Enantioselective Synthesis of Chiral Heterocyclic Biaryls via Asymmetric Suzuki–Miyaura Cross-coupling of 3-bromopyridine-4-carboxamides

Wang Xia,[a] Zhenwei Zhang,[b] Yongsu Li,[a] Xiaoding Jiang,[a] Hao Liang,[a] Yaqi Zhang,[a] Rihui Cao[a] and Liqin Qiu[a]*

[a.] School of Chemistry, The Key Laboratory of Low-carbon Chemistry & Energy Conservation of Guangdong Province, South China Sea Bio-Resource Exploitation and Utilization Collaborative Innovation Center, Guangdong Engineering Research Center of Chiral Drugs, Sun Yat-Sen University, No. 135 Xingangxi Road, Guangzhou 510275, People's Republic of China. E-mail: qiuliqin@mail.sysu.edu.cn
[b.] College of Pharmacy, Guangxi Zhuang-Yao Medicine Center of Engineering and Technology, Guangxi University of Chinese Medicine, Nanning, Guangxi 530200, People's Republic of China.

Supporting information

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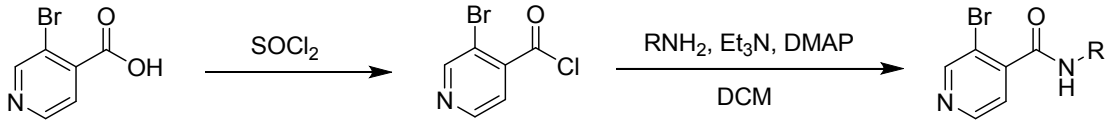
General Considerations

All reactions and manipulations were performed in a nitrogen-filled glovebox or under nitrogen using standard Schlenk techniques unless otherwise noted. Commercially available compounds were used without further purification. Solvents were dried according to standard procedures. Column chromatography was carried out using silica gel (200–300 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer (400 and 100 MHz respectively). Chemical shifts (δ) were referenced to tetramethylsilane as an internal standard (^{1}H NMR, ^{13}C NMR). High-resolution mass spectra were obtained with Shimazu LCMS-IT-TOF mass spectrometer. Optical rotations were measured on Perkin-Elmer 341 polarimeter. Enantiomeric excesses (ee values) of the products were determined by chiral HPLC analysis using an Aglient HP 1200 instrument (*n*-hexane/2-propanol as eluent) with a Chialcel AD-H or OD-H.

Experimental Section

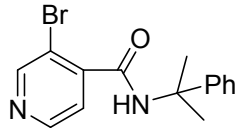
(1) General Procedure for the Synthesis of compounds 1a-1d



1a-1d

A mixture of 3-bromoisonicotinic acid (5.0 mmol) and $SOCl_2$ (8 mL) was heated to reflux for 3 h. The resulting mixture was then cooled down to room temperature and concentrated with the aid of a rotary evaporator. To the obtained residue, toluene (30 mL) was added and the resulting solution was concentrated with the aid of a rotary evaporator. Then the residue was dissolved in DCM (10 mL) and added to a solution containing RNH_2 (1.2 eq), Et_3N (1.5 eq), DMAP (5%) and DCM (10 mL). The mixture was then stirred at room temperature over night. The resulting mixture was diluted with EA (40 mL) and washed twice with water and once with brine. The organic layer was dried and concentrated in vacuo. The crude product was purified by flash chromatography.

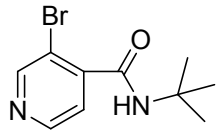
3-bromo-N-(2-phenyl-2-propyl)isonicotinamide (1a)



1a

The title compound was obtained in 78% yield as a pale yellow solid from 3-bromoisonicotinic acid by adopting the general procedure. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.78 (s, 1H), 8.60 (d, *J* = 4.0 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.29-7.47 (m, 4H), 6.38 (s, 1H), 1.87 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.01, 152.63, 148.66, 145.93, 144.82, 128.55, 127.08, 124.83, 123.45, 117.07, 57.29, 28.80.

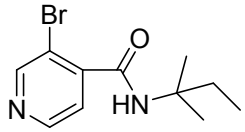
3-bromo-N-(tert-butyl)isonicotinamide (1b)



1b

The title compound was obtained in 82% yield as a white solid from 3-bromoisonicotinic acid by adopting the general procedure. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (s, 1H), 8.56 (d, *J* = 4.0 Hz, 1H), 7.40 (d, *J* = 4.0 Hz, 1H), 5.92 (s, 1H), 1.49 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.49, 152.47, 148.52, 145.34, 123.08, 117.14, 52.71, 28.66.

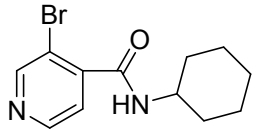
3-bromo-N-(2-ethyl-2-propyl)isonicotinamide (1c)



1c

The title compound was obtained in 76% yield as a white solid from 3-bromoisonicotinic acid by adopting the general procedure. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.77 (s, 1H), 8.59 (d, *J* = 4.0 Hz, 1H), 7.43 (d, *J* = 4.0 Hz, 1H), 5.73 (s, 1H), 1.84-1.90 (m, 2H), 1.45 (s, 6H), 0.97 (t, *J* = 4.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.45, 152.48, 148.49, 145.39, 123.14, 117.07, 55.56, 32.85, 26.29, 8.47.

3-bromo-N-(cyclohexyl)isonicotinamide (1d)



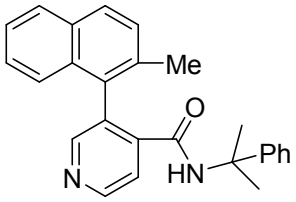
1d

The title compound was obtained in 96% yield as a white solid from 3-bromoisonicotinic acid by adopting the general procedure. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.78 (s, 1H), 8.60 (d, *J* = 4.0 Hz, 1H), 7.47 (d, *J* = 4.0 Hz, 1H), 5.99 (s, 1H), 4.03 (d, *J* = 8.0 Hz, 1H), 2.08 (d, *J* = 12.0 Hz, 2H),1.67-1.80 (m, 3H), 1.41-1.50 (m, 2H), 1.23-1.35 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.31, 152.51, 148.52, 144.77, 123.31, 117.20, 49.15, 32.75, 25.41, 24.70.

(2) General Procedure for the asymmetric Suzuki–Miyaura coupling

An oven-dried one-necked flask (15 mL) was charged with pyridyl bromide **1** (0.5 mmol, 1.0 equiv), $Pd_2(dba)_3$ (0.01 mmol, 4 mol% Pd), ligand **L1** (0.024 mmol, 4.8 mol%), 2-alkyl-1-naphthylboronic acid (1 mmol, 2.0 equiv), and K_3PO_4 (1.5 mmol, 3 equiv) in a glovebox, then dry degassed DME (5 mL) was injected into the flask. The racemic products were prepared by using S-phos as the ligand and all the racemic reactions were performed at 110 °C in toluene for 24−48 h. For the asymmetric catalytic reaction, the mixture was stirred vigorously in in DME at 80 °C for 36−96 h. The reaction was monitored by TLC. After the reaction completion, the reaction mixture was diluted with ethyl acetate and water. Followed by extraction twice, the combined organic layers was then dried over anhydrous Na_2SO_4 and then concentrated. The crude product was purified by flash chromatography on silica gel. The enantiomeric excesses (ee values) of the products were determined by HPLC with a chiral AD-H or OD-H column.

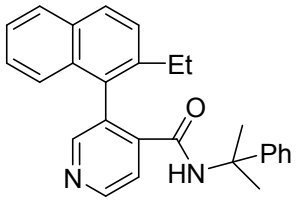
3-(2-methyl-1-naphthyl)-N-(2-phenyl-2-propyl)isonicotinamide (3aA)



3aA

The reaction was conducted for 36 h at 80 °C according to the general procedure to give the title compound **3aA** (182 mg, 96% yield) as a pale yellow oil in 87% ee. $[\alpha]_D^{25}$ = +18.9 (c = 1.8, CH_2Cl_2). The enantiomeric excess was determined by HPLC analysis using a chiral stationary phase column [Daicel chiracel® AD-H, 254 nm, n-hexane : i-PrOH = 90 : 10 as the eluent, flow rate: 1 mL/min, retention times: 17.5 min (major isomer) and 13.6 min (minor isomer)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.84 (d, *J* = 8.0 Hz, 1H), 8.56 (s, 1H), 7.88-7.94 (m, 3H), 7.44-7.52 (m, 3H), 7.30 (d, *J* = 12.0 Hz, 1H), 7.04-7.17 (m, 3H), 6.68-6.70 (m, 2H), 5.75 (s, 1H), 2.25 (s, 3H), 1.10 (s, 3H), 1.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.08, 151.79, 149.97, 145.61, 143.26, 129.11, 128.82, 128.52, 128.49, 128.13, 128.10, 127.51, 126.52, 126.49, 125.87, 125.84, 124.75, 124.72, 124.34, 123.21, 55.60, 28.03, 27.70, 20.76.

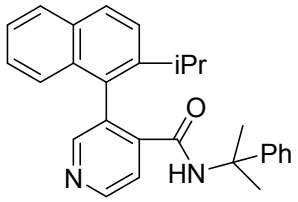
3-(2-ethyl-1-naphthyl)-N-(2-phenyl-2-propyl)isonicotinamide (3aB)



3aB

The reaction was conducted for 96 h at 80 °C according to the general procedure to give the title compound **3aB** (152 mg, 77% yield) as a pale yellow oil in 79% ee. $[\alpha]_D^{25}$ = +17.2 (c = 1.0, CH_2Cl_2). The enantiomeric excess was determined by HPLC analysis using a chiral stationary phase column [Daicel chiracel® AD-H, 254 nm, n-hexane : i-PrOH = 90 : 10 as the eluent, flow rate: 1 mL/min, retention times: 14.6 min (major isomer) and 10.7 min (minor isomer)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.85 (d, *J* = 4.0 Hz, 1H), 8.59 (s, 1H), 7.93-7.97 (m, 3H), 7.44-7.58 (m, 3H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.07-7.14 (m, 3H), 6.66-6.68 (m, 2H), 5.79 (s, 1H), 2.51-2.58 (m, 2H), 1.16 (t, *J* = 8.0 Hz, 3H), 1.08 (s, 3H), 1.02 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.86, 151.93, 149.98, 145.54, 143.16, 140.98, 132.83, 132.11, 131.36, 130.85, 129.48, 128.47, 128.09, 127.53, 127.32, 126.46, 125.96, 124.99, 124.34, 123.32, 55.53, 28.04, 27.76, 27.05, 15.27. ESI-HRMS Calcd. for $C_{27}H_{26}N_2O$ $[M+Na]^+$: 417.1937; found 417.1948.

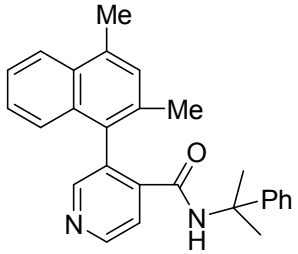
3-(2-isopropyl -1-naphthyl)-N-(2-phenyl-2-propyl)isonicotinamide (3aC)



3aC

The reaction was conducted for 96 h at 80 °C according to the general procedure to give the title compound **3aC** (106 mg, 52% yield) as a pale yellow oil in 92% ee. $[\alpha]_D^{25}$ = +11.7 (c = 0.6, CH_2Cl_2). The enantiomeric excess was determined by HPLC analysis using a chiral stationary phase column [Daicel chiracel® AD-H, 254 nm, n-hexane : i-PrOH = 90 : 10 as the eluent, flow rate: 1 mL/min, retention times: 17.7 min (major isomer) and 8.4 min (minor isomer)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.85 (d, *J* = 4.0 Hz, 1H), 8.59 (s, 1 H), 7.96-8.02 (m, 3H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.44-7.55 (m, 2H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.03-7.09 (m, 3H), 6.62-6.64 (m, 2H), 5.84 (s, 1H), 2.76-2.83 (m, 1H), 1.20-1.25 (m, 6H), 1.11 (s, 3H), 0.98 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.79, 151.79, 149.98, 145.49, 145.35, 143.08, 132.77, 132.07, 130.95, 130.50, 129.77, 128.47, 128.12, 127.54, 126.43, 126.04, 125.32, 124.34, 124.20, 123.36, 55.50, 30.91, 28.22, 27.73, 24.40, 23.11. ESI-HRMS Calcd. for $C_{28}H_{28}N_2O$ [M+Na]$^+$: 431.2094; found 431.2100.

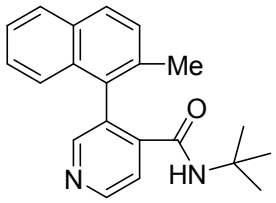
3-(2,4-methyl -1-naphthyl)-N-(2-phenyl-2-propyl)isonicotinamide (3aD)



3aD

The reaction was conducted for 60 h at 80 °C according to the general procedure to give the title compound **3aD** (181 mg, 92% yield) as a pale yellow oil in 80% ee. $[\alpha]_D^{25}$ = +22.6 (c = 1.6, CH_2Cl_2). The enantiomeric excess was determined by HPLC analysis using a chiral stationary phase column [Daicel chiracel® AD-H, 254 nm, n-hexane : i-PrOH = 90 : 10 as the eluent, flow rate: 1 mL/min, retention times: 11.1 min (major isomer) and 9.8 min (minor isomer)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.84 (d, *J* = 4.0 Hz, 1H), 8.55 (s, 1 H), 8.08 (d, *J* = 8.0 Hz, 1H), 7.95-7.96 (m, 1H), 7.54-7.58 (m, 1H), 7.44-7.48 (m, 1H), 7.34 (s, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.06-7.14 (m, 3H), 6.66-6.69 (m, 2H), 5.82 (s, 1H), 2.76 (s, 3H), 2.20 (s, 3H), 1.09 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.02, 152.08, 149.88, 145.70, 143.12, 135.67, 134.64, 132.88, 131.43, 131.36, 130.28, 129.54, 128.09, 128.04, 127.12, 126.46, 125.68, 125.35, 124.63, 124.28, 123.23, 55.61, 27.86, 27.62, 20.60, 19.43. ESI-HRMS Calcd. for $C_{27}H_{26}N_2O$ [M+Na]$^+$: 417.1937; found 417.1936.

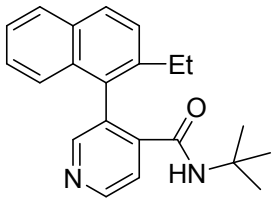
3-(2-methyl-1-naphthyl)-N-(tert-butyl)isonicotinamide (3bA)



3bA

The reaction was conducted for 60 h at 80 °C according to the general procedure to give the title compound **3bA** (135 mg, 85% yield) as a pale yellow oil in 62% ee. $[\alpha]_D^{25}$ = +20.7 (c = 1.0, CH_2Cl_2). The enantiomeric excess was determined by HPLC analysis using a chiral stationary phase column [Daicel chiracel® AD-H, 254 nm, n-hexane : i-PrOH = 90 : 10 as the eluent, flow rate: 1 mL/min, retention times: 8.7 min (major isomer) and 7.2 min (minor isomer)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.84 (d, *J* = 4.0 Hz, 1H), 8.56 (s, 1 H), 7.90-7.98 (m, 3H), 7.41-7.50 (m, 3H), 7.26 (d, *J* = 8.0 Hz, 1H), 5.16 (s, 1H), 2.23 (s, 3H), 0.69 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.74, 151.69, 149.92, 143.88, 135.02, 132.76, 132.08, 128.93, 128.80, 128.39, 127.44, 125.73, 124.59, 122.59, 50.97, 27.63, 27.59, 20.64. ESI-HRMS Calcd. for $C_{21}H_{22}N_2O$ $[M+Na]^+$: 341.1624; found 341.1623.

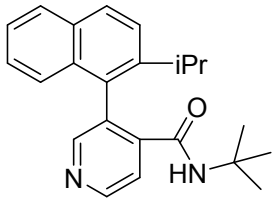
3-(2-ethyl-1-naphthyl)-N-(tert-butyl)isonicotinamide (3bB)



3bB

The reaction was conducted for 96 h at 80 °C according to the general procedure to give the title compound **3bB** (138 mg, 83% yield) as a pale yellow oil in 64% ee. $[\alpha]_D^{25}$ = +17.9 (c = 1.5, CH_2Cl_2). The enantiomeric excess was determined by HPLC analysis using a chiral stationary phase column [Daicel chiracel® AD-H, 254 nm, n-hexane : i-PrOH = 90 : 10 as the eluent, flow rate: 1 mL/min, retention times: 7.6 min (major isomer) and 6.2 min (minor isomer)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.85 (d, *J* = 4.0 Hz, 1H), 8.58 (s, 1 H), 7.91-7.97 (m, 3H), 7.41-7.56 (m, 3H), 7.24 (d, *J* = 8.0 Hz, 1H), 5.22 (s, 1H), 2.47-2.57 (m, 2H), 1.15 (t, *J* = 8.0 Hz, 3H), 0.67 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.50, 151.85, 149.95, 143.82, 140.88, 132.77, 132.00, 131.32, 130.82, 129.25, 128.32, 127.41, 127.30, 125.80, 124.82, 123.04, 50.98, 27.62, 26.94, 15.26. ESI-HRMS Calcd. for $C_{22}H_{24}N_2O$ $[M+Na]^+$: 355.1781; found 355.1778.

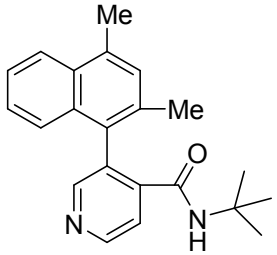
3-(2-isopropyl-1-naphthyl)-N-(tert-butyl)isonicotinamide (3bC)



3bC

The reaction was conducted for 96 h at 80 °C according to the general procedure to give the title compound **3bC** (109 mg, 63% yield) as a colorless oil in 75% ee. $[\alpha]_D^{25}$ = +20.8 (c = 0.7, CH_2Cl_2). The enantiomeric excess was determined by HPLC analysis using a chiral stationary phase column [Daicel chiracel® AD-H, 254 nm, n-hexane : i-PrOH = 90 : 10 as the eluent, flow rate: 1 mL/min, retention times: 7.5 min (major isomer) and 5.5 min (minor isomer)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.84 (d, *J* = 4.0 Hz, 1H), 8.56 (s, 1 H), 7.89-8.00 (m, 3H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.41-7.50 (m, 2H), 7.20 (d, *J* = 8.0 Hz, 1H), 5.27 (s, 1H), 2,72-2.76 (m, 1H), 1,19-1.22 (m, 6H), 0.65 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.40, 151.67, 145.93, 145.24, 143.76, 132.68, 131.93, 130.94, 130.44, 129.52, 128.31, 127.42, 125.87, 125.09, 124.13, 123.08, 50.98, 30.83, 27.65, 24.31, 23.12. ESI-HRMS Calcd. for $C_{23}H_{26}N_2O$ $[M+H]^+$: 347.2118; found 347. 2120. ESI-HRMS Calcd. for $C_{22}H_{24}N_2O$ $[M+H]^+$: 333.1961; found 333.1959.

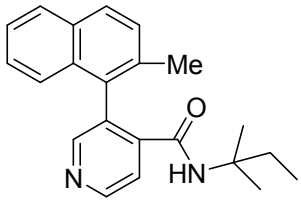
3-(2,4-dimethyl-1-naphthyl)-N-(tert-butyl)isonicotinamide (3bD)



3bD

The reaction was conducted for 96 h at 80 °C according to the general procedure to give the title compound **3bD** (146 mg, 88% yield) as a colorless oil in 57% ee. $[\alpha]_D^{25}$ = +14.4 (c = 0.7, CH_2Cl_2). The enantiomeric excess was determined by HPLC analysis using a chiral stationary phase column [Daicel chiracel® OD-H, 254 nm, n-hexane : i-PrOH = 97 : 3 as the eluent, flow rate: 1 mL/min, retention times: 11.5 min (major isomer) and 14.0 min (minor isomer)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (s, 1H), 8.53 (s, 1 H), 8.06 (d, *J* = 4.0 Hz, 1H), 7.90 (s, 1H), 7.49-7.51 (m, 1H), 7.40-7.43 (m, 1H), 7.23(s, 1H), 7.25-7.27 (m, 1H), 5.23 (s, 1H), 2.75 (s, 3H), 2.17 (s, 3H), 0.67 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.67, 151.95, 149.83, 143.81, 135.46, 134.52, 132.81, 131.42, 131.25, 130.22, 129.49, 127.04, 125.55, 125.18, 124.53, 122.96, 50.96, 27.58, 20.55, 19.40. ESI-HRMS Calcd. for $C_{22}H_{24}N_2O$ $[M+H]^+$: 333.1961; found 333.1966.

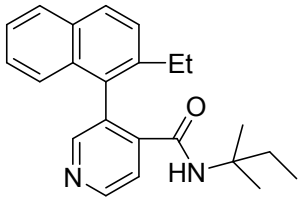
3-(2-methyl-1-naphthyl)-N-(2-ethyl-2-propyl)isonicotinamide (3cA)



3cA

The reaction was conducted for 60 h at 80 °C according to the general procedure to give the title compound **3cA** (144 mg, 87% yield) as a colorless oil in 60% ee. $[\alpha]_D^{25}$ = +21.3 (c = 1.1, CH_2Cl_2). The enantiomeric excess was determined by HPLC analysis using a chiral stationary phase column [Daicel chiracel® AD-H, 254 nm, n-hexane : i-PrOH = 90 : 10 as the eluent, flow rate: 1 mL/min, retention times: 8.0 min (major isomer) and 6.7 min (minor isomer)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.83 (d, *J* = 8.0 Hz, 1H), 8.53 (s, 1 H), 7.90-7.94 (m, 3H), 7.40-7.49 (m, 3H), 7.25 (d, *J* = 8.0 Hz, 1H), 5.15 (s, 1H), 2,22 (s, 3H), 1,08-1.15 (m, 2H), 0.66 (s, 3H), 0.65 (s, 3H), 0.27 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.48, 151.73, 149.89, 143.70, 134.97, 132.73, 132.11, 131.13, 128.90, 128.77, 128.33, 127.35, 125.67, 124.59, 123.01, 53.95, 32.46, 25.22, 25.11, 20.64, 7.56. ESI-HRMS Calcd. for $C_{22}H_{24}N_2O$ $[M+H]^+$: 333.1961; found 333.1966.

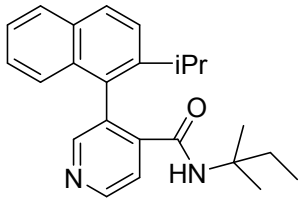
3-(2-ethyl-1-naphthyl)-N-(2-ethyl-2-propyl)isonicotinamide (3cB)



3cB

The reaction was conducted for 96 h at 80 °C according to the general procedure to give the title compound **3cB** (163 mg, 94% yield) as a pale yellow oil in 59% ee. $[\alpha]_D^{25}$ = +19.8 (c = 1.7, CH_2Cl_2). The enantiomeric excess was determined by HPLC analysis using a chiral stationary phase column [Daicel chiracel® AD-H, 254 nm, n-hexane : i-PrOH = 90 : 10 as the eluent, flow rate: 1 mL/min, retention times: 7.3 min (major isomer) and 6.1 min (minor isomer)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.85 (d, *J* = 4.0 Hz, 1H), 8.56 (s, 1 H), 7.91-7.97 (m, 3H), 7.42-7.55 (m, 3H), 7.23 (d, *J* = 8.0 Hz, 1H), 5.19 (s, 1H), 2,44-2.57 (m, 2H), 1.15 (t, *J* = 8.0 Hz, 3H), 1,05-1.21 (m, 2H), 0.66 (s, 3H), 0.62 (s, 3H), 0.27 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.36, 151.94, 149.95, 143.69, 140.93, 132.80, 132.10, 131.39, 130.81, 129.31, 128.35, 127.41, 127.32, 125.83, 124.89, 123.15, 54.03, 32.38, 27.02, 25.26, 25.15, 15.21, 7.65, 7.51. ESI-HRMS Calcd. for $C_{23}H_{26}N_2O$ $[M+H]^+$: 347.2118; found 347.2128.

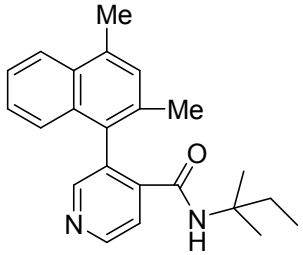
3-(2-isopropyl-1-naphthyl)-N-(2-ethyl-2-propyl)isonicotinamide (3cC)



3cC

The reaction was conducted for 96 h at 80 °C according to the general procedure to give the title compound **3cC** (136 mg, 76% yield) as a pale yellow oil in 80% ee. $[\alpha]_D^{25}$ = +25.3 (c = 1.2, CH_2Cl_2). The enantiomeric excess was determined by HPLC analysis using a chiral stationary phase column [Daicel chiracel® AD-H, 254 nm, n-hexane : i-PrOH = 90 : 10 as the eluent, flow rate: 1 mL/min, retention times: 7.7 min (major isomer) and 5.6 min (minor isomer)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.86 (d, *J* = 4.0 Hz, 1H), 8.56 (s, 1 H), 7.91-8.01 (m, 3H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.41-7.52 (m, 2H), 7.21 (d, *J* = 8.0 Hz, 1H), 5.23 (s, 1H), 2,72-2.79 (m, 1H), 1.22 (t, *J* = 8.0 Hz, 6H), 1,00-1.17 (m, 2H), 0.69 (s, 3H), 0.57 (s, 3H), 0.26 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.26, 151.78, 149.94, 145.31, 143.60, 132.71, 132.02, 130.89, 130.50, 129.56, 128.32, 127.41, 125.88, 125.16, 124.16, 123.18, 54.05, 32.27, 30.86, 25.31, 25.18, 24.31, 23.09, 7.66. ESI-HRMS Calcd. for $C_{24}H_{28}N_2O$ $[M+H]^+$: 361.2274; found 361.2280.

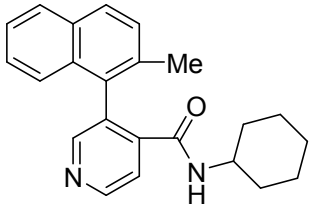
3-(2,4-dimethyl-1-naphthyl)-N-(2-ethyl-2-propyl)isonicotinamide (3cD)



3cD

The reaction was conducted for 96 h at 80 °C according to the general procedure to give the title compound **3cD** (157 mg, 91% yield) as a pale yellow oil in 64% ee. $[\alpha]_D^{25}$ = +17.4 (c = 1.5, CH_2Cl_2). The enantiomeric excess was determined by HPLC analysis using a chiral stationary phase column [Daicel chiracel® OD-H, 254 nm, n-hexane : i-PrOH = 97 : 3 as the eluent, flow rate: 1 mL/min, retention times: 14.2 min (major isomer) and 11.0 min (minor isomer)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82 (s, 1H), 8.52 (s, 1 H), 8.06 (d, *J* = 4.0 Hz, 1H), 7.94 (s, 1H), 7.49-7.51 (m, 1H), 7.40-7.43 (m, 1H), 7.23(s, 1H), 7.25-7.27 (m, 1H), 5.22 (s, 1H), 2.75 (s, 3H), 2.18 (s, 3H), 1.06-1.13 (m, 2H), 0.65 (s, 6H), 0.25 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.48, 152.03, 149.86, 143.60, 135.52, 134.59, 132.83, 131.41, 131.33, 130.28, 129.54, 127.05, 125.59, 125.25, 124.55, 123.10, 53.93, 32.46, 25.24, 25.14, 20.59, 19.40, 7.55. ESI-HRMS Calcd. for $C_{23}H_{26}N_2O$ $[M+H]^+$: 347.2118; found 347.2116.

