Supporting Information For

Preparation of novel cadmium-containing coordination polymer and catalytic application in the synthesis of N-alkylated aminoquinoline derivatives *via* the borrowing hydrogen approach†

Jiahao Li,[a] Anruo Mao,[a,b] Xinyu Hu,[a] Likui Wang,[a] Dawei Wang*[a] and Zheng-Chao Duan*[a,c]

[a] *Key Laboratory of Synthetic and Biological Colloids, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122, PR China.*

[b] *Department of Chemistry, University of Manchester, Oxford Road, Manchester M13 9PL, UK.*

[c] *School of Chemical and Environmental Engineering, Hubei Minzu University, Enshi 445000, PR China.*

Contents

1. Materials and Methods

1.1. Catalyst Characterization

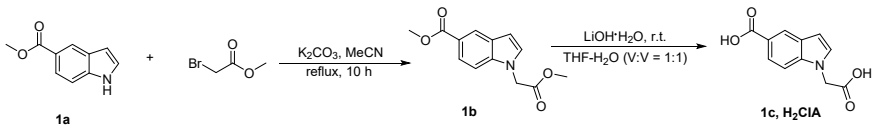
FT-IR spectra (Thermo Fisher Co., Waltham, MA, USA) were recorded on a Nicolet 360 FT-IR instrument (KBr discs) in the 4000–525 cm^{-1} regions. Single crystal X-ray diffraction data were collected using a Bruker D8 VENTURE CMOS X-ray diffractometer with Cu-Kα1 radiation at 293 K. Cell parameters were refined on all observed reflections using the APEX3 program. XPS data were recorded with an electron energy analyzer (ESCALAB 250Xi, Thermo Fisher Co., Waltham, MA, USA). Flash column chromatography was performed on 230–430 mesh silica gel. Analytical thin layer chromatography was performed with precoated glass baked plates (250 μ) and visualized via fluorescence and charring after treatment with potassium permanganate stain. ^{1}H NMR and ^{13}C NMR spectra were obtained on a Bruker Advance III HD (Switzerland) 400 MHz spectrometer and referenced to $CDCl_3$ (7.26 ppm for ^{1}H, and 77.1 ppm for ^{13}C) or DMSO-d_6 (2.50 ppm for ^{1}H, and 39.5 ppm for ^{13}C) with tetramethylsilane as the internal standard (0 ppm). High resolution mass spectra (HRMS) were recorded on LTQ-FTUHRA mass spectrometer.

1.2. Chemicals

The following chemicals were used as received: Methyl indole-5-carboxylate (98%, Energy Chemical, Anhui, China), Potassium carbonate (K_2CO_3, Sinopharm, Beijing, China), Methyl bromoacetate (98%, Energy Chemical, Anhui, China), Lithium hydroxide hydrate ($LiOH•H_2O$, 98%, Sinopharm, Beijing, China), Acetonitrile (CH_3CN, 99.5%, Sinopharm, Beijing, China), Tetrahydrofuran (THF, 99.5%, Energy Chemical, Anhui, China), Hydrochloric acid (HCl, 37.5%, Sinopharm, Beijing, China), Anhydrous magnesium sulfate ($MgSO_4$, 99%, Sinopharm, Beijing, China), Cadmium acetate dihydrate ($Cd(OAc)_2•2H_2O$, 98%, Energy Chemical, Anhui, China), 1,10-Phenanthroline (99%, Energy Chemical, Anhui, China), Triethylamine (NEt_3, 99.5%, Sigma, Shanghai, China), ethanol (99%, Sigma, Shanghai, China), Sodium hydroxide (NaOH, 97%, Sinopharm, Beijing, China), Toluene (99.5%, Sinopharm, Beijing, China), benzyl alcohol derivatives (98%, Energy Chemical, Anhui, China), 8-Aminoquinoline (98%, Energy Chemical, Anhui, China), 2-Aminoquinoline (97%, Energy Chemical, Anhui, China), Unless otherwise noted, all commercial reagents and solvents were obtained from the commercial provider and used without further purification.

2. **Preparation of Cd-containing Coordination Polymer.**

2.1 The synthesis of 1-(carboxymethyl)-1*H*-indole-5-carboxylic acid (H_2CIA) ligand. (**1c**)



(1) To 500 mL round-bottom bottle was successively added methyl indole-5-carboxylate (**1a**) (3.504 g, 20 mmol), methyl 2-bromoacetate (7.649 g, 50 mmol), anhydrous potassium carbonate (11.057 g, 80 mmol) and MeCN (100 mL).The reaction mixture was refluxed for twenty hours and monitored by TLC until complete disappearance of methyl indole-5-carboxylate (**1a**) was confirmed. Then the mixture was added water and extracted with ethyl acetate. The combined organic phases were washed with dried over anhydrous $MgSO_4$.The solvent was removed under reduced pressure and purification of the crude product by column chromatography on silica-gel (petroleum ether/ethyl acetate = 5:1) afforded the title compound methyl 1-(2-methoxy-2-oxoethyl)-1H-indole-5-carboxylate (**1b)** in 88 % yield as pale yellow solid.

(2) To a mixed solution of THF-H_2O (v/v = 1:1) (200 mL) and LiOH•H_2O (1 g) was successively added the solution of **1b** (20 mmol) in THF/H_2O (1:1) (200 mL) at room temperature. After eight hours, the reaction was acidified to pH=2 by adding an aqueous solution of 1N HCl, the acid product 1-(carboxymethyl)-1H-indole-5-carboxylic acid (H_2CIA) (**1c**) was washed with H_2O, then evaporated to dryness to afford **1c** in 95 % yield.

2.2. The synthesis of $[Cd(CIA)(phen)_2(H_2O)]_n$.

Complex was prepared from a mixture of $Cd(OAc)_2$•$2H_2O$ (0.106 g, 0.4 mmol), ligand H_2CIA (0.131 g, 0.6 mmol), 1,10-phen (0.144 g, 0.80 mmol), and 10 mL of H_2O. The mixture was stirred and the pH value was adjusted to 10-11 with NEt_3. After being stirred for another 20 min, the mixture was transferred to a 25 mL Teflonlined stainless steel bomb and kept at 120 ^oC under autogenously pressure for 3 days. The reaction system was cooled to room temperature during 24 h. A large amount of brownness crystals $[Cd(CIA)(phen)_2(H_2O)]_n$ was obtained.

