Supporting Information

Aerobic cross-dehydrogenative couplings of N-heteroarenes with toluene derivatives at room temperature

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1. General Information

All reactions were carried out with magnetic stirring and in dried glassware. Standard syringe techniques were applied for transfer of dry solvents. All reagents and solvents were commercially available and used without any further purification unless specified. Proton (¹H NMR) and carbon (¹³C NMR) nuclear magnetic resonance spectra were recorded at 400 MHz and 100MHz, respectively. The chemical shifts are given in parts per million (ppm) on the delta (δ) scale. The solvent peak was used as a reference value, for ¹H NMR: TMS = 0.00 ppm, for ¹³C NMR: CDCl₃ = 77.00 ppm. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, td = triplet of doublet, q = quartet, m = multiplet, and br = broad. Analytical TLC was performed on precoated silica gel plates. High-resolution mass spectra (HRMS) were obtained on an Agilent mass spectrometer using ESI-TOF (electrospray ionization-time of flight).

2. Experiment Section

2.1 Typical experimental procedure for the benzylation



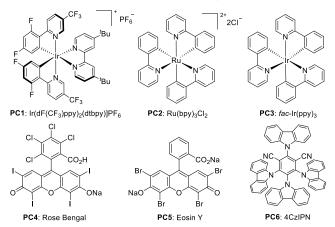
To a Schlenk tube were added **1** (0.2 mmol), **2** (2 mmol, 10.0 eqiuv), **PC1** (0.004 mmol, 2 mol%), NH₄Br (0.1 mmol, 0.5 equiv), H₂O (2 mmol, 10.0 equiv), acetone (3 mL). Then the mixture was stirred at room temperature in oxygen atmosphere (1 atm) under 35 W blue LED light for 20 h until complete consumption of starting material as monitored by TLC and GC-MS analysis. After the reaction was finished, the reaction mixture was washed with brine. The aqueous phase was re-extracted with EtOAc (3×10 mL). The combined organic extracts were dried over Na₂SO₄ and concentrated in vacuum. The residue was purified by silica gel flash column chromatography (hexane/ethyl acetate = 15 : 1 to 5 : 1) to afford the desired products **3** or **4**.

2.2 Optimization of reaction conditions

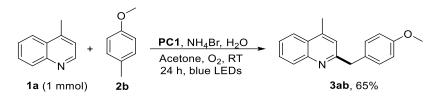
Table S1

N 1a	PC1 (2 mol%) NH ₄ Br (0.5 equiv) H ₂ O (10.0 equiv) 35 W blue LED light, O ₂ Acetone (3 mL), 20 h 3a	aa
entry	variation from the standard conditions	yield $(\%)^b$
1	none	74
2	without PC1	0
3	without light	0
4	PC2 instead of PC1	trace
5	PC3 instead of PC1	trace
6	PC4 instead of PC1	trace
7	PC5 instead of PC1	trace
8	PC6 instead of PC1	18
9	without NH ₄ Br	0
10	LiBr instead of NH4Br	51
11	NaBr instead of NH4Br	20
12	TBAB instead of NH ₄ Br	32
13	LiCl instead of NH4Br	0
14	NH4I instead of NH4Br	0
15	CH ₃ CN instead of Acetone	38
16	1,4-dioxane instead of Acetone	56
17	DMSO instead of Acetone	0
18	DCM instead of Acetone	68
19	PhCl instead of Acetone	62
20	NMP instead of Acetone	0
21	under air	65
22 4 D (i)	without H ₂ O	58

^{<i>a</i>} Reaction conditions: 1a (0.2 mmol), 2a (2 mmol, 10 equiv), catalyst (2 mol%),
additive (0.5 equiv), H ₂ O (10 equiv), solvent (3 mL), at 35 °C under O ₂ atmosphere
and 35 W blue LED irradiation for 20 h. ^b Isolated yield.



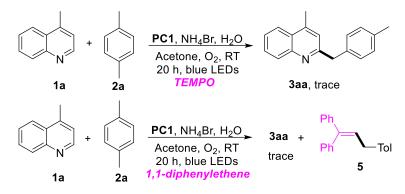
2.3 Scale-up experiment:



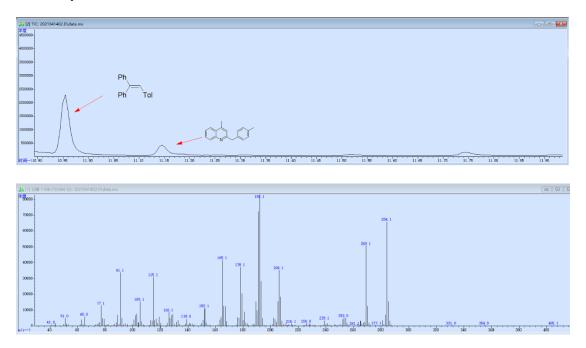
A 50 mL Schlenk tube were added 4-methylquinoline (**1a**, 1.0 mmol, 1.0 equiv), 1-methoxy-4methylbenzene (**2b**, 10 mmol, 10.0 equiv), **PC1** (0.02 mmol, 2 mol%), NH₄Br (0.5 mmol, 0.5 equiv), H₂O (10 mmol, 10.0 equiv), acetone (15 mL). Then the mixture was stirred at room temperature in oxygen atmosphere (1 atm) under 35 W blue LED light for 24 h. After the reaction was finished, the reaction mixture was washed with brine. The aqueous phase was re-extracted with EtOAc (3×10 mL). The combined organic extracts were dried over Na₂SO₄ and concentrated in vacuum. The residue was purified by silica gel flash column chromatography (hexane/ethyl acetate = 10 : 1) to afford the desired products **3ab** in 65% yield.

3. Mechanistic studies

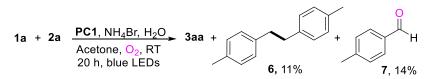
3.1 Radical trapping experiments



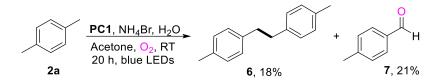
Two reactions of radical trapping experiments were performed. A solution of TEMPO (3.0 equiv, 0.6 mmol), or 1,1-diphenylethene (3 equiv, 0.6 mmol), 4-methylquinoline (**1a**, 0.2 mmol), *p*-xylene (**2a**, 2 mmol, 10 equiv), **PC1** (0.004 mmol, 2 mol%), NH₄Br (0.1 mmol, 0.5 equiv), H₂O (2 mmol, 10.0 equiv), Acetone (3 mL). Then the mixture was stirred at room temperature in oxygen atmosphere (1 atm) under 35 W blue LED light for 20 h. The benzylation were completely quenched and no benzylation products were detected. The benzyl trapping product (3-(*p*-tolyl)prop-1-ene-1,1-diyl)dibenzene (**5**) could be detected by GC-MS.



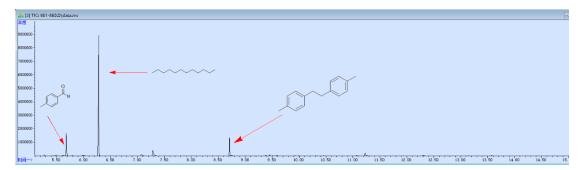
3.2 Side reaction



To a Schlenk tube were added 4-methylquinoline (1a, 0.2 mmol), *p*-xylene (2a, 2 mmol, 10.0 equiv), PC1 (0.004 mmol, 2 mol%), NH₄Br (0.1 mmol, 0.5 equiv), H₂O (2 mmol, 10.0 equiv), acetone (3 mL). Then the mixture was stirred at room temperature in oxygen atmosphere (1 atm) under 35 W blue LED light for 20 h. 4-Methylbenzaldehyde (6) and 1,2-di-*p*-tolylethane (7) could be detected by GC-MS and the yield was determined by GC analysis of the crude reaction mixture using dodecane as the internal standard.

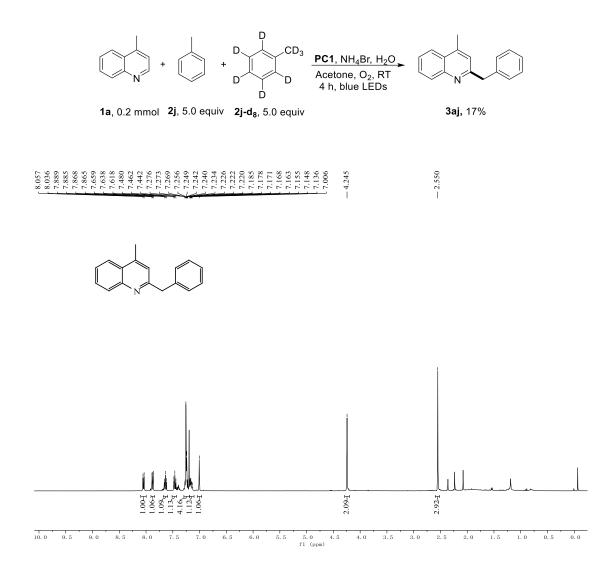


To a Schlenk tube were added *p*-xylene (**2a**, 0.2 mmol), **PC1** (0.004 mmol, 2 mol%), NH₄Br (0.1 mmol, 0.5 equiv), H₂O (2 mmol, 10.0 equiv), acetone (3 mL). Then the mixture was stirred at room temperature in oxygen atmosphere (1 atm) under 35 W blue LED light for 20 h. 4-Methylbenzaldehyde and 1,2-di*p*-tolylethane could be detected by GC-MS and the yield was determined by GC analysis of the crude reaction mixture using dodecane as the internal standard.

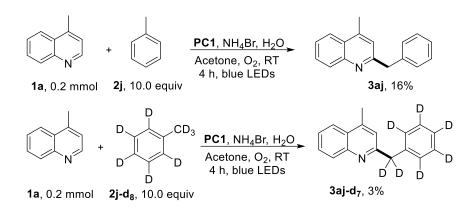


3.2 Kinetic isotope effect

(a) A solution of toluene (**2j**, 5.0 equiv, 92.14 mg), and toluene-d₈ (**2j-d**₈, 5.0 equiv, 100.19 mg), 4methylquinoline (**1a**, 0.2 mmol), **PC1** (0.004 mmol, 2 mol%), NH₄Br (0.1 mmol, 0.5 equiv), H₂O (2 mmol, 10.0 equiv), acetone (3 mL). Then the mixture was stirred at room temperature in oxygen atmosphere (1 atm) under 35 W blue LED light for 4 h. the reaction mixture was washed with brine. The aqueous phase was re-extracted with EtOAc ($3 \times 10 \text{ mL}$). The combined organic extracts were dried over Na₂SO₄ and concentrated in vacuum. The residue was purified by silica gel flash column chromatography (hexane/ethyl acetate = 10 : 1) to afford product **3aj** in 17% yield.



(b) Two parallel reactions of toluene (**2j**) or toluene-d₈ (**2j**-d₈) were performed. A solution of toluene (**2j**, 10.0 equiv, 184.28 mg), or toluene- d₈ (**2j**-d₈, 10.0 equiv, 200.38 mg), 4-methylquinoline (**1a**, 0.2 mmol), **PC1** (0.004 mmol, 2 mol%), NH₄Br (0.1 mmol, 0.5 equiv), H₂O (2 mmol, 10.0 equiv), Acetone (3 mL). Then the mixture was stirred at room temperature in oxygen atmosphere (1 atm) under 35 W blue LED light for 4 h. the reaction mixture was washed with brine. The aqueous phase was re-extracted with EtOAc (3×10 mL). The combined organic extracts were dried over Na₂SO₄ and concentrated in vacuum. The solvent was removed on a rotary evaporator under reduced pressure. The residue was measured by GC, and the product **3aj** in 16% yield and **3aj-d**₇ in 3% yield by using dodecane as the internal standard.

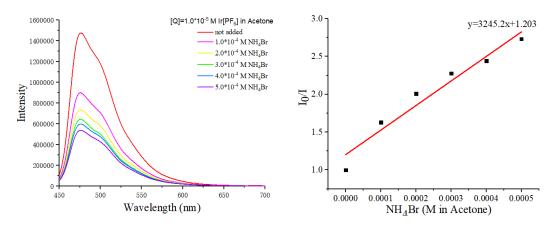


3.3. Stern–Volmer Quenching¹

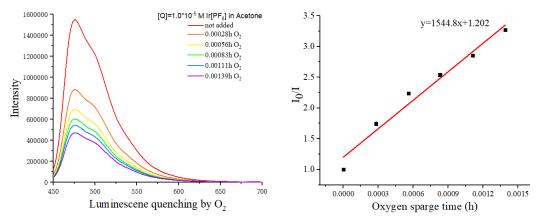
Formulation solution: 4-Methylquinoline (357.7 mg) was dissolved in acetone in a 25 mL volumetric flask to set the concentration to be 0.1 M. *p*-Xylene (616.5 μ L) was dissolved in acetone in a 25 mL volumetric flask to set the concentration to be 0.5 M. NH₄Br (122.4 mg) was dissolved in acetone in a 25 mL volumetric flask to set the concentration to be 0.05 M. Photocatalyst Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (2.8 mg) was dissolved in acetone (25.0 mL) to set the concentration to be 0.1 mM.

Experimental procedure: The resulting 0.1 M solution (50 μ L) was added to cuvette to obtain different concentrations of catalyst solution. This solution was then diluted to a volume of 2.0 mL by adding further solvent (acetone) to prepare a 2.5 μ M solution. The resulting mixture was sparged with nitrogen for 3 minutes and then irradiated at 375 nm. Fluorescence emission spectra were recorded (3 trials per sample). Into this solution, 10.0 μ L of a 4-methylquinoline solution was successively added and uniformly stirred, and the resulting mixture was bubbled with nitrogen for 3 minutes and irradiated at 375 nm. Fluorescence emission for 3 minutes and irradiated at 375 nm. Fluorescence emission spectra were recorded (3 trials per sample). Into this solution, 10.0 μ L of a 4-methylquinoline solution was successively added and uniformly stirred, and the resulting mixture was bubbled with nitrogen for 3 minutes and irradiated at 375 nm. Fluorescence emission spectra of 0 μ L, 20.0 μ L, 40.0 μ L, 60.0 μ L, 80.0 μ L, 100.0 μ L, fluorescence intensity. Follow this method and make changes to the amount to obtain the Stern–Volmer relationship in turn.

(a) Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ quenched by NH₄Br in acetone



The emission intensity of the $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ catalyst solution strongly affected by the gradual increase of the amount of NH_4Br .

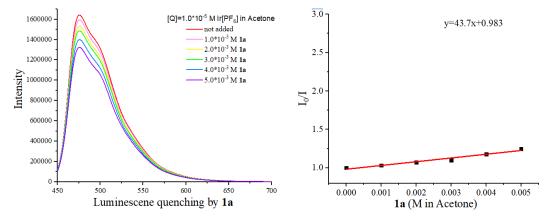


(b) $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ quenched by O_2 in acetone

The emission intensity of the $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ catalyst solution strongly affected by the

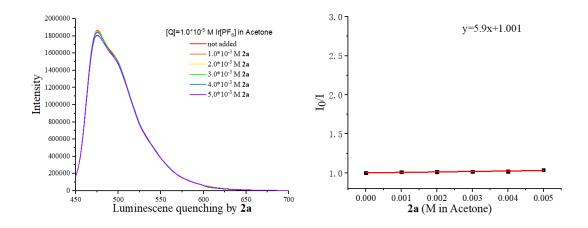
gradual increase of the amount of O2.

(c) $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ quenched by **1a** in acetone.



The emission intensity of the $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ catalyst solution slightly affected by the gradual increase of the amount of **1a**.

(d) $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ quenched by **2a** in acetone. Linear quenching is not observed.



3.4 Quantum yield determination

Determination of the light intensity at 415 nm:

According to the procedure of Yoon² the photon flux of the blue LED ($\lambda_{max} = 415$ nm) was determined by standard ferrioxalate actinometry. A 0.15 M solution of ferrioxalate was prepared by dissolving 2.21 g of potassium ferrioxalate hydrate in 30 mL of 0.05 M H₂SO₄. A buffered solution of phenanthroline was prepared by dissolving 50 mg of phenanthroline and 11.25 g of sodium acetate in 50 mL of 0.5 M H₂SO₄. Both solutions were stored in the dark. To determine the photon flux of the spectrophotometer, 2.0 mL of the ferrioxalate solution was placed in a cuvette and irradiated for 90.0 seconds at $\lambda = 415$ nm with an emission slit width at 10.0 nm. After irradiation, 0.35 mL of the phenanthroline solution was added to the cuvette. The solution was then allowed to rest for 1 h to allow the ferrous ions to completely coordinate to the phenanthroline. The absorbance of the solution was measured at 510 nm. A nonirradiated sample was also prepared and the absorbance at 510 nm measured. Conversion was calculated using eq 1.

mol of Fe²⁺ =
$$\frac{V \cdot \Delta A_{510} nm}{l \cdot \varepsilon}$$
 (1)
(0.00235 L) · (0.913)

mol of Fe²⁺ =
$$\frac{(0.00235 L) \cdot (0.913)}{(1.00 cm) \cdot (11,100 \frac{L}{mol} cm^{-1})} = 1.933 \times 10^{-7}$$

Where V is the total volume (0.00235 L) of the solution after addition of phenanthroline, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, 1 is the path length (1.000 cm), and ϵ is the molar absorptivity of the ferrioxalate actinometer at 510 nm (11,100 L mol⁻¹ cm⁻¹).³ The photon flux can be calculated using eq 2.

