Supplementary Information (SI) for Green Chemistry.
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Red-Light-Driven Enantioselective Minisci-type Addition to Heteroarenes via Recyclable Heterogeneous Catalysis

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Supporting Information

Contents

1. General Information

All reactions were performed under argon atmosphere with glass storage tube unless otherwise stated. Reagents were purchased from commercial sources and were used as received. Solvents were purified by VG-P7 solvent drying system or commercial dry solvent. Thin layer chromatography (TLC) was performed to monitor reactions by UV light (254 nm) or phosphomolybdate chromogenic agent. Silica gel column chromatography was performed using 200-300 Mesh silica gel.

^{1}H and ^{13}C NMR spectra were recorded at 400 MHz, 100 MHz on a Bruker Avance 400 spectrometer. All chemical shifts in ^{1}H NMR spectra are reported in parts per million (ppm) relative to residual $CDCl_3$ (7.26 ppm) as internal standards. ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, br = broad), the number of protons (n) for a given resonance was indicated by *n*H. Coupling constants were reported as a *J* value in Hz. ^{19}F NMR chemical shiftswere reported in ppm. ^{13}C NMR chemical shifts are reported in ppm relative to the central peak of $CDCl_3$ (77.16 ppm) as internal standards. HRMS data were obtained by ESI or APCI method with Bruker mass spectrometer (MAXIS). The enantiomeric excess (*ee*) of products were determined by chiral phase HPLC analysis on a Thermo Scientific DIONEX UltiMate U3000 HPLC machine. X-Ray crystallographic analyses were performed on Bruker D8 Venture. HRMS data were obtained by ESI or APCI method with Bruker mass spectrometer (MAXIS). Optical rotations were measured in $CHCl_3$ on a Shanghai Zhuoguang fully automatic Polarimeter using a sodium lamp (λ 589 nm, D-line). The X-Ray Diffraction (XRD) patterns were collected on Rigaku D/Max2550VB+/PC (Cu Kα source) at a scan rate of 2.4^{o} min^{-1}. Scanning Electron Microscopy (SEM) images were obtained on a field emission scanning electron microscope (HITACHI SU8220 microscope). Transmission Electron Microscopy (TEM) images and element mapping were obtained by a Tecnai G2 F20 transmission electron microscopy (FEI, USA).

A 10 mL liquid storage sealed tube with a polytetrafluoroethylene thread plug was used for all the experiments, The photoreactor was an optical parallel reaction instrument produced by TaoBao and a 50 W*2 red LED lamp was used. (Figure S1).

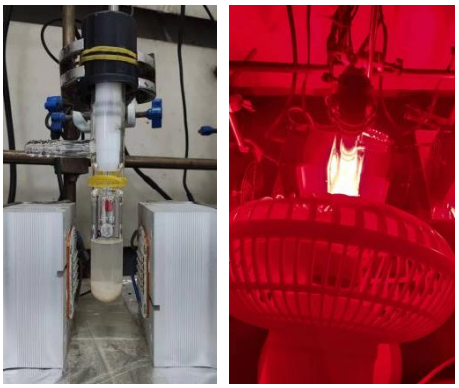
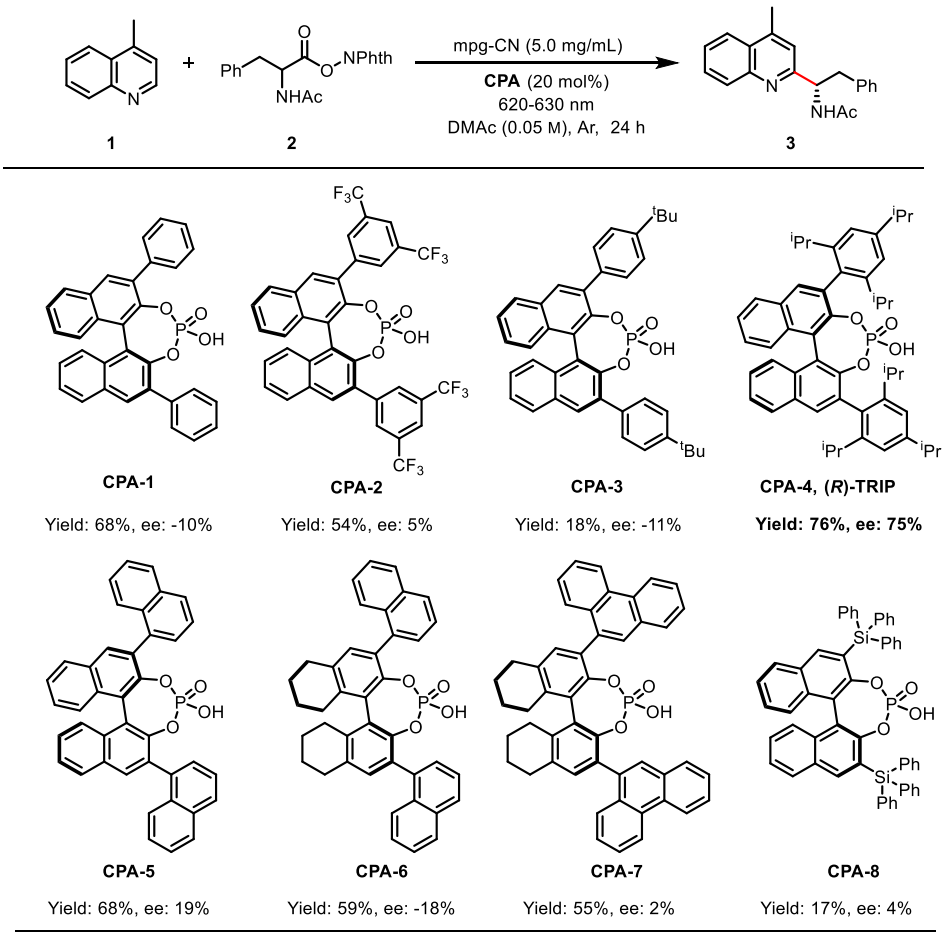


Figure S1. Pictures of photoreactors

(Note: The reaction was conducted at room temperature)

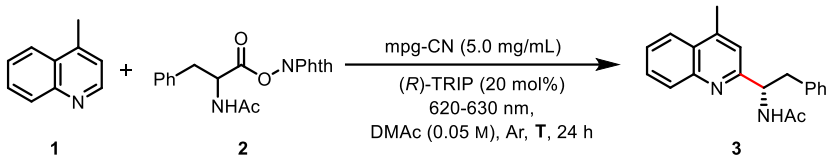
2. Optimization of reaction conditions

Scheme S1. Screening of chiral phosphoric acid (CPA).



Reaction conditions: **1** (0.1 mmol), **2** (1.5 equiv.), mpg-CN (5.0 mg/mL), CPA (20 mol%), 620-630 nm, DMAc (0.05 M), Ar, at ambient temperature (25-28 °C), 24 h. Yields were determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as internal standard.

Table S1. Screening of temperature.

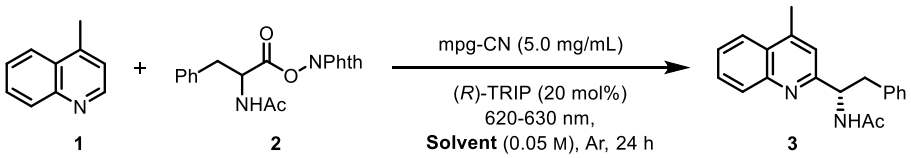


1 **2** **3**

Entry	**T** (^{o}C)	Yield (%)	ee (%)
1	**25**	**76**	**75**
2	45	81	72
3	65	60	51

Reaction conditions: **1** (0.1 mmol), **2** (1.5 equiv.), mpg-CN (5.0 mg/mL), (*R*)-TRIP (20 mol%), 620-630 nm, DMAc (0.05 M), Ar, 24 h. Yields were determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as internal standard.

Table S2. Screening of solvent.

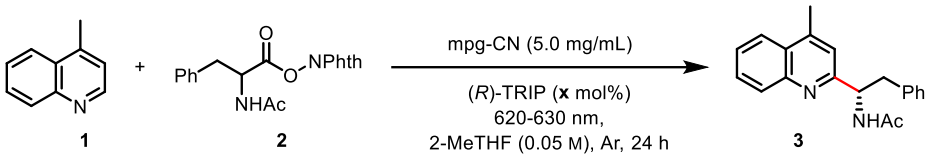


1 **2** **3**

Entry	**Solvent**	Yield (%)	ee (%)
1	DMAc	76	75
2	DMF	30	67
3	1,4-dioxane	15	83
4	THF	26	80
5	CH_3CN	trace	-
6	DCM	N.R	--
7	**2-MeTHF**	**69**	**95**
8	1,3-dioxolane	42	94
9	toluene	trace	-
10	H_2O	N.R	-

Reaction conditions: **1** (0.1 mmol), **2** (1.5 equiv.), mpg-CN (5.0 mg/mL), (*R*)-TRIP (20 mol%), 620-630 nm, Solvent (0.05 M), at ambient temperature (25-28 °C), 24 h. Yields were determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as internal standard.

Table S3. Screening of chiral phosphoric acid (CPA) loading.

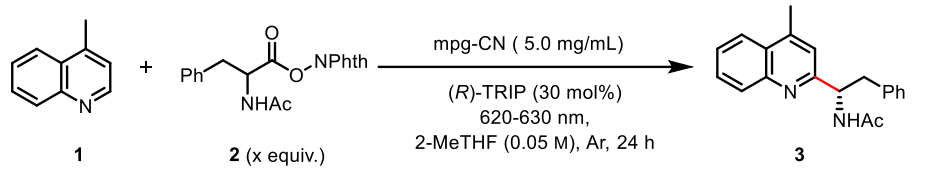


1 **2** **3**

Entry	(*R*)-TRIP-PA (**x** mol%)	Yield (%)	ee (%)
1	5	16	86
2	10	42	93
3	15	52	93
4	20	69	95
5	25	75	94
6	**30**	**91**	**95**

Reaction conditions: **1** (0.1 mmol), **2** (1.5 equiv.), mpg-CN (5.0 mg/mL), (*R*)-TRIP (x mol%), 620-630 nm, 2-MeTHF (0.05 M), Ar, 24 h, at ambient temperature (25-28 °C), 24 h. Yields were determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as internal standard.

Table S4. Screening of the substrates loading.

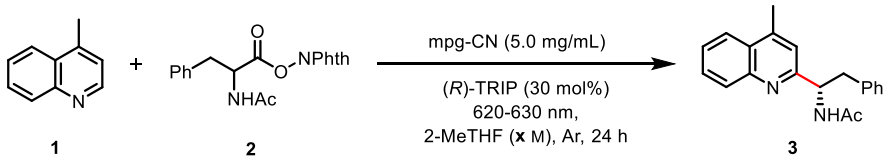


1 **2** (x equiv.) **3**

Entry	**2** (x equiv.)	Yield (%)	*ee (%)*
1	1.5	91	95
2	**2.0**	**93**	**95**
3	2.5	88	94

Reaction conditions: **1** (0.1 mmol), **2** (x equiv.), mpg-CN (5 mg/mL), (*R*)-TRIP (30 mol%), 620-630 nm, 2-MeTHF (0.05 M), Ar, 24 h, at ambient temperature (25-28 °C), 24 h. Yields were determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as internal standard.

Table S5. Screening of concentration.

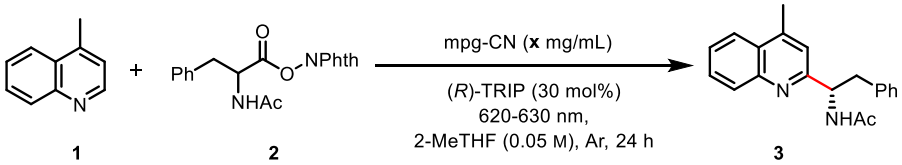


1 2 3

Entry	2-MeTHF (**x** M)	Yield (%)	ee (%)
1	0.067	65	93
2	**0.050**	**93**	**95**
3	0.040	87	92
4	0.033	83	92

Reaction conditions: **1** (0.1 mmol), **2** (2.0 equiv.), mpg-CN (5.0 mg/mL), (*R*)-TRIP (30 mol%), 620-630 nm, 2-MeTHF (x M), Ar, at ambient temperature (25-28 °C), 24 h. Yields were determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as internal standard.

Table S6. Screening of mpg-CN loading.

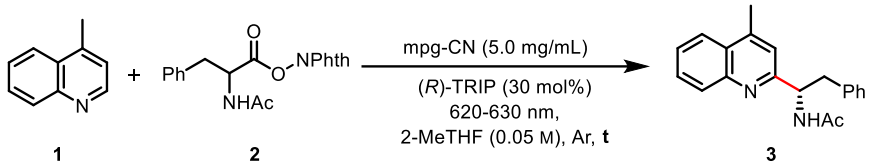


1 2 3

Entry	mpg-CN (**x** mg/mL)	Yield (%)	ee (%)
1	1.0	42	94
2	3.5	84	94
3	**5.0**	**93**	**95**
4	7.5	94	94

Reaction conditions: **1** (0.1 mmol), **2** (2.0 equiv.), mpg-CN (x mg/mL), (*R*)-TRIP (30 mol%), 620-630 nm, 2-MeTHF (0.05 M), Ar, at ambient temperature (25-28 °C), 24 h. Yields were determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as internal standard.

Table S7. Screening of reaction time.

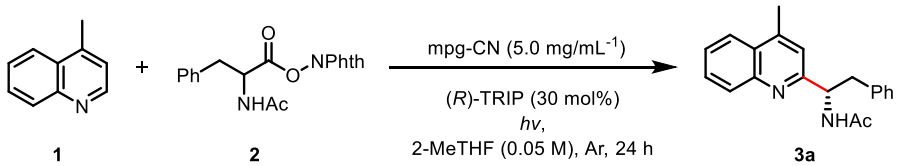


1 2 3

Entry	**t** (h)	Yield (%)	ee (%)
1	12	56	93
2	16	79	93
3	20	87	94
4	**24**	**93**	**95**
5	28	94	94

Reaction conditions: **1** (0.1 mmol), **2** (2.0 equiv.), mpg-CN (5 mg/mL), (*R*)-TRIP (30 mol%), 620-630 nm, 2-MeTHF (0.05 M), Ar, at ambient temperature (25-28 °C). Yields were determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as internal standard.

Table S8. Screening of different light sources.

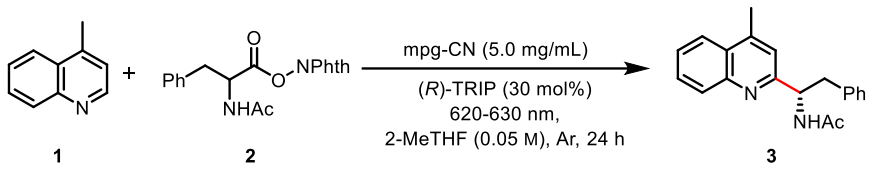


1 2 3a

Entry	*hv* (nm)	luminous power (W)	Temp.(°C)	Yield (%)	ee (%)
1	390-395 nm	50*2	ambient temperature	86	94
2	460-465 nm	50*2	ambient temperature	92	93
3	**620-630 nm**	**50*2**	ambient temperature	**93**	**95**
4	620-630 nm	50*2	60	92	53

Reaction conditions: **1** (0.1 mmol), **2** (2.0 equiv.), mpg-CN (5 mg/mL), (*R*)-TRIP (30 mol%), *hv*, 2-MeTHF (0.05 M), Ar, at ambient temperature (25-28 °C), 24 h. Yields were determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as internal standard.

Table S9. Control experiments.



1 2 3

Entry	Deviation from the standard conditions	Yield (%)	ee (%)
1	standard conditions	93	95
2	standard conditions, no light	trace	-
3	standard conditions, no mpg-CN	trace	-
4	standard conditions, no (*R*)-TRIP-PA	N.R	-

Reaction conditions: **1** (0.1 mmol), **2** (2.0 equiv.), mpg-CN (5 mg/mL), (*R*)-TRIP (30 mol%), 620-630 nm, 2-MeTHF (0.05 M), Ar, at ambient temperature (25-28 °C), 24 h. Yields were determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as internal standard.

3. Preparation of mpg-CN and redox-active esters (RAEs).

3.1 Preparation of mpg-CN

mpg-CN was synthesized according to the literature procedure[1]. A mixture of cyanamide (3.00 g) and colloidal silica aqueous solution (Ludox HS-40, 40 wt.%, 7.50 g) was stirred in a glass vial at room temperature for about 15 minutes until cyanamide was dissolved completely. Water was slowly evaporated upon stirring the mixture overnight at 60 °C. Magnetic stirring bar was removed and the white solid was transferred into a porcelain crucible and calcinated at 550 °C for ca. 4h under flow of nitrogen in a muffle oven. The oven was allowed to cool to room temperature, the content from the crucible was transferred into a polypropylene bottle, The resulting brown-yellow powder was treated with a 4M NH_4HF_2 for 24 h to remove the silica template. The powders were then centrifuged and washed three times with distilled water and twice with ethanol, and dried overnight in a vacuum oven (60 °C).

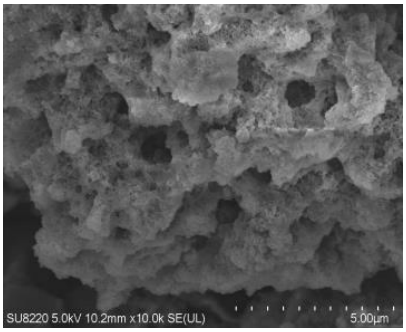


Fig. S1 SEM images of mpg-CN

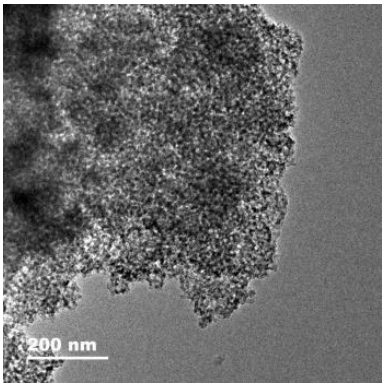


Fig. S2 TEM images of mpg-CN

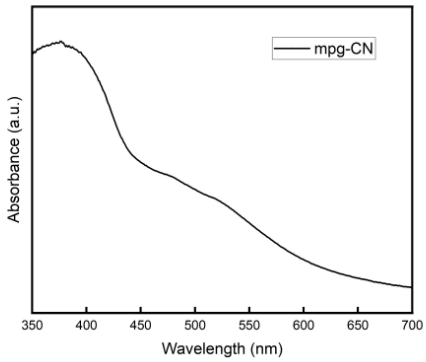


Fig. S3 Diffuse reflectance UV-Vis absorption spectrum of mpg-CN.

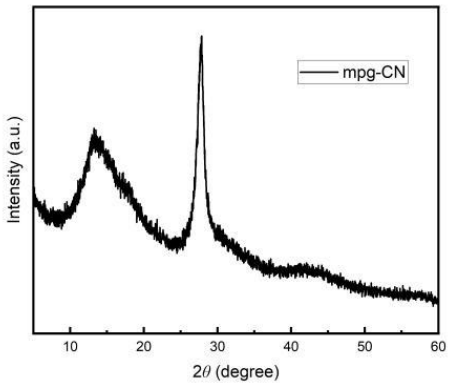
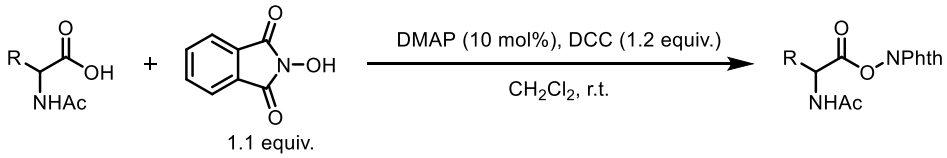


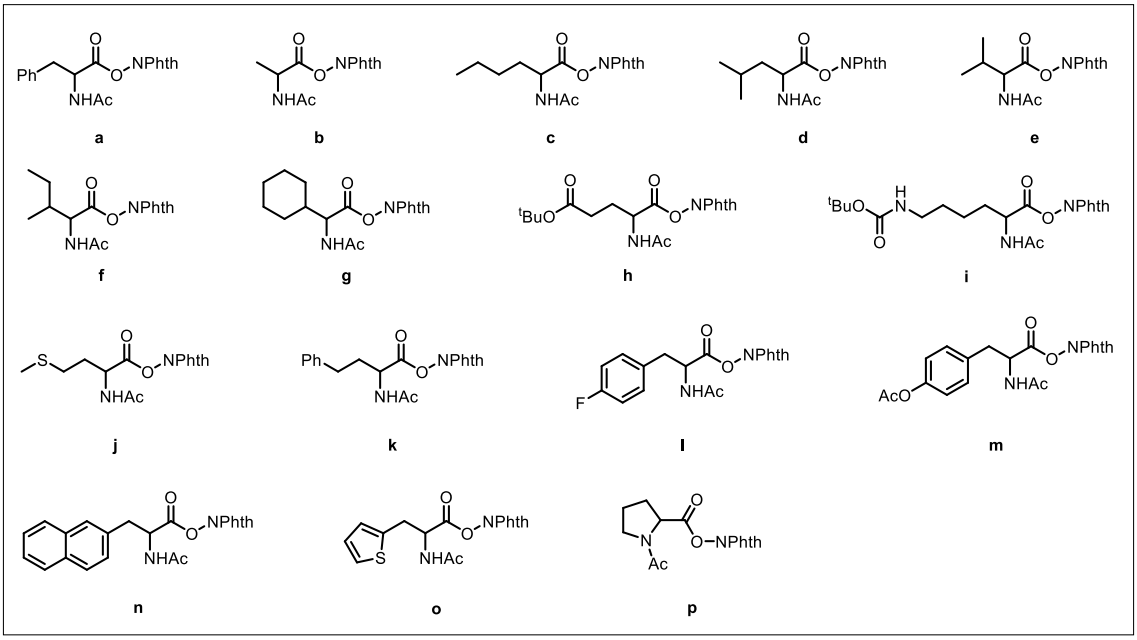
Fig. S4. Powder X-Ray diffraction pattern of mpg-CN.

3.2 General procedure for preparation of redox active esters (RAEs).



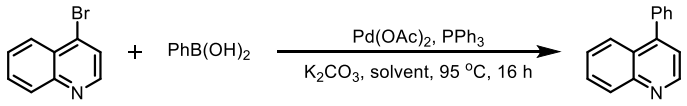
RAEs were prepared using enantiopure *N*-acetyl amino acids as starting materials according to the

literature procedure.[2] The corresponding alkyl carboxylic acid (10.0 mmol, 1.0 equiv.), *N*-hydroxyphthalimide (11.0 mmol, 1.1 equiv.), and 4-dimethylaminopyridine (1.0 mmol, 10 mol%) were mixed in a flask with a magnetic stirring bar. Dry CH_2Cl_2 (40 mL) was added. Then a solution of *N*, *N*´-dicyclohexylcarbodiimide (11.0 mmol, 1.1 equiv.) in CH_2Cl_2 (15 mL) was added slowly at room temperature. The reaction mixture was monitored by TLC at room temperature. After completed, the white precipitate was filtered off and the solution was concentrated under vacuum. Corresponding redox active esters were purified by column chromatography on silica gel (petroleum ether/ethyl acetate as eluent).



3.3 Procedure for the preparation of 4-phenylquinoline

4-phenylquinoline was synthesized according to the literature procedure.[3]

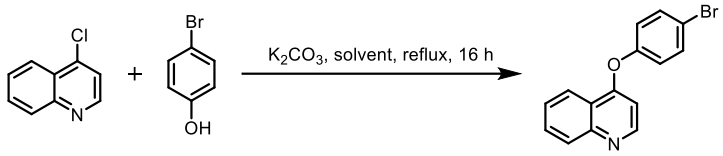


A vessel was charged with 4-bromoquinoline (416 mg, 2.0 mmol, 1.0 equiv.), and ethanol (2 mL), water (4 mL), toluene (8 mL), phenylboronic acid (366 mg, 3.0 mmol, 1.5 equiv.), K_2CO_3 (1.10 g, 8.0 mmol, 4.0 equiv.), PPh_3 (88 mg, 0.30 mmol, 15 mol%), and $Pd(OAc)_2$ (22 mg, 0.10 mmol, 5 mol%) were added. The green reaction mixture was heated at 95 °C for 16 hours. After cooling to room temperature, the biphasic solution was diluted with saturated aqueous NH_4Cl (10 mL) and CH_2Cl_2 (10 mL). The aqueous phase was extracted with CH_2Cl_2 (2 x 10 mL) and the combined organic layers were washed with water

(10 mL) and saturated aqueous $NaHCO_3$ (10 mL). The organic phase was dried over $MgSO_4$ and filtered. The filtrate was concentrated in vacuo and purified by flash column chromatography eluting with 40% EtOAc in petroleum ether (40-60) to afford 4-phenylquinoline (395 mg, 1.92 mmol, 96%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δH 8.95 (d, *J* = 4.4 Hz, 1H), 8.19 (d, *J* = 8.0 Hz, 1H), 7.92 (dd, *J* = 8.5, 0.9 Hz, 1H), 7.74-7.70 (m, 1H), 7.57-7.44 (m, 6H), 7.33 (d, *J* = 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δC 150.0, 148.7, 148.5, 138.0, 129.9, 129.6, 129.3, 128.6, 128.4, 126.8, 126.6, 125.9, 121.3.

3.4 Procedure for the preparation of 4-(4-bromophenoxy)quinoline.

4-(4-Bromophenoxy)quinoline was synthesized according to the literature procedure.[3]

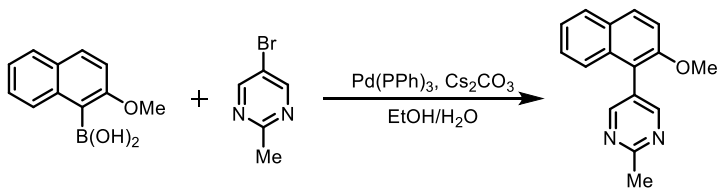


S-c **S-d** **S-2**

4-Chloroquinoline, (327 mg, 2.00 mmol), 4-bromophenol (410 mg, 4.40 mmol, 1.2 equiv.) and K_2CO_3 (830 mg, 6.00 mmol, 3.0 equiv.) were suspended in dry dimethylformamide (DMF, 2.5 mL). The resulting mixture was heated under reflux and vigorous stirring for 14 h. The reaction mass was diluted with water (12.5 mL) and extracted with dichloromethane (3 x 30 mL). Finally, the organic phases were dehydrated using Na_2SO_4, concentrated under vacuum and the crude mixture purified by flash column chromatography eluting with 25% EtOAc in petroleum ether (40-60) to afford 4-(4-bromophenoxy)quinoline (573 mg, 1.90 mmol, 95%) as white wax block-shaped solid.

^{1}H NMR (400 MHz, $CDCl_3$) δH 8.69 (d, *J* = 5.1 Hz, 1H), 8.32 (dd, *J* = 8.4, 1.0 Hz, 1H), 8.11 (d, *J* = 8.5 Hz, 1H), 7.79-7.75 (m, 1H), 7.62-7.53 (m, 3H), 7.11-7.03 (m, 2H), 6.57 (d, *J* = 5.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δC 161.4. 153.6, 151.0, 149.8, 133.4, 130.3, 129.1, 126.4, 122.8, 121.7, 121.4, 118.5, 104.5.

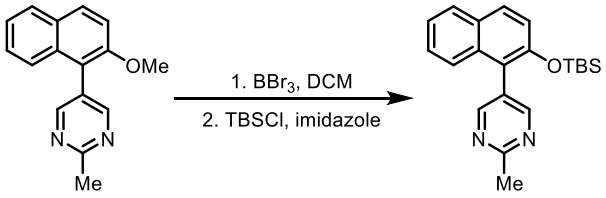
3.5 Procedure for the preparation of 5-Arylimidine. [4]



S-e **S-f** **S-3**

The (2-methoxynaphthalen-1-yl)boronic acid (10 mmol, 1.0 equiv.), 5-bromo-2-methyl-pyrimidine (10

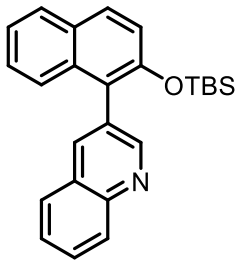
mmol, 1.0 equiv.), $Pd(PPh_3)_4$ (0.25 mmol, 0.025 equiv.) and Cs_2CO_3 (25 mmol, 2.5 equiv.) were dissolved into EtOH (20 mL) and H_2O (10 mL). The resulting solution was stirred at 80 °C for overnight. After completion of the reaction (TLC), the reaction was diluted with Et_2O (100 mL) and washed with H_2O. The organic layer was washed with brine, dried over Na_2SO_4. The product was purified by flash column chromatography on silica gel using (petroleum ether/ethyl acetate) as eluent to afford **S-3** as a yellow solid.



S-3 **S-4**

To a solution of S3 (1.0 equiv.) in CH_2Cl_2 (0.1 M) was added BBr_3 (1.2 equiv.) slowly, and the mixture was stirred at room temperature under argon until the reaction was complete (TLC). The mixture was diluted with water and extracted with CH_2Cl_2. The aqueous layer was extracted with DCM and the combined organic extracts were washed with brine, dried over Na_2SO_4, the solvent was removed under vacuum and the residue was subjected to column chromatography on SiO_2 with EtOAc-Petroleum ether as an eluent to give a colorless oil. Then the colorless oil (1.0 equiv.) and imidazole (3.0 equiv.) were dissolved into CH_2Cl_2 (0.1 M), then tert-Butyldimethylsilyl chloride (2.0 equiv.) was added to the resulting solution at room temperature. The reaction mixture was stirred overnight. After completion, the precipitate was removed by filtration and the filtrate was concentrated under reduced pressure to afford a crude product, which was purified by silica-gel column chromatography (petroleum ether/ethyl acetate) to afford **S-4**

1H NMR (400 MHz, $CDCl_3$) δH 8.69 (s, 2H), 7.86-7.80 (m, 2H), 7.47-7.38 (m, 3H), 7.18 (d, *J* = 8.9 Hz, 1H), 2.84 (s, 3H), 0.77 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δC 166.5, 158.9, 151.1, 133.5, 130.3, 129.3, 128.3, 127.6, 127.0, 124.1, 120.7, 120.0, 25.7, 25.4, 18.0, -4.2.



S-5

^{1}H NMR (400 MHz, $CDCl_3$) δH 8.83 (d, *J* = 1.8 Hz, 1H), 8.14-8.06 (m, 2H), 7.78-7.71 (m, 3H), 7.69-7.63 (m, 1H), 7.52-7.40 (m, 2H), 7.31-7.22 (m, 2H), 7.16-7.09 (m, 1H), 0.55 (s, 9H), -0.15 (t, *J* = 4.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 153.2, 151.0, 146.9, 138.1, 133.8, 130.1, 129.7, 129.4, 129.4, 129.2, 128.1, 128.0, 127.7, 126.7, 126.7, 124.7, 123.8, 123.6, 121.0, 25.3, 17.9, -4.3.

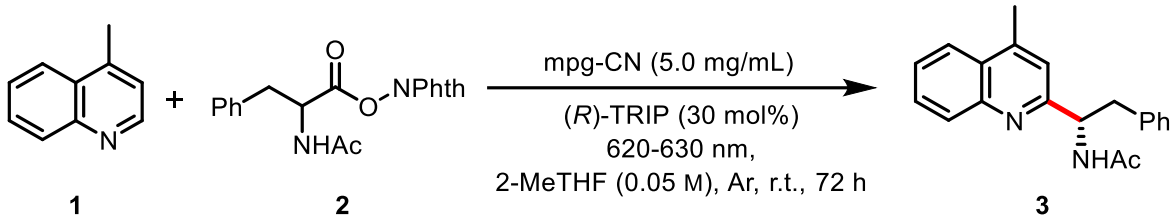
4. General procedure for the catalytic reactions

4.1 Standard procedure for the synthesis of products

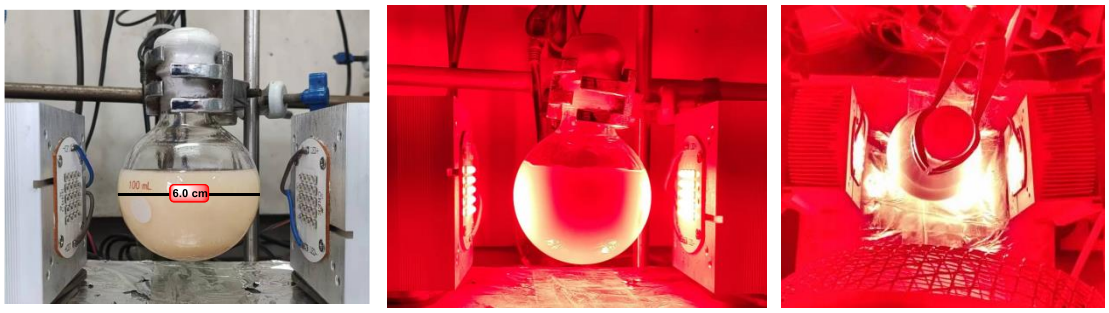
To an oven-dried 10 mL glass storage tube with a stir bar were added *N*-heteroarene (1.0 equiv., 0.3 mmol), redox active ester (2.0 equiv., 0.6 mmol), mpg-CN (30 mg) and (*R*)-TRIP-PA (30 mol%). The mixture was evacuated and backfilled with argon for 3 times before 2-MeTHF (6.0 mL) were added. The reaction mixture was placed in a photo reactor, and maintained at approximately room temperature. The mixture was then stirred rapidly and irradiated for 24-48 hours. mpg-CN was obtained by rapid filtration of the reaction mixture, and the filtrate was concentrated under vacuo. The product was purified via flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1~2:1).

4.2 Standard procedure for gram-scale synthesis

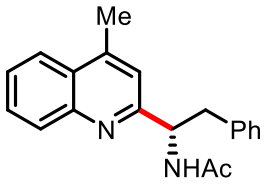
An oven-dried 100 mL flask equipped with a magnetic stir bar was sequentially charged with *N*-heteroarene (1.0 equiv., 3.0 mmol), redox active ester (2.0 equiv., 6.0 mmol), mpg-CN (300 mg) and (*R*)-TRIP (30 mol%), 2-Me THF (60.0 mL) in the glove box. The flask was sealed and removed from the glove box. The reaction mixture was placed in a photo reactor, and maintained at approximately room temperature. The mixture was then stirred rapidly and irradiated for 72 h. mpg-CN was obtained by rapid filtration of the reaction mixture, and the filtrate was concentrated under vacuo. The product was purified via flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1~2:1).



1 **2** **3**



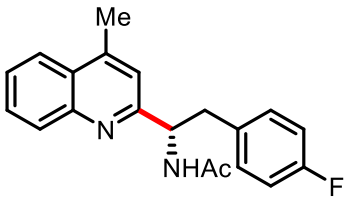
4.3 Characterization of compounds



(*S*)-*N*-(1-(4-methylquinolin-2-yl)-2-phenylethyl)acetamide (**3**)[3]: white solid, 87% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 8.03 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.70 (t, *J* = 7.9 Hz, 1H), 7.55 (t, *J* = 7.9 Hz, 1H), 7.23 (br s, 1H), 7.16-7.14 (m, 3H), 6.95-6.93 (m, 2H), 6.80 (s, 1H), 5.41-5.36 (m, 1H), 3.34 (d, *J* = 13.3, 5.2 Hz, 1H), 3.16 (q, *J* = 13.5, 8.1 Hz, 1H), 2.58 (s, 3H), 2.08 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 169.5, 158.7, 147.1, 144.6, 137.2, 129.7, 129.4, 129.3, 128.1, 127.4, 126.4, 126.2, 123.8, 121.5, 55.5, 42.2, 23.6, 18.7.

Chiral HPLC analysis, Chiralpak IC (70:30 Hexane:i-PrOH, flow rate 1.0 mL/min, 254 nm, 25 °C), t_r(minor) = 11.48 min, t_r(major) = 13.37 min, 95% ee.

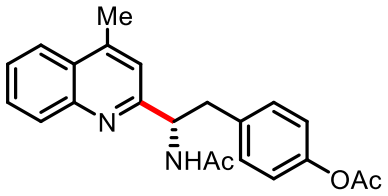


(*S*)-*N*-(2-(4-fluorophenyl)-1-(4-methylquinolin-2-yl)ethyl)acetamide (**4**)[5]: white solid, 69% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 8.00 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.69 (t, *J* = 8.1 Hz, 1H), 7.54 (t, *J* = 8.0 Hz, 1H), 7.28 (bt d, *J* = 7.2 Hz, 1H), 6.89-6.80 (m, 5H), 5.36 (dt, *J* = 7.6, 7.5 Hz, 1H), 3.28 (dd, *J* = 13.4, 5.0 Hz, 1H), 3.16 (dd, *J* = 13.4, 7.8, Hz, 1H), 2.59 (s, 3H), 2.07 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 169.5, 162.8, 160.4, 158.5, 147.1, 144.7, 132.9 (d, *J* = 3.2 Hz), 131.1(d, *J* = 7.9

Hz), 129.4 (d, *J* = 8.5 Hz), 127.4, 126.2, 123.8, 121.4, 114.9 (d, *J* = 21.2 Hz), 55.4, 41.2, 23.6, 18.7; ^{19}F NMR (376 MHz, $CDCl_3$) δF -166.69.

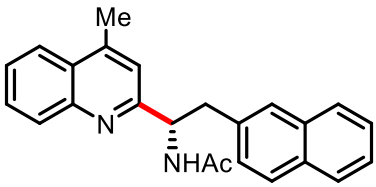
Chiral HPLC analysis, Chiralpak AD-H (95:5 Hexane:i-PrOH, flow rate 1.0 mL/min, 254 nm, 25 °C),, t_r(major) = 9.30 min., t_r(minor) = 10.52 min, 96% ee.



(*S*)-4-(2-acetamido-2-(4-methylquinolin-2-yl)ethyl)phenyl acetate (**5**): light yellow solid, 50% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δH 8.03 (d, *J* = 8.3 Hz, 1H), 7.96 (d, *J* = 8.3 Hz, 1H), 7.73 (dt, *J* = 8.2, 7.0 Hz, 1H), 7.55 (dt, *J* = 8.2, 7.0 Hz, 1H), 7.33 (br d, *J* = 4.6 Hz, 1H), 6.93 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 9.4 Hz, 2H), 6.79 (s, 1H), 5.36 (dt, *J* = 7.8, 5.0 Hz, 1H), 3.34 (dd, *J* = 13.3, 5.0 Hz, 1H), 3.14 (dd, *J* = 13.3, 8.1 Hz, 1H), 2.59 (s, 3H), 2.26 (s, 3H), 2.08 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 169.5, 169.5, 158.4, 149.3, 147.1, 144.8, 134.9, 130.6, 129.4, 129.3, 127.4, 126.2, 123.9, 121.5, 121.2, 55.4, 41.5, 23.6, 21.2, 18.7.

HRMS(ESI$^+$) m/z: [M + H]$^+$calcd. for $[C_{22}H_{23}N_2O_3]^+$ expect 363.1703; found 363.1707.

Chiral HPLC analysis, Chiralpak OD (85:15 Hexane:i-PrOH, flow rate 1.0 mL/min, 220 nm, 25 °C), t_r(minor) = 9.69 min., t_r(major) = 11.02 min; $[\alpha]_D^{27.4}$ = +48.7 (*c* 1.0, $CHCl_3$), 93% ee.

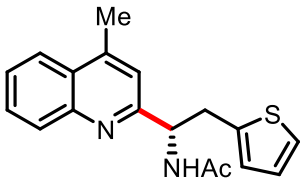


(*S*)-*N*-(1-(4-methylquinolin-2-yl)-2-(naphthalen-2-yl)ethyl)acetamide (**6**): light yellow solid, 56% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 8.03 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.3 Hz, 1H), 7.76 (t, *J* = 3.5 Hz 1H), 7.70-7.62 (m, 3H), 7.56-7.53 (t, *J* = 7.5 Hz, 1H), 7.46 (s, 1H), 7.42-7.39 (m, 2H), 7.28 (d, *J* = 7.1 Hz, 1H), 7.06 (d, *J* = 8.4 Hz, 1H), 6.83 (s, 1H), 5.50 (q, *J* = 6.9 Hz, 1H), 3.51 (dd, *J* = 13.3, 5.0 Hz, 1H), 3.36 (dd, *J* = 13.2, 7.9 Hz, 1H), 2.52 (s, 3H), 2.08 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 169.4, 158.7, 147.1, 144.6, 134.8, 133.3, 132.2, 129.4, 129.2, 128.3, 128.0, 127.5, 127.5, 127.5, 127.4, 126.1, 125.8, 125.3, 123.8, 121.4, 55.4, 42.2, 23.5, 18.5.

HRMS(ESI$^+$) m/z: [M + H]$^+$calcd. for $[C_{24}H_{23}N_2O]^+$ expect 355.1805; found 355.1807.

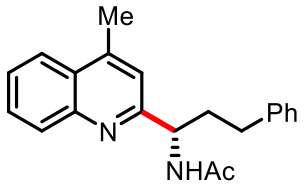
Chiral HPLC analysis, Chiralpak IF (80:20 Hexane:i-PrOH, flow rate 1.0 mL/min, 220 nm, 25 °C), t_r(major) = 10.35 min., t_r(minor) = 11.73 min. $[\alpha]_D^{27.6}$ = + 88.8 (*c* 1.0, $CHCl_3$), 93% ee.



(*S*)-*N*-(1-(4-methylquinolin-2-yl)-2-(thiophen-2-yl)ethyl)acetamide (**7**): light yellow solid, 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δH 8.02 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 8.3 Hz, 1H), 7.69 (t, *J* = 6.9 Hz 1H), 7.54 (t, *J* = 7.0 Hz 1H), 7.30 (br s, 1H), 7.04-7.02 (m, 2H), 6.79 (t, *J* = 5.0 Hz, 1H), 6.56 (d, *J* = 3.2 Hz 1H), 5.42 (dd, *J* = 12.4, 7.0 Hz 1H), 3.59-3.48 (m, 2H), 2.64 (s, 3H), 2.10 (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$) δC 169.6, 158.2, 147.0, 144.9, 138.9, 129.5, 129.3, 127.5, 126.6, 126.5, 126.2, 124.2, 123.8, 121.1, 55.0, 35.6, 23.6, 18.8.

HRMS(ESI$^+$) m/z: $[M + H]^+$calcd. for $[C_{20}H_{27}N_2O_3]^+$ expect 311.1213; found 311.1214.

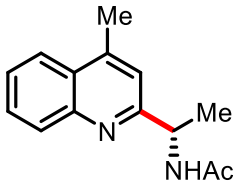
Chiral HPLC analysis, Chiralpak AD-H (95:5 Hexane:i-PrOH, flow rate 1.0 mL/min, 220 nm, 25 °C), t_r (major) = 17.42 min., t_r(minor) = 18.65 min, 88% ee; $[\alpha]_D^{27.6}$ = -23.5 (*c* 1.0, $CHCl_3$).



(*S*)-*N*-(1-(4-methylquinolin-2-yl)-3-phenylpropyl)acetamide (**8**)[3]: white solid, 90% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 8.08 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 8.3 Hz, 1H), 7.75-7.69 (m, 1H), 7.60-7.53 (m, 1H), 7.28 (br d, *J* = 3.6 Hz, 1H), 7.25 (t, *J* = 8.0 Hz, 2H), 7.14 (t, *J* = 8.0 Hz, 4H), 5.30 (q, *J* = 6.4 Hz, 1H), 2.69 (s, 3H), 2.66-2.61 (m, 1H), 2.59-2.52 (m, 1H), 2.41-2.32 (m, 1H), 2.22-2.13 (m, 1H), 2.09 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 169.7, 159.5, 147.2, 145.2, 141.7, 129.5, 129.4, 128.4, 128.3, 127.5, 126.2, 125.8, 123.9, 121.0, 53.9, 37.7, 31.6, 23.6, 18.8.

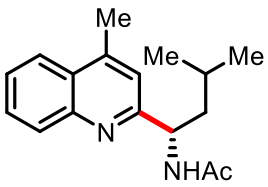
Chiral HPLC analysis, Chiralpak IF (85:15 Hexane:i-PrOH, flow rate 1.0 mL/min, 220 nm, 25 °C), t_r(major) = 11.200 min., t_r(minor) = 13.630 min, 92% ee.



(*S*)-*N*-(1-(4-methylquinolin-2-yl)ethyl)acetamide (**9**)[3]: white solid, 85% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 8.07 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 8.3 Hz, 1H), 7.72 (t, *J* = 7.3 Hz, 1H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.48 (s, 1H), 7.16 (s, 1H), 5.21 (p, *J* = 6.8 Hz, 1H), 2.71 (s, 3H), 2.11 (s, 3H), 1.54 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δC 169.6, 160.6, 147.0, 145.6, 129.6, 129.4, 127.6, 126.3, 123.9, 120.5, 50.1, 23.8, 22.8, 18.9.

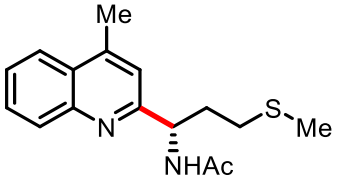
Chiral HPLC analysis, Chiralpak IC (70:30 Hexane:i-PrOH, flow rate 1.0 mL/min, 220 nm, 25 °C) t_r(minor) = 12.86 min, t_r(major) = 16.04 min, 89% ee.



(*S*)-*N*-(3-methyl-1-(4-methylquinolin-2-yl)butyl)acetamide (**10**)[5]: white solid, 80% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 8.3 Hz, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.19 (s, 1H), 6.96 (d, *J* = 1.8 Hz, 1H), 5.26 (dd, *J* = 14.6, 7.8 Hz, 1H), 2.69 (s, 3H), 2.05 (s, 3H), 1.77-1.67 (m, 2H), 1.65-1.58 (m, 1H), 0.98 (d, *J* = 6.4 Hz, 3H), 0.94 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 160.9, 147.4, 145.0, 129.4, 129.3, 127.4, 126.0, 123.8, 121.2, 52.6, 46.1, 25.0, 23.6, 23.0, 22.7, 18.8.

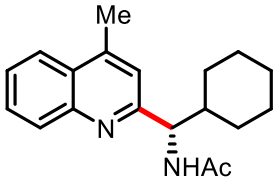
Chiral HPLC analysis, Chiralpak IC (70:30 Hexane:i-PrOH, flow rate 1.0 mL/min, 254 nm, 25 °C), t_r(minor) = 6.96 min, t_r(major) = 9.66 min, 82% ee.



(*S*)-*N*-(1-(4-methylquinolin-2-yl)-3-(methylthio)propyl)acetamide (**11**)[3]: white solid, 77% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 8.04 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.71 (t, *J* = 7.9 Hz, 1H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.27 (s, 1H), 7.20 (s, 1H), 5.32 (q, *J* = 6.4 Hz, 1H), 2.70 (s, 3H), 2.55-2.48 (m, 1H), 2.40-2.25 (m, 2H), 2.17-2.07 (m, 7H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 169.7, 158.9, 147.1, 145.4, 129.5, 129.4, 127.5, 126.3, 123.8, 120.9, 53.2, 35.8, 30.0, 23.6, 18.8, 15.4.

Chiral HPLC analysis, Chiralpak IC (70:30 Hexane:i-PrOH, flow rate 1.0 mL/min, 254 nm, 25 °C), t_r(minor) = 12.93 min., t_r(major) = 16.46 min, 92% ee.

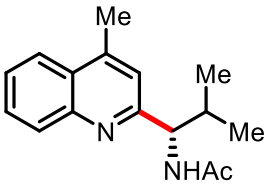


(*S*)-*N*-(cyclohexyl(4-methylquinolin-2-yl)methyl)acetamide (**12**): white solid, 91% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 8.03 (d, *J* = 8.4Hz, 1H), 7.96 (d, *J* = 8.3 Hz, 1H), 7.75-7.63 (m, 1H), 7.56-7.48 (m, 1H), 7.13 (s, 1H), 7.10 (d, *J* = 8.8 Hz, 1H), 5.03 (dd, *J* = 6.0, 1.1 Hz, 1H), 2.68 (s, 3H), 2.06 (s, 3H), 1.90-1.82 (m, 1H), 1.73-1.54 (m, 5H), 1.19-0.97(m, 5H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 169.6, 159.6, 147.3, 144.3, 129.5, 129.2, 127.4, 126.0, 123.8, 122.2, 58.6, 44.0, 29.9, 29.0, 26.3, 26.2, 26.1, 23.7, 18.8.

HRMS(ESI$^+$) m/z: [M + H]$^+$calcd. for $[C_{19}H_{25}N_2O]^+$ expect 297.1961; found 297.1964.

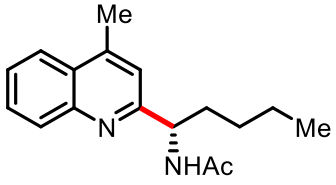
Chiral HPLC analysis, Chiralpak IC (70:30 Hexane:i-PrOH, flow rate 1.0 mL/min, 254 nm, 25 °C), t_r(minor) = 8.71 min., t_r(major) = 13.84 min, 91% ee; $[\alpha]_D^{27.4}$ = -119.8 (*c* 1.0, $CHCl_3$).



(*S*)-*N*-(2-methyl-1-(4-methylquinolin-2-yl)propyl)acetamide (**13**)[3]: white solid, 87% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 8.03 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 8.3 Hz, 1H), 7.68 (t, J = 7.1 Hz, 1H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.14 (s, 1H), 7.11 (br d, *J* = 8.2 Hz, 1H), 5.05 (dd, *J* = 8.5, 7.8 Hz, 1H), 2.67 (s, 3H), 2.27-2.19 (m, 1H), 2.08 (s, 3H), 0.92 (d, *J* = 6.8 Hz, 3H), 0.87 (d, *J* = 6.8 Hz, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 169.7, 159.5, 147.2, 144.4, 129.5, 129.2, 127.4, 126.0, 123.8, 122.0, 59.0, 34.2, 23.7, 19.4, 18.8, 18.4.

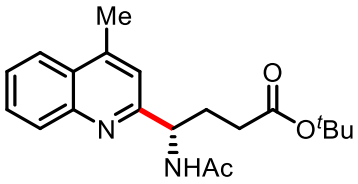
Chiral HPLC analysis, Chiralpak IC (70:30 Hexane:i-PrOH, flow rate 1.0 mL/min, 254 nm, 25 °C), t_r(minor) = 8.53 min, t_r(major) = 13.53 min, 92% ee.



(*S*)-*N*-(1-(4-methylquinolin-2-yl)pentyl)acetamide (**14**)[2]: white solid, 88% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 8.04 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.3 Hz, 1H), 7.67 (t, *J* = 7.3 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.29 (br d, *J* = 7.2 Hz, 1H), 7.15 (s, 1H), 5.18 (q, *J* = 6.7 Hz, 1H), 2.67 (s, 3H), 2.06 (s, 3H), 1.98-1.93 (m, 1H), 1.87-1.78 (m, 1H), 1.30-1.19 (m, 4H), 0.81 (t, J = 6.5 Hz, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 169.5, 160.1, 147.2, 144.9, 129.4, 129.3, 127.4, 126.0, 123.8, 121.1, 54.1, 36.1, 27.5, 23.6, 22.7, 18.8, 14.0.

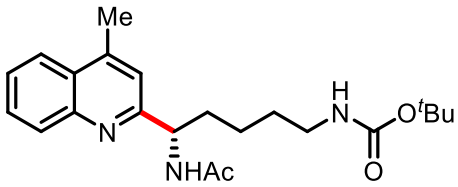
Chiral HPLC analysis, Chiralpak IC (70:30 Hexane:i-PrOH, flow rate 1.0 mL/min, 220 nm, 25 °C), t_r(minor) = 8.11 min., t_r(major) = 11.14 min, 90% ee.



tert-butyl (*S*)-4-acetamido-4-(4-methylquinolin-2-yl)butanoate (**15**)[3]: white solid, 79% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 8.00 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.65 (t, *J* = 9.6 Hz, 1H), 7.50 (br t, *J* = 9.4 Hz, 1H), 7.37 (br d, *J* = 7.4 Hz, 1H), 7.16 (s, 1H), 5.22 (dd, *J* = 12.8, 7.9 Hz, 1H), 2.64 (s, 3H), 2.34-2.24 (m, 2H), 2.18-2.13 (m, 1H), 2.06-2.02 (m, 4H), 1.35 (s, 9H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 172.4, 169.6, 159.0, 146.9, 145.1, 129.3, 129.2, 127.3, 126.0, 123.6, 120.6, 80.1, 53.1, 31.2, 31.1, 27.8, 23.4, 18.6.

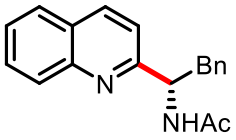
Chiral HPLC analysis, Chiralpak IC (70:30 Hexane:i-PrOH, flow rate 1.0 mL/min, 220 nm, 25 °C), t_r(minor) = 14.85 min., t_r(major) = 25.52 min, 87% ee.



tert-butyl (*S*)-(5-acetamido-5-(4-methylquinolin-2-yl)pentyl)carbamate (**16**)[3]: white solid, 74% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 8.04 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.70 (t, *J* = 7.2 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 1H), 7.22 (d, *J* = 7.4 Hz, 1H), 7.15 (s, 1H), 5.18 (q, *J* = 6.5 Hz, 1H), 4.54 (br s, 1H), 3.04 (d, *J* = 6.0 Hz, 2H), 2.70 (s, 3H), 2.09 (s, 3H), 2.01-1.95 (m, 1H), 1.87-1.79 (m, 1H), 1.48-1.40 (m, 11H), 1.34-1.28 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δC 169.7, 159.8, 156.1, 147.2, 145.2, 129.5, 129.4, 127.5, 126.2, 123.8, 121.0, 79.0, 54.0, 40.3, 36.1, 29.9, 28.5, 23.7, 22.5, 18.9.

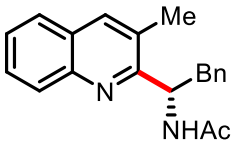
Chiral HPLC analysis, Chiralpak IC (70:30 Hexane:i-PrOH, flow rate 1.0 mL/min, 220 nm, 25 °C), t_r(minor) = 13.51 min., t_r(major) = 20.01 min, 88% ee.



(*S*)-*N*-(2-phenyl-1-(quinolin-2-yl)ethyl)acetamide (**17**)[3]: white solid, 60% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 8.03 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 8.3 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.71 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.3 Hz, 1H), 7.28 (d, *J* = 6.1 Hz, 1H), 7.16-7.14 (m, 3H), 6.95-6.93 (m, 3H), 5.44 (dd, *J* = 6.8, 5.6 Hz, 1H), 3.37 (dd, *J* = 13.1, 3.8 Hz, 1H), 3.15 (dd, *J* = 12.0, 8.5 Hz, 1H), 2.09 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 169.5, 159.2, 147.4, 137.1, 136.3, 129.7, 129.6, 128.9, 128.2, 127.7, 127.4, 126.5, 126.4, 120.9, 55.8, 42.4, 23.6.

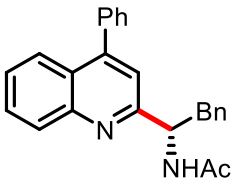
Chiral HPLC analysis, Chiralpak IC (70:30 Hexane:i-PrOH, flow rate 1.0 mL/min, 220 nm, 25 °C), t_r(minor) = 10.25 min., t_r(major) = 11.07 min, 91% ee.



(*S*)-*N*-(1-(3-methylquinolin-2-yl)-2-phenylethyl)acetamide (**18**)[3]: white solid, 84% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 8.03 (d, *J* = 8.4 Hz, 1H), 7.80 (s, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.67 (t, *J* = 7.3 Hz, 1H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.27 (d, *J* = 7.8 Hz, 1H), 7.15-7.13 (m, 3H), 6.91-6.8 (m, 2H), 5.70 (q, *J* = 6.2 Hz, 1H), 3.29-3.19 (m, 2H), 2.17 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δC 169.2, 159.4, 146.1, 137.0, 136.4, 129.7, 129.3, 128.7, 128.5, 128.1, 127.6, 126.9, 126.4, 126.4, 51.7, 42.5, 23.6, 18.4.

Chiral HPLC analysis, Chiralpak IC (70:30 Hexane:i-PrOH, flow rate 1.0 mL/min, 220 nm, 25 °C), t_r(minor) = 7.83 min., t_r(major) = 8.58 min, 97% ee.

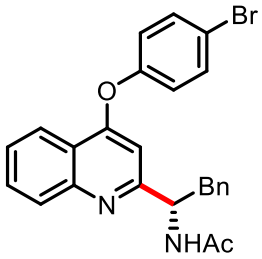


(*S*)-*N*-(2-phenyl-1-(4-phenylquinolin-2-yl)ethyl)acetamide (**19**)[2]: white solid, 58% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 8.12 (d, *J* = 9.2 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.72 (dt, *J* = 8.3, 1.3 Hz, 1H), 7.50-7.46 (m, 4H), 7.35-7.26 (m, 3H), 7.19-7.17 (m, 3H), 6.99 (dd, *J* = 7.0, 3.6 Hz, 2H), 6.80

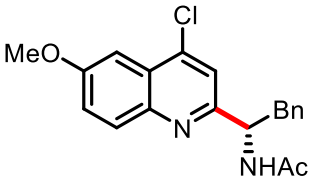
(s, 1H), 5.49-5.43 (m, 1H), 3.44 (dd, *J* = 13.1, 5.2 Hz, 1H), 3.11 (dd, *J* = 13.1, 8.4 Hz, 1H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δC 169.5, 158.6, 148.5, 147.9, 137.7, 137.3, 129.7, 129.5, 129.3, 128.5, 128.4, 128.3, 126.5, 126.5, 125.9, 125.9, 121.2, 55.8, 42.6, 23.6. (one carbon signals were overlapped)

Chiral HPLC analysis, Chiralpak IC (70:30 Hexane:i-PrOH, flow rate 1.0 mL/min, 220 nm, 25 °C), t_r(minor) = 9.64 min., t_r(major) = 11.37 min, 92% ee.



(*S*)-*N*-(1-(4-(4-bromophenoxy)quinolin-2-yl)-2-phenylethyl)acetamide (**20**)[3]: white solid, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δH 8.24 (d, *J* = 8.3, 0.8 Hz, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.75 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.55 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.46 (m, 2H), 7.33 (d, *J* = 7.4 Hz, 1H), 7.18-7.12 (m, 3H), 6.91 (dd, *J* = 7.9, 1.5 Hz, 2H), 6.76-6.72 (m, 2H), 5.93 (s, 1H), 5.21-5.16 (m, 1H), 3.35 (dd, *J* = 13.0, 5.0 Hz, 1H), 2.91 (dd, *J* = 13.0, 9.3 Hz, 1H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δC 169.2, 160.7, 160.2, 152.8, 148.9, 137.2, 133.1, 130.3, 129.4, 128.4, 128.1, 126.3, 125.9, 122.5, 121.6, 120.3, 118.3, 104.0, 56.1, 42.7, 23.4.

Chiral HPLC analysis, Chiralpak IF (85:15 Hexane:i-PrOH, flow rate 1.0 mL/min, 254 nm, 25 °C), t_r(major) = 9.01 min., t_r(minor) = 11.18 min, 96% ee.

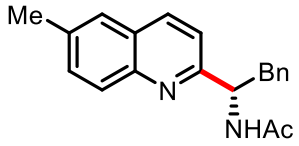


(*S*)-*N*-(1-(4-chloro-6-methoxyquinolin-2-yl)-2-phenylethyl)acetamide (**21**): light yellow solid, 55% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 7.93 (d, *J* = 8.9 Hz, 1H), 7.43 (d, *J* = 6.7 Hz, 2H), 7.17 (s, 3H), 7.04 (d, *J* = 12.0 Hz, 2H), 6.95 (s, 2H), 5.37 (q, *J* = 6.4 Hz, 1H), 3.96 (s, 3H), 3.31 (dd, *J* = 13.3, 5.0 Hz, 1H), 3.14 (dd, *J* = 12.3, 7.8 Hz, 1H), 2.06 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 169.5, 158.6, 156.6, 144.2, 141.0, 136.9, 130.8, 129.6, 128.3, 126.7, 126.6, 123.4, 121.0, 101.7, 55.7, 55.3, 42.1, 23.6.

HRMS(ESI$^+$) m/z: $[M+H]^+$ calcd. for $[C_{20}H_{20}ClN_2O_2]^+$ expect 355.1208; found 355.1215.

Chiral HPLC analysis, Chiralpak IF (85:15 Hexane:i-PrOH, flow rate 1.0 mL/min, 220 nm, 25 °C), t_r(minor) = 10.17 min., t_r(major) = 14.75 min, 95% ee; $[\alpha]_D^{27.4}$ = -12.7 (*c* 1.0, $CHCl_3$).

