Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.


# Supporting Information

## One-Pot Stepwise Approach to Axially Chiral Quinoline-3-Carbaldehydes Enabled by Iminium-Allenamine Cascade Catalysis

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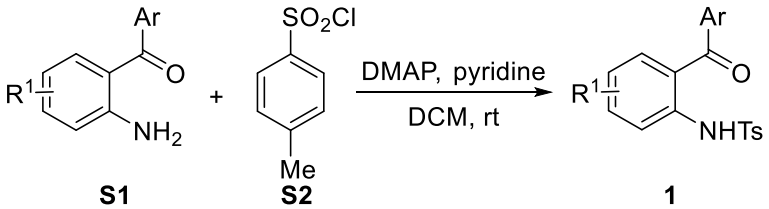
## General Information

$^{1}H$ and $^{13}C$ NMR spectra were recorded on a Bruker AC-400 FT (400 MHz for $^{1}H$ NMR and 100 MHz for $^{13}C$ NMR, respectively) using tetramethylsilane as an internal reference. Chemical shifts (δ) and coupling constants (*J*) were expressed in ppm and Hz, respectively. High resolution mass spectra (HRMS) were recorded on a LC-TOF spectrometer (Micromass). ESI-HRMS data were acquired using a Thermo LTQ Orbitrap XL Instrument equipped with an ESI source and controlled by Xcalibur software. High pressure liquid chromatography (HPLC) analyses were performed on a Thermo Scientific UltiMate 3000 instrument equipped with an isostatic pump, using a chiral stationary phase column (Daicel Co. CHIRALPAK). The chiral HPLC methods were calibrated with the corresponding racemic mixtures. Optical Rotation was measured on an Anton Paar MCP 100/150 polarimeter. X-ray crystallography analysis of single crystal was performed on a SuperNova, Dual, Cu at zero, Eos diffractometer.

Chloroform was distilled over calcium hydride. Other solvents and chemicals were purchased from the Sinopharm Chemical Reagent Co., Adamas, Acros, Alfa Aesar, and TCI, and used as received. 2-Alkynals **2** were prepared according to the literature.[1] Catalysts **C1-6** and **C8-9** were purchased from Daicel Chiral Technologies (China) CO., LTD. and used directly.

## Preparation and Analytic Data of 2-(Tosylamino)aryl Ketones 1

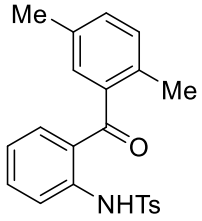
2-(Tosylamino)aryl ketones **1** were prepared from the corresponding 2-aminoaryl ketones **S1**[2] and 4-toluenesulfonyl chloride **S2** via the following procedure. The new compounds were characterized in this report.




**S1** **S2** **1**

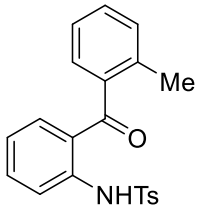
To a solution of **S1** (1.0 mmol) in dichloromethane (5.0 mL) were added pyridine (0.5 mL), DMAP (24.4 mg, 0.20 mmol) and 4-toluenesulfonyl chloride **S2** (286.0 mg, 1.5 mmol) at 0 °C successively. The mixture was then allowed to stir at room temperature for 24 h. Dilute the reaction with 50 mL of dichloromethane. The reaction mixture was washed twice with a saturated aqueous solution of $CuSO_4$ (2 × 30 mL) and once with brine (30 mL). The organic

layer was dried with anhydrous $Na_2SO_4$ and concentrated in vacuo. The crude product was then purified by chromatography on silica gel (petroleum ether/ethyl acetate) to give **1**.



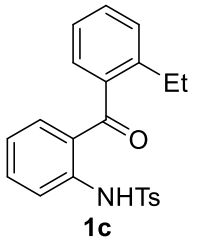
**1a**

*N*-(2-(2,5-Dimethylbenzoyl)phenyl)-4-methylbenzenesulfonamide **1a** was obtained as a white solid in 90% yield. $R_f$ = 0.40 (petroleum ether/ethyl acetate = 5:1); m.p. 106-107 °C; $^1$H NMR (400 MHz, $CDCl_3$): δ 11.06 (br., s, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.52-7.44 (m, 1H), 7.30-7.24 (m, 1H), 7.23-7.15 (m, 3H), 7.11 (d, *J* = 8.0 Hz, 1H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.71 (s, 1H), 2.35 (s, 3H), 2.29 (s, 3H), 2.04 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 202.4, 143.8, 140.2, 138.5, 136.6, 134.9, 134.8, 134.5, 132.8, 131.2, 130.8, 129.7, 128.3, 127.3, 124.3, 123.0, 120.7, 21.5, 20.9, 19.0; HRMS (ESI) calcd for $C_{22}H_{22}NO_3S$ $(M+H)^+$ 380.1315, found 380.1316.



**1b**

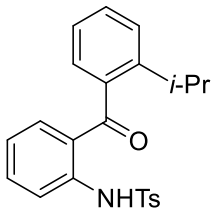
4-Methyl-*N*-(2-(2-methylbenzoyl)phenyl)benzenesulfonamide **1b** was obtained as a white solid in 92% yield. $R_f$ = 0.40 (petroleum ether/ethyl acetate = 5:1); m.p. 99-100 °C; $^1$H NMR (400 MHz, $CDCl_3$): δ 11.03 (br., s, 1H), 7.80 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.53-7.45 (m, 1H), 7.40-7.33 (m, 1H), 7.28-7.14 (m, 5H), 7.02-6.94 (m, 1H), 6.88 (dd, *J* = 7.6, 1.2 Hz, 1H), 2.36 (s, 3H), 2.12 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 202.1, 143.9, 140.3, 138.5, 136.5, 136.1, 134.9, 134.5, 130.9, 130.5, 129.7, 128.0, 127.3, 125.2, 124.3, 123.0, 120.7, 21.5, 19.6; HRMS (ESI) calcd for $C_{21}H_{18}NO_3S$ $(M-H)^-$ 364.1013, found 364.1036.



**1c**

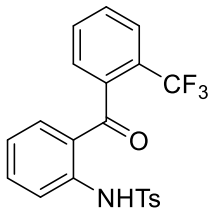
*N*-(2-(2-Ethylbenzoyl)phenyl)-4-methylbenzenesulfonamide **1c** was obtained as a yellowish

oil in 93% yield. $R_f$ = 0.40 (petroleum ether/ethyl acetate = 5:1); $^1$H NMR (400 MHz, $CDCl_3$): δ 11.12 (br., s, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.52-7.44 (m, 1H), 7.43-7.37 (m, 1H), 7.32-7.24 (m, 2H), 7.23-7.13 (m, 3H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 7.2 Hz, 1H), 2.47 (q, *J* = 7.6 Hz, 2H), 2.36 (s, 3H), 1.08 (t, *J* = 7.6 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 202.3, 143.9, 142.4, 140.4, 138.2, 136.5, 134.9, 134.7, 130.5, 129.7, 129.4, 127.8, 127.3, 125.1, 124.2, 122.9, 120.5, 26.2, 21.5, 15.7; HRMS (ESI) calcd for $C_{22}H_{20}NO_3S$ $(M-H)^-$ 378.1169, found 378.1187.



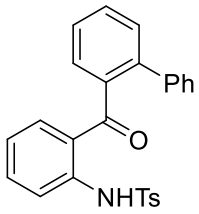
**1d**

*N*-(2-(2-Isopropylbenzoyl)phenyl)-4-methylbenzenesulfonamide **1d** was obtained as a white solid in 89% yield. $R_f$ = 0.40 (petroleum ether/ethyl acetate = 8:1); m.p. 104-105 °C; $^1$H NMR (400 MHz, $CDCl_3$): δ 11.27 (br., s, 1H), 7.80 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.51-7.45 (m, 1H), 7.44-7.38 (m, 2H), 7.28-7.20 (m, 3H), 7.19-7.13 (m, 1H), 6.99-6.92 (m, 1H), 6.82 (dd, *J* = 7.6, 1.2 Hz, 1H), 2.80-2.69 (m, 1H), 2.38 (s, 3H), 1.13 (d, *J* = 6.8 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 202.8, 146.6, 143.9, 140.6, 138.0, 136.6, 135.1, 134.9, 130.4, 129.7, 127.3, 127.0, 126.1, 125.2, 123.9, 122.7, 120.1, 30.4, 24.0, 21.6; HRMS (ESI) calcd for $C_{23}H_{24}NO_3S$ $(M+H)^+$ 394.1471, found 394.1482.



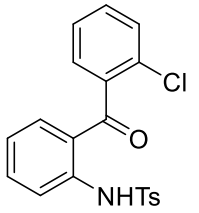
**1e**

4-Methyl-*N*-(2-(2-(trifluoromethyl)benzoyl)phenyl)benzenesulfonamide **1e** was obtained as a white solid in 92% yield. $R_f$ = 0.40 (petroleum ether/ethyl acetate = 8:1); m.p. 109-110 °C; $^1$H NMR (400 MHz, $CDCl_3$): δ 10.09 (br., s, 1H), 7.82-7.72 (m, 4H), 7.65-7.55 (m, 2H), 7.52-7.46 (m, 1H), 7.28-7.22 (m, 2H), 7.15 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.11-7.05 (m, 1H), 6.98-6.92 (m, 1H), 2.39 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 199.1, 144.1, 140.9, 137.5 (q, *J* = 2.1 Hz), 136.4, 135.6, 134.9, 131.4. 130.1, 129.7, 127.9, 127.8 (q, *J* = 32.2 Hz), 127.3, 126.8 (q, *J* = 4.5 Hz), 123.4 (q, *J* = 272.3 Hz), 122.6, 122.4, 119.6, 21.5; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -58.15; HRMS (ESI) calcd for $C_{21}H_{15}F_3NO_3S$ $(M-H)^-$ 418.0730, found 418.0749.



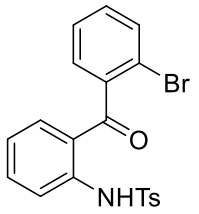

**1f**

*N*-(2-(Biphenylcarbonyl)phenyl)-4-methylbenzenesulfonamide **1f** was obtained as a yellowish oil in 90% yield. $R_f$ = 0.40 (petroleum ether/ethyl acetate = 5:1); $^1$H NMR (400 MHz, $CDCl_3$): δ 11.05 (br., s, 1H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.61 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.58-7.52 (m, 1H), 7.46 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.41-7.35 (m, 1H), 7.35-7.27 (m, 2H), 7.24-7.15 (m, 7H), 7.12 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.86-6.79 (m, 1H), 2.38 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 202.0, 143.9, 141.1, 140.3, 139.8, 138.5, 136.7, 134.8, 134.5, 130.7, 130.3, 129.7, 128.7, 128.6, 128.5, 127.5, 127.3, 126.9, 123.3, 122.3, 119.0, 21.6; HRMS (ESI) calcd for $C_{26}H_{22}NO_3S$ $(M+H)^+$ 428.1315, found 428.1319.




**1g**

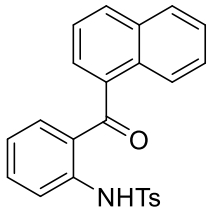
*N*-(2-(2-Chlorobenzoyl)phenyl)-4-methylbenzenesulfonamide **1g** was obtained as a yellow solid in 94% yield. $R_f$ = 0.40 (petroleum ether/ethyl acetate = 5:1); m.p. 116-117 °C; $^1$H NMR (400 MHz, $CDCl_3$): δ 11.08 (br., s, 1H), 7.80 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.53-7.47 (m, 1H), 7.46-7.38 (m, 2H), 7.37-7.31 (m, 1H), 7.27-7.19 (m, 3H), 7.17-7.11 (m, 1H), 7.02-6.94 (m, 1H), 2.36 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 198.7, 144.1, 140.6, 138.2, 136.5, 135.5, 134.6, 131.4, 130.9, 130.0, 129.8, 128.7, 127.4, 126.8, 122.9, 122.7, 120.0, 21.5; HRMS (ESI) calcd for $C_{20}H_{15}ClNO_3S$ $(M-H)^-$ 384.0467, found 384.0487.




**1h**

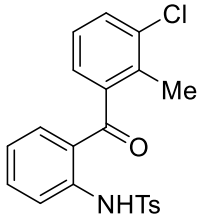
*N*-(2-(2-Bromobenzoyl)phenyl)-4-methylbenzenesulfonamide **1h** was obtained as a yellow solid in 92% yield. $R_f$ = 0.30 (petroleum ether/ethyl acetate = 5:1); m.p. 84-85 °C; $^1$H NMR (400 MHz, $CDCl_3$): δ 11.10 (br., s, 1H), 7.82 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.77 (d, *J* = 8.0 Hz,

2H), 7.59 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.53-7.46 (m, 1H), 7.42-7.31 (m, 2H), 7.23 (d, *J* = 8.0 Hz, 3H), 7.12 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.01-6.93 (m, 1H), 2.37 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 199.4, 144.0, 140.8, 140.2, 136.6, 135.5, 134.7, 133.1, 131.4, 129.8, 128.6, 127.4, 127.3, 122.9, 122.3, 119.9, 119.2, 21.5; HRMS (ESI) calcd for $C_{20}H_{15}BrNO_3S$ $(M-H)^-$ 427.9962, found 427.9958.



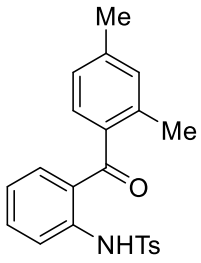

**1i**

*N*-(2-(1-Naphthoyl)phenyl)-4-methylbenzenesulfonamide **1i** was obtained as a yellow solid in 94% yield. $R_f$ = 0.40 (petroleum ether/ethyl acetate = 5:1); m.p. 117-118 °C; $^1$H NMR (400 MHz, $CDCl_3$): δ 11.00 (br., s, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.92-7.82 (m, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.54-7.47 (m, 2H), 7.45-7.37 (m, 2H), 7.27-7.22 (m, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.10 (dd, *J* = 7.2, 1.2 Hz, 1H), 6.97-6.89 (m, 1H), 2.35 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 201.3, 144.0, 140.2, 136.5, 136.2, 134.9, 134.7, 133.5, 131.5, 130.5, 129.8, 128.5, 127.4, 127.4, 126.6, 125.4, 125.2, 124.2, 123.2, 121.3, 21.6; HRMS (ESI) calcd for $C_{24}H_{18}NO_3S$ $(M-H)^-$ 400.1013, found 400.1038.



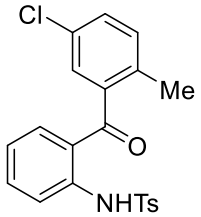

**1j**

*N*-(2-(3-Chloro-2-methylbenzoyl)phenyl)-4-methylbenzenesulfonamide **1j** was obtained as a yellow solid in 89% yield. $R_f$ = 0.40 (petroleum ether/ethyl acetate = 5:1); m.p. 105-106 °C; $^1$H NMR (400 MHz, $CDCl_3$): δ 11.09 (br., s, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.54-7.43 (m, 2H), 7.23 (d, *J* = 7.6 Hz, 3H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.02-6.94 (m, 1H), 6.84 (d, *J* = 7.6 Hz, 1H), 2.37 (s, 3H), 2.08 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 201.1, 144.0, 140.6, 136.5, 135.8, 135.4, 134.5, 133.6, 131.0, 129.7, 127.3, 126.5, 125.7, 123.3, 123.0, 120.4, 21.5, 17.0; HRMS (ESI) calcd for $C_{21}H_{17}ClNO_3S$ $(M-H)^-$ 398.0623, found 398.0646.



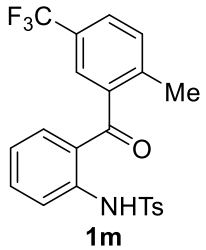
**1k**

*N*-(2-(2,4-Dimethylbenzoyl)phenyl)-4-methylbenzenesulfonamide **1k** was obtained as a white solid in 91% yield. $R_f$ = 0.40 (petroleum ether/ethyl acetate = 5:1); m.p. 103-104 °C; $^1$H NMR (400 MHz, $CDCl_3$): δ 10.92 (br., s, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.50-7.44 (m, 1H), 7.29-7.23 (m, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.06 (s, 1H), 7.01-6.93 (m, 2H), 6.75 (d, *J* = 8.0 Hz, 1H), 2.36 (s, 3H), 2.34 (s, 3H), 2.12 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 201.9, 143.9, 141.0, 140.0, 136.6, 136.4, 135.6, 134.5, 134.3, 131.8, 129.7, 128.7, 127.3, 125.8, 125.0, 123.0, 121.0, 21.5, 21.4, 19.7; HRMS (ESI) calcd for $C_{22}H_{20}NO_3S$ $(M-H)^-$ 378.1169, found 378.1187.



**1l**

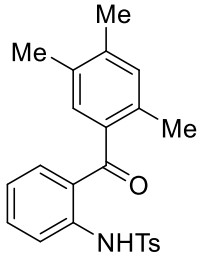
*N*-(2-(5-Chloro-2-methylbenzoyl)phenyl)-4-methylbenzenesulfonamide **1l** was obtained as a yellowish oil in 90% yield. $R_f$ = 0.40 (petroleum ether/ethyl acetate = 5:1); $^1$H NMR (400 MHz, $CDCl_3$): δ 10.82 (br., s, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.57-7.49 (m, 1H), 7.33 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.25-7.15 (m, 4H), 7.07-7.00 (m, 1H), 6.77 (d, *J* = 2.4 Hz, 1H), 2.37 (s, 3H), 2.10 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 200.4, 144.2, 140.2, 139.8, 136.2, 135.3, 134.6, 134.2, 132.4, 131.1, 130.4, 129.8, 127.6, 127.3, 124.1, 123.5, 121.4, 21.6, 19.0; HRMS (ESI) calcd for $C_{21}H_{17}ClNO_3S$ $(M-H)^-$ 398.0623, found 398.0636.



**1m**

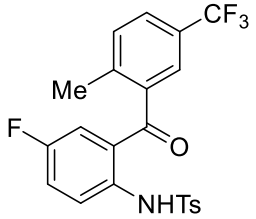
4-Methyl-*N*-(2-(2-methyl-5-(trifluoromethyl)benzoyl)phenyl)benzenesulfonamide **1m** was

obtained as a yellowish oil in 91% yield. $R_f$ = 0.40 (petroleum ether/ethyl acetate = 5:1); $^1$H NMR (400 MHz, $CDCl_3$): δ 10.92 (br., s, 1H), 7.83 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.62 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.57-7.51 (m, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.24-7.16 (m, 3H), 7.14 (s, 1H), 7.06-6.98 (m, 1H), 2.35 (s, 3H), 2.20 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 200.5, 144.2, 140.5, 140.3, 139.0, 136.3, 135.5, 134.2, 131.6, 129.7, 128.0 (q, *J* = 32.7 Hz), 127.3, 126.9 (q, *J* = 3.6 Hz), 124.4 (q, *J* = 3.8 Hz), 123.7 (q, *J* = 270.5 Hz), 123.6, 123.3, 121.1, 21.4, 19.6; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -62.46; HRMS (ESI) calcd for $C_{22}H_{17}F_3NO_3S$ $(M-H)^-$ 432.0887, found 432.0902.



**1n**

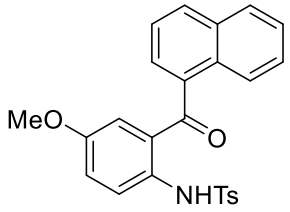
4-Methyl-*N*-(2-(2,4,5-trimethylbenzoyl)phenyl)benzenesulfonamide **1n** was obtained as a yellow solid in 90% yield. $R_f$ = 0.55 (petroleum ether/ethyl acetate = 5:1); m.p. 97-98 °C; $^1$H NMR (400 MHz, $CDCl_3$): δ 10.95 (br., s, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.51-7.44 (m, 1H), 7.31-7.26 (m, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.02-6.95 (m, 2H), 6.64 (s, 1H), 2.34 (s, 3H), 2.26 (s, 3H), 2.18 (s, 3H), 2.05 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 202.1, 143.8, 140.0, 139.6, 136.5, 136.0, 134.5, 134.4, 133.8, 133.4, 132.3, 129.6, 129.6, 127.3, 125.0, 123.1, 121.0, 21.5, 19.7, 19.2, 19.1; HRMS (ESI) calcd for $C_{23}H_{22}NO_3S$ $(M-H)^-$ 392.1326, found 392.1338.



**1o**

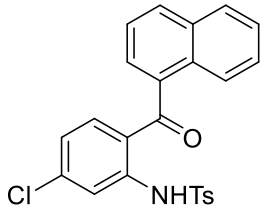
(2-Amino-5-fluorophenyl)(2-methyl-5-(trifluoromethyl)phenyl)methanone **1o** was obtained as a yellowish oil in 91% yield. $R_f$ = 0.20 (petroleum ether/ethyl acetate 8:1); $^1$H NMR (400 MHz, $CDCl_3$): δ 10.43 (br., s, 1H), 7.87 (dd, *J* = 9.2, 4.8 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 3H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.32-7.25 (m, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.02 (s, 1H), 6.83 (dd, *J* = 8.4, 2.8 Hz, 1H), 2.34 (s, 3H), 2.20 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 199.1 (d, $^4J_{C-F}$ = 2.1 Hz), 158.1 (d, $^1J_{C-F}$ = 245.1 Hz), 144.4, 140.6, 138.1, 136.3, 136.2, 135.9, 131.8, 129.8, 128.1 (q, *J* = 32.9 Hz), 127.4 (q, *J* = 3.5 Hz), 127.2, 125.7 (d, $^3J_{C-F}$ = 5.8 Hz), 124.6, 124.5,

124.4 (q, $J$ = 3.8 Hz), 123.6 (q, $J$ = 270.5 Hz), 122.6 (d, $^2J_{C\text{-}F}$ = 22.4 Hz), 119.6 (d, $^2J_{C\text{-}F}$ = 23.5 Hz), 21.4, 19.6; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -62.49, -116.35; HRMS (ESI) calcd for $C_{22}H_{16}F_4NO_3S$ $(M-H)^-$ 450.0793, found 450.0806.



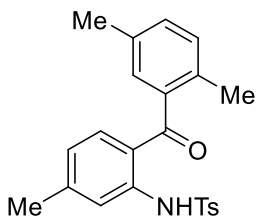

**1p**

*N*-(2-(1-Naphthoyl)-4-methoxyphenyl)-4-methylbenzenesulfonamide **1p** was obtained as a white solid in 93% yield. $R_f$ = 0.30 (petroleum ether/ethyl acetate 5:1); m.p. 104-105 °C; $^1$H NMR (400 MHz, $CDCl_3$): δ 10.13 (br., s, 1H), 7.97 (d, $J$ = 8.4 Hz, 1H), 7.89 (d, $J$ = 8.4 Hz, 1H), 7.83 (d, $J$ = 9.2 Hz, 1H), 7.70 (dd, $J$ = 8.4, 1.20 Hz, 1H), 7.59 (d, $J$ = 8.0 Hz, 2H), 7.55-7.49 (m, 1H), 7.47-7.39 (m, 1H), 7.38-7.32 (m, 1H), 7.13-7.07 (m, 3H), 6.88 (dd, $J$ = 7.2, 1.2 Hz, 1H), 6.69 (d, $J$ = 3.2 Hz, 1H), 3.56 (s, 3H), 2.31 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 200.3, 155.7, 143.7, 136.1, 135.5, 133.6, 132.4, 132.0, 130.6, 129.7, 128.6, 128.5, 128.2, 127.6, 127.4, 126.6, 125.4, 125.2, 123.9, 119.9, 118.9, 55.6, 21.5; HRMS (ESI) calcd for $C_{25}H_{22}NO_4S$ $(M+H)^+$ 432.1264, found 432.1272.



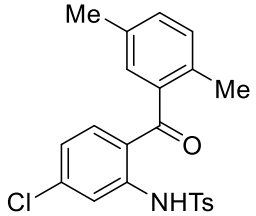

**1q**

*N*-(2-(1-Naphthoyl)-5-chlorophenyl)-4-methylbenzenesulfonamide **1q** was obtained as a yellow solid in 94% yield. $R_f$ = 0.40 (petroleum ether/ethyl acetate = 5:1); m.p. 109-110 °C; $^1$H NMR (400 MHz, $CDCl_3$): δ 11.15 (br., s, 1H), 7.99 (d, $J$ = 8.0 Hz, 1H), 7.90 (d, $J$ = 8.0 Hz, 1H), 7.87 (d, $J$ = 2.0 Hz, 1H), 7.79 (d, $J$ = 8.0 Hz, 2H), 7.59 (d, $J$ = 8.4 Hz, 1H), 7.55-7.50 (m, 1H), 7.47-7.39 (m, 2H), 7.27-7.22 (m, 2H), 7.21-7.15 (m, 2H), 6.88 (dd, $J$ = 8.4, 2.0 Hz, 1H), 2.39 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 200.5, 144.3, 141.5, 141.3, 136.3, 135.9, 135.8, 133.6, 131.7, 130.4, 129.9, 128.6, 127.5, 127.4, 127.2, 126.7, 125.0, 124.3, 123.2, 123.1, 120.6, 21.6; HRMS (ESI) calcd for $C_{24}H_{17}ClNO_3S$ $(M-H)^-$ 434.0623, found 434.0642.



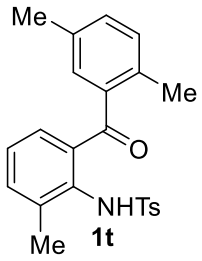

**1r**

*N*-(2-(2,5-Dimethylbenzoyl)-5-methylphenyl)-4-methylbenzenesulfonamide **1r** was obtained as a white solid in 90% yield. $R_f$ = 0.40 (petroleum ether/ethyl acetate = 5:1); m.p. 110-111 $^oC$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 10.18 (br., s, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.61 (s, 1H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.18-7.12 (m, 2H), 7.11-7.07 (m, 1H), 6.78 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.72 (d, *J* = 2.0 Hz, 1H), 2.37 (s, 3H), 2.36 (s, 3H), 2.28 (s, 3H), 2.02 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 202.1, 146.4, 143.8, 140.4, 138.8, 136.6, 134.8, 134.7, 132.5, 130.9, 130.7, 129.8, 129.6, 128.1, 127.9, 127.3, 124.0, 121.7, 121.0, 22.1, 21.5, 20.9, 19.0; HRMS (ESI) calcd for $C_{23}H_{22}NO_3S$ $(M-H)^-$ 392.1326, found 392.1323.



**1s**

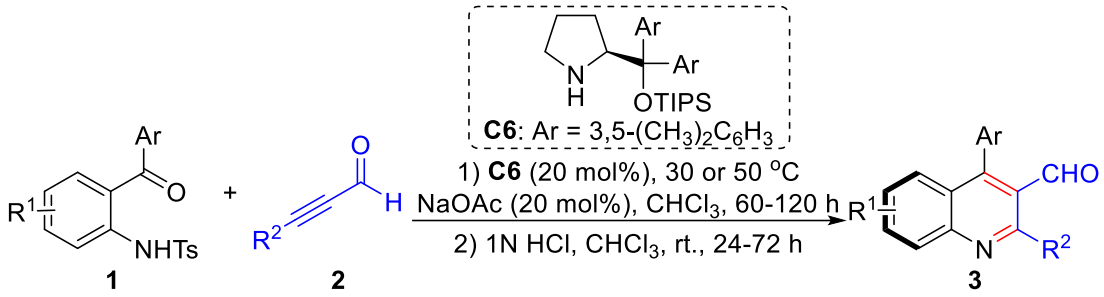
*N*-(5-Chloro-2-(2,5-dimethylbenzoyl)phenyl)-4-methylbenzenesulfonamide **1s** was obtained as a yellow solid in 89% yield. $R_f$ = 0.40 (petroleum ether/ethyl acetate = 5:1); m.p. 108-109 $^oC$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 11.20 (br., s, 1H), 7.82 (d, *J* = 2.0 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.27-7.22 (m, 3H), 7.21-7.16 (m, 1H), 7.15-7.09 (m, 1H), 6.93 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.74 (s, 1H), 2.38 (s, 3H), 2.29 (s, 3H), 2.05 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 201.6, 144.3, 141.5, 141.2, 138.1, 136.3, 135.6, 135.1, 132.8, 131.4, 130.9, 129.8, 128.2, 127.3, 123.1, 122.1, 120.1, 21.6, 20.9, 19.0; HRMS (ESI) calcd for $C_{22}H_{19}ClNO_3S$ $(M-H)^-$ 412.0780, found 412.0795.



**1t**

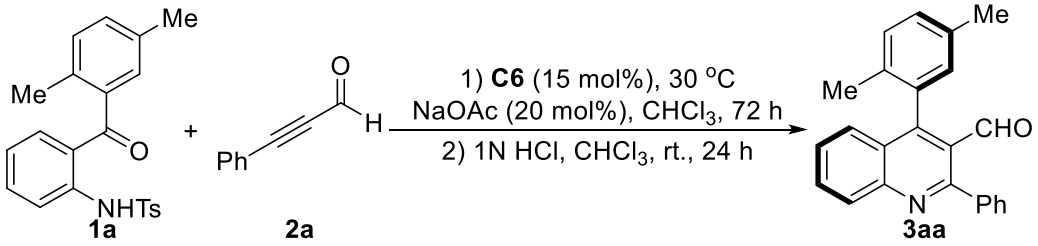
*N*-(2-(2,5-Dimethylbenzoyl)-6-methylphenyl)-4-methylbenzenesulfonamide **1t** was obtained as a colorless oil in 82% yield. $R_f$ = 0.60 (petroleum ether/ethyl acetate = 5:1); $^1H$ NMR (400 MHz, $CDCl_3$): δ 9.25 (br., s, 1H), 7.54-7.41 (m, 3H), 7.16-7.05 (m, 3H), 7.04-6.94 (m, 3H), 6.22 (s, 1H), 2.66 (s, 3H), 2.23 (s, 6H), 2.17 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 200.1, 143.4, 139.9, 136.4, 136.3, 135.9, 135.7, 135.4, 133.7, 133.1, 131.8, 131.2, 130.8, 130.8, 129.3, 128.0, 125.9, 21.4, 20.9, 19.9, 19.8; HRMS (ESI) calcd for $C_{23}H_{24}NO_3S$ $(M+H)^+$ 394.1471, found 394.1484.

## General Procedure for the Atroposelective Aza-Michael-aldol-aromatization Sequence




To a flame dried sealed tube equipped with a magnetic stirring bar were added 2-(tosylamino)aryl ketones **1** (0.10 mmol), catalyst **C6** (9.3 mg, 0.020 mmol), NaOAc (1.6 mg, 0.020 mmol), 2-alkynals **2** (0.12 mmol) and anhydrous chloroform (1.0 mL) successively. The mixture was stirred at 30 °C or 50 °C for 60-120 h. After full conversion of the first step as detected by TLC, chloroform (1.0 mL) and 1N HCl (1.5 mL) were added to the reaction mixture for the second step, and the resulting solution was stirred at room temperature for another 24-72 h. Then the reaction was diluted with ethyl acetate (10 mL) and neutralized with saturated $NaHCO_3$ solution (10 mL). The organic layer is separated, and the aqueous layer is extracted with ethyl acetate (2 × 10 mL). The combined organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, filtered and concentrated in vacuo to give a crude residue which was purified by flash column chromatography (petroleum ether/ethyl acetate = 30:1 to 5:1) to give **3**.

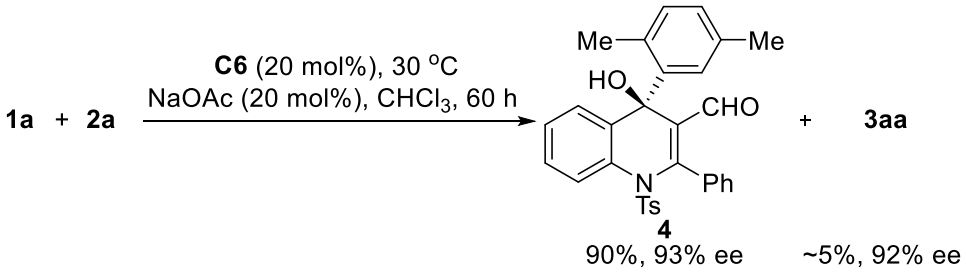
## Procedure for the Scale-up Experiment



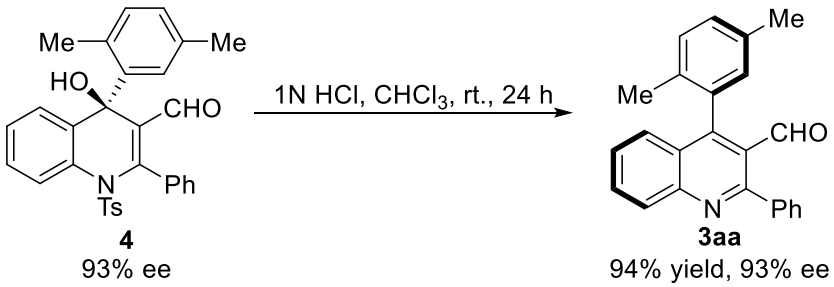

To a flame dried sealed tube (120 mL) equipped with a magnetic stirring bar were added *N*-(2-(2,5-dimethylbenzoyl)phenyl)-4-methylbenzenesulfonamide **1a** (379.1 mg, 1.0 mmol), catalyst **C6** (69.8 mg, 0.15 mmol), NaOAc (16.4 mg, 0.20 mmol), 3-phenylpropiolaldehyde **2a** (156.1 mg, 1.20 mmol) and anhydrous chloroform (10.0 mL) successively. The mixture was stirred at 30 °C for 72 h. After full conversion of the first step as detected by TLC, 1N HCl (15.0 mL) were added to the reaction mixture for the second step, and the resulting solution was stirred at room temperature for another 24 h. Then the reaction was diluted with ethyl acetate (30 mL) and neutralized with saturated $NaHCO_3$ solution (20 mL). The organic layer is separated, and the aqueous layer is extracted with ethyl acetate (2 × 30 mL). The

combined organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, filtered and concentrated in vacuo to give a crude residue which was purified by flash column chromatography (petroleum ether/ethyl acetate = 20:1 to 5:1) to give **3aa** as a yellow oil in 92% yield (311.4 mg) and 93% ee.

## Procedure for the Stepwise Synthesis

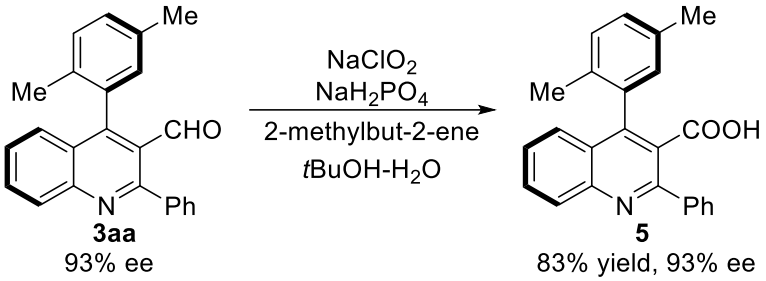



To a flame dried sealed tube equipped with a magnetic stirring bar were added **1a** (75.8 mg, 0.20 mmol), catalyst **C6** (18.6 mg, 0.040 mmol), NaOAc (3.3 mg, 0.040 mmol), **2a** (31.2 mg, 0.24 mmol) and anhydrous chloroform (2.0 mL) successively. The mixture was stirred at 30 °C for 60 h. Solvent was evaporated, the crude mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 70:30) to give **4** in 90% yield (91.6 mg) and 93% ee along with **3aa** (3.4 mg, 5% yield, 92% ee).

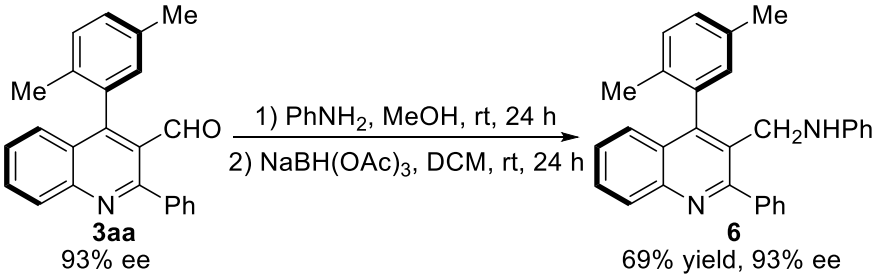



To a stirred solution of aldehyde **4** (50.9 mg, 0.10 mmol) in $CHCl_3$ (1.0 mL), 1N HCl (1.5 mL) were added, and the resulting solution was stirred at room temperature for 24 h. Then the reaction was diluted with ethyl acetate (10 mL) and neutralized with saturated $NaHCO_3$ solution (10 mL). The organic layer is separated, and the aqueous layer is extracted with ethyl acetate (2 × 10 mL). The combined organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, filtered and concentrated in vacuo to give a crude residue which was purified by flash column chromatography (petroleum ether/ethyl acetate = 20:1 to 5:1) to give **3aa** in 94% yield (31.7 mg) and 93% ee.

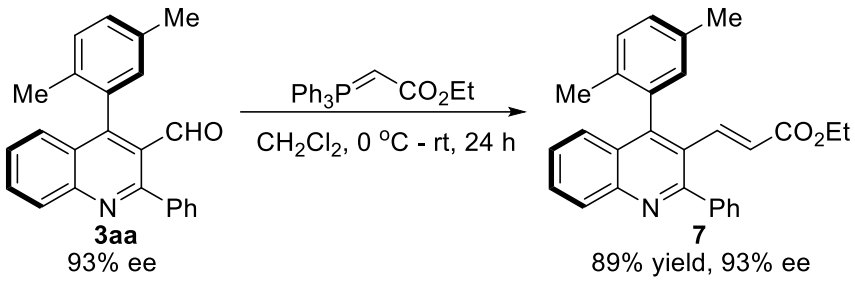
## Procedure for the Transformations of Products 3



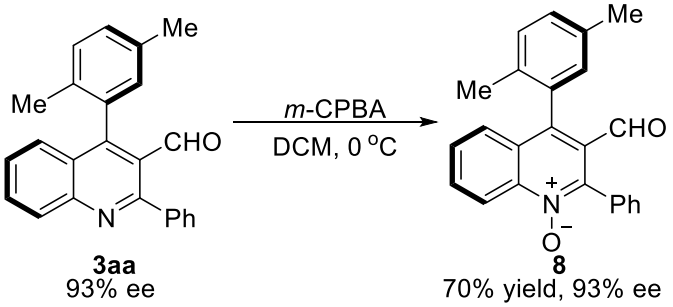

To a suspension of compound **3aa** (33.7 mg, 0.10 mmol) and 2-methylbut-2-ene (911.7 mg, 1.3 mmol) in *t*BuOH (3.0 mL) were added a saturated solution of $NaClO_2$ (33.5 mg, 0.37 mmol) and $NaH_2PO_4$ (56.0 mg, 0.50 mmol). The mixture was stirred at room temperature for 3 h. The mixture was quenched with saturated $NH_4Cl$ (10 mL) and extracted with EtOAc (4 × 10 mL). The combined organic layers were washed with brine, dried over anhydrous $Na_2SO_4$, filtered and concentrated in vacuo to give a crude residue which was purified by flash column chromatography (petroleum ether/ethyl acetate = 70:30) to give **5** as a yellow solid in 83% yield (29.3 mg) and 93% ee.[3]



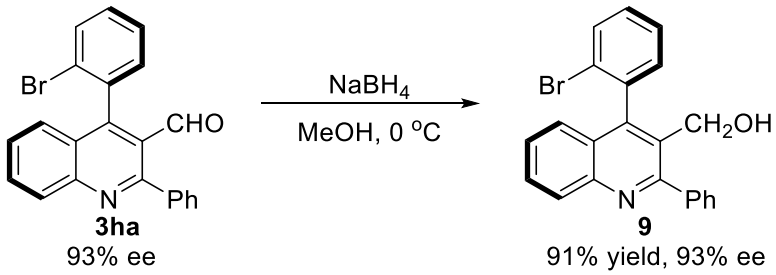

To a suspension of (*S*)-**3aa** (33.7 mg, 0.10 mmol) in methanol (3.0 mL) were added aniline (10.0 uL, 0.11 mmol) and 4-toluenesulfonic acid monohydrate (3.8 mg, 0.020 mmol). After stirring at room temperature for 24 h, the mixture was concentrated in vacuo. Then, DCM (2.0 mL), $NaBH(OAc)_3$ (63.6 mg, 0.30 mmol) and $CH_3COOH$ (17.0 uL, 0.30 mmol) were added successively. The mixture was stirred at room temperature for another 24 h, quenched with sat. $NaHCO_3$ (10 mL) and extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with brine, dried over anhydrous $Na_2SO_4$, filtered and concentrated in vacuo to give a crude residue which was purified by flash column chromatography (petroleum ether/ethyl acetate = 90:10) to give **6** as a yellow solid in 69% yield (28.6 mg) and 93% ee.




To a stirred solution of aldehyde (*S*)-**3aa** (33.7 mg, 0.10 mmol) in $CH_2Cl_2$ (2.0 mL) was added ethyl 2-(triphenylphosphoranylidene)acetate (41.8 mg, 0.12 mmol) at 0 °C. The resultant mixture was allowed to warm to rt and stirred for 24 h. The crude mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 90:10) to give **7** as a yellow oil in 89% yield (36.2 mg) and 93% ee.[4]



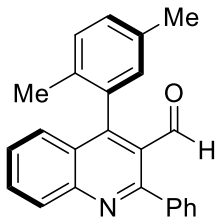

*m*-CPBA (40.6 mg, 85%, 0.20 mmol) was added to a solution of (*S*)-**3aa** (33.7 mg, 0.10 mmol) in $CH_2Cl_2$ (2.0 mL) at 0 °C. After stirring for 24 h, the reaction mixture was quenched with sat. $Na_2SO_3$ (5 mL) and stirred at this temperature for 10 minutes. Then, saturated aqueous $NaHCO_3$ solution (5 mL) was added. After being extracted with $CH_2Cl_2$ (3 × 10 mL), the organic phases were combined and washed with brine, dried over anhydrous $Na_2SO_4$, filtered and concentrated in vacuo to give a crude residue which was purified by flash column chromatography (petroleum ether/ethylacetate = 70:30) to give **8** as a yellowish oil in 70% yield (24.7 mg) and 93% ee.[2]




To a suspension of (*S*)-**3ha** (38.7 mg, 0.10 mmol) in methanol (3.0 mL) was added $NaBH_4$ (7.6 mg, 0.20 mmol) at 0 °C, After stirring at this temperature for 20 minutes, the mixture was

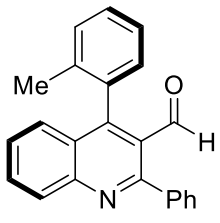
quenched with sat. $NH_4Cl$ (10 mL) at 0 °C and extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with brine, dried over anhydrous $Na_2SO_4$, filtered and concentrated in vacuo to give a crude residue which was purified by flash column chromatography (petroleum ether/ethyl acetate = 70:30) to give **9** as a white solid in 91% yield (35.4 mg) and 93% ee.[2]

## Analytic Data for the Products




**3aa**

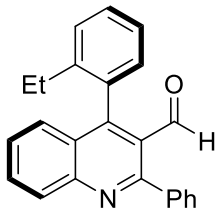
4-(2,5-Dimethylphenyl)-2-phenylquinoline-3-carbaldehyde **3aa** was obtained as a yellowish oil in 96% yield (32.3 mg) and 94% ee (step 1, 30 °C, 60 h; step 2, rt, 24 h). $R_f$ = 0.40 (petroleum ether/ethyl acetate 10:1). The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane (10:90), 1.0 mL/min, λ = 254 nm, $t_r$ (major) = 6.98 min, $t_r$ (minor) = 7.56 min]. $[\alpha]_D^{25}$ = −9.00 (c = 1.0, EtOAc); $^1$H NMR (400 MHz, $CDCl_3$): δ 10.02 (s, 1H), 8.24 (d, *J* = 8.4 Hz, 1H), 7.84-7.77 (m, 1H), 7.69-7.63 (m, 2H), 7.53-7.43 (m, 5H), 7.28-7.20 (m, 2H), 6.98 (s, 1H), 2.36 (s, 3H), 1.97 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 192.3, 159.2, 152.4, 148.7, 139.6, 135.3, 134.3, 133.2, 132.1, 130.0, 129.9, 129.8, 129.7, 129.6, 129.0, 128.5, 127.5, 127.2, 126.5, 126.2, 21.1, 19.5; HRMS (ESI) calcd for $C_{24}H_{20}NO$ $(M+H)^+$ 338.1539, found 338.1541.




**3ba**

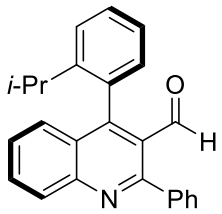
2-Phenyl-4-*o*-tolylquinoline-3-carbaldehyde **3ba** was obtained as a yellow solid in 95% yield (30.7 mg) and 93% ee (step 1, 30 °C, 60 h; step 2, rt, 24 h). $R_f$ = 0.40 (petroleum ether/ethyl acetate 10:1). The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak AD-H, isopropanol/hexane (10:90), 1.0 mL/min, λ = 254 nm, $t_r$ (minor) = 7.42 min, $t_r$ (major) = 9.68 min]. m.p. 111-112 °C; $[\alpha]_D^{25}$ = −6.34 (c = 1.0, EtOAc); $^1$H NMR (400 MHz, $CDCl_3$): δ 10.01 (s, 1H), 8.26 (d, *J* = 8.4 Hz, 1H), 7.88-7.78 (m, 1H), 7.72-7.61 (m, 2H), 7.57-7.46 (m, 4H), 7.46-7.30 (m, 4H), 7.16 (d, *J* = 7.6 Hz, 1H), 2.02 (s, 3H); $^{13}$C NMR (100

MHz, $CDCl_3$): δ 192.2, 159.4, 151.9, 148.7, 139.4, 136.2, 134.6, 132.1, 130.1, 129.9, 129.1, 129.0, 128.8, 128.6, 127.5, 127.1, 126.4, 126.2, 125.8, 20.0; HRMS (ESI) calcd for $C_{23}H_{18}NO$ $(M+H)^+$ 324.1383, found 324.1389.




**3ca**

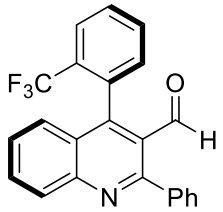
4-(2-Ethylphenyl)-2-phenylquinoline-3-carbaldehyde **3ca** was obtained as a yellowish oil in 86% yield (29.0 mg) and 97% ee (step 1, 30 °C, 72 h; step 2, rt, 24 h). $R_f$ = 0.50 (petroleum ether/ethyl acetate 10:1). The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak AD-H, isopropanol/hexane (10:90), 1.0 mL/min, λ = 254 nm, $t_r$ (minor) = 6.30 min, $t_r$ (major) = 8.28 min]. $[\alpha]_D^{25}$ = −17.85 (c = 1.0, EtOAc); $^1$H NMR (400 MHz, $CDCl_3$): δ 10.01 (s, 1H), 8.25 (d, *J* = 8.8 Hz, 1H), 7.87-7.79 (m, 1H), 7.66 (d, *J* = 6.4 Hz, 2H), 7.57-7.40 (m, 7H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.14 (d, *J* = 7.2 Hz, 1H), 2.39-2.25 (m, 2H), 1.02 (t, *J* = 7.6 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 192.2, 159.3, 152.1 148.5, 142.1, 139.4, 133.9, 132.1, 129.8, 129.8, 129.2, 129.1, 129.0, 128.5, 128.3, 127.4, 127.3, 126.6, 125.8, 26.4, 14.7; HRMS (ESI) calcd for $C_{24}H_{20}NO$ $(M+H)^+$ 338.1539, found 338.1545.




**3da**

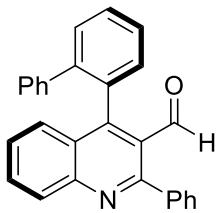
4-(2-Isopropylphenyl)-2-phenylquinoline-3-carbaldehyde **3da** was obtained as a yellowish oil in 81% yield (28.4 mg) and 99% ee (step 1, 30 °C, 72 h; step 2, rt, 24 h). $R_f$ = 0.50 (petroleum ether/ethyl acetate 10:1). The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak AD-H, isopropanol/hexane (10:90), 1.0 mL/min, λ = 254 nm, $t_r$ (minor) = 4.87 min, $t_r$ (major) = 7.65 min]. $[\alpha]_D^{25}$ = −20.63 (c = 1.0, EtOAc); $^1$H NMR (400 MHz, $CDCl_3$): δ 10.02 (s, 1H), 8.27 (d, *J* = 8.8 Hz, 1H), 7.88-7.79 (m, 1H), 7.70-7.62 (m, 2H), 7.58-7.41 (m, 7H), 7.36-7.29 (m, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 2.53-2.39 (m, 1H), 1.13 (d, *J* = 7.2 Hz, 3H), 1.04 (d, *J* = 6.8 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 192.1, 159.2, 152.3, 148.3, 147.0, 139.3, 133.1, 132.1, 129.8, 129.7, 129.2, 129.1, 129.0, 128.5, 127.4, 127.3,

126.8, 126.7, 125.8, 125.7, 31.0, 24.1, 23.7; HRMS (ESI) calcd for $C_{25}H_{22}NO$ $(M+H)^+$ 352.1696, found 352.1704.




**3ea**

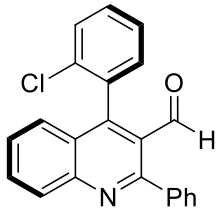
2-Phenyl-4-(2-(trifluoromethyl)phenyl)quinoline-3-carbaldehyde **3ea** was obtained as a yellowish oil in 85% yield (32.2 mg) and 98% ee (step 1, 30 °C, 60 h; step 2, rt, 48 h). $R_f$ = 0.50 (petroleum ether/ethyl acetate 10:1). The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak AD-H, isopropanol/hexane (10:90), 1.0 mL/min, λ = 254 nm, $t_r$ (major) = 8.44 min, $t_r$ (minor) = 9.07 min]. $[\alpha]_D^{25}$ = −5.14 (c = 1.0, EtOAc); $^1$H NMR (400 MHz, $CDCl_3$): δ 9.98 (s, 1H), 8.29 (d, *J* = 8.8 Hz, 1H), 7.91-7.81 (m, 2H), 7.74-7.63 (m, 4H), 7.59-7.47 (m, 4H), 7.35-7.29 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 191.5, 159.7, 148.3, 148.1, 138.4, 134.4 (q, *J* = 2.0 Hz), 132.2, 131.6, 130.8, 130.2, 130.1, 129.6, 129.4, 128.8 (q, *J* = 30.4 Hz), 128.7, 128.6, 127.5, 127.4, 127.0, 126.6, 126.4 (q, *J* = 4.9 Hz), 125.9, 123.7 (q, *J* = 272.3 Hz); $^{19}$F NMR (376 MHz, $CDCl_3$) δ -59.64; HRMS (ESI) calcd for $C_{23}H_{15}F_3NO$ $(M+H)^+$ 378.1100, found 378.1108.




**3fa**

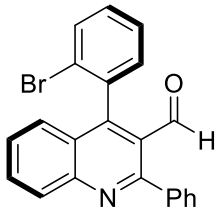
4-(Biphenyl-2-yl)-2-phenylquinoline-3-carbaldehyde **3fa** was obtained as a white solid in 64% yield (24.7 mg) and 98% ee (step 1, 50 °C, 120 h; step 2, rt, 24 h). $R_f$ = 0.30 (petroleum ether/ethyl acetate 10:1). The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak AD-H, isopropanol/hexane (10:90), 1.0 mL/min, λ = 254 nm, $t_r$ (minor) = 7.90 min, $t_r$ (major) = 10.01 min]. m.p. 106-107 °C; $[\alpha]_D^{25}$ = −7.67 (c = 1.0, EtOAc); $^1$H NMR (400 MHz, $CDCl_3$): δ 9.77 (s, 1H), 8.17 (d, *J* = 8.4 Hz, 1H), 7.83-7.76 (m, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.63-7.57 (m, 1H), 7.56-7.48 (m, 3H), 7.47-7.37 (m, 5H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.10-6.95 (m, 5H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 192.0, 159.3, 151.4, 148.5, 142.0, 140.4, 139.2, 133.7, 131.9, 130.2, 130.1, 129.8, 129.7, 129.1, 129.0, 128.9, 128.5, 127.9, 127.5, 127.4, 127.3, 127.1, 126.8, 126.5; HRMS (ESI) calcd for $C_{28}H_{20}NO$ $(M+H)^+$ 386.1539,

found 386.1543.



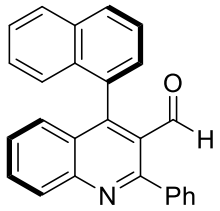

**3ga**

4-(2-Chlorophenyl)-2-phenylquinoline-3-carbaldehyde **3ga** was obtained as a yellow solid in 93% yield (32.0 mg) and 90% ee (step 1, 30 °C, 72 h; step 2, rt, 48 h). $R_f$ = 0.40 (petroleum ether/ethyl acetate 10:1). The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak AD-H, isopropanol/hexane (10:90), 1.0 mL/min, λ = 254 nm, $t_r$ (minor) = 9.55 min, $t_r$ (major) = 10.26 min]. m.p. 116-117 °C; $[\alpha]_D^{25}$ = +52.15 (c = 1.2, EtOAc); $^1$H NMR (400 MHz, $CDCl_3$): δ 10.02 (s, 1H), 8.28 (d, *J* = 8.4 Hz, 1H), 7.88-7.82 (m, 1H), 7.73-7.67 (m, 2H), 7.61-7.48 (m, 6H), 7.48-7.42 (m, 2H), 7.33-7.27 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 191.5, 159.6, 148.8, 148.1, 138.8, 134.5, 132.8, 132.1, 130.8, 130.0, 130.0, 129.9, 129.7, 129.3, 128.7, 127.6, 126.9, 126.7, 126.2, 125.9; HRMS (ESI) calcd for $C_{22}H_{15}ClNO$ $(M+H)^+$ 344.0837, found 344.0842.



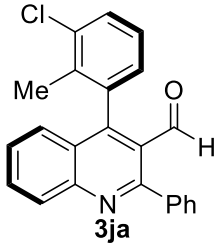

**3ha**

4-(2-Bromophenyl)-2-phenylquinoline-3-carbaldehyde **3ha** was obtained as a yellowish oil in 94% yield (36.4 mg) and 93% ee (step 1, 30 °C, 72 h; step 2, rt, 24 h). $R_f$ = 0.30 (petroleum ether/ethyl acetate 10:1). The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak AD-H, isopropanol/hexane (05:95), 1.0 mL/min, λ = 254 nm, $t_r$ (minor) = 14.34 min, $t_r$ (major) = 15.28 min]. $[\alpha]_D^{25}$ = +42.08 (c = 1.2, EtOAc); $^1$H NMR (400 MHz, $CDCl_3$): δ 10.03 (s, 1H), 8.27 (d, *J* = 8.0 Hz, 1H), 7.88-7.81 (m, 1H), 7.76 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.72-7.67 (m, 2H), 7.58-7.47 (m, 5H), 7.45-7.37 (m, 2H), 7.30 (dd, *J* = 7.6, 1.6 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 191.5, 159.6, 149.7, 148.9, 138.9, 136.6, 132.9, 132.2, 130.8, 130.1, 130.1, 129.9, 129.3, 128.7, 127.7, 127.4, 126.9, 126.0, 125.8, 122.7; HRMS (ESI) calcd for $C_{22}H_{15}BrNO$ $(M+H)^+$ 388.0332, found 388.0341.



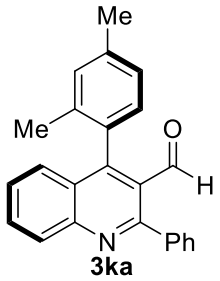

**3ia**

4-(Naphthalen-1-yl)-2-phenylquinoline-3-carbaldehyde **3ia** was obtained as a yellow solid in 92% yield (33.0 mg) and 92% ee (step 1, 30 °C, 60 h; step 2, rt, 24 h). $R_f$ = 0.40 (petroleum ether/ethyl acetate 10:1). The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak AD-H, isopropanol/hexane (20:80), 1.0 mL/min, λ = 254 nm, $t_r$ (major) = 6.88 min, $t_r$ (minor) = 8.25 min]. m.p. 84-85 °C; $[\alpha]_D^{25}$ = +44.75 (c = 1.2, EtOAc); $^1$H NMR (400 MHz, $CDCl_3$): δ 9.92 (s, 1H), 8.29 (d, *J* = 8.4 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.85-7.77 (m, 1H), 7.73-7.67 (m, 2H), 7.66-7.58 (m, 1H), 7.56-7.47 (m, 4H), 7.44 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.40-7.30 (m, 3H), 7.26-7.21 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 192.0, 159.2, 151.0, 148.5, 139.4, 133.3, 132.4, 132.1, 132.1, 129.8, 129.8, 129.1, 129.0, 128.5, 128.5, 127.7, 127.4, 127.4, 127.4, 126.9, 126.9, 126.4, 125.5, 125.1; HRMS (ESI) calcd for $C_{26}H_{18}NO$ $(M+H)^+$ 360.1383, found 360.1389.



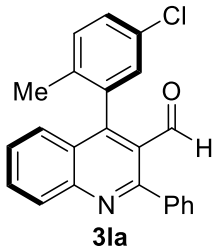

**3ja**

4-(3-Chloro-2-methylphenyl)-2-phenylquinoline-3-carbaldehyde **3ja** was obtained as a yellow solid in 89% yield (31.8 mg) and 93% ee (step 1, 30 °C, 60 h; step 2, rt, 24 h). $R_f$ = 0.40 (petroleum ether/ethyl acetate 10:1). The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane (10:90), 1.0 mL/min, λ = 254 nm, $t_r$ (major) = 6.41 min, $t_r$ (minor) = 6.86 min]. m.p. 118-119 °C; $[\alpha]_D^{25}$ = −7.13 (c = 1.0, EtOAc); $^1$H NMR (400 MHz, $CDCl_3$): δ 10.01 (s, 1H), 8.26 (d, *J* = 8.4 Hz, 1H), 7.90-7.81 (m, 1H), 7.73-7.63 (m, 2H), 7.58-7.47 (m, 5H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.26 (d, *J* = 7.2 Hz, 1H), 7.05 (d, *J* = 7.6 Hz, 1H), 2.05 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 191.8, 159.6, 150.4, 148.7, 139.0, 136.8, 135.3, 134.6, 132.2, 130.0, 129.9, 129.6, 129.3, 128.7, 127.7, 127.5, 127.0, 126.7, 126.2, 126.0, 17.6; HRMS (ESI) calcd for $C_{23}H_{17}ClNO$ $(M+H)^+$ 358.0993, found 358.0996.



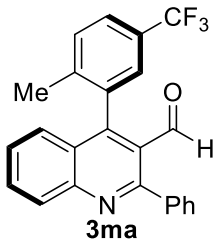
**3ka**

4-(2,4-Dimethylphenyl)-2-phenylquinoline-3-carbaldehyde **3ka** was obtained as a yellowish oil in 91% yield (30.7 mg) and 92% ee (step 1, 30 °C, 72 h; step 2, rt, 24 h). $R_f$ = 0.40 (petroleum ether/ethyl acetate 10:1). The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane (10:90), 1.0 mL/min, λ = 254 nm, $t_r$ (major) = 7.17 min, $t_r$ (minor) = 7.81 min]. $[\alpha]_D^{25}$ = −8.33 (c = 1.0, EtOAc); $^1$H NMR (400 MHz, $CDCl_3$): δ 10.01 (s, 1H), 8.27 (d, *J* = 8.4 Hz, 1H), 7.87-7.80 (m, 1H), 7.70-7.63 (m, 2H), 7.57-7.43 (m, 5H), 7.21 (s, 1H), 7.16 (d, *J* = 8.4 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 2.45 (s, 3H), 1.98 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 192.3, 159.2, 152.4, 148.4, 139.3, 138.6, 136.0, 132.1, 131.4, 130.9, 129.8, 129.7, 129.1, 129.0, 128.5, 127.4, 127.1, 126.6, 126.5, 126.4, 21.3, 19.9; HRMS (ESI) calcd for $C_{24}H_{20}NO$ $(M+H)^+$ 338.1539, found 338.1545.



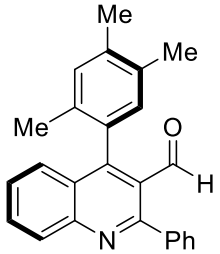
**3la**

4-(5-Chloro-2-methylphenyl)-2-phenylquinoline-3-carbaldehyde **3la** was obtained (step 1, 30 °C, 60 h; step 2, rt, 48 h) as a yellow solid in 90% yield (30.7 mg) and 91% ee. $R_f$ = 0.40 (petroleum ether/ethyl acetate 10:1). The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane (10:90), 1.0 mL/min, λ = 254 nm, $t_r$ (major) = 6.58 min, $t_r$ (minor) = 6.94 min]. m.p. 99-100 °C; $[\alpha]_D^{25}$ = −9.40 (c = 1.0, EtOAc); $^1$H NMR (400 MHz, $CDCl_3$): δ 10.02 (s, 1H), 8.28 (d, *J* = 8.8 Hz, 1H), 7.90-7.81 (m, 1H), 7.72-7.63 (m, 2H), 7.58-7.48 (m, 4H), 7.45-7.37 (m, 2H), 7.32 (d, *J* = 8.4 Hz, 1H), 7.14 (d, *J* = 2.0 Hz, 1H), 1.98 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 191.8, 159.6, 149.7, 148.7, 138.8, 136.7, 135.0, 132.3, 131.6, 131.4, 130.0, 129.9, 129.4, 128.7, 128.7, 128.6, 127.8, 126.9, 126.2, 125.9, 19.4; HRMS (ESI) calcd for $C_{23}H_{17}ClNO$ $(M+H)^+$ 358.0993, found 358.0999.



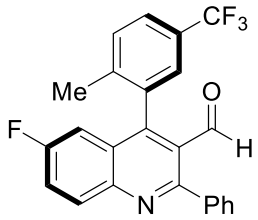

**3ma**

4-(2-Methyl-5-(trifluoromethyl)phenyl)-2-phenylquinoline-3-carbaldehyde **3ma** was obtained as a white solid in 92% yield (36.0 mg) and 93% ee (step 1, 30 °C, 60 h; step 2, rt, 72 h). $R_f$ = 0.50 (petroleum ether/ethyl acetate 10:1). The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak AD-H, isopropanol/hexane (08:92), 1.0 mL/min, λ = 254 nm, $t_r$ (minor) = 5.34 min, $t_r$ (major) = 5.76 min]. m.p. 123-124 °C; $[\alpha]_D^{25}$ = −8.50 (c = 1.0, EtOAc); $^1$H NMR (400 MHz, $CDCl_3$): δ 10.01 (s, 1H), 8.29 (d, *J* = 8.4 Hz, 1H), 7.90-7.83 (m, 1H), 7.74-7.65 (m, 3H), 7.60-7.47 (m, 5H), 7.39 (s, 1H), 7.35 (d, *J* = 8.8 Hz, 1H), 2.08 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 191.7, 159.8, 149.2, 148.8, 140.8, 138.7, 136.0, 132.3, 130.4, 130.1, 130.0, 129.4, 128.7, 128.4 (q, *J* = 32.5 Hz), 127.9, 126.7, 126.2, 125.9, 125.4 (q, *J* = 3.7 Hz), 124.1 (q, *J* = 270.4 Hz), 20.0; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -62.13; HRMS (ESI) calcd for $C_{24}H_{17}F_3NO$ $(M+H)^+$ 392.1257, found 392.1263.



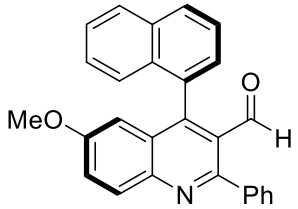

**3na**

2-Phenyl-4-(2,4,5-trimethylphenyl)quinoline-3-carbaldehyde **3na** was obtained as a yellowish oil in 91% yield (32.0 mg) and 93% ee (step 1, 30 °C, 72 h; step 2, rt, 24 h). $R_f$ = 0.40 (petroleum ether/ethyl acetate 10:1). The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane (10:90), 1.0 mL/min, λ = 254 nm, $t_r$ (major) = 6.90 min, $t_r$ (minor) = 7.64 min]. $[\alpha]_D^{25}$ = −61.35 (c = 1.0, EtOAc); $^1$H NMR (400 MHz, $CDCl_3$): δ 10.01 (s, 1H), 8.25 (d, *J* = 8.4 Hz, 1H), 7.86-7.79 (m, 1H), 7.69-7.61 (m, 2H), 7.55-7.44 (m, 5H), 7.15 (s, 1H), 6.93 (s, 1H), 2.35 (s, 3H), 2.27 (s, 3H), 1.95 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 192.4, 159.1, 152.7, 148.5, 139.5, 137.2, 133.9, 133.4, 132.0, 131.5, 131.4, 130.3, 129.7, 128.9, 128.4, 127.3, 127.2, 126.6, 126.4, 19.6, 19.4, 19.3; HRMS (ESI) calcd for $C_{25}H_{22}NO$ $(M+H)^+$ 352.1696, found 352.1698.




**3oa**

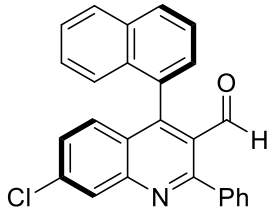
6-Fluoro-4-(2-methyl-5-(trifluoromethyl)phenyl)-2-phenylquinoline-3-carbaldehyde **3oa** was obtained as a white solid in 80% yield (32.7 mg) and 91% ee (step 1, 30 °C, 72 h; step 2, rt, 72 h). $R_f$ = 0.50 (petroleum ether/ethyl acetate 10:1). The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane (05:95), 1.0 mL/min, λ = 254 nm, $t_r$ (major) = 4.94 min, $t_r$ (minor) = 5.17 min]. m.p. 131-132 °C; $[\alpha]_D^{25}$ = −11.13 (c = 1.0, EtOAc); $^1$H NMR (400 MHz, $CDCl_3$): δ 10.01 (s, 1H), 8.30 (dd, *J* = 9.2, 5.2 Hz, 1H), 7.74-7.67 (m, 3H), 7.66-7.60 (m, 1H), 7.59-7.47 (m, 4H), 7.37 (s, 1H), 6.93 (dd, *J* = 9.6, 2.8 Hz, 1H), 2.09 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 191.5, 161.2 (d, $^1J_{C\text{-}F}$ = 249.2 Hz), 159.1 (d, $^4J_{C\text{-}F}$ = 2.7 Hz), 148.4 (d, $^3J_{C\text{-}F}$ = 5.9 Hz), 145.9, 140.7, 138.3, 135.5, 132.6 (d, $^3J_{C\text{-}F}$ = 9.1 Hz), 130.6, 130.1, 129.8, 129.6, 128.8, 128.6 (q, *J* = 32.6 Hz), 127.9, 126.9 (d, $^3J_{C\text{-}F}$ = 9.4 Hz), 126.8, 125.7 (q, *J* = 3.6 Hz), 125.3 (q, *J* = 3.6 Hz), 124.0 (q, *J* = 270.5 Hz), 122.6 (d, $^2J_{C\text{-}F}$ = 25.9 Hz), 109.9 (d, $^2J_{C\text{-}F}$ = 23.0 Hz), 20.0; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -62.18. -109.35; HRMS (ESI) calcd for $C_{24}H_{16}F_4NO$ $(M+H)^+$ 410.1163, found 410.1173.




**3pa**

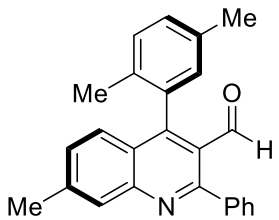
6-Methoxy-4-(naphthalen-1-yl)-2-phenylquinoline-3-carbaldehyde **3pa** was obtained as a yellow solid in 86% yield (33.3 mg) and 89% ee (step 1, 30 °C, 72 h; step 2, rt, 24 h). $R_f$ = 0.30 (petroleum ether/ethyl acetate 10:1). The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak AD-H, isopropanol/hexane (20:80), 1.0 mL/min, λ = 254 nm, $t_r$ (major) = 7.68 min, $t_r$ (minor) = 9.19 min]. m.p. 113-114 °C; $[\alpha]_D^{25}$ = −19.00 (c = 1.0, EtOAc); $^1$H NMR (400 MHz, $CDCl_3$): δ 9.90 (s, 1H), 8.20 (d, *J* = 9.2 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.71-7.60 (m, 3H), 7.52-7.41 (m, 6H), 7.39-7.31 (m, 1H), 7.30-7.22 (m, 1H), 6.54 (d, *J* = 2.8 Hz, 1H), 3.50 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 192.3, 158.4, 156.8, 149.1, 144.8, 139.4, 133.3, 132.7, 131.9, 131.2, 129.8, 129.1, 128.8, 128.5, 128.4, 128.0, 127.6, 127.6, 126.9, 126.3, 125.4, 125.2, 124.6, 104.9, 55.3; HRMS (ESI)

calcd for $C_{27}H_{20}NO_2$ $(M+H)^+$ 390.1489, found 390.1496.



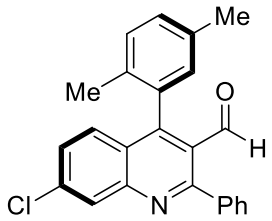

**3qa**

7-Chloro-4-(naphthalen-1-yl)-2-phenylquinoline-3-carbaldehyde **3qa** was obtained as a yellow solid in 90% yield (35.4 mg) and 92% ee (step 1, 30 °C, 60 h; step 2, rt, 36 h). $R_f$ = 0.40 (petroleum ether/ethyl acetate 10:1). The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak AD-H, isopropanol/hexane (10:90), 1.0 mL/min, λ = 254 nm, $t_r$ (major) = 7.51 min, $t_r$ (minor) = 8.69 min]. m.p. 116-117 °C; $[\alpha]_D^{25}$ = +11.47 (c = 1.0, EtOAc); $^1$H NMR (400 MHz, $CDCl_3$): δ 9.90 (s, 1H), 8.28 (d, *J* = 2.0 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.72-7.66 (m, 2H), 7.62 (t, *J* = 8.0 Hz, 1H), 7.56-7.47 (m, 4H), 7.42 (d, *J* = 6.8 Hz, 1H), 7.38-7.29 (m, 2H), 7.28-7.23 (m, 1H), 7.20 (d, *J* = 8.4 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 191.7, 160.4, 150.9, 149.0, 139.0, 138.4, 133.4, 132.0, 131.9, 129.9, 129.4, 129.4, 128.8, 128.8, 128.7, 128.6, 128.6, 127.7, 127.6, 127.2, 126.5, 125.4, 125.3, 125.2; HRMS (ESI) calcd for $C_{26}H_{17}ClNO$ $(M+H)^+$ 394.0993, found 394.0994.



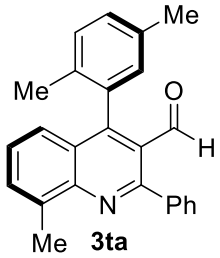

**3ra**

4-(2,5-Dimethylphenyl)-7-methyl-2-phenylquinoline-3-carbaldehyde **3ra** was obtained as a yellow solid in 93% yield (32.8 mg) and 94% ee (step 1, 30 °C, 72 h; step 2, rt, 24 h). $R_f$ = 0.40 (petroleum ether/ethyl acetate 10:1). The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak AD-H, isopropanol/hexane (10:90), 1.0 mL/min, λ = 254 nm, $t_r$ (minor) = 5.37 min, $t_r$ (major) = 6.68 min]. m.p. 171-172 °C; $[\alpha]_D^{25}$ = +6.80 (c = 1.0, EtOAc); $^1$H NMR (400 MHz, $CDCl_3$): δ 9.99 (s, 1H), 8.03 (s, 1H), 7.68-7.61 (m, 2H), 7.54-7.45 (m, 3H), 7.37-7.29 (m, 2H), 7.27-7.20 (m, 2H), 6.97 (s, 1H), 2.58 (s, 3H), 2.36 (s, 3H), 1.97 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 192.3, 159.5, 152.3, 148.9, 143.0, 139.7, 135.3, 134.5, 133.1, 130.0, 129.8, 129.7, 129.7, 129.5, 128.9, 128.4, 126.9, 125.7, 124.3, 22.0, 21.0, 19.5; HRMS (ESI) calcd for $C_{25}H_{22}NO$ $(M+H)^+$ 352.1696, found 352.1703.



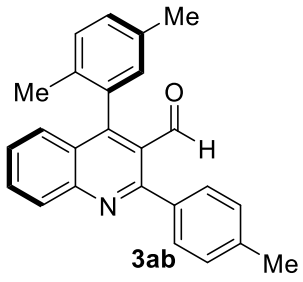

**3sa**

7-Chloro-4-(2,5-dimethylphenyl)-2-phenylquinoline-3-carbaldehyde **3sa** was obtained as a yellow solid in 89% yield (33.0 mg) and 95% ee (step 1, 30 °C, 60 h; step 2, rt, 36 h). $R_f$ = 0.40 (petroleum ether/ethyl acetate 10:1). The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak AD-H, isopropanol/hexane (10:90), 1.0 mL/min, λ = 254 nm, $t_r$ (minor) = 5.34 min, $t_r$ (major) = 6.18 min]. m.p. 171-172 °C; $[\alpha]_D^{25}$ = +10.75 (c = 1.0, EtOAc); $^1$H NMR (400 MHz, $CDCl_3$): δ 9.99 (s, 1H), 8.24 (d, *J* = 2.0 Hz, 1H), 7.69-7.59 (m, 2H), 7.57-7.47 (m, 3H), 7.46-7.34 (m, 2H), 7.30-7.20 (m, 2H), 6.95 (s, 1H), 2.37 (s, 3H), 1.96 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 191.9, 160.4, 152.2, 148.9, 139.0, 138.2, 135.4, 133.8, 133.0, 130.1, 129.8, 129.5, 129.3, 128.7, 128.5, 128.5, 128.4, 126.5, 124.7, 21.0, 19.4; HRMS (ESI) calcd for $C_{24}H_{19}ClNO$ $(M+H)^+$ 372.1150, found 372.1157.



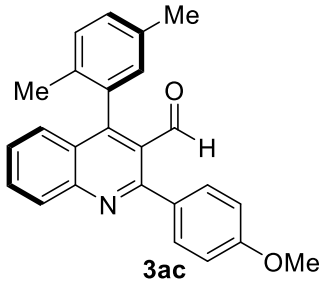

**3ta**

4-(2,5-Dimethylphenyl)-8-methyl-2-phenylquinoline-3-carbaldehyde **3ta** was obtained as a yellowish oil in 54% yield (19.0 mg) and 95% ee (step 1, 30 °C, 96 h; step 2, rt, 72 h). $R_f$ = 0.60 (petroleum ether/ethyl acetate 10:1). The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane (05:95), 1.0 mL/min, λ = 254 nm, $t_r$ (major) = 5.16 min, $t_r$ (minor) = 5.41 min]. $[\alpha]_D^{25}$ = −9.71 (c = 1.0, EtOAc); $^1$H NMR (400 MHz, $CDCl_3$): δ 10.04 (d, *J* = 2.0 Hz, 1H), 7.75-7.70 (m, 2H), 7.67 (d, *J* = 6.8 Hz, 1H), 7.54-7.47 (m, 3H), 7.39-7.33 (m, 1H), 7.29-7.20 (m, 3H), 6.96 (s, 1H), 2.89 (s, 3H), 2.37 (s, 3H), 1.96 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 192.8, 157.5, 152.3, 147.6, 139.9, 137.9, 135.2, 134.8, 133.1, 132.0, 130.3, 129.9, 129.7, 129.4, 128.9, 128.9, 128.3, 127.2, 127.0, 126.1, 126.0, 125.0, 21.0, 19.5, 18.1; HRMS (ESI) calcd for $C_{25}H_{22}NO$ $(M+H)^+$ 352.1696, found 352.1706.



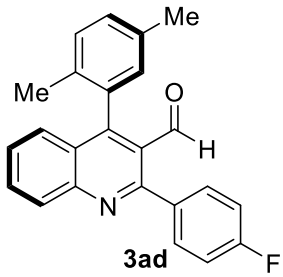
**3ab**

3-(2,5-Dimethylphenyl)-2-*p*-tolylquinoline-3-carbaldehyde **3ab** was obtained as a yellow solid in 90% yield (31.6 mg) and 94% ee (step 1, 30 °C, 60 h; step 2, rt, 24 h). $R_f$ = 0.40 (petroleum ether/ethyl acetate 10:1). The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak AD-H, isopropanol/hexane (10:90), 1.0 mL/min, λ = 254 nm, $t_r$ (minor) = 5.77 min, $t_r$ (major) = 8.89 min]. m.p. 106-107 °C; $[\alpha]_D^{25}$ = −17.67 (c = 1.0, EtOAc); $^1$H NMR (400 MHz, $CDCl_3$): δ 10.02 (s, 1H), 8.24 (d, *J* = 8.4 Hz, 1H), 7.85-7.76 (m, 1H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.50-7.41 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.28-7.16 (m, 2H), 6.96 (s, 1H), 2.44 (s, 3H), 2.36 (s, 3H), 1.97 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 192.4, 159.2, 152.2, 148.6, 139.1, 136.5, 135.3, 134.4, 133.1, 132.0, 130.0, 129.8, 129.7, 129.7, 129.5, 129.3, 127.3, 127.1, 126.5, 126.2, 21.4, 21.0, 19.5; HRMS (ESI) calcd for $C_{25}H_{22}NO$ $(M+H)^+$ 352.1696, found 352.1702.



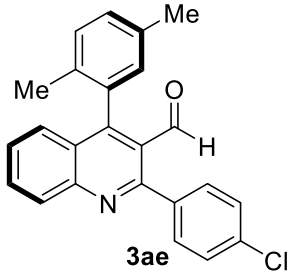
**3ac**

4-(2,5-Dimethylphenyl)-2-(4-methoxyphenyl)quinoline-3-carbaldehyde **3ac** was obtained as a yellow solid in 89% yield (32.7 mg) and 92% ee (step 1, 30 °C, 72 h; step 2, rt, 24 h). $R_f$ = 0.30 (petroleum ether/ethyl acetate 10:1). The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak AD-H, isopropanol/hexane (10:90), 1.0 mL/min, λ = 254 nm, $t_r$ (minor) = 8.61 min, $t_r$ (major) = 13.89 min]. m.p. 150-151 °C; $[\alpha]_D^{25}$ = −21.56 (c = 1.0, EtOAc); $^1$H NMR (400 MHz, $CDCl_3$): δ 10.02 (s, 1H), 8.23 (d, *J* = 8.4 Hz, 1H), 7.85-7.76 (m, 1H), 7.68-7.59 (m, 2H), 7.50-7.39 (m, 2H), 7.30-7.19 (m, 2H), 7.09-7.01 (m, 2H), 6.96 (s, 1H), 3.88 (s, 3H), 2.37 (s, 3H), 1.96 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 192.4, 160.5, 158.7, 152.1, 148.6, 135.2, 134.4, 133.1, 131.9, 131.7, 131.4, 129.9, 129.6, 129.5, 127.1, 127.1, 126.4, 126.0, 114.0, 55.4, 21.0, 19.5; HRMS (ESI) calcd for $C_{25}H_{22}NO_2$ $(M+H)^+$ 368.1645, found 368.1651.



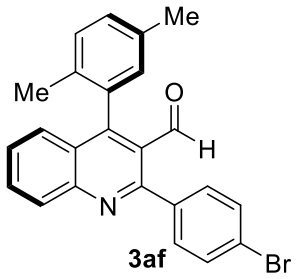
**3ad**

4-(2,5-Dimethylphenyl)-2-(4-fluorophenyl)quinoline-3-carbaldehyde **3ad** was obtained as a white solid in 91% yield (32.3 mg) and 92% ee (step 1, 30 °C, 72 h; step 2, rt, 48 h). $R_f$ = 0.40 (petroleum ether/ethyl acetate 10:1). The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak AD-H, isopropanol/hexane (10:90), 1.0 mL/min, λ = 254 nm, $t_r$ (minor) = 6.58 min, $t_r$ (major) = 9.18 min]. m.p. 127-128 °C; $[\alpha]_D^{25}$ = −11.22 (c = 1.0, EtOAc); $^1$H NMR (400 MHz, $CDCl_3$): δ 10.00 (s, 1H), 8.22 (d, *J* = 8.4 Hz, 1H), 7.88-7.78 (m, 1H), 7.69-7.59 (m, 2H), 7.54-7.41 (m, 2H), 7.30-7.26 (m, 1H), 7.25-7.14 (m, 3H), 6.99 (s, 1H), 2.38 (s, 3H), 1.97 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 192.2, 163.3 (d, $^1J_{C\text{-}F}$ = 247.2 Hz), 157.9, 153.2, 148.5, 135.7 (d, $^4J_{C\text{-}F}$ = 3.3 Hz), 135.4, 133.9, 133.1, 132.3, 131.6 (d, $^3J_{C\text{-}F}$ = 8.4 Hz), 130.1, 129.8, 129.7, 127.6, 127.1, 126.2, 126.1, 115.5 (d, $^2J_{C\text{-}F}$ = 21.7 Hz), 21.0, 19.5; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -112.22; HRMS (ESI) calcd for $C_{24}H_{19}FNO$ $(M+H)^+$ 356.1445, found 356.1448.



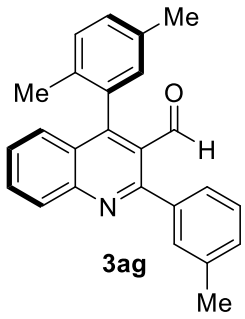
**3ae**

2-(4-Chlorophenyl)-4-(2,5-dimethylphenyl)quinoline-3-carbaldehyde **3ae** was obtained as a yellowish oil in 87% yield (32.3 mg) and 93% ee (step 1, 30 °C, 72 h; step 2, rt, 24 h). $R_f$ = 0.40 (petroleum ether/ethyl acetate 10:1). The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak AD-H, isopropanol/hexane (10:90), 1.0 mL/min, λ = 254 nm, $t_r$ (minor) = 7.17 min, $t_r$ (major) = 10.50 min]. $[\alpha]_D^{25}$ = −20.90 (c = 1.0, EtOAc); $^1$H NMR (400 MHz, $CDCl_3$): δ 9.99 (s, 1H), 8.23 (d, *J* = 8.4 Hz, 1H), 7.89-7.79 (m, 1H), 7.59 (d, *J* = 8.8 Hz, 2H), 7.54-7.41 (m, 4H), 7.32-7.22 (m, 2H), 6.99 (s, 1H), 2.38 (s, 3H), 1.97 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 192.1, 157.7, 153.4, 148.5, 138.1, 135.4, 135.1, 133.7, 133.1, 132.3, 131.0, 130.1, 129.8, 129.8. 129.8, 128.6, 127.7, 127.0, 126.2, 126.1, 21.0, 19.5; HRMS (ESI) calcd for $C_{24}H_{19}ClNO$ $(M+H)^+$ 372.1150, found 372.1155.



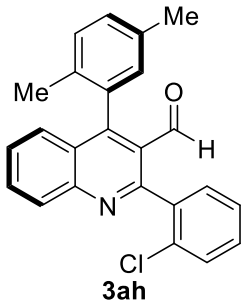
**3af**

2-(4-Bromophenyl)-4-(2,5-dimethylphenyl)quinoline-3-carbaldehyde **3af** was obtained as a yellowish oil in 85% yield (35.3 mg) and 94% ee (step 1, 30 °C, 72 h; step 2, rt, 48 h). $R_f$ = 0.40 (petroleum ether/ethyl acetate 10:1). The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak AD-H, isopropanol/hexane (10:90), 1.0 mL/min, λ = 254 nm, $t_r$ (minor) = 7.12 min, $t_r$ (major) = 10.49 min]. $[\alpha]_D^{25}$ = −23.15 (c = 1.0, EtOAc); $^1$H NMR (400 MHz, $CDCl_3$): δ 9.99 (s, 1H), 8.22 (d, *J* = 8.4 Hz, 1H), 7.90-7.77 (m, 1H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.56-7.40 (m, 4H), 7.31-7.21 (m, 2H), 6.99 (s, 1H), 2.38 (s, 3H), 1.97 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 192.1, 157.7, 153.5, 148.6, 138.7, 135.5, 133.7, 133.1, 132.3, 131.6, 131.3, 130.1, 129.9, 129.9, 129.8, 127.7, 127.0, 126.2, 126.1, 123.5, 21.0, 19.5; HRMS (ESI) calcd for $C_{24}H_{19}BrNO$ $(M+H)^+$ 416.0645, found 416.0651.



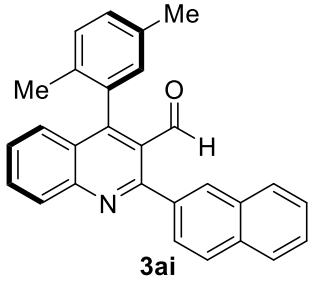
**3ag**

4-(2,5-Dimethylphenyl)-2-(*m*-tolyl)quinoline-3-carbaldehyde **3ag** was obtained as a yellowish oil in 93% yield (32.6 mg) and 93% ee (step 1, 30 °C, 72 h; step 2, rt, 24 h). $R_f$ = 0.40 (petroleum ether/ethyl acetate 10:1). The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak AD-H, isopropanol/hexane (10:90), 1.0 mL/min, λ = 254 nm, $t_r$ (minor) = 5.26 min, $t_r$ (major) = 6.52 min]. $[\alpha]_D^{25}$ = −12.60 (c = 1.0, EtOAc); $^1$H NMR (400 MHz, $CDCl_3$): δ 10.01 (s, 1H), 8.25 (d, *J* = 8.4 Hz, 1H), 7.87-7.78 (m, 1H), 7.55-7.43 (m, 3H), 7.42-7.35 (m, 2H), 7.32-7.20 (m, 3H), 6.97 (s, 1H), 2.46 (s, 3H), 2.37 (s, 3H), 1.97 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 192.3, 159.5, 152.2, 148.5, 139.3, 138.3, 135.3, 134.4, 133.1, 132.0, 130.3, 130.0, 129.9, 129.8, 129.6, 129.5, 128.3, 127.4, 127.2, 127.1, 126.5, 126.2, 21.6, 21.0, 19.5; HRMS (ESI) calcd for $C_{25}H_{22}NO$ $(M+H)^+$ 352.1696, found 352.1707.




