Supporting Information

Asymmetric Synthesis of Isoquinolinonaphthyridines Catalyzed by a Chiral Brønsted Acid

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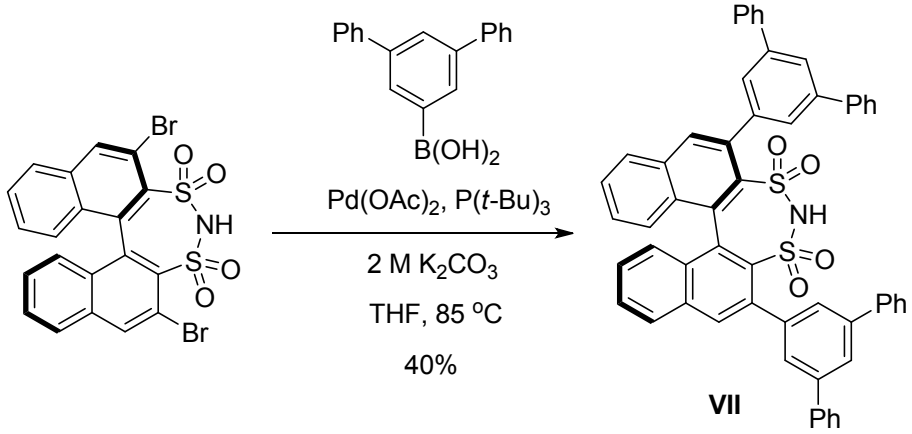
1. General Information

Unless otherwise noted, all reagents were obtained commercially and used without further purification. Unless otherwise specified, all other reagents were purchased from Acros, Aldrich, Fisher, Adamas-beta Co. Ltd. or TCI and used without further purification. The NMR spectra were recorded on a Varian MERCURY plus-400 (400 MHz, ^{1}H; 100 MHz, ^{13}C) spectrometer with chemical shifts reported in ppm relative to the residual deuterated solvent and the internal standard tetramethylsilane. Data for 1H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant(s) in Hz, integration). Chromatography was carried out with silica gel (200-300 mesh) or neutral alumina (200-300 mesh) using mixtures of petroleum ether (b.p. 60-90 ºC) and ethyl acetate as eluents. The enantiomeric ratios of products were detected on HPLC (Shimadzu LC-LabSolutions) using a Daicel chiral column. Mass Spectra were obtained by using an electrospray spectrometer Waters Micromass Q-TOF Premier Mass Spectrometer from East China University of Science and Technology mass spectral facility.

2. Procedure for the synthesis of catalysts

Catalysts **I**,[1a] **II**,[1b] **III**,[1c] **IV**,[1d,1e] **V**,[1f] **VI**,[1g] and **VIII**[1h] were known in the literature and **VII** were prepared according to the literature methods.[1a]

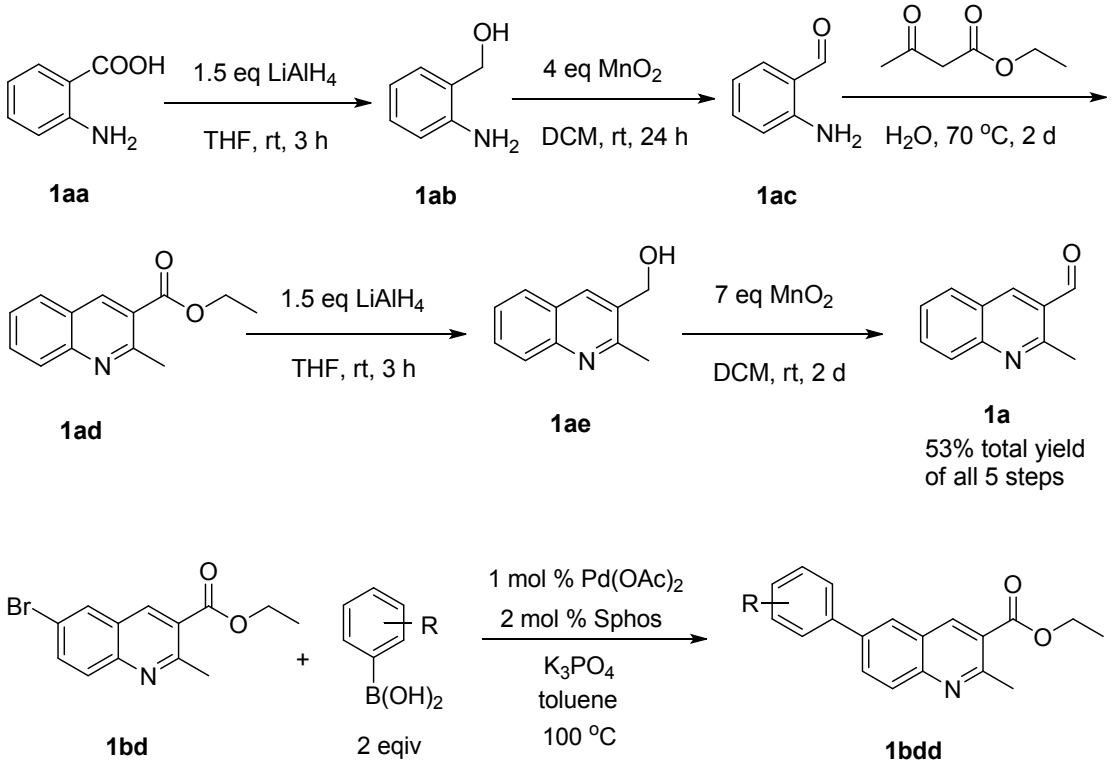


***(R)*-(-)-3,3'-bis(3,5-Diphenylphenyl)-1,1'-binaphthalene-2,2'-sulfonimide VII:** To a solution of *(R)*-(-)-3,3'-Dibromo-1,1'-binaphthalene-2,2'-sulfonimide (1.16 g, 2.1 mmol, 1 equiv), $Pd(OAc)_2$ (24 mg, 1.05 mmol, 0.05 equiv), and (3,5-diphenylphenyl)boronic acid (1.73 g, 6.3 mmol, 3 equiv) in THF (60 mL) under the protection of N_2, was added 2 M aqueous K_2CO_3 (13 mL). Then P(*t*-Bu)$_3$ (1M in hexane, 0.21 mL, 0.1 equiv) was added quickly. The reaction mixture was heated for 24 h at 85 °C. After the reaction was completed, the resulting mixture was acidified with 1 M HCl and extracted with $CHCl_3$ (30 mL×3). The combined organic phase was dried over Na_2SO_4 followed by filtration and concentrated in vacuo. The crude product was purified by silica gel column chromatography (petroleum ether/EtOAc 3:1). Then the product was dissolved in DCM and acidified with a 2 M HCl aqueous solution. The combined organic phase was evaporated to give the desired product as a white solid (702 mg, 40% yield). ^{1}H NMR (400 MHz, $CDCl_3$): 8.20 (s, 2H), 8.03 (d, J = 8.0 Hz,

2H), 7.87 (s, 2H), 7.82 (s, 2H), 7.66-7.77 (m, 12H), 7.33-7.49 (m, 14H), 7.22 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 141.4, 140.8, 140.7, 139.9, 138.5, 136.7, 134.4, 133.9, 132.3, 132.0, 129.9, 128.9, 128.8, 128.5, 128.2, 127.6, 127.5, 127.4, 126.3, 125.6; HRMS (ESI) calcd for $C_{56}H_{31}NO_4S_2$ $[M-H]^-$ 850.2086, found 850.2085.

3. General procedure for the synthesis of compound 2-methylquinolin-3-carbaldehyde derivatives 1[2-4] **and Characterization data**

Unless otherwise specified, 2-methylquinoline-3-carbaldehyde (as examples) derivatives were synthesized via the following 5 steps:



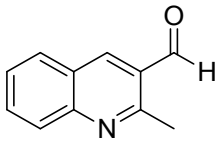
1ab,[2] **1ac**,[3] **1ad**[4] were prepared according to the literature.

1ae: To an ice-cooled solution of 2-methyl-3-quinolinecarboxylic acid ethyl ester **1ad** (17.66 g, 82.1 mmol) in dry THF (100 mL), a solution of $LiAlH_4$ in THF (1M, 125 mL) was added dropwise. The resulting mixture was stirred for 3 h at room temperature. The mixture was slowly treated with ethyl acetate (100 mL), partitioned by saturated $NaHCO_3$ (200 mL), and extracted with ethyl acetate three times. The combined organic phase was washed with brine, dried over $MgSO_4$, filtered and concentrated to afford 2-methyl-3-quinolinemethanol **1ae** quantitatively without further purification.

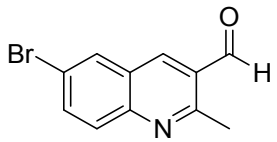
1a: To a solution of 2-methyl-3-quinolinemethanol **1ad** (14 g, 81 mmol) in DCM (300 mL) was treated with MnO_2 (50 g, 567 mmol). The mixture was stirred for 2 d at room temperature. After the reaction was completed (monitored by TLC, PE/EA 3:1, Rf = 0.6), the resulting mixture was filtered through celite, washed with DCM, and the combined organic phase was evaporated. The crude product was purified by silica gel column chromatography (PE/EA 12:1) to give the pure product 2-methylquinolin-3-

carbaldehyde **1a** (7.45 g, 53% total yield).

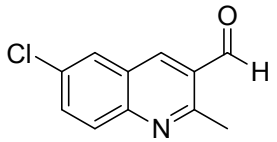
1bdd: To a solution of $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), Sphos (8.2 mg, 0.02 mmol), K_3PO_4 (849 mg, 4 mmol), 6-bromo-2-methylquinoline-3-carboxylate **1bd** (294 mg, 1 mmol) in toluene was added relevant phenylboronic acid (2 equiv, 2 mmol). Then the reaction was stirred at 100 °C for 24 h. After the reaction was completed (monitored by TLC), the mixture was filtered and evaporated. The crude product was purified by flash silica gel column chromatography to give the product.



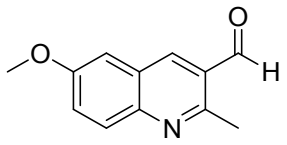
2-Methylquinolin-3-carbaldehyde (1a): yellow solid, 53% total yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.39 (s, 1H), 8.60 (s, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.85 (t, *J* = 8 Hz, 1H), 7.59 (t, *J* = 8 Hz, 1H), 3.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.5, 158.3, 149.2, 142.5, 132.7, 129.1, 128.8, 128.0, 127.0, 126.1, 24.0; HRMS (EI) m/z calcd for $C_{11}H_9NO$ (M) 171.0684, found 171.0685.



6-Bromo-2-methylquinoline-3-carbaldehyde (1b): yellow solid, 22% total yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.38 (s, 1H), 8.50 (s, 1H), 8.10 (s, 1H), 7.88-7.96 (m, 2H), 3.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.1, 158.8, 147.8, 141.0, 136.0, 130.8, 130.5, 128.5, 127.2, 120.7, 24.0; HRMS (EI) m/z calcd for $C_{11}H_8BrNO$ (M) 248.9789, found 248.9786.

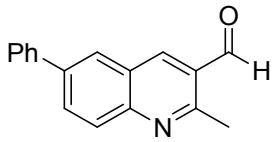


6-Chloro-2-methylquinoline-3-carbaldehyde (1c): yellow solid, 14% total yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.37 (s, 1H), 8.49 (s, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.91 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 3.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.1, 158.6, 147.6, 141.2, 133.5, 132.7, 130.4, 128.6, 127.5, 126.7, 23.9; HRMS (EI) m/z calcd for $C_{11}H_8ClNO$ (M) 205.0294, found 205.0296.

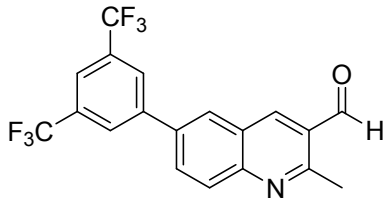


6-Methoxy-2-methylquinoline-3-carbaldehyde (1d): pale yellow solid, 12% total

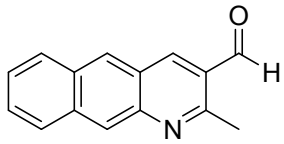
yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.31 (s, 1H), 8.47 (s, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.37 (s, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 3.98 (s, 3H), 3.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.1, 163.5, 159.0, 151.3, 141.6, 130.2, 126.2, 121.2, 120.2, 106.9, 55.8, 23.8; HRMS (EI) m/z calcd for $C_{12}H_{11}NO_2$ (M) 201.0790, found 201.0791.



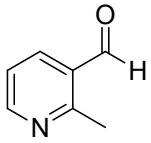
2-Methyl-6-phenylquinoline-3-carbaldehyde (1e): yellow solid, 16% total yield. The title compound was prepared from **1bd** and phenylboronic acid according to the above steps of **1bdd**, **1ae** and **1a**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.41 (s, 1H), 8.65 (s, 1H), 8.09-8.16 (m, 3H), 7.71-7.72 (m, 2H), 7.50-7.54 (m, 2H), 7.41-7.45 (m, 1H), 3.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.4, 158.3, 148.6, 142.6, 139.8, 139.7, 132.5, 129.2, 129.1, 128.4, 128.1, 127.4, 126.5, 126.3, 24.0; HRMS (EI) m/z calcd for $C_{17}H_{13}NO$ (M) 247.0997, found 247.0998.



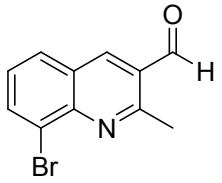
6-(3,5-bis(Trifluoromethyl)phenyl)-2-methylquinoline-3-carbaldehyde (1f): yellow solid, 14% total yield. The title compound was prepared from **1bd** and 3,5-bis(Trifluoromethyl)phenylboronic acid according to the above steps of **1bdd**, **1ae** and **1a**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.42 (s, 1H), 8.70 (s, 1H), 8.08-8.23 (m, 5H), 7.94 (s, 1H), 3.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.1, 159.4, 149.0, 142.5, 141.9, 136.7, 132.7, 132.4, 131.5, 130.1, 128.8, 127.4, 126.3, 124.6, 121.9, 121.7, 24.1; HRMS (EI) m/z calcd for $C_{19}H_{11}F_6NO$ (M) 383.0745, found 383.0743.



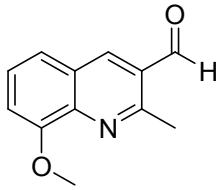
2-Methylbenzo[g]quinoline-3-carbaldehyde (1g): yellow solid, 4% total yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.36 (s, 1H), 8.77 (s, 1H), 8.63 (s, 1H), 8.55 (s, 1H), 8.09 (t, *J* = 8.0 Hz, 2H), 7.55-7.63 (m, 2H), 3.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.3, 158.3, 144.9, 144.5, 135.9, 131.9, 129.2, 128.6, 128.5, 128.1, 127.8, 126.6, 126.5, 124.3, 24.7; HRMS (EI) m/z calcd for $C_{15}H_{11}NO$ (M) 221.0841, found 221.0842.



2-Methylnicotinaldehyde (1h): yellow oil, 42% total yield. The title compound was prepared from commercial availability ethyl 2-methylnicotinate, according to a simple procedure of **1ae** and **1a**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.34 (s, 1H), 8.69 (d, J = 8.0 Hz, 1H), 8.11 (d, J = 8.0 Hz, 1H), 7.34 (t, J = 8.0 Hz, 1H), 2.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.4, 160.3, 153.2, 138.3, 129.5, 121.8, 22.3; HRMS (EI) m/z calcd for C_7H_7NO (M) 121.0528, found 121.0529.



8-Bromo-2-methylquinoline-3-carbaldehyde (1i): white solid, 24% total yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.41 (s, 1H), 8.57 (s, 1H), 8.15 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.43 (t, J = 8.0 Hz, 1H), 3.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.0, 159.5, 146.1, 142.4, 136.1, 128.9, 128.5, 127.4, 127.3, 124.4, 24.3; HRMS (EI) m/z calcd for $C_{11}H_8BrNO$ (M) 248.9789, found 248.9787.

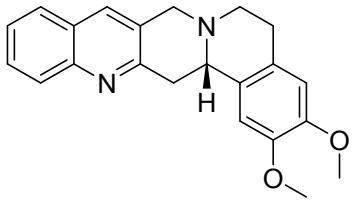


8-Methoxy-2-methylquinoline-3-carbaldehyde (1j): yellow solid, 27% total yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.42 (s, 1H), 8.60 (s, 1H), 7.53 (d, J = 4.0 Hz, 2H), 7.21 (t, J = 4.0 Hz, 1H), 4.13 (s, 3H), 3.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.5, 157.4, 154.8, 141.1, 140.9, 128.4, 127.2, 127.1, 120.7, 110.7, 56.3, 24.2; HRMS (EI) m/z calcd for $C_{12}H_{11}NO_2$ (M) 201.0790, found 201.0788.

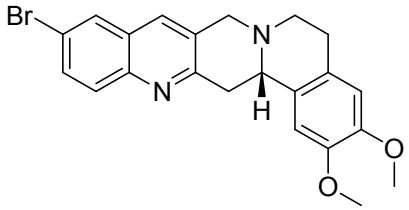
Unless otherwise noted, all compounds **2** were obtained commercially and used without further purification. Compound **2d** was prepared according to the literature methods.[5]

4. General procedure for the synthesis of compound 2,3-dimethoxy-6,8,15,15a-tetrahydro-5H-benzo[b]isoquinolino[2,1-*g*][1,6]naphthyridine derivatives 3 and Characterization Data

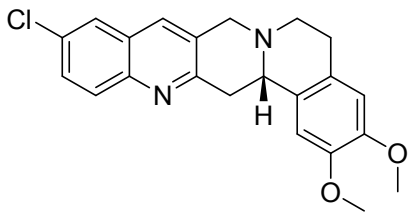
Under N_2, a mixture of **1a** (0.1 mmol) and catalyst **VII** (0.03 mmol) was stirred in toluene (1.0 mL) for 30 min at room temperature. Then 3 Å molecular sieves (50 mg), secondary amine **2a** (0.13 mmol) were added and the reaction was heated to 60 ^{o}C. After the reaction was completed (monitored by TLC), the mixture was cooled to room temperature, filtered, and washed with DCM. The combined organic phase was evaporated and purified by column chromatography (neutral alumina) to give the corresponding product **3a**.



(*S*)-2,3-Dimethoxy-6,8,15,15a-tetrahydro-5H-benzo[b]isoquinolino[2,1-g][1,6]naphthyridine (3a): yellow solid, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 12.0 Hz, 1H), 7.88 (s, 1H), 7.76 (d, *J* = 12.0 Hz, 1H), 7.67 (t, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 1H), 6.84 (s, 1H), 6.65 (s, 1H), 4.26 (d, *J* = 16.0 Hz, 1H), 3.89 (s, 6H), 3.79-3.86 (m, 3H), 3.15-3.27 (m, 3H), 2.67-2.75 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.5, 147.6, 147.5, 147.1, 132.7, 129.1, 129.0, 128.4, 128.2, 127.3, 127.0, 126.2, 126.0, 111.3, 108.2, 59.7, 58.0, 55.9, 55.8, 51.5, 40.9, 29.0; HRMS (EI) m/z calcd for $C_{22}H_{22}N_2O_2$ (M) 346.1681, found 346.1679. (Chiralpak OD-3, *i*-PrOH/hexane = 20/80, flow rate = 1.0 mL/min, λ = 210 nm): t_{major} = 15.14 min, t_{minor} = 21.69 min, e.r. = 86:14, $[\alpha]_D^{25}$ = 19.2° (*c* = 0.15, CH_2Cl_2).

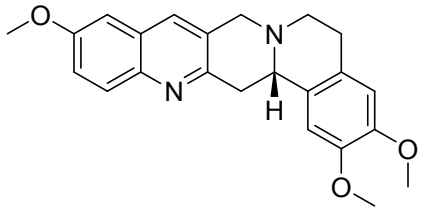


(*S*)-11-Bromo-2,3-dimethoxy-6,8,15,15a-tetrahydro-5H-benzo[b]isoquinolino[2,1-g][1,6]naphthyridine (3b): yellow solid, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (s, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.78 (s, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 6.81 (s, 1H), 6.65 (s, 1H), 4.25 (d, *J* = 16.0 Hz, 1H), 3.75-3.89 (m, 9H), 3.16-3.27 (m, 3H), 2.67-2.75 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.1, 147.6, 146.6, 132.5, 131.6, 130.2, 129.3, 128.9, 128.1, 126.2, 119.7, 111.3, 108.2, 59.6, 57.8, 55.9, 55.9, 51.5, 40.9, 28.9; HRMS (EI) m/z calcd for $C_{22}H_{21}BrN_2O_2$ (M) 424.0786, found 424.0779. (Chiralpak OD-3, *i*-PrOH/hexane = 20/80, flow rate = 1.0 mL/min, λ = 210 nm): t_{major} = 15.91 min, t_{minor} = 24.12 min, e.r. = 90:10; $[\alpha]_D^{25}$ = 5.3° (*c* = 0.16, CH_2Cl_2)

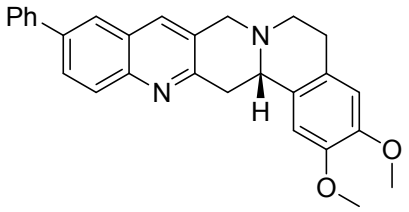


(*S*)-11-Chloro-2,3-dimethoxy-6,8,15,15a-tetrahydro-5H-benzo[b]isoquinolino[2,1-g][1,6]naphthyridine (3c): yellow solid, 41% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.0 Hz, 1H), 7.79 (s, 1H), 7.75 (s, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 6.81 (s, 1H), 6.65 (s, 1H), 4.26 (d, *J* = 12.0 Hz, 1H), 3.76-3.89 (m,

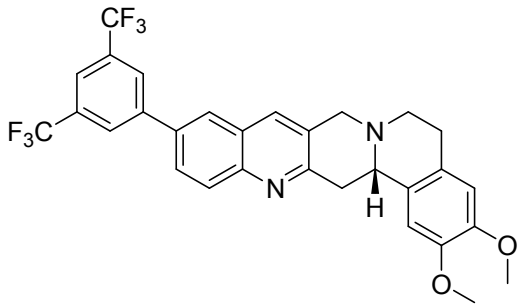
9H), 3.14-3.27 (m, 3H), 2.68-2.75 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.0, 147.7, 145.4, 131.7, 131.6, 130.1, 130.0, 129.3, 128.9, 127.6, 126.2, 125.9, 111.28, 108.2, 59.6, 57.9, 55.9, 55.8, 51.5, 40.8, 29.0; HRMS (EI) m/z calcd for $C_{22}H_{21}ClN_2O_2$ (M) 380.1292, found 4380.1284. (Chiralpak OD-3, *i*-PrOH/hexane = 20/80, flow rate = 1.0 mL/min, λ = 210 nm): t_{major} = 13.47 min, t_{minor} = 21.77 min, e.r. = 87:13; $[\alpha]_D^{25}$ = 8.8° (*c* = 0.2, CH_2Cl_2).



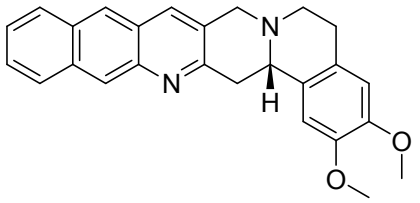
(*S*)-2,3,11-Trimethoxy-6,8,15,15a-tetrahydro-5H-benzo[b]isoquinolino[2,1-g][1,6]naphthyridine (3d): yellow solid, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (s, 1H), 7.64 (d, *J* = 12.0 Hz, 1H), 7.35 (s, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 6.83 (s, 1H), 6.65 (s, 1H), 4.21 (d, *J* = 16.0 Hz, 1H), 3.74-3.98 (m, 12H), 3.16-3.25 (m, 3H), 2.66-2.75 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ160.5, 156.4, 148.7, 147.6, 147.5, 132.5, 129.1, 128.3, 126.2, 125.9, 122.3, 119.3, 111.3, 108.2, 106.4, 59.7, 57.8, 55.9, 55.5, 51.5, 40.8, 29.0; HRMS (EI) m/z calcd for $C_{23}H_{24}N_2O_3$ (M) 376.1787, found 376.1789. (Chiralpak OD-3, *i*-PrOH/hexane = 20/80, flow rate = 1.0 mL/min, λ = 220 nm): t_{major} = 14.40 min, t_{minor} = 22.10 min, e.r. = 66:34; $[\alpha]_D^{25}$ = 12.2° (*c* = 0.15, CH_2Cl_2).



