Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Chiral Phosphoric Acid Catalyzed Atroposelective and Diastereoselective Synthesis of 9-Aryltetrahydroacridines

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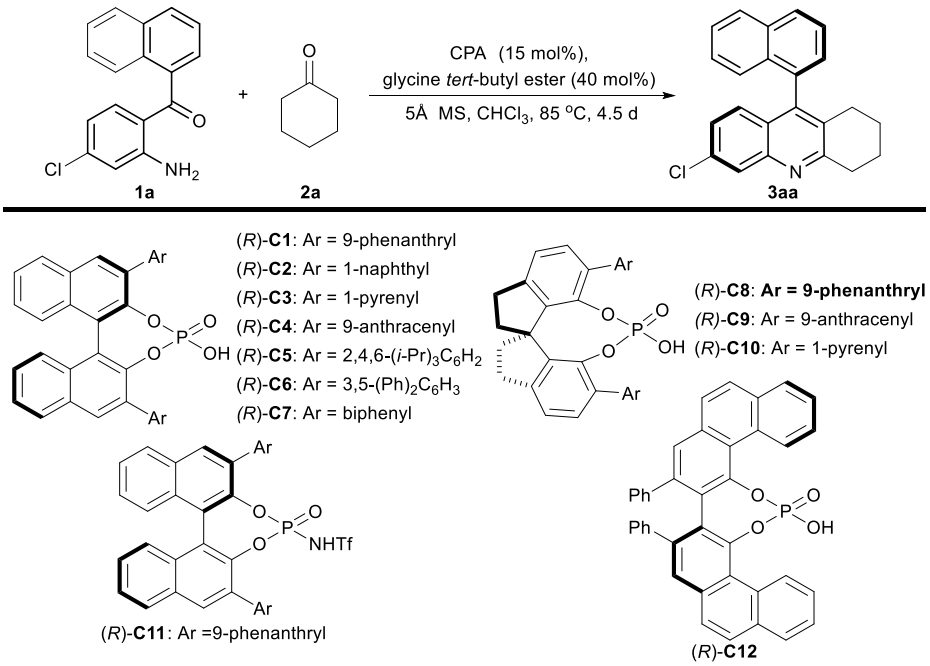
General Information

^{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.

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. Catalysts (*R*)-**C1-C7** were prepared according to the literatures.[1] Catalysts (*R*)-**C8-C12** were purchased from Daicel Chiral Technologies (China) CO., LTD. and used directly. 2-Aminoaryl ketones **1** were prepared in accordance with literature methods.[2-4]

Screening of Catalysts and Condition Optimization

Table S1. Screening of catalysts.[a]

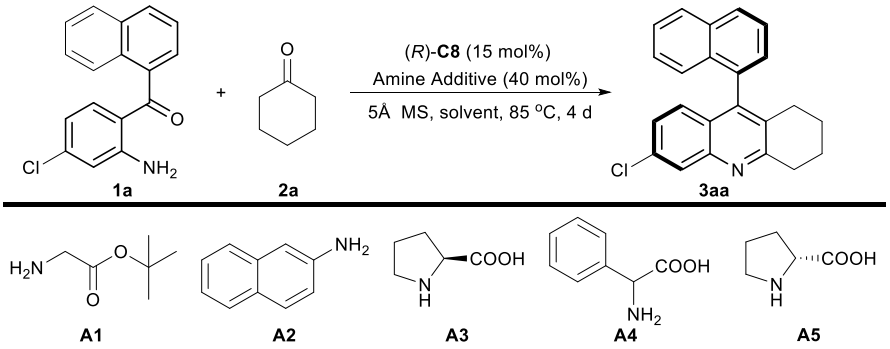


Entry	CPA	Yield[b] [%]	ee[c] [%]
1	(*R*)-**C1**	54	55

2	(*R*)-**C2**	58	23
3	(*R*)-**C3**	56	49
4	(*R*)-**C4**	60	55
5	(*R*)-**C5**	trace	15
6	(*R*)-**C6**	43	1
7	(*R*)-**C7**	50	3
8	(*R*)-**C8**	**67**	**89**
9	(*R*)-**C9**	61	82
10	(*R*)-**C10**	63	84
11	(*R*)-**C11**	trace	30
12	(*R*)-**C12**	52	24

[a] All reactions were carried out with (2-amino-4-chlorophenyl)(naphthalen-1-yl)methanone **1a** (28.1 mg, 0.10 mmol), cyclohexanone **2a** (29.4 mg, 31.0 uL, 0.30 mmol), catalyst CPA (15 mol%), glycine *tert*-butyl ester (40 mol%) and $CHCl_3$ (1.0 mL) in sealed tube for 4.5 d. [b] Isolated yield. [c] Determined by chiral stationary phase HPLC analysis.

Table S2. Screening of additives, solvents, temperatures *et al*.[a]

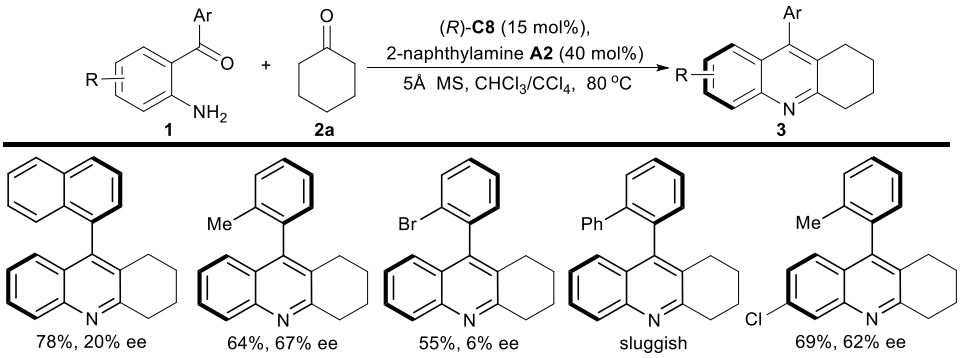


Entry	Solvent	Amine Additive	Yield[b] [%]	ee[c] [%]
1	$CHCl_3$	**A1**	67	89
2	**$CHCl_3$**	**A2**	**72**	**90**
3	$CHCl_3$	**A3**	61	87
4	$CHCl_3$	**A4**	49	86
5	$CHCl_3$	**A5**	60	86
6	Toluene	**A2**	trace	ND
7	CH_3CN	**A2**	NP	ND

8	EtOAc	**A2**	trace	ND
9	CCl_4	**A2**	81	82
10	DCE	**A2**	trace	ND
11	*n*-hexane	**A2**	80	66
12	MTBE	**A2**	73	81
13[d]	**$CHCl_3$:CCl_4=4:1**	**A2**	**77**	**92**
14[d]	$CHCl_3$:CCl_4=3:2	**A2**	79	90
15[d,e]	$CHCl_3$:CCl_4=4:1	**A2**	73	90
16[d,f]	$CHCl_3$:CCl_4=4:1	**A2**	67	87
17[d,g]	$CHCl_3$:CCl_4=4:1	**A2**	74	91
18[d,h]	$CHCl_3$:CCl_4=4:1	**A2**	trace	ND

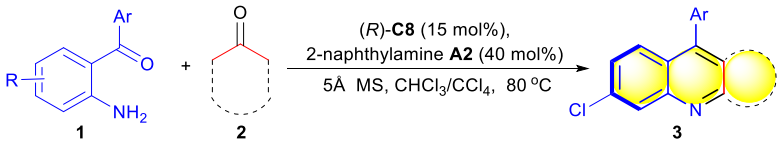
[a] Unless otherwise stated, all reactions were carried out with (2-amino-4-chlorophenyl)(naphthalen-1-yl)methanone **1a** (28.1 mg, 0.10 mmol), cyclohexanone **2a** (29.4 mg, 31.0 uL, 0.30 mmol), catalyst (*R*)-**C8** (10.0 mg, 15 mol%), amine additive (40 mol%) and solvent (1.0 mL) in sealed tube at 85 ℃ for 4.5 d. [b] Isolated yield. [c] Determined by chiral stationary phase HPLC analysis. [d] The reaction was run at 80 ℃ for 4 d . [e] The reaction was run with 0.70 mmol **2a**. [f] The reaction was run with 0.15 mmol **2a**. [g] The reaction was run with 60 mol% of **A2**. [h] The reaction was run with 100 mol% of **A2**.

Table S3. Preliminary investigations on the different combinations of substrates.[a]



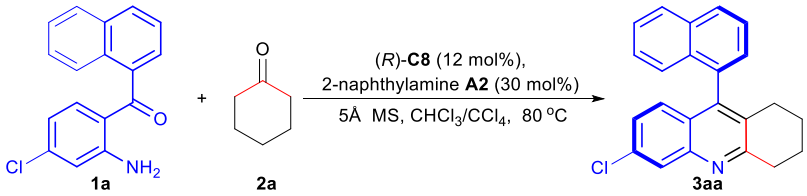
[a] All reactions were carried out with **1** (0.10 mmol), cyclohexanone **2a** (0.30 mmol), (*R*)-**C8** (15 mol%), 2-naphthylamine **A2** (40 mol%) and 5 Å molecular sieves (100 mg) in $CHCl_3$ (0.8 mL) and CCl_4 (0.2 mL) at 80 ºC in sealed tube for 4 d. Yields refer to isolated pure compounds. The ee values were determined by chiral stationary phase HPLC analysis.

General Procedure for the Atroposelective and Diastereoselective Synthesis of 9-Aryltetrahydroacridines



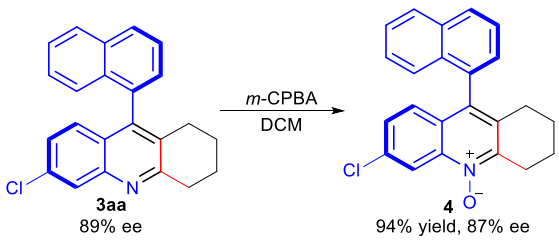
To a flame dried sealed tube equipped with a magnetic stirring bar were added powdered 5 Å molecular sieves (100 mg), chiral phosphoric acid (*R*)-**C8** (10.0 mg, 0.015 mmol), 2-naphthylamine **A2** (5.7 mg, 0.040 mmol), 2-aminoaryl ketone **1** (0.10 mmol), carbon tetrachloride (0.2 mL), anhydrous chloroform (0.8 mL) and alicyclic ketone **2** (0.30 mmol) successively. The resulting mixture was stirred at 80 °C for 4-5 d, and directly charged onto silica gel. Product **3** was isolated using petroleum ether/ethyl acetate (30:1 to 5:1) as eluent.

Procedure for Scale-up Experiment



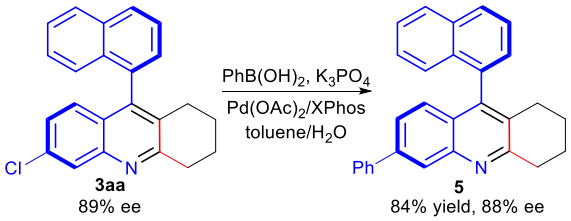
To a flame dried sealed tube equipped with a magnetic stirring bar were added powdered 5 Å molecular sieves (1.00 g), chiral phosphoric acid (*R*)-**C8** (80.1 mg, 0.12 mmol), 2-naphthylamine **A2** (43.0 mg, 0.30 mmol), **1a** (281.1 mg, 1.0 mmol), carbon tetrachloride (4.0 mL), anhydrous chloroform (6.0 mL) and **2a** (245.4 mg, 259.0 uL, 2.5 mmol) successively. After stirring at 80 °C for 4.5 d, the reaction was quenched with saturated sodium bicarbonate solution (10.0 mL). After being extracted with dichloromethane (3 × 15 mL), the organic phases were combined and washed with brine, dried over anhydrous sodium sulfate, filtered and concentrated in vacuo to give a crude residue which was purified by flash column chromatography (petroleum ether/ethylacetate = 20:1) to give **3aa** (240.2 mg, 70% yield, 89% ee) as a yellow solid.

Procedure for the Transformation of Product 3aa



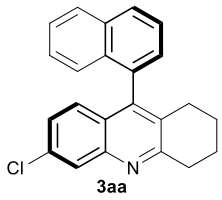
m-CPBA (37.0 mg, 0.15 mmol) was added to a solution of (*S*)-**3aa** (34.3 mg, 0.10 mmol) in dichloromethane (5.0 mL) at 0 °C. After stirring for 2 h, the reaction mixture was adjusted to pH = 10 by 1 N NaOH. After being extracted with dichloromethane (3 × 10 mL), the organic phases were combined and washed with brine, dried over anhydrous sodium sulfate, filtered and concentrated in vacuo to give a crude residue which was purified by flash column

chromatography (petroleum ether/ethylacetate = 70:30) to give **4** (33.8 mg, 94% yield) as a white solid.[4]

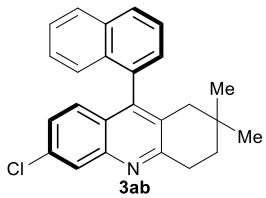


To a flame dried Schlenk flask were added **3aa** (34.3 mg, 0.10 mmol), $Pd(OAc)_2$ (0.50 mg, 0.002 mmol), XPhos (2.0 mg, 0.004 mmol), phenylboronic acid (24.4 mg, 0.20 mmol) and K_3PO_4 (85.0 mg, 0.40 mmol) successively. The flask was evacuated and backfilled with nitrogen three times, then toluene (0.80 mL) and H_2O (0.20 mL) were added. After stirring at 70 °C for 16 hours, the reaction mixture was cooled to room temperature, diluted with ethyl acetate (10 mL) and washed with aqueous NaOH (1 N, 10 mL). After being extracted with ethyl acetate (2 × 10 mL), the combined organic layers were washed with brine (10 mL), dried over anhydrous sodium sulfate, filtered and concentrated in vacuo to give a crude residue which was purified by flash column chromatography (petroleum ether/ethylacetate = 30:1–5:1) to give **5** (32.4 mg, 84% yield) as a yellow oil.[5]

Analytic Data for the Products

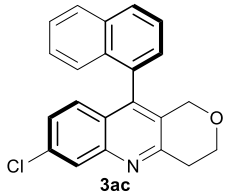


6-Chloro-9-(naphthalen-1-yl)-1,2,3,4-tetrahydroacridine **3aa** was obtained as a white solid in 77% yield (26.4 mg) and 92% ee. The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane (03:97), 1.0 mL/min, λ = 254 nm, t_r (minor) = 7.63 min, t_r (major) = 8.06 min]. m.p. 133-134 °C; $[\alpha]_D^{25}$ = +27.74 (c = 1.0, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 2.0 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.35-7.27 (m, 2H), 7.17-7.09 (m, 2H), 7.03 (d, *J* = 8.8 Hz, 1H), 3.23 (t, *J* = 6.8 Hz, 2H), 2.62-2.47 (m, 1H), 2.38-2.26 (m, 1H), 2.01-1.90 (m, 2H), 1.78-1.65 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.5, 146.7, 145.0, 134.3, 134.2, 133.7, 131.3. 130.0, 128.6, 128.5, 127.4, 127.3, 126.9, 126.7, 126.5, 126.3, 125.7, 125.6, 125.2, 34.3, 27.5, 22.8, 22.8; HRMS (ESI) calcd for $C_{23}H_{19}ClN$ $(M+H)^+$ 344.1201, found 344.1200.



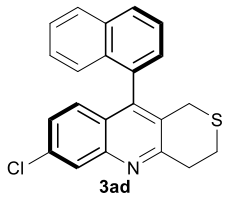
6-Chloro-2,2-dimethyl-9-(naphthalen-1-yl)-1,2,3,4-tetrahydroacridine **3ab** was obtained as a

white solid in 69% yield (25.6 mg) and 91% ee. The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak AD-H, isopropanol/hexane (03:97), 1.0 mL/min, λ = 254 nm, t_r (major) = 9.12 min, t_r (minor) = 9.93 min]. m.p. >240 °C; $[\alpha]_D^{25}$ = +16.67 (c = 1.0, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (s, 1H), 7.99 (t, *J* = 8.8 Hz, 2H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.36-7.22 (m, 2H), 7.18-7.05 (m, 2H), 6.99 (d, *J* = 8.8 Hz, 1H), 3.27 (t, *J* = 6.8 Hz, 2H), 2.34 (d, *J* = 16.8 Hz, 1H), 2.10 (d, *J* = 16.8 Hz, 1H), 1.77 (t, *J* = 6.8 Hz, 2H), 0.90 (s, 3H), 0.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 146.8, 145.5, 134.3, 134.2, 133.7, 131.4, 129.4, 128.5, 128.5, 127.4, 126.9, 126.7, 126.5, 126.3, 125.7, 125.6, 125.2, 41.2 35.6, 31.0, 29.5, 28.4, 27.4; HRMS (ESI) calcd for $C_{25}H_{23}ClN$ $(M+H)^+$ 372.1514, found 372.1513.



3ac

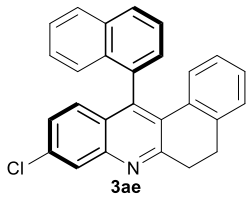
7-Chloro-10-(naphthalen-1-yl)-3,4-dihydro-1*H*-pyrano[4,3-*b*]quinoline **3ac** was obtained as a yellow solid in 70% yield (24.2 mg) and 90% ee. The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane (10:90), 1.0 mL/min, λ = 254 nm, t_r (minor) = 8.10 min, t_r (major) = 9.53 min]. m.p. 141-142 °C; $[\alpha]_D^{25}$ = +14.74 (c = 1.0, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, *J* = 2.0 Hz, 1H), 8.05-7.95 (m, 2H), 7.66-7.59 (m, 1H), 7.56-7.49 (m, 1H), 7.38-7.29 (m, 2H), 7.24 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.12 (d, *J* = 9.2 Hz, 2H), 4.56 (d, *J* = 16.0 Hz, 1H), 4.31 (d, *J* = 16.0 Hz, 1H), 4.18-4.05 (m, 2H), 3.42-3.28 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.3, 146.2, 141.5, 134.0, 132.6, 131.0, 129.9, 128.1, 127.6, 126.6, 126.4, 126.1, 126.1, 126.0, 125.8, 125.5, 124.5, 124.4, 123.9, 65.6, 64.5, 32.0; HRMS (ESI) calcd for $C_{22}H_{17}ClNO$ $(M+H)^+$ 346.0993, found 346.0992.



3ad

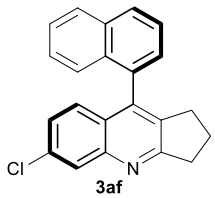
7-Chloro-10-(naphthalen-1-yl)-3,4-dihydro-1*H*-thiopyrano[4,3-*b*]quinoline **3ad** was obtained as a yellow solid in 74% yield (26.7 mg) and 89% ee. The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane (07:93), 1.0 mL/min, λ = 254 nm, t_r (minor) = 6.96 min, t_r (major) = 7.54 min]. m.p. 78-79 °C; $[\alpha]_D^{25}$ = +15.63 (c = 1.0, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, *J* = 2.0 Hz, 1H), 8.03-7.94 (m, 2H), 7.67-7.58 (m, 1H), 7.55-7.48 (m, 1H), 7.38-7.31 (m, 2H), 7.22 (dd, *J* = 8.8, 2.0 Hz,

1H), 7.16 (d, *J* = 8.8 Hz, 1H), 7.10 (d, *J* = 9.2 Hz, 1H), 3.56-3.45 (m, 3H), 3.39 (d, *J* = 5.2 Hz, 1H), 3.16-3.03 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.4, 147.0, 143.3, 135.0, 133.6, 132.9, 131.6, 129.1, 128.7, 128.6, 127.9, 127.6, 127.3, 127.2, 127.0, 126.5, 125.8, 125.5, 125.3, 34.7, 27.0, 25.8; HRMS (ESI) calcd for $C_{22}H_{17}ClNS$ $(M+H)^+$ 362.0765, found 362.0764.



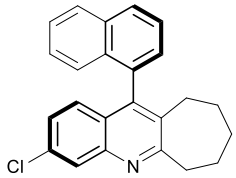
3ae

9-Chloro-12-(naphthalen-1-yl)-5,6-dihydrobenzo[*a*]acridine **3ae** was obtained as a pink solid in 80% yield (31.3 mg) and 81% ee. 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) = 8.49 min, t_r (major) = 9.03 min]. m.p. 97-98 °C; $[\alpha]_D^{25}$ = +12.44 (c = 1.0, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, *J* = 2.4 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 2H), 7.55-7.46 (m, 2H), 7.35-7.30 (m, 2H), 7.28-7.23 (m, 1H), 7.22-7.18 (m, 1H), 7.16 (dd, *J* = 9.2, 2.4 Hz, 1H), 7.08 (d, *J* = 9.2 Hz, 1H), 7.04-6.98 (m, 1H), 6.61-6.55 (m, 2H), 3.41-3.32 (m, 1H), 3.31-3.22 (m, 1H), 3.11-2.97 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.5, 146.7, 142.2, 139.6, 135.4, 135.0, 133.6, 132.5, 128.8, 128.8, 128.7, 128.4, 127.8, 127.8, 127.7, 127.7, 127.6, 127.0, 126.9, 126.8, 126.4, 126.0, 126.0, 125.8, 34.8, 29.3; HRMS (ESI) calcd for $C_{27}H_{19}ClN$ $(M+H)^+$ 392.1201, found 392.1199.



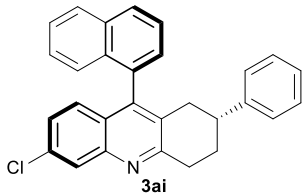
3af

6-Chloro-9-(naphthalen-1-yl)-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline **3af** was obtained as a white solid in 81% yield (26.7 mg) and 80% ee. 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 (minor) = 8.82 min, t_r (major) = 9.42 min]. m.p. 85-86 °C; $[\alpha]_D^{25}$ = +13.57 (c = 1.0, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12-8.08 (m, 1H), 7.97 (t, *J* = 8.4 Hz, 2H), 7.64-7.57 (m, 1H), 7.53-7.48 (m, 1H), 7.39-7.31 (m, 2H), 7.24-7.19 (m, 3H), 3.31-3.24 (m, 2H), 2.80-2.70 (m, 1H), 2.66-2.55 (m, 1H), 2.19-2.09 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.8, 148.3, 141.4, 135.5, 134.2, 133.9, 133.7, 131.2, 128.7, 128.6, 127.8, 127.3, 126.9, 126.6, 126.5, 126.3, 125.6, 125.5, 125.4, 35.2, 30.0, 23.2; HRMS (ESI) calcd for $C_{22}H_{17}ClN$ $(M+H)^+$ 330.1044, found 330.1044.



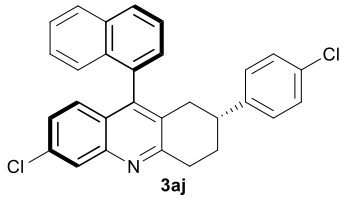
3ag

3-Chloro-11-(naphthalen-1-yl)-7,8,9,10-tetrahydro-6*H*-cyclohepta[*b*]quinoline **3ag** was obtained as a white solid in 70% yield (25.0 mg) and 80% ee. 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) =7.27 min, t_r (major) = 7.74 min]. m.p. 99-100 °C; $[\alpha]_D^{25}$ = +12.86 (c = 1.0, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 2.0 Hz, 1H), 7.96 (t, *J* = 9.2 Hz, 2H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.34-7.26 (m, 2H), 7.18-7.09 (m, 2H), 6.94 (d, *J* = 8.8 Hz, 1H), 3.37-3.25 (m, 2H), 2.60-2.49 (m, 2H), 1.95-1.75 (m, 4H), 1.56-1.39 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1, 146.3, 143.8, 135.4, 134.7, 134.1, 133.5, 132.0, 128.5, 128.4, 127.9, 127.6, 127.1, 126.6, 126.6, 126.3, 125.9, 125.7, 125.4, 40.3, 31.9, 30.9, 28.3, 27.0; HRMS (ESI) calcd for $C_{24}H_{21}ClN$ $(M+H)^+$ 358.1357, found 358.1356.



3ai

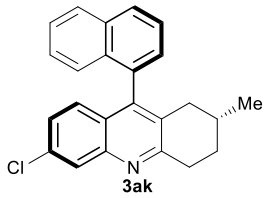
6-Chloro-9-(naphthalen-1-yl)-2-phenyl-1,2,3,4-tetrahydroacridine **3ai** was obtained as a yellow solid in 71% yield (29.8 mg), 90:10 dr and 92% ee for the major diastereoisomer. The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak AD-H, isopropanol/hexane (05:95), 1.0 mL/min, λ = 254 nm, t_r (major) = 11.15 min, t_r (minor) = 12.06 min]. m.p. 217-218 °C; $[\alpha]_D^{25}$ = +115.78 (c = 1.0, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 2.4 Hz, 1H), 7.97-7.89 (m, 2H), 7.64-7.55 (m, 1H), 7.50-7.43 (m, 1H), 7.35-7.27 (m, 2H), 7.22-7.07 (m, 7H), 7.03 (d, *J* = 8.8 Hz, 1H), 3.51-3.27 (m, 2H), 3.08-2.93 (m, 1H), 2.86-2.76 (m, 1H), 2.49-2.38 (m, 1H), 2.32-2.22 (m, 1H), 2.19-2.09 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 146.8, 145.5, 145.4, 134.6, 133.9, 133.8, 131.4, 129.4, 128.7, 128.7, 128.5, 128.5, 127.5, 127.4, 126.8, 126.8, 126.7, 126.6, 126.4, 126.3, 125.7, 125.7, 125.6, 125.1, 40.4, 35.1, 34.3, 30.1; HRMS (ESI) calcd for $C_{29}H_{23}ClN$ $(M+H)^+$ 420.1514, found 420.1512.



3aj

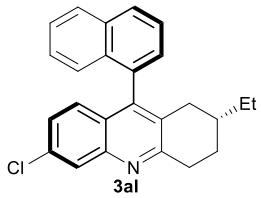
6-Chloro-2-(4-chlorophenyl)-9-(naphthalen-1-yl)-1,2,3,4-tetrahydroacridine **3aj** was obtained

as a yellow solid in 74% yield (33.5 mg), 88:12 dr and 92% ee for the major diastereoisomer. 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 (major) = 10.08 min, t_r (minor) = 10.95 min]. m.p. 214-215 °C; $[\alpha]_D^{25}$ = +128.30 (c = 1.0, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 2.4 Hz, 1H), 7.95 (t, *J* = 7.6 Hz, 2H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.37-7.28 (m, 2H), 7.21-7.13 (m, 3H), 7.10 (d, *J* = 8.4 Hz, 1H), 7.03 (t, *J* = 8.0 Hz, 3H), 3.51-3.27 (m, 2H), 3.08-2.93 (m, 1H), 2.86-2.76 (m, 1H), 2.49-2.38 (m, 1H), 2.32-2.22 (m, 1H), 2.19-2.09 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 146.9, 145.4, 143.7, 134.6, 133.7, 133.7, 132.0, 131.2, 128.9, 128.7, 128.6, 128.5, 128.1, 127.4, 127.4, 126.8, 126.7, 126.6, 126.3, 125.6, 125.5, 125.0, 39.7, 35.0, 34.0, 29.9; HRMS (ESI) calcd for $C_{29}H_{22}Cl_2N$ $(M+H)^+$ 454.1124, found 454.1123.



3ak

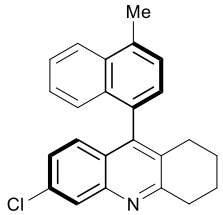
6-Chloro-2-methyl-9-(naphthalen-1-yl)-1,2,3,4-tetrahydroacridine **3ak** was obtained as a yellow solid in 68% yield (24.3 mg), 75:25 dr and 87% ee for the major diastereoisomer. The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak OD-H, isopropanol/hexane (04:96), 1.0 mL/min, λ = 254 nm, t_r (major) = 5.09 min, t_r (minor) = 5.46 min]. m.p. 117-118 °C; $[\alpha]_D^{25}$ = +68.14 (c = 1.0, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 2.0 Hz, 1H), 7.97 (t, *J* = 8.8 Hz, 2H), 7.64-7.58 (m, 1H), 7.52-7.46 (m, 1H), 7.33-7.27 (m, 2H), 7.16-7.08 (m, 2H), 7.02 (d, *J* = 8.8 Hz, 1H), 3.39-3.30 (m, 1H), 3.27-3.15 (m, 1H), 2.65-2.55 (m, 1H), 2.08-2.00 (m, 1H), 1.92-1.80 (m, 1H), 1.66-1.53 (m, 2H), 0.87 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1, 146.8, 145.0, 134.3, 134.2, 133.7, 131.4, 129.6, 128.6, 128.5, 127.4, 127.4, 126.7, 126.7, 126.5, 126.3, 125.7, 125.6, 125.3, 35.5, 33.8, 31.0, 29.0, 21.5; HRMS (ESI) calcd for $C_{24}H_{21}ClN$ $(M+H)^+$ 358.1357, found 358.1356.



3al

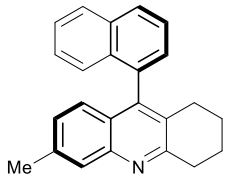
6-Chloro-2-ethyl-9-(naphthalen-1-yl)-1,2,3,4-tetrahydroacridine **3al** was obtained as a white solid in 75% yield (27.8 mg), 88:12 dr and 91% ee for the major diastereoisomer. The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak AD-H, isopropanol/hexane (03:97), 1.0 mL/min, λ = 254 nm, t_r (major) = 8.47 min, t_r (minor) = 9.70 min]. m.p. 135-136 °C; $[\alpha]_D^{25}$ = +80.71 (c = 1.0, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07

(d, *J* = 2.0 Hz, 1H), 7.99 (t, *J* = 8.4 Hz, 2H), 7.67-7.60 (m, 1H), 7.54-7.47 (m, 1H), 7.35-7.27 (m, 2H), 7.16 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.10 (d, *J* = 8.4 Hz, 1H), 7.02 (d, *J* = 8.8 Hz, 1H), 3.39-3.29 (m, 1H), 3.25-3.11 (m, 1H), 2.68-2.56 (m, 1H), 2.18-2.06 (m, 1H), 2.04-1.95 (m, 1H), 1.68-1.51 (m, 2H), 1.25-1.15 (m, 2H), 0.78 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.5, 146.8, 145.1, 134.3, 134.2, 133.7, 131.4, 129.7, 128.6, 128.5, 128.5, 127.4, 127.4, 126.7, 126.5, 126.3, 125.7, 125.6, 125.3, 35.5, 33.7, 33.5, 28.4, 28.2, 11.5; HRMS (ESI) calcd for $C_{25}H_{23}ClN$ $(M+H)^+$ 372.1514, found 372.1512.



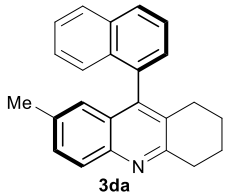
3ba

6-Chloro-9-(4-methylnaphthalen-1-yl)-1,2,3,4-tetrahydroacridine **3ba** was obtained as a white solid in 79% yield (28.2 mg) and 92% ee. 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 (minor) = 7.24 min, t_r (major) = 7.68 min]. m.p. 95-96 °C; $[\alpha]_D^{25}$ = +30.05 (c = 1.0, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19-7.94 (m, 2H), 7.58-7.40 (m, 2H), 7.35-7.26 (m, 1H), 7.21-6.98 (m, 4H), 3.33-3.14 (m, 2H), 2.80 (s, 3H), 2.60-2.25 (m, 2H), 2.01-1.61 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.4, 146.7, 145.4, 135.0, 134.2, 132.8. 132.4, 131.4, 130.2, 127.4, 127.4, 126.6, 126.4, 126.4, 126.3, 126.1, 125.9, 125.8, 124.7, 34.4, 27.5, 22.9, 22.8, 19.6; HRMS (ESI) calcd for $C_{24}H_{21}ClN$ $(M+H)^+$ 358.1357, found 358.1356.



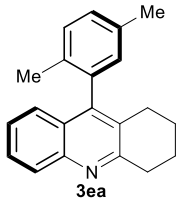
3ca

6-Methyl-9-(naphthalen-1-yl)-1,2,3,4-tetrahydroacridine **3ca** was obtained as a yellow solid in 82% yield (26.5 mg) and 90% ee. The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak AS-H, isopropanol/hexane (03:97), 1.0 mL/min, λ = 254 nm, t_r (major) = 7.23 min, t_r (minor) = 8.07 min]. m.p. 118-119 °C; $[\alpha]_D^{25}$ = +15.17 (c = 1.0, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00-7.90 (m, 2H), 7.87 (s, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.34-7.23 (m, 2H), 7.16 (d, *J* = 8.4 Hz, 1H), 7.07-6.94 (m, 2H), 3.24 (t, *J* = 6.8 Hz, 2H), 2.59-2.42 (m, 4H), 2.36-2.24 (m, 1H), 2.00-1.86 (m, 2H), 1.79-1.60 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.0, 146.5, 144.9, 138.7, 135.0, 133.6, 131.5, 128.8, 128.5, 128.2, 127.8, 127.3, 126.8, 126.5, 126.2, 125.6, 125.6, 125.4, 125.3, 34.2, 27.4, 23.0, 23.0, 21.8; HRMS (ESI) calcd for $C_{24}H_{22}N$ $(M+H)^+$ 324.1747, found 324.1745.



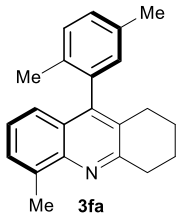
3da

7-Methyl-9-(naphthalen-1-yl)-1,2,3,4-tetrahydroacridine **3da** was obtained as a white solid in 77% yield (24.9 mg) and 70% ee. 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 (major) = 8.09 min, t_r (minor) = 8.96 min]. m.p. 179-180 °C; $[\alpha]_D^{25}$ = +9.85 (c = 1.0, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02-7.88 (m, 3H), 7.59 (t, *J* = 8.0 Hz, 1H), 7.50-7.38 (m, 2H), 7.31-7.25 (m, 2H), 7.19 (d, *J* = 8.4 Hz, 1H), 6.86 (s, 1H), 3.23 (t, *J* = 6.8 Hz, 2H), 2.55-2.44 (m, 1H), 2.35-2.25 (m, 1H), 2.21 (s, 3H), 1.99-1.89 (m, 2H), 1.76-1.61 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.0, 145.0, 144.3, 135.3, 135.1, 133.7, 131.5, 130.9, 129.6, 128.5, 128.2, 127.2, 126.9, 126.6, 126.2, 125.7, 125.5, 124.6, 34.3, 27.5, 23.1, 23.0, 21.7; HRMS (ESI) calcd for $C_{24}H_{22}N$ $(M+H)^+$ 324.1747, found 324.1746.



3ea

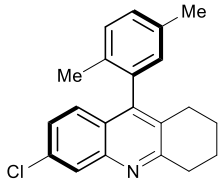
9-(2,5-Dimethylphenyl)-1,2,3,4-tetrahydroacridine **3ea** was obtained as a white solid in 73% yield (21.0 mg) and 76% ee. The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak AD-H, isopropanol/hexane (10:90), 1.0 mL/min, λ = 254 nm, t_r (minor) = 4.44 min, t_r (major) = 5.77 min]. m.p. 134-135 °C; $[\alpha]_D^{25}$ = −5.86 (c = 1.0, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8.4 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.35-7.12 (m, 4H), 6.87 (s, 1H), 3.21 (t, *J* = 6.8 Hz, 2H), 2.66-2.50 (m, 1H), 2.45-2.38 (m, 1H), 2.36 (s, 3H), 2.04-1.91 (m, 2H), 1.86 (s, 3H), 1.83-1.73 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 146.5, 146.3, 136.5, 135.6, 132.6, 130.1, 129.4, 128.7, 128.5, 128.4, 126.4, 125.5, 34.3, 27.7, 23.0, 23.0, 21.0, 19.0; HRMS (ESI) calcd for $C_{21}H_{22}N$ $(M+H)^+$ 288.1747, found 288.1746.



3fa

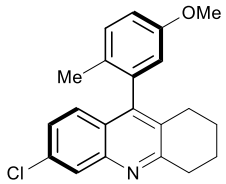
9-(2,5-Dimethylphenyl)-5-methyl-1,2,3,4-tetrahydroacridine **3fa** was obtained as a white

solid in 82% yield (24.7 mg) and 94% ee. The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak AD-H, isopropanol/hexane (03:97), 1.0 mL/min, λ = 254 nm, t_r (minor) = 3.37 min, t_r (minor) = 3.95 min]. m.p. 130-131 °C; $[\alpha]_D^{25}$ = +12.43 (c = 1.0, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, *J* = 7.2 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.20-7.13 (m, 2H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.85 (s, 1H), 3.21 (t, *J* = 6.8 Hz, 2H), 2.83 (s, 3H), 2.63-2.51 (m, 1H), 2.42-2.30 (m, 4H), 2.00-1.91 (m, 2H), 1.87-1.71 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.0, 146.4, 146.3, 137.0, 136.2, 135.5, 132.6, 130.1, 129.4, 128.6, 128.5, 128.0, 126.3, 125.1, 123.5, 34.7, 27.7, 23.2, 23.2, 21.1, 19.1, 18.2; HRMS (ESI) calcd for $C_{22}H_{24}N$ $(M+H)^+$ 302.1903, found 302.1902.



3ga

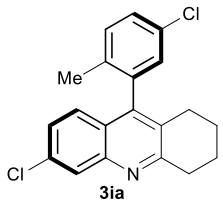
6-Chloro-9-(2,5-dimethylphenyl)-1,2,3,4-tetrahydroacridine **3ga** was obtained as a yellow solid in 78% yield (25.1 mg) and 95% ee. The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak AD-H, isopropanol/hexane (03:97), 1.0 mL/min, λ = 254 nm, t_r (minor) = 7.24 min, t_r (major) = 9.42 min]. m.p. 129-130 °C; $[\alpha]_D^{25}$ = +22.86 (c = 1.0, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 2.0 Hz, 1H), 7.28-7.21 (m, 2H), 7.20-7.16 (m, 1H), 7.14 (d, *J* = 8.8 Hz, 1H), 6.85 (s, 1H), 3.18 (t, *J* = 6.8 Hz, 2H), 2.64-2.53 (m, 1H), 2.43-2.37 (m, 1H), 2.36 (s, 3H), 2.00-1.92 (m, 2H), 1.85 (s, 3H), 1.83-1.72 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.5, 146.7, 146.5, 136.9, 135.7, 134.2, 132.5, 130.3, 129.2, 129.0, 128.8, 127.4, 126.9, 126.4, 124.9, 34.3, 27.6, 22.9, 21.0, 19.0; HRMS (ESI) calcd for $C_{21}H_{21}ClN$ $(M+H)^+$ 322.1357, found 322.1356.



3ha

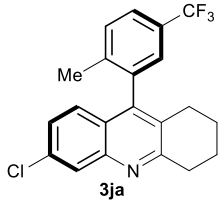
6-Chloro-9-(5-methoxy-2-methylphenyl)-1,2,3,4-tetrahydroacridine **3ha** was obtained as a yellow solid in 64% yield (21.6 mg) and 94% ee. The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak AD-H, isopropanol/hexane (10:90), 1.0 mL/min, λ = 254 nm, t_r (minor) = 5.66 min, t_r (major) = 8.51 min]. m.p. 131-132 °C; $[\alpha]_D^{25}$ = +33.33 (c = 1.0, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 2.0 Hz, 1H), 7.31-7.22 (m, 2H), 7.17 (d, *J* = 9.2 Hz, 1H), 6.92 (dd, *J* = 8.4, 2.8 Hz, 1H), 6.62 (d, *J* = 2.8 Hz, 1H),

3.79 (s, 3H), 3.18 (t, *J* = 6.8 Hz, 2H), 2.69-2.55 (m, 1H), 2.48-2.35 (m, 1H), 2.04-1.91 (m, 2H), 1.88-1.72 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.5, 158.0, 146.7, 146.1, 137.0, 134.2, 131.4, 128.8, 127.5, 127.4, 126.9, 126.5, 124.7, 114.1, 113.7, 55.3, 34.2, 27.5, 22.9, 22.8, 18.5; HRMS (ESI) calcd for $C_{21}H_{21}ClNO$ $(M+H)^+$ 338.1306, found 338.1305.



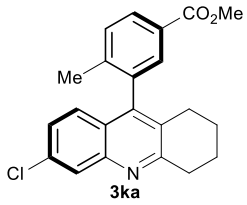
3ia

6-Chloro-9-(5-chloro-2-methylphenyl)-1,2,3,4-tetrahydroacridine **3ia** was obtained as a white solid in 80% yield (27.3 mg) and 94% ee. 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) = 7.05 min, t_r (major) = 8.42 min]. m.p. 107-108 °C; $[\alpha]_D^{25}$ = +27.75 (c = 1.0, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 2.0 Hz, 1H), 7.38-7.34 (m, 1H), 7.33-7.24 (m, 2H), 7.14-7.03 (m, 2H), 3.18 (t, *J* = 6.8 Hz, 2H), 2.65-2.53 (m, 1H), 2.42-2.30 (m, 1H), 2.01-1.93 (m, 2H), 1.86 (s, 3H), 1.85-1.74 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.6, 146.7, 144.7, 137.8, 134.4, 134.3, 132.0, 131.8, 128.8, 128.6, 128.4, 127.6, 126.8, 126.4, 124.4, 34.2, 27.6, 22.8, 18.9; HRMS (ESI) calcd for $C_{20}H_{18}Cl_2N$ $(M+H)^+$ 342.0811, found 342.0810.



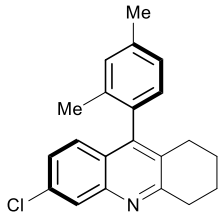
3ja

6-Chloro-9-(2-methyl-5-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroacridine **3ja** was obtained as a yellow solid in 76% yield (28.5 mg) and 91% ee. 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 (major) = 4.63 min, t_r (minor) = 5.04 min]. m.p. 149-150 °C; $[\alpha]_D^{25}$ = −15.57 (c = 1.0, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, *J* = 2.0 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.35 (s, 1H), 7.28 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.04 (d, *J* = 9.2 Hz, 1H), 3.20 (t, *J* = 6.8 Hz, 2H), 2.62-2.50 (m, 1H), 2.41-2.28 (m, 1H), 2.04-1.93 (m, 5H), 1.90-1.72 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.7, 146.7, 144.5, 140.2, 136.8, 134.5, 131.0, 129.0 (q, *J* = 32.4 Hz), 128.8, 127.7, 126.9, 126.2, 125.7 (q, *J* = 3.7 Hz), 125.2 (q, *J* = 3.7 Hz), 124.3, 124.1 (q, *J* = 270.4 Hz), 34.2, 27.6, 22.8, 22.7, 19.5; HRMS (ESI) calcd for $C_{21}H_{18}ClF_3N$ $(M+H)^+$ 376.1074, found 376.1073.



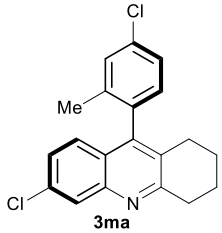
3ka

Methyl 3-(6-chloro-1,2,3,4-tetrahydroacridin-9-yl)-4-methylbenzoate **3ka** was obtained as a yellow solid in 62% yield (22.6 mg) and 95% ee. The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak AD-H, isopropanol/hexane (15:85), 1.0 mL/min, λ = 254 nm, t_r (minor) = 7.69 min, t_r (major) = 13.74 min]. m.p. 162-163 °C; $[\alpha]_D^{25}$ = +35.16 (c = 1.0, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11-8.00 (m, 2H), 7.77 (d, *J* = 2.0 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.26 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.06 (d, *J* = 8.8 Hz, 1H), 3.90 (s, 3H), 3.20 (t, *J* = 6.8 Hz, 2H), 2.65-2.51 (m, 1H), 2.41-2.29 (m, 1H), 2.04-1.93 (m, 5H), 1.90-1.72 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 160.6, 146.7, 145.0, 141.5, 136.4, 134.4, 130.7, 130.1, 129.5, 128.9, 128.5, 127.6, 126.8, 126.4, 124.5, 52.2, 34.2, 27.6, 22.8, 22.8, 19.7; HRMS (ESI) calcd for $C_{22}H_{21}ClNO_2$ $(M+H)^+$ 366.1255, found 366.1254.



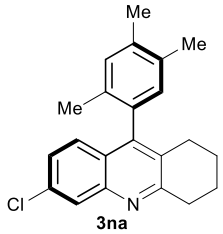
3la

6-Chloro-9-(2,4-dimethylphenyl)-1,2,3,4-tetrahydroacridine **3la** was obtained as a yellow solid in 66% yield (21.2 mg) and 94% ee. The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane (07:93), 1.0 mL/min, λ = 254 nm, t_r (minor) = 5.51 min, t_r (major) = 6.04 min]. m.p. 95-96 °C; $[\alpha]_D^{25}$ = +20.14 (c = 1.0, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 2.0 Hz, 1H), 7.22 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.18 (s, 1H), 7.14-7.10 (m, 2H), 6.92 (d, *J* = 7.6 Hz, 1H), 3.18 (t, *J* = 6.8 Hz, 2H), 2.64-2.53 (m, 1H), 2.42 (s, 3H), 2.41-2.34 (m, 1H), 2.00-1.92 (m, 2H), 1.86 (s, 3H), 1.84-1.72 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.5, 146.7, 146.4, 137.9, 135.4, 134.2, 133.0, 131.1, 129.1, 128.7, 127.4, 127.0, 126.9, 126.4, 125.1, 34.3, 27.6, 22.9, 21.3, 19.4; HRMS (ESI) calcd for $C_{21}H_{21}ClN$ $(M+H)^+$ 322.1357, found 322.1356.



