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Rhodium-Catalyzed Synthesis of Imines and Esters from Benzyl Alcohols and Nitroarenes: Change in Catalyst Reactivity Depending on the Presence or Absence of the Phosphine Ligand

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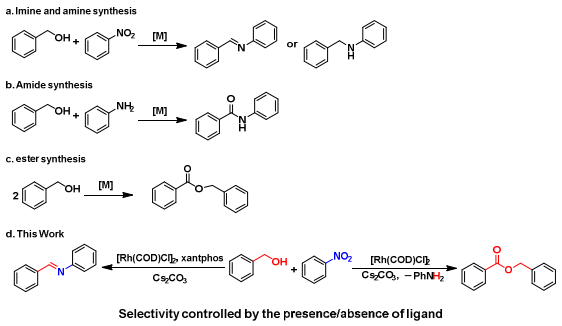
ABSTRACT: $[Rh(COD)Cl]_2$/xantphos/Cs_2CO_3 efficiently catalyzes the reductive N-alkylation of aryl nitro compounds with alcohols by a borrowing-hydrogen strategy to afford the corresponding imine products in good to excellent yield. In the absence of xantphos, the $[Rh(COD)Cl]_2$/Cs_2CO_3 catalytic system behaves as an effective catalyst for the dehydrogenative coupling of alcohols to esters, with nitrobenzene as hydrogen-acceptor. The reactivity of the rhodium catalytic system can be easily manipulated to selectively afford the imine or ester.

Imines and esters are important industrial products that serve as useful intermediates for the introduction of other functional groups.[1] Therefore, methods for their synthesis and conversion are of prime importance in the fine and bulk chemical industry.[2] Despite well-established methodologies, the development of mild procedures for the synthesis of imines and esters continues to attract considerable interest.

Catalytic alcohol dehydrogenation (CAD) has been well-developed as a convenient, atom-economical approach for alcohol oxidation without the need of an oxidant.[3] Subsequently, reactive carbonyl compounds generated from CAD can be transformed into other useful organic materials including imines, amide, and esters (Scheme 1). For example, dehydrogenation of primary alcohols affords aldehydes and a sequential condensation with amines leads to the formation of a hemiaminal intermediate. Imine is formed by liberating water from the hemiaminal intermediate (Scheme 1a),[4] whereas amide is produced by elimination of hydrogen from the same intermediate (Scheme 1b).[5] An ester is produced via dehydrogenation of the intermediate hemiacetal, formed when the primary dehydrogenation aldehyde product reacts with excess alcohol (Scheme 1c).[6] It is challenging that development of a catalytic system can control the selectivity between two different reactions by a simple modification of a catalytic system. Recently, a catalytic system that can control the selectivity between imine and amide formation by a modification of a catalytic system has been reported by Huynh and Mashima groups.[7] However, as far as we are aware, there have been no reports on the switch of the reaction between imination and esterification by a simple modification of a catalytic system (Scheme 1d).

Recently, we reported[8] a rhodium/DPEphos-catalyzed carbonylative [2+2+1] cycloaddition of alkynes, using alcohol as a source of carbon monoxide, for the formation of cyclopentenones. In this rhodium-catalyzed reaction, the alcohol is initially oxidized to the corresponding carbonyl compound, accompanied with the generation of a metal-hydride intermediate. A metal-hydride has been proposed as an intermediate in the transition metal-catalyzed N-alkylation of amines with alcohols by the borrowing-hydrogen strategy.[9] Thus, our focus to use the metal-hydride intermediate in other reactions led to the study of reductive N-alkylation of nitroarenes with alcohols to form imines via a borrowing-hydrogen strategy. While studying the Rh-catalyzed N-alkylation of nitroarenes with alcohols, we discovered that an imine was afforded as the major product, accompanied by an ester as a byproduct. Our concern to the generation of the ester revealed that the presence of a phosphine compound was critical to the yield of the imine, while the ester was isolated in high yield in its absence. Thus, a switch of the reaction pathways of the oxidative coupling of alcohols and amines, from imination to esterification, was exposed for the first time. Herein, we report our results.

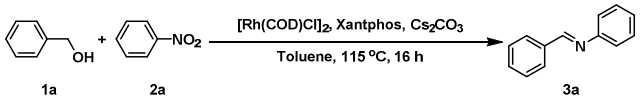
Scheme 1. Dehydrogenative coupling reaction of alcohols and nitroarenes (or amines)



The Rh-catalyzed synthesis of N-(phenylmethylene)benzeneamine was discovered from the reaction of benzyl alcohol and nitrobenzene in the

presence of Cs_2CO_3, 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (xantphos) and $[Rh(COD)Cl]_2$ in toluene at 115 °C for 16 h. We screened various reaction conditions (Table 1 and SI). Ligand exchange from xantphos to DPEphos and other bidentate phosphines was ineffective (Table 1, entry 2 and SI). Thus, we supposed that the ligand plays a crucial role in stabilizing the rhodium hydride intermediate or the hydride transfer transition state. Other bases and solvents were also screened (see the SI). The best yield (93%) was observed when 8 mol% catalyst was used at 115 °C. As expected, no product was formed in the absence of the rhodium catalyst (Table 1, entry 3); however, a significant amount of product was isolated in the absence of Cs_2CO_3 and xantphos (Table 1, entries 4 and 5). When aniline was used instead of nitrobenzene, a slightly lower yield (81%) was observed (Table 1, entry 6). Interestingly, the use of benzaldehyde instead of benzyl alcohol also afforded the corresponding imine in low yield (33%; Table 1, entry 7).Thus, the optimum conditions were established from these results as follows: 0.3 mmol nitrobenzene, 5 equivalents benzyl alcohol, 8 mol% $[Rh(COD)Cl]_2$, 16 mol% xantphos, 20 mol% Cs_2CO_3, and 1.5 mL toluene at 115 °C for 16 h.

