Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Kinetic resolution of 2*H*-azirines *via* Cu(I)-catalyzed asymmetric 1,3-dipolar cycloaddition of azomethine ylides

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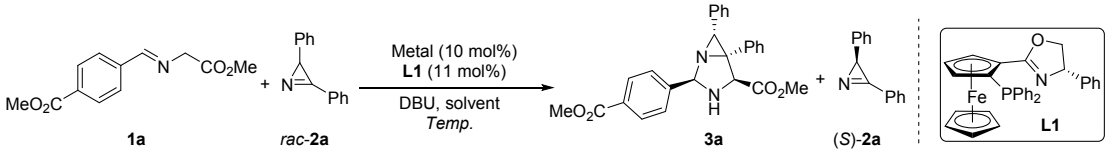
General information

^{1}H NMR spectrum were recorded on a Bruker AVANCE III 400 MHz or Bruker-Ultrashield PLUS 500 MHz spectrometers in $CDCl_3$ or acetone-d_6. Chemical shifts were reported in ppm with the internal TMS signal at 0.0 ppm as a standard. The spectrums are interpreted as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, brs = broad singlet, coupling constant(s) *J* are reported in Hz and relative integrations are reported. ^{13}C NMR (100 MHz) spectrums were recorded on a Bruker AVANCE III 400 MHz or Bruker-Ultrashield PLUS 500 MHz spectrometers in $CDCl_3$ or acetone-d_6. Chemical shifts were reported in ppm with the internal chloroform signal at 77.16 ppm (acetone signal at 29.84 ppm) as a standard. Optical rotations were measured on an AUTOPOL V. Diastereomeric ratios and enantiomeric excesses were determined from crude ^{1}H NMR spectroscopy interpretation or by analysis of HPLC traces, obtained by using chiralpak AD-H, IF and chiralcel OD-H columns with *n*-hexane and *i*-propanol or ethanol as solvents. (chiralpak AD-H, IF, AS-H and chiralcel OD-H columns were purchased from Daicel Chemical Industries, LTD.) Melting points were obtained in open capillary tubes using SGW X-4 micro melting point apparatus which were uncorrected. Mass spectrums were recorded on TOF mass Waters GCT Premier spectrometer. Solvents were dried and distilled following usual protocols. Commercially available materials purchased from Adamas-beta, Bidepharm or TCI were used as received. Imino esters[1] and 2*H*-azirines[2] were prepared according to the literature procedure.

Table S1. Optimization of the reaction conditions

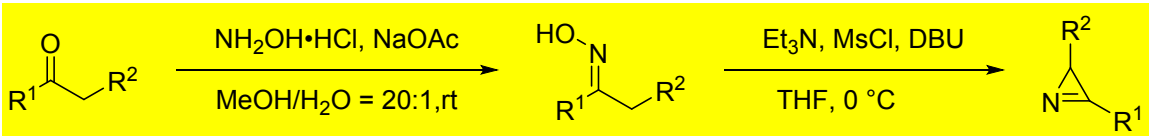


Entry	Base (mol%)	Solvent	Metal	*T* (°C)	**2a**/**1a**	**3a**		(*S*)-**2a**		*S*[d]
						Yield(%)[b]	ee(%)[c]	Yield(%)[b]	ee(%)[c]	
1	DBU(20)	THF	$CuBF_4$	rt	2:1	42	98	48	67	200
2	DBU(50)	THF	$CuBF_4$	rt	2:1	41	98	48	65	195
3	DBU(100)	THF	$CuBF_4$	rt	2:1	42	98	46	65	195
4	DBU(20)	CH_2Cl_2	$CuBF_4$	rt	2:1	40	96	47	47	78
5	DBU(20)	$(CH_2Cl)_2$	$CuBF_4$	rt	2:1	41	97	45	71	140
6	DBU(20)	toluene	$CuBF_4$	rt	2:1	42	97	46	55	114
7	DBU(20)	THF	$CuPF_6$	rt	2:1	42	98	42	60	183
8	DBU(20)	THF	$Cu(OTf)_2$	rt	2:1	46	94	47	41	48
9	DBU(20)	THF	AgOAc	rt	2:1	41	94	43	46	51
10	DBU(20)	THF	$CuBF_4$	0	2:1	42	98	48	68	203
11	DBU(20)	THF	$CuBF_4$	-20	2:1	44	99	46	54	343
12	**DBU(20)**	**THF**	**$CuBF_4$**	**-40**	**2:1**	**44**	**99**	**45**	**73**	**438**
13	DBU(20)	THF	$CuBF_4$	-60	2:1	41	99	50	66	397
14	DBU(20)	THF	$CuBF_4$	-78	2:1	trace	-	-	-	-
15	DBU(20)	THF	$CuBF_4$	-40	2:1.2	45	98	42	60	183
16	DBU(20)	THF	$CuBF_4$	-40	2:1.5	47	97	43	70	138

a) All reactions were performed with **1a** (0.1 mmol), *rac*-**2a** (0.2 mmol) in 1.5 mL of solvent, under an N_2 atmosphere. b) Isolated yield based on *rac*-**2a**, and >20:1 dr was determined by ^{1}H NMR of crude product. c) The ee was determined by chiral HPLC analysis. d) Selectivity factors *S*, calculated according to the following equations: $S = \ln[(1-C)(1-ee_{2a})]/\ln[(1-C)(1+ee_{2a})]$, $C = (ee_{2a})/(ee_{2a}+ee_3)$.

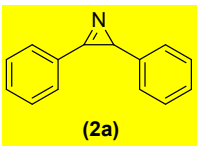
The preparation of 2*H*-azirine substrates

2*H*-azirines (**2**) were prepared as previously described.[2]

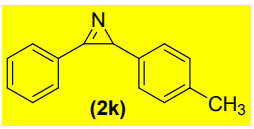


The mixture of ketone (1 equiv), $NH_2OH{\cdot}HCl$ (1.5 equiv) and sodium acetate were dissolved in $MeOH/H_2O$ (20:1) at room temperature and monitored by TLC. After the reaction completed, the solution was sequentially washed with sat. $NaHCO_3$ and brine. The organic layer was dried over Na_2SO_4. Concentration led to the oxime which was used directly for the next step.

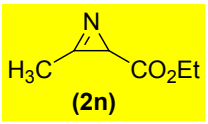
Triethylamine (1.5 equiv) and methanesulfonyl chloride (1.5 equiv) was added sequentially to the solution of oxime (1 equiv) in dry THF at 0 ℃. The solution got cloudy after the addition of methanesulfonyl chloride. Then, the resulting mixture was stirred for 30 min, and DBU (1.5 equiv) was added over 10 min. After stirring for additional 30 min, the reaction mixture was passed through a pad of silica gel and washed with EtOAc. The mixture was concentrated in vacuo and the resulting residue was purified by column chromatography on silica gel to give the 2*H*-azirine.



2,3-Diphenyl-2*H*-azirine **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 – 7.87 (m, 2H), 7.65-7.51 (m, 3H), 7.39-7.21 (m, 3H), 7.21-7.13 (m, 2H), 3.33 (s, 1H).

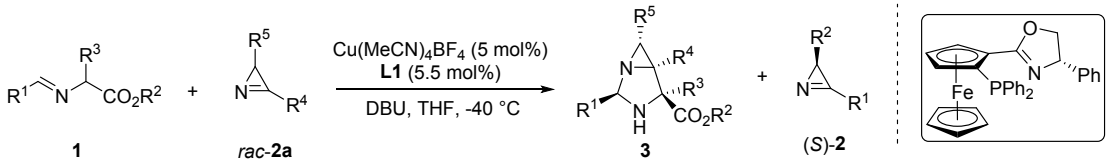


3-Phenyl-2-(*p-tolyl*)-2*H*-azirine **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93-7.84 (m, 2H), 7.64-7.48 (m, 3H), 7.12-6.96 (m, 4H), 3.30 (s, 1H), 2.31 (s, 3H).

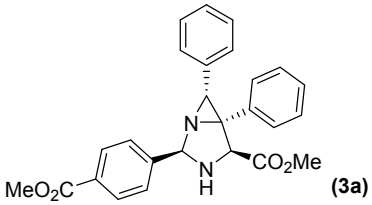


Ethyl 3-methyl-2*H*-azirine-2-carboxylate **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.28 – 4.07 (m, 2H), 2.53 (s, 3H), 2.44 (s, 1H), 1.28 (t, J = 7.1 Hz, 3H).

General procedure

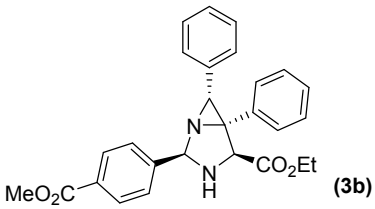


At a nitrogen atmosphere, $Cu(CH_3CN)_4BF_4$ (1.6 mg, 0.005 mmol) and **L1** (2.9 mg, 0.0055mmol) were dissolved in 1.5 mL dry THF, subsequently stirred at room temperature for about 1 h. Then, iminoester **1** (0.1 mmol) and DBU (3 μL, 0.02 mmol) were added, the mixture was cooled to -40 °C and 2*H*-azirine **2** (0.2 mmol) was added. Once starting material was consumed (0.5-3 h mostly), the mixture was concentrated and the residue was purified by silica gel flash chromatography (petroleum ether/ethyl acetate 15:1 to 6:1) to afford the corresponding recovered **2** and product **3**.



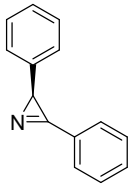
(3a)

Methyl (2*R*,4*S*,5*R*,6*R*)-2-(4-(methoxycarbonyl)phenyl)-5,6-diphenyl-1,3-diazabicyclo[3.1.0]hexane-4-carboxylate White solid, yield: 38.5 mg, 45%; m.p.: 69-70 °C; $[\alpha]_D^{25}$ = -0.93 (*c* 1.00, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 08.0 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.28 – 7.02 (m, 10H), 5.76 (d, *J* = 10.3 Hz, 1H), 4.20 (d, *J* = 9.4 Hz, 1H), 3.88 (s, 3H), 3.79 (s, 3H), 3.20 (s, 1H), 3.13 (t, *J* = 10.9 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.6, 166.8, 142.8, 135.4, 134.8, 130.0 (2C), 129.4 (2C), 128.1 (2C), 127.9 (3C), 127.9 (2C), 127.8, 127.0, 126.9 (2C), 82.5, 67.6, 61.5, 52.6, 52.2, 38.6. **HRMS** (EI-TOF, *m/z*) calcd for $C_{26}H_{24}N_2O_4$ $[M]^+$: 420.1731, found: 420.1740; **HPLC** (Chiralcel OD-H, *n*-hexane/*i*-propanol = 95/5, 1.0 mL/min, 220 nm) t_R = 10.41 min, 12.80 min.



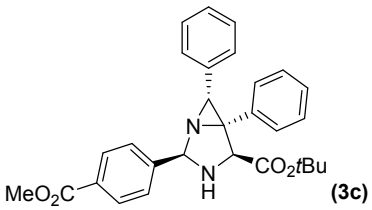
(3b)

Ethyl (2*R*,4*S*,5*R*,6*R*)-2-(4-(methoxycarbonyl)phenyl)-5,6-diphenyl-1,3-diazabicyclo[3.1.0]hexane-4-carboxylate White solid, yield: 41.7 mg, 48%; m.p.: 52-54 °C; $[\alpha]_D^{25}$ = -1.30 (*c* 1.03, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 8.1 Hz, 2H), 7.25 – 6.97 (m, 10H), 5.77 (d, *J* = 10.2 Hz, 1H), 4.37 – 4.20 (m, 2H), 4.17 (d, *J* = 9.5 Hz, 1H), 3.88 (s, 3H), 3.19 (s, 1H), 3.14 (t, *J* = 10.6 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.0, 166.8, 142.8, 135.5, 134.9, 130.0 (2C), 130.0, 129.6 (2C), 128.1 (2C), 127.9 (2C), 127.9 (2C), 127.8, 127.0, 126.9 (2C), 82.5, 67.7, 61.9, 61.5, 52.2, 38.6, 14.3. **HRMS** (ESI-TOF, *m/z*) calcd for $C_{27}H_{26}N_2O_4$ $[M]^+$: 442.1887, found: 442.1894; **HPLC** (Chiralpak AD-H, *n*-hexane/*i*-propanol = 95/5, 1.0 mL/min, 220 nm) t_R = 19.95 min, 26.06 min.



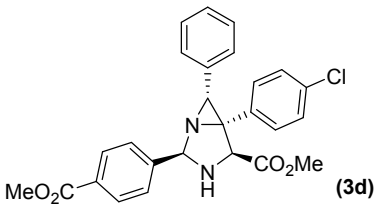
(S)-2a

2,3-diphenyl-*2H*-azirine (S)-2a yield: 47%; $[\alpha]_D^{25}$ = -388.5 (*c* 0.11, 91% ee, CH_2Cl_2); **HPLC** (Chiralpak AD-H, *n*-hexane/*i*-propanol = 97/3, 1.0 mL/min, 254 nm) t_R = 8.27 min, 8.76 min.



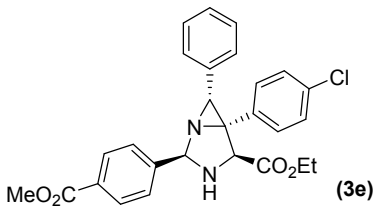
(3c)

***tert*-Butyl (2*R*,4*S*,5*R*,6*R*)-2-(4-(methoxycarbonyl)phenyl)-5,6-diphenyl-1,3-diazabicyclo[3.1.0]hexane-4-carboxylate** White solid, yield: 40.5 mg, 43%; m.p.: 56-58 °C; $[\alpha]_D^{25}$ = -1.61 (*c* 1.07, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.25 – 7.15 (m, 5H), 7.17 – 7.09 (m, 3H), 7.10 – 7.02 (m, 2H), 5.77 (s, 1H), 4.09 (s, 1H), 3.89 (s, 3H), 3.13 (brs, 2H), 1.46 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.0, 166.9, 143.0, 135.7, 135.1, 130.0 (2C), 129.9, 129.8 (2C), 128.0 (2C), 127.9 (2C), 127.8 (2C), 127.7, 127.0, 126.9 (2C), 82.9, 82.5, 68.4, 61.3, 52.3, 38.6, 28.1 (3C). **HRMS** (ESI-TOF, *m/z*) calcd for $C_{29}H_{30}N_2O_4$ $[M]^+$: 470.2200, found: 470.2205; **HPLC** (Chiralpak AD-H, *n*-hexane/*i*-propanol = 92/8, 1.0 mL/min, 220 nm) t_R = 7.10 min, 8.53 min.



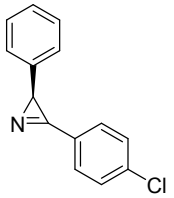
(3d)

Methyl (2*R*,4*S*,5*R*,6*R*)-5-(4-chlorophenyl)-2-(4-(methoxycarbonyl)phenyl)-6-phenyl-1,3-diazabicyclo[3.1.0]hexane-4-carboxylate White solid, yield: 41.6 mg, 45%; m.p.: 60-62 °C; $[\alpha]_D^{25}$ = -1.02 (*c* 0.97, CH_2Cl_2); **^{1}H NMR** (400 MHz, Acetone-d_6) δ 7.98 (d, *J* = 8.3 Hz, 2H), 7.71 (d, *J* = 8.1 Hz, 2H), 7.33 – 7.20 (m, 4H), 7.17 – 7.04 (m, 5H), 5.77 (d, *J* = 10.3 Hz, 1H), 4.22 (d, *J* = 9.7 Hz, 1H), 3.86 (s, 3H), 3.82 (s, 3H), 3.45 (s, 1H), 3.41 (t, *J* = 10.3 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) **^{13}C NMR** (100 MHz, Acetone-d_6) δ 171.8, 166.9, 144.2, 136.6, 135.4, 133.7, 132.1 (2C), 130.8, 130.3 (2C), 128.8 (2C), 128.6 (2C), 128.5 (2C), 127.8 (2C), 127.6, 82.3, 67.8, 61.1, 52.8, 52.3, 39.2. **HRMS** (ESI-TOF, *m/z*) calcd for $C_{26}H_{23}ClN_2O_4$ $[M]^+$: 462.1341, found: 462.1348; **HPLC** (Chiralpak AD-H, *n*-hexane/*i*-propanol = 95/5, 1.0 mL/min, 220 nm) t_R = 18.51 min, 32.11 min.



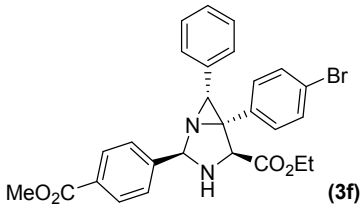
(3e)

Ethyl (2*R*,4*S*,5*R*,6*R*)-5-(4-chlorophenyl)-2-(4-(methoxycarbonyl)phenyl)-6-phenyl-1,3-diazabicyclo[3.1.0]hexane-4-carboxylate White solid, yield: 40.1 mg, 42%; m.p.: 59-60 °C; $[\alpha]_D^{25}$ = -1.33 (*c* 0.95, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.3 Hz, 2H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.24 – 7.08 (m, 7H), 7.09 – 7.01 (m, 2H), 5.74 (d, *J* = 11.2 Hz, 1H), 4.39 – 4.20 (m, 2H), 4.13 (d, *J* = 10.3 Hz, 1H), 3.89 (s, 3H), 3.18 (s, 1H), 3.13 (t, *J* = 11.1 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.8, 166.8, 142.6, 135.0, 133.7, 133.6, 130.9 (2C), 130.0 (3C), 128.4 (2C), 128.1 (2C), 127.8 (2C), 127.2, 126.8 (2C), 82.4, 67.5, 62.0, 60.8, 52.3, 38.6, 14.3. **HRMS** (ESI-TOF, *m/z*) calcd for $C_{27}H_{25}ClN_2O_4$ $[M]^+$: 476.1497, found: 476.1502; **HPLC** (Chiralpak AD-H, *n*-hexane/*i*-propanol = 97/3, 1.0 mL/min, 220 nm) t_R = 25.80 min, 33.87 min.



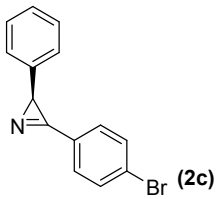
(2b)

3-(4-chlorophenyl)-2-phenyl-*2H*-azirine (S)-2b yield: 42%; $[\alpha]_D^{25}$ = -525.3 (*c* 0.10, 96% ee, CH_2Cl_2); **HPLC** (Chiralpak AD-H, *n*-hexane/*i*-propanol = 97/3, 1.0 mL/min, 254 nm) t_R = 8.73 min, 9.65 min.



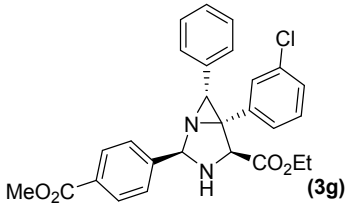
(3f)

Ethyl (2*R*,4*S*,5*R*,6*R*)-5-(4-bromophenyl)-2-(4-(methoxycarbonyl)phenyl)-6-phenyl-1,3-diazabicyclo[3.1.0]hexane-4-carboxylate White solid, yield: 41.7 mg, 40%; m.p.: 61-63 °C; $[\alpha]_D^{25}$ = -1.33 (*c* 0.90, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.1 Hz, 2H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 7.21 – 6.97 (m, 7H), 5.74 (d, *J* = 9.7 Hz, 1H), 4.37 – 4.20 (m, 2H), 4.13 (d, *J* = 8.8 Hz, 1H), 3.89 (s, 3H), 3.18 (s, 1H), 3.13 (t, *J* = 10.0 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.8, 166.8, 142.6, 135.0, 134.1, 131.3 (2C), 131.3 (2C), 130.0 (2C), 128.1 (2C), 127.8 (2C), 127.2 (2C), 126.8 (2C), 122.0, 82.4, 67.5, 62.0, 60.8, 52.3, 38.6, 14.4. **HRMS** (ESI-TOF, *m/z*) calcd for $C_{27}H_{25}{}^{79}BrN_2O_4$ $[M]^+$: 520.0992, found: 520.1000, for $C_{27}H_{25}{}^{81}BrN_2O_4$ $[M]^+$: 522.0972, found: 522.0975; **HPLC** (Chiralpak AD-H, *n*-hexane/*i*-propanol = 95/5, 1.0 mL/min, 220 nm) t_R = 19.12 min, 23.46 min.



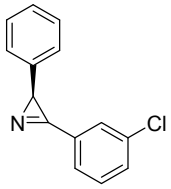
(2c)

2-Phenyl-3-(4-bromophenyl)-2*H*-azirine (S)-2c yield: 40%; $[\alpha]_D^{25}$ = -460.5 (*c* 0.26, 98% ee, CH_2Cl_2); **HPLC** (Chiralpak AD-H, *n*-hexane/*i*-propanol = 97/3, 1.0 mL/min, 254 nm) t_R = 9.46 min, 10.30 min.



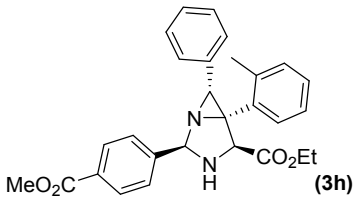
(3g)

Ethyl (2*R*,4*S*,5*R*,6*R*)-5-(3-chlorophenyl)-2-(4-(methoxycarbonyl)phenyl)-6-phenyl-1,3-diazabicyclo[3.1.0]hexane-4-carboxylate White solid, yield: 40.0 mg, 42%; m.p.: 49-51 °C; $[\alpha]_D^{25}$ = -1.11 (*c* 0.93, CH_2Cl_2); **^{1}H NMR** (400 MHz, Acetone-d_6) δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.1 Hz, 2H), 7.38 – 7.31 (m, 1H), 7.27 – 7.18 (m, 3H), 7.18 – 7.04 (m, 5H), 5.80 (d, *J* = 10.9 Hz, 1H), 4.44 – 4.31 (m, 1H), 4.31 – 4.18 (m, 2H), 3.85 (s, 3H), 3.44 (s, 1H), 3.40 (t, *J* = 10.5 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, Acetone-d_6) δ 171.3, 166.9, 144.2, 138.8, 136.5, 133.9, 130.8, 130.4, 130.3, 130.3 (2C), 129.0, 128.7 (2C), 128.5 (2C), 128.4, 127.8 (2C), 127.7, 82.3, 67.8, 62.3, 61.2, 52.3, 39.2, 14.5. **HRMS** (ESI-TOF, *m/z*) calcd for $C_{27}H_{25}ClN_2O_4$ $[M]^+$: 476.1497, found: 476.1502; **HPLC** (Chiralpak AD-H, *n*-hexane/*i*-propanol = 97/3, 1.0 mL/min, 220 nm) t_R = 23.36 min, 31.53 min.



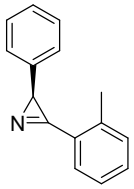
(2d)

3-(3-chlorophenyl)-2-phenyl-*2H*-azirine (S)-2d yield: 42%; $[\alpha]_D^{25}$ = -448.5 (*c* 0.15, 83% ee, CH_2Cl_2); **HPLC** (Chiralpak AD-H, *n*-hexane/*i*-propanol = 97/3, 1.0 mL/min, 254 nm) t_R = 9.28 min, 10.19 min.



(3h)

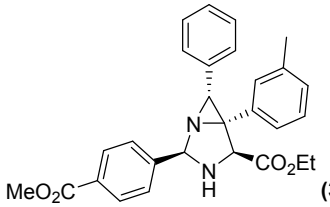
Ethyl (2*R*,4*S*,5*R*,6*R*)-2-(4-(methoxycarbonyl)phenyl)-6-phenyl-5-(*o*-tolyl)-1,3-diazabicyclo[3.1.0]hexane-4-carboxylate White solid, yield: 42.2 mg, 46%; m.p.: 67-69 °C; $[\alpha]_D^{25}$ = -1.54 (*c* 1.00, CH_2Cl_2); **^{1}H NMR** (400 MHz, Acetone-d_6) δ 7.95 (d, *J* = 8.2 Hz, 2H), 7.68 (d, *J* = 8.1 Hz, 2H), 7.28 – 7.11 (m, 5H), 7.01 – 6.75 (m, 4H), 5.72 (d, *J* = 10.7 Hz, 1H), 4.36 – 4.15 (m, 2H), 4.12 (d, *J* = 10.0 Hz, 1H), 3.83 (s, 3H), 3.38 – 3.21 (m, 2H), 2.14 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.5, 169.4, 135.5, 135.3, 133.7, 133.6, 131.3 (2C), 130.5 (2C), 129.9, 129.3, 128.2, 127.8 (2C), 127.7 (2C), 127.4, 127.3, 126.9, 70.1, 66.9, 60.5, 52.1, 49.9, 47.4, 25.9, 13.8. **HRMS** (ESI-TOF, *m/z*) calcd for $C_{28}H_{28}N_2O_4$ $[M]^+$: 456.2044, found: 456.2046; **HPLC** (Chiralpak AD-H, *n*-hexane/*i*-propanol = 97/3, 1.0 mL/min, 220 nm) t_R = 15.67 min, 36.64 min.



(2e)

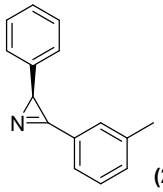
2-phenyl-3-(o-tolyl)-*2H*-azirine (S)-2e yield: 46%; $[\alpha]_D^{25}$ = -465.9 (*c* 0.14, 92% ee, CH_2Cl_2); **HPLC**

(Chiralpak AS, *n*-hexane/*i*-propanol = 97/3, 1.0 mL/min, 254 nm) t_R = 5.33 min, 6.21 min.



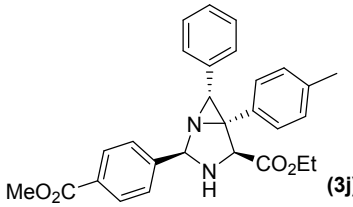
(3i)

Ethyl (2*R*,4*S*,5*R*,6*R*)-2-(4-(methoxycarbonyl)phenyl)-6-phenyl-5-(*m*-tolyl)-1,3-diazabicyclo[3.1.0]hexane-4-carboxylate White solid, yield: 44.7 mg, 49%; m.p.: 46-48 °C; $[\alpha]_D^{25}$ = -1.69 (*c* 1.06, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.18 – 6.98 (m, 8H), 6.88 (d, *J* = 7.4 Hz, 1H), 5.76 (s, 1H), 4.39 – 4.19 (m, 2H), 4.16 (s, 1H), 3.89 (s, 3H), 3.17 (s, 1H), 3.14 (s, 1H), 2.27 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.1, 166.9, 142.9, 137.7, 135.5, 134.7, 130.2, 130.0 (2C), 129.9, 128.6, 127.9 (2C), 127.9 (2C), 127.8, 127.0, 126.9 (2C), 126.6, 82.6, 67.8, 61.9, 61.5, 52.3, 38.6, 21.5, 14.3. **HRMS** (ESI-TOF, *m/z*) calcd for $C_{28}H_{28}N_2O_4$ $[M]^+$: 456.2044, found: 456.2045; **HPLC** (Chiralpak AD-H, *n*-hexane/*i*-propanol = 95/5, 1.0 mL/min, 220 nm) t_R = 16.86 min, 21.71 min.



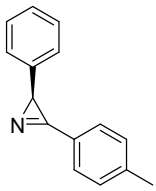
(2f)

2-Phenyl-3-(m-tolyl)-2*H*-azirine (S)-2f yield: 49%; $[\alpha]_D^{25}$ = -540.0 (*c* 0.15, 96% ee, CH_2Cl_2); **HPLC** (Chiralpak AS-H, *n*-hexane/*i*-propanol = 98/2, 1.0 mL/min, 254 nm) t_R = 6.58 min, 8.48 min.



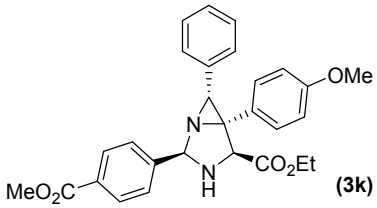
(3j)

Ethyl (2*R*,4*S*,5*R*,6*R*)-2-(4-(methoxycarbonyl)phenyl)-6-phenyl-5-(*p*-tolyl)-1,3-diazabicyclo[3.1.0]hexane-4-carboxylate White solid, yield: 33.9 mg, 37%; m.p.: 53-55 °C; $[\alpha]_D^{25}$ = -1.81 (*c* 1.00, CH_2Cl_2); **^{1}H NMR** (400 MHz, Acetone-d_6) δ 7.98 (d, *J* = 8.3 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.21 – 7.07 (m, 7H), 7.06 – 6.94 (m, 2H), 5.74 (d, *J* = 10.1 Hz, 1H), 4.39 – 4.18 (m, 2H), 4.17 – 4.08 (m, 1H), 3.85 (s, 3H), 3.37 (s, 1H), 3.32 (t, *J* = 11.6 Hz, 1H), 2.23 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, Acetone-d_6) δ 171.6, 166.9, 144.5, 137.8, 137.1, 133.3, 130.7, 130.3 (2C), 130.2 (2C), 129.3 (2C), 128.6 (2C), 128.5 (2C), 127.8 (2C), 127.4, 82.5, 68.4, 62.1, 61.8, 52.3, 39.0, 21.2, 14.5. **HRMS** (ESI-TOF, *m/z*) calcd for $C_{28}H_{28}N_2O_4$ $[M]^+$: 456.2044, found: 456.2046; **HPLC** (Chiralpak AD-H, *n*-hexane/*i*-propanol = 95/5, 1.0 mL/min, 220 nm) t_R = 22.63 min, 28.47 min.



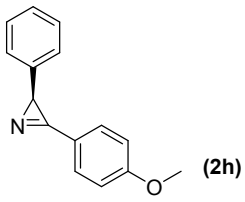
(2g)

2-Phenyl-3-(p-tolyl)-2*H*-azirine (S)-2g yield: 40%; $[\alpha]_D^{25}$ = -240.0 (*c* 0.18, 99% ee, CH_2Cl_2); **HPLC** (Chiralpak AD-H, *n*-hexane/*i*-propanol = 97/3, 1.0 mL/min, 220 nm) t_R = 7.17 min, 7.67 min.



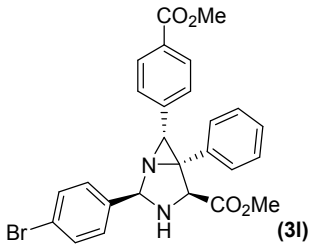
(3k)

Ethyl (2*R*,4*S*,5*R*,6*R*)-2-(4-(methoxycarbonyl)phenyl)-5-(4-methoxyphenyl)-6-phenyl-1,3-diazabicyclo[3.1.0]hexane-4-carboxylate White solid, yield: 28.6 mg, 30%; m.p.: 70-72 °C; $[\alpha]_D^{25}$ = -1.46 (*c* 1.00, CH_2Cl_2); **^{1}H NMR** (400 MHz, Acetone-d_6) δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.1 Hz, 2H), 7.24 – 7.03 (m, 7H), 6.82 – 6.73 (m, 2H), 5.74 (d, *J* = 9.0 Hz, 1H), 4.38 – 4.19 (m, 2H), 4.13 (d, *J* = 8.3 Hz, 1H), 3.86 (s, 3H), 3.73 (s, 3H), 3.42 – 3.23 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, Acetone-d_6) δ 171.6, 166.9, 160.0, 144.5, 137.1, 131.5 (2C), 130.7, 130.3 (2C), 128.6 (2C), 128.5 (2C), 128.1, 127.8 (2C), 127.4, 114.0 (2C), 82.4, 68.5, 62.1, 61.5, 55.4, 52.3, 39.0, 14.5. **HRMS** (ESI-TOF, *m/z*) calcd for $C_{28}H_{28}N_2O_5$ $[M]^+$: 472.1993, found: 472.1998; **HPLC** (Chiralpak AD-H, *n*-hexane/*i*-propanol = 97/3, 1.0 mL/min, 220 nm) t_R = 40.43 min, 49.22 min.



(2h)

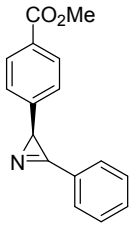
3-(4-methoxyphenyl)-2-phenyl-*2H*-azirine (S)-2h yield: 30%; $[\alpha]_D^{25}$ = -279.3 (*c* 0.15, 81% ee, CH_2Cl_2); **HPLC** (Chiralpak AD, *n*-hexane/*i*-propanol = 97/3, 1.0 mL/min, 254 nm) t_R = 17.48 min, 20.69 min.



(3l)

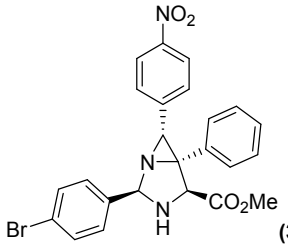
Methyl (2*R*,4*S*,5*R*,6*R*)-2-(4-bromophenyl)-6-(4-(methoxycarbonyl)phenyl)-5-phenyl-1,3-diazabicyclo[3.1.0]hexane-4-carboxylate White solid, yield: 49.8 mg, 49%; m.p.: 73-75 °C; $[\alpha]_D^{25}$ = -1.35 (*c* 0.96, CH_2Cl_2); **^{1}H NMR** (400 MHz, Acetone-d_6) δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.52 (s, 4H), 7.28 – 7.13 (m, 7H), 5.69 (d, *J* = 10.5 Hz, 1H), 4.21 (d, *J* = 9.9 Hz, 1H), 3.81 (s, 3H), 3.79 (s, 3H), 3.54 (s, 1H), 3.35 (t, *J* = 10.8 Hz, 1H). **^{13}C NMR** (100 MHz, Acetone-d_6) δ 171.9, 167.0, 142.7, 138.5, 135.8, 132.3 (2C), 130.2 (2C), 129.6 (2C), 129.5 (2C), 129.5, 128.7 (2C), 128.7 (2C), 128.4, 122.4, 82.1, 68.0,

62.4, 52.7, 52.2, 38.8. **HRMS** (ESI-TOF, *m/z*) calcd for $C_{26}H_{23}{}^{79}BrN_2O_4$ $[M]^+$: 506.0836, found: 506.0844, for $C_{26}H_{23}{}^{81}BrN_2O_4$ $[M]^+$: 508.0815, found: 508.0822, **HPLC** (Chiralpak AD-H, *n*-hexane/*i*-propanol = 95/5, 1.0 mL/min, 220 nm) t_R = 22.52 min, 31.04 min.



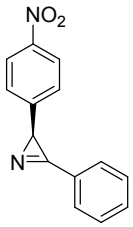
(2i)

Methyl 4-(3-phenyl-2*H*-azirin-2-yl)-benzoate (S)-2i yield: 49%; $[\alpha]_D^{25}$ = -361.0 (*c* 0.1, 92% ee, CH_2Cl_2); **HPLC** (Chiralpak AD-H, *n*-hexane/*i*-propanol = 97/3, 1.0 mL/min, 254 nm) t_R = 20.84 min, 23.25 min.



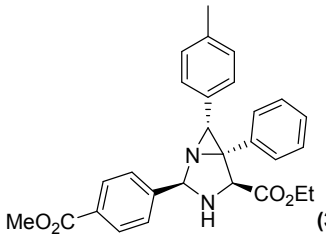
(3m)

Methyl (2*R*,4*S*,5*R*,6*R*)-2-(4-bromophenyl)-6-(4-nitrophenyl)-5-phenyl-1,3-diazabicyclo[3.1.0]hexane-4-carboxylate White solid, yield: 46.8 mg, 47%; m.p.:80-82°C; $[\alpha]_D^{25}$ = -1.81 (*c* 1.00, CH_2Cl_2); **^{1}H NMR** (400 MHz, Acetone-d_6) δ 7.97 (d, *J* = 8.7 Hz, 2H), 7.53 (s, 4H), 7.39 (d, *J* = 8.7 Hz, 2H), 7.30 – 7.16 (m, 5H), 5.71 (d, *J* = 10.4 Hz, 1H), 4.24 (d, *J* = 9.8 Hz, 1H), 3.82 (s, 3H), 3.65 (s, 1H), 3.40 (t, *J* = 10.2 Hz, 1H). **^{13}C NMR** (100 MHz, Acetone-d_6) δ 171.7, 147.7, 145.2, 138.4, 135.4, 132.4 (2C), 130.1 (2C), 129.6 (4C), 128.9 (2C), 128.6, 123.5 (2C), 122.4, 82.0, 68.0, 62.8, 52.8, 38.6. **HRMS** (ESI-TOF, *m/z*) calcd for $C_{24}H_{20}{}^{79}BrN_3O_4$ $[M]^+$: 493.0632, found: 493.0635 for $C_{24}H_{20}{}^{81}BrN_3O_4$ $[M]^+$: 495.0611, found: 495.0625; **HPLC** (Chiralpak AD-H, *n*-hexane/*i*-propanol = 95/5, 1.0 mL/min, 220 nm) t_R = 23.41 min, 29.64 min.



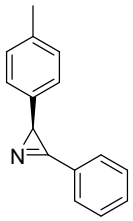
(2j)

2-(4-nitrophenyl)-3-phenyl-2H-azirine (S)-2j yield: 47%; $[\alpha]_D^{25}$ = -613.9 (*c* 0.17, 97% ee, CH_2Cl_2); **HPLC** (Chiralpak AS, *n*-hexane/*i*-propanol = 97/3, 1.0 mL/min, 254 nm) t_R = 26.46 min, 34.15 min.



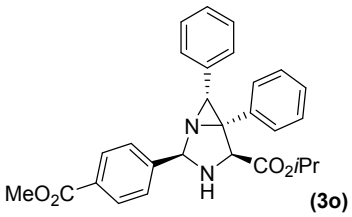
(3n)

Ethyl (2*R*,4*S*,5*R*,6*R*)-2-(4-(methoxycarbonyl)phenyl)-5-phenyl-6-(*p*-tolyl)-1,3-diazabicyclo[3.1.0]hexane-4-carboxylate White solid, yield: 41.8 mg, 47%; m.p.: 53-55 °C; $[\alpha]_D^{25}$ = -1.42 (*c* 1.00, CH_2Cl_2); **^{1}H NMR** (400 MHz, Acetone-d_6) δ 7.98 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.32 – 7.14 (m, 5H), 7.00 (d, *J* = 7.9 Hz, 2H), 6.91 (d, *J* = 7.9 Hz, 2H), 5.75 (d, *J* = 10.6 Hz, 1H), 4.39 – 4.17 (m, 2H), 4.15 (d, *J* = 9.9 Hz, 1H), 3.85 (s, 3H), 3.39 – 3.25 (m, 2H), 2.17 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, Acetone-d_6) δ 171.5, 166.9, 144.5, 136.9, 136.4, 133.9, 130.7, 130.4 (2C), 130.3 (2C), 129.2 (2C), 128.6 (2C), 128.5 (2C), 128.3, 127.8 (2C), 82.5, 68.3, 62.2, 61.8, 52.3, 38.9, 21.0, 14.5. **HRMS** (ESI-TOF, *m/z*) calcd for $C_{28}H_{28}N_2O_4$ $[M]^+$: 456.2044, found: 456.2048; **HPLC** (Chiralpak AD-H, *n*-hexane/*i*-propanol = 97/3, 1.0 mL/min, 220 nm) t_R = 32.28 min, 37.39 min.



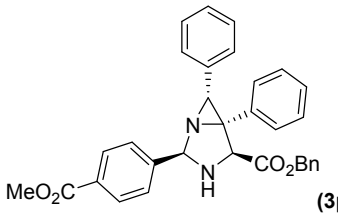
(2k)

3-phenyl-2-(p-tolyl)-2H-azirine (S)-2k yield: 47%; $[\alpha]_D^{25}$ = -380.0 (*c* 0.10, 92% ee, CH_2Cl_2); **HPLC** (Chiralpak AS, *n*-hexane/*i*-propanol = 97/3, 1.0 mL/min, 254 nm) t_R = 6.35 min, 7.97 min.



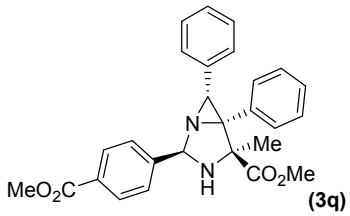
(3o)

***iso*-Propyl (2*R*,4*S*,5*R*,6*R*)-2-(4-(methoxycarbonyl)phenyl)-5,6-diphenyl-1,3-diazabicyclo[3.1.0]hexane-4-carboxylate** White solid, yield: 33.0 mg, 36%; m.p.: 49-51 °C; $[\alpha]_D^{25}$ = -1.20 (*c* 1.00, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.23 – 7.02 (m, 10H), 5.76 (d, *J* = 11.1 Hz, 1H), 5.23 – 5.09 (m, 1H), 4.14 (d, *J* = 10.2 Hz, 1H), 3.89 (s, 3H), 3.18 (s, 1H), 3.14 (t, *J* = 11.1 Hz, 1H), 1.24 (dd, *J* = 8.1, 6.2 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.5, 166.9, 142.9, 135.5, 134.9, 130.0 (2C), 130.0, 129.7 (2C), 128.0 (2C), 127.9 (2C), 127.9 (2C), 127.8, 127.0, 126.9 (2C), 82.6, 69.9, 67.9, 61.5, 52.2, 38.6, 21.9, 21.8. **HRMS** (ESI-TOF, *m/z*) calcd for $C_{28}H_{28}N_2O_4$ $[M]^+$: 456.2044, found: 456.2048; **HPLC** (Chiralpak AD-H, *n*-hexane/*i*-propanol = 95/5, 1.0 mL/min, 220 nm) t_R = 13.52 min, 21.40 min.



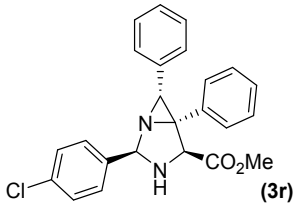
(3p)

Benzyl (2*R*,4*S*,5*R*,6*R*)-2-(4-(methoxycarbonyl)phenyl)-5,6-diphenyl-1,3-diazabicyclo[3.1.0]hexane-4-carboxylate White solid, yield: 42.6 mg, 42%; m.p.: 53-54 °C; $[\alpha]_D^{25}$ = -1.53 (*c* 0.95, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.38 – 7.27 (m, 5H), 7.19 – 7.06 (m, 6H), 7.03 – 6.93 (m, 4H), 5.76 (d, *J* = 7.1 Hz, 1H), 5.36 (d, *J* = 12.0 Hz, 1H), 5.13 (d, *J* = 12.0 Hz, 1H), 4.22 (d, *J* = 5.8 Hz, 1H), 3.89 (s, 3H), 3.15 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.0, 166.9, 142.8, 135.3, 135.0, 134.6, 130.0 (2C), 130.0, 129.6 (2C), 129.1 (2C), 128.8, 128.7 (2C), 128.0 (2C), 127.9 (2C), 127.8 (2C), 127.7, 127.0, 126.9 (2C), 82.6, 67.7, 67.6, 61.4, 52.3, 38.6. **HRMS** (ESI-TOF, *m/z*) calcd for $C_{32}H_{28}N_2O_4$ $[M]^+$: 504.2044, found: 504.2050; **HPLC** (Chiralpak AD-H, *n*-hexane/*i*-propanol = 95/5, 1.0 mL/min, 220 nm) t_R = 25.20 min, 47.95 min.



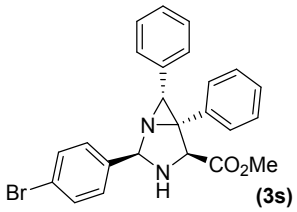
(3q)

Methyl (2*R*,4*S*,5*S*,6*R*)-2-(4-(methoxycarbonyl)phenyl)-4-methyl-5,6-diphenyl-1,3-diazabicyclo[3.1.0]hexane-4-carboxylate White solid, yield: 30.2 mg, 34%; m.p.: 56-57 °C; $[\alpha]_D^{25}$ = -1.80 (*c* 1.06, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.65 – 7.58 (m, 3H), 7.40 – 6.91 (m, 8H), 6.66 (s, 1H), 5.77 (s, 1H), 3.89 (s, 3H), 3.85 (s, 3H), 3.57 (s, 1H), 3.21 (s, 1H), 1.33 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.9, 166.9, 143.1, 135.7, 133.3, 131.0, 130.0 (2C), 129.9, 129.4, 127.8 (2C), 127.7 (4C), 127.5, 126.9 (2C), 126.9, 80.3, 69.7, 64.8, 53.0, 52.2, 40.3, 21.8. **HRMS** (ESI-TOF, *m/z*) calcd for $C_{27}H_{26}N_2O_4$ $[M]^+$: 442.1887, found: 442.1894; **HPLC** (Chiralpak AD-H, *n*-hexane/*i*-propanol = 95/5, 1.0 mL/min, 220 nm) t_R = 6.94 min, 13.00 min.



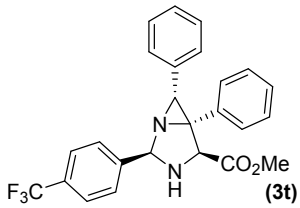
(3r)

Methyl (2*R*,4*S*,5*R*,6*R*)-2-(4-chlorophenyl)-5,6-diphenyl-1,3-diazabicyclo[3.1.0]hexane-4-carboxylate White solid, yield: 38.2 mg, 47%; m.p.: 57-59 °C; $[\alpha]_D^{25}$ = -1.77 (*c* 1.00, CH_2Cl_2); **^{1}H NMR** (400 MHz, Acetone-d_6) δ 7.59 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.27 – 7.17 (m, 5H), 7.14 – 7.04 (m, 5H), 5.69 (d, *J* = 10.8 Hz, 1H), 4.17 (d, *J* = 10.1 Hz, 1H), 3.80 (s, 3H), 3.42 (s, 1H), 3.30 (t, *J* = 10.5 Hz, 1H). **^{13}C NMR** (100 MHz, Acetone-d_6) δ 172.1, 138.3, 137.0, 136.3, 134.1, 130.2 (2C), 129.3 (2C), 129.3 (2C), 128.6 (2C), 128.6 (2C), 128.5 (2C), 128.2, 127.5, 82.1, 68.2, 61.9, 52.7, 39.0. **HRMS** (ESI-TOF, *m/z*) calcd for $C_{24}H_{21}ClN_2O_2$ $[M]^+$: 404.1286, found: 404.1296; **HPLC** (Chiralpak IF, *n*-hexane/*i*-propanol = 97/3, 1.0 mL/min, 220 nm) t_R = 7.38 min, 7.86 min.