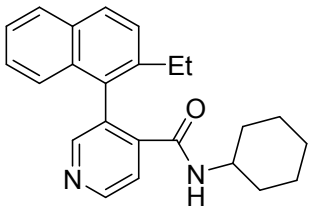
3-(2-methyl-1-naphthyl)-N-(cyclohexyl)isonicotinamide (3dA)



3dA

The reaction was conducted for 96 h at 80 °C according to the general procedure to give the title compound **3dA** (153 mg, 89% yield) as a colorless oil in 57% ee. $[\alpha]_D^{25}$ = +15.2 (c = 1.2, CH_2Cl_2). The enantiomeric excess was determined by HPLC analysis using a chiral stationary phase column [Daicel chiracel® AD-H, 254 nm, n-hexane : i-PrOH = 90 : 10 as the eluent, flow rate: 1 mL/min, retention times: 31.3 min (major isomer) and 26.7 min (minor isomer)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.85 (d, *J* = 4.0 Hz, 1H), 8.54 (s, 1 H), 7.90-7.98 (m, 3H), 7.41-7.51 (m, 3H), 7.26 (d, *J* = 8.0 Hz, 1H), 5.32 (s, 1H), 3.52-3.54 (m, 1H), 2.22 (s, 3H), 0.80-1.35 (m, 8H), 0.18-1.37 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.38, 151.84, 149.85, 142.83, 134.95, 132.63, 132.09, 131.96, 131.31, 128.99, 128.75, 128.35, 127.36, 125.71, 124.56, 124.46, 123.20, 47.63, 31.62, 31.55, 25.09, 23.68, 20.69. ESI-HRMS Calcd. for $C_{23}H_{24}N_2O$ $[M+H]^+$: 345.1961; found 345.1968.

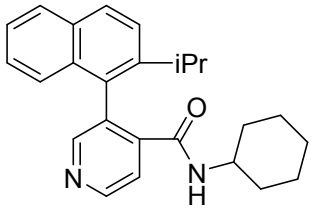
3-(2-ethyl-1-naphthyl)-N-(cyclohexyl)isonicotinamide (3dB)



3dB

The reaction was conducted for 96 h at 80 °C according to the general procedure to give the title compound **3dB** (93 mg, 52% yield) as a pale yellow oil in 70% ee. $[\alpha]_D^{25}$ = +20.6 (c = 0.8, CH_2Cl_2). The enantiomeric excess was determined by HPLC analysis using a chiral stationary phase column [Daicel chiracel® AD-H, 254 nm, n-hexane : i-PrOH = 90 : 10 as the eluent, flow rate: 1 mL/min, retention times: 10.7 min (major isomer) and 9.2 min (minor isomer)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.83 (d, *J* = 4.0 Hz, 1H), 8.54 (s, 1 H), 7.88-7.99 (m, 3H), 7.38-7.53 (m, 3H), 7.21 (d, *J* = 8.0 Hz, 1H), 5.37 (s, 1H), 3.50-3.52 (m, 1H), 2.47-2.52 (m, 2H), 0.78-1.34 (m, 11H), 0.14-0.31 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.22, 151.99, 149.84, 142.82, 140.87, 132.66, 132.06, 131.21, 131.00, 129.36, 128.33, 127.33, 127.30, 125.81, 124.82, 123.24, 47.60, 31.62, 31.45, 26.97, 25.07, 23.64, 23.59, 15.28. ESI-HRMS Calcd. for $C_{24}H_{26}N_2O$ $[M+H]^+$: 359.2118; found 359.2115.

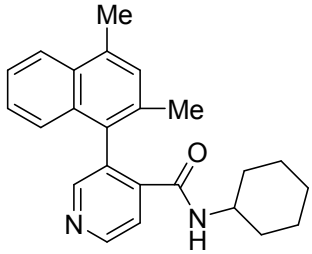
3-(2-isopropyl-1-naphthyl)-N-(cyclohexyl)isonicotinamide (3dC)



3dC

The reaction was conducted for 96 h at 80 °C according to the general procedure to give the title compound **3dC** (61 mg, 33% yield) as a pale yellow oil in 67% ee. $[\alpha]_D^{25}$ = +12.6 (c = 1.5, CH_2Cl_2). The enantiomeric excess was determined by HPLC analysis using a chiral stationary phase column [Daicel chiracel® AD-H, 254 nm, n-hexane : i-PrOH = 90 : 10 as the eluent, flow rate: 1 mL/min, retention times: 12.3 min (major isomer) and 8.3 min (minor isomer)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.86 (d, *J* = 4.0 Hz, 1H), 8.56 (s, 1 H), 7.99-8.02 (m, 2H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.41-7.52 (m, 2H), 7.20 (d, *J* = 8.0 Hz, 1H), 5.37 (s, 1H), 3.46-3.59 (m, 1H), 2.73-2.76 (m, 1H), 0.82-1.35 (m, 14H), 0.20-0.28 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.15, 151.88, 149.93, 145.27, 142.69, 132.57, 132.06, 131.11, 130.41, 129.86, 128.31, 127.42, 125.94, 125.17, 124.13, 123.40, 47.66, 31.71, 31.46, 30.90, 25.09, 24.18, 23.57, 23.23. ESI-HRMS Calcd. for $C_{25}H_{28}N_2O$ $[M+H]^+$: 373.2274; found 373.2276.

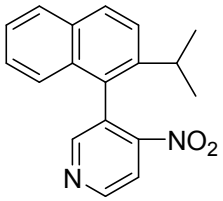
3-(2-methyl-1-naphthyl)-N-(cyclohexyl)isonicotinamide (3dD)



3dD

The reaction was conducted for 96 h at 80 °C according to the general procedure to give the title compound **3dD** (161 mg, 90% yield) as a pale yellow oil in 62% ee. $[\alpha]_D^{25}$ = +19.8 (c = 1.8, CH_2Cl_2). The enantiomeric excess was determined by HPLC analysis using a chiral stationary phase column [Daicel chiracel® OD-H, 254 nm, n-hexane : i-PrOH = 97 : 3 as the eluent, flow rate: 1 mL/min, retention times: 14.3 min (major isomer) and 19.7 min (minor isomer)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82 (s, 1H), 8.52 (s, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.97 (s, 1H), 7.49-7.51 (m, 1H), 7.39-7.43 (m, 1H), 7.33(s, 1H), 7.24-7.26 (m, 1H), 5.42 (s, 1H), 3.46-3.63 (m, 1H), 2.74 (s, 3H), 2.17 (s, 3H), 0.81-1.25 (m, 8H), 0.18-0.42 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.37, 152.10, 149.76, 142.79, 135.56, 134.53, 132.74, 131.57, 131.33, 130.16, 129.52, 127.01, 125.58, 125.21, 124.53, 123.22, 47.45, 31.51, 31.40, 25.18, 23.49, 23.40, 20.58, 19.40. ESI-HRMS Calcd. for $C_{24}H_{26}N_2O$ $[M+H]^+$: 359.2118; found 359.2120.

3-(2-isopropylnaphthalen-1-yl)-4-nitropyridine (3eC)

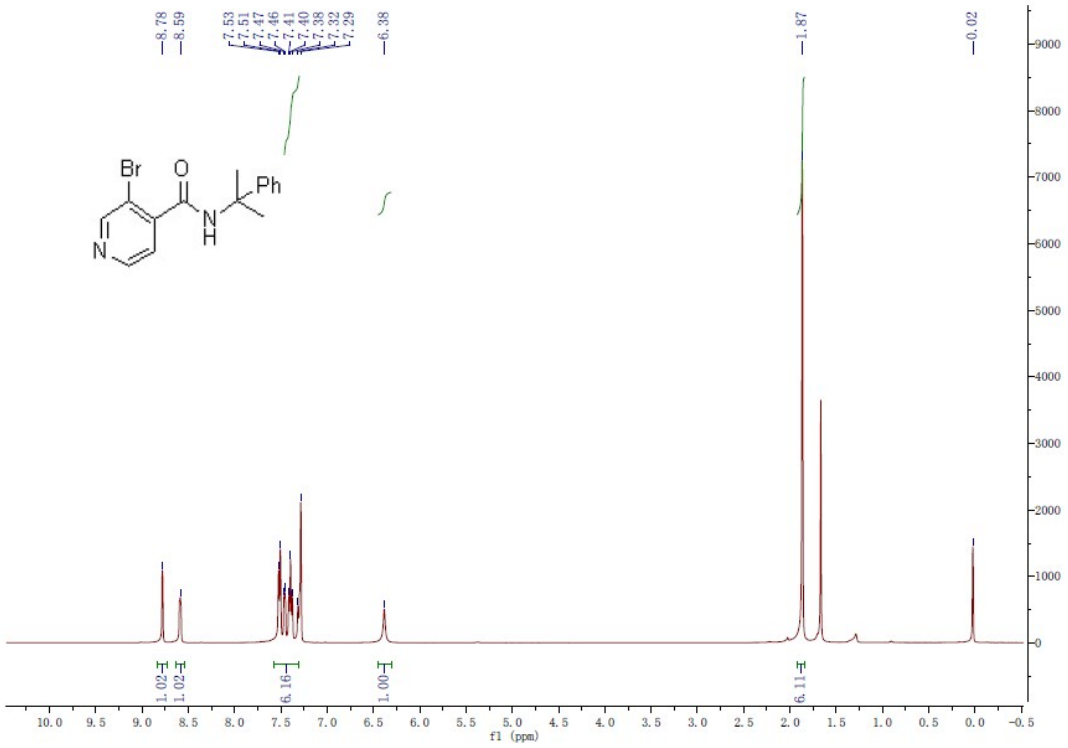


3eC

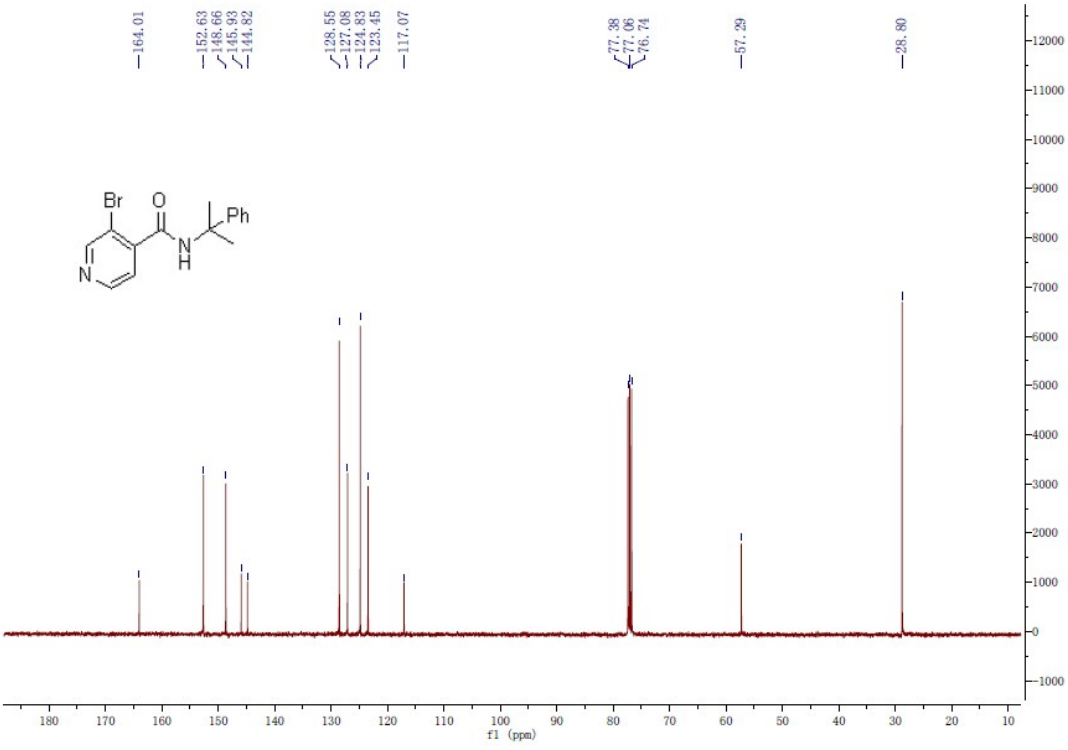
The reaction was conducted for 96 h at 80 °C according to the general procedure to give the title compound **3eC** (63 mg, 43% yield) as a pale yellow oil in 73% ee. The enantiomeric excess was determined by HPLC analysis using a chiral stationary phase column [Daicel chiracel® OJ-H, 214 nm, n-hexane : i-PrOH = 95 : 5 as the eluent, flow rate: 1 mL/min, retention times: 43.0 min (major isomer) and 24.8 min (minor isomer)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.89 (d, *J* = 4.0 Hz, 1H), 8.72 (s, 1H), 7.92-7.96 (m, 2H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.42-7.46 (m, 1H), 7.33-7.38 (m, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 2.59-2.64 (m, 1H), 1.19-1.24 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ. 155.08, 154.57, 151.06, 144.83, 132.23, 131.86, 129.75, 128.23, 128.15, 127.17, 126.83, 125.52, 124.93, 123.65, 116.62, 31.60, 24.26, 23.11. ESI-HRMS Calcd. for $C_{18}H_{16}N_2O_2$ $[M+H]^+$: 293.1285; found 293.1275.

NMR Spectra

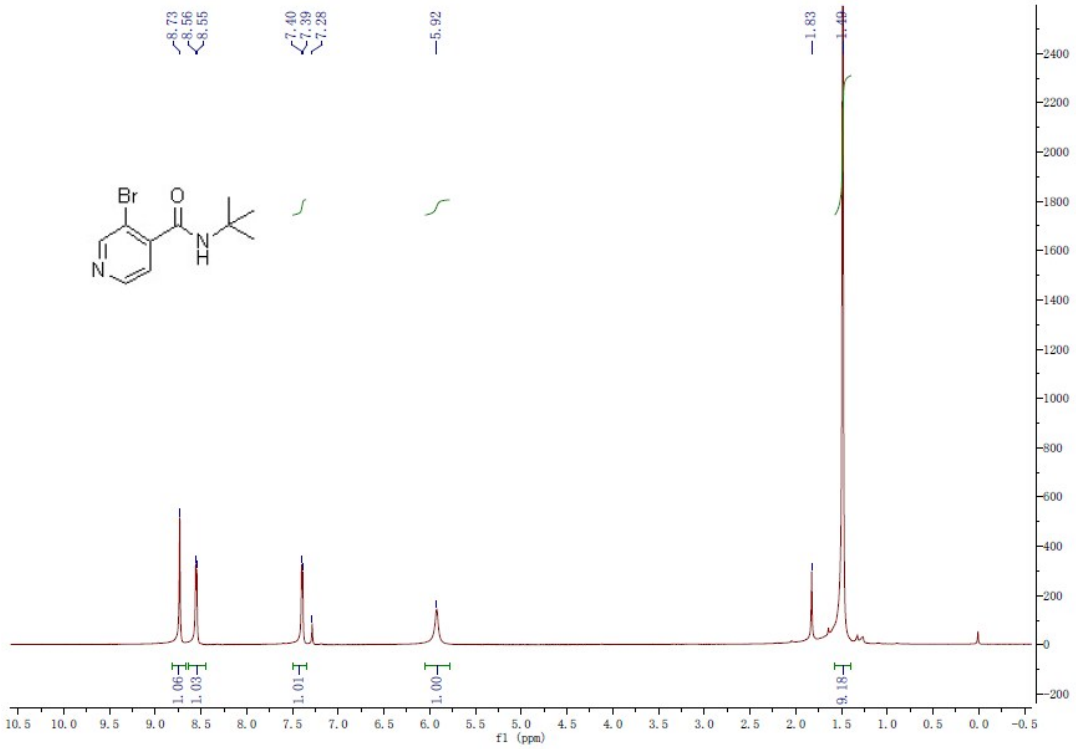
^{1}H NMR (400 MHz, $CDCl_3$) of **1a**



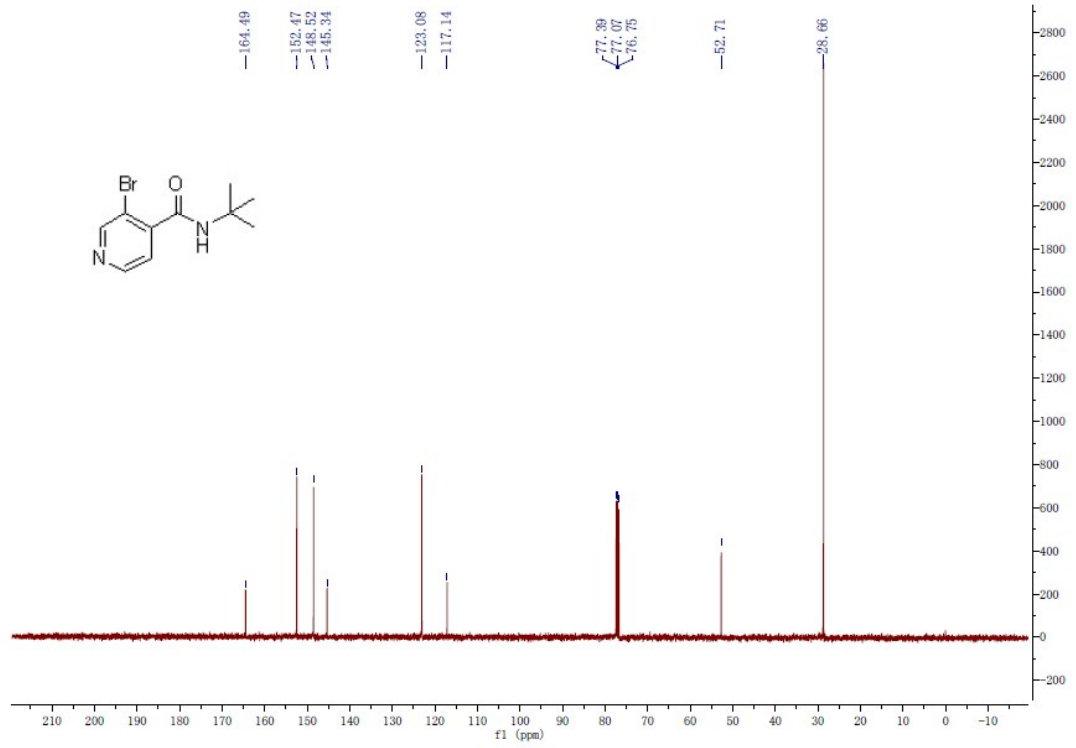
^{13}C NMR (100 MHz, $CDCl_3$) of **1a**



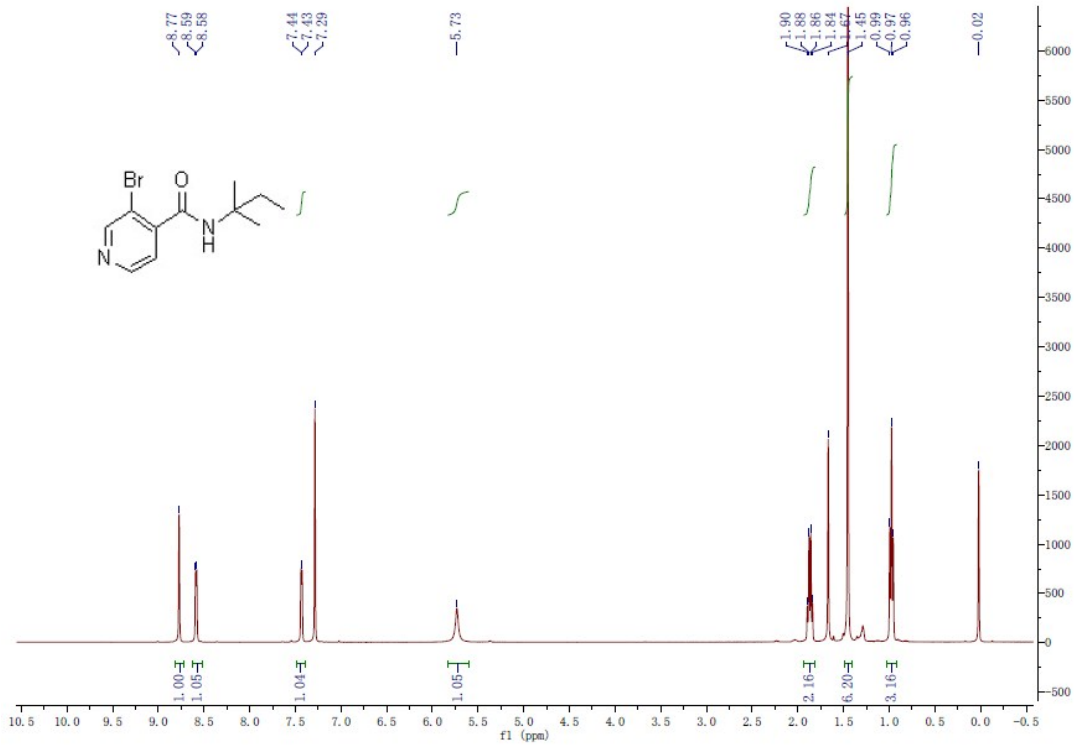
^{1}H NMR (400 MHz, $CDCl_3$) of **1b**



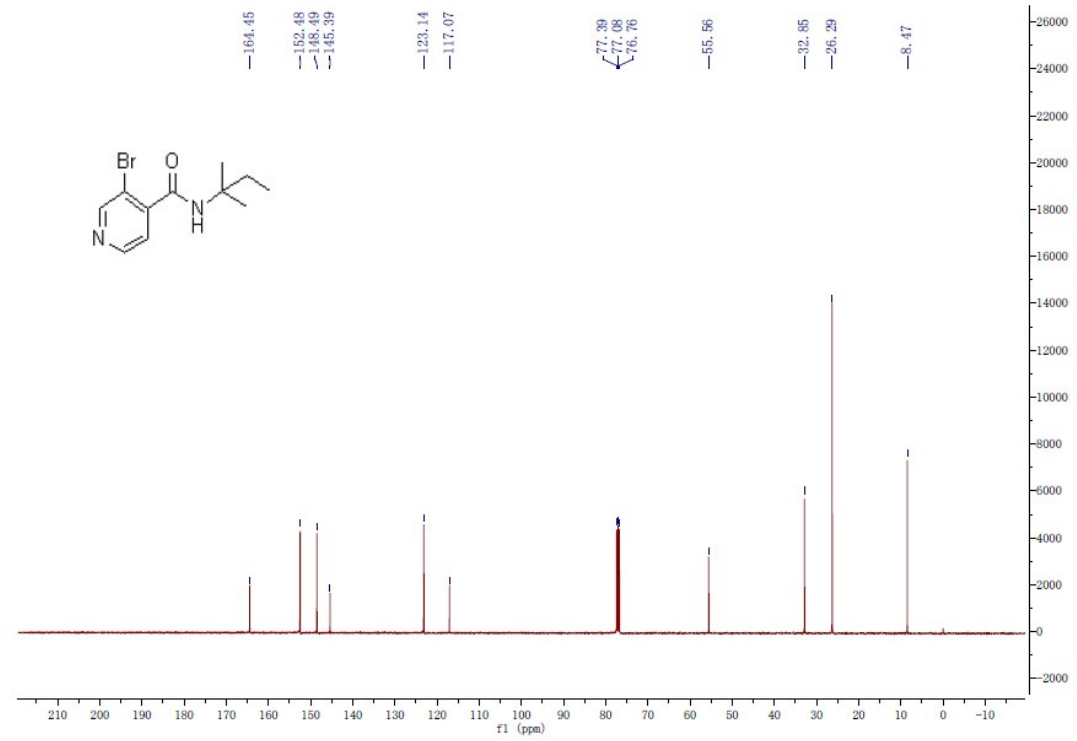
^{13}C NMR (100 MHz, $CDCl_3$) of **1b**



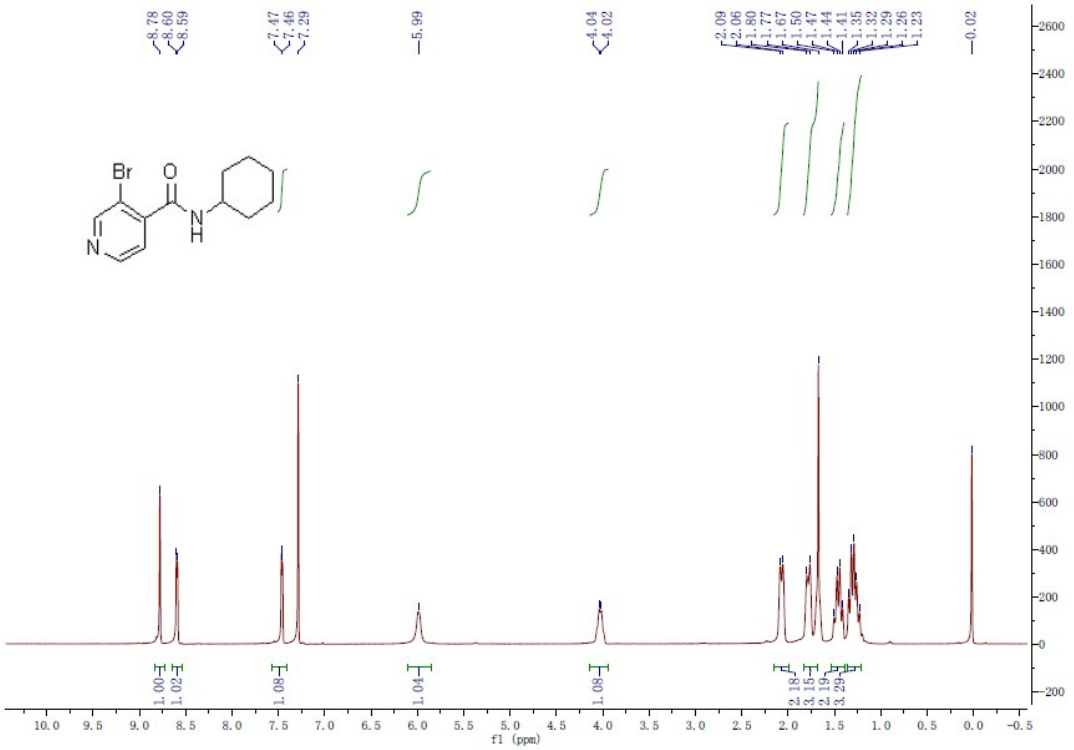
^{1}H NMR (400 MHz, $CDCl_3$) of **1c**



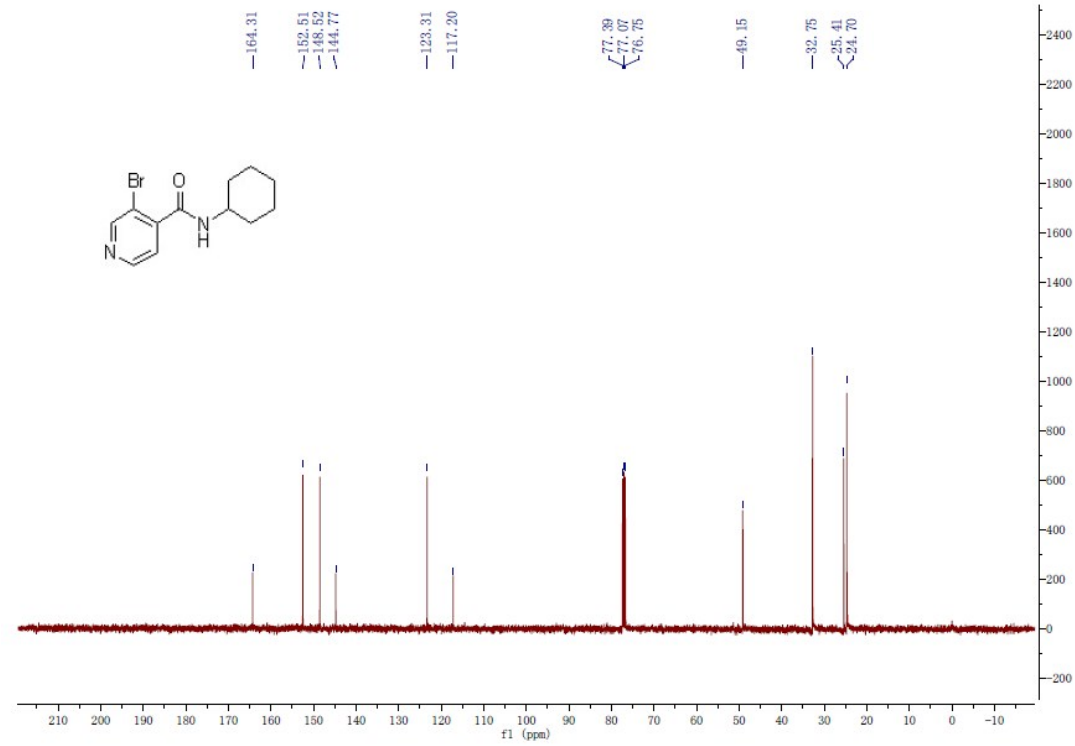
^{13}C NMR (100 MHz, $CDCl_3$) of **1c**