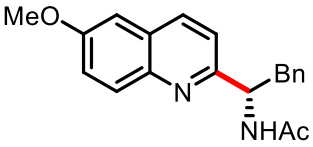


(*S*)-*N*-(1-(6-methylquinolin-2-yl)-2-phenylethyl)acetamide (**22**): light yellow solid, 88% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 7.84 (d, *J* = 9.1 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.50-7.45 (m, 2H), 7.21-7.17 (m, 1H), 7.08-7.05 (m, 3H), 6.85-6.81 (m, 3H), 5.37-5.31 (m, 1H), 3.27 (dd, *J* = 13.2, 4.9 Hz, 1H), 3.06 (dd, *J* = 13.2, 8.1 Hz, 1H), 2.45 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δC 169.4, 158.1, 145.9, 137.1, 136.2, 135.5, 131.8, 129.6, 128.5, 128.1, 127.3, 126.5, 126.3, 120.8, 55.5, 42.3, 23.5, 21.5.

HRMS(ESI$^+$) m/z: $[M+H]^+$ calc'd for $[C_{20}H_{21}N_2O]^+$ expect 305.1648; found 305.1647.

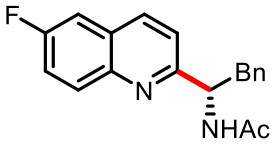
Chiral HPLC analysis, Chiralpak AD-H (85:15 Hexane:i-PrOH, flow rate 1.0 mL/min, 220 nm, 25 °C), t_r(minor) = 9.19 min, t_r(major) = 11.35 min, 90% ee; $[\alpha]_D^{27.5}$ = +32.8 (*c* 1.0, $CHCl_3$).



(*S*)-*N*-(1-(6-methoxyquinolin-2-yl)-2-phenylethyl)acetamide (**23**)[3]: white solid, 81% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 7.92 (d, *J* = 9.2 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.35 (dd, *J* = 9.0, 2.3 Hz, 1H), 7.22 (d, *J* = 6.9 Hz, 1H), 7.16-7.13 (m, 3H), 7.04 (d, *J* = 2.3 Hz, 1H), 6.93-6.91 (m, 2H), 6.88 (d, *J* = 8.4 Hz, 1H), 5.42-5.37 (m, 1H), 3.92 (s, 3H), 3.35 (dd, *J* = 13.2, 5.0 Hz, 1H), 3.12 (dd, *J* = 13.1, 8.2 Hz, 1H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δC 169.4, 157.7, 156.5, 143.4, 137.2, 134.9, 130.3, 129.7, 128.3, 128.1, 126.4, 122.3, 121.1, 105.1, 55.6, 55.5 42.3, 23.5.

Chiral HPLC analysis, Chiralpak AD-H (85:15 Hexane:i-PrOH, flow rate 1.0 mL/min, 220 nm, 25 °C), t_r(minor) = 8.92 min., t_r(major) = 11.66 min, 88% ee.

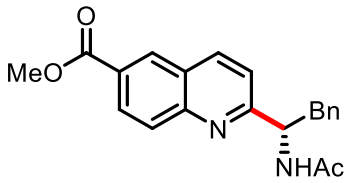


(*S*)-*N*-(1-(6-fluoroquinolin-2-yl)-2-phenylethyl)acetamide (**24**)[3]: white solid, 65% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 8.02 (dd, *J* = 9.2, 5.3 Hz, 1H), 7.91 (d, *J* = 8.5 Hz, 1H), 7.46 (dt, *J* = 8.6, 2.8 Hz, 1H), 7.39 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.19-7.14 (m, 4H), 6.96 (d, *J* = 8.5 Hz, 1H), 6.93-6.91 (m,

2H), 5.47-5.42 (m, 1H), 3.35 (dd, *J* = 13.2, 5.2 Hz, 1H), 3.14 (dd, *J* = 13.3, 8.1Hz, 1H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δC 169.5, 160.3 (d, *J* = 247 Hz), 158.6 (d, *J* = 3.0 Hz), 144.4, 137.0, 135.5 (d, *J* = 5 Hz), 131.3 (d, *J* = 9 Hz), 129.6, 128.2, 127.9 (d, *J* = 10 Hz), 126.5, 121.6, 119.8 (d, *J* = 26 Hz), 110.7 (d, *J* = 21 Hz), 55.6, 42.3, 23.6.

Chiral HPLC analysis, Chiralpak AD-H (85:15 Hexane:i-PrOH, flow rate 1.0 mL/min, 220 nm, 25 °C), t_r(minor) = 7.66 min., t_r(major) = 9.82 min, 94% ee.

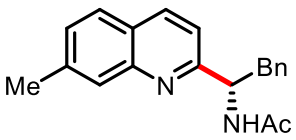


methyl (*S*)-2-(1-acetamido-2-phenylethyl)quinoline-6-carboxylate (**25**): white solid, 64% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 8.54 (s, 1H), 8.29 (d, *J* = 8.8 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 6.7 Hz, 1H), 7.14 (m, 3H), 7.01 (d, *J* = 8.4 Hz, 1H), 6.92 (m, 2H), 5.47 (d, *J* = 6.8 Hz, 1H), 3.99 (s, 3H), 3.35 (dd, *J* = 13.1, 3.8 Hz, 1H), 3.15 (dd, *J* = 12.6, 8.4 Hz, 1H), 2.09 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 169.0, 166.7, 161.7, 149.3, 137.5, 136.9, 130.9, 129.7, 129.3, 128.3, 128.1, 126.7, 126.6, 121.7, 55.8, 52.6, 42.4, 23.6. (From the DEPT(135°) spectrum, it can be observed that there are two types of carbon signals at 129.3 ppm, which overlap with each other.)

HRMS(ESI$^+$) m/z: $[M+H]^+$ calc'd for $[C_{21}H_{21}N_2O_3]^+$ expect 349.1547; found 349.1556.

Chiral HPLC analysis, Chiralpak AD-H, (85:15 Hexane:i-PrOH, flow rate 1.0 mL/min, 220 nm, 25 °C), t_r(minor) = 11.32 min., t_r(major) = 13.68 min, 84% ee; $[\alpha]_D^{27.5}$ = +19.4 (*c* 1.0, $CHCl_3$).



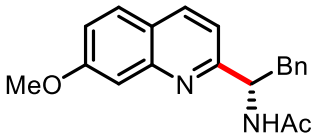
(*S*)-*N*-(1-(7-methylquinolin-2-yl)-2-phenylethyl)acetamide (**26**): white solid, 60% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 7.92 (d, *J* = 8.4 Hz, 1H), 7.82 (s, 1H), 7.67 (d, *J* = 8.3 Hz, 1H), 7.35 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.28 (d, *J* = 7.0 Hz, 1H), 7.14 (t, *J* = 3.0 Hz, 3H), 6.94-6.92 (m, 2H), 6.87 (d, *J* = 8.4 Hz, 1H), 5.45-5.39 (m, 1H), 3.36 (dd, *J* = 13.2, 5.1 Hz, 1H), 3.14 (dd, *J* = 13.2, 8.2 Hz, 1H), 2.56 (s, 3H), 2.08 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 169.4, 159.0, 147.6, 140.0, 137.2, 135.9, 129.7, 128.7, 128.1, 127.9, 127.3, 126.4, 125.4, 120.1, 55.7, 42.4, 23.6, 21.9.

HRMS(ESI$^+$) m/z: $[M+H]^+$ calcd. for $[C_{20}H_{21}N_2O]^+$ expect 305.1648; found 305.1647.

Chiral HPLC analysis, Chiralpak AD-H (85:15 Hexane:i-PrOH, flow rate 1.0 mL/min, 220 nm, 25 °C),

t_r(minor) = 5.98 min., t_r(major) = 9.75 min, 82% ee; $[\alpha]_D^{27.4}$ = +49.0 (*c* 1.0, $CHCl_3$).

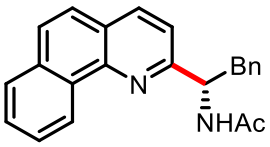


(*S*)-*N*-(1-(7-methoxyquinolin-2-yl)-2-phenylethyl)acetamide (**27**): light yellow solid, 72% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 7.80 (d, *J* = 8.2 Hz, 1H), 7.57 (d, *J* = 8.9 Hz, 1H), 7.28 (s, 1H), 7.16 (d, *J* = 6.5 Hz, 1H), 7.10-7.06 (m, 4H), 6.86 (s, 2H), 6.74 (d, *J* = 8.2 Hz, 1H), 5.32(d, *J* = 6.8 Hz, 1H), 3.88 (s, 3H), 3.27 (d, *J* = 10.4 Hz, 1H), 3.06 (dd, *J* = 12.9, 8.2 Hz, 1H), 2.00 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 169.4, 160.9, 159.3, 149.1, 137.2, 135.9, 129.7, 128.7, 128.2, 126.4, 122.6, 119.5, 118.7, 107.0, 55.7, 55.5, 42.4, 23.6.

HRMS(ESI$^+$) m/z: $[M+H]^+$ calc'd for $[C_{20}H_{21}N_2O_2]^+$ expect 321.1598; found 321.1605.

Chiral HPLC analysis, Chiralpak IF (85:15 Hexane:i-PrOH, flow rate 1.0 mL/min, 220 nm, 25 °C), t_r(minor) = 11.93 min., t_r(major) = 13.40 min, 91% ee; $[\alpha]_D^{27.6}$ = +80.3 (*c* 1.0, $CHCl_3$).

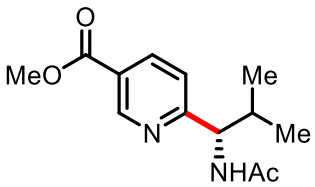


(*S*)-*N*-(1-(benzo[h]quinolin-2-yl)-2-phenylethyl)acetamide (**28**): white solid, 60% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 9.17 (d, *J* = 7.7 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.84 (d, *J* = 7.3 Hz, 1H), 7.71 (d, *J* = 8.8 Hz, 1H), 7.67-7.61 (m, 2H), 7.56 (d, *J* = 8.8 Hz, 1H), 7.11 (d, *J* = 7.1 Hz, 1H), 7.06-7.04 (m, 3H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.90-6.88 (m, 2H), 5.47-5.42 (m, 1H), 3.36 (dd, *J* = 13.1, 5.1 Hz, 1H), 3.14 (dd, *J* = 13.1, 8.5 Hz, 1H), 2.04 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 169.4, 157.7, 145.6, 137.3, 136.1, 133.8, 131.1, 129.7, 128.3, 128.2, 128.0, 127.6, 126.9, 126.4, 125.4, 125.2, 124.2, 121.4, 55.9, 42.8, 23.7.

HRMS(ESI$^+$) m/z: $[M+H]^+$ calcd. for $[C_{21}H_{21}N_2O_3]^+$ expect 349.1547; found 349.1556.

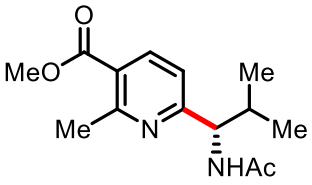
Chiral HPLC analysis, Chiralpak IF (85:15 Hexane:i-PrOH, flow rate 1.0 mL/min, 220 nm, 25 °C), t_r(minor) = 11.21 min., t_r(major) = 12.37 min, 88% ee; $[\alpha]_D^{27.4}$ = +85.4 (*c* 1.0, $CHCl_3$).



methyl (*S*)-6-(1-acetamido-2-methylpropyl)nicotinate (**29**)[3]: light yellow solid, 76% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 9.07 (s, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 7.8 Hz, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 4.88 (t, *J* = 7.6 Hz, 1H), 3.88 (s, 3H), 2.10-2.01 (m, 1H), 1.97 (s, 3H), 0.86 (d, *J* = 6.8 Hz, 3H), 0.72 (d, *J* = 6.8 Hz, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 169.7, 165.6, 163.8, 150.4, 137.3, 124.7, 122.7, 59.0, 52.4, 33.8, 23.4, 19.1, 18.5.

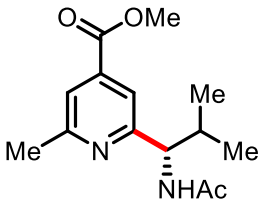
Chiral HPLC analysis, Chiralpak IC (70:30 Hexane:i-PrOH, flow rate 1.0 mL/min, 254 nm, 25 °C), t_r(minor) = 14.43 min., t_r(major) = 20.86 min, 87% ee.



methyl (*S*)-6-(1-acetamido-2-methylpropyl)-2-methylnicotinate (**30**)[3]: white solid, 88% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 8.10 (d, *J* = 8.0 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.78 (d, *J* = 8.2 Hz, 1H), 4.86 (t, *J* = 7.9 Hz, 1H), 3.88 (s, 3H), 2.78 (s, 3H), 2.14-2.05 (m, 1H), 2.02 (s, 3H), 0.89 (d, *J* = 6.8 Hz, 3H), 0.76 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δC 169.6, 166.8, 161.7, 159.6, 138.7, 123.8, 120.1, 58.7, 52.2, 33.8, 24.9, 23.5, 19.1, 18.5.

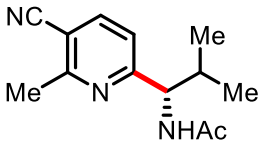
Chiral HPLC analysis, Chiralpak IC (80:20 Hexane:i-PrOH, flow rate 1.0 mL/min, 254 nm, 25 °C), t_r(minor) = 15.89 min., t_r(major) = 27.08 min, 96% ee.



methyl (*S*)-2-(1-acetamido-2-methylpropyl)-6-methylisonicotinate (**31**)[3]: white solid, 69% yield.

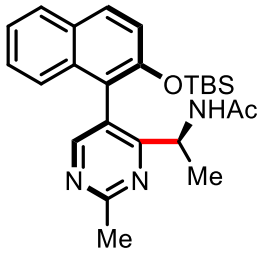
^{1}H NMR (400 MHz, $CDCl_3$) δH 7.59 (s, 1H), 7.52 (s, 1H), 6.72 (d, *J* = 5.8 Hz, 1H), 4.91 (t, *J* = 7.9 Hz, 1H), 3.93 (s, 3H), 2.59 (s, 3H), 2.16-2.08 (m, 1H), 2.03 (s, 3H), 0.92 (d, *J* = 6.7 Hz, 3H), 0.78 (d, *J* = 6.7 Hz, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 169.6, 165.8, 159.9, 159.1, 137.8, 121.2, 119.2, 59.0, 52.7, 33.9, 24.4, 23.5, 19.2, 18.6.

Chiral HPLC analysis, Chiralpak IC (70:30 Hexane:i-PrOH, flow rate 1.0 mL/min, 254 nm, 25 °C), t_r(minor) = 11.06 min., t_r(major) = 21.69 min, 94% ee.



(*S*)-*N*-(1-(5-cyano-6-methylpyridin-2-yl)-2-methylpropyl)acetamide (**32**)[3]: white solid, 49% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δH 7.81 (d, *J* = 7.9 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 1H), 6.58 (d, *J* = 7.9Hz, 1H), 4.87 (t, *J* = 7.6 Hz, 1H), 2.74 (s, 3H), 2.12-2.05 (m, 1H), 2.03 (s, 3H), 0.90 (d, *J* = 6.8 Hz, 3H), 0.78 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δC 169.6, 163.0, 161.2, 140.1, 120.2, 116.8, 107.5, 59.0, 33.6, 23.7, 23.4, 19.1, 18.4.

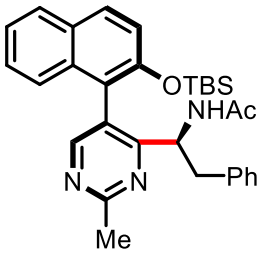
Chiral HPLC analysis, Chiralpak IC (70:30 Hexane:i-PrOH, flow rate 1.0 mL/min, 254 nm, 25 °C), t_r(minor) = 21.60 min., t_r(major) = 27.18 min, 96% ee.



N-((*S*)-1-(5-((*R*)-2-((tert-butyldimethylsilyl)oxy)naphthalen-1-yl)-2-methylpyrimidin-4-yl)ethyl)acetamide (**33**)[4]: white solid, 74% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH (ppm) 8.42 (s, 1H), 7.86-7.82 (m, 2H), 7.39-7.35 (m, 2H), 7.25-7.21 (m, 2H), 7.17 (d, *J* = 8.9 Hz, 1H), 5.06-5.00 (m, 1H), 2.84 (s, 3H), 1.98 (s, 3H), 0.98 (d, *J* = 6.7 Hz, 3H), 0.65 (s, 9H), 0.22 (s, 3H), -0.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δC (ppm) 168.7, 168.6, 166.8, 159.3, 150.6, 133.7, 130.6, 129.3, 128.4, 127.0, 125.2, 124.0, 123.8, 120.5, 118.9, 47.4, 25.8, 25.0, 23.5, 21.9, 17.7, -3.8, -4.6.

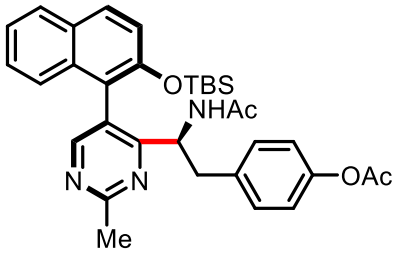
Chiral HPLC analysis, Chiralpak IC (97:3 Hexane:i-PrOH, flow rate 1.0 mL/min, 220 nm, 25 °C), t_r(major) = 6.84 min., t_r(minor) = 10.62 min, >99% ee , >19:1 dr.



N-((*S*)-1-(5-((*R*)-2-((tert-butyldimethylsilyl)oxy)naphthalen-1-yl)-2-methylpyrimidin-4-yl)-2-phenylethyl)acetamide (**34**)[4]: white solid, 76% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 8.47 (s, 1H), 7.89-7.84 (m, 2H), 7.37-7.32 (m, 2H), 7.25-7.20 (m, 2H), 7.06-7.00 (m, 3H), 6.78 (d, *J* = 7.7 Hz, 1H), 6.58 (d, *J* = 7.8 Hz, 2H), 5.40-5.35 (m, 1H), –2.93 (dd, *J* = 13.6, 6.0 Hz, 1H), 2.70 (s, 3H), 2.43 (dd, *J* = 13.6, 5.0 Hz, 1H), 1.91 (s, 3H), 0.65 (s, 9H), 0.21 (s, 3H), -0.11 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 168.5, 166.9, 166.3, 159.3, 150.7, 136.2, 133.5, 130.6, 129.7, 129.4, 128.4, 127.7, 127.2, 126.3, 125.7, 124.0, 123.8, 120.7, 119.0, 51.6, 40.2, 25.7, 25.1, 23.4, 17.7, -3.8, -4.7.

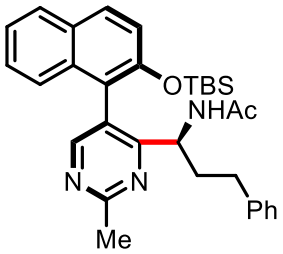
Chiral HPLC analysis, Chiralpak OD (99:1 Hexane:i-PrOH, flow rate 1.0 mL/min, 220 nm, 25 °C), t_r(major) = 15.48 min, t_r(minor) = 22.82 min, 98% ee , >19:1 dr.



5-((*S*)-2-acetamido-2-(5-((*R*)-2-((tert-butyldimethylsilyl)oxy)naphthalen-1-yl)-2-methylpyrimidin-4-yl)ethyl)phenyl acetate (**35**)[4]: white solid, 51% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 8.48 (s, 1H), 7.89-7.84 (m, 2H), 7.38-7.34 (m, 2H), 7.22-7.20 (m, 2H), 6.81 (d, *J* = 7.7 Hz, 1H), 6.75 (d, *J* = 8.4 Hz, 2H), 6.58 (d, *J* = 8.5 Hz, 2H), 5.39-5.34 (m, 1H), 2.92 (dd, *J* = 13.7, 6.1 Hz, 1H), 2.72 (s, 3H), 2.42 (dd, *J* = 13.7, 5.0 Hz, 1H), 2.26 (s, 3H), 1.93 (s, 3H), 0.65 (s, 9H), 0.21 (s, 3H), -0.11 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 169.4, 168.6, 166.7, 166.4, 159.3, 150.7, 149.2, 133.8, 133.4, 130.7, 130.6, 129.4, 128.5, 127.3, 125.7, 124.1, 123.6, 120.8, 120.7, 118.8, 51.5, 39.6, 25.6, 25.1, 23.4, 21.1, 17.7, -3.8, -4.7.

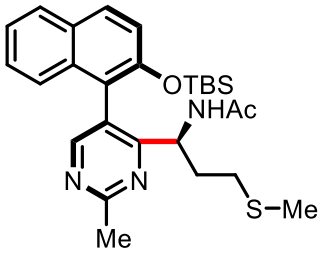
Chiral HPLC analysis, Chiralpak OD (97:3 Hexane:i-PrOH, flow rate 1.0 mL/min, 220 nm, 25 °C), t_r (major) = 12.83 min, t_r(minor) = 16.54 min, 98% ee , >19:1 dr.



N-((*S*)-1-(5-((*R*)-2-((tert-butyldimethylsilyl)oxy)naphthalen-1-yl)-2-methylpyrimidin-4-yl)-3-phenylpropyl)acetamide (**36**)[4]: white solid, 74% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 8.45 (s, 1H), 7.86-7.83 (m, 2H), 7.40-7.34 (m, 2H), 7.23 (d, *J* = 2.2 Hz, 1H), 7.16 (d, *J* = 8.9 Hz, 1H), 7.13 (d, *J* = 7.7 Hz, 1H), 7.07-7.01 (m, 3H), 6.69 (dd, *J* = 7.7, 1.92 Hz, 2H), 5.20-5.15 (m, 1H), 2.84 (s, 3H), 2.21-2.17 (m, 2H), 1.98 (s, 3H), 1.79 – 1.71 (m, 1H), 1.52-1.43 (m, 1H), 0.65 (s, 9H), 0.23 (s, 3H), -0.07 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 168.8, 167.6, 166.5, 159.4, 150.7, 141.4, 133.7, 130.6, 129.3, 128.5, 128.1, 128.0, 127.1, 125.5, 125.5, 124.0, 123.8, 120.5, 118.8, 50.9, 37.1, 31.2, 25.9, 25.1, 23.5, 17.7, -3.8, -4.7.

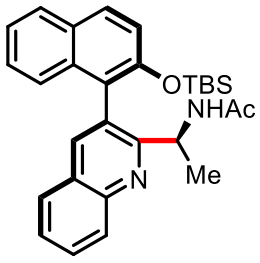
Chiral HPLC analysis, Chiralpak OD (97:3 Hexane:i-PrOH, flow rate 1.0 mL/min, 254 nm, 25 °C), t_r(major) = 9.23 min, t_r(minor) = 12.73 min, >99% ee, >19:1 dr.



N-((*S*)-1-(5-((*R*)-2-((tert-butyldimethylsilyl)oxy)naphthalen-1-yl)-2-methylpyrimidin-4-yl)-3-(methylthio)propyl) acetamide (**37**)[4]: white solid, 63% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 8.45 (s, 1H), 7.87-7.83 (m, 2H), 7.39-7.36 (m, 2H), 7.24 (d, *J* = 5.5 Hz, 1H), 7.19 (d, *J* = 9.0 Hz, 1H), 7.10 (d, *J* = 7.7 Hz, 1H), 5.16-5.11 (m, 1H), 2.83 (s, 3H), 1.98 (s, 3H), 1.75-1.68 (m, 1H), 1.53-1.40 (m, 5H), 0.89-0.80 (m, 1H), 0.65 (s, 9H), 0.23 (s, 3H), -0.07 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 168.9, 167.2, 166.6, 159.4, 150.7, 133.7, 130.7, 129.4, 128.5, 127.2, 125.5, 124.1, 123.8, 120.6, 118.7, 50.5, 35.7, 29.8, 25.8, 25.0, 23.5, 17.7, 14.8, -3.8, -4.7.

Chiral HPLC analysis, Chiralpak OD (95:5 Hexane:i-PrOH, flow rate 1.0 mL/min, 220 nm, 25 °C), t_r(major) = 6.03 min., t_r(minor) = 7.61 min, >99% ee, >19:1 dr.

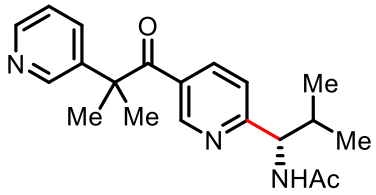


6-*N*-((*S*)-1-(3-((*R*)-2-((tert-butyldimethylsilyl)oxy)naphthalen-1-yl)quinolin-2-yl)ethyl)acetamide (**38**)[4]: white solid, 71% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 8.16 (d, *J* = 8.4 Hz, 1H), 7.99 (s, 1H), 7.88-7.75 (m, 5H), 7.57 (t, *J* = 7.1 Hz, 1H), 7.38-7.33 (m, 3H), 7.21 (d, *J* = 8.9 Hz, 1H), 5.25-5.18 (m, 1H), 2.06 (s, 3H), 1.01 (d, *J* = 6.6

Hz, 3H), 0.52 (s, 9H), 0.20 (s, 3H), -0.18 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 168.7, 161.5, 150.4, 146.4, 139.3, 134.1, 130.1, 129.5, 129.5, 129.0, 128.7, 128.3, 127.4, 127.3, 126.7, 126.5, 124.5, 123.8, 122.5, 120.6, 48.3, 24.9, 23.7, 22.3, 17.6, -3.9, -4.7.

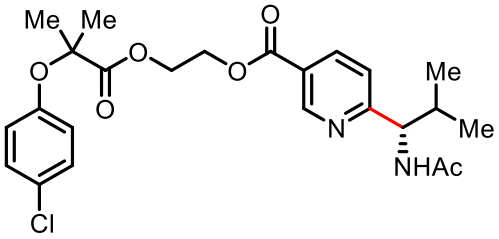
Chiral HPLC analysis, Chiralpak OD (95:5 Hexane:i-PrOH, flow rate 1.0 mL/min, 220 nm, 25 °C), t_r (major) = 5.21 min, t_r(minor) = 8.88 min, >99% ee, >19:1 dr.



(S)-*N*-(2-methyl-1-(5-(2-methyl-2-(pyridin-4-yl)propanoyl)pyridin-2-yl)propyl)acetamide (**41**)[3] : light yellow solid, 57% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 8.60 (s, 2H), 8.55 (d, *J* = 4.5Hz, 1H), 7.71 (d, *J* = 8.1, 1.6 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.31-7.28 (m, 1H), 7.09 (d, *J* = 8.2 Hz, 1H), 6.56 (d, *J* = 8.6 Hz, 1H), 4.83 (t, *J* = 7.7 Hz, 1H), 2.05-1.99 (m, 1H), 1.98 (s, 3H), 1.65 (s, 6H), 0.86 (d, *J* = 6.8 Hz, 3H), 0.73 (d, *J* = 6.8 Hz, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 200.8, 169.6, 162.7, 150.4, 148.7, 147.5, 139.9, 137.3, 133.4, 129.7, 124.0, 122.5, 58.8, 50.3, 33.7, 27.4, 27.3, 23.4, 19.2, 18.5.

Chiral HPLC analysis, Chiralpak IC (60:40 Hexane:i-PrOH, flow rate 1.0 mL/min, 220 nm, 25 °C), t_r (major) = 19.73 min., t_r(minor) = 27.86 min, 93% ee.



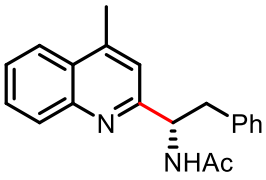
2-((3-(4-chlorophenyl)-2,2-dimethylpropanoyl)oxy)ethyl (S)-6-(1-acetamido-2-methylpropyl)-Nicotinate (**43**)[3] : light yellow solid, 51% yield.

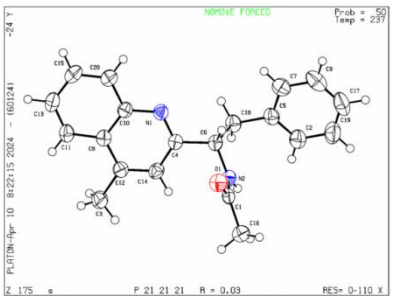
^{1}H NMR (400 MHz, $CDCl_3$) δH 9.00 (s, 1H), 8.05 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.27-7.25 (m, 1H), 7.09 (d, *J* = 7.3 Hz, 2H), 6.86 (t, *J* = 8.1 Hz, 1H), 6.73 (d, *J* = 8.8 Hz, 2H), 4.97 (t, *J* = 7.2 Hz, 1H), 4.51 (d, *J* = 3.4 Hz, 4H), 2.14-2.09 (m, 1H), 2.03 (s, 3H), 1.58 (s, 6H), 0.93 (d, *J* = 6.7 Hz, 3H), 0.78 (d, *J* = 6.7 Hz, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 173.9, 169.8, 164.6, 164.0, 153.9, 150.3, 137.4, 129.2, 127.2, 124.2, 122.9, 120.1, 79.3, 63.0, 62.7, 59.0, 33.8, 25.3, 25.2, 23.4, 19.2, 18.6.

Chiral HPLC analysis, Chiralpak AD-H (80:20 Hexane:i-PrOH, flow rate 1.0 mL/min, 220 nm, 25 °C),

t_r(minor) = 7.63 min., t_r(major) = 10.22 min, 89% ee.

4.4 Determination of absolute configuration of compound 3a





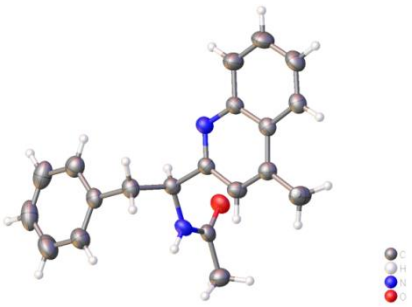


Table 1 Crystal data and structure refinement for 3a.

Identification code	3a
Empirical formula	$C_{20}H_{20}N_2O$
Formula weight	304.38
Temperature/K	237.00
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	8.8814(3)
b/Å	9.6260(3)
c/Å	19.8518(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1697.18(10)
Z	4
ρ_{calc}g/cm^3	1.191
μ/mm^{-1}	0.580
F(000)	648.0
Crystal size/mm^3	0.3 × 0.2 × 0.1
Radiation	CuKα (λ = 1.54178)

2Θ range for data collection/°	10.212 to 136.752
Index ranges	-10 ≤ h ≤ 10, -11 ≤ k ≤ 11, -23 ≤ l ≤ 23
Reflections collected	28669
Independent reflections	3077 [R_{int} = 0.0373, R_{sigma} = 0.0169]
Data/restraints/parameters	3077/0/210
Goodness-of-fit on F^2	1.058
Final R indexes [I>=2σ (I)]	R_1 = 0.0261, wR_2 = 0.0703
Final R indexes [all data]	R_1 = 0.0264, wR_2 = 0.0706
Largest diff. peak/hole / e $Å^{-3}$	0.11/-0.10
Flack parameter	0.10(5)

5. References

1. I. Ghosh, J. Khamrai, A. Savateev, N. Shlapakov, M. Antonietti, B. König. Organic semiconductor photocatalyst can bifunctionalize arenes and heteroarenes. *Science*, 2019, **365**, 360-366.

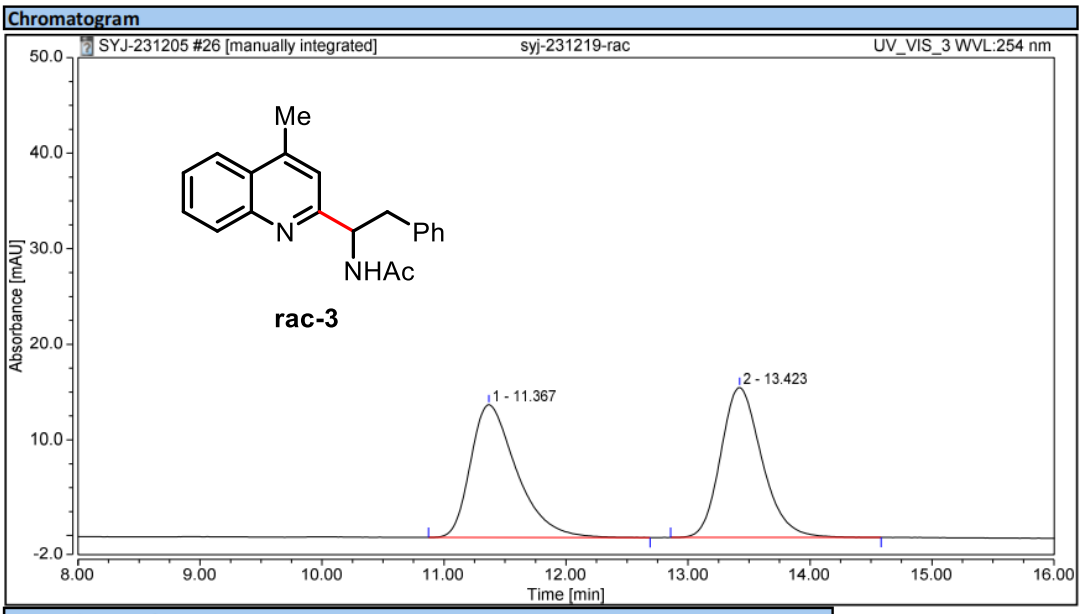
2. M-C. Fu, R. S, B. Zhao, B. Wang, Y. Fu. Photocatalytic decarboxylative alkylations mediated by triphenylphosphine and sodium iodide. *Science*, 2019, **363**, 1429-1434.

3. R. S. J. Proctor, H. J. Davis, R. J. Phipps. Catalytic enantioselective Minisci-type addition to heteroarenes. *Science*, 2018, **360**, 419-422.

4. D. Liang, J-R. Chen, L-P. Tan, Z-W. He, W-J. Xiao. Catalytic Asymmetric Construction of Axially and Centrally Chiral Heterobiaryls by Minisci Reaction. *J. Am. Chem. Soc*., 2022, **144**, 6040−6049.

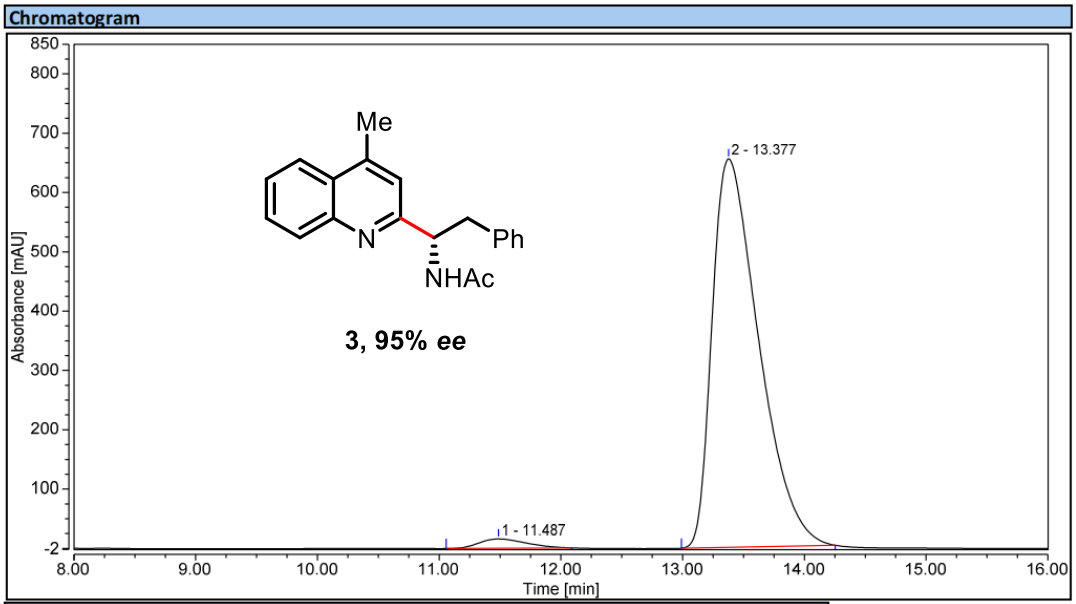
5. J. Li, S. S. Tan, S. H. Kyne, P. W. Hong Chan. Minisci-Type Alkylation of N-Heteroarenes by N-(Acyloxy)phthalimide Esters Mediated by a Hantzsch Ester And Blue LED Light. *Adv. Synth. Catal*., 2022, **364**, 802-810.

6. HPLC spectra of products



Integration Results

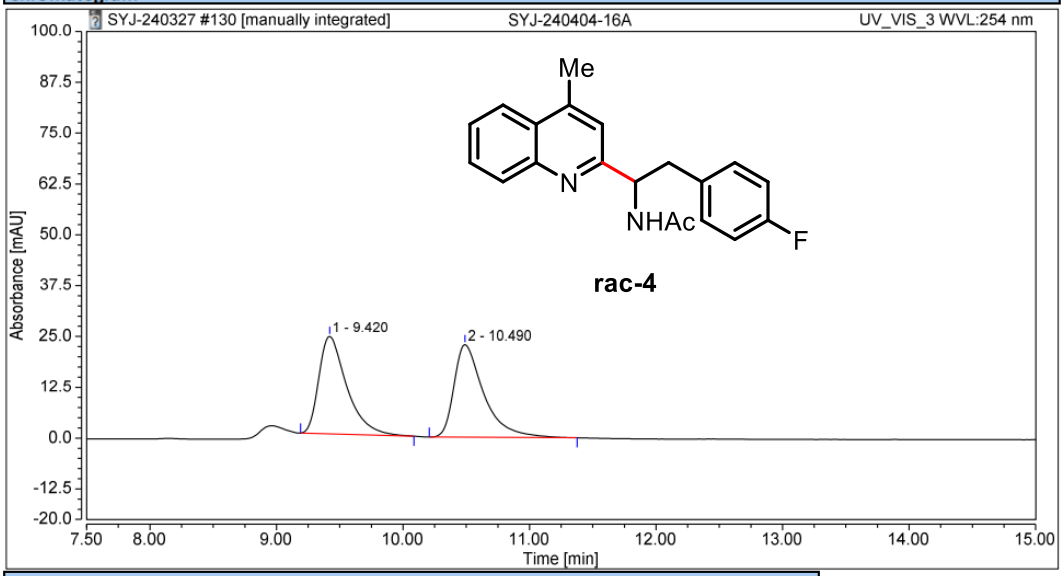
No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	11.367	6.079	49.74	46.96	n.a.
2	13.423	6.142	50.26	53.04	n.a.
Total:		**12.222**	**100.00**	**100.00**	



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	11.487	7.035	2.37	2.35	n.a.
2	13.377	290.117	97.63	97.65	n.a.
Total:		**297.152**	**100.00**	**100.00**	

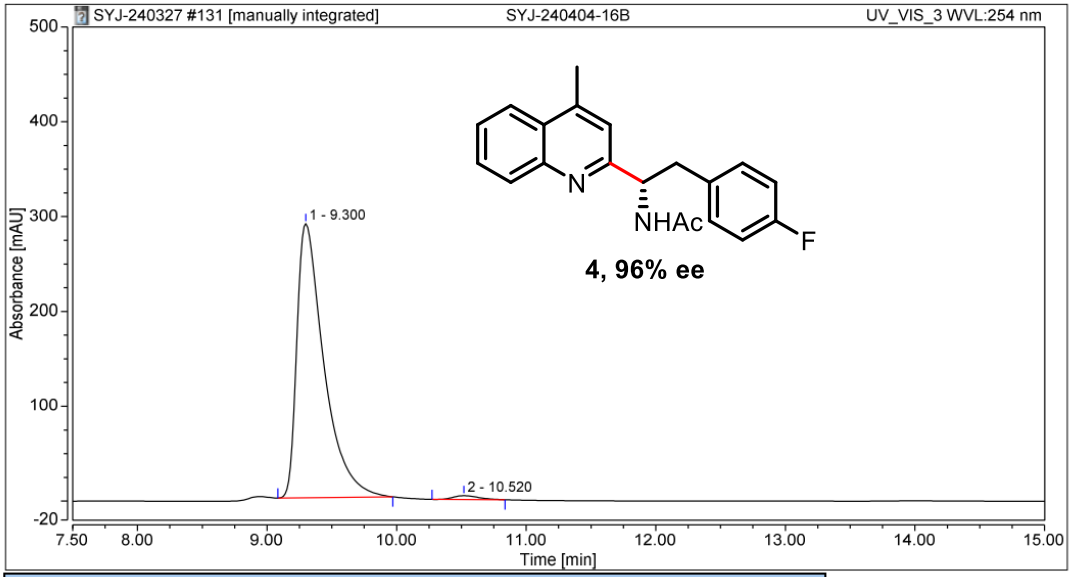
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	9.420	6.141	49.63	51.30	n.a.
2	10.490	6.232	50.37	48.70	n.a.
Total:		**12.373**	**100.00**	**100.00**	

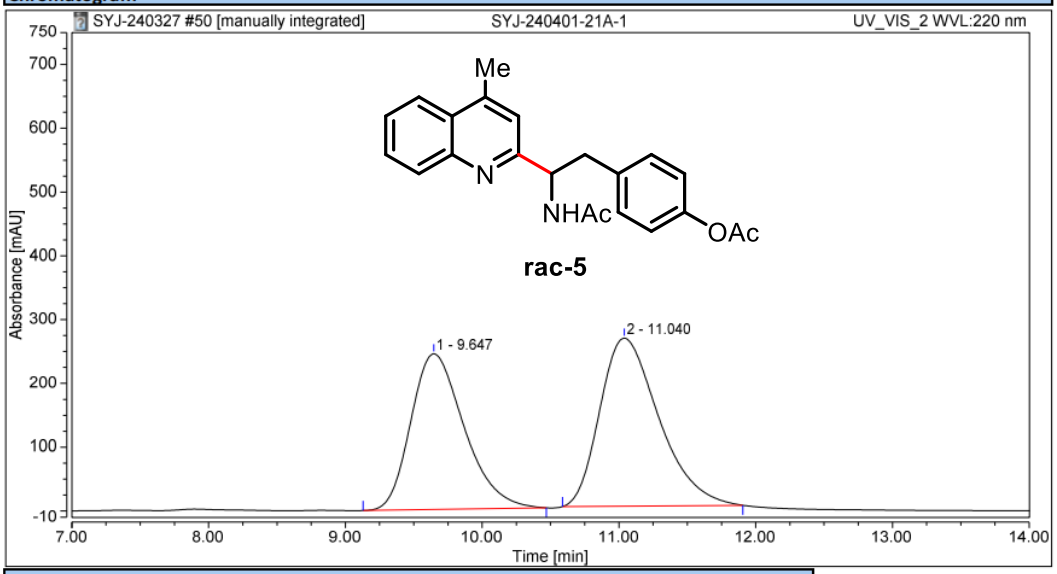
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	9.300	69.797	98.66	98.60	n.a.
2	10.520	0.947	1.34	1.40	n.a.
Total:		**70.745**	**100.00**	**100.00**	

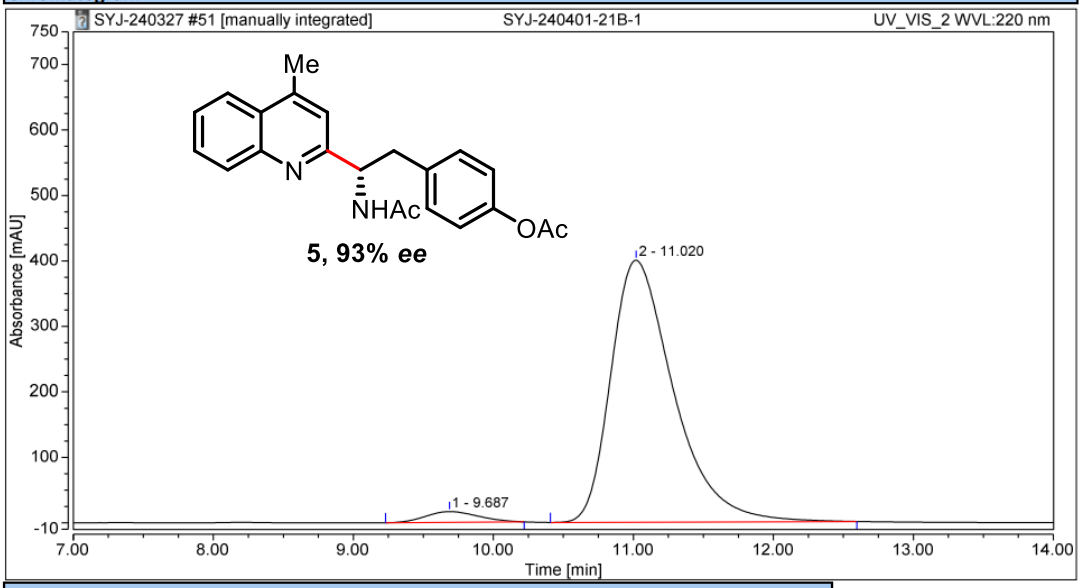
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	9.647	110.391	45.61	48.10	n.a.
2	11.040	131.640	54.39	51.90	n.a.
Total:		**242.031**	**100.00**	**100.00**	

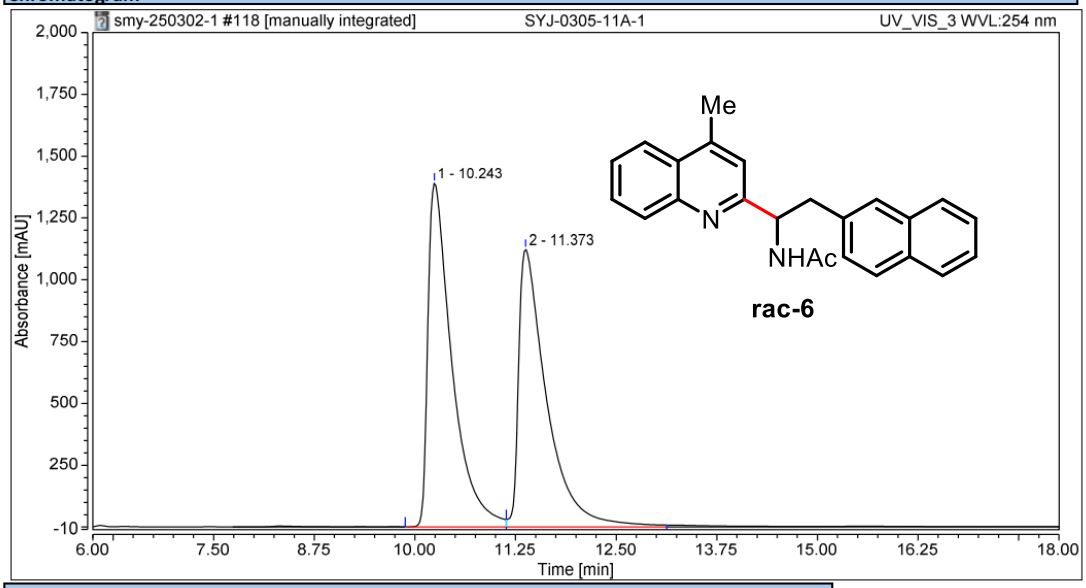
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	9.687	7.128	3.32	3.94	n.a.
2	11.020	207.771	96.68	96.06	n.a.
Total:		**214.898**	**100.00**	**100.00**	

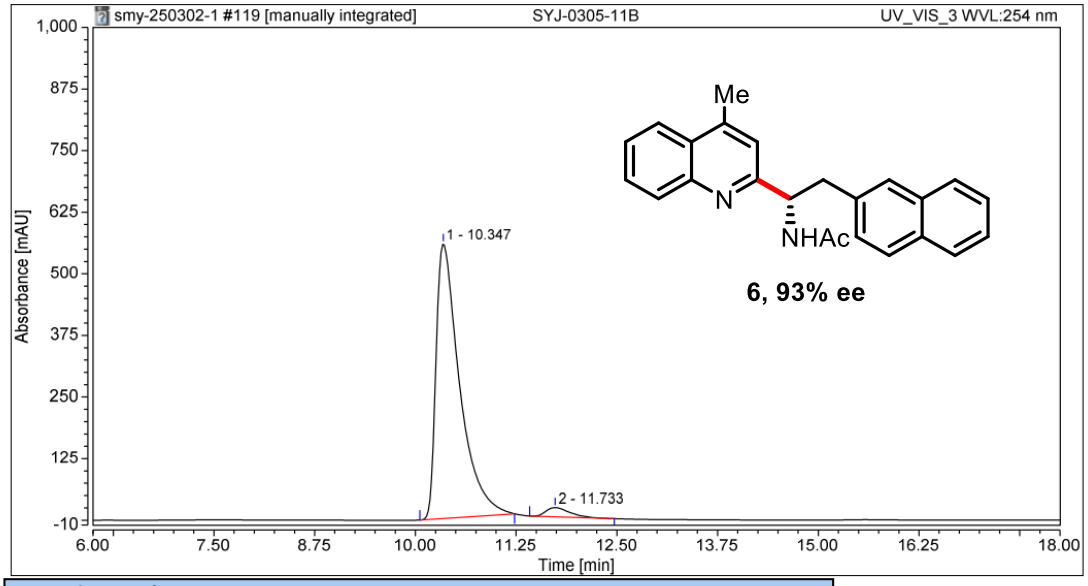
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	10.243	479.114	51.42	55.34	n.a.
2	11.373	452.618	48.58	44.66	n.a.
Total:		**931.731**	**100.00**	**100.00**	

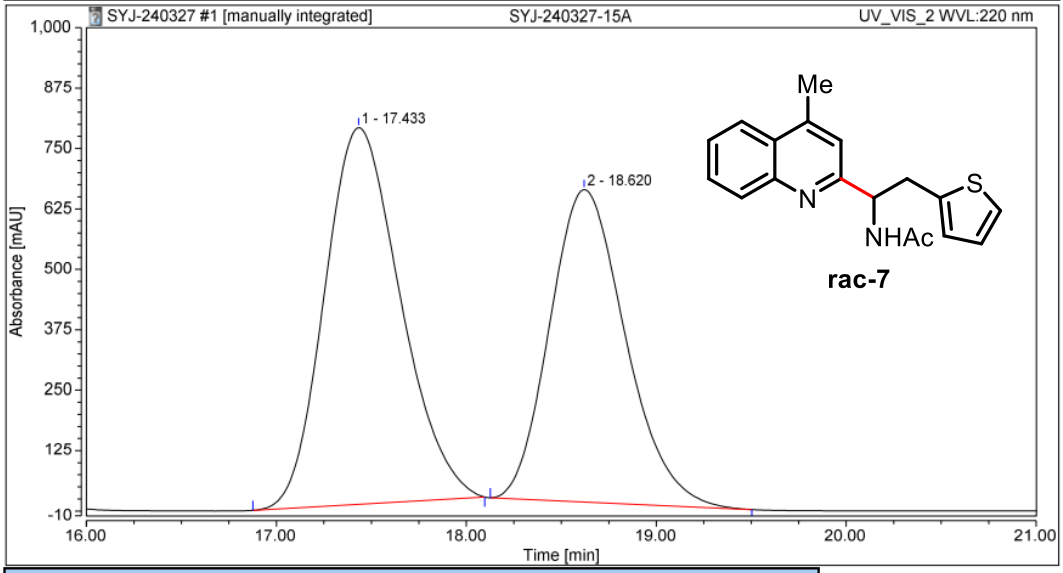
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	10.347	188.437	96.69	96.74	n.a.
2	11.733	6.441	3.31	3.26	n.a.
Total:		**194.879**	**100.00**	**100.00**	

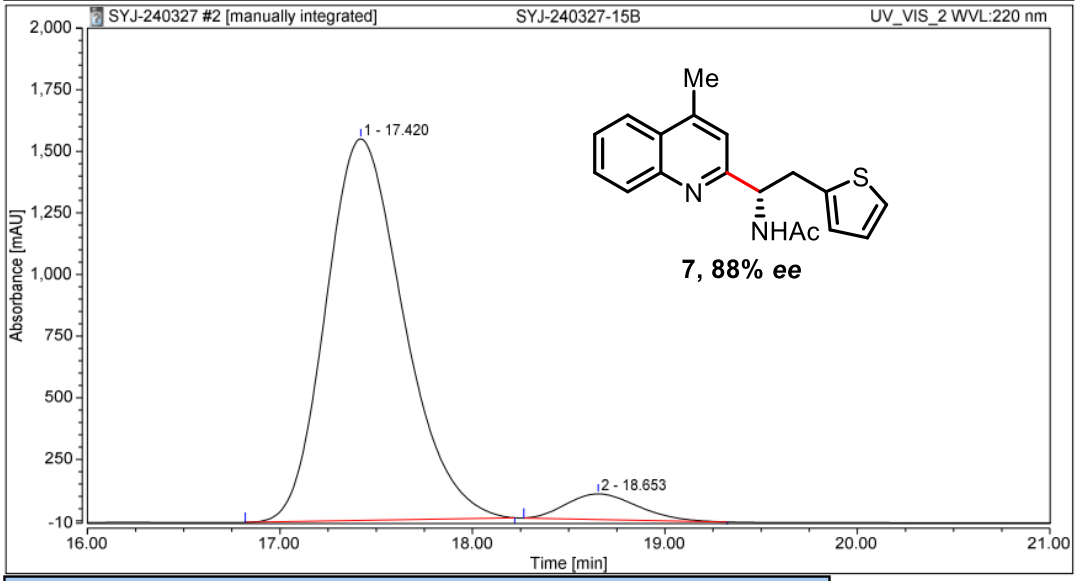
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	17.433	359.962	54.71	54.66	n.a.
2	18.620	298.040	45.29	45.34	n.a.
Total:		**658.001**	**100.00**	**100.00**	

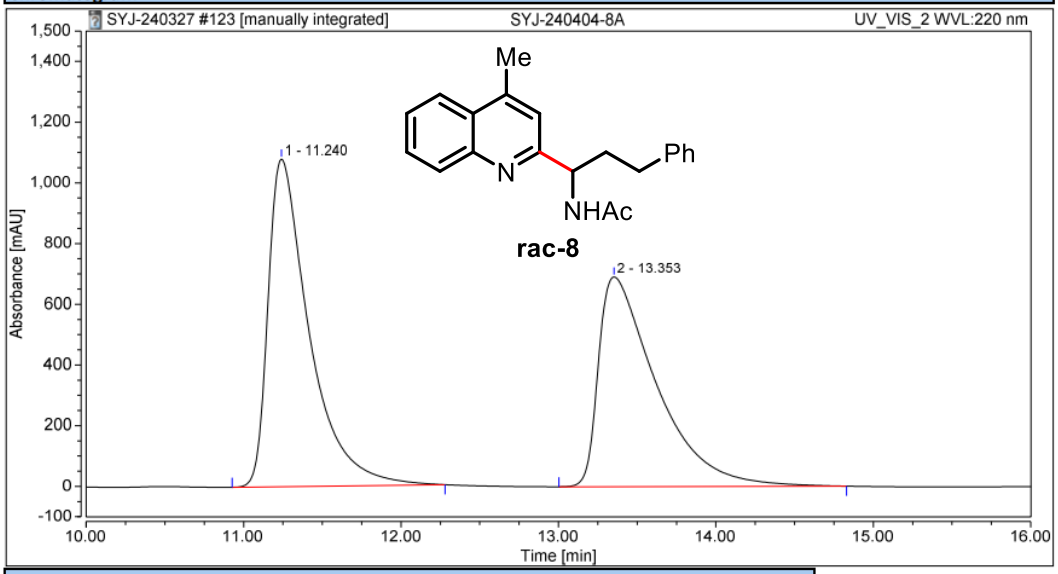
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	17.420	724.976	94.22	93.72	n.a.
2	18.653	44.458	5.78	6.28	n.a.
Total:		**769.434**	**100.00**	**100.00**	

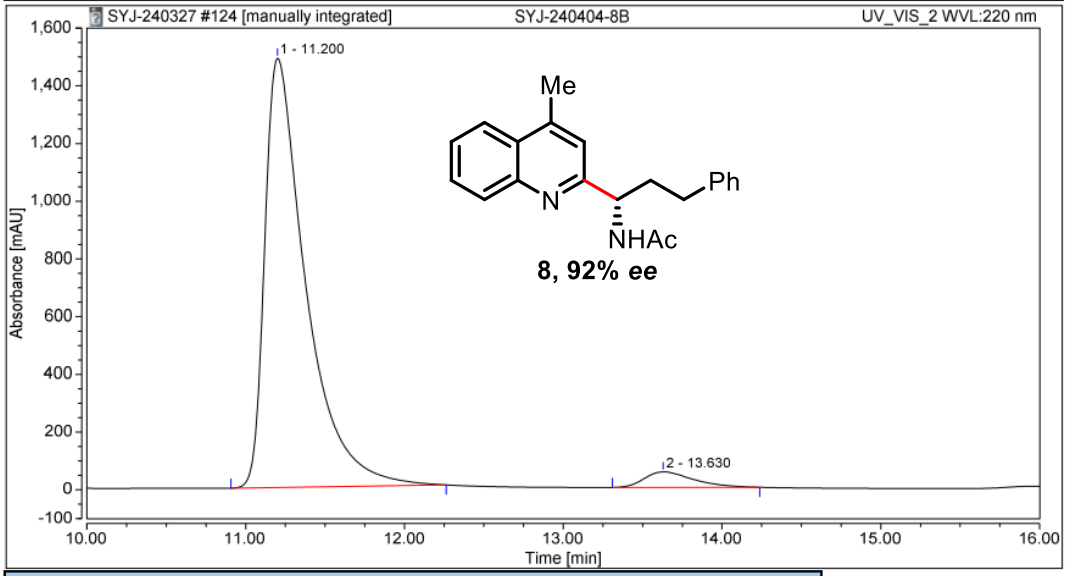
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	11.240	326.696	52.56	60.97	n.a.
2	13.353	294.848	47.44	39.03	n.a.
Total:		**621.544**	**100.00**	**100.00**	

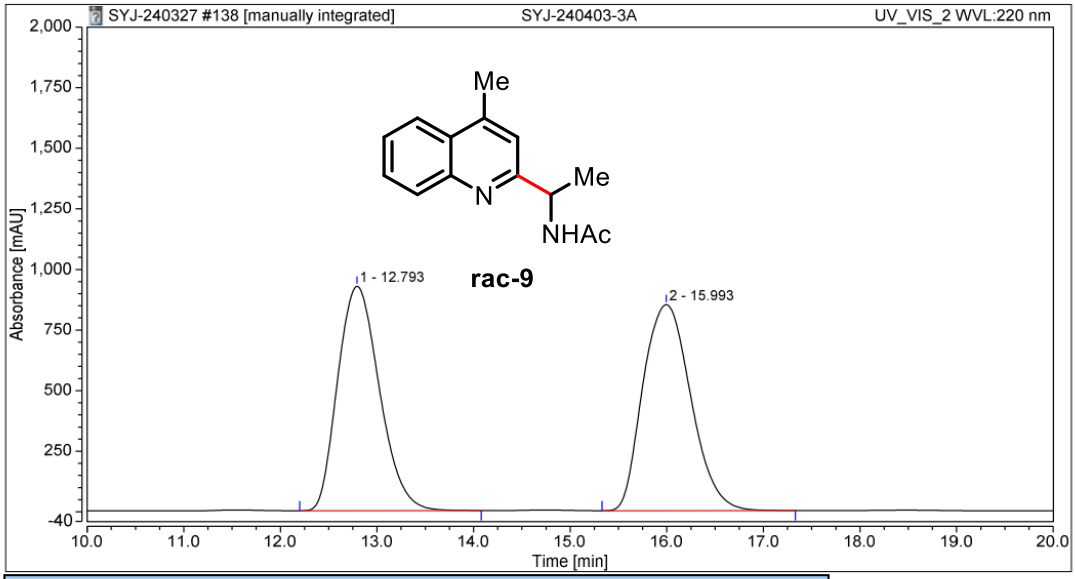
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	11.200	445.516	95.85	96.50	n.a.
2	13.630	19.306	4.15	3.50	n.a.
Total:		**464.822**	**100.00**	**100.00**	

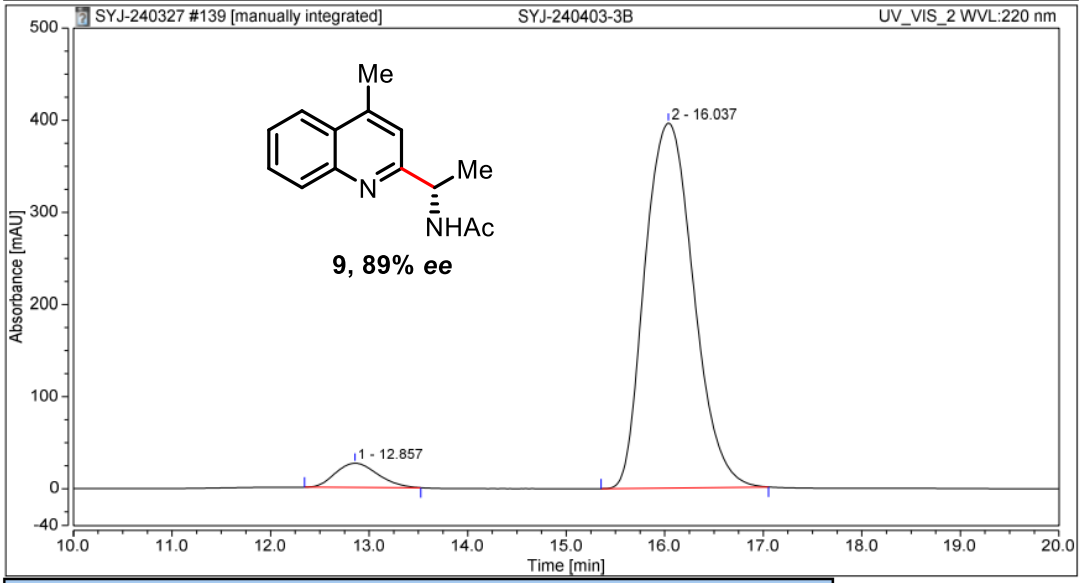
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	12.793	463.452	48.67	52.14	n.a.
2	15.993	488.849	51.33	47.86	n.a.
Total:		**952.301**	**100.00**	**100.00**	

