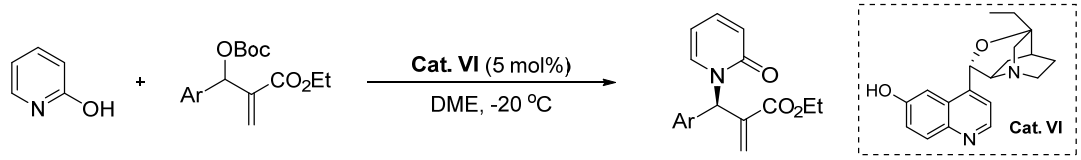
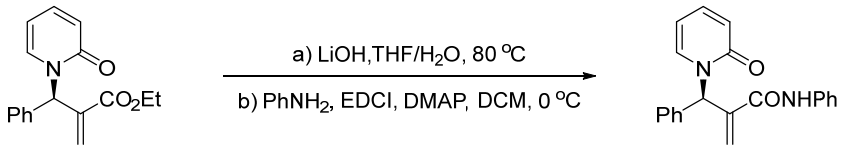
6. Scale-up reaction for synthesis of product 3aa and 3at



1a: 1.0 mmol **2**: 1.5 mmol **3aa:** Ar = Ph, 98% yield, 96% ee
3at: Ar = 2-BrC_6H_4, 97% yield, 93% ee

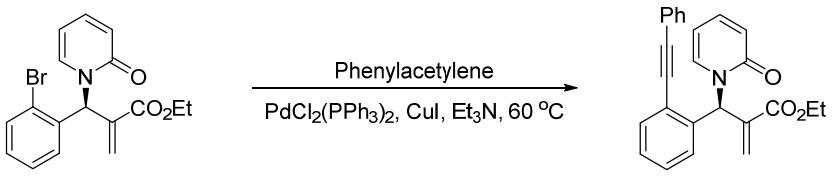
In the glovebox, a Schlenk tube was charged with **Cat. VI** (5 mol%), **1a** (0.0951 g, 1.0 mmol), **2a** (0.4590 g, 1.5 mmol) or **2t** (0.5760 g, 1.5 mmol) and DME (10.0 mL). Then, the mixture was stirred at -20 °C. After completion of the reaction (monitored by TLC), the resulting mixture was concentrated under reduced pressure. The resulting crude material was purified by flash column chromatography to afford the desired products **3aa** (0.2794 g, 98% yield, 96% ee) and **3at** (0.3495 g, 97% yield, 93% ee). The enantiomeric excess of the products **3aa** and **3at** were determined by HPLC with chiral columns.

7. Further synthetic transformations of product 3aa and 3at



3aa: 96% ee **5**: 45% yield (two steps); 95% ee

Synthesis of compound 5[9]: To a stirred solution of **3aa** (28.3 mg, 0.1 mmol) in THF (0.8 mL) added LiOH (12.0 mg, 0.5 mmol) in H_2O (0.2 mL) and the resulting mixture was refluxed for 8 h. Acidify the solution with the 1M HCl, followed by adding water and diethyl ether. The aqueous phase was separated and extracted three times with diethyl ether. The combined organic phases were dried over anhydrous sodium sulfate and the solvents were removed in vacuo. Add aniline (1.0 eq.) to a stirred solution of 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDCI) (1.0 eq.), above residue and 4-dimethyl-aminopyridine (DMAP) (0.1 eq.) in DCM at 0 °C. After completion of the reaction (monitored by TLC), then extracted three times with DCM. Dry the organic layer with anhydrous sodium sulfate. The crude residue was purified by column chromatography (dichloromethane/ethyl acetate = 20/1) to afford the desired compound **5** as a white solid (15.0 mg, 45% yield for two steps, 95% ee), Mp: 265.0-269.3 °C. Unknown compound, $[\alpha]^{20}_D$ = -190.89 (*c* 0.055, $CHCl_3$), R_f= 0.20 (dichloromethane/ethyl acetate 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.45 (s, 1H), 7.72–7.61 (m, 2H), 7.54–7.37 (m, 4H), 7.37–7.28 (m, 4H), 7.24–7.18 (m, 1H), 7.18–7.00 (m, 2H), 6.80–6.66 (m, 1H), 6.41 (s, 1H), 6.32–6.17 (m, 1H), 5.40 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 163.3, 144.6, 140.4, 138.3, 135.6, 135.4, 129.4, 129.2, 129.1, 129.0, 125.2, 124.5, 120.7, 120.2, 107.2, 59.6. HPLC (AD-H, *n*-hexane/*i*-propanol = 70/30, flow rate = 0.5 mL/min, l = 230 nm) tR = 17.6 min (minor) and 20.5 min (major); HRMS (ESI-QEplus) m/z: $[M+H]^+$ Calcd for $C_{21}H_{19}N_2O_2$ 331.1441; found 331.1434.