3. **Characterization of Cd-containing Coordination Polymer.**

Table S1. Crystallographic data for $[Cd(CIA)(phen)_2(H_2O)]_n$

Empirical formula	$C_{35}\ H_{25}\ Cd\ N_5\ O_5$
Formula weight	708.01
Temperature	298(2) K
Wavelength	0.71076 Å
Crystal system	Orthorhombic
Space group	Pbca
Unit cell dimensions	a = 16.325 alpha = 90°
	b = 15.0860(8) Å beta =90°
	c = 23.0509(14) Å gamma =90°
Volume	5677.0(6) $Å^3$
Z	8
Density (calculated)	1.657 Mg/m^3
Absorption coefficient	0.826 mm^{-1}
F(000)	2864
Crystal size / mm^3	0.25 x 0.16 x 0.12
Theta range for data collection	2.972 to 27.236°
Index ranges	-20<=h<=19, -19<=k<=19, -29<=l<=26
Reflections collected	30406
Independent reflections	6275 [R(int) = 0.0384]
Completeness to theta=27.236°	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. Transmission	0.764 and 0.577
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6275 / 48 / 456
Goodness-of-fit on F^2	1.021
Final R indices [I>2sigma(I)]	R1 = 0.0280, wR2 = 0.0671
R indices (all data)	R1 = 0.0388, wR2 = 0.0743
Largest diff. peak and hole	0.456 and -0.740 $e.Å^{-3}$

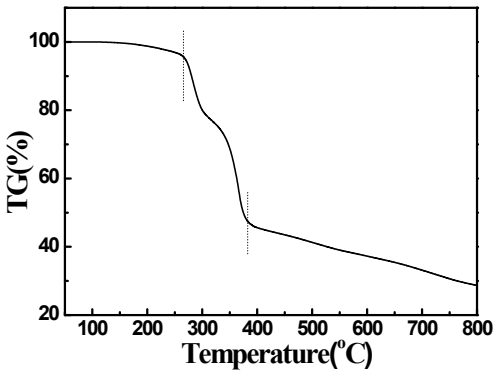


Fig. S1. TGA spectra of $[Cd(CIA)(phen)_2(H_2O)]_n$.

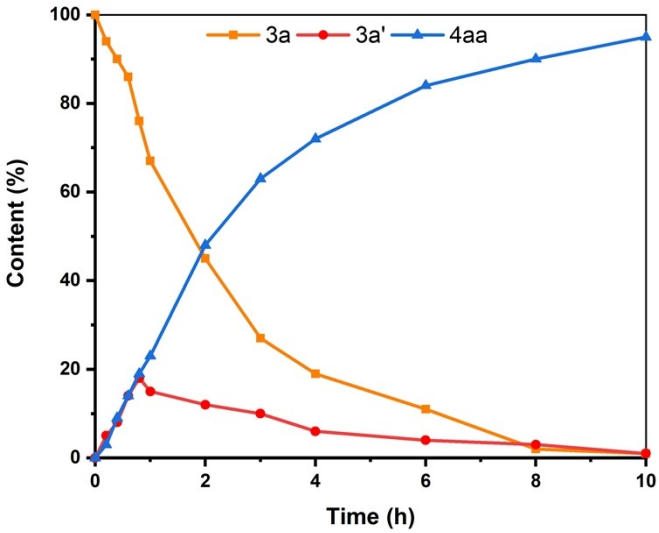


Fig. S2. Kinetic investigations for the synthesis of **4aa**.

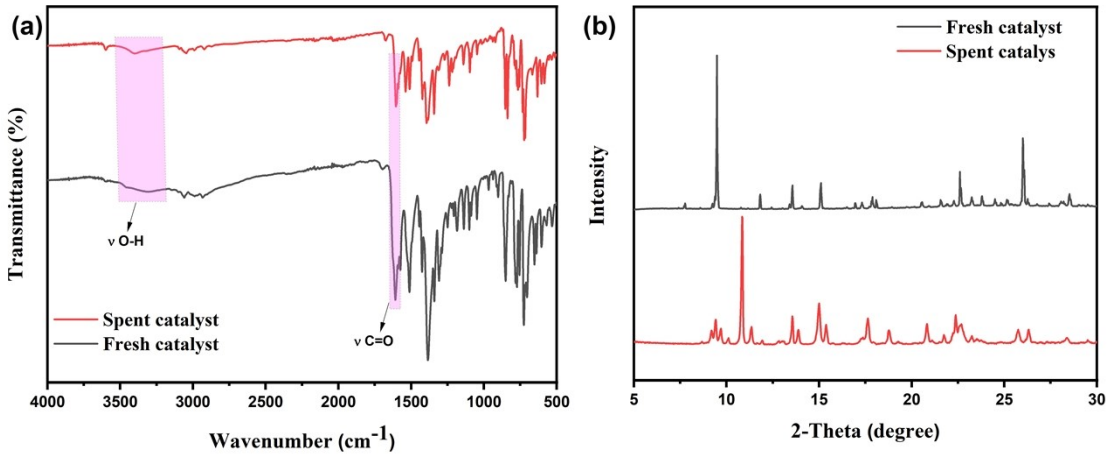


Fig. S3. (a) FT-IR images of $[Cd(CIA)(phen)_2(H_2O)]_n$ after five runs, (b) PXRD images of $[Cd(CIA)(phen)_2(H_2O)]_n$ after five runs.

