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An Efficient Synthesis of Substituted Quinolines *via* Indium(III) Chloride Catalyzed Reaction of Imines with Alkynes

Mei Zhu,[†] Weijun Fu,[†,*] Chen Xun,[†] and Guanglong Zou[‡]

[†]*College of Chemistry and Chemical Engineering, Luoyang Normal University, Luoyang 471022, P.R. China*
[*]*E-mail: wjfu@lynu.edu.cn*
[‡]*School of Chemistry and Environmental Science, Guizhou University for Nationalities, Guiyang 550025, P.R. China*
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An efficient synthetic method for the preparation of quinolines through indium(III) chloride-catalyzed tandem addition-cyclization-oxidation reactions of imines with alkynes was developed. The processes can provide a diverse range of quinoline derivatives in good yields from simple imines and alkynes.

Key Words : Indium(III), Quinoline, Imine, Alkyne

Introduction

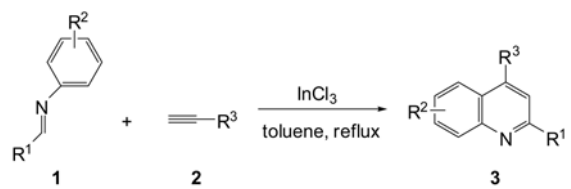
Quinolines represent an important class of heterocyclic compounds as they are pivotal skeletons in many biologically active natural products as well as numerous pharmacologically interesting compounds.[1] A variety of compounds with quinoline units have been used as anesthetic, tumorcidal, angina pectoris, antihypertensive, and antibacterial activities and also act as insecticidal agents.[2] Moreover, quinolines also found wide utility as synthetic intermediates or synthons for formation of conjugated molecules and polymers or ligands for the preparation of OLED phosphorescent complexes.[3] As a consequence, much attention has been paid to synthesize and functionalize them since the late 1800s. In addition to classical methods (e.g., the Conrad-Limpach-Knorr synthesis,[4] the Skraup synthesis,[5] and the Friedländer synthesis[6]), numerous transition-metal-catalyzed heteroannulation reactions have been developed with remarkable improvements in terms of efficiency and wide scope of application.[7] These include rhodium-catalyzed cyclization of trifluoroacetimidoyl chloride with alkynes,[8] Zn(II), indium (III) or gold(I)-catalyzed cyclization of 2-aminoaryl ketones with alkynes.[9] Nevertheless, the development of new and efficient methodologies for the synthesis of substituted quinolines from simple, readily available starting materials remains an important research theme in organic chemistry despite many strategies already existed.[10]

Indium salts as effective, alternative, and promising transition-metal catalysts have received much more attention in recent years because of their intriguing chemical properties of reactivity, selectivity, and low toxicity.[11] Over the past decade, many efficient indium-mediated organic reactions such as the Diels-Alder,[12] Friedel-Crafts,[13] Mukaiyama aldol,[14] Sakurai-Hosomi allylation reactions[15] and other specific reactions[16] have been intensively investigated. Recently, the design of indium-catalyzed hydroarylation of alkynes has attracted attention because of the application to efficient construction of molecular structures.[17] As a continuation of our interest in the design and discovery of new reactions for the synthesis of heterocycles,[18] herein we present our recent results on the $InCl_3$-catalyzed tandem addition-cyclization-oxidation reactions of imines with alkynes to afford quinoline derivatives (Scheme 1).

Results and Discussion

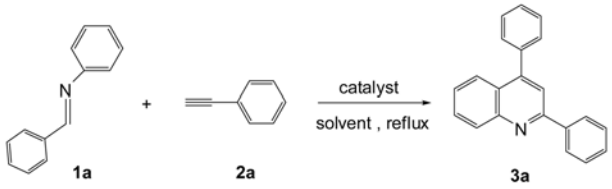
We focused our initial efforts on establishing optimal conditions for the tandem addition-cyclization-oxidation reactions between benzaldimine **1a** and phenylacetylene **2a**, which were selected as the first substrates for screening of the catalytic activity of a variety of indium salts, and the results are summarized in Table 1. The reaction of **1a** with **2a** in toluene at 120 °C in the absence of any catalyst did not yield any desired product (Table 1, entry 1). As anticipated, when 20 mol % of $InCl_3$ was used as catalyst, the tandem addition-cyclization-oxidation reactions proceeded smoothly and generated the desired product **3a** in 90% yield. Other indium salts such as $InBr_3$, InI_3, $In(CF_3SO_3)_3$, and $In(CH_3COO)_3$ were also active and the corresponding quinolines were obtained in 76, 78, 86, and 72% yields, respectively (Table 1, entries 3-6). With respect to the catalyst loading, 20 mol % of $InCl_3$ was found to be optimal. When a lower loading of $InCl_3$ (10 mol %), the reaction also proceeded but sluggishly (Table 1, entry 7). However, no significant improvement was observed with 30 mol % of $InCl_3$ (Table 1, entry 8). On using other solvent such as 1,4-dioxane, 1,2-dichloroethane, CH_3NO_2 the desired product **3a** could be isolated in slightly lower yield (Table 1, entries 9-11).

