

Supporting Information

Rh(III)-Catalyzed C(sp³)-H Acetoxylation of 8-Methylquinolines

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1. General Information

All the commercially available chemicals and solvents were used without further purification. Anhydrous solvents were prepared according to standard methods. Reagents used to prepare the substrates were purchased from Sigma-Aldrich, Alfa, TCI and J&K. $[\text{Cp}^*\text{Rh}(\text{MeCN})_3](\text{SbF}_6)_2$ was synthesised according to the literature.¹ ^1H NMR and ^{13}C NMR spectra were recorded on Bruker-DRX (500 MHz and 125 MHz, respectively) instruments internally referenced to chloroform signals. High Resolution Mass Spectra were recorded at the Center For Mass Spectrometry, Nanjing University.

2. Experimental Section

2.1 General Procedure for the Preparation of the Substrates

The substrates **1b-q** were prepared according to the literature.²

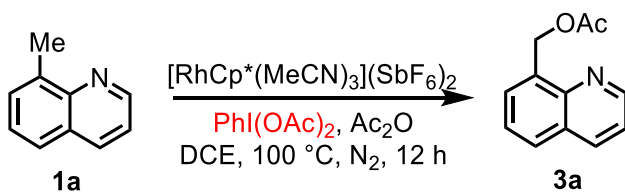
Synthesis to **1l**: Glycerin (1.1 g, 12 mmol) was added dropwise over a period 30 minutes to a solution of 3-iodo-2-methylaniline (2.3 g, 10 mmol) and NaI (20 mg, 0.13 mmol) in 80% aqueous H_2SO_4 (5.5 g, 3.18 ml) at 140 °C. The mixture was then heated at 145 °C for 3.5 h while distilling the water formed during this period. Upon cooling to room temperature, the dark solution was carefully poured into ice (10 g) and then neutralized with 25% NaOH (10.9 g, 6.9 mmol) to basic pH 8-11. The mixture was extracted with ethyl acetate (3 × 20 ml), and then dried with anhydrous sodium sulfate. After ethyl acetate was removed, the residue was purified by flash column chromatography on silica gel to give the 7-iodo-8-methylquinoline (2.3g, 85%).

8-methylquinoline- d_3 was prepared according to the literature.³

The substrates **1p**, **1s** were prepared according to the literature.⁴

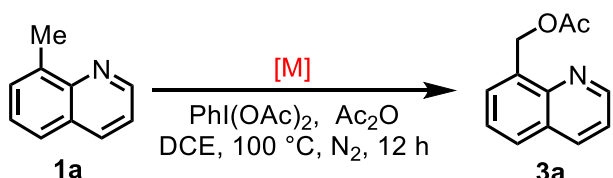
2.2 Optimization Studies

Table S1. Selected observations from initial screening of the amount of $\text{PhI}(\text{OAc})_2$ ^{a, b}

		
Entry	$\text{PhI}(\text{OAc})_2$	Yield ^b
1	0.15 mmol	36%
2	0.30 mmol	43%
3	0.45 mmol	60%

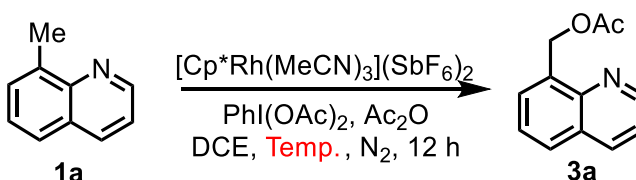
^aConditions: **1a** (0.1 mmol), $[\text{Cp}^*\text{Rh}(\text{MeCN})_3](\text{SbF}_6)_2$ (10 mol%), Ac_2O (1.6 mmol), and DCE (2 ml) under N_2 , 12 h, 100 °C. ^bThe yield was determined by ^1H NMR analysis of crude product using 1,3,5-trimethoxybenzene as an internal standard.

Table S2. Selected observations from initial screening of catalyst system^{a, b}

		
Entry	[M]	Yield ^b
1	$[\text{Cp}^*\text{RhCl}_2]_2$	NR
2	$[\text{Cp}^*\text{RhCl}_2]_2 + \text{AgSbF}_6$	58%
3	$[\text{Cp}^*\text{Rh}(\text{MeCN})_3](\text{SbF}_6)_2$	60%
4 ^c	$[\text{Cp}^*\text{Rh}(\text{MeCN})_3](\text{SbF}_6)_2$	NR
5 ^d	-----	NR

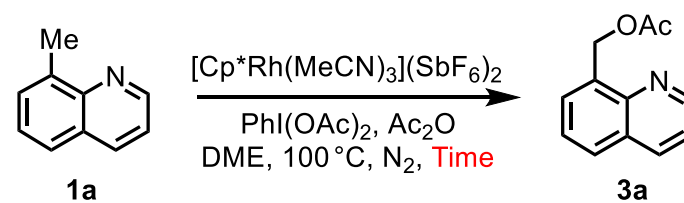
^aConditions: **1a** (0.1 mmol), M (10 mol%), Ac_2O (1.6 mmol), $\text{PhI}(\text{OAc})_2$ (0.45 mmol) and DCE (2 ml) under N_2 , 12 h, 100 °C. ^bThe yield was determined by ^1H NMR analysis of crude product using 1,3,5-trimethoxybenzene as an internal standard. ^cwithout $\text{PhI}(\text{OAc})_2$. ^dwithout Rh catalysts.

Table S3. Selected observations from initial screening of temperature^{a, b}

		
Entry	Temp. (°C)	Yield ^b
1	60	18%
2	80	57%
3	100	60%
4	120	50%

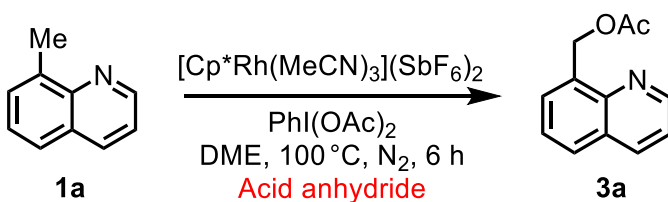
^aConditions: **1a** (0.1 mmol), [Cp*Rh(MeCN)₃](SbF₆)₂ (10 mol%), Ac₂O (1.6 mmol), PhI(OAc)₂ (0.45 mmol) and DCE (2 ml) under N₂, 12 h. ^bThe yield was determined by ¹H NMR analysis of crude product using 1,3,5-trimethoxybenzene as an internal standard.

Table S4. Selected observations from initial screening of time^{a, b}

		
Entry	Time (h)	Yield ^b
1	1	38%
2	3	74%
3	6	93%
4	9	93%

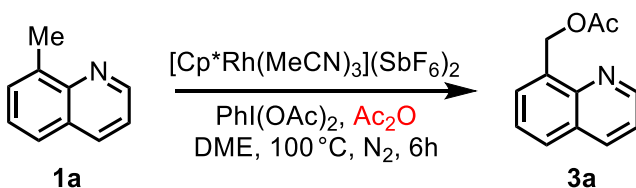
^aConditions: **1a** (0.1 mmol), [Cp*Rh(MeCN)₃](SbF₆)₂ (10 mol%), Ac₂O (1.6 mmol), PhI(OAc)₂ (0.45 mmol) and DME (2 ml) under N₂, 100 °C. ^bThe yield was determined by ¹H NMR analysis of crude product using 1,3,5-trimethoxybenzene as an internal standard.

Table S5. Selected observations from initial screening of acid-anhydride^{a,b}

		
Entry	Acid anhydride	Yield ^b
1	Trimethylacetic anhydride	48%
2	Isobutyric anhydride	46%
3	Ac ₂ O	93%

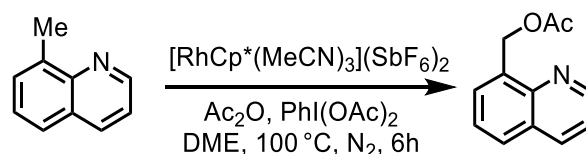
^aConditions: **1a** (0.1 mmol), [Cp*Rh(MeCN)₃](SbF₆)₂ (5), Acid anhydride (1.6 mmol), PhI(OAc)₂ (0.45 mmol) and DME (2 ml) under N₂, 100 °C, 6 h. ^bThe yield was determined by ¹H NMR analysis of crude product using 1,3,5-trimethoxybenzene as an internal standard.