Table 1. Screening the reaction conditions for imine[a]

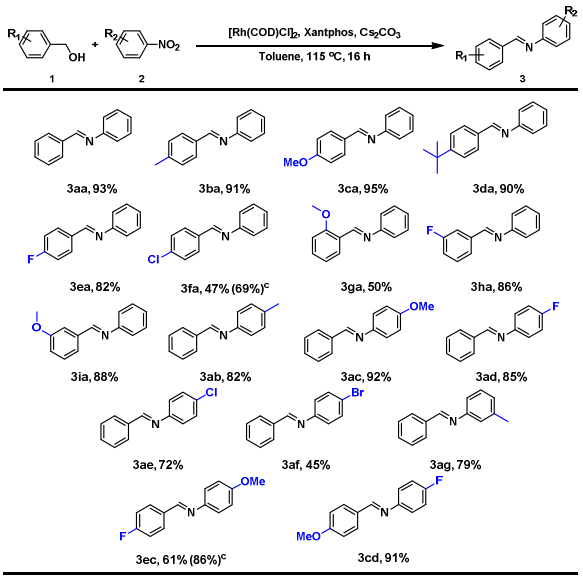


entry	variation from standard conditions	yield[b] (%)
1	None	93
2	DPEphos instead of xantphos	trace
3	Without $[Rh(COD)Cl]_2$	N.R.
4	Without Cs_2CO_3	31
5	Without xantphos	29
6	Aniline instead of nitrobenzene	81
7	Benzaldehyde instead of benzyl alcohol	33

[a]Reaction conditions: 0.3 mmol of **2a**, 5 equiv of **1a**, 8 mol % of $[Rh(COD)Cl]_2$, 16 mol % of xantphos, 20 mol % of Cs_2CO_3, and 1.5 mL of toluene. [b]Yield determined by NMR analysis of crude reaction mixture using benzyl formate as an internal standard. N.R. = No reaction

With the optimum reaction conditions established, the substrate scope was next studied (Scheme 2). First, the scope of benzyl alcohol derivatives was screened (Scheme 2, entries **3aa**–**3ia**). The desired products were generally afforded in good to excellent yield. Electron-rich and -neutral benzyl alcohols reacted smoothly to produce the corresponding imines in high yield (Scheme 2, entries **3aa**–**3da**; ≤95%). On the other hand, benzyl alcohols with electron-withdrawing fluoro- or chloro-groups at the para-position afforded the corresponding imine products in moderate to high yield [Scheme 2, entries **3ea** and **3fa**; **3ea** (82%) and **3fa** (47%)]. However, lengthening the reaction time to 24 h led to increase the yield from 47% to 69%. Although 4-tert-butylbenzyl alcohol was expected to exhibit a steric effect, it still afforded the imine product in high yield (Scheme 2, entry **3da**; 90%). Meta-substituted benzyl alcohols reacted smoothly to produce the corresponding imines in high yields (**3ha**, 86%; **3ia**, 88%). Conversely, the ortho-substituted group in benzyl alcohols significantly hampered the N-alkylation reaction (Scheme 2, entry **3ga**; 50%). Following benzyl alcohol screening, the scope of the nitroarene substrates was investigated (Scheme 2, entries **3ab**–**3ag**). The reaction could be carried out smoothly, regardless of the electron-withdrawing or -donating group on the aromatic ring. However, relatively lower yields (Scheme 2, entry **3ae**, 72%; entry **3af**, 45%) were observed for 1-chloro-4-nitrobenzene and 1-bromo-4-nitrobenzene. Lengthening the reaction time did not affect the yield of **3af**. However, the yield of **3ec** was highly sensitive to the reaction time (61% for 16 h and 86% for 24 h, respectively). 3-Methylnitrobenzene was also a good substrate (**3ag**, 79%). However, neither alkyl alcohol nor nitroalkyl was a good substrate.

Scheme 2. Scope with various nitroarenes and alcohols[a,b]



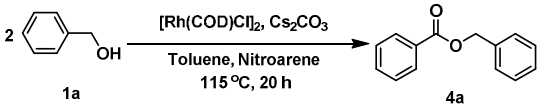
[a]Reaction conditions: 0.3 mmol of **2**, 5 equiv of **1**, 8 mol % of $[Rh(COD)Cl]_2$, 16 mol % of xantphos, 20 mol % of Cs_2CO_3, and 1.5 mL of toluene. [b]Yield determined by NMR analysis of crude reaction mixture using benzyl formate as an internal standard. [c]24 h.

Having identified $[Rh(COD)Cl]_2$ as a suitable catalyst for the imination of nitroarenes and benzyl alcohols, we further explored other possibilities by varying the conditions for the selective formation of esters from nitroarenes and benzyl alcohols using the same catalyst precursor. The addition of oxidants favors ester formation in many catalyzed reactions.[10] Therefore, our experiments were carried out in the presence of an oxidant/ligand combination (see the SI); however, no reaction was observed. Interestingly, the Rh-catalyzed synthesis of benzyl benzoate was discovered from the reaction of benzyl alcohol and nitrobenzene under the reaction conditions for

imine formation, but without xantphos (Cs_2CO_3 and $[Rh(COD)Cl]_2$ in toluene at 115 °C for 20 h; 69% yield). In the reaction, nitroarene acted as a hydrogen-acceptor.[11]

We next screened various reaction conditions (Table 2 and SI). In the presence of xantphos, only 12% ester product was formed. Conversely, a good yield (69%) was observed in the absence of xantphos (Table 2, entry 5). Other nitroarenes were also screened. Thus, we opted for 1-fluoro-2-nitrobenzene as the hydrogen-acceptor (Table 2, entry 1 and SI). Moreover, other bases and solvents were also examined, whereby the yield was highly sensitive to the base (see the SI). As expected, no product was formed in the absence of the rhodium catalyst or Cs_2CO_3 (Table 2, entries 2 and 3). Thus, we concluded that the presence of rhodium and a base was critical for a successful reaction. However, 16% ester product formed in the absence of a nitroarene (Table 2, entry 4). From these results, the optimum conditions were established as follows: 0.6 mmol benzyl alcohol, 0.3 equivalent 1-fluoro-2-nitrobenzene, 5 mol% $[Rh(COD)Cl]_2$, 20 mol% Cs_2CO_3, and 2.0 mL toluene at 115 °C for 20 h. Some ruthenium-catalyzed reactions were carried out at higher temperatures, namely, 147 °C for $Ru_3(CO)_{12}$ and 180 °C for $RuH_2(PPh_3)_4$.[12,13]