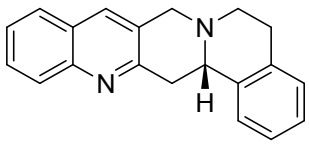
(*S*)-2,3-Dimethoxy-11-phenyl-6,8,15,15a-tetrahydro-5H-benzo[b]isoquinolino[2,1-g][1,6]naphthyridine (3e): yellow solid, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 8.0 Hz, 1H), 7.91-7.94 (m, 3H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.50 (t, *J* = 8.0 Hz, 2H), 7.40 (t, *J* = 8.0 Hz, 1H), 6.84 (s, 1H), 6.65 (s, 1H), 4.28 (d, *J* = 16.0 Hz, 1H), 3.80-3.91 (m, 9H), 3.16-3.28 (m, 3H), 2.68-2.76 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.5, 147.6, 147.5, 146.5, 140.5, 138.7, 132.8, 129.1, 129.0, 128.9, 128.8, 128.6, 127.6, 127.4, 127.2, 126.2, 125.0, 111.3, 108.2, 59.7, 58.0, 55.9, 55.8, 51.5, 40.9, 29.0; HRMS (EI) m/z calcd for $C_{28}H_{26}N_2O_2$ (M) 422.1994, found 422.1995. (Chiralpak OD-3, *i*-PrOH/hexane = 20/80, flow rate = 1.0 mL/min, λ = 210 nm): t_{major} = 19.84 min, t_{minor} = 29.97 min, e.r. = 76:24; $[\alpha]_D^{25}$ = 21.8° (*c* = 0.2, CH_2Cl_2).



(*S*)-11-(3,5-bis(Trifluoromethyl)phenyl)-2,3-dimethoxy-6,8,15,15a-tetrahydro-5H-benzo[b]isoquinolino[2,1-g][1,6]naphthyridine (3f): yellow solid, 43% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (m, 3H), 7.99 (d, J = 8.0 Hz, 2H), 7.92 (d, J = 8.0 Hz, 2H), 6.84 (s, 1H), 6.66 (s, 1H), 4.31 (d, J = 16.0 Hz, 1H), 3.82-3.94 (m, 9H), 3.17-3.31 (m, 3H), 2.71-2.77 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.8, 147.7, 146.9, 142.6, 135.6, 133.0, 132.5, 132.2, 129.7, 129.3, 128.8, 128.1, 127.4, 127.1, 126.2, 125.9, 124.7, 122.0, 121.2, 111.3, 108.2, 59.6, 57.9, 55.9, 55.8, 51.5, 41.0, 29.0; HRMS (EI) m/z calcd for $C_{30}H_{24}F_6N_2O_2$ (M) 558.1742, found 558.1735. (Chiralpak OD-3, *i*-PrOH/hexane = 20/80, flow rate = 1.0 mL/min, λ = 210 nm): t_{minor} = 18.00 min, t_{major} = 22.70 min, e.r. = 88:12; $[\alpha]_D^{25}$ = 44.7° (c = 0.15, CH_2Cl_2).

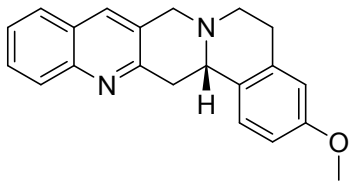


(*S*)-2,3-Dimethoxy-6,8,17,17a-tetrahydro-5H-isoquinolino[2,1-g]naphtho[2,3-b][1,6]naphthyridine (3g): yellow solid, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (s, 1H), 8.35 (s, 1H), 8.00-8.07 (m, 3H), 7.50 (t, J = 4.0 Hz, 2H), 6.86 (s, 1H), 6.66 (s, 1H), 4.34 (d, J = 16.0 Hz, 1H), 3.87- 3.96 (m, 9H), 3.19-3.32 (m, 3H), 2.71-2.77 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.1, 147.7, 143.7, 133.8, 132.4, 131.6, 129.1, 128.5, 128.0, 127.9, 126.2, 126.1, 126.0, 125.9, 125.8, 125.7, 111.3, 108.3, 104.6, 59.8, 58.3, 56.0, 55.9, 51.6, 41.4, 29.0; HRMS (EI) m/z calcd for $C_{26}H_{24}N_2O_2$ (M) 396.1838, found 396.1834. (Chiralpak OD-3, *i*-PrOH/hexane = 15/85, flow rate = 1.0 mL/min, λ = 254 nm): t_{major} = 32.55 min, t_{minor} = 50.00 min, e.r. = 92:8; $[\alpha]_D^{25}$ = 6.6° (c = 0.2, CH_2Cl_2).

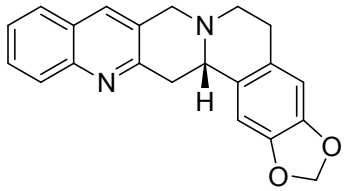


(*S*)-6,8,15,15a-Tetrahydro-5H-benzo[b]isoquinolino[2,1-g][1,6]naphthyridine (3i): yellow solid, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, J = 8.0 Hz, 1H), 7.87 (s, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.66 (t, J = 8.0 Hz, 1H), 7.48 (t, J = 8.0 Hz, 1H), 7.36

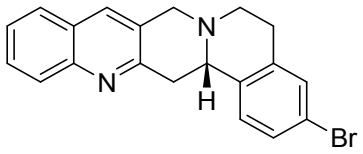
(d, J = 8.0 Hz, 1H), 7.17-7.28 (m, 3H), 4.26 (d, J = 16.0 Hz, 1H), 3.81-3.91 (m, 3H), 3.21-3.30 (m, 3H), 2.72-2.85 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.6, 147.1, 137.3, 134.2, 132,6, 129.0, 128.9, 128.5, 128.2, 127.2, 127.0, 126.4, 126.0, 125.6, 60.1, 58.0, 51.3, 40.7, 29.5; HRMS (EI) m/z calcd. for $C_{20}H_{18}N_2$ (M) 286.1470, found 286.1469. (Chiralpak AD-3, *i*-PrOH/hexane = 20/80, flow rate = 1.0 mL/min, λ = 210 nm): t_{minor} = 8.49 min, t_{major} = 12.36 min, e.r. = 73:27; $[\alpha]_D^{25}$ = -25.7° (c = 0.15, CH_2Cl_2).



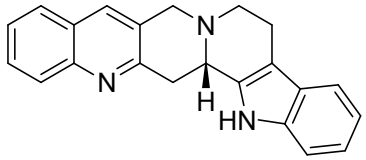
(*S*)-3-Methoxy-6,8,15,15a-tetrahydro-5H-benzo[b]isoquinolino[2,1-g][1,6]naphthyridine (3j): yellow solid, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, J = 8.0 Hz, 1H), 7.86 (s, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.66 (t, J = 8.0 Hz, 1H), 7.48 (t, J = 8.0 Hz, 1H), 7.26-7.28 (m, 1H), 6.83 (d, J = 8.0 Hz, 1H), 6.70 (s, 1H), 4.25 (d, J = 16.0 Hz, 1H), 3.78-3.90 (m, 6H), 3.17-3.27 (m, 3H), 2.67-2.81 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.9, 156.6, 147.1, 135.5, 132.6, 129.6, 129.0, 128.5, 128.2, 127.2, 127.0, 126.6, 125.9, 113.3, 112.6, 59.7, 58.0, 55.3, 51.3, 40.9, 29.7; HRMS (EI) m/z calcd for $C_{21}H_{20}N_2O$ (M) 316.1576, found 316.1583. (Chiralpak AD-3, *i*-PrOH/hexane = 20/80, flow rate = 1.0 mL/min, λ = 210 nm): t_{minor} = 11.94 min, t_{major} = 23.58 min, e.r. = 76:24; $[\alpha]_D^{25}$ = 32.9° (c = 0.2, CH_2Cl_2).



(*S*)-6,8,15,15a-Tetrahydro-5H-[1,3]dioxolo[4',5':6,7]isoquinolino[2,1-g]benzo[b][1,6]naphthyridine (3k): yellow solid, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, J = 8.0 Hz, 1H), 7.79 (s, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.58 (t, J = 8.0 Hz, 1H), 7.41 (t, J = 8.0 Hz, 1H), 6.73 (s, 1H), 6.54 (s, 1H), 5.87 (s, 2H), 4.16 (d, J = 16.0 Hz, 1H), 3.63-3.81 (m, 3H), 3.05-3.15 (m, 3H), 2.57-2.65 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.4, 147.1, 146.4, 146.2, 132.6, 130.2, 129.1, 128.4, 128.1, 127.4, 127.2, 127.0, 126.0, 108.4, 105.5, 100.9, 60.0, 57.9, 51.3, 40.9, 29.5; HRMS (EI) m/z calcd for $C_{21}H_{18}N_2O_2$ (M) 330.1368, found 330.1364. (Chiralpak AD-3, *i*-PrOH/hexane = 20/80, flow rate = 1.0 mL/min, λ = 210 nm): t_{minor} = 12.73 min, t_{major} = 24.99 min, e.r. = 71:29; $[\alpha]_D^{25}$ = -30.7° (c = 0.2, CH_2Cl_2).



(*S*)-3-Bromo-6,8,15,15a-tetrahydro-5H-benzo[b]isoquinolino[2,1-g][1,6]naphthyridine (3l): yellow solid, 55% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 8.0 Hz, 1H), 7.86 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.66 (t, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.32 (s, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 4.24 (d, *J* = 16.0 Hz, 1H), 3.75-3.90 (m, 3H), 3.17-3.23 (m, 3H), 2.64-2.80 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.1, 147.1, 136.6, 136.4, 132.7, 131.6, 129.5, 129.2, 128.4, 128.0, 127.3, 127.2, 127.0, 126.1, 120.2, 59.7, 57.8, 50.9, 40.5, 29.3; HRMS (EI) m/z calcd for $C_{20}H_{17}BrN_2$ (M) 364.0575, found 364.0571. (Chiralpak AD-3, *i*-PrOH/hexane = 20/80, flow rate = 1.0 mL/min, λ = 210 nm): t_{minor} = 11.26 min, t_{major} = 18.33 min, e.r. = 62:38; $[\alpha]_D^{25}$ = 23.5° (*c* = 0.15, CH_2Cl_2).



(*S*)-5,6,8,15,15a,16-Hexahydrobenzo[b]indolo[2',3':3,4]pyrido[1,2-g][1,6]naphthyridine (3m): yellow solid, 62% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 8.0 Hz, 1H), 7.91 (s, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.67 (t, *J* = 8.0 Hz, 1H), 7.49-7.56 (m, 2H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.12-7.21 (m, 2H), 4.35 (d, *J* = 16.0 Hz, 1H), 3.96-4.00 (m, 2H), 3.67 (d, *J* = 16.0 Hz, 1H), 3.32-3.41 (m, 2H), 3.08-3.11 (m, 1H), 2.81-2.91 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.4, 146.9, 136.5, 133.8, 133.2, 129.3, 128.3, 128.2, 127.3, 127.1, 127.0, 126.2, 121.8, 119.5, 118.2, 111.1, 108.5, 57.2, 56.5, 52.3, 38.7,21.5; HRMS (EI) m/z calcd for $C_{22}H_{19}N_3$ (M) 325.1579, found 325.1577. (Chiralpak AD-3, *i*-PrOH/hexane = 20/80, flow rate = 1.0 mL/min, λ = 210 nm): t_{minor} = 14.19 min, t_{major} = 22.38 min, e.r. = 63:37; $[\alpha]_D^{25}$ = 54.1° (*c* = 0.17, CH_2Cl_2).

5. Determination of X-ray crystallographic structure 3b

The data were collected on an Agilent Technologies Gemini Atlas Ultra diffractometer using a ultra Cu radiation (l=1.54184Å) with collimating mirror monochromators and at 293 K. Data collection, unit cell refinement and data reduction were performed using Agilent Technologies CrysAlisPro V 1.171.35.11.1 The structure was solved by direct methods and refined by full-matrix least-squares on F2 with anisotropic displacement parameters for the non-H atoms using Olex2/ SHELXTL program package.2 The hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms). The hydrogen atoms bound to nitrogen were located in a ΔF map and

refined with isotropic displacement parameters.

1. CrysAlisPro, Agilent Technologies, Version 1.171.35.11 (release 16-05-2011 CrysAlis171 .NET) (compiled May 16 2011, 17:55:39) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

2. Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339-341.

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) t_0m_a

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: t_0m_a

Bond precision: C-C = 0.0050 A Wavelength=1.54178

Cell: a=9.1340(3) b=10.0111(4) c=11.6697(4)
alpha=66.936(2) beta=86.111(2) gamma=76.562(2)
Temperature: 301 K

	Calculated	Reported
Volume	954.60(6)	954.60(6)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C22 H21 Br N2 O2	C22 H21 Br N2 O2
Sum formula	C22 H21 Br N2 O2	C22 H21 Br N2 O2
Mr	425.31	425.32
Dx,g cm-3	1.480	1.480
Z	2	2
Mu (mm-1)	3.089	3.089
F000	436.0	436.0
F000'	435.70	
h,k,lmax	11,12,14	11,12,14
Nref	3487	3426
Tmin,Tmax	0.566,0.539	
Tmin'	0.513	

Correction method= Not given

Data completeness= 0.983 Theta(max)= 68.291

R(reflections)= 0.0451(2646) wR2(reflections)= 0.1247(3426)

S = 1.006 Npar= 246

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT052_ALERT_1_C	Info on Absorption Correction Method Not Given	Please	Do !
PLAT906_ALERT_3_C	Large K value in the Analysis of Variance	2.805	Check
PLAT911_ALERT_3_C	Missing # FCF Refl Between THmin & STh/L= 0.600	55	Report

Alert level G

PLAT154_ALERT_1_G	The s.u.'s on the Cell Angles are Equal ..(Note)	0.002	Degree
PLAT793_ALERT_4_G	The Model has Chirality at C11 (Centro SPGR)	S	Verify
PLAT912_ALERT_4_G	Missing # of FCF Reflections Above STh/L= 0.600	7	Note
PLAT913_ALERT_3_G	Missing # of Very Strong Reflections in FCF	1	Note
PLAT978_ALERT_2_G	Number C-C Bonds with Positive Residual Density	6	Note

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
3 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
5 **ALERT level G** = General information/check it is not something unexpected

2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
1 ALERT type 2 Indicator that the structure model may be wrong or deficient
3 ALERT type 3 Indicator that the structure quality may be low
2 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

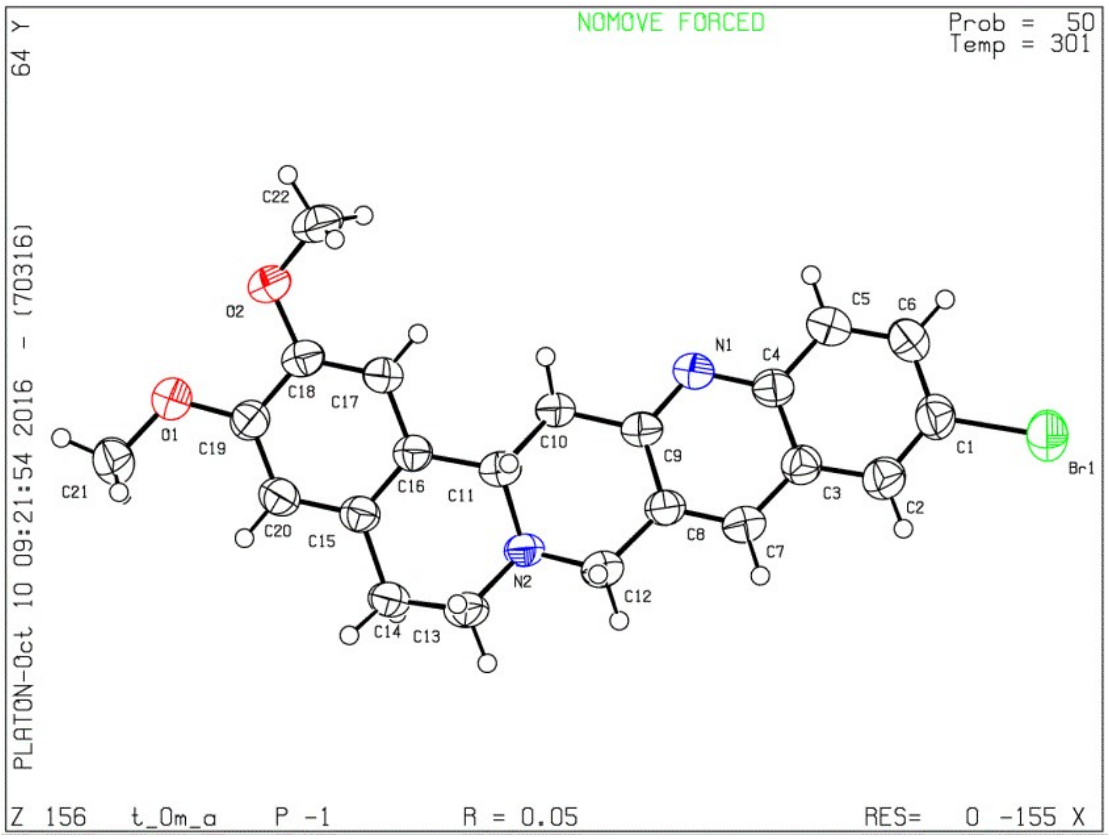
Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 11/08/2016; check.def file version of 04/08/2016



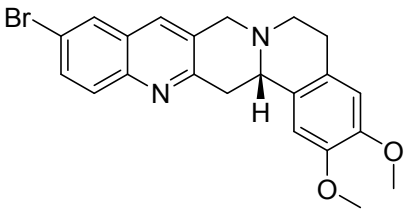


Fig S1. The X-ray crystallographic structure of compound **3b**

6. References

[1] (a) He, H.; Chen, L. Y.; Wong, W. Y.; Chan, W. H.; Lee, A. W. M. *Eur. J. Org. Chem*. **2010**, 4181-4184. (b) Hisashi Morita; Junji Itoh; Kohei Fuchibe; Takahiko Akiyama *Org. Lett*., **2005**, *7*, 2583-2585. (c) Boris J. Nachtsheim; Rene M. Koenigs; Winai Ieawsuwan; Magnus Rueping *Chem. Eur. J*. **2010**, *16*, 13116-13126. (d) Berkessel, A.; Christ, P.; Leconte, N.; Neudörfl, J. M.; Schafer, M. *Eur. J. Org. Chem.* **2010**, 5165-5170. (e) Shengjun Ni; Veluru Ramesh Naidu; Johan Franzén *Eur. J. Org. Chem.* **2016**, 1708-1713. (f) Jia-Hui Tay; Alonso J. Arguelles; Pavel Nagorny *Org. Lett.*, **2015**, *17*, 3774-3777. (g) Mahlau, M.; García-García, P.; List, B. *Chem.-Eur. J.* **2012**, *18*, 16283-16287. (h) Qinggang Wang; Markus Leutzsch; Manuel van Gemmeren; Benjamin List *J. Am. Chem. Soc*. **2013**, *135*, 15334-15337.

[2] Jia, M. Q.; You, S. L. *ACS Catal*. **2013**, *3*, 622-624.

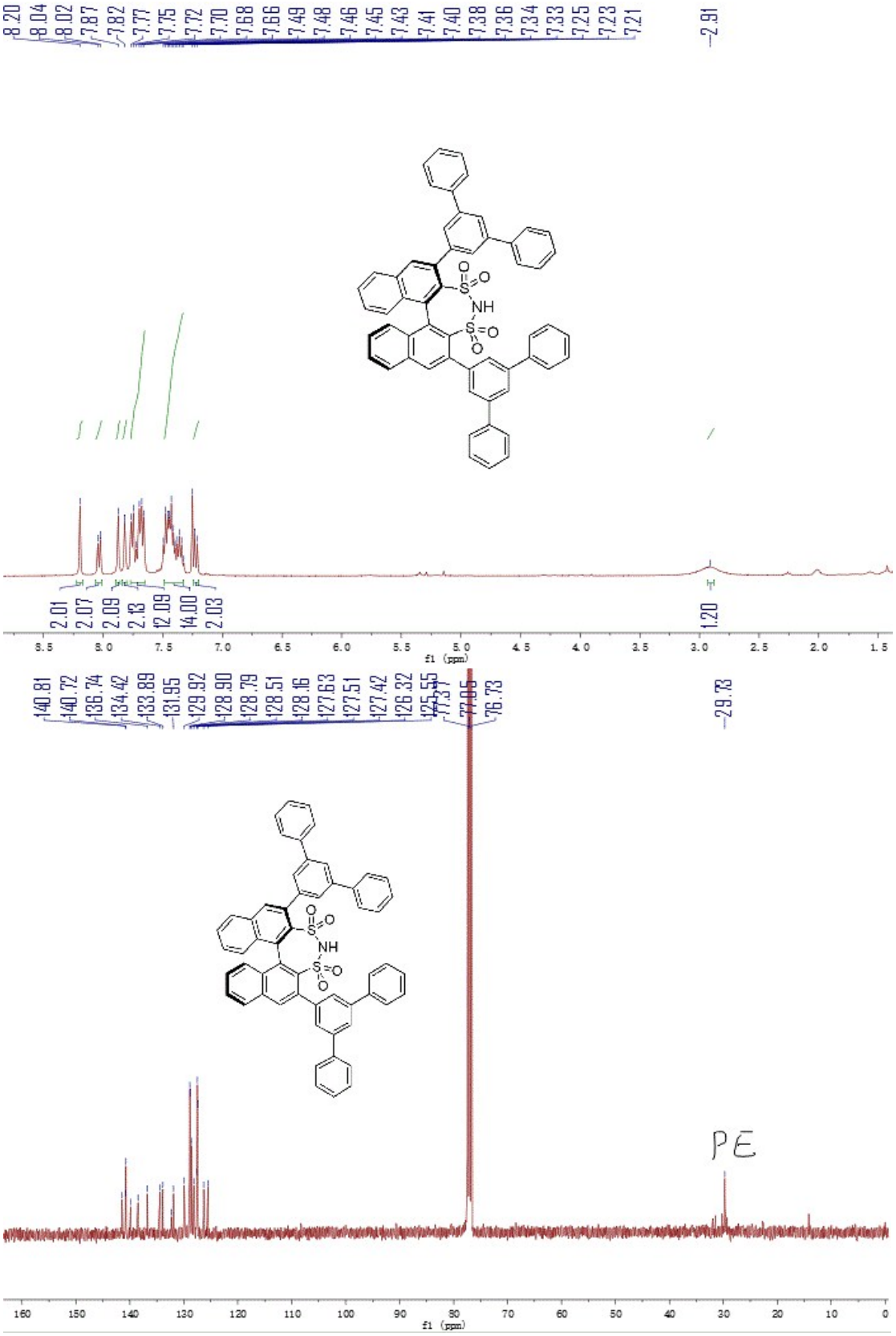
[3] Matteo Chiurato; Rajaa Boulahjar; Sylvain Routier; Yves Troin; Gérald Guillaumet *Tetrahedron*, **2010**, *66*, 4647-4653.

[4] Shen Q.; Yu J. J.; Liu, M. T.; Qiu J.; Fang L.; Guo F. L.; Tang J.; Wang, L. M

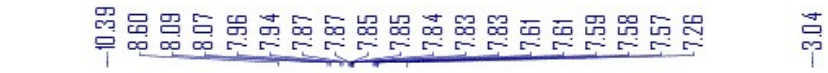
Synthesis, **2012**, *44*, 389-392
[5] Kaliyamoorthy Alagiri, Kandikere Ramaiah Prabhu *Org. Biomol. Chem.*, **2012**, *10*, 835-842.