Table S6. Selected observations from initial screening of the amount of Ac₂O^{a,b}

		
Entry	Ac ₂ O	Yield ^b
1	-----	24%
2	0.1 mmol	45%
3	0.2 mmol	93%
4	0.3 mmol	87%
5	0.4 mmol	75%

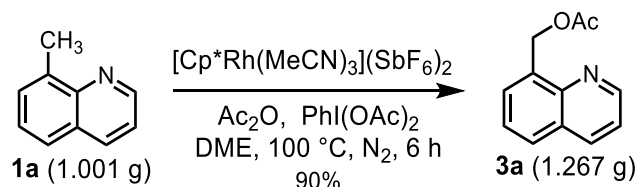
^aConditions: **1a** (0.1 mmol), [Cp*Rh(MeCN)₃](SbF₆)₂ (10 mol%), PhI(OAc)₂ (0.45 mmol) and DME (2 ml) under N₂, 100 °C, 6 h. ^bThe yield was determined by ¹H NMR analysis of crude product using 1,3,5-trimethoxybenzene as an internal standard.

2.3 General Procedure for Rh(III)-Catalyzed C–H Acetoxylation



To a 25 ml Schlenk-type sealed tube equipped with a magnetic stirring bar was added the substrate (0.1 mmol), $[\text{Cp}^*\text{Rh}(\text{MeCN})_3](\text{SbF}_6)_2$ (8.0 mg, 0.01 mmol), Ac_2O (0.2 mmol), $\text{PhI}(\text{OAc})_2$ (145 mg, 0.45 mmol) and dry DME (2.0 ml) under N_2 atmosphere. The tube was capped, and then submerged into a pre-heated $100\text{ }^\circ\text{C}$ heating mantle for 6 h. After cooled to room temperature, the reaction mixture was filtered through a pad of Celite. The filtrate was concentrated in vacuo to afford crude product, which was purified by flash column chromatography on silica gel to give the pure product.

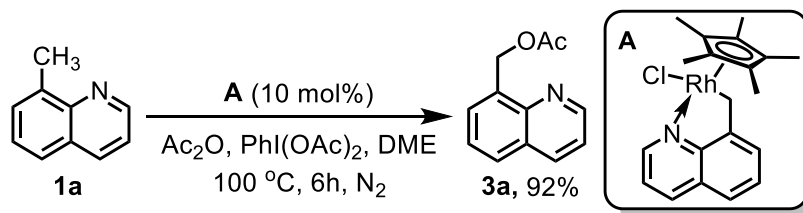
2.4 Gram-Scale Synthesis



To a 350 ml Schlenk-type sealed tube equipped with a magnetic stirring bar was added the substrate **1a** (1.001g, 7 mmol), $[\text{Cp}^*\text{Rh}(\text{MeCN})_3](\text{SbF}_6)_2$ (560 mg, 0.7 mmol), Ac_2O (14 mmol), $\text{PhI}(\text{OAc})_2$ (10 g, 31.5 mmol) and dry DME (45 ml) under N_2 atmosphere. The tube was capped, and submerged into a pre-heated $100\text{ }^\circ\text{C}$ oil for 6 h. After cooled to room temperature, the reaction mixture was filtered through a pad of Celite. The filtrate was concentrated in vacuo to afford crude product, which was purified by flash column chromatography on silica gel with a gradient eluent of petroleum ether/ethyl acetate (5/1) to give the pure product **3a** (1.267g, 90%).

2.5 Mechanism Study

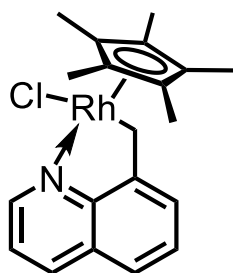
2.5.1 Catalytic Activity of Five-Membered Rhodacycle



To a 25ml Schlenk-type sealed tube equipped with a magnetic string bar was added the substrate **1a** (0.1 mmol), **A** (4.2 mg, 0.01 mmol), AgSbF_6 (6.8 mg, 0.02 mmol), Ac_2O (0.2 mmol), $\text{PhI}(\text{OAc})_2$ (145mg, 0.45 mmol), and dry DME (2 ml) under N_2 atmosphere. The tube was capped, and then submerged into a pre-heated $100\text{ }^\circ\text{C}$ heating mantle for 6 h. After cooled to room temperature, the reaction mixture was filtered through a pad of Celite, which was purified by flash column chromatography on silica gel to give 92% desired product.

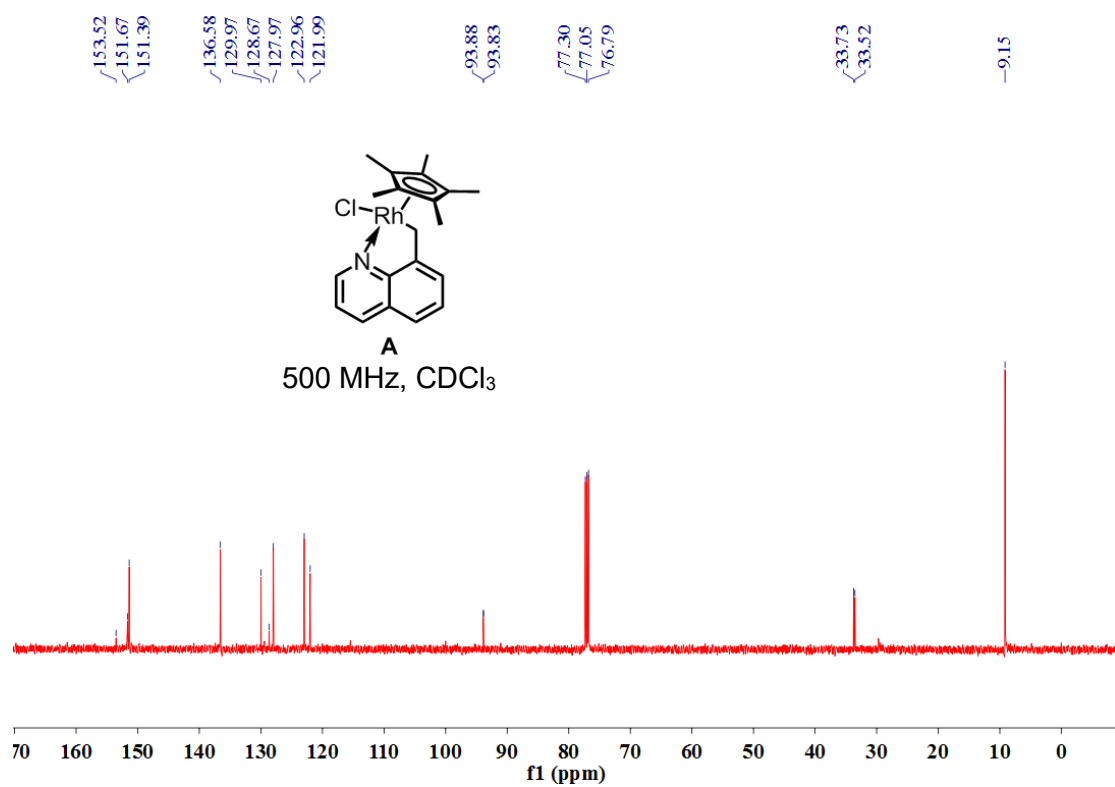
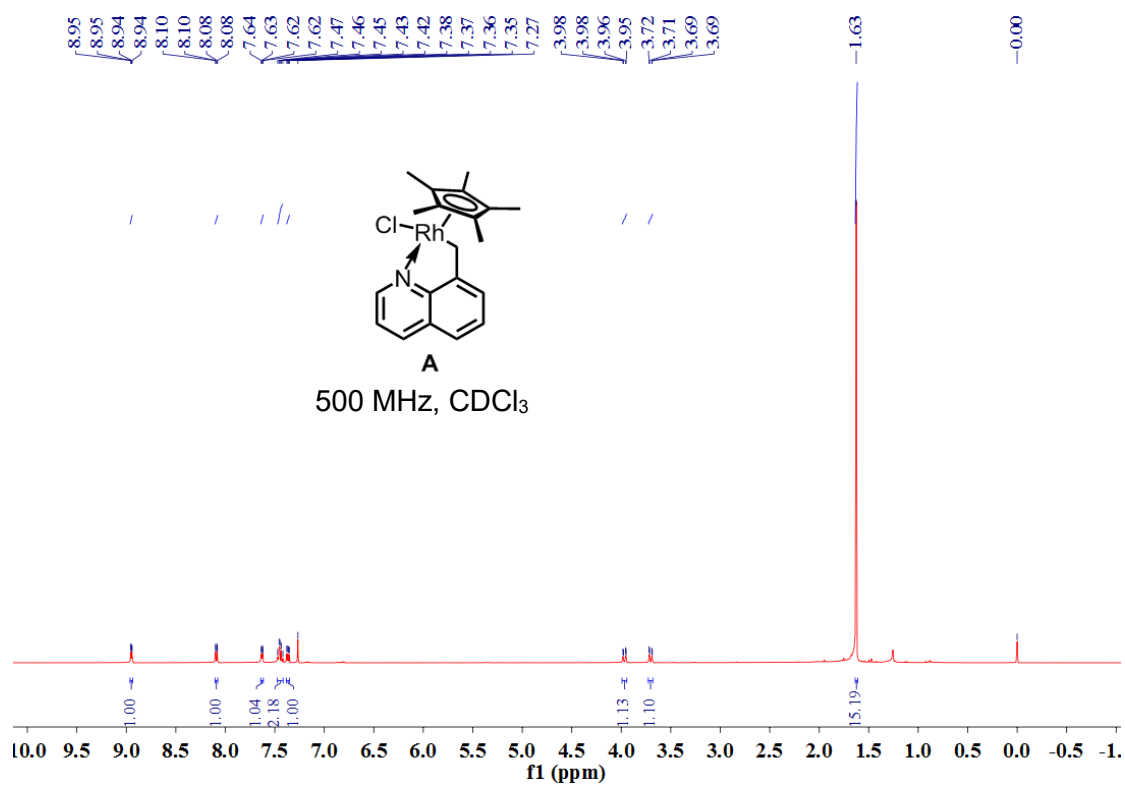
Preparation of Intermediate A:⁵