After having established the optimized conditions for the present reaction, various imine derivatives **1a-m** and terminal



Scheme 1. $InCl_3$-catalyzed reactions of imines with alkynes.

Table 1. Optimization of the reaction conditions[a]



Entry	Catalyst	Solvent	Time (h)	Yield (%)[b]
1	No catalyst	toluene	24	NR
2	$InCl_3$	toluene	24	90
3	$InBr_3$	toluene	24	76
4	InI_3	toluene	24	78
5	$In(OTf)_3$	toluene	24	86
6	$In(OAc)_3$	toluene	24	72
7[c]	$InCl_3$	toluene	36	88
8[d]	$InCl_3$	toluene	24	90
9	$InCl_3$	1,4-dioxane	30	62
10	$InCl_3$	DCE	36	68
11	$InCl_3$	CH_3NO_2	30	75

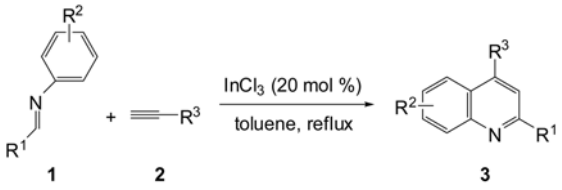
[a]Reaction conditions: **1a** (1 equiv), **2a** (1.5 equiv), catalyst (20 mol %), solvent (3.0 mL), unless otherwise noted. [b]Isolated yield. [c]In the present of $InCl_3$ (10 mol %). [d]In the present of $InCl_3$ (30 mol %).

alkynes **1n-q** were subjected to the above conditions, and the results are summarized in Table 2. As indicated, the addition-cyclization-oxidation reactions proceeded smoothly to provide the corresponding products **3a-q** in moderate to good yields. The reaction could tolerate various substituents on the aromatic groups. For imines **1** having electron-withdrawing group including chloro, fluoro and electron-donating group such as methoxy on the benzene ring, the reaction proceeded well to give the products **3**. In addition, the reaction was no sensitive to steric effects. For imines **1** with aryl groups including *o*-bromo, *m*-chloro, *o*-chloro and *o*-methyl, the desired products were also obtained in 80, 82, 81 and 83% yields, respectively (Table 2, entries 7-8 and 12-13). Subsequently, the scope of alkynes in this reaction was further investigated, and it was found that substituted phenylacetylenes with electron-donating or electron-withdrawing groups were perfectly suitable substrates for this transformation, and the expected products were obtained in moderate to excellent yields (Table 2, entries 14-17). Interestingly, aliphatic alkyne like 1-hexyne with benzaldimine **1a** also reacted smoothly to give 4-butyl-2-phenylquinoline **3r** in 75% yield (Table 2, entry 18).

To understand the reaction mechanism for the formation of quinolines, we conducted the reaction of the propargylamine **4** with $InCl_3$ (20 mol %) in toluene at 120 °C. As a consequence, the desired product **3a** was obtained in 85% yield after 24 h. This indicates that propargylamines are the most probable intermediates (Scheme 2).

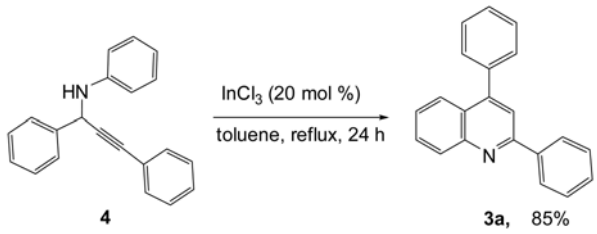
On the basis of the above observations, a plausible mechanisms is proposed for this $InCl_3$-catalyzed transformation (Scheme 3). Initially, The catalyst $InCl_3$ would be first reacted with terminal alkyne to form a stable In^{III} alkynyl ate complex **A**,[19] which then underwent nucleophilic addition to

Table 2. Synthesis of substituted quinolines[a]