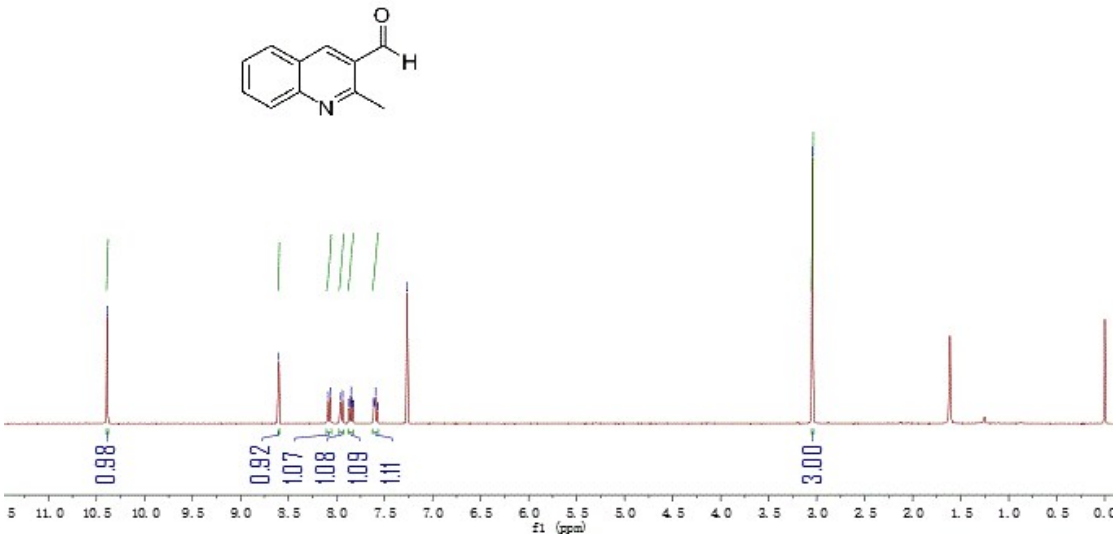
7. ^{1}H and ^{13}C-NMR spectra

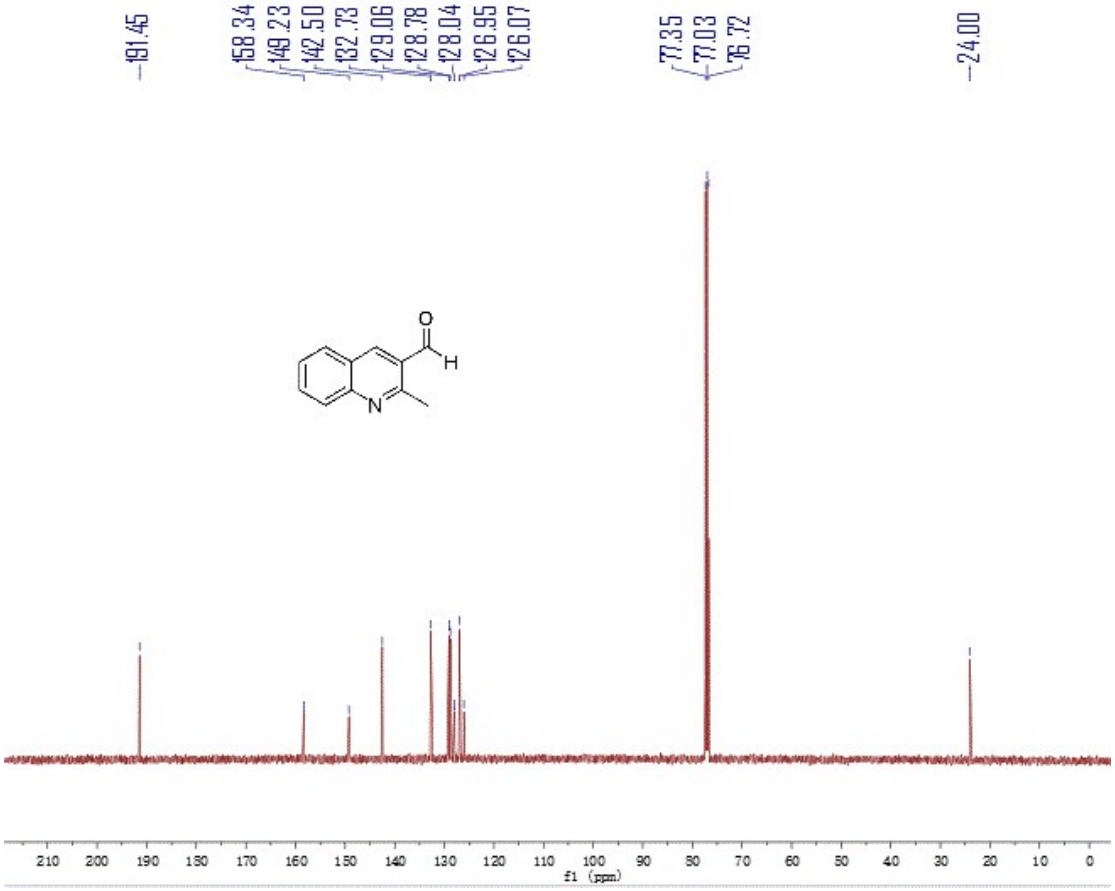
***(R)*-(–)-3,3'-bis(3,5-Diphenylphenyl)-1,1'-Binaphthalene-2,2'-sulfonimide (VII)**



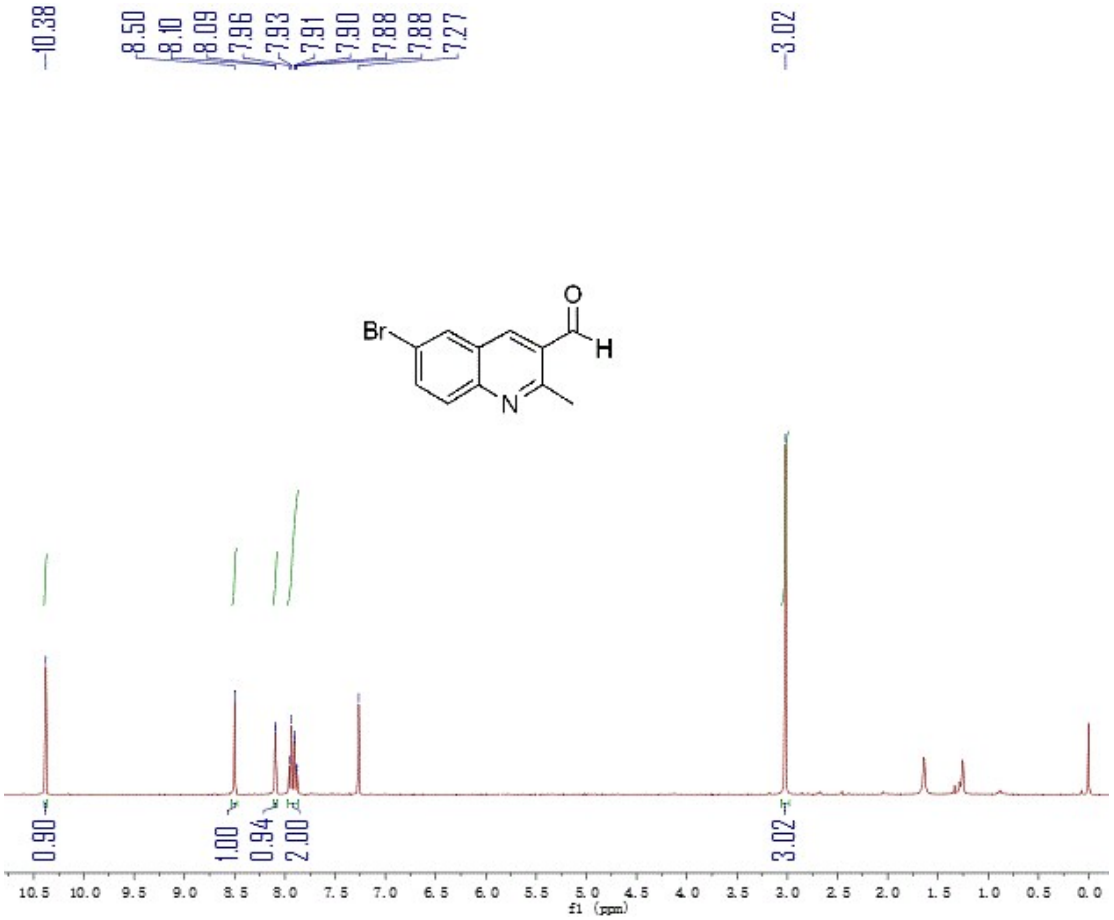
2-Methylquinolin-3-carbaldehyde (1a)







6-Bromo-2-methylquinoline-3-carbaldehyde (1b)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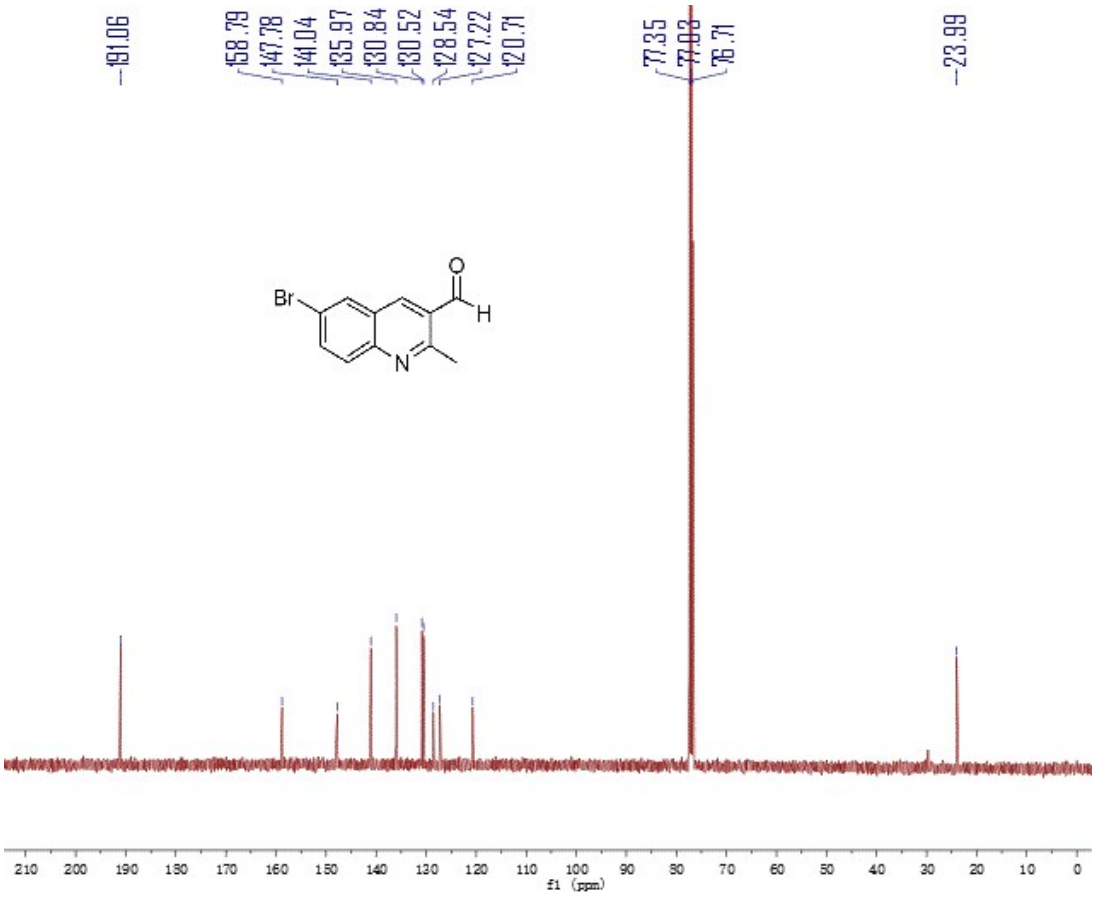
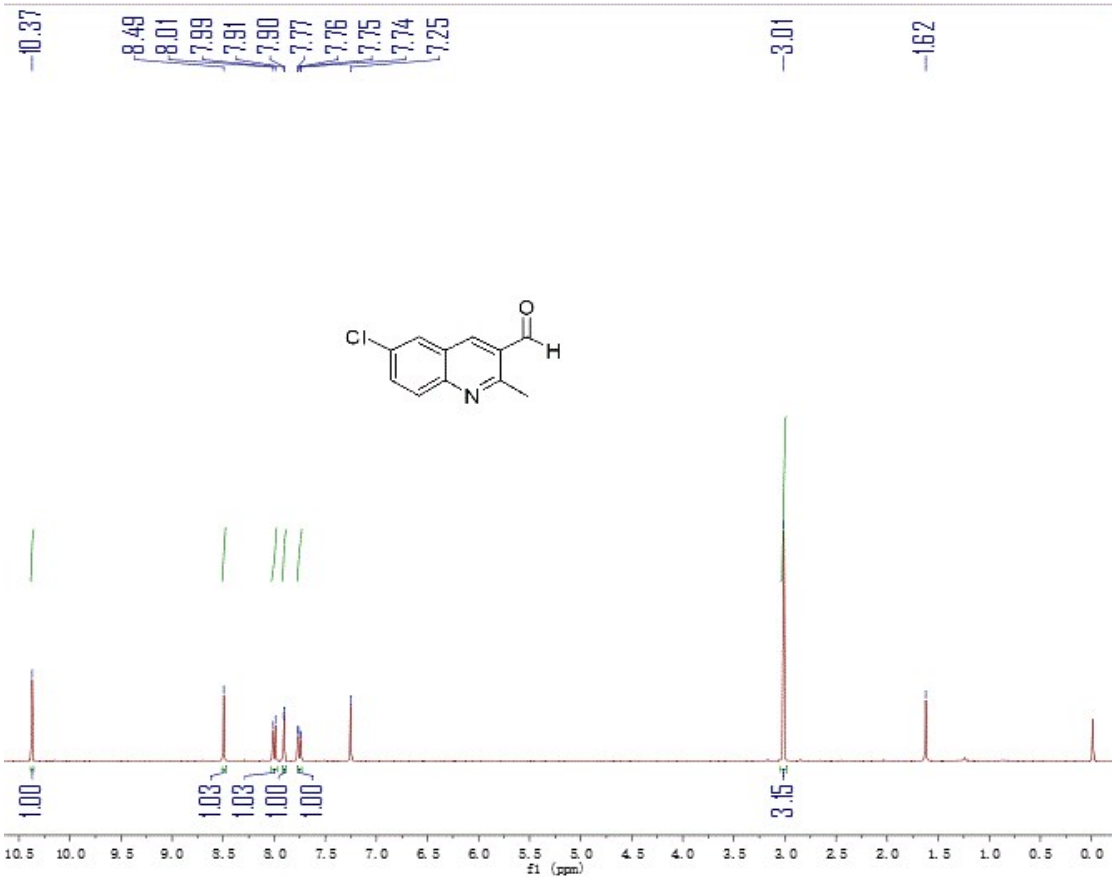
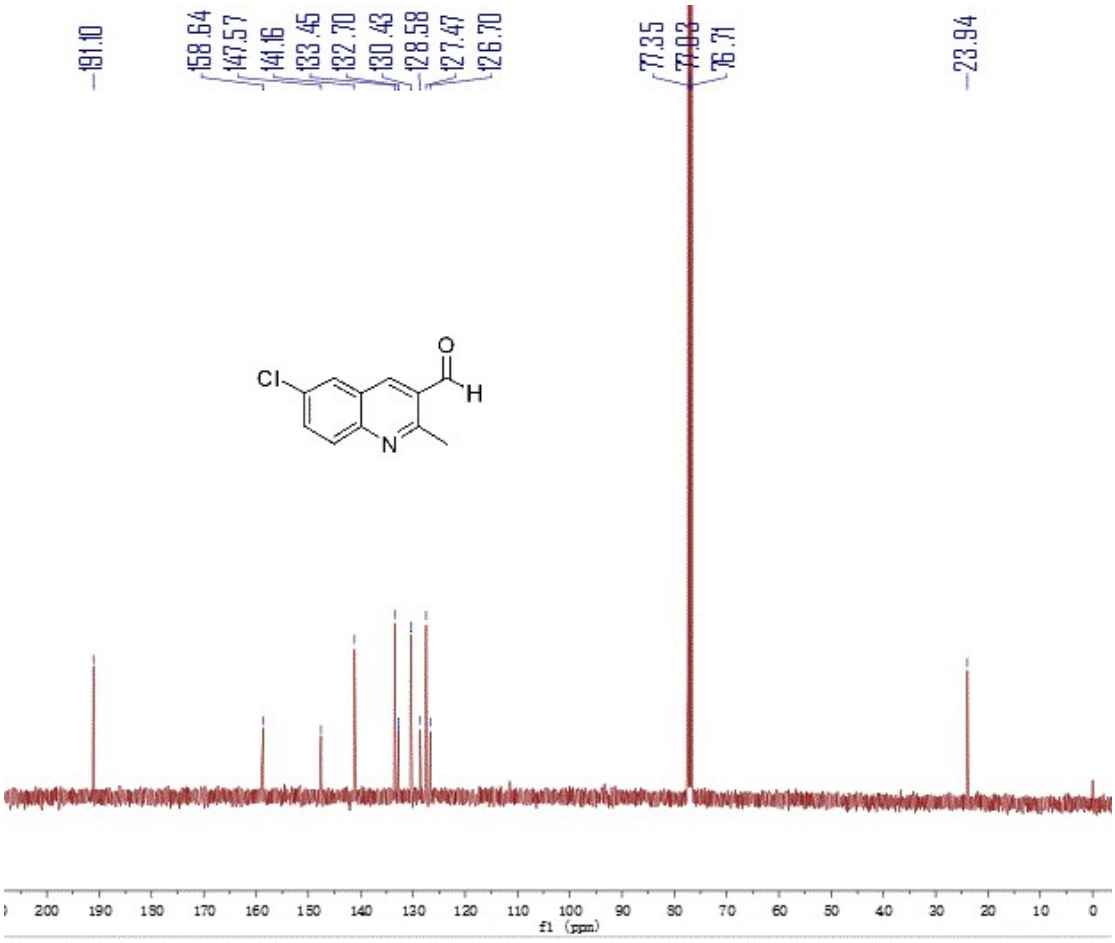
8.50
8.10
8.09
7.96
7.93
7.91
7.90
7.88
7.88
7.27
3.02
Br
O
H
N
0.90
1.00
0.94
2.00
3.02
f1 (ppm)

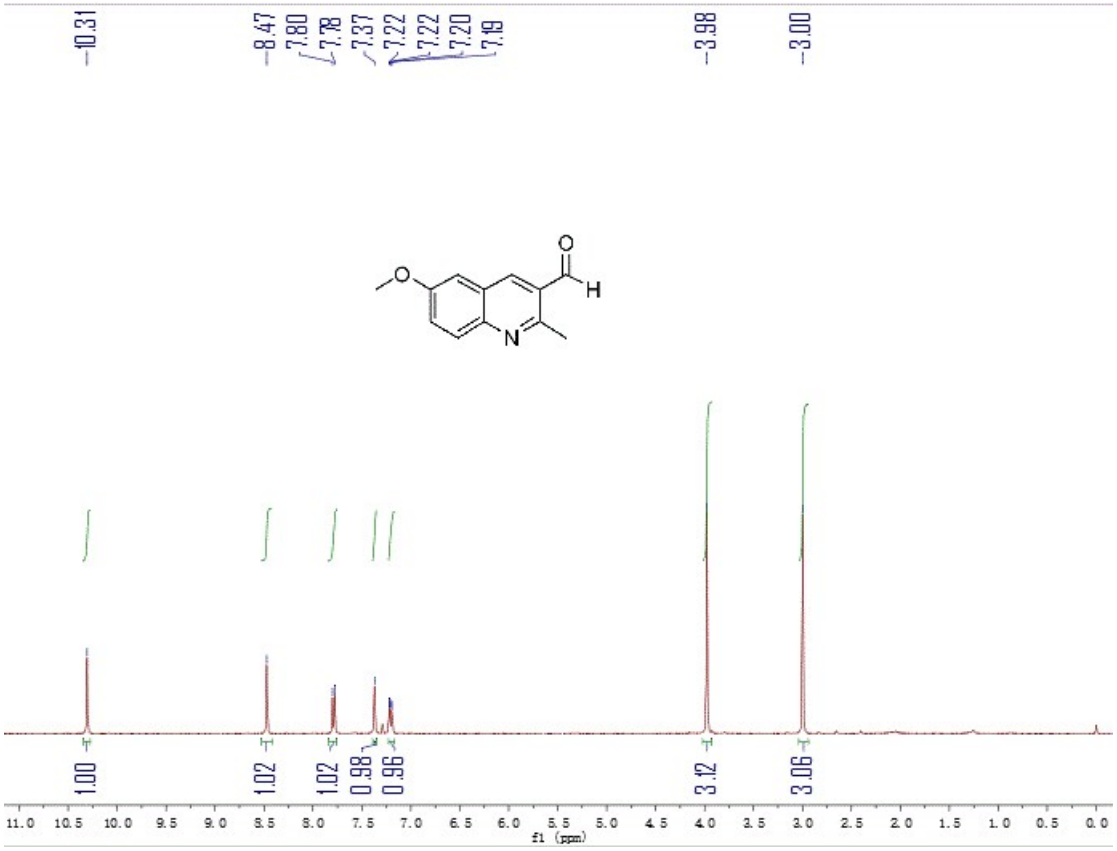

191.06
158.79
147.78
141.04
135.97
130.84
130.52
128.54
127.22
120.71
77.35
77.03
76.71
23.99
Br
O
H
N
f1 (ppm)

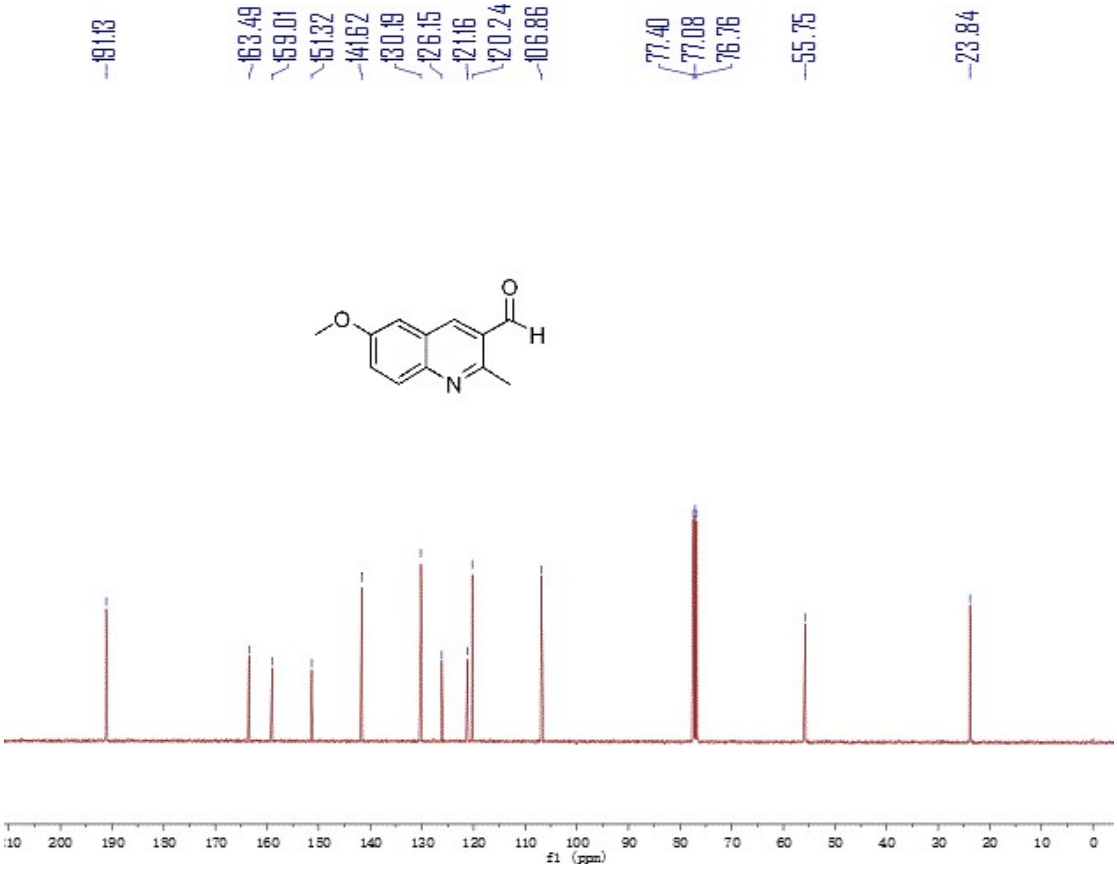
6-Chloro-2-methylquinoline-3-carbaldehyde (1c)



