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Note

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Copper-Catalyzed Synthesis of Substituted Quinolines *via* C-N Coupling/Condensation from *ortho*-Acylanilines and Alkenyl Iodides

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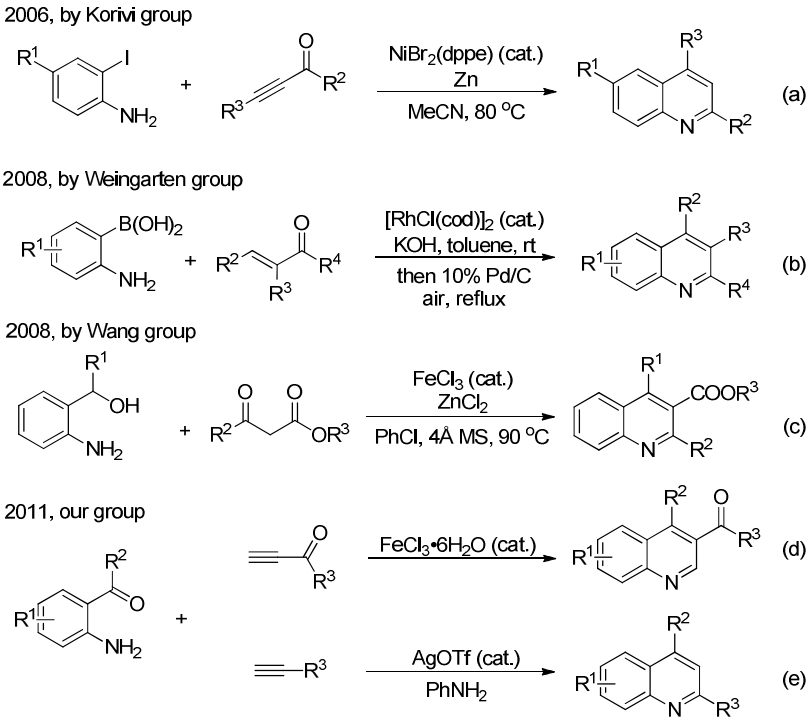
Abstract. An efficient cascade copper-catalyzed intermolecular Ullmann-type C-N coupling/enamine condensation reaction is described, in which *ortho*-acylanilines and alkenyl iodides converted to multi-substituted quinolines in good to excellent yields.

Quinolines are widely found in natural products[1] and broadly used in medicinal chemistry particularly as antiviral, anticancer, antituberculosis, and antimalarial agents.[2] Furthermore, quinolines as building blocks were applied to prepare functional materials with enhanced physical properties.[3] The traditional methods for constructing quinolines include the Combes synthesis from anilines and 1,3-diketones, the Skraup synthesis from anilines and glycerins, and the Friedlander (Pfitzinger, Niementowski) synthesis from *ortho*-acylanilines and α-methylene aldehydes/ketones.[4] In recent years, new approaches based on transition-metal-catalyzed C-N/C-C bond formation attracted much attention due to mild reaction conditions and expanded substrate scope.[5] Among them, *ortho*-substituted anilines as important starting materials has a special position in the synthesis of quinolines. In 2006, A novel cascade reaction of nickel-catalyzed Michael addition/deiodination was developed by Korivi group

(Scheme 1, a).[5j] In 2008, Weingarten and coworkers reported a two-step method from *ortho*-amino arylboronic acids *via* rhodium-catalyzed conjugate addition and direct palladium-catalyzed borylation (Scheme 1, b).[5g] In the same year, a useful cascade synthesis of substituted 3-quinolinecarboxylic esters *via* iron-catalyzed benzylation/cyclization was achieved by Wang group (Scheme 1, c).[5h] During the course of our ongoing study on the development of transition-metal-mediated heterocycle-forming protocols,[6] we have reported two methods for yielding 2,4- and 3,4-substituted quinolines from *ortho*-acylanilines and alkynones or alkynes catalyzed by Fe or Ag, respectively (Scheme 1, d-e).[7]

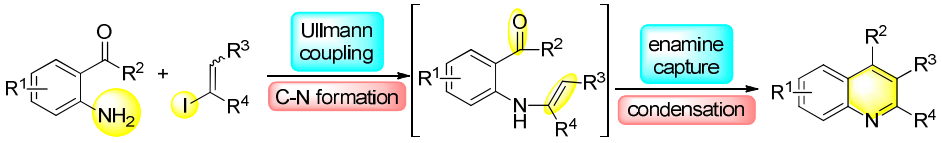
Scheme 1. Metal-Catalyzed Synthesis of Quinolines from *ortho*-Substituted Anilines