Photo flux =
$$\frac{mol \ of \ Fe^{2+}}{\phi \cdot t \cdot f}$$
 (2)

Photo flux =
$$\frac{1.933 \times 10^{-7}}{(1.12) \cdot (90 \text{ s}) \cdot (1)} = 1.92 \times 10^{-9} \text{ einstein/s}$$

Where Φ is the quantum yield for the ferrioxalate actinometer (1.12 at $\lambda = 415$ nm),⁴ t is the time (90.0 s), and f is the fraction of light absorbed at 415 nm by the ferrioxalate actinometer. This value is calculated using eq 3 where A₄₁₅ nm is the absorbance of the ferrioxalate solution at 415 nm. An absorption spectrum gave an A₄₁₅ nm value of > 3, indicating that the fraction of absorbed light (f) is > 0.999.

$$f = 1 - 10^{-A_{415} nm}$$
(3)

The photon flux was thus calculated to be 1.92 $\times 10^{\text{-9}}$ einsteins s ^-1

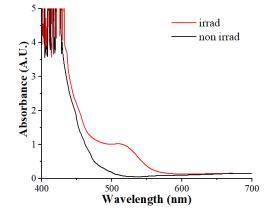
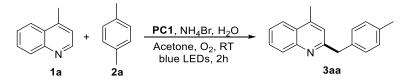


Figure S1. Absorbance of the ferrioxalate actinometer solution.

Determination of the reaction quantum yield.



A cuvette was charged with 4-methylquinoline (**1a**, 0.2 mmol), *p*-xylene (**2a**, 2 mmol, 10.0 eqiuv), **PC1** (0.004 mmol, 2 mol%), NH₄Br (0.1 mmol, 0.5 equiv), H₂O (2 mmol, 10.0 equiv), acetone (3 mL). The reaction mixture was stirred at room temperature for 2 h (7,200 s) under blue LED irradiation (λ = 415 nm). The solvent was removed in vacuo and the yield of formed product was determined by ¹H NMR based on dibromomethane as internal standard. The quantum yield was determined using eq 4.

$$\phi = \frac{mol \ of \ product}{flux \cdot t \cdot f} \qquad (4)$$

$$\phi = \frac{7.2 \times 10^{-5}}{(1.92 \times 10^{-9} einstein \ s^{-1}) \cdot (7200) \cdot (0.995)} = 0.52$$

The photon flux is 1.92×10^{-9} einsteins s⁻¹, t is the reaction time (7,200 s). f is the fraction of incident light absorbed by the catalyst, determined using eq 3. An absorption spectrum of the catalyst (0.001 M)

gave an absorbance value of 2.31 at 415 nm (figure S2), indicating that the fraction of light absorbed by the photocatalyst (f) is 0.995.

Absorbance of catalyst:

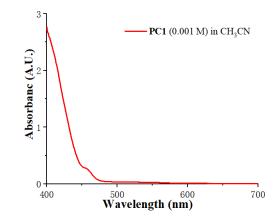
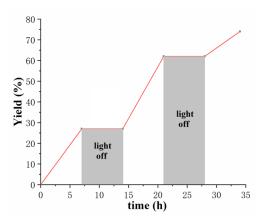


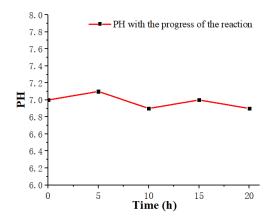
Figure S2. Absorption spectrum of PC1 [0.001 M] in acetonitrile

3.5 Light on/off experiment



The above depicted reaction was performed according to the general protocol established. The reaction was irradiated with Blue LEDs for 7 hour and then stirred in the dark for 7 hour. This procedure was repeated for 35 hours, and the yield of the product was determined by ¹H NMR with dibromomethane as an internal standard at each point the light was turned off or on. The results are shown in the graph above. This result shows that constant light irradiation is needed to progress the reaction.

3.6 System PH with the progress of the reaction

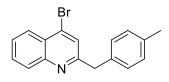


The above depicted reaction was performed according to the general protocol established. The PH of the reaction was measured at 5 hours intervals by PH meter. The results are shown in the graph above. This result indicates that the H+ which is generated from HBr can not acidifies the system.

4. Analytical data

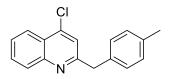
4-Methyl-2-(4-methylbenzyl)quinoline (3aa)⁵

Yield: 36.6 mg, 74%; yellow solid; mp 63-65 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ: 8.11 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.71-7.67 (m, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.21 (d, *J* = 7.6 Hz, 2H), 7.11 (d, *J* = 7.6 Hz, 2H), 7.06 (s, 1H), 4.27 (s, 2H), 2.60 (s, 3H), 2.31 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 161.1, 147.5, 144.6, 136.2, 136.0, 129.4, 129.3, 129.1, 129.0, 126.8, 125.7, 123.6, 122.1, 45.0, 21.0, 18.7.



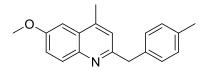
4-Bromo-2-(4-methylbenzyl)quinoline (3ba)

Yield: 42.3 mg, 68%; yellow solid; mp 68-71 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ : 8.13-8.07 (m, 2H), 7.74 (t, *J* = 8.0 Hz, 1H), 7.58 (t, *J* = 8.0 Hz, 1H), 7.51 (s, 1H), 7.20 (d, *J* = 7.6 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 4.26 (s, 2H), 2.33 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 161.3, 148.2, 136.3, 135.3, 1345, 130.4, 129.4, 129.3, 129.1, 127.1, 126.6, 126.3, 125.3, 44.6, 21.0. HRMS (ESI) m/z calcd for C₁₇H₁₄BrNNa⁺ (M+Na)⁺ 312.0382, found 312.0386.



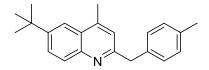
4-Chloro-2-(4-methylbenzyl)quinoline (3ca)

Yield: 40.6 mg, 76%; yellow solid; mp 71-75 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ : 8.16 (d, J = 8.4 Hz, 1H), 8.10 (d, J = 8.4 Hz, 1H), 7.75 (t, J = 8.0 Hz, 1H), 7.59 (t, J = 7.2 Hz, 1H), 7.30 (s, 1H), 7.20 (d, J = 7.6 Hz, 2H), 7.13 (d, J = 7.6 Hz, 2H), 4.27 (s, 2H), 2.32 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 161.4, 148.4, 142.9, 136.3, 135.3, 130.4, 129.4, 129.2, 129.1, 126.9, 125.0, 123.9, 121.4, 44.8, 21.0. HRMS (ESI) m/z calcd for C₁₇H₁₄ClNNa⁺ (M+Na)⁺ 290.0707, found 290.0709.



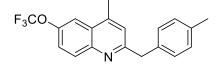
6-Methoxy-4-methyl-2-(4-methylbenzyl)quinoline (3da)

Yield: 24.9 mg, 45%; white solid; mp 121-123 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ : 8.00 (d, J = 9.2 Hz, 1H), 7.35 (dd, J = 9.2, 2.8 Hz, 1H), 7.20 (d, J = 7.6 Hz, 2H), 7.14 (d, J = 2.8 Hz, 2H), 7.11 (d, J = 7.6 Hz, 2H), 7.03 (s, 1H), 4.22 (s, 2H), 3.93 (s, 3H), 2.55 (s, 3H), 2.31 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 158.5, 157.2, 143.3, 143.2, 136.5, 135.9, 130.8, 129.2, 129.0, 127.6, 122.3, 121.1, 102.1, 55.5, 44.7, 21.0, 18.9. HRMS (ESI) m/z calcd for C₁₉H₂₀NO⁺ (M+H)⁺ 278.1539, found 278.1546.



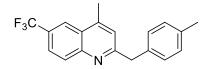
6-(tert-Butyl)-4-methyl-2-(4-methylbenzyl)quinoline (4ea)

Yield: 28.5 mg, 47%; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ : 8.04 (d, *J* = 8.8 Hz, 1H), 7.83 (s, 1H), 7.79 (d, *J* = 8.8, Hz, 1H), 7.18 (d, *J* = 7.8 Hz, 2H), 7.10 (d, *J* = 7.8 Hz, 2H), 7.03 (s, 1H), 4.24 (s, 2H), 2.60 (s, 3H), 2.31 (s, 3H), 1.43 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ : 160.3, 148.5, 145.8, 144.6, 136.4, 135.9, 129.2, 129.0, 128.8, 128.0, 126.3, 122.2, 118.4, 44.8, 35.0, 31.3, 21.0, 18.8. HRMS (ESI) m/z calcd for C₂₂H₂₆N⁺ (M+H)⁺ 304.2060, found 304.2065.



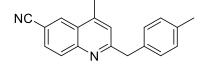
4-Methyl-2-(4-methylbenzyl)-6-(trifluoromethoxy)quinoline (3fa)

Yield: 53.6 mg, 81%; yellow solid; mp 96-99 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ : 8.12 (d, J = 9.2 Hz, 1H), 7.72 (s, 1H), 7.57-7.54 (m, 1H), 7.19 (d, J = 8.0 Hz, 2H), 7.13-7.11 (m, 3H), 4.25 (s, 2H), 2.58 (s, 3H), 2.32 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 161.7, 146.4, 145.9, 144.5, 136.1, 135.9, 131.6, 129.3, 129.0, 127.2, 123.1, 123.0, 120.6 (d, J = 255.9 Hz), 114.5, 44.9, 21.0, 18.6. HRMS (ESI) m/z calcd for C₁₉H₁₆F₃NONa⁺ (M+Na)⁺ 354.1076, found 354.1079.



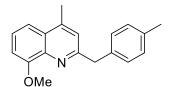
4-Methyl-2-(4-methylbenzyl)-6-(trifluoromethyl)quinoline (3ga)

Yield: 47.9 mg, 76%; yellow solid; mp 97-99 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ : 8.12 (d, J = 9.2 Hz, 1H), 7.72 (s, 1H), 7.57-7.54 (m, 1H), 7.19 (d, J = 8.0 Hz, 2H), 7.13-7.11 (m, 3H), 4.256 (s, 2H), 2.58 (s, 3H), 2.32 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 163.5, 148.6, 145.6, 136.2, 135.6, 130.5, 129.4, 129.0, 127.3 (d, J = 32.1 Hz), 126.0, 124.9 (d, J = 3.3 Hz), 124.2 (d, J = 270.5 Hz), 123.3, 121.6 (q, J = 13.0 Hz), 45.0, 21.0, 18.6. HRMS (ESI) m/z calcd for C₁₉H₁₇F₃N⁺ (M+H)⁺ 316.1308, found 316.1311.



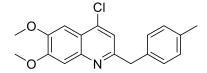
4-Methyl-2-(4-methylbenzyl)quinoline-6-carbonitrile (3ha)

Yield: 44.6 mg, 82%; white solid; mp 87-90 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ : 8.33 (s, 1H), 8.15 (d, *J* = 8.8 Hz, 1H), 7.83 (d, *J* = 8.8 Hz, 1H), 7.19 (t, *J* = 8.0 Hz, 3H), 7.13 (d, *J* = 7.6 Hz, 2H), 4.27 (s, 2H), 2.63 (s, 3H), 2.33 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 164.5, 148.7, 145.2, 136.4, 135.3, 130.9, 131.2, 130.0, 129.4, 129.0, 126.5, 123.7, 119.0, 109.2, 45.1, 21.0, 18.6. HRMS (ESI) m/z calcd for C₂₀H₁₉N₂Na⁺ (M+Na)⁺ 295.1206, found 295.1209.



8-Methoxy-4-methyl-2-(4-methylbenzyl)quinoline (3ia)

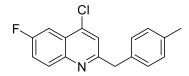
Yield: 22.7 mg, 41%; brown solid; mp 91-94 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ : 7.50 (dd, J = 8.4, 1.2 Hz, 1H), 7.44 (t, J = 8.0 Hz, 1H), 7.20 (d, J = 7.6 Hz, 2H), 7.12 (d, J = 7.6 Hz, 2H), 7.07 (d, J = 7.6 Hz, 1H), 7.03 (s, 1H), 4.36 (s, 2H), 4.10 (s, 3H), 2.57 (s, 3H), 2.33 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 160.2, 155.4 144.6, 139.1, 136.3, 135.9, 129.3, 129.2, 127.9, 125.7, 122.6, 115.5, 107.6, 56.1, 45.0, 21.0, 19.2. HRMS (ESI) m/z calcd for C₁₉H₁₉NNaO⁺ (M+Na)⁺ 300.1359, found 300.1361.



4-Chloro-6,7-dimethoxy-2-(4-methylbenzyl)quinoline (3ja)

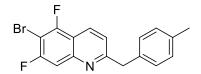
Yield: 30.7 mg, 47%; yellow solid; mp 151-153 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ: 7.42 (s, 1H), 7.34 (s, 1H), 7.18 (t, *J* = 8.0 Hz, 3H), 7.13 (d, *J* = 7.6 Hz, 2H), 4.21 (s, 2H), 4.04 (s, 6H), 2.32 (s, 1H), 7.18 (t, *J* = 8.0 Hz, 3H), 7.13 (d, *J* = 7.6 Hz, 2H), 4.21 (s, 2H), 4.04 (s, 6H), 2.32 (s, 1H), 7.18 (t, *J* = 8.0 Hz, 3H), 7.18 (t, J = 8.0 Hz, 3H), 7.18 (t, J

3H); ¹³C NMR (100 MHz, CDCl₃) δ: 159.2, 153.0, 150.01, 145.5, 140.8, 136.1, 135.7, 129.3, 129.0, 120.2, 119.6, 108.0, 101.6, 56.2, 56.1, 44.5, 21.0. HRMS (ESI) m/z calcd for C₁₉H₁₈ClNNaO₂⁺ (M+Na)⁺ 350.0918, found 350.0921.



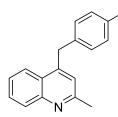
4-Chloro-6-fluoro-2-(4-methylbenzyl)quinoline (3ka)

Yield: 41.6 mg, 73%; yellow solid; mp 86-89 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ : 8.09 (dd, J = 9.2, 5.6 Hz, 1H), 7.78 (dd, J = 9.2, 2.8 Hz, 1H), 7.51 (ddd, J = 9.2, 8.0, 2.8 Hz, 1H), 7.33 (s, 1H), 7.19 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 4.25 (s, 2H), 2.33 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 160.8 (d, J = 246.9 Hz), 160.8 (d, J = 2.8 Hz), 145.5, 142.0, 136.4, 135.2, 131.9 (d, J = 8.9 Hz), 129.5, 129.0, 125.9 (d, J = 10.2 Hz), 122.0, 120.5 (d, J = 25.5 Hz), 107.8 (d, J = 24.1 Hz), 44.70, 21.04. HRMS (ESI) m/z calcd for C₁₇H₁₃ClFNNa⁺ (M+Na)⁺ 308.0613, found 308.0617.



6-Bromo-5,7-difluoro-2-(4-methylbenzyl)quinoline (3la)

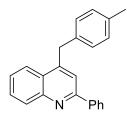
Yield: 52.7 mg, 76%; yellow solid; mp 125-127 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ : 8.23 (d, *J* = 8.8 Hz, 1H), 7.66 (d, *J* = 9.2 Hz, 1H), 7.28 (d, *J* = 8.8 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 4.28 (s, 2H), 2.32 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 164.14, 158.8 (dd, *J* = 249.0, 5.4 Hz), 155.5 (dd, *J* = 254.4, 6.1 Hz), 146.8, 144.5, 136.42, 135.16, 129.46, 129.06, 121.7 (dd, *J* = 3.4, 3.4 Hz), 114.8 (dd, *J* = 16.7, 1.3 Hz), 113.8, 109.6 (dd, *J* = 22.1, 4.5 Hz), 45.02, 21.04. HRMS (ESI) m/z calcd for C₁₇H₁₂BrF₂NNa⁺ (M+Na)⁺ 370.0013, found 370.0016.



2-Methyl-4-(4-methylbenzyl)quinoline (3ma)

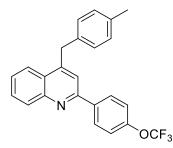
Yield: 27.2 mg, 55%; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ: 8.09 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.69 (t, *J* = 8.0 Hz, 1H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.11 (d, *J* = 8.0

Hz, 2H), 7.06 (s, 1H), 4.25 (s, 2H), 2.60 (s, 3H), 2.32 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 161.1, 147.5, 144.6, 136.2, 135.9, 129.4, 129.3, 129.1, 129.0, 126.8, 125.7, 123.6, 122.1, 45.0, 21.0, 18.7. HRMS (ESI) m/z calcd for C₁₈H₁₈N⁺ (M+H)⁺ 248.1434, found 248.1437.