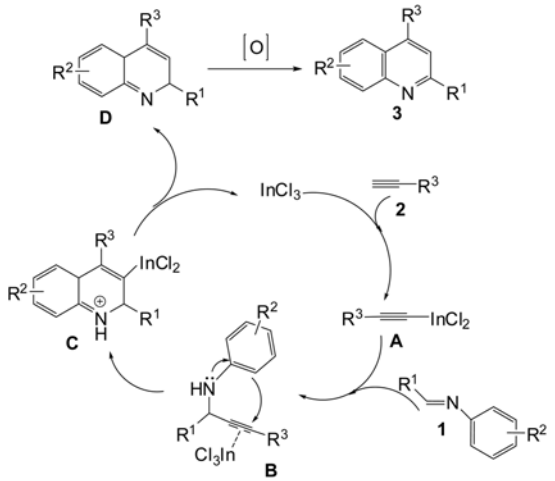


Entry	R^1, R^2	R^3	Yield (%)[b]
1	Ph, H	Ph	**3a**, 90
2	4-MeC_6H_4, H	Ph	**3b**, 92
3	4-$MeOC_6H_4$, H	Ph	**3c**, 89
4	4-ClC_6H_4, H	Ph	**3d**, 85
5	4-BrC_6H_4, H	Ph	**3e**, 88
6	4-FC_6H_4, H	Ph	**3f**, 83
7	2-BrC_6H_4, H	Ph	**3g**, 80
8	3-ClC_6H_4, H	Ph	**3h**, 82
9	Ph, 4-Me	Ph	**3i**, 85
10	Ph, 4-MeO	Ph	**3j**, 87
11	Ph, 4-Cl	Ph	**3k**, 89
12	Ph, 2-Cl	Ph	**3l**, 81
13	Ph, 2-Me	Ph	**3m**, 83
14	Ph, H	4-MeC_6H_4	**3n**, 88
15	Ph, H	4-$MeOC_6H_4$	**3o**, 90
16	Ph, H	4-ClC_6H_4	**3p**, 85
17	Ph, H	4-FC_6H_4	**3q**, 87
18	Ph, H	*n*-Bu	**3r**, 75

[a]Reaction conditions: **1** (0.5 mmoL), **2** (1.5 equiv), catalyst (20 mol %), toluene (3.0 mL) at reflux for 24 h. [b]Isolated yield.



Scheme 2. $InCl_3$-catalyzed cyclization of propargyl amine **4**.



Scheme 3. Possible mechanisms of the $InCl_3$-catalyzed transformation.

imine affording propargylamine **B**. $InCl_3$ as Lewis acid coordinates to the triple bond to enhance the electrophilicity of the alkyne. The subsequent intramolecular nucleophilic attack by the *N*-substituted aromatic ring to give intermediate **C**. Protonolysis of the resulting intermediate **C** gives dihydroquinoline **D** and regenerates the In(III) catalyst. In the presence of air oxygen, the generated dihydroquinoline could be oxidized by O_2 to afford the corresponding quinoline product **3**.

Conclusion

In conclusion, we have developed a $InCl_3$-catalyzed tandem addition-cyclization-oxidation reactions and applied the reaction for divergent syntheses of quinolines from readily available imines with alkynes. The method has advantages of broad substrate scope, simple operation, mild reaction conditions, and high effectiveness. Further studies, including the reaction mechanism and synthetic application of this methodology, are in progress.

Experimental Section. Chemicals used were obtained from commercial suppliers and used without further purifications. ^{1}H NMR spectra and ^{13}C NMR spectra were measured in $CDCl_3$ and recorded on Bruker Avance-400 spectrometer (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR) with TMS as an internal standard.

Typical Procedure for Synthesis of Quinolines 3. The mixture of imine **1** (0.5 mmoL), alkyne **2** (0.75 mmoL) and $InCl_3$ (20 mol %) in toluene (5 mL) was stirred at 120 °C until the substrates were consumed completely in a 25 mL two-necked round-bottom flask. The mixture was cooled to room temperature and the solvent was evaporated, the residue was purified by flash chromatography to give the corresponding product **3**.

2,4-Diphenylquinoline (3a)[6e]**.** ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (d, *J* = 8.4 Hz, 1H), 8.16-8.14 (m, 2H), 7.82-7.84 (m, 1H), 7.74 (s, 1H), 7.62-7.65 (m, 1H), 7.36-7.45 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.6, 148.9, 148.70, 139.4, 138.2, 130.0, 129.4, 129.3, 129.2,128.6, 128.4, 128.2, 127.4, 126.1, 125.6, 125.4, 119.1.

