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Brønsted acid catalyzed synthesis of 1,3-di(2-quinolyl)propane derivatives via tandem C(sp^3)–H functionalization

Jia-jia Jin [a], Dong-chao Wang [a], Hong-ying Niu [b,*], Shan Wu [a], Gui-rong Qu [a], Zhong-bo Zhang [a], Hai-ming Guo [a,*]

[a] School of Chemistry and Chemical Engineering, Key Laboratory of Green Chemical Media and Reactions of Ministry of Education, Henan Normal University, Xinxiang 453007, China
[b] School of Chemistry and Chemical Engineering, Henan Institute of Science and Technology, Xinxiang 453003, China

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ABSTRACT

A novel protocol for Brønsted acid catalyzed reaction of 2-methyl azaarenes and aromatic aldehyde to give 1,3-di(2-quinolyl)propane derivatives through tandem C(sp^3)–H bond functionalization has been developed. This approach provides a new access to a variety of 1,3-di(2-quinolyl)propane derivatives, which are potentially of great importance in pharmaceuticals and ligand fields.

1. Introduction

Since aromatic heterocycles have extremely potent biological, chemical, and pharmaceutical utilities,[1] the chemical transformation of pyridines and quinolines is of great significance in organic synthesis. Additionally, 1,3-di(2-pyridyl)propane derivatives have found their application in preparing palladium complexes to catalyze the polymerization reaction of norbornene.[2] The preparation of 1,3-di(2-pyridyl)propane derivatives was reported by Chung and co-workers via the reaction of benzaldehydes and lithiated 2-picoline in somewhat low yield, and this synthetic strategy required lithium reagents and multi-step synthetic sequences. Furthermore, only one substrate was used in this reaction. As far as we know, there is few report on the synthesis of 1,3-di(2-quinolyl)propane derivatives up to now.[3] Recent studies have demonstrated that the direct C(sp^3)–H bond functionalization of 2-alkyl azaarenes is an efficient and atom economical synthetic strategy to access various substituted azaarene derivatives.[4–9] For example, Huang and co-workers reported iron-catalyzed direct alkenylation of 2-alkyl azaarenes with *N*-sulfonyl aldimines via C–H bond activation.[5c] Matsunaga et al. and Kanai et al. reported Lewis acid catalyzed direct addition of alkyl-substituted azaarenes to the C=C double bonds of enones.[8b] Li and Yang reported the benzylic C–H bond functionalization of azaarenes by a Brønsted acid.[3b,9] Recently, we also reported the copper-catalyzed addition of 2-alkyl azaarenes to ethyl glyoxylate via direct C(sp^3)–H activation.[10]

Based on the above mentioned successful achievement and our continued interest[11] in C–H bond activation, we reasoned that the synthesis of 1,3-di(2-quinolyl)propane derivatives would be realized via tandem C(sp^3)–H bond functionalization of 2-alkyl-substituted azaarenes. Our working hypothesis is shown in Scheme 1. First, alkyl-substituted azaarene **1** reacted with aromatic aldehyde, affording a reactive intermediate 2-alkenylated azaarene **A**.[6c,12] Next, the addition of another molecule alkyl-substituted azaarenes to the C=C double bonds of intermediate **A** catalyzed by Brønsted acid gave 1,3-di(2-quinolyl)propane **3** (Scheme 1).

To test the viability of our hypothesis, 2-methyl quinoline **1a** and benzaldehyde **2a** were chosen as model substrates in the reaction designed to deliver product **3aa**. The optimization studies were summarized in Table 1. A screening of potential catalysts indicated that the reaction gave product **3aa** in higher yield with 10 mol % of TsOH than any other Brønsted acids (Table 1, entries 1–4). Then the effect of solvents was examined and it was found that the reaction proceeded much better in nonpolar solvents than in polar ones and *p*-xylene was the best solvent (Table 1, entries 4–8). When the

* Corresponding authors. E-mail addresses: niu_hy@163.com (H.-ying Niu), guohm518@hotmail.com (H.-ming Guo).

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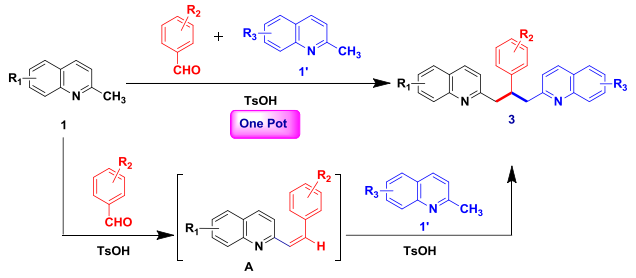
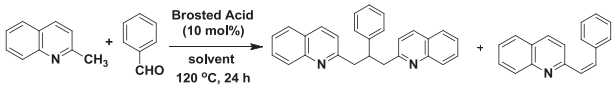


Scheme 1. Working hypothesis.

Table 1
Optimization of reaction conditions[a]



1a 2a 3aa 3a

Entry	Brønsted acid	Solvent	Yield/%[b]
1[c]	CF_3COOH	*p*-Xylene	14 (12)
2	PhCOOH	*p*-Xylene	32 (10)
3	*p*-$CH_3OC_6H_4COOH$	*p*-Xylene	31 (11)
4	**TsOH**	***p*-Xylene**	**86**
5	TsOH	Toluene	78 (11)
6	TsOH	DMF	Trace
7	TsOH	THF	13 (11)
8	TsOH	CH_2ClCH_2Cl	13 (7)
9	TsOH	*p*-Xylene	75[d]
10	TsOH	*p*-Xylene	85[e]
11	TsOH	*p*-Xylene	72[f]
12	TsOH	*p*-Xylene	23 (41)[g]
13[h]	$Cu(OTf)_2$	*p*-Xylene	Trace

The optimized reaction conditions are in bold.