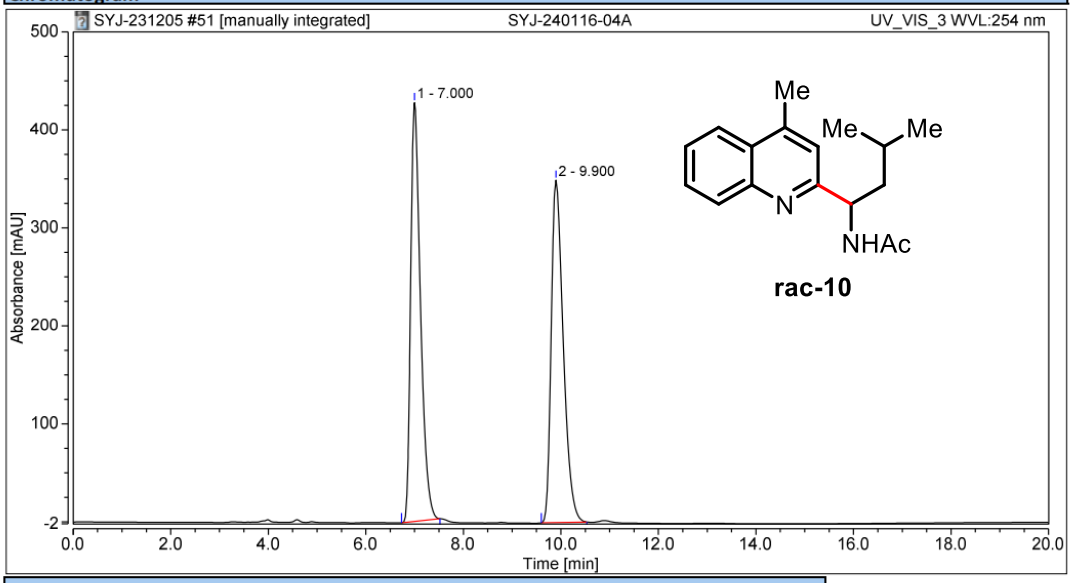
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	12.857	13.025	5.43	6.21	n.a.
2	16.037	226.868	94.57	93.79	n.a.
Total:		**239.894**	**100.00**	**100.00**	

Chromatogram

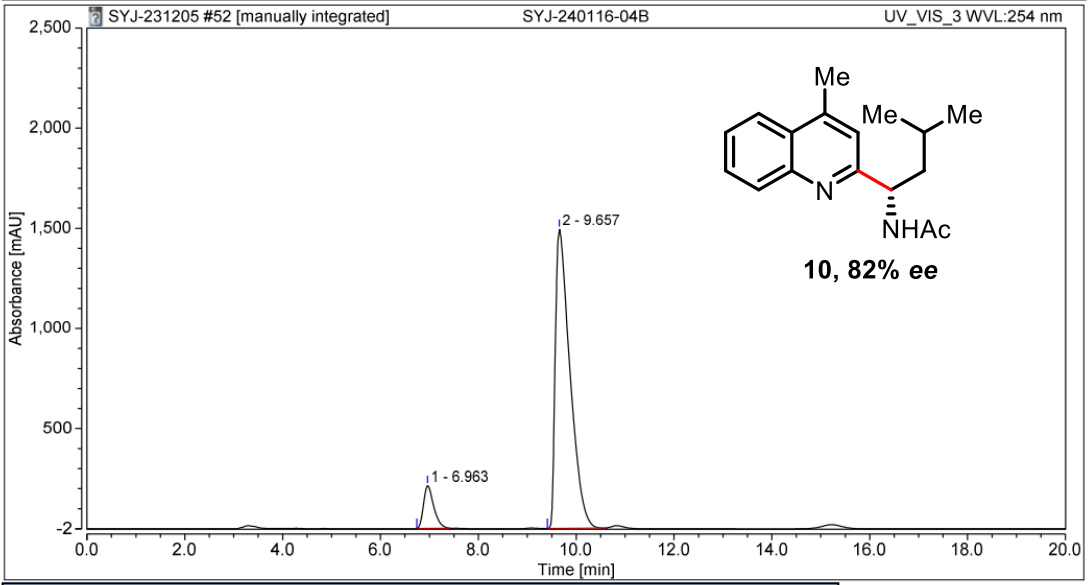


rac-10

Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	7.000	99.598	50.05	55.02	n.a.
2	9.900	99.402	49.95	44.98	n.a.
Total:		**199.000**	**100.00**	**100.00**	

Chromatogram

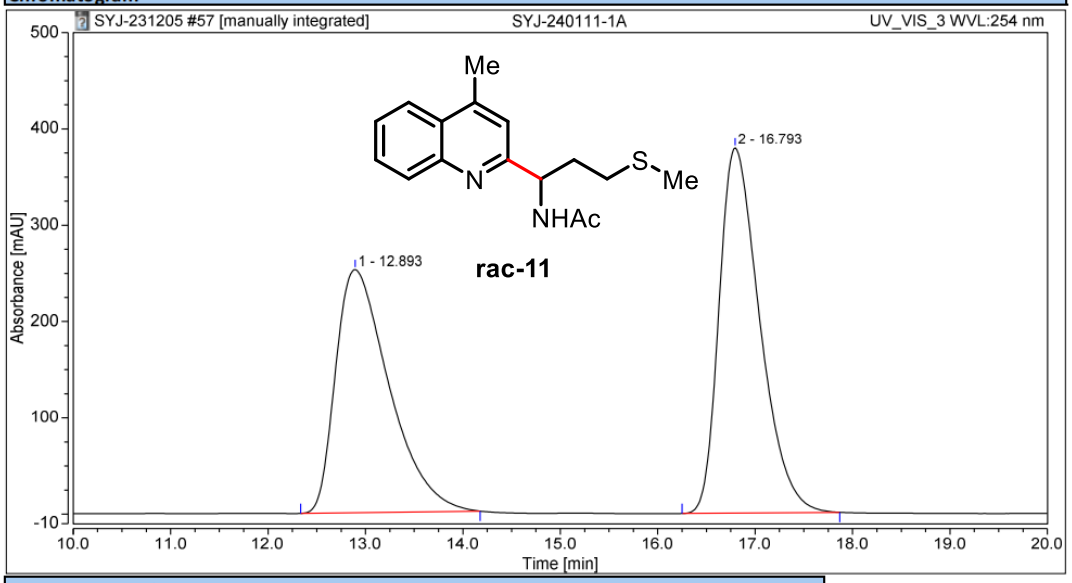


10, 82% *ee*

Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	6.963	51.347	9.04	12.52	n.a.
2	9.657	516.651	90.96	87.48	n.a.
Total:		**567.998**	**100.00**	**100.00**	

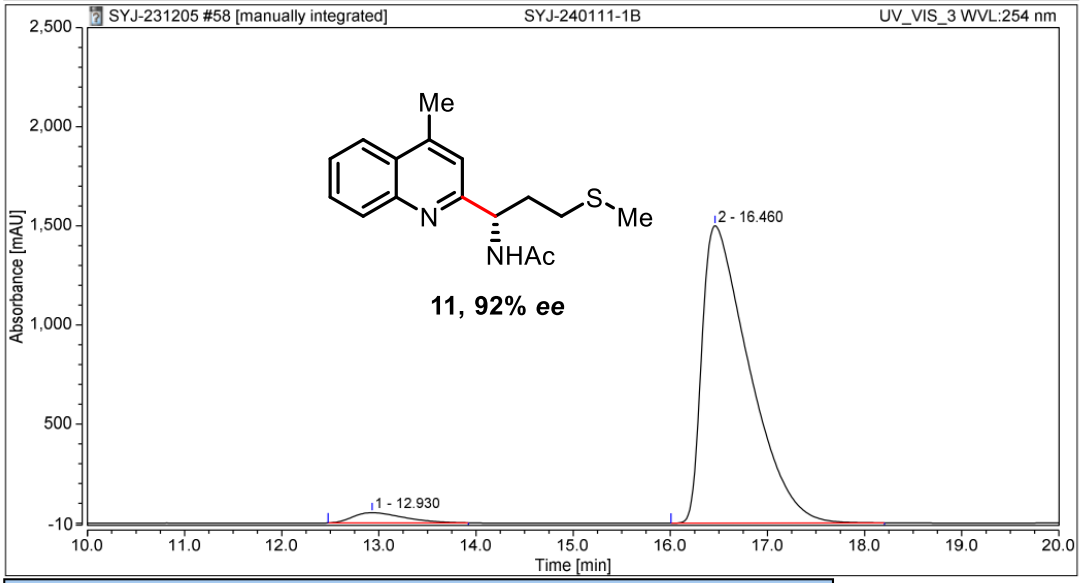
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	12.893	160.769	46.69	39.96	n.a.
2	16.793	183.598	53.31	60.04	n.a.
Total:		**344.367**	**100.00**	**100.00**	

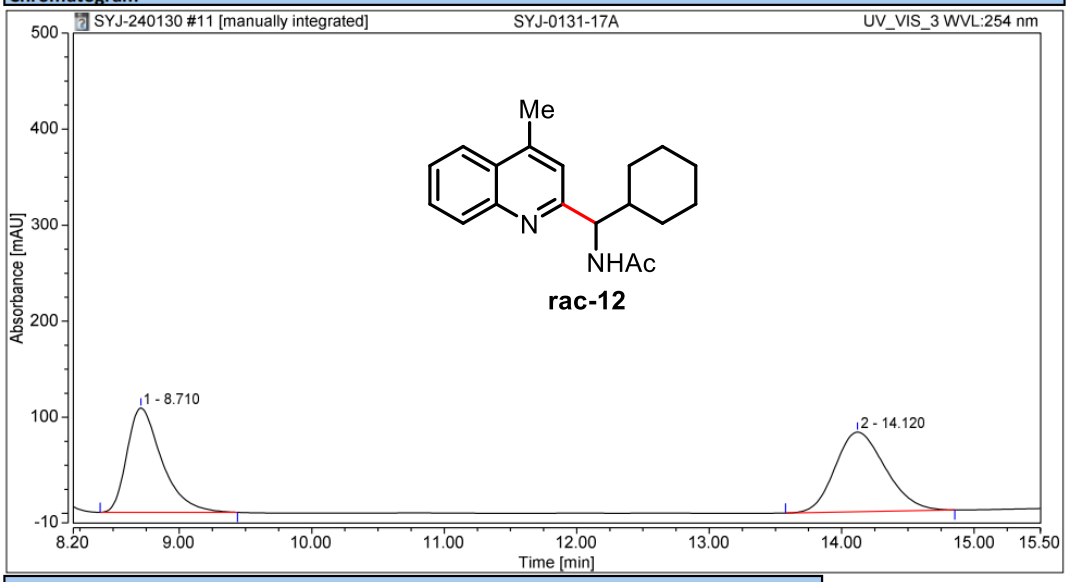
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	12.930	31.438	3.59	3.34	n.a.
2	16.460	843.662	96.41	96.66	n.a.
Total:		**875.100**	**100.00**	**100.00**	

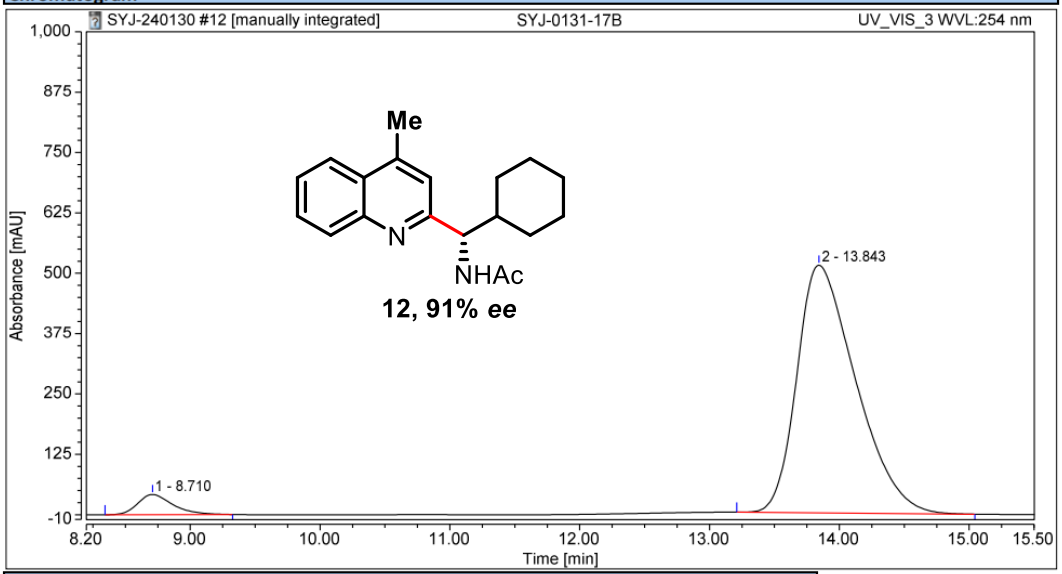
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	8.710	33.277	47.70	56.71	n.a.
2	14.120	36.479	52.30	43.29	n.a.
Total:		**69.757**	**100.00**	**100.00**	

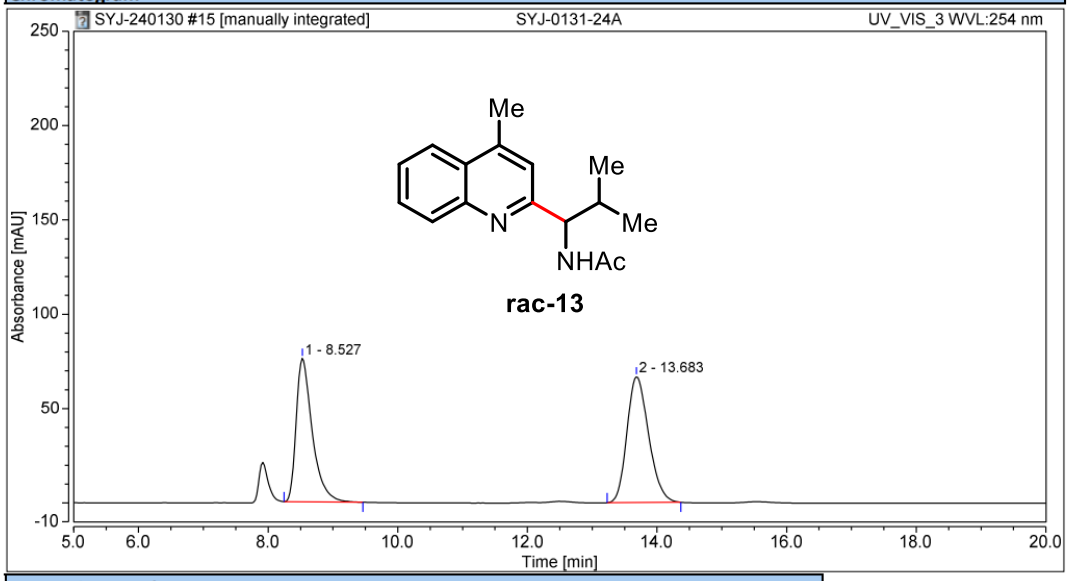
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	8.710	13.058	4.62	7.52	n.a.
2	13.843	269.888	95.38	92.48	n.a.
Total:		**282.946**	**100.00**	**100.00**	

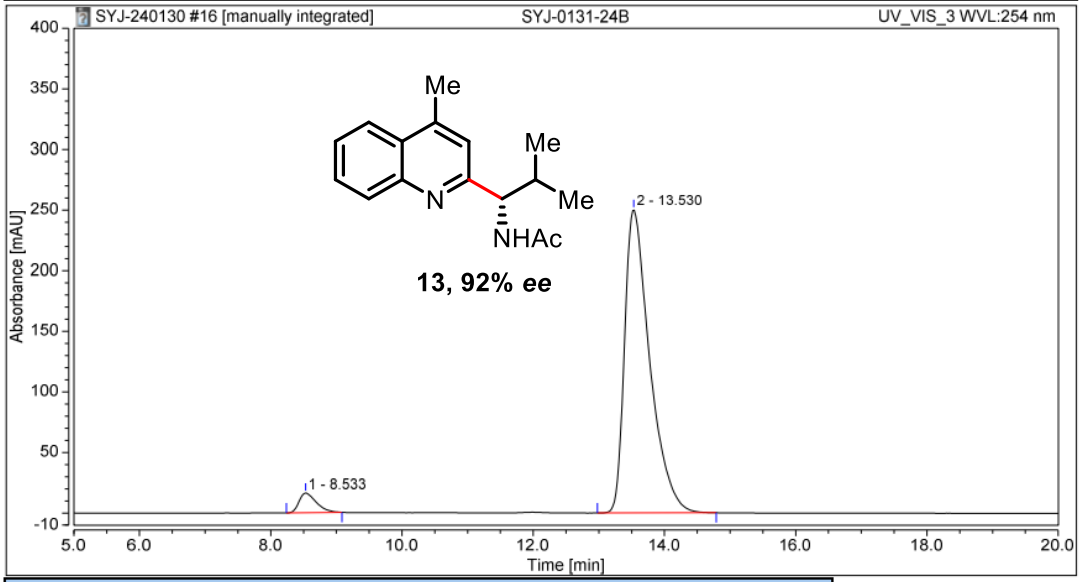
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	8.527	21.893	45.84	53.28	n.a.
2	13.683	25.869	54.16	46.72	n.a.
Total:		**47.763**	**100.00**	**100.00**	

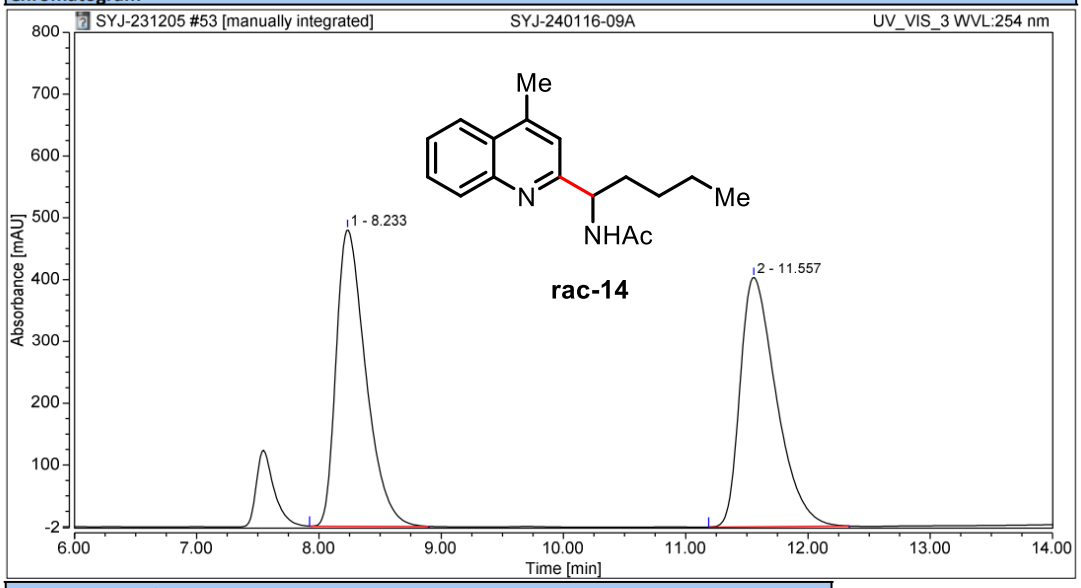
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	8.533	4.966	4.28	6.10	n.a.
2	13.530	110.958	95.72	93.90	n.a.
Total:		**115.924**	**100.00**	**100.00**	

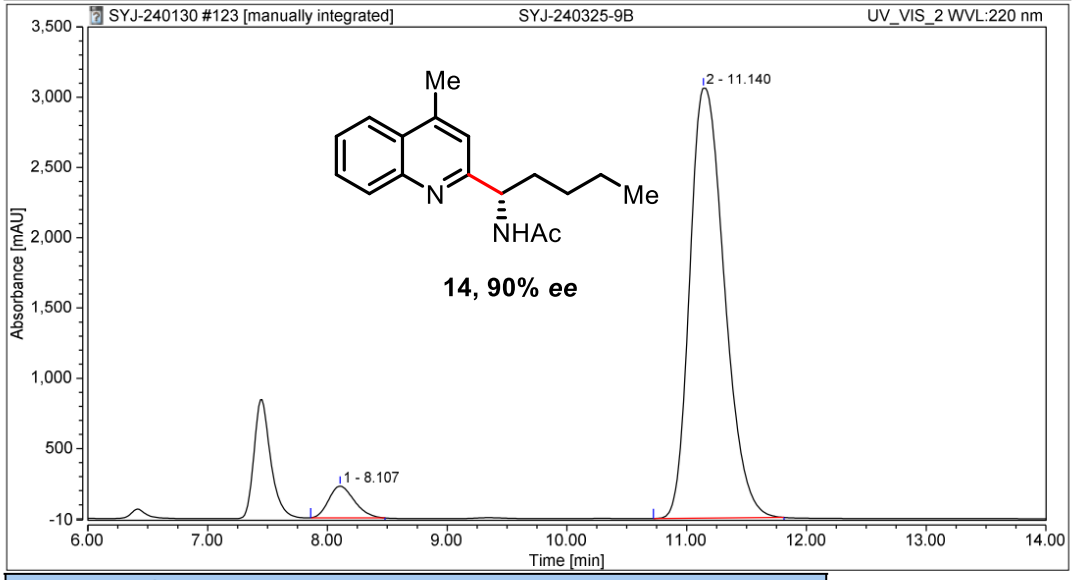
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	8.233	134.400	49.32	54.32	n.a.
2	11.557	138.110	50.68	45.68	n.a.
Total:		**272.511**	**100.00**	**100.00**	

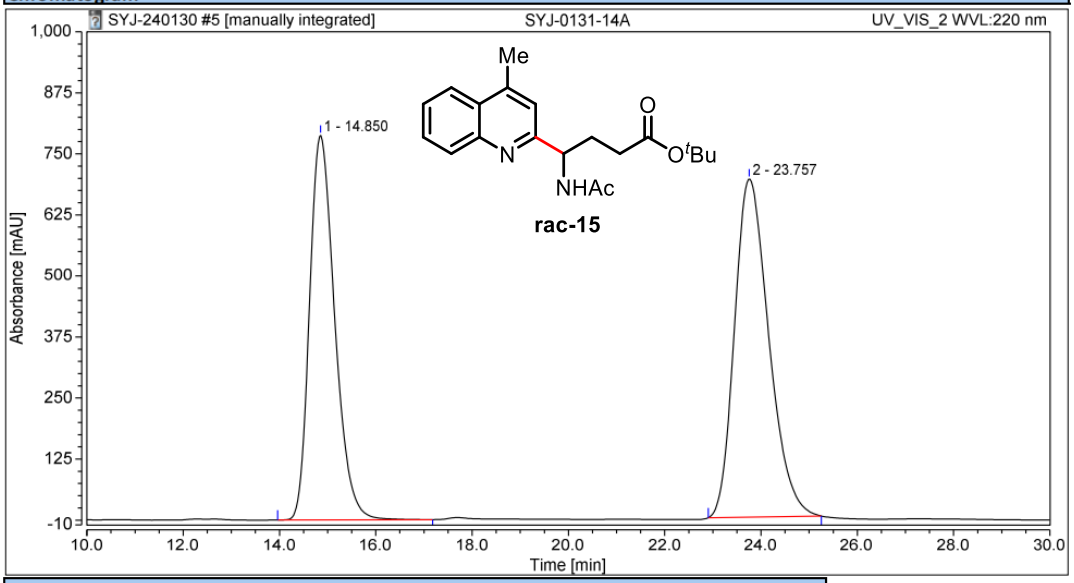
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	8.107	56.067	5.18	6.87	n.a.
2	11.140	1025.273	94.82	93.13	n.a.
Total:		**1081.340**	**100.00**	**100.00**	

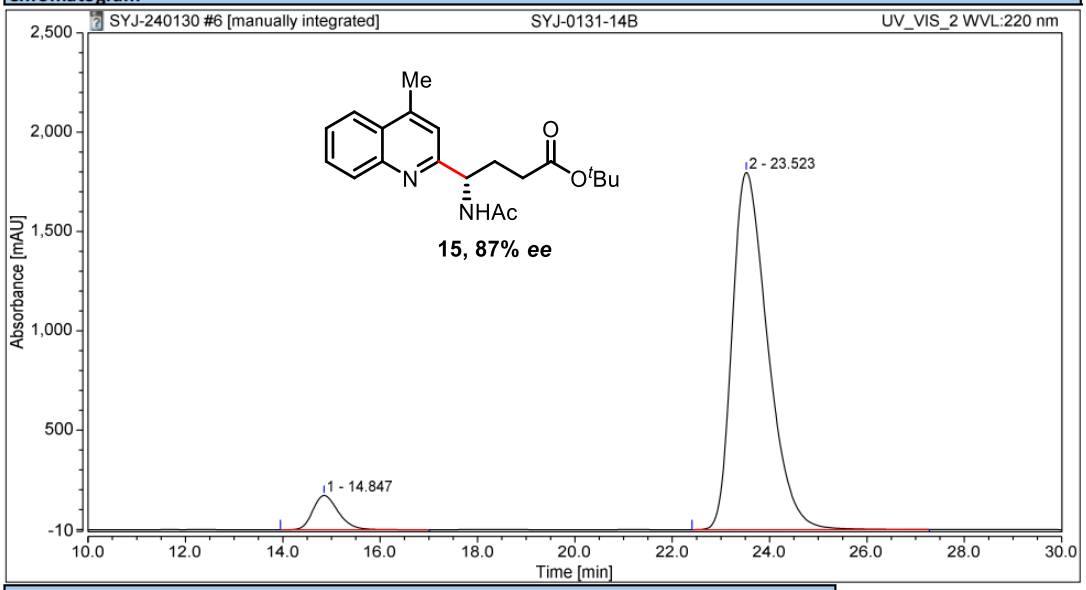
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	14.850	476.066	45.52	53.21	n.a.
2	23.757	569.875	54.48	46.79	n.a.
Total:		**1045.942**	**100.00**	**100.00**	

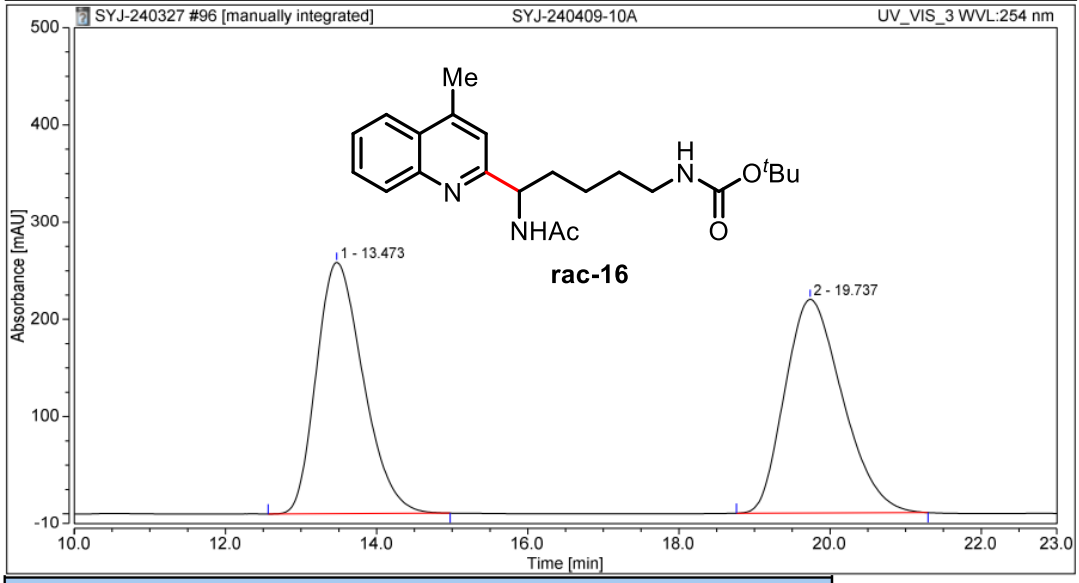
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	14.847	104.103	6.44	8.75	n.a.
2	23.523	1511.313	93.56	91.25	n.a.
Total:		**1615.416**	**100.00**	**100.00**	

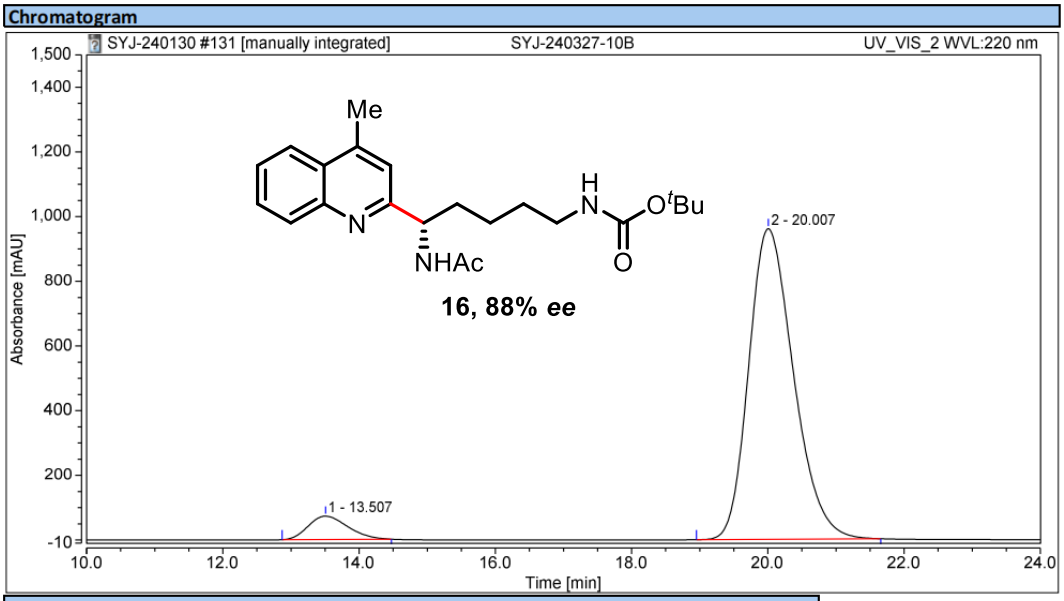
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	13.473	185.500	48.85	54.04	n.a.
2	19.737	194.237	51.15	45.96	n.a.
Total:		**379.737**	**100.00**	**100.00**	

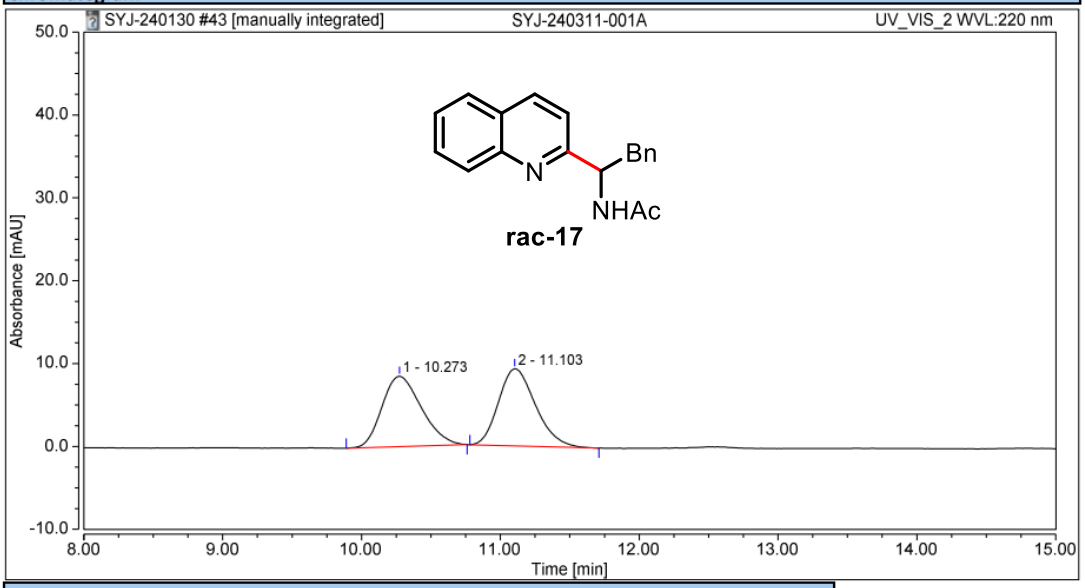
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	13.507	48.576	6.23	7.00	n.a.
2	20.007	730.619	93.77	93.00	n.a.
Total:		**779.195**	**100.00**	**100.00**	

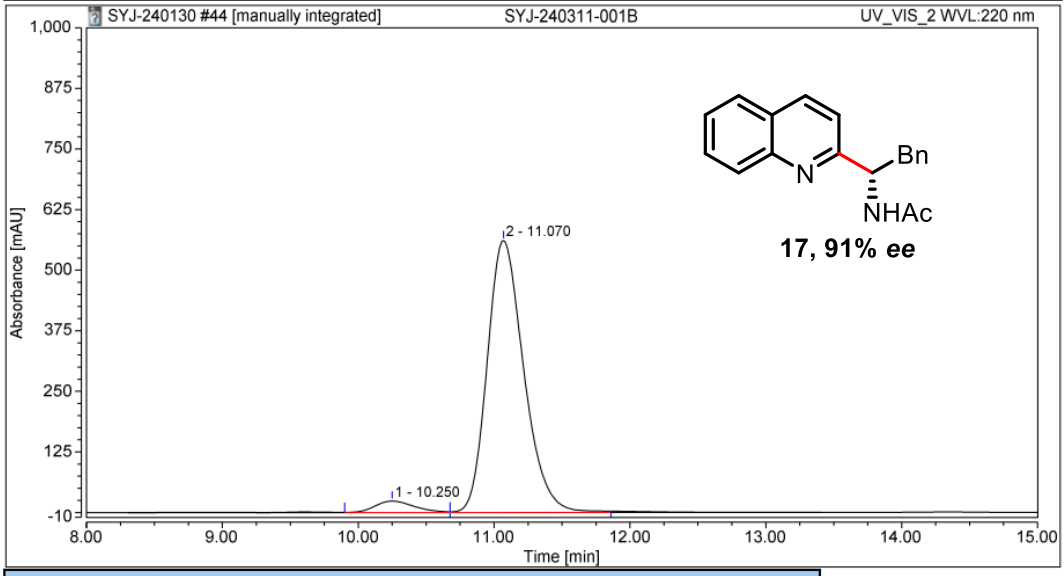
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	10.273	2.786	49.18	47.68	n.a.
2	11.103	2.879	50.82	52.32	n.a.
Total:		**5.665**	**100.00**	**100.00**	

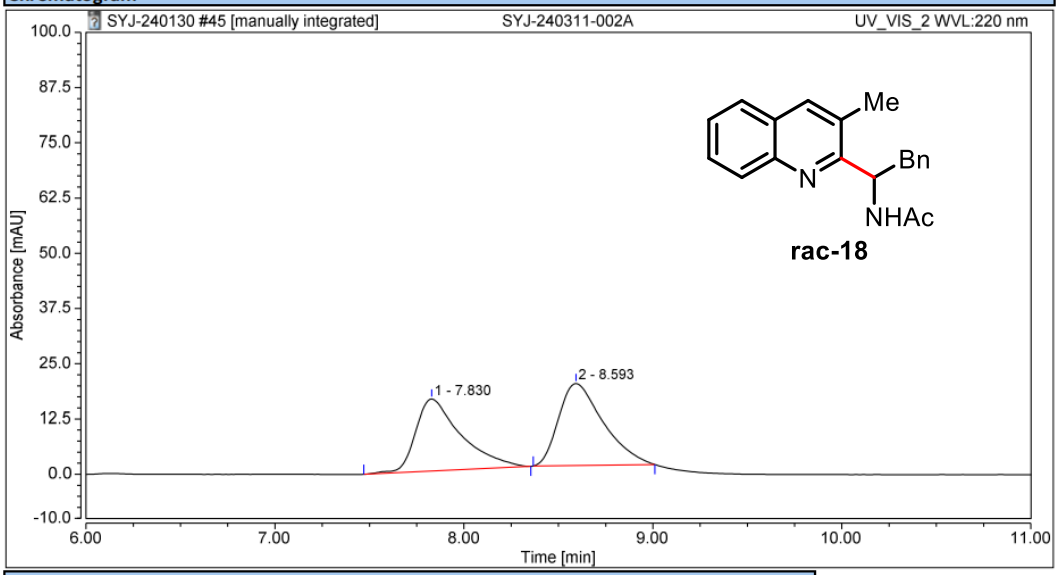
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	10.250	7.925	4.33	4.05	n.a.
2	11.070	175.017	95.67	95.95	n.a.
Total:		**182.942**	**100.00**	**100.00**	

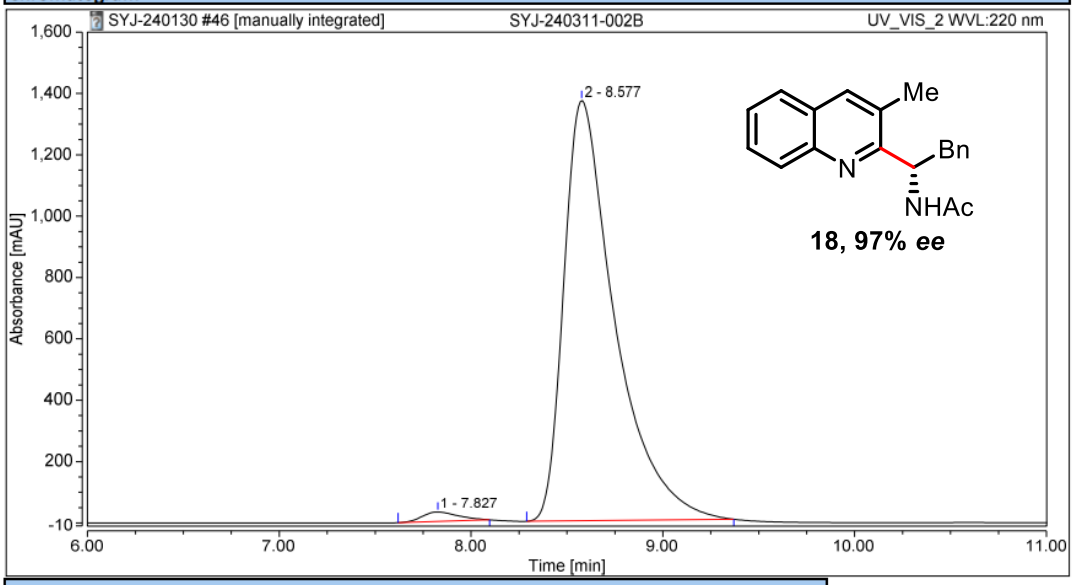
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	7.830	4.527	47.16	46.79	n.a.
2	8.593	5.073	52.84	53.21	n.a.
Total:		**9.600**	**100.00**	**100.00**	

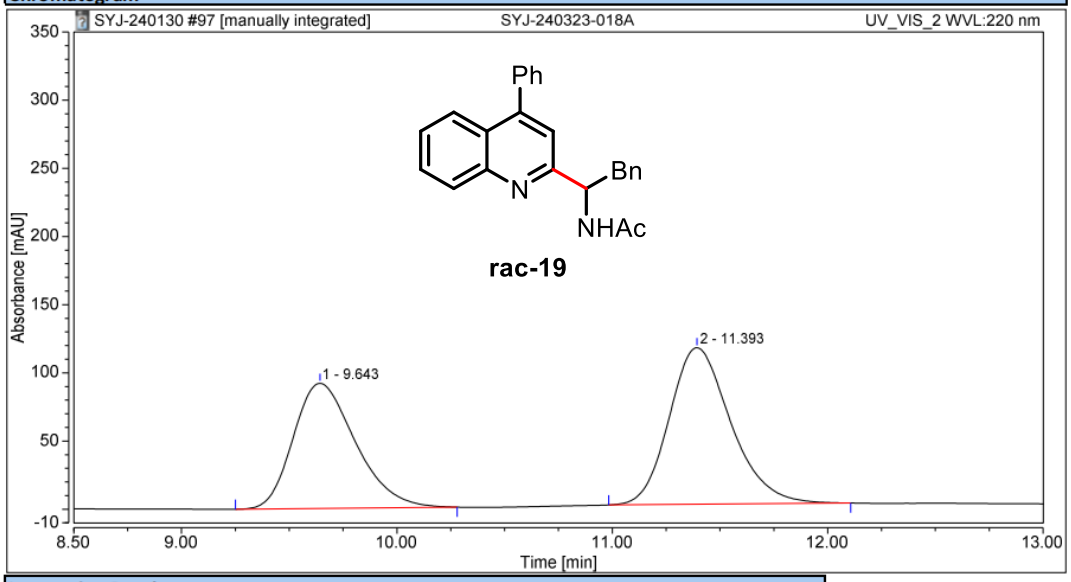
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	7.827	6.701	1.56	2.20	n.a.
2	8.577	421.696	98.44	97.80	n.a.
Total:		**428.397**	**100.00**	**100.00**	

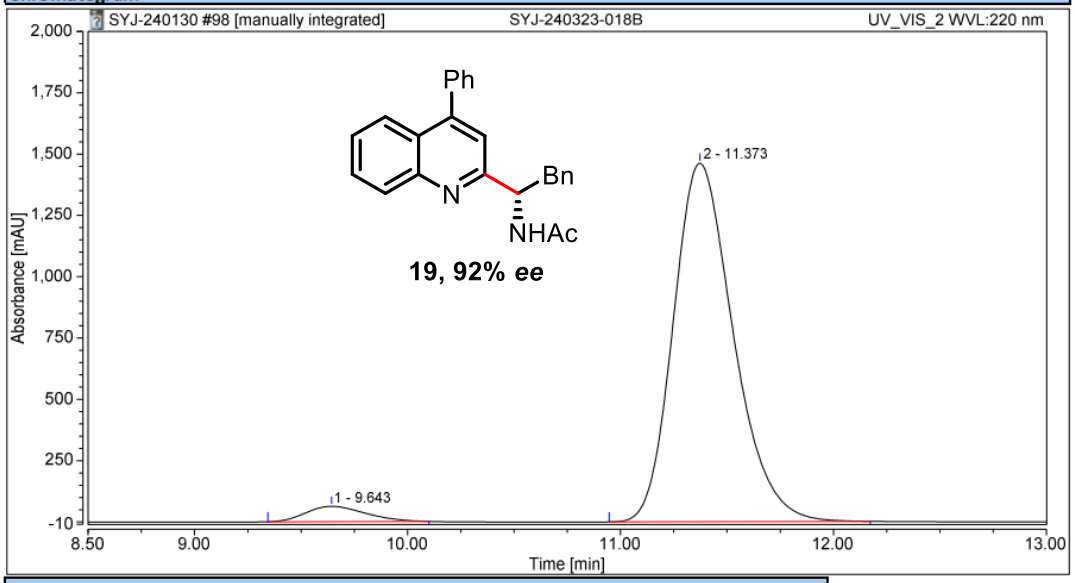
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	9.643	30.703	44.67	44.42	n.a.
2	11.393	38.033	55.33	55.58	n.a.
Total:		**68.736**	**100.00**	**100.00**	

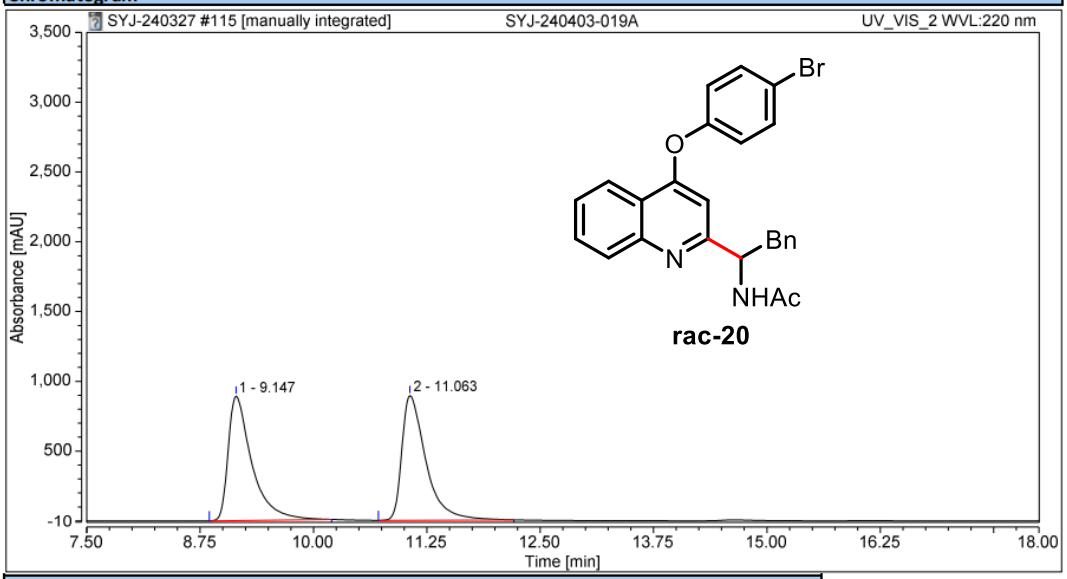
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	9.643	20.196	4.07	4.09	n.a.
2	11.373	476.477	95.93	95.91	n.a.
Total:		**496.673**	**100.00**	**100.00**	

Chromatogram

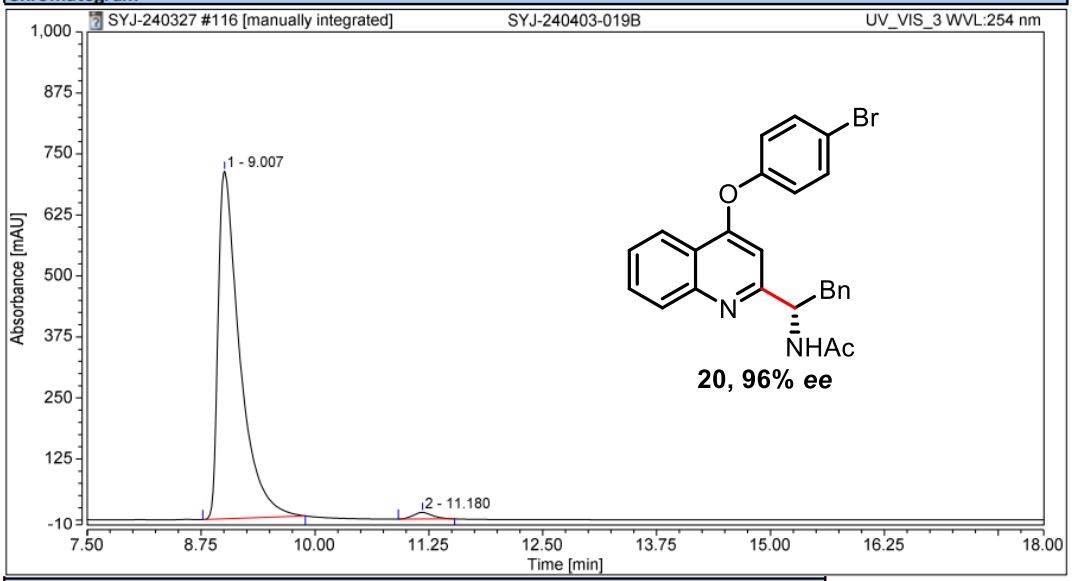


rac-20

Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	9.147	269.248	49.62	49.96	n.a.
2	11.063	273.403	50.38	50.04	n.a.
Total:		**542.652**	**100.00**	**100.00**	

Chromatogram

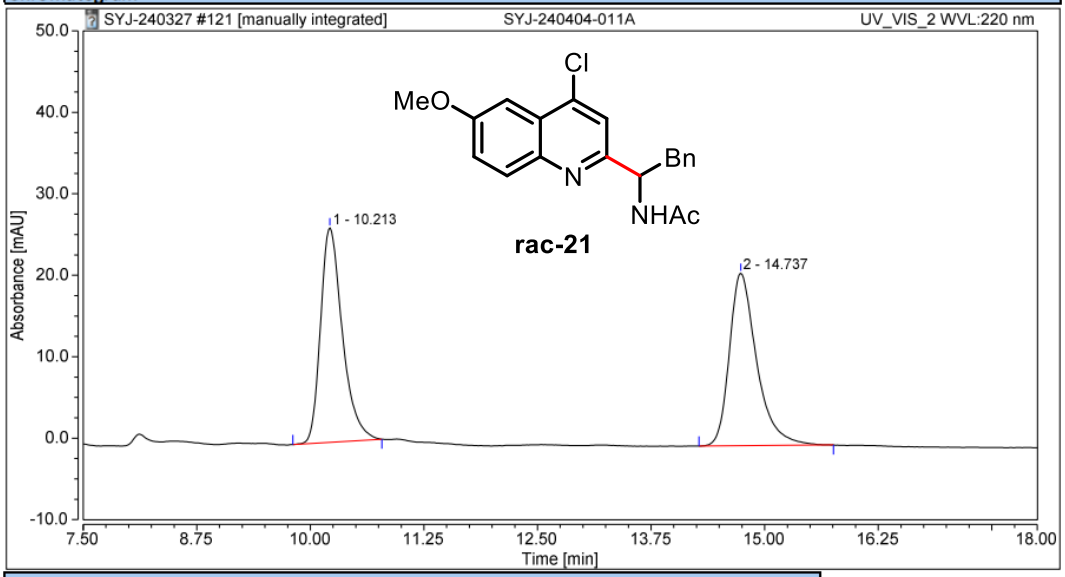


20, 96% *ee*

Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	9.007	195.420	98.32	98.13	n.a.
2	11.180	3.330	1.68	1.87	n.a.
Total:		**198.750**	**100.00**	**100.00**	

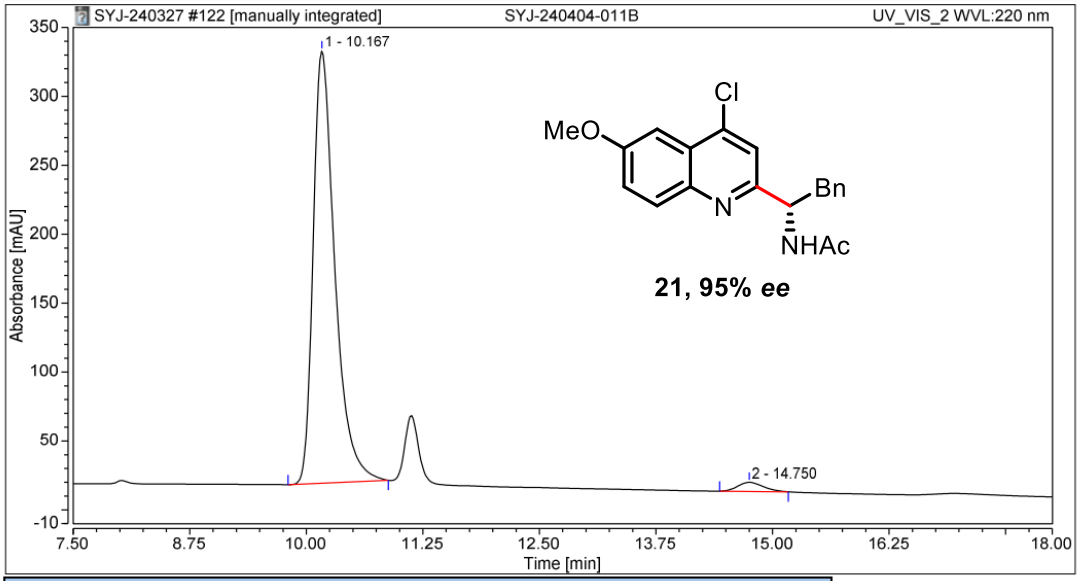
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	10.213	7.330	49.85	55.43	n.a.
2	14.737	7.373	50.15	44.57	n.a.
Total:		**14.703**	**100.00**	**100.00**	

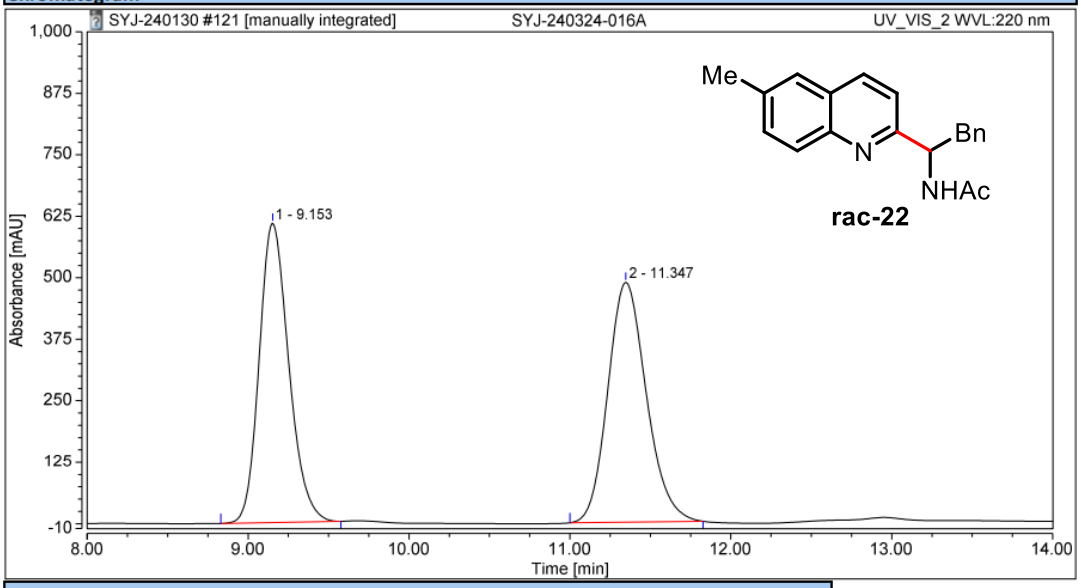
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	10.167	84.562	97.59	97.94	n.a.
2	14.750	2.084	2.41	2.06	n.a.
Total:		**86.647**	**100.00**	**100.00**	

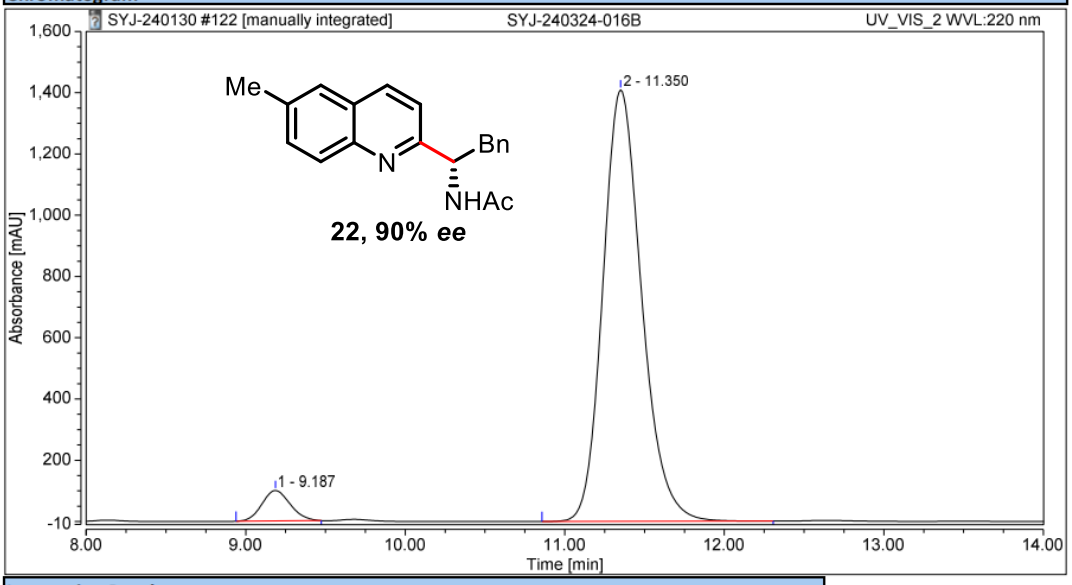
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	9.153	129.561	48.95	55.53	n.a.
2	11.347	135.100	51.05	44.47	n.a.
Total:		**264.660**	**100.00**	**100.00**	

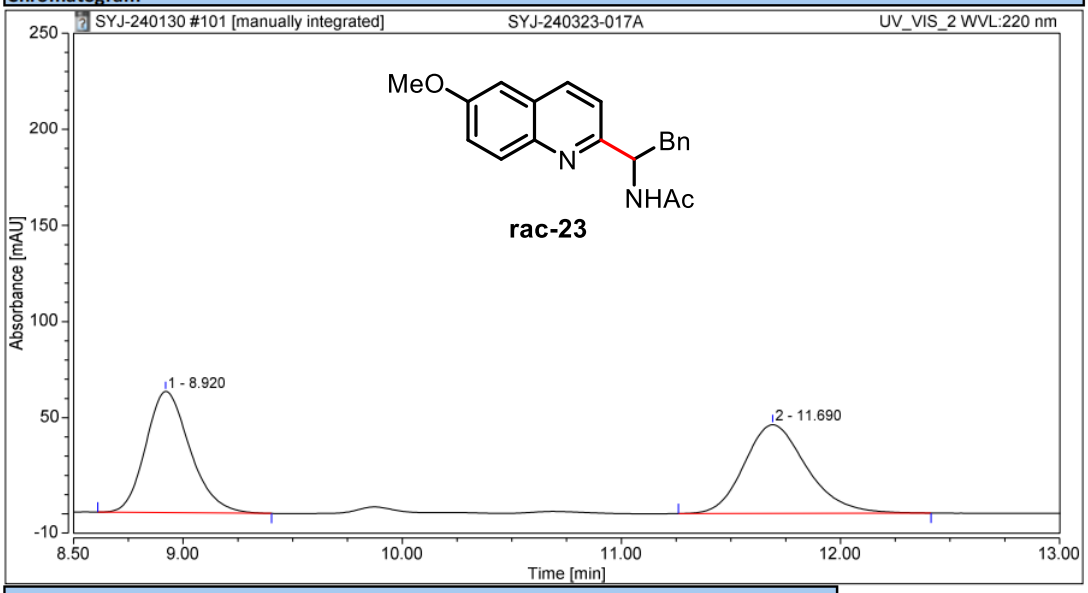
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	9.187	20.444	4.91	6.59	n.a.
2	11.350	395.910	95.09	93.41	n.a.
Total:		**416.354**	**100.00**	**100.00**	

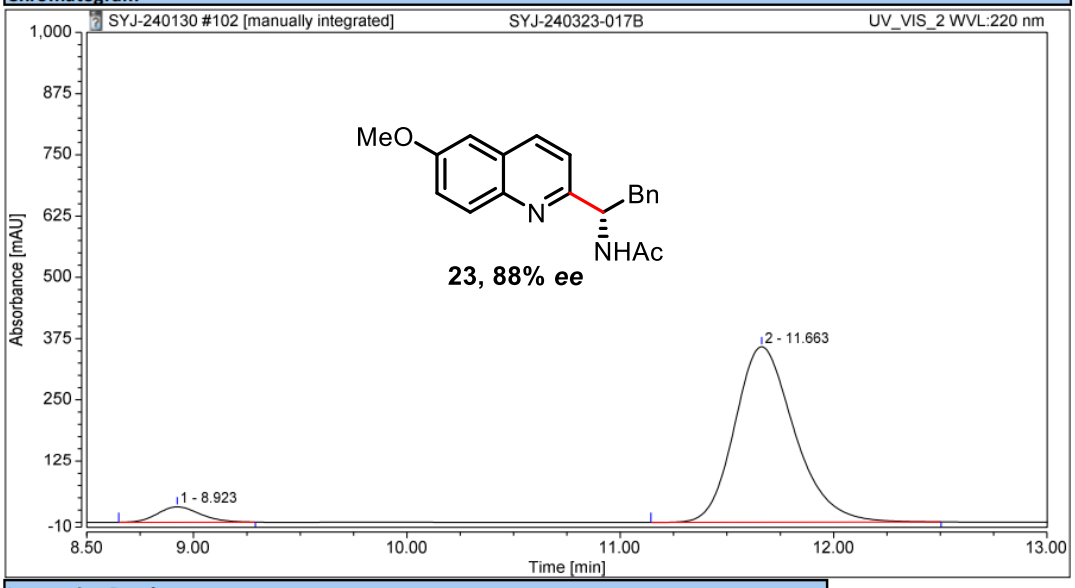
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	8.920	14.775	49.17	57.75	n.a.
2	11.690	15.276	50.83	42.25	n.a.
Total:		**30.051**	**100.00**	**100.00**	