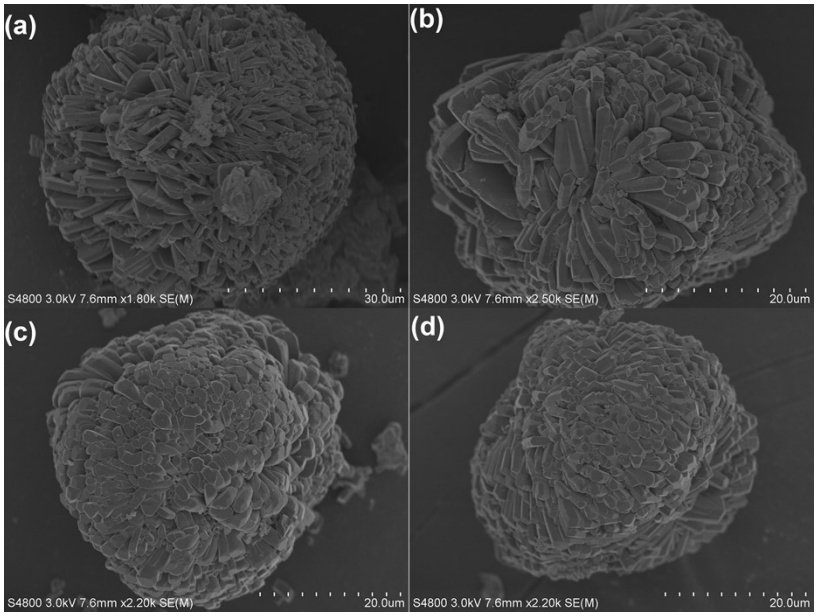


Fig. S4. (a,b) SEM images of $[Cd(CIA)(phen)_2(H_2O)]_n$, (c, d) SEM images of $[Cd(CIA)(phen)_2(H_2O)]_n$ after five runs.

4. General procedure for 4

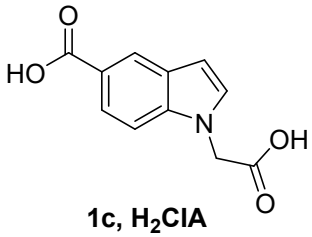
To 10 mL reaction tube was added 2-aminoquinoline (0.5 mmol), benzyl alcohol (0.6 mmol), $[Cd(CIA)(phen)_2(H_2O)]_n$ (2 mol% Cd), NaOH (1.0 equiv.). Then, toluene (2.0 mL) was added and the mixture was stirred at 100 ^oC for 10 h. The solvent was removed under reduced pressure carefully and purification of the crude product by column chromatography on silica-gel (petroleum ether/ethyl acetate = 5:1) afforded the compound **4**.

5. General procedure for 6

To 10 mL reaction tube was added 8-aminoquinoline (0.5 mmol), benzyl alcohol (0.6 mmol), $[Cd(CIA)(phen)_2(H_2O)]_n$ (2 mol% Cd), NaOH (1.0 equiv.). Then, toluene (2.0 mL) was added and the mixture was stirred at 100 ^oC for 10 h. The solvent was removed under reduced pressure carefully and purification of the crude product by column chromatography on silica-gel (petroleum ether/ethyl acetate = 5:1) afforded the compound **6**.

6. Analytical data of the obtained compounds

(1) 1-(carboxymethyl)-1*H*-indole-5-carboxylic acid (H_2CIA)

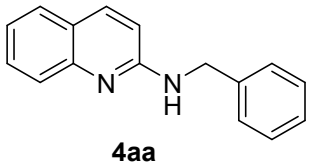


1c, H_2CIA

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.58 (s, 2H), 8.04 (m, 2H), 7.48 (d, J = 7.0 Hz, 1H), 7.22 (m, 2H), 5.13 (s, 2H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 170.32, 166.05, 137.45, 136.82, 126.74, 122.81, 121.81, 121.19, 111.14, 107.46, 47.80.

(2) N-benzylquinolin-2-amine (4aa)

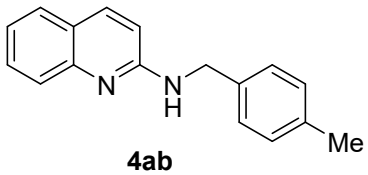


4aa

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (ddd, J = 17.0, 8.8, 1.2 Hz, 2H), 7.63 – 7.53 (m, 2H), 7.46 – 7.38 (m, 2H), 7.39 – 7.33 (m, 2H), 7.32 – 7.27 (m, 1H), 7.24 (ddd, J = 8.1, 6.9, 1.2 Hz, 1H), 6.60 (d, J = 8.9 Hz, 1H), 5.18 (s, 1H), 4.73 (d, J = 5.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.91, 148.18, 139.52, 137.54, 129.73, 128.79, 127.92, 127.61, 127.44, 126.38, 123.72, 122.29, 111.52, 45.96.

(3) N-(4-methylbenzyl)quinolin-2-amine (4ab).

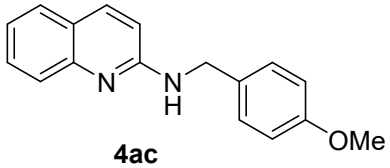


4ab

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, J = 8.9, 0.8 Hz, 1H), 7.72 (dd, J = 8.3, 1.0 Hz, 1H), 7.60 – 7.51 (m, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.25 – 7.20 (m, 1H), 7.15 (d, J = 7.9 Hz, 2H), 6.61 (d, J = 8.9 Hz, 1H), 5.09 (s, 1H), 4.66 (d, J = 4.5 Hz, 2H), 2.35 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.92, 148.11, 137.55, 137.10, 136.33, 129.71, 129.45, 127.87, 127.57, 126.27, 123.65, 122.24, 111.40, 45.79, 21.23.

(4) N-(4-methoxybenzyl)quinolin-2-amine (4ac).

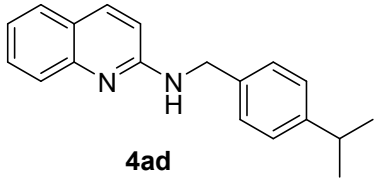


4ac

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 8.9, 0.8 Hz, 1H), 7.73 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.60 – 7.51 (m, 2H), 7.32 (d, *J* = 8.7 Hz, 2H), 7.22 (ddd, *J* = 8.0, 7.0, 1.2 Hz, 1H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.59 (d, *J* = 8.9 Hz, 1H), 5.11 (s, 1H), 4.64 (d, *J* = 5.2 Hz, 2H), 3.78 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.01, 156.87, 148.10, 137.51, 131.45, 129.71, 129.22, 127.59, 126.27, 123.65, 122.24, 114.14, 111.55, 55.40, 45.45.

(5) N-(4-isopropylbenzyl)quinolin-2-amine (4ad).

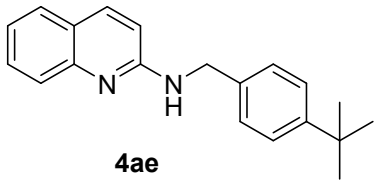


4ad

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.76 (m, 2H), 7.66 – 7.54 (m, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.27 – 7.22 (m, 3H), 6.61 (d, *J* = 8.9 Hz, 1H), 5.22 (s, 1H), 4.71 (d, *J* = 4.8 Hz, 2H), 2.95 (p, *J* = 7.0 Hz, 1H), 1.30 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.00, 148.21, 148.15, 137.52, 136.84, 129.74, 128.04, 127.99, 127.64, 126.87, 126.36, 123.71, 122.26, 111.61, 45.77, 33.98, 24.23.