**3ah**

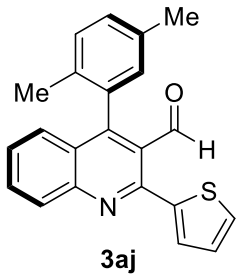
2-(2-Chlorophenyl)-4-(2,5-dimethylphenyl)quinoline-3-carbaldehyde **3ah** was obtained as a yellowish oil as a mixture of rotamers in a 1.4:1 ratio in 90% yield (33.5 mg) and 97% ee (step 1, 30 ºC, 60 h; step 2, rt, 24 h). $R_f$ = 0.40 (petroleum ether/ethyl acetate 10:1). The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak AD-H, isopropanol/hexane (10:90), 1.0 mL/min, λ = 254 nm, $t_r$ (minor) = 6.17 min, $t_r$ (major) = 8.49 min]. $[\alpha]_D^{25}$ = −35.60 (c = 1.0, EtOAc); $^1$H NMR (400 MHz, $CDCl_3$): δ 9.94-9.85 (1H; minor rotamer: 9.91, major rotamer: 9.87), 8.25 (d, *J* = 8.4 Hz, 1H), 7.89-7.81 (m, 1H), 7.65-7.57 (m, 1H), 7.57-7.48 (m, 2H), 7.47-7.38 (m, 3H), 7.31-7.24 (m, 2H), 7.15-6.94 (1H; minor rotamer: 7.13, major rotamer: 6.98), 2.44-2.33 (3H; minor rotamer: 2.41, major rotamer: 2.37), 2.09-1.87 (3H; major rotamer: 2.06, minor rotamer: 1.91); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 191.4, 156.2, 148.7, 139.4, 135.6, 133.2, 133.2, 132.3, 131.9, 130.4, 130.3, 130.3, 130.2, 129.9, 129.9, 129.3, 127.9, 127.3, 127.3, 126.9, 126.5, 126.3, 21.0, 19.5; HRMS (ESI) calcd for $C_{24}H_{19}ClNO$ $(M+H)^+$ 372.1150, found 372.1158.




**3ai**

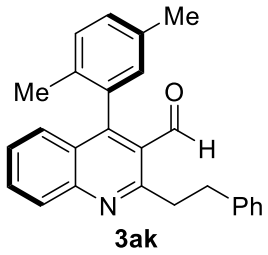
4-(2,5-Dimethylphenyl)-2-(naphthalen-2-yl)quinoline-3-carbaldehyde **3ai** was obtained as a yellowish oil in 95% yield (36.9 mg) and 93% ee (step 1, 30 ºC, 60 h; step 2, rt, 24 h). $R_f$ = 0.30 (petroleum ether/ethyl acetate 10:1). The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak AD-H, isopropanol/hexane (10:90), 1.0 mL/min, λ = 254 nm, $t_r$ (minor) = 8.39 min, $t_r$ (major) = 13.31 min]. $[\alpha]_D^{25}$ = −27.00 (c = 1.0, EtOAc); $^1$H NMR (400 MHz, $CDCl_3$): δ 10.05 (s, 1H), 8.28 (d, *J* = 8.4 Hz, 1H), 8.13 (s, 1H), 8.01-7.88 (m, 3H), 7.87-7.75 (m, 2H), 7.59-7.41 (m, 4H), 7.30-7.23 (m, 2H), 7.00 (s, 1H), 2.37 (s, 3H), 2.00 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 192.2, 159.1, 152.5, 148.6, 136.9, 135.3, 134.2, 133.4, 133.1, 133.1, 132.1, 130.0, 129.8, 129.7, 129.6, 129.6, 128.6, 128.1, 127.8, 127.5,

127.1, 127.1, 126.8, 126.6, 126.4, 126.2, 21.0, 19.5; HRMS (ESI) calcd for $C_{28}H_{22}NO$ $(M+H)^+$ 388.1696, found 388.1700.




**3aj**

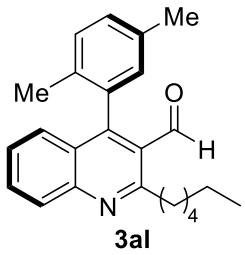
4-(2,5-Dimethylphenyl)-2-(thiophen-2-yl)quinoline-3-carbaldehyde **3aj** was obtained as a yellow solid in 92% yield (31.6 mg) and 93% ee (step 1, 30 °C, 72 h; step 2, rt, 24 h). $R_f$ = 0.40 (petroleum ether/ethyl acetate 10:1). The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak AD-H, isopropanol/hexane (10:90), 1.0 mL/min, λ = 254 nm, $t_r$ (minor) = 5.90 min, $t_r$ (major) = 7.99 min]. m.p. 46-47 °C; $[\alpha]_D^{25}$ = −39.70 (c = 1.0, EtOAc); $^1$H NMR (400 MHz, $CDCl_3$): δ 10.17 (s, 1H), 8.18 (d, *J* = 8.4 Hz, 1H), 7.83-7.74 (m, 1H), 7.59-7.52 (m, 1H), 7.48-7.42 (m, 1H), 7.41-7.34 (m, 2H), 7.28-7.20 (m, 2H), 7.18-7.11 (m, 1H), 6.94 (s, 1H), 2.36 (s, 3H), 1.95 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 192.4, 151.4, 148.6, 142.5, 135.3, 134.3, 133.2, 131.9, 130.5, 130.0, 129.6, 129.6, 129.5, 129.4, 128.0, 127.4, 127.1, 126.5, 126.0, 21.0, 19.5; HRMS (ESI) calcd for $C_{22}H_{18}NOS$ $(M+H)^+$ 344.1104, found 344.1113.




**3ak**

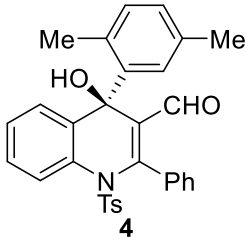
4-(2,5-Dimethylphenyl)-2-phenethylquinoline-3-carbaldehyde **3ak** was obtained as a yellowish oil in 85% yield (31.1 mg) and 97% ee (step 1, 30 °C, 60 h; step 2, rt, 24 h). $R_f$ = 0.50 (petroleum ether/ethyl acetate 10:1). The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak AD-H, isopropanol/hexane (10:90), 1.0 mL/min, λ = 254 nm, $t_r$ (minor) = 5.35 min, $t_r$ (major) = 6.20 min]. $[\alpha]_D^{25}$ = −8.86 (c = 1.0, EtOAc); $^1$H NMR (400 MHz, $CDCl_3$): δ 9.91 (s, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 7.86-7.77 (m, 1H), 7.48-7.42 (m, 1H), 7.39 (dd, *J* = 8.4, 1.6 Hz, 3H), 7.33-7.24 (m, 4H), 7.24-7.17 (m, 1H), 6.99 (s, 1H), 3.74-3.61 (m, 2H), 3.21-3.05 (m, 2H), 2.37 (s, 3H), 1.92 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 193.4, 160.7, 155.8, 148.7, 142.0, 135.6, 133.3, 133.2, 132.2, 130.5, 130.2, 129.9, 129.2, 128.8, 128.3, 126.9, 126.7, 125.9, 125.8, 125.3, 39.5, 35.7, 20.9, 19.5; HRMS (ESI)

calcd for $C_{26}H_{24}NO$ $(M+H)^+$ 366.1852, found 366.1861.



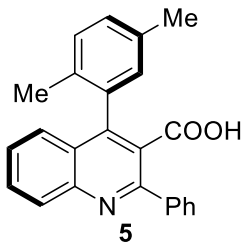

**3al**

4-(2,5-Dimethylphenyl)-2-hexylquinoline-3-carbaldehyde **3al** was obtained as a yellowish oil in 91% yield (31.4 mg) and 98% ee (step 1, 30 °C, 72 h; step 2, rt, 48 h). $R_f$ = 0.60 (petroleum ether/ethyl acetate 10:1). The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak AD-H, isopropanol/hexane (05:95), 1.0 mL/min, λ = 254 nm, $t_r$ (minor) = 4.48 min, $t_r$ (major) = 5.53 min]. $[\alpha]_D^{25}$ = −17.64 (c = 1.0, EtOAc); $^1$H NMR (400 MHz, $CDCl_3$): δ 9.96 (s, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.84-7.76 (m, 1H), 7.46-7.33 (m, 2H), 7.28-7.20 (m, 2H), 6.99 (s, 1H), 3.45-3.28 (m, 2H), 2.37 (s, 3H), 1.92 (s, 3H), 1.84-1.69 (m, 3H), 1.55-1.46 (m, 2H), 1.39-1.31 (m, 3H), 0.90 (t, *J* = 6.8 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 193.3, 162.1, 155.8, 148.5, 135.6, 133.4, 133.2, 132.2, 130.4, 130.2, 129.9, 129.0, 126.7, 126.6, 125.7, 125.1, 37.6, 31.8, 30.0, 29.6, 22.7, 20.9, 19.4, 14.1; HRMS (ESI) calcd for $C_{24}H_{28}NO$ $(M+H)^+$ 346.2165, found 346.2168.



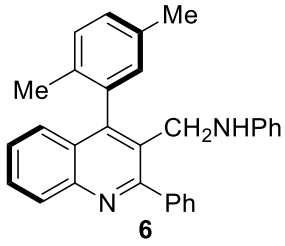

**4**

4-(2,5-Dimethylphenyl)-4-hydroxy-2-phenyl-1-tosyl-1,4-dihydroquinoline-3-carbaldehyde **4** was obtained as a yellowish oil in 90% yield (91.6 mg) and 93% ee. $R_f$ = 0.20 (petroleum ether/ethyl acetate 10:1). The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane (10:90), 1.0 mL/min, λ = 254 nm, $t_r$ (major) = 6.39 min, $t_r$ (minor) = 6.90 min]. $[\alpha]_D^{25}$ = −16.78 (c = 1.0, EtOAc); $^1$H NMR (400 MHz, $CDCl_3$): δ 9.87 (s, 1H), 9.04 (d, *J* = 8.4 Hz, 1H), 8.16-8.08 (m, 1H), 7.80-7.72 (m, 3H), 7.65-7.56 (m, 2H), 7.56-7.52 (m, 2H), 7.49 (t, *J* = 8.0 Hz, 2H), 7.32 (s, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.97 (s, 1H), 2.39 (s, 3H), 2.35 (s, 3H), 1.99 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 188.7, 159.9, 156.9, 142.1, 140.5, 139.8, 136.5, 136.0, 132.7, 131.9, 131.9, 130.9, 130.7, 130.5, 130.3, 129.0, 128.9, 128.6, 127.8, 127.4, 127.2, 125.9, 124.0, 21.3, 21.0, 19.5, 17.7; HRMS (ESI) calcd for $C_{31}H_{28}NO_4S$ $(M+H)^+$ 510.1734, found 510.1740.



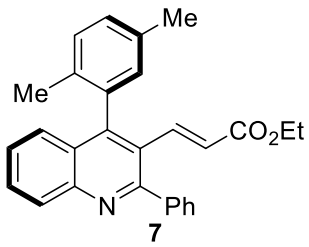

**5**

4-(2,5-Dimethylphenyl)-2-phenylquinoline-3-carboxylic acid **5** was obtained as a yellow solid in 83% yield (29.3 mg) and 93% ee. $R_f$ = 0.20 (petroleum ether/ethyl acetate 1:1). The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak AD-H, isopropanol/hexane (05:95), 1.0 mL/min, λ = 254 nm, $t_r$ (minor) = 7.09 min, $t_r$ (major) = 10.81 min]. m.p. 232-233 ºC; $[\alpha]_D^{25}$ = −68.85 (c = 1.0, EtOAc); $^1$H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.4 Hz, 1H), 7.73-7.59 (m, 3H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.37-7.25 (m, 4H), 7.07 (s, 2H), 6.91 (s, 1H), 2.24 (s, 3H), 1.89 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 155.8, 147.4, 146.8, 139.3, 134.8, 134.8, 133.6, 130.7, 129.9, 129.7, 129.3, 128.9, 128.9, 128.7, 128.3, 127.2, 126.3, 125.7, 20.9, 19.4; HRMS (ESI) calcd for $C_{24}H_{20}NO_2$ $(M+H)^+$ 354.1489, found 354.1498.



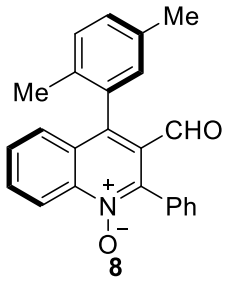

**6**

*N*-((4-(2,5-Dimethylphenyl)-2-phenylquinolin-3-yl)methyl)aniline **6** was obtained as a yellow solid in 69% yield (28.6 mg) and 93% ee. $R_f$ = 0.30 (petroleum ether/ethyl acetate 5:1). The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak AD-H, isopropanol/hexane (10:90), 1.0 mL/min, λ = 254 nm, $t_r$ (minor) = 5.07 min, $t_r$ (major) = 7.37 min]. m.p. 186-187 ºC; $[\alpha]_D^{25}$ = +4.45 (c = 1.0, EtOAc); $^1$H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, *J* = 8.4 Hz, 1H), 7.82-7.75 (m, 2H), 7.74-7.66 (m, 1H), 7.53-7.39 (m, 4H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.28-7.25 (m, 1H), 7.21-7.16 (m, 1H), 7.05 (s, 1H), 7.00 (t, *J* = 8.0 Hz, 2H), 6.61 (t, *J* = 7.2 Hz, 1H), 6.20 (d, *J* = 8.0 Hz, 2H), 4.30 (d, *J* = 13.2 Hz, 1H), 4.05 (d, *J* = 13.2 Hz, 1H), 2.36 (s, 3H), 1.94 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 160.5, 147.3, 135.6, 135.5, 132.9, 130.9, 130.4, 129.8, 129.5, 129.3, 128.9, 128.8, 128.7, 128.6, 128.1, 126.8, 126.7, 126.1, 117.7, 113.3, 43.6, 21.0, 19.4; HRMS (ESI) calcd for $C_{30}H_{27}N_2$ $(M+H)^+$ 415.2169, found 415.2172.



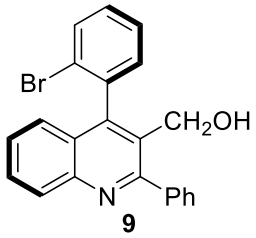

**7**

Ethyl (*E*)-3-(4-(2,5-dimethylphenyl)-2-phenylquinolin-3-yl)acrylate **7** was obtained as a yellow solid in 89% yield (36.2 mg) and 93% ee. $R_f$ = 0.30 (petroleum ether/ethyl acetate 10:1). The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane (03:97), 1.0 mL/min, λ = 254 nm, $t_r$ (minor) = 11.56 min, $t_r$ (major) = 12.31 min]. m.p. 102-103 °C; $[\alpha]_D^{25}$ = −11.30 (c = 1.0, EtOAc); $^1$H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, *J* = 8.4 Hz, 1H), 7.76-7.69 (m, 1H), 7.68-7.61 (m, 2H), 7.53 (d, *J* = 16.4 Hz, 1H), 7.51-7.39 (m, 4H), 7.35 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.26-7.17 (m, 2H), 6.96 (s, 1H), 5.38 (d, *J* = 16.4 Hz, 1H), 4.04 (q, *J* = 7.2 Hz, 2H), 2.37 (s, 3H), 1.90 (s, 3H), 1.15 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 166.3, 159.3, 149.0, 147.2, 141.3, 140.4, 135.7, 135.6, 132.7, 130.4, 130.3, 129.8, 129.5, 129.5, 129.5, 128.7, 128.4, 127.0, 126.6, 126.5, 125.2, 124.5, 60.3, 21.0, 19.2, 14.1; HRMS (ESI) calcd for $C_{28}H_{26}NO_2$ $(M+H)^+$ 408.1958, found 408.1965.




**8**

4-(2,5-Dimethylphenyl)-3-formyl-2-phenylquinoline 1-oxide **8** was obtained as a yellowish oil in 70% yield (24.7 mg) and 93% ee. $R_f$ = 0.30 (petroleum ether/ethyl acetate 3:1). The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak AD-H, isopropanol/hexane (30:70), 1.0 mL/min, λ = 254 nm, $t_r$ (minor) = 8.91 min, $t_r$ (major) = 11.81 min]. $[\alpha]_D^{25}$ = −12.70 (c = 1.0, EtOAc); $^1$H NMR (400 MHz, $CDCl_3$): δ 9.70 (s, 1H), 8.91 (d, *J* = 8.8 Hz, 1H), 7.90 (t, *J* = 8.0 Hz, 1H), 7.66-7.44 (m, 7H), 7.31-7.20 (m, 2H), 7.01 (s, 1H), 2.37 (s, 3H), 2.00 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 189.7, 144.9, 142.9, 140.6, 135.6, 133.7, 133.0, 132.8, 131.2, 130.3, 130.2, 130.0, 129.5, 129.4, 128.8, 128.7, 128.2, 128.0, 120.6, 21.0, 19.5; HRMS (ESI) calcd for $C_{24}H_{20}NO_2$ $(M+H)^+$ 354.1489, found 354.1497.




**9**

(4-(2-Bromophenyl)-2-phenylquinolin-3-yl)methanol **9** was obtained as a white solid in 91% yield (35.4 mg) and 93% ee. $R_f$ = 0.20 (petroleum ether/ethyl acetate 10:1). The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak AD-H, isopropanol/hexane (20:80), 1.0 mL/min, λ = 254 nm, $t_r$ (minor) = 7.90 min, $t_r$ (major) = 10.86 min]. m.p. 169-170 °C; $[\alpha]_D^{25}$ = +21.60 (c = 1.0, EtOAc); $^1$H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, *J* = 8.4 Hz, 1H), 7.85-7.77 (m, 3H), 7.76-7.70 (m, 1H), 7.54-7.43 (m, 5H), 7.43-7.35 (m, 2H), 7.27-7.22 (m, 1H), 4.54 (d, *J* = 12.0 Hz, 1H), 4.38 (d, *J* = 12.0 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 160.9, 148.2, 147.2, 140.3, 137.4, 133.1, 131.5, 130.2, 130.0, 129.6, 129.2, 129.0, 128.6, 128.4, 127.7, 127.0, 126.2, 125.9, 123.4, 60.2; HRMS (ESI) calcd for $C_{22}H_{17}BrNO$ $(M+H)^+$ 390.0488, found 390.0495.

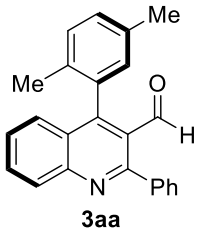
## Investigation on the Racemization Barrier of 3aa

The reaction was conducted at 1 mg/mL concentration in a sealed tube and heated at the specified temperature. The change in enantiomeric excess over time was determined by HPLC. The barrier to rotation for **3aa** was obtained by kinetic of racemization of an enantiomer.

This data was plotted as ($\ln[ee_0/ee_t]$) versus time (seconds). The gradient of this graph gives the racemization constant ($k_{racemization} = 2 \times k_{enantiomerization}$) at the specified temperature. The barrier to rotation, $\Delta G^{\neq}_{enantiomerization}$, was calculated using the following Eyring equation, R = Gas constant = 8.3145 $J \cdot K^{-1} \cdot mol^{-1}$, h = Planck constant = 6.62608 x $10^{-34}$ J·s, $k_B$ = Boltzmann constant = 1.38066 x $10^{-23}$ $J \cdot K^{-1}$, and $T_1$ = temperature racemization study was conducted at, in Kelvin.

$$\Delta G^{\neq}_{enantiomerization} = RT_1 \ln \frac{k_B T_1}{h k_{enantiomerization}}$$

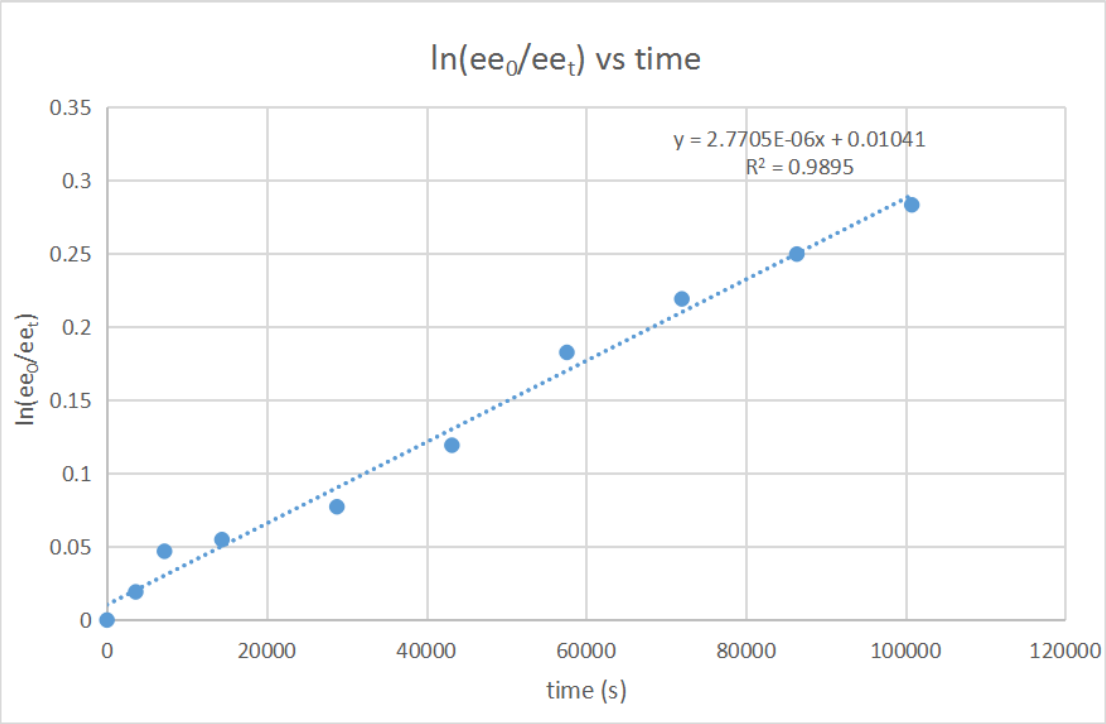
Racemization of **3aa** in *i*-PrOH at 140 °C




**3aa**

**Table S1. Investigation on the racemization barrier of 3aa**

| Time (seconds) | Enantiomeric Excess (ee) | First Order Racemization ($ln[ee_0/ee_t]$) |
|---|---|---|
| 0 | 92.58 | 0.00000 |
| 3600 | 90.82 | 0.01919 |
| 7200 | 88.34 | 0.04688 |
| 14400 | 87.64 | 0.05484 |
| 28800 | 85.70 | 0.07722 |
| 43200 | 82.18 | 0.11916 |
| 57600 | 77.14 | 0.18245 |
| 72000 | 74.38 | 0.21889 |
| 86400 | 72.14 | 0.24946 |
| 100800 | 69.76 | 0.28301 |




$k_{racemization}$ (140 °C) = 2.7705 × $10^{-6}$ $s^{-1}$

$k_{enantiomerization}$ (140 °C) = 1.38525 × $10^{-6}$ $s^{-1}$

$\Delta G^{\neq}_{enantiomerization}$ = 148.654 KJ/mol = 35.51 kcal/mol

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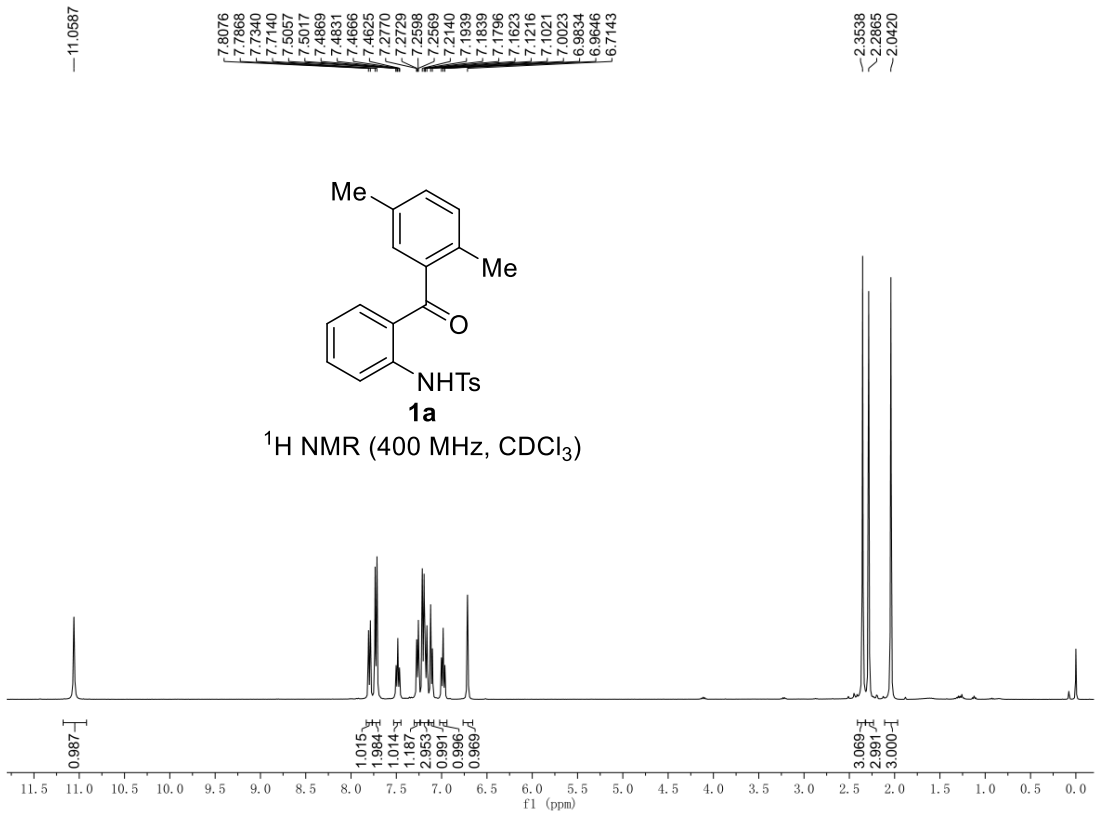
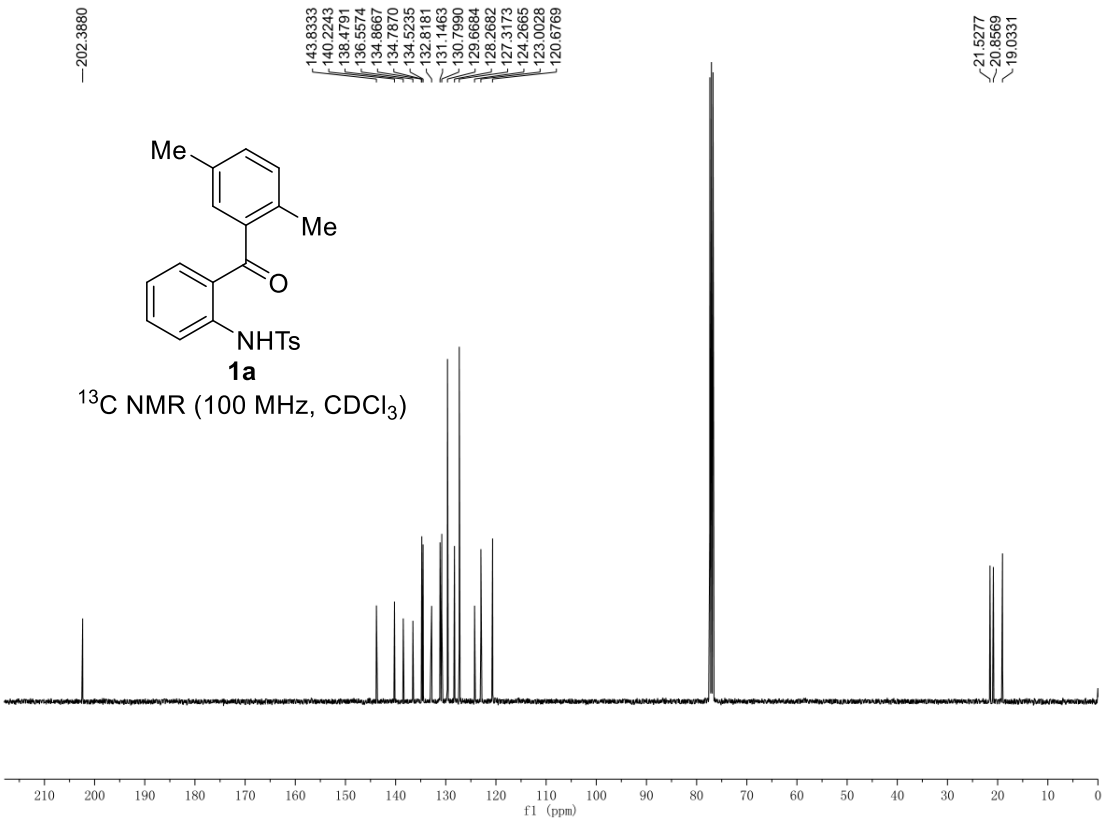
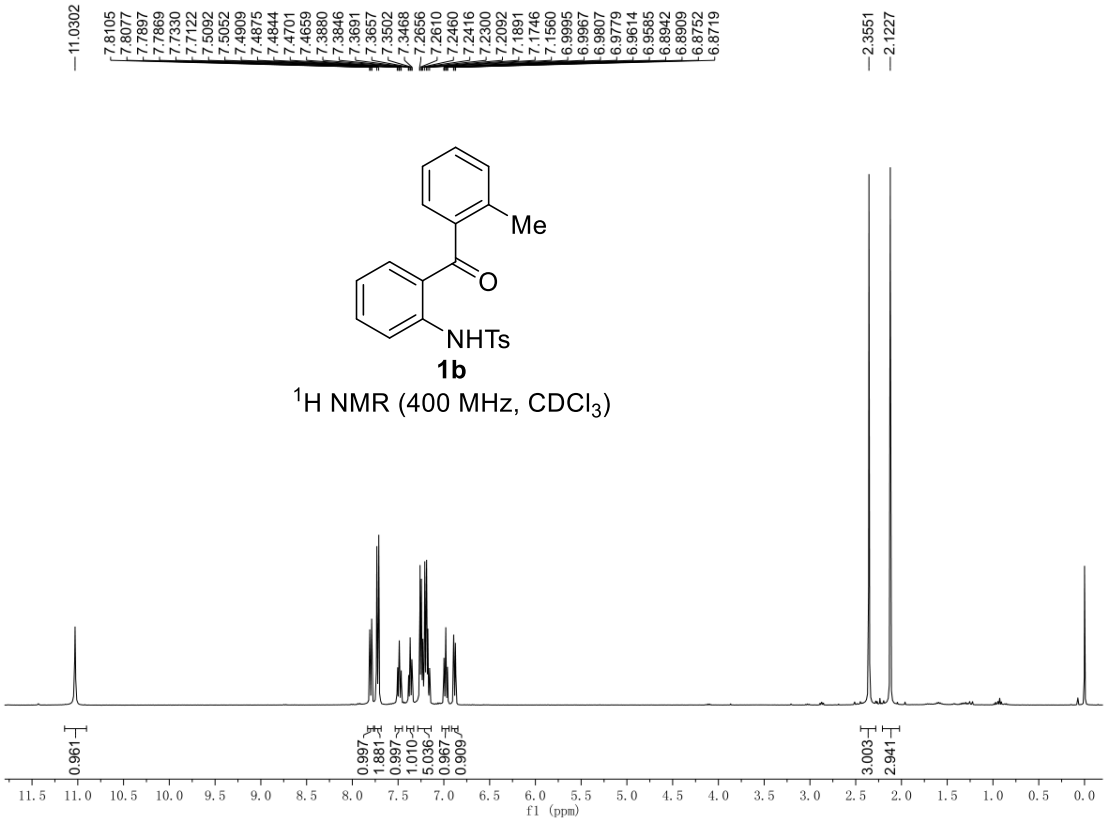
## NMR Spectra of 2-Aminoaryl Ketones 1

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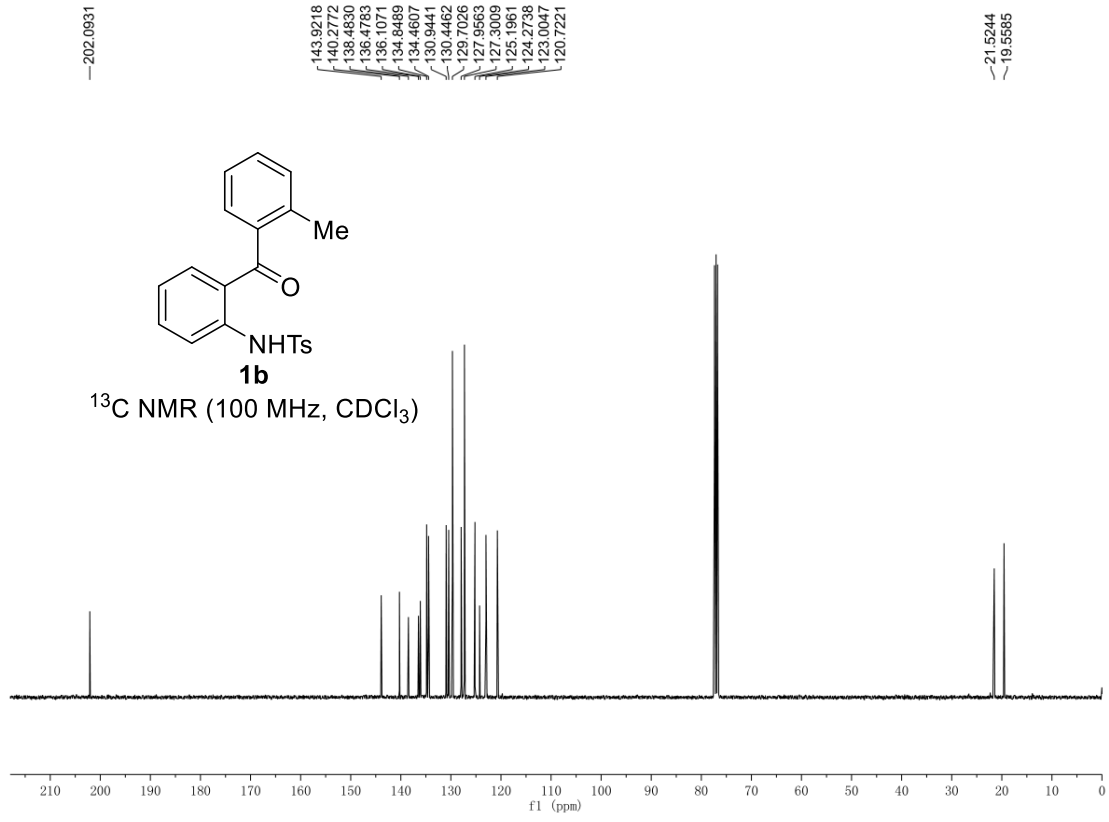
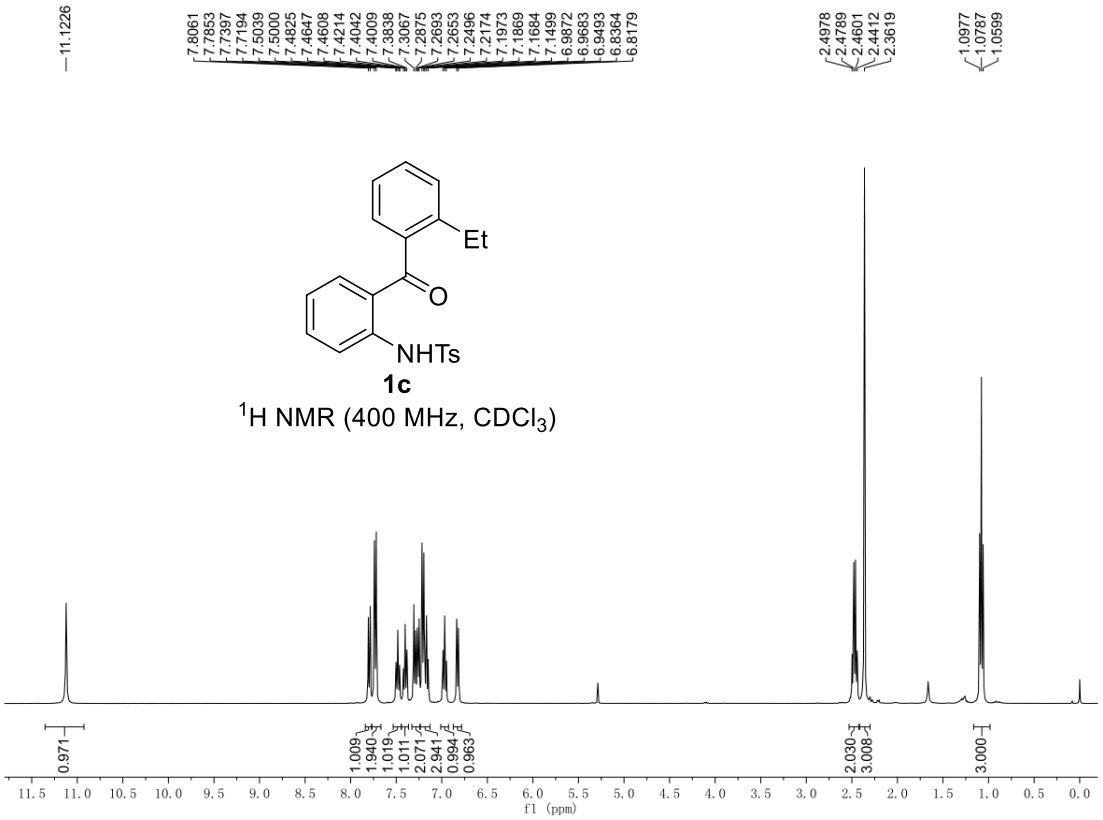
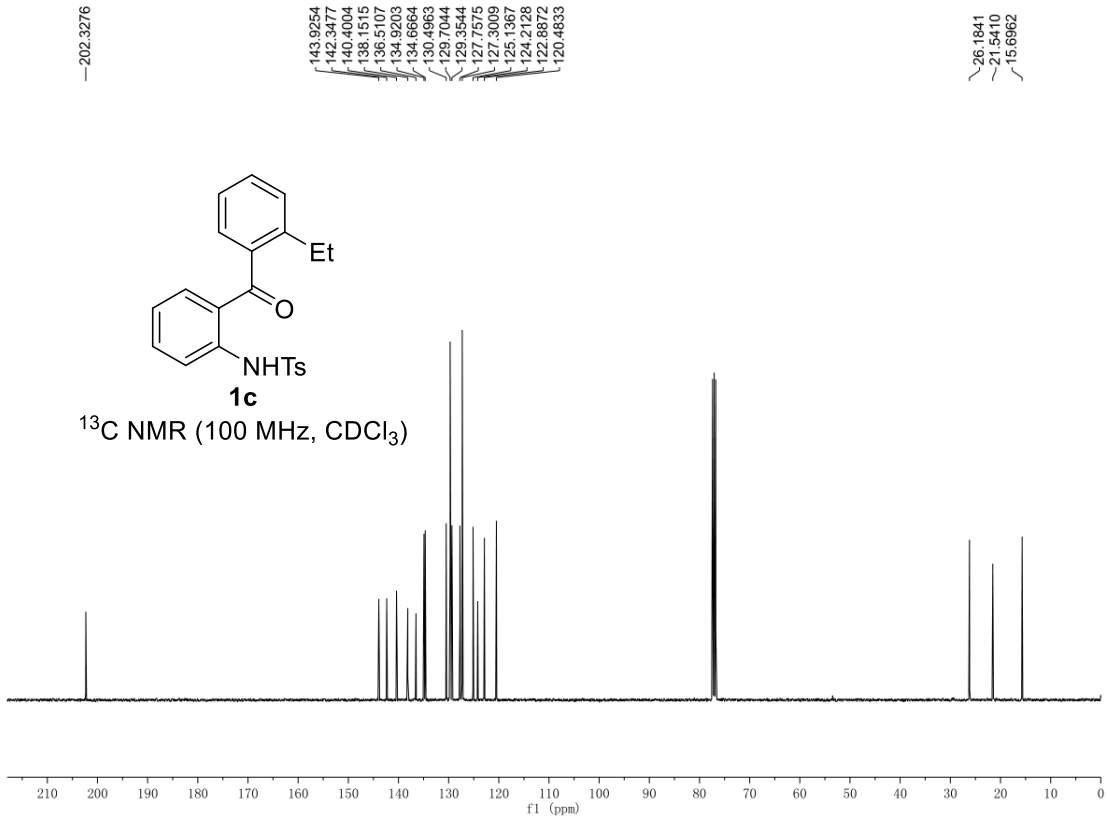
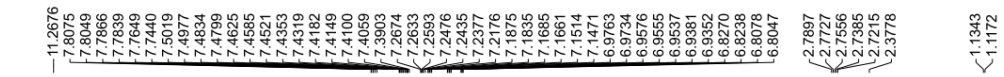
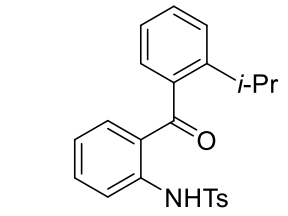
7.8105
7.8077
7.7897
7.7869
7.7330
7.7122
7.5092
7.5052
7.4909
7.4875
7.4844
7.4701
7.4659
7.3880
7.3846
7.3691
7.3657
7.3502
7.3468
7.2656
7.2610
7.2460
7.2416
7.2300
7.2092
7.1891
7.1746
7.1560
6.9995
6.9967
6.9807
6.9779
6.9614
6.9585
6.8942
6.8909
6.8752
6.8719
2.3551
2.1227
Me
O
NHTs
1b
1H NMR (400 MHz, CDCl3)
0.961
0.997
1.881
0.997
1.010
5.036
0.967
0.909
3.003
2.941
f1 (ppm)


202.0931
143.9218
140.2772
138.4830
136.4783
136.1071
134.8489
134.4607
130.9441
130.4462
129.7026
127.9563
127.3009
125.1961
124.2738
123.0047
120.7221
21.5244
19.5585
Me
O
NHTs
1b
13C NMR (100 MHz, CDCl3)
f1 (ppm)


11.1226
7.8061
7.7853
7.7397
7.7194
7.5039
7.5000
7.4825
7.4647
7.4608
7.4214
7.4042
7.4009
7.3838
7.3067
7.2875
7.2693
7.2653
7.2496
7.2174
7.1973
7.1869
7.1684
7.1499
6.9872
6.9683
6.9493
6.8364
6.8179
2.4978
2.4789
2.4601
2.4412
2.3619
1.0977
1.0787
1.0599
Et
O
NHTs
1c
1H NMR (400 MHz, CDCl3)
0.971
1.009
1.940
1.019
1.011
2.071
2.941
0.994
0.963
2.030
3.008
3.000
f1 (ppm)


202.3276
143.9254
142.3477
140.4004
138.1515
136.5107
134.9203
134.6664
130.4963
129.7044
129.3544
127.7575
127.3009
125.1367
124.2128
122.8872
120.4833
26.1841
21.5410
15.6962
Et
O
NHTs
1c
13C NMR (100 MHz, CDCl3)
f1 (ppm)



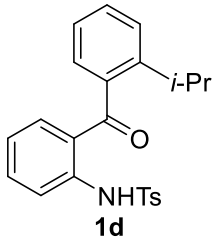




**1d**

$^{1}$H NMR (400 MHz, $CDCl_3$)

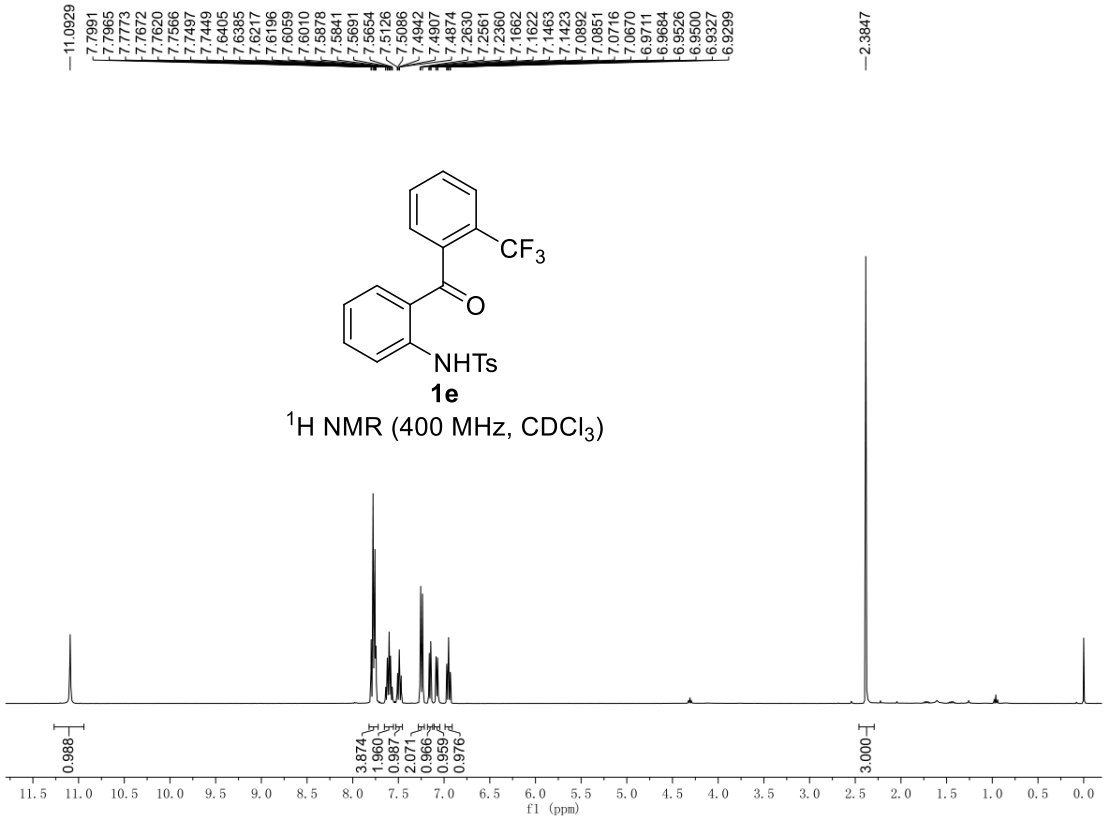


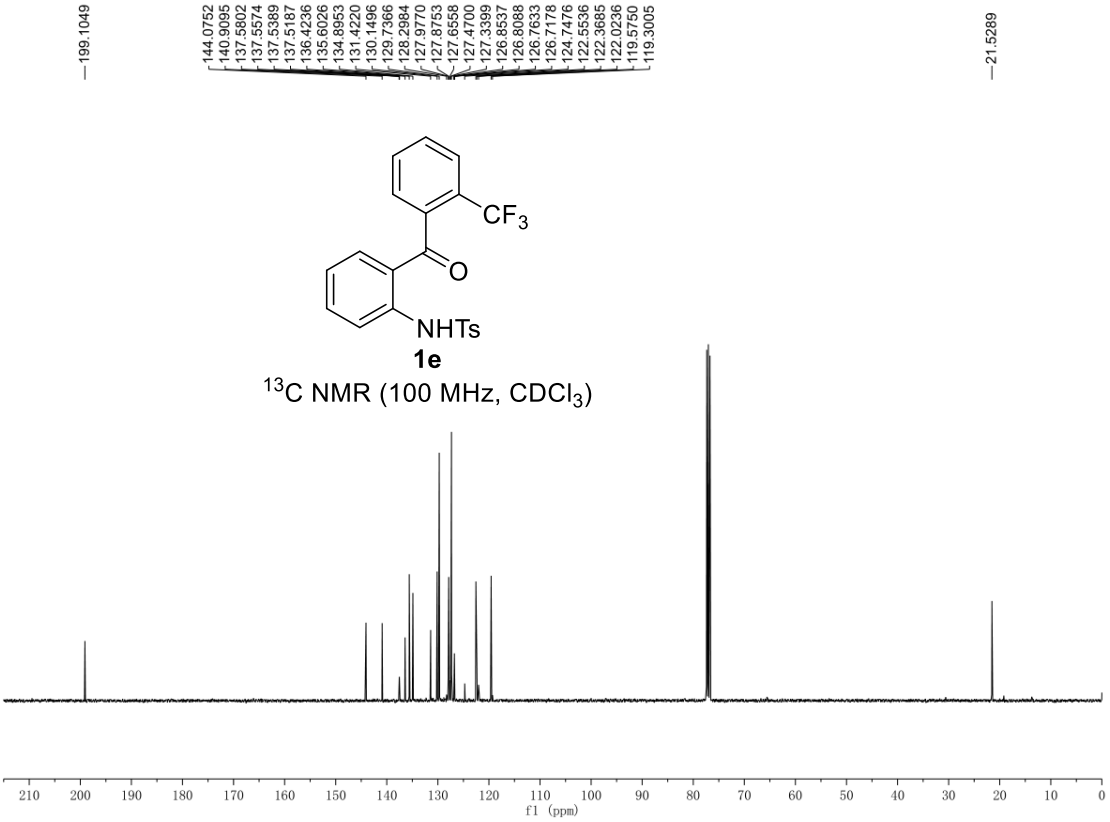


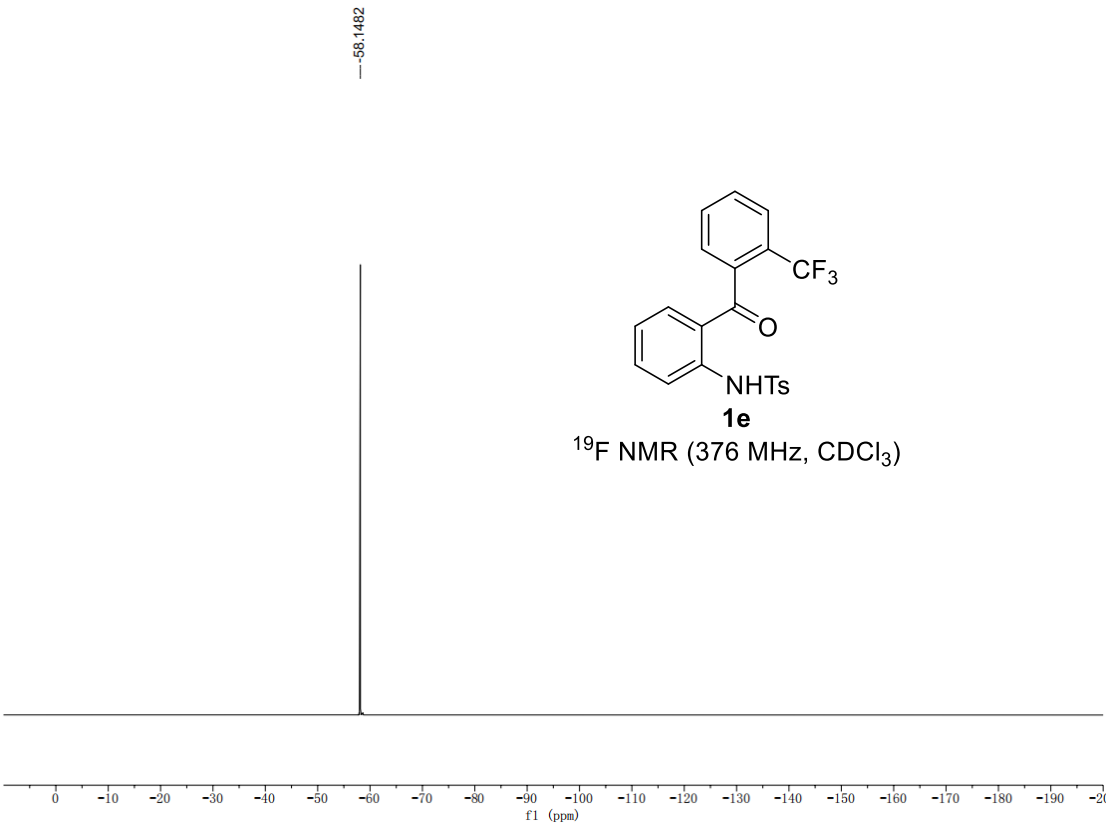



**1d**

$^{13}$C NMR (100 MHz, $CDCl_3$)

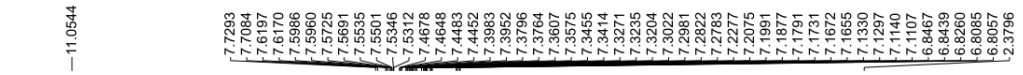

11.0929
7.7991
7.7965
7.7773
7.7672
7.7620
7.7566
7.7497
7.7449
7.6405
7.6385
7.6217
7.6196
7.6059
7.6010
7.5878
7.5841
7.5691
7.5654
7.5126
7.5086
7.4942
7.4907
7.4874
7.2630
7.2561
7.2360
7.1662
7.1622
7.1463
7.1423
7.0892
7.0851
7.0716
7.0670
6.9711
6.9684
6.9526
6.9500
6.9327
6.9299
2.3847
CF3
O
NHTs
1e
1H NMR (400 MHz, CDCl3)
0.988
3.874
1.960
0.987
2.071
0.966
0.959
0.976
3.000
f1 (ppm)

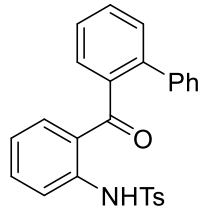

199.1049
144.0752
140.9095
137.5802
137.5574
137.5389
137.5187
136.4236
135.6026
134.8953
131.4220
130.1496
129.7366
128.2984
127.9770
127.8753
127.6558
127.4700
127.3399
126.8537
126.8088
126.7633
126.7178
124.7476
122.5536
122.3685
122.0236
119.5750
119.3005
21.5289
CF3
O
NHTs
1e
13C NMR (100 MHz, CDCl3)
f1 (ppm)




**1e**

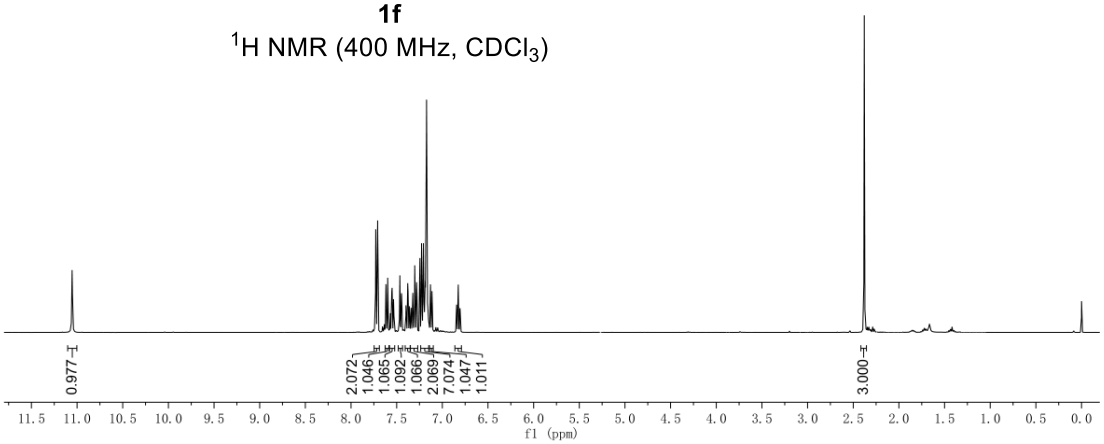
$^{19}F$ NMR (376 MHz, $CDCl_3$)



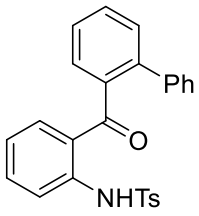




**1f**

$^{1}$H NMR (400 MHz, $CDCl_3$)

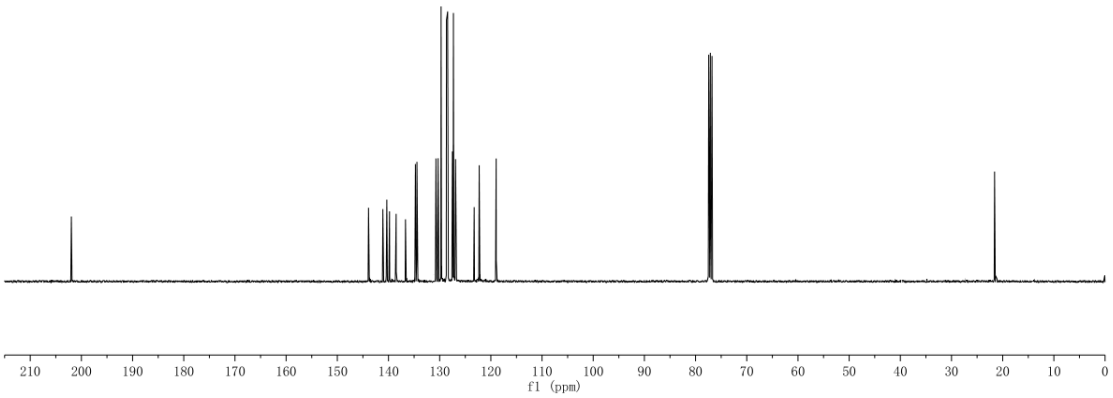


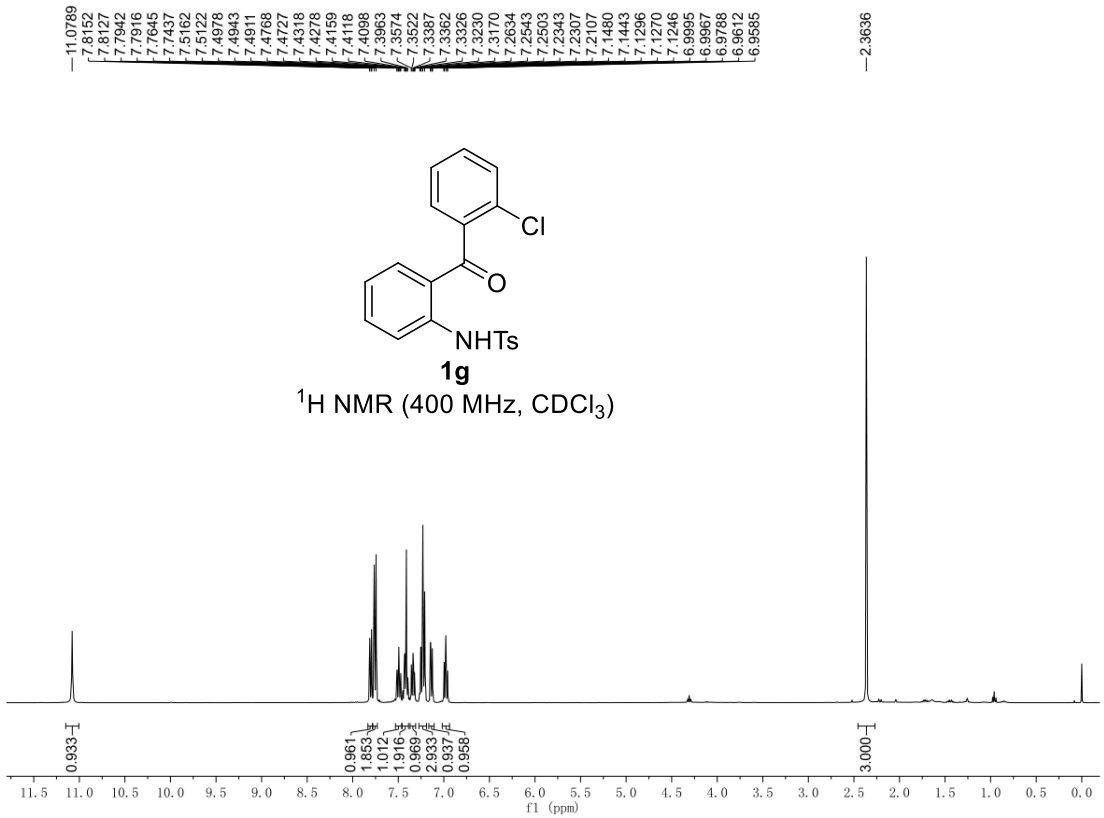





**1f**

$^{13}$C NMR (100 MHz, $CDCl_3$)

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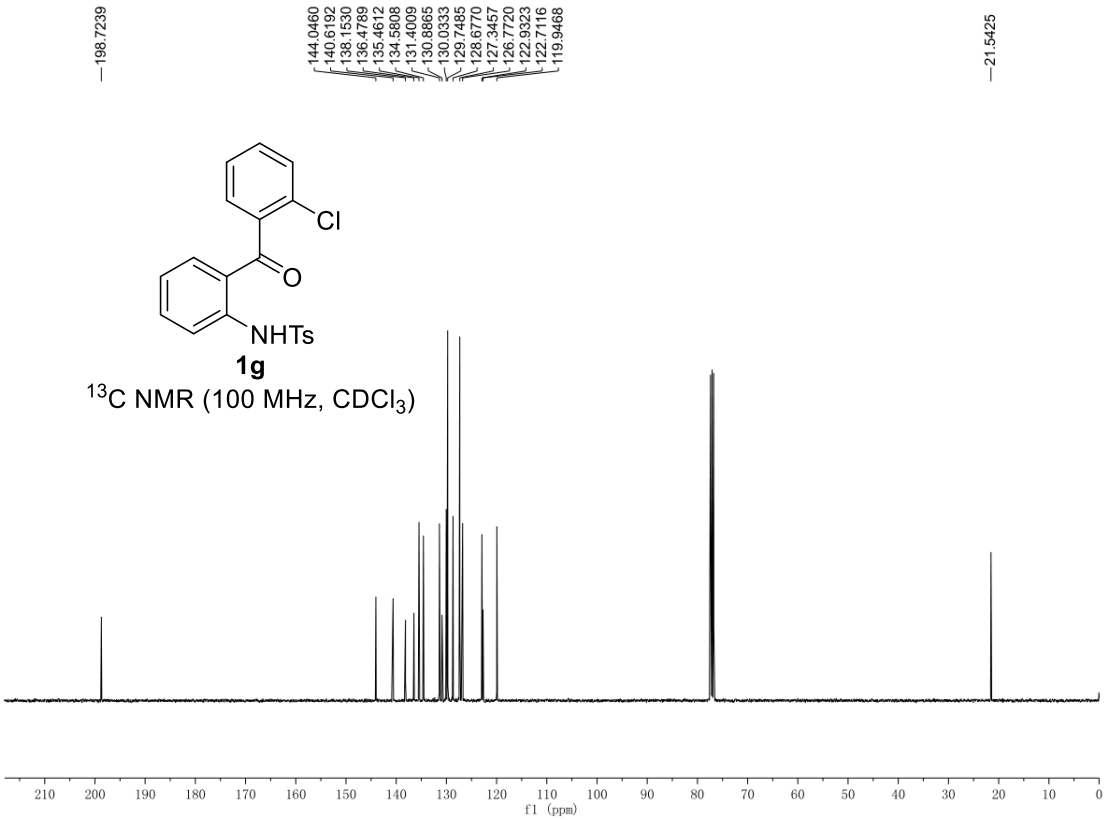
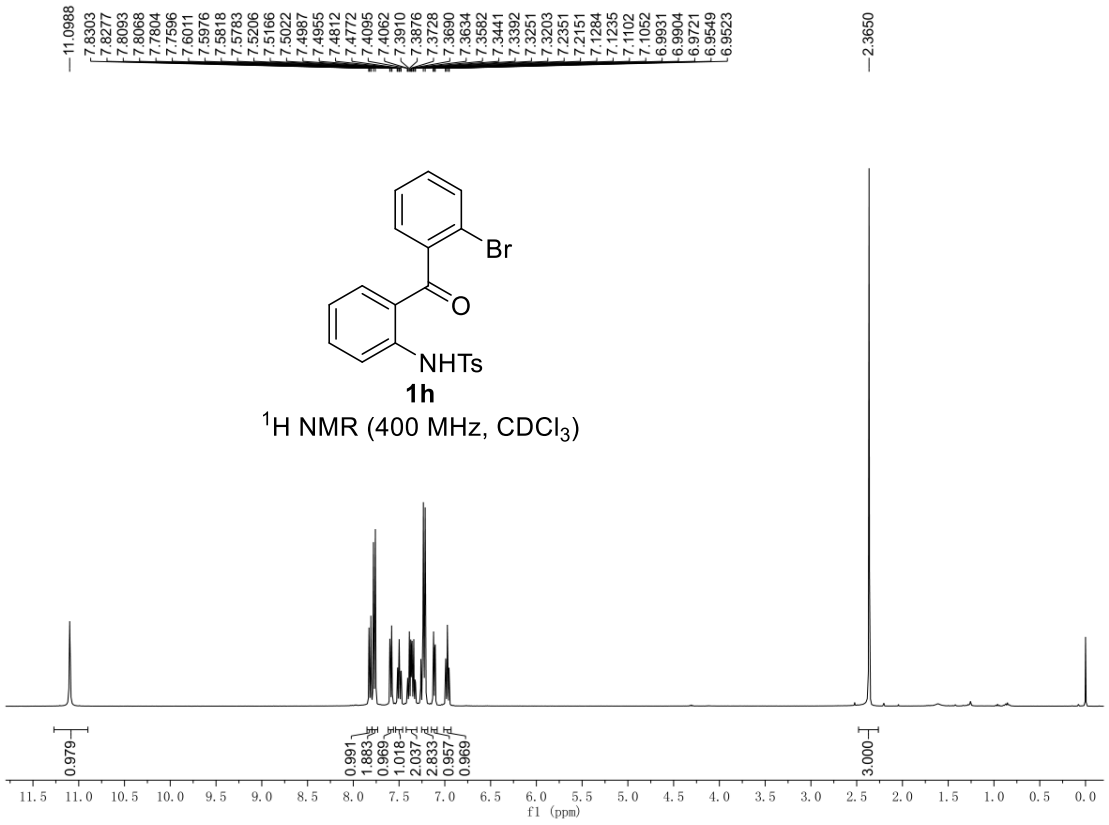
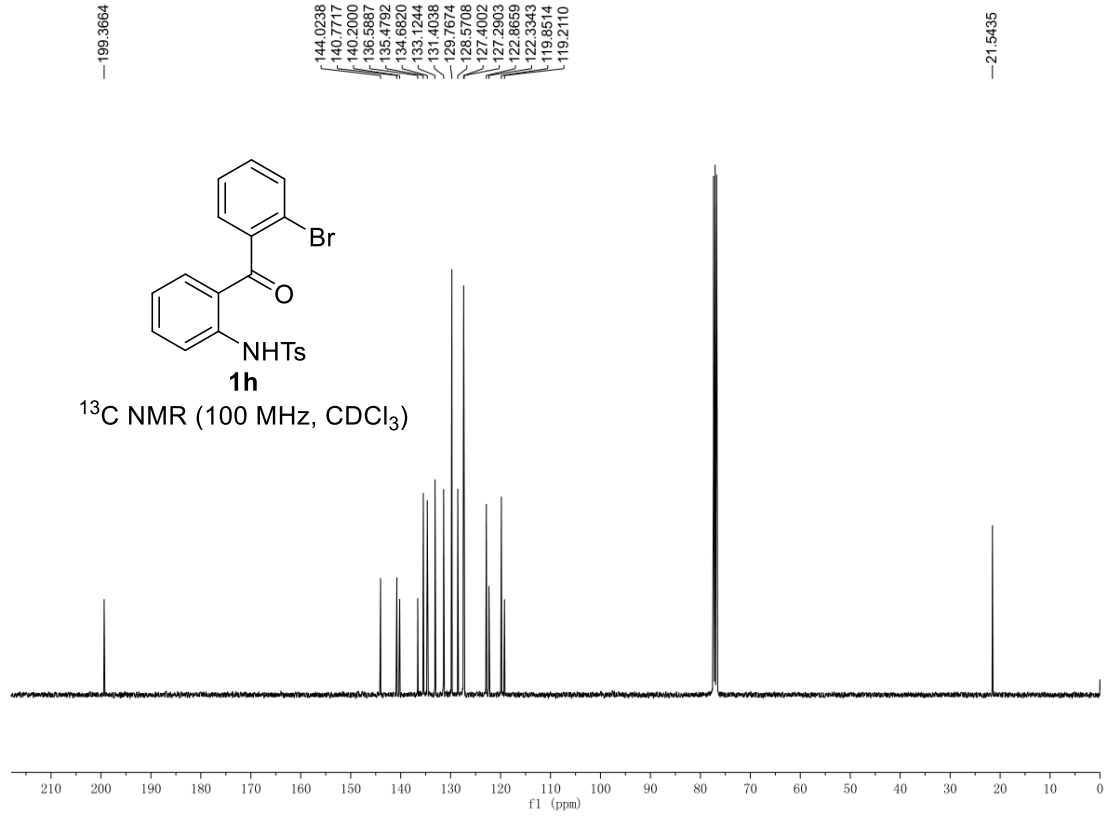
7.8152
7.8127
7.7942
7.7916
7.7645
7.7437
7.5162
7.5122
7.4978
7.4943
7.4911
7.4768
7.4727
7.4318
7.4278
7.4159
7.4118
7.4098
7.3963
7.3574
7.3522
7.3387
7.3362
7.3326
7.3230
7.3170
7.2634
7.2543
7.2503
7.2343
7.2307
7.2107
7.1480
7.1443
7.1296
7.1270
7.1246
6.9995
6.9967
6.9788
6.9612
6.9585
2.3636
Cl
O
NHTs
1g
1H NMR (400 MHz, CDCl3)
0.933
0.961
1.853
1.012
1.916
0.969
2.933
0.937
0.958
3.000
f1 (ppm)


198.7239
144.0460
140.6192
138.1530
136.4789
133.4612
134.5808
131.4009
130.8865
130.0333
129.7485
128.6770
127.3457
126.7720
122.9323
122.7116
119.9468
21.5425
Cl
O
NHTs
1g
13C NMR (100 MHz, CDCl3)
f1 (ppm)


11.0988
7.8303
7.8277
7.8093
7.8068
7.7804
7.7596
7.6011
7.5976
7.5818
7.5783
7.5206
7.5166
7.5022
7.4987
7.4955
7.4812
7.4772
7.4095
7.4062
7.3910
7.3876
7.3728
7.3690
7.3634
7.3582
7.3441
7.3392
7.3251
7.3203
7.2351
7.2151
7.1284
7.1235
7.1102
7.1052
6.9931
6.9904
6.9721
6.9549
6.9523
2.3650
Br
O
NHTs
1h
$^1$H NMR (400 MHz, CDCl$_3$)
0.979
0.991
1.883
0.969
1.018
2.037
2.833
0.957
0.969
3.000
f1 (ppm)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140.7717
140.2000
136.5887
135.4792
134.6820
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131.4038
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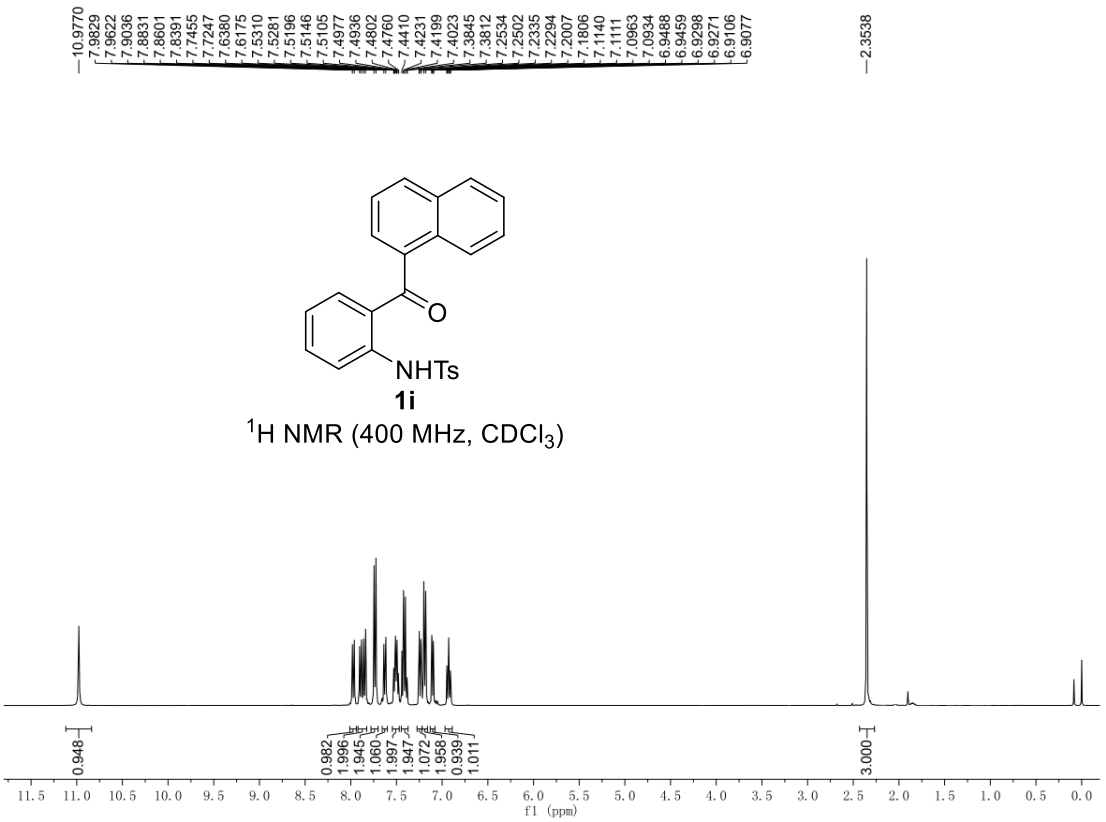
128.5708
127.4002
127.2903
122.8659
122.3343
119.8514
119.2110
21.5435
Br
O
NHTs
1h
$^{13}$C NMR (100 MHz, CDCl$_3$)
f1 (ppm)


10.9770
7.9829
7.9622
7.9036
7.8831
7.8601
7.8391
7.7455
7.7247
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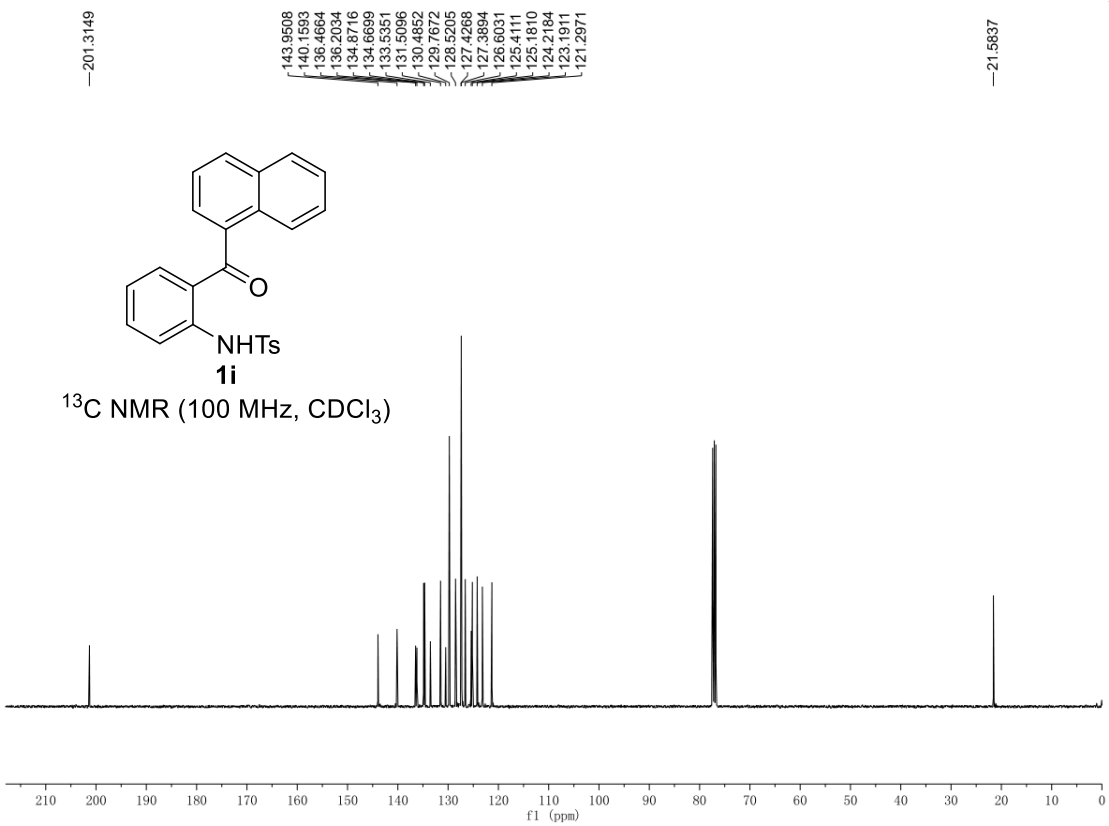
7.6175
7.5310
7.5281
7.5196
7.5146
7.5105
7.4977
7.4936
7.4802
7.4760
7.4410
7.4231
7.4199
7.4023
7.3845
7.3812
7.2534
7.2502
7.2335
7.2294
7.2007
7.1806
7.1140
7.1111
7.0963
7.0934
6.9488
6.9459
6.9298
6.9271
6.9106
6.9077
2.3538
O
NHTs
1i
1H NMR (400 MHz, CDCl3)
0.948
0.982
1.996
1.945
1.060
1.997
1.947
1.072
1.958
0.939
1.011
3.000
f1 (ppm)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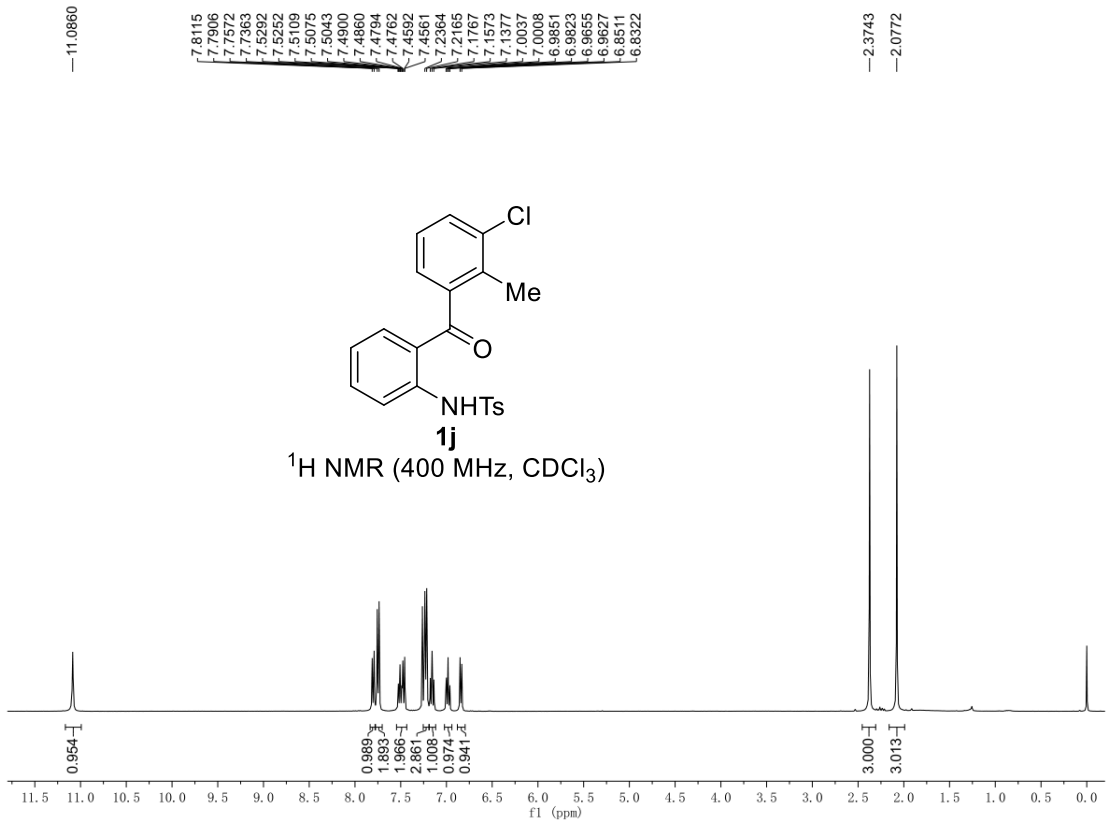
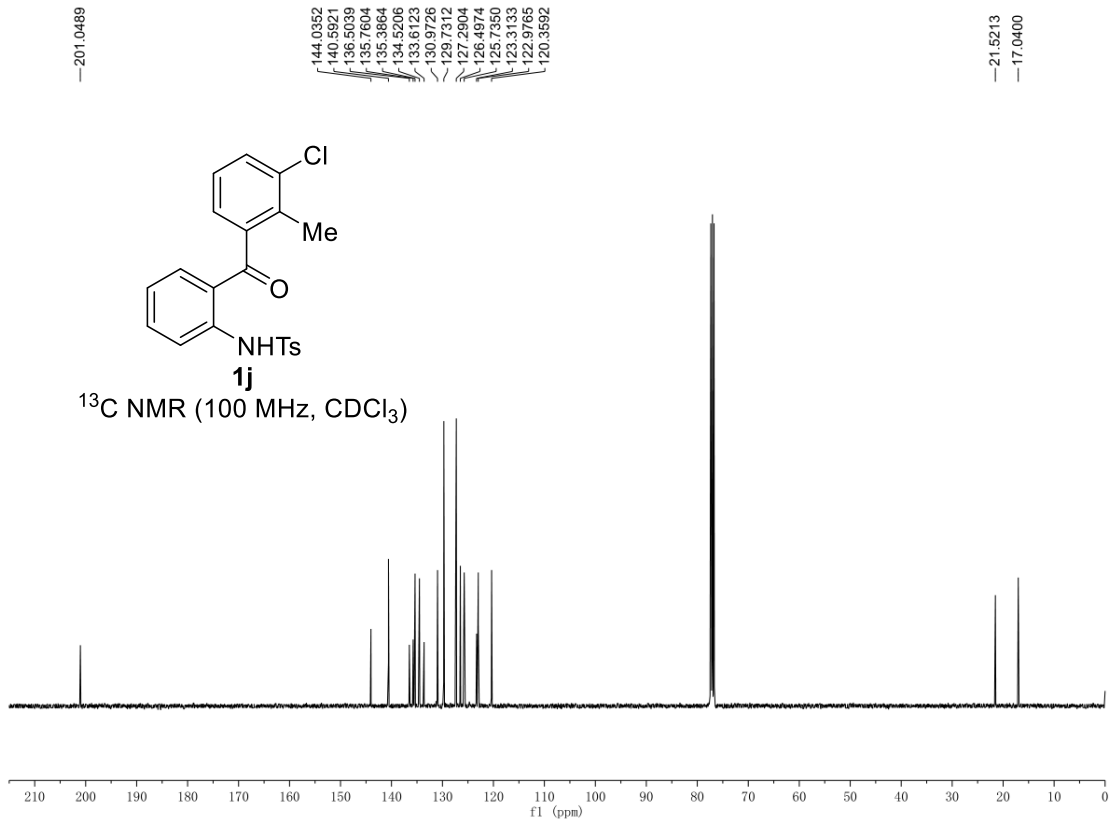
140.1593
136.4664
136.2034
134.8716
134.6699
133.5351
131.5096
130.4852
129.7672
128.5205
127.4268
127.3894
126.6031
125.4111
125.1810
124.2184
123.1911
121.2971
21.5837
O
NHTs
1i
13C NMR (100 MHz, CDCl3)
f1 (ppm)



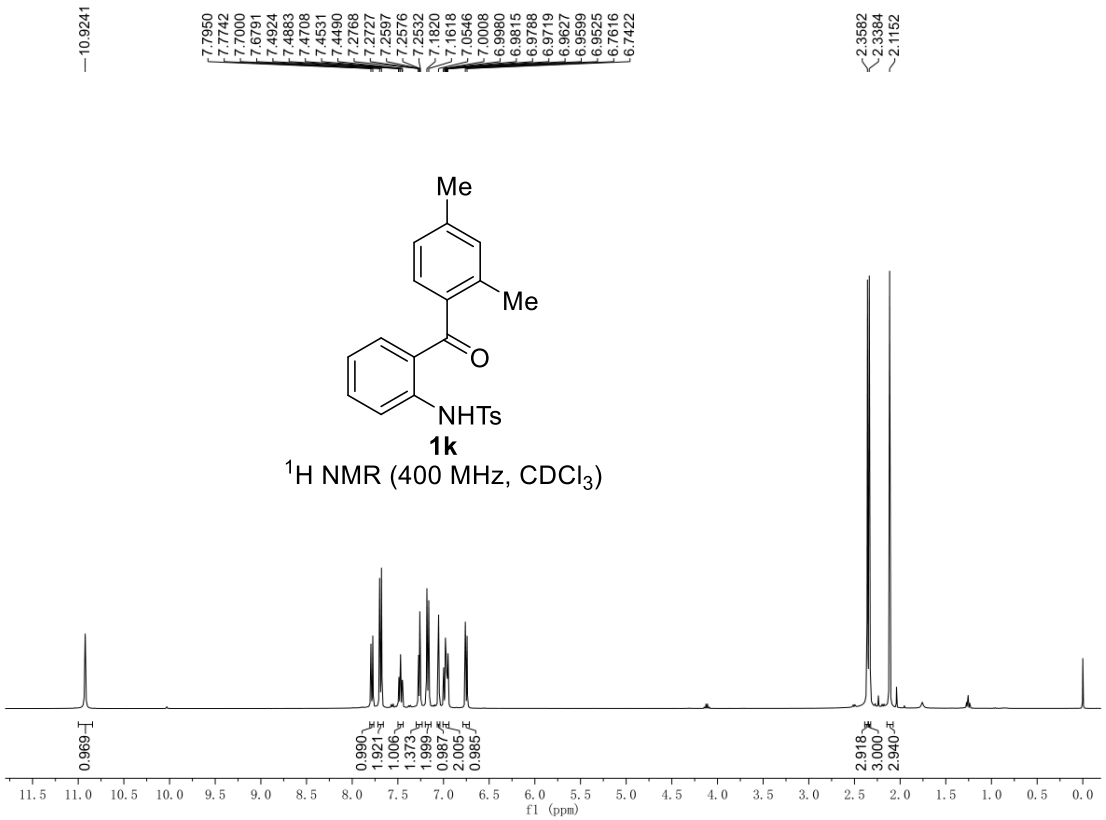

**1j**

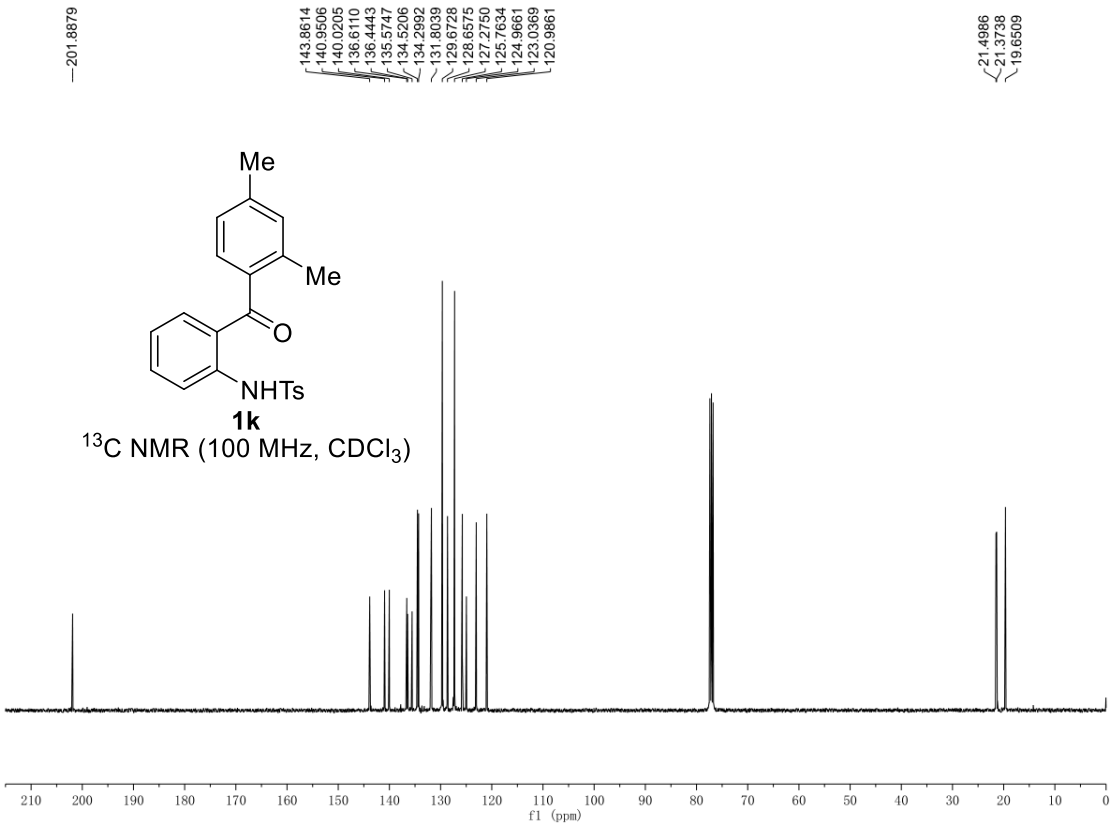
$^{1}$H NMR (400 MHz, $CDCl_3$)

