Supporting information for

Organocatalyzed Nucleophilic Addition of Pyrazoles to 2H-Azirines: Asymmetric Synthesis of 3,3-Disubstituted Aziridines and Kinetic Resolution of Racemic 2H-Azirines

Dong An, Xukai Guan, Rui Guan, Lajiao Jin, Guangliang Zhang, Suoqin Zhang*

College of Chemistry, Jilin University, 2699 Qianjin Street, Changchun 130012, China

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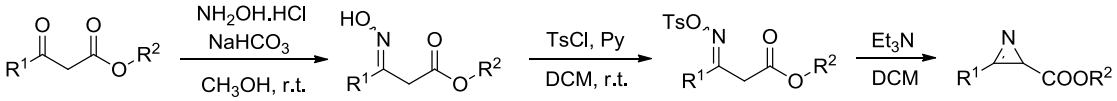
General Remarks: All reagents were used without purification. All solvents were purified and dried according to standard methods. The reaction products were purified by flash column chromatography on 200-300 mesh silica gel. The melting point was recorded on a melting point apparatus (MPA100, Stanford Research Systems, Inc.). Optical rotations were measured with a Jasco-P-2000 digital polarimeter at 20 or 25 ℃ and concentrations (*c*) are given in g×(100 mL)$^{-1}$. ^{1}H and ^{13}C NMR spectra were recorded with Bruker 400 MHz spectrometers (400 MHz for ^{1}H NMR, 101 MHz for ^{13}C NMR); chemical shifts (δ) are given in ppm. High-resolution mass spectral analysis (HRMS) data were measured on a Bruker ApexII mass spectrometer by means of the ESI technique. Analytical HPLC was recorded on a HPLC machine equipped with Elite P1201 series or Ichrom 5100 series quaternary pump with a UV diode array detector. Enantiomeric excess values were measured by analytical HPLC with Daicel ChiralPak AS-H or Daicel Chiralcel OD-H column. 5-aryl-1H-pyrazole-3-carboxylic esters **1** were synthesized according to literature procedures.[1]

General procedure and characterization data for racemic 2H-azirine carboxylic esters 2:

Racemic 2H-azirine carboxylic esters **2** were synthesized according to literature procedures.[2] Compounds **2a**, **2b**, **2d**, **2i**, **2j**, **2m** and **2o** are known compounds.[1] Compounds **2c**, **2e-2h**, **2k**, **2l** and **2n** were first synthesized in this work and the characterization data was given.

General procedure for aliphatic substituded 2H-azirine carboxylic esters **2a-2i**:

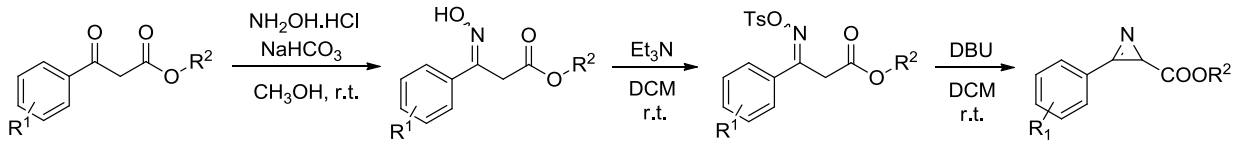


To a solution of $NH_2OH·HCl$ (11 mmol, 1.1 equiv.) in 20 mL CH_3OH was added aliphatic substituded β-ketoester (10 mmol, 1.0 equiv.) dropwise and the solution was stirred for 1-2 h. After completion of reaction, the solvent was removed under reduced pressure. 30 mL ethyl acetate and 5 mL water was added and the organic and the aqueous layer were separated. The aqueous layer was extracted twice with ethyl acetate. The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo to give crude product without purification. (The products ketoximes are unstable and should be used for next step as soon as possible.)

To the ketoxime produced in the previous step, TsCl (12 mmol, 1.2 equiv.) and pyridine (12 mmol, 1.2 equiv.) were added. The solution was stirred for 6 h at 25^{o}C. After the reaction was completed, the solvent was removed in vacuo and the crude material was purified by column chromatography.

To a solution of ketoximetosylate (5 mmol, 1 equiv.) in 10 mL CH_2Cl_2, Et_3N (5.5 mmol, 1.1 equiv.) was added dropwise at 0 ℃. After stirring at 0 ℃ for 15-30 min, the mixture was stirred at 25 ^{o}C for 6h. After the reaction was completed, the solvent was removed in vacuo and the crude material was purified by column chromatography.

General procedure for aromatic substituded 2H-azirine carboxylic esters **2j-2o**:



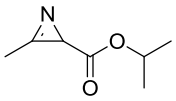
To a solution of $NH_2OH·HCl$ (11 mmol, 1.1 equiv.) in 20 mL CH_3OH was added aromatic substituded β-ketoester (10 mmol, 1.0 equiv.) dropwise and the solution was stirred for 4-8 h. After completion of reaction, the solvent was removed under reduced pressure. 30 mL ethyl acetate and 5 mL water was added and the

organic and the aqueous layer were separated. The aqueous layer was extracted twice with ethyl acetate. The combined organic layers were washed with 10 mL saturated Na_2CO_3 and saturated brine (10 ml × 3), dried over $MgSO_4$ and concentrated in vacuo to give crude product without purification. (The products ketoximes are unstable and should be used for next step as soon as possible.)

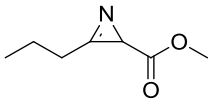
To the ketoxime produced in the previous step, TsCl (6 mmol, 1.2 equiv.) and pyridine (6 mmol, 1.2 equiv.) were added. The solution was stirred for 3 h at 0 ^oC. After the reaction was completed, the solvent was removed in vacuo and the crude material was purified by column chromatography.

To a solution of ketoximetosylate (5 mmol, 1 equiv.) in 10 mL CH_2Cl_2, DBU (6.0 mmol, 1.2 equiv.) was added dropwise at 0 ℃. After stirring at 0 ℃ for 15-30 min, the mixture was stirred at 25 ^oC for 2h. After the reaction was completed, 20 mL ethyl acetate and 5 mL water was added. The aqueous layer was extracted twice with ethyl acetate. The combined organic layers were washed with saturated brine (10 ml × 3), dried over $MgSO_4$ and concentrated in vacuo. The crude material was purified by column chromatography.

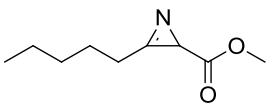
Characterization data for racemic 2H-azirine carboxylic esters **2**:



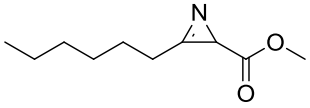
Isopropyl 3-methyl-2H-azirine-2-carboxylate (±)-**2c**: colorless oil, 79% yield (from the corresponding keto ester), ^1H NMR (400 MHz, $CDCl_3$) δ 5.08-4.99 (m, 1H), 2.53 (s, 3H), 2.41 (s, 1H), 1.24 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.43, 159.10, 68.50, 28.91, 21.73, 21.68, 12.45. HRMS(ESI) *m/z* calcd for $C_7H_{12}NO_2$ ($[M+H]^+$): 142.0868, found: 142.0862.



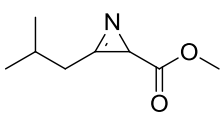
Methyl 3-propyl-2H-azirine-2-carboxylate (±)-**2e**: colorless oil, 66% yield (from the corresponding keto ester), ^1H NMR (400 MHz, $CDCl_3$) δ 3.73 (s, 3H), 2.81 (t, *J* = 7.2 Hz, 2H), 2.45 (s, 1H), 1.81 (q, *J* = 7.2 Hz, 2H), 1.07 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.47, 161.77, 51.98, 28.46, 28.35, 17.74, 13.54. HRMS(ESI) *m/z* calcd for $C_7H_{12}NO_2$ ($[M+H]^+$): 142.0868, found: 142.0866.



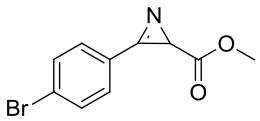
Methyl 3-pentyl-2H-azirine-2-carboxylate (±)-**2f**: colorless oil, 67% yield (from the corresponding keto ester), ^1H NMR (300 MHz, $CDCl_3$) δ 3.72 (s, 3H), 2.82 (t, *J* = 7.4 Hz, 2H), 2.44 (s, 1H), 1.81-1.72 (m, 2H), 1.48-1.32 (m, 4H), 0.92 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.50, 161.94, 52.02, 31.06, 28.48, 26.59, 23.76, 22.08, 13.72. HRMS(ESI) *m/z* calcd for $C_9H_{16}NO_2$ ($[M+H]^+$): 170.1181, found: 170.1176.



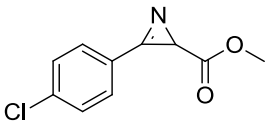
Methyl 3-hexyl-2H-azirine-2-carboxylate (±)-**2g**: colorless oil, 55% yield (from the corresponding keto ester), ^1H NMR (400 MHz, $CDCl_3$) δ 3.72 (s, 3H), 2.82 (t, *J* = 7.3 Hz, 2H), 2.44 (s, 1H), 1.82-1.70 (m, 2H), 1.45-1.40 (m, 2H), 1.39-1.26 (m, 4H), 0.90 (t, *J* = 6.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.50, 161.94, 52.03, 31.19, 28.63, 28.49, 26.63, 24.06, 22.31, 13.88. HRMS(ESI) *m/z* calcd for $C_{10}H_{18}NO_2$ ($[M+H]^+$): 184.1338, found: 184.1334.



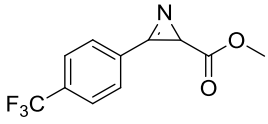
Methyl 3-isobutyl-2H-azirine-2-carboxylate (±)-**2h**: colorless oil, 14% yield (from the corresponding keto ester), ^1H NMR (400 MHz, $CDCl_3$) δ 3.73 (s, 3H), 2.73 (d, *J* = 6.8 Hz, 2H), 2.42 (s, 1H), 2.23-2.13 (m, 1H), 1.07 (t, *J* = 9.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.53, 161.24, 52.05, 35.31, 28.20, 25.32, 22.34. HRMS(ESI) *m/z* calcd for $C_8H_{14}NO_2$ ($[M+H]^+$): 156.1025, found: 156.1028.



Methyl 3-(4-bromophenyl)-2H-azirine-2-carboxylate (±)-**2k**: white solid, 17% yield, (from the corresponding keto ester), m.p. 68.2-68.7 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.68 (m, 4H), 3.75 (s, 3H), 2.87 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.64, 157.99, 132.72, 131.54, 128.97, 121.06, 52.29, 29.54. HRMS(ESI) *m/z* calcd for $C_{10}H_9BrNO_2$ ($[M+H]^+$): 253.9811, found: 253.9800.



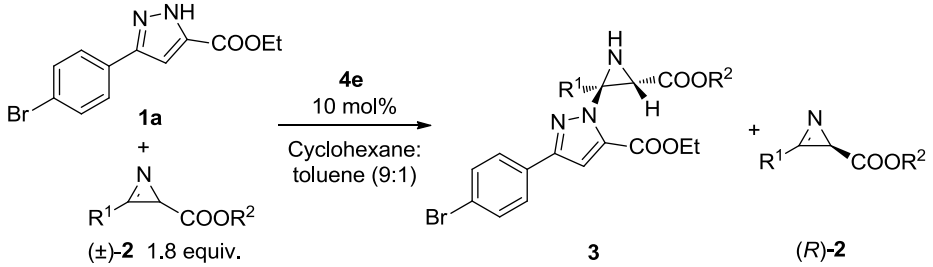
Methyl 3-(4-chlorophenyl)-2H-azirine-2-carboxylate (±)-**2l**: white solid, 11% yield (from the corresponding keto ester), m.p. 63.4-64.2 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.0 Hz, 2H), 7.57 (d, *J* = 7.0 Hz, 2H), 3.75 (s, 3H), 2.87 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.70, 157.82, 140.37, 131.51, 129.77, 120.66, 52.31, 29.57. HRMS(ESI) *m/z* calcd for $C_{10}H_9ClNO_2$ ($[M+H]^+$): 210.0316, found: 210.0309.



Methyl 3-(4-(trifluoromethyl)phenyl)-2H-azirine-2-carboxylate (±)-**2n**: colorless oil, 26% yield (from the corresponding keto ester), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.0 Hz, 2H), 7.86 (d, *J* = 8.0 Hz, 2H), 3.76 (s, 3H), 2.94 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.36, 158.53, 135.25 (q, *J* = 32.7 Hz), 130.57, 126.30 (q, *J* = 3.7 Hz), 125.71, 123.25 (q, *J* = 271.3 Hz), 52.29, 29.91. HRMS(ESI) *m/z* calcd for $C_{11}H_9F_3NO_2$ ($[M+H]^+$): 244.0580, found: 244.0567.

General procedure and characterization data for chiral 2H-azirine carboxylic esters (*R*)-2:

General procedure for chiral 2H-azirine carboxylic esters (*R*)-**2**:

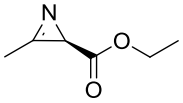


For **2a-d**: A solution of ethyl 3-(4-bromophenyl)-1H-pyrazole-5-carboxylate **1a** (0.1 mmol) and catalyst **4e** (10 mol %, 0.01 mmol) in 0.9 mL cyclohexane and 0.1 mL toluene was stirred at -20 °C for 10 min, then racemic 2H-azirine carboxylic esters **2** (0.18 mmol) was added. The reaction mixture was stirred at -20 ℃ for 3 d. After removal of the solvent, the residue was purified by flash column chromatography to afford the pure products.

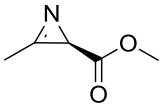
For **2e**, **2g** and **2i**: A solution of ethyl 3-(4-bromophenyl)-1H-pyrazole-5-carboxylate **1a** (0.1 mmol) and catalyst **4e** (10 mol %, 0.01 mmol) in 0.9 mL cyclohexane and 0.1 mL toluene was stirred at 0 °C for 10 min, then racemic 2H-azirine carboxylic esters **2** (0.18 mmol) was added. The reaction mixture was stirred at 0 ℃ for 3 d. After removal of the solvent, the residue was purified by flash column chromatography to afford the pure products.

For **2k**, **2l** and **2n**: A solution of ethyl 3-(4-bromophenyl)-1H-pyrazole-5-carboxylate **1a** (0.1 mmol) and catalyst **4e** (10 mol %, 0.01 mmol) in 0.9 mL cyclohexane and 0.1 mL toluene was stirred at 25 °C for 10 min, then racemic 2H-azirine carboxylic esters **2** (0.18 mmol) was added. The reaction mixture was stirred at 25 ℃ for 6 d. After removal of the solvent, the residue was purified by flash column chromatography to afford the pure products.

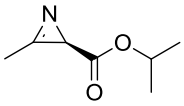
Characterization data for chiral 2H-azirine carboxylic esters (*R*)-**2**:



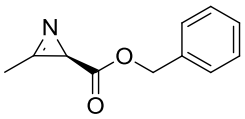
(*R*)-ethyl 3-methyl-2H-azirine-2-carboxylate (*R*)-**2a**: colorless oil, 49% yield, 98% ee [Daicel Chiralcel OD-H column, *n*-hexane / *i*-PrOH = 98 : 2, 1.0 ml/min, λ = 210 nm, t (minor) = 8.55 min, t (major) = 12.77 min]; $[\alpha]_D^{25}$ = -223.2 (c = 0.112, EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.25-4.12 (m, 2H), 2.53 (s, 3H), 2.44 (s, 1H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.92, 159.07, 61.02, 28.71, 14.12, 12.48. HRMS(ESI) *m/z* calcd for $C_6H_{10}NO_2$ ($[M+H]^+$): 128.0712, found: 128.0716.



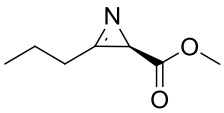
(*R*)-methyl 3-methyl-2H-azirine-2-carboxylate (*R*)-**2b**: colorless oil, 48% yield, 99% ee [Daicel Chiralcel OD-H column, *n*-hexane / *i*-PrOH = 99 : 1, 1.0 ml/min, λ = 210 nm, t (minor) = 12.39 min, t (major) = 18.23 min]; $[\alpha]_D^{25}$ = -140.5 (c = 0.195, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.73 (s, 3H), 2.54 (s, 3H), 2.46 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.25, 158.96, 51.97, 28.46, 12.38. HRMS(ESI) *m/z* calcd for $C_5H_8NO_2$ ($[M+H]^+$): 114.0555, found: 114.0563.



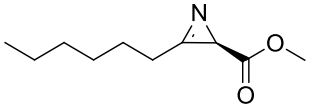
(*R*)-isopropyl 3-methyl-2H-azirine-2-carboxylate (*R*)-**2c**: colorless oil, 48% yield, 99% ee [Daicel Chiralcel OD-H column, *n*-hexane / *i*-PrOH = 99 : 1, 1.0 ml/min, λ = 210 nm, t (minor) = 8.51min, t (major) = 10.74 min]; $[\alpha]_D^{25}$ = -161.5 (c = 0.112, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.16-4.97 (m, 1H), 2.52 (s, 3H), 2.41 (s, 1H), 1.25 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.57, 159.24, 68.65, 28.94, 21.75, 12.46. HRMS(ESI) *m/z* calcd for $C_7H_{12}NO_2$ ($[M+H]^+$): 142.0868, found: 142.0856.



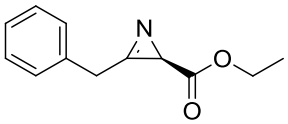
(*R*)-benzyl 3-methyl-2H-azirine-2-carboxylate (*R*)-**2d**: colorless oil, 49% yield, 99% ee [Daicel Chiralcel OD-H column, *n*-hexane / *i*-PrOH = 98 : 2, 0.5 ml/min, λ = 225 nm, t (minor) = 15.92 min, t (major) = 25.96 min]; $[\alpha]_D^{25}$ = -129.8 (c = 0.168, EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45-7.29 (m, 5H), 5.19 (d, *J* = 12.3 Hz, 1H), 5.14 (d, *J* = 12.3 Hz, 1H), 2.52 (s, 3H), 2.49 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.77, 158.89, 135.49, 128.46, 128.22, 128.12, 66.71, 28.68, 12.44. HRMS(ESI) *m/z* calcd for $C_{11}H_{12}NO_2$ ($[M+H]^+$): 190.0868, found: 190.0864.



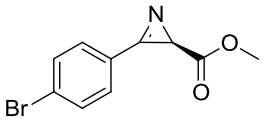
(*R*)-methyl 3-propyl-2H-azirine-2-carboxylate (*R*)-**2e**: colorless oil, 48% yield, 97% ee [Daicel Chiralcel OD-H column, *n*-hexane / *i*-PrOH = 99 : 1, 1.0 ml/min, λ = 210 nm, t (minor) = 9.43 min, t (major) = 20.27 min]; $[\alpha]_D^{25}$ = -195.0 (c = 0.121, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.73 (s, 3H), 2.81 (t, *J* = 7.2 Hz, 2H), 2.45 (s, 1H), 1.81 (q, *J* = 7.2 Hz, 2H), 1.07 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.47, 161.77, 51.98, 28.46, 28.35, 17.74, 13.54. HRMS(ESI) *m/z* calcd for $C_7H_{12}NO_2$ ($[M+H]^+$): 142.0868, found: 142.0866.



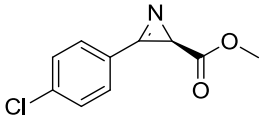
(*R*)-methyl 3-hexyl-2H-azirine-2-carboxylate (*R*)-**2g**: colorless oil, 49% yield, 99% ee [Daicel Chiralcel OD-H column, *n*-hexane / *i*-PrOH = 98 : 2, 1.0 ml/min, λ = 210 nm, t (minor) = 6.29 min, t (major) = 9.75 min]; $[\alpha]_D^{25}$ = -216.1 (c = 0.161, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.72 (s, 3H), 2.82 (t, *J* = 7.3 Hz, 2H), 2.44 (s, 1H), 1.82-1.70 (m, 2H), 1.45-1.40 (m, 2H), 1.39-1.26 (m, 4H), 0.90 (t, *J* = 6.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.50, 161.94, 52.03, 31.19, 28.63, 28.49, 26.63, 24.06, 22.31, 13.88. HRMS(ESI) *m/z* calcd for $C_{10}H_{18}NO_2$ ($[M+H]^+$): 184.1338, found: 184.1334.



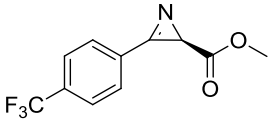
(*R*)-ethyl 3-benzyl-2H-azirine-2-carboxylate (*R*)-**2i**: colorless oil, 45% yield, 94% ee [Daicel Chiralcel OD-H column, *n*-hexane / *i*-PrOH = 98 : 2, 1.0 ml/min, λ = 225 nm, t (minor) = 16.40min, t (major) = 24.27 min]; $[\alpha]_D^{25}$ = -275.2 (c = 0.164, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.28 (m, 5H), 4.25-4.09 (m, 4H), 2.51 (s, 1H), 1.21 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.65, 161.29, 131.57, 128.89, 128.70, 127.65, 61.04, 32.89, 29.15, 14.05. HRMS(ESI) *m/z* calcd for $C_{12}H_{14}NO_2$ ($[M+H]^+$): 204.1025, found: 204.1018.



(*R*)-methyl 3-(4-bromophenyl)-2H-azirine-2-carboxylate (*R*)-**2k**: white solid, 48% yield, 97% ee [Daicel Chiralcel OD-H column, *n*-hexane / *i*-PrOH = 95 : 5, 1.0 ml/min, λ = 254 nm, t (minor) = 10.27 min, t (major) = 15.90 min]; m.p. 68.2-68.7 ^{o}C, $[\alpha]_D^{25}$ = -377.3 (c = 0.220, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.68 (m, 4H), 3.75 (s, 3H), 2.87 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.64, 157.99, 132.72, 131.54, 128.97, 121.06, 52.29, 29.54. HRMS(ESI) *m/z* calcd for $C_{10}H_9BrNO_2$ ($[M+H]^+$): 253.9811, found: 253.9800.



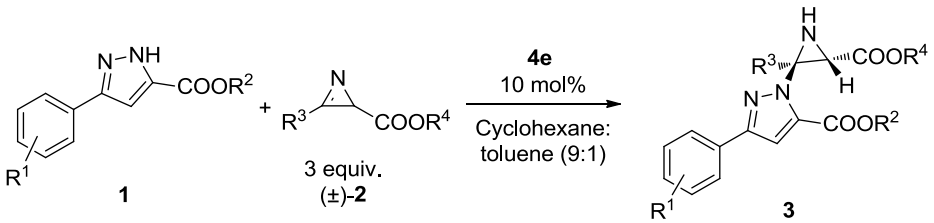
(*R*)-methyl 3-(4-chlorophenyl)-2H-azirine-2-carboxylate (*R*)-**2l**: white solid, 49% yield, 96% ee [Daicel Chiralcel OD-H column, *n*-hexane / *i*-PrOH = 95 : 5, 1.0 ml/min, λ = 254 nm, t (minor) = 9.32 min, t (major) = 14.10 min]; m.p. 63.4-64.2 ^{o}C, $[\alpha]_D^{25}$ = -602.2 (c = 0.184, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.0 Hz, 2H), 7.57 (d, *J* = 7.0 Hz, 2H), 3.75 (s, 3H), 2.87 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.70, 157.82, 140.37, 131.51, 129.77, 120.66, 52.31, 29.57. HRMS(ESI) *m/z* calcd for $C_{10}H_9ClNO_2$ ($[M+H]^+$): 210.0316, found: 210.0309.



(*R*)-methyl 3-(4-(trifluoromethyl)phenyl)-2H-azirine-2-carboxylate (*R*)-**2n**: colorless oil, 46% yield, 98% ee [Daicel Chiralcel OD-H column, *n*-hexane / *i*-PrOH = 97 : 3, 1.0 ml/min, λ = 254 nm, t (minor) = 9.49 min, t (major) = 17.24 min]; $[\alpha]_D^{25}$ = -518.2 (c = 0.203, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.0 Hz, 2H), 7.86 (d, *J* = 8.0 Hz, 2H), 3.76 (s, 3H), 2.94 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.36, 158.53, 135.25 (q, *J* = 32.7 Hz), 130.57, 126.30 (q, *J* = 3.7 Hz), 125.71, 123.25 (q, *J* = 271.3 Hz), 52.29, 29.91. HRMS(ESI) *m/z* calcd for $C_{11}H_9F_3NO_2$ ($[M+H]^+$): 244.0580, found: 244.0567.

General procedure and characterization data for chiral arylpyrazole substituted aziridines 3:

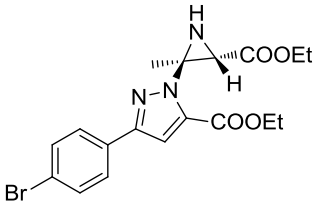
General procedure for chiral arylpyrazole substituted aziridines **3**:



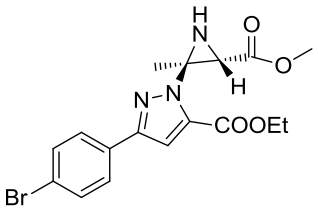
For **3a-3i** and **3p-3w**: A solution of 5-aryl-1H-pyrazole-3-carboxylic esters **1** (0.1 mmol) and catalyst **4e** (10 mol %, 0.01 mmol) in 0.9 mL cyclohexane and 0.1 mL toluene was stirred at -20 ^{o}C for 10 min, then racemic 2H-azirine carboxylic esters **2** (0.3 mmol) was added. The reaction mixture was stirred at -20 ℃ until the reaction was completed. After removal of the solvent, the residue was purified by flash column chromatography to afford the pure products.

For **3k**-**3o**: A solution of 5-aryl-1H-pyrazole-3-carboxylic esters **1** (0.1 mmol) and catalyst **4e** (10 mol %, 0.01 mmol) in 0.9 mL cyclohexane and 0.1 mL toluene was stirred at 25 ^{o}C for 10 min, then racemic 2H-azirine carboxylic esters **2** (0.3 mmol) was added. The reaction mixture was stirred at 25 ℃ until the reaction was completed. After removal of the solvent, the residue was purified by flash column chromatography to afford the pure products.

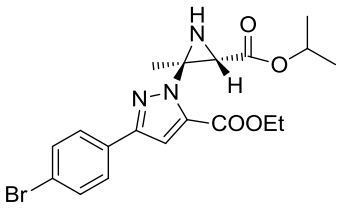
Characterization data for chiral arylpyrazole substituted aziridines **3**:



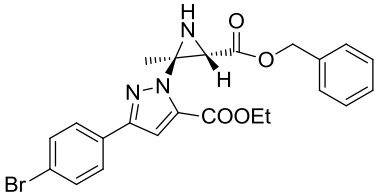
Ethyl 3-(4-bromophenyl)-1-((2*R*,3*S*)-3-(ethoxycarbonyl)-2-methylaziridin-2-yl)-1H-pyrazole-5-carboxylate **3a**: colourless oil, 97% yield, 99.9% ee [Daicel Chiralcel AS-H column, *n*-hexane / *i*-PrOH = 90 : 10, 1.0 ml/min, λ = 254 nm, t (major) = 7.73 min, t (minor) = 15.77 min]; $[\alpha]_D^{25}$ = +257.4 (c = 0.408, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.09 (s, 1H), 4.48-4.28 (m, 4H), 3.16 (s, 1H), 2.04 (brs, 1H), 1.93 (s, 3H), 1.45-1.36 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.35, 158.67, 149.29, 134.20, 131.74, 131.16, 127.33, 122.25, 108.68, 62.21, 61.36, 58.42, 42.17, 18.48, 14.20. HRMS(ESI) *m/z* calcd for $C_{18}H_{21}BrN_3O_4$ ($[M+H]^+$): 422.0715, found: 422.0715.



Ethyl 3-(4-bromophenyl)-1-((2*R*,3*S*)-3-(methoxycarbonyl)-2-methylaziridin-2-yl)-1H-pyrazole-5-carboxylate **3b**: colourless oil, 96% yield, 99.9% ee [Daicel Chiralcel AS-H column, *n*-hexane / *i*-PrOH = 90 : 10, 1.0 ml/min, λ = 254 nm, t (major) = 9.20 min, t (minor) = 18.72 min]; $[\alpha]_D^{25}$ = +226.1 (c = 0.452, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.1 Hz, 2H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.09 (s, 1H), 4.48-4.33 (m, 2H), 3.90 (s, 3H), 3.18 (s, 1H), 2.04 (brs, 1H), 1.93 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.70, 158.63, 149.27, 134.13, 131.71, 131.06, 127.28, 122.23, 108.72, 61.36, 58.43, 52.89, 42.01, 18.51, 14.16. HRMS(ESI) *m/z* calcd for $C_{17}H_{19}BrN_3O_4$ ($[M+H]^+$): 408.0559, found: 408.0559.

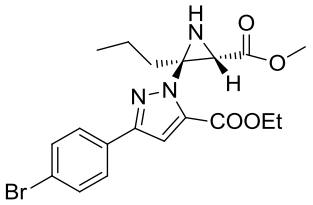


Ethyl 3-(4-bromophenyl)-1-((2*R*,3*S*)-3-(isopropoxycarbonyl)-2-methylaziridin-2-yl)-1H-pyrazole-5-carboxylate **3c**: colourless oil, 98% yield, 99.9% ee [Daicel Chiralcel AS-H column, *n*-hexane / *i*-PrOH = 90 : 10, 1.0 ml/min, λ = 254 nm, t (major) = 7.84 min, t (minor) = 14.96 min]; $[\alpha]_D^{25}$ = +222.1 (c = 0.426, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.08 (s, 1H), 5.23-5.14 (m, 1H), 4.49-4.31 (m, 2H), 3.12 (s, 1H), 2.01 (brs, 1H), 1.93 (s, 3H), 1.46-1.30 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.71, 158.62, 149.21, 134.21, 131.73, 131.16, 127.33, 122.21, 108.62, 70.04, 61.29, 58.29, 42.35, 21.86, 21.77, 18.43, 14.22. HRMS(ESI) *m/z* calcd for $C_{19}H_{23}BrN_3O_4$ ($[M+H]^+$): 436.0872, found: 436.0869.

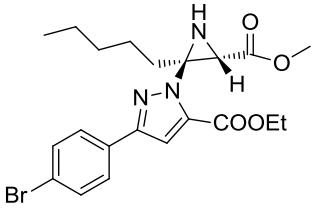


Ethyl 1-((2*R*,3*S*)-3-((benzyloxy)carbonyl)-2-methylaziridin-2-yl)-3-(4-bromophenyl)-1H-pyrazole-5-carboxylate **3d**: colourless oil, 98% yield, 99.9% ee [Daicel Chiralcel AS-H column, *n*-hexane / *i*-PrOH = 90 : 10, 1.0 ml/min, λ = 254 nm, t (major) = 13.13 min, t (minor) = 26.15 min]; $[\alpha]_D^{25}$ = +246.5 (c = 0.473, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.8 Hz, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.49-7.30 (m, 5H), 7.08 (s, 1H), 5.33 (s, 2H), 4.40-4.35 (m, 2H), 3.21 (s, 1H), 2.04 (brs, 1H), 1.92 (s, 3H), 1.44-1.32 (t, J = 6.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.11, 158.61,

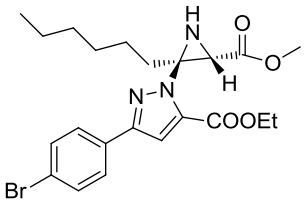
149.29, 135.07, 134.10, 131.72, 131.00, 128.60, 128.52, 128.34, 127.30, 122.25, 108.69, 67.70, 61.34, 58.48, 42.17, 18.54, 14.18. HRMS(ESI) *m/z* calcd for $C_{23}H_{23}BrN_3O_4$ ($[M+H]^+$): 484.0872, found: 484.0861.



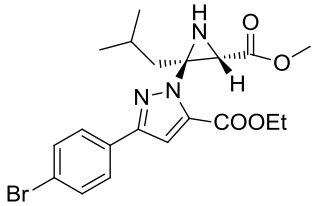
Ethyl 3-(4-bromophenyl)-1-((2*R*,3*S*)-3-(methoxycarbonyl)-2-propylaziridin-2-yl) -1H-pyrazole-5-carboxylate **3e**: white solid, 96% yield, 99.6% ee [Daicel Chiralcel AS-H column, *n*-hexane / *i*-PrOH = 90 : 10, 1.0 ml/min, λ = 254 nm, t (major) = 6.55 min, t (minor) = 18.88 min]; m.p. 130.6-131.2 °C, $[\alpha]_D^{25}$ = +252.4 (c = 0.416, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.12 (s, 1H), 4.40 (q, *J* = 6.0 Hz, 2H), 3.89 (s, 3H), 3.25 (s, 1H), 2.37 (s, 1H), 2.04-1.95 (m, 2H), 1.41 (t, *J* = 7.1 Hz, 3H), 1.26-1.17 (m, 2H), 0.86 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.84, 158.67, 148.79, 134.47, 131.72, 131.20, 127.32, 122.19, 109.12, 61.50, 61.34, 52.88, 41.89, 33.87, 18.71, 14.19, 13.49. HRMS(ESI) *m/z* calcd for $C_{19}H_{23}BrN_3O_4$ ($[M+H]^+$): 436.0872, found: 436.0870.



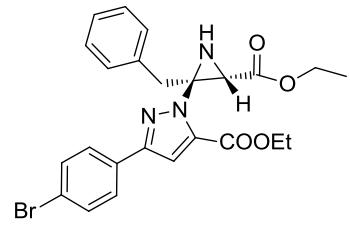
Ethyl 3-(4-bromophenyl)-1-((2*R*,3*S*)-3-(methoxycarbonyl)-2-pentylaziridin-2-yl) -1H-pyrazole-5-carboxylate **3f**: white solid, 92% yield, 99.4% ee [Daicel Chiralcel AS-H column, *n*-hexane / *i*-PrOH = 90 : 10, 1.0 ml/min, λ = 254 nm, t (major) = 5.41 min, t (minor) = 12.31 min]; m.p. 100.3-101.1 °C, $[\alpha]_D^{25}$ = +304.3 (c = 0.370, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.12 (s, 1H), 4.40 (q, *J* = 7.0 Hz, 2H), 3.89 (s, 3H), 3.25 (s, 1H), 2.37 (s, 1H), 2.10-1.92 (m, 2H), 1.41 (t, *J* = 7.1 Hz, 3H), 1.29-1.11 (m, 6H), 0.80 (t, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.77, 158.67, 148.78, 134.45, 131.71, 131.20, 127.31, 122.18, 109.14, 61.64, 61.33, 52.86, 41.92, 31.87, 31.04, 24.90, 22.28, 14.19, 13.81. HRMS(ESI) *m/z* calcd for $C_{19}H_{23}BrN_3O_4$ ($[M+H]^+$): 464.1179, found: 464.1180.



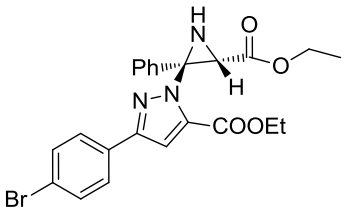
Ethyl 3-(4-bromophenyl)-1-((2*R*,3*S*)-2-hexyl-3-(methoxycarbonyl)aziridin-2-yl)-1H-pyrazole-5-carboxylate **3g**: white solid, 86% yield, 99.9% ee [Daicel Chiralcel AS-H column, *n*-hexane / *i*-PrOH = 90 : 10, 1.0 ml/min, λ = 254 nm, t (major) = 4.99 min, t (minor) = 9.88 min]; m.p. 97.2-97.7 °C, $[\alpha]_D^{25}$ = +313.1 (c = 0.411, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.5 Hz, 2H), 7.53 (d, *J* = 7.9 Hz, 2H), 7.13 (s, 1H), 4.40 (q, *J* = 6.0 Hz, 2H), 3.89 (s, 3H), 3.25 (s, 1H), 2.38 (brs, 1H), 2.02 (t, *J* = 6.0 Hz, 2H), 1.41 (t, *J* = 5.6 Hz, 3H), 1.29-1.09 (m, 8H), 0.82 (t, *J* = 5.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.82, 158.68, 148.78, 134.45, 131.71, 131.22, 127.31, 122.20, 109.14, 61.64, 61.33, 52.91, 41.94, 31.94, 31.45, 28.56, 25.32, 22.40, 14.19, 13.92. HRMS(ESI) *m/z* calcd for $C_{22}H_{29}BrN_3O_4$ ($[M+H]^+$): 478.1336, found: 478.1337.



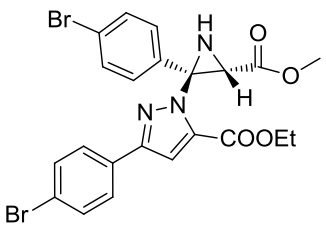
Ethyl 3-(4-bromophenyl)-1-((2*R*,3*S*)-2-isobutyl-3-(methoxycarbonyl)aziridin-2-yl)-1H-pyrazole-5-carboxylate **3h**: white solid, 93% yield, 99.3% ee [Daicel Chiralcel AS-H column, *n*-hexane / *i*-PrOH = 90 : 10, 1.0 ml/min, λ = 254 nm, t (major) = 5.38 min, t (minor) = 11.07 min]; m.p. 123.2-123.8 °C, $[\alpha]_D^{25}$ = +358.9 (c = 0.418, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.8 Hz, 2H), 7.52 (d, *J* = 7.5 Hz, 2H), 7.12 (s, 1H), 4.42-4.32 (m, 2H), 3.88 (s, 3H), 3.29 (s, 1H), 2.43 (brs, 1H), 1.93-1.73 (m, 1H), 1.41 (t, *J* = 6.8 Hz, 3H), 1.35-1.18 (m, 2H), 0.89 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.96, 158.65, 148.53, 134.49, 131.72, 131.23, 127.24, 122.16, 109.12, 61.31, 60.87, 52.85, 41.72, 39.65, 25.34, 22.86, 21.76, 14.19. HRMS(ESI) *m/z* calcd for $C_{20}H_{25}BrN_3O_4$ ($[M+H]^+$): 450.1028, found: 450.1029.



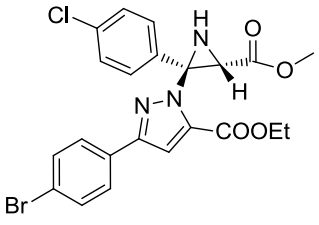
Ethyl 3-(4-bromophenyl)-1-((2*R*,3*S*)-3-(ethoxycarbonyl)-2-phenethylaziridin -2-yl)-1H-pyrazole-5-carboxylate **3i**: white solid, 91% yield, 97% ee [Daicel Chiralcel AS-H column, *n*-hexane / *i*-PrOH = 90 : 10, 1.0 ml/min, λ = 254 nm, t (major) = 8.35 min, t (minor) = 21.40 min]; m.p. 84.5-85.2 ^{o}C, $[\alpha]_D^{25}$ = +219.5 (c = 0.307, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.18-7.11 (m, 3H), 7.05 (s, 1H), 6.92-6.84 (m, 2H), 4.43-4.29 (m, 4H), 3.71 (d, *J* = 14.3 Hz, 1H), 3.39 (d, *J* = 14.8 Hz, 1H), 3.33 (s, 1H), 2.28 (brs, 1H), 1.40 (t, *J* = 7.6 Hz, 3H), 1.38 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.37, 158.63, 148.87, 135.22, 134.76, 131.63, 131.14, 129.35, 128.07, 127.39, 126.87, 122.16, 109.19, 62.20, 61.59, 61.29, 42.44, 38.20, 14.21. HRMS(ESI) *m/z* calcd for $C_{24}H_{25}BrN_3O_4$ ($[M+H]^+$): 498.1023, found: 498.1026.



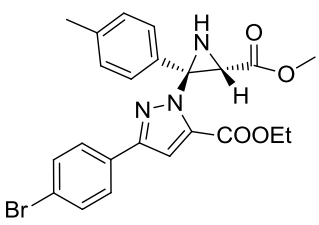
Ethyl 3-(4-bromophenyl)-1-((2*R*,3*S*)-3-(ethoxycarbonyl)-2-phenylaziridin-2-yl)-1H-pyrazole-5-carboxylate **3j**: white solid, 89% yield, 98% ee [Daicel Chiralcel AS-H column, *n*-hexane / *i*-PrOH = 90 : 10, 1.0 ml/min, λ = 254 nm, t (major) = 13.76 min, t (minor) = 21.66 min]; m.p. 127.0-127.8 ^{o}C, $[\alpha]_D^{25}$ = +507.1 (c = 0.435, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.1 Hz, 2H), 7.62-7.52 (m, 4H), 7.34-7.26 (m, 3H), 7.09 (s, 1H), 4.32 (q, *J* = 6.9 Hz, 2H), 4.06 (q, *J* = 6.9 Hz, 2H), 3.77 (s, 1H), 2.99 (brs, 1H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.08 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.58, 158.34, 149.31, 134.87, 133.70, 131.75, 131.17, 128.81, 127.89, 127.79, 127.39, 122.30, 109.37, 61.85, 61.23, 43.70, 14.17, 13.89. HRMS(ESI) *m/z* calcd for $C_{23}H_{23}BrN_3O_4$ ($[M+H]^+$): 484.0866, found: 484.0857.



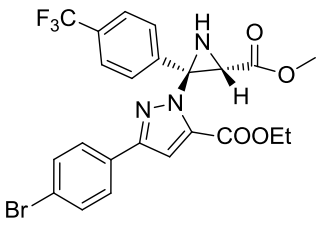
Ethyl 3-(4-bromophenyl)-1-((2*R*,3*S*)-2-(4-bromophenyl)-3-(methoxycarbonyl) aziridin-2-yl)-1H-pyrazole-5-carboxylate **3k**: white solid, 91% yield, 99.7% ee [Daicel Chiralcel AS-H column, *n*-hexane / *i*-PrOH = 90 : 10, 1.0 ml/min, λ = 254 nm, t (major) = 13.05 min, t (minor) = 22.37 min]; m.p. 151.2-151.8 ^{o}C, $[\alpha]_D^{25}$ = +444.4 (c = 0.496, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 6.8 Hz, 2H), 7.55 (d, *J* = 7.9 Hz, 2H), 7.43 (s, 4H), 7.09 (s, 1H), 4.38-4.24 (m, 2H), 3.80 (s, 1H), 3.66 (s, 3H), 2.92 (brs, 1H), 1.33 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.05, 158.29, 149.60, 134.81, 132.79, 131.80, 131.17, 130.93, 129.46, 127.37, 123.19, 122.48, 109.44, 61.38, 52.86, 43.60, 14.17. HRMS(ESI) *m/z* calcd for $C_{22}H_{20}Br_2N_3O_4$ ($[M+H]^+$): 547.9815, found: 547.9820.