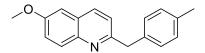
4-(4-Methylbenzyl)-2-phenylquinoline (3na)

Yield: 35.8 mg, 58%; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ : 8.22 (d, *J* = 8.4 Hz, 1H), 8.12 (d, *J* = 8.0 Hz, 2H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.73-7.71 (m, 1H), 7.66 (s, 1H), 7.54-7.44 (m, 4H), 7.16-7.10 (m, 4H), 4.46 (s, 2H), 2.34 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 157.1, 148.4, 147.4, 139.7, 136.1, 135.5, 130.3, 129.4, 129.3, 129.2, 128.7, 128.7, 127.5, 126.6, 126.2, 123.7, 119.8, 38.1, 21.0. HRMS (ESI) m/z calcd for C₂₃H₁₉NNa⁺ (M+Na)⁺ 332.1410, found 332.1413.



4-(4-Methylbenzyl)-2-(4-(trifluoromethoxy)phenyl)quinoline (3oa)

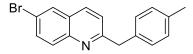
Yield: 51.1 mg, 65%; yellow solid; mp 85-88 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ : 8.18 (d, J = 8.4 Hz, 1H), 8.14-8.12 (m, 2H), 8.03 (d, J = 8.4 Hz, 1H), 7.71 (ddd, J = 8.4, 6.8, 1.6 Hz, 1H), 7.59 (s, 1H), 7.51 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.34 (d, J = 8.0 Hz, 2H), 7.12 (s, 4H), 4.46 (s, 2H), 2.33 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 155.6, 150.0, 148.3, 147.8, 138.3, 136.3, 135.4, 130.3, 129.6, 129.4, 129.0, 128.7, 126.6, 126.5, 123.8, 121.1, 120.4 (d, J = 255.8 Hz), 119.3, 38.1, 21.0. HRMS (ESI) m/z calcd for C₂₄H₁₈F₃NNaO⁺ (M+Na)⁺ 416.1233, found 416.1237.



6-Methoxy-2-(4-methylbenzyl)quinoline (3pa)

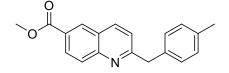
Yield: 21.0 mg, 40%; yellow solid; mp 59-63 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ : 7.99 (d, J = 9.2 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.35 (dd, J = 9.2, 2.8 Hz, 1H), 7.18 (t, J = 8.0 Hz, 3H), 7.11 (d,

 $J = 7.6 \text{ Hz}, 2\text{H}, 7.03 \text{ (d, } J = 2.8 \text{ Hz}, 1\text{H}, 4.27 \text{ (s, } 2\text{H}, 3.91 \text{ (s, } 3\text{H}), 2.31 \text{ (s, } 3\text{H}); {}^{13}\text{C} \text{ NMR} (100 \text{ MHz}, CDCl_3) \delta: 159.0, 157.3, 143.6, 136.3, 136.0, 135.4, 130.2, 129.3, 129.0, 127.6, 122.0, 121.7, 105.1, 55.5, 44.8, 21.0. HRMS (ESI) m/z calcd for C_{18}H_{18}NO^+ (M+H)^+ 264.1383, found 264.1387.$



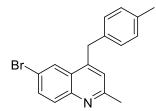
6-Bromo-2-(4-methylbenzyl)quinoline (3qa)

Yield: 41.0 mg, 66%; yellow solid; mp 84-87 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ : 7.97-7.91 (m, 3H), 7.76 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.24 (d, *J* = 8.4 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 4.29 (s, 2H), 2.32 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 162.0, 146.2, 136.2, 135.5, 132.9, 130.6, 129.5, 129.4, 129.1, 128.1, 127.8, 122.3, 119.7, 45.0, 21.0. HRMS (ESI) m/z calcd for C₁₇H₁₅BrN⁺ (M+H)⁺ 312.0382, found 3121.0383.



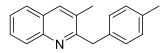
Methyl 2-(4-methylbenzyl)quinoline-6-carboxylate (3ra)

Yield: 41.9 mg, 72%; yellow solid; mp 119-121 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ : 8.53 (s, 1H), 8.29 (d, *J* = 8.8 Hz, 1H), 8.13 (d, *J* = 8.8 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 1H), 7.21 (d, *J* = 7.6 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 4.33 (s, 2H), 3.99 (s, 3H), 2.32 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 166.7, 163.9, 149.5, 137.8, 136.3, 135.5, 130.7, 129.4, 129.4, 129.1, 129.1, 127.5, 125.9, 122.3, 45.1, 21.0. HRMS (ESI) m/z calcd for C₁₉H₁₈NO₂⁺ (M+H)⁺ 292.1332, found 292.1336.



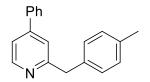
6-Bromo-2-methyl-4-(4-methylbenzyl)quinoline (3sa)

Yield: 40.9 mg, 63%; white solid; mp 135-138 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ : 8.14 (s, 1H), 7.89 (d, *J* = 8.8 Hz, 1H), 7.73-7.70 (m, 1H), 7.14 (d, *J* = 7.6 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.01 (s, 1H), 4.30 (s, 2H), 2.66 (s, 3H), 2.34 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 159.3, 146.5, 146.1, 136.4, 134.9, 132.5, 130.9, 129.4, 128.8, 1272, 126.0, 132.2, 119.6, 37.5, 25.3, 21.0. HRMS (ESI) m/z calcd for C₁₈H₁₇BrN⁺ (M+H)⁺ 326.0539, found 326.0542.



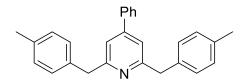
3-Methyl-2-(4-methylbenzyl)quinoline (3ta)

Yield: 25.7 mg, 52%; yellow solid; mp 58-61 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ : 8.10 (d, J = 8.4 Hz, 1H), 7.81 (s, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.64 (t, J = 8.0 Hz, 1H), 7.46 (d, J = 7.2 Hz, 1H), 7.10 (d, J = 8.0 Hz, 2H), 7.04 (d, J = 8.0 Hz, 2H), 4.38 (s, 2H), 2.33 (s, 3H), 2.27 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 160.4, 146.4, 136.4, 135.6, 135.3, 130.3, 129.0, 128.6, 128.5, 128.4, 127.5, 126.7, 125.9, 42.8, 20.9, 19.3. HRMS (ESI) m/z calcd for C₁₈H₁₈N⁺ (M+H)⁺ 248.1434, found 248.1435.



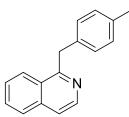
2-(4-Methylbenzyl)-4-phenylpyridine (3ua)

Yield: 19.3 mg, 37%; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ : 8.58 (d, *J* = 6.4 Hz, 1H), 7.58-7.55 (m, 2H), 7.47-7.40 (m, 3H), 7.33-7.31 (m, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 4.18 (s, 2H), 2.31 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 161.7, 149.6, 149.0, 138.3, 136.3, 135.9, 129.3, 129.0, 128.9, 128.9, 127.0, 121.0, 119.3, 44.3, 21.0. HRMS (ESI) m/z calcd for C₁₉H₁₈N⁺ (M+H)⁺ 260.1434, found 260.1438.



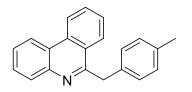
2,6-Bis(4-methylbenzyl)-4-phenylpyridine (3ua')

Yield: 10.9 mg, 15%; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ : 7.47-7.44 (m, 2H), 7.41-7.35 (m, 3H), 7.21 (d, *J* = 7.6 Hz, 4H), 7.13-7.08 (m, 6H), 4.19 (s, 4H), 2.32 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ : 161.1, 138.6, 136.4, 135.8, 129.2, 129.0, 128.8, 128.7, 128.1, 127.1, 118.7, 44.1, 21.1. HRMS (ESI) m/z calcd for C₂₇H₂₆N⁺ (M+H)⁺ 364.2060, found 364.2063.



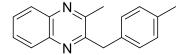
1-(4-Methylbenzyl)isoquinoline (3va)

Yield: 28.5 mg, 61%; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ : 8.49 (d, *J* = 5.6 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.56-7.50 (m, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 4.63 (s, 2H), 2.27 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 160.3, 141.9, 136.5, 136.3, 135.7, 129.8, 129.2, 128.4, 127.3, 127.2, 127.1, 125.8, 119.8, 41.6, 21.0. HRMS (ESI) m/z calcd for C₁₇H₁₆N⁺ (M+H)⁺ 234.1277, found 234.1284.



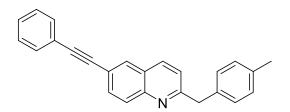
6-(4-Methylbenzyl)phenanthridine (3wa)

Yield: 36.8 mg, 65%; white solid; mp 100-102 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ : 8.58 (d, *J* = 8.0 Hz, 1H), 8.52 (d, *J* = 8.4 Hz, 1H), 8.19 (t, *J* = 8.0 Hz, 2H), 7.73 (t, *J* = 7.6 Hz, 2H), 7.63 (t, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 7.6 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 7.6 Hz, 2H), 4.71 (s, 2H), 2.25 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 160.3, 143.6, 135.9, 135.7, 133.2, 130.3, 129.7, 129.2, 128.6, 128.3, 127.3, 127.0, 126.6, 125.3, 123.9, 122.3, 121.9, 42.6, 21.0. HRMS (ESI) m/z calcd for C₂₁H₁₇NNa⁺ (M+Na)⁺ 306.1253, found 306.1259.



2-Methyl-3-(4-methylbenzyl)quinoxaline (3xa)

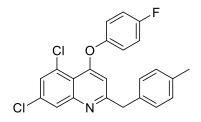
Yield: 28.8 mg, 58%; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ : 8.09-8.07 (m, 1H), 8.01-7.98 (m, 1H), 7.71-7.69 (m, 2H), 7.12-7.07 (m, 4H), 4.36 (s, 2H), 2.64 (s, 3H), 2.30 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 155.1, 153.7, 141.0, 141.0, 136.3, 134.0, 129.3, 129.2, 129.0, 128.7, 128.6, 128.2, 42.3, 23.0, 21.0. HRMS (ESI) m/z calcd for C₁₇H₁₇N₂⁺ (M+H)⁺ 249.1386, found 249.1394.



2-(4-Methylbenzyl)-6-(phenylethynyl)quinoline (3ya)

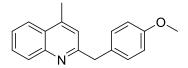
Yield: 28.8 mg, 58%; white solid; mp 72-74 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ : 8.06 (d, J = 8.8 Hz, 1H), 8.00 (t, J = 8.4 Hz, 1H), 7.81 (d, J = 8.4 Hz, 1H), 7.59-7.56 (m, 2H), 7.39-7.35 (m, 3H),

7.23 (dd, J = 14.4, 8.8 Hz, 3H), 7.13 (d, J = 7.6 Hz, 2H), 4.31 (s, 2H), 2.32 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 162.2, 136.3, 136.2, 135.8, 132.3, 131.6, 131.6, 130.8, 129.4, 129.1, 128.9, 128.5, 128.4, 126.5, 123.0, 122.2, 120.9, 90.4, 89.1, 45.0, 21.1. HRMS (ESI) m/z calcd for C₂₅H₂₀N ⁺ (M+H)⁺ 334.1590, found 334.1596.



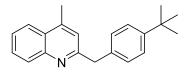
5,7-Dichloro-4-(4-fluorophenoxy)-2-(4-methylbenzyl)quinoline (3za)

Yield: 21.4 mg, 26%; yellow solid; mp 100-103 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ : 7.99 (d, *J* = 2.1 Hz, 1H), 7.52 (d, *J* = 2.1 Hz, 1H), 7.12-7.06 (m, 6H), 7.04-7.00 (m, 2H), 6.45 (s, 1H), 4.08 (s, 2H), 2.29 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 164.1, 162.5, 159.8 (d, *J* = 242.7 Hz), 151.2, 149.9, 136.2, 135.1, 135.0, 130.0, 129.3, 128.9, 128.7, 127.4, 121.9 (d, *J* = 8.4 Hz), 116.9 (d, *J* = 23.4 Hz), 116.8, 107.3, 44.7, 21.0. HRMS (ESI) m/z calcd for C₂₃H₁₆Cl₂FNNaO ⁺ (M+Na)⁺ 434.0485, found 434.0489.



2-(4-Methoxybenzyl)-4-methylquinoline (3ab)

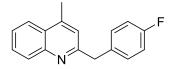
Yield: 41.0 mg, 74%; yellow solid; mp 74-76 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ : 8.09 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.69 (t, J = 8.3 Hz, 1H), 7.51 (t, J = 8.2 Hz, 1H), 7.23 (d, J = 8.4 Hz, 2H), 7.05 (s, 1H), 6.85 (d, J = 8.8 Hz, 2H), 4.23 (s, 2H), 3.78 (s, 3H), 2.61 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 161.2, 158.2, 147.8, 144.6, 131.4, 130.1, 129.4, 129.2, 126.8, 125.7, 123.6, 122.1, 114.0, 55.2, 44.5, 18.7. HRMS (ESI) m/z calcd for C₁₈H₁₈NO⁺ (M+H)⁺ 264.1383, found 264.1390.



2-(4-(tert-Butyl)benzyl)-4-methylquinoline (3ac)

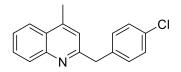
Yield: 46.2 mg, 80%; yellow solid; ¹H NMR (400 MHz, CDCl₃) δ:8.10 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.69 (t, *J* = 8.3 Hz, 1H), 7.52 (t, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.26-.25 (m, 2H),

7.10 (s, 1H), 4.27 (s, 1H), 2.62 (s, 3H), 1.30 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ: 161.0, 149.2, 147.4, 144.7, 136.2, 129.3, 129.2, 128.8, 126.9, 125.7, 125.5, 123.6, 122.2, 44.9, 34.4, 31.3, 18.8. HRMS (ESI) m/z calcd for C₂₁H₂₃N⁺ (M+H)⁺ 290.1903, found 290.1913.



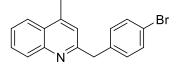
2-(4-Fluorobenzyl)-4-methylquinoline (3ad)⁶

Yield: 29.1 mg, 58%; yellow solid; mp 110.4-112.0 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ : 8.08 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.0 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.28-7.25 (m, 2H), 7.04 (s, 1H), 7.00-6.96 (m, 2H), 4.25 (s, 2H), 2.61 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 161.6 (d, *J* = 242.9 Hz), 160.5, 147.6, 144.8, 135.0 (d, *J* = 3.2 Hz), 130.5 (d, *J* = 7.8 Hz), 129.5, 129.2, 126.9, 125.8, 123.6, 122.0, 115.3 (d, *J* = 21.1 Hz), 44.6, 18.7.



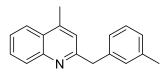
2-(4-Chlorobenzyl)-4-methylquinoline (3ae)⁵

Yield: 27.8 mg, 52%; orange solid; mp 51-52 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ: 8.08 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.94 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.70 (t, *J* = 7.7 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.28-7.22 (m, 4H), 7.03 (s, 1H), 4.25 (s, 2H), 2.61 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 160.2, 147.7, 144.9, 137.8, 132.3, 130.5, 129.4, 129.3, 128.7, 126.9, 125.9, 123.6, 122.0, 44.7, 18.7.



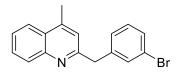
2-(4-Bromobenzyl)-4-methylquinoline (3af)⁵

Yield: 29.2 mg, 47%; brown solid; mp 70-71 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ: 8.07 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.02 (s, 1H), 4.23 (s, 2H), 2.61 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 160.1, 147.5, 144.9, 138.3, 131.6, 130.8, 129.4, 129.3, 126.8, 125.9, 123.6, 122.0, 120.3, 44.7, 18.7.



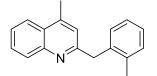
4-Methyl-2-(3-methylbenzyl)quinoline (3ag)⁶

Yield: 28.7 mg, 58%; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ : 8.09 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.69 (t, J = 8.3 Hz, 1H), 7.51 (t, J = 8.1 Hz, 1H), 7.19 (t, J = 7.4 Hz, 1H), 7.11 (d, J = 8.0 Hz, 2H), 7.06-7.03 (m, 2H), 4.25 (s, 2H), 2.60 (s, 3H), 2.31 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 161.0, 147.6, 144.5, 139.2, 138.2, 130.0, 129.5, 129.1, 128.4, 127.2, 126.9, 126.2, 125.7, 123.6, 122.2, 45.4, 21.4, 18.7.



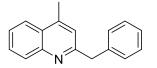
2-(3-Bromobenzyl)-4-methylquinoline (3ah)⁶

Yield: 25.5 mg, 41%; white solid; mp 55-56 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ: 8.08 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 7.6 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 8.2 Hz, 1H), 7.46 (s, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.16 (t, *J* = 7.8 Hz, 1H), 7.04 (s, 1H), 4.25 (s, 2H), 2.62 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 159.8, 147.6, 144.9, 141.6, 132.1, 130.1, 129.6, 129.5, 129.3, 127.8, 126.9, 125.9, 123.6, 122.6, 122.0, 44.9, 18.7.



