JOC Article

Selective Conversion of Diallylanilines and Arylimines to Quinolines

Josemon Jacob and William D. Jones*

Department of Chemistry, University of Rochester, Rochester, New York 14627

jones@chem.rochester.edu

Received November 19, 2002

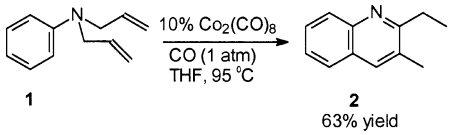
A variety of diallylanilines are shown to undergo cobalt−carbonyl catalyzed rearrangement to quinolines. Diallylanilines are also used as allyl transfer reagents to convert benzaldimines into quinolines. Substitution in the 2- and 3-positions of the quinoline is featured in all transformations.

Introduction

Transition metal catalyzed heteroannulation provides a useful and convenient tool for the construction of *N*-heterocycles.[1−3] Quinolines and their derivatives form an interesting class of compounds in that they display attractive applications as pharmaceuticals as well as being general synthetic building blocks due to their chemical and biological relevance.[4,5] Many transition metal catalyzed processes have been developed for the synthesis of quinolines. For example, several ruthenium,[6] rhodium,[7] palladium,[8] and iron[9] complexes have been shown to catalyze the formation of 2,3-substituted quinolines from nitrobenzene and aldehydes or alcohols in the presence of CO. Also, aniline was shown to undergo *N*-heterocyclization to generate quinolines with aliphatic aldehydes with use of ruthenium,[10] rhodium,[11] and palladium complexes.[12,13] Recently, $RuCl_3/SnCl_2$ was shown to catalyze formation of 2,3-disubstituted quinolines from aniline and triallylamine at 180 °C.[14] A new Domino synthesis of quinolines from aniline and styrene has also been reported.[15] Despite the advances in methodology toward the construction of quinoline derivatives, the development of catalytic routes toward their synthesis remains an active area of research. We recently discovered a cobalt-catalyzed conversion of mono- and diallylanilines to quinolines.[16] Arylimines have also been found to undergo selective cross-coupling with diallylanilines to generate quinolines, and the results of a detailed investigation are reported here.

Results and Discussion

Conversion of Diallylanilines to 2,3-Substituted Quinolines. *N*,*N*-Diallylaniline (**1**), when heated with 10 mol % of $Co_2(CO)_8$ and 1 atm of CO at 95 °C, leads to the selective formation of 2-ethyl-3-methylquinoline (**2**) in 63% isolated yield (eq 1). Aniline and propene are also



(1)

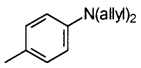
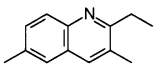
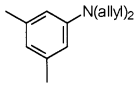
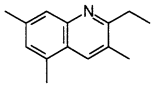
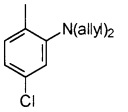
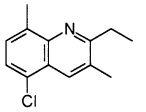
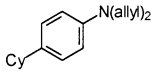
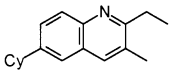
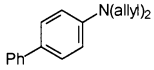
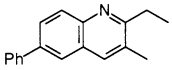
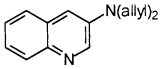
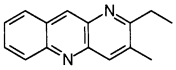
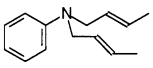
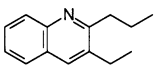
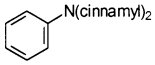
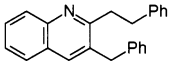
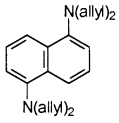
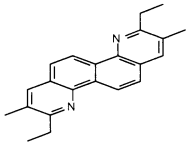
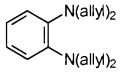
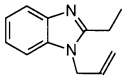
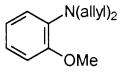
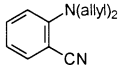
observed as products in the reaction. The presence of CO is necessary to stabilize $Co_2(CO)_8$ under the reaction conditions. The reaction is easily extended to a range of diallylanilines with varying substituents on the aromatic ring. The results are summarized in Table 1. The 2-ethyl-3-methyl-substitution pattern in the product is common to all quinolines derived from diallylanilines.

Similar product selectivity and substitution pattern have been reported in the literature for quinoline synthesis from aniline and allyl alcohols or α,β-unsaturated aldehydes catalyzed by ruthenium complexes.[6,10,11] Substituents are easily introduced at the 5-, 6-, 7-, and 8-positions of the quinoline skeleton. For entry 6, almost equimolar amounts of both regioisomers are formed in the reaction. Reaction of a four-carbon allyl fragment as

(1) Hegedus, L. S. *Angew*. Chem., Int. Ed. Engl. **1988**, 27, 1113.
(2) Hegedus, L. S.; Allen, G. F.; Bozell, J. J. *J. Am. Chem. Soc.* **1978**, 100, 5800.
(3) Diamond, S. E.; Szalkiewicz, A.; Mares, F. *J. Am. Chem. Soc.* **1979**, 101, 490.
(4) Balasubramanian, M.; Keay, J. G. In *Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R., Rees, C. W., Scriven, E. F. V., Eds.; Pergamon Press: Oxford, UK, 1996; Vol. 5, p 245.
(5) Jones, G. In *Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R., Rees, C. W., Scriven, E. F. V., Eds.; Pergamon Press: Oxford, UK, 1996; Vol. 5, p167.
(6) Watanabe, Y.; Tsuji, Y.; Ohsuji, Y. *Tetrahedron Lett.* **1981**, *22*, 2667.
(7) Watanabe, Y.; Suzuki, N.; Tsuji, Y.; Shim, S. C.; Mitsudo, T. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1116.
(8) Watanabe, Y.; Tsuji, Y.; Shida, J. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 435.
(9) Watanabe, Y.; Takatsuki, K.; Shim, S. C.; Mitsudo, T.; Takegami, Y. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 3397.
(10) Watanabe, Y.; Tsuji, Y.; Ohsugi, Y.; Shida, J. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2452.
(11) Watanabe, Y.; Shim, S. C.; Mitsudo, T. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3460.
(12) Larock, R. C.; Hightower, T. R.; Hasvold, L. A.; Peterson, K. P. *J. Org. Chem.* 1996, *61*, 3584.
(13) Larock, R. C.; Kuo, M.-Y. *Tetrahedron Lett.* **1991**, *32*, 572.
(14) Cho, S. C.; Ho Oh, B.; Shim, S. C. *Tetrahedron Lett.* **1999**, *40*, 1499.
(15) Beller, M.; Thiel, O. R.; Trauthwein, H.; Hartung, C. G. *Chem. Eur. J.* **2000**, *6*, 2513.
(16) Proceedings from the 10th ISRHHC: Jacob, J.; Cavalier, C. K.; Jones, W. D.; Godleski, S. A.; Valente, R. R. *J. Mol. Catal. A* **2002**, *183*, 565−570.