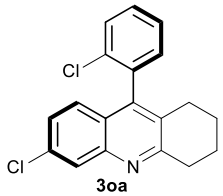
3ma

6-Chloro-9-(4-chloro-2-methylphenyl)-1,2,3,4-tetrahydroacridine **3ma** was obtained as a yellow solid in 70% yield (23.9 mg) and 94% ee. The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak AD-H, isopropanol/hexane (03:97), 1.0 mL/min, λ = 254 nm, t_r (minor) = 4.82 min, t_r (major) = 6.70 min]. m.p. 115-116 °C; $[\alpha]_D^{25}$ = +27.50 (c = 1.0, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 2.0 Hz, 1H), 7.38 (d, *J* = 2.4 Hz, 1H), 7.32 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.26 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.10 (d, *J* = 8.8 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 3.18 (t, *J* = 6.8 Hz, 2H), 2.61-2.50 (m, 1H), 2.41-2.31 (m, 1H), 2.02-1.93 (m, 2H), 1.89 (s, 3H), 1.86-1.74 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.6, 146.7, 145.0, 137.8, 134.5, 134.4, 134.0, 130.4, 130.1, 129.0, 127.6, 126.7, 126.6, 126.4, 124.6, 34.2, 27.6, 22.8, 19.4; HRMS (ESI) calcd for $C_{20}H_{18}Cl_2N$ $(M+H)^+$ 342.0811, found 342.0810.



3na

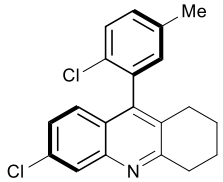
6-Chloro-9-(2,4,5-trimethylphenyl)-1,2,3,4-tetrahydroacridine **3na** was obtained as a yellow solid in 81% yield (27.2 mg) and 93% ee. The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak AD-H, isopropanol/hexane (05:95), 1.0 mL/min, λ = 254 nm, t_r (minor) = 4.58 min, t_r (major) = 6.43 min]. m.p. 129-130 °C; $[\alpha]_D^{25}$ = +33.75 (c = 1.0, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 2.0 Hz, 1H), 7.23 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.18-7.10 (m, 2H), 6.80 (s, 1H), 3.18 (t, *J* = 6.8 Hz, 2H), 2.65-2.54 (m, 1H), 2.44-2.35 (m, 1H), 2.33 (s, 3H), 2.27 (s, 3H), 2.00-1.91 (m, 2H), 1.85-1.71 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.5, 146.7, 146.6, 136.5, 134.3, 134.1, 133.3, 132.8, 131.6, 129.8, 129.0, 127.3, 127.1, 126.3, 125.1, 34.3, 27.7, 22.9, 19.6, 19.4, 18.9; HRMS (ESI) calcd for $C_{22}H_{23}ClN$ $(M+H)^+$ 336.1514, found 336.1512.



3oa

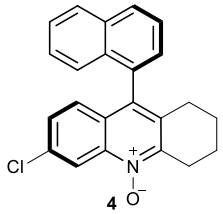
6-Chloro-9-(2-chlorophenyl)-1,2,3,4-tetrahydroacridine **3oa** was obtained as a yellow solid in 71% yield (23.2 mg) and 80% ee. The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak AD-H, isopropanol/hexane (10:90), 1.0 mL/min, λ = 254 nm, t_r (minor) = 5.61 min, t_r (major) = 8.46 min]. m.p. 139-140 °C; $[\alpha]_D^{25}$ = +13.17 (c = 1.0, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 2.0 Hz, 1H), 7.59-7.53 (m, 1H),

7.47-7.38 (m, 2H), 7.26 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.19-7.14 (m, 1H), 7.11 (d, *J* = 8.8 Hz, 1H), 3.27-3.10 (m, 2H), 2.63-2.45 (m, 2H), 2.05-1.91 (m, 2H), 1.88-1.75 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.5, 146.7, 143.7, 135.5, 134.3, 133.2, 130.6, 130.0, 129.7, 129.3, 127.5, 127.2, 126.7, 126.5, 124.5, 34.2, 27.4, 22.8, 22.7; HRMS (ESI) calcd for $C_{19}H_{16}Cl_2N$ $(M+H)^+$ 328.0654, found 328.0653.



3pa

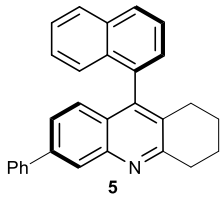
6-Chloro-9-(2-chloro-5-methylphenyl)-1,2,3,4-tetrahydroacridine **3pa** was obtained as a yellow solid in 72% yield (24.6 mg) and 86% ee. The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak AD-H, isopropanol/hexane (05:95), 1.0 mL/min, λ = 254 nm, t_r (minor) = 8.45 min, t_r (major) = 10.16 min]. m.p. 150-151 °C; $[\alpha]_D^{25}$ = +38.42 (c = 1.0, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 2.0 Hz, 1H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.31-7.20 (m, 2H), 7.13 (d, *J* = 8.8 Hz, 1H), 6.97 (d, *J* = 2.4 Hz, 1H), 3.25-3.11 (m, 2H), 2.54 (t, *J* = 6.4 Hz, 2H), 2.39 (s, 3H), 2.03-1.92 (m, 2H), 1.86-1.76 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.5, 146.6, 143.9, 137.2, 135.1, 134.3, 131.0, 130.5, 130.1, 129.6, 129.3, 127.5, 126.6, 126.6, 124.6, 34.2, 27.4, 22.8, 22.7, 20.9; HRMS (ESI) calcd for $C_{20}H_{18}Cl_2N$ $(M+H)^+$ 342.0811, found 342.0810.



4

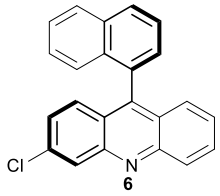
6-Chloro-9-(naphthalen-1-yl)-1,2,3,4-tetrahydroacridine 10-oxide **4** was obtained as a white solid in 94% yield (33.8 mg) and 87% ee. The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak AD-H, isopropanol/hexane (30:70), 1.0 mL/min, λ = 254 nm, t_r (minor) = 14.87 min, t_r (major) = 18.22 min]. m.p. 91-92 °C; $[\alpha]_D^{25}$ = +17.78 (c = 1.0, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.88 (d, *J* = 2.4 Hz, 1H), 8.05-7.94 (m, 2H), 7.64 (t, *J* = 7.2 Hz, 1H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.38-7.31 (m, 2H), 7.27 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.17 (d, *J* = 8.4 Hz, 1H), 7.10 (d, *J* = 8.8 Hz, 1H), 3.34 (t, *J* = 6.8 Hz, 2H), 2.59-2.47 (m, 1H), 2.36-2.25 (m, 1H), 2.01-1.90 (m, 2H), 1.75-1.60 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.3, 138.9, 135.1, 134.4, 132.7, 132.0, 130.7, 130.5, 128.0, 127.7, 127.6, 127.0, 126.6, 126.0, 125.9, 125.4, 124.6, 123.9, 117.8, 26.6, 25.7, 20.8, 20.6; HRMS (ESI) calcd for

$C_{23}H_{19}ClNO$ $(M+H)^+$ 360.1150, found 360.1149.



5

9-(Naphthalen-1-yl)-6-phenyl-1,2,3,4-tetrahydroacridine **5** was obtained as a yellow oil in 84% yield (32.4 mg) and 88% ee. The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak OD-H, isopropanol/hexane (03:97), 1.0 mL/min, λ = 254 nm, t_r (major) = 11.11 min, t_r (minor) = 12.35 min]. $[\alpha]_D^{25}$ = −41.50 (c = 1.0, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (s, 1H), 7.97 (t, *J* = 7.6 Hz, 2H), 7.71 (d, *J* = 7.6 Hz, 2H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.53-7.40 (m, 4H), 7.38-7.27 (m, 3H), 7.23-7.11 (m, 2H), 3.29 (t, *J* = 6.8 Hz, 2H), 2.64-2.50 (m, 1H), 2.41-2.29 (m, 1H), 2.03-1.90 (m, 2H), 1.81-1.64 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.55, 146.41, 145.04, 141.17, 140.38, 134.64, 133.65, 131.41, 129.68, 128.88, 128.48, 128.34, 127.63, 127.31, 126.85, 126.61, 126.37, 126.21, 125.83, 125.57, 125.35, 125.19, 34.16, 27.48, 22.89, 22.86; HRMS (ESI) calcd for $C_{29}H_{24}N$ $(M+H)^+$ 386.1903, found 386.1925.



6

3-Chloro-9-(naphthalen-1-yl)acridine **6** was obtained as a yellow solid in 34% yield (11.5 mg) and 84% ee. The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak AD-H, isopropanol/hexane (03:97), 1.0 mL/min, λ = 254 nm, t_r (major) = 6.74 min, t_r (minor) = 7.14 min]. m.p. 213-214 °C; $[\alpha]_D^{25}$ = +30.04 (c = 1.0, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38-8.24 (m, 2H), 8.10 (d, *J* = 8.4 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.79 (t, *J* = 7.6 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.56-7.47 (m, 2H), 7.47-7.31 (m, 3H), 7.30-7.19 (m, 2H), 6.99 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.3, 147.7, 145.2, 135.2, 132.5, 132.0, 131.4, 129.9, 129.7, 128.5, 128.1, 127.8, 127.4, 127.0, 126.1, 126.0, 125.8, 125.4, 125.1, 125.0, 124.9, 124.3, 123.3; HRMS (ESI) calcd for $C_{23}H_{15}ClN$ $(M+H)^+$ 340.0888, found 340.0887.

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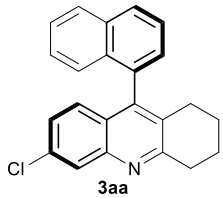
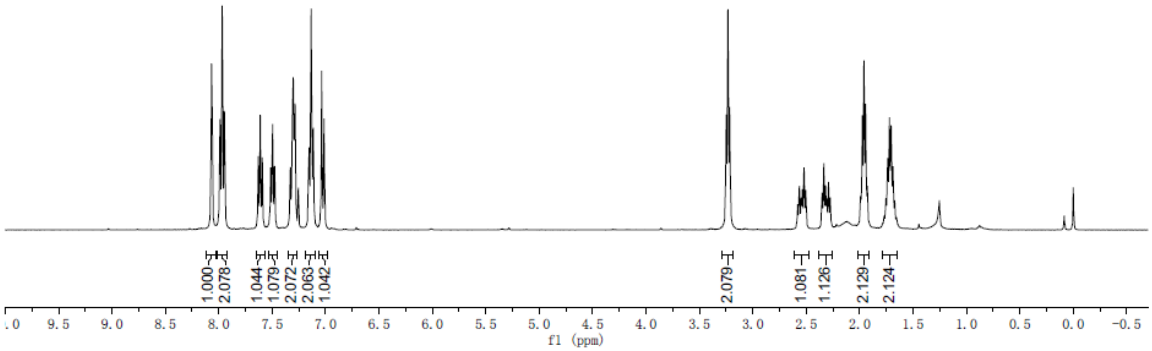
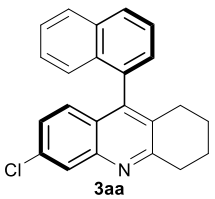
^{1}H and ^{13}C NMR Spectra



3aa

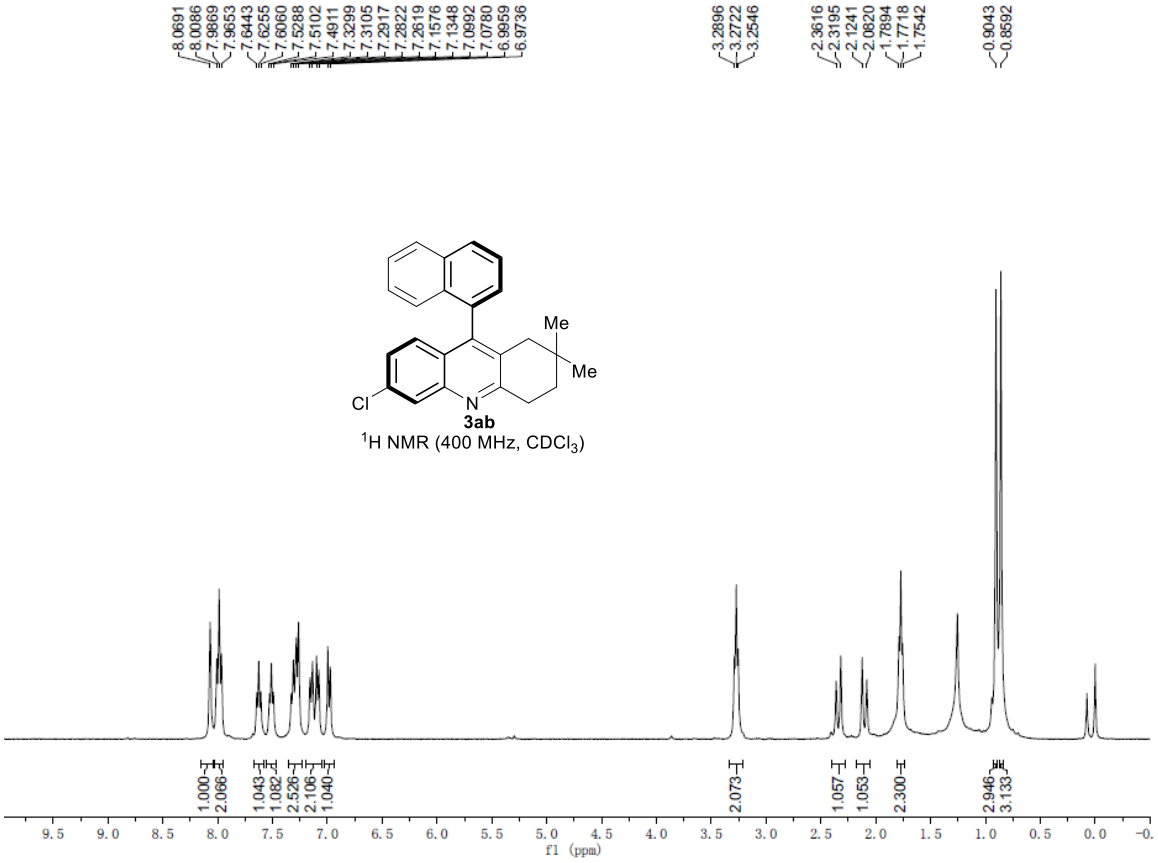
^{1}H NMR (400 MHz, $CDCl_3$)





3aa

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



3ab

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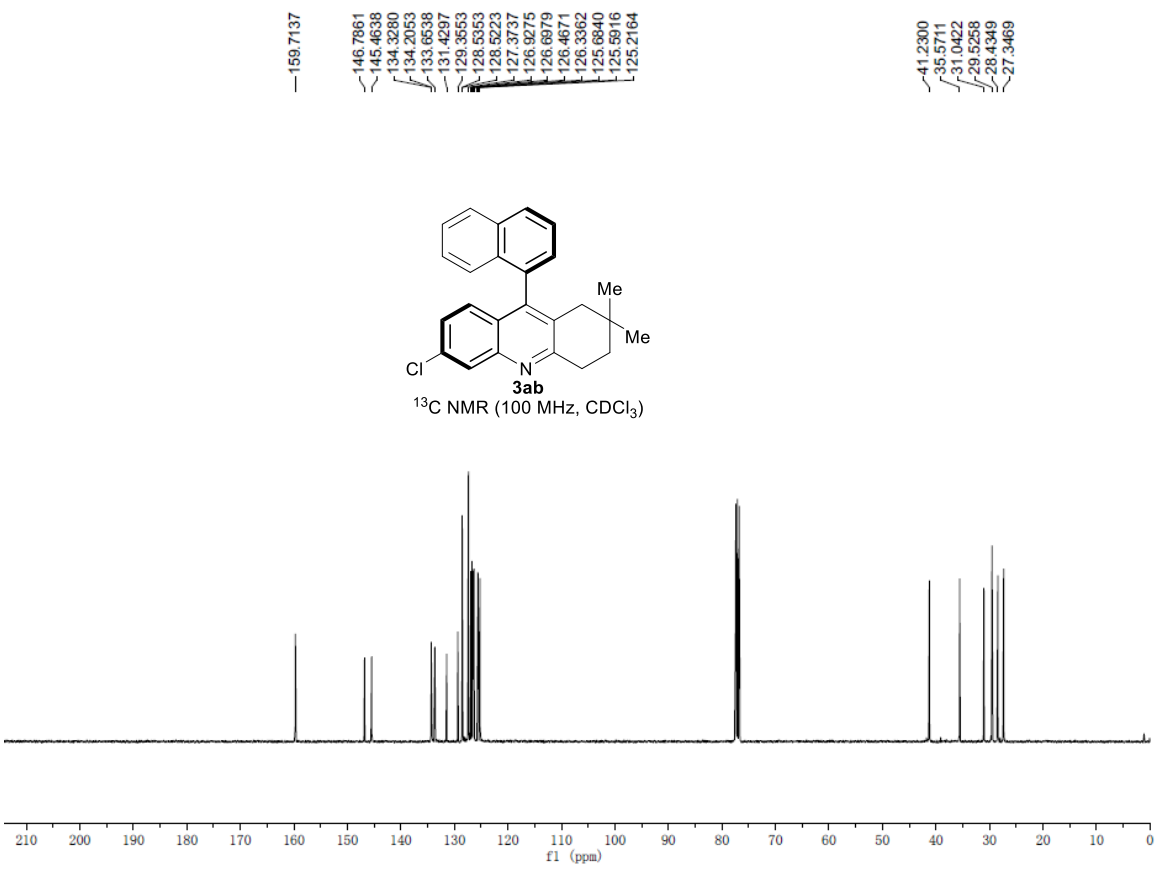
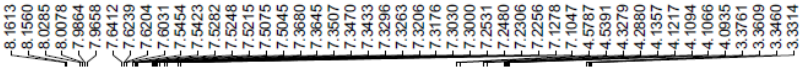
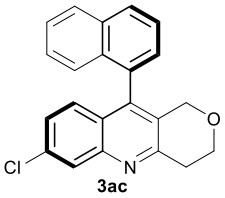


3ab

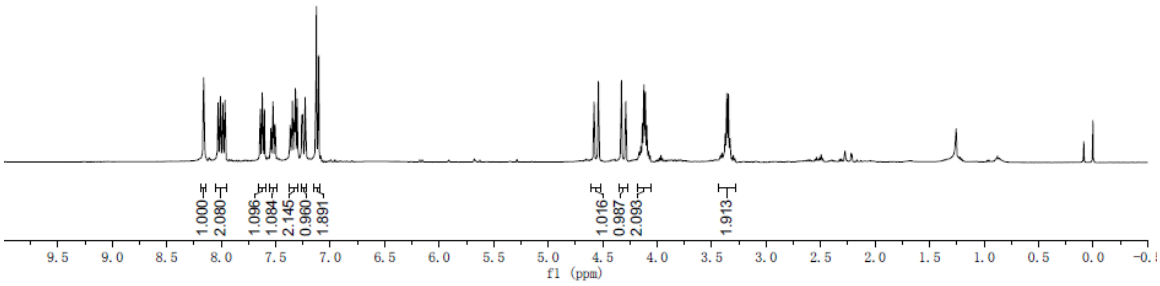
^{13}C NMR (100 MHz, $CDCl_3$)

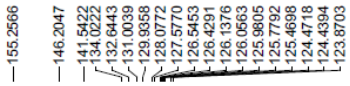


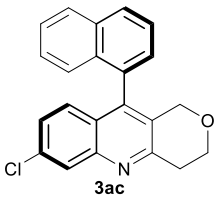


3ac

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

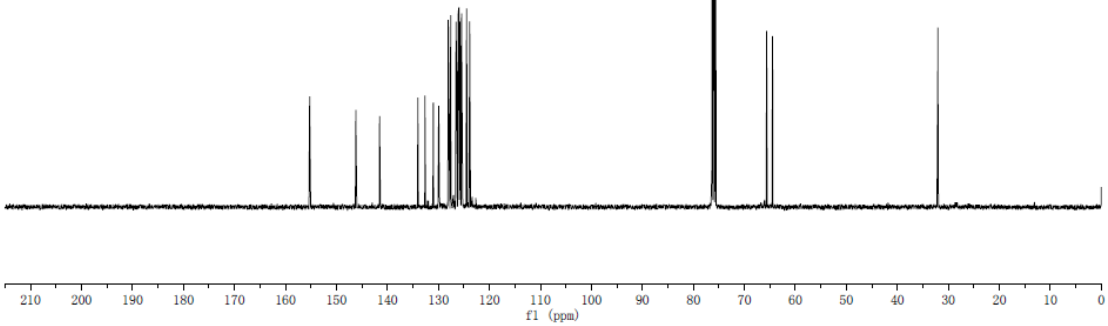


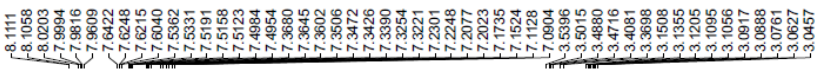


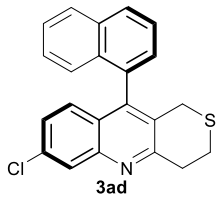


3ac

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

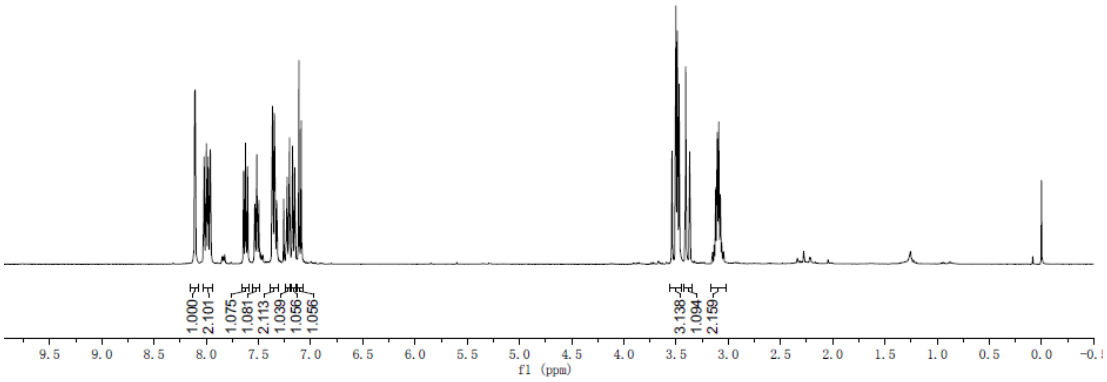


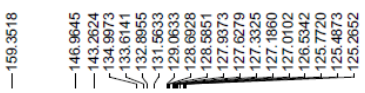


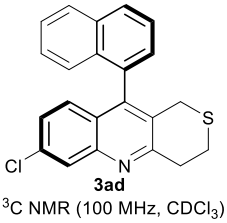


3ad

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

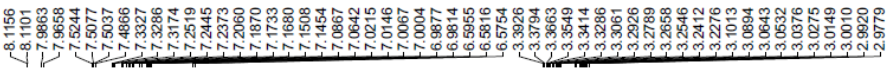


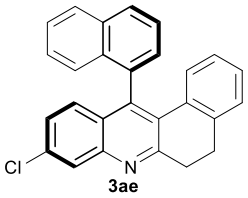




3ad

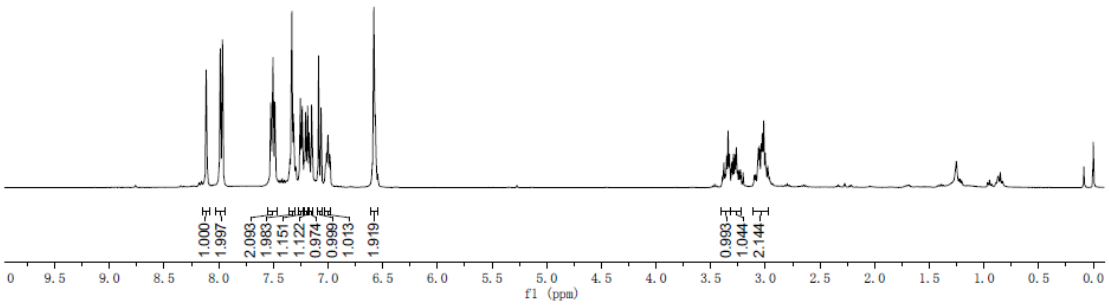
^{13}C NMR (100 MHz, $CDCl_3$)

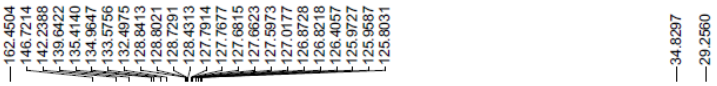


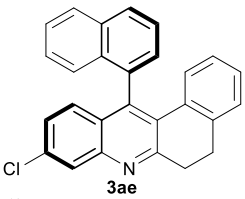


3ae

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

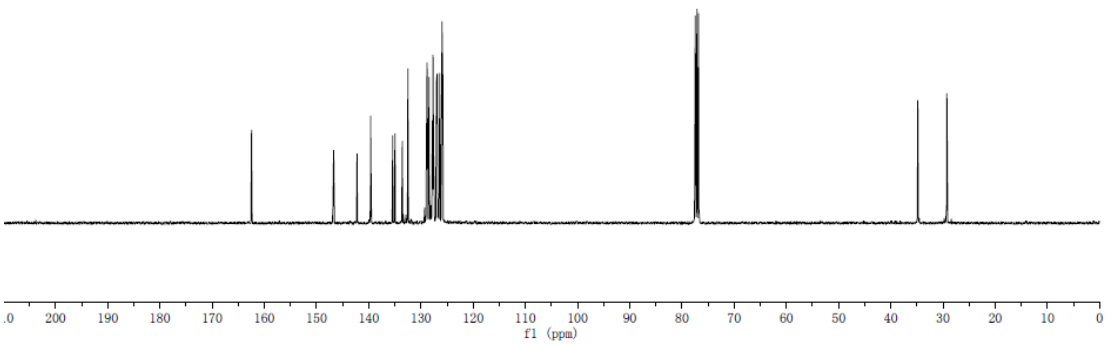


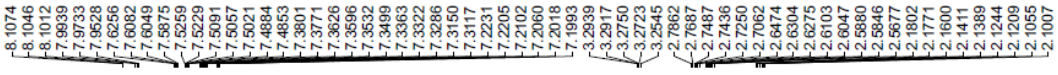


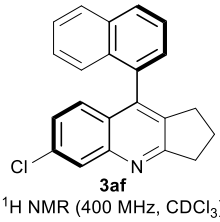


3ae

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

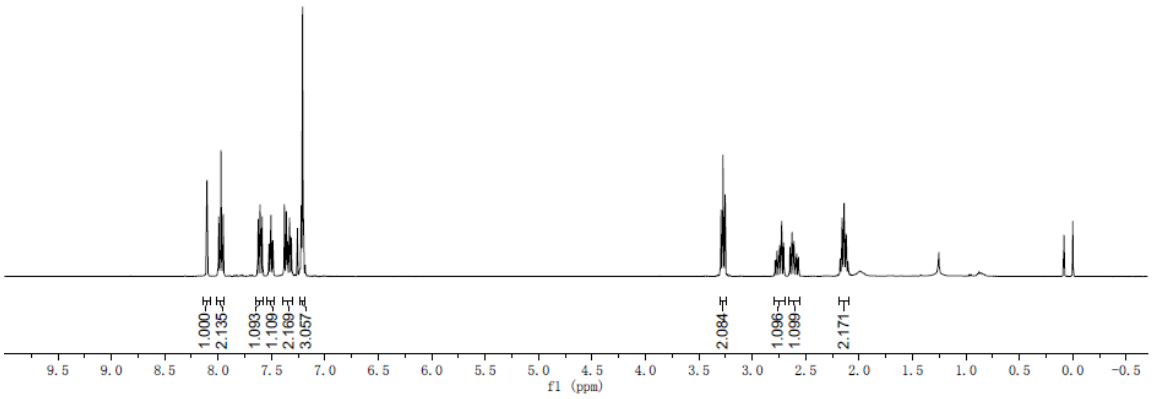


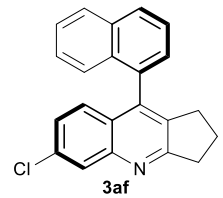




3af

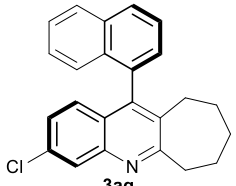
^{1}H NMR (400 MHz, $CDCl_3$)





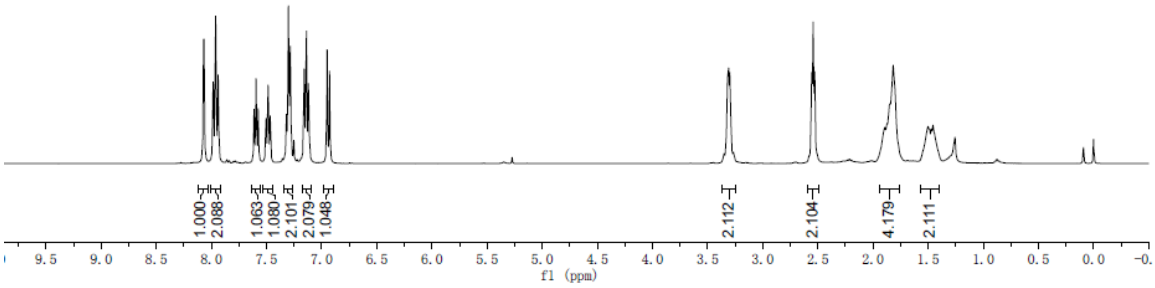
3af

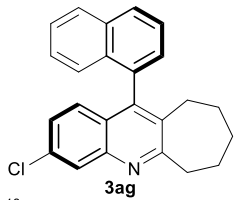
^{13}C NMR (100 MHz, $CDCl_3$)



3ag

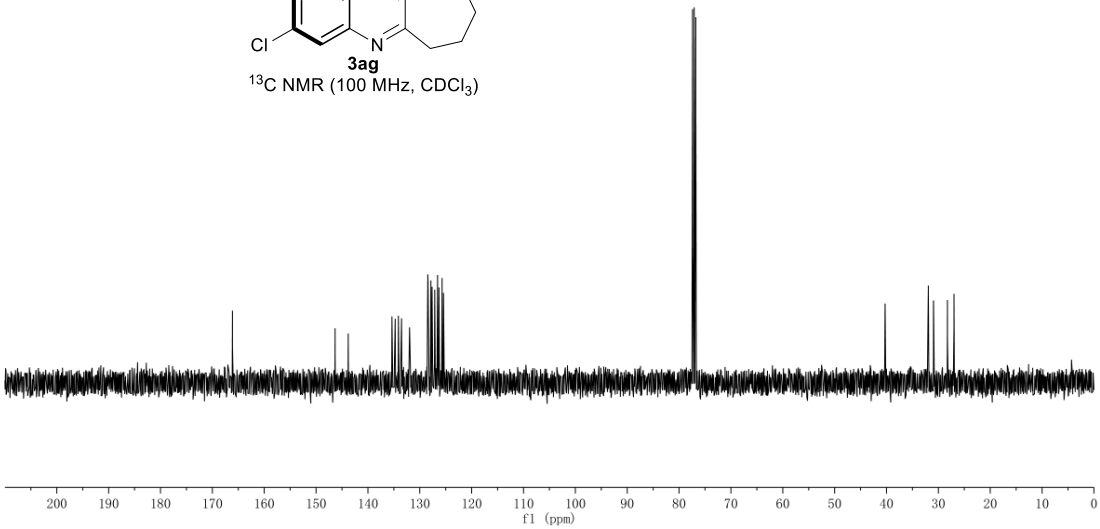
^{1}H NMR (400 MHz, $CDCl_3$)

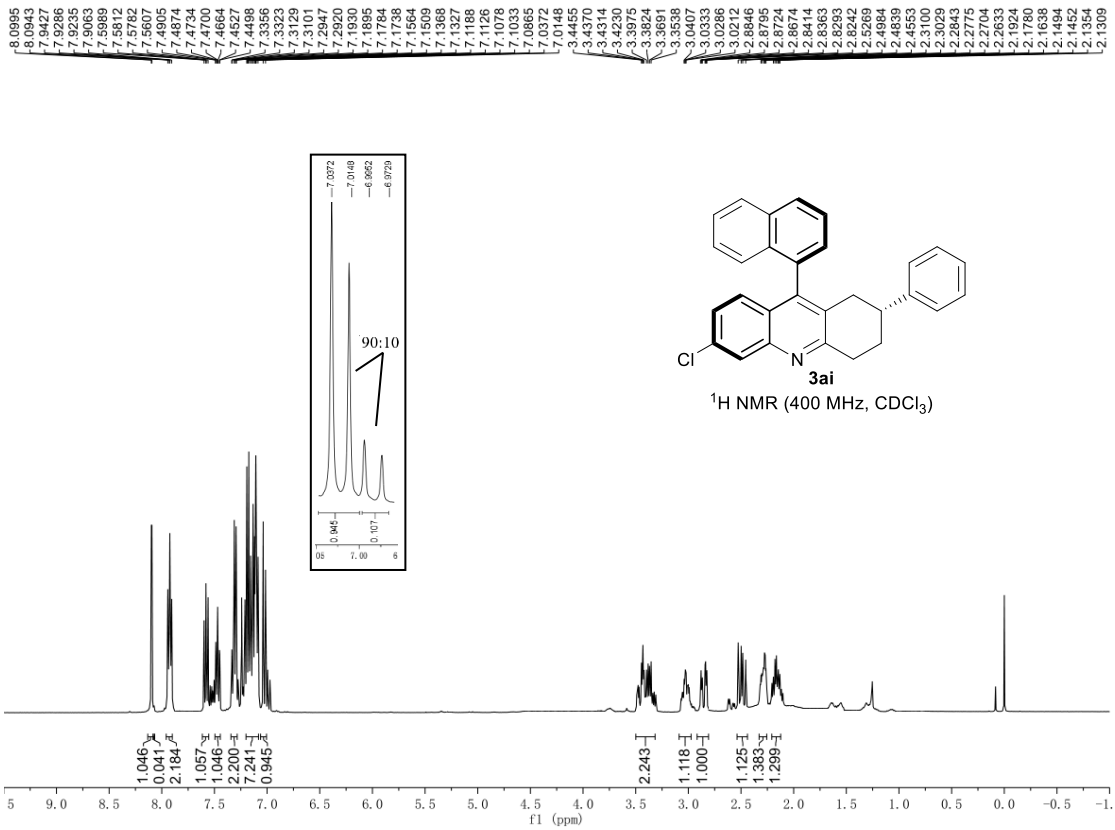


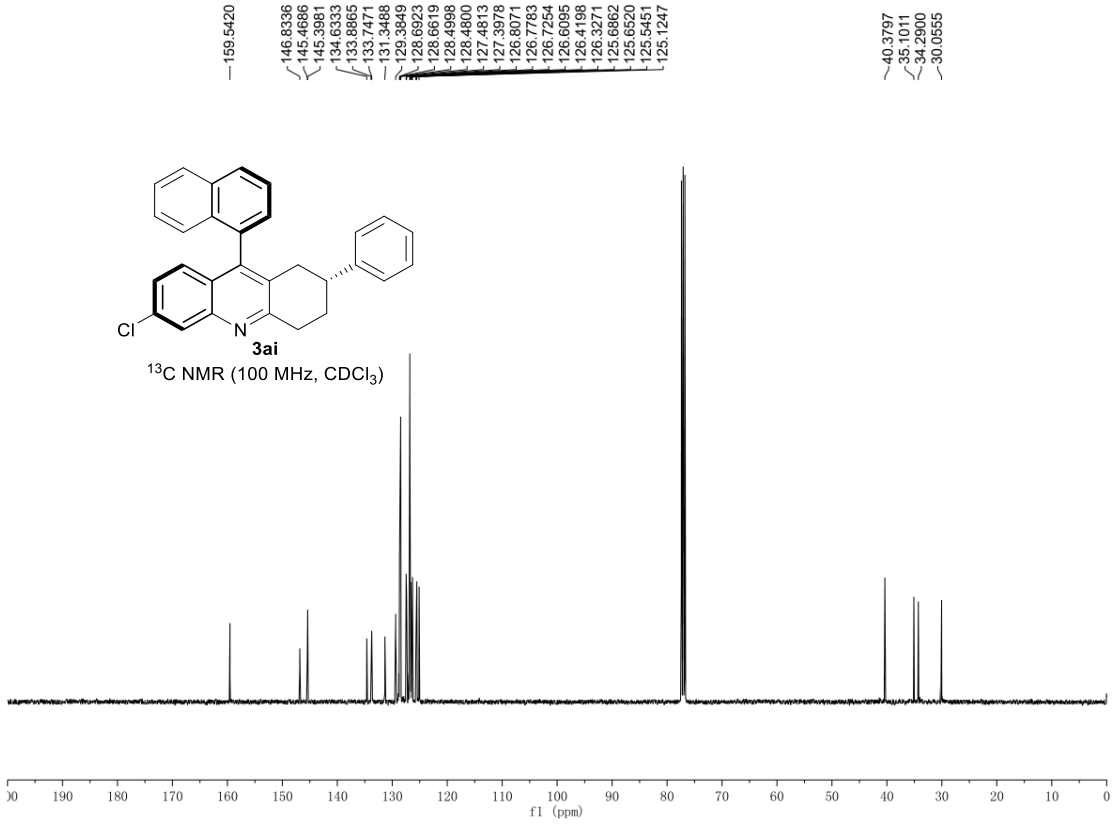


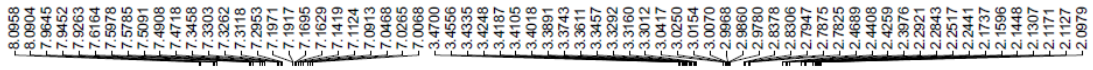
3ag

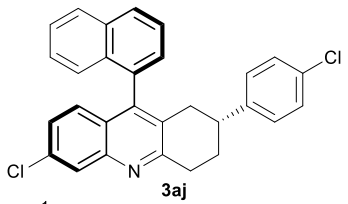
^{13}C NMR (100 MHz, $CDCl_3$)




90:10
Cl
N
3ai
1H NMR (400 MHz, CDCl3)
f1 (ppm)

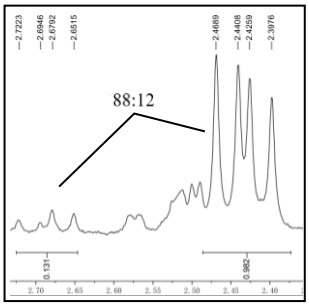

Cl
N
3ai
13C NMR (100 MHz, CDCl3)
f1 (ppm)

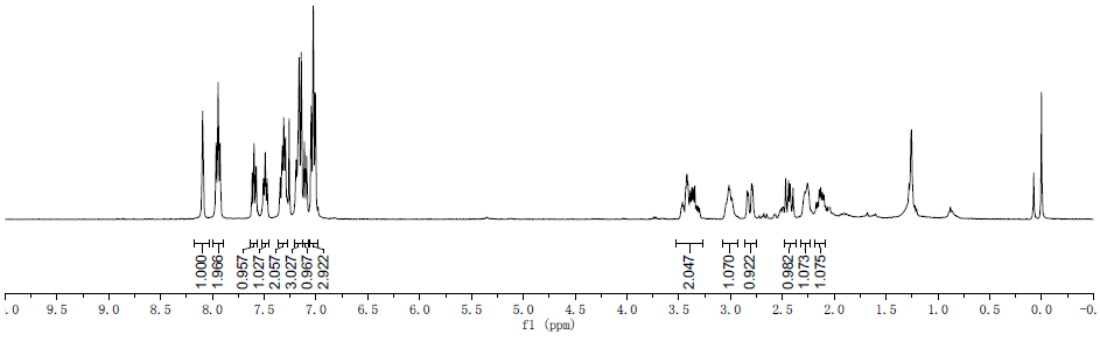


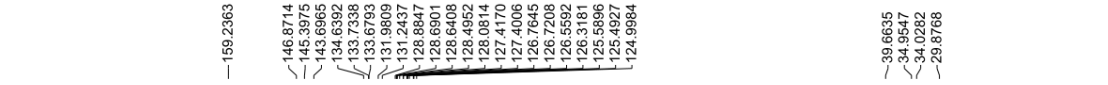


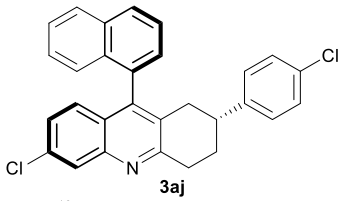
3aj

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



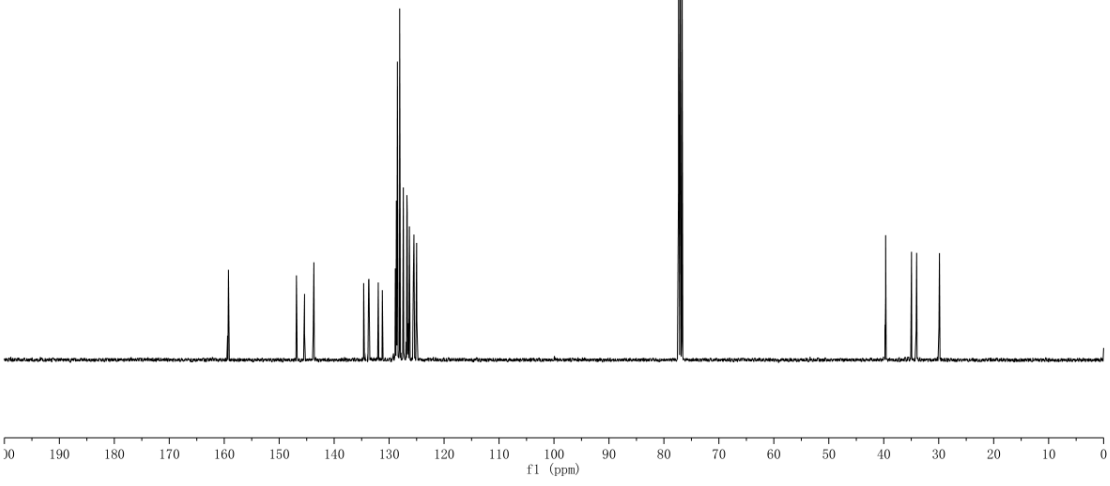


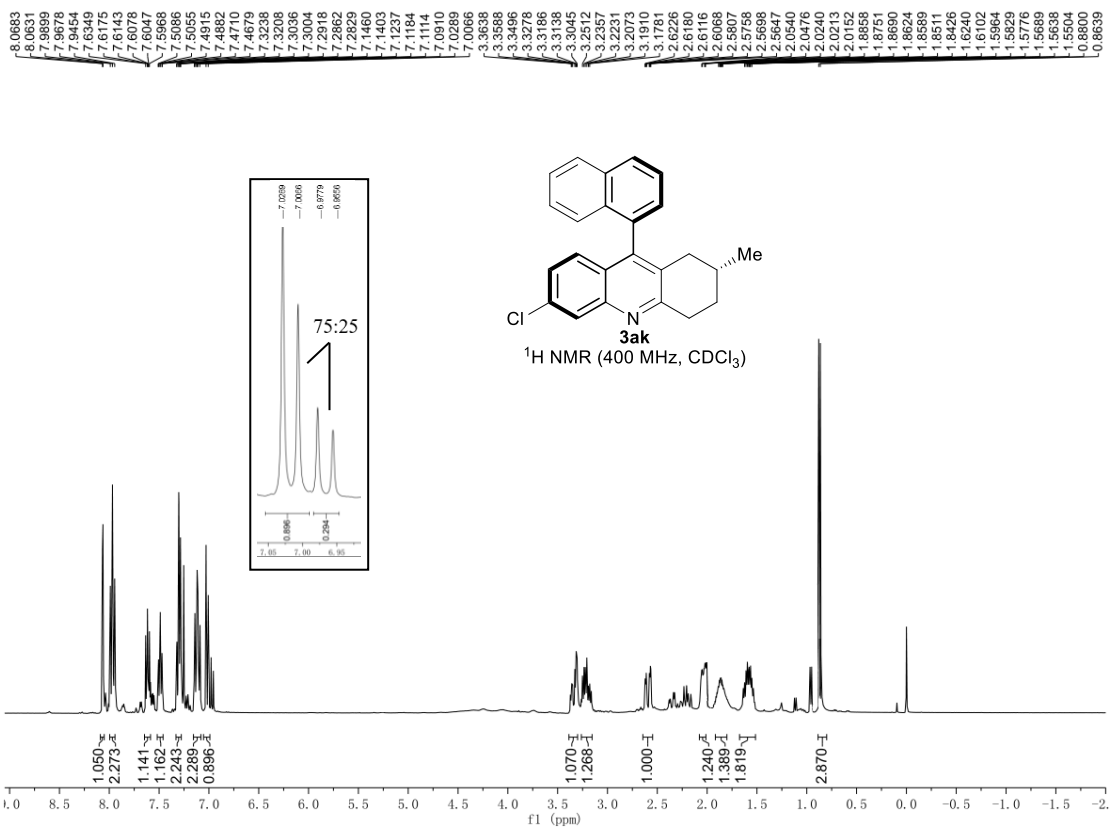


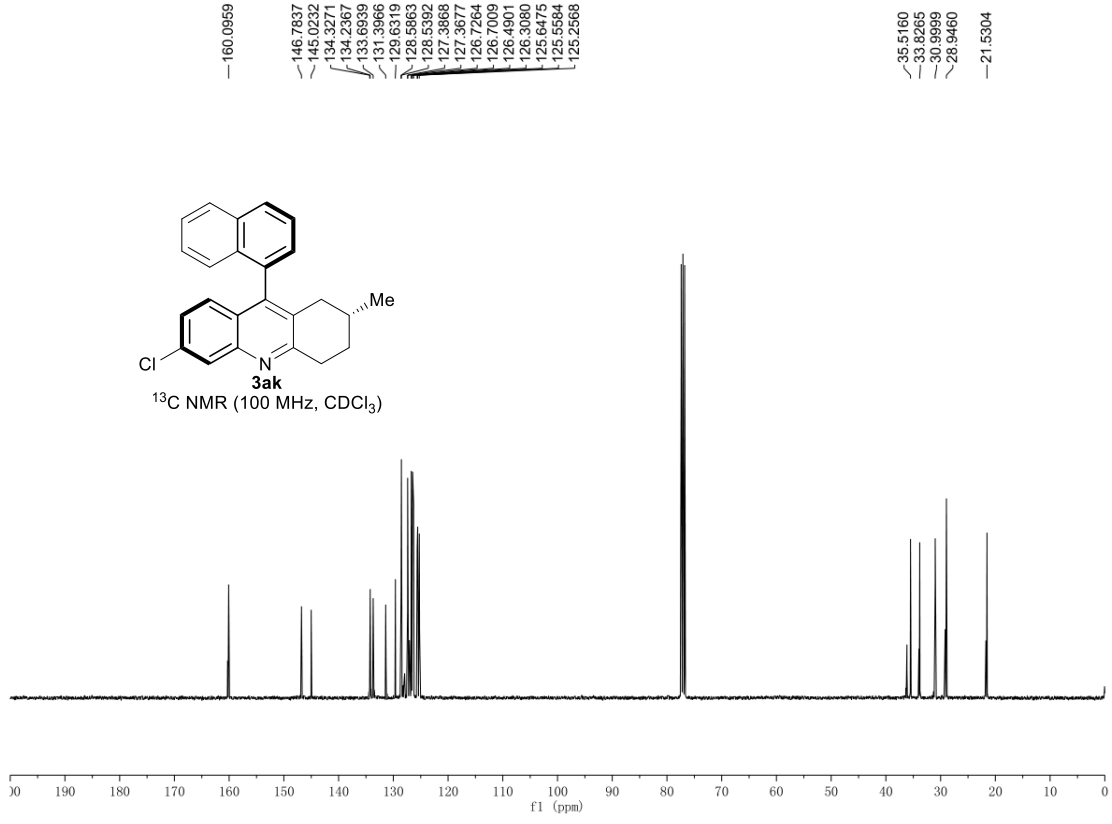


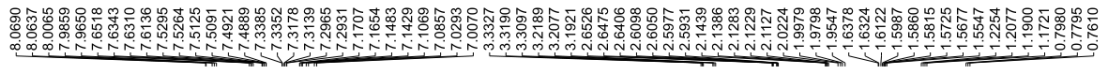
3aj

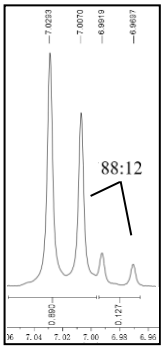
^{13}C NMR (100 MHz, $CDCl_3$)