Regarding the economy and easy-handle-system of copper-catalyzed C-N coupling, important breakthroughs with the discovery of versatile and very efficient new copper/ligand systems have led to a spectacular resurgence of interest in Ullmann-type reactions in the last decade.[8] More recently, ligand-assisted copper catalyzed modern versions of the Ullmann-Goldberg reactions between vinyl halides and amides have been developed.[9] However, few reports focused on *N*-vinylation of amines, especially in which *ortho*-substituted anilines as substrate only gave moderate yield.[10] The difficulties might be

caused by the bulky groups around the reactive site and unstable enamine products. We envisioned that if anilines bearing an *ortho*-substituted electrophilic group were employed, it might capture the reactive enamine formed through the C-N coupling reaction to undergo further intramolecular cyclization (Scheme 2). Herein, we reported a cascade copper-catalyzed intermolecular Ullmann-type C-N coupling/enamine condensation reaction for the synthesis of substituted quinolines starting from *ortho*-acylanilines and alkenyl iodides. This is the first report of Ullmann coupling reactions using sterically hindered aniline derivatives and vinyl halides as substrates to prepare quinoline derivatives, to the best of our knowledge.

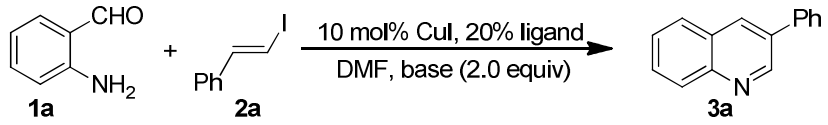
Scheme 2. Synthesis of Quinolines *via* C-N Coupling/Condensation from *ortho*-Acylanilines



The reaction of 2-aminobenzaldehyde (**1a**) with 2 equiv of (*E*)-1-(2-iodovinyl)benzene (**2a**) was screened to optimize reaction conditions, and the results are summarized in Table 1. Initially, our investigation began with an attempt of **1a**, using 10 mol % of CuI as catalyst, 20 mol % *N,N′*-dimethylethylenediamine (DMEDA) as ligand and 2.0 equiv of K_2CO_3 as base in DMF at 130 ^oC under N_2 atmosphere (entry 1). The desired quinoline derivative **3a** could be isolated in 72% yield within 6 h. This result encouraged us to examine various common ligands, such as *N,N,N′,N′*-tetramethylethylenediamine (TMEDA), *N,N′*-dimethyl-1,2-cyclohexanediamine (DMCHDA), 1,10-phenanthroline, 2,2'-dipyridyl, *DL*-proline, and glycine, and the target product **3a** was obtained in 35%-91% yields (entries 2-7). To our delight, the glycine which is commercially available has the highest activity for this reaction (91% yield, entry 7). Then the reaction conditions were further investigated, and the results showed that 10 h reaction time-span, 130 ^oC reaction temperature and nitrogen atmosphere were essential for this catalytic system (entries 7-10). The excellent yield (95%) of **3a** could be achieved under these reaction conditions while only 36% yield under ambient air (entry 8 vs 10).

Finally, the effect of base were evaluated, and the further studies showed that other bases like Na_2CO_3 and ^tBuOK were less effective affording 43% and 35% yield, respectively (entries 11 and 12).

Table 1. Optimization of Reaction Conditions [a]

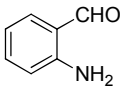
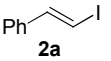
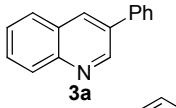
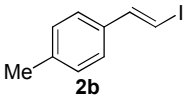
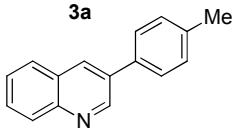
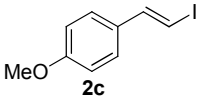
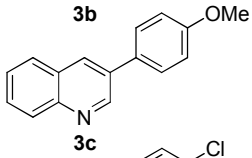
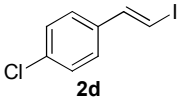
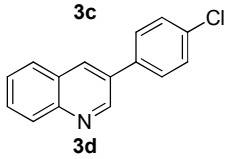
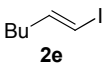
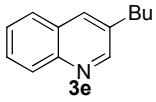
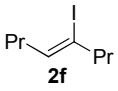
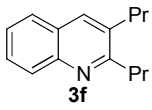
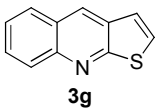
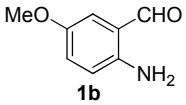
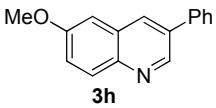
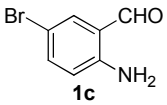
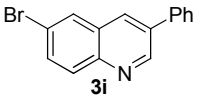
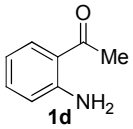
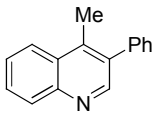
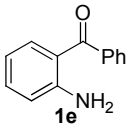
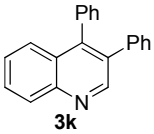