Table 2. Screening the reaction conditions for ester[a]



1a 4a

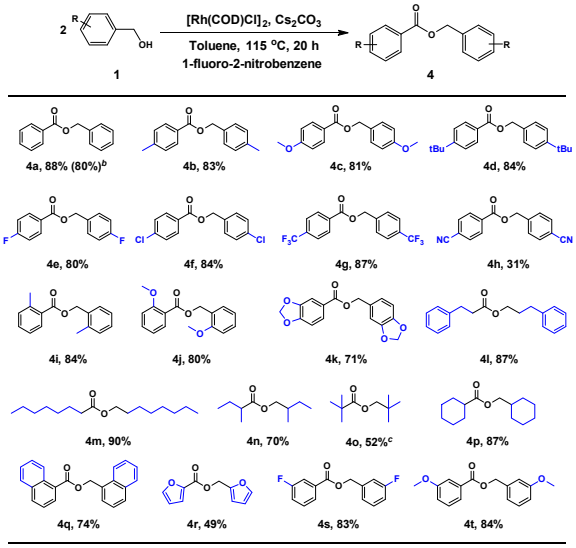
entry	variation from standard conditions	yield[d] (%)
1	Using 1-fluro-2-nitrobenzene	88
2	Without $[Rh(COD)Cl]_2$	N.R.
3	Without Cs_2CO_3	N.R.
4	Without nitroarene	16
5[b]	Using nitrobenzene	69
6[b,c]	Presence of xantphos	12

[a]Reaction conditions: 0.6 mmol of **1a**, 0.3 equiv of nitroarene, 5 mol % of $[Rh(COD)Cl]_2$, 20 mol % of Cs_2CO_3, and 2 mL of toluene. [b]Reaction conditions: 0.3 mmol of **2a**, 5 equiv of **1a**, 8 mol % of $[Rh(COD)Cl]_2$, 20 mol % of Cs_2CO_3, and 1.5 mL of toluene. [c]16mol % of xantphos. [d]Yield determined by NMR analysis of crude reaction mixture using benzyl formate as an internal standard. N.R.: No reaction.

Using the optimized conditions, we next investigated the substrate scope for the selective esterification of alcohols. The results are summarized in Scheme 3. Various primary alcohols were converted to the corresponding esters in fair to good yield. Benzyl alcohols were converted to the corresponding benzyl benzoates in good yield (Scheme 3, entries **4a**–**4g**, **4i**–**4j**), except for 4-(hydroxymethyl)benzonitrile (Scheme 3, entry **4h**; 31%). The esterification of 4-(hydroxymethyl)benzonitrile has not been reported date,[14] while a slightly lower yield (71%) was observed for 1,3-benzodioxole-5-methanol (Scheme 3, entry **4k**).[15] The steric effect of the substituent on the aromatic ring in benzyl alcohols was not significant (Scheme 3, entries **4b** *vs* **4i**, entries **4c** *vs* **4j** *vs* **4t**, and entries **4e** *vs* **4s**). Aliphatic alcohols, such as 3-phenylpropan-1-ol, were also suitable substrates (Scheme 3, entry **4l**; 87%), while 1-octanol (higher alcohol) was converted to octyl octanoate in 90% yield (entry **4m**). The proposed catalytic system was also effective for branched aliphatic alcohols such as 2-methyl-1-butanol and neopentyl alcohol (Scheme 3, entries **4n** and **4o**, respectively), with 70% of the corresponding ester being isolated from the former alcohol. The highly sterically crowed neopentyl alcohol, known to be inert in the presence of some catalysts,[16] afforded the corresponding ester in 52% yield. To the best of our knowledge, this is the first report on the formation of neopentyl pivalate via a dehydrogenative coupling strategy of alcohols.[16] Other aliphatic alcohols, including steric hindrance alcohols, cyclohexylmethanol and 1-naphthalenemethanol, and an allylic alcohol, furfuryl alcohol, could be converted to the corresponding ester in reasonable to high yields (**4p**, 87%; **4q**, 74%; **4r**, 49%). When a gram scale reaction was performed, **4a** was isolated in 80% (0.79 g). Thus, it proves the practicality of the developed method.

To gain some insight into the possible reaction mechanism, the following reactions were studied (Scheme 4).

Scheme 3. Scope with various alcohols[a]

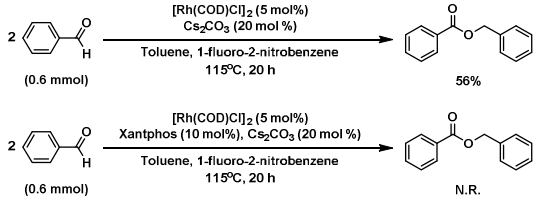


[a]Reaction conditions: 0.6 mmol of **1**, 0.3 equiv of 1-fluoro-2-nitrobenzene, 5 mol % of $[Rh(COD)Cl]_2$, 20 mol % of Cs_2CO_3, and 2 mL of toluene. [b]Gram scale experiment: 1.0 g of benzyl alcohol used. [c]Yield determined by NMR analysis of crude reaction mixture using benzyl formate as an internal standard.

