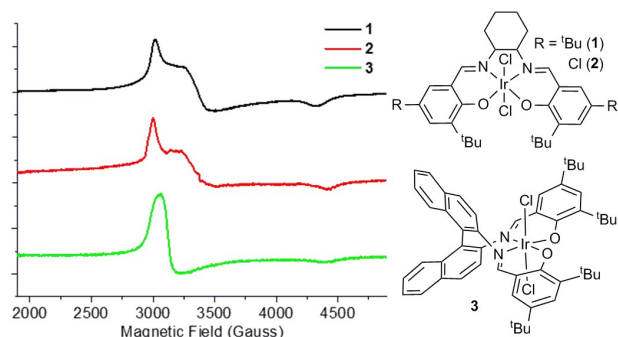


Fig. 1 X-band EPR spectra of [Ir<sup>IV</sup>(salen)Cl<sub>2</sub>] (salen = L<sup>1</sup>: **1**, L<sup>2</sup>: **2**, L<sup>3</sup>: **3**) in frozen CH<sub>2</sub>Cl<sub>2</sub> at 10 K. H<sub>2</sub>L<sup>1</sup> = bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine; H<sub>2</sub>L<sup>2</sup> = bis(3-*tert*-butyl-5-chlorosalicylidene)-1,2-cyclohexanediamine; H<sub>2</sub>L<sup>3</sup> = bis(3,5-di-*tert*-butylsalicylidene)-1,1'-binaphthyl-2,2'-diamine.

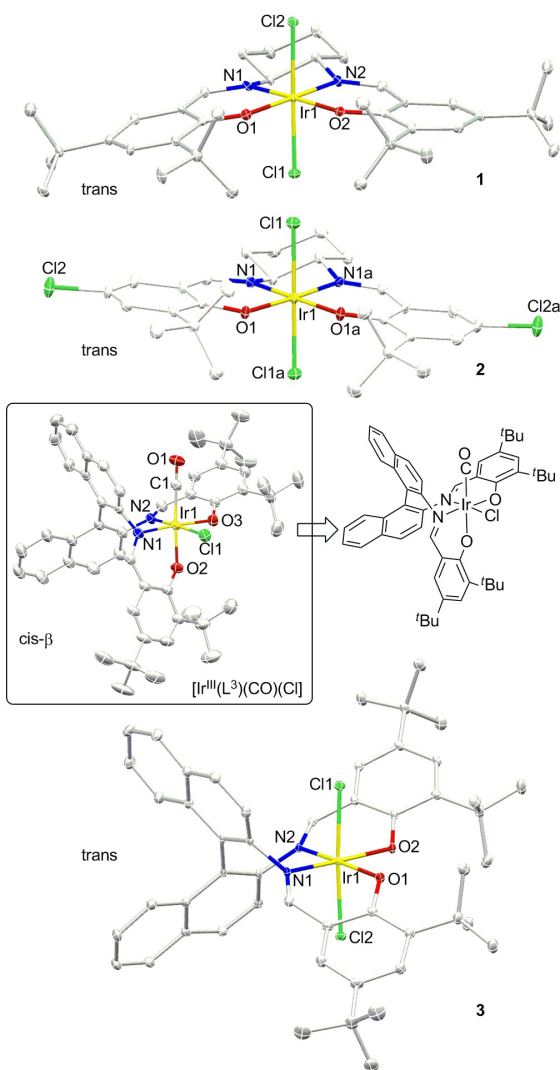
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2.14,  $g_x = 2.12$ ,  $g_z = 1.51$  for **2** (Fig. S6, ESI†). Complex **3** gives an axial signal with simulated  $g_x \sim g_y = 2.17$  and  $g_z = 1.52$  (Fig. S7, ESI†). These  $g$  values for **1–3** are comparable to those of previously reported Ir(IV) complexes ( $g_x = 2.15–2.48$ ,  $g_y = 2.15–2.42$ ,  $g_z = 1.56–1.96$ ).<sup>6,7,8b</sup> In contrast,  $[\text{Ir}^{\text{III}}(\text{L}^3)(\text{Cl})(\text{CO})]$  is diamagnetic, showing a well-resolved  $^1\text{H}$  NMR spectrum which is not sensitive to temperature (from  $-40$  to  $50$  °C, Fig. S8, ESI†).