entry	ligand	base	temperature (°C)	time (h)	yield (%) [b]
1	DMEDA	K_2CO_3	130	6	72
2	TMEDA	K_2CO_3	130	6	67
3	DMCHDA	K_2CO_3	130	6	89
4	1,10-phenanthroline	K_2CO_3	130	6	75
5	2,2'-dipyridyl	K_2CO_3	130	8	35
6	*DL*-proline	K_2CO_3	130	6	62
7	glycine	K_2CO_3	130	6	91
8	glycine	K_2CO_3	130	10	95
9	glycine	K_2CO_3	100	20	62
10[c]	glycine	K_2CO_3	130	10	36
11	glycine	^tBuOK	130	16	35
12	glycine	Na_2CO_3	130	10	43

[a] Unless otherwise noted, all reactions were carried out under N_2 atmosphere in 0.5 mmol scale with the ratio of **1a**:**2a** = 1:2. [b] Isolated yield. [c] The reaction was carried out under air.

With the standard reaction conditions (Table 1, entry 8), the substrate scope of the reaction by employing a variety of *ortho*-acylanilines **1** and alkenyl iodides **2** was explored. Firstly, the screening of different structures of alkenyl iodides **2** with 2-aminobenzaldehyde **1a** was summarized in Table 2, entries 1-7. For aryl alkenyl iodides **2a**-**2d**, the substrates with electron-donating substituents on the benzene ring offered higher yields (88% and 92%) compared with those with electron-withdrawing substituents on the benzene ring (69%) (entries 2 and 3 vs 4). For alkyl alkenyl iodides **2e** and **2f**, the reaction also proceeded well, and **3e** and **3f** were obtained in 72% and 78% yields, respectively (entries 5 and 6). Remarkably, raising the temperature to 160 °C in DMA, the heterocyclic iodides **2g** gave

Table 2. Synthesis of Various Quinoline 3 [a]

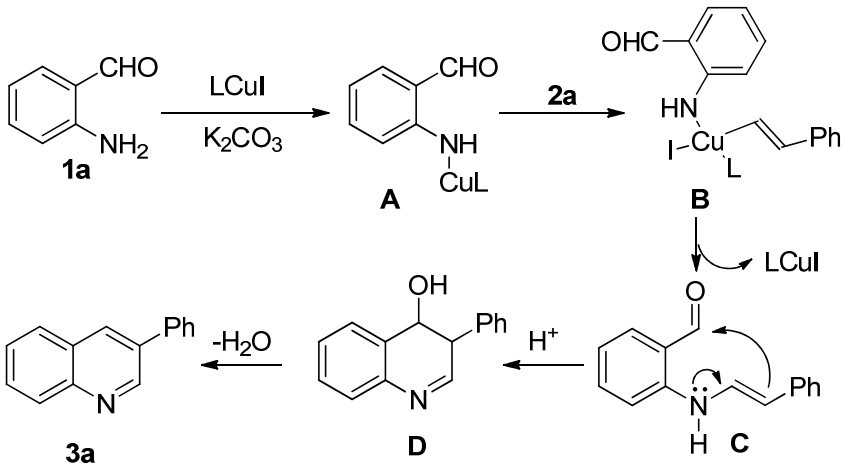
entry	substrate	vinyliodo	product	time (h)	yield (%) [b]
1	 **1a**	 **2a**	 **3a**	10	95
2	**1a**	 **2b**	 **3b**	10	88
3	**1a**	 **2c**	 **3c**	15	92
4	**1a**	 **2d**	 **3d**	20	69
5	**1a**	 **2e**	 **3e**	25	78
6	**1a**	 **2f**	 **3f**	25	72
7[c]	**1a**	 **2g**	 **3g**	20	57
8	 **1b**	**2a**	 **3h**	20	78
9	 **1c**	**2a**	 **3i**	15	84
10	 **1d**	**2a**	 **3j**	12	83
11	 **1e**	**2a**	 **3k**	15	93

[a] Unless otherwise noted, all reactions were carried out under N_2 atmosphere in 0.5 mmol scale with the ratio of **1a**:**2a** = 1:2. [b] Isolated yield. [c] The reaction carried out at 160 °C in DMA.