When benzaldehyde was reacted with 1-fluoro-2-nitrobenzene under the reaction conditions employed for imine formation, no reaction was observed. However, treatment of benzaldehyde with/without 1-fluoro-2-nitrobenzene under the reaction conditions employed in ester formation afforded benzyl benzoate in 56% yield. Therefore, we supposed that a Tishchenko-type reaction occurs under our proposed reaction conditions.[17,18] The presence or absence of nitrobenzene did not impact the outcome of the reaction. Our preliminary DFT calcula-

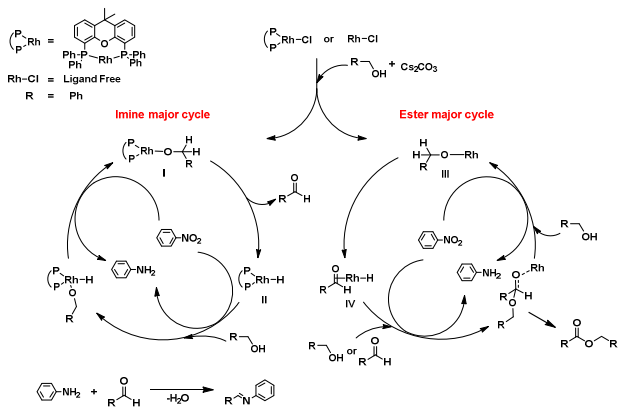
tions revealed that formation of Rh(H)(xantphos) and free aldehyde is energetically more favorable than (xantphos)Rh(H)(η²-benzaldehyde) or Rh(alkoxide)(xantphos) (see the SI). Due to the electronic effect of xantphos, a large portion of in situ generated benzaldehyde may be free. Thus, we postulated that the aldehyde liberated from the electron-rich rhodium-xantphos species condensed with aniline to form an imine, while the aldehyde coordinated to Rh(COD) reacted with another alcohol to produce an ester.

Scheme 4. Reactions of benzaldehyde in presence/absence xantphos



From the above and other reported[19] observations, we next proposed a possible mechanism (Scheme 5) based on the widely accepted mechanism for imine and ester formation:[20] treatment of the catalyst precursor $[Rh(COD)Cl]_2$ with xantphos affords Rh(xantphos)Cl species, which further react with alcohol in the presence of a base to form a rhodium(xantphos) alkoxide species. β-Hydride elimination of the rhodium(xantphos) alkoxide affords a rhodium hydride intermediate and an aldehyde. The rhodium hydride then reacts with nitrobenzene to form aniline. Subsequently, the condensation reaction of the liberated aldehyde with this amine produces the corresponding imine. In the absence of xantphos, we suppose that $[Rh(COD)Cl]_2$ reacts with the base and alcohol to afford a Rh(COD)(alkoxide) species. This forms a rhodium(COD)(hydrido)(η²-aldehyde) species, which reacts with nitrobenzene and another alcohol or aldehyde to produces esters and aniline. According to our calculation, the reaction of the rhodium(COD)(hydrido)(η²-aldehyde) with an alkoxide is more favorable than that with aniline (see SI). Thus, it leads to esters as a major product. However, the actual mechanism is probably much more complex and a more detailed study on the reaction mechanism is required.

Scheme 5. Proposed reaction mechanism



In conclusion, we have demonstrated the rhodium-catalyzed synthesis of imines and esters from benzyl alcohols and nitroarenes in the presence or absence of xantphos, respectively. This reaction can be easily manipulated to provide the imine or ester selectively and cleanly, in high yield. The catalytic system tolerates a wide range of benzyl alcohols and aniline substrates for imine formation and aliphatic alcohols, including benzyl alcohols for ester formation. A detailed study on the reaction mechanism is currently underway.

EXPERIMENTAL SECTION

All solvents were dried and distilled according to standard methods before use. Reagents were purchased from chemical companies and were used as received. Reactions were monitored by thin-layer chromatography on 0.25 mm E. Merck silica gel plates (60F-254). The TLC plates were visualized by UV-light (254 nm) and treated with acidic p-anisaldehyde and $KMnO_4$ stain followed by gentle heating. Workup procedures were done in air. Flash column chromatography was carried out on Merck 60 silica gel (230 – 400 mesh). ^1H and ^{13}C NMR spectra were recorded with Agilent 400-MR DD2 (400 MHz and 100 MHz, respectively) spectrometer. ^1H NMR spectra were taken in $CDCl_3$ and were referenced to residual TMS (7.26 ppm) and reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublet, m = multiplet). Proton-decoupled $^{13}C\{^1H\}$ NMR spectra were recorded at 100 MHz and the chemical shifts were measured relative to $CDCl_3$ (77.16 ppm). High-Resolution Mass Spectra were obtained at the Korea Basic Science Institute (Daegu, South Korea) on a Jeol JMS 700 high-resolution mass spectrometer. GC-MS analyses were performed with a HP-6890 series with a HP-5 capillary column (30 m x 0.25 mm; coating thickness 0.25 μm) and Agilent 5973 Network Mass Selective detector. Yields of imine products were determined by ^1H NMR analysis of crude reaction mixture using benzyl formate as an internal standard.

General procedure for the entries reported in Table 1: reactions of nitroarenes and alcohols. Reactions were performed in a Schlenk-type tube equipped with a stirring bar and capped with a rubber septum. The followings were placed in the tube in order: 5-10 mol% of $[Rh(COD)Cl]_2$, 10-20 mol% of ligand, 14-50 mol% of base, 3-10 equivalents of benzyl alcohol, 0.3 mmol (31 μl) of nitrobenzene, and 1.5 mL of toluene. The mixture was heated with stirring at 115 °C for 16 h. The yield of the products were determined by ^1H NMR analysis of crude reaction mixture using benzyl formate as an internal standard.

General procedure for the entries reported in Scheme 2: reactions of nitroarenes and alcohols. Reactions were performed in a Schlenk-type tube equipped with a stirring bar and capped with a rubber septum. The followings were placed in the tube in order: 11.8 mg (8 mol%) of $[Rh(COD)Cl]_2$, 27.8 mg of xantphos (16 mol%), 19.5 mg of Cs_2CO_3 (20 mol%), 5 equivalents of alcohol, 0.3 mmol of nitroarenes, and 1.5 mL of toluene. The mixture was stirred at 115 °C for 16 h. The reaction products were

identified by NMR analysis and the yield of the products were determined by ^{1}H NMR analysis of crude reaction mixture using benzyl formate as an internal standard.

General Procedure for the entries reported in Table 2: reactions of benzyl alcohols. Reactions were performed in a Schlenk-type tube equipped with a stirring bar and capped with a rubber septum. The followings were placed in the tube in order: 3-7 mol% of $[Rh(COD)Cl]_2$, 7-30 mol% of base, 0.6 mmol (62 µl) of benzyl alcohol, 30 mol% of nitroarene, and 2 mL of toluene. The reaction mixture was heated with stirring at 115 °C for 20 h. The reaction products were identified by NMR analysis and the yield of the products were determined by ^{1}H NMR analysis of crude reaction mixture using benzyl formate as an internal standard.