To a 25ml Schlenk-type sealed tube equipped with a magnetic string bar was added the substrate 8-methyl-quinoline (85.9 mg, 0.6 mmol), $[\text{Cp}^*\text{RhCl}_2]_2$ (18.6 mg, 0.03 mmol, 5.0 mol %), NaOAc (24.6 mg, 0.3 mmol) and MeOH (1 mL) under N_2 atmosphere. The tube was capped, and then submerged into a pre-heated $80\text{ }^\circ\text{C}$ heating mantle overnight. After cooled to room temperature, the reaction mixture was filtered through a pad of Celite, which was purified by flash column chromatography on silica gel (petroleum ether:EA = 1:2).



Intermediate A

Orange-red solid. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.95 (dd, $J_1 = J_2 = 2.5\text{ Hz}$, 1 H), 8.09 (dd, $J_1 = J_2 = 5\text{ Hz}$, 1 H), 7.63 (dd, $J_1 = 5\text{ Hz}$, $J_2 = 7.5\text{ Hz}$, 1 H), 7.45 (m, 2 H), 7.37 (dd, $J_1 = 2.5\text{ Hz}$, $J_2 = 4\text{ Hz}$, 1 H), 3.97 (dd, $J_1 = 5\text{ Hz}$, $J_2 = 12.5\text{ Hz}$, 1 H), 3.70 (dd, $J_1 = 7.5\text{ Hz}$, $J_2 = 12.5\text{ Hz}$, 1 H), 1.63 (s, 15 H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 153.5, 151.7, 151.4, 136.6, 130.0, 128.7, 128.0, 123.0, 122.0, 93.9, 93.8, 33.7, 33.5, 9.15.



Crystallographic Data for Intermediate A

General Procedure for Crystal Preparation: Compound A (around 30 mg) was dissolved in trichloromethane (1 ml) and the vial was capped with an open-top cap. The single crystals were grown in the vial via slow evaporation of solvents at room temperature.

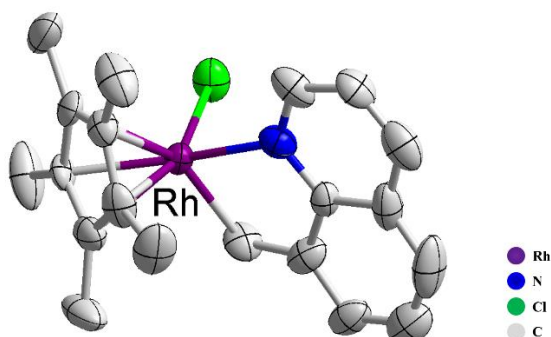


Figure S1 Crystal structure of Compound A with displacement ellipsoids drawn at the 50% probability level

X-ray Structure Determination of A:

Crystallographic data for **A** was collected on a Bruker Smart Apex II CCD area-detector diffractometer with graphite-monochromated Mo $\text{K}\alpha$ radiation ($1\frac{1}{4}$ 0.71073 Å) at 296 (2) K using the ω -scan technique. The diffraction data were integrated using the SAINT program,⁶ which was also used for the intensity corrections for the Lorentz and polarization effects. Semi-empirical absorption correction was applied using the SADABS program.⁷ The structures were solved by direct methods, and all nonhydrogen atoms were refined anisotropically on F^2 by the fullmatrix least-squares technique using the SHELXL-2018 crystallographic software package. The hydrogen atoms were generated geometrically and refined isotropically using the riding model. Crystal data and experimental details of the structure determination are listed in Table S7 and S8.

CCDC 978941 contains the supplementary crystallographic data for this crystall. These data can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/>, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

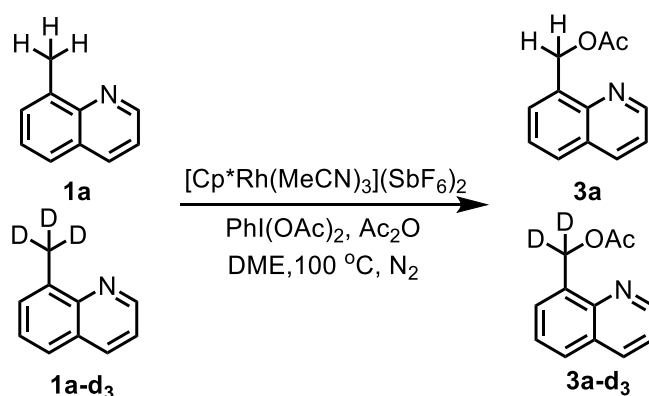
Table S7 Crystal data and structure refinements for A

Formula	C ₂₀ H ₂₃ ClNRh
Formula weight	415.75
T (K)	296(2)
Crystal system	Orthorhombic
Space group	<i>Pna</i> 2 ₁
<i>a</i> (Å)	15.2959(16)
<i>b</i> (Å)	8.5347(8)
<i>c</i> (Å)	13.7129(13)
<i>V</i> (Å ³)	1790.2(3)
<i>Z</i>	4
<i>D</i> _{calc} (g cm ⁻³)	1.543
μ (mm ⁻¹)	1.102
<i>F</i> (000)	848
θ for data collection (°)	2.733–27.513
Reflections collected	14961
Unique reflections	4082
Goodness-of-fit on <i>F</i> ²	1.001
<i>R</i> ₁ ^a [<i>I</i> > 2 σ (<i>I</i>)]	0.0390
<i>wR</i> ₂ ^b [<i>I</i> > 2 σ (<i>I</i>)]	0.1204
<i>R</i> ₁ ^a [all data]	0.0465
<i>wR</i> ₂ ^b [all data]	0.1304