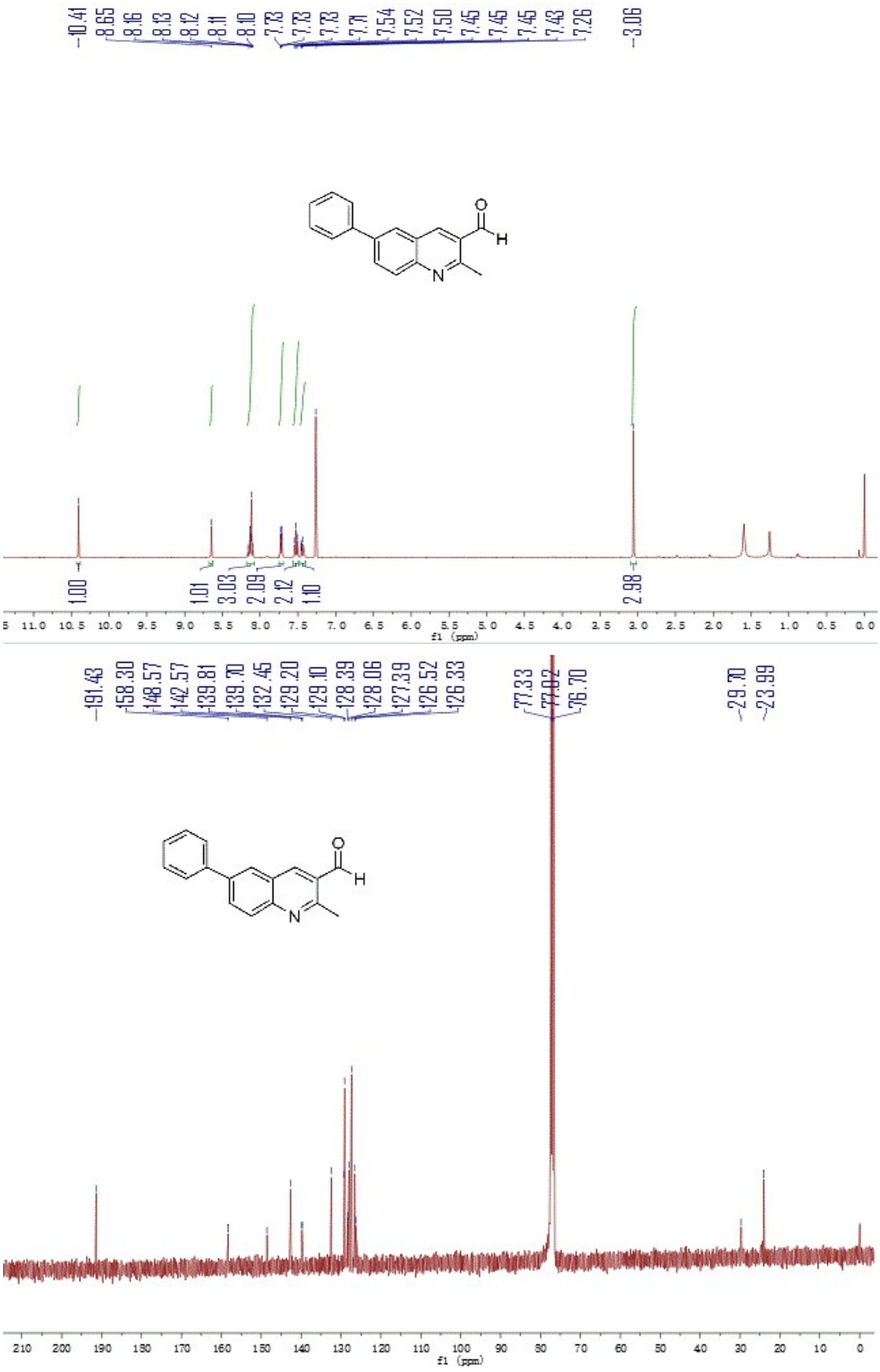


6-Methoxy-2-methylquinoline-3-carbaldehyde (1d)

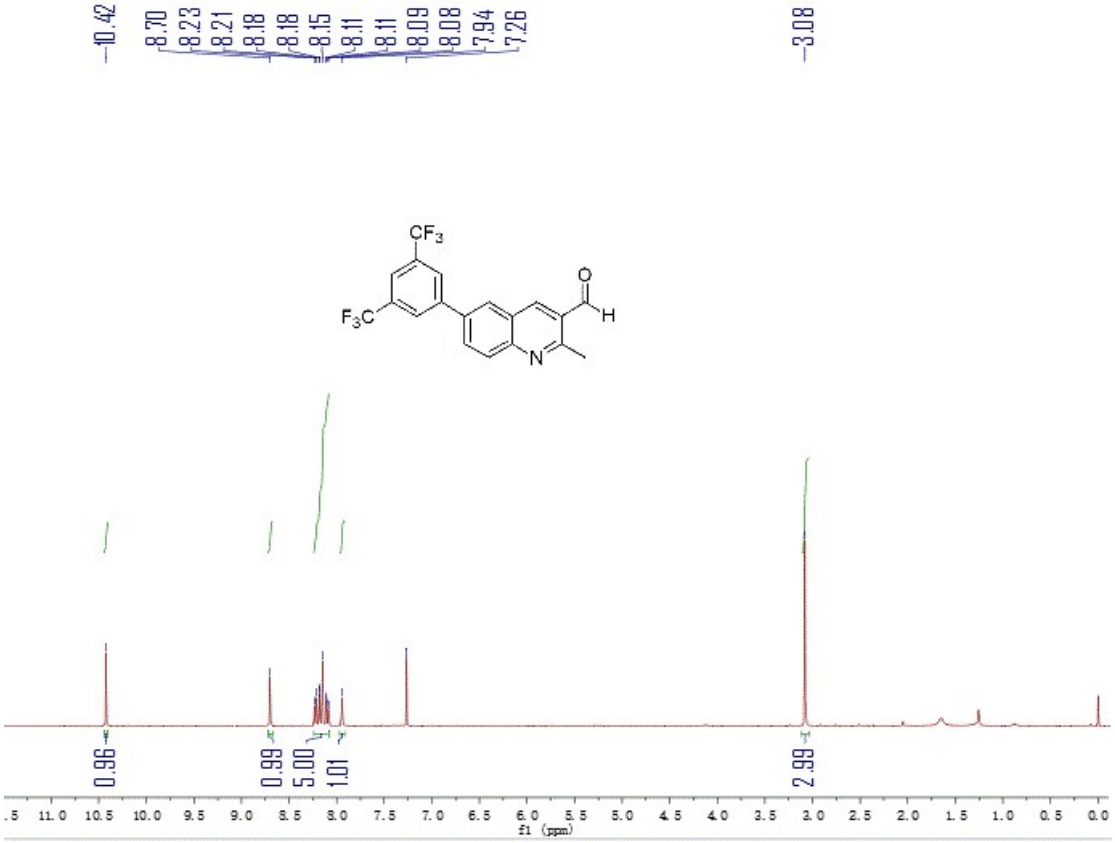


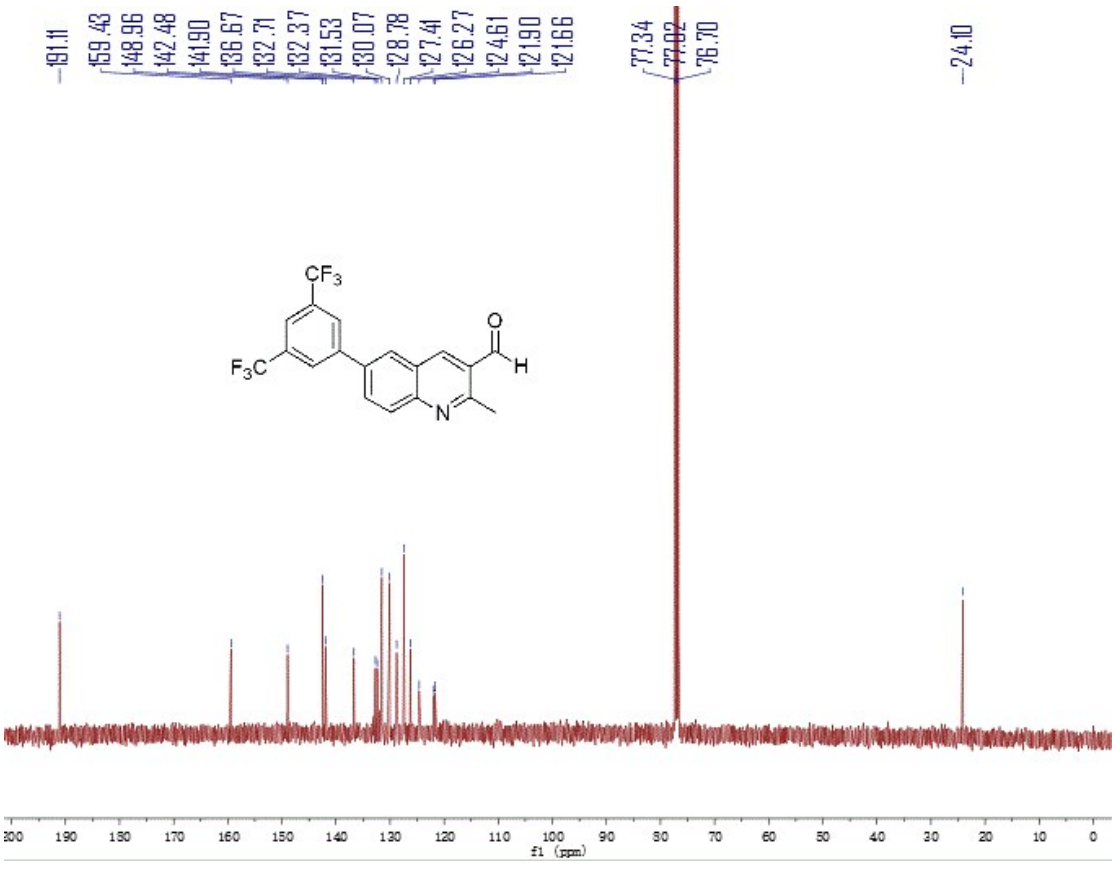


2-Methyl-6-phenylquinoline-3-carbaldehyde (1e)

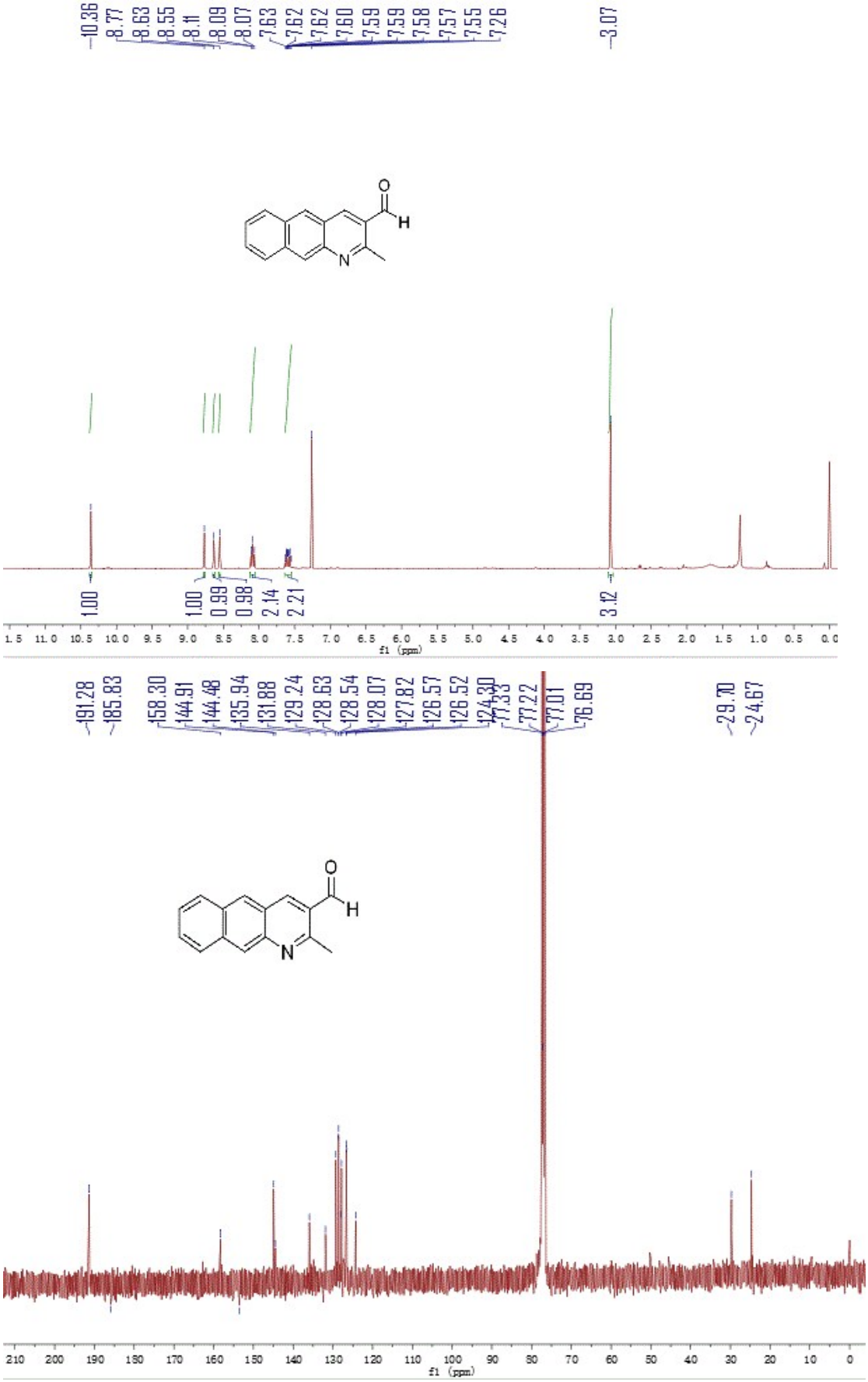


6-(3,5-bis(Trifluoromethyl)phenyl)-2-methylquinoline-3-carbaldehyde (1f)

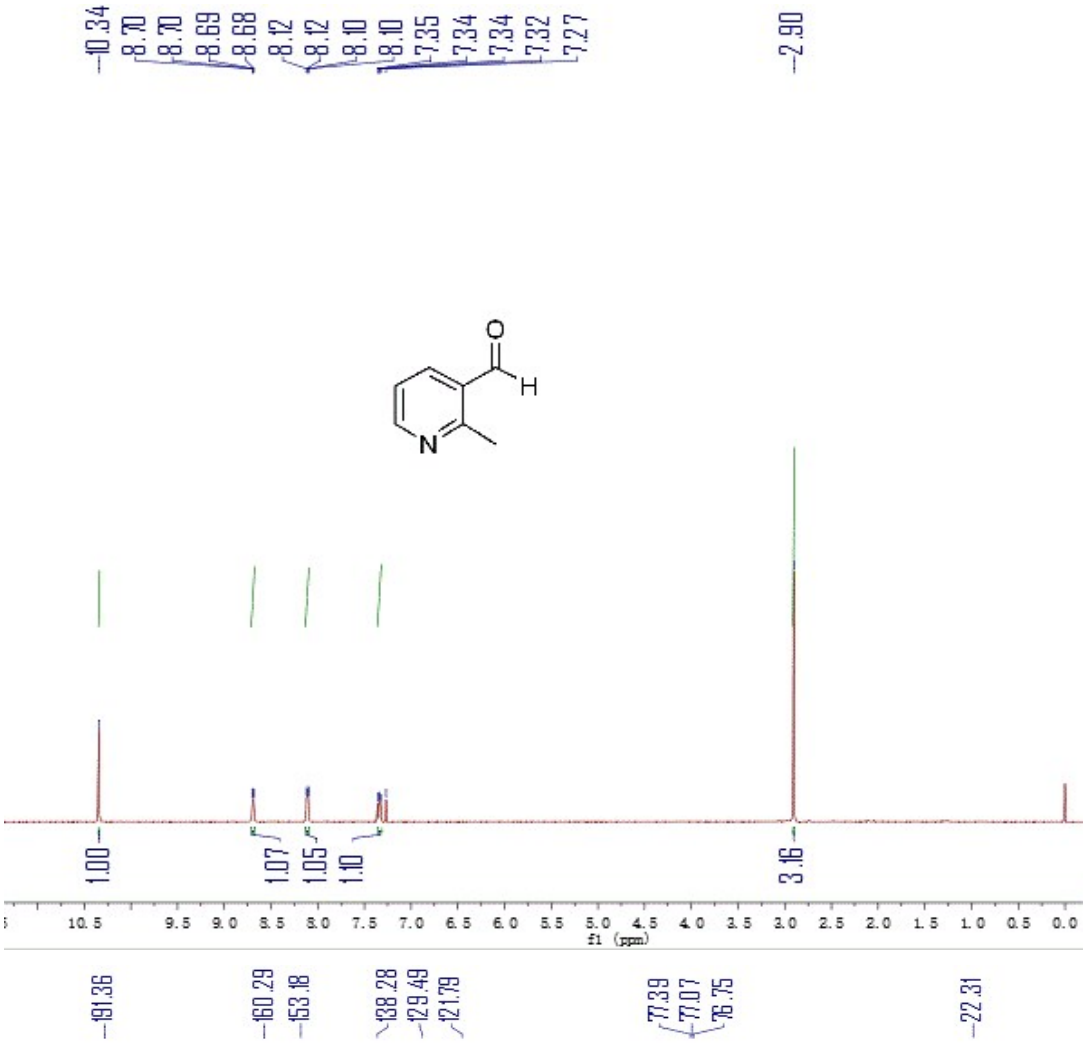


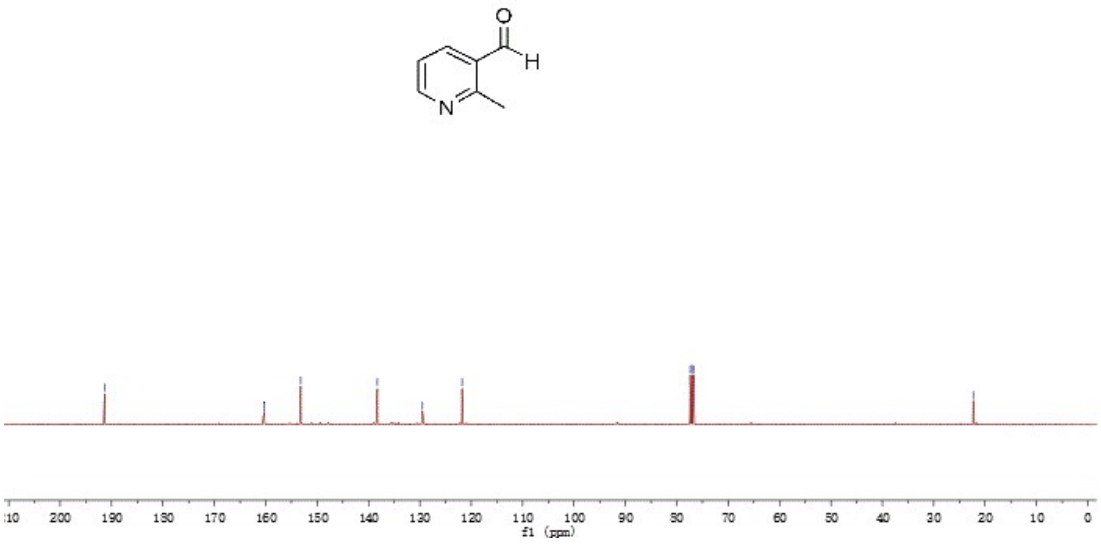


2-Methylbenzo[g]quinoline-3-carbaldehyde (1g)

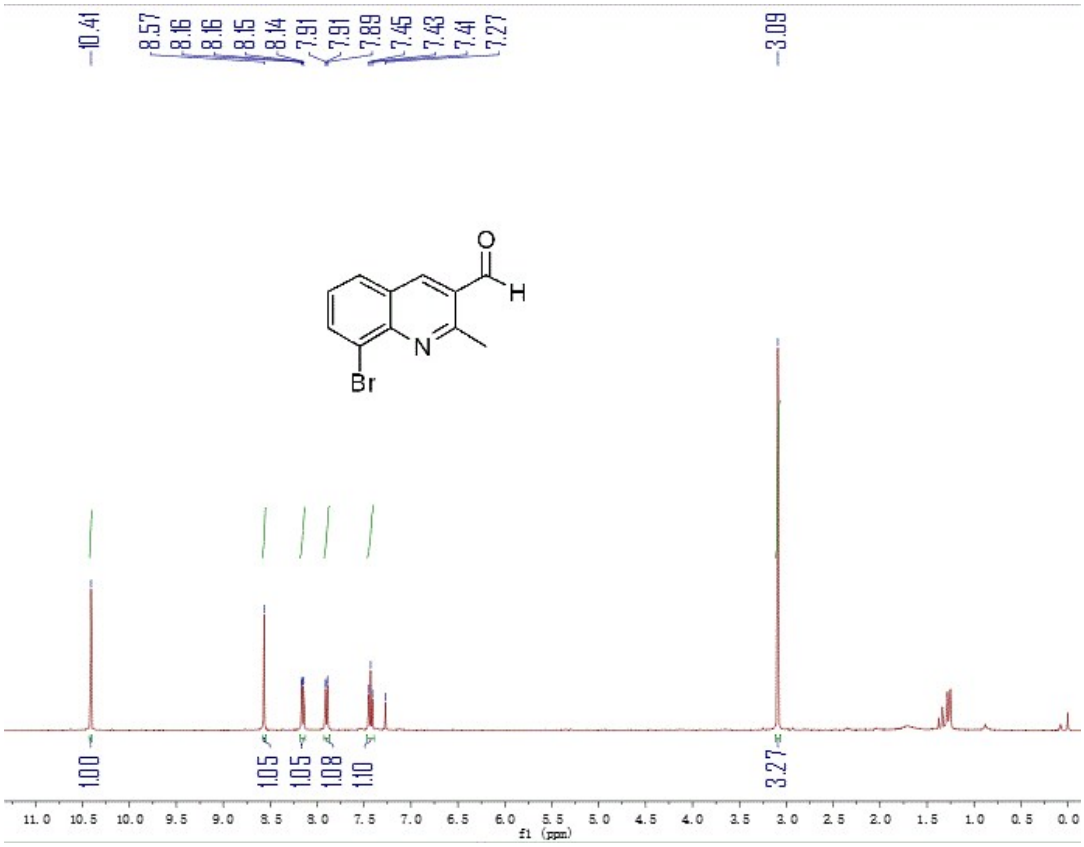


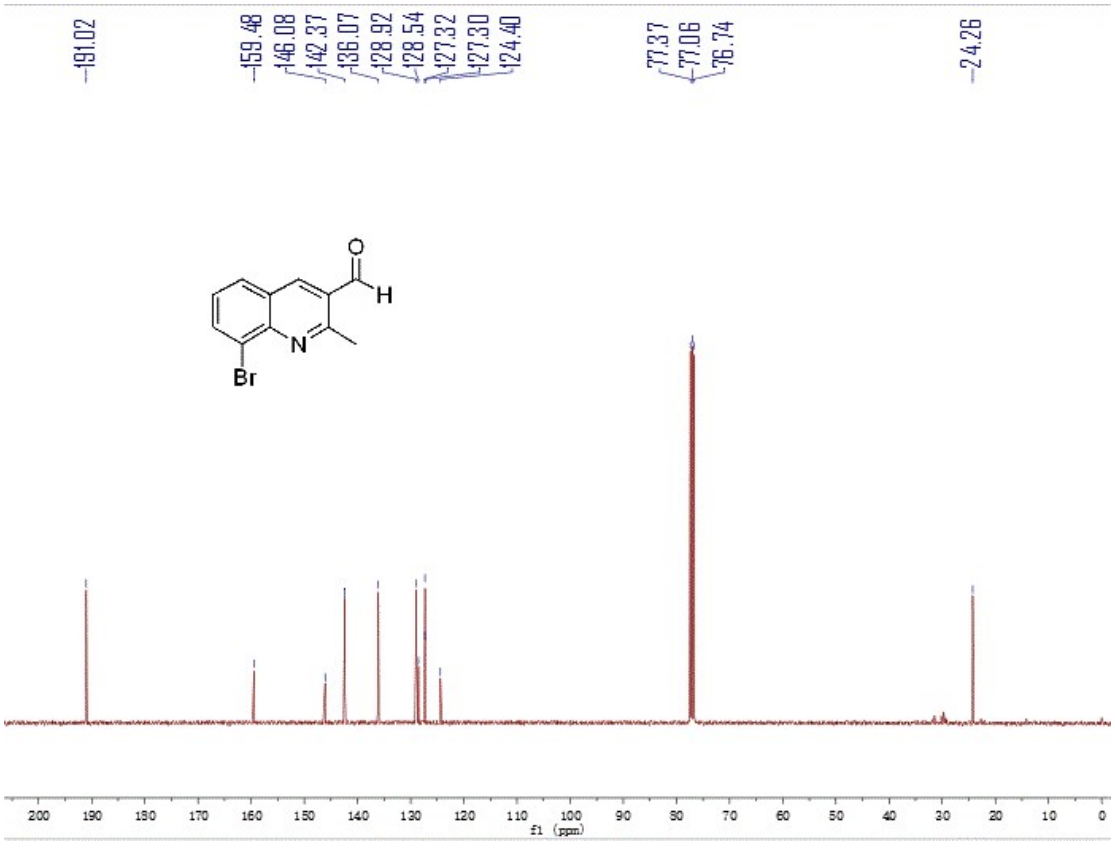
2-Methylnicotinaldehyde (1h)