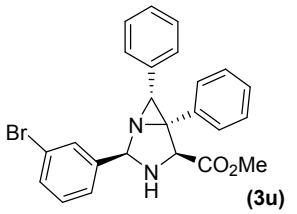
(3s)

Methyl (2*R*,4*S*,5*R*,6*R*)-2-(4-bromophenyl)-5,6-diphenyl-1,3-diazabicyclo[3.1.0]hexane-4-carboxylate White solid, yield: 43.4 mg, 48%; m.p.: 56-58 °C; $[\alpha]_D^{25}$ = -1.14 (*c* 0.95, CH_2Cl_2); **^{1}H NMR** (500 MHz, Acetone-d_6) δ 7.53 (brs, 4H), 7.29 – 7.14 (m, 5H), 7.15 – 6.99 (m, 5H), 5.67 (dd, *J* = 10.9, 0.8 Hz, 1H), 4.17 (d, *J* = 10.2 Hz, 1H), 3.80 (s, 3H), 3.42 (d, *J* = 0.8 Hz, 1H), 3.31 (t, *J* = 10.6 Hz, 1H). **^{13}C NMR** (126 MHz, Acetone-d_6) δ 172.0, 138.8, 136.9, 136.3, 132.3 (2C), 130.2 (2C), 129.7 (2C), 128.6 (2C), 128.6 (2C), 128.5 (2C), 128.2, 127.5, 122.3, 82.1, 68.1, 61.9, 52.7, 38.9. **HRMS** (ESI-TOF, *m/z*) calcd for $C_{24}H_{21}{}^{79}BrN_2O_2$ $[M]^+$: 448.0781, found: 448.0784, for $C_{24}H_{21}{}^{81}BrN_2O_2$ $[M]^+$: 450.0760, found: 450.0780; **HPLC** (Chiralpak AD-H, *n*-hexane/*i*-propanol = 97/3, 1.0 mL/min, 220 nm) t_R = 17.22 min, 18.32 min.



(3t)

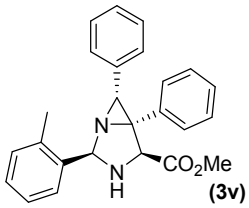
Methyl (2*R*,4*S*,5*R*,6*R*)-5,6-diphenyl-2-(4-(trifluoromethyl)phenyl)-1,3-diazabicyclo[3.1.0]hexane-4-carboxylate White solid, yield: 42.3 mg, 48%; m.p.: 53-55 °C; $[\alpha]_D^{25}$ = -0.95 (*c* 0.99, CH_2Cl_2); **^{1}H NMR** (500 MHz, Acetone-d_6) δ 7.81 (d, *J* = 8.1 Hz, 2H), 7.70 (d, *J* = 8.1 Hz, 2H), 7.29 – 7.24 (m, 2H), 7.23 – 7.17 (m, 3H), 7.14 – 7.04 (m, 5H), 5.78 (d, *J* = 10.6 Hz, 1H), 4.21 (d, *J* = 10.1 Hz, 1H), 3.80 (s, 3H), 3.47 (s, 1H), 3.41 (t, *J* = 10.4 Hz, 1H). **^{13}C NMR** (126 MHz, Acetone-d_6) δ 172.0, 143.8, 136.9, 136.2, 130.3 (q, *J* = 32.1 Hz), 130.2 (2C), 125.2 (q, *J* = 272.0 Hz), 128.7 (2C), 128.6 (2C), 128.5 (2C), 128.4 (2C), 128.3, 127.5, 126.2 (q, *J* = 3.9 Hz, 2C), 82.2, 68.1, 61.9, 52.7, 39.1. **HRMS** (ESI-TOF, *m/z*) calcd for $C_{25}H_{21}F_3N_2O_2$ $[M]^+$: 438.1550, found: 438.1556; **HPLC** (Chiralpak AD-H, *n*-hexane/*i*-propanol = 97/3, 1.0 mL/min, 220 nm) t_R = 10.97 min, 12.15 min.



(3u)

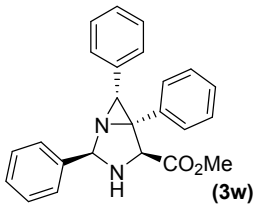
Methyl (2*R*,4*S*,5*R*,6*R*)-2-(3-bromophenyl)-5,6-diphenyl-1,3-diazabicyclo[3.1.0]hexane-4-carboxylate White solid, yield: 37.8 mg, 42%; m.p.: 113-114 °C; $[\alpha]_D^{25}$ = -1.43 (*c* 1.08, CH_2Cl_2); **^{1}H NMR** (500 MHz, Acetone-d_6) δ 7.76 (s, 1H), 7.59 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.49 (dt, *J* = 8.1, 1.3 Hz, 1H), 7.31 (t, *J* = 7.9 Hz, 1H), 7.28 – 7.21 (m, 2H), 7.24 – 7.16 (m, 3H), 7.16 – 7.00 (m, 5H), 5.70 (d, *J* = 10.5 Hz, 1H), 4.18 (d, *J* = 10.0 Hz, 1H), 3.80 (s, 3H), 3.47 (s, 1H), 3.37 (t, *J* = 10.4 Hz, 1H). **^{13}C NMR** (126 MHz, Acetone-d_6) δ 172.0, 142.0, 136.9, 136.3, 131.8, 131.3, 130.7, 130.2 (2C), 128.6 (2C),

128.5 (2C), 128.5 (2C), 128.2, 127.5, 126.5, 122.8, 81.9, 68.0, 61.8, 52.7, 39.1. **HRMS** (ESI-TOF, *m/z*) calcd $C_{24}H_{21}{}^{79}BrN_2O_2$ $[M]^+$: 448.0781, found: 448.0781, for $C_{24}H_{21}{}^{81}BrN_2O_2$ $[M]^+$: 450.0760, found: 450.0752; **HPLC** (Chiralpak AD-H, *n*-hexane/*i*-propanol = 97/3, 1.0 mL/min, 220 nm) t_R = 15.63 min, 19.52 min.



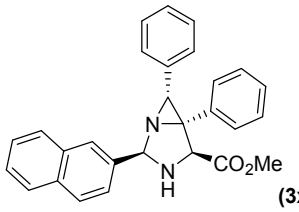
(3v)

Methyl (2*R*,4*S*,5*R*,6*R*)-5,6-diphenyl-2-(*o*-tolyl)-1,3-diazabicyclo[3.1.0]hexane-4-carboxylate White solid, yield: 34.7 mg, 45%; m.p.: 49-50 °C; $[\alpha]_D^{25}$ = -0.82 (*c* 1.00, CH_2Cl_2); **^{1}H NMR** (500 MHz, Acetone-d_6) δ 7.50 (d, *J* = 7.7 Hz, 1H), 7.29 – 7.24 (m, 2H), 7.23 – 7.16 (m, 5H), 7.14 – 7.05 (m, 6H), 5.72 (d, *J* = 10.8 Hz, 1H), 4.16 (d, *J* = 10.0 Hz, 1H), 3.80 (s, 3H), 3.56 (s, 1H), 3.17 (t, *J* = 10.4 Hz, 1H), 2.59 (s, 3H). **^{13}C NMR** (126 MHz, Acetone-d_6) δ 172.3, 138.1, 137.1, 136.8, 136.6, 131.3, 130.2 (2C), 128.8, 128.7 (2C), 128.6 (2C), 128.5 (2C), 128.1, 127.4, 126.4, 126.1, 80.6, 68.0, 60.7, 52.6, 39.3, 19.9. **HRMS** (ESI-TOF, *m/z*) calcd for $C_{25}H_{24}N_2O_2$ $[M]^+$: 384.1832, found: 384.1839; **HPLC** (Chiralpak AD-H, *n*-hexane/*i*-propanol = 90/10, 1.0 mL/min, 220 nm) t_R = 6.52 min, 7.52 min.



(3w)

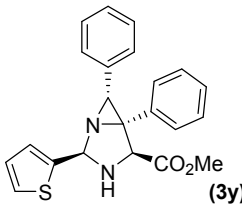
Methyl (2*R*,4*S*,5*R*,6*R*)-2,5,6-triphenyl-1,3-diazabicyclo[3.1.0]hexane-4-carboxylate White solid, yield: 33.5 mg, 45%; m.p.: 116-118 °C; $[\alpha]_D^{25}$ = -1.04 (*c* 1.01, CH_2Cl_2); **^{1}H NMR** (500 MHz, Acetone-d_6) δ 7.58 (d, *J* = 7.3 Hz, 2H), 7.39 – 7.27 (m, 3H), 7.26 – 7.23 (m, 2H), 7.22 – 7.16 (m, 3H), 7.14 – 7.03 (m, 5H), 5.70 (d, *J* = 11.0 Hz, 1H), 4.16 (d, *J* = 10.3 Hz, 1H), 3.87 – 3.71 (m, 3H), 3.38 (s, 1H), 3.24 (t, *J* = 10.8 Hz, 1H). **^{13}C NMR** (126 MHz, Acetone-d_6) δ 172.2, 139.4, 137.1, 136.4, 130.3 (2C), 129.3 (2C), 128.8, 128.6 (2C), 128.6 (2C), 128.4 (2C), 128.2, 127.5 (2C), 127.4, 82.8, 68.2, 61.9, 52.7, 38.9. **HRMS** (ESI-TOF, *m/z*) calcd for $C_{24}H_{22}N_2O_2$ $[M]^+$: 370.1676, found: 370.1678; **HPLC** (Chiralpak AD-H, *n*-hexane/*i*-propanol = 97/3, 1.0 mL/min, 220 nm) t_R = 16.73 min, 19.53 min.



(3x)

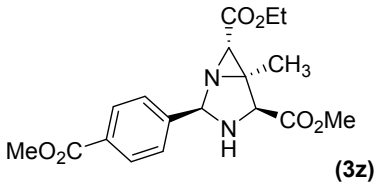
Methyl (2*R*,4*S*,5*R*,6*R*)-2-(naphthalen-2-yl)-5,6-diphenyl-1,3-diazabicyclo[3.1.0]hexane-4-carboxylate White solid, yield: 34.7 mg, 41%; m.p.: 58-60 °C; $[\alpha]_D^{25}$ = -1.06 (*c* 1.02, CH_2Cl_2); **^{1}H NMR** (500 MHz, Acetone-d_6) δ 8.08 (s, 1H), 7.88 (dd, *J* = 8.9, 4.1 Hz, 2H), 7.84 – 7.78 (m, 1H), 7.76 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.53 – 7.45 (m, 2H), 7.32 – 7.25 (m, 2H), 7.24 – 7.18 (m, 3H), 7.16 – 7.13 (m, 2H), 7.12 – 7.02 (m, 3H), 5.86 (d, *J* = 10.4 Hz, 1H), 4.23 (d, *J* = 9.8 Hz, 1H), 3.82 (s, 3H), 3.48 (s, 1H),

3.42 (t, *J* = 10.5 Hz, 1H). **^{13}C NMR** (126 MHz, Acetone-d_6) δ 172.2, 137.2, 137.0, 136.6, 134.1, 134.0, 130.3 (2C), 128.9, 128.9, 128.7 (4C), 128.5, 128.4 (2C), 128.2, 127.4, 127.1, 127.0, 126.2, 125.9, 82.9, 68.3, 61.9, 52.7, 39.1. **HRMS** (ESI-TOF, *m/z*) calcd for $C_{28}H_{24}N_2O_2$ $[M]^+$: 420.1832, found: 420.1837; **HPLC** (Chiralpak AD-H, *n*-hexane/*i*-propanol = 90/10, 1.0 mL/min, 220 nm) t_R = 13.94 min, 30.49 min.



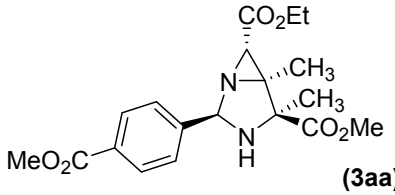
(3y)

Methyl (2*R*,4*S*,5*R*,6*R*)-5,6-diphenyl-2-(thiophen-2-yl)-1,3-diazabicyclo[3.1.0]hexane-4-carboxylate White solid, yield: 31.8 mg, 42%; m.p.: 78-80 °C; $[\alpha]_D^{25}$ = -1.11 (*c* 1.06, CH_2Cl_2); **^{1}H NMR** (500 MHz, Acetone-d_6) δ 7.40 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.27 – 7.22 (m, 2H), 7.23 – 7.14 (m, 4H), 7.13 – 7.03 (m, 5H), 7.00 (dd, *J* = 5.1, 3.5 Hz, 1H), 5.81 (d, *J* = 10.4 Hz, 1H), 4.16 (d, *J* = 10.0 Hz, 1H), 3.81 (s, 3H), 3.54 (s, 1H), 3.35 (t, *J* = 10.3 Hz, 1H). **^{13}C NMR** (126 MHz, Acetone-d_6) δ 172.0, 141.7, 136.9, 136.3, 130.2 (2C), 128.7 (2C), 128.6 (2C), 128.4 (2C), 128.3, 127.6, 127.4, 126.3, 126.1, 79.4, 68.1, 62.1, 52.8, 39.5. **HRMS** (ESI-TOF, *m/z*) calcd for $C_{22}H_{20}N_2O_2S$ $[M]^+$: 376.1240, found: 376.1243; **HPLC** (Chiralcel OD-H, *n*-hexane/*i*-propanol = 97/3, 1.0 mL/min, 220 nm) t_R = 10.19 min, 13.03 min.



(3z)

6-ethyl 4-methyl (2R,4S,5R,6S)-2-(4-(methoxycarbonyl)phenyl)-5-methyl-1,3-diazabicyclo[3.1.0] hexane-4,6-dicarboxylate Colorless oil, yield: 31.2 mg, 43%; $[\alpha]_D^{25}$ = -13.80 (*c* 1.00, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.2 Hz, 2H), 5.36 (d, *J* = 10.9 Hz, 1H), 4.30 - 4.10 (m, 2H), 3.91 (s, 3H), 3.84 (s, 3H), 2.74 (t, *J* = 10.9 Hz, 1H), 2.28 (s, 1H), 1.72 (s, 1H), 1.60 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 168.5, 166.7, 141.9, 130.1, 129.9 (2C), 126.5 (2C), 81.0, 65.8, 61.4, 53.9, 52.9, 52.2, 34.9, 14.2, 13.4. **HRMS** (EI-TOF, *m/z*) calcd for $C_{18}H_{22}N_2O_6$ $[M]^+$: 362.1472, found: 362.1476; **HPLC** (Chiralpak AD-H, *n*-hexane/ethanol = 90/10, 1.0 mL/min, 220 nm) t_R = 23.91 min, 30.90 min.

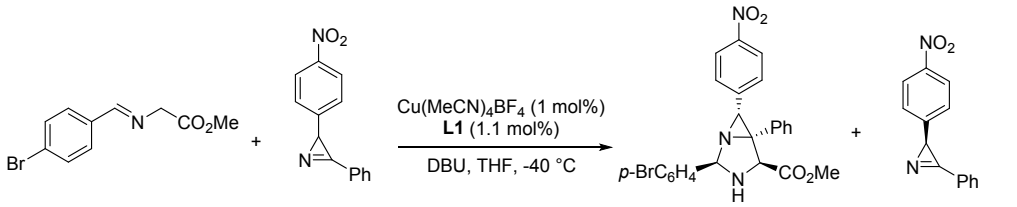


(3aa)

6-ethyl 4-methyl (2R,4S,5S,6S)-2-(4-(methoxycarbonyl)phenyl)-4,5-dimethyl-1,3-diazabicyclo [3.1.0] hexane-4,6-dicarboxylate White solid, yield: 26.5 mg, 35%; m.p.: 74-78 °C; $[\alpha]_D^{25}$ = -12.50 (*c* 1.00, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 7.8 Hz, 2H), 5.40 (d, *J* = 11.2 Hz, 1H), 4.28 – 4.11 (m, 2H), 3.91 (s, 3), 3.82 (s, 3H), 3.10 (d, *J* = 11.6 Hz, 1H), 2.29 (d, *J*

= 0.8 Hz, 1H), 1.57 (s, 3H), 1.52 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H); ^{13}C **NMR** (100 MHz, $CDCl_3$) δ 173.0, 168.8, 166.9, 142.4, 130.1, 130.0 (2C), 126.7 (2C), 79.2, 69.1, 61.4, 56.2, 53.2, 52.3, 36.9, 20.6, 14.4, 10.9. **HRMS** (EI-TOF, *m/z*) calcd for $C_{19}H_{24}N_2O_6$ $[M]^+$: 376.1629, found: 376.1631; **HPLC** (Chiralpak AD-H, *n*-hexane/*i*-propanol = 90/10, 1.0 mL/min, 220 nm) t_R = 13.00 min, 13.77 min.

Gram scale procedure



1d, 1.28 g (5 mmol) | *rac*-**2j**, 2.38 g (10 mmol) | **3m**, 2.37 g (49% yield, 99% ee) | (*S*)-**2j**, 1.14 g (48% yield, 96% ee)

Under a nitrogen atmosphere, $Cu(CH_3CN)_4BF_4$ (15.7 mg, 0.05 mmol) and **L1** (28.3 mg, 0.055 mmol) were dissolved in dry THF (60 mL), and stirred at room temperature for about 1 h. Then, glycine imine **1d** (1.28 g, 5.0 mmol) and DBU (0.15 mL, 1.0 mmol) were added, the mixture was cooled to -40 °C and azirine **2j** (2.38 g, 10 mmol) was added. Once starting material was consumed (monitored by TLC, about 5 h), the mixture was filtered through celite and the filtrate was concentrated, then the residue was purified by column chromatography (petroleum ether/ethyl acetate 10:1 to 4:1) on silica gel to afford the corresponding product **3m** and **2j**.

References

(1) (a) A. López-Pérez, J. Adrio, J. C. Carretero, *J. Am. Chem. Soc*. 2008, **130**, 10084. (b) C.-J. Wang, G. Liang, Z.-Y. Xue, F. Gao, *J. Am. Chem. Soc*. 2008, **130**, 17250.

(2) (a) H. Hu, Y. Liu, L. Lin, Y. Zhang, X. Liu, X. Feng, *Angew. Chem. Int. Ed*. 2016, **55**, 10098 – 10101. (b) Y. Wang, X. Lei, Y. Tang, *Chem. Commun*. 2015, **51**, 4507-4510.

The absolute configuration determination of 3m

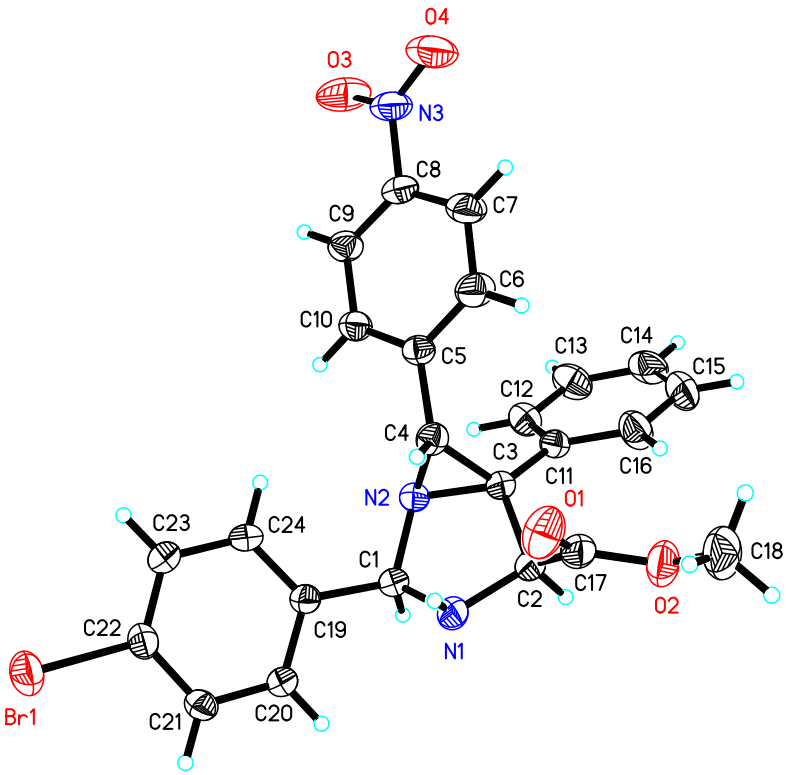


Fig S2. X-ray structure of (2*R*,4*S*,5*R*,6*R*)-**3m**

Ellipsoids are drawn at the 30% probability level.

Crystal data and structure refinement for CCDC 2008510

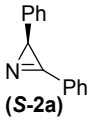
(CCDC **2008510** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.)

Table S2. Crystal data and structure refinement for (2*R*,4*S*,5*R*,6*R*)-**3m**.

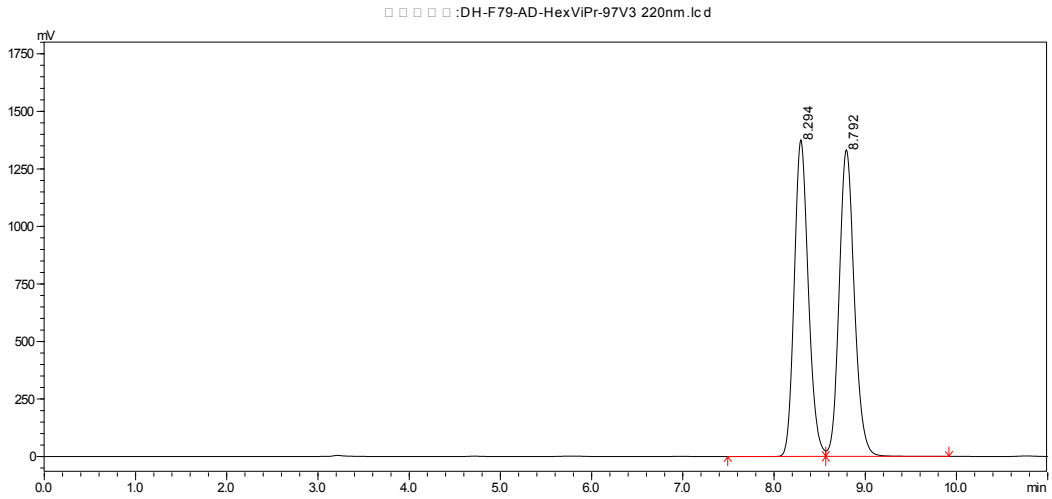
Identification code	(2*R*,4*S*,5*R*,6*R*)-**3m**	
Empirical formula	C24 H20 Br N3 O4	
Formula weight	494.34	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 9.1040(4) Å	α= 90°.
	b = 18.5010(7) Å	β= 93.6690(10)°.
	c = 13.3317(6) Å	γ = 90°.
Volume	2240.90(16) Å^3	

Z	4
Density (calculated)	1.465 Mg/m^3
Absorption coefficient	1.870 mm^{-1}
F(000)	1008
Crystal size	0.160 x 0.140 x 0.100 mm^3
Theta range for data collection	2.242 to 25.997°.
Index ranges	-11<=h<=11, -22<=k<=22, -16<=l<=16
Reflections collected	33837
Independent reflections	8745 [R(int) = 0.0518]
Completeness to theta = 25.242°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.3477
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8745 / 1 / 588
Goodness-of-fit on F^2	1.010
Final R indices [I>2sigma(I)]	R1 = 0.0352, wR2 = 0.0699
R indices (all data)	R1 = 0.0628, wR2 = 0.0801
Absolute structure parameter	0.022(5)
Extinction coefficient	0.0065(9)
Largest diff. peak and hole	0.299 and -0.327 $e.Å^{-3}$

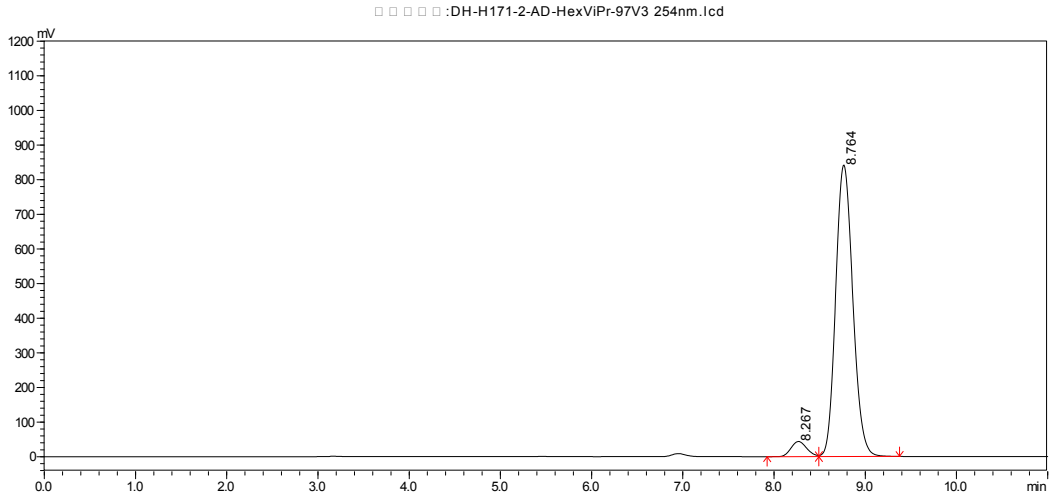
Chiral HPLC Chromatograms



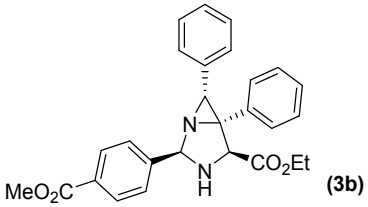
(*S*-2a)



#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	8.294	1376600	14792863	49.091
2	8.792	1333228	15340934	50.909

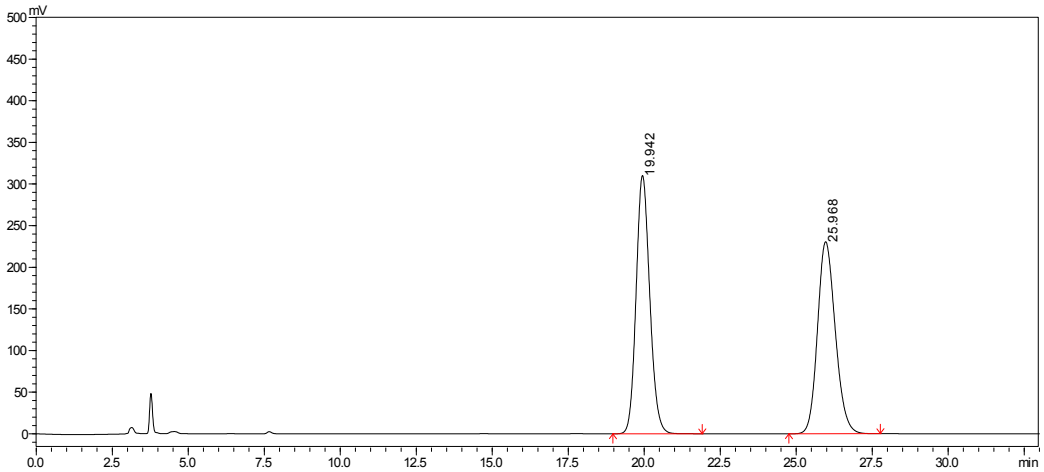


#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	8.267	43766	527234	4.573
2	8.764	841960	11001940	95.427



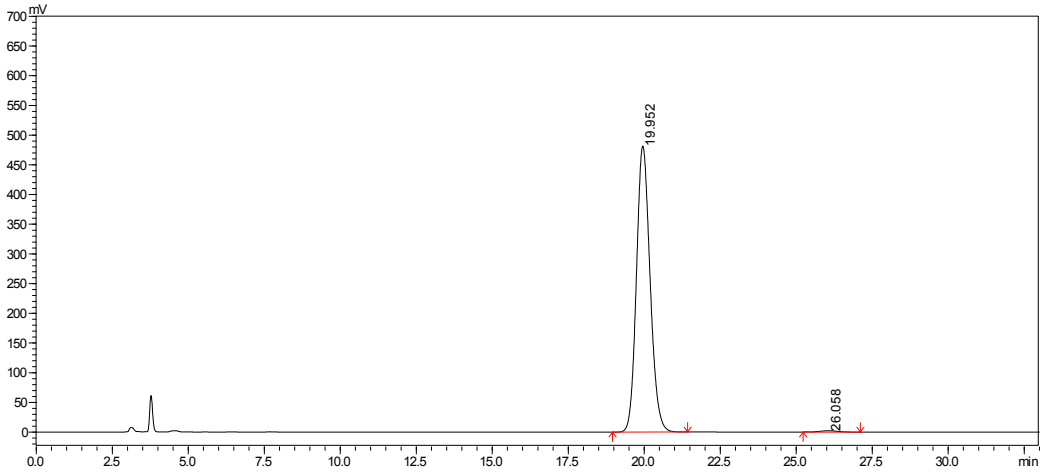
(3b)

□ □ □ □ □ :DH-H16A-AD-HexViPr-95V5 220nm.lcd

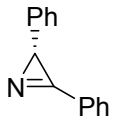


#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	19.942	310282	9694517	50.793
2	25.968	230639	9391954	49.207

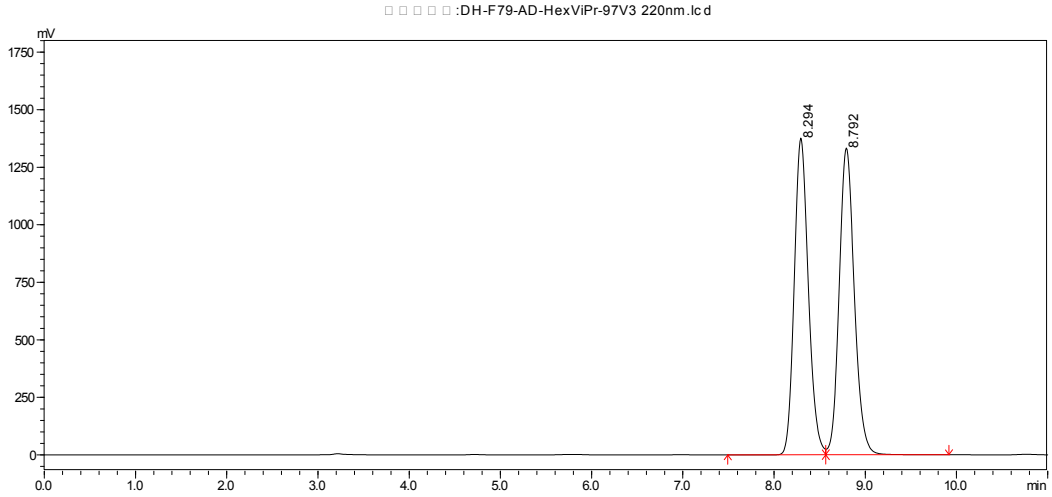
□ □ □ □ □ :DH-H16B2-AD-HexViPr-95V5 220nm.lcd



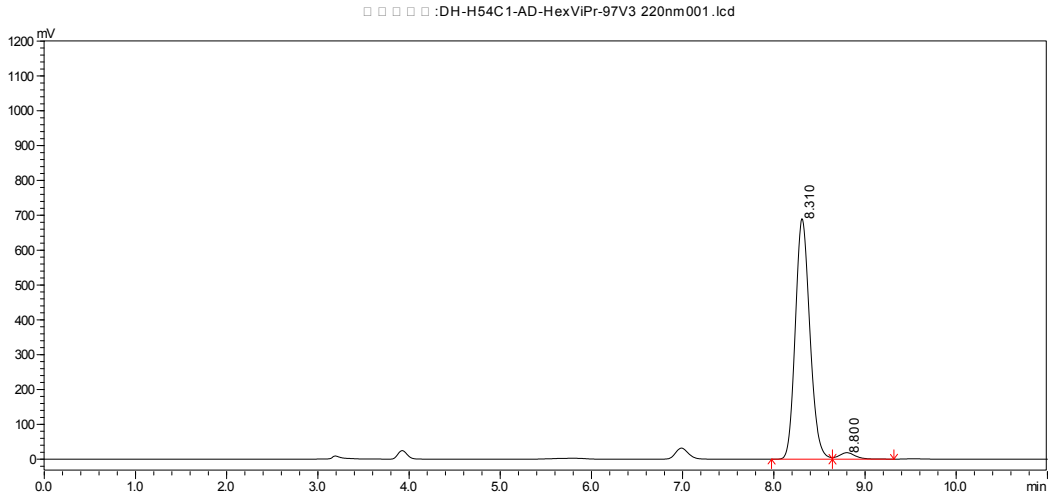
#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	19.952	481628	15049197	99.402
2	26.058	2274	90544	0.598



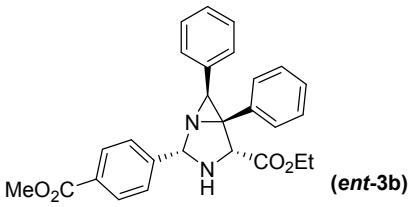
(*R*-2a)



#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	8.294	1376600	14792863	49.091
2	8.792	1333228	15340934	50.909

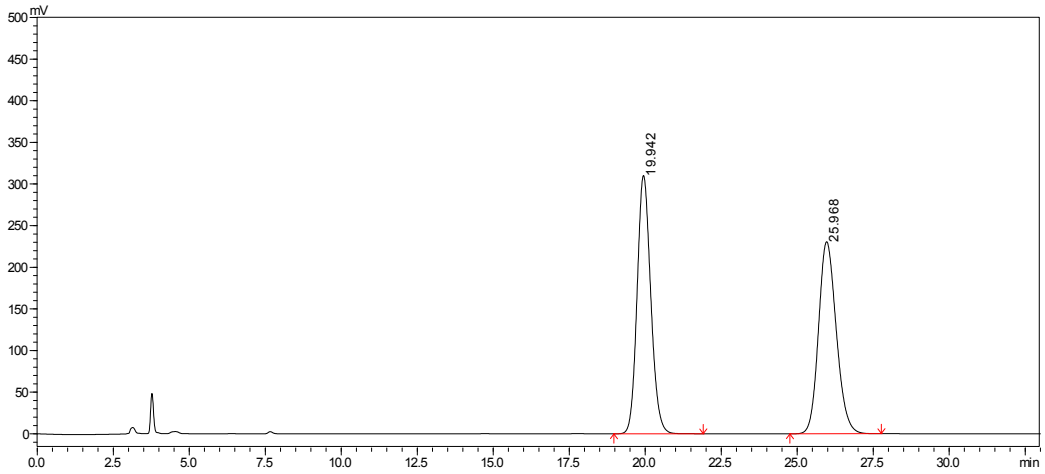


#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	8.310	690228	7658029	97.105
2	8.800	18466	228298	2.895



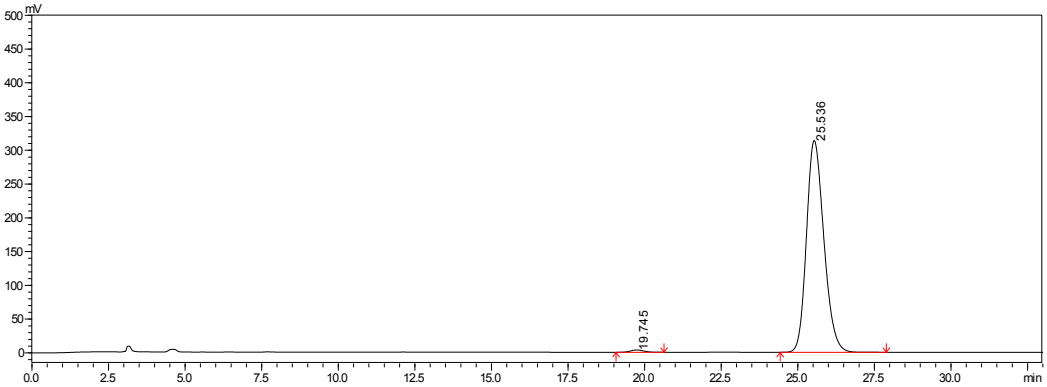
(***ent*-3b**)

□ □ □ □ □ :DH-H16A-AD-HexViPr-95V5 220nm.lcd

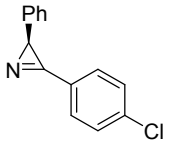


#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	19.942	310282	9694517	50.793
2	25.968	230639	9391954	49.207

□ □ □ □ □ :DH-H54C2-AD-HexViPr-95V5 220nm001.lcd

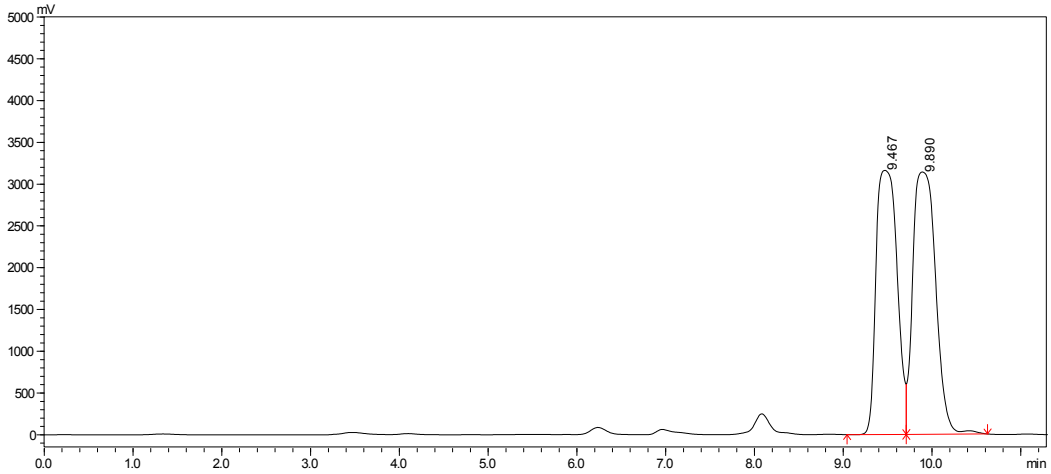


#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	19.745	3412	103024	0.825
2	25.536	313496	12387312	99.175



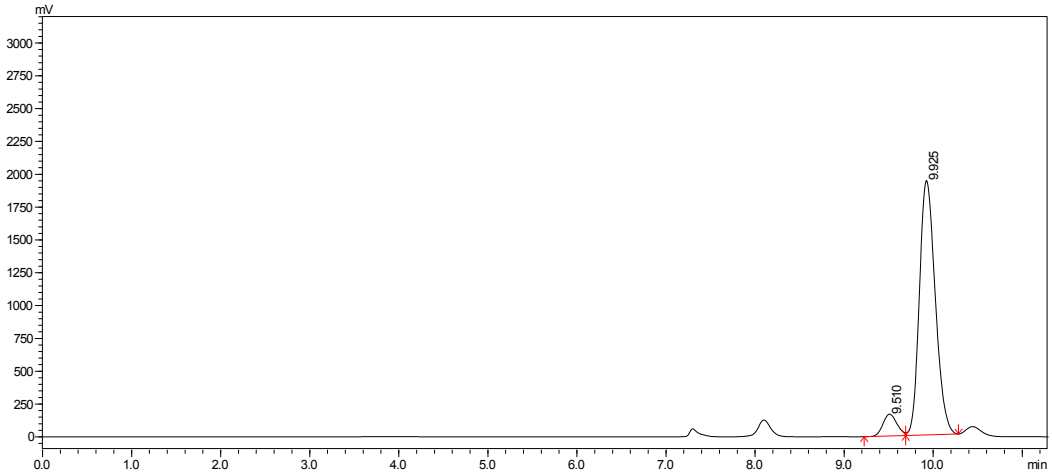
(2b)

□ □ □ □ □ :DH-G45-AD-HexViPr-97V3 254nm001.lcd

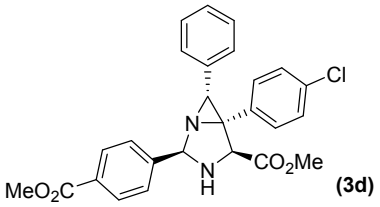


#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	9.467	3152138	51932032	49.901
2	9.890	3053912	52137789	50.099

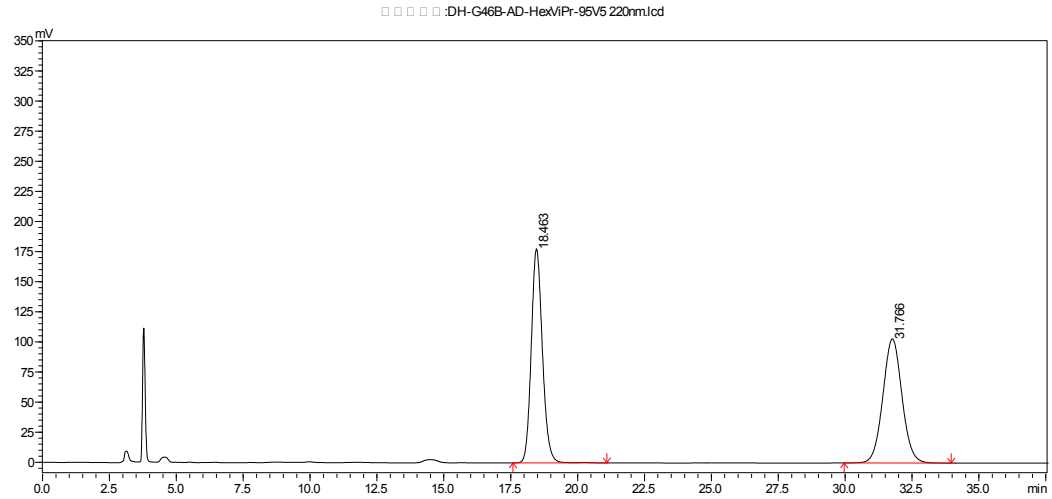
□ □ □ □ □ :DH-H071-AD-HexViPr-97V3 254nm001.lcd



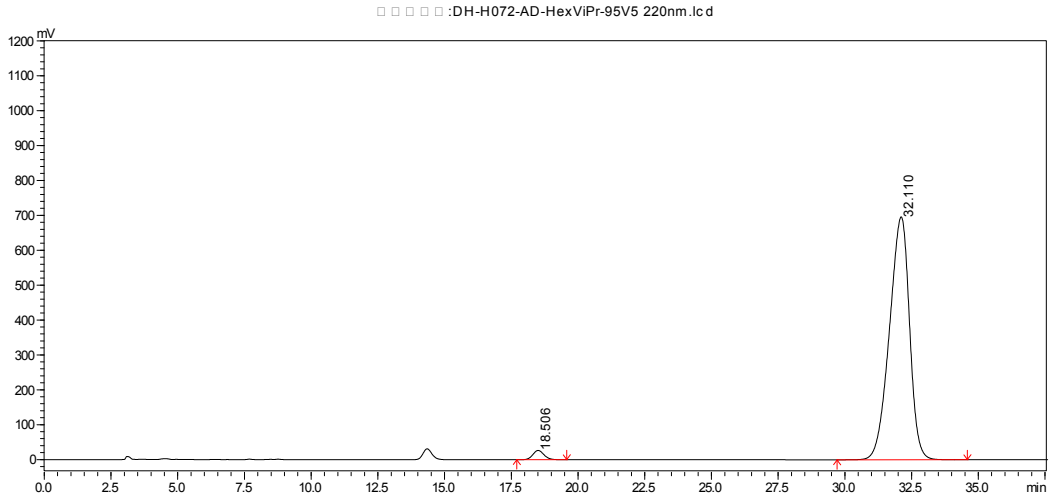
#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	9.510	166570	1816414	7.036
2	9.925	1939621	24000606	92.964



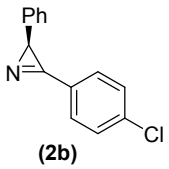
(3d)



#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	18.463	177887	5125263	49.995
2	31.766	103139	5126324	50.005

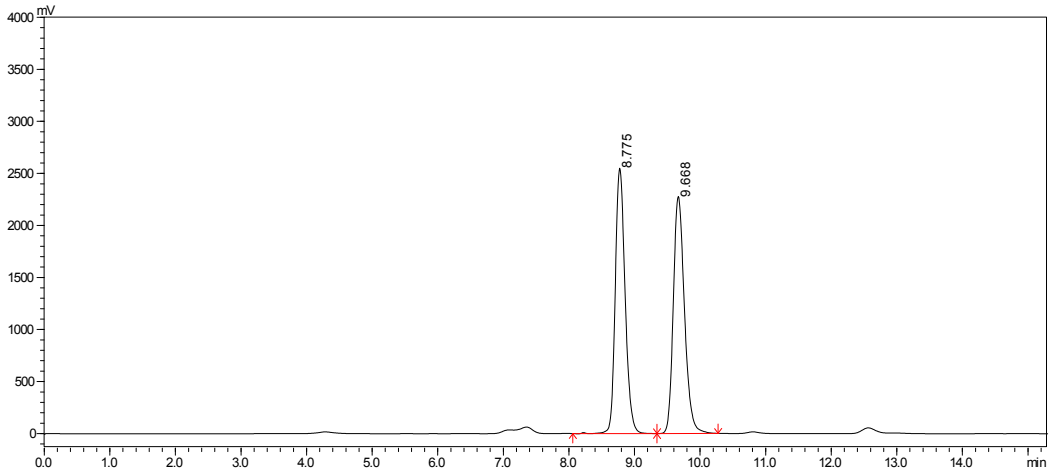


#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	18.506	26610	777733	2.091
2	32.110	696169	36407946	97.909



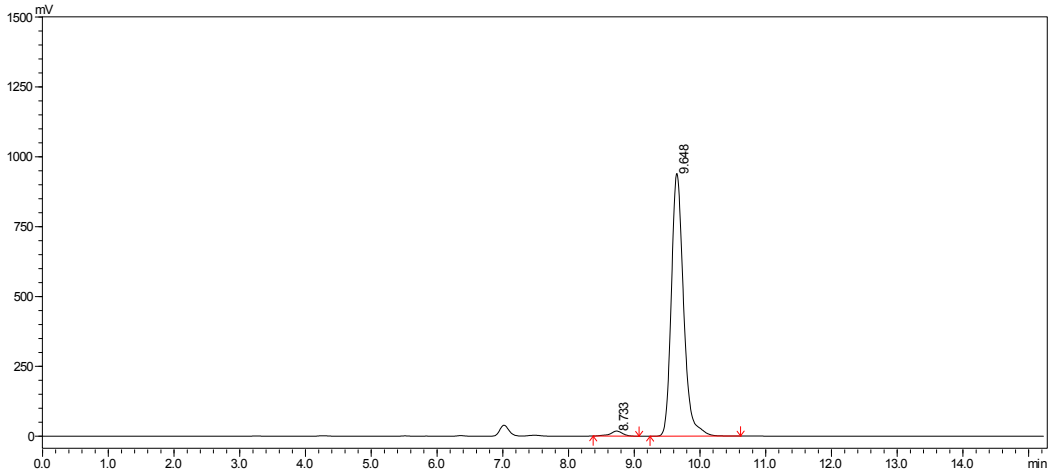
(2b)

□ □ □ □ □ :DH-G45(p-Cl)-AD-HexViPr-97V3 254nm001.lcd

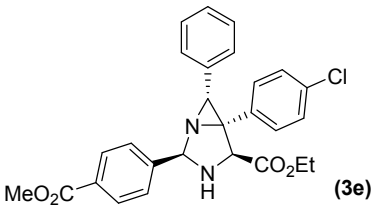


#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	8.775	2549884	26593856	49.652
2	9.668	2277498	26966506	50.348

