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Dual-Reagent Catalysis within Ir−Sn Domain: Highly Selective Alkylation of Arenes and Heteroarenes with Aromatic Aldehydes

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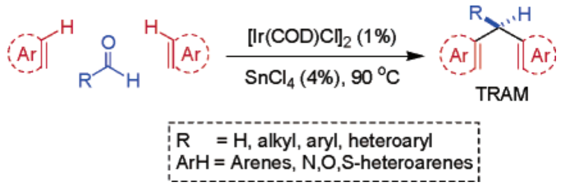
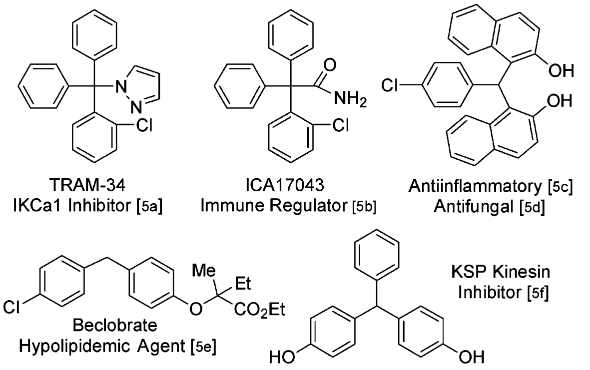


Reactions of arenes and heteroarenes with aromatic aldehydes proceeded smoothly in the presence of a catalytic combination of $[Ir(COD)Cl]_2-SnCl_4$ to afford the corresponding triarylmethane derivatives (TRAMs) in high yields. This 100% TRAM selective transformation is clean and eliminates the use of acid systems.

Even after 125 years since its discovery, Friedel−Crafts alkylation (FCA) remains a fundamental tool for the construction of various organic architectures of pharmaceutical and industrial relevance.[1] Within the FCA domain, there has been multiprong development in the area of alkylation of arenes and heteroarenes. Tuning a FCA catalyst to deliver high turnover frequency (TOF), substrate and alkylating agent selectivity, and envirotolerability continues to be an important exercise. Toward this pursuit, the evolution/resurgence of d- and f-block metal catalysts (either simple salts or designer complexes) is quite breathtaking.[2] Our continuing success in developing an efficient bimetallic pathway for carbon−carbon bond formation[3] led us to recently propose a dual-reagent catalyst system comprised of Ir(I) and Sn(IV) for the FCA of arenes using alcohols.[4] Herein we demonstrate the further utility of the reagent combination for the bisarylation of aldehydes leading to highly selective formation of triarylmethanes (TRAMs).

CHART 1. **Representative Bioactive TRAMs and Analogues**



Motifs bearing triarylmethane (TRAM) and their heterocyclic variants constitute an integral part of a number of bioactive compounds, prodrugs, pharmaceuticals, and dyes (Chart 1).[5] They are also well exploited as building blocks for dendrimers, and NLOs.[6] Routes to TRAMs, via Lewis acid (LA) catalyzed alkylation of arenes with aldehyde as alkylating agent, are often restricted by the formation of a multitude of products, a high (even stoichiometric) amount of catalyst loading, and at times drastic reaction conditions.[7] While LA-catalyzed reductive alkylations of arenes with aldehydes do not suffer from the said process limitations, they afford exclusively the corresponding diarylmethanes.[8] Two most recent reports on TRAM-selective transformations using catalytic $BF_3{:}H_2O$ or $AuCl_3/3AgOTf$ are

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[1] (a) Olah, G. A. *Friedel Crafts and Related Reactions*; Wiley-Interscience: New York, 1964; Vol. II, Part I. (b) Olah, G. A. *A Life of Magic Chemistry. Autobiographical reflections of a Nobel Prize winner*; Wiley-Interscience: New York, 2001. (c) Roberts, R. M.; Khalaf, A. A. *Friedel-Crafts Alkylation Chemistry. A Century of Discovery*; Marcel Dekker: New York, 1984.