10.1021/jo026737j CCC: $25.00
Published on Web 04/04/2003

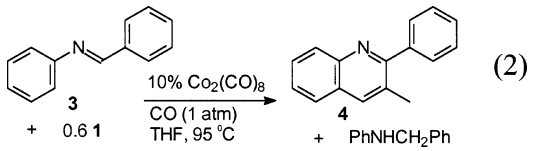
TABLE 1. Isolated Yields for the Conversion of Diallylanilines to Quinolines[a]

entry	substrate	product	temp (°C)	yield (%)
1			105	59
2			105	56
3			110	45
4			105	62
5			105	52
6			120	32[b]
7			110	53
8			120	27
9			120	26
10			120	15[c]
11		--	120	--
12		--	120	--

[a] 10% $Co_2(CO)_8$ used in all the experiments; typical reaction time is 36−48 h. [b] Both regioisomers are formed in an approximately 1:1 ratio. [c] Stoichiometric reaction.

in entry 7 led to 2-propyl-3-ethyl substitution in the quinoline product. A dicinnamylaniline as in entry 8 leads to more of the reduction products, namely aniline and *β*-methylstyrene. Although a 4-methoxy substituent is easily introduced to the quinoline skeleton, coordinating substituents at the 2-position of the diallylaniline largely inhibit the reaction. While entry 10 gave a 15% yield of the benzimidazole derivative in a stoichiometric reaction, no reaction was observed with entries 11 and 12 even at 120 °C. This is most likely due to the initial formation of a stable chelate complex with $Co_2(CO)_8$, which is rendered unreactive.

Cross-Coupling of Arylimines with Diallylanilines. Allylcobalt tricarbonyl[17] and monoallylaniline are the only intermediates observed in the reaction when followed by ^{1}H NMR spectroscopy. The ability of cobalt hydrides to isomerize double bonds[18] suggested that imines are likely intermediates in the reaction. To test this, the cross-coupling of imine **3** was studied with diallylaniline in the presence of 10 mol % of $Co_2(CO)_8$. As anticipated, the cross-coupled quinoline product **4** was isolated in 47% yield (eq 2). A small amount (<5%) of

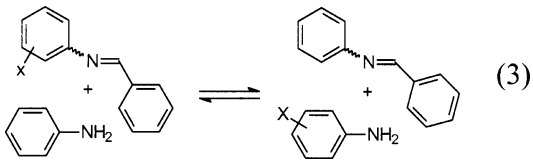


(2)

quinoline formed from diallylaniline by the reaction reported above is also observed in the reaction. The only other products observed are the secondary amine (formed by reduction of the imine) and aniline (formed from diallylaniline after transfer of its two allyl groups). This greatly improves the scope of this cobalt-catalyzed reaction in that it allows for the introduction of varying substituents at the 2-position of the quinoline skeleton.

This unique cross-coupling reaction is easily extended to a range of arylimines as recorded in Table 2.[19] For these experiments, 0.6−0.7 equiv of diallylaniline was used as the allyl source. The yields reported are based on the starting imine. The same secondary amine formed by reduction of the imine is also observed for all substrates. The reaction is quite versatile for imines derived from aniline and various ortho- and para-substituted aldehydes. No cross-coupling product and only 2-ethyl-3-methylquinoline was observed for entry 6 in Table 2. This is most likely due to the formation of a stable chelate complex with $Co_2(CO)_8$.

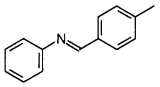
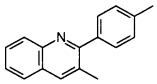
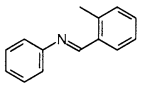
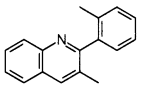
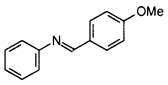
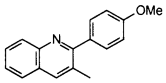
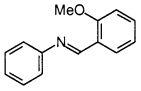
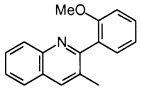
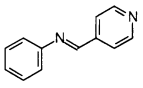
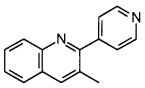
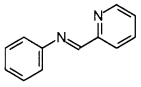
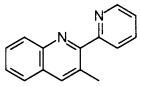
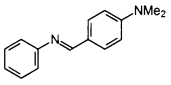
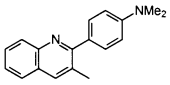
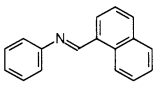
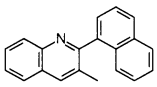
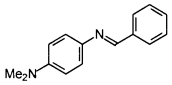
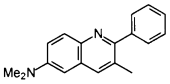
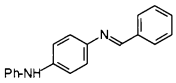
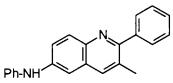
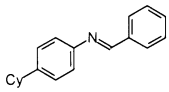
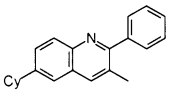
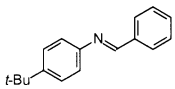
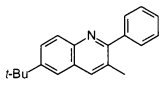
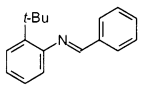
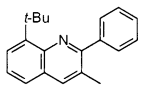
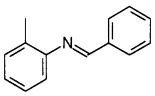
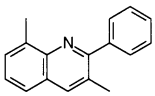
Small amounts (2−4%) of a carbonylation product were observed for entry 7 in Table 2. In the absence of diallylaniline, the other conditions remaining the same, this carbonylation product is the sole product in the system although the reaction is very slow (14 days at 120 °C). This product was identified as a five-membered-ring lactam.[20] For entries 9−14 where the imine is derived from anilines bearing a ring substituent, the aniline formed in the reaction could undergo an imine exchange reaction with the substrate as shown in eq 3. Although