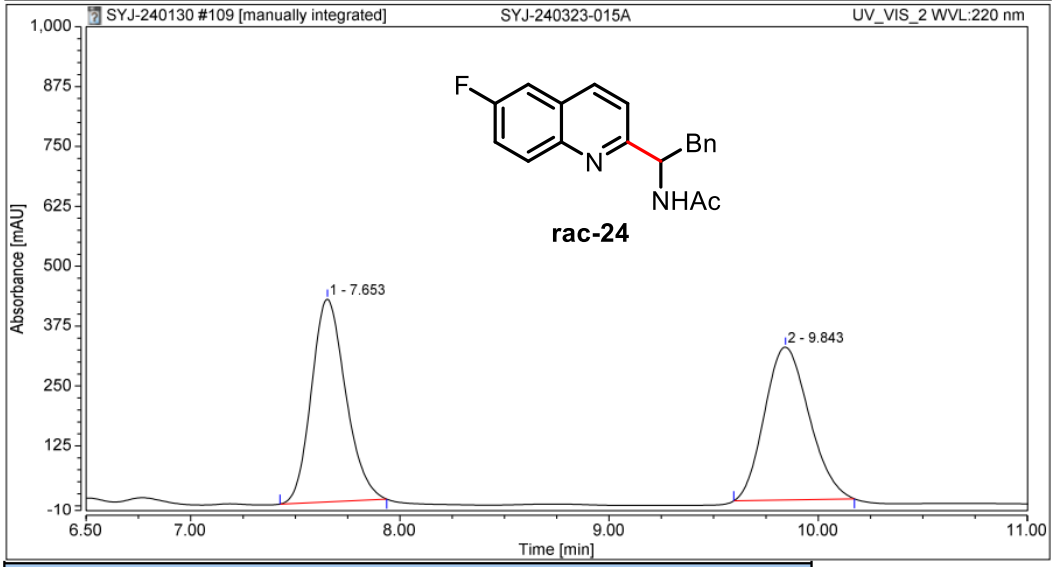
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	8.923	7.315	5.91	8.10	n.a.
2	11.663	116.362	94.09	91.90	n.a.
Total:		**123.676**	**100.00**	**100.00**	

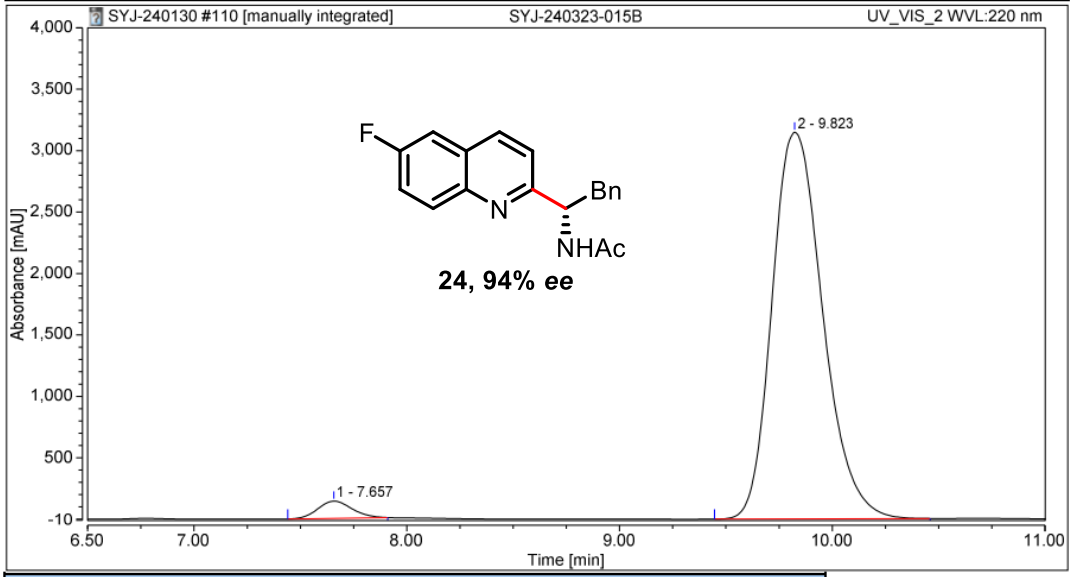
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	7.653	80.270	50.47	57.00	n.a.
2	9.843	78.782	49.53	43.00	n.a.
Total:		**159.052**	**100.00**	**100.00**	

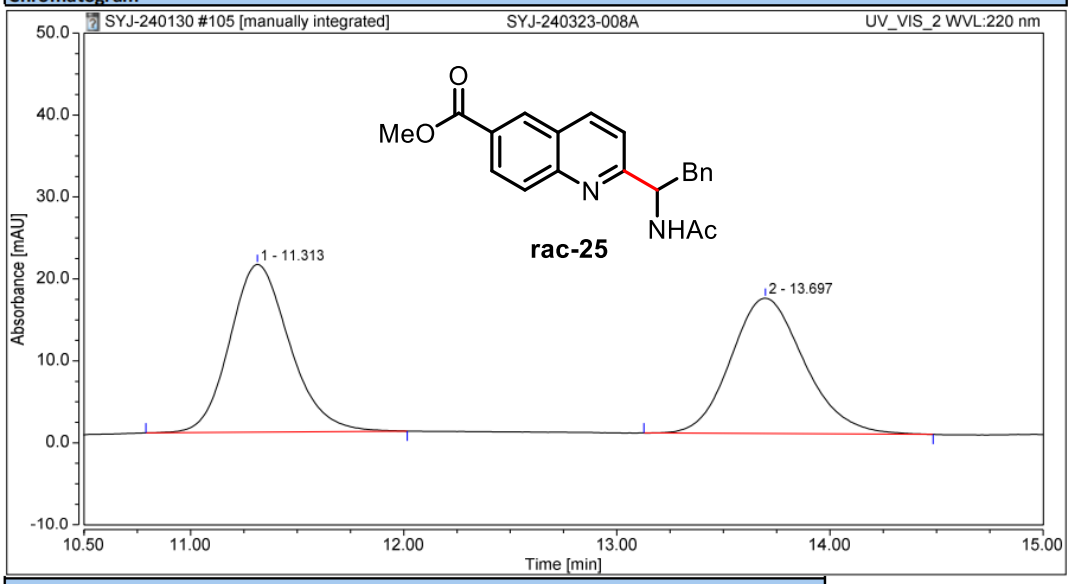
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	7.657	26.062	2.91	4.26	n.a.
2	9.823	868.348	97.09	95.74	n.a.
Total:		**894.410**	**100.00**	**100.00**	

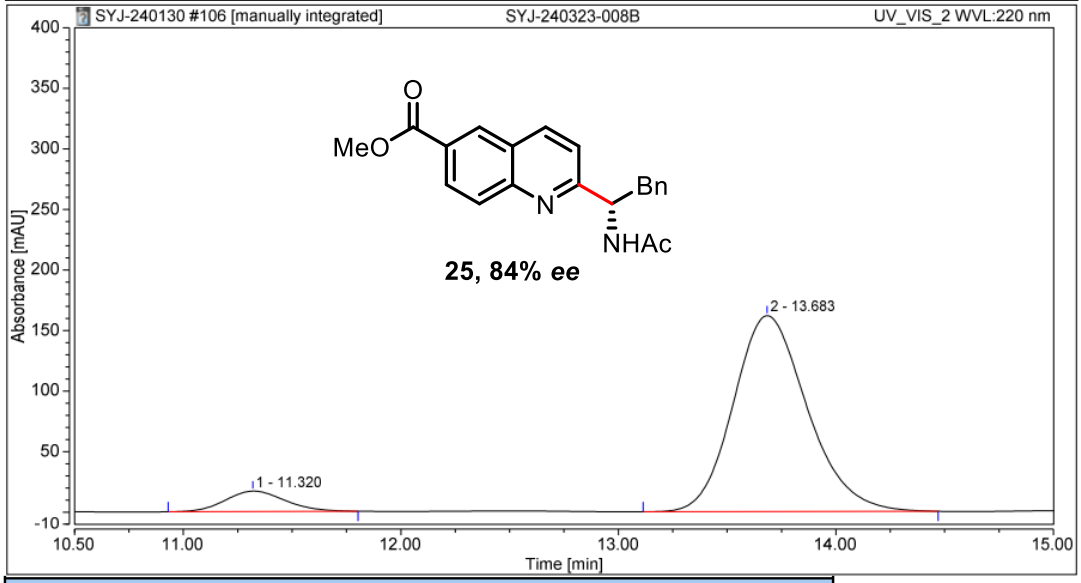
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	11.313	6.664	50.22	55.33	n.a.
2	13.697	6.605	49.78	44.67	n.a.
Total:		**13.269**	**100.00**	**100.00**	

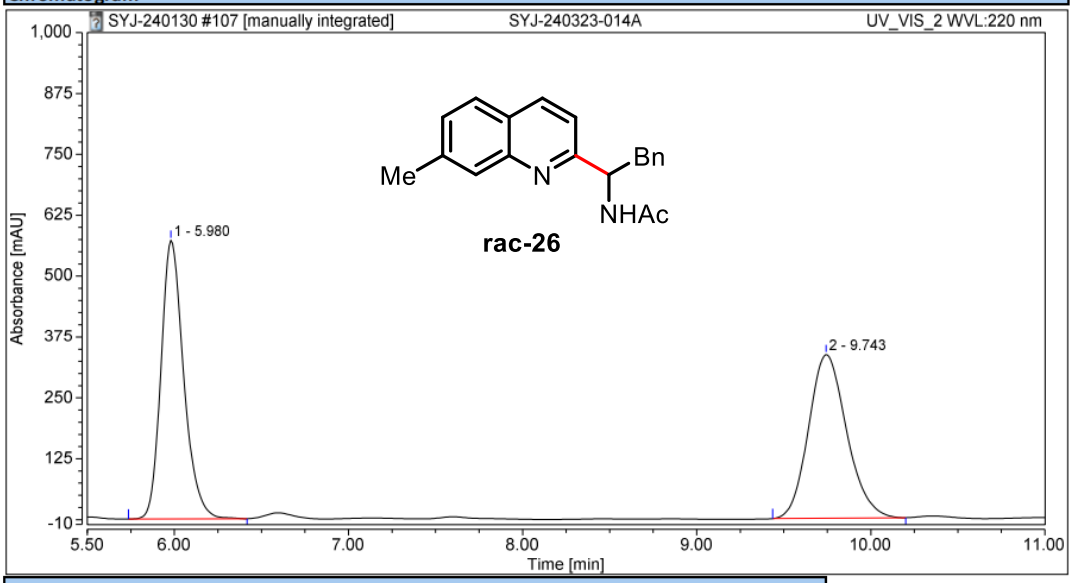
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	11.320	5.393	7.80	9.47	n.a.
2	13.683	63.762	92.20	90.53	n.a.
Total:		**69.155**	**100.00**	**100.00**	

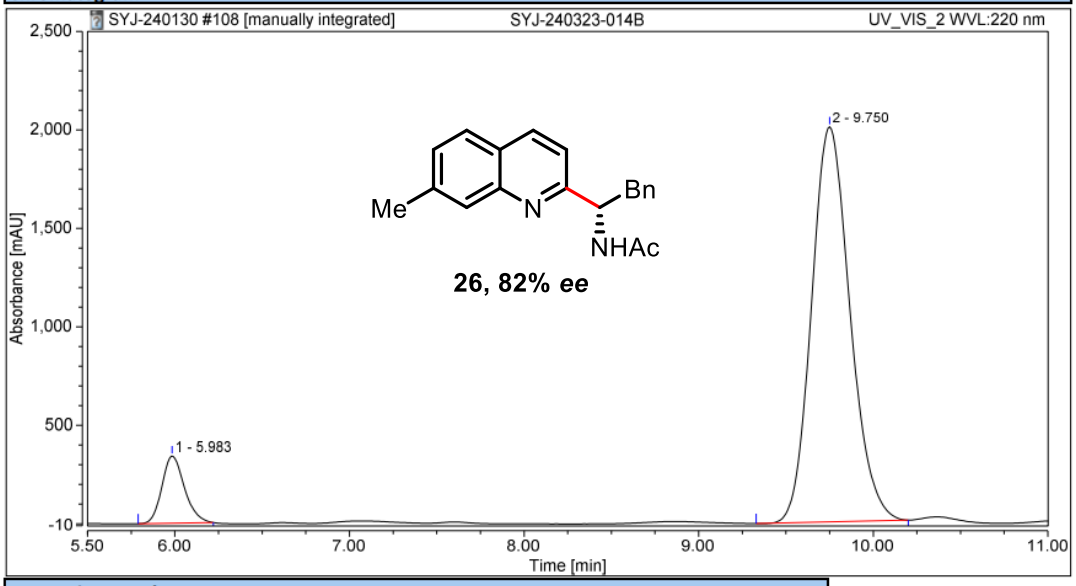
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	5.980	86.478	50.39	62.98	n.a.
2	9.743	85.091	49.58	37.01	n.a.
3	24.700	0.047	0.03	0.01	n.a.
Total:		**171.616**	**100.00**	**100.00**	

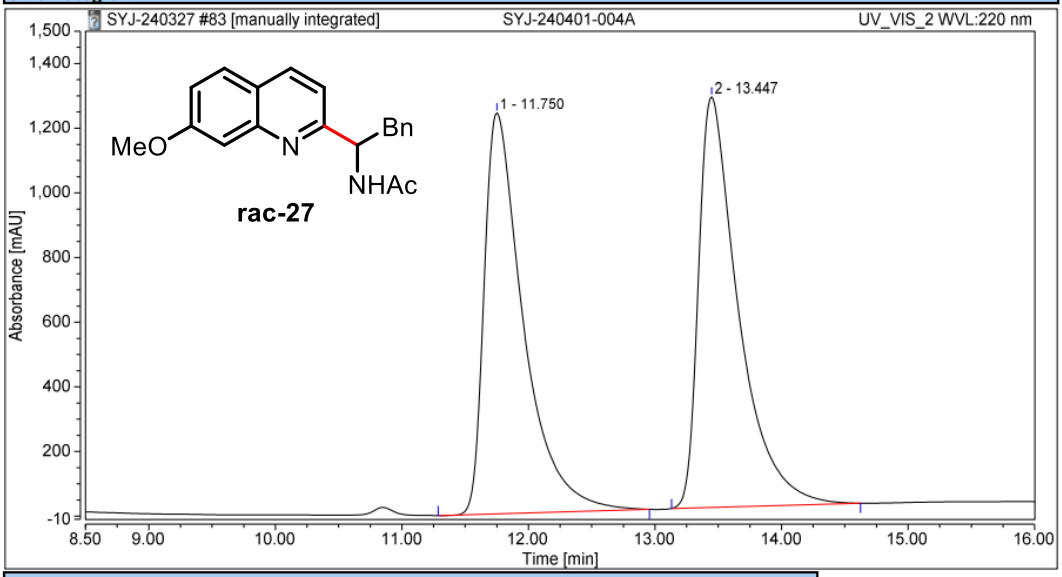
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	5.983	50.959	9.06	14.54	n.a.
2	9.750	511.355	90.94	85.46	n.a.
Total:		**562.314**	**100.00**	**100.00**	

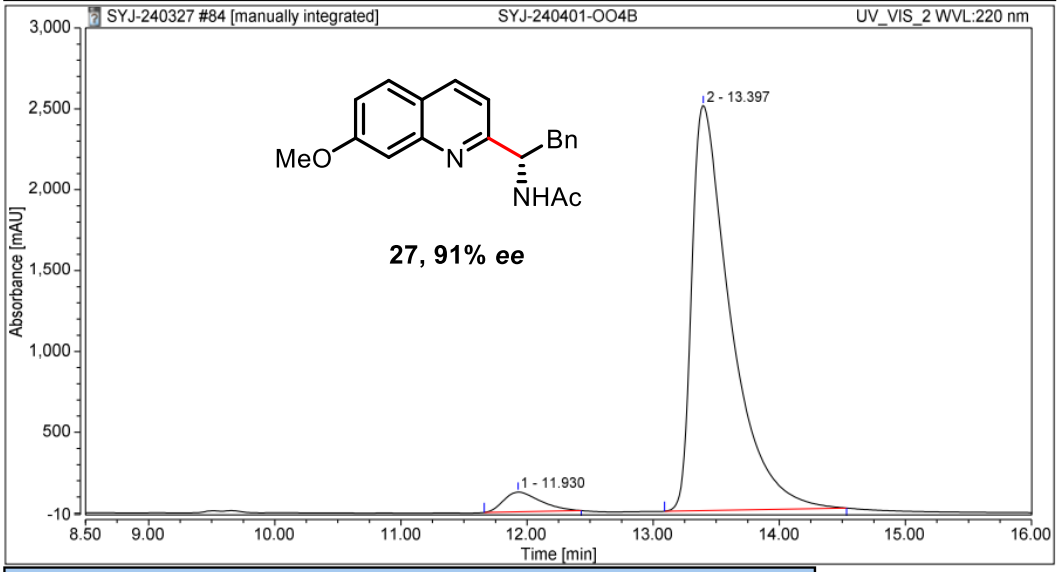
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	11.750	445.043	49.02	49.42	n.a.
2	13.447	462.837	50.98	50.58	n.a.
Total:		**907.880**	**100.00**	**100.00**	

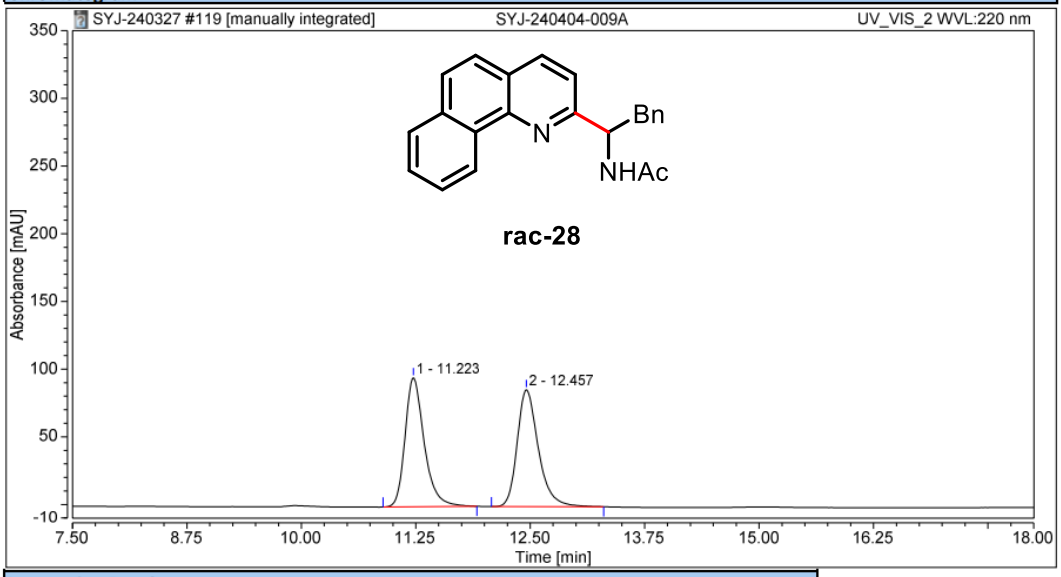
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	11.930	41.072	4.41	4.63	n.a.
2	13.397	890.800	95.59	95.37	n.a.
Total:		**931.872**	**100.00**	**100.00**	

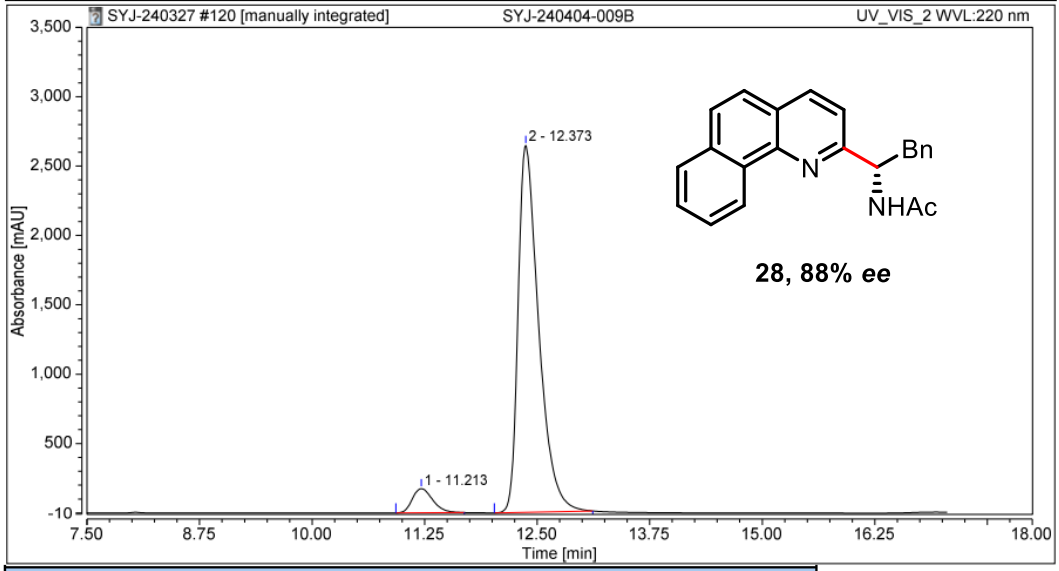
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	11.223	23.213	50.03	52.46	n.a.
2	12.457	23.189	49.97	47.54	n.a.
Total:		**46.401**	**100.00**	**100.00**	

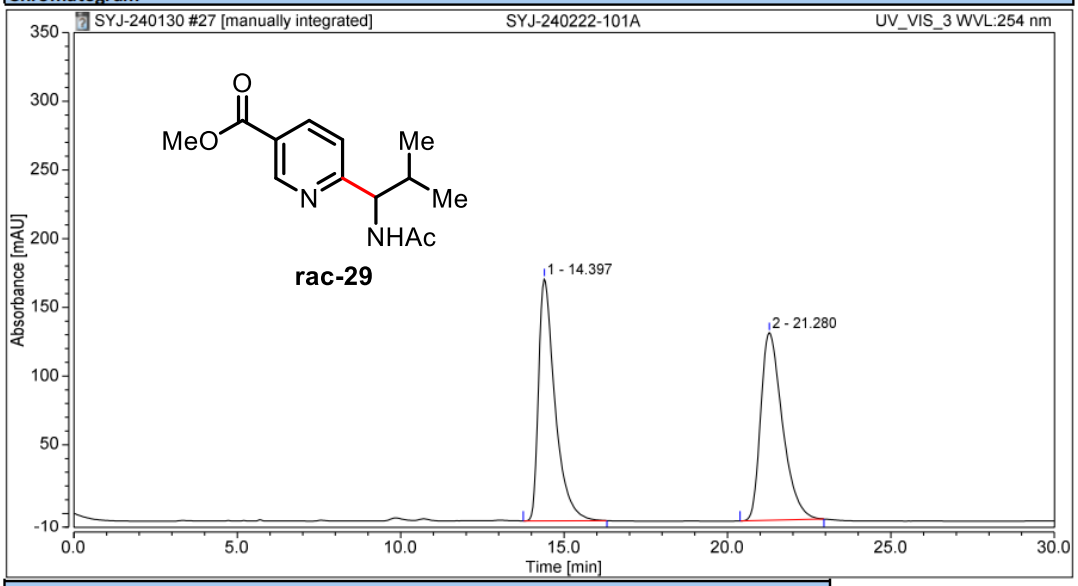
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	11.213	45.553	6.10	6.16	n.a.
2	12.373	701.240	93.90	93.84	n.a.
Total:		**746.793**	**100.00**	**100.00**	

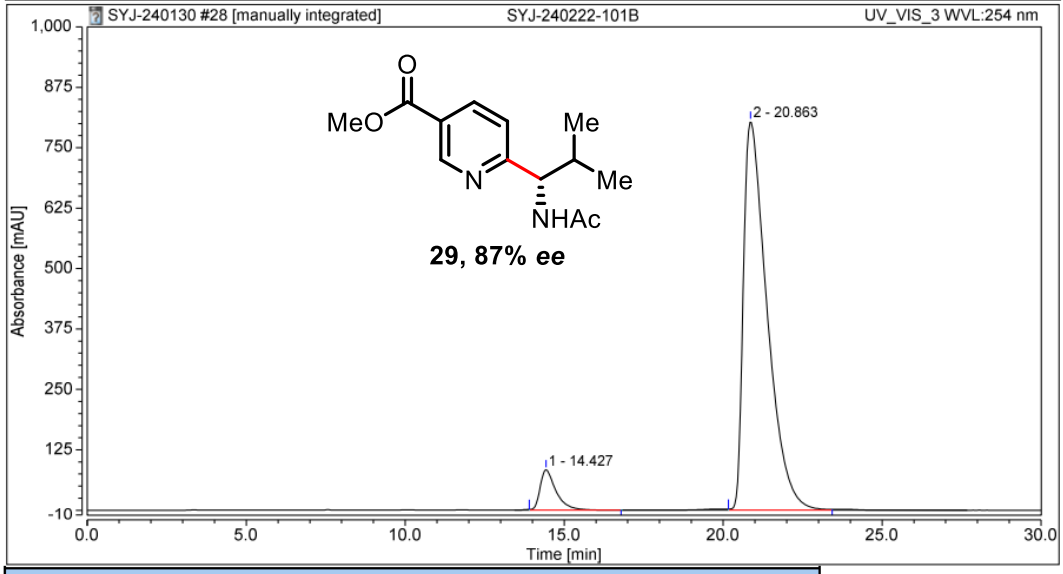
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	14.397	102.942	49.36	56.33	n.a.
2	21.280	105.617	50.64	43.67	n.a.
Total:		**208.559**	**100.00**	**100.00**	

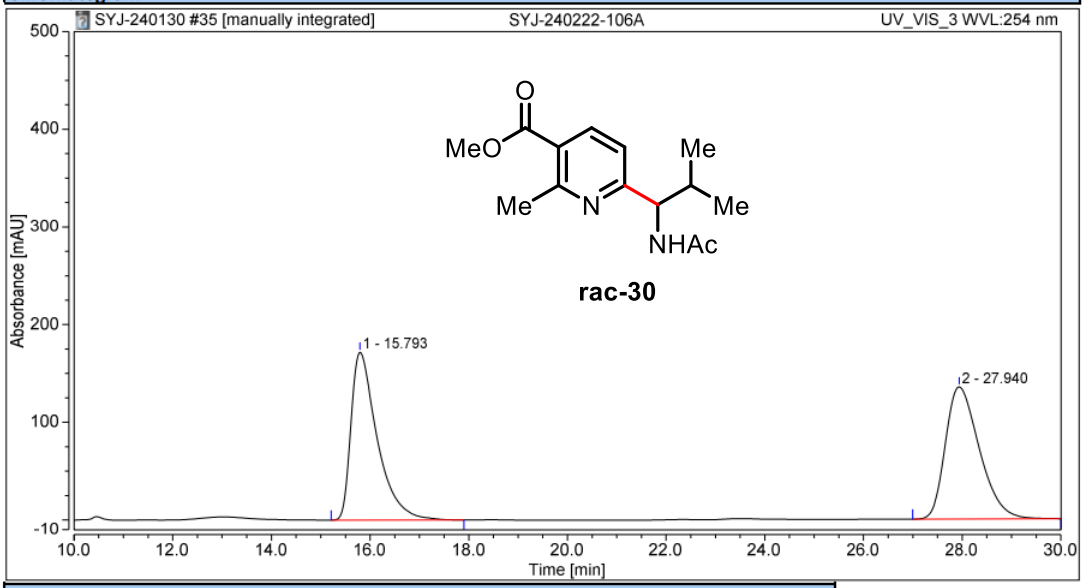
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	14.427	48.639	6.54	9.39	n.a.
2	20.863	694.753	93.46	90.61	n.a.
Total:		**743.392**	**100.00**	**100.00**	

Chromatogram



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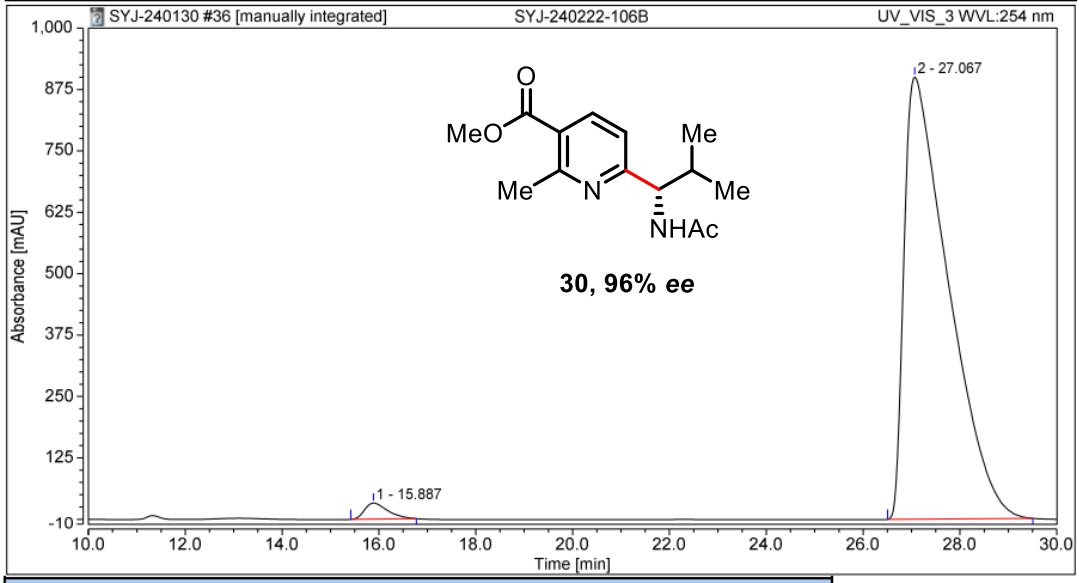
Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	15.793	106.031	49.60	55.95	n.a.
2	27.940	107.751	50.40	44.05	n.a.
Total:		**213.782**	**100.00**	**100.00**	

Chromatogram

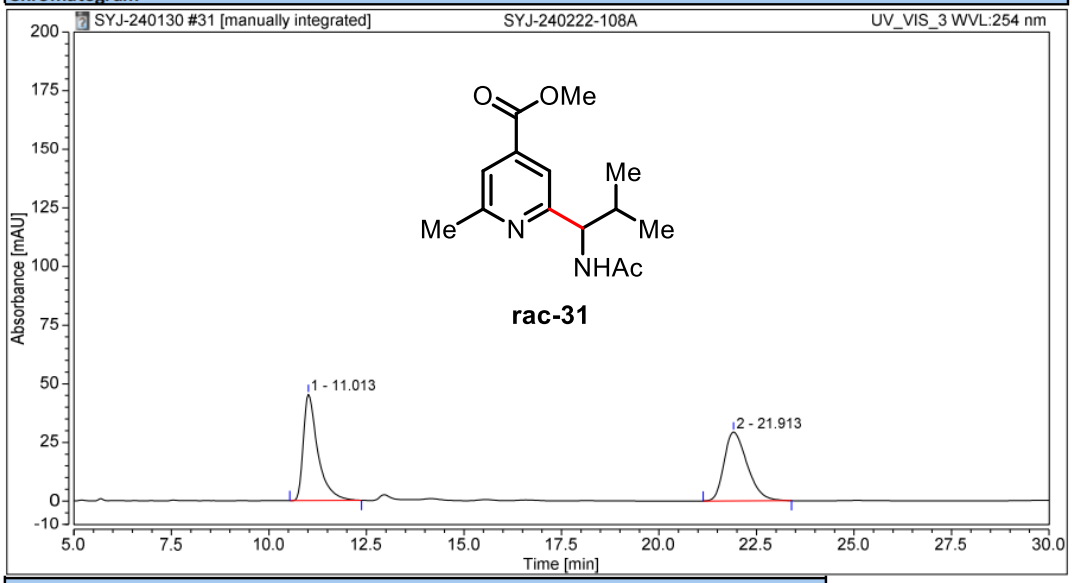


30, 96% *ee*

Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	15.887	18.169	1.87	3.52	n.a.
2	27.067	952.477	98.13	96.48	n.a.
Total:		**970.646**	**100.00**	**100.00**	

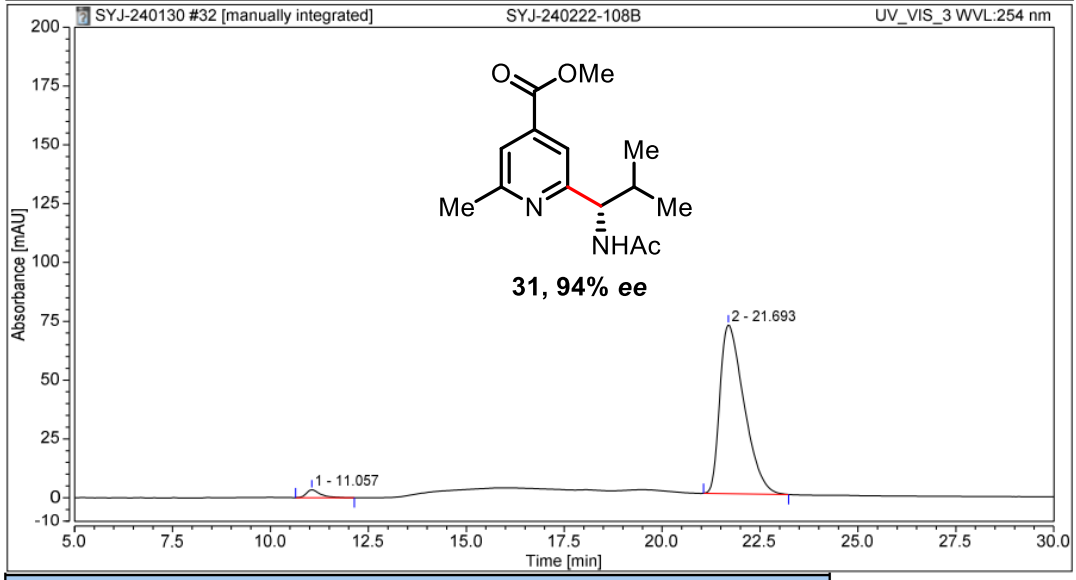
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	11.013	19.577	49.33	60.67	n.a.
2	21.913	20.112	50.67	39.33	n.a.
Total:		**39.689**	**100.00**	**100.00**	

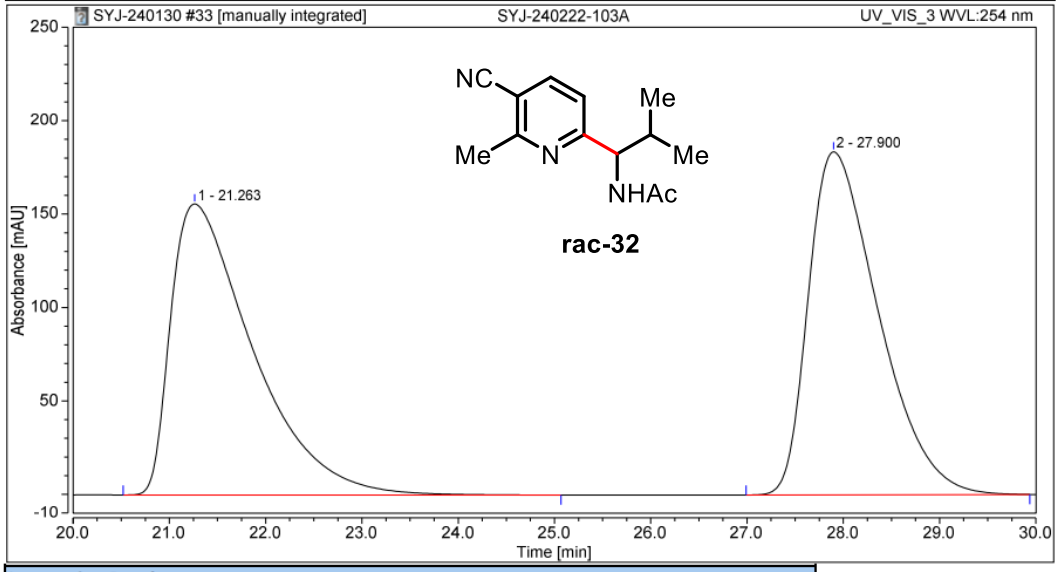
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	11.057	1.405	2.66	4.45	n.a.
2	21.693	51.385	97.34	95.55	n.a.
Total:		**52.790**	**100.00**	**100.00**	

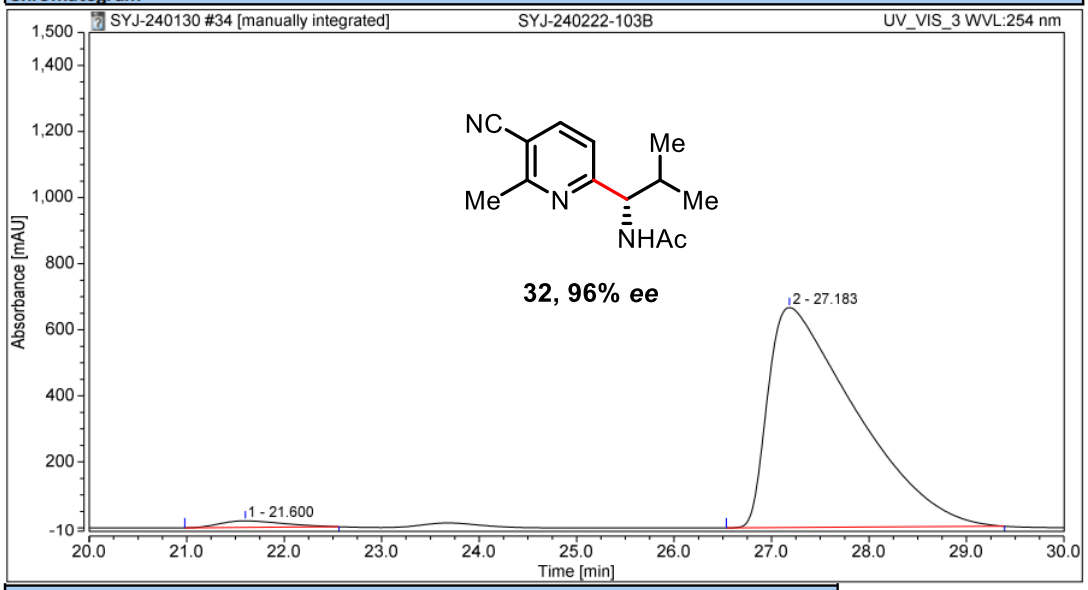
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	21.263	153.111	49.70	45.91	n.a.
2	27.900	154.933	50.30	54.09	n.a.
Total:		**308.044**	**100.00**	**100.00**	

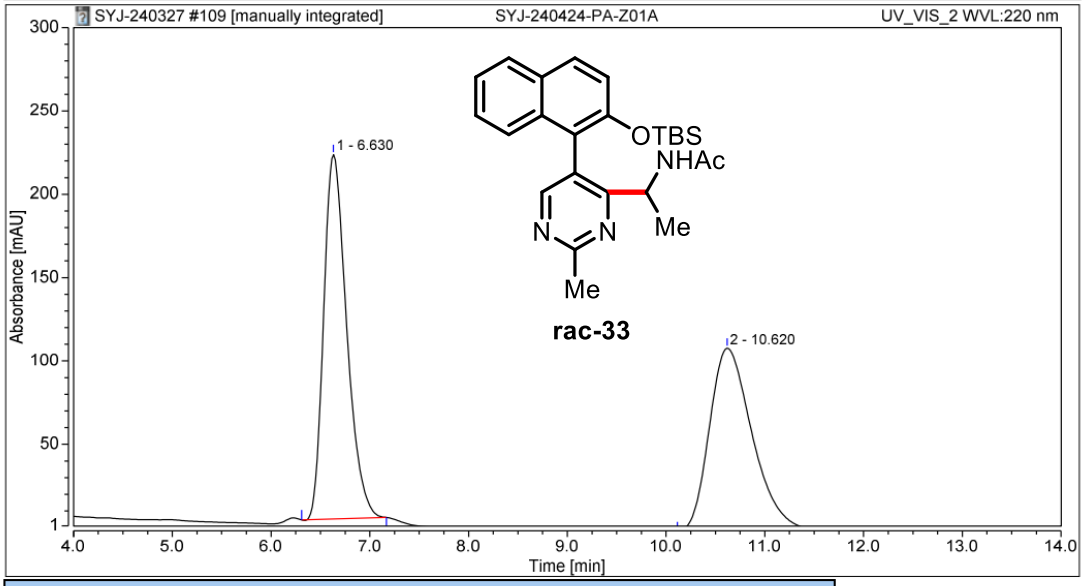
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	21.600	14.932	2.11	2.88	n.a.
2	27.183	694.370	97.89	97.12	n.a.
Total:		**709.302**	**100.00**	**100.00**	

Chromatogram



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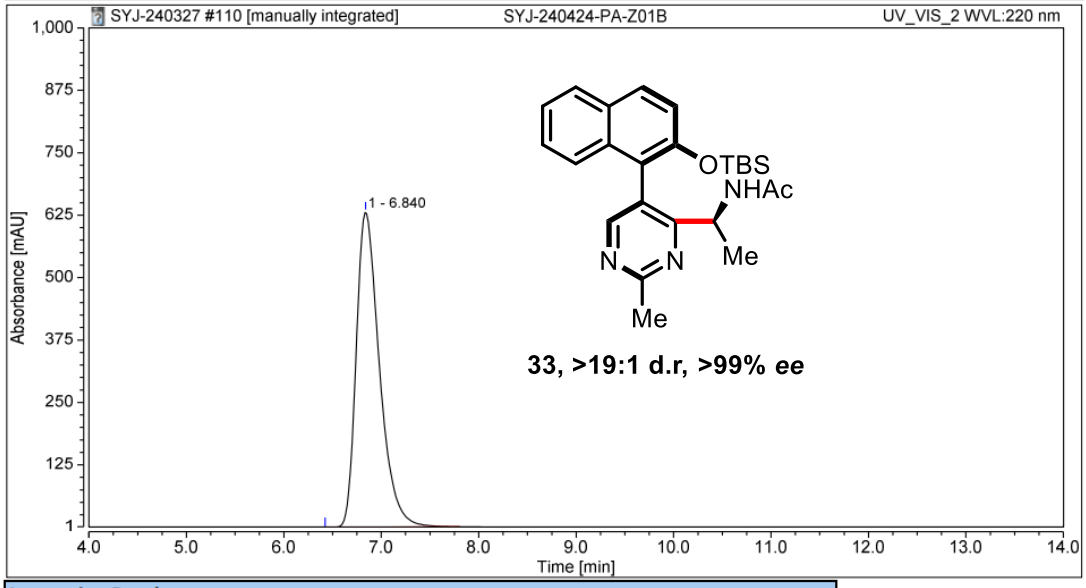
Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	6.630	58.999	51.46	66.52	n.a.
2	10.620	55.657	48.54	33.48	n.a.
Total:		**114.655**	**100.00**	**100.00**	

Chromatogram

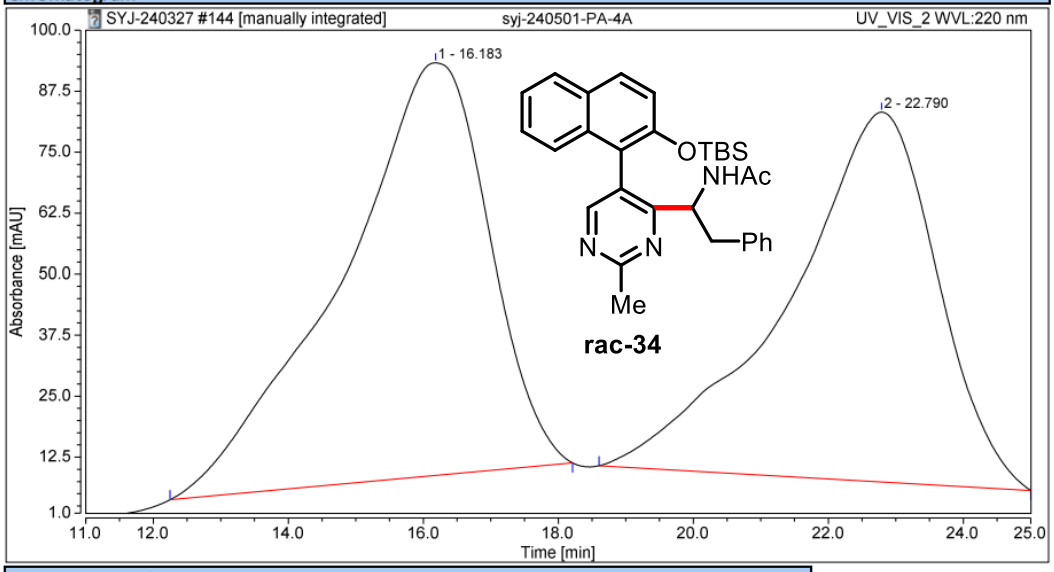


33, >19:1 d.r, >99% *ee*

Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	6.840	174.140	100.00	100.00	n.a.
Total:		**174.140**	**100.00**	**100.00**	

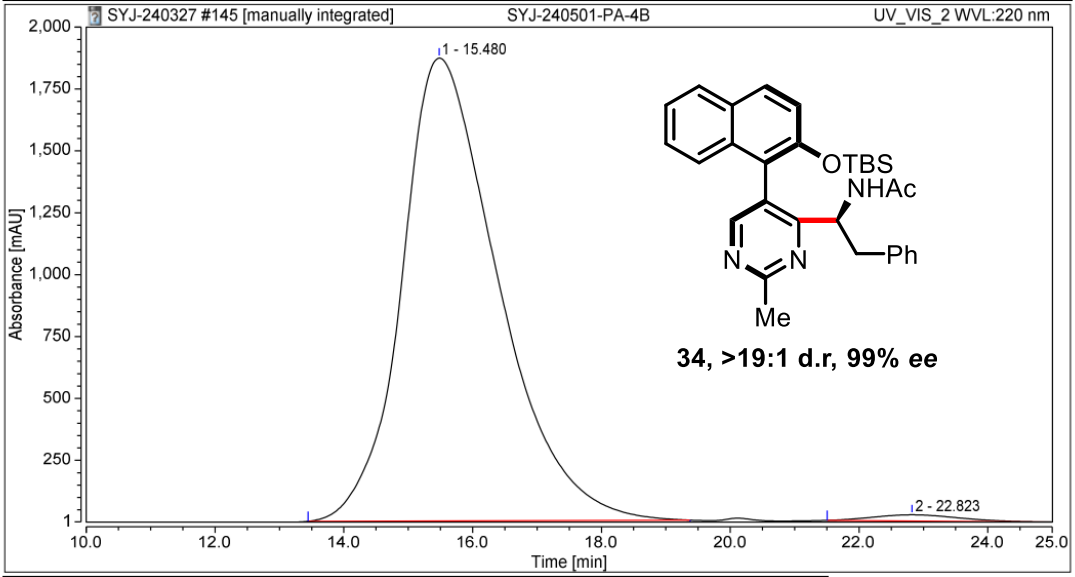
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	16.183	215.235	52.65	52.73	n.a.
2	22.790	193.592	47.35	47.27	n.a.
Total:		**408.827**	**100.00**	**100.00**	

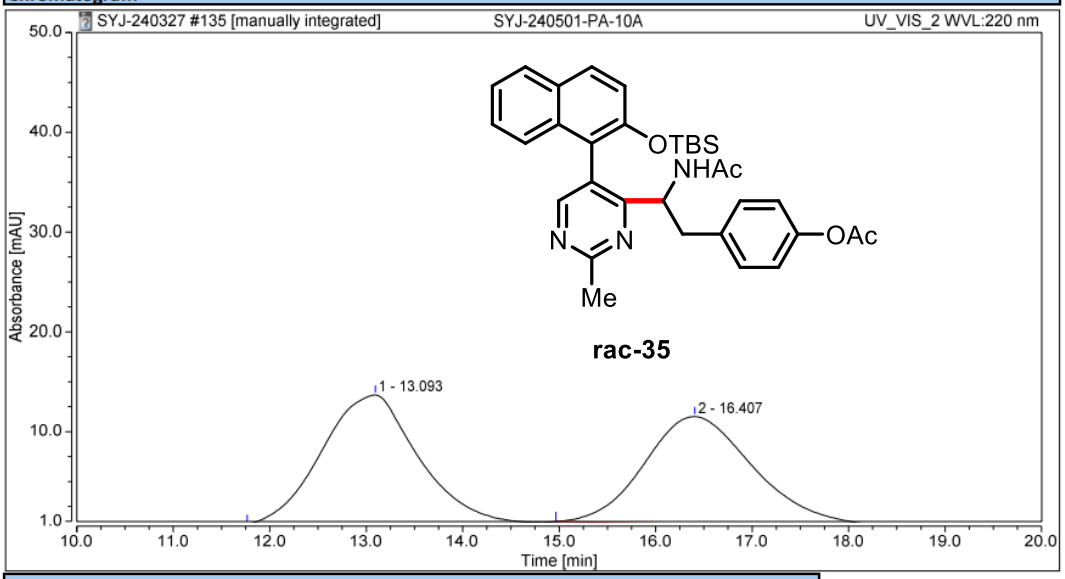
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	15.480	3239.140	98.85	98.69	n.a.
2	22.823	37.763	1.15	1.31	n.a.
Total:		**3276.903**	**100.00**	**100.00**	

Chromatogram



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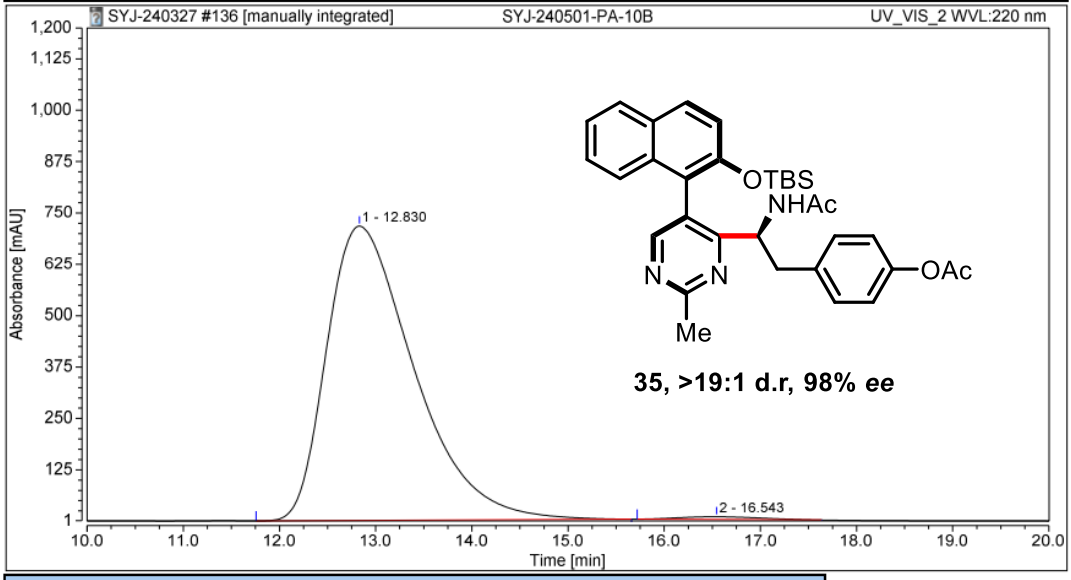
Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	13.093	14.841	51.04	54.51	n.a.
2	16.407	14.234	48.96	45.49	n.a.
Total:		**29.075**	**100.00**	**100.00**	

Chromatogram

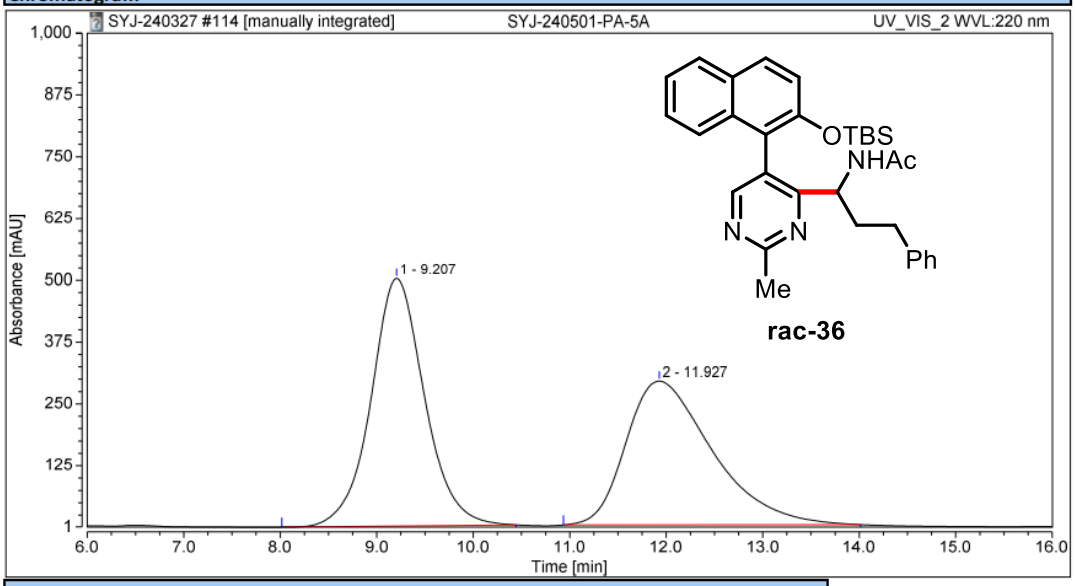


35, >19:1 d.r, 98% *ee*

Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	12.830	753.140	99.12	99.06	n.a.
2	16.543	6.712	0.88	0.94	n.a.
Total:		**759.852**	**100.00**	**100.00**	

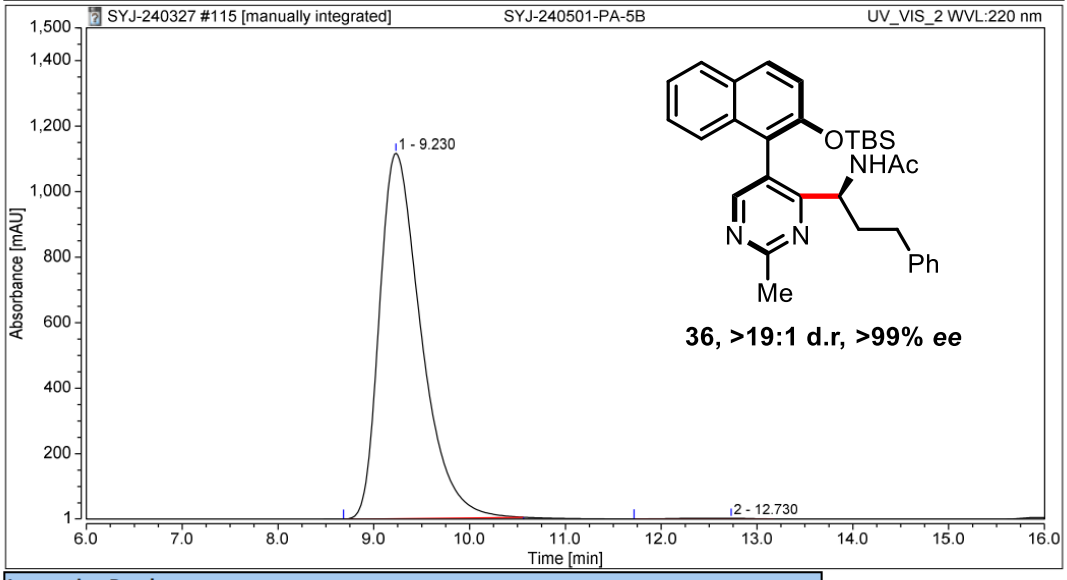
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	9.207	321.453	51.60	63.28	n.a.
2	11.927	301.540	48.40	36.72	n.a.
Total:		**622.994**	**100.00**	**100.00**	

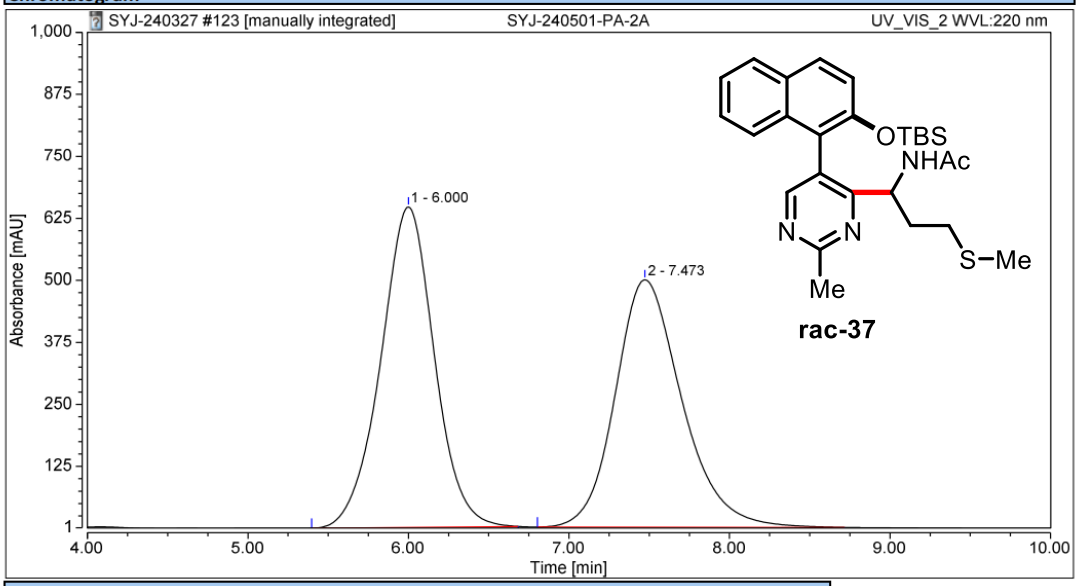
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	9.230	560.660	99.62	99.78	n.a.
2	12.730	2.139	0.38	0.22	n.a.
Total:		**562.800**	**100.00**	**100.00**	

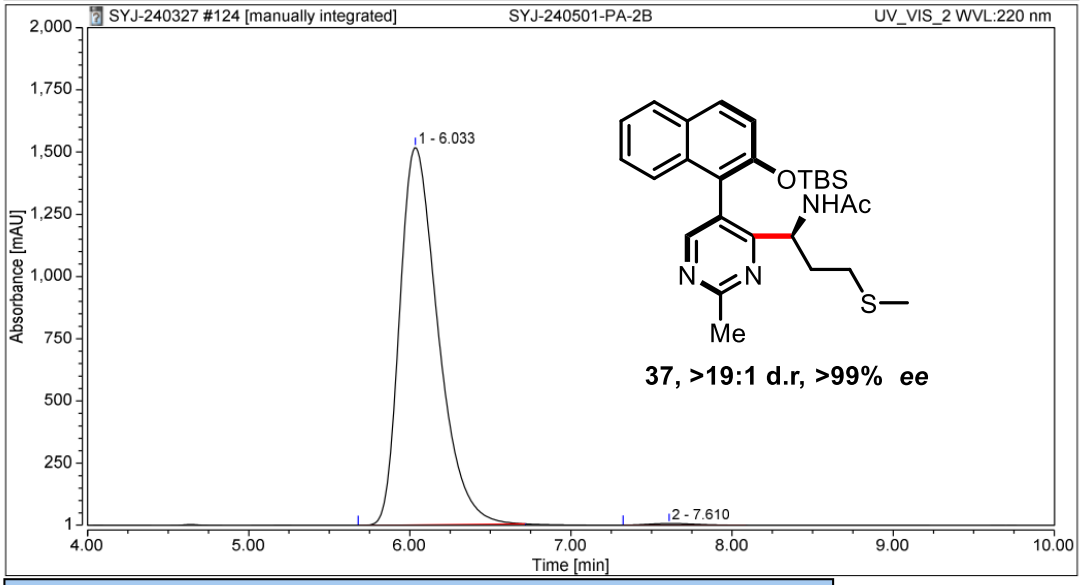
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	6.000	249.882	51.05	56.44	n.a.
2	7.473	239.574	48.95	43.56	n.a.
Total:		**489.456**	**100.00**	**100.00**	

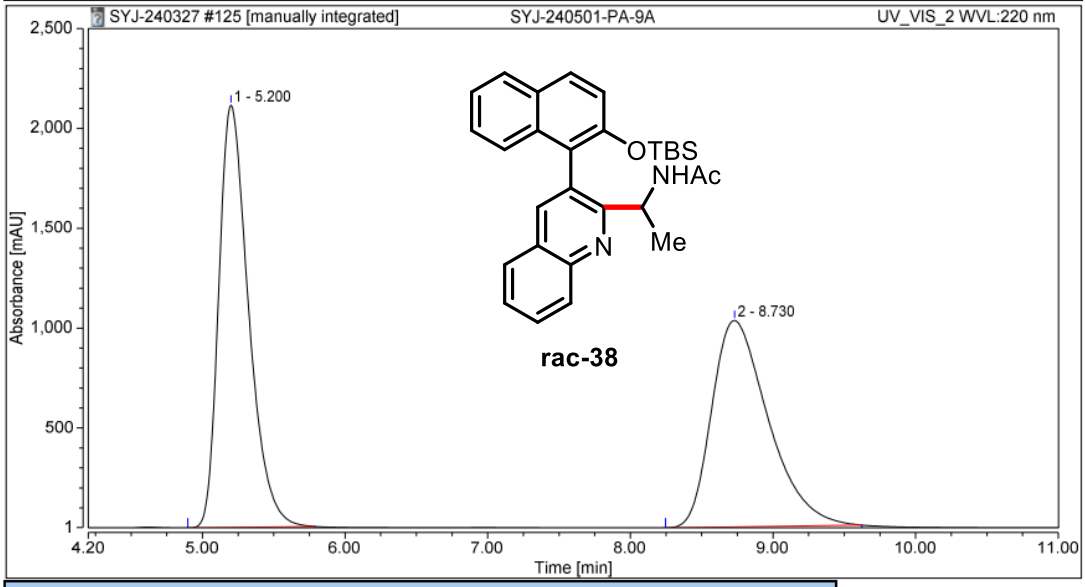
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	6.033	417.418	99.39	99.54	n.a.
2	7.610	2.545	0.61	0.46	n.a.
Total:		**419.962**	**100.00**	**100.00**	