[a] Reaction conditions: all reactions were carried out with **1a** (3 equiv), **2a** (0.5 mmol), catalyst (10 mol %), solvent (0.8 mL) in Schlenk tube at 120 °C for 24 h.

[b] Isolated yield of **3aa** based on **2a**, and the value in parentheses is the isolated yield of **3a**.

[c] 2 equiv of CF_3COOH was used.

[d] The temperature was 100 °C.

[e] The reaction time was 48 h.

[f] The loading of TsOH was 5 mol %.

[g] 3 equiv of **2a** was used.

[h] No target product got catalyzed by Lewis acid $Cu(OTf)_2$ in the reaction conditions.

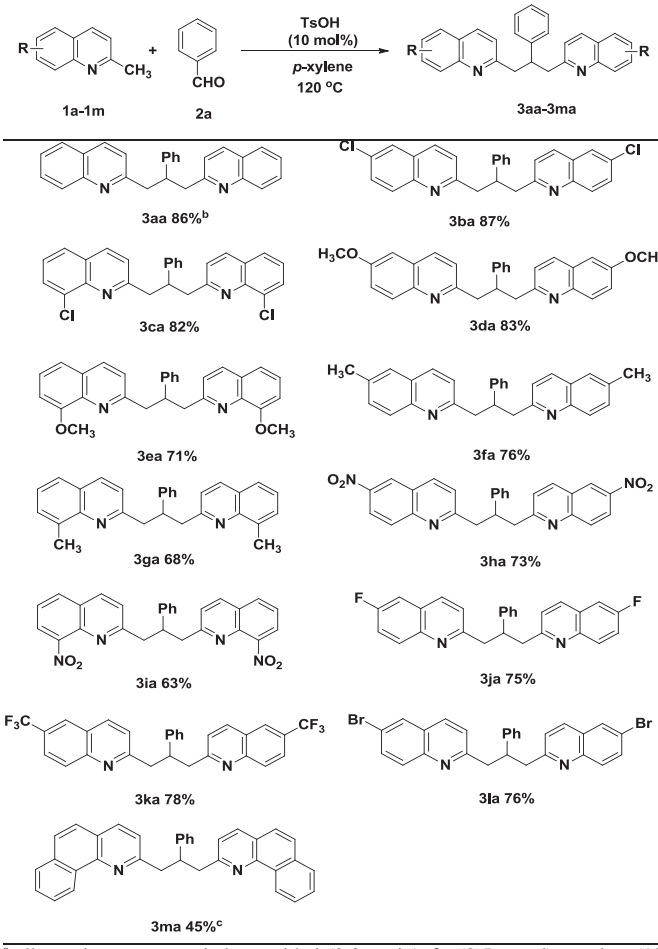
reaction time was extended to 48 h, the yield was almost the same (Table 1, entries 4 vs 10). And the test of the reaction temperature showed that 120 °C was suitable for the reaction (entries 4 vs 9). The by-product **3a** was given in very low yields (7%–12%) when 3.0 equiv of **1a** was used, while **3a** became the main product when **1a** and **2a** were the same equivalent (entry 12).

2. Results and discussion

Under the optimized reaction conditions, the scope of this transformation with various 2-alkyl quinolines with electron-neutral, electron-donating or electron-withdrawing groups was then examined (Table 2). In general, the C8-substituted 2-methyl quinolines gave lower yields than the C6-substituted 2-methyl quinolines, which might be caused by the steric effect. Moreover, various functional groups like F, Cl, Br, CF_3, and NO_2 were tolerated in the quinoline ring. When 2-methyl-7,8-benzoquinoline **1m** was used as the substrate, the reaction proceeded at 150 °C and yield of the corresponding product **3ma** was only 45%.[13]

Next, the effect of various aromatic aldehydes was investigated (Table 3). The reaction of 2-methyl quinoline **1a** and aromatic aldehyde **2b**–**j**, which bear electron-withdrawing groups, provided the corresponding products **4ab**–**aj** in good yields (74%–85%).

Table 2
Scope of 2-methyl azaarenes[a]



[a] all reactions were carried out with **1** (3.0 equiv), **2a** (0.5 mmol), catalyst (10 mol%), solvent (0.8 mL) in Schlenk tube at 120 °C for 24 h.

[b] Isolated yields based on **2a**.

[c] The temperature was 150 °C.

However, the aromatic aldehyde (**2k**–**m**) bearing electron-donating groups afforded the corresponding products in relatively low yields. For example, *p*-methoxy benzaldehyde gave the corresponding product **4al** in 43% yield. Notably, 2-pyridinecarboxaldehyde **2n** and 2-furaldehyde **2o** could also react with 2-methyl quinoline **1a** to form **4an** and **4ao** in good yields.

At last, we explored the reaction of benzaldehyde **2a** and two different substituted azaarenes (Scheme 2), in order to find if the competition reactions of different substituted azaarenes had influence on the products. The experimental result shows that the reaction gave three kinds of products, including one non-symmetrical 2-phenyl-1,3-di(2-quinolyl)propane derivative **5a** and two kinds of symmetrical products. Although the total yields of the reactions were good (85%), the nonsymmetrical products **5a** had no advantage over the symmetrical products.

The reaction of 2-ethyl quinoline or 2-methyl pyridines with benzaldehyde **2a** was also tested. Unfortunately, the desired reaction didn't occur in our hands. We also explored the addition of 1 equiv of the intermediate **3a** to the substrate **1a** (Scheme 3). The desired product **3aa** was obtained in 73% yield. This verified our hypothesis that the synthesis of 1,3-di(2-quinolyl)propane was realized via tandem C(sp^3)–H bond activation of 2-alkyl-substituted azaarenes.