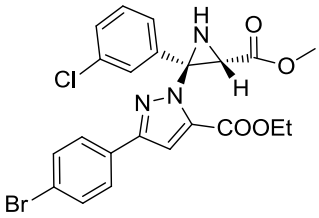
Ethyl 3-(4-bromophenyl)-1-((2*R*,3*S*)-2-(4-chlorophenyl)-3-(methoxycarbonyl) aziridin-2-yl)-1H-pyrazole-5-carboxylate **3l**: white solid, 93% yield, 99.9% ee [Daicel Chiralcel AS-H column, *n*-hexane / *i*-PrOH = 90 : 10, 1.0 ml/min, λ = 254 nm, t (major) = 7.59 min, t (minor) = 12.92 min]; m.p. 148.2-148.7 ^{o}C, $[\alpha]_D^{25}$ = +592.3 (c = 0.468, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 7.10 (s, 1H), 4.32 (q, *J* = 7.2 Hz, 2H), 3.80 (s, 1H), 3.66 (s, 3H), 2.05 (brs, 1H) 1.34 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.05, 158.33, 149.61, 134.89, 132.28, 131.83, 130.94, 129.18, 128.25, 127.37, 122.47, 109.44, 99.94, 61.38, 52.85, 43.63, 14.16. HRMS(ESI) *m/z* calcd for $C_{22}H_{20}BrClN_3O_4$ ($[M+H]^+$): 504.0320, found: 504.0321.



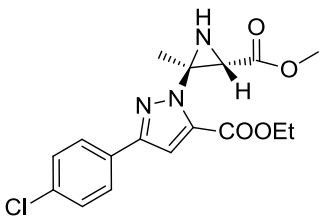
Ethyl 3-(4-bromophenyl)-1-((2*R*,3*S*)-3-(methoxycarbonyl)-2-(p-tolyl)aziridin-2-yl)-1H-pyrazole-5-carboxylate **3m**: white solid, 74% yield, 99.5% ee [Daicel Chiralcel AS-H column, *n*-hexane / *i*-PrOH = 95 : 5, 1.0 ml/min, λ = 254 nm, t (major) = 17.58 min, t (minor) = 29.89 min]; m.p. 134.5-135.2 °C, $[\alpha]_D^{25}$ = +403.9 (c = 0.359, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.6 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 7.1 Hz, 2H), 7.09 (d, *J* = 7.1 Hz, 2H), 7.08 (s, 1H) 4.32 (q, *J* = 6.5 Hz, 2H), 3.75 (s, 1H), 3.65 (s, 3H), 2.95 (brs, 1H), 2.29 (s, 3H), 1.34 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.43, 158.37, 149.32, 138.78, 134.76, 131.75, 131.19, 130.70, 128.70, 127.56, 127.39, 122.29, 109.35, 61.25, 52.78, 43.59, 21.21, 14.19. HRMS(ESI) *m/z* calcd for $C_{23}H_{23}BrN_3O_4$ ($[M+H]^+$): 484.0872, found: 484.0867.



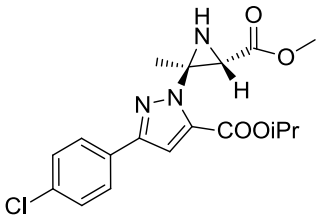
Ethyl 3-(4-bromophenyl)-1-((2*R*,3*S*)-3-(methoxycarbonyl)-2-(4-(trifluoromethyl)phenyl)aziridin-2-yl)-1H-pyrazole-5-carboxylate **3n**: white solid, 90% yield, 99.9% ee [Daicel Chiralcel AS-H column, *n*-hexane / *i*-PrOH = 90 : 10, 1.0 ml/min, λ = 254 nm, t (major) = 8.68 min, t (minor) = 13.26 min]; m.p. 138.5-139.2 °C, $[\alpha]_D^{25}$ = +576.4 (c = 0.483, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.8 Hz, 2H), 7.69 (d, *J* = 7.4 Hz, 2H), 7.56 (d, *J* = 7.7 Hz, 4H), 7.11 (s, 1H), 4.31 (q, *J* = 6.4 Hz, 2H), 3.84 (s, 1H), 3.65 (s, 3H), 3.00 (brs, 1H), 1.34 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.73, 158.22, 149.78, 137.65, 135.03, 131.79, 130.87, 130.82 (q, *J* = 32.3 Hz), 128.25, 127.35, 125.12, 124.87 (d, *J* = 3.5 Hz), 123.78 (q, *J* = 271.1 Hz), 109.45, 61.37, 52.64, 43.80, 14.04. HRMS(ESI) *m/z* calcd for $C_{23}H_{20}BrF_3N_3O_4$ ($[M+H]^+$): 538.0584, found: 538.0581.



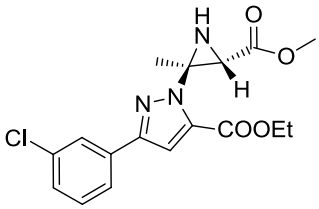
Ethyl 3-(4-bromophenyl)-1-((2*R*,3*S*)-2-(3-chlorophenyl)-3-(methoxycarbonyl) aziridin-2-yl)-1H-pyrazole-5-carboxylate **3o**: white solid, 86% yield, 99% ee [Daicel Chiralcel AS-H column, *n*-hexane / *i*-PrOH = 95 : 5, 1.0 ml/min, λ = 254 nm, t (major) = 18.37 min, t (minor) = 39.18 min]; m.p. 143.3-144.0 °C, $[\alpha]_D^{25}$ = +501.4 (c = 0.434, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.60-7.55 (m, 3H), 7.47 (d, *J* = 6.2 Hz, 1H), 7.30-7.19 (m, 2H), 7.11 (s, 1H), 4.33 (q, *J* = 6.8 Hz, 2H), 3.79 (s, 1H), 3.67 (s, 3H), 2.90 (brs, 1H), 1.35 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.93, 158.30, 149.69, 135.68, 134.87, 133.92, 131.81, 130.92, 129.24, 129.15, 128.03, 127.40, 125.99, 122.50, 109.52, 61.44, 52.85, 43.70, 14.17. HRMS(ESI) *m/z* calcd for $C_{22}H_{20}BrClN_3O_4$ ($[M+H]^+$): 504.0326, found: 504.0321.



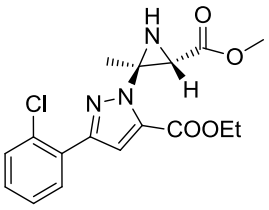
Ethyl 3-(4-chlorophenyl)-1-((2*R*,3*S*)-3-(methoxycarbonyl)-2-methylaziridin-2-yl)-1H-pyrazole-5-carboxylate **3p**: white solid, 98% yield, 99.9% ee [Daicel Chiralcel AS-H column, *n*-hexane / *i*-PrOH = 95 : 5, 1.0 ml/min, λ = 254 nm, t (major) = 11.93 min, t (minor) = 27.15 min]; m.p. 93.3-94.0 °C, $[\alpha]_D^{25}$ = +234.2 (c = 0.357, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.09 (s, 1H), 4.52-4.30 (m, 2H), 3.90 (s, 3H), 3.19 (s, 1H), 2.04 (brs, 1H), 1.93 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.85, 158.68, 149.30, 134.14, 134.07, 130.64, 128.80, 127.03, 108.75, 61.38, 58.45, 52.93, 42.05, 18.55, 14.19. HRMS(ESI) *m/z* calcd for $C_{17}H_{19}ClN_3O_4$ ($[M+H]^+$): 364.1064, found: 364.1065.



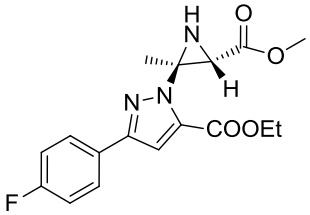
Isopropyl 3-(4-chlorophenyl)-1-((2*R*,3*S*)-3-(methoxycarbonyl)-2-methylaziridin -2-yl)-1H-pyrazole-5-carboxylate **3q**: white solid, 97% yield, 99.9% ee [Daicel Chiralcel AS-H column, *n*-hexane / *i*-PrOH = 90 : 10, 1.0 ml/min, λ = 254 nm, t (major) = 6.63 min, t (minor) = 10.25 min]; m.p. 113.3-114.1 °C, $[\alpha]_D^{25}$ = +240.0 (c = 0.365, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.06 (s, 1H), 5.32-5.23 (m, 1H), 3.90 (s, 3H), 3.19 (s, 1H), 2.04 (brs, 1H), 1.94 (s, 3H), 1.40 (d, *J* = 4.0 Hz, 3H), 1.39 (d, *J* = 4.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.84, 158.24, 149.18, 134.58, 134.01, 130.70, 128.78, 127.02, 108.62, 69.19, 58.47, 52.91, 41.99, 21.81, 18.55. HRMS(ESI) *m/z* calcd for $C_{18}H_{21}ClN_3O_4$ ($[M+H]^+$): 378.1221, found: 378.1218.



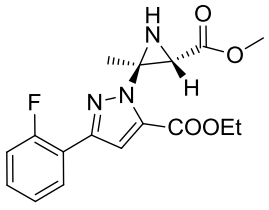
Ethyl 3-(3-chlorophenyl)-1-((2*R*,3*S*)-3-(methoxycarbonyl)-2-methylaziridin-2-yl)-1H-pyrazole-5-carboxylate **3r**: white solid, 97% yield, 99.9% ee [Daicel Chiralcel AS-H column, *n*-hexane / *i*-PrOH = 90 : 10, 1.0 ml/min, λ = 254 nm, t (major) = 7.87 min, t (minor) = 16.21 min]; m.p. 87.1-87.8 °C, $[\alpha]_D^{25}$ = +252.1 (c = 0.357, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.69 (d, *J* = 7.2 Hz, 1H), 7.37-7.28 (m, 2H), 7.11 (s, 1H), 4.51-4.32 (m, 2H), 3.90 (s, 3H), 3.20 (s, 1H), 2.05 (brs, 1H), 1.93 (s, 3H), 1.42 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.81, 158.62, 149.01, 134.63, 134.16, 133.89, 129.85, 128.20, 125.79, 123.83, 108.89, 61.37, 58.48, 52.90, 42.00, 18.50, 14.16. HRMS(ESI) *m/z* calcd for $C_{17}H_{19}ClN_3O_4$ ($[M+H]^+$): 364.1064, found: 364.1056.



Ethyl 3-(2-chlorophenyl)-1-((2*R*,3*S*)-3-(methoxycarbonyl)-2-methylaziridin-2-yl)-1H-pyrazole-5-carboxylate **3s**: colorless oil, 97% yield, 99.9% ee [Daicel Chiralcel AS-H column, *n*-hexane / *i*-PrOH = 90 : 10, 1.0 ml/min, λ = 254 nm, t (major) = 8.02 min]; $[\alpha]_D^{25}$ = +237.5 (c = 0.347, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.4 Hz, 1H), 7.44 (d, *J* = 7.5 Hz, 1H), 7.38-7.27 (m, 3H), 4.51-4.32 (m, 2H), 3.89 (s, 3H), 3.22 (s, 1H), 2.05 (brs, 1H), 1.95 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.77, 158.83, 147.97, 133.20, 132.28, 131.04, 130.66, 130.22, 129.32, 126.85, 112.78, 61.34, 58.48, 52.89, 42.02, 18.57, 14.20. HRMS(ESI) *m/z* calcd for $C_{17}H_{19}ClN_3O_4$ ($[M+H]^+$): 364.1064, found: 364.1072.

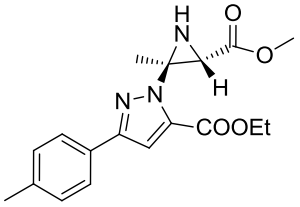


Ethyl 3-(4-fluorophenyl)-1-((2*R*,3*S*)-3-(methoxycarbonyl)-2-methylaziridin-2-yl)-1H-pyrazole-5-carboxylate **3t**: colorless oil, 98% yield, 99.6% ee [Daicel Chiralcel AS-H column, *n*-hexane / *i*-PrOH = 90 : 10, 1.0 ml/min, λ = 254 nm, t (major) = 9.11 min, t (minor) = 18.54 min]; $[\alpha]_D^{25}$ = +208.2 (c = 0.341, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89-7.73 (m, 2H), 7.18-7.00 (m, 3H), 4.49-4.32 (m, 2H), 3.90 (s, 3H), 3.19 (s, 1H), 2.04 (brs, 1H), 1.93 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.64, 162.85 (d, *J* = 245.3 Hz), 158.70, 149.50, 134.16, 128.41, 127.51 (d, *J* = 8.1 Hz), 115.49 (d, *J* = 21.5 Hz), 108.55, 61.28, 58.37, 52.74, 42.06, 18.53, 14.13. HRMS(ESI) *m/z* calcd for $C_{17}H_{19}FN_3O_4$ ($[M+H]^+$): 348.1360, found: 348.1349.

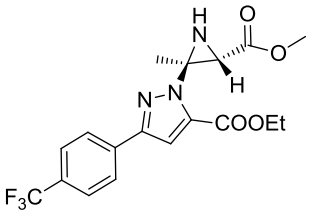


Ethyl 3-(2-fluorophenyl)-1-((2*R*,3*S*)-3-(methoxycarbonyl)-2-methylaziridin-2-yl)-1H-pyrazole-5-carboxylate **3u**: colorless oil, 97% yield, 99.9% ee [Daicel Chiralcel AS-H column, *n*-hexane / *i*-PrOH = 90 : 10, 1.0 ml/min, λ = 254 nm, t (major) = 7.91 min, t (minor) = 15.81 min]; $[\alpha]_D^{25}$ = +179.8 (c = 0.337, EtOAc). ^{1}H NMR (400 MHz,

$CDCl_3$) δ 8.05 (t, *J* = 7.6 Hz, 1H), 7.35-7.28 (m, 1H), 7.26-7.24 (m, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.17-7.09 (m, 1H), 4.46-4.35 (m, 2H), 3.90 (s, 3H), 3.21 (s, 1H), 2.10 (brs, 1H), 1.94 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.68, 160.11 (d, *J* = 248.4 Hz), 158.76, 144.95, 133.75, 129.55 (d, *J* = 8.3 Hz), 128.52 (d, *J* = 3.0 Hz), 124.14 (d, *J* = 3.2 Hz), 120.04 (d, *J* = 11.3 Hz), 115.89 (d, *J* = 22.0 Hz), 112.18 (d, *J* = 9.7 Hz), 61.21, 58.43, 52.69, 41.98, 18.50, 14.10. HRMS(ESI) *m/z* calcd for $C_{17}H_{19}FN_3O_4$ ($[M+H]^+$): 348.1360, found: 348.1361.



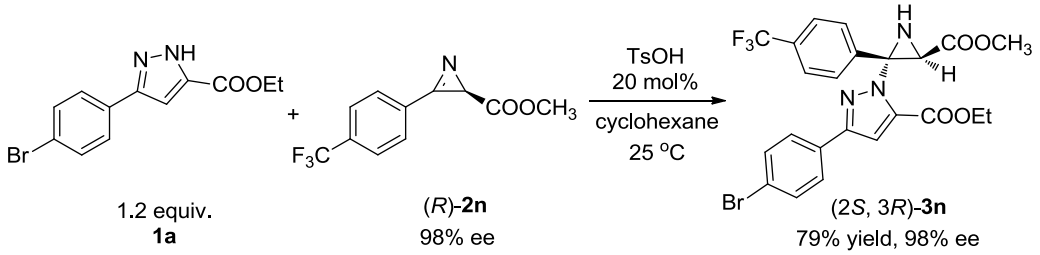
Ethyl 1-((2*R*,3*S*)-3-(methoxycarbonyl)-2-methylaziridin-2-yl)-3-(p-tolyl)-1H-pyrazole-5-carboxylate **3v**: colorless oil, 98% yield, 99.9% ee [Daicel Chiralcel AS-H column, *n*-hexane / *i*-PrOH = 90 : 10, 1.0 ml/min, λ = 254 nm, t (major) = 7.48 min, t (minor) = 14.22 min]; $[\alpha]_D^{25}$ = +203.8 (c = 0.320, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.2 Hz, 2H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.16 (s, 1H), 4.55-4.32 (m, 2H), 3.91 (s, 3H), 3.20 (s, 1H), 2.06 (brs, 1H), 1.95 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.86, 158.87, 150.49, 138.10, 133.85, 129.30, 125.67, 108.65, 61.26, 58.34, 52.88, 42.09, 21.24, 18.58, 14.20. HRMS(ESI) *m/z* calcd for $C_{18}H_{22}N_3O_4$ ($[M+H]^+$): 344.1605, found: 344.1608.



Ethyl 1-((2*R*,3*S*)-3-(methoxycarbonyl)-2-methylaziridin-2-yl)-3-(4-(trifluoromethyl)phenyl)-1H-pyrazole-5-carboxylate **3w**: white solid, 72% yield, 99% ee [Daicel Chiralcel AS-H column, *n*-hexane / *i*-PrOH = 90 : 10, 1.0 ml/min, λ = 254 nm, t (major) = 7.15 min, t (minor) = 12.98 min]; m.p. 85.1-85.8 °C, $[\alpha]_D^{25}$ = +306.6 (c = 0.286, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 8.1 Hz, 2H), 7.16 (s, 1H), 4.52-4.29 (m, 2H), 3.91 (s, 3H), 3.20 (s, 1H), 2.06 (brs, 1H), 1.95 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.59, 158.58, 148.92, 135.62, 134.45, 130.10 (q, *J* = 32.1 Hz), 125.93, 125.54 (d, *J* = 3.8 Hz), 124.07 (q, *J* = 260.9 Hz), 109.09, 61.41, 58.56, 52.78, 42.03, 18.50, 14.11. HRMS(ESI) *m/z* calcd for $C_{18}H_{19}F_3N_3O_4$ ($[M+H]^+$): 398.1328, found: 398.1330.

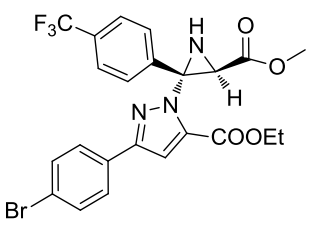
General procedure and characterization data for chiral arylpyrazole substituted aziridine (2*S*, 3*R*)-3n:

General procedure for chiral arylpyrazole substituted aziridine (2*S*, 3*R*)-**3n**:



A solution of 5-aryl-1H-pyrazole-3-carboxylic ester **1a** (0.12 mmol) and TsOH (20 mol %, 0.02 mmol) in 1.0 mL cyclohexane was stirred at 25 °C for 10 min, then chiral 2H-azirine carboxylic ester (*R*)-**2n** (0.1 mmol) was added. The reaction mixture was stirred at 25 ℃ until the reaction was completed. After removal of the solvent, the residue was purified by flash column chromatography to afford the pure product.

Characterization data for chiral arylpyrazole substituted aziridine (2*S*, 3*R*)-**3n**:



Ethyl 3-(4-bromophenyl)-1-((2*S*,3*R*)-3-(methoxycarbonyl)-2-(4-(trifluoromethyl) phenyl)aziridin-2-yl)-1H-pyrazole-5-carboxylate (2*S*, 3*R*)-**3n**: white solid, 79% yield, 98% ee [Daicel Chiralcel AS-H column, *n*-hexane / *i*-PrOH = 90 : 10, 1.0 ml/min, λ = 254 nm, t (minor) = 9.12 min, t (major) = 14.53 min]; m.p. 138.3-139.2 ^{o}C, $[\alpha]_D^{25}$ = -532.3 (c = 0.426, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.8 Hz, 2H), 7.69 (d, *J* = 7.4 Hz, 2H), 7.56 (d, *J* = 7.7 Hz, 4H), 7.11 (s, 1H), 4.31 (q, *J* = 6.4 Hz, 2H), 3.84 (s, 1H), 3.65 (s, 3H), 3.00 (brs, 1H), 1.34 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.73, 158.22, 149.78, 137.65, 135.03, 131.79, 130.87, 130.82 (q, *J* = 32.3 Hz), 128.25, 127.35, 125.12, 124.87 (d, *J* = 3.5 Hz), 123.78 (q, *J* = 271.1 Hz), 109.45, 61.37, 52.64, 43.80, 14.04. HRMS(ESI) *m/z* calcd for $C_{23}H_{20}BrF_3N_3O_4$ ($[M+H]^+$): 538.0584, found: 538.0581.

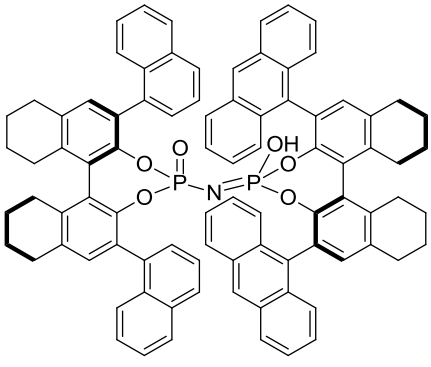
General procedure and characterization data for H_8-BINOL derived chiral imidodiphosphoric acids 4:

H_8-BINOL derived chiral imidodiphosphoric acids **4a**-**4e** were synthesized according to our previous work.[3] Catalyst **4e** were first synthesized in this work and the characterization data was given.

General procedure for H_8-BINOL derived chiral imidodiphosphoric acids **4e**:

NaH (60% in oil, 3 mmol) was added to a stirred solution of 9-anthracenyl substituted H_8-BINOL-type phosphoryl chloride (1.2 mmol) in dry DMF (10 ml) under nitrogen atmosphere at room termperature. After stirring for 5 min, 1-naphthyl substituted H_8-BINOL-type phosphoramide (1 mmol) was added and the mixture was stirred for another 1 h. After the reaction was completed, 30 ml CH_2Cl_2 was added to the flask and the mixture was washed with saturated brine (50 ml × 5). The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified with silica gel column chromatography. Then the product was dissolved in CH_2Cl_2, acidified with 3 M HCl (10 ml), washed with brine (30 ml × 5), dried over Na_2SO_4 and concentrated in vacuo. The product was further purified by recrystallization in THF and methanol to give catalyst **4e**.

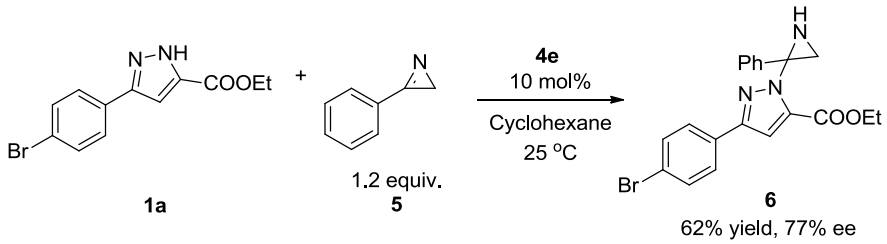
Characterization data for H_8-BINOL derived chiral imidodiphosphoric acids **4e**:



H_8-BINOL derived chiral imidodiphosphoric acids **4e**: white soild, 52% yield, ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 (s, 2H), 8.06 (d, *J* = 6.4 Hz, 1H), 7.94-7.85 (m, 1H), 7.77 (t, *J* = 6.4 Hz, 1H), 7.69-7.45 (m, 12H), 7.38-7.34 (m, 3H), 7.30-7.16 (m, 3H), 7.04-6.76 (m, 4H), 6.68 (t, *J* = 7.2 Hz, 1H), 6.60-6.50 (m, 4H), 6.32 (s, 1H), 6.20-5.92 (m, 3H), 5.69-5.60 (m, 1H), 2.99-2.28 (m, 16H), 2.12-1.75 (m, 16H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.59, 145.32, 145.00, 143.75, 138.01, 137.21, 136.75, 135.05, 134.83, 134.62, 133.71, 133.48, 133.20, 132.99, 132.65, 132.38, 132.06, 131.80, 130.85, 130.67, 130.42, 130.20, 129.71, 128.40, 128.11, 127.82, 127.32, 127.19, 126.84, 126.45, 126.19, 125.86, 125.27, 124.76, 124.50, 124.11, 123.97, 123.28, 29.64, 29.51, 29.42, 29.13, 28.98, 28.89, 28.47, 28.13, 27.95, 27.71, 23.17, 23.08, 22.85, 22.80, 22.77, 22.64, 22.52. ^{31}P NMR (162 MHz, $CDCl_3$) δ 6.73, 6.31, 5.41, 4.99. HRMS(ESI) *m/z* calcd for $C_{88}H_{70}NO_6P_2$ ($[M+H]^+$): 1298.4678, found: 1298.4686.

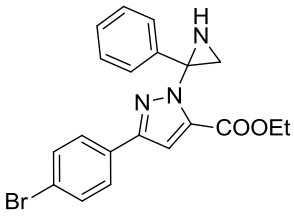
General procedure and characterization data for chiral arylpyrazole substituted aziridines 6:

General procedure for chiral arylpyrazole substituted aziridines **6**:



A solution of 5-aryl-1H-pyrazole-3-carboxylic esters **1a** (0.1 mmol) and catalyst **4e** (10 mol %, 0.01 mmol) in 1.0 mL cyclohexane was stirred at 25 °C for 10 min, then 3-phenyl-2H-azirine **5** (0.12 mmol) was added. The reaction mixture was stirred at 25 ℃ for 6 d. After removal of the solvent, the residue was purified by flash column chromatography to afford the pure products.

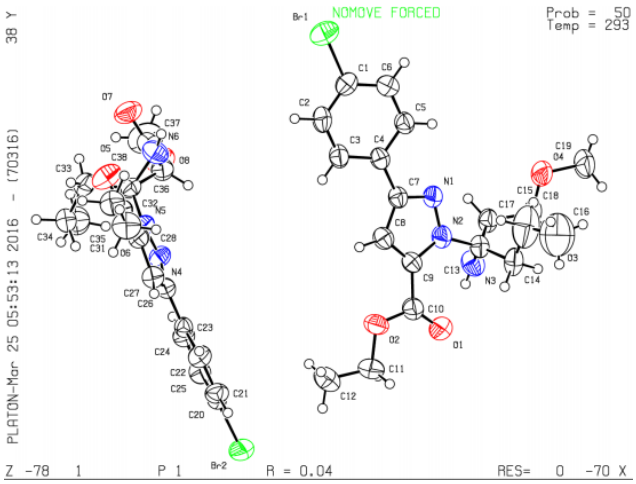
Characterization data for chiral arylpyrazole substituted aziridines **6**:



Ethyl 3-(4-bromophenyl)-1-(2-phenylaziridin-2-yl)-1H-pyrazole-5-carboxylate **6**: colorless oil, 62% yield, 77% ee [Daicel Chiralcel OD-H column, *n*-hexane / *i*-PrOH = 95 : 5, 1.0 ml/min, λ = 254 nm, t (minor) = 15.14 min, t (major) = 18.76 min]; $[\alpha]_D^{25}$ = +144.7 (c = 0.253, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.6 Hz, 2H), 7.55 (d, *J* = 7.3 Hz, 2H), 7.37-7.26 (m, 3H), 7.20 (s, 1H), 7.12 (d, *J* = 7.1 Hz, 2H), 4.26 (q, *J* = 6.5 Hz, 2H), 2.87 (s, 1H), 2.65 (s, 1H), 1.62 (brs, 1H), 1.27 (t, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 158.44, 148.81, 140.39, 136.21, 132.21, 131.66, 128.70, 127.99, 127.76, 125.09, 121.95, 109.33, 61.36, 14.30. HRMS(ESI) *m/z* calcd for $C_{20}H_{19}BrN_3O_2$ ($[M+H]^+$): 412.0661, found: 412.0652.

X-Ray Structures of 3e:

Good quality crystal of **3e** was obtained by recrystallization in ethanol. CCDC 1486543 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



(1) (a) Çalışkan, B.; Yılmaz, A.; Evren, İ.; Menevşe, S.; Uludag, O.; Banoglu, E. *Med. Chem. Res.* **2012**, *22*, 782. (b) Kamal, A.; Shaik, A. B.; Polepalli, S.; Reddy, V. S.; Kumar, G. B.; Gupta, S.; Krishna, K. V.; Nagabhushana, A.; Mishra, R. K.; Jain, N. *Org. Biomol. Chem.* **2014**, *12*, 7993. (c) Nagarapu, L.; Mateti, J.; Gaikwad, H. K.; Bantu, R.; Sheeba Rani, M.; Prameela Subhashini, N. J. *Bioorg. Med. Chem. Lett.* **2011**, *21*, 4138.
(2) (a) Wang, Y.; Lei, X.; Tang, Y. *Chem. Commun*. **2015**, *51*, 4507. (b) Ryu, T.; Baek, Y.; Lee, P. H. *J. Org. Chem*. **2015**, *80*, 2376. (c) Loy, N. S. Y.; Kim, S.; Park, C. M. *Org. Lett*. **2015**, *17*, 395. (d) Loy, N. S. Y.; Singh, A.; Xu, X.; Park, C. M. *Angew. Chem*. **2013**, *125*, 2268.
(3) Fan, Y.-S.; Jiang, Y.-J.; An, D.; Sha, D.; Antilla, J. C.; Zhang, S. *Org. Lett*. **2014**, *16*, 6112.

NMR spectra:

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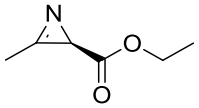

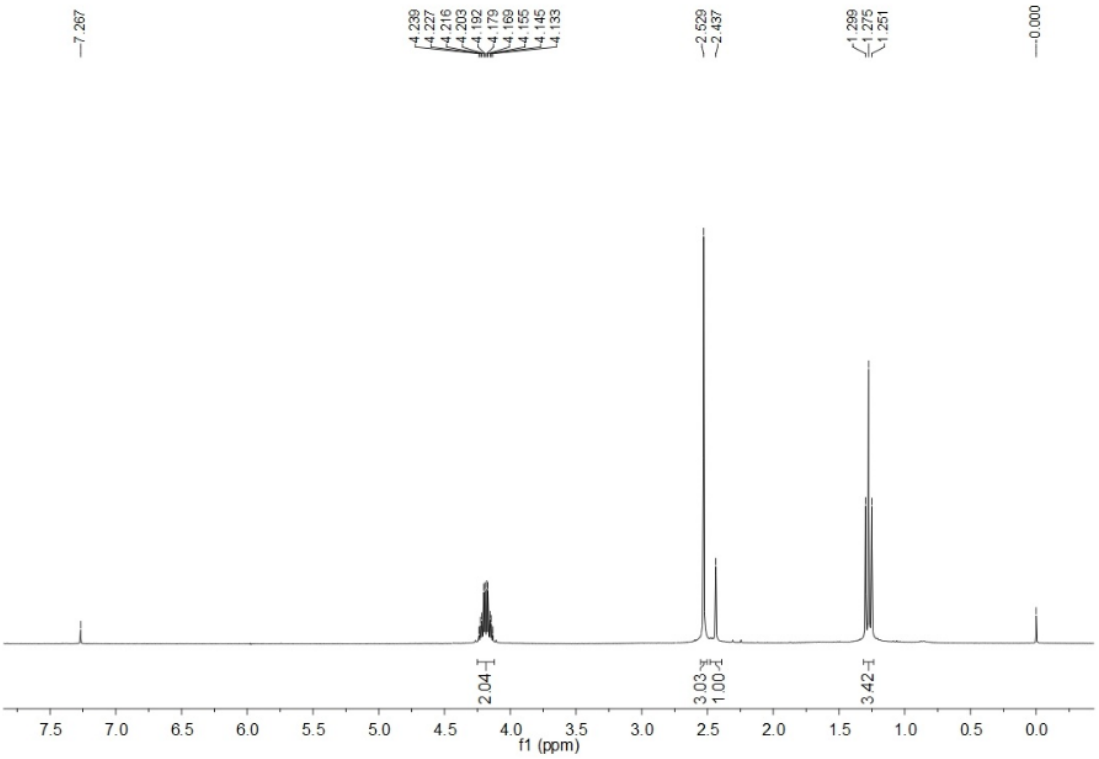

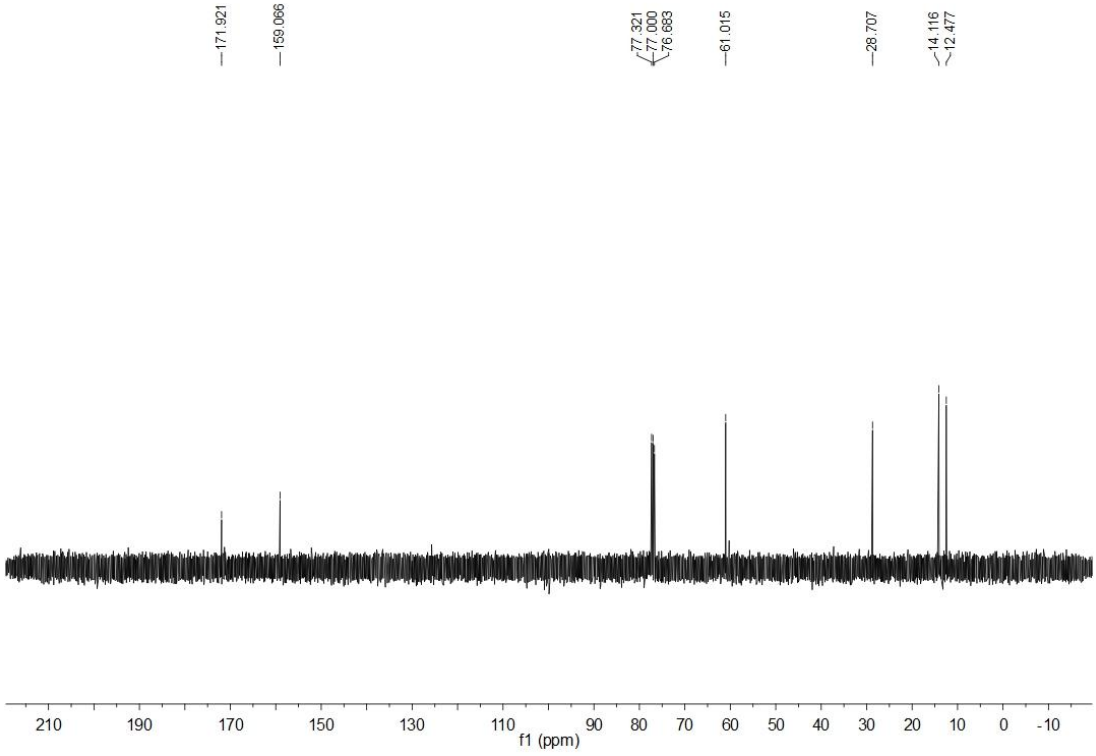

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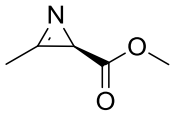
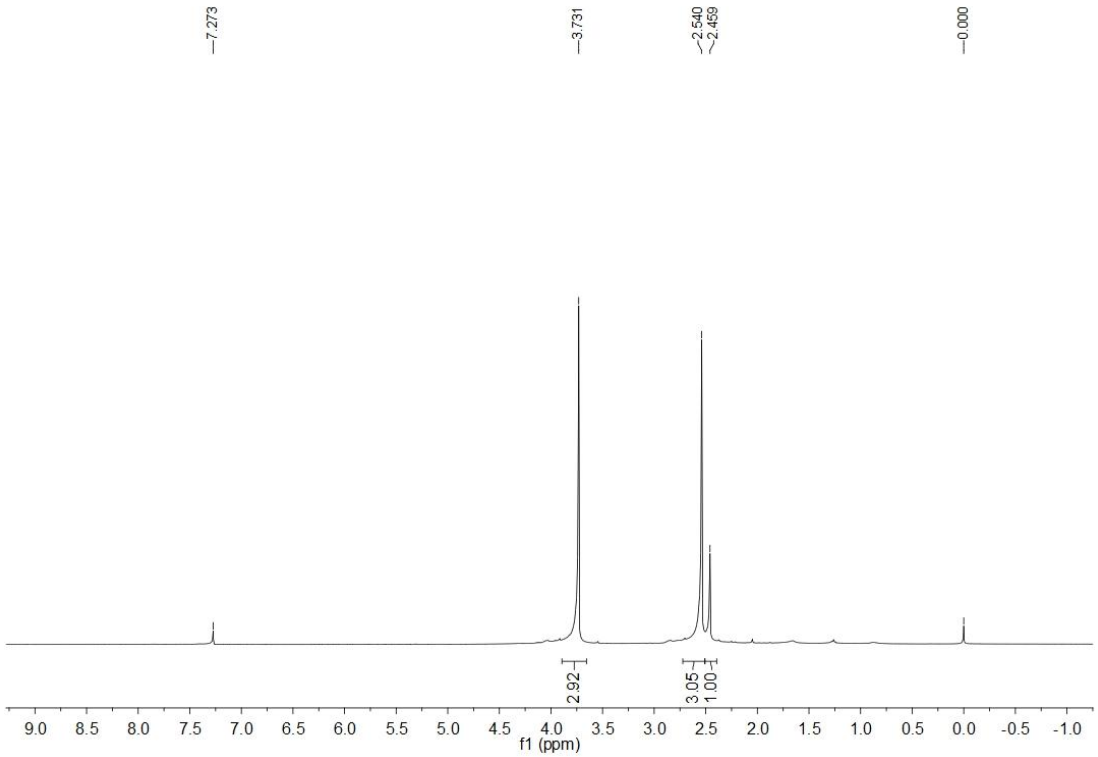
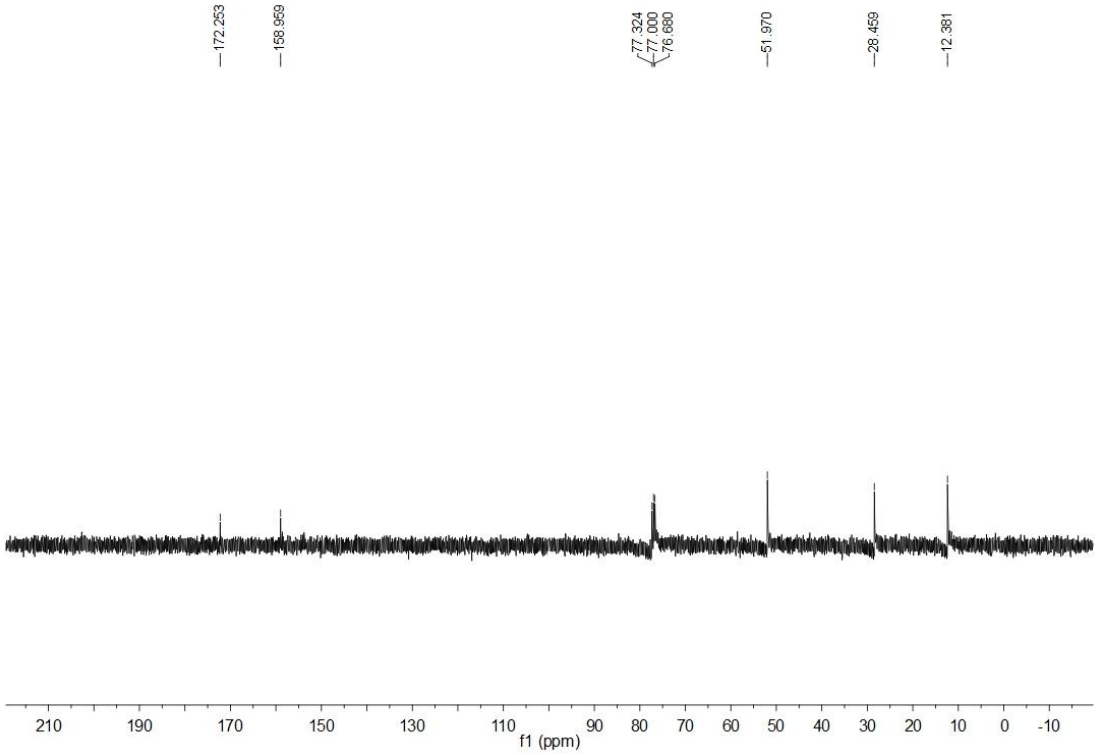

N
O
O


7.273
3.731
2.540
2.459
0.000
2.92
3.05
1.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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12.381
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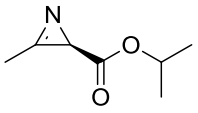
f1 (ppm)

2c: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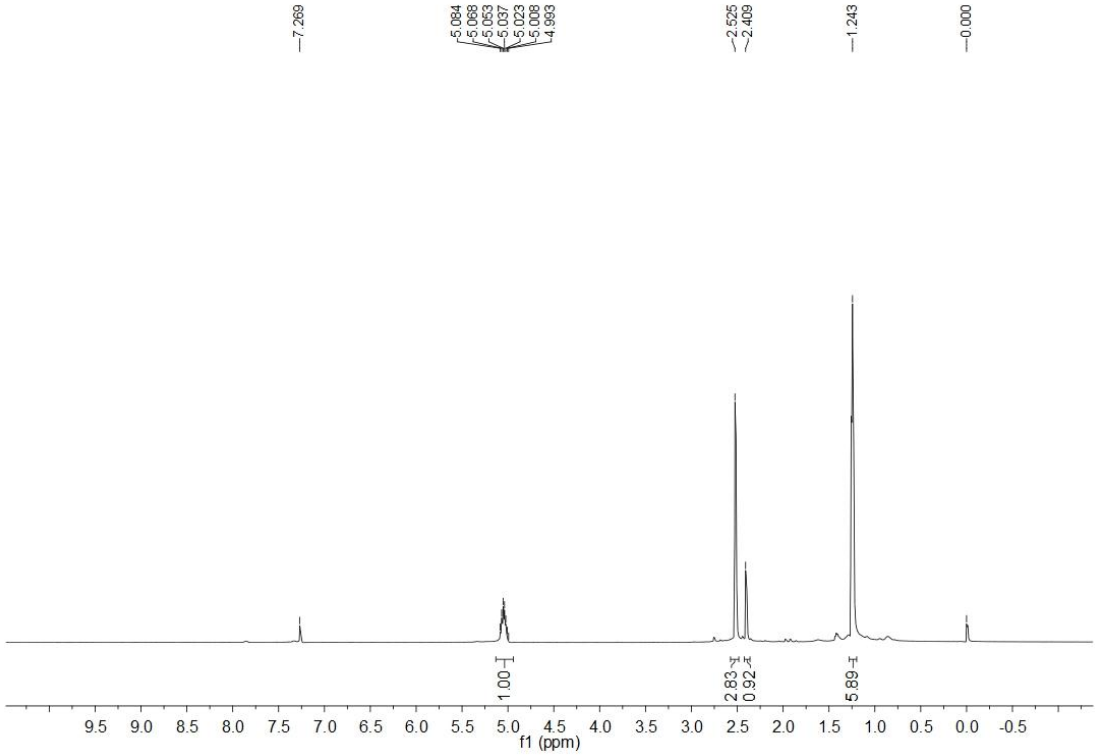
O
O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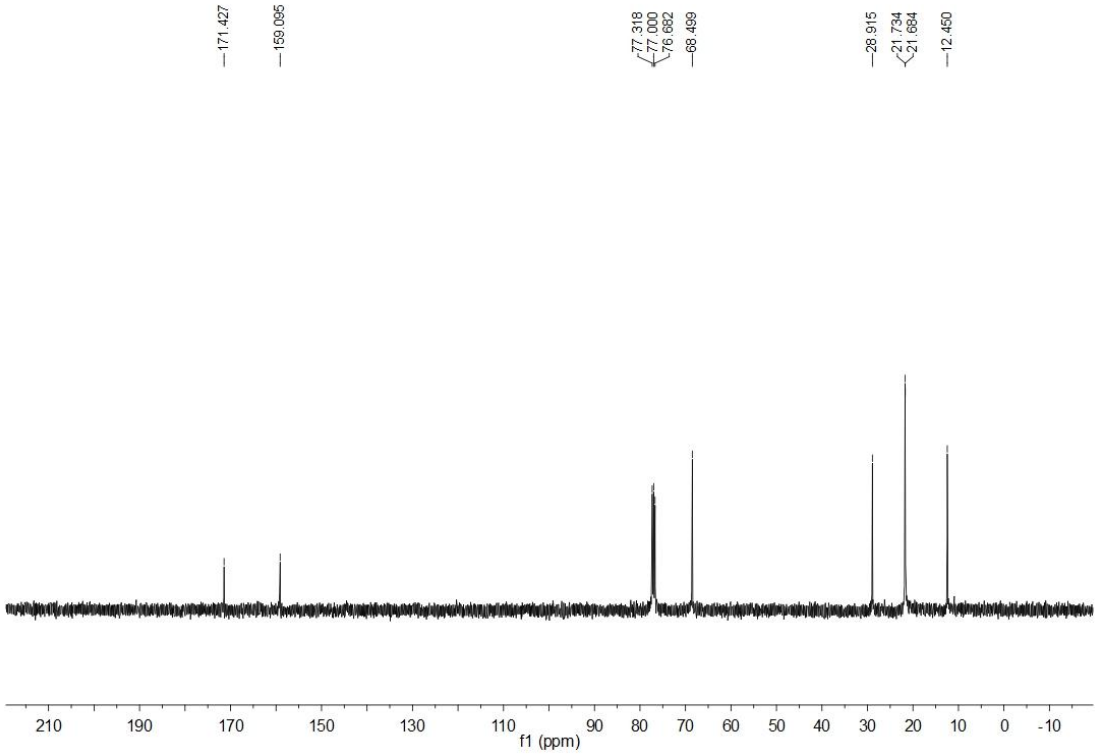
5.068
5.053
5.037
5.023
5.008
4.993
2.525
2.409
1.243
0.000
1.00
2.83
0.92
5.89
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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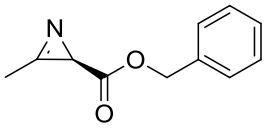
159.095
77.318
77.000
76.682
68.499
28.915
21.734
21.684
12.450
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