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[3] (a) Sinha, P.; Roy, S. *Organometallics* **2004**, *23*, 67. (b) Banerjee, M.; Roy, S. *Org. Lett.* **2004**, *6*, 2137. (c) Banerjee, M.; Roy, S. *J. Mol. Catal. A*: *Chem.* **2006**, *246*, 231.

[4] Choudhury, J.; Podder, S.; Roy, S. *J. Am. Chem. Soc.* **2005**, *127*, 6162.

[5] (a) Wulff, H.; Miller, M. J.; Hänsel, W.; Grissmer, S.; Cahalan, M. D.; Chandy, K. G. *Proc. Natl. Acad. Sci. U.S.A.* **2000**, *97*, 8151. (b) McNaughton-Smith, G. A.; Rigdon G. C.; Stocker, J. W. Icagen, Inc., U.S.A., PCT Int. Appl. WO-2000050026, 2000 [CAN *133*, 187954]. (c) Lacroix, R.; Poupelin, J. P.; Lacroix, J.; Reynouard, F.; Combescot, C. *Ann. Pharm. Fr.* **1979**, *37*, 131. (d) Poupelin, J. P.; Saint-Ruf, G.; Foussard-Blanpin, O.; Narcisse, G.; Uchida-Ernouf, G.; Lacroix, R. *Eur. J. Med. Chem.* **1978**, *13*, 67. (e) Manzoni, C.; Lovati, M. R.; Bonelli, A.; Galli, G.; Sirtori, C. R. *Eur. J. Pharmacol.* **1990**, *190*, 39. (f) Finer, J. T.; Chabala J. C.; Lewis, E. Cytokinetics, Inc., U.S.A., PCT Int. Appl. WO-2002056880, 2005, [CAN *137*, 124985]. (g) Mibu, N.; Yokomizo, K.; Uyeda, M.; Sumoto, K. *Chem. Pharm. Bull.* **2003**, *51*, 1325. (h) Oclarit, J. M.; Ohta, S.; Kamimura, K.; Yamaoka, Y.; Shimizu, T.; Ikegami, S. *Nat. Prod. Lett.* **1994**, *4*, 309.

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[7] Selected references: (a) Roberts, R. M.; EI-Khawaga, A. M.; Sweeney K. M.; EI-Zohry, M. F. *J. Org. Soc.* **1987**, *52*, 1591 and references cited therein. (b) Mibu, N.; Yokomizo, K.; Uyeda, M.; Sumoto, K. *Chem. Pharm. Bull.* **2003**, *51*, 1325.

[8] (a) Hashimoto, Y.; Hirata, K.; Kagoshima, H.; Kihara, N.; Hasegawa, M.; Saigo, K. *Tetrahedron* **1993**, *49*, 5969. (b) Tsuchimoto, T.; Tobita, K.; Hiyama, T.; Fukuzawa, S-I. *J. Org. Soc.* **1997**, *62*, 6997. (c) Miyai, T.; Oniishi, Y.; Baba, A. *Tetrahedron* **1999**, *55*, 1017.

10.1021/jo062633n CCC: $37.00

SCHEME 1. Synthesis of TRAM 3: Model Studies with Aldehyde 1 and Arene 2

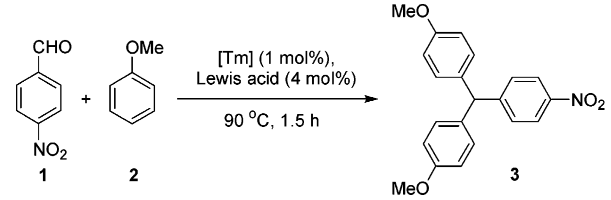


TABLE 1. Bisarylation of 4-Nitrobenzaldehyde with Anisole in the Presence of Catalytic Tm−Sn Combination[a]

entry	Tm partner	yield of **3** (%)
1	Nil	11
2[b]	$[Ir(COD)Cl]_2$	77
3[c]	$[Ir(COD)Cl]_2$	<1
4	$IrCl_3$	12
5	$IrCl(CO)(PPh_3)_2$	25
6	$RhCl(CO)(PPh_3)_2$	34
7	$RhCl(PPh_3)_3$	10
8	$[Rh(COD)Cl]_2$	17
9	$CoCl(PPh_3)_3$	9
10	$NiCl_2(PPh_3)_2$	10
11	$PdCl_2(PPh_3)_2$	10
12	$PtCl_2(PPh_3)_2$	12