General Procedure for the entries reported in Scheme 3: reactions of alcohols. Reactions were performed in a Schlenk-type tube equipped with a stirring bar and capped with a rubber septum. The followings were placed in the tube in order: 14.8 mg (5 mol%) of $[Rh(COD)Cl]_2$, 39 mg of Cs_2CO_3 (20 mol%), 0.6 mmol of alcohol, 19 µl of 1-fluoro-2-nitrobenzene, and 2 mL of toluene. The reaction mixture was heated with stirring at 115 °C for 20 h. The reaction products were purified by flash chromatography on silica gel (n-hexane/ethyl acetate).

Physical and spectroscopic data, as well as literature for known compounds, are as follows:

(*E*)-N,1-diphenylmethanimine (3aa).[21] Yellow oil product (93% NMR yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1 H), 7.86 – 7.81 (m, 2 H), 7.43 – 7.39 (m, 3 H), 7.33 (t, J = 7.7 Hz, 2 H), 7.18 – 7.13 (m, 3 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.6, 152.2, 136.4, 131.5, 129.3, 128.9, 128.9, 126.1, 121.0.

(*E*)-N-phenyl-1-(p-tolyl)methanimine (3ba).[21] Yellow oil product (91% NMR yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1 H), 7.71 (d, J = 8.0 Hz, 2 H), 7.30 (t, J = 7.8 Hz, 2 H), 7.19 (d, J = 7.9 Hz, 2 H), 7.13 (m, 3 H), 2.33 (s, 3 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.5, 152.4, 142.0, 133.8, 129.6, 129.2, 128.9, 125.9, 121.0, 21.8.

(*E*)-1-(4-methoxyphenyl)-N-phenylmethanimine (3ca).[22] Yellow solid product (95% NMR yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1 H), 7.77 (d, J = 8.6 Hz, 2 H), 7.30 (t, J = 7.7 Hz, 2 H), 7.13 (t, J = 8.6 Hz, 3 H), 6.91 (d, J = 8.6 Hz, 2 H), 3.79 (s, 3 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.4, 159.8, 152.5, 130.6, 129.4, 129.2, 125.7, 121.0, 114.3, 55.6.

(*E*)-1-(4-(tert-butyl)phenyl)-N-phenylmethanimine (3da). Brown oil product (90% NMR yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1 H), 7.75 (d, J = 8.3 Hz, 2 H), 7.41 (d, J = 8.3 Hz, 2 H), 7.29 (d, J = 7.6 Hz, 2 H), 7.17 – 7.09 (m, 3 H), 1.27 (s, 9 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.4, 155.1, 152.5, 133.7, 129.2, 128.8, 125.9, 125.8, 121.0, 35.2, 31.3.; HRMS (EI) calc. for $[C_{17}H_{19}N, M]$+: 237.1517, found 237.1516

(*E*)-1-(4-fluorophenyl)-N-phenylmethanimine (3ea).[21] Brown solid product (82% NMR yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1 H), 7.83 (m, 2 H), 7.32 (m, 2 H), 7.20 – 7.06 (m, 5 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.8 (d, J = 252.2 Hz), 159.0, 152.0, 132.7 (d, J = 3.0 Hz), 130.9 (d, J = 8.8 Hz), 129.3, 126.1, 121.0, 116.1 (d, J = 22.0 Hz).

(*E*)-1-(4-chlorophenyl)-N-phenylmethanimine (3fa).[21] Light brown solid product (47% NMR yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1 H), 7.75 (m, 2 H), 7.38 – 7.28 (m, 4 H), 7.19 – 7.10 (m, 3 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.9, 151.8, 137.5, 134.8, 130.1, 129.3, 129.2, 126.3, 121.0.

(*E*)-1-(2-methoxyphenyl)-N-phenylmethanimine (3ga).[23] Yellow oil product (50% NMR yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (s, 1 H), 8.06 (m, 1 H), 7.33 – 7.23 (m, 3 H), 7.14 – 7.07 (m, 3 H), 6.92 (m, 1 H), 6.81 (d, J = 8.3 Hz, 1 H), 3.74 (s, 3 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.6, 156.5, 152.8, 132.8, 129.1, 127.6, 125.7, 124.8, 121.1, 120.9, 111.2, 55.6.

(E)-1-(3-fluorophenyl)-N-phenylmethanimine (3ha).[25] Yellow oil product (86% NMR yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1 H), 7.62 (dd, *J* = 20.3, 8.5 Hz, 2 H), 7.44 – 7.34 (m, 3 H), 7.26 – 7.10 (m, 4 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.2 (d, *J* = 246.9 Hz), 158.9 (d, *J* = 3.0 Hz), 151.6, 138.6 (d, *J* = 7.3 Hz), 130.4 (d, *J* = 8.0 Hz), 129.3, 126.4, 125.1 (d, *J* = 2.8 Hz), 121.0, 118.4 (d, *J* = 21.7 Hz), 114.7 (d, *J* = 22.2 Hz).

(E)-1-(3-methoxyphenyl)-N-phenylmethanimine (3ia).[33] Light green product (88% NMR yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1 H), 7.51 (s, 1 H), 7.42 – 7.32 (m, 4 H), 7.21 (t, *J* = 8.7 Hz, 3 H), 7.02 (d, *J* = 7.9 Hz, 1 H), 3.85 (s, 3 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.3, 160.1, 152.1, 137.7, 129.8, 129.2, 126.0, 122.4, 121.0, 118.4, 111.9, 55.5.

(*E*)-1-phenyl-N-(p-tolyl)methanimine (3ab).[21] Brown oil product (82% NMR yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1 H), 7.82 (m, 2 H), 7.42 – 7.35 (m, 3 H), 7.09 (m, 4 H), 2.29 (s, 3 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.7, 149.6, 136.5, 135.9, 131.3, 129.9, 128.9, 128.8, 120.9, 21.1.