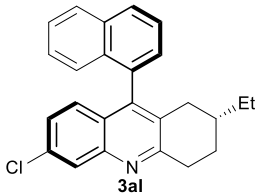



Me
Cl
N
3ak
^{1}H NMR (400 MHz, CDCl$_3$)
75:25
f1 (ppm)


Me
Cl
N
3ak
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)

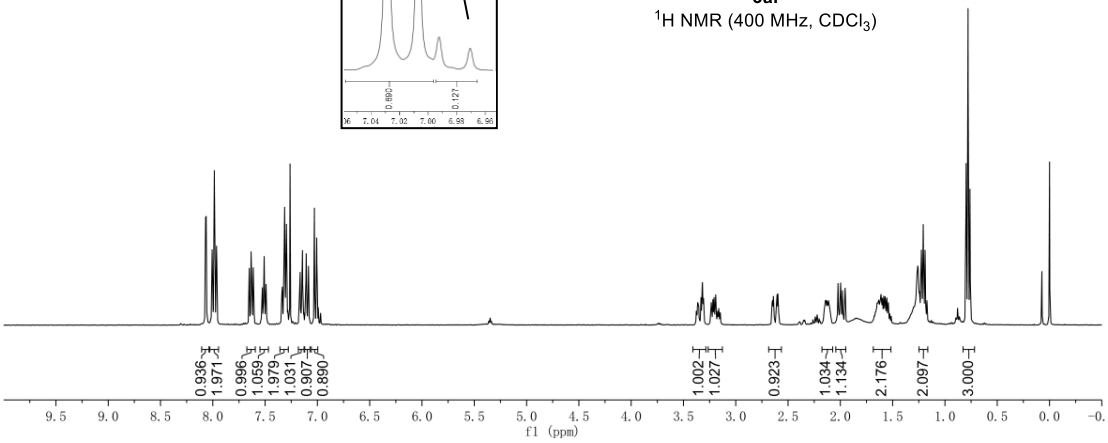


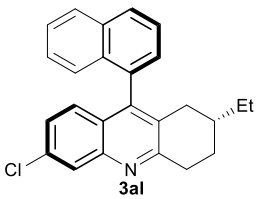




3al

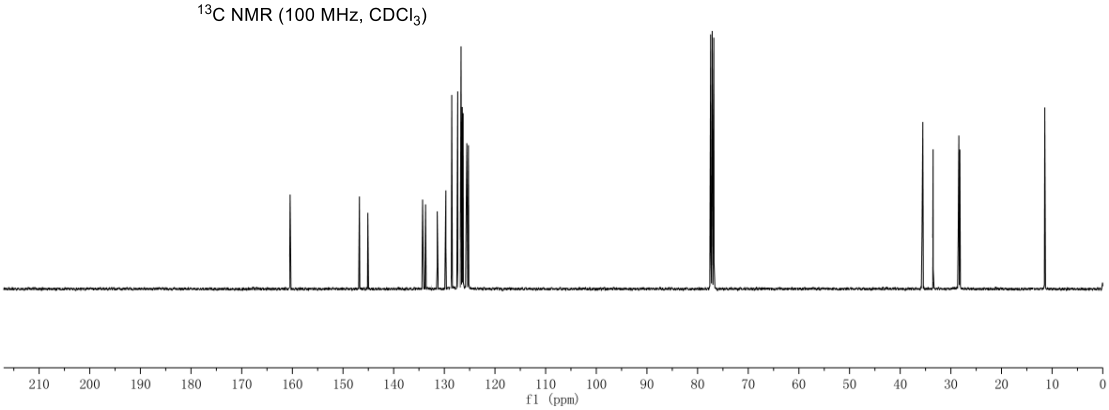
^{1}H NMR (400 MHz, $CDCl_3$)

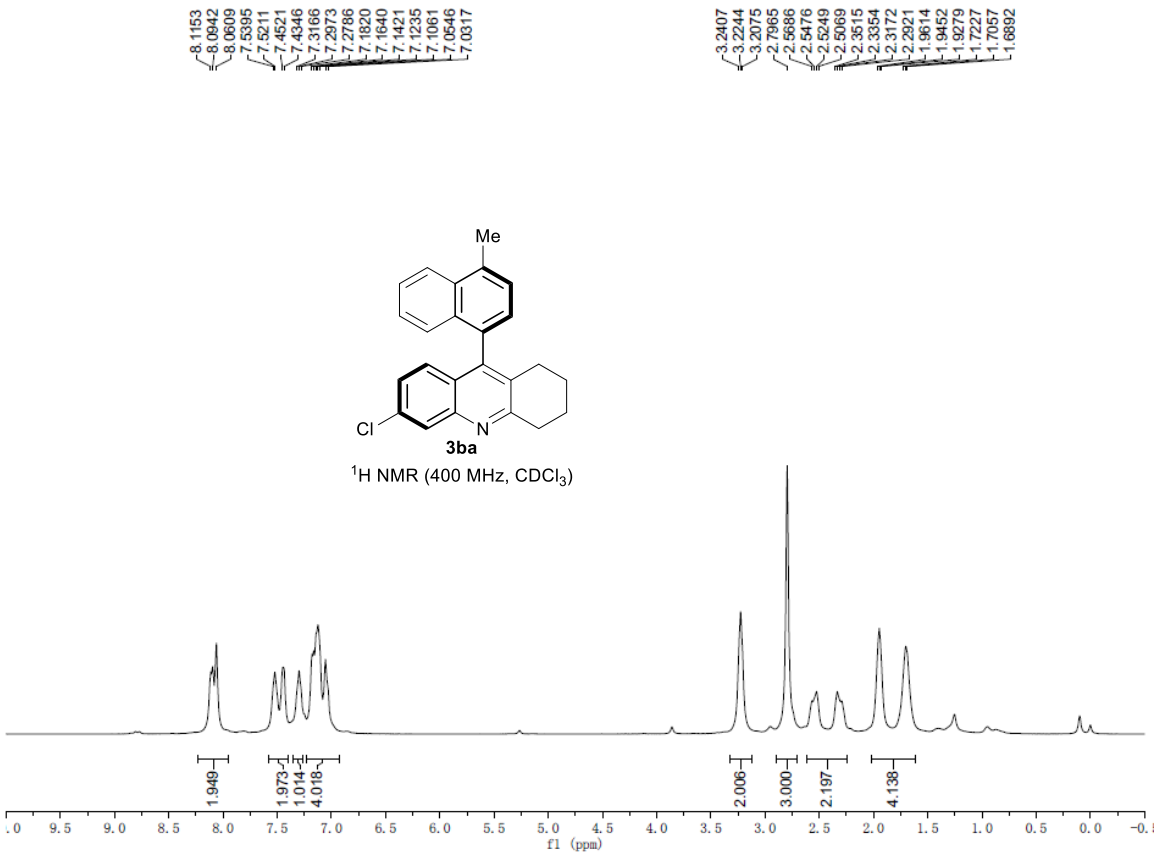


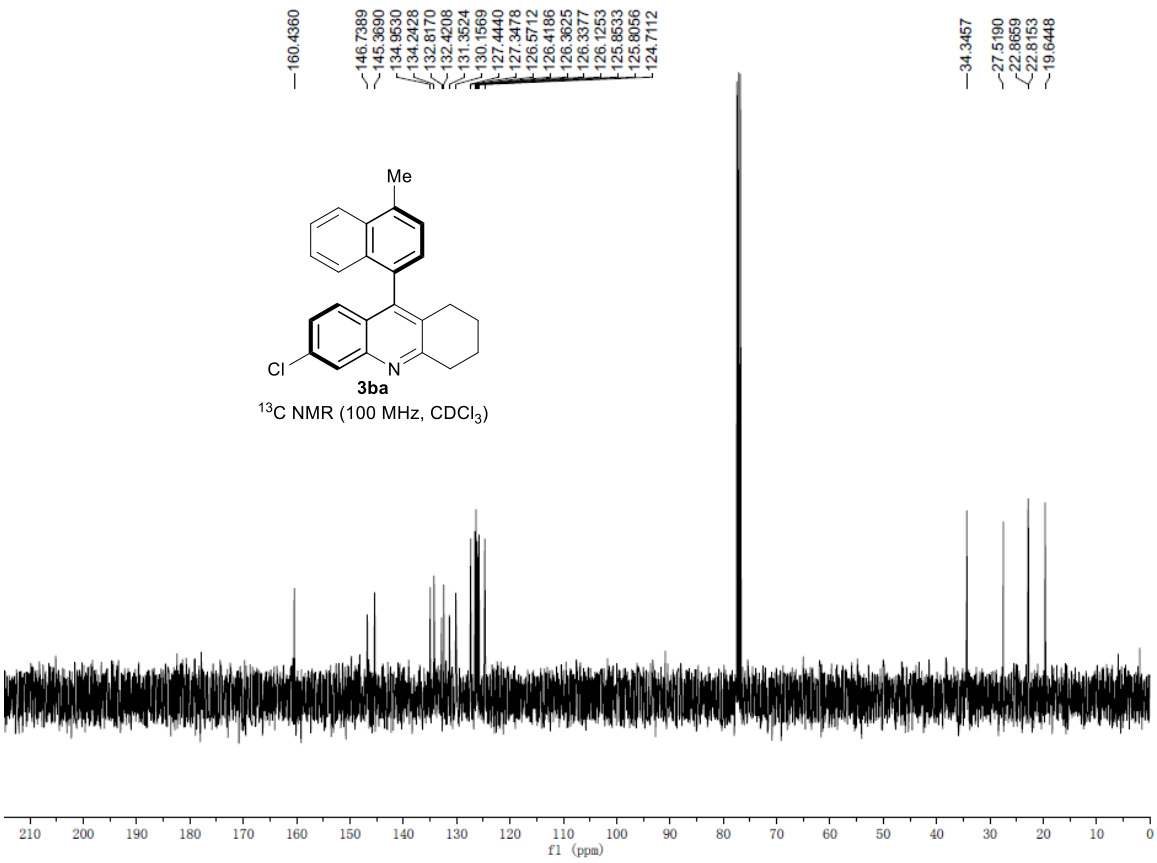


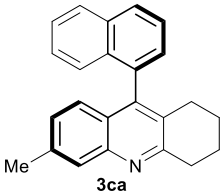
3al

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



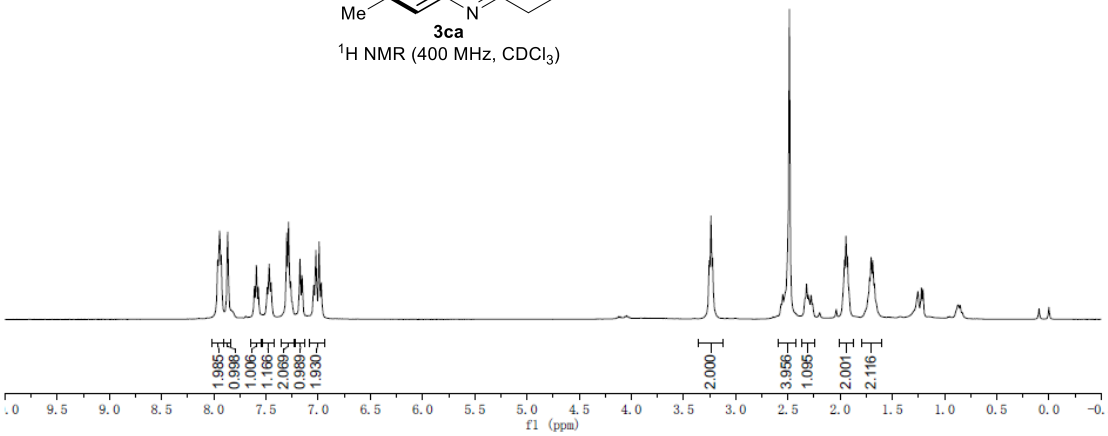

8.1153
8.0942
8.0609
7.5395
7.5211
7.4521
7.4346
7.3166
7.2973
7.2786
7.1820
7.1640
7.1421
7.1235
7.1061
7.0546
7.0317
3.2407
3.2244
3.2075
2.7965
2.5686
2.5476
2.5249
2.5069
2.3515
2.3354
2.3172
2.2921
1.9614
1.9452
1.9279
1.7227
1.7057
1.6892
Me
Cl
N
3ba
1H NMR (400 MHz, CDCl3)
1.949
1.973
1.014
4.018
2.006
3.000
2.197
4.138
f1 (ppm)

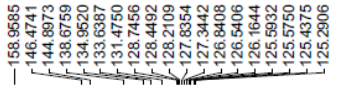

160.4360
146.7389
145.3690
134.9530
134.2428
132.8170
132.4208
131.3524
130.1569
127.4440
127.3478
126.5712
126.4186
126.3625
126.3377
126.1253
125.8533
125.8056
124.7112
34.3457
27.5190
22.8659
22.8153
19.6448
Me
Cl
N
3ba
13C NMR (100 MHz, CDCl3)
f1 (ppm)

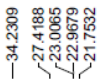


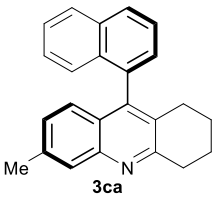
3ca

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



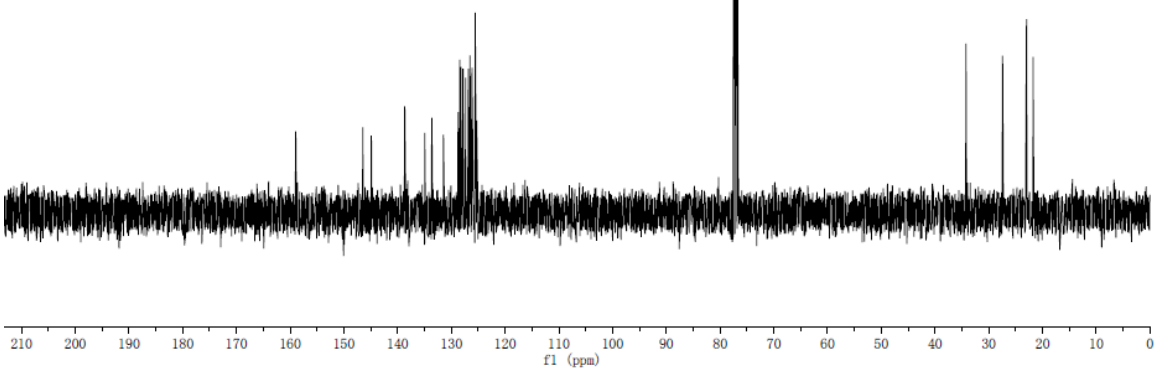


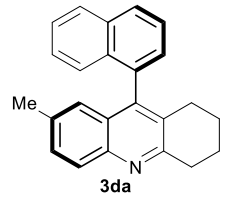




3ca

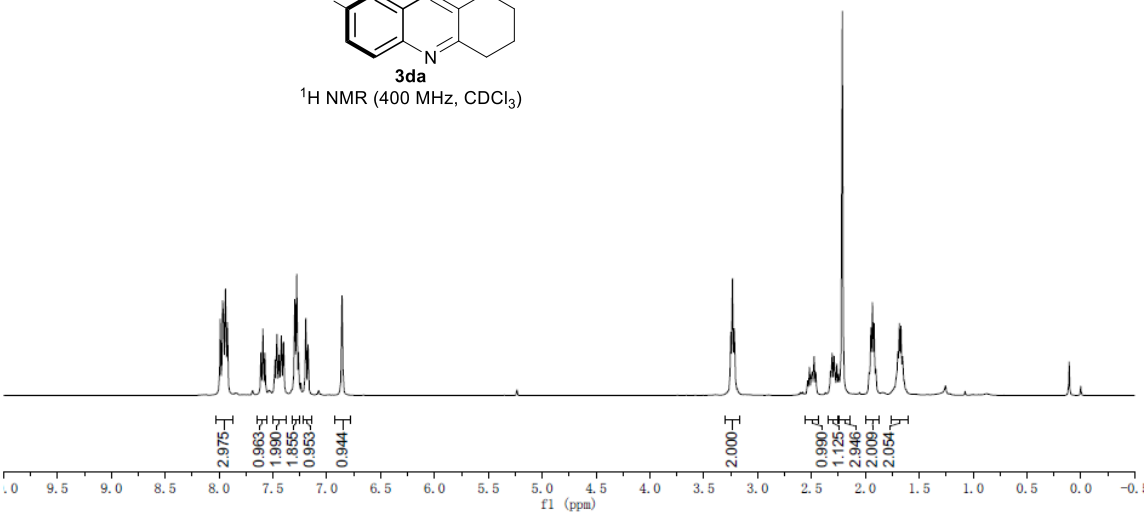
^{13}C NMR (100 MHz, $CDCl_3$)

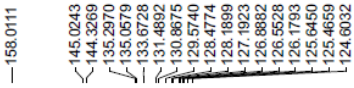


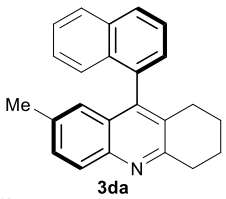


3da

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

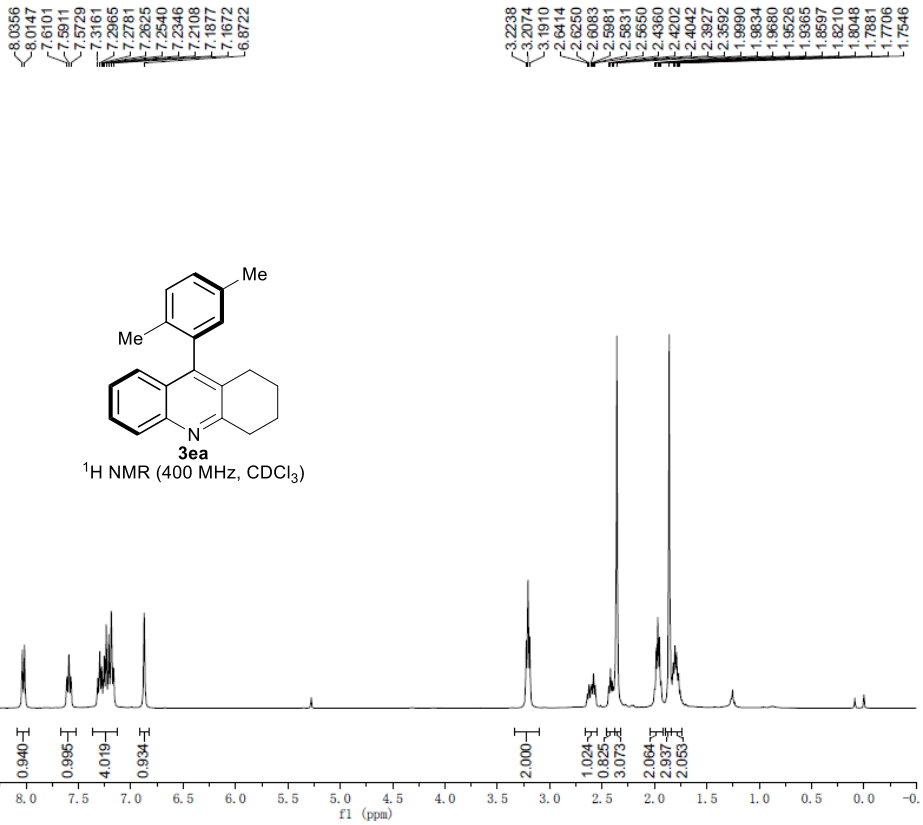


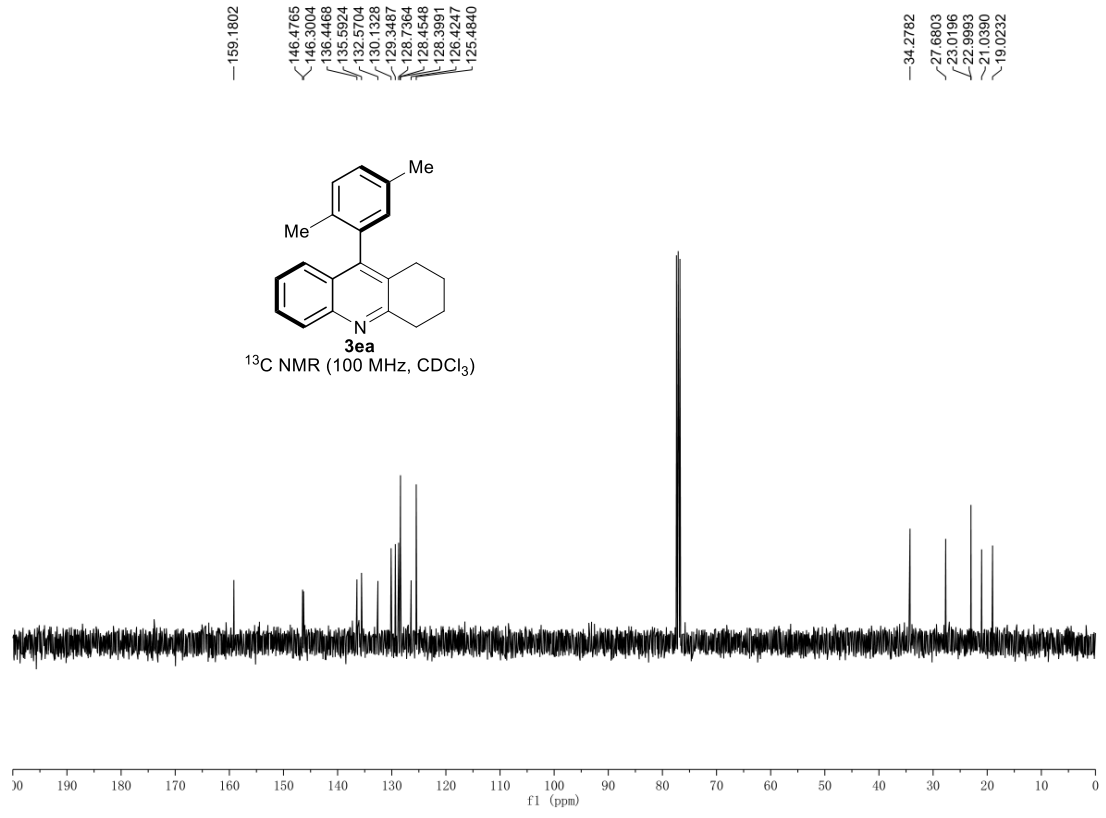


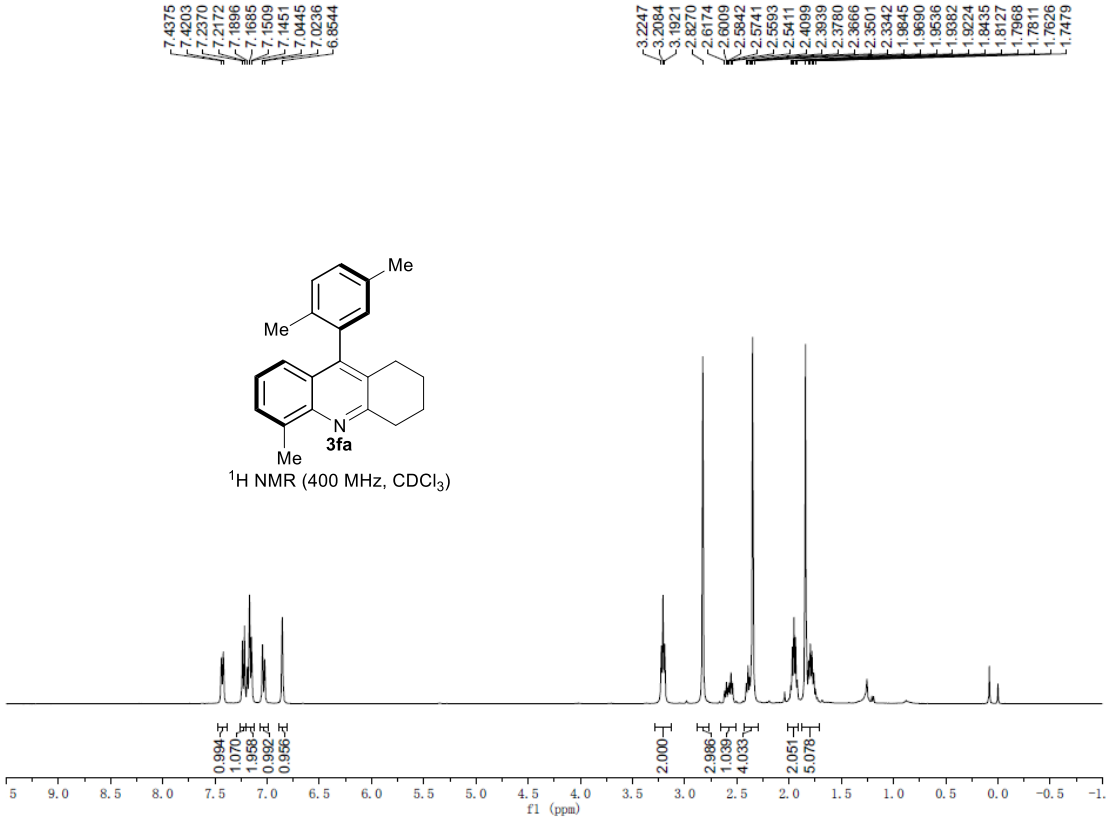


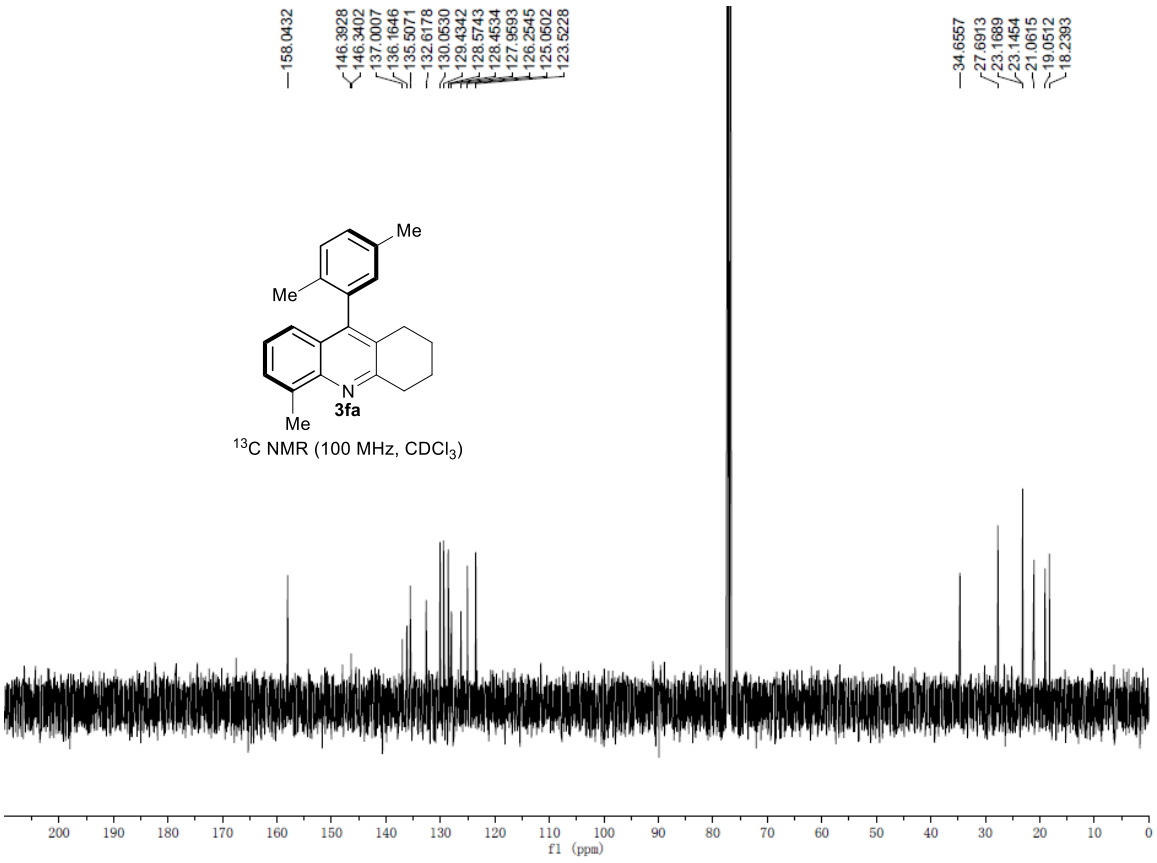
3da

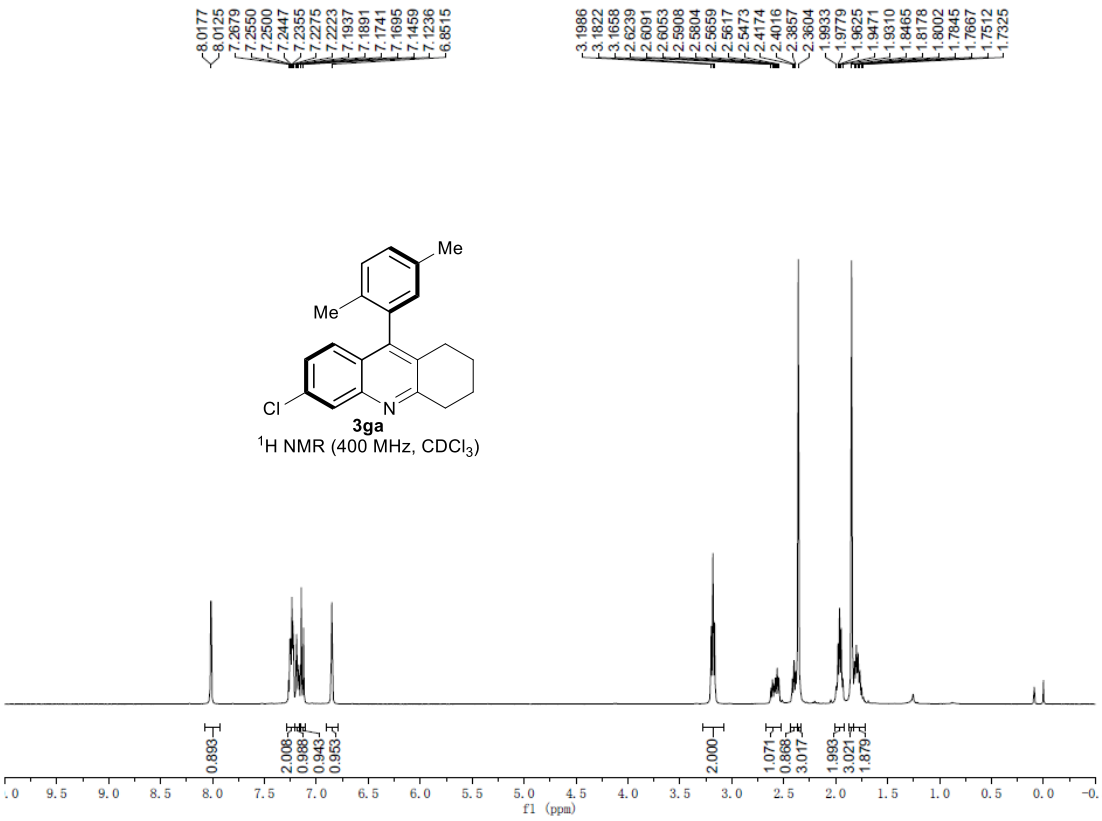
^{13}C NMR (100 MHz, $CDCl_3$)

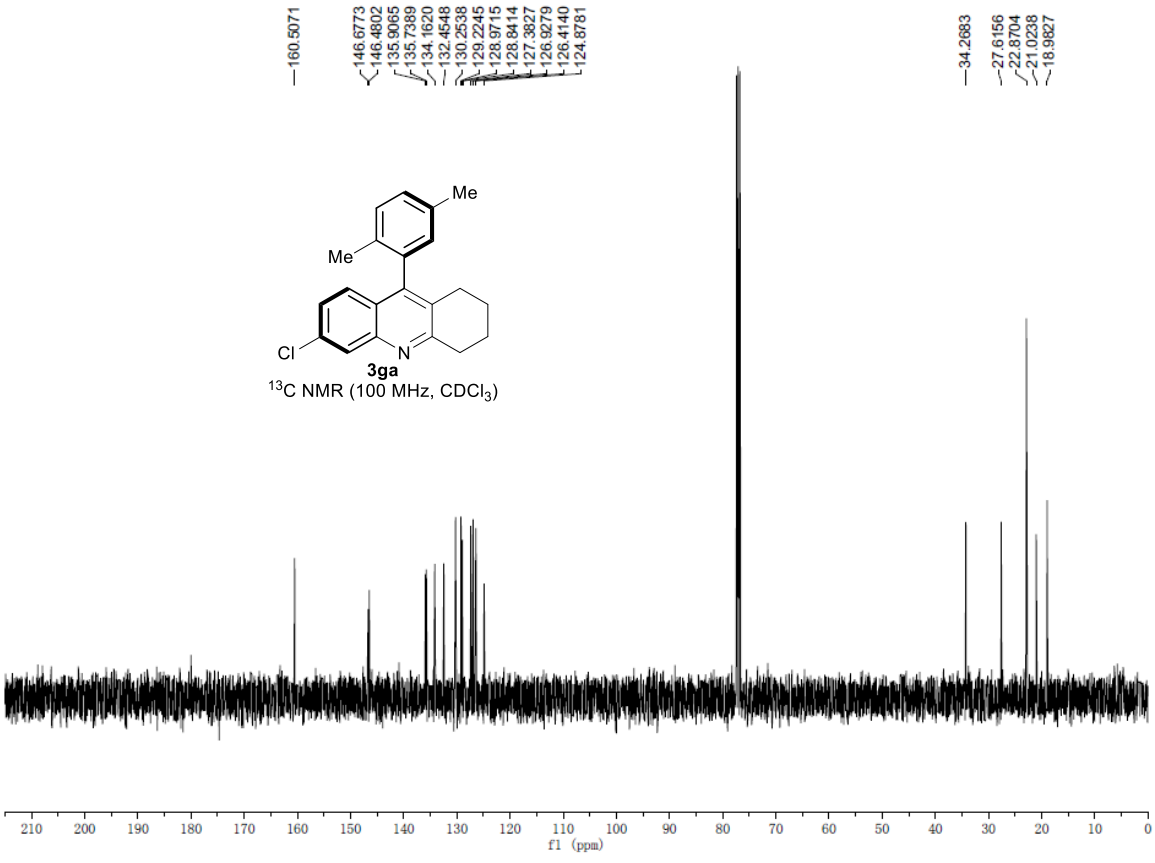

8.0356
8.0147
7.6101
7.5911
7.5729
7.3161
7.2965
7.2781
7.2625
7.2540
7.2346
7.2108
7.1877
7.1672
6.8722
3.2238
3.2074
3.1910
2.6414
2.6250
2.6083
2.5981
2.5831
2.5650
2.4360
2.4202
2.4042
2.3927
2.3592
1.9990
1.9834
1.9680
1.9526
1.9365
1.8597
1.8210
1.8048
1.7881
1.7706
1.7546
Me
Me
N
3ea
1H NMR (400 MHz, CDCl3)
0.940
0.995
4.019
0.934
2.000
1.024
0.825
3.073
2.064
2.937
2.053
f1 (ppm)

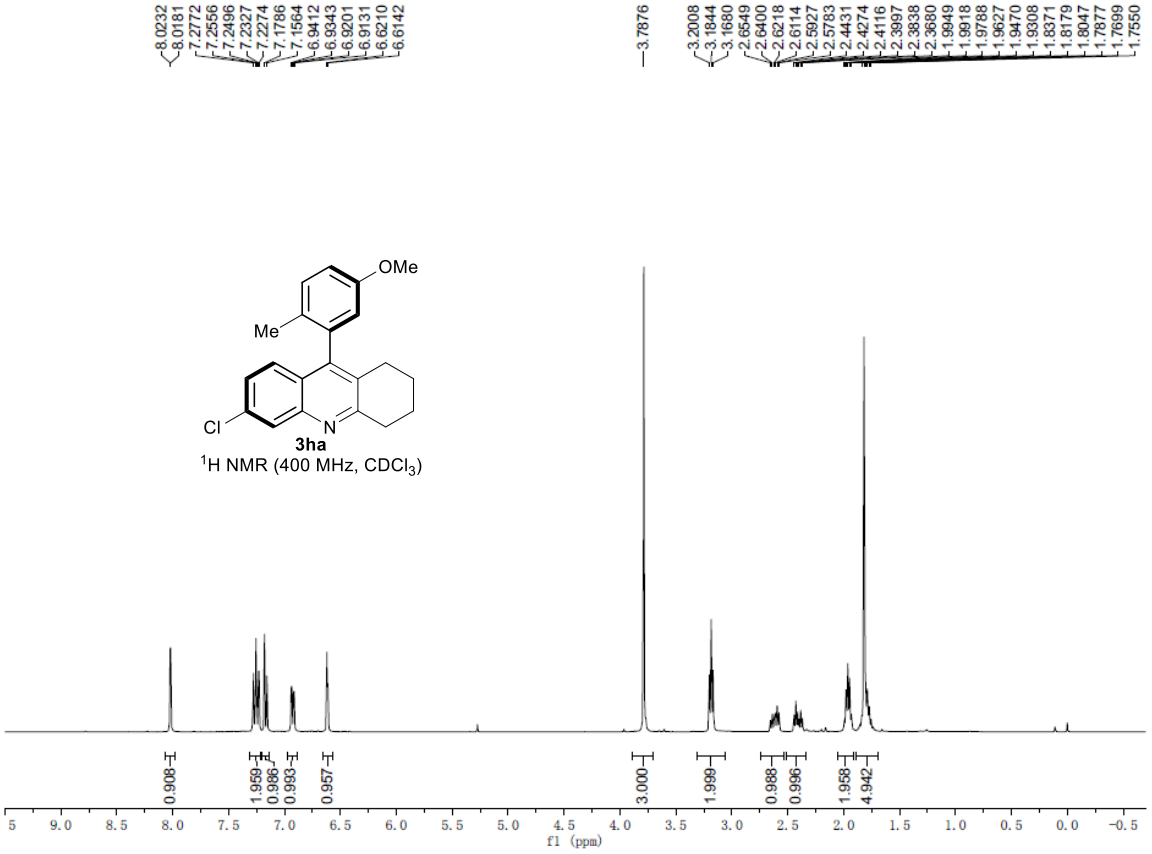

159.1802
146.4765
146.3004
136.4468
135.5924
132.5704
130.1328
129.3487
128.7364
128.4548
128.3991
126.4247
125.4840
34.2782
27.6803
23.0196
22.9993
21.0390
19.0232
Me
Me
N
3ea
13C NMR (100 MHz, CDCl3)
f1 (ppm)

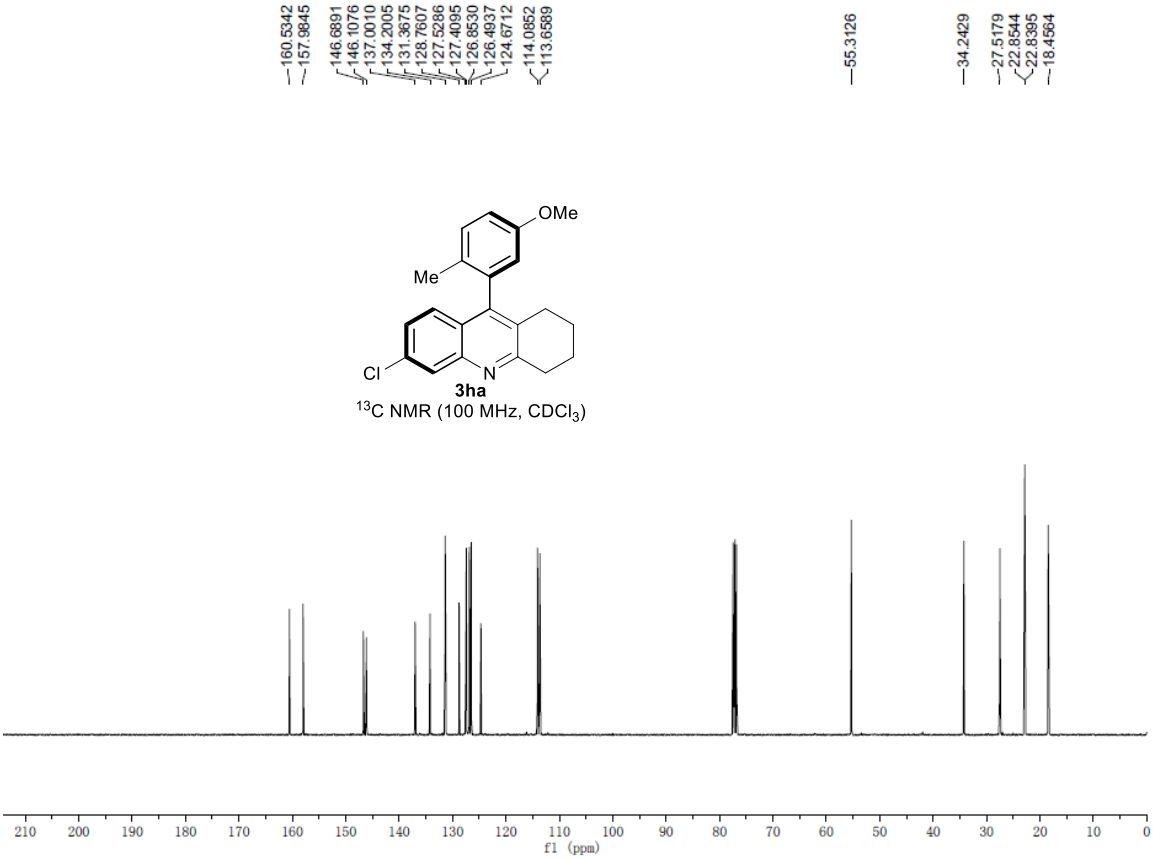

7.4375
7.4203
7.2370
7.2172
7.1896
7.1685
7.1509
7.1451
7.0445
7.0236
6.8544
3.2247
3.2084
3.1921
2.8270
2.6174
2.6009
2.5842
2.5741
2.5593
2.5411
2.4099
2.3939
2.3780
2.3666
2.3501
2.3342
1.9845
1.9690
1.9536
1.9382
1.9224
1.8435
1.8127
1.7968
1.7811
1.7626
1.7479
Me
Me
N
Me
3fa
^{1}H NMR (400 MHz, $CDCl_3$)
0.994
1.070
1.968
0.992
0.956
2.000
2.986
1.039
4.033
2.051
5.078
f1 (ppm)