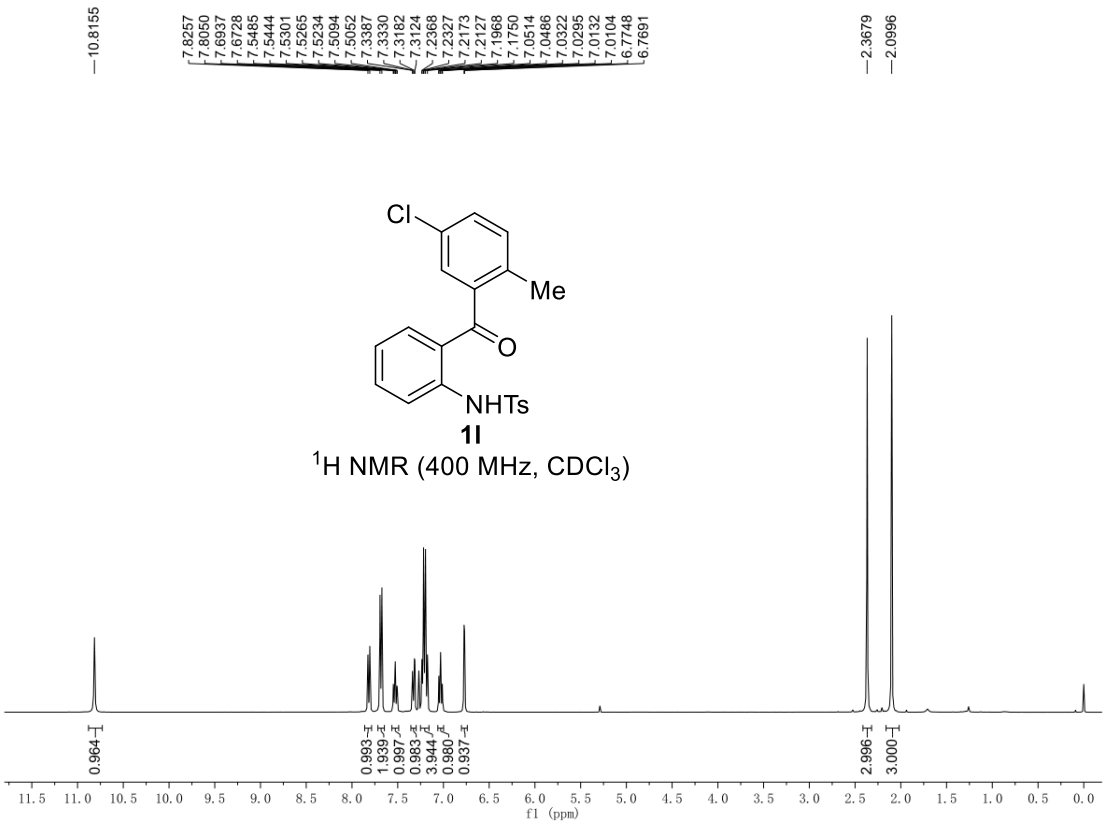


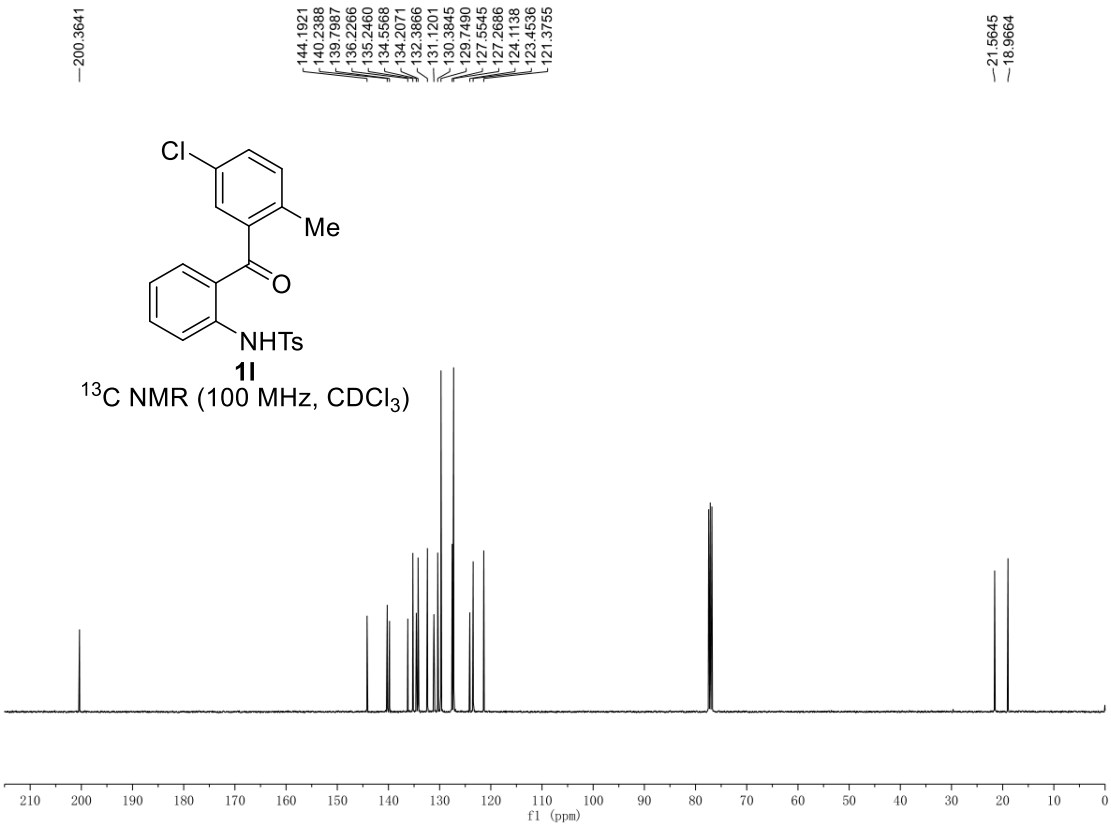

**1j**

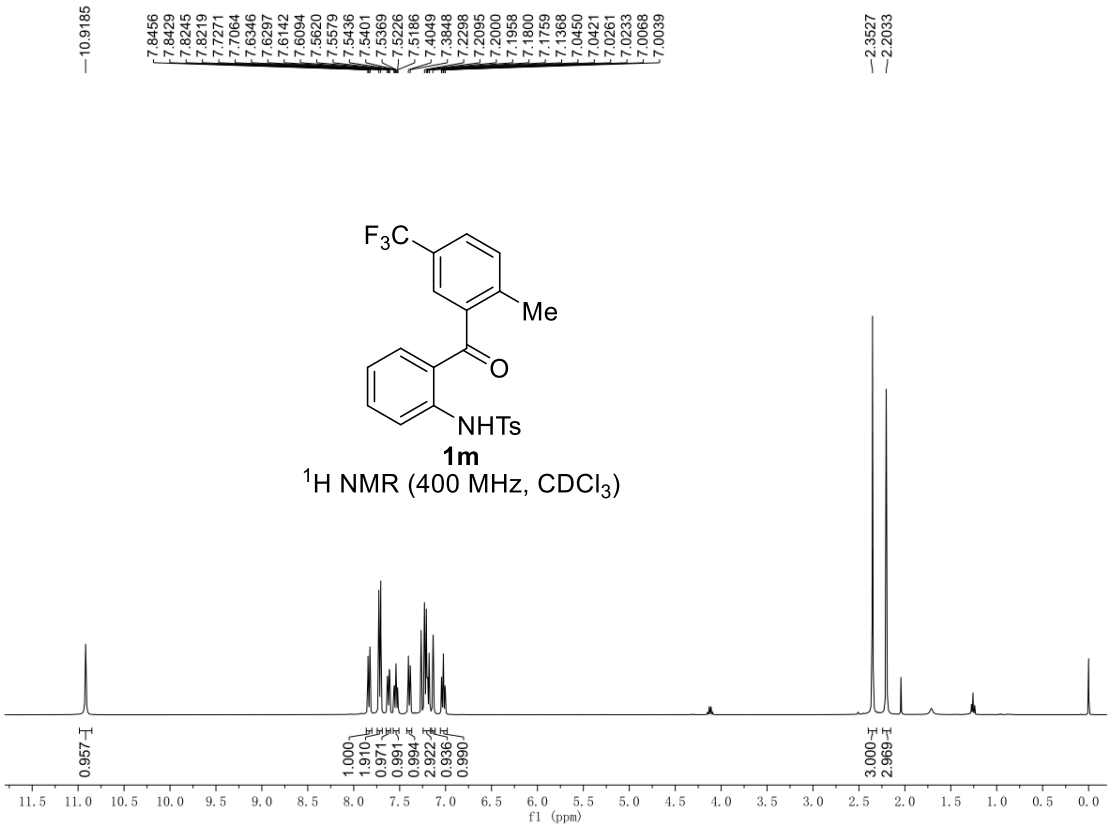
$^{13}$C NMR (100 MHz, $CDCl_3$)


10.9241
7.7950
7.7742
7.7000
7.6791
7.4924
7.4883
7.4708
7.4531
7.4490
7.2768
7.2727
7.2597
7.2576
7.2532
7.1820
7.1618
7.0546
7.0008
6.9980
6.9815
6.9788
6.9719
6.9627
6.9599
6.9525
6.7616
6.7422
2.3582
2.3384
2.1152
Me
Me
O
NHTs
1k
1H NMR (400 MHz, CDCl3)
0.969
0.990
1.921
1.006
1.373
1.999
0.987
2.005
0.985
2.918
3.000
2.940
f1 (ppm)


201.8879
143.8614
140.9506
140.0205
136.6110
136.4443
135.5747
134.5206
134.2992
131.8039
129.6728
128.6575
127.2750
125.7634
124.9661
123.0369
120.9861
21.4986
21.3738
19.6509
Me
Me
O
NHTs
1k
13C NMR (100 MHz, CDCl3)
f1 (ppm)


10.8155
7.8257
7.8050
7.6937
7.6728
7.5485
7.5444
7.5301
7.5265
7.5234
7.5094
7.5052
7.3387
7.3330
7.3182
7.3124
7.2368
7.2327
7.2173
7.2127
7.1968
7.1750
7.0514
7.0486
7.0322
7.0295
7.0132
7.0104
6.7748
6.7691
2.3679
2.0996
Cl
Me
O
NHTs
1l
1H NMR (400 MHz, CDCl3)
0.964
0.993
1.939
0.997
0.983
3.944
0.980
0.937
2.996
3.000
f1 (ppm)


200.3641
144.1921
140.2388
139.7987
136.2266
135.2460
134.5568
134.2071
132.3866
131.1201
130.3845
129.7490
127.5545
127.2686
124.1138
123.4536
121.3755
21.5645
18.9664
Cl
Me
O
NHTs
1l
13C NMR (100 MHz, CDCl3)
f1 (ppm)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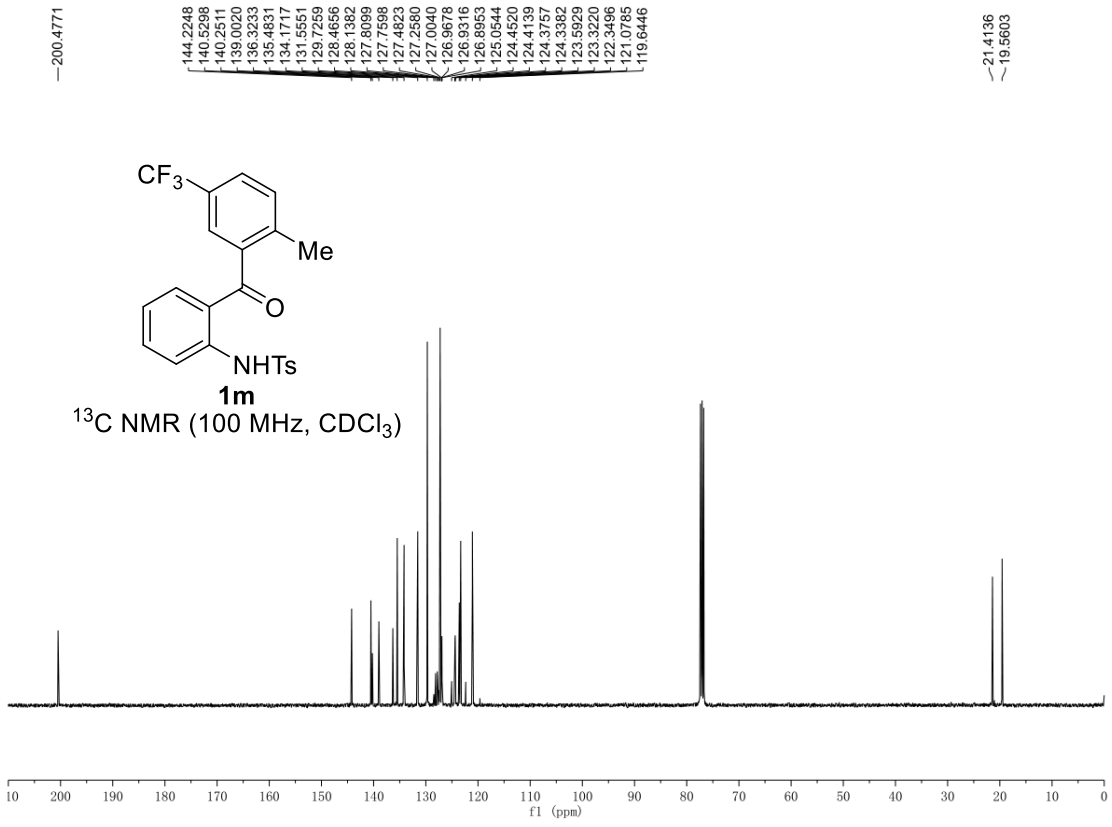
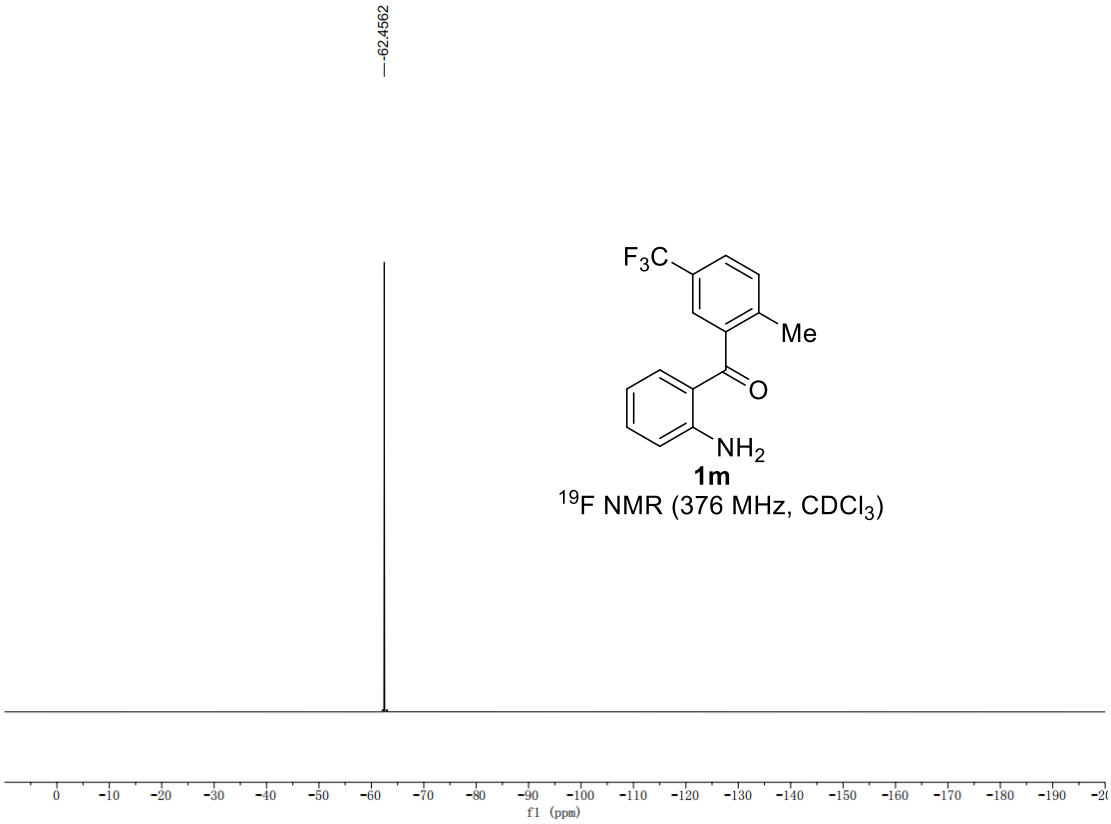
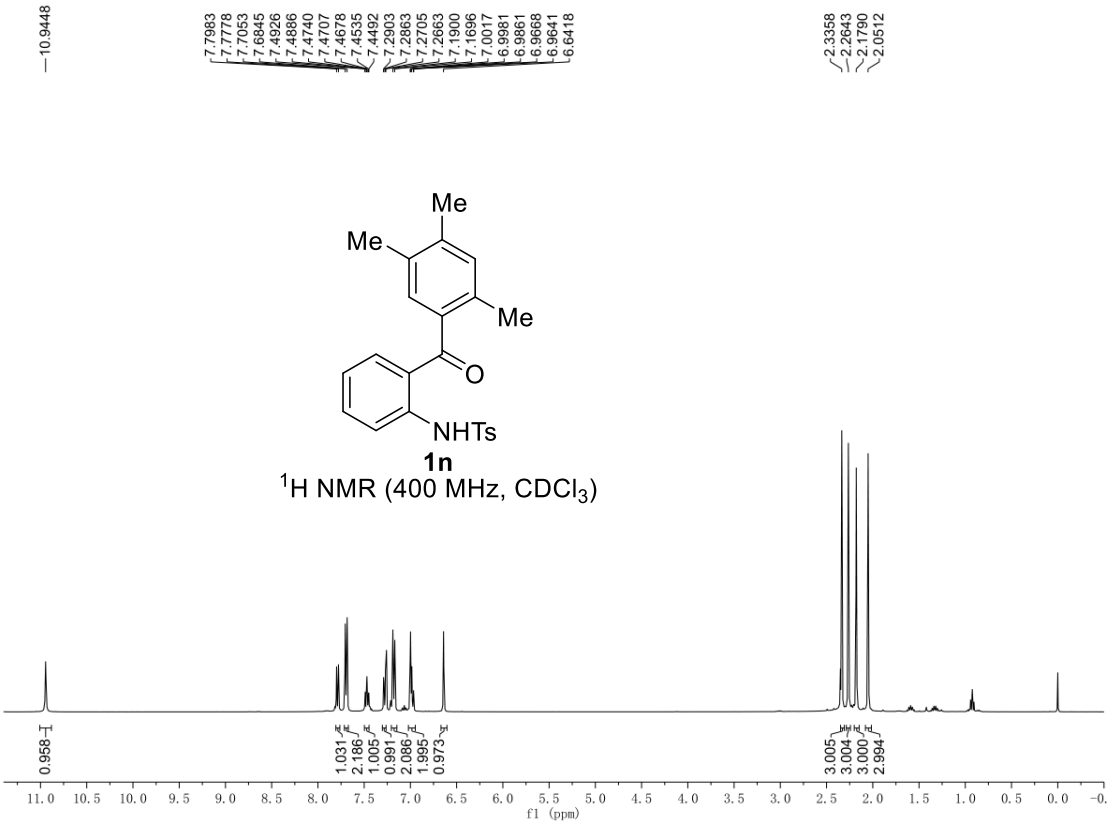
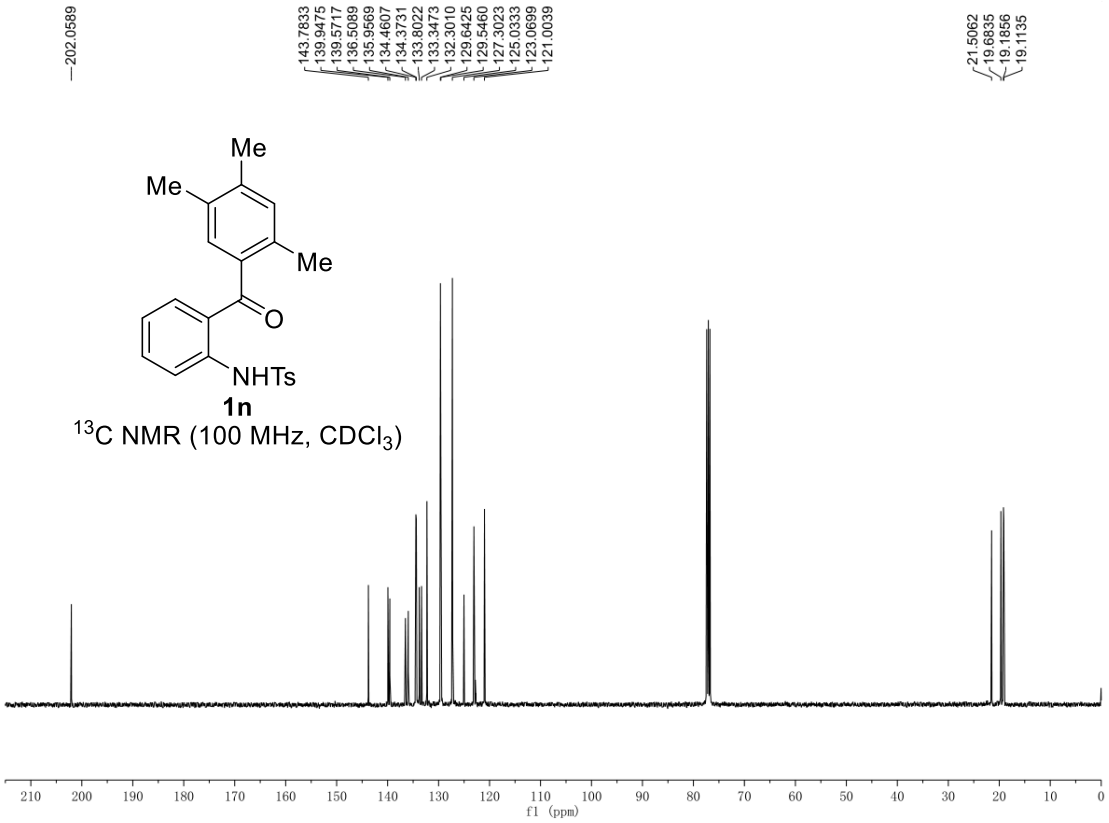
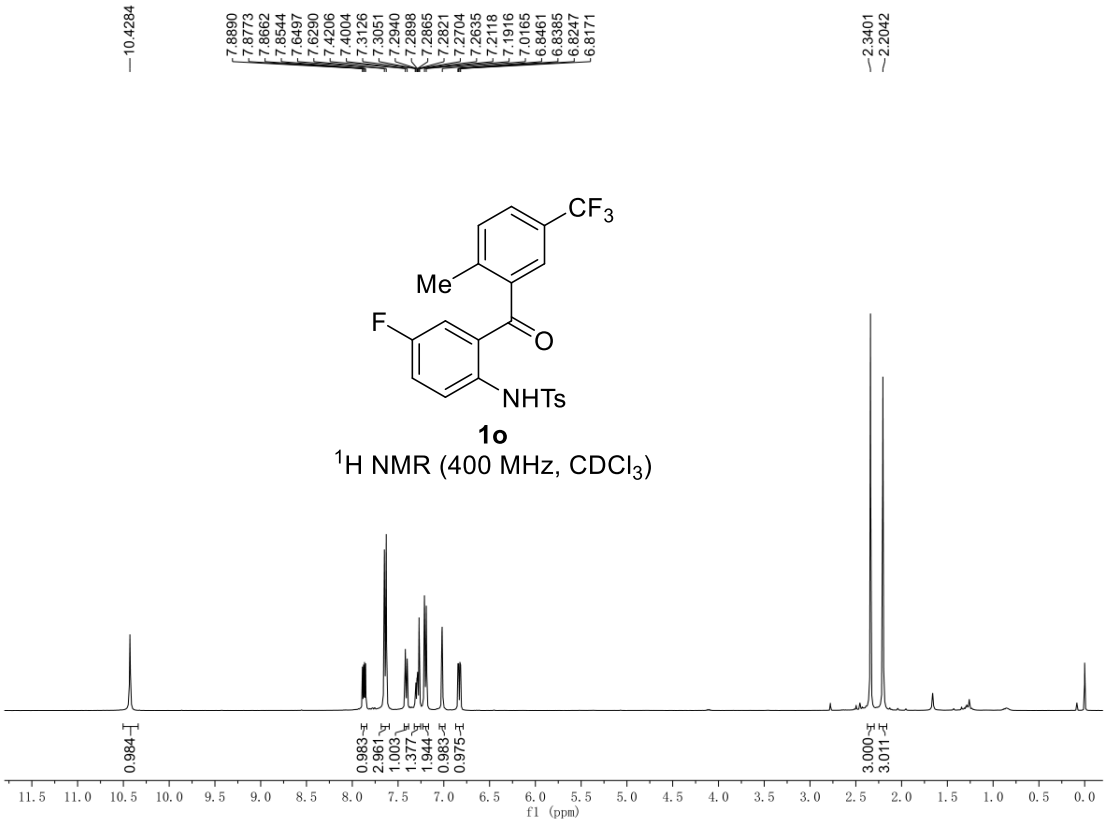
7.8456
7.8429
7.8245
7.8219
7.7271
7.7064
7.6346
7.6297
7.6142
7.6094
7.5620
7.5579
7.5436
7.5401
7.5369
7.5226
7.5186
7.4049
7.3848
7.2298
7.2095
7.2000
7.1958
7.1800
7.1759
7.1388
7.0450
7.0421
7.0261
7.0233
7.0068
7.0039
2.3527
2.2033
F3C
Me
O
NHTs
1m
1H NMR (400 MHz, CDCl3)
0.957
1.000
1.910
0.971
0.991
0.994
2.922
0.936
0.990
3.000
2.969
f1 (ppm)

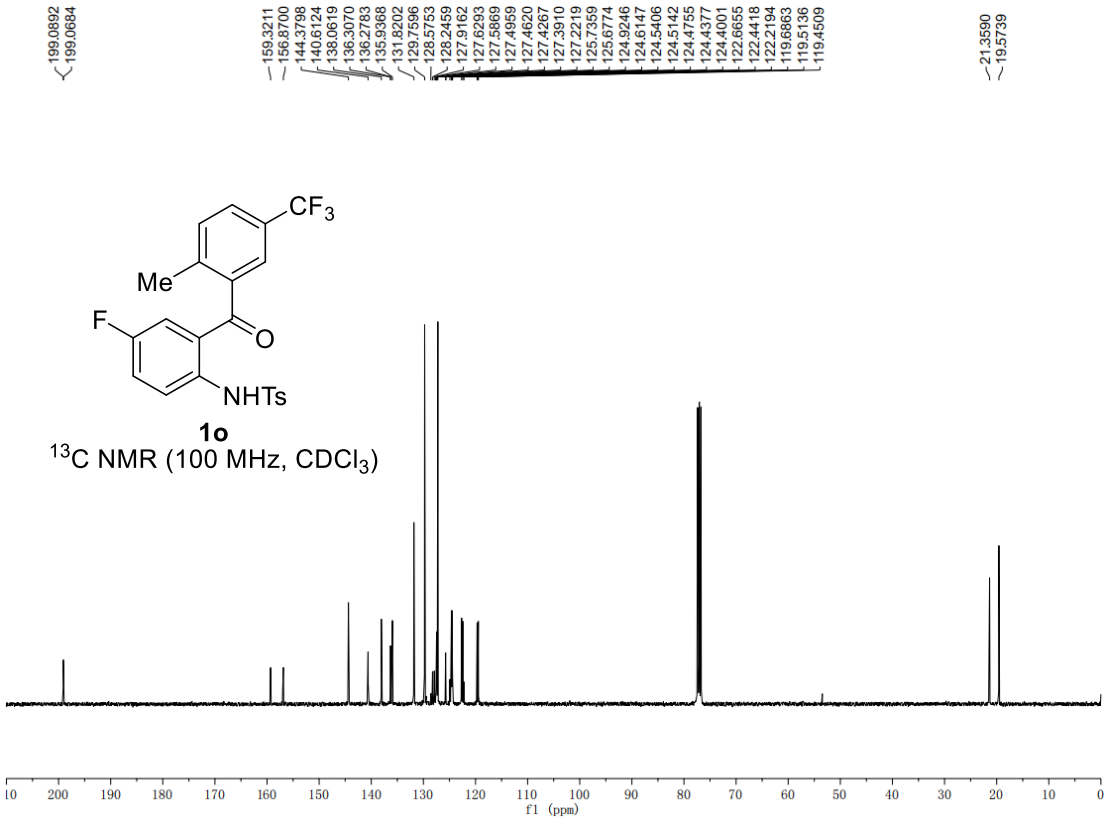

200.4771
144.2248
140.5298
140.2511
139.0020
136.3233
135.4831
134.1717
131.5551
129.7259
128.4656
128.1382
127.8099
127.7598
127.4823
127.2580
127.0040
126.9678
126.9316
126.8953
125.0544
124.4520
124.4139
124.3757
124.3382
123.5929
123.3220
122.3496
121.0785
119.6446
21.4136
19.5603
CF3
Me
O
NHTs
1m
13C NMR (100 MHz, CDCl3)
f1 (ppm)

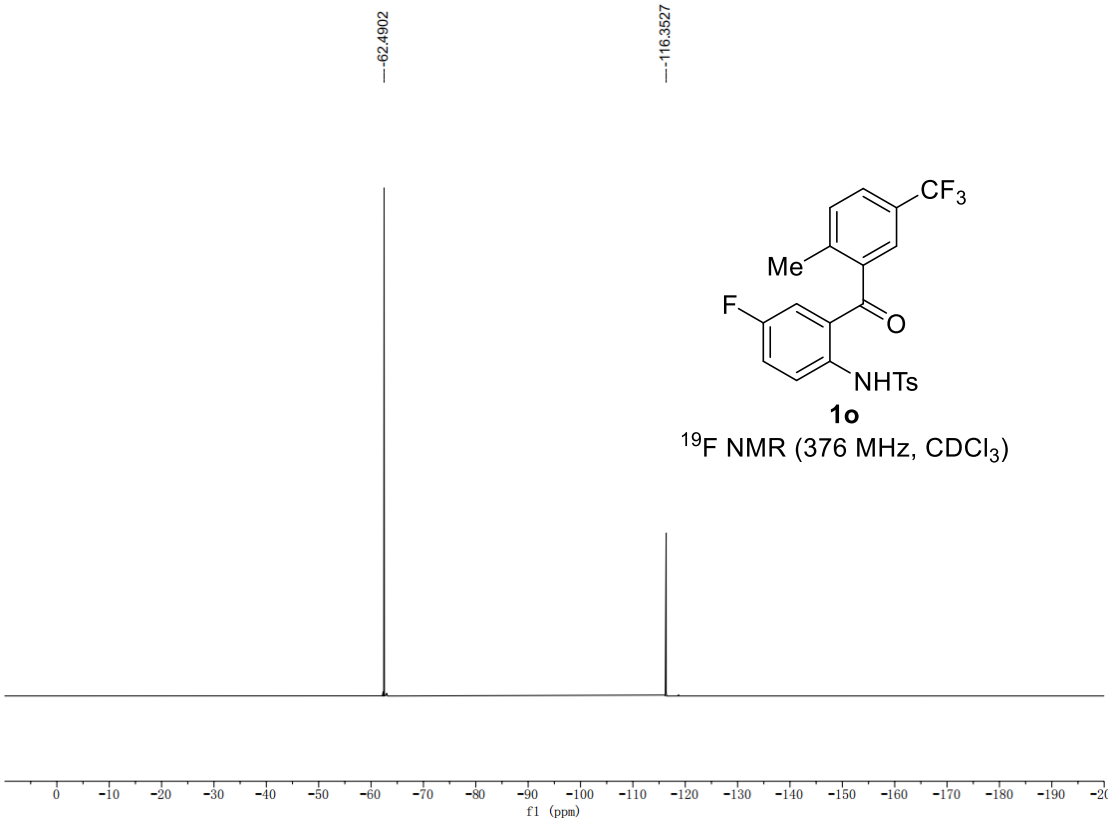

-62.4562
F3C
Me
O
NH2
1m
19F NMR (376 MHz, CDCl3)
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

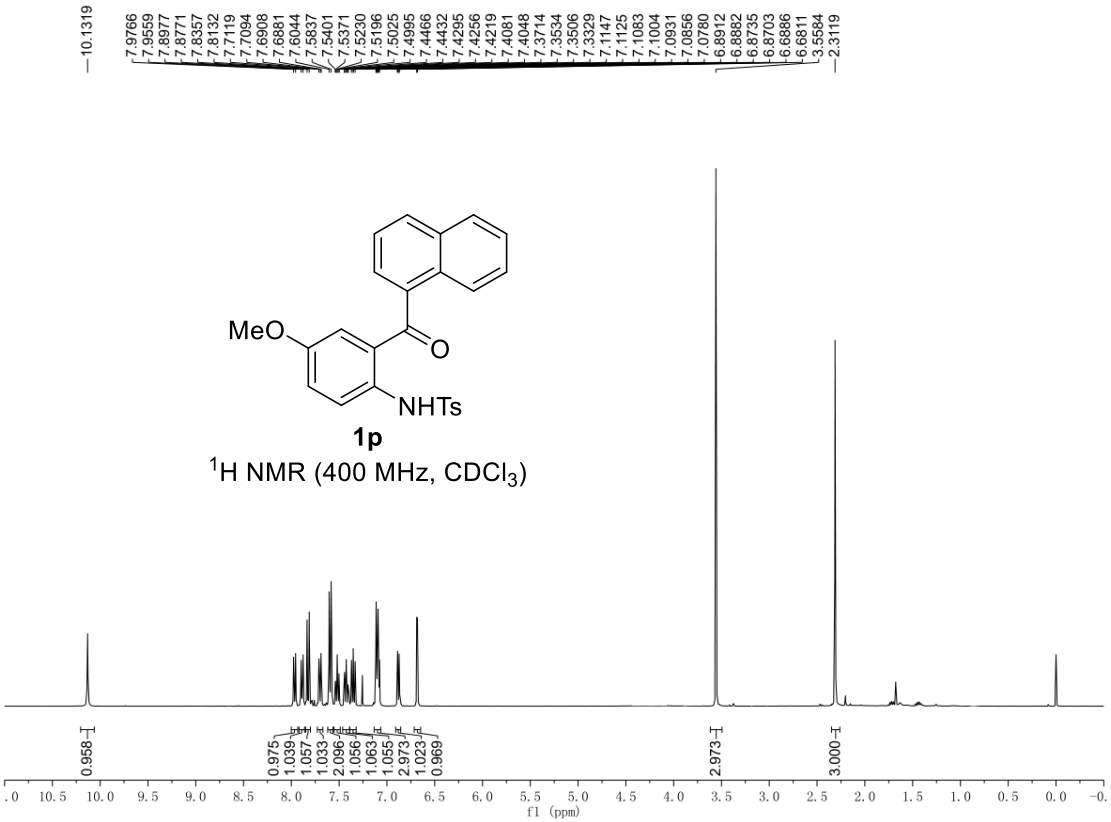

10.9448
7.7983
7.7778
7.7053
7.6845
7.4926
7.4886
7.4740
7.4707
7.4678
7.4535
7.4492
7.2903
7.2863
7.2705
7.2663
7.1900
7.1696
7.0017
6.9981
6.9861
6.9668
6.9641
6.6418
2.3358
2.2643
2.1790
2.0512
Me
Me
Me
O
NHTs
1n
1H NMR (400 MHz, CDCl3)
0.958
1.031
2.186
1.005
0.991
2.086
1.995
0.973
3.005
3.004
3.000
2.994
f1 (ppm)

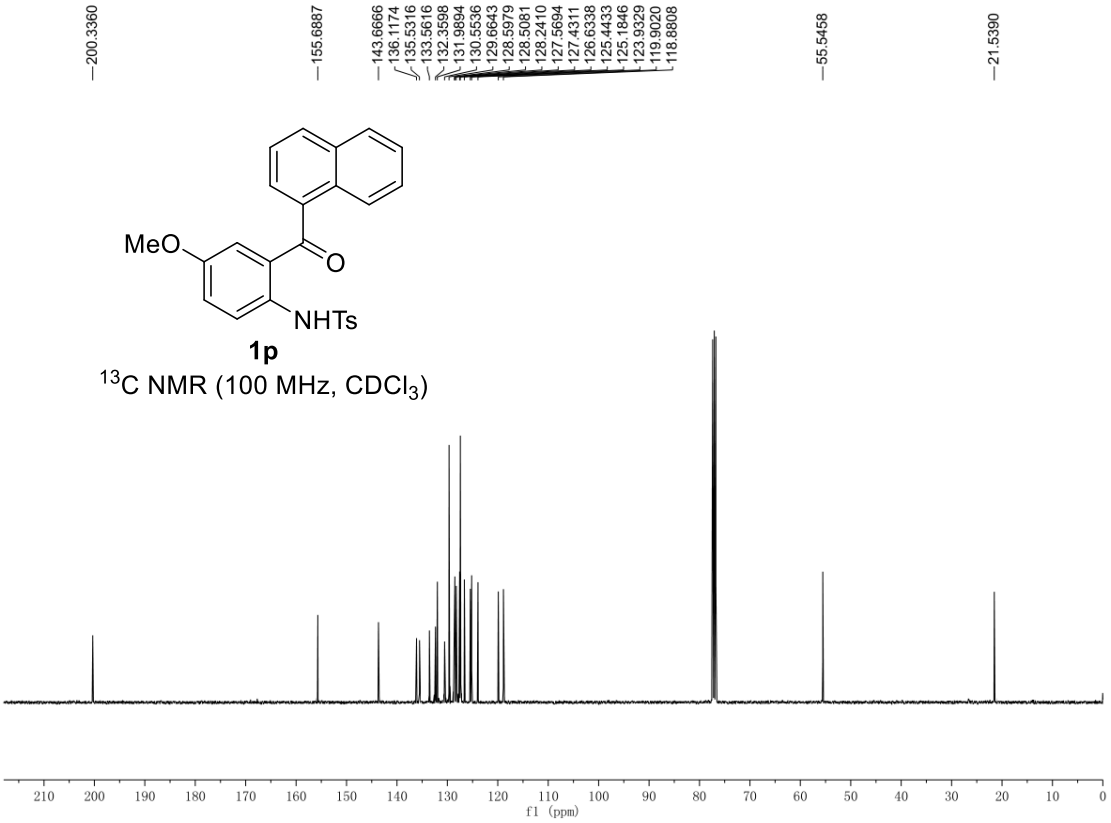

202.0589
143.7833
139.9475
139.5717
136.5089
135.9569
134.4607
134.3731
133.8022
133.3473
132.3010
129.6425
129.5460
127.3023
125.0333
123.0699
121.0039
21.5062
19.6835
19.1856
19.1135
Me
Me
Me
O
NHTs
1n
13C NMR (100 MHz, CDCl3)
f1 (ppm)

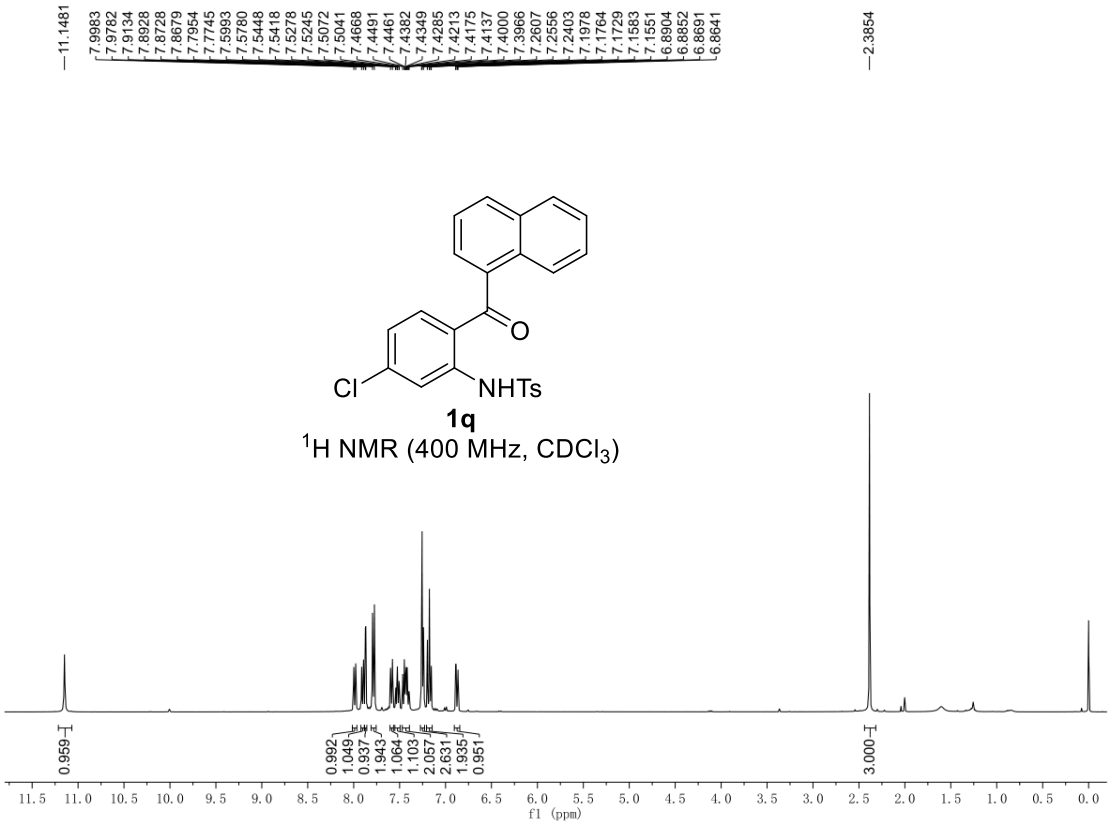

10.4284
7.8890
7.8773
7.8662
7.8544
7.6497
7.6290
7.4206
7.4004
7.3126
7.3051
7.2940
7.2898
7.2865
7.2821
7.2704
7.2635
7.2118
7.1916
7.0165
6.8461
6.8385
6.8247
6.8171
2.3401
2.2042
CF3
Me
F
O
NHTs
1o
1H NMR (400 MHz, CDCl3)
0.984
0.983
2.961
1.003
1.377
1.944
0.983
0.975
3.000
3.011
f1 (ppm)

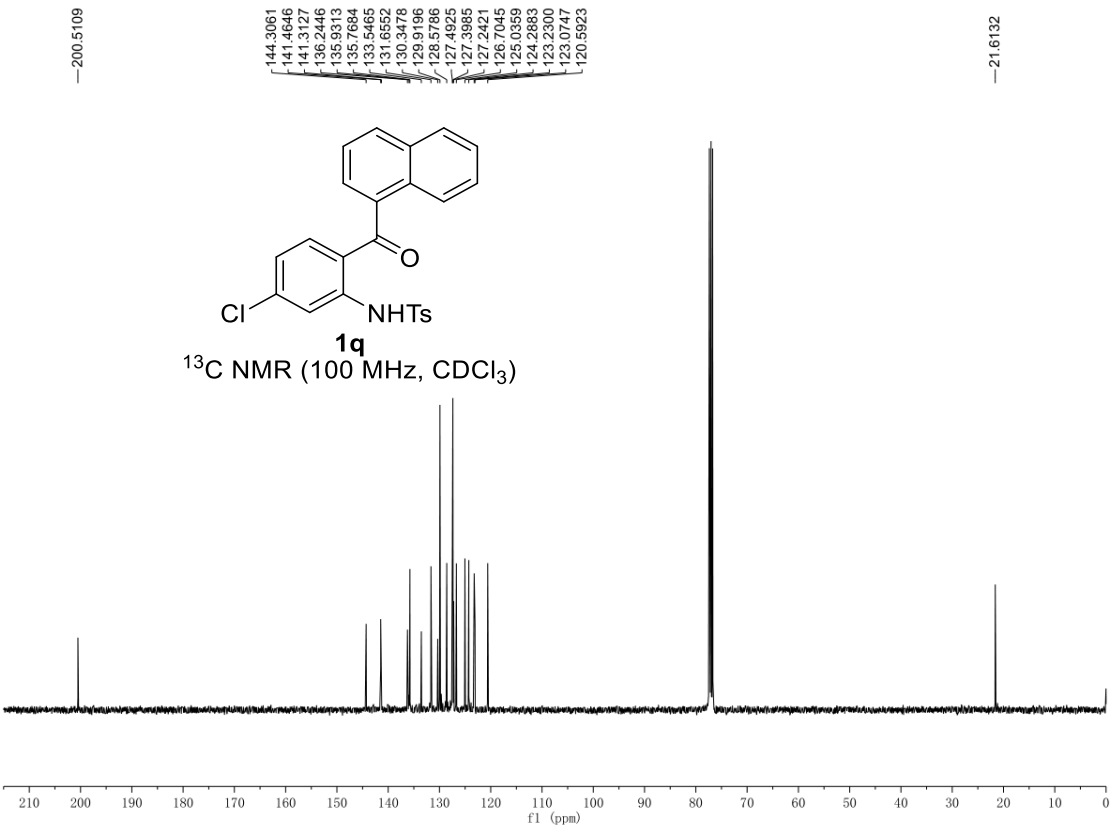

199.0892
199.0684
159.3211
156.8700
144.3798
140.6124
138.0619
136.3070
136.2783
135.9368
131.8202
129.7596
128.5753
128.2459
127.9162
127.6293
127.5869
127.4959
127.4620
127.4267
127.3910
127.2219
125.7359
125.6774
124.9246
124.6147
124.5406
124.5142
124.4755
124.4377
124.4001
122.6655
122.4418
122.2194
119.6863
119.5136
119.4509
21.3590
19.5739
CF3
Me
F
O
NHTs
1o
13C NMR (100 MHz, CDCl3)
f1 (ppm)

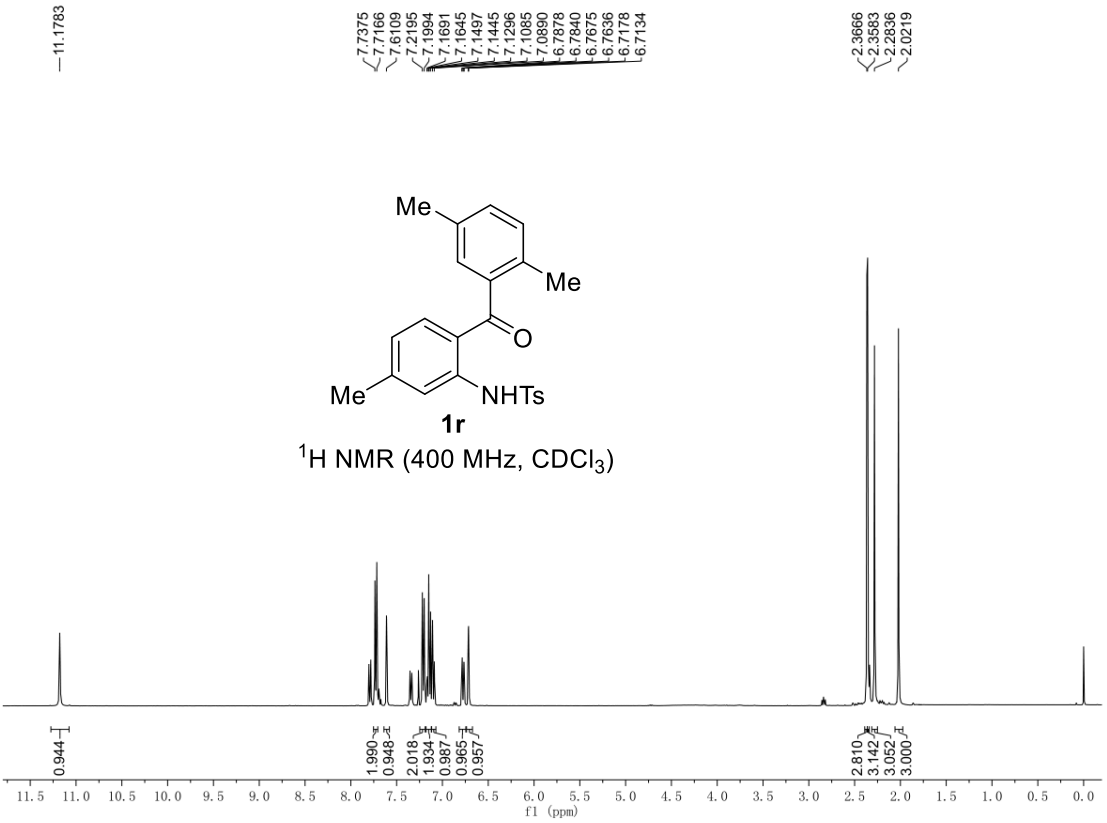

-62.4902
-116.3527
CF3
Me
F
O
NHTs
1o
19F NMR (376 MHz, CDCl3)
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
f1 (ppm)

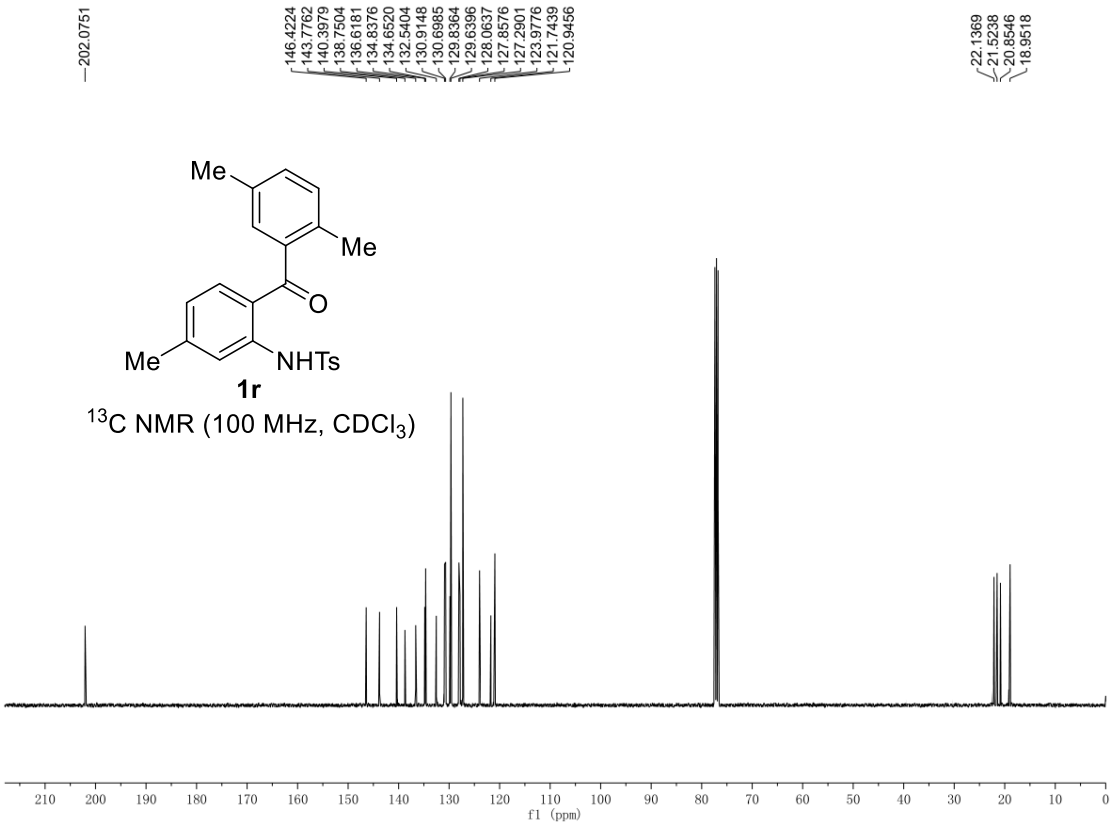

10.1319
7.9766
7.9559
7.8977
7.8771
7.8357
7.8132
7.7119
7.7094
7.6908
7.6881
7.6044
7.5837
7.5401
7.5371
7.5230
7.5196
7.5025
7.4995
7.4466
7.4432
7.4295
7.4256
7.4219
7.4081
7.4048
7.3714
7.3534
7.3506
7.3329
7.1147
7.1125
7.1083
7.1004
7.0931
7.0856
7.0780
6.8912
6.8882
6.8735
6.8703
6.6886
6.6811
3.5584
2.3119
MeO
O
NHTs
1p
1H NMR (400 MHz, CDCl3)
0.958
0.975
1.039
1.057
1.033
2.096
1.056
1.063
1.055
2.973
1.023
0.969
2.973
3.000
f1 (ppm)

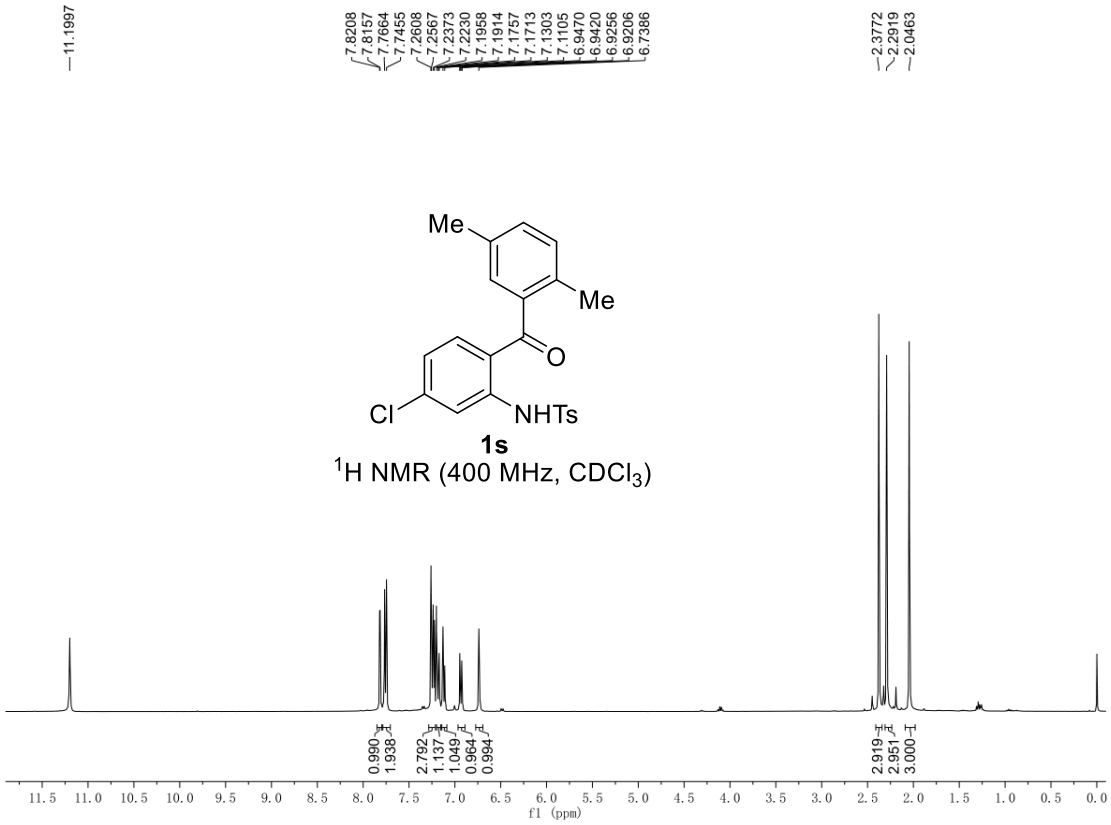

200.3360
155.6887
143.6666
136.1174
135.5316
133.5616
132.3598
131.9894
130.5536
129.6643
128.5979
128.5081
128.2410
127.5694
127.4311
126.6338
125.4433
125.1846
123.9329
119.9020
118.8808
55.5458
21.5390
MeO
O
NHTs
1p
13C NMR (100 MHz, CDCl3)
f1 (ppm)

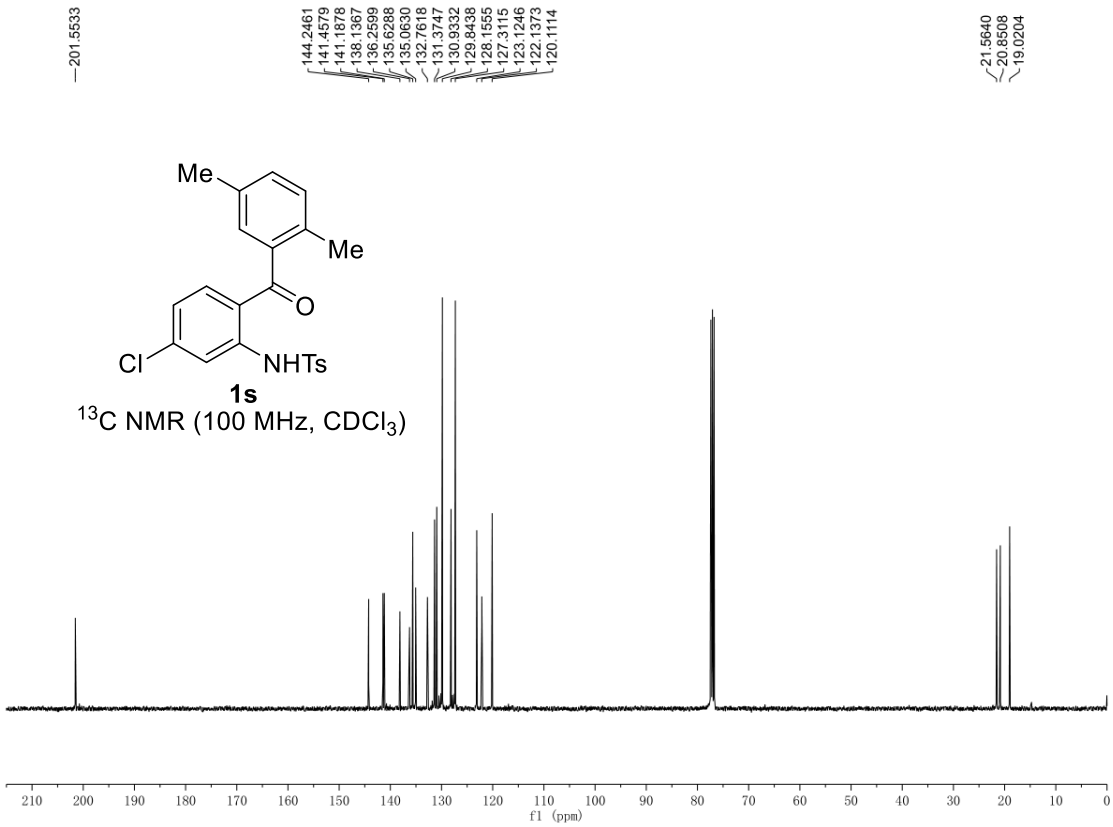

11.1481
7.9983
7.9782
7.9134
7.8928
7.8728
7.8679
7.7954
7.7745
7.5993
7.5780
7.5448
7.5418
7.5278
7.5245
7.5072
7.5041
7.4668
7.4491
7.4461
7.4382
7.4349
7.4285
7.4213
7.4175
7.4137
7.4000
7.3966
7.2607
7.2556
7.2403
7.1978
7.1764
7.1729
7.1583
7.1551
6.8904
6.8852
6.8691
6.8641
2.3854
O
Cl
NHTs
1q
$^{1}$H NMR (400 MHz, $CDCl_3$)
0.959
0.992
1.049
0.937
1.943
1.064
1.103
2.057
2.631
1.935
0.951
3.000
f1 (ppm)

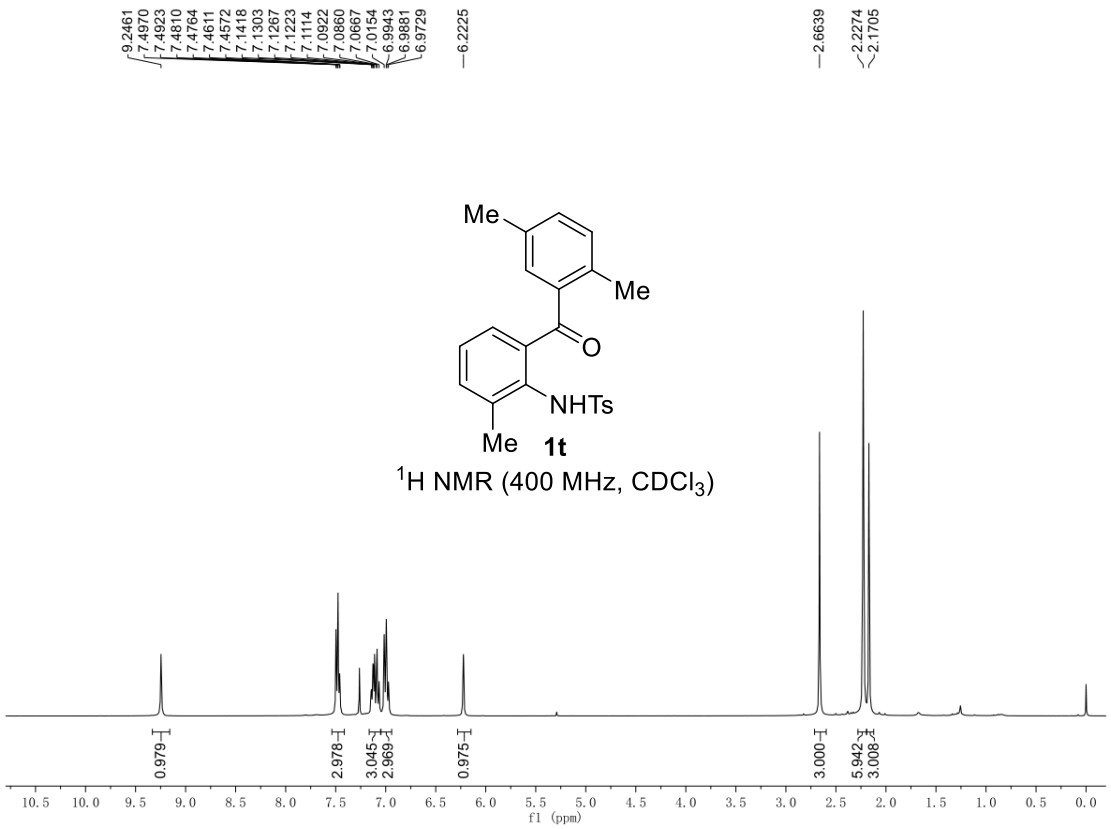

200.5109
144.3061
141.4646
141.3127
136.2446
135.9313
135.7684
133.5465
131.6552
130.3478
129.9196
128.5786
127.4925
127.3985
127.2421
126.7045
125.0359
124.2883
123.2300
123.0747
120.5923
21.6132
O
Cl
NHTs
1q
$^{13}$C NMR (100 MHz, $CDCl_3$)
f1 (ppm)

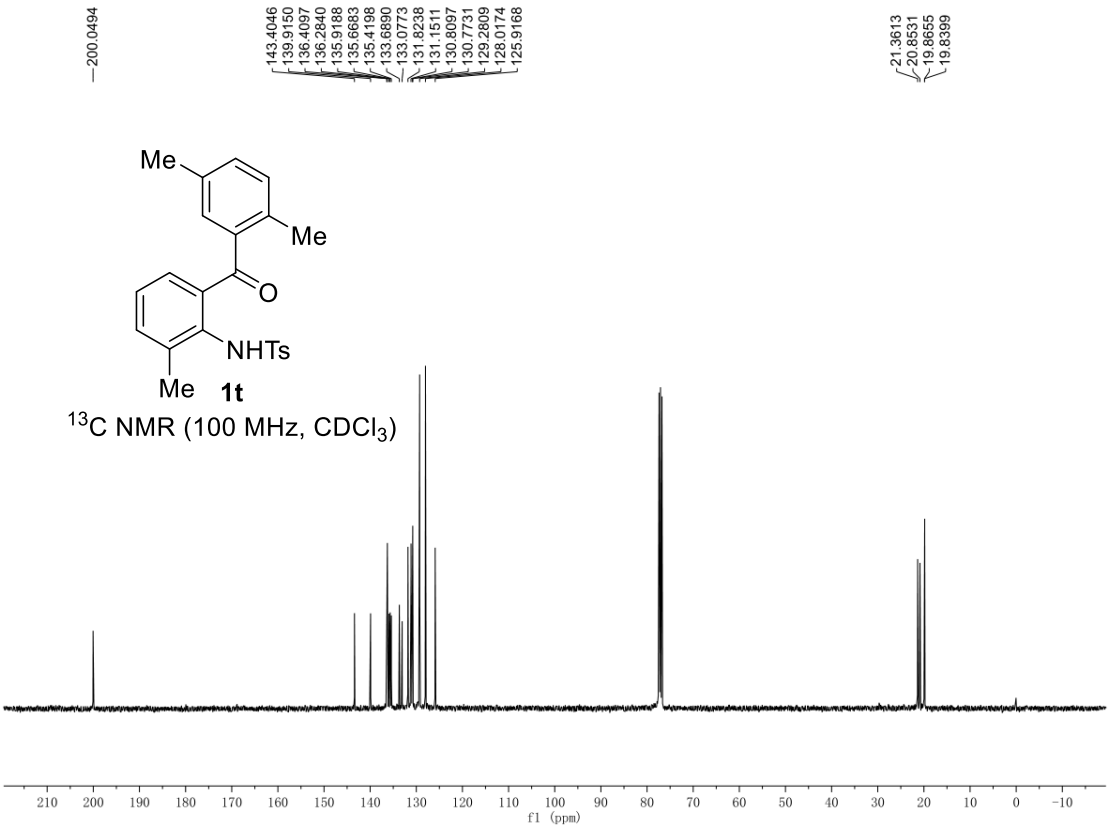

11.1783
7.7375
7.7166
7.6109
7.2195
7.1994
7.1691
7.1645
7.1497
7.1445
7.1296
7.1085
7.0890
6.7878
6.7840
6.7675
6.7636
6.7178
6.7134
2.3666
2.3583
2.2836
2.0219
Me
Me
O
Me
NHTs
1r
1H NMR (400 MHz, CDCl3)
0.944
1.990
0.948
2.018
1.934
0.987
0.965
0.957
2.810
3.142
3.052
3.000
f1 (ppm)


202.0751
146.4224
143.7762
140.3979
138.7504
136.6181
134.8376
134.6520
132.5404
130.9148
130.6985
129.8364
129.6396
128.0637
127.8576
127.2901
123.9776
121.7439
120.9456
22.1369
21.5238
20.8546
18.9518
Me
Me
O
Me
NHTs
1r
13C NMR (100 MHz, CDCl3)
f1 (ppm)

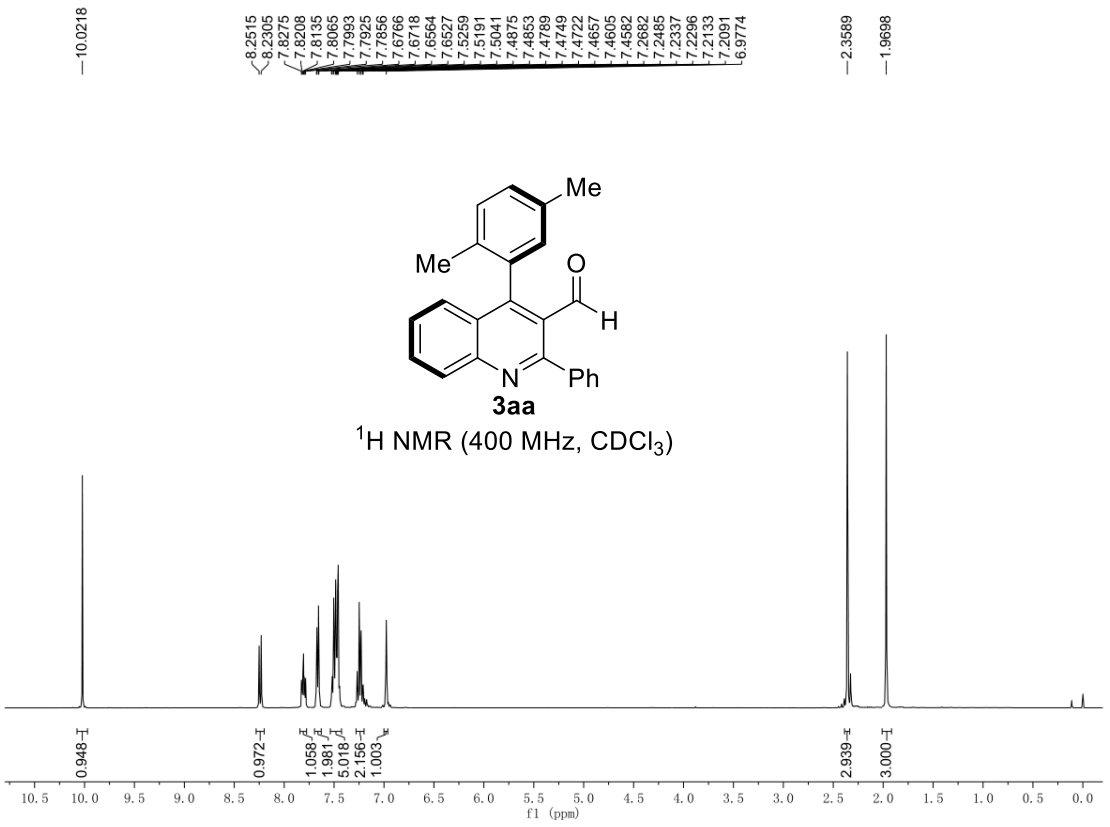

11.1997
7.8208
7.8157
7.7664
7.7455
7.2608
7.2567
7.2373
7.2230
7.1958
7.1914
7.1757
7.1713
7.1303
7.1105
6.9470
6.9420
6.9256
6.9206
6.7386
2.3772
2.2919
2.0463
Me
Me
O
Cl
NHTs
1s
1H NMR (400 MHz, CDCl3)
0.990
1.938
2.792
1.137
1.049
0.964
0.994
2.919
2.951
3.000
f1 (ppm)

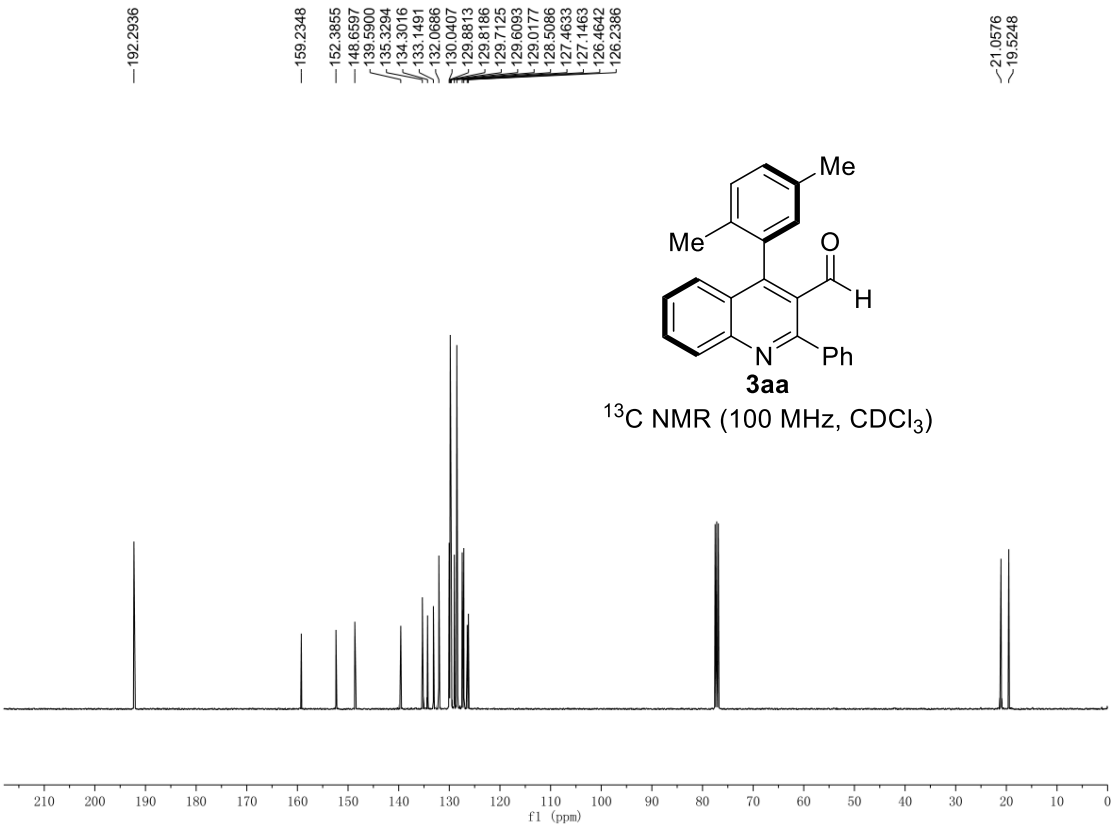

201.5533
144.2461
141.4579
141.1878
138.1367
136.2599
135.6288
135.0630
132.7618
131.3747
130.9332
129.8438
128.1555
127.3115
123.1246
122.1373
120.1114
21.5640
20.8508
19.0204
Me
Me
O
Cl
NHTs
1s
13C NMR (100 MHz, CDCl3)
f1 (ppm)

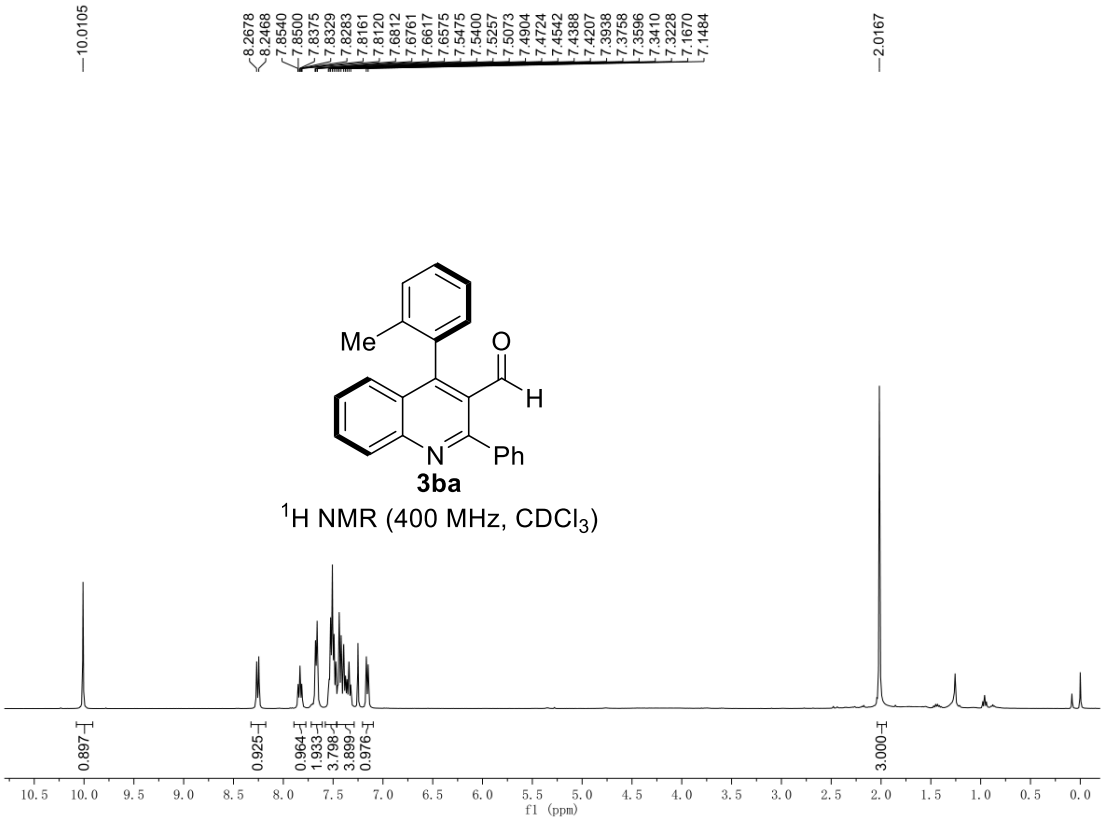

9.2461
7.4970
7.4923
7.4810
7.4764
7.4611
7.4572
7.1418
7.1303
7.1267
7.1223
7.1114
7.0922
7.0860
7.0667
7.0154
6.9943
6.9881
6.9729
6.2225
2.6639
2.2274
2.1705
Me
Me
O
NHTs
Me
1t
1H NMR (400 MHz, CDCl3)
0.979
2.978
3.045
2.969
0.975
3.000
5.942
3.008
f1 (ppm)

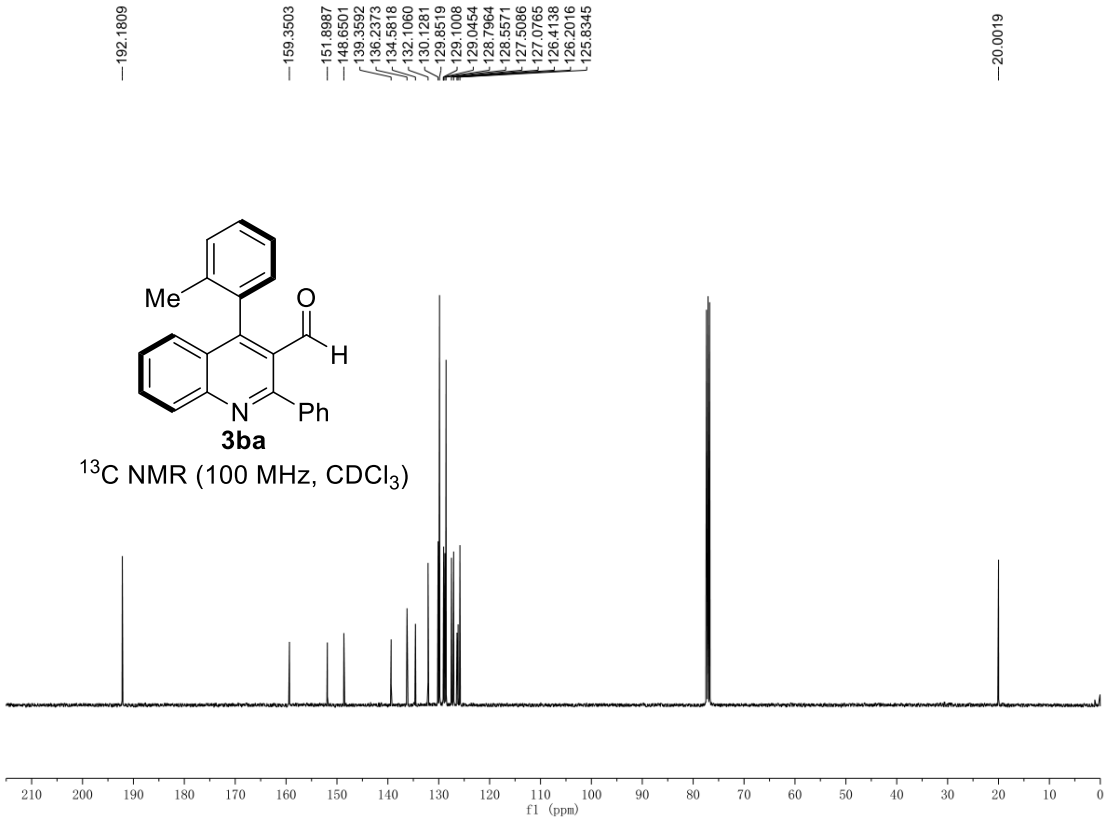

200.0494
143.4046
139.9150
136.4097
136.2840
135.9188
135.6683
135.4198
133.6890
133.0773
131.8238
131.1511
130.8097
130.7731
129.2809
128.0174
125.9168
21.3613
20.8531
19.8655
19.8399
Me
Me
O
NHTs
Me
1t
13C NMR (100 MHz, CDCl3)
f1 (ppm)