□ □ □ □ □ :DH-H30A1-AD-HexViPr-97V3 254nm.lcd

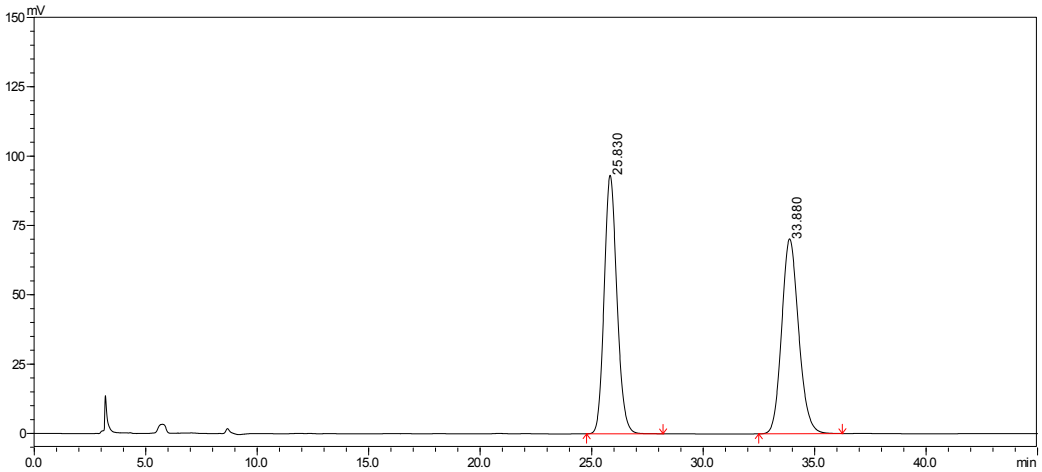


#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	8.733	18207	239627	1.933
2	9.648	939655	12154184	98.067



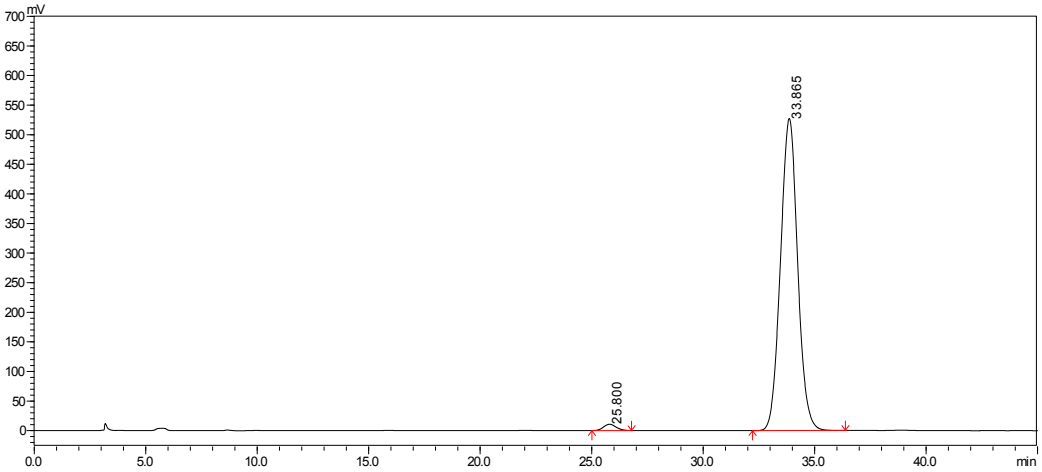
(3e)

□ □ □ □ □ :DH-H29A-AD-HexViPr-97V3 220nm.lcd

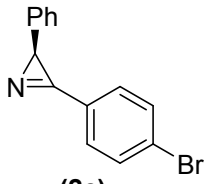


#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	25.830	93226	3714686	49.981
2	33.880	70267	3717467	50.019

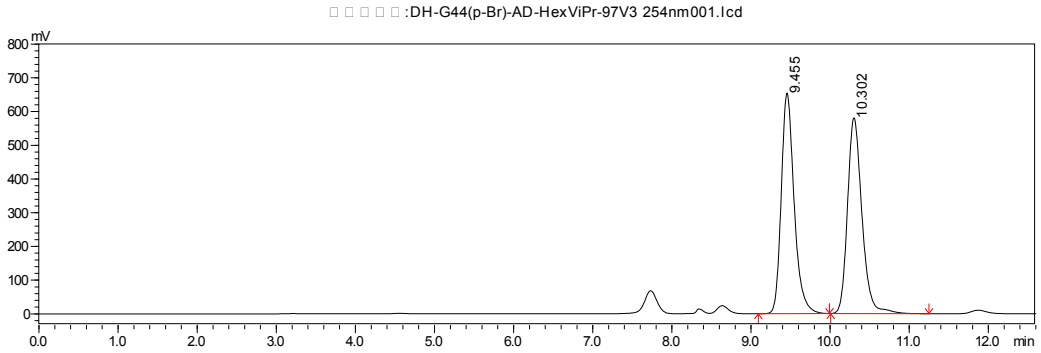
□ □ □ □ □ :DH-H30A2-AD-HexViPr-97V3 220nm.lcd



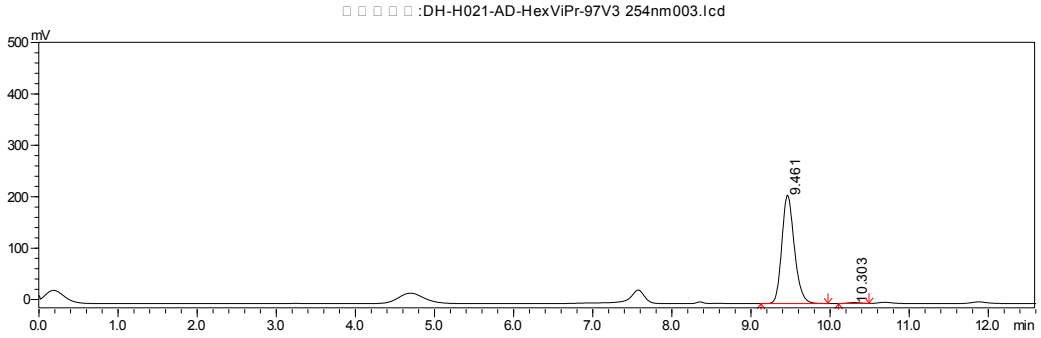
#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	25.800	10680	419945	1.466
2	33.865	527431	28231837	98.534



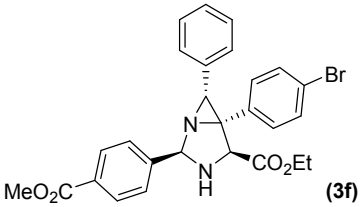
(2c)



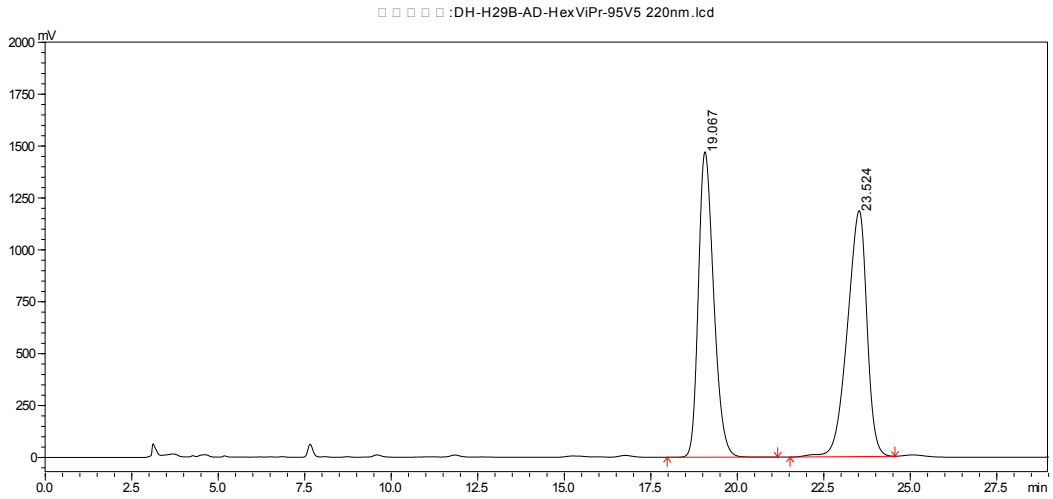
#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	9.455	654418	7417307	50.142
2	10.302	580852	7375171	49.858



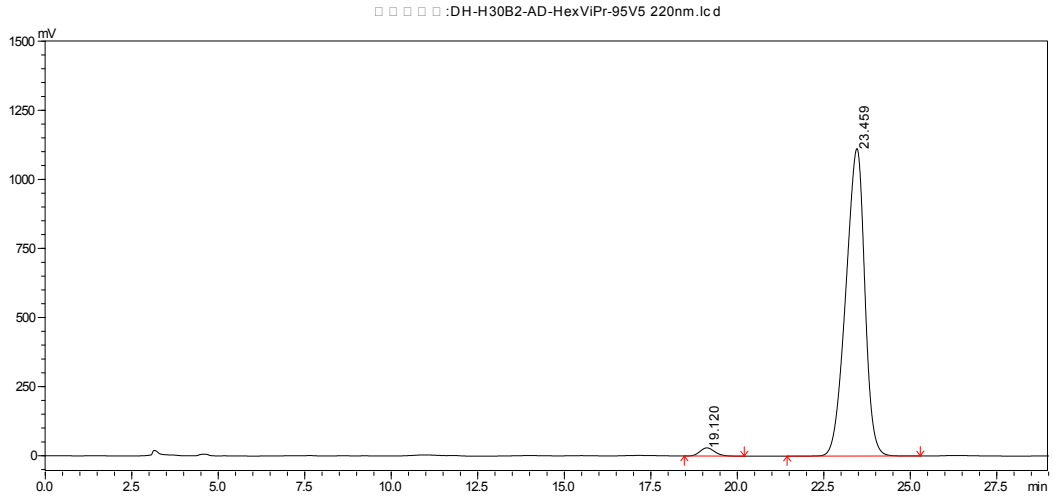
#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	9.461	210799	2324538	99.151
2	10.303	1632	17539	0.849



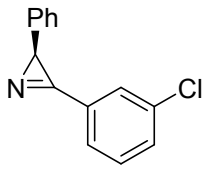
(3f)



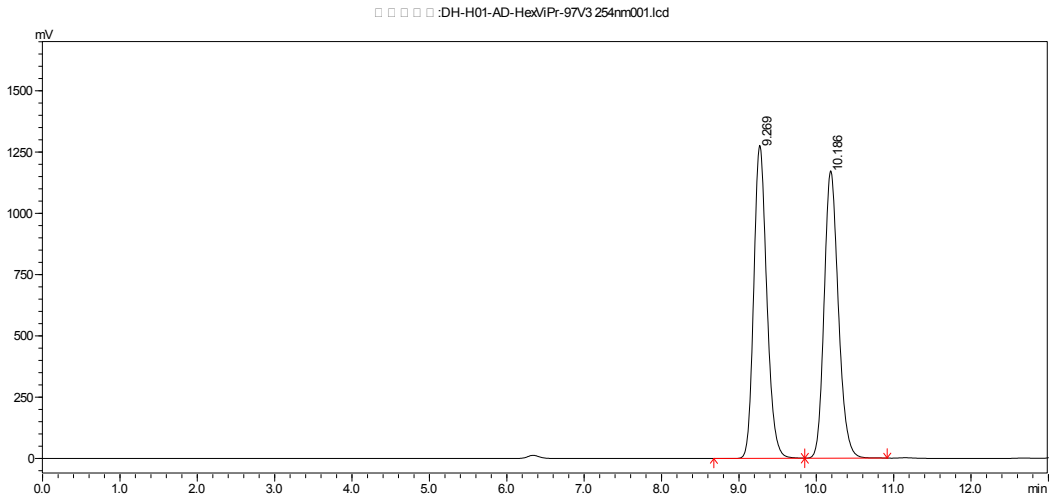
#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	19.067	1470661	45118974	49.923
2	23.524	1176676	45257776	50.077



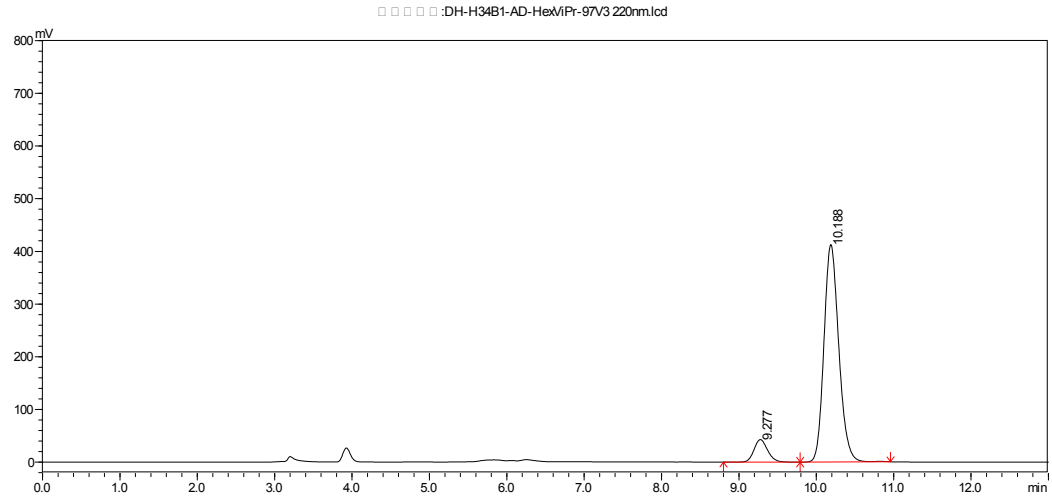
#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	19.120	29789	888552	2.055
2	23.459	1112884	42340822	97.945



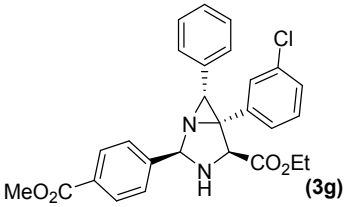
(2d)



#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	9.269	1277161	14946251	49.978
2	10.186	1172791	14959530	50.022

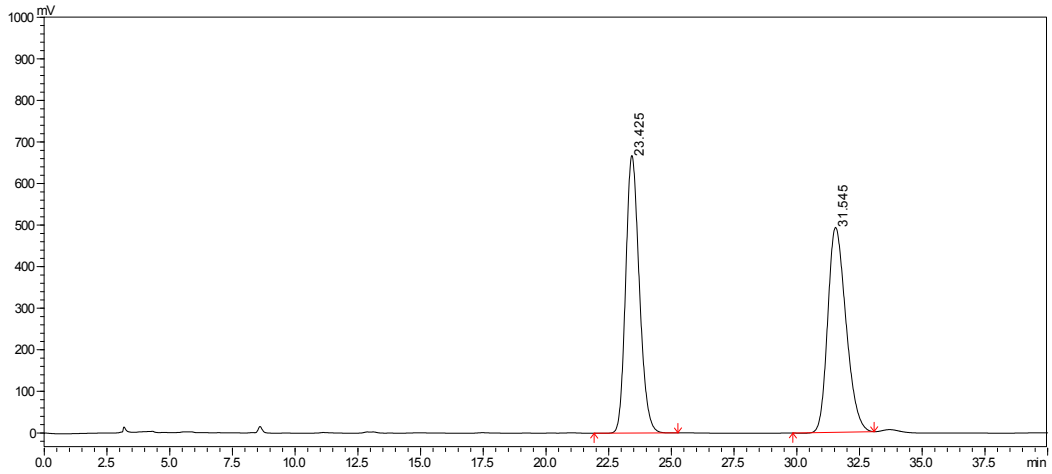


#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	9.277	42702	520199	8.648
2	10.188	412424	5495328	91.352



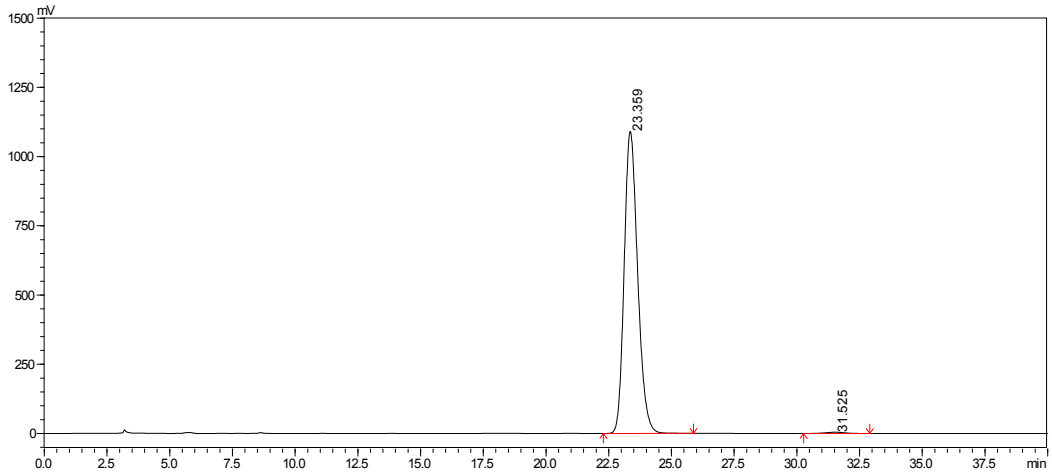
(3g)

□ □ □ □ □ :DH-H33B-AD-HexViPr-97V3 220nm.lcd

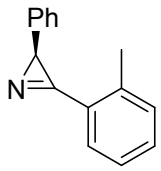


#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	23.425	667784	25251431	50.333
2	31.545	492981	24917593	49.667

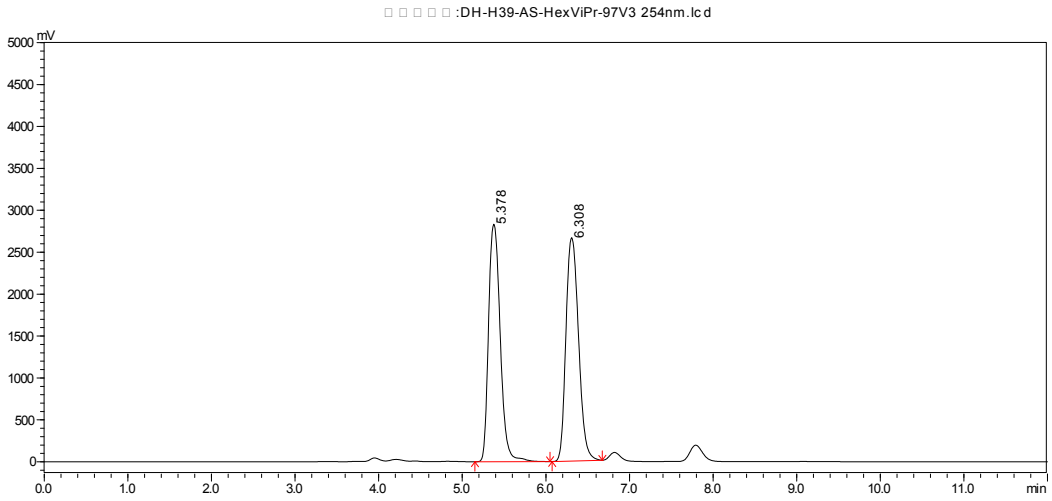
□ □ □ □ □ :DH-H34B2-AD-HexViPr-97V3 220nm.lcd



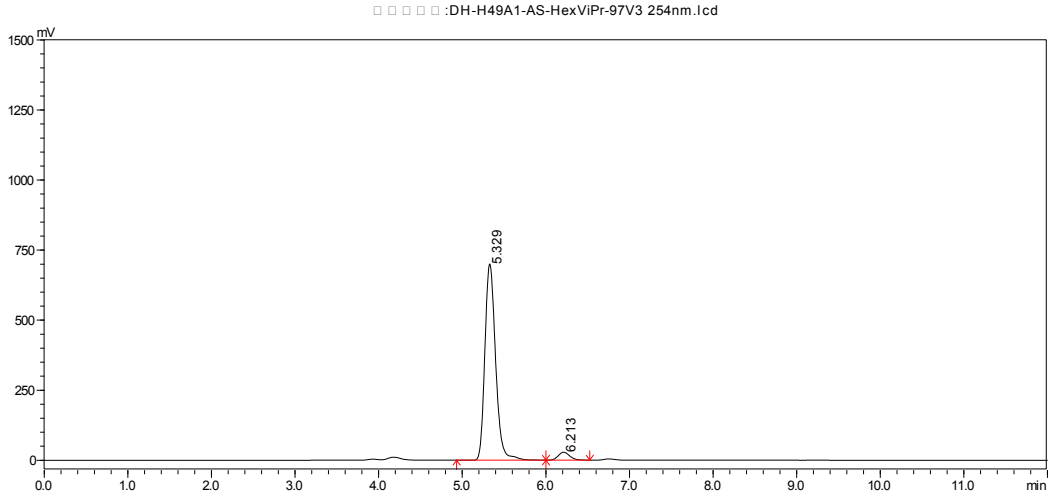
#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	23.359	1090855	40725658	99.396
2	31.525	4655	247521	0.604



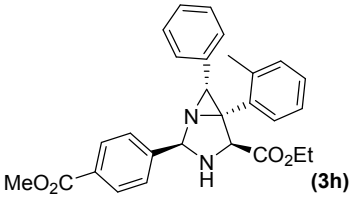
(2e)



#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	5.378	2831939	27516207	49.621
2	6.308	2663493	27936221	50.379

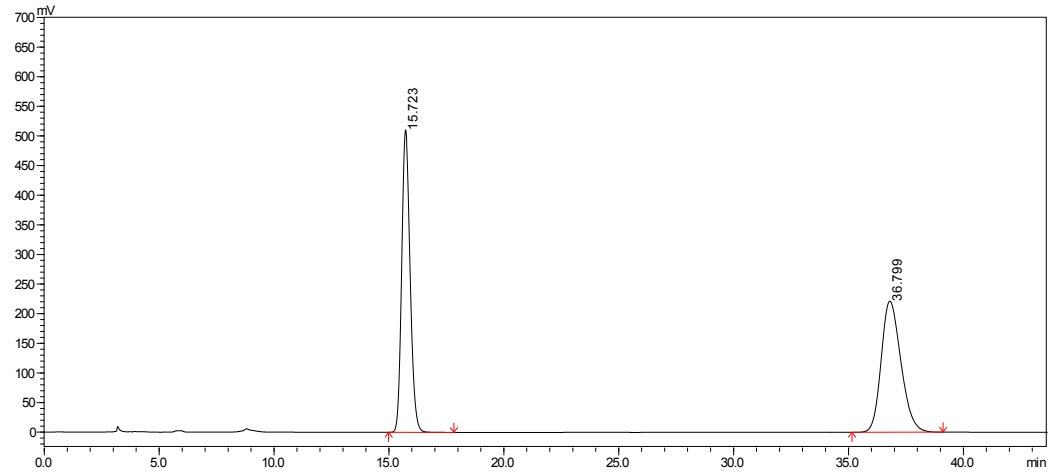


#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	5.329	700139	6230261	95.850
2	6.213	28265	269772	4.150



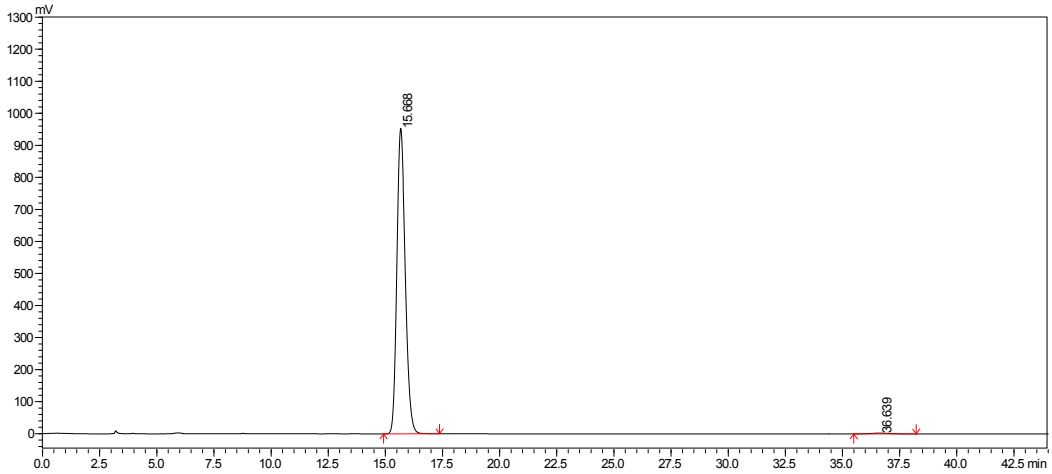
(3h)

□ □ □ □ □ :DH-H46B-AD-HexViPr-97V3 220nm.lcd

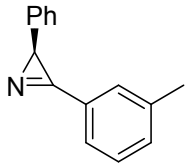


#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	15.723	510526	13185982	49.981
2	36.799	221405	13195806	50.019

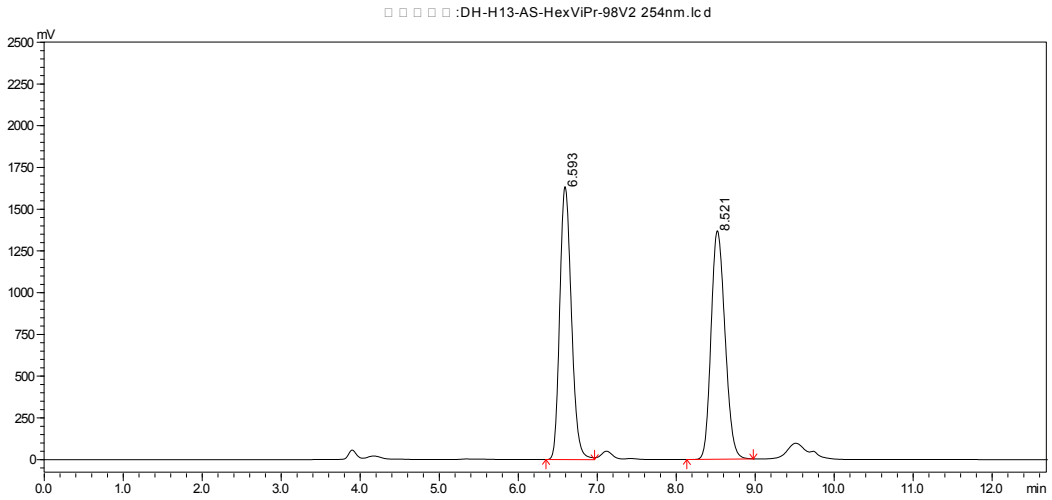
□ □ □ □ □ :DH-H49A2-AD-HexViPr-97V3 220nm.lcd



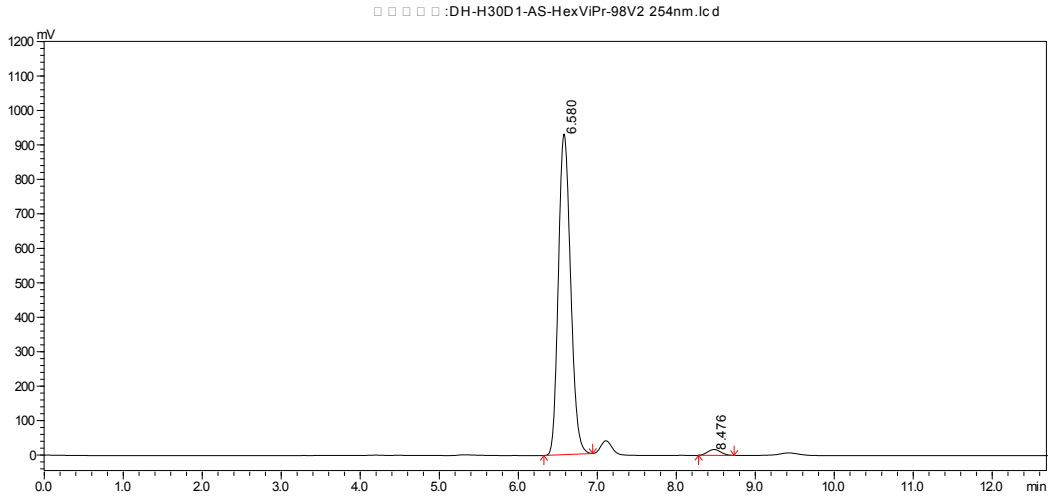
#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	15.668	953553	24485995	99.427
2	36.639	2474	141075	0.573



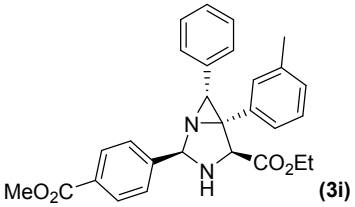
(2f)



#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	6.593	1634379	16763755	49.917
2	8.521	1367858	16819714	50.083

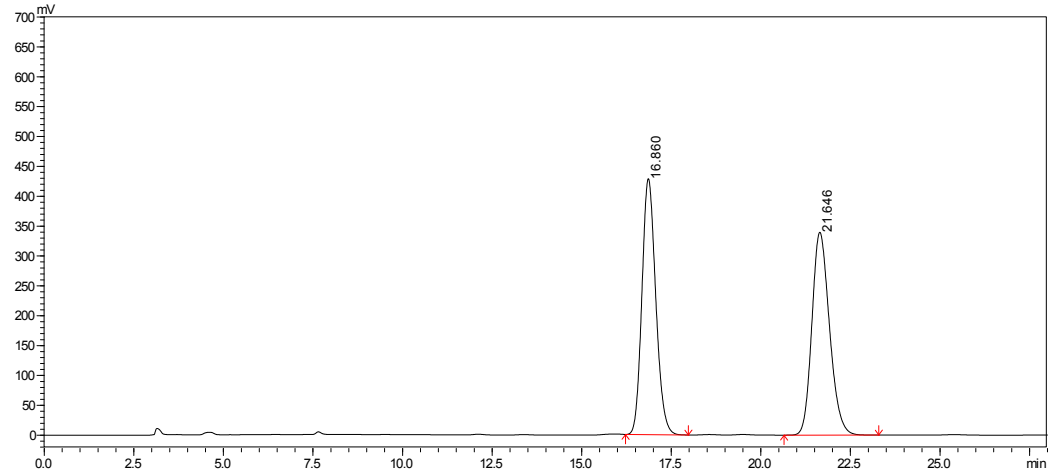


#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	6.580	930440	10014415	98.055
2	8.476	17007	198594	1.945



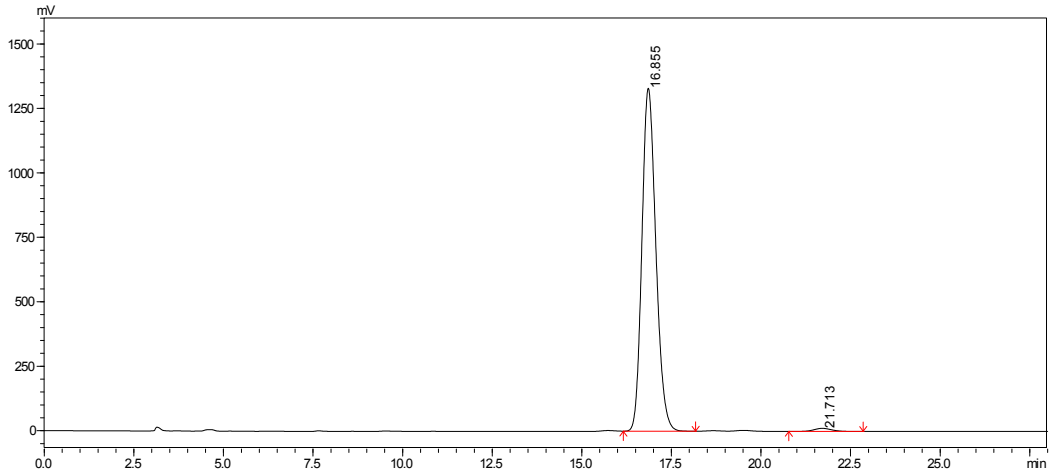
(3i)

□ □ □ □ □ :DH-H29D-AD-HexViPr-95V5 220nm.lcd

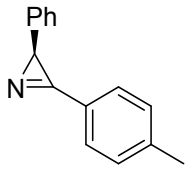


#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	16.860	428498	11523282	49.833
2	21.646	339377	11600712	50.167

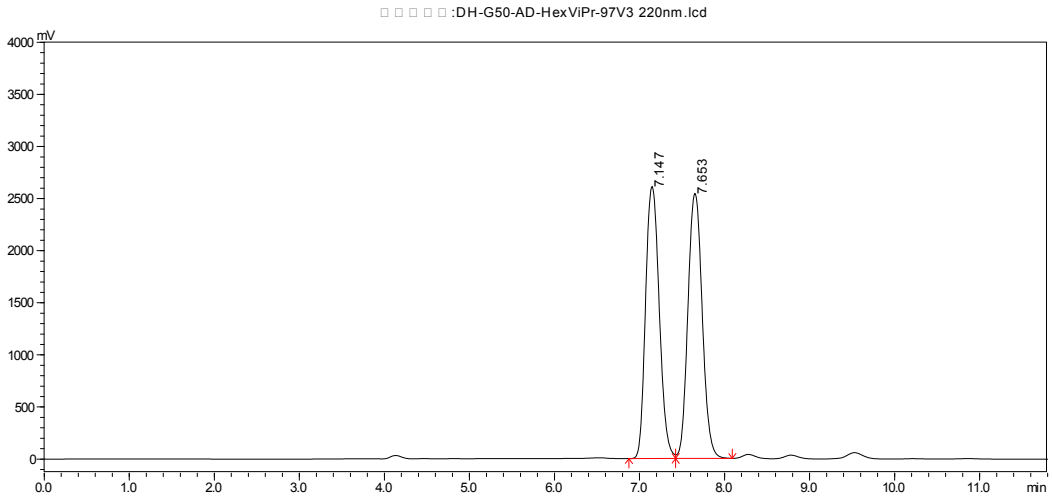
□ □ □ □ □ :DH-H30D2-AD-HexViPr-95V5 220nm.lcd



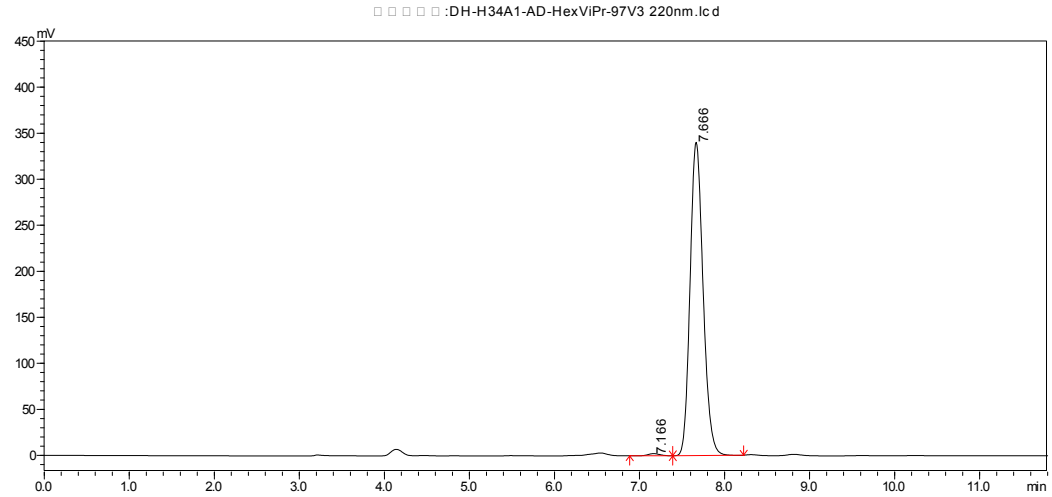
#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	16.855	1330019	36078089	98.882
2	21.713	12026	407940	1.118



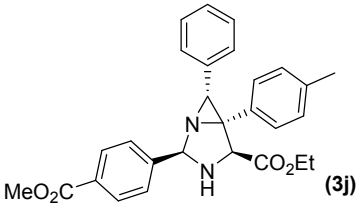
(2g)



#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	7.147	2610304	29233811	49.549
2	7.653	2543735	29765988	50.451

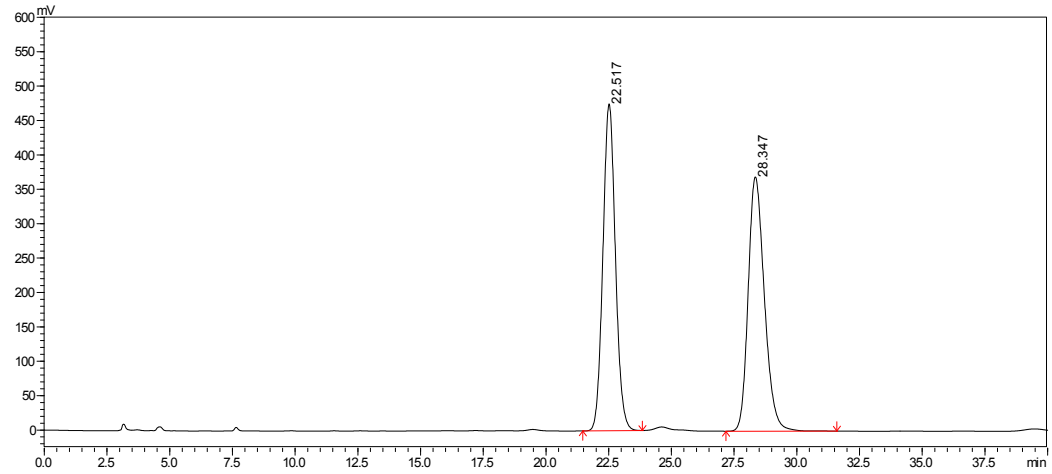


#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	7.166	2385	23198	0.636
2	7.666	340429	3622066	99.364



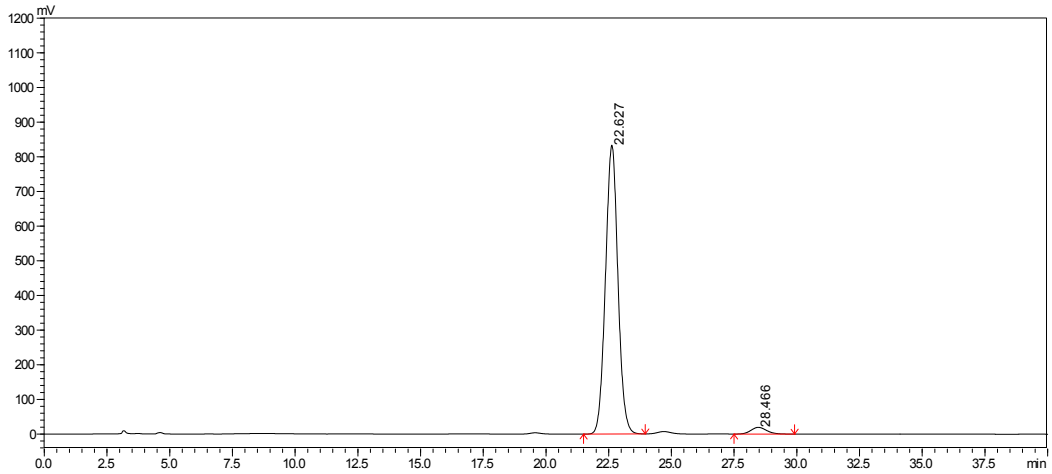
(3j)

□ □ □ □ □ :DH-H33A-AD-HexViPr-95V5 220nm.lcd

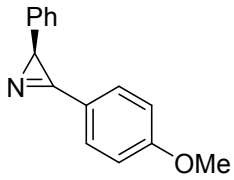


#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	22.517	475320	16487306	49.816
2	28.347	369555	16608923	50.184

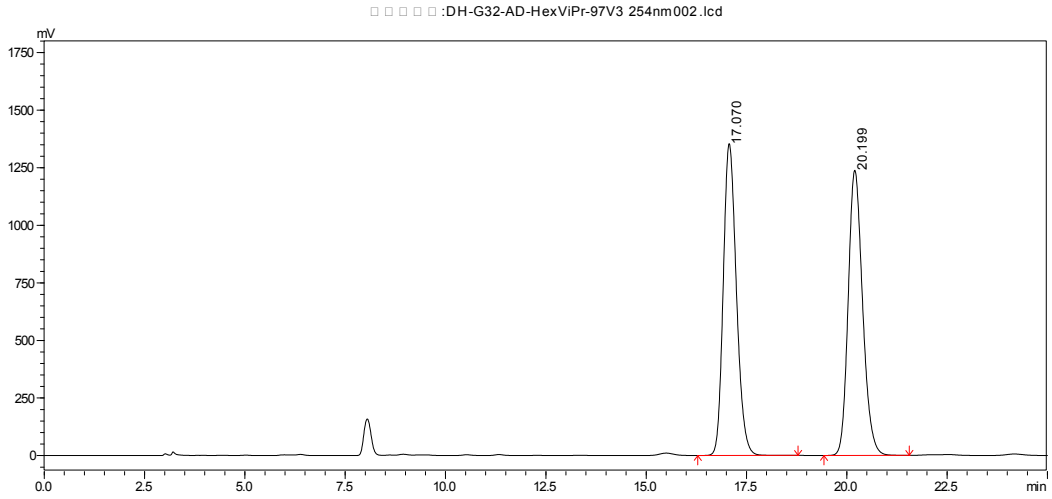
□ □ □ □ □ :DH-H34A2-AD-HexViPr-95V5 220nm.lcd



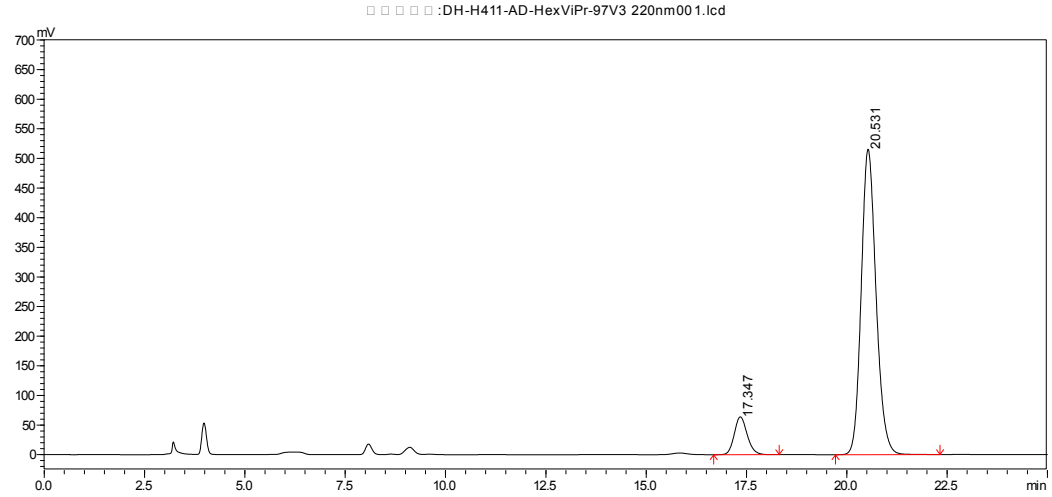
#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	22.627	833522	28829605	97.482
2	28.466	18456	744636	2.518



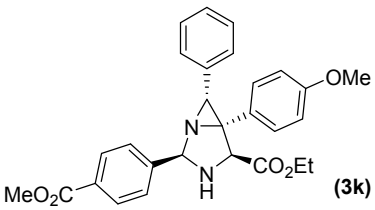
(2h)



#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	17.070	1354343	30814999	49.891
2	20.199	1238345	30949948	50.109

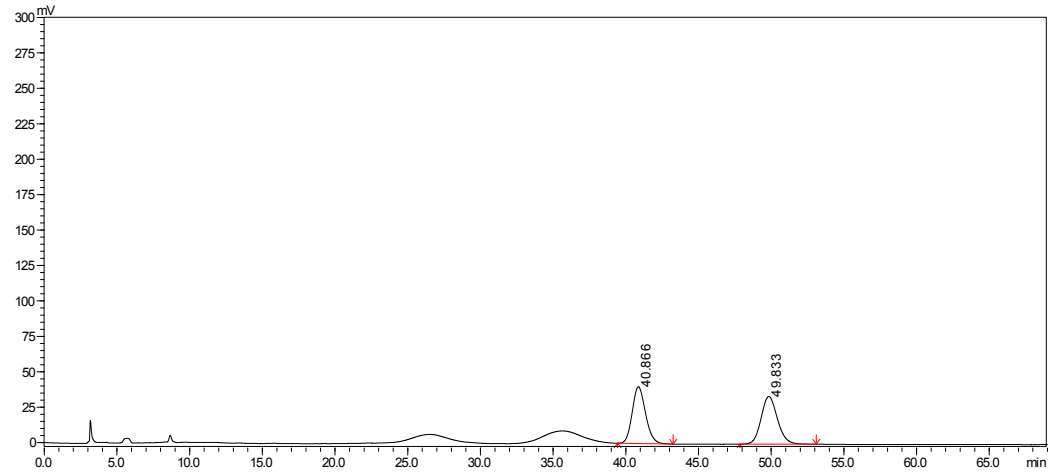


#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	17.483	60364	1375306	9.702
2	20.693	486027	12800761	90.298



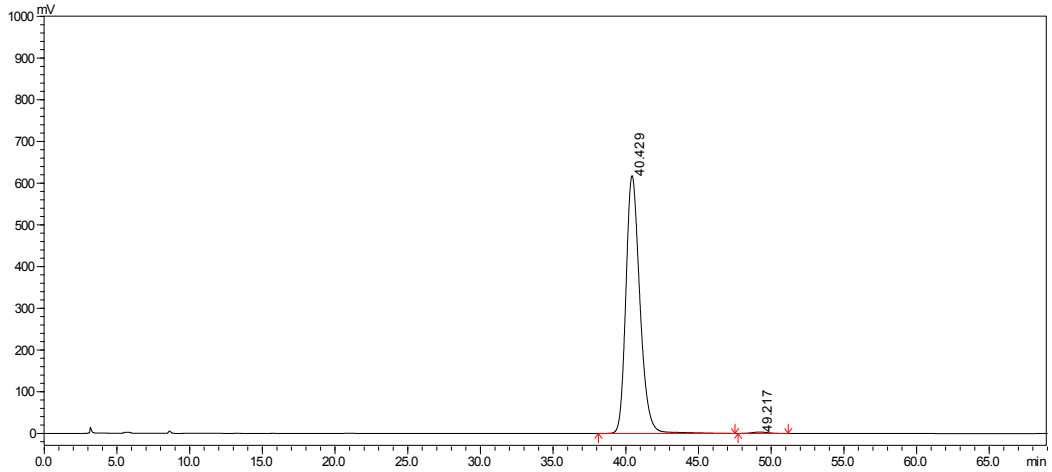
(3k)