The crystal structures of **1–3** and  $[\text{Ir}^{\text{III}}(\text{L}^3)(\text{Cl})(\text{CO})]$  have been determined by X-ray crystallographic studies (Fig. 2). Complexes **1** and **2** adopt planar ONNO arrangement as usually found for metal complexes with this type of salen ligands.<sup>15</sup> The Ir(IV) ions of **1** and **2** are each situated in an axially elongated octahedral environment with two trans Ir–Cl axial bonds (cf. Ir–Cl 2.328(2)–2.347(3) Å vs Ir–O 1.997(8)–2.003(7) Å and Ir–N 1.964(4)–1.983(9) Å). The trans-Cl–Ir–Cl moiety is basically linear (bond angles:  $177.89(12)^\circ$  for **1**,  $178.15(6)^\circ$  for **2**) and nearly perpendicular to the ONNO plane (e.g. Cl–Ir–O angles:  $87.8(2)^\circ$ – $91.5(2)^\circ$  in **1** and  $88.65(10)^\circ$ – $90.03(10)^\circ$  in **2**).

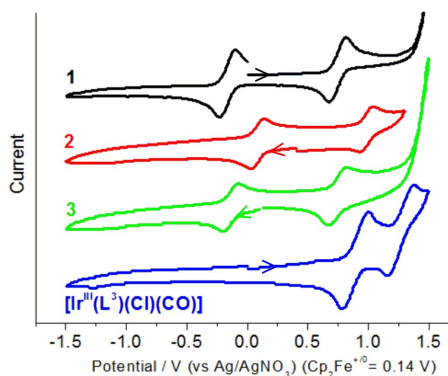


**Fig. 2** ORTEP drawings of **1–3** (for each of **1** and **2**, only one of the two crystallographically independent molecules is shown) and  $[\text{Ir}^{\text{III}}(\text{L}^3)(\text{Cl})(\text{CO})]$ . Hydrogen atoms are not shown. Thermal ellipsoid probability: 30%.

For the binaphthyl salen complex  $[\text{Ir}^{\text{III}}(\text{L}^3)(\text{Cl})(\text{CO})]$ , its crystal structure reveals a distorted octahedral coordination geometry with a *cis*-β configuration (non-planar ONNO; Ir–Cl 2.3486(9) Å), like previously reported metal complexes with tetradentate binaphthyl salen ligands.<sup>18</sup> Intriguingly, upon converting this *cis*-β Ir(III)-L<sup>3</sup> complex to the Ir(IV)-L<sup>3</sup> complex **3**, **3** adopts a *trans* configuration (planar ONNO, Fig. 2) with a distorted  $\text{IrO}_2\text{N}_2\text{Cl}_2$  octahedron (Ir–Cl 2.3325(13)–2.3372(12) Å, Ir–O 2.000(4)–2.007(4) Å, Ir–N 2.001(4)–2.011(4) Å, Cl–Ir–Cl 176.23(5)°, Cl–Ir–O 87.32(11)°–91.22(11)°) similar to that in **1** and **2**. Possibly, a *cis*-Ir<sup>IV</sup>Cl<sub>2</sub> configuration of **3** is destabilized by the imine/phenolate groups trans to Cl<sup>−</sup> and/or by the repulsion between the *cis* Cl<sup>−</sup> ligands. The Ir–Cl distances in **1–3** (2.328(2)–2.347(3) Å) compare well with those in *trans*- $[\text{Ir}^{\text{IV}}(\text{N}^{\wedge}\text{O})_2\text{Cl}_2]$  (2.3195(9)–2.3473(15) Å, N<sup>∧</sup>O = 2-(pyridin-2-yl)propan-2-oate),<sup>8b</sup> and slightly longer than those in  $[\text{Ir}^{\text{IV}}(\text{O}^{\wedge}\text{O})\text{Cl}_3]$  (2.2781(9)–2.2895(9) Å; all Ir–Cl bonds are *cis* to each other; O<sup>∧</sup>O = Kläui tripodal ligand).<sup>11</sup>