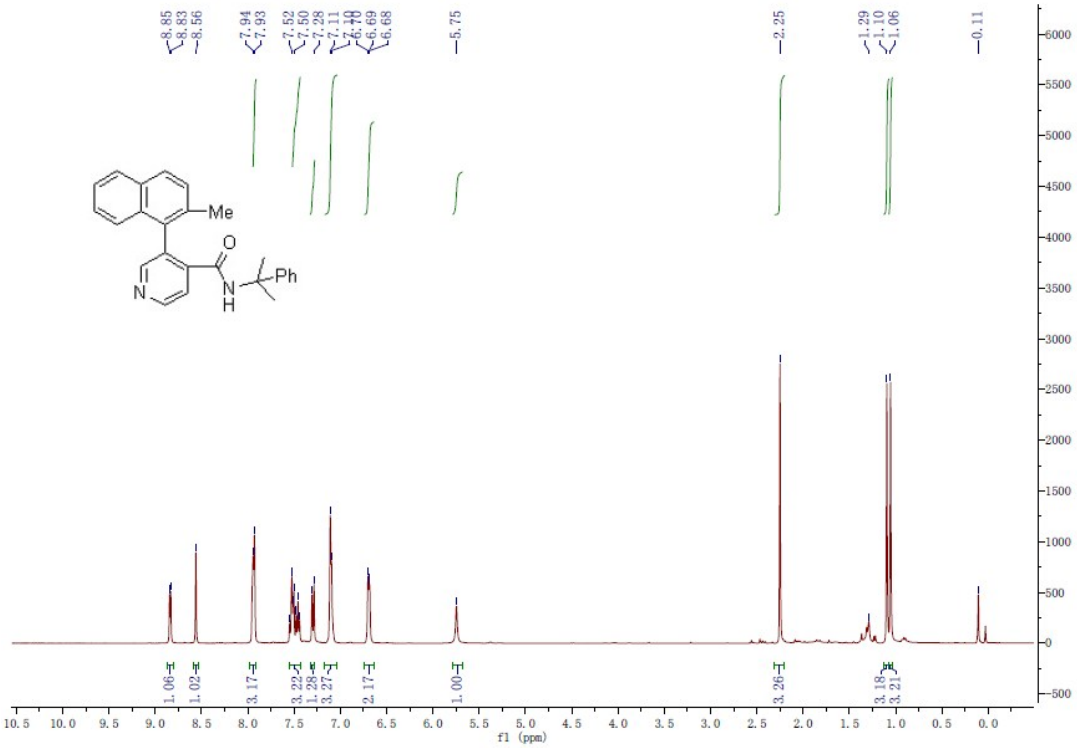
^{1}H NMR (400 MHz, $CDCl_3$) of **1d**



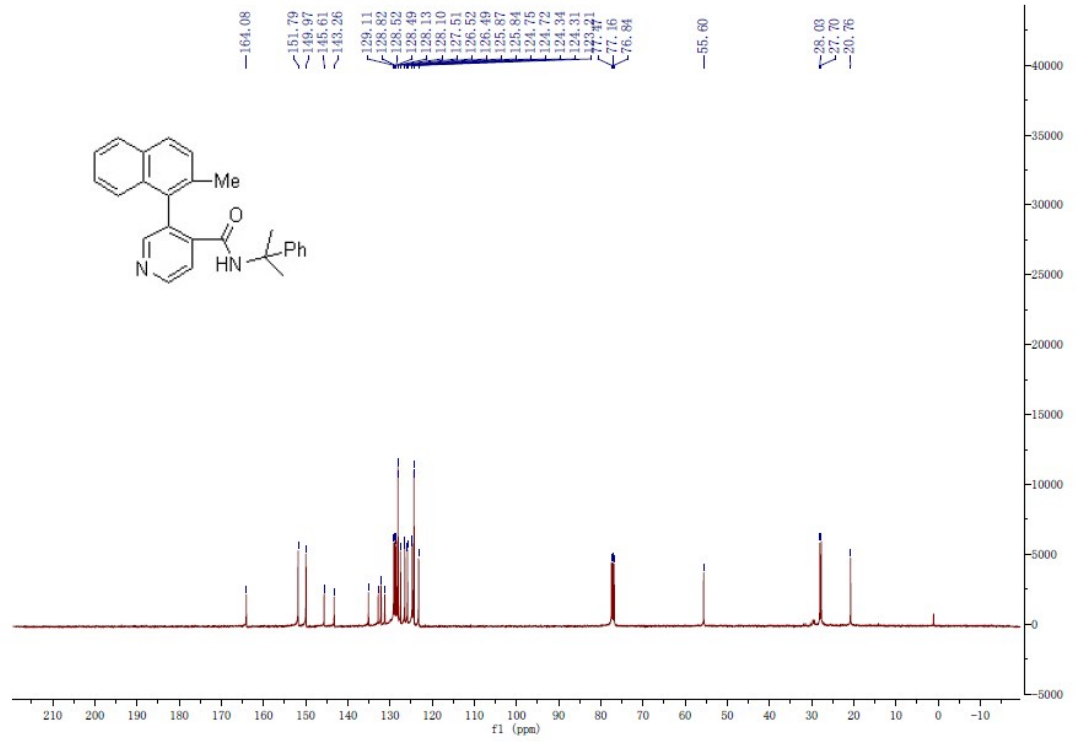
^{13}C NMR (100 MHz, $CDCl_3$) of **1d**



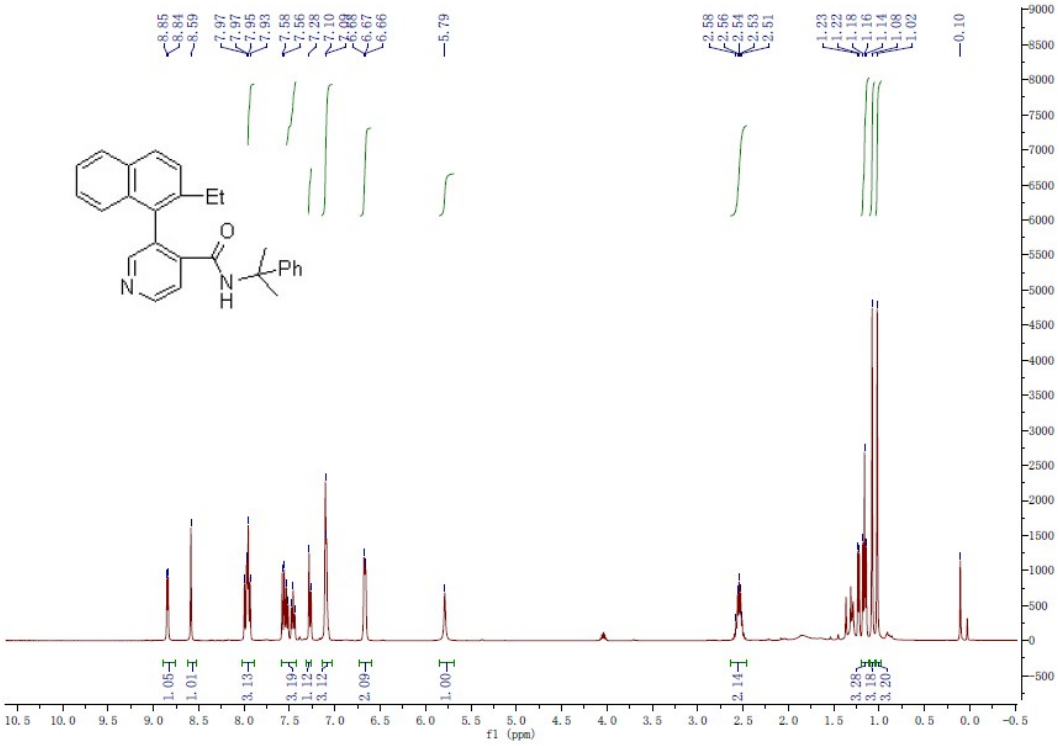
^{1}H NMR (400 MHz, $CDCl_3$) of **3aA**



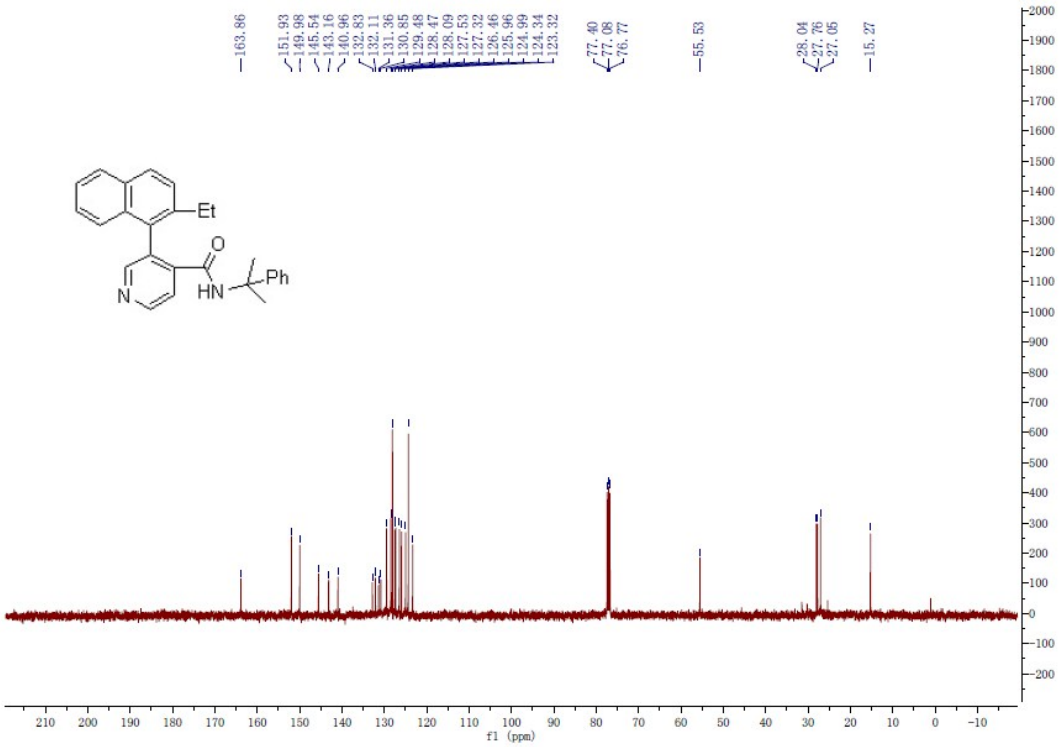
^{13}C NMR (100 MHz, $CDCl_3$) of **3aA**



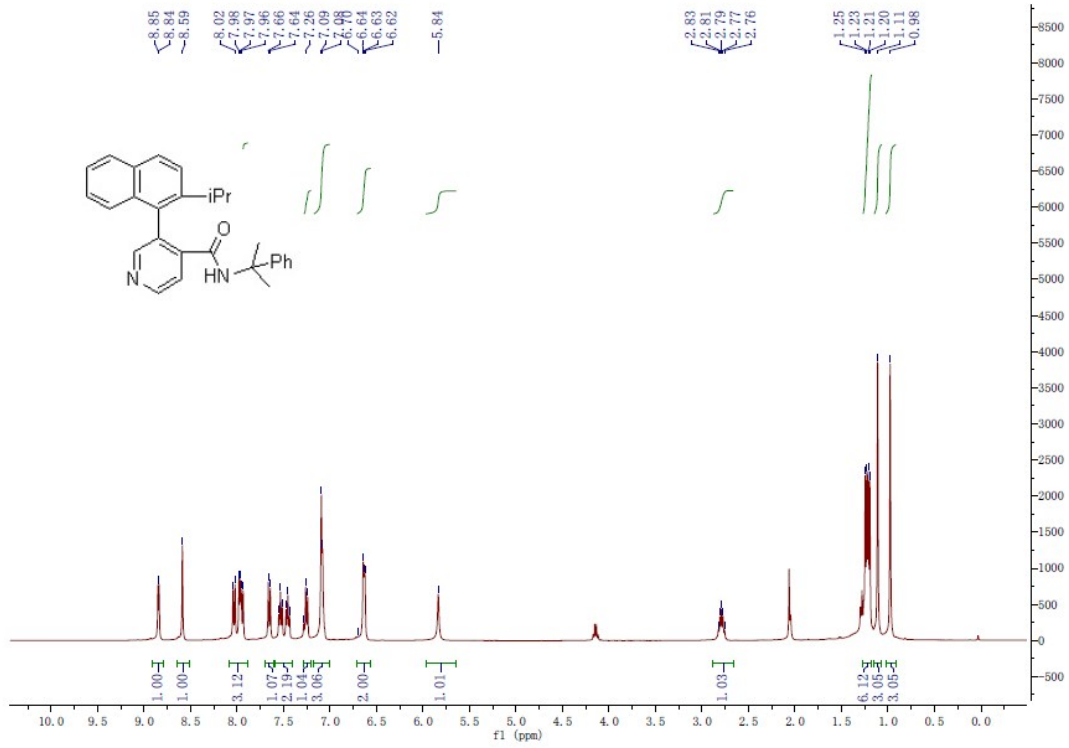
^{1}H NMR (400 MHz, $CDCl_3$) of **3aB**



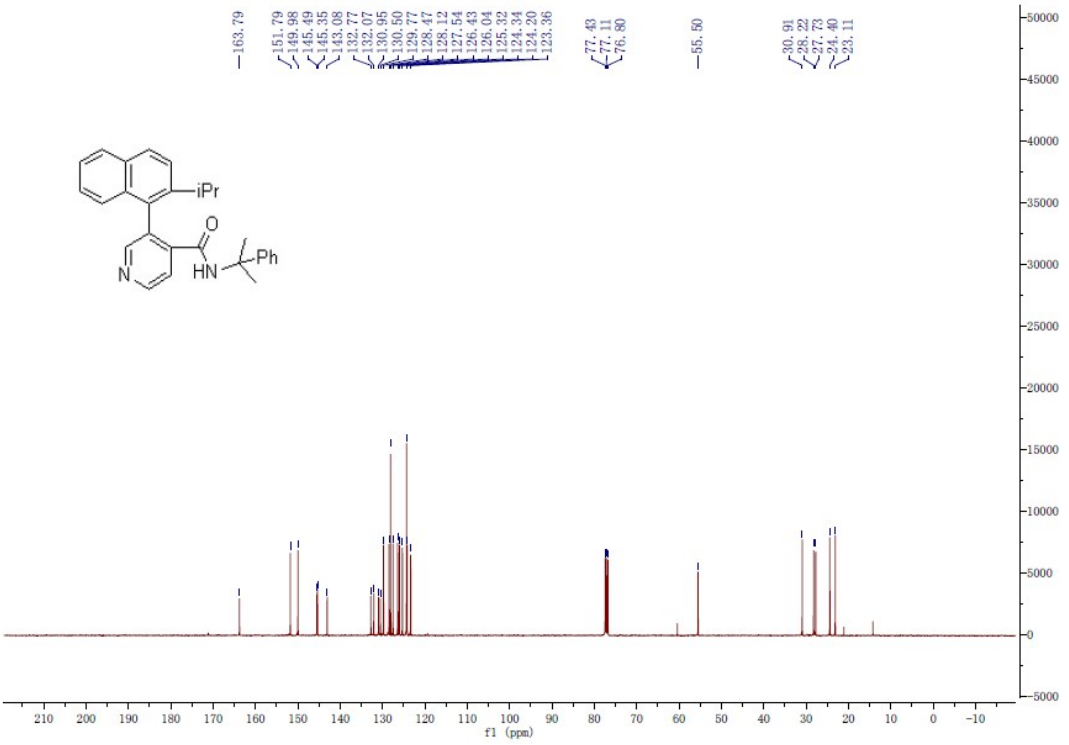
^{13}C NMR (100 MHz, $CDCl_3$) of **3aB**



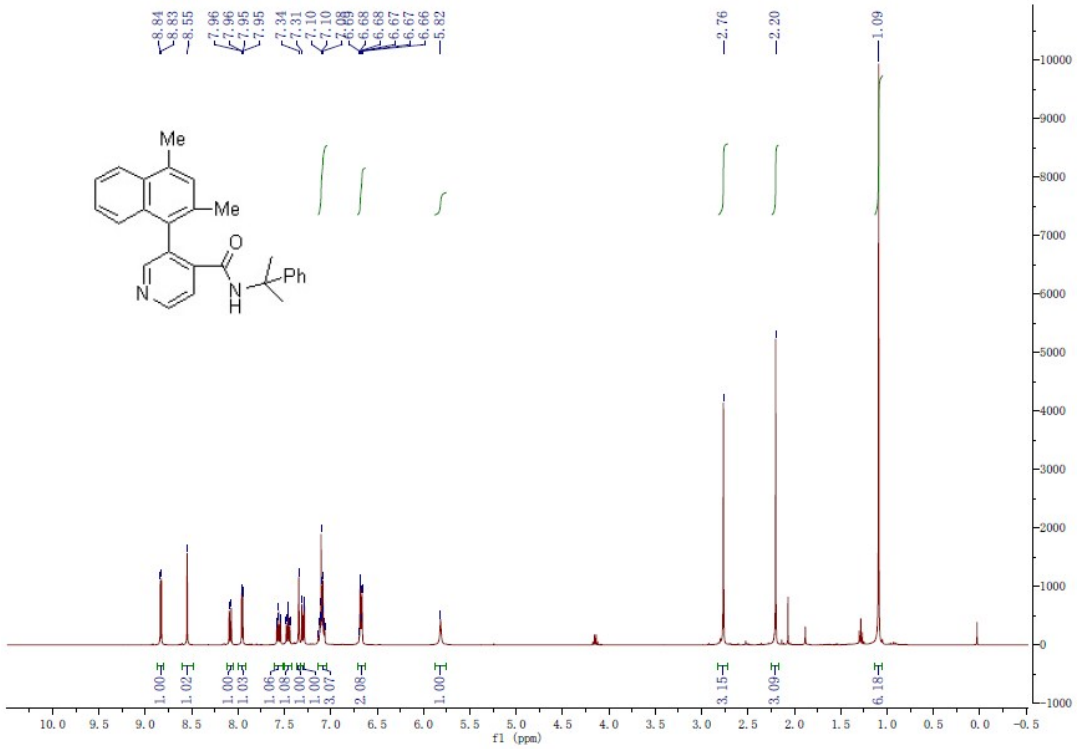
^{1}H NMR (400 MHz, $CDCl_3$) of **3aC**



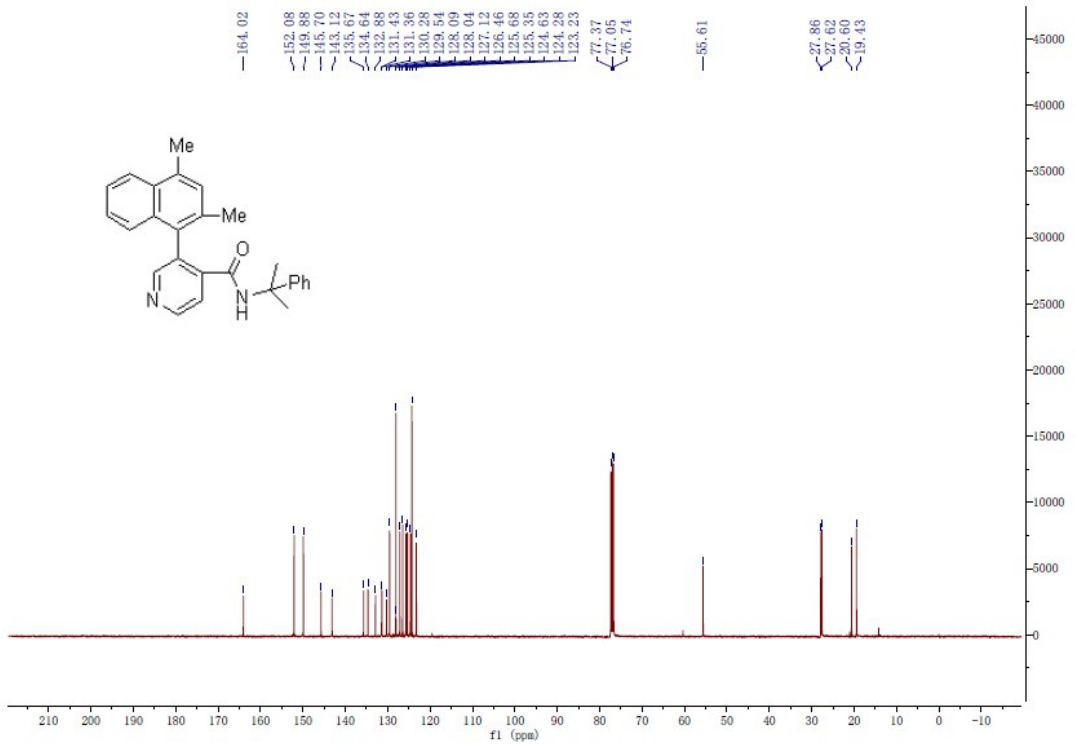
^{13}C NMR (100 MHz, $CDCl_3$) of **3aC**



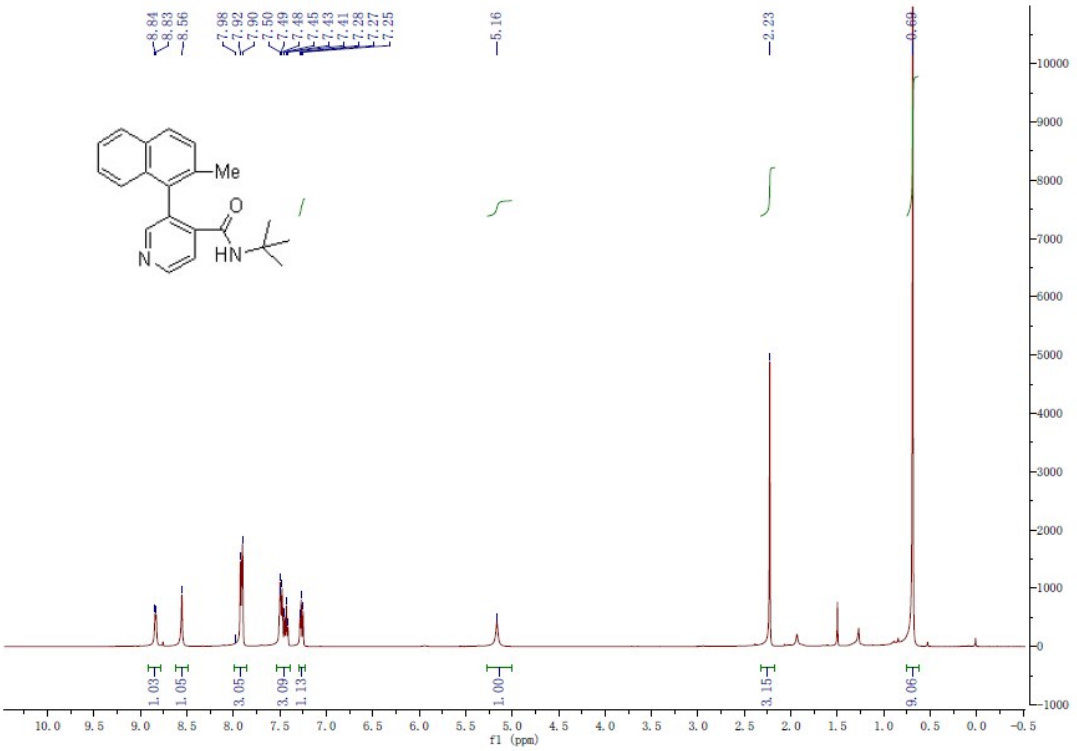
^{1}H NMR (400 MHz, $CDCl_3$) of **3aD**



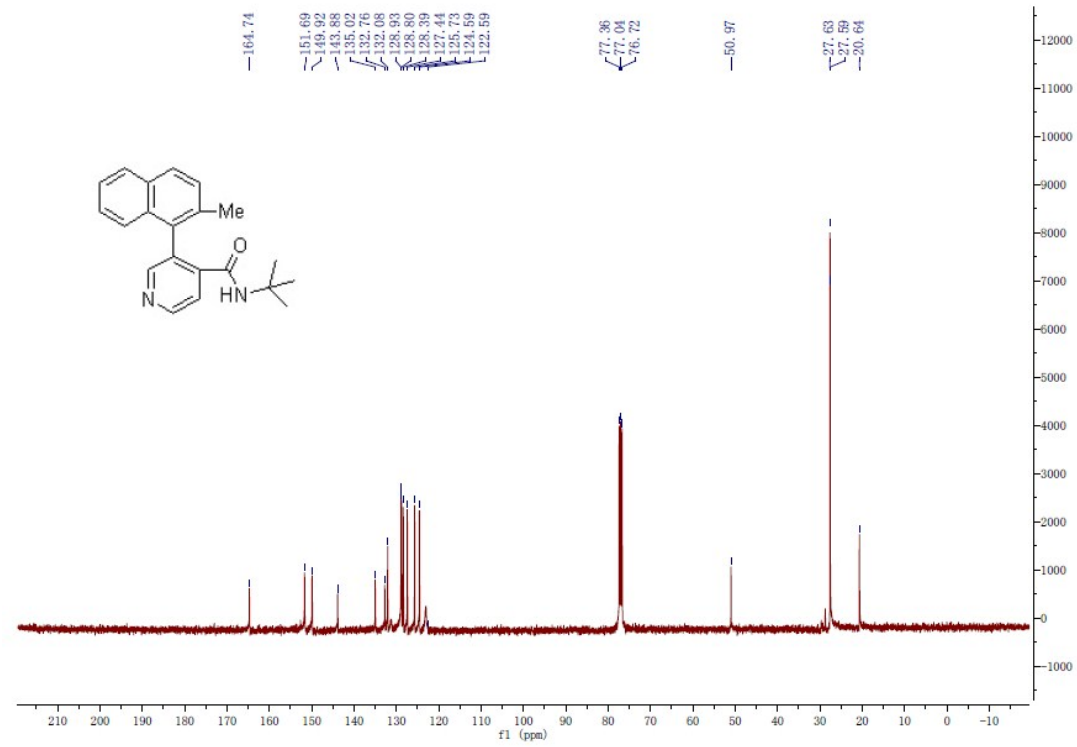
^{13}C NMR (100 MHz, $CDCl_3$) of **3aD**