moderate yield (57%) of desired product **3g** (entry 7). Secondly, the different substituted *ortho*-acylanilines **1b-1e** were examined in this catalytic system, resulting in 78%-93% yields of the desired quinolines (entries 8-11). Furthermore, 3,4-substituted quinolines **3j** and **3k** could be smoothly accessed

under the exact same conditions using *ortho*-aminophenyl ketones **1d** and **1e** as substrate in high yields (83% and 93%), of which the synthetic methods are not very sufficient (entries 10 and 11).[5-7]

Scheme 3. A Proposed Mechanism



On the basis of the reported work,[11] a plausible mechanism is proposed with model substrates **1a** and **2a** as outlined in Scheme 3. The process began with the ligand exchange with 2-aminobenzaldehyde **1a** affords copper-coordinated intermediate **A** in the presence of K_2CO_3. Then, alkenyl iodide **2a** reacts with intermediate **A** through oxidative addition, furnishing the intermediate **C** after reductive elimination. Intramolecular cyclization of the *ß*-carbon of enamine **C** to acyl group forms intermediate **D**, which further undergoes aromatization to give the desired quinoline **3a**.

In conclusion, we have developed an efficient procedure of the cascade copper-catalyzed C-N coupling/cyclization reaction to construct various substituted quinoline derivatives. This catalytic system, which sterically hindered anilines and vinyl iodides were used in Ullmann coupling reactions, gave a variety of 3- or 3,4-substituted quinolines in good to excellent yields.

Experimental Section

High-resolution mass spectra were performed on a mass spectrometer with a TOF (for EI or ESI) or FT-ICR (for MALDI) analyzer.

Typical Procedure. To a solution of *ortho*-acylaniline **1** (0.5 mmol) in DMF (2.0 mL) was added alkenyl iodide **2** (1.0 mmol), copper(I) iodide (9.5 mg, 0.05 mmol), glycine (7.5 mg, 0.1 mmol) and K_2CO_3 (138.2 mg, 1.0 mmol) at room temperature. Then the mixture was slowly warmed up to 130 ^oC and stirred for corresponding time. After that the mixture was quenched with deionized water, extracted with ethyl acetate, washed with brine and dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to afford product **3**.

*3-Phenylquinoline (**3a**)*:[12] Yellow oil, 95% yield (98 mg). ^1H NMR (400 MHz, $CDCl_3$) δ7.42-7.59 (m, 4H), 7.70-7.74 (m, 3H), 7.87 (d, J = 7.6 Hz, 1H), 8.15 (d, J = 8.4 Hz, 1H), 8.29 (d, J = 2.0 Hz, 1H), 9.20 (d, J = 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 127.0, 127.4, 128.0, 128.1 (2C), 129.2, 129.2, 129.4, 133.2, 133.8, 137.9, 147.4, 150.0.

*3-(p-Tolyl)quinoline (**3b**)*:[13] Light yellow solid, 88% yield (96 mg), mp 81-82 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 2.44 (s, 3H), 7.34 (d, J = 7.6 Hz, 2H), 7.57 (t, J = 7.6 Hz, 1H), 7.62 (d, J = 8.0 Hz, 2H), 7.71 (t, J = 7.2 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 8.13 (d, J = 8.4 Hz, 1H), 8.28 (d, J = 2.0 Hz, 1H), 9.18 (d, J = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 127.0, 127.3, 128.0, 128.1, 129.3 (2C), 130.0, 132.9, 133.8, 135.0, 138.1, 147.3, 150.0.

*3-(4-Methoxyphenyl)quinoline (**3c**)*:[12] Light yellow solid, 92% yield (108 mg), mp 80-81 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 3.85 (s, 3H), 7.01-7.06 (m, 2H), 7.53-7.56 (m, 1H), 7.61-7.70 (m, 3H), 7.82 (t, J = 7.2 Hz, 1H), 8.12 (d, J = 8.4 Hz, 1H), 8.20 (d, J = 5.6 Hz, 1H), 9.15 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.3, 114.6, 126.9, 127.8, 128.1, 128.5, 129.0, 129.2, 130.2, 132.3, 133.4, 147.0, 149.8, 159.8.

*3-(4-Chlorophenyl)quinoline (**3d**)*:[13] Light yellow solid, 69% yield (82 mg), mp 149-150 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ7.45 (d, J = 8.0 Hz, 2H), 7.53-7.60 (m, 3H), 7.71 (t, J = 8.0 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 8.13 (d, J = 8.6 Hz, 1H), 8.21 (s, 1H), 9.11 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 127.1, 127.8, 128.0, 128.6, 129.2, 129.3, 129.6, 132.5, 133.1, 134.3, 136.2, 147.4, 149.4.