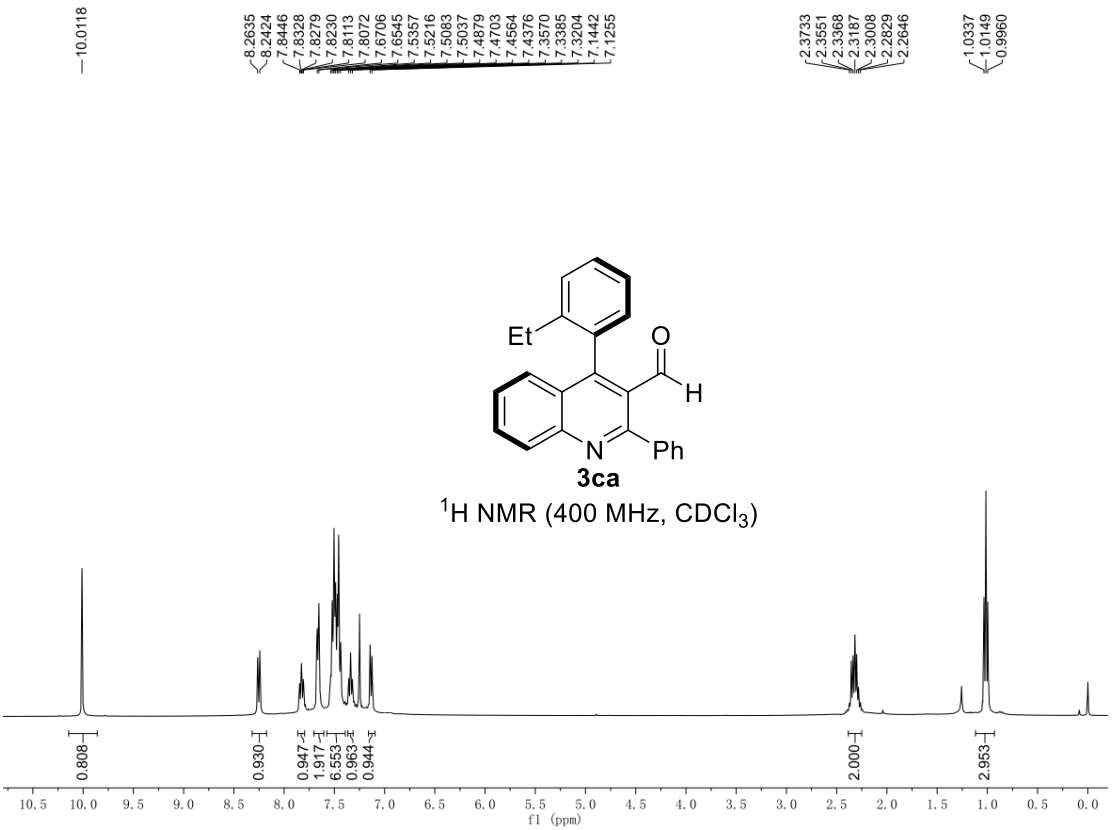
## NMR Spectra of Products

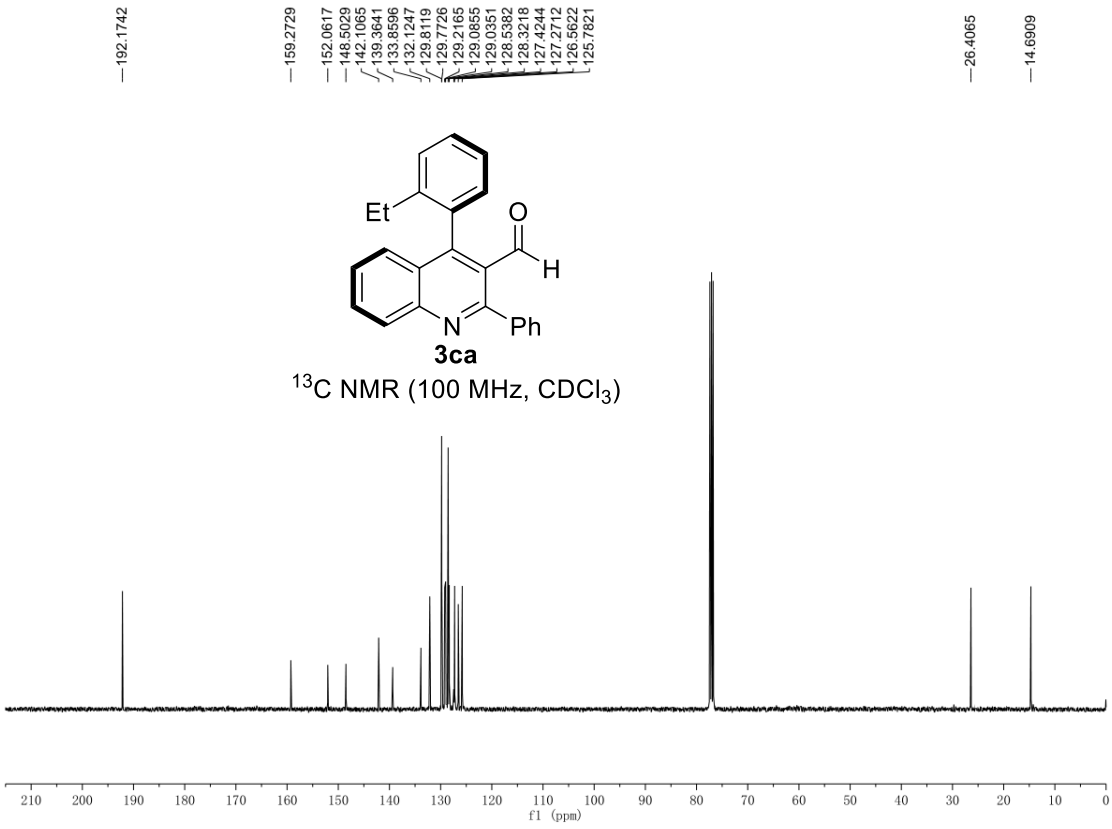


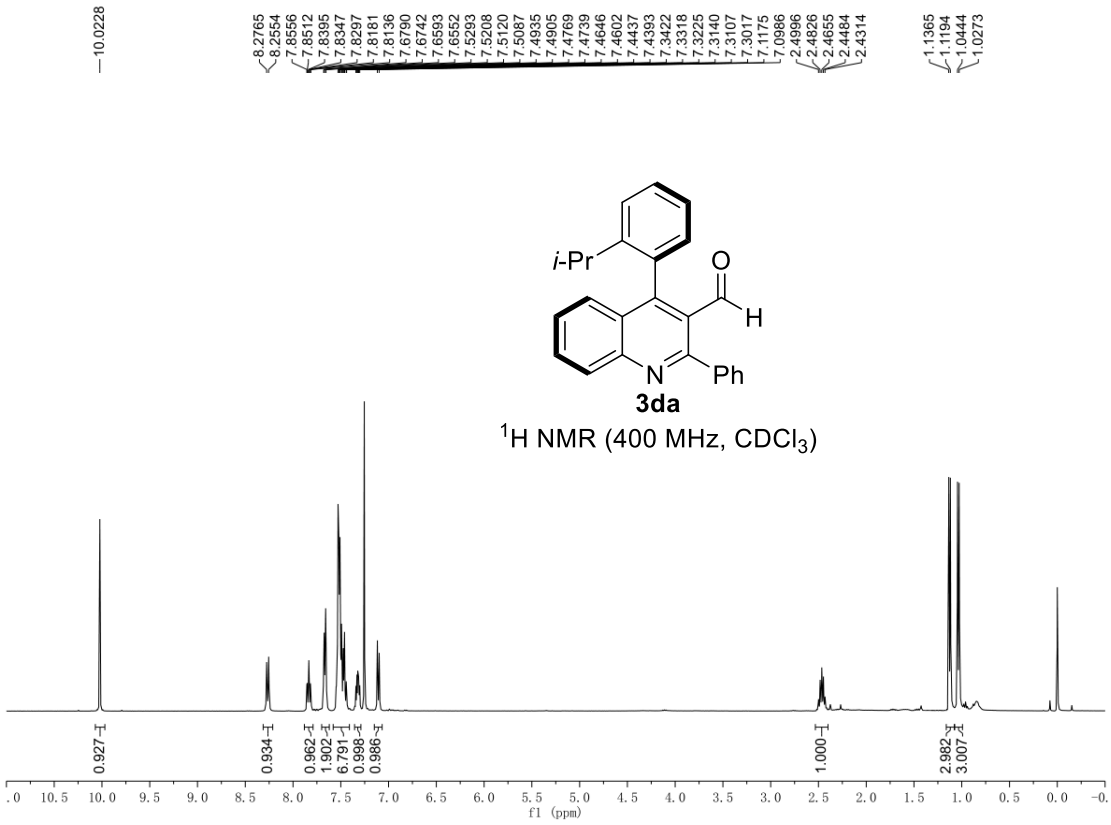



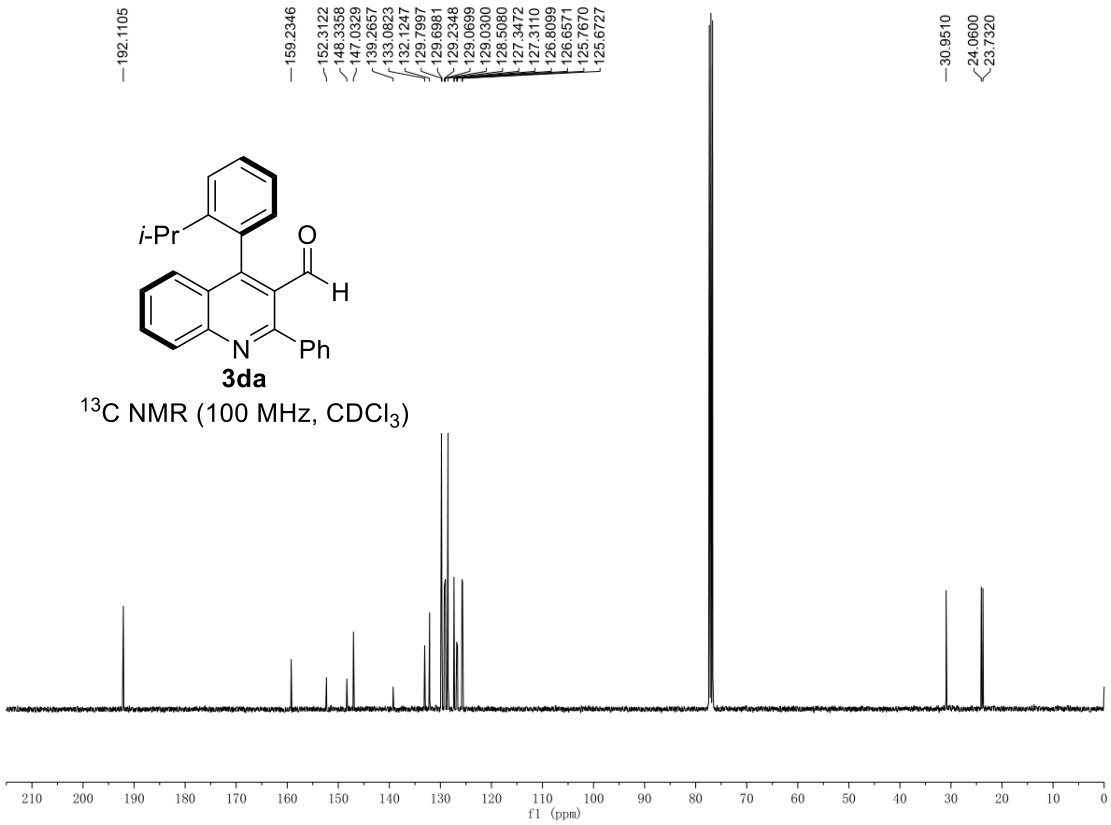

10.0105
8.2678
8.2468
7.8540
7.8500
7.8375
7.8329
7.8283
7.8161
7.8120
7.6812
7.6761
7.6617
7.6575
7.5475
7.5400
7.5257
7.5073
7.4904
7.4724
7.4542
7.4388
7.4207
7.3938
7.3758
7.3596
7.3410
7.3228
7.1670
7.1484
2.0167
Me
O
H
N
Ph
3ba
1H NMR (400 MHz, CDCl3)
0.897
0.925
0.964
1.933
3.798
3.899
0.976
3.000
f1 (ppm)

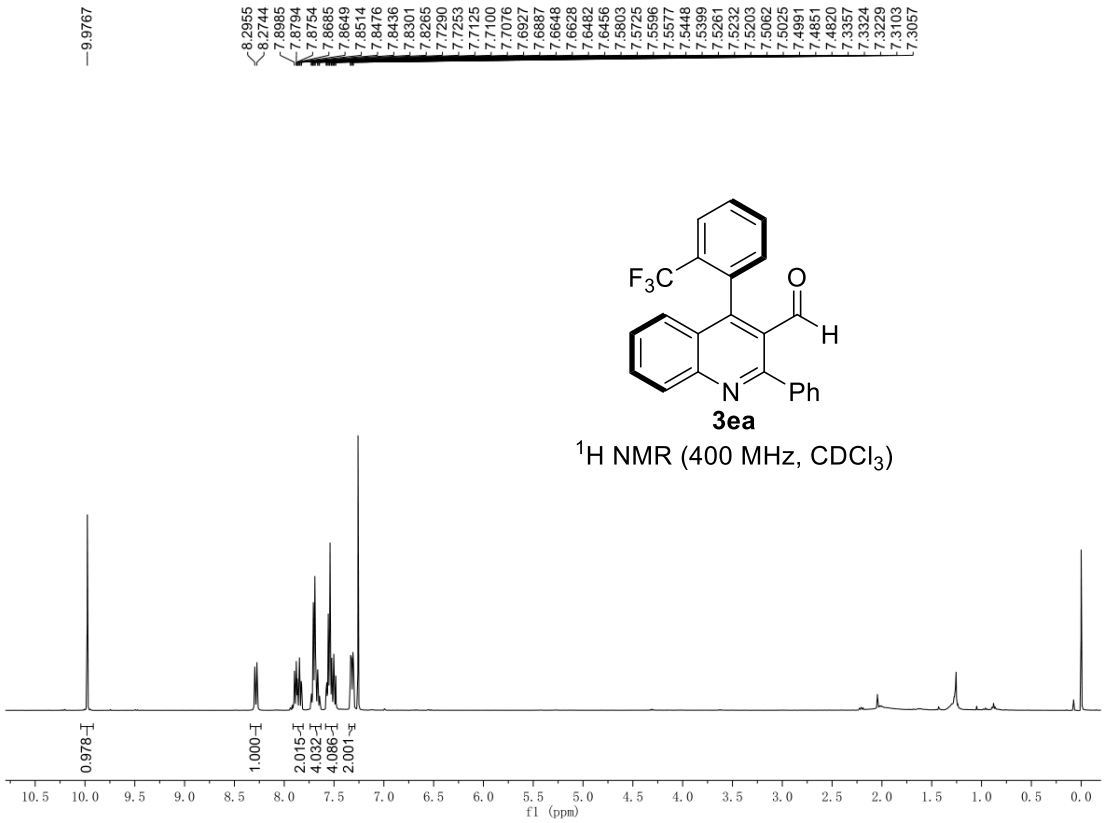

192.1809
159.3503
151.8987
148.6501
139.3592
136.2373
134.5818
132.1060
130.1281
129.8519
129.1008
129.0454
128.7964
128.5571
127.5086
127.0765
126.4138
126.2016
125.8345
20.0019
Me
O
H
N
Ph
3ba
13C NMR (100 MHz, CDCl3)
f1 (ppm)

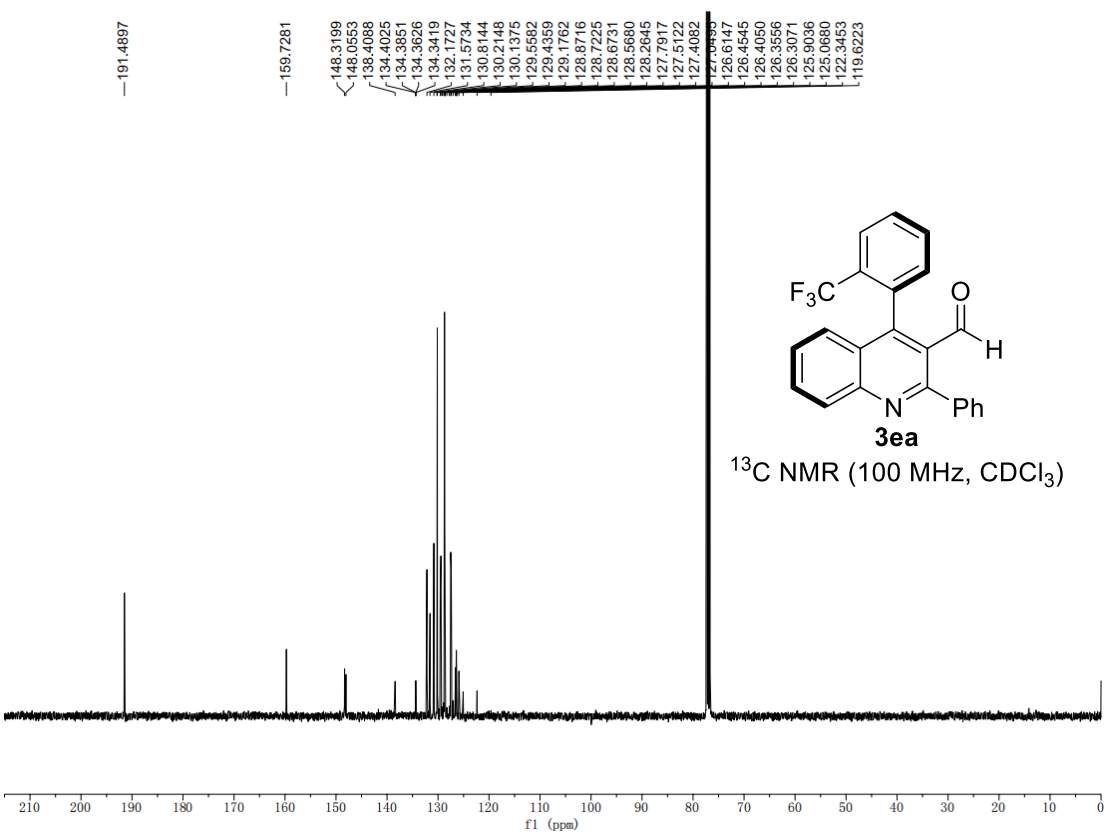

10.0118
8.2635
8.2424
7.8446
7.8328
7.8279
7.8230
7.8113
7.8072
7.6706
7.6645
7.5357
7.5216
7.5083
7.5037
7.4879
7.4703
7.4564
7.4376
7.3570
7.3385
7.3204
7.1442
7.1255
2.3733
2.3551
2.3368
2.3187
2.3008
2.2829
2.2646
1.0337
1.0149
0.9960
Et
O
H
N
Ph
3ca
1H NMR (400 MHz, CDCl3)
0.808
0.930
0.947
1.917
6.553
0.963
0.944
2.000
2.953
f1 (ppm)

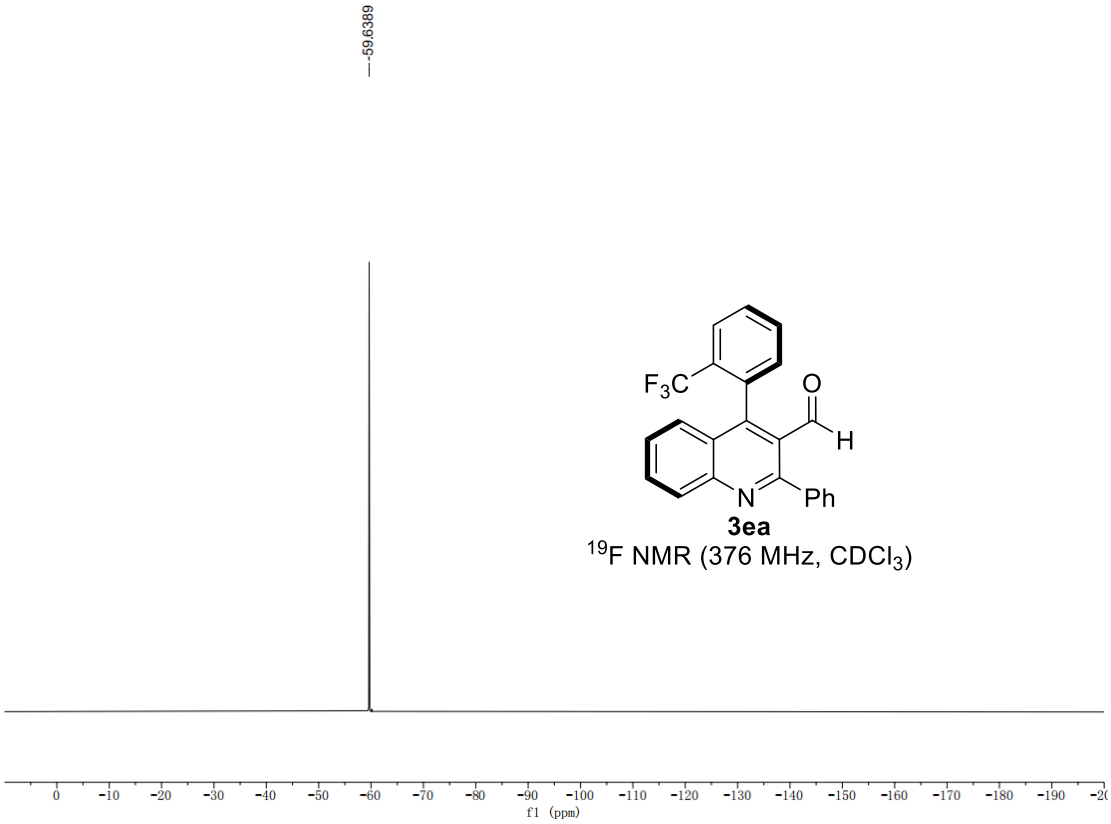

192.1742
159.2729
152.0617
148.5029
142.1065
139.3641
133.8596
132.1247
129.8119
129.7726
129.2165
129.0855
129.0351
128.5382
128.3218
127.4244
127.2712
126.5622
125.7821
26.4065
14.6909
Et
O
H
N
Ph
3ca
13C NMR (100 MHz, CDCl3)
f1 (ppm)


10.0228
8.2765
8.2554
7.8556
7.8512
7.8395
7.8347
7.8297
7.8181
7.8136
7.6790
7.6742
7.6593
7.6552
7.5293
7.5208
7.5120
7.5087
7.4935
7.4905
7.4769
7.4739
7.4646
7.4602
7.4437
7.4393
7.3422
7.3318
7.3225
7.3140
7.3107
7.3017
7.1175
7.0986
2.4996
2.4826
2.4655
2.4484
2.4314
1.1365
1.1194
1.0444
1.0273
i-Pr
O
H
N
Ph
3da
1H NMR (400 MHz, CDCl3)
0.927
0.934
0.962
1.902
6.791
0.998
0.986
1.000
2.982
3.007
f1 (ppm)


192.1105
159.2346
152.3122
148.3358
147.0329
139.2657
133.0823
132.1247
129.7997
129.6981
129.2348
129.0699
129.0300
128.5080
127.3472
127.3110
126.8099
126.6571
125.7670
125.6727
30.9510
24.0600
23.7320
i-Pr
O
H
N
Ph
3da
13C NMR (100 MHz, CDCl3)
f1 (ppm)

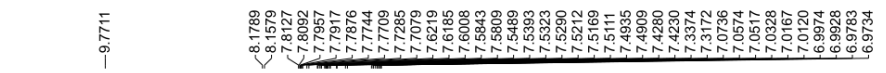

9.9767
8.2955
8.2744
7.8985
7.8794
7.8754
7.8685
7.8649
7.8514
7.8476
7.8436
7.8301
7.8265
7.7290
7.7253
7.7125
7.7100
7.7076
7.6927
7.6887
7.6648
7.6628
7.6482
7.6456
7.5803
7.5725
7.5596
7.5577
7.5448
7.5399
7.5261
7.5232
7.5203
7.5062
7.5025
7.4991
7.4851
7.4820
7.3357
7.3324
7.3229
7.3103
7.3057
F3C
O
H
N
Ph
3ea
1H NMR (400 MHz, CDCl3)
0.978
1.000
2.015
4.032
4.086
2.001
f1 (ppm)

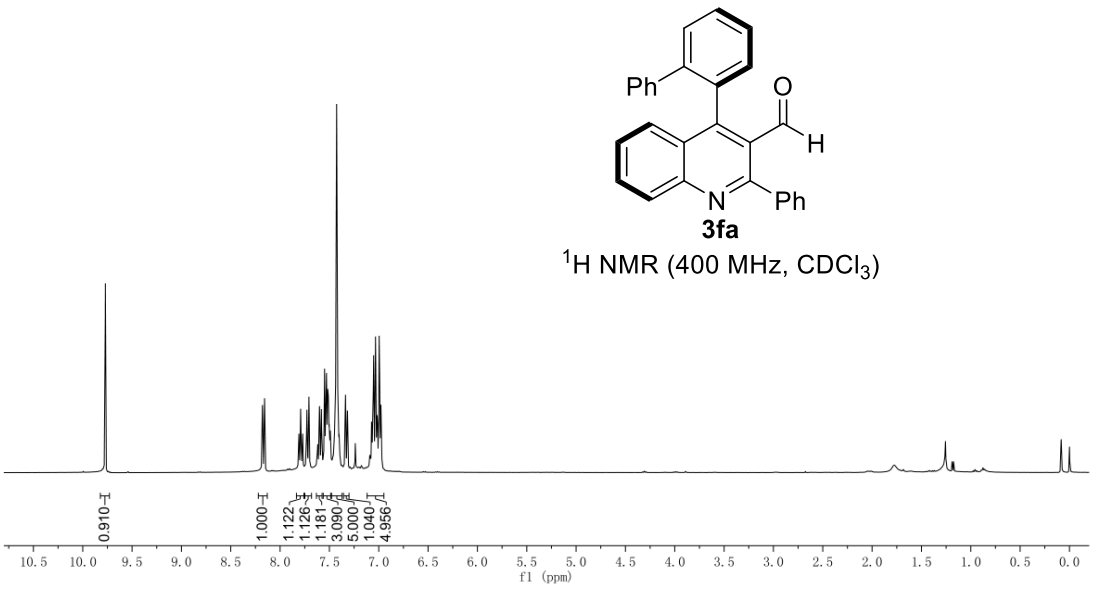

191.4897
159.7281
148.3199
148.0553
138.4088
134.4025
134.3851
134.3626
134.3419
132.1727
131.5734
130.8144
130.2148
130.1375
129.5582
129.4359
129.1762
128.8716
128.7225
128.6731
128.5680
128.2645
127.7917
127.5122
127.4082
126.6147
126.4545
126.4050
126.3556
126.3071
125.9036
125.0680
122.3453
119.6223
F3C
O
H
N
Ph
3ea
13C NMR (100 MHz, CDCl3)
f1 (ppm)




**3ea**

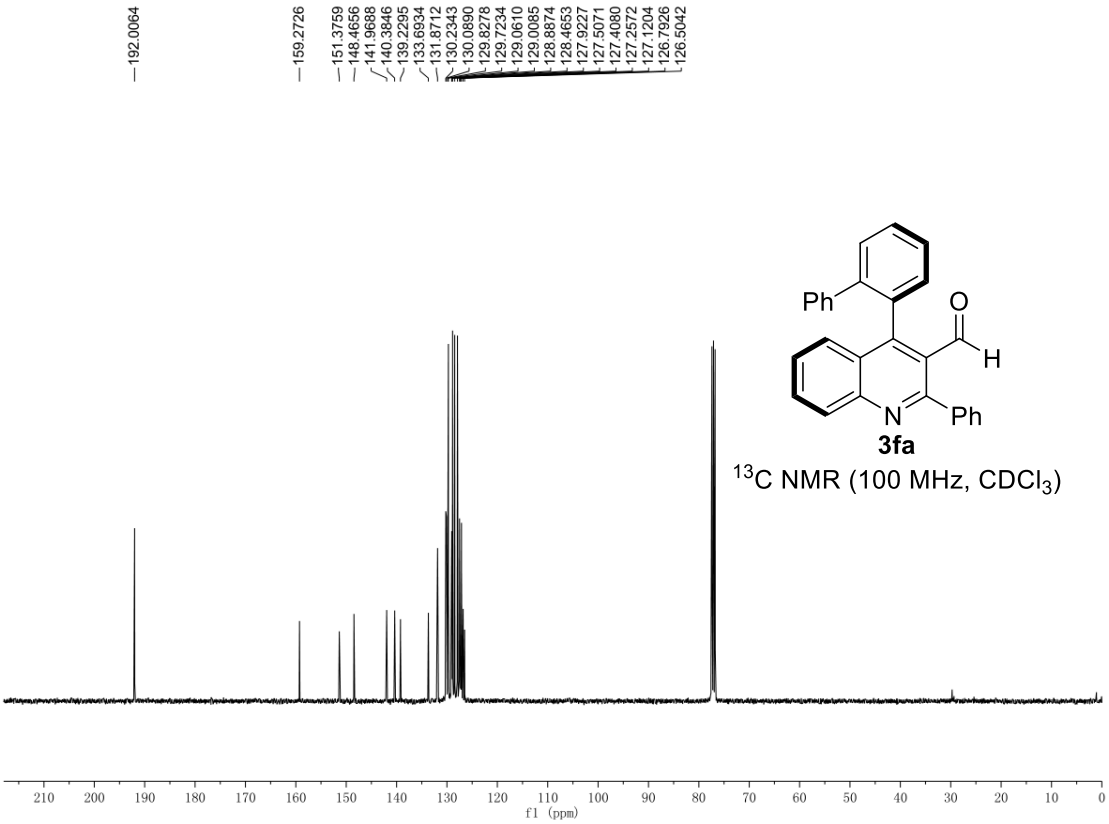
$^{19}$F NMR (376 MHz, $CDCl_3$)



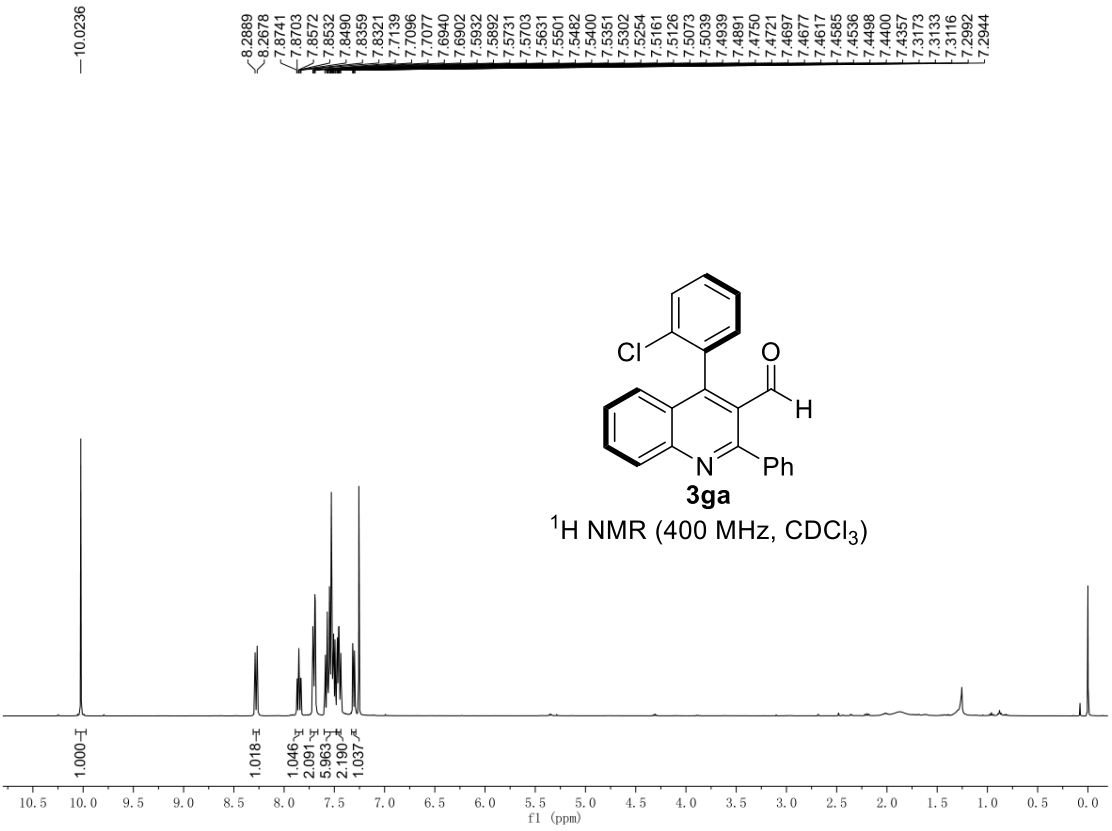

**3fa**

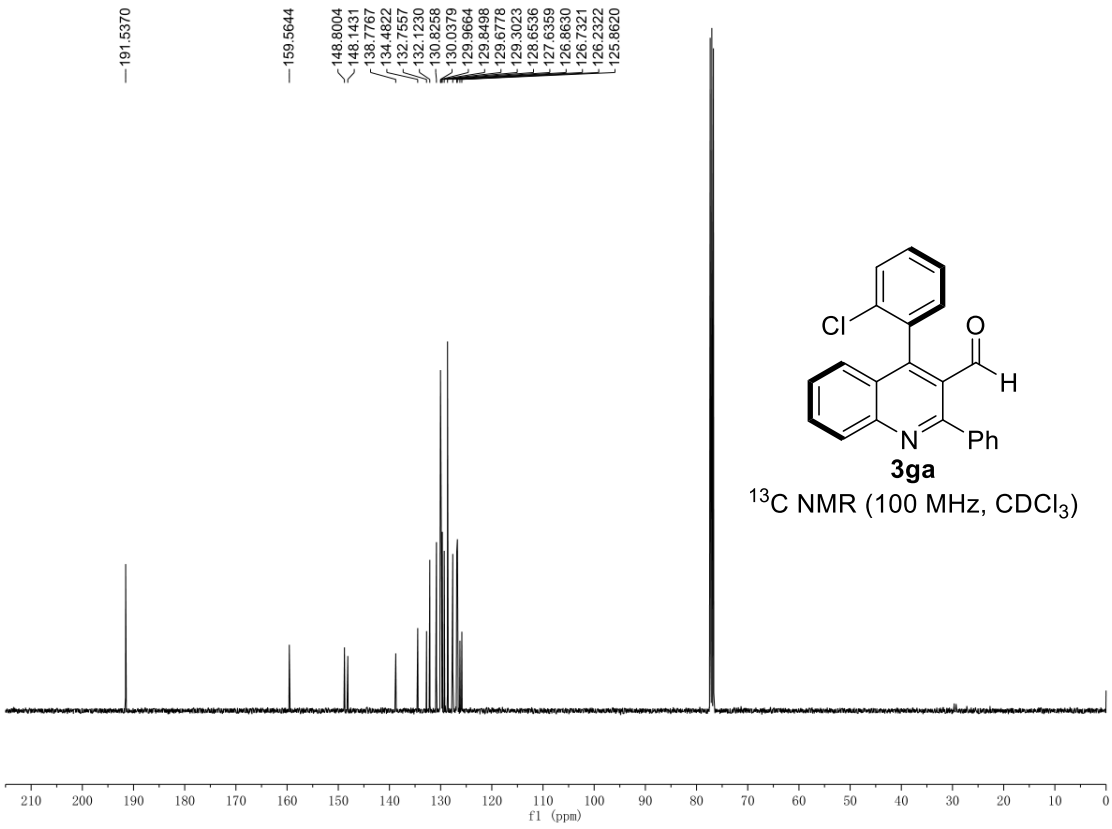
$^{1}$H NMR (400 MHz, $CDCl_3$)

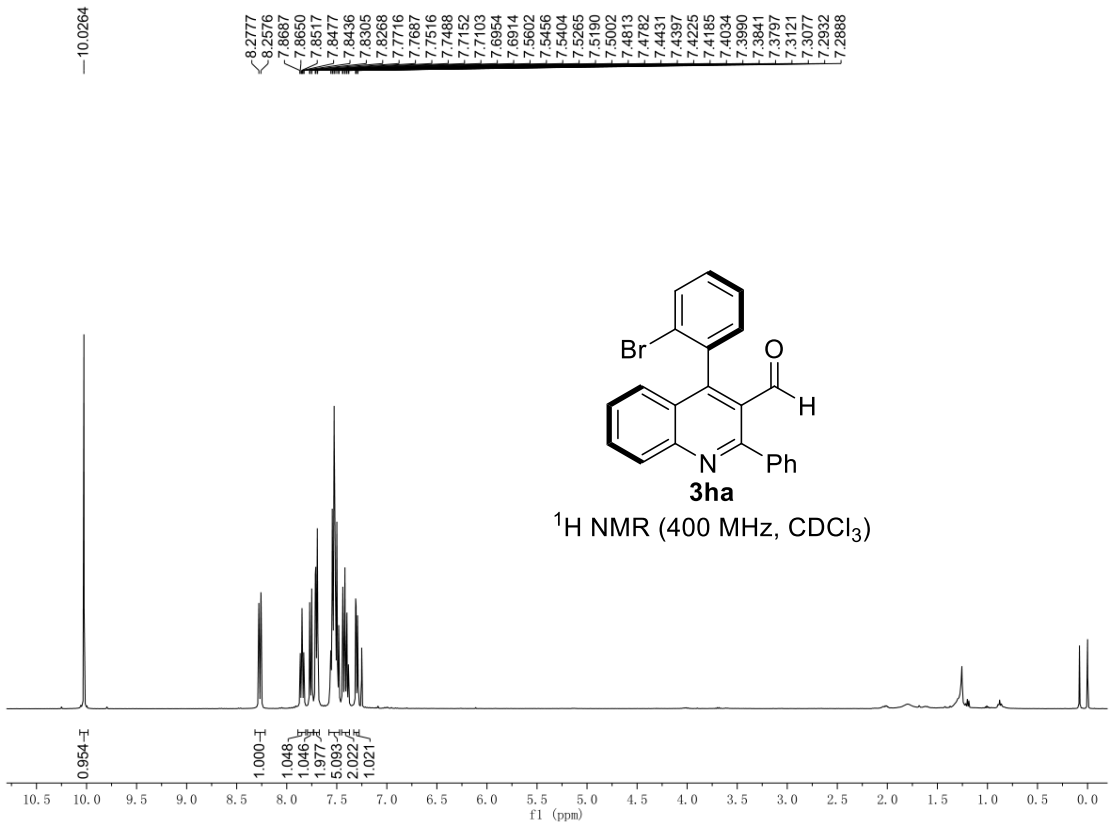


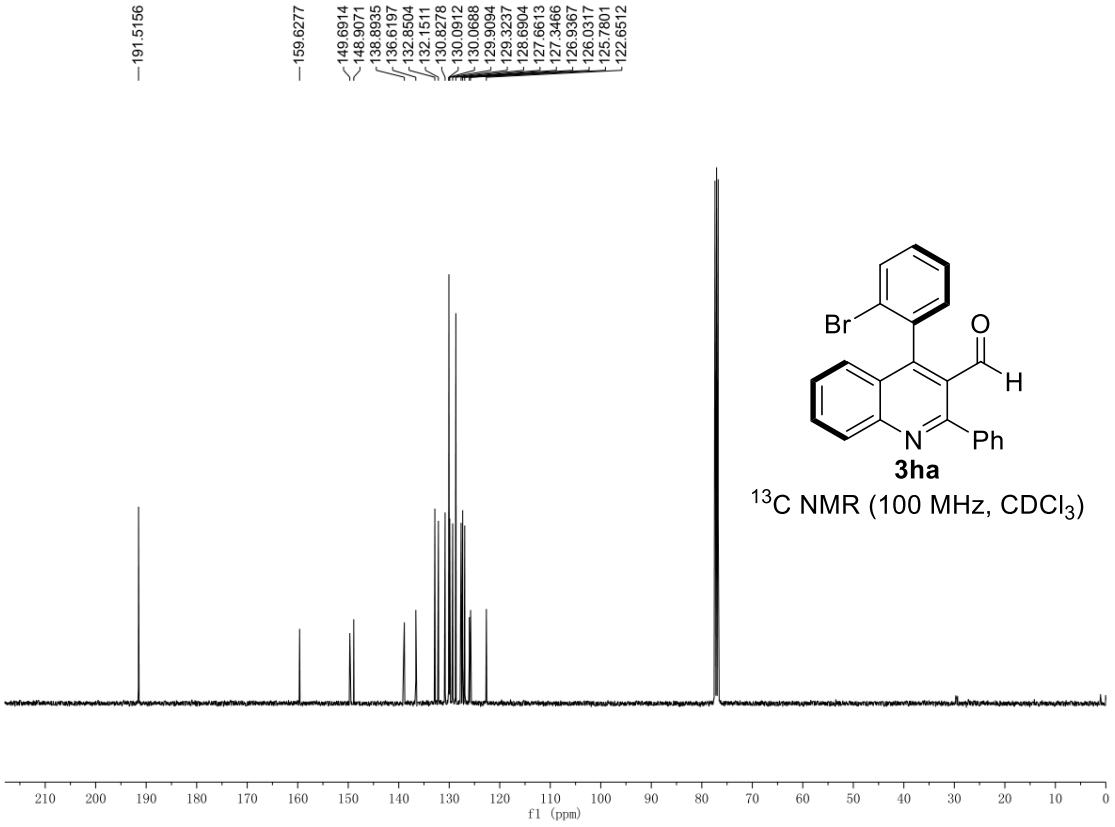

**3fa**

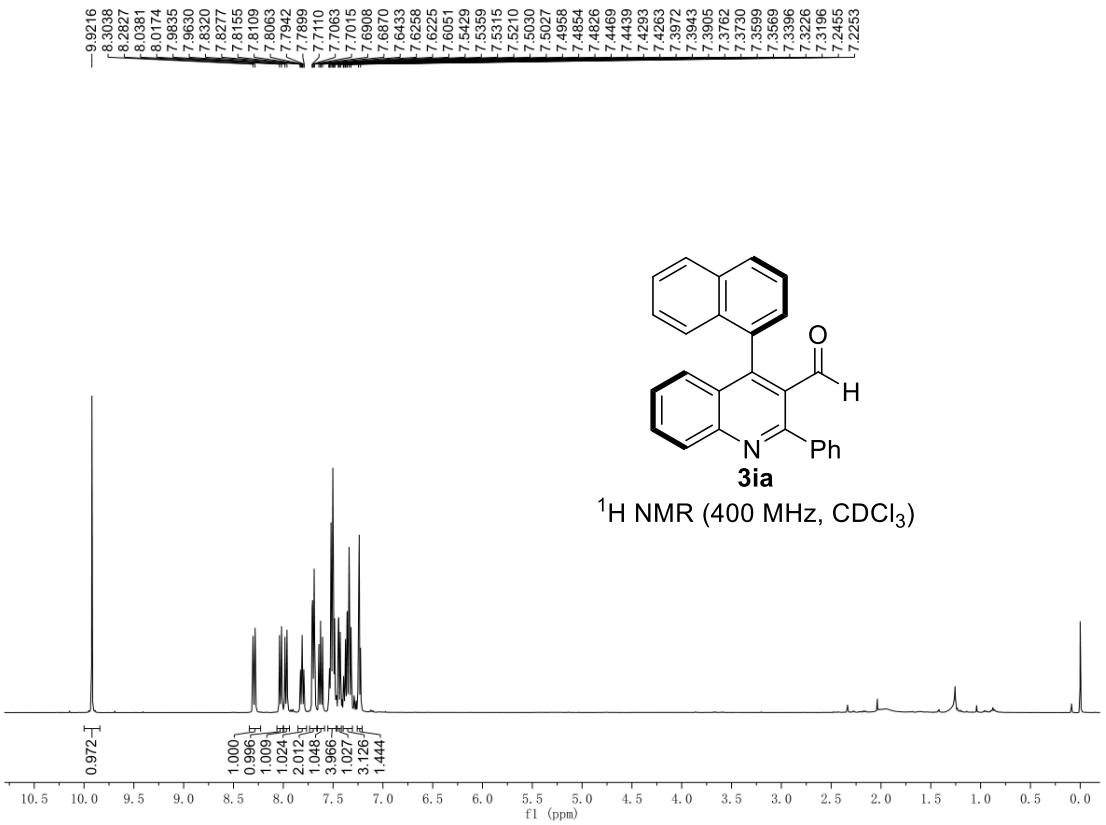
$^{13}$C NMR (100 MHz, $CDCl_3$)

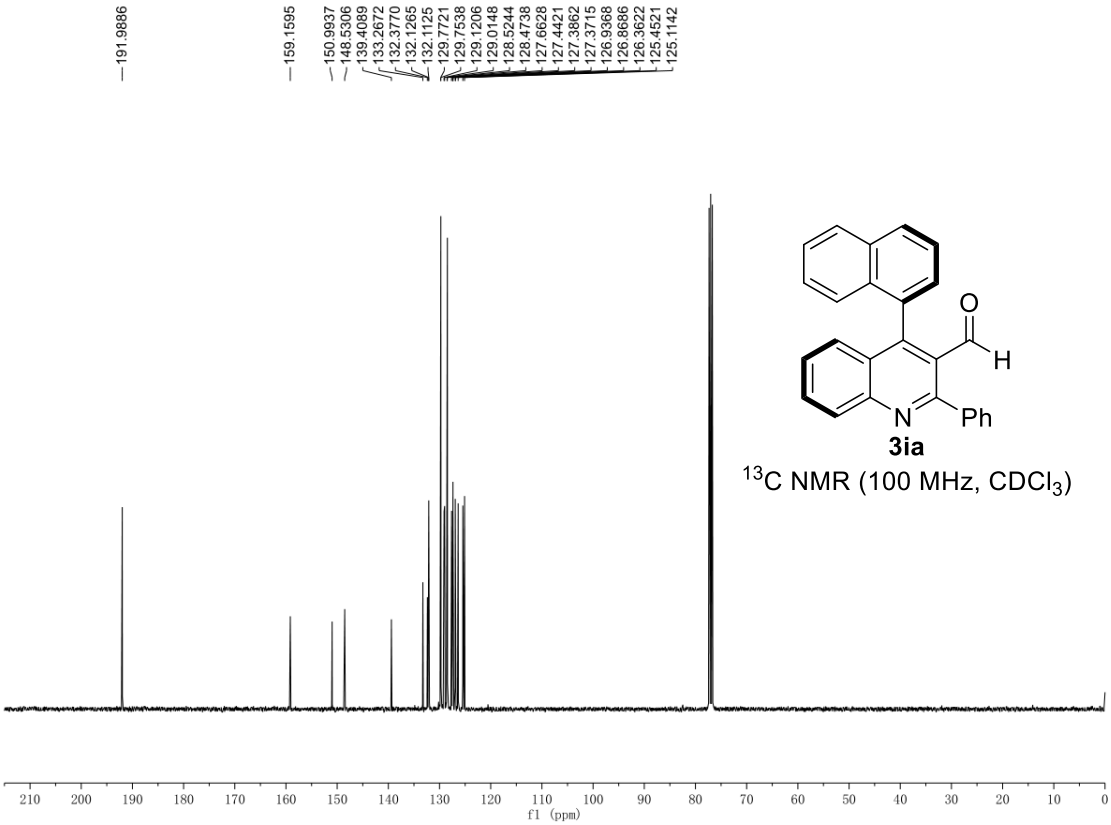

10.0236
8.2889
8.2678
7.8741
7.8703
7.8572
7.8532
7.8490
7.8359
7.8321
7.7139
7.7096
7.7077
7.6940
7.6902
7.5932
7.5892
7.5731
7.5703
7.5631
7.5501
7.5482
7.5400
7.5351
7.5302
7.5254
7.5161
7.5126
7.5073
7.5039
7.4939
7.4891
7.4750
7.4721
7.4697
7.4677
7.4617
7.4585
7.4536
7.4498
7.4400
7.4357
7.3173
7.3133
7.3116
7.2992
7.2944
Cl
O
H
N
Ph
3ga
1H NMR (400 MHz, CDCl3)
1.000
1.018
1.046
2.091
5.963
2.190
1.037
f1 (ppm)

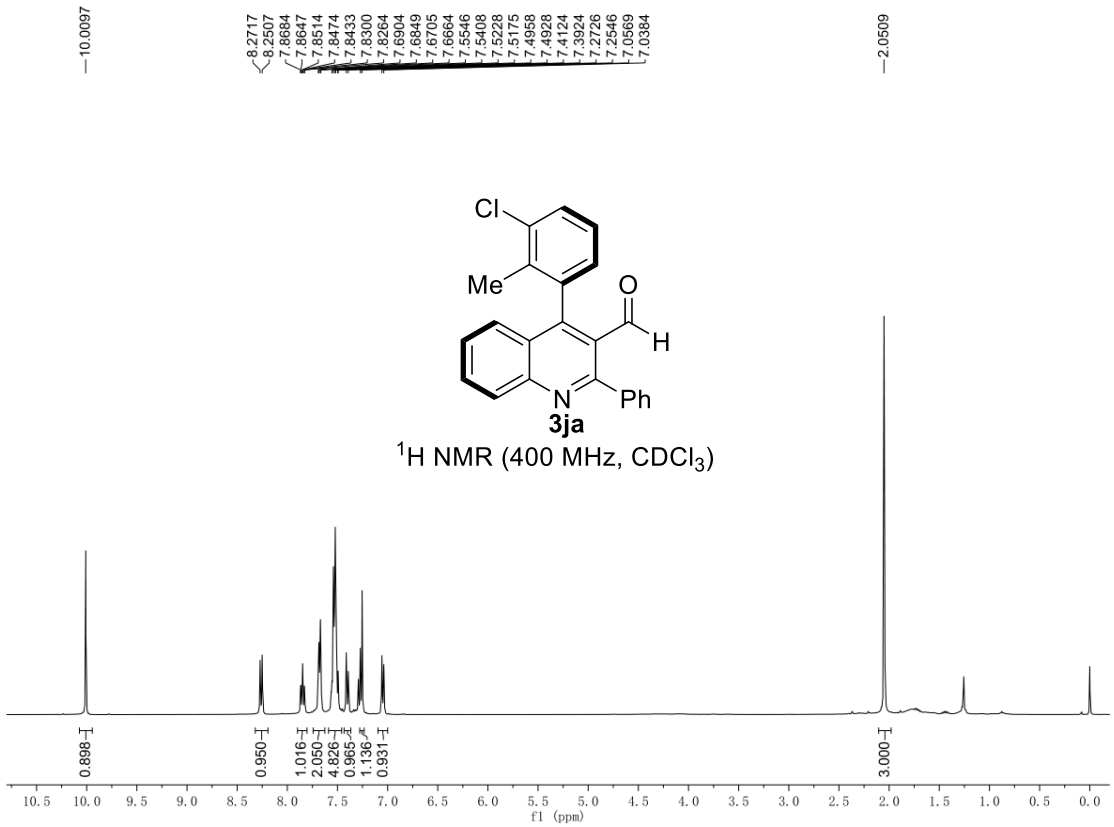

191.5370
159.5644
148.8004
148.1431
138.7767
134.4822
132.7557
132.1230
130.8258
130.0379
129.9664
129.8498
129.6778
129.3023
128.8536
127.6359
126.8630
126.7321
126.2322
125.8620
Cl
O
H
N
Ph
3ga
13C NMR (100 MHz, CDCl3)
f1 (ppm)


10.0264
8.2777
8.2576
7.8687
7.8650
7.8517
7.8477
7.8436
7.8305
7.8268
7.7716
7.7687
7.7516
7.7488
7.7152
7.7103
7.6954
7.6914
7.5602
7.5456
7.5404
7.5265
7.5190
7.5002
7.4813
7.4782
7.4431
7.4397
7.4225
7.4185
7.4034
7.3990
7.3841
7.3797
7.3121
7.3077
7.2932
7.2888
Br
O
H
N
Ph
3ha
1H NMR (400 MHz, CDCl3)
0.954
1.000
1.048
1.046
1.977
5.093
2.022
1.021
f1 (ppm)

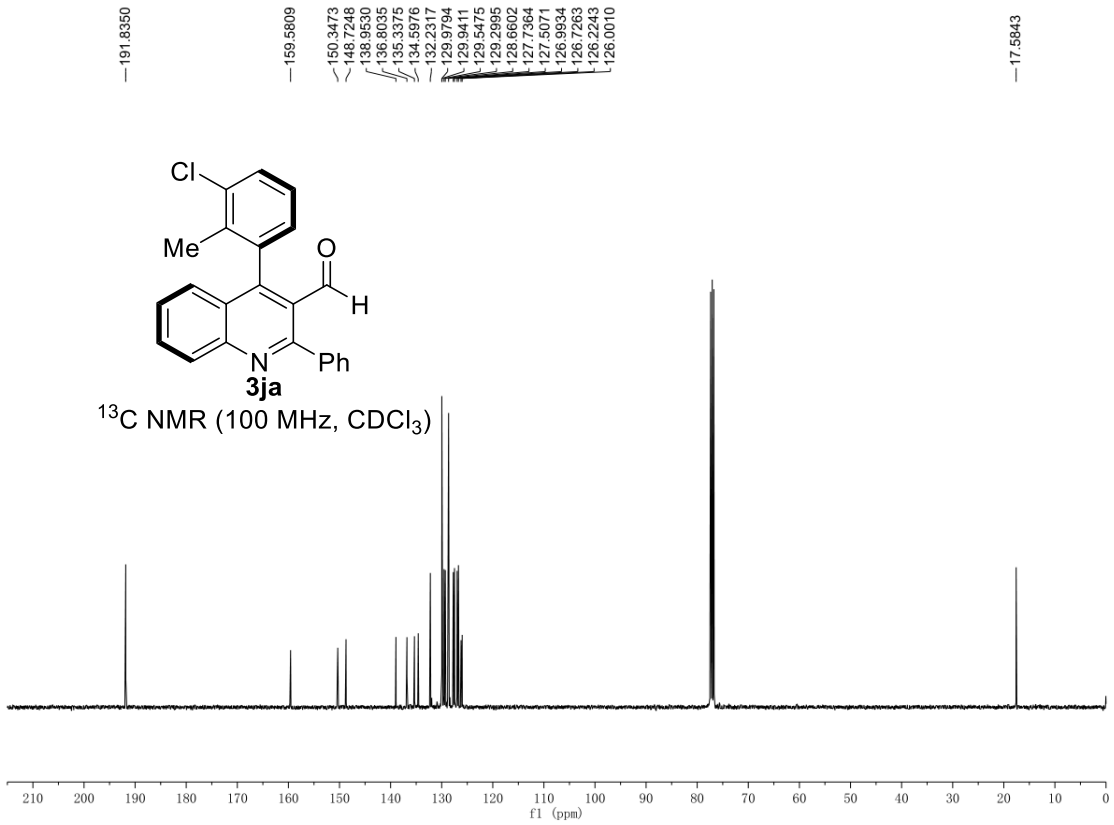

191.5156
159.6277
149.6914
148.9071
138.8935
136.6197
132.8504
132.1511
130.8278
130.0912
130.0688
129.9094
129.3237
128.6904
127.6613
127.3466
126.9367
126.0317
125.7801
122.6512
Br
O
H
N
Ph
3ha
13C NMR (100 MHz, CDCl3)
f1 (ppm)


9.9216
8.3038
8.2827
8.0381
8.0174
7.9835
7.9630
7.8320
7.8277
7.8155
7.8109
7.8063
7.7942
7.7899
7.7110
7.7063
7.7015
7.6908
7.6870
7.6433
7.6258
7.6225
7.6051
7.5429
7.5359
7.5315
7.5210
7.5030
7.5027
7.4958
7.4854
7.4826
7.4469
7.4439
7.4293
7.4263
7.3972
7.3943
7.3905
7.3762
7.3730
7.3599
7.3569
7.3396
7.3226
7.3196
7.2455
7.2253
O
H
N
Ph
3ia
1H NMR (400 MHz, CDCl3)
0.972
1.000
0.996
1.009
1.024
2.012
1.048
3.966
1.027
3.126
1.444
f1 (ppm)

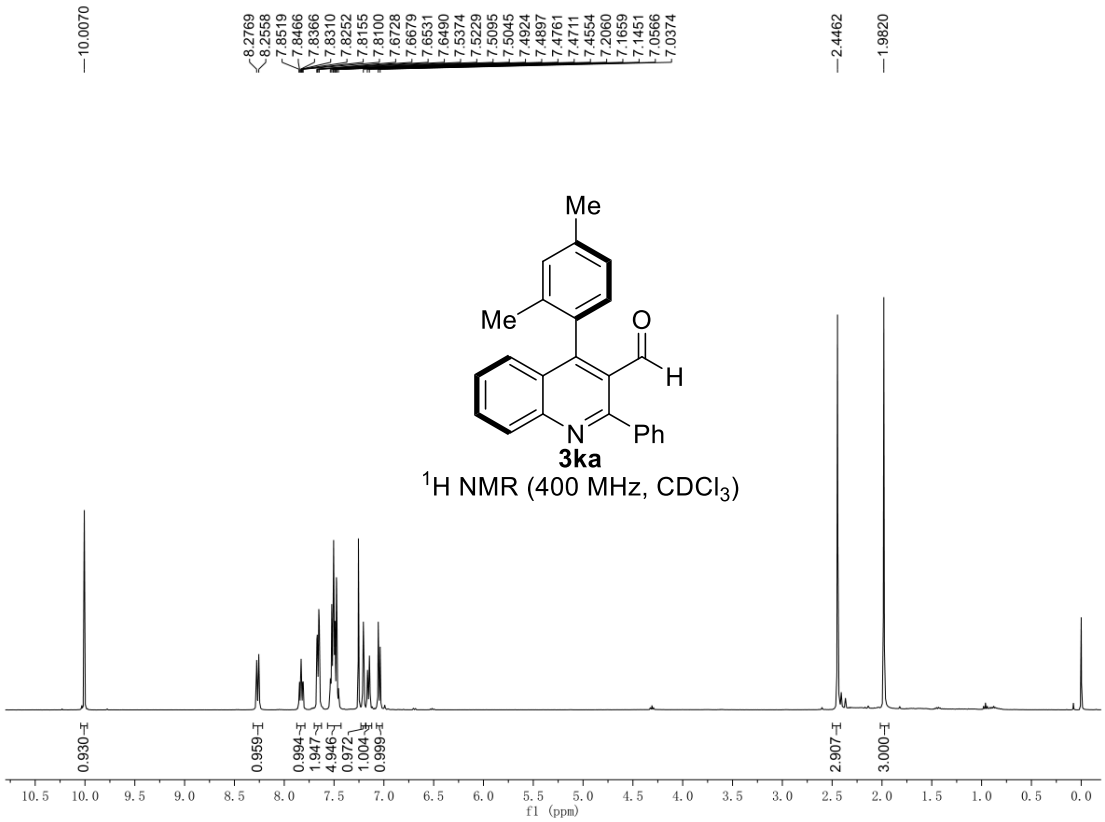

191.9886
159.1595
150.9937
148.5306
139.4089
133.2672
132.3770
132.1265
132.1125
129.7721
129.7538
129.1206
129.0148
128.5244
128.4738
127.6628
127.4421
127.3862
127.3715
126.9368
126.8686
126.3622
125.4521
125.1142
O
H
N
Ph
3ia
13C NMR (100 MHz, CDCl3)
f1 (ppm)

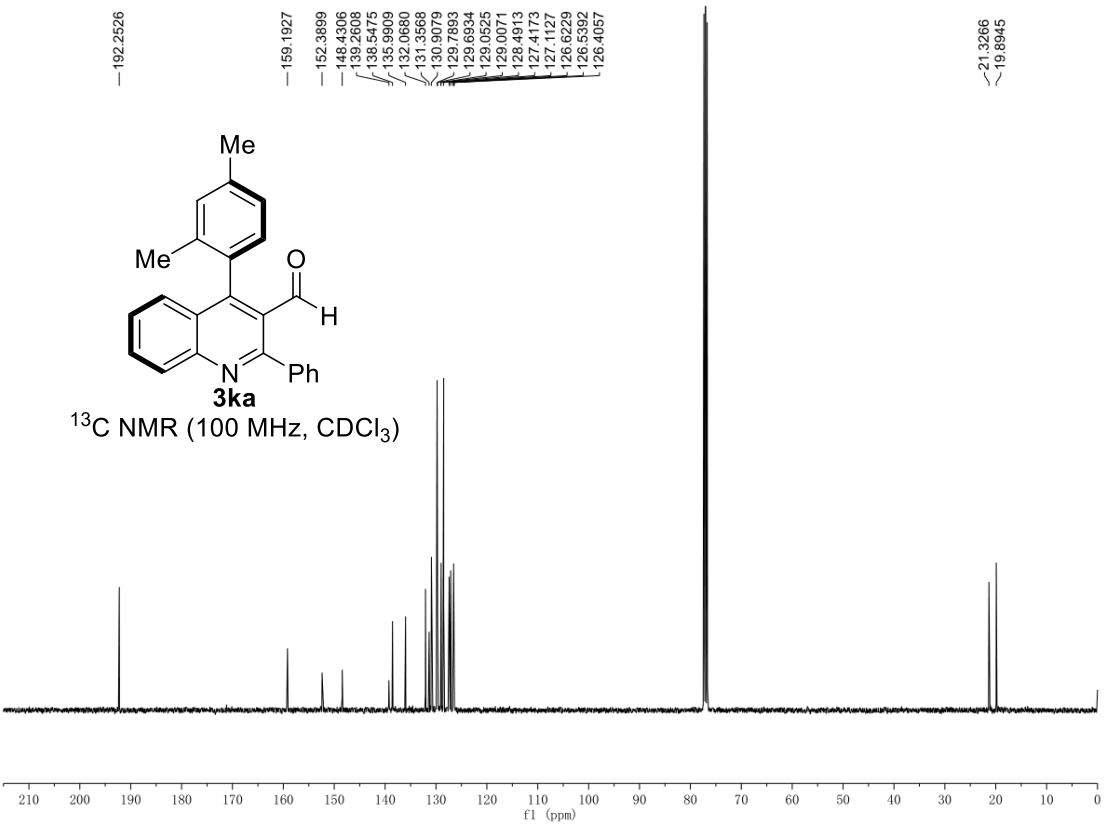


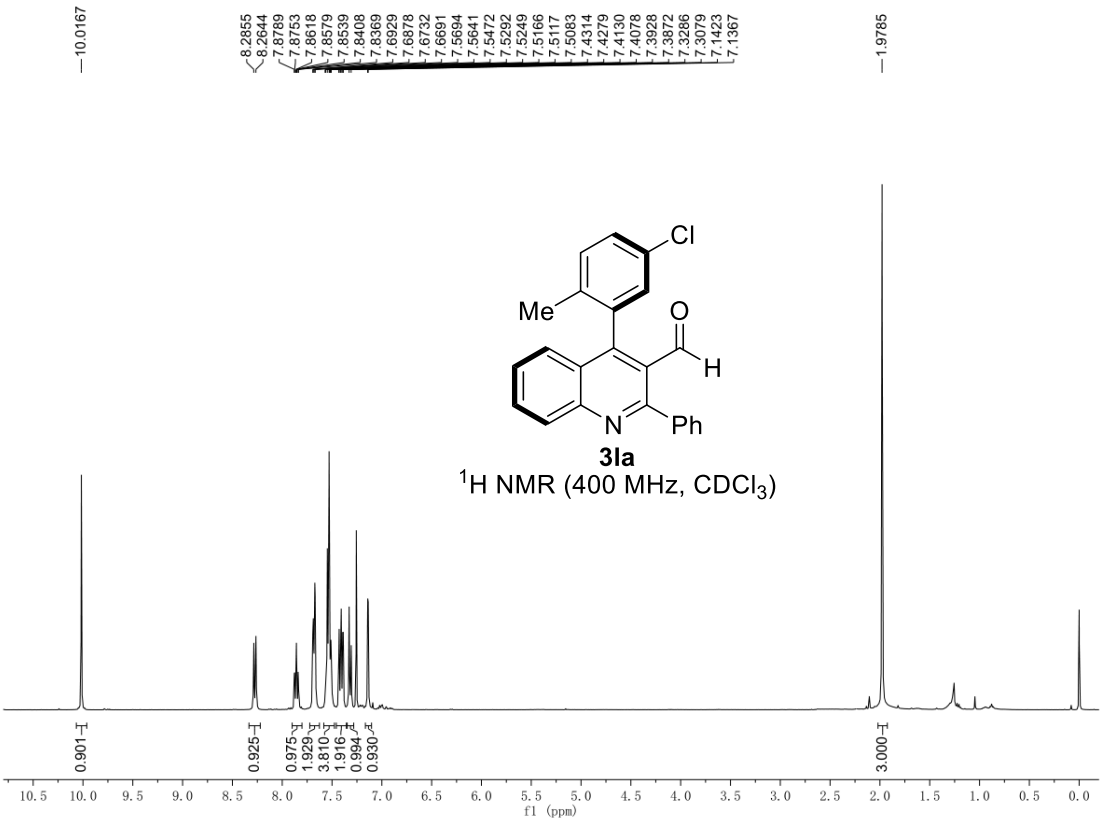

$^{1}$H NMR (400 MHz, $CDCl_3$)




$^{13}$C NMR (100 MHz, $CDCl_3$)

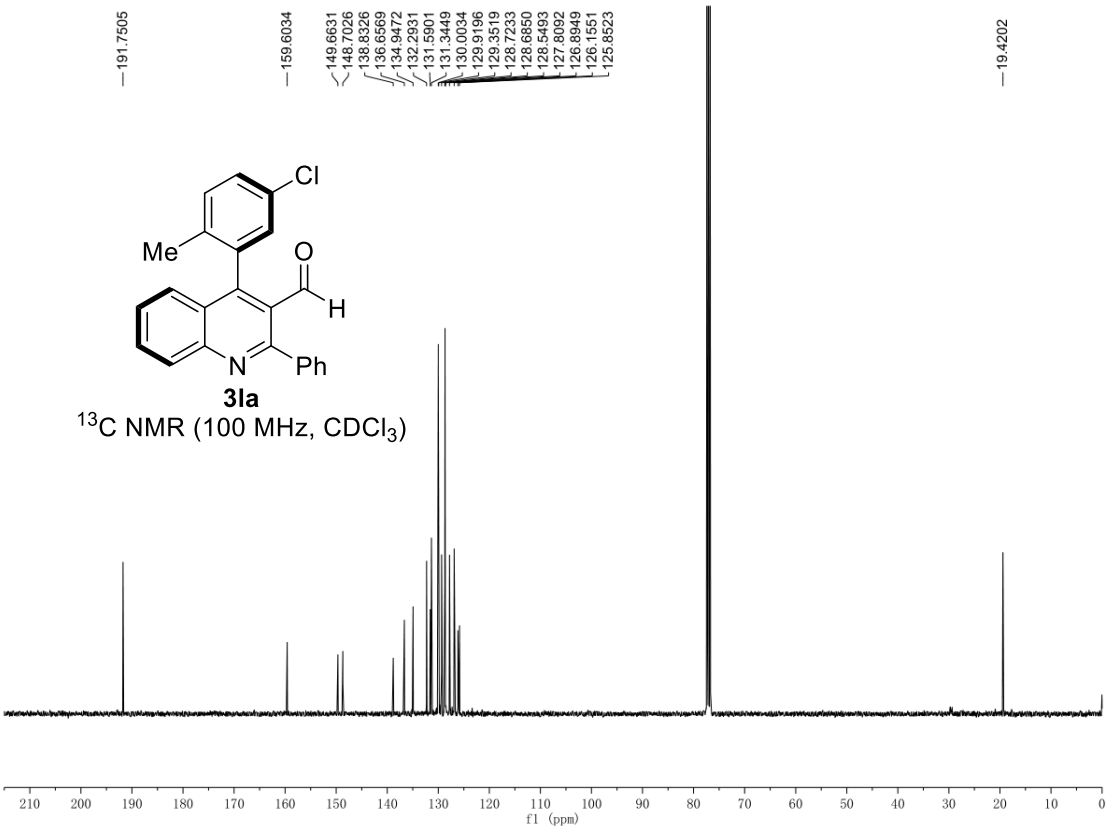

10.0070
8.2769
8.2558
7.8519
7.8466
7.8366
7.8310
7.8252
7.8155
7.8100
7.6728
7.6679
7.6531
7.6490
7.5374
7.5229
7.5095
7.5045
7.4924
7.4897
7.4761
7.4711
7.4554
7.2060
7.1659
7.1451
7.0566
7.0374
2.4462
1.9820
Me
Me
O
H
N
Ph
3ka
1H NMR (400 MHz, CDCl3)
0.930
0.959
0.994
1.947
4.946
0.972
1.004
0.999
2.907
3.000
f1 (ppm)


192.2526
159.1927
152.3899
148.4306
139.2608
138.5475
135.9909
132.0680
131.3568
130.9079
129.7893
129.6934
129.0525
129.0071
128.4913
127.4173
127.1127
126.6229
126.5392
126.4057
21.3266
19.8945
Me
Me
O
H
N
Ph
3ka
13C NMR (100 MHz, CDCl3)
f1 (ppm)



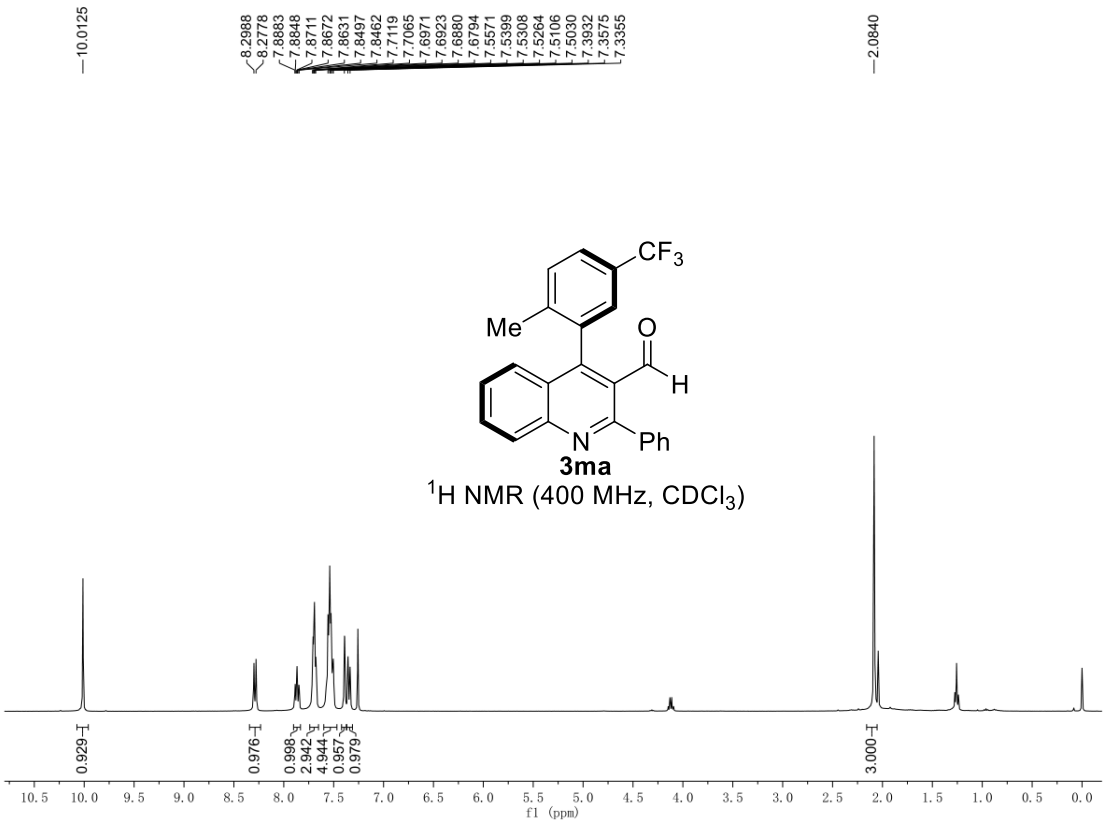

**3la**

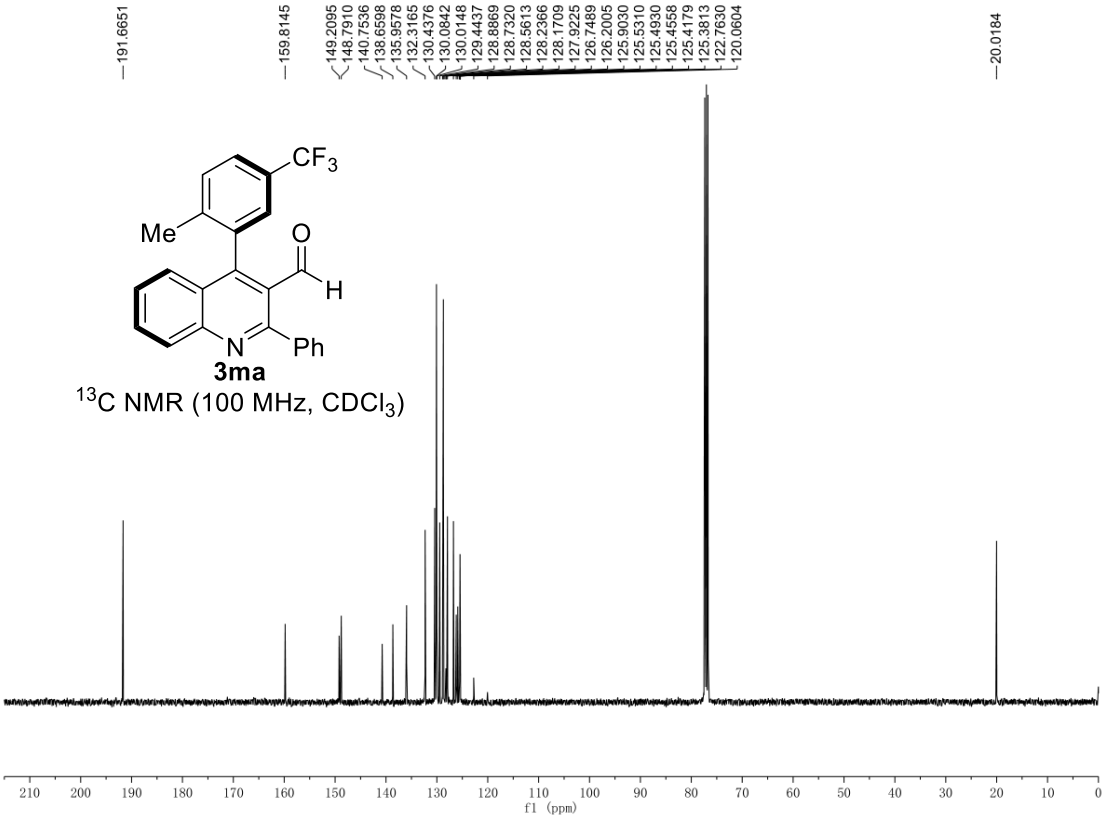
$^{1}$H NMR (400 MHz, $CDCl_3$)

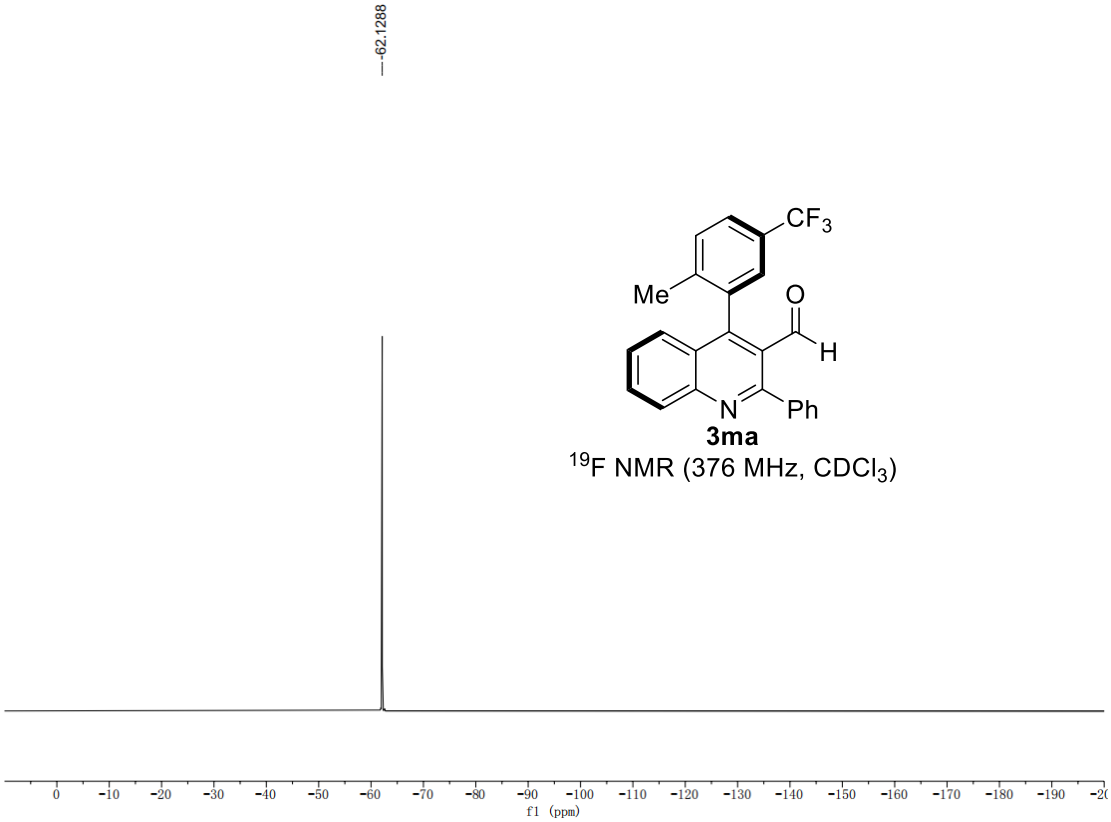



**3la**

$^{13}$C NMR (100 MHz, $CDCl_3$)

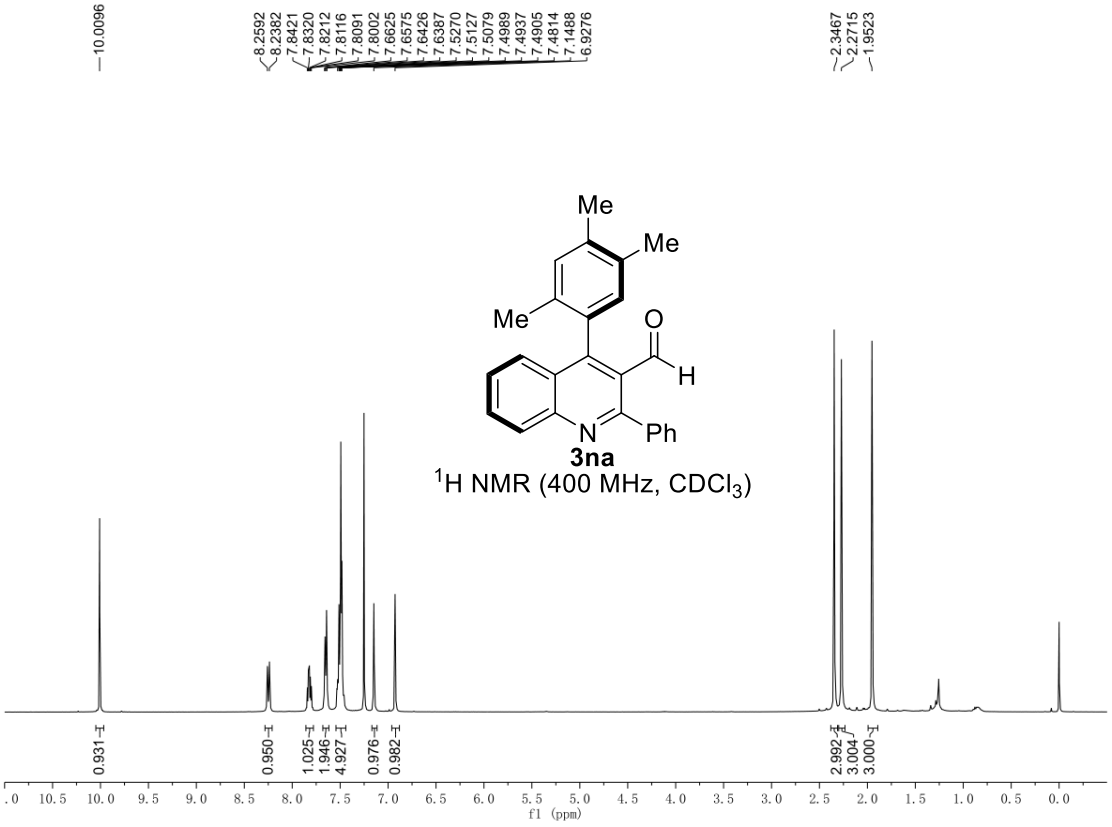

10.0125
8.2988
8.2778
7.8883
7.8848
7.8711
7.8672
7.8631
7.8497
7.8462
7.7119
7.7065
7.6971
7.6923
7.6880
7.6794
7.5571
7.5399
7.5308
7.5264
7.5106
7.5030
7.3932
7.3575
7.3355
2.0840
CF3
Me
O
H
N
Ph
3ma
1H NMR (400 MHz, CDCl3)
0.929
0.976
0.998
2.942
4.944
0.957
0.979
3.000
f1 (ppm)

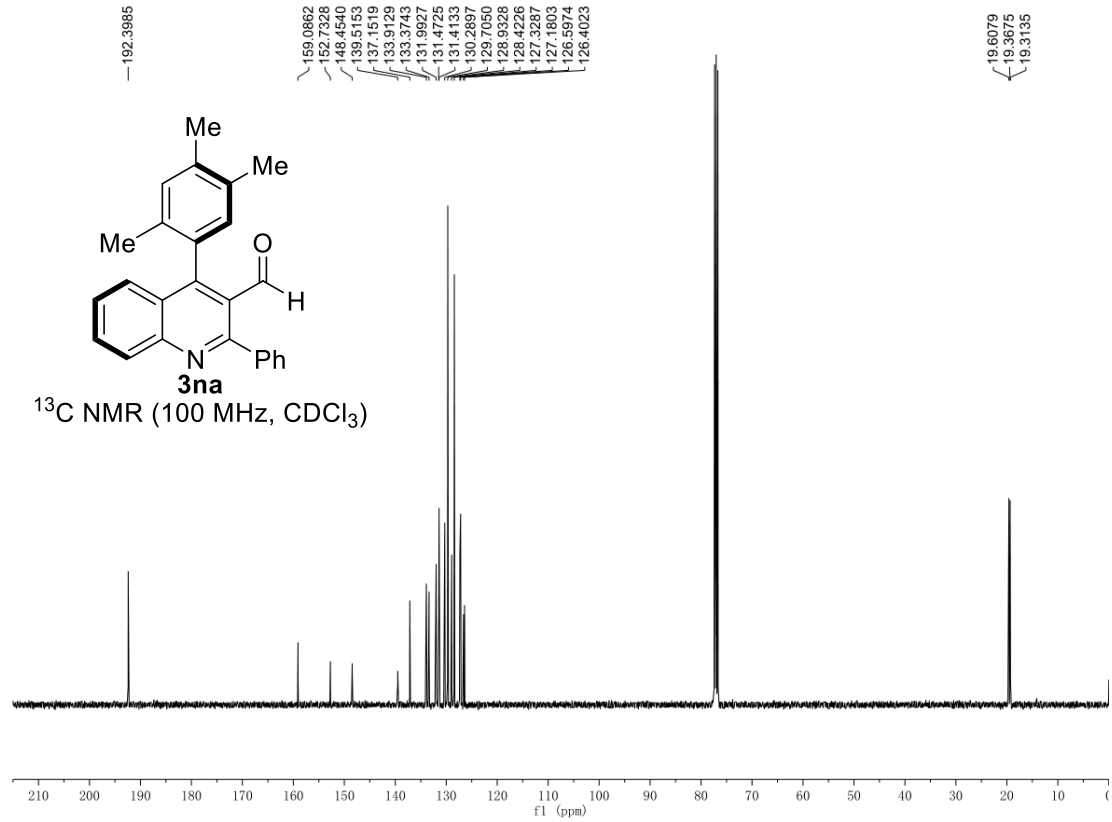

191.6651
159.8145
149.2095
148.7910
140.7536
138.6598
135.9578
132.3165
130.4376
130.0842
130.0148
129.4437
128.8869
128.7320
128.5613
128.2366
128.1709
127.9225
126.7489
126.2005
125.9030
125.5310
125.4930
125.4558
125.4179
125.3813
122.7630
120.0604
20.0184
CF3
Me
O
H
N
Ph
3ma
13C NMR (100 MHz, CDCl3)
f1 (ppm)

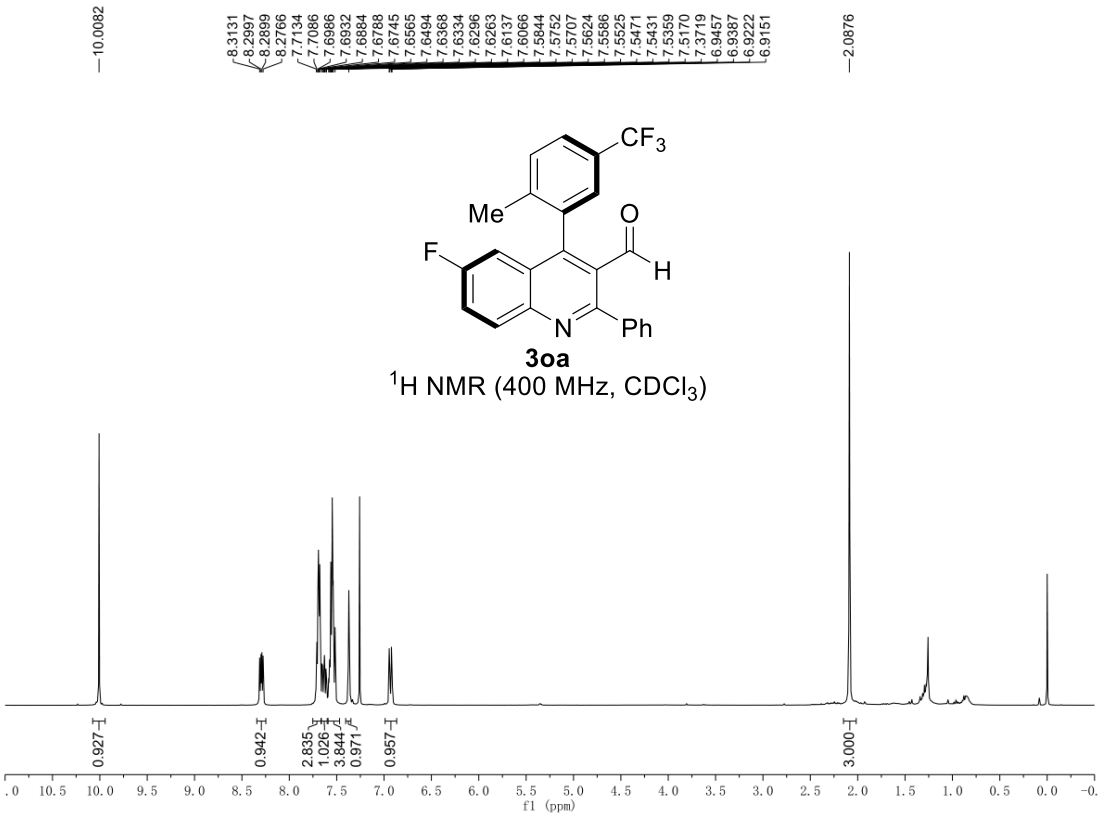


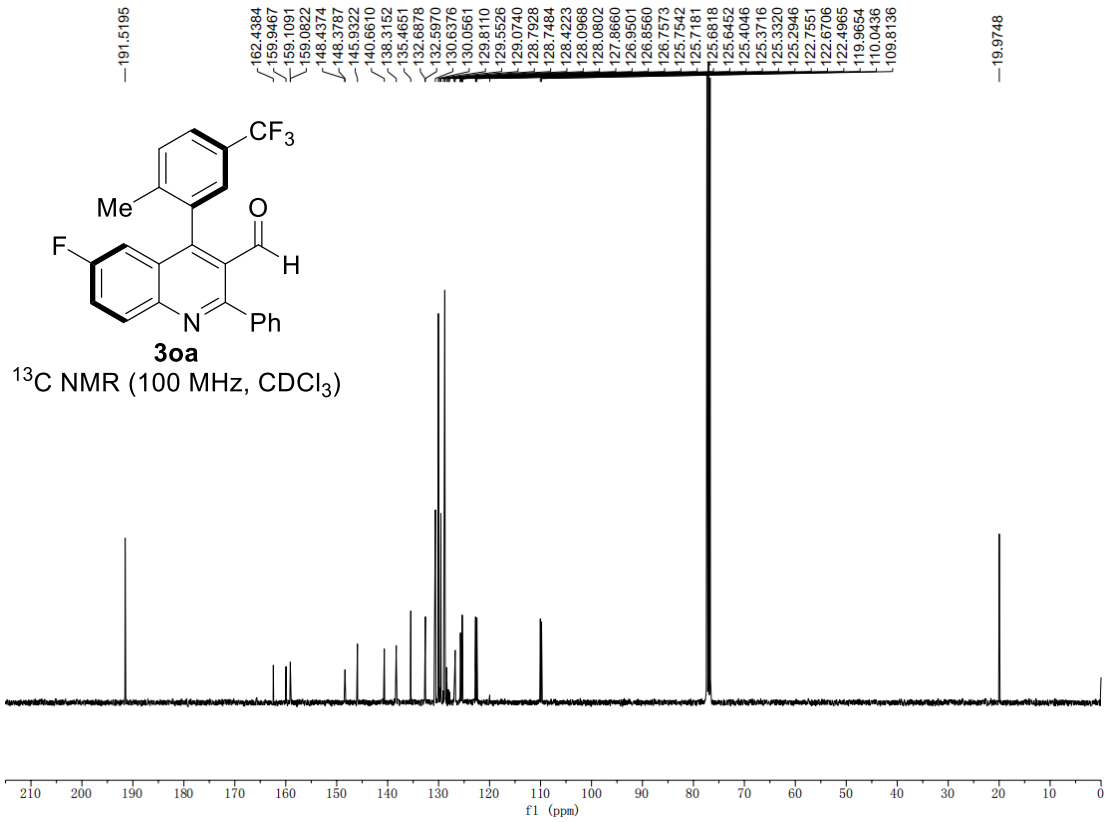

**3ma**

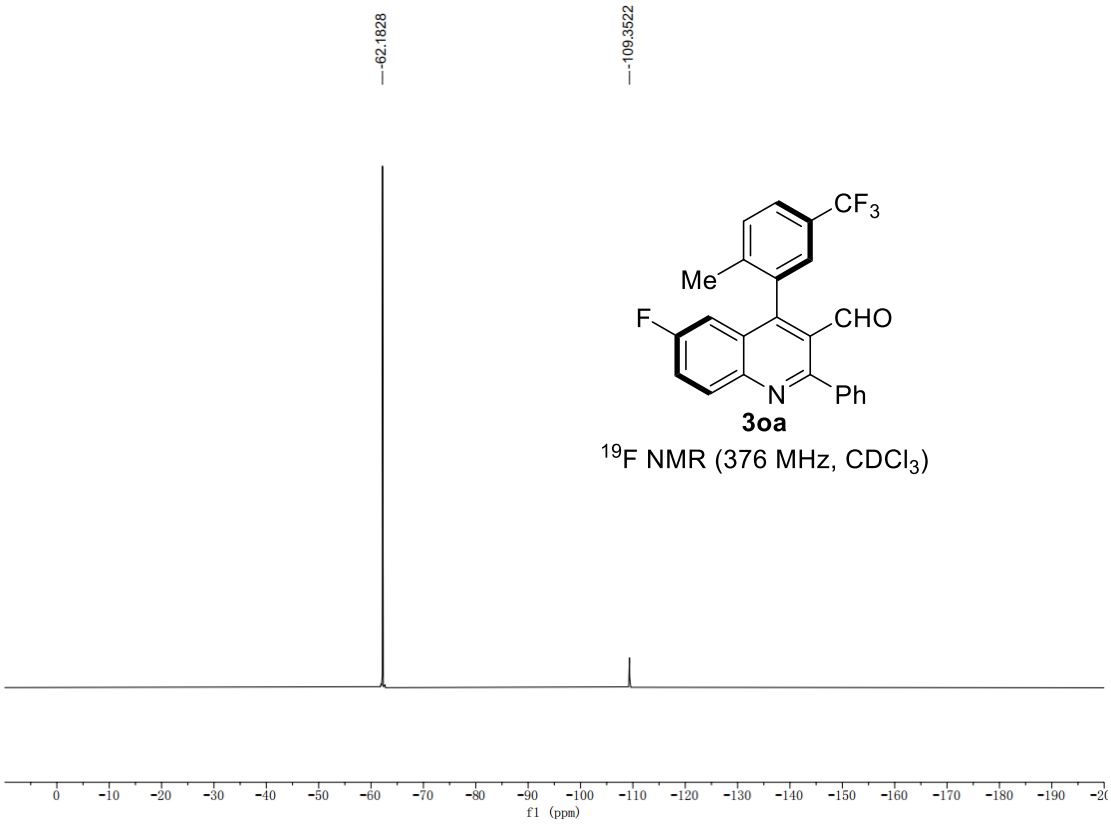
$^{19}$F NMR (376 MHz, $CDCl_3$)