□ □ □ □ □ :DH-H32-(29C)-AD-HexViPr-97V3 220nm.lcd

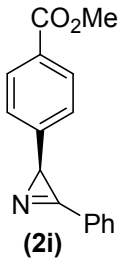


#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	40.866	40078	2555615	49.373
2	49.833	33651	2620511	50.627

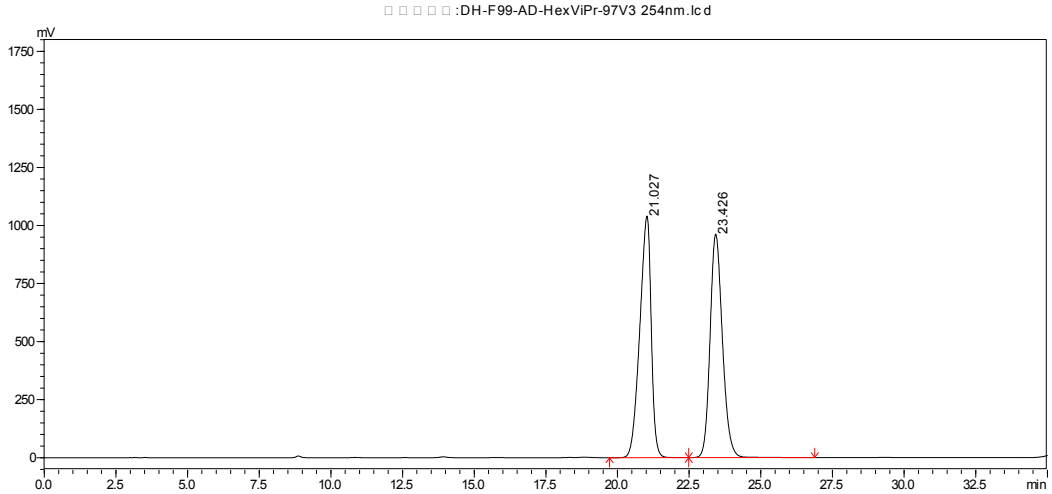
□ □ □ □ □ :DH-H30C2-AD-HexViPr-97V3 220nm.lcd



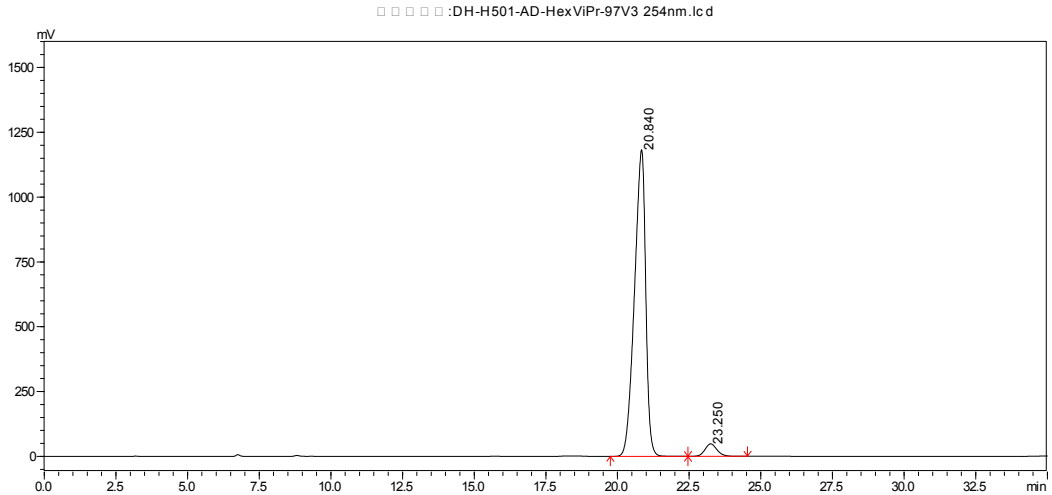
#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	40.429	618154	41351210	99.383
2	49.217	3391	256626	0.617



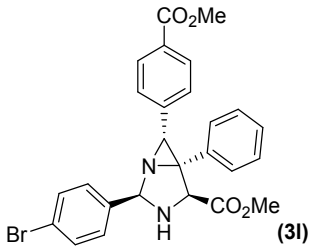
(2i)



#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	21.027	1040551	28823506	49.926
2	23.426	962171	28908388	50.074

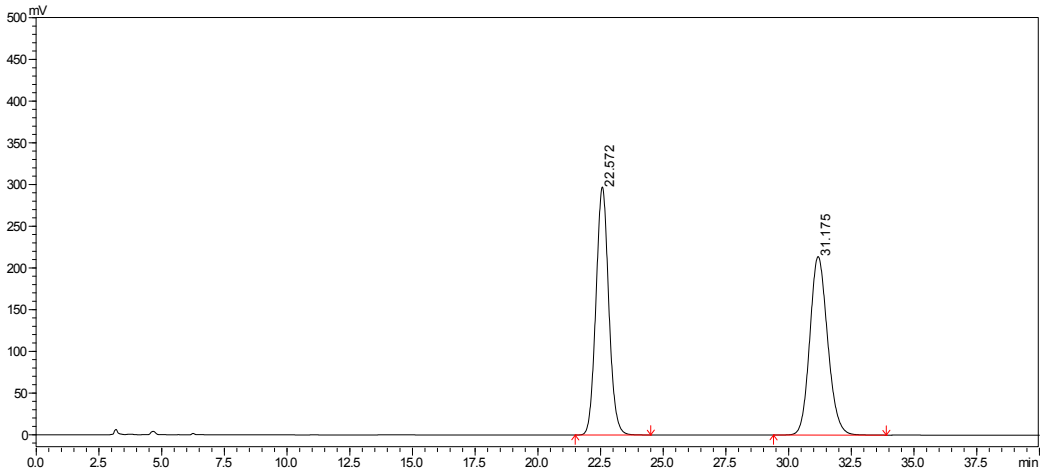


#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	20.840	1182603	32242856	95.819
2	23.250	48079	1406836	4.181



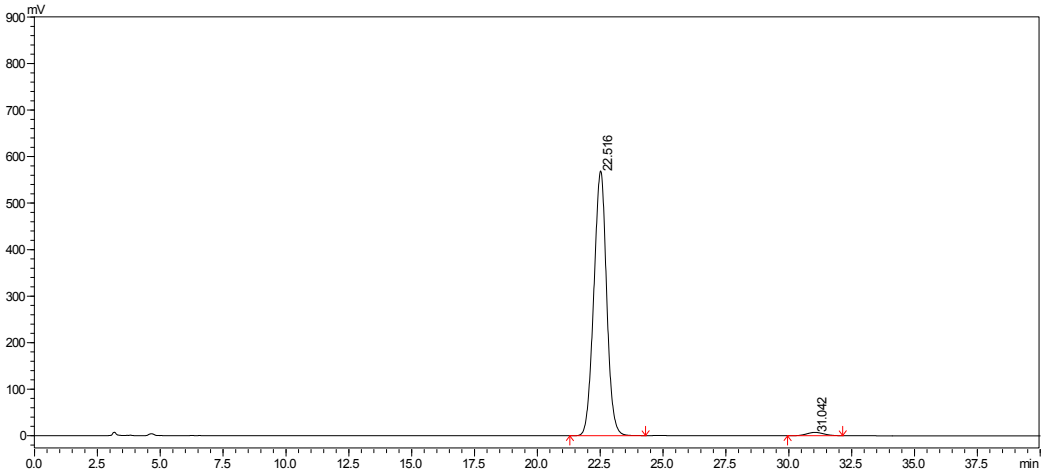
(3l)

□ □ □ □ □ :DH-H45-AD-HexViPr-95V5 220nm.lcd

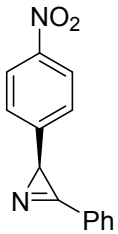


#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	22.572	297244	10558154	49.919
2	31.175	214054	10592282	50.081

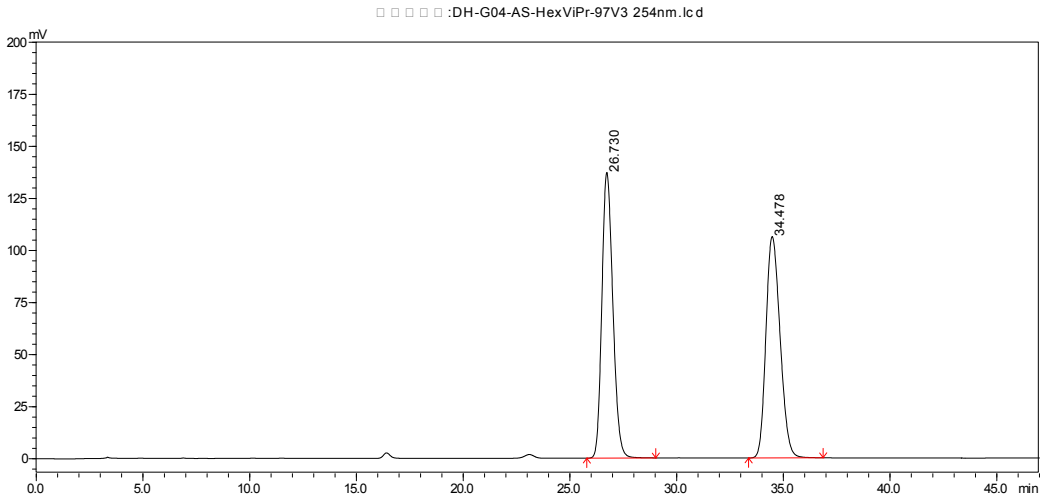
□ □ □ □ □ :DH-H502-AD-HexViPr-95V5 220nm.lcd



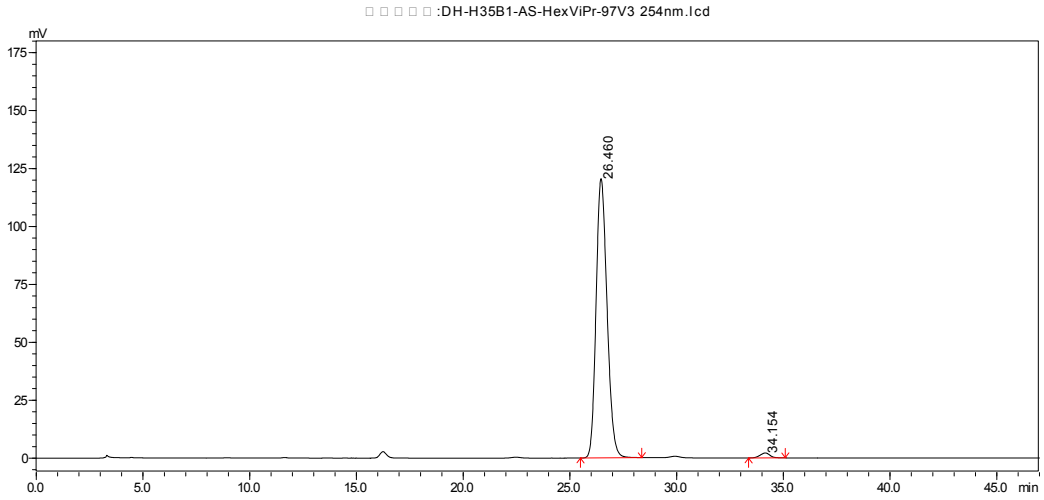
#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	22.516	569087	20148153	98.347
2	31.042	7172	338587	1.653



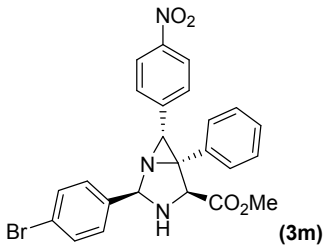
(2j)



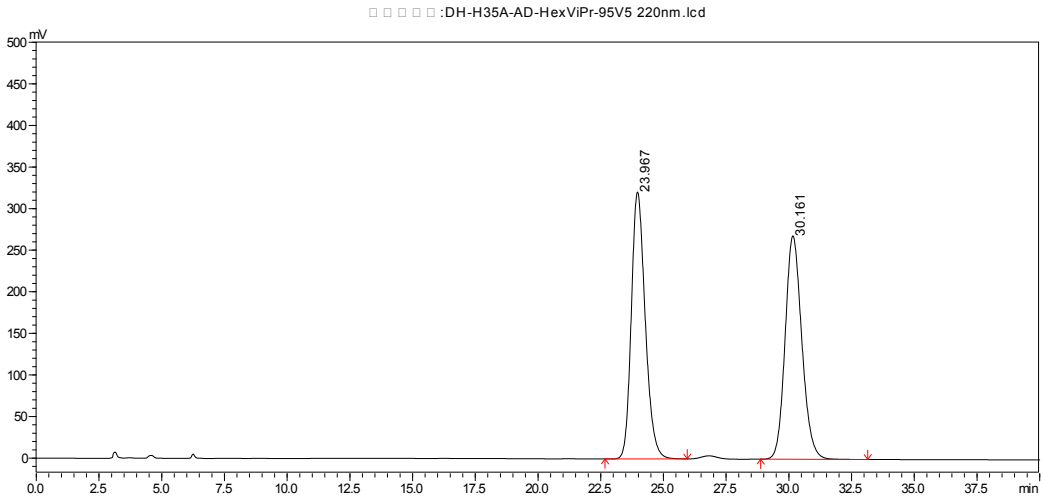
#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	26.730	137184	4905966	50.003
2	34.478	106336	4905355	49.997



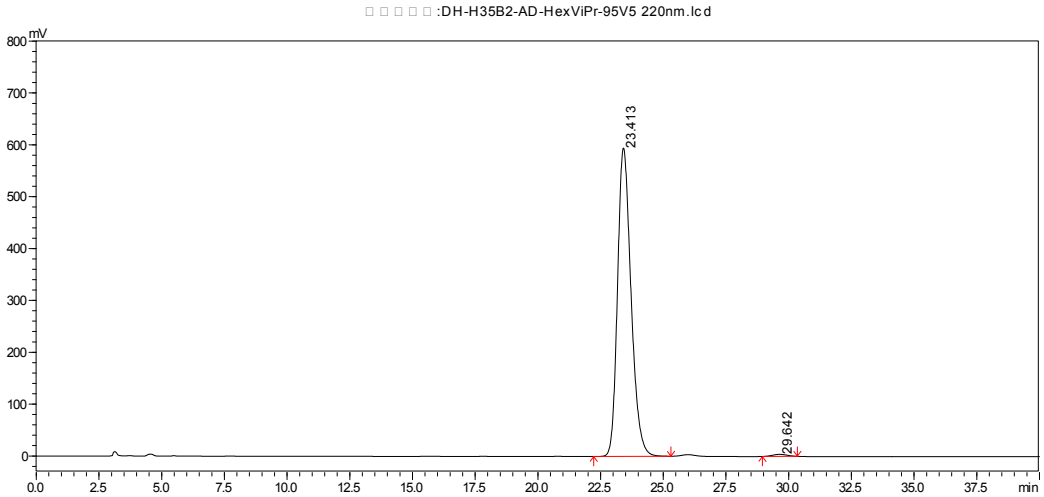
#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	26.460	120508	4301557	98.428
2	34.154	2130	68701	1.572



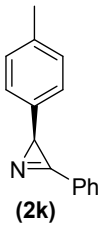
(3m)



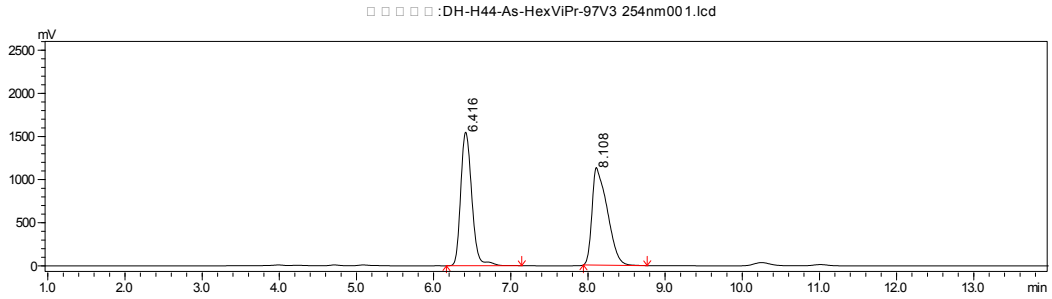
#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	23.967	320973	12385992	49.878
2	30.161	268489	12446763	50.122



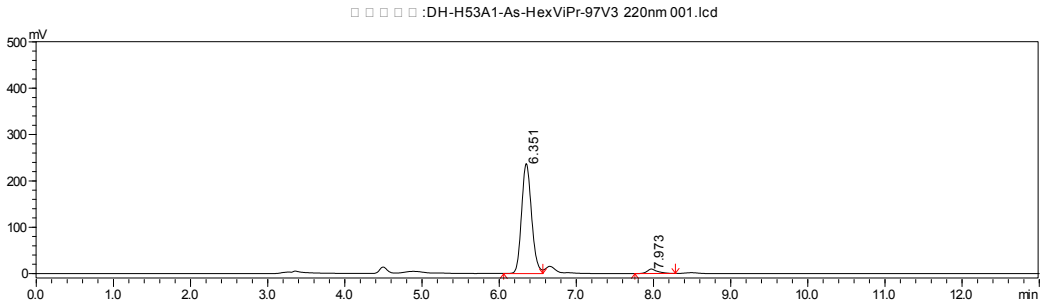
#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	23.413	594506	22279186	99.286
2	29.642	3956	160281	0.714



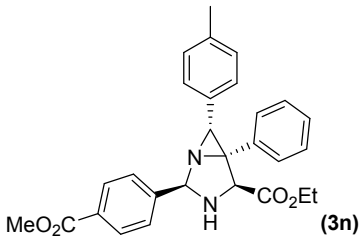
(2k)



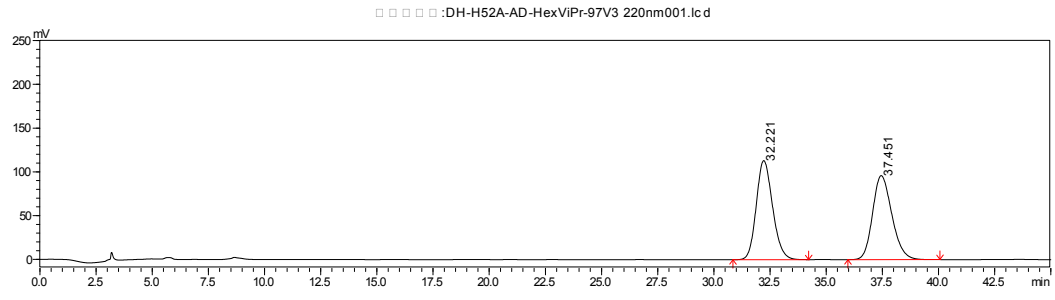
#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	6.416	1549016	15486327	50.071
2	8.108	1131096	15442425	49.929



#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	6.351	237372	2141757	95.969
2	7.973	9815	89971	4.031

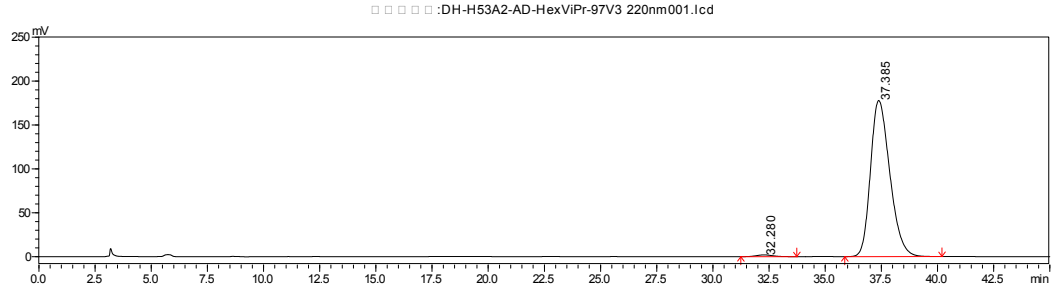


(3n)

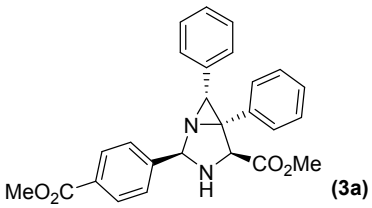


#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)

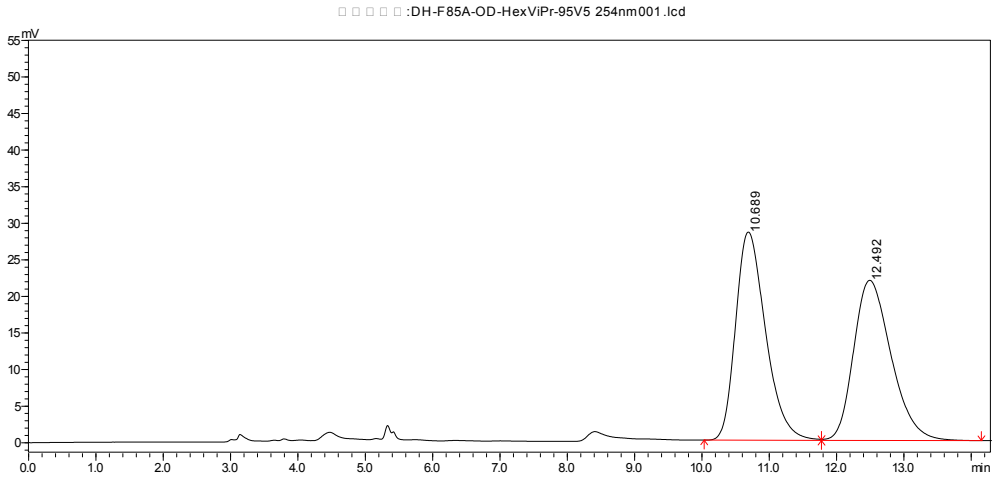
1	32.221	113216	5729151	49.980
2	37.451	95948	5733770	50.020



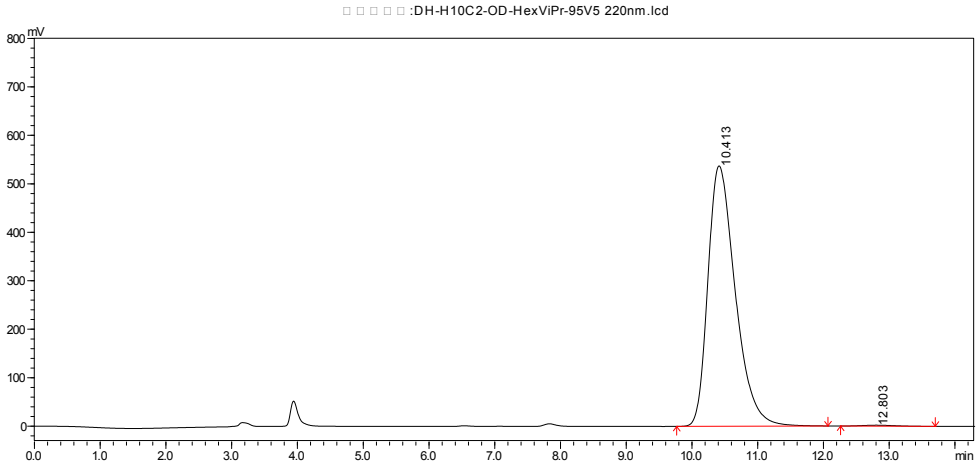
#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	32.280	2018	102145	0.949
2	37.385	177840	10663465	99.051



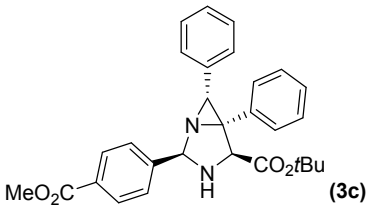
(3a)



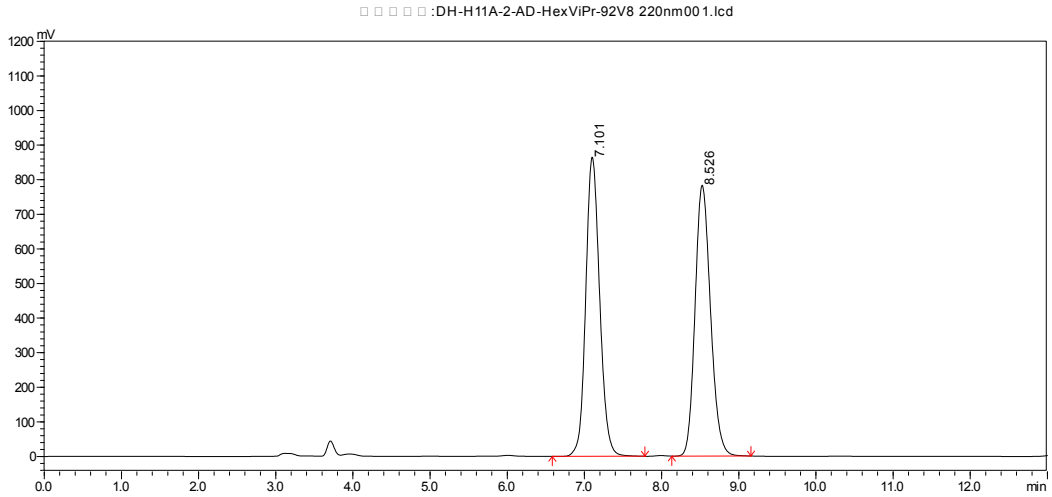
#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	10.689	27920	841165	50.103
2	12.492	21794	837719	49.897



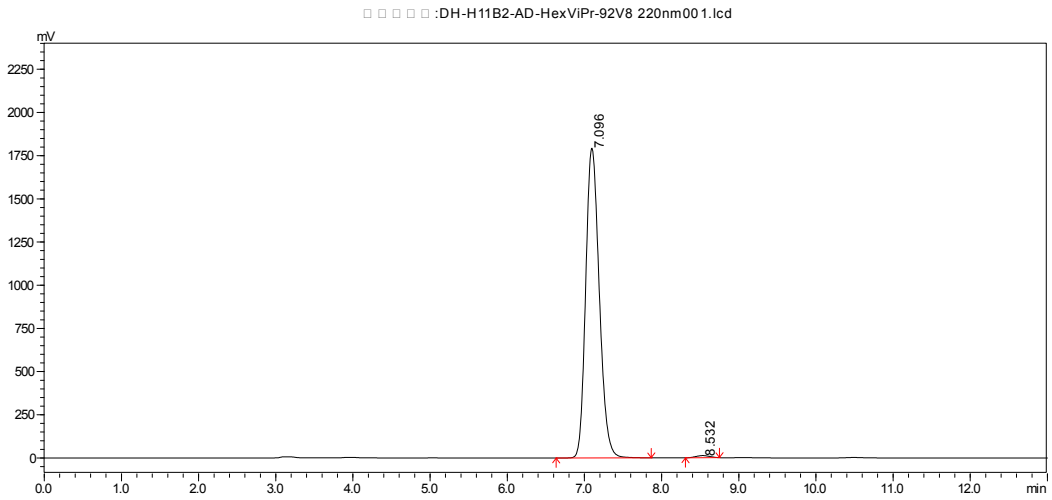
#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	10.413	537218	15535891	99.582
2	12.803	1938	65245	0.418



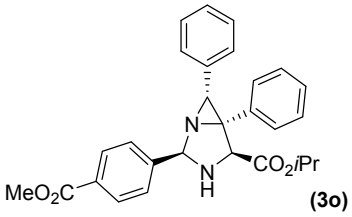
(3c)



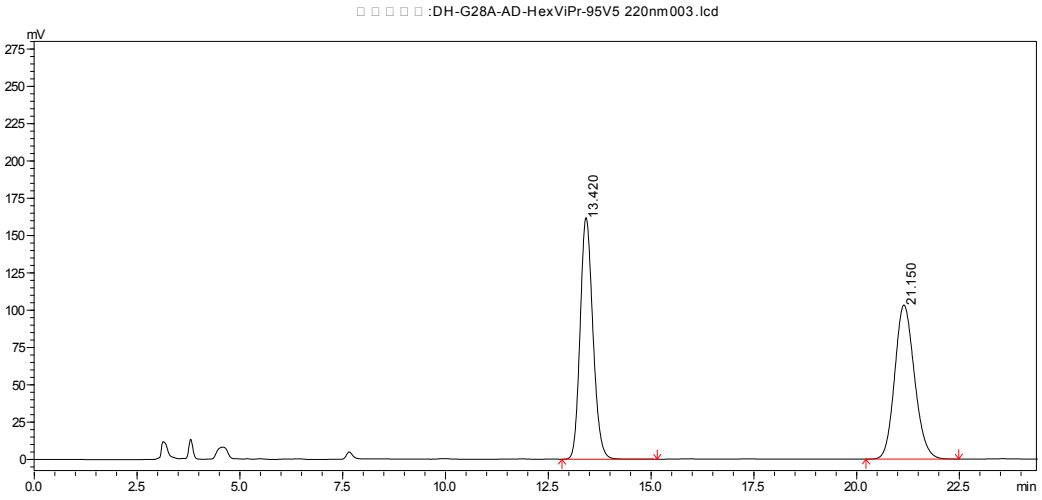
#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	7.101	864843	10835516	49.842
2	8.526	783037	10904133	50.158



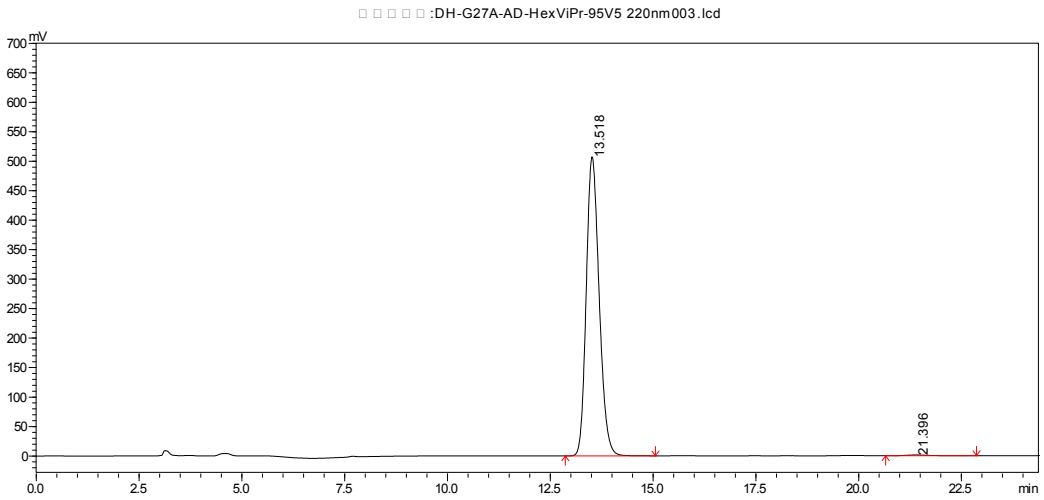
#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	7.096	1792391	21915508	99.274
2	8.532	12592	160303	0.726



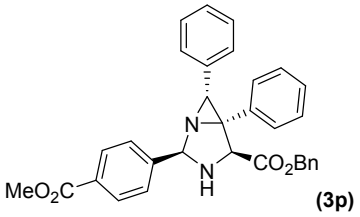
(3o)



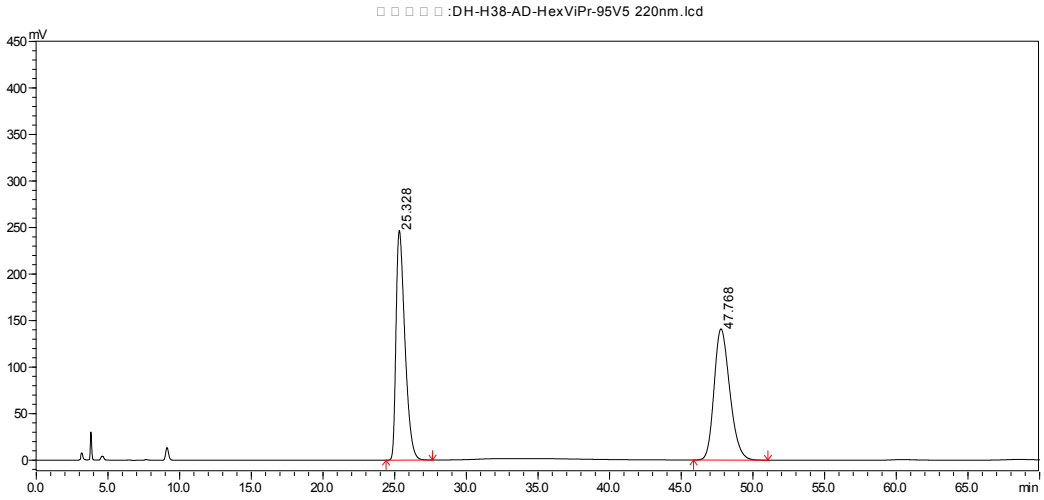
#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	13.420	161854	3491273	50.297
2	21.150	103293	3450043	49.703



#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	13.518	507312	11082497	99.541
2	21.396	1308	51132	0.459

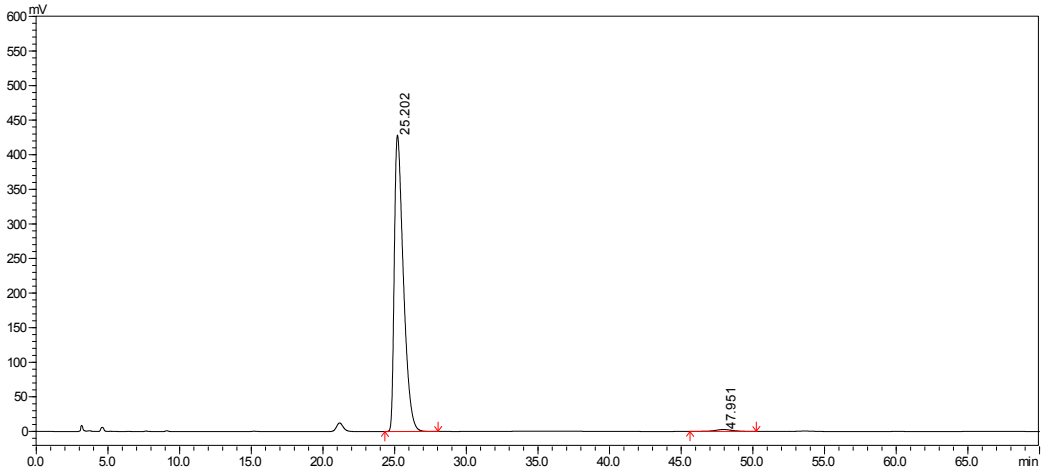


(3p)

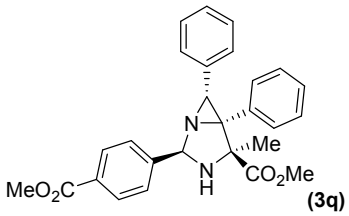


#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	25.328	246830	10641015	49.768
2	47.768	140933	10740393	50.232

□ □ □ □ □ :DH-H27B-AD-HexViPr-95V5 220nm.lcd

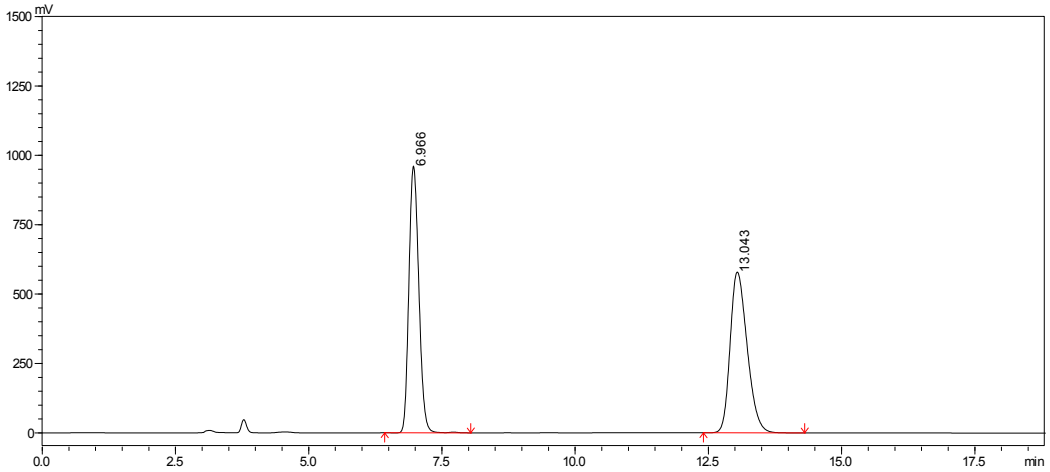


#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	25.202	428561	18891672	98.803
2	47.951	2768	228875	1.197

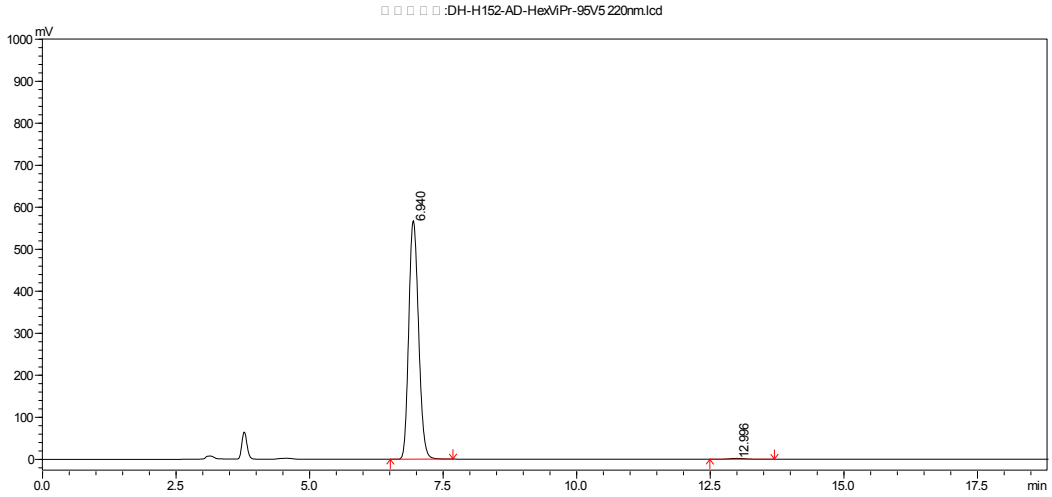


(3q)

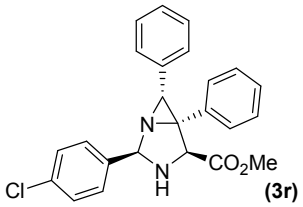
□ □ □ □ □ :DH-H14A-AD-HexViPr-95V5 220nm.lcd



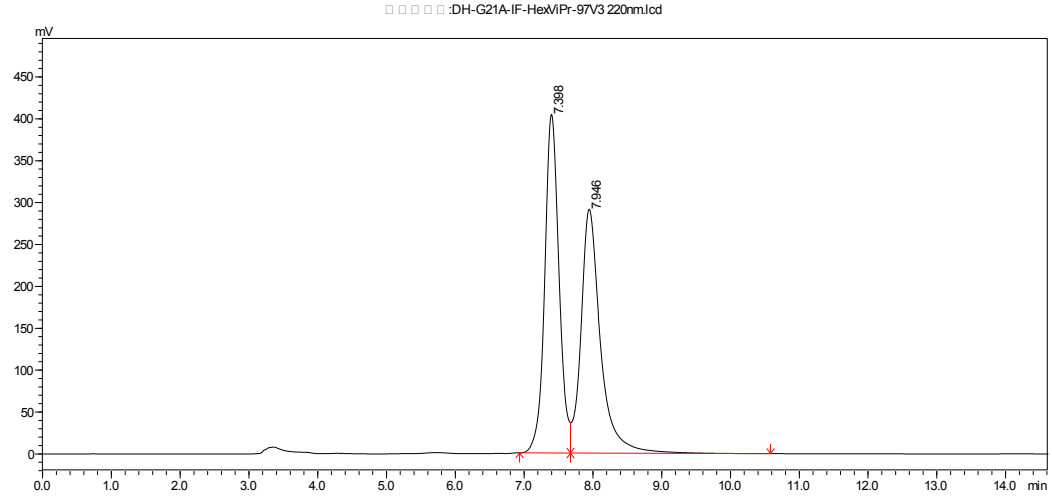
#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	6.966	961730	12452628	49.310
2	13.043	578664	12800913	50.690



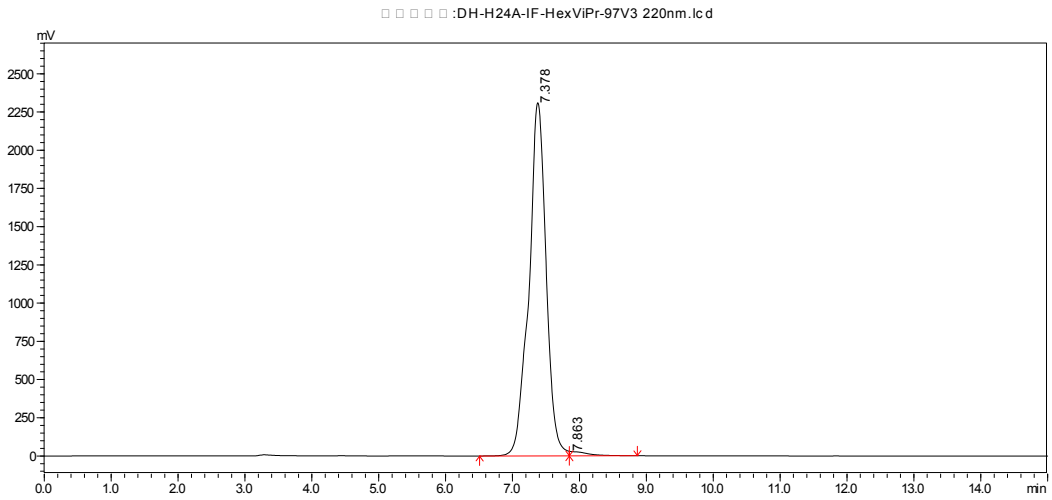
#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	6.940	567755	7228873	99.342
2	12.996	2219	47857	0.658



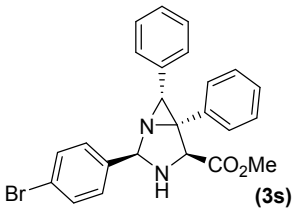
(3r)



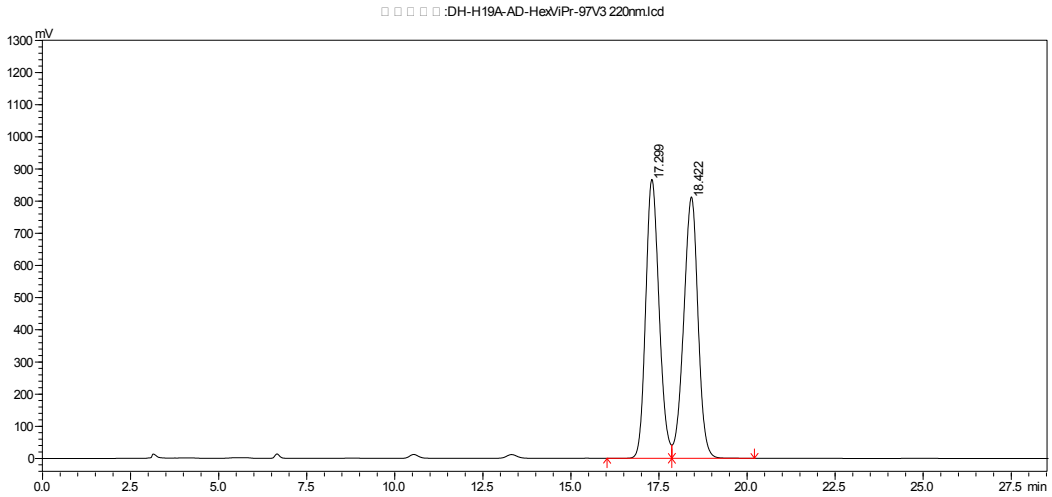
#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	7.398	404435	5822008	50.476
2	7.946	291013	5712212	49.524



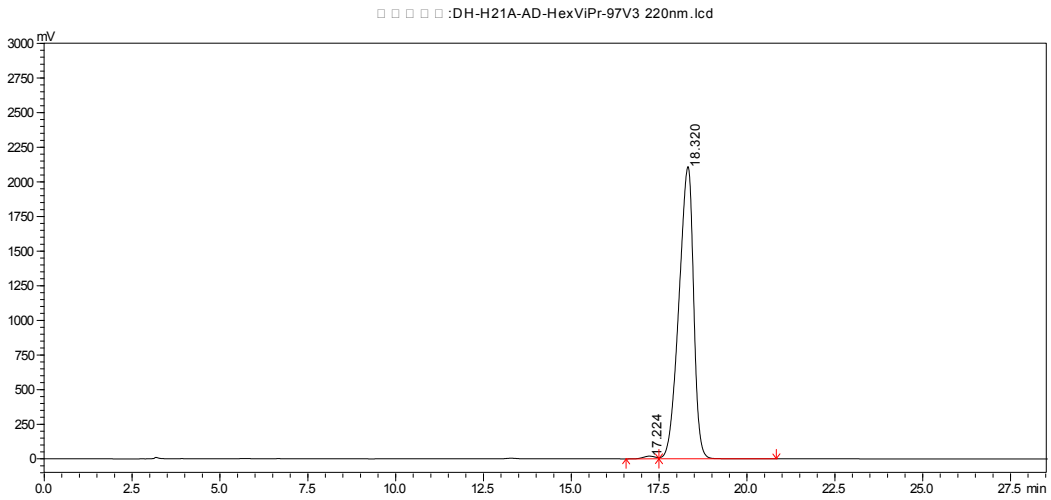
#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	7.378	2309884	41382025	98.759
2	7.863	29074	519882	1.241



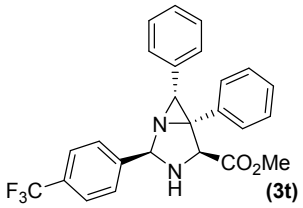
(3s)