(3)

there is no significant effect of this equilibration for

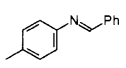
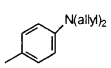
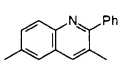
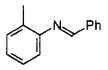
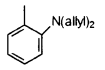
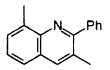
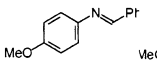
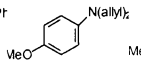
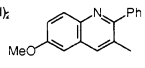
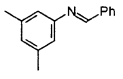
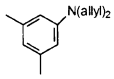
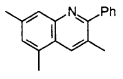
(17) Heck, R. F.; Breslow, D. S. *J. Am. Chem. Soc.* **1961**, *83*, 1097.
(18) Kumobayashi, H.; Akutagawa, S.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 3949.
(19) For a recent comprehensive account of transition metal catalyzed cross-coupling reactions, see: Stang, P. J.; Diederich, F. *Metal-Catalyzed Cross-coupling Reactions*; Wiley-VCH: New York, 1998.
(20) Similar reactivity of imines has been reported with transition metal carbonyls in the literature, see: Bruce, D. W.; Liu, X.-H. J. *Chem. Soc., Chem.* Commun. **1994**, 729. See Experimental Section for data on this compound, 6-(dimethylamino)-*N*-phenylphthalimidine.

TABLE 2. Isolated Yields of Quinoline Derivatives by Cross-Coupling with Diallylaniline[a]

entry	imine	cross coupled product	temp (°C)	yield (%)
1			105	43
2			110	51
3			105	39
4			100	64[b]
5			120	50[c]
6			120	--
7			100	58
8			110	47
9			105	47
10			100	49
11			105	56
12			100	53
13			100	17[b]
14			100	29

[a] 0.6−0.7 equiv of diallylaniline was used as the allyl source in all the reactions; 10% $Co_2(CO)_8$ and 1 atm of CO is used in all the reactions; typical reaction time is 36−48 h. [b] NMR yield. [c] Small amounts (2−4%) of a carbonylation product are also observed in the reaction.

TABLE 3. Isolated Yields of Quinolines by Cross-Coupling of Imines with Diallylaniline[a]

entry	imine	diallyl aniline	product	temp (°C)	yield (%)
1				100	61
2				100	33
3				105	60
4				105	73
5				105	55
6				105	54

[a] The yields reported are based on the starting imine; 10% catalyst loading; typical reaction time is 36−48 h.

imines derived from aniline bearing a para substutuent (entries 9−12), it is significant for imines derived from ortho-substituted anilines (13 and 14). For entry 13, there is significant equilibration and the major product observed is **4**, which can be explained by an aniline−imine exchange as in eq 3. For entry 14, an approximately 1:1 mixture of the two quinolines is observed.

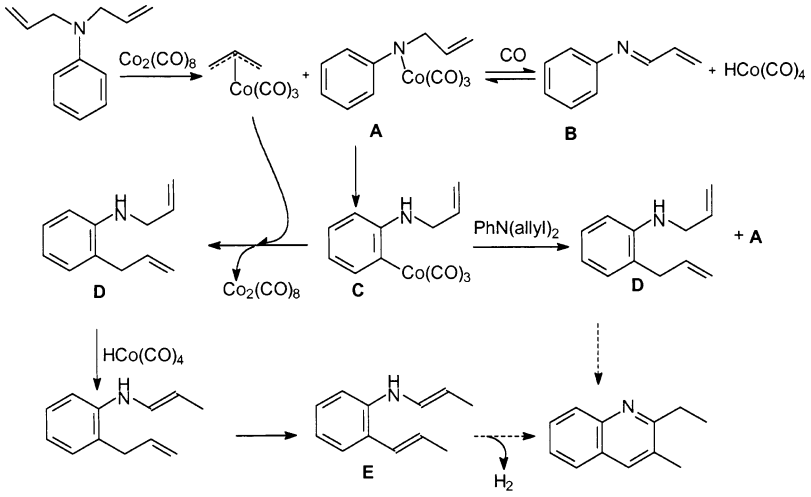
To circumvent this problem, the cross-coupling was studied by using diallylanilines derived from the same aniline fragment as the imine. The results are recorded in Table 3. This modification significantly improves the yields of this cross-coupling reaction while avoiding any side reactions leading from aniline−imine exchange. It can be seen from Tables 2 and 3 that arylimines with alkyl, alkoxy, dialkylamino, arylamino, and aryl substituents on either side of the ring undergo this cross-coupling very efficiently. Although preliminary studies were done on an NMR scale, the reaction is easily scaled up to 200 mg without reduction in product yield.

Mechanistic Considerations. While oxidative addition of a substrate to a transition metal is often a key elementary step in many catalytic processes, the only intermediates spectroscopically observed in this system are allylcobalttricarbonyl and monoallylaniline. With certain substrates, palladium and ruthenium complexes have been shown in the past to cleave allylic C−N bonds.[21,22] While these types of bond cleavages and double bond migrations are likely to be involved, a mechanistic discussion at this point would have to be quite spectulative without further experiments.

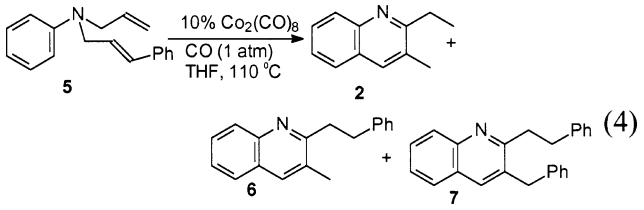
Although the overall reaction is the heteroannulation of diallylaniline to give quinoline with elimination of

(21) Moberg, C.; Antonsson, T. *Organometallics* **1994**, *13*, 1878.
(22) Hiraki, K.; Matsunaga, T.; Kawano, H. *Organometallics* **1994**, *13*, 1878.

SCHEME 1. Proposed Mechanistic Sequence



hydrogen, the detection and isolation of allylcobalttricarbonyl suggested that the reaction is not intramolecular. Also, kinetic studies showed a *second order* dependence of initial rate on the concentration of diallylaniline, again suggesting the possibility of allyl group transfer between substrates. To test this, substrate **5** was synthesized and its reactivity studied in the presence of $Co_2(CO)_8$ (eq 4). Analysis of the reaction by GC-MS



showed formation of three quinoline products: **2**, **6**, and **7** (the ratio from NMR of **2**:**6**:**7** is 1:4.8:5.8). If the reaction were intramolecular, only **6** (or its isomer) is expected as a product. This intermolecular allyl transfer was further confirmed by reacting diallylaniline with dicinnamyl−aniline. Detection of **6** in the reaction by NMR and by GC-MS further supports intermolecular allyl transfer.