10.0096
8.2592
8.2382
7.8421
7.8320
7.8212
7.8116
7.8091
7.8002
7.6625
7.6575
7.6426
7.6387
7.5270
7.5127
7.5079
7.4989
7.4937
7.4905
7.4814
7.1488
6.9276
2.3467
2.2715
1.9523
Me
Me
Me
O
H
N
Ph
3na
1H NMR (400 MHz, CDCl3)
0.931
0.950
1.025
1.946
4.927
0.976
0.982
2.992
3.004
3.000
f1 (ppm)


192.3985
159.0862
152.7328
148.4540
139.5153
137.1519
133.9129
133.3743
131.9927
131.4725
131.4133
130.2897
129.7050
128.9328
128.4226
127.3287
127.1803
126.5974
126.4023
19.6079
19.3675
19.3135
Me
Me
Me
O
H
N
Ph
3na
13C NMR (100 MHz, CDCl3)
f1 (ppm)

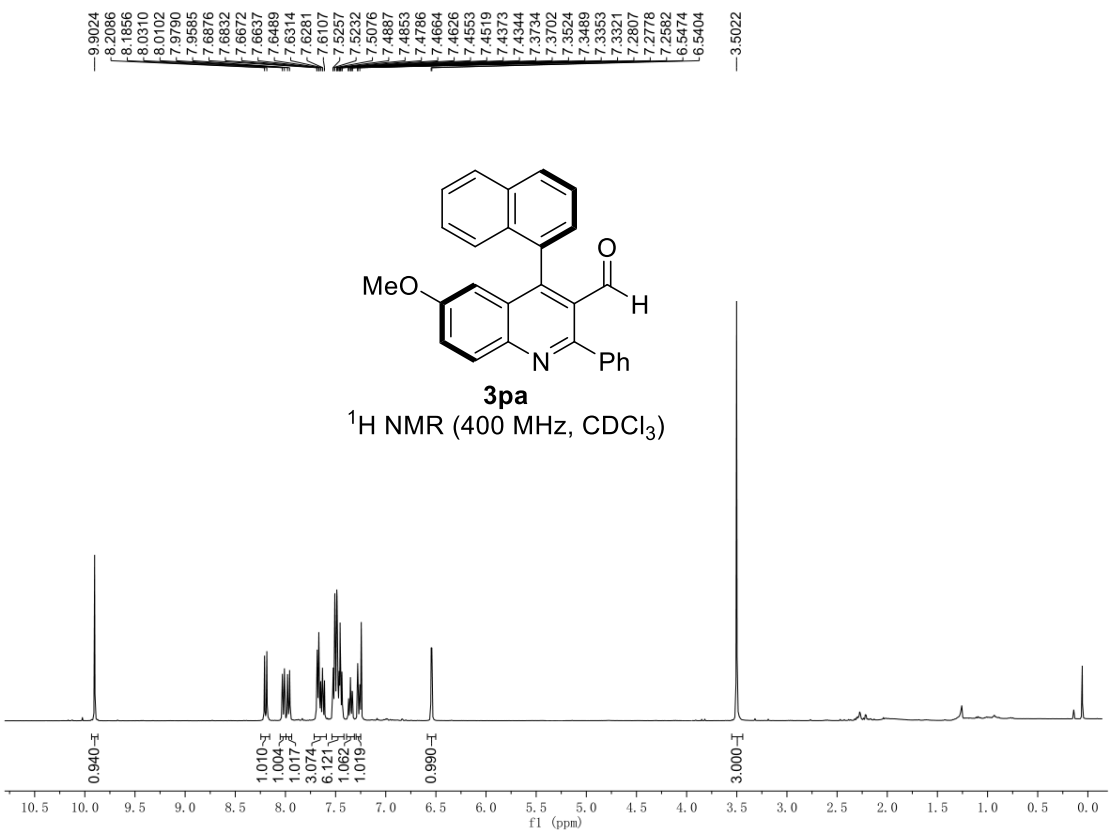

10.0082
8.3131
8.2997
8.2899
8.2766
7.7134
7.7086
7.6986
7.6932
7.6884
7.6788
7.6745
7.6565
7.6494
7.6368
7.6334
7.6296
7.6263
7.6137
7.6066
7.5844
7.5752
7.5707
7.5624
7.5586
7.5525
7.5471
7.5431
7.5359
7.5170
7.3719
6.9457
6.9387
6.9222
6.9151
2.0876
CF3
Me
O
F
H
N
Ph
3oa
1H NMR (400 MHz, CDCl3)
0.927
0.942
2.835
1.026
3.844
0.971
0.957
3.000
f1 (ppm)


191.5195
162.4384
159.9467
159.1091
159.0822
148.4374
148.3787
145.9322
140.6610
138.3152
135.4651
132.6878
132.5970
130.6376
130.0561
129.8110
129.5526
129.0740
128.7928
128.7484
128.4223
128.0968
128.0802
127.8660
126.9501
126.8560
126.7573
125.7542
125.7181
125.6818
125.6452
125.4046
125.3716
125.3320
125.2946
122.7551
122.6706
122.4965
119.9654
110.0436
109.8136
19.9748
CF3
Me
O
F
H
N
Ph
3oa
13C NMR (100 MHz, CDCl3)
f1 (ppm)



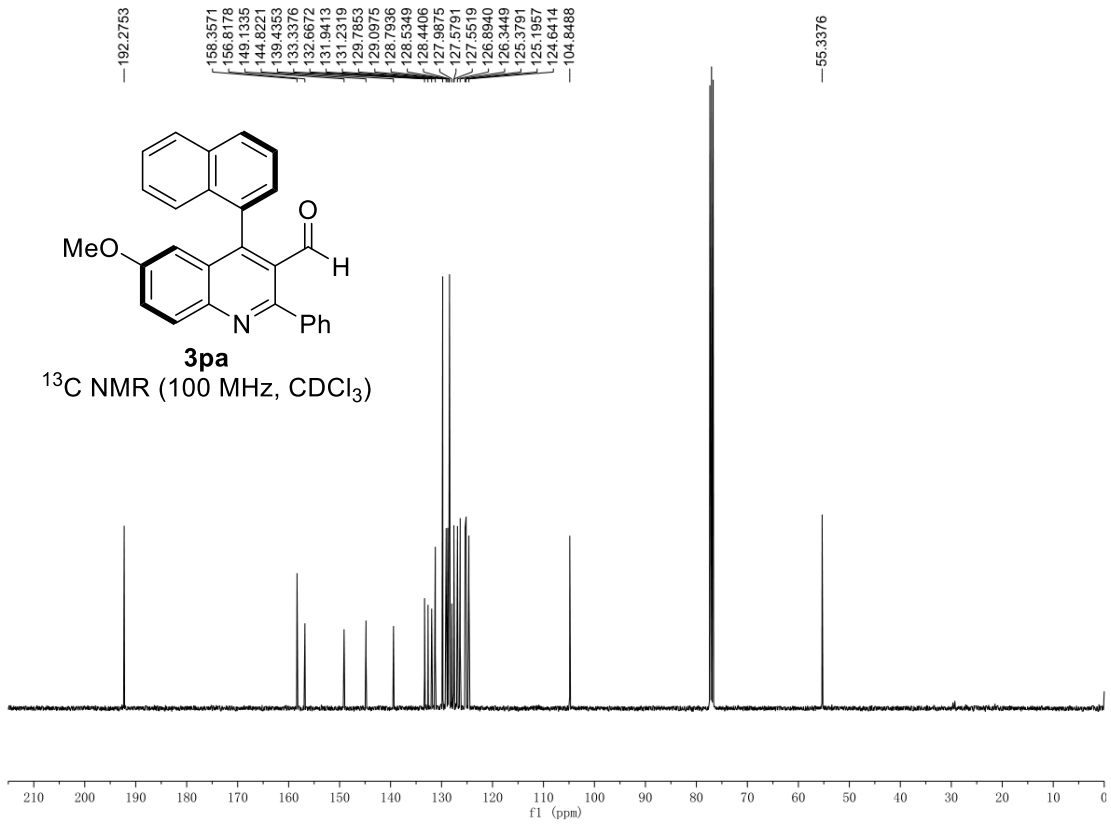

**3oa**

$^{19}F$ NMR (376 MHz, $CDCl_3$)



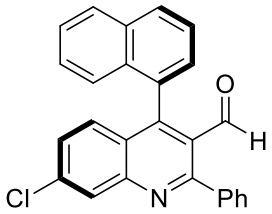

**3pa**

$^{1}$H NMR (400 MHz, $CDCl_3$)



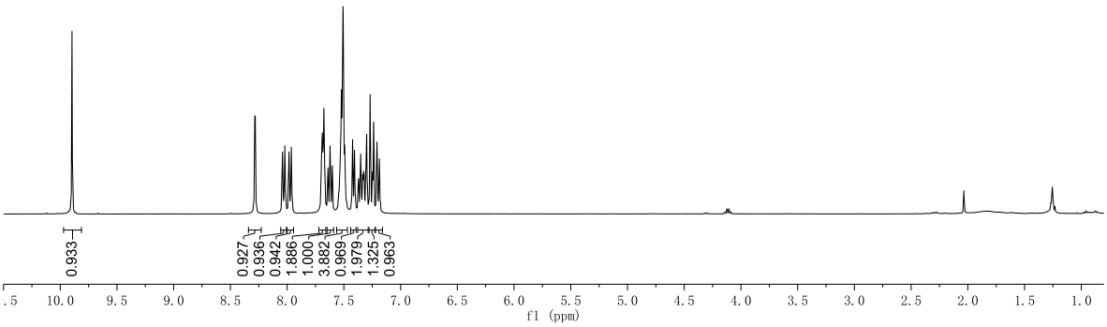

**3pa**

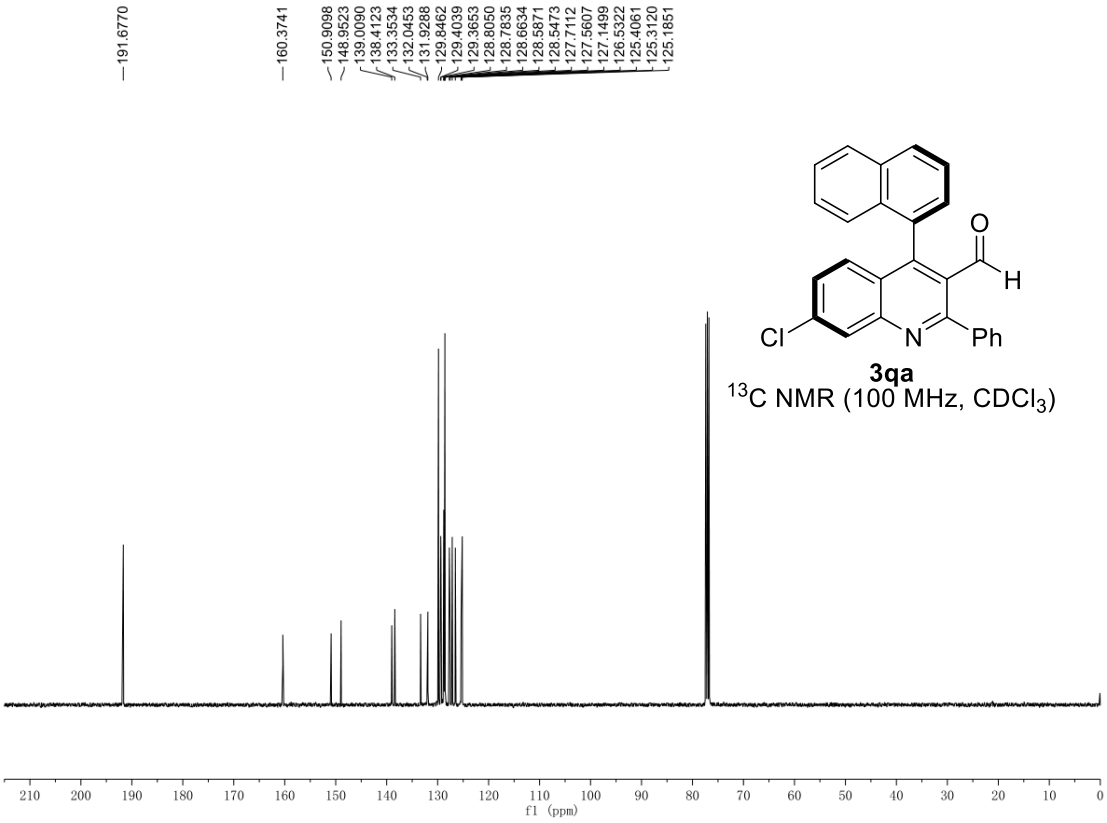
$^{13}$C NMR (100 MHz, $CDCl_3$)


**3qa**

$^{1}$H NMR (400 MHz, $CDCl_3$)



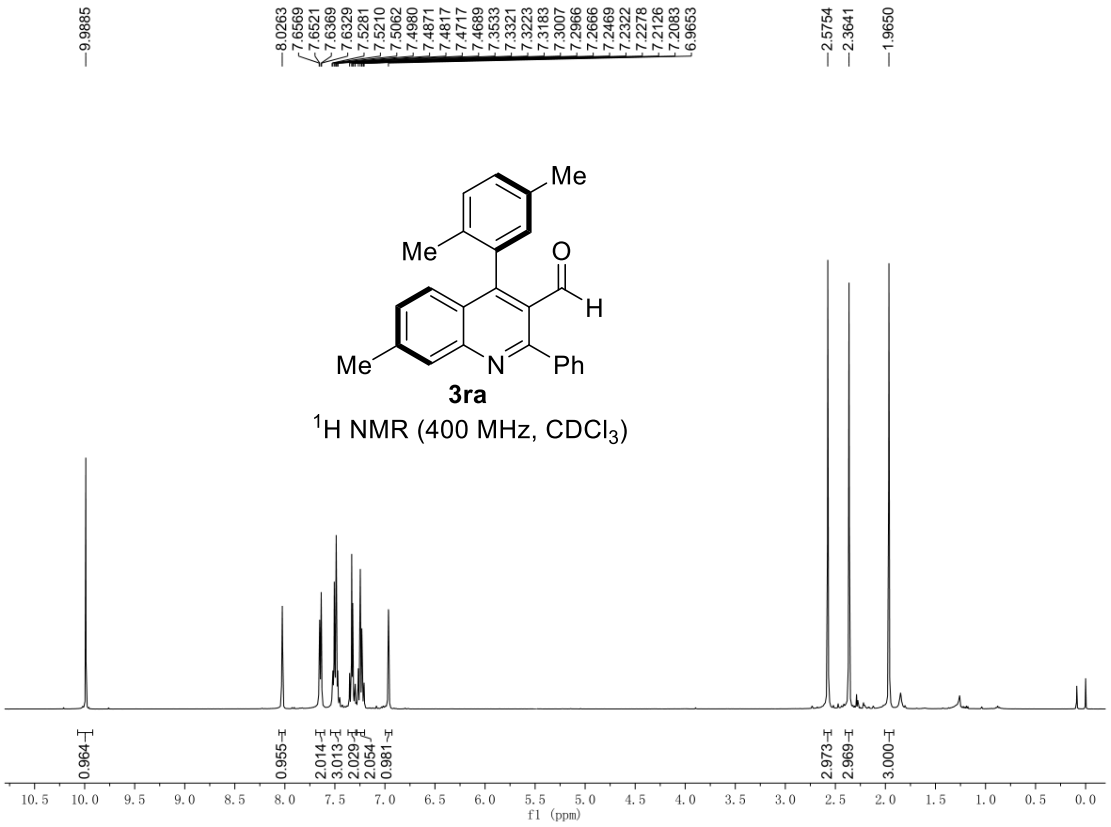



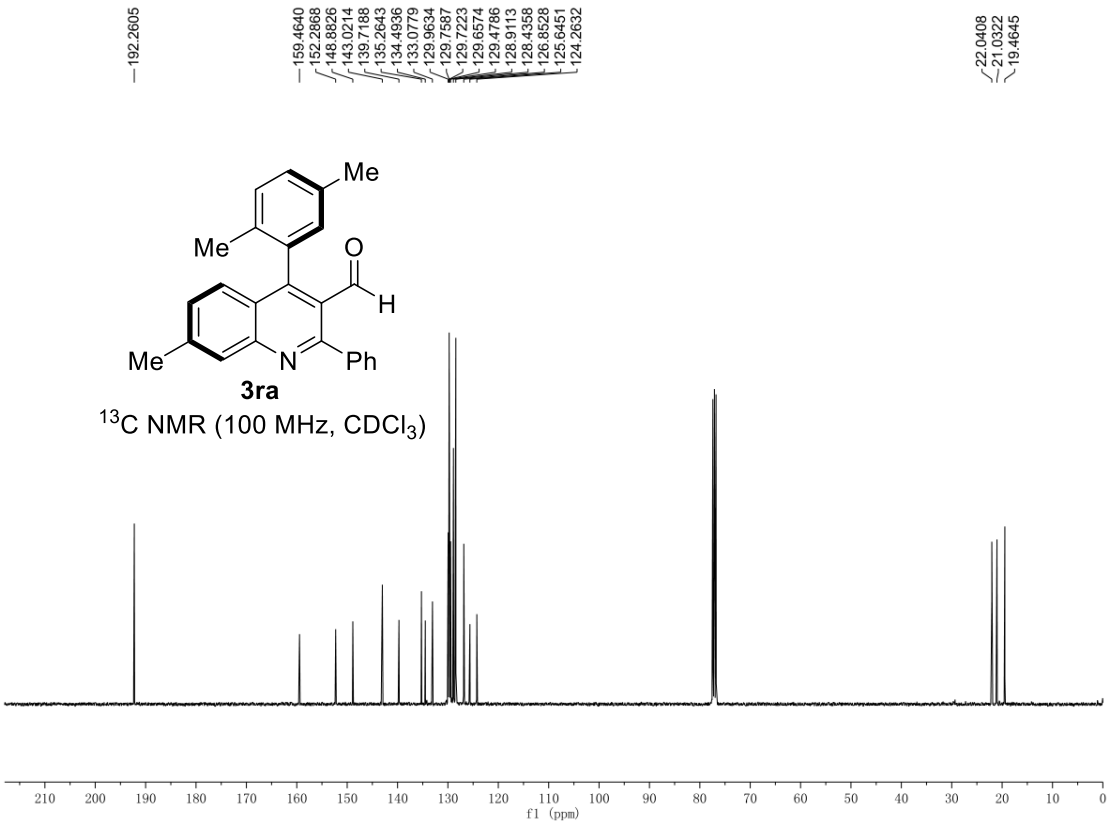


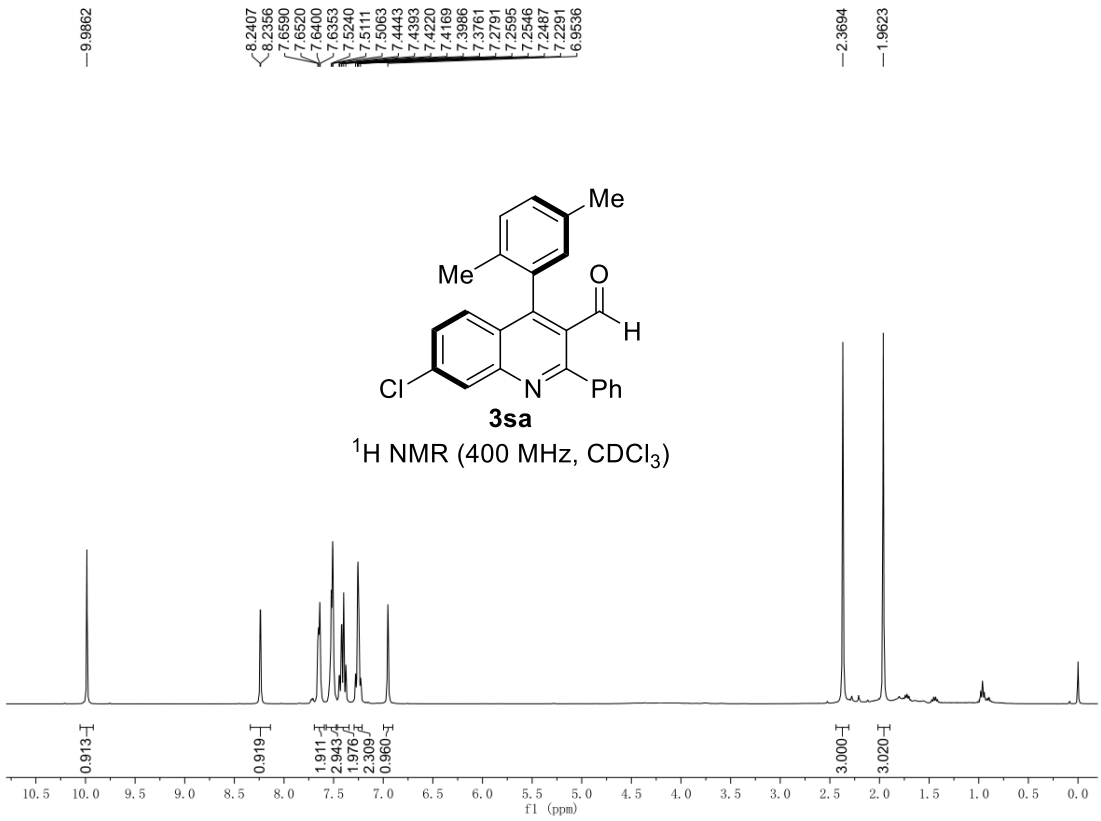


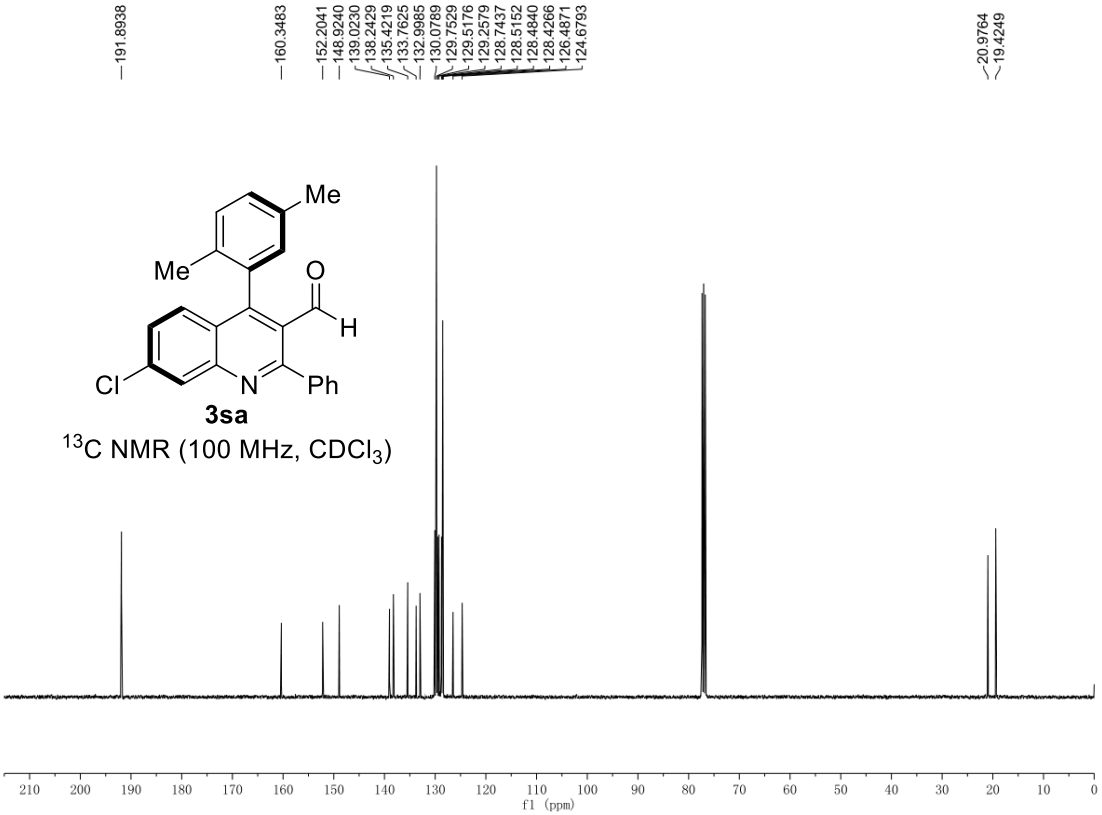
**3qa**

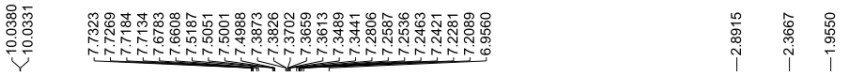
$^{13}$C NMR (100 MHz, $CDCl_3$)

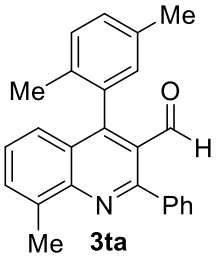

9.9885
8.0263
7.6569
7.6521
7.6369
7.6329
7.5281
7.5210
7.5062
7.4980
7.4871
7.4817
7.4717
7.4689
7.3533
7.3321
7.3223
7.3183
7.3007
7.2966
7.2666
7.2469
7.2322
7.2278
7.2126
7.2083
6.9653
2.5754
2.3641
1.9650
Me
Me
O
H
Me
N
Ph
3ra
1H NMR (400 MHz, CDCl3)
0.964
0.955
2.014
3.013
2.029
2.054
0.981
2.973
2.969
3.000
f1 (ppm)


192.2605
159.4640
152.2868
148.8826
143.0214
139.7188
135.2643
134.4936
133.0779
129.9634
129.7587
129.7223
129.6574
129.4786
128.9113
128.4358
126.8528
125.6451
124.2632
22.0408
21.0322
19.4645
Me
Me
O
H
Me
N
Ph
3ra
13C NMR (100 MHz, CDCl3)
f1 (ppm)


9.9862
8.2407
8.2356
7.6590
7.6520
7.6400
7.6353
7.5240
7.5111
7.5063
7.4443
7.4393
7.4220
7.4169
7.3986
7.3761
7.2791
7.2595
7.2546
7.2487
7.2291
6.9536
2.3694
1.9623
Me
Me
O
H
Cl
N
Ph
3sa
1H NMR (400 MHz, CDCl3)
0.913
0.919
1.911
2.943
1.976
2.309
0.960
3.000
3.020
f1 (ppm)

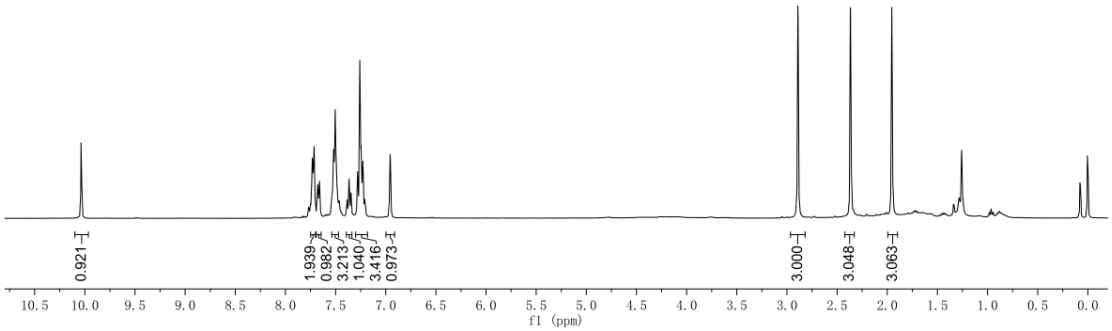

191.8938
160.3483
152.2041
148.9240
139.0230
138.2429
135.4219
133.7625
132.9985
130.0789
129.7529
129.5176
129.2579
128.7437
128.5152
128.4840
128.4266
126.4871
124.6793
20.9764
19.4249
Me
Me
O
H
Cl
N
Ph
3sa
13C NMR (100 MHz, CDCl3)
f1 (ppm)

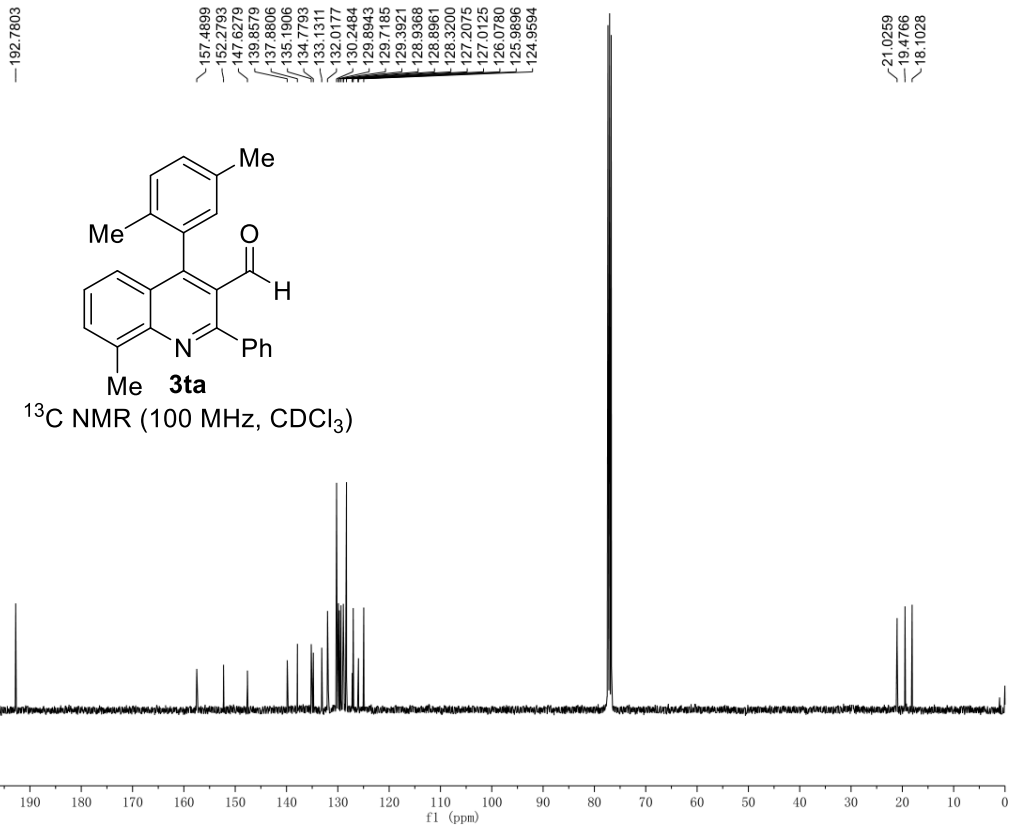



**3ta**

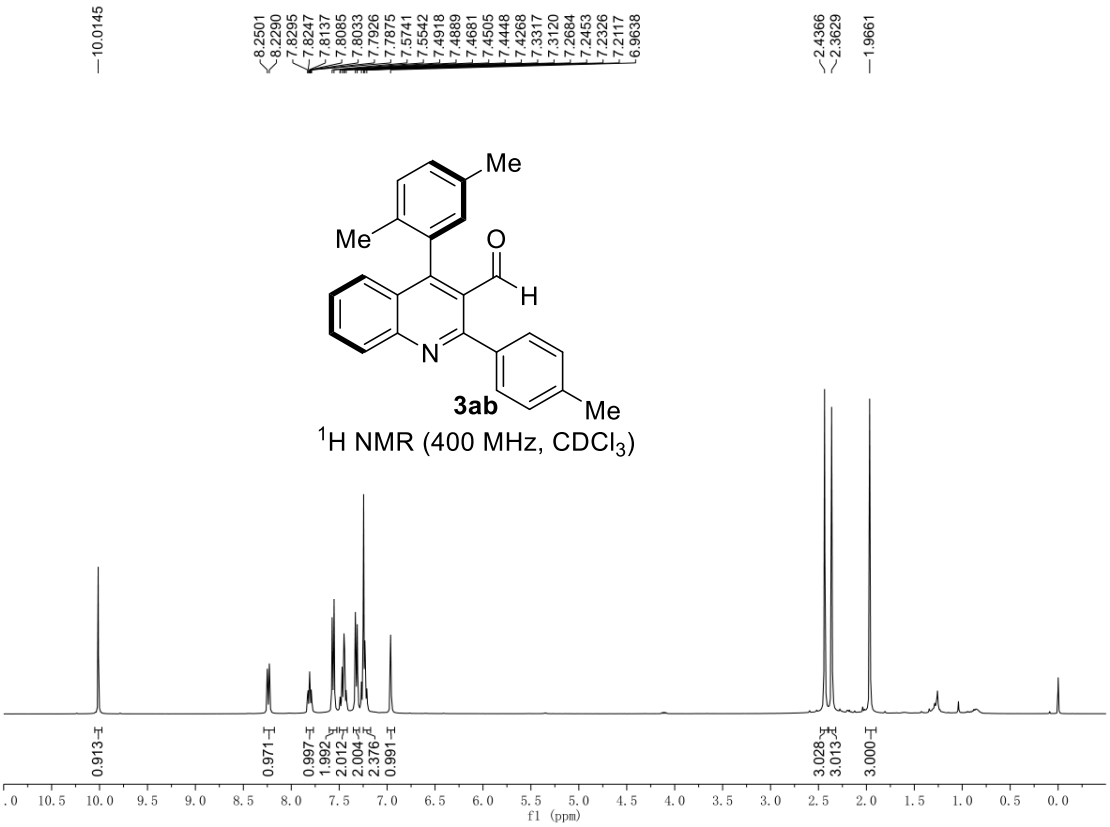
$^{1}$H NMR (400 MHz, $CDCl_3$)



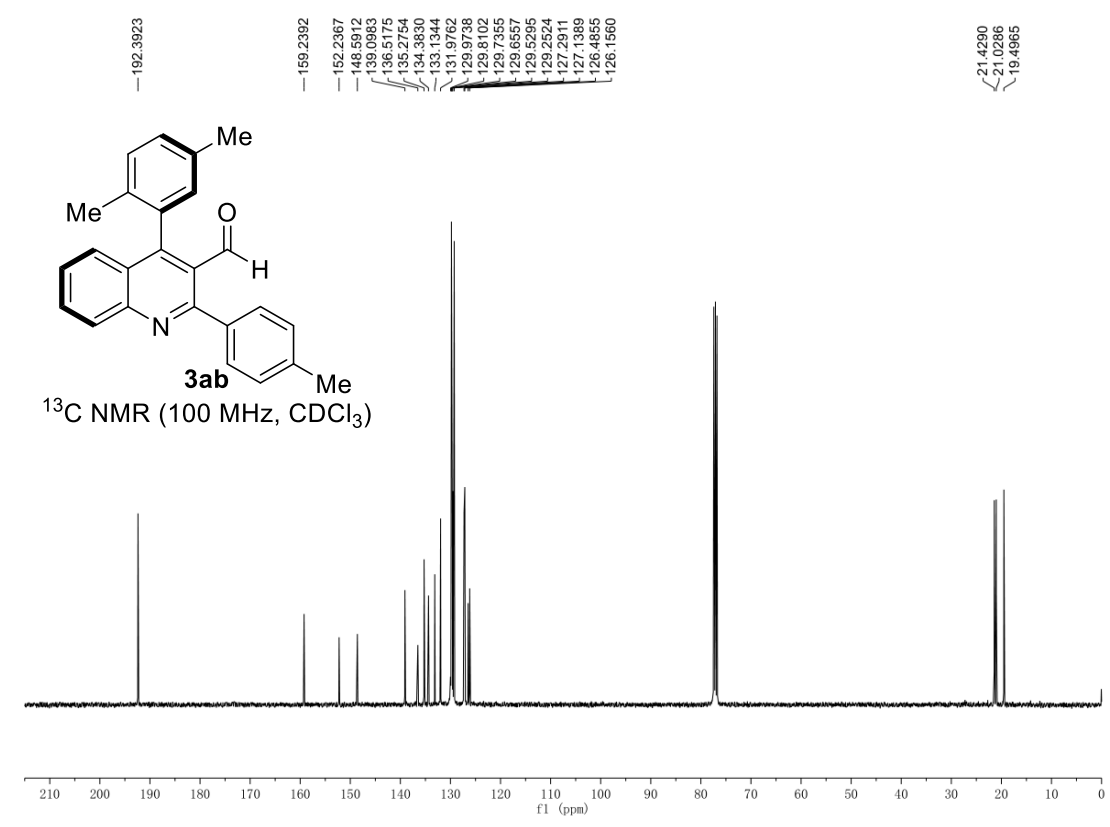




**3ta**

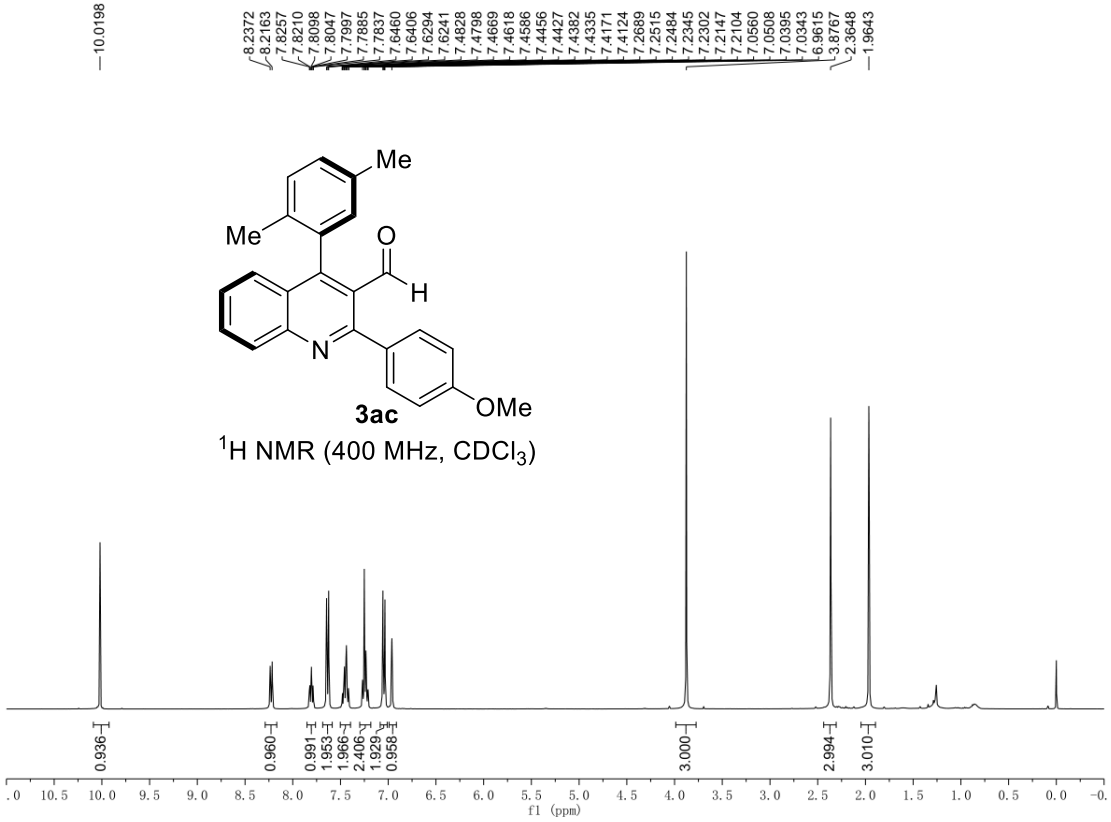
$^{13}$C NMR (100 MHz, $CDCl_3$)

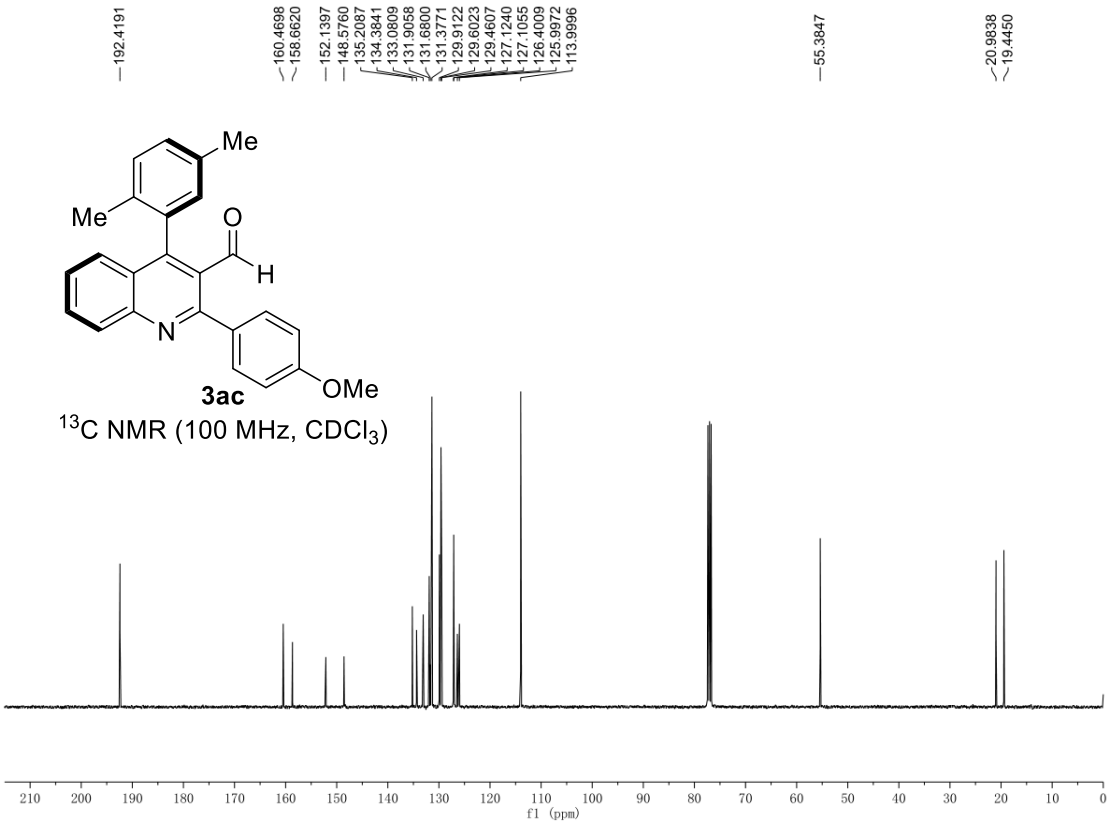


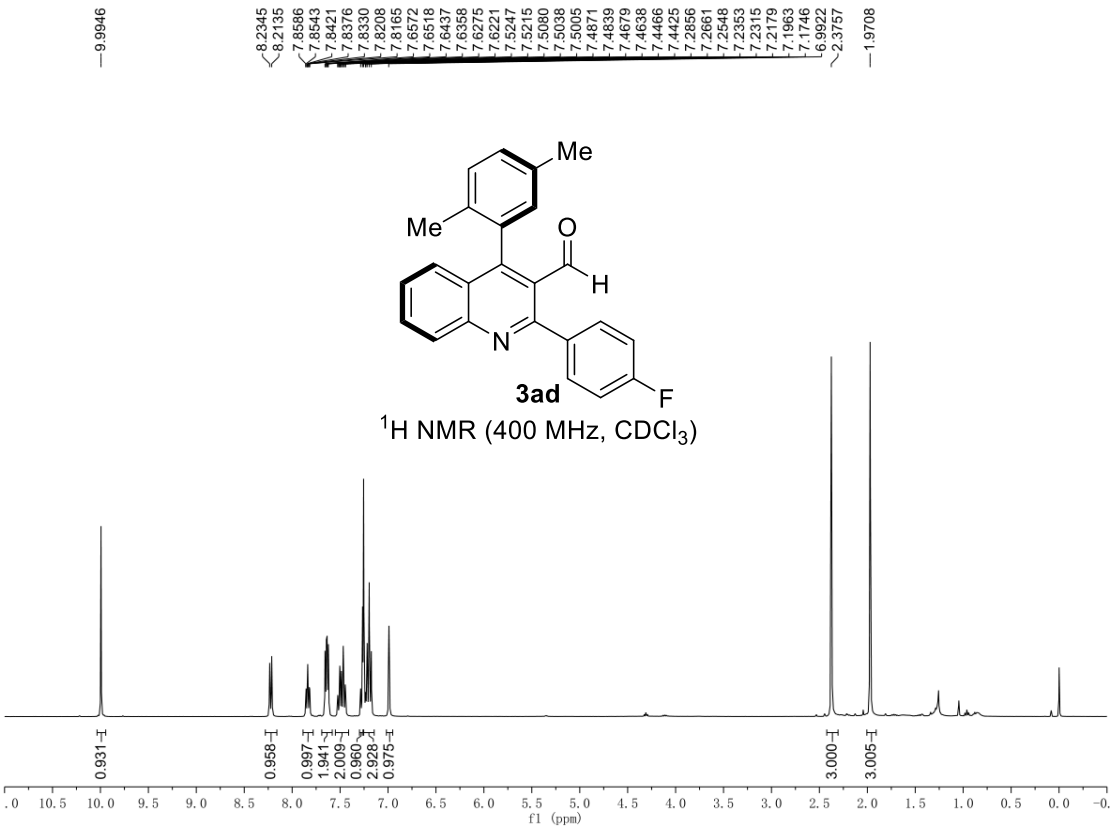

$^1$H NMR (400 MHz, $CDCl_3$)

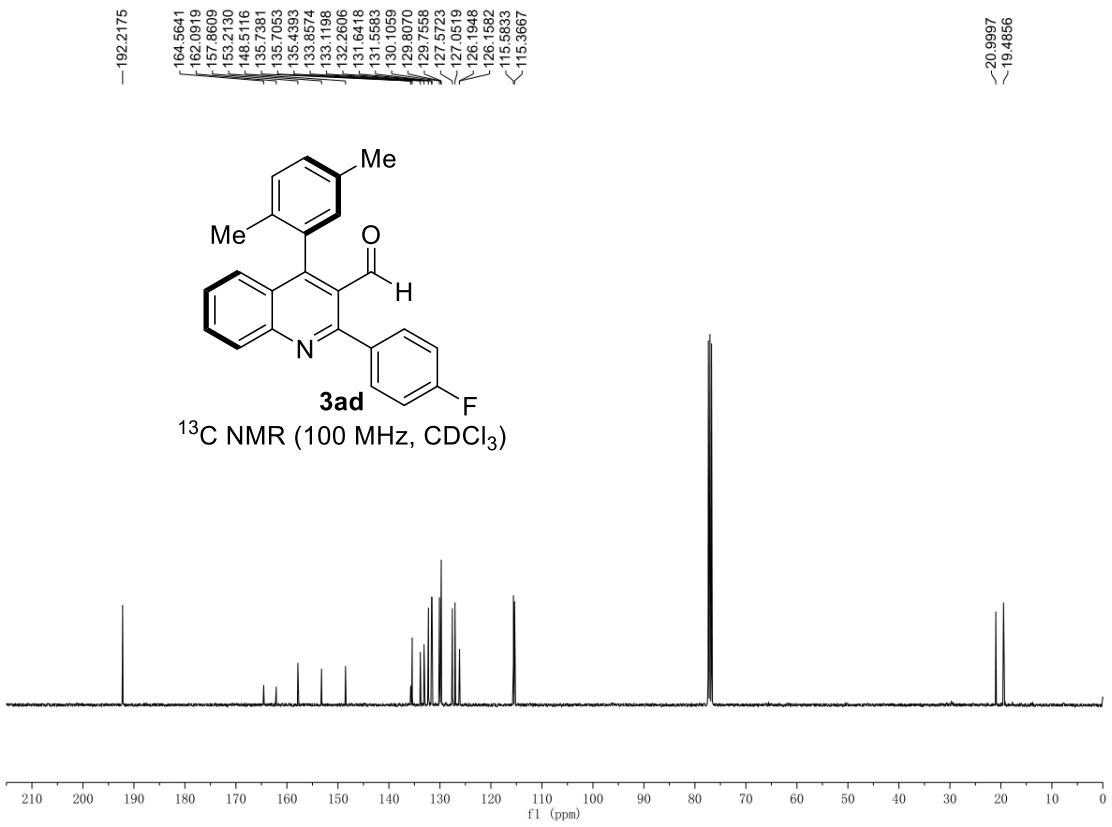


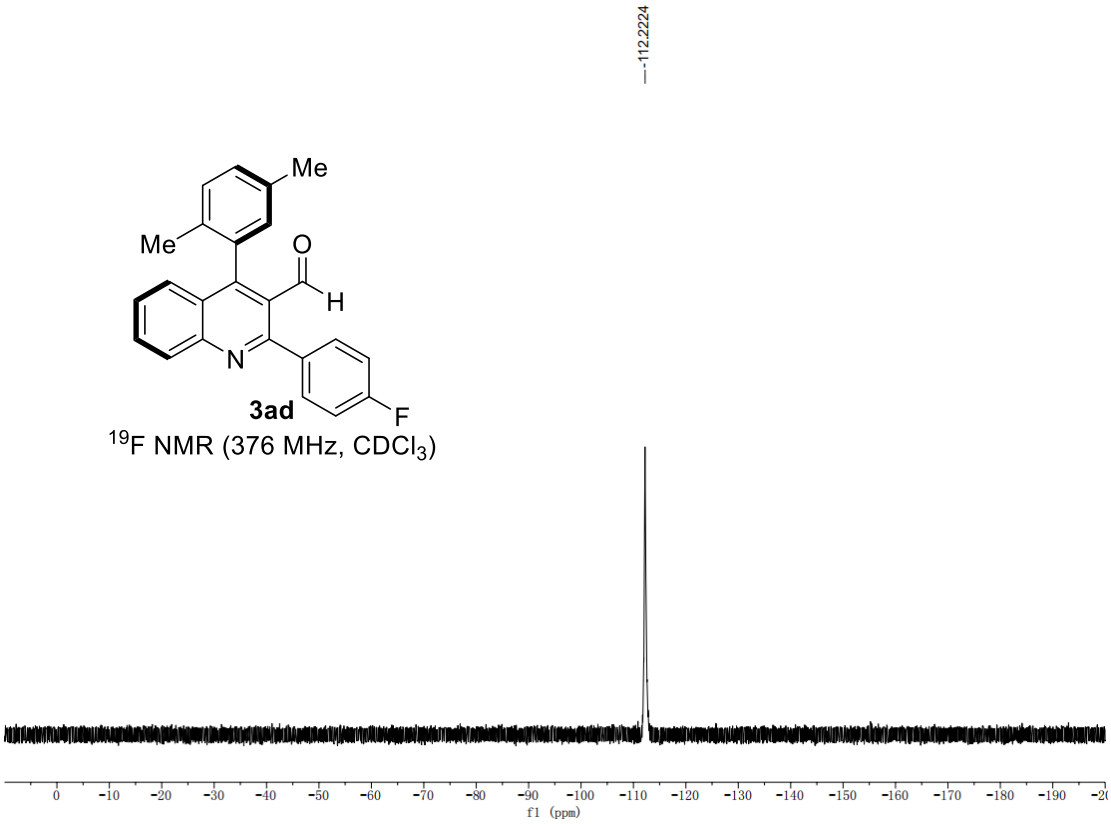

$^{13}$C NMR (100 MHz, $CDCl_3$)

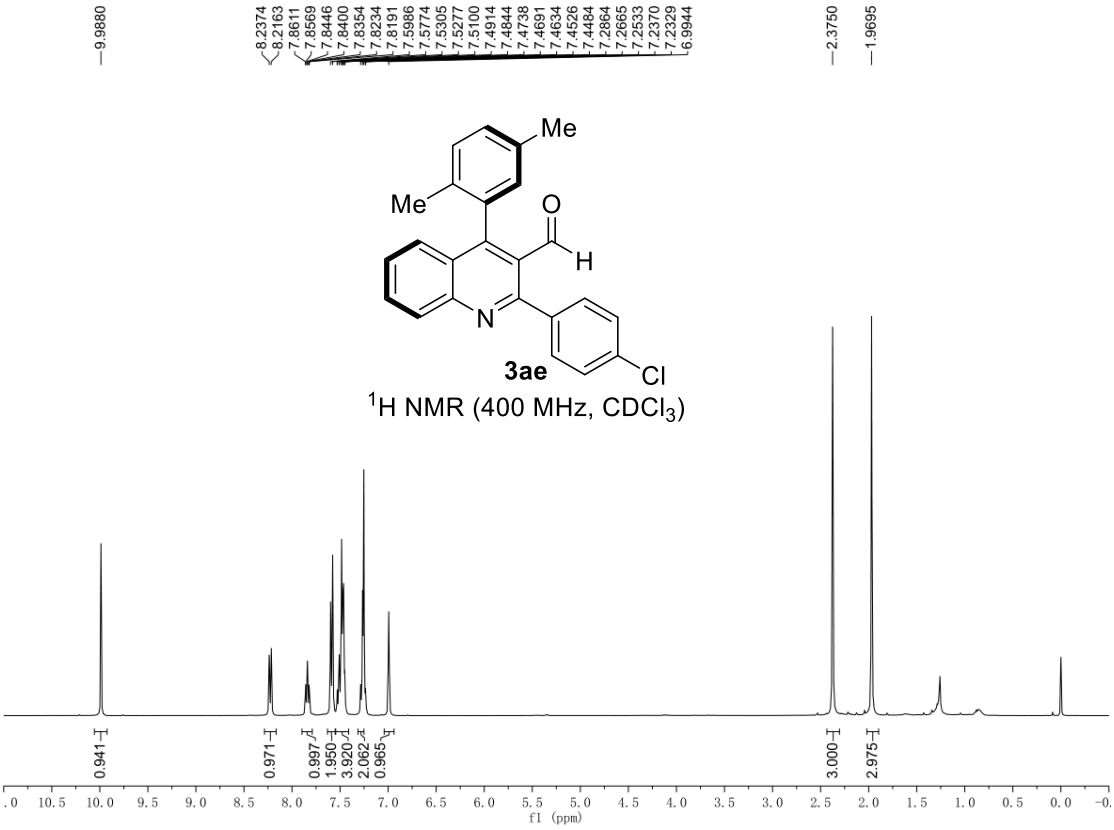

10.0198
8.2372
8.2163
7.8257
7.8210
7.8098
7.8047
7.7997
7.7885
7.7837
7.6460
7.6406
7.6294
7.6241
7.4828
7.4798
7.4669
7.4618
7.4586
7.4456
7.4427
7.4382
7.4335
7.4171
7.4124
7.2689
7.2515
7.2484
7.2345
7.2302
7.2147
7.2104
7.0560
7.0508
7.0395
7.0343
6.9615
3.8767
2.3648
1.9643
Me
Me
O
H
N
OMe
3ac
$^1$H NMR (400 MHz, CDCl$_3$)
0.936
0.960
0.991
1.953
1.966
2.406
1.929
0.958
3.000
2.994
3.010
f1 (ppm)


192.4191
160.4698
158.6620
152.1397
148.5760
135.2087
134.3841
133.0809
131.9058
131.6800
131.3771
129.9122
129.6023
129.4607
127.1240
127.1055
126.4009
125.9972
113.9996
55.3847
20.9838
19.4450
Me
Me
O
H
N
OMe
3ac
$^{13}$C NMR (100 MHz, CDCl$_3$)
f1 (ppm)

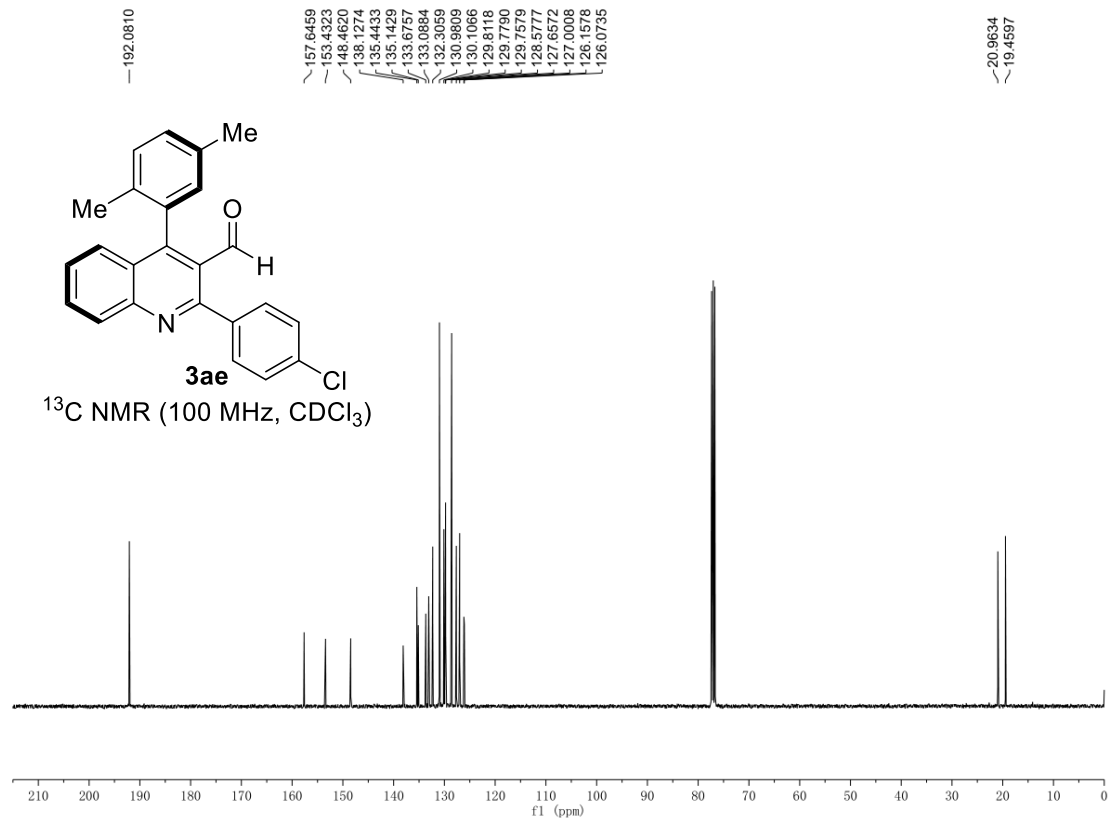

9.9946
8.2345
8.2135
7.8586
7.8543
7.8421
7.8376
7.8330
7.8208
7.8165
7.6572
7.6518
7.6437
7.6358
7.6275
7.6221
7.5247
7.5215
7.5080
7.5038
7.5005
7.4871
7.4839
7.4679
7.4638
7.4466
7.4425
7.2856
7.2661
7.2548
7.2353
7.2315
7.2179
7.1963
7.1746
6.9922
2.3757
1.9708
Me
Me
O
H
N
F
3ad
$^1$H NMR (400 MHz, CDCl$_3$)
0.931
0.958
0.997
1.941
2.009
0.960
2.928
0.975
3.000
3.005
f1 (ppm)


192.2175
164.5641
162.0919
157.8609
153.2130
148.5116
135.7381
135.7053
135.4393
133.8574
133.1198
132.2606
131.6418
131.5583
130.1059
129.8070
129.7558
127.5723
127.0519
126.1948
126.1582
115.5833
115.3667
20.9997
19.4856
Me
Me
O
H
N
F
3ad
$^{13}$C NMR (100 MHz, CDCl$_3$)
f1 (ppm)

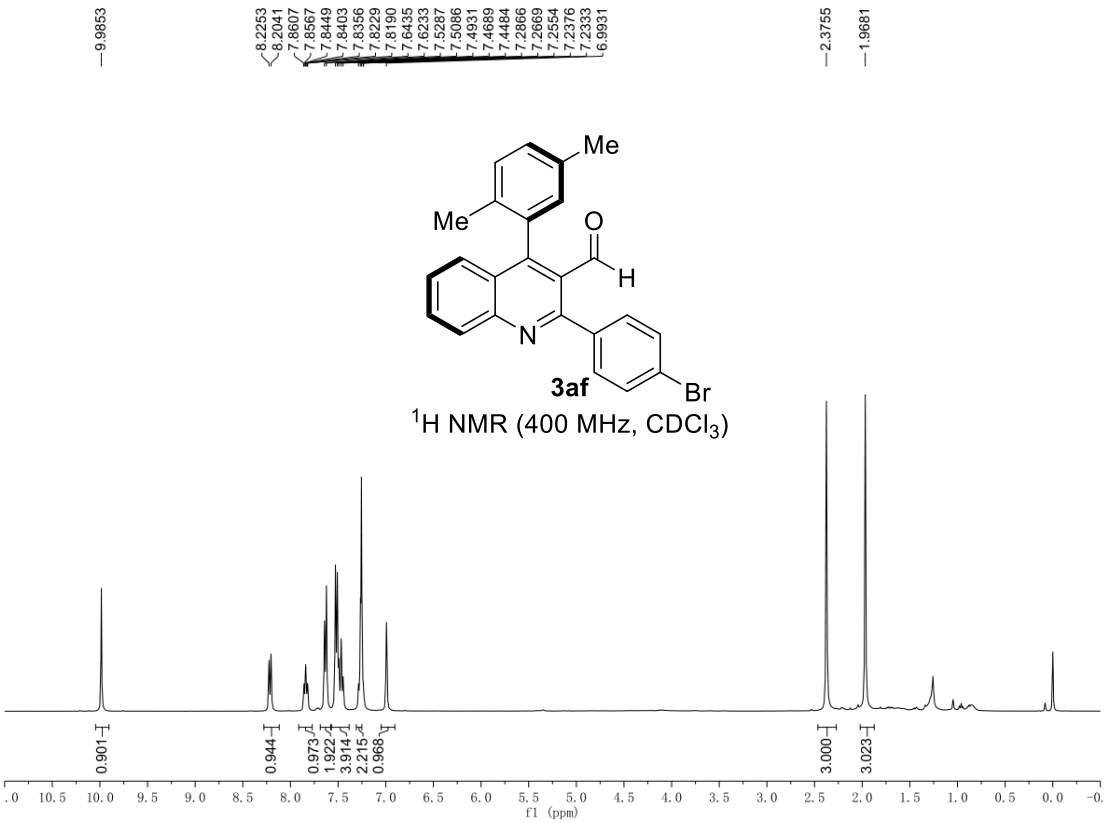

-112.2224
Me
Me
O
H
N
F
3ad
19F NMR (376 MHz, CDCl3)
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

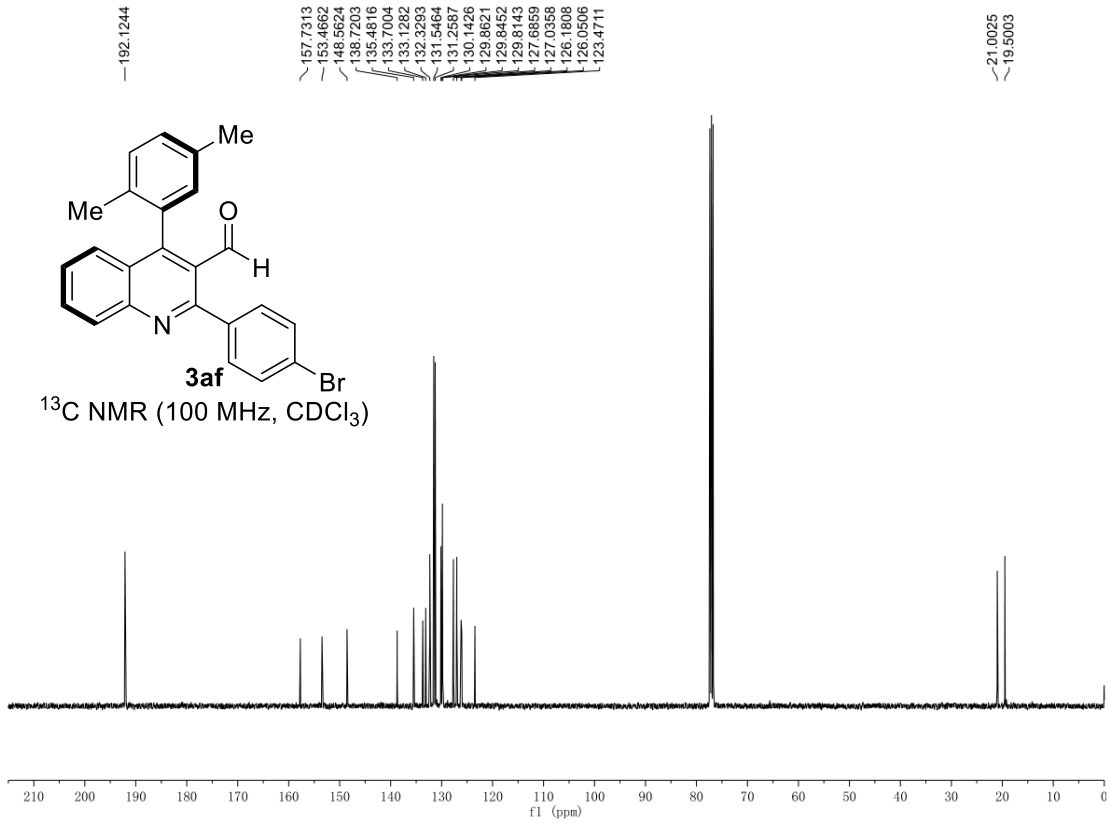


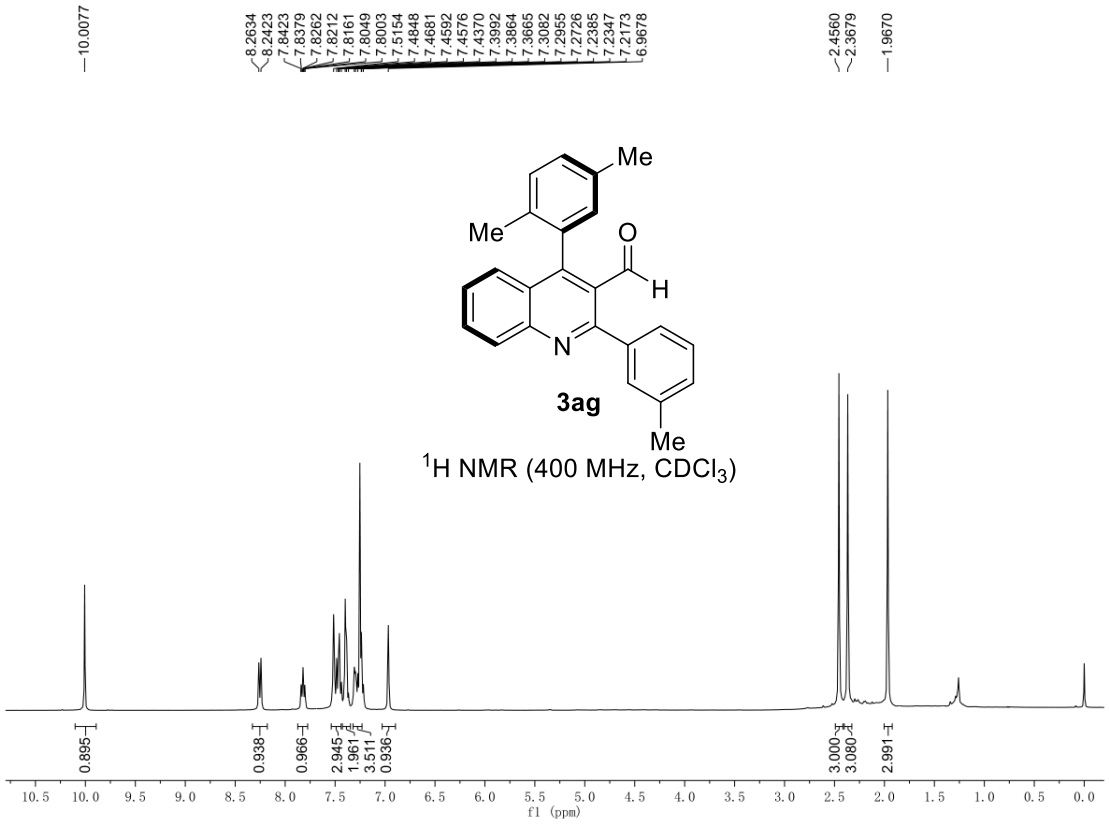

$^{1}$H NMR (400 MHz, $CDCl_3$)

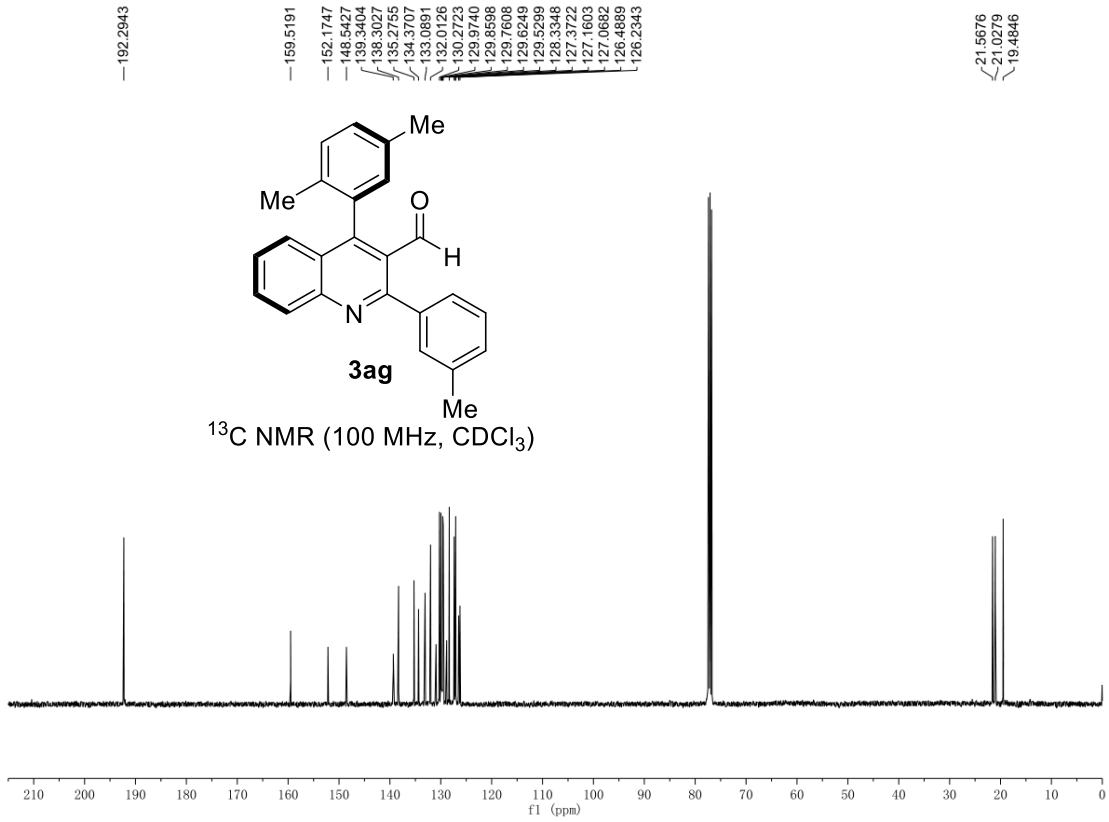


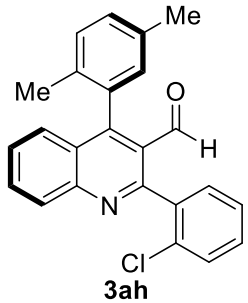

$^{13}$C NMR (100 MHz, $CDCl_3$)


9.9853
8.2253
8.2041
7.8607
7.8567
7.8449
7.8403
7.8356
7.8229
7.8190
7.6435
7.6233
7.5287
7.5086
7.4931
7.4689
7.4484
7.2866
7.2669
7.2554
7.2376
7.2333
6.9931
2.3755
1.9681
Me
Me
O
H
N
Br
3af
$^1$H NMR (400 MHz, CDCl$_3$)
0.901
0.944
0.973
1.922
3.914
2.215
0.968
3.000
3.023
f1 (ppm)


192.1244
157.7313
153.4662
148.5624
138.7203
135.4816
133.7004
133.1282
132.3293
131.5464
131.2587
130.1426
129.8621
129.8452
129.8143
127.6859
127.0358
126.1808
126.0506
123.4711
21.0025
19.5003
Me
Me
O
H
N
Br
3af
$^{13}$C NMR (100 MHz, CDCl$_3$)
f1 (ppm)

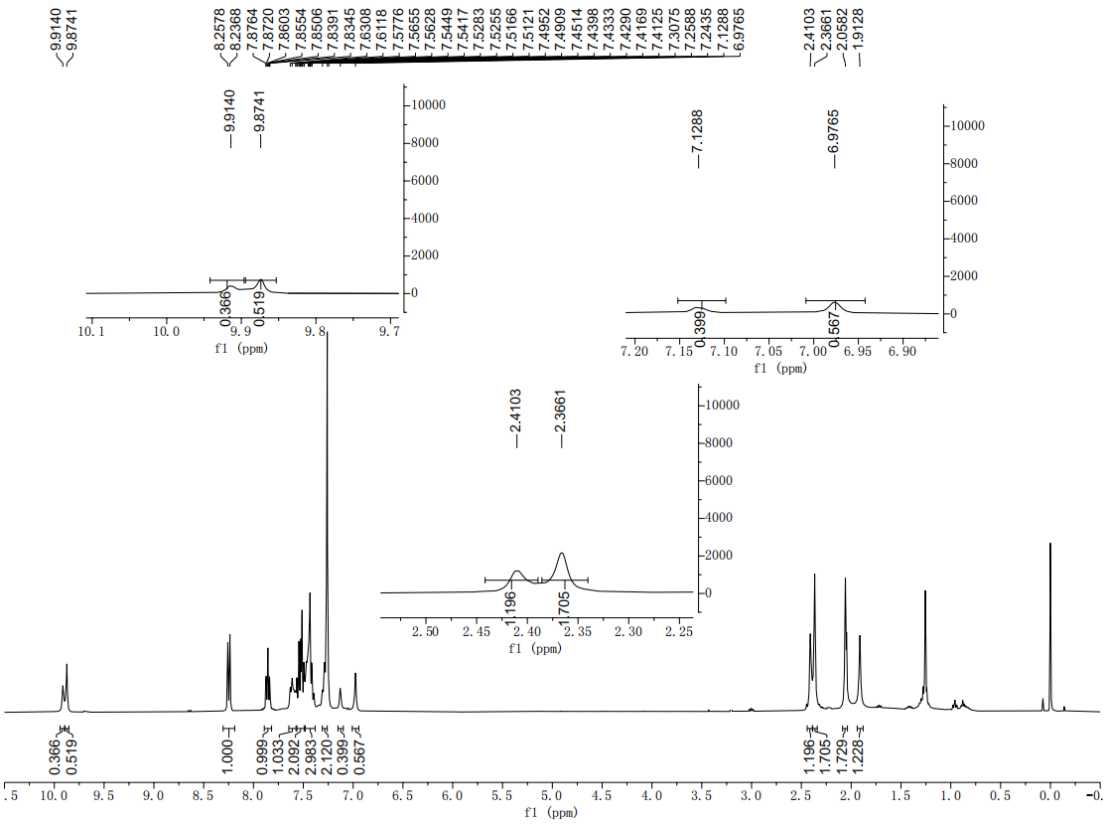

10.0077
8.2634
8.2423
7.8423
7.8379
7.8262
7.8212
7.8161
7.8049
7.8003
7.5154
7.4848
7.4681
7.4592
7.4576
7.4370
7.3992
7.3864
7.3665
7.3082
7.2955
7.2726
7.2385
7.2347
7.2173
6.9678
2.4560
2.3679
1.9670
Me
Me
O
H
N
3ag
Me
1H NMR (400 MHz, CDCl3)
0.895
0.938
0.966
2.945
1.961
3.511
0.936
3.000
3.080
2.991
f1 (ppm)

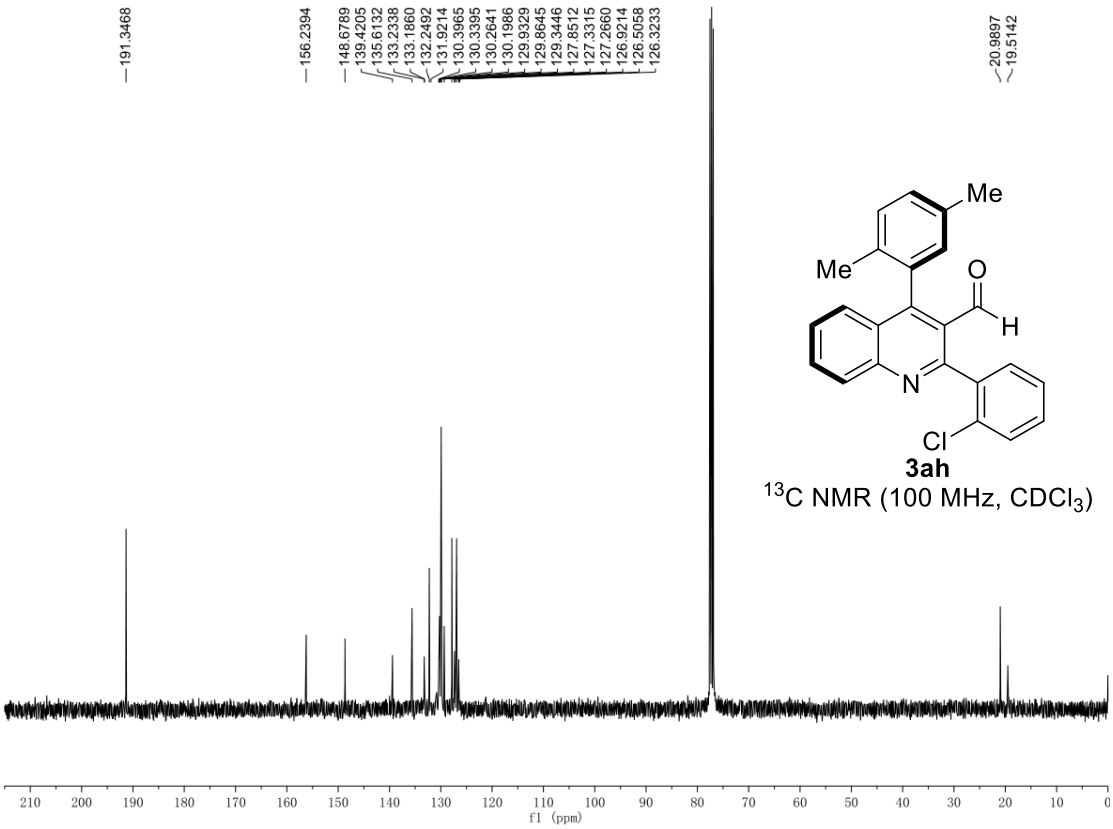

192.2943
159.5191
152.1747
148.5427
139.3404
138.3027
135.2755
134.3707
133.0891
132.0126
130.2723
129.9740
129.8598
129.7608
129.6249
129.5299
128.3348
127.3722
127.1603
127.0682
126.4889
126.2343
21.5676
21.0279
19.4846
Me
Me
O
H
N
3ag
Me
13C NMR (100 MHz, CDCl3)
f1 (ppm)

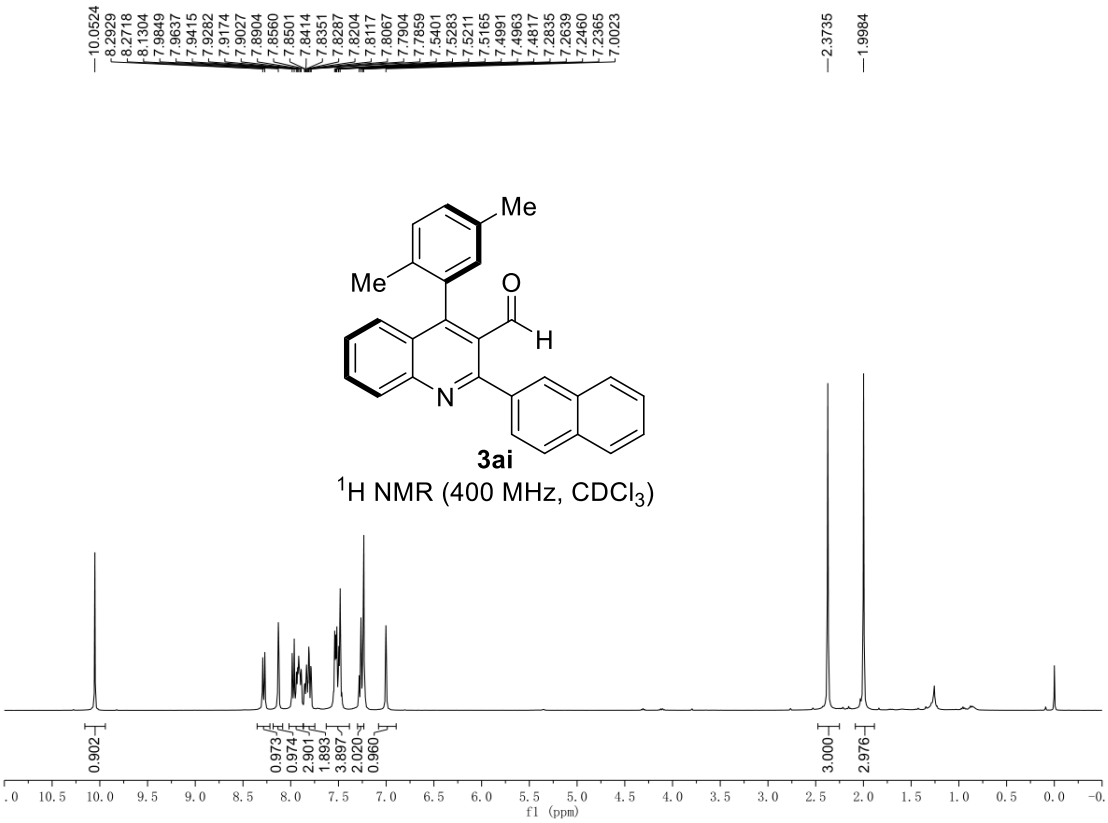


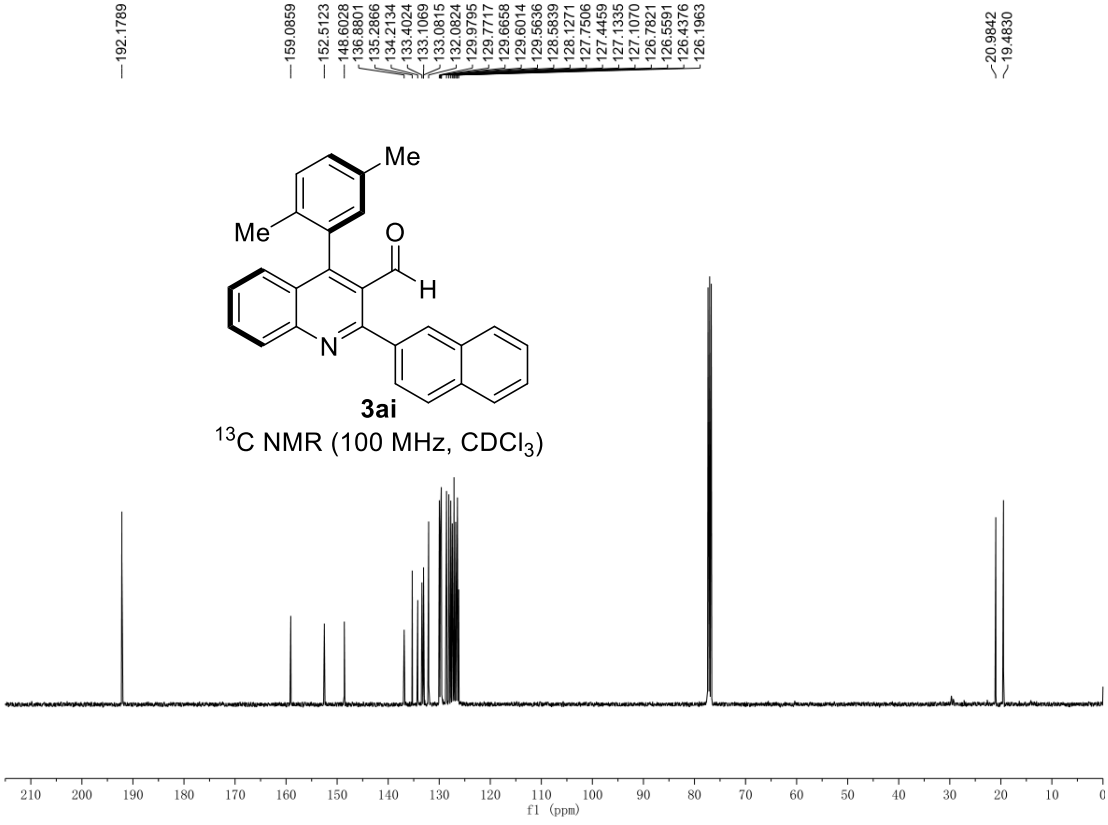

**3ah**

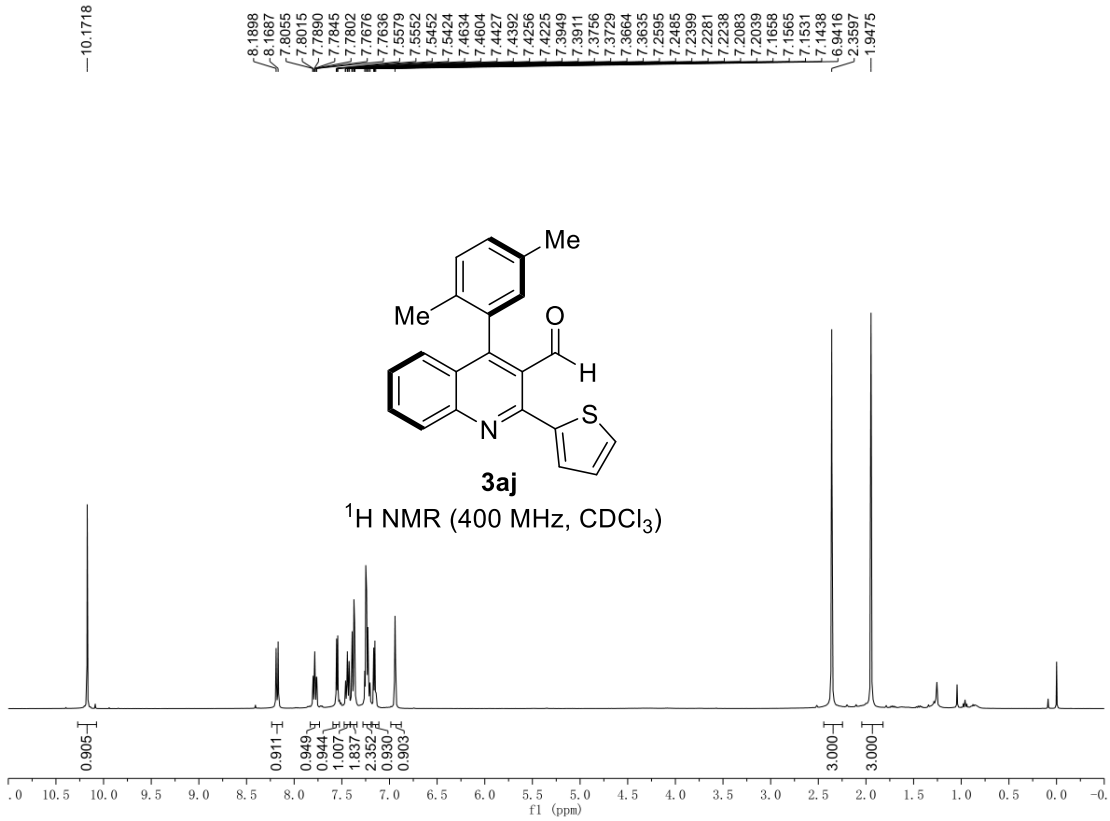
$^1$H NMR (400 MHz, $CDCl_3$)