The cyclic voltammograms of **1–3** in dichloromethane each display two redox couples (reversible or quasi-reversible): an oxidation couple at  $E_{1/2} = 0.75–0.99$  V and a reduction couple at  $E_{1/2} = 0.08$  to  $-0.17$  V (vs 0.1 M Ag/AgNO<sub>3</sub> in MeCN, Fig. 3). The potentials of both the oxidation and reduction couples are affected by the substituents on the salen ligand, with the  $E_{1/2}$  values showing an anodic shift from 0.75 and  $-0.17$  V for **1** to 0.99 and 0.08 V for **2**, respectively, upon replacing two electron-donating <sup>t</sup>Bu groups of **1** with two electron-withdrawing Cl groups to give **2**. Complexes **1** and **3**, which differ in their salen backbones (cyclohexyl vs binaphthyl), exhibit the redox couples at similar potentials, indicating that the backbone of the salen ligand has little effect on the  $E_{1/2}$  values. The oxidation couple for **1–3** is tentatively assigned to a ligand-based process, as an oxidation couple similar to that for the Ir(IV)-L<sup>3</sup> complex **3** has also been observed for  $[\text{Ir}^{\text{III}}(\text{L}^3)(\text{Cl})(\text{CO})]$  (Fig. 3). The reduction couples for **1–3** at  $E_{1/2} = -0.06$  to  $-0.31$  V vs Cp<sub>2</sub>Fe<sup>+0</sup> (0.08 to  $-0.17$  V vs 0.1 M Ag/AgNO<sub>3</sub>, Fig. 3) are attributable to reduction of Ir<sup>IV</sup> to Ir<sup>III</sup> (note the absence of significant reduction wave for  $[\text{Ir}^{\text{III}}(\text{L}^3)(\text{Cl})(\text{CO})]$  in Fig. 3); these potentials are comparable to the reported  $E_{1/2}(\text{Ir}^{\text{IV}}/\text{Ir}^{\text{III}})$  values for *fac*- $[\text{Ir}^{\text{IV}}(\text{N}^{\wedge}\text{O})_3]^+$ <sup>8a</sup> and *trans*- $[\text{Ir}^{\text{IV}}(\text{N}^{\wedge}\text{O})_2\text{Cl}_2]$ <sup>8b</sup> in dichloromethane ( $-0.176$  and  $-0.387$  V vs Cp<sub>2</sub>Fe<sup>+0</sup>, respectively).

Complexes **1–3** exhibit similar UV-vis absorption spectra in dichloromethane (Fig. S1, S2, S4, ESI†). The high energy bands at  $\sim 350$  nm and below 300 nm are dominated by intra-ligand charge-



**Fig. 3** Cyclic voltammograms of **1–3** and  $[\text{Ir}^{\text{III}}(\text{L}^3)(\text{Cl})(\text{CO})]$  in  $\text{CH}_2\text{Cl}_2$  (0.1 M [<sup>t</sup>Bu<sub>4</sub>N]PF<sub>6</sub>). Scan rate: 100 mV s<sup>−1</sup>. Redox potentials and peak separations are shown in Table S5 (ESI†).

transfer (ILCT) transitions of the coordinated salen ligands. The bands with  $\lambda_{\text{max}}$  at 413–575 nm can be assigned to ligand-to-metal charge-transfer (LMCT) transitions, similar to the assignment of the visible absorption bands for Ir(IV)-N<sup>+</sup>O complexes.<sup>8</sup> There are also bands in the near-IR region, analogous to the case of Ir(IV)-N<sup>+</sup>O complexes,<sup>8b</sup> with  $\lambda_{\text{max}}$  being, for example 775 and 931 nm for **1**. Such low energy bands for **2** and **3** appear at  $\lambda_{\text{max}}$  of 747–944 nm.