4-Phenyl-2-P-Tolylquinoline (3b)[7f]**.** ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (d, *J* = 8.4 Hz, 1H), 8.05 (d, *J* = 7.8 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.70 (s, 1H), 7.68-7.64 (m, 1H), 7.50-7.44 (m, 5H), 7.43-7.40 (m, 1H), 7.28 (d, *J* = 7.8 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.7, 148.8, 148.7, 139.5, 138.3, 136.9, 130.0, 129.5, 129.3, 128.5, 128.3, 127.3, 126.2, 125.6, 125.5, 119.3, 21.2.

2-(4-Methoxyphenyl)-4-Phenylquinoline (3c)[7h]**.** ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, *J* = 8.4 Hz, 1H), 8.16 (d, *J* = 8.8 Hz, 2H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.74 (s, 1H), 7.73-7.68 (m, 1H), 7.51-7.45 (m, 5H), 7.44-7.39 (m, 1H), 7.05 (d, *J* = 8.8 Hz, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.8, 156.3, 148.9, 148.7, 138.4, 132.1, 129.8, 129.5, 129.4, 128.8, 128.5, 128.3, 125.9, 125.6, 125.5, 118.8, 114.1, 55.3.

2-(4-Chlorophenyl)-4-Phenylquinoline (3d)[7g]**.** ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, *J* = 8.0 Hz, 1H), 8.17 (d, *J* = 8.4 Hz, 2H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.80-7.73 (m, 2H), 7.55-7.46 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.4, 149.4, 148.6, 138.1, 137.9, 135.5, 129.9,129.7, 129.5, 129.0, 128.9, 128.7, 128.6, 126.5, 125.8, 125.7, 118.8.

2-(4-Bromophenyl)-4-Phenylquinoline (3e)[7g]**.** ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, *J* = 8.4 Hz, 1H), 8.10 (d, *J* = 8.4 Hz, 2H), 7.85-7.79 (m, 1H), 7.76 (s, 1H), 7.74-7.68 (m, 1H), 7.62-7.58 (m, 2H), 7.52-7.41 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.4, 149.3, 148.7, 138.3, 138.1, 131.9, 129.9, 129.6, 129.5, 129.0, 128.6, 128.4, 126.5, 125.8, 125.6, 123.9, 118.7.

2-(4-Fluorophenyl)-4-Phenylquinoline (3f)[19]**.** ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23-8.17 (m, 3H), 7.90-7.88 (m, 1H), 7.77-7.73 (m, 2H), 7.54-7.47 (m, 6H), 7.25-7.18 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.5, 155.6, 149.3, 148.8, 138.3, 129.9, 129.7, 129.6, 129.4, 129.1, 129.0, 128.9, 128.5, 126.4, 125.6, 118.9, 117.7, 115.8, 115.5, 112.9.

2-(2-Bromophenyl)-4-Phenylquinoline (3g)[19]**.** ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.78-7.69 (m, 4H), 7.55-7.44 (m, 7H), 7.31-7.27 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.5, 148.6, 148.0, 141.4, 137.9, 133.1, 131.6, 130.0, 129.9, 129.8, 129.5, 128.6, 128.5, 127.7, 126.9, 125.6, 125.5, 122.8, 121.8.

2-(3-Chlorophenyl)-4-Phenylquinoline (3h)[7f]**.** ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, *J* = 8.4 Hz, 1H), 7.96-7.93 (m, 1H), 7.75-7.68 (m, 2H), 7.67 (s, 1H), 7.54-7.43 (m, 7H), 7.41-7.30 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.4, 148.5, 148.0, 139.4, 137.1, 132.3, 131.7, 130.0, 129.9, 129.8, 129.6, 129.5, 128.5, 128.3, 127.0, 126.7, 125.7, 125.5, 122.9.

6-Methyl-2,4-Diphenylquinoline (3i)[7c]**.** ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16-8.12 (m, 3H), 7.76 (s, 1H), 7.63 (s, 1H), 7.55-7.44 (m, 9H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.9, 148.3, 147.3, 139.7, 138.6, 136.3, 131.8, 129.8, 129.5, 129.1, 128.8, 128.5, 128.3, 127.4, 125.6, 124.3, 119.3, 21.8.

6-Methoxyl-2,4-Diphenylquinoline(3j)[20]**.** ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16-8.14 (m, 3H), 7.77 (s, 1H), 7.58-7.35 (m, 9H), 7.19 (d, *J* = 2.4 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.7,154.6, 147.7, 144.8, 139.7, 138.6, 131.5, 129.3, 128.9, 128.7, 128.6, 128.3, 127.2,126.5, 121.8, 119.6, 103.5, 55.4.