For the cross-coupling of imines with diallylanilines to form quinolines, the formation of secondary amine by reduction of the imine is an undesirable side reaction. For every molecule of product, one molecule of hydrogen is released in the system. $Co_2(CO)_8$ is known to form $HCo(CO)_4$ in the presence of H_2, which could reduce the imine. In an attempt to eliminate the reduction product, the reaction was performed in the presence of a 10-fold excess of *tert*-butylethylene. Although this eliminated the reduction of the imine almost completely as evidenced by GC, only a 50% conversion of the imine was observed after 5 days. Use of a smaller mole ratio of the olefin was less successful in eliminating the reduction reaction. In another attempt, the reaction was done in 1,4-dioxane but with a constant purge of CO. This was again not successful since the allylcobalttricarbonyl formed in the reaction is very volatile and escapes the system.

The proposed mechanistic sequence is outlined in Scheme 1, although as mentioned above, the pathway is speculative in the absence of a more thorough study. As the reaction is conducted under an atmosphere of CO, carbonyl loss and addition are likely to be reversible in many of these species. Intermediate **A**, formed via *N*-allyl cleavage, is proposed to undergo reaction in one of two pathways; it can either form a conjugated imine as in **B** generating hydridocobaltcarbonyl or undergo orthometalation to generate an intermediate of type **C**. Intermediate **C** can react with allylcobalt tricarbonyl to form intermediate **D** and regenerate $Co_2(CO)_8$. $HCo(CO)_4$ has been shown in the literature to effect double bond isomerizations and hence **D** can undergo isomerization to generate **E**.[18] Also, when diallylaniline was treated with $(Ph_3P)_3CoH$ synthesized independently, both allylic double bonds were found to isomerize to the enamine within minutes when followed by NMR spectroscopy. [23] **E** is poised for cyclization to generate quinoline with elimination of H_2. Alternatively, **C** can react with another molecule of substrate to generate intermediates **D** and **A** and continue the catalytic cycle. The observed cross-coupling of imines with diallylanilines strongly suggests the intermediacy of imines as in **B**, which can enter the catalytic cycle as well. The formation of monoallylaniline in the system can be accounted for by the reaction of **A** with $HCo(CO)_4$.

Although many other organometallic complexes were screened for reactivity toward allylic C−N bonds, none of them exhibited selectivity similar to $Co_2(CO)_8$. Complexes tested include $Ni(cod)_2$, $(Cy_3P)_2Ni(CH_2{=}CH_2)$, $Mn_2(CO)_{10}$, $(Ph_3P)_2Ni(CO)_2$, $Mo(CO)_6$, $(CH_3CN)_3Mo(CO)_3$, $(CH_3CN)_3W(CO)_3$, $(Ph_3P)_2RhCl(CO)$, $(Ph_3P)_3RuClH(CO)$, Rh_6CO_{16} (cod = cyclooctadiene, Cy = cyclohexyl), $(Ph_3P)_3$-$RhH(CO)$, $Ru_3(CO)_{12}$, $[(cod)RhCl]_2$, $[(Ph_3P)_3Co(CH_2CH_2)]_2$, $[(dippe)NiH]_2$ (dippe = 1,2-bis(diisopropyl-phosphino)-ethane), and $(Ph_3P)_3CoH(N_2)$.

In conclusion, $Co_2(CO)_8$ is an efficient catalyst for the conversion of diallylanilines and imines to 2-*R*-3-methylquinolines. The ready availability of catalyst and starting reagents makes this an attractive method for the synthesis of quinolines.

Experimental Section

General Considerations. Most manipulations were performed under an N_2 atmosphere, either on a high-vacuum line with modified Schlenk techniques or in a glovebox. Tetrahy-

(23) Whitfield, J. M.; Watkins, S. F.; Tupper, G. B.; Baddley, W. H. *J. Chem. Soc., Dalton Trans.* 1977, 407.

drofuran was distilled from sodium/benzophenone ketyl solution. $Co_2(CO)_8$ was used as received. The diallylanilines used in this study were synthesized from the corresponding aniline by reaction with allylbromide and sodium carbonate in methanol. The diallylanilines were distilled and dried over KOH prior to use. The arylimines were synthesized by direct condensation of the corresponding aniline and aldehyde in absolute ethanol and recrystallized from hexanes.

All ^{1}H and ^{13}C NMR spectra were recorded either on an AMX400 spectrometer or an AVANCE400 spectrometer. All ^{1}H chemical shifts are reported in ppm (δ) relative to tetramethylsilane and referenced using chemical shifts of residual solvent resonances (THF-d_8, 1.73; C_6D_6, 7.15). All isolated quinolines gave satisfactory NMR and mass spectral data.

General Procedure for the Conversion of Diallylanilines to Quinolines. For the quinolines recorded in Table 1, a general procedure with 4-methyl-*N*,*N*-diallylaniline is as follows: In a 50-mL round-bottomed flask equipped with a Teflon seal, 149.0 mg (0.8 mmol) of 4-methyl-*N*,*N*-diallylaniline (Table 1 entry 1), and 27.4 mg of $Co_2(CO)_8$ (0.08 mmol) are added to 5 mL of dry THF in a glovebox. The flask is then connected to a Schlenk line and any dissolved nitrogen is removed by freeze−pump−thawing the solution three times. Carbon monoxide is then introduced at 1 atm and the reaction is heated in an oil bath at 105 °C for 48 h with stirring. The solution is then concentrated to ∼1 mL and chromatographed, using 0−10% ethyl acetate in hexane. The isolated yield of 2-ethyl-3,6-dimethylquinoline as a colorless viscous liquid was 86.5 mg.