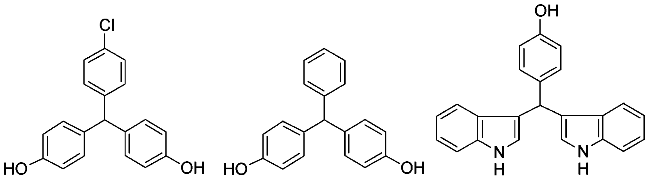
[a] Reaction conditions: aldehyde (1 mmol), anisole (3 mmol), Tm complex (0.01 mmol, 1%), $SnCl_4$ (0.04 mmol, 4%), 90 °C, 1.5 h. [b] Additionally 12% of another isomer (4-nitrophenyl)(2-methoxyphenyl)(4-methoxyphenyl)methane **3′** was obtained. [c] Without $SnCl_4$.

TABLE 2. Bisarylation of 4-Nitrobenzaldehyde with Anisole in the Presence of Catalytic Ir−LA Combination[a]

entry	Lewis acid partner	yield of **3** (%)[b]
1	$AlCl_3$	5(5)
2	$InCl_3$	4(4)
3	$TiCl_4$	11(11)
4	$BF_3.Et_2O$	3(3)
5	$CdCl_2$	0
6	$Sc(OTf)_3$	2(2)
7	$SnCl_2$	13(13)
8	$ZnCl_2$	<1(<1)

[a] Reaction conditions: aldehyde (1 mmol), anisole (3 mmol), $[Ir(COD)Cl]_2$ (0.01 mmol, 1%), Lewis acid (0.04 mmol, 4%), 90 °C, 1.5 h. [b] Yields in parentheses are in the absence of $[Ir(COD)Cl]_2$

CHART 2. Synthesis of Bioactive TRAMs [24−26] with Catalytic Ir−Sn Combination



24, 65% Antiviral [5g]

25, 56% KSP Kinesin Inhibitor [5f]

26, 82% Antimicrobial [5h]

noteworthy.[9] However, in our hand, the latter failed in a model reaction (see discussion later).

For model studies we had chosen the bisarylation of 4-nitrobenzaldehyde (**1**) with anisole (**2**) for the synthesis of the desired TRAM (4-nitrophenyl)bis(4-methoxyphenyl)methane (**3**) (Scheme 1). Initial catalyst screening included a combination of a low-valent late transition metal organometallic complex (1 mol %) with $SnCl_4$ (4 mol %). Among these, Ir^I and Rh^I were promising Tm partners to $SnCl_4$ (Table 1, entries 2, 5, and 6). Unsurpassed catalytic efficiency was observed in the case of $[Ir(COD)Cl]_2$ as the partner, which afforded **3** in 77% yield after 1.5 h (entry 2). Most gratifyingly, the reaction is highly selective toward triarylmethane, and no diarylmethane or other realkylation products were formed. Note that individually either $[Ir(COD)Cl]_2$ or $SnCl_4$ was poorly active, and even a simple combination of $IrCl_3$ and $SnCl_4$ was also ineffective (entries 1, 3, and 4). The above results prompted us to test whether LAs, other than $SnCl_4$, can be used as a partner to iridium. The model reaction was, therefore, executed with a dual combination of $[Ir(COD)Cl]_2$ (1 mol %) and a Lewis acid (4 mol %) representing each of the four groups in Olah's seminal paper.[10] Surprisingly, all of the LAs inclusive of $AlCl_3$, $InCl_3$, $TiCl_4$, $BF_3.Et_2O$, $CdCl_2$, $Sc(OTf)_3$, $SnCl_2$, and $ZnCl_2$ were ineffective (Table 2). Finally, the model reaction was tested with reported $AuCl_3$ (1 mol %), as well as a combination of $AuCl_3$ (1 mol %) and AgOTf (3 mol %) catalysts, but in both cases there was no conversion, and starting materials were isolated back satisfactorily.