(*E*)-N-(4-methoxyphenyl)-1-phenylmethanimine (3ac).[24] Yellow solid product (92% NMR yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1 H), 7.82 (m, 2 H), 7.42 – 7.36 (m, 3 H), 7.20 – 7.14 (m, 2 H), 6.87 (d, J = 8.8 Hz, 2 H), 3.76 (s, 3 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.6, 158.4, 145.0, 136.6, 131.2, 128.9, 128.7, 122.3, 114.5, 55.7.

(*E*)-N-(4-fluorophenyl)-1-phenylmethanimine (3ad).[24] Yellow solid product (85% NMR yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1 H), 7.81 (m, 2 H), 7.43 – 7.35 (m, 3 H), 7.14 – 7.08 (m, 2 H), 6.99 (m, 2 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.6, 160.2 (d, J = 16.1 Hz), 148.1, 136.2, 131.6, 128.9 (d, J = 3.0 Hz), 122.4 (d, J = 8.3 Hz), 116.1, 115.9.

(*E*)-N-(4-chlorophenyl)-1-phenylmethanimine (3ae).[21] Brown solid product (72% NMR yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1 H), 7.82 (m, 2 H), 7.44 – 7.38 (m, 3 H), 7.28 (d, J = 8.6 Hz, 2 H), 7.08 (d, J = 8.6 Hz, 2 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.9, 150.7, 136.1, 131.8, 131.6, 129.4, 129.0, 129.0, 122.3.

(*E*)-N-(4-bromophenyl)-1-phenylmethanimine (3af).[24] Brown solid product (45% NMR yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1 H), 7.86 – 7.79 (m, 2 H), 7.42 (m, 5 H), 7.02 (d, J = 8.5 Hz, 2 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.9, 151.2, 136.1, 132.3, 131.8, 129.0, 129.0, 122.7, 119.5.

(E)-1-phenyl-N-(m-tolyl)methanimine (3ag).[21] Brown oil product (79% NMR yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1 H), 7.88 (dd, *J* = 6.5, 2.7 Hz, 2 H), 7.50 – 7.42 (m, 3 H), 7.26 (t, *J* = 7.7 Hz, 1 H), 7.02 (t, *J* = 8.9 Hz, 3 H), 2.38 (s, 3 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.2, 152.2, 139.0, 136.4, 131.4, 129.1, 128.9, 128.8, 126.8, 121.7, 117.9, 21.5.

(*E*)-1-(4-fluorophenyl)-N-(4-methoxyphenyl)methanimine (3ec).[25] Yellow solid product (61% NMR yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1 H), 7.84 – 7.73 (m, 2 H), 7.13 (d, J = 8.5 Hz, 2 H), 7.05 (m, 2 H), 6.84 (d, J = 8.5 Hz, 2H), 3.73 (s, 3 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.6 (d, J = 251.6 Hz), 158.4, 156.9, 144.7, 132.9 (d, J = 3.0 Hz), 130.6 (d, J = 8.7 Hz), 122.2, 115.9 (d, J = 22.0 Hz), 114.5, 55.6.

(E)-N-(4-fluorophenyl)-1-(4-methoxyphenyl)methanimine (3cd).[26] Yellow solid product (91% NMR yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1 H), 7.74 (d, J = 8.6 Hz, 2 H), 7.08 (m, 2 H), 6.97 (t, J = 8.6 Hz, 2 H), 6.89 (d, J = 8.6 Hz, 2 H), 3.77 (s, 3 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.4 (d, J = 8.9 Hz), 159.9, 159.6, 148.4, 130.6, 129.2, 122.3 (d, J = 8.2 Hz), 115.9 (d, J = 22.4 Hz), 114.3, 55.5.

Benzyl benzoate (4a).[15] Purification by flash chromatography on silica gel (*n*-hexane/ethyl acetate = 20/1) afforded light yellow oil product (88%, 56 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.4 Hz, 2 H), 7.46 (t, *J* = 7.4 Hz, 1 H), 7.40 – 7.22 (m, 7 H), 5.28 (s, 2 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.5, 136.2, 133.1, 130.2, 129.8, 128.7, 128.5, 128.4, 128.3, 66.8.

4-methylbenzyl 4-methylbenzoate (4b).[27] Purification by flash chromatography on silica gel (*n*-hexane/ethyl acetate = 20/1) afforded yellow greenish oil product (83%, 60 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.1 Hz, 2 H), 7.25 (d, *J* = 7.9 Hz, 2 H), 7.11 (m, 4 H), 5.22 (s, 2 H), 2.30 (s, 3 H), 2.27 (s, 3 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.7, 143.7, 138.1, 133.3, 129.8, 129.3, 129.2, 128.4, 127.6, 66.6, 21.8, 21.3.

4-methoxybenzyl 4-methoxybenzoate (4c).[15] Purification by flash chromatography on silica gel (*n*-hexane/ethyl acetate = 8/1) afforded yellow brownish oil product (81%, 66 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.7 Hz, 2 H), 7.29 (d, *J* = 8.4 Hz, 2 H), 6.81 (m, 4 H), 5.18 (s, 2 H), 3.74 (s, 3 H), 3.71 (s, 3 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.3, 163.4, 159.6, 131.8, 130.1, 128.5, 122.7, 114.0, 113.7, 66.3, 55.5, 55.4.

4-(*tert*-butyl)benzyl 4-(*tert*-butyl)benzoate (4d). Purification by flash chromatography on silica gel (*n*-hexane/ethyl acetate = 20/1) afforded light green oil product (84%, 82 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.5 Hz, 2 H), 7.35 (d, *J* = 8.5 Hz, 2 H), 7.30 (d, *J* = 2.8 Hz, 4 H), 5.24 (s, 2 H), 1.24 (s, 18 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.6, 156.7, 151.3, 133.4, 129.7, 128.1, 127.6, 125.6, 125.4, 66.4, 35.2, 34.7, 31.4, 31.2.; HRMS (EI) calc. for [$C_{22}H_{28}O_2$, M]$^+$: 324.2089, found 324.2086

4-fluorobenzyl 4-fluorobenzoate (4e).[27] Purification by flash chromatography on silica gel (*n*-hexane/ethyl acetate = 20/1) afforded light orange oil product (80%, 60 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (m, 2 H), 7.33 (m, 2 H), 7.00 (m, 4 H), 5.22 (s, 2 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 167.2, 165.5, 164.4 (d, *J* = 65.1 Hz), 161.6, 132.4 (d, *J* = 9.4 Hz), 131.9 (d, *J* = 3.3 Hz), 130.4 (d, *J* = 8.3 Hz), 126.4, 115.7 (d, *J* = 21.8 Hz), 66.2.