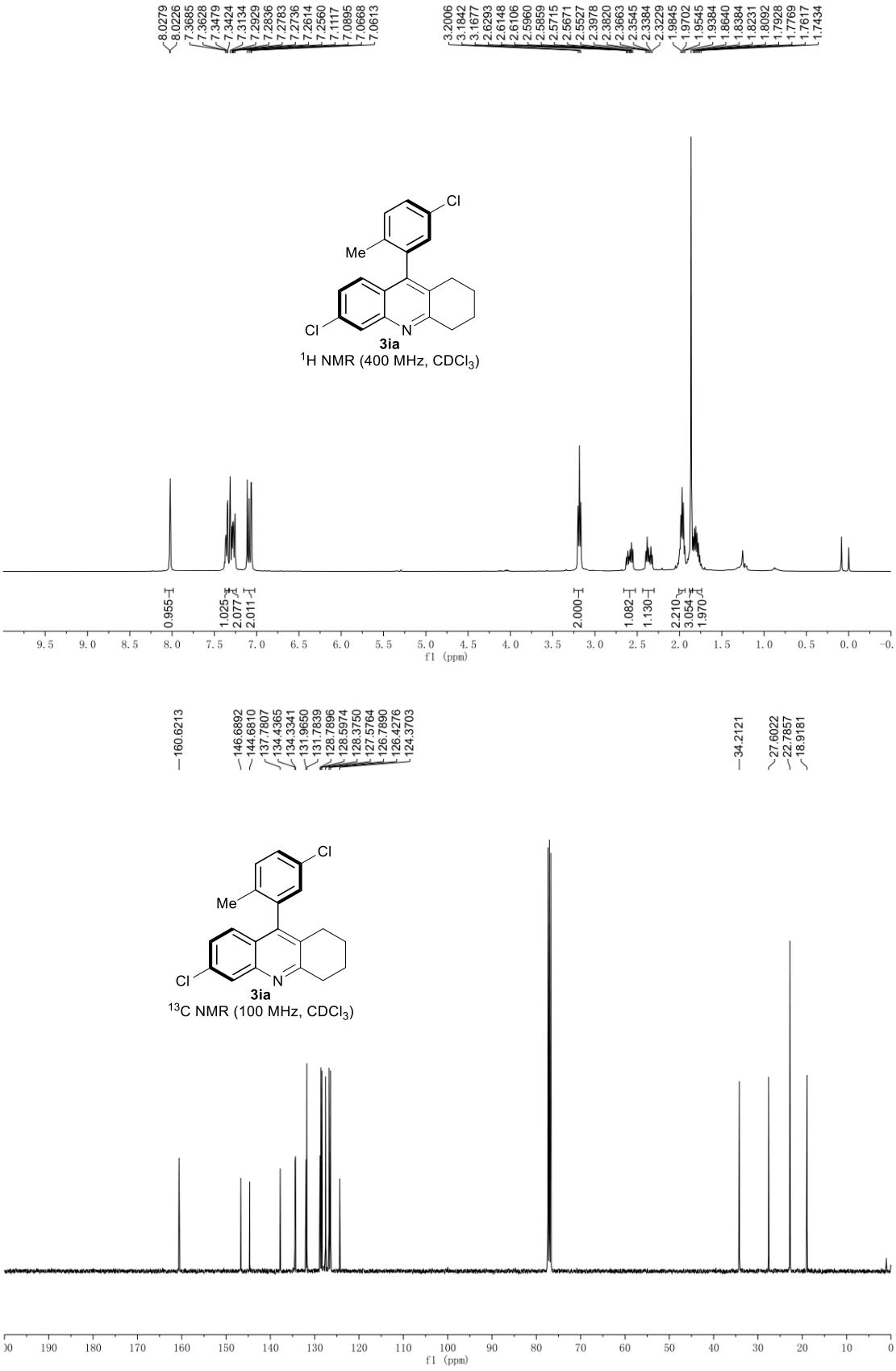

158.0432
146.3928
146.3402
137.0007
136.1646
135.5071
132.6178
130.0530
129.4342
128.5743
128.4534
127.9593
126.2545
125.0502
123.5228
34.6557
27.6913
23.1689
23.1454
21.0615
19.0512
18.2393
Me
Me
N
Me
3fa
^{13}C NMR (100 MHz, $CDCl_3$)
f1 (ppm)

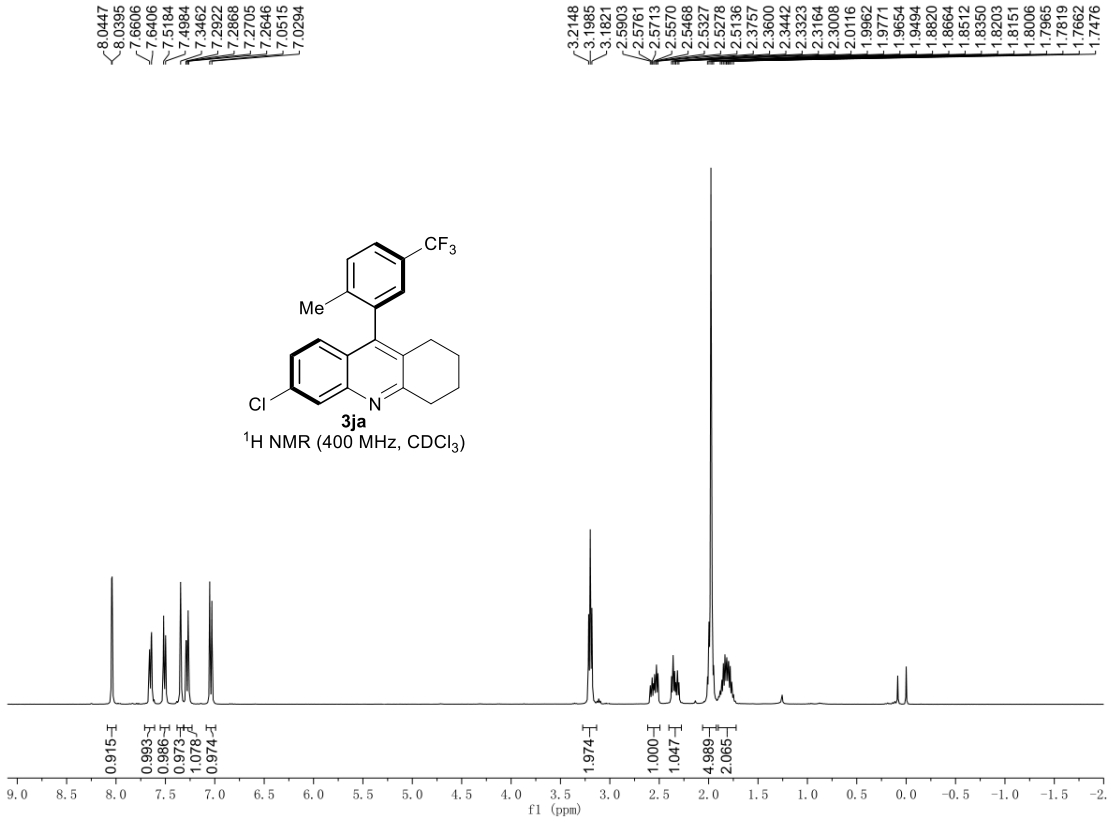

8.0177
8.0125
7.2679
7.2550
7.2500
7.2447
7.2355
7.2275
7.2223
7.1937
7.1891
7.1741
7.1695
7.1459
7.1236
6.8515
3.1986
3.1822
3.1658
2.6239
2.6091
2.6053
2.5908
2.5804
2.5659
2.5617
2.5473
2.4174
2.4016
2.3857
2.3604
1.9833
1.9779
1.9625
1.9471
1.9310
1.8465
1.8178
1.8002
1.7845
1.7667
1.7512
1.7325
Me
Me
Cl
N
3ga
1H NMR (400 MHz, CDCl3)
0.893
2.008
0.988
0.943
0.953
2.000
1.071
0.868
3.017
1.993
3.021
1.879
f1 (ppm)

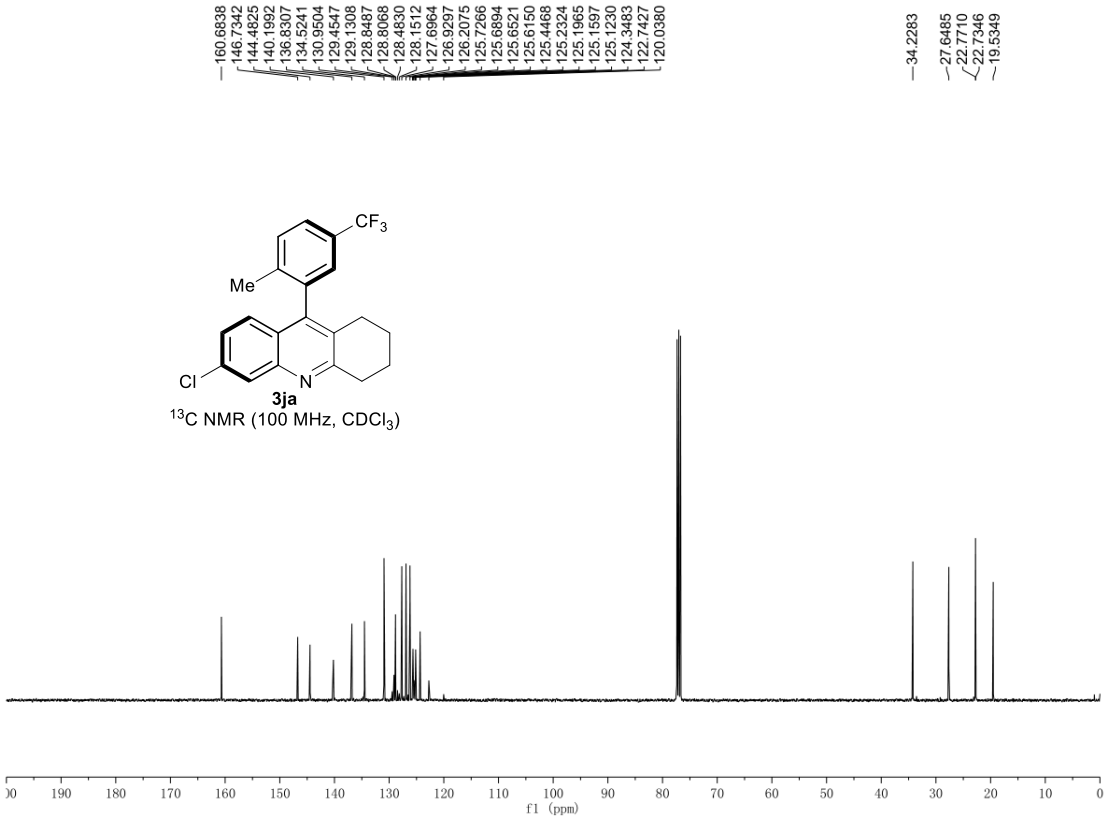

160.5071
146.6773
146.4802
135.9065
135.7389
134.1620
132.4548
130.2538
129.2245
128.9715
128.8414
127.3827
126.9279
126.4140
124.8781
34.2683
27.6156
22.8704
21.0238
18.9827
Me
Me
Cl
N
3ga
13C NMR (100 MHz, CDCl3)
f1 (ppm)

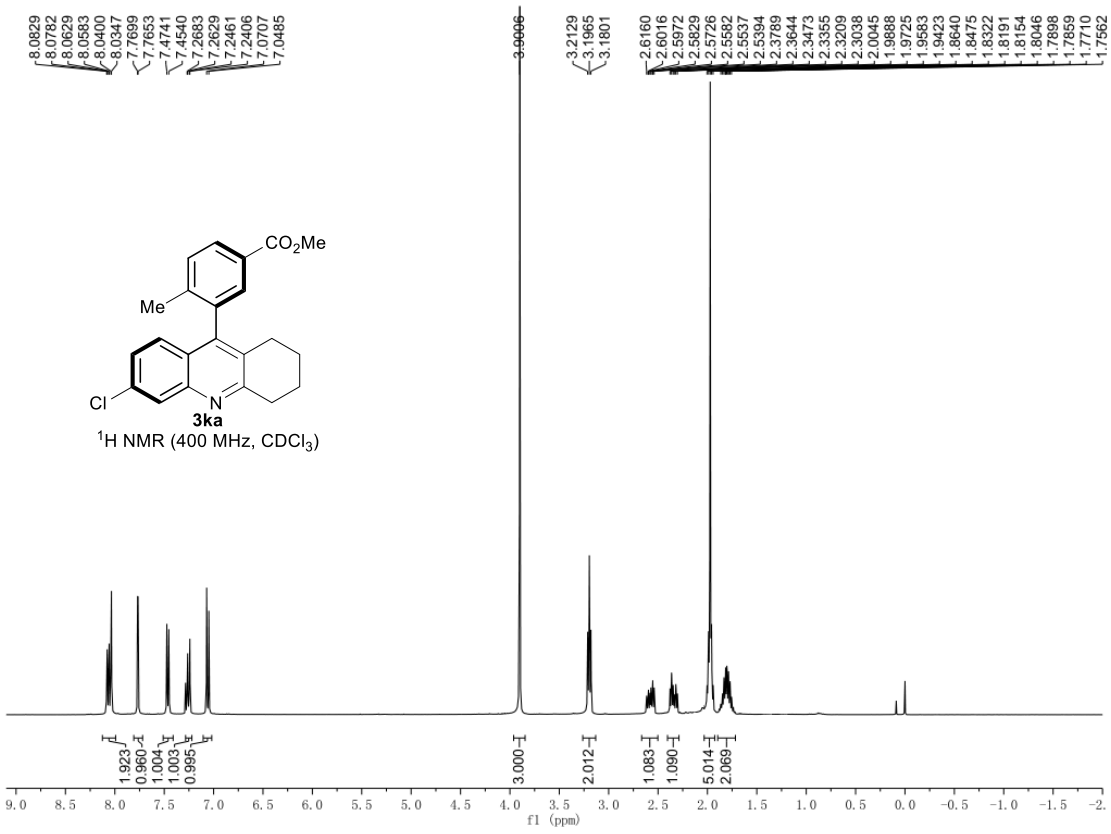

8.0232
8.0181
7.2772
7.2556
7.2496
7.2327
7.2274
7.1786
7.1564
6.9412
6.9343
6.9201
6.9131
6.6210
6.6142
3.7876
3.2008
3.1844
3.1680
2.6549
2.6400
2.6218
2.6114
2.5927
2.5783
2.4431
2.4274
2.4116
2.3997
2.3838
2.3680
1.9949
1.9918
1.9788
1.9627
1.9470
1.9308
1.8371
1.8179
1.8047
1.7877
1.7699
1.7550
OMe
Me
Cl
N
3ha
1H NMR (400 MHz, CDCl3)
0.908
1.959
0.986
0.993
0.957
3.000
1.999
0.988
0.996
1.958
4.942
f1 (ppm)

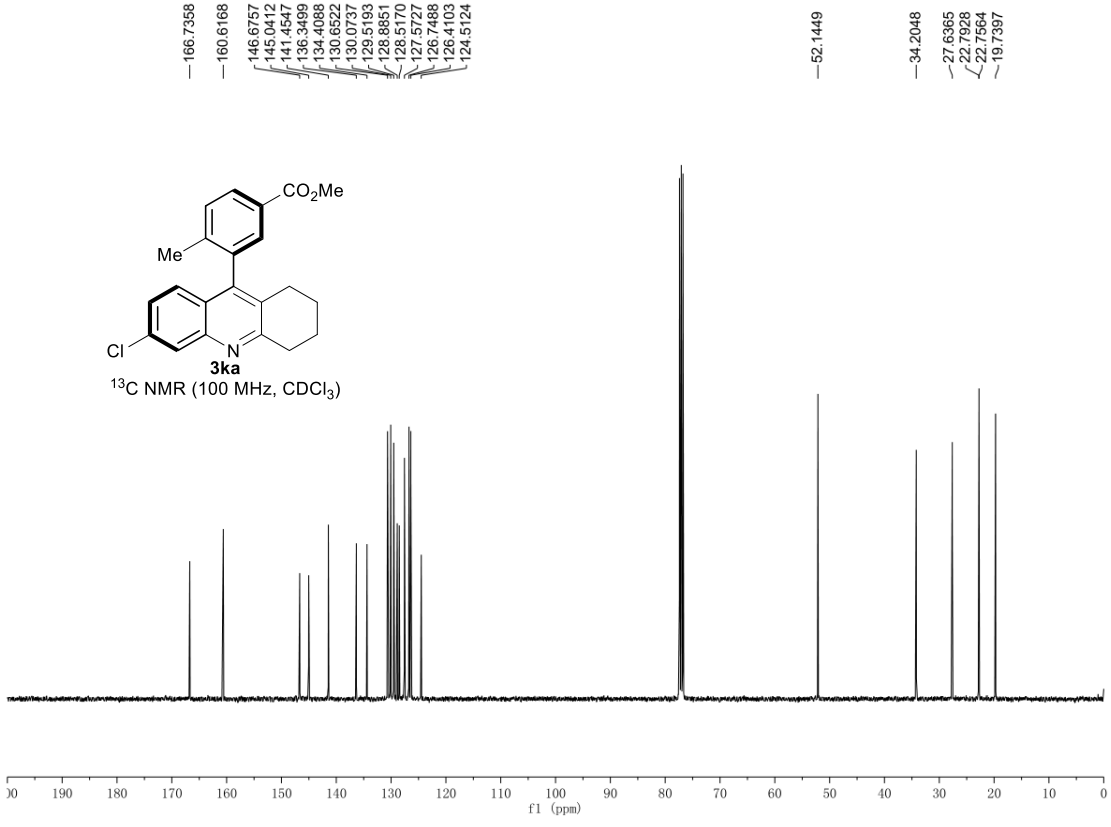

160.5342
157.9845
146.6891
146.1076
137.0010
134.2005
131.3675
128.7607
127.5286
127.4095
126.8530
126.4937
124.6712
114.0852
113.6589
55.3126
34.2429
27.5179
22.8544
22.8395
18.4564
OMe
Me
Cl
N
3ha
13C NMR (100 MHz, CDCl3)
f1 (ppm)

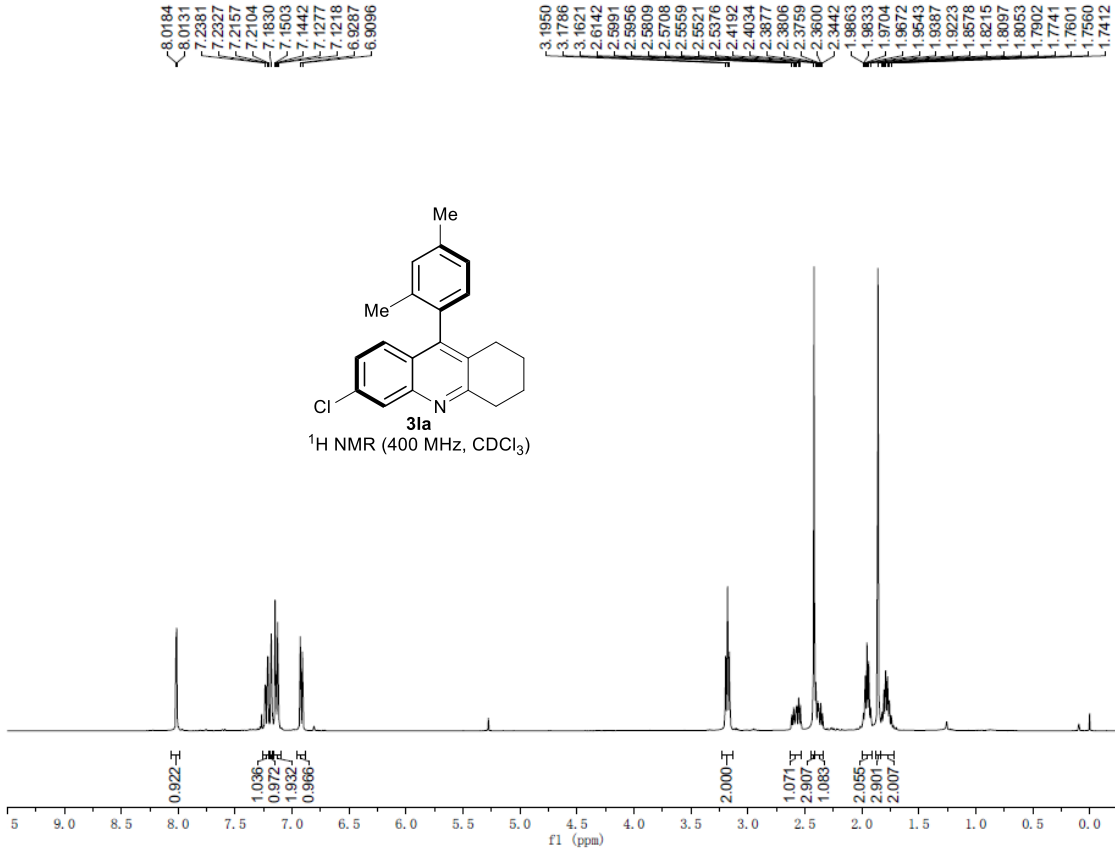

8.0279
8.0226
7.3685
7.3628
7.3479
7.3424
7.3134
7.2929
7.2836
7.2783
7.2736
7.2614
7.2560
7.1117
7.0895
7.0668
7.0613
3.2006
3.1842
3.1677
2.6293
2.6148
2.6106
2.5960
2.5859
2.5715
2.5671
2.5527
2.3978
2.3820
2.3663
2.3545
2.3384
2.3229
1.9845
1.9702
1.9545
1.9384
1.8640
1.8384
1.8231
1.8092
1.7928
1.7769
1.7617
1.7434
Cl
Me
Cl
N
3ia
1H NMR (400 MHz, CDCl3)
0.955
1.025
2.077
2.011
2.000
1.082
1.130
2.210
3.054
1.970
f1 (ppm)
160.6213
146.6892
144.6810
137.7807
134.4365
134.3341
131.9650
131.7839
128.7896
128.5974
128.3750
127.5764
126.7890
126.4276
124.3703
34.2121
27.6022
22.7857
18.9181
Cl
Me
Cl
N
3ia
13C NMR (100 MHz, CDCl3)
f1 (ppm)

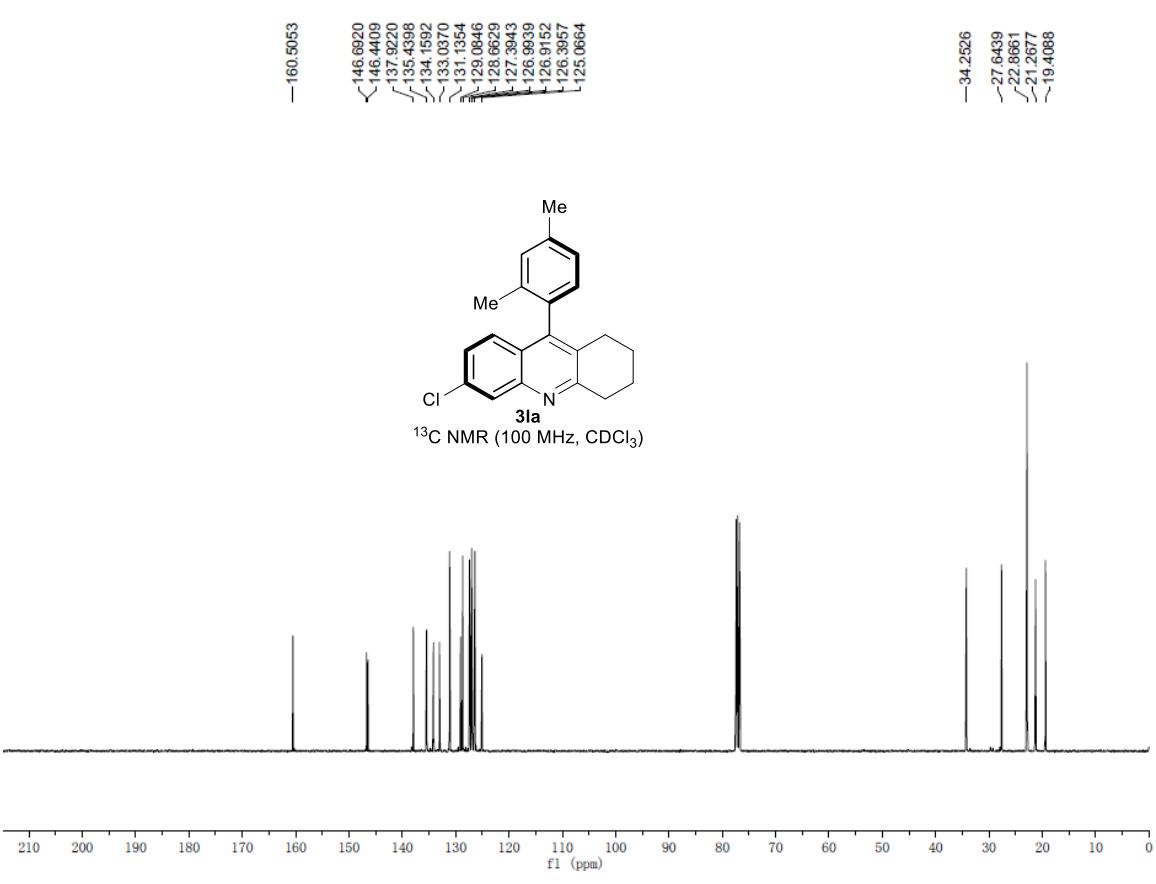

8.0447
8.0395
7.6606
7.6406
7.5184
7.4984
7.3462
7.2922
7.2868
7.2705
7.2646
7.0515
7.0294
3.2148
3.1985
3.1821
2.5903
2.5761
2.5713
2.5570
2.5468
2.5327
2.5278
2.5136
2.3757
2.3600
2.3442
2.3323
2.3164
2.3008
2.0116
1.9962
1.9771
1.9654
1.9494
1.8820
1.8664
1.8512
1.8350
1.8203
1.8151
1.8006
1.7965
1.7819
1.7662
1.7476
CF3
Me
Cl
N
3ja
1H NMR (400 MHz, CDCl3)
0.915
0.993
0.986
0.973
1.078
0.974
1.974
1.000
1.047
4.989
2.065
f1 (ppm)

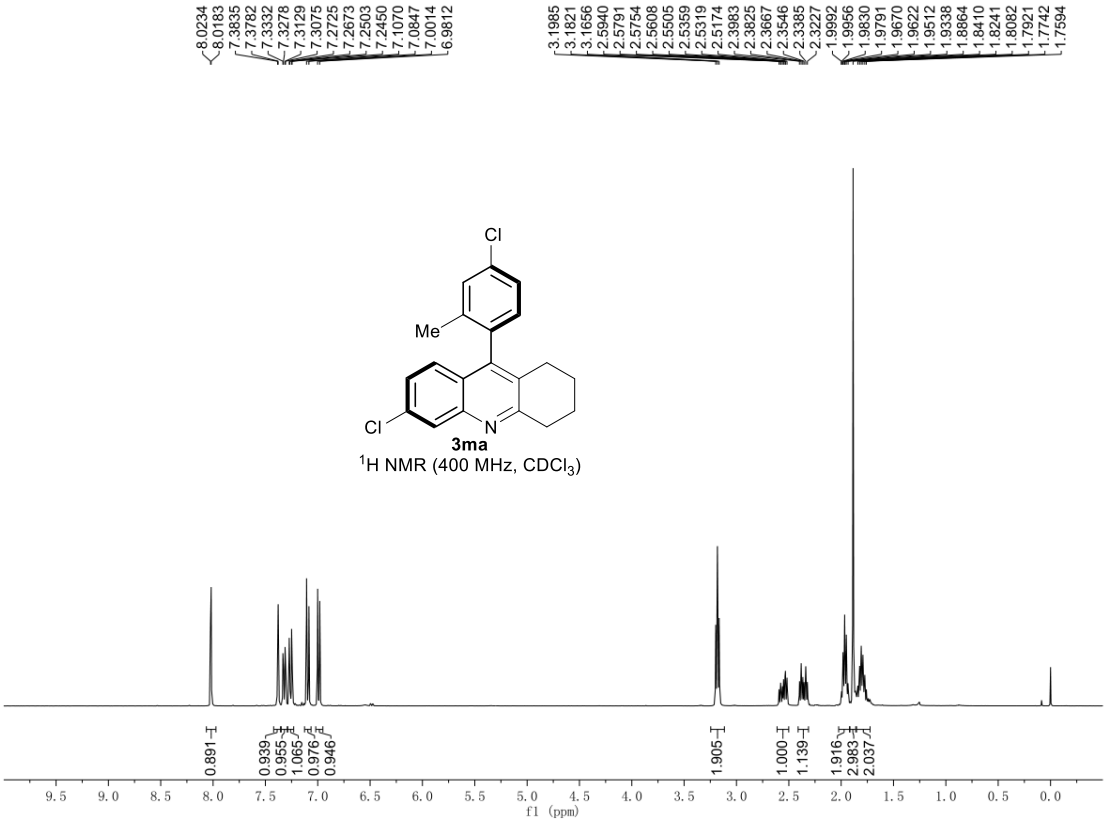

160.6838
146.7342
144.4825
140.1992
136.8307
134.5241
130.9504
129.4547
129.1308
128.8487
128.8068
128.4830
128.1512
127.6964
126.9297
126.2075
125.7266
125.6894
125.6521
125.6150
125.4468
125.2324
125.1965
125.1597
125.1230
124.3483
122.7427
120.0380
34.2283
27.6485
22.7710
22.7346
19.5349
CF3
Me
Cl
N
3ja
13C NMR (100 MHz, CDCl3)
f1 (ppm)

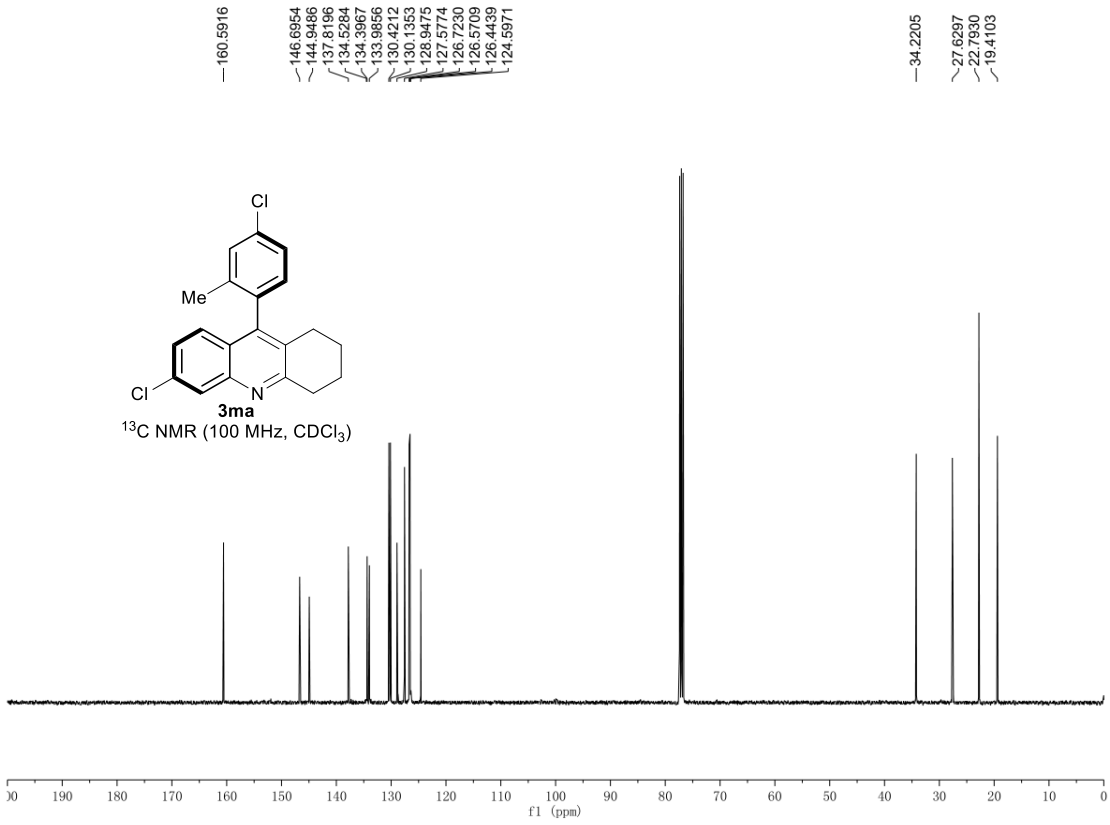

8.0829
8.0782
8.0629
8.0583
8.0400
8.0347
7.7699
7.7653
7.4741
7.4540
7.2683
7.2629
7.2461
7.2406
7.0707
7.0485
3.9006
3.2129
3.1965
3.1801
2.6160
2.6016
2.5972
2.5829
2.5726
2.5582
2.5537
2.5394
2.3789
2.3644
2.3473
2.3355
2.3209
2.3038
2.0045
1.9888
1.9725
1.9583
1.9423
1.8640
1.8475
1.8322
1.8191
1.8154
1.8046
1.7898
1.7859
1.7710
1.7562
CO2Me
Me
Cl
N
3ka
1H NMR (400 MHz, CDCl3)
1.923
0.960
1.004
1.003
0.995
3.000
2.012
1.083
1.090
5.014
2.069
f1 (ppm)

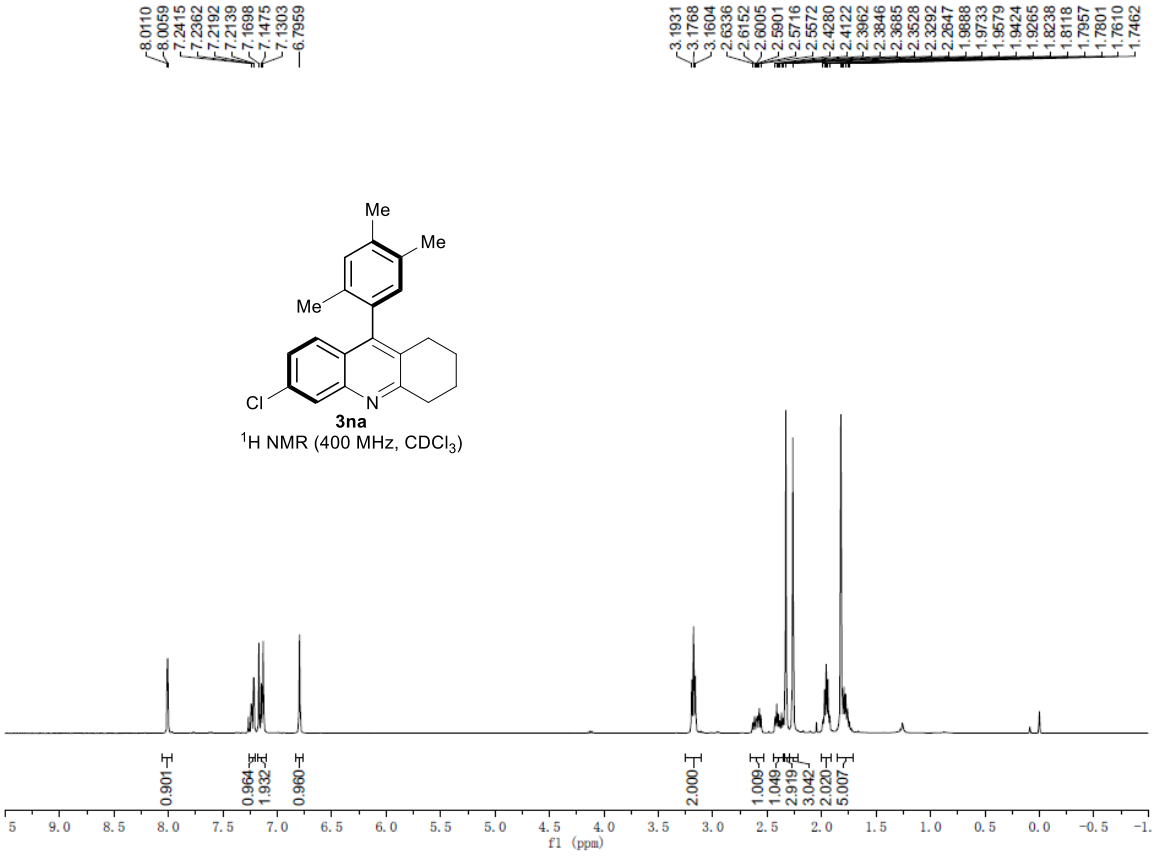

166.7358
160.6168
146.6757
145.0412
141.4547
136.3499
134.4088
130.6522
130.0737
129.5193
128.8851
128.5170
127.5727
126.7488
126.4103
124.5124
52.1449
34.2048
27.6365
22.7928
22.7564
19.7397
CO2Me
Me
Cl
N
3ka
13C NMR (100 MHz, CDCl3)
f1 (ppm)

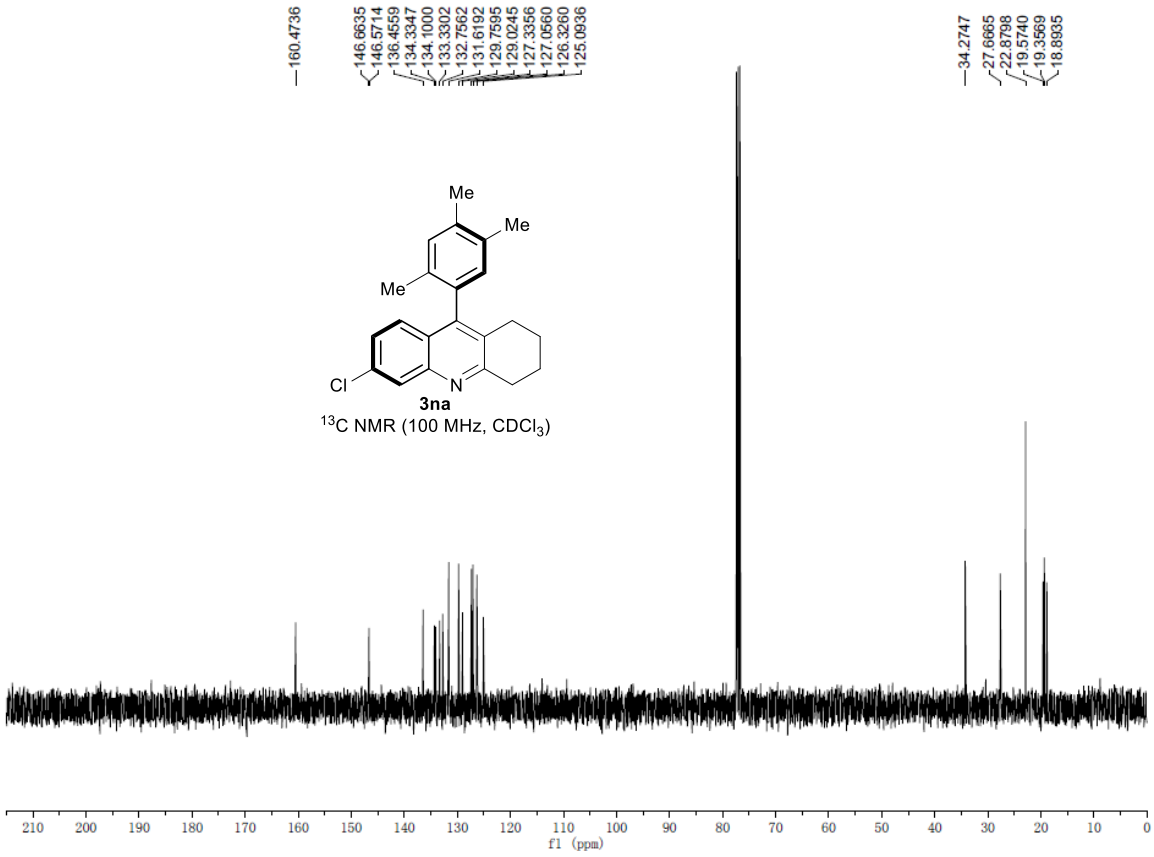

8.0184
8.0131
7.2381
7.2327
7.2157
7.2104
7.1830
7.1503
7.1442
7.1277
7.1218
6.9287
6.9096
3.1950
3.1786
3.1621
2.6142
2.5991
2.5956
2.5809
2.5708
2.5559
2.5521
2.5376
2.4192
2.4034
2.3877
2.3806
2.3759
2.3600
2.3442
1.9863
1.9833
1.9704
1.9672
1.9543
1.9387
1.9223
1.8578
1.8215
1.8097
1.8053
1.7902
1.7741
1.7601
1.7560
1.7412
Me
Me
Cl
N
3la
1H NMR (400 MHz, CDCl3)
0.922
1.036
0.972
1.932
0.966
2.000
1.071
2.907
1.083
2.055
2.901
2.007
f1 (ppm)

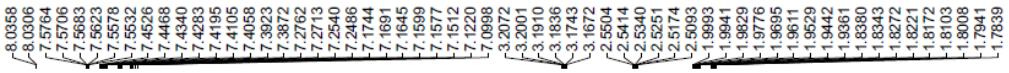

160.5053
146.6920
146.4409
137.9220
135.4398
134.1592
133.0370
131.1354
129.0846
128.6629
127.3943
126.9939
126.9152
126.3957
125.0664
34.2526
27.6439
22.8661
21.2677
19.4088
Me
Me
Cl
N
3la
13C NMR (100 MHz, CDCl3)
f1 (ppm)

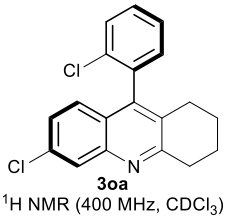

8.0234
8.0183
7.3835
7.3782
7.3332
7.3278
7.3129
7.3075
7.2725
7.2673
7.2503
7.2450
7.1070
7.0847
7.0014
6.9812
3.1985
3.1821
3.1656
2.5940
2.5791
2.5754
2.5608
2.5505
2.5359
2.5319
2.5174
2.3983
2.3825
2.3667
2.3546
2.3385
2.3227
1.9992
1.9956
1.9830
1.9791
1.9670
1.9622
1.9512
1.9338
1.8864
1.8410
1.8241
1.8082
1.7921
1.7742
1.7594
Cl
Me
Cl
N
3ma
1H NMR (400 MHz, CDCl3)
0.891
0.939
0.955
1.065
0.976
0.946
1.905
1.000
1.139
1.916
2.983
2.037
f1 (ppm)


160.5916
146.6954
144.9486
137.8196
134.5284
134.3967
133.9856
130.4212
130.1353
128.9475
127.5774
126.7230
126.5709
126.4439
124.5971
34.2205
27.6297
22.7930
19.4103
Cl
Me
Cl
N
3ma
13C NMR (100 MHz, CDCl3)
f1 (ppm)


8.0110
8.0059
7.2415
7.2362
7.2192
7.2139
7.1698
7.1475
7.1303
6.7959
3.1931
3.1768
3.1604
2.6336
2.6152
2.6005
2.5901
2.5716
2.5572
2.4280
2.4122
2.3962
2.3846
2.3685
2.3528
2.3292
2.2647
1.9888
1.9733
1.9579
1.9424
1.9265
1.8238
1.8118
1.7957
1.7801
1.7610
1.7462
Me
Me
Me
Cl
N
3na
1H NMR (400 MHz, CDCl3)
0.901
0.964
1.932
0.960
2.000
1.009
1.049
2.919
3.042
2.020
5.007
f1 (ppm)

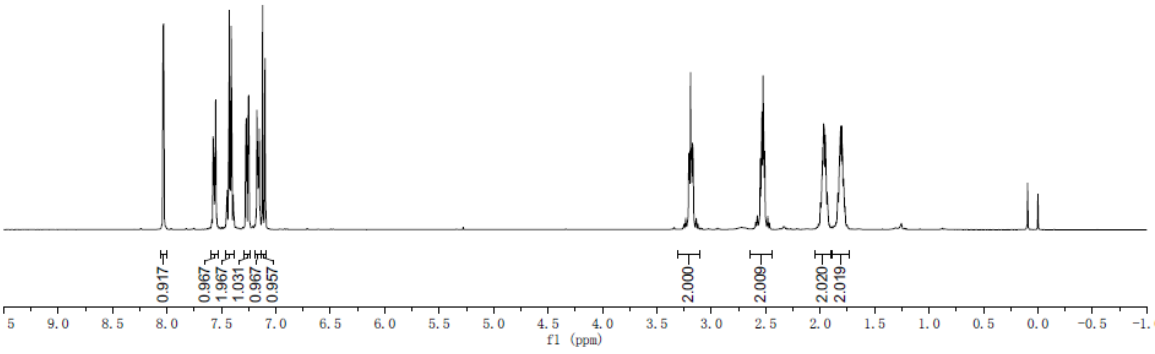

160.4736
146.6635
146.5714
136.4559
134.3347
134.1000
133.3302
132.7562
131.6192
129.7595
129.0245
127.3356
127.0560
126.3260
125.0936
34.2747
27.6665
22.8798
19.5740
19.3569
18.8935
Me
Me
Me
Cl
N
3na
13C NMR (100 MHz, CDCl3)
f1 (ppm)