*3-Butylquinoline (**3e**)*:[14] Light yellow oil, 78% yield (72 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (t, J = 7.6 Hz, 3H), 1.34-1.40 (m, 2H), 1.62-1.68 (m, 2H), 2.74 (t, J = 7.6 Hz, 2H), 7.47 (t, J = 7.2 Hz, 1H), 7.61 (t, J = 7.2 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.85 (s, 1H), 8.06 (d, J = 8.6 Hz, 1H), 8.76 (d, J = 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 22.0, 32.7, 33.0, 126.4, 127.2, 128.1, 128.4, 129.1, 134.0, 135.3, 146.7, 152.1.

*2,3-Dipropylquinoline (**3f**)*: Light yellow oil, 72% yield (76 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98-1.09 (m, 6H), 1.66-1.76 (m, 2H), 1.79-1.89 (m, 2H), 2.75 (t, J = 8.0 Hz, 2H), 2.95 (t, J = 8.0 Hz, 2H), 7.42 (t, J = 7.2 Hz, 1H), 7.59 (t, J = 7.8 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.81(s, 1H), 8.02 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 14.2, 22.8, 23.4, 34.3, 37.7, 125.5, 126.9, 127.2, 128.3, 128.5, 133.9, 134.8, 146.5, 162.1. HRMS (EI) for $C_{15}H_{19}N$ [M^+] calcd 213.1517, found 213.1521.

*Thieno[2,3-b]quinoline (**3g**)*:[15] Light yellow oil, 57% yield (52 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 6.0 Hz, 1H), 7.52-7.58 (m, 2H), 7.72-7.77 (m, 1H), 7.95 (d, J = 8.0 Hz, 1H), 8.15-8.18 (m, 1H), 8.52 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 121.2, 125.5, 125.6, 128.3, 128.4, 128.5, 129.3, 130.1, 131.5, 146.7, 163.4.

*6-Methoxy-3-phenylquinoline (**3h**)*:[13] Light yellow solid, 78% yield (92 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.96 (s, 3H), 7.14 (d, J = 2.4 Hz, 1H), 7.38 (dd, J = 2.4, 9.2 Hz, 1H), 7.44 (t, J = 7.6 Hz, 1H), 7.53 (t, J = 7.6 Hz, 2H), 7.71 (d, J = 7.6 Hz, 2H), 8.03 (d, J = 9.2 Hz, 1H), 8.21 (s, 1 H), 9.03 (d, J = 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.5, 105.3, 122.3, 127.5, 128.1, 129.2, 129.2, 130.7, 132.2, 134.2, 138.1, 143.6, 147.5, 158.2.

*6-Bromo-3-phenylquinoline (**3i**)*:[13] Light yellow solid, 84% yield (119 mg), mp 114-115 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (t, J = 7.6 Hz, 1H), 7.53 (t, J = 8.0 Hz, 2H), 7.68-7.70 (m, 2H), 7.70 (dd, J = 2.0, 8.8 Hz, 1H), 7.98-8.02 (m, 2H), 8.18 (d, J = 2.4 Hz, 1H), 9.17 (d, J = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 120.9, 127.5, 128.5, 129.2, 129.3, 130.0, 131.0, 132.1, 132.8, 134.7, 137.4, 145.9, 150.4.

*4-Methyl-3-phenylquinoline (**3j**)*: Light yellow solid, 83% yield (90 mg), mp 58-61 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.50 (s, 3H), 7.25-7.38 (m, 5H), 7.46 (t, J = 7.6 Hz, 1H), 7.58 (t, J = 7.6 Hz, 1H), 7.93

(d, J = 8.4 Hz, 1H), 8.03 (d, J = 8.4 Hz, 1H), 8.70 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.4, 124.1, 126.6, 127.5, 127.9, 128.4, 128.8, 129.9, 129.9, 134.3, 138.5, 140.5, 146.9, 151.5. HRMS (ESI) for $C_{16}H_{14}N$ [M+H$^+$] calcd 220.1126, found 220.1123.

*3,4-Diphenylquinoline (**3k**)*:[16] Light yellow solid, 93% yield (130 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17-7.24 (m, 7H), 7.33-7.35 (m, 3H), 7.47 (t, J = 7.6 Hz, 1H), 7.69-7.73 (m, 2H), 8.20 (d, J = 8.0 Hz, 1H), 9.01 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 126.6, 126.9, 127.1, 127.2, 127.7, 128.1, 128.2, 129.1, 129.5, 130.2, 130.5, 133.1, 136.3 138.1, 145.5, 147.6 151.9.

Supporting Information Available. NMR spectra for all products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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