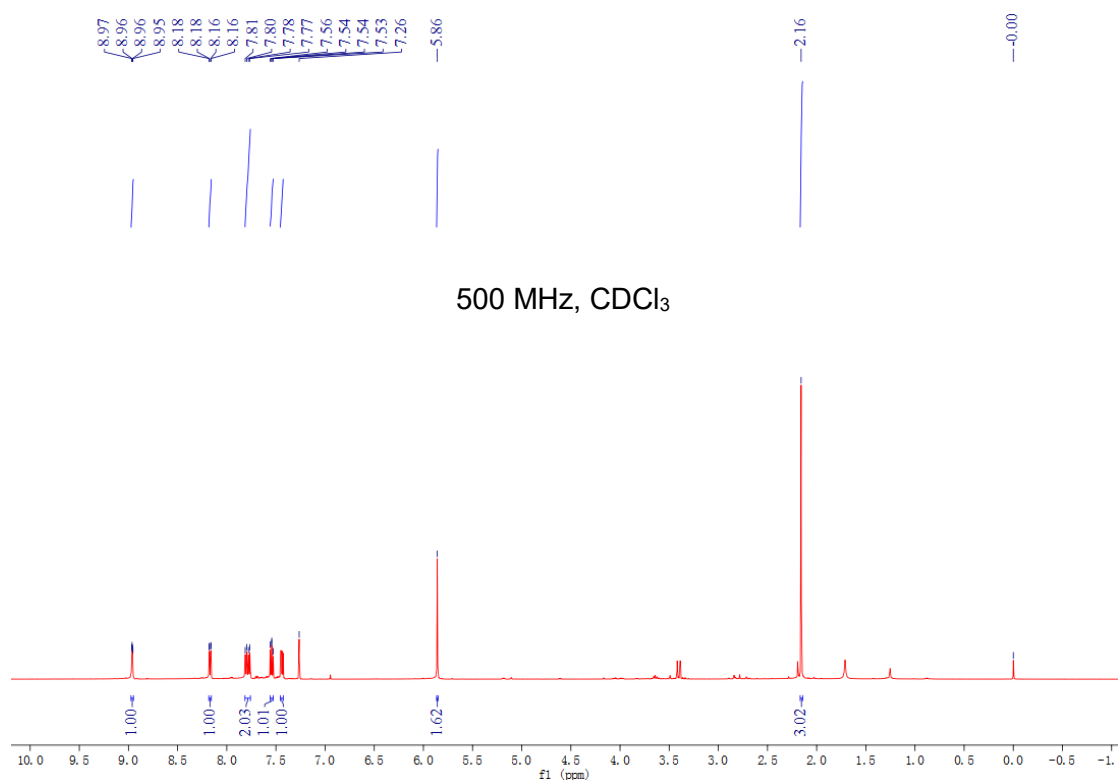
Table S8 Bond lengths [Å] and angles [°] for Intermediate A

Rh(1)-N(1)	2.082(7)	Rh(1)-C(19)	2.109(8)
Rh(1)-C(10)	2.132(8)	Rh(1)-C(20)	2.164(8)
Rh(1)-C(16)	2.169(6)	Rh(1)-C(18)	2.231(7)
Rh(1)-C(17)	2.240(7)	Rh(1)-Cl(1)	2.415(2)
N(1)-Rh(1)-C(19)	99.2(3)	N(1)-Rh(1)-C(10)	79.8(3)
C(19)-Rh(1)-C(10)	108.9(4)	N(1)-Rh(1)-C(20)	131.9(3)
C(19)-Rh(1)-C(20)	38.8(3)	C(10)-Rh(1)-C(20)	92.3(4)
N(1)-Rh(1)-C(16)	161.6(3)	C(19)-Rh(1)-C(16)	64.5(3)
C(10)-Rh(1)-C(16)	112.6(3)	C(20)-Rh(1)-C(16)	38.5(3)
N(1)-Rh(1)-C(18)	99.4(3)	C(19)-Rh(1)-C(18)	38.7(4)
C(10)-Rh(1)-C(18)	147.4(3)	C(20)-Rh(1)-C(18)	63.7(3)
C(16)-Rh(1)-C(18)	62.7(3)	N(1)-Rh(1)-C(17)	128.5(3)
C(19)-Rh(1)-C(17)	63.3(4)	C(10)-Rh(1)-C(17)	150.5(3)
C(20)-Rh(1)-C(17)	63.4(3)	C(16)-Rh(1)-C(17)	37.9(3)
C(18)-Rh(1)-C(17)	36.1(3)	N(1)-Rh(1)-Cl(1)	92.91(19)
C(19)-Rh(1)-Cl(1)	161.0(3)	C(10)-Rh(1)-Cl(1)	87.6(3)
C(20)-Rh(1)-Cl(1)	134.4(3)	C(16)-Rh(1)-Cl(1)	100.8(2)
C(18)-Rh(1)-Cl(1)	124.9(2)	C(17)-Rh(1)-Cl(1)	97.7(3)

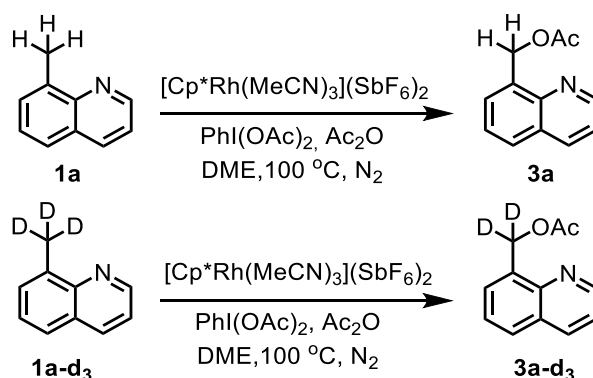
2.5.2 Intermolecular Kinetic Isotope Effects in the Acetoxylation Reaction



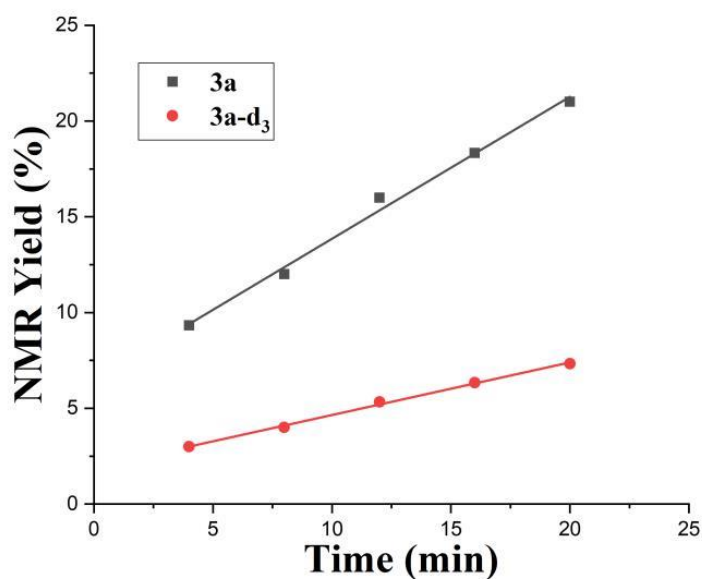
To a 25ml Schlenk-type sealed tube equipped with a magnetic string bar was added the substrate **1a** (0.1 mmol) and **1a-d₃** (0.1 mmol), $[\text{Cp}^*\text{Rh}(\text{MeCN})_3](\text{SbF}_6)_2$ (8 mg, 0.01 mmol), Ac_2O (0.2 mmol), $\text{PhI}(\text{OAc})_2$ (145mg, 0.45 mmol), and dry DME (2 ml) under N_2 atmosphere. The tube was capped, and then submerged into a pre-heated $100\text{ }^\circ\text{C}$ heating mantle for 40 minutes. After cooled to room temperature, the reaction mixture was filtered through a pad of Celite, which was purified by flash column chromatography on silica gel to give 18% mixed products. The ratio was $K_{\text{H}}: K_{\text{D}} = 4.3$ determined by ^1H NMR spectrum.