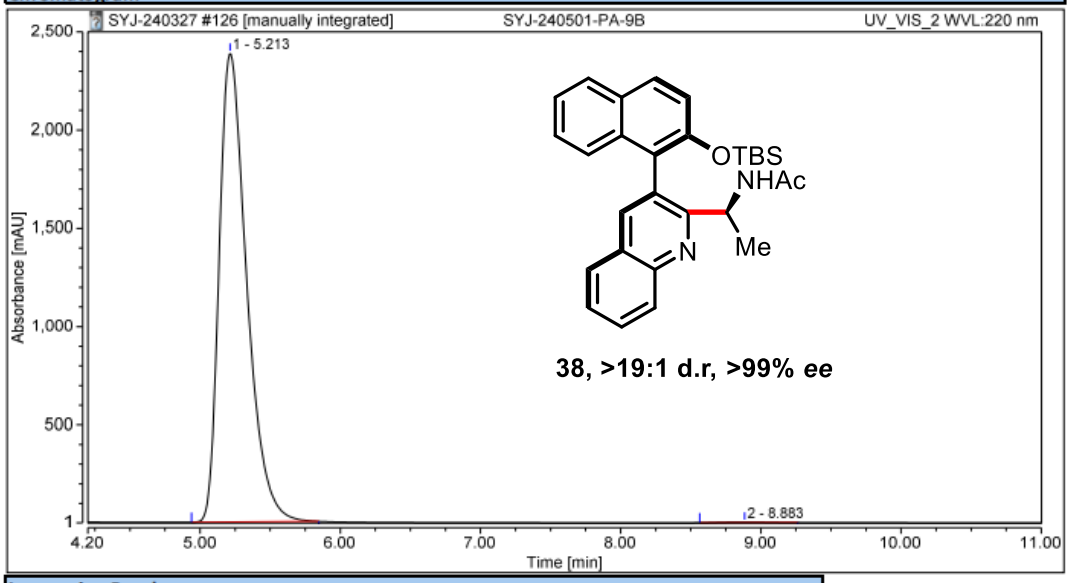
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	5.200	510.914	51.81	67.16	n.a.
2	8.730	475.215	48.19	32.84	n.a.
Total:		**986.129**	**100.00**	**100.00**	

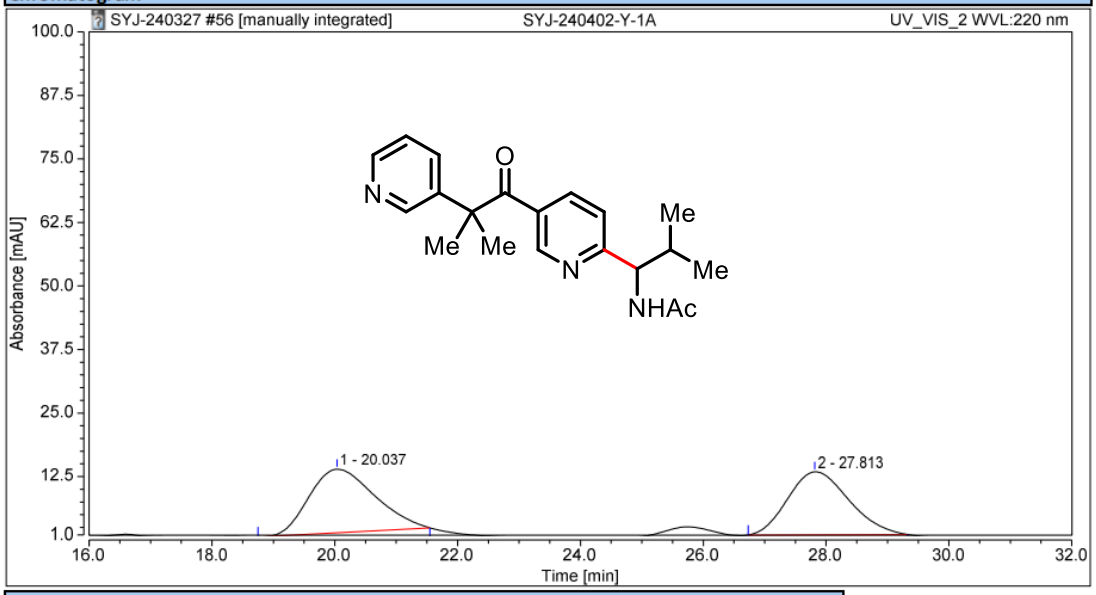
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	5.213	541.547	99.71	99.83	n.a.
2	8.883	1.560	0.29	0.17	n.a.
Total:		**543.107**	**100.00**	**100.00**	

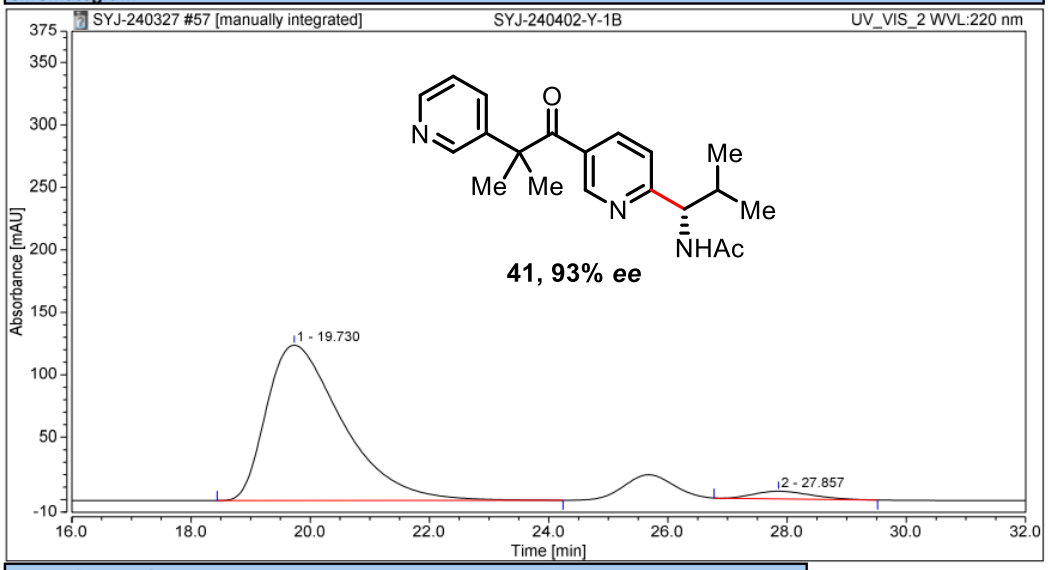
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	20.037	15.409	51.91	50.23	n.a.
2	27.813	14.276	48.09	49.77	n.a.
Total:		**29.684**	**100.00**	**100.00**	

Chromatogram

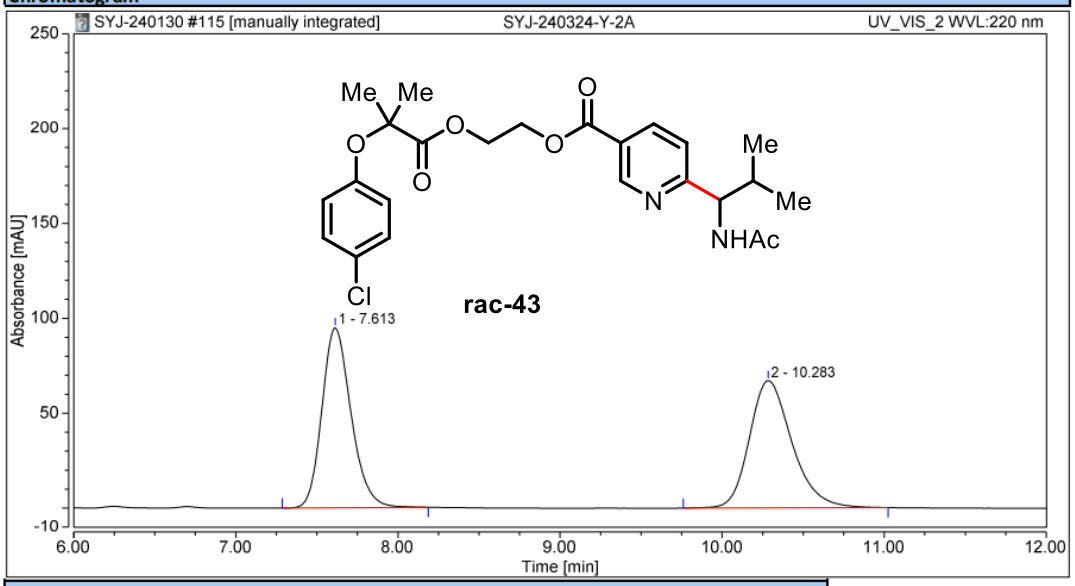


41, 93% *ee*

Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	19.730	183.779	96.46	95.34	n.a.
2	27.857	6.753	3.54	4.66	n.a.
Total:		**190.532**	**100.00**	**100.00**	

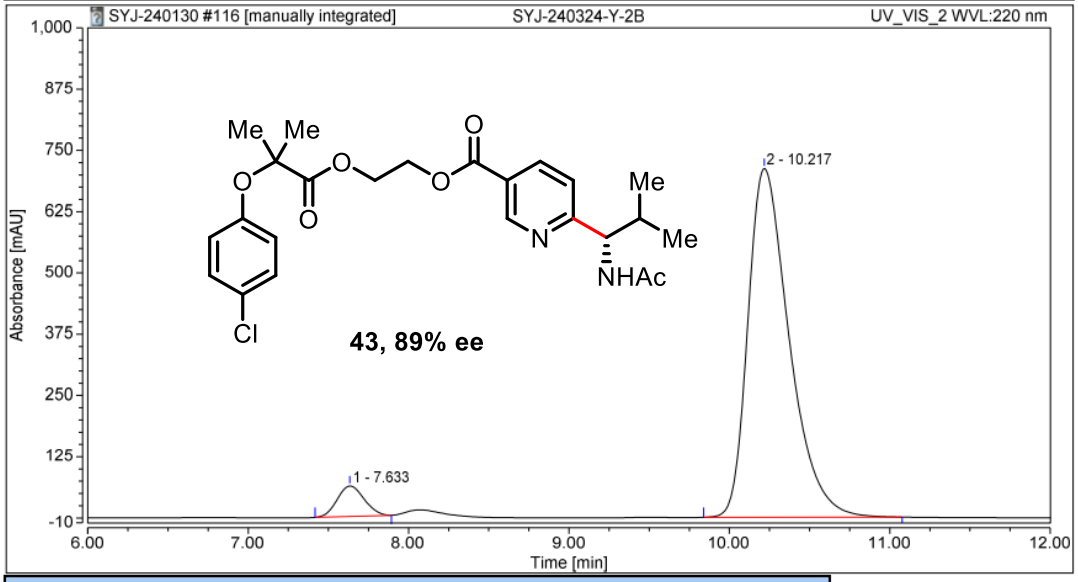
Chromatogram



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	7.613	19.752	49.15	58.57	n.a.
2	10.283	20.432	50.85	41.43	n.a.
Total:		**40.183**	**100.00**	**100.00**	

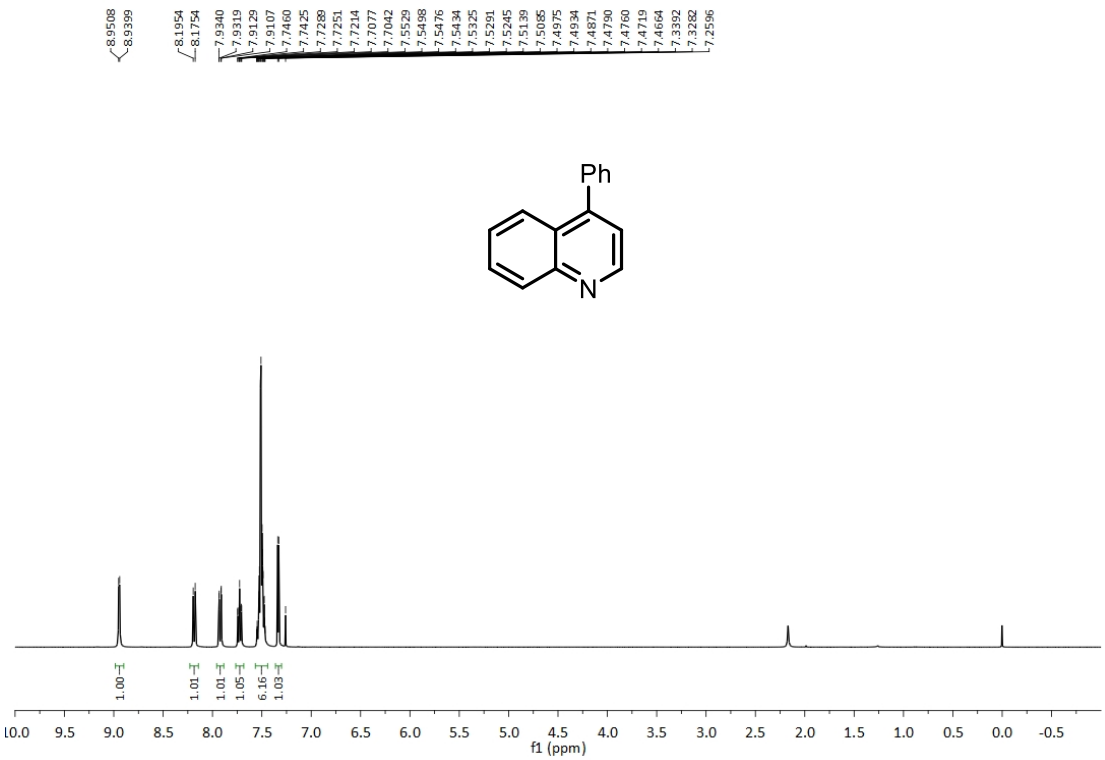
Chromatogram



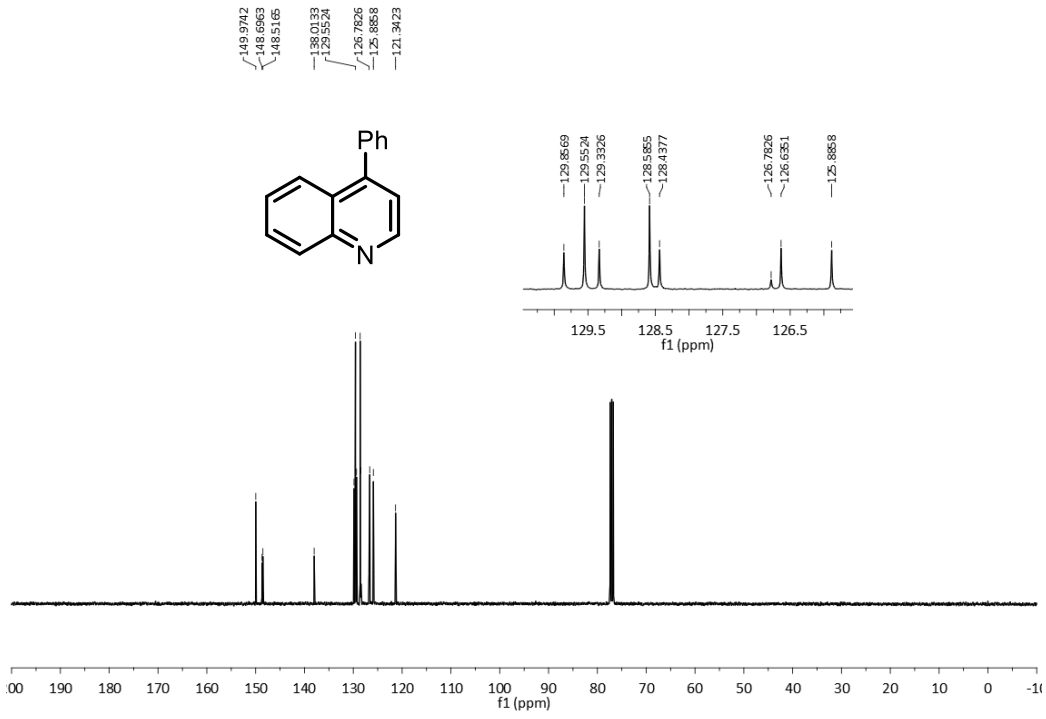
Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %	Relative Height %	Amount n.a.
1	7.633	12.102	5.40	8.06	n.a.
2	10.217	211.993	94.60	91.94	n.a.
Total:		**224.095**	**100.00**	**100.00**	

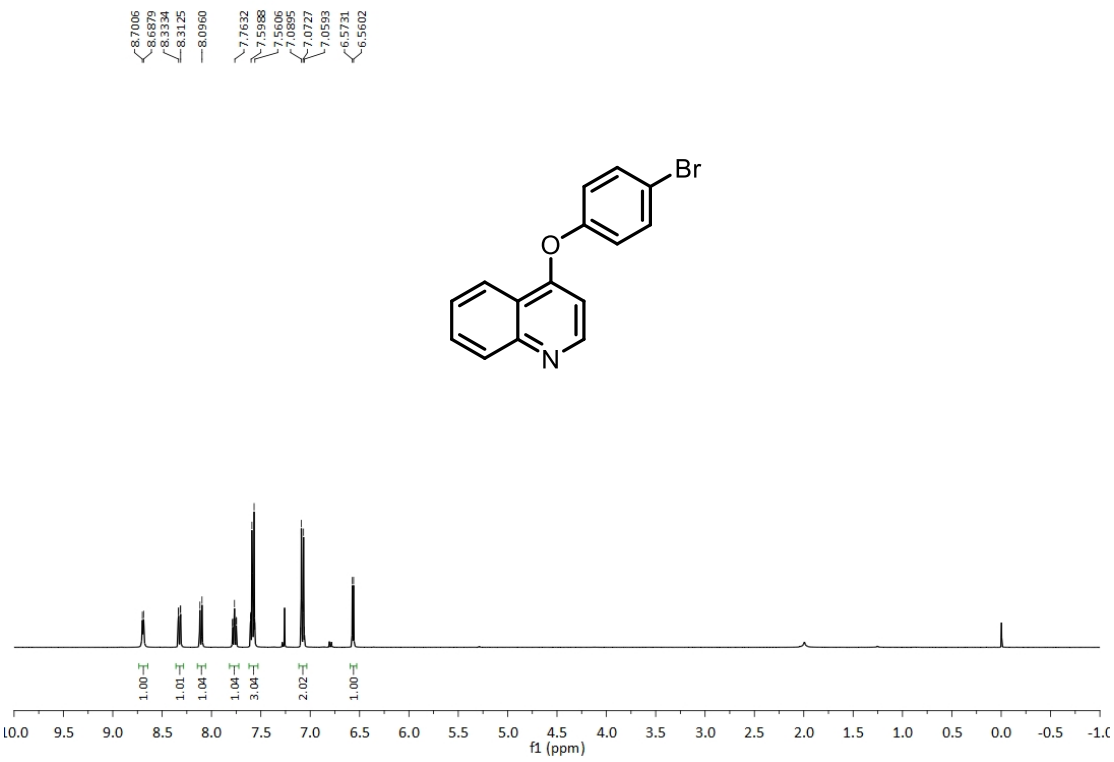
7. NMR spectral data for compounds



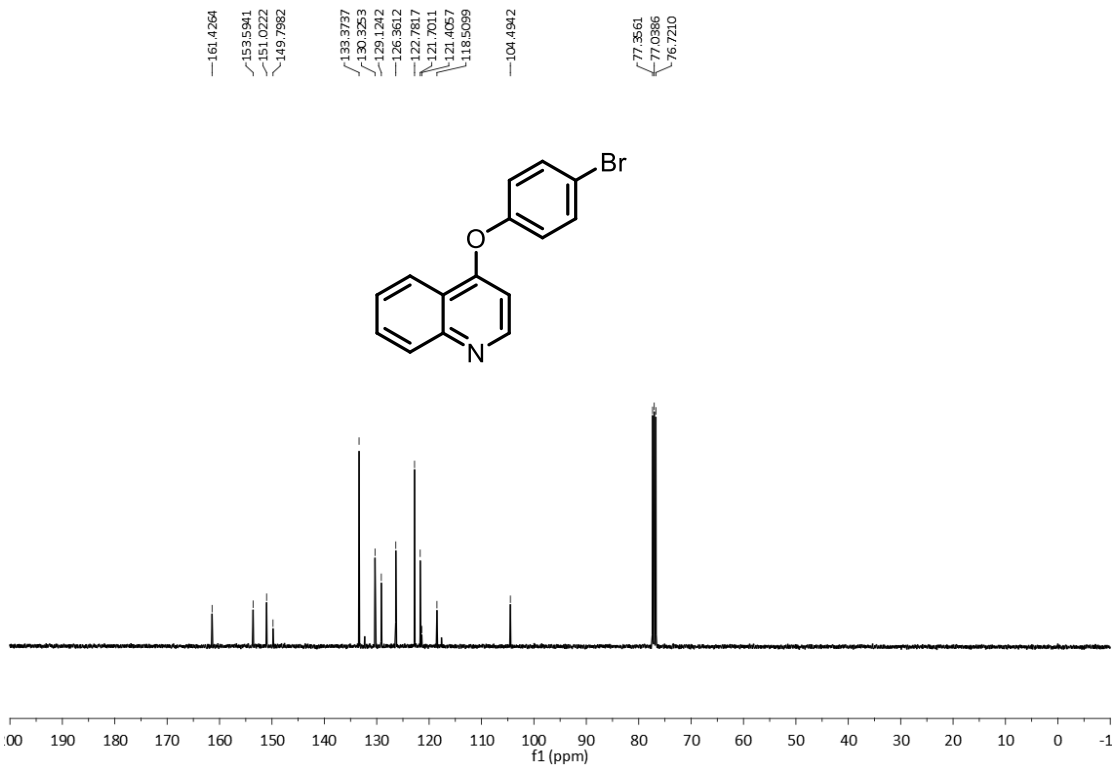
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **S-1**



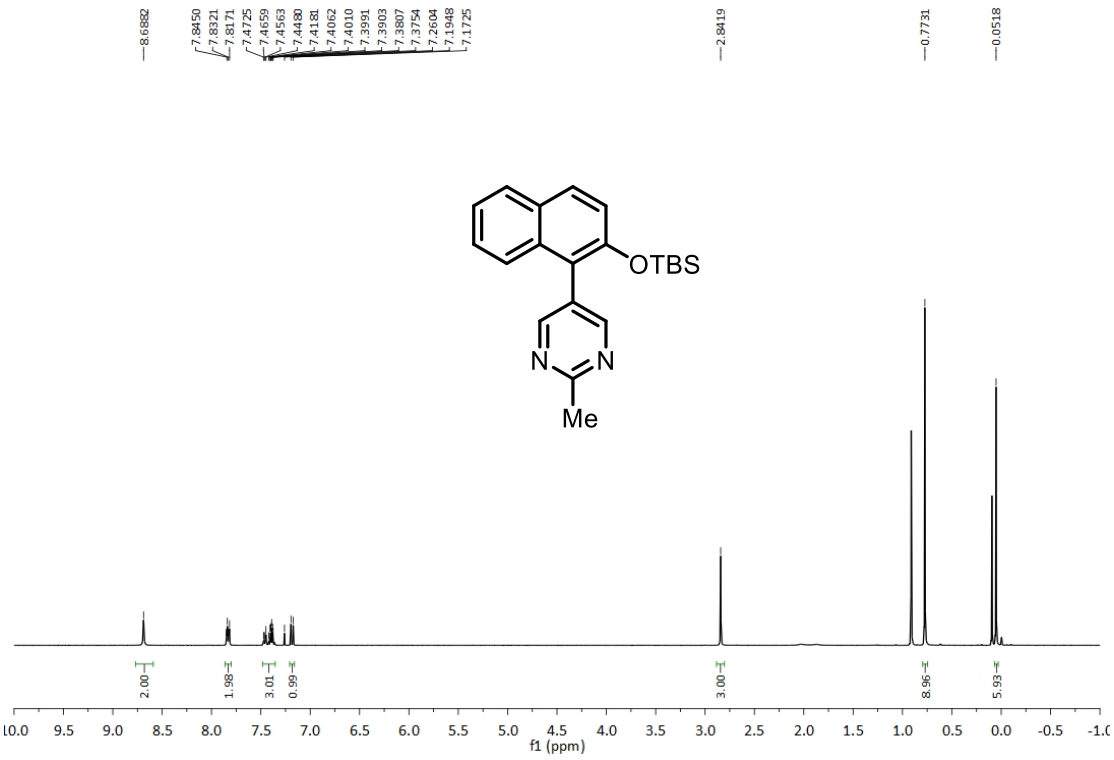
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **S-1**



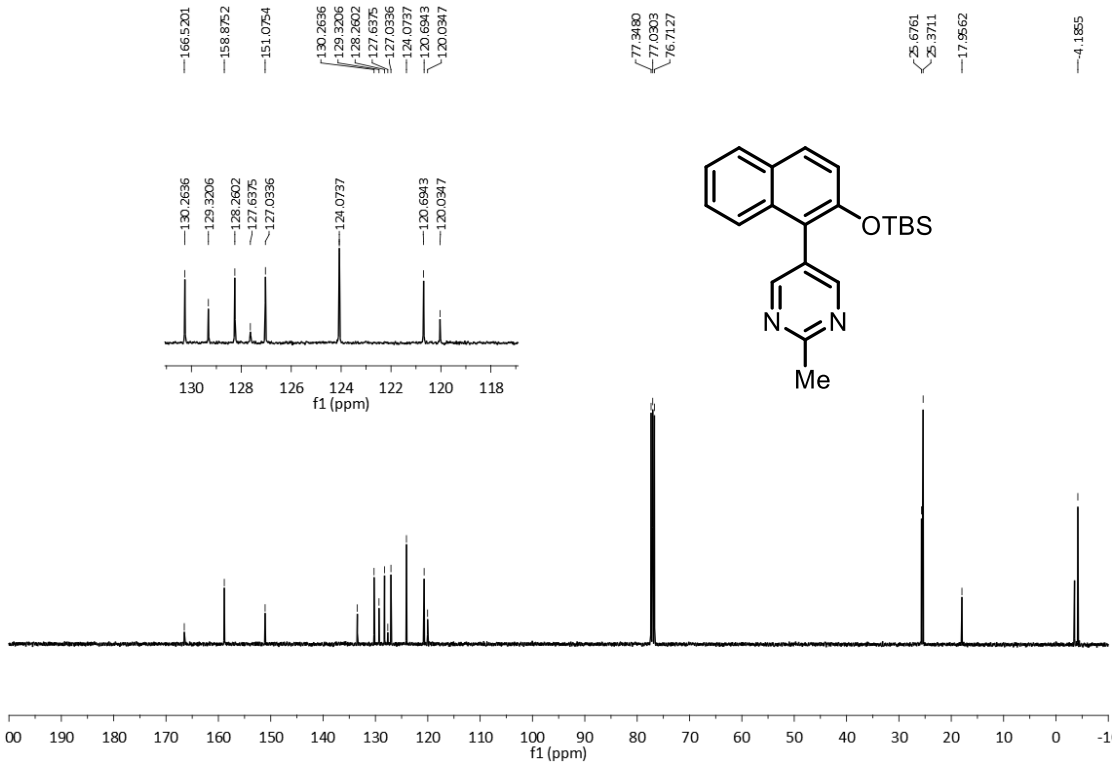
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **S-2**



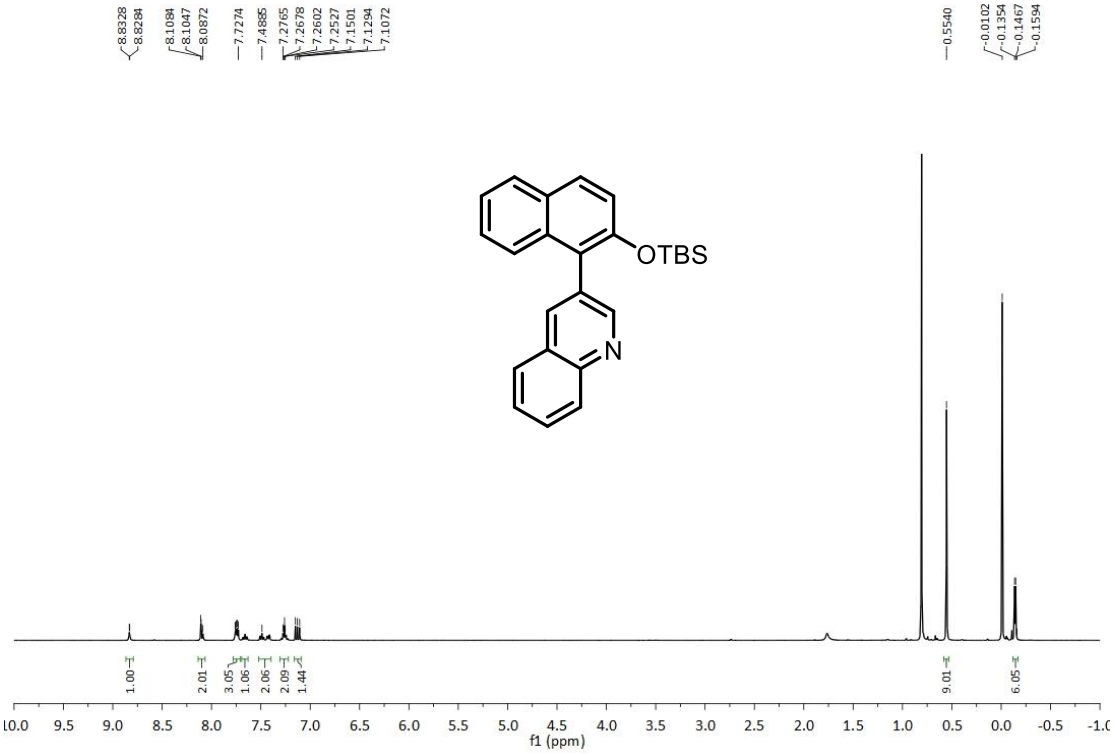
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **S-2**



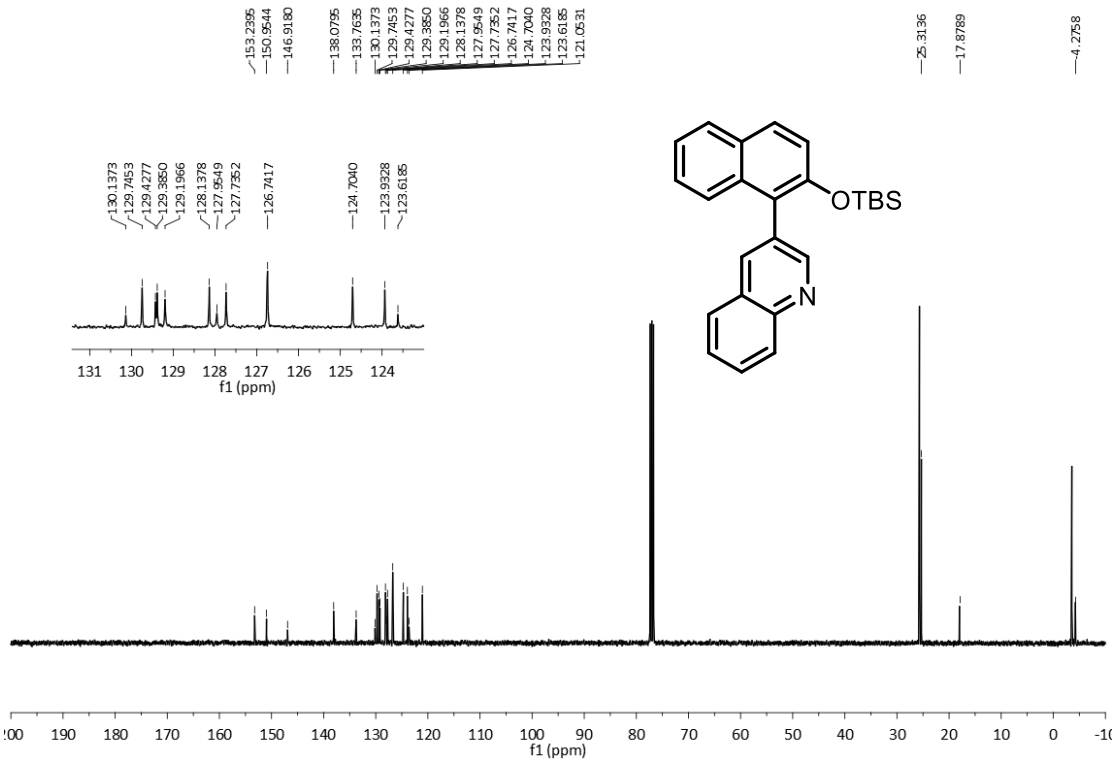
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **S-4**



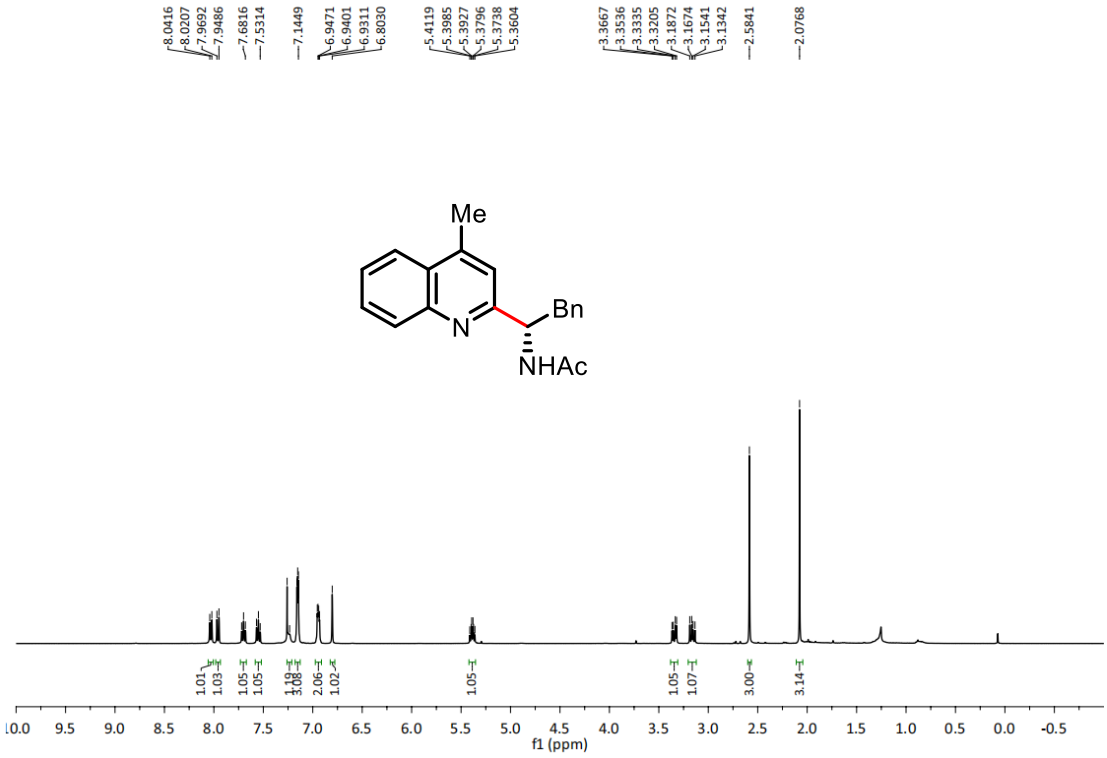
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **S-4**



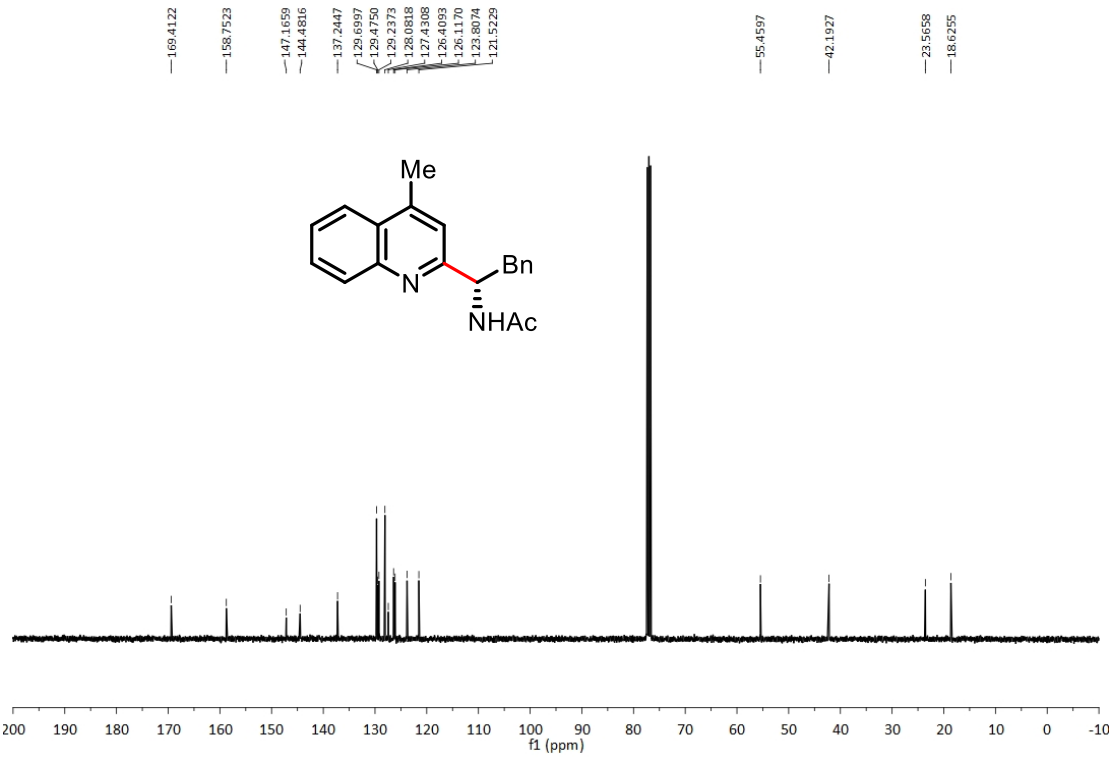
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **S-5**



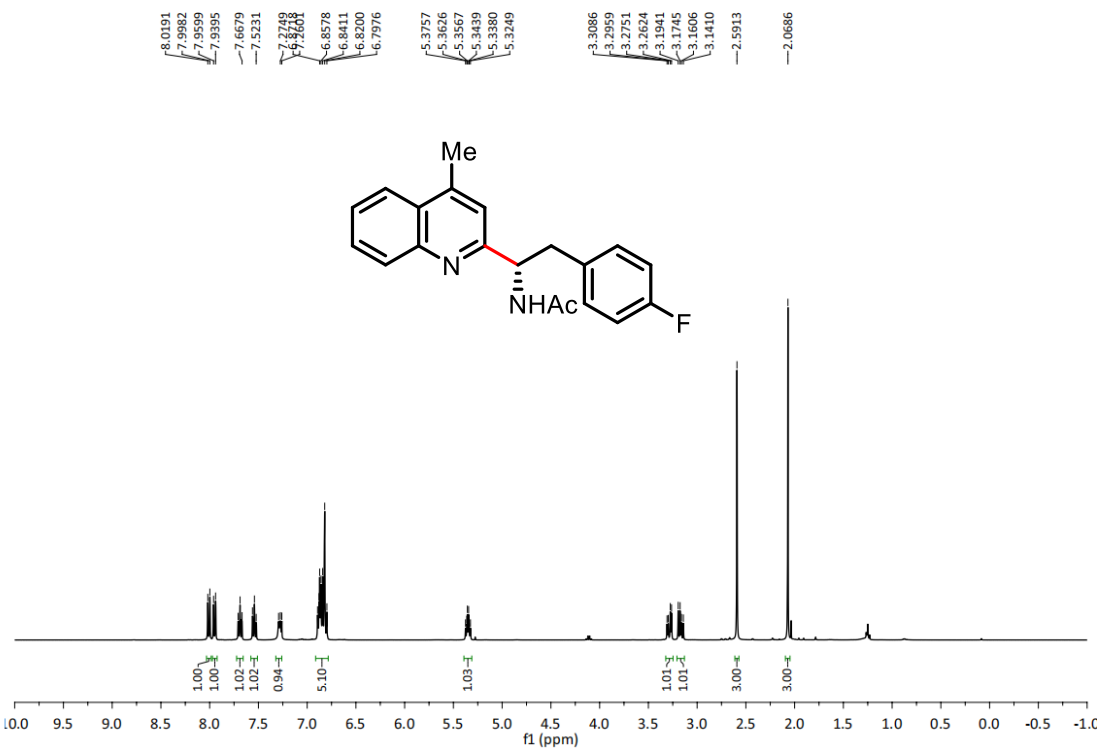
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **S-5**



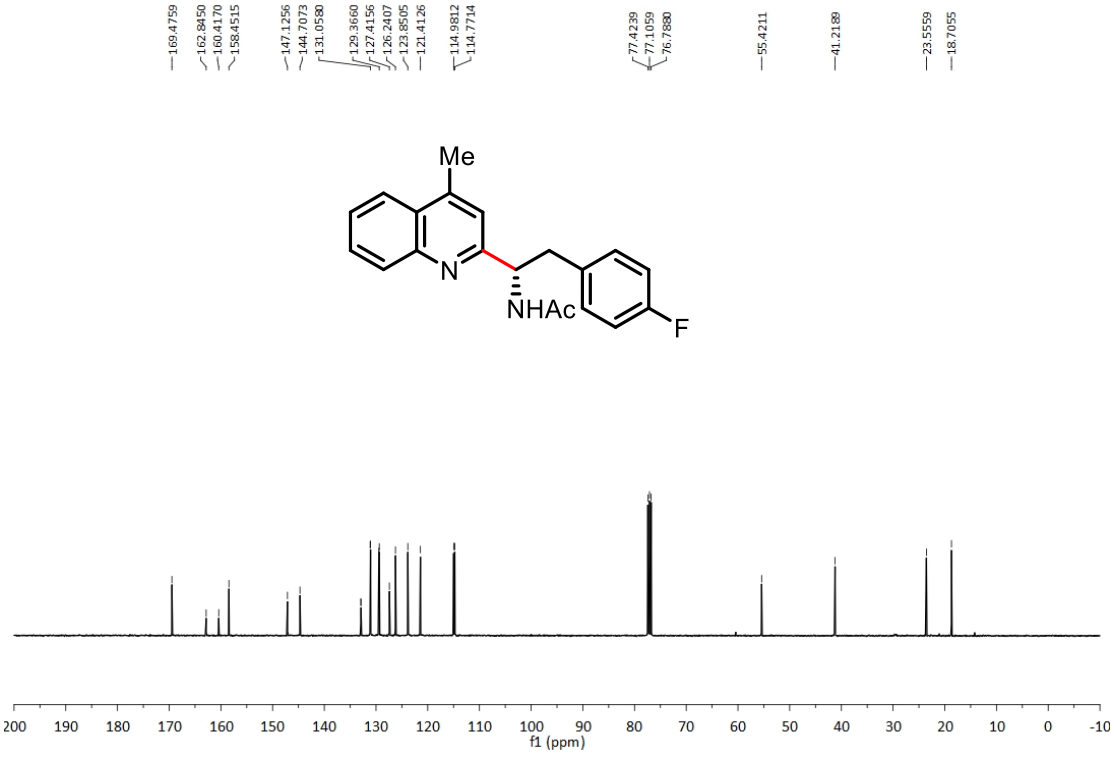
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3**



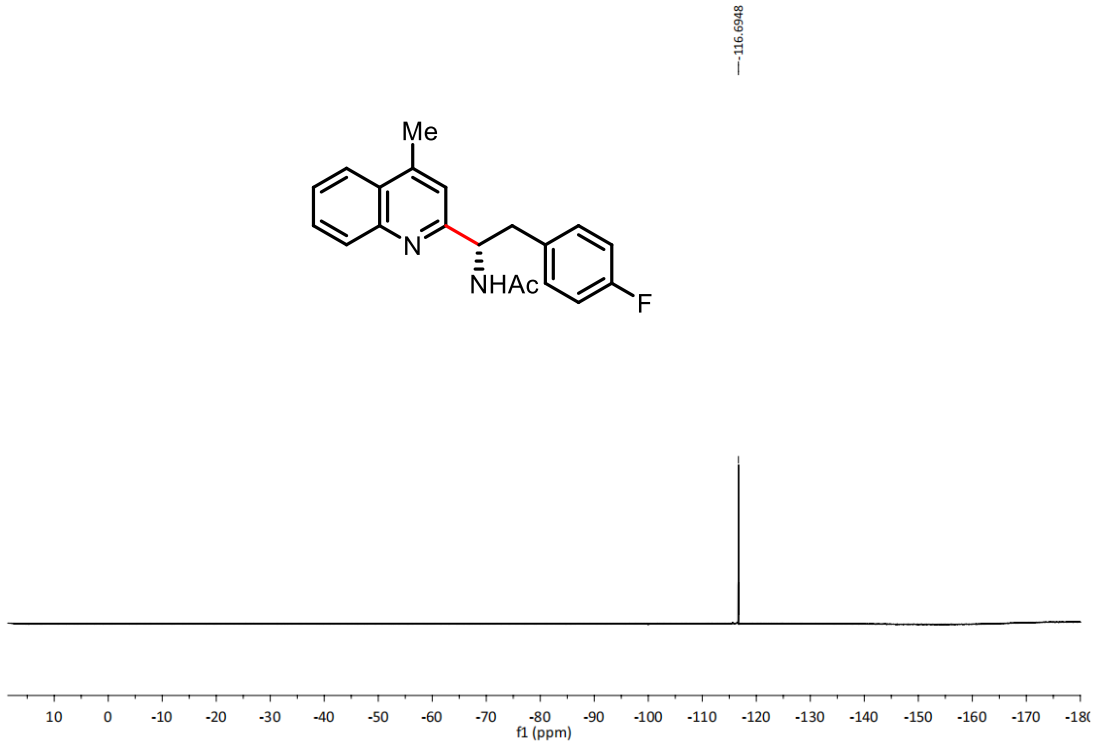
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3**



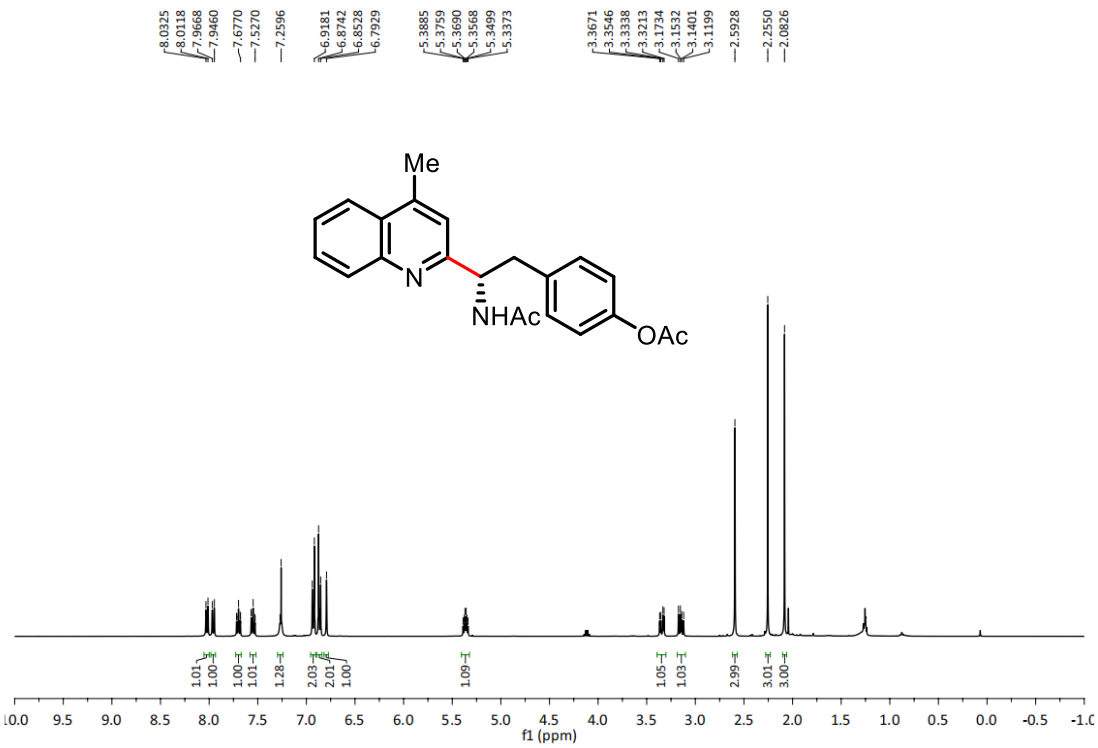
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4**



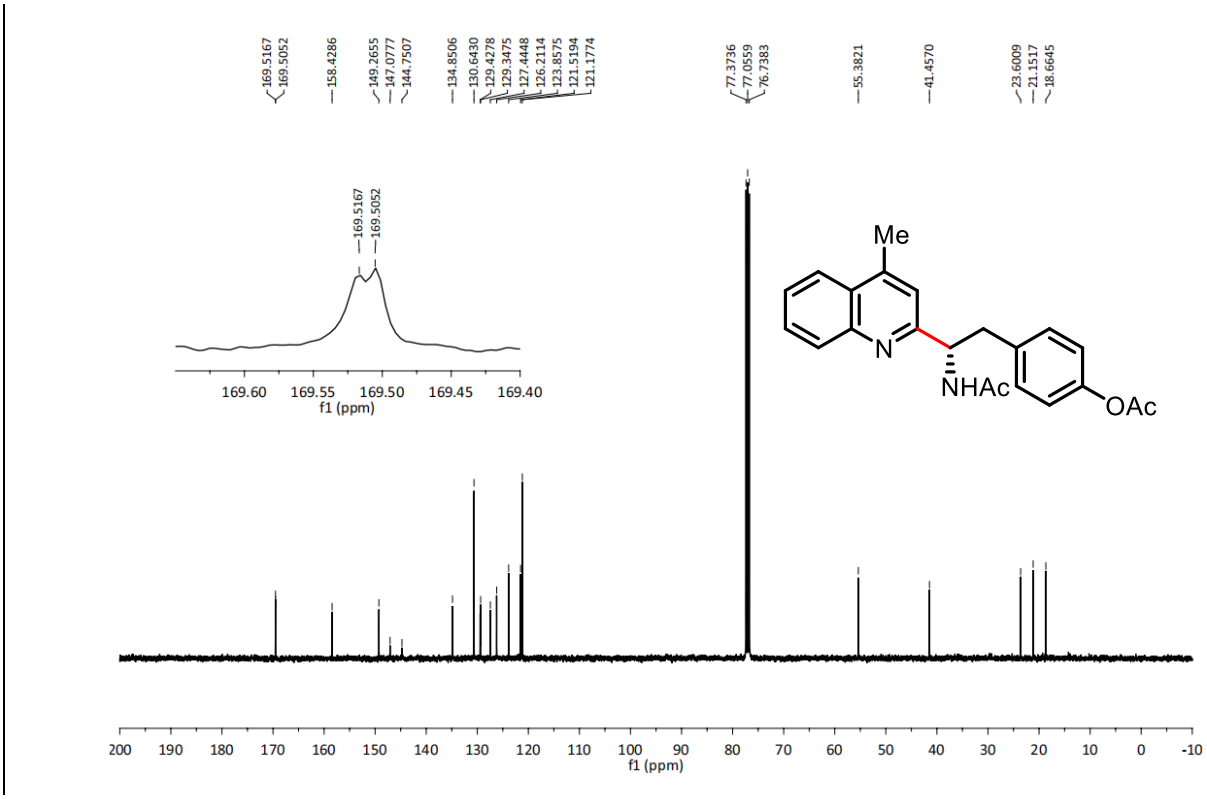
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4**



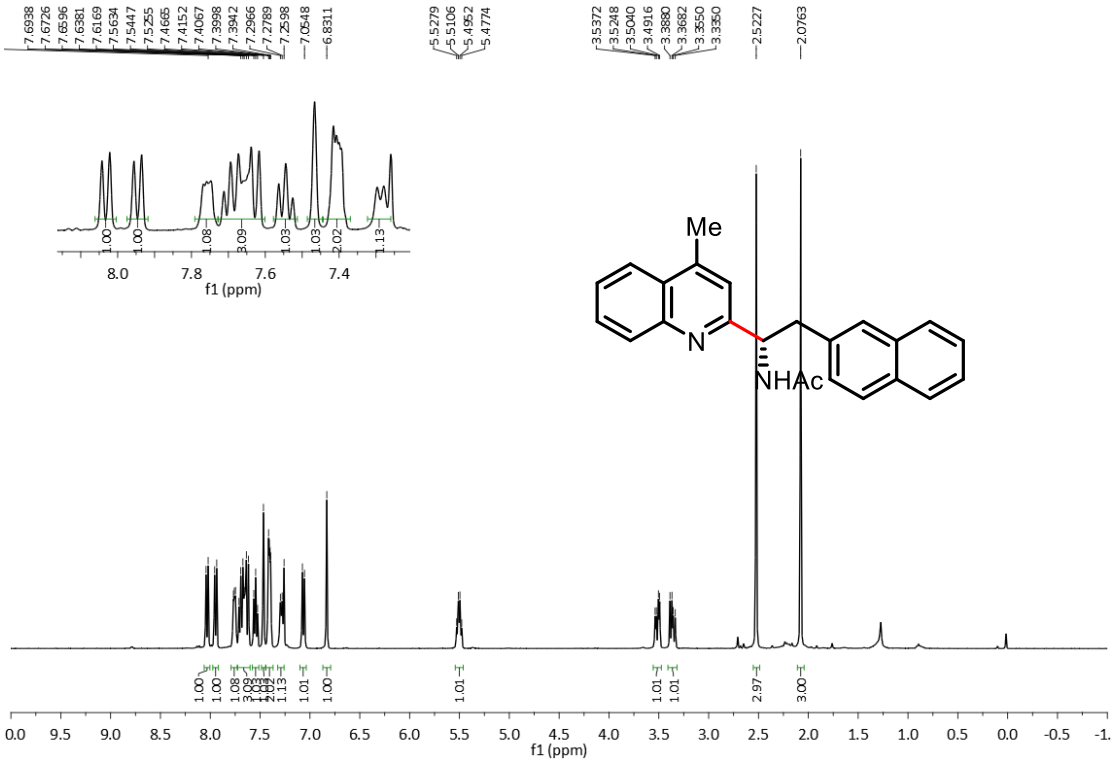
^{19}F NMR (100 MHz, $CDCl_3$) spectrum of compound **4**



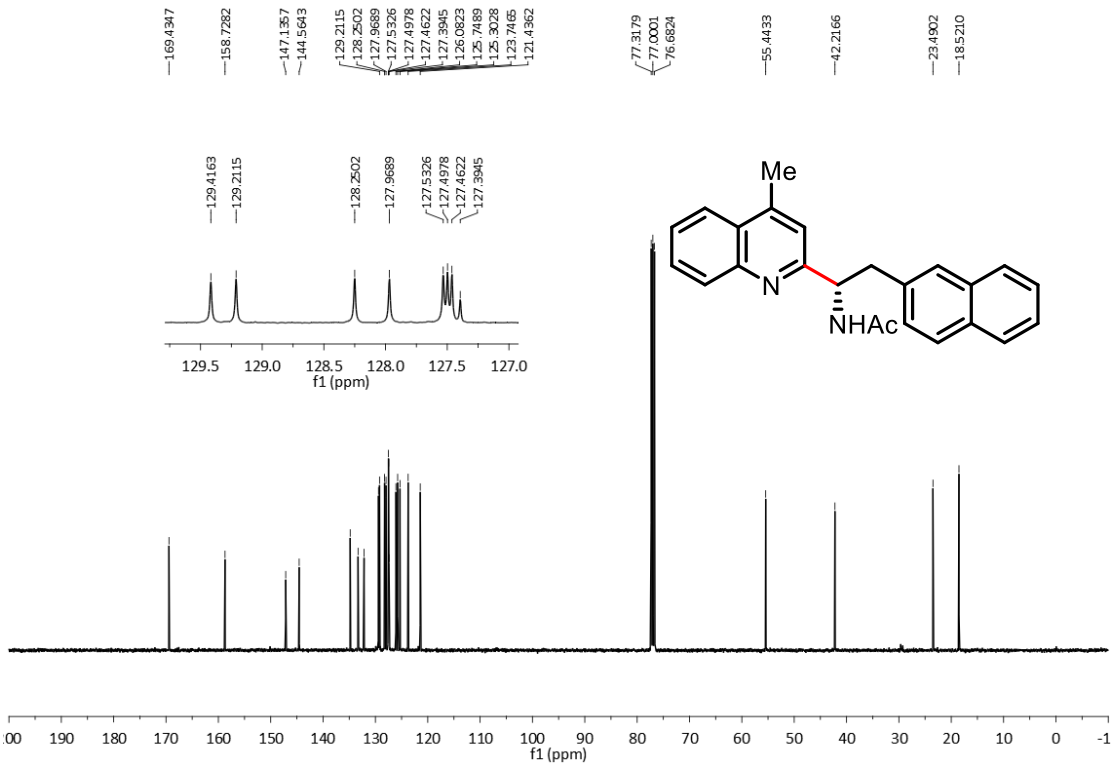
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5**



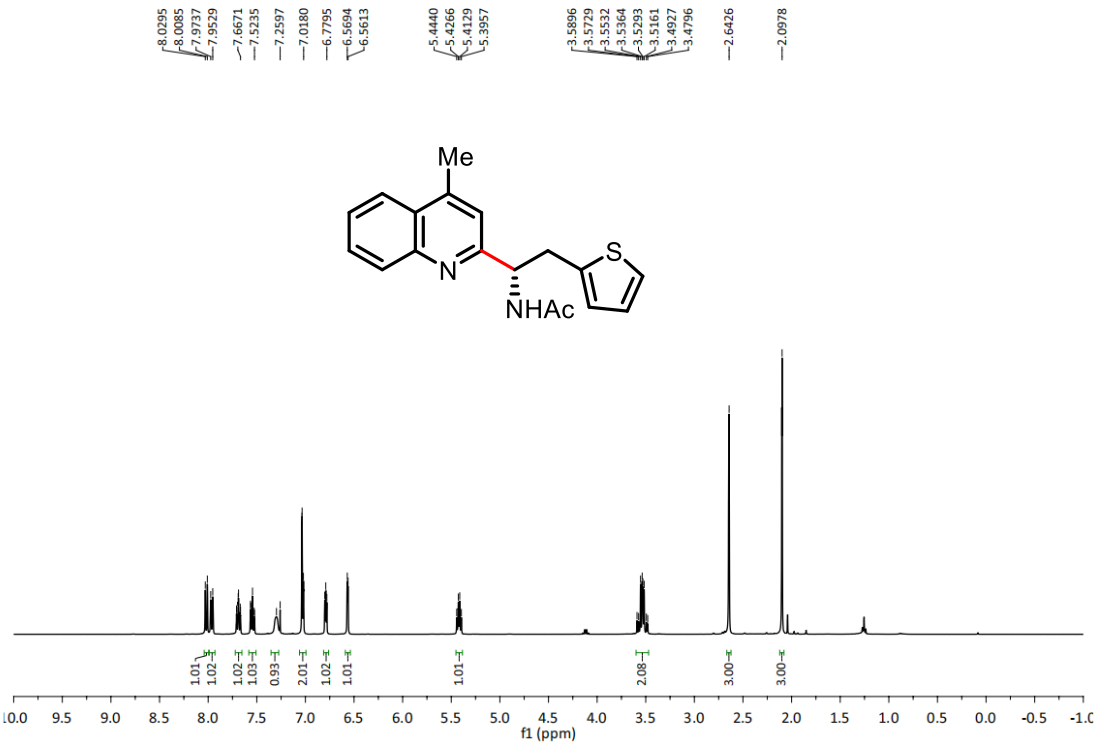
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5**