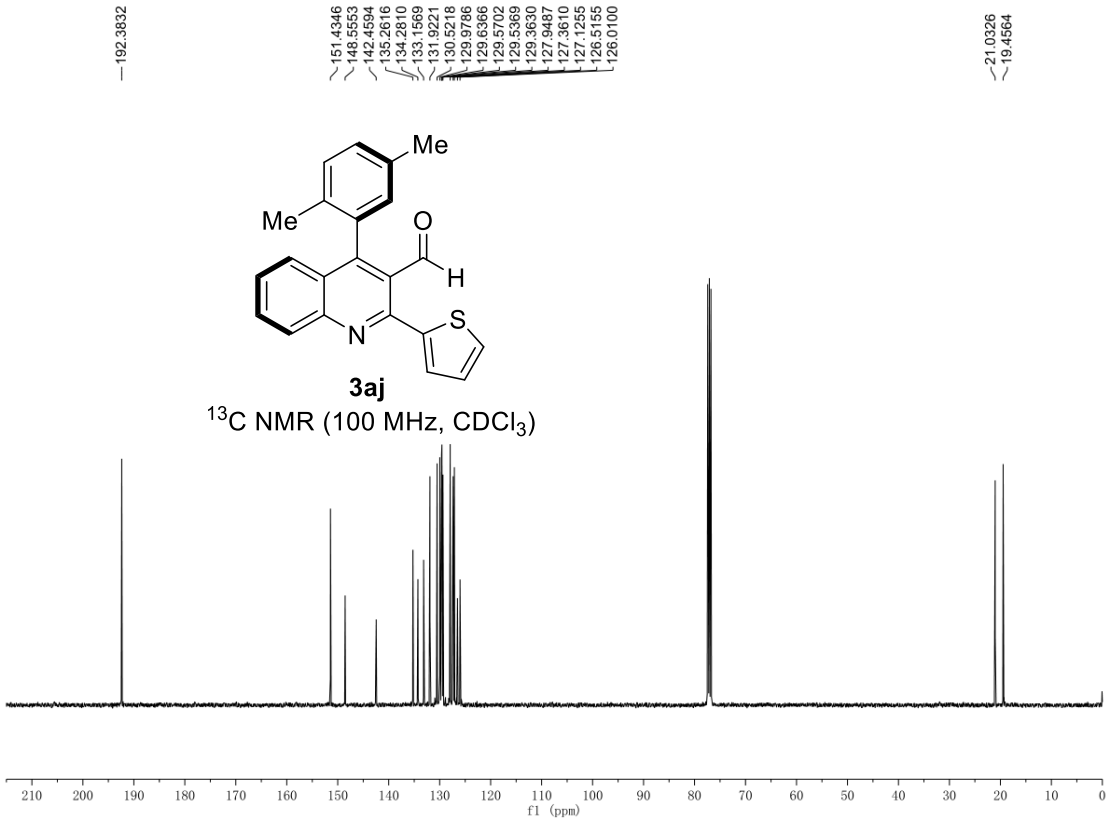


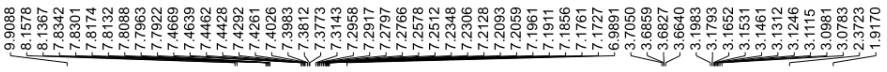

191.3468
156.2394
148.6789
139.4205
135.6132
133.2338
133.1860
132.2492
131.9214
130.3965
130.3395
130.2641
130.1986
129.9329
129.8645
129.3446
127.8512
127.3315
127.2660
126.9214
126.5058
126.3233
20.9897
19.5142
Me
Me
O
H
N
Cl
3ah
13C NMR (100 MHz, CDCl3)
f1 (ppm)

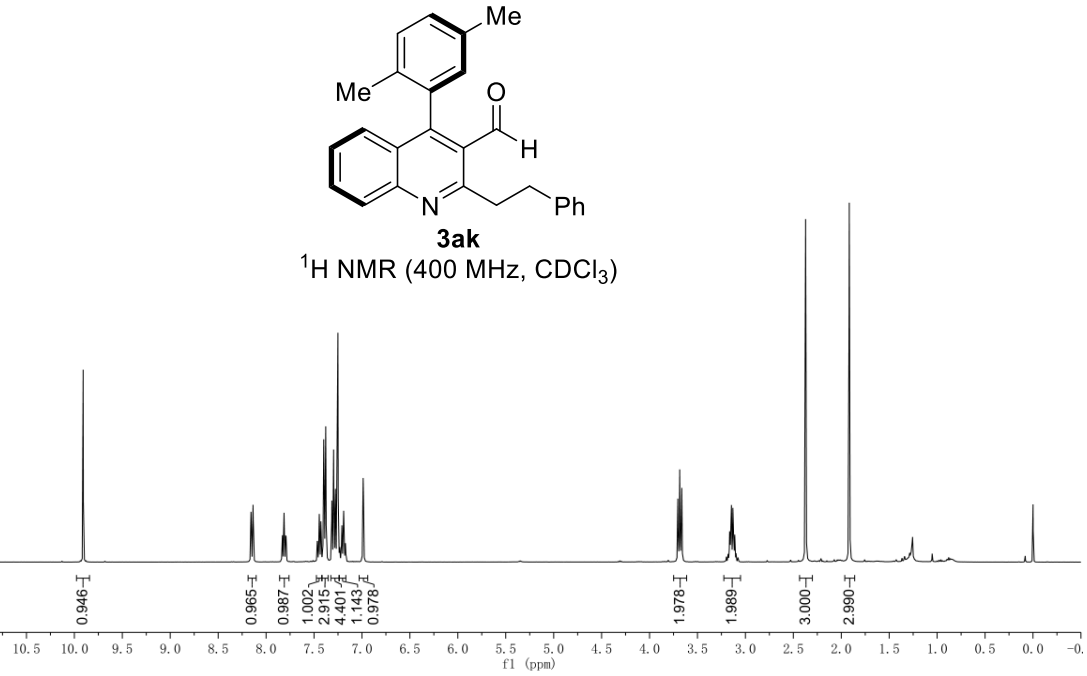

10.0524
8.2929
8.2718
8.1304
7.9849
7.9637
7.9415
7.9282
7.9174
7.9027
7.8904
7.8560
7.8501
7.8414
7.8351
7.8287
7.8204
7.8117
7.8067
7.7904
7.7859
7.5401
7.5283
7.5211
7.5165
7.4991
7.4963
7.4817
7.2835
7.2639
7.2460
7.2365
7.0023
2.3735
1.9984
Me
Me
O
H
N
3ai
1H NMR (400 MHz, CDCl3)
0.902
0.973
0.974
2.901
1.893
3.897
2.020
0.960
3.000
2.976
f1 (ppm)


192.1789
159.0859
152.5123
148.6028
136.8801
135.2866
134.2134
133.4024
133.1069
133.0815
132.0824
129.9795
129.7717
129.6658
129.6014
129.5636
128.5839
128.1271
127.7506
127.4459
127.1335
127.1070
126.7821
126.5591
126.4376
126.1963
20.9842
19.4830
Me
Me
O
H
N
3ai
13C NMR (100 MHz, CDCl3)
f1 (ppm)


10.1718
8.1898
8.1687
7.8055
7.8015
7.7890
7.7845
7.7802
7.7676
7.7636
7.5579
7.5552
7.5452
7.5424
7.4634
7.4604
7.4427
7.4392
7.4256
7.4225
7.3949
7.3911
7.3756
7.3729
7.3664
7.3635
7.2595
7.2485
7.2399
7.2281
7.2238
7.2083
7.2039
7.1658
7.1565
7.1531
7.1438
6.9416
2.3597
1.9475
Me
Me
O
H
N
S
3aj
$^1$H NMR (400 MHz, CDCl$_3$)
0.905
0.911
0.949
0.944
1.007
1.837
2.352
0.930
0.903
3.000
3.000
f1 (ppm)


192.3832
151.4346
148.5553
142.4594
135.2616
134.2810
133.1569
131.9221
130.5218
129.9786
129.6366
129.5702
129.5369
129.3630
127.9487
127.3610
127.1255
126.5155
126.0100
21.0326
19.4564
Me
Me
O
H
N
S
3aj
$^{13}$C NMR (100 MHz, CDCl$_3$)
f1 (ppm)

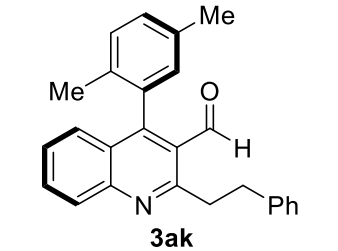





**3ak**

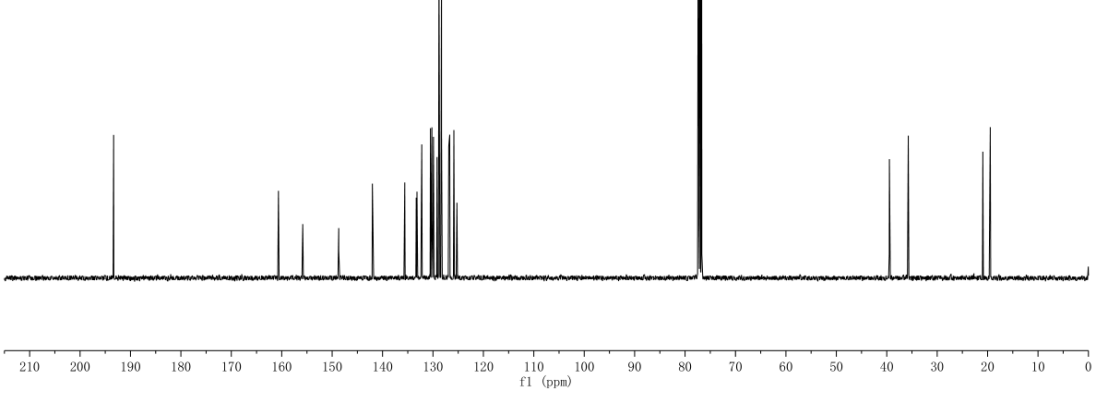
$^{1}$H NMR (400 MHz, $CDCl_3$)

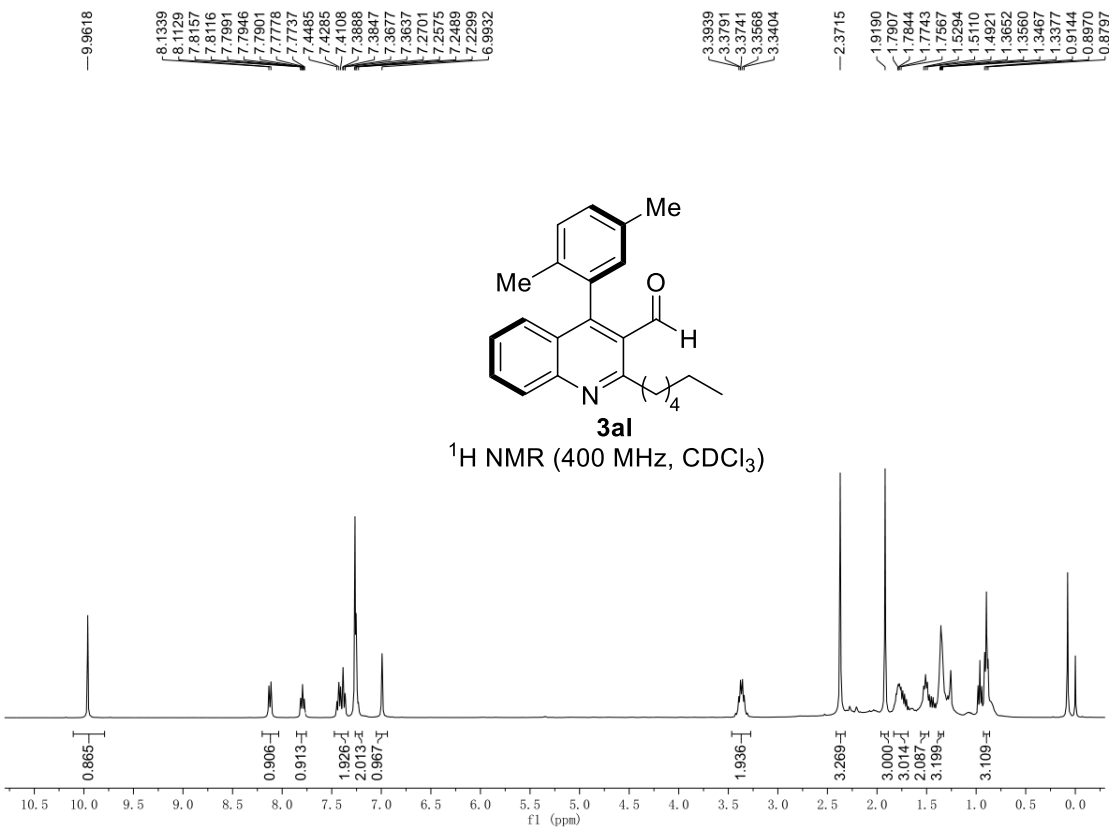


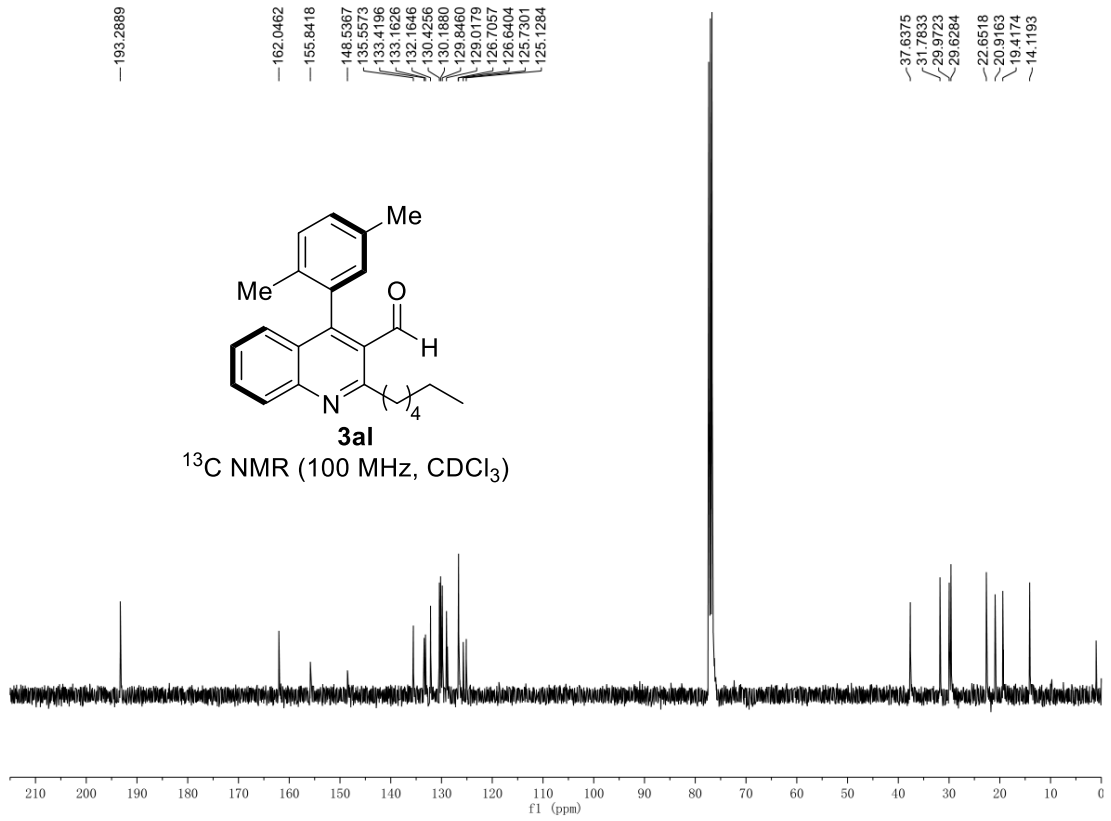


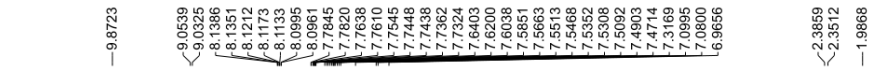

**3ak**

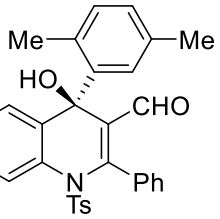
$^{13}$C NMR (100 MHz, $CDCl_3$)




9.9618
8.1339
8.1129
7.8157
7.8116
7.7991
7.7946
7.7901
7.7778
7.7737
7.4485
7.4285
7.4108
7.3888
7.3847
7.3677
7.3637
7.2701
7.2575
7.2489
7.2299
6.9932
3.3939
3.3791
3.3741
3.3568
3.3404
2.3715
1.9190
1.7907
1.7844
1.7743
1.7567
1.5294
1.5110
1.4921
1.3652
1.3560
1.3467
1.3377
0.9144
0.8970
0.8797
Me
Me
O
H
N
4
3al
1H NMR (400 MHz, CDCl3)
0.865
0.906
0.913
1.926
2.013
0.967
1.936
3.269
3.000
3.014
2.087
3.199
3.109
f1 (ppm)

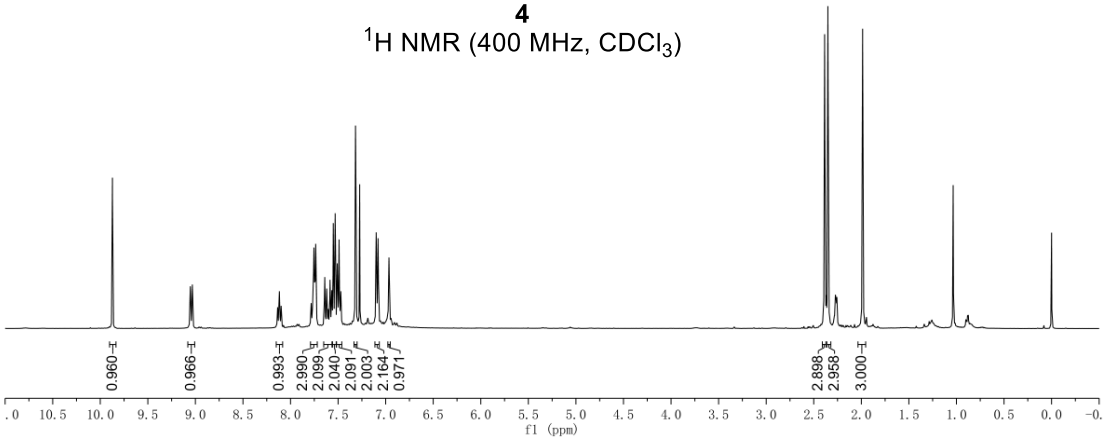

193.2889
162.0462
155.8418
148.5367
135.5573
133.4196
133.1626
132.1646
130.4256
130.1880
129.8460
129.0179
126.7057
126.6404
125.7301
125.1284
37.6375
31.7833
29.9723
29.6284
22.6518
20.9163
19.4174
14.1193
Me
Me
O
H
N
4
3al
13C NMR (100 MHz, CDCl3)
f1 (ppm)

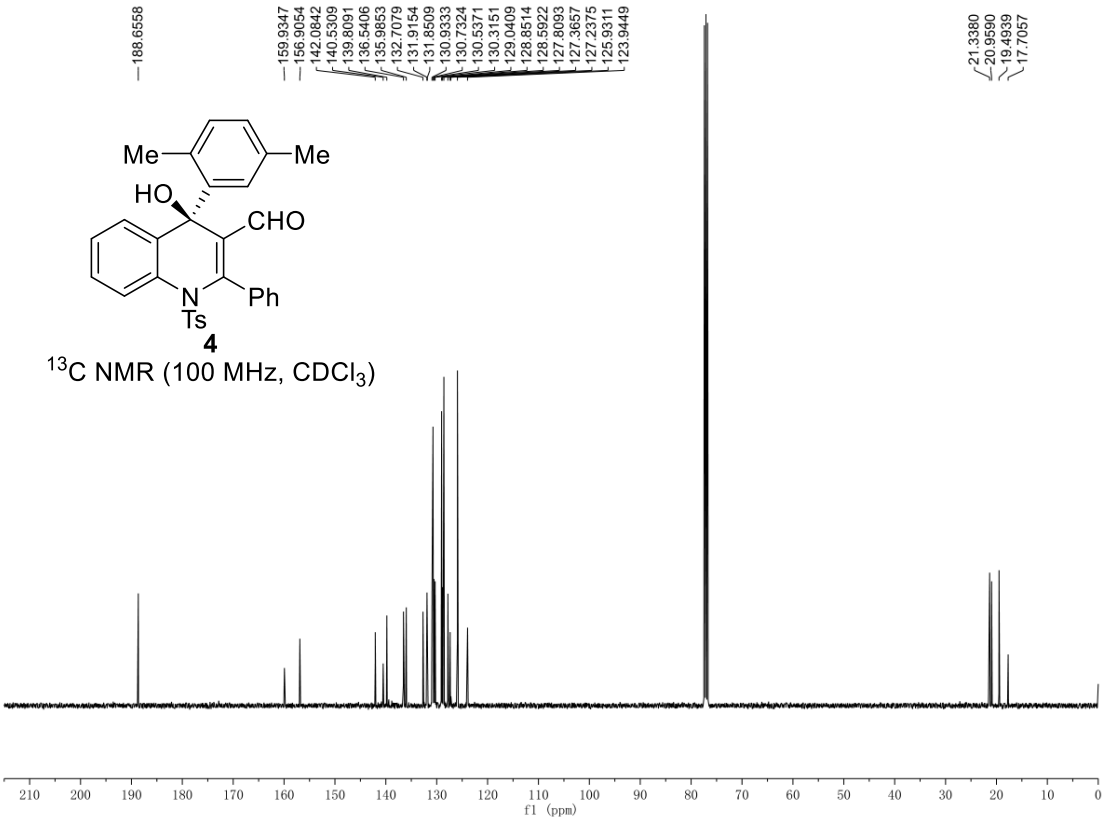



**4**

$^{1}$H NMR (400 MHz, $CDCl_3$)



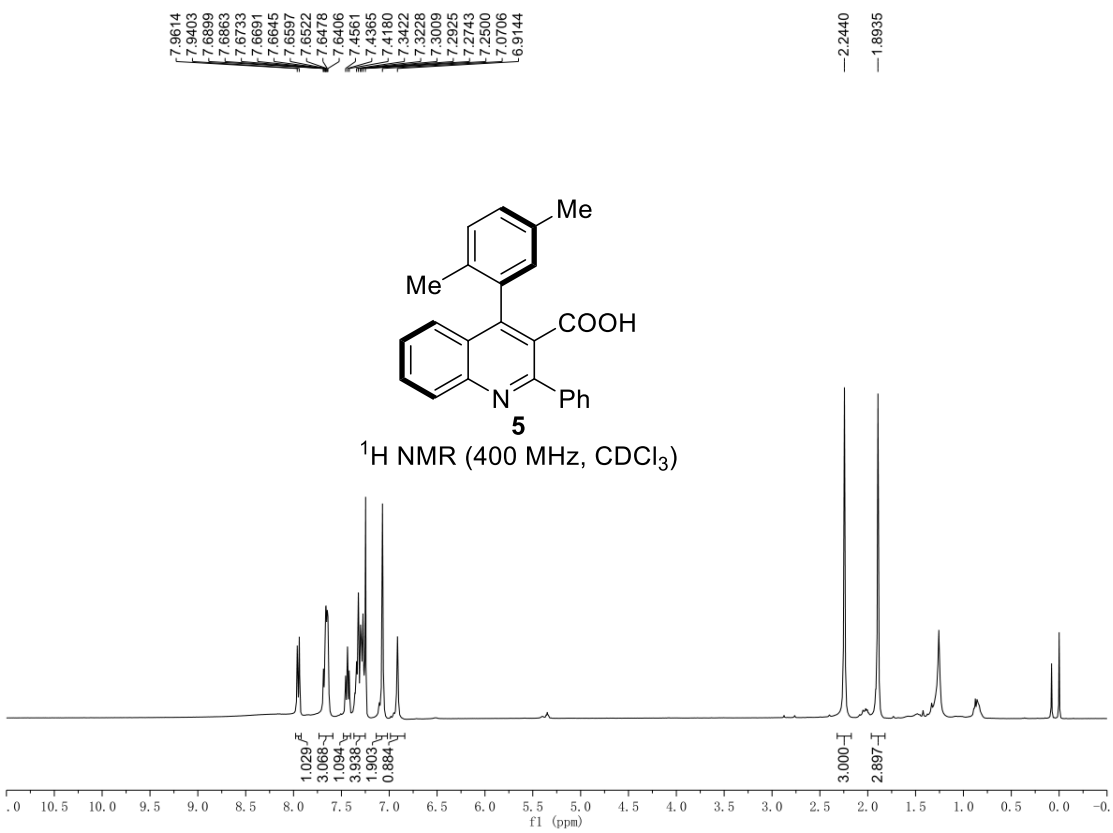



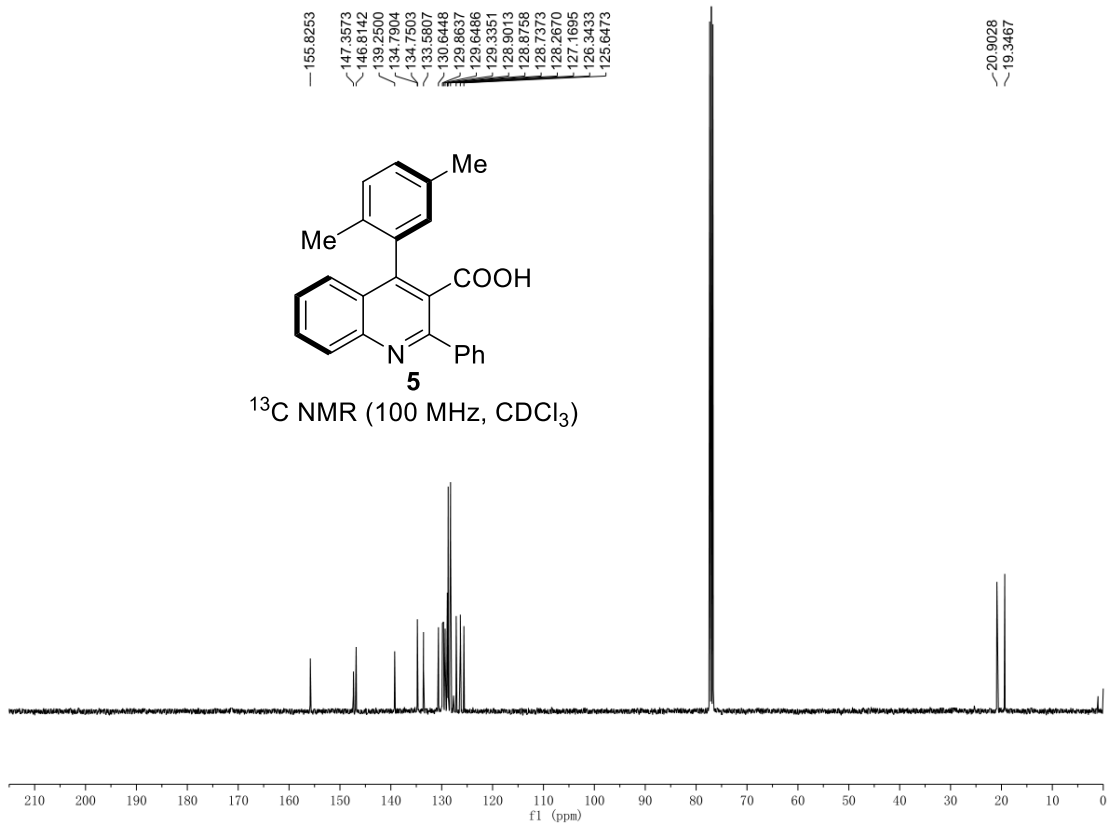


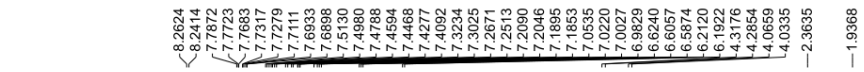


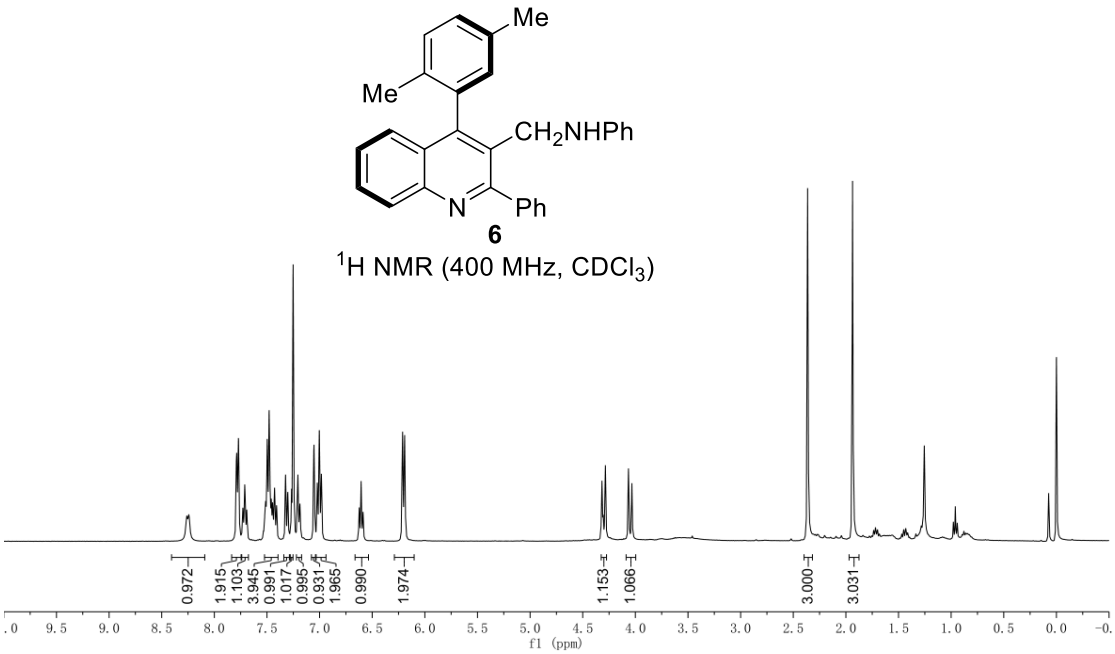
**4**

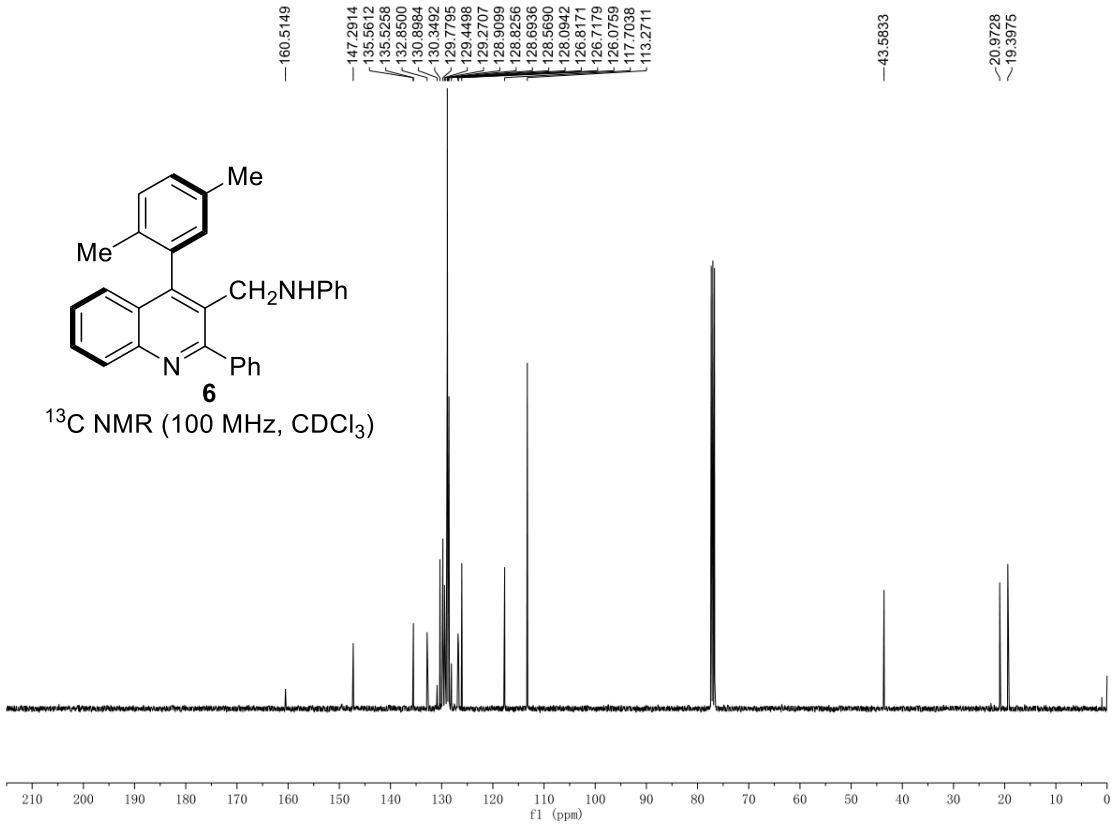
$^{13}$C NMR (100 MHz, $CDCl_3$)

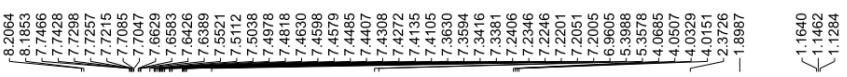

7.9614
7.9403
7.6899
7.6863
7.6733
7.6691
7.6645
7.6597
7.6522
7.6478
7.6406
7.4561
7.4365
7.4180
7.3422
7.3228
7.3009
7.2925
7.2743
7.2500
7.0706
6.9144
2.2440
1.8935
Me
Me
COOH
N
Ph
5
1H NMR (400 MHz, CDCl3)
1.029
3.068
1.094
3.938
1.903
0.884
3.000
2.897
f1 (ppm)

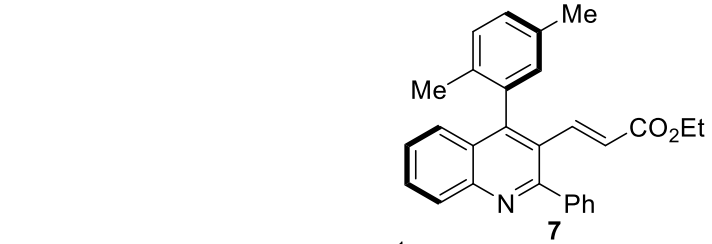

155.8253
147.3573
146.8142
139.2500
134.7904
134.7503
133.5807
130.6448
129.8637
129.6486
129.3351
128.9013
128.8758
128.7373
128.2670
127.1695
126.3433
125.6473
20.9028
19.3467
Me
Me
COOH
N
Ph
5
13C NMR (100 MHz, CDCl3)
f1 (ppm)


8.2624
8.2414
7.7872
7.7723
7.7683
7.7317
7.7279
7.7111
7.6933
7.6898
7.5130
7.4980
7.4788
7.4594
7.4468
7.4277
7.4092
7.3234
7.3025
7.2671
7.2513
7.2090
7.2046
7.1895
7.1853
7.0535
7.0220
7.0027
6.9829
6.6240
6.6057
6.5874
6.2120
6.1922
4.3176
4.2854
4.0659
4.0335
2.3635
1.9368


Me
Me
CH2NHPh
N
Ph
6
1H NMR (400 MHz, CDCl3)
0.972
1.915
1.103
3.945
0.991
1.017
0.995
0.931
1.965
0.990
1.974
1.153
1.066
3.000
3.031
f1 (ppm)

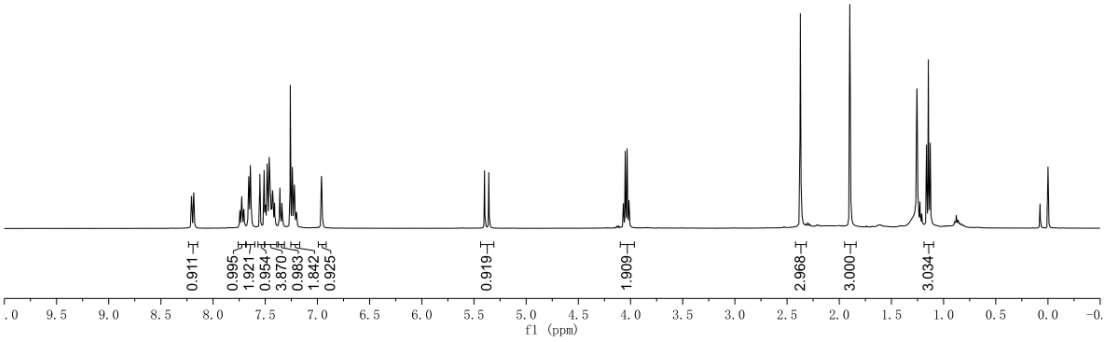

160.5149
147.2914
135.5612
135.5258
132.8500
130.8984
130.3492
129.7795
129.4498
129.2707
128.9099
128.8256
128.6936
128.5690
128.0942
126.8171
126.7179
126.0759
117.7038
113.2711
43.5833
20.9728
19.3975
Me
Me
CH2NHPh
N
Ph
6
13C NMR (100 MHz, CDCl3)
f1 (ppm)

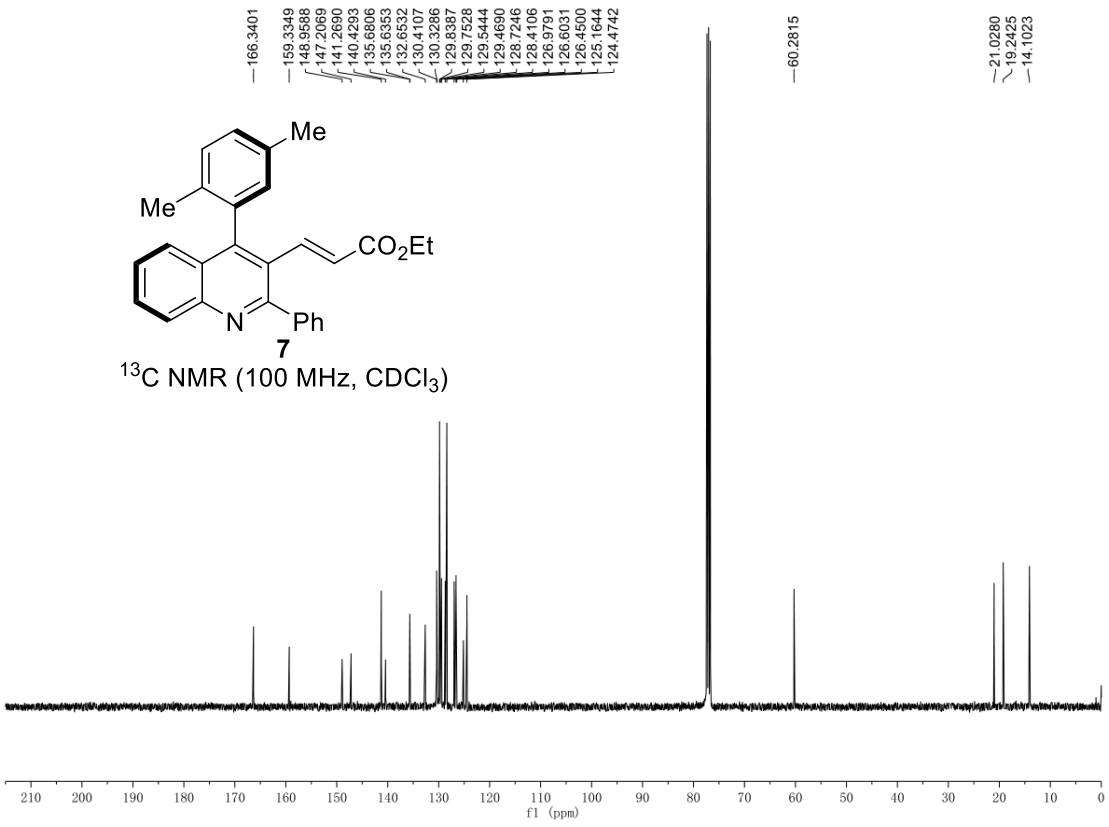



**7**

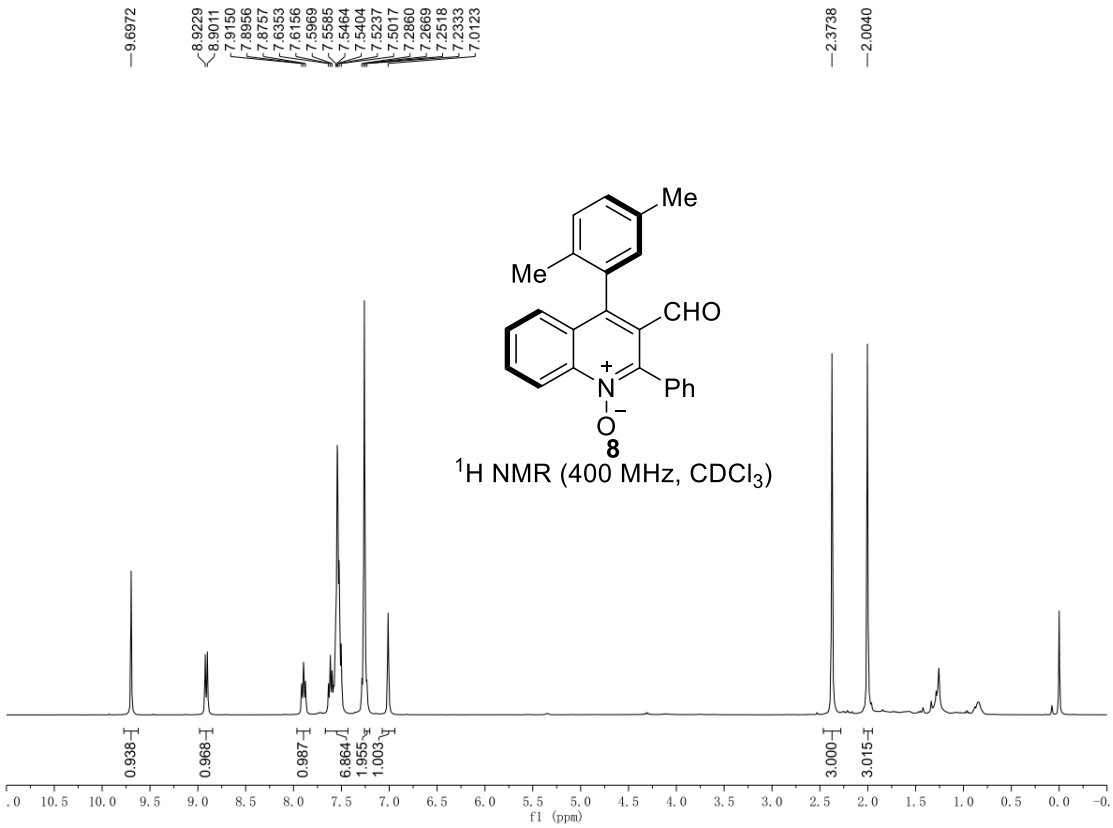
$^{1}$H NMR (400 MHz, $CDCl_3$)



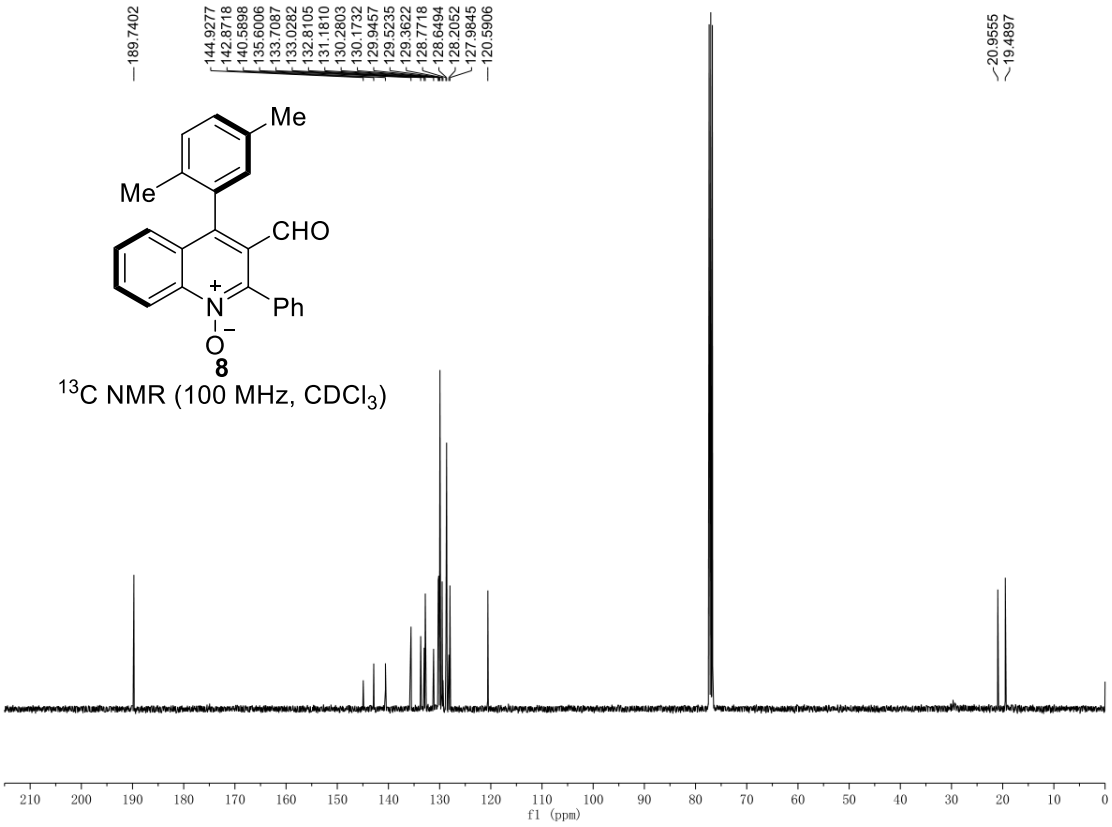




**7**

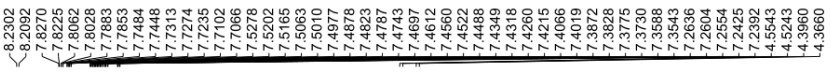
$^{13}$C NMR (100 MHz, $CDCl_3$)

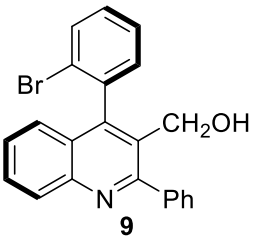



$^{1}$H NMR (400 MHz, $CDCl_3$)



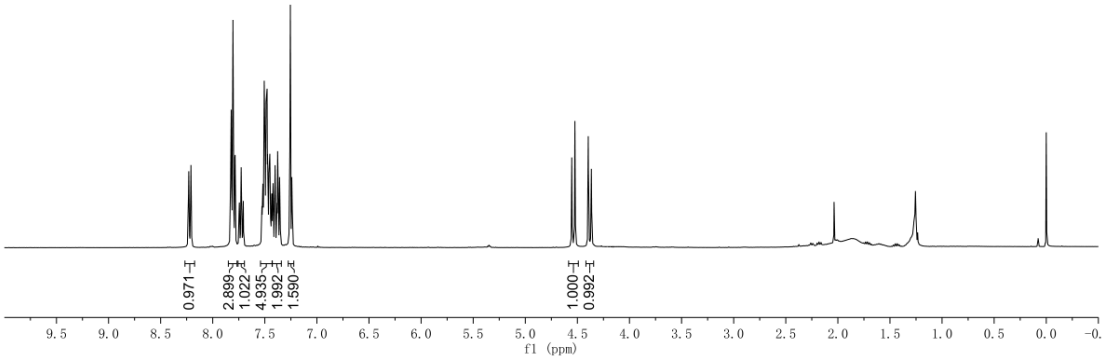

$^{13}$C NMR (100 MHz, $CDCl_3$)



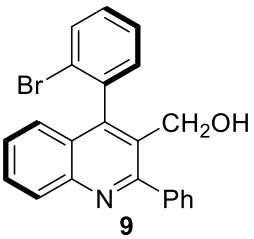




**9**

$^{1}$H NMR (400 MHz, $CDCl_3$)



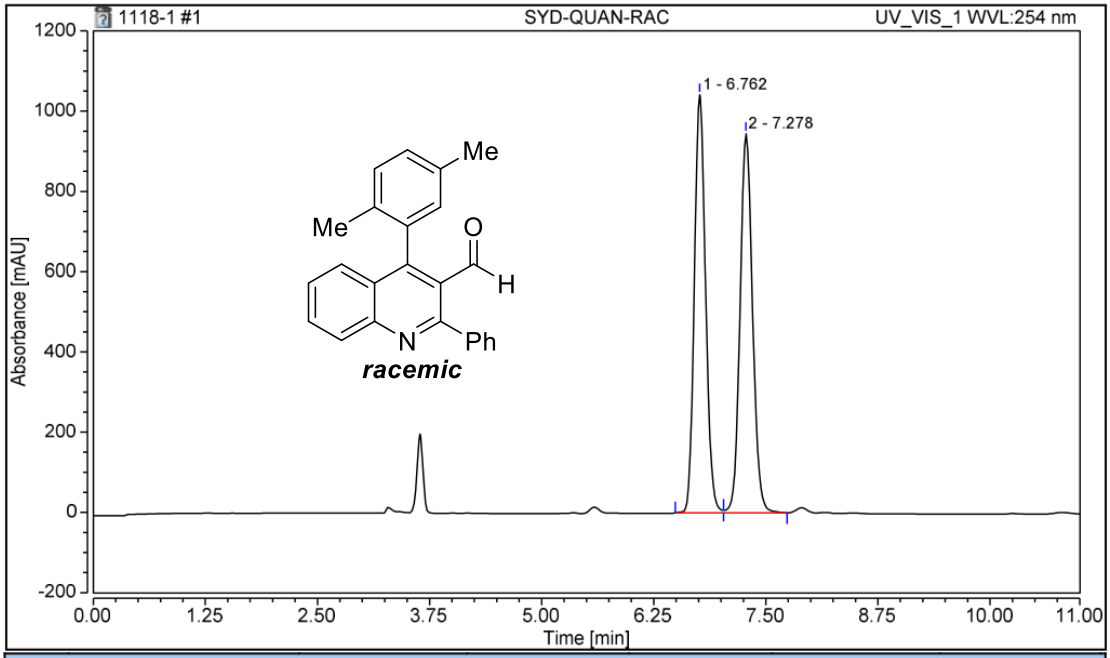





**9**

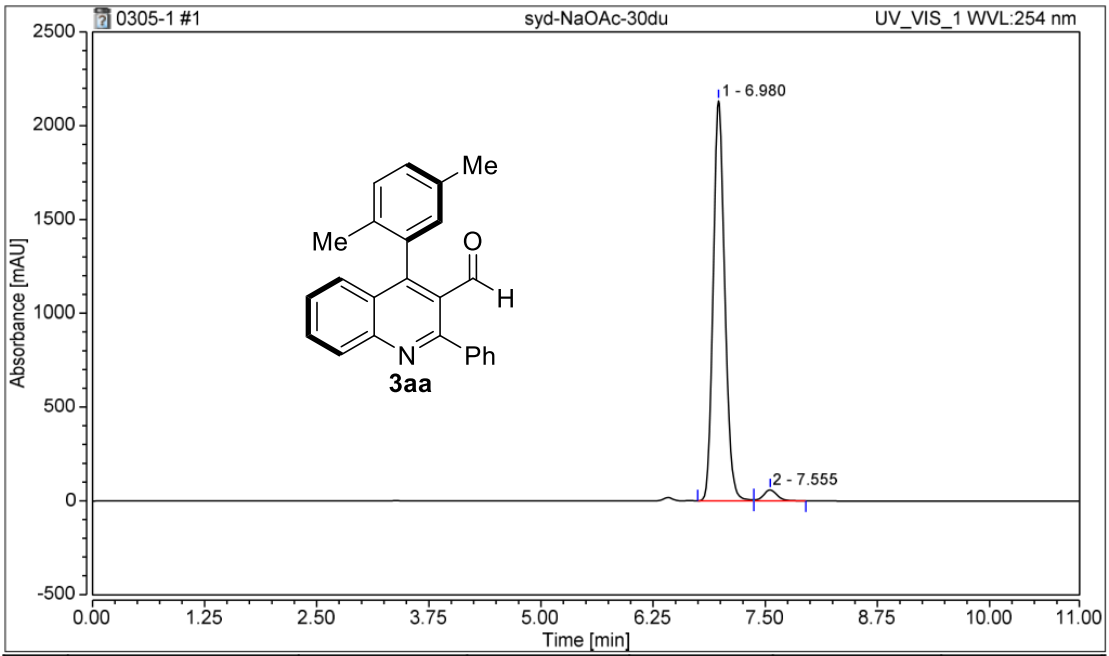
$^{13}$C NMR (100 MHz, $CDCl_3$)

## HPLC Traces



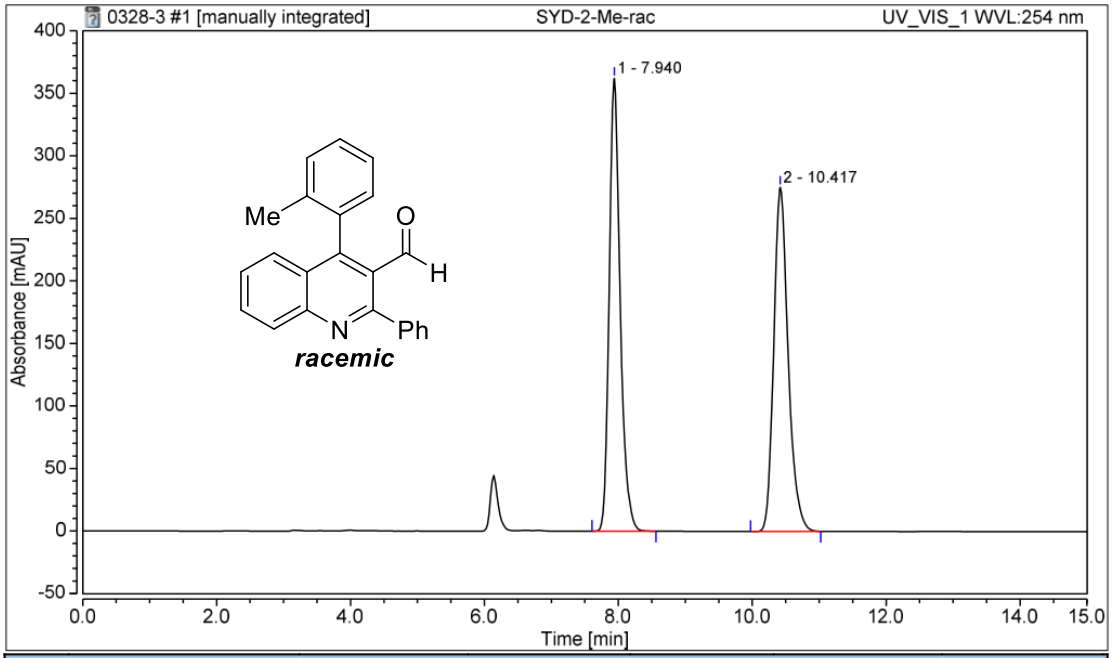

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 6.762 | 150.836 | 1042.174 | 49.65 | 1.13 | 0.23 |
| 2 | 7.278 | 152.962 | 945.210 | 50.35 | 1.10 | 0.25 |
| **Total:** | | **303.798** | **1987.384** | **100.00** | | |



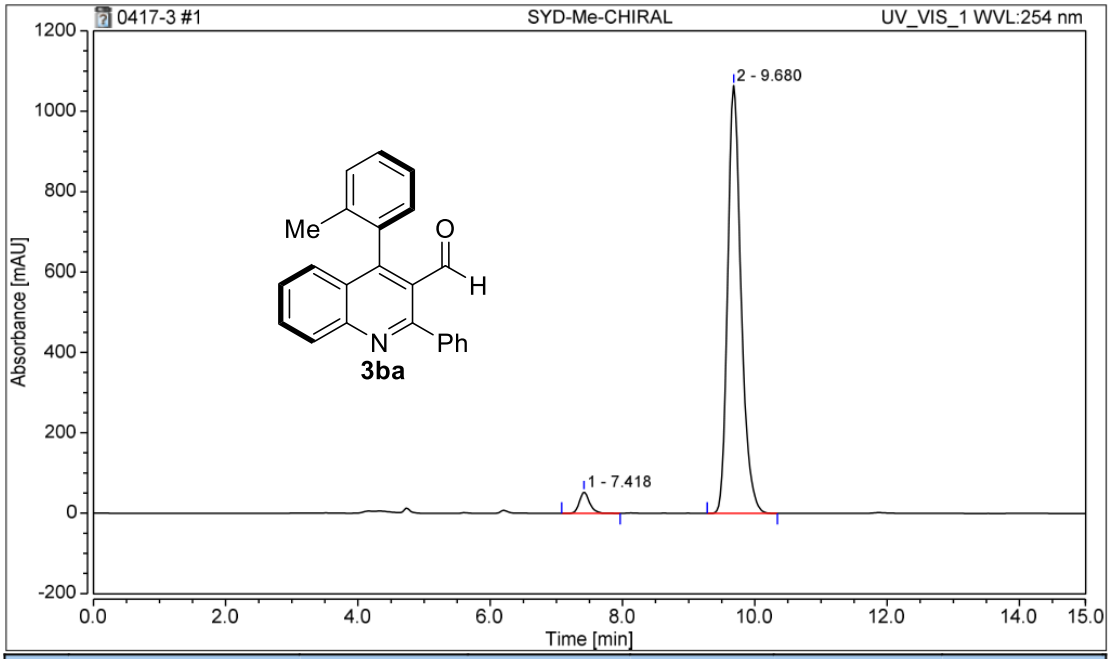

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 6.980 | 319.680 | 2133.181 | 96.85 | 1.15 | 0.23 |
| 2 | 7.555 | 10.384 | 58.426 | 3.15 | n.a. | 0.27 |
| **Total:** | | **330.065** | **2191.608** | **100.00** | | |



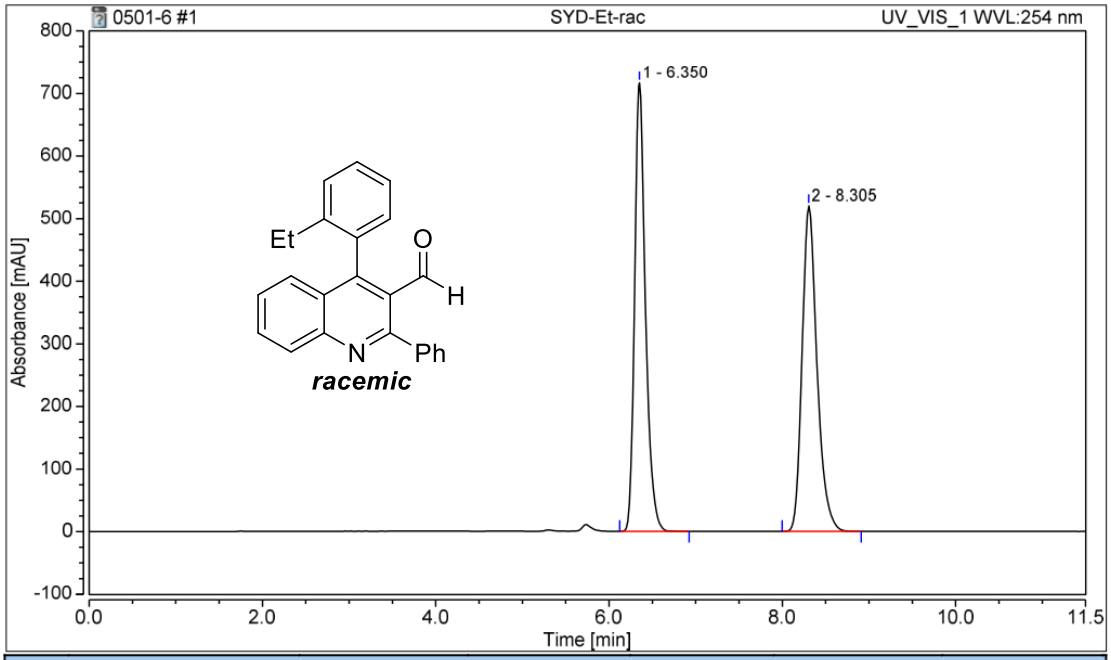

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 7.940 | 68.695 | 362.158 | 50.18 | 1.26 | 0.29 |
| 2 | 10.417 | 68.205 | 275.296 | 49.82 | 1.26 | 0.37 |
| **Total:** | | **136.900** | **637.455** | **100.00** | | |



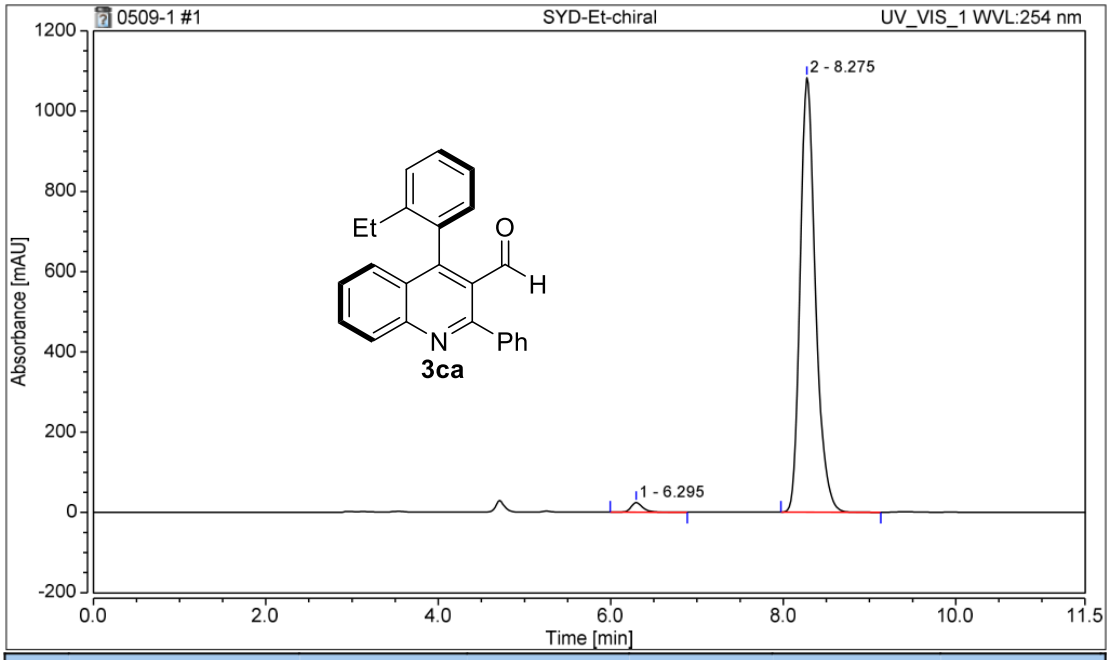

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 7.418 | 9.504 | 53.041 | 3.66 | 1.23 | 0.27 |
| 2 | 9.680 | 250.383 | 1064.463 | 96.34 | 1.27 | 0.36 |
| **Total:** | | **259.887** | **1117.505** | **100.00** | | |



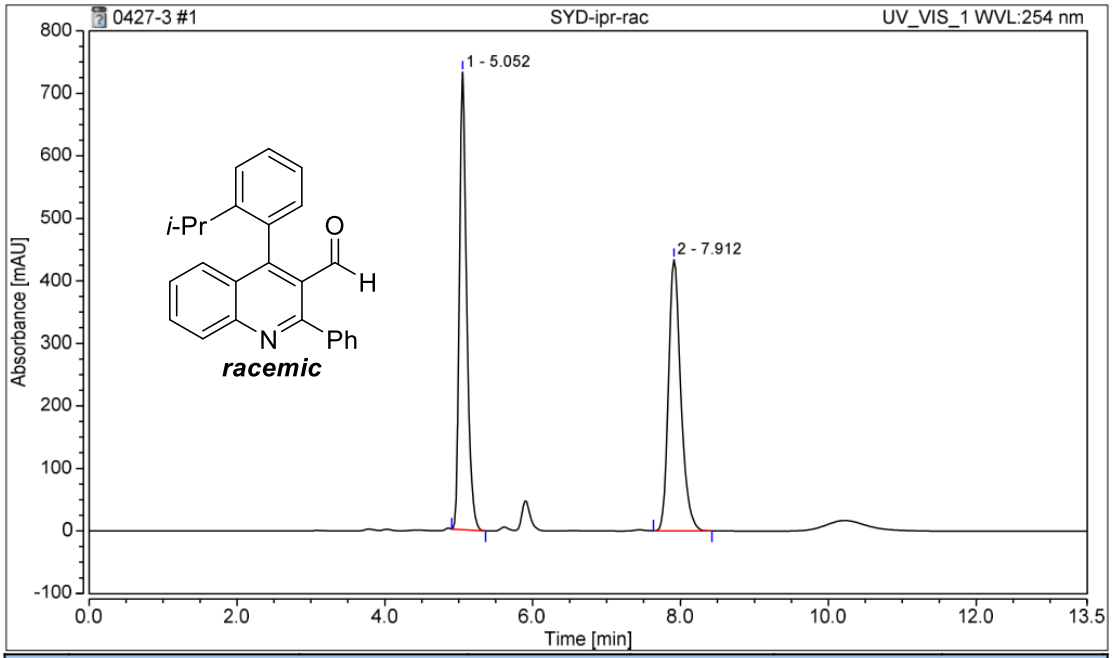

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 6.350 | 103.701 | 716.868 | 49.99 | 1.30 | 0.22 |
| 2 | 8.305 | 103.740 | 520.343 | 50.01 | 1.28 | 0.31 |
| **Total:** | | **207.441** | **1237.211** | **100.00** | | |



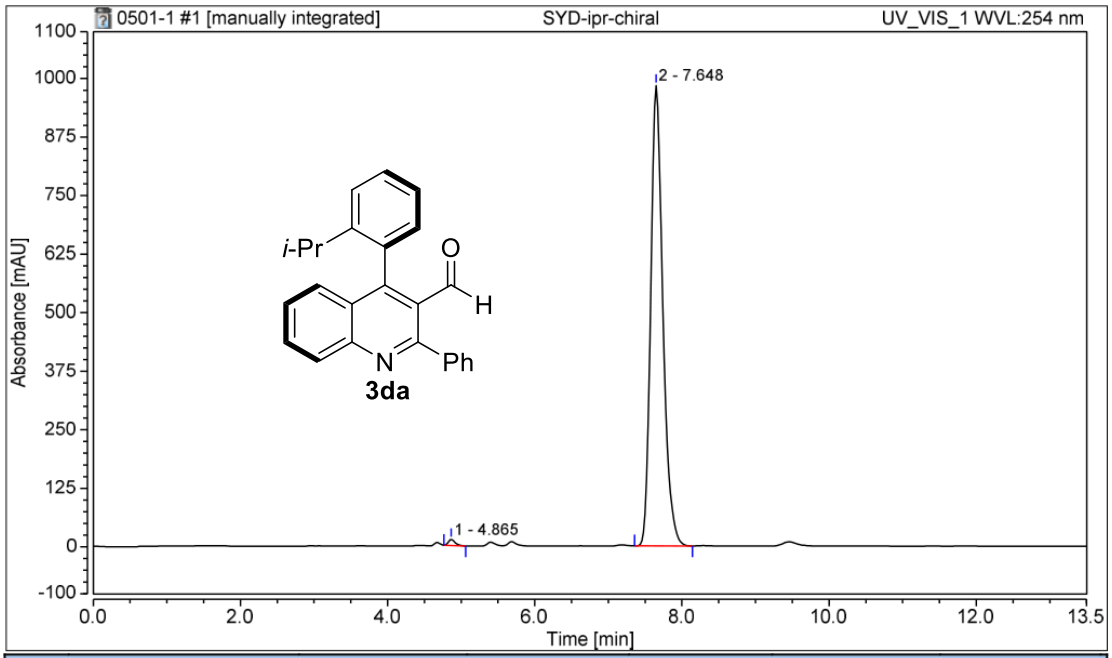

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 6.295 | 3.753 | 23.917 | 1.65 | 1.27 | 0.24 |
| 2 | 8.275 | 223.022 | 1082.979 | 98.35 | 1.28 | 0.31 |
| **Total:** | | **226.775** | **1106.896** | **100.00** | | |



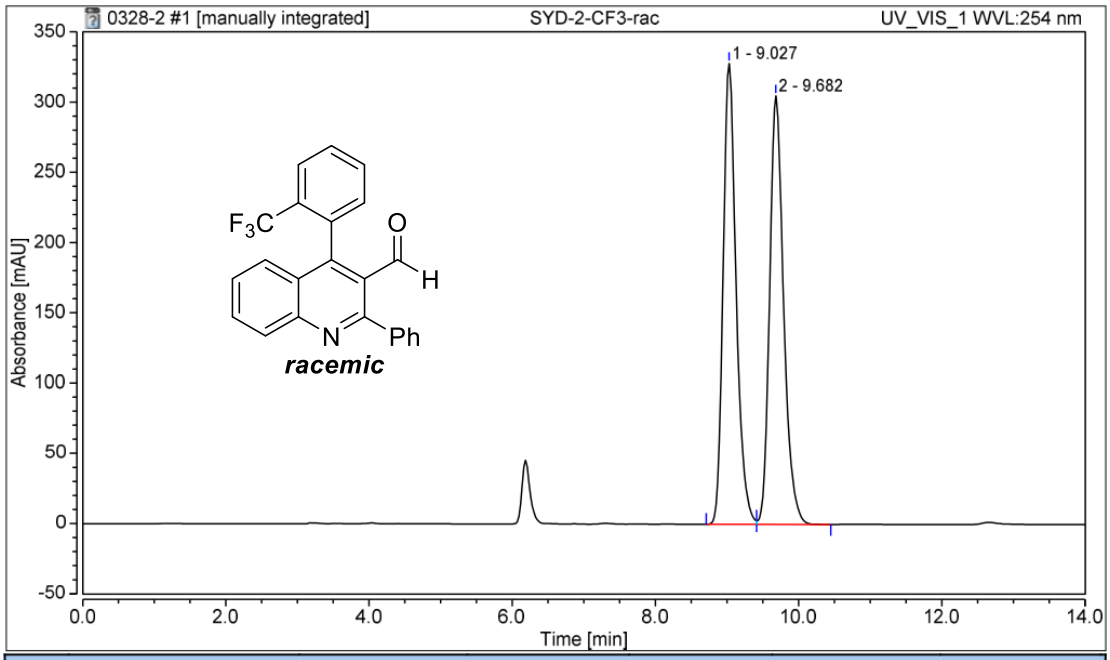

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 5.052 | 83.727 | 731.893 | 49.96 | 1.33 | 0.18 |
| 2 | 7.912 | 83.849 | 434.128 | 50.04 | 1.27 | 0.30 |
| **Total:** | | **167.575** | **1166.021** | **100.00** | | |



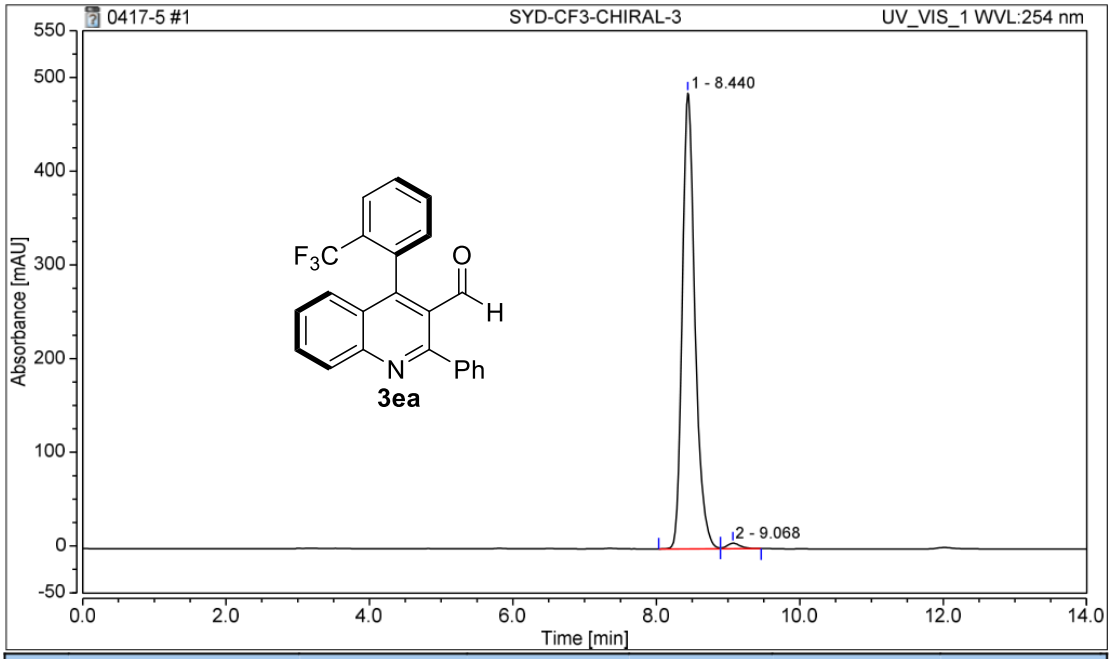

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 4.865 | 1.309 | 12.873 | 0.69 | 1.33 | 0.16 |
| 2 | 7.648 | 188.421 | 983.340 | 99.31 | 1.28 | 0.29 |
| **Total:** | | **189.730** | **996.213** | **100.00** | | |



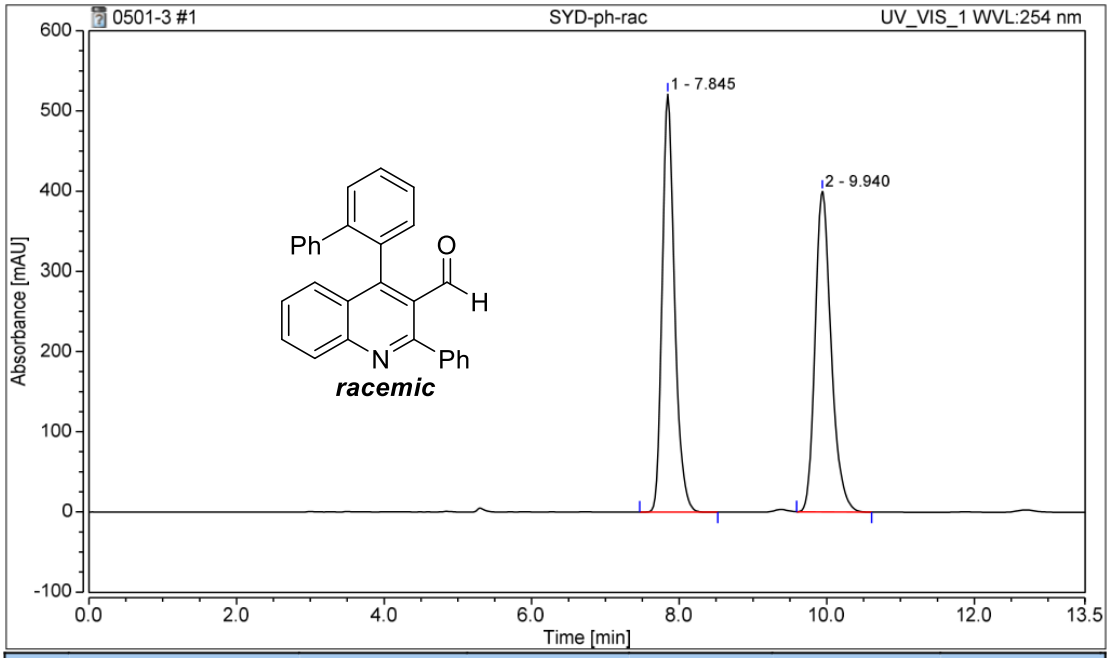

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 9.027 | 68.906 | 327.979 | 49.94 | 1.25 | 0.33 |
| 2 | 9.682 | 69.086 | 304.935 | 50.06 | 1.25 | 0.34 |
| **Total:** | | **137.992** | **632.914** | **100.00** | | |



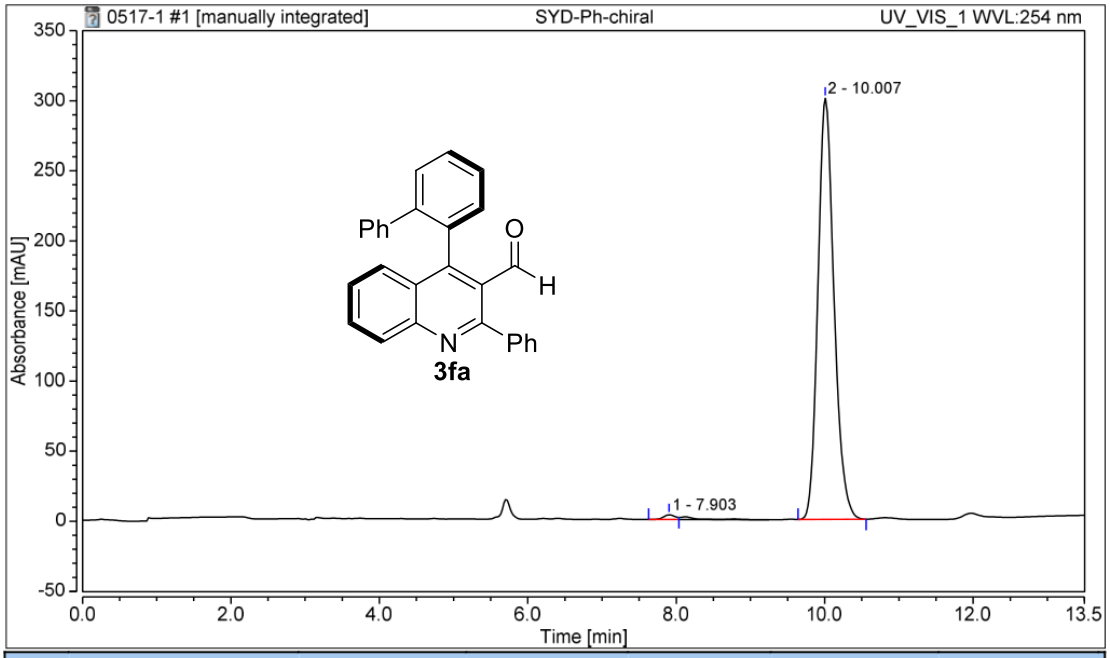

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 8.440 | 99.871 | 486.598 | 98.74 | 1.29 | 0.31 |
| 2 | 9.068 | 1.279 | 5.953 | 1.26 | n.a. | 0.33 |
| **Total:** | | **101.150** | **492.551** | **100.00** | | |



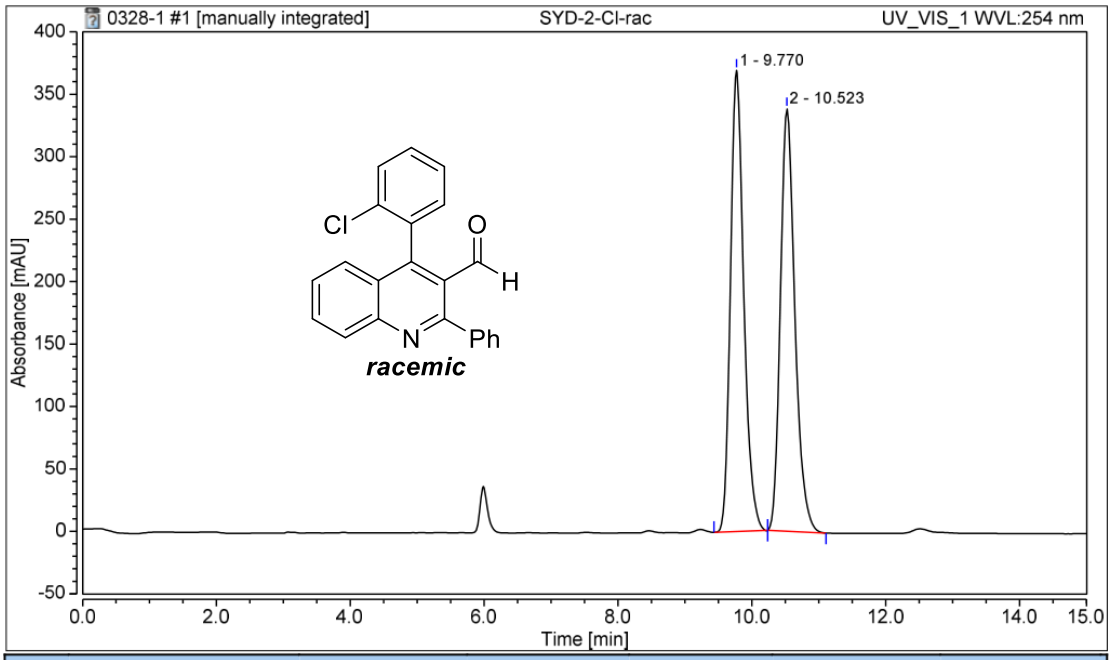

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 7.845 | 101.431 | 521.248 | 50.06 | 1.27 | 0.30 |
| 2 | 9.940 | 101.172 | 399.857 | 49.94 | 1.26 | 0.39 |
| **Total:** | | **202.603** | **921.105** | **100.00** | | |



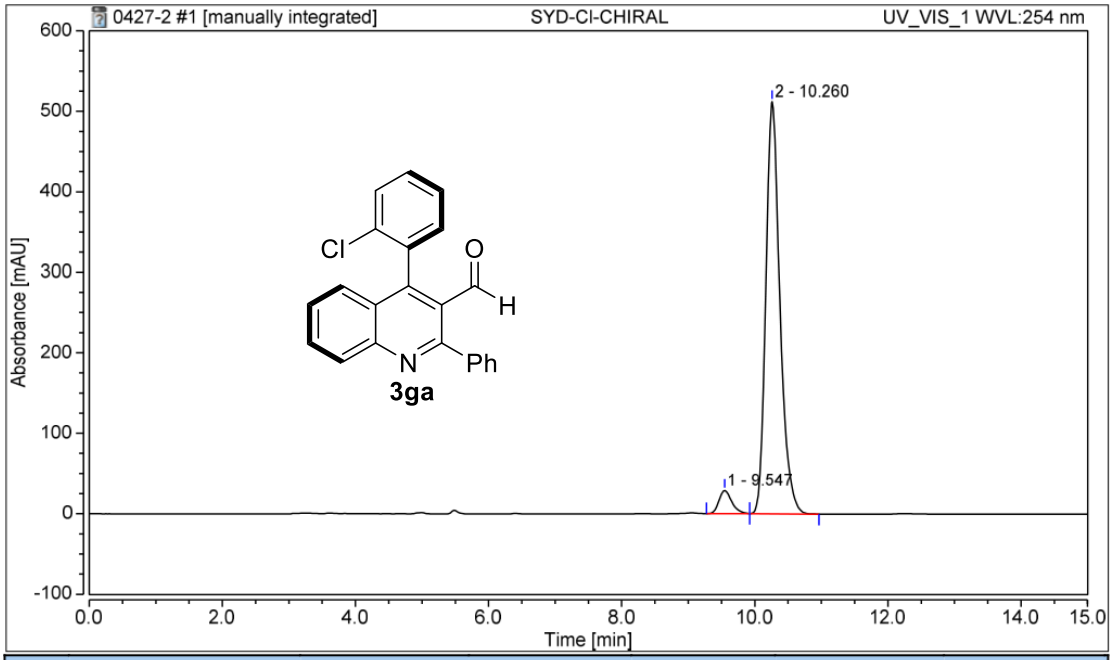

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 7.903 | 0.615 | 3.384 | 0.81 | n.a. | 0.31 |
| 2 | 10.007 | 75.797 | 300.497 | 99.19 | 1.20 | 0.39 |
| **Total:** | | **76.412** | **303.881** | **100.00** | | |