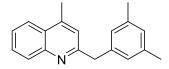
4-Methyl-2-(2-methylbenzyl)quinoline (3ai)⁶

Yield: 25.7 mg, 52%; white solid; mp 53-55 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ : 8.08 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.69 (t, *J* = 8.4 Hz, 1H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.20-7.16 (m, 4H), 6.94 (s, 1H), 4.31 (s, 2H), 2.58 (s, 3H), 2.30 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 160.6, 147.5, 144.6, 137.4, 137.1, 130.4, 130.1, 129.4, 129.1, 126.8, 126.8, 126.1, 125.7, 123.6, 121.6, 43.2, 19.9, 18.7.



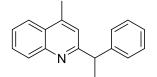
2-Benzyl-4-methylquinoline (3aj)⁶

Yield: 27.0 mg, 58%; yellow solid; mp 63-65 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ: 8.09 (d, *J* = 8.4, 1H), 7.92 (d, *J* = 8.4, Hz, 1H), 7.69 (t, *J* = 8.4 Hz, 1H), 7.51 (t, *J* = 8.2 Hz, 1H), 7.33-7.28 (m, 4H), 7.25-7.20 (m, 1H), 7.06 (s, 1H), 4.29 (s, 2H), 2.60 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 160.8, 147.6, 144.6, 139.3, 129.4, 129.2, 129.1, 128.6, 126.8, 126.4, 125.7, 123.6, 122.1, 45.4, 18.7.



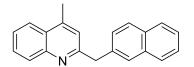
2-(3,5-Dimethylbenzyl)-4-methylquinoline (3ak)

Yield: 36.0 mg, 69%; yellow solid; mp 68-70 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ : 8.10 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.69 (t, J = 8.4 Hz, 1H), 7.51 (t, J = 8.2 Hz, 1H), 7.07 (s, 1H), 6.93 (s, 2H), 6.86 (s, 1H), 4.22 (s, 2H), 2.61 (s, 3H), 2.27 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ : 161.1, 147.5, 144.5, 139.1, 138.1, 129.5, 129.1, 128.1, 127.0, 126.9, 125.7, 123.6, 122.2, 45.4, 21.2, 18.7. HRMS (ESI) m/z calcd for C₁₉H₂₀N⁺ (M+H)⁺ 262.1590, found 262.1598.



4-Methyl-2-(1-phenylethyl)quinoline (3al)

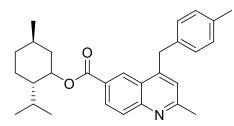
Yield: 22.2 mg, 45%; yellow solid; mp 65-68 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ : 8.11 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 7.6 Hz, 1H), 7.68 (t, J = 8.4 Hz, 1H), 7.50 (t, J = 8.2 Hz, 1H), 7.36 (d, J = 7.6 Hz, 2H), 7.30 (t, J = 7.6 Hz, 2H), 7.20 (t, J = 7.2 Hz, 1H), 7.02 (s, 1H), 4.45 (q, J = 7.2 Hz, 1H), 2.59 (s, 3H), 1.78 (d, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 164.8, 147.4, 144.7, 144.3, 129.7, 129.0, 128.4, 127.8, 127.0, 126.3, 125.7, 123.5, 121.2, 48.0, 20.4, 18.8. HRMS (ESI) m/z calcd for C₁₈H₁₇N⁺ (M+H)⁺ 248.1434, found 248.1443.



4-Methyl-2-(naphthalen-2-ylmethyl)quinoline (3am)⁵

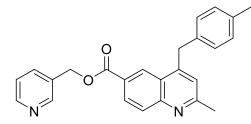
Yield: 18.7 mg, 33%; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ: 8.12 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.81-7.76 (m, 4H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.47-7.41 (m, 3H), 7.08 (s, 1H), 4.45 (s, 2H), 2.58 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 160.7, 147.6, 144.7, 136.9, 133.6,

132.2, 129.5, 129.2, 128.2, 127.7, 127.6, 127.6, 127.5, 126.9, 126.0, 125.8, 125.5, 123.6, 122.3, 45.6, 18.6.



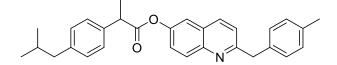
(2S,5R)-2-Isopropyl-5-methylcyclohexyl 2-methyl-4-(4-methylbenzyl)quinoline-6-carboxylate (4a)

Yield: 38.6 mg, 45%; yellow solid; mp 110.4-112.0 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ : 8.81 (s, 1H), 8.25 (dd, *J* = 8.8, 1.6 Hz, 1H), 8.05 (d, *J* = 8.8 Hz, 1H), 7.13 (s, 4H), 7.08 (s, 1H), 4.97 (td, *J* = 10.9, 4.4 Hz, 1H), 4.46-4.36 (m, 2H), 2.70 (s, 3H), 2.33 (s, 3H), 2.18-2.15 (m, 1H), 2.00-1.96 (m, 1H), 1.78-1.72 (m, 2H), 1.64-1.56 (m, 2H), 1.17-1.08 (m, 2H), 0.94 (d, *J* = 7.2 Hz, 7H), 0.80 (d, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 165.8, 161.1, 149.9, 148.4, 136.2, 135.1, 129.4, 129.3, 128.8, 128.7, 127.7, 126.8, 125.1, 123.1, 75.1, 47.2, 40.9, 37.7, 34.3, 31.4, 26.5, 25.5, 23.6, 22.0, 21.0, 20.8, 16.5. HRMS (ESI) m/z calcd for C₂₉H₃₅NNaO₂⁺ (M+Na)⁺ 452.2560, found 452.2567.



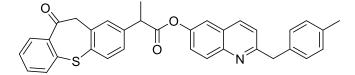
Pyridin-3-ylmethyl 2-methyl-4-(4-methylbenzyl)quinoline-6-carboxylate (4b)

Yield: 39.0 mg, 51%; yellow solid; mp 110.4-112.0 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ : 8.83 (s, 1H), 8.75 (s, 1H), 8.64 (d, *J* = 4.9 Hz, 1H), 8.26 (d, *J* = 8.8 Hz, 1H), 8.08 (d, *J* = 8.8 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.36 (dd, *J* = 7.6, 4.8 Hz, 1H), 7.13-7.08 (m, 5H), 5.42 (s, 2H), 4.40 (s, 2H), 2.72 (s, 3H), 2.33 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 166.0, 161.5, 149.7, 149.7, 136.4, 136.1, 134.9, 131.5, 129.5, 129.4, 129.3, 128.9, 128.8, 127.2, 126.6, 126.6, 125.2, 123.6, 123.3, 64.4, 37.7, 25.4, 21.1. HRMS (ESI) m/z calcd for C₂₅H₂₂N₂NaO₂⁺ (M+Na)⁺ 391.1417, found 391.1421.

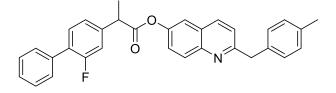


2-(4-Methylbenzyl)quinolin-6-yl 2-(4-isobutylphenyl)propanoate (4c)

Yield: 59.5 mg, 68%; yellow solid; mp 110.4-112.0 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ : 8.06 (d, *J* = 9.2 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.41 (s, 1H), 7.33 (d, *J* = 8.0 Hz, 3H), 7.23-7.16 (m, 5H), 7.11 (d, *J* = 8.0 Hz, 2H), 4.28 (s, 2H), 3.99 (q, *J* = 7.2 Hz, 1H), 2.48 (d, *J* = 7.2 Hz, 2H), 2.31 (s, 3H), 1.90-1.86 (m, 1H), 1.64 (d, *J* = 7.2 Hz, 3H), 0.93 (s, 3H), 0.91 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 173.3, 161.3, 148.2, 140.9, 137.0, 136.2, 136.1, 135.9, 130.2, 129.6, 129.3, 129.0, 127.2, 126.9, 124.5, 122.0, 118.0, 45.3, 45.1, 44.9, 30.2, 22.4, 21.1, 18.5. HRMS (ESI) m/z calcd for C₃₀H₃₂NO₂⁺ (M+H)⁺ 438.2428, found 438.2438.

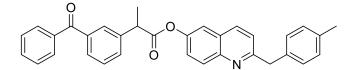


2-(4-Methylbenzyl)quinolin-6-yl 2-(10-oxo-10,11-dihydrodibenzo[*b*,*f*]thiepin-2-yl)propanoate (4d) Yield:56.0 mg, 53%; yellow solid; mp 110.4-112.0 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ : 8.21 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.06 (d, *J* = 8.8 Hz, 1H), 7.96 (d, *J* = 8.8 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 1.6 Hz, 1H), 7.47-7.40 (m, 2H), 7.34-7.27 (m, 3H), 7.22-7.16 (m, 3H), 7.10 (d, *J* = 8.0 Hz, 2H), 4.40 (s, 2H), 4.28 (s, 2H), 4.02 (q, *J* = 7.2 Hz, 1H), 2.31 (s, 3H), 1.63 (d, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 191.2, 172.4, 161.4, 148.0, 145.5, 142.0, 140.0, 138.2, 136.3, 136.1, 135.8, 133.6, 132.5, 131.7, 131.5, 130.8, 130.3, 129.3, 129.3, 129.0, 129.0, 128.7, 126.9, 126.3, 124.3, 122.1, 118.0, 51.0, 45.3, 44.9, 21.0, 18.5. HRMS (ESI) m/z calcd for C₃₄H₂₈NNaO₃S⁺ (M+H)⁺ 530.1784, found 530.1799.



2-(4-Methylbenzyl)quinolin-6-yl 2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoate (4e)

Yield: 57.0 mg, 60%; yellow solid; mp 110.4-112.0 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ : 8.09 (d, *J* = 9.2 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.58-7.55 (m, 2H), 7.49-7.43 (m, 4H), 7.4-7.36 (m, 2H), 7.30-7.23 (m, 2H), 7.23-7.17 (m, 3H), 7.11 (d, *J* = 7.6 Hz, 2H), 4.29 (s, 2H), 4.05 (q, *J* = 7.2 Hz, 1H), 2.31 (s, 3H), 1.69 (d, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 172.5, 161.4, 159.8 (d, *J* = 247.2 Hz), 148.1, 145.6, 141.0 (d, *J* = 7.5 Hz), 136.3, 136.1 135.8, 135.3, 131.1 (d, *J* = 3.8 Hz), 130.3, 129.3, 129.0, 128.9, 128.9, 128.5, 127.7, 126.9, 124.3, 123.6 (d, *J* = 3.3 Hz), 122.1, 118.0, 115.3 (d, *J* = 23.7 Hz), 45.1, 44.9, 21.0, 18.4. HRMS (ESI) m/z calcd for $C_{32}H_{26}FNNaO_2^+$ (M+Na)⁺ 498.1840, found 498.1856.



2-(4-Methylbenzyl)quinolin-6-yl 2-(3-benzoylphenyl)propanoate (4f)

Yield: 68.9 mg, 71%; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ : 8.08 (d, *J* = 8.8 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.90 (s, 1H), 7.83 (d, *J* = 7.2 Hz, 2H), 7.75 (d, *J* = 7.6, 1.6 Hz, 1H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.60 (d, *J* = 7.4 Hz, 1H), 7.54-7.44 (m, 4H), 7.35 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.23 (d, *J* = 8.4 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 4.29 (s, 2H), 4.12 (q, *J* = 7.2 Hz, 1H), 2.31 (s, 3H), 1.70 (d, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 196.4, 172.6, 161.5, 148.1, 145.6, 140.2, 138.1, 137.4, 136.2, 136.1, 135.9, 132.6, 131.5, 130.3, 130.1, 129.3, 129.2, 129.0, 128.9, 128.8, 128.3, 126.9, 124.3, 122.1, 118.0, 45.5, 44.9, 21.0, 18.5. HRMS (ESI) m/z calcd for C₃₃H₂₇NNaO₃⁺ (M+Na)⁺ 508.1883, found 508.1893.

5. Reference

[1] Nacsa, E. D.; MacMillan, D. W. C. Spin-Center Shift-Enabled Direct Enantioselective α-Benzylation of Aldehydes with Alcohols. *J. Am. Chem. Soc.* **2018**, *140*, 3322–3330.

[2] Cismesia M. A.; Yoon, T. P. Characterizing chain processes in visible light photoredox catalysis. *Chem. Sci.* **2015**, *6*, 5426-5434.

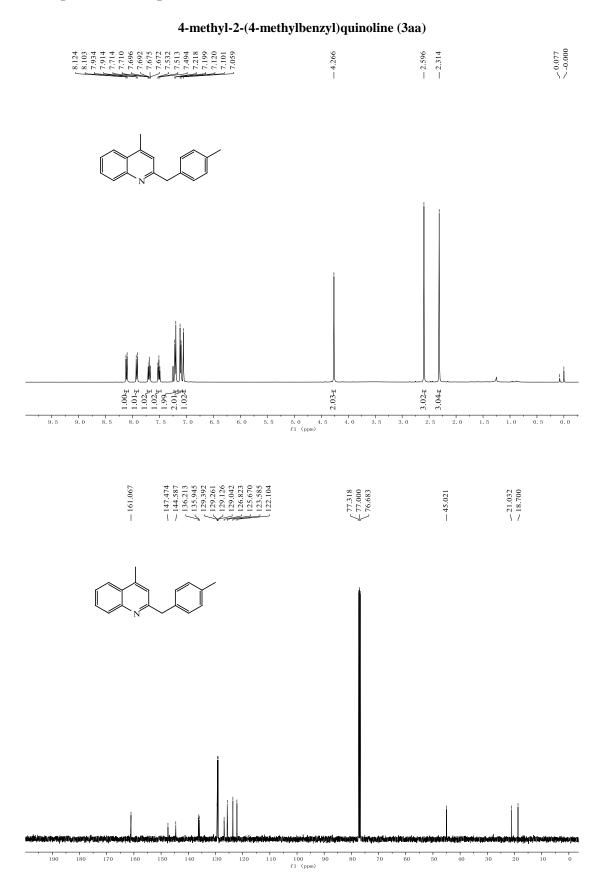
[3] Hatchard, C. G.; Parker, C. A. Proc. Roy. Soc. (London) 1956, A235, 518-536.

[4] Kim, I.; Park, B.; Kang, G.; Kim, J.; Jung, H.; Lee, H.; Baik, M.-H.; Hong, S. Angew. Chem. Int. Ed. 2018, 57, 15517-15522.