(6) N-(4-(tert-butyl)benzyl)quinolin-2-amine (4ae).

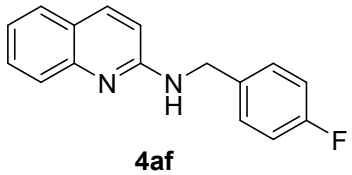


4ae

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.74 (m, 2H), 7.63 – 7.53 (m, 2H), 7.42 – 7.35 (m, 4H), 7.24 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1H), 6.61 (d, *J* = 8.8 Hz, 1H), 5.14 (s, 1H), 4.72 (d, *J* = 5.5 Hz, 2H), 1.36 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.95, 150.41, 148.23, 137.47, 136.48, 129.71, 127.76, 127.61, 126.40, 125.69, 123.71, 122.30, 111.64, 45.66, 34.66, 31.57.

(7) N-(4-fluorobenzyl)quinolin-2-amine (4af).

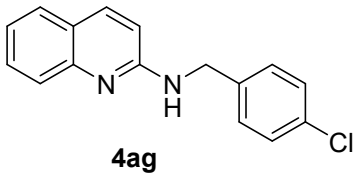


4af

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 8.9, 0.8 Hz, 1H), 7.70 (dt, *J* = 8.5, 0.9 Hz, 1H), 7.63 – 7.50 (m, 2H), 7.40 – 7.33 (m, 2H), 7.22 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 1H), 7.01 (t, *J* = 8.7 Hz, 2H), 6.61 (d, *J* = 8.9 Hz, 1H), 5.06 (s, 1H), 4.68 (d, *J* = 5.5 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.20 (d, *J* = 245.2 Hz), 156.63, 147.98, 137.62, 135.23 (d, *J* = 3.0 Hz), 129.63 (d, *J* = 26.3 Hz), 127.58, 126.33, 123.69, 122.36, 115.59, 115.38, 111.46, 45.18.

(8) N-(4-chlorobenzyl)quinolin-2-amine (4ag).

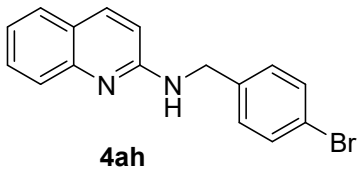


4ag

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.78 (m, 1H), 7.71 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.62 – 7.50 (m, 2H), 7.32 – 7.21 (m, 5H), 6.60 (d, *J* = 8.9 Hz, 1H), 5.32 (s, 1H), 4.71 – 4.62 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.54, 147.62, 137.98, 137.84, 133.08, 129.91, 129.16, 128.83, 127.63, 126.07, 123.63, 122.54, 111.40, 45.15.

(9) N-(4-bromobenzyl)quinolin-2-amine (4ah).

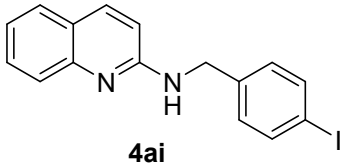


4ah

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 8.9, 0.8 Hz, 1H), 7.70 (dd, *J* = 8.4, 1.0 Hz, 1H), 7.62 – 7.50 (m, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.27 – 7.21 (m, 3H), 6.59 (d, *J* = 8.9 Hz, 1H), 5.18 (s, 1H), 4.65 (d, *J* = 4.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.63, 147.98, 138.63, 137.66, 131.77, 129.81, 129.54, 127.62, 126.32, 123.72, 122.46, 121.15, 111.44, 45.18.

(10) N-(4-iodobenzyl)quinolin-2-amine (4ai).

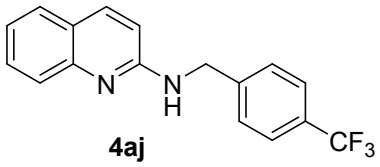


4ai

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.77 (m, 1H), 7.71 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.63 – 7.60 (m, 2H), 7.59 – 7.51 (m, 2H), 7.25 – 7.20 (m, 1H), 7.13 – 7.08 (m, 2H), 6.58 (d, *J* = 8.9 Hz, 1H), 5.40 (s, 1H), 4.63 (d, *J* = 4.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.61, 147.77, 139.27, 137.77, 137.73, 129.86, 129.72, 127.63, 126.14, 123.66, 122.45, 111.42, 92.69, 45.26.

(11) N-(4-(trifluoromethyl)benzyl)quinolin-2-amine (4aj).

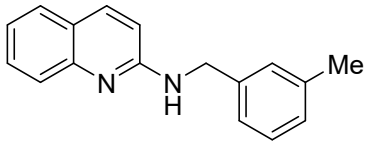


4aj

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 8.8, 0.8 Hz, 1H), 7.70 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.61 – 7.48 (m, 6H), 7.25 – 7.20 (m, 1H), 6.62 (d, *J* = 8.9 Hz, 1H), 5.13 (d, *J* = 6.2 Hz, 1H), 4.79 (d, *J* = 5.7 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.48, 147.96, 143.86, 137.70, 129.80, 129.38, 127.96, 127.59, 126.42, 125.63, 125.59, 123.77, 122.54, 111.44, 45.25.

(12) N-(3-methylbenzyl)quinolin-2-amine (4ak).

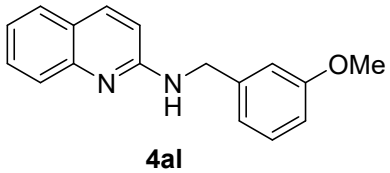


4ak

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.9 Hz, 1H), 7.72 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.62 – 7.51 (m, 2H), 7.26 – 7.19 (m, 4H), 7.10 (d, *J* = 7.1 Hz, 1H), 6.62 (d, *J* = 8.9 Hz, 1H), 5.07 (s, 1H), 4.68 (d, *J* = 5.3 Hz, 2H), 2.34 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.88, 148.11, 139.31, 138.47, 137.56, 129.70, 128.68, 128.62, 128.20, 127.56, 126.30, 124.93, 123.66, 122.25, 111.39, 46.00, 21.53.