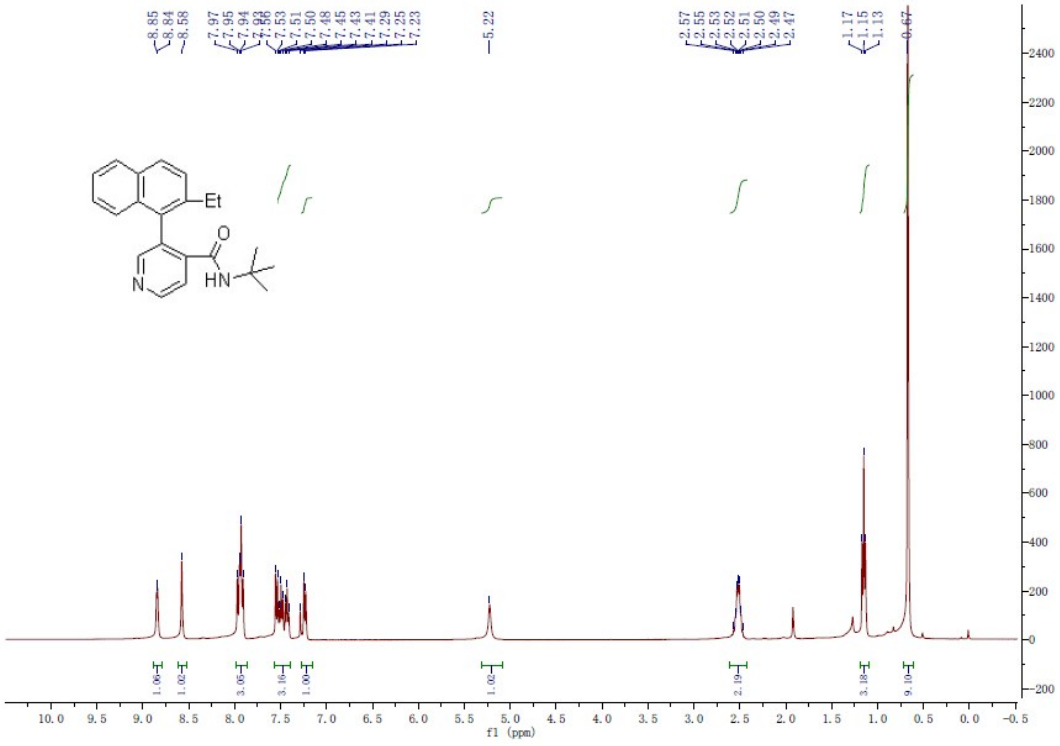
^{1}H NMR (400 MHz, $CDCl_3$) of **3bA**



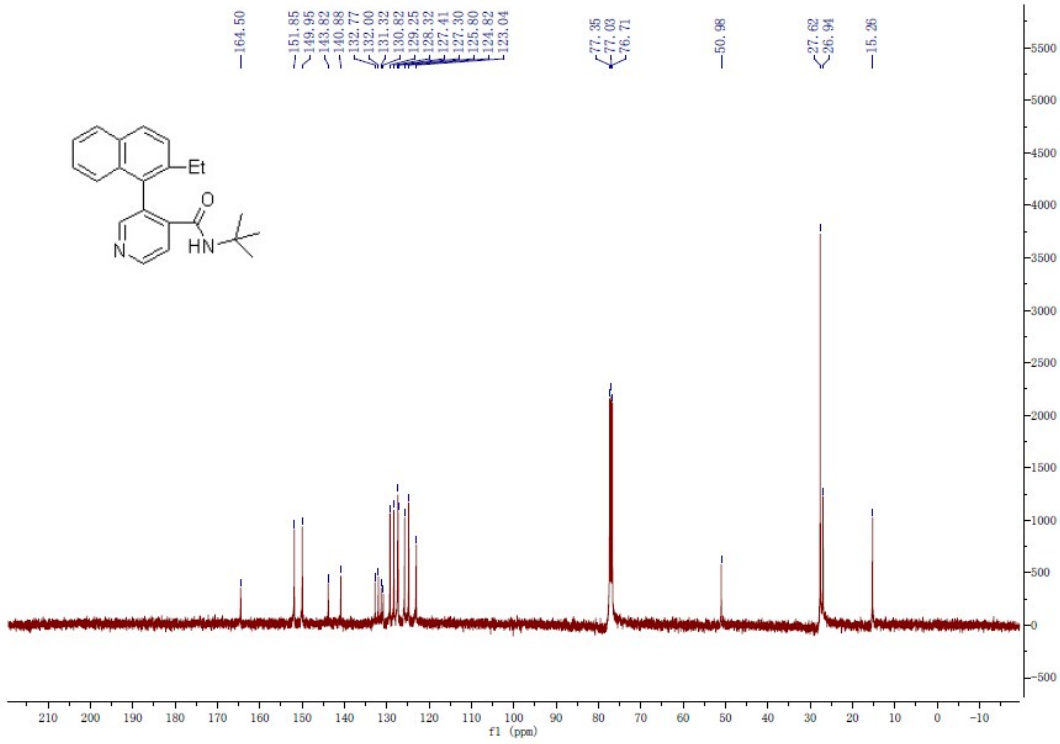
^{13}C NMR (100 MHz, $CDCl_3$) of **3bA**



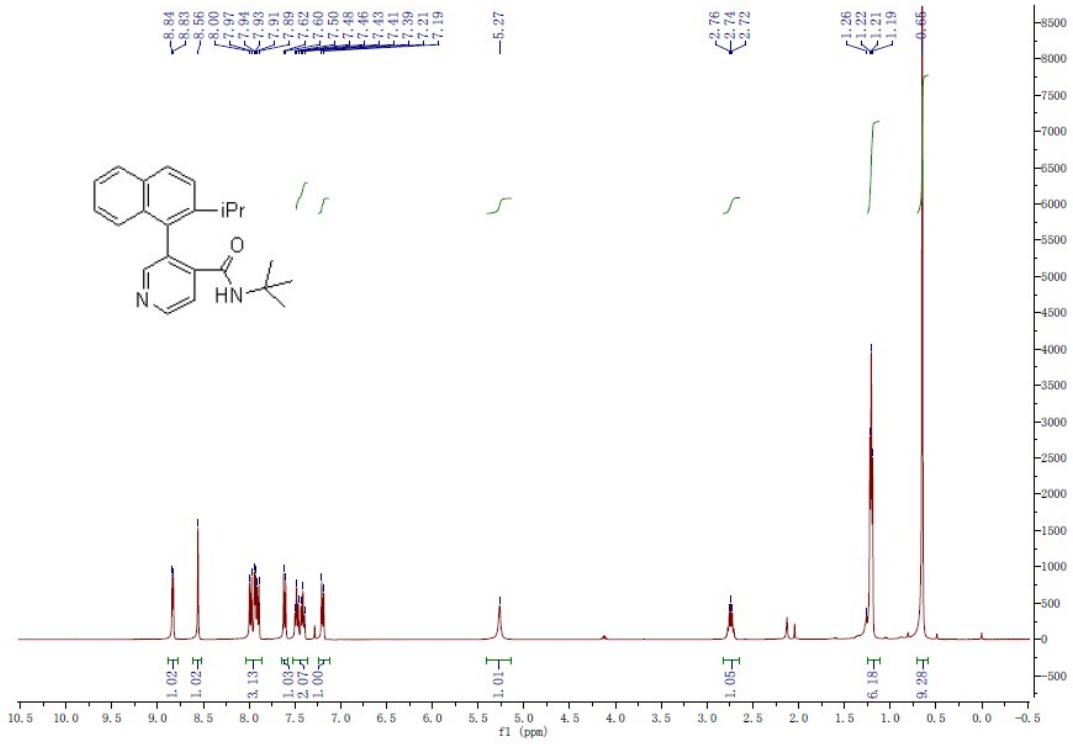
^{1}H NMR (400 MHz, $CDCl_3$) of **3bB**



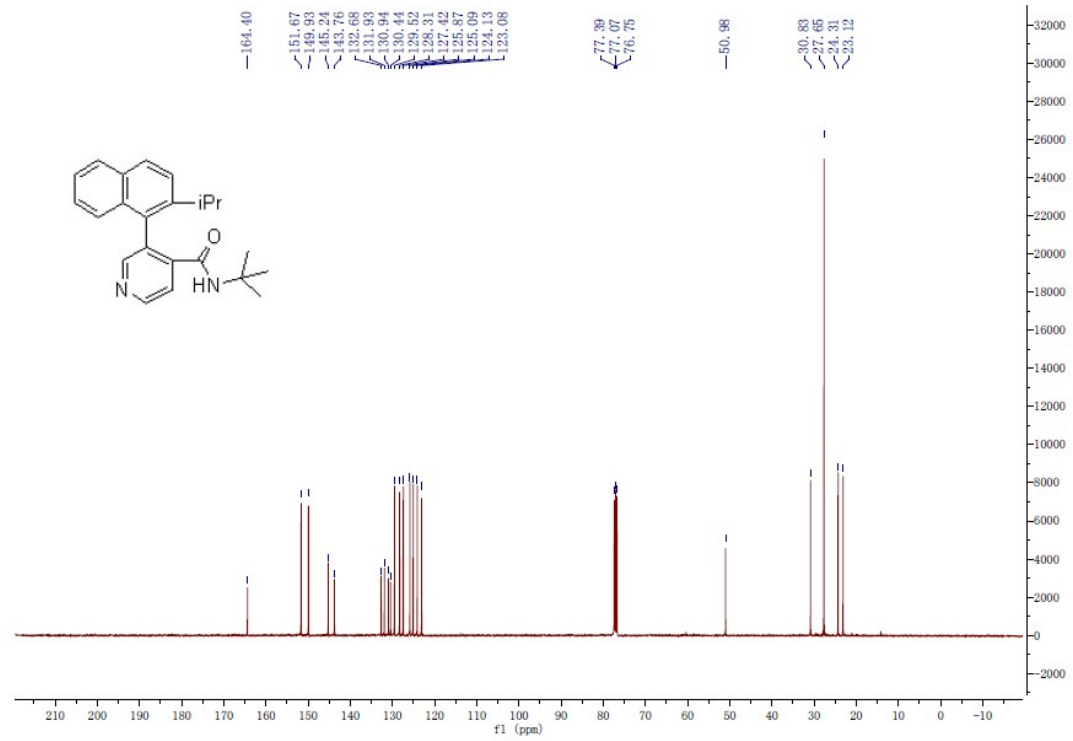
^{13}C NMR (100 MHz, $CDCl_3$) of **3bB**



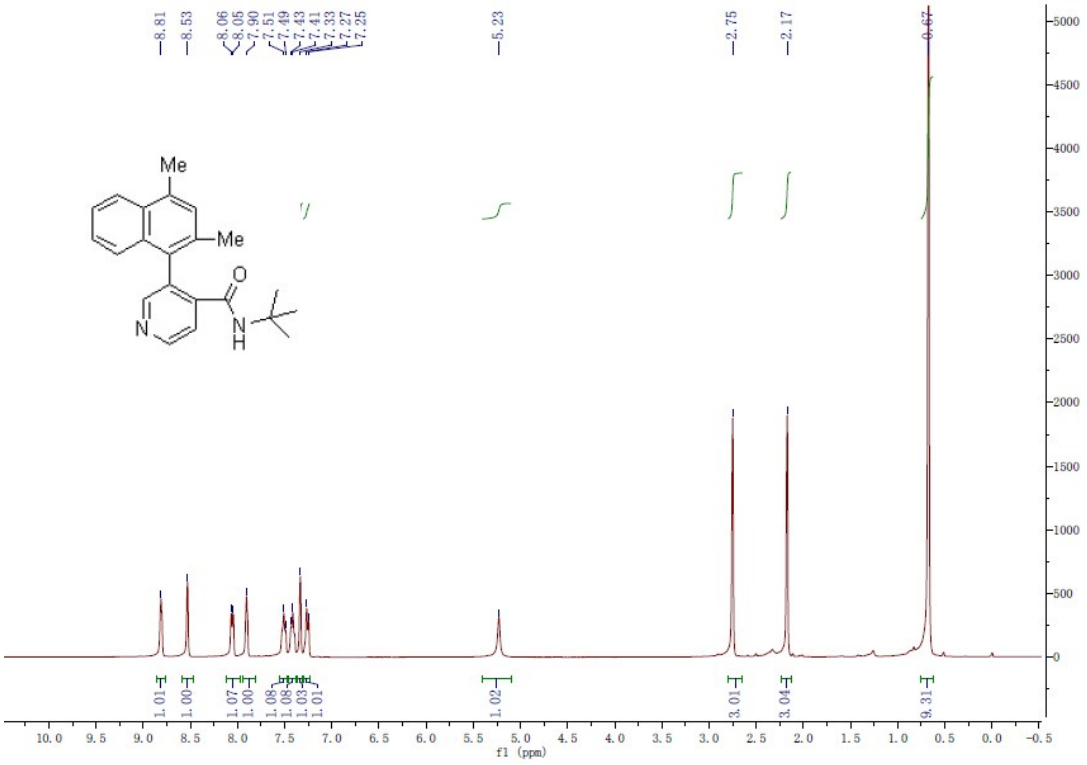
^{1}H NMR (400 MHz, $CDCl_3$) of **3bC**



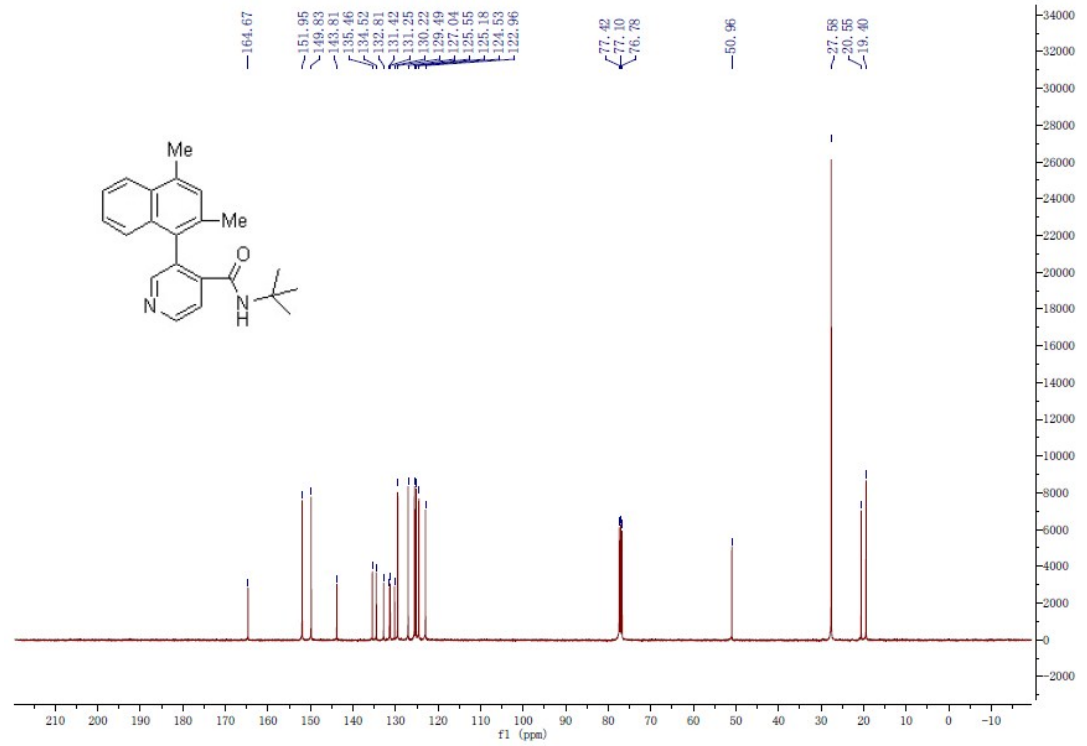
^{13}C NMR (100 MHz, $CDCl_3$) of **3bC**



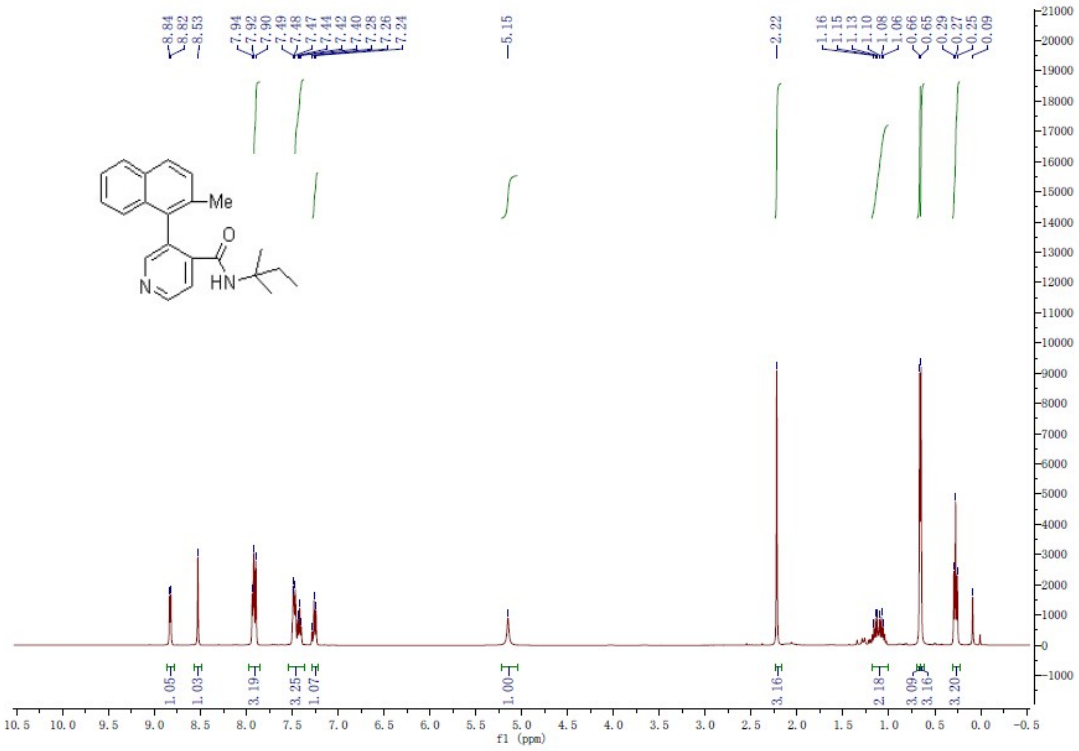
^{1}H NMR (400 MHz, $CDCl_3$) of **3bD**



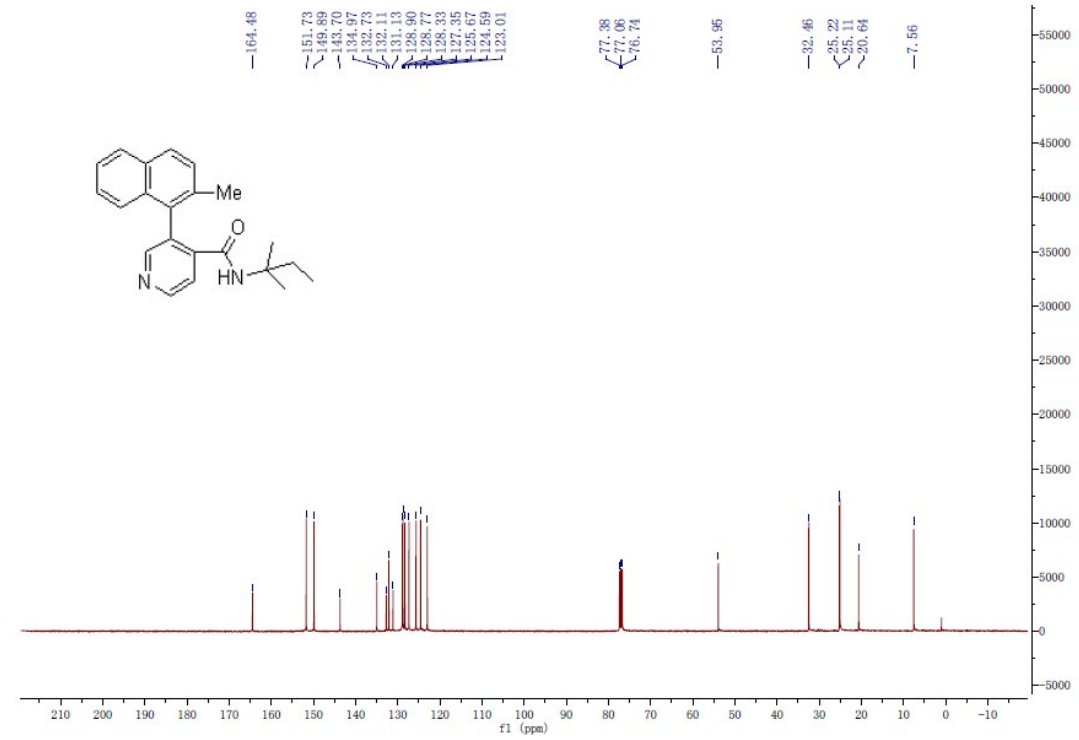
^{13}C NMR (100 MHz, $CDCl_3$) of **3bD**



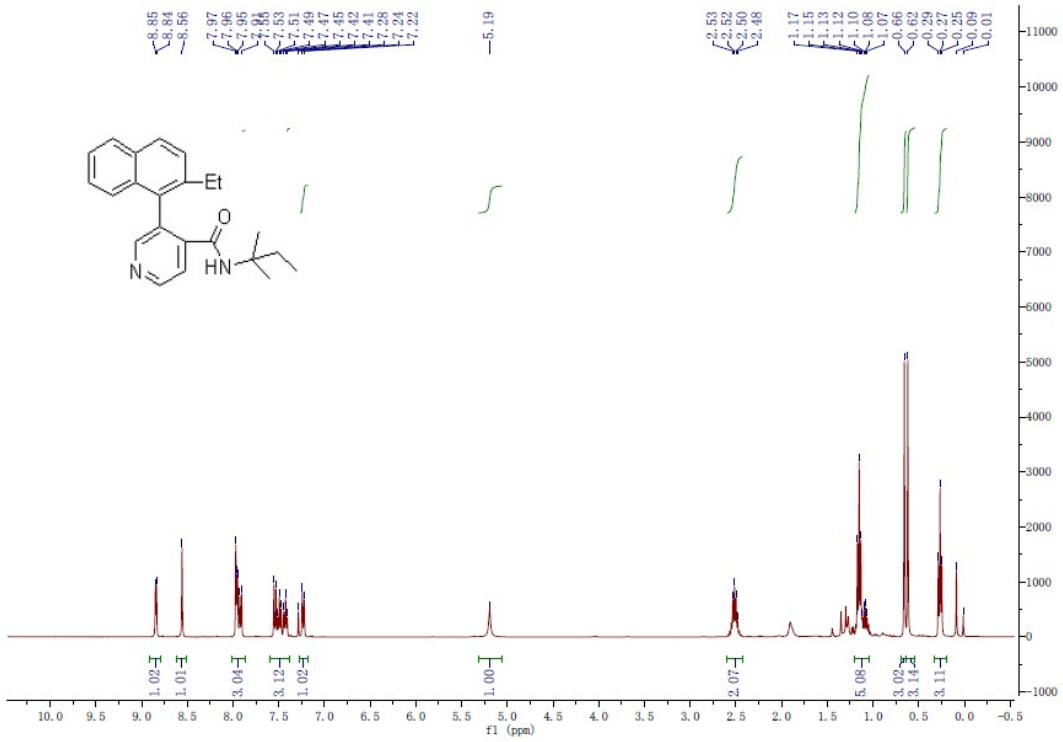
^{1}H NMR (400 MHz, $CDCl_3$) of **3cA**



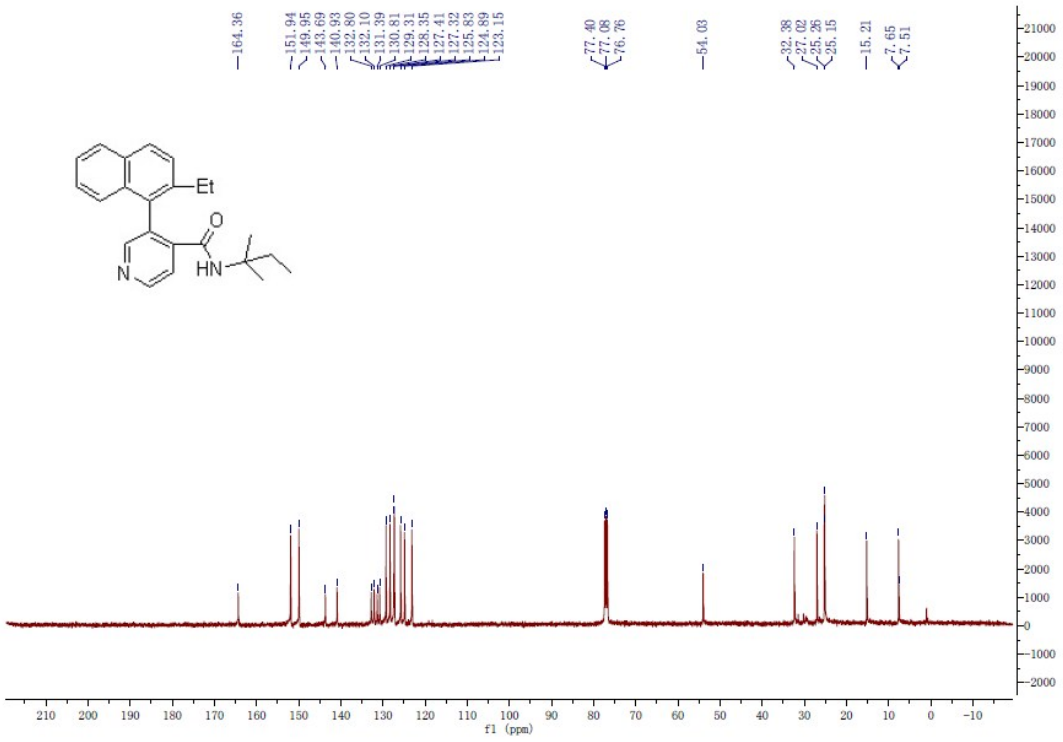
^{13}C NMR (100 MHz, $CDCl_3$) of **3cA**



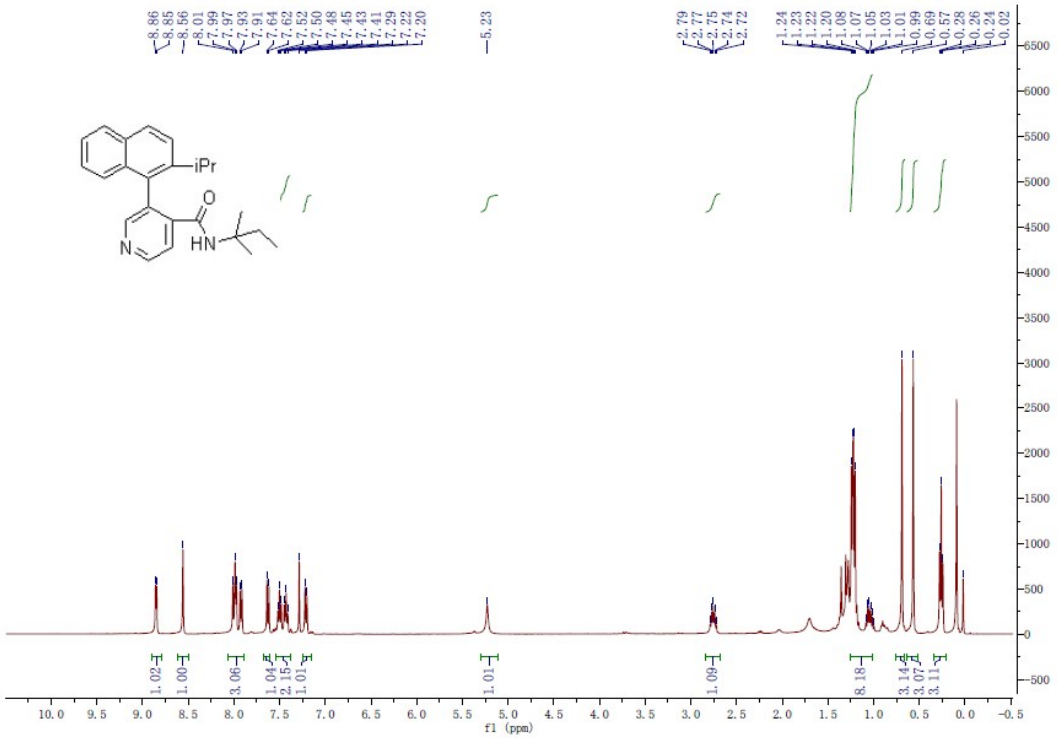
^{1}H NMR (400 MHz, $CDCl_3$) of **3cB**