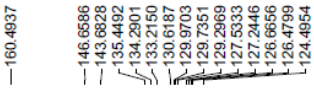


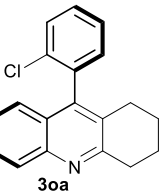


3oa

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

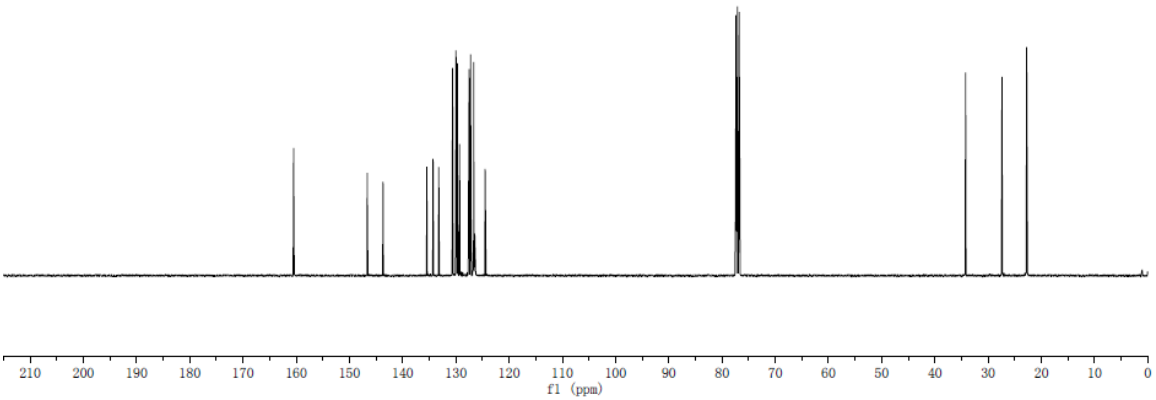


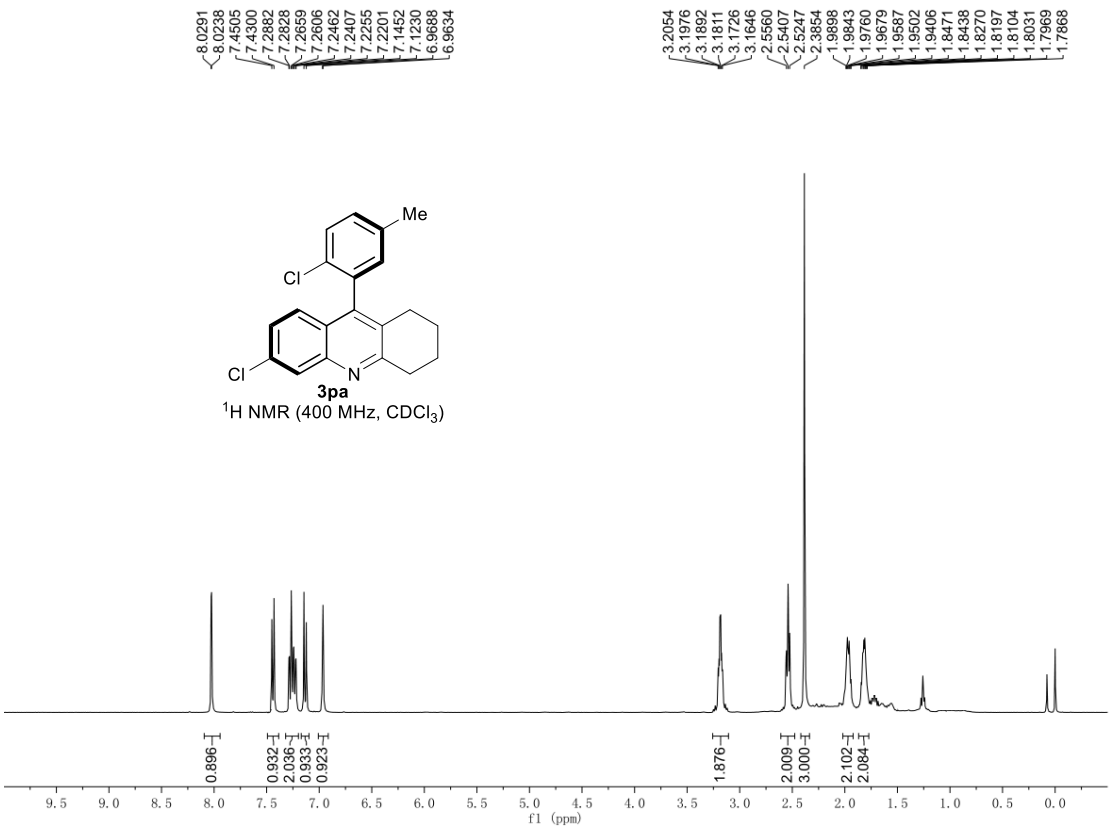




3oa

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




8.0291
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7.2201
7.1452
7.1230
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6.9634
3.2054
3.1976
3.1892
3.1811
3.1726
3.1646
2.5560
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2.5247
2.3854
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1.9843
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1.9679
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1.9502
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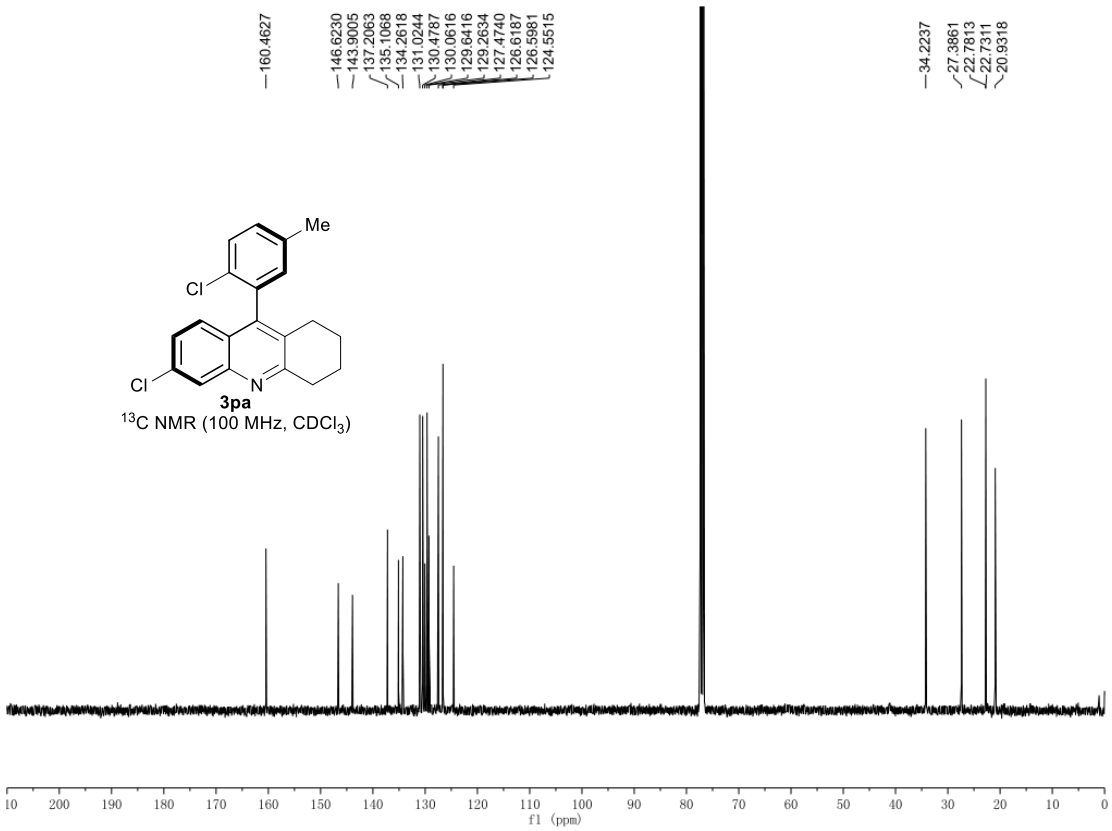
1.8471
1.8438
1.8270
1.8197
1.8104
1.8031
1.7969
1.7868
Me
Cl
Cl
N
3pa
1H NMR (400 MHz, CDCl3)
0.896
0.932
2.036
0.933
0.923
1.876
2.009
3.000
2.102
2.084
f1 (ppm)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22.7311
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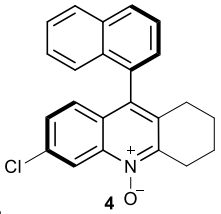
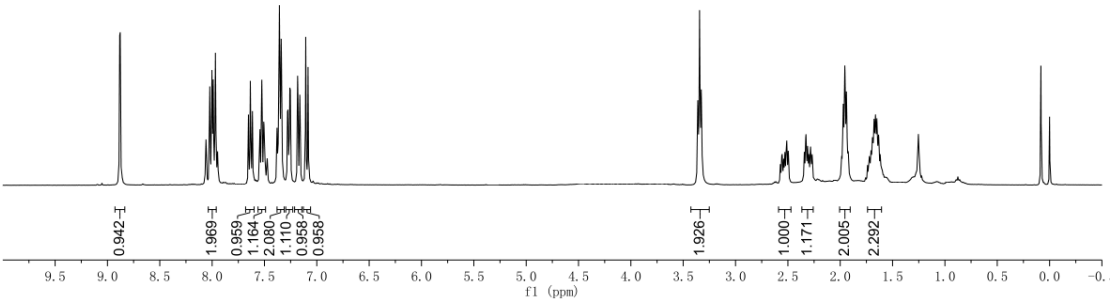
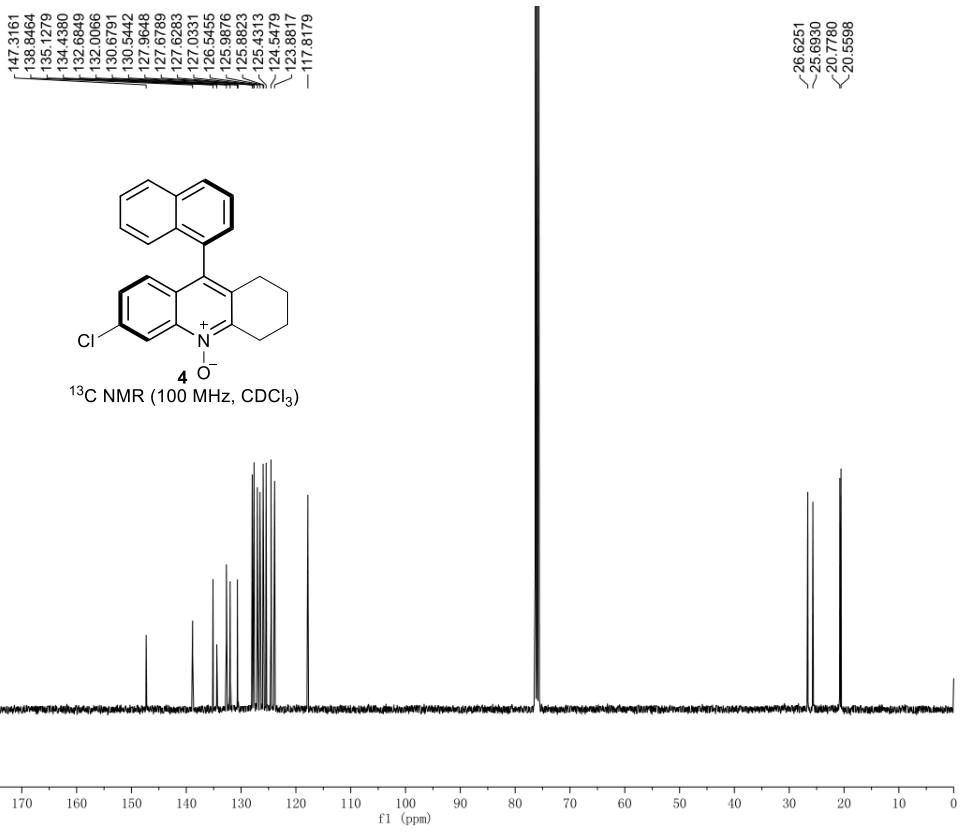
Me
Cl
Cl
N
3pa
13C NMR (100 MHz, CDCl3)
f1 (ppm)

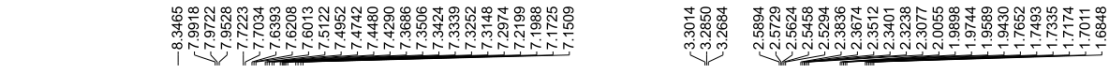


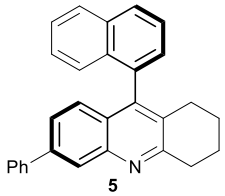
^{1}H NMR (400 MHz, $CDCl_3$)





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





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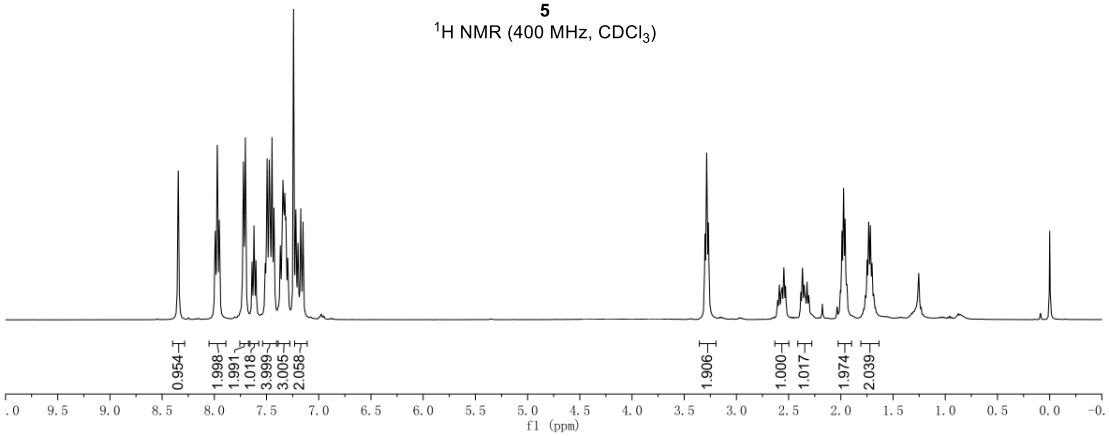
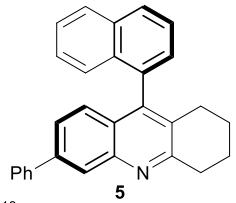
^{1}H NMR (400 MHz, $CDCl_3$)





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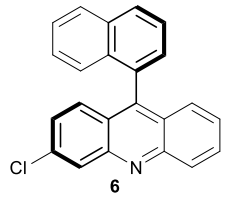
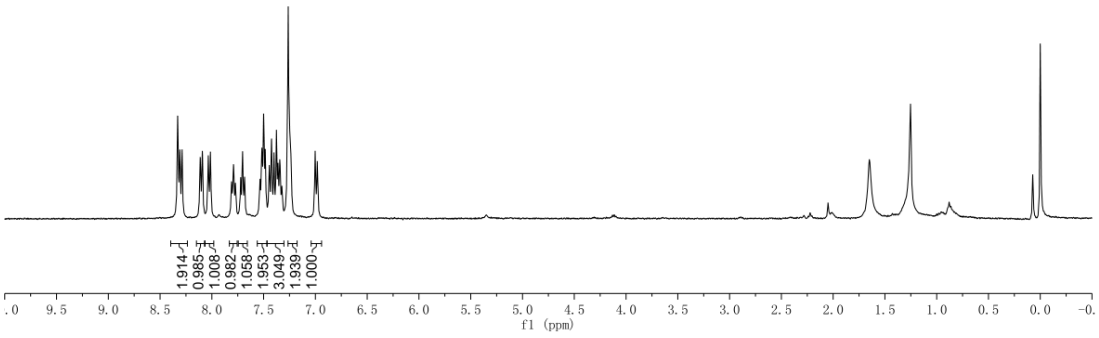
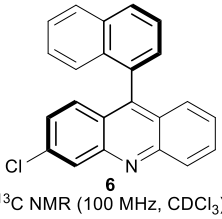
^{13}C NMR (100 MHz, $CDCl_3$)



6

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

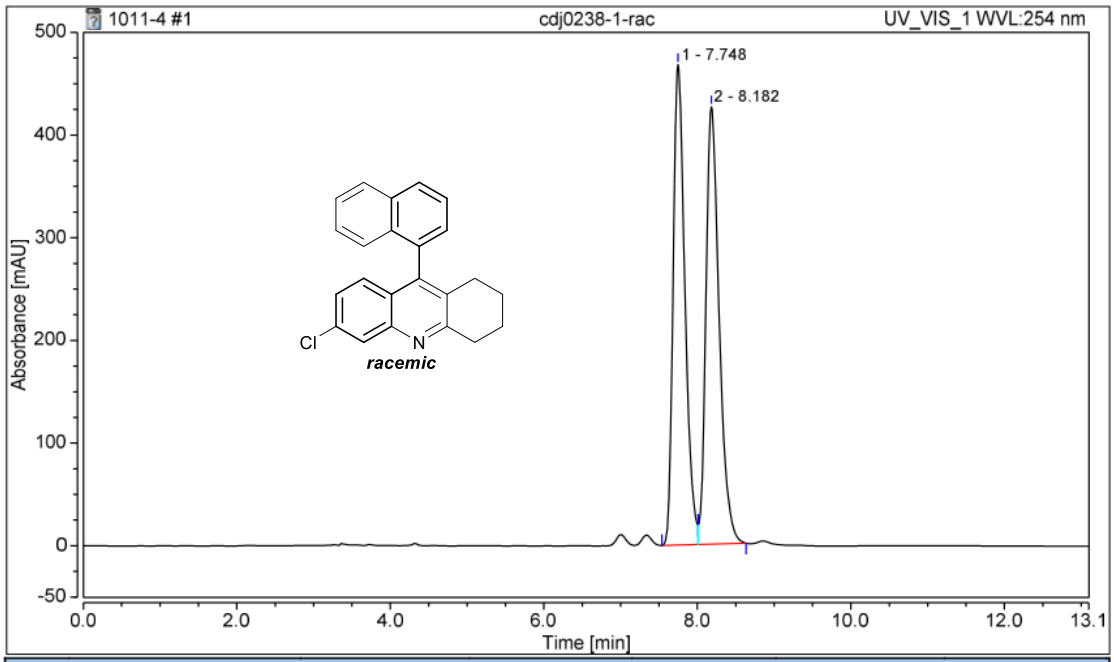




6

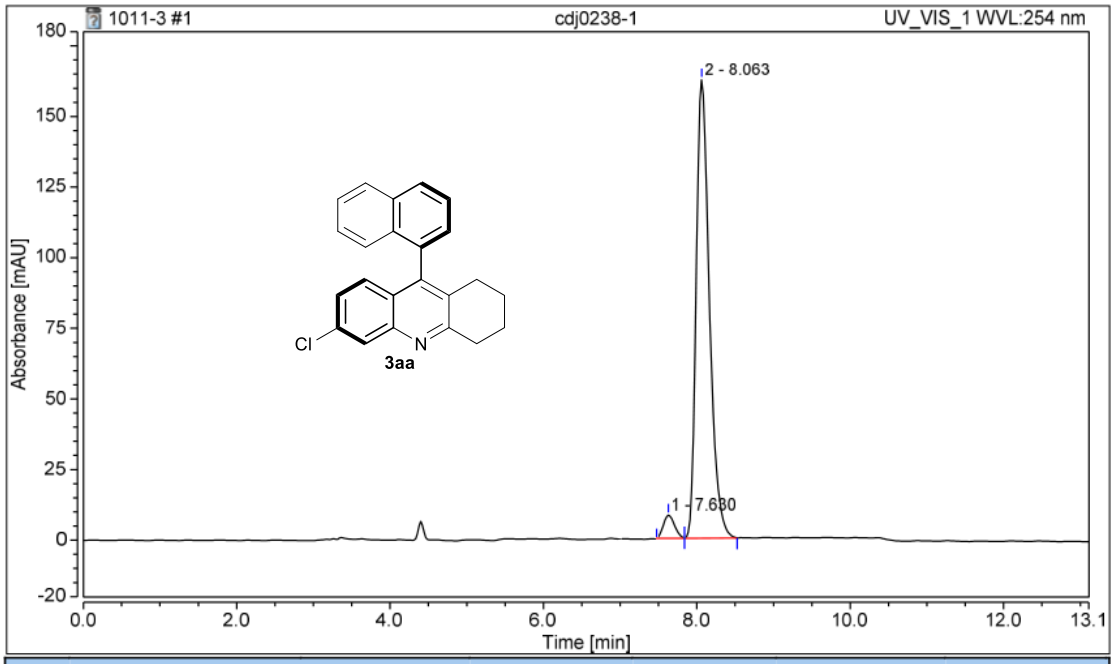
^{13}C NMR (100 MHz, $CDCl_3$)

HPLC Traces



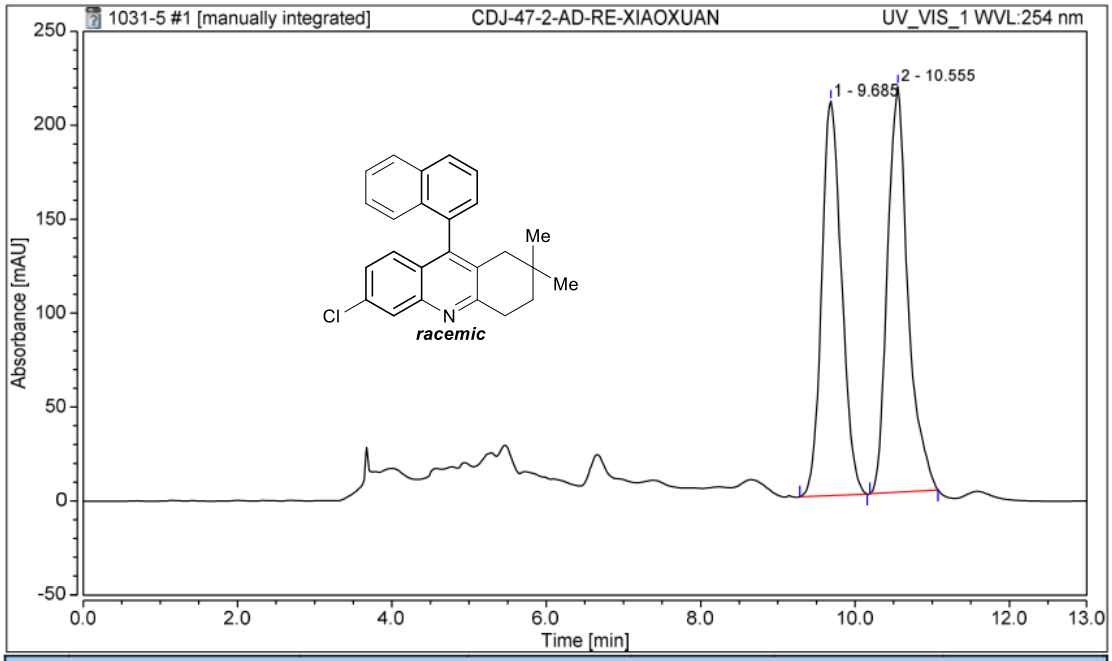
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	7.748	83.183	468.021	49.42	1.38	0.28
2	8.182	85.124	426.153	50.58	1.35	0.31
Total:		**168.307**	**894.173**	**100.00**		



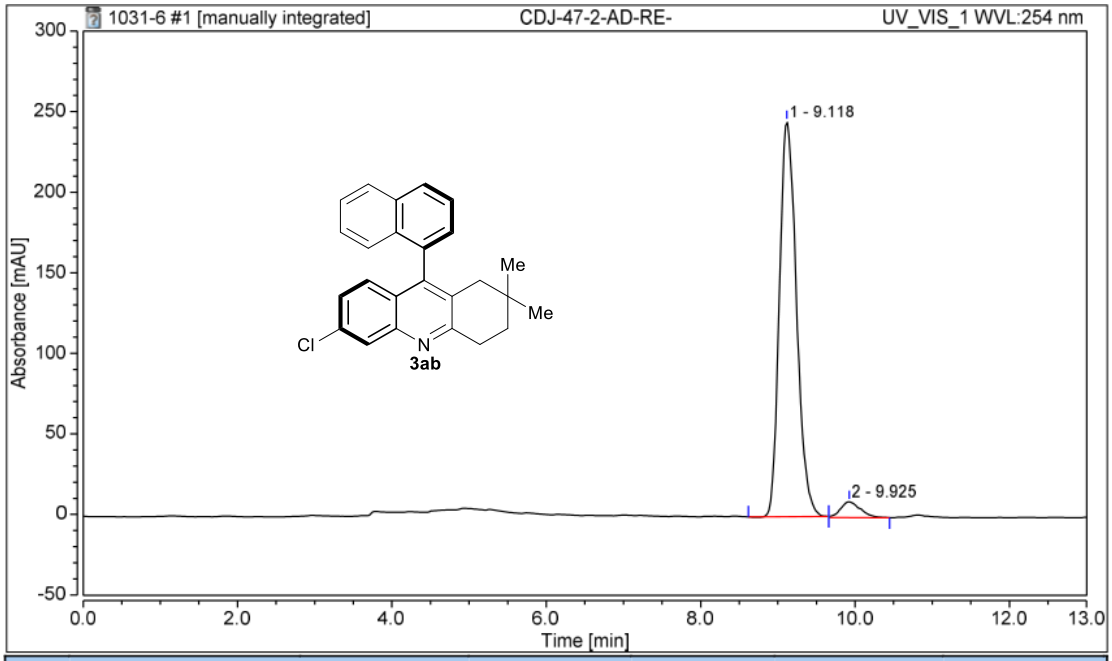
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	7.630	1.380	8.189	4.09	1.15	0.27
2	8.063	32.362	162.274	95.91	1.39	0.31
Total:		**33.742**	**170.463**	**100.00**		



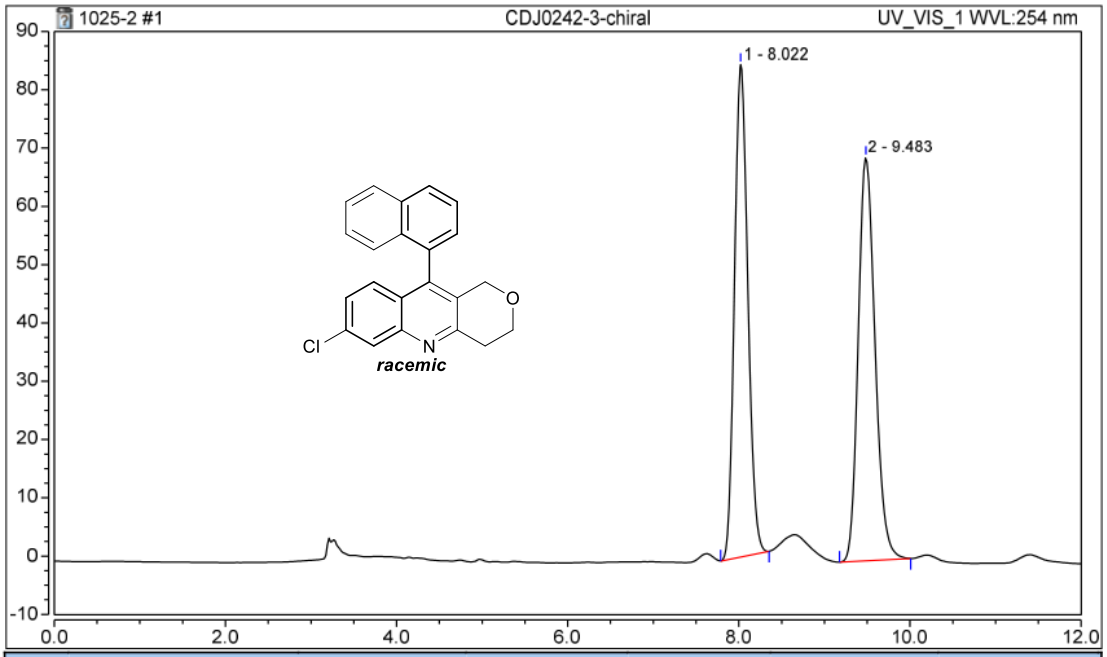
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	9.685	62.749	210.040	48.46	1.13	0.45
2	10.555	66.745	216.242	51.54	1.25	0.44
Total:		**129.495**	**426.282**	**100.00**		



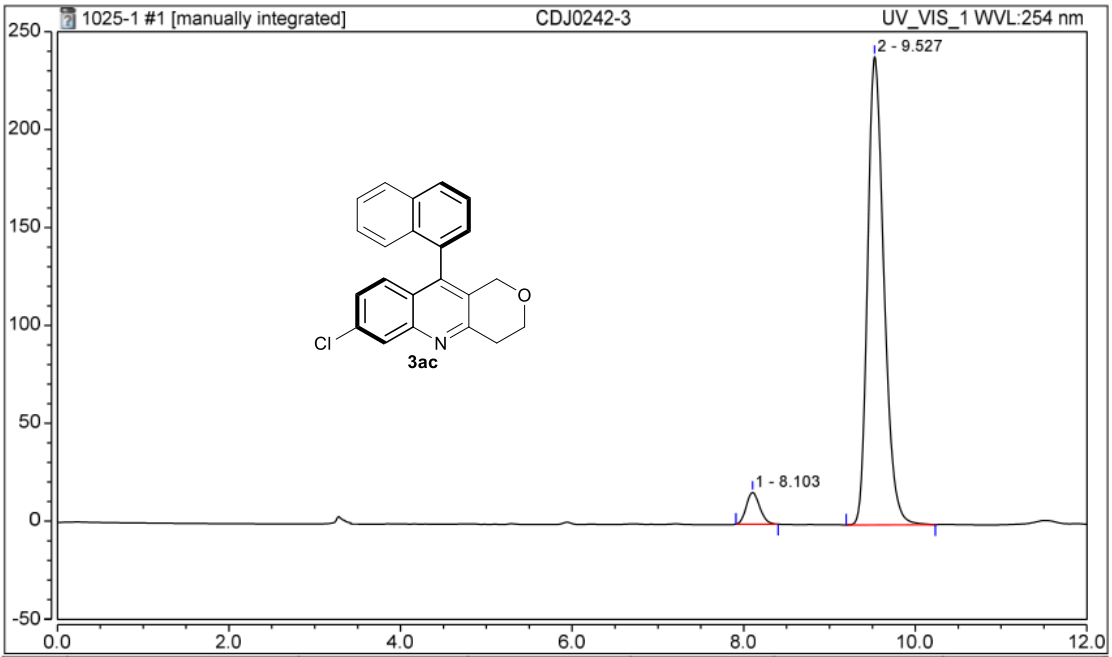
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	9.118	62.733	245.102	95.59	1.23	0.50
2	9.925	2.892	9.725	4.41	n.a.	0.43
Total:		**65.626**	**254.827**	**100.00**		



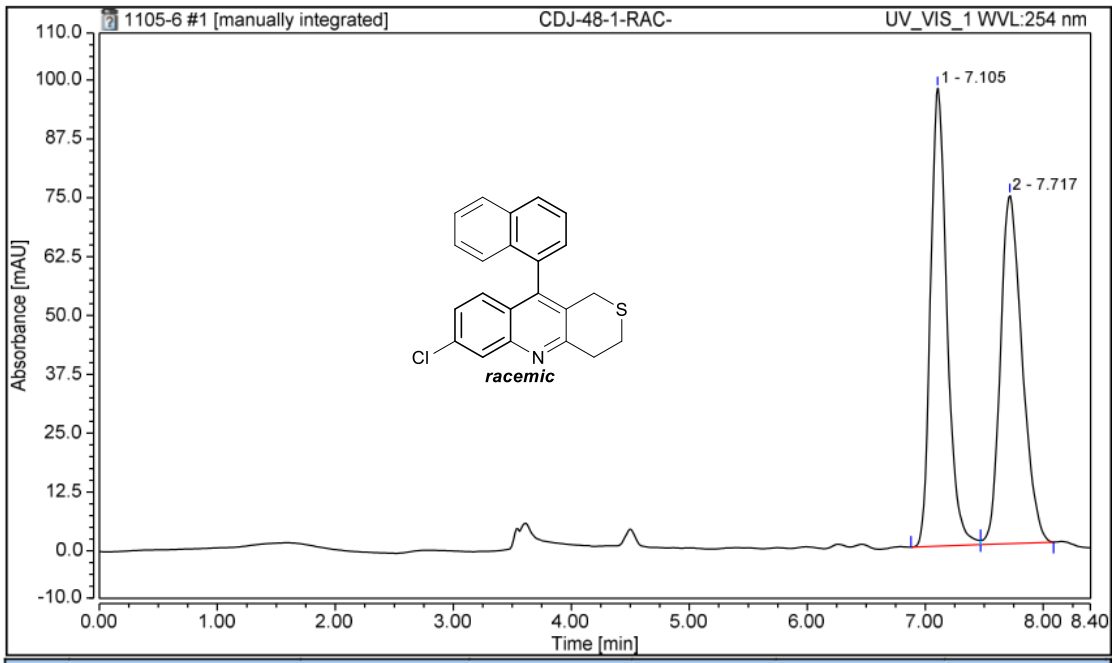
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	8.022	15.206	84.537	49.17	1.15	0.28
2	9.483	15.718	69.221	50.83	1.21	0.36
Total:		**30.924**	**153.758**	**100.00**		



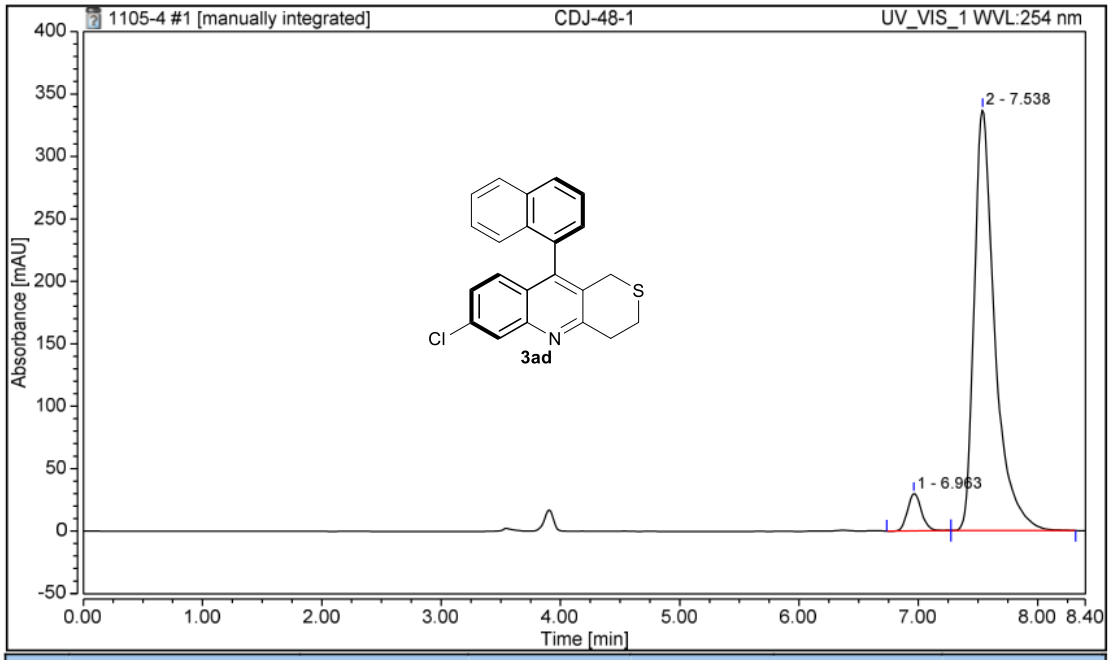
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	8.103	2.953	16.299	5.27	1.14	0.29
2	9.527	53.087	239.158	94.73	1.27	0.34
Total:		**56.039**	**255.457**	**100.00**		



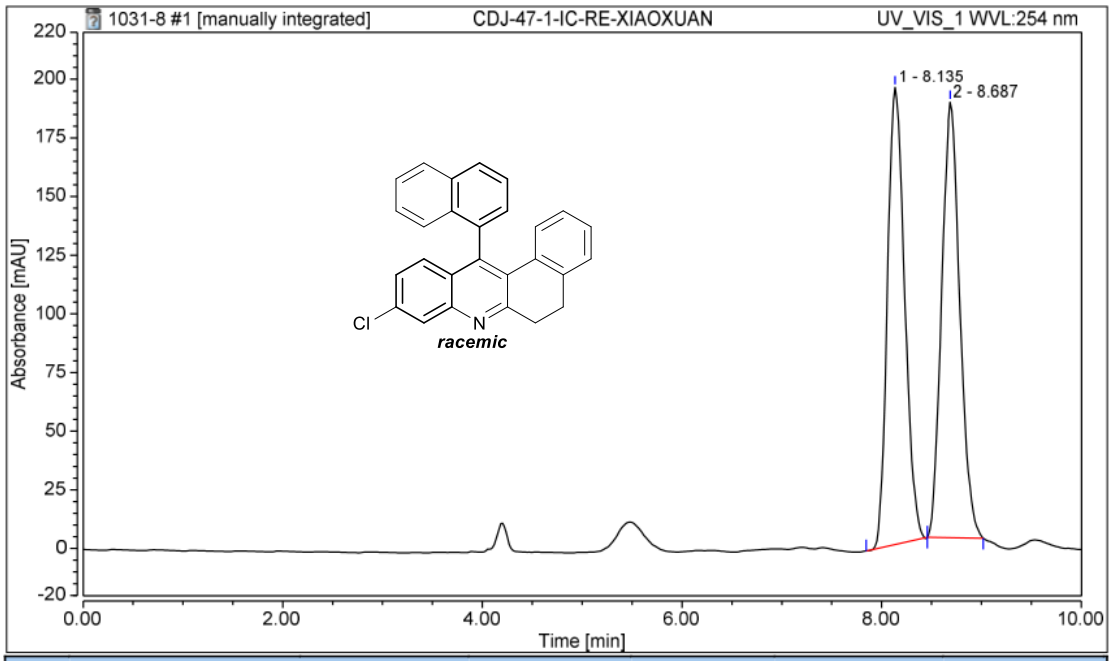
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	7.105	15.659	97.336	49.77	1.29	0.24
2	7.717	15.806	74.080	50.23	1.25	0.32
Total:		**31.465**	**171.416**	**100.00**		



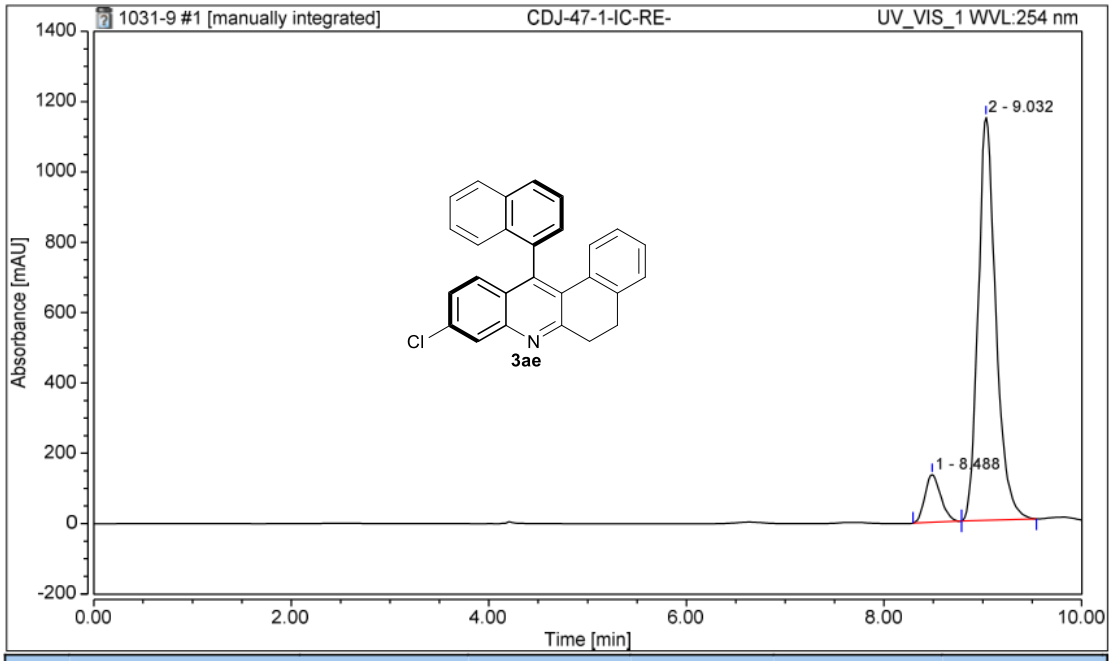
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	6.963	3.994	29.872	5.58	1.14	0.21
2	7.538	67.542	337.078	94.42	1.60	0.29
Total:		**71.536**	**366.950**	**100.00**		



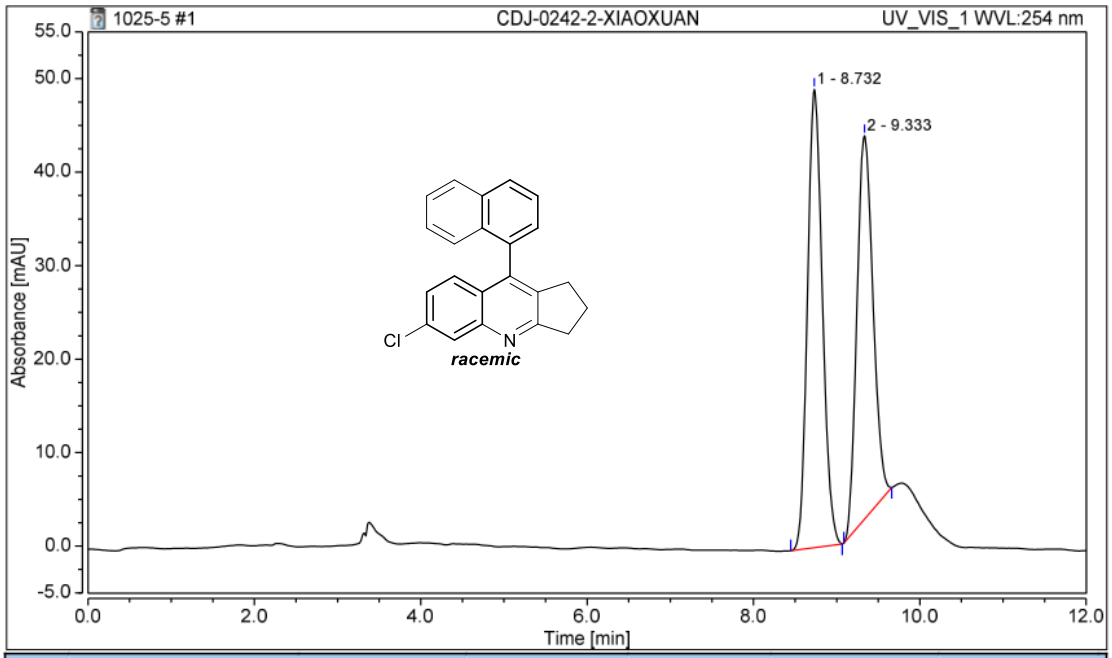
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	8.135	38.689	194.888	49.82	1.20	0.30
2	8.687	38.962	185.792	50.18	1.15	0.35
Total:		**77.651**	**380.680**	**100.00**		



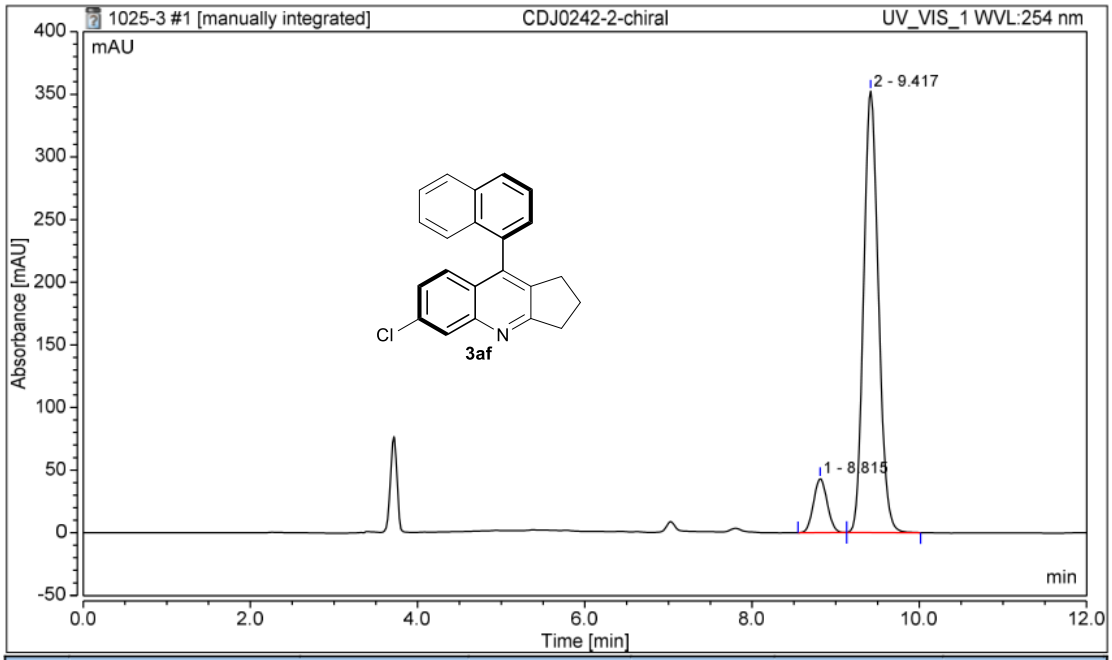
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	8.488	24.874	134.761	9.46	1.18	0.29
2	9.032	238.190	1146.390	90.54	1.26	0.30
Total:		**263.064**	**1281.151**	**100.00**		