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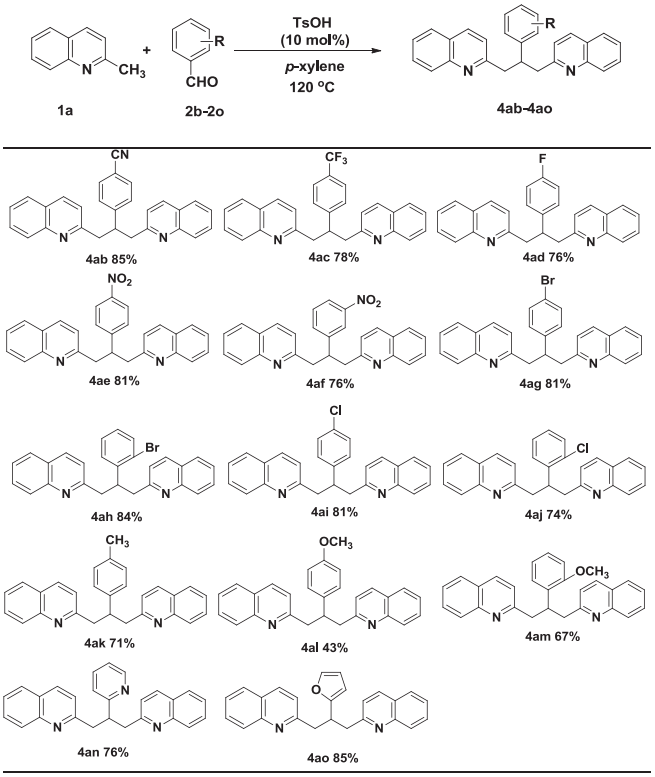
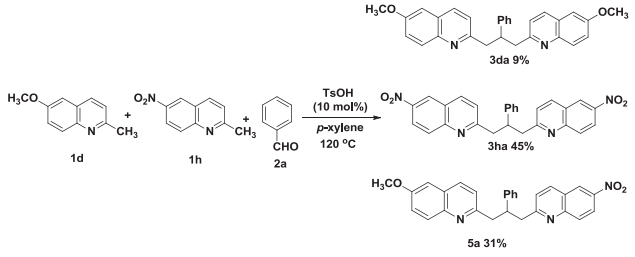
Table 3
Scope of 2-methyl azaarenes[a]

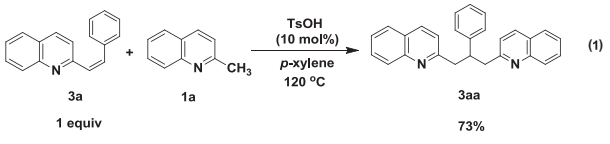


[a] all reactions were carried out with **1a** (3.0 equiv), **2** (0.5 mmol), catalyst (10 mol%), solvent (0.8 mL) in Schlenk tube at 120 ºC for 24 h.

[b] Isolated yields based on **2**.



Scheme 2. Cross coupling of two different azaarenes.



Scheme 3. The reaction of 2-methyl quinoline with **3a**.

3. Conclusion

We have developed an efficient Brønsted acid catalyzed reaction of 2-methyl azaarenes and aromatic aldehydes to give 1,3-di(2-quinolyl)propane derivatives through tandem C(sp^3)–H bond functionalization. This protocol provides a simple and rapid approach to access a variety of 1,3-di(2-quinolyl)propane derivatives, which are potentially of great importance in pharmaceutical and ligand fields. Further studies to apply this method for generating new C–C bond, as well as to understand the detailed mechanism, are ongoing in our laboratory.

4. Experimental section

4.1. General information

Melting points were recorded with a micro melting point apparatus and uncorrected. NMR spectra were recorded with a 400 NMR spectrometer for ^{1}H NMR, 100 MHz for ^{13}C NMR. Proton chemical shifts δ were given in parts per million relative to tetramethylsilane (0.00 ppm) in $CDCl_3$ for ^{1}H or $CDCl_3$ in ^{13}C NMR spectroscopy. High resolution mass spectra were taken with a 3000 mass spectrometer, using Waters Q-TofMS/MS system. For column chromatography 200–300 mesh silica gel (GF254) was used as the stationary phase. All reactions were monitored by thin layer chromatography (TLC). *p*-Xylene used in reactions was reagent grade and distilled from sodium. All reagents and solvents were purchased from commercial sources and purified commonly before used. All known quinolines (**1a**–**m**) were prepared according to literature procedures.[14] All aromatic aldehyde are commercially available compounds.

4.2. General procedure for the Brønsted acid catalyzed synthesis of 1,3-di(2-quinolyl)propane derivatives via direct C(sp^3)–H functionalization

TsOH (8.2 mg, 10 mol %), 2-methyl quinoline **1a** (205 μL, 1.5 mmol), and benzaldehyde **2a** (52 μL, 0.5 mmol) were mixed in a Schlenk tube and then dry *p*-xylene (0.8 mL) was added. The mixture was stirred at 120 °C in a closed reaction vessel. The reaction was monitored by TLC. After completion of the reaction, the solvent was evaporated under reduced pressure and the residue purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to give the desired product.

4.3. General procedure for cross coupling reaction

TsOH (8.2 mg, 10 mol %), 2-methyl-6-trifluoromethyl quinoline **1h** (94 mg, 0.5 mmol), 2-methyl-6-methoxyl quinoline **1d** (86 mg, 0.5 mmol), and benzaldehyde **2a** (52 μL, 0.5 mmol) were mixed in a Schlenk tube and then dry *p*-xylene (0.8 mL) was added. The mixture was stirred at 120 °C in a closed reaction vessel. The reaction was monitored by TLC. After completion of the reaction, the solvent was evaporated under reduced pressure and the residue purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to give the desired product.