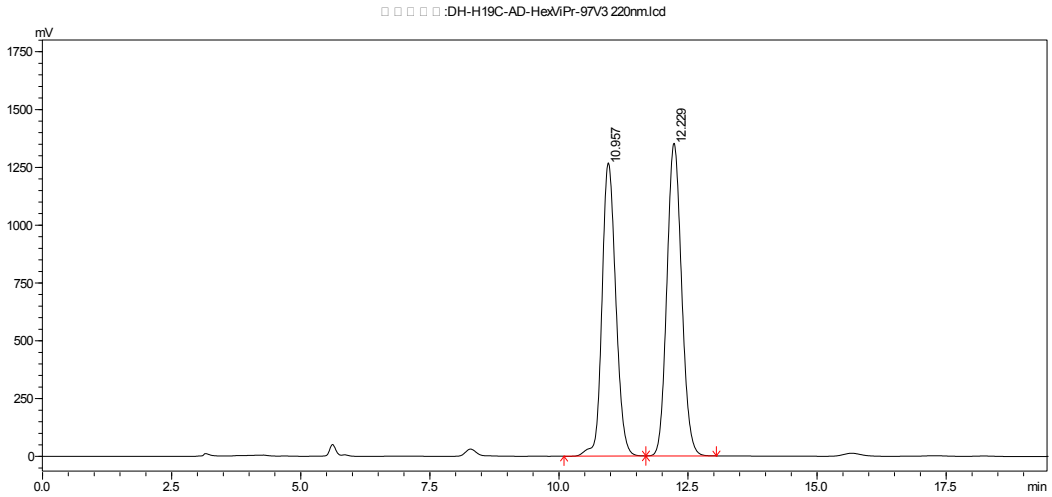
#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	17.299	867836	22917278	49.968
2	18.422	812976	22946749	50.032



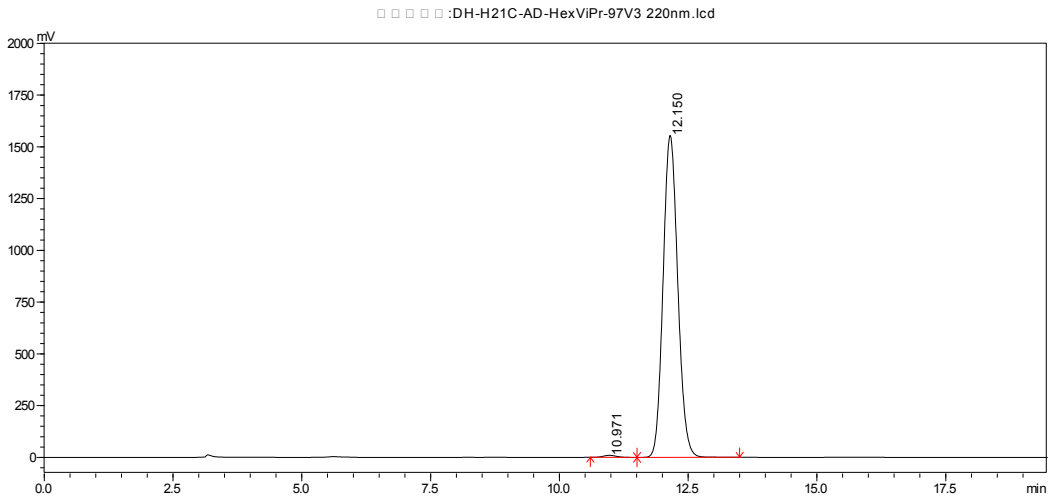
#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	17.224	19683	443010	0.717
2	18.320	2110275	61323733	99.283



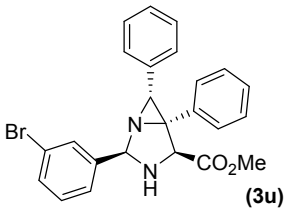
(3t)



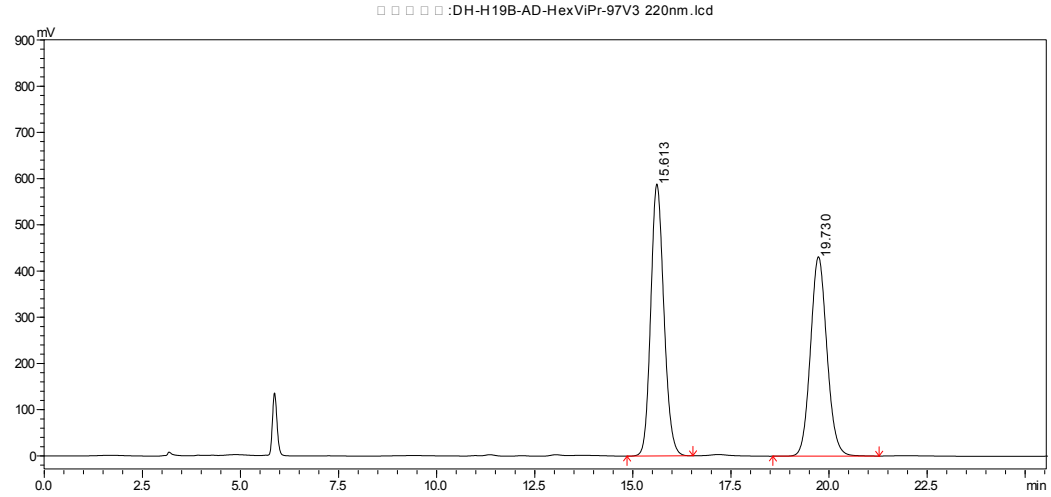
#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	10.957	1268572	24947754	49.463
2	12.229	1352248	25489929	50.537



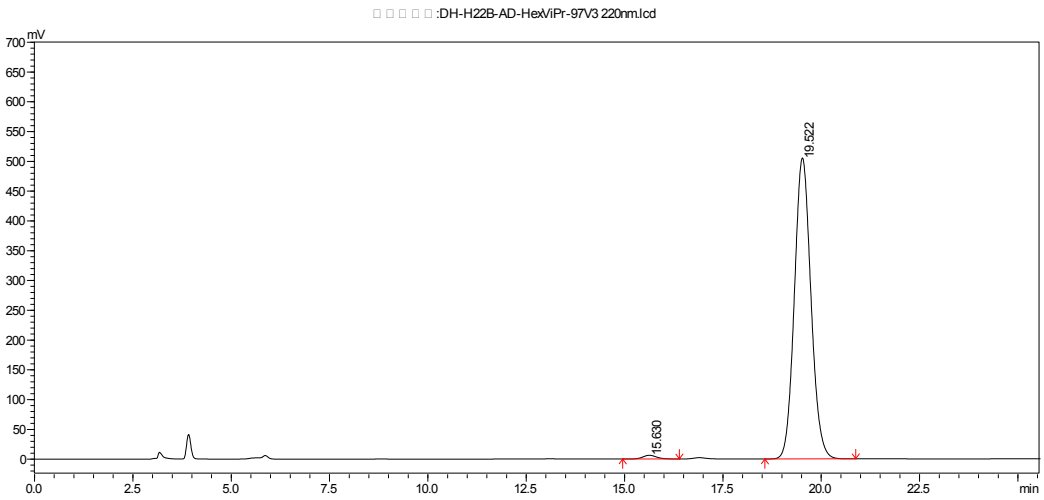
#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	10.971	9522	166604	0.538
2	12.150	1555492	30807953	99.462



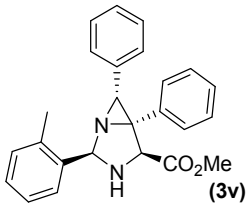
(3u)



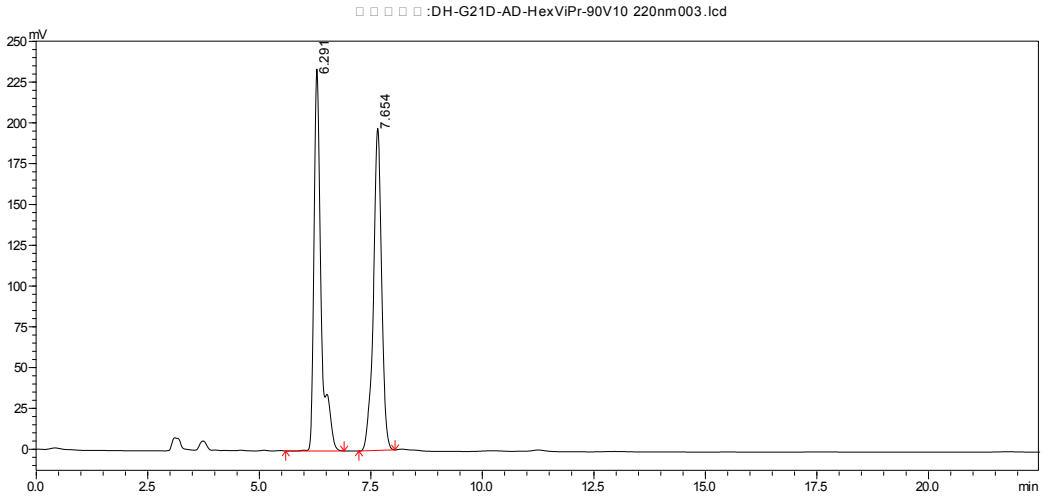
#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	15.613	575131	12887212	50.577
2	19.730	431519	12593207	49.423



#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	15.630	6222	150877	1.009
2	19.522	505312	14801949	98.991

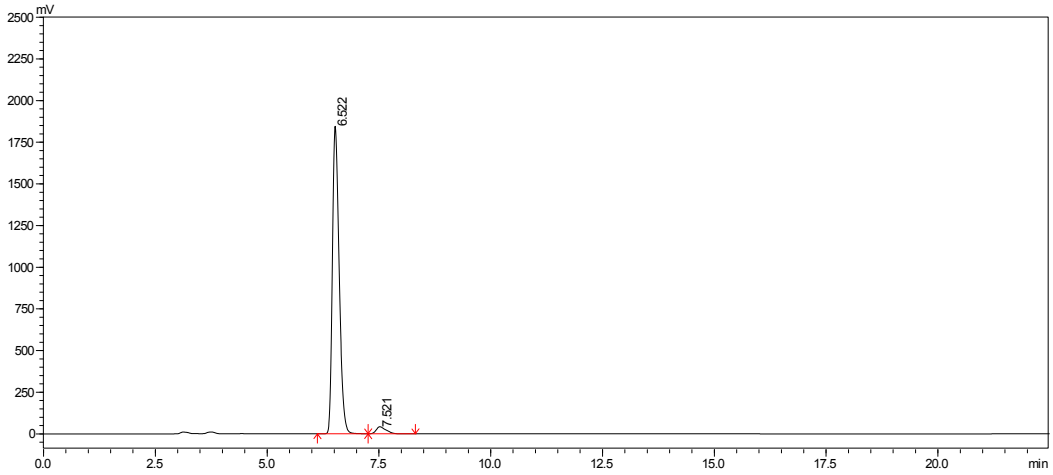


(3v)

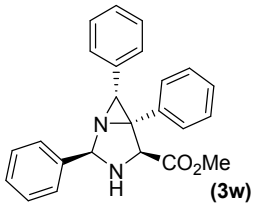


#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	6.291	234099	2589283	50.503
2	7.654	197420	2537686	49.497

□ □ □ □ □ :DH-H26C-AD-HexViPr-90V10 220nm001.lcd

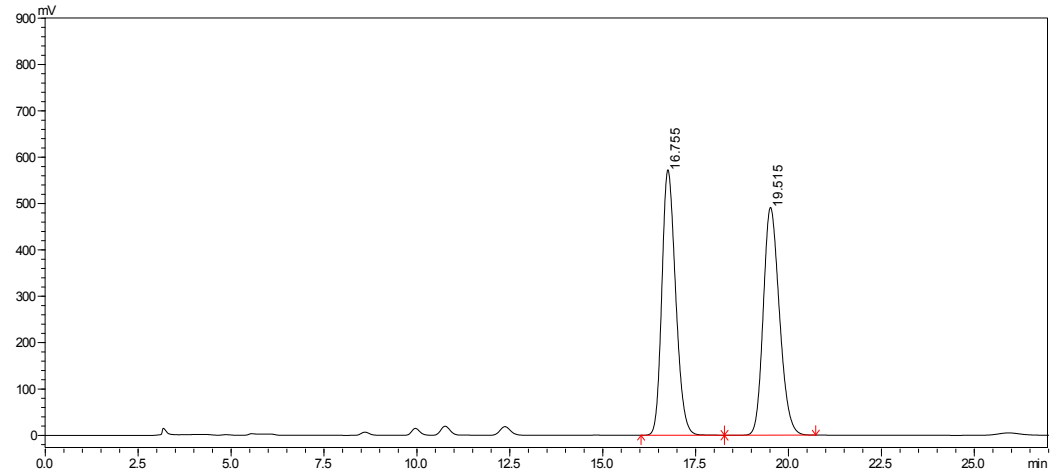


#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	6.522	1845035	19476044	96.753
2	7.521	42629	653678	3.247

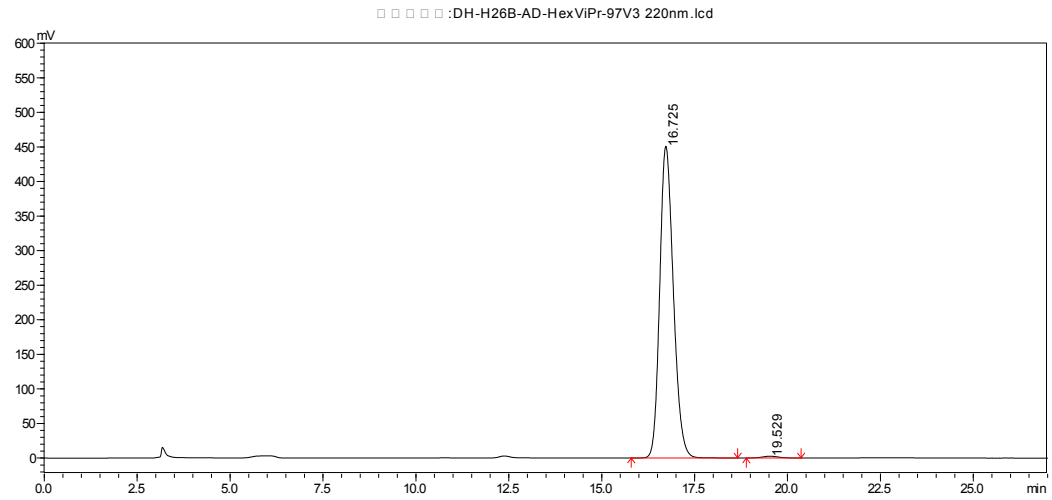


(3w)

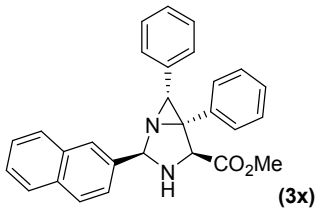
□ □ □ □ □ :DH-G33B-AD-HexViPr-97V3 220nm.lcd



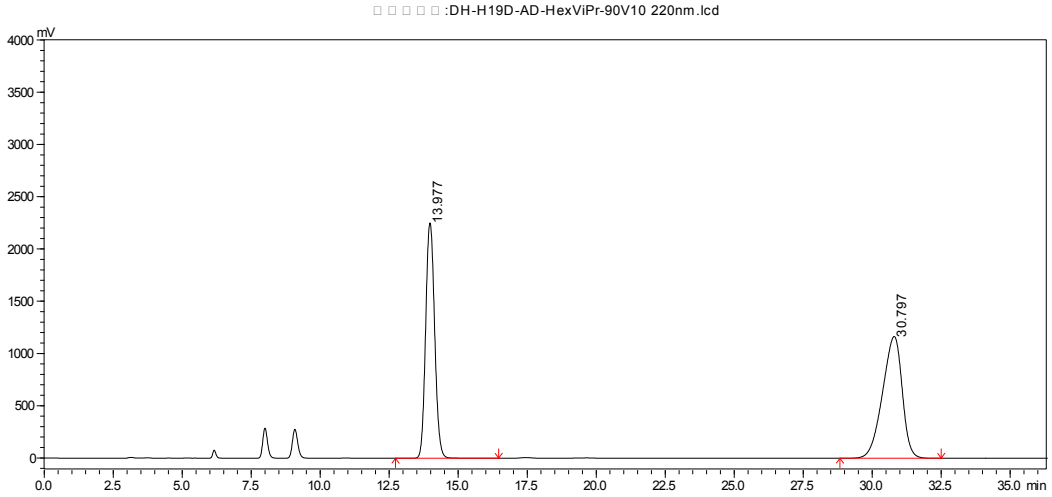
#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	16.755	572551	14783780	49.914
2	19.515	491442	14834806	50.086



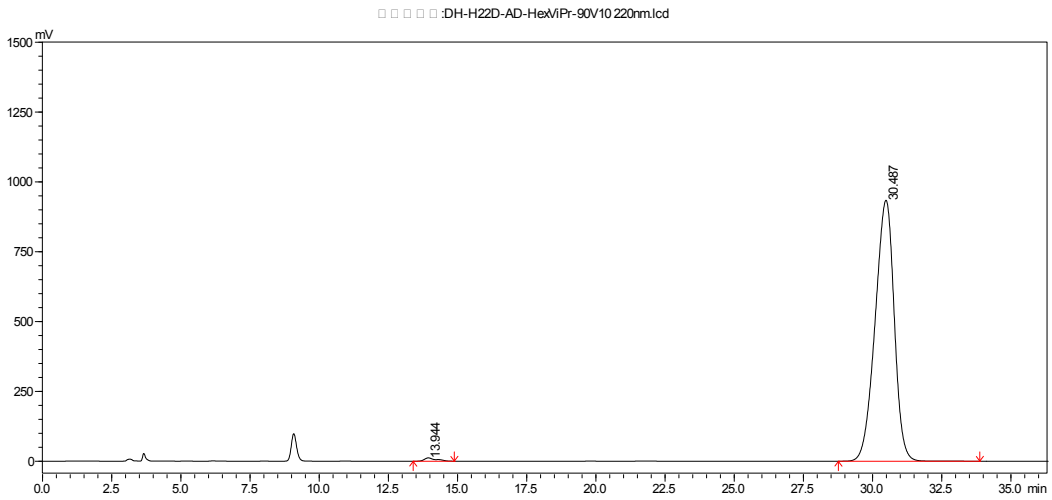
#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	16.725	450723	11500148	99.340
2	19.529	2582	76359	0.660



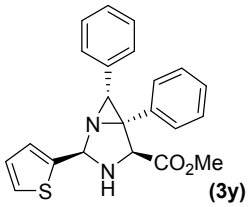
(3x)



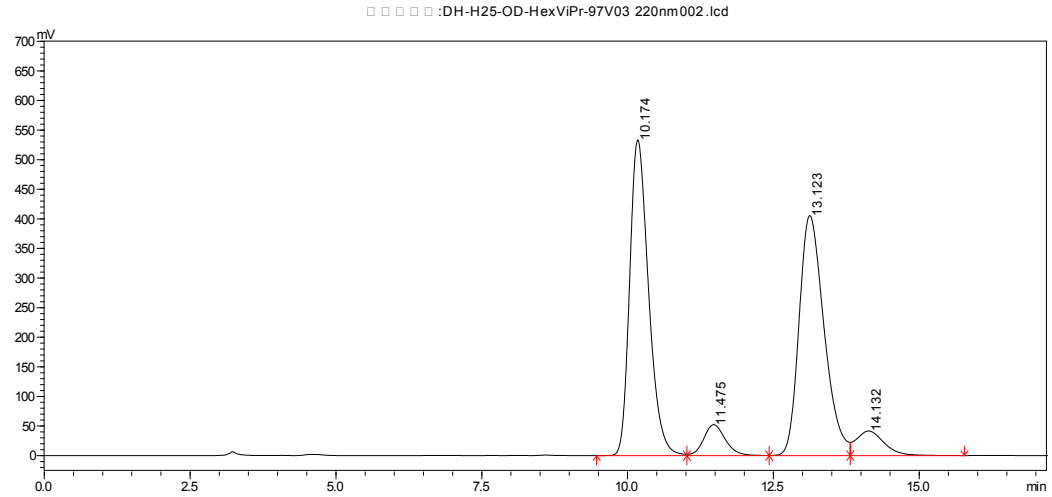
#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	13.977	2251648	50847363	49.789
2	30.797	1108155	51278609	50.211



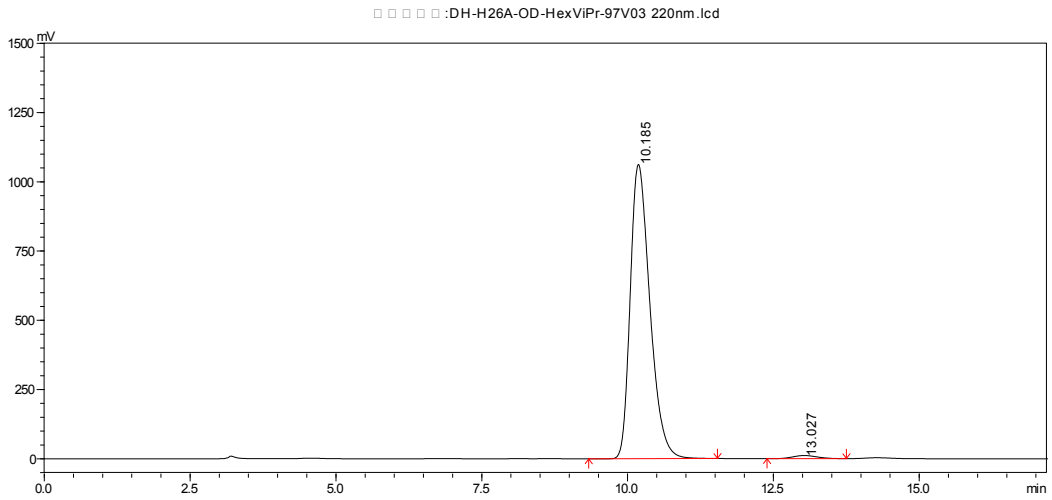
#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	13.944	11970	270856	0.601
2	30.487	934324	44832018	99.399



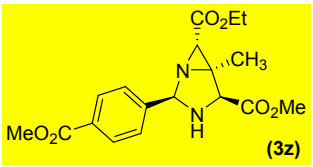
(3y)

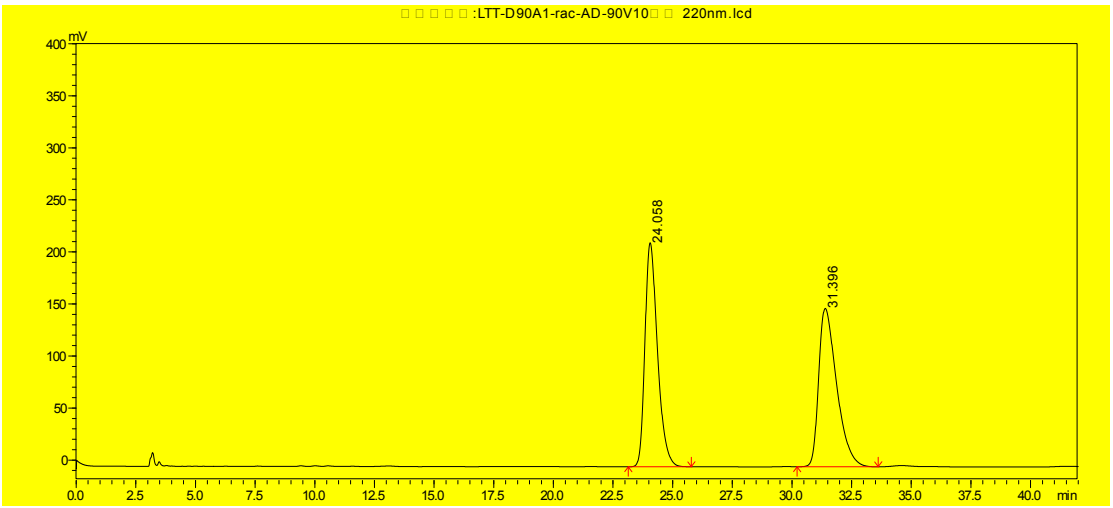


#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	10.174	533539	12019123	44.749
2	11.475	52286	1352001	5.034
3	13.123	405479	12136612	45.186
4	14.132	41492	1351421	5.032

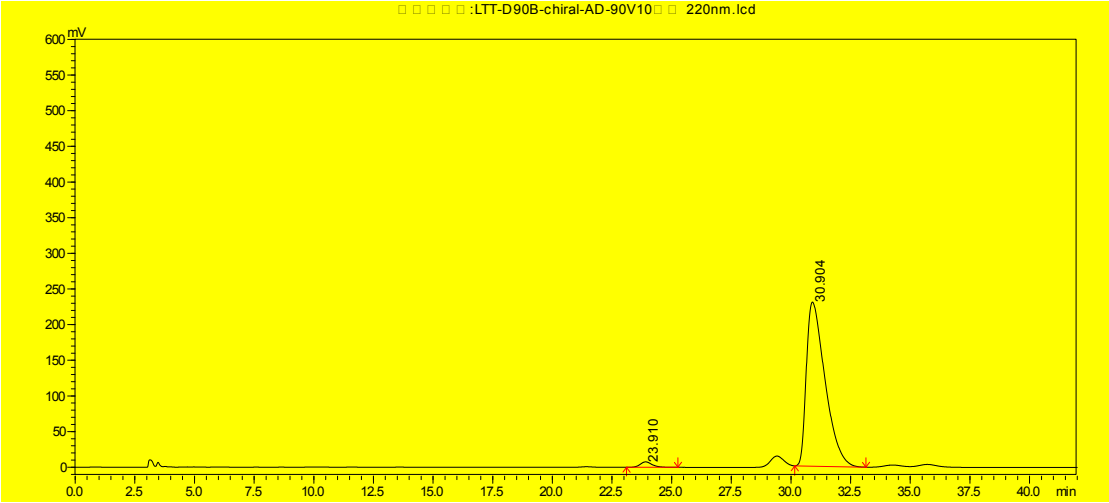


#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	10.185	1062352	24902264	98.851
2	13.027	10599	289406	1.149

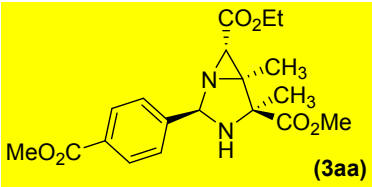


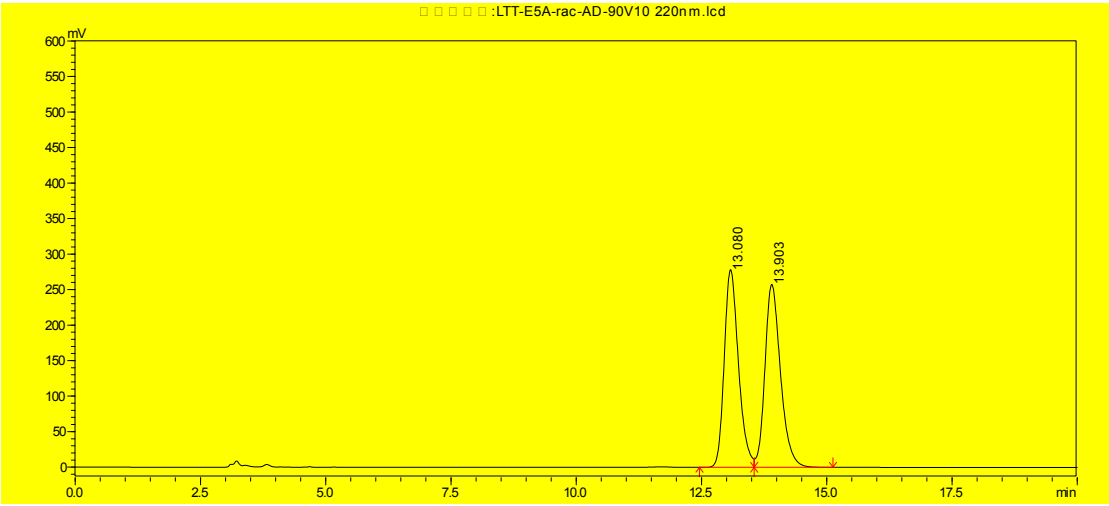


#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	24.058	215238	7876063	49.673
2	31.396	152067	7979676	50.327

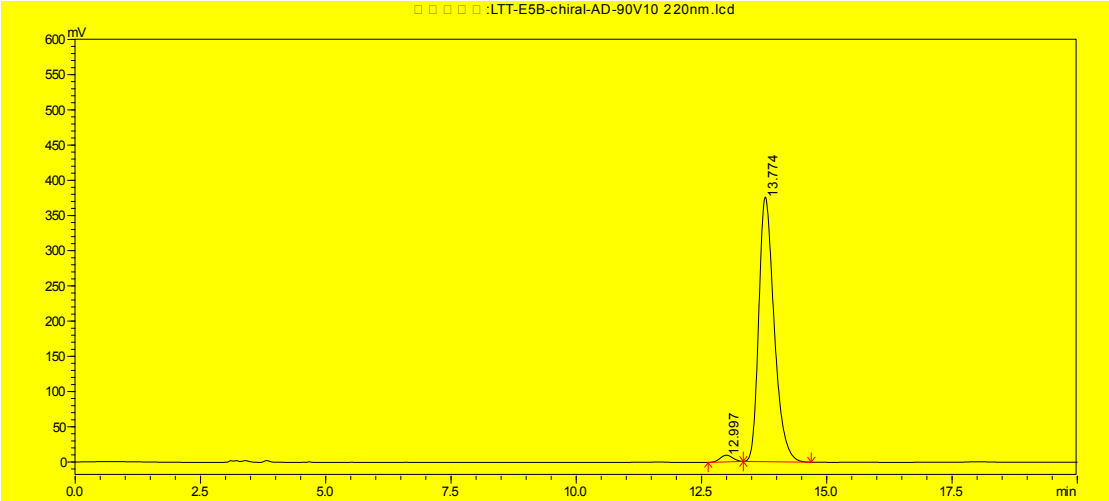


#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	23.910	7625	266005	2.074
2	30.904	230261	12558636	97.926





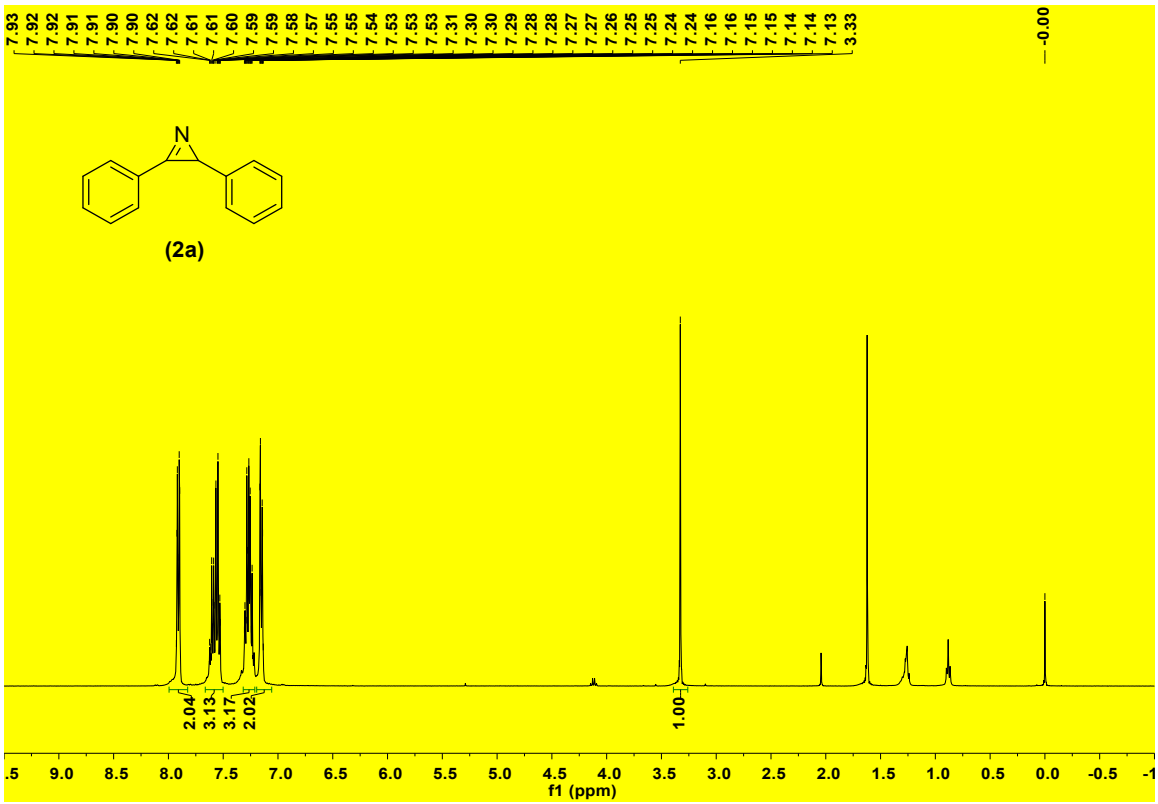
#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	13.080	278252	5493249	49.608
2	13.903	257666	5580125	50.392



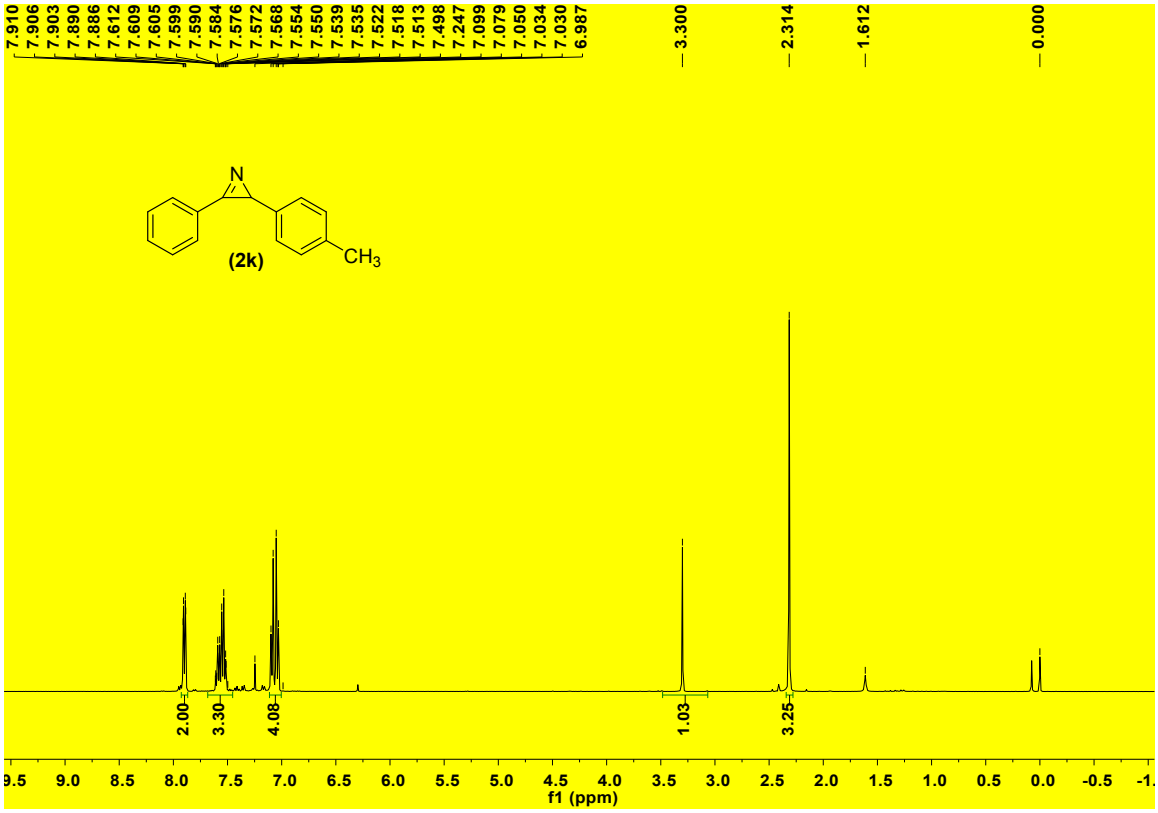
#	Ret Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	12.997	9496	165332	2.019
2	13.774	375819	8025155	97.981

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

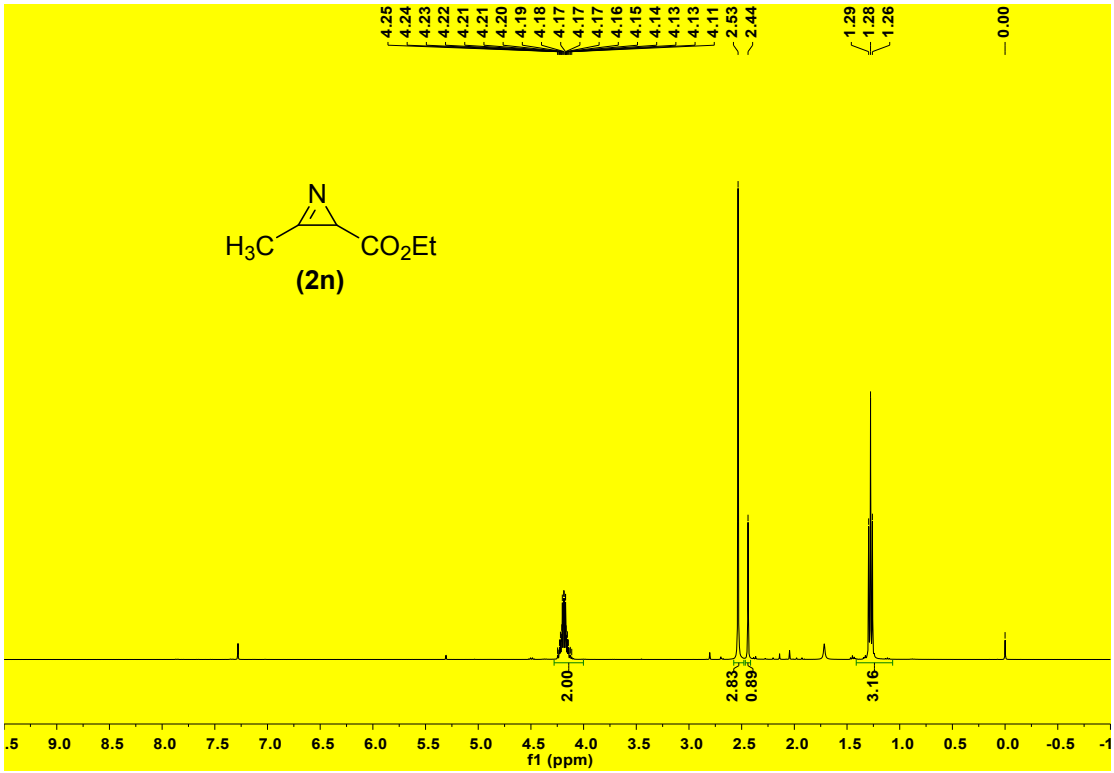
^{1}H NMR spectrum of compound **2a** ($CDCl_3$)



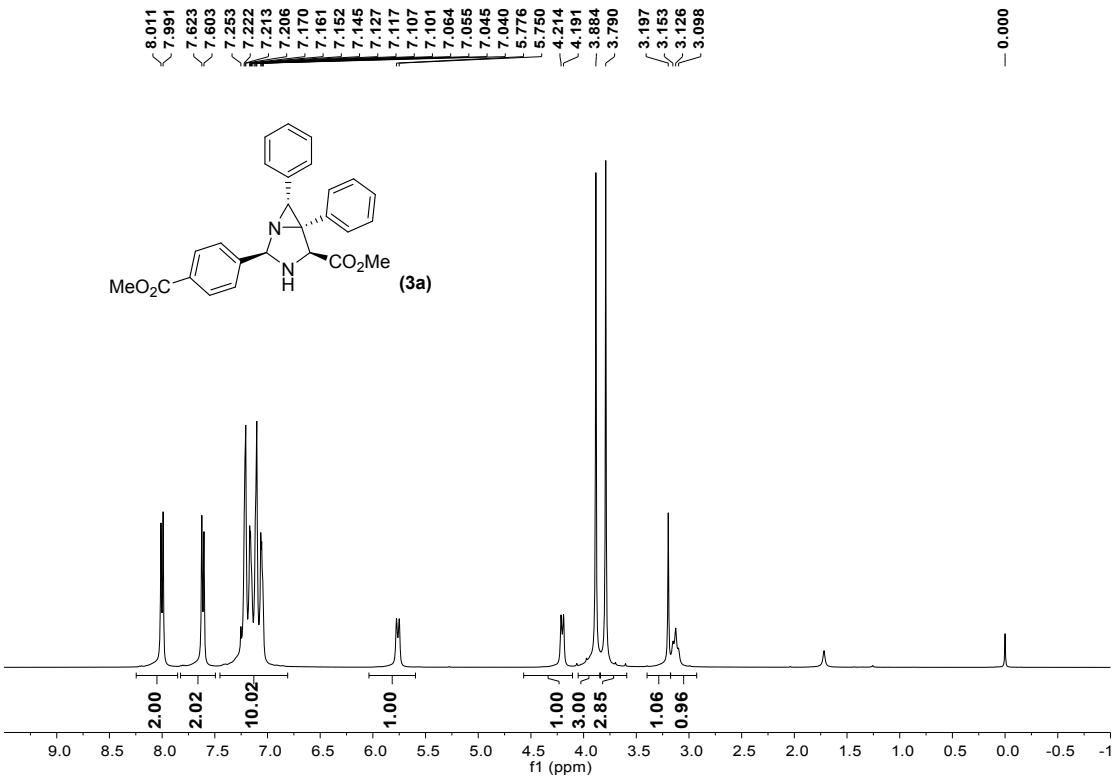
^{1}H NMR spectrum of compound **2k** ($CDCl_3$)



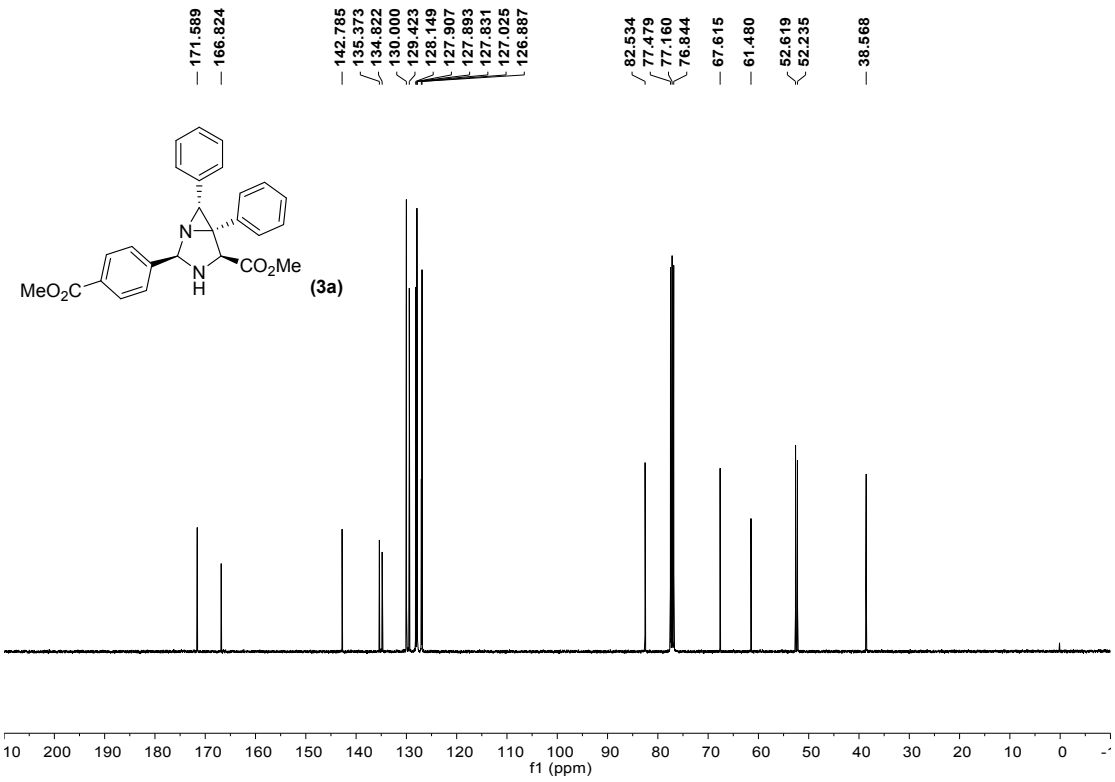
^{1}H NMR spectrum of compound **2n** ($CDCl_3$)



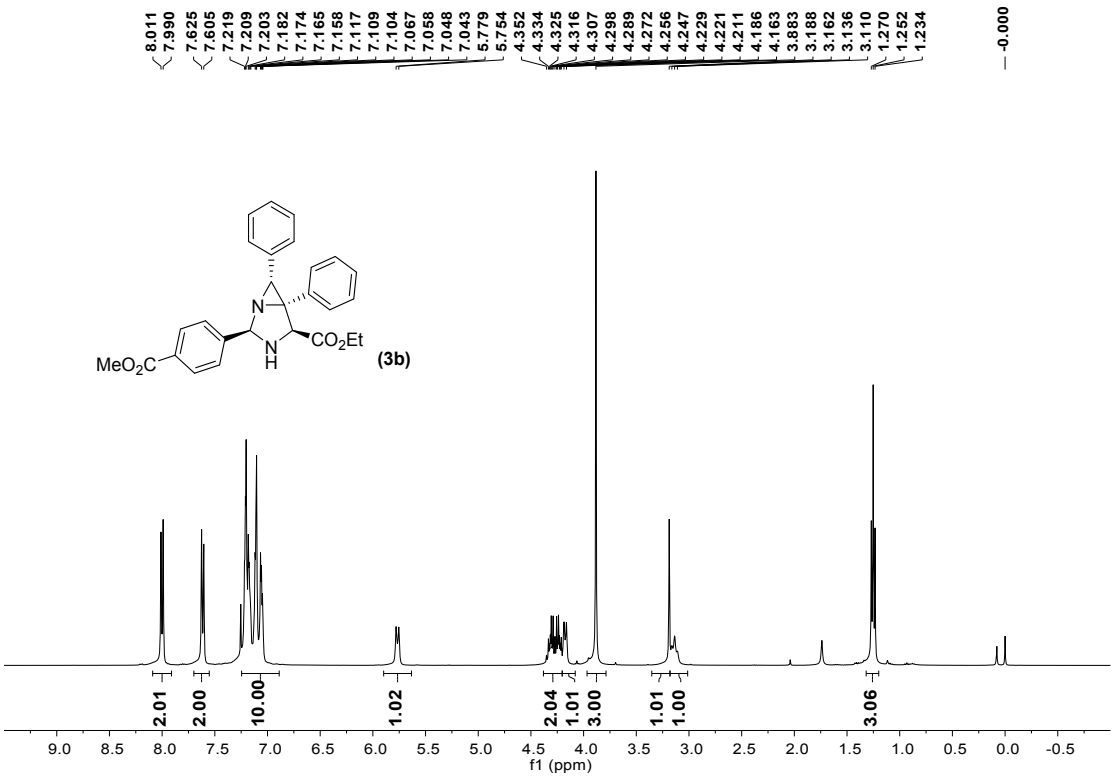
^{1}H NMR spectrum of compound **3a** ($CDCl_3$)