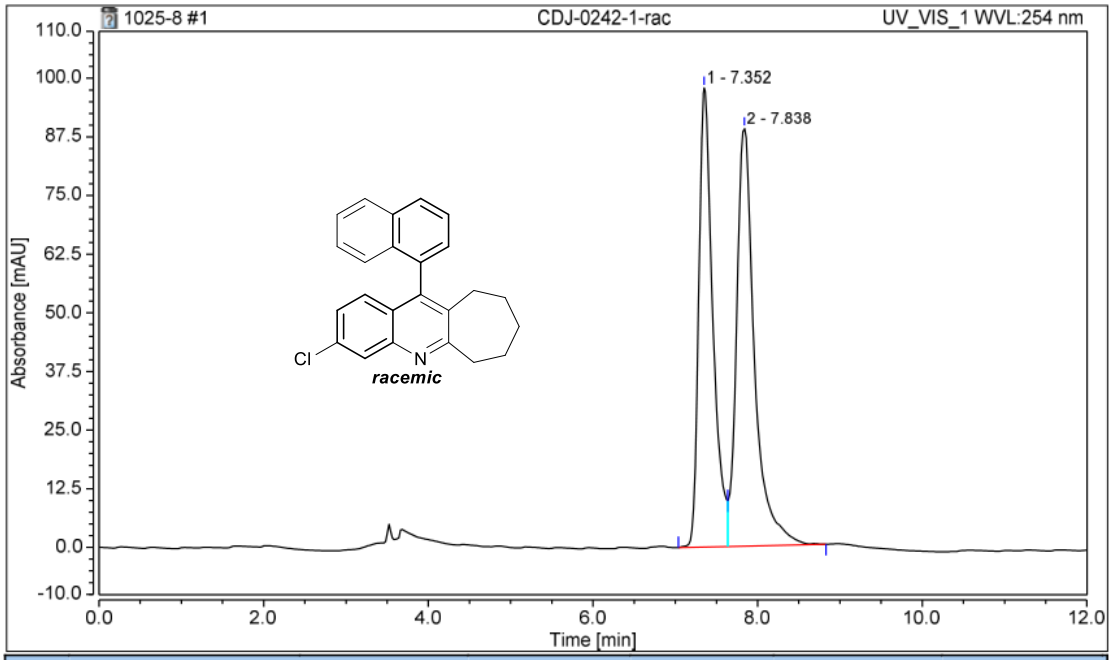
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	8.732	10.153	49.049	52.53	1.15	0.32
2	9.333	9.175	41.025	47.47	1.15	0.36
Total:		**19.328**	**90.074**	**100.00**		



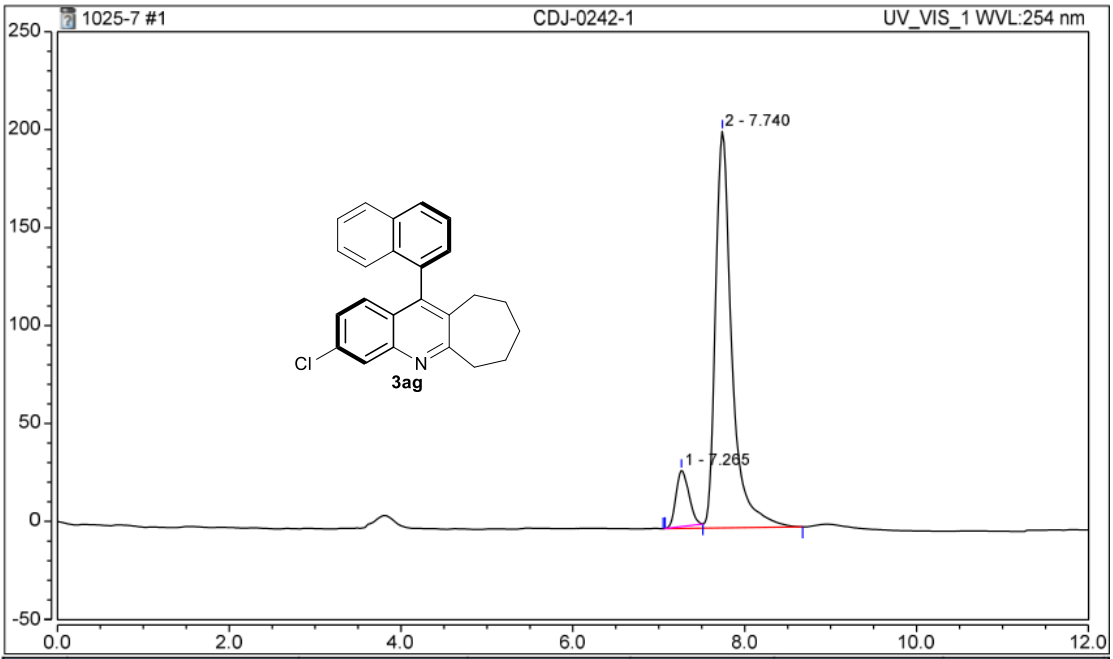
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	8.815	8.136	43.043	10.11	1.06	0.30
2	9.417	72.347	352.439	89.89	1.13	0.33
Total:		**80.483**	**395.482**	**100.00**		



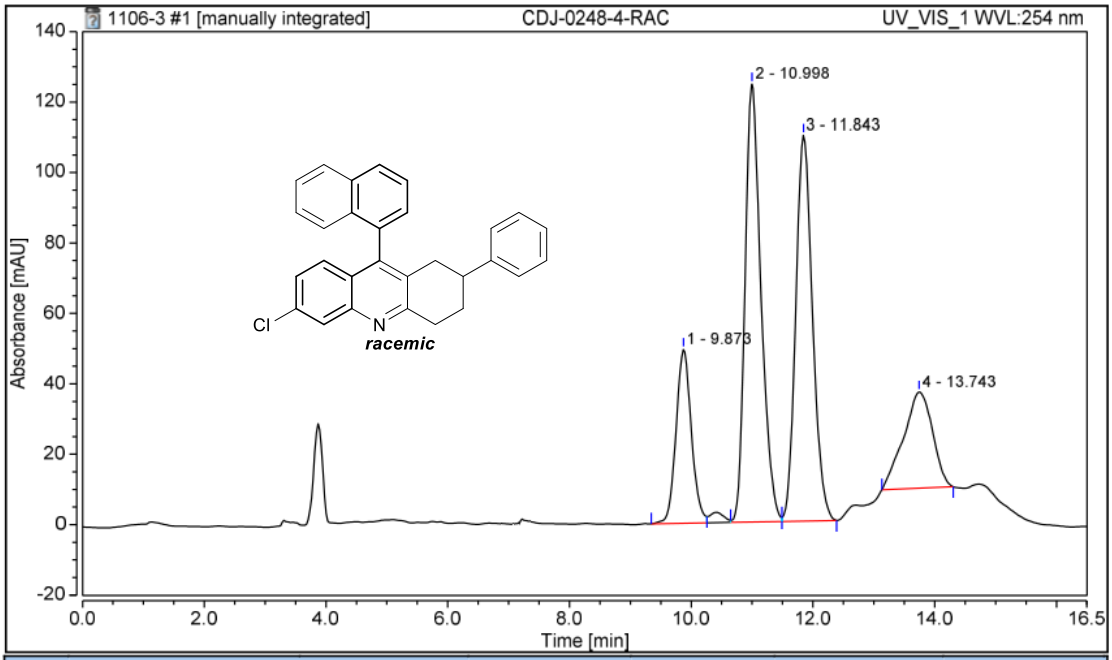
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	7.352	19.385	97.895	46.28	n.a.	0.29
2	7.838	22.501	89.051	53.72	n.a.	0.35
Total:		**41.885**	**186.947**	**100.00**		



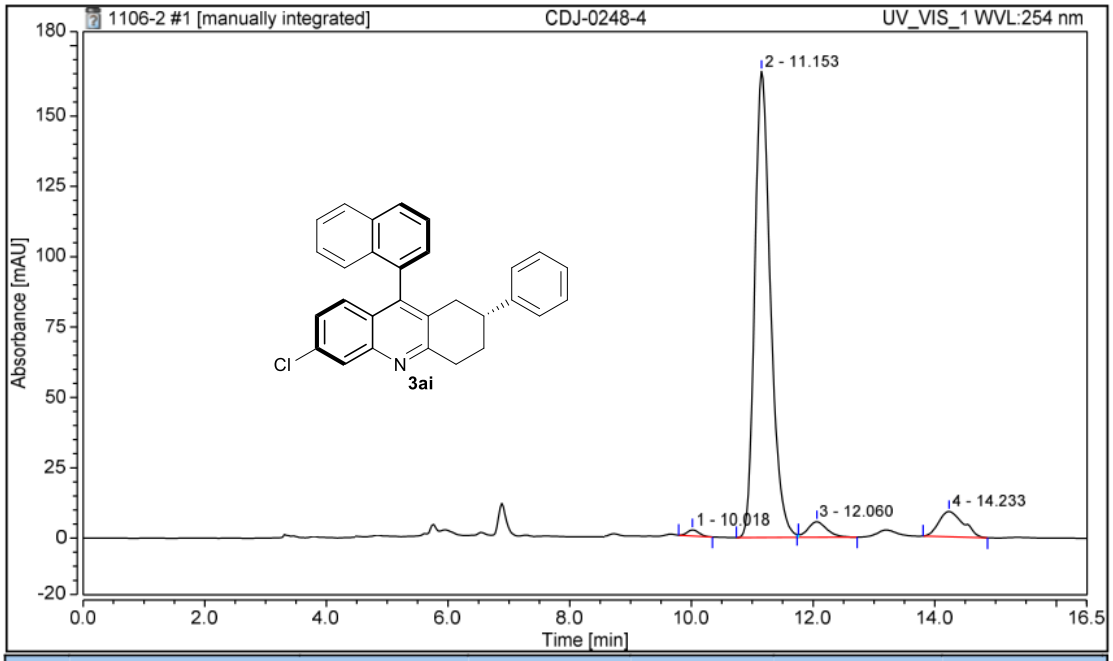
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	7.265	4.923	28.669	9.84	n.a.	n.a.
2	7.740	45.128	202.541	90.16	1.55	0.31
Total:		**50.051**	**231.210**	**100.00**		



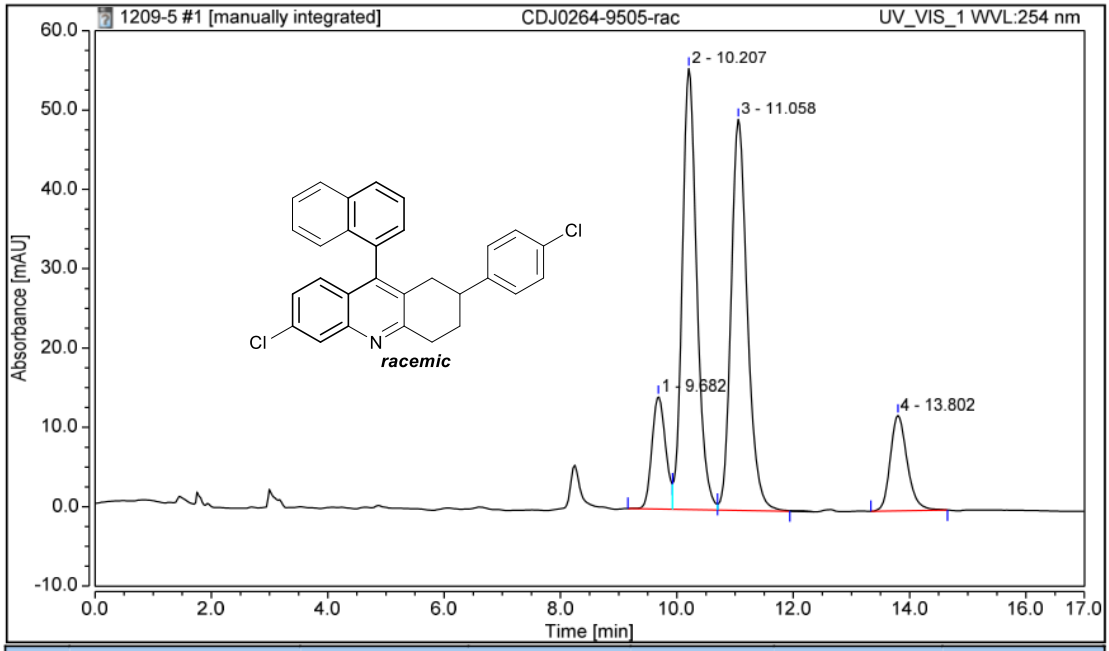
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	9.873	14.415	49.400	14.11	1.11	0.45
2	10.998	37.722	124.412	36.93	1.28	0.46
3	11.843	34.946	109.596	34.22	1.17	0.52
4	13.743	15.052	27.353	14.74	0.91	0.92
Total:		**102.136**	**310.762**	**100.00**		



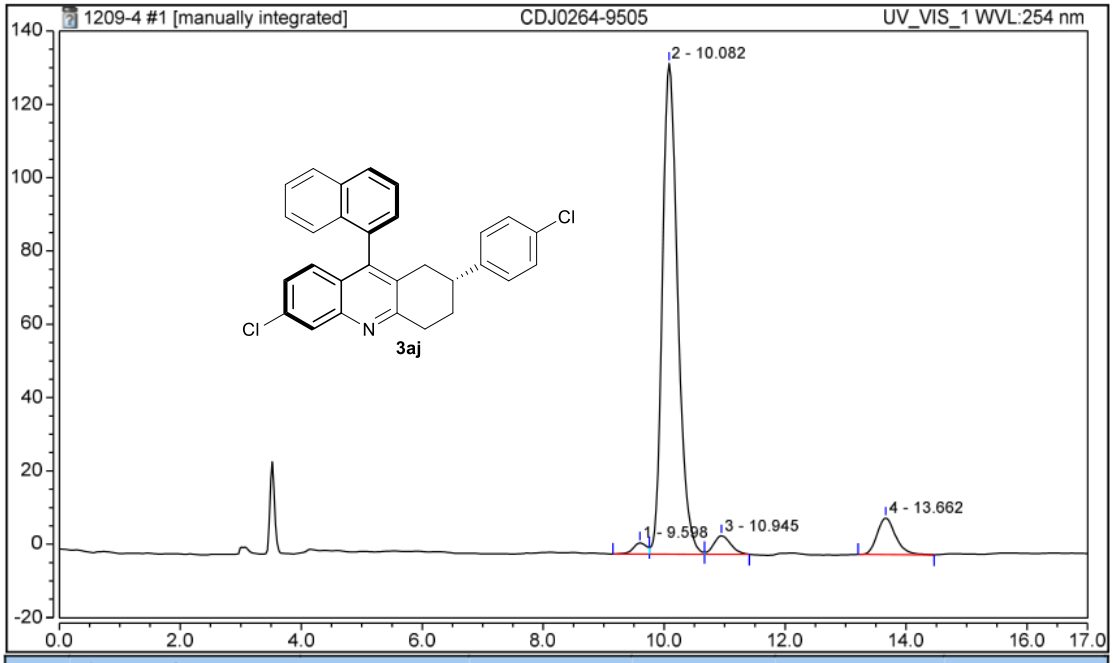
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	10.018	0.468	2.131	0.83	1.13	0.34
2	11.153	49.944	165.678	88.24	1.28	0.45
3	12.060	2.004	5.513	3.54	n.a.	0.58
4	14.233	4.184	8.950	7.39	1.21	0.74
Total:		**56.600**	**182.271**	**100.00**		



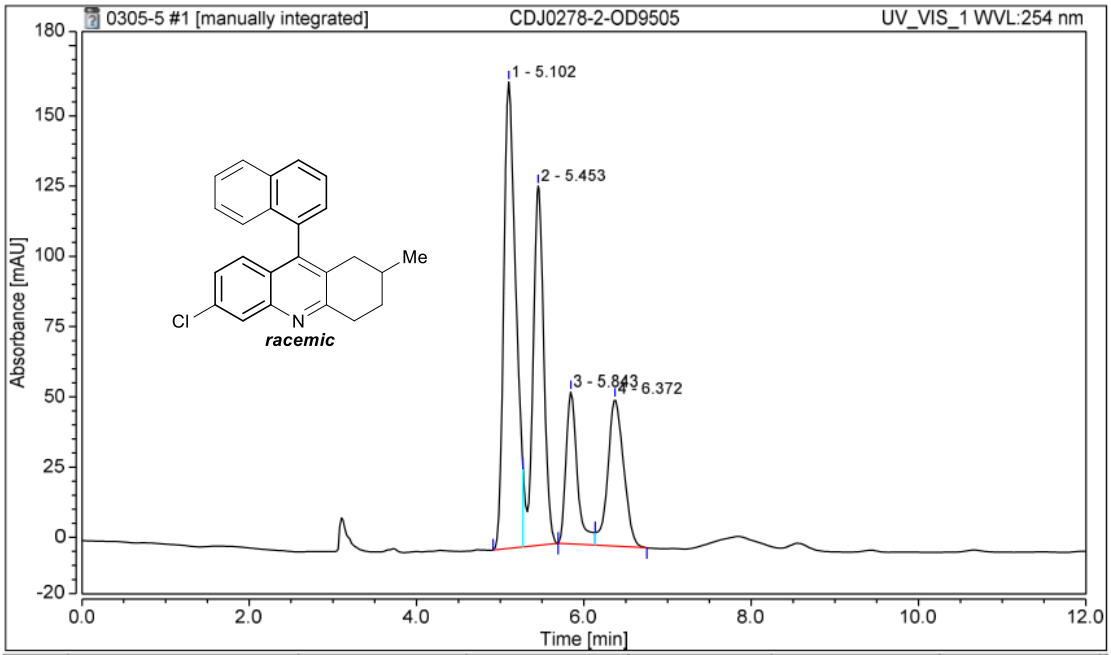
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	9.682	3.858	14.188	9.64	n.a.	0.44
2	10.207	16.127	55.607	40.29	n.a.	0.45
3	11.058	15.968	49.304	39.89	1.23	0.50
4	13.802	4.077	12.057	10.19	1.21	0.52
Total:		**40.030**	**131.156**	**100.00**		



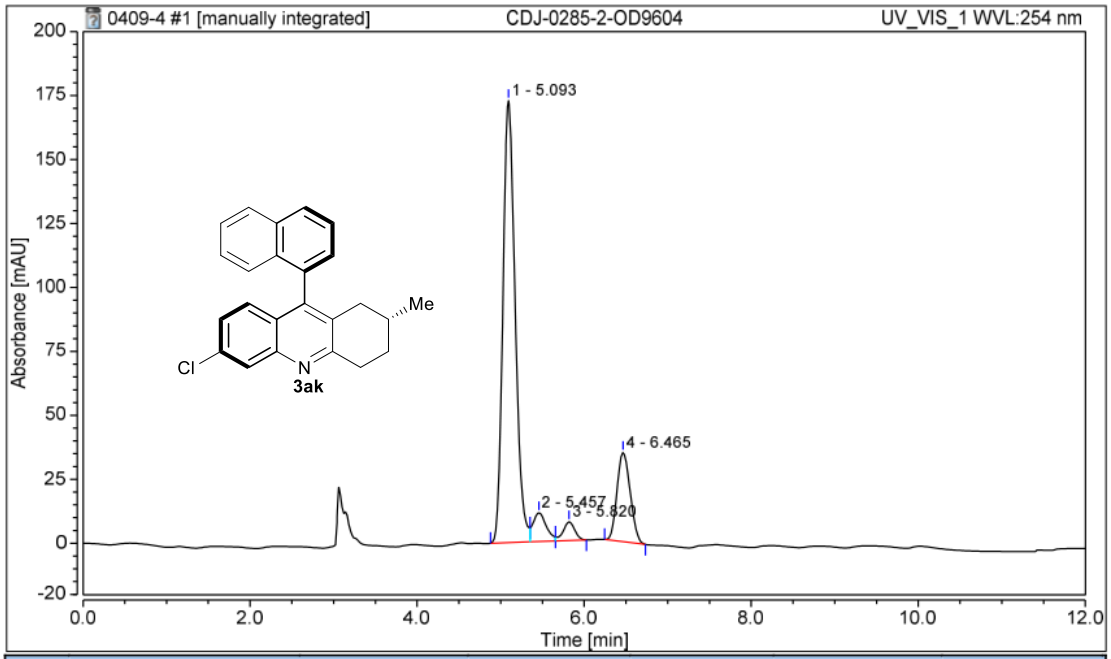
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	9.598	0.793	3.055	1.75	n.a.	0.49
2	10.082	39.503	133.931	86.90	1.27	0.46
3	10.945	1.635	5.024	3.60	n.a.	0.51
4	13.662	3.526	9.967	7.76	1.22	0.55
Total:		**45.457**	**151.977**	**100.00**		



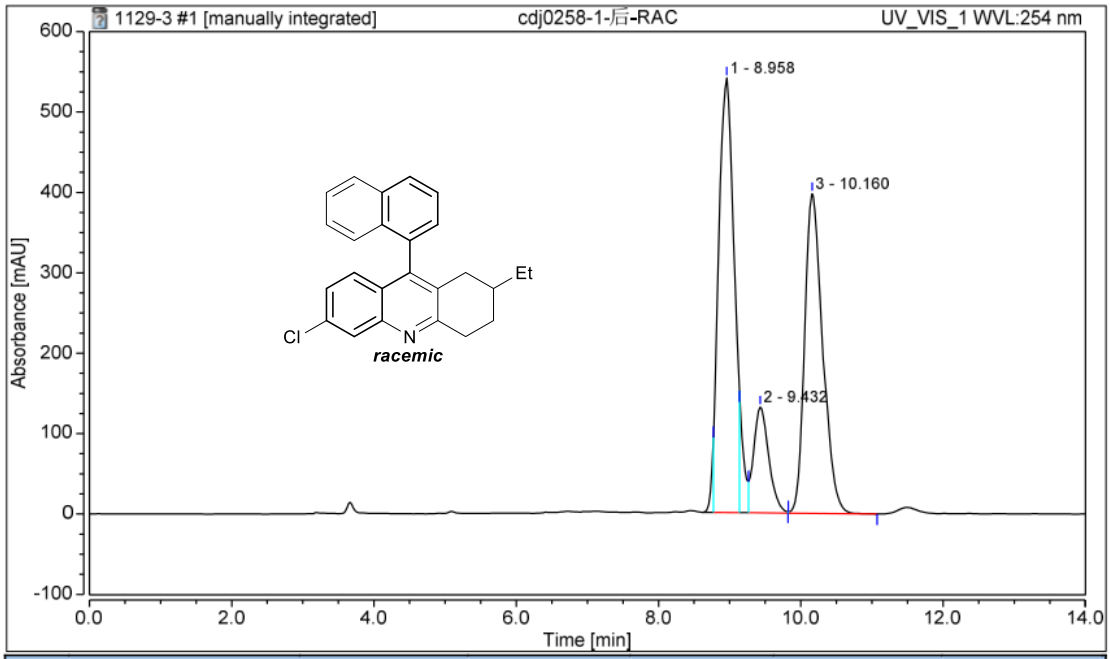
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	5.102	23.542	165.999	35.27	n.a.	0.27
2	5.453	23.243	127.965	34.82	n.a.	0.23
3	5.843	9.893	54.133	14.82	n.a.	0.23
4	6.372	10.065	52.259	15.08	n.a.	0.34
Total:		**66.744**	**400.356**	**100.00**		



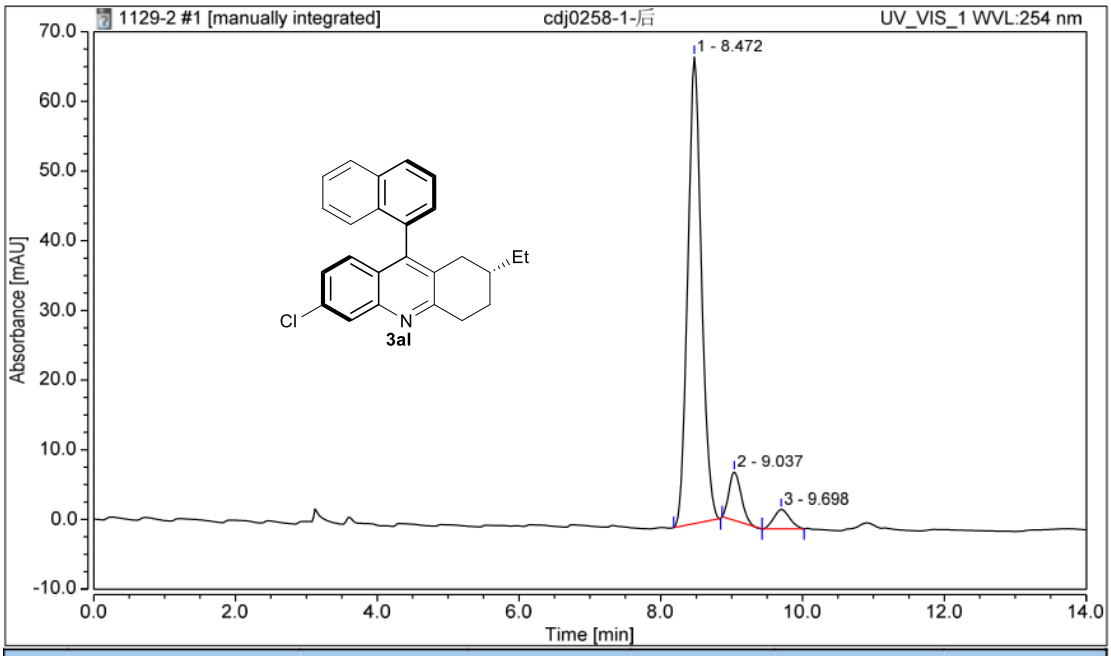
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	5.093	29.232	172.834	75.25	1.22	0.27
2	5.457	2.054	11.279	5.29	n.a.	0.31
3	5.820	1.177	7.302	3.03	n.a.	0.25
4	6.465	6.383	34.882	16.43	1.13	0.30
Total:		**38.846**	**226.296**	**100.00**		



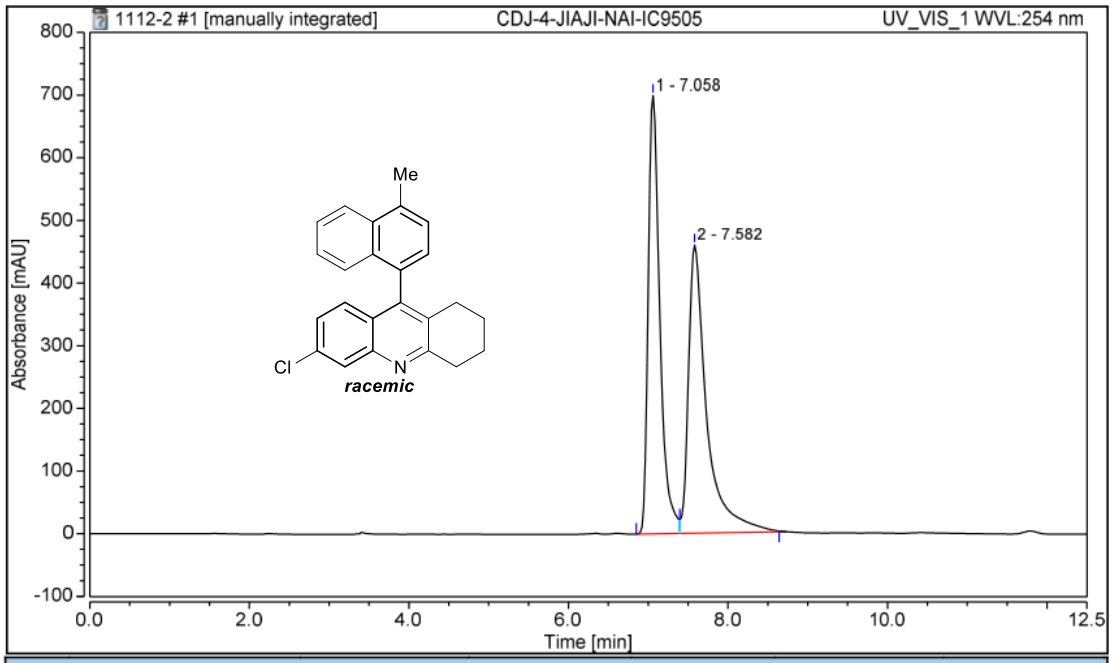
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	8.958	128.773	540.529	46.90	n.a.	0.43
2	9.432	128.773	131.718	11.60	n.a.	0.39
3	10.160	128.773	397.550	41.50	1.30	0.46
Total:		**386.319**	**1069.797**	**100.00**		



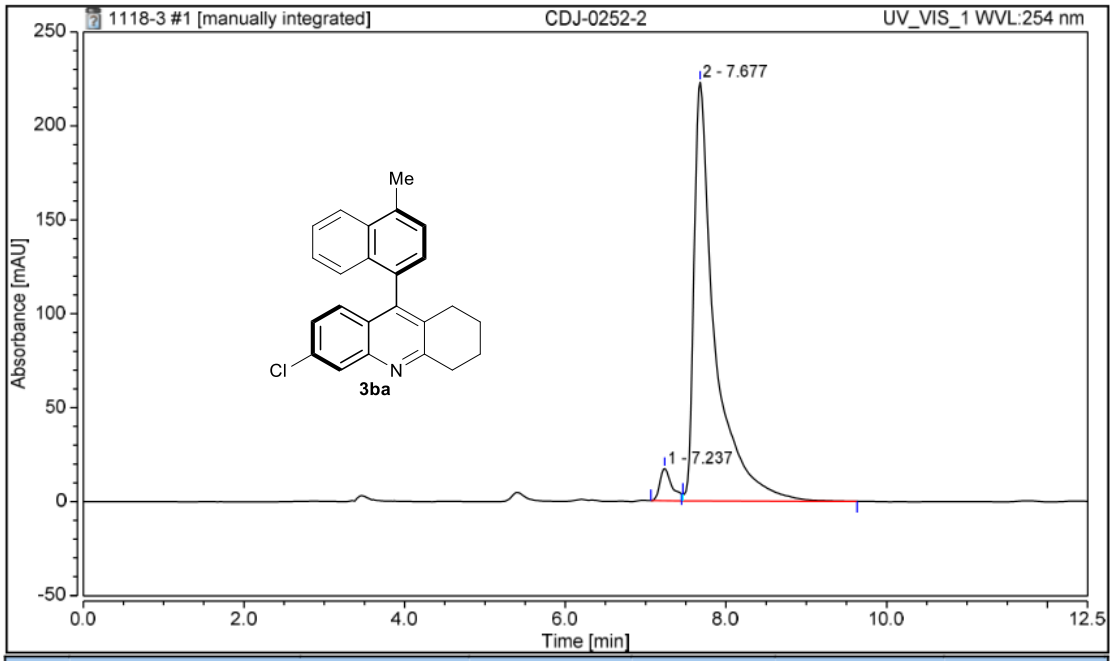
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	8.472	14.988	67.026	87.68	1.12	0.37
2	9.037	1.388	6.945	8.12	1.22	0.32
3	9.698	0.717	2.763	4.20	1.15	0.42
Total:		**17.093**	**76.734**	**100.00**		



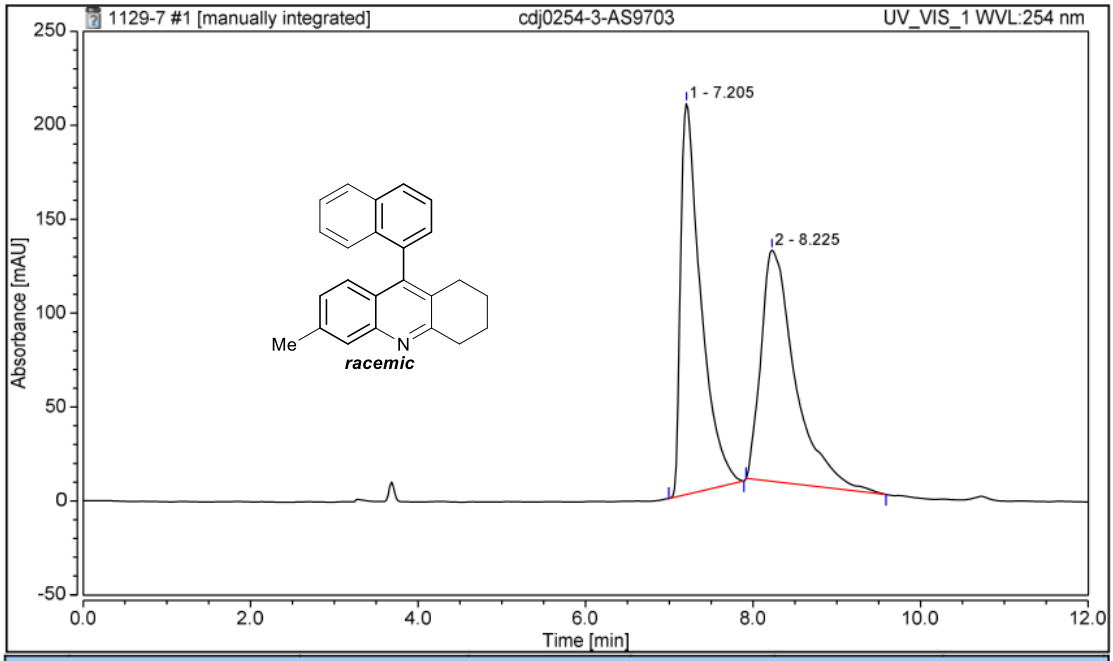
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	7.058	118.124	699.523	49.37	1.62	0.25
2	7.582	121.148	460.024	50.63	2.09	0.34
Total:		**239.272**	**1159.548**	**100.00**		



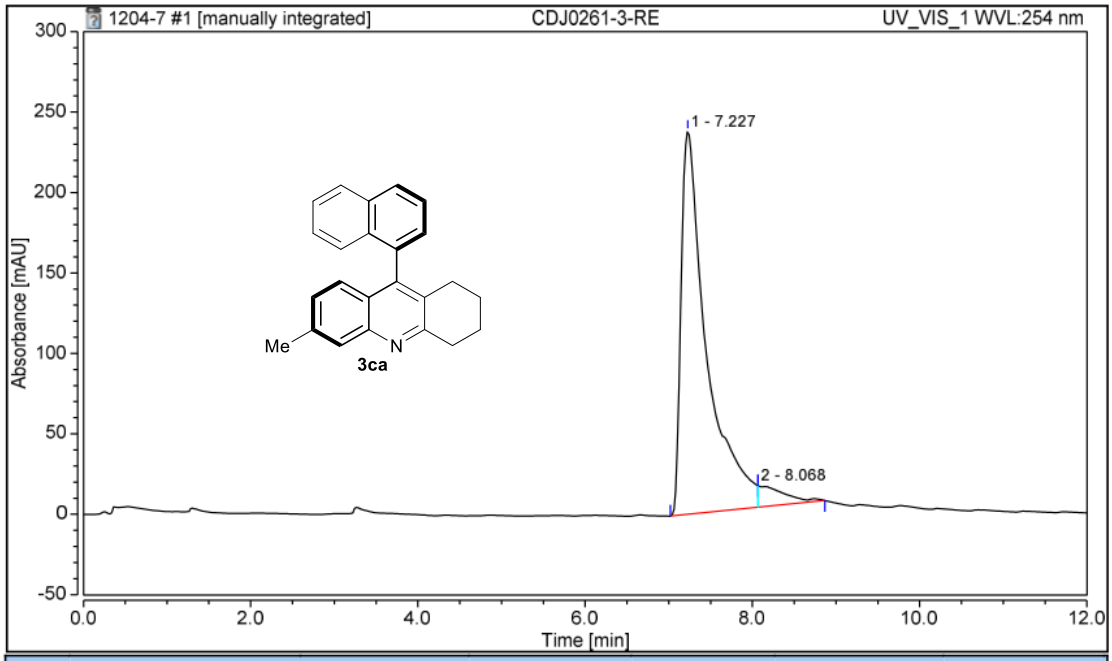
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	7.237	2.943	17.145	4.20	n.a.	0.25
2	7.677	67.049	222.881	95.80	2.75	0.37
Total:		**69.992**	**240.026**	**100.00**		



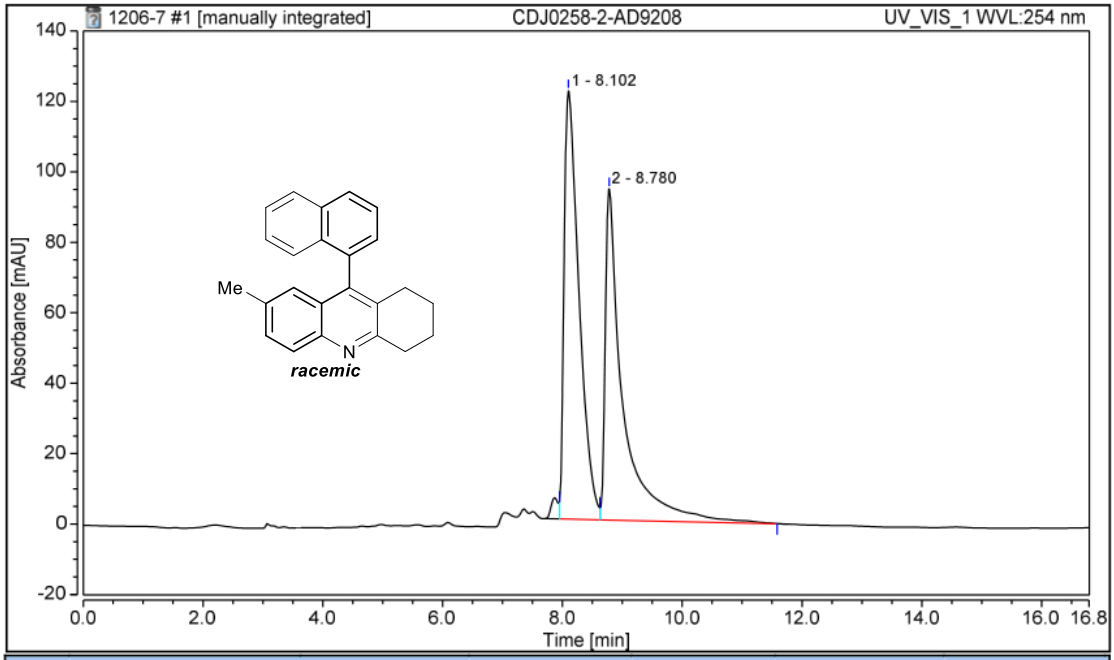
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	7.205	58.289	208.278	50.00	2.38	0.41
2	8.225	58.285	123.108	50.00	1.98	0.64
Total:		**116.574**	**331.386**	**100.00**		



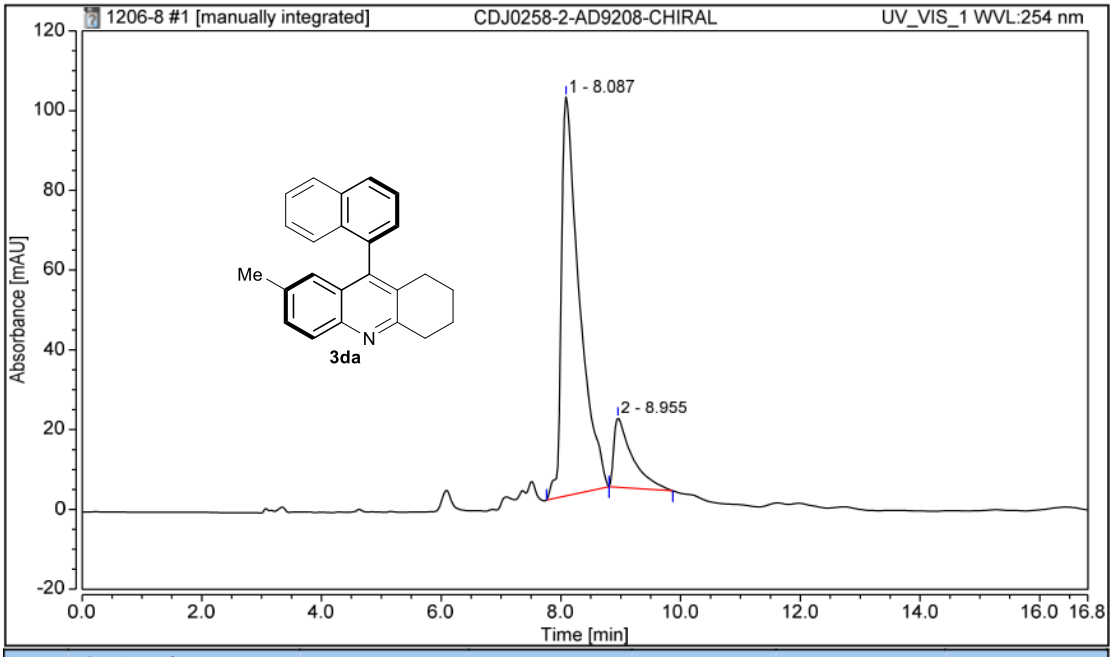
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	7.227	83.757	238.103	94.78	n.a.	0.45
2	8.068	4.615	13.263	5.22	n.a.	n.a.
Total:		**88.372**	**251.366**	**100.00**		



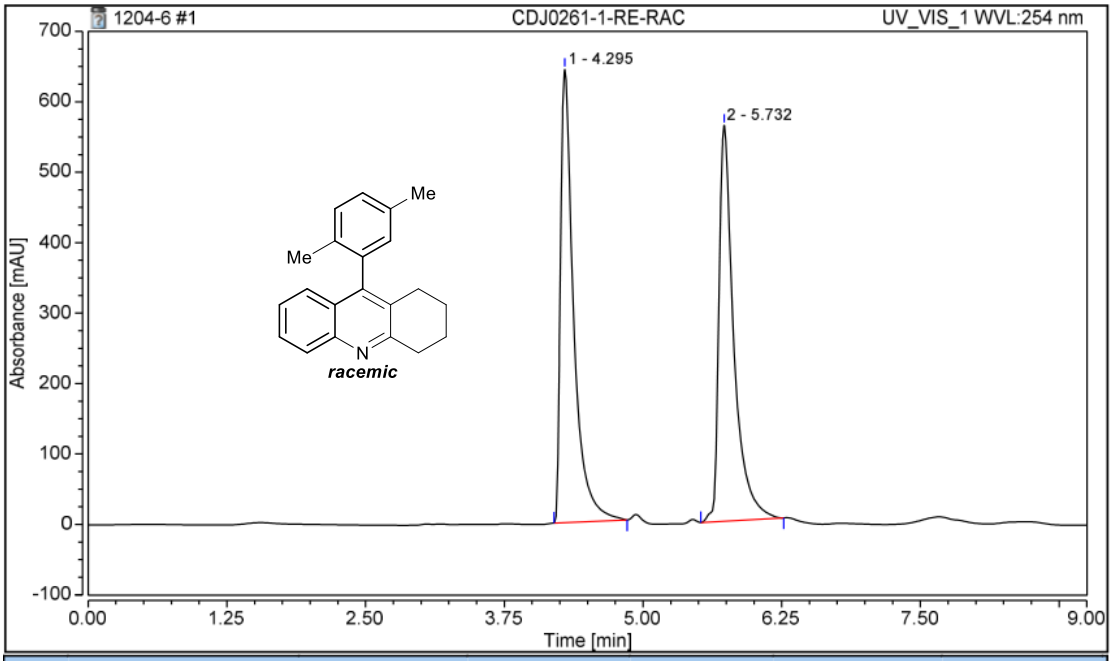
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	8.102	35.186	121.625	52.22	2.13	0.45
2	8.780	32.191	94.053	47.78	4.17	0.37
Total:		**67.376**	**215.678**	**100.00**		



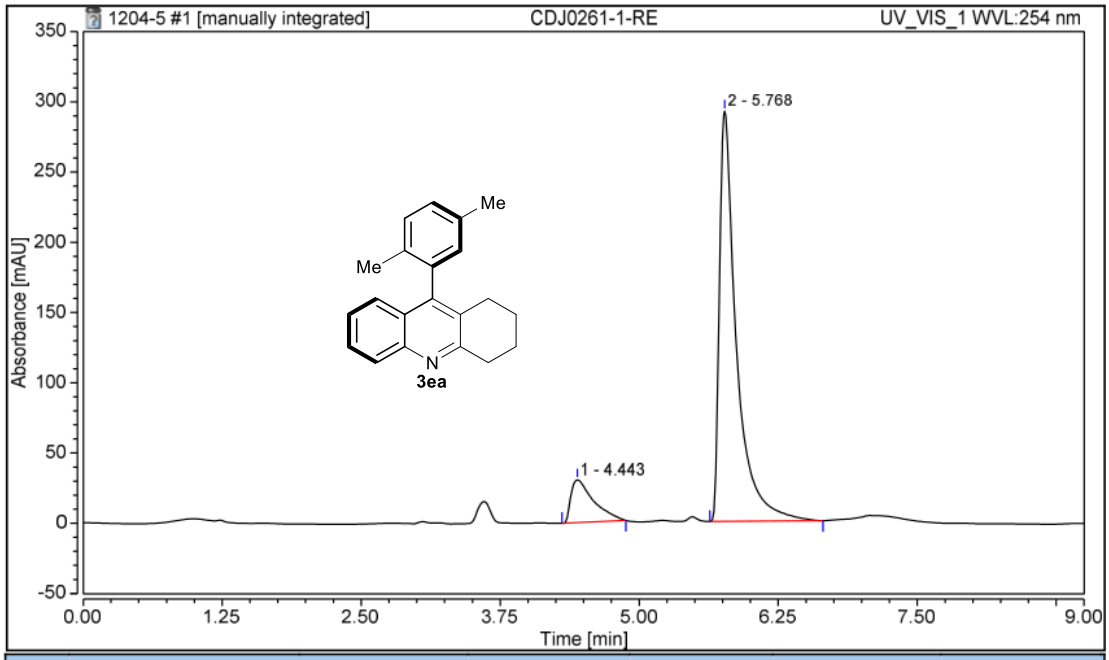
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	8.087	34.936	100.024	84.95	2.43	0.51
2	8.955	6.189	17.344	15.05	3.45	0.48
Total:		**41.125**	**117.368**	**100.00**		