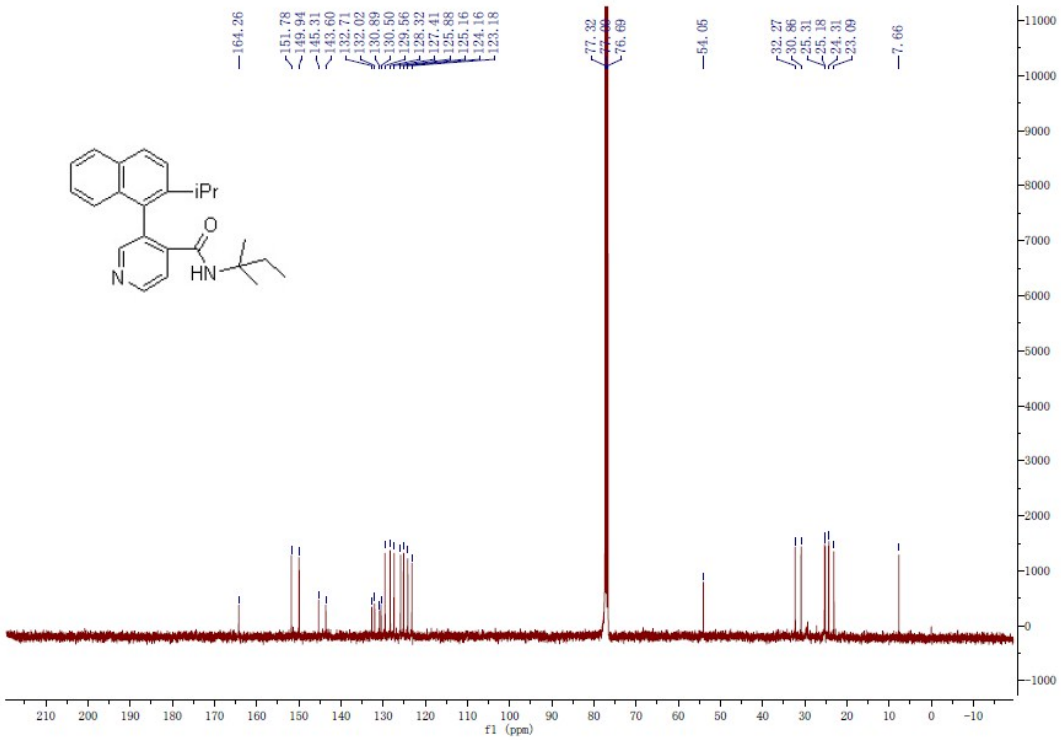
^{13}C NMR (100 MHz, $CDCl_3$) of **3cB**



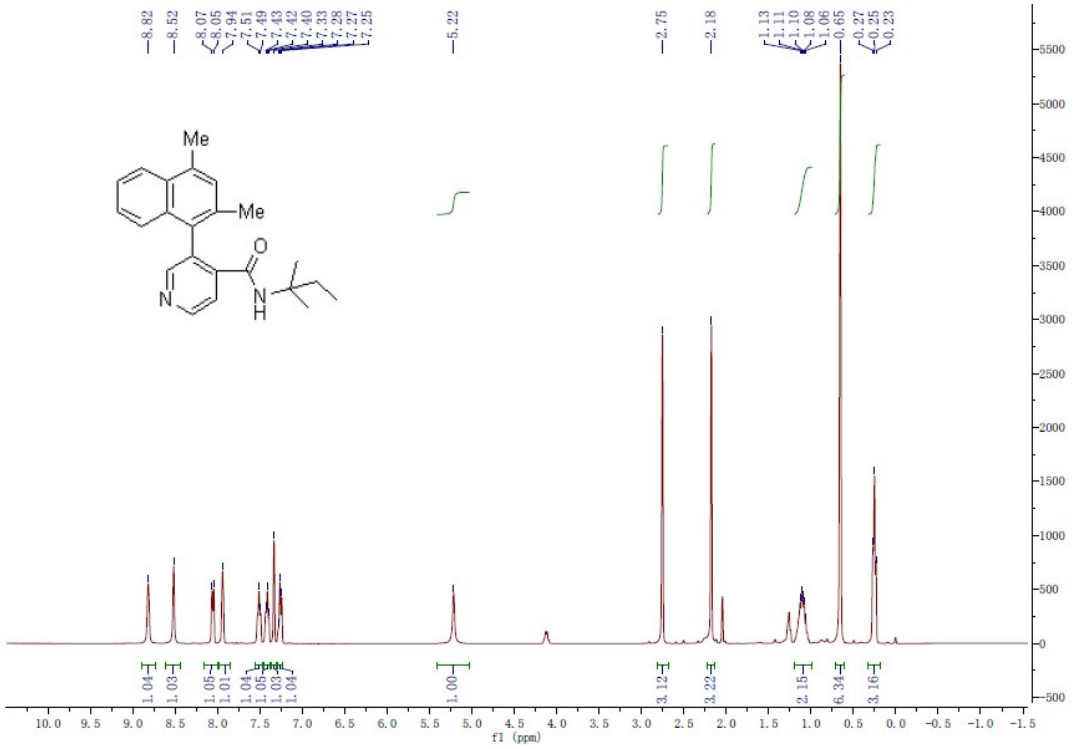
^{1}H NMR (400 MHz, $CDCl_3$) of **3cC**



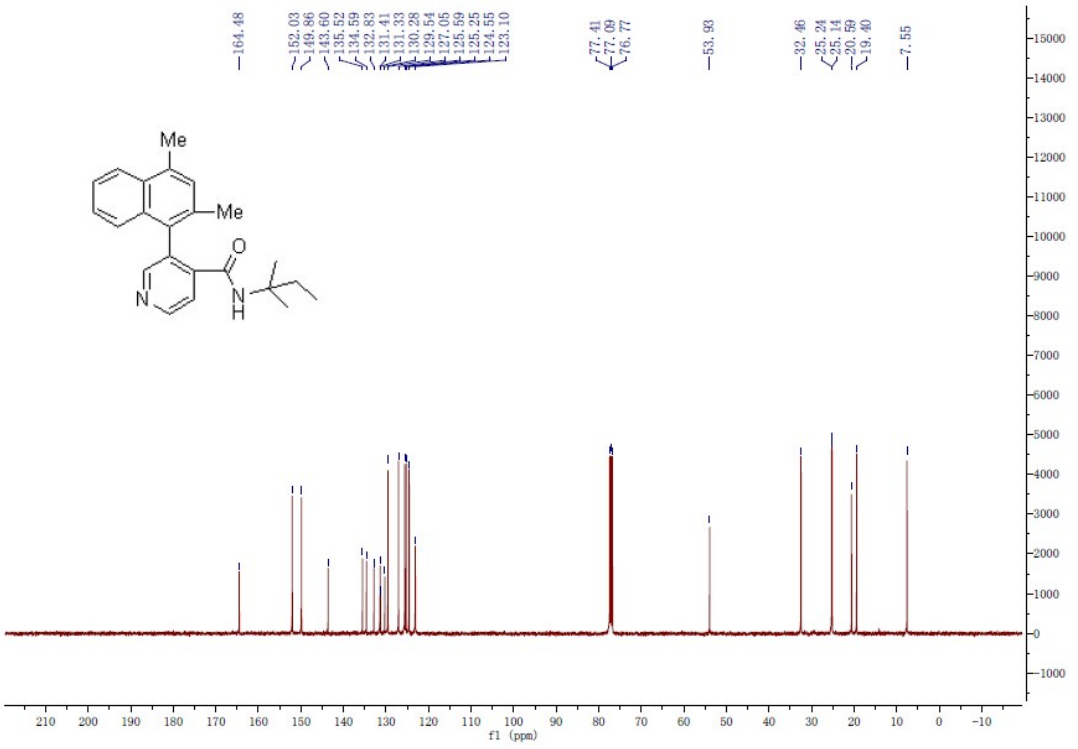
^{13}C NMR (100 MHz, $CDCl_3$) of **3cC**



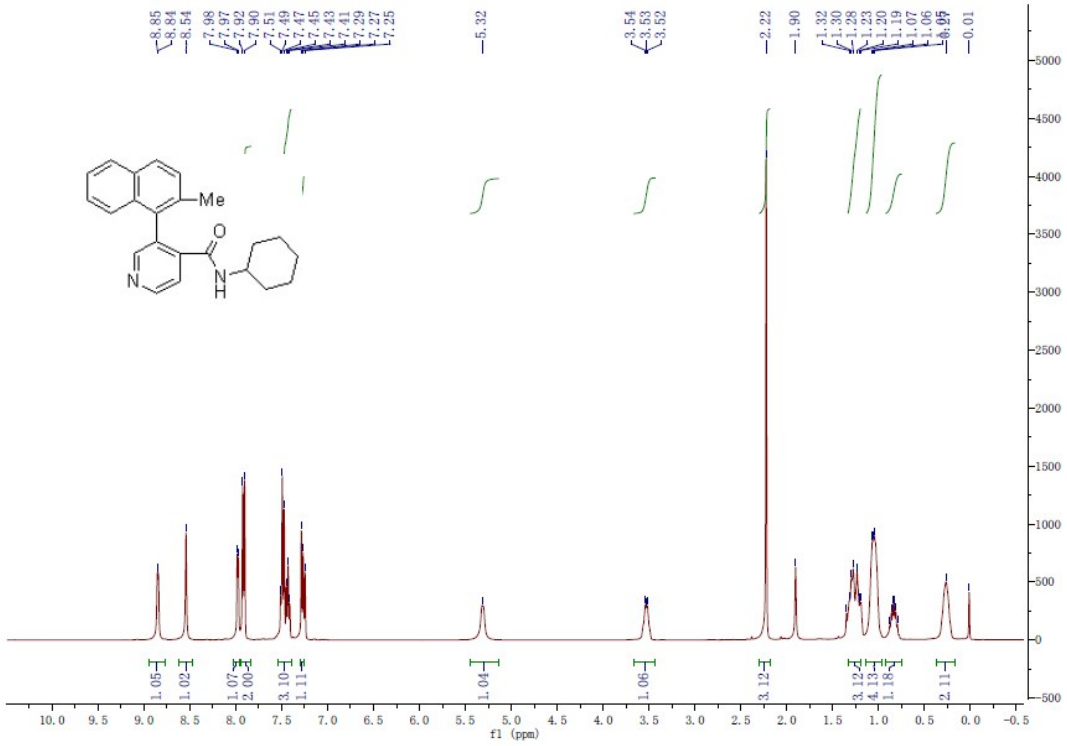
^{1}H NMR (400 MHz, $CDCl_3$) of **3cD**



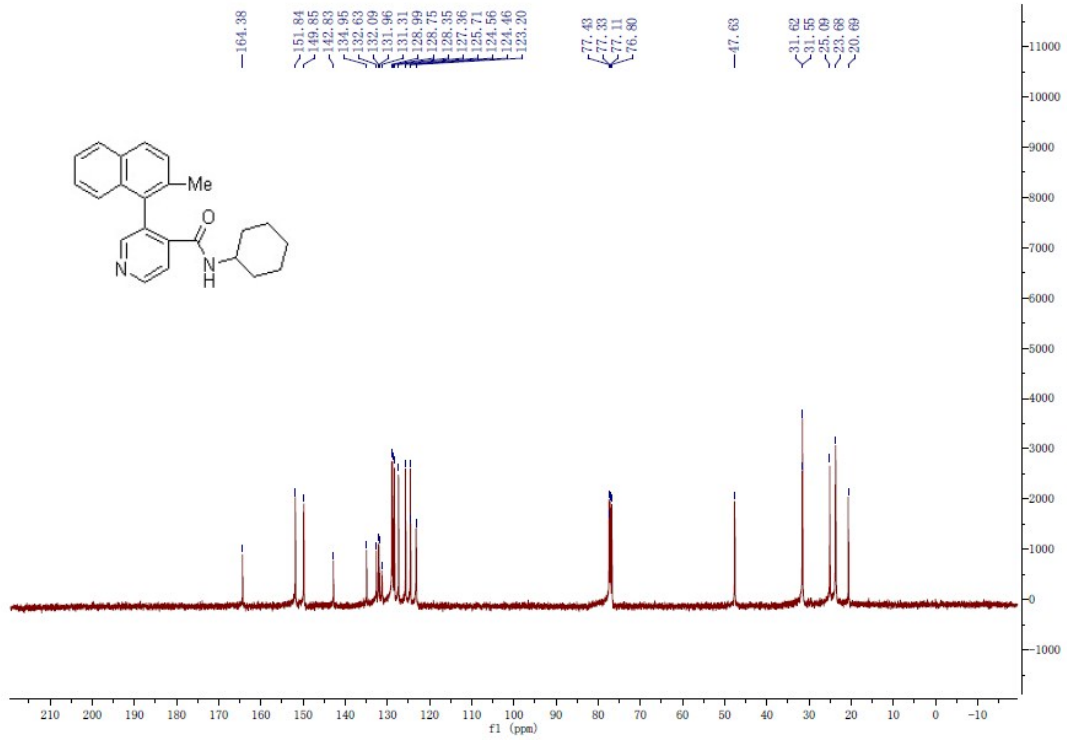
^{13}C NMR (100 MHz, $CDCl_3$) of **3cD**



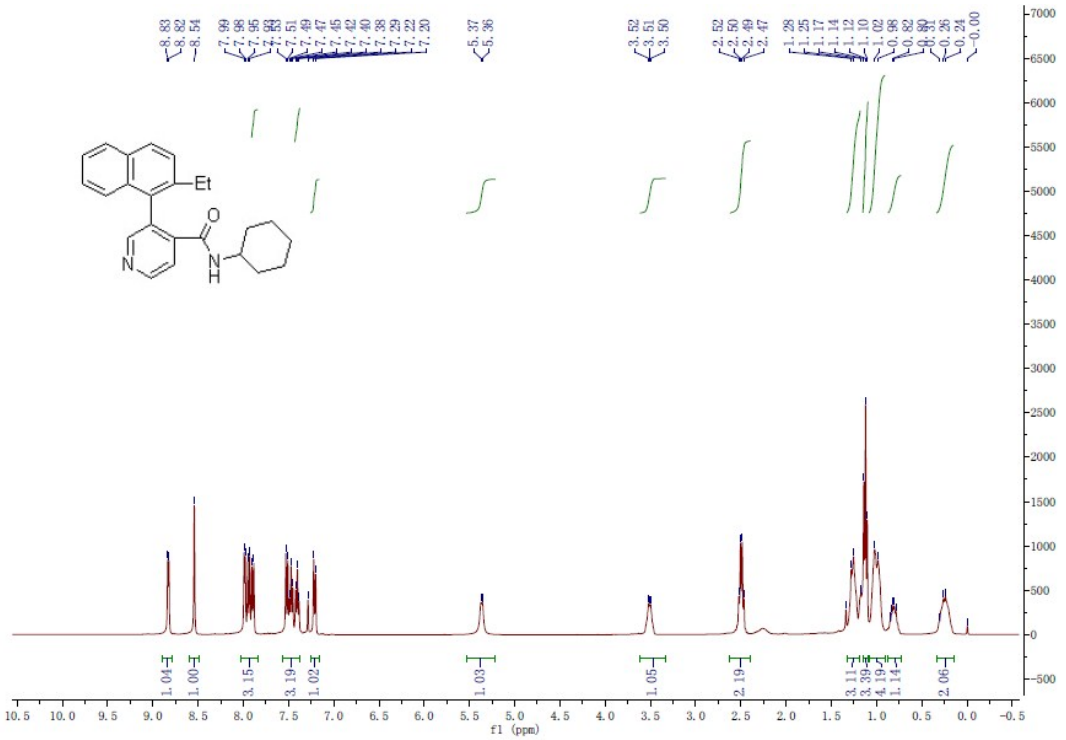
^{1}H NMR (400 MHz, $CDCl_3$) of **3dA**



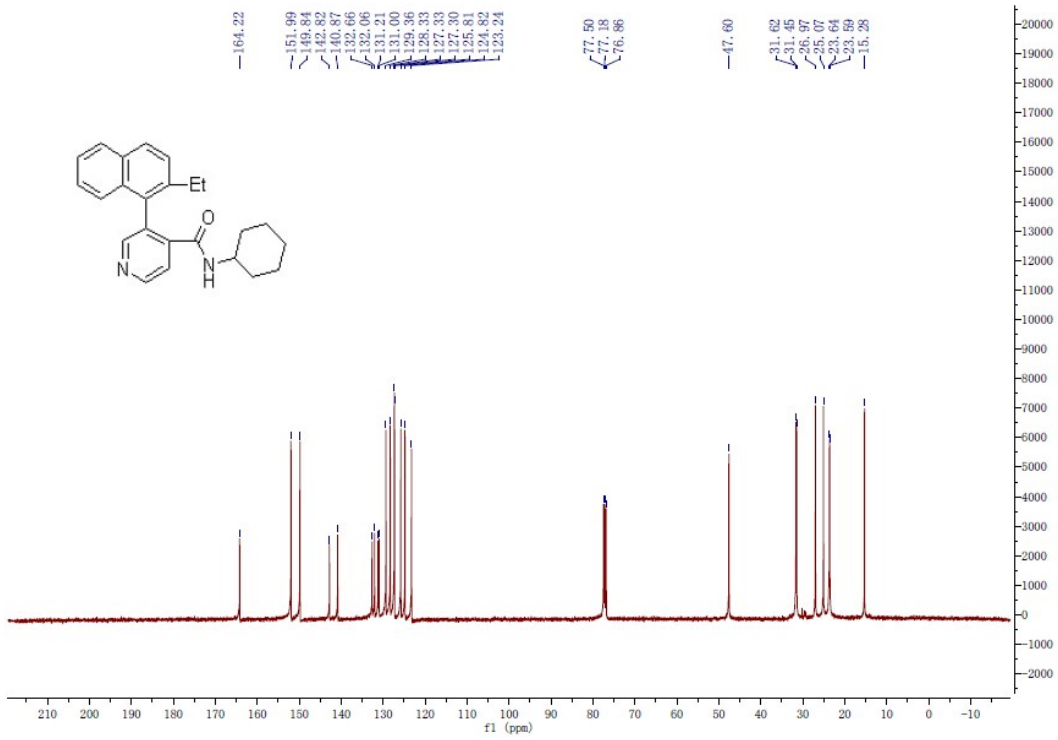
^{13}C NMR (100 MHz, $CDCl_3$) of **3dA**



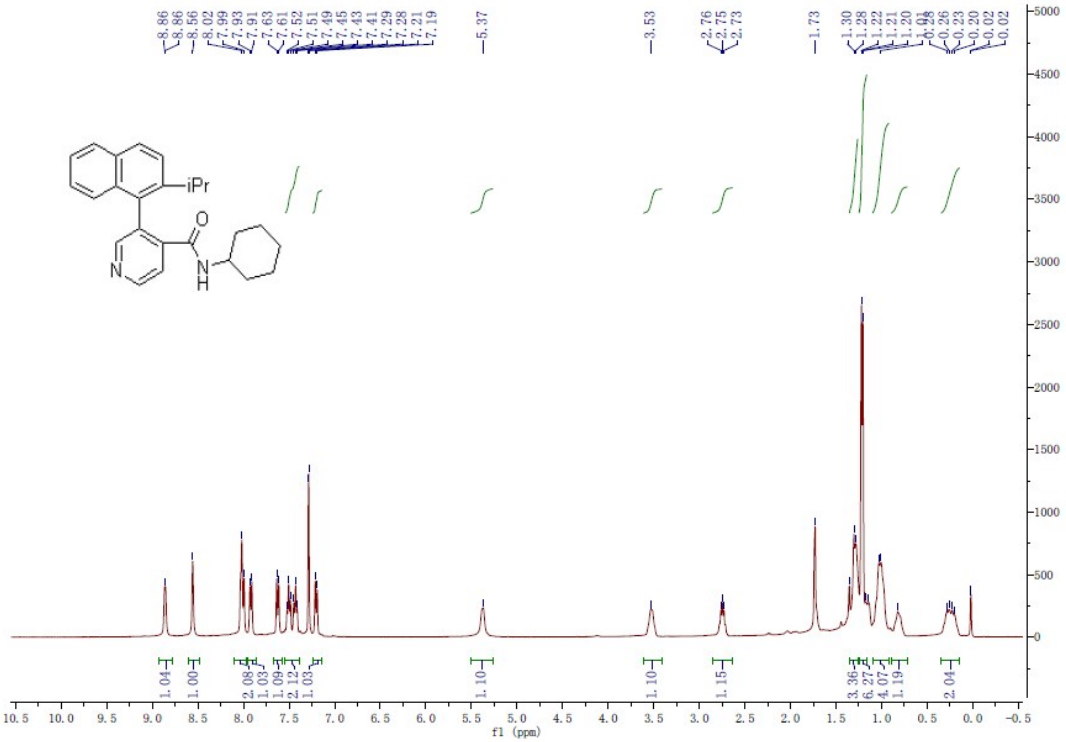
^{1}H NMR (400 MHz, $CDCl_3$) of **3dB**



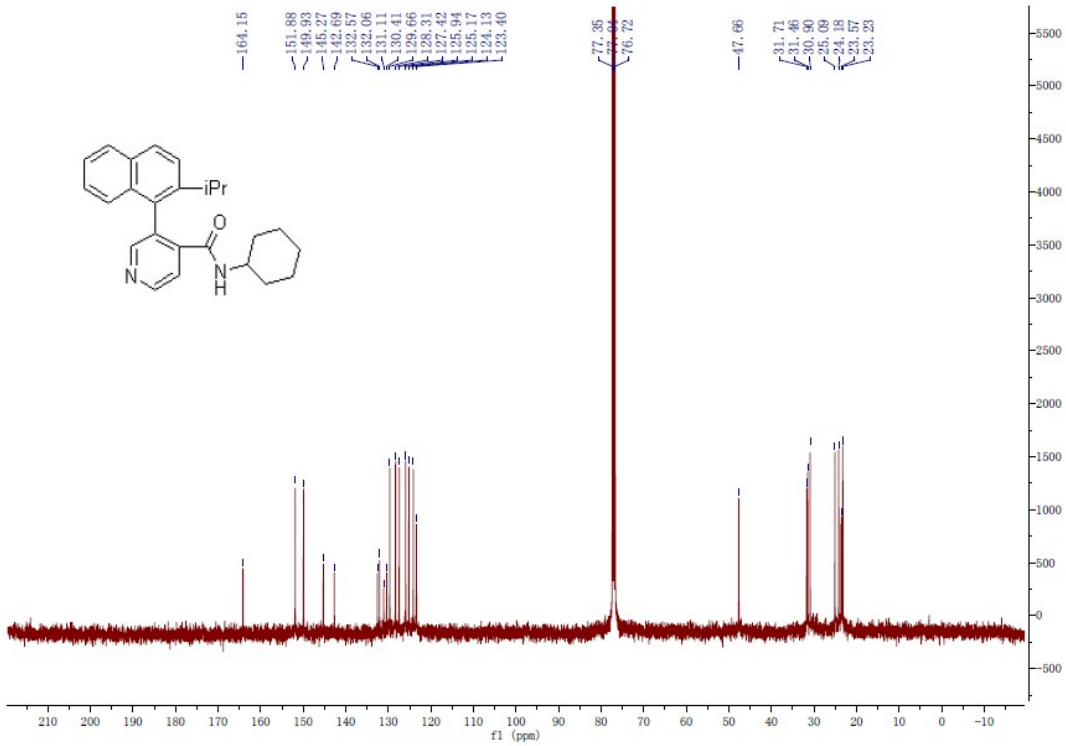
^{13}C NMR (100 MHz, $CDCl_3$) of **3dB**



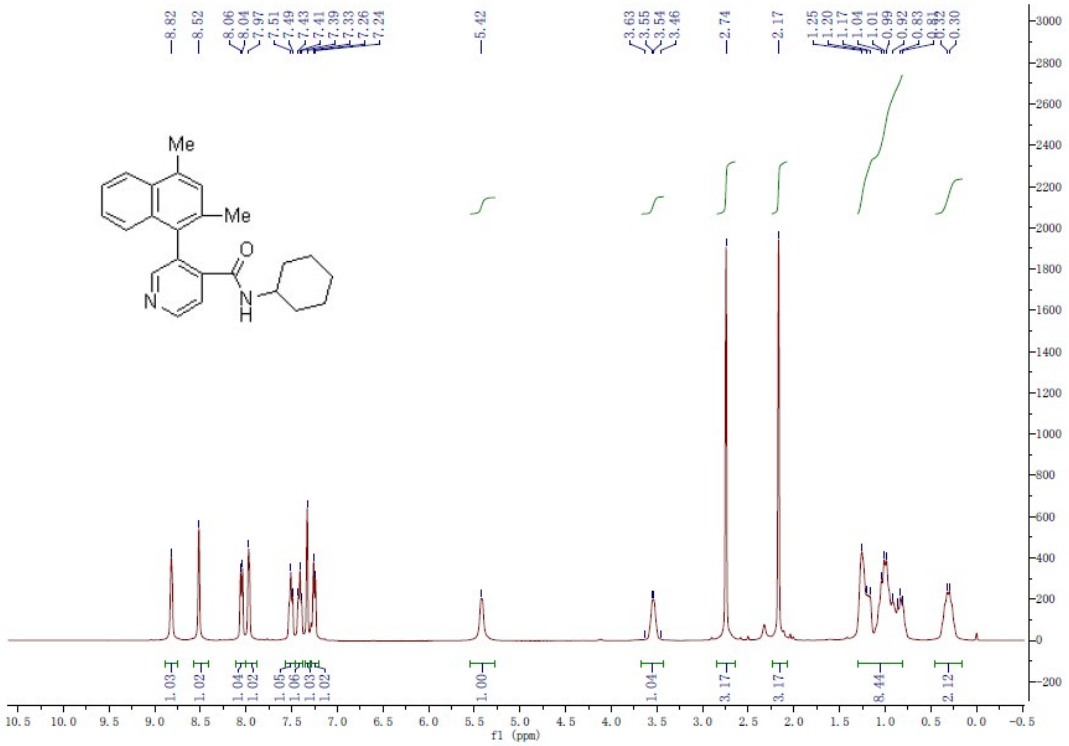
^{1}H NMR (400 MHz, $CDCl_3$) of **3dC**