*4.3.1. (Z)-2-Styrylquinoline (**3a**).* Orange liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, J=8.4 Hz, 1H), 8.08 (d, J=8.4 Hz, 1H), 7.80 (d, J=8.0 Hz, 1H), 7.73–7.64 (m, 5H), 7.50 (t, J=7.4 Hz, 1H), 7.44–7.39 (m, 3H), 7.33 (t, J=7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.0, 148.2, 136.5, 136.4, 129.8, 129.2, 129.0, 128.8, 128.7, 127.5, 127.4, 127.3, 126.2, 119.3; HRMS: calcd for $C_{17}H_{14}N$ $[M+H]^+$ 232.1121, found 232.1118; IR (KBr) ν/cm^{-1}: 3057, 3033, 1595, 1503, 1428, 749.

*4.3.2. 2,2′-(2-Phenylpropane-1,3-diyl)diquinoline (**3aa**).* Light yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, J=8.4 Hz, 2H), 7.84 (d, J=8.8 Hz, 2H), 7.64 (t, J=7.2 Hz, 4H), 7.43 (t, J=7.6 Hz, 2H), 7.23–7.07 (m, 7H), 4.09–4.01 (m, 1H), 3.52–3.39 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.7, 147.6, 143.7, 135.9, 129.3, 128.6, 128.3, 127.9, 127.4, 126.7, 126.4, 125.7, 122.1, 46.3, 45.6; HRMS: calcd for $C_{27}H_{23}N_2$ $[M+H]^+$ 375.1856, found 375.1849; IR (NaCl) ν/cm^{-1}: 3058, 2922, 1599, 1504, 1426, 755.

*4.3.3. 2,2′-(2-Phenylpropane-1,3-diyl)bis(6-chloroquinoline) (**3ba**).* Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, J=9.2 Hz, 2H), 7.75 (d, J=8.8 Hz, 2H), 7.63 (s, 1H), 7.58–7.55 (m, 4H), 7.18–7.07 (m, 7H), 4.02–3.95 (m, 1H), 3.48–3.35 (m, 4H); ^{13}C NMR (100 MHz,

$CDCl_3$): δ 161.0, 146.0, 143.4, 134.9, 131.4, 130.2, 130.1, 128.4, 127.8, 127.2, 126.5, 126.0, 122.9, 46.1, 45.5; HRMS: calcd for $C_{27}H_{20}Cl_2N_2Na$ $[M+Na]^+$ 465.0896, found 465.0900; IR (NaCl) ν/cm^{-1}: 3059, 2923, 1597, 1489, 1452, 765.

*4.3.4. 2,2′-(2-Phenylpropane-1,3-diyl)bis(8-chloroquinoline) (**3ca**).* Yellow liquid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, J=8.4 Hz, 2H), 7.75 (d, J=7.6 Hz, 2H), 7.55 (d, J=8.0 Hz, 2H), 7.33–7.29 (m, 4H), 7.26–7.18 (m, 4H), 7.11 (t, J=7.2 Hz, 1H), 4.33–4.26 (m, 1H), 3.61–3.44 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.7, 144.2, 143.8, 135.9, 133.0, 129.2, 128.2, 128.0, 127.9, 126.5, 126.3, 125.4, 123.1, 45.2, 45.0; HRMS: calcd for $C_{27}H_{20}Cl_2N_2Na$ $[M+Na]^+$ 465.0896, found 465.0899; IR (KBr) ν/cm^{-1}: 3059, 2912, 2882, 1598, 1496, 1424, 759.

*4.3.5. 2,2′-(2-Phenylpropane-1,3-diyl)bis(6-methoxyquinoline) (**3da**).* Dark yellow liquid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, J=9.2 Hz, 2H), 7.75 (d, J=8.4 Hz, 2H), 7.30–7.26 (m, 2H), 7.20–7.02 (m, 7H), 6.93 (d, J=2.8 Hz, 2H), 3.97–3.91 (m, 1H), 3.88 (s, 6H), 3.44–3.31 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.1, 157.1, 143.9, 143.8, 134.6, 130.1, 128.2, 127.9, 127.5, 126.2, 122.3, 121.7, 105.0, 55.4, 46.3, 45.4; HRMS: calcd for $C_{29}H_{27}N_2O_2$ $[M+H]^+$ 435.2067, found 435.2071; IR (NaCl) ν/cm^{-1}: 3059, 2936, 2836, 1600, 1500, 1462, 1232, 732.

*4.3.6. 2,2′-(2-Phenylpropane-1,3-diyl)bis(8-methoxyquinoline) (**3ea**).* Yellow liquid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, J=8.4 Hz, 2H), 7.34 (t, J=8.0 Hz, 2H), 7.26–7.24 (m, 2H), 7.20 (d, J=7.2 Hz, 2H), 7.14 (t, J=7.2 Hz, 2H), 7.08 (d, J=8.4 Hz, 3H), 6.99 (d, J=6.8 Hz, 2H), 4.06 (s, 6H), 4.01–3.96 (m, 1H), 3.57–3.43 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 155.0, 143.7, 139.7, 135.5, 128.2, 128.1, 127.8, 126.2, 125.6, 122.6, 119.4, 107.7, 56.1, 46.0, 45.7; HRMS: calcd for $C_{29}H_{27}N_2O_2$ $[M+H]^+$ 435.2067, found 435.2068; IR (NaCl) ν/cm^{-1}: 3057, 2933, 2834, 1602, 1504, 1471, 1259, 731.