4-chlorobenzyl 4-chlorobenzoate (4f).[27] Purification by flash chromatography on silica gel (*n*-hexane/ethyl acetate = 20/1) afforded yellow greenish solid product (84%, 71 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.5 Hz, 2 H), 7.31 (d, *J* = 8.5 Hz, 2 H), 7.27 (s, 4 H), 5.22 (s, 2 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.5, 139.7, 134.4, 134.4, 131.2, 129.8, 128.9, 128.9, 128.4, 66.2.

4-(trifluoromethyl)benzyl 4-(trifluoromethyl)benzoate (4g).[28] Purification by flash chromatography on silica gel (*n*-hexane/ethyl acetate = 20/1) afforded white solid product (87%, 90 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.1 Hz, 2 H), 7.63 (d, *J* = 8.2 Hz, 2 H), 7.57 (d, *J* = 8.1 Hz, 2 H), 7.48 (d, *J* = 8.0 Hz, 2 H), 5.36 (s, 2 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.2, 139.7, 134.9 (d, *J* = 32.7 Hz), 133.1, 130.8 (d, *J* = 32.6 Hz), 130.3, 128.4, 125.8 (q, *J* = 3.8 Hz), 125.7 (q, *J* = 3.7 Hz), 125.3 (d, *J* = 40.1 Hz), 122.6 (d, *J* = 40.7 Hz), 66.4.

4-cyanobenzyl 4-cyanobenzoate (4h).[29] Purification by flash chromatography on silica gel (*n*-hexane/ethyl acetate = 8/1) afforded yellow solid product (31%, 24 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.4 Hz, 2 H), 7.70 (d, *J* = 8.4 Hz, 2 H), 7.63 (d, *J* = 8.2 Hz, 2 H), 7.48 (d, *J* = 8.1 Hz, 2 H), 5.37 (s, 2 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.6, 140.6, 133.4, 132.7, 132.5, 130.3, 128.6, 118.5, 117.9, 117.0, 112.6, 66.4.

2-methylbenzyl 2-methylbenzoate (4i).[30] Purification by flash chromatography on silica gel (*n*-hexane/ethyl acetate = 20/1) afforded yellow greenish oil product (84%, 61 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.7 Hz, 1 H), 7.36 – 7.25 (m, 2 H), 7.19 – 7.08 (m, 5 H), 5.26 (s, 2 H), 2.52 (s, 3 H), 2.32 (s, 3 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ

167.4, 140.5, 137.1, 134.2, 132.2, 131.8, 130.8, 130.5, 129.5, 129.4, 128.6, 126.2, 125.8, 65.0, 21.9, 19.1.

2-methoxybenzyl 2-methoxybenzoate (4j).[30] Purification by flash chromatography on silica gel (*n*-hexane/ethyl acetate = 8/1) afforded brown oil product (80%, 65 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (m, 1 H), 7.35 (m, 2 H), 7.25 – 7.16 (m, 1 H), 6.91 – 6.83 (m, 3 H), 6.80 (d, *J* = 8.2 Hz, 1 H), 5.31 (s, 2 H), 3.80 (s, 3 H), 3.75 (s, 3 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.1, 159.3, 157.4, 133.5, 131.8, 129.4, 129.3, 124.7, 120.5, 120.3, 120.1, 112.1, 110.4, 62.1, 56.0, 55.5.

Benzo[*d*][1,3]dioxol-5-ylmethyl benzo[*d*][1,3]dioxole-5-carboxylate (4k).[15] Purification by flash chromatography on silica gel (*n*-hexane/ethyl acetate = 8/1) afforded brown solid product (71%, 64 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.4 Hz, 1 H), 7.39 (s, 1 H), 6.82 (m, 2 H), 6.72 (t, *J* = 7.7 Hz, 2 H), 5.93 (s, 2 H), 5.88 (s, 2 H), 5.13 (s, 2 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.8, 151.8, 147.9, 147.8, 147.7, 130.0, 125.6, 124.2, 122.3, 109.7, 109.1, 108.3, 108.0, 101.9, 101.3, 66.7.

3-phenylpropyl 3-phenylpropanoate (4l).[30] Purification by flash chromatography on silica gel (*n*-hexane/ethyl acetate = 20/1) afforded colorless oil product (87%, 70 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (m, 4 H), 7.15 – 7.08 (m, 4 H), 7.06 (d, *J* = 7.1 Hz, 2 H), 4.00 (t, *J* = 6.5 Hz, 2 H), 2.87 (t, *J* = 7.8 Hz, 2 H), 2.54 (m, 4 H), 1.84 (m, 2 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.0, 141.3, 140.6, 128.6, 128.5, 128.5, 128.4, 126.4, 126.1, 63.9, 36.0, 32.2, 31.1, 30.3.

Octyl octanoate (4m).[31] Purification by flash chromatography on silica gel (*n*-hexane/ethyl acetate = 20/1) afforded colorless oil product (90%, 69 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.98 (t, *J* = 6.7 Hz, 2 H), 2.22 (t, *J* = 7.5 Hz, 2 H), 1.54 (m, 4 H), 1.32 – 1.13 (m, 18 H), 0.81 (t, *J* = 6.4 Hz, 6 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 174.1, 64.5, 34.5, 31.9, 31.8, 29.3, 29.3, 29.2, 29.1, 28.8, 26.1, 25.2, 22.8, 22.7, 14.2, 14.2.