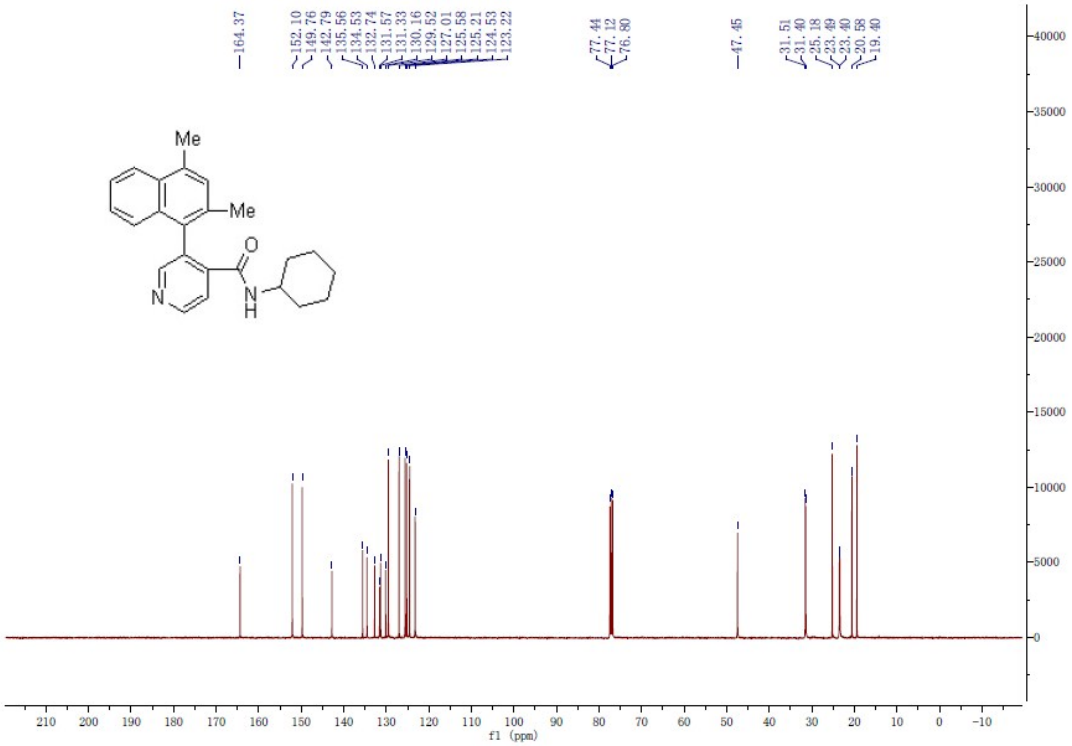
^{13}C NMR (100 MHz, $CDCl_3$) of **3dC**



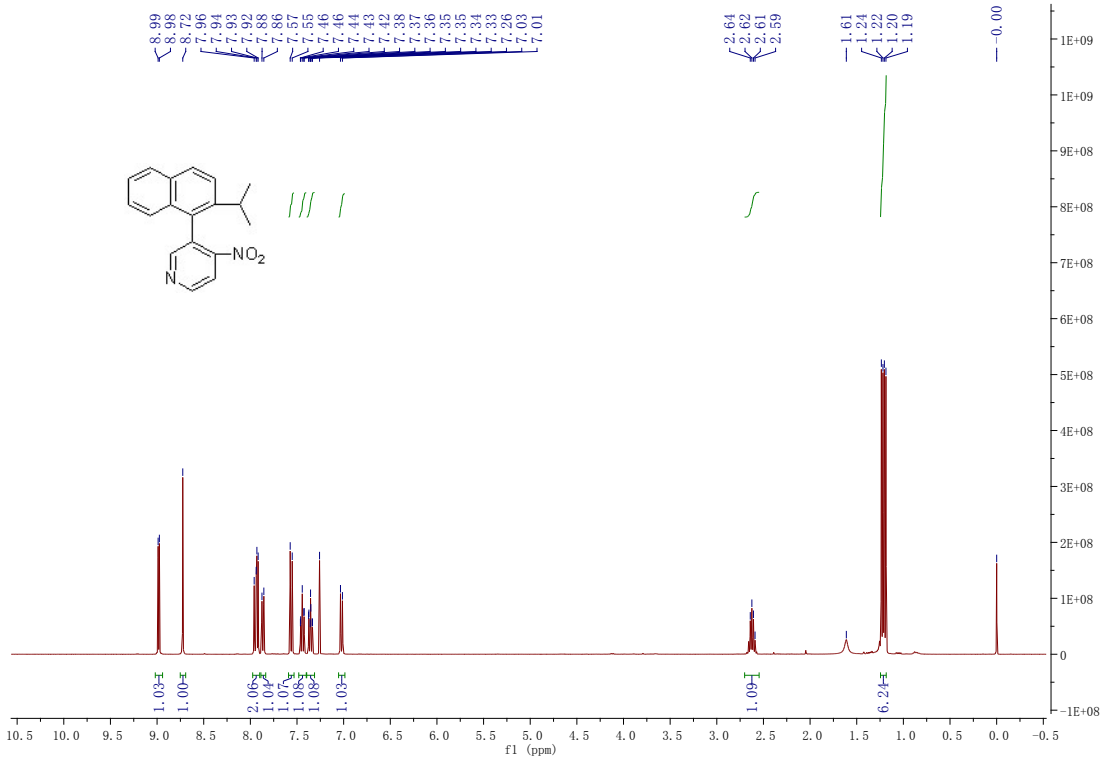
^{1}H NMR (400 MHz, $CDCl_3$) of **3dD**



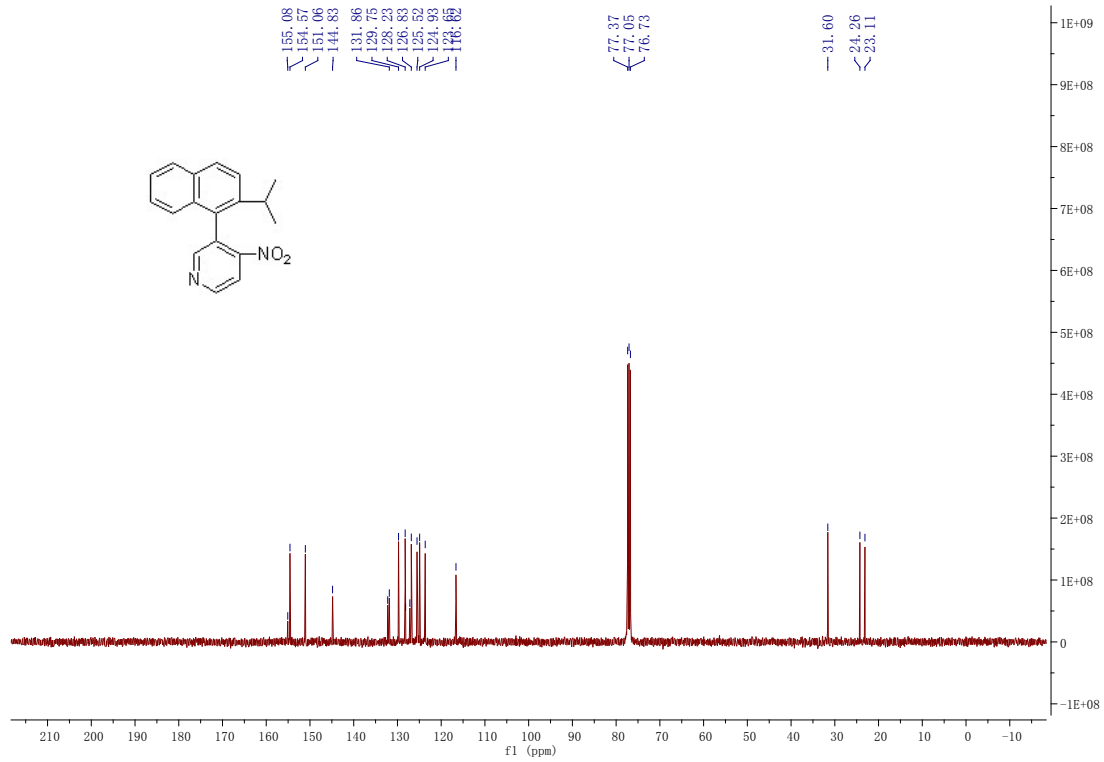
^{13}C NMR (100 MHz, $CDCl_3$) of **3dD**



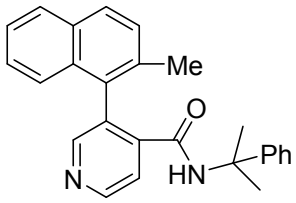
^{1}H NMR (400 MHz, $CDCl_3$) of **3eC**



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

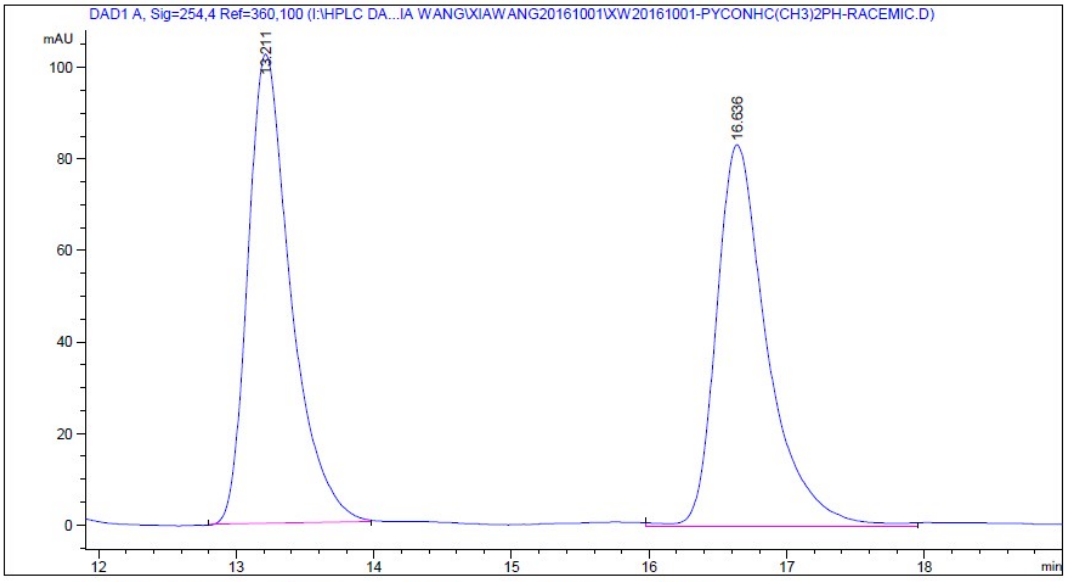


HPLC SPECTRA

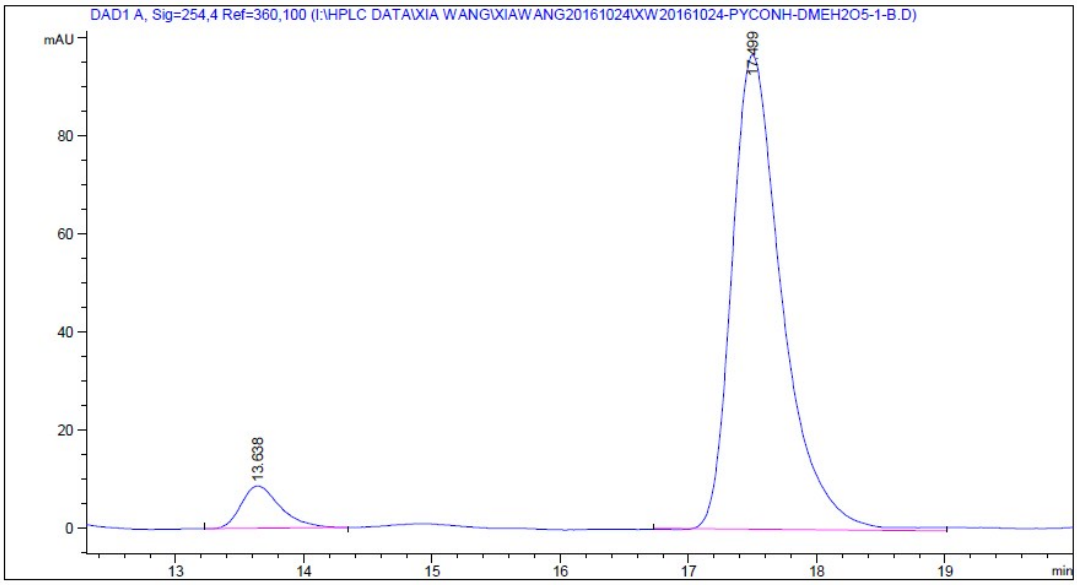


3aA

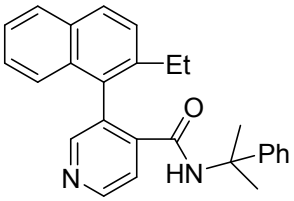
The top one is racemic and the bottom one is chiral.



Entry #	RetTime [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.211	0.3607	2218.73779	102.51774	50.5974
2	16.636	0.4322	2166.34131	83.53082	49.4026

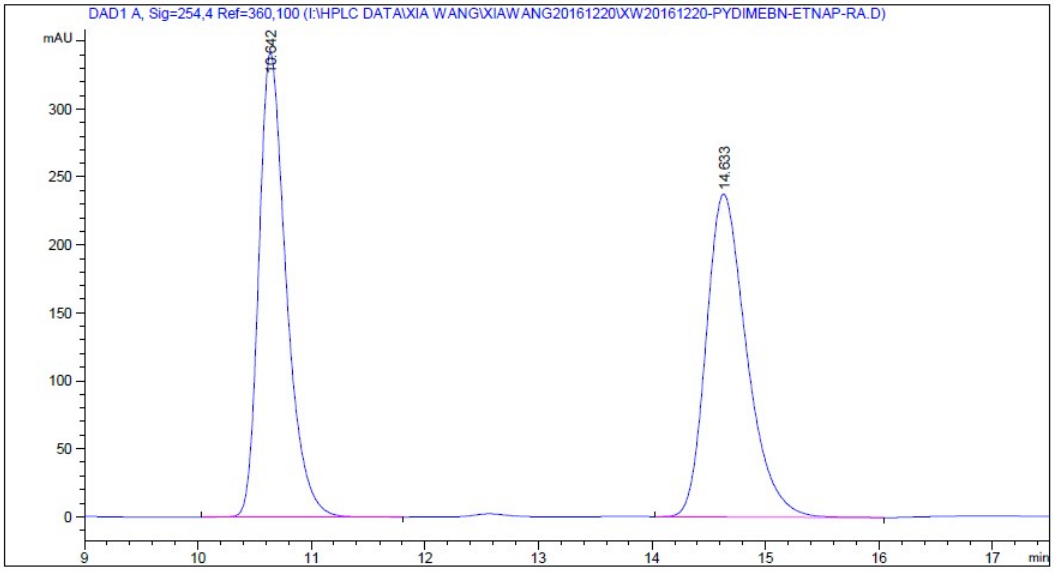


Entry #	RetTime [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.638	0.3198	183.62384	8.64611	6.5210
2	17.499	0.4535	2632.27002	96.74740	93.4790

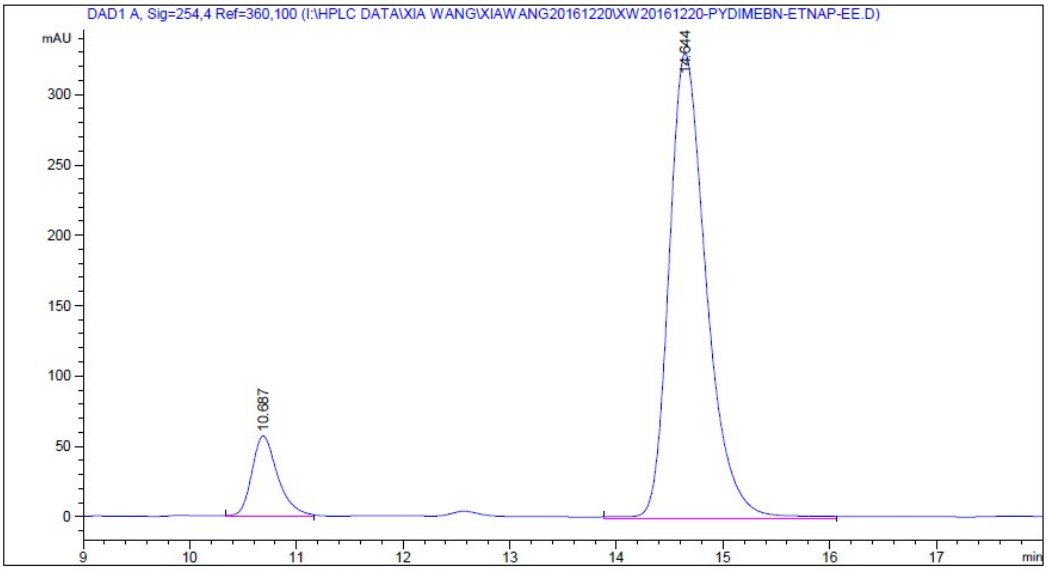


3aB

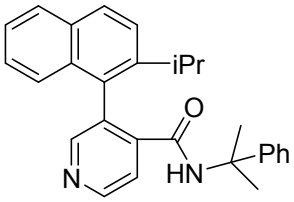
The top one is racemic and the bottom one is chiral.



Entry #	RetTime [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.642	0.2535	5723.98633	341.65698	49.3289
2	14.633	0.3768	5879.73535	237.54837	50.6711

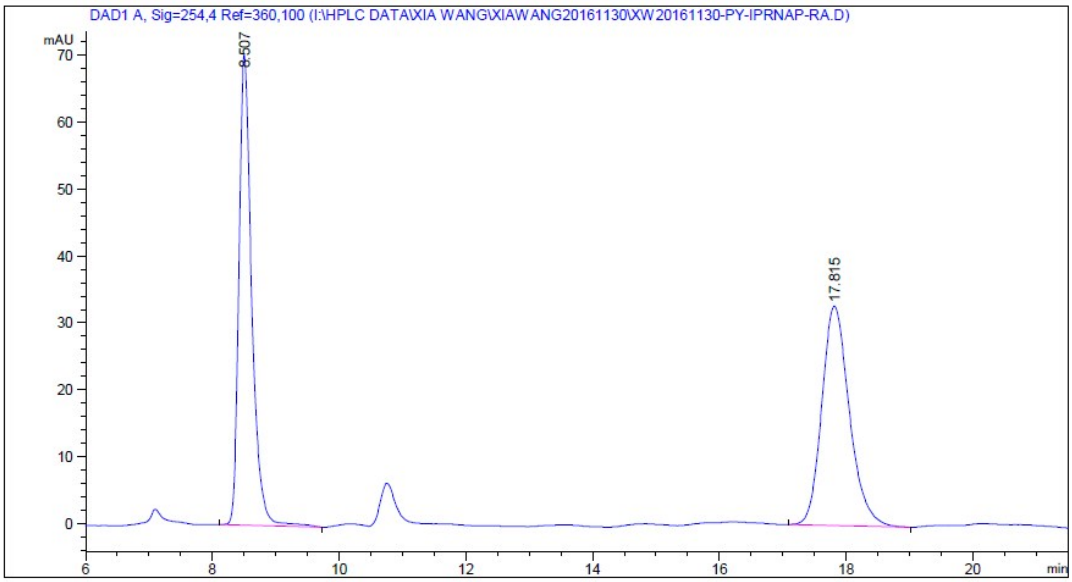


Entry #	RetTime [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.687	0.2786	947.46765	56.68844	10.5199
2	14.644	0.4061	8058.95752	330.70770	89.4801

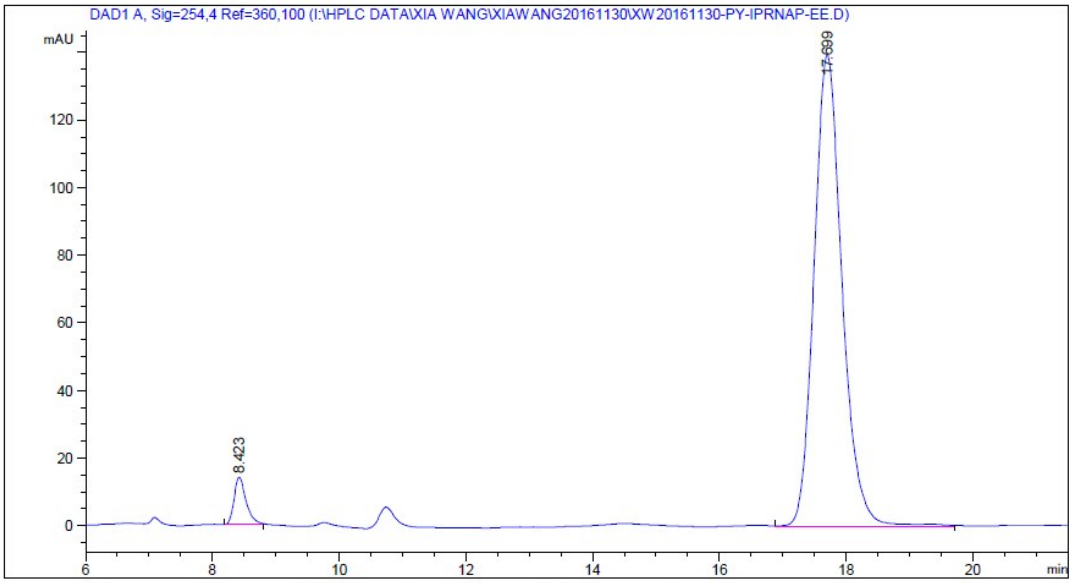


3aC

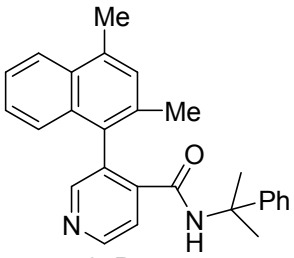
The top one is racemic and the bottom one is chiral.



Entry #	RetTime [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.507	0.2115	984.89172	70.27605	49.8303
2	17.815	0.4645	991.59888	32.81821	50.1697

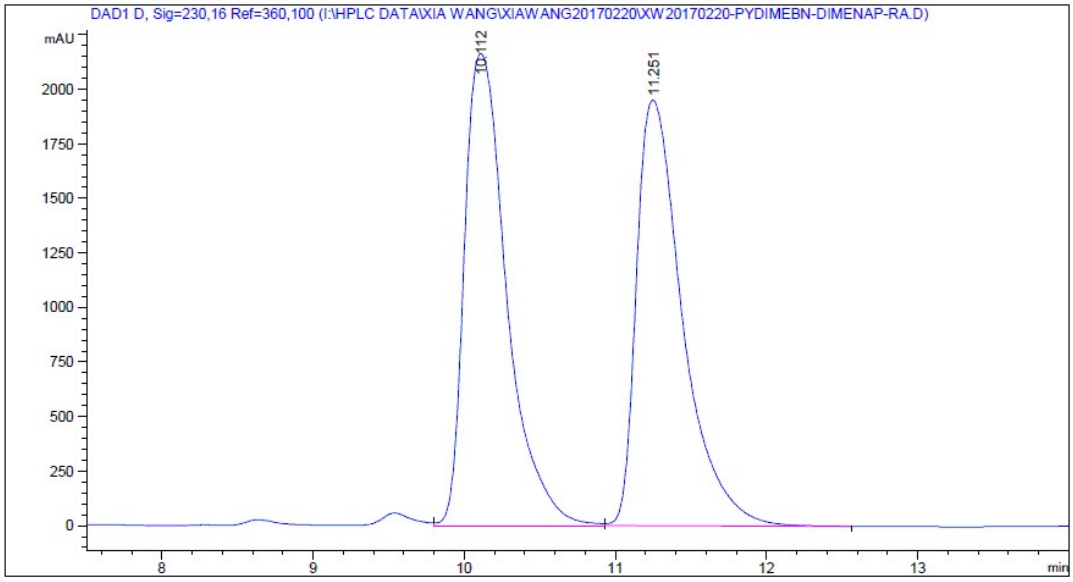


Entry #	RetTime [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.423	0.2150	178.16154	13.80914	3.9713
2	17.699	0.5141	4308.11377	139.65761	96.0287

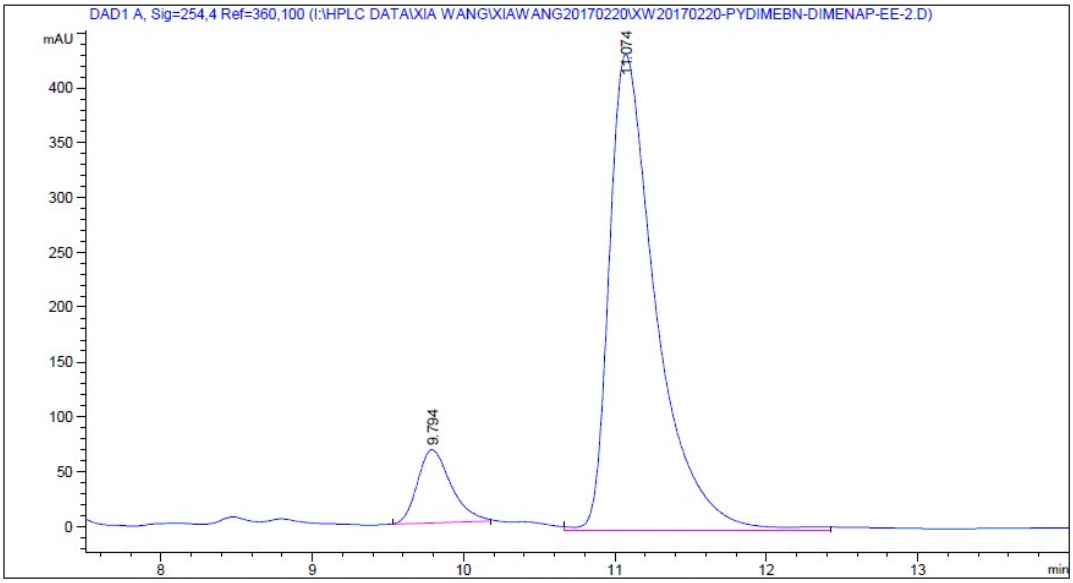


3aD

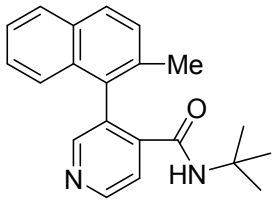
The top one is racemic and the bottom one is chiral.



Entry #	RetTime [min]	width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.112	0.2994	4.21107e4	2160.39893	50.5008
2	11.251	0.3229	4.12756e4	1950.33093	49.4992

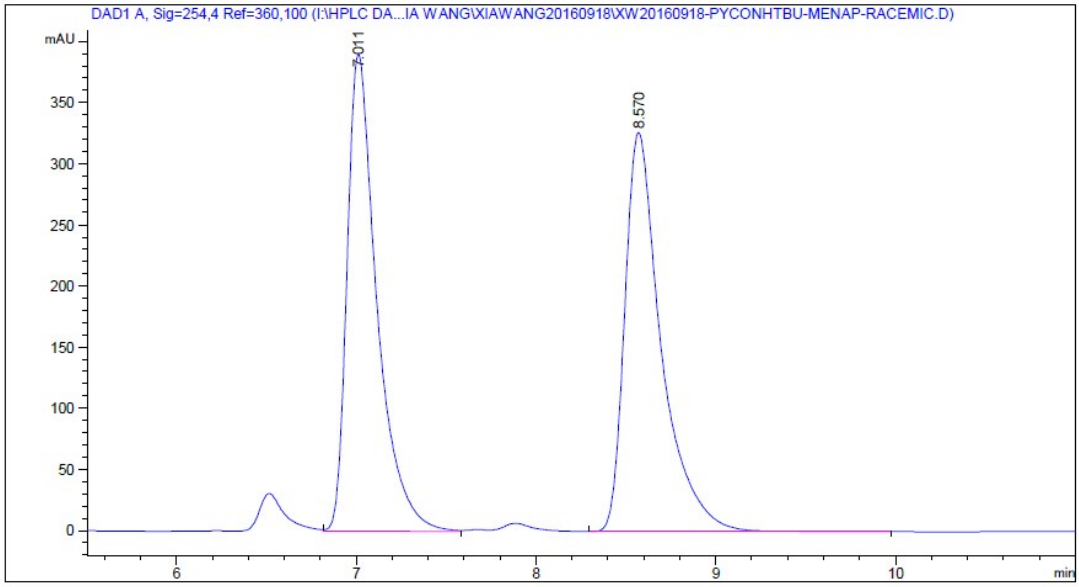


Entry #	RetTime [min]	width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.794	0.2564	1027.95007	66.82371	9.9017
2	11.074	0.3588	9353.57715	434.45944	90.0983

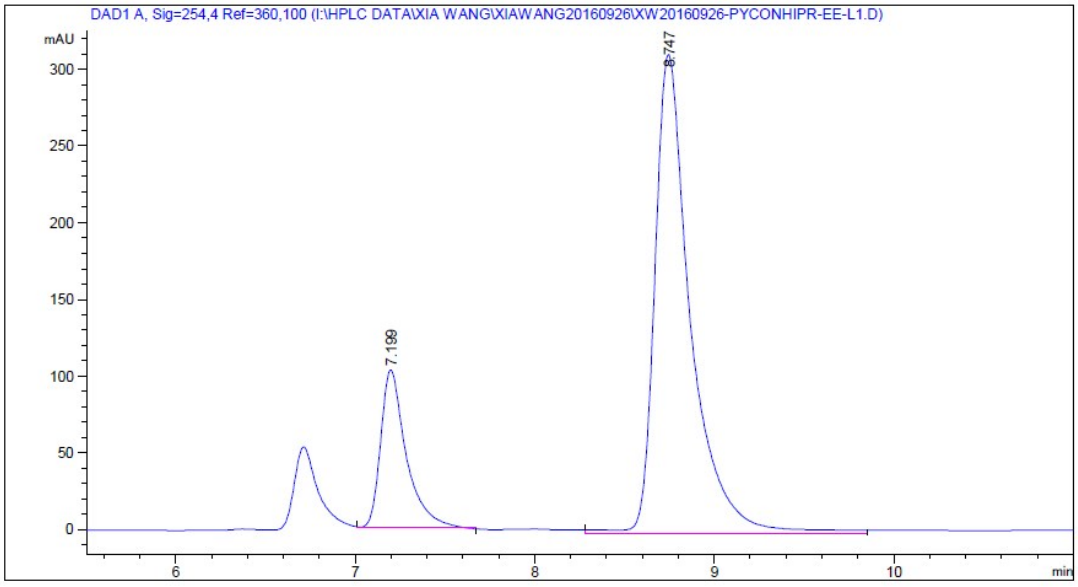


3bA

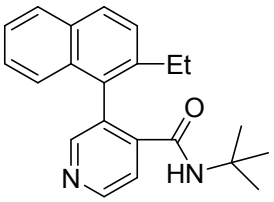
The top one is racemic and the bottom one is chiral.