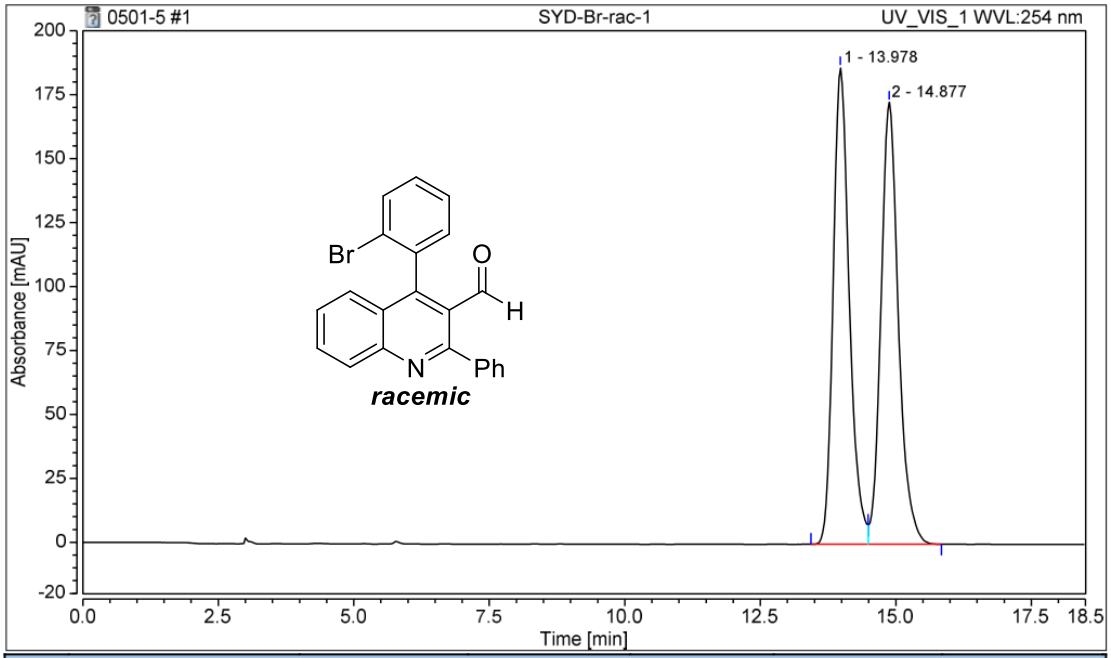

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 9.770 | 85.245 | 369.383 | 49.99 | 1.24 | 0.35 |
| 2 | 10.523 | 85.292 | 338.367 | 50.01 | 1.25 | 0.40 |
| **Total:** | | **170.538** | **707.750** | **100.00** | | |



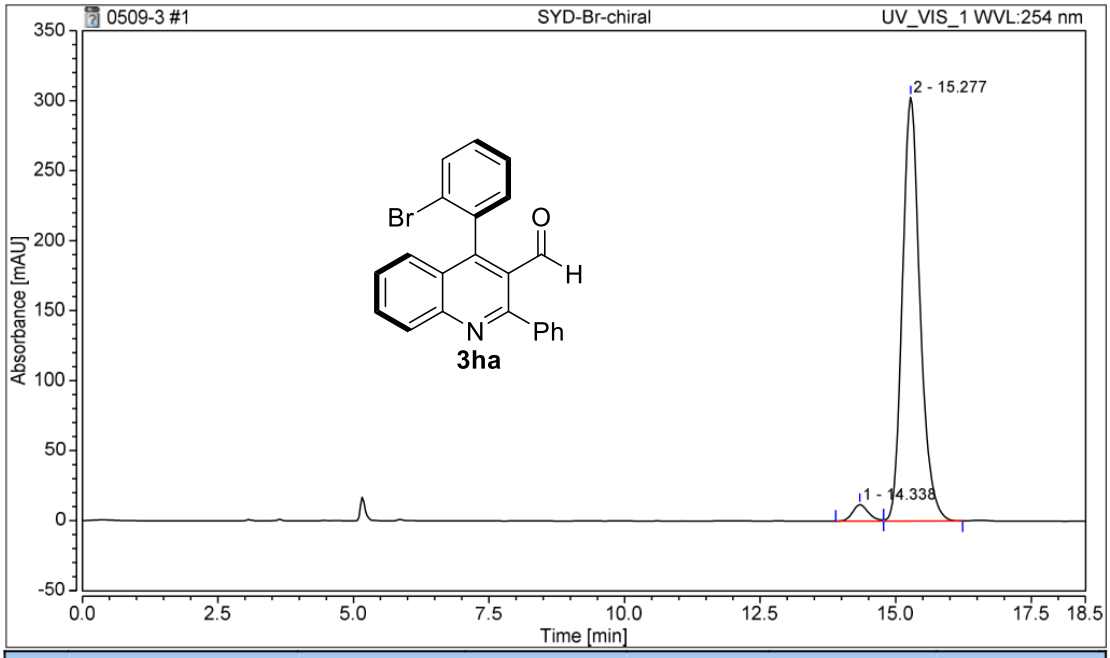

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 9.547 | 6.445 | 28.928 | 4.87 | 1.30 | 0.33 |
| 2 | 10.260 | 126.007 | 512.046 | 95.13 | 1.27 | 0.37 |
| **Total:** | | **132.452** | **540.973** | **100.00** | | |



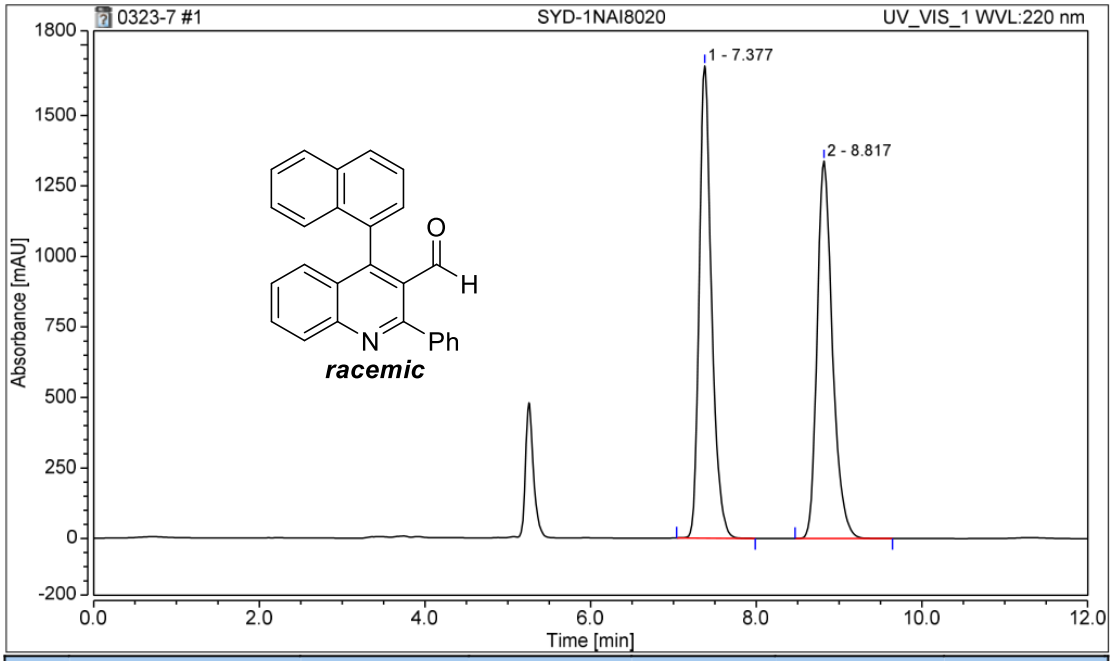

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 13.978 | 64.280 | 186.293 | 49.78 | 1.27 | 0.53 |
| 2 | 14.877 | 64.853 | 172.759 | 50.22 | 1.18 | 0.57 |
| **Total:** | | **129.132** | **359.053** | **100.00** | | |



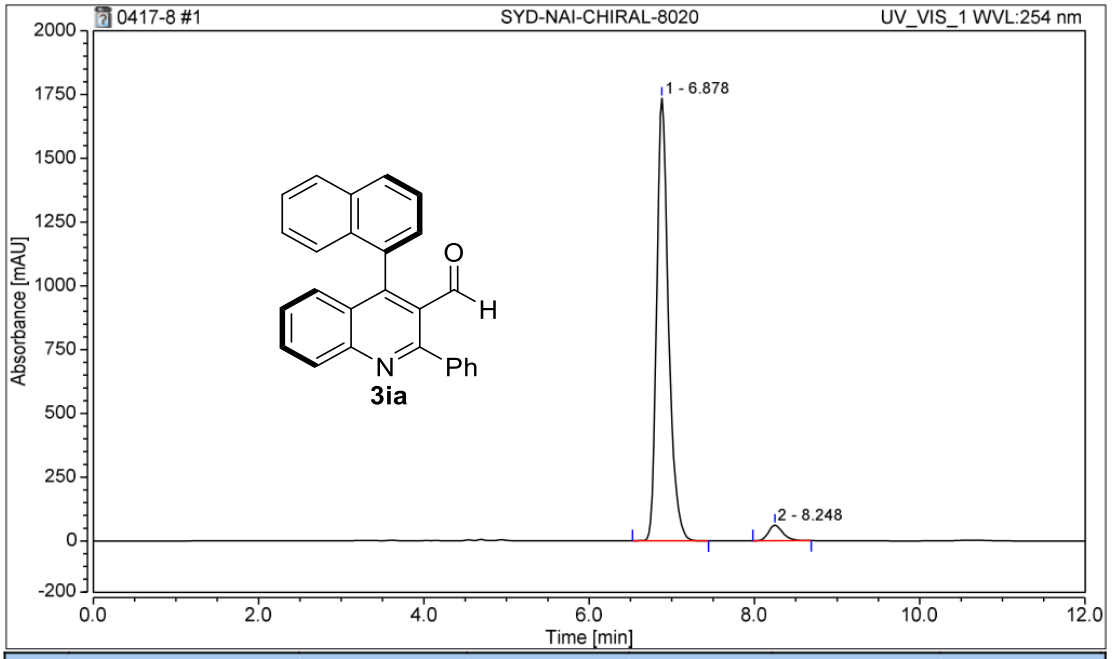

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 14.338 | 3.983 | 11.806 | 3.36 | n.a. | 0.52 |
| 2 | 15.277 | 114.374 | 303.039 | 96.64 | 1.20 | 0.58 |
| **Total:** | | **118.357** | **314.845** | **100.00** | | |



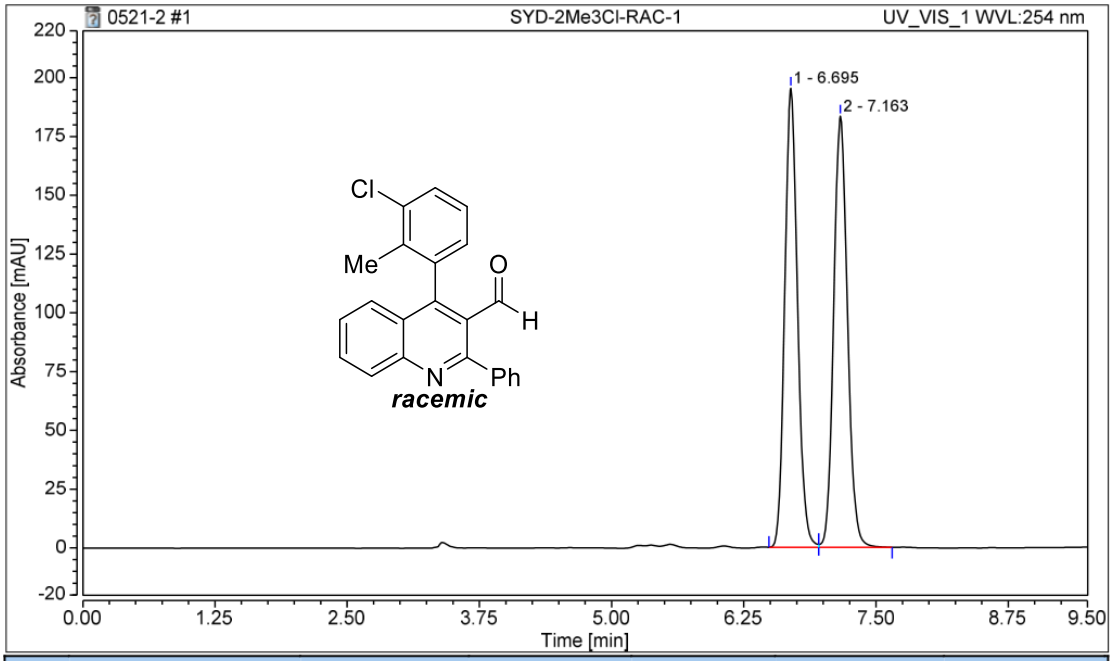

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 7.377 | 289.025 | 1674.266 | 50.12 | 1.31 | 0.26 |
| 2 | 8.817 | 287.661 | 1338.867 | 49.88 | 1.29 | 0.32 |
| **Total:** | | **576.686** | **3013.133** | **100.00** | | |



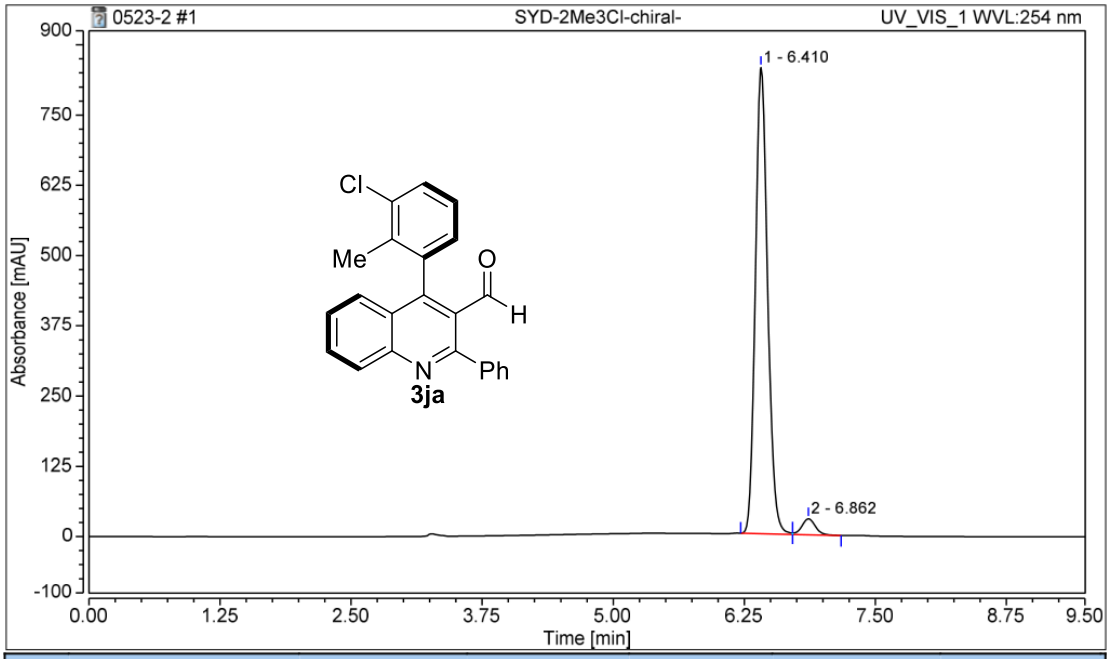

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 6.878 | 287.316 | 1734.650 | 95.91 | 1.34 | 0.25 |
| 2 | 8.248 | 12.266 | 60.827 | 4.09 | 1.23 | 0.31 |
| **Total:** | | **299.582** | **1795.478** | **100.00** | | |



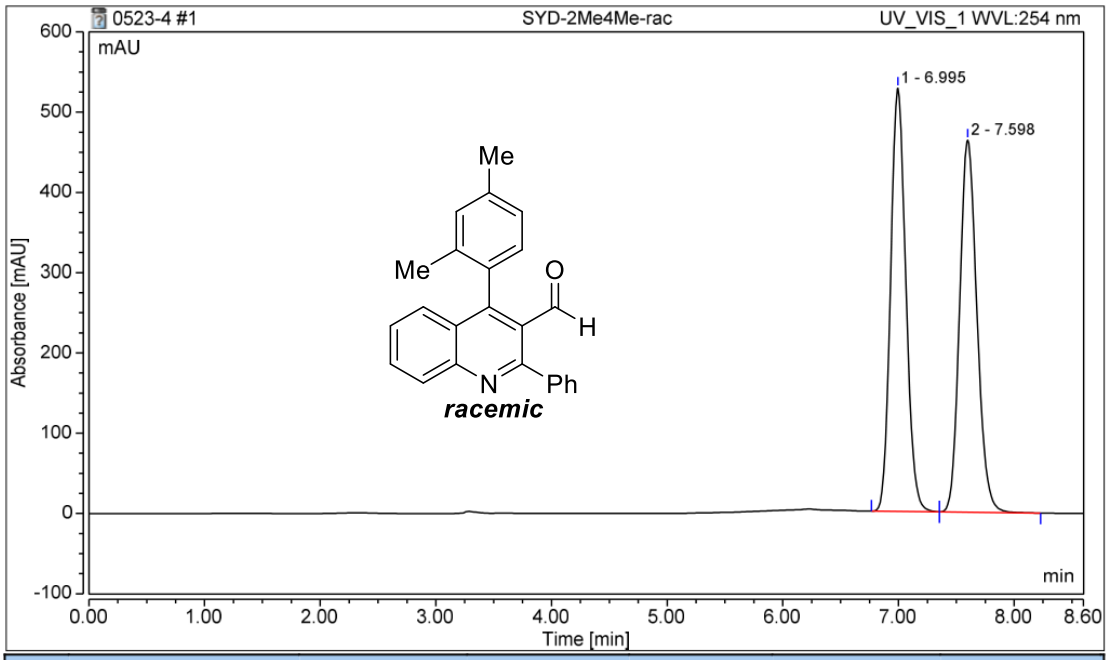

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 6.695 | 27.373 | 195.295 | 49.72 | 1.12 | 0.22 |
| 2 | 7.163 | 27.686 | 183.440 | 50.28 | 1.10 | 0.24 |
| **Total:** | | **55.060** | **378.735** | **100.00** | | |



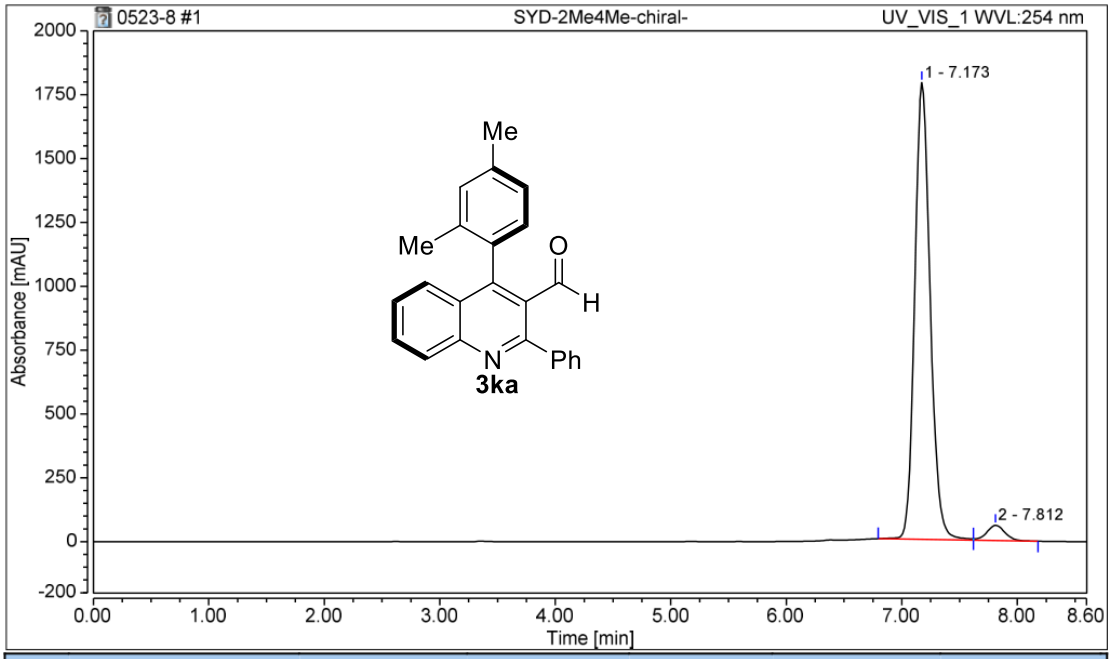

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 6.410 | 112.488 | 829.784 | 96.34 | 1.14 | 0.21 |
| 2 | 6.862 | 4.275 | 28.522 | 3.66 | n.a. | 0.23 |
| **Total:** | | **116.762** | **858.306** | **100.00** | | |



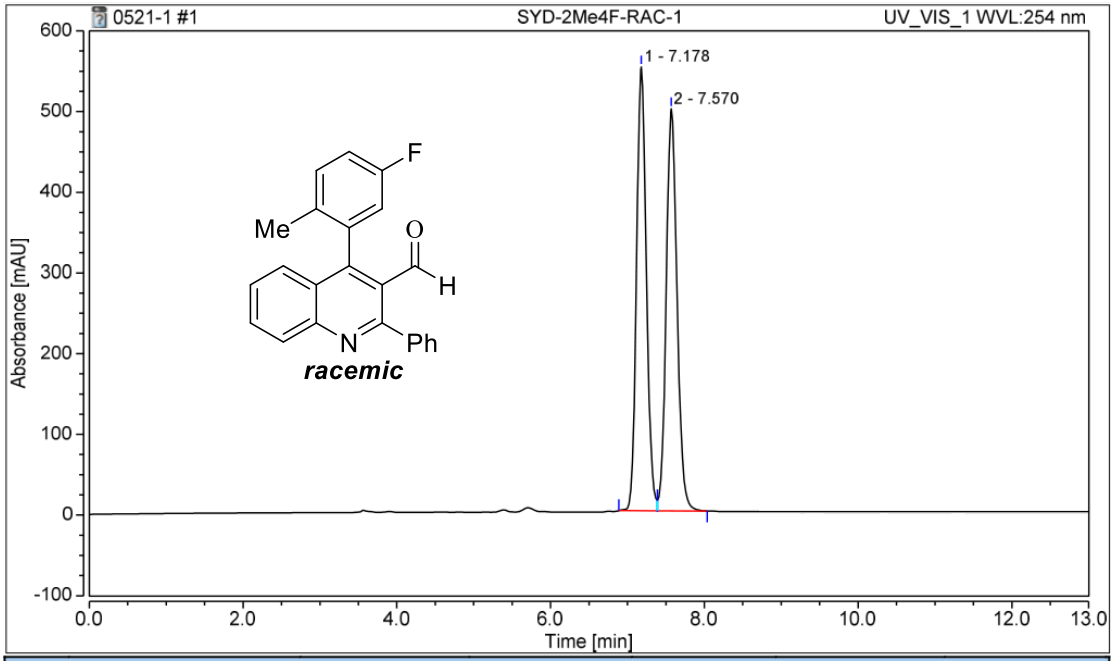

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 6.995 | 80.494 | 527.402 | 49.94 | 1.12 | 0.24 |
| 2 | 7.598 | 80.672 | 463.611 | 50.06 | 1.15 | 0.27 |
| **Total:** | | **161.166** | **991.013** | **100.00** | | |



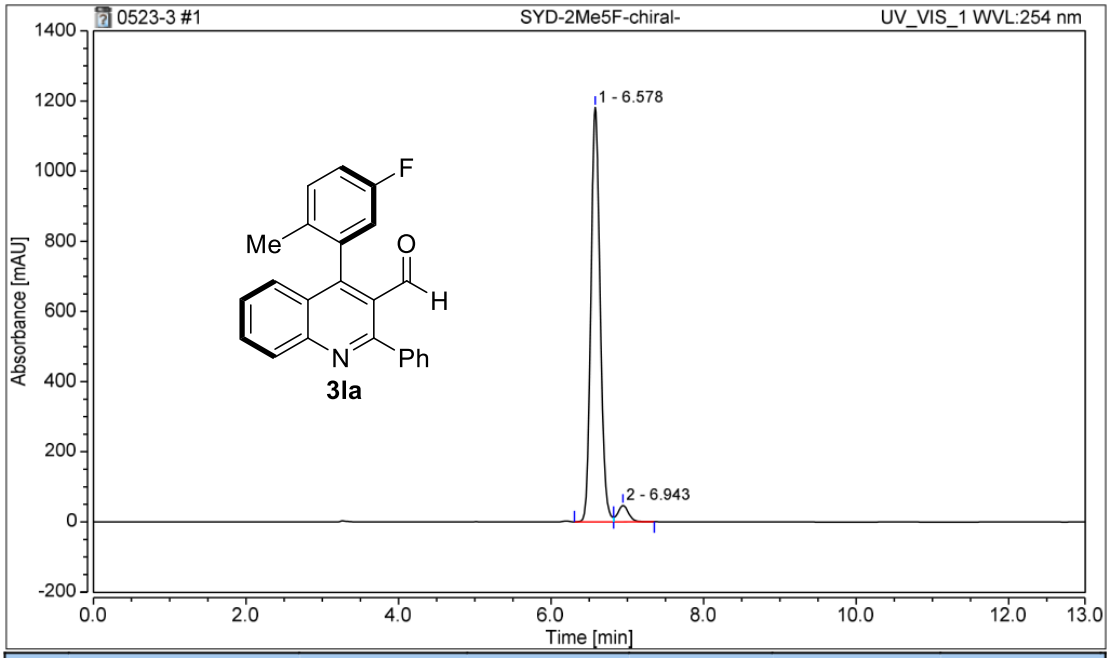

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 7.173 | 277.257 | 1788.909 | 96.20 | 1.15 | 0.24 |
| 2 | 7.812 | 10.946 | 59.646 | 3.80 | n.a. | 0.28 |
| **Total:** | | **288.203** | **1848.555** | **100.00** | | |



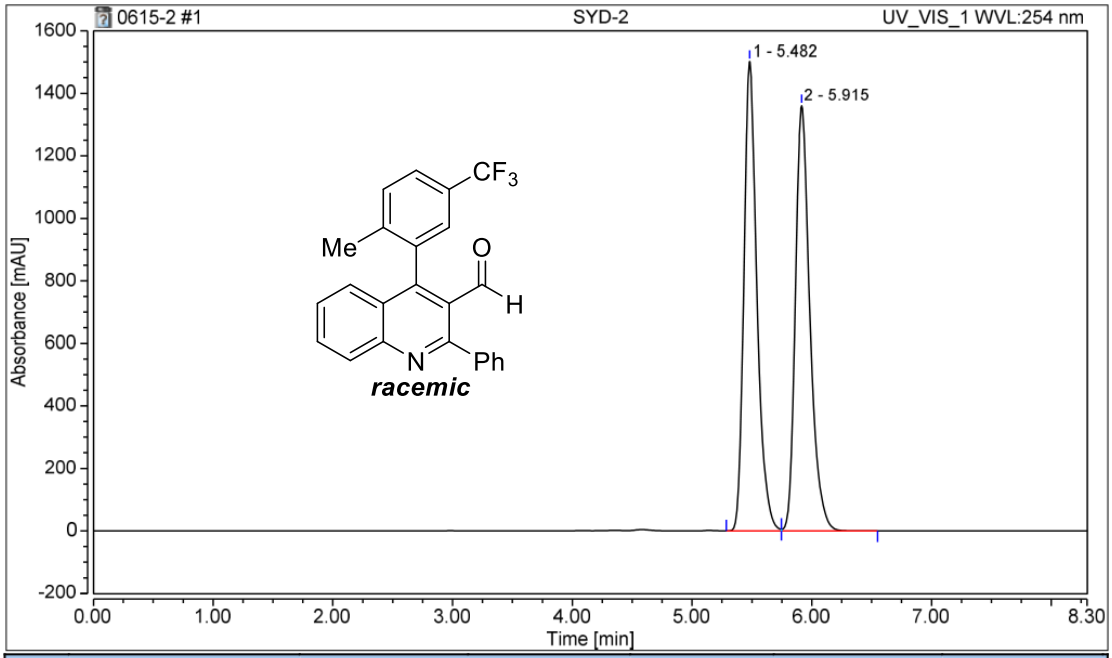

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 7.178 | 81.216 | 549.879 | 49.96 | 1.12 | 0.23 |
| 2 | 7.570 | 81.353 | 498.222 | 50.04 | 1.12 | 0.25 |
| **Total:** | | **162.569** | **1048.101** | **100.00** | | |



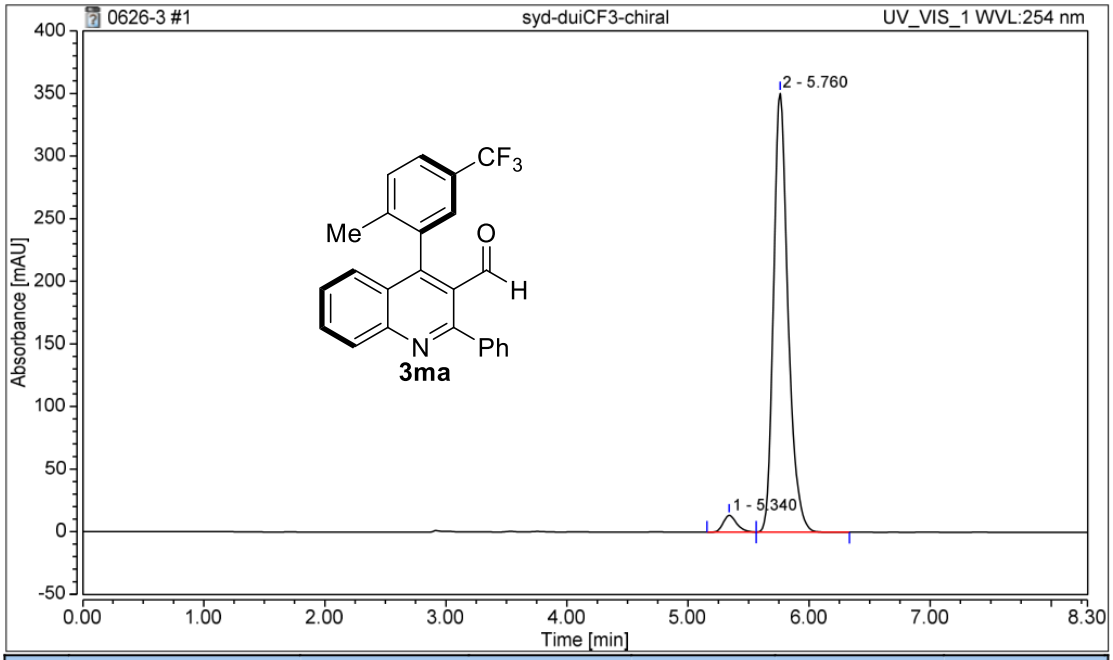

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 6.578 | 165.261 | 1181.485 | 95.61 | 1.14 | 0.22 |
| 2 | 6.943 | 7.594 | 46.693 | 4.39 | n.a. | 0.26 |
| **Total:** | | **172.854** | **1228.177** | **100.00** | | |



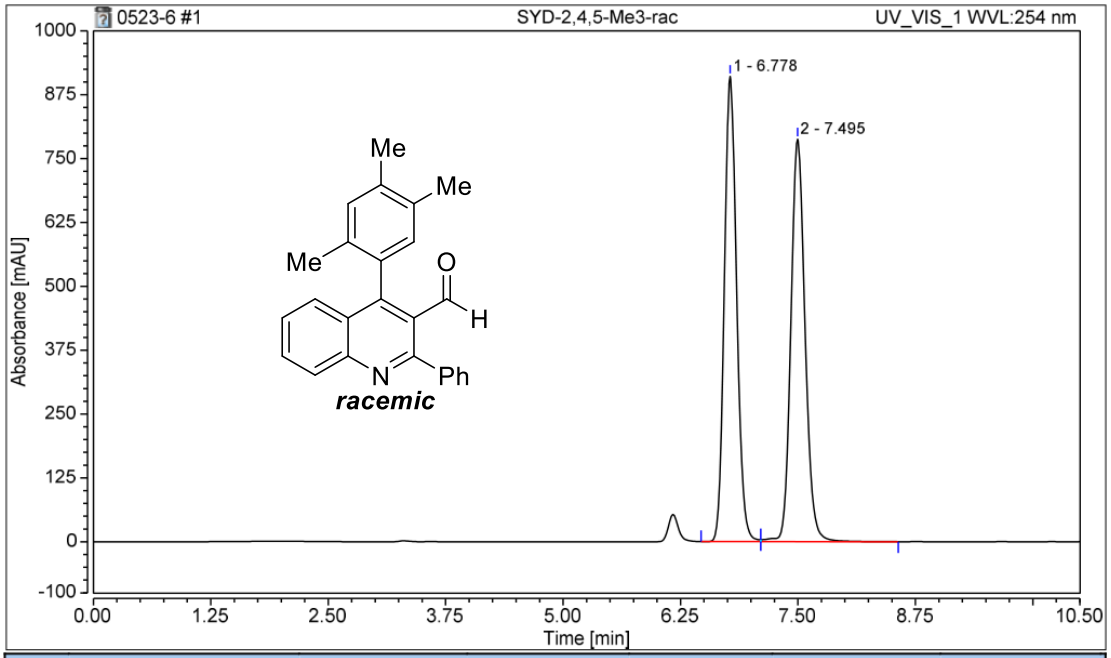

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 5.482 | 189.054 | 1501.708 | 49.72 | 1.29 | 0.19 |
| 2 | 5.915 | 191.167 | 1360.459 | 50.28 | 1.34 | 0.21 |
| **Total:** | | **380.221** | **2862.168** | **100.00** | | |



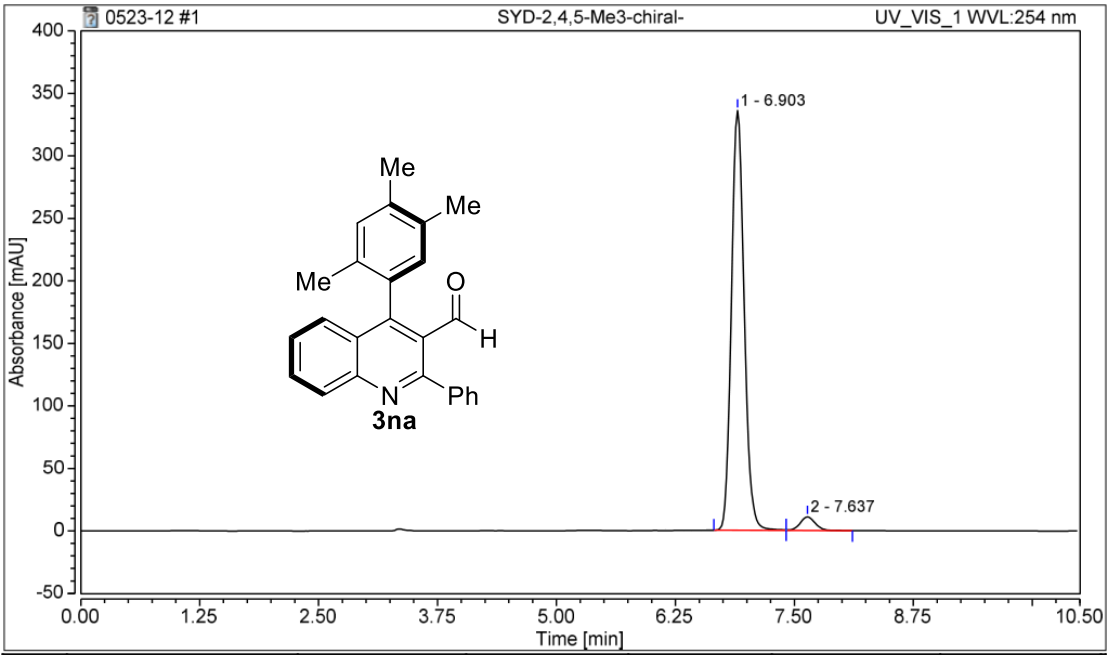

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 5.340 | 1.749 | 13.511 | 3.47 | 1.26 | 0.20 |
| 2 | 5.760 | 48.669 | 351.030 | 96.53 | 1.27 | 0.21 |
| **Total:** | | **50.418** | **364.540** | **100.00** | | |



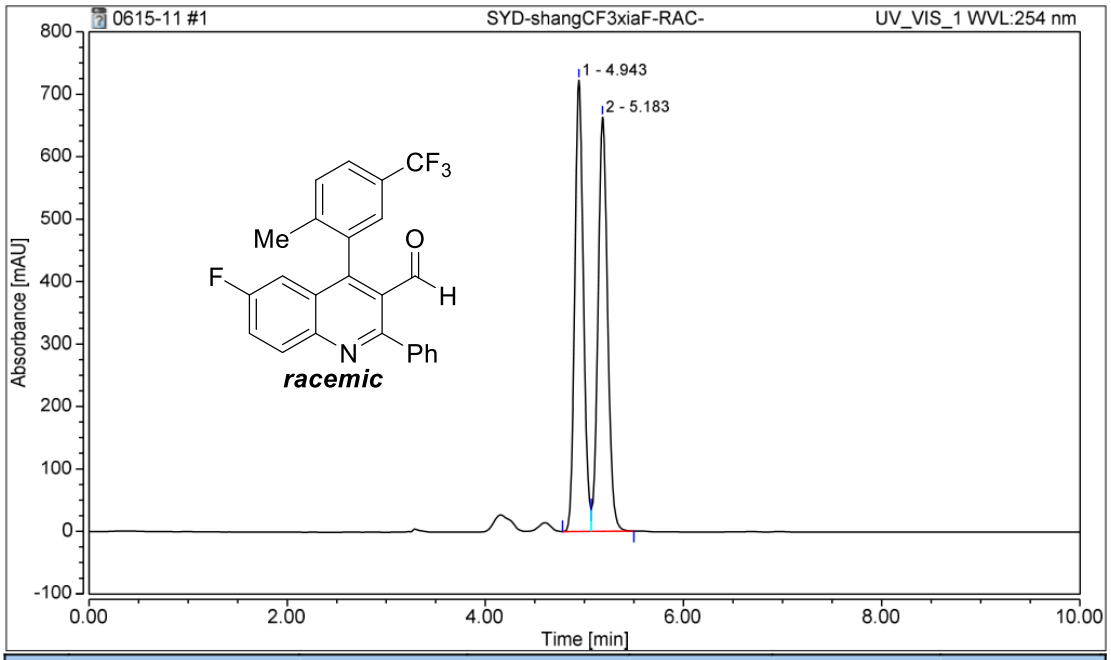

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 6.778 | 137.114 | 910.984 | 49.67 | 1.12 | 0.24 |
| 2 | 7.495 | 138.936 | 788.099 | 50.33 | 1.14 | 0.27 |
| **Total:** | | **276.050** | **1699.083** | **100.00** | | |



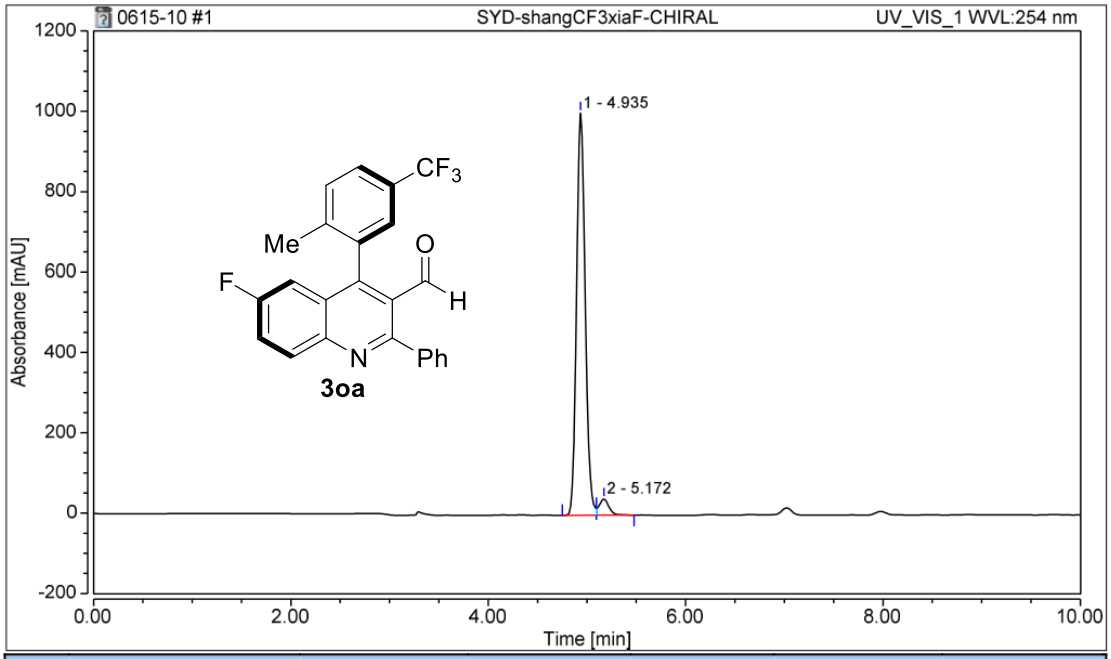

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 6.903 | 51.980 | 335.832 | 96.31 | 1.12 | 0.24 |
| 2 | 7.637 | 1.993 | 10.846 | 3.69 | 1.07 | 0.28 |
| **Total:** | | **53.973** | **346.678** | **100.00** | | |



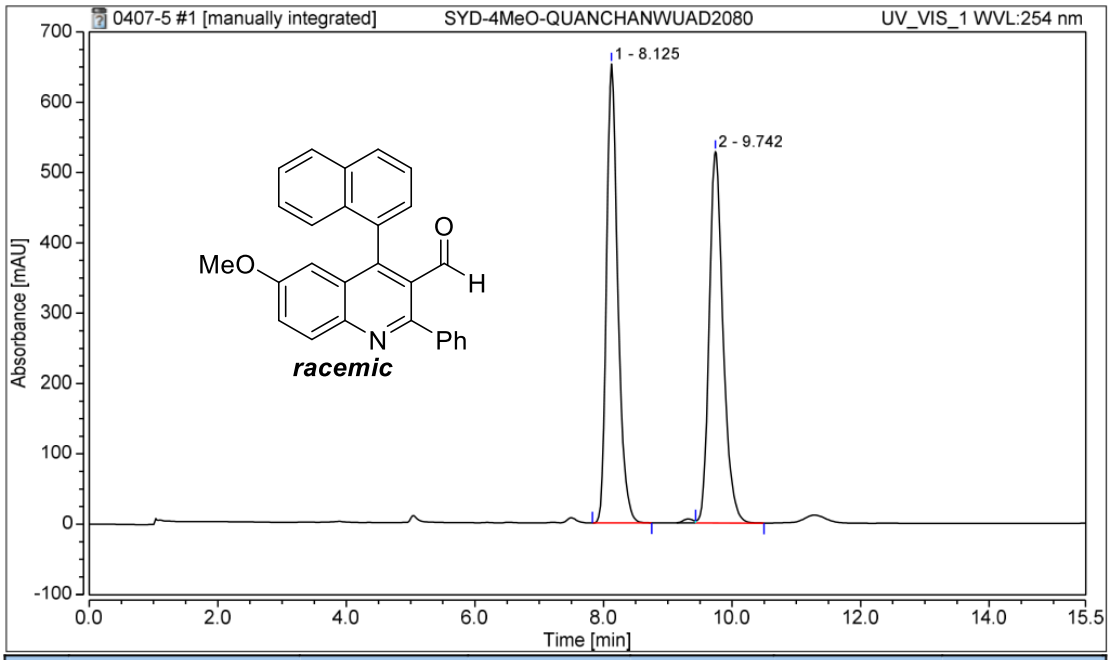

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 4.943 | 72.834 | 722.825 | 49.65 | 1.16 | 0.16 |
| 2 | 5.183 | 73.849 | 663.222 | 50.35 | n.a. | 0.17 |
| **Total:** | | **146.683** | **1386.048** | **100.00** | | |



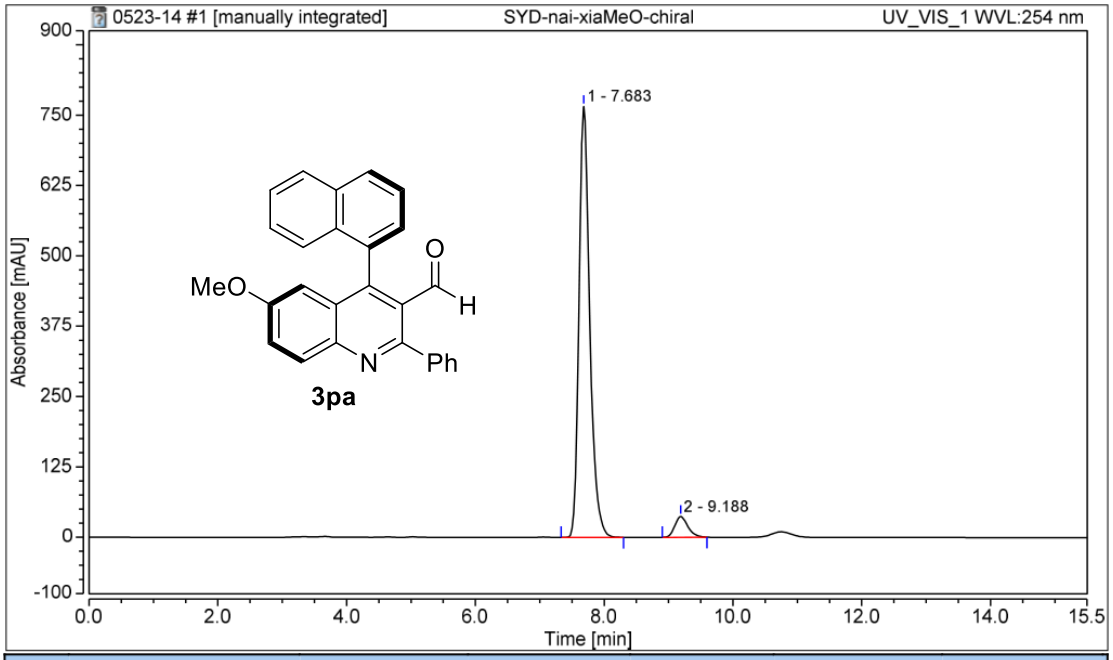

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 4.935 | 101.267 | 1001.232 | 95.59 | 1.15 | 0.16 |
| 2 | 5.172 | 4.667 | 40.222 | 4.41 | n.a. | 0.19 |
| **Total:** | | **105.934** | **1041.454** | **100.00** | | |



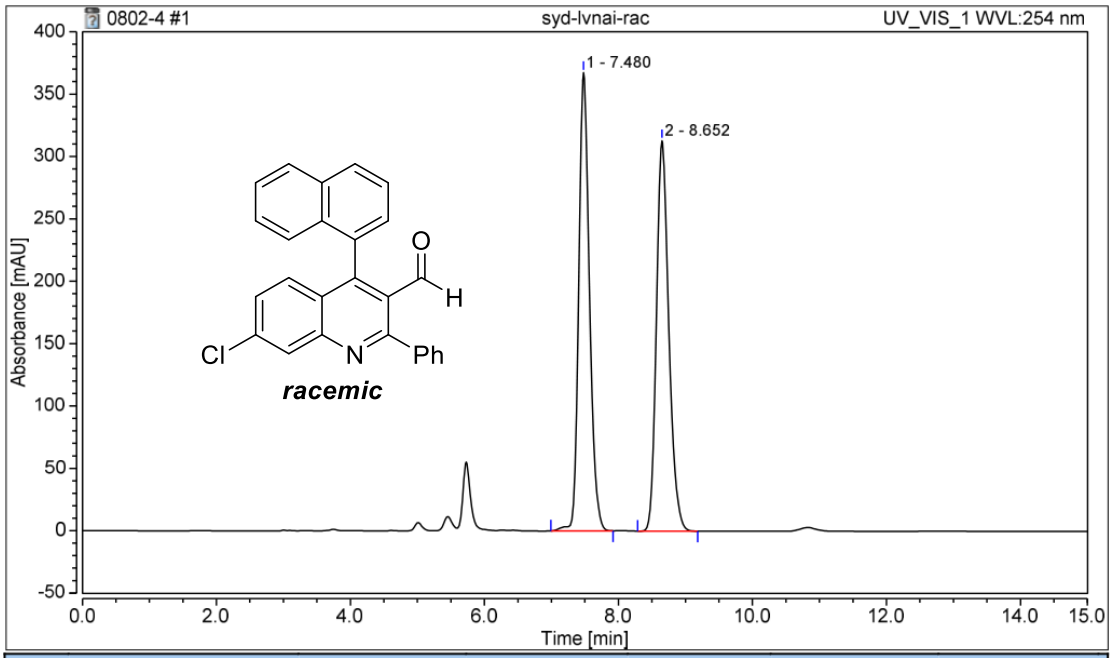

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 8.125 | 132.630 | 652.678 | 50.06 | 1.30 | 0.30 |
| 2 | 9.742 | 132.325 | 528.300 | 49.94 | 1.26 | 0.42 |
| **Total:** | | **264.955** | **1180.978** | **100.00** | | |



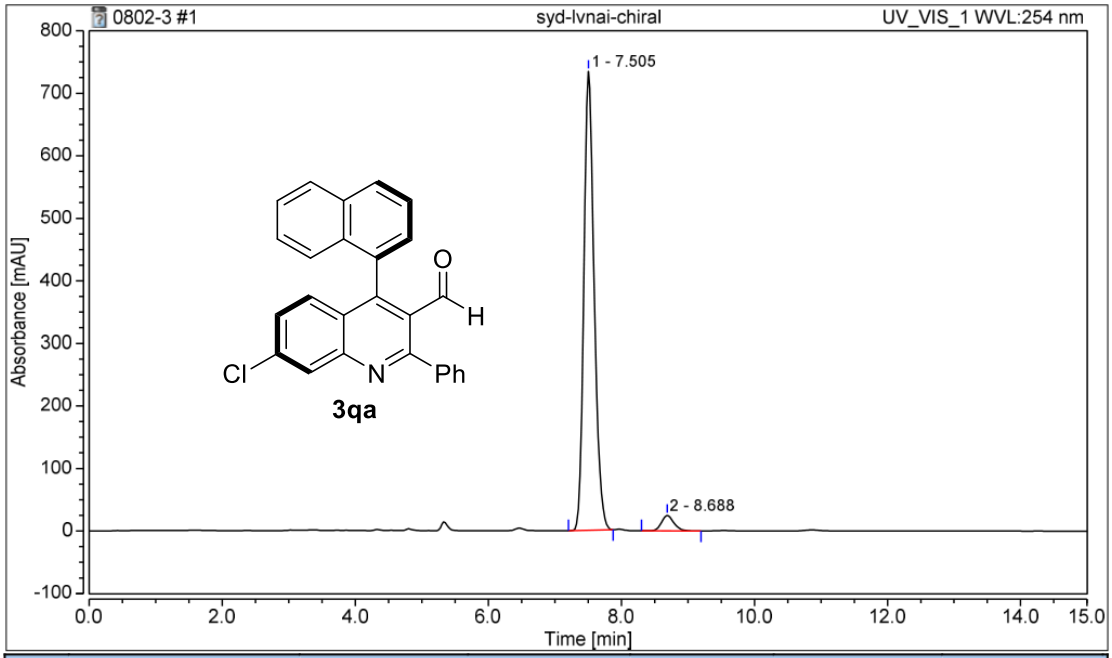

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 7.683 | 148.821 | 766.027 | 94.47 | 1.30 | 0.30 |
| 2 | 9.188 | 8.710 | 37.062 | 5.53 | 1.24 | 0.36 |
| **Total:** | | **157.531** | **803.090** | **100.00** | | |



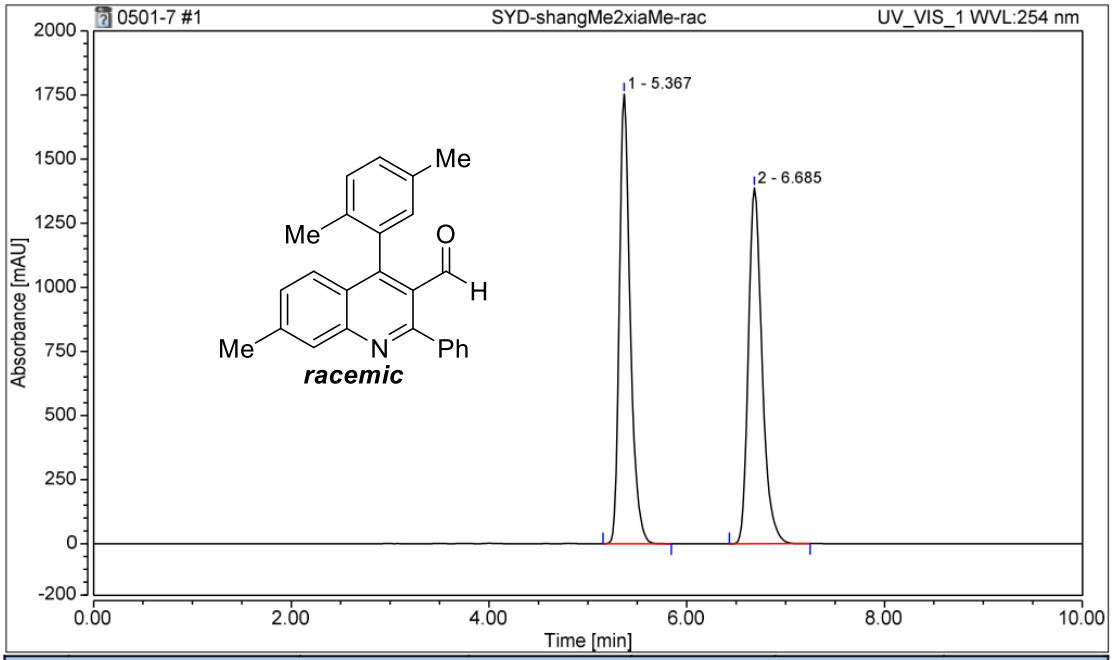

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 7.480 | 68.227 | 367.444 | 50.35 | 1.22 | 0.29 |
| 2 | 8.652 | 67.287 | 312.987 | 49.65 | 1.21 | 0.33 |
| **Total:** | | **135.514** | **680.432** | **100.00** | | |



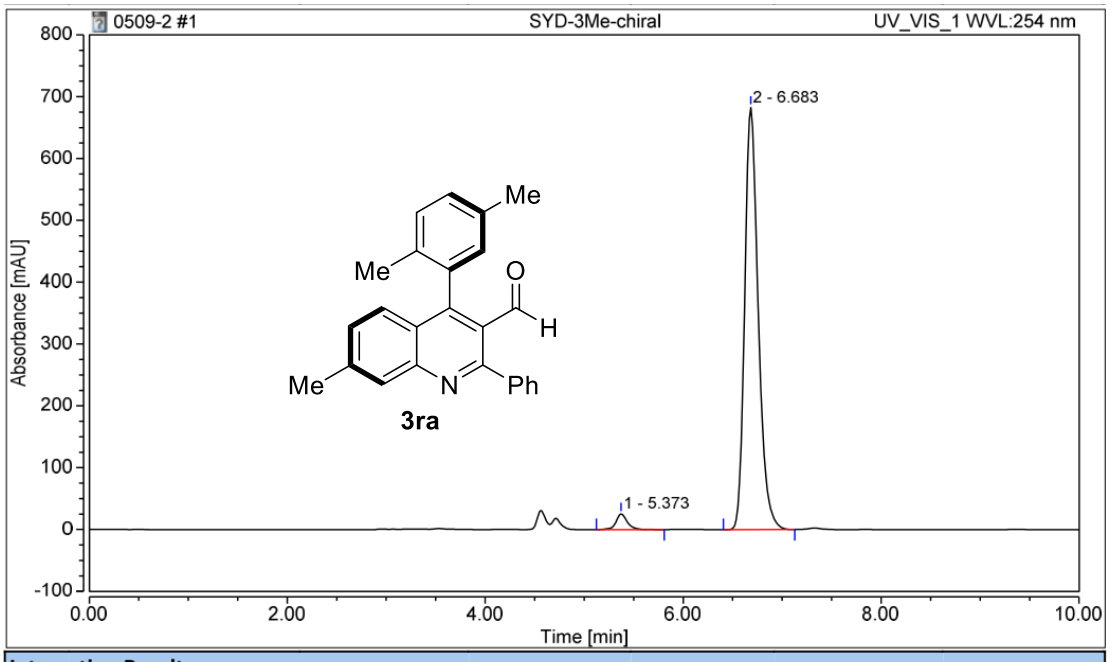

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 7.505 | 131.693 | 733.982 | 96.11 | 1.22 | 0.28 |
| 2 | 8.688 | 5.336 | 24.638 | 3.89 | 1.16 | 0.34 |
| **Total:** | | **137.029** | **758.621** | **100.00** | | |



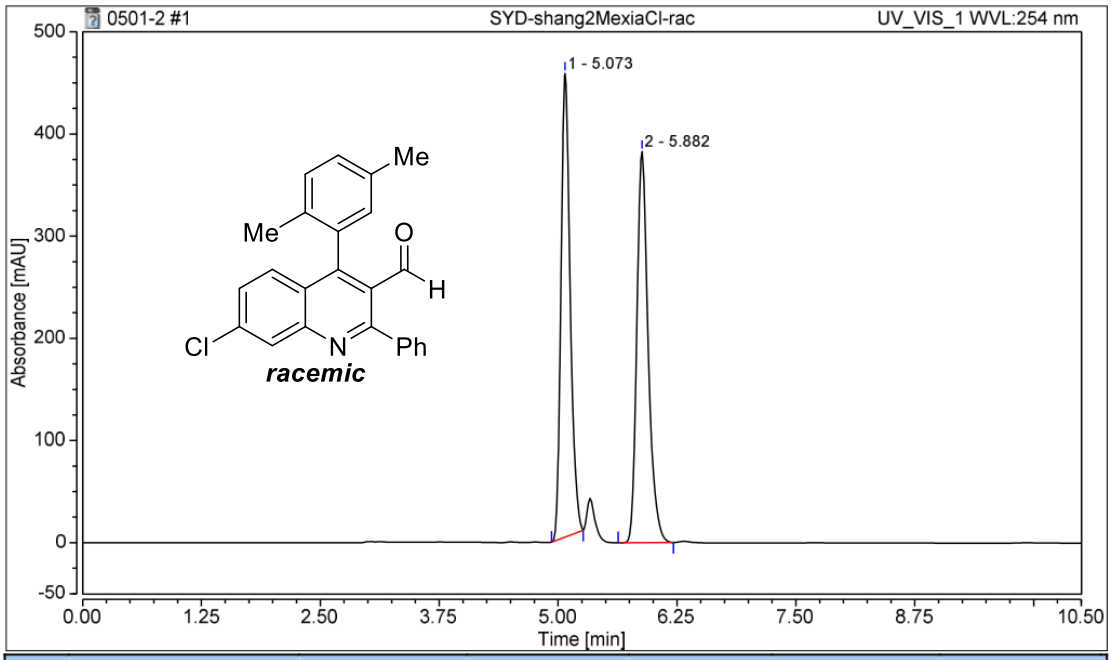

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 5.367 | 223.125 | 1754.106 | 50.04 | 1.35 | 0.19 |
| 2 | 6.685 | 222.807 | 1388.302 | 49.96 | 1.30 | 0.25 |
| **Total:** | | **445.932** | **3142.408** | **100.00** | | |



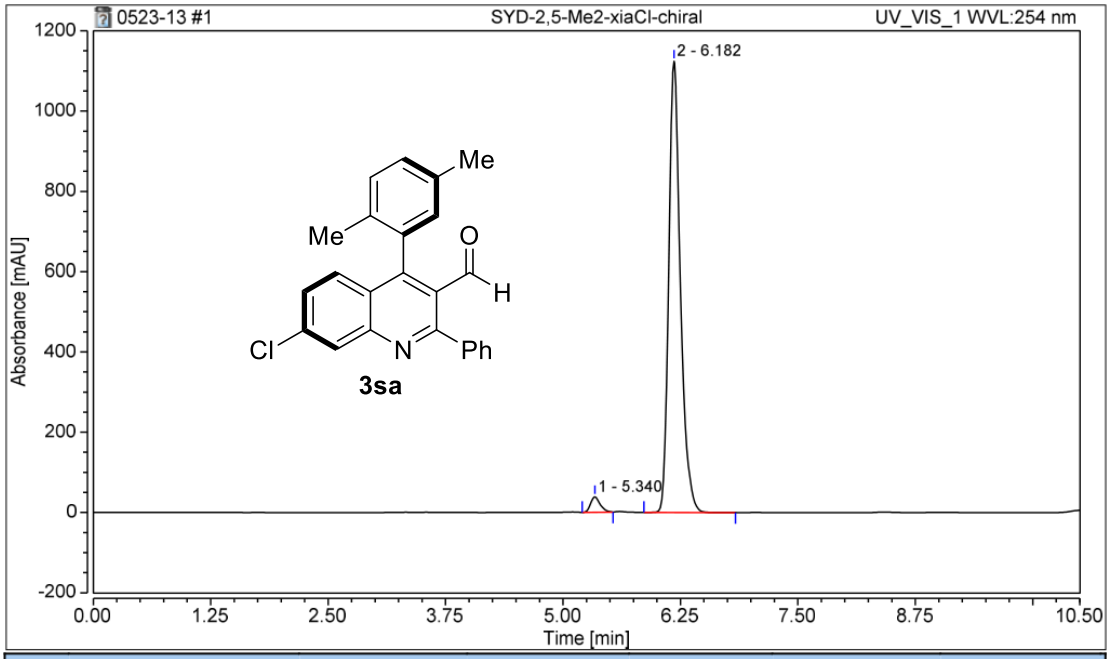

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 5.373 | 3.370 | 25.468 | 3.01 | 1.07 | 0.19 |
| 2 | 6.683 | 108.585 | 683.120 | 96.99 | 1.25 | 0.25 |
| **Total:** | | **111.955** | **708.588** | **100.00** | | |



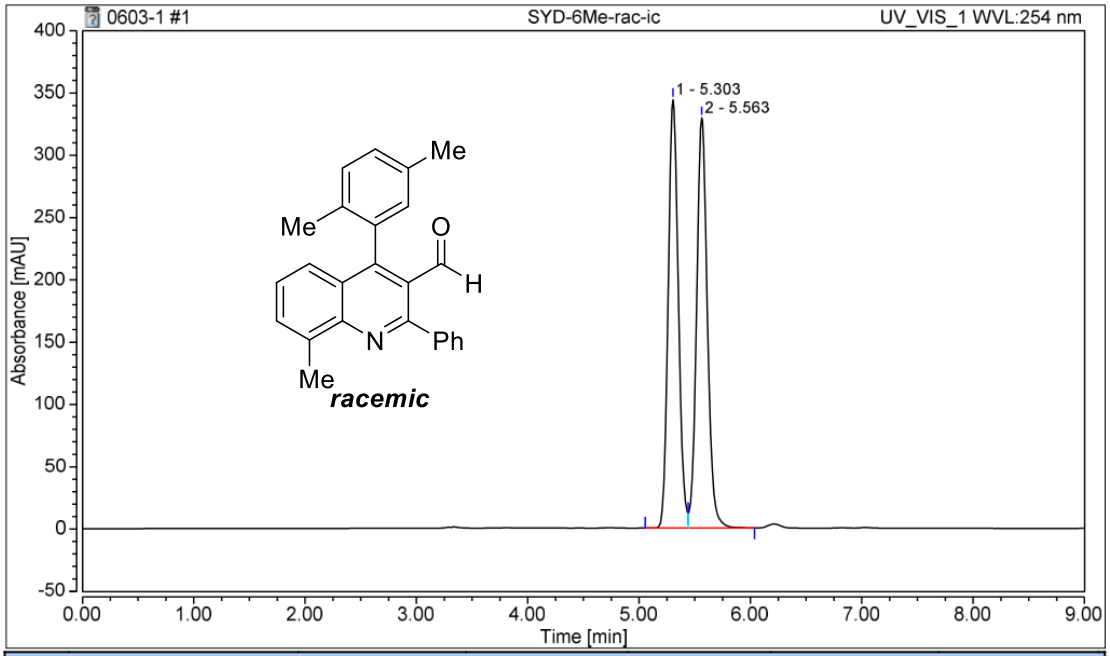

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 5.073 | 50.625 | 453.944 | 48.93 | 1.25 | 0.17 |
| 2 | 5.882 | 52.839 | 382.929 | 51.07 | 1.28 | 0.21 |
| **Total:** | | **103.464** | **836.873** | **100.00** | | |



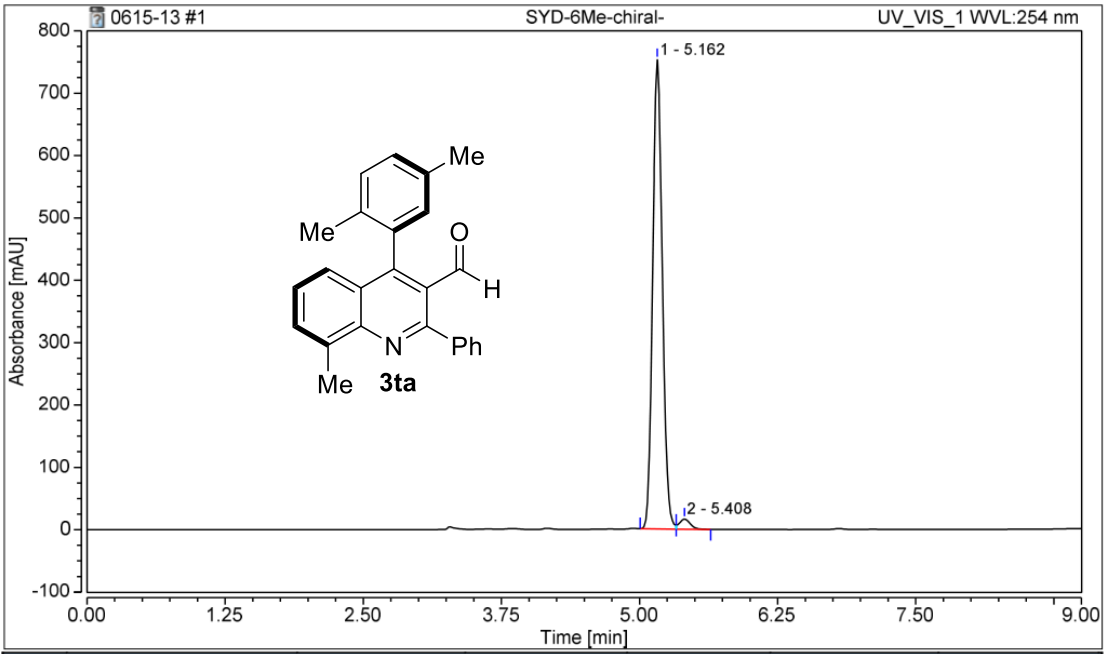

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 5.340 | 4.508 | 38.838 | 2.70 | 1.26 | 0.18 |
| 2 | 6.182 | 162.226 | 1124.442 | 97.30 | 1.28 | 0.21 |
| **Total:** | | **166.734** | **1163.280** | **100.00** | | |



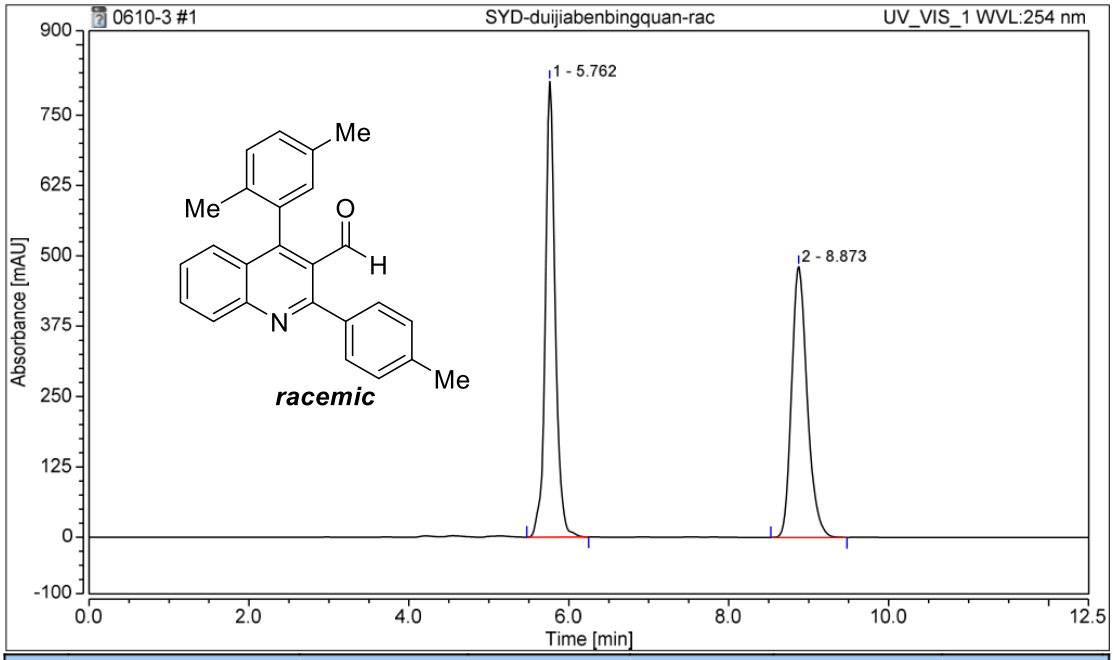

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 5.303 | 36.138 | 344.044 | 49.45 | 1.14 | 0.16 |
| 2 | 5.563 | 36.948 | 329.389 | 50.55 | 1.08 | 0.17 |
| **Total:** | | **73.086** | **673.433** | **100.00** | | |



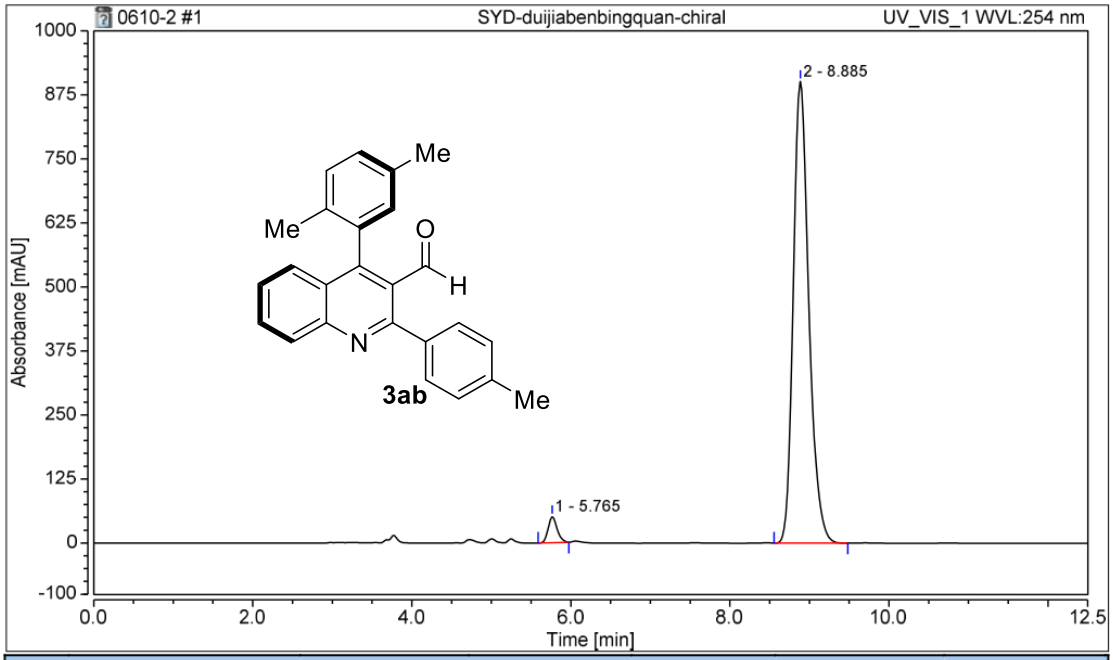

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 5.162 | 75.854 | 752.432 | 97.64 | 1.10 | 0.16 |
| 2 | 5.408 | 1.831 | 16.223 | 2.36 | n.a. | 0.19 |
| **Total:** | | **77.685** | **768.655** | **100.00** | | |



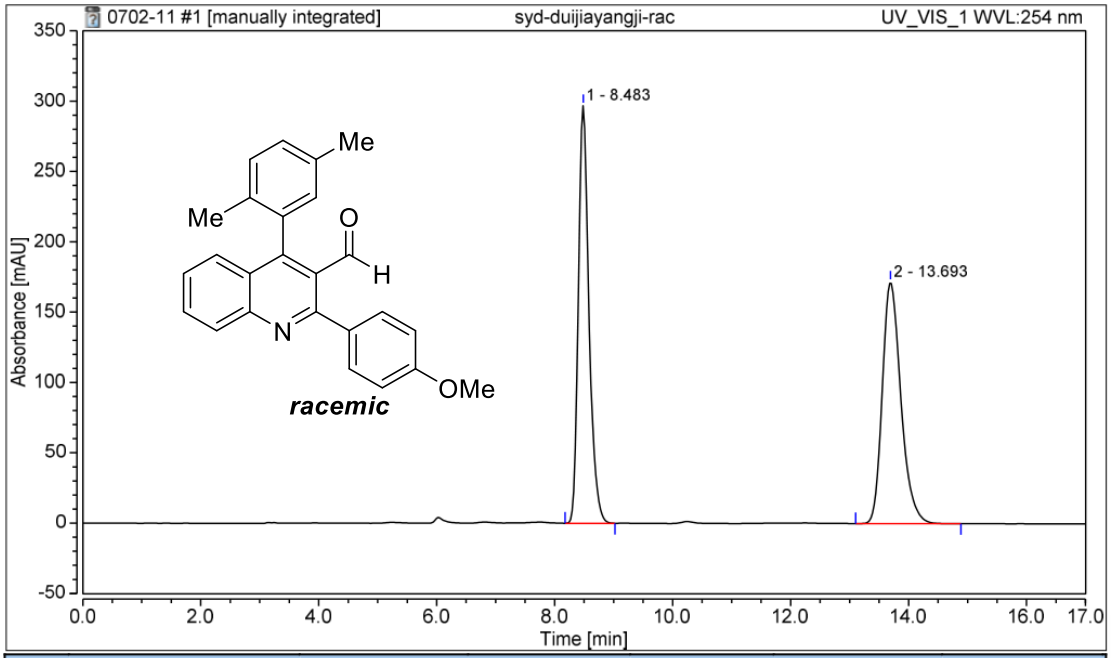

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 5.762 | 116.320 | 809.828 | 51.67 | 1.06 | 0.21 |
| 2 | 8.873 | 108.821 | 481.148 | 48.33 | 1.25 | 0.35 |
| **Total:** | | **225.142** | **1290.976** | **100.00** | | |



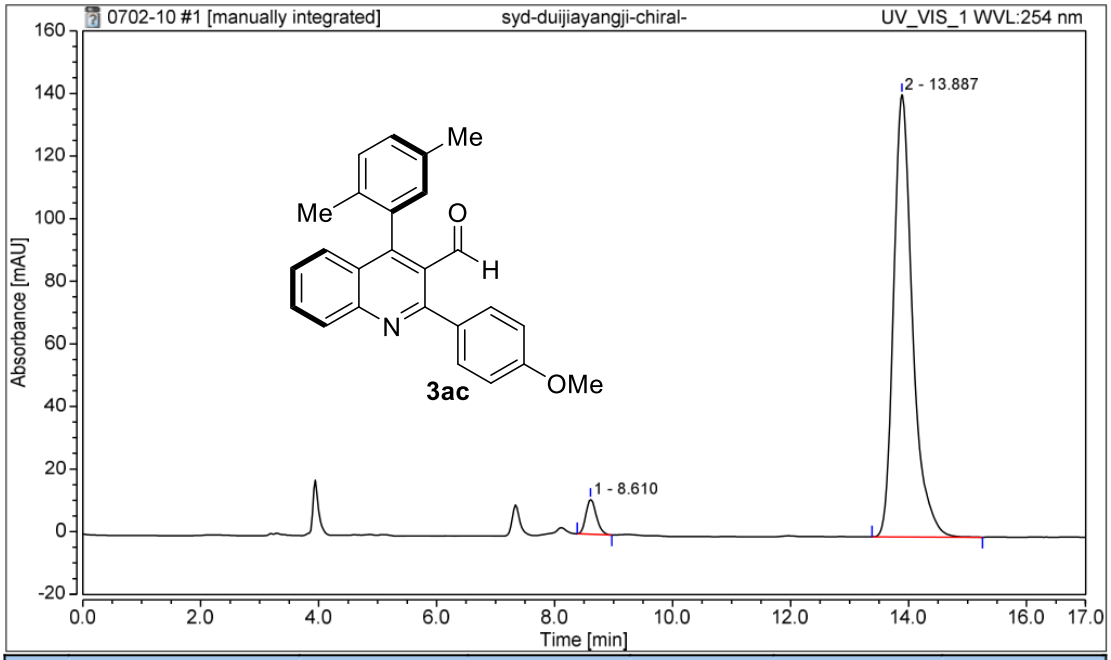

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 5.765 | 6.609 | 50.920 | 3.13 | 1.21 | 0.20 |
| 2 | 8.885 | 204.275 | 901.775 | 96.87 | 1.25 | 0.35 |
| **Total:** | | **210.883** | **952.695** | **100.00** | | |



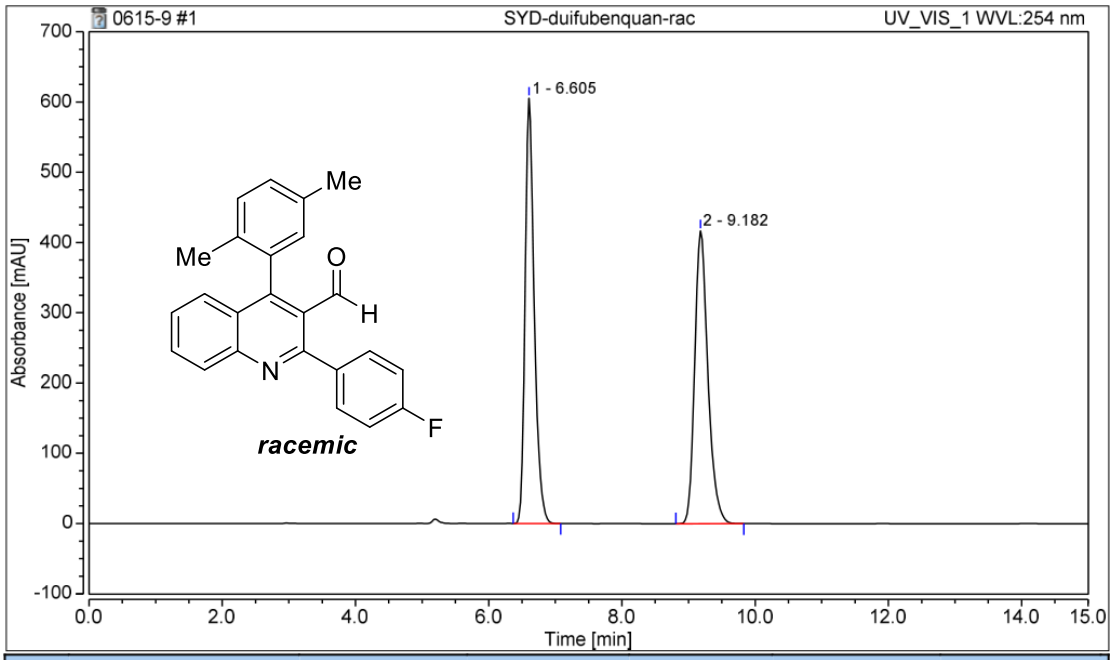

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 8.483 | 61.947 | 296.855 | 49.73 | 1.27 | 0.32 |
| 2 | 13.693 | 62.620 | 171.718 | 50.27 | 1.27 | 0.57 |
| **Total:** | | **124.566** | **468.572** | **100.00** | | |



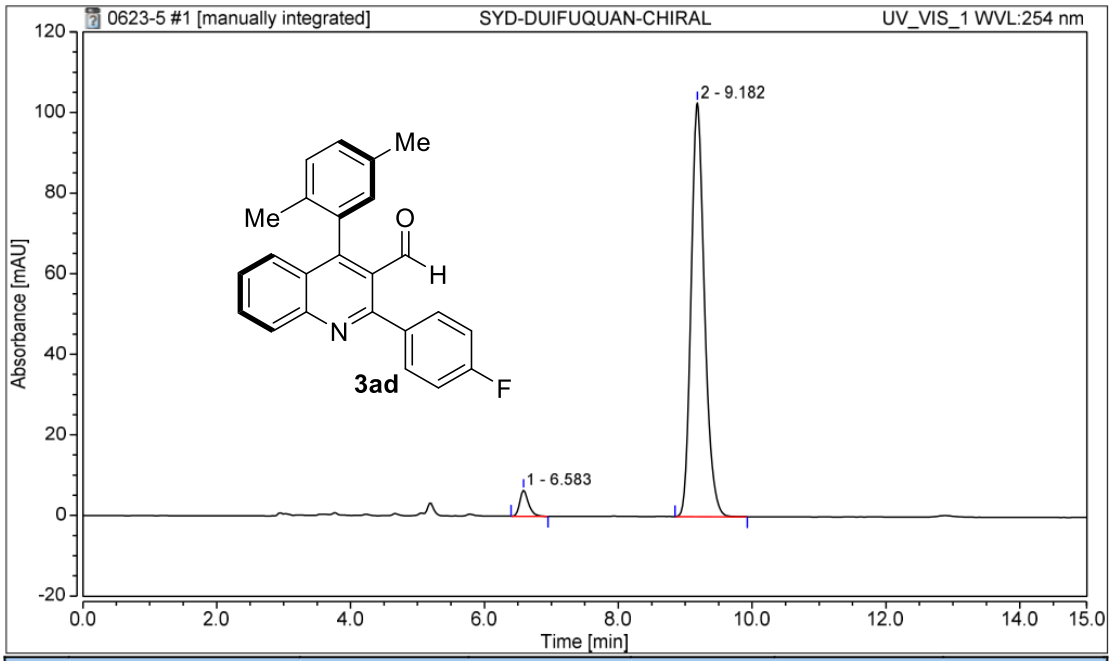

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 8.610 | 2.263 | 11.141 | 4.15 | 1.21 | 0.31 |
| 2 | 13.887 | 52.318 | 141.336 | 95.85 | 1.37 | 0.54 |
| **Total:** | | **54.581** | **152.477** | **100.00** | | |



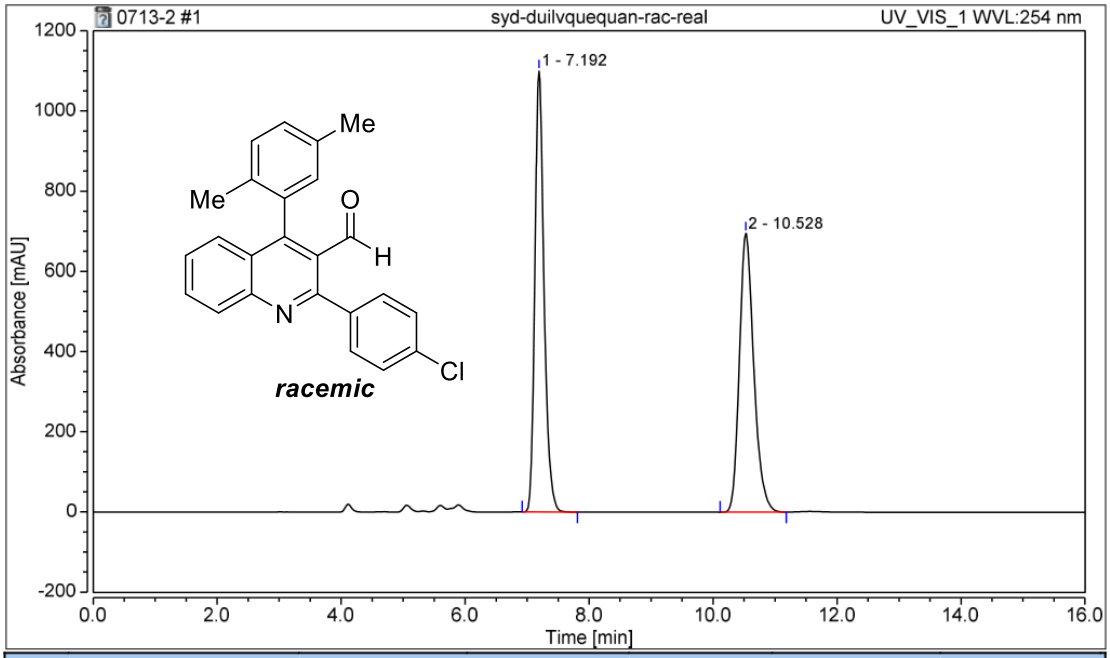

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 6.605 | 96.138 | 605.392 | 50.11 | 1.33 | 0.24 |
| 2 | 9.182 | 95.726 | 416.635 | 49.89 | 1.27 | 0.35 |
| **Total:** | | **191.864** | **1022.027** | **100.00** | | |