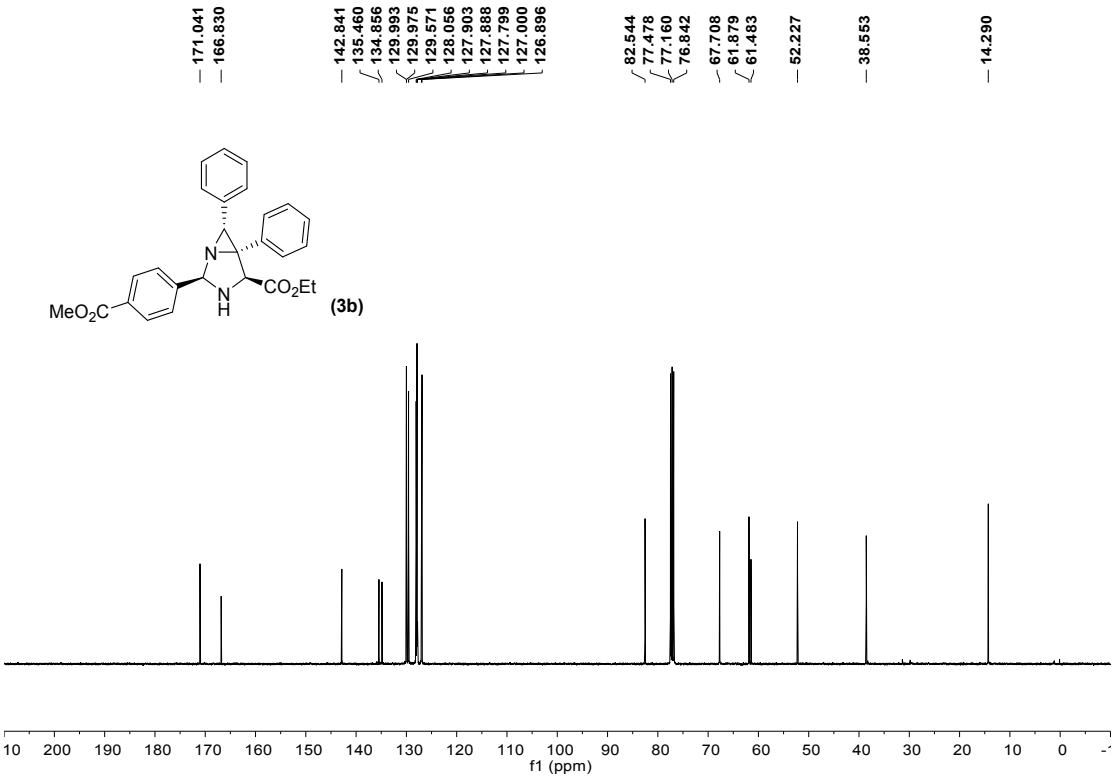
^{13}C NMR spectrum of compound **3a** ($CDCl_3$)



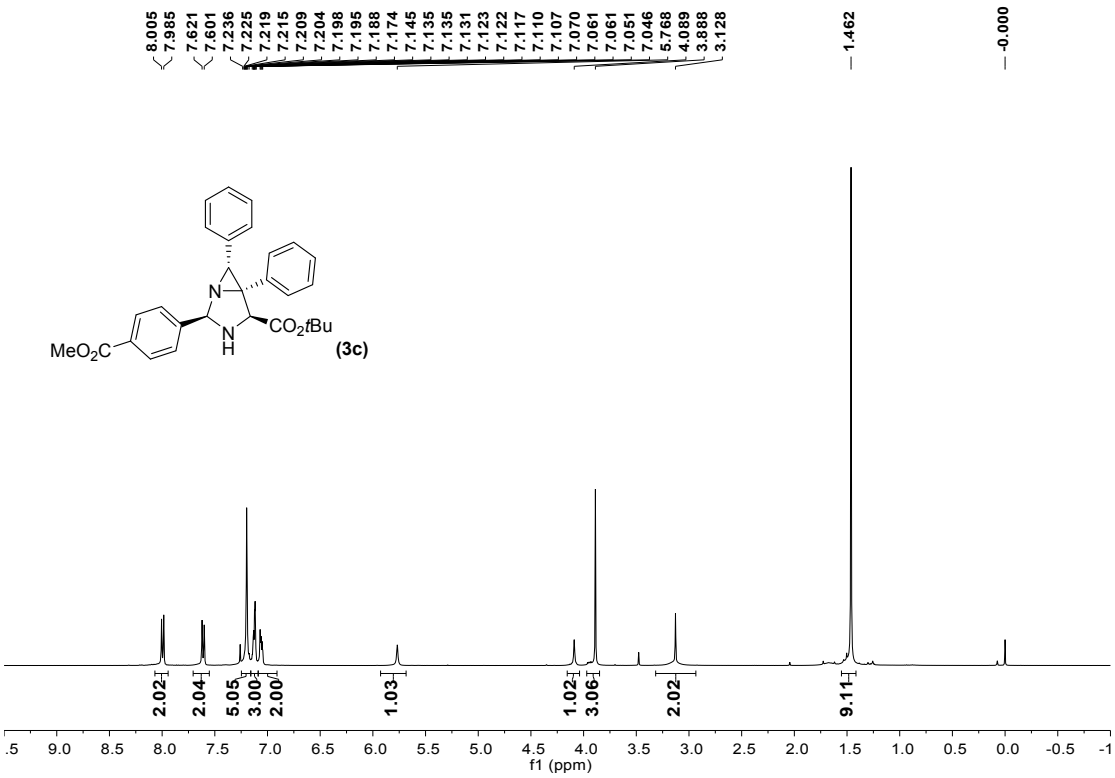
^{1}H NMR spectrum of compound **3b** ($CDCl_3$)



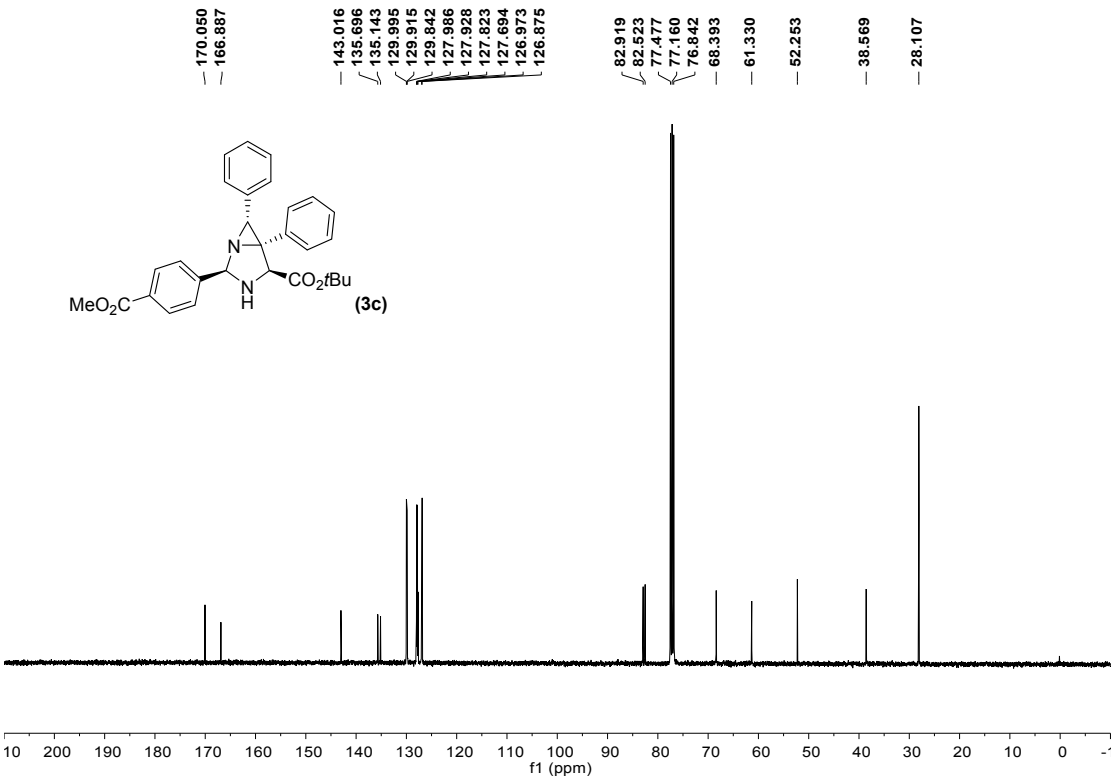
^{13}C NMR spectrum of compound **3b** ($CDCl_3$)



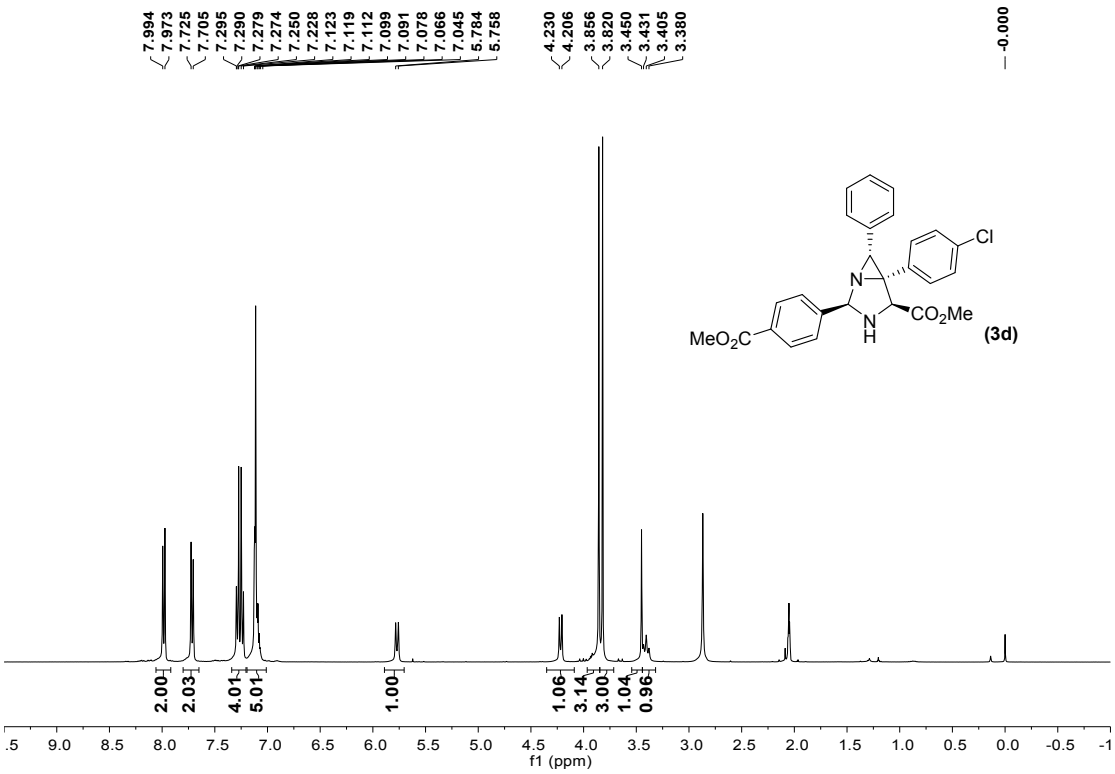
^{1}H NMR spectrum of compound **3c** ($CDCl_3$)



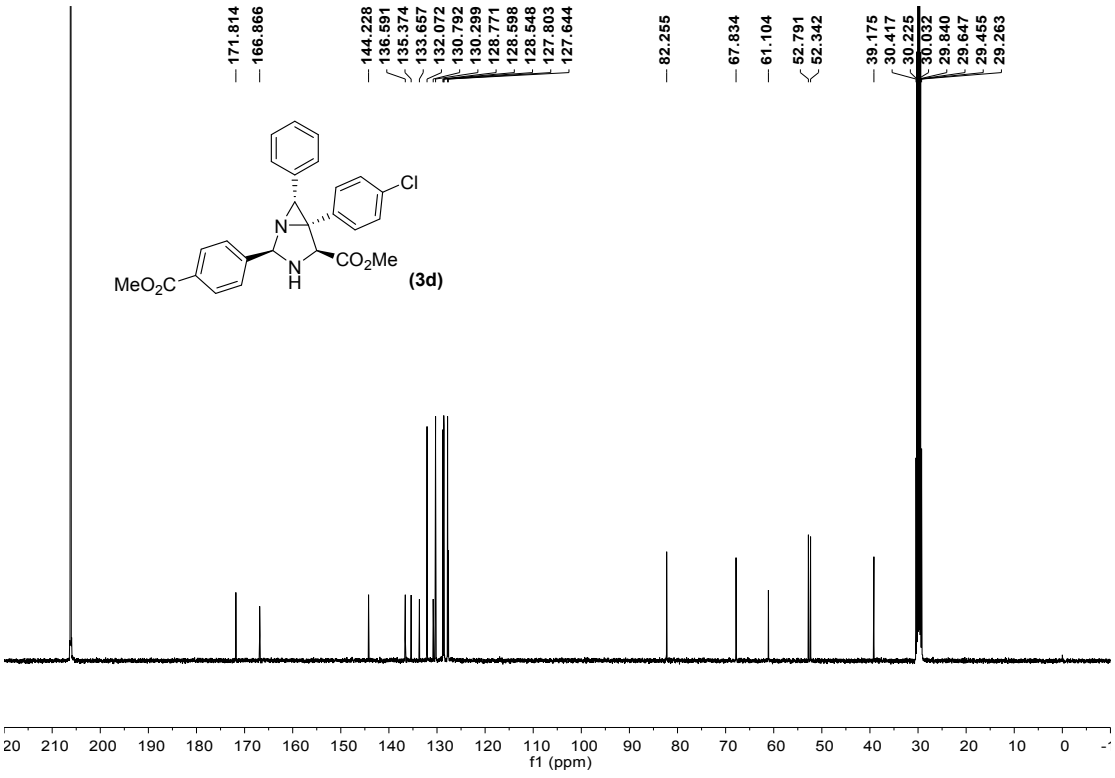
^{13}C NMR spectrum of compound **3c** ($CDCl_3$)



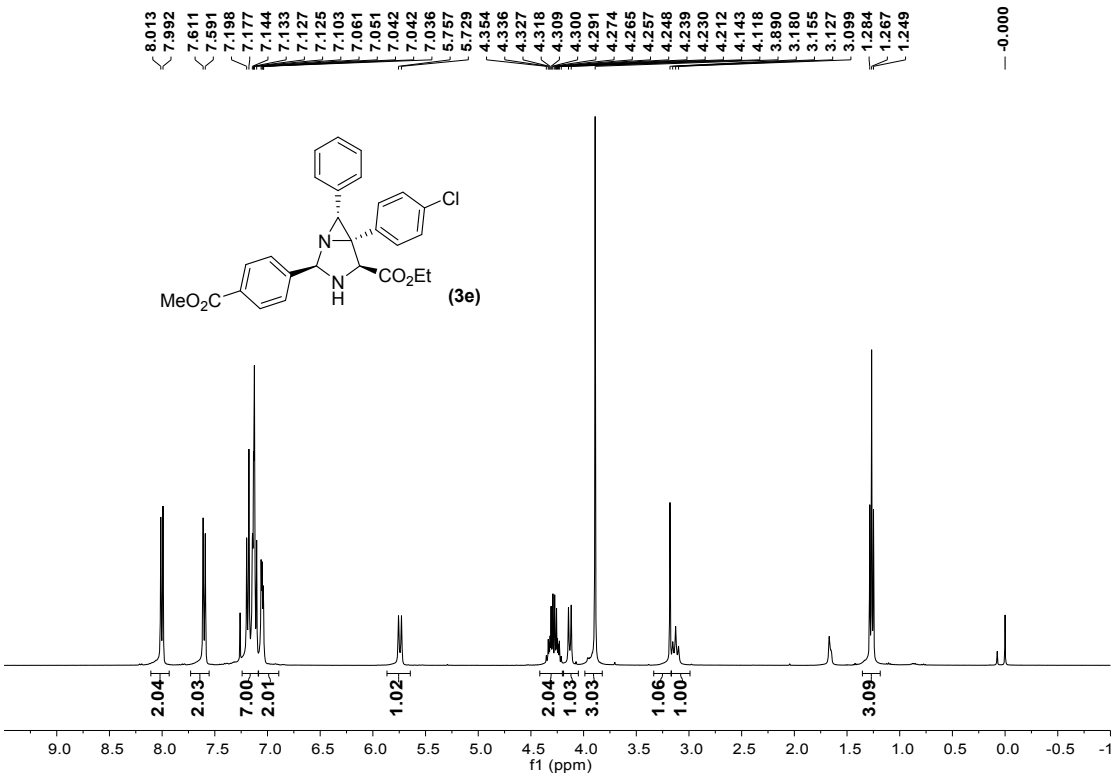
^{1}H NMR spectrum of compound **3d** (Acetone-d_6)



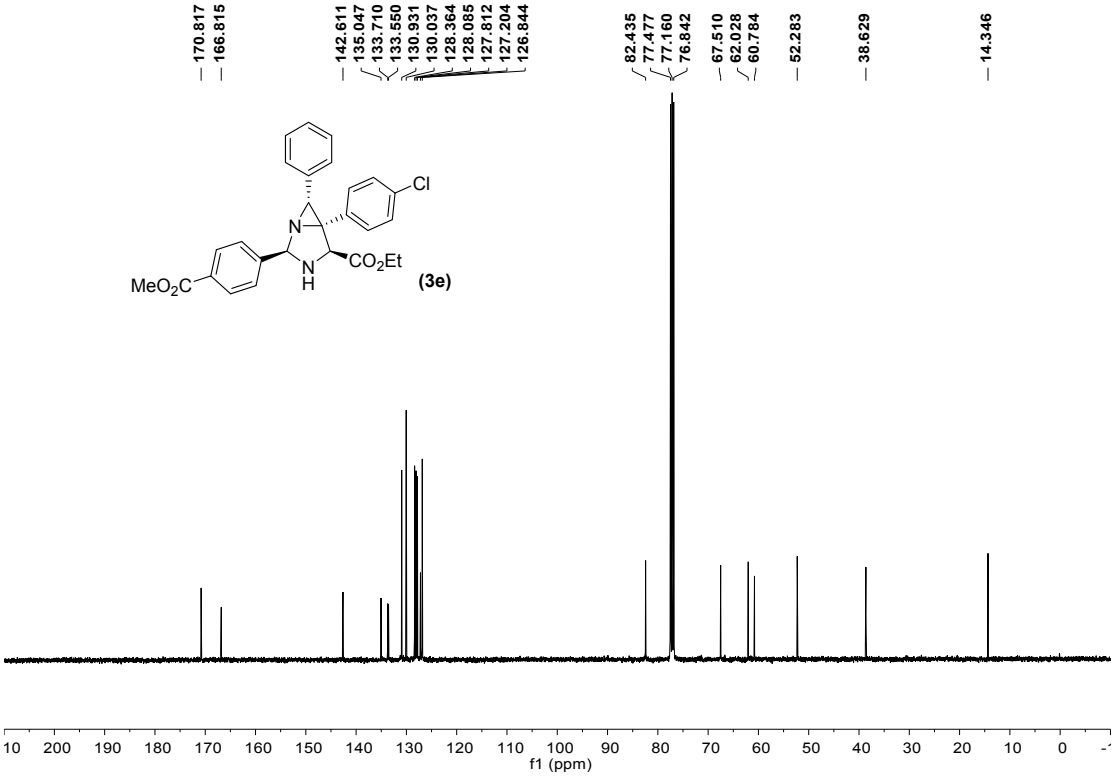
^{13}C NMR spectrum of compound **3d** (Acetone-d_6)



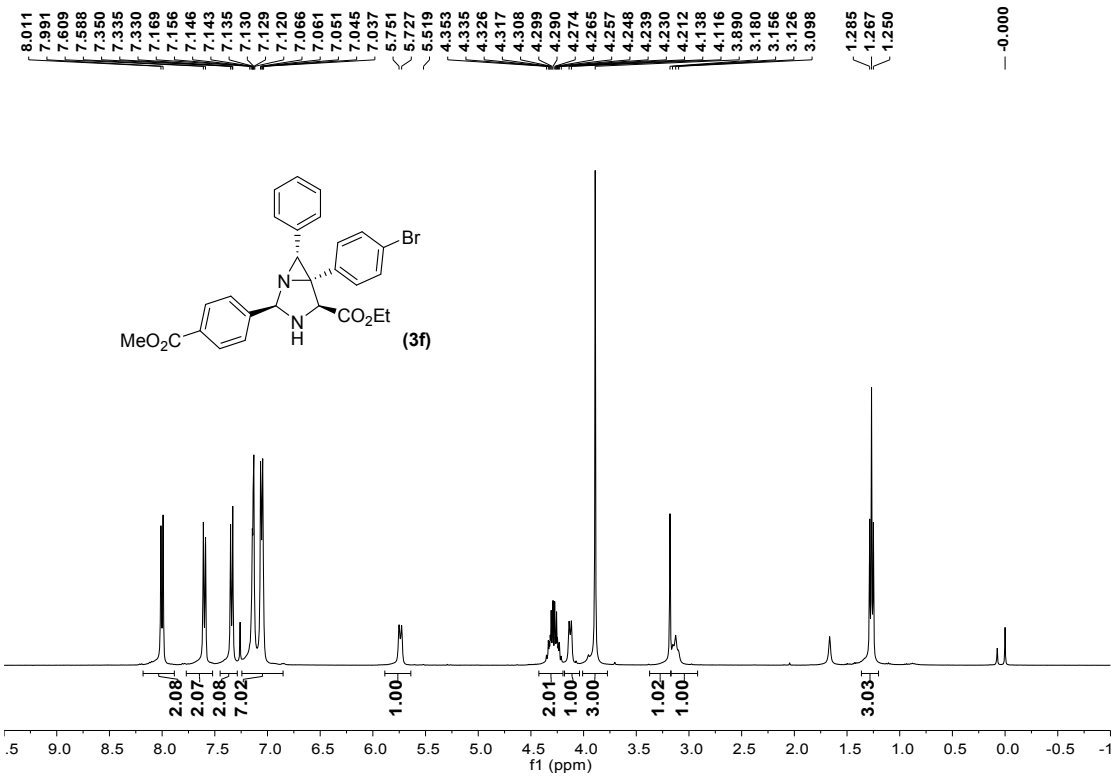
^{1}H NMR spectrum of compound **3e** ($CDCl_3$)



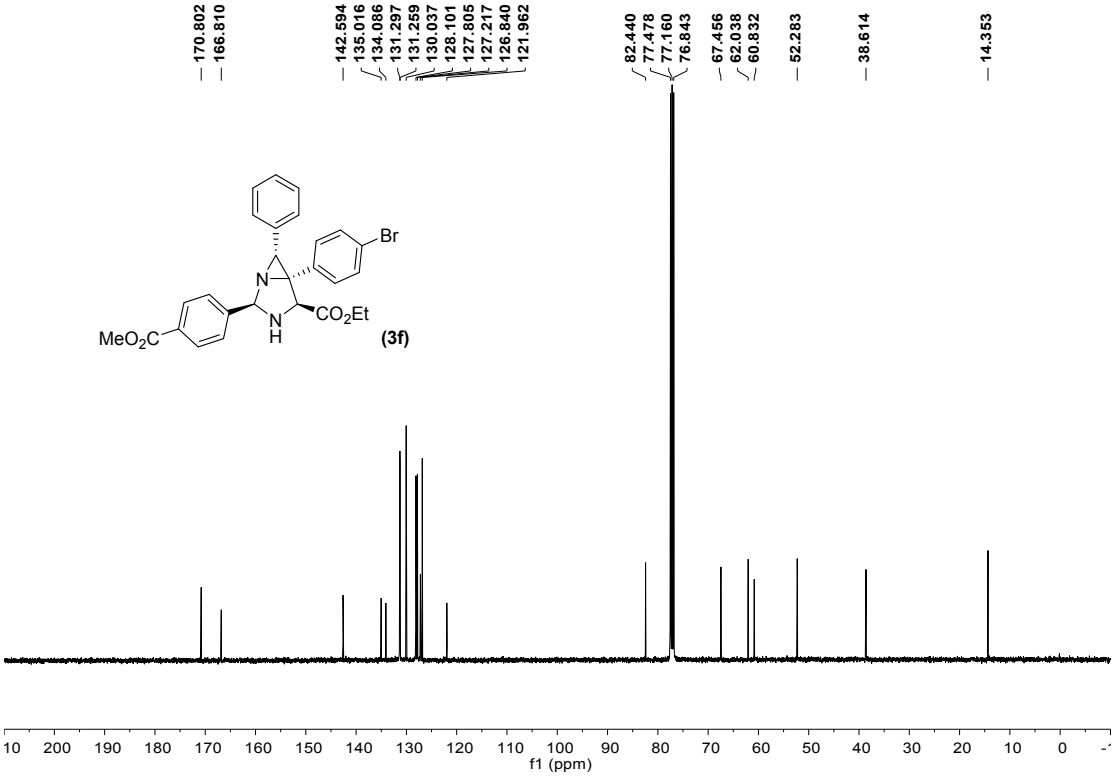
^{13}C NMR spectrum of compound **3e** ($CDCl_3$)



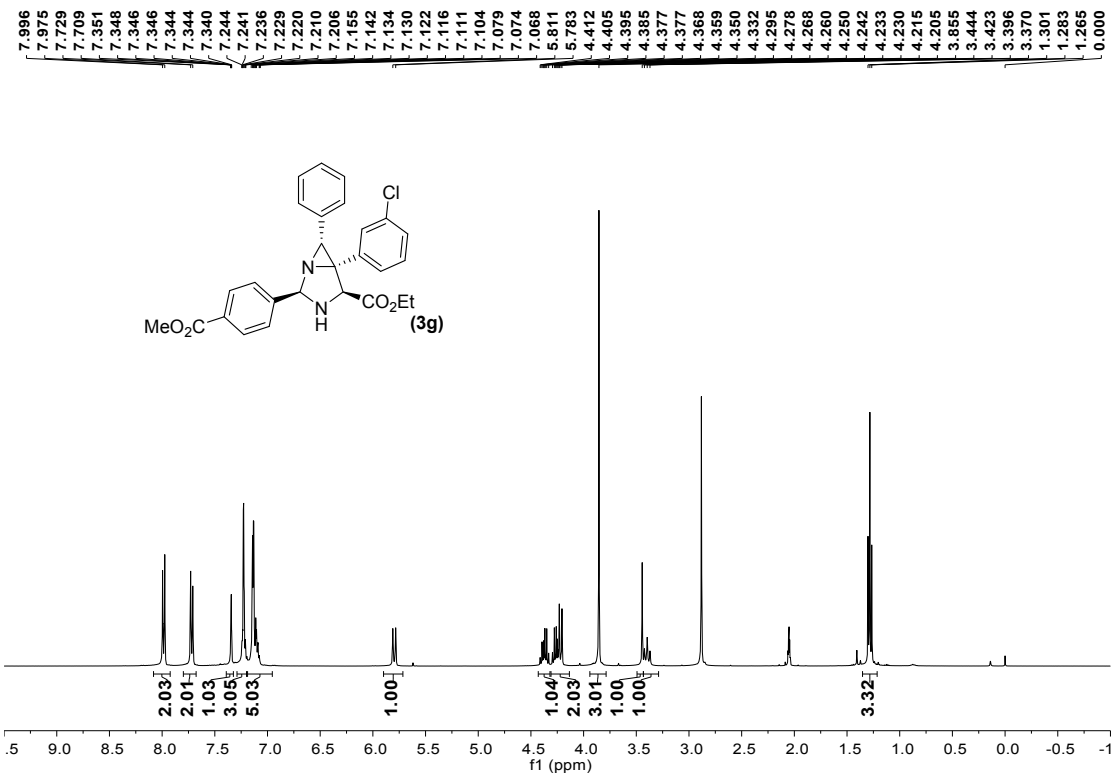
^{1}H NMR spectrum of compound **3f** ($CDCl_3$)



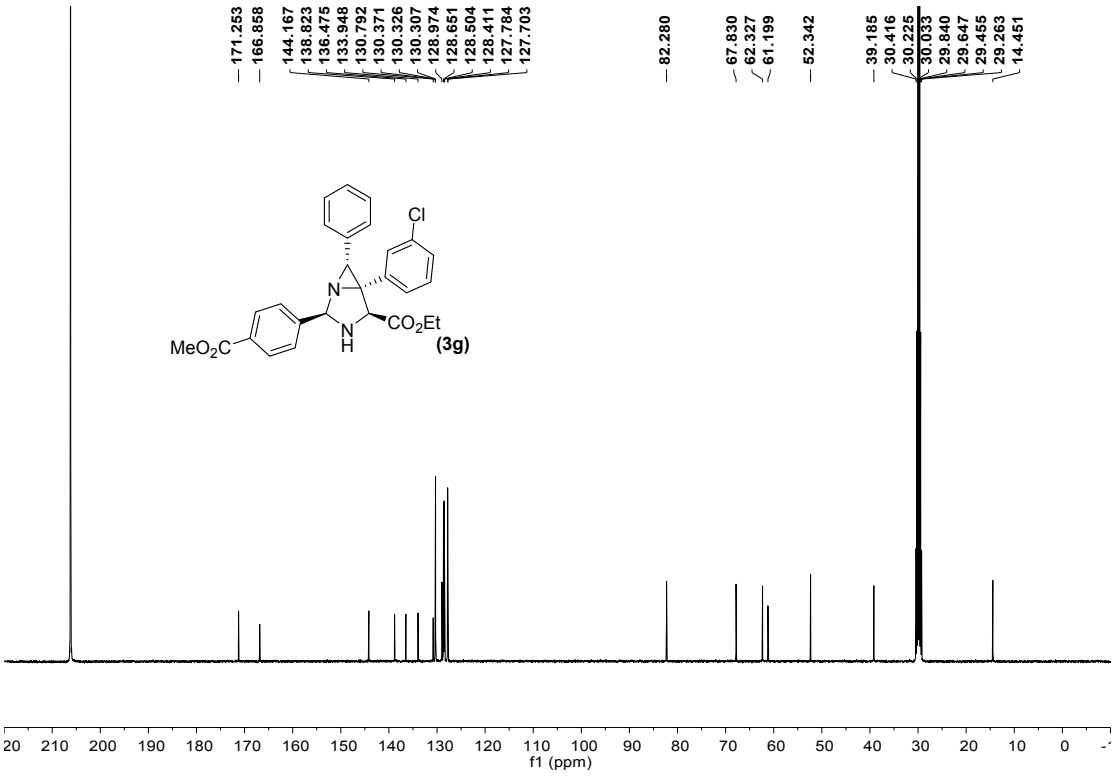
^{13}C NMR spectrum of compound **3f** ($CDCl_3$)



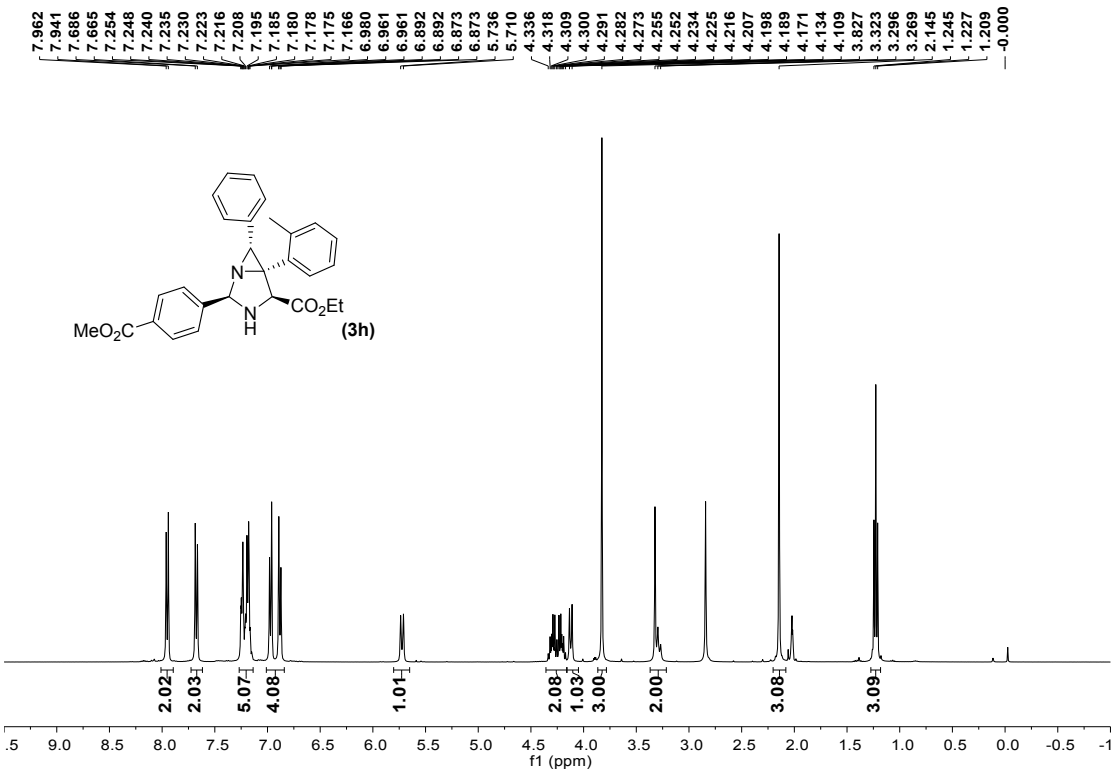
^{1}H NMR spectrum of compound **3g** (Acetone-d_6)



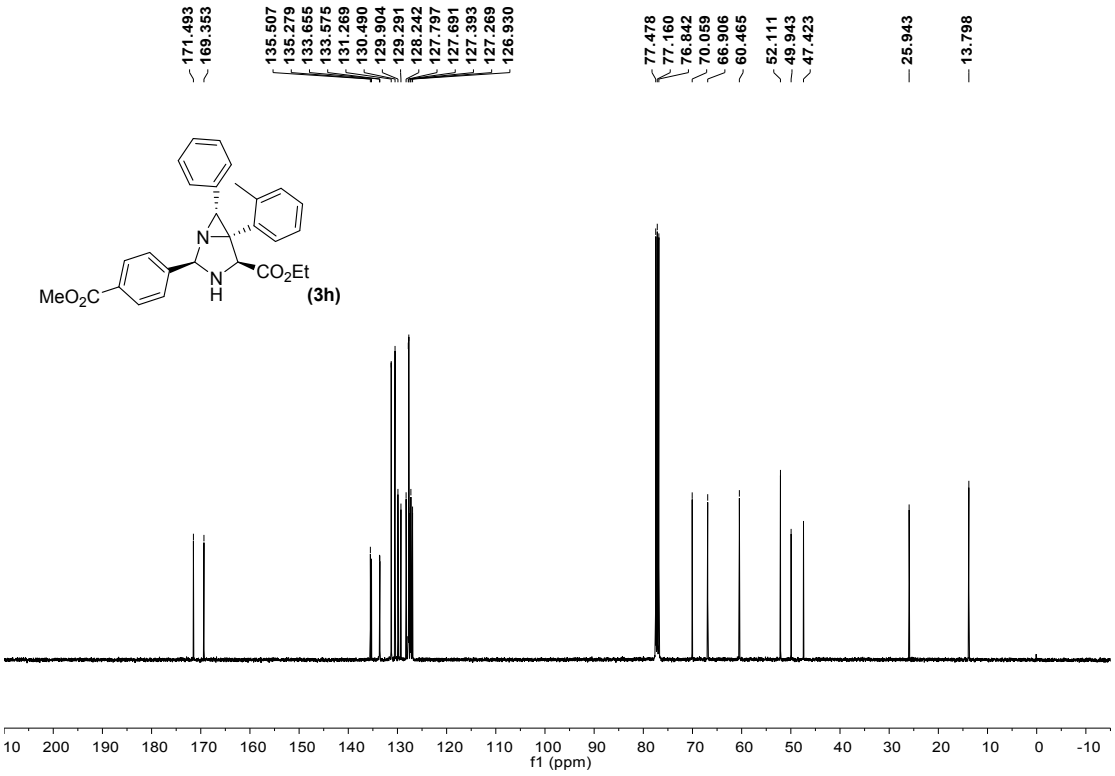
^{13}C NMR spectrum of compound **3g** (Acetone-d_6)



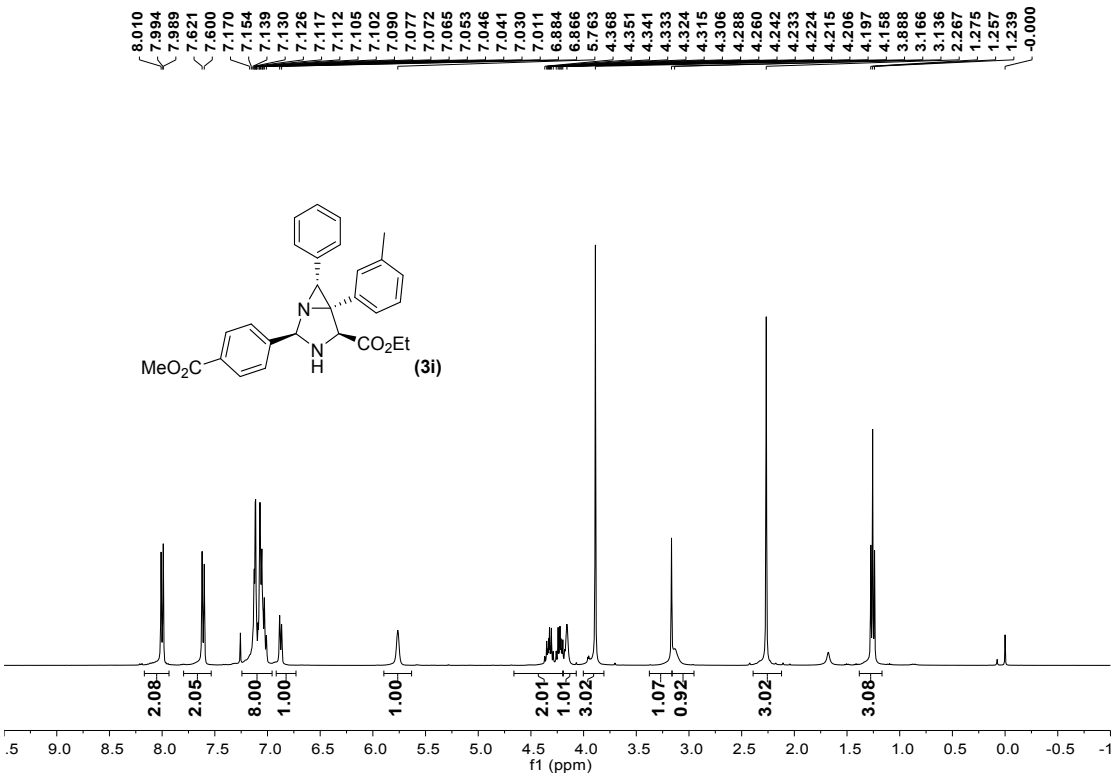
^{1}H NMR spectrum of compound **3h** (Acetone-d_6)



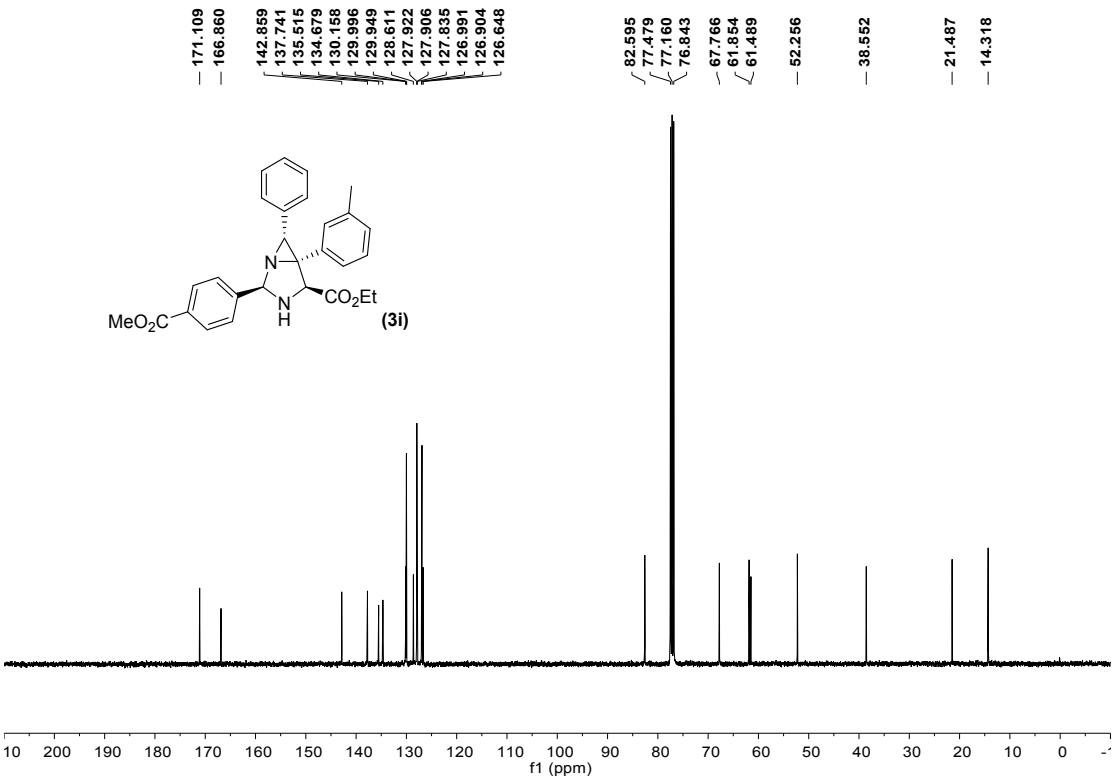
^{13}C NMR spectrum of compound **3h** ($CDCl_3$)



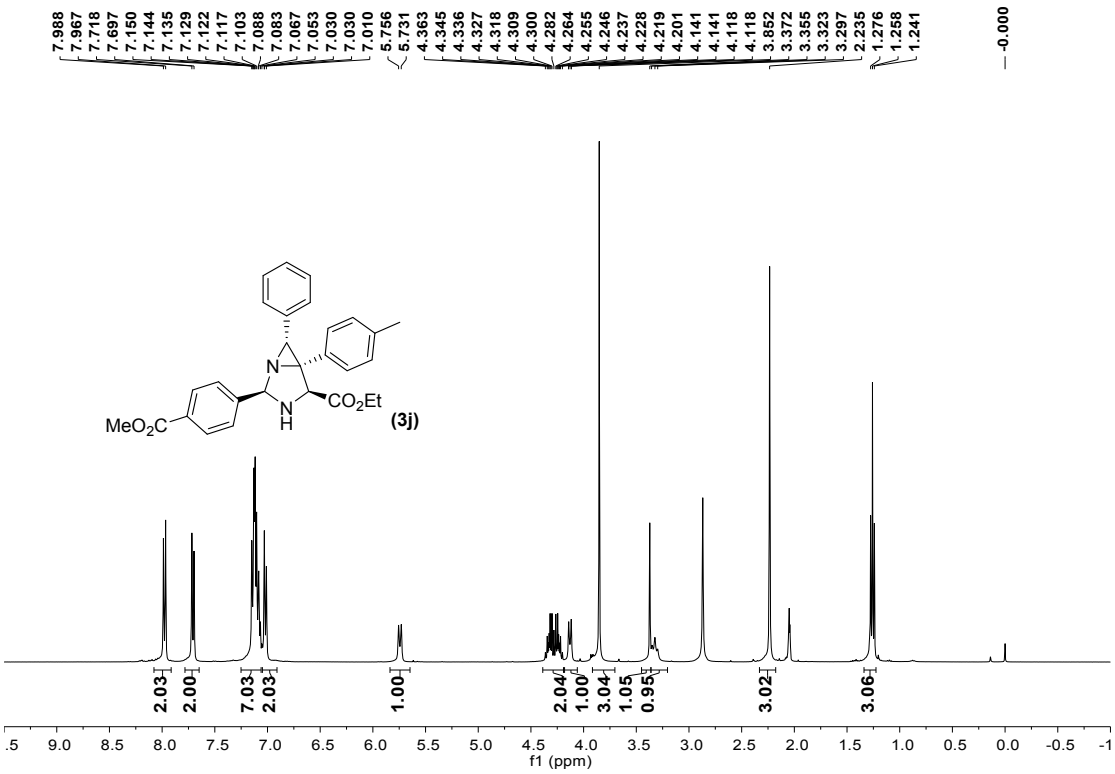
^{1}H NMR spectrum of compound **3i** ($CDCl_3$)



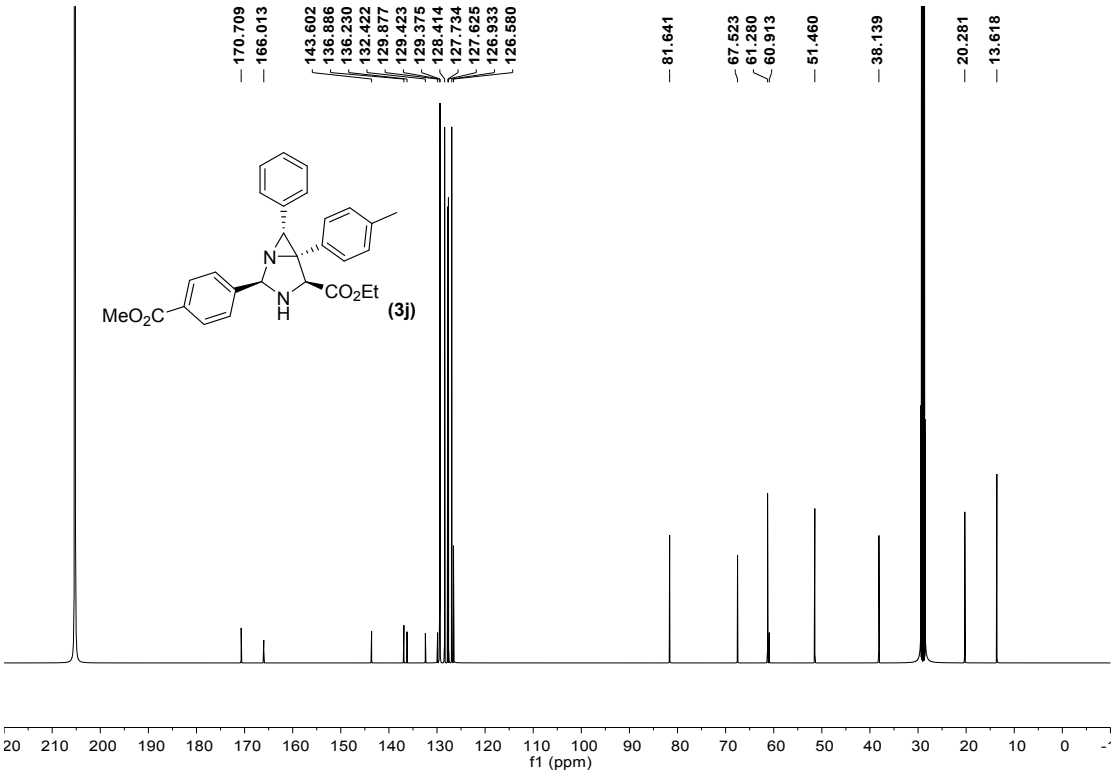
^{13}C NMR spectrum of compound **3i** ($CDCl_3$)