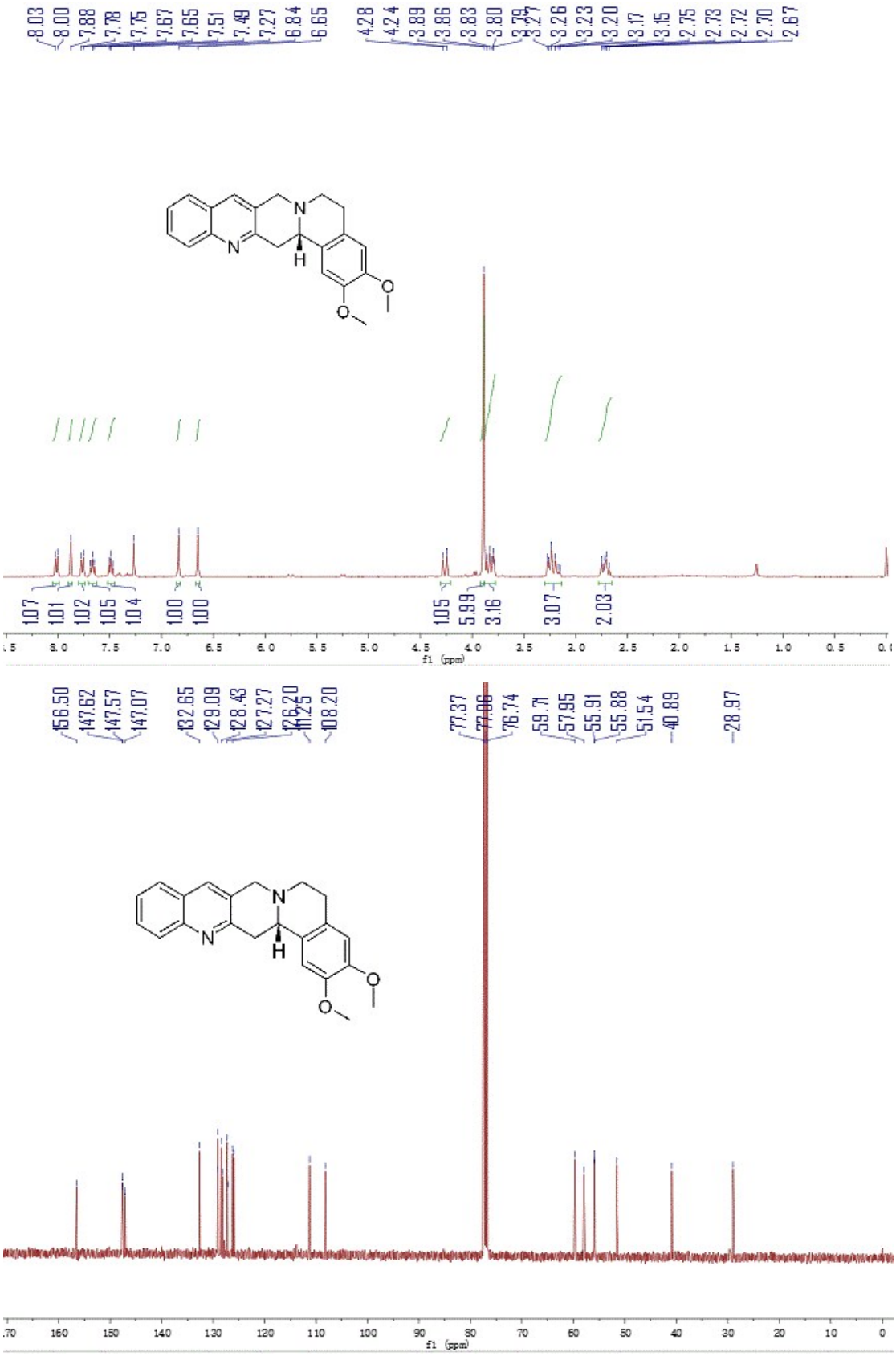
8-Bromo-2-methylquinoline-3-carbaldehyde (1i)



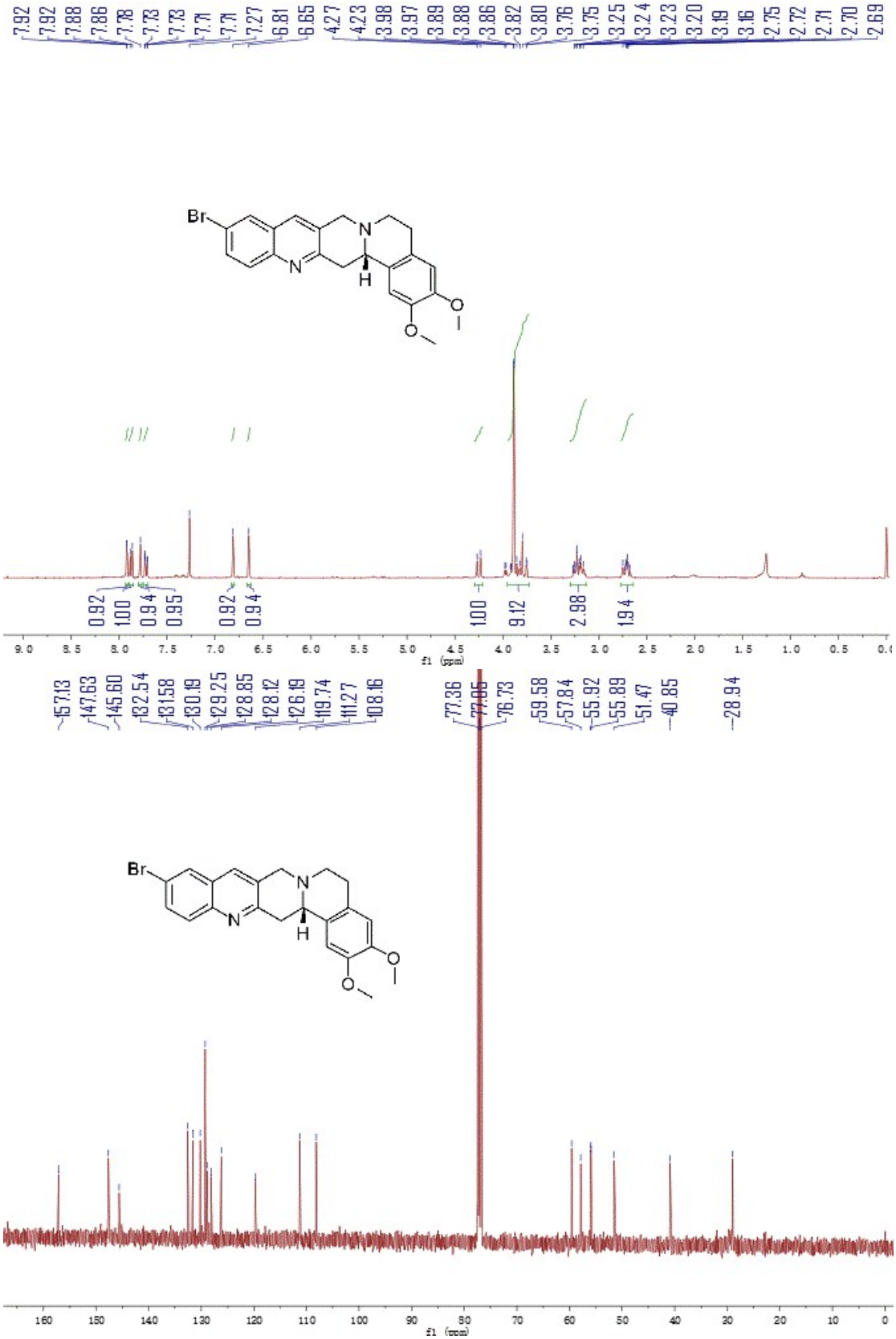


8-Methoxy-2-methylquinoline-3-carbaldehyde (1j)

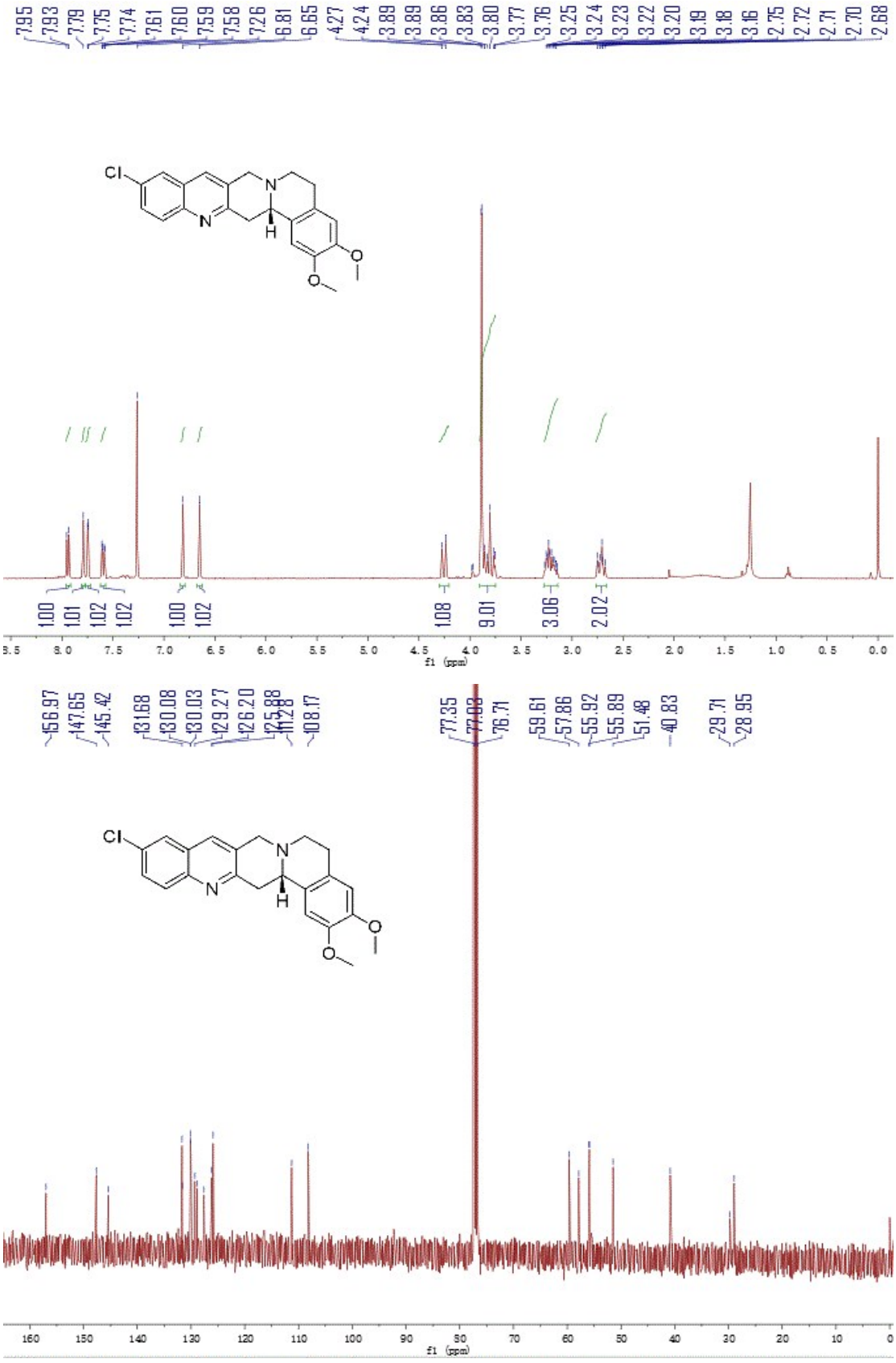
(*S*)-2,3-Dimethoxy-6,8,15,15a-tetrahydro-5H-benzo[b]isoquinolino[2,1-g][1,6]naphthyridine (3a)



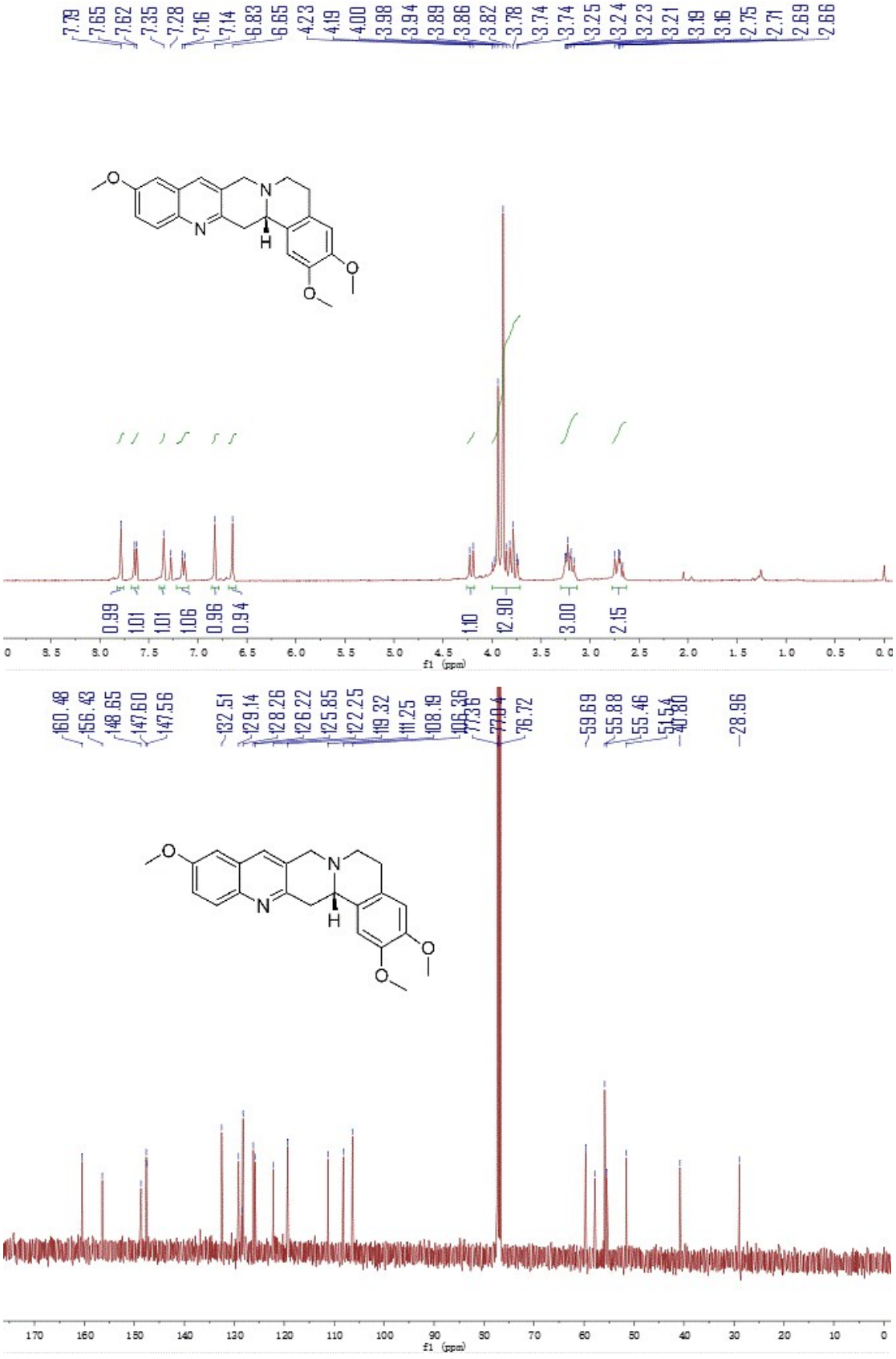
(*S*)-11-Bromo-2,3-dimethoxy-6,8,15,15a-tetrahydro-5H-benzo[b]isoquinolino[2,1-g][1,6]naphthyridine (3b)



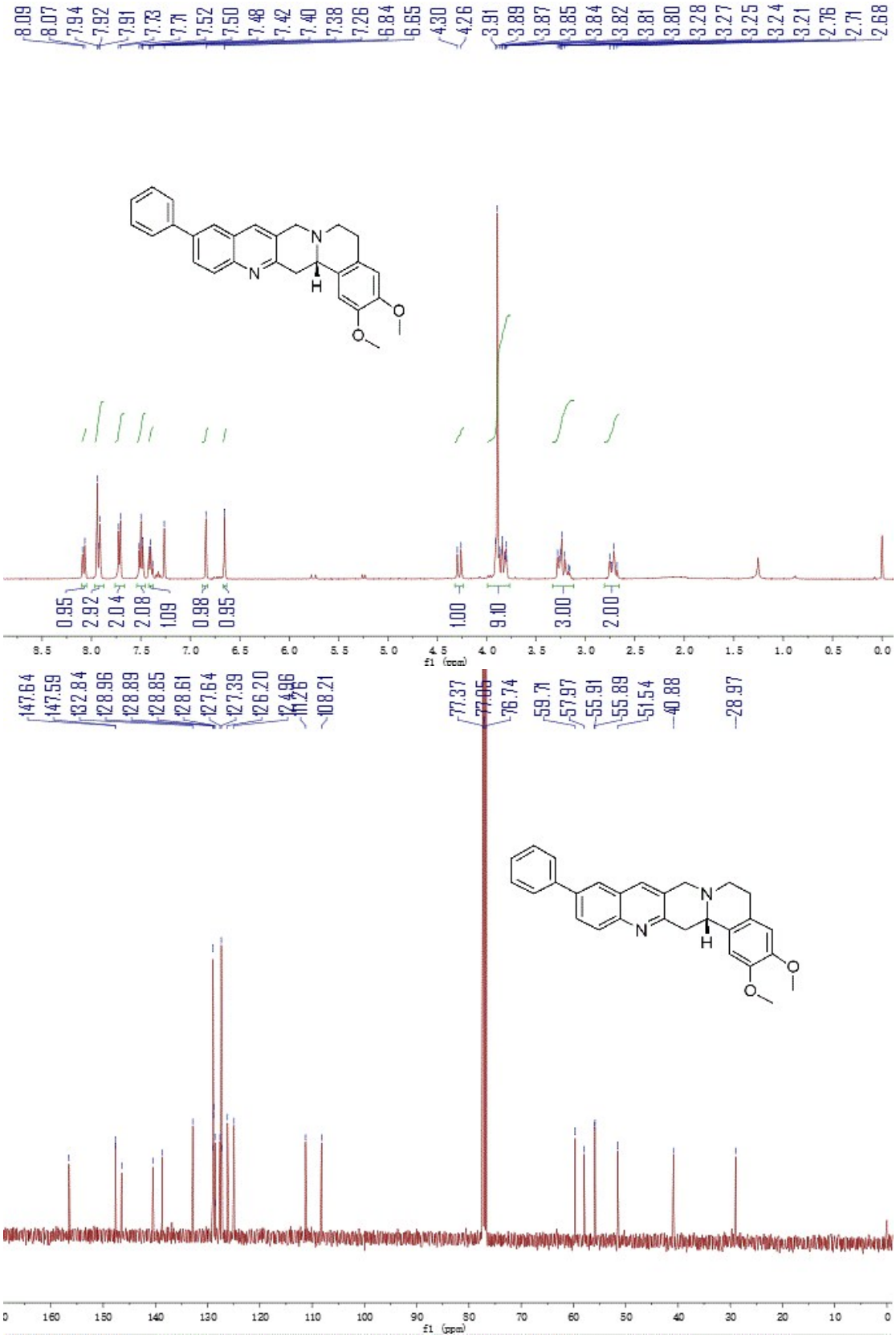
(*S*)-11-Chloro-2,3-dimethoxy-6,8,15,15a-tetrahydro-5H-benzo[b]isoquinolino[2,1-g][1,6]naphthyridine (3c)



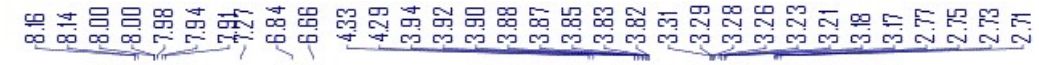
(*S*)-2,3,11-Trimethoxy-6,8,15,15a-tetrahydro-5H-benzo[b]isoquinolino[2,1-g][1,6]naphthyridine (3d)

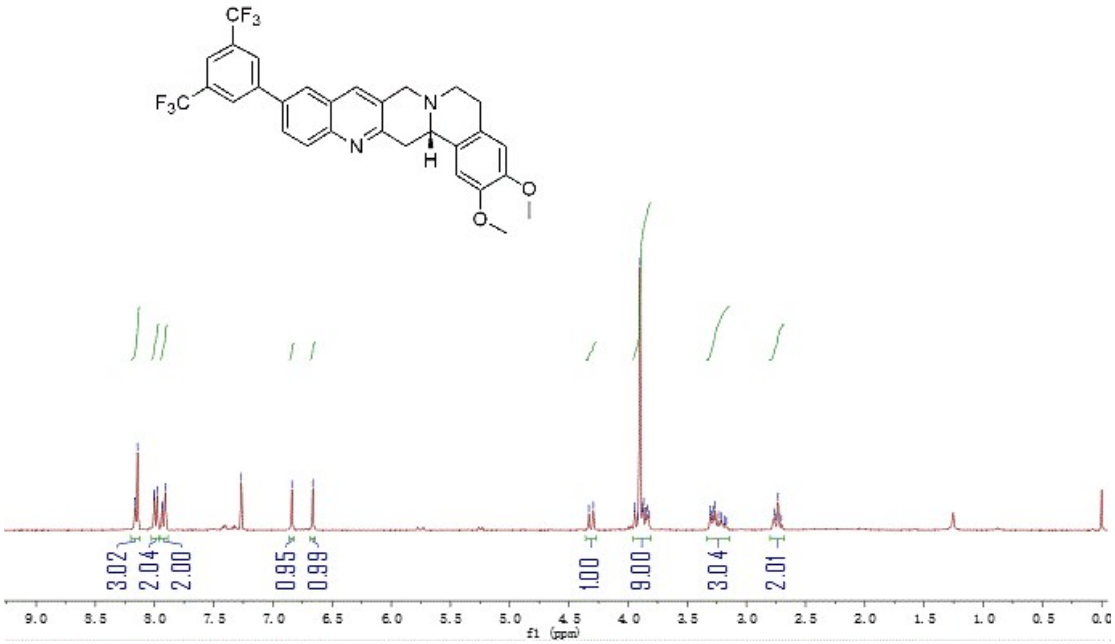


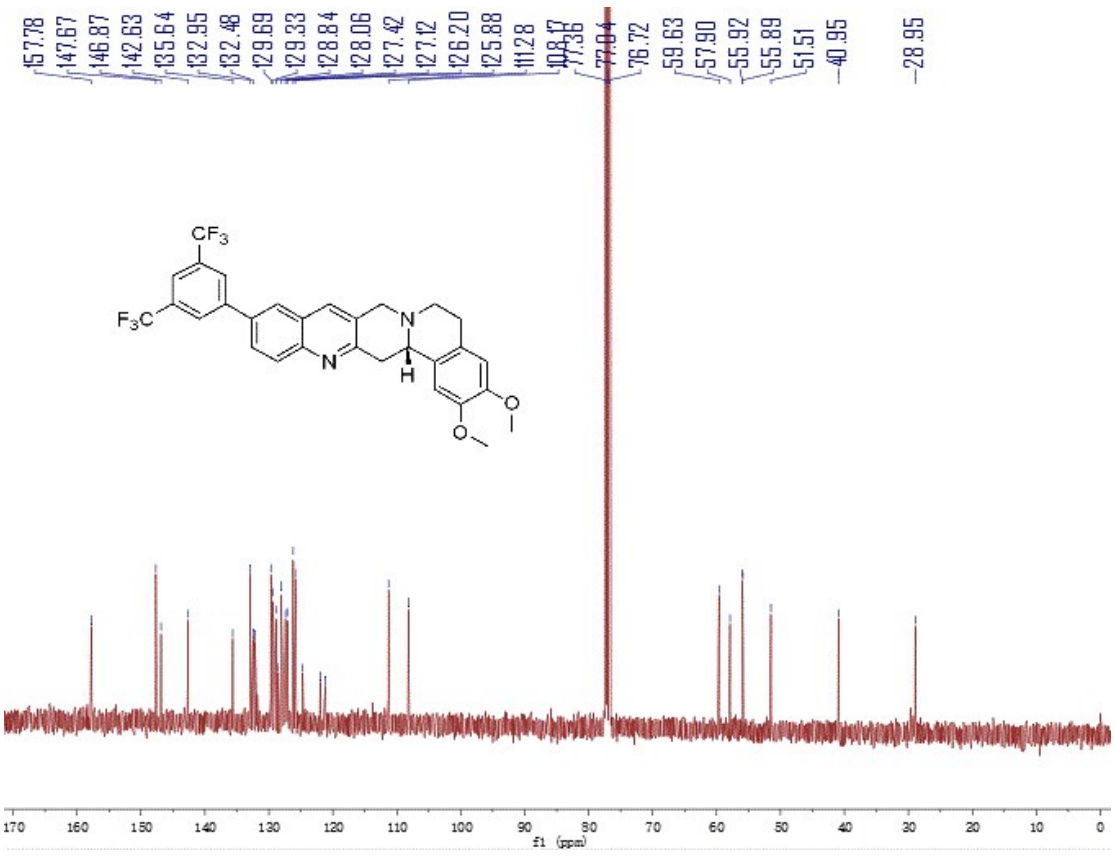
(*S*)-2,3-Dimethoxy-11-phenyl-6,8,15,15a-tetrahydro-5H-benzo[b]isoquinolino[2,1-g][1,6]naphthyridine (3e)