The catalytic properties of the Ir(IV)-salen complexes were examined with *ortho*-azidobenzamides (**4**), a type of aryl azides previously reported to undergo intramolecular C(sp<sup>3</sup>)-H amination to give dihydroquinazolinones (**5**) and quinazolinones (**6**) in the presence of iron porphyrin catalyst [Fe<sup>III</sup>(F<sub>20</sub>TPP)Cl] (H<sub>2</sub>F<sub>20</sub>TPP = *meso*-tetrakis(pentafluorophenyl)porphyrin) with **5** being the dominant products (up to 83% yield; yields of **6**: up to 17%).<sup>19</sup> Interestingly,

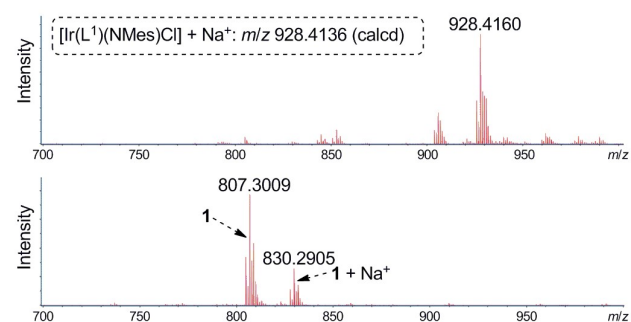
**Table 1** Microwave-accelerated dihydroquinazolinone or quinazolinone formation<sup>a</sup>

Entry	Cat.	Substrate	<b>5</b> (Yield <sup>b</sup> )	<b>6</b> (Yield <sup>b</sup> )
1	<b>1</b>			
2	<b>2</b>			
		<b>4a</b>	<b>5a<sup>c</sup></b>	<b>6a</b> (96%, <sup>d</sup> 92% <sup>e</sup> )
3	<b>1</b>			
		<b>4b</b>	<b>5b<sup>c</sup></b>	<b>6b</b> (93%)
4	<b>1</b>			
		<b>4c</b>	<b>5c<sup>c</sup></b>	<b>6c</b> (69%)
5	<b>1</b>			
		<b>4d</b>	<b>5d<sup>c</sup></b>	<b>6d</b> (74%)
6	<b>1</b>			
		<b>4e</b>	<b>5e<sup>c</sup></b>	<b>6e</b> (57%)
7	<b>3</b>			
		<b>4a</b>	<b>5a</b> (40%)	<b>6a<sup>c</sup></b>
8	<i>f</i>			
		<b>4a</b>	<b>5a</b> (68%)	<b>6a<sup>c</sup></b>
9 <sup>g</sup>				
		<b>4a</b>	<b>5a<sup>c</sup></b>	<b>6a<sup>c</sup></b>

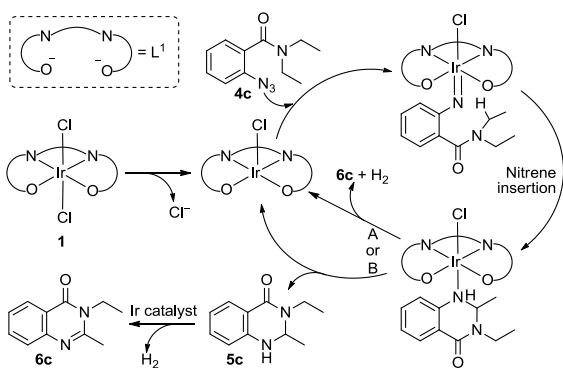
<sup>a</sup> Reactions were performed with substrate **4a–4e** (0.1 mmol) and catalyst (5 mol%) in DCE under N<sub>2</sub>. <sup>b</sup> Isolated yield. <sup>c</sup> Not obtained. <sup>d</sup> Catalyst **1**. <sup>e</sup> Catalyst **2**. <sup>f</sup> [Ir<sup>III</sup>(L<sup>3</sup>)(Cl)(CO)]. <sup>g</sup> Control experiment without catalyst.