3at: 93% ee **6**: 86% yield; 95% ee

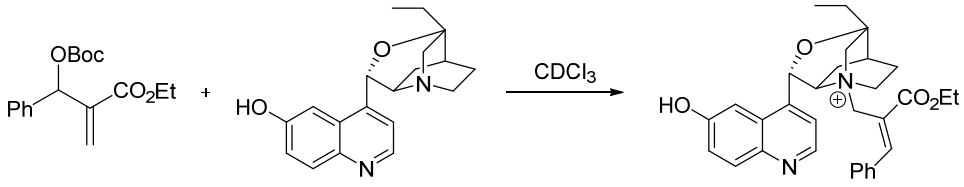
Synthesis of compound 6[10]: Under nitrogen atmosphere, the mixture of CuI (0.6 mg, 0.003 mmol), $PdCl_2(PPh_3)_2$ (3.5 mg, 0.005 mmol), **3at** (36.2 mg, 0.1 mmol) and phenylacetylene (12.2 mg, 0.12 mmol) in Et_3N (1.0 mL) was stirred overnight in 60 °C oil bath. After completion of the reaction (monitored by TLC), dilute the reaction mixture in diethyl ether. Remove the solid by filtration. Evaporate the solvent under reduced pressure. The resulting crude material was purified by flash column chromatography (petroleum ether/ethyl acetate = 3/1) to afford the desired compound **6** as a yellow solid (32.9 mg, 86% yield, 95% ee), Mp: 138.2-142.5 °C. Unknown compound, $[\alpha]^{20}_D$ = -102.62 (*c* 0.38, $CHCl_3$), R_f = 0.20 (petroleum ether/ethyl acetate 2/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73–7.59 (m, 1H), 7.59–7.42 (m, 3H), 7.40–7.26 (m, 6H), 7.22–7.13 (m, 1H), 7.09–6.97 (m, 1H), 6.76–6.45 (m, 2H), 6.21–5.95 (m, 1H), 5.31 (s, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 1.10 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 162.0, 139.3, 139.3, 139.0, 135.4, 133.4, 132.1, 128.7, 128.6, 128.5, 128.5, 128.2, 128.1, 124.4, 122.9, 121.2, 105.8, 96.0, 86.3, 61.3, 58.3, 14.1. HPLC (IA, *n*-hexane/*i*-propanol = 70/30, flow rate = 0.5 mL/min, l = 230 nm) tR = 11.6 min (minor) and 14.8 min (major); HRMS (ESI-QEplus) *m*/*z*: $[M+H]^+$ Calcd for $C_{25}H_{22}NO_3$ 384.1594; found 384.1588.