With the reliable bimetallic combination of catalytic $[Ir(COD)Cl]_2/SnCl_4$, we next explored the bisarylation of aldehyde **1** with various arenes and heteroarenes for the synthesis of corresponding TRAMs. The results represented in Table 3 show that all the reactions gave selective formation of triarylmethane derivatives. Electron-rich arenes and heteroarenes such as anisole, 1,2-dimethoxybenzene, 1,3,5-trimethoxybenzene, 1-methoxynaphthalene, thiophenol, 2,5-dimethylfuran, thiophene, and 4-methylphenol gave the corresponding TRAMs in moderate to good yields (entries 1−4 and 6−9). The reaction of 1,4-dimethoxybenzene was comparatively slower and workup after 12 h led to the isolation of desired product **7** in 37% yield along with ~52% of unreacted aldehyde (entry 5). Reaction of phenol afforded the corresponding TRAMs **13** and **13′** in 56% and 35% yields, respectively (entry 11). Incorporation of electrowithdrawing substituent as in 4-chlorophenol caused lowering in the yield of TRAM (entry 10).

Henceforth we have tested the generality of the present reaction with anisole varying the aldehyde partner (Table 4). Reactions were facile with aromatic or heteroaromatic aldehydes having an electron-withdrawing substituent on the aromatic ring (entries 1−5 and 8). For terephthaldehyde having two aldehyde moieties in the same substrate, anisole was used in excess (10 equiv with respect to aldehyde) and the desired product **15** was obtained in 71% yield (entry 2). Noteworthy is the fact that the reaction can tolerate other carbonyl groups such as keto, ester, and carboxylic acid in the alkylating agent, which is indicative of aldehyde selectivity (entries 3−5), and the corresponding TRAMs **16**−**18** were obtained in excellent yields. Facile reaction of 5-nitrofurfural afforded TRAM **21** in 88% yield (entry 8). In contrast to the above results, reactions of benzaldehyde and 4-methylbenzaldehyde led to a decrease in product yield (entries 6 and 7), possibly due to the decrease in electrophilicity at the aldehydic carbon atom. In our hand, 4-methoxybenzaldehyde

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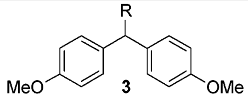
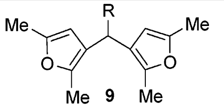
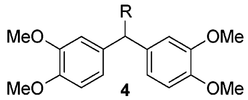
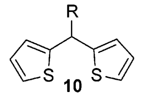
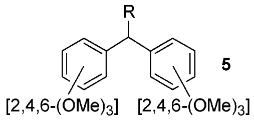
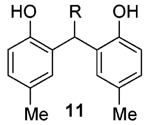
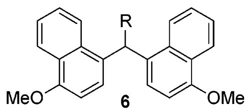
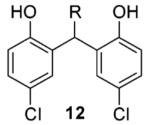
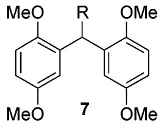
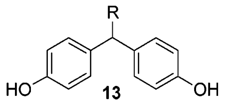
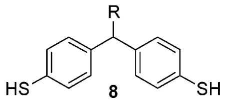
(9) (a) BF_3:H_2O as catalyst: Prakash, G. K. S.; Paknia, F.; Mathew T.; Olah, G. A. *Abstracts of Papers*; 230th National Meeting of the American Chemical Society, Washington, DC, Aug 28−Sept 1, 2005; American Chemical Society: Washington, DC, 2005. (b) Prakash, G. K. S.; Shah, E; Panja, C.; Mathew, T.; Shakhmin, A.; Olah, G. A. *Abstracts of Papers*; 232nd National Meeting of the American Chemical Society, San Francisco, CA, Sept. 10−14, 2006; American Chemical Society: Washington, DC, 2006. (c) $AuCl_3$/3AgOTf as catalyst: Nair, V.; Abhilash, K. G.; Vidya, N. *Org. Lett.* **2005**, *7*, 5857.