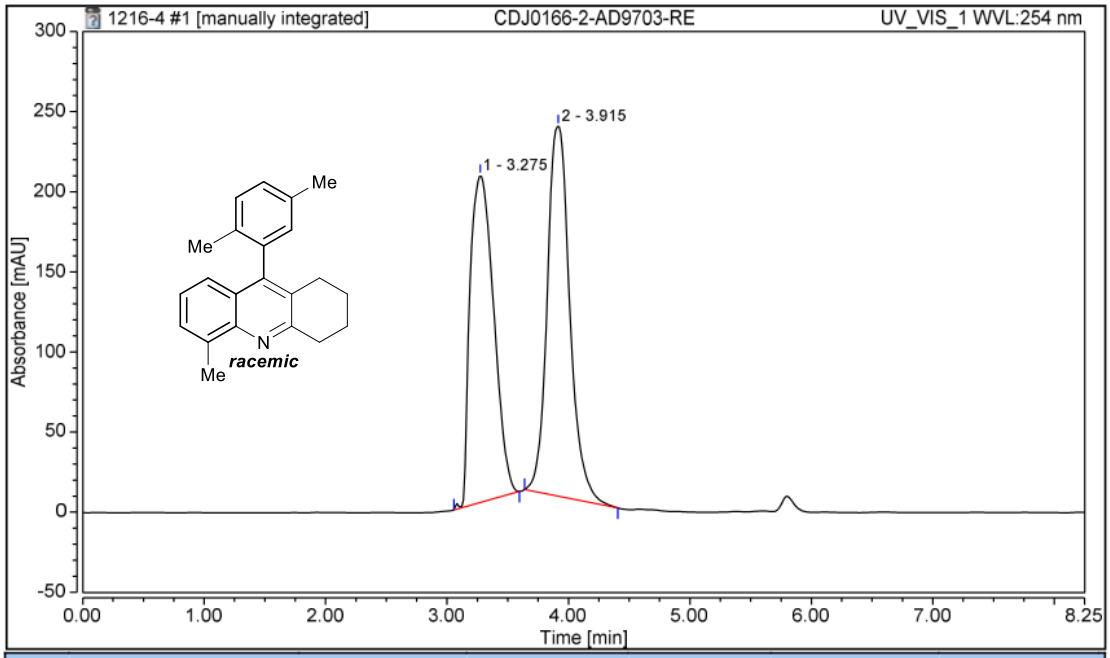
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	4.295	88.719	643.701	50.47	2.27	0.19
2	5.732	87.073	562.053	49.53	1.97	0.22
Total:		**175.791**	**1205.754**	**100.00**		



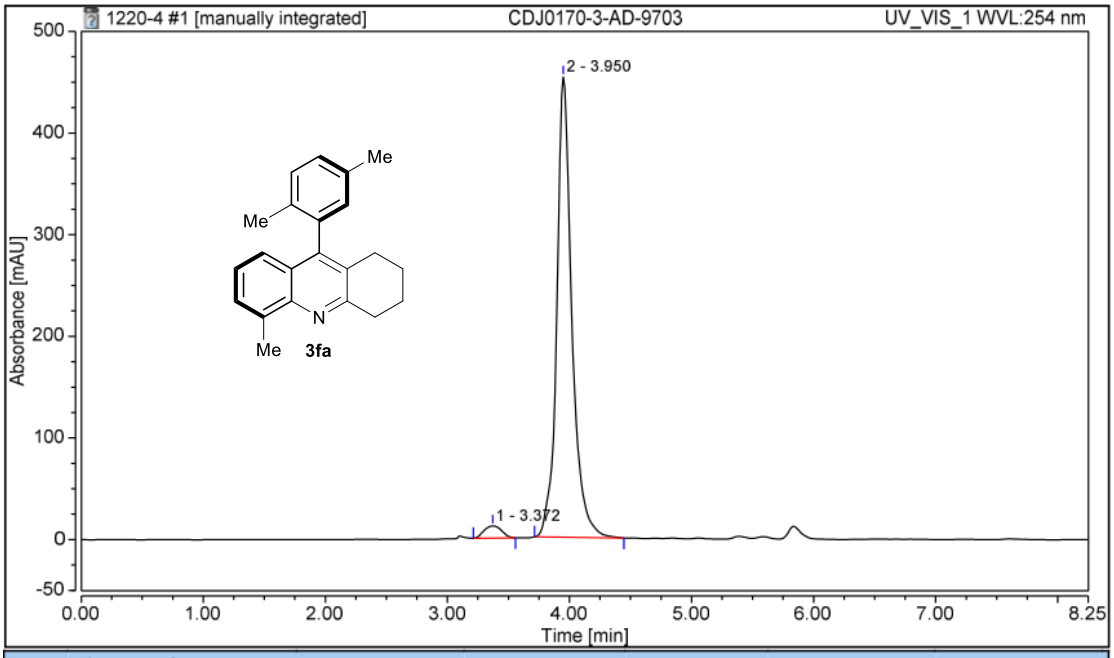
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	4.443	7.191	30.427	12.22	2.41	0.34
2	5.768	51.648	292.015	87.78	2.42	0.24
Total:		**58.839**	**322.442**	**100.00**		



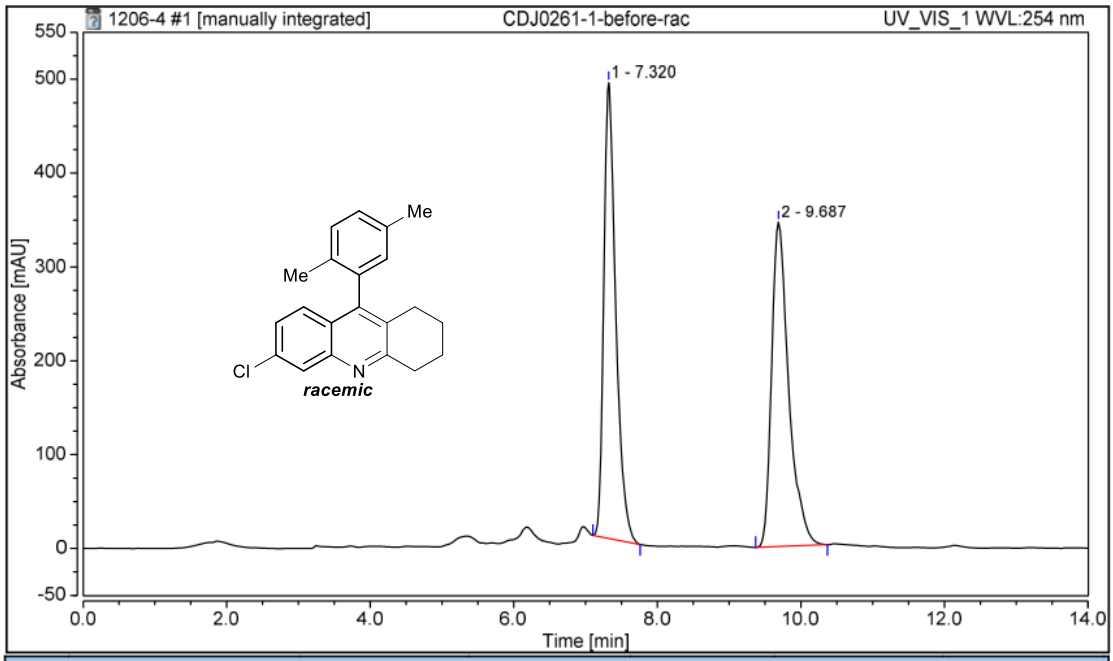
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	3.275	45.714	203.998	47.98	1.41	0.35
2	3.915	49.560	231.041	52.02	1.15	0.30
Total:		**95.274**	**435.039**	**100.00**		



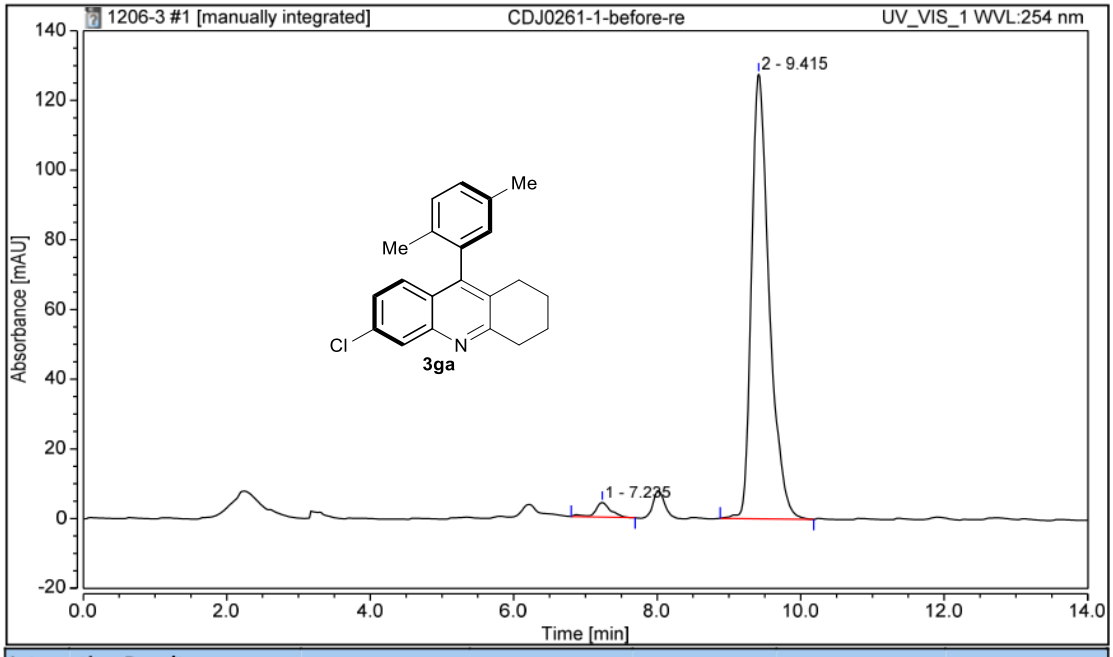
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	3.372	1.972	11.767	2.95	1.05	0.26
2	3.950	64.805	452.912	97.05	1.15	0.20
Total:		**66.777**	**464.679**	**100.00**		



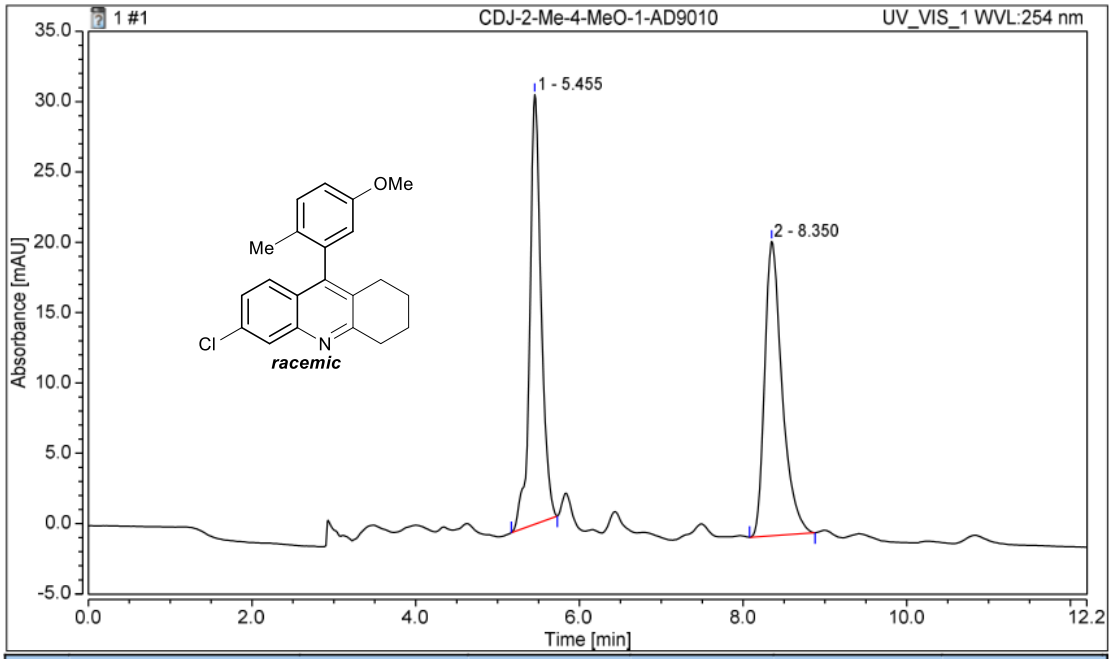
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	7.320	93.921	485.959	49.60	1.46	0.29
2	9.687	95.419	345.866	50.40	1.50	0.41
Total:		**189.340**	**831.826**	**100.00**		



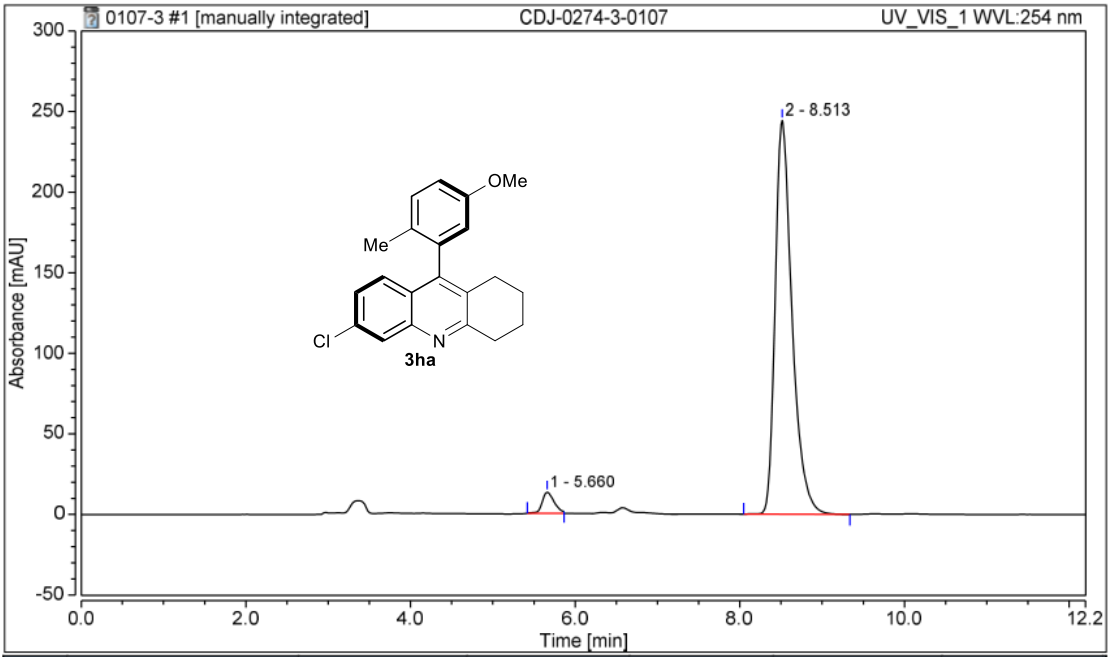
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	7.235	1.045	4.189	2.77	0.87	0.32
2	9.415	36.639	127.629	97.23	1.43	0.43
Total:		**37.684**	**131.819**	**100.00**		



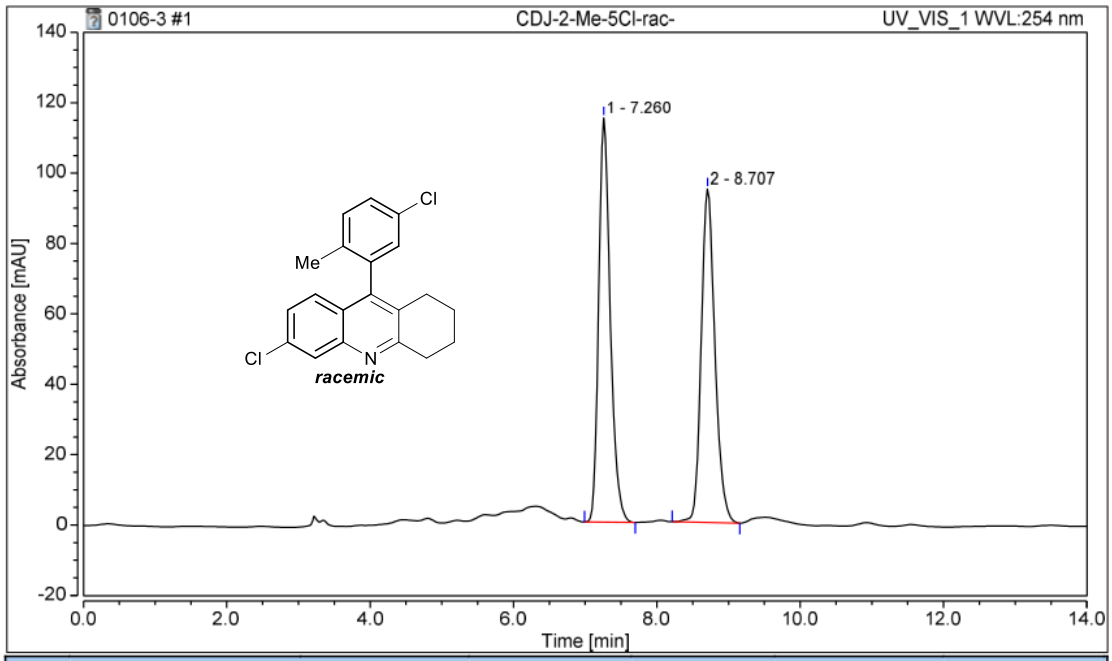
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	5.455	4.922	30.554	48.71	1.00	0.24
2	8.350	5.184	20.929	51.29	1.46	0.37
Total:		**10.106**	**51.483**	**100.00**		



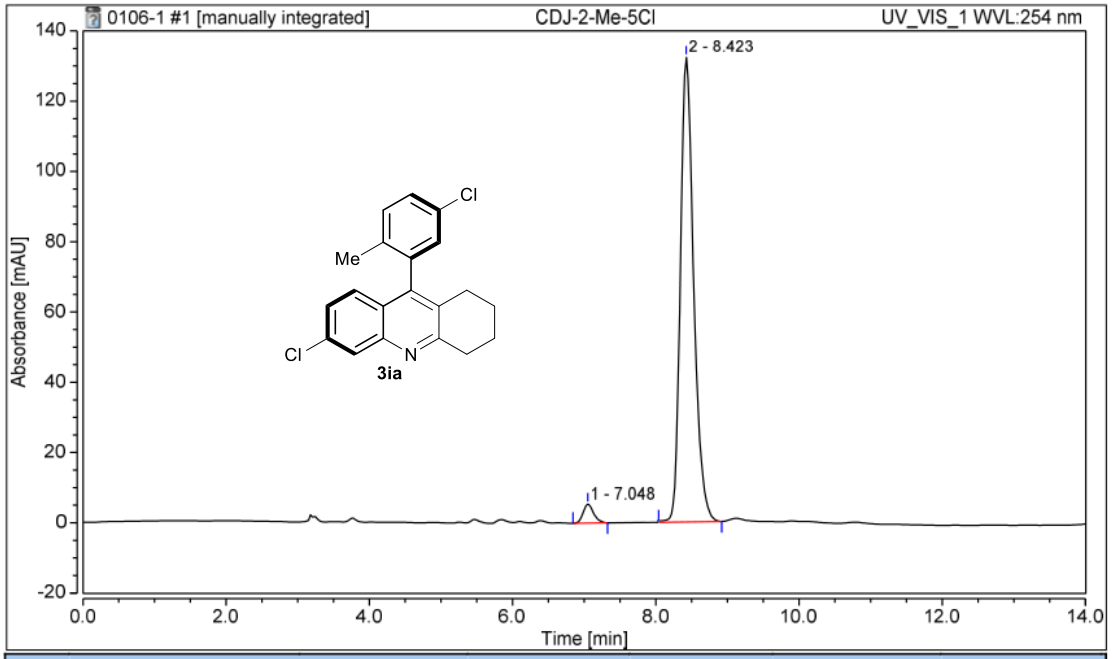
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	5.660	2.209	13.171	3.65	n.a.	0.26
2	8.513	58.265	244.437	96.35	1.43	0.36
Total:		**60.474**	**257.608**	**100.00**		



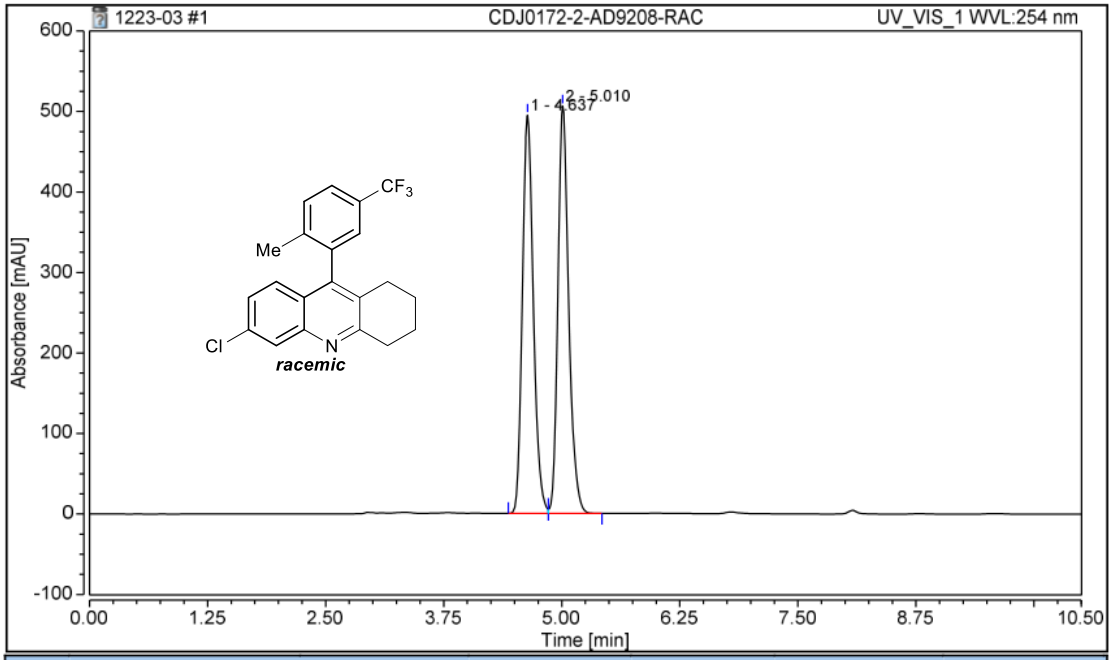
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	7.260	21.529	114.848	50.61	1.27	0.28
2	8.707	21.009	94.805	49.39	1.21	0.35
Total:		**42.537**	**209.652**	**100.00**		



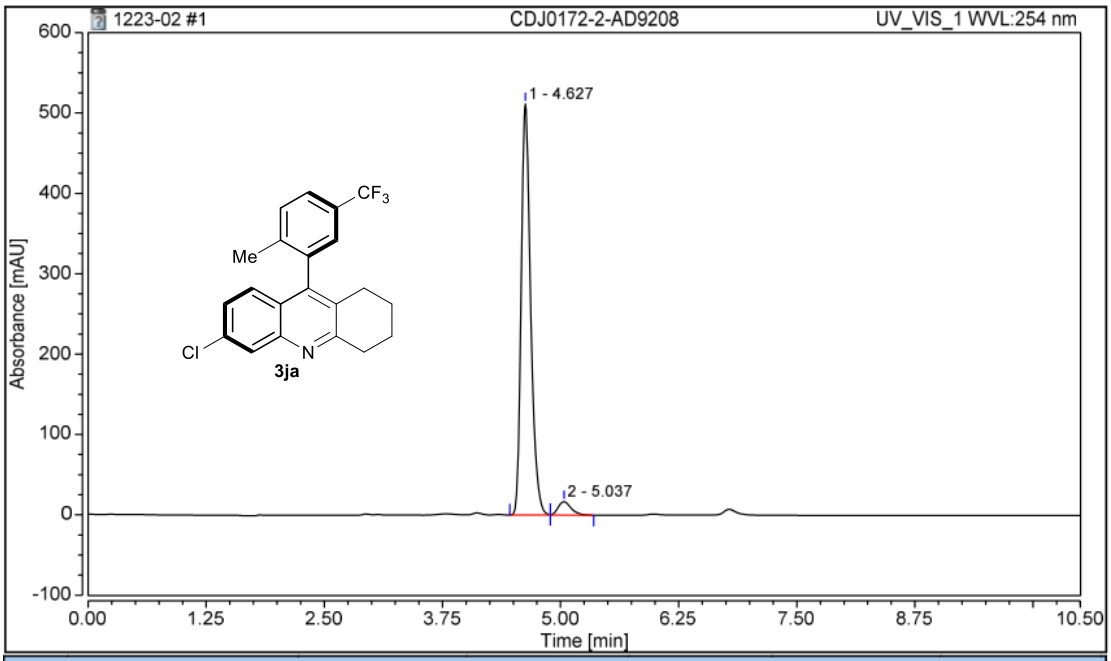
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	7.048	0.917	5.403	3.12	1.23	0.26
2	8.423	28.428	132.281	96.88	1.28	0.32
Total:		**29.344**	**137.683**	**100.00**		



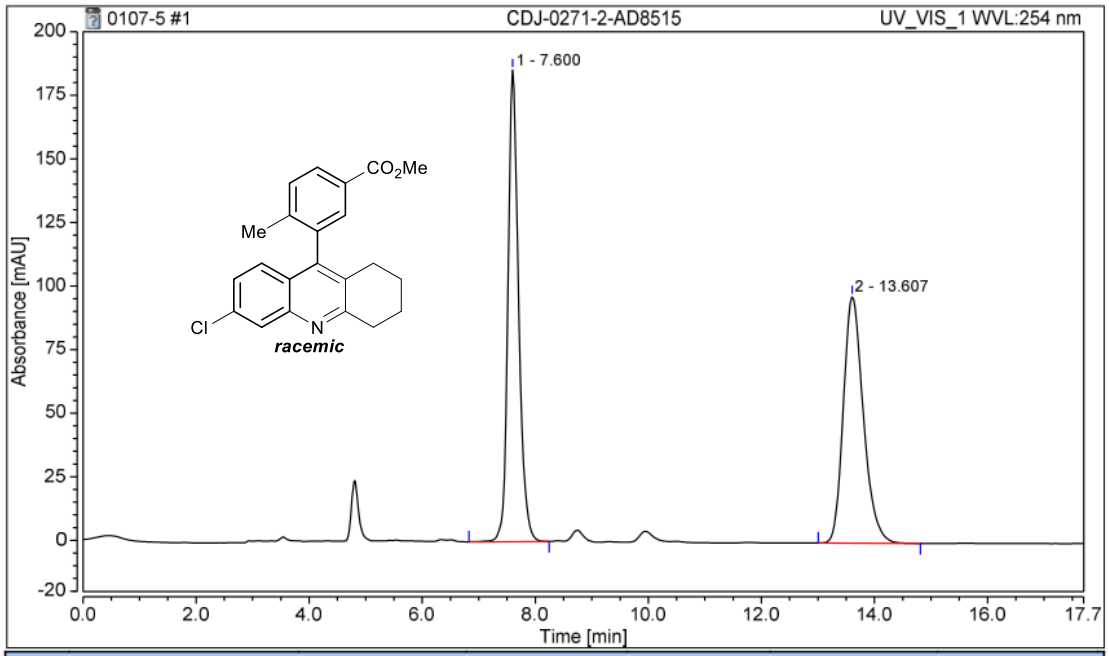
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	4.637	67.054	494.745	49.94	1.19	0.21
2	5.010	67.225	505.984	50.06	1.25	0.20
Total:		**134.279**	**1000.729**	**100.00**		



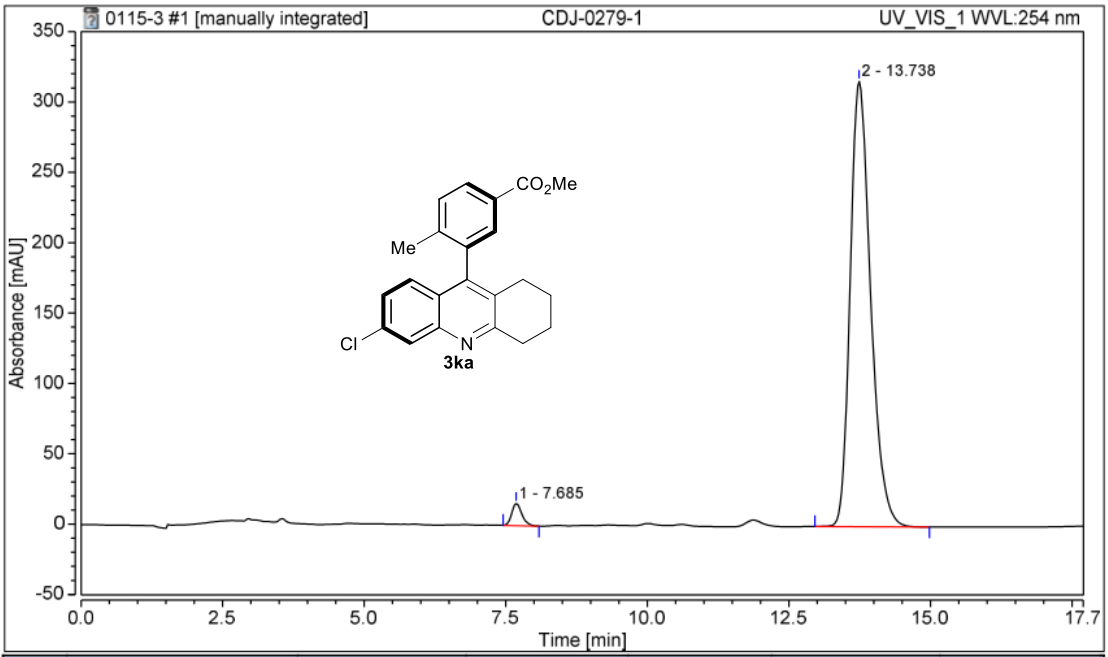
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	4.627	58.631	511.665	95.58	1.32	0.18
2	5.037	2.714	16.719	4.42	1.27	0.25
Total:		**61.346**	**528.384**	**100.00**		



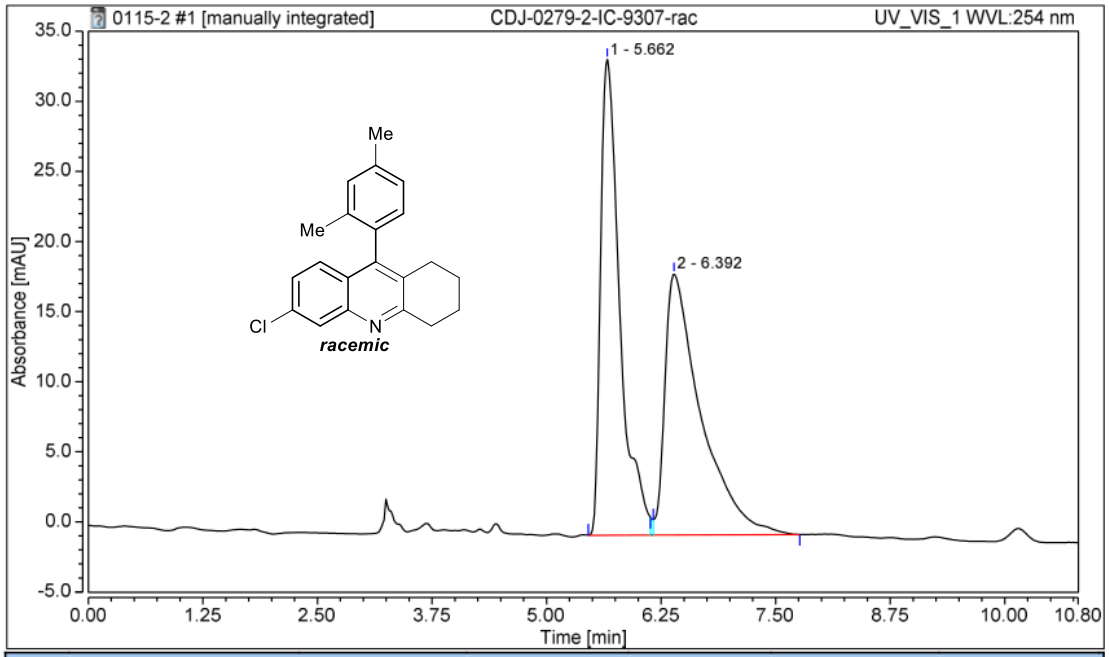
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	7.600	40.320	185.495	50.34	1.22	0.33
2	13.607	39.783	96.897	49.66	1.25	0.63
Total:		**80.103**	**282.393**	**100.00**		



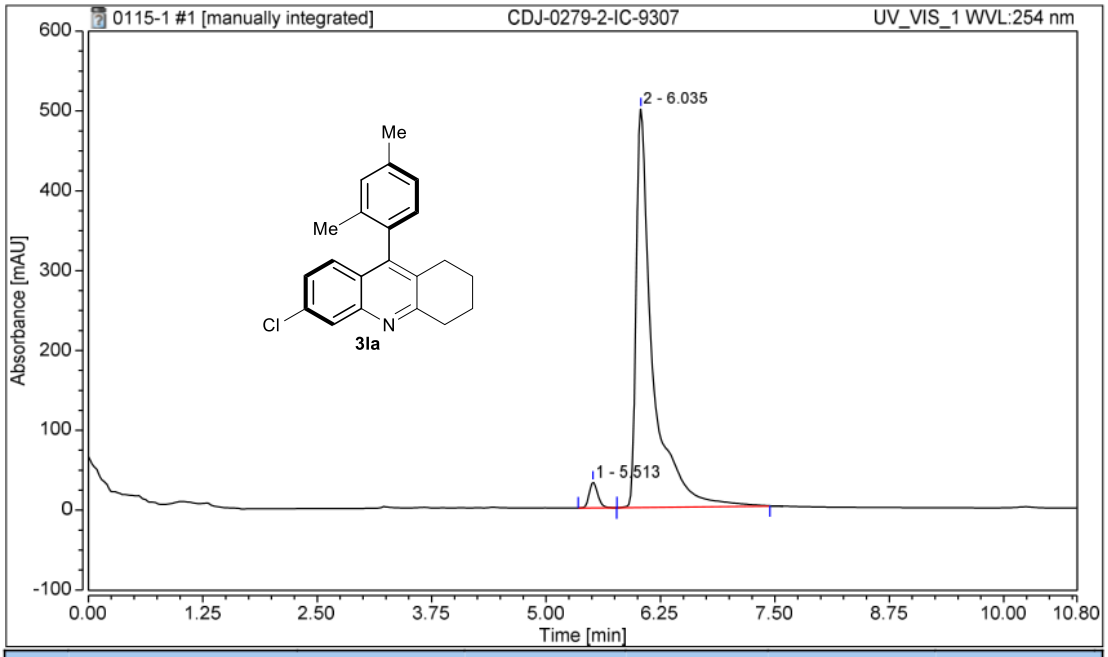
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	7.685	3.255	15.742	2.40	1.26	0.33
2	13.738	132.278	316.524	97.60	1.29	0.65
Total:		**135.533**	**332.266**	**100.00**		



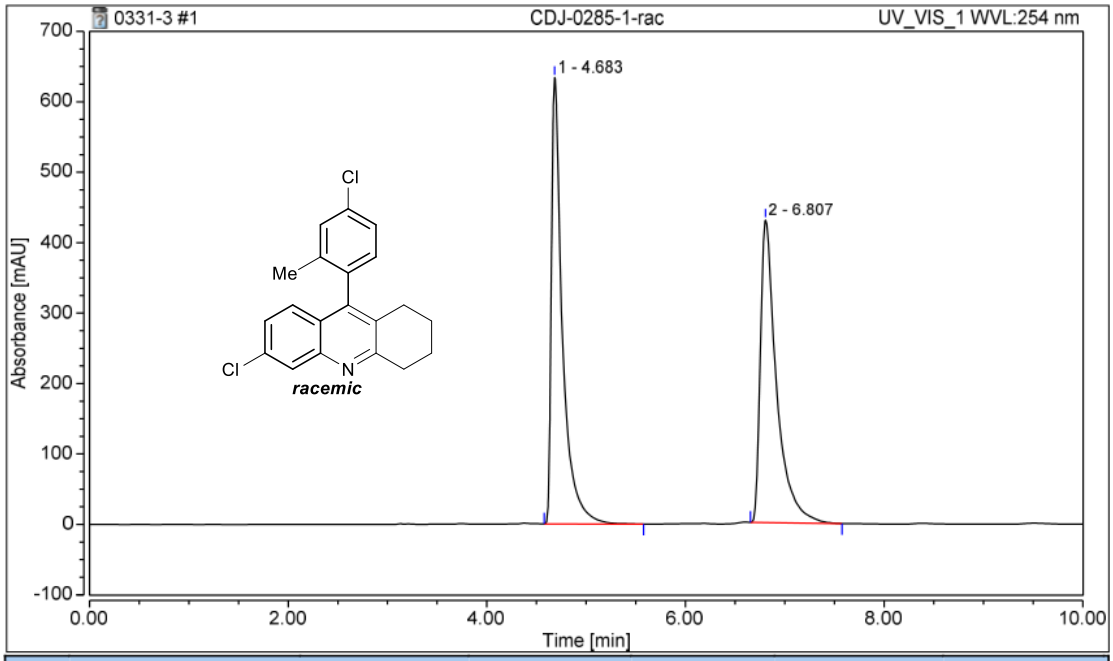
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	5.662	8.268	33.929	49.46	2.07	0.35
2	6.392	8.447	18.631	50.54	n.a.	0.63
Total:		**16.715**	**52.560**	**100.00**		



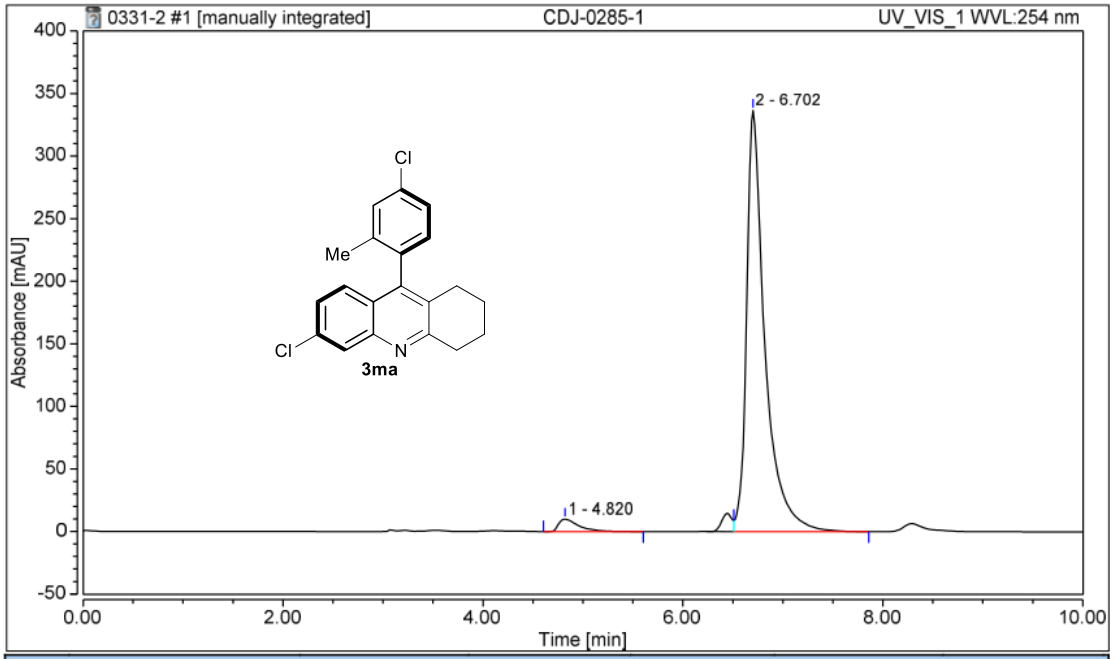
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	5.513	3.451	32.121	3.19	1.21	0.17
2	6.035	104.768	499.225	96.81	2.88	0.25
Total:		**108.220**	**531.346**	**100.00**		



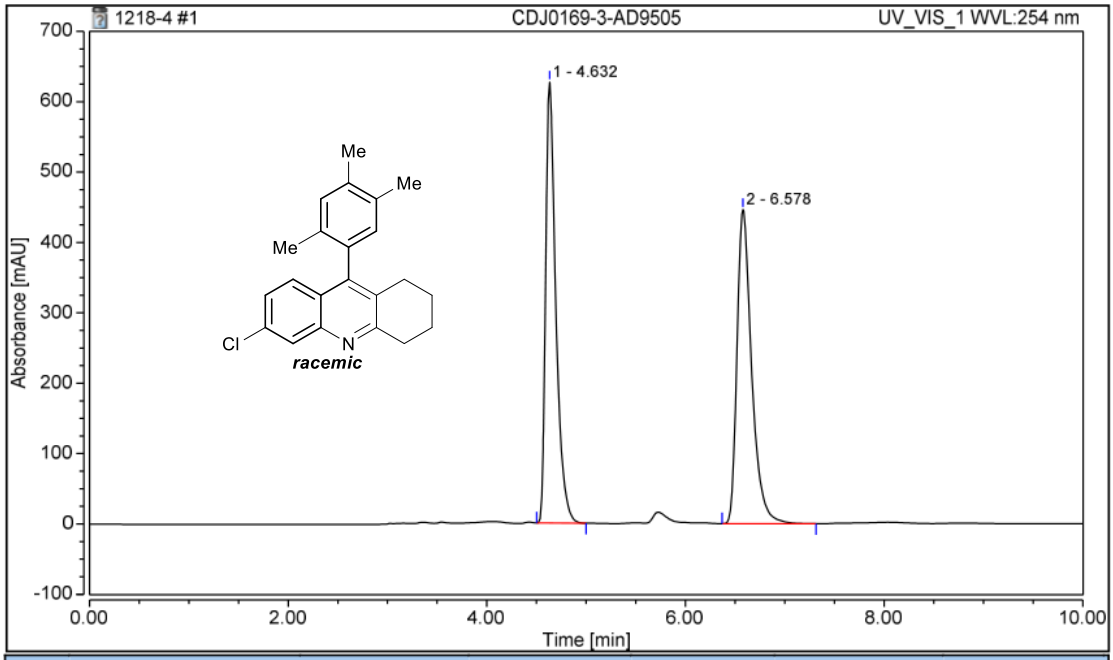
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	4.683	81.016	633.637	50.06	2.47	0.17
2	6.807	80.834	429.489	49.94	2.14	0.26
Total:		**161.849**	**1063.126**	**100.00**		



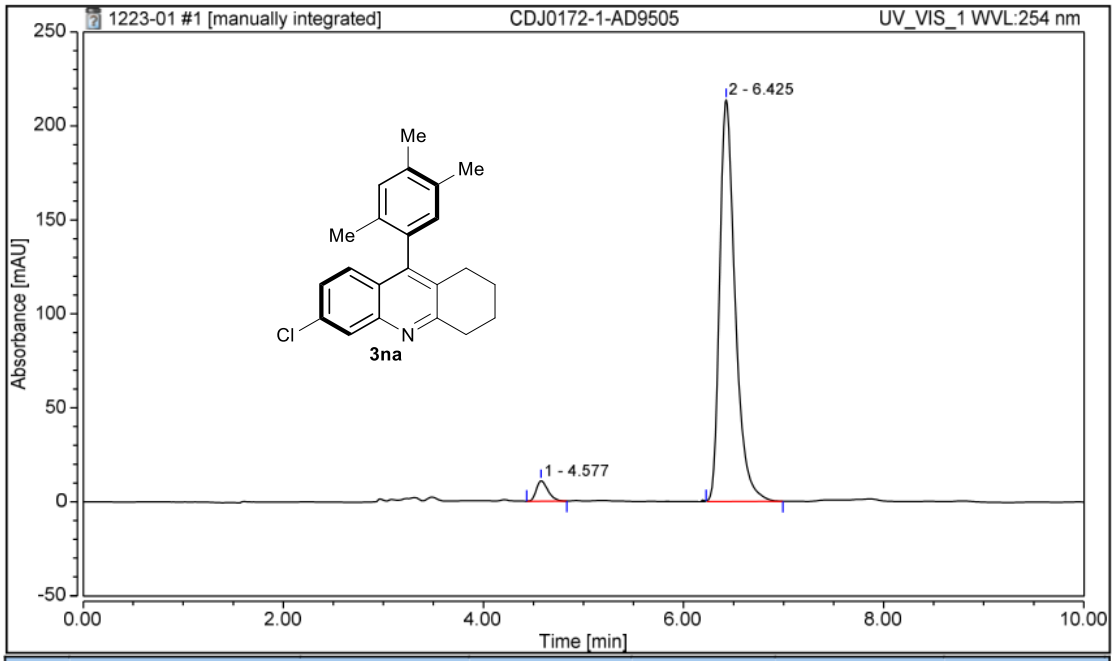
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	4.820	2.365	9.936	3.20	2.24	0.33
2	6.702	71.474	336.617	96.80	1.71	0.29
Total:		**73.839**	**346.552**	**100.00**		