*4.3.7. 2,2′-(2-Phenylpropane-1,3-diyl)bis(6-methylquinoline) (**3fa**).* Dark yellow liquid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, J=8.4 Hz, 2H), 7.76 (d, J=8.4 Hz, 2H), 7.48–7.46 (m, 2H), 7.41 (s, 2H), 7.21–7.12 (m, 4H), 7.09–7.03 (m, 3H), 4.03–3.95 (m, 1H), 3.50–3.36 (m, 4H), 2.47 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8, 146.1, 143.7, 135.5, 135.3, 131.5, 128.2, 127.9, 126.7, 126.3, 122.1, 46.4, 45.4, 21.5; HRMS: calcd for $C_{29}H_{27}N_2$ $[M+H]^+$ 403.2169, found 403.2172; IR (NaCl) ν/cm^{-1}: 3058, 2917, 1600, 1496, 1451, 829.

*4.3.8. 2,2′-(2-Phenylpropane-1,3-diyl)bis(8-methylquinoline) (**3ga**).* Yellow liquid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, J=8.4 Hz, 2H), 7.52 (q, J=8.0 Hz, 4H), 7.33 (t, J=7.2 Hz, 2H), 7.27–7.25 (m, 2H), 7.19–7.07 (m, 5H), 4.30–4.22 (m, 1H), 3.55–3.38 (m, 4H), 2.81 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 146.8, 144.7, 136.9, 135.7, 129.1, 128.0, 126.5, 126.0, 125.3, 125.2, 121.8, 45.3, 18.0; HRMS: calcd for $C_{29}H_{27}N_2$ $[M+H]^+$ 403.2169, found 403.2167; IR (KBr) ν/cm^{-1}: 3041, 2951, 2915, 2882, 1600, 1500, 1426, 760.

*4.3.9. 2,2′-(2-Phenylpropane-1,3-diyl)bis(6-nitroquinoline) (**3ha**).* Red solid. ^1H NMR (400 MHz, $CDCl_3$): δ 8.65 (d, J=2.4 Hz, 2H), 8.42–8.39 (m, 2H), 8.08 (q, J=8.0 Hz, 4H), 7.23 (d, J=8.4 Hz, 2H), 7.17–7.09 (m, 5H), 4.12–4.04 (m, 1H), 3.56–3.43 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.7, 149.8, 144.9, 142.8, 137.3, 130.5, 128.5, 127.7, 126.7, 125.3, 124.2, 123.9, 122.7, 45.8, 45.7; HRMS: calcd for $C_{27}H_{21}N_4O_4$ $[M+H]^+$ 465.1557, found 465.1562; IR (KBr) ν/cm^{-1}: 3097, 2920, 1610, 1490, 1465, 1341, 702.

*4.3.10. 2,2′-(2-Phenylpropane-1,3-diyl)bis(8-nitroquinoline) (**3ia**).* Gray solid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, J=8.8 Hz, 2H), 7.89 (d, J=7.2 Hz, 2H), 7.80 (d, J=8.0 Hz, 2H), 7.50–7.41 (m, 3H), 7.32 (d, J=8.8 Hz, 2H), 7.28(s, 1H), 7.23–7.10 (m, 3H), 4.27–4.18 (m, 1H), 3.51–3.36 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.6, 147.9, 144.0, 138.7, 135.5, 133.7, 131.3, 130.2, 128.5, 128.3, 127.8, 127.4, 126.4, 124.1, 44.9, 44.0; HRMS: calcd for $C_{27}H_{21}N_4O_4$ $[M+H]^+$ 465.1557, found 465.1565; IR (KBr) ν/cm^{-1}: 3065, 2922, 1601, 1500, 1431, 1380, 751.

*4.3.11. 2,2′-(2-Phenylpropane-1,3-diyl)bis(6-fluoroquinoline) (**3ja**).* Yellow liquid. ^1H NMR (400 MHz, $CDCl_3$): δ 8.00 (q, J=4.8 Hz, 2H), 7.78 (d, J=8.4 Hz, 2H), 7.43–7.34 (m, 2H), 7.28–7.25 (m, 2H), 7.20–7.07 (m, 7H), 4.03–3.95 (m, 1H), 3.48–3.35 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0, 144.6, 143.5, 135.3, 135.2, 131.0, 130.9, 129.9, 128.3, 127.8, 127.2, 127.1, 126.4, 122.9, 119.5, 119.2, 110.5, 110.3, 46.2, 45.3; HRMS: calcd for $C_{27}H_{21}F_2N_2$ $[M+H]^+$ 411.1667, found 411.1666; IR (KBr) ν/cm^{-1}: 3059, 2933, 1605, 1503, 1476, 1228, 698.

*4.3.12. 2,2′-(2-Phenylpropane-1,3-diyl)bis(6-(trifluoromethyl)quinoline) (**3ka**).* Yellow liquid. ^1H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, J=8.4 Hz, 2H), 7.94–7.90 (m, 4H), 7.81–7.78 (m, 2H), 7.20–7.11 (m, 7H), 4.10–4.03 (m, 1H), 3.55–3.42 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.1, 148.5, 143.3, 136.5, 129.9, 129.7, 128.4, 128.3, 127.8, 127.7, 127.5, 126.6, 125.5, 125.4, 125.3, 125.3, 125.0, 123.3, 122.7, 46.0, 45.6; HRMS: calcd for $C_{29}H_{21}F_6N_2$ $[M+H]^+$ 511.1603, found 511.1610; IR (NaCl) ν/cm^{-1}: 3062, 2924, 1604, 1483, 1453, 1120, 700.