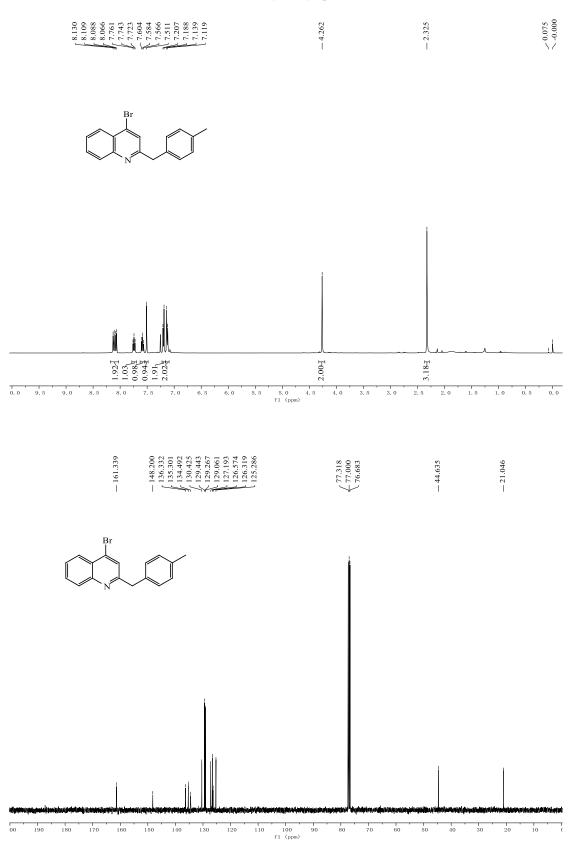
[5] Z. Wang, Q. Liu, X. Ji, G.-J. Deng, H, Huang, Bromide-Promoted Visible-Light-Induced Reductive Minisci Reaction with Aldehydes. ACS Catal. 2020, 10, 154-159

[6] S. Zhong, G.-J. Deng, Z. Dai, H, Huang, Visible-light-induced 4CzIPN/LiBr system: a tireless electron shuttle to enable reductive deoxygenation of N-heteroaryl carbonyls. *Org. Chem. Front.*, **2021**, doi: 10.1039/D1Q000634G

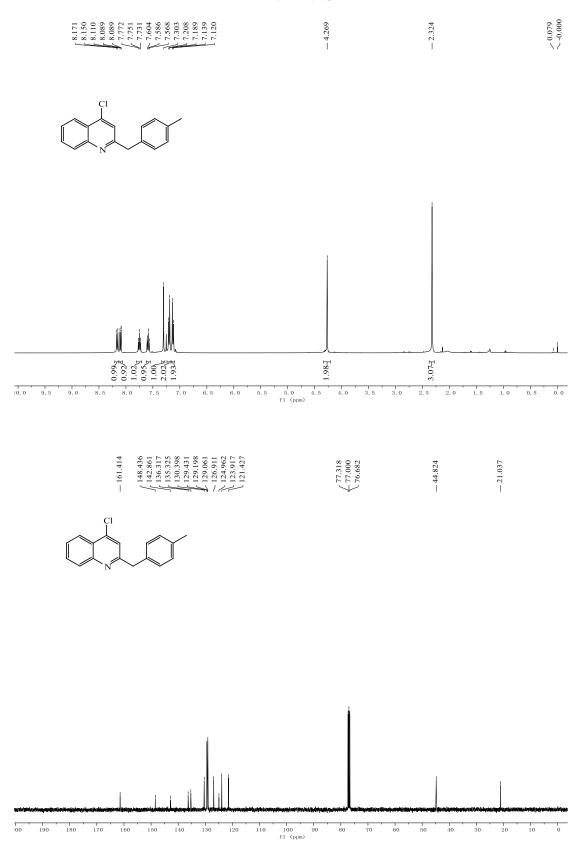
6. Copies of NMR spectra



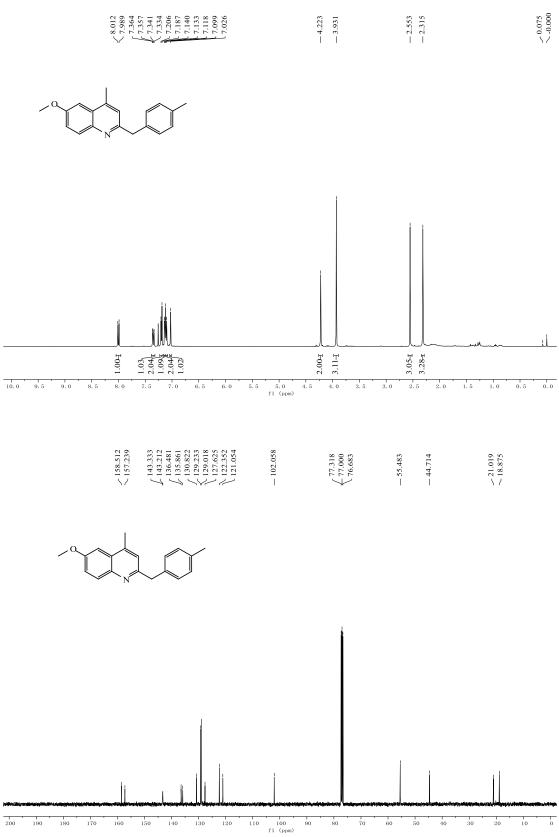
4-bromo-2-(4-methylbenzyl)quinoline (3ba)



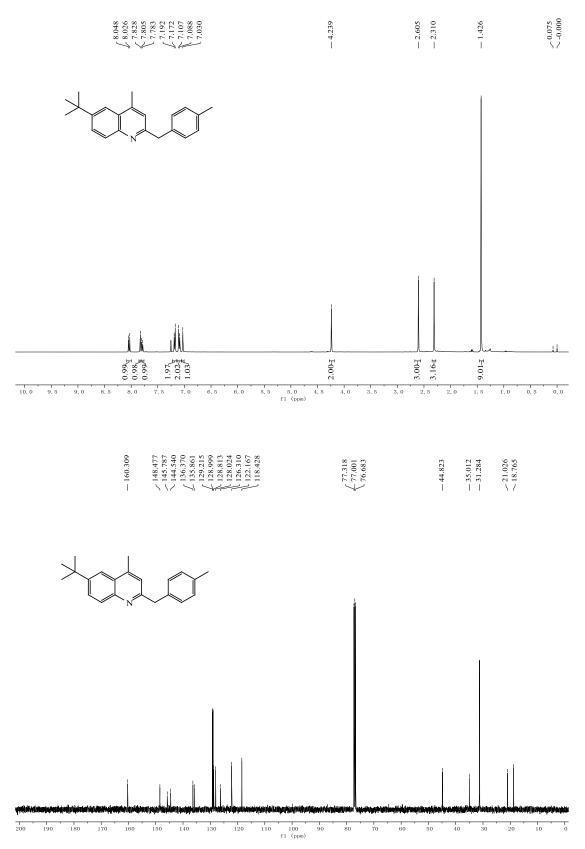
4-chloro-2-(4-methylbenzyl)quinoline (3ca)



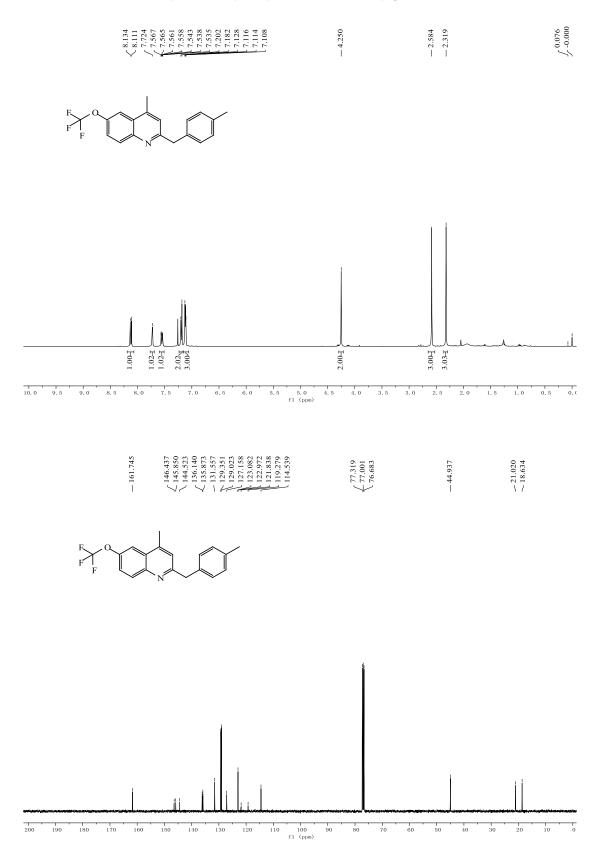


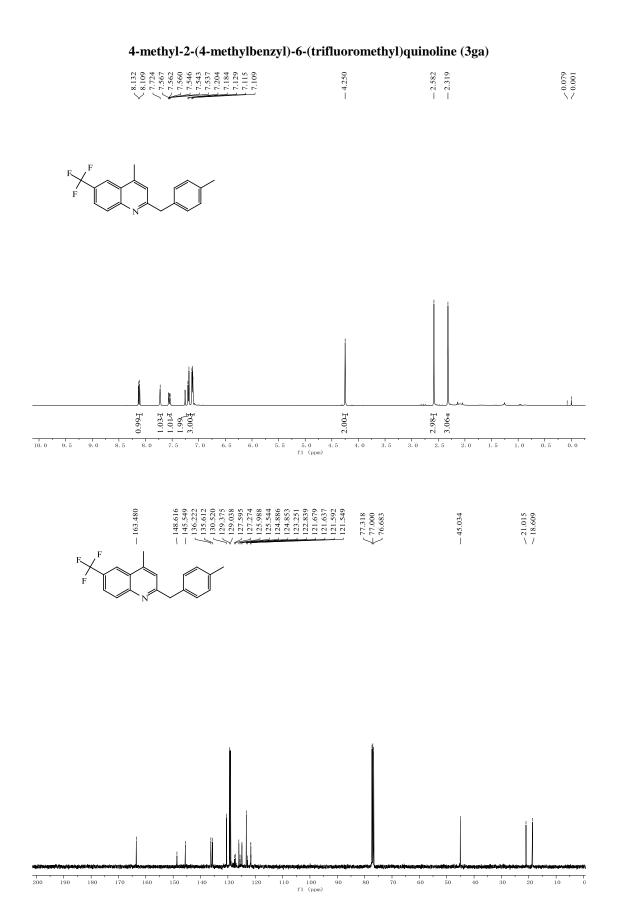






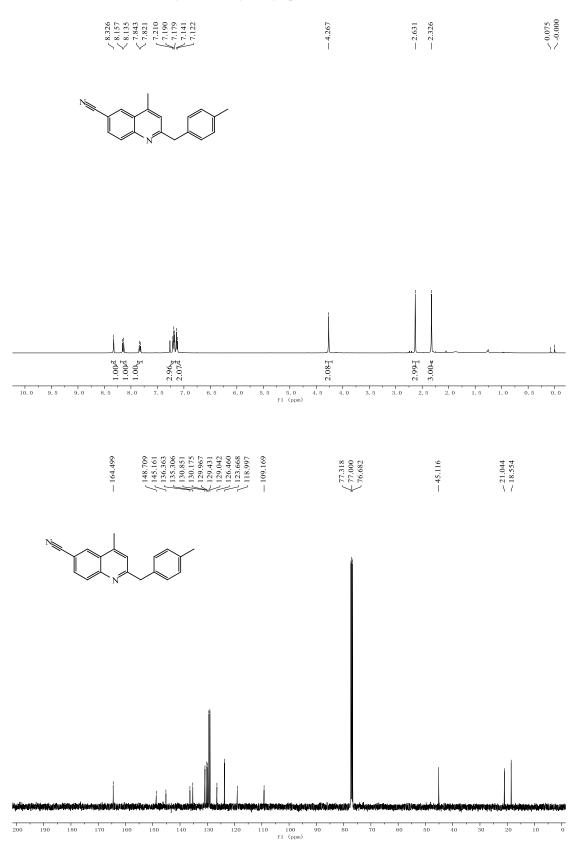
4-methyl-2-(4-methylbenzyl)-6-(trifluoromethoxy)quinoline (3fa)



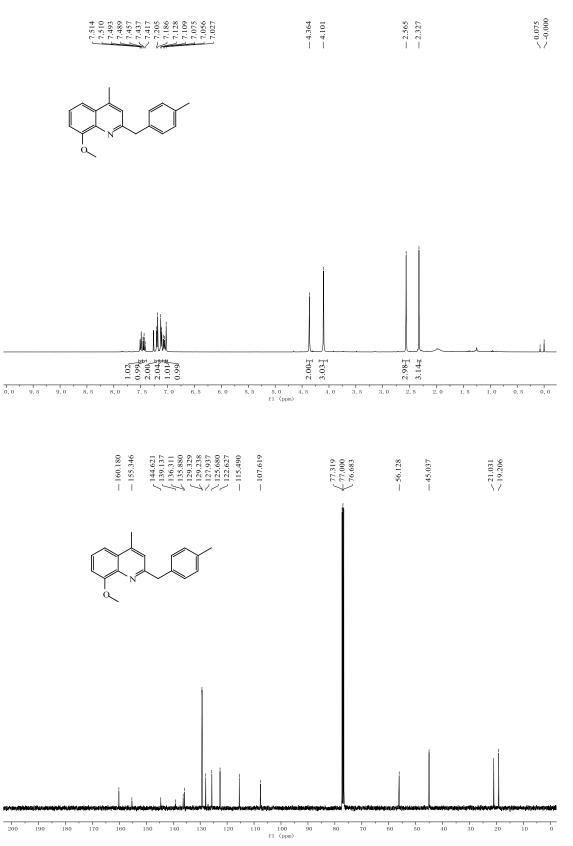


S35

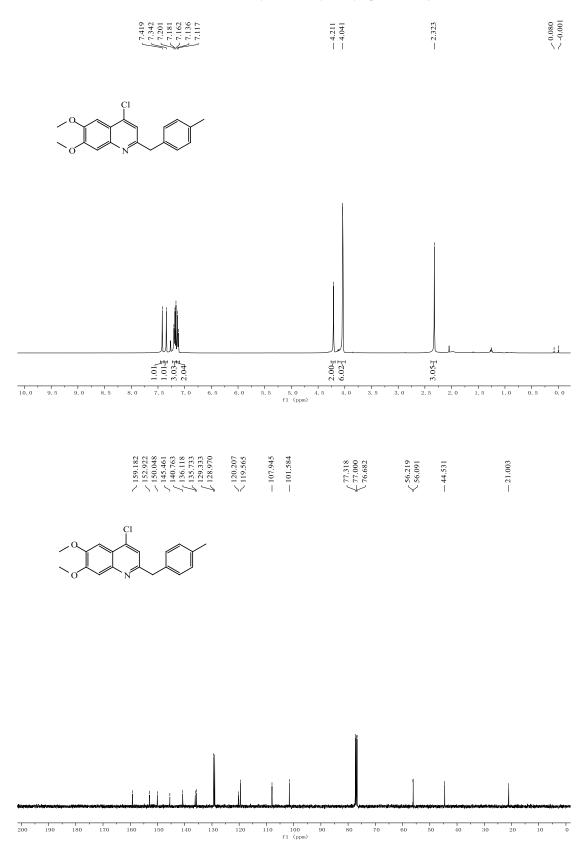
4-methyl-2-(4-methylbenzyl)quinoline-6-carbonitrile (3ha)



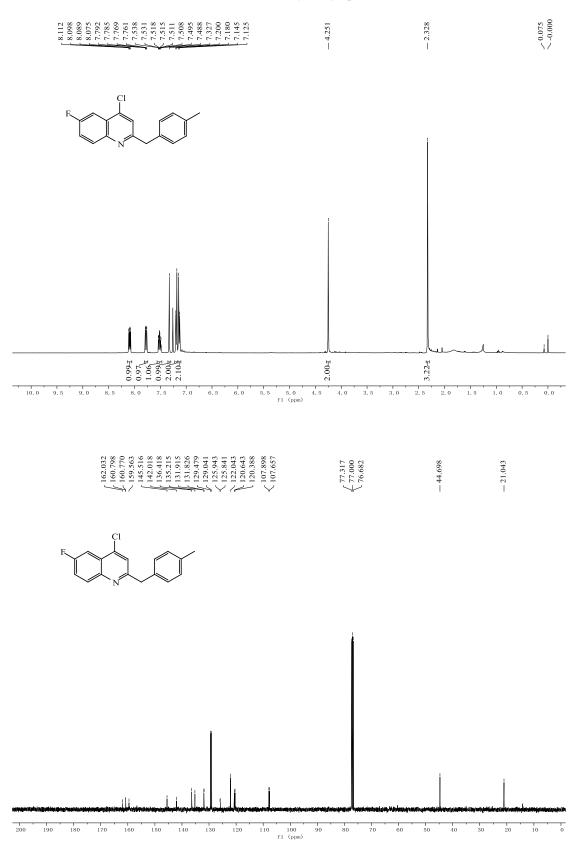
8-methoxy-4-methyl-2-(4-methylbenzyl)quinoline (3ia)



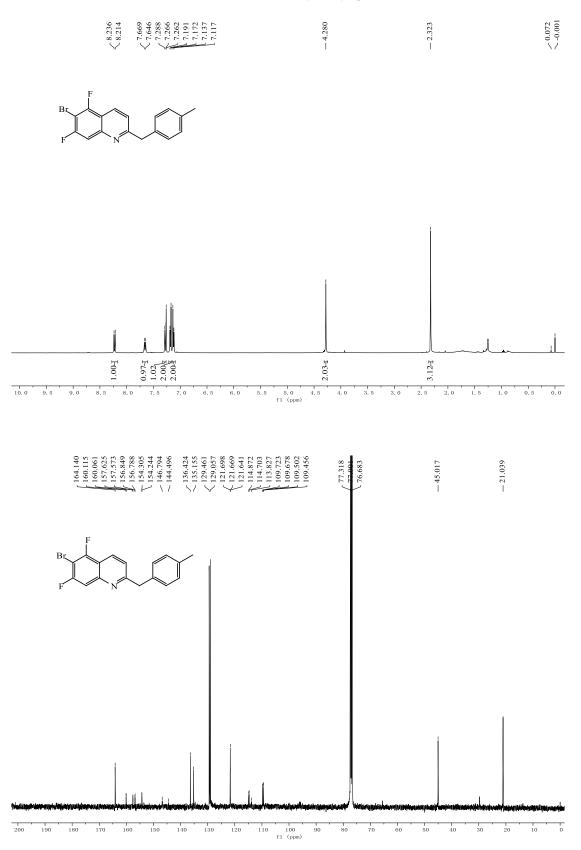
4-chloro-6,7-dimethoxy-2-(4-methylbenzyl)quinoline (3ja)