2d: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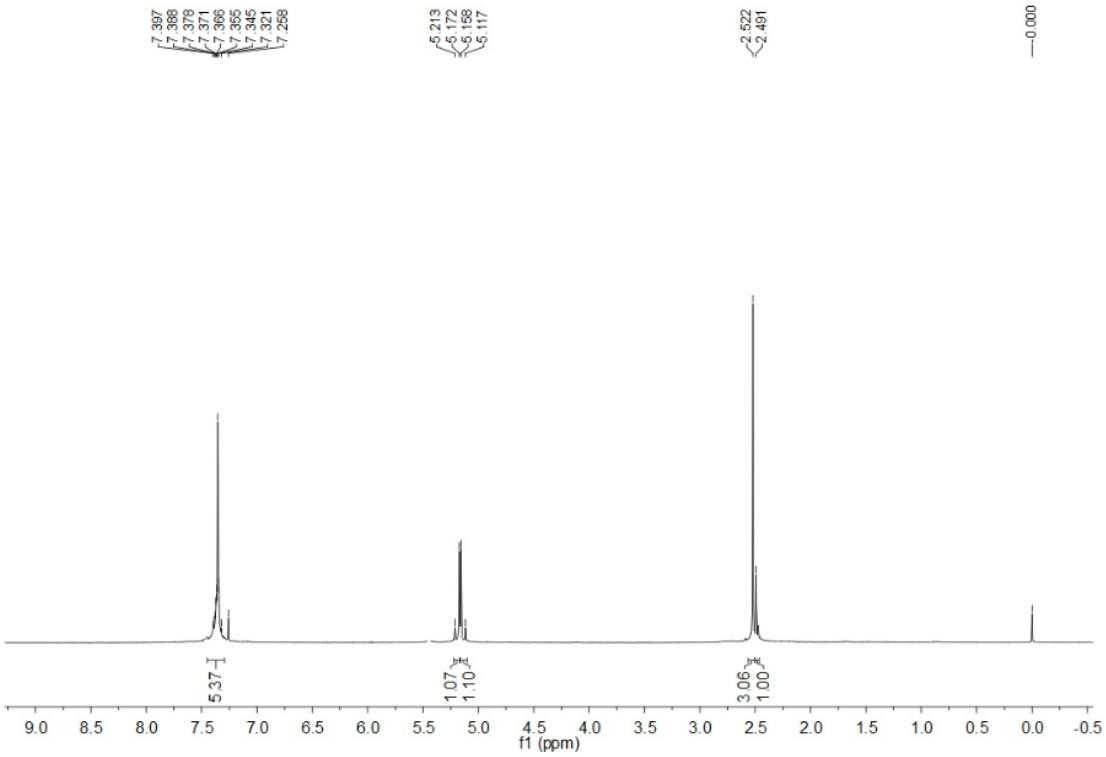
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7.388
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7.371
7.366
7.355
7.345
7.321
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5.213
5.172
5.158
5.117
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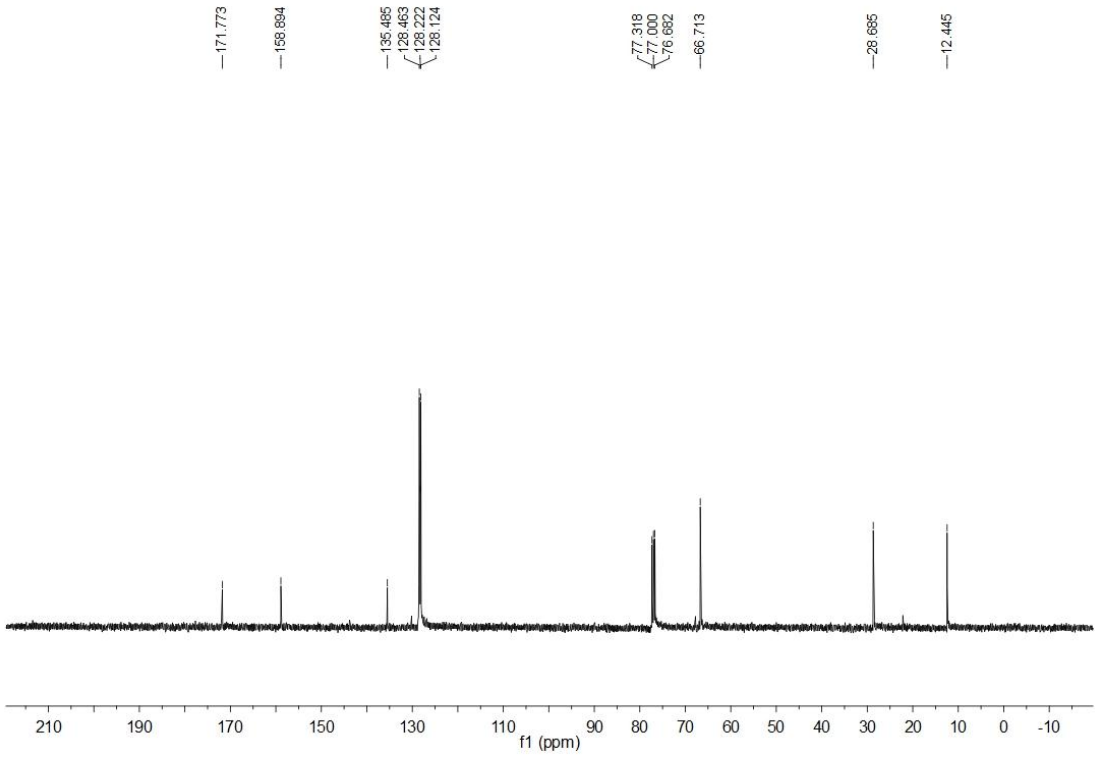
2.491
0.000
5.37
1.07
1.10
3.06
1.00
f1 (ppm)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77.000
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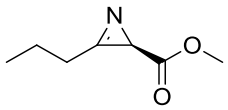
66.713
28.685
12.445
f1 (ppm)

2e: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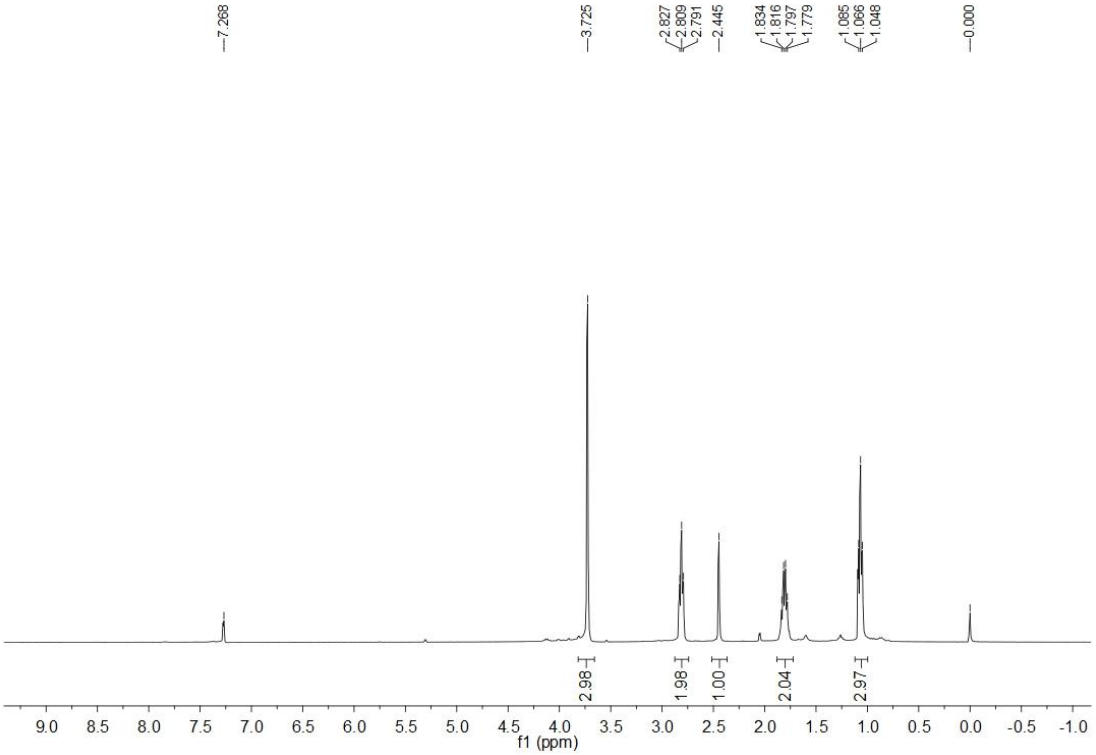
O
O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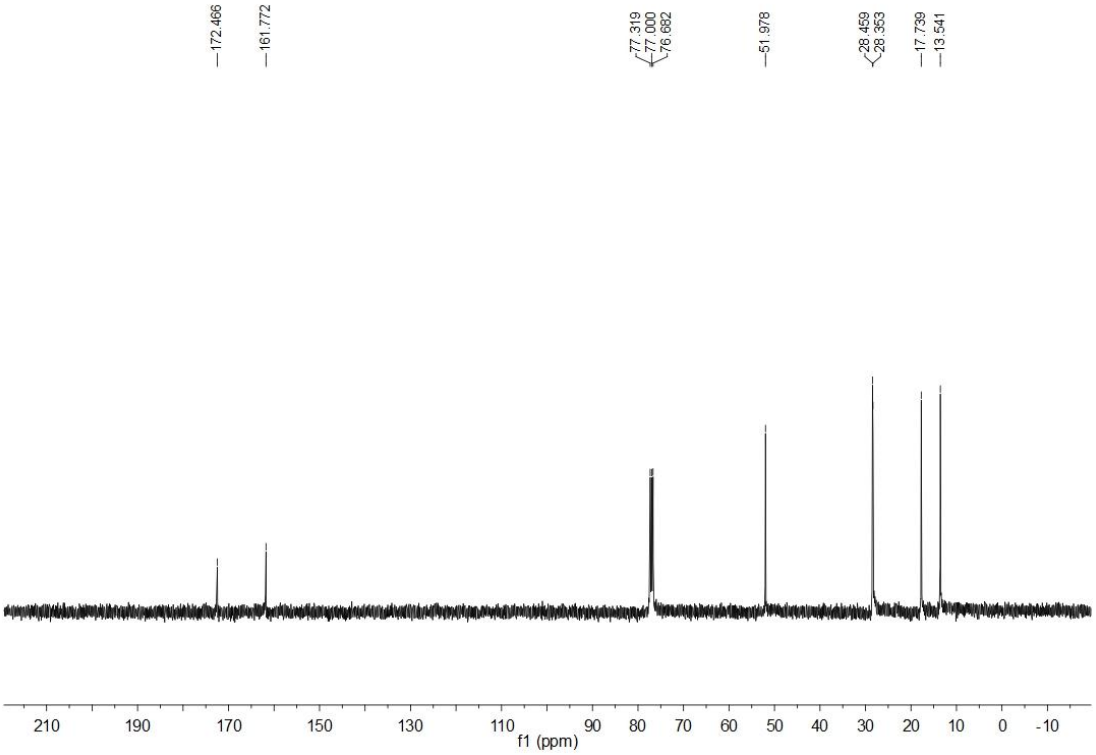
1.00
2.04
2.97
f1 (ppm)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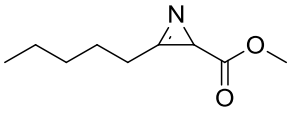
f1 (ppm)

2f: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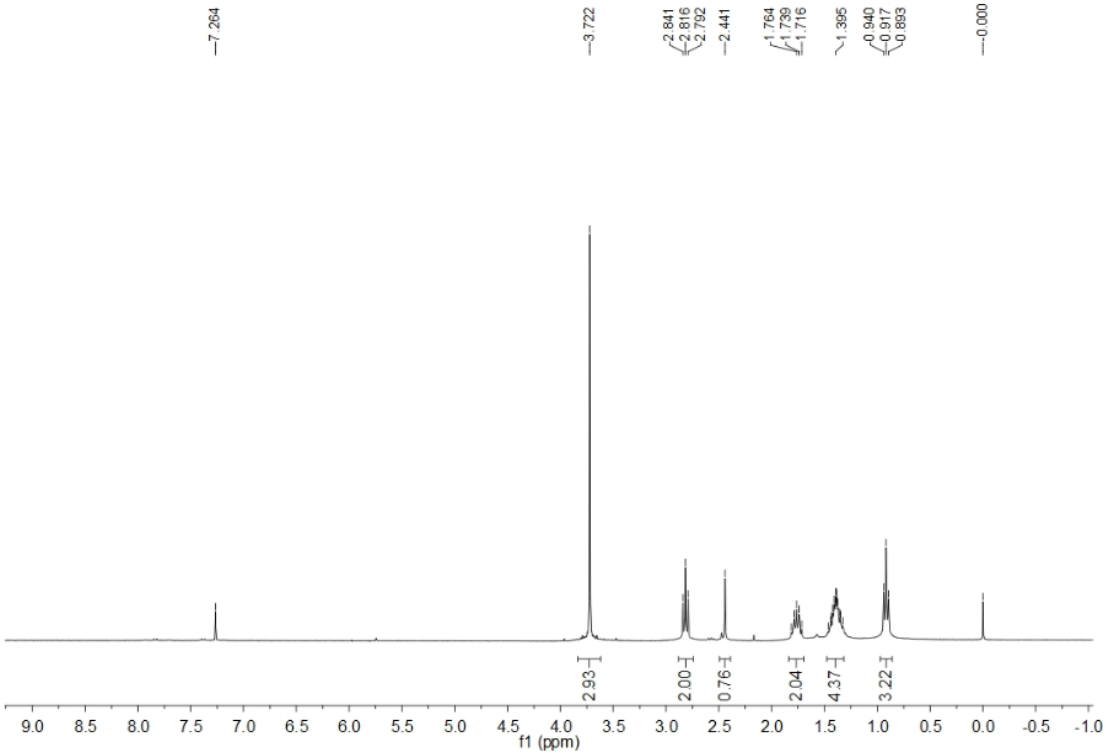
O
O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2.04
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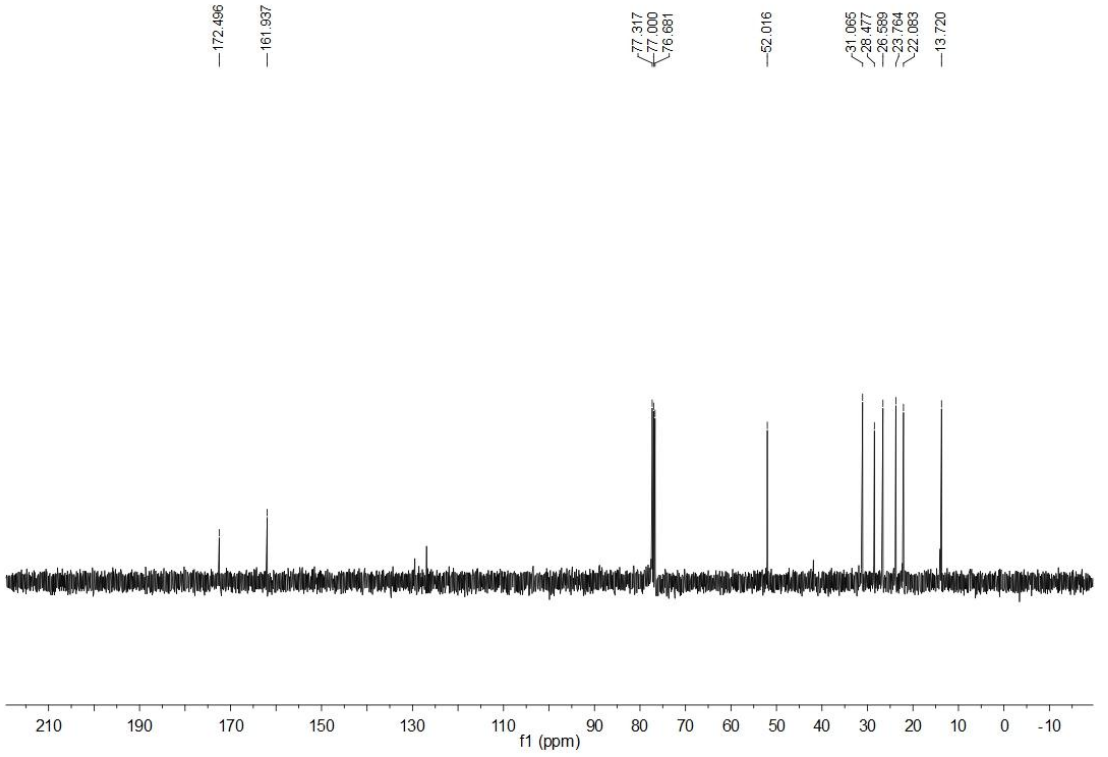
3.22
f1 (ppm)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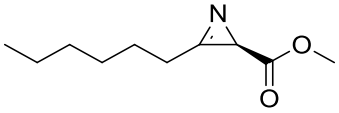
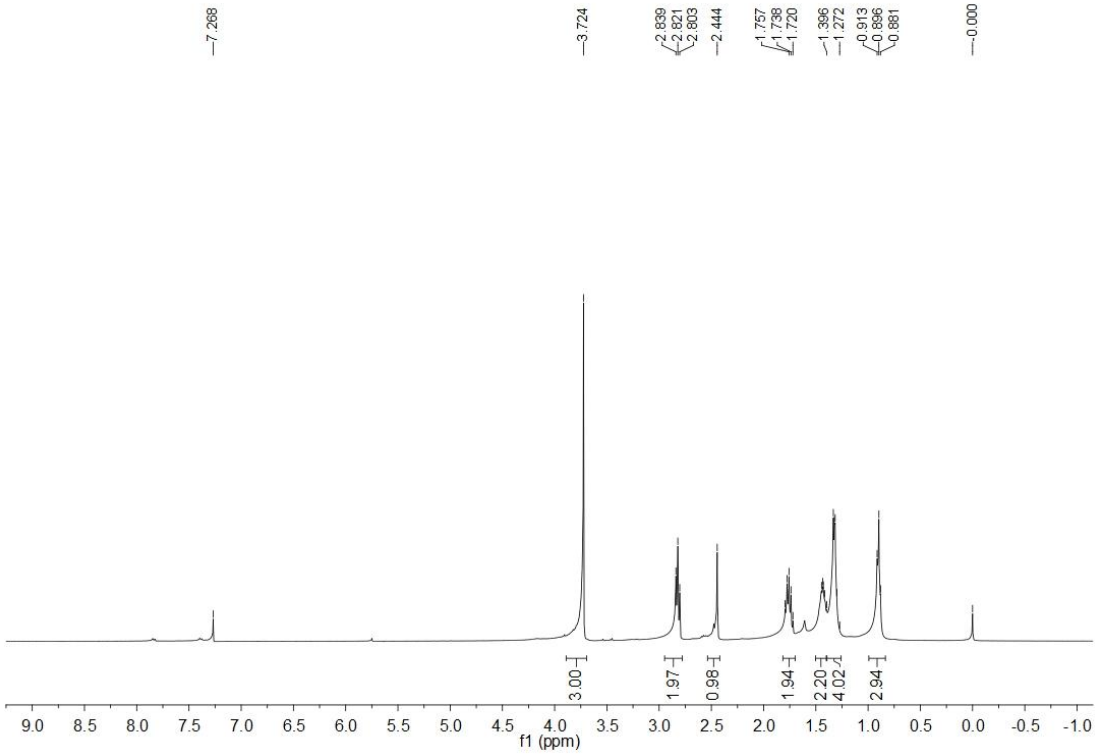
f1 (ppm)

2g:


N
O
O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1.720
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1.272
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0.896
0.881
0.000
3.00
1.97
0.98
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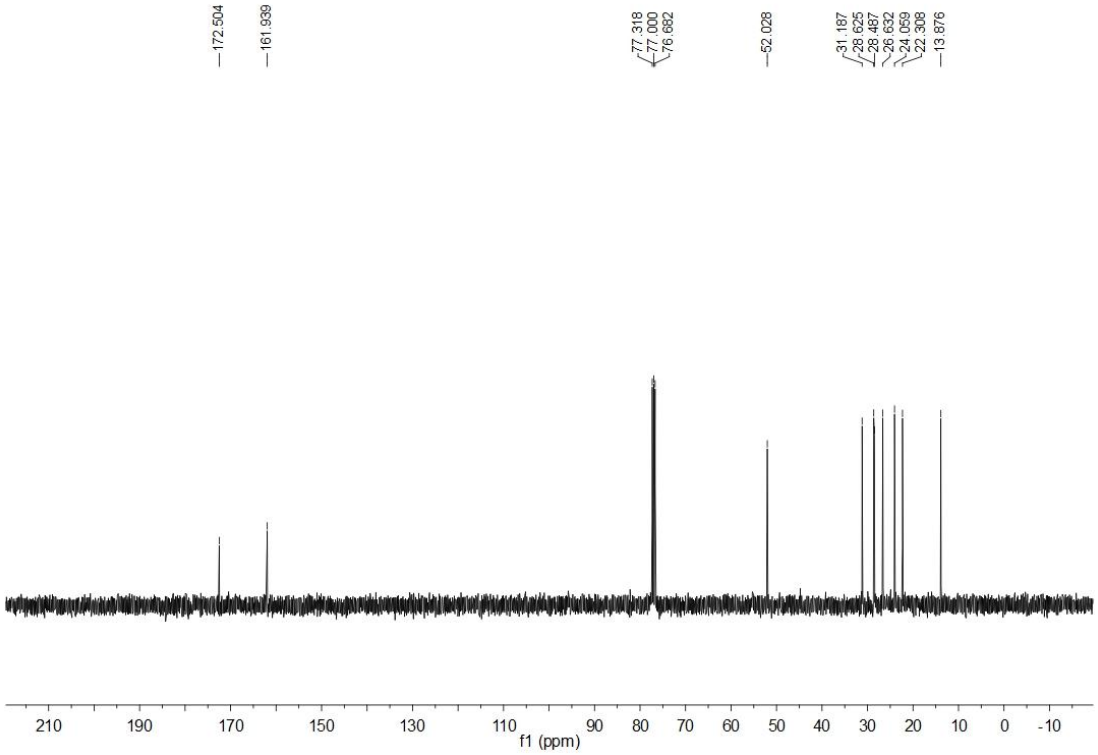
2.94
f1 (ppm)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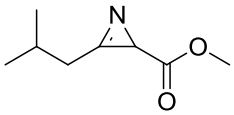
f1 (ppm)

2h: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O
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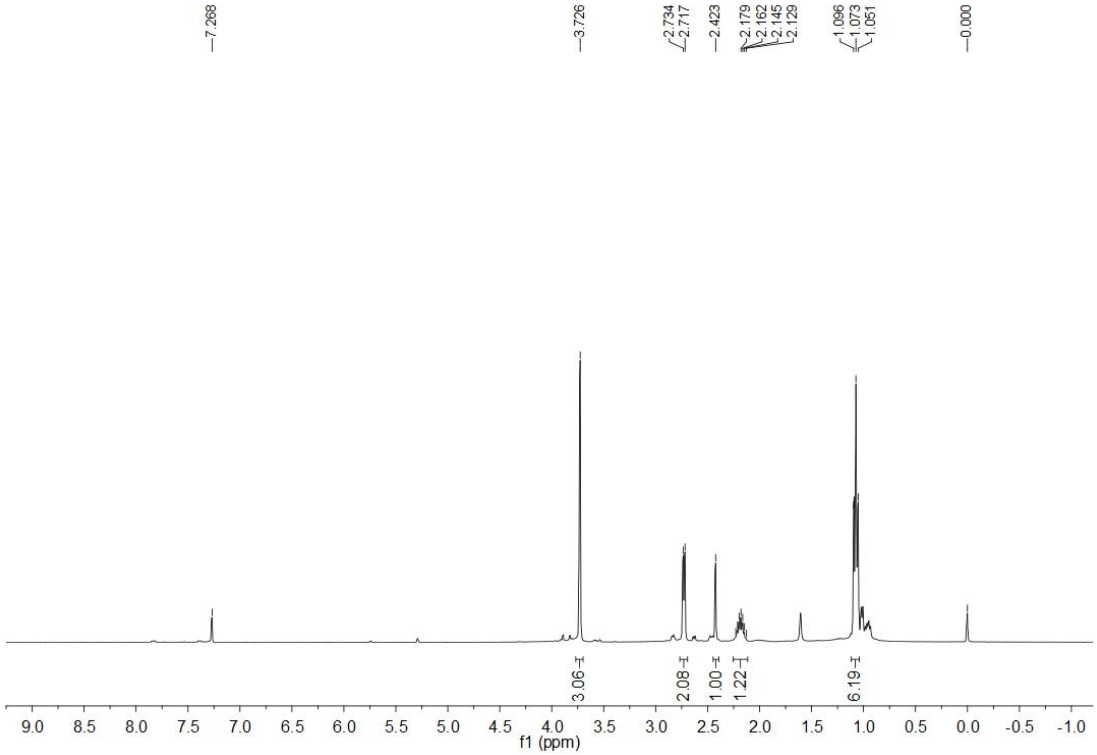
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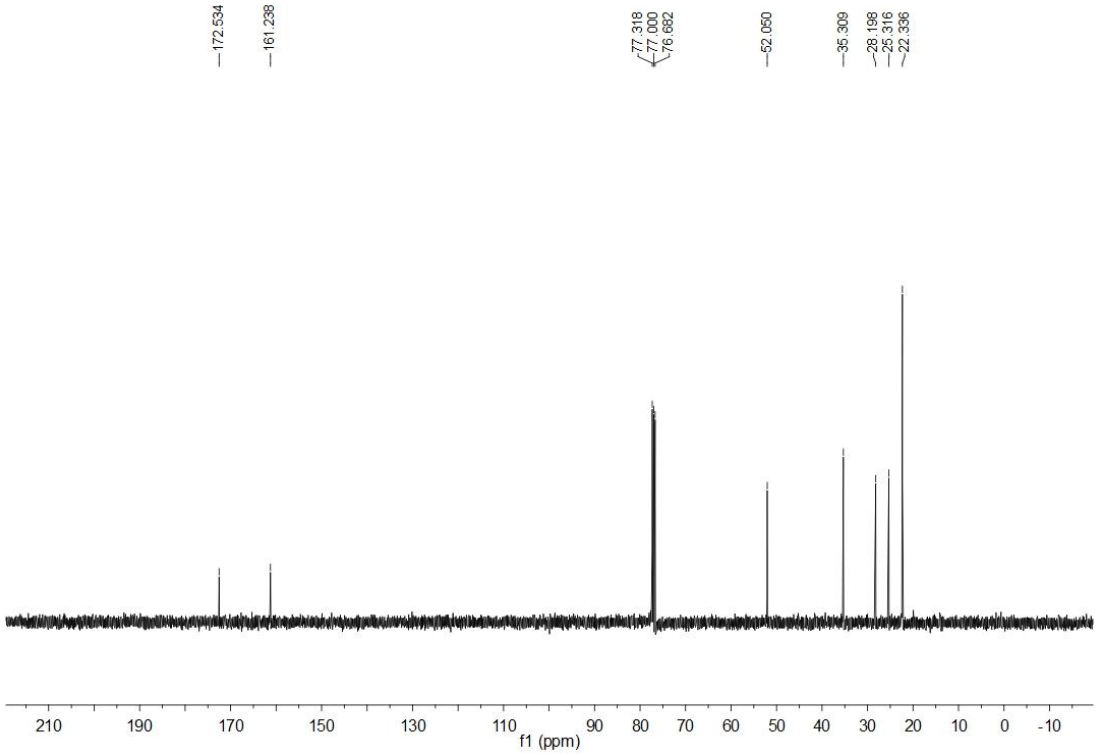
f1 (ppm)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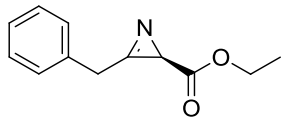
N
O
O


7.383
7.365
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7.328
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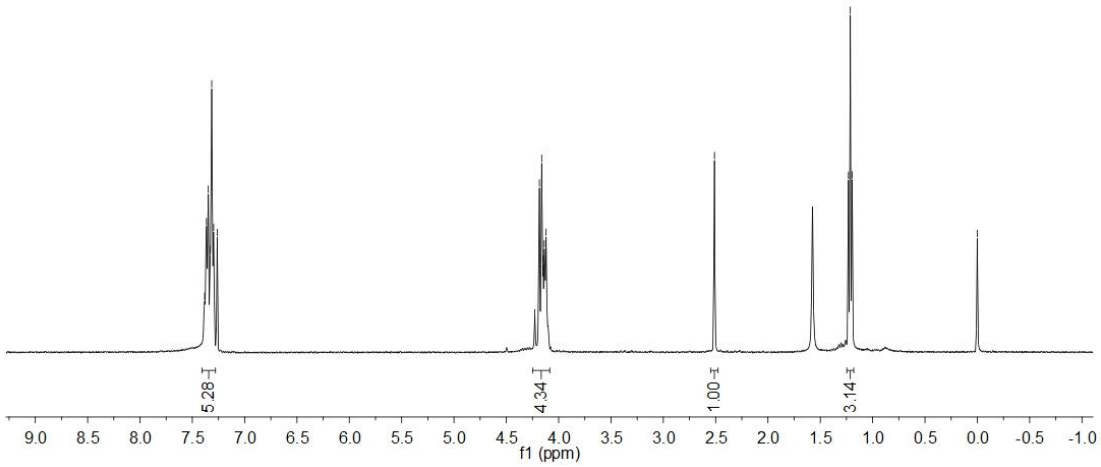
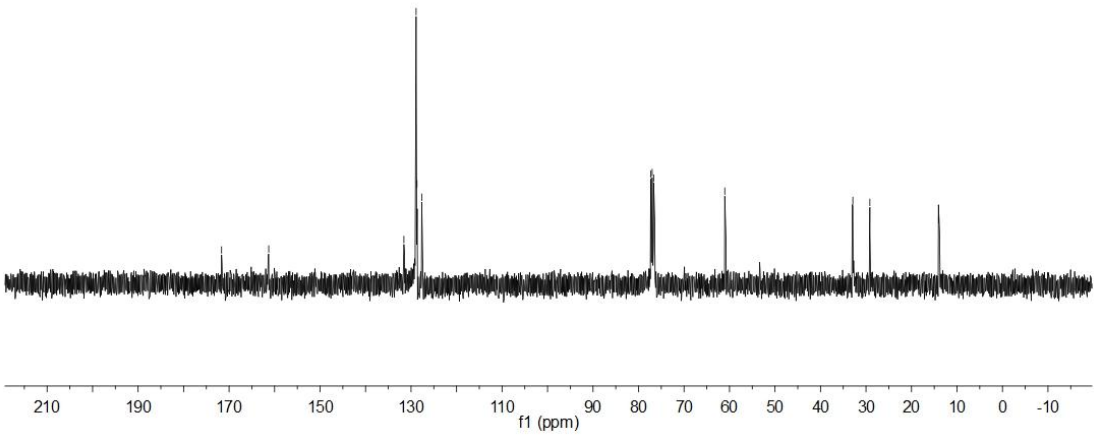
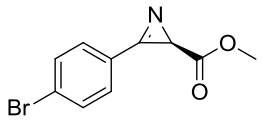
7.262
4.229
4.184
4.162
4.149
4.138
4.120
2.511
1.231
1.213
1.196
0.000

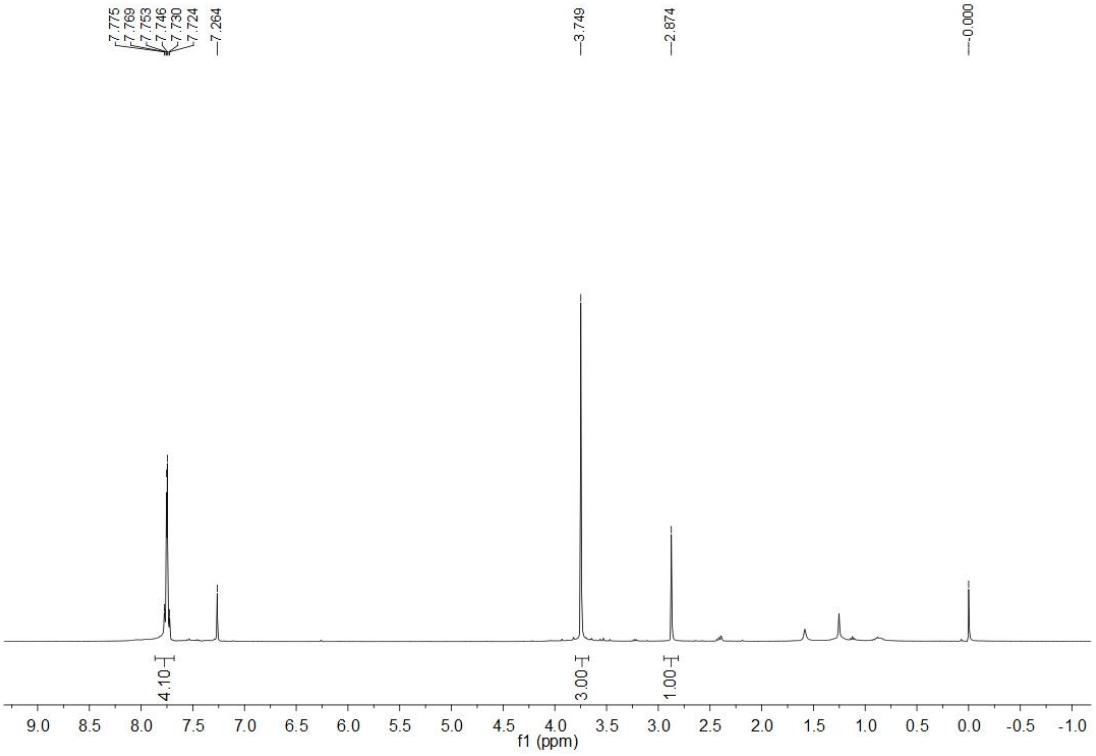

5.28
4.34
1.00
3.14
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

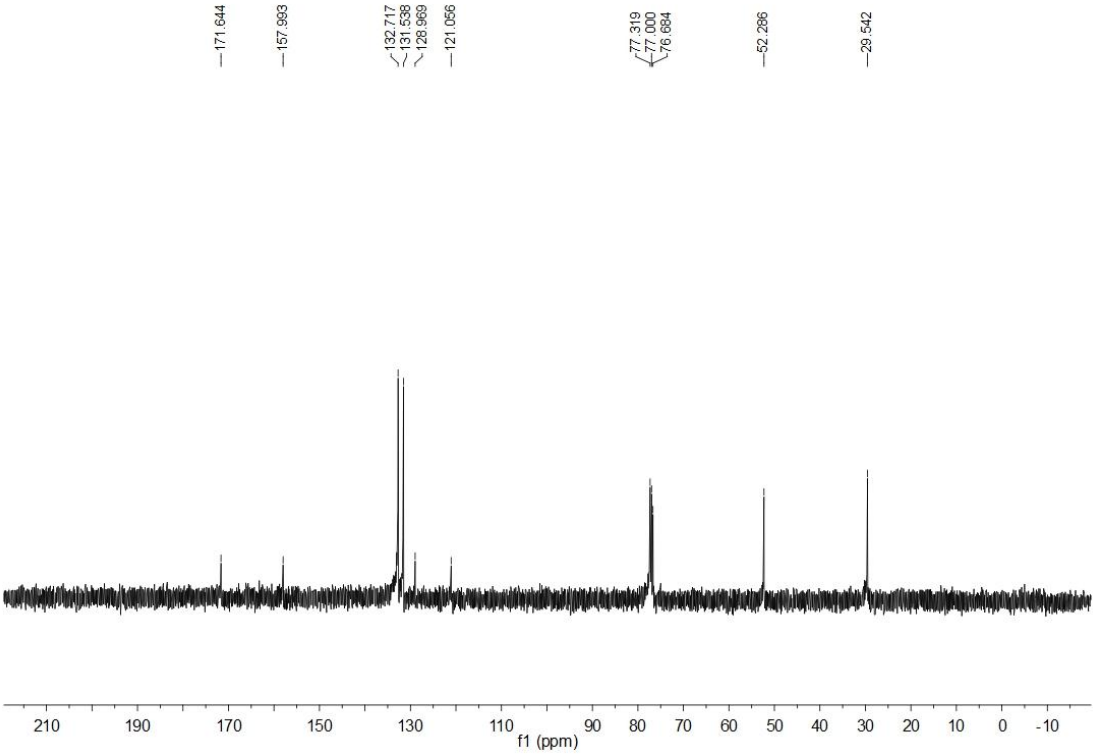

171.651
161.288
131.574
128.891
128.700
127.664
77.317
77.000
76.676
61.044
32.893
29.151
14.051


210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

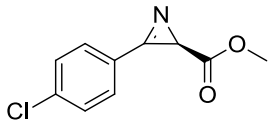
2k:

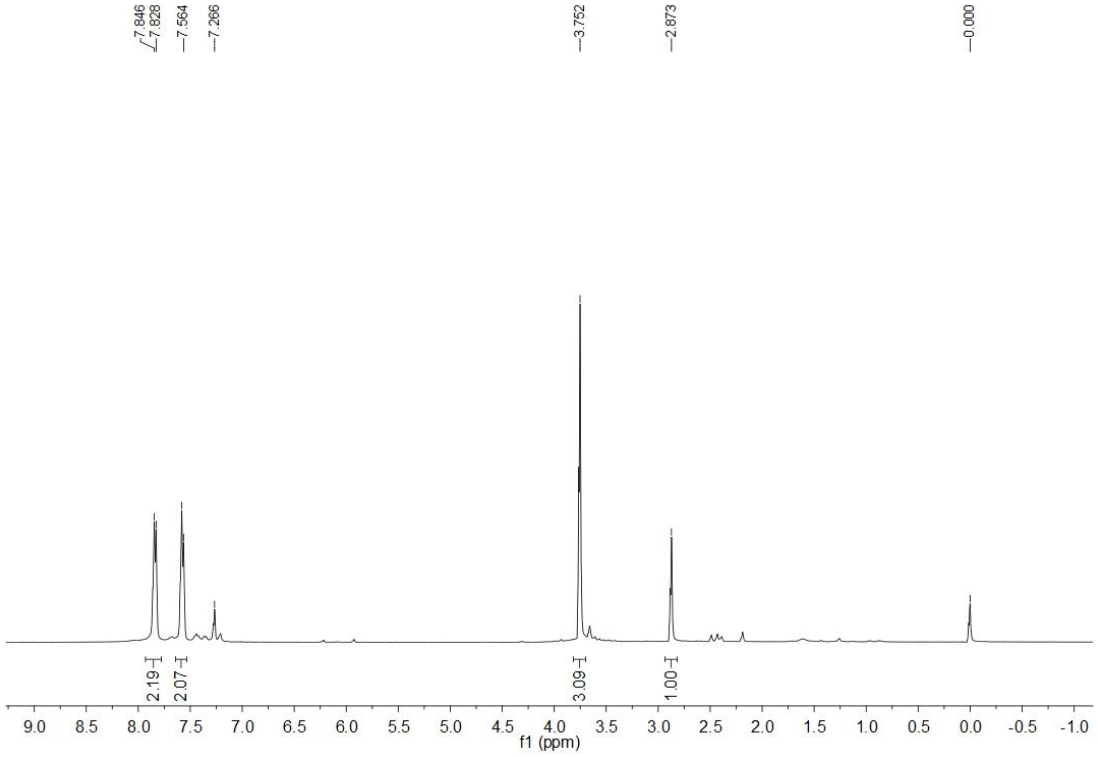

N
O
O
Br

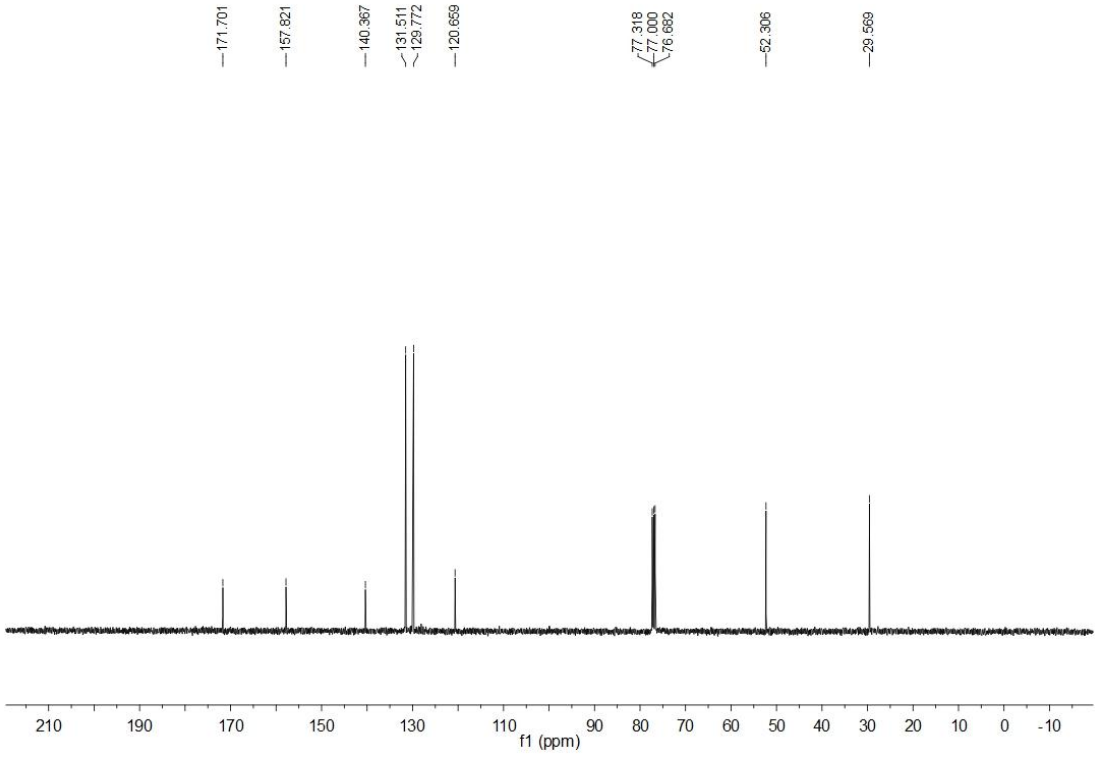

7.775
7.769
7.753
7.746
7.730
7.724
7.264
3.749
2.874
0.000
4.10
3.00
1.00
f1 (ppm)