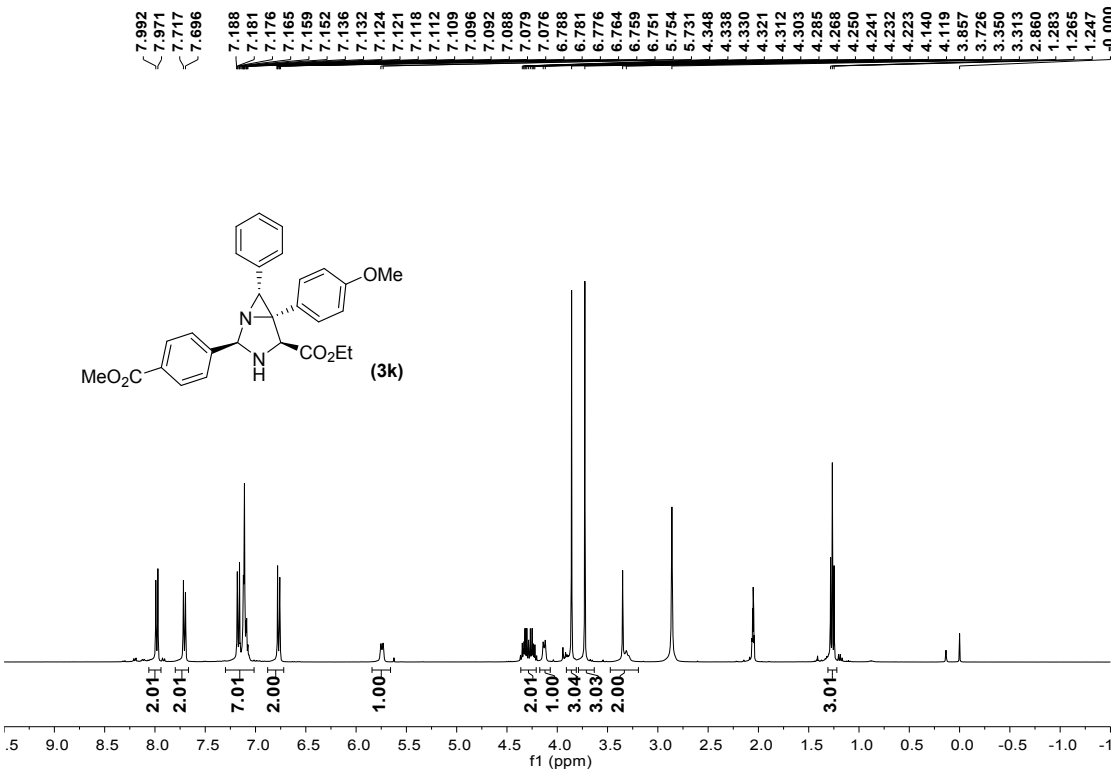
^{1}H NMR spectrum of compound **3j** (Acetone-d_6)



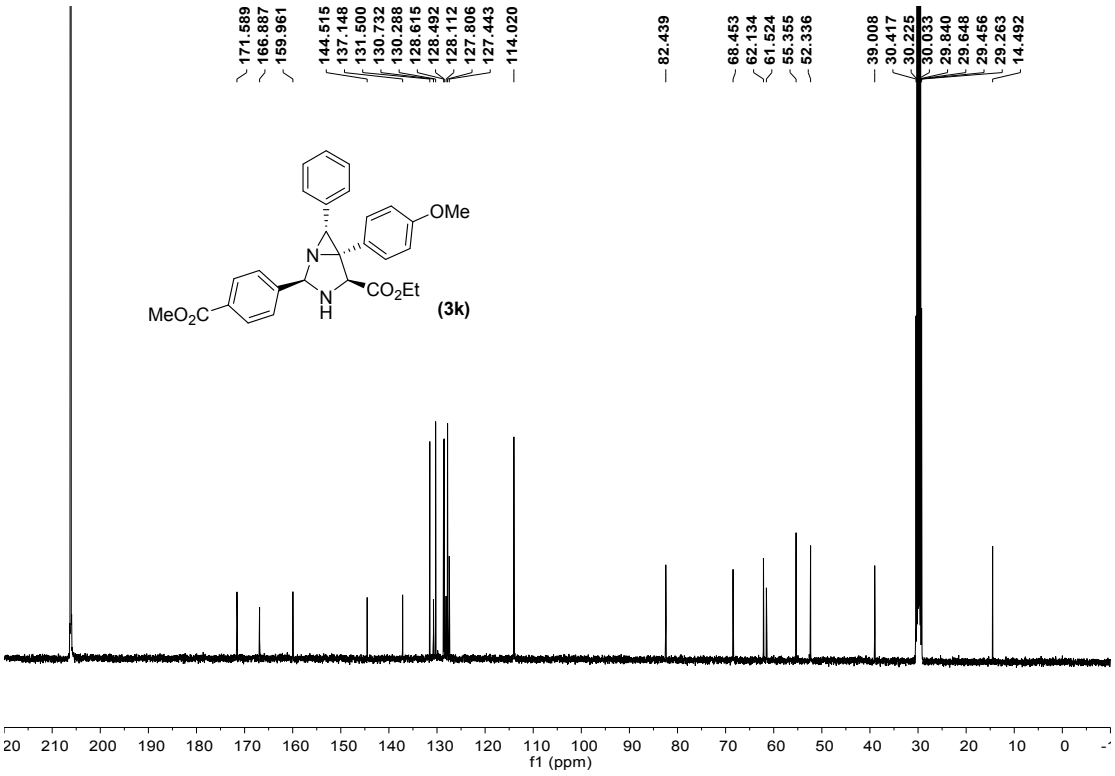
^{13}C NMR spectrum of compound **3j** (Acetone-d_6)



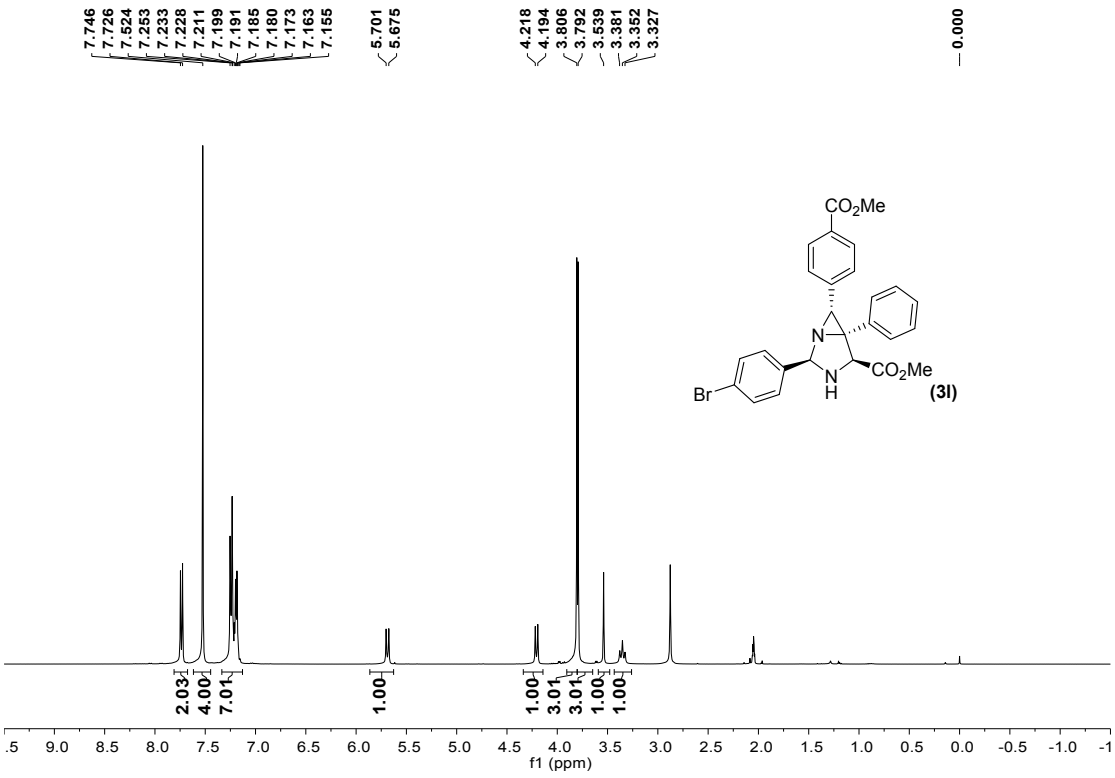
^{1}H NMR spectrum of compound **3k** (Acetone-d_6)



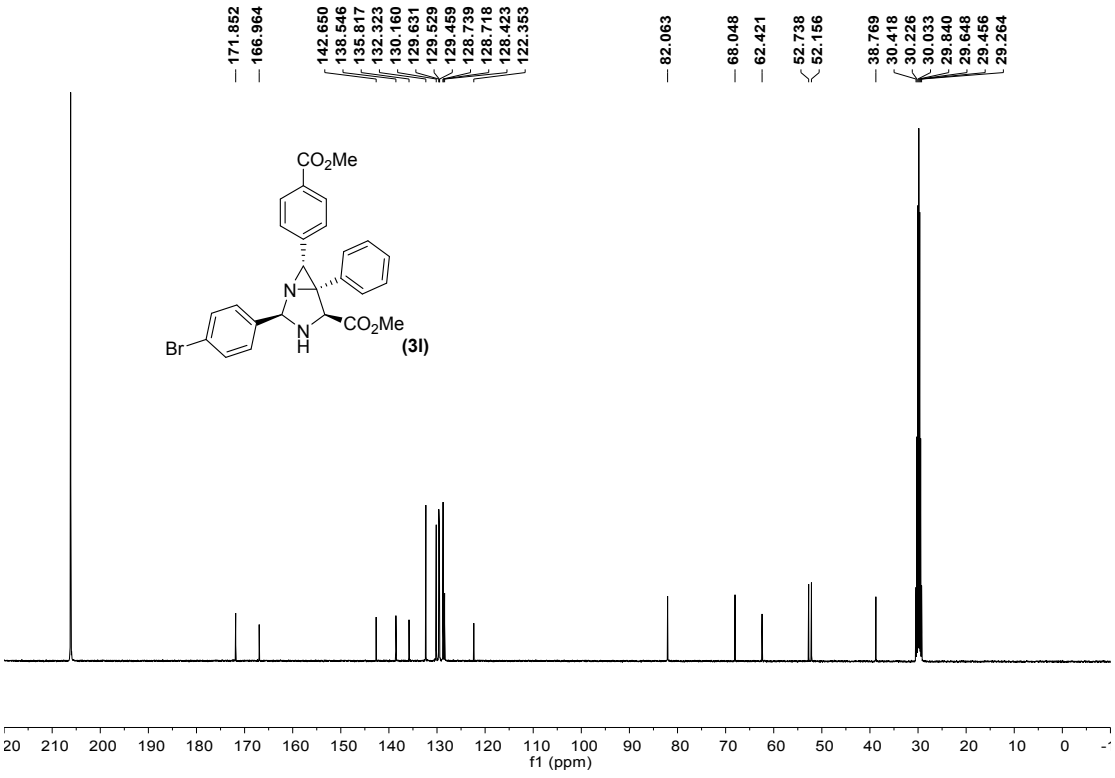
^{13}C NMR spectrum of compound **3k** (Acetone-d_6)



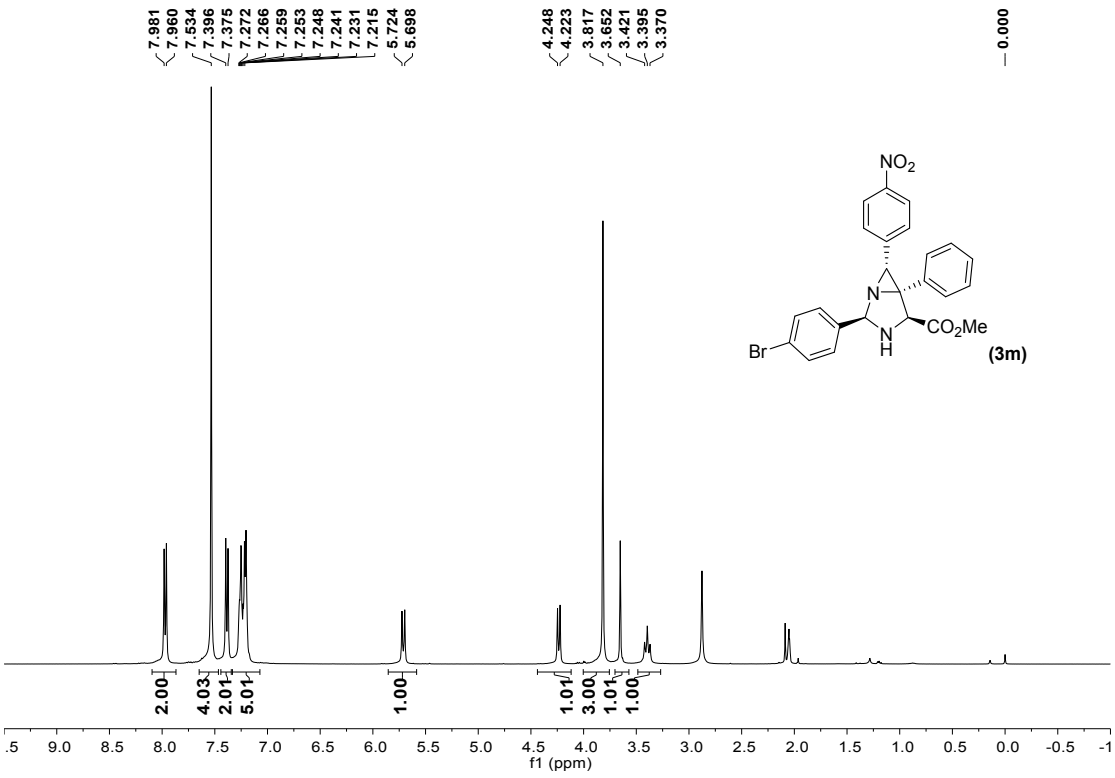
^{1}H NMR spectrum of compound **3l** (Acetone-d_6)



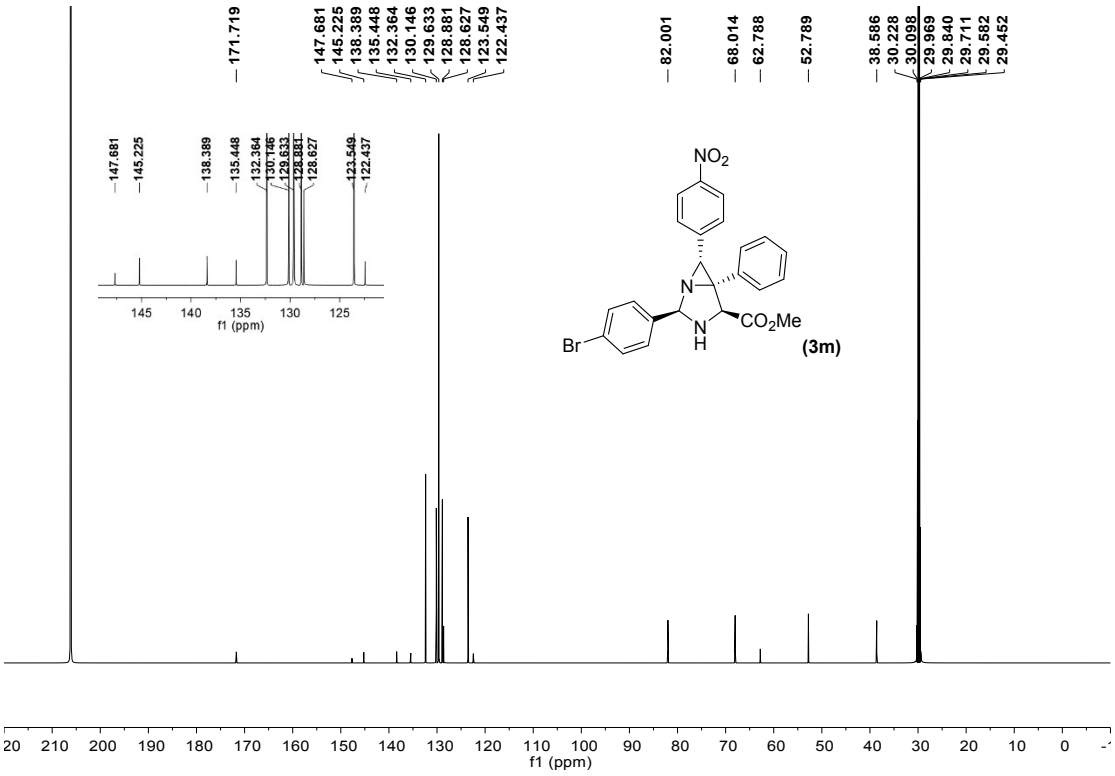
^{13}C NMR spectrum of compound **3l** (Acetone-d_6)



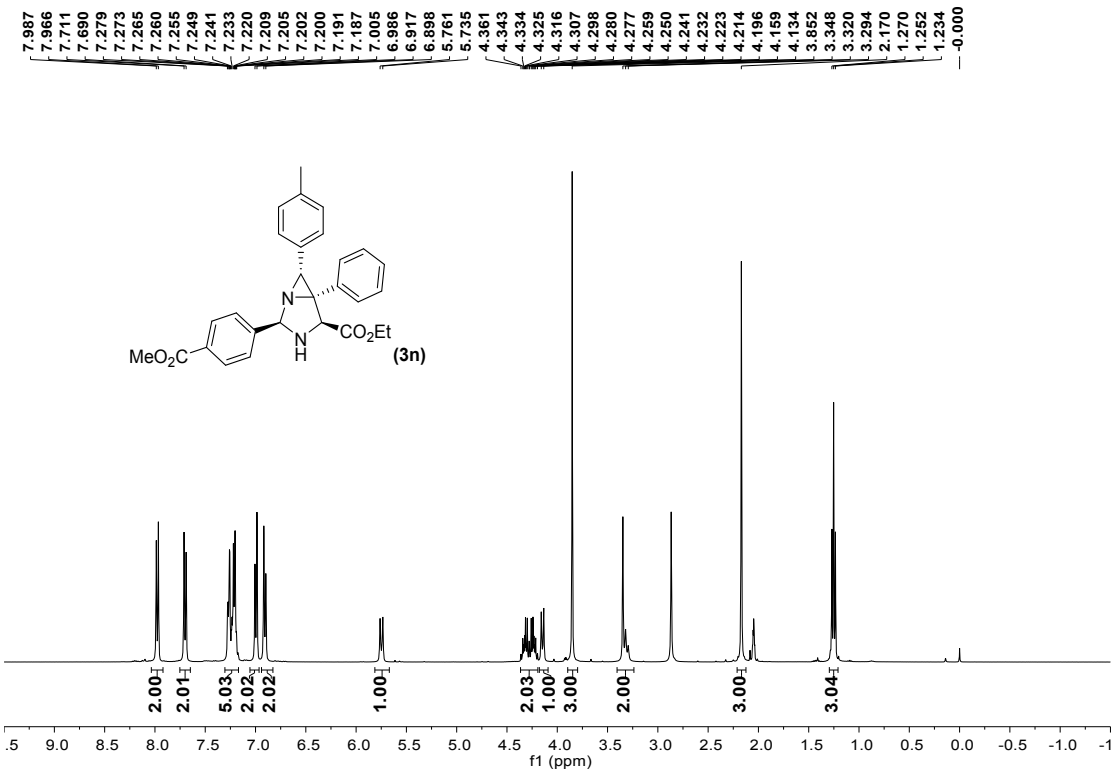
^{1}H NMR spectrum of compound **3m** (Acetone-d_6)



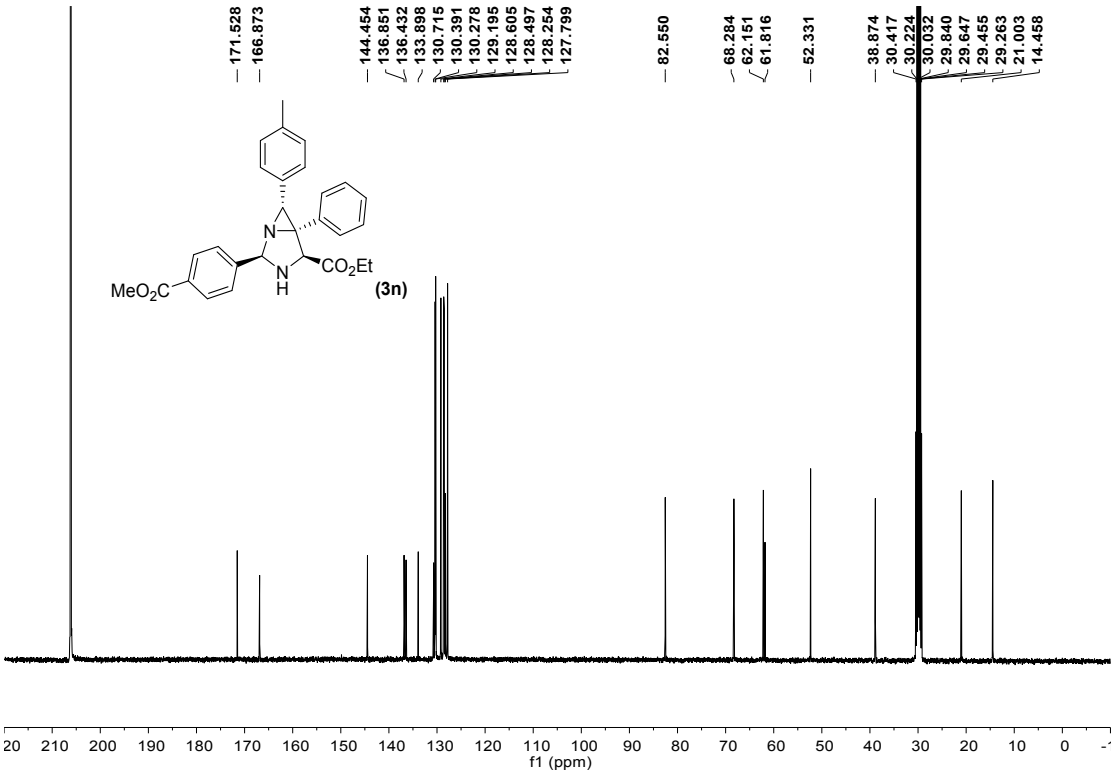
^{13}C NMR spectrum of compound **3m** (Acetone-d_6)



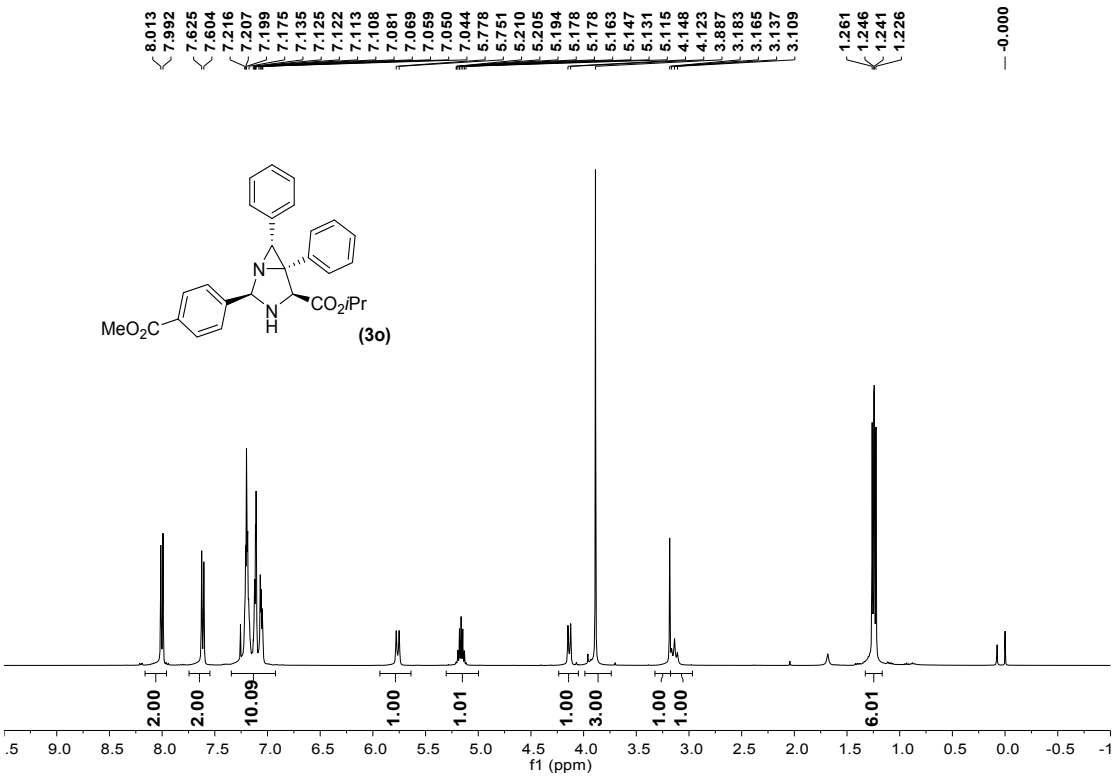
^{1}H NMR spectrum of compound **3n** (Acetone-d_6)



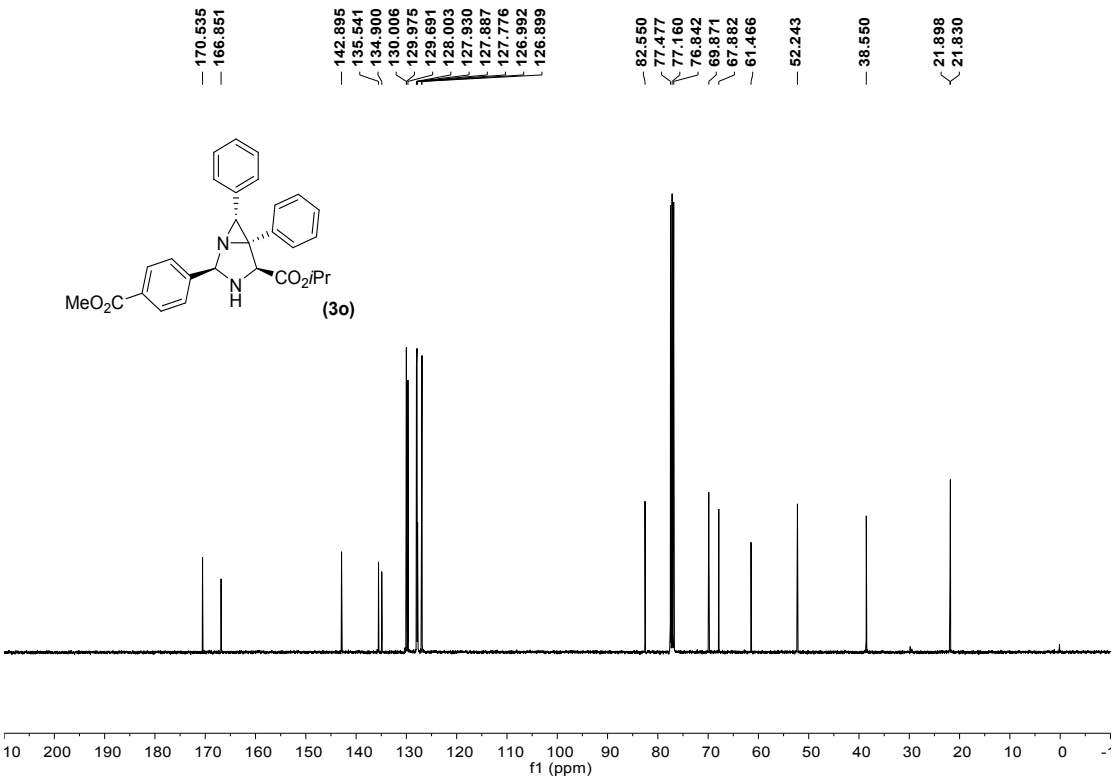
^{13}C NMR spectrum of compound **3n** (Acetone-d_6)



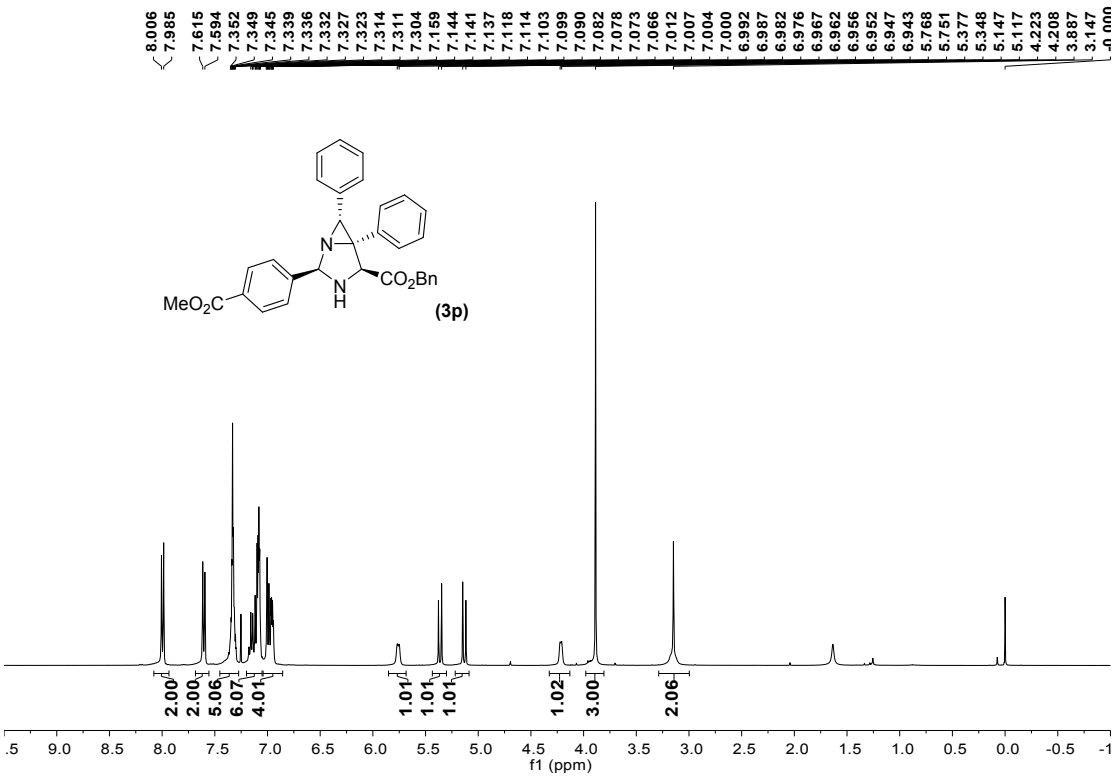
^{1}H NMR spectrum of compound **3o** ($CDCl_3$)



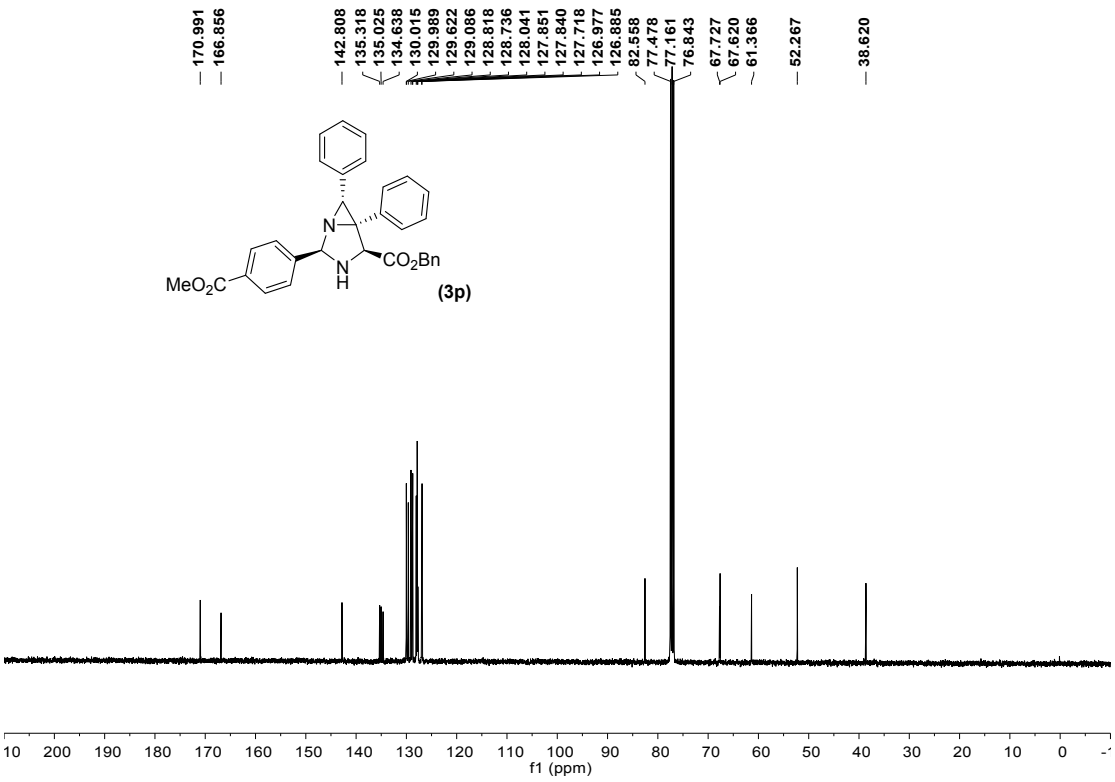
^{13}C NMR spectrum of compound **3o** ($CDCl_3$)



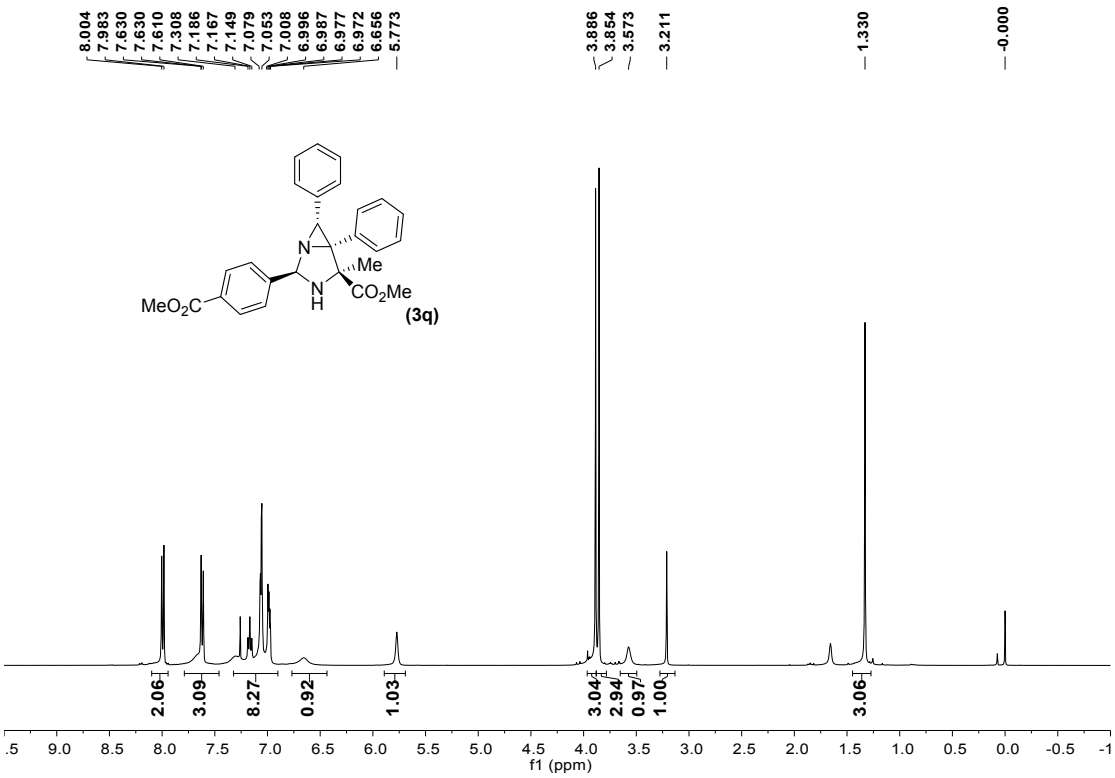
^{1}H NMR spectrum of compound **3p** ($CDCl_3$)



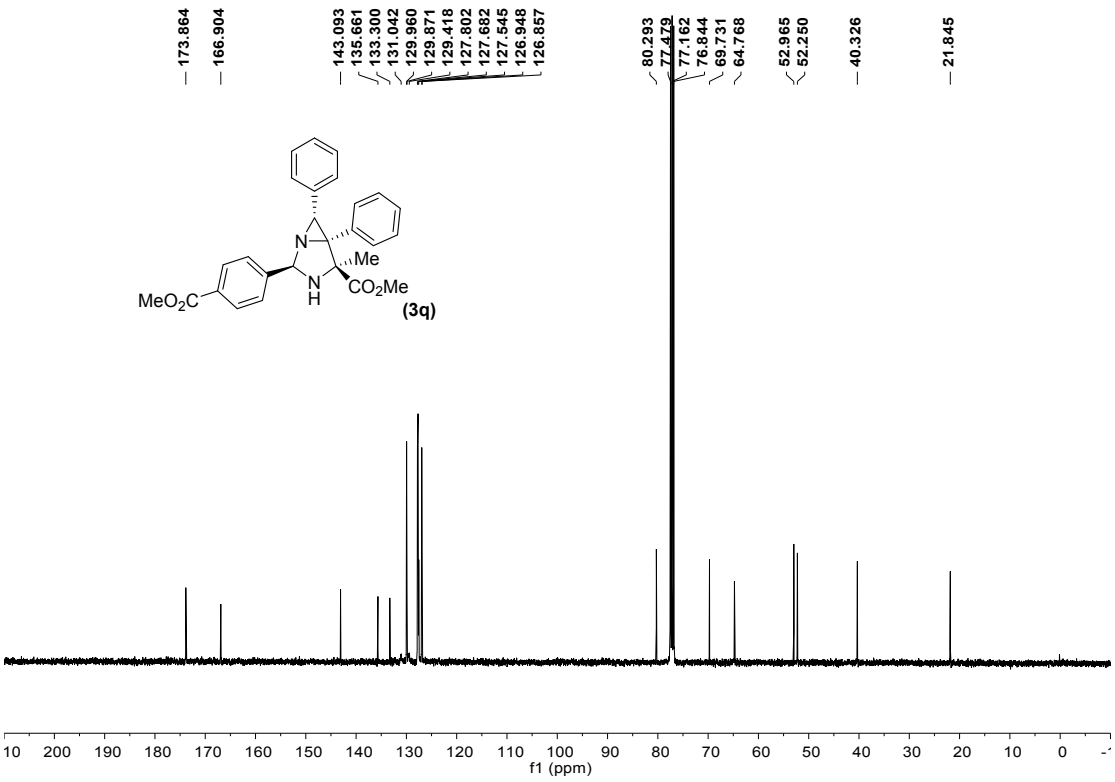
^{13}C NMR spectrum of compound **3p** ($CDCl_3$)



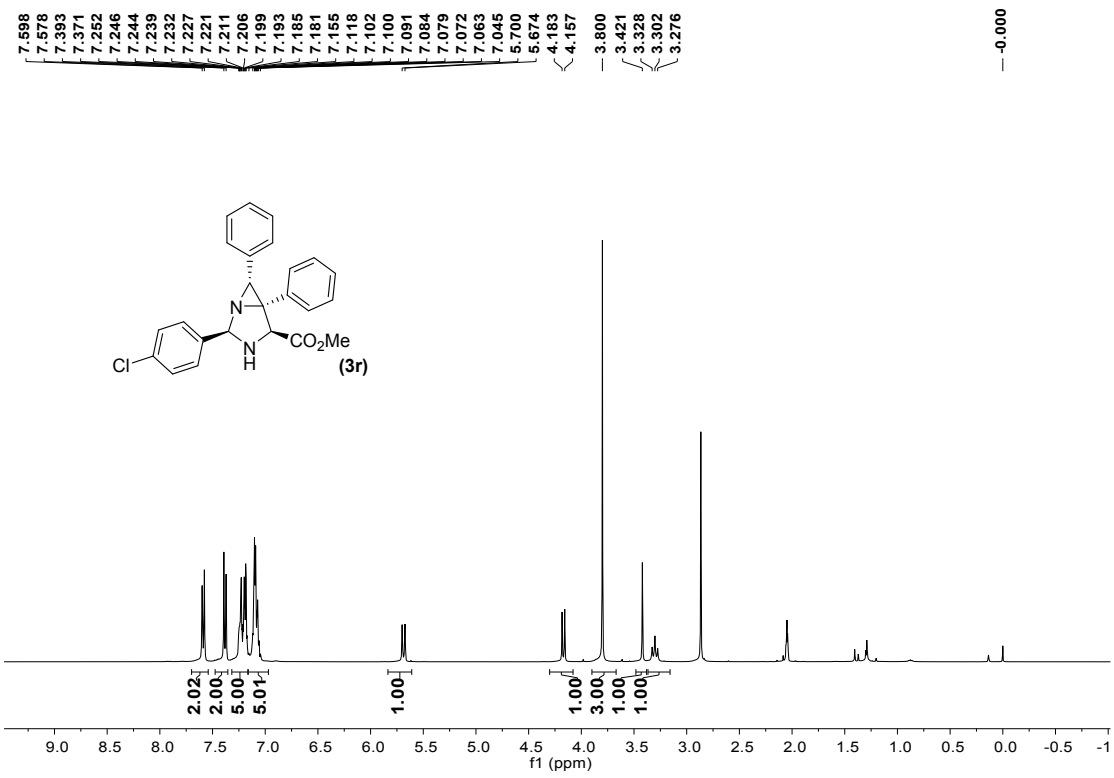
^{1}H NMR spectrum of compound **3q** ($CDCl_3$)



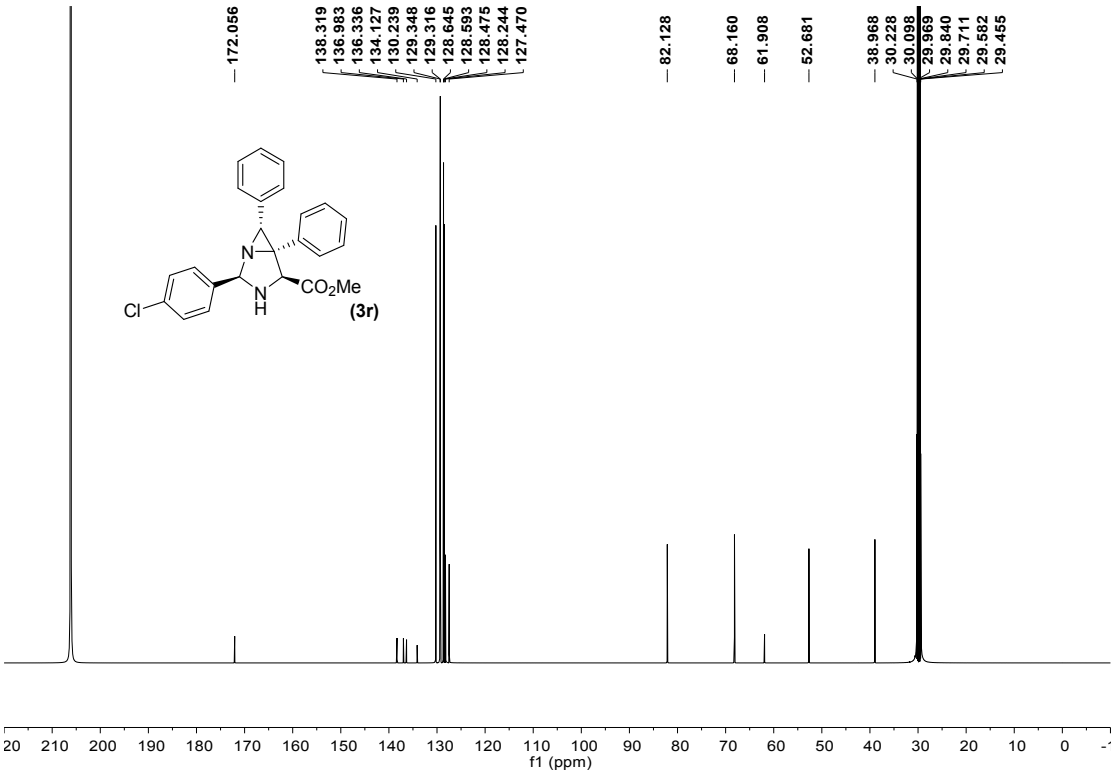
^{13}C NMR spectrum of compound **3q** ($CDCl_3$)



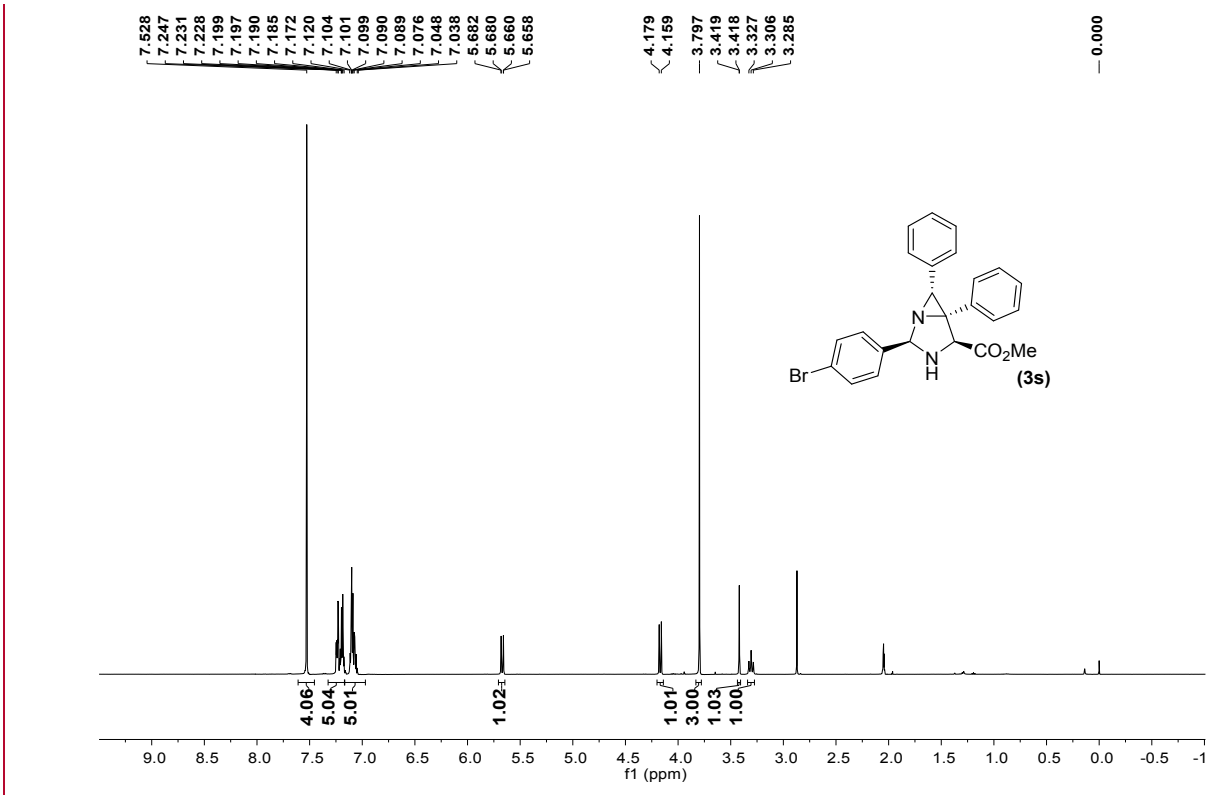
^{1}H NMR spectrum of compound **3r** (Acetone-d_6)