2-methylbutyl 2-methylbutanoate (4n).[16] Purification by flash chromatography on silica gel (*n*-hexane/ether = 20/1) afforded yellow oil product (70%, 36 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.89 (m, 1 H), 3.84 – 3.76 (m, 1 H), 2.31 (m, 1 H), 1.62 (m, 2 H), 1.45 – 1.32 (m, 2 H), 1.19 – 1.04 (m, 4 H), 0.89 – 0.78 (m, 9 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 177.0, 68.9, 41.4, 34.3, 27.0, 26.2, 16.8, 16.6, 11.8, 11.4.

Neopentyl pivalate (4o).[17] Purification by flash chromatography on silica gel (*n*-hexane/ehter= 20/1) afforded yellow oil product (52%, NMR yield using benzyl formate as a standard).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.67 (s, 2 H), 1.15 (s, 9 H), 0.88 (s, 9 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 178.7, 73.7, 39.1, 31.6, 27.4, 26.6.

Cyclohexylmethyl cyclohexanecarboxylate (4p).[32] Purification by flash chromatography on silica gel (*n*-hexane/ ehter = 20/1) afforded yellow greenish oil product (87%, 58 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.87 (d, *J* = 6.5 Hz, 2 H), 2.29 (m, *J* = 14.9, 7.5, 3.6 Hz, 1 H), 1.90 (m, *J* = 12.7 Hz, 2 H), 1.80 – 1.60 (m, 9 H), 1.51 – 1.38 (m, 2 H), 1.34 – 1.13 (m, 6 H), 0.97 (m, *J* = 21.7, 11.6 Hz, 2 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.3, 69.4, 43.5, 37.3, 29.8, 29.2, 26.5, 25.9, 25.8, 25.6.

Naphthalen-1-ylmethyl 1-naphthoate (4q).[32] Purification by flash chromatography on silica gel (*n*-hexane/ ethyl acetate = 20/1) afforded yellow greenish oil product (74%, 69 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (d, *J* = 8.6 Hz, 1 H), 8.12 – 8.02 (m, 2 H), 7.85 (d, *J* = 8.2 Hz, 1 H), 7.81 – 7.71 (m, 3 H), 7.57 (d, *J* = 6.8 Hz, 1 H), 7.42 (m, 5 H), 7.29 (m, *J* = 7.7 Hz, 1 H), 5.79 (s, 2 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 167.4, 133.9, 133.6, 131.9, 131.7 131.6 130.6, 129.5 128.9 128.6, 127.9, 127.8, 126.9, 126.8, 126.3, 126.1, 125.9, 125.5, 124.6, 123.8, 65.3.

Furan-2-ylmethyl furan-2-carboxylate (4r).[15] Purification by flash chromatography on silica gel (*n*-hexane/ ethyl acetate = 15/1) afforded brown oil product (49%, 28 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 0.6 Hz, 1 H), 7.44 (d, *J* = 0.9 Hz, 1 H), 7.20 (d, *J* = 3.5 Hz, 1 H), 6.50 (m, *J* = 3.2 Hz, 2 H), 6.40 – 6.36 (m, 1 H), 5.29 (s, 2 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.4, 149.2, 146.6, 144.4, 143.6, 118.6, 112.0, 111.3, 110.8, 58.4.

3-fluorobenzyl 3-fluorobenzoate (4s).[34] Purification by flash chromatography on silica gel (*n*-hexane/ ethyl acetate = 20/1) afforded light orange oil product (83%, 62 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.7 Hz, 1 H), 7.70 – 7.63 (m, 1 H), 7.37 – 7.23 (m, 2 H), 7.21 – 7.15 (m, 1 H), 7.12 (d, *J* = 7.6 Hz, 1 H), 7.06 (d, *J* = 9.5 Hz, 1 H), 6.99 – 6.92 (m, 1 H), 5.26 (s, 2 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.2 (d, *J* = 3.0 Hz), 164.1 (d, *J* = 32.6 Hz), 161.6 (d, *J* = 33.3 Hz), 138.3 (d, *J* = 7.4 Hz), 132.1 (d, *J* = 7.5 Hz), 130.4 (d, *J* = 8.2 Hz), 130.2 (d, *J* = 7.8 Hz), 125.6 (d, *J* = 3.1 Hz), 123.7 (d, *J* = 3.0 Hz), 120.4 (d, *J* = 21.2 Hz), 116.7 (d, *J* = 23.2 Hz), 115.4 (d, *J* = 21.1 Hz), 115.1 (d, *J* = 21.9 Hz), 66.3 (d, *J* = 2.0 Hz).

3-methoxybenzyl 3-methoxybenzoate (4t).[27] Purification by flash chromatography on silica gel (*n*-hexane/ ethyl acetate = 10/1) afforded colorless oil product (84%, 68 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.6 Hz, 1 H), 7.51 (s, 1 H), 7.28 – 7.16 (m, 2 H), 7.05 – 6.98 (m, 1 H), 6.97 – 6.86 (m, 2 H), 6.79 (d, *J* = 8.2 Hz, 1 H), 5.25 (s, 2 H), 3.75 (s, 3 H), 3.73 (s, 3 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.4, 159.9, 159.7, 137.7, 131.5, 129.8, 129.5, 122.2, 120.4, 119.6, 114.3, 113.7, 113.7, 66.7, 55.6, 55.4.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publication website.

Experimental procedure, characterization and NMR spectral data (PDF)

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Notes

The authors declare no competing financial interest.

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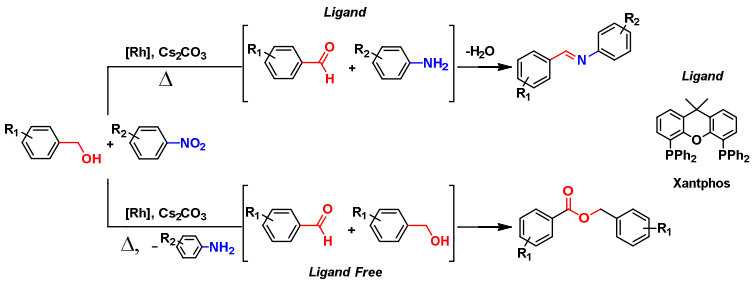
Ligand
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