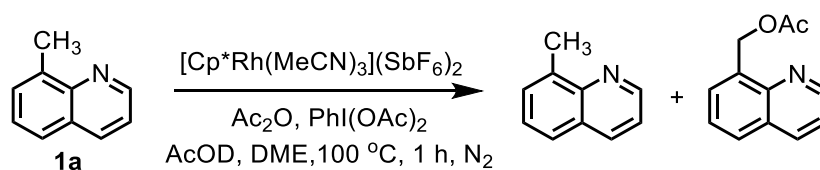
2.5.3 Parallel Kinetic Isotope Effects in the Acetoxylation Reaction



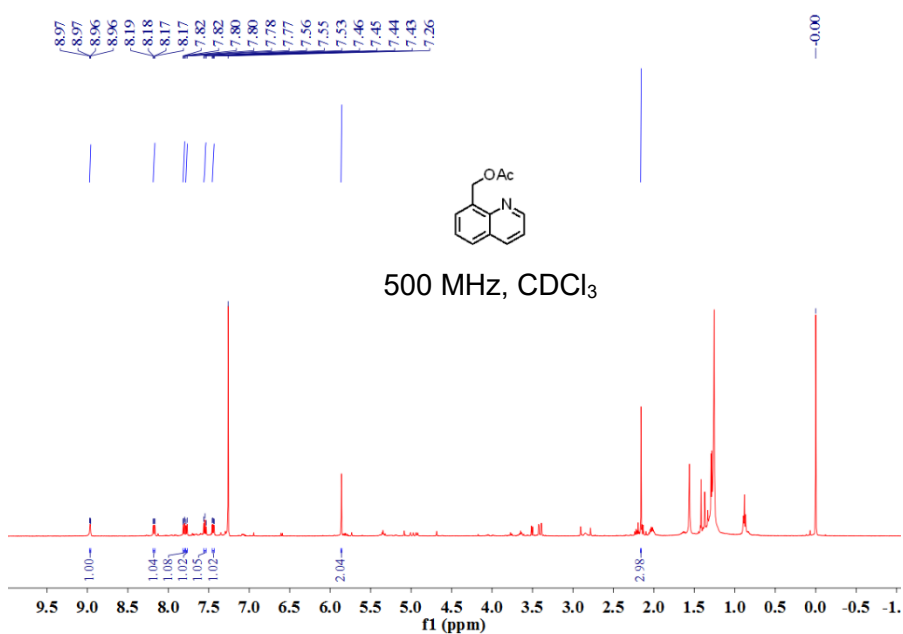
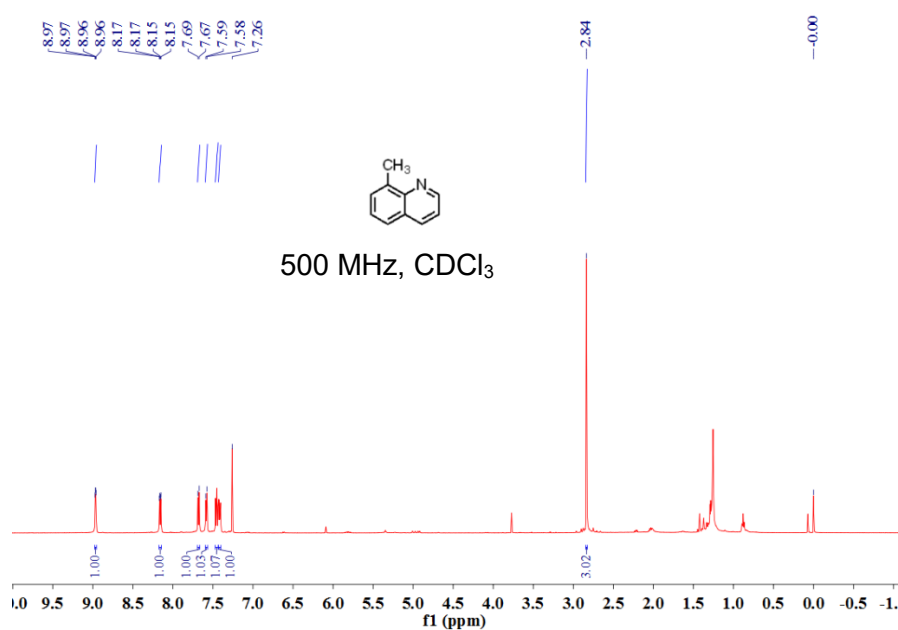
To a 25ml Schlenk-type sealed tube equipped with a magnetic string bar was added the substrate **1a** (0.1 mmol) or **1a-d₃** (0.1 mmol), [Cp^{*}Rh(MeCN)₃](SbF₆)₂ (8 mg, 0.01 mmol), Ac₂O (0.2 mmol), PhI(OAc)₂ (145mg, 0.45 mmol), and dry DME (2 ml) under N₂ atmosphere. The tube was capped, and the reaction mixture was submerged into a pre-heated 100 °C heating mantle for the indicated time. After cooled to room temperature, the reaction mixture was filtered through a pad of Celite, The filtrate was concentrated in vacuo. The yield was determined by ¹H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as the internal standard. For 3a, $y = 0.742x + 6.431$, $R^2 = 0.9963$; 3a-d₃, $y = 0.275x + 1.901$, $R^2 = 0.9987$. KIE value (2.7) was determined by comparing the relative initial rates.



2.5.3 H-D Exchange Studies



To a 25ml Schlenk-type sealed tube equipped with a magnetic stirring bar was added the substrate **1a** (0.1 mmol), $[\text{Cp}^*\text{Rh}(\text{MeCN})_3](\text{SbF}_6)_2$ (8 mg, 0.01 mmol), Ac_2O (0.2 mmol), $\text{PhI}(\text{OAc})_2$ (145mg, 0.45mmol), AcOD (1 mmol) and dry DME (2 ml) under N_2 atmosphere. The tube was capped, and the reaction mixture was submerged into a pre-heated 100°C heating mantle for 1 h. After cooled to room temperature, the reaction mixture was filtered through a pad of Celite, no deuterated substrate or product was detected.



2.5.4 The Effect of Ac₂O on the Reaction

To a 25 ml Schlenk-type sealed tube equipped with a magnetic stirring bar was added the substrate (0.1 mmol), [Cp*Rh(MeCN)₃](SbF₆)₂ (8.0 mg, 0.01 mmol), with and without Ac₂O (0.2 mmol), PhI(OAc)₂ (145 mg, 0.45 mmol) and dry DME (2.0 ml) under N₂ atmosphere. The tube was capped, and then submerged into a pre-heated 100 °C heating mantle for the indicated time. Each data point was determined by ¹H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as the internal standard.

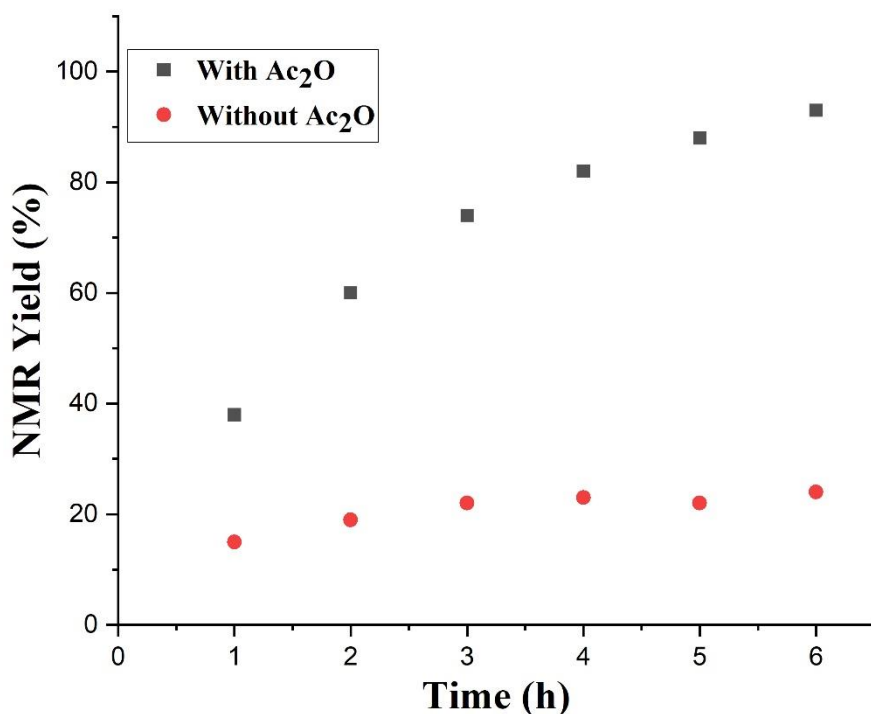
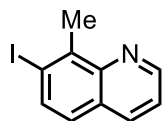


Figure S2 The effect of Ac₂O on the rate profile

3. References

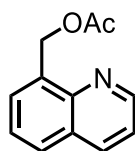
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7. G.M. Sheldrick, SADABS, University of Göttingen, Göttingen, Germany.