Entry #	RetTime [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.011	0.1707	4506.50977	390.28690	49.4630
2	8.570	0.2085	4604.35742	326.50708	50.5370

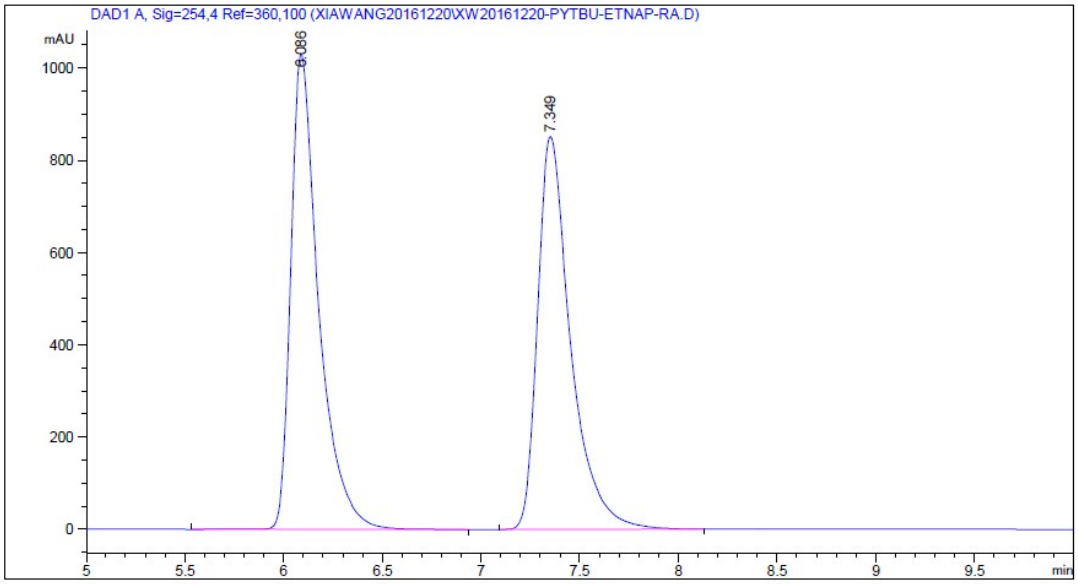


Entry #	RetTime [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.199	0.1651	1022.46057	103.18622	19.0700
2	8.747	0.2315	4339.15234	312.34509	80.9300

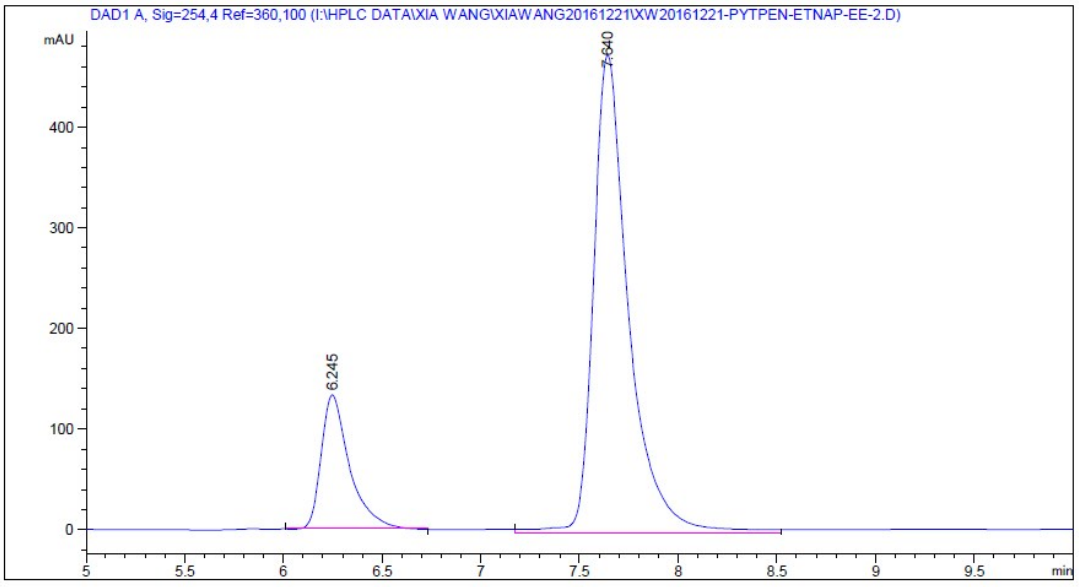


3bB

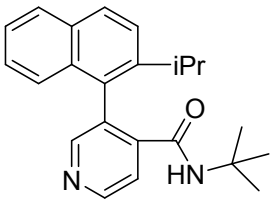
The top one is racemic and the bottom one is chiral.



Entry #	RetTime [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.086	0.1444	1.01118e4	1031.05371	50.5577
2	7.349	0.1714	9888.68164	852.07458	49.4423

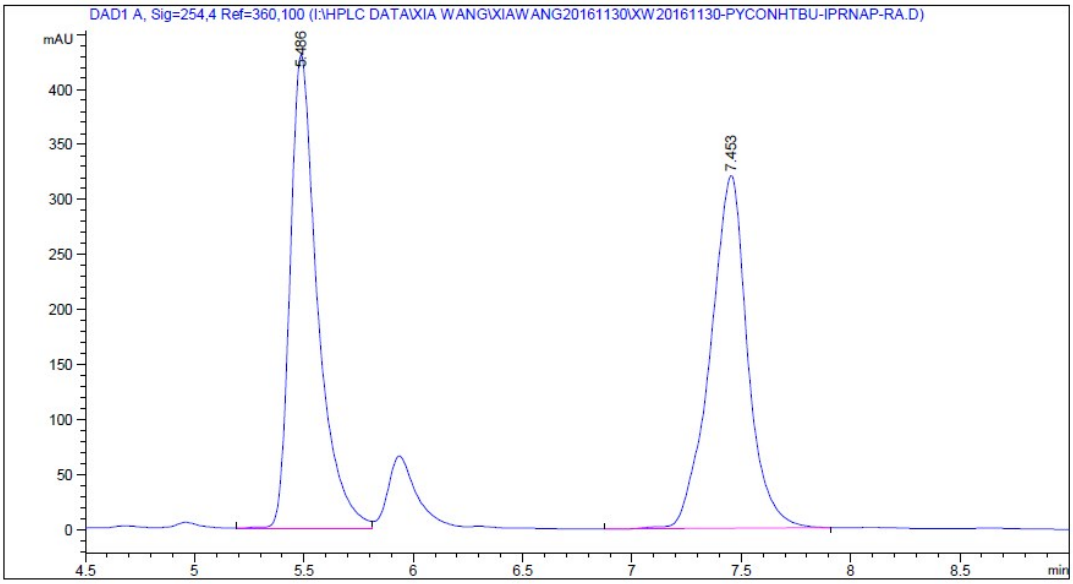


Entry #	RetTime [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.245	0.1630	1295.63660	132.49916	17.8688
2	7.640	0.2087	5955.19336	475.62863	82.1312

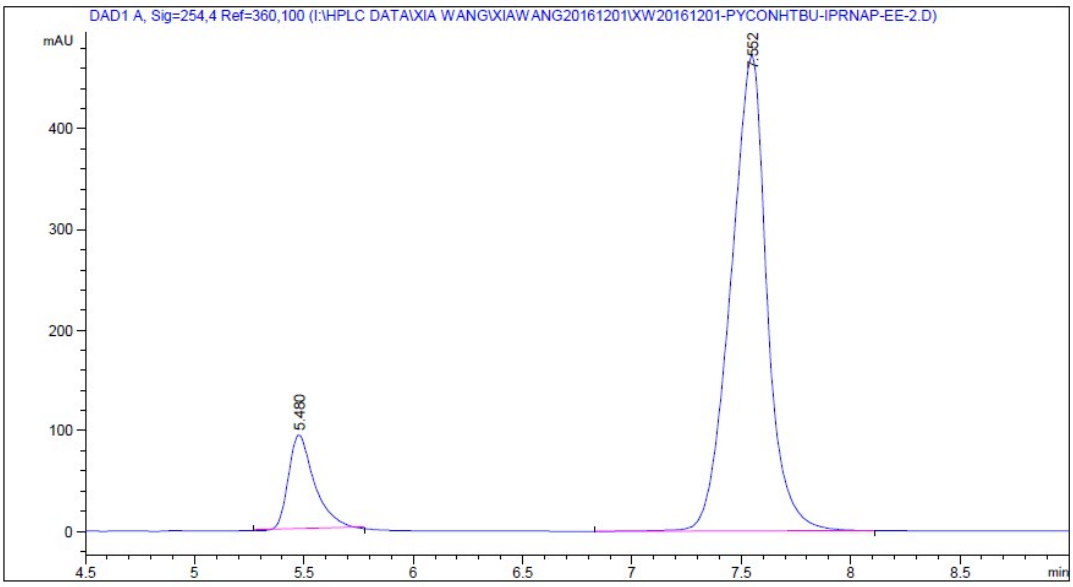


3bC

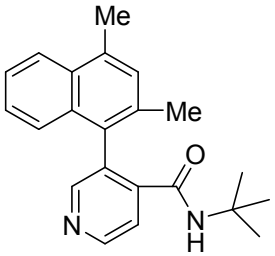
The top one is racemic and the bottom one is chiral.



Entry #	RetTime [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.486	0.1282	3770.06909	430.57407	49.7349
2	7.453	0.1786	3810.25952	320.61801	50.2651

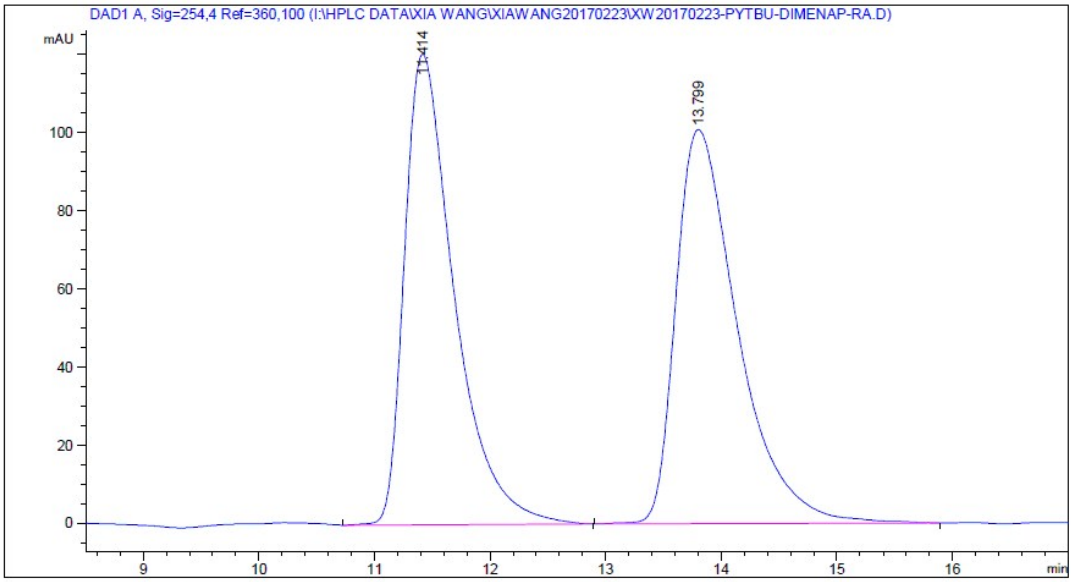


Entry #	RetTime [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.480	0.1368	766.10443	93.33291	12.3646
2	7.552	0.1721	5429.83887	472.46365	87.6354

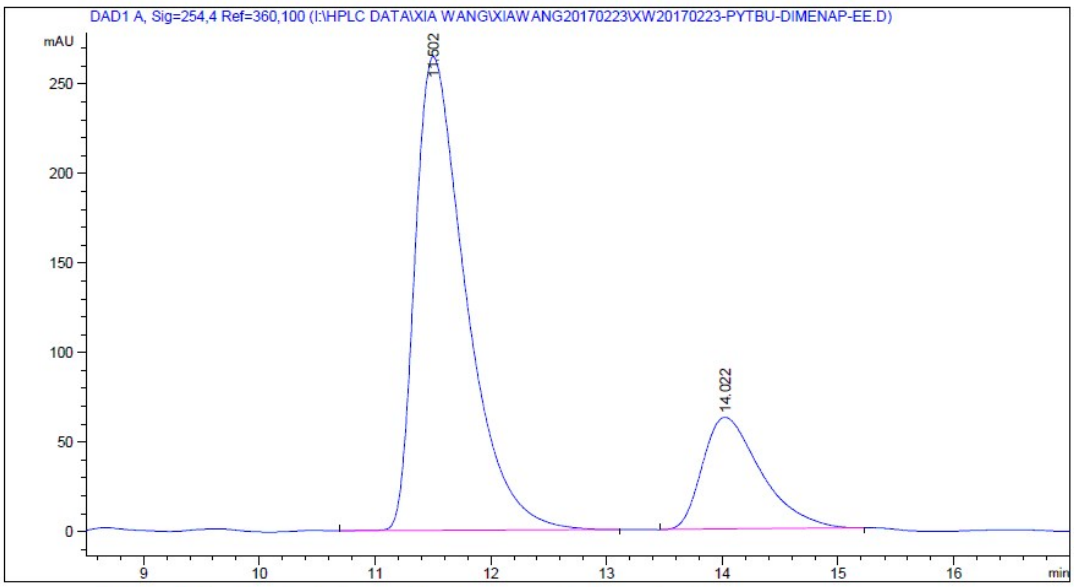


3bD

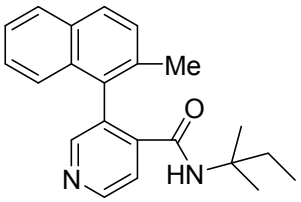
The top one is racemic and the bottom one is chiral.



Entry #	RetTime [min]	width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.414	0.4479	3607.91089	120.29056	49.1025
2	13.799	0.5649	3739.80786	100.78046	50.8975

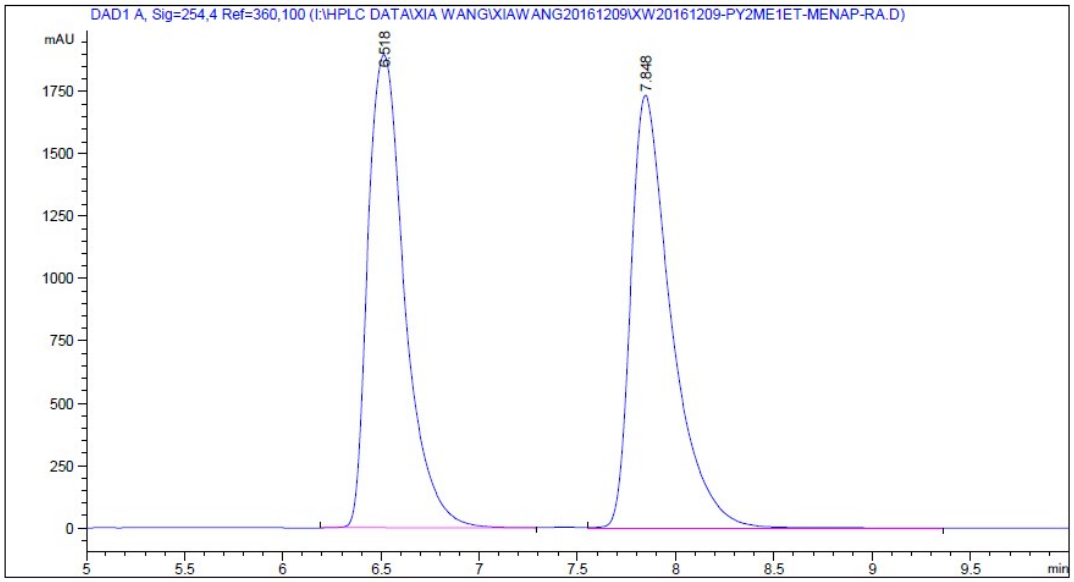


Entry #	RetTime [min]	width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.502	0.4575	8069.39014	264.79230	78.6408
2	14.022	0.5348	2191.68481	62.54187	21.3592

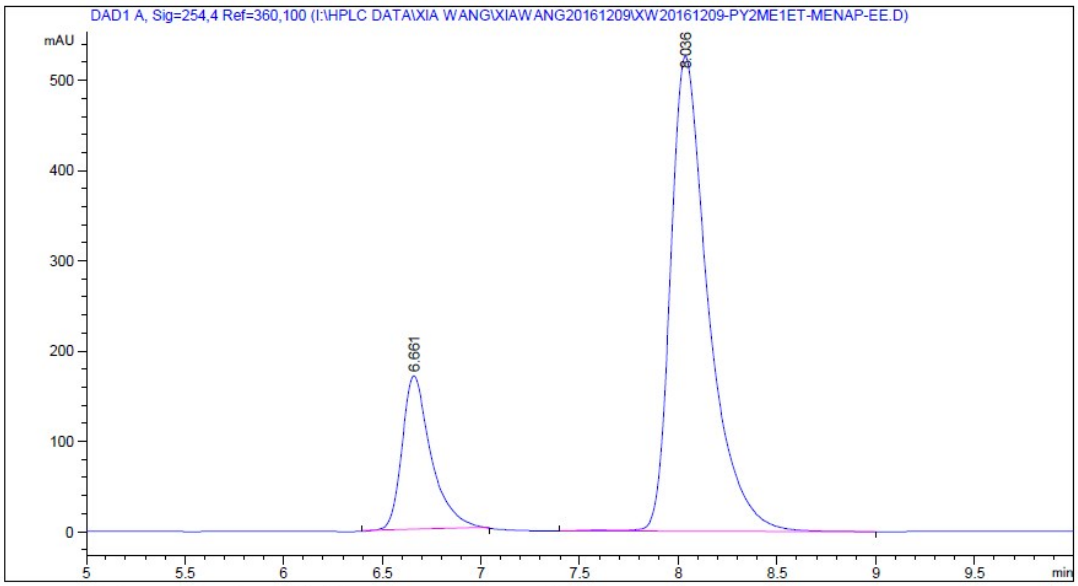


3cA

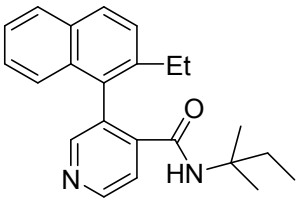
The top one is racemic and the bottom one is chiral.



Entry #	RetTime [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.518	0.2035	2.46551e4	1899.24976	49.9545
2	7.848	0.2119	2.47000e4	1736.52881	50.0455

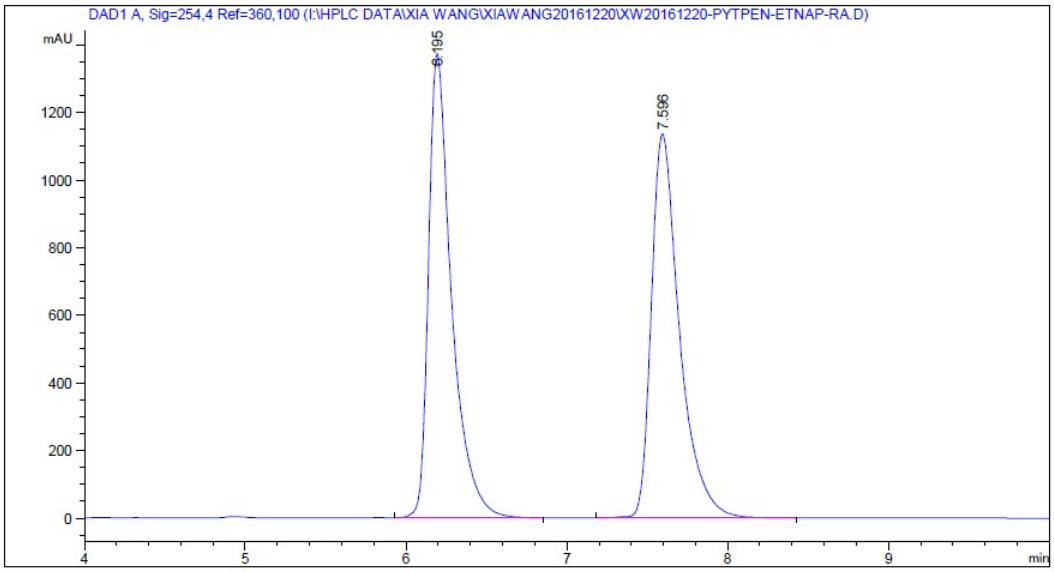


Entry #	RetTime [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.661	0.1696	1727.05225	169.70766	19.8066
2	8.036	0.1969	6992.54102	526.82397	80.1934

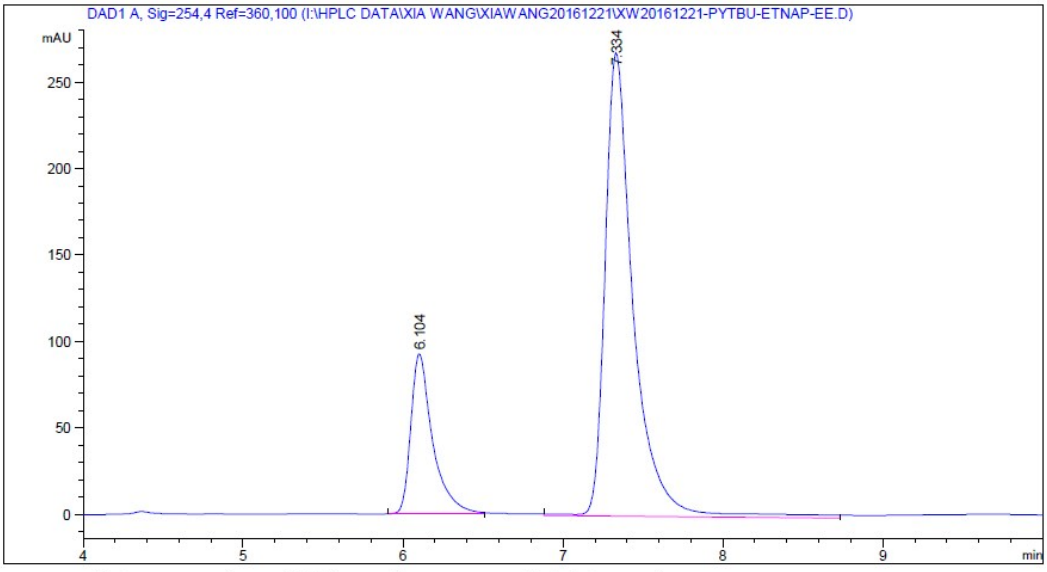


3cB

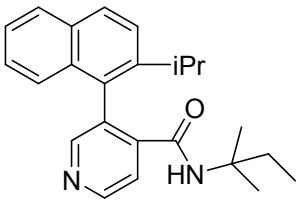
The top one is racemic and the bottom one is chiral.



Entry #	RetTime [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.195	0.1462	1.36754e4	1372.99609	49.6774
2	7.596	0.1842	1.38530e4	1136.85229	50.3226

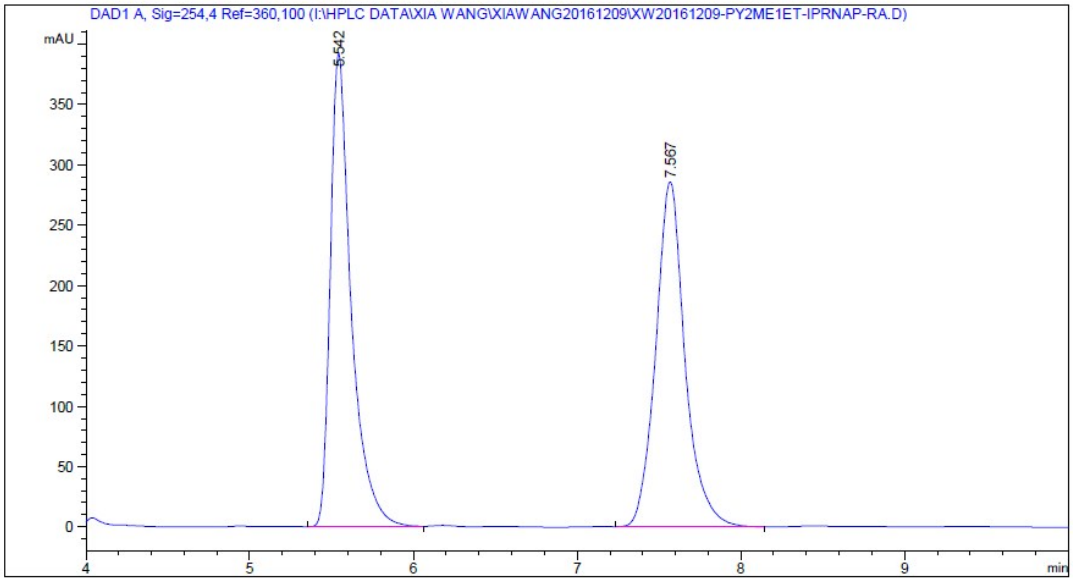


Entry #	RetTime [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.104	0.1560	863.26782	92.20815	20.5267
2	7.334	0.2078	3342.32153	268.06708	79.4733

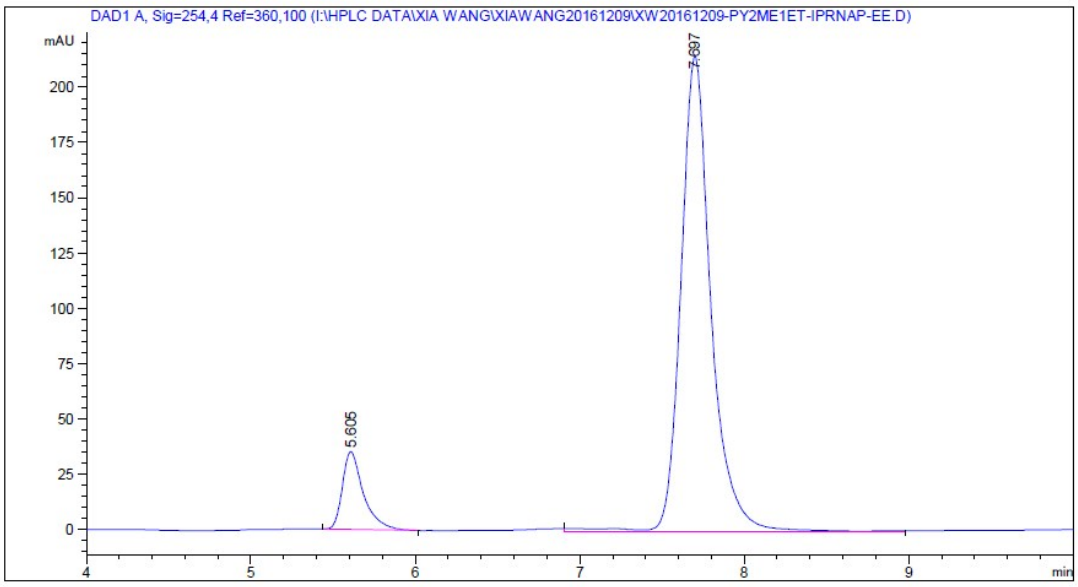


3cC

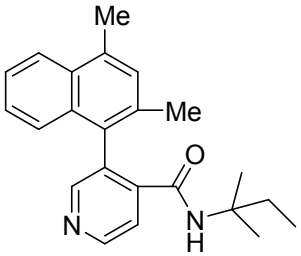
The top one is racemic and the bottom one is chiral.