*4.3.13. 2,2′-(2-Phenylpropane-1,3-diyl)bis(6-bromoquinoline) (**3la**).* Yellow liquid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, J=8.8 Hz, 2H), 7.77 (s, 2H), 7.86 (q, J=8.0 Hz, 4H), 7.17–7.05 (m, 7H), 4.03–3.96 (m, 1H), 3.48–3.35 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.1, 146.1, 143.4, 134.8, 132.6, 130.4, 129.4, 128.4, 127.8, 127.7, 126.5, 122.9, 119.5, 46.1, 45.5; HRMS: calcd for $C_{27}H_{20}Br_2N_2Na$ $[M+Na]^+$ 522.9885, found 522.9886; IR (KBr) ν/cm^{-1}: 3054, 2925, 1595, 1486, 1456, 833, 699.

*4.3.14. 2,2′-(2-Phenylpropane-1,3-diyl)bis(benzo[h]quinoline) (**3ma**).* Yellow liquid. ^1H NMR (400 MHz, $CDCl_3$): δ 9.41–9.39 (m, 2H), 7.89–7.87 (m, 4H), 7.72–7.65 (m, 6H), 7.56 (d, J=8.8 Hz, 2H), 7.33–7.21 (m, 2H), 7.22–7.18 (m, 4H), 7.13–7.09 (m, 1H), 4.49–4.42 (m, 1H), 3.66–3.49 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 145.9, 135.4, 133.6, 131.5, 128.2, 128.0, 127.8, 127.5, 126.6, 126.6, 126.0, 125.2, 124.7, 124.3, 122.5, 45.7, 45.3; HRMS: calcd for $C_{35}H_{27}N_2$ $[M+H]^+$ 475.2169, found 475.2175; IR (KBr) ν/cm^{-1}: 3049, 2921, 1595, 1505, 1449, 1395, 843.

*4.3.15. 4-(1,3-Di(quinolin-2-yl)propan-2-yl)benzonitrile (**4ab**).* Yellow liquid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, J=8.4 Hz, 2H), 7.91 (d, J=8.4 Hz, 2H), 7.71–7.64 (m, 4H), 7.48–7.40 (m, 4H), 7.30 (d, J=8.0 Hz, 2H), 7.09 (d, J=8.4 Hz, 2H), 4.23–4.15 (m, 1H), 3.53–3.34 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 149.6, 147.8, 136.0, 132.0, 129.4, 128.8, 127.5, 126.6, 125.9, 121.8, 119.0, 110.0, 45.9, 45.0; HRMS: calcd for $C_{28}H_{22}N_3$ $[M+H]^+$ 400.1808, found 400.1800; IR (KBr) ν/cm^{-1}: 3041, 2924, 2224, 1598, 1504, 1426, 827.

*4.3.16. 2,2′-(2-(4-(Trifluoromethyl)phenyl)propane-1,3-diyl)diquinoline (**4ac**).* Yellow liquid. ^1H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, J=9.2 Hz, 2H), 7.88 (d, J=8.4 Hz, 2H), 7.71–7.64 (m, 4H), 7.47–7.39 (m, 4H), 7.33 (d, J=8.0 Hz, 2H), 7.10 (d, J=8.4 Hz, 2H), 4.21–4.13 (m, 1H), 3.57–3.40 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0, 147.9, 147.4, 136.3, 130.2, 129.6, 128.3, 128.2, 127.5, 126.7, 126.0, 125.2, 125.2, 122.0, 46.0, 44.9; HRMS: calcd for $C_{28}H_{22}F_3N_2$ $[M+H]^+$ 443.1730, found 443.1729; IR (KBr) ν/cm^{-1}: 3058, 2926, 1600, 1506, 1426, 1326, 837.

*4.3.17. 2,2′-(2-(4-Fluorophenyl)propane-1,3-diyl)diquinoline (**4ad**).* Yellow liquid. ^1H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, J=8.0 Hz, 2H), 7.88 (d, J=8.4 Hz, 2H), 7.70–7.63 (m, 4H), 7.44 (t, J=7.6 Hz, 2H), 7.15–7.07 (m, 4H), 6.82 (t, J=8.8 Hz, 2H), 4.08–4.00 (m, 1H), 3.50–3.33 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.4, 147.8, 139.3, 139.3, 135.9, 129.3, 129.2, 128.8, 127.5, 126.7, 125.8, 122.0, 115.1,

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114.9, 45.7, 45.4; HRMS: calcd for $C_{27}H_{22}FN_2$ $[M+H]^+$ 393.1762, found 393.1754; IR (KBr) ν/cm^{-1}: 3060, 2926, 1600, 1507, 1427, 1224, 831.

*4.3.18. 2,2′-(2-(4-Nitrophenyl)propane-1,3-diyl)diquinoline (**4ae**).* Gray solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99–7.91 (m, 6H), 7.72–7.65 (m, 4H), 7.46 (t, J=7.2 Hz, 2H), 7.36 (d, J=8.4 Hz, 2H), 7.12 (d, J=8.4 Hz, 2H), 4.32–4.24 (m, 1H), 3.56–3.37 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 151.8, 147.8, 146.4, 136.1, 129.5, 128.8, 128.8, 127.5, 126.7, 126.0, 123.4, 121.8, 45.7, 45.1; HRMS: calcd for $C_{27}H_{22}N_3O_2$ $[M+H]^+$ 420.1707, found 420.1700; IR (KBr) ν/cm^{-1}: 3059, 2931, 1599, 1508, 1426, 1343, 826.