4. Characterization of Substrate 1l and Acetoxylation Products



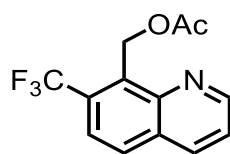
7-iodo-8-methylquinoline (1l): white solid, petroleum ether/ethyl acetate (10/1)

¹H NMR (500 MHz, CDCl₃) δ 8.91 (dd, *J*₁ = 4.3, *J*₂ = 1.9 Hz, 1 H), 8.09 (dd, *J*₁ = 8.2, *J*₂ = 1.9 Hz, 1 H), 7.91 (d, *J* = 8.8 Hz, 1 H), 7.41 (dd, *J*₁ = 8.2, *J*₂ = 4.3 Hz, 1 H), 7.36 (d, *J* = 8.7 Hz, 1 H), 3.00 (s, 3 H). **¹³C NMR** (125 MHz, CDCl₃) δ 149.8, 147.0, 141.2, 136.6, 136.3, 127.8, 126.7, 121.2, 102.8, 23.4. **HRMS (EI-TOF):** *m/z* Calcd. For C₁₀H₈INNa⁺ [M+Na]⁺: 291.9594, found 291.9592.



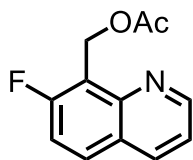
quinolin-8-ylmethyl acetate (3a): white solid (20.8 mg, 93%) petroleum ether/ethyl acetate (5/1)

¹H NMR (500 MHz, CDCl₃) δ 8.96 (dd, *J*₁ = 1.5 Hz, *J*₂ = 4.3 Hz, 1 H), 8.18 (dd, *J*₁ = 2 Hz, *J*₂ = 8.5 Hz, 1 H), 7.81 (d, *J* = 8.5 Hz, 1 H), 7.78 (d, *J* = 7 Hz, 1 H), 7.55 (dd, *J*₁ = 7 Hz, *J*₂ = 8 Hz, 1 H), 7.45 (dd, *J*₁ = 4.5 Hz, *J*₂ = 8.3 Hz, 1 H), 5.86 (s, 2 H), 2.16 (s, 3 H); **¹³C NMR** (125 MHz, CDCl₃) δ 171.1, 149.9, 146.1, 136.4, 134.1, 128.9, 128.2, 128.2, 126.2, 121.3, 62.8, 21.2. **HRMS (EI-TOF):** *m/z* Calcd. For C₁₂H₁₁NNaO₂⁺ [M+Na]⁺: 224.0682, found 224.0683.



(7-(trifluoromethyl)quinolin-8-yl)methyl acetate (3b): light yellow solid (21.5 mg, 80%) petroleum ether/ethyl acetate (4/1)

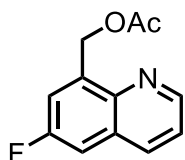
¹H NMR (500 MHz, CDCl₃) δ 9.07 (dd, *J*₁ = 1.5 Hz, *J*₂ = 4.3 Hz, 1 H), 8.30 (dd, *J*₁ = 2 Hz, *J*₂ = 8.3 Hz, 1 H), 7.98 (d, *J* = 8.5 Hz, 1 H), 7.84 (d, *J* = 8.5 Hz, 1 H), 7.56 (dd, *J*₁ = 4 Hz, *J*₂ = 8.5 Hz, 1 H), 6.02 (s, 2 H), 2.07 (s, 3 H); **¹³C NMR** (125 MHz, CDCl₃) δ 170.7, 151.5, 146.8, 136.1, 133.5 (*J* = 2.5 Hz), 130.9 (*J* = 30 Hz), 129.7, 129.5, 125.1, 123.0, 122.6 (q, *J* = 5 Hz), 57.8 (*J* = 1.3 Hz), 20.9. **HRMS (EI-TOF):** *m/z* Calcd. For C₁₃H₁₀F₃NNaO₂⁺ [M+Na]⁺: 292.0556, found 292.0557.



(7-fluoroquinolin-8-yl)methyl acetate (3c): white solid (19.9 mg, 91%)

petroleum ether/ethyl acetate (5/1)

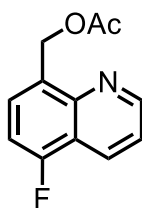
¹H NMR (500 MHz, CDCl₃) δ 9.01 (dd, $J_1 = 2$ Hz, $J_2 = 4.3$ Hz, 1 H), 8.18 (dd, $J_1 = 2$ Hz, $J_2 = 8.3$ Hz, 1 H), 7.86 (dd, $J_1 = 6$ Hz, $J_2 = 9$ Hz, 1 H), 7.43 (dd, $J_1 = 4$ Hz, $J_2 = 8.3$, 1 H), 7.39 (t, $J = 9$ Hz, 1 H), 5.84 (s, 2 H), 2.08 (s, 3 H); **¹³C NMR** (125 MHz, CDCl₃) δ 171.0, 161.9 ($J = 251.3$ Hz), 151.1, 136.4, 130.6 ($J = 11.3$ Hz), 125.3, 120.6, 120.6, 118.3 ($J = 13.8$ Hz), 117.0 ($J = 26.3$ Hz), 55.5 ($J = 5$ Hz), 21.0. **HRMS (EI-TOF):** m/z Calcd. For C₁₂H₁₁FNO₂⁺ [M+H]⁺: 220.0768, found 220.0770.



(6-fluoroquinolin-8-yl)methyl acetate (3d): white solid (18.0 mg, 82%)

petroleum ether/ethyl acetate (5/1)

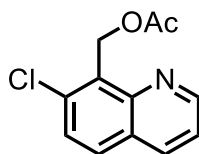
¹H NMR (500 MHz, CDCl₃) δ 8.90 (dd, $J_1 = 2$ Hz, $J_2 = 4.3$ Hz, 1 H), 8.12 (dd, $J_1 = 2$ Hz, $J_2 = 8.5$ Hz, 1 H), 7.55 (m, 1 H), 7.46 (dd, $J_1 = 4$ Hz, $J_2 = 8.5$ Hz, 1 H), 7.39 (dd, $J_1 = 3$ Hz, $J_2 = 8.5$ Hz, 1 H), 5.86 (s, 2 H), 2.20 (s, 3 H); **¹³C NMR** (125 MHz, CDCl₃) δ 170.77, 160.18 ($J = 247.5$ Hz), 148.7, 148.7, 136.4, 136.3, 129.0, 122.1, 118.7 ($J_{C-F} = 27.5$ Hz), 110.5 ($J_{C-F} = 21.3$ Hz), 62.2, 21.1. **HRMS (EI-TOF):** m/z Calcd. For C₁₂H₁₁FNO₂⁺ [M+H]⁺: 220.0768, found 220.0771.



(5-fluoroquinolin-8-yl)methyl acetate (3e): white solid (16.9 mg, 77%)

petroleum ether/ethyl acetate (5/1)

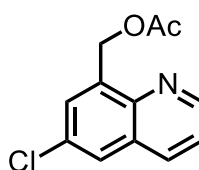
¹H NMR (500 MHz, CDCl₃) δ 9.01 (dd, $J_1 = 1.5$ Hz, $J_2 = 4.3$ Hz, 1 H), 8.45 (dd, $J_1 = 2$ Hz, $J_2 = 8.5$ Hz, 1 H), 7.73 (dd, $J_1 = 6$ Hz, $J_2 = 8$ Hz, 1 H), 7.50 (dd, $J_1 = 4.5$ Hz, $J_2 = 8.3$ Hz, 1 H), 7.21 (dd, $J_1 = 8$ Hz, $J_2 = 9.5$ Hz, 1 H), 5.78 (s, 2 H), 2.14 (s, 3 H); **¹³C NMR** (125 MHz, CDCl₃) δ 171.0, 157.8 ($J_{C-F} = 255$ Hz), 150.8, 146.7, 130.3 ($J_{C-F} = 3.8$ Hz), 129.5 ($J_{C-F} = 5$ Hz), 129.0 ($J_{C-F} = 8.8$ Hz), 121.4 ($J_{C-F} = 2.5$ Hz), 119.0 ($J_{C-F} = 16.3$ Hz), 109.7 ($J_{C-F} = 18.8$ Hz), 62.4, 21.2. **HRMS (EI-TOF):** m/z Calcd. For C₁₂H₁₁FNO₂⁺ [M+H]⁺: 220.0768, found 220.0770.