General Procedure for the Cross-Coupling of Imines with Diallylanilines. For the cross-coupling of imines with diallylanilines (results recorded in Tables 2 and 3), a general procedure using entry 1 in Table 3 is as follows: 200 mg (1.02 mmol) of *N*-(4-methyl)phenylbenzaldehyde imine is added to 10 mL of THF in a 100-mL RB flask equipped with a Teflon seal in a glovebox. To this is added 134.0 mg (0.71 mmol) of 4-methyl-*N*,*N*-diallylaniline followed by 35.1 mg of Co_2CO_8 (0.1 mmol) with stirring. The flask is then connected to a Schlenk line and the solution is freeze−pump−thawed three times. CO is introduced at 1 atm and the reaction is heated at 100 °C in an oil bath for 48 h. The reaction volume is then concentrated to ∼1 mL, 0.5 g of silica is added, and the solvent is pumped dry. The crude sample on silica is then chromatographed with 0−10% ethyl acetate in hexane. The isolated yield of 3,6-dimethyl-2-phenylquinoline as a yellow oil was 145.3 mg

2-Ethyl-3,6-dimethylquinoline (entry 1, Table 1). ^{1}H NMR: δ 8.17 (d, 1H, J = 8.4 Hz), 7.29 (s, 1H), 7.18 (s, 1H), 7.14 (d, 1H, J = 8.4 Hz), 2.71 (q, 2H, J = 7.6 Hz), 2.18 (s, 3H), 1.96 (s, 3H), 1.40 (t, 3H, J = 7.6 Hz). ^{13}C NMR: δ 161.80, 146.28, 135.10, 134.70, 130.55, 129.48, 129.42, 128.32, 125.96, 29.25, 21.52, 18.95, 12.37. MS: *m*/*e* 185, 184 (bp), 157, 142, 128, 102, 77, 63. Oily liquid.

2-Ethyl-3,5,7-trimethylquinoline (entry 2, Table 1). ^{1}H NMR: δ 8.02 (s, 1H), 7.61 (s, 1H), 6.86 (s, 1H), 2.78 (q, 2H, J = 7.6 Hz), 2.31 (s, 3H), 2.20 (s, 3H), 2.03 (s, 3H), 1.44 (t, 3H, J = 7.6 Hz). ^{13}C NMR: δ 162.14, 148.29, 137.72, 133.09, 131.69, 128.67, 127.97, 127.33, 125.07, 29.30, 21.72, 19.18, 18.50, 12.48. MS: *m*/*e* 199, 198 (bp), 171, 128, 115, 91, 77. White solid. Anal. Calcd: C 84.36; H 8.60; N 7.03. Found: C 84.40; H 8.57; N 7.01.

5-Chloro-2-ethyl-3,8-dimethylquinoline (entry 3, Table 1). ^{1}H NMR: δ 8.21 (s, 1H), 7.42 (d, 1H, J = 7.6 Hz), 7.39 (d, 1H, J = 7.6 Hz), 3.0 (q, 2H, J = 7.2 Hz), 2.73 (s, 3H), 2.52 (s, 3H), 1.42 (t, 3H). ^{13}C NMR: δ 167.69, 141.90, 137.32, 136.32, 133.49, 133.18, 130.89, 34.39, 23.85, 22.67, 16.93. MS: *m*/*e* 219, 218 (bp), 191, 168, 154, 127, 102, 90, 77. Light yellow solid.

6-Cyclohexyl-2-ethyl-3-methylquinoline (entry 4, Table 1). ^{1}H NMR: δ 8.26 (d, 1H, J = 8.8 Hz), 7.38 (s, 1H), 7.33 (d, 1H, J = 1.6 Hz), 7.26 (dd, 1H, J = 8.8, 1.6 Hz), 2.75 (q, 2H, J = 7.6 Hz), 2.45 (m, 1H), 2.00 (s, 3H), 1.85−1.69 (m, 5H), 1.42 (t, 3H), 1.40−1.14 (m, 5H). ^{13}C NMR: δ 161.95, 146.73, 145.30, 135.12, 129.58, 129.34, 128.64, 127.85, 123.63, 44.83, 34.77, 29.32, 27.28, 26.57, 19.00, 12.49. MS: *m*/*e* 253, 252 (bp), 225, 210, 196, 184, 169, 115, 77. White solid.

2-Ethyl-3-methyl-4-phenylquinoline (entry 5, Table 1). ^{1}H NMR: δ 8.30 (d, 1H, J = 8.4 Hz), 7.69 (s, 1H), 7.62 (d, 1H, J = 8.8 Hz), 7.50 (d, 2H, J = 7.2 Hz), 7.33 (s, 1H), 7.22 (t, 2H, J = 7.2 Hz), 7.13 (t, 1H, J 6.8 Hz), 2.73 (q, 2H, J = 7.2 Hz), 1.96 (s, 3H), 1.42 (t, 3H, J = 7.6 Hz). ^{13}C NMR: δ 162.86, 147.04, 141.39, 138.65, 135.50, 130.11, 129.94, 129.17, 128.34, 128.20, 127.98, 127.61, 124.89, 29.38, 18.97, 12.35. MS: *m*/*e* 247, 246 (bp), 219, 203, 189, 165, 123, 102, 77, 63. White solid.

2-Ethyl-3-methyl-1,10-diazaanthracene (entry 6, Table 1). ^{1}H NMR: δ 9.39 (s, 1H), 8.61 (s, 1H), 8.53 (d, 1H, J = 7.6 Hz), 8.18 (dd, 1H, J = 8.0, 1.6 Hz), 7.73 (m, 2H), 3.04 (q, 2H, J = 7.6 Hz), 2.62 (s, 3H), 1.41 (t, 3H). ^{13}C NMR: δ 166.19, 156.64, 146.39, 142.50, 136.89, 132.30, 132.16, 130.80, 129.35, 128.55, 125.52, 124.40, 31.19, 21.74, 14.19. MS: *m*/*e* 222, 221 (bp), 197, 182, 63. Oily liquid.

3-Ethyl-2-propylquinoline (entry 7, Table 1). ^{1}H NMR: δ 7.92 (d, 1H, J = 8.8 Hz), 7.91 (s, 1H), 7.74 (d, 1H, J = 8.0 Hz), 7.56 (dd, 1H, J = 8.0, 7.6 Hz), 7.41 (dd, 1H, J = 8.0, 7.6 Hz), 2.95 (t, 2H, J = 7.6 Hz), 2.84 (q, 2H, J = 7.2 Hz), 1.91 (pentet, 2H, J = 7.6 Hz), 1.32 (t, 3H, J = 7.2 Hz), 1.06 (t, 3H, J = 7.2 Hz). ^{13}C NMR: δ 166.74, 152.55, 140.99, 138.88, 134.54, 133.50, 133.21, 132.51, 130.94, 42.85, 30.73, 27.44, 19.54, 19.45. MS: *m*/*e* 199, 184, 171 (bp), 156, 143, 128, 102, 77, 51. Liquid.