171.644
157.993
132.717
131.538
128.969
121.056
77.319
77.000
76.684
52.286
29.542
f1 (ppm)

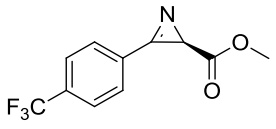
2l:

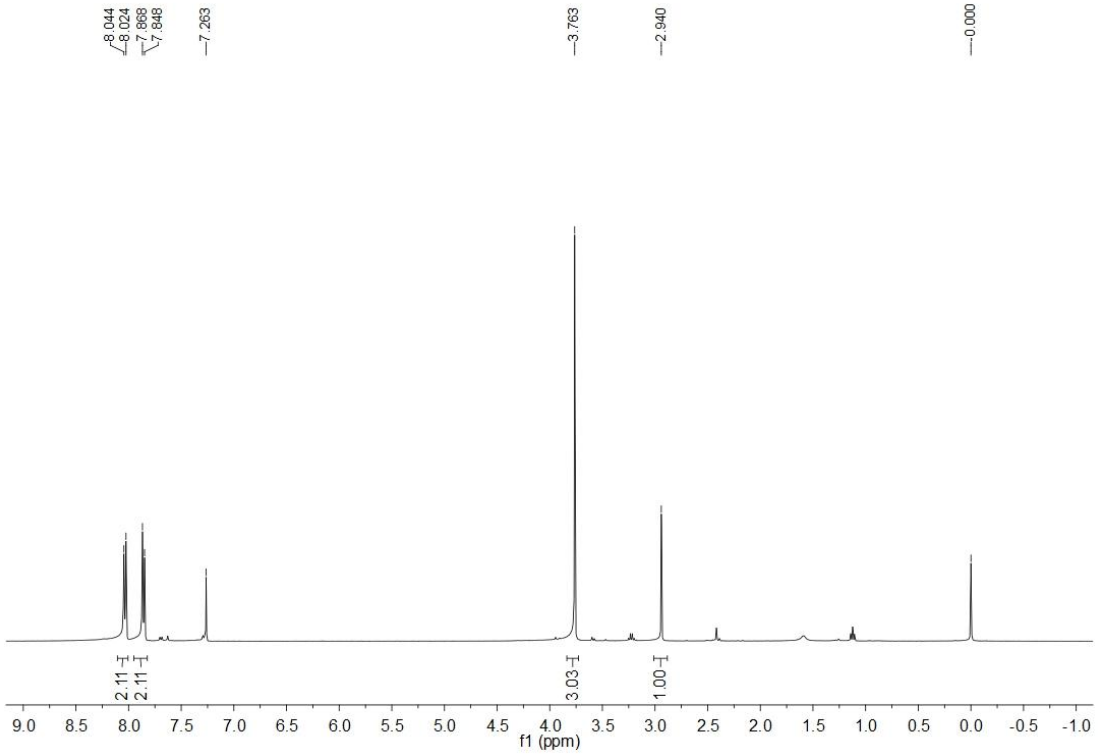

N
O
O
Cl

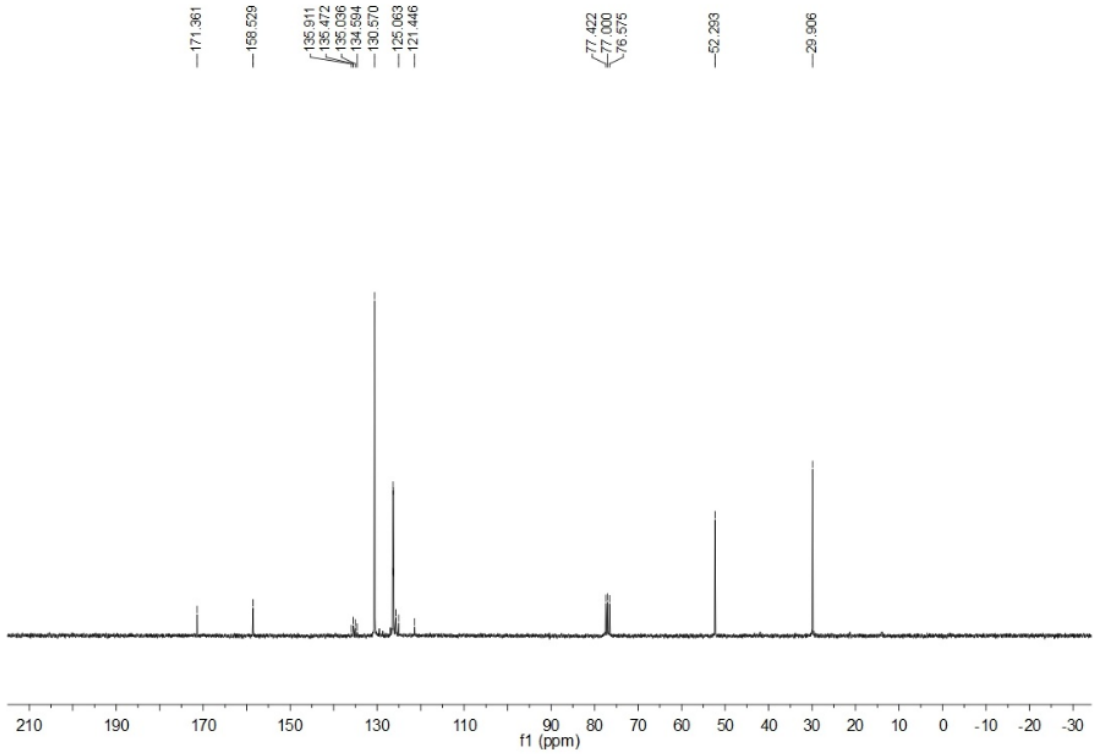

7.846
7.828
7.564
7.266
3.752
2.873
0.000
2.19
2.07
3.09
1.00
f1 (ppm)


171.701
157.821
140.367
131.511
129.772
120.659
77.318
77.000
76.682
52.306
29.569
f1 (ppm)

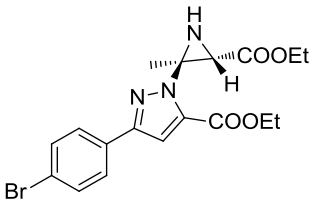
2n:


N
O
O
F3C

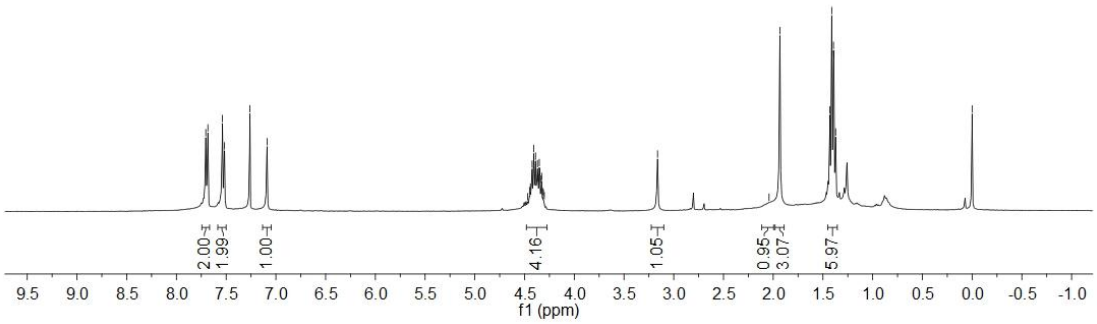

8.044
8.024
7.868
7.848
7.263
3.763
2.940
0.000
2.11
2.11
3.03
1.00
f1 (ppm)


171.361
158.529
135.911
135.472
135.036
134.594
130.570
125.063
121.446
77.422
77.000
76.575
52.293
29.906
f1 (ppm)

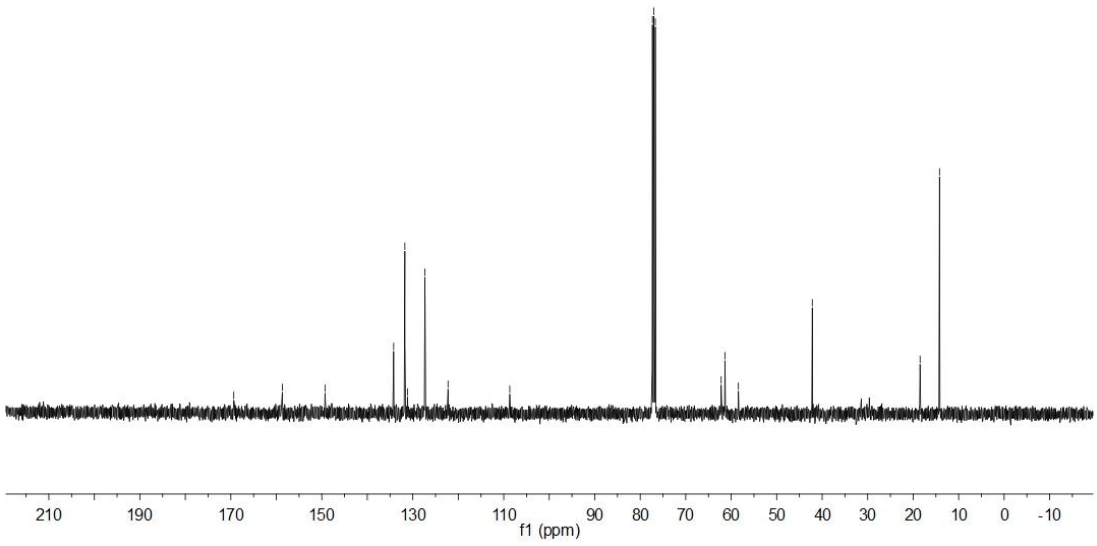
3a:


H
N
COOEt
H
N
N
COOEt
Br

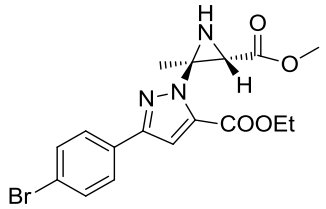

7.705
7.684
7.537
7.516
7.261
7.089
4.450
4.441
4.424
4.407
4.390
4.370
4.363
4.351
4.346
4.333
4.328
4.319
4.310
4.301
3.163
2.042
1.932
1.430
1.412
1.394
1.390
1.372
0.000

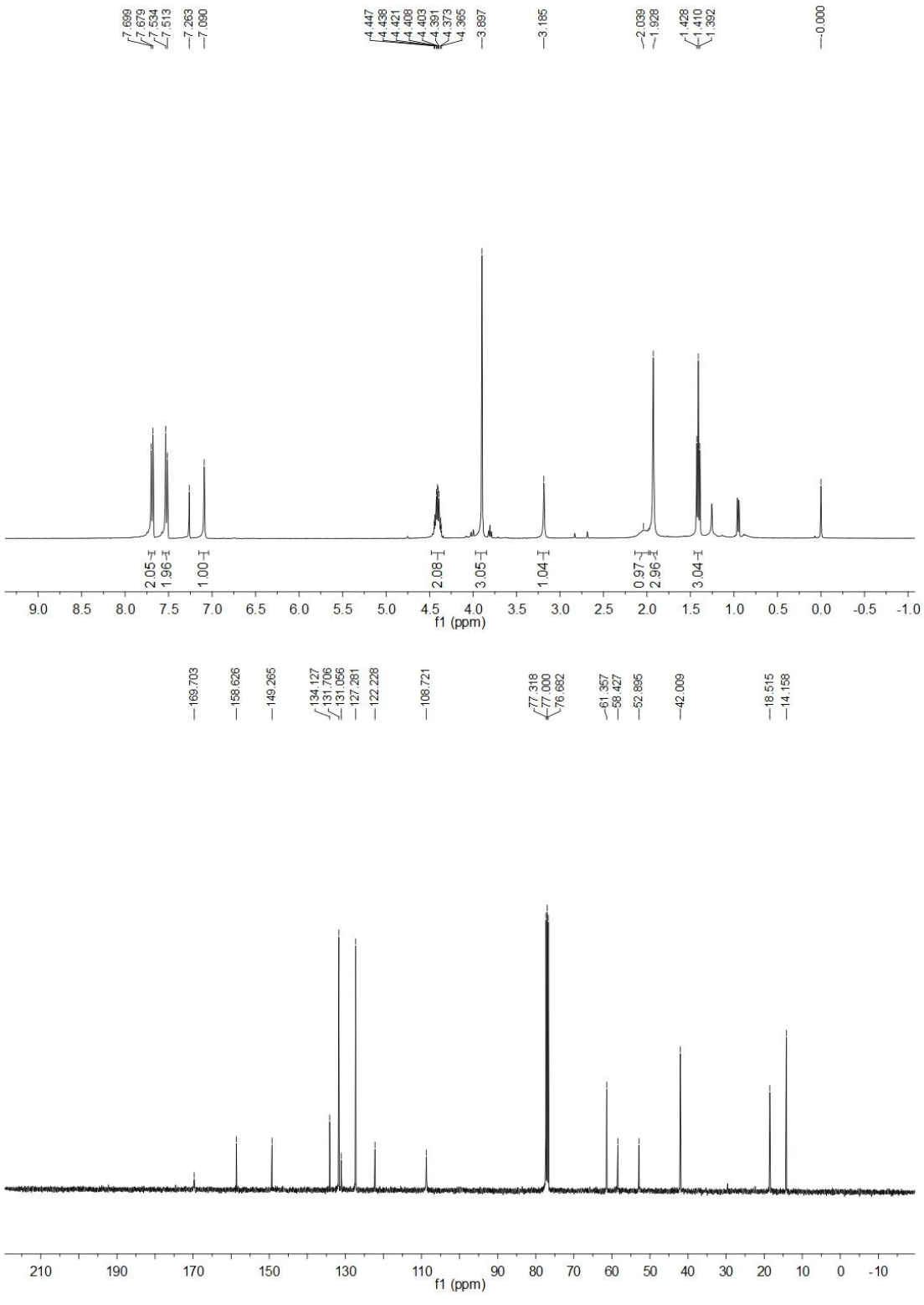

2.00
1.99
1.00
4.16
1.05
0.95
3.07
5.97
f1 (ppm)


169.353
158.670
149.292
134.204
131.741
131.155
127.330
122.249
108.676
77.318
77.000
76.682
62.208
61.359
58.419
42.173
18.479
14.203

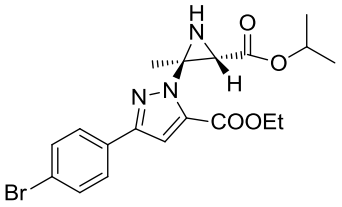

f1 (ppm)

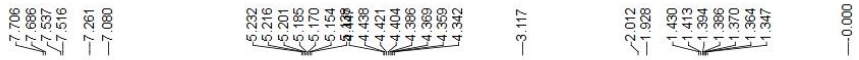
3b:

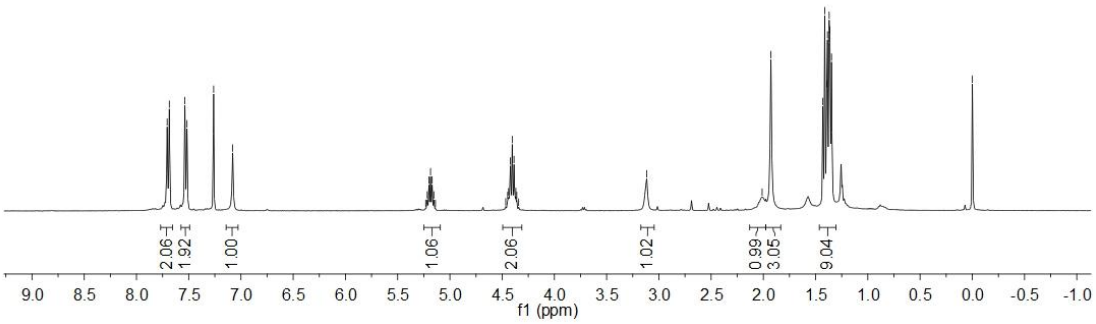

H
N
O
O
H
N
N
COOEt
Br


7.699
7.679
7.534
7.513
7.263
7.090
4.447
4.438
4.421
4.408
4.403
4.391
4.373
4.365
3.897
3.185
2.039
1.928
1.428
1.410
1.392
0.000
2.05
1.96
1.00
2.08
3.05
1.04
0.97
2.96
3.04
f1 (ppm)
169.703
158.626
149.265
134.127
131.706
131.056
127.281
122.228
108.721
77.318
77.000
76.682
61.357
58.427
52.895
42.009
18.515
14.158
f1 (ppm)

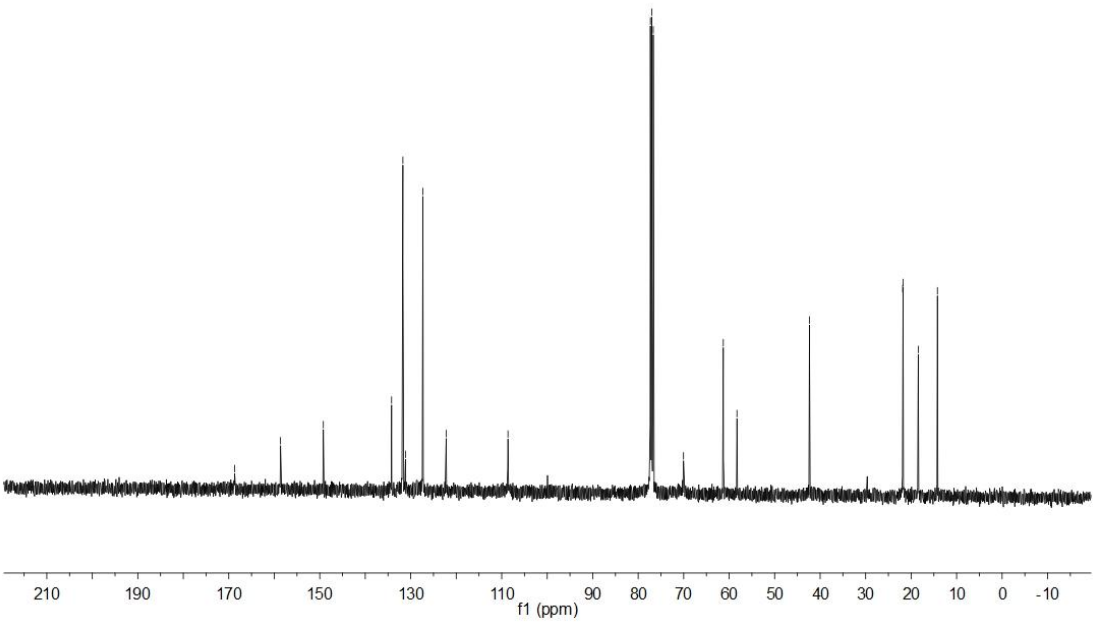
3c:


H
N
O
O
H
N
N
COOEt
Br

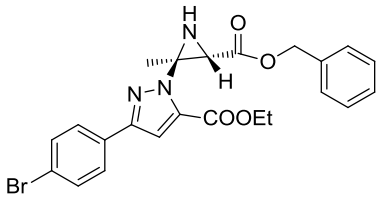

7.706
7.686
7.537
7.516
7.261
7.080
5.232
5.216
5.201
5.185
5.170
5.154
4.438
4.421
4.404
4.386
4.369
4.359
4.342
3.117
2.012
1.928
1.430
1.413
1.394
1.386
1.370
1.364
1.347
0.000


2.06
1.92
1.00
1.06
2.06
1.02
0.99
3.05
9.04
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

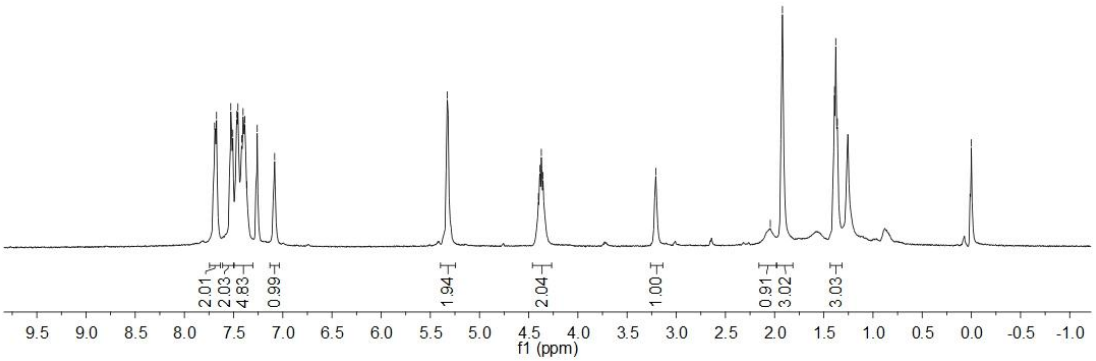

168.710
158.624
149.214
134.209
131.726
131.163
127.326
122.208
108.624
77.318
77.000
76.683
70.036
61.292
58.286
42.352
21.856
21.770
18.431
14.216


210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

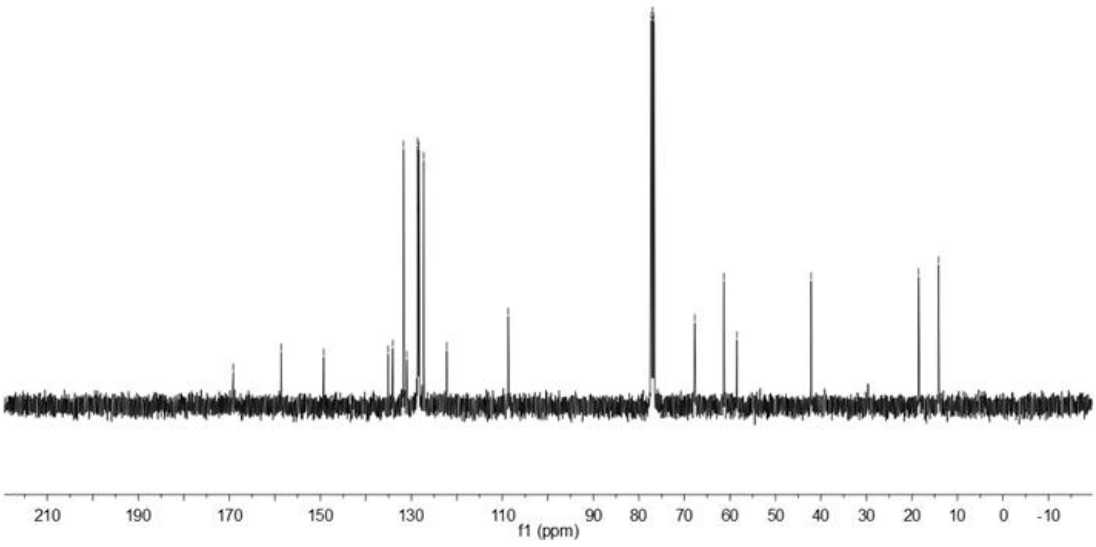
3d:


H
N
O
O
H
N
N
COOEt
Br

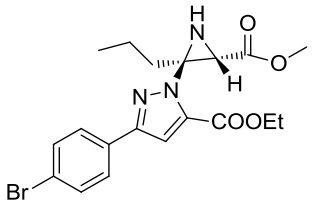

7.693
7.673
7.528
7.508
7.467
7.456
7.417
7.404
7.386
7.364
7.260
7.083
5.327
4.401
4.385
4.372
4.354
3.207
2.044
1.921
1.391
1.379
1.362
0.000

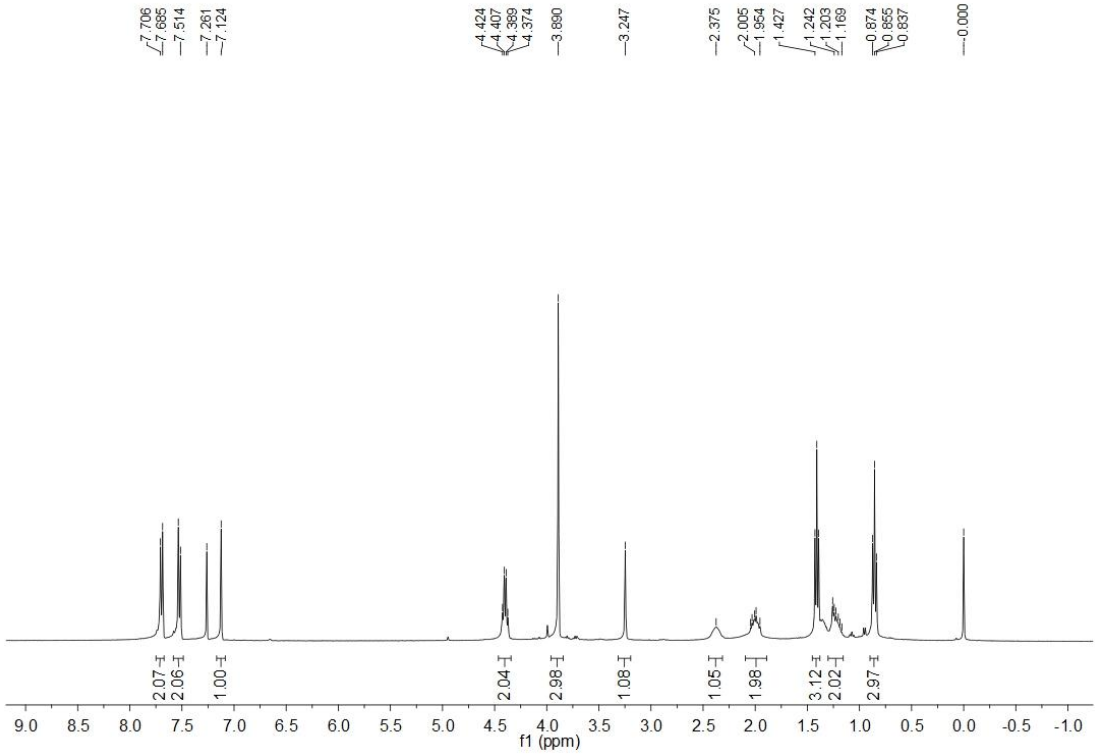

2.01
2.03
4.83
0.99
1.94
2.04
1.00
0.91
3.02
3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

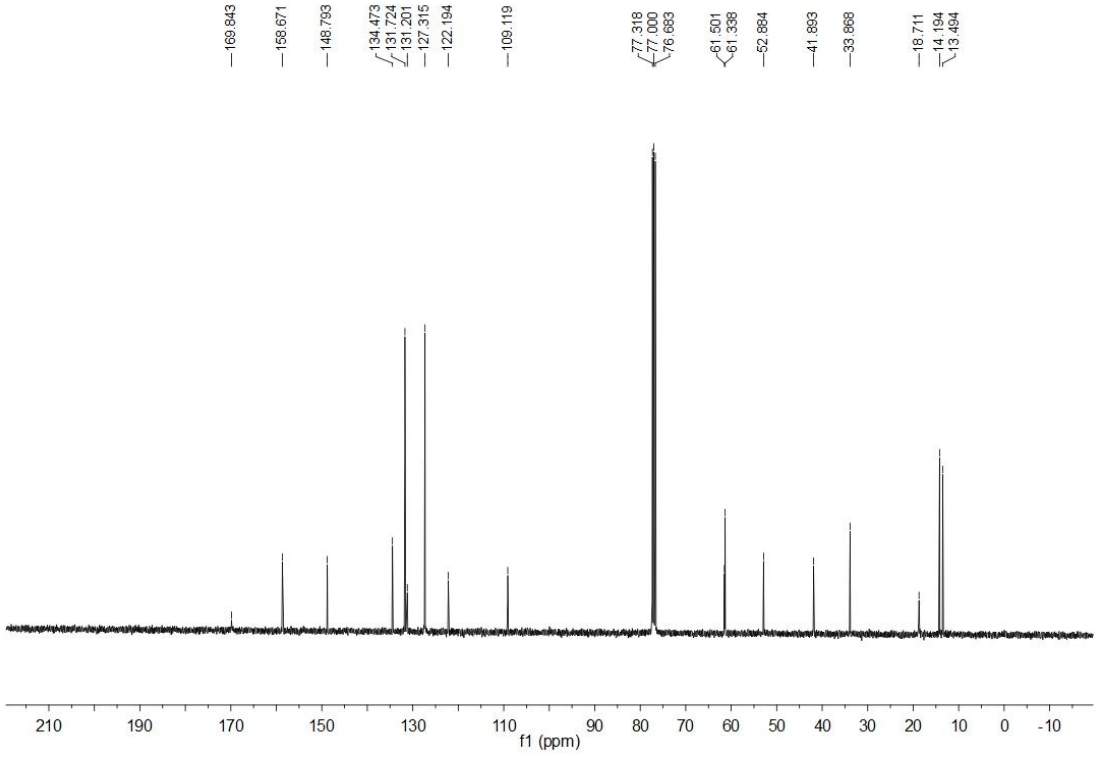

169.114
158.610
149.289
131.716
128.600
128.522
128.339
127.301
122.247
108.690
77.316
77.000
76.681
67.700
61.345
58.483
42.174
18.542
14.183


210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

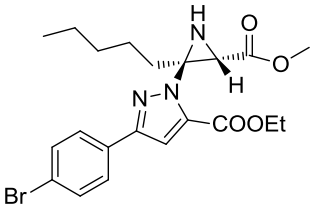
3e:

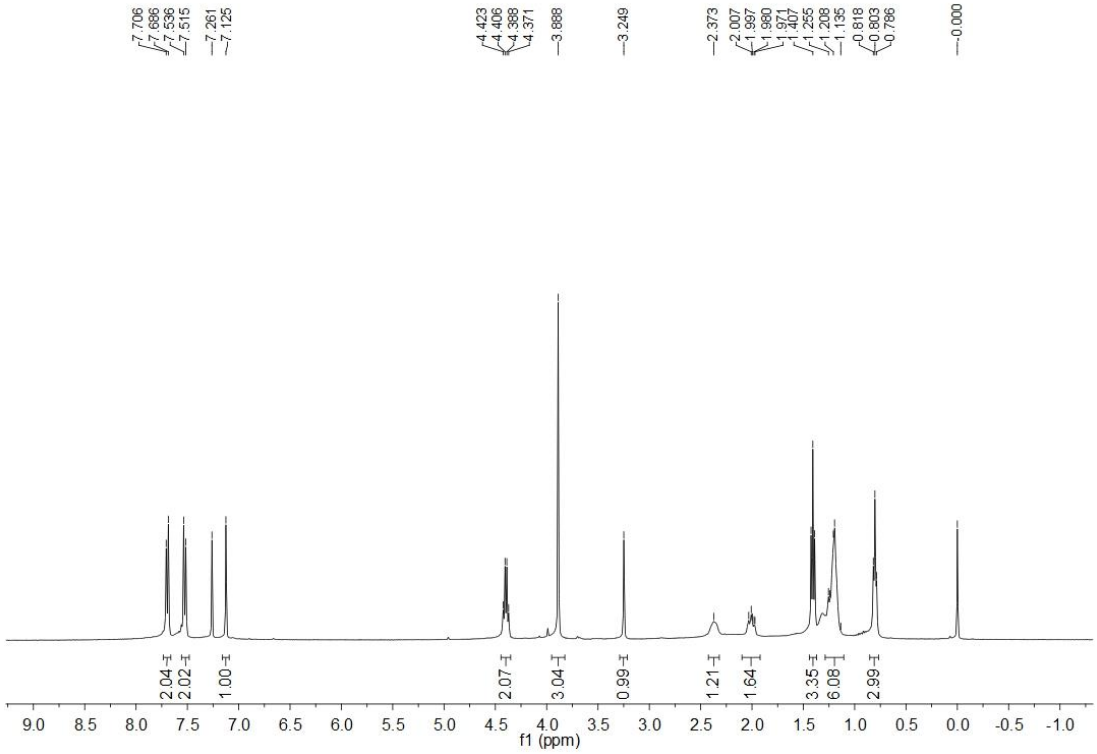

H
N
O
O
H
N
N
COOEt
Br

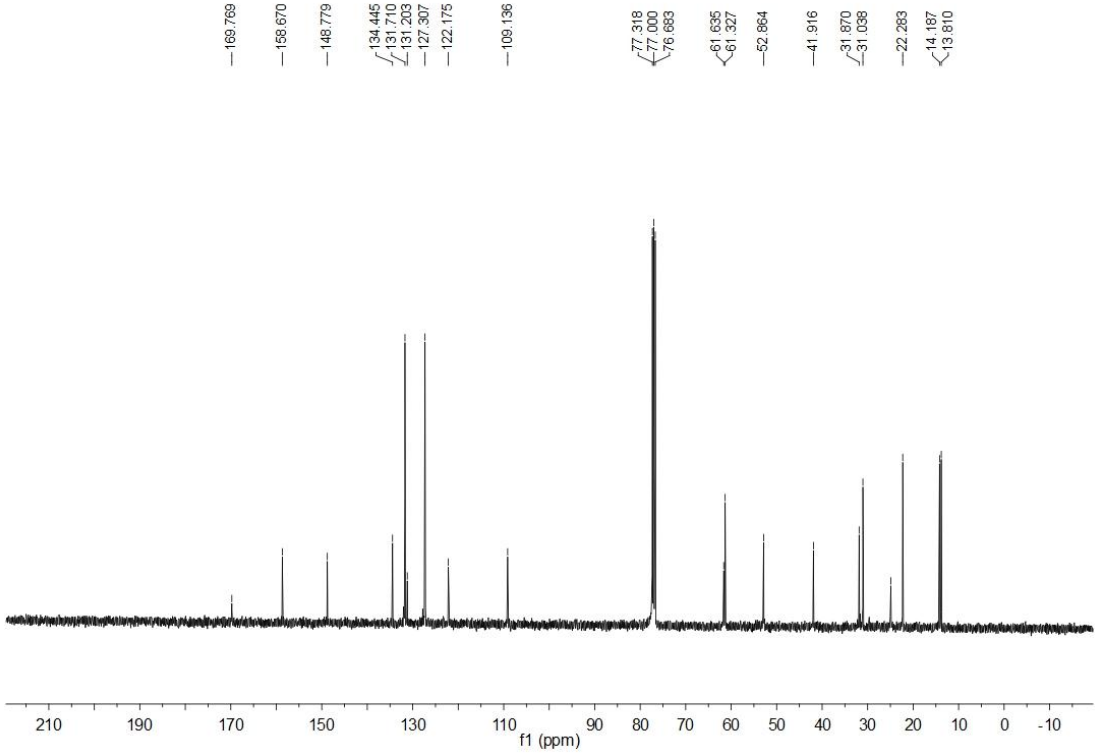

7.706
7.695
7.514
7.261
7.124
4.424
4.407
4.389
4.374
3.890
3.247
2.375
2.005
1.954
1.427
1.242
1.203
1.169
0.874
0.855
0.837
0.000
2.07
2.06
1.00
2.04
2.98
1.08
1.05
1.98
3.12
2.02
2.97
f1 (ppm)


169.843
158.671
148.793
134.473
131.724
131.201
127.315
122.194
109.119
77.318
77.000
76.683
61.501
61.338
52.884
41.893
33.868
18.711
14.194
13.494
f1 (ppm)

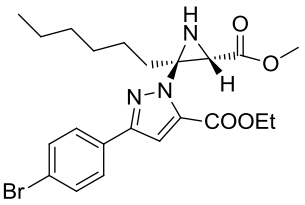
3f:

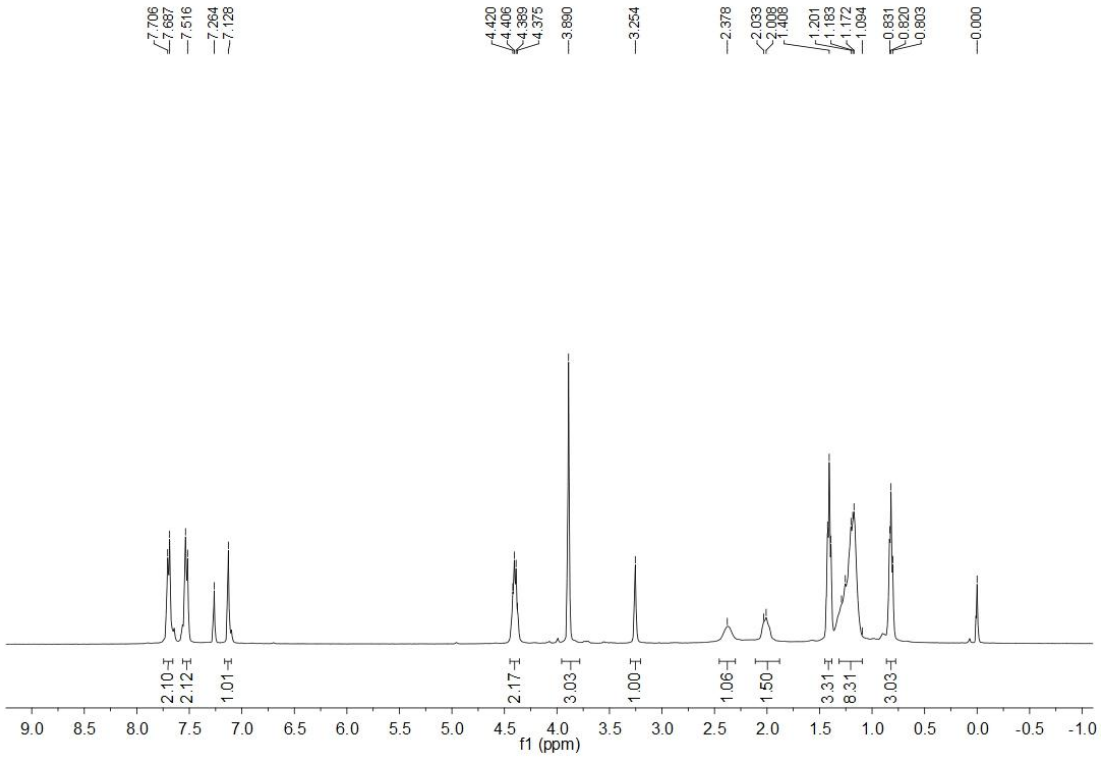

H
N
O
O
H
N
N
COOEt
Br

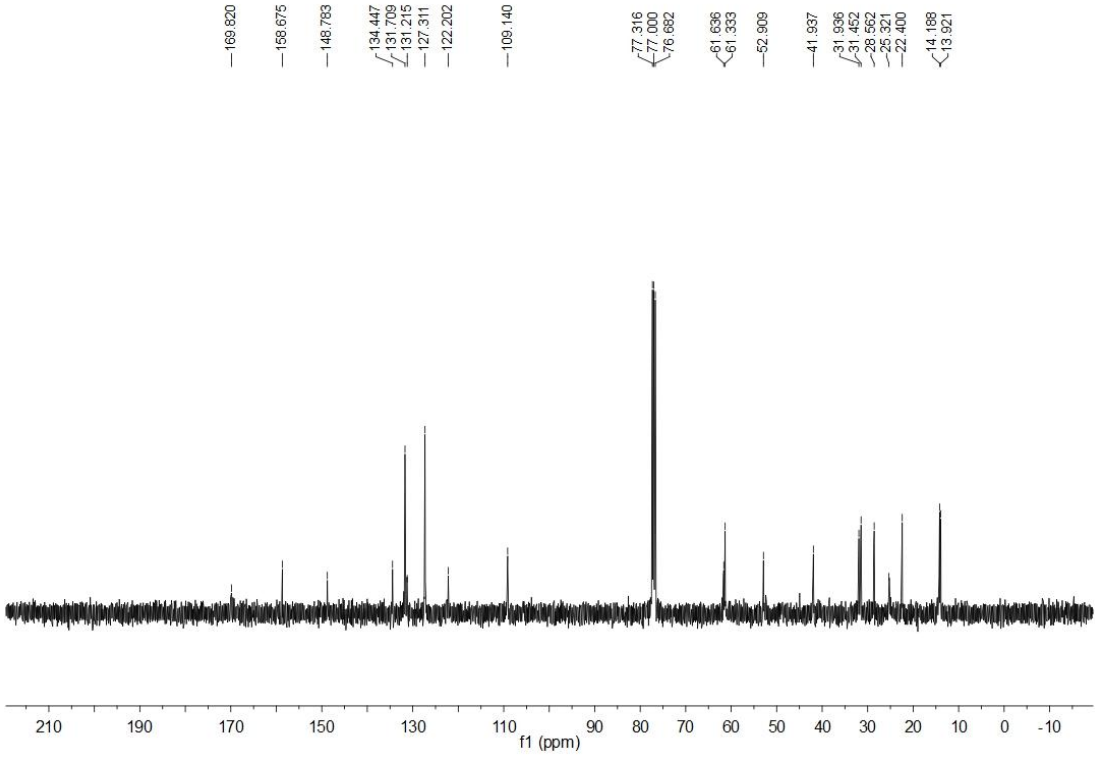

7.706
7.686
7.536
7.515
7.261
7.125
4.423
4.406
4.388
4.371
3.888
3.249
2.373
2.007
1.997
1.980
1.971
1.407
1.255
1.208
1.135
0.818
0.803
0.786
0.000
2.04
2.02
1.00
2.07
3.04
0.99
1.21
1.64
3.35
6.08
2.99
f1 (ppm)


169.769
158.670
148.779
134.445
131.710
131.203
127.307
122.175
109.136
77.318
77.000
76.683
61.635
61.327
52.864
41.916
31.870
31.038
22.283
14.187
13.810
f1 (ppm)

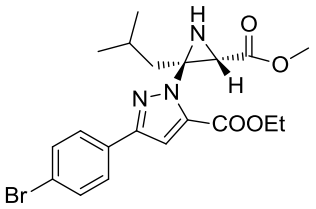
3g:

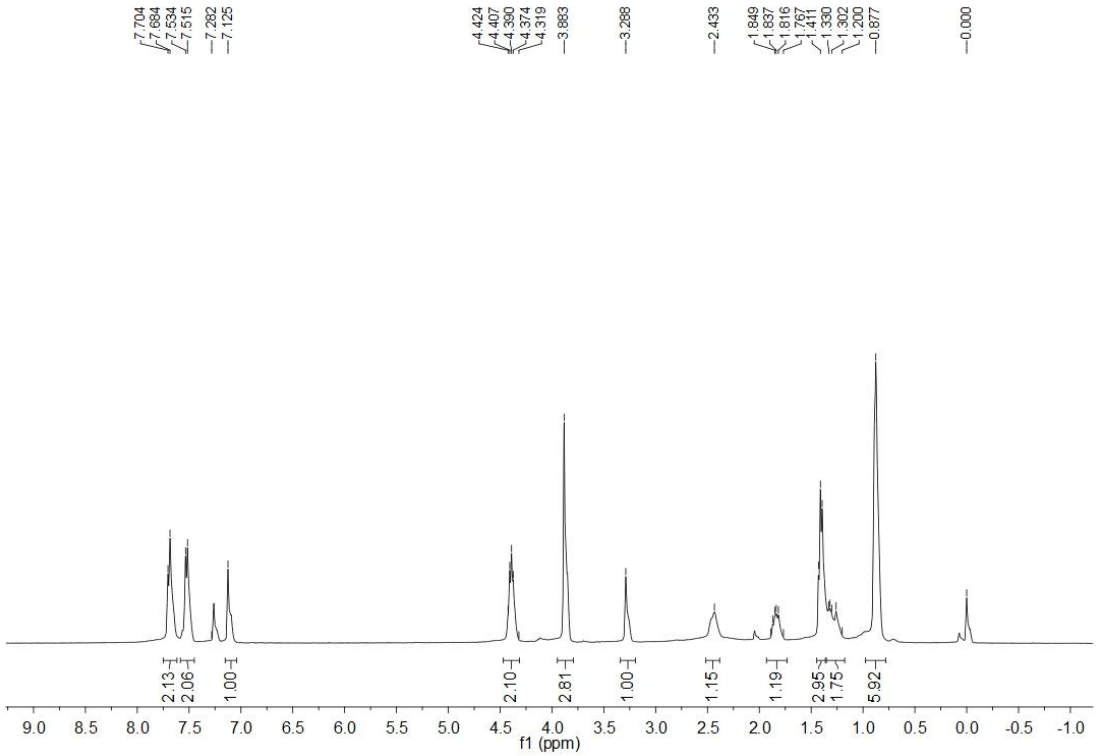

H
N
O
O
H
N
N
COOEt
Br

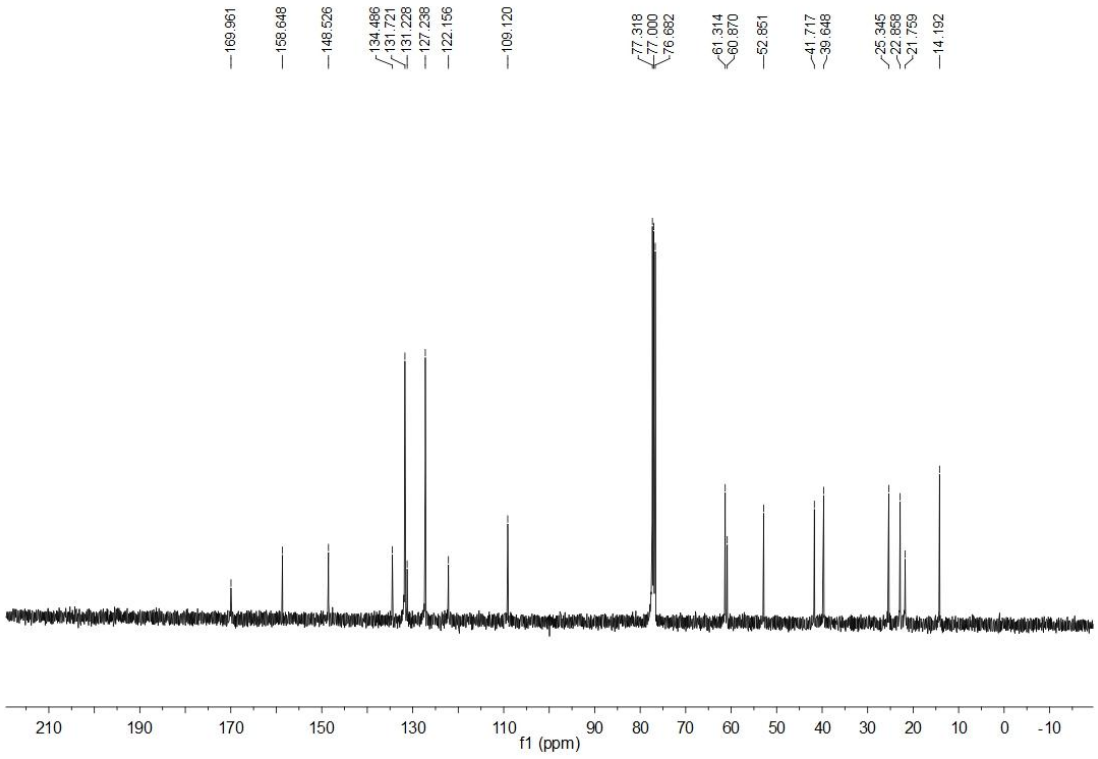

7.706
7.687
7.516
7.264
7.128
4.420
4.406
4.389
4.375
3.890
3.254
2.378
2.033
2.008
1.408
1.201
1.183
1.172
1.094
0.831
0.820
0.803
0.000
2.10
2.12
1.01
2.17
3.03
1.00
1.06
1.50
3.31
8.31
3.03
f1 (ppm)


169.820
158.675
148.783
134.447
131.709
131.215
127.311
122.202
109.140
77.316
77.000
76.682
61.636
61.333
52.909
41.937
31.936
31.452
28.562
25.321
22.400
14.188
13.921
f1 (ppm)

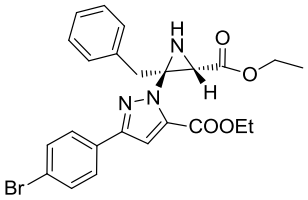
3h:

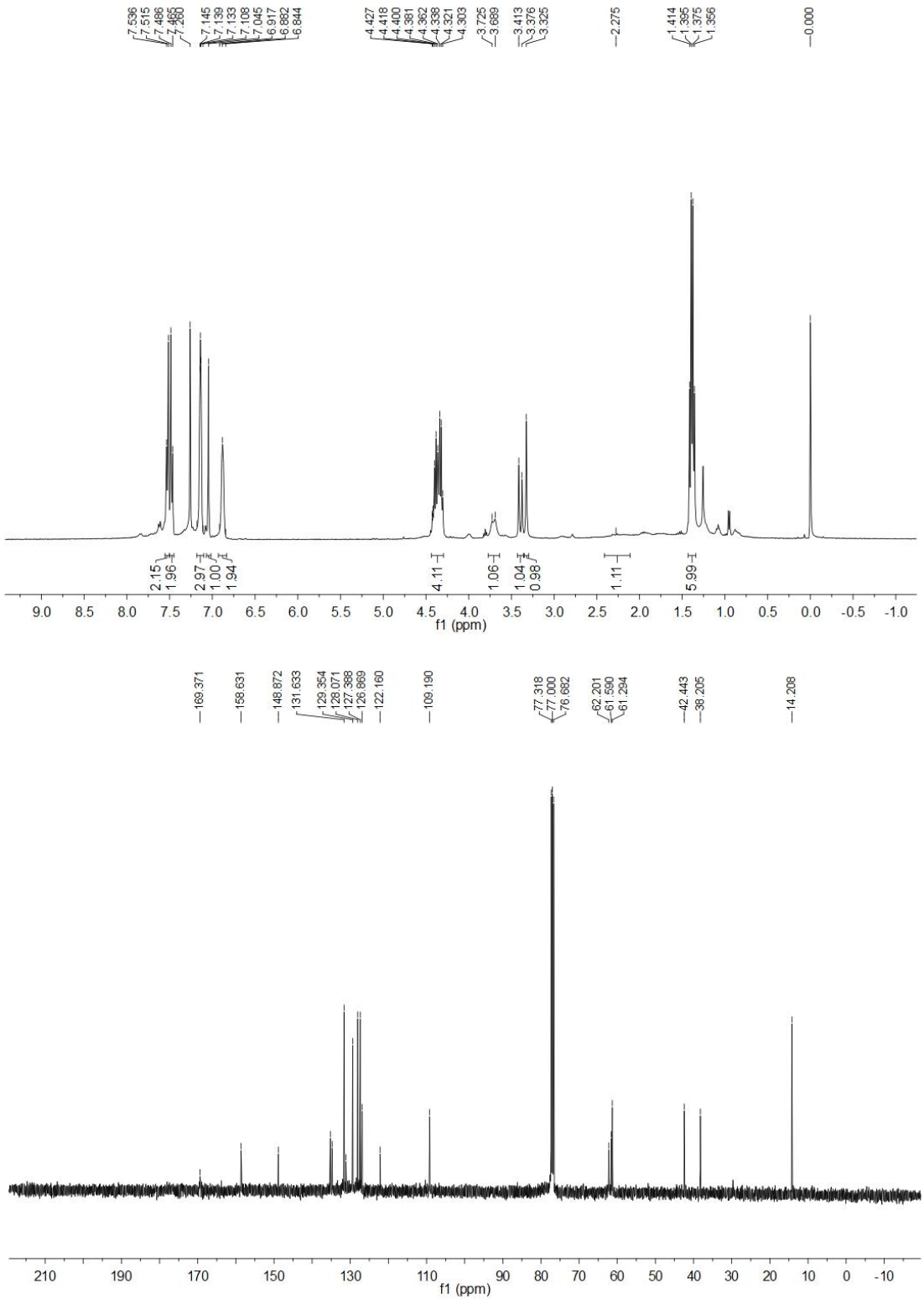

H
N
O
O
H
N
N
COOEt
Br


7.704
7.684
7.534
7.515
7.282
7.125
4.424
4.407
4.390
4.374
4.319
3.883
3.288
2.433
1.849
1.837
1.816
1.767
1.411
1.330
1.302
1.200
0.877
0.000
2.13
2.06
1.00
2.10
2.81
1.00
1.15
1.19
2.95
1.75
5.92
f1 (ppm)

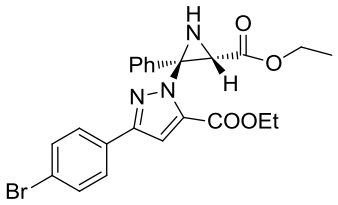

169.961
158.648
148.526
134.486
131.721
131.228
127.238
122.156
109.120
77.318
77.000
76.682
61.314
60.870
52.851
41.717
39.648
25.345
22.858
21.759
14.192
f1 (ppm)

3i:

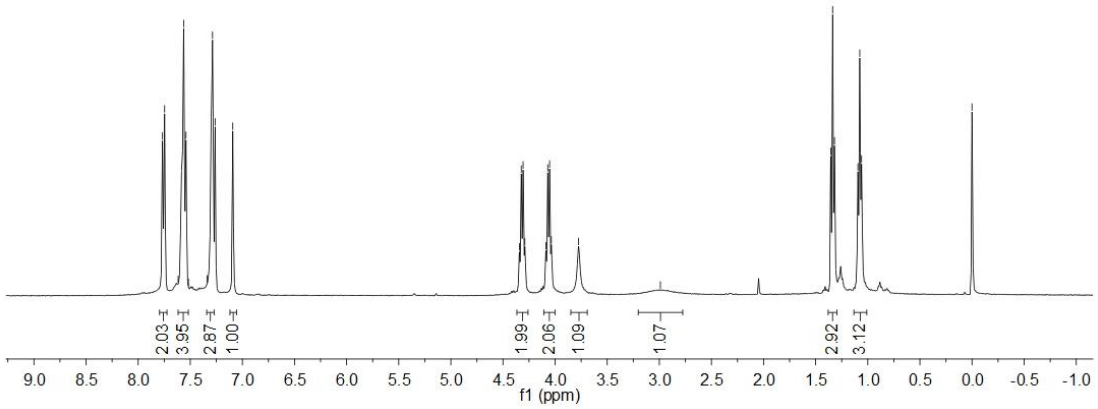

H
N
O
O
H
N
N
COOEt
Br

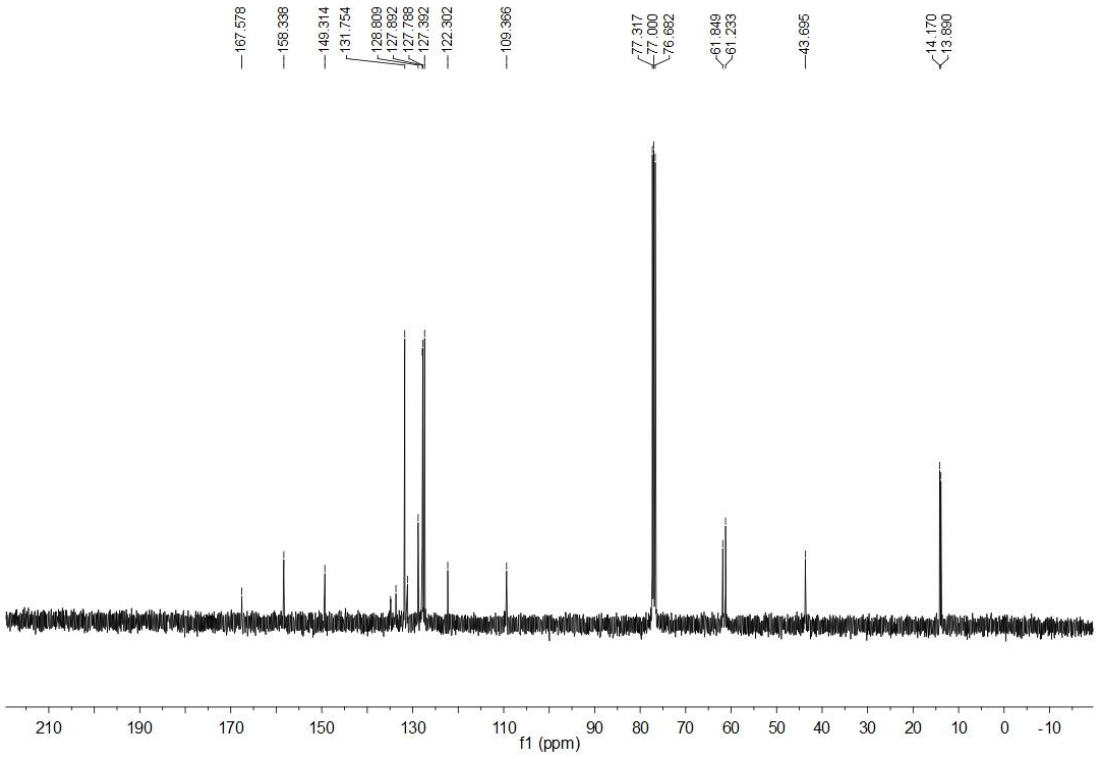

7.536
7.515
7.486
7.465
7.260
7.145
7.139
7.133
7.108
7.045
6.917
6.882
6.844
4.427
4.418
4.400
4.381
4.362
4.338
4.321
4.303
3.725
3.689
3.413
3.376
3.325
2.275
1.414
1.395
1.375
1.356
0.000
2.15
1.96
2.97
1.00
1.94
4.11
1.06
1.04
0.98
1.11
5.99
f1 (ppm)
169.371
158.631
148.872
131.633
129.354
128.071
127.388
126.869
122.160
109.190
77.318
77.000
76.682
62.201
61.590
61.294
42.443
38.205
14.208
f1 (ppm)

3j:

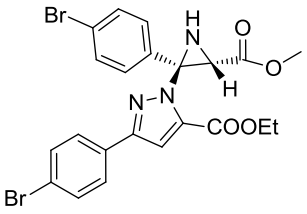

H
N
O
Ph
O
H
N
N
COOEt
Br

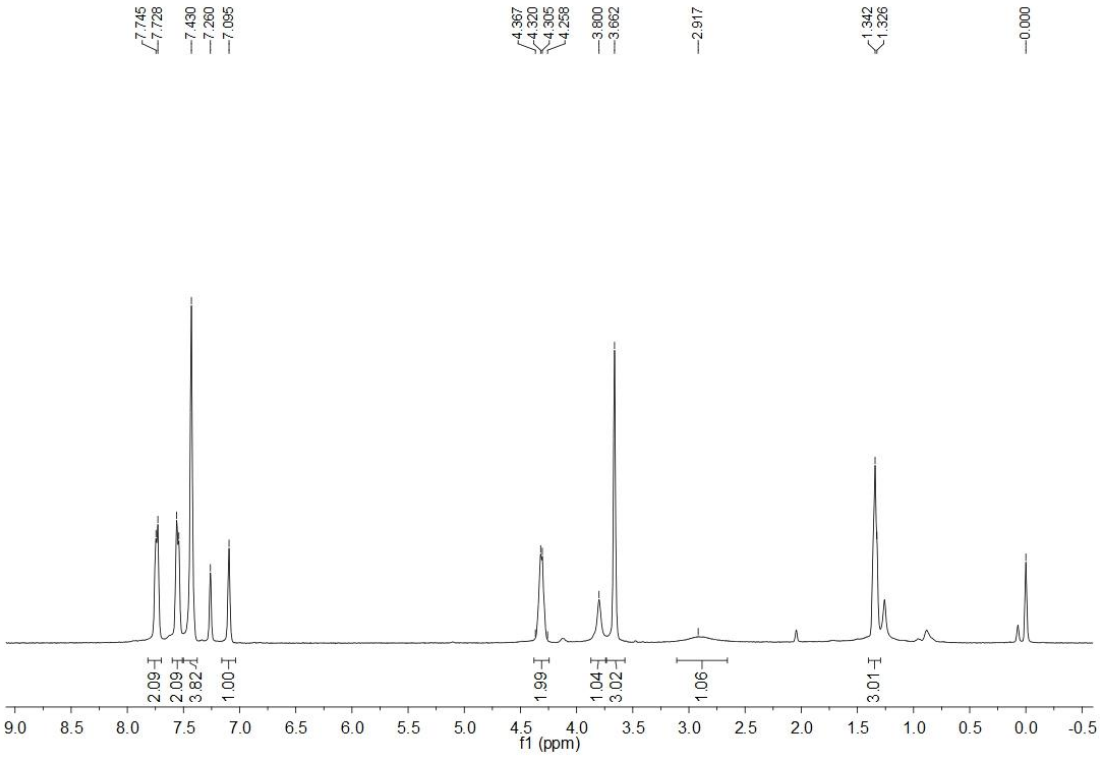

7.766
7.746
7.616
7.563
7.541
7.518
7.262
7.092
4.342
4.325
4.307
4.290
4.036
3.774
2.990
1.355
1.337
1.320
1.095
1.077
1.060
0.000

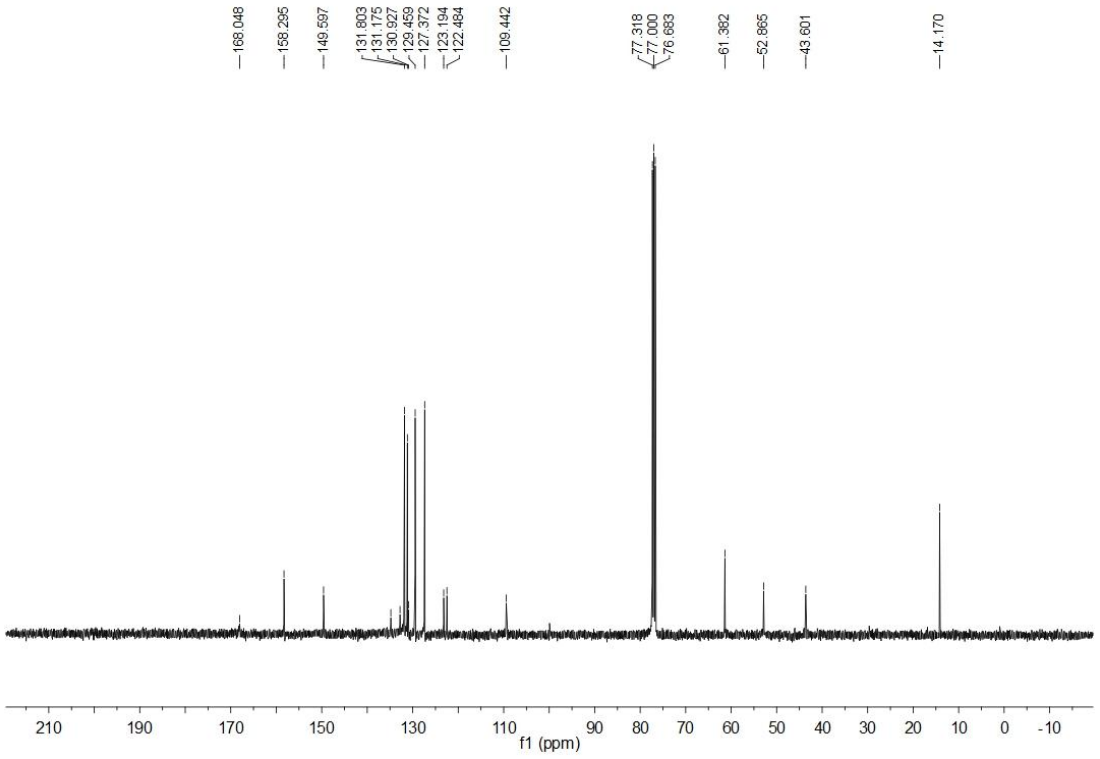

2.03
3.95
2.87
1.00
1.99
2.06
1.09
1.07
2.92
3.12
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


167.578
158.338
149.314
131.754
128.809
127.892
127.788
127.392
122.302
109.366
77.317
77.000
76.682
61.849
61.233
43.695
14.170
13.890
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

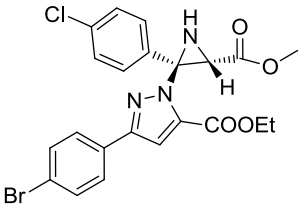
3k:

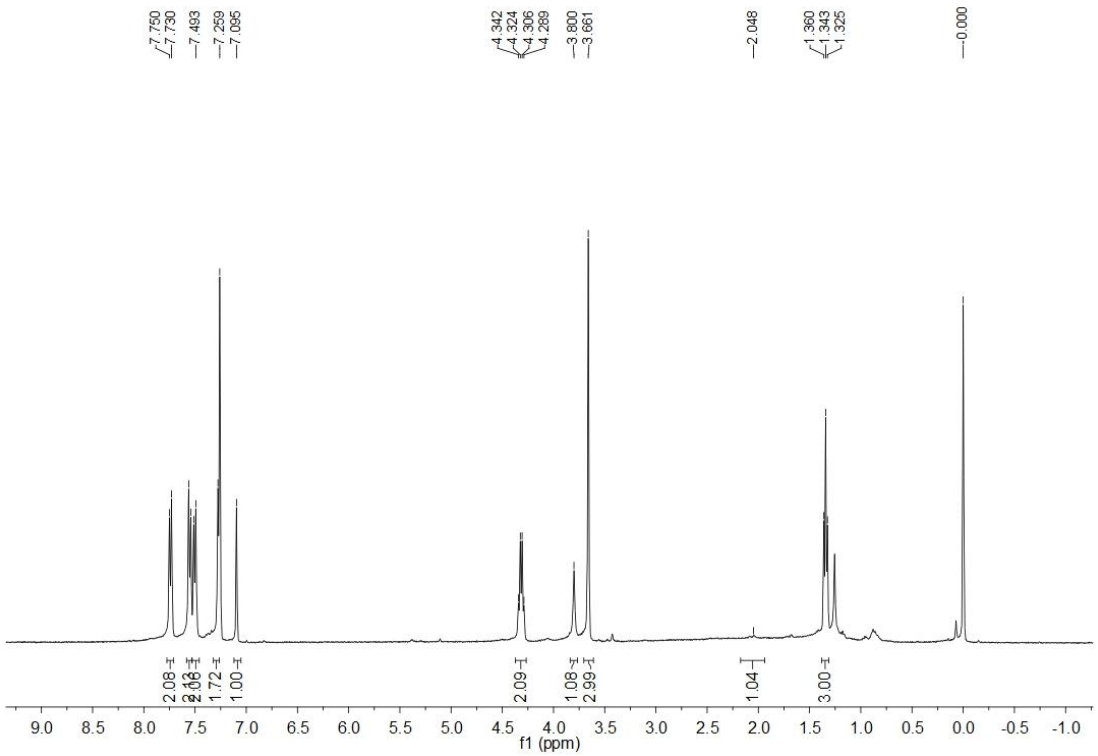

Br
H
N
O
O
H
N
N
COOEt
Br

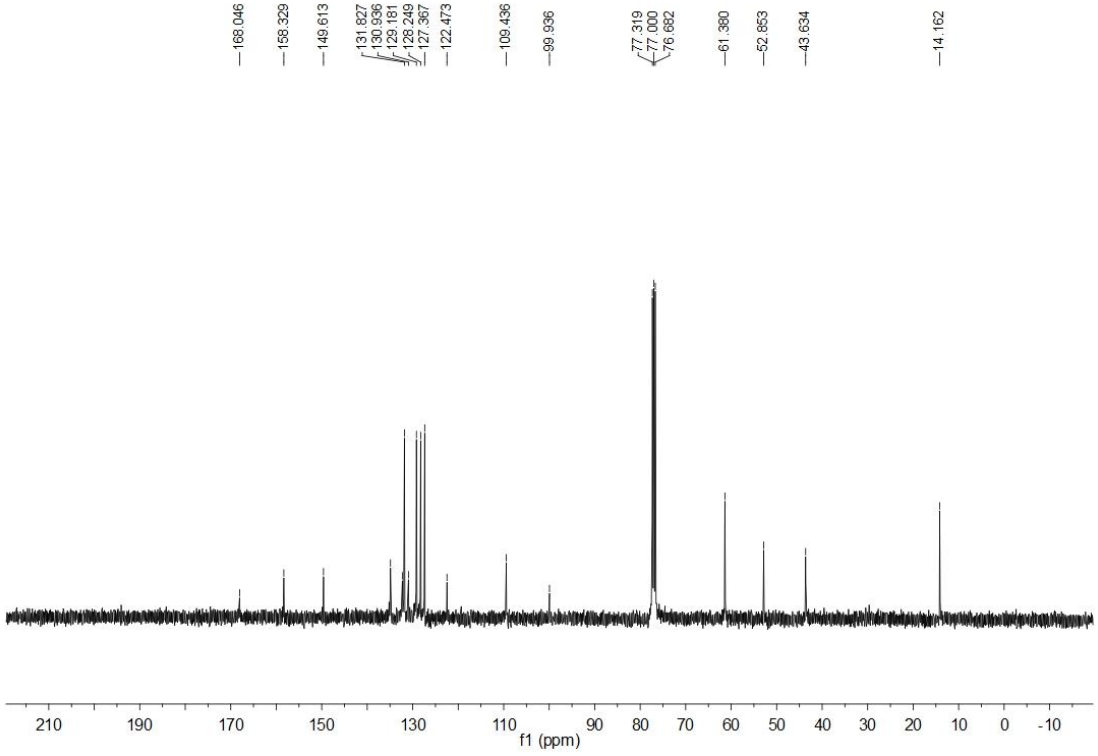

7.745
7.728
7.430
7.260
7.095
4.367
4.320
4.305
4.258
3.800
3.662
2.917
1.342
1.326
0.000
2.09
2.09
3.82
1.00
1.99
1.04
3.02
1.06
3.01
f1 (ppm)


168.048
158.295
149.597
131.803
131.175
130.927
129.459
127.372
123.194
122.484
109.442
77.318
77.000
76.683
61.382
52.865
43.601
14.170
f1 (ppm)

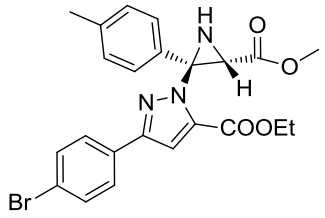
3l:

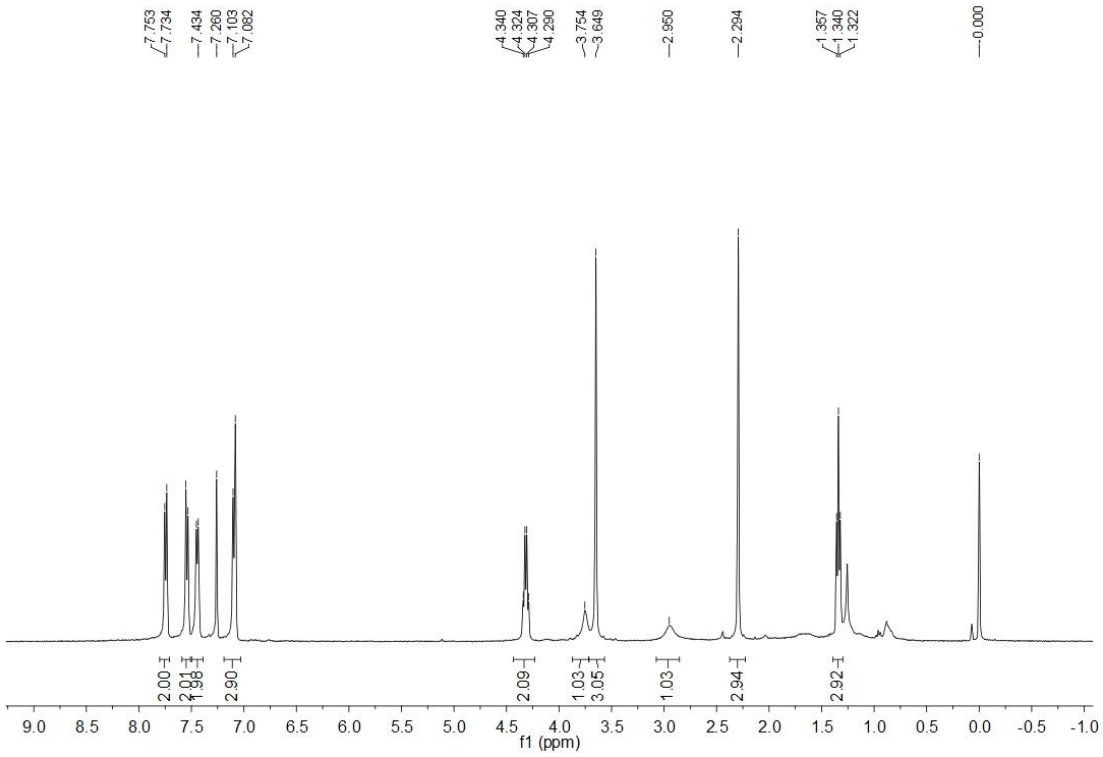

Cl
H
N
O
O
H
N-N
COOEt
Br

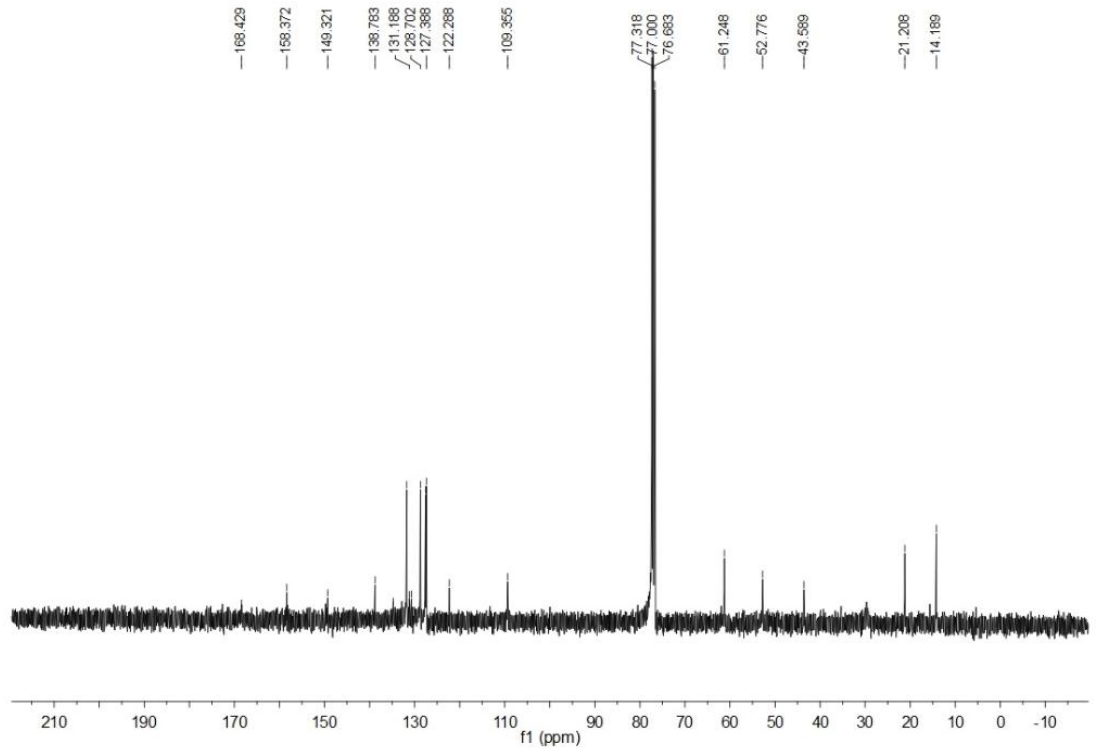

7.750
7.730
7.493
7.259
7.095
4.342
4.324
4.306
4.289
3.800
3.661
2.048
1.360
1.343
1.325
0.000
2.08
2.13
2.06
1.72
1.00
2.09
1.08
2.99
1.04
3.00
f1 (ppm)


168.046
158.329
149.613
131.827
130.936
129.161
128.249
127.367
122.473
109.436
99.936
77.319
77.000
76.682
61.380
52.853
43.634
14.162
f1 (ppm)

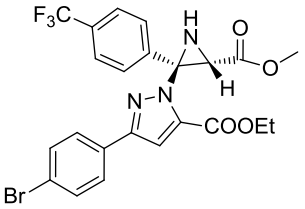
3m:

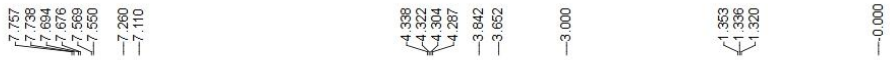

H
N
O
O
H
N
N
COOEt
Br

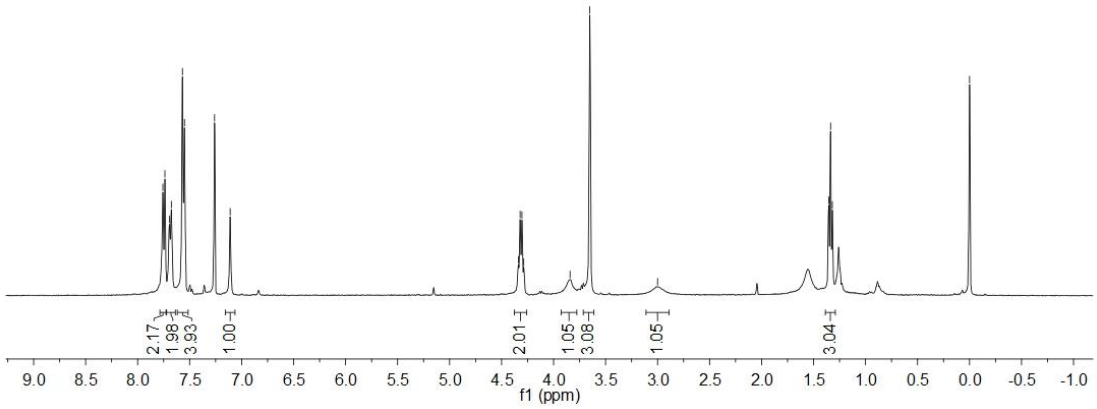

7.753
7.734
7.434
7.260
7.103
7.082
4.340
4.324
4.307
4.290
3.754
3.649
2.950
2.294
1.357
1.340
1.322
0.000
2.00
2.01
1.98
2.90
2.09
1.03
3.05
1.03
2.94
2.92
f1 (ppm)

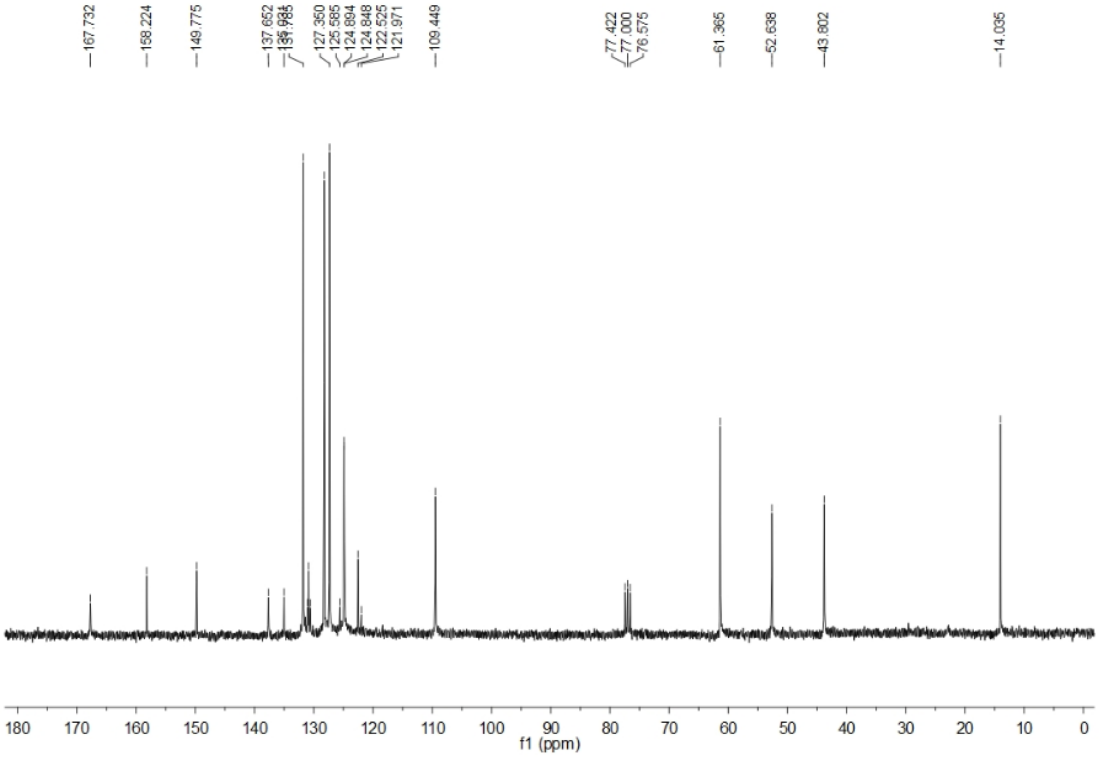

168.429
159.372
149.321
136.783
131.188
128.702
127.388
122.288
109.355
77.318
77.000
76.683
61.248
52.776
43.589
21.208
14.189
f1 (ppm)

3n:

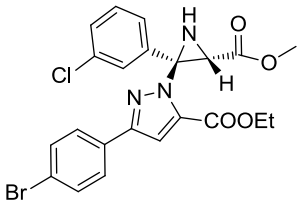

F3C
H
N
O
O
H
N
N
COOEt
Br

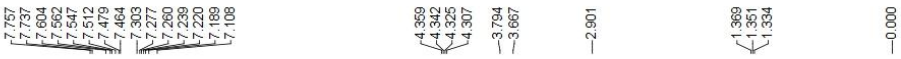

7.757
7.738
7.694
7.676
7.569
7.550
7.260
7.110
4.338
4.322
4.304
4.287
3.842
3.652
3.000
1.353
1.336
1.320
0.000

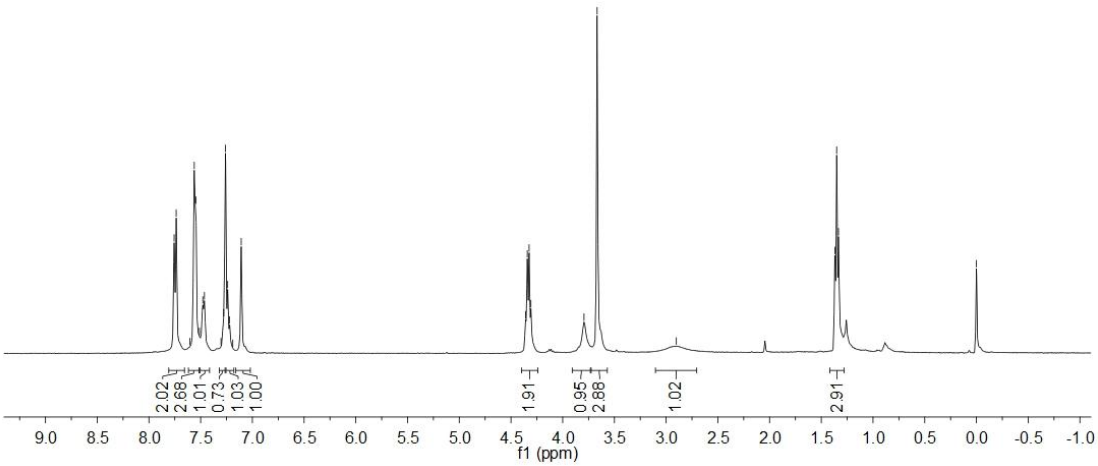

2.17
1.98
3.93
1.00
2.01
1.05
3.08
1.05
3.04
f1 (ppm)


167.732
158.224
149.775
137.652
127.350
125.585
124.894
124.848
122.525
121.971
109.449
77.422
77.000
76.575
61.365
52.638
43.802
14.035
f1 (ppm)

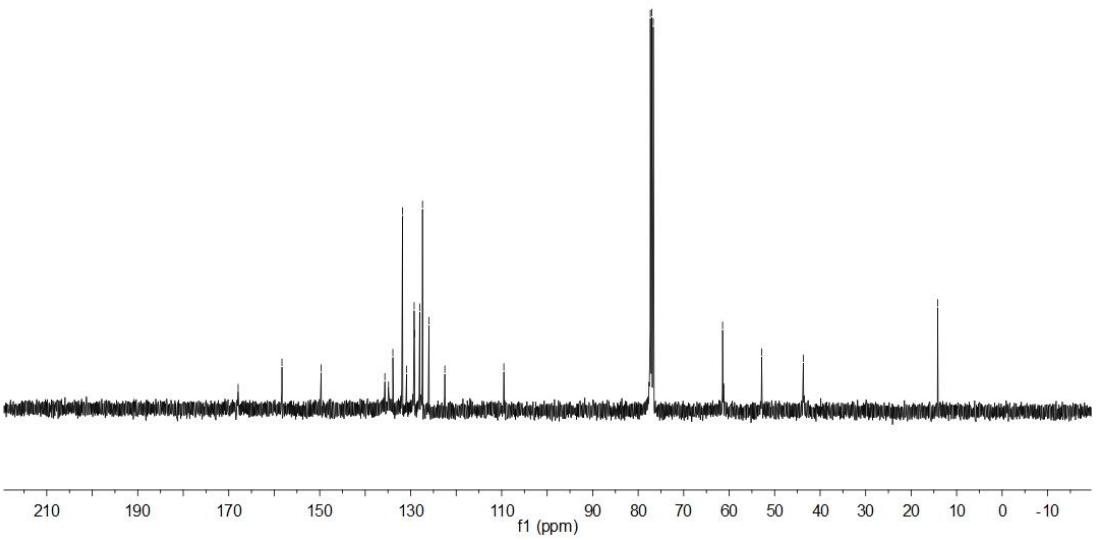
3o:


H
N
O
Cl
O
H
N
N
COOEt
Br

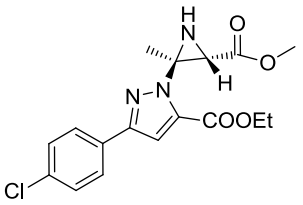

7.757
7.737
7.604
7.562
7.547
7.512
7.479
7.464
7.303
7.277
7.260
7.239
7.220
7.189
7.108
4.359
4.342
4.325
4.307
3.794
3.667
2.901
1.369
1.351
1.334
0.000