(13) N-(3-methoxybenzyl)quinolin-2-amine (4al).

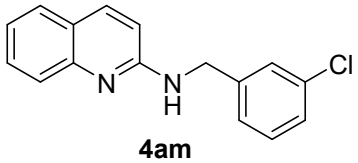


4al

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 8.9, 0.8 Hz, 1H), 7.73 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.60 – 7.51 (m, 2H), 7.27 – 7.19 (m, 2H), 7.01 – 6.96 (m, 2H), 6.82 (ddd, *J* = 8.3, 2.6, 1.0 Hz, 1H), 6.60 (d, *J* = 8.9 Hz, 1H), 5.21 (s, 1H), 4.70 – 4.67 (m, 2H), 3.77 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.98, 156.88, 148.05, 141.13, 137.59, 129.80, 129.74, 127.60, 126.26, 123.68, 122.30, 120.10, 113.40, 112.87, 111.45, 55.32, 45.94.

(14) N-(3-chlorobenzyl)quinolin-2-amine (4am).

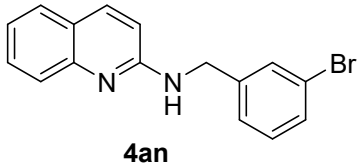


4am

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 8.9, 0.8 Hz, 1H), 7.71 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.61 – 7.51 (m, 2H), 7.39 (q, *J* = 0.7 Hz, 1H), 7.31 – 7.21 (m, 4H), 6.60 (d, *J* = 8.9 Hz, 1H), 5.16 (s, 1H), 4.70 (d, *J* = 5.7 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.54, 147.95, 141.76, 137.68, 134.53, 129.99, 129.79, 127.87, 127.60, 127.51, 126.36, 125.93, 123.74, 122.47, 111.46, 45.22.

(15) N-(3-bromobenzyl)quinolin-2-amine (4an).

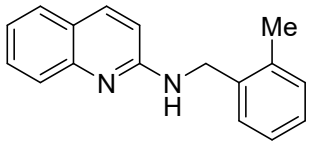


4an

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.9 Hz, 1H), 7.69 (dd, *J* = 8.4, 1.0 Hz, 1H), 7.59 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.55 – 7.51 (m, 2H), 7.39 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.34 – 7.30 (m, 1H), 7.25 – 7.18 (m, 2H), 6.61 (dd, *J* = 8.8, 1.0 Hz, 1H), 5.08 (s, 1H), 4.67 (d, *J* = 13.5 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.51, 147.93, 141.99, 137.72, 130.78, 130.46, 130.30, 129.80, 127.58, 126.40, 125.44, 123.74, 122.79, 122.48, 111.39, 45.21.

(16) N-(2-methylbenzyl)quinolin-2-amine (4ao).

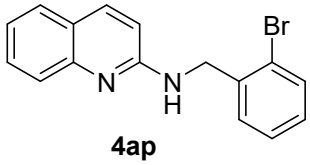


4ao

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 8.9, 0.8 Hz, 1H), 7.72 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.59 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.57 – 7.51 (m, 1H), 7.37 – 7.34 (m, 1H), 7.23 – 7.16 (m, 4H), 6.61 (d, *J* = 8.8 Hz, 1H), 4.94 (s, 1H), 4.69 (d, *J* = 5.1 Hz, 2H), 2.40 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.70, 147.90, 137.63, 136.98, 136.70, 130.59, 129.77, 128.64, 127.69, 127.57, 126.28, 126.19, 123.57, 122.31, 111.42, 44.11, 19.23.

(17) N-(2-bromobenzyl)quinolin-2-amine (4ap).

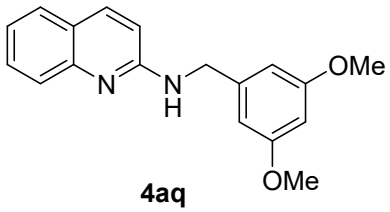


4ap

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.73 (m, 2H), 7.58 (dtd, *J* = 8.5, 3.5, 1.5 Hz, 3H), 7.51 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.23 (dtd, *J* = 7.6, 6.8, 1.2 Hz, 2H), 7.12 (dd, *J* = 7.7, 1.8 Hz, 1H), 6.58 (d, *J* = 8.9 Hz, 1H), 5.48 (s, 1H), 4.79 (d, *J* = 2.9 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.74, 148.07, 138.47, 137.69, 132.89, 130.03, 129.81, 128.97, 127.72, 127.68, 126.38, 123.81, 123.76, 122.42, 111.43, 46.00.

(18) N-(3,5-dimethoxybenzyl)quinolin-2-amine (4aq).

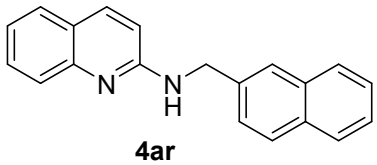


4aq

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.9 Hz, 1H), 7.70 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.60 – 7.50 (m, 2H), 7.21 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 6.64 – 6.55 (m, 3H), 6.37 (t, *J* = 2.3 Hz, 1H), 5.16 (s, 1H), 4.65 (d, *J* = 5.6 Hz, 2H), 3.75 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.14, 156.81, 148.00, 141.92, 137.59, 129.72, 127.57, 126.26, 123.67, 122.30, 111.40, 105.70, 99.31, 55.43, 46.11.

(19) N-(naphthalen-2-ylmethyl)quinolin-2-amine (4ar).

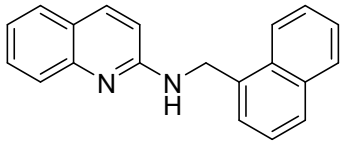


4ar

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.74 (m, 6H), 7.61 – 7.44 (m, 5H), 7.26 – 7.20 (m, 1H), 6.63 (d, *J* = 8.8 Hz, 1H), 5.26 (s, 1H), 4.87 (d, *J* = 5.1 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.94, 148.11, 137.66, 136.92, 133.57, 132.87, 129.79, 128.55, 127.88, 127.83, 127.62, 126.31, 126.26, 126.12, 125.92, 123.73, 122.34, 111.42, 46.08.

(20) N-(naphthalen-1-ylmethyl)quinolin-2-amine (4as).