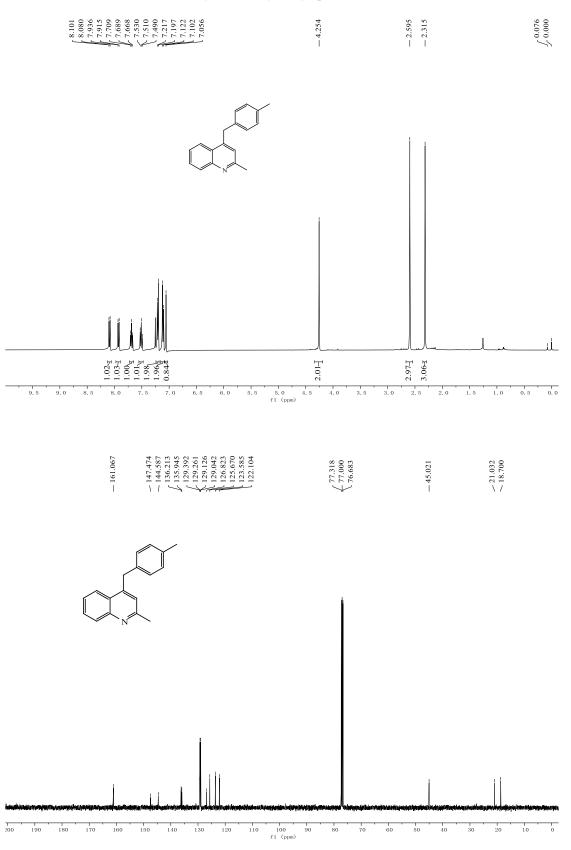
4-chloro-6-fluoro-2-(4-methylbenzyl)quinoline (3ka)

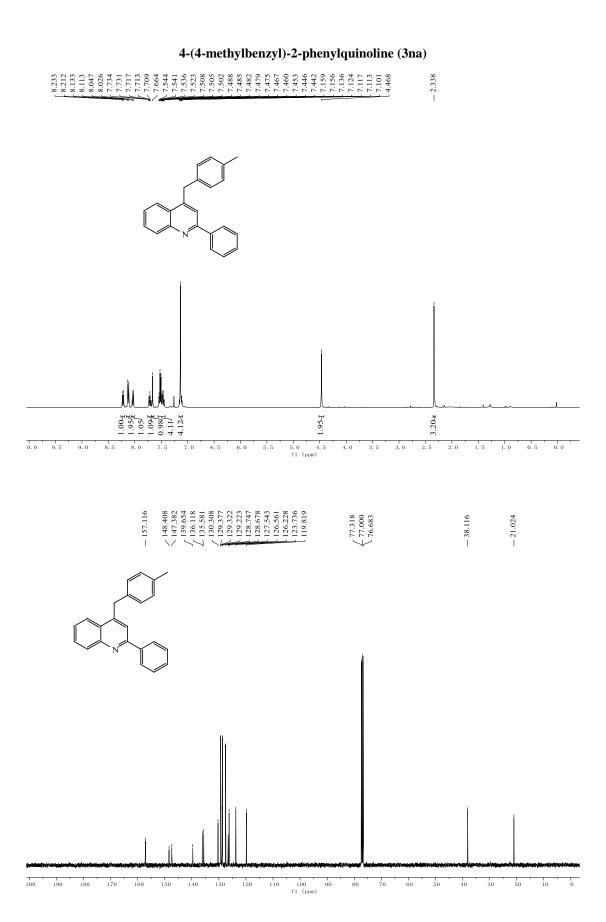


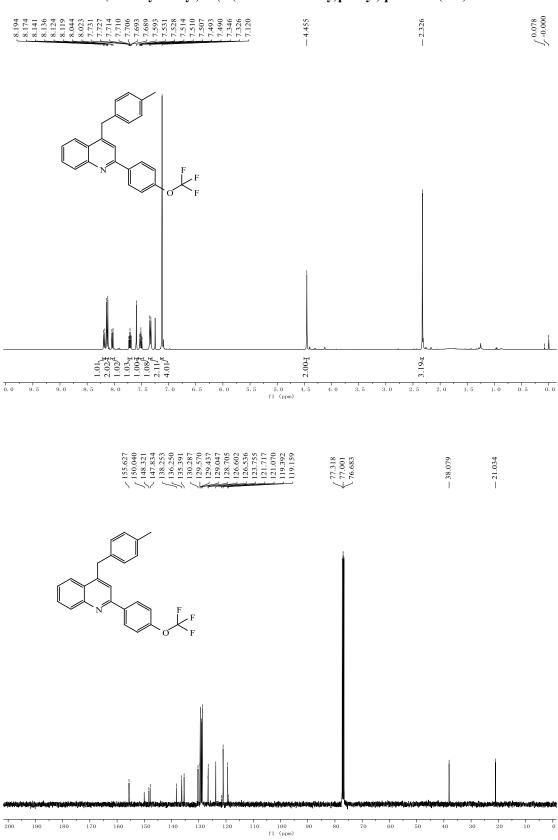
6-bromo-5,7-difluoro-2-(4-methylbenzyl)quinolone (3la)



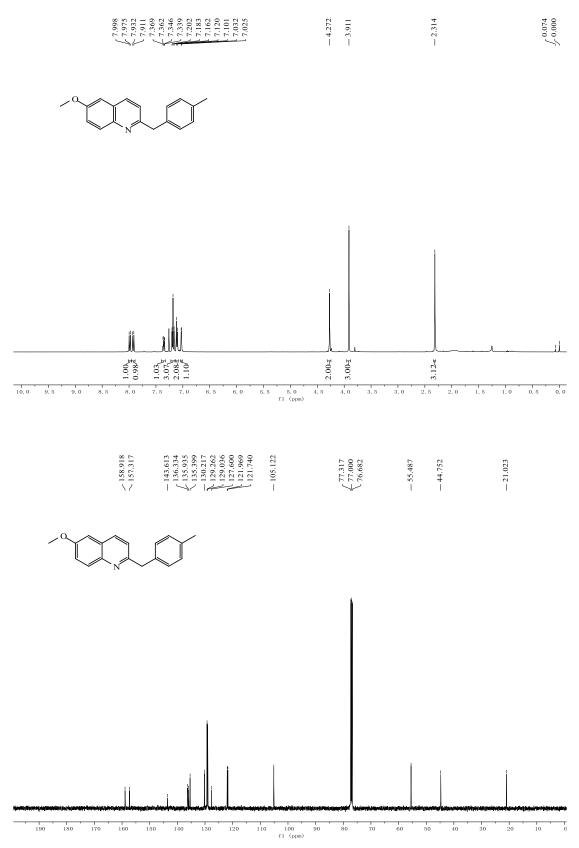
2-methyl-4-(4-methylbenzyl)quinoline (3ma)



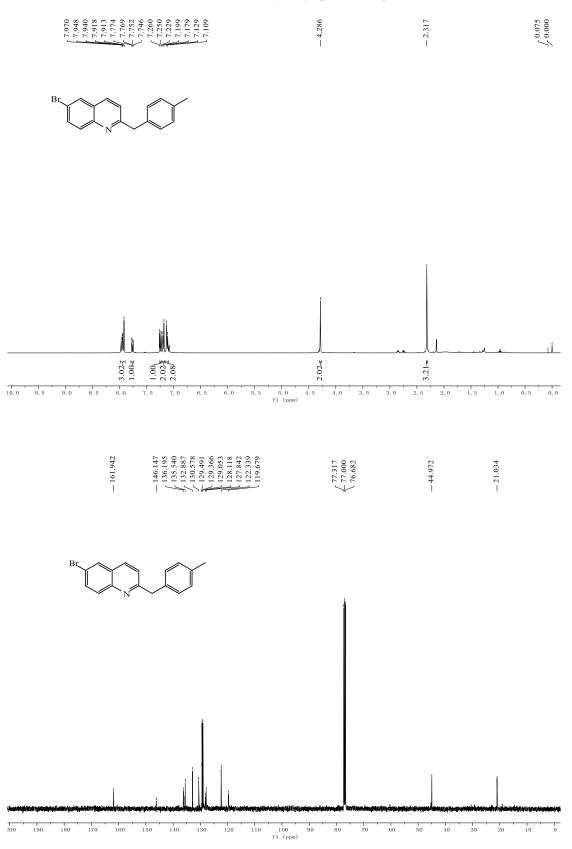




6-methoxy-2-(4-methylbenzyl)quinoline (3pa)



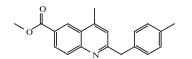
6-bromo-2-(4-methylbenzyl)quinoline (3qa)

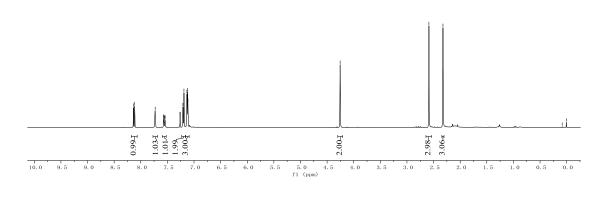


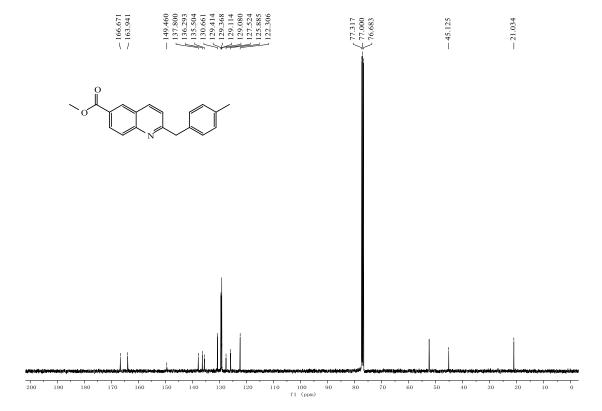
S45

methyl 2-(4-methylbenzyl)quinoline-6-carboxylate (3ra)





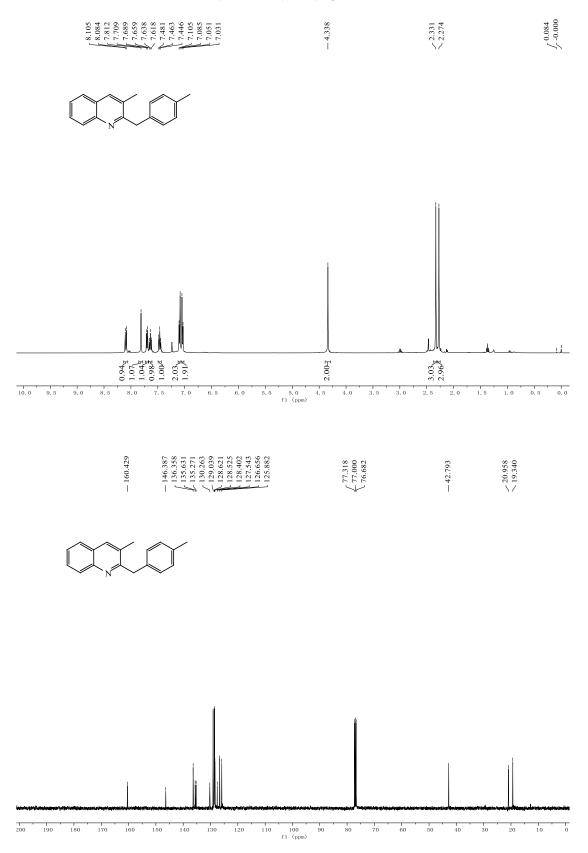




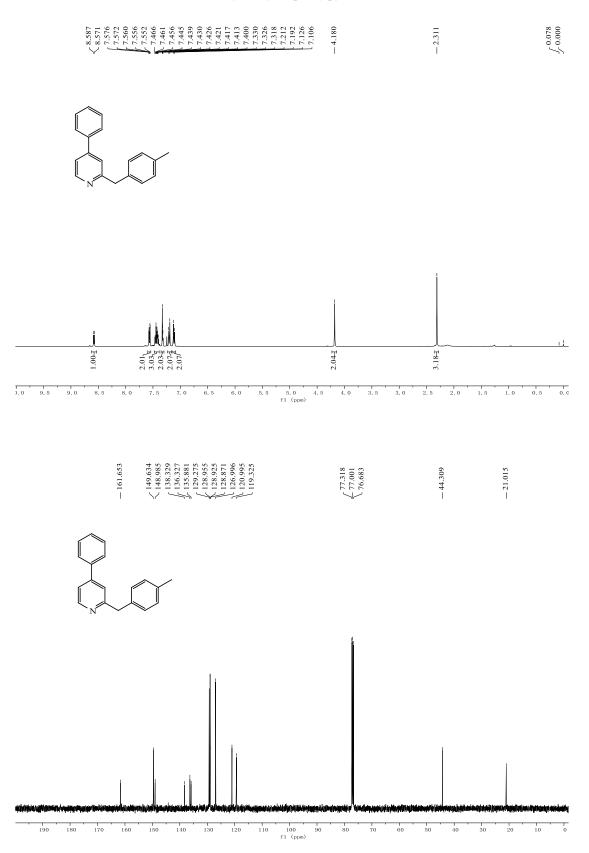
6-bromo-2-methyl-4-(4-methylbenzyl)quinoline (3sa)



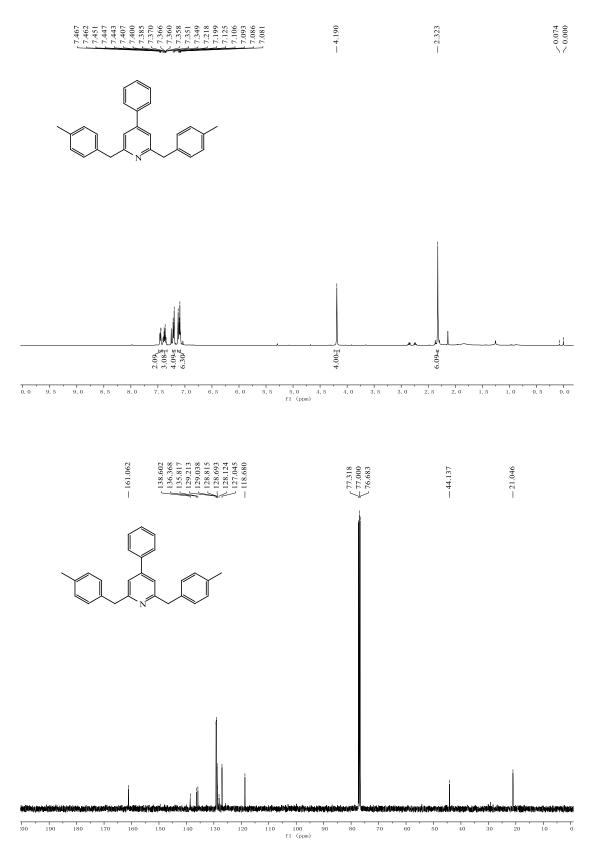
3-methyl-2-(4-methylbenzyl)quinoline (3ta)



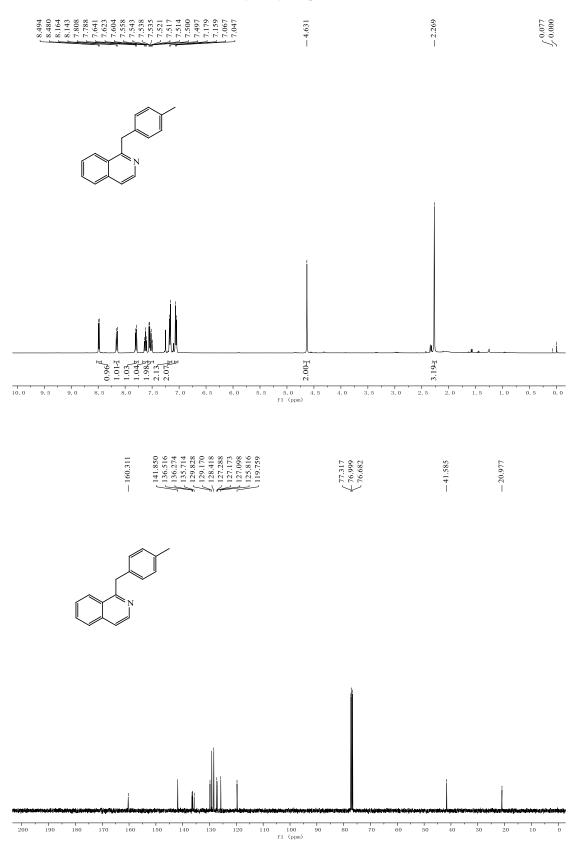
2-(4-methylbenzyl)-4-phenylpyridine (3ua)