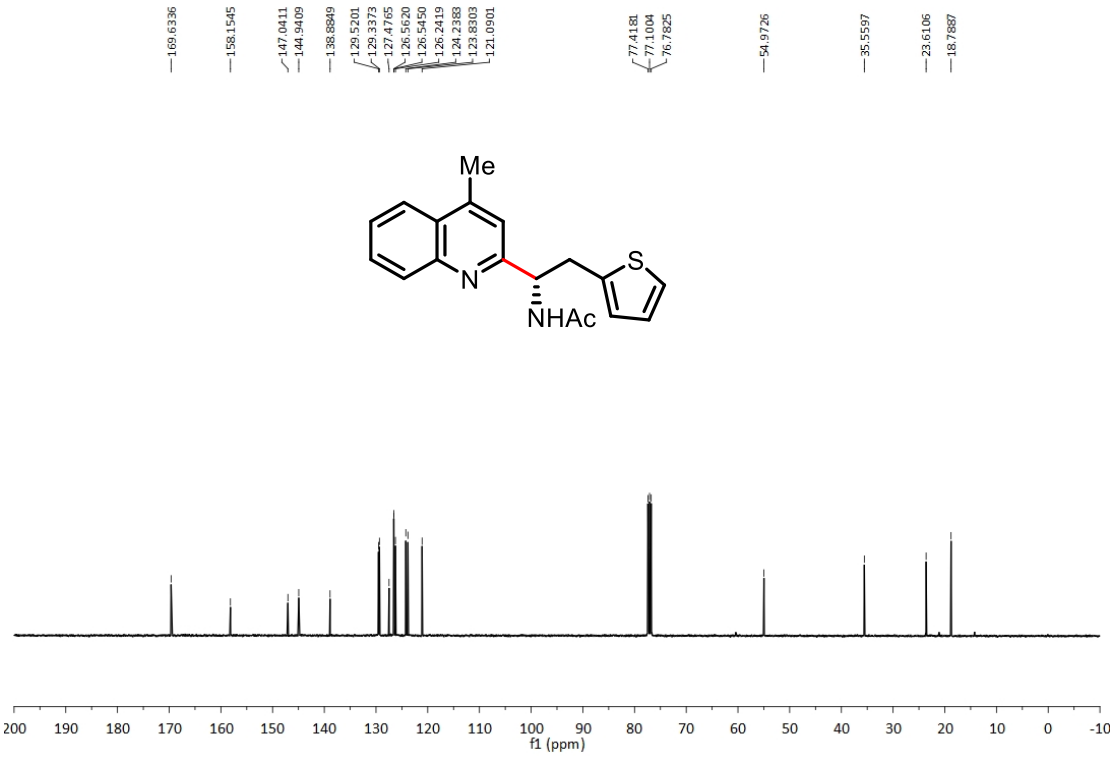
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6**



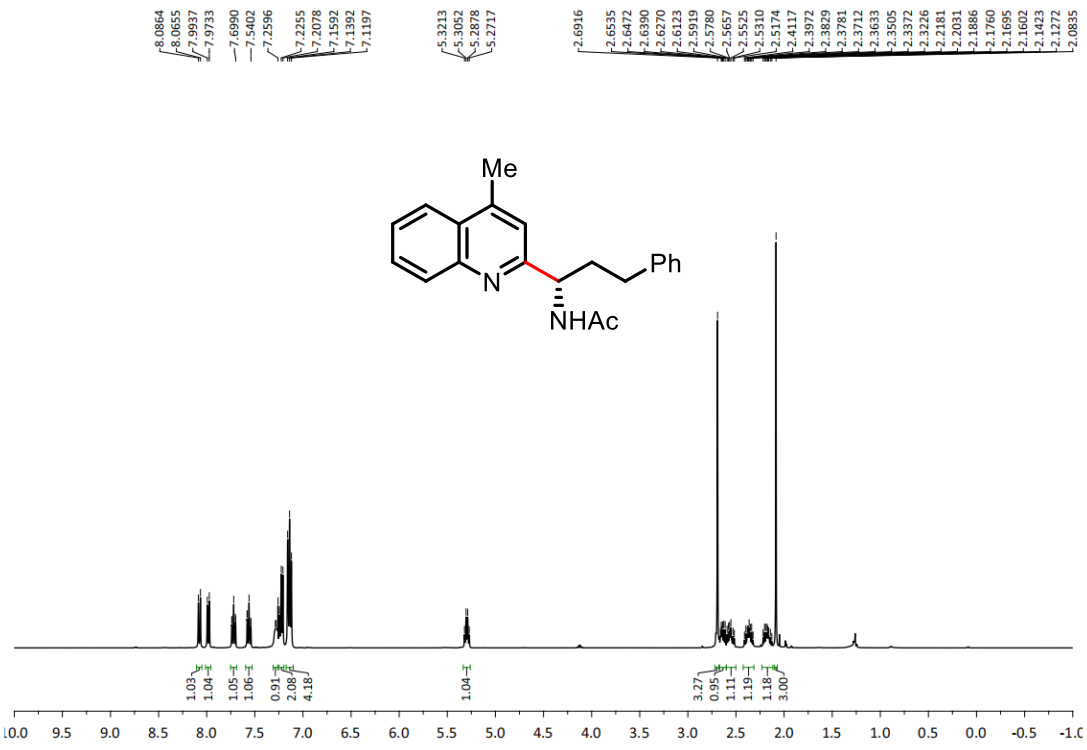
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **6**



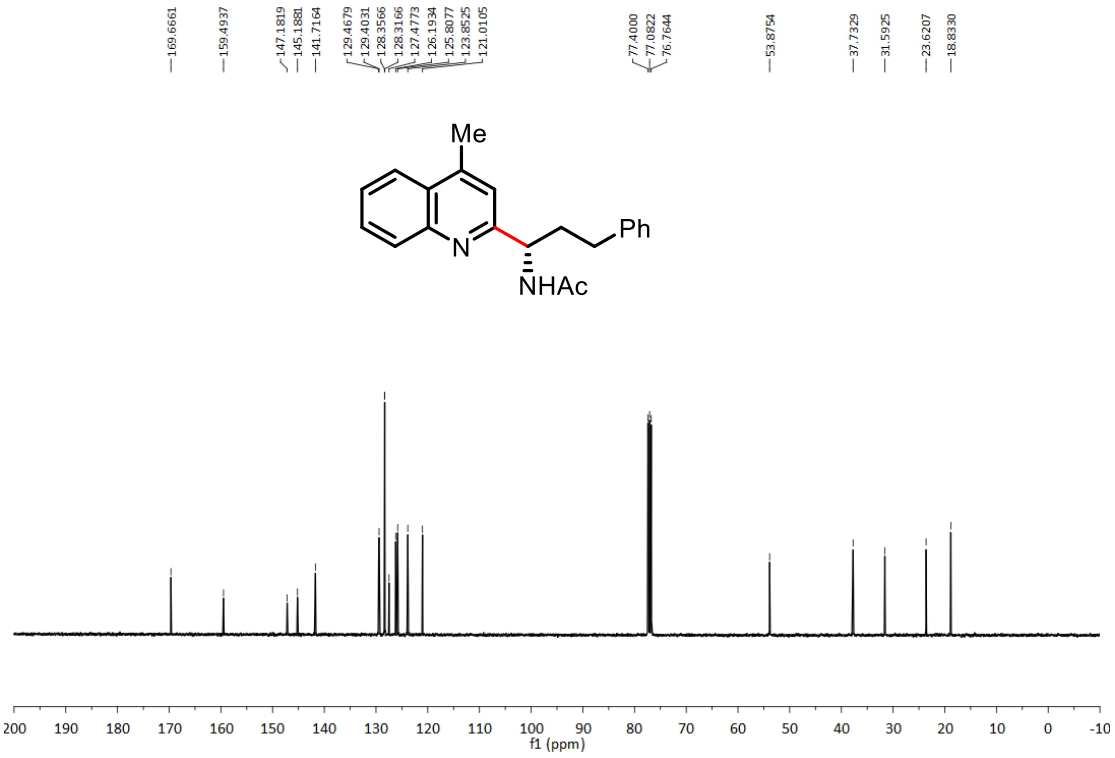
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **7**



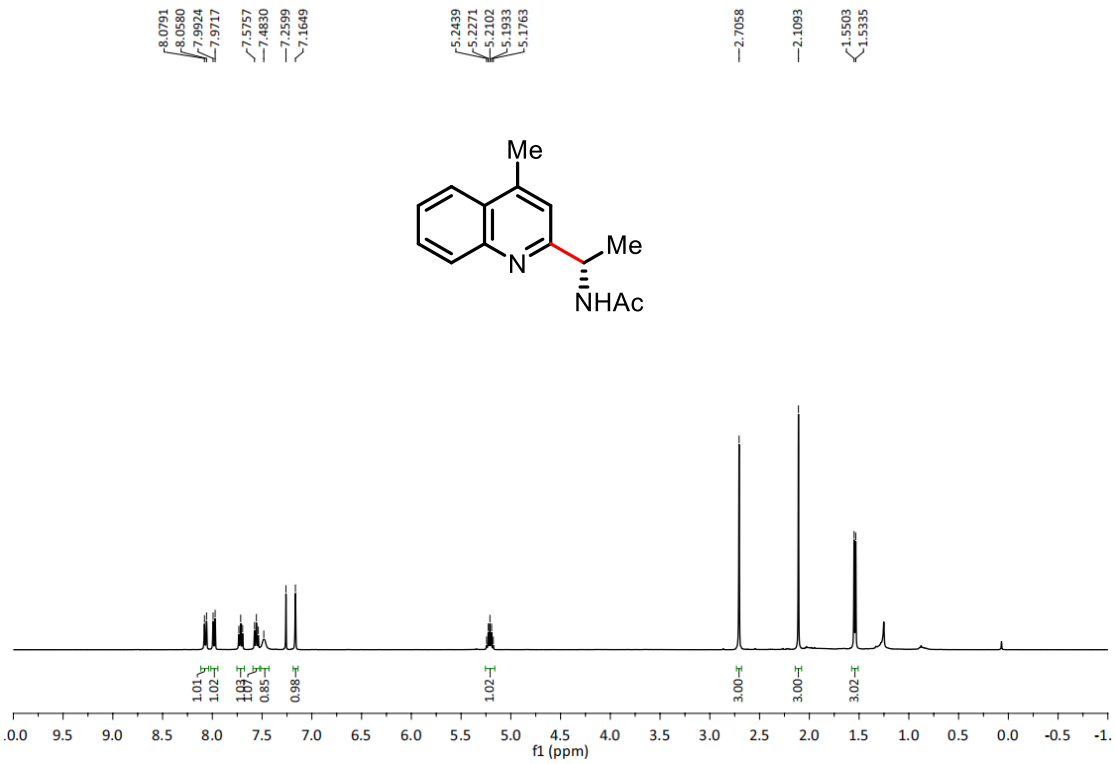
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **7**



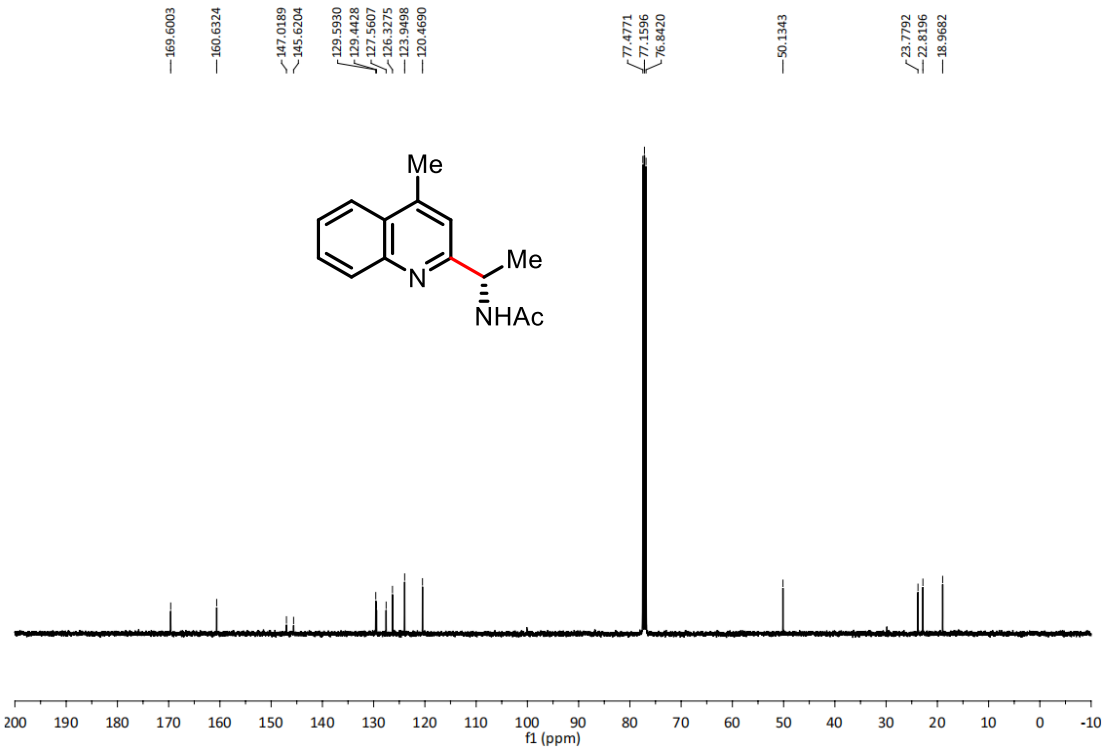
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **8**



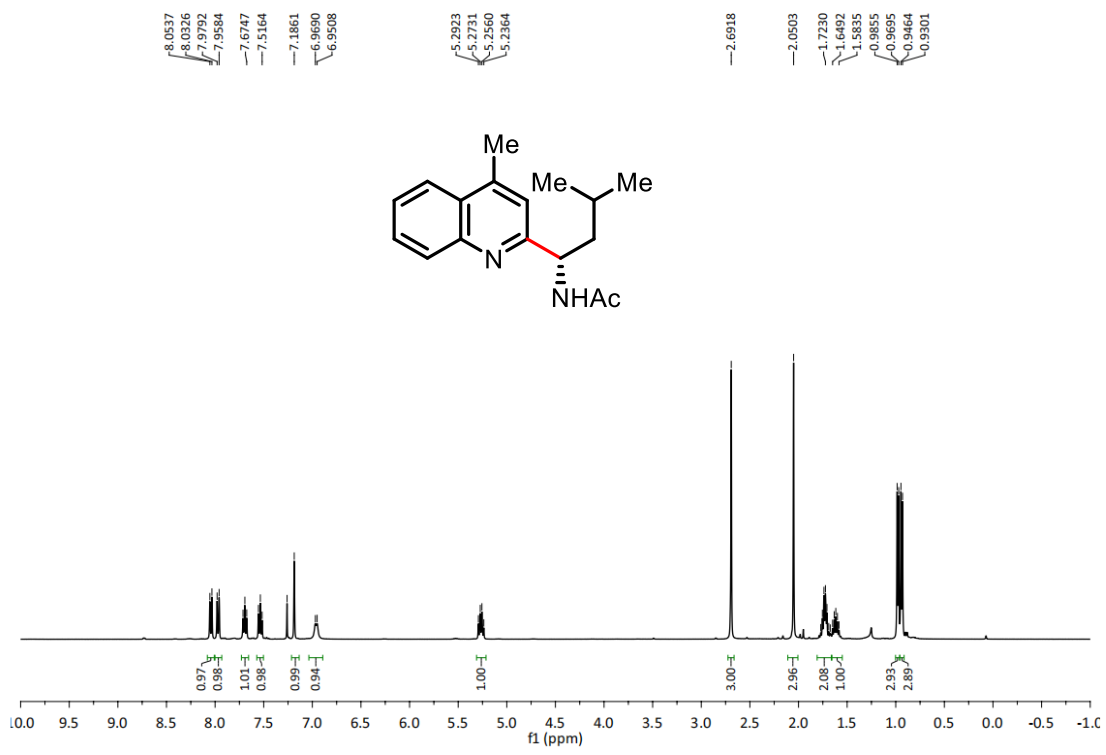
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **8**



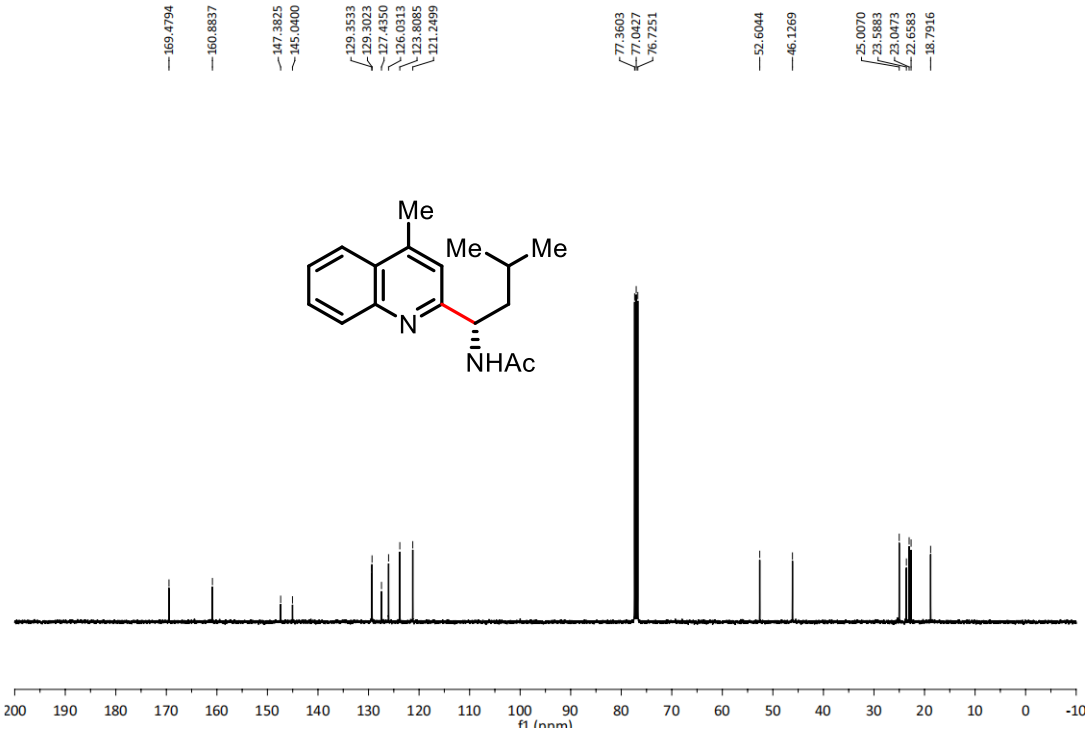
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **9**



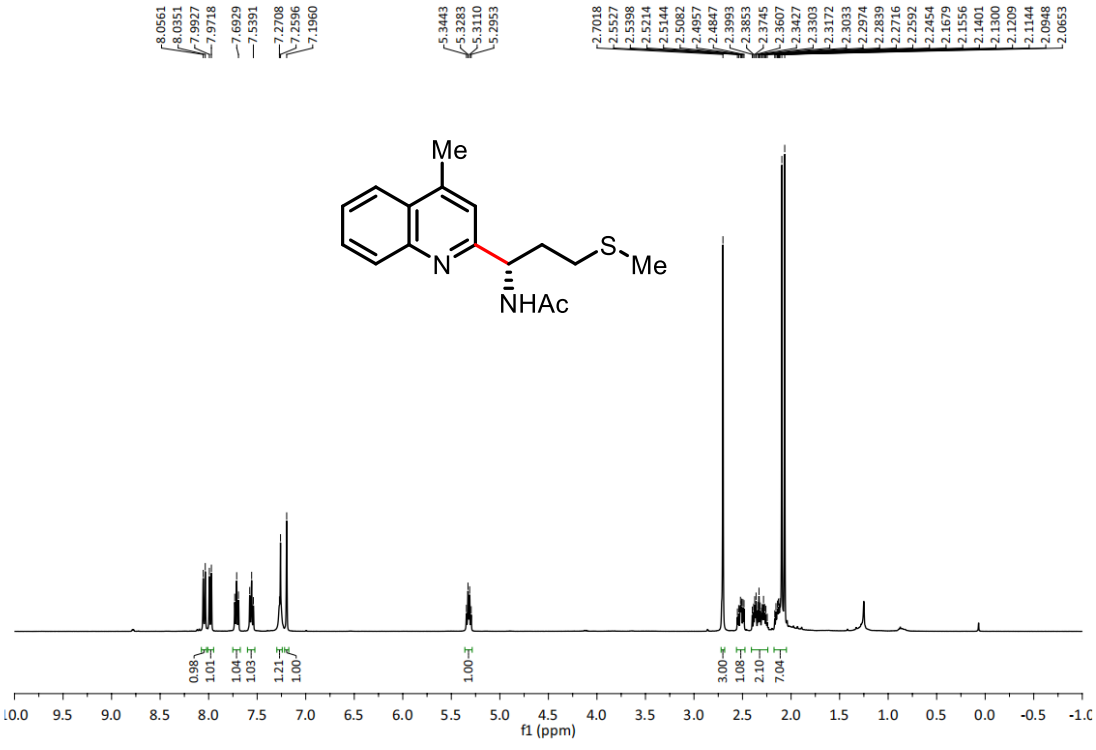
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **9**



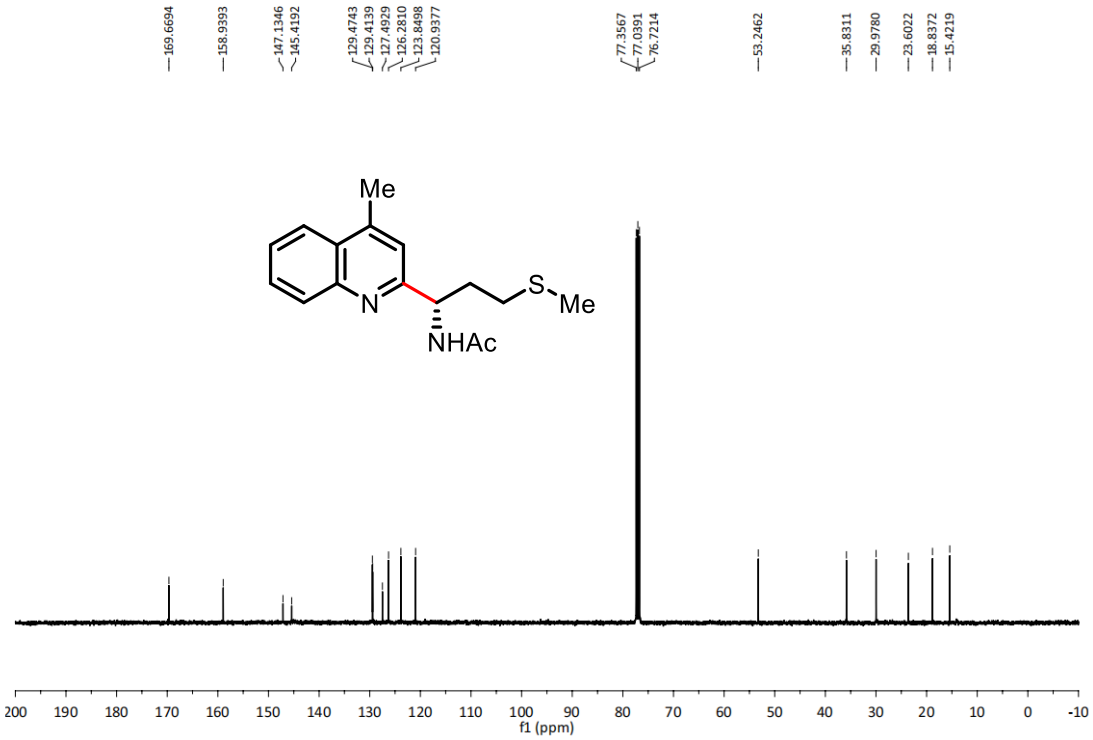
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **10**



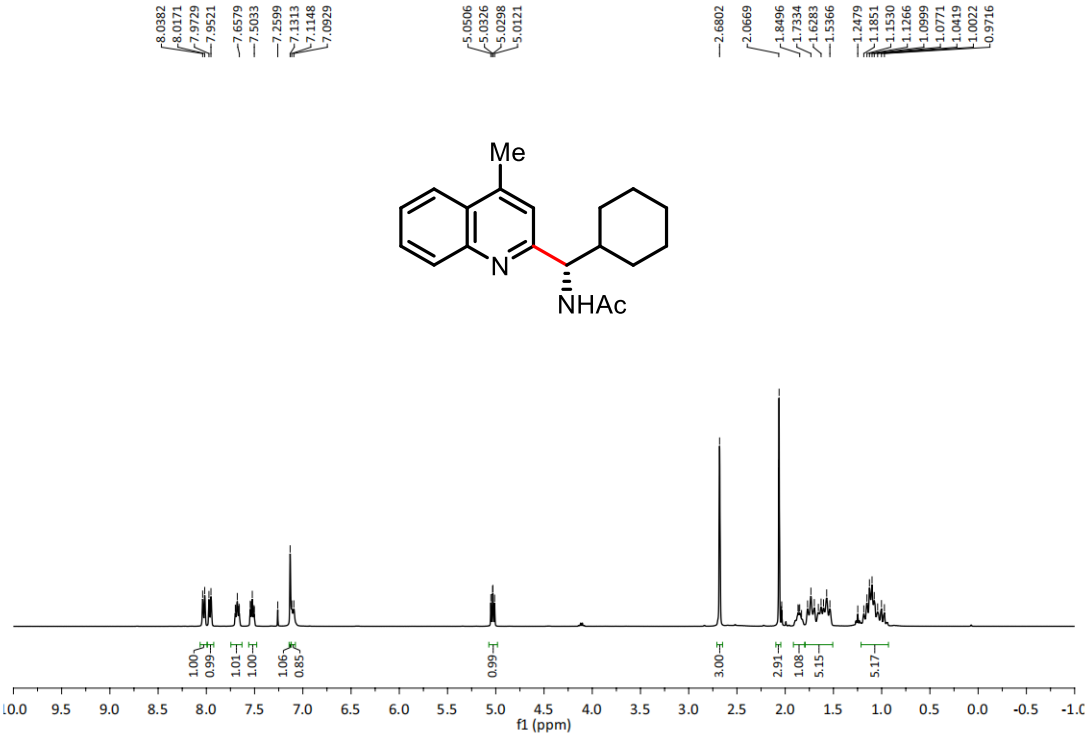
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **10**



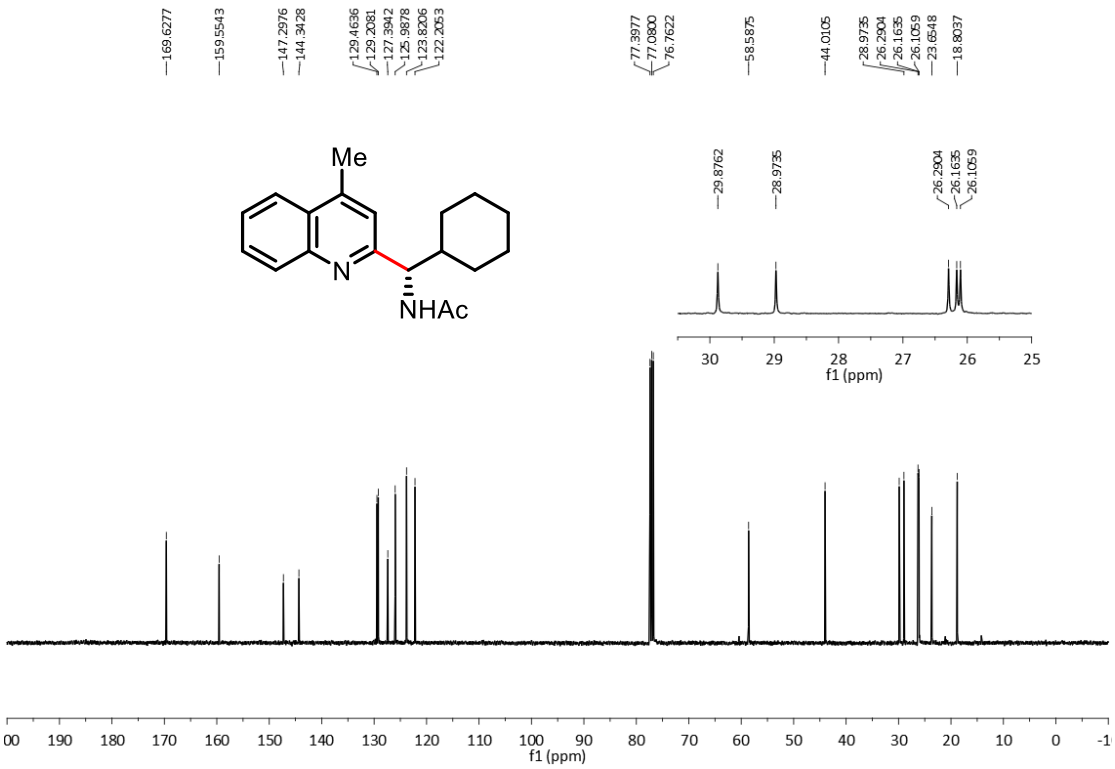
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **11**



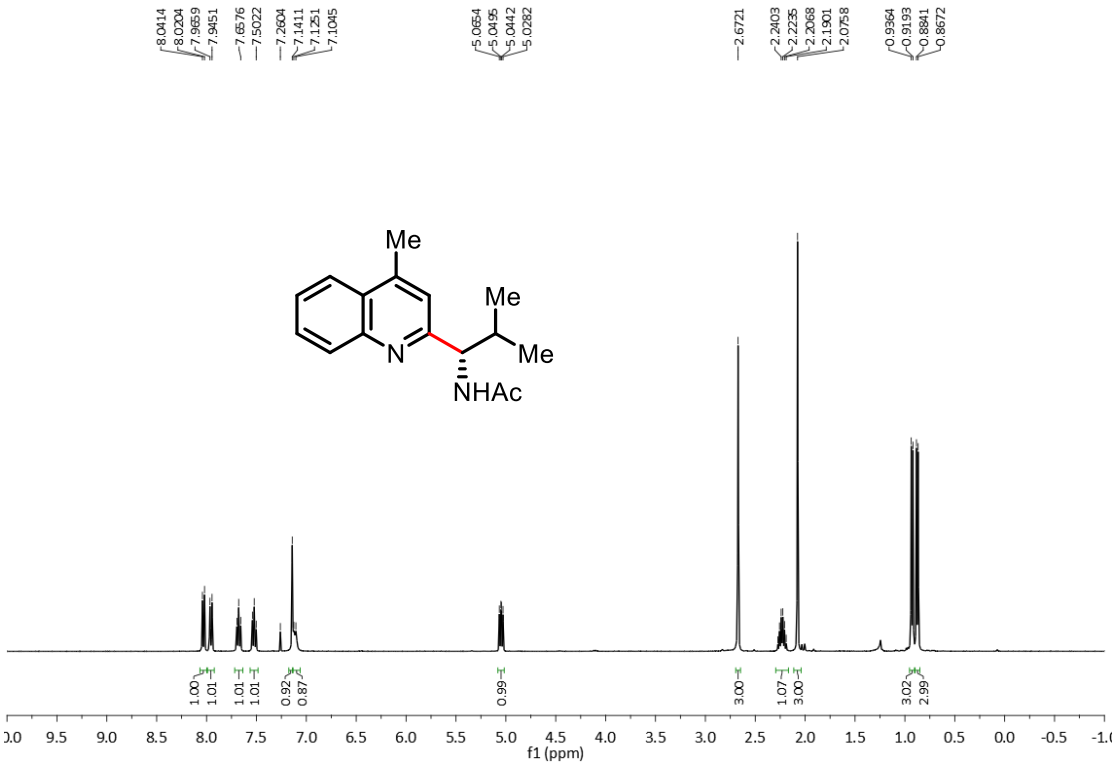
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **11**



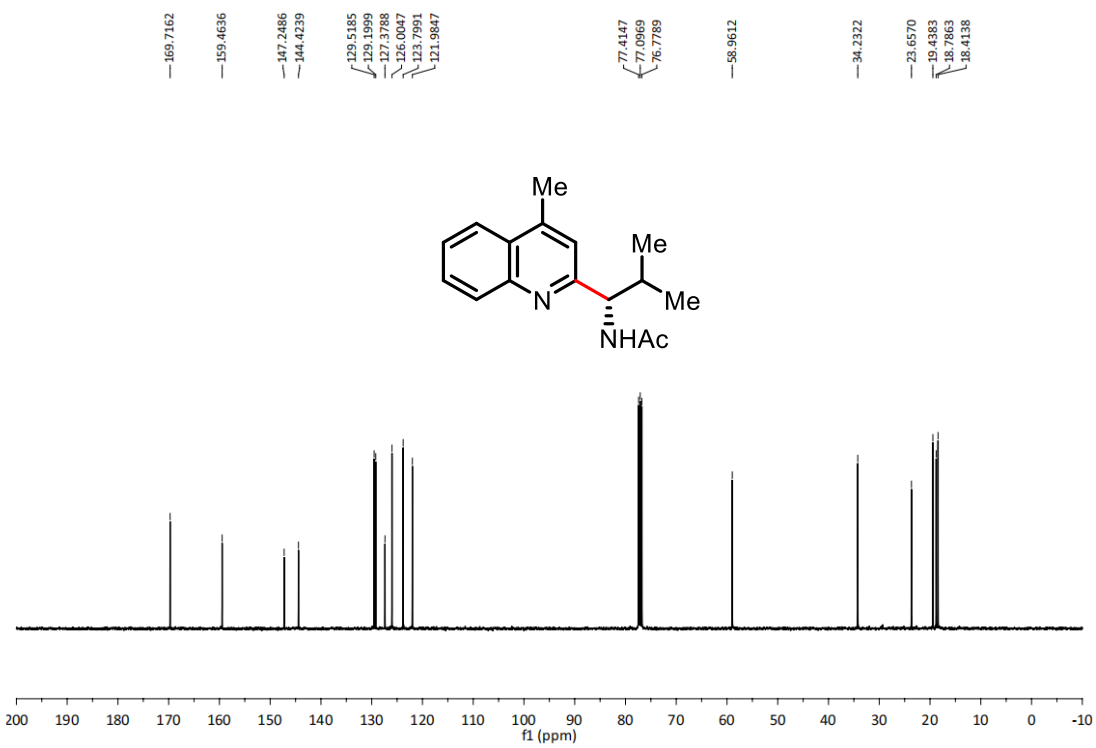
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **12**



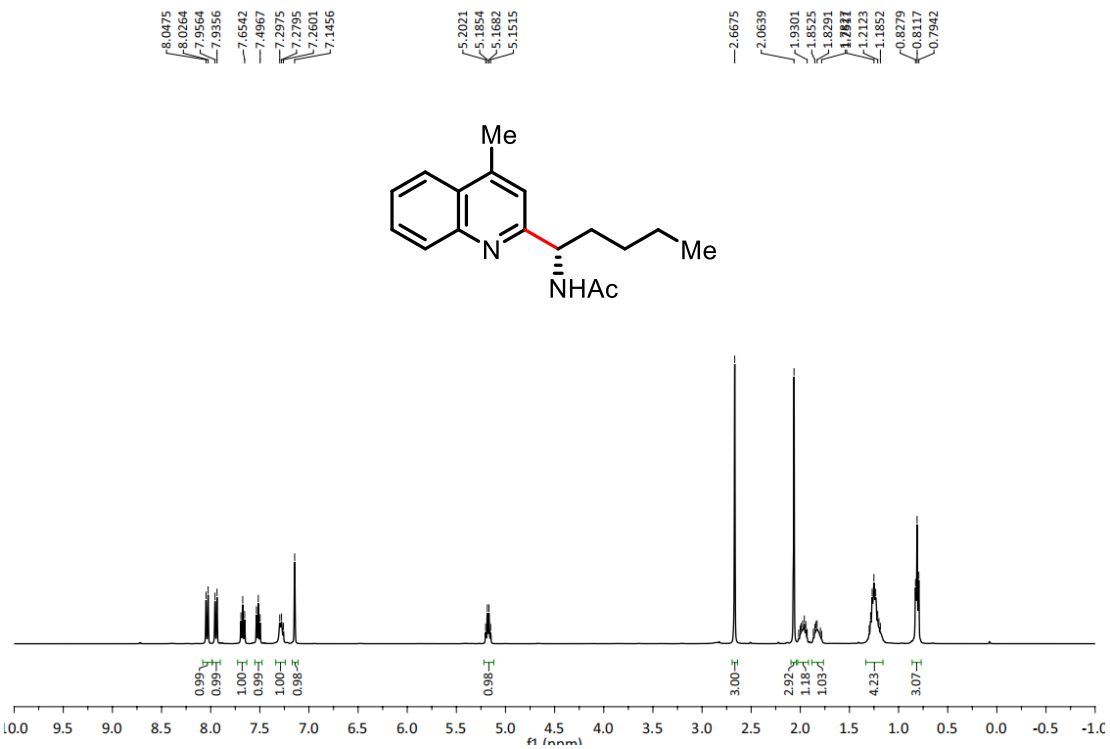
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **12**



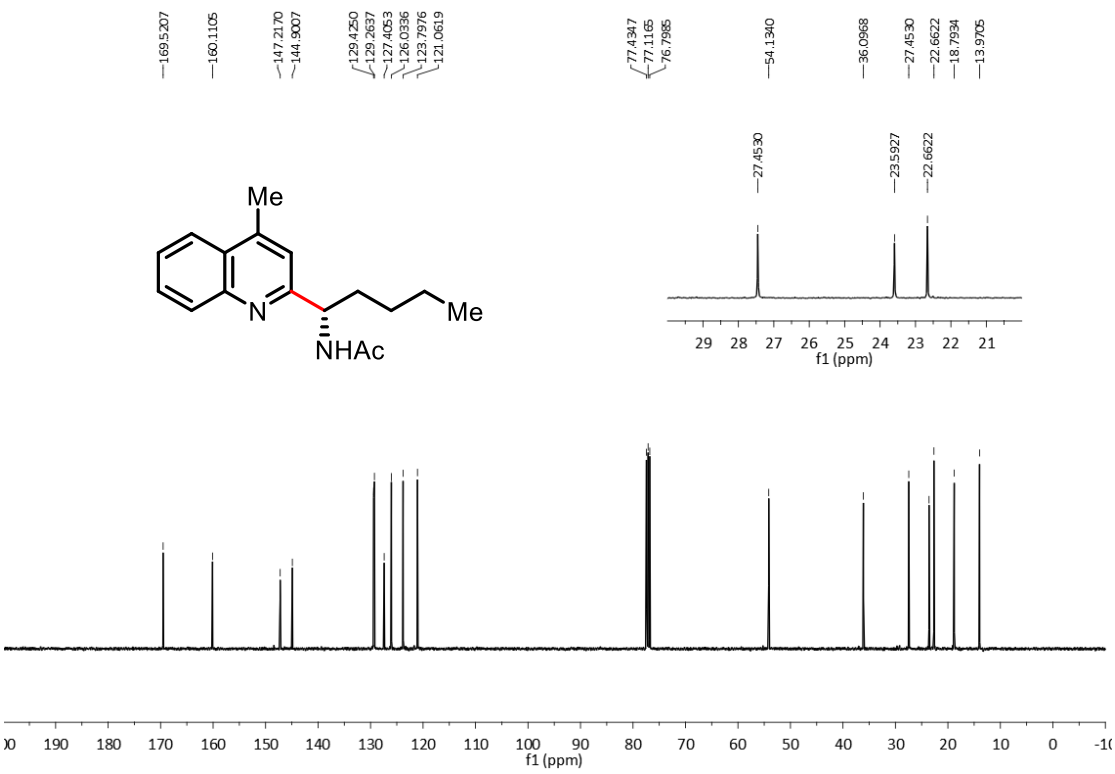
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **13**



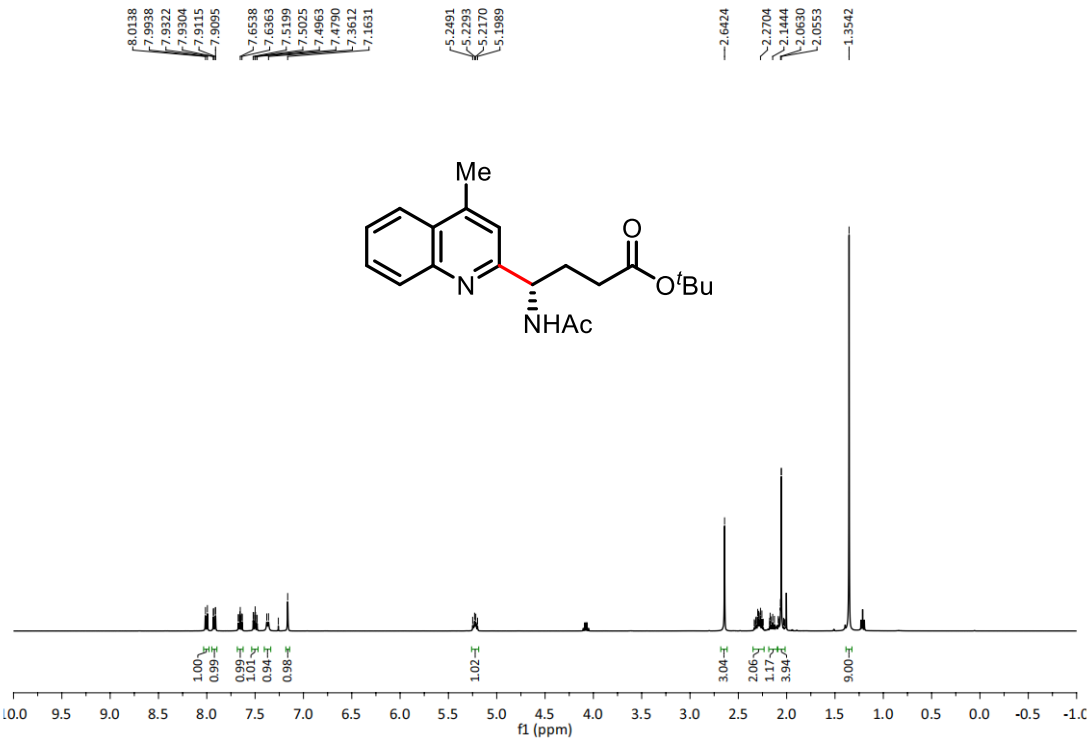
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **13**



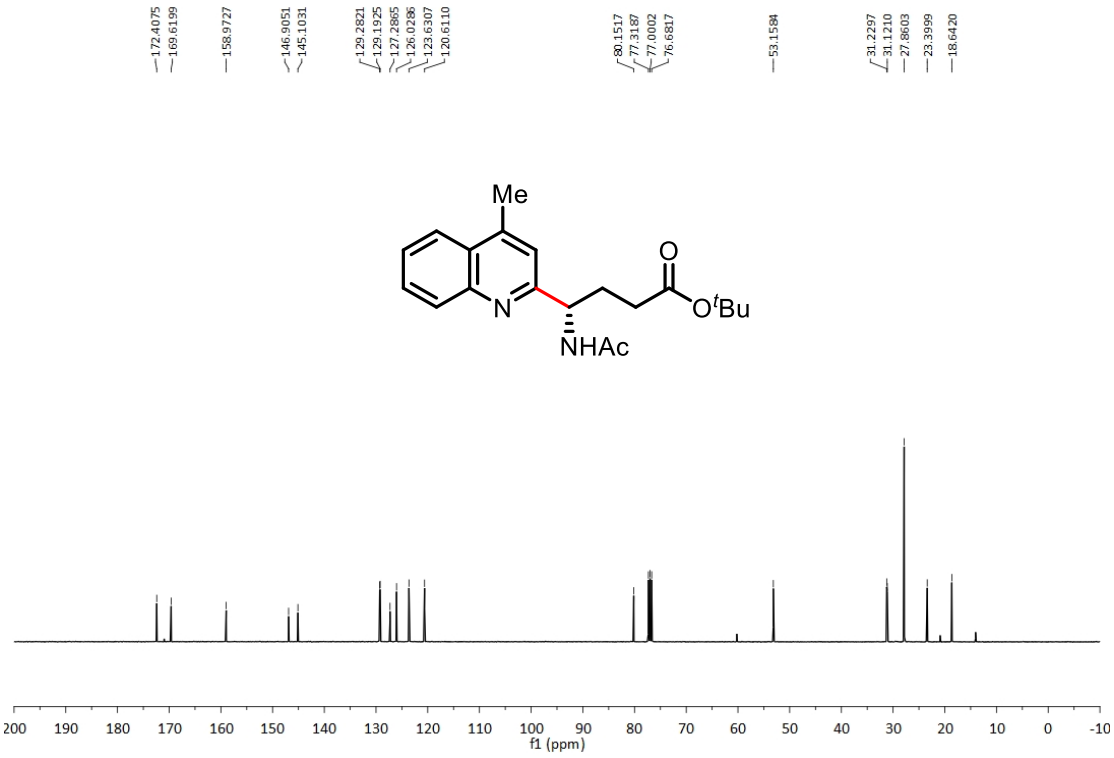
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **14**



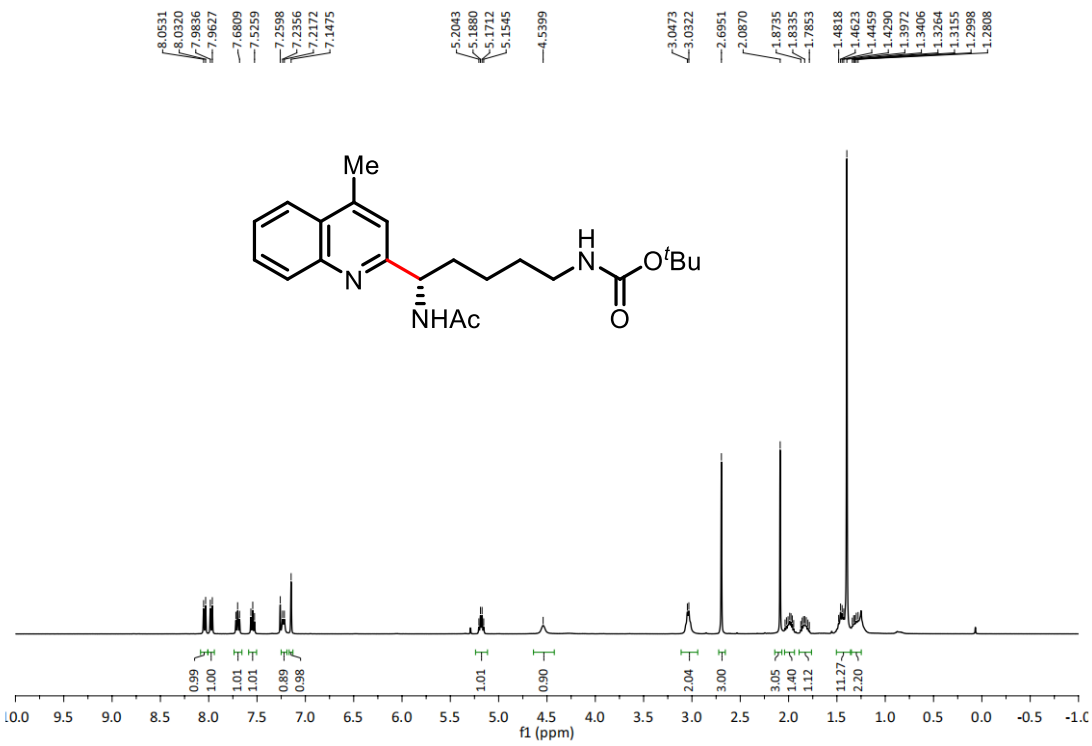
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **14**



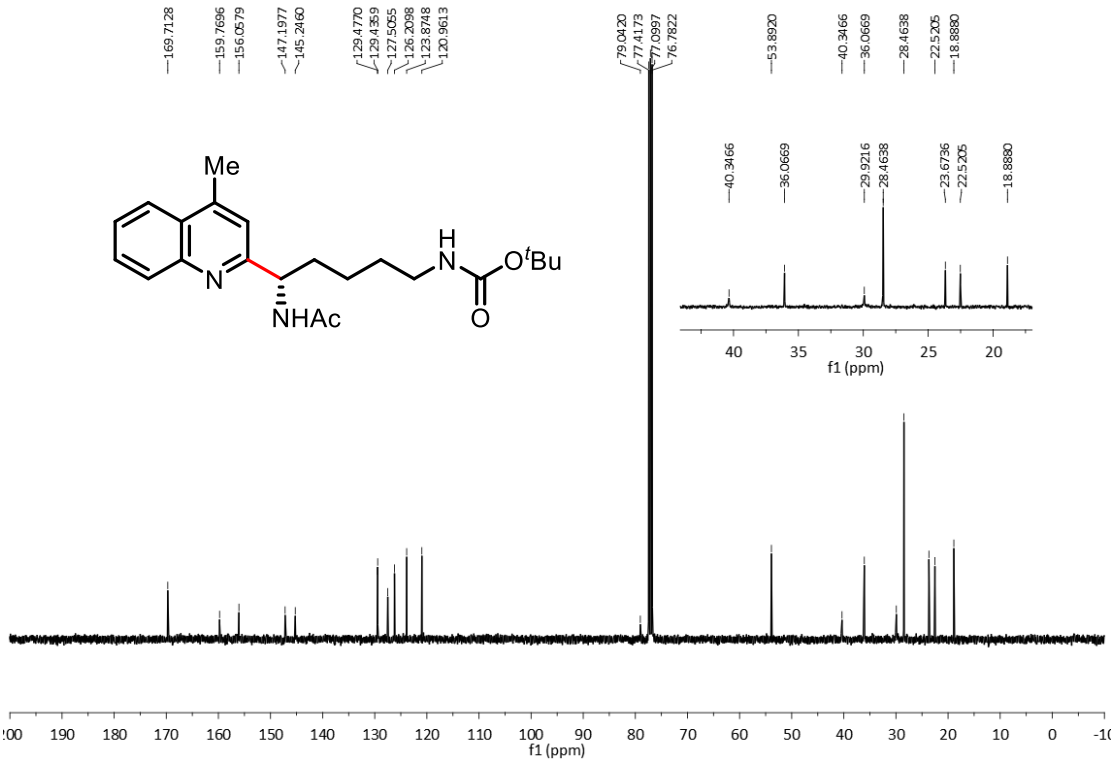
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **15**



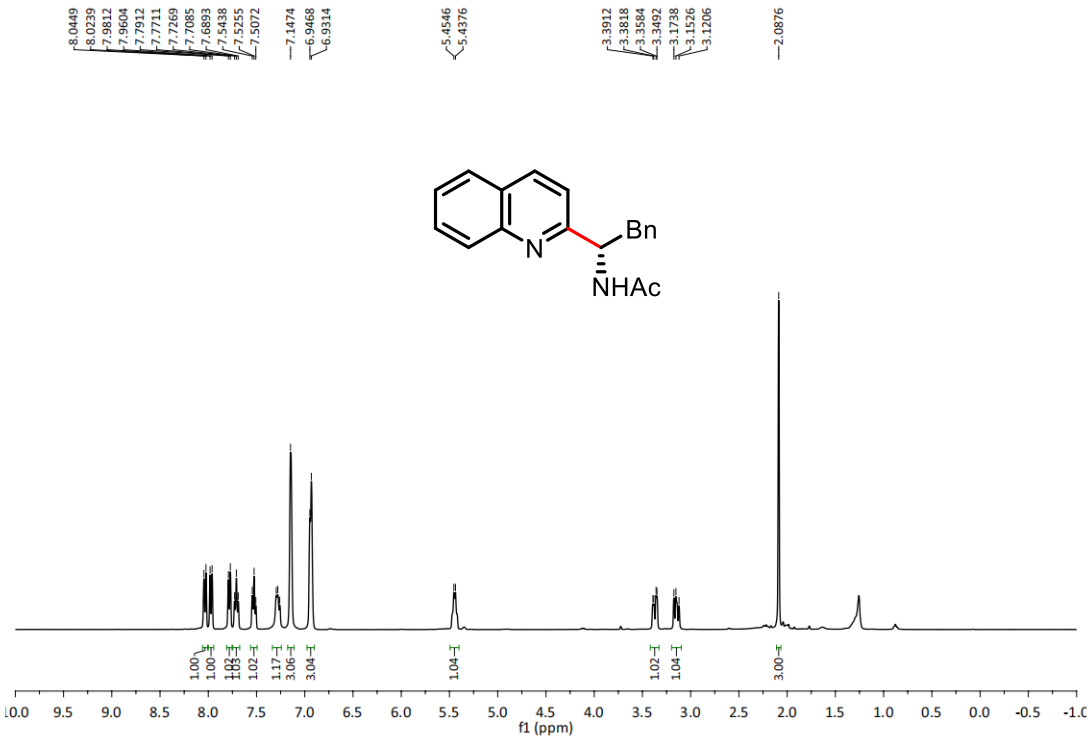
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **15**



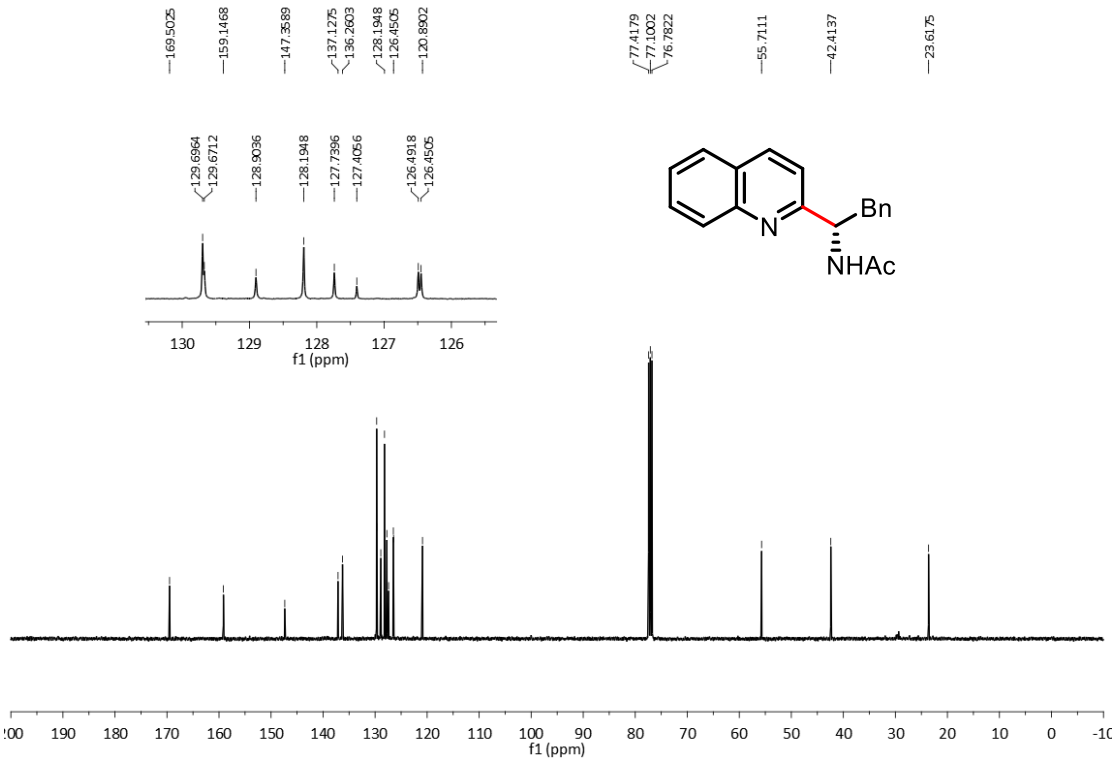
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **16**



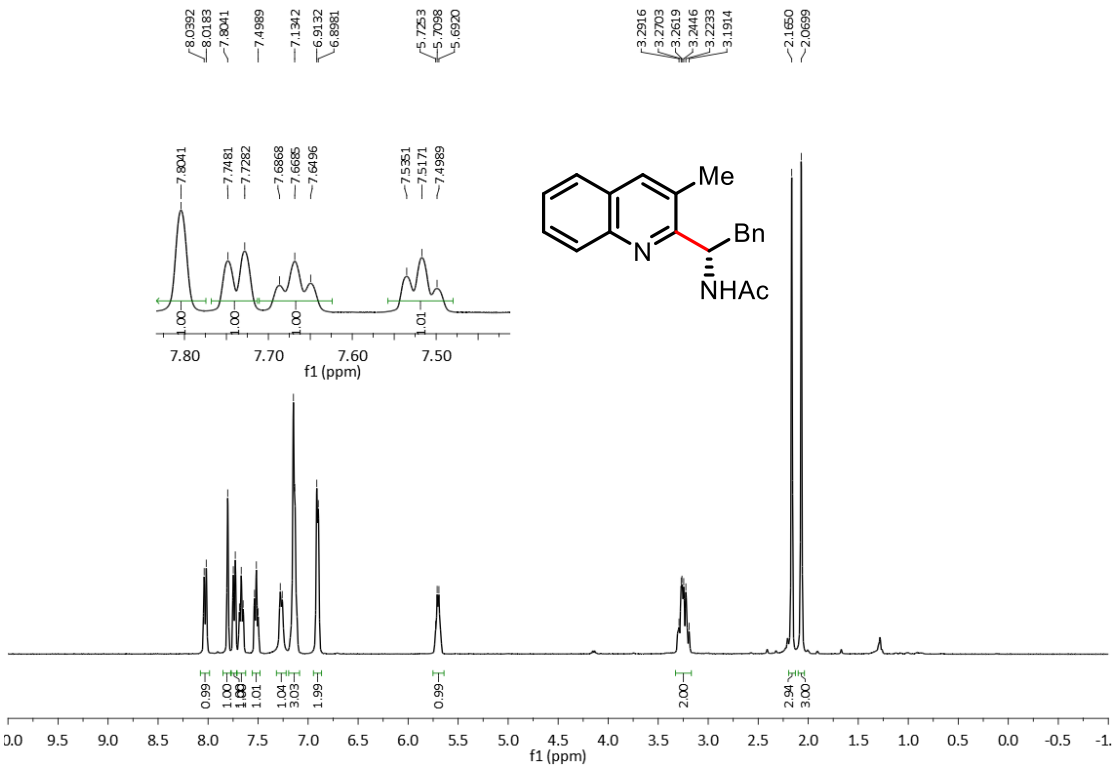
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **16**



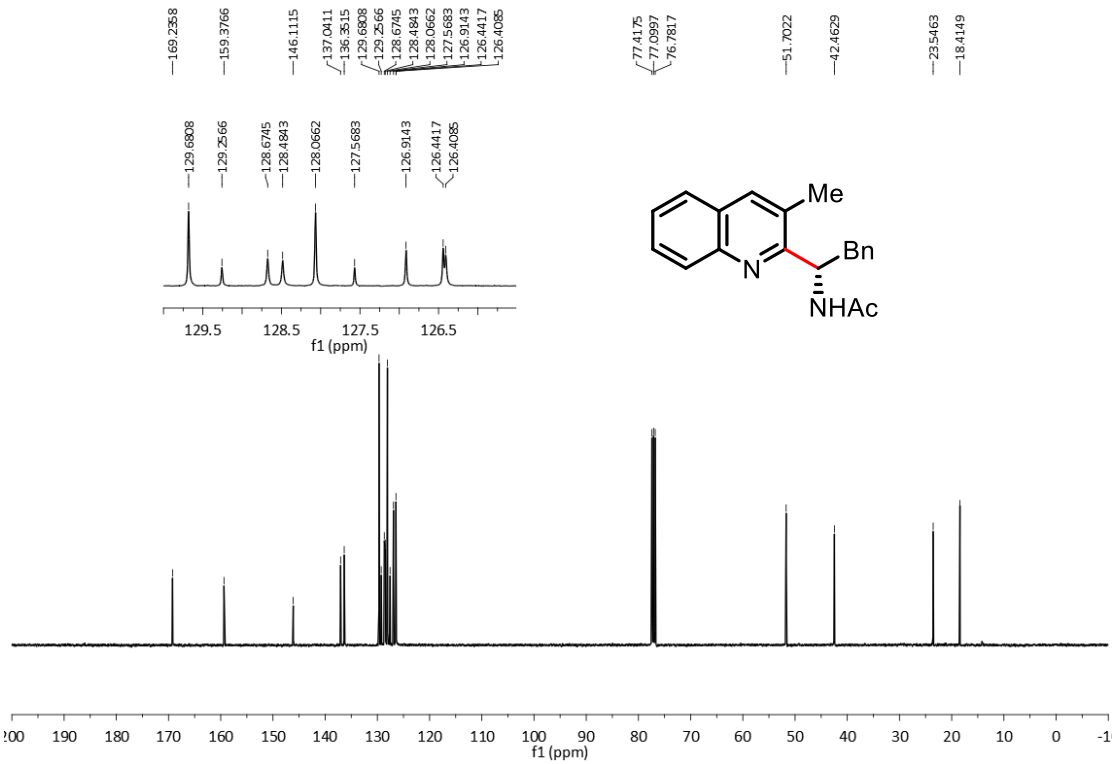
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **17**



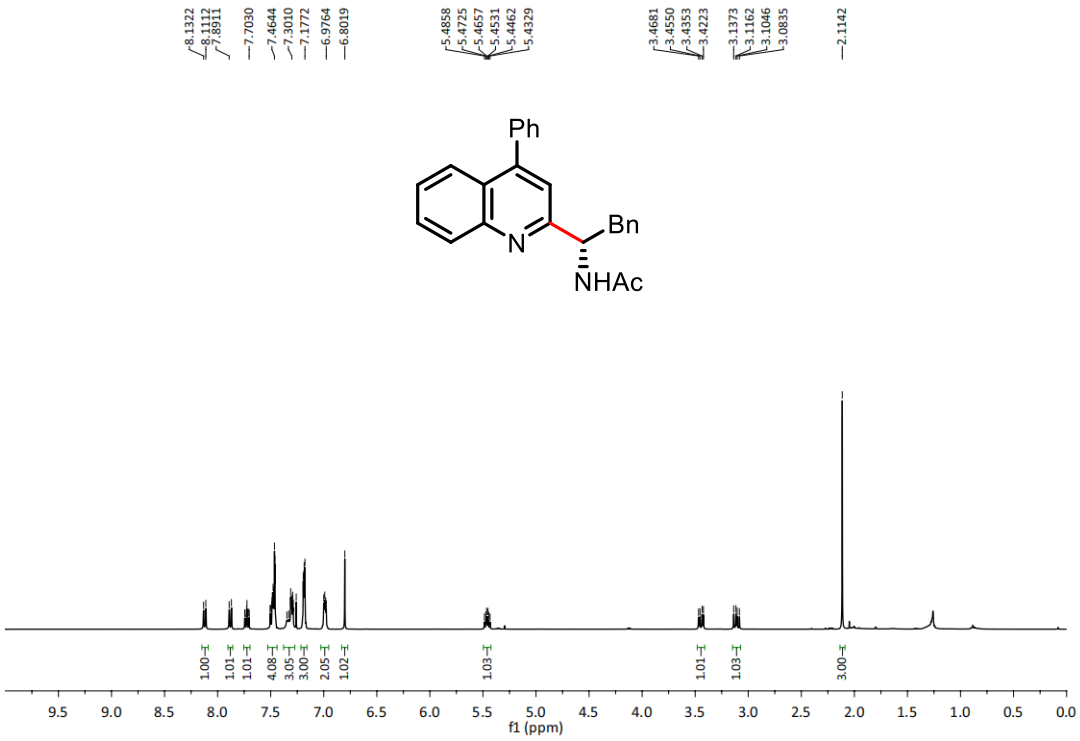
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **17**