2.02
2.68
1.01
0.73
1.03
1.00
1.91
0.95
2.88
1.02
2.91
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

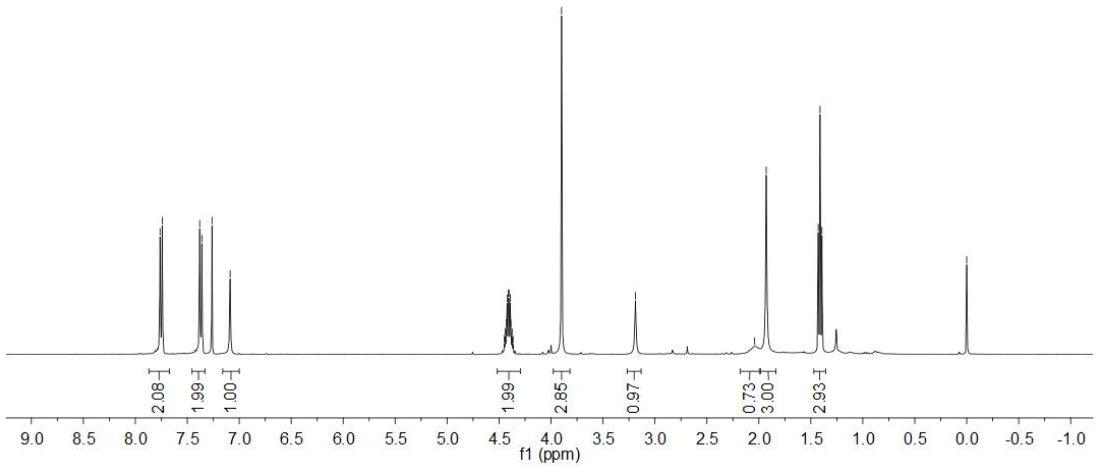

167.934
158.300
149.687
134.873
131.807
129.244
128.026
125.987
122.500
109.523
77.317
77.000
76.683
61.439
52.851
43.704
14.165

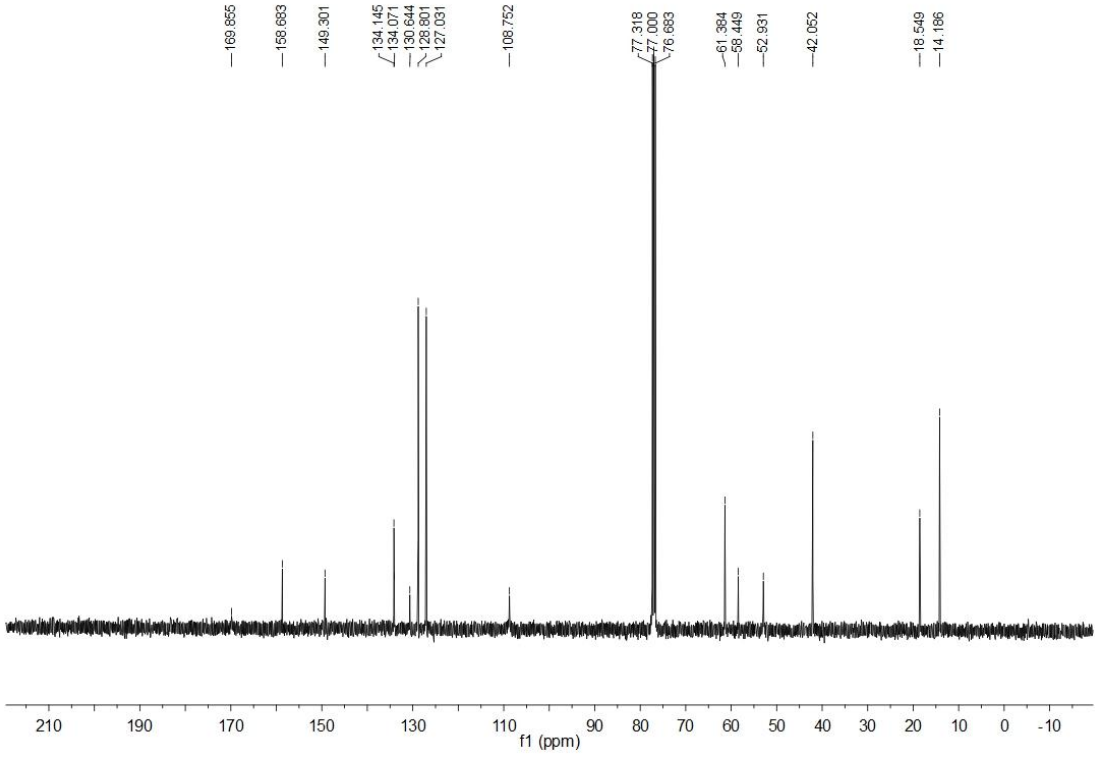

210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3p:

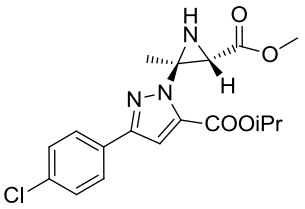

H
N
O
O
H
N
N
COOEt
Cl


7.762
7.741
7.381
7.262
7.088
4.449
4.440
4.428
4.422
4.410
4.404
4.392
4.387
4.375
4.366
3.898
3.188
2.041
1.929
1.429
1.411
1.393
0.000

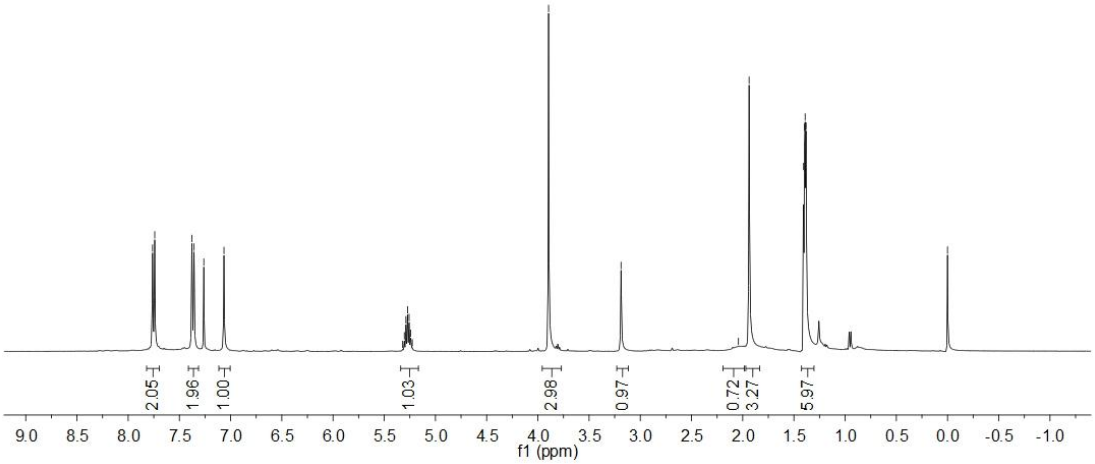

2.08
1.99
1.00
1.99
2.85
0.97
0.73
3.00
2.93
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


169.855
158.683
149.301
134.145
134.071
130.644
128.801
127.031
108.752
77.318
77.000
76.683
61.384
58.449
52.931
42.052
18.549
14.186
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

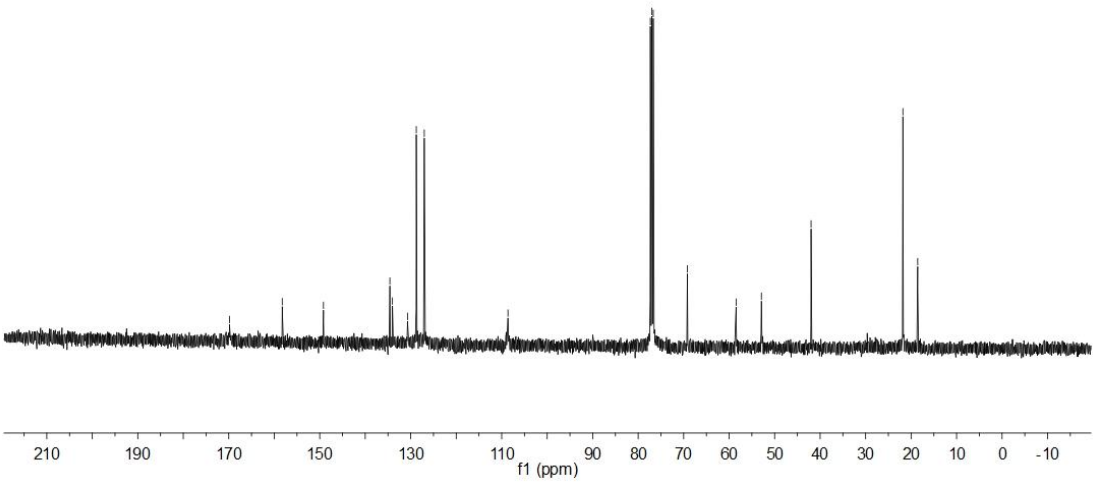
3q:


H
N
O
O
H
N
N
COOiPr
Cl

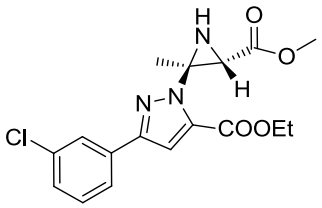

7.762
7.741
7.378
7.262
7.065
5.320
5.304
5.289
5.273
5.257
5.242
5.226
3.896
3.188
2.042
1.938
1.406
1.396
1.390
1.381
0.000


2.05
1.96
1.00
1.03
2.98
0.97
0.72
3.27
5.97
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

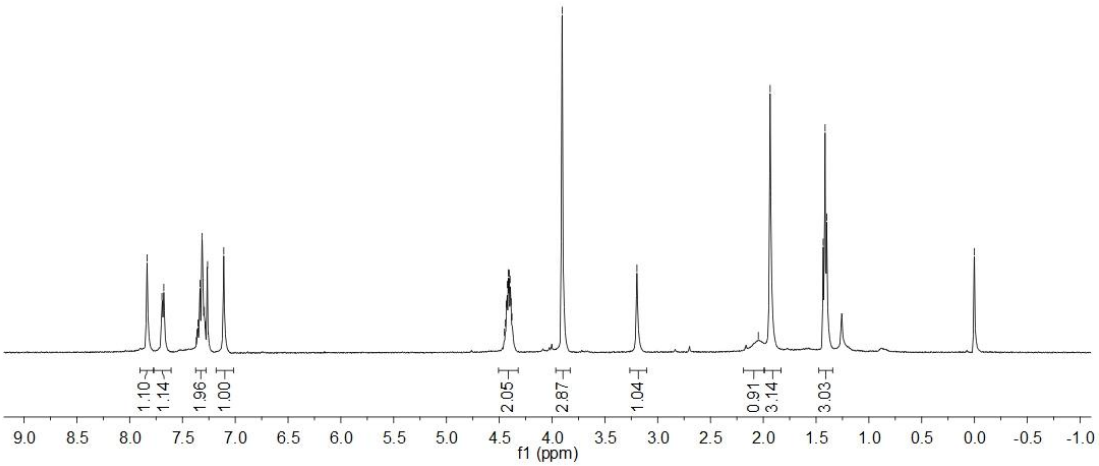

169.835
158.243
149.182
134.581
134.013
130.702
128.775
127.018
108.624
77.318
77.000
76.683
69.187
58.469
52.909
41.988
21.807
18.552


210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

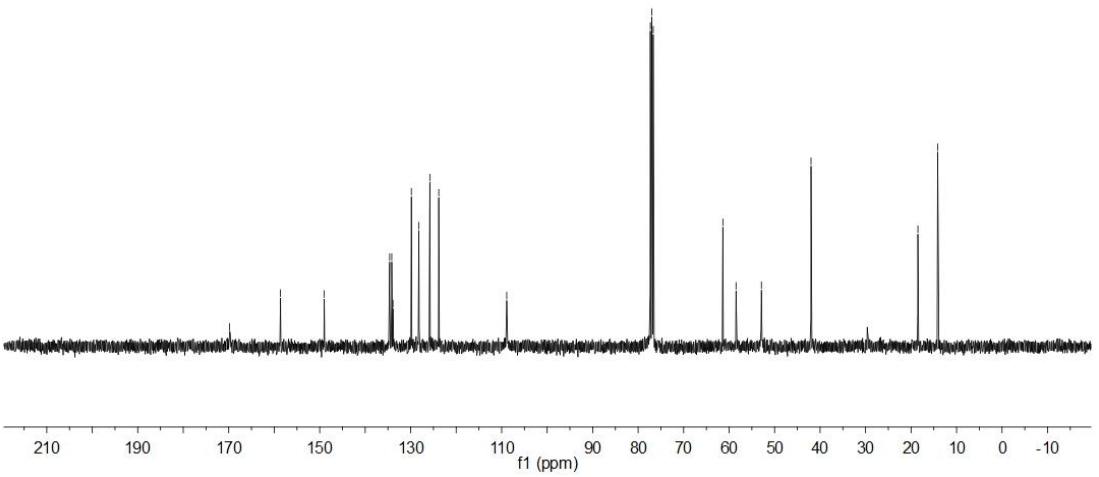
3r:


H
N
O
O
H
N
N
Cl
COOEt

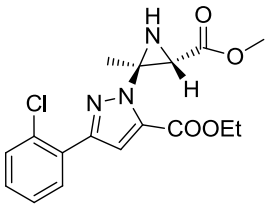

7.895
7.694
7.677
7.334
7.262
7.109
4.451
4.441
4.433
4.424
4.415
4.406
4.398
4.389
4.380
3.904
3.196
2.047
1.935
1.432
1.415
1.399
0.000

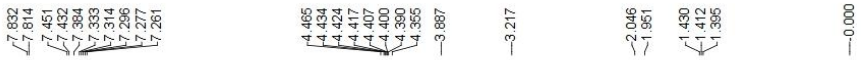

1.10
1.14
1.96
1.00
2.05
2.87
1.04
0.91
3.14
3.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

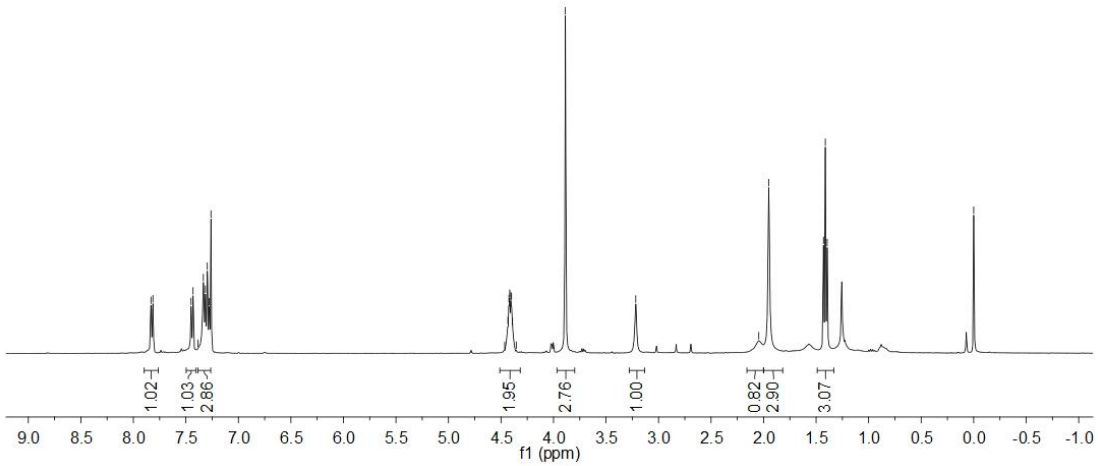

169.813
158.620
149.006
134.627
134.160
133.895
129.853
128.201
125.790
123.831
108.886
77.318
77.000
76.683
61.372
58.478
52.902
41.995
18.500
14.158


210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

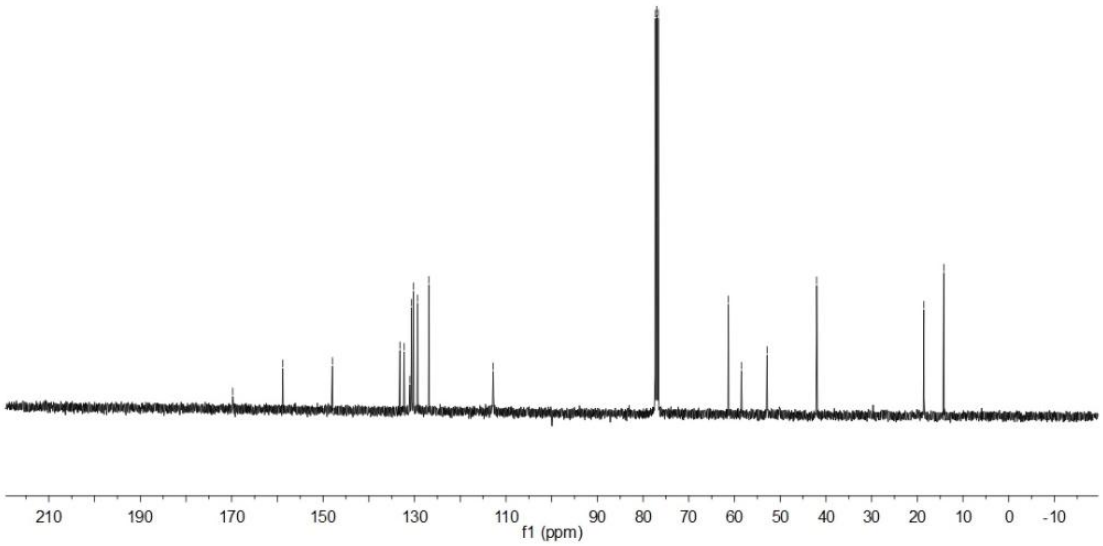
3s:


H
N
O
O
H
Cl
N
N
COOEt

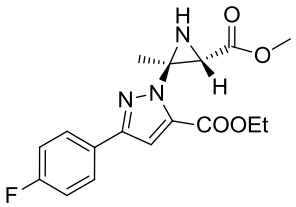

7.832
7.814
7.451
7.432
7.384
7.333
7.314
7.296
7.277
7.261
4.465
4.434
4.424
4.417
4.407
4.400
4.390
4.355
3.887
3.217
2.046
1.951
1.430
1.412
1.395
0.000

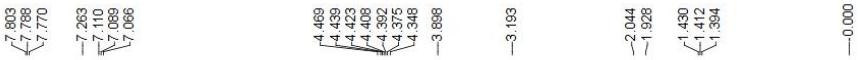

1.02
1.03
2.86
1.95
2.76
1.00
0.82
2.90
3.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

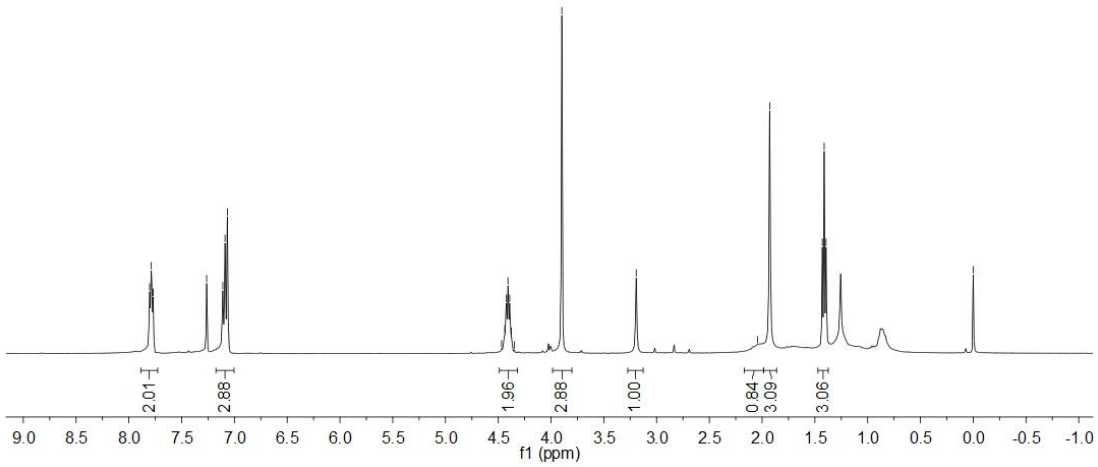

169.772
158.829
147.969
133.205
132.276
131.039
130.661
130.216
129.316
126.847
112.785
77.318
77.000
76.683
61.337
58.483
52.887
42.020
18.575
14.199


210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

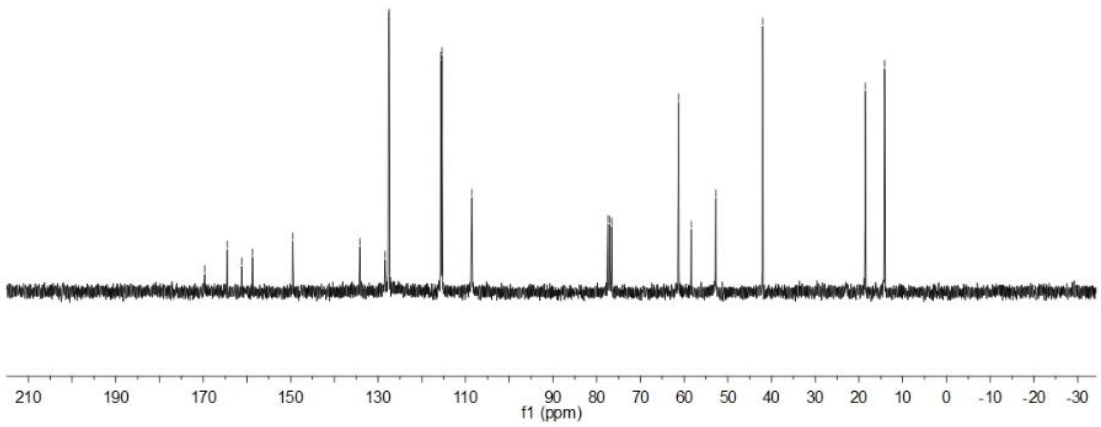
3t:


H
N
O
O
H
N–N
COOEt
F

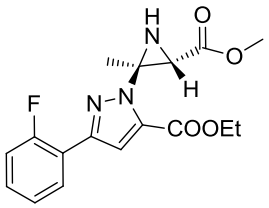

7.803
7.788
7.770
7.263
7.110
7.089
7.066
4.469
4.439
4.423
4.408
4.392
4.375
4.348
3.898
3.193
2.044
1.928
1.430
1.412
1.394
0.000

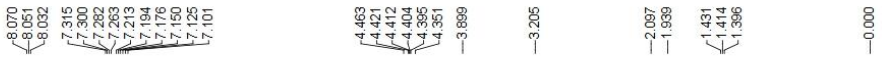

2.01
2.88
1.96
2.88
1.00
0.84
3.09
3.06
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

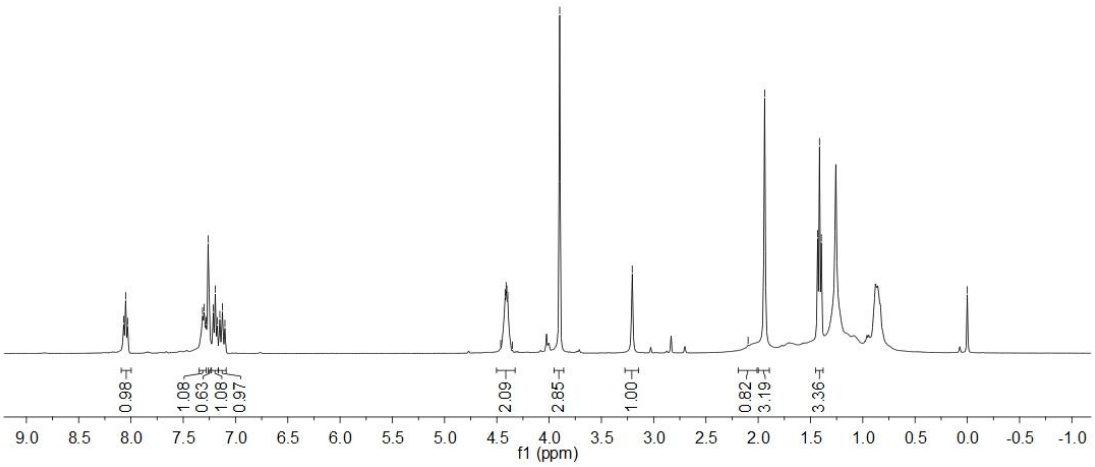

169.639
164.481
161.205
158.704
149.504
134.157
127.561
127.453
115.636
115.349
108.549
77.427
77.000
76.578
61.285
58.365
52.743
42.055
18.534
14.126


210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)

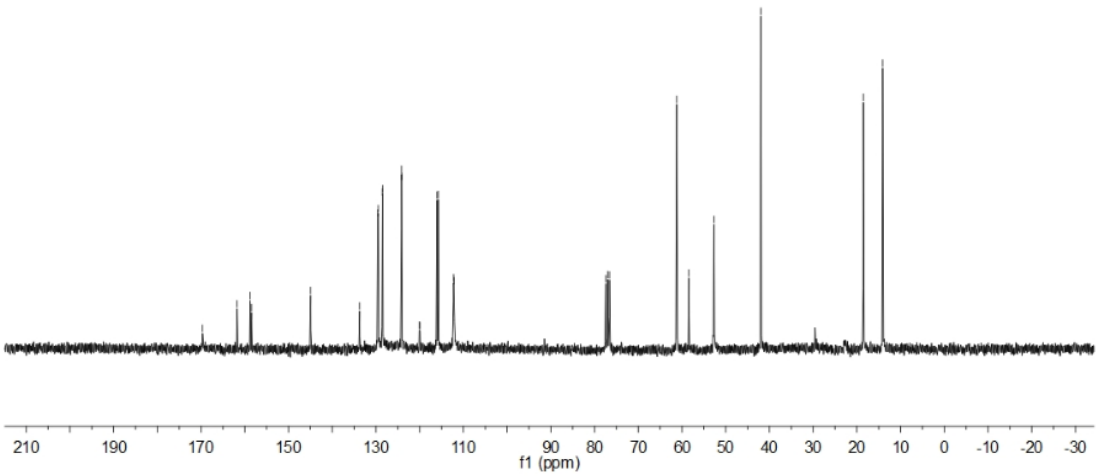
3u:


H
N
O
O
H
F
N
N
COOEt

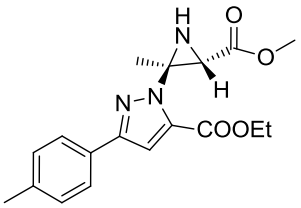

8.070
8.051
8.032
7.315
7.300
7.282
7.263
7.213
7.194
7.176
7.150
7.125
7.101
4.463
4.421
4.412
4.404
4.395
4.351
3.899
3.205
2.097
1.939
1.431
1.414
1.396
0.000

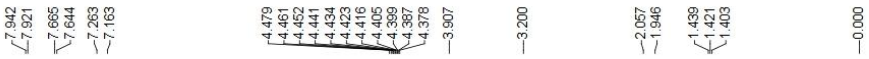

0.98
1.08
0.63
1.08
0.97
2.09
2.85
1.00
0.82
3.19
3.36
f1 (ppm)

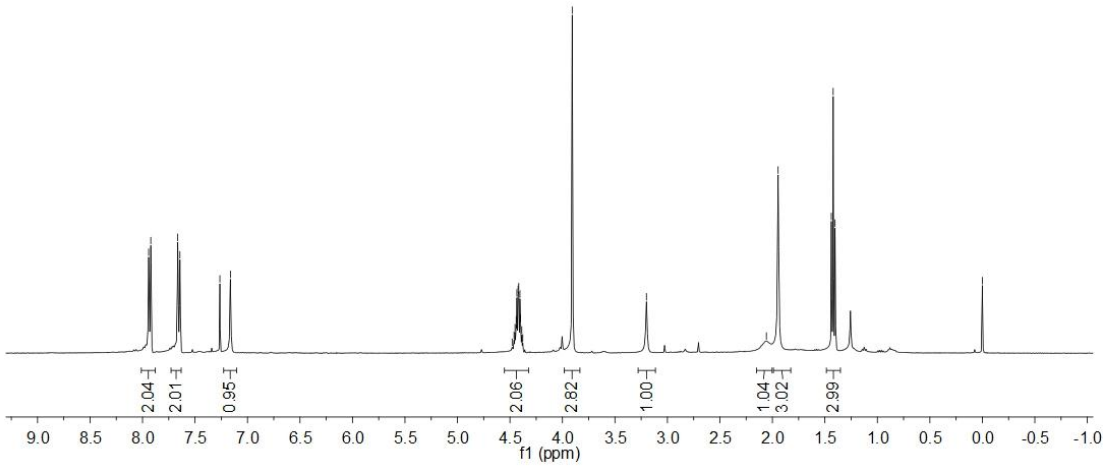

169.677
161.767
158.759
158.455
144.952
133.748
128.497
124.118
119.961
116.039
115.746
112.248
112.119
77.424
77.000
76.575
61.209
58.433
52.693
41.980
18.503
14.096

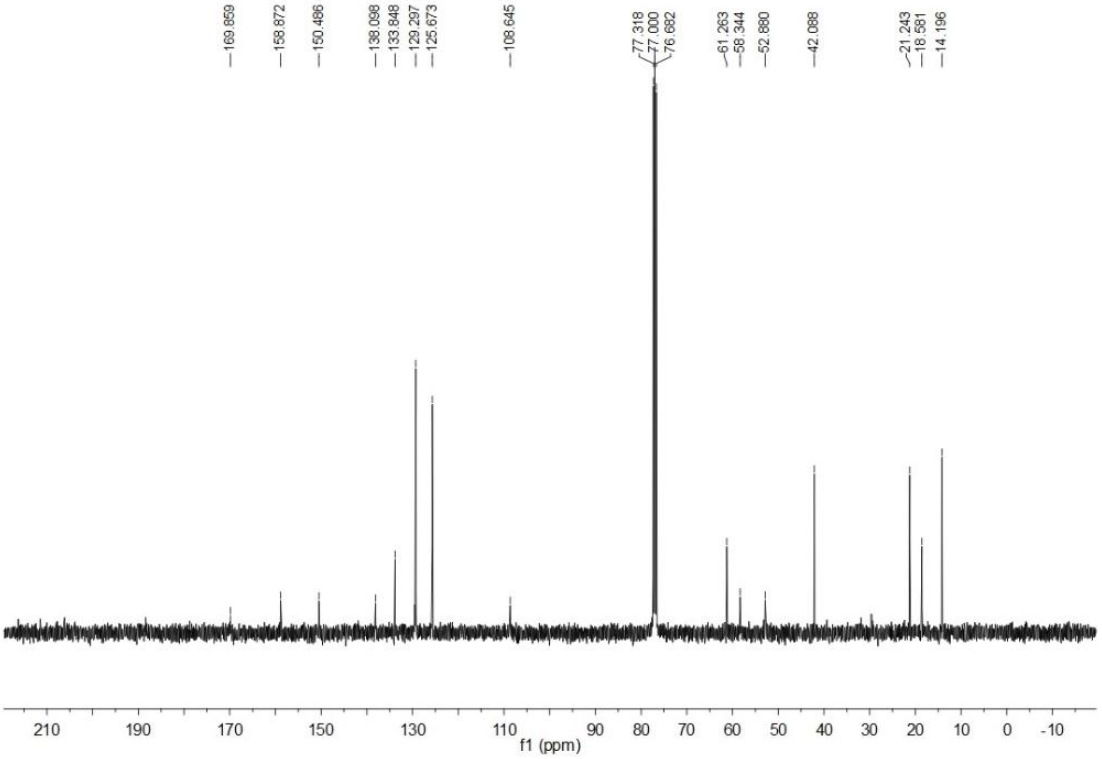

f1 (ppm)

3v:

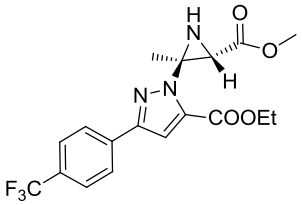

H
N
O
O
H
N-N
COOEt

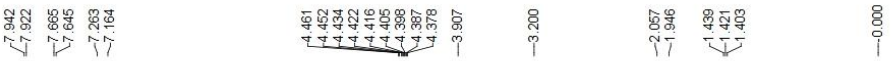

7.942
7.921
7.665
7.644
7.263
7.163
4.479
4.461
4.452
4.441
4.434
4.423
4.416
4.405
4.399
4.387
4.378
3.907
3.200
2.057
1.946
1.439
1.421
1.403
0.000

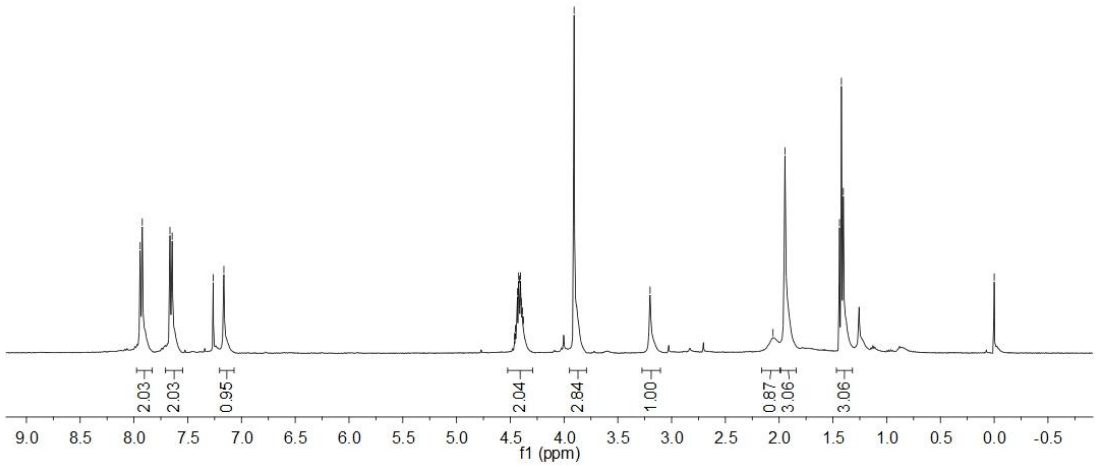

2.04
2.01
0.95
2.06
2.82
1.00
1.04
3.02
2.99
f1 (ppm)


169.859
158.872
150.486
138.098
133.848
129.297
125.673
108.645
77.318
77.000
76.682
61.263
58.344
52.880
42.088
21.243
18.581
14.196
f1 (ppm)

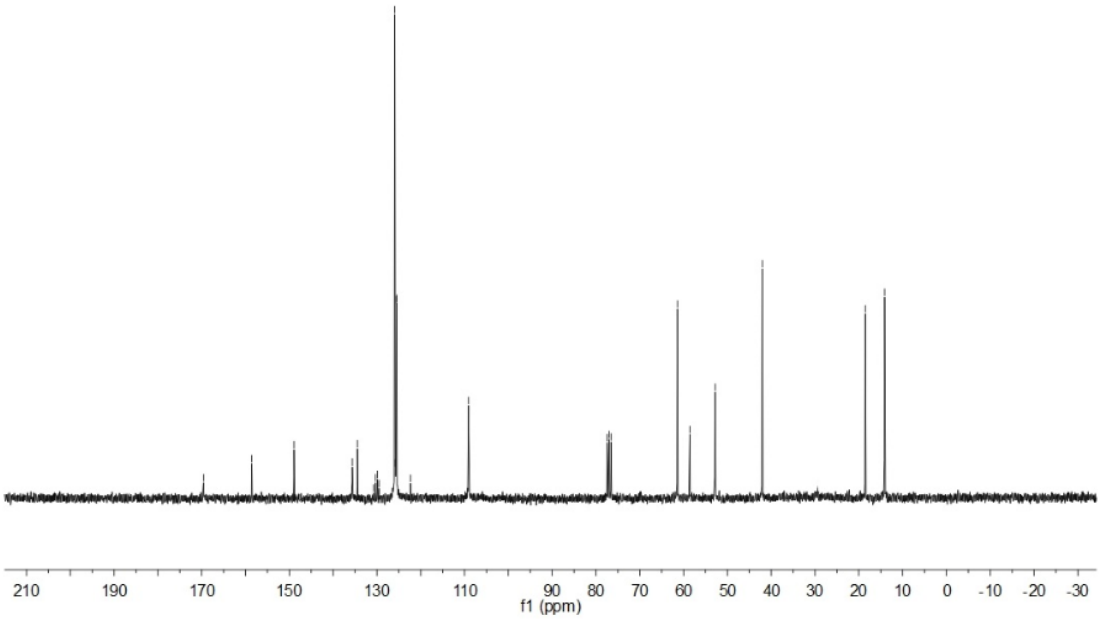
3w:


H
N
O
O
H
N-N
COOEt
F3C

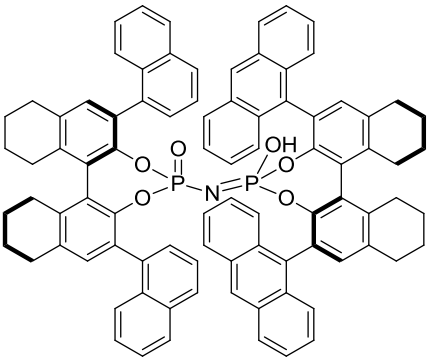

7.942
7.922
7.665
7.645
7.263
7.164
4.461
4.452
4.434
4.422
4.416
4.405
4.398
4.387
4.378
3.907
3.200
2.057
1.946
1.439
1.421
1.403
0.000

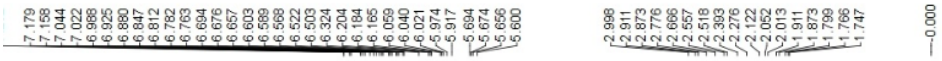

2.03
2.03
0.95
2.04
2.84
1.00
0.87
3.06
3.06
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

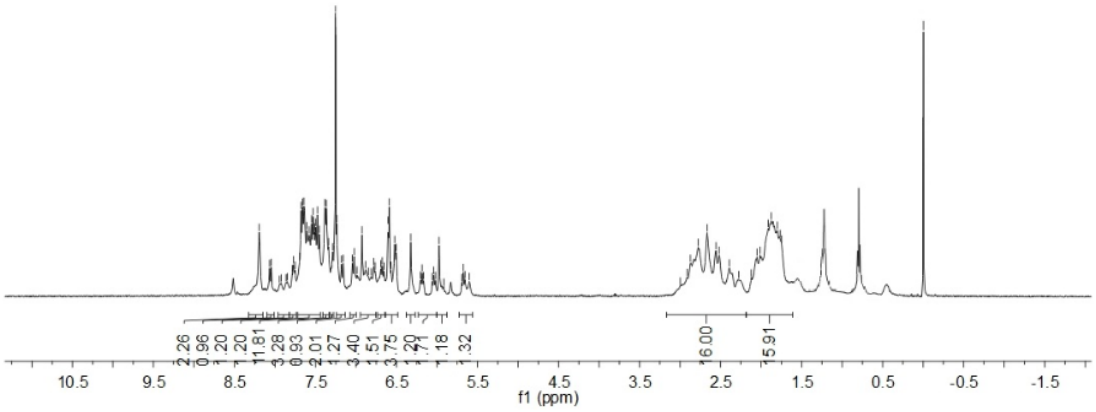

169.590
159.583
148.917
135.617
134.450
129.533
125.927
125.519
122.332
109.088
77.424
77.000
76.577
61.407
58.560
52.784
42.027
18.504
14.113

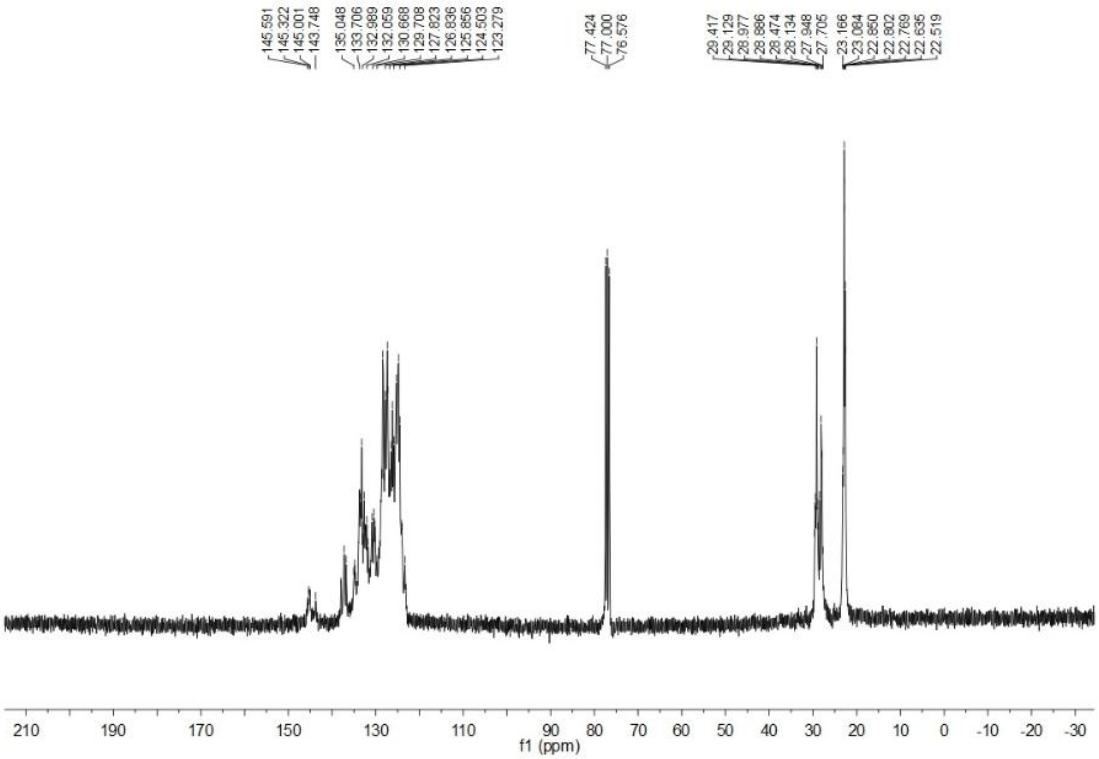

210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)