3at: 93% ee **7**: 91% yield; 92% ee

Synthesis of compound 7[11]: Under nitrogen atmosphere, the mixture of $PdCl_2$(dppf) (3.6 mg, 0.005 mmol), bis(pinacolato)diboron (63.5 mg, 0.25 mmol), AcOK (24.5 mg, 0.25 mmol) and **3at** (36.2 mg, 0.1 mmol) in dry toluene (1.0 mL) was stirred overnight in 80 °C oil bath. After completion of the reaction (monitored by TLC), dilute with acetone and filter. Evaporate the solvent under reduced pressure. The resulting crude material was purified by flash column chromatography (petroleum ether/ethyl acetate = 2/1) to afford the desired compound **7** as a yellow oil (37.2 mg, 91% yield, 92% ee) Unknown compound, $[\alpha]^{20}_D$ = -27.60 (*c* 0.56, $CHCl_3$), R_f = 0.25 (petroleum ether/ethyl acetate 1/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95–7.84 (m, 1H), 7.61 (s, 1H), 7.43–7.36 (m, 1H), 7.35–7.27 (m, 2H), 7.15–7.06 (m, 1H), 7.05–6.90 (m, 1H), 6.67–6.56 (m, 1H), 6.55 (s, 1H), 6.14–5.99 (m, 1H), 5.22 (s, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 1.26 (s, 12H), 1.14 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 162.1, 142.9, 141.5, 139.0, 137.2, 135.7, 131.4, 129.0, 127.5, 127.1, 121.4, 105.1, 84.1, 61.1, 59.2, 24.9, 24.8, 14.2. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.39. HPLC (OD-H, *n*-hexane/*i*-propanol = 70/30, flow rate = 0.5 mL/min, l =

230 nm) tR = 7.9 min (major) and 8.8 min (minor); HRMS (ESI-QEplus) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{29}BNO_5$ 410.2133; found 410.2129.