(7-chloroquinolin-8-yl)methyl acetate (3f): white solid (19.3 mg, 82%)

petroleum ether/ethyl acetate (5/1)

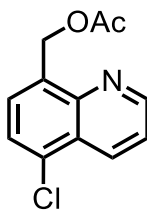
¹H NMR (500 MHz, CDCl₃) δ 8.99 (dd, *J*₁ = 1 Hz, *J*₂ = 3.8 Hz, 1 H), 8.16 (dd, *J*₁ = 2 Hz, *J*₂ = 8.3 Hz, 1 H), 7.79 (d, *J* = 8.5 Hz, 1 H), 7.58 (d, *J* = 9 Hz, 1 H), 7.44 (dd, *J*₁ = 4.5 Hz, *J*₂ = 8.3 Hz, 1 H), 5.97 (s, 2 H), 2.09 (s, 3 H); **¹³C NMR** (125 MHz, CDCl₃) δ 171.0, 151.1, 147.5, 137.2, 136.2, 131.3, 129.7, 128.2, 126.9, 121.4, 59.1, 20.9. **HRMS (EI-TOF):** *m/z* Calcd. For C₁₂H₁₁ClNO₂⁺ [M+H]⁺: 236.0473, found 236.0474.



(6-chloroquinolin-8-yl)methyl acetate (3g): white solid (20.7 mg, 88%)

petroleum ether/ethyl acetate (5/1)

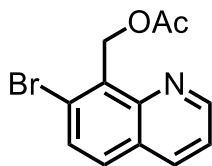
¹H NMR (500 MHz, CDCl₃) δ 8.95 (dd, *J*₁ = 1.5 Hz, *J*₂ = 4.3 Hz, 1 H), 8.12 (dd, *J*₁ = 1.5 Hz, *J*₂ = 8.3 Hz, 1 H), 7.79 (d, *J* = 2.5 Hz, 1 H), 7.72 (dd, *J*₁ = 1 Hz, *J*₂ = 2.3 Hz, 1 H), 7.49 (dd, *J*₁ = 4.5 Hz, *J*₂ = 8.3 Hz, 1 H), 5.84 (s, 2 H), 2.20 (s, 3 H); **¹³C NMR** (125 MHz, CDCl₃) δ 170.8, 149.8, 143.9, 136.3, 135.8, 132.3, 129.2, 128.9, 126.4, 122.2, 62.1, 21.1. **HRMS (EI-TOF):** *m/z* Calcd. For C₁₂H₁₁ClNO₂⁺ [M+H]⁺: 236.0473, found 236.0474.



(5-chloroquinolin-8-yl)methyl acetate (3h): white solid (18.3 mg, 78%)

petroleum ether/ethyl acetate (5/1)

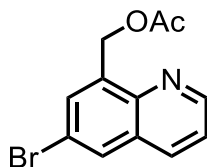
¹H NMR (500 MHz, CDCl₃) δ 8.99 (dd, *J*₁ = 1.5 Hz, *J*₂ = 4.3 Hz, 1 H), 8.59 (dd, *J*₁ = 2 Hz, *J*₂ = 8.5 Hz, 1 H), 7.69 (d, *J* = 8 Hz, 1 H), 7.62 (d, *J* = 7.5 Hz, 1 H), 7.55 (dd, *J*₁ = 4 Hz, *J*₂ = 8.5 Hz, 1 H), 5.81 (s, 2 H), 2.16 (s, 3 H); **¹³C NMR** (125 MHz, CDCl₃) δ 171.0, 150.5, 146.6, 133.6, 133.1, 131.4, 128.4, 126.2, 126.2, 122.1, 62.5, 21.1. **HRMS (EI-TOF):** *m/z* Calcd. For C₁₂H₁₀ClNNaO₂⁺ [M+Na]⁺: 258.0292, found 258.0295.



(7-bromoquinolin-8-yl)methyl acetate (3i): white solid (23.7 mg, 85%)

petroleum ether/ethyl acetate (5/1)

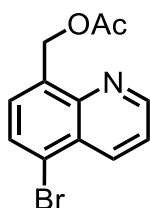
¹H NMR (500 MHz, CDCl₃) δ 8.98 (dd, *J*₁ = 2 Hz, *J*₂ = 4 Hz, 1 H), 8.15 (dd, *J*₁ = 2 Hz, *J*₂ = 8.3 Hz, 1 H), 7.75 (d, *J* = 9 Hz, 1 H), 7.71 (d, *J* = 8.5 Hz, 1 H), 7.46 (dd, *J*₁ = 4 Hz, *J*₂ = 8 Hz, 1 H), 5.98 (s, 2 H), 2.10 (s, 3 H); **¹³C NMR** (125 MHz, CDCl₃) δ 171.0, 151.0, 147.6, 136.2, 133.4, 131.0, 129.8, 127.8, 127.3, 121.6, 61.6, 20.9. **HRMS (EI-TOF):** *m/z* Calcd. For C₁₂H₁₁BrNO₂⁺ [M+H]⁺: 279.9968, found 279.9970.



(6-bromoquinolin-8-yl)methyl acetate (3j): white solid (25.1 mg, 90%)

petroleum ether/ethyl acetate (5/1)

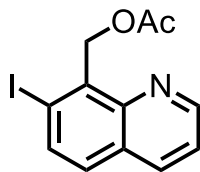
¹H NMR (500 MHz, CDCl₃) δ 8.94 (dd, *J*₁ = 2 Hz, *J*₂ = 4.3 Hz, 1 H), 8.07 (dd, *J*₁ = 2 Hz, *J*₂ = 8.5 Hz, 1 H), 7.95 (d, *J* = 2 Hz, 1 H), 7.82 (dd, *J*₁ = 1 Hz, *J*₂ = 2.3 Hz, 1 H), 7.45 (dd, *J*₁ = 4 Hz, *J*₂ = 8.3 Hz, 1 H), 5.82 (s, 2 H), 2.19 (s, 3 H); **¹³C NMR** (125 MHz, CDCl₃) δ 170.8, 150.1, 144.6, 136.6, 135.2, 131.4, 129.7, 129.3, 122.2, 120.2, 62.0, 21.1. **HRMS (EI-TOF):** *m/z* Calcd. For C₁₂H₁₀BrNNaO₂⁺ [M+Na]⁺: 301.9787, found 301.9791.



(5-bromoquinolin-8-yl)methyl acetate (3k): white solid (22.9 mg, 82%)

petroleum ether/ethyl acetate (5/1)

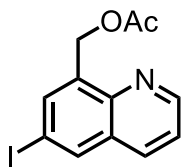
¹H NMR (500 MHz, CDCl₃) δ 8.96 (dd, *J*₁ = 1.5 Hz, *J*₂ = 3.3 Hz, 1 H), 8.55 (dd, *J*₁ = 1.5 Hz, *J*₂ = 8.5 Hz, 1 H), 7.82 (d, *J* = 7.5 Hz, 1 H), 7.63 (d, *J* = 8 Hz, 1 H), 7.54 (dd, *J*₁ = 4.5 Hz, *J*₂ = 8.8 Hz, 1 H), 5.80 (s, 2 H), 2.16 (s, 3 H); **¹³C NMR** (125 MHz, CDCl₃) δ 171.0, 150.5, 146.7, 135.7, 134.4, 130.0, 128.8, 127.5, 122.4, 122.0, 62.5, 21.1. **HRMS (EI-TOF):** *m/z* Calcd. For C₁₂H₁₁BrNO₂⁺ [M+H]⁺: 279.9968, found 279.9970.



(7-iodoquinolin-8-yl)methyl acetate (3l): white solid (28.4 mg, 87%)

petroleum ether/ethyl acetate (5/1)

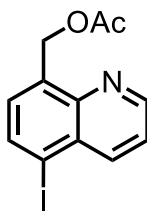
¹H NMR (500 MHz, CDCl₃) δ 8.94 (dd, $J_1 = 1.5$ Hz, $J_2 = 4.3$ Hz, 1 H), 8.19 (d, $J = 1.5$ Hz, 1 H), 8.04 (dd, $J_1 = 1.5$ Hz, $J_2 = 8.3$, 1 H), 7.98 (d, $J = 2$ Hz, 1 H), 7.44 (dd, $J_1 = 4.5$ Hz, $J_2 = 8.3$ Hz, 1 H), 5.80 (s, 2 H), 2.19 (s, 3 H); **¹³C NMR** (125 MHz, CDCl₃) δ 170.8, 150.3, 145.0, 136.7, 136.6, 136.3, 135.0, 129.7, 122.0, 91.8, 61.9, 21.1. **HRMS (EI-TOF):** m/z Calcd. For C₁₂H₁₀INNaO₂⁺ [M+Na]⁺: 349.9648, found 349.9652



(6-iodoquinolin-8-yl)methyl acetate (3m): white solid (27.8 mg, 85%)

petroleum ether/ethyl acetate (5/1)

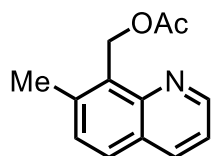
¹H NMR (500 MHz, CDCl₃) δ 8.95 (dd, $J_1 = 1.5$ Hz, $J_2 = 4.3$ Hz, 1 H), 8.14 (dd, $J_1 = 2$ Hz, $J_2 = 8.5$ Hz, 1 H), 8.00 (d, $J = 8.5$ Hz, 1 H), 7.54 (d, $J = 9$ Hz, 1 H), 7.46 (dd, $J_1 = 4$ Hz, $J_2 = 8$ Hz, 1 H), 5.97 (s, 2 H), 2.11 (s, 3 H); **¹³C NMR** (125 MHz, CDCl₃) δ 171.0, 150.8, 147.1, 137.3, 137.0, 136.2, 129.8, 127.9, 121.8, 104.1, 66.0, 21.0. **HRMS (EI-TOF):** m/z Calcd. For C₁₂H₁₀INNaO₂⁺ [M+Na]⁺: 349.9648, found 349.9651.