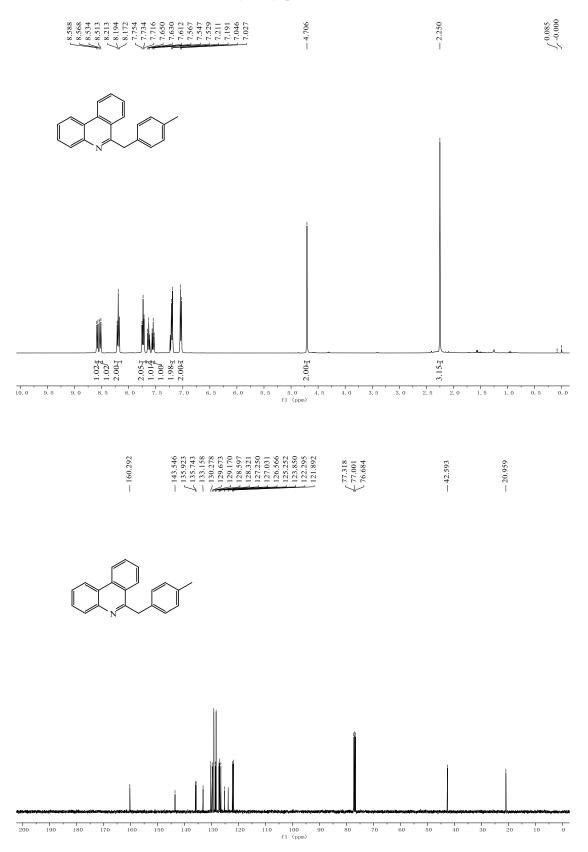
2,6-bis(4-methylbenzyl)-4-phenylpyridine (3ua')



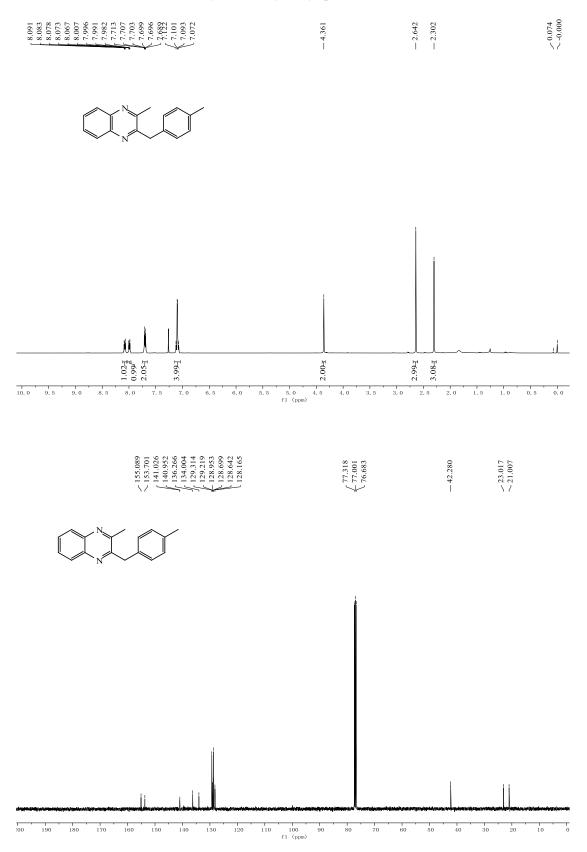
1-(4-methylbenzyl)isoquinoline (3va)



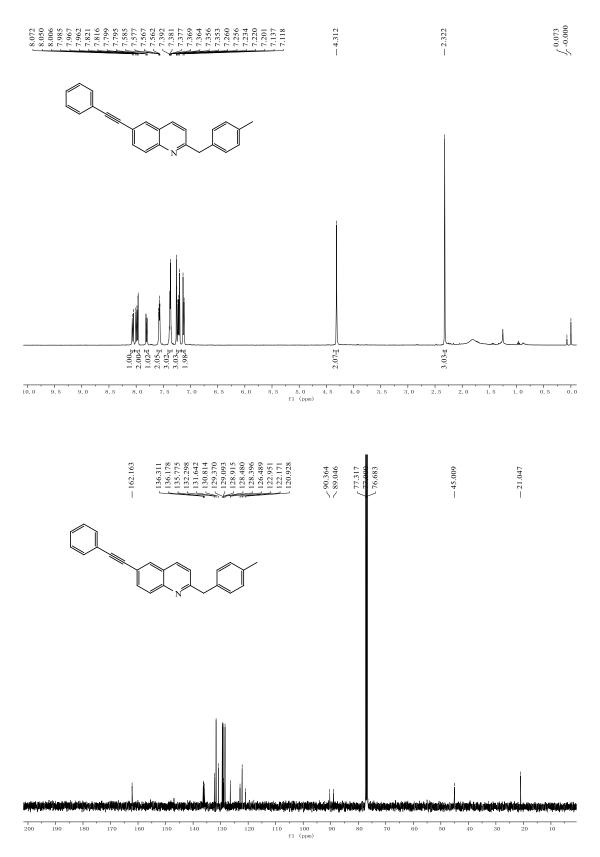
6-(4-methylbenzyl)phenanthridine (3wa)



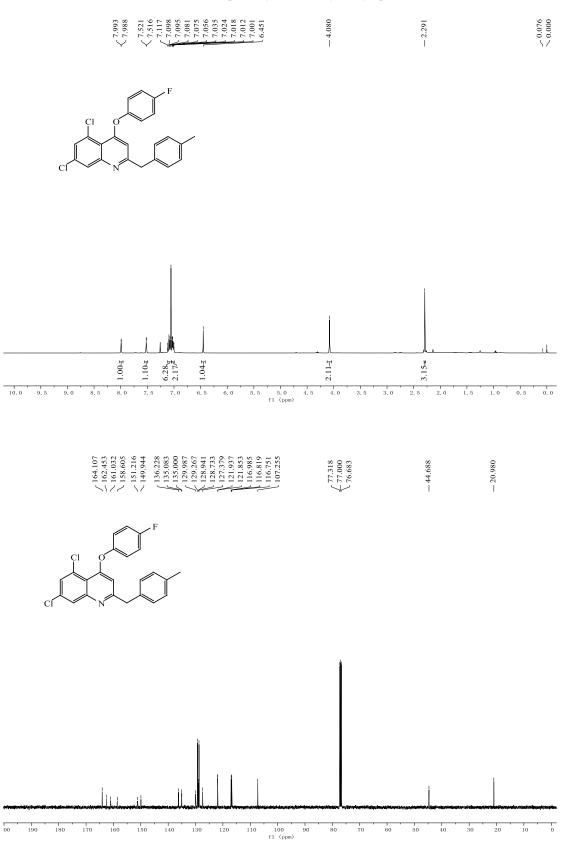
2-methyl-3-(4-methylbenzyl)quinoxaline (3xa)



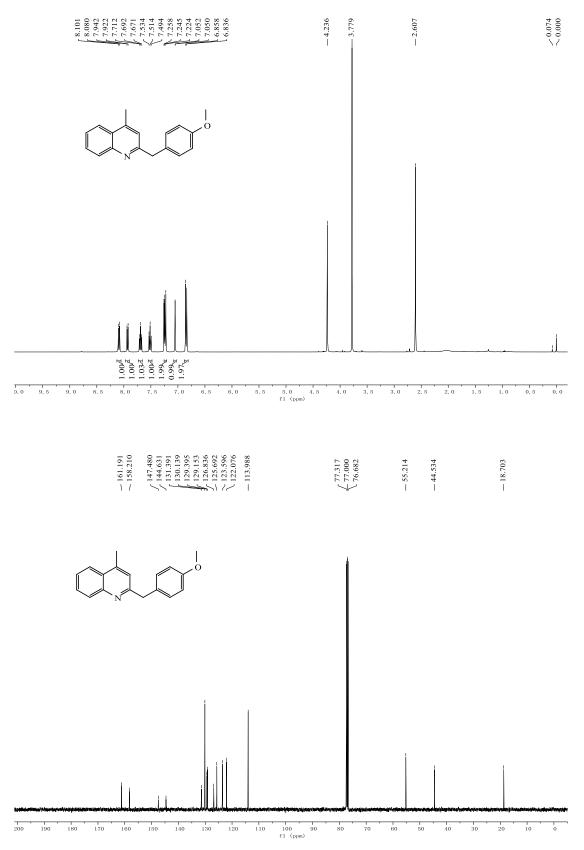
2-(4-methylbenzyl)-6-(phenylethynyl)quinoline (3ya)



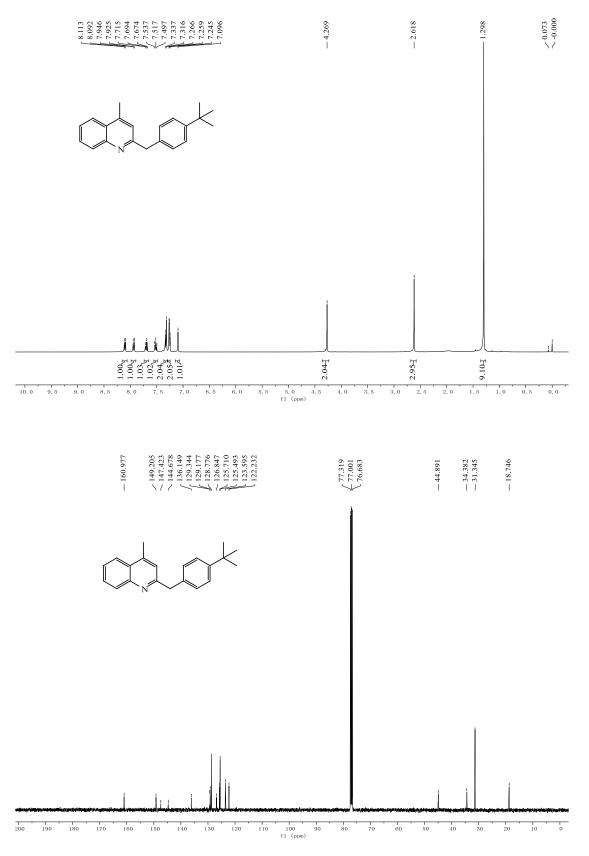
5,7-dichloro-4-(4-fluorophenoxy)-2-(4-methylbenzyl)quinoline (3za)



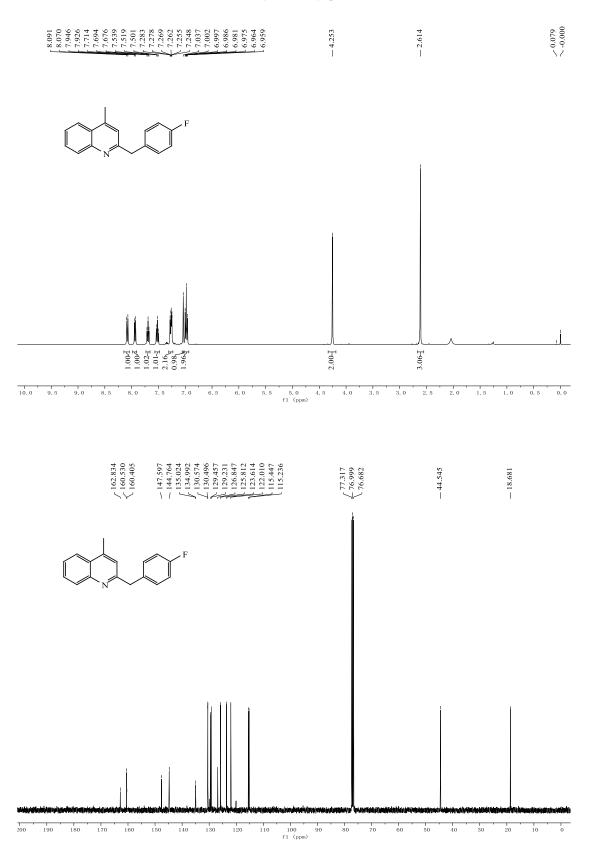
2-(4-methoxybenzyl)-4-methylquinoline (3ab)



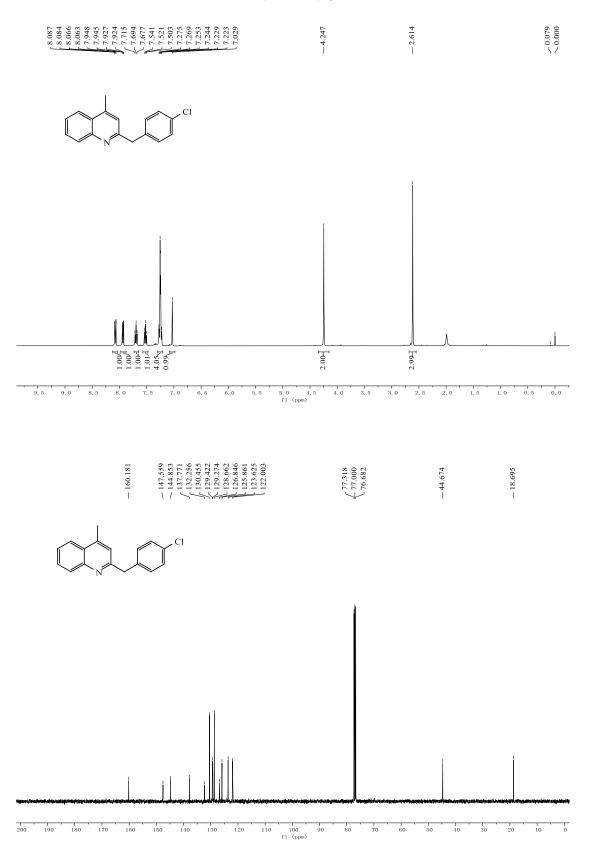
2-(4-(tert-butyl)benzyl)-4-methylquinoline (3ac)



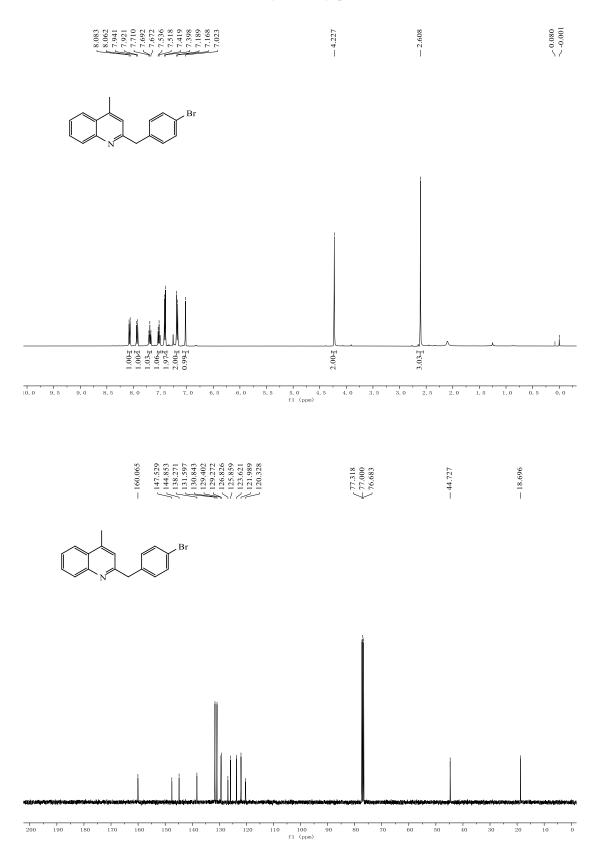
2-(4-fluorobenzyl)-4-methylquinoline (3ad)



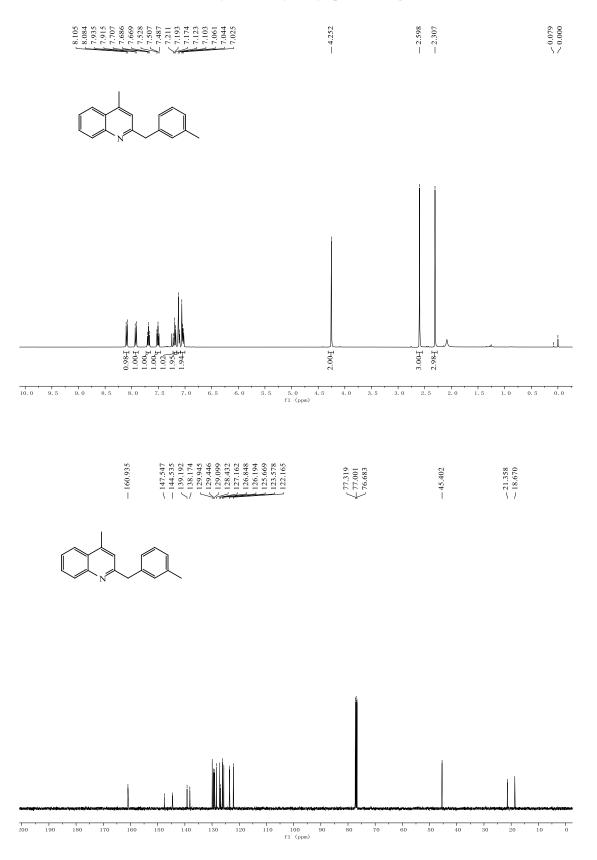
2-(4-chlorobenzyl)-4-methylquinoline (3ae)