6-Chloro-2,4-diphenylquinoline (3k)[7c]**.** ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18-8.15 (m, 3H), 7.86 (d, *J* = 2.4 Hz, 1H), 7.82 (s, 1H), 7.66-7.63 (m, 1H), 7.58-7.43 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.9, 148.4, 147.1, 139.1, 137.6, 132.1, 131.7, 130.4, 129.6, 129.4, 129.0, 128.9, 128.8, 128.7, 127.5, 126.4, 124.4, 119.9.

8-Chloro-2,4-Diphenylquinoline (3l)[7c]**.** ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31-8.29 (m, 2H), 7.87 (s, 1H), 7.81-7.76 (m, 2H), 7.52-7.33 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.7, 149.7, 144.8, 138.9, 138.1, 134.3, 129.8, 129.6, 129.5, 128.8, 128.7, 128.5, 127.7, 127.1, 125.9, 124.7, 119.8.

8-Methyl-2,4-Diphenylquinoline (3m)[7f]**.** ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29-8.26 (m, 2H), 7.82 (s, 1H), 7.73-7.69 (m, 1H), 7.52-7.31 (m, 10H), 2.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9, 149.2, 147.7, 139.8, 138.9, 137.90, 129.6, 129.5, 129.2, 128.7, 128.3, 128.2, 127.4, 125.9, 125.6,

123.5, 118.6, 18.4.

2-Phenyl-4-P-Tolylquinoline (3n)[21]**.** ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, J = 8.4 Hz, 1H), 8.19-8.17 (m, 2H), 7.96-7.93 (m, 1H), 7.80 (s, 1H), 7.75-7.71 (m, 1H), 7.53-7.49 (m, 2H), 7.47-7.44 (m, 4H), 7.35 (d, J = 8.4 Hz, 1H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.9, 149.3, 148.7, 139.6, 138.3, 135.4, 130.00, 129.4, 129.3, 128.8, 127.6, 126.2, 125.8, 125.7, 119.3, 21.3.

4-(4-Methoxyphenyl)-2-Phenylquinoline (3o)[7e]**.** ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, J = 8.4 Hz, 1H), 8.22 (d, J = 7.2 Hz, 2H), 7.98 (d, J = 8.4 Hz, 1H), 7.81 (s, 1H), 7.75-7.72 (m, 1H), 7.55-7.45 (m, 6H), 7.10-7.03 (m, 2H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8, 156.7, 148.7, 148.8, 139.6, 130.7, 130.5, 130.0, 129.4, 129.3, 128.8, 127.5, 126.1, 125.9, 125.7, 119.3, 113.9, 55.4.

4-(4-Chlorophenyl)-2-Phenylquinoline (3p)[21]**.** ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24-8.22 (m, 1H), 8.21-8.16 (m, 2H), 7.84-7.80 (m, 1H), 7.77 (s, 1H), 7.74-7.69 (m, 1H), 7.55-7.43 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.8, 148.7, 147.8, 139.4, 136.7, 134.5, 130.8, 130.1, 129.6, 129.4, 128.8, 128.7, 127.6, 126.5, 125.3, 125.2, 119.1.

4-(4-Fluorophenyl)-2-Phenylquinoline (3q)[7e]**.** ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26-8.22 (m, 1H), 8.17-8.15 (m, 2H), 7.84-7.81 (m, 1H), 7.75 (s, 1H), 7.75-7.70 (m, 1H), 7.55-7.43 (m, 6H), 7.23-7.18 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.1, 161.6, 156.8, 148.7, 148.0, 139.4, 134.3, 134.2, 131.2, 131.1, 130.0, 129.5, 129.4, 128.8, 127.5, 126.4, 125.7, 125.2, 119.3, 115.8, 115.49

4-Butyl-2-Phenylquinoline (3r)[7c]**.** ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, J = 8.0 Hz, 1H), 8.14 (d, J = 8.8 Hz, 2H), 8.05 (d, J = 8.8 Hz, 1H), 7.71-7.67 (m, 2H), 7.57-7.46 (m, 4H), 3.16 (t, J = 8.0 Hz, 2H), 1.83-1.76 (m, 2H), 1.53-1.48 (m, 2H), 0.98 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CD Cl_3): δ 157.0, 149.5, 148.4, 140.0, 130.5, 129.3, 128.9, 128.6, 127.7, 126.6, 126.1, 123.5, 118.8, 32.4, 32.3, 22.7, 13.8.

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