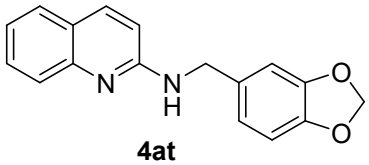


4as

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.11 (m, 1H), 7.98 – 7.80 (m, 3H), 7.75 (dt, *J* = 9.0, 1.0 Hz, 1H), 7.61 (ddd, *J* = 6.2, 5.1, 2.9 Hz, 2H), 7.53 (td, *J* = 6.2, 2.7 Hz, 3H), 7.44 (dd, *J* = 8.2, 7.0 Hz, 1H), 7.33 – 7.26 (m, 1H), 6.50 (d, *J* = 8.9 Hz, 1H), 5.17 (s, 2H), 5.13 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.74, 148.29, 137.47, 134.76, 134.06, 131.84, 129.81, 128.94, 128.46, 127.73, 126.60, 126.51, 126.10, 125.72, 124.03, 123.77, 122.36, 111.94, 44.01.

(21) N-(benzo[*d*][1,3]dioxol-5-ylmethyl)quinolin-2-amine (4at).

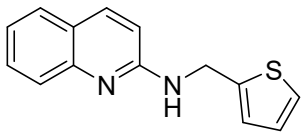


4at

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 9.0, 0.8 Hz, 1H), 7.72 (dt, *J* = 8.4, 0.9 Hz, 1H), 7.62 – 7.47 (m, 2H), 7.22 (ddd, *J* = 8.0, 7.0, 1.2 Hz, 1H), 6.90 (d, *J* = 1.7 Hz, 1H), 6.86 – 6.81 (m, 1H), 6.75 (d, *J* = 7.9 Hz, 1H), 6.59 (d, *J* = 8.9 Hz, 1H), 5.91 (s, 2H), 5.15 (s, 1H), 4.60 (d, *J* = 5.4 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.77, 148.07, 147.95, 146.89, 137.53, 133.38, 129.73, 127.59, 126.30, 123.67, 122.29, 121.07, 111.54, 108.52, 108.39, 101.11, 45.72.

(22) N-(thiophen-2-ylmethyl)quinolin-2-amine (4au).

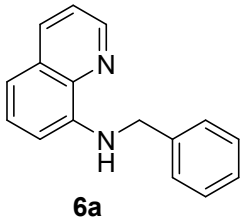


4au

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.9 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.64 – 7.53 (m, 2H), 7.26 (s, 1H), 7.21 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.07 (dd, *J* = 3.6, 1.2 Hz, 1H), 6.96 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.66 (d, *J* = 8.9 Hz, 1H), 5.35 (s, 1H), 4.91 (d, *J* = 5.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.92, 142.07, 137.90, 129.90, 127.51, 126.80, 125.84, 125.72, 124.97, 123.50, 122.62, 111.43, 40.77.

(23) N-benzylquinolin-8-amine (6a).

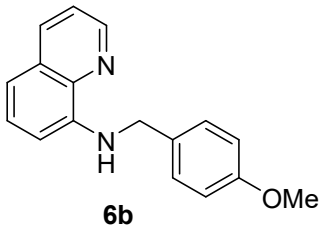


6a

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.05 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.43 (d, *J* = 7.0 Hz, 2H), 7.39 – 7.22 (m, 5H), 7.05 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.64 (dd, *J* = 7.7, 1.1 Hz, 2H), 4.55 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.06, 144.75, 139.42, 138.36, 136.27, 128.85, 128.80, 127.98, 127.60, 127.32, 121.58, 114.34, 105.37, 47.89.

(24) N-(4-methoxybenzyl)quinolin-8-amine (6b).

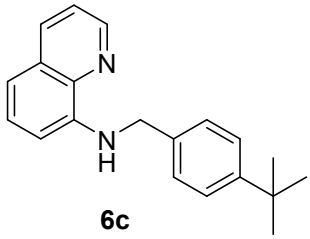


6b

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.09 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.48 – 7.34 (m, 4H), 7.10 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.94 (d, *J* = 8.6 Hz, 2H), 6.78 – 6.53 (m, 2H), 4.53 (d, *J* = 4.9 Hz, 2H), 3.84 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.94, 147.01, 144.75, 138.36, 136.12, 131.34, 128.84, 128.77, 127.92, 121.51, 114.19, 114.15, 105.21, 55.39, 47.29.

(25) N-(4-(tert-butyl)benzyl)quinolin-8-amine (6c).

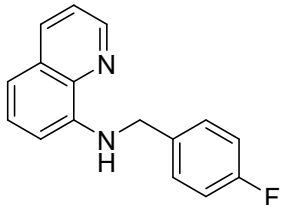


6c

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.11 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.50 – 7.38 (m, 6H), 7.13 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.79 – 6.61 (m, 2H), 4.59 (d, *J* = 5.1 Hz, 2H), 1.42 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.20, 147.00, 144.87, 138.39, 136.33, 136.11, 128.79, 127.95, 127.45, 125.67, 121.52, 114.18, 105.18, 47.55, 34.64, 31.57.

(26) N-(4-fluorobenzyl)quinolin-8-amine (6d).

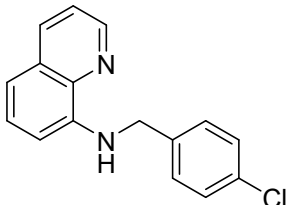


6d

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (dd, *J* = 4.2, 1.7 Hz, 1H), 7.99 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.40 – 7.23 (m, 4H), 7.08 – 6.90 (m, 3H), 6.57 (dd, *J* = 7.6, 1.2 Hz, 2H), 4.44 (d, *J* = 4.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.13 (d, *J* = 244.8 Hz), 147.06, 144.51, 138.32, 136.14, 135.01 (d, *J* = 3.1 Hz), 129.02 (d, *J* = 8.0 Hz), 128.76, 127.84, 121.55, 115.51 (d, *J* = 21.4 Hz), 114.47, 105.28, 47.07.

(27) N-(4-chlorobenzyl)quinolin-8-amine (6e).

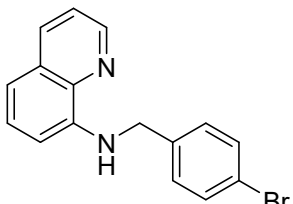


6e

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.10 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.48 – 7.31 (m, 6H), 7.12 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.76 – 6.58 (m, 2H), 4.56 (d, *J* = 4.7 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.13, 144.42, 138.33, 137.93, 136.17, 132.88, 128.85, 128.75, 127.82, 121.60, 114.58, 105.35, 47.12.