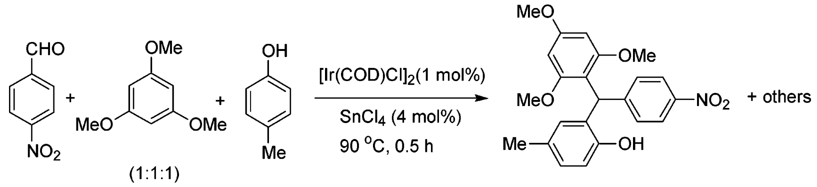
(10) Olah, G. A.; Kobayashi, S.; Tashiro, M. *J. Am. Chem. Soc.* **1972**, *94*, 7443.

TABLE 3. Bisarylation of 4-Nitrobenzaldehyde (RCHO) with Various Arenes (Ar−H) Leading to Product TRAM ($RCHAr_2$)[a]

#	Arene	product	t (h)	yield (%)	#	Arene	product	t (h)	yield (%)
1[b]	Anisole	 3	1.5	77	7	2,5-Me_2-furan	 9	1	77
2	1,2-$(MeO)_2$-benzene	 4	1.5	86	8	Thiophene	 10	3	63
3	1,3,5-$(MeO)_3$ benzene	 5	1	99	9	4-Me-phenol	 11	1	81
4	1-MeO-naphthalene	 6	1	87	10	4-Cl-phenol	 12	12	51
5	1,4-$(MeO)_2$-benzene	 7	12	37	11[c]	Phenol	 13	1	56
6	Thiophenol	 8	1	74					

[a] Reaction conditions: aldehyde **1** (1 mmol), arene (3 mmol), $[Ir(COD)Cl]_2$ (0.01 mmol), $SnCl_4$ (0.04 mmol), 90 °C. [b] Plus 12% of (4-nitrophenyl)(2-methoxy phenyl)(4-methoxyphenyl)methane **3′**. [c] Plus 35% of (4-nitrophenyl)(2-hydroxyphenyl)(4-hydroxyphenyl)methane **13′**.

SCHEME 2. Control Experiments on the Intermediacy of Secondary Alcohol



28 (37%)

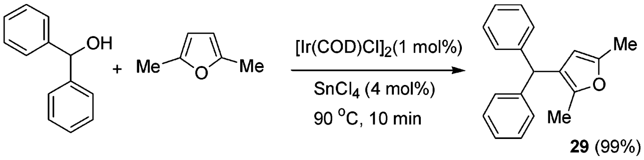
failed to give the desired TRAM. While the reactions of aromatic and heteroaromatic aldehydes having electron-withdrawing substituent on the aromatic ring are generally facile, those of aliphatic aldehydes are comparatively low yielding. For example, with *p*-formaldehyde a mixture of regioisomer was obtained in 66% overall yield (entry 9). Due to its low boiling point, the reaction of propanal was performed at 50 °C and the desired product **23** was isolated in 30% yield (entry 10).

While further scope and limitation of the bisarylation of aldehyde using the bimetallic Ir−Sn catalyst combination is under study, Chart 2 shows the synthesis of three bioactive TRAMs **24**−**26** varying the aldehyde and arene motifs. In each case, exclusive TRAM selectivity was noticed and no byproduct was formed.

Even though we are far away from realizing the exact mechanism for the present dual-reagent catalysis, the following experimental results may be noted.