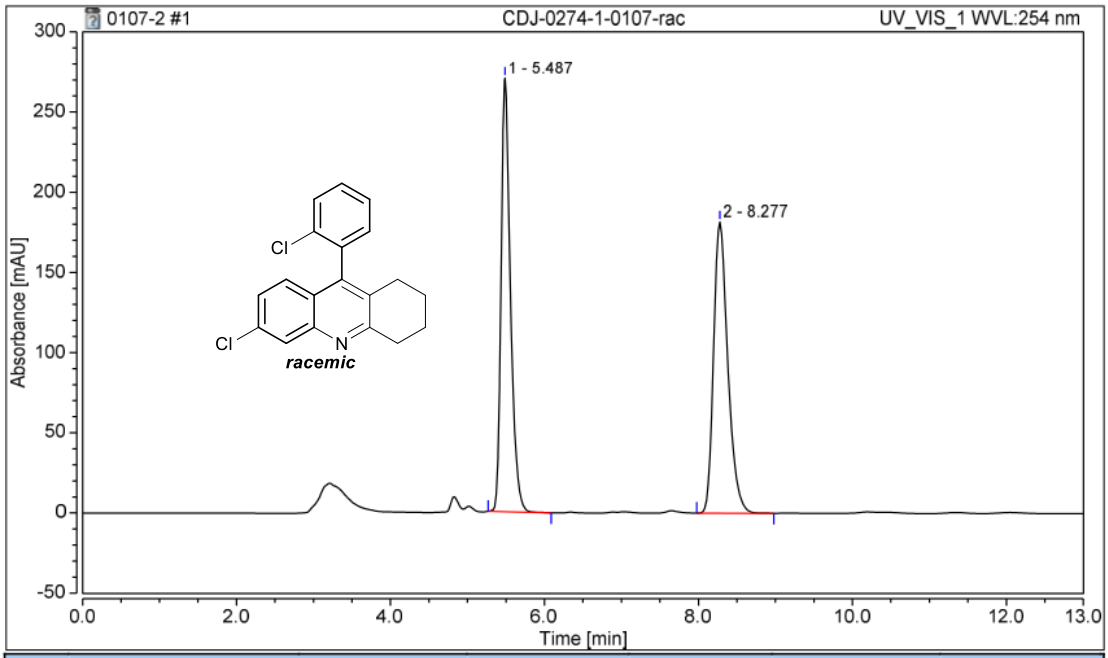
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	4.632	74.335	626.715	49.46	1.59	0.18
2	6.578	75.968	446.470	50.54	1.46	0.26
Total:		**150.303**	**1073.184**	**100.00**		



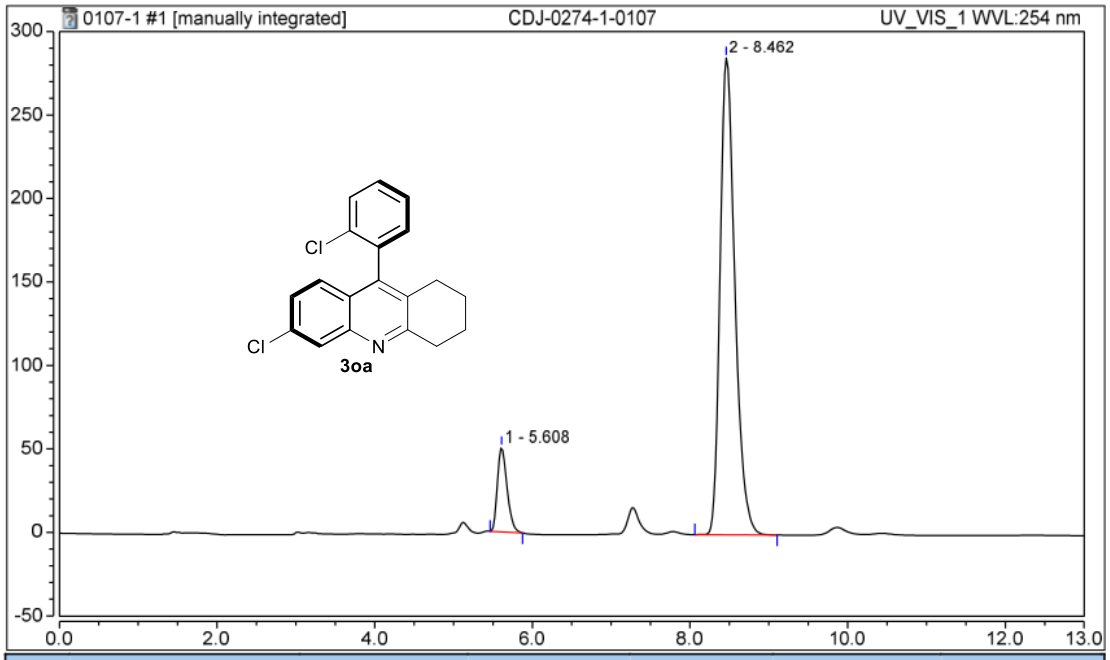
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	4.577	1.458	10.870	3.67	1.36	0.21
2	6.425	38.250	213.767	96.33	1.43	0.27
Total:		**39.709**	**224.637**	**100.00**		



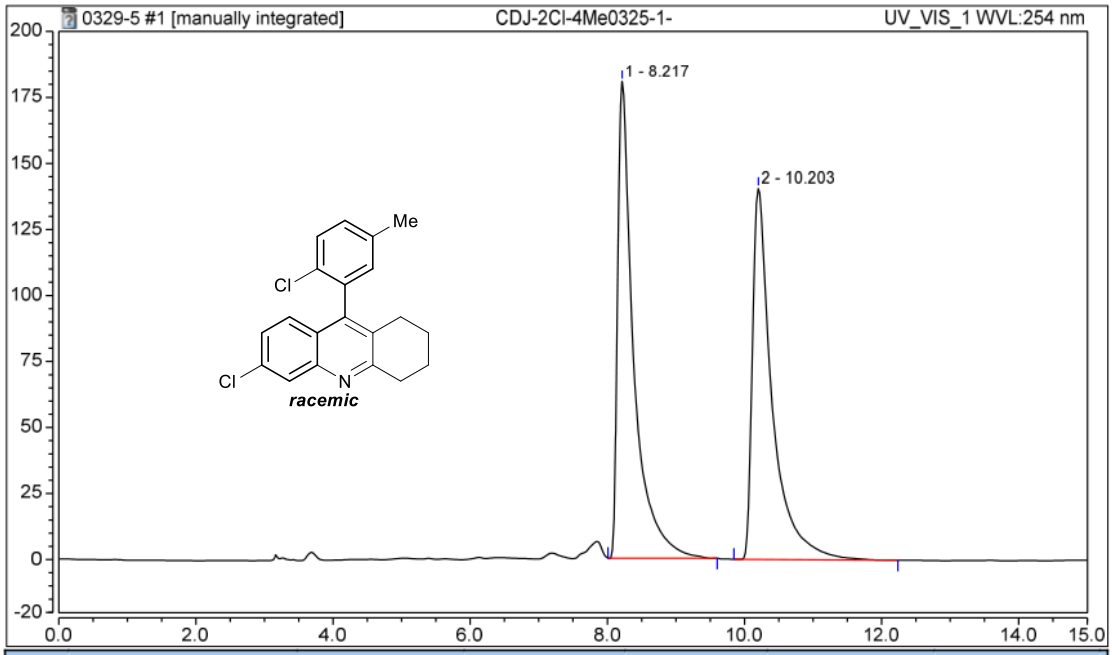
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	5.487	37.944	270.432	49.40	1.38	0.21
2	8.277	38.867	181.674	50.60	1.32	0.33
Total:		**76.810**	**452.106**	**100.00**		



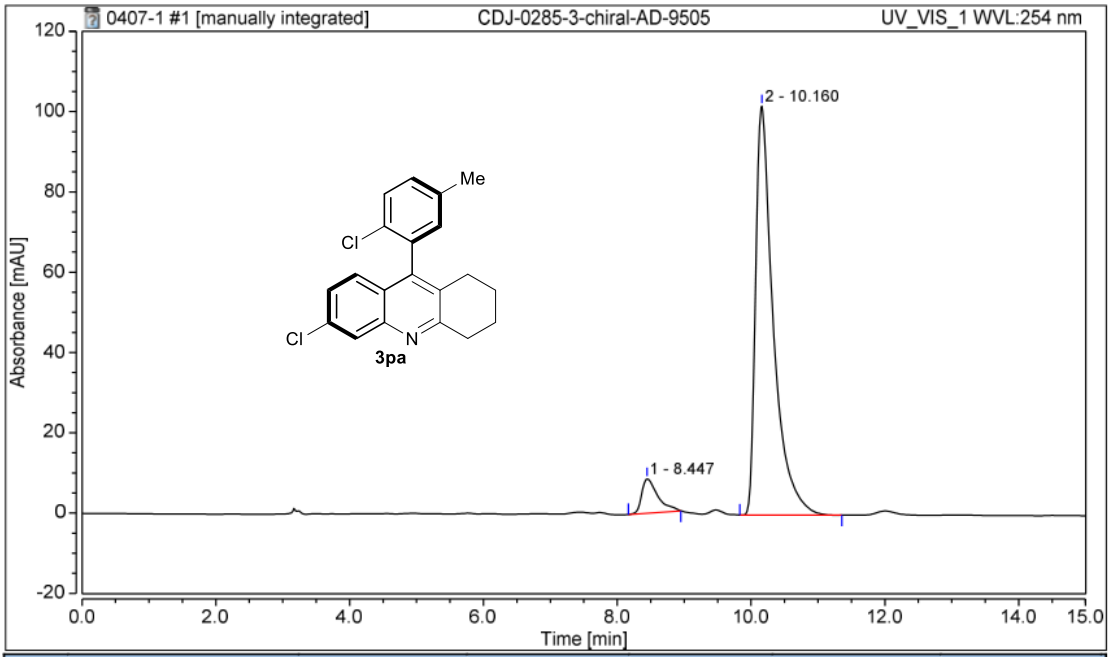
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	5.608	7.093	50.527	10.24	1.33	0.22
2	8.462	62.173	285.716	89.76	1.32	0.34
Total:		**69.266**	**336.244**	**100.00**		



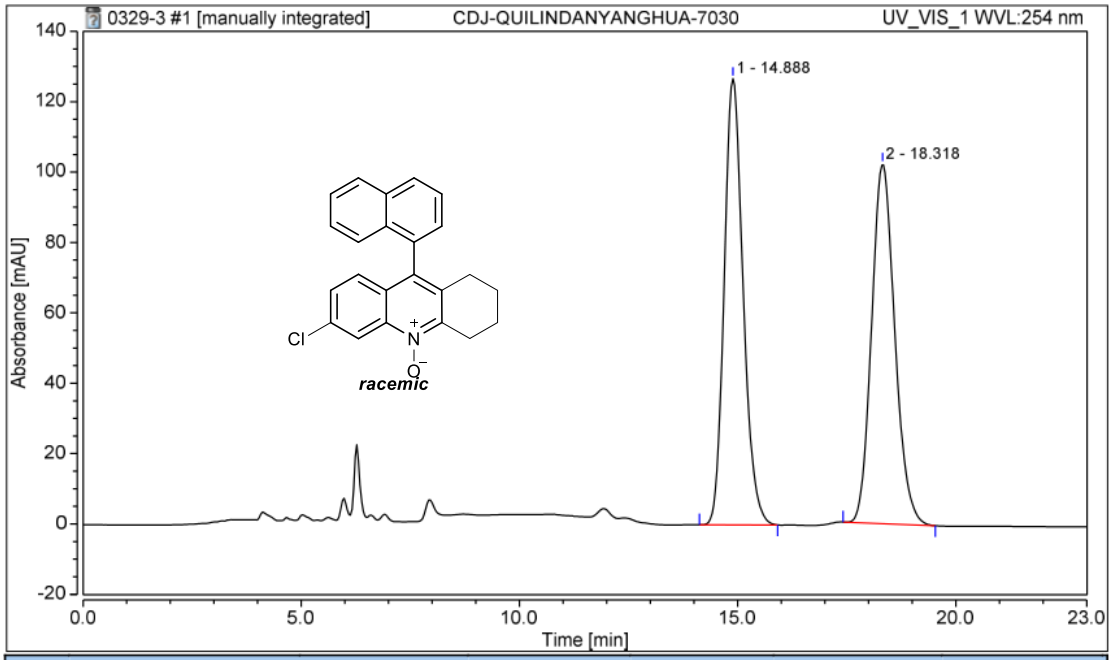
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	8.217	48.834	180.556	50.96	2.81	0.35
2	10.203	46.991	140.620	49.04	2.50	0.46
Total:		**95.825**	**321.176**	**100.00**		



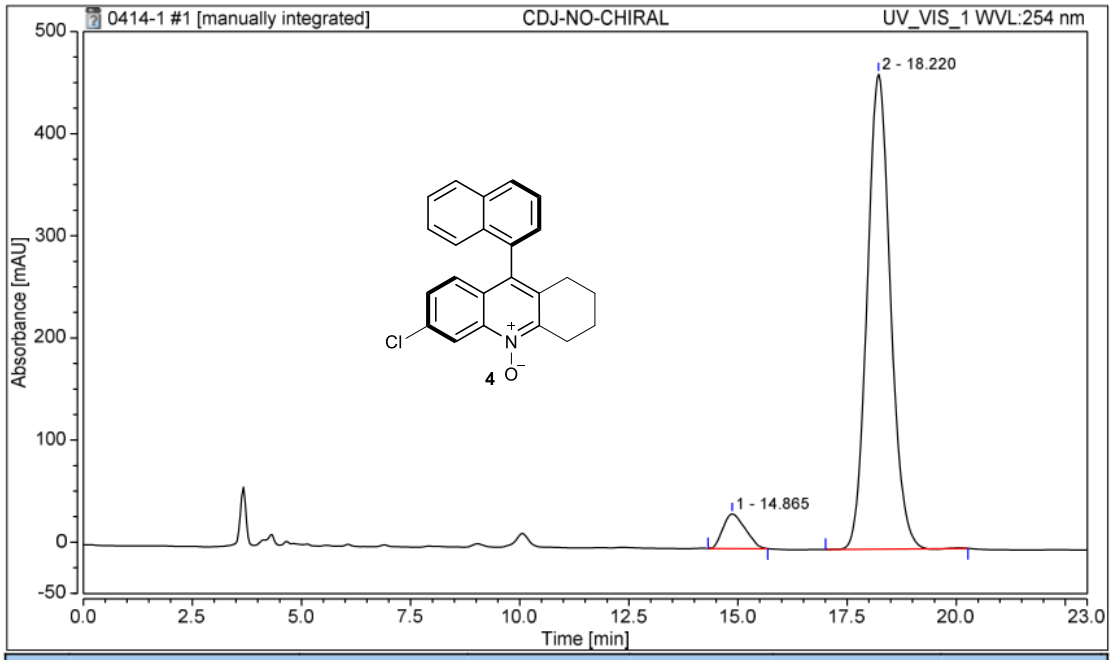
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	8.447	2.391	8.554	7.14	1.79	0.41
2	10.160	31.074	101.889	92.86	1.98	0.43
Total:		**33.465**	**110.443**	**100.00**		



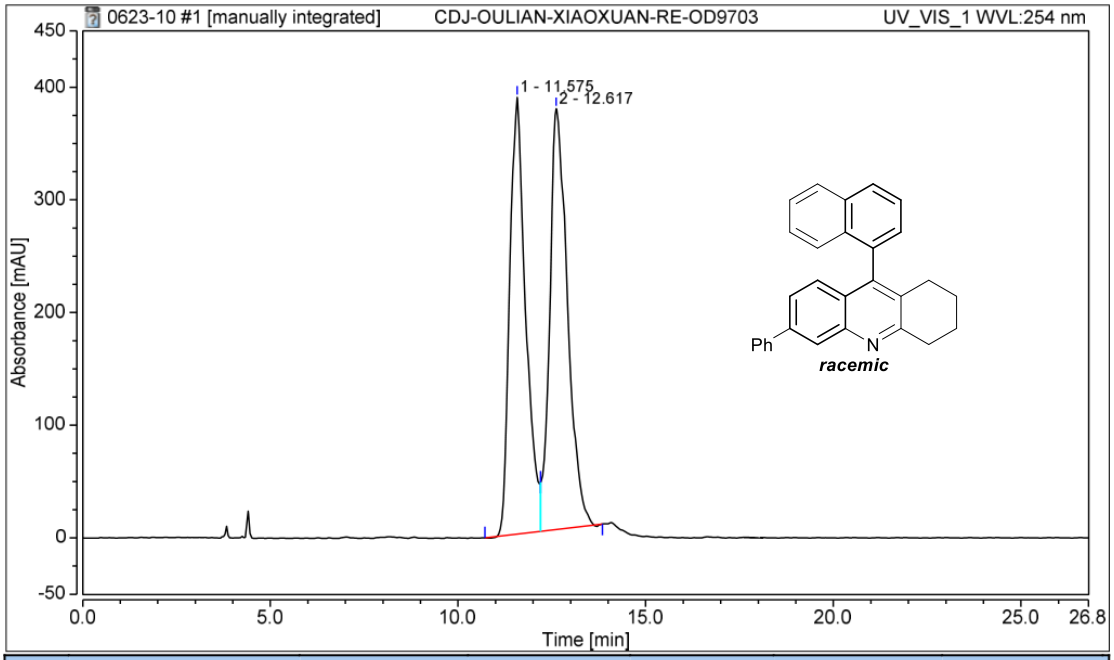
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	14.888	63.720	126.870	50.33	1.19	0.78
2	18.318	62.878	102.223	49.67	1.15	0.98
Total:		**126.597**	**229.093**	**100.00**		



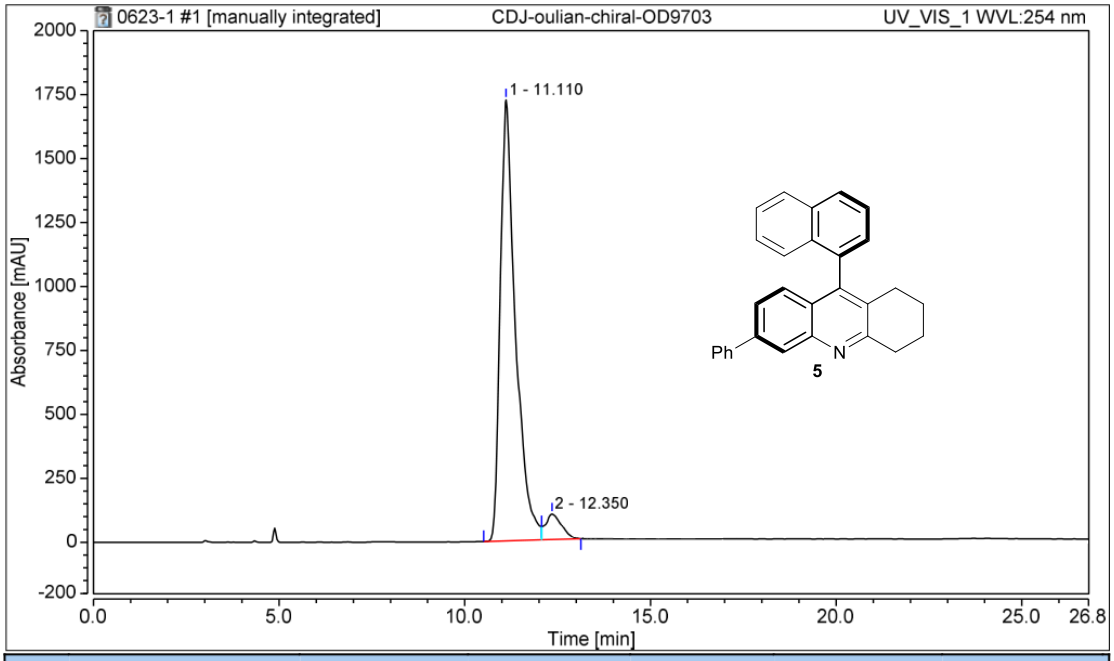
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	14.865	20.545	34.391	6.68	1.27	1.02
2	18.220	286.874	465.264	93.32	1.10	0.97
Total:		**307.419**	**499.656**	**100.00**		



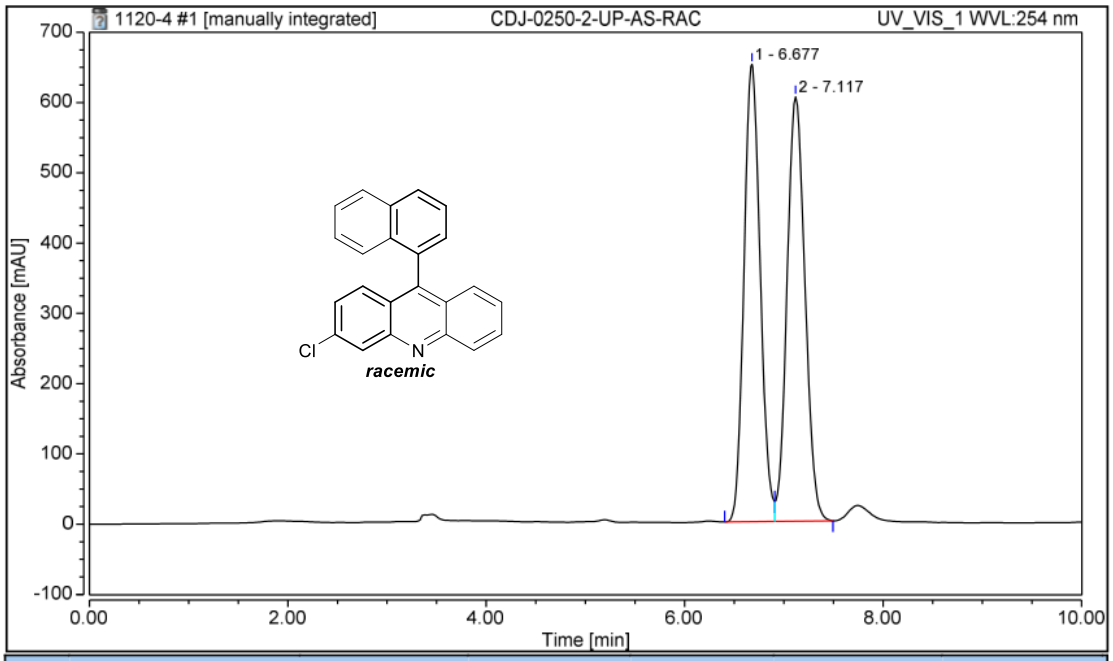
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	11.575	191.004	387.659	48.17	n.a.	0.99
2	12.617	205.530	373.531	51.83	n.a.	0.87
Total:		**396.534**	**761.190**	**100.00**		



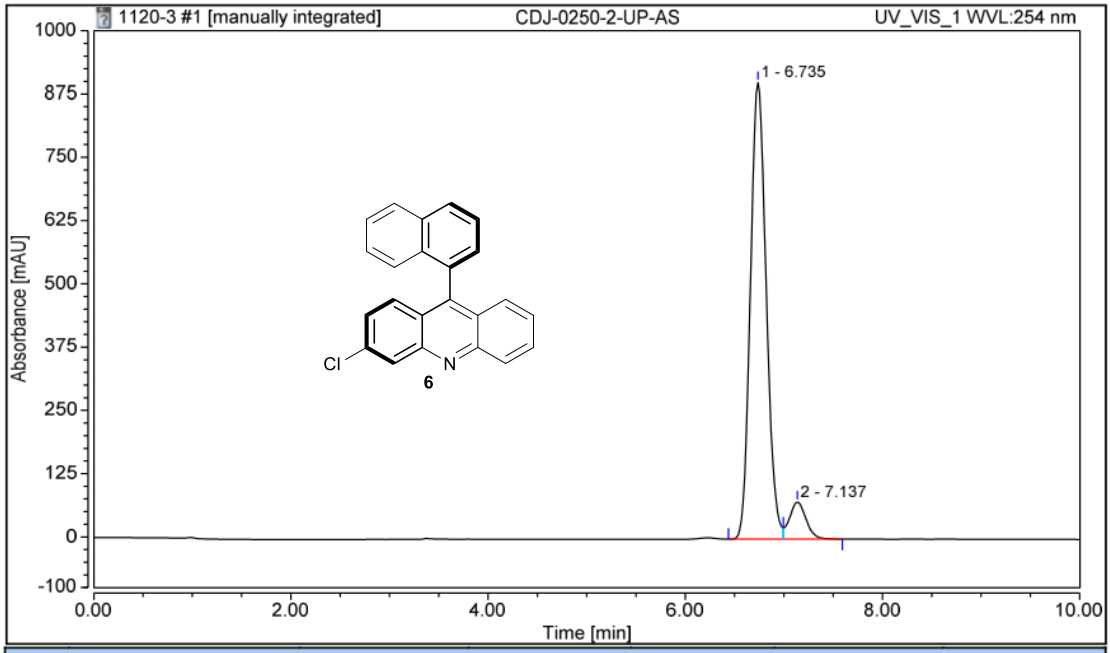
Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	11.110	820.365	1723.729	94.13	1.70	0.73
2	12.350	51.184	99.650	5.87	n.a.	0.76
Total:		**871.549**	**1823.379**	**100.00**		



Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	6.677	122.921	650.959	49.25	1.13	0.30
2	7.117	126.641	604.088	50.75	1.07	0.34
Total:		**249.562**	**1255.046**	**100.00**		



Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Asymmetry (EP)	Peak Width min
1	6.735	167.938	902.390	92.18	1.14	0.30
2	7.137	14.248	73.226	7.82	n.a.	0.31
Total:		**182.187**	**975.616**	**100.00**		

X-ray Crystallographic Information

CCDC 1998526 (**3aa**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

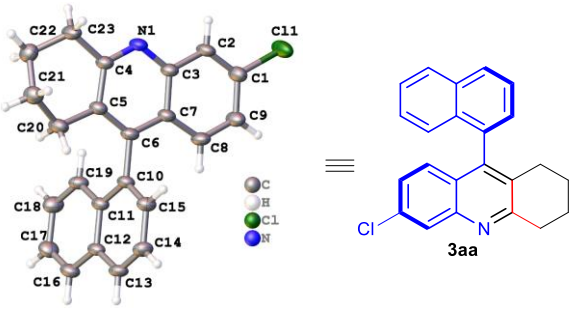


Table S4. Crystal data and structure refinement

Identification code	ndj-hz-3-300k	
Empirical formula	C23H18ClN	
Formula weight	343.83	
Temperature	299.61(10) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 9.4300(2) Å	α= 90°.
	b = 8.4784(2) Å	β= 110.650(2)°.
	c = 11.9996(2) Å	γ = 90°.
Volume	897.74(3) $Å^3$	
Z	2	
Density (calculated)	1.272 Mg/m^3	
Absorption coefficient	1.892 mm^{-1}	
F(000)	360	
Crystal size	? x ? x ? mm^3	
Theta range for data collection	3.937 to 76.831°.	
Index ranges	-11<=h<=11, -10<=k<=10, -14<=l<=9	
Reflections collected	9452	
Independent reflections	3392 [R(int) = 0.0334]	
Completeness to theta = 67.684°	99.8%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.70534	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3392 / 31 / 245	
Goodness-of-fit on F^2	1.313	
Final R indices [I>2sigma(I)]	R1 = 0.0425, wR2 = 0.1525	
R indices (all data)	R1 = 0.0467, wR2 = 0.1547	
Absolute structure parameter	0.040(15)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.247 and -0.216 e.$Å^{-3}$	

Table S5. Atomic coordinates (x10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl(1)	192(1)	4424(3)	1109(1)	102(1)
N(1)	5411(3)	4407(5)	4265(2)	54(1)
C(21)	8601(12)	3720(20)	7682(13)	70(4)
C(16)	3020(5)	6157(6)	9535(4)	62(1)
C(11)	3620(4)	5116(5)	7859(3)	49(1)
C(12)	3096(4)	4850(5)	8823(3)	50(1)
C(7)	3288(4)	4139(5)	4967(3)	50(1)
C(19)	4004(5)	6668(5)	7647(4)	58(1)
C(6)	4324(4)	4037(5)	6152(3)	50(1)
C(4)	6345(4)	4314(6)	5372(3)	52(1)
C(5)	5861(4)	4124(5)	6372(3)	52(1)
C(10)	3739(4)	3803(5)	7156(3)	50(1)
C(3)	3896(4)	4317(6)	4046(3)	52(1)
C(15)	3334(5)	2334(5)	7397(4)	58(1)
C(14)	2791(5)	2086(6)	8342(4)	61(1)
C(8)	1694(4)	4073(6)	4639(3)	63(1)
C(13)	2679(5)	3312(5)	9031(3)	57(1)
C(2)	2909(4)	4396(7)	2853(3)	60(1)
C(23)	8009(4)	4398(8)	5552(3)	71(1)
C(20)	7014(5)	4029(7)	7613(3)	70(1)
C(18)	3926(6)	7887(6)	8366(4)	67(1)
C(9)	754(4)	4168(8)	3477(3)	70(1)
C(17)	3441(6)	7621(6)	9325(4)	69(1)
C(1)	1393(4)	4318(7)	2590(3)	67(1)
C(22)	9006(18)	4740(20)	6813(9)	70(4)
C(22A)	9054(13)	3900(20)	6742(7)	76(4)
C(21A)	8568(10)	4620(20)	7704(9)	72(3)

Table S6. Bond lengths [Å] and angles [°].

Cl(1)-C(1)	1.740(4)
N(1)-C(4)	1.311(4)
N(1)-C(3)	1.361(4)
C(21)-C(20)	1.493(10)
C(21)-C(22)	1.506(12)
C(16)-C(12)	1.416(6)
C(16)-C(17)	1.354(7)
C(11)-C(12)	1.428(4)
C(11)-C(19)	1.412(6)
C(11)-C(10)	1.424(5)
C(12)-C(13)	1.409(6)
C(7)-C(6)	1.415(5)
C(7)-C(3)	1.422(4)
C(7)-C(8)	1.415(5)
C(19)-C(18)	1.365(6)
C(6)-C(5)	1.381(5)
C(6)-C(10)	1.505(4)
C(4)-C(5)	1.435(4)
C(4)-C(23)	1.509(5)
C(5)-C(20)	1.505(5)
C(10)-C(15)	1.363(6)
C(3)-C(2)	1.407(5)
C(15)-C(14)	1.415(5)
C(14)-C(13)	1.355(6)
C(8)-C(9)	1.365(6)
C(2)-C(1)	1.353(5)
C(23)-C(22)	1.501(10)
C(23)-C(22A)	1.483(9)
C(20)-C(21A)	1.518(9)
C(18)-C(17)	1.399(6)
C(9)-C(1)	1.402(5)
C(22A)-C(21A)	1.515(11)
C(4)-N(1)-C(3)	118.5(3)
C(20)-C(21)-C(22)	110.8(12)
C(17)-C(16)-C(12)	121.6(4)
C(19)-C(11)-C(12)	118.5(3)
C(19)-C(11)-C(10)	122.9(3)
C(10)-C(11)-C(12)	118.6(3)
C(16)-C(12)-C(11)	118.1(4)
C(13)-C(12)-C(16)	122.7(3)
C(13)-C(12)-C(11)	119.1(3)

C(6)-C(7)-C(3)	117.6(3)
C(8)-C(7)-C(6)	124.5(3)
C(8)-C(7)-C(3)	117.9(3)
C(18)-C(19)-C(11)	121.2(4)
C(7)-C(6)-C(10)	119.6(3)
C(5)-C(6)-C(7)	119.7(3)
C(5)-C(6)-C(10)	120.7(3)
N(1)-C(4)-C(5)	123.8(3)
N(1)-C(4)-C(23)	115.8(3)
C(5)-C(4)-C(23)	120.4(3)
C(6)-C(5)-C(4)	117.9(3)
C(6)-C(5)-C(20)	122.0(3)
C(4)-C(5)-C(20)	120.2(3)
C(11)-C(10)-C(6)	119.9(3)
C(15)-C(10)-C(11)	120.1(3)
C(15)-C(10)-C(6)	120.0(3)
N(1)-C(3)-C(7)	122.6(3)
N(1)-C(3)-C(2)	117.8(3)
C(2)-C(3)-C(7)	119.5(3)
C(10)-C(15)-C(14)	120.9(4)
C(13)-C(14)-C(15)	120.2(4)
C(9)-C(8)-C(7)	121.7(3)
C(14)-C(13)-C(12)	121.0(3)
C(1)-C(2)-C(3)	120.0(3)
C(22)-C(23)-C(4)	113.8(7)
C(22A)-C(23)-C(4)	115.4(6)
C(21)-C(20)-C(5)	115.1(6)
C(5)-C(20)-C(21A)	113.3(5)
C(19)-C(18)-C(17)	120.3(4)
C(8)-C(9)-C(1)	118.9(3)
C(16)-C(17)-C(18)	120.2(4)
C(2)-C(1)-Cl(1)	119.3(3)
C(2)-C(1)-C(9)	121.9(3)
C(9)-C(1)-Cl(1)	118.7(3)
C(23)-C(22)-C(21)	111.4(11)
C(23)-C(22A)-C(21A)	110.0(9)
C(22A)-C(21A)-C(20)	110.8(10)

Table S7. Anisotropic displacement parameters ($Å^2x10^3$). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11}+ ... +2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	57(1)	205(2)	43(1)	2(1)	15(1)	6(1)
N(1)	49(1)	84(2)	38(1)	4(2)	25(1)	4(2)
C(21)	61(7)	92(9)	54(6)	11(7)	19(5)	9(6)
C(16)	62(2)	88(3)	44(2)	-1(2)	30(2)	7(2)
C(11)	45(2)	71(2)	37(2)	5(1)	21(1)	6(2)
C(12)	43(2)	78(3)	36(2)	5(2)	21(1)	6(2)
C(7)	53(2)	68(2)	38(2)	1(2)	26(1)	3(2)
C(19)	61(2)	74(3)	50(2)	6(2)	35(2)	4(2)
C(6)	56(2)	64(2)	41(2)	3(2)	29(1)	4(2)
C(4)	49(2)	73(2)	41(2)	3(2)	24(1)	4(2)
C(5)	53(2)	71(2)	38(2)	3(2)	24(1)	6(2)
C(10)	49(2)	72(3)	35(2)	4(2)	23(1)	3(2)
C(3)	50(2)	73(2)	42(2)	2(2)	26(1)	4(2)
C(15)	64(2)	67(2)	51(2)	0(2)	33(2)	1(2)
C(14)	65(2)	71(3)	58(2)	11(2)	34(2)	0(2)
C(8)	53(2)	96(3)	49(2)	5(2)	31(2)	1(2)
C(13)	54(2)	84(3)	42(2)	12(2)	29(2)	4(2)
C(2)	56(2)	97(3)	36(2)	5(2)	26(1)	7(2)
C(23)	51(2)	120(4)	48(2)	6(3)	26(2)	3(3)
C(20)	61(2)	110(4)	42(2)	7(2)	24(2)	7(2)
C(18)	73(3)	70(3)	72(3)	-2(2)	41(2)	0(2)
C(9)	49(2)	119(4)	49(2)	3(3)	23(2)	5(3)
C(17)	73(3)	81(3)	61(2)	-13(2)	35(2)	4(2)
C(1)	54(2)	106(3)	42(2)	4(2)	18(1)	4(2)
C(22)	54(6)	87(8)	67(7)	4(6)	20(5)	-3(6)
C(22A)	56(5)	119(9)	58(5)	14(5)	26(4)	17(6)
C(21A)	60(5)	111(8)	43(4)	-1(5)	17(3)	-2(6)

Table S8. Hydrogen coordinates (x10^4) and isotropic displacement parameters (Å^{2}x10^3).

	x	y	z	U(eq)
H(21A)	8703	2616	7505	84
H(21B)	9294	3929	8483	84
H(16)	2672	6005	10163	74
H(19)	4316	6864	7006	69
H(15)	3416	1484	6933	69
H(14)	2510	1079	8490	74
H(8)	1275	3961	5230	75
H(13)	2322	3135	9650	68
H(2)	3300	4502	2245	72
H(23A)	8317	3402	5310	85
H(23B)	8161	5214	5038	85
H(23C)	8194	3742	4955	85
H(23D)	8251	5476	5414	85
H(20A)	6998	5015	8019	84
H(20B)	6712	3199	8040	84
H(20C)	7102	2941	7879	84
H(20D)	6657	4644	8144	84
H(18)	4197	8898	8217	81
H(9)	-292	4134	3277	85
H(17)	3407	8453	9820	82
H(22A)	8901	5841	6990	84
H(22B)	10056	4558	6901	84
H(22C)	10078	4232	6849	92
H(22D)	9048	2759	6802	92
H(21C)	8542	5764	7625	86
H(21D)	9300	4359	8480	86

Table S9. Torsion angles [°].

N(1)-C(4)-C(5)-C(6)	0.0(7)
N(1)-C(4)-C(5)-C(20)	-179.9(4)
N(1)-C(4)-C(23)-C(22)	163.8(9)
N(1)-C(4)-C(23)-C(22A)	-165.4(9)
N(1)-C(3)-C(2)-C(1)	-179.7(5)
C(16)-C(12)-C(13)-C(14)	-178.9(4)
C(11)-C(12)-C(13)-C(14)	1.0(6)
C(11)-C(19)-C(18)-C(17)	-0.8(7)
C(11)-C(10)-C(15)-C(14)	0.0(6)
C(12)-C(16)-C(17)-C(18)	1.8(7)
C(12)-C(11)-C(19)-C(18)	2.1(6)
C(12)-C(11)-C(10)-C(6)	-178.5(3)
C(12)-C(11)-C(10)-C(15)	1.1(5)
C(7)-C(6)-C(5)-C(4)	-0.1(6)
C(7)-C(6)-C(5)-C(20)	179.8(4)
C(7)-C(6)-C(10)-C(11)	-99.9(4)
C(7)-C(6)-C(10)-C(15)	80.5(5)
C(7)-C(3)-C(2)-C(1)	0.6(8)
C(7)-C(8)-C(9)-C(1)	0.7(8)
C(19)-C(11)-C(12)-C(16)	-1.4(5)
C(19)-C(11)-C(12)-C(13)	178.7(4)
C(19)-C(11)-C(10)-C(6)	1.2(6)
C(19)-C(11)-C(10)-C(15)	-179.2(4)
C(19)-C(18)-C(17)-C(16)	-1.1(7)
C(6)-C(7)-C(3)-N(1)	-0.7(6)
C(6)-C(7)-C(3)-C(2)	178.9(4)
C(6)-C(7)-C(8)-C(9)	-179.6(5)
C(6)-C(5)-C(20)-C(21)	164.6(9)
C(6)-C(5)-C(20)-C(21A)	-162.9(7)
C(6)-C(10)-C(15)-C(14)	179.6(4)
C(4)-N(1)-C(3)-C(7)	0.5(7)
C(4)-N(1)-C(3)-C(2)	-179.1(5)
C(4)-C(5)-C(20)-C(21)	-15.5(11)
C(4)-C(5)-C(20)-C(21A)	17.0(9)
C(4)-C(23)-C(22)-C(21)	47.0(18)
C(4)-C(23)-C(22A)-C(21A)	-45.3(16)
C(5)-C(6)-C(10)-C(11)	81.3(5)
C(5)-C(6)-C(10)-C(15)	-98.3(5)
C(5)-C(4)-C(23)-C(22)	-16.8(10)
C(5)-C(4)-C(23)-C(22A)	14.0(10)
C(5)-C(20)-C(21A)-C(22A)	-48.8(14)
C(10)-C(11)-C(12)-C(16)	178.3(3)

C(10)-C(11)-C(12)-C(13)	-1.6(5)
C(10)-C(11)-C(19)-C(18)	-177.6(4)
C(10)-C(6)-C(5)-C(4)	178.6(4)
C(10)-C(6)-C(5)-C(20)	-1.5(7)
C(10)-C(15)-C(14)-C(13)	-0.6(7)
C(3)-N(1)-C(4)-C(5)	-0.1(7)
C(3)-N(1)-C(4)-C(23)	179.2(4)
C(3)-C(7)-C(6)-C(5)	0.5(6)
C(3)-C(7)-C(6)-C(10)	-178.3(4)
C(3)-C(7)-C(8)-C(9)	0.3(7)
C(3)-C(2)-C(1)-Cl(1)	179.8(4)
C(3)-C(2)-C(1)-C(9)	0.4(9)
C(15)-C(14)-C(13)-C(12)	0.1(6)
C(8)-C(7)-C(6)-C(5)	-179.6(4)
C(8)-C(7)-C(6)-C(10)	1.6(6)
C(8)-C(7)-C(3)-N(1)	179.4(4)
C(8)-C(7)-C(3)-C(2)	-1.0(7)
C(8)-C(9)-C(1)-Cl(1)	179.5(5)
C(8)-C(9)-C(1)-C(2)	-1.1(9)
C(23)-C(4)-C(5)-C(6)	-179.3(4)
C(23)-C(4)-C(5)-C(20)	0.8(7)
C(23)-C(22A)-C(21A)-C(20)	63.5(18)
C(20)-C(21)-C(22)-C(23)	-62(2)
C(17)-C(16)-C(12)-C(11)	-0.6(6)
C(17)-C(16)-C(12)-C(13)	179.3(4)
C(22)-C(21)-C(20)-C(5)	45.3(17)

CCDC 1998519 (**3ac**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

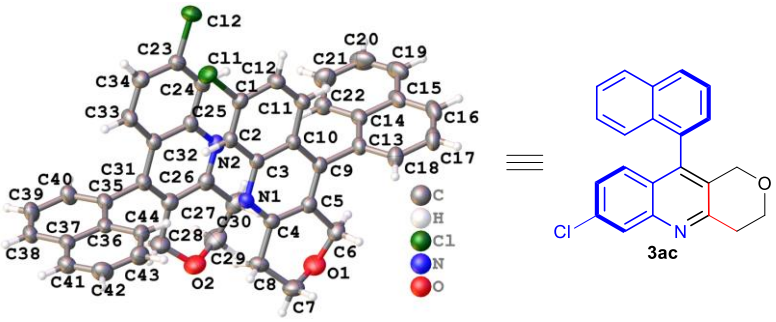


Table S10. Crystal data and structure refinement

Identification code	ndj-hz-2-300k	
Empirical formula	C22H16ClNO	
Formula weight	345.81	
Temperature	299.69(10) K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 9.35760(10) Å	α= 90°.
	b = 18.24240(10) Å	β= 90°.
	c = 20.28210(10) Å	γ = 90°.
Volume	3462.26(4) Å^3	
Z	8	
Density (calculated)	1.327 Mg/m^3	
Absorption coefficient	2.011 mm^{-1}	
F(000)	1440	
Crystal size	? x ? x ? mm^3	
Theta range for data collection	3.258 to 77.281°.	
Index ranges	-11<=h<=11, -23<=k<=20, -23<=l<=25	
Reflections collected	46005	
Independent reflections	7109 [R(int) = 0.0370]	
Completeness to theta = 67.684°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.83498	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7109 / 0 / 451	
Goodness-of-fit on F^2	1.051	
Final R indices [I>2sigma(I)]	R1 = 0.0385, wR2 = 0.1143	
R indices (all data)	R1 = 0.0403, wR2 = 0.1162	
Absolute structure parameter	-0.002(5)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.503 and -0.300 e.Å^{-3}	

CCDC 1998518 (**3aj**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

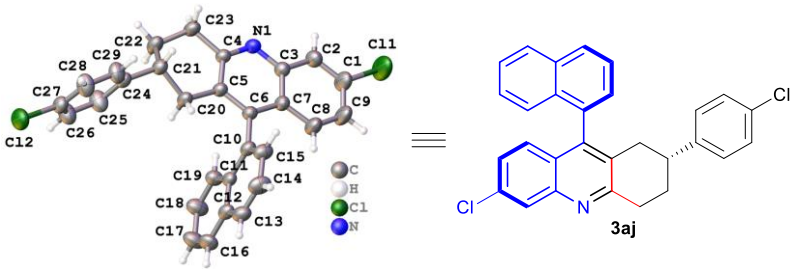


Table S11. Crystal data and structure refinement

Identification code	ndj-hz-1-300k	
Empirical formula	C29H21Cl2N	
Formula weight	454.37	
Temperature	299.60(10) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 10.8865(3) Å	α= 90°.
	b = 8.8581(3) Å	β= 97.528(2)°.
	c = 12.0837(4) Å	γ = 90°.
Volume	1155.23(6) $Å^3$	
Z	2	
Density (calculated)	1.306 Mg/m^3	
Absorption coefficient	2.644 mm^{-1}	
F(000)	472	
Crystal size	? x ? x ? mm^3	
Theta range for data collection	3.690 to 76.873°.	
Index ranges	-12<=h<=13, -11<=k<=10, -14<=l<=15	
Reflections collected	12833	
Independent reflections	4168 [R(int) = 0.0348]	
Completeness to theta = 67.684°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.74959	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4168 / 1 / 289	
Goodness-of-fit on F^2	1.079	
Final R indices [I>2sigma(I)]	R1 = 0.0611, wR2 = 0.1885	
R indices (all data)	R1 = 0.0646, wR2 = 0.1934	
Absolute structure parameter	0.05(3)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.262 and -0.196 e.$Å^{-3}$	