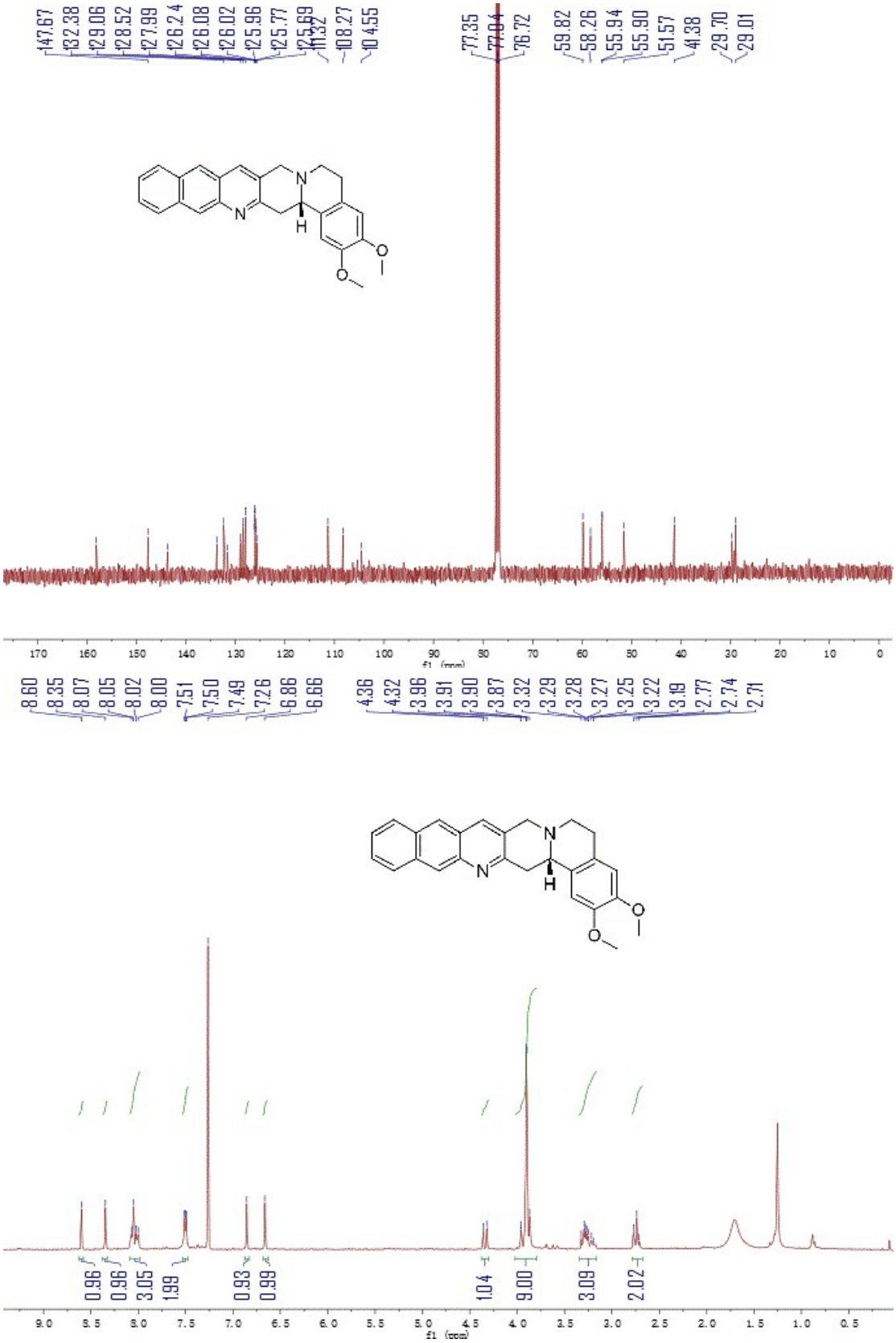
(*S*)-11-(3,5-bis(Trifluoromethyl)phenyl)-2,3-dimethoxy-6,8,15,15a-tetrahydro-5H-benzo[b]isoquinolino[2,1-g][1,6]naphthyridine (3f)





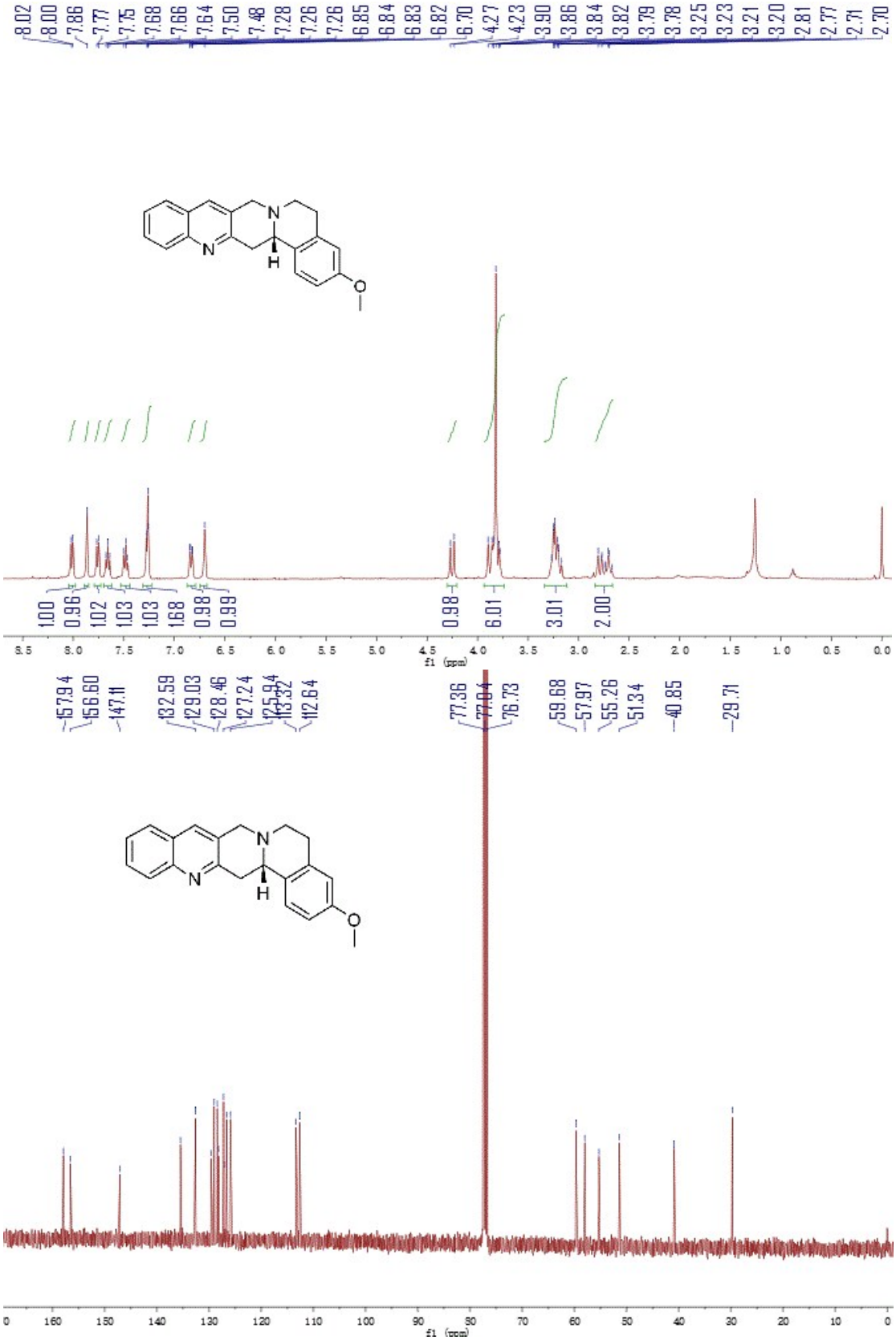


(*S*)-2,3-Dimethoxy-6,8,17,17a-tetrahydro-5H-isoquinolino[2,1-g]naphtho[2,3-b][1,6]naphthyridine **(3g)**



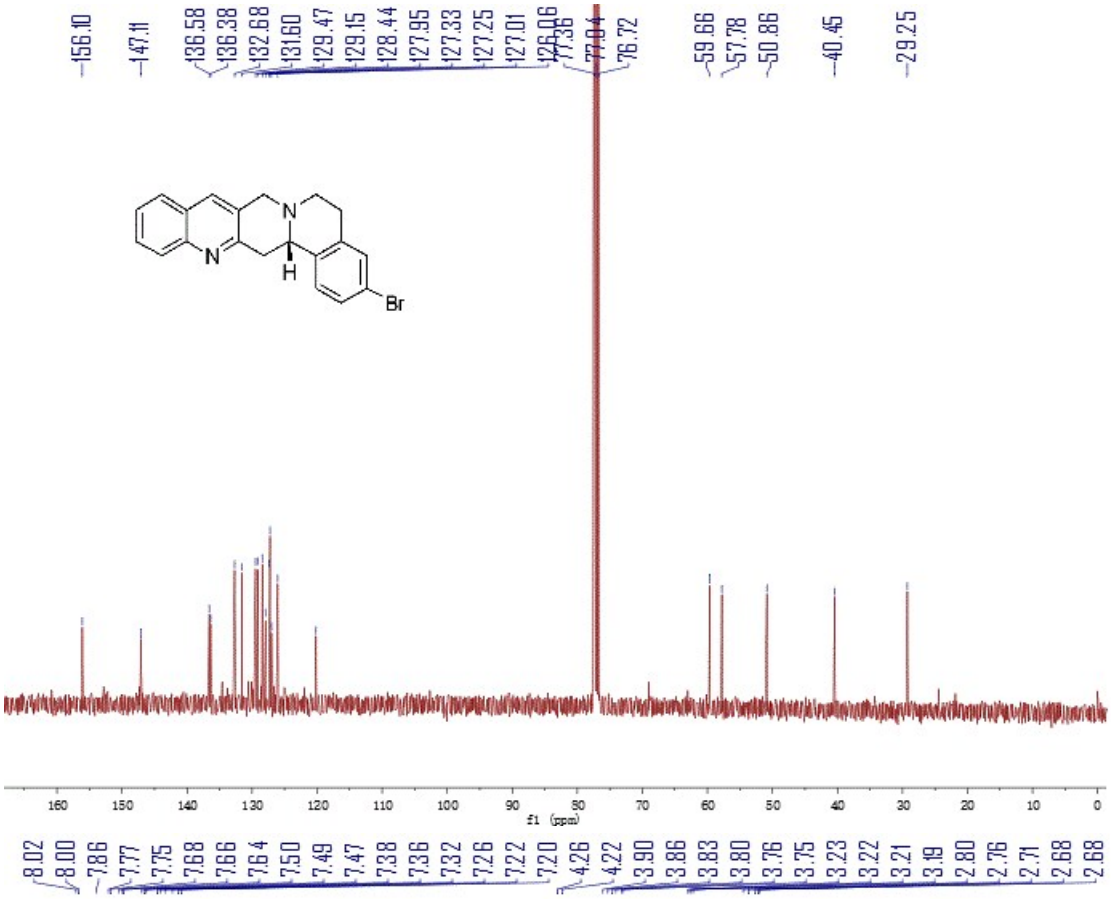
(*S*)-6,8,15,15a-Tetrahydro-5H-benzo[b]isoquinolino[2,1-g][1,6]naphthyridine (3i)

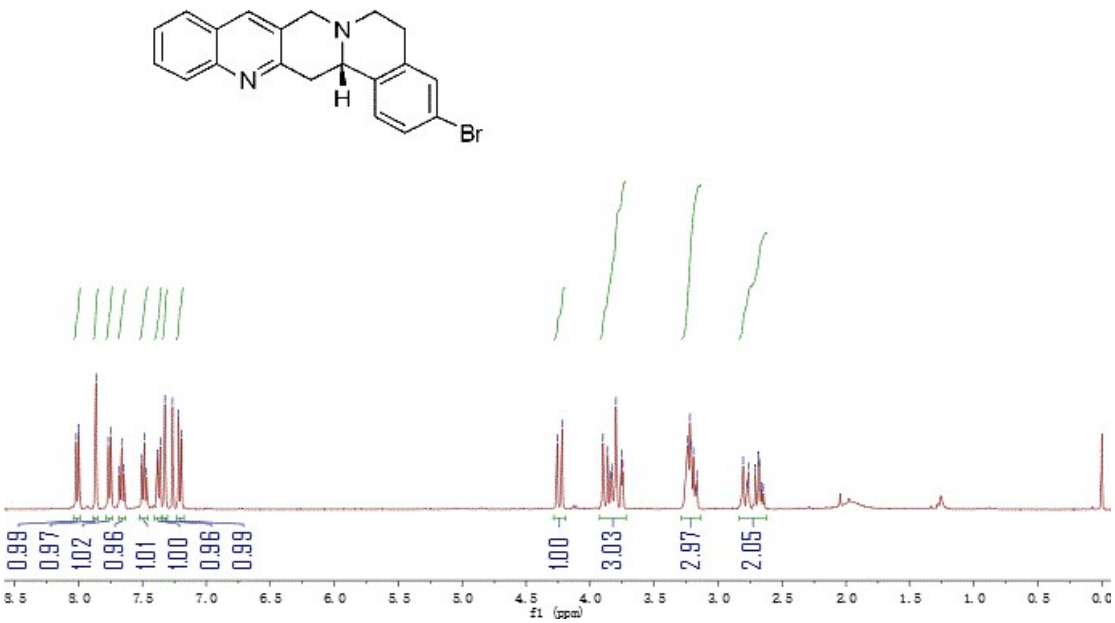
(*S*)-3-Methoxy-6,8,15,15a-tetrahydro-5H-benzo[b]isoquinolino[2,1-g][1,6]naphthyridine (3j)



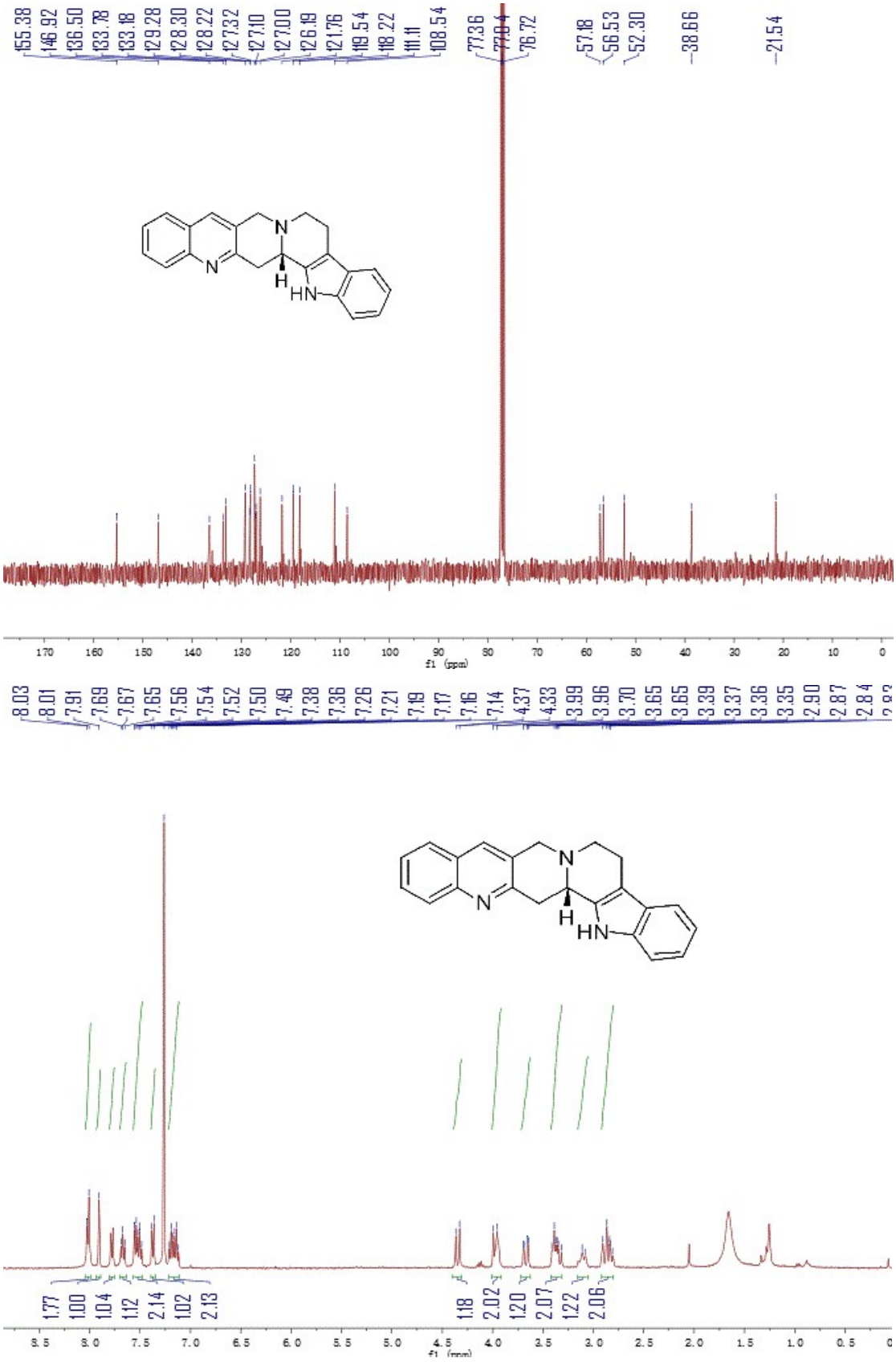
(*S*)-6,8,15,15a-Tetrahydro-5H-[1,3]dioxolo[4',5':6,7]isoquinolino[2,1-g]benzo[b][1,6]naphthyridine(3k)

(*S*)-3-Bromo-6,8,15,15a-tetrahydro-5H-benzo[b]isoquinolino[2,1-g][1,6]naphthyridine (3l)





(*S*)-5,6,8,15,15a,16-Hexahydrobenzo[b]indolo[2',3':3,4]pyrido[1,2-g][1,6]naphthyridine (3m)



8. Chiral HPLC analysis spectra

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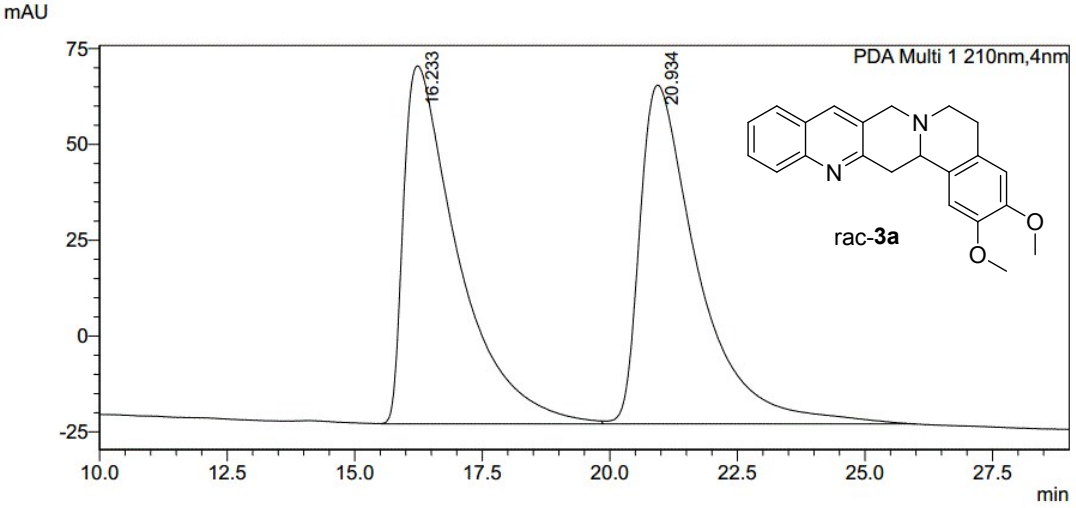

<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	16.233	6947623	93405	49.719	%	SV	RT:16.233
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Total		13973805	181741				

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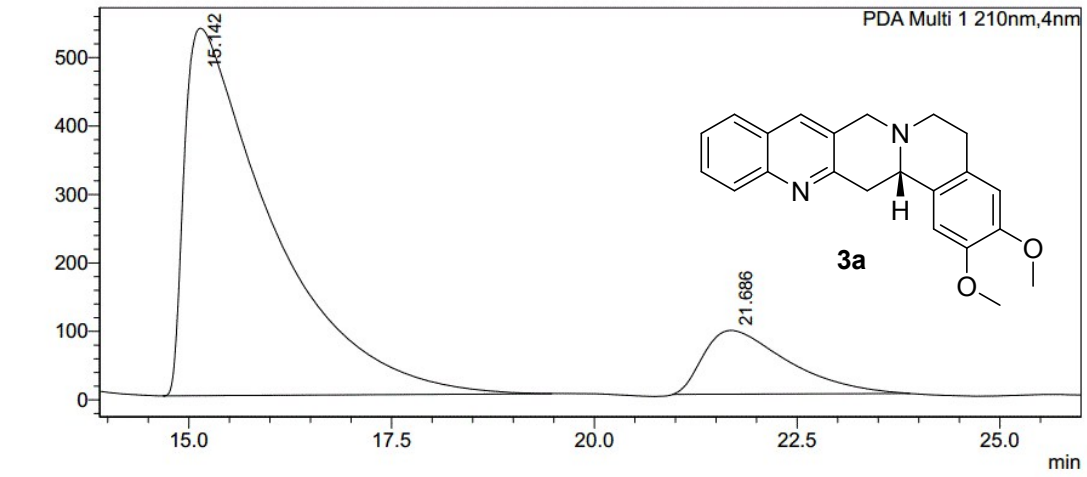

<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.142	40224330	536771	85.668	%		RT:15.142
2	21.686	6729656	93048	14.332	%		RT:21.686
Total		46953986	629819				

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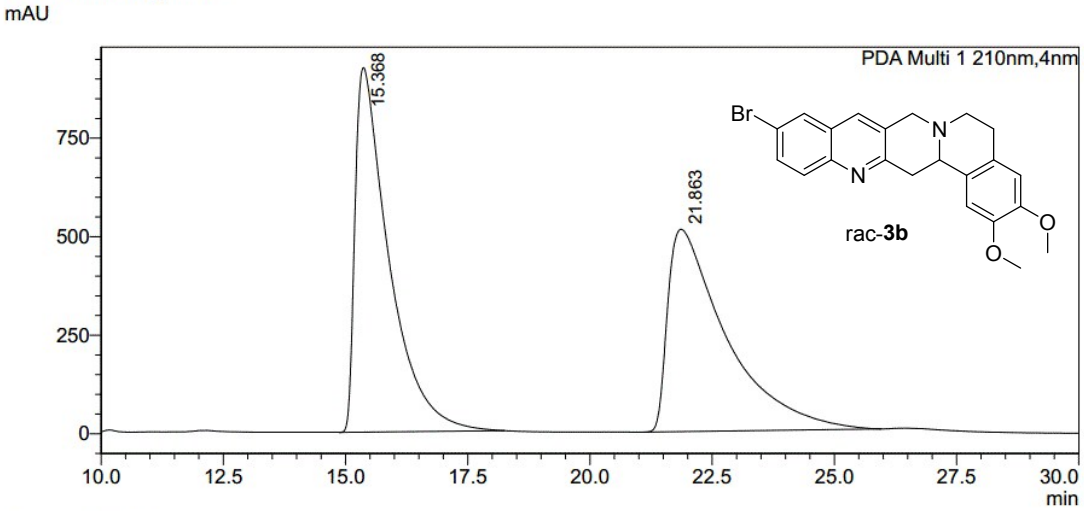

<Peak Table>

PDA Ch1 210nm

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1	15.368	44517336	925091	51.012	%		RT:15.368
2	21.863	42750723	513323	48.988	%		RT:21.863
Total		87268059	1438413				