(1) Reaction of $[IrCl(COD)]_2$ in dichloromethane with $SnCl_4$ in benzene under ambient condition led to the isolation of a

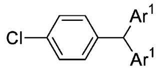
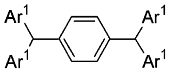
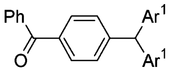
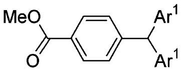
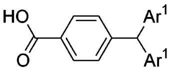
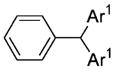
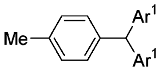
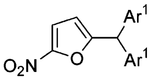
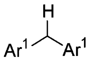
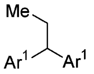
SCHEME 3. Reaction of Secondary Alcohol with Heteroarene



29 (99%)

heterobimetallic complex $[Ir_2(COD)_2(SnCl_3)_2(Cl)_2(\mu\text{-}Cl)_2]$ (**27**) having $Ir^{III}-Sn^{IV}$ motif.[4] With **27** as catalyst (1 mol %), the model reaction of 4-nitrobenzaldehyde (**1**) with anisole (**2**) at 90 °C afforded the desired TRAM (4-nitrophenyl)bis(4-methoxy-phenyl)methane (**3**) in 40% yield after 1.5 h, indicating a distinct heterobimetallic reactivity. Several attempts were made to isolate the active catalyst, which is equal in turn-over frequency to that of the combination of $[Ir(COD)Cl]_2/4SnCl_4$ in the TRAM forming reaction. This endeavor remained unsuccessful until now.

TABLE 4. Bisarylation of Different Aldehydes (R^1CHO) with Anisole (Ar^1−H) Leading to Product TRAM ($R^1CHAr^1_2$)[a]

#	aldehyde	product	t (h)	yield (%)
1	4-Cl-benzaldehyde	 **14**	1.5	84
2[b]	4-CHO-benzaldehyde	 **15**	1	71
3	4-COPh-benzaldehyde	 **16**	1	72
4	4-CO_2Me-benzaldehyde	 **17**	3	94
5	4-CO_2H-benzaldehyde	 **18**	5	81
6	benzaldehyde	 **19**	6	51
7	4-Me-benzaldehyde	 **20**	12	41
8	5-NO_2-furfural	 **21**	0.5	88
9[c]	*para*-formaldehyde	 **22**	1	37
10[d]	propanal	 **23**	24	30

[a] Reaction conditions: anisole (3 mmol), aldehyde (1 mmol), $[Ir(COD)Cl]_2$ (0.01 mmol), $SnCl_4$ (0.04 mmol), 90 °C. [b] Aldehyde:arene 1:10. [c] Plus 29% of (2-methoxyphenyl)(4-methoxyphenyl)methane **22′**. [d] At 50 °C.

(2) The reaction of 4-nitrobenzaldehyde (1 mmol) with a mixture of two arenes, namely 1,3,5-trimethoxybenzene (1 mmol) and 4-methylphenol (1 mmol), in the presence of catalytic Ir−Sn afforded the cross-coupled TRAM product **28** in 37% yield besides self-coupled products (Scheme 2). TRAM **28** can only arise via the possible intermediacy of secondary alcohol as an intermediate. Indeed under the mediation of Ir−Sn as catalyst, diphenylcarbinol reacted spontaneously with 2,5-dimethylfuran affording the corresponding TRAM product **29** in very high yield (99%) in just 10 min (Scheme 3).

(3) While studies are underway in our laboratory to understand the detailed mechanism, an electrophilic aromatic substitution pathway is indicated by the formation of regioisomers in a few cases (Table 3, entries 1 and 11, and Table 4, entry 9). One may also note that in a number of cases bisarylation was 100% regioselective giving rise to a single product.

(4) Plausible complexation/interaction of the carbonyl functionality at the tin center is indicated by preliminary in situ FT−IR and ^{13}C NMR experiments.[11]

In summary, we have developed a facile protocol using a dual reagent catalysis concept for the bisarylation of aldehydes that is 100% TRAM selective. While the exact nature of the active catalyst from the dual combination of $[Ir(COD)Cl]_2$/$4SnCl_4$ remains to be established, control experiments suggested the plausible involvement of a heterobimetallic Ir−Sn core in the present catalysis.