*4.3.19. 2,2′-(2-(3-Nitrophenyl)propane-1,3-diyl)diquinoline (**4af**).* Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (s, 1H), 7.99 (d, J=8.4 Hz, 2H), 7.92 (t, J=8.4 Hz, 3H), 7.71–7.65 (m, 4H), 7.52–7.44 (m, 3H), 7.29–7.25 (m, 1H), 7.14 (d, J=8.4 Hz, 2H), 4.34–4.26 (m, 1H), 3.56–3.38 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 148.1, 147.8, 146.2, 136.0, 134.5, 129.4, 128.9, 128.8, 127.5, 126.7, 125.9, 122.9, 121.8, 121.4, 45.3, 45.1; HRMS: calcd for $C_{27}H_{22}N_3O_2$ $[M+H]^+$ 420.1707, found 420.1705; IR (KBr) ν/cm^{-1}: 3057, 2905, 1600, 1522, 1426, 1349, 834.

*4.3.20. 2,2′-(2-(4-Bromophenyl)propane-1,3-diyl)diquinoline (**4ag**).* Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, J=8.4 Hz, 2H), 7.88 (d, J=8.4 Hz, 2H), 7.69–7.65 (m, 4H), 7.46–7.42 (m, 2H), 7.25 (d, J=8.4 Hz, 2H), 7.07 (q, J=4.0 Hz, 4H), 4.09–4.01 (m, 1H), 3.48–3.32 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.2, 147.8, 142.8, 135.9, 131.3, 129.7, 129.3, 128.8, 127.5, 126.7, 125.8, 122.0, 45.5; HRMS: calcd for $C_{27}H_{22}BrN_2$ $[M+H]^+$ 453.0961, found 453.0968; IR (KBr) ν/cm^{-1}: 3052, 2930, 1598, 1503, 1427, 1009, 821.

*4.3.21. 2,2′-(2-(4-Bromophenyl)propane-1,3-diyl)diquinoline (**4ah**).* Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, J=8.4 Hz, 2H), 7.87 (d, J=8.4 Hz, 2H), 7.67–7.61 (m, 4H), 7.46–7.40 (m, 4H), 7.19 (d, J=8.4 Hz, 3H), 6.97–6.93 (m, 1H), 4.67–4.59 (m, 1H), 3.50–3.40 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1, 147.7, 142.7, 135.8, 132.8, 129.2, 128.9, 127.8, 127.6, 127.4, 126.7, 125.7, 121.7, 44.4; HRMS: calcd for $C_{27}H_{22}BrN_2$ $[M+H]^+$ 453.0961, found 453.0955; IR (NaCl) ν/cm^{-1}: 3056, 2921, 1599, 1504, 1426, 1020, 754.

*4.3.22. 2,2′-(2-(4-Chlorophenyl)propane-1,3-diyl)diquinoline (**4ai**).* Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, J=8.8 Hz, 2H), 7.89 (d, J=8.4 Hz, 2H), 7.67 (q, J=8.4 Hz, 4H), 7.45 (d, J=7.6 Hz, 2H), 7.11–7.08 (m, 6H), 4.08–4.01 (m, 1H), 3.49–3.33 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3, 147.8, 142.2, 135.9, 131.8, 129.3, 128.8, 128.3, 127.4, 126.7, 125.8, 122.0, 45.5, 45.4; HRMS: calcd for $C_{27}H_{22}ClN_2$ $[M+H]^+$ 409.1466, found 409.1461; IR (KBr) ν/cm^{-1}: 3055, 2923, 1599, 1502, 1425, 828.

*4.3.23. 2,2′-(2-(2-Chlorophenyl)propane-1,3-diyl)diquinoline (**4aj**).* Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, J=8.4 Hz, 2H), 7.87 (d, J=8.4 Hz, 2H), 7.67–7.62 (m, 4H), 7.43 (q, J=8.0 Hz, 3H), 7.22–7.13 (m, 4H), 7.02 (t, J=7.6 Hz, 1H), 4.69–4.61 (m, 1H), 3.48 (d, J=7.2 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.2, 147.6, 141.0, 135.9, 134.1, 129.5, 129.2, 128.7, 127.4, 127.4, 126.9, 126.7, 125.7, 121.7, 44.1; HRMS: calcd for $C_{27}H_{22}ClN_2$ $[M+H]^+$ 409.1466, found 409.1459; IR (NaCl) ν/cm^{-1}: 3057, 2923, 1599, 1504, 1426, 754.

*4.3.24. 2,2′-(2-(p-Tolyl)propane-1,3-diyl)diquinoline (**4ak**).* Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, J=8.4 Hz, 2H), 7.84 (d, J=8.4 Hz, 2H), 7.67–7.62 (m, 4H), 7.42 (t, J=7.2 Hz, 2H), 7.11 (t, J=8.8 Hz, 4H), 6.97 (d, J=8.0 Hz, 2H), 4.06–3.98 (m, 1H), 3.49–3.37 (m, 4H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.9, 147.8, 140.7, 135.8, 129.2, 129.0, 128.7, 127.7, 127.4, 126.7, 125.7, 122.1, 45.7, 45.7, 21.0; HRMS: calcd for $C_{28}H_{25}N_2$ $[M+H]^+$ 389.2012, found 389.2008; IR (KBr) ν/cm^{-1}: 3059, 2956, 2916, 1599, 1503, 1426, 824.