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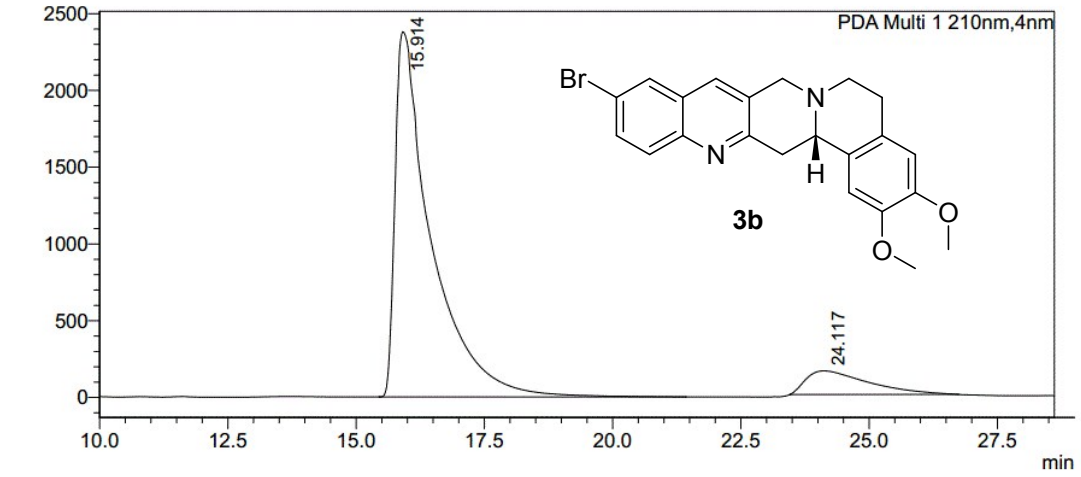

<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.914	116500609	2378902	89.942	%		RT:15.914
2	24.117	13028161	153852	10.058	%		RT:24.117
Total		129528770	2532755				

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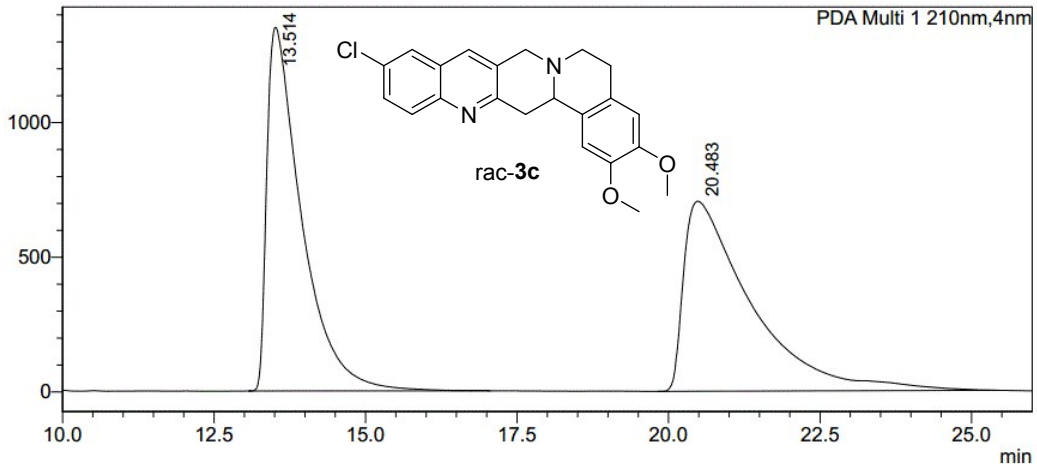
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.514	53860753	1350776	49.582	%		RT:13.514
2	20.483	54769239	705480	50.418	%		RT:20.483
Total		108629991	2056256				

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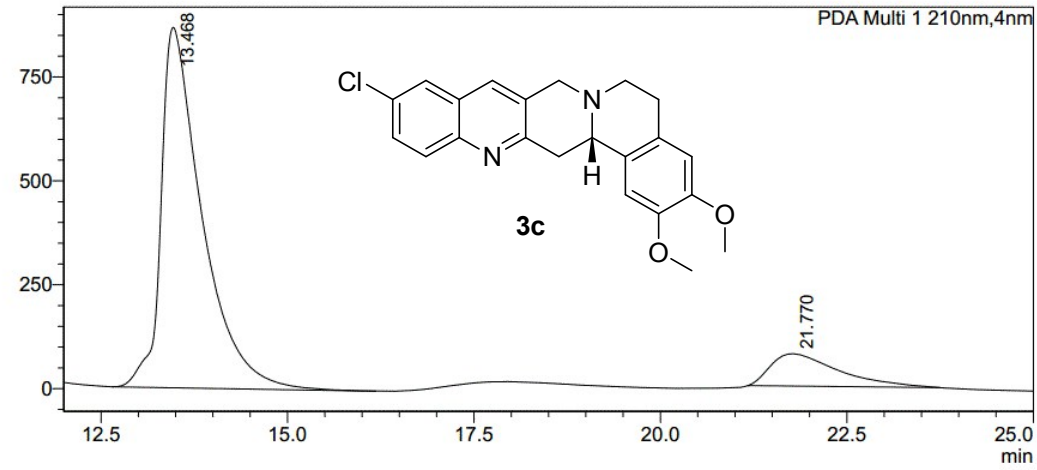
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.468	33155378	867208	87.048	%		RT:13.468
2	21.770	4933360	77780	12.952	%		RT:21.770
Total		38088737	944989				

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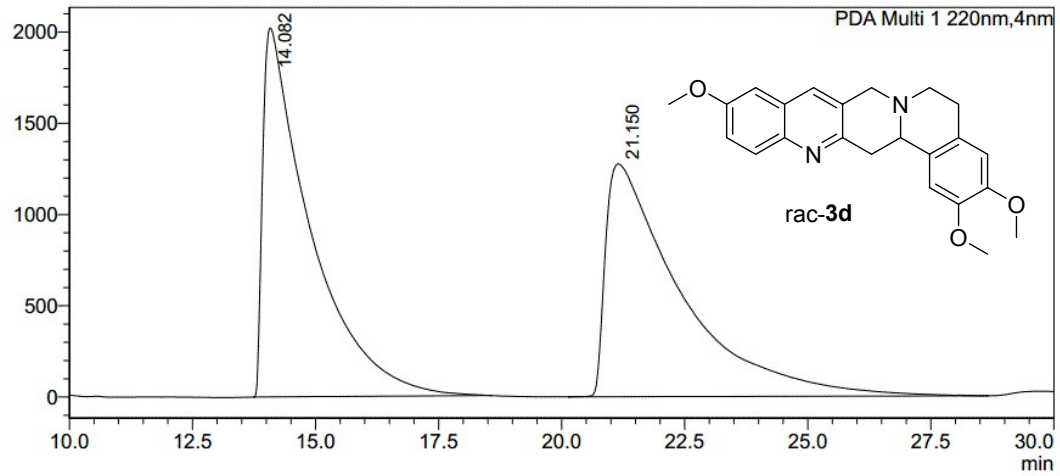

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PDA Ch1 220nm

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1	14.082	135195674	2021199	49.859	%		RT:14.082
2	21.150	135958307	1275340	50.141	%		RT:21.150
Total		271153980	3296539				

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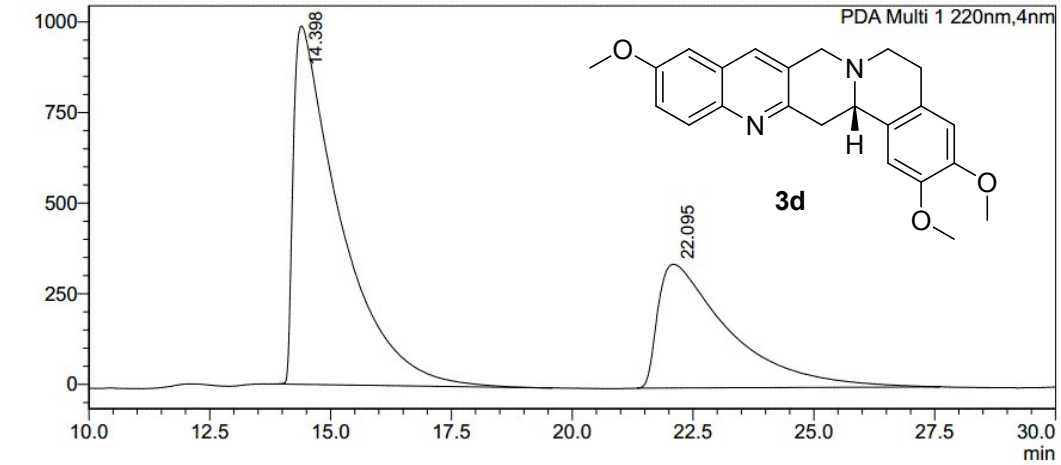
mAU



<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.398	66348104	988553	65.505	%		RT:14.398
2	22.095	34939467	341219	34.495	%		RT:22.095
Total		101287571	1329771				

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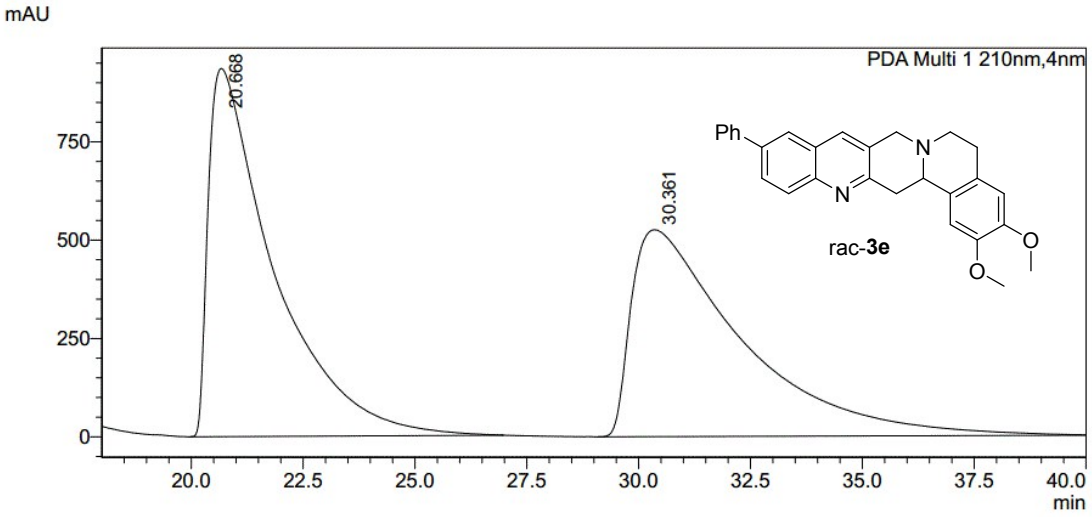

<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	20.668	94869944	935940	51.182	%		RT:20.668
2	30.361	90487284	526128	48.818	%		RT:30.361
Total		185357228	1462069				

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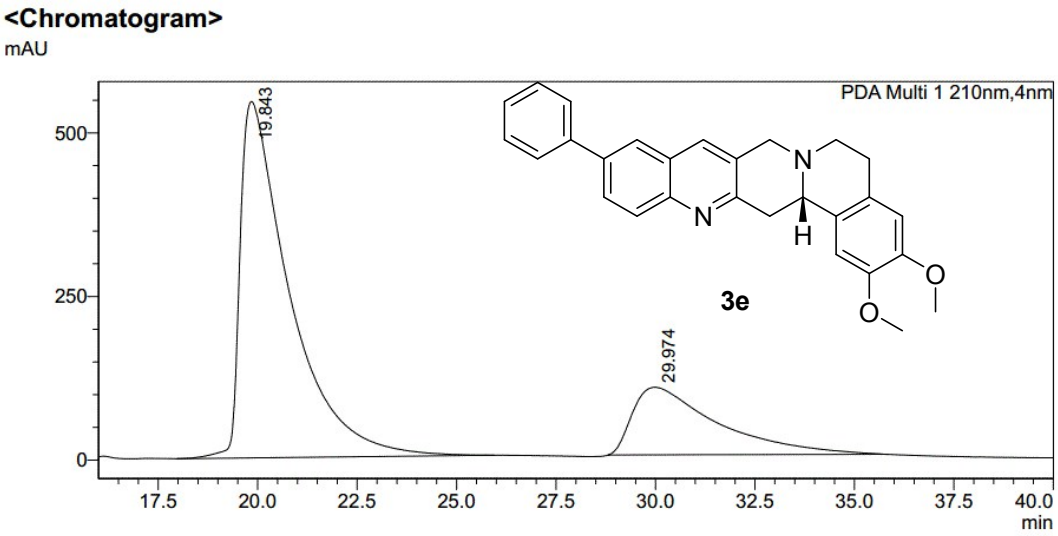


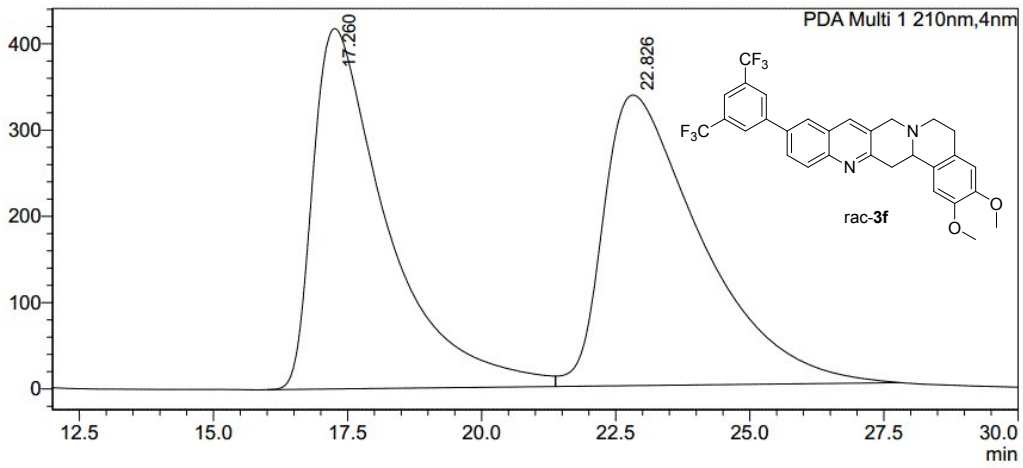
<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	19.843	46899831	544586	75.422	%	S	RT:19.843
2	29.974	15282993	103228	24.578	%		RT:29.974
Total		62182824	647814				

<Chromatogram>

mAU



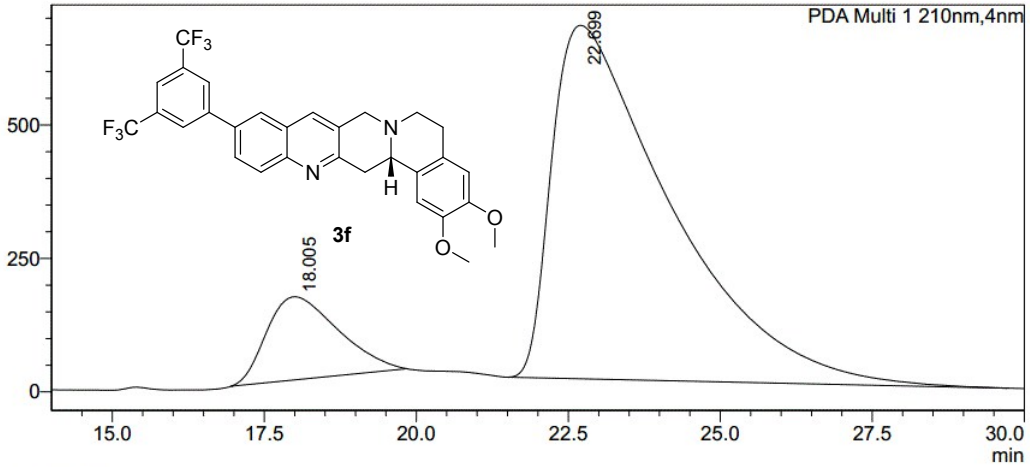
<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	17.260	40297887	417528	48.345	%		RT:17.260
2	22.826	43056956	336701	51.655	%	V	RT:22.826
Total		83354843	754229				

<Chromatogram>

mAU



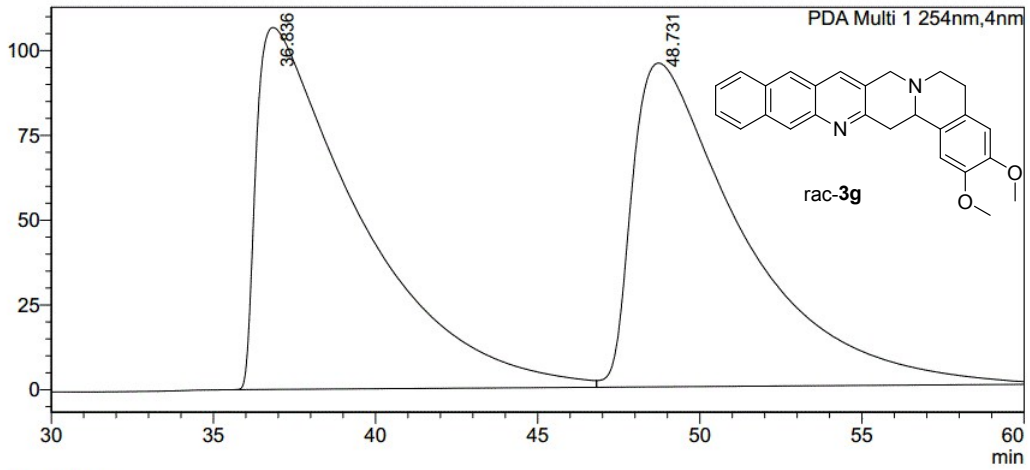
<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	18.005	12720563	155673	12.356	%		RT:18.005
2	22.699	90225962	662381	87.644	%		RT:22.699
Total		102946525	818054				

<Chromatogram>

mAU



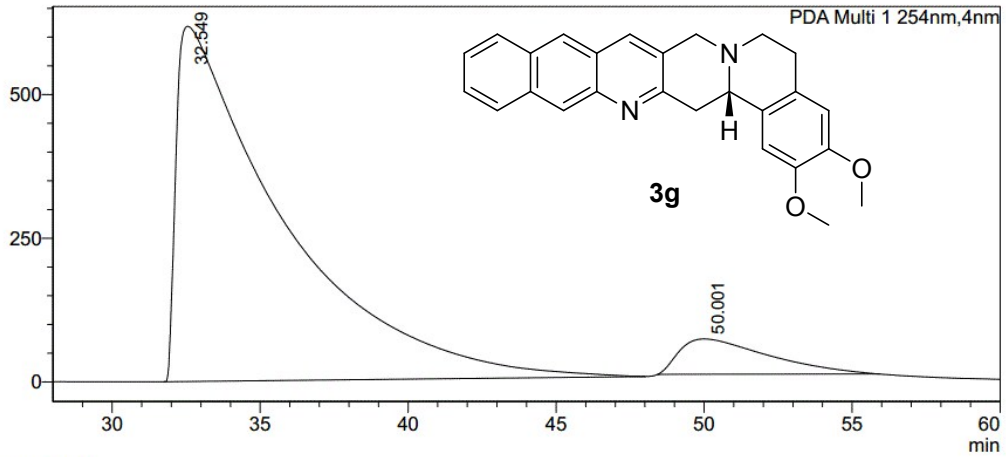
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	36.836	23572235	106709	50.671	%		RT:36.836
2	48.731	22947718	95468	49.329	%	SV	RT:48.731
Total		46519953	202177				

<Chromatogram>

mAU



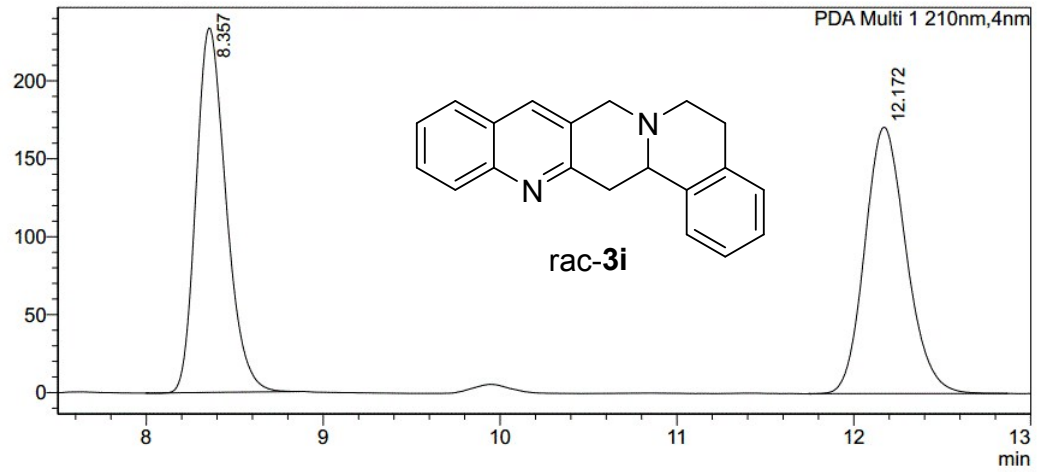
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	32.549	153654060	618178	92.295	%		RT:32.549
2	50.001	12828045	61383	7.705	%		RT:50.001
Total		166482105	679561				

<Chromatogram>

mAU



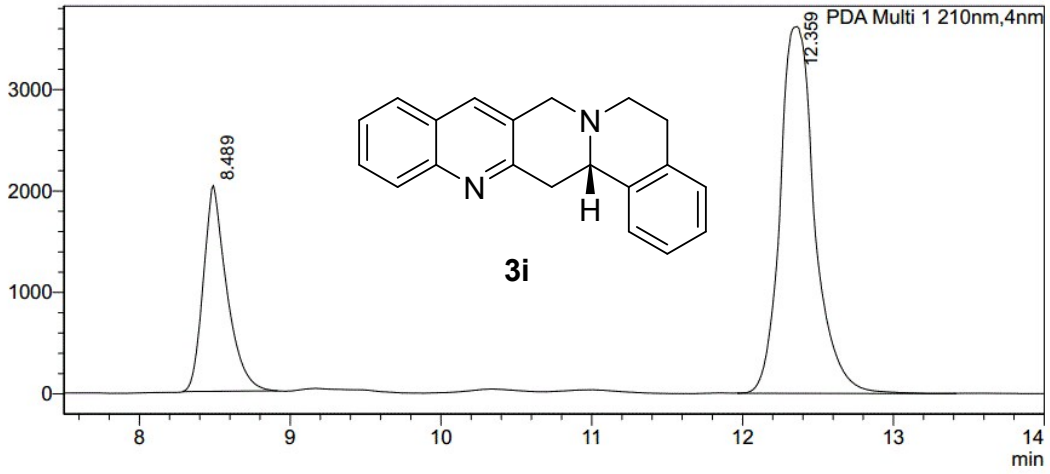
<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.357	2760198	227935	49.751	%	M	RT:8.357
2	12.172	2787862	169641	50.249	%		RT:12.172
Total		5548060	397576				

<Chromatogram>

mAU

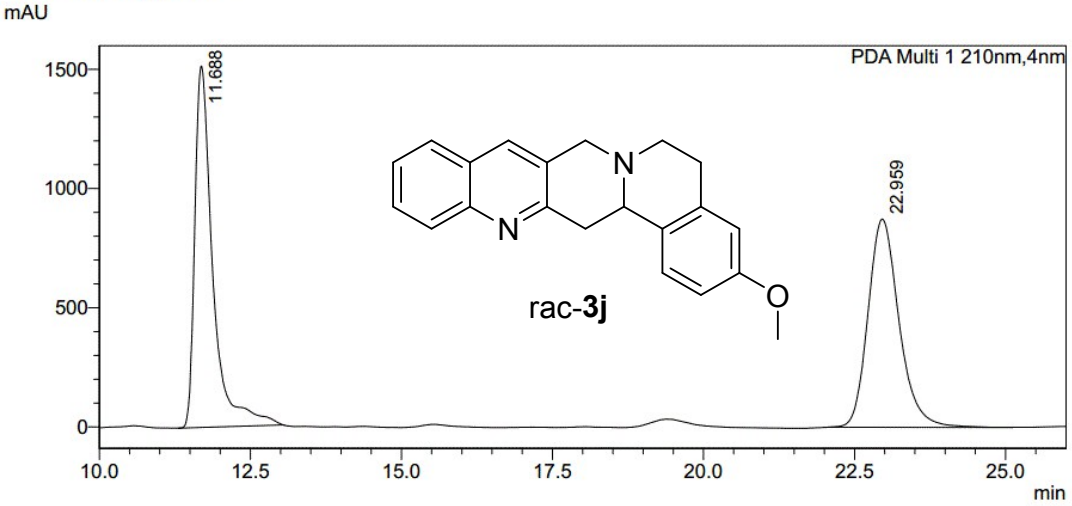


<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.489	21885599	2031733	27.517	%		RT:8.489
2	12.359	57650011	3615642	72.483	%		RT:12.359
Total		79535610	5647375				