3-Benzyl-2-(2-phenylethyl)quinoline (entry 8, Table 1). ^{1}H NMR: δ 8.01 (d, 1H, J = 8.Hz), 7.79 (s, 1H), 7.73 (d, 1H, J = 8.0 Hz), 7.66 (t, 1H, J = 7.2 Hz), 7.48 (t, 1H, J = 7.2 Hz), 7.39−7.13 (m, 10H), 4.11 (s, 2H), 3.18 (t, 2H, J = 6.4 Hz), 3.06 (t, 2H, J = 6.4 Hz). ^{13}C NMR: δ 163.28, 144.43, 141.70, 138.38, 134.88, 131.14 (2 overlapping peaks), 130.84 (2 peaks), 130.74 (2 peaks), 130.50 (2 peaks), 129.37, 129.35, 128.63, 128.05, 40.83, 39.70, 36.94. MS: *m*/*e* 323, 322 (bp), 232, 91. Liquid.

3,9-Diethyl-2,8-dimethyl-4,10-diazachrysene (entry 9, Table 1). ^{1}H NMR: δ 9.92 (d, 2H, J = 8.8 Hz), 7.76 (d, 2H, J = 8.8 Hz), 7.43 (s, 1H), 2.90 (q, 2H, J = 7.2 Hz), 2.05 (s, 6H), 1.57 (t, 6H, J = 7.2 Hz). ^{13}C NMR: δ 161.32, 144.49, 136.10, 132.03, 129.87, 126.44, 125.60, 123.34, 29.45, 18.78, 12.50. MS: *m*/*e* 314 (bp), 313, 298, 286, 207, 156, 143. Brown solid.

***N*-Allyl-2-ethylbenzimidazole (entry 10, Table 1).** ^{1}H NMR: δ 7.55 (m, 1H), 7.27 (m, 1H), 7.09 (m, 2H), 6.01 (m, 1H), 5.12 (d, 1H, J = 10.4 Hz), 4.89 (d, 1H, J = 17.2 Hz), 4.79 (d, 2H, J = 4.8 Hz), 2.82 (q, 2H, J = 7.6 Hz), 1.39 (t, 3H, J = 7.6 Hz). ^{13}C NMR: δ 149.18, 141.36, 138.96, 133.87, 126.57, 124.74, 121.41, 114.75, 50.76, 26.03, 16.78. MS: *m*/*e* 186 (bp), 171, 157, 145, 132, 92, 77, 51.

2-(4-Methylphenyl)-3-methylquinoline (entry 1, Table 2). ^{1}H NMR: δ 8.06 (s, 1H), 7.99 (d, 1H, J = 8.4 Hz), 7.61 (t, 1H), J = 7.2 Hz), 7.55 (d, 2H, J = 7.6 Hz), 7.47 (t, 1H, J = 7.2 Hz), 7.27 (d, 2H, J = 7.6 Hz), 2.50(s, 3H), 2.36(s, 3H). ^{13}C NMR: δ 160.89, 146.96, 138.33, 137.01, 129.69, 129.59, 129.30, 129.13, 129.00, 127.5, 127.05, 127.00, 126.61, 21.67, 21.06. MS: 233, 232 (bp), 217, 115, 108, 89, 63. Oily liquid.

2-(2-Methylphenyl)-3-methylquinoline (entry 2, Table 2). ^{1}H NMR: δ 8.09 (s, 1H), 7.97 (d, 1H, J = 8.4 Hz), 7.82 (d, 1H, J = 8.0 Hz), 7.62 (t, 1H, J = 8.0 Hz), 7.50 (t, 1H, J = 8.0 Hz), 7.30−7.19 (m, 4H), 2.46 (s, 3H), 2.08 (s, 3H). ^{13}C NMR: δ 166.87, 152.63, 146.77, 141.29, 141.16, 135.61, 135.35, 135.07, 134.03, 133.91, 133.59, 133.36, 132.47, 131.81, 131.09, 24.58, 24.46. MS: *m*/*e* 233, 232, 218 (bp), 113, 108, 89, 63. Oily liquid.

2-(4-Methoxyphenyl)-3-methylquinoline (entry 3, Table 2). ^{1}H NMR: δ 8.05 (s, 1H), 7.98 (d, 1H, J = 8.4 Hz), 7.78 (d, 1H, J = 8.0 Hz), 7.62 (d, 2H, J = 8.4 Hz), 7.60 (t, 1H, J = 8.0 Hz), 7.46(t, 1H, J = 8.0 Hz), 7.00 (d, 2H, J = 8.4 Hz), 3.85 (s, 3H), 2.52 (s, 3H). ^{13}C NMR: δ 165.68, 165.29, 152.83, 142.07, 139.36, 136.22, 135.02, 134.75, 133.88, 133.24, 132.28, 131.54, 118.82, 60.30, 25.95. MS: *m*/*e* 249, 248 (bp), 233, 218, 204, 124, 102, 89, 63. Oily liquid.

2-(2-Methoxyphenyl)-3-methylquinoline (entry 4, Table 2). ^{1}H NMR: δ 7.98 (s, 1H), 7.96 (d, 1H, J = 8.0 Hz), 7.79 (d,

1H, J = 8.0 Hz), 7.59 (t, 1H, J = 7.6 Hz), 7.47 (t, 1H, J = 7.6 Hz), 7.39 (t, 1H, J = 7.2 Hz), 7.29 (d, 1H, J = 7.2 Hz), 7.05 (m, 2H), 3.74 (s, 3H), 2.28 (s, 3H). ^{13}C NMR: δ 164.91, 162.78, 152.70, 140.21, 136.74, 136.60, 136.11, 135.11, 134.96, 133.64, 133.54, 132.34, 131.58, 126.06, 116.29, 60.36, 24.19. MS: *m/e* 249, 248 (bp), 233, 218, 204, 124, 102, 89, 63. Oily liquid.