*4.3.25. 2,2′-(2-(4-Methoxyphenyl)propane-1,3-diyl)diquinoline (**4al**).* Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, J=8.4 Hz, 2H), 7.87 (d, J=8.4 Hz, 2H), 7.69–7.63 (m, 4H), 7.46–7.42 (m, 2H), 7.09 (t, J=8.0 Hz, 4H), 6.68 (d, J=8.8 Hz, 2H), 4.00–3.91 (m, 1H), 3.70 (s, 3H), 3.47–3.33 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.8, 157.9, 147.7, 135.7, 135.7, 129.2, 128.8, 128.7, 127.4, 126.7, 125.6, 122.1, 113.6, 107.0, 55.1, 45.9, 45.4; HRMS: calcd for $C_{28}H_{25}N_2O$ $[M+H]^+$ 405.1961, found 405.1953; IR (NaCl) ν/cm^{-1}: 3057, 2929, 2835, 1600, 1512, 1426, 1248, 828.

*4.3.26. 2,2′-(2-(2-Methoxyphenyl)propane-1,3-diyl)diquinoline (**4am**).* Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, J=8.4 Hz, 2H), 7.84 (d, J=8.4 Hz, 2H), 7.66–7.60 (m, 4H), 7.41 (t, J=7.6 Hz, 2H), 7.26–7.06 (m, 4H), 6.80 (t, J=7.6 Hz, 1H), 6.71 (d, J=8.0 Hz, 1H), 4.45–4.38 (m, 1H), 3.61 (s, 3H), 3.46 (d, J=7.6 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.3, 157.3, 147.7, 135.5, 131.8, 129.0, 128.8, 128.4, 127.3, 127.2, 126.6, 125.5, 122.0, 120.5, 110.5, 55.2, 44.2, 39.5; HRMS: calcd for $C_{28}H_{25}N_2O$ $[M+H]^+$ 405.1961, found 405.1954; IR (KBr) ν/cm^{-1}: 3051, 2966, 2925, 1602, 1503, 1425, 1236, 766.

*4.3.27. 2,2′-(2-(Pyridin-2-yl)propane-1,3-diyl)diquinoline (**4an**).* Red liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57 (s, 1H), 8.01 (d, J=8.0 Hz, 2H), 7.85 (d, J=8.4 Hz, 2H), 7.67–7.61 (m, 4H), 7.43–7.28 (m, 3H), 7.08 (d, J=8.4 Hz, 2H), 6.99–6.88 (m, 2H), 4.24–4.19 (m, 1H), 3.62–3.46 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.7, 160.7, 149.2, 147.8, 135.9, 135.7, 129.2, 128.8, 127.4, 126.6, 125.7, 123.8, 122.2, 121.4, 47.8, 44.2; HRMS: calcd for $C_{26}H_{22}N_3$ $[M+H]^+$ 376.1808, found 376.1804; IR (NaCl) ν/cm^{-1}: 3056, 2925, 1598, 1503, 1426, 1310, 749.

*4.3.28. 2,2′-(2-(Furan-2-yl)propane-1,3-diyl)diquinoline (**4ao**).* Black liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, J=8.8 Hz, 2H), 7.92 (d, J=8.4 Hz, 2H), 7.71–7.63 (m, 4H), 7.45 (t, J=7.6 Hz, 2H), 7.31 (s, 1H), 7.11 (d, J=8.4 Hz, 2H), 6.10 (d, J=2.0 Hz, 1H), 5.80 (d, J=2.8 Hz, 1H), 4.17–4.10 (m, 1H), 3.48–3.38 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3, 156.4, 147.8, 141.0, 135.8, 129.2, 128.8, 127.4, 126.7, 125.7, 121.9, 109.9, 106.3, 43.2, 39.7; HRMS: calcd for $C_{25}H_{21}N_2O$ $[M+H]^+$ 365.1648, found 365.1656; IR (NaCl) ν/cm^{-1}: 3056, 2925, 2360, 1600, 1505, 1426, 827.

*4.3.29. 2,2′-(2-Methylpropane-1,3-diyl)diquinoline (**4ap**).* Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06–8.00 (m, 4H), 7.75 (d, J=8.0 Hz, 2H), 7.70–7.66 (m, 2H), 7.48 (d, J=7.2 Hz, 2H), 7.30 (d, J=8.4 Hz, 2H), 3.15–2.91 (m, 4H), 2.85–2.78 (m, 1H), 3.84 (s, 3H), 0.98 (d, J=6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.6, 147.9, 136.0, 129.3, 128.9, 127.5, 126.8, 125.7, 122.2, 46.4, 35.0, 19.6; HRMS: calcd for $C_{22}H_{21}N_2$ $[M+H]^+$ 313.1699, found 313.1691; IR (NaCl) ν/cm^{-1}: 3056, 2955, 2925, 1599, 1504, 1426, 758.

*4.3.30. 6-Methoxy-2-(3-(6-nitroquinolin-2-yl)-2-phenylpropyl)quinoline (**5a**).* Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (d, J=2.4 Hz, 1H), 8.35–8.32 (m, 1H), 8.02 (d, J=9.2 Hz, 1H), 7.34–7.27 (m, 2H), 7.73 (d, J=8.4 Hz, 1H), 7.29–7.27 (m, 1H), 7.21–7.02 (m, 7H), 6.89 (d, J=2.8 Hz, 1H), 4.07–3.99 (m, 1H), 3.84 (s, 3H), 3.52–3.34 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.1, 157.7, 157.2, 149.7, 144.8, 143.7, 143.6, 137.0, 134.7, 130.4, 130.1, 128.4, 127.7, 127.5, 126.5, 125.2, 124.2, 122.5, 122.3, 121.8, 105.0, 55.4, 46.0, 45.7, 45.6; HRMS: calcd for $C_{28}H_{24}N_3O_3$ $[M+H]^+$ 450.1812, found 450.1819; IR (NaCl) ν/cm^{-1}: 3061, 2935, 2835, 1622, 1495, 1463, 1232, 701.

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