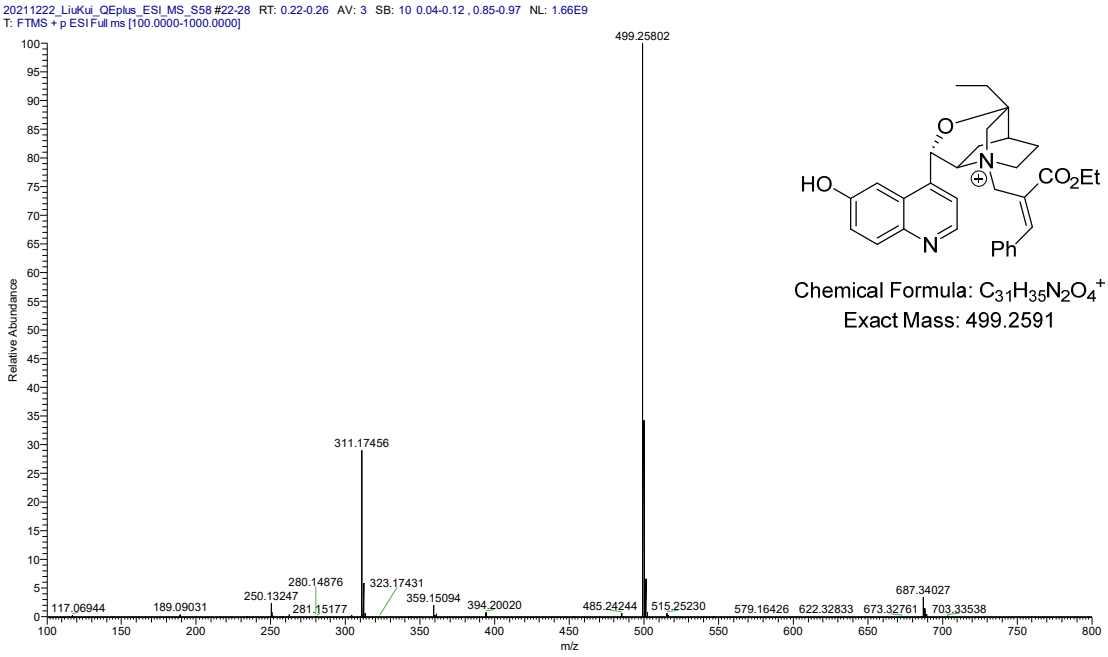
8. Mechanism studies

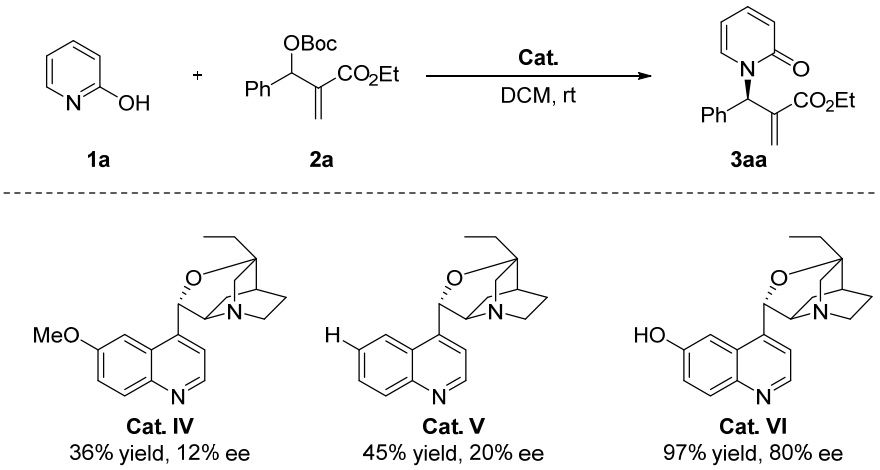


2a **Cat. VI** **INT**

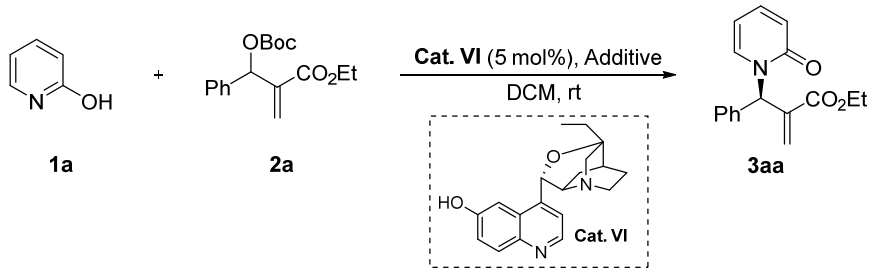
HRMS (ESI-QEplus) *m/z*: 499.2591; found 499.2580.

In the glovebox, a Schlenk tube was charged with **Cat. VI** (6.2 mg, 0.02 mmol), **2a** (6.1 mg, 0.02 mmol) and $CDCl_3$ (1.0 mL). Then, the mixture was stirred at -20 °C until starting material **2a** was consumed (monitored by TLC). The intermediate **INT** was observed by the high resolution mass spectrometry (HRMS). HRMS (ESI-QEplus) *m/z*: $[M]^+$ Calcd for $C_{31}H_{35}N_2O_4$ 499.2591; found 499.2580.





In the glovebox, a Schlenk tube was charged with **Cat.** (5 mol%), **1a** (9.5 mg, 0.1 mmol), **2a** (30.6 mg, 0.1 mmol) and DCM (1.0 mL). Then, the mixture was stirred at room temperature. After completion of the reaction (monitored by TLC), the resulting mixture was concentrated under reduced pressure. The resulting crude material was purified by flash column chromatography to afford the desired products **3aa**. The enantiomeric excess of the products **3aa** was determined by HPLC with chiral columns.



Entry	Additive	**3aa** Yield (%)	**3aa** ee (%)
1	TFE (10 eq.)	16	74
2	TFE (as solvent)	N.R.	-
3	MeOH (as solvent)	2	41

In the glovebox, a Schlenk tube was charged with **Cat. VI** (5 mol%), **1a** (9.5 mg, 0.1 mmol), **2a** (30.6 mg, 0.1 mmol) additive (x eq.) and DCM (1.0 mL). Then, the mixture was stirred at room temperature. After completion of the reaction (monitored by TLC), the resulting mixture was concentrated under reduced pressure. The resulting crude material was purified by flash column chromatography to afford the desired products **3aa**. The enantiomeric excess of the products **3aa** was determined by HPLC with chiral columns.