(28) N-(4-bromobenzyl)quinolin-8-amine (6f).

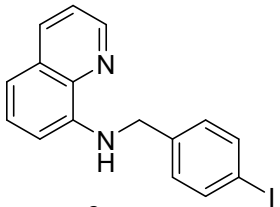


6f

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.10 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.44 – 7.30 (m, 4H), 7.11 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.81 – 6.55 (m, 2H), 4.59 – 4.47 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.18, 144.42, 138.51, 138.36, 136.23, 131.84, 129.14, 128.79, 127.84, 121.65, 121.00, 114.64, 105.40, 47.22.

(29) N-(4-iodobenzyl)quinolin-8-amine (6g).

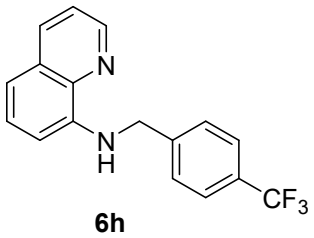


6g

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.10 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.45 – 7.34 (m, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.11 (dd, *J* = 8.2, 1.1 Hz, 1H), 6.77 – 6.54 (m, 2H), 4.61 – 4.49 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.12, 144.36, 139.15, 138.30, 137.73, 136.16, 129.37, 128.72, 127.81, 121.59, 114.58, 105.35, 92.48, 47.23.

(30) N-(4-(trifluoromethyl)benzyl)quinolin-8-amine (6h).

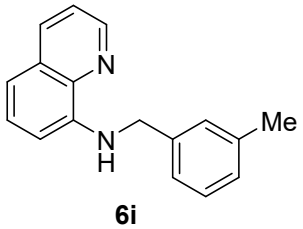


6h

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.06 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.65 – 7.46 (m, 4H), 7.40 – 7.26 (m, 2H), 7.07 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.78 – 6.50 (m, 2H), 4.72 – 4.48 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.24, 144.34, 143.74, 138.34, 136.34,129.57 (q, *J* = 32.4 Hz), 128.86, 127.86, 127.57, 125.74 (q, *J* = 3.8 Hz), 124.34 (q, *J* = 271 Hz), 121.72, 114.86, 105.50, 47.41.

(31) N-(3-methylbenzyl)quinolin-8-amine (6i).

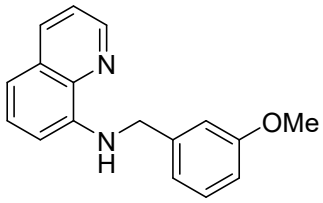


6i

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.10 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.48 – 7.24 (m, 5H), 7.19 – 7.05 (m, 2H), 6.76 – 6.55 (m, 2H), 4.56 (d, *J* = 5.3 Hz, 2H), 2.39 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.08, 144.85, 139.35, 138.44, 138.42, 136.19, 128.82, 128.69, 128.37, 128.10, 127.98, 124.69, 121.57, 114.26, 105.28, 47.93, 21.63.

(32) N-(3-methoxybenzyl)quinolin-8-amine (6j).

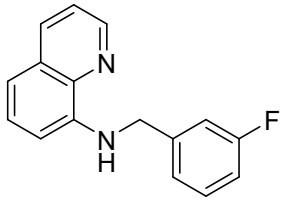


6j

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.09 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.44 – 7.26 (m, 3H), 7.14 – 7.01 (m, 3H), 6.86 (ddd, *J* = 8.3, 2.7, 0.9 Hz, 1H), 6.68 (dd, *J* = 7.6, 1.2 Hz, 2H), 4.58 (d, *J* = 4.8 Hz, 2H), 3.82 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.11, 147.09, 144.76, 141.19, 138.41, 136.19, 129.80, 128.80, 127.94, 121.49, 119.84, 114.37, 113.11, 112.74, 105.37, 55.38, 47.90.

(33) N-(3-fluorobenzyl)quinolin-8-amine (6k).

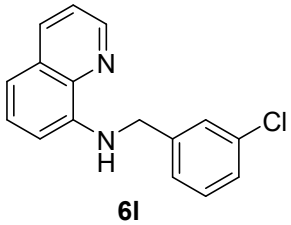


6k

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.00 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.34 – 7.20 (m, 3H), 7.18 – 7.08 (m, 2H), 7.03 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.95 – 6.87 (m, 1H), 6.72 – 6.52 (m, 2H), 4.49 (d, *J* = 4.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.30 (d, *J* = 245.9 Hz), 147.11, 144.42, 142.30 (d, *J* = 6.8 Hz), 138.32, 136.16, 130.19 (d, *J* = 8.2 Hz), 128.76, 127.82, 122.83 (d, *J* = 2.8 Hz), 121.58, 114.60, 114.23 (d, *J* = 12.9 Hz), 114.02 (d, *J* = 12.3 Hz), 105.35, 47.27.

(34) N-(3-chlorobenzyl)quinolin-8-amine (6l).

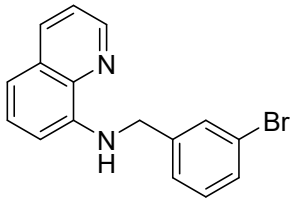


6l

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.10 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.48 (dt, *J* = 1.6, 0.9 Hz, 1H), 7.44 – 7.26 (m, 5H), 7.12 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.77 – 6.60 (m, 2H), 4.57 (d, *J* = 4.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.15, 144.38, 141.70, 138.33, 136.18, 134.64, 130.01, 128.76, 127.83, 127.47, 127.43, 125.47, 121.62, 114.66, 105.36, 47.30.

(35) N-(3-bromobenzyl)quinolin-8-amine (6m).

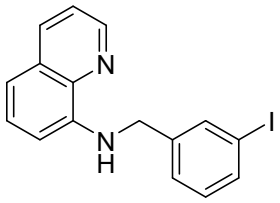


6m

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.10 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.64 (t, *J* = 1.8 Hz, 1H), 7.47 – 7.34 (m, 4H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.13 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.80 – 6.59 (m, 2H), 4.56 (d, *J* = 5.9 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.09, 144.32, 141.92, 138.27, 136.11, 130.33, 130.30, 130.25, 128.70, 127.78, 125.88, 122.86, 121.56, 114.62, 105.31, 47.20.