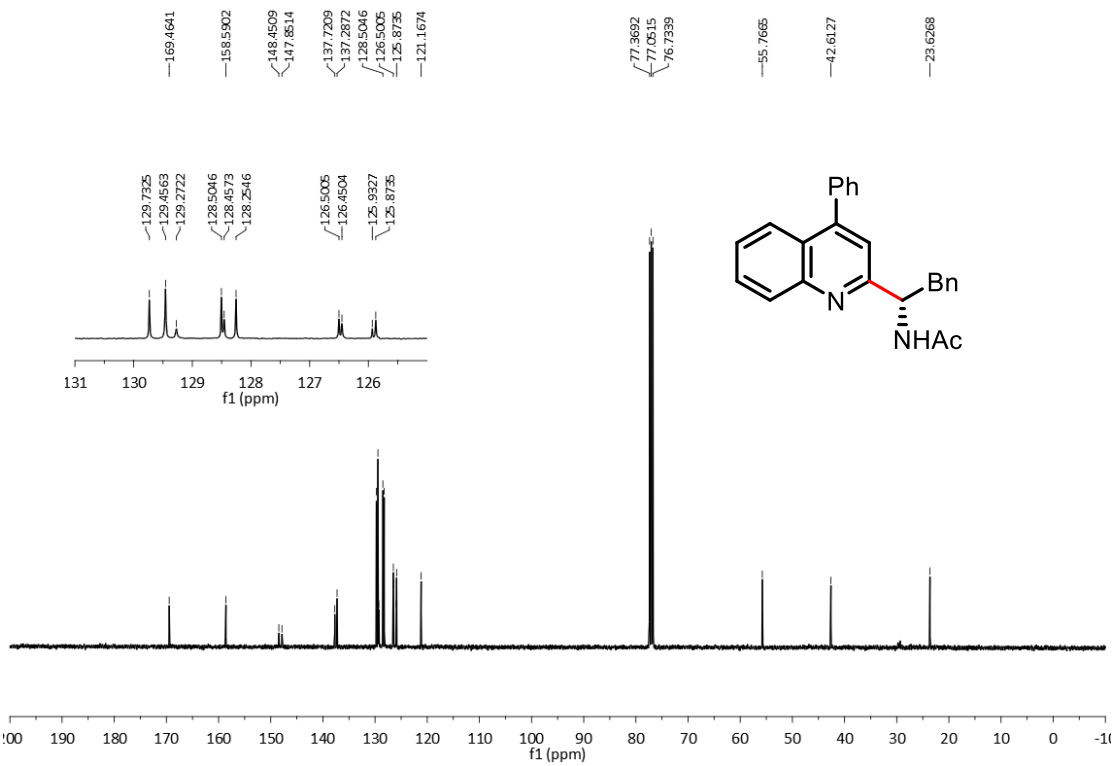
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **18**



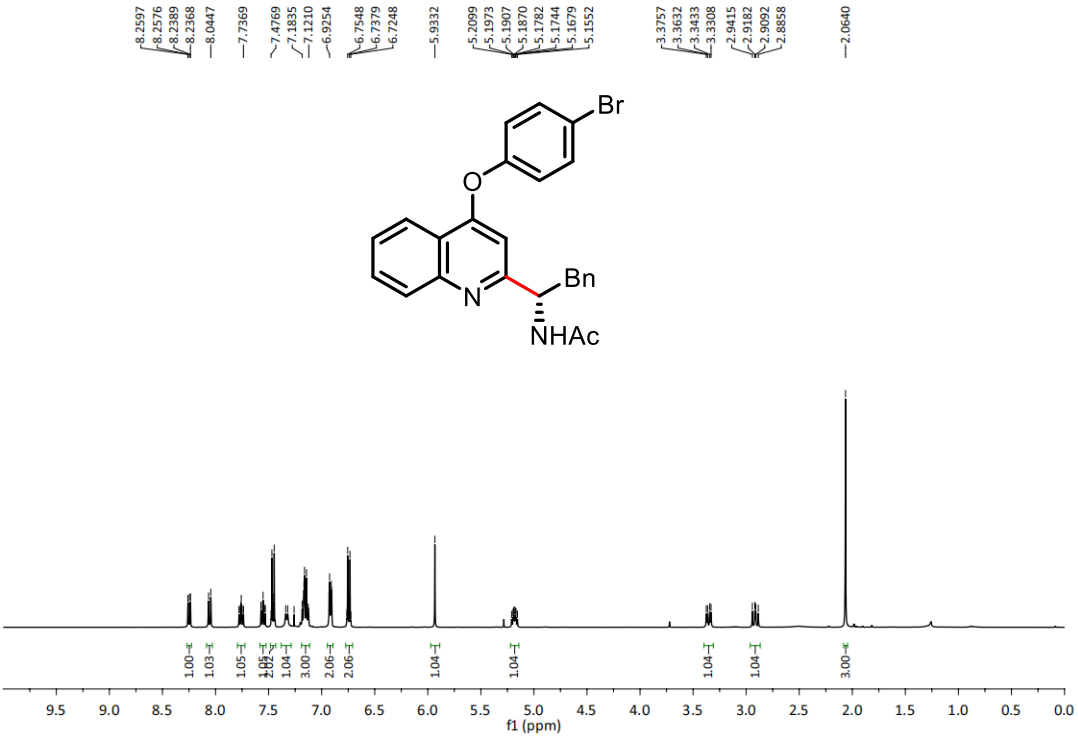
^{13}C NMR (100 MHz, CDC_{l3}) spectrum of compound **18**



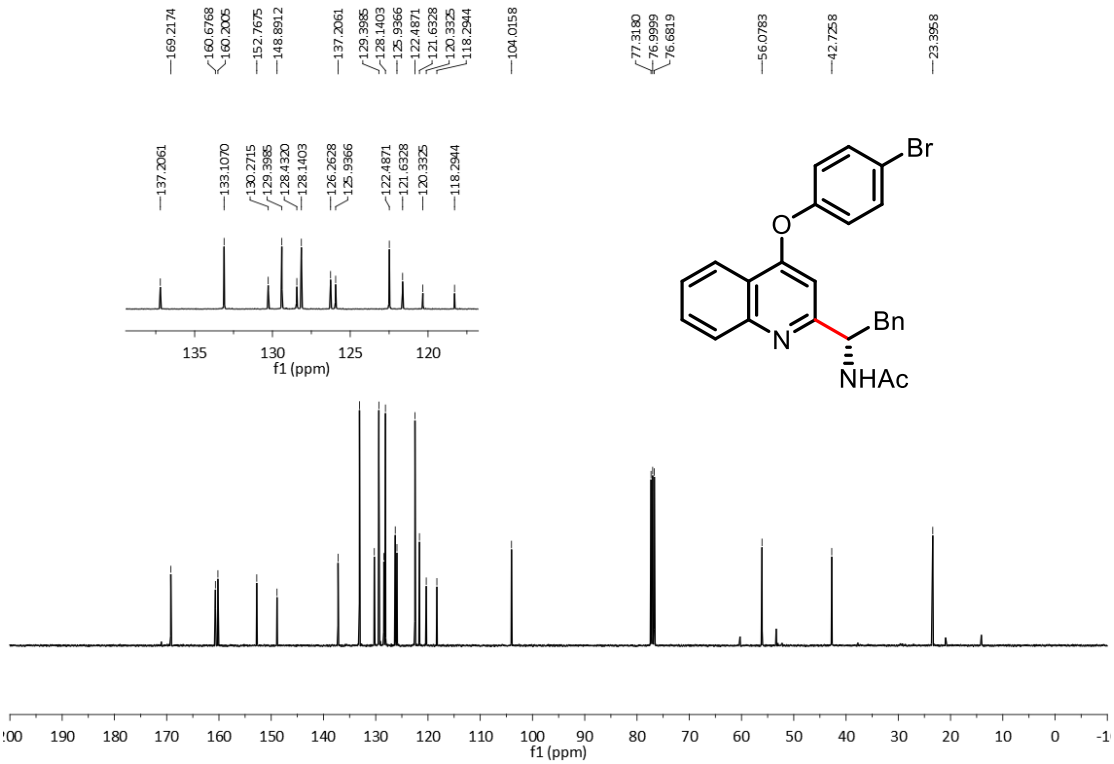
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **19**



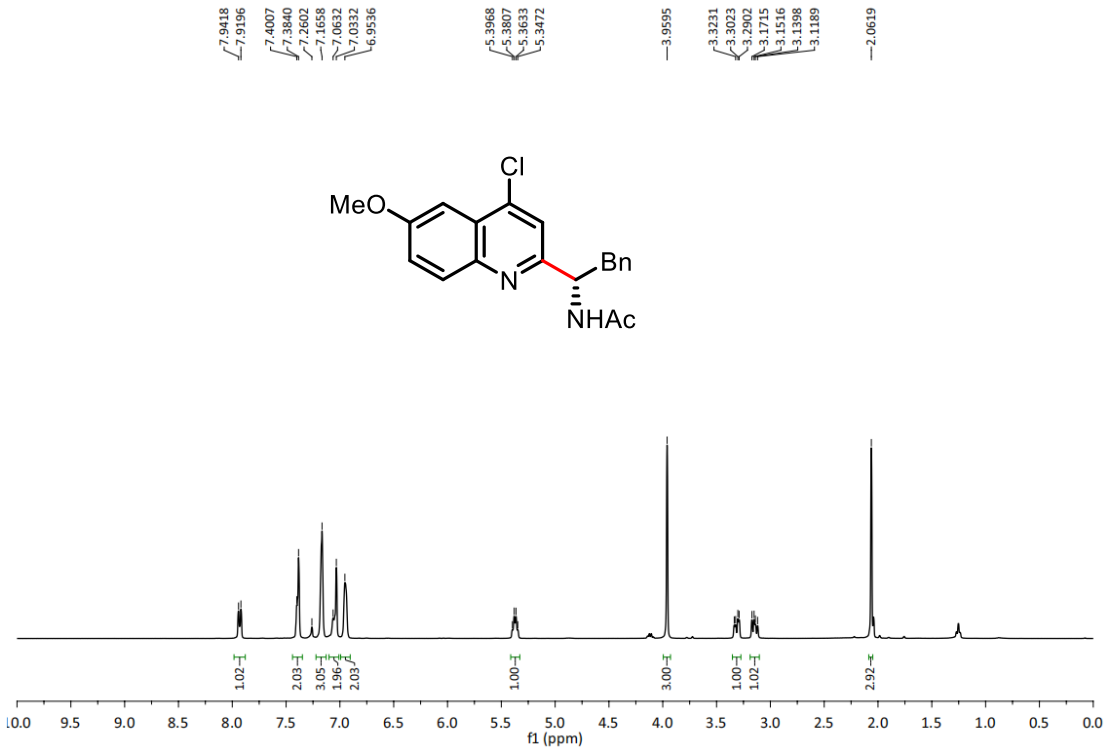
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **19**



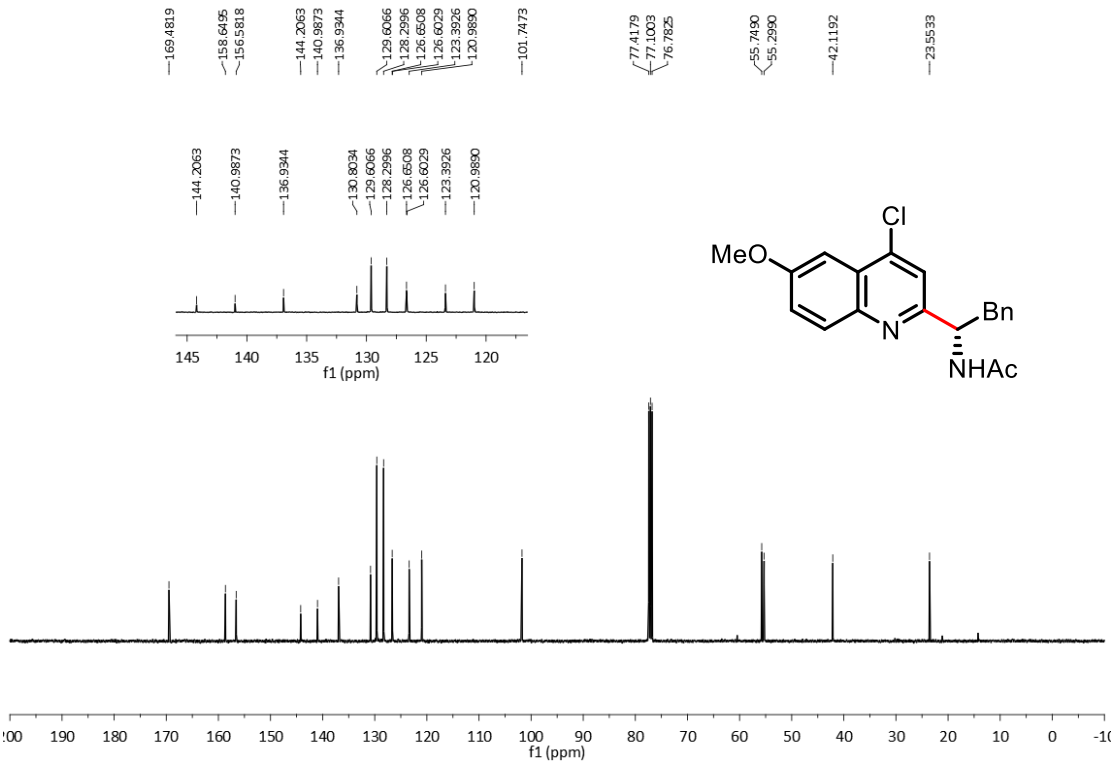
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **20**



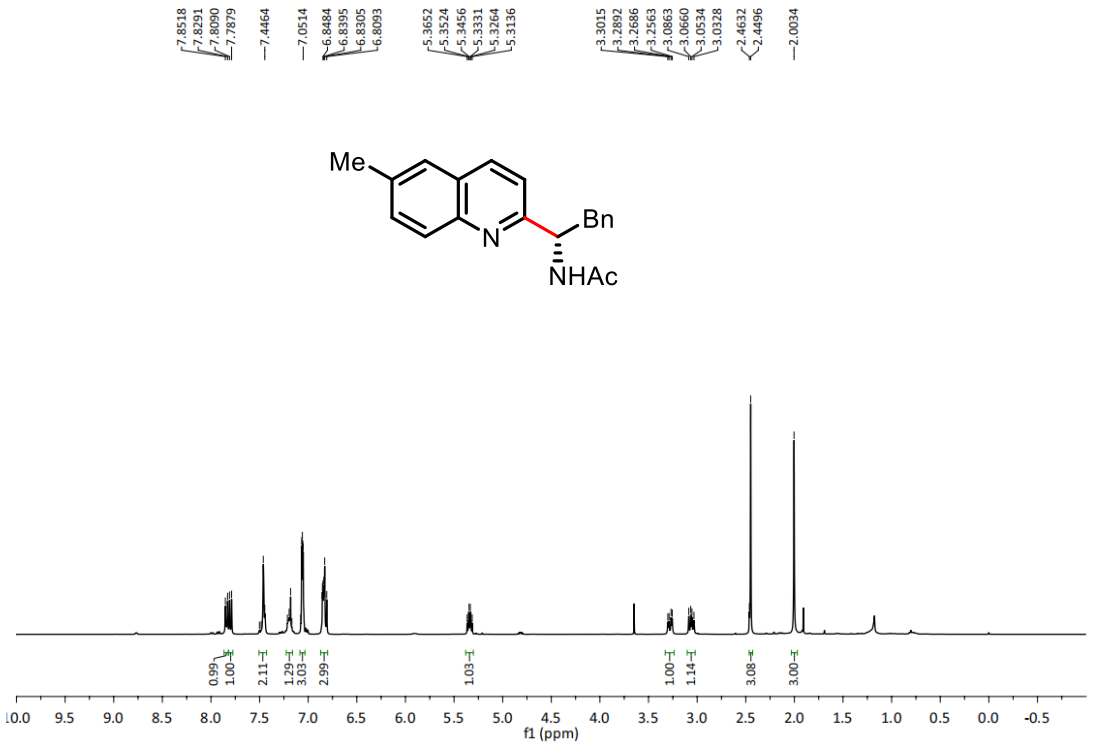
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **20**



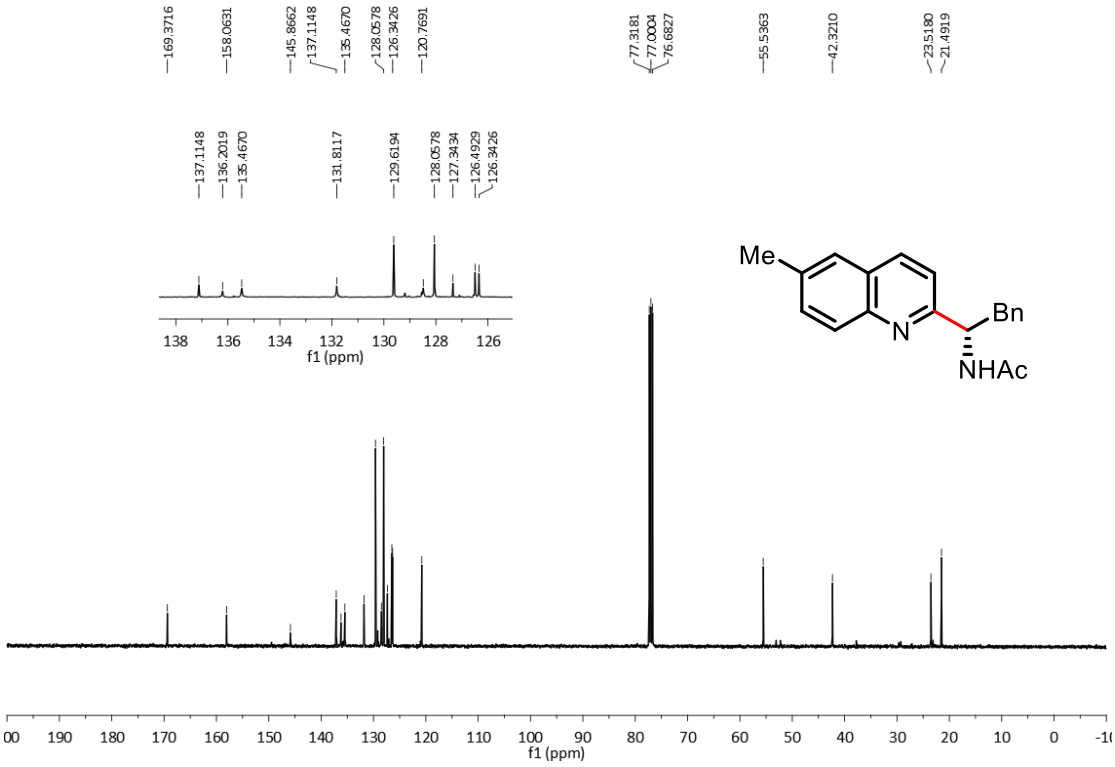
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **21**



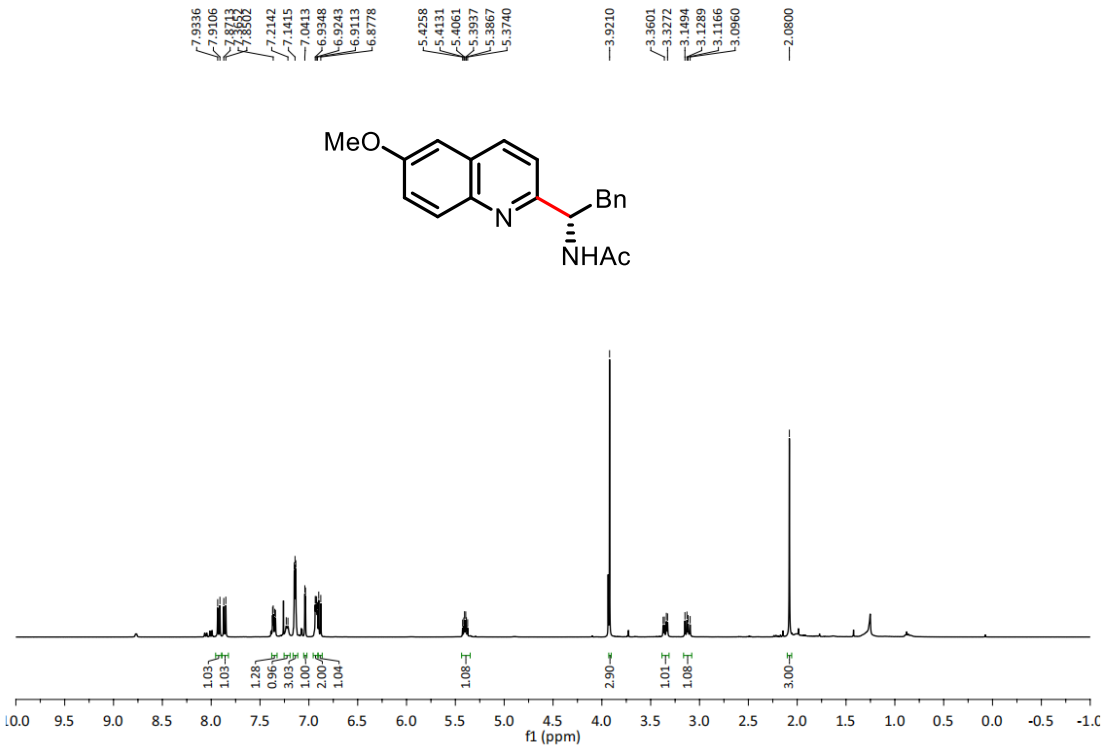
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **21**



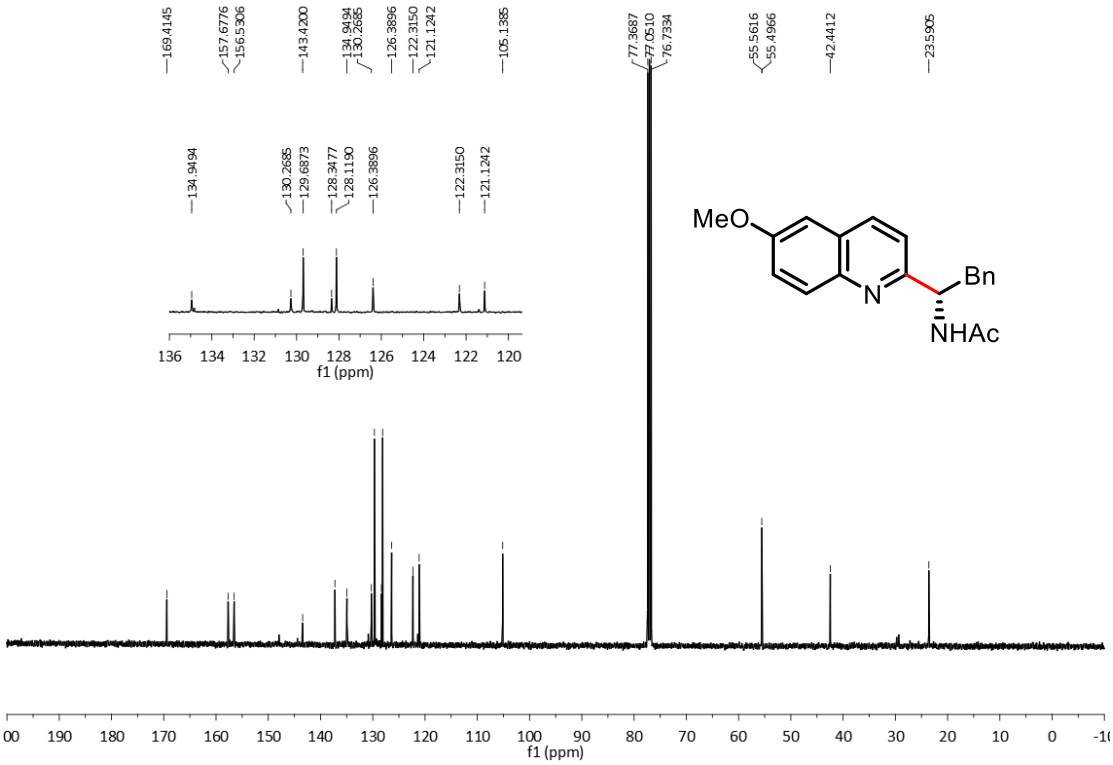
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **22**



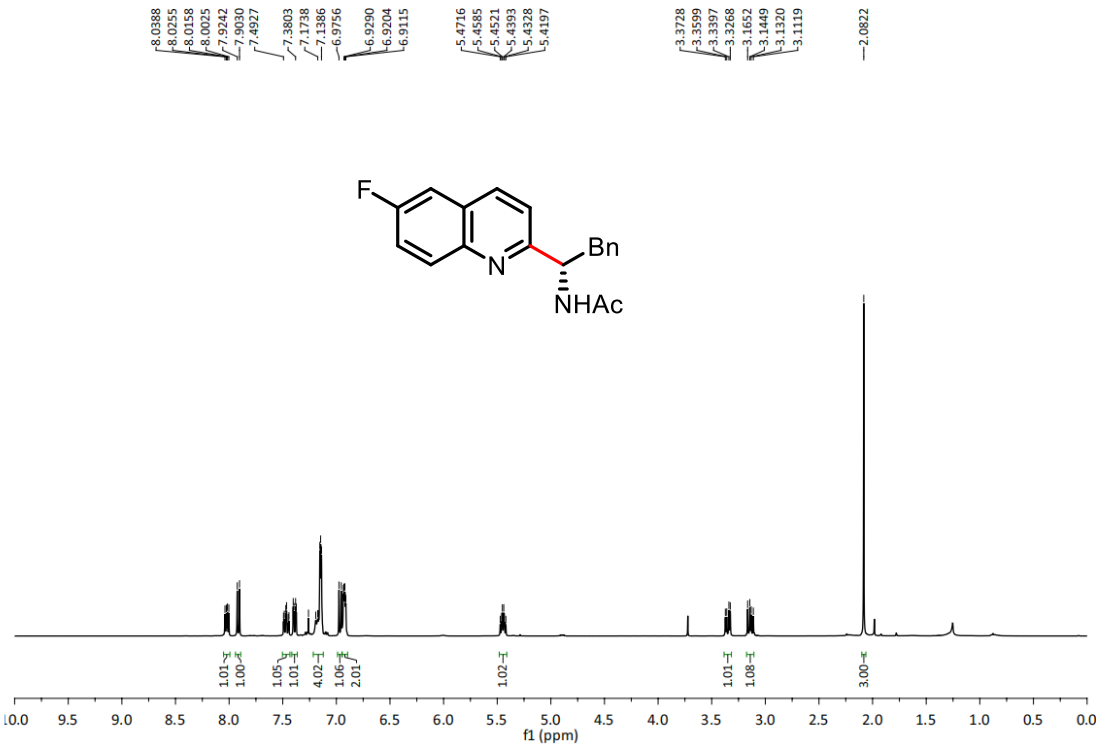
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **22**



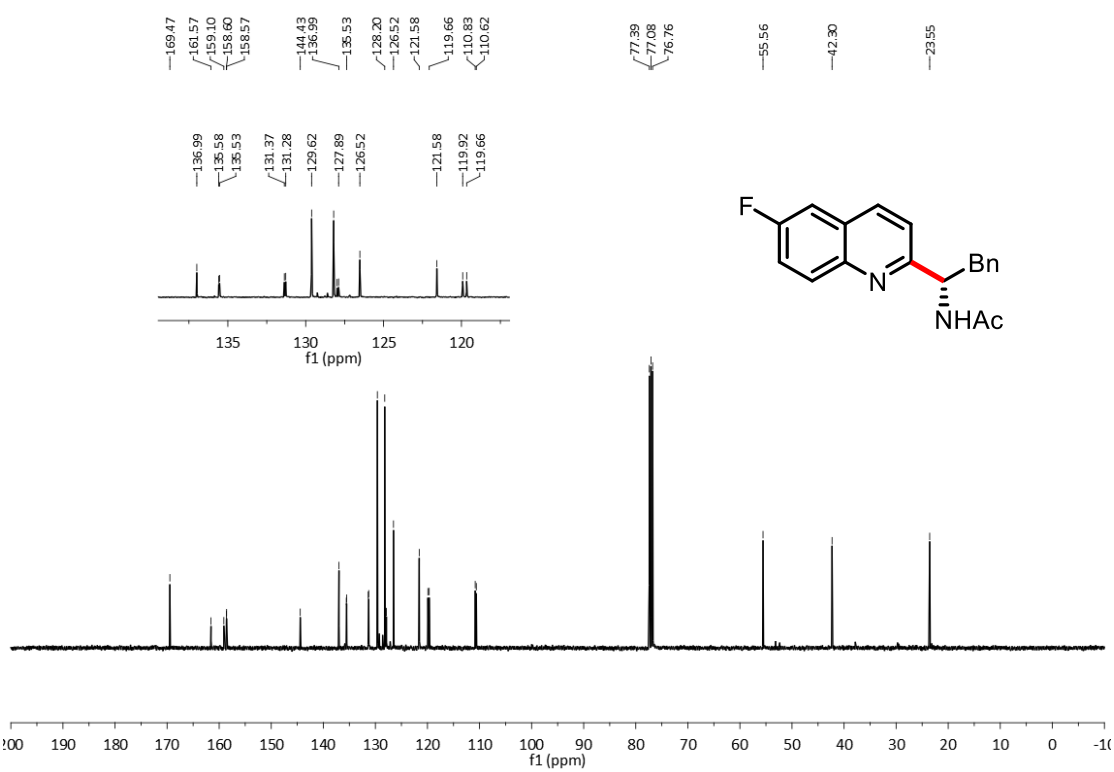
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **23**



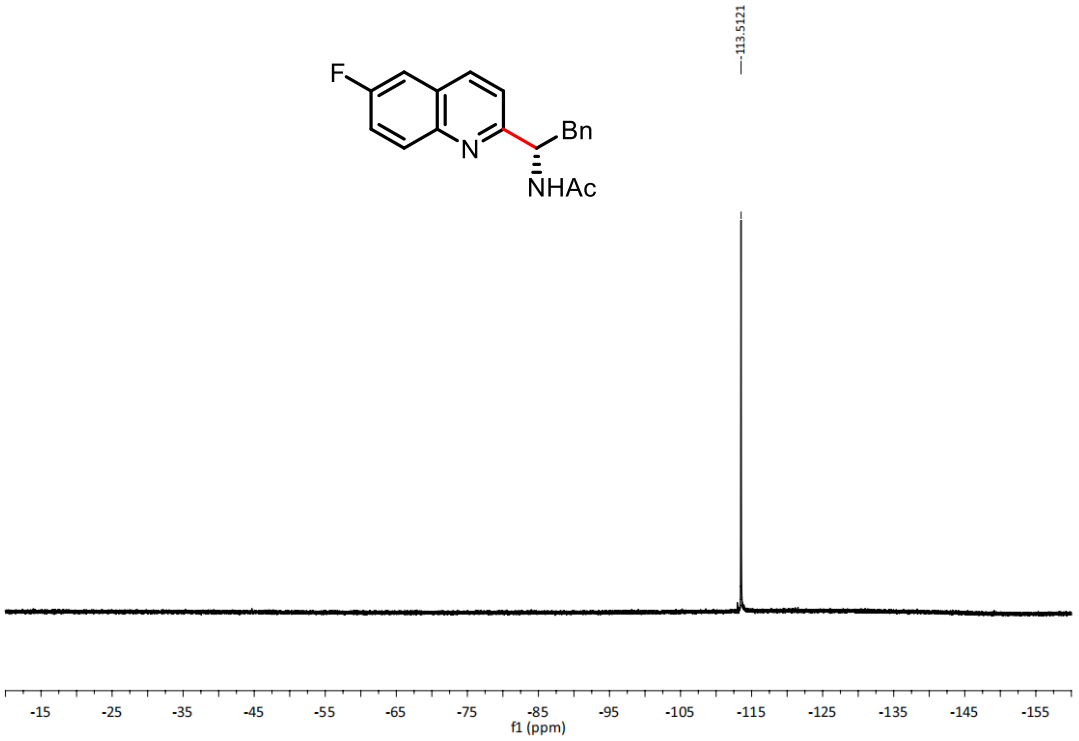
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **23**



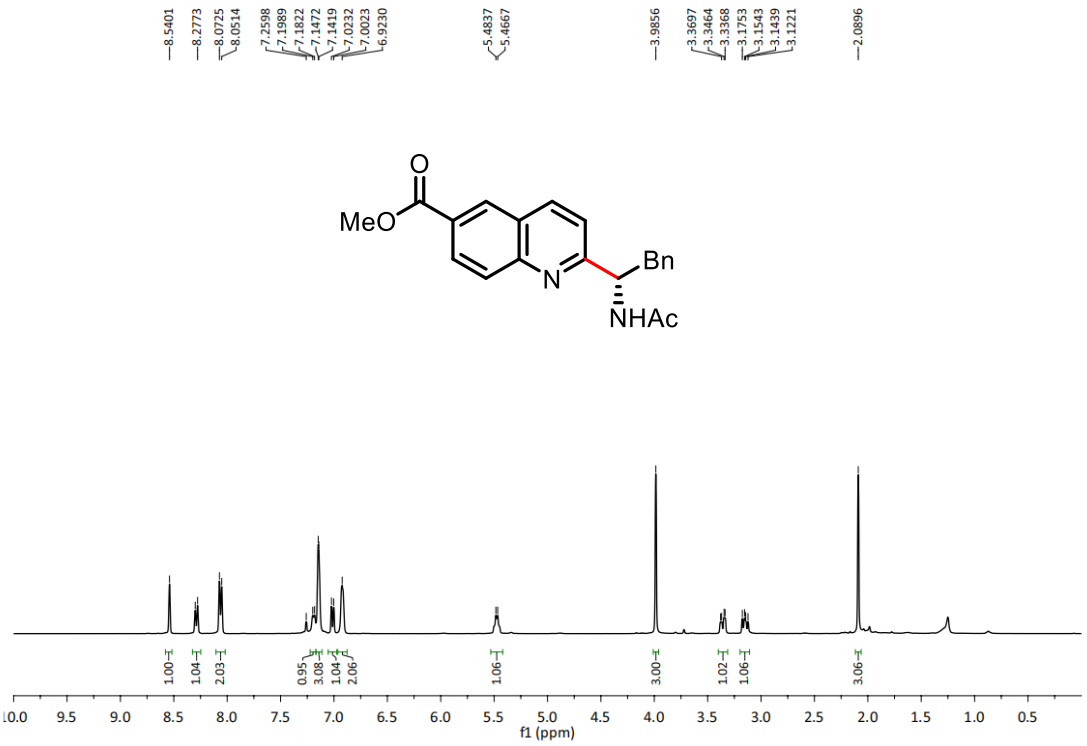
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **24**



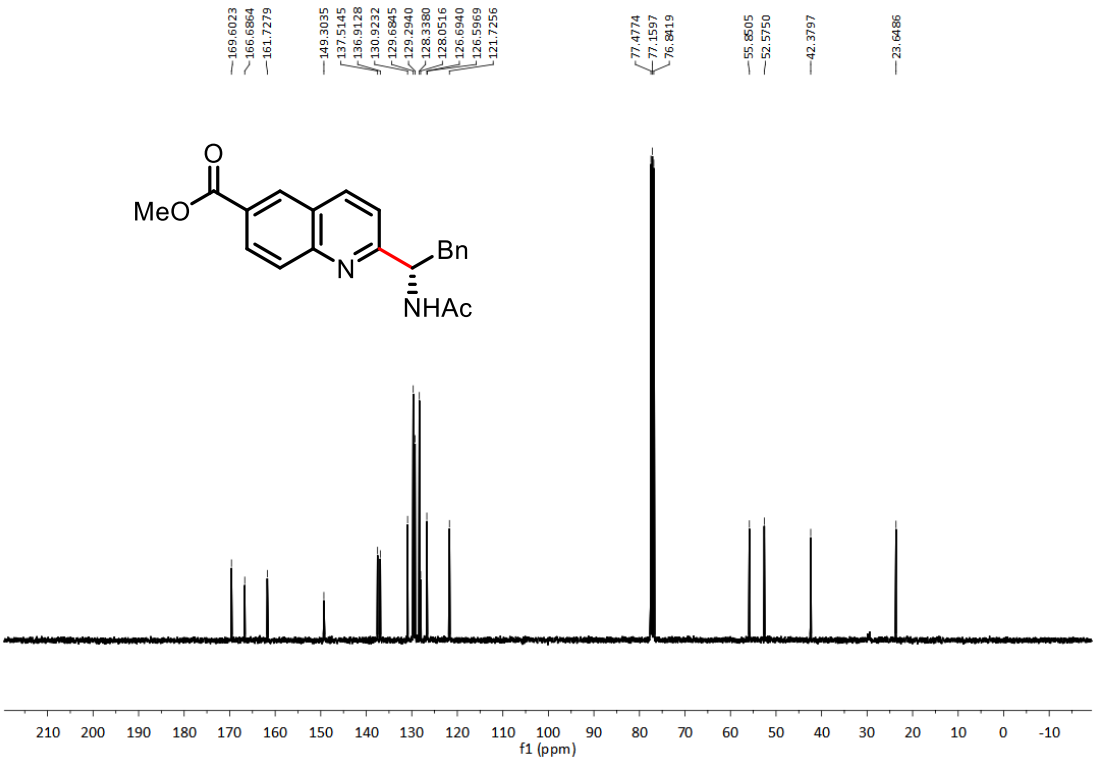
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **24**



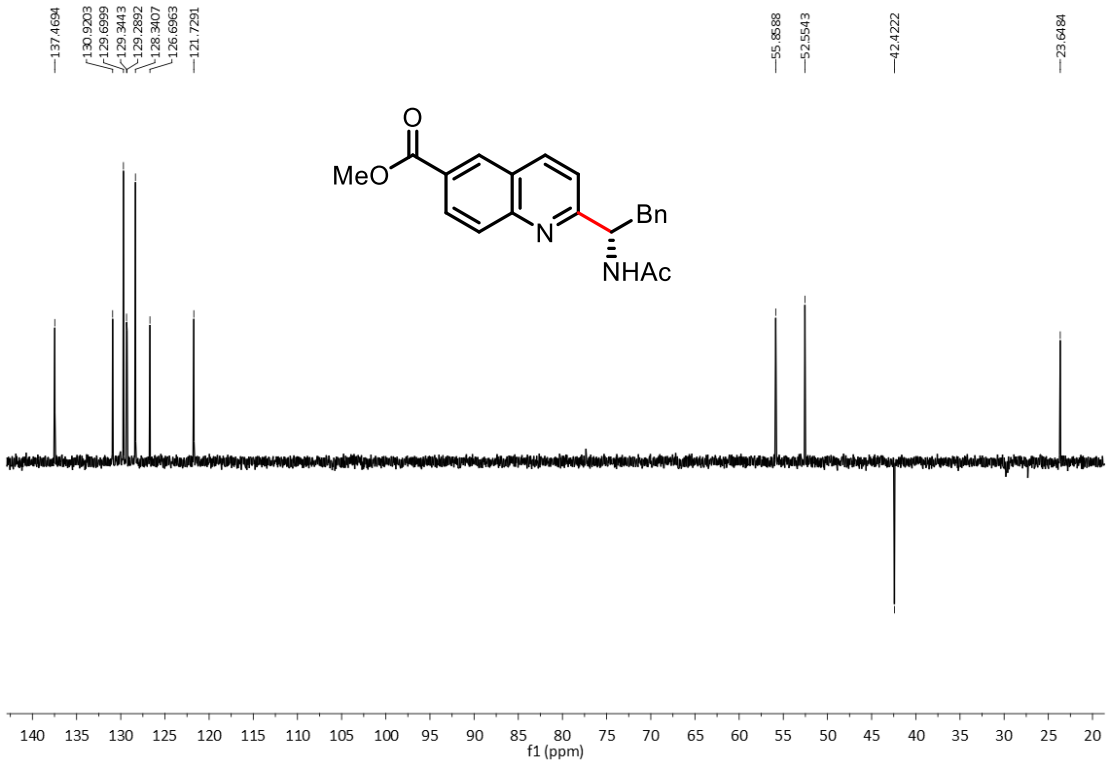
^{19}F NMR (100 MHz, $CDCl_3$) spectrum of compound **24**



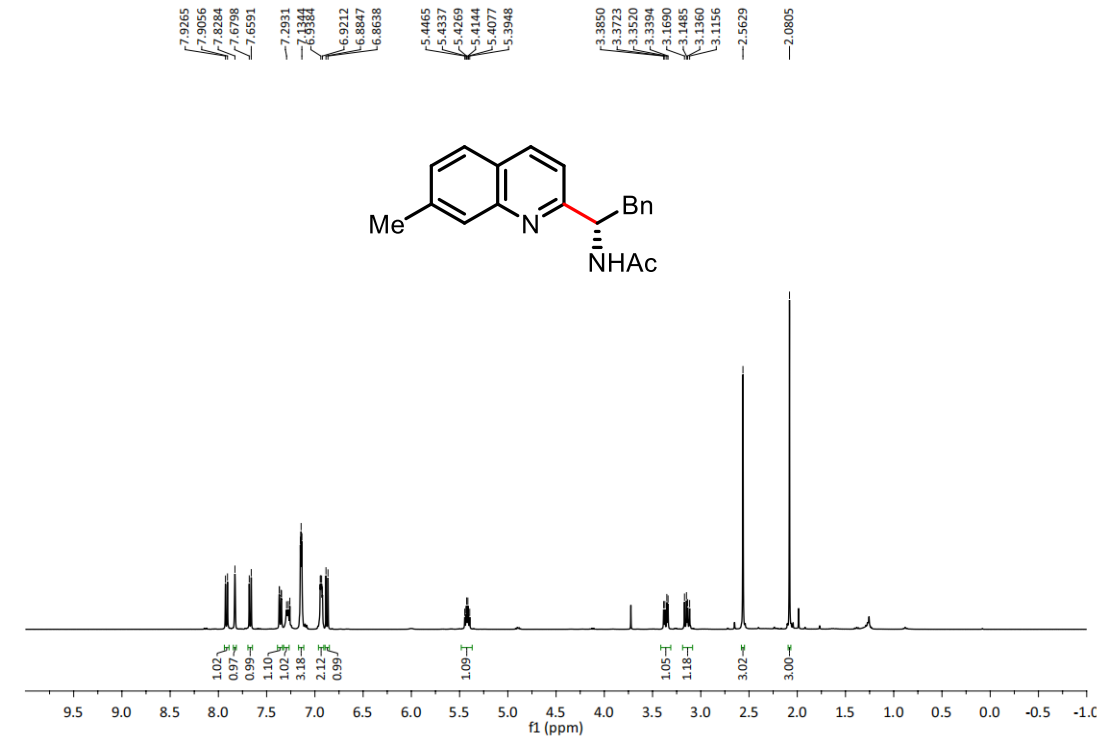
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **25**



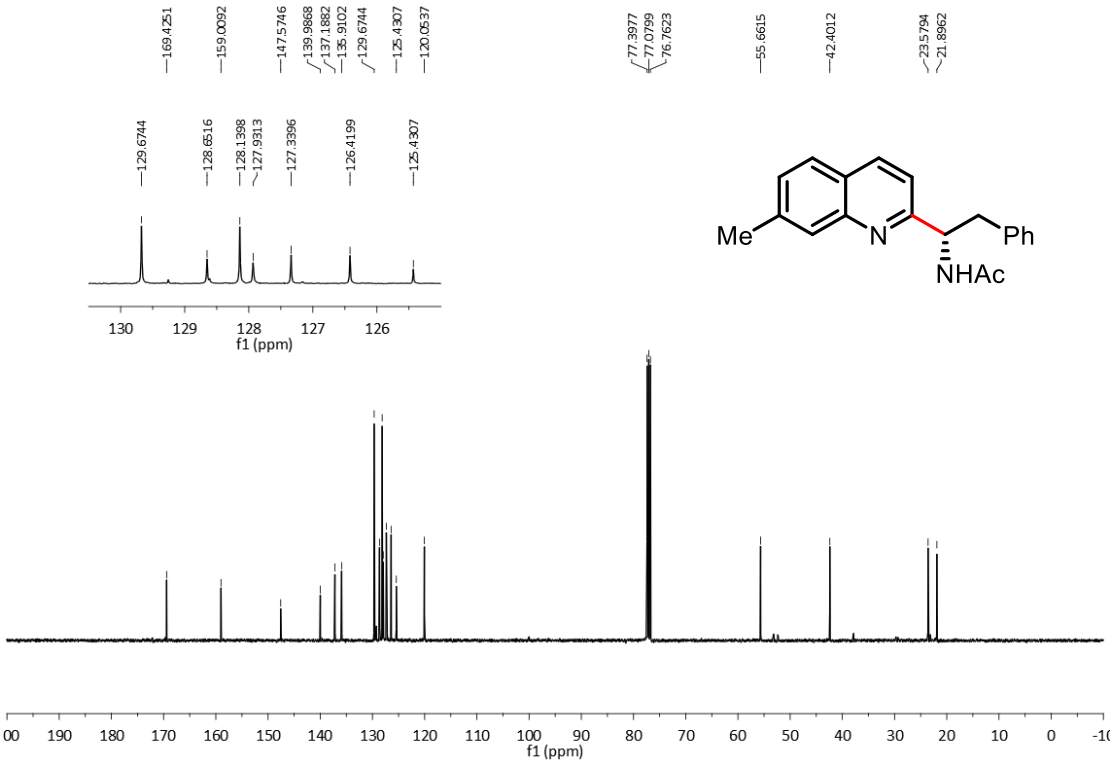
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **25**



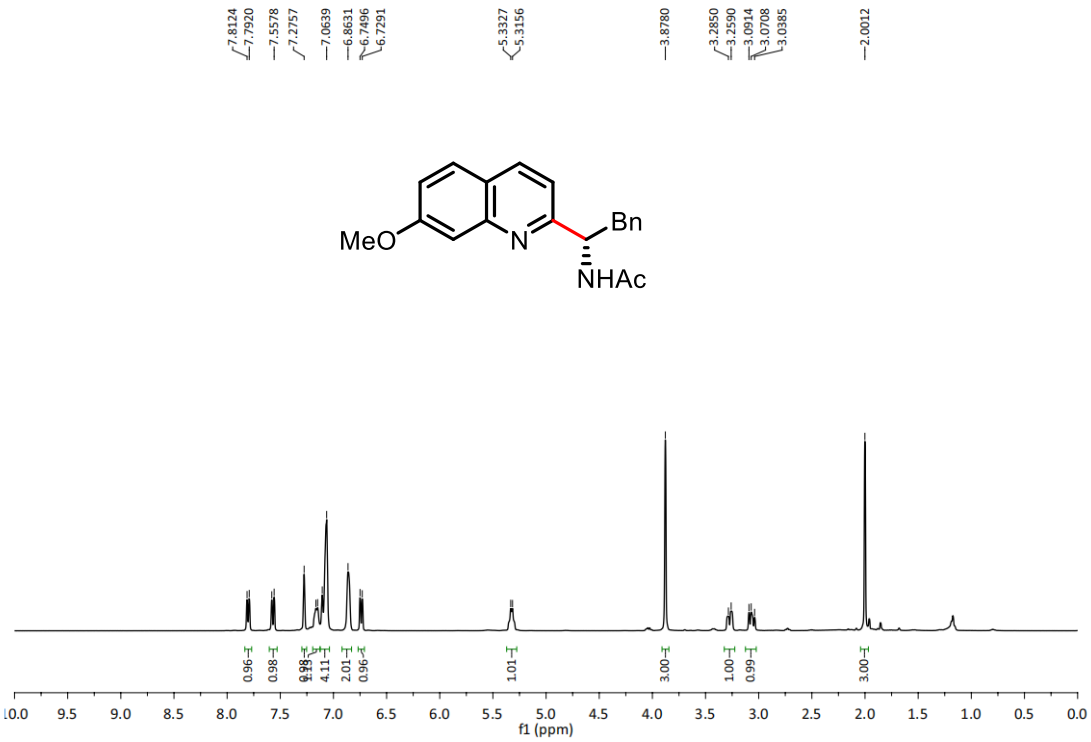
^{13}C NMR (100 MHz, $CDCl_3$) Dept 135 spectrum of compound **25**



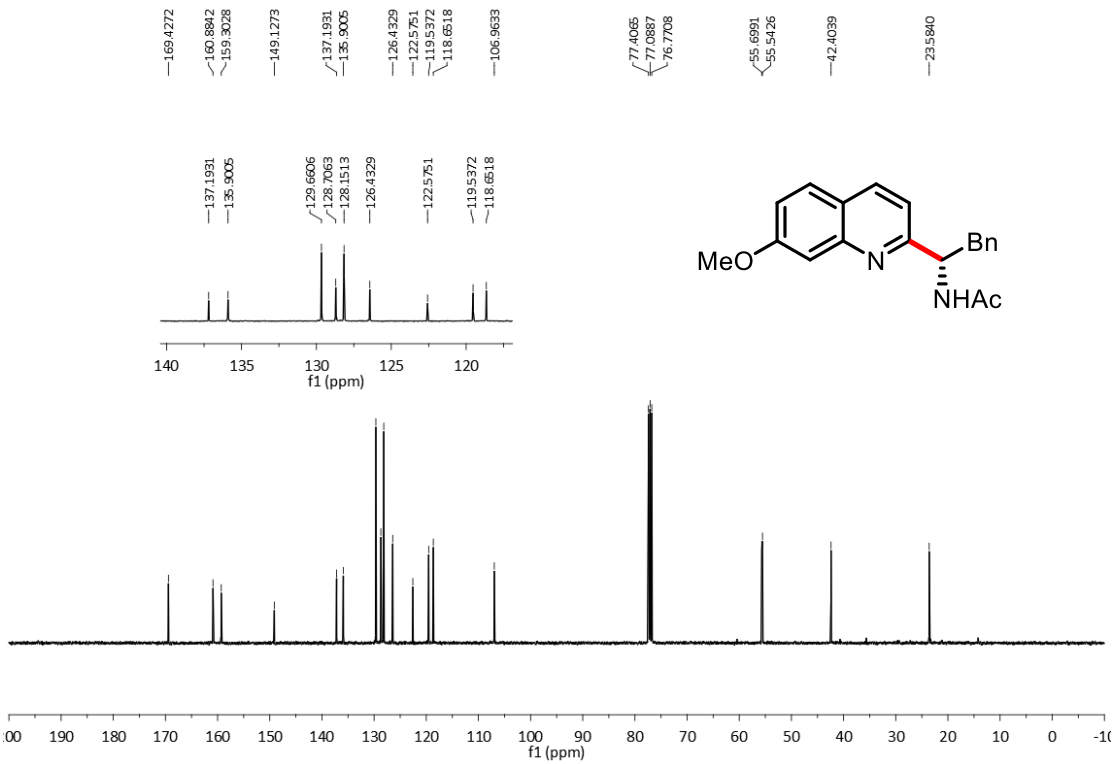
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **26**



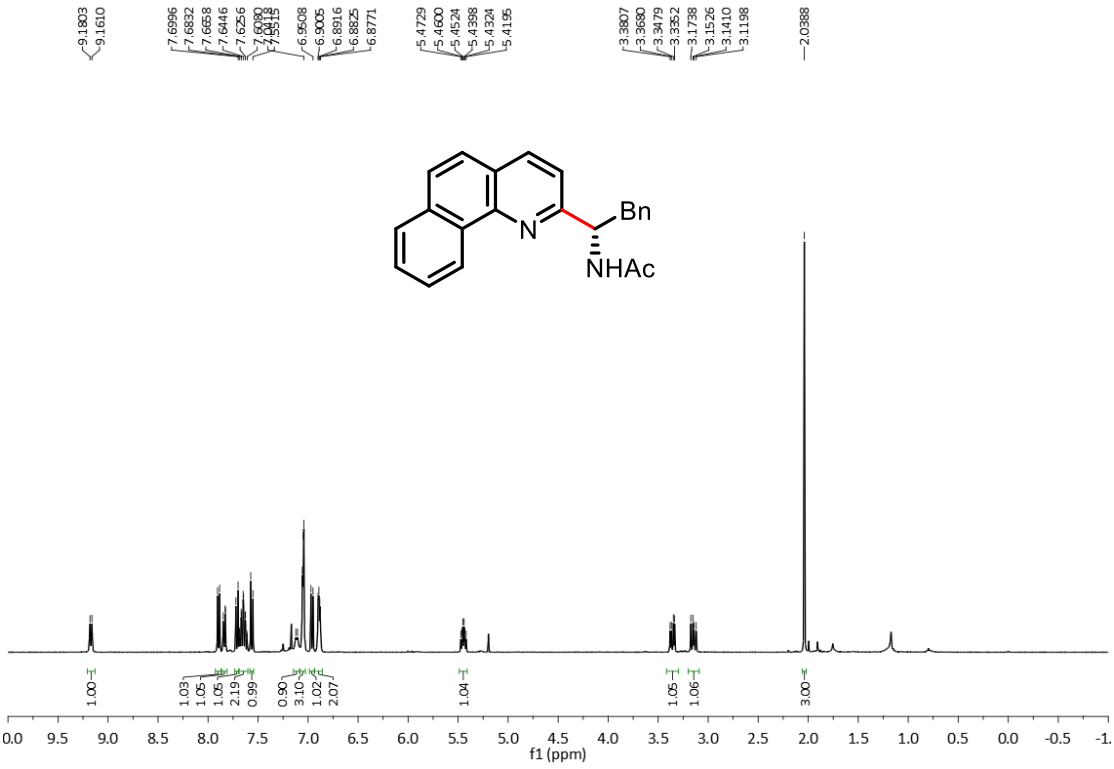
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **26**



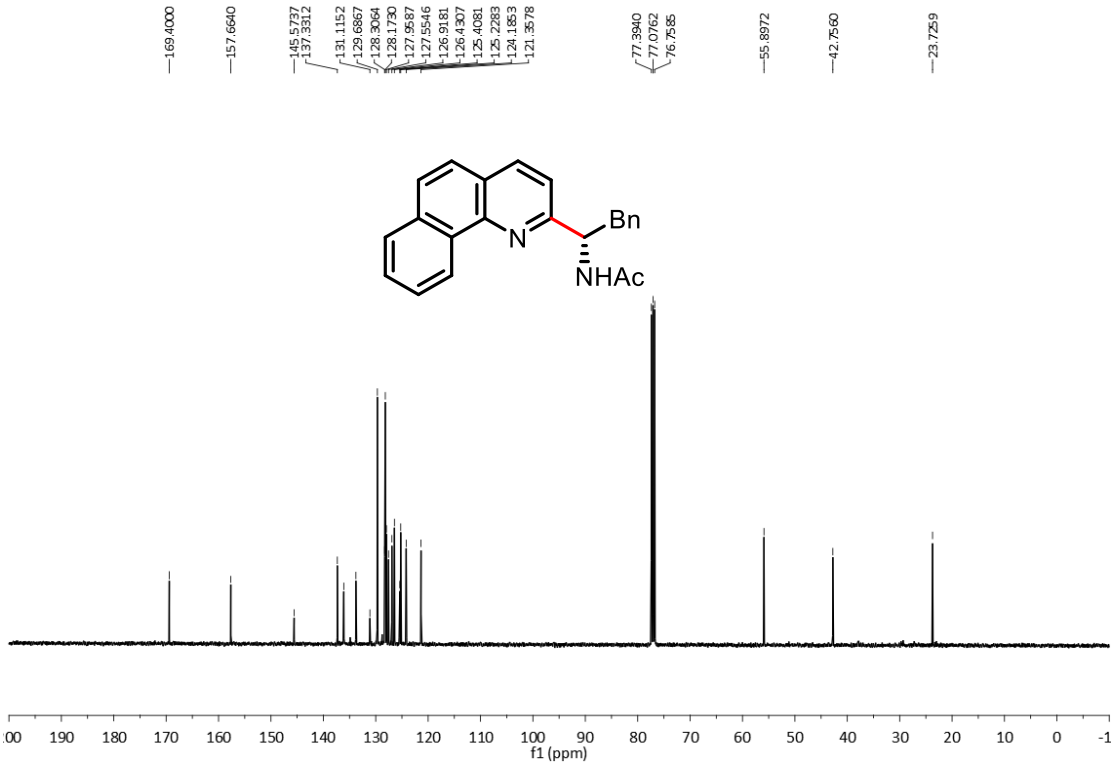
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **27**



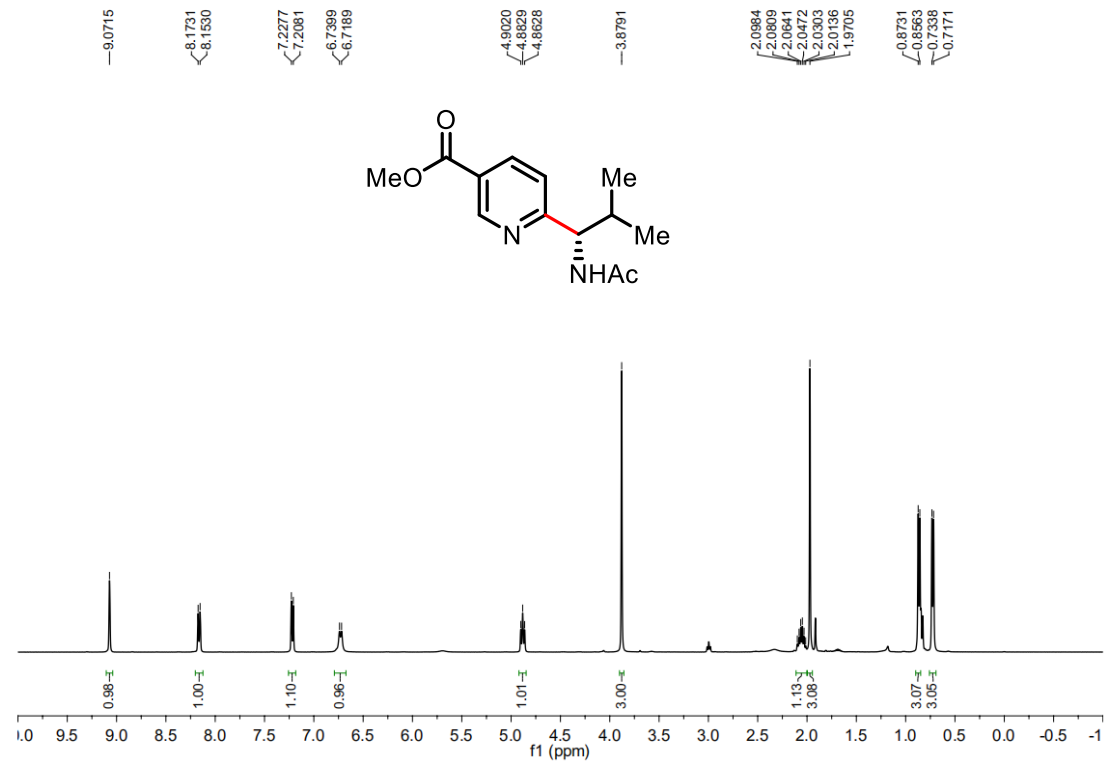
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **27**