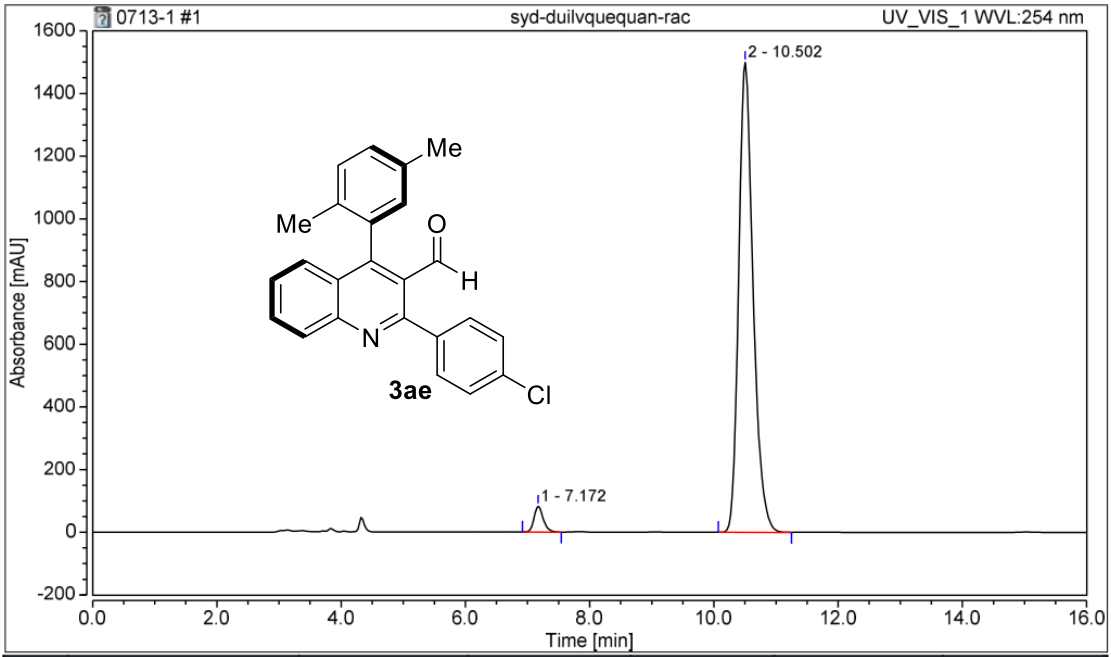

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 6.583 | 0.975 | 6.428 | 3.93 | 1.32 | 0.23 |
| 2 | 9.182 | 23.851 | 102.716 | 96.07 | 1.21 | 0.36 |
| **Total:** | | **24.826** | **109.144** | **100.00** | | |



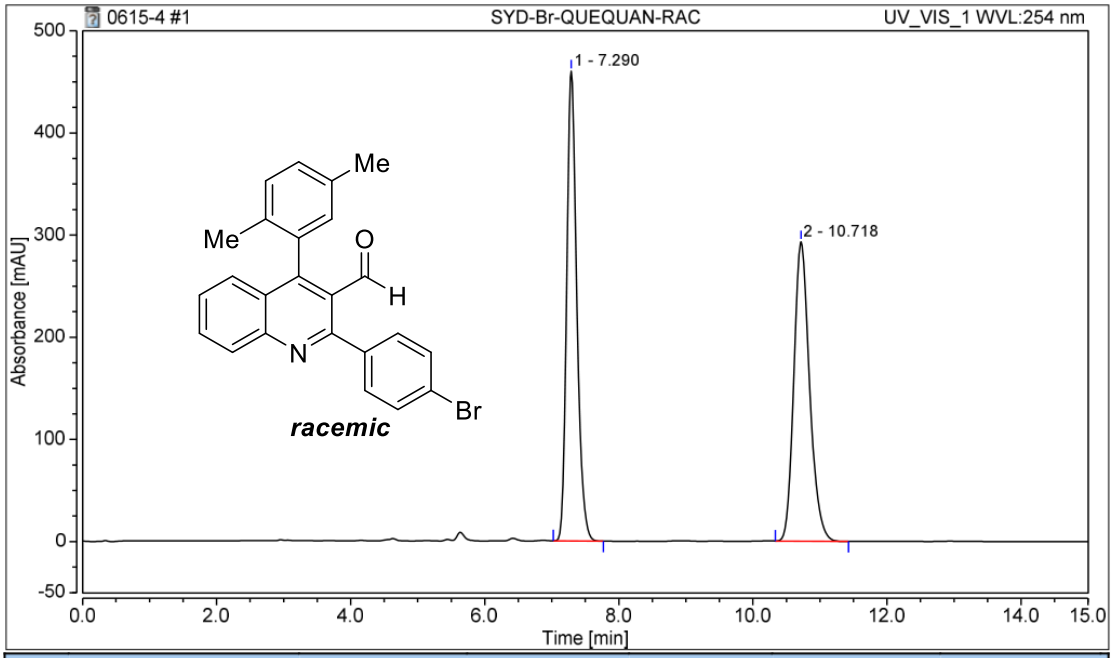

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 7.192 | 187.916 | 1099.904 | 50.08 | 1.26 | 0.26 |
| 2 | 10.528 | 187.329 | 695.796 | 49.92 | 1.25 | 0.41 |
| **Total:** | | **375.246** | **1795.700** | **100.00** | | |



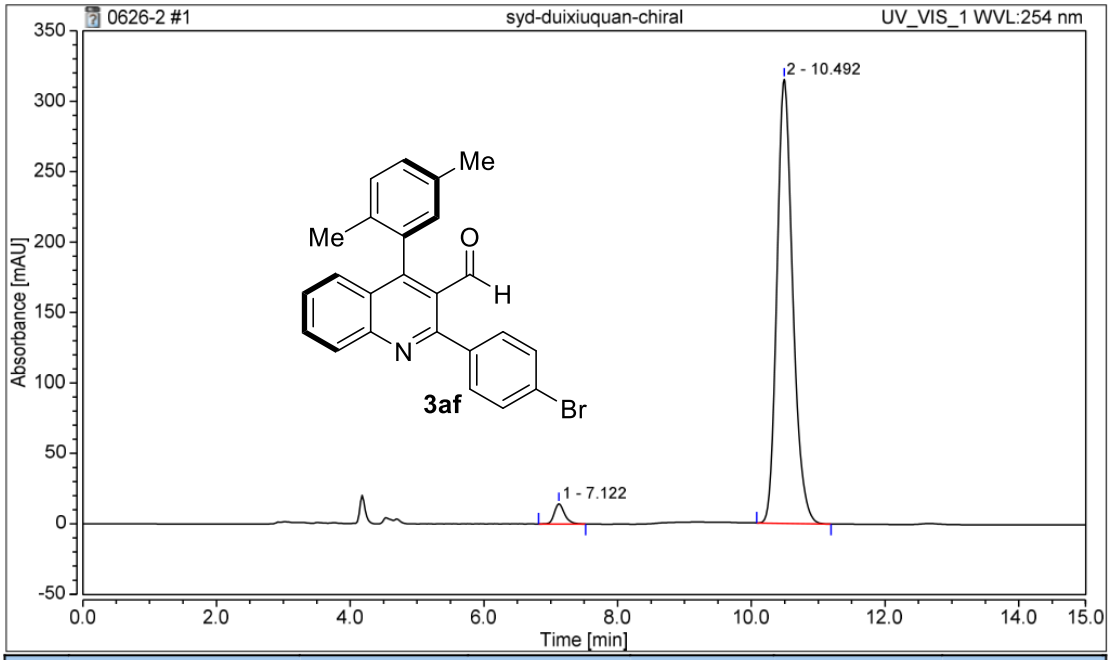

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 7.172 | 14.122 | 83.064 | 3.38 | 1.24 | 0.26 |
| 2 | 10.502 | 403.326 | 1499.526 | 96.62 | 1.27 | 0.42 |
| **Total:** | | **417.449** | **1582.590** | **100.00** | | |



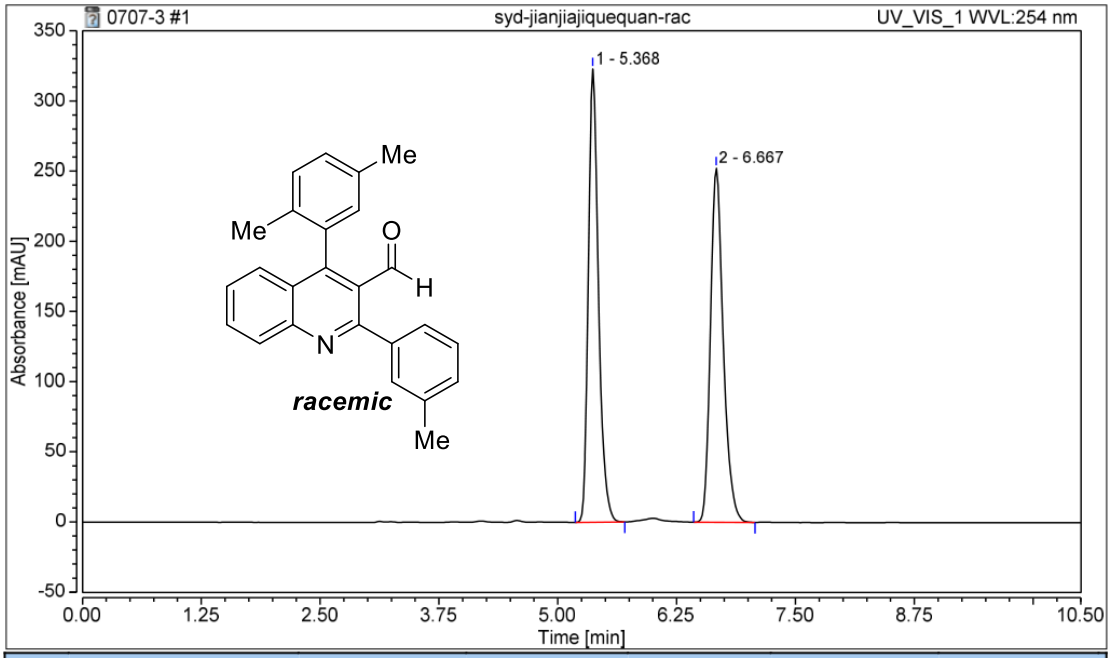

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 7.290 | 80.229 | 459.932 | 50.08 | 1.24 | 0.27 |
| 2 | 10.718 | 79.977 | 293.020 | 49.92 | 1.21 | 0.43 |
| **Total:** | | **160.206** | **752.952** | **100.00** | | |



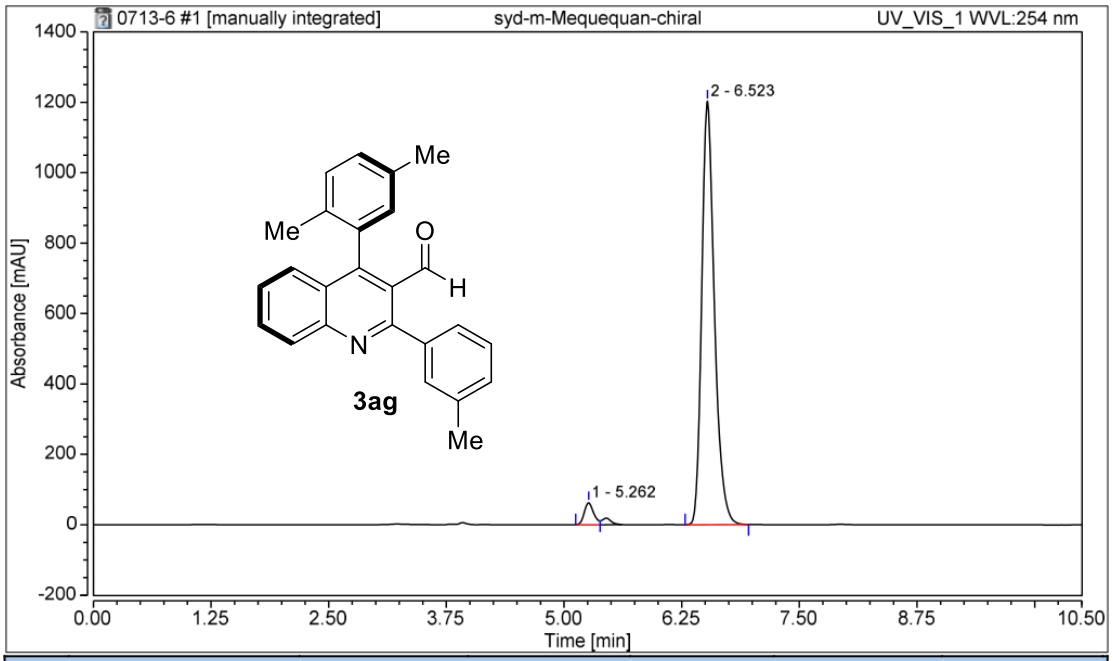

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 7.122 | 2.571 | 14.415 | 2.88 | 1.26 | 0.27 |
| 2 | 10.492 | 86.554 | 315.393 | 97.12 | 1.22 | 0.43 |
| **Total:** | | **89.125** | **329.808** | **100.00** | | |



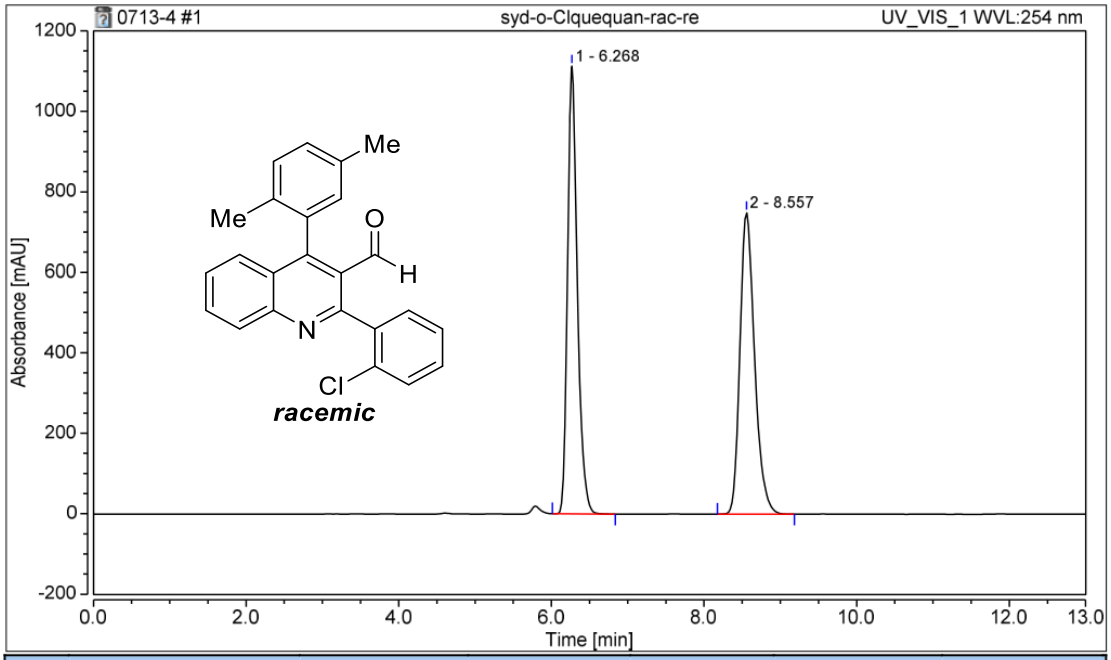

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 5.368 | 39.778 | 323.047 | 50.12 | 1.30 | 0.19 |
| 2 | 6.667 | 39.590 | 252.403 | 49.88 | 1.26 | 0.24 |
| **Total:** | | **79.368** | **575.450** | **100.00** | | |



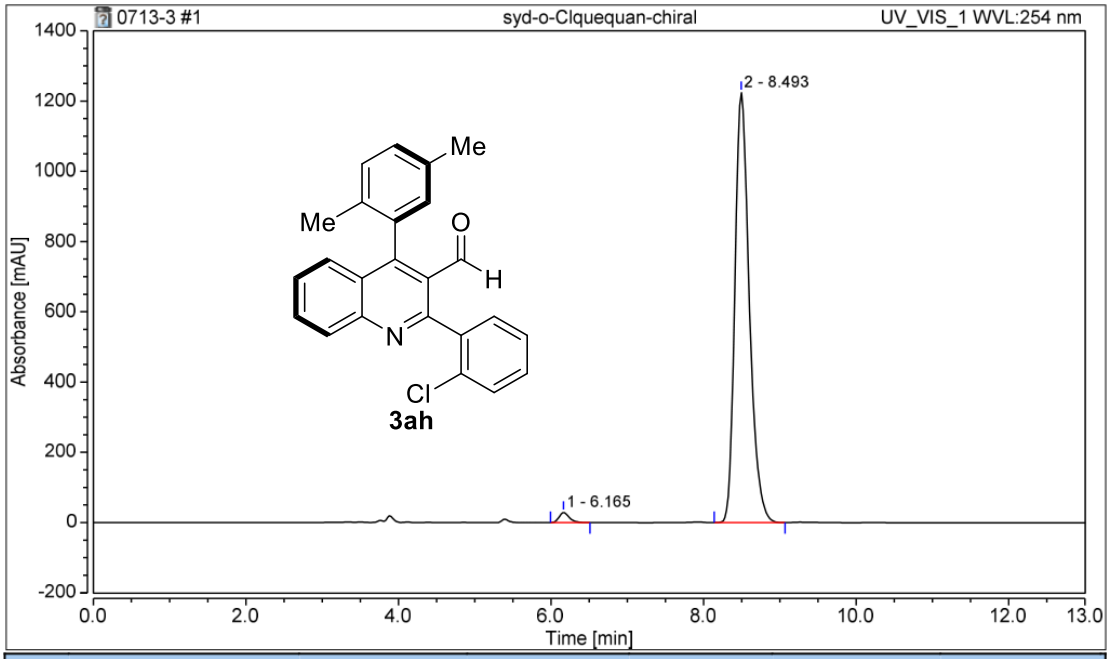

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 5.262 | 7.277 | 62.416 | 3.71 | n.a. | 0.18 |
| 2 | 6.523 | 189.013 | 1202.775 | 96.29 | 1.28 | 0.24 |
| **Total:** | | **196.290** | **1265.191** | **100.00** | | |



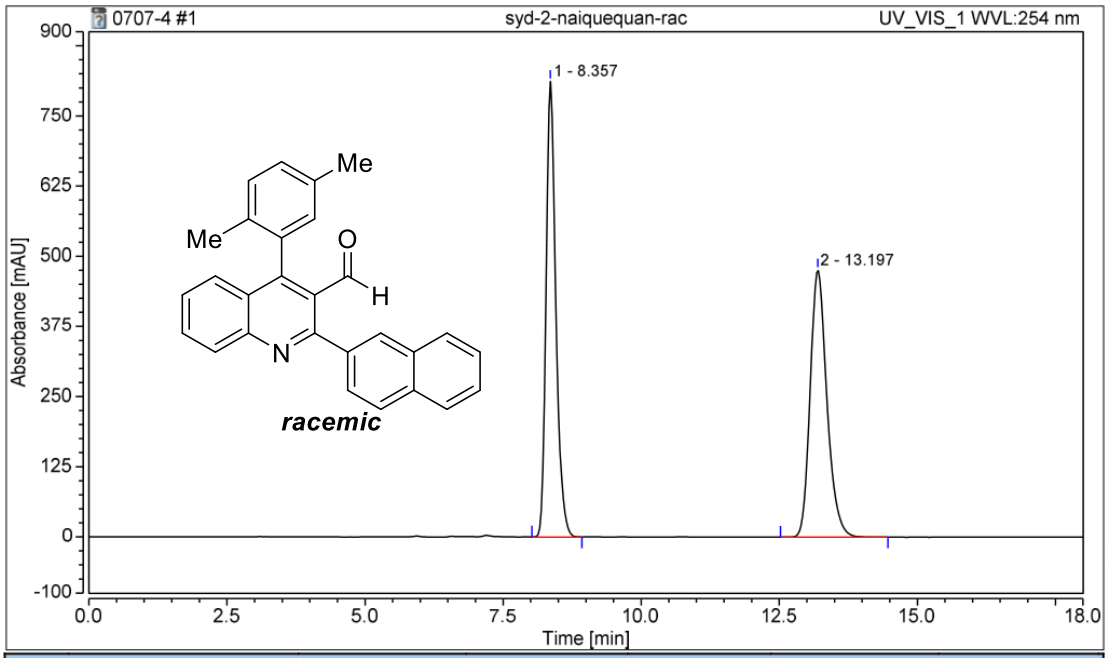

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 6.268 | 165.352 | 1113.171 | 49.77 | 1.30 | 0.22 |
| 2 | 8.557 | 166.861 | 749.501 | 50.23 | 1.27 | 0.34 |
| **Total:** | | **332.214** | **1862.672** | **100.00** | | |



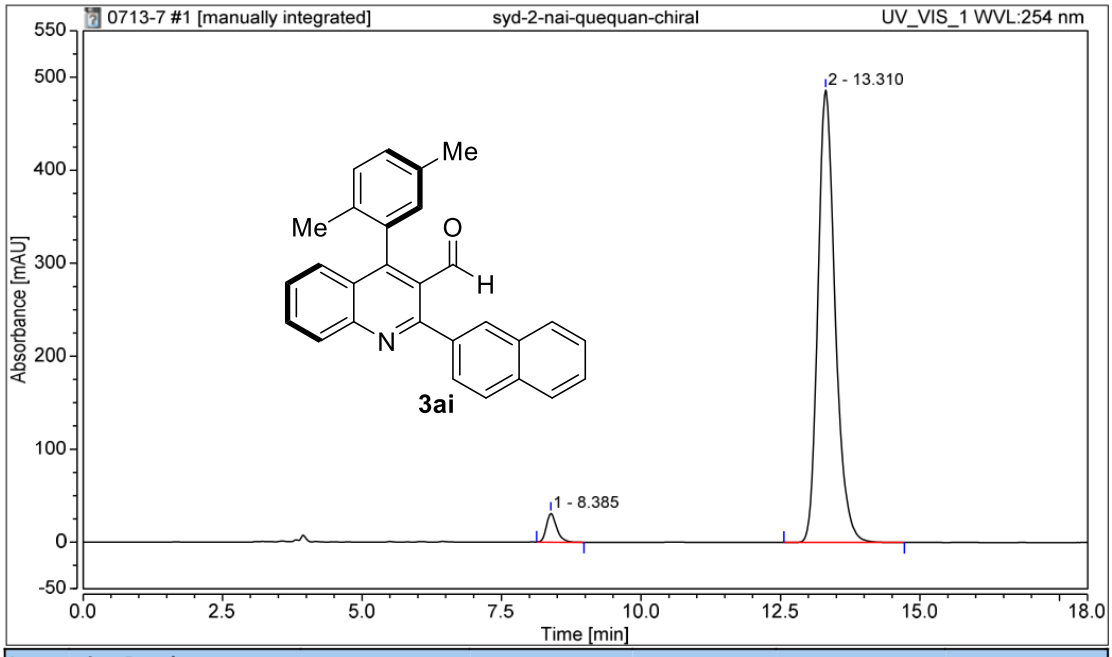

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 6.165 | 4.511 | 28.919 | 1.65 | 1.29 | 0.24 |
| 2 | 8.493 | 268.682 | 1224.357 | 98.35 | 1.29 | 0.34 |
| **Total:** | | **273.194** | **1253.275** | **100.00** | | |



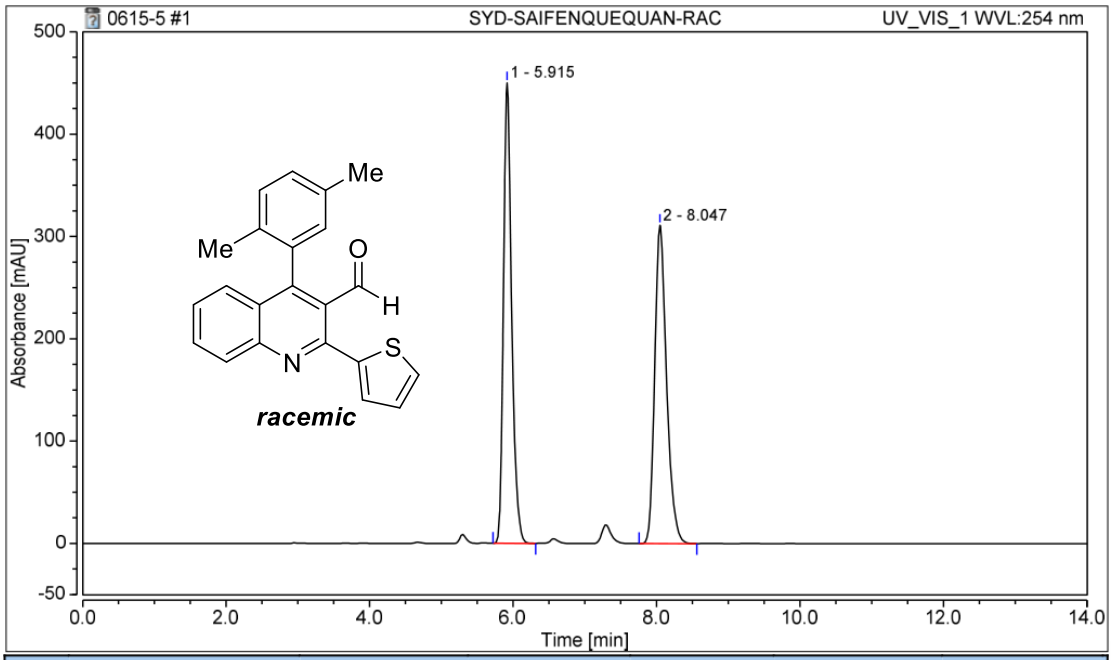

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 8.357 | 166.537 | 812.155 | 49.95 | 1.27 | 0.31 |
| 2 | 13.197 | 166.877 | 476.200 | 50.05 | 1.24 | 0.53 |
| **Total:** | | **333.414** | **1288.355** | **100.00** | | |



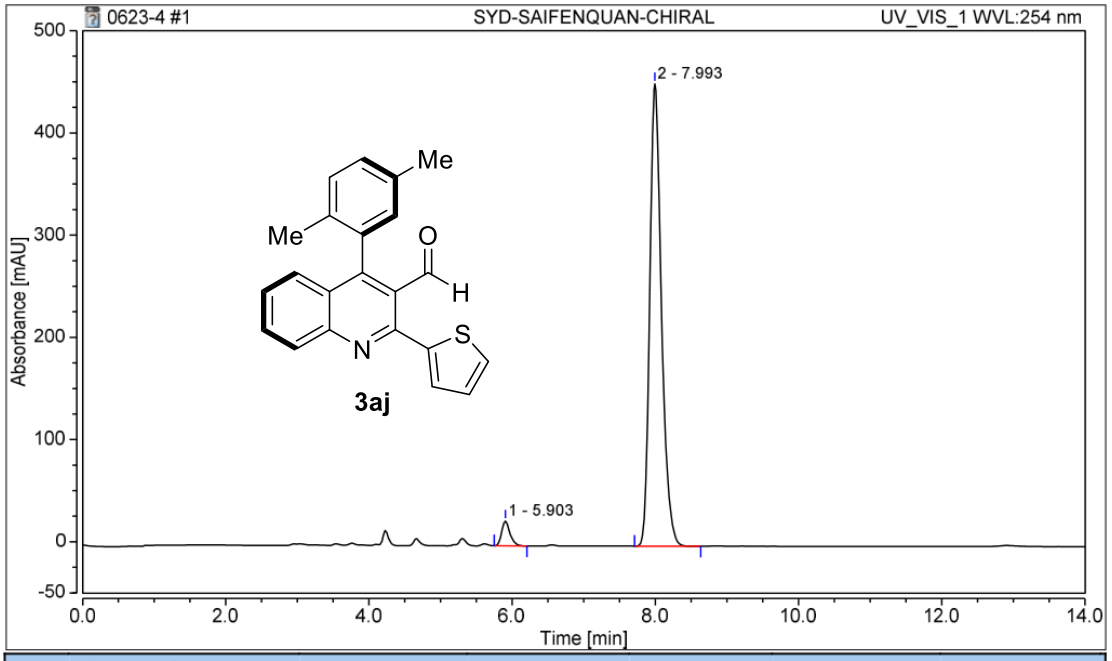

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 8.385 | 6.594 | 31.079 | 3.65 | 1.31 | 0.33 |
| 2 | 13.310 | 174.092 | 486.607 | 96.35 | 1.24 | 0.57 |
| **Total:** | | **180.686** | **517.685** | **100.00** | | |



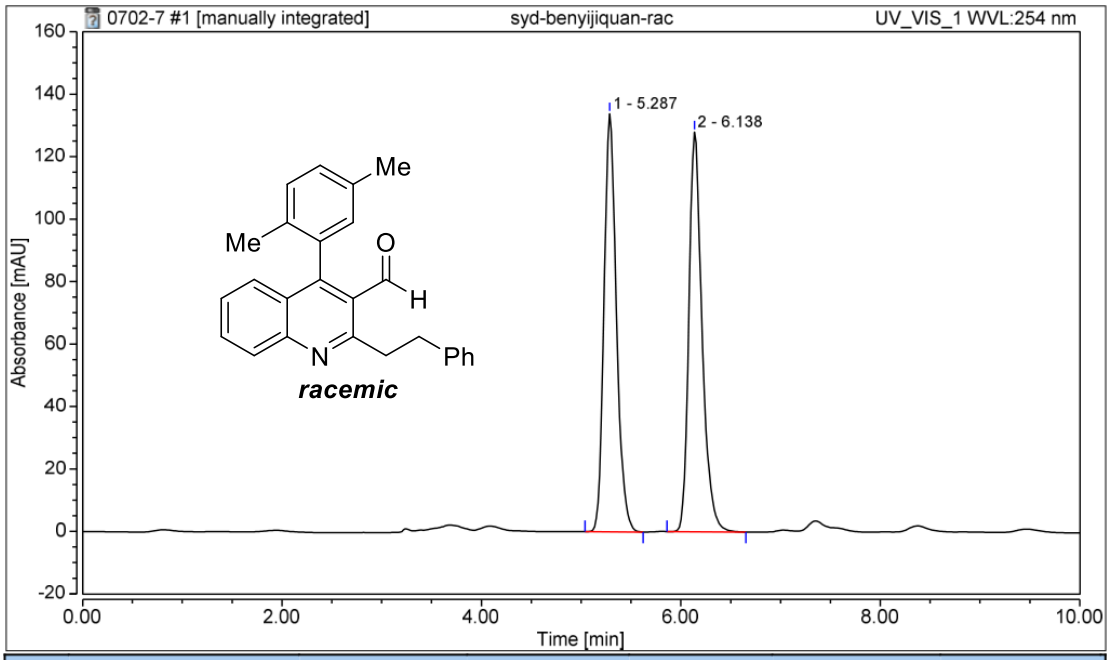

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 5.915 | 59.414 | 449.976 | 49.94 | 1.30 | 0.20 |
| 2 | 8.047 | 59.553 | 311.131 | 50.06 | 1.27 | 0.30 |
| **Total:** | | **118.967** | **761.107** | **100.00** | | |



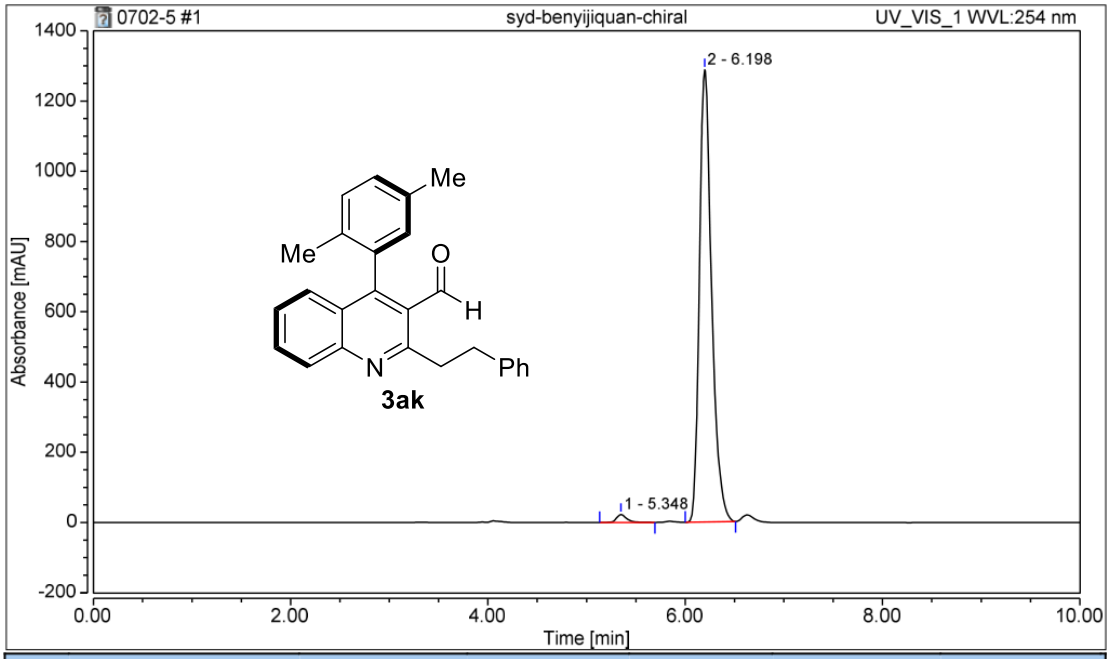

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 5.903 | 3.277 | 24.362 | 3.69 | 1.31 | 0.21 |
| 2 | 7.993 | 85.558 | 452.427 | 96.31 | 1.27 | 0.29 |
| **Total:** | | **88.835** | **476.789** | **100.00** | | |



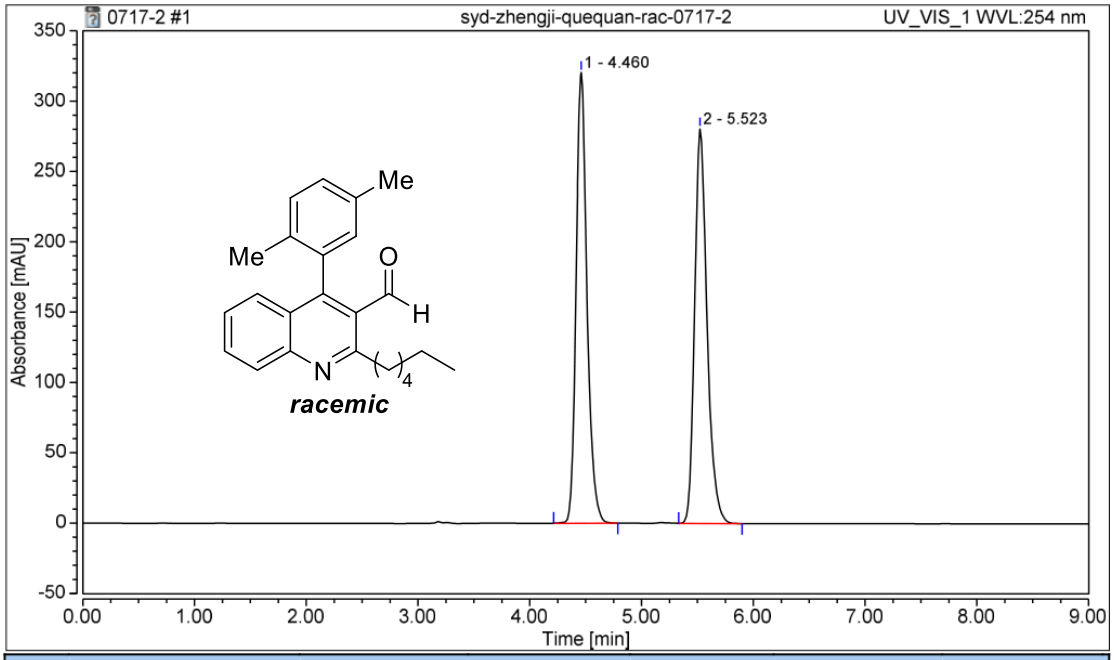

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 5.287 | 19.247 | 133.885 | 49.53 | 1.20 | 0.22 |
| 2 | 6.138 | 19.614 | 127.984 | 50.47 | 1.29 | 0.24 |
| **Total:** | | **38.861** | **261.869** | **100.00** | | |



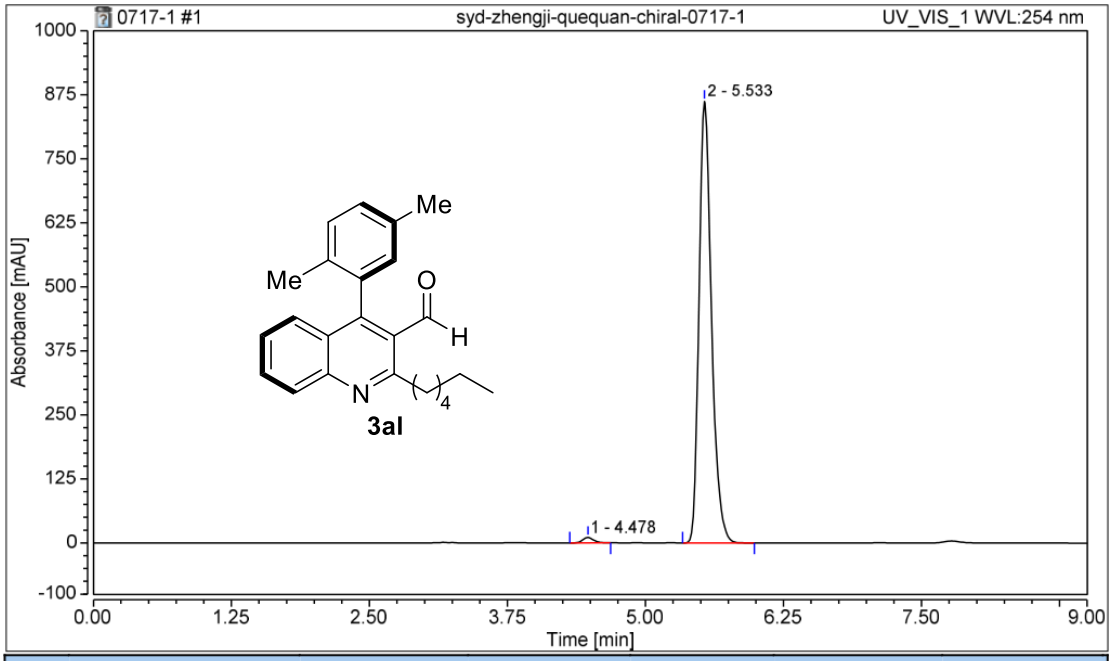

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 5.348 | 2.720 | 22.825 | 1.46 | 1.36 | 0.17 |
| 2 | 6.198 | 184.026 | 1287.826 | 98.54 | 1.33 | 0.21 |
| **Total:** | | **186.746** | **1310.651** | **100.00** | | |



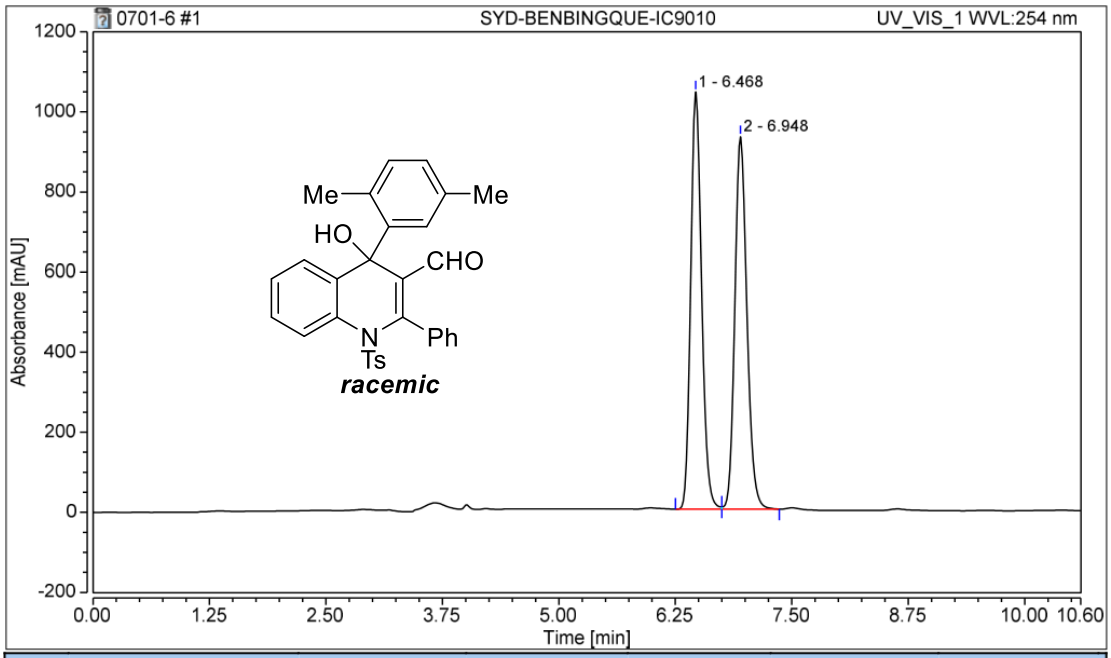

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 4.460 | 36.080 | 320.437 | 49.98 | 1.22 | 0.17 |
| 2 | 5.523 | 36.111 | 280.464 | 50.02 | 1.29 | 0.20 |
| **Total:** | | **72.191** | **600.901** | **100.00** | | |



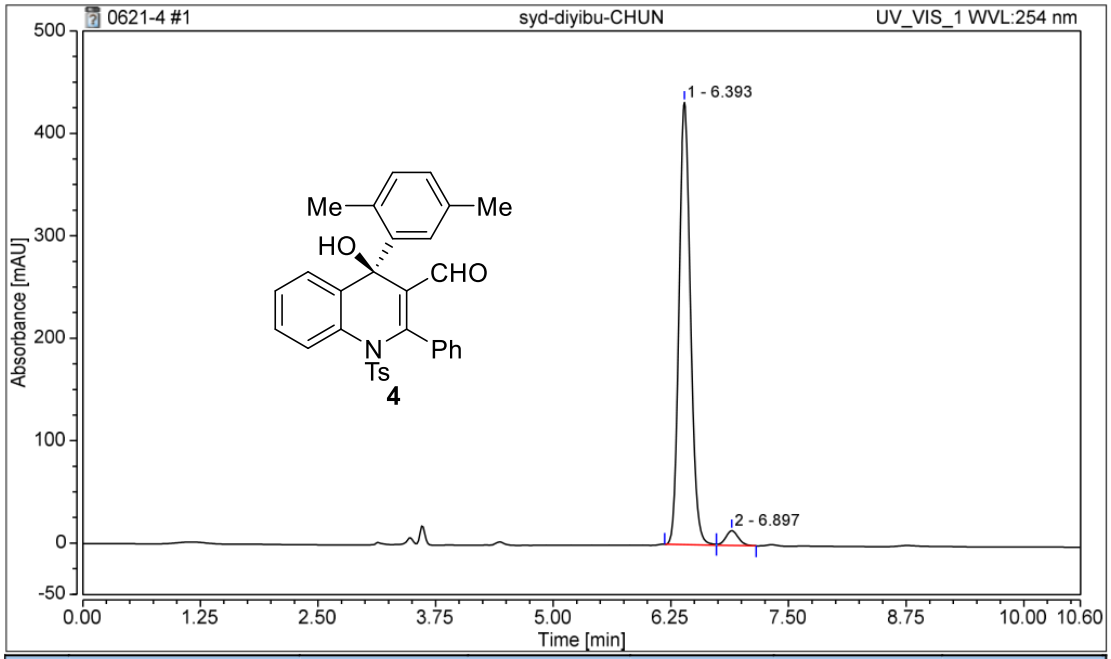

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 4.478 | 1.196 | 10.542 | 1.05 | 1.15 | 0.18 |
| 2 | 5.533 | 112.975 | 862.036 | 98.95 | 1.31 | 0.20 |
| **Total:** | | **114.171** | **872.578** | **100.00** | | |



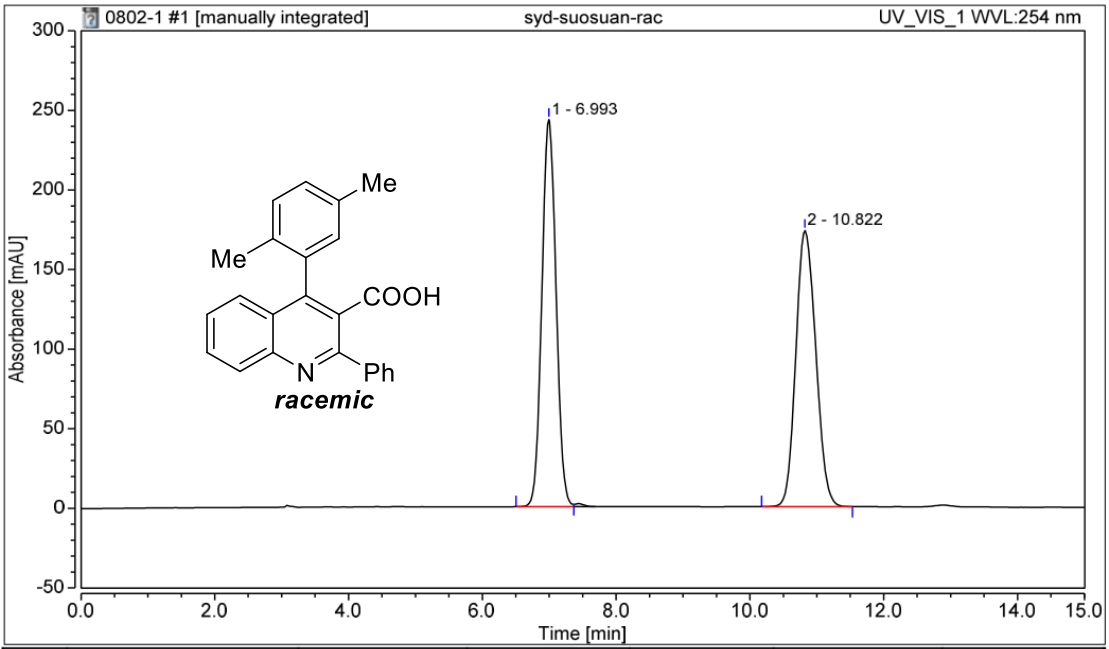

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 6.468 | 140.961 | 1041.749 | 50.16 | 1.17 | 0.21 |
| 2 | 6.948 | 140.056 | 930.102 | 49.84 | 1.17 | 0.23 |
| **Total:** | | **281.018** | **1971.850** | **100.00** | | |



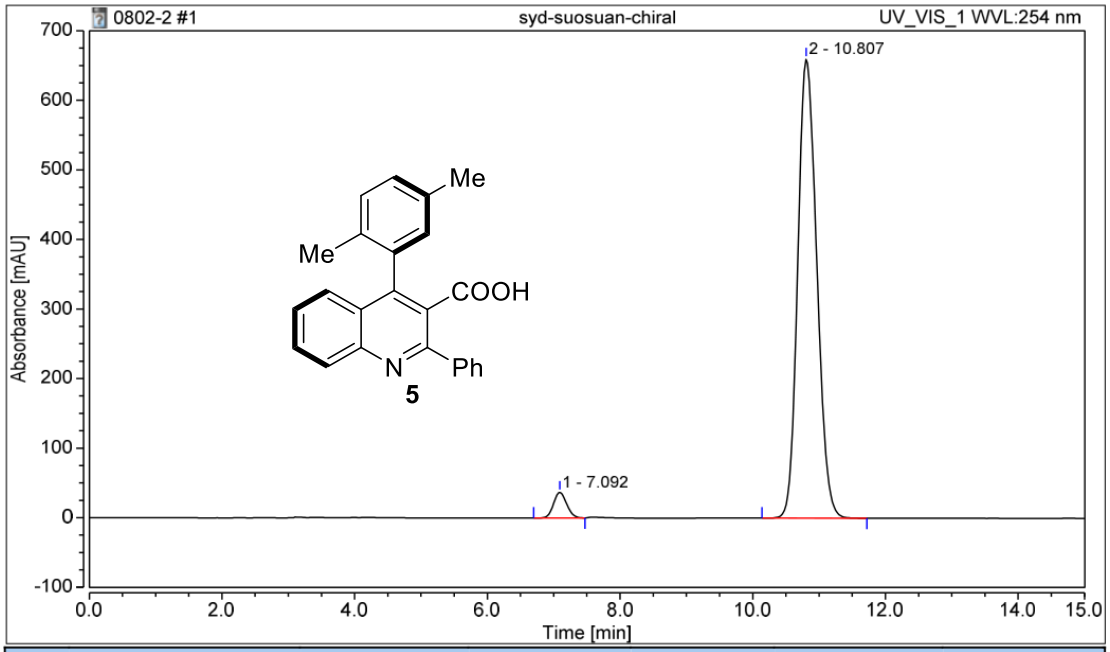

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 6.393 | 61.165 | 431.835 | 96.43 | 1.13 | 0.22 |
| 2 | 6.897 | 2.267 | 14.448 | 3.57 | n.a. | 0.25 |
| **Total:** | | **63.432** | **446.283** | **100.00** | | |



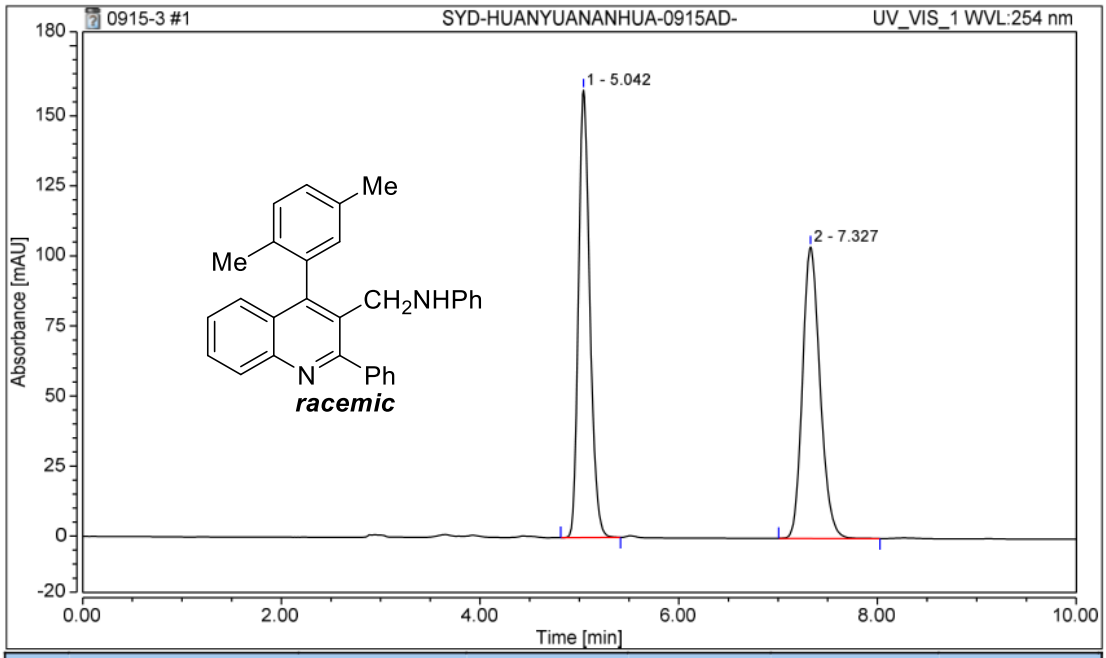

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 6.993 | 59.872 | 243.356 | 49.93 | 1.05 | 0.39 |
| 2 | 10.822 | 60.031 | 173.510 | 50.07 | 1.13 | 0.55 |
| **Total:** | | **119.903** | **416.866** | **100.00** | | |



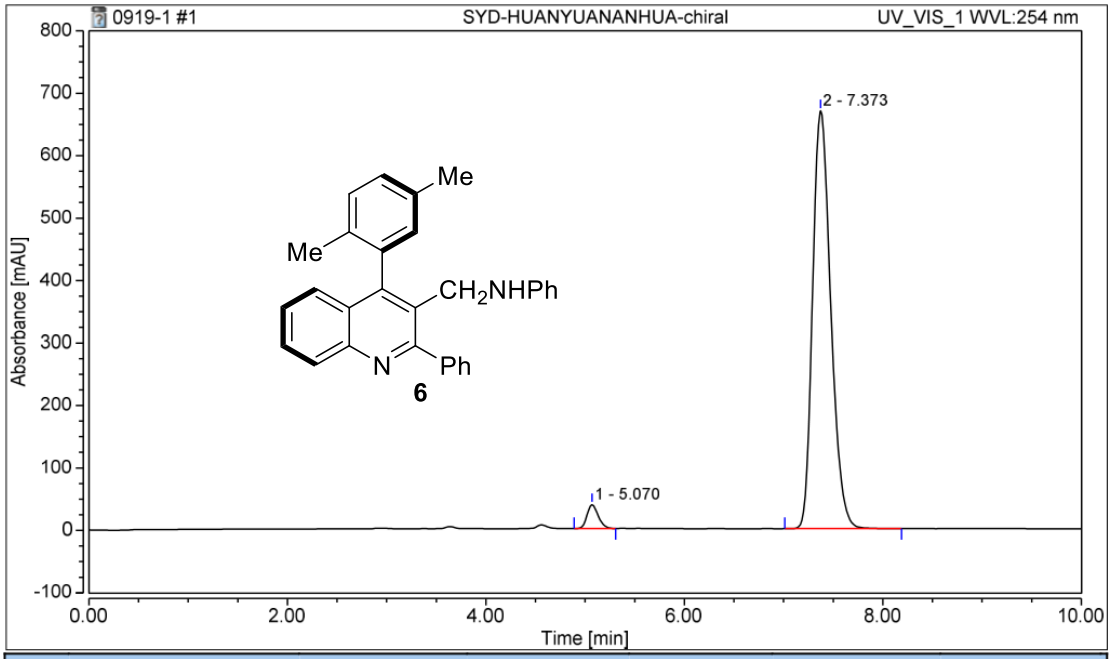

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 7.092 | 8.472 | 36.967 | 3.72 | 1.09 | 0.36 |
| 2 | 10.807 | 219.366 | 660.168 | 96.28 | 1.17 | 0.52 |
| **Total:** | | **227.838** | **697.135** | **100.00** | | |



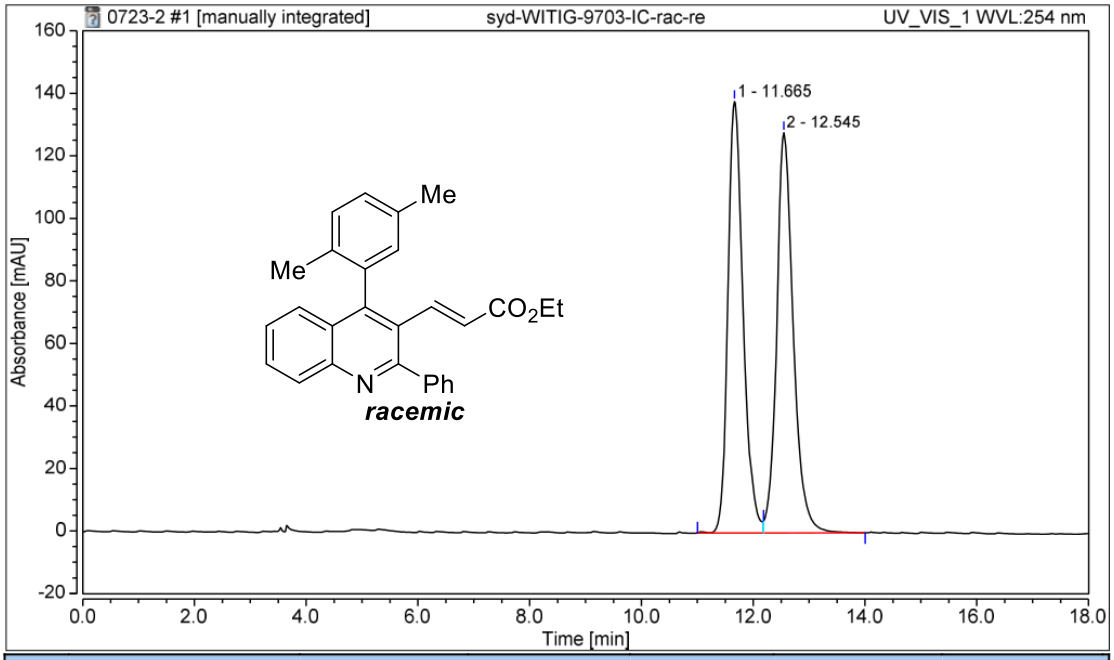

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 5.042 | 21.157 | 159.709 | 49.84 | 1.24 | 0.21 |
| 2 | 7.327 | 21.293 | 104.042 | 50.16 | 1.19 | 0.32 |
| **Total:** | | **42.450** | **263.750** | **100.00** | | |



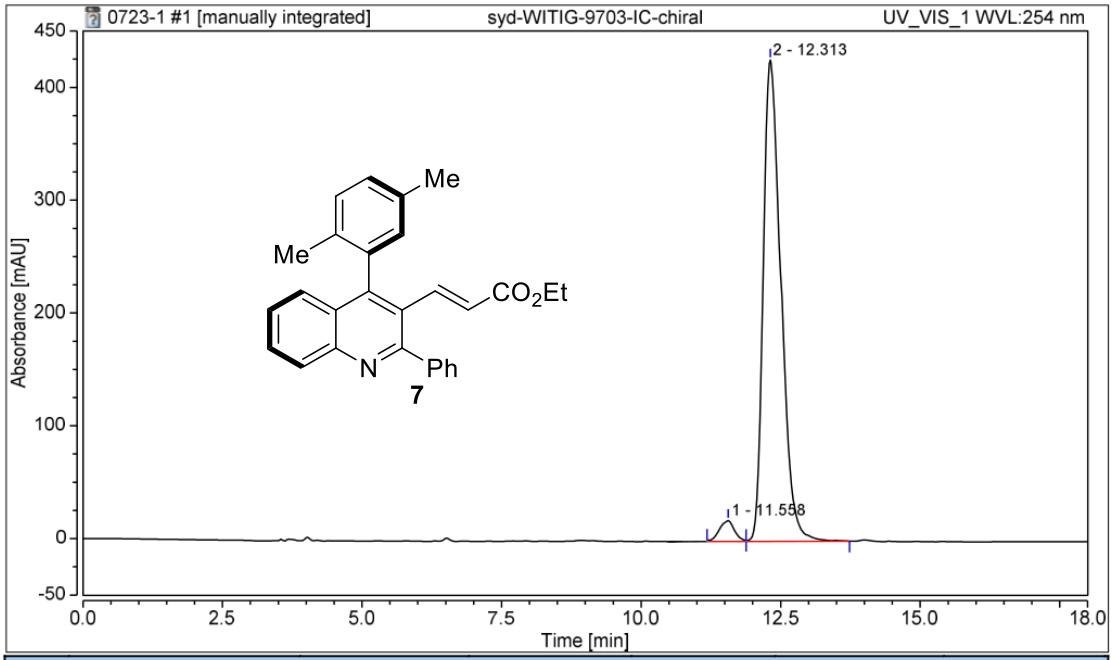

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 5.070 | 5.010 | 38.429 | 3.41 | 1.21 | 0.21 |
| 2 | 7.373 | 141.740 | 668.973 | 96.59 | 1.26 | 0.33 |
| **Total:** | | **146.750** | **707.402** | **100.00** | | |



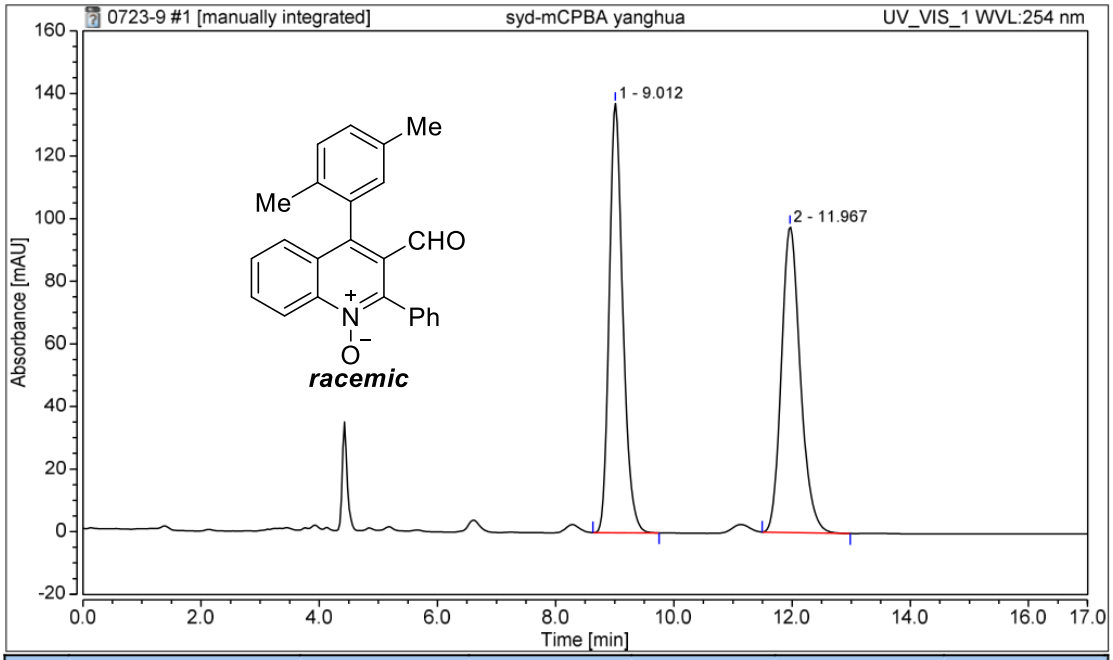

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 11.665 | 43.409 | 138.022 | 49.61 | 1.26 | 0.48 |
| 2 | 12.545 | 44.089 | 128.022 | 50.39 | 1.22 | 0.51 |
| **Total:** | | **87.498** | **266.043** | **100.00** | | |



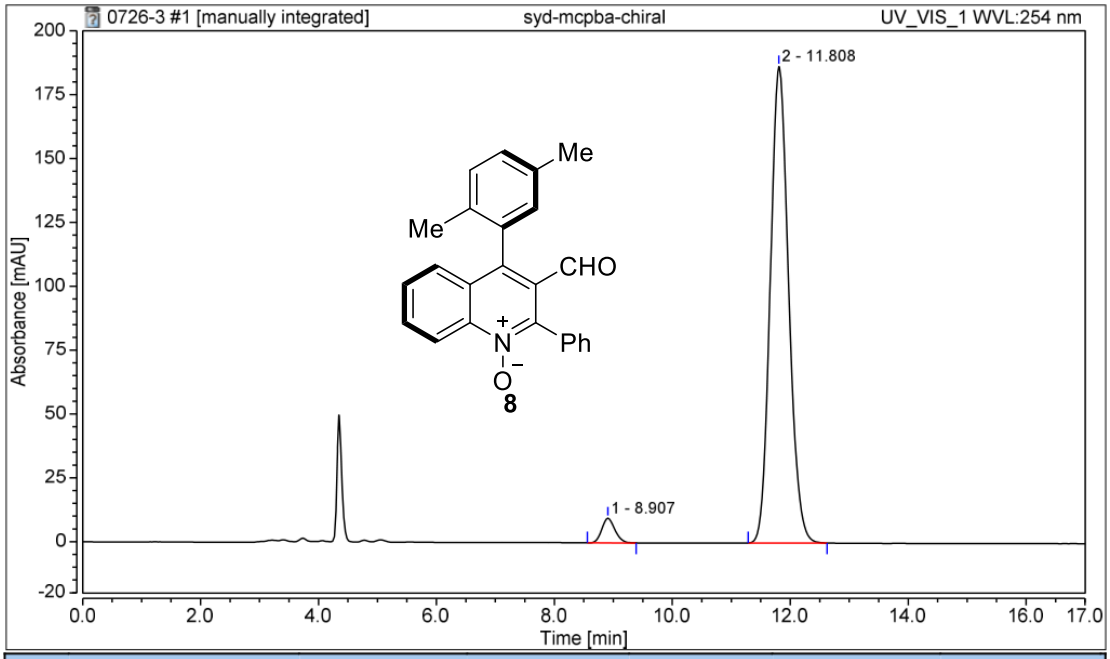

**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 11.558 | 5.813 | 18.635 | 3.56 | n.a. | 0.76 |
| 2 | 12.313 | 157.358 | 426.709 | 96.44 | 1.39 | 0.60 |
| **Total:** | | **163.171** | **445.344** | **100.00** | | |




**Integration Results**

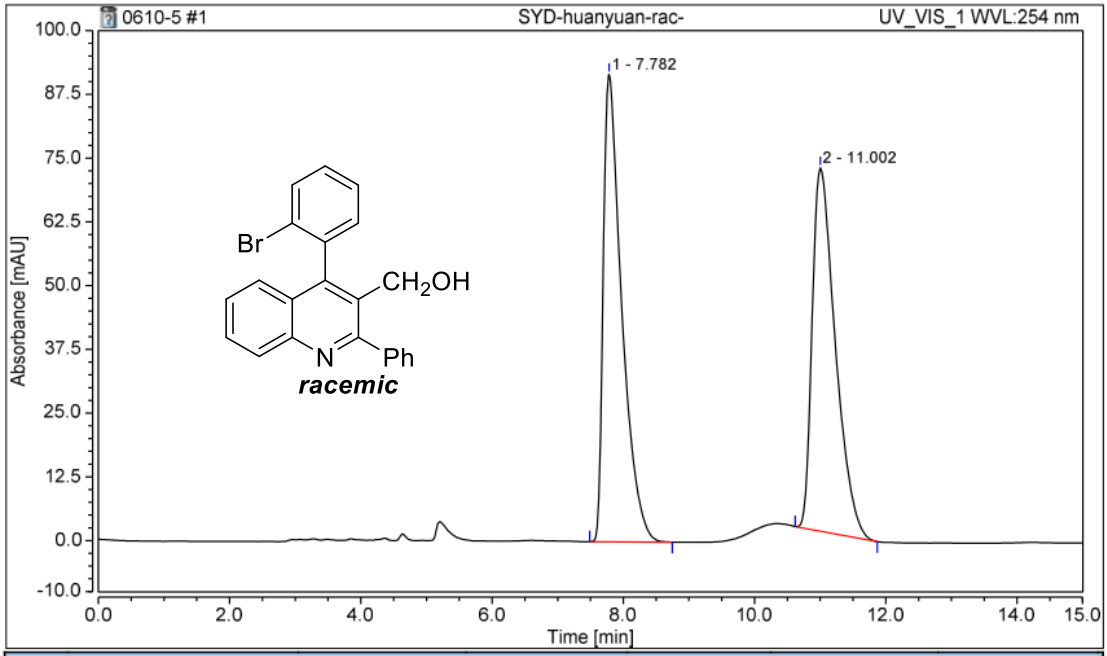
| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 9.012 | 36.565 | 137.183 | 50.07 | 1.23 | 0.41 |
| 2 | 11.967 | 36.468 | 97.746 | 49.93 | 1.21 | 0.58 |
| **Total:** | | **73.033** | **234.929** | **100.00** | | |




**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 8.907 | 2.489 | 9.641 | 3.56 | 1.15 | 0.41 |
| 2 | 11.808 | 67.338 | 186.502 | 96.44 | 1.13 | 0.57 |
| **Total:** | | **69.827** | **196.143** | **100.00** | | |

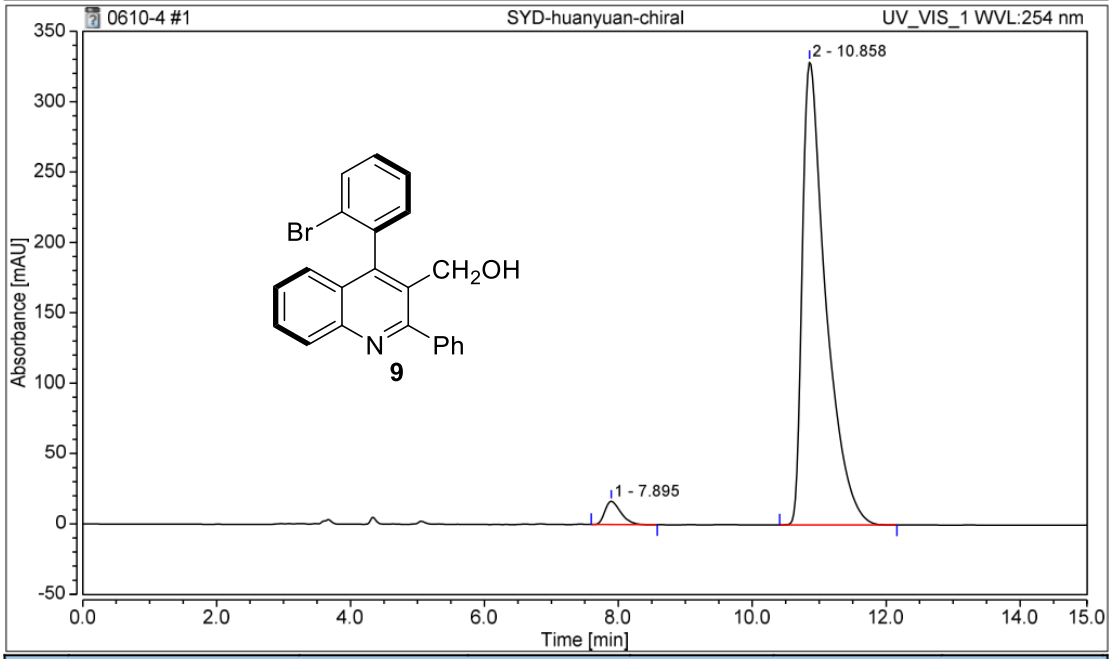
**Chromatogram**




**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 7.782 | 29.924 | 91.654 | 50.72 | 2.05 | 0.50 |
| 2 | 11.002 | 29.069 | 71.267 | 49.28 | 1.66 | 0.64 |
| **Total:** | | **58.992** | **162.921** | **100.00** | | |

**Chromatogram**




**Integration Results**

| No. | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Asymmetry (EP) | Peak Width min |
|---|---|---|---|---|---|---|
| 1 | 7.895 | 4.574 | 16.569 | 3.29 | 1.42 | 0.43 |
| 2 | 10.858 | 134.299 | 329.204 | 96.71 | 2.04 | 0.59 |
| **Total:** | | **138.872** | **345.773** | **100.00** | | |

## X-ray Crystallographic Information

The absolute configuration of compound **9** was assigned to be (a*S*) by the single crystal X-ray analysis. The crystal data of compound **9** have been deposited in CCDC with number 2021435.

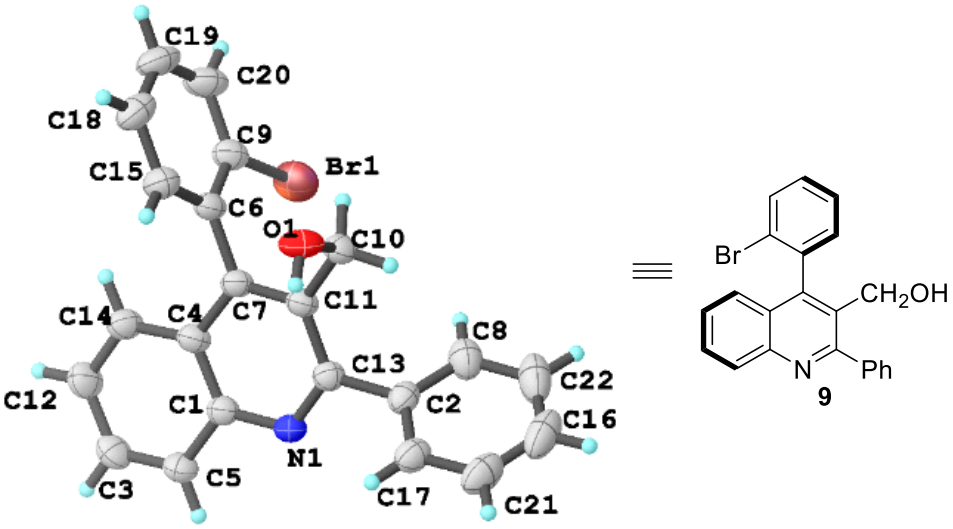



**Table S2. Crystal data and structure refinement for NDJ-HZ-300K.**

| | |
|---|---|
| Identification code | NDJ-HZ-300K |
| Empirical formula | $C_{22}H_{16}BrNO$ |
| Formula weight | 390.27 |
| Temperature/K | 300.91(10) |
| Crystal system | monoclinic |
| Space group | C2 |
| a/Å | 16.7622(2) |
| b/Å | 7.97140(10) |
| c/Å | 13.42690(10) |
| α/° | 90 |
| β/° | 100.2810(10) |
| γ/° | 90 |
| Volume/Å$^3$ | 1765.27(3) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.468 |
| μ/mm$^{-1}$ | 3.232 |
| F(000) | 792.0 |
| Crystal size/mm$^3$ | ? × ? × ? |
| Radiation | Cu Kα (λ = 1.54184) |
| 2Θ range for data collection/° | 6.69 to 154.394 |
| Index ranges | -14 ≤ h ≤ 20, -9 ≤ k ≤ 9, -16 ≤ l ≤ 16 |

| | |
|---|---|
| Reflections collected | 9327 |
| Independent reflections | 3420 [$R_{int}$ = 0.0231, $R_{sigma}$ = 0.0242] |
| Data/restraints/parameters | 3420/1/228 |
| Goodness-of-fit on $F^2$ | 0.858 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0276, $wR_2$ = 0.0934 |
| Final R indexes [all data] | $R_1$ = 0.0280, $wR_2$ = 0.0946 |
| Largest diff. peak/hole / e $Å^{-3}$ | 0.23/-0.60 |
| Flack parameter | -0.04(2) |

**Table S3. Fractional Atomic Coordinates (×$10^4$) and Equivalent Isotropic Displacement Parameters (Å²×$10^3$) for NDJ-HZ-300K. $U_{eq}$ is defined as 1/3 of of the trace of the orthogonalised $U_{IJ}$ tensor.**

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| Br1 | 8459.8(2) | 2191.9(6) | 1880.5(3) | 63.71(16) |
| O1 | 8798.2(14) | 7822(3) | 3865.0(17) | 49.7(5) |
| N1 | 6925.1(13) | 4180(3) | 4505.9(16) | 36.9(5) |
| C1 | 6455.1(15) | 4245(4) | 3566.7(19) | 37.0(5) |
| C2 | 8194.1(16) | 4438(4) | 5636.7(19) | 38.9(6) |
| C3 | 5130.6(16) | 3835(5) | 2543(2) | 49.1(7) |
| C4 | 6763.1(16) | 4700(4) | 2688(2) | 37.3(5) |
| C5 | 5618.4(16) | 3829(4) | 3473(2) | 43.2(6) |
| C6 | 7955.9(14) | 5613(4) | 1914.7(18) | 37.8(5) |
| C7 | 7598.4(14) | 5166(3) | 2820.4(18) | 35.6(5) |
| C8 | 8892.2(19) | 3444(5) | 5783(3) | 54.7(7) |
| C9 | 8352.7(16) | 4442(4) | 1415(2) | 43.5(6) |
| C10 | 8883.0(15) | 6050(4) | 3948(2) | 41.1(6) |
| C11 | 8054.3(14) | 5218(3) | 3776.7(18) | 35.5(5) |
| C12 | 5435.9(18) | 4278(5) | 1673(2) | 51.7(7) |
| C13 | 7698.6(16) | 4627(3) | 4601.9(19) | 36.1(5) |
| C14 | 6241.5(18) | 4696(4) | 1743(2) | 44.2(6) |
| C15 | 7900.0(17) | 7259(6) | 1534(2) | 48.3(6) |
| C16 | 9357(2) | 3302(6) | 6745(3) | 69.2(11) |
| C17 | 7969.0(18) | 5245(4) | 6454(2) | 47.6(6) |
| C18 | 8230(2) | 7675(5) | 695(2) | 56.3(8) |
| C19 | 8633(2) | 6499(5) | 224(2) | 58.8(8) |
| C20 | 8698(2) | 4867(6) | 580(2) | 57.4(8) |
| C21 | 8448(3) | 5104(6) | 7412(2) | 63.8(10) |
| C22 | 9145(3) | 4142(6) | 7541(3) | 72.4(12) |

**Table S4. Anisotropic Displacement Parameters ($Å^2×10^3$) for NDJ-HZ-300K. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.**

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| Br1 | 66.4(2) | 51.7(2) | 77.0(3) | -4.24(16) | 23.50(16) | 6.76(15) |
| O1 | 51.8(11) | 52.9(12) | 50.5(11) | -10.0(9) | 26.0(9) | -16.3(9) |
| N1 | 33.8(9) | 42.5(12) | 36.3(10) | 3.0(9) | 11.5(8) | -1.2(9) |
| C1 | 34.7(11) | 41.1(13) | 36.5(11) | -0.8(9) | 9.6(9) | -0.7(10) |
| C2 | 40.5(12) | 41.0(15) | 34.3(11) | 4.7(10) | 4.3(9) | -5.8(10) |
| C3 | 32.2(11) | 59.6(18) | 54.8(15) | -0.5(13) | 5.7(11) | -5.7(11) |
| C4 | 32.0(11) | 44.2(14) | 37.1(11) | -5.1(10) | 9.8(9) | -2.9(10) |
| C5 | 34.8(11) | 52.4(16) | 44.2(13) | 3.4(11) | 11.9(10) | -4.1(11) |
| C6 | 29.8(10) | 51.1(14) | 33.5(10) | -3.1(10) | 8.6(8) | -3.7(10) |
| C7 | 33.9(10) | 41.1(13) | 33.9(10) | -1.9(9) | 11.3(8) | -1.4(9) |
| C8 | 49.4(15) | 53.5(17) | 58.3(17) | 7.3(13) | 1.6(13) | 4.4(13) |
| C9 | 38.7(11) | 53.5(16) | 39.8(12) | -6.2(11) | 11.0(10) | -3.1(10) |
| C10 | 32.3(11) | 52.8(15) | 39.2(12) | -0.5(11) | 8.8(9) | -4.0(11) |
| C11 | 30.7(10) | 41.3(13) | 35.8(11) | -2.3(9) | 9.7(8) | -1.7(9) |
| C12 | 37.9(12) | 72(2) | 43.1(14) | -7.9(14) | 0.4(11) | -4.3(13) |
| C13 | 36.0(11) | 39.0(13) | 33.9(11) | -2.2(9) | 7.9(9) | -2.4(9) |
| C14 | 40.6(12) | 58.2(18) | 35.1(12) | -4.6(11) | 10.1(9) | -5.3(12) |
| C15 | 51.0(12) | 54.4(15) | 42.1(12) | 3.2(14) | 15.1(9) | 1.6(15) |
| C16 | 55.0(17) | 63(2) | 81(3) | 23.3(19) | -11.6(18) | 0.9(15) |
| C17 | 49.4(14) | 56.2(17) | 36.9(12) | -0.6(11) | 7.2(11) | -9.3(12) |
| C18 | 66.6(18) | 64(2) | 38.6(13) | 7.3(12) | 9.4(13) | -13.9(14) |
| C19 | 62.5(17) | 83(2) | 35.2(12) | -1.5(14) | 19.1(11) | -18.0(17) |
| C20 | 52.3(15) | 78(2) | 47.4(14) | -13.3(15) | 23.7(12) | -6.5(15) |
| C21 | 76(2) | 77(3) | 36.6(14) | -1.2(15) | 2.5(14) | -22.7(19) |
| C22 | 79(2) | 82(3) | 47.4(17) | 18.7(18) | -14.2(16) | -25(2) |

**Table S5. Bond Lengths for NDJ-HZ-300K.**

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| Br1 | C9 | 1.898(3) | C6 | C9 | 1.387(4) |
| O1 | C10 | 1.422(4) | C6 | C15 | 1.405(5) |
| N1 | C1 | 1.363(3) | C7 | C11 | 1.373(3) |
| N1 | C13 | 1.329(3) | C8 | C16 | 1.389(5) |
| C1 | C4 | 1.417(4) | C9 | C20 | 1.392(4) |
| C1 | C5 | 1.425(4) | C10 | C11 | 1.519(3) |
| C2 | C8 | 1.398(4) | C11 | C13 | 1.429(3) |
| C2 | C13 | 1.494(3) | C12 | C14 | 1.378(4) |

| | | | | | |
|---|---|---|---|---|---|
| C2 | C17 | 1.381(4) | C15 | C18 | 1.381(4) |
| C3 | C5 | 1.365(4) | C16 | C22 | 1.361(7) |
| C3 | C12 | 1.401(5) | C17 | C21 | 1.393(4) |
| C4 | C7 | 1.429(3) | C18 | C19 | 1.374(6) |
| C4 | C14 | 1.407(4) | C19 | C20 | 1.384(6) |
| C6 | C7 | 1.492(3) | C21 | C22 | 1.382(7) |

**Table S6. Bond Angles for NDJ-HZ-300K.**

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C13 | N1 | C1 | 118.2(2) | C6 | C9 | C20 | 122.0(3) |
| N1 | C1 | C4 | 122.9(2) | C20 | C9 | Br1 | 117.8(3) |
| N1 | C1 | C5 | 118.0(2) | O1 | C10 | C11 | 110.2(2) |
| C4 | C1 | C5 | 119.0(2) | C7 | C11 | C10 | 119.8(2) |
| C8 | C2 | C13 | 120.1(3) | C7 | C11 | C13 | 118.4(2) |
| C17 | C2 | C8 | 119.5(3) | C13 | C11 | C10 | 121.6(2) |
| C17 | C2 | C13 | 120.4(3) | C14 | C12 | C3 | 120.3(3) |
| C5 | C3 | C12 | 121.0(2) | N1 | C13 | C2 | 115.7(2) |
| C1 | C4 | C7 | 117.2(2) | N1 | C13 | C11 | 123.3(2) |
| C14 | C4 | C1 | 119.4(2) | C11 | C13 | C2 | 121.0(2) |
| C14 | C4 | C7 | 123.4(2) | C12 | C14 | C4 | 120.3(3) |
| C3 | C5 | C1 | 120.0(3) | C18 | C15 | C6 | 120.8(3) |
| C9 | C6 | C7 | 122.0(3) | C22 | C16 | C8 | 120.5(4) |
| C9 | C6 | C15 | 117.3(2) | C2 | C17 | C21 | 120.1(3) |
| C15 | C6 | C7 | 120.6(2) | C19 | C18 | C15 | 120.8(4) |
| C4 | C7 | C6 | 119.2(2) | C18 | C19 | C20 | 119.8(3) |
| C11 | C7 | C4 | 119.6(2) | C19 | C20 | C9 | 119.3(3) |
| C11 | C7 | C6 | 121.2(2) | C22 | C21 | C17 | 119.7(4) |
| C16 | C8 | C2 | 119.6(3) | C16 | C22 | C21 | 120.6(3) |
| C6 | C9 | Br1 | 120.2(2) | | | | |

**Table S7. Torsion Angles for NDJ-HZ-300K.**

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| Br1 | C9 | C20 | C19 | -179.8(2) | C7 | C11 | C13 | N1 | -6.7(4) |
| O1 | C10 | C11 | C7 | 72.4(3) | C7 | C11 | C13 | C2 | 171.8(2) |
| O1 | C10 | C11 | C13 | -101.4(3) | C8 | C2 | C13 | N1 | 122.8(3) |
| N1 | C1 | C4 | C7 | -2.5(4) | C8 | C2 | C13 | C11 | -55.8(4) |
| N1 | C1 | C4 | C14 | 178.4(3) | C8 | C2 | C17 | C21 | 1.7(5) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| N1 | C1 | C5 | C3 | -178.2(3) | C8 | C16 | C22 | C21 | 2.3(7) |
| C1 | N1 | C13 | C2 | -176.7(3) | C9 | C6 | C7 | C4 | -93.9(3) |
| C1 | N1 | C13 | C11 | 1.9(4) | C9 | C6 | C7 | C11 | 87.1(3) |
| C1 | C4 | C7 | C6 | 178.5(3) | C9 | C6 | C15 | C18 | 0.0(4) |
| C1 | C4 | C7 | C11 | -2.4(4) | C10 | C11 | C13 | N1 | 167.2(3) |
| C1 | C4 | C14 | C12 | 0.9(5) | C10 | C11 | C13 | C2 | -14.3(4) |
| C2 | C8 | C16 | C22 | -1.0(6) | C12 | C3 | C5 | C1 | -1.3(5) |
| C2 | C17 | C21 | C22 | -0.5(5) | C13 | N1 | C1 | C4 | 2.7(4) |
| C3 | C12 | C14 | C4 | -0.7(6) | C13 | N1 | C1 | C5 | -177.5(3) |
| C4 | C1 | C5 | C3 | 1.5(5) | C13 | C2 | C8 | C16 | 178.8(3) |
| C4 | C7 | C11 | C10 | -167.3(3) | C13 | C2 | C17 | C21 | -178.0(3) |
| C4 | C7 | C11 | C13 | 6.7(4) | C14 | C4 | C7 | C6 | -2.4(4) |
| C5 | C1 | C4 | C7 | 177.8(3) | C14 | C4 | C7 | C11 | 176.6(3) |
| C5 | C1 | C4 | C14 | -1.3(4) | C15 | C6 | C7 | C4 | 86.1(3) |
| C5 | C3 | C12 | C14 | 0.9(6) | C15 | C6 | C7 | C11 | -93.0(3) |
| C6 | C7 | C11 | C10 | 11.7(4) | C15 | C6 | C9 | Br1 | 179.78(19) |
| C6 | C7 | C11 | C13 | -174.3(3) | C15 | C6 | C9 | C20 | 1.2(4) |
| C6 | C9 | C20 | C19 | -1.1(5) | C15 | C18 | C19 | C20 | 1.3(5) |
| C6 | C15 | C18 | C19 | -1.2(5) | C17 | C2 | C8 | C16 | -1.0(5) |
| C7 | C4 | C14 | C12 | -178.1(3) | C17 | C2 | C13 | N1 | -57.5(4) |
| C7 | C6 | C9 | Br1 | -0.3(3) | C17 | C2 | C13 | C11 | 123.9(3) |
| C7 | C6 | C9 | C20 | -178.9(3) | C17 | C21 | C22 | C16 | -1.6(6) |
| C7 | C6 | C15 | C18 | -179.9(2) | C18 | C19 | C20 | C9 | -0.1(5) |

**Table S8. Hydrogen Atom Coordinates (Å×10$^4$) and Isotropic Displacement Parameters (Å$^2$×10$^3$) for NDJ-HZ-300K.**

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| H1 | 8498.27 | 8151.35 | 4244.21 | 74 |
| H3 | 4587.52 | 3540.12 | 2485.17 | 59 |
| H5 | 5404.6 | 3553.85 | 4044.93 | 52 |
| H8 | 9044.54 | 2881.43 | 5240.15 | 66 |
| H10A | 9176.68 | 5760.59 | 4615.26 | 49 |
| H10B | 9191.49 | 5643.88 | 3450.82 | 49 |
| H12 | 5093.46 | 4289.24 | 1046.89 | 62 |
| H14 | 6441.42 | 4977.78 | 1161.37 | 53 |
| H15 | 7638.18 | 8076.97 | 1849.95 | 58 |
| H16 | 9816.98 | 2627.05 | 6846.42 | 83 |
| H17 | 7497.46 | 5884.26 | 6364.62 | 57 |
| H18 | 8177.77 | 8765.66 | 444.79 | 68 |
| H19 | 8861.9 | 6799.02 | -332.25 | 71 |

| | | | | |
|---|---|---|---|---|
| H20 | 8968.92 | 4062.31 | 265.55 | 69 |
| H21 | 8298.59 | 5653.61 | 7961.38 | 77 |
| H22 | 9471.25 | 4069.18 | 8176.29 | 87 |