9. The details of DFT calculations and discussion

All calculations were carried out with Gaussian 16 program.[12] Geometrical optimizations and vibrational frequency analysis were performed at the M06-2X[13]/6-31G(d) level. Frequency calculations of optimized structures were performed to confirm that each stationary point was a transition state (one imaginary frequency) or a minimum (no imaginary frequency) and to obtain the thermodynamic corrections. Intrinsic reaction coordinate (IRC) calculations were conducted for each transition state to verify the direct connection between the corresponding reactant and product. The subsequent single-point calculations were carried out at the level of M06-2X/6-311+G(d,p) together with SMD implicit solvent model[14] for considering the solvation effect. The diethyl ether solvent, which was implanted in Gaussian 16, was used for considering 1,2-dimethoxyethane solvation effect. Gibbs free energies in solution described in the text were obtained from such single-point energy calculations including gas-phase free energy corrections. The conformational search for key structures, especially for the transition states related to stereoselectivity, were performed. We found that although bi- and tri-molecules participate in the transformations, the key structures are not as flexible as it seems due to the existence of multiple hydrogen bond interactions including a strong O–H···O hydrogen bond. A few conformations are mainly derived from the different orientations of ester group of MBH carbonate substrate and/or the ethyl group of catalyst. The different conformations of **TS4** and **TS4′** are given in Figures S6 and S7, and the most stable conformations are given in the energy profile for discussion. The three-dimensional images of the optimized structures were prepared using CYLview software.[15] Noncovalent interactions were performed with Multiwfn[16] to investigate the hydrogen-bonding interactions between the substrate and catalyst, and were visualized with visual molecular dynamics (VMD).[17]

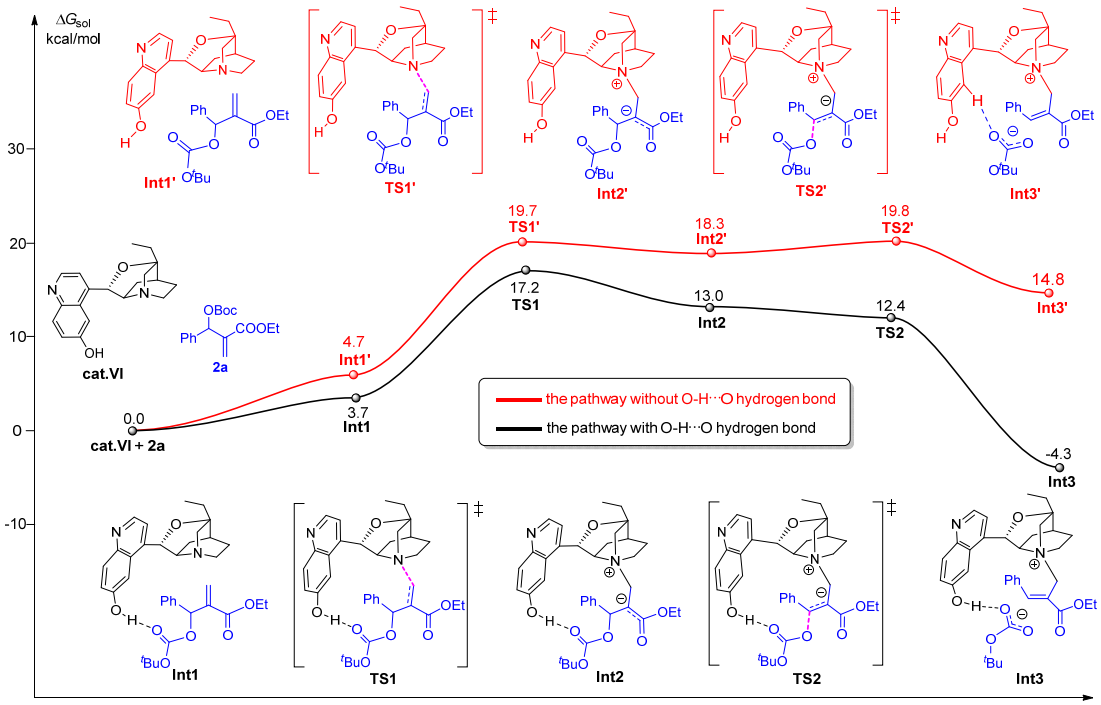


Figure S1. Energy profiles (kcal/mol) of the initial processes of electrophilic attack (C–N formation) and OBoc removal (C–O cleavage) with or without O–H···O hydrogen bond.