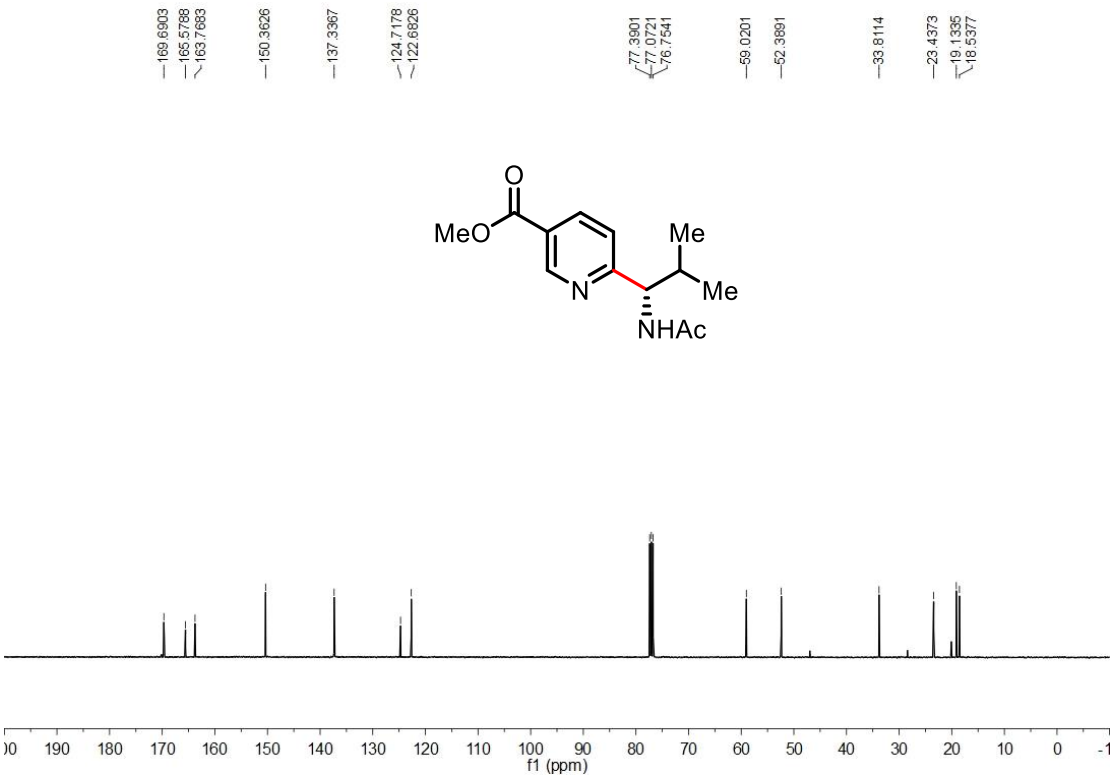
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **28**



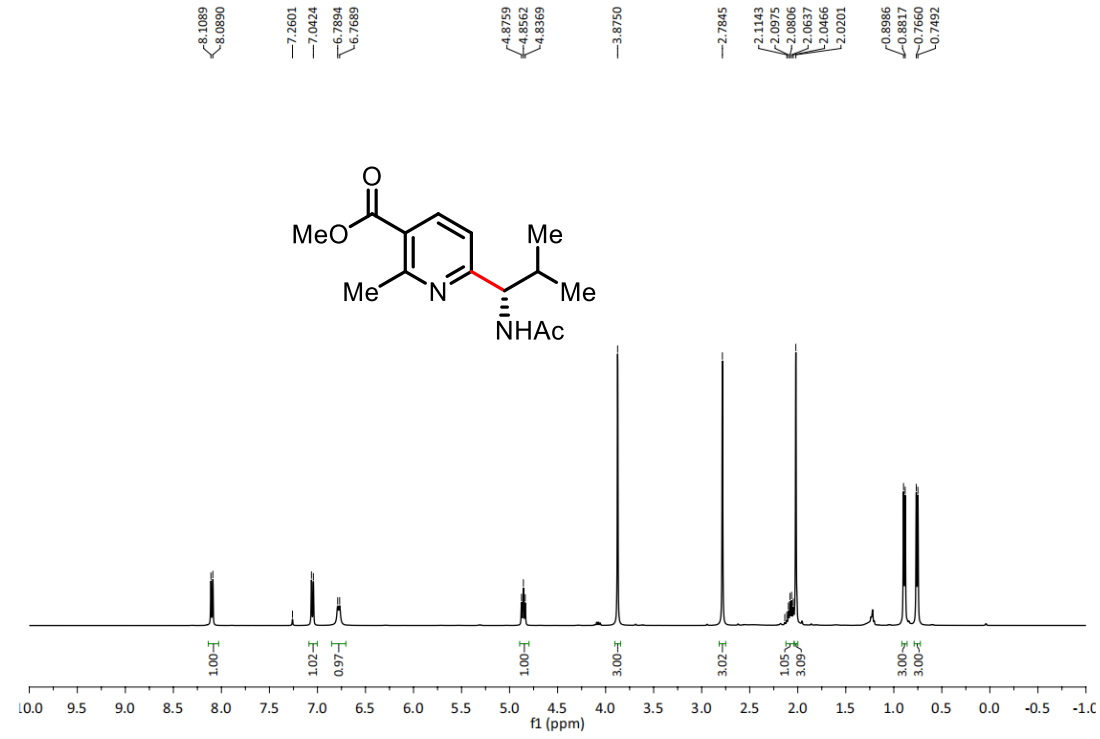
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **28**



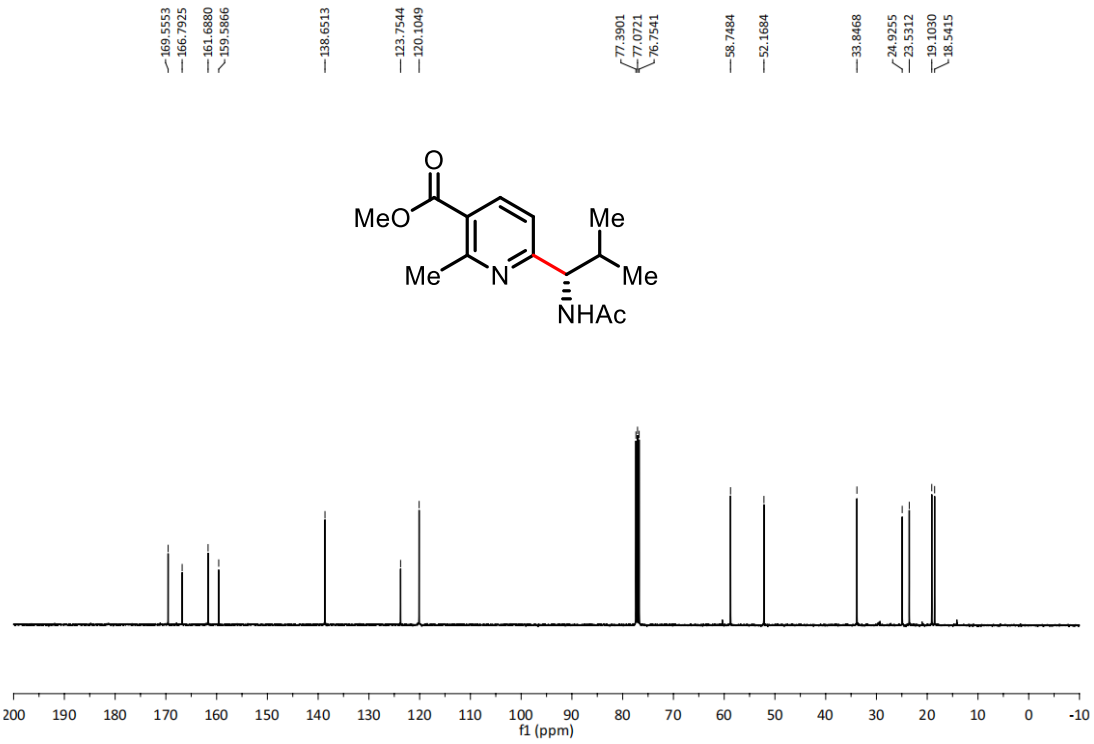
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **29**



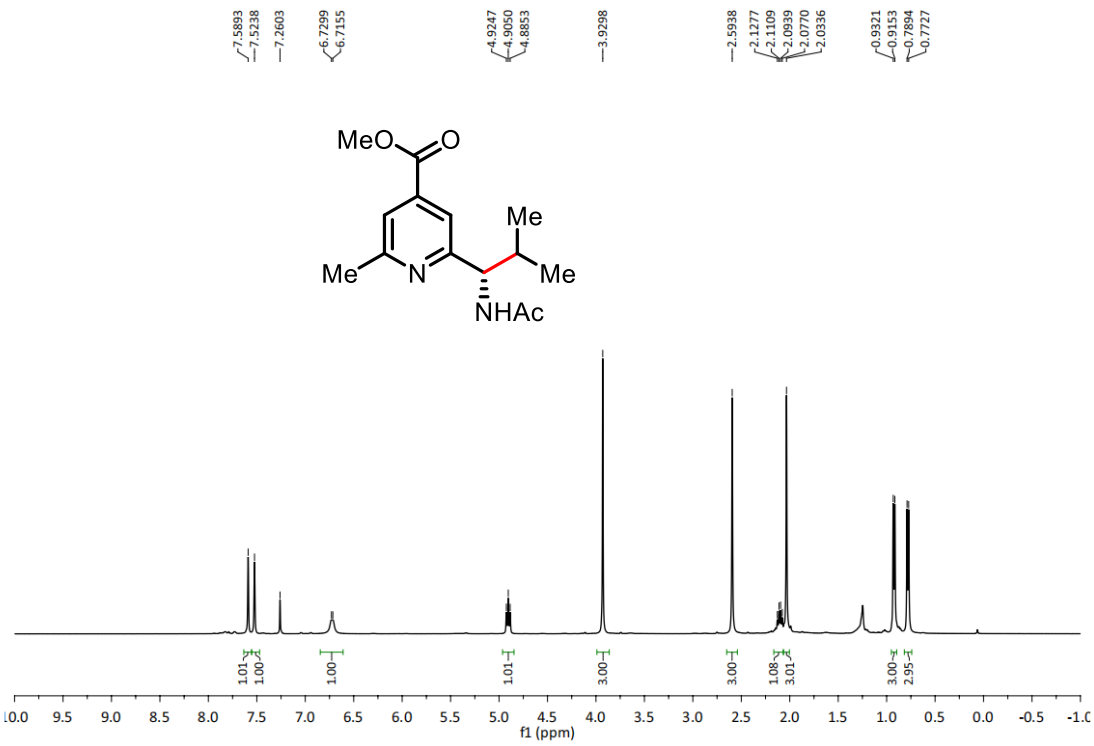
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **29**



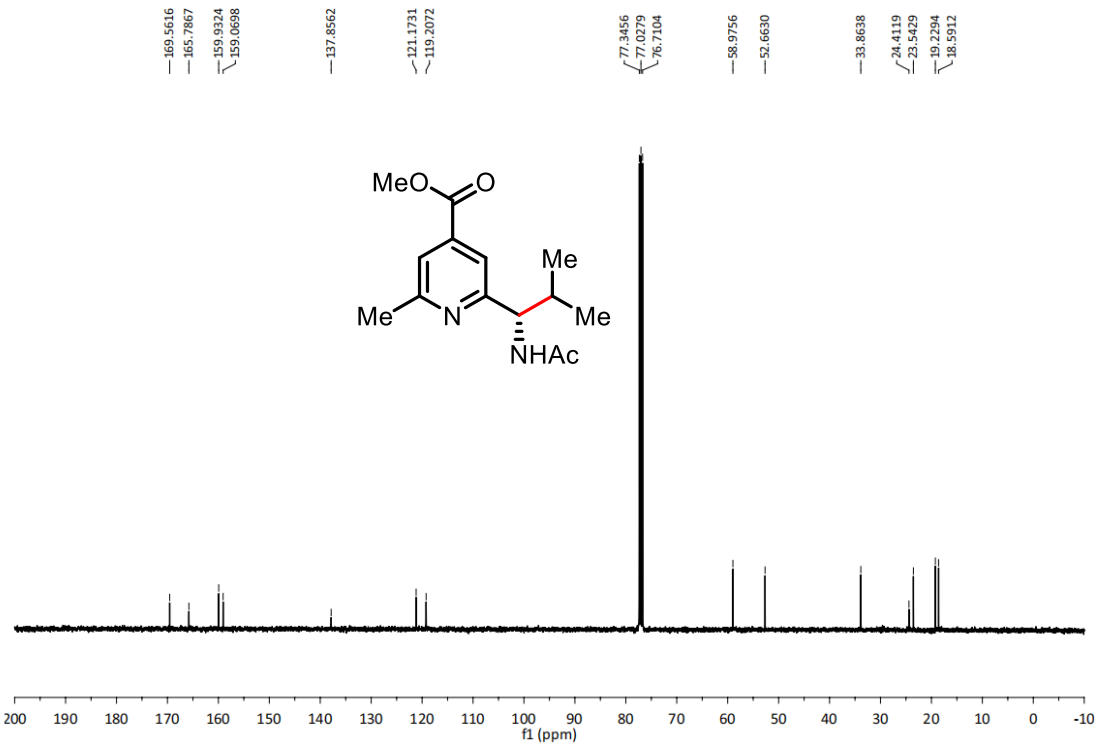
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **30**



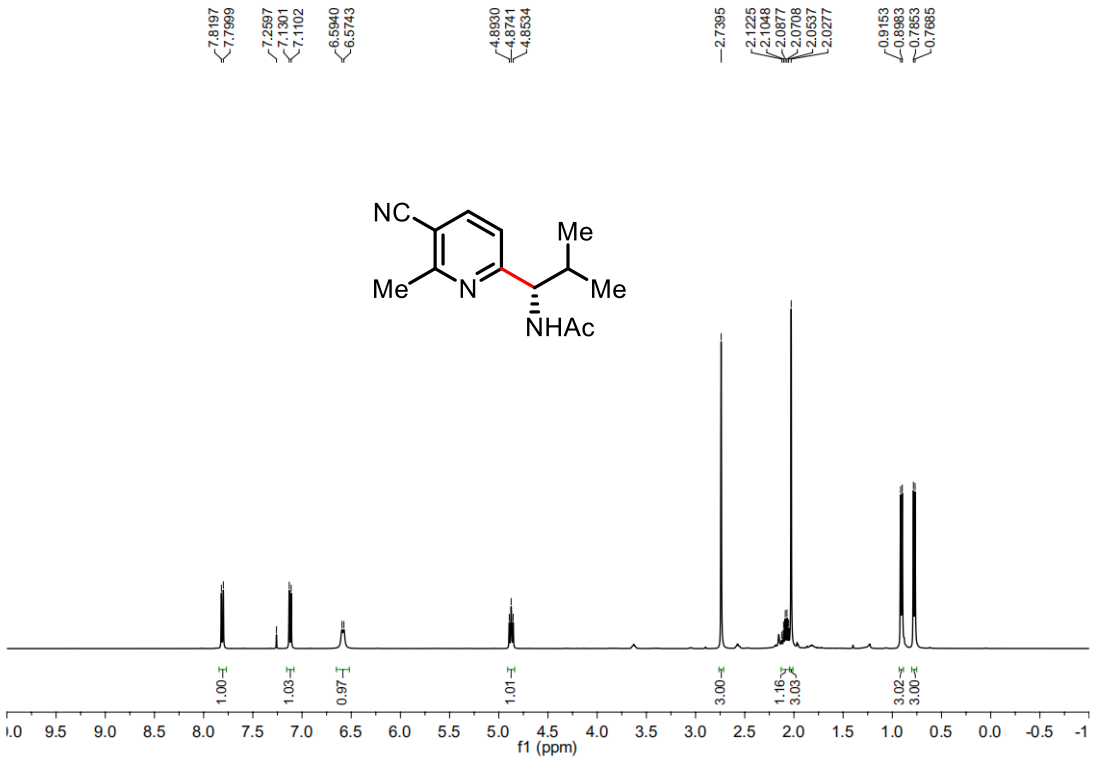
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **30**



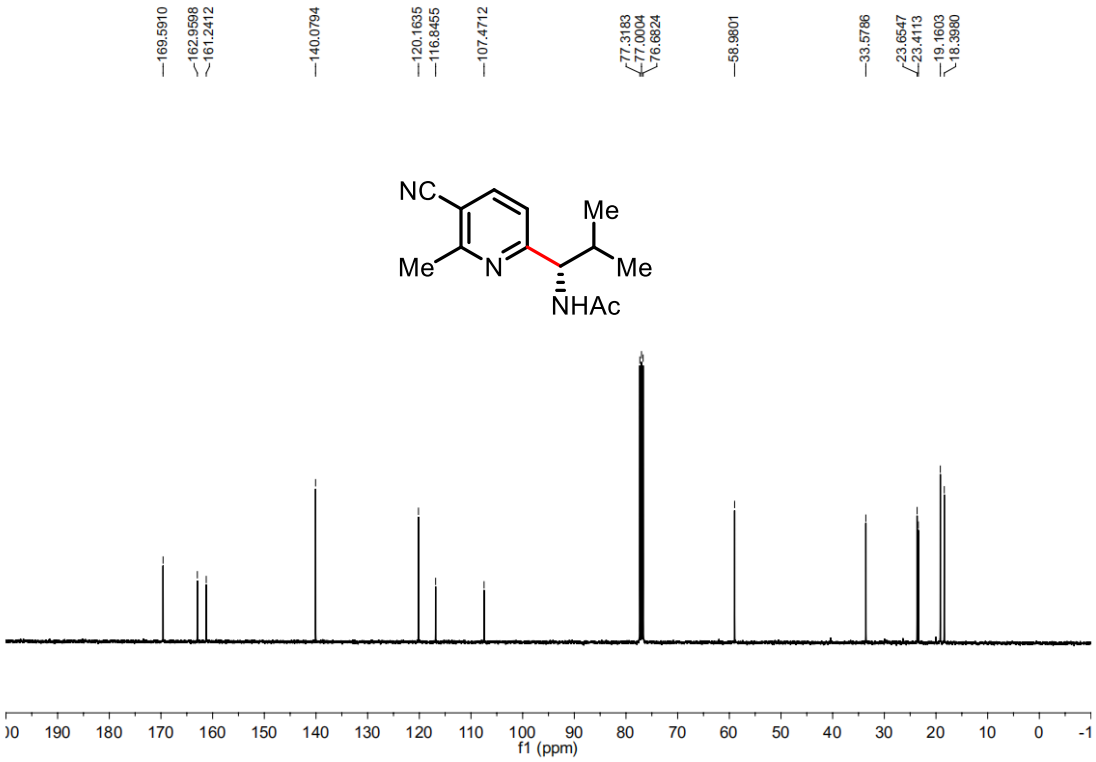
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **31**



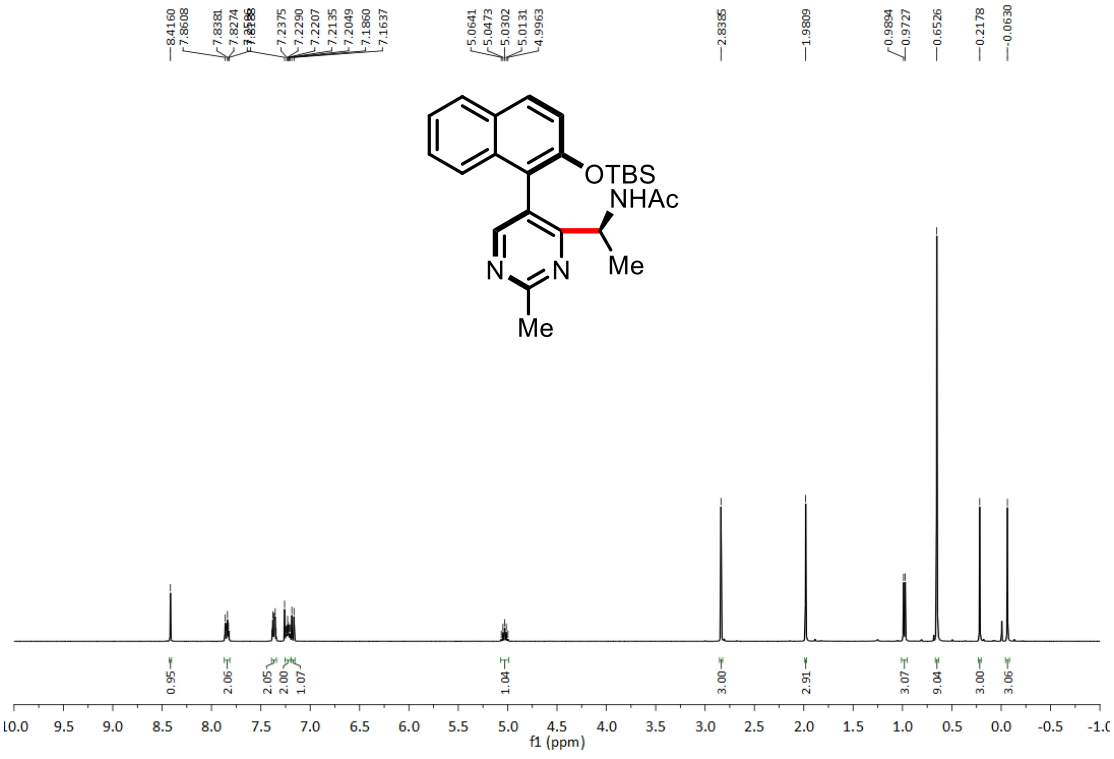
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **31**



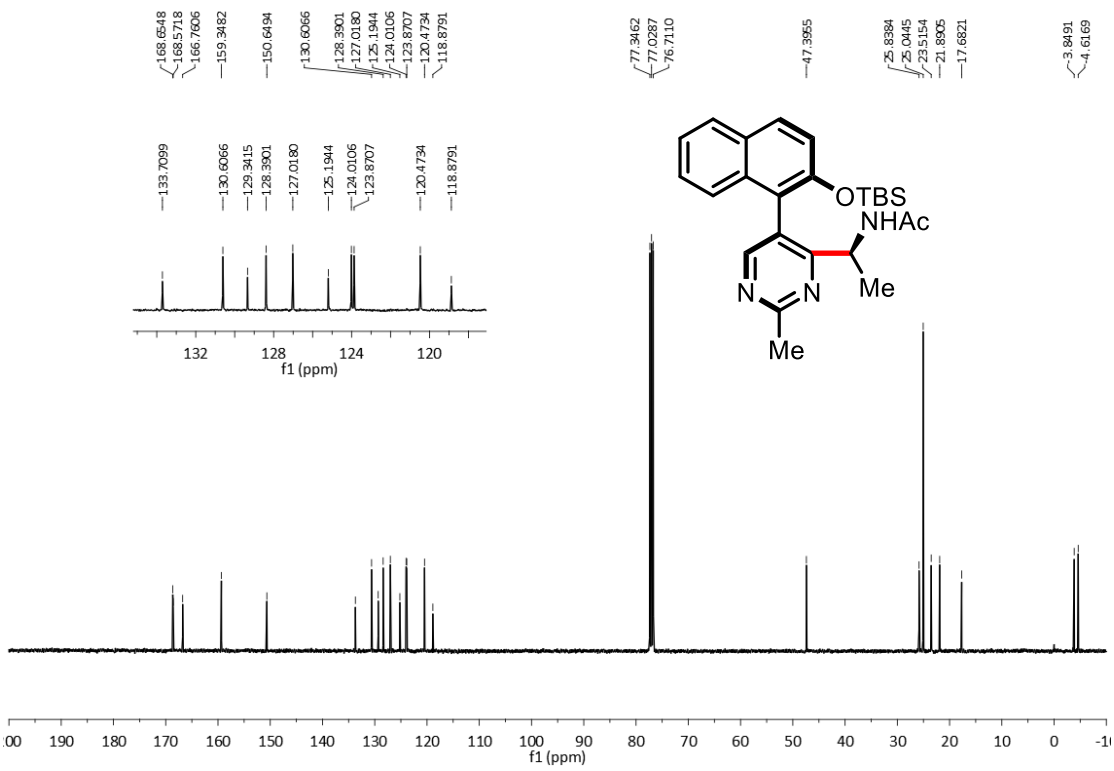
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **32**



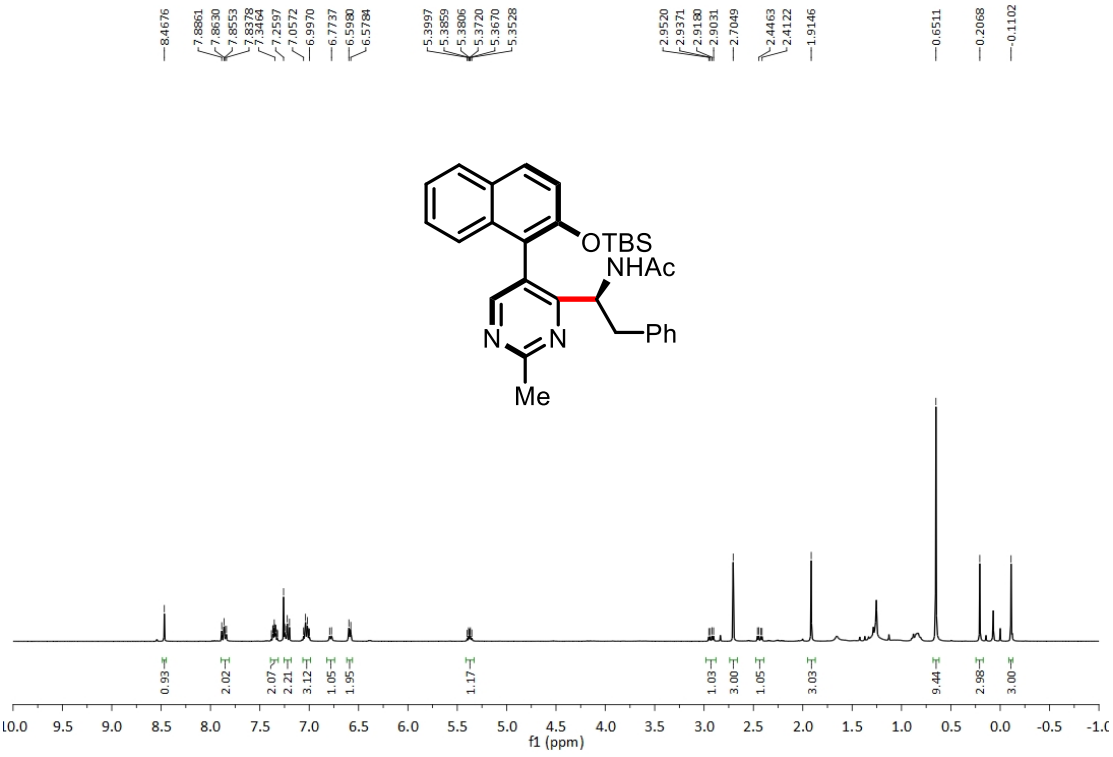
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **32**



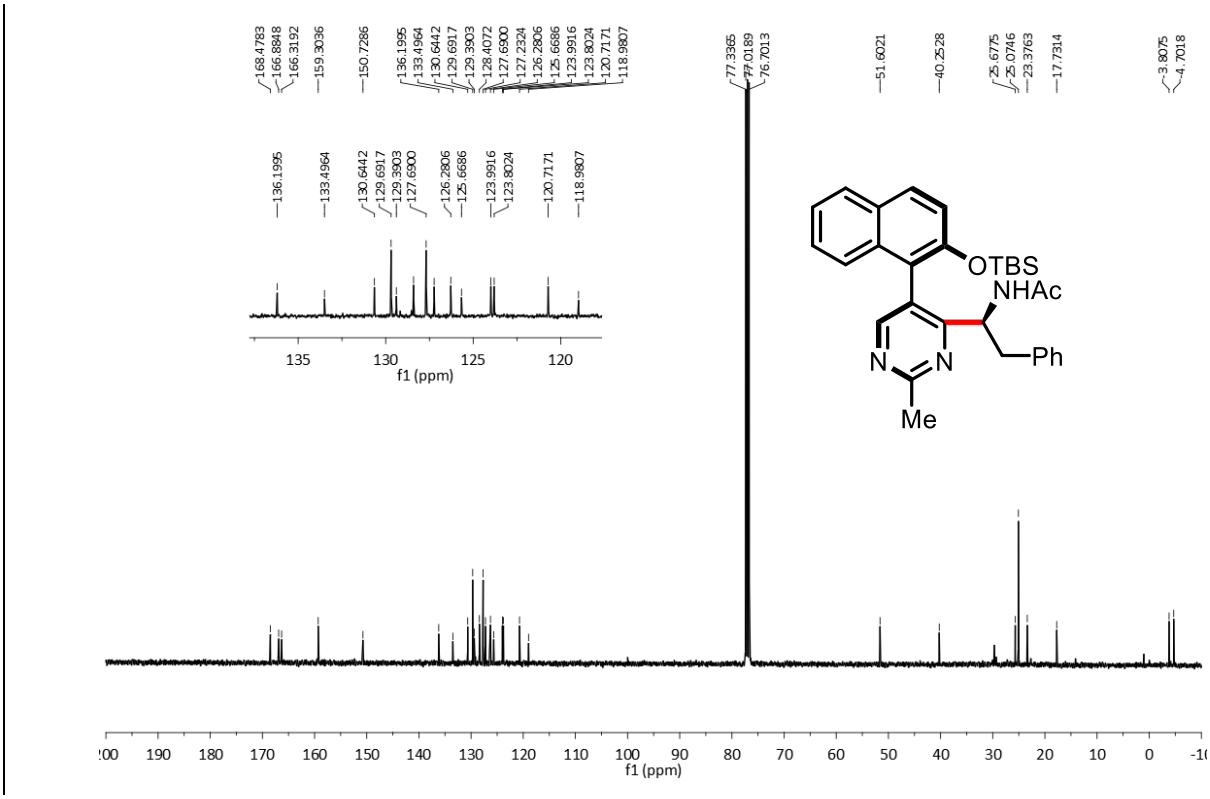
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **33**



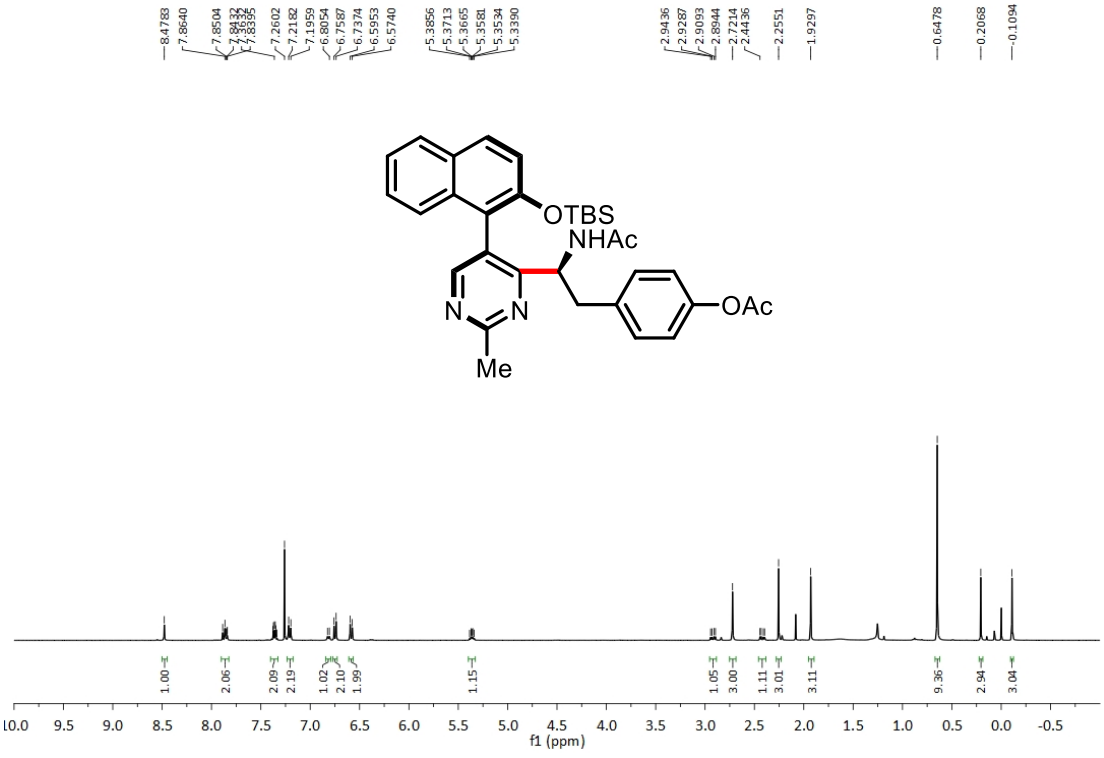
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **33**



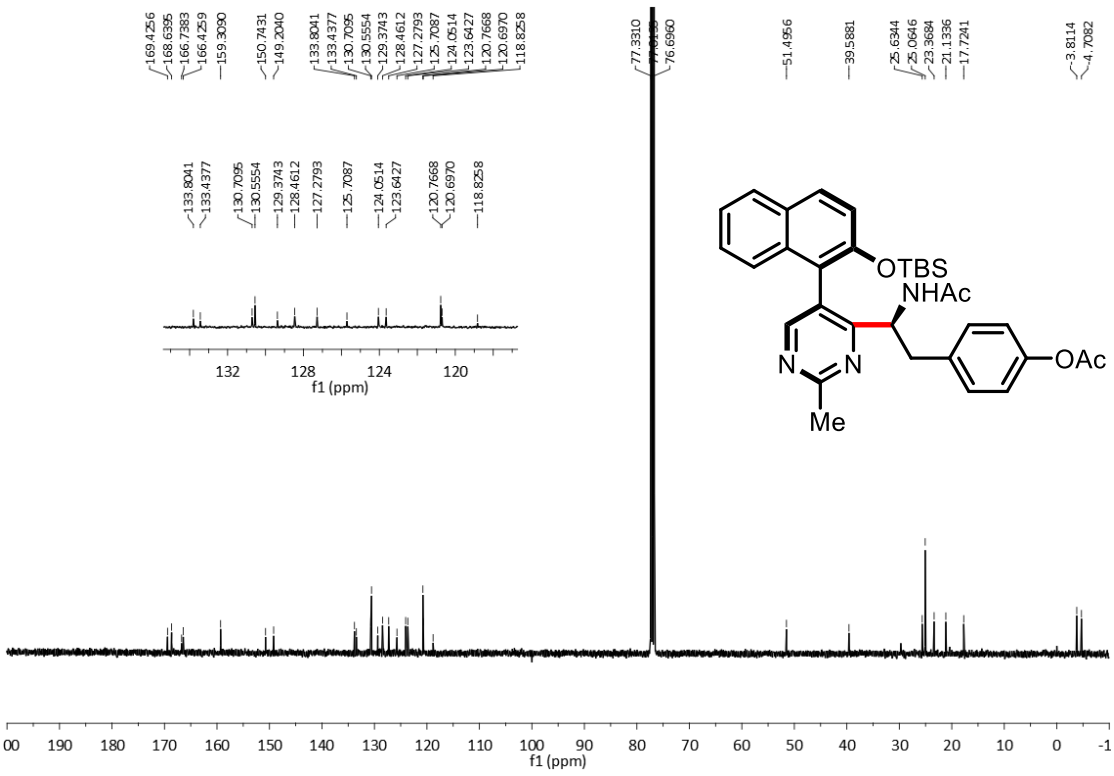
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **34**



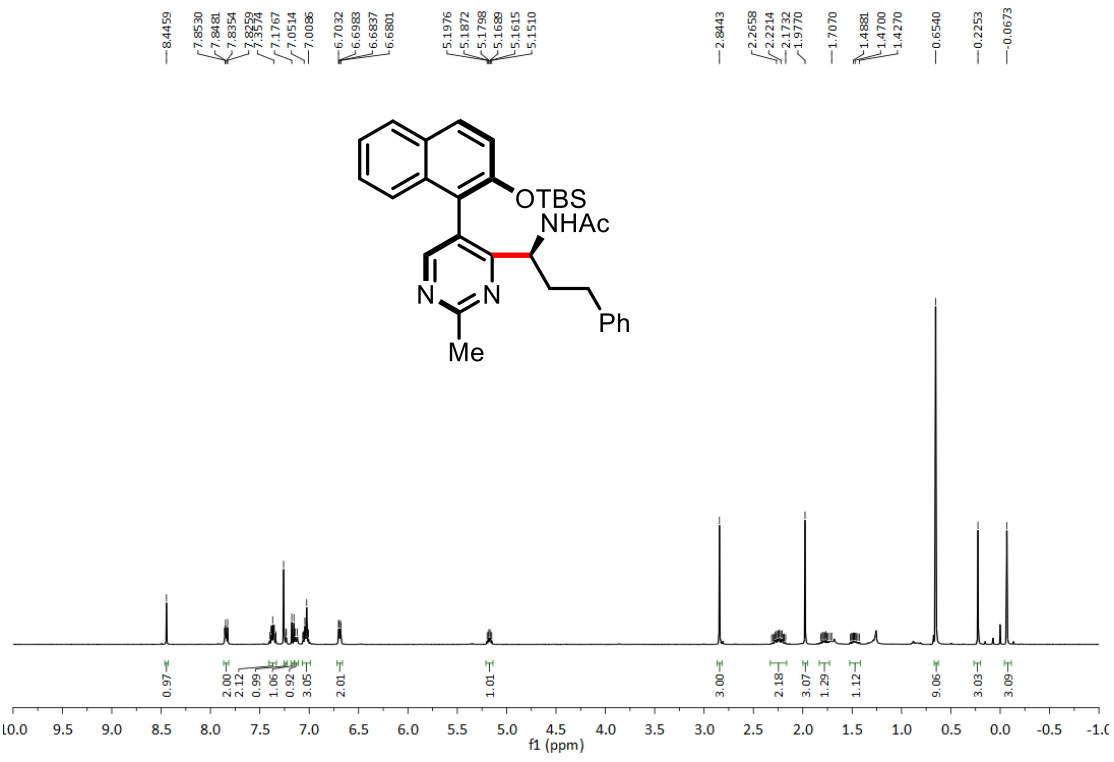
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **34**



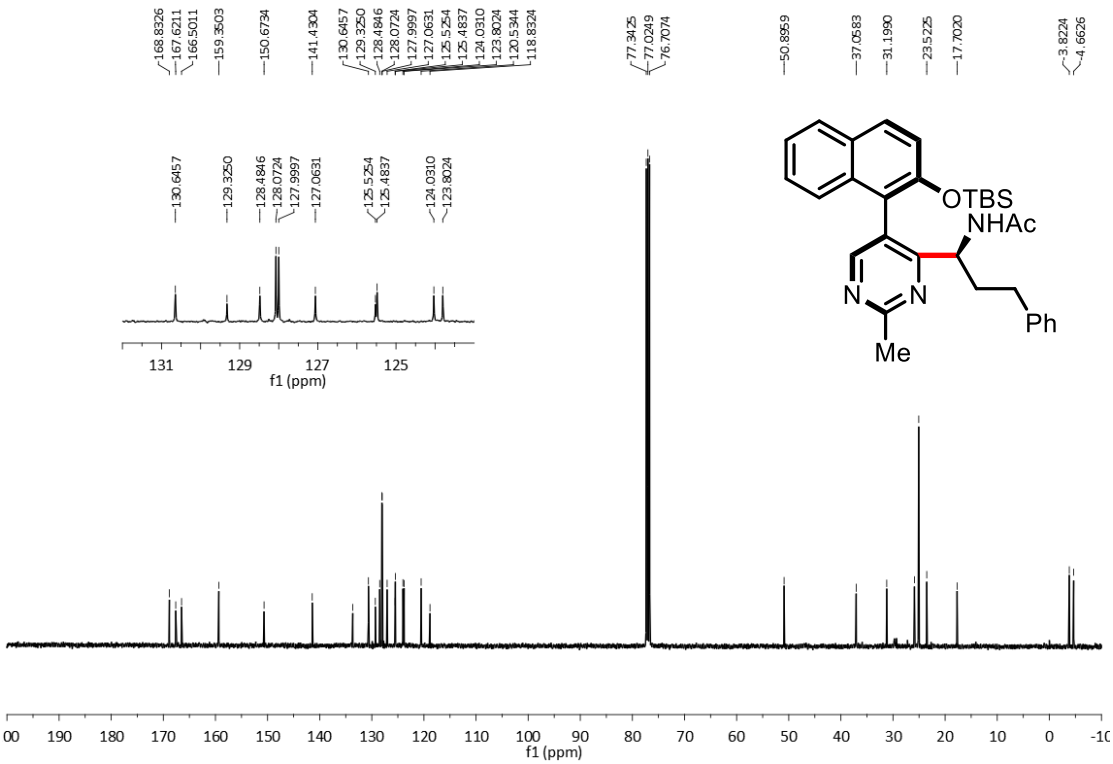
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **35**



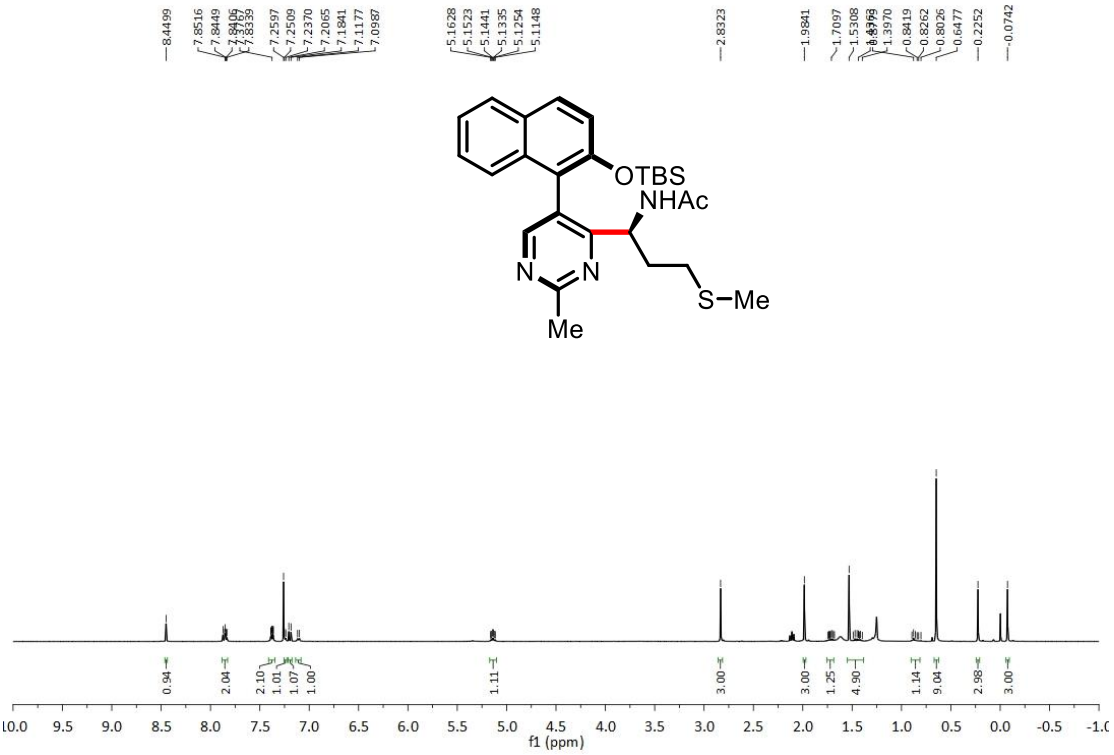
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **35**



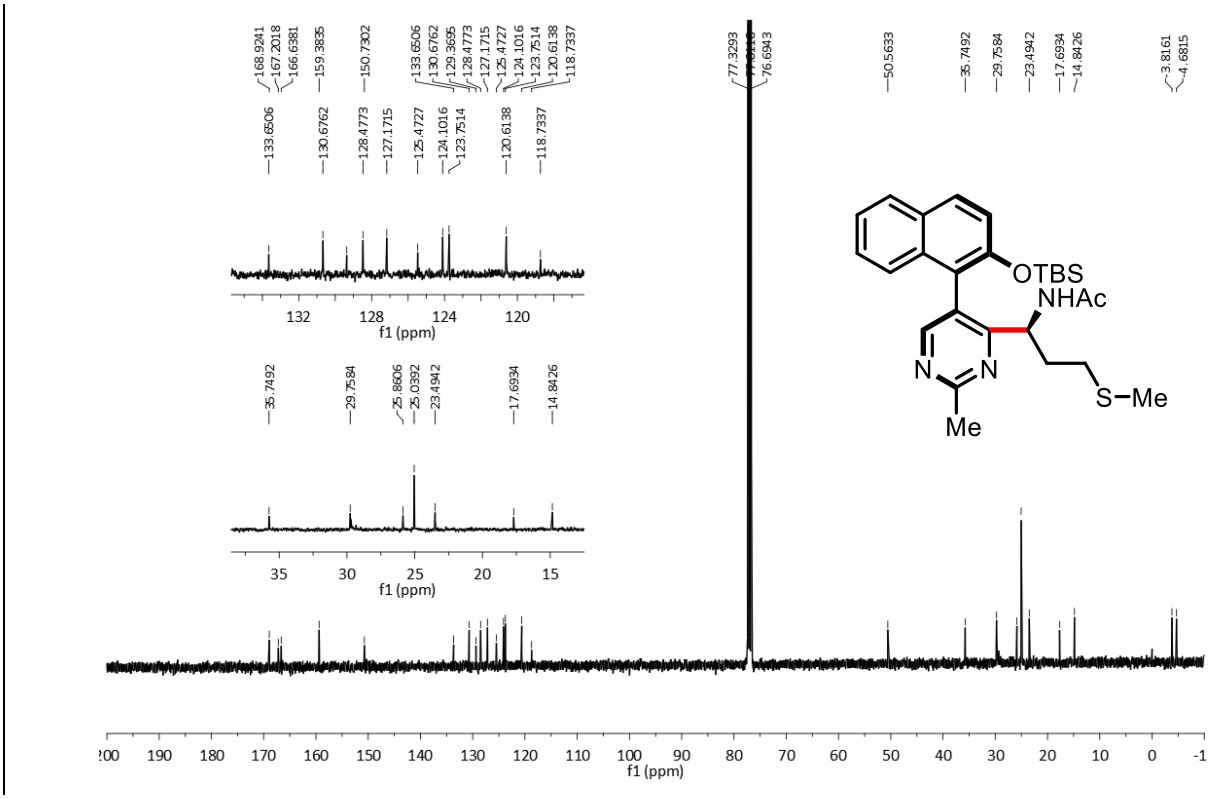
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **36**



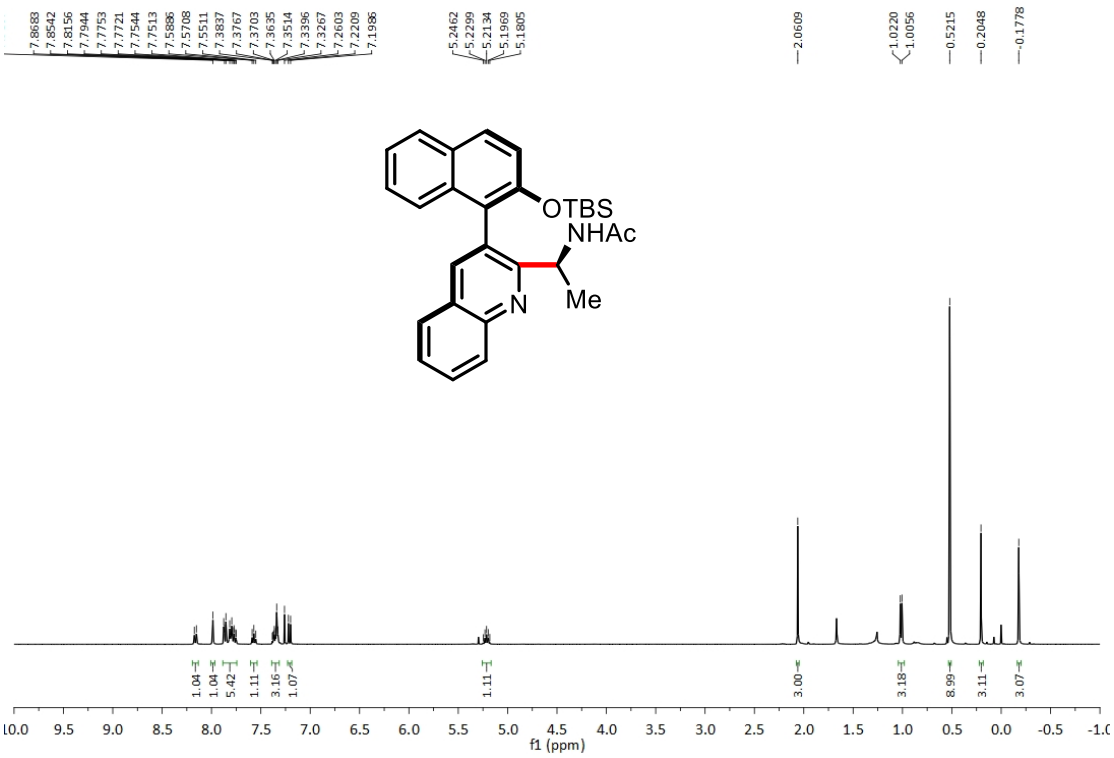
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **36**



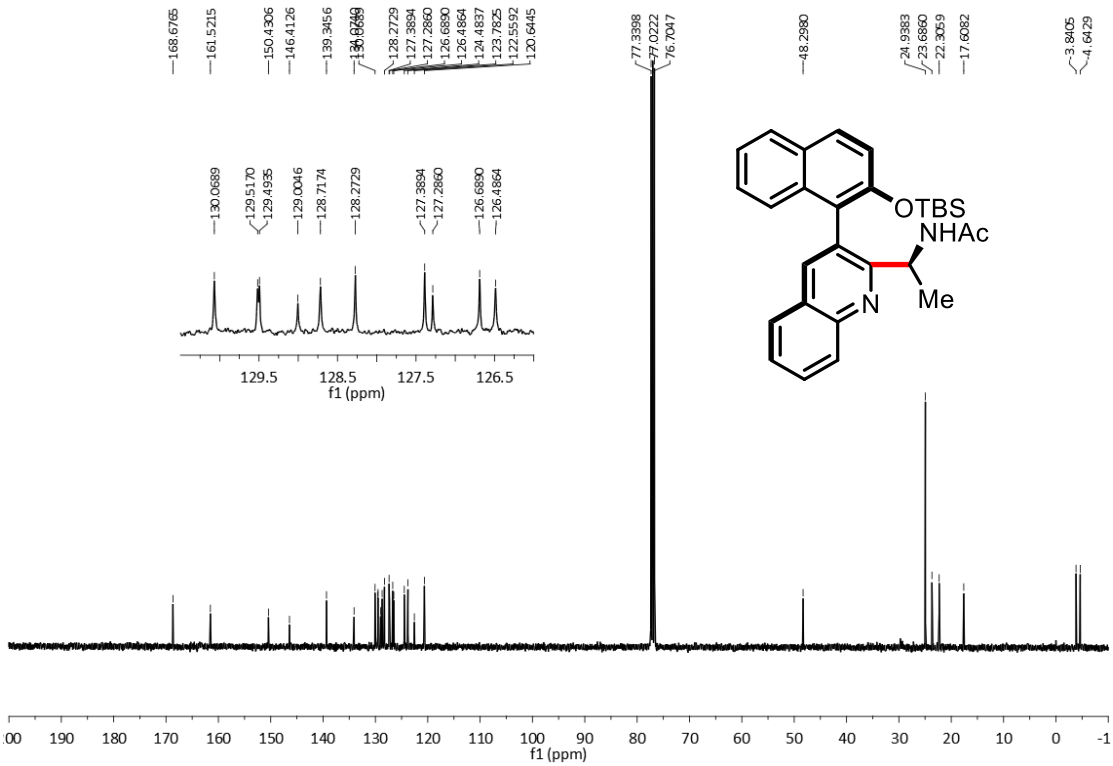
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **37**



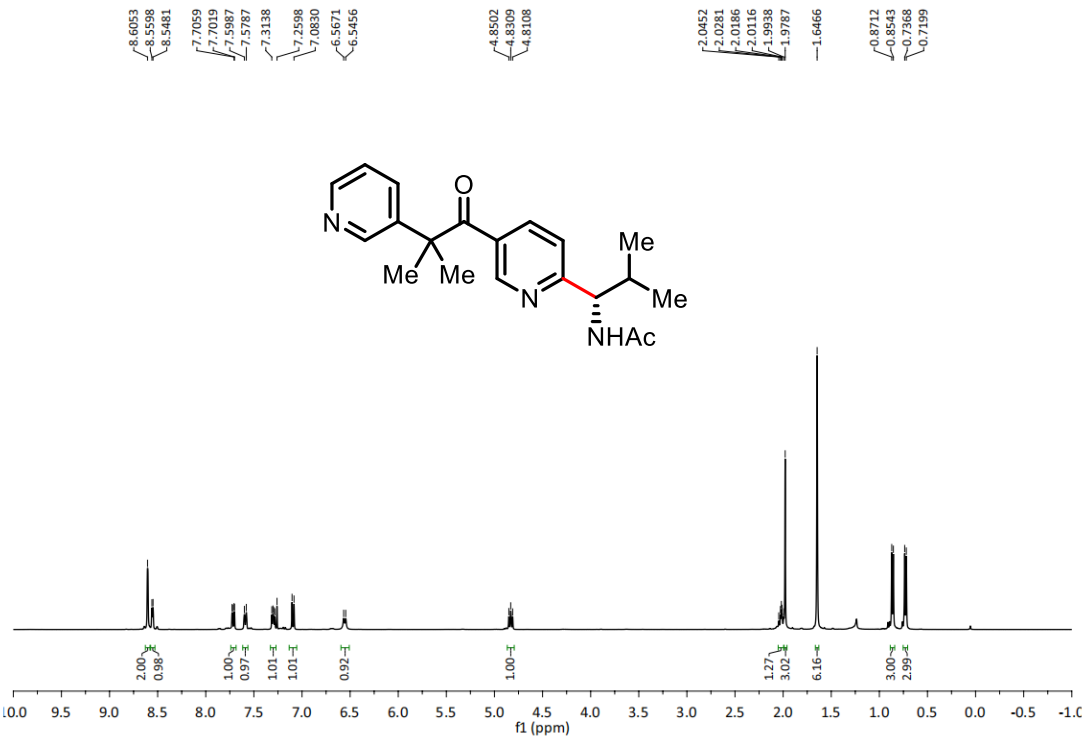
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **37**



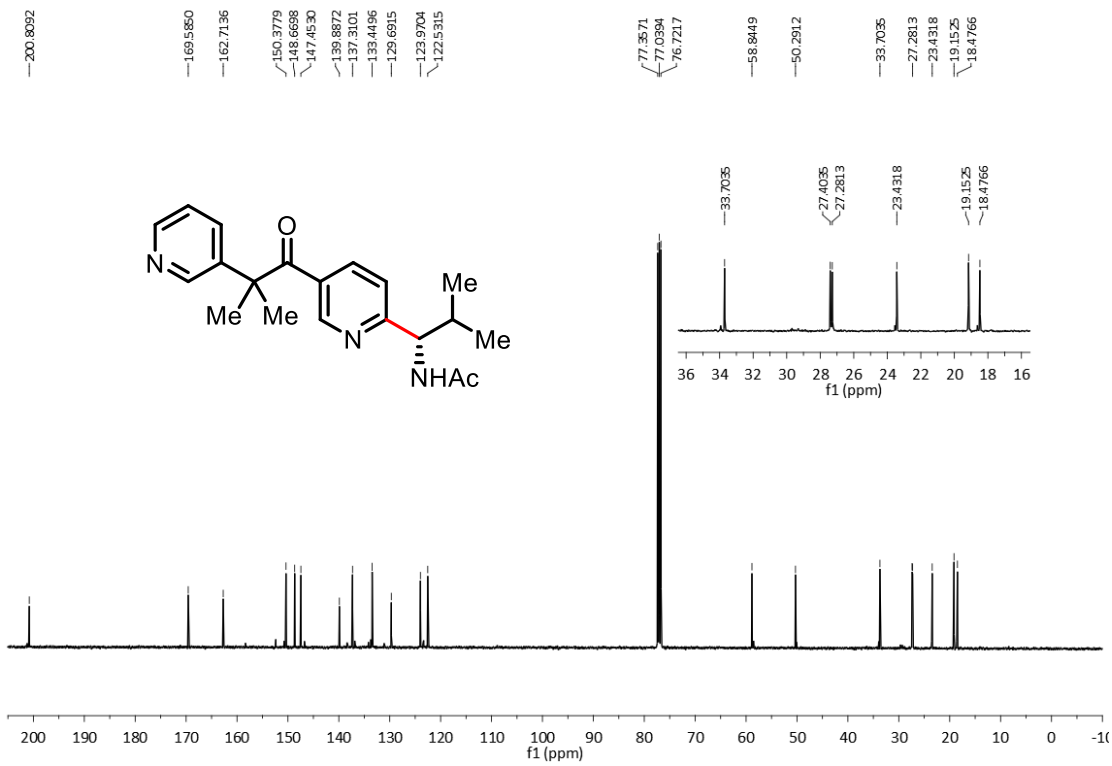
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **38**



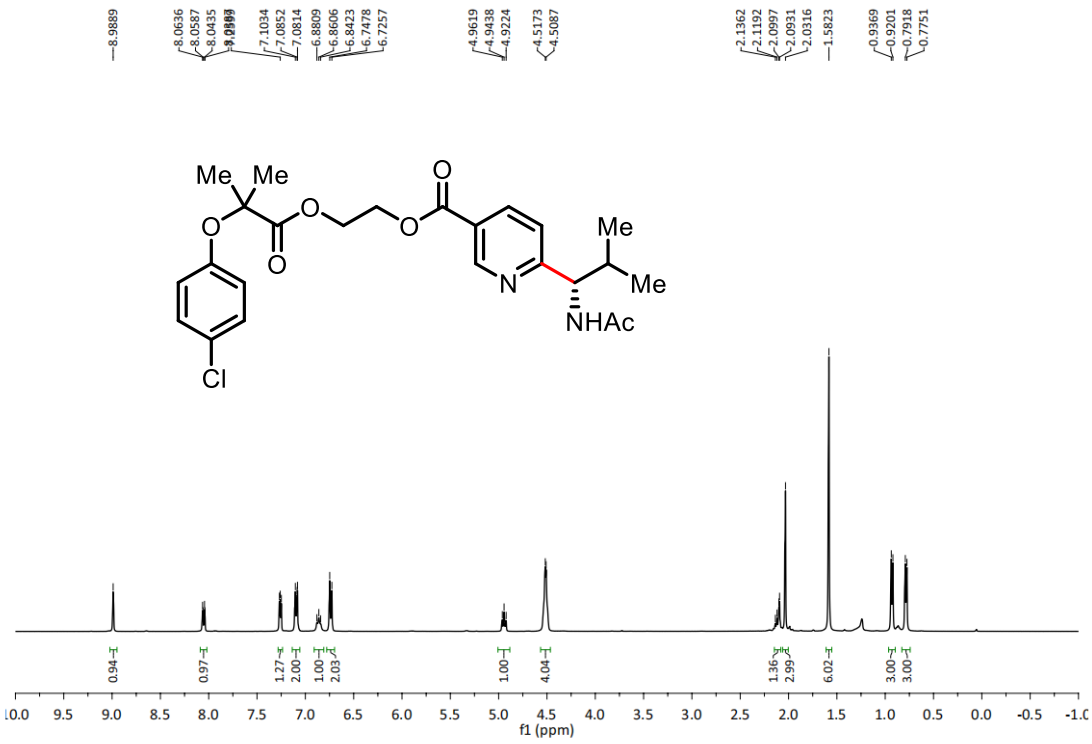
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **38**



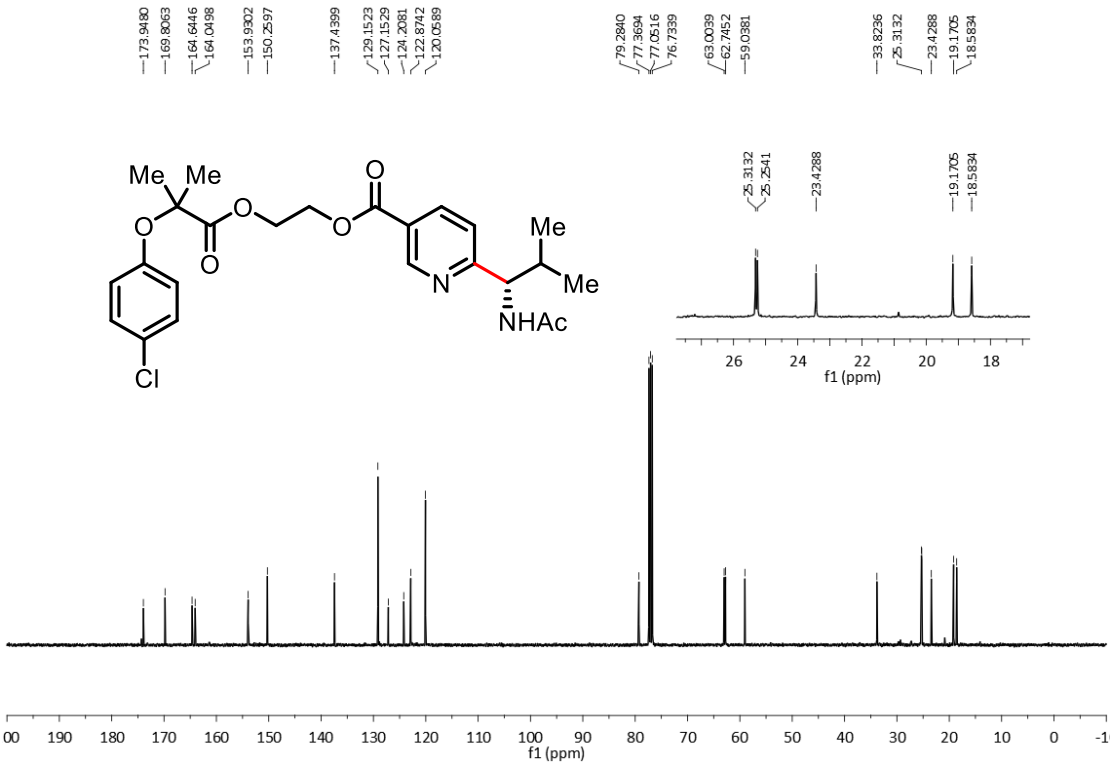
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **41**



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **41**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **43**



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **43**