3-Methyl-2-(4-pyridyl)quinoline (entry 5, Table 2). ^{1}H NMR: δ 8.76 (dd, 2H, J = 4.8, 1.2 Hz), 8.09 (d, 1H, J = 8.8 Hz), 8.05 (s, 1H), 7.81 (m, 1H), 7.69 (t, 1H, J = 6.8 Hz), 7.54 (m, 3H), 2.47 (s, 3H). ^{13}C NMR: δ 157.82, 149.96, 148.97, 146.97, 137.65, 129.69, 129.64, 129.58, 128.90, 128.22, 127.48, 127.17, 20.59. MS: *m/e* 220, 219 (bp), 192, 110, 95, 83. Oily liquid.

2-(4-(Dimethylamino)phenyl)-3-methylquinoline (entry 7, Table 2). ^{1}H NMR: δ 7.99 (s, 1H), 7.97 (d, 1H, J = 7.6 Hz), 7.74 (d, 1H, J = 7.6 Hz), 7.60 (m, 3H), 7.42(t, 1H, J = 6.8 Hz), 6.81 (d, 2H, J = 8.8 Hz), 3.00 (s, 6H), 2.55 (s, 3H). ^{13}C NMR: δ 165.68, 156.28, 152.96, 141.95, 135.97, 134.95, 134.80, 133.69, 133.01, 132.23, 131.12, 117.08, 45.33, 26.30. MS: *m/e* 262, 261 (bp), 245, 217, 130, 108, 89, 63. Oily liquid.

3-Methyl-2-(1-naphthyl)quinoline (entry 8, Table 2). ^{1}H NMR: δ 8.15 (s, 1H), 8.02 (d, 1H, J = 8.4 Hz), 7.95 (d, 2H, J = 8.4 Hz), 7.88 (d, 1H, J = 8.0 Hz), 7.64 (t, 1H), 7.58−7.34 (m, 6H), 2.18 (s, 3H). ^{13}C NMR: δ 165.90, 152.77, 144.91, 141.34, 139.57, 137.46, 136.22, 135.23, 134.08, 133.97, 133.79, 133.74, 132.57, 132.05, 131.90, 131.75, 131.40, 131.26, 130.90, 24.68 ppm. MS: *m/e* 269, 268 (bp), 267, 253, 133, 89, 63. Oily liquid.

6-(Dimethylamino)-3-methyl-2-phenylquinoline (entry 9, Table 2). ^{1}H NMR: δ 8.22 (d, 1H, J = 9.2 Hz), 7.70 (m, 2H), 7.47 (s, 1H), 7.24 (m, 2H), 7.17 (m, 1H), 6.97 (dd, 1H, J = 9.2, 2.8 Hz), 6.61 (d, 1H, J = 2.4 Hz), 2.52 (s, 6H), 2.21 (s, 3H). ^{13}C NMR: δ 156.49, 148.86, 142.34, 142.16, 135.05, 130.85, 129.88, 129.60, 129.26, 128.21, 127.78, 119.07, 104.55, 40.37, 20.90. Oily liquid. MS: *m/e* 262, 261 (bp), 245, 217, 202, 130, 122, 96, 63. Anal. Calcd: C 82.39; H 6.92; N 10.69. Found: C 82.46; H 7.02; N 10.52.

3-Methyl-2-pheny-6-(*N*-phenylamino)quinoline (entry 10, Table 2). ^{1}H NMR: δ 7.85 (d, 1H, J = 10.0 Hz), 7.84 (s, 1H), 7.68 (s, br, 1H), 7.63 (m, 2H), 7.45−7.37 (m, 5H), 7.34−7.20 (m, 4H), 6.90 (m, 1H), 2.44 (s, 3H). ^{13}C NMR: δ 162.31, 149.09, 148.69, 147.94, 147.40, 140.43, 136.07, 134.90, 134.78, 134.67, 133.33, 133.08, 127.97, 126.48, 123.87, 119.75, 113.27, 25.73. MS: *m/e* 310 (bp), 309, 217, 154, 77, 51. Yellow solid.

6-Cyclohexyl-3-methyl-2-phenylquinoline (entry 11, Table 2). ^{1}H NMR: δ 8.29 (d, 1H, J = 8.8 Hz), 7.63 (d, 2H, J = 7.2 Hz), 7.50 (s, 1H), 7.35 (s, 1H), 7.29−7.15 (m, 4H), 2.46 (m, 1H), 2.16 (s, 3H), 1.86−1.71 (m, 5H), 1.39−1.25 (m, 5H). ^{13}C NMR: δ 159.74, 146.80, 146.18, 141.97, 136.54, 130.08, 129.77, 129.23, 129.03, 128.33, 128.26, 128.14, 123.58, 44.87, 34.71, 27.25, 26.55, 20.76. MS: *m/e* 301, 300 (bp), 281, 244, 207, 115, 96, 73. White solid.

6-*tert*-Butyl-3-methyl-2-phenylquinoline (entry 12, Table 2). ^{1}H NMR: δ 8.04 (s, 1H), 7.93 (d, 1H, J = 8.8 Hz), 7.76 (d, 1H, J = 8.8 Hz), 7.75 (s, 1H), 7.63 (d, 2H, J = 8.0 Hz), 7.46−7.38 (m, 3H), 2.48 (s, 3H), 1.44 (s, 9H). ^{13}C NMR: δ 164.97, 154.54, 151.39, 147.23, 142.19, 134.89, 134.69, 134.42, 133.40, 133.37, 133.11, 132.91, 127.32, 40.38, 36.39, 25.70. MS: *m/e* 275, 274 (bp), 260, 2245, 231, 217, 115. White solid.

3,8-Dimethyl-2-phenylquinoline (entry 14, Table 2). ^{1}H NMR: δ 8.05 (s, 1H), 7.67−7.63 (m, 3H), 7.49−7.36 (m, 5H), 2.75 (s, 3H), 2.51 (s, 3H). ^{13}C NMR: δ 164.35, 151.62, 147.39, 142.85, 142.55, 134.98, 134.36, 134.16, 133.46, 133.42, 133.34, 131.67, 130.39, 25.60, 22.87. MS: *m/e* 233, 232 (bp), 217, 127, 115, 102, 77, 63. Oily liquid.

3,6-Dimethyl-2-phenylquinoline (entry 1, Table 3). ^{1}H NMR: δ 8.22 (d, 1H, J = 8.8 Hz), 7.61 (m, 2H), 7.44 (s, 1H), 7.24−7.13 (m, 5H), 2.18 (s, 3H), 2.14 (s, 3H).^{13}C NMR: δ 159.70, 146.40, 141.90, 136.16, 136.09, 131.17, 129.92, 129.74, 129.18, 128.26, 128.15, 128.09, 125.91, 21.61, 20.75. MS: *m/e* 233, 232 (bp), 115, 89, 77, 63. Oily liquid.