(36) N-(3-iodobenzyl)quinolin-8-amine (6n).

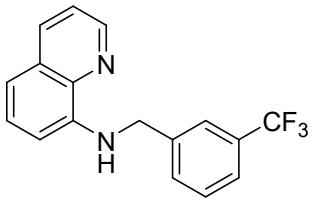


6n

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.10 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.85 (d, *J* = 1.7 Hz, 1H), 7.65 (dt, *J* = 8.0, 1.1 Hz, 1H), 7.47 – 7.34 (m, 3H), 7.20 – 7.02 (m, 2H), 6.77 – 6.59 (m, 2H), 4.53 (d, *J* = 5.8 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.08, 144.32, 141.93, 138.26, 136.29, 136.12, 130.42, 128.69, 127.79, 127.49, 126.55, 121.56, 114.61, 105.32, 94.81, 47.12.

(37) N-(3-(trifluoromethyl)benzyl)quinolin-8-amine (6o).

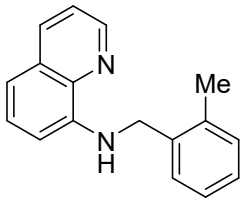


6o

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.11 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.77 (s, 1H), 7.70 – 7.56 (m, 2H), 7.52 – 7.35 (m, 3H), 7.15 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.84 – 6.60 (m, 2H), 4.64 (d, *J* = 5.4 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.21, 144.40, 140.63, 138.38, 136.20, 131.04 (q, *J* = 31.9 Hz), 130.67, 129.21, 128.80, 127.82, 124.40 (q, *J* = 271.0 Hz), 124.18 (q, *J* = 4.0 Hz), 124.11, 121.65, 114.84, 105.40, 47.45.

(38) N-(2-methylbenzyl)quinolin-8-amine (6p).

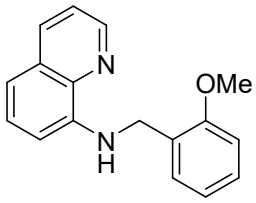


6p

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (dd, *J* = 4.2, 1.7 Hz, 1H), 7.92 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.41 – 7.06 (m, 6H), 6.98 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.65 – 6.34 (m, 2H), 4.39 (d, *J* = 5.1 Hz, 2H), 2.33 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.89, 144.78, 138.28, 136.79, 136.28, 135.97, 130.42, 128.69, 128.05, 127.87, 127.33, 126.18, 121.41, 114.08, 104.94, 45.86, 19.03.

(39) N-(2-methoxybenzyl)quinolin-8-amine (6q).

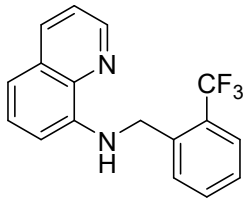


6q

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.10 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.51 – 7.37 (m, 3H), 7.33 (td, *J* = 7.8, 1.7 Hz, 1H), 7.12 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.02 – 6.94 (m, 2H), 6.82 – 6.67 (m, 2H), 4.68 (d, *J* = 5.3 Hz, 2H), 3.94 (d, *J* = 0.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.52, 146.91, 144.94, 138.45, 136.06, 128.79, 128.51, 128.23, 127.94, 127.23, 121.42, 120.61, 113.93, 110.32, 105.23, 55.41, 42.61.

(40) N-(2-(trifluoromethyl)benzyl)quinolin-8-amine (6r).

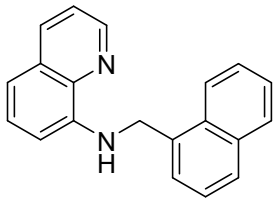


6r

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.02 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.73 – 7.59 (m, 2H), 7.45 – 7.22 (m, 4H), 7.04 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.82 – 6.46 (m, 2H), 4.77 (d, *J* = 5.5 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.20, 144.27, 138.36, 136.25, 132.31, 128.83, 128.40, 127.96 (q, *J* = 32 Hz), 127.90, 127.08, 126.14 (q, *J* = 5.7 Hz), 124.87 (q, *J* = 272 Hz), 121.65, 114.72, 105.38, 44.04.

(41) N-(naphthalen-1-ylmethyl)quinolin-8-amine (6s).

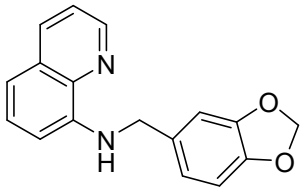


6s

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.13 (dd, *J* = 8.3, 1.7 Hz, 1H), 8.03 – 7.84 (m, 4H), 7.66 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.60 – 7.51 (m, 2H), 7.49 – 7.39 (m, 2H), 7.17 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.96 – 6.75 (m, 2H), 4.79 (d, *J* = 5.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.01, 144.71, 138.37, 136.85, 136.06, 133.63, 132.86, 128.73, 128.44, 127.88, 127.87, 127.78, 126.15, 125.86, 125.77, 125.70, 121.48, 114.32, 105.37, 47.93.

(42) N-(benzo[*d*][1,3]dioxol-5-ylmethyl)quinolin-8-amine (6t).

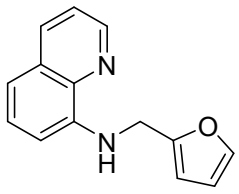


6t

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.06 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.40 – 7.31 (m, 2H), 7.07 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.98 – 6.88 (m, 2H), 6.79 (d, *J* = 7.9 Hz, 1H), 6.70 – 6.50 (m, 2H), 5.93 (s, 2H), 4.46 (d, *J* = 4.5 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.05, 147.04, 146.81, 144.57, 138.29, 136.17, 133.28, 128.75, 127.88, 121.54, 120.64, 114.32, 108.42, 108.13, 105.27, 101.09, 47.62.

(43) N-(furan-2-ylmethyl)quinolin-8-amine (6u).



6u

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (dd, *J* = 4.3, 1.6 Hz, 1H), 7.94 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.35 – 7.21 (m, 3H), 6.98 (d, *J* = 8.2 Hz, 1H), 6.66 (d, *J* = 7.7 Hz, 1H), 6.50 – 6.13 (m, 3H), 4.43 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.78, 147.16, 144.34, 142.08, 138.44, 136.17, 128.77, 127.81, 121.58, 114.75, 110.46, 107.18, 105.34, 41.06.