Experimental Section

Bisarylation of 4-Nitrobenzaldehyde with Anisole. A 10-mL Schlenk flask equipped with a magnetic bar was charged with $[Ir(COD)Cl]_2$ (0.01 mmol), $SnCl_4$ (0.04 mmol), and anisole (3 mmol). The flask was degassed with argon and placed into a constant temperature bath at 90 °C. After the mixture was stirred vigorously for 5 min, 4-nitrobenzaldehyde (1 mmol) was added to it, and the reaction was allowed to continue at 90 °C (TLC monitoring; petroleum ether 60−80 °C/ethylacetate (9:1)). After completion of the reaction, the mixture was quenched with aqueous NH_4F solution and extracted with diethyl ether. The combined extract was washed with water and brine and dried over $MgSO_4$, and the solvent was removed under reduced pressure. Purification by silica gel column chromatography (60/120 mesh, petroleum ether 60−80 °C/ethylacetate (97:3)) afforded triarylmethane **3** (269 mg, 77%, R_f 0.30 petroleum ether 60−80 °C/EtOAc (9:1)), along with another regioisomer **3′** (42 mg, 12%, R_f 0.37 petroleum ether 60−80 °C/EtOAc (9:1)).

Spectral data for **3**: ^1H NMR (200 MHz, $CDCl_3$, 25 °C) δ 3.79 (s, 6H; 2 OCH_3), 5.53 (s, 1H; C*H*), 6.84 (d, $^3J(H,H) = 8.7$ Hz, 4H; C*H* aromatic), 6.99 (d, $^3J(H,H) = 8.7$ Hz, 4H; C*H* aromatic), 7.26 (d, $^3J(H,H) = 8.6$ Hz, 2H; C*H* aromatic), 8.13 (d, $^3J(H,H) = 8.6$ Hz, 2H; C*H* aromatic); ^{13}C NMR (54.6 MHz, $CDCl_3$, 25 °C) δ 54.9, 55.2, 113.9, 123.4, 130.0, 130.1, 134.7, 146.3, 152.3, 158.3; HRMS calcd for $C_{21}H_{19}NO_4 + H^+$ 350.1392, found 350.1384. Anal. ($C_{21}H_{19}NO_4$) Calcd: C, 72.18; H, 5.48; N, 4.01. Found: C, 72.29; H, 5.50; N, 4.03.

Spectral data for isomer **3′**: ^1H NMR (200 MHz, $CDCl_3$, 25 °C) δ 3.71 (3H, s, OCH_3), 3.79 (3H, s, OCH_3), 5.91 (1H, s, C*H*), 6.77−7.00 (8H, m, C*H* aromatic), 7.23 (2H, d, $J = 8.8$ Hz, C*H* aromatic), 8.11 (2H, d, $J = 8.8$ Hz, C*H* aromatic); ^{13}C NMR (54.6 MHz, $CDCl_3$, 25 °C) δ 48.9, 55.1, 55.4, 110.7, 113.8, 120.4, 123.3, 128.1, 129.8, 129.9, 130.3, 131.3, 134.1, 146.3, 152.3, 156.8, 158.2. HRMS: calcd for $C_{21}H_{19}NO_4 + H^+$ 350.1392, found 350.1375.Anal. ($C_{21}H_{19}NO_4$) Calcd: C, 72.18; H, 5.48; N, 4.01. Found: C, 72.31, H, 5.60, N, 4.09.

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Supporting Information Available: Additional experimental details and spectral and analytical data for all products. This material is available free of charge via the Internet at http://pubs.acs.org.

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[11] For 4-methylbenzaldehyde, the shifts in the carbonyl frequency ($\Delta\nu$, cm^{-1}) after the addition of $SnCl_4$, complex **27**, and $[Ir(COD)Cl]_2$/$4SnCl_4$ are 111, 102, and 110, respectively. The corresponding shifts in ^{13}C NMR signal of −CHO ($\Delta\delta$, ppm) are 6.62, 0.52, and 0.79, respectively. Similar behavior was also observed (in FT-IR) with Tm-$SnCl_4$ combinations where $Ir(CO)Cl(PPh_3)_2$ and $Rh(CO)Cl(PPh_3)_2$ are the Tm partners. See the Supporting Information.