treatment of **4a** with **1** (5 mol%) in refluxing benzene for 18 h afforded quinazolinone **6a** as the major product in 89% yield whereas dihydroquinazolinone **5a** was obtained in only 9% yield (entry 1 in Table S6, ESI<sup>†</sup>). Changing the solvent to 1,2-dichloroethane (DCE) increased the yield of **6a** to 95% (no **5a** was obtained, entry 4 in Table S6, ESI<sup>†</sup>), and the same yield of **6a** was obtained when **4a** was treated with **1** (5 mol%) in DCE under irradiation with an incandescent lamp (150 W) for 12 h (entry 1 in Table S7, ESI<sup>†</sup>). Notably, under microwave-assisted conditions, the reaction time for the **1**-catalyzed transformation of **4a** to **6a** was dramatically shortened to 1 h, affording **6a** in 96% yield (entry 1, Table 1; yield of **6a** using catalyst **2**: 92%, entry 2, Table 1). Similar reactions of *ortho*-azidobenzamides **4b–4e** gave quinazolinones **6b–6e** in 57–93% yields (entries 3–6, Table 1). For all of **4a–4e**, their reactions catalyzed by **1** under microwave-assisted conditions for 1 h gave product yields comparable to those obtained under irradiation of incandescent lamp (150 W) for 12 h (**6a–6e**: 61–95% yields, Table S7, ESI<sup>†</sup>). Unexpectedly, upon changing the catalyst to **3** (5 mol%), no **6a** was obtained from the reaction of **4a** under microwave-assisted conditions for 1 h; instead, dihydroquinazolinone **5a** was isolated in 40% yield (entry 7, Table 1), albeit lower than the 68% yield of **5a** isolated from the reaction catalyzed by [Ir<sup>III</sup>(L<sup>3</sup>)(Cl)(CO)] under the same conditions (entry 8, Table 1). In control experiment using **4a** in the absence of the iridium catalysts, neither **5a** nor **6a** was obtained (entry 9, Table 1).

To gain insight into the mechanism of the catalytic reactions, we examined a reaction mixture of **1** with **4c** (1 equiv) in refluxing DCE under N<sub>2</sub> by ESI-MS, which showed a cluster peak at *m/z* 962.4 attributable to [Ir(L<sup>1</sup>)(Cl)(**5c**)] (Fig. S9, ESI<sup>†</sup>). GC analysis of the head space of the reaction mixture in a sealed Schlenk tube revealed the presence of H<sub>2</sub>. By treating **1** with mesityl azide (MesN<sub>3</sub>, 3 equiv) in degassed DCE under microwave-assisted conditions for 10 min, high-resolution ESI-MS spectra showed a cluster peak at *m/z* 928.4160 which, together with the isotope distribution pattern, matches the formulation of an Ir-imido species [Ir(L<sup>1</sup>)(NMes)Cl] + Na<sup>+</sup> (Fig. 4). Based on these experiments and previous studies in [Fe<sup>III</sup>(F<sub>20</sub>TPP)Cl]-catalyzed analogues,<sup>19</sup> the following mechanism for the Ir(IV)-catalyzed intramolecular C(sp<sup>3</sup>)-H bond amination is proposed (Scheme 1): The **1**-catalyzed system initially generated a mono(chloro) species (from **1**) with a vacant site for aryl azide coordination. Decomposition of the coordinated aryl azide gave an Ir-imido intermediate; this intermediate underwent intramolecular nitrene C(sp<sup>3</sup>)-H insertion to afford dihydroquinazolinone intermediate **5** (or its bound form), which is converted to quinazolinone **6** by Ir-



**Fig. 4** High-resolution ESI-MS spectrum of **1** before (lower) and after (upper) treatment with MesN<sub>3</sub> (3 equiv) in degassed DCE under microwave irradiation.



**Scheme 1** Possible mechanism for **1**-catalyzed reaction of **4** (**4c** as example) to give **6**. Charges of the Ir- $L^1$  intermediates, if any, are omitted.

catalyzed dehydrogenation, analogous to previous examples of Ir-catalyzed dehydrogenation of secondary amines to imines.<sup>1a</sup> Indeed, treatment of **5a** with **1** (5 mol%) in DCE under microwave-assisted conditions for 1 h afforded **6a** in 92% yield (Scheme S3, ESI†); for the same treatment with the Ir- $L^3$  complex **3** or  $[Ir^{III}(L^3)(Cl)(CO)]$ , no reaction was observed, possibly owing to the larger steric hindrance of their binaphthyl salen ligand  $L^3$ .

In conclusion, we have prepared and characterized a series of Ir(IV)-salen complexes (**1**–**3**). Complex **1** exhibited a high catalytic reactivity toward aryl azides for a consecutive nitrene  $C(sp^3)$ -H insertion followed by dehydrogenation, providing a tandem catalytic system for the formation of quinazolinones.

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## Conflicts of interest

There are no conflicts to declare.

## Notes and references

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