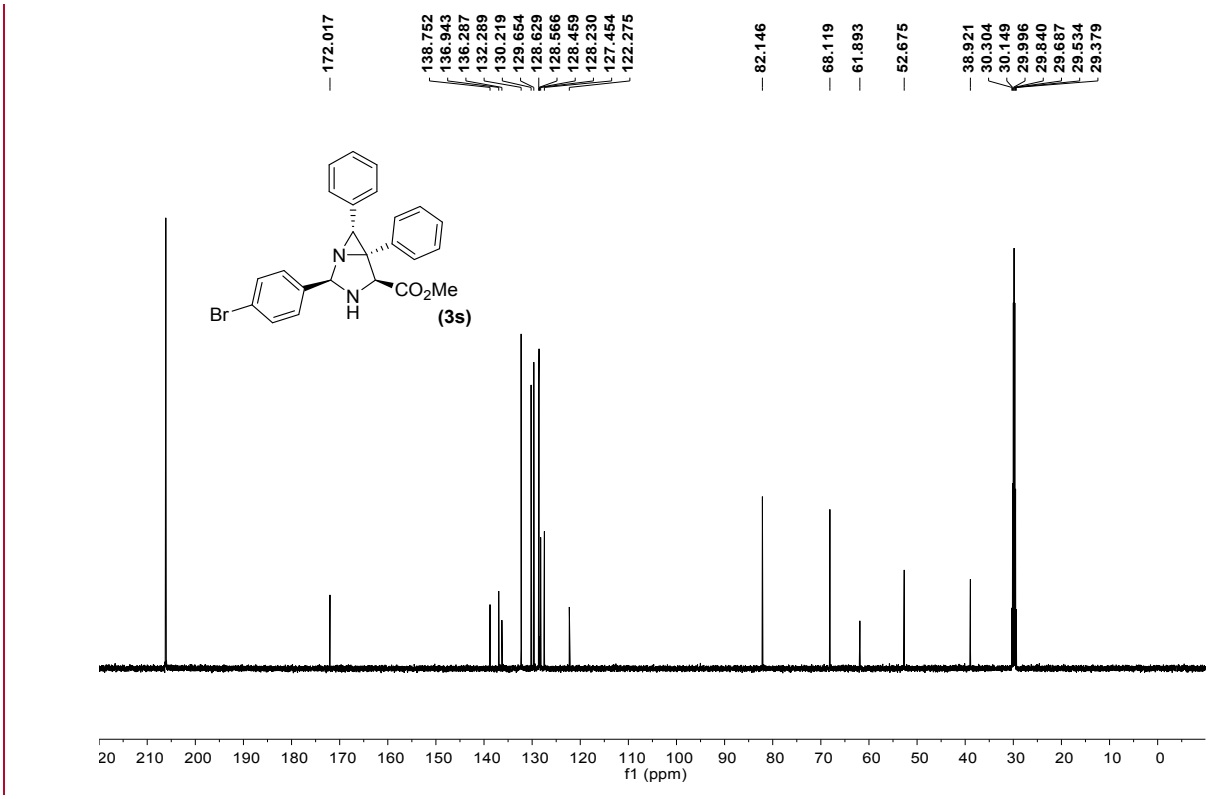
^{13}C NMR spectrum of compound **3r** (Acetone-d_6)



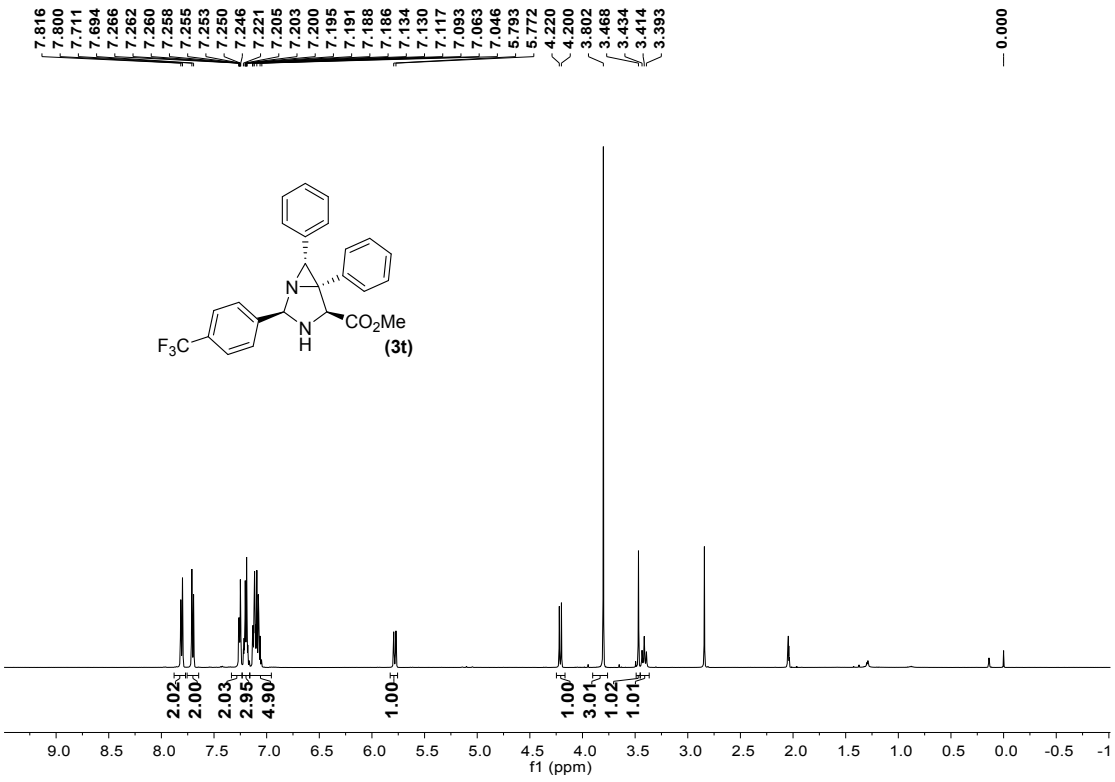
^{1}H NMR spectrum of compound **3s** (Acetone-d_6)



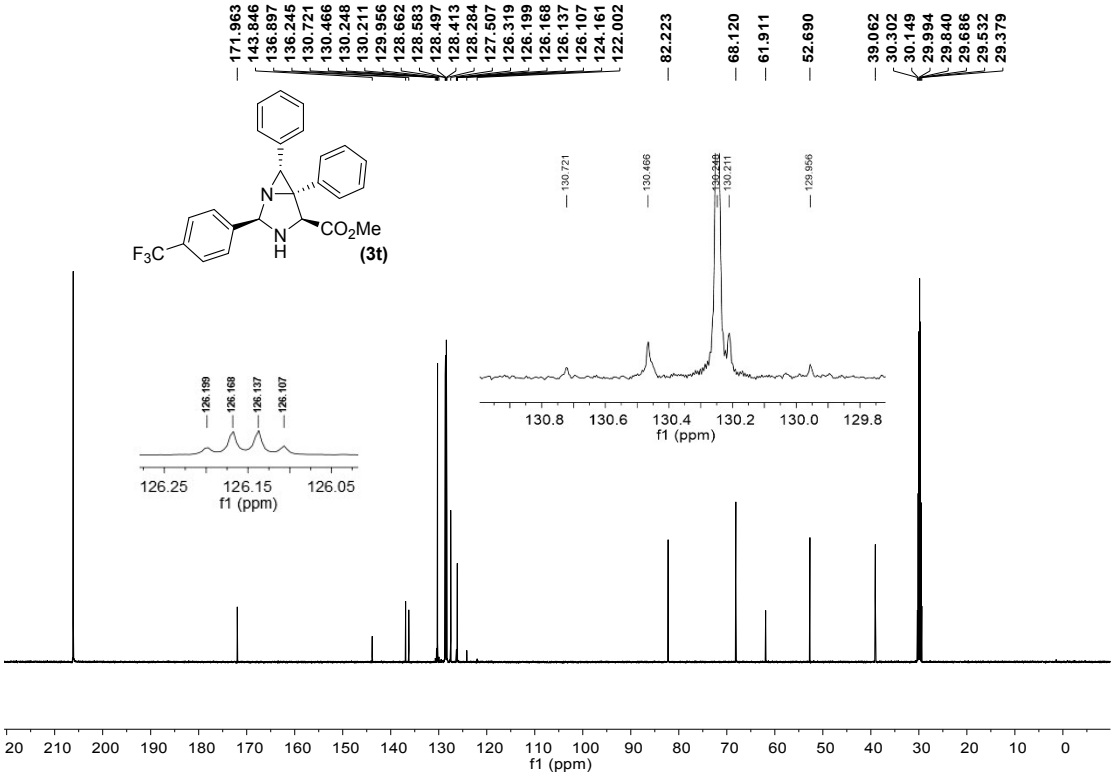
^{13}C NMR spectrum of compound **3s** (Acetone-d_6)



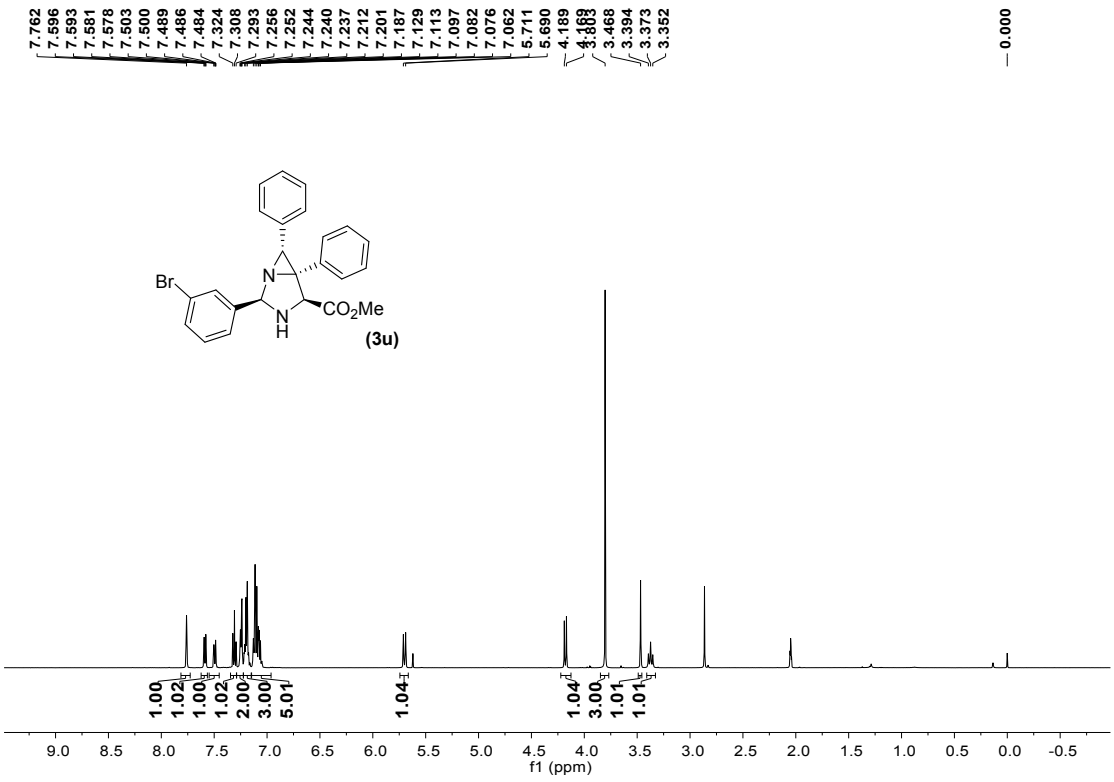
^{1}H NMR spectrum of compound **3t** (Acetone-d_6)



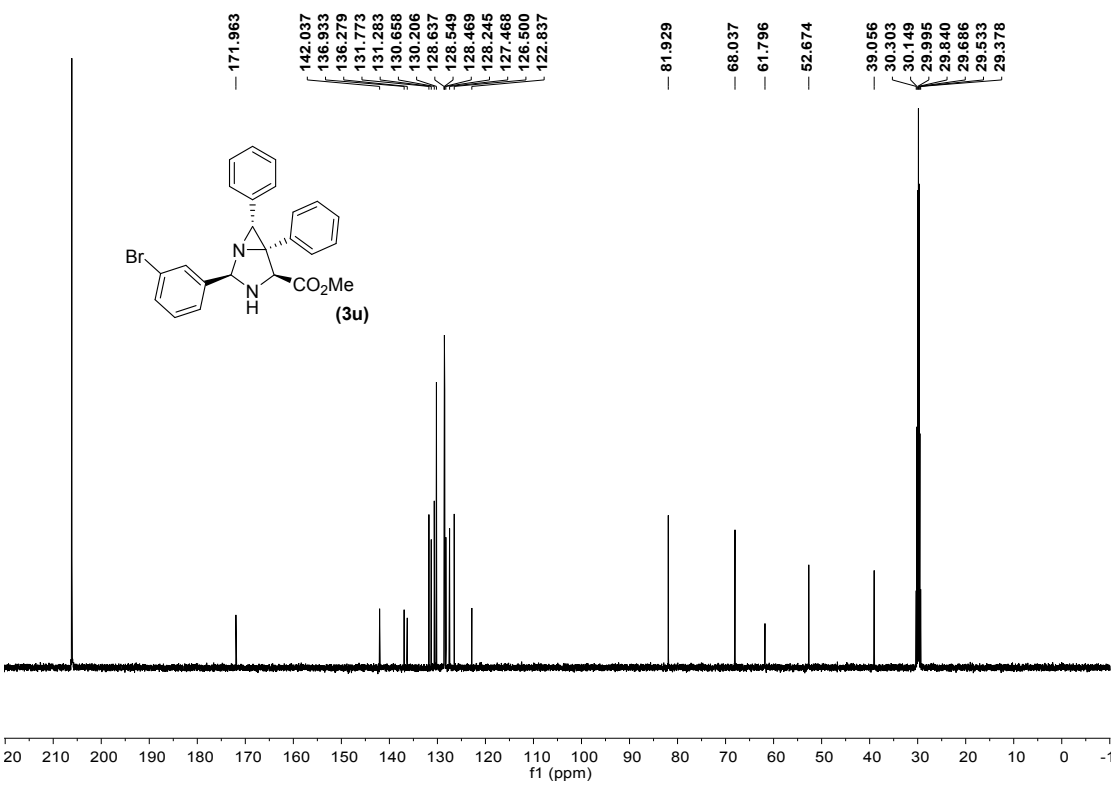
^{13}C NMR spectrum of compound **3t** (Acetone-d_6)



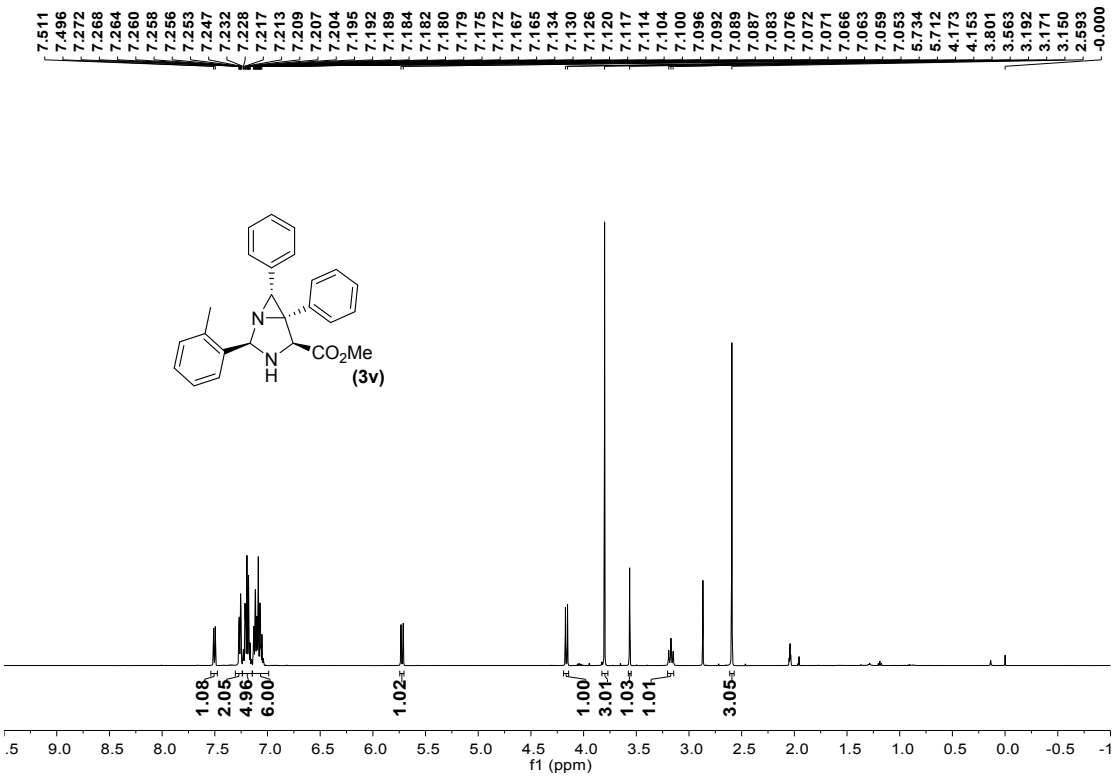
^{1}H NMR spectrum of compound **3u** (Acetone-d_6)



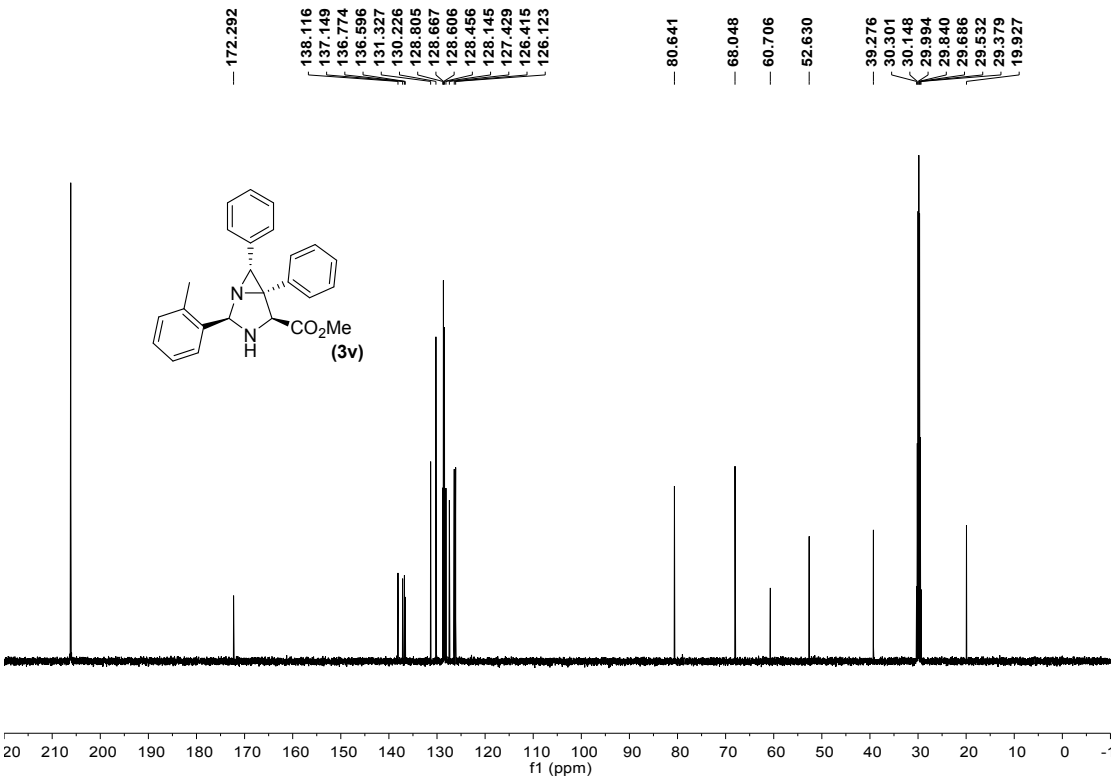
^{13}C NMR spectrum of compound **3u** (Acetone-d_6)



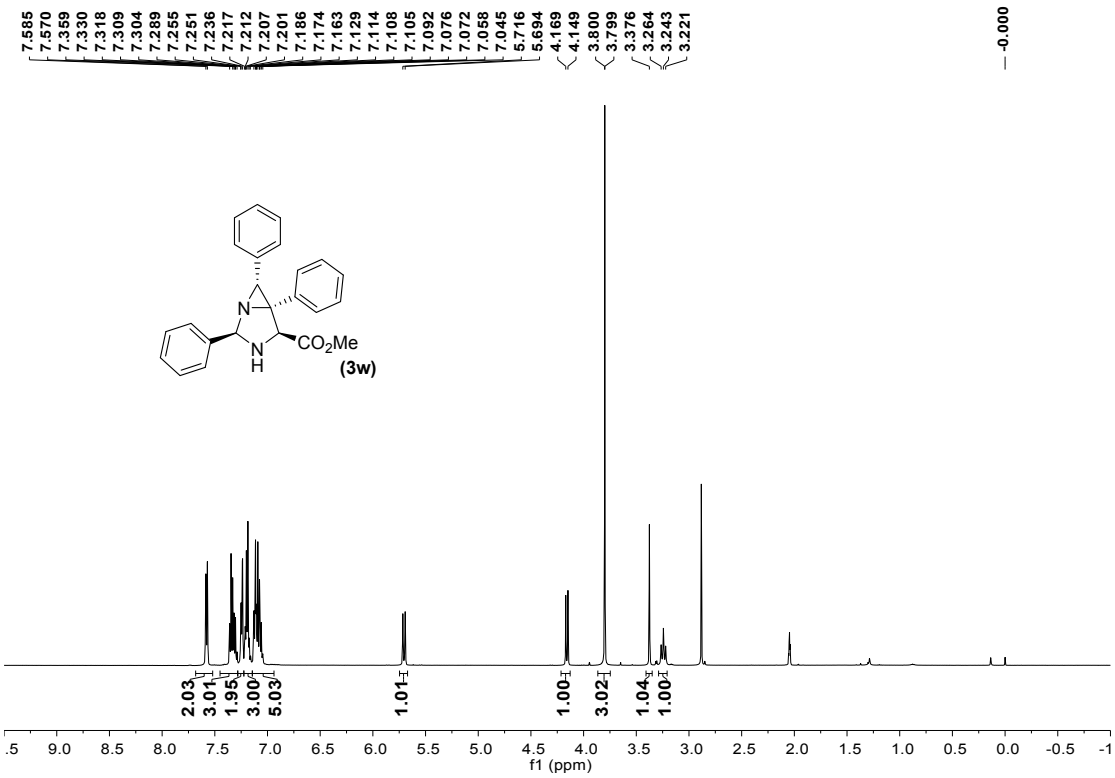
^{1}H NMR spectrum of compound **3v** (Acetone-d_6)



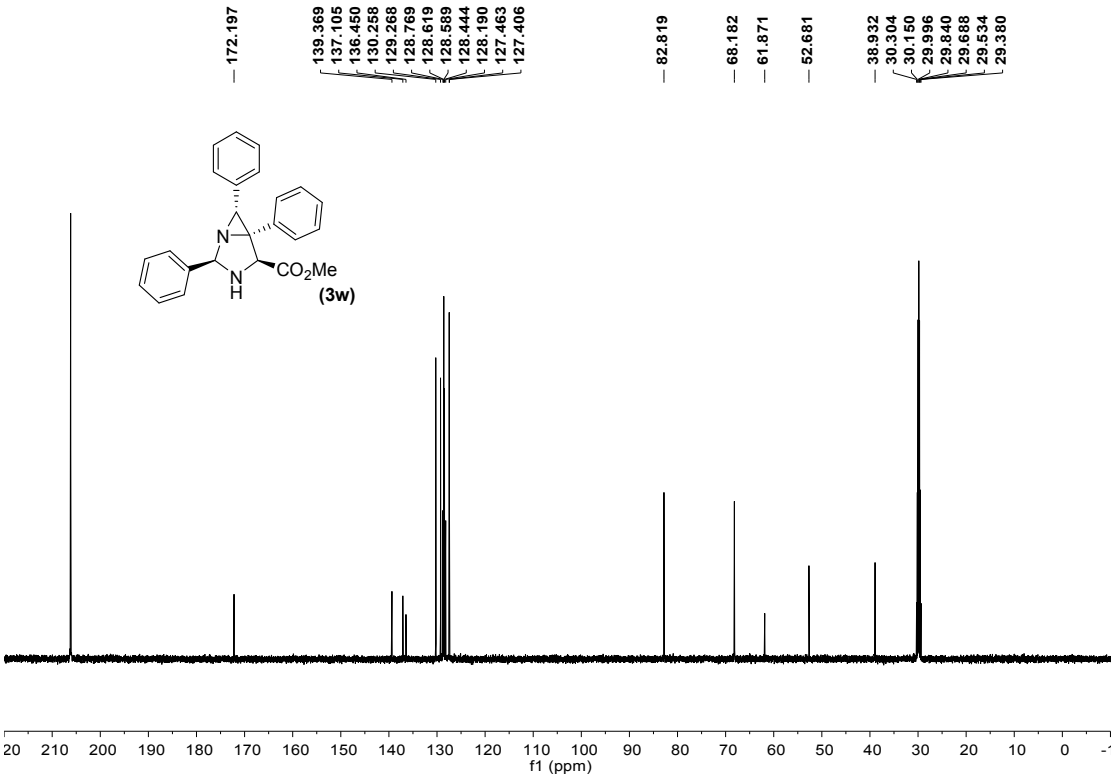
^{13}C NMR spectrum of compound **3v** (Acetone-d_6)



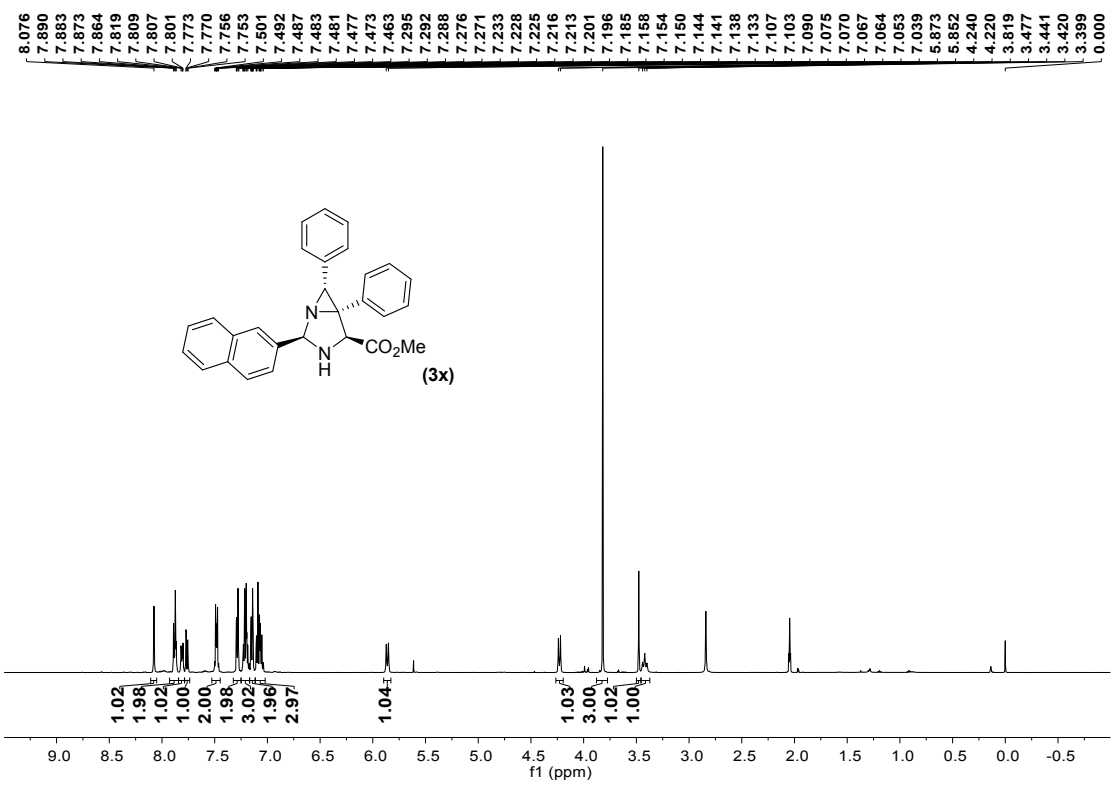
^{1}H NMR spectrum of compound **3w** (Acetone-d_6)



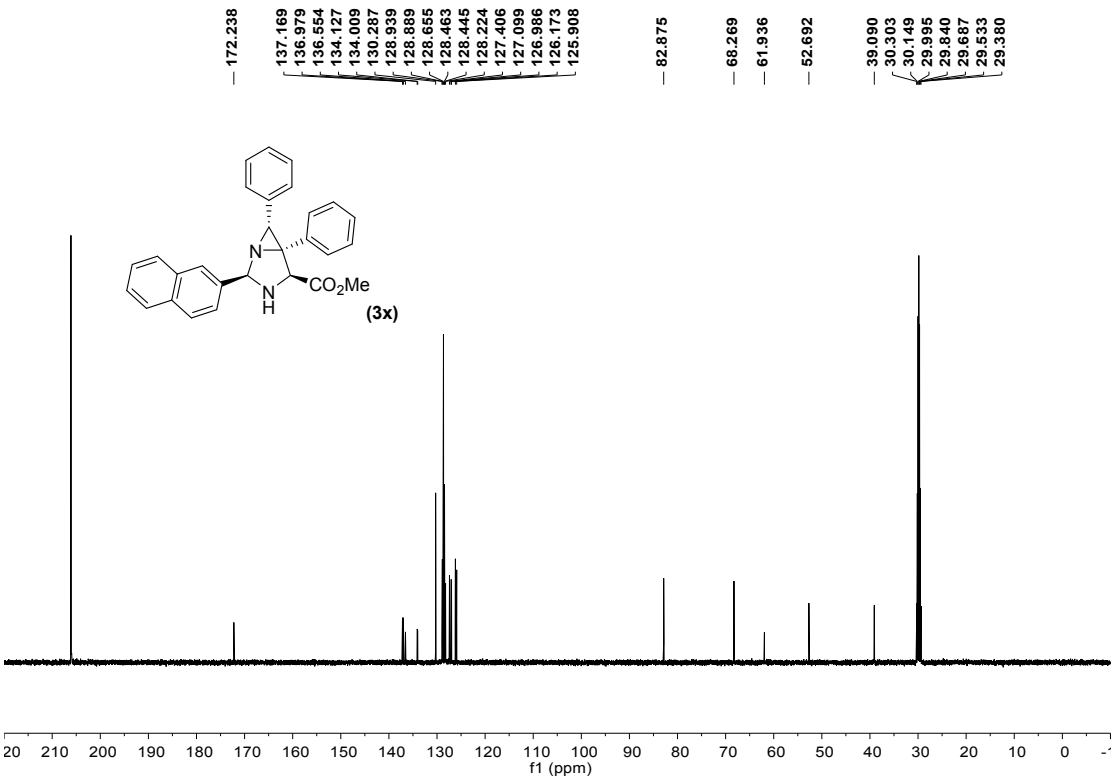
^{13}C NMR spectrum of compound **3w** (Acetone-d_6)



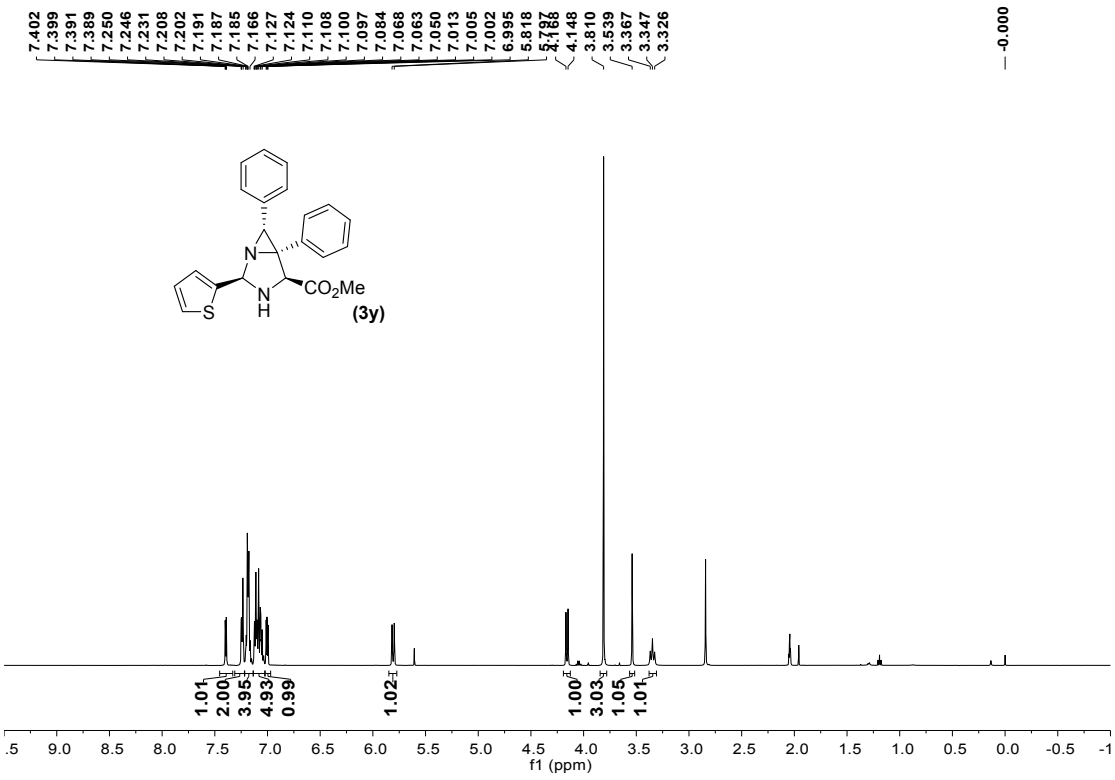
^{1}H NMR spectrum of compound **3x** (Acetone-d_6)



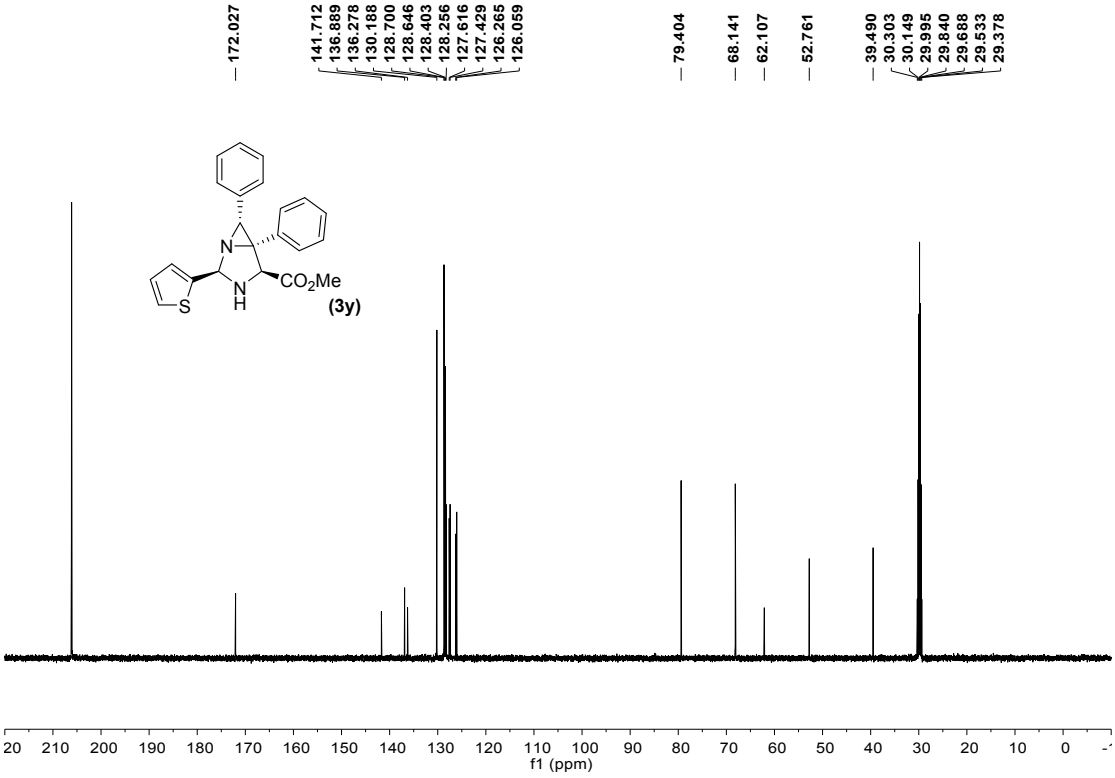
^{13}C NMR spectrum of compound **3x** (Acetone-d_6)



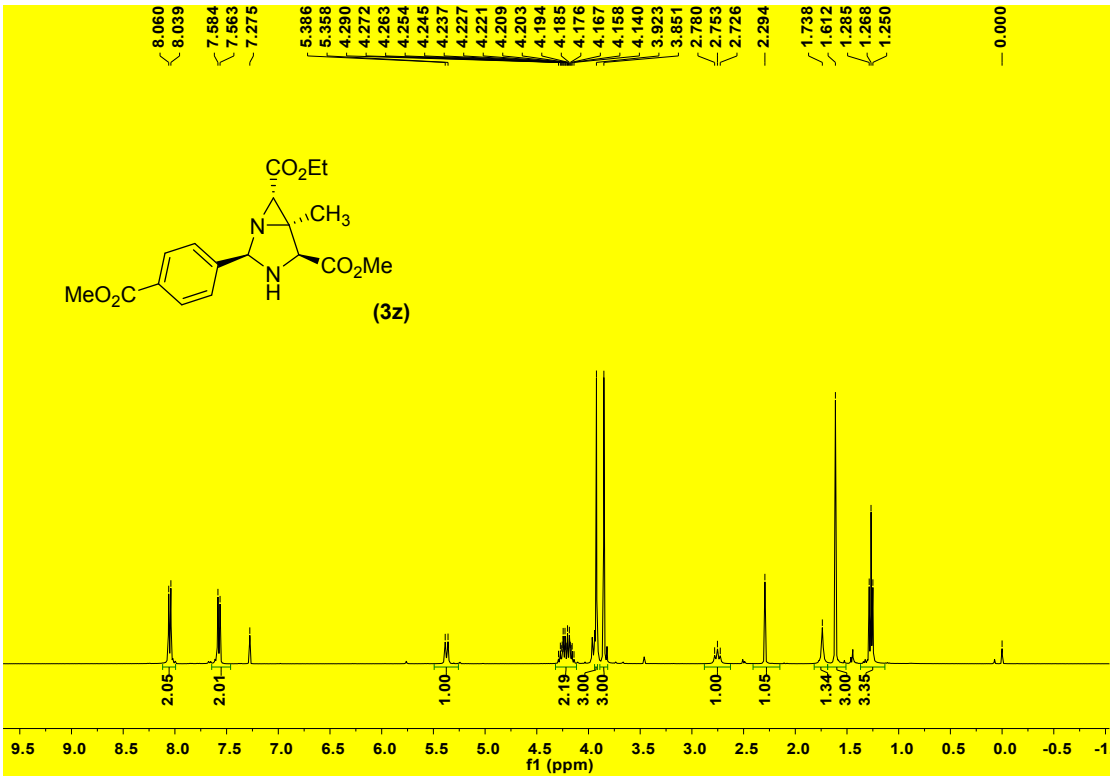
^{1}H NMR spectrum of compound **3y** (Acetone-d_6)



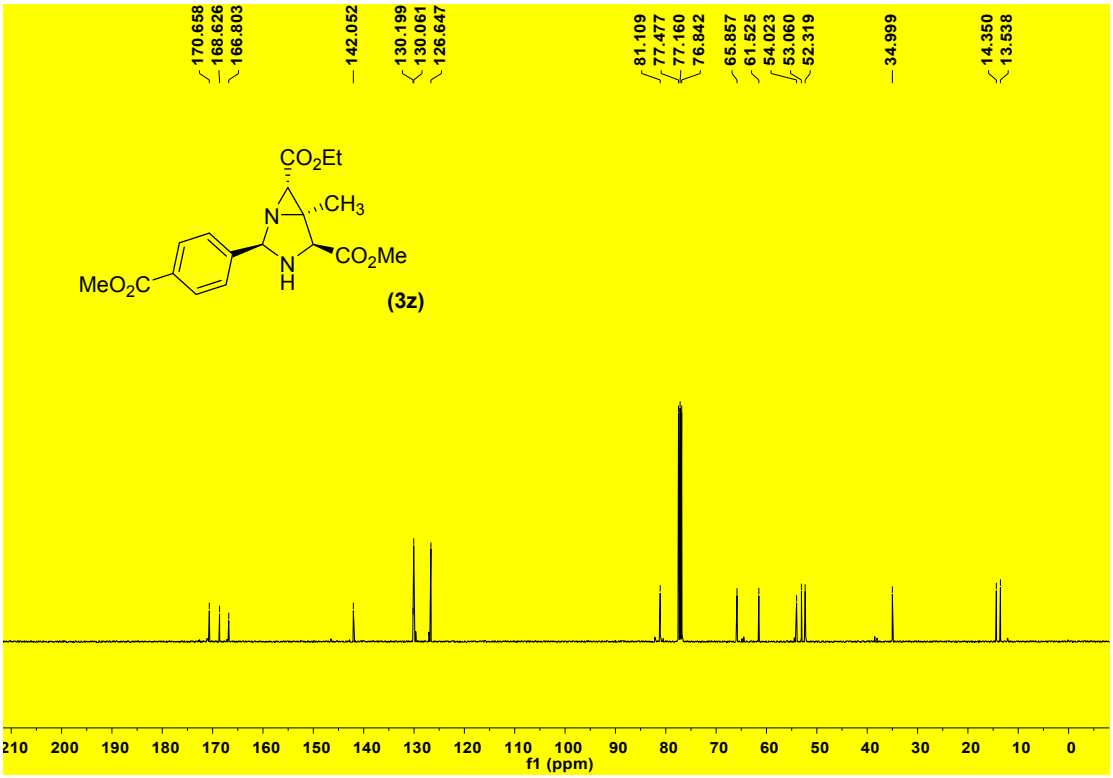
^{13}C NMR spectrum of compound **3y** (Acetone-d_6)



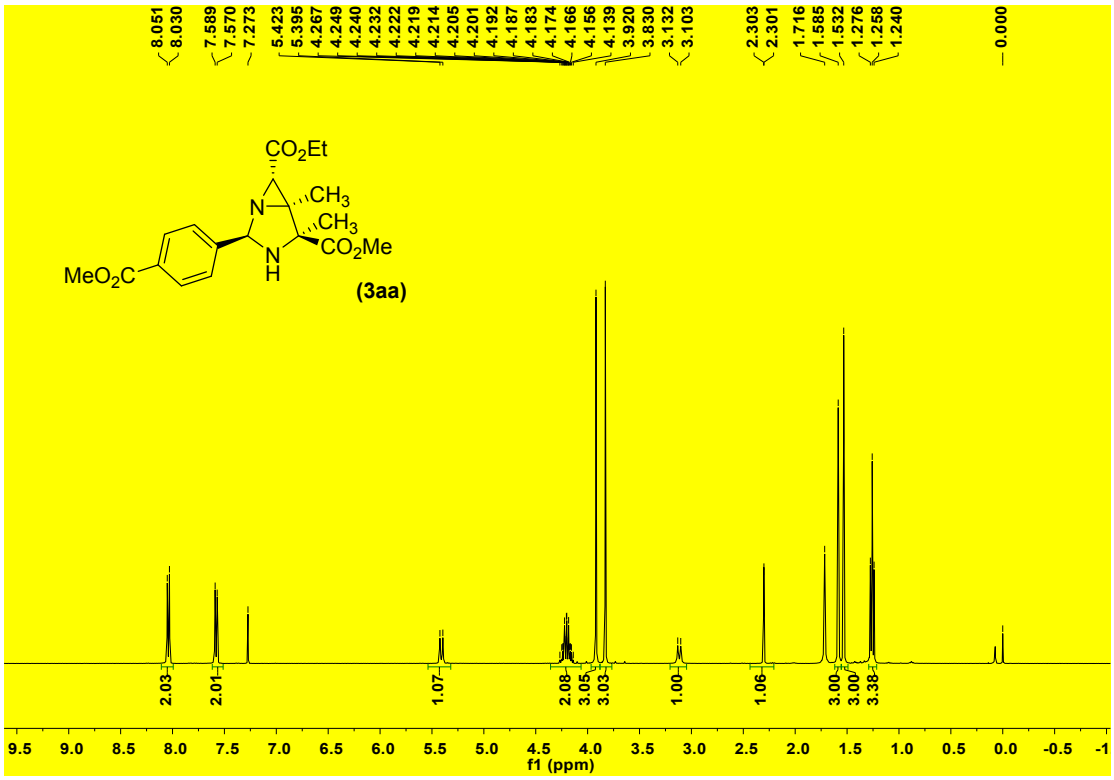
^{1}H NMR spectrum of compound **3z** ($CDCl_3$)



^{13}C NMR spectrum of compound **3z** ($CDCl_3$)



^{1}H NMR spectrum of compound **3aa** ($CDCl_3$)



^{13}C NMR spectrum of compound **3aa** ($CDCl_3$)