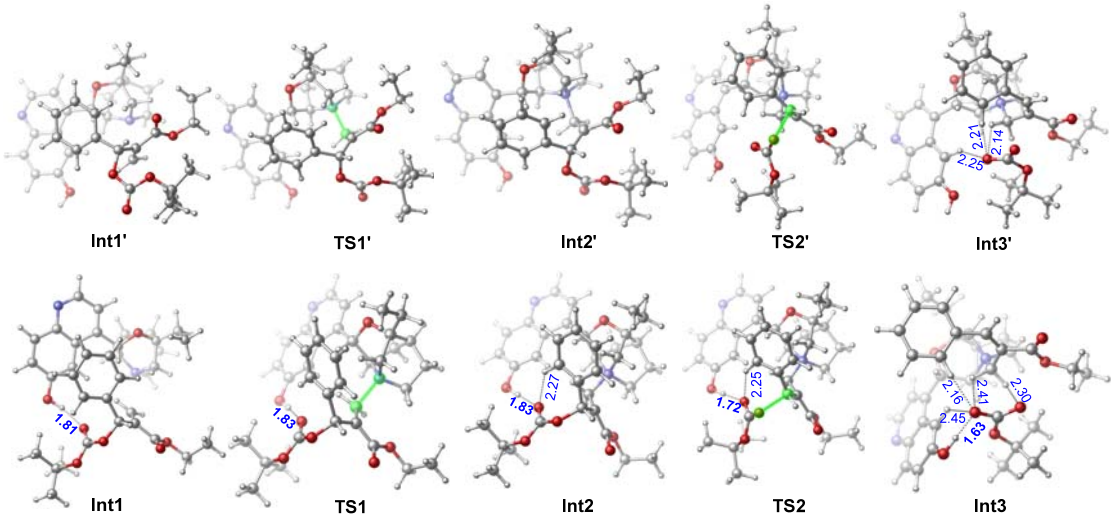


Figure S2. Optimized structures involved in the energy profiles shown in Figure S1. Bond distances are given in Å.

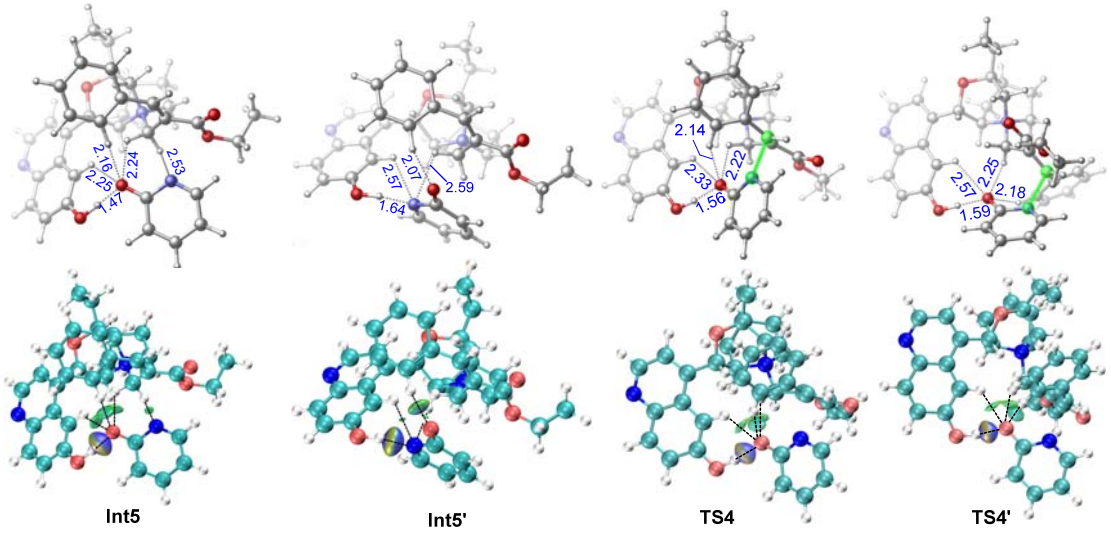


Figure S3. Computational analysis (kcal/mol) of optimized key intermediates and transition states and their visualization of noncovalent interactions (NCIs, isovalue = 0.015) of hydrogen bonds. Bond distances are given in Å.