Entry #	RetTime [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.542	0.1318	3492.20898	392.32745	49.6122
2	7.567	0.1847	3546.81055	285.95004	50.3878

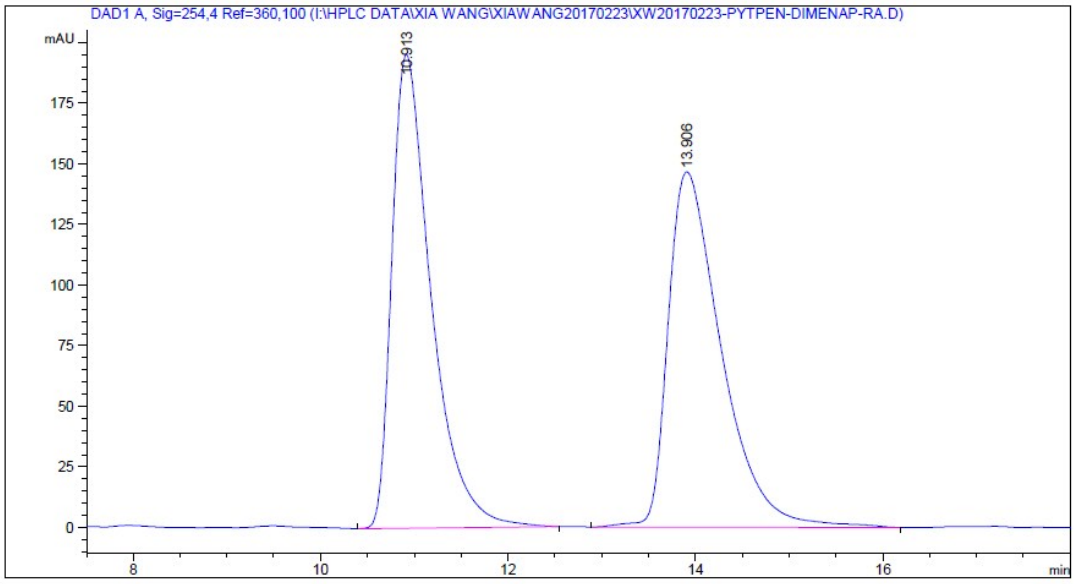


Entry #	RetTime [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.605	0.1311	311.63617	35.24758	10.1691
2	7.697	0.2133	2752.91064	215.12625	89.8309

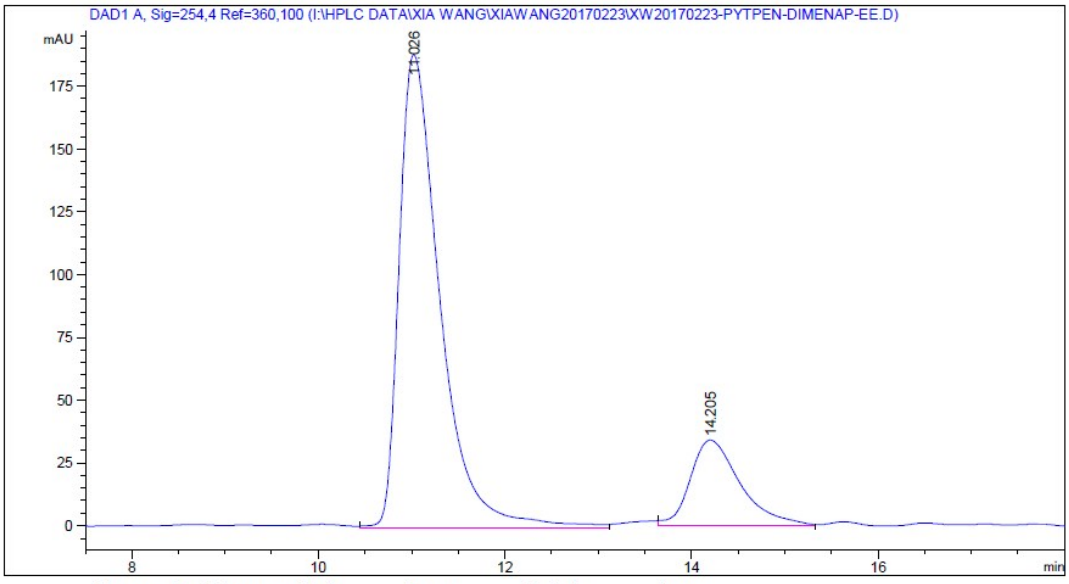


3cD

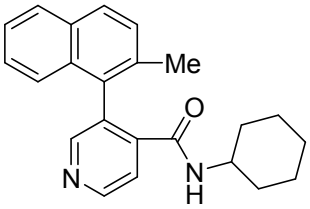
The top one is racemic and the bottom one is chiral.



Entry #	RetTime [min]	width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.913	0.4377	5689.66748	195.38008	49.6134
2	13.906	0.5982	5778.33838	146.50122	50.3866

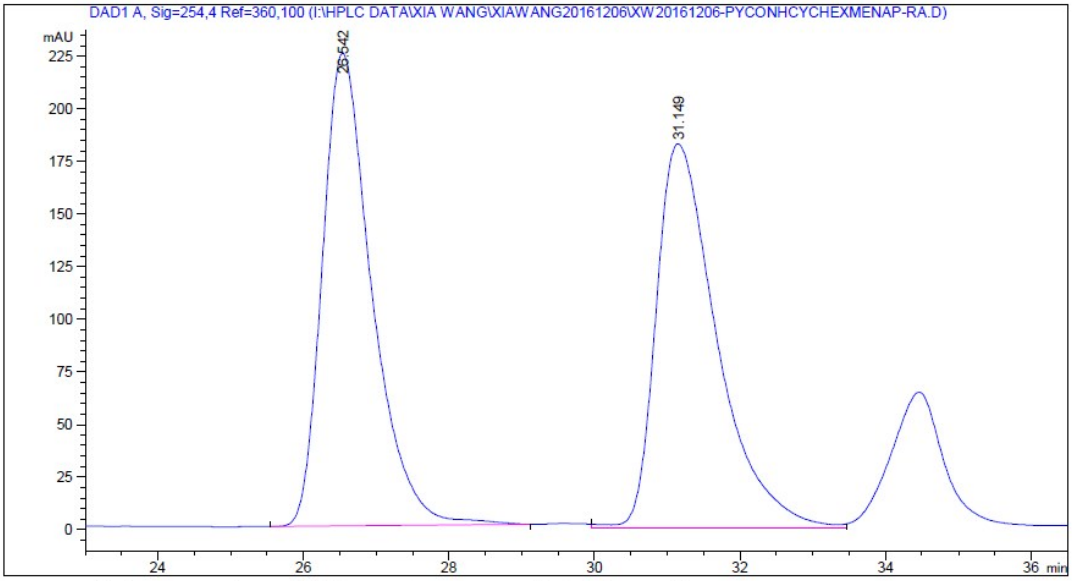


Entry #	RetTime [min]	width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.026	0.5087	5754.23340	188.51701	82.1810
2	14.205	0.6146	1247.67102	33.83545	17.8190

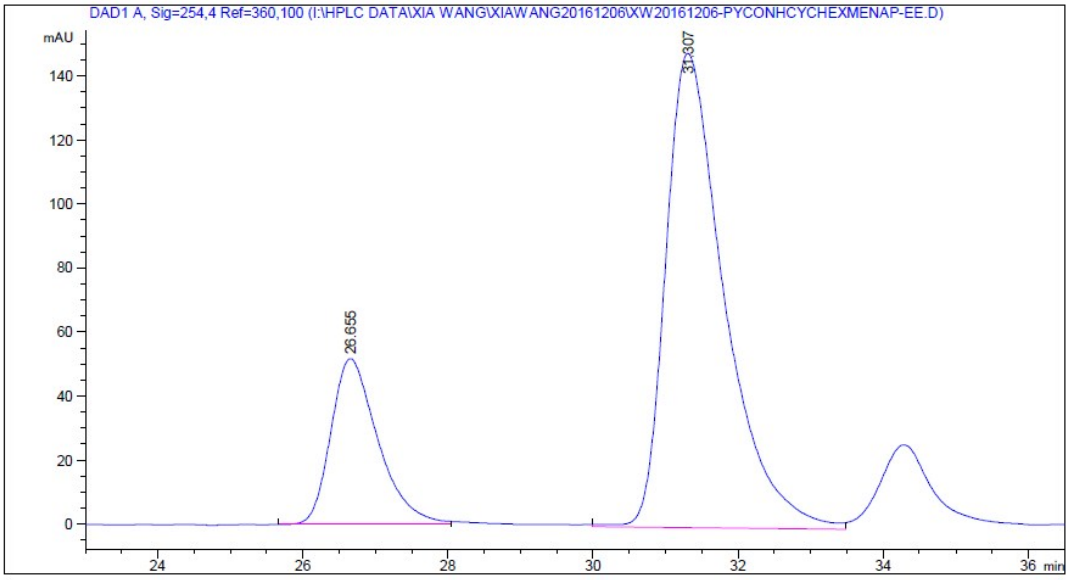


3dA

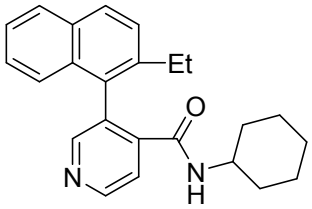
The top one is racemic and the bottom one is chiral.



Entry #	RetTime [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.542	0.7106	1.06422e4	224.67596	50.0823
2	31.149	0.9686	1.06072e4	182.51378	49.9177

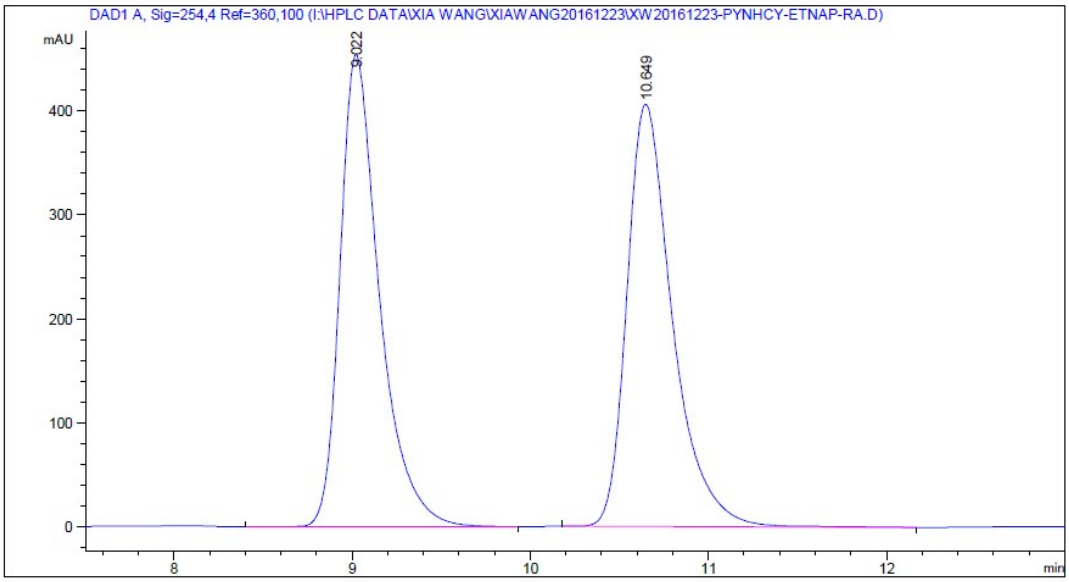


Entry #	RetTime [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.655	0.7474	2315.91943	51.64578	21.7333
2	31.307	0.9386	8340.19238	148.09572	78.2667

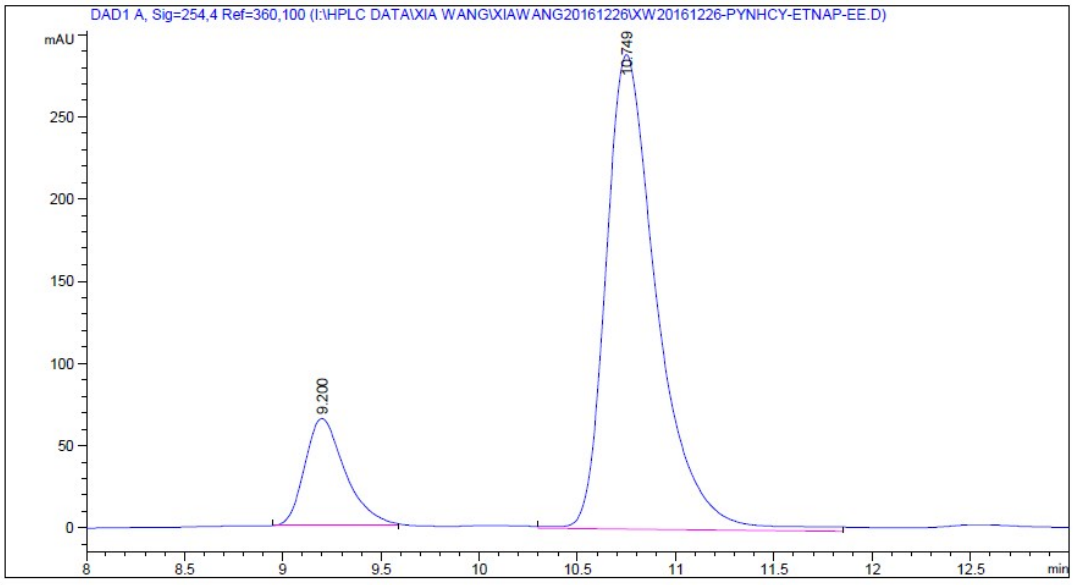


3dB

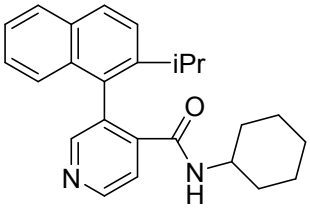
The top one is racemic and the bottom one is chiral.



Entry #	RetTime [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.022	0.2301	7009.31787	454.00830	49.2145
2	10.649	0.2696	7233.05469	406.43881	50.7855

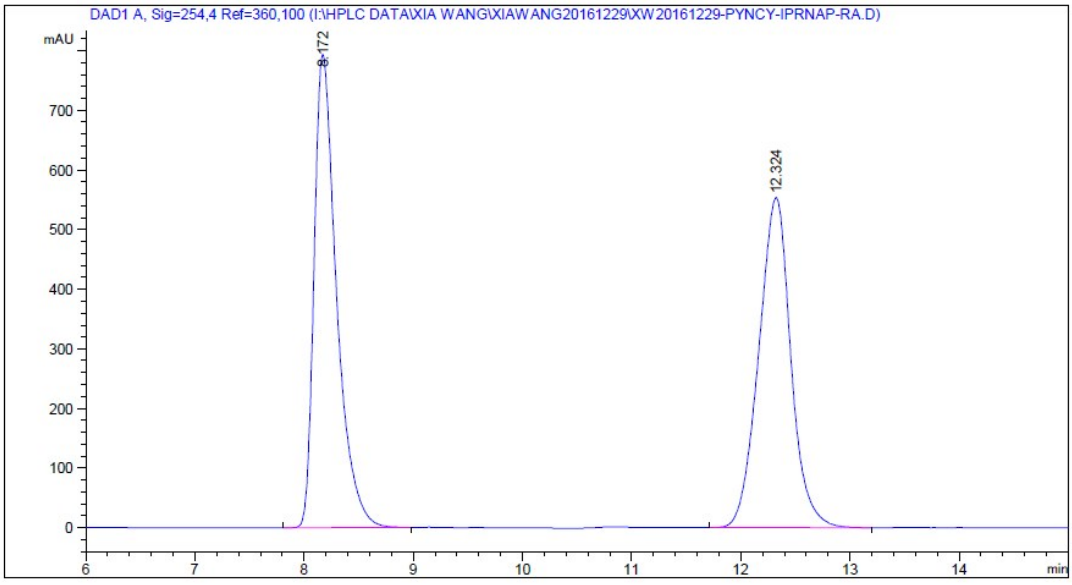


Entry #	RetTime [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.200	0.2376	927.31354	65.03564	15.0544
2	10.749	0.3023	5232.43262	288.51877	84.9456

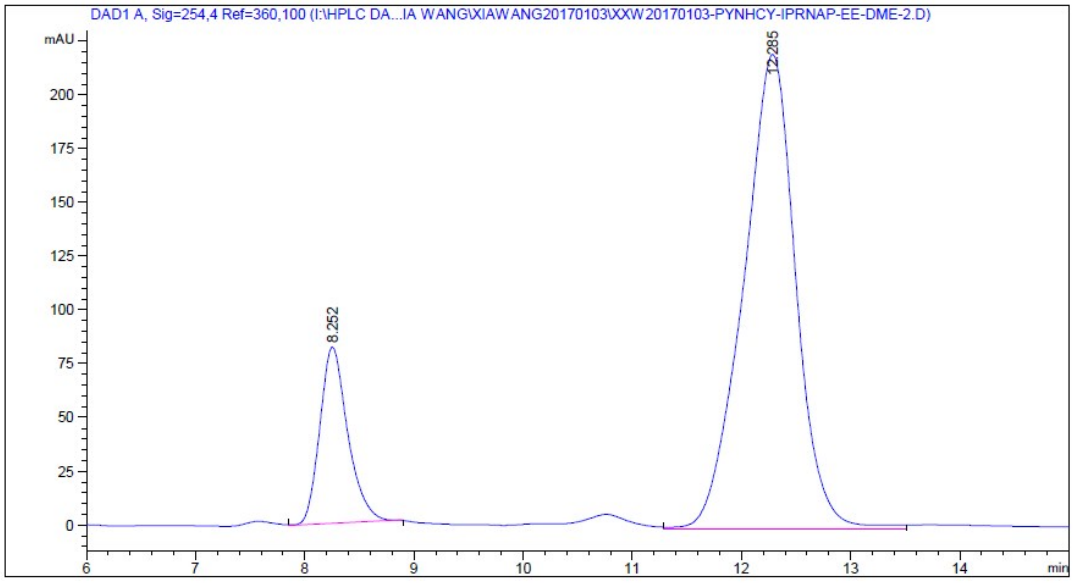


3dC

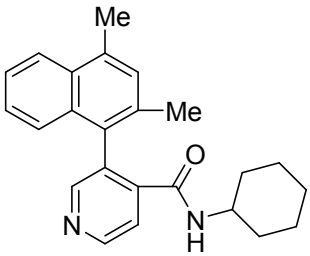
The top one is racemic and the bottom one is chiral.



Entry #	RetTime [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.172	0.2165	1.13222e4	793.34668	50.0822
2	12.324	0.3079	1.12850e4	553.35583	49.9178

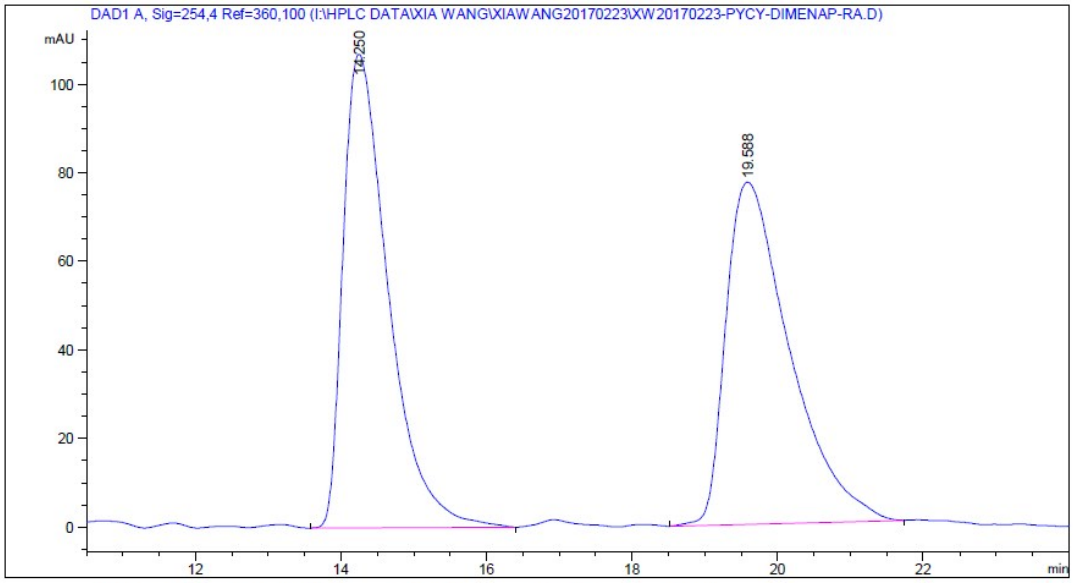


Entry #	RetTime [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.252	0.2964	1459.71570	82.08865	16.5990
2	12.285	0.5540	7334.29150	220.65257	83.4010

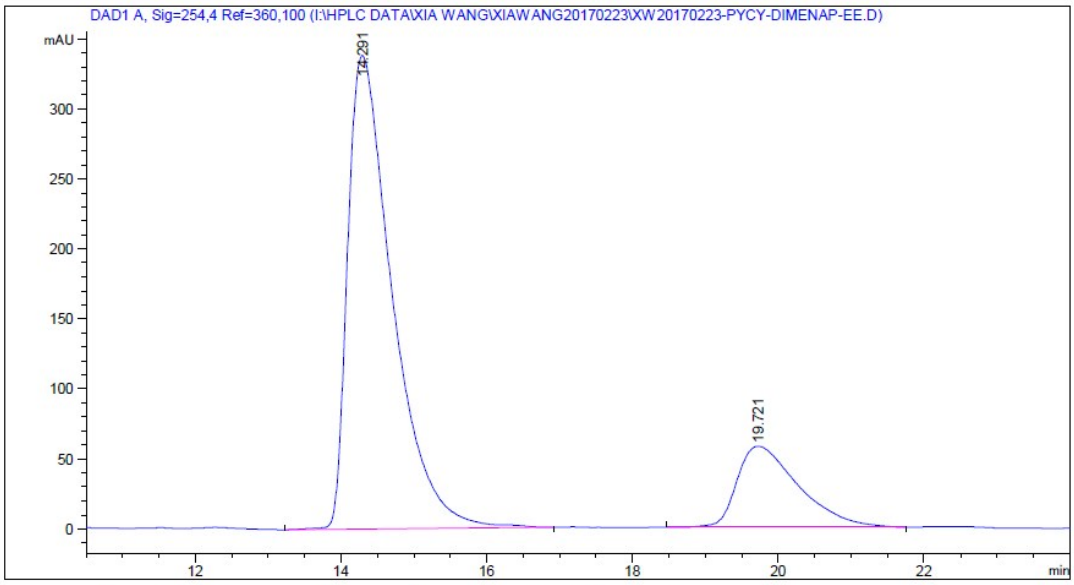


3dD

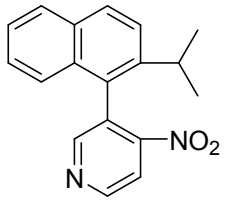
The top one is racemic and the bottom one is chiral.



Entry #	RetTime [min]	width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.250	0.6582	4620.58936	106.90955	49.5235
2	19.588	0.9054	4709.51416	77.23880	50.4765

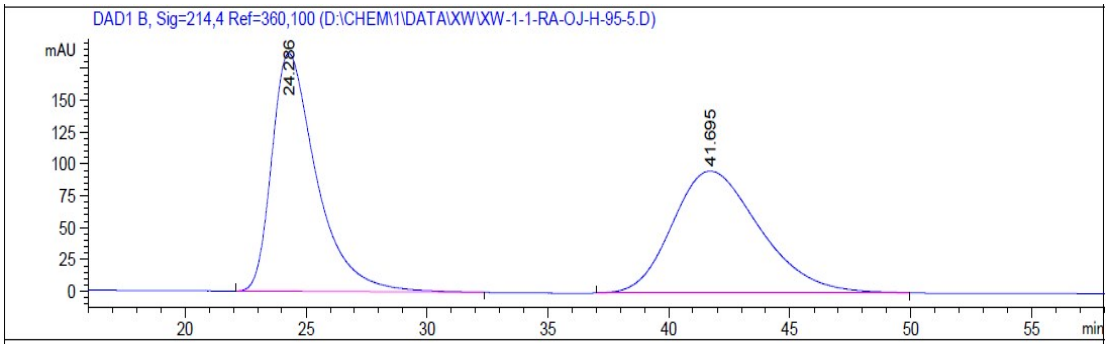


Entry #	RetTime [min]	width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.291	0.6407	1.44024e4	338.31573	80.9058
2	19.721	0.8864	3399.02783	57.93806	19.0942

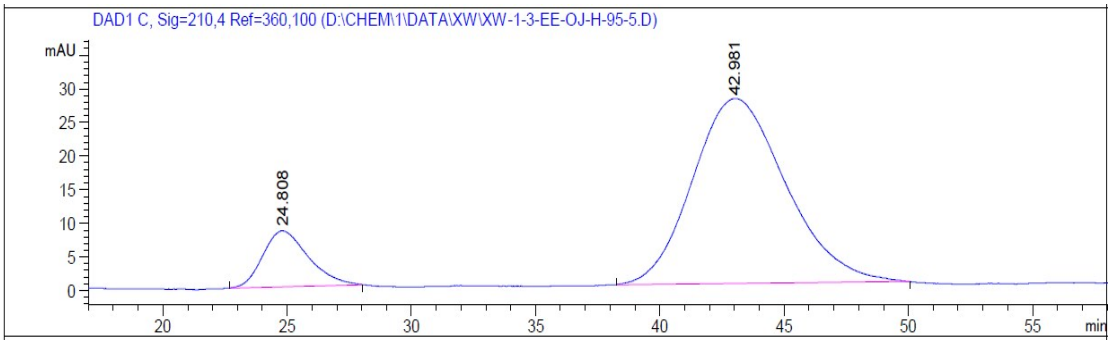


3eC

The top one is racemic and the bottom one is chiral.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.286	BB	1.8953	2.40786e4	186.86816	49.9862
2	41.695	BB	2.9767	2.40919e4	95.64397	50.0138



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.813	BB	1.5428	1365.80103	10.45008	13.2920
2	42.994	BB	3.0646	8909.54688	34.16272	86.7080