(5-iodoquinolin-8-yl)methyl acetate (3n): white solid (26.8 mg, 82%)

petroleum ether/ethyl acetate (5/1)

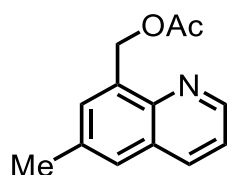
¹H NMR (500 MHz, CDCl₃) δ 8.91 (dd, $J_1 = 1.5$ Hz, $J_2 = 4$ Hz, 1 H), 8.39 (dd, $J_1 = 1.5$ Hz, $J_2 = 8.5$ Hz, 1 H), 8.11 (d, $J = 7.5$ Hz, 1 H), 7.49 (m, 2 H), 5.81 (s, 2 H), 2.16 (s, 3 H); **¹³C NMR** (125 MHz, CDCl₃) δ 170.9, 150.6, 146.4, 140.5, 137.4, 135.5, 129.9, 129.4, 122.9, 98.5, 62.5, 21.1. **HRMS (EI-TOF):** m/z Calcd. For C₁₂H₁₀INNaO₂⁺ [M+Na]⁺: 349.9648, found 349.9650.



(7-methylquinolin-8-yl)methyl acetate (3o): white solid (18.9 mg, 88%)

petroleum ether/ethyl acetate (5/1)

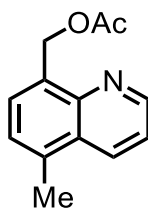
¹H NMR (500 MHz, CDCl₃) δ 8.97 (dd, *J*₁ = 2 Hz, *J*₂ = 4.5 Hz, 1 H), 8.15 (dd, *J*₁ = 2 Hz, *J*₂ = 8 Hz, 1 H), 7.76 (d, *J* = 8.5 Hz, 1 H), 7.44 (d, *J* = 8.5 Hz, 1 H), 7.39 (dd, *J*₁ = 4.5 Hz, *J*₂ = 8.3 Hz, 1 H), 5.95 (s, 2 H), 2.61 (s, 3 H), 2.08 (s, 3 H); **¹³C NMR** (125 MHz, CDCl₃) δ 171.3, 150.0, 146.9, 140.5, 136.4, 130.6, 129.9, 128.4, 126.7, 120.5, 58.9, 21.1, 19.9. **HRMS (EI-TOF):** *m/z* Calcd. For C₁₃H₁₃NNaO₂⁺ [M+Na]⁺: 238.0838, found 238.0839.



(6-methylquinolin-8-yl)methyl acetate (3p): white solid (19.6 mg, 91%)

petroleum ether/ethyl acetate (5/1)

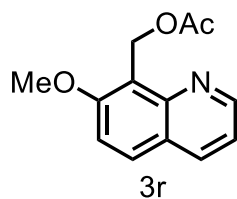
¹H NMR (500 MHz, CDCl₃) δ 8.89 (dd, *J*₁ = 1.5 Hz, *J*₂ = 4.3 Hz, 1 H), 8.08 (dd, *J*₁ = 1.5 Hz, *J*₂ = 8.3 Hz, 1 H), 7.60 (s, 1 H), 7.57 (s, 1 H), 7.40 (dd, *J*₁ = 4 Hz, *J*₂ = 8 Hz, 1 H), 5.82 (s, 2 H), 2.54 (s, 3 H), 2.16 (s, 3 H); **¹³C NMR** (125 MHz, CDCl₃) δ 171.1, 149.0, 144.7, 136.1, 135.7, 133.7, 131.3, 128.4, 127.0, 121.3, 62.8, 21.7, 21.2. **HRMS (EI-TOF):** *m/z* Calcd. For C₁₃H₁₃NNaO₂⁺ [M+Na]⁺: 238.0838, found 238.0840.



(5-methylquinolin-8-yl)methyl acetate (3q): white solid (21.1 mg, 98%)

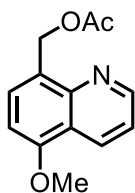
petroleum ether/ethyl acetate (5/1)

¹H NMR (500 MHz, CDCl₃) δ 8.96 (dd, *J*₁ = 1.5 Hz, *J*₂ = 4.3 Hz, 1 H), 8.33 (dd, *J*₁ = 1.5 Hz, *J*₂ = 8.5 Hz, 1 H), 7.65 (d, *J* = 7 Hz, 1 H), 7.46 (dd, *J*₁ = 4 Hz, *J*₂ = 8.5 Hz, 1 H), 7.36 (d, *J* = 7 Hz, 1 H), 5.81 (s, 2 H), 2.68 (s, 3 H), 2.14 (s, 3 H); **¹³C NMR** (125 MHz, CDCl₃) δ 171.1, 149.5, 146.5, 135.1, 132.6, 132.2, 128.8, 127.6, 126.6, 120.9, 63.0, 21.2, 18.7. **HRMS (EI-TOF):** *m/z* Calcd. For C₁₃H₁₃NNaO₂⁺ [M+Na]⁺: 238.0838, found 238.0843.



(7-methoxyquinolin-8-yl)methyl acetate (3r): white solid (19.4 mg, 84%) petroleum ether/ethyl acetate (4/1)

¹H NMR (500 MHz, CDCl₃) δ 9.04 (d, *J* = 2 Hz, 1 H), 8.27 (d, *J* = 4 Hz, 1 H), 7.94 (d, *J* = 4.5 Hz, 1 H), 7.45 (d, *J* = 4.5 Hz, 1 H), 7.41 (dd, *J*₁ = 4 Hz, *J*₂ = 4.5 Hz, 1 H), 5.88 (s, 2 H), 4.04 (s, 3 H), 2.09 (s, 3 H); **¹³C NMR** (125 MHz, CDCl₃) δ 171.3, 159.8, 149.8, 138.4, 138.4, 130.6, 123.5, 119.0, 117.3, 114.3, 56.7, 56.4, 21.3. **HRMS (EI-TOF):** *m/z* Calcd. For C₁₃H₁₃NNaO₃⁺ [M+Na]⁺: 254.0788, found 254.0789.



(5-methylquinolin-8-yl)methyl acetate (3s): white solid (18.9 mg, 82%) petroleum ether/ethyl acetate (4/1):

¹H NMR (500 MHz, CDCl₃) δ 9.00 (dd, *J*₁ = 1.5 Hz, *J*₂ = 3 Hz, 1 H), 8.65 (dd, *J*₁ = 1.5 Hz, *J*₂ = 8 Hz, 1 H), 7.73 (d, *J* = 8 Hz, 1 H), 7.46 (dd, *J*₁ = 4 Hz, *J*₂ = 8.5 Hz, 1 H), 6.86 (d, *J* = 8 Hz, 1 H), 5.75 (s, 2 H), 4.02 (s, 3 H), 2.11 (s, 3 H); **¹³C NMR** (125 MHz, CDCl₃) δ 171.2, 155.6, 149.9, 146.2, 131.9, 131.0, 125.4, 121.0, 120.4, 103.9, 62.8, 55.9, 21.3. **HRMS (EI-TOF):** *m/z* Calcd. For C₁₃H₁₃NNaO₂⁺ [M+Na]⁺: 254.0788, found 254.0793.

5. NMR Spectra for Substrate 11 and Acetoxylation Products