<Chromatogram>

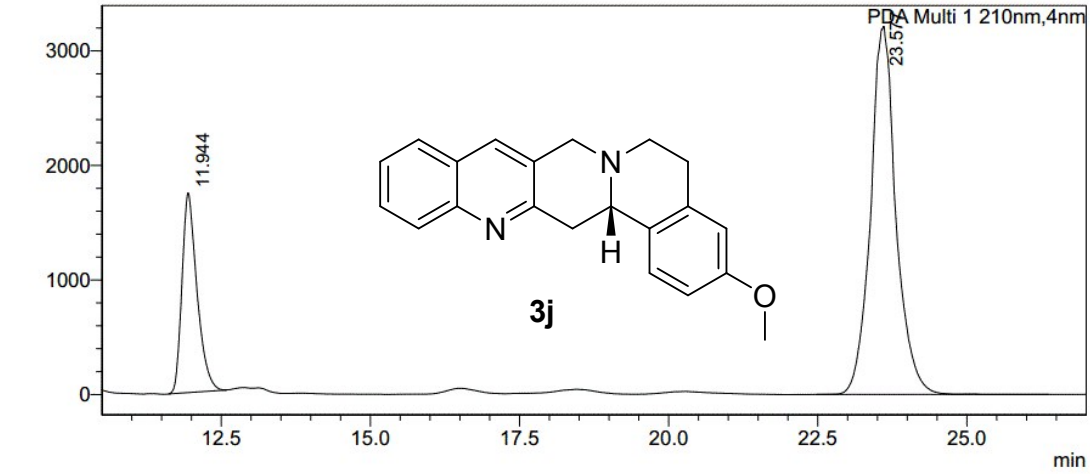


<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.688	31333809	1516358	50.108	%		RT:11.688
2	22.959	31198711	873313	49.892	%		RT:22.959
Total		62532519	2389670				

<Chromatogram>



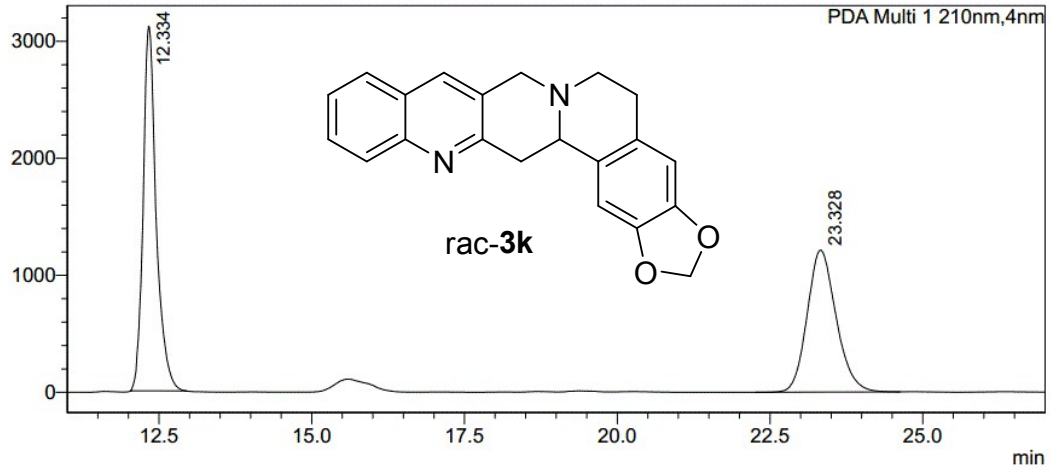
<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.944	30426970	1742190	24.179	%		RT:11.944
2	23.577	95415069	3190786	75.821	%	S	RT:23.577
Total		125842039	4932976				

<Chromatogram>

mAU



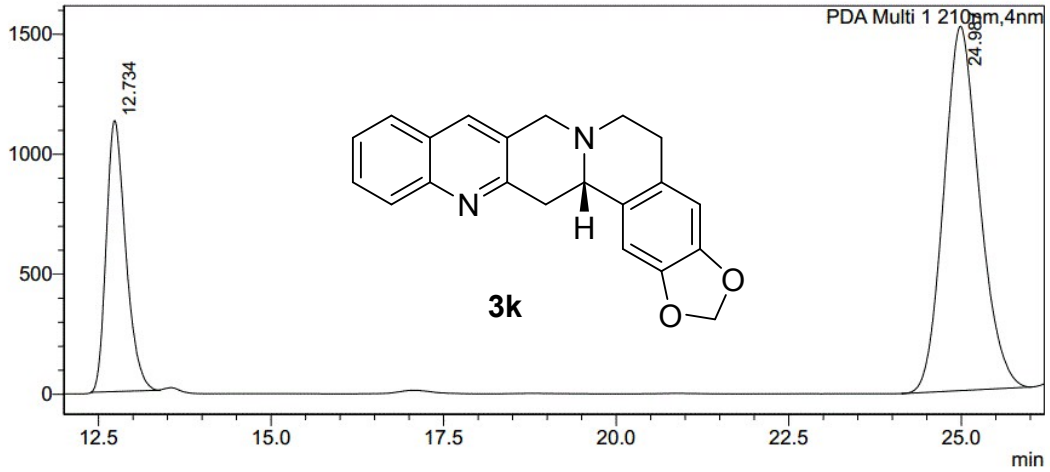
<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.334	46440122	3118335	53.752	%		RT:12.334
2	23.328	39956661	1213567	46.248	%		RT:23.328
Total		86396782	4331902				

<Chromatogram>

mAU

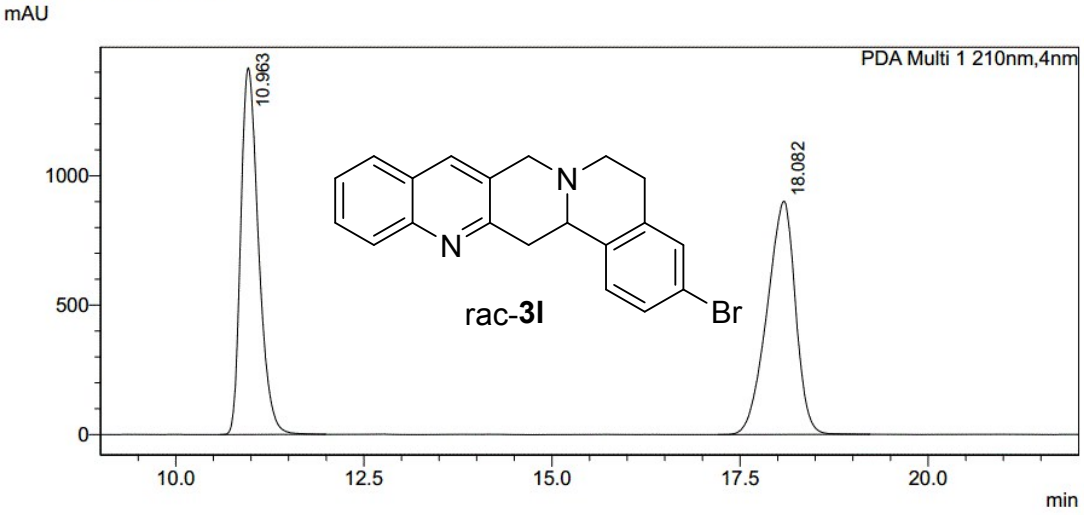


<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.734	22199881	1129525	28.848	%		RT:12.734
2	24.987	54754828	1518513	71.152	%		RT:24.987
Total		76954709	2648038				

<Chromatogram>

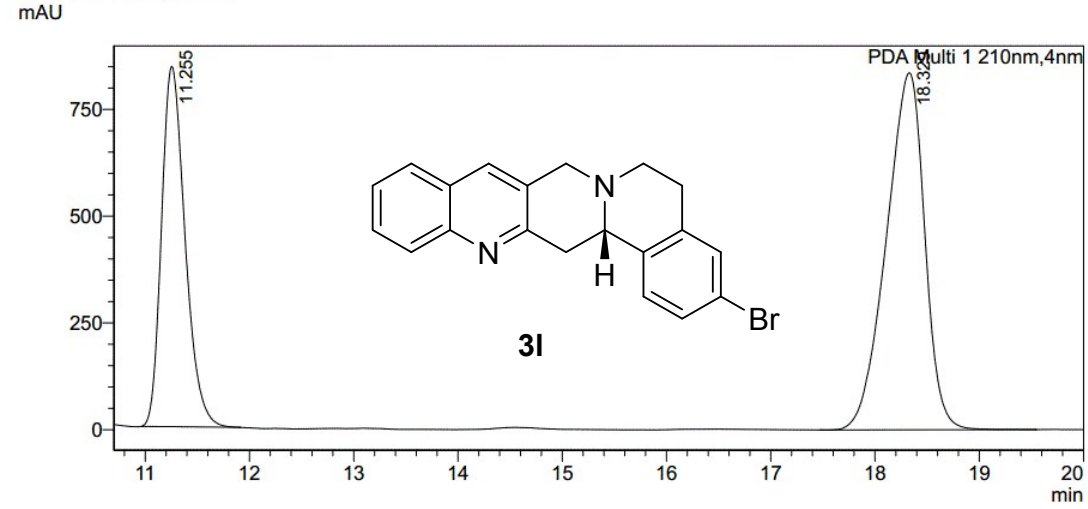


<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.963	23271217	1417022	49.520	%		RT:10.963
2	18.082	23722105	900559	50.480	%		RT:18.082
Total		46993322	2317582				

<Chromatogram>

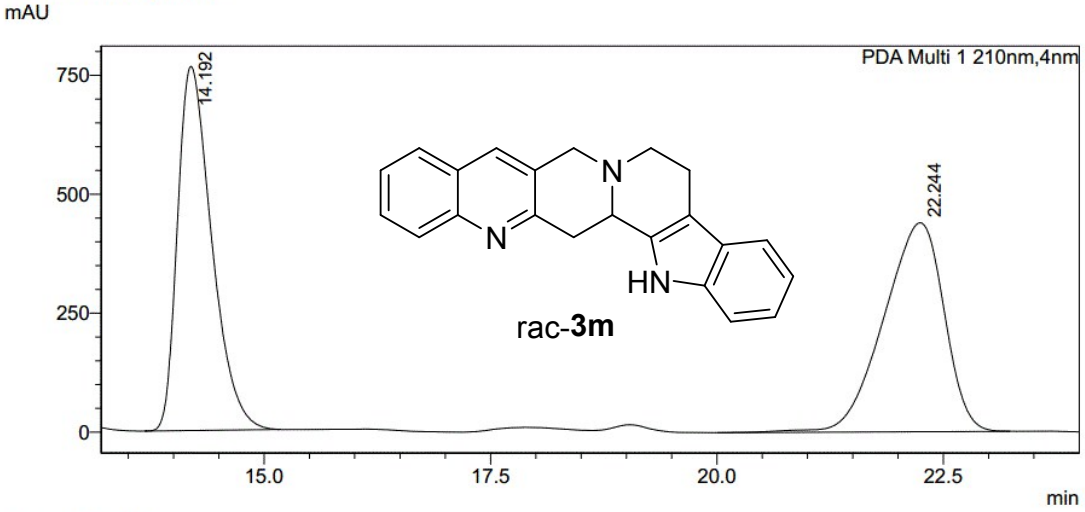


<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.255	13248869	844339	38.258	%		RT:11.255
2	18.329	21381638	836298	61.742	%	S	RT:18.329
Total		34630507	1680637				

<Chromatogram>

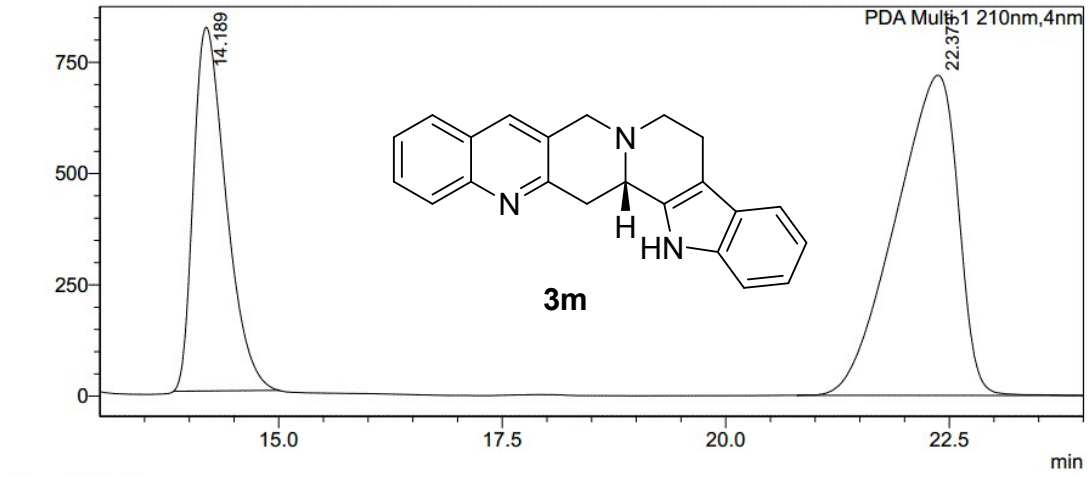


<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.192	20090465	765292	49.617	%		RT:14.192
2	22.244	20400559	439358	50.383	%		RT:22.244
Total		40491024	1204650				

<Chromatogram>

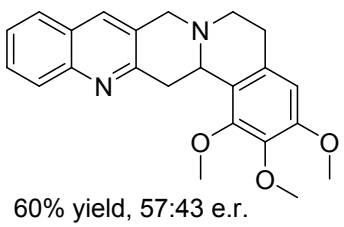


<Peak Table>

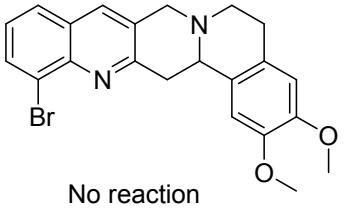
PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.189	20753320	817352	37.169	%		RT:14.189
2	22.373	35081515	719207	62.831	%		RT:22.373
Total		55834835	1536559				

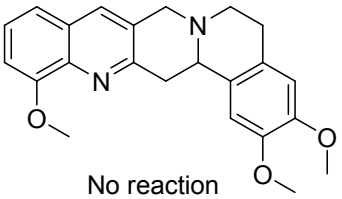
9. Other Substrates



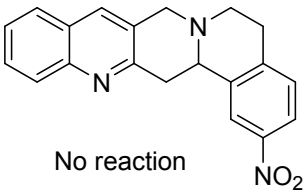
60% yield, 57:43 e.r.



No reaction



No reaction



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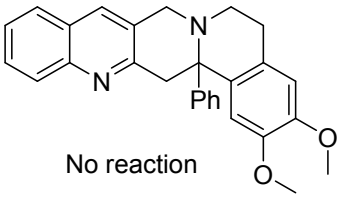
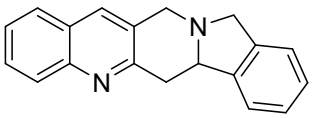


No reaction



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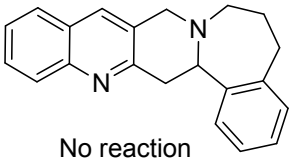

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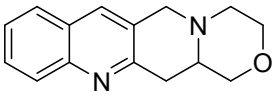
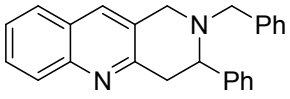
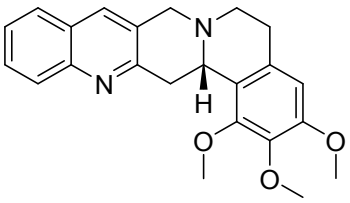


No reaction

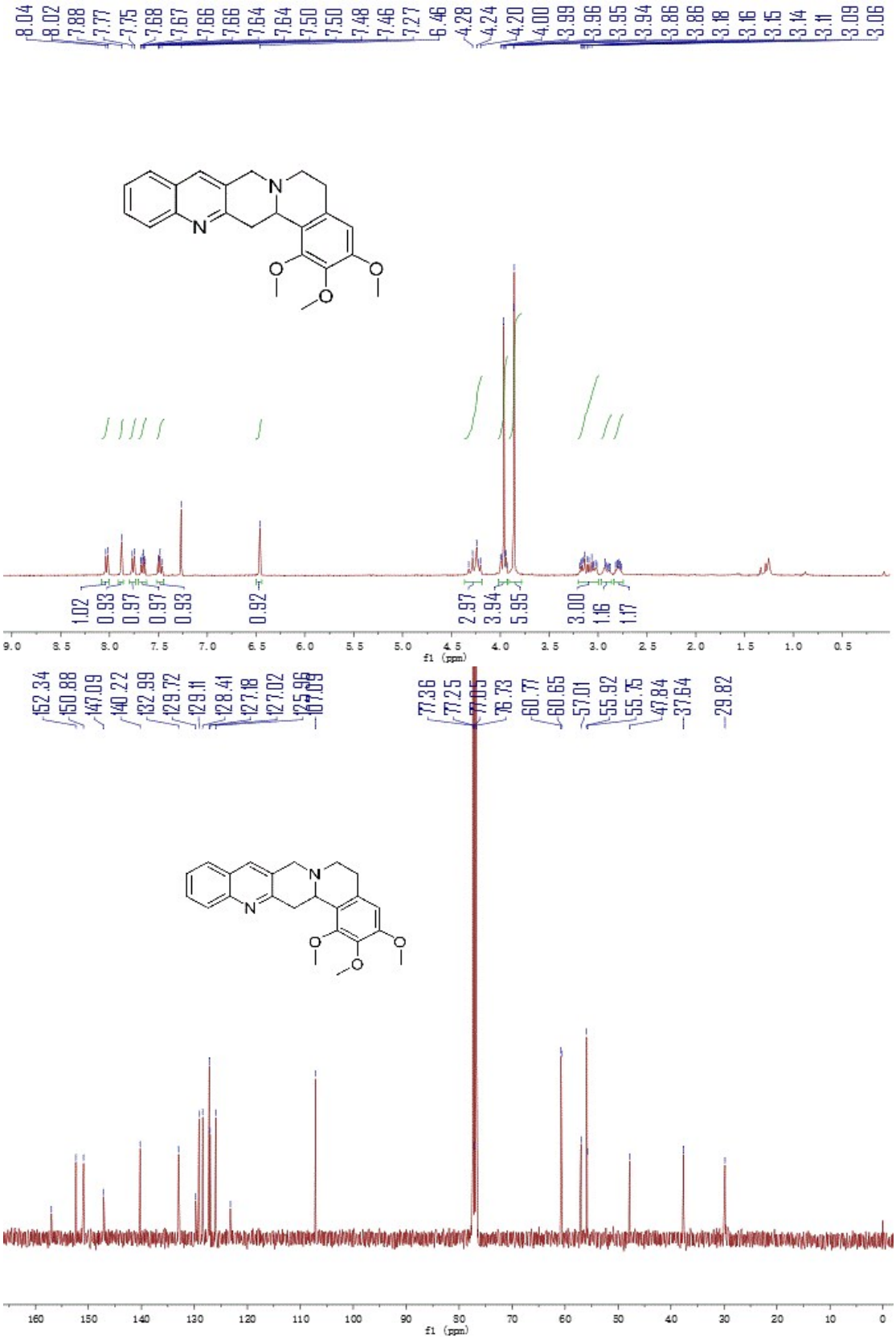


No reaction



(*S*)-1,2,3-Trimethoxy-6,8,15,15a-tetrahydro-5H-benzo[b]isoquinolino[2,1-g][1,6]naphthyridine: yellow solid, 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8.0 Hz, 1H), 7.88 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.66 (t, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 1H), 6.46 (s, 1H), 4.20-4.32 (m, 3H), 3.93-4.00 (m, 1H), 3.96 (s, 3H), 3.86 (s, 6H), 3.01-3.19 (m, 3H), 2.88-2.93 (m, 1H), 2.76-2.82 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.9, 152.3, 150.9, 147.1, 140.2, 133.0, 129.7, 129.1, 128.4, 127.3, 127.2, 127.0, 125.9, 123.2, 107.1, 60.8, 60.7, 57.0, 55.9, 55.8, 47.8, 37.6, 29.8; HRMS (EI) m/z calcd for $C_{23}H_{24}N_2O_3$ (M) 376.1787, found 376.1788.

(*S*)-1,2,3-Trimethoxy-6,8,15,15a-tetrahydro-5H-benzo[b]isoquinolino[2,1-g][1,6]naphthyridine



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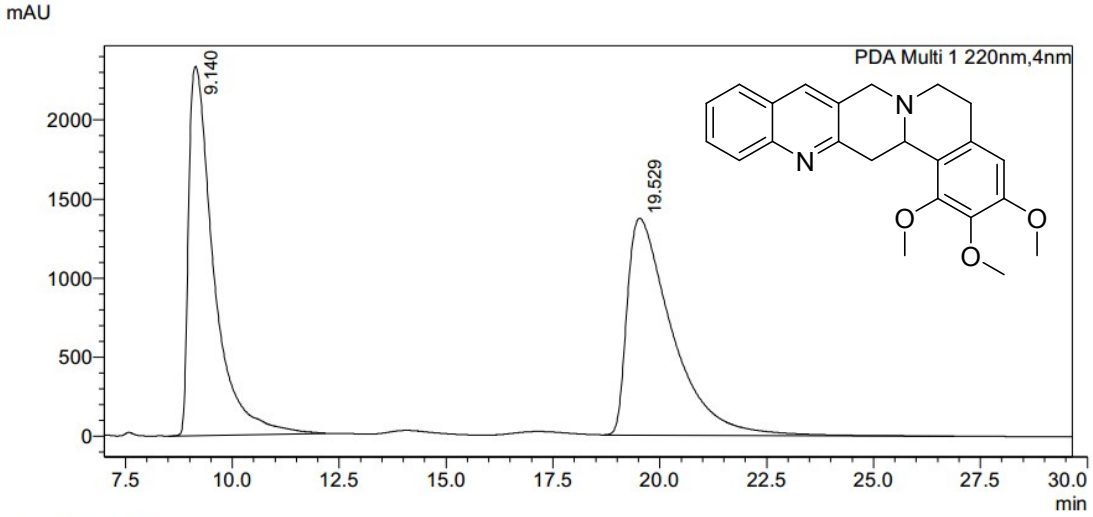
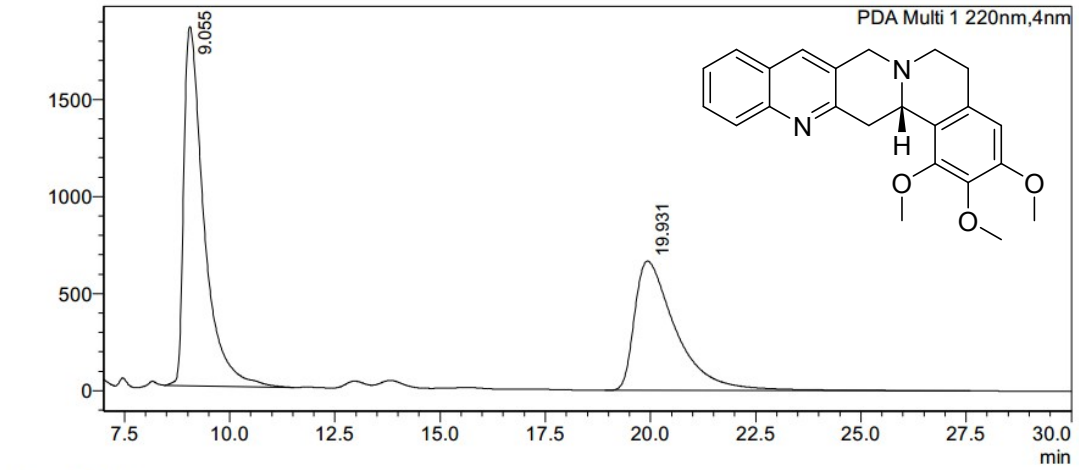


<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.140	95166961	2334574	48.593	%		RT:9.140
2	19.529	100676140	1370386	51.407	%		RT:19.529
Total		195843101	3704960				

<Chromatogram>



<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.055	61703446	1848361	57.331	%		RT:9.055
2	19.931	45923854	666574	42.669	%		RT:19.931
Total		107627299	2514935				