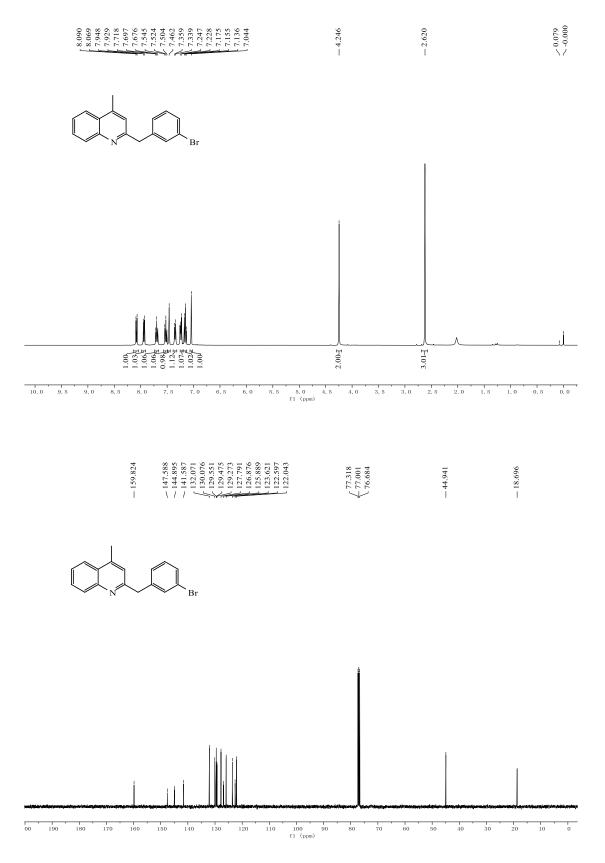
2-(4-bromobenzyl)-4-methylquinoline (3af)



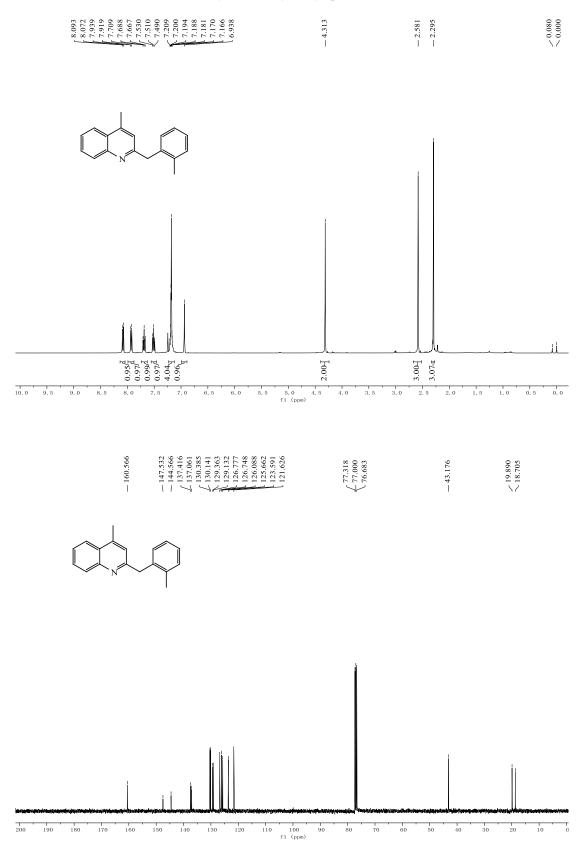
4-methyl-2-(3-methylbenzyl)quinoline (3ag)



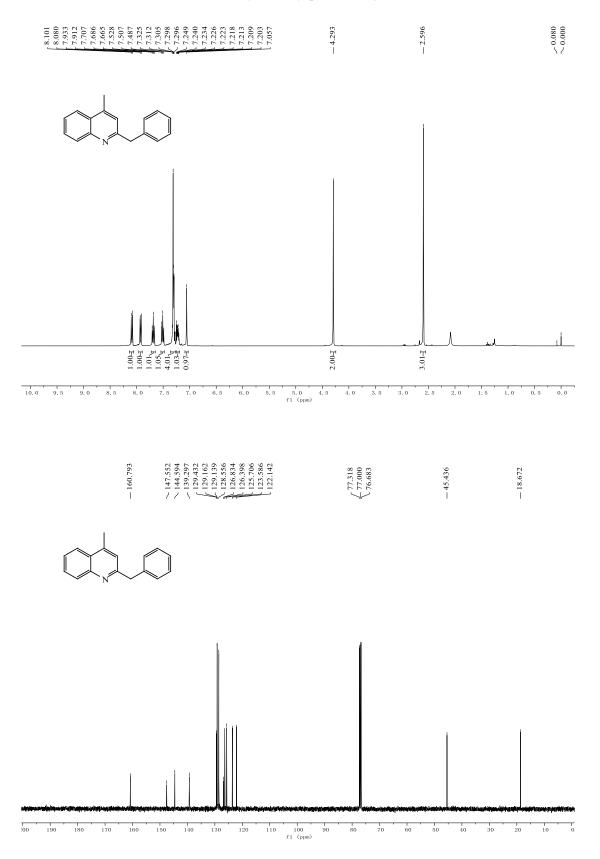
2-(3-bromobenzyl)-4-methylquinoline (3ah)



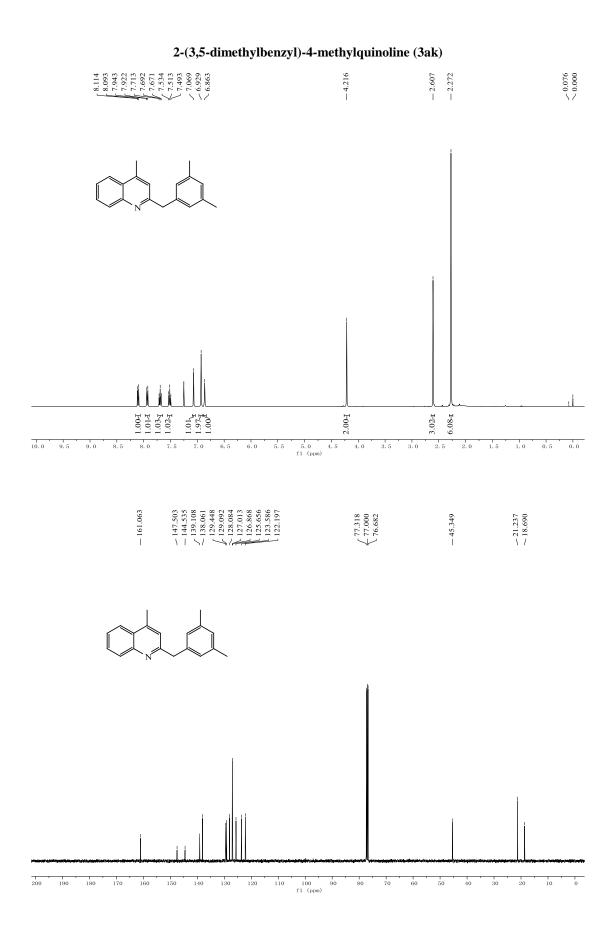
4-methyl-2-(2-methylbenzyl)quinoline (3ai)

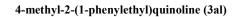


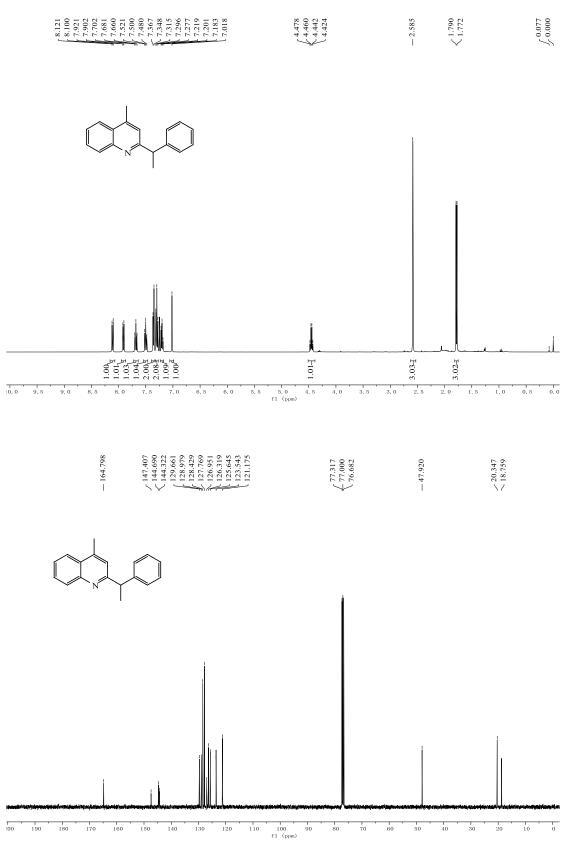
2-benzyl-4-methylquinoline (3aj)



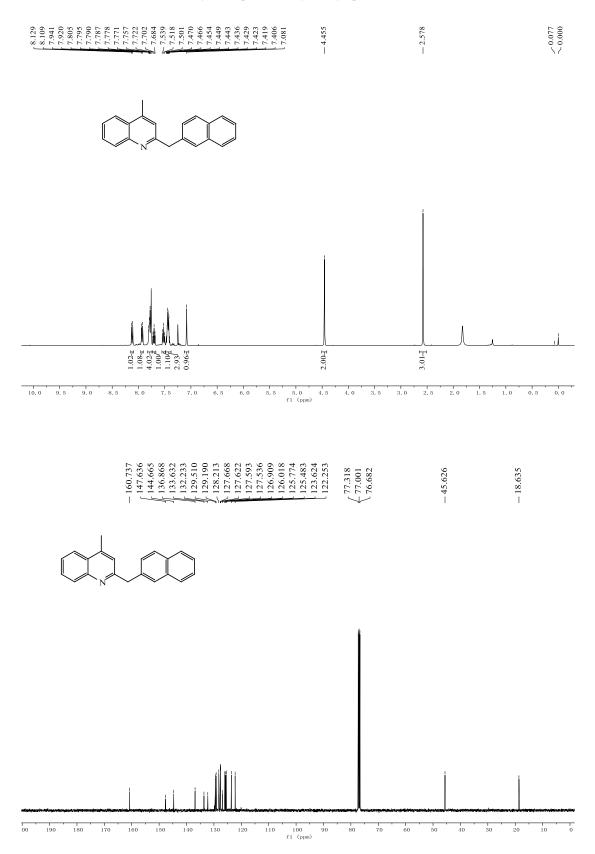
S64

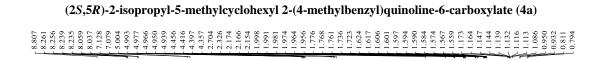


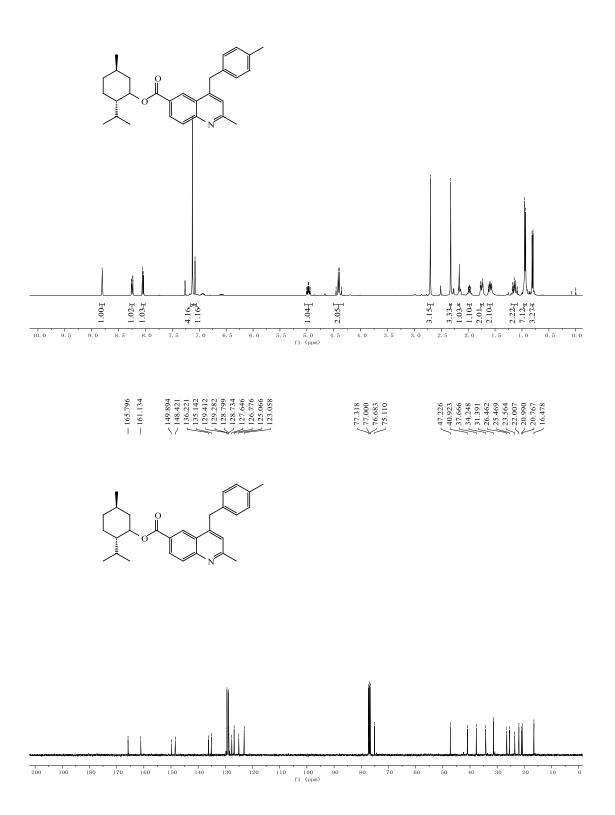


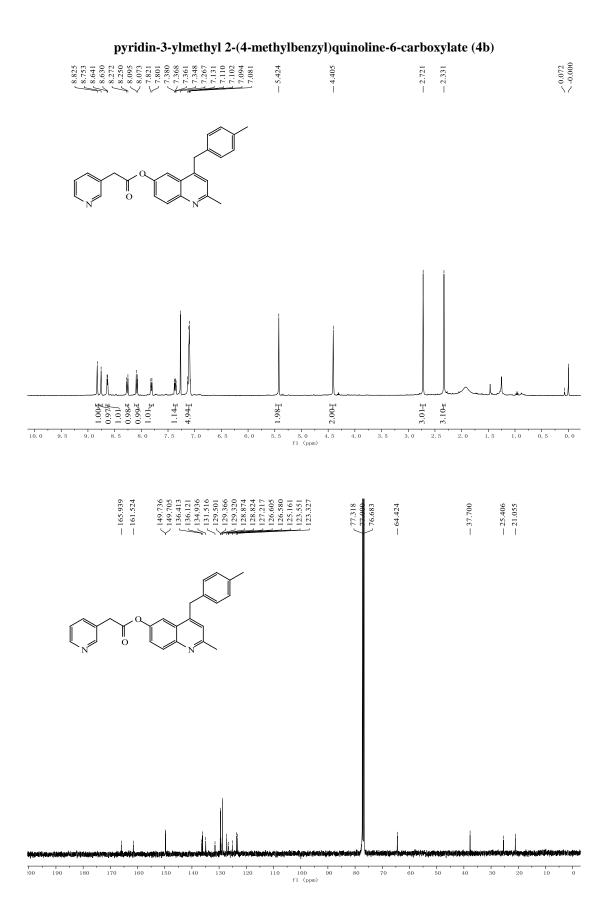


4-methyl-2-(naphthalen-2-ylmethyl)quinoline (3am)





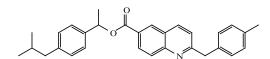


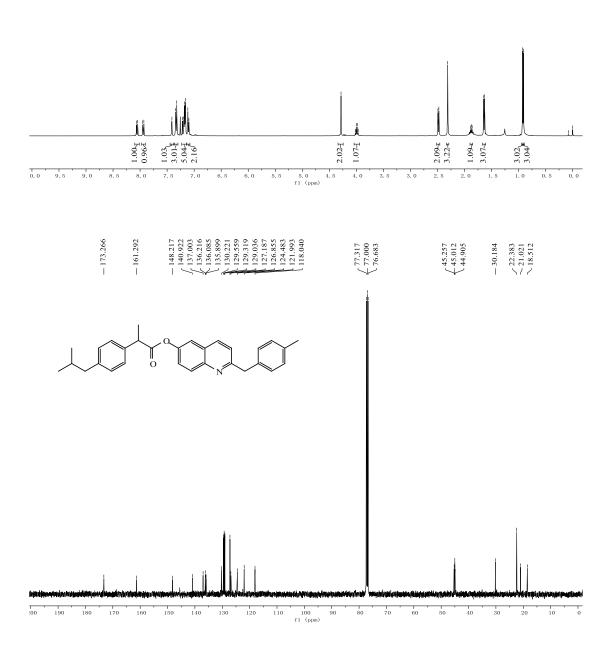


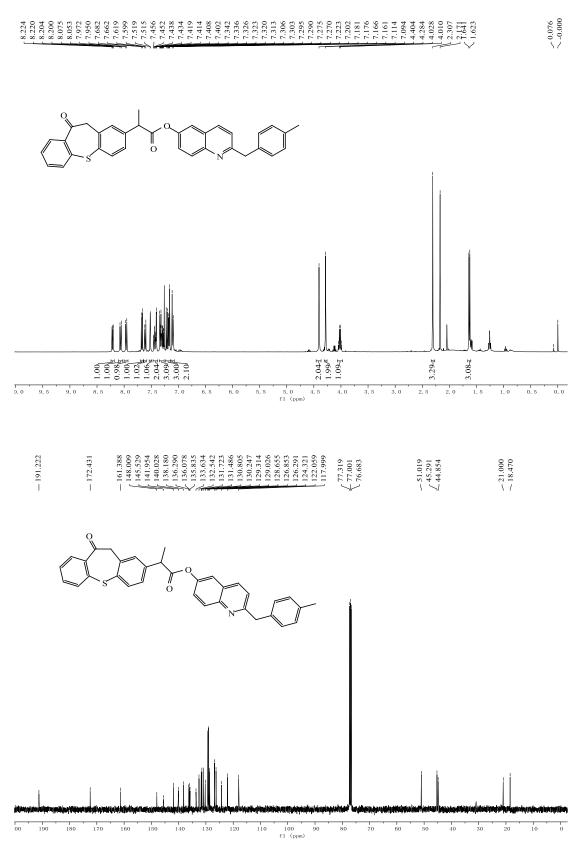
S69

2-(4-methylbenzyl)quinolin-6-yl 2-(4-isobutylphenyl)propanoate (4c)









 $\label{eq:linear} 2-(4-methylbenzyl) quinolin-6-yl\ 2-(10-oxo-10,11-dihydrodibenzo[\textit{b,f}] thiepin-2-yl) propanoate\ (4d)$