6-Methoxy-3-methyl-2-phenylquinoline (entry 3, Table 3). ^{1}H NMR: δ 8.27 (d, 1H, J = 9.2 Hz), 7.72 (d, 2H, J = 7.6 Hz), 7.49 (s, 1H), 7.33−7.22 (m, 4H), 6.80 (d, 1H), 3.44 (s, 3H), 2.26 (s, 3H). ^{13}C NMR: δ 163.75, 163.05, 148.87, 147.23, 141.07, 136.46, 134.91, 134.79, 134.39, 133.40, 133.25, 126.82, 109.75, 60.55, 25.73. MS: *m/e* 249, 248 (bp), 217, 205, 124, 102, 77. Yellow solid.

3,5,7-Trimethyl-2-phenylquinoline (entry 4, Table 3). ^{1}H NMR: δ 8.02 (s, 1H), 7.73 (s, 1H), 7.66 (d, 2H, J = 8.0 Hz), 7.24 (t, 2H, J = 8.0 Hz), 7.16 (t, 1H, J = 7.6 Hz), 6.88 (s, 1H), 2.31 (s, 3H), 2.19 (s, 3H), 2.18 (s, 3H). ^{13}C NMR: δ 159.87, 148.35, 142.03, 138.33, 133.18, 129.79, 129.41, 128.26, 128.15, 127.98, 127.85, 127.64, 125.38, 21.75, 20.94, 18.47. MS: *m/e* 247, 246 (bp), 230, 216, 122, 115, 102, 77, 63. Light yellow solid. Anal. Calcd: C 87.40; H 6.93; N 5.67. Found: C 87.24; H 6.96; N 5.70.

6-Chloro-3-methyl-4-phenylquinoline (entry 5, Table 3). ^{1}H NMR: δ 8.04 (s, 1H), 8.00 (d, 1H, J = 4.8 Hz), 7.80 (s, 1H), 7.63 (m, 3H), 7.45 (m, 3H), 2.49 (s, 3H). ^{13}C NMR: δ 166.21, 151.07, 146.65, 141.36, 137.32, 136.92, 136.07, 134.90, 134.84, 134.05, 133.77, 133.55, 131.16, 25.74. MS: *m/e* 253, 252 (bp), 217, 207, 125, 108, 79, 63. Yellow solid.

3-Methyl-2,6-diphenylquinoline (entry 6, Table 3). ^{1}H NMR: δ 8.33 (d, 1H, J = 8.8 Hz), 7.72 (d, 1H, J = 1.6 Hz), 7.66−7.63 (m, 3H), 7.53 (m, 2H), 7.47 (s, 1H), 7.25−7.11 (m, 6H), 2.14 (s, 3H). ^{13}C NMR: δ 160.51, 147.13, 141.76, 141.23, 139.40, 137.00, 130.64, 129.74, 129.59, 129.22, 128.76, 128.20, 128.09, 127.97, 127.61, 127.17, 124.82, 20.77. MS: *m/e* 295, 294 (bp), 207, 147, 115, 77, 51. White solid. Anal. Calcd: C 89.45; H 5.81; N 4.75. Found: C 88.88; H 5.87; N 4.87.

Reaction of *N*-Phenyl-4-(dimethylamino)benzaldehyde Imine (Table 2, entry 7) with $Co_2(CO)_8$ and CO. In an NMR experiment, 11.6 mg of the imine was dissolved in 0.7 mL of THF-d_8 and 10.0 mg of $Co_2(CO)_8$ (0.5 equiv), in a glovebox. The reaction mixture was freeze−pump−thawed three times to remove any dissolved nitrogen and then CO was introduced at 1 atm. The sample was heated in an oil bath at 120 °C. Complete consumption of starting material to form a single product was observed when followed by NMR in two weeks. This product was isolated by using preparative TLC and identified as 6-(dimethylamino)-*N*-phenylphthalimidine. ^{1}H NMR: δ 7.86 (m, 2H, J = 8.8 Hz), 7.40 (m, 2H), 7.32 (d, 1H, J = 8.4 Hz), 7.18 (d, 1H, J = 2.4 Hz), 7.14 (m, 1H), 6.95 (dd, 1H, J = 8.4, 2.4 Hz), 4.74 (s, 2H), 3.00 (s, 6H). ^{13}C NMR: δ 168.62, 151.34, 140.23, 134.45, 129.41, 128.13, 124.49, 123.26, 119.70, 117.29, 106.79, 50.59, 41.17. MS: *m/e* 252 (bp), 251, 224, 208, 89, 77, 51.

Screening of Other Organometallic Compounds. The following complexes were screened for catalytic activity and showed no reaction toward diallylaniline at 120 °C: $Ni(cod)_2$, $(Cy_3P)_2Ni(CH_2{=}CH_2)$, $Mn_2(CO)_{10}$, $Mo(CO)_6$, $(CH_3CN)_3Mo(CO)_3$, $(CH_3CN)_3W(CO)_3$, $(Ph_3P)_2Ni(CO)_2$, $(Ph_3P)_2Rh(Cl)(CO)$, $(Ph_3P)_3Ru(Cl)(H)(CO)$, and Rh_6CO_{16} (cod = cyclooctadiene, Cy = cyclohexyl).

Complexes $(Ph_3P)_3Rh(H)(CO)$, $Ru_3(CO)_{12}$, and $[(cod)RhCl]_2$ led to a complex mixture of reaction products at 120 °C. When $[(dippe)NiH]_2$ [dippe = 1,2-bis(diisopropylphosphino)ethane] was reacted with diallylaniline (1:1), a nickel−olefin complex was formed at both double bonds. This complex decomposed on heating at 100 °C. Complexes $[(Ph_3P)_3Co(CH_2CH_2)]_2$ and $(Ph_3P)_3Co(H)(N_2)$ caused isomerization of both double bonds to the enamine in a fast reaction when treated with diallylaniline.

Acknowledgment is made to the National Science Foundation (CHE-9616601) for their support of this work.

Supporting Information Available: A description of the kinetics of the reaction of diallylaniline with $Co_2(CO)_8$. This material is available free of charge via the Internet at http://pubs.acs.org.

JO026737J