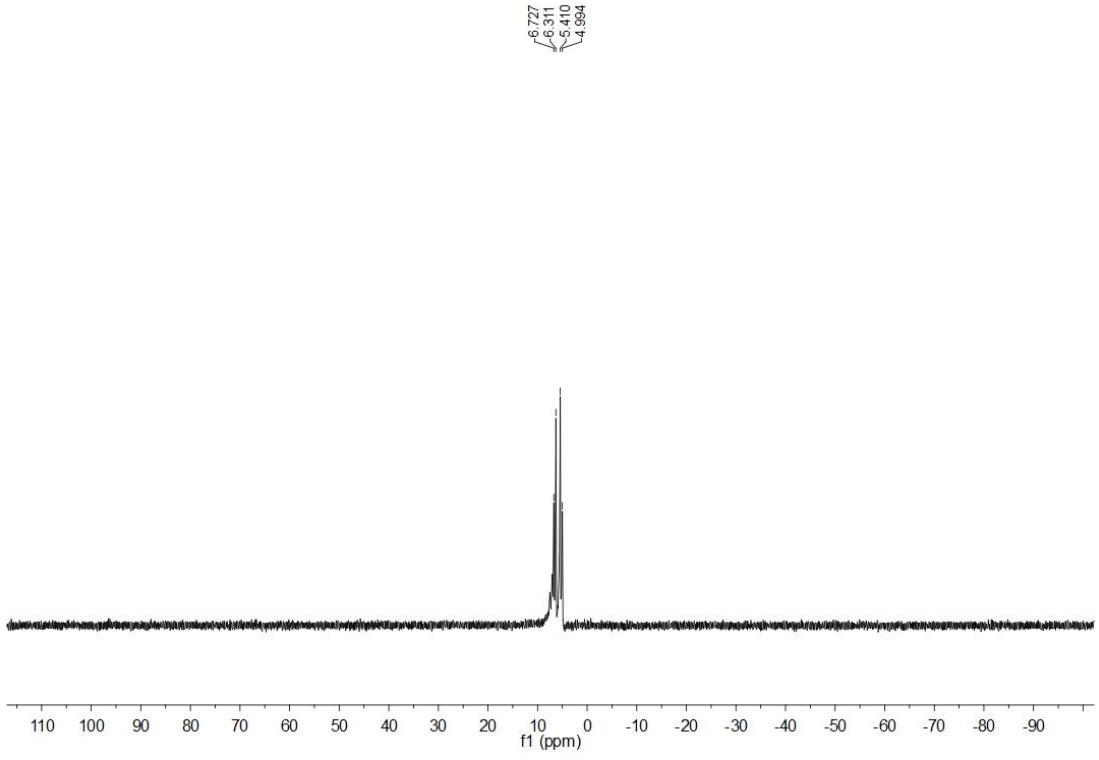
4e:


OH
O
P
N
P
O

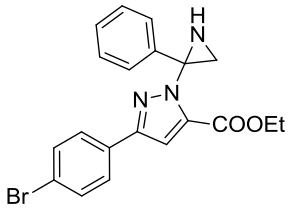

7.179
7.158
7.044
7.022
6.988
6.925
6.880
6.847
6.812
6.782
6.763
6.694
6.676
6.657
6.603
6.589
6.568
6.522
6.503
6.324
6.204
6.184
6.165
6.059
6.040
6.021
5.974
5.917
5.694
5.674
5.656
5.600
2.998
2.911
2.873
2.776
2.666
2.557
2.518
2.393
2.276
2.122
2.052
2.013
1.911
1.873
1.799
1.766
1.747
0.000

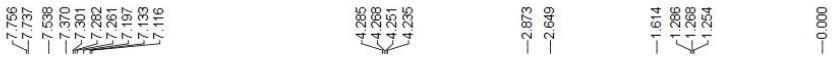

2.26
0.96
1.20
1.20
11.81
3.28
0.93
2.01
1.27
3.40
1.51
3.75
1.20
1.71
1.18
1.32
16.00
15.91
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5
f1 (ppm)

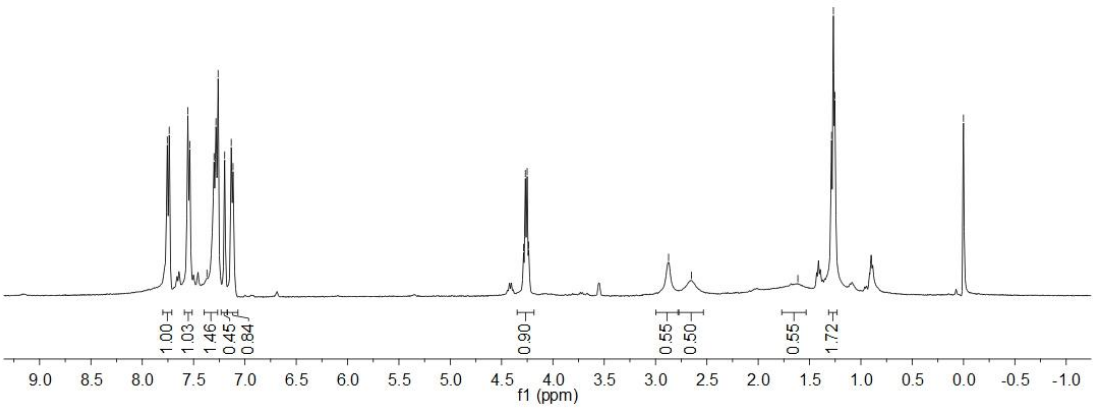

145.591
145.322
145.001
143.748
135.048
133.706
132.989
132.059
130.668
129.708
127.823
126.836
125.856
124.503
123.279
77.424
77.000
76.576
29.417
29.129
28.977
28.886
28.474
28.134
27.948
27.705
23.166
23.084
22.850
22.802
22.769
22.635
22.519
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)

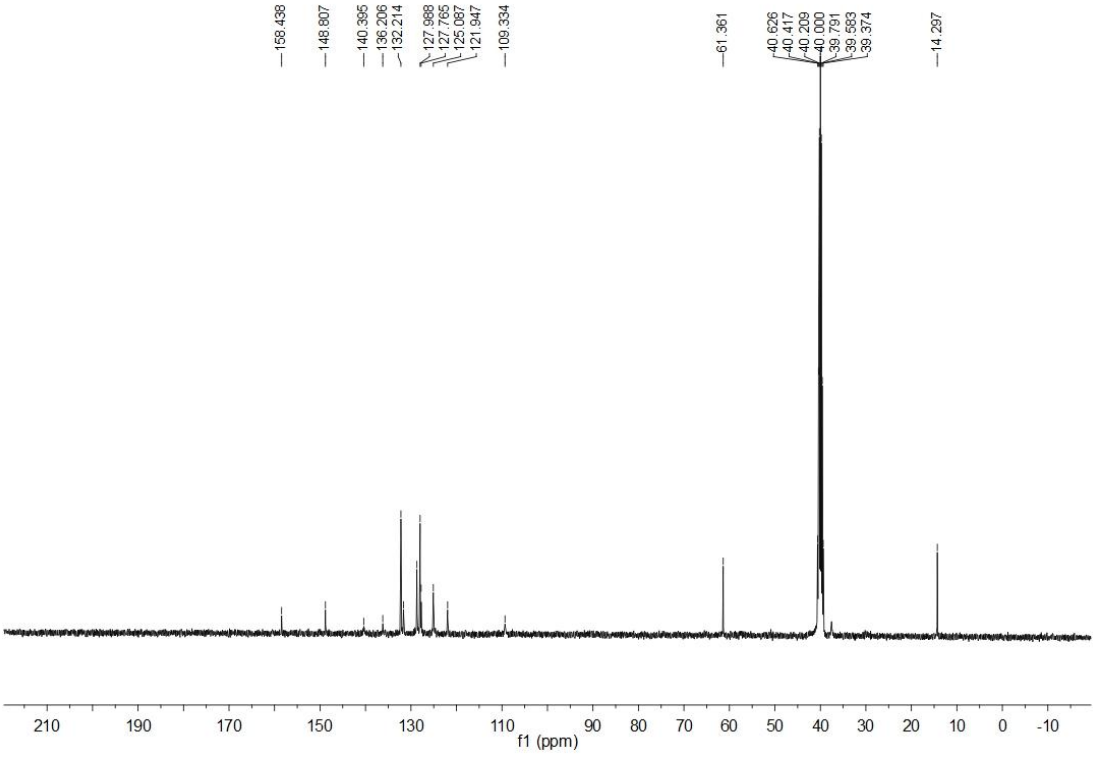

6.727
6.311
5.410
4.994
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

6:


H
N
N
N
COOEt
Br

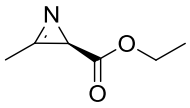

7.756
7.737
7.538
7.370
7.301
7.282
7.261
7.197
7.133
7.116
4.285
4.268
4.251
4.235
2.873
2.649
1.614
1.286
1.268
1.254
0.000

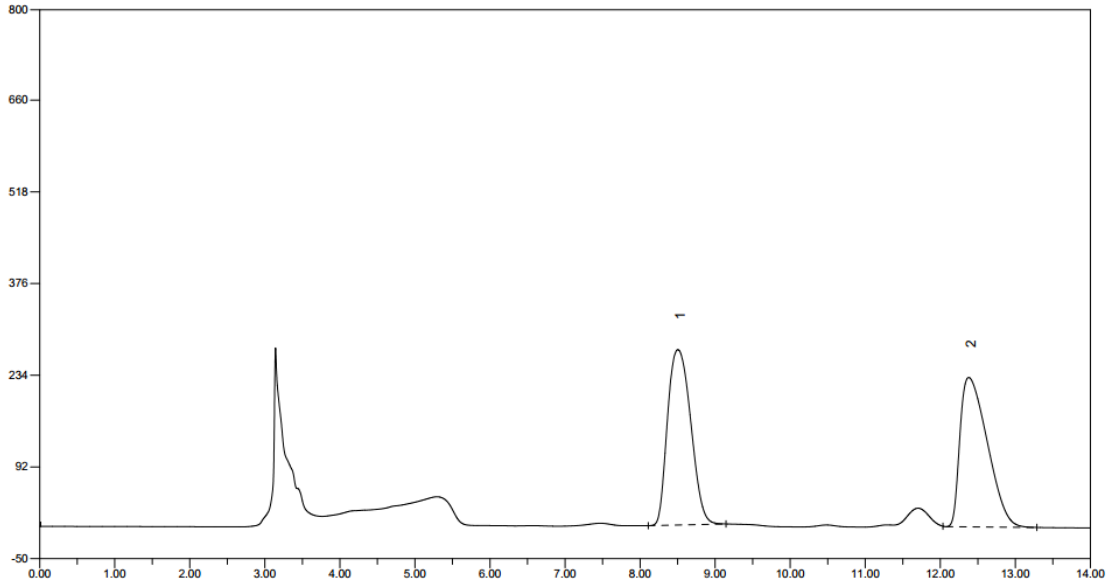

1.00
1.03
1.46
0.45
0.84
0.90
0.55
0.50
0.55
1.72
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


158.438
148.807
140.395
136.206
132.214
127.988
127.765
125.087
121.947
109.334
61.361
40.626
40.417
40.209
40.000
39.791
39.583
39.374
14.297
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

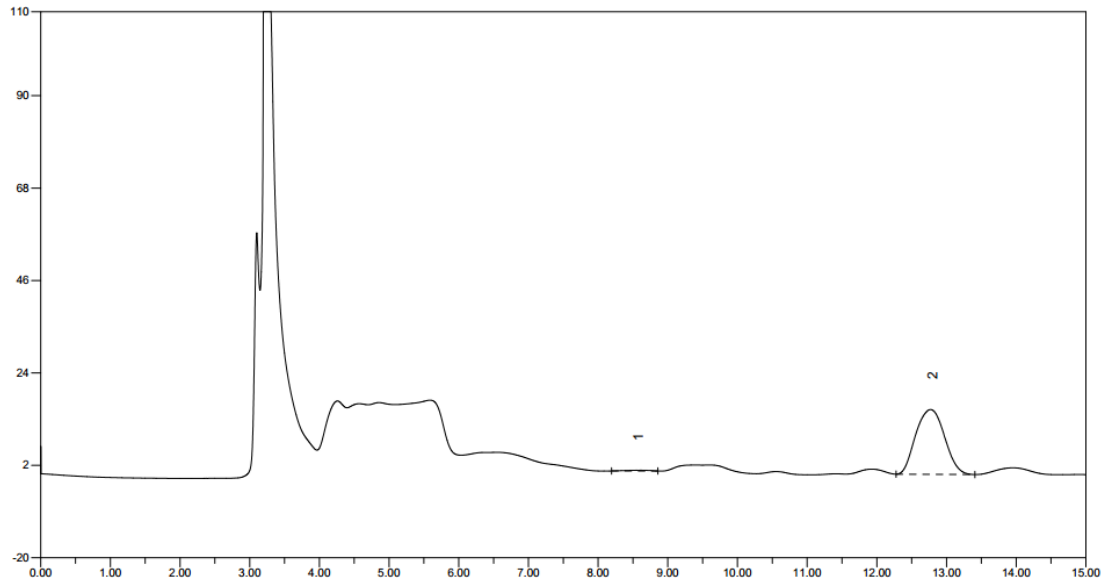
HPLC spectra of racemic and enantioenriched products:

2a:



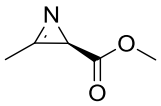


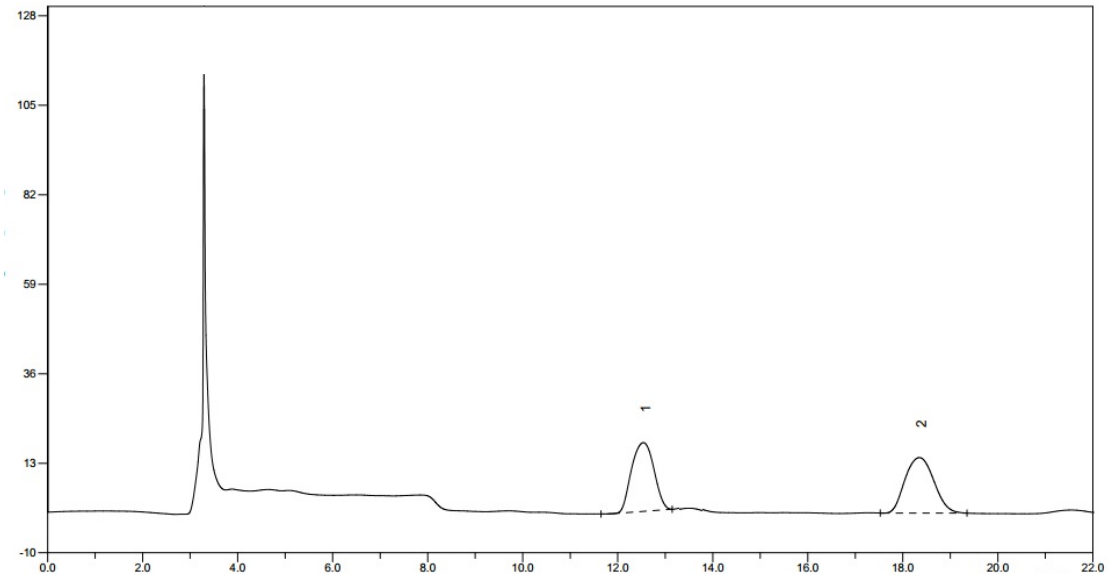
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	8.50333	271.59	54.04282	5839.07	50.0657
2	12.37917	230.95	45.95718	5823.74	49.9343



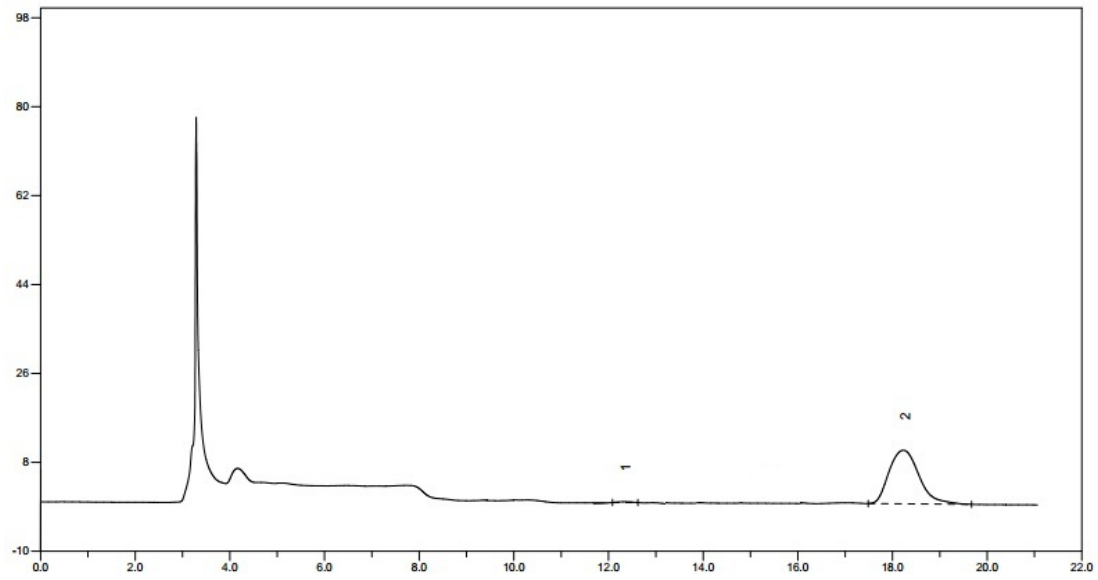
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	8.54583	0.17	1.08655	4.14	0.9266
2	12.77083	15.41	98.91345	442.82	99.0734

2b:



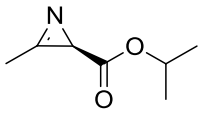


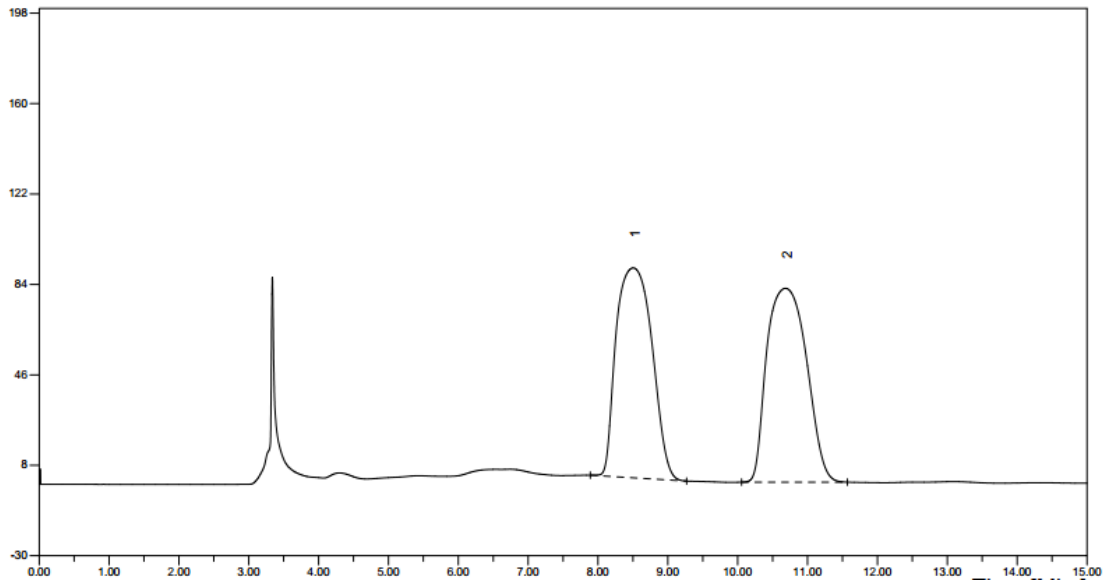
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	12.54000	17.62	55.27070	574.67	48.8665
2	18.34500	14.26	44.72930	601.33	51.1335



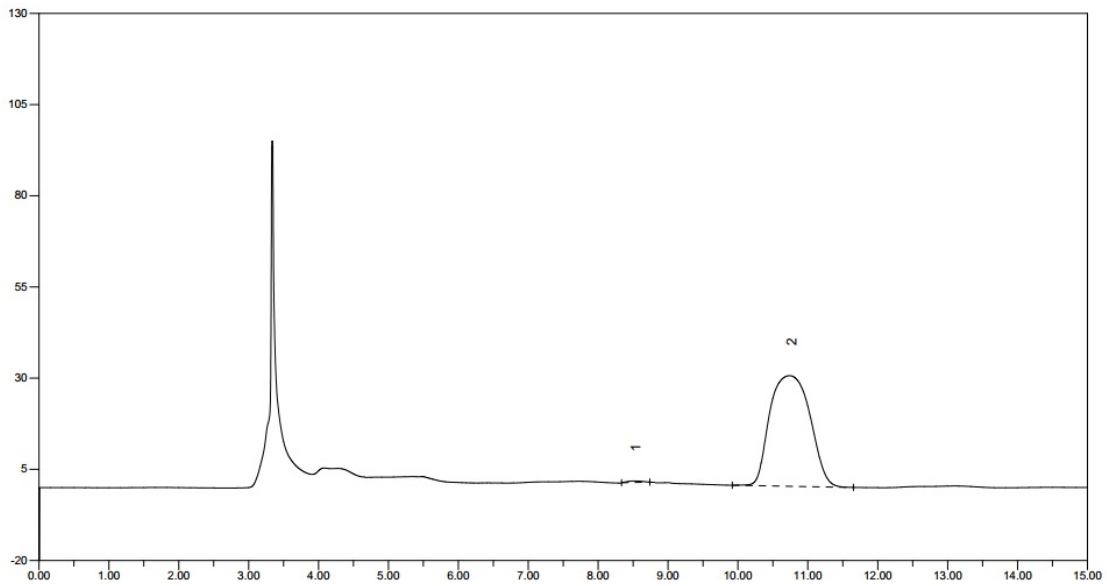
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	12.38665	0.15	1.38392	3.04	0.6345
2	18.22917	10.86	98.61608	476.24	99.3655

2c:



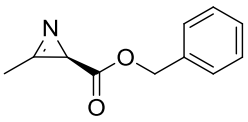


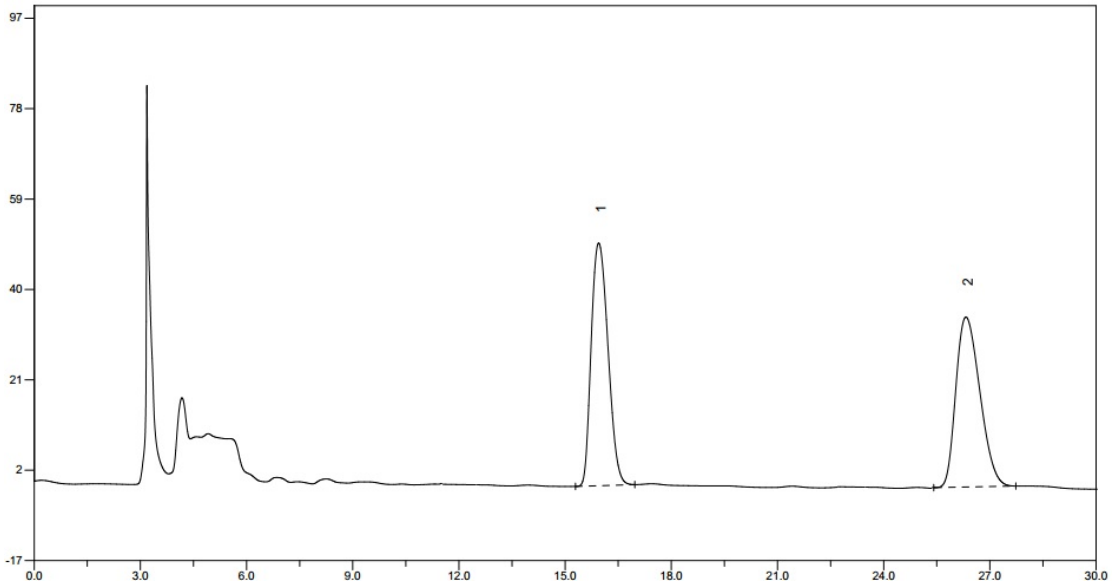
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	8.50333	88.18	51.98659	3154.66	49.4276
2	10.68167	81.44	48.01341	3227.73	50.5724



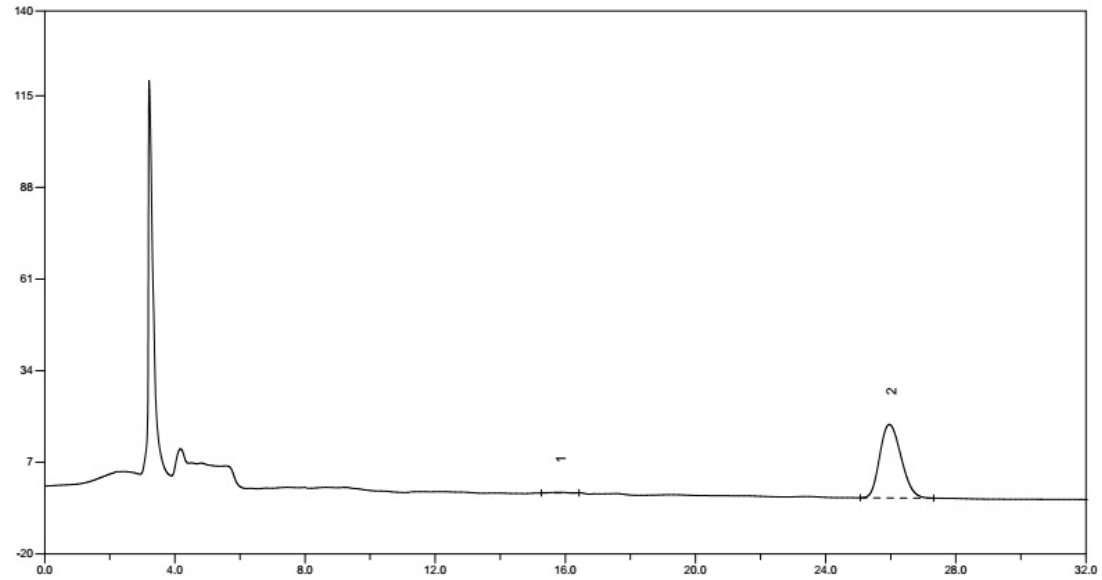
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	8.51254	0.39	1.27614	5.81	0.4766
2	10.73833	30.31	98.72386	1213.80	99.5234

2d:



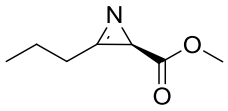


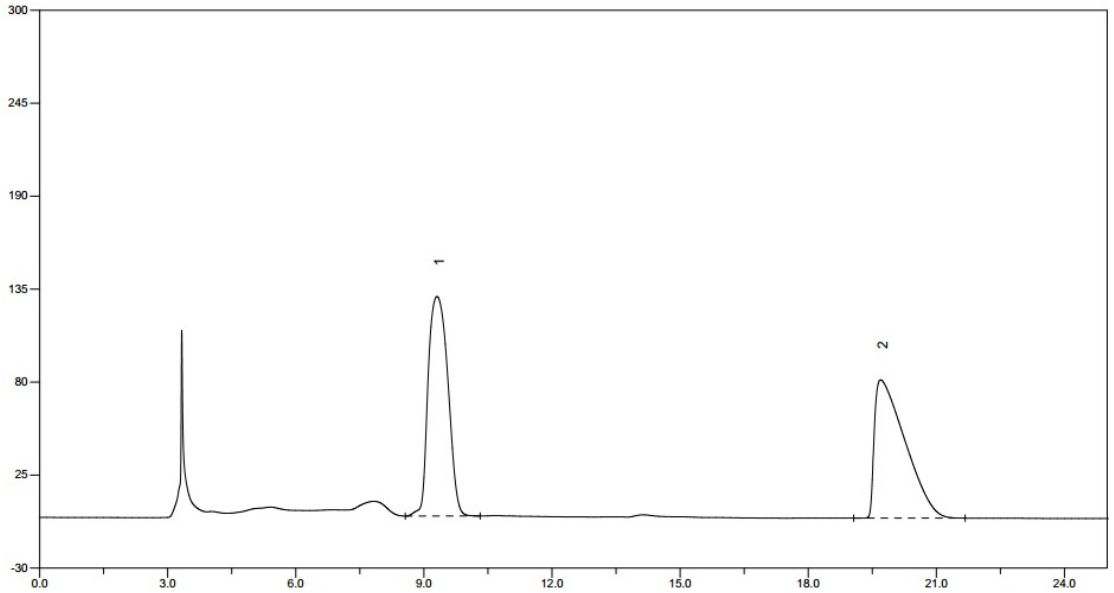
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	15.94917	51.04	58.80747	1679.73	49.9390
2	26.32333	35.75	41.19253	1683.84	50.0610



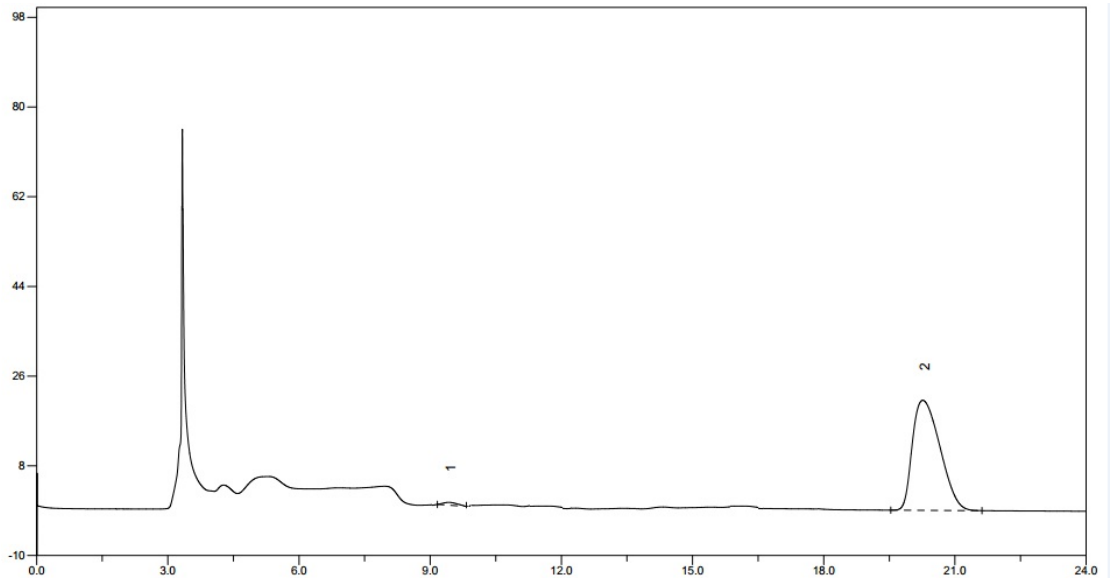
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	15.92354	0.16	0.75336	4.98	0.5035
2	25.95750	21.67	99.24664	983.43	99.4965

2e:



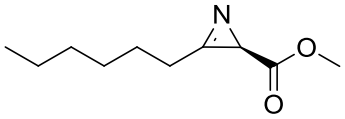


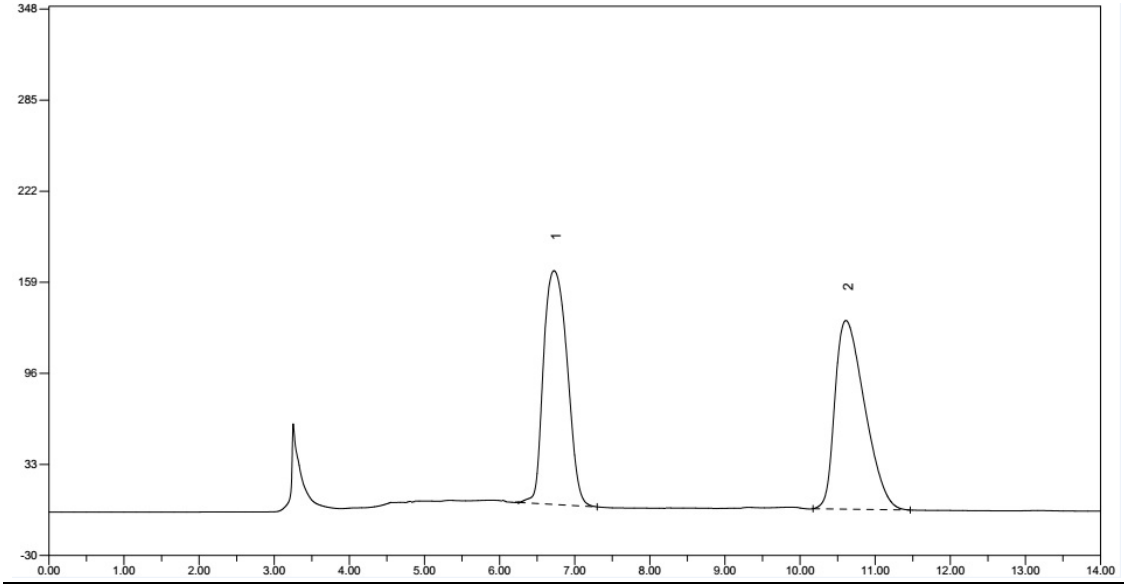
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	9.30583	129.85	61.34985	4176.49	50.6608
2	19.69667	81.81	38.65015	4067.53	49.3392



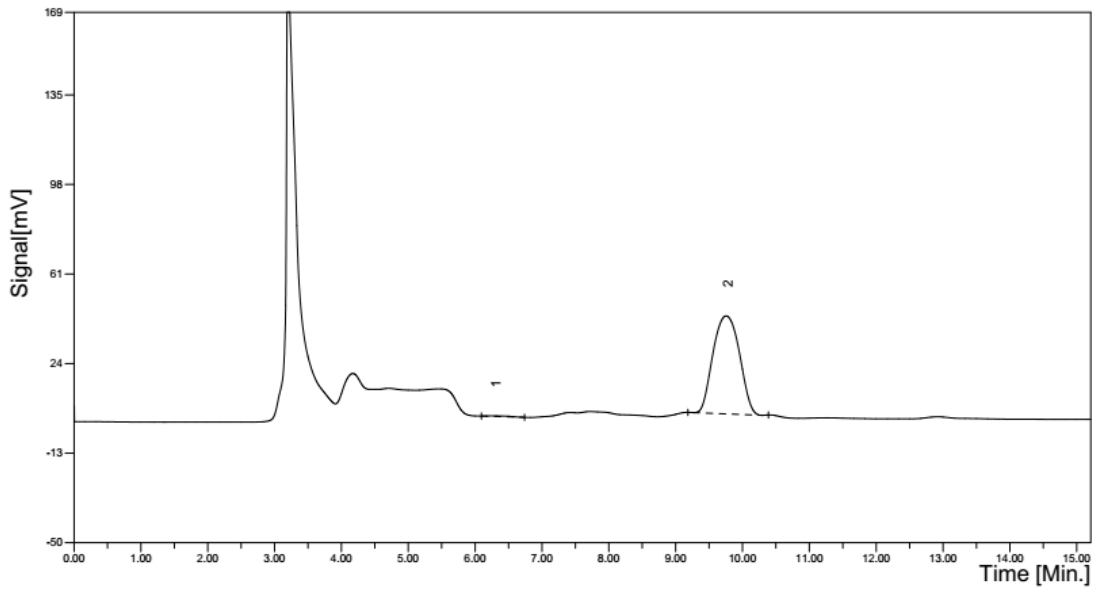
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	9.42833	0.58	2.53855	13.33	1.3582
2	20.26500	22.09	97.46145	967.98	98.6418

2g:



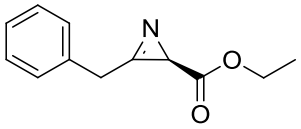


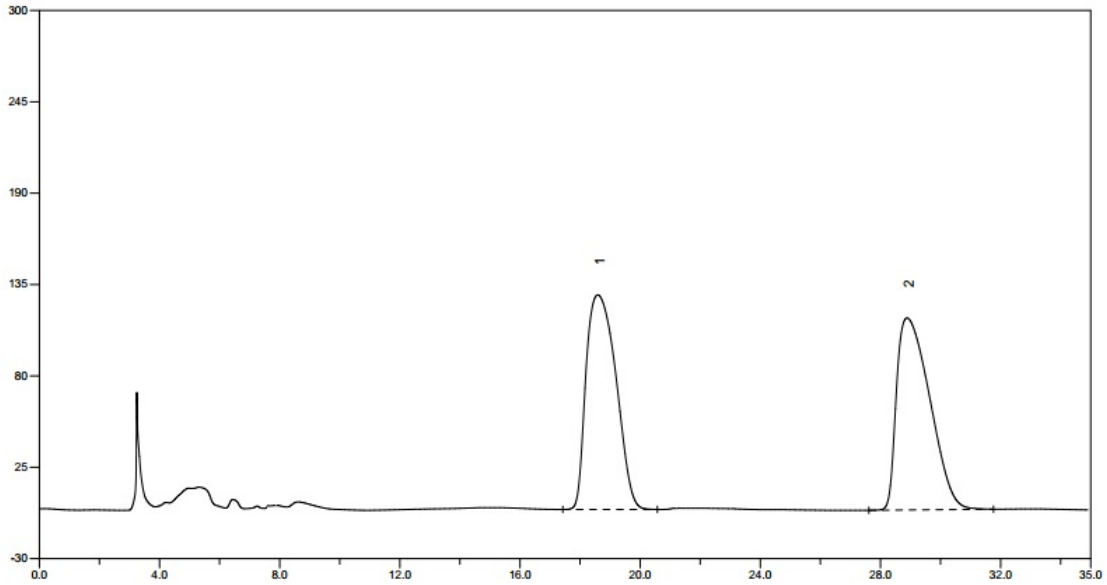
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	6.72500	161.76	55.34529	3545.74	49.6431
2	10.61083	130.51	44.65471	3596.73	50.3569



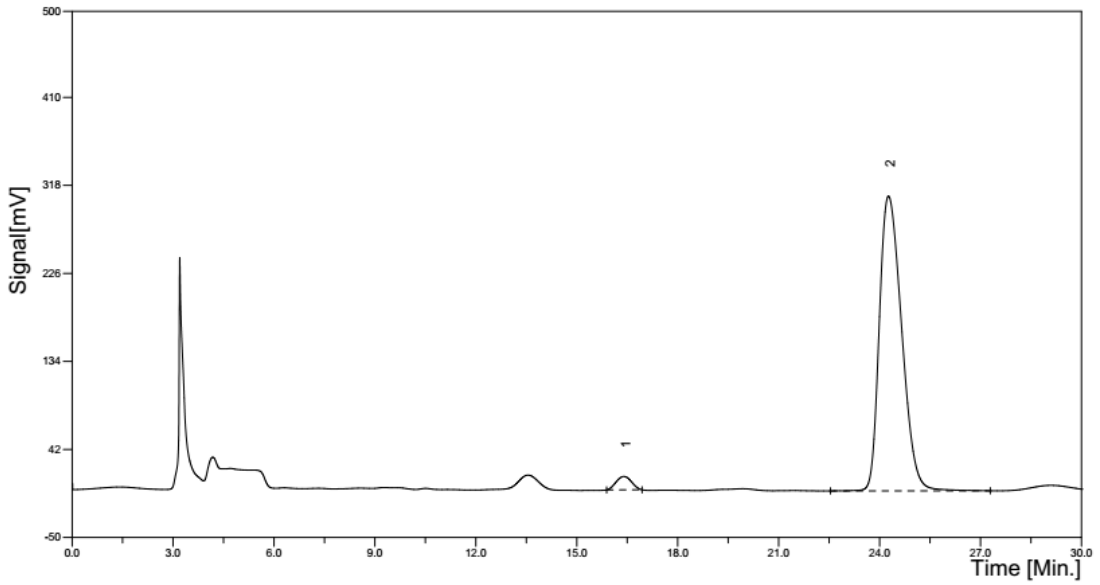
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	6.28500	0.23	0.55490	6.03	0.5418
2	9.75417	40.36	99.44510	1107.22	99.4582

2i:



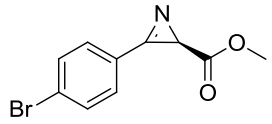


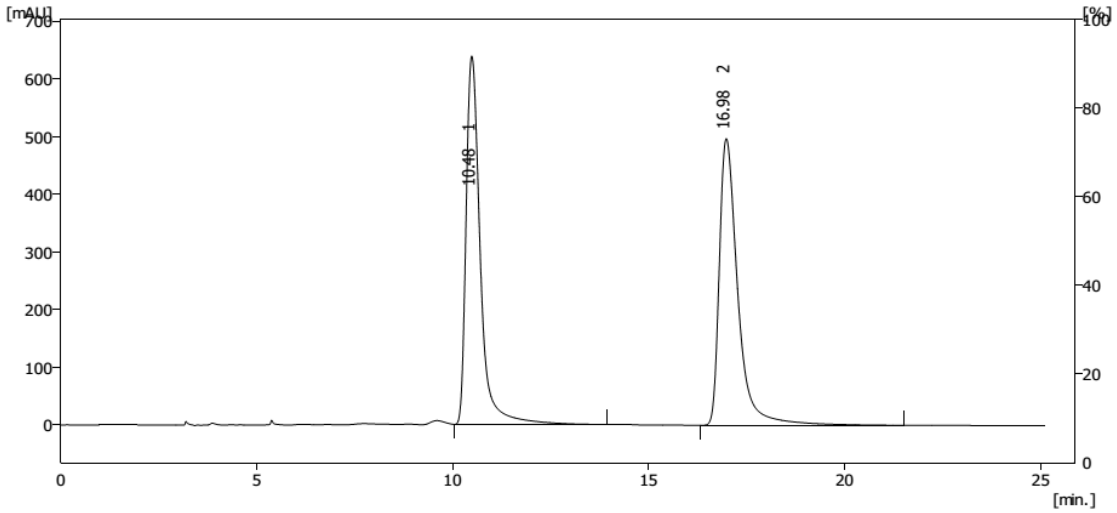
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	18.59167	129.18	52.78138	8936.56	50.1498
2	28.88667	115.57	47.21862	8883.17	49.8502



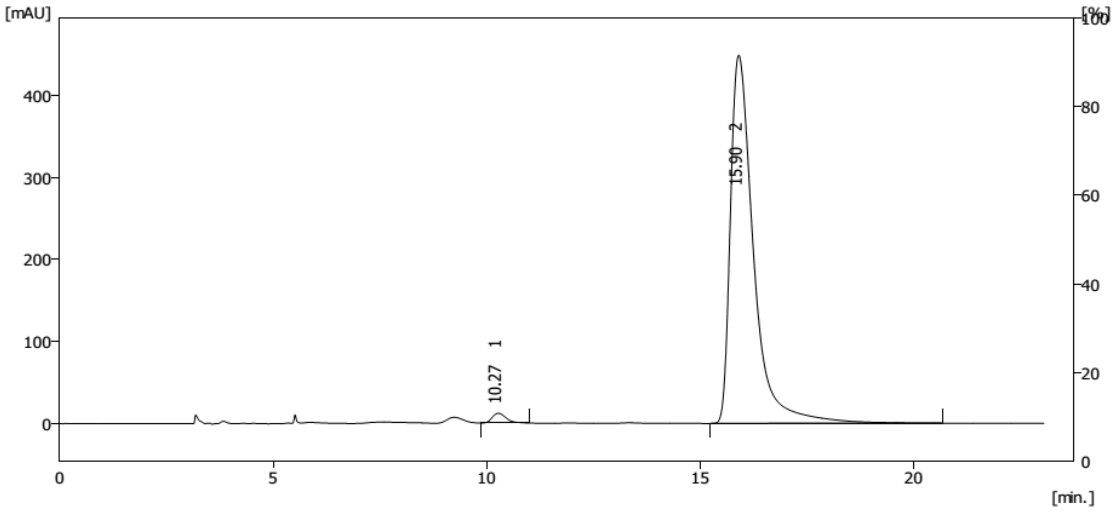
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	16.39917	13.99	4.34273	443.58	3.0337
2	24.26500	308.21	95.65727	14178.15	96.9663

2k:



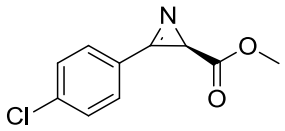


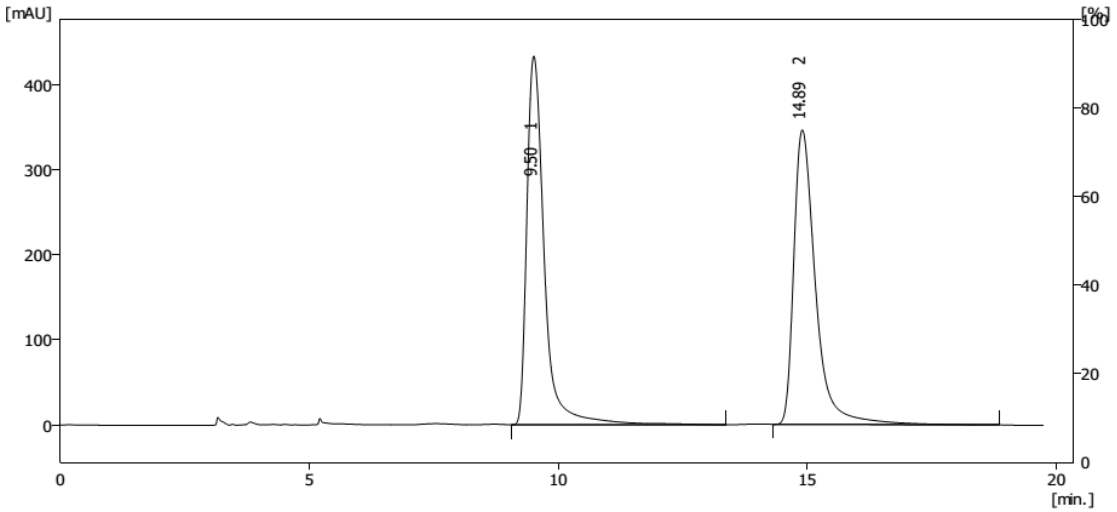
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	10.484	638.436	56.2	16068.870	49.6562
2	16.977	496.953	43.8	16291.368	50.3438



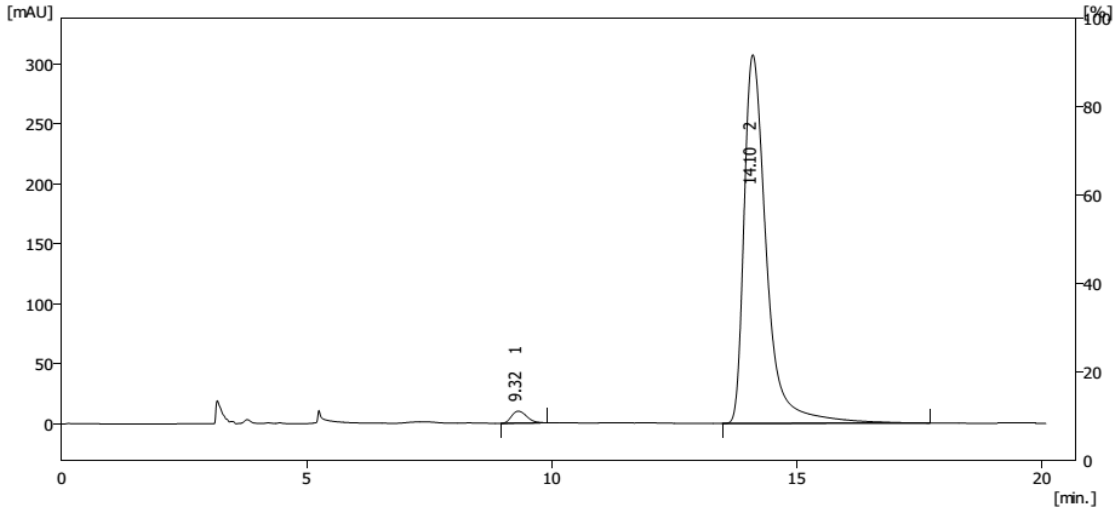
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	10.272	11.856	2.6	270.250	1.5708
2	15.902	448.647	97.4	16934.868	98.4292

2l:



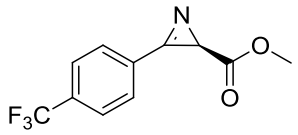


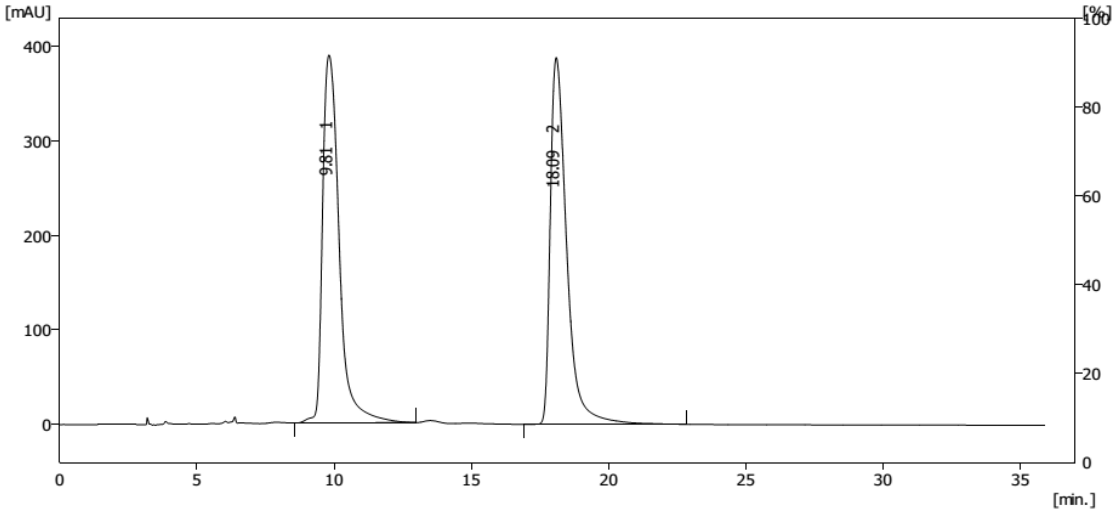
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	9.504	433.082	55.6	10559.807	50.1620
2	14.894	346.090	44.4	10491.595	49.8380



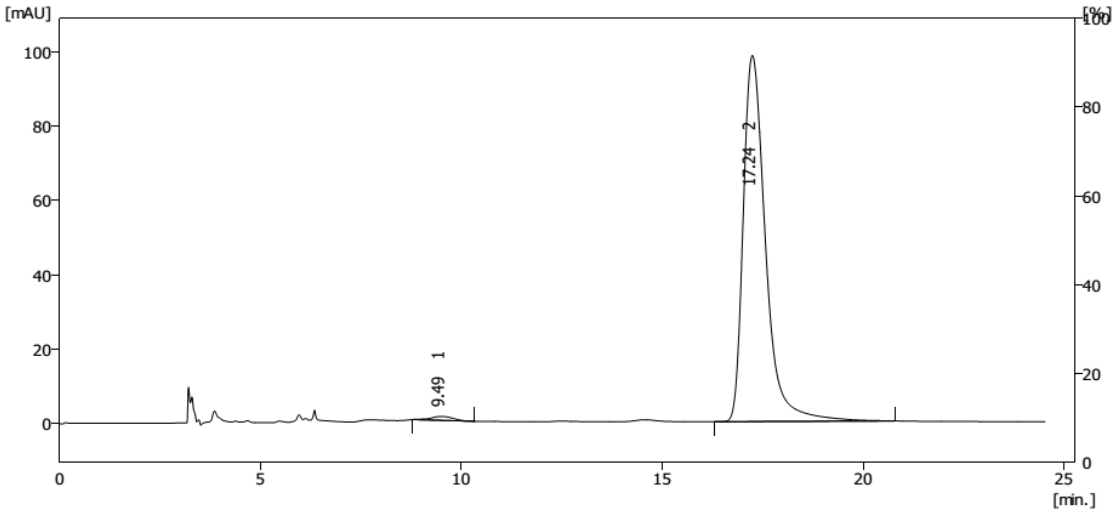
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	9.316	9.980	3.1	216.453	2.1718
2	14.100	307.047	96.9	9750.201	97.8282

2n:



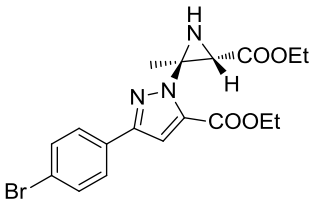


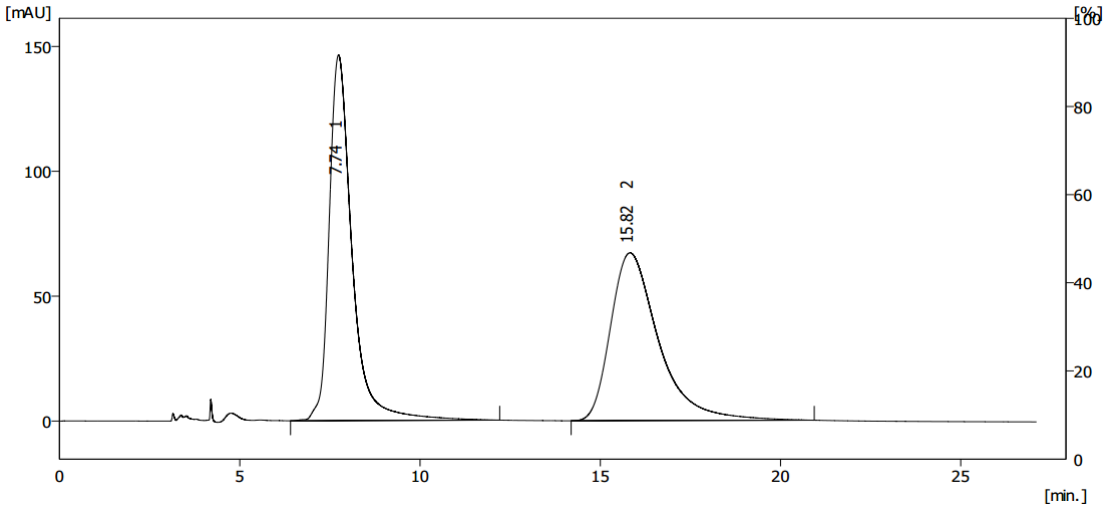
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	9.811	388.482	50.1	16301.858	50.3592
2	18.087	387.509	49.9	16069.279	49.6408



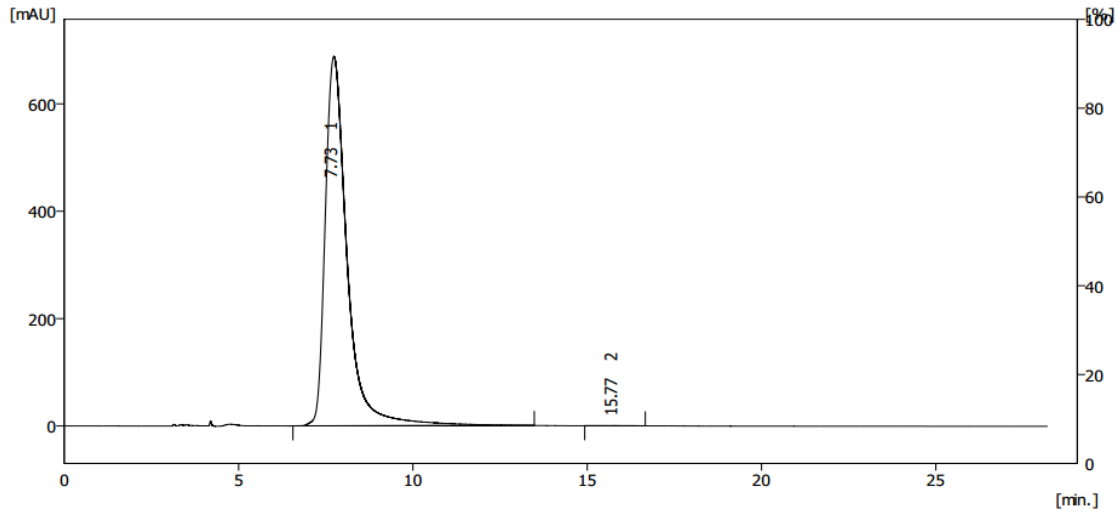
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	9.492	1.055	1.1	40.952	1.0676
2	17.240	98.457	98.9	3795.001	98.9324

3a:



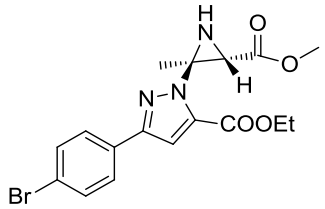


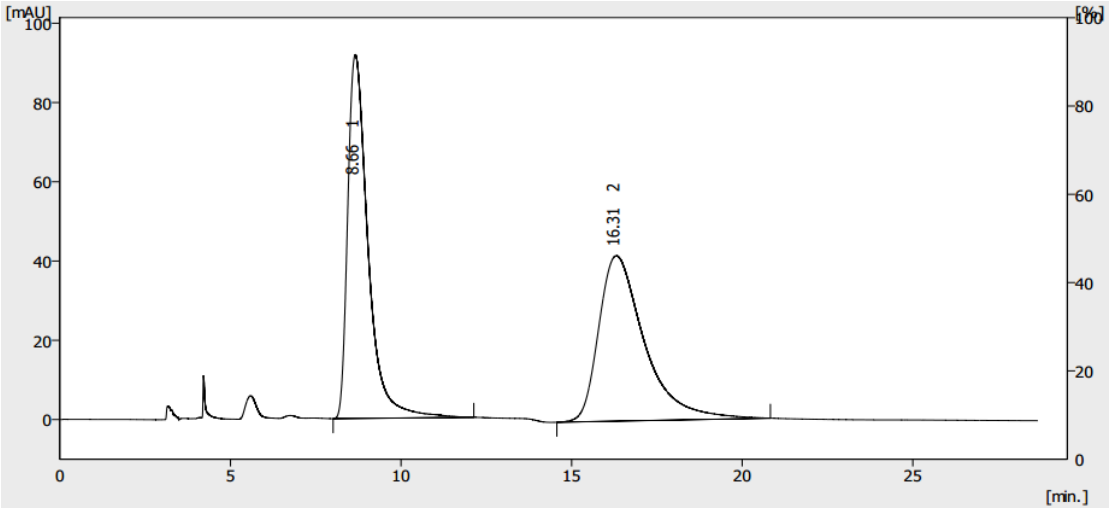
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	7.739	146.395	68.5	6467.712	50.9820
2	15.823	67.211	31.5	6218.546	49.0180



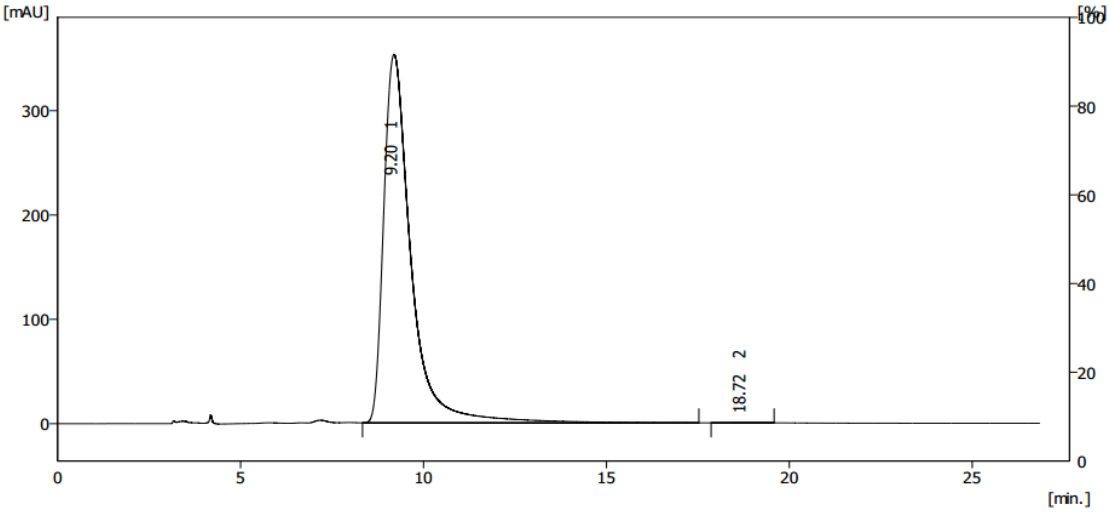
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	7.734	687.979	100.0	29925.474	99.9625
2	15.770	0.188	0.0	11.221	0.0375

3b:



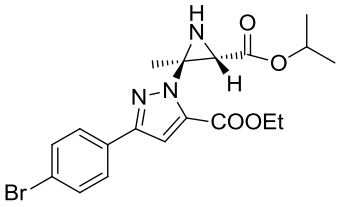


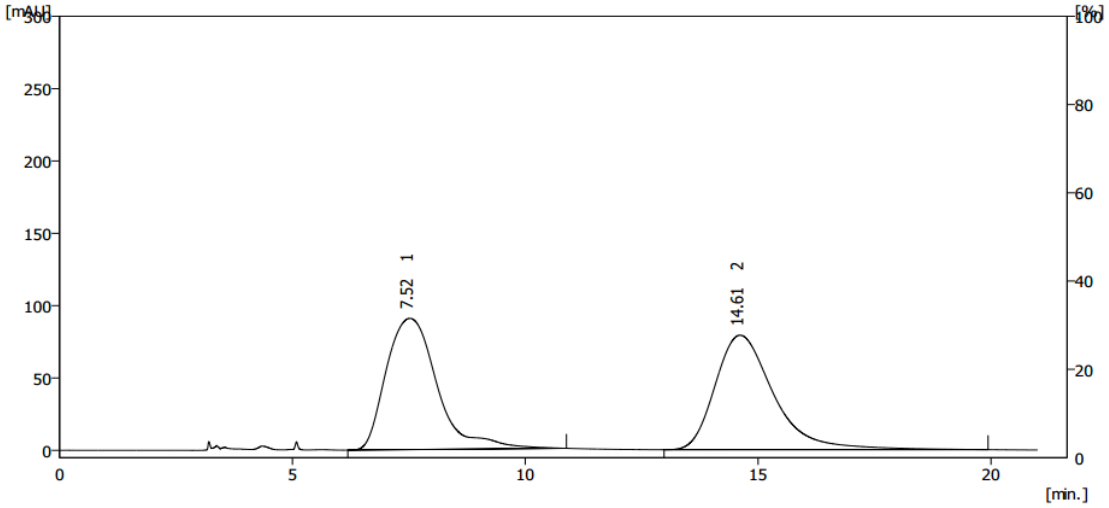
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	8.661	91.854	68.8	3793.823	49.3700
2	16.309	41.745	31.2	3890.643	50.6300



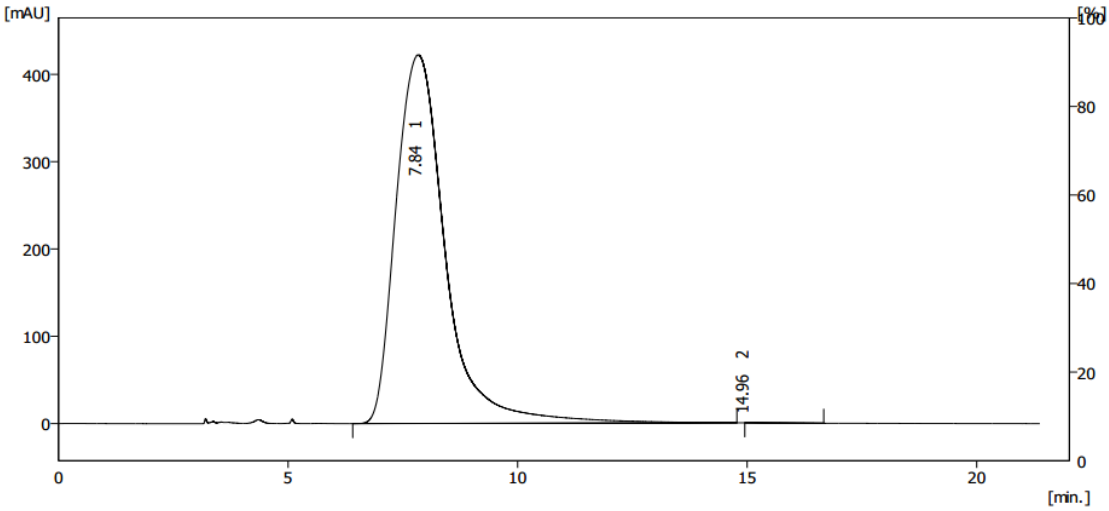
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	9.196	353.210	100.0	18285.441	99.9450
2	18.715	0.161	0.0	10.055	0.0550

3c:



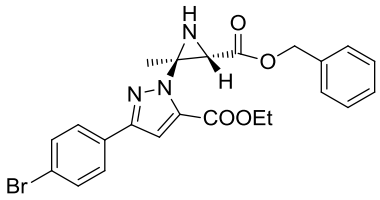


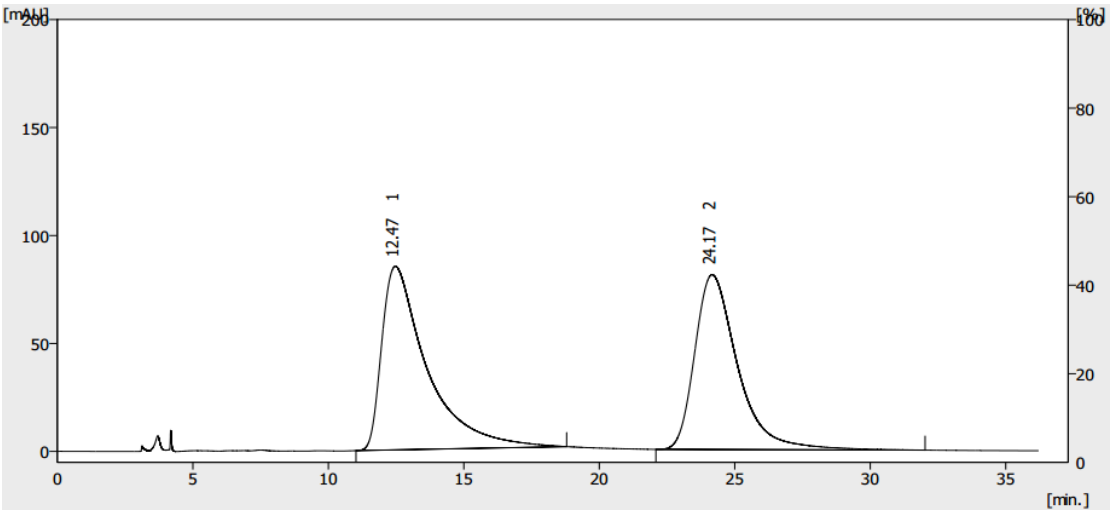
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	7.521	90.745	53.4	6924.902	50.0414
2	14.613	79.164	46.6	6913.450	49.9586



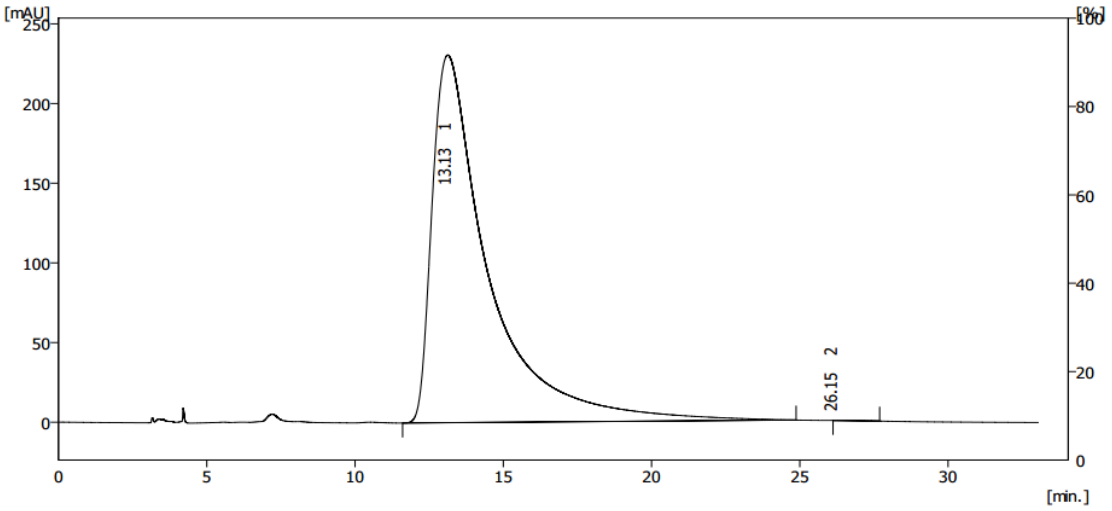
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	7.835	422.273	100.0	31608.543	99.9820
2	14.958	0.004	0.0	5.687	0.0180

3d:



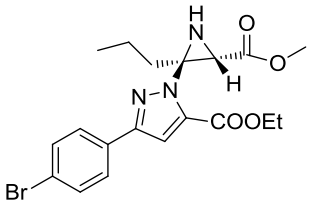


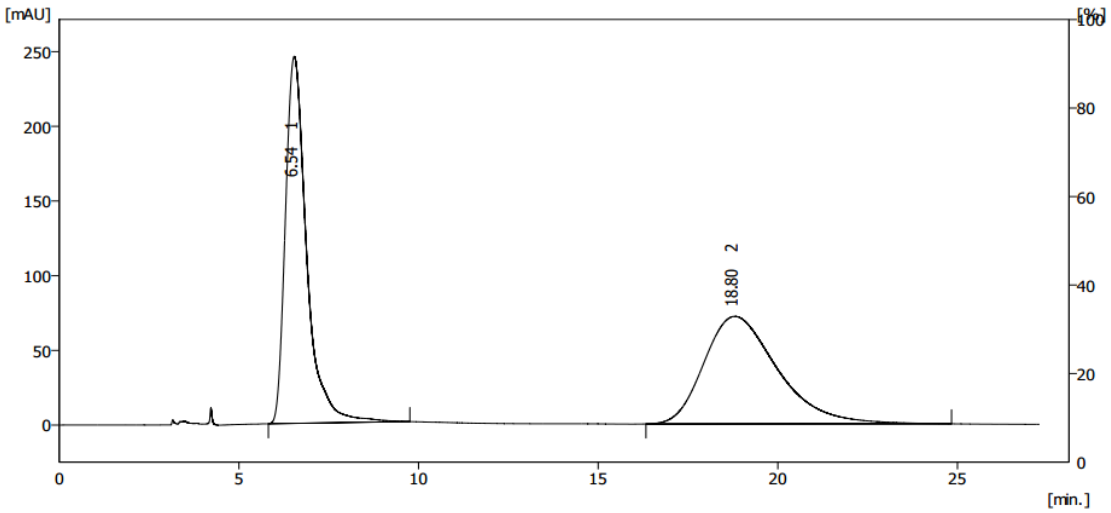
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	12.473	85.018	51.2	9869.518	52.5921
2	24.168	80.979	48.8	8896.633	47.4079



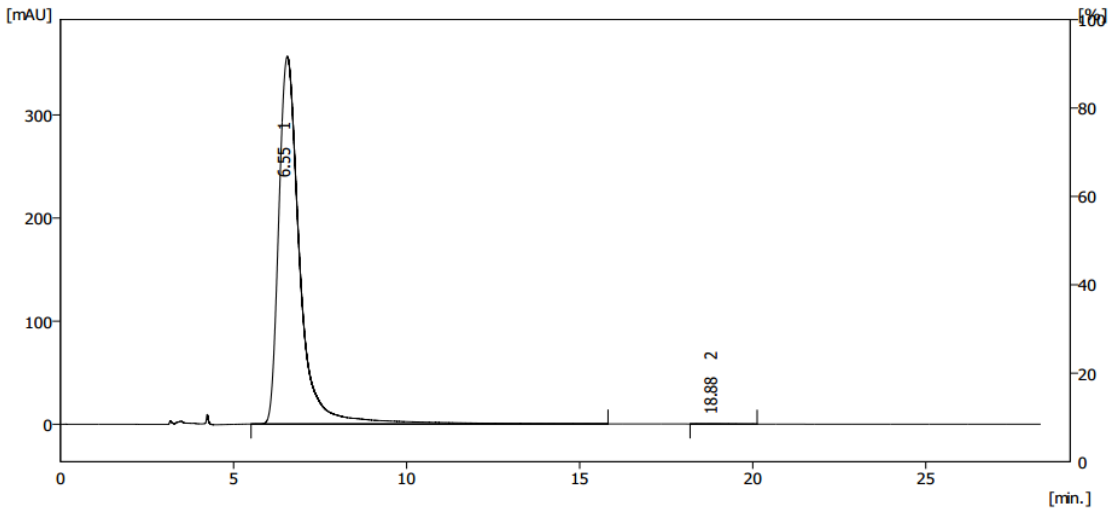
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	13.128	230.794	100.0	30472.473	99.9830
2	26.153	0.010	0.0	5.174	0.0170

3e:



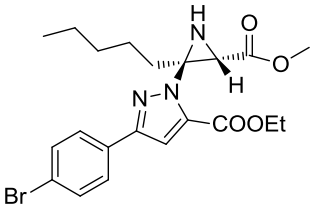


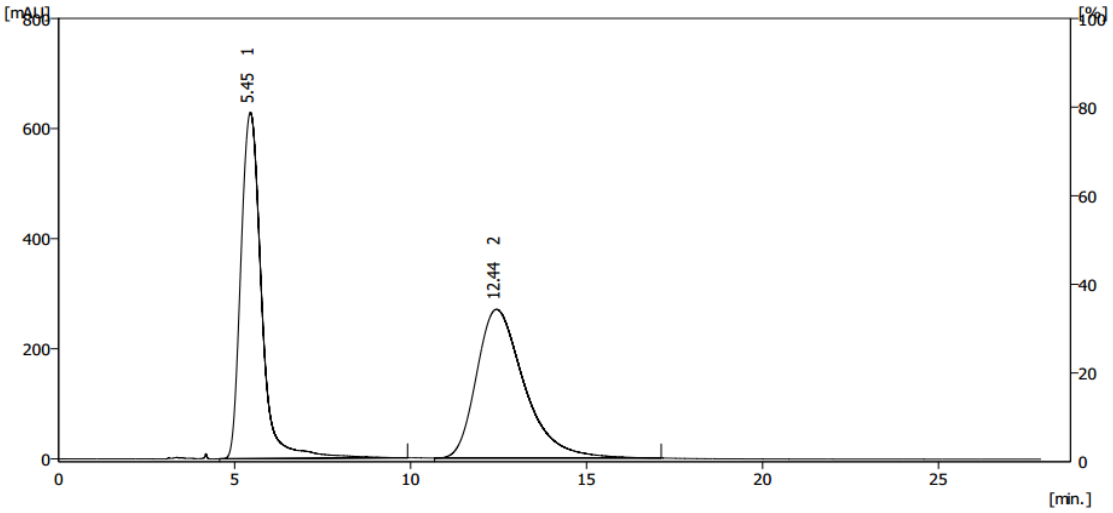
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	6.540	245.709	77.3	10070.872	49.5698
2	18.801	71.997	22.7	10245.657	50.4302



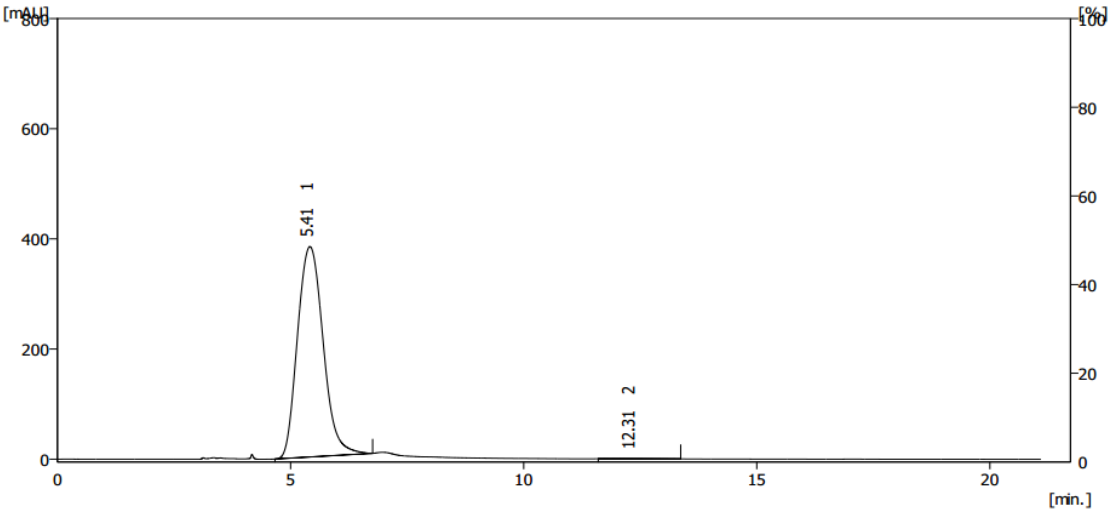
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	6.553	356.456	100.0	15064.703	99.9514
2	18.877	0.149	0.0	7.324	0.0486

3f:



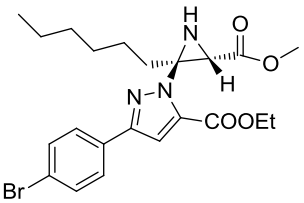


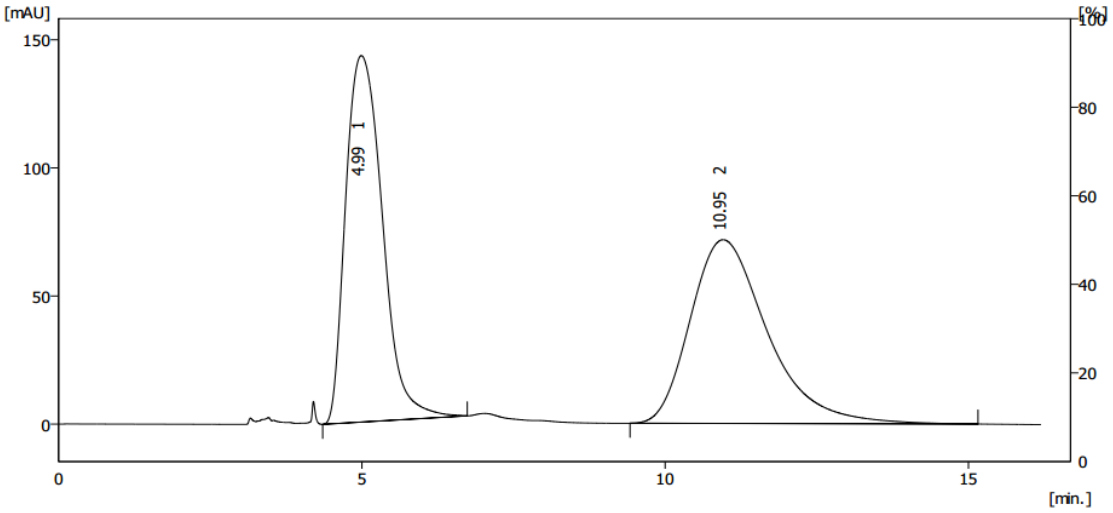
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	5.447	628.695	69.9	25575.661	50.1330
2	12.441	270.294	30.1	25439.955	49.8670



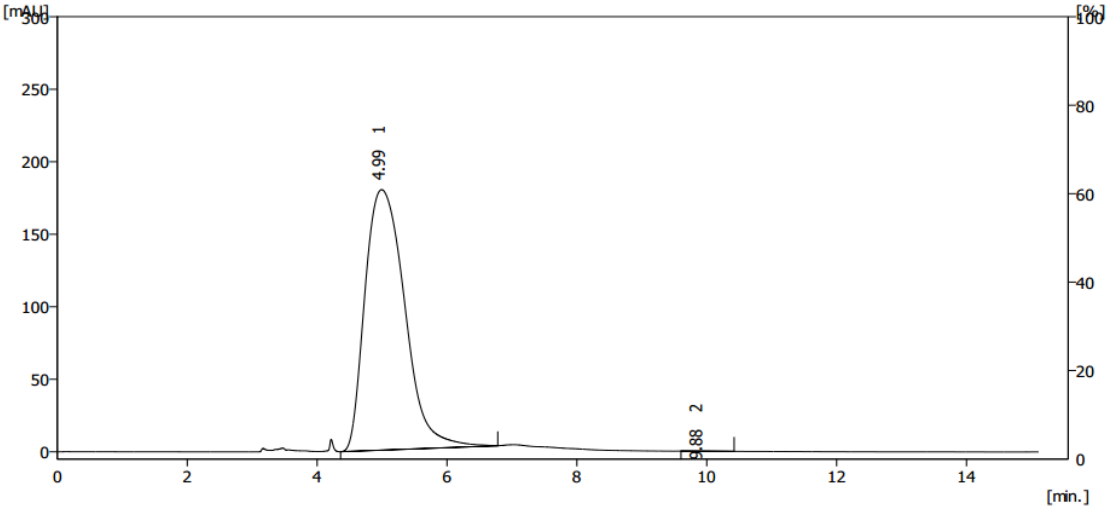
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	5.414	382.084	99.9	14621.391	99.7845
2	12.313	0.509	0.1	31.582	0.2155

3g:



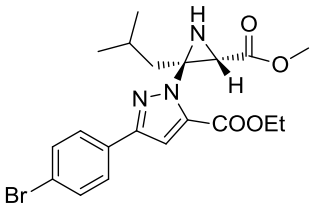


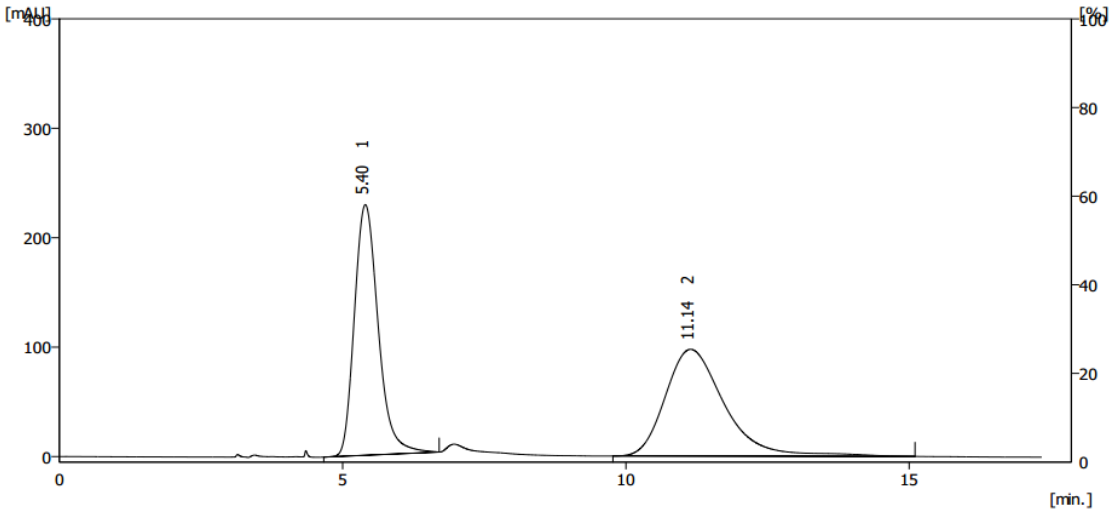
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	4.990	143.086	66.6	6040.164	48.7919
2	10.953	71.733	33.4	6339.281	51.2081



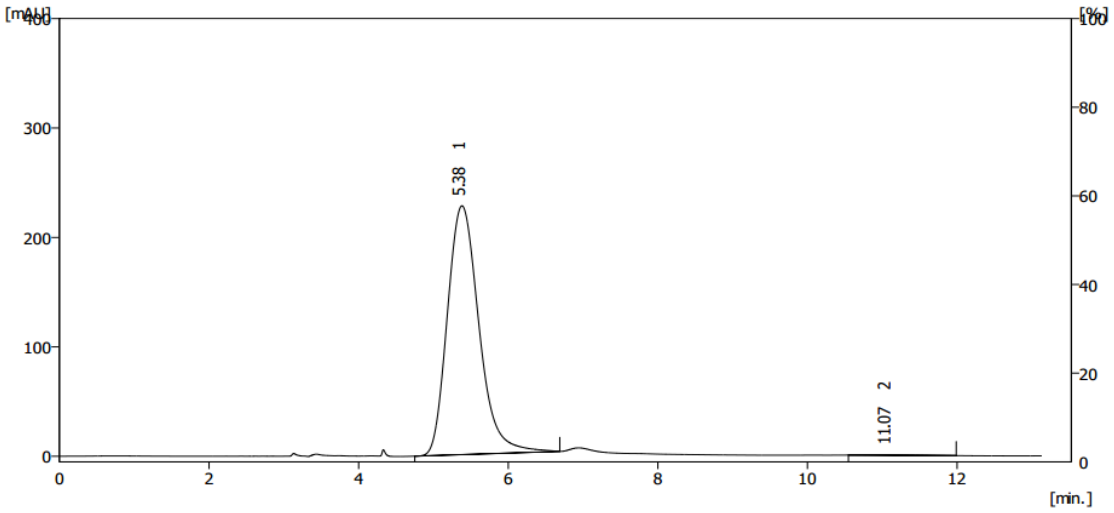
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	4.993	179.666	100.0	7660.563	99.9816
2	9.882	0.061	0.0	1.413	0.0184

3h:



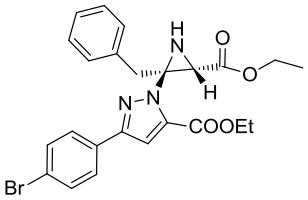


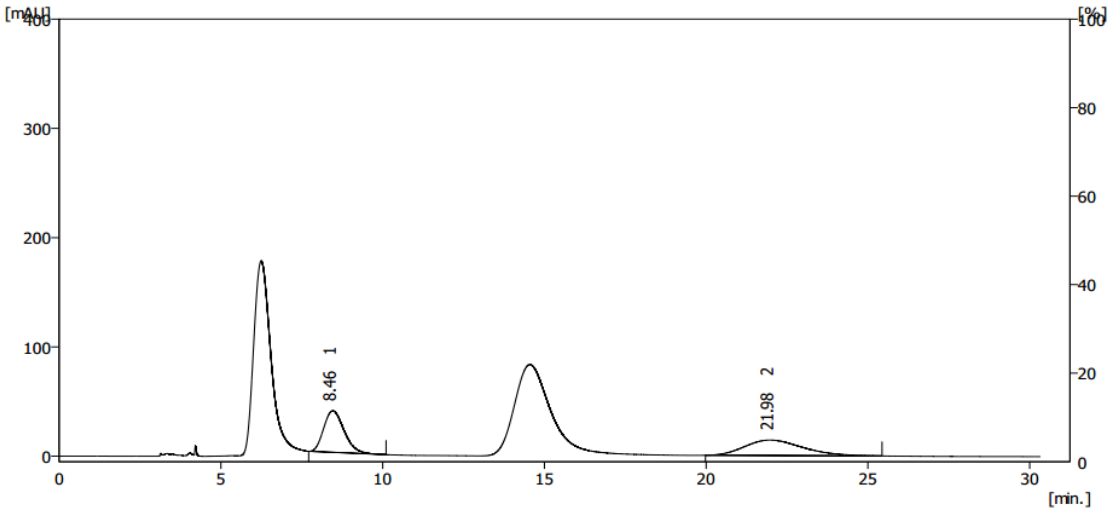
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	5.399	229.103	70.1	6685.291	48.5864
2	11.140	97.600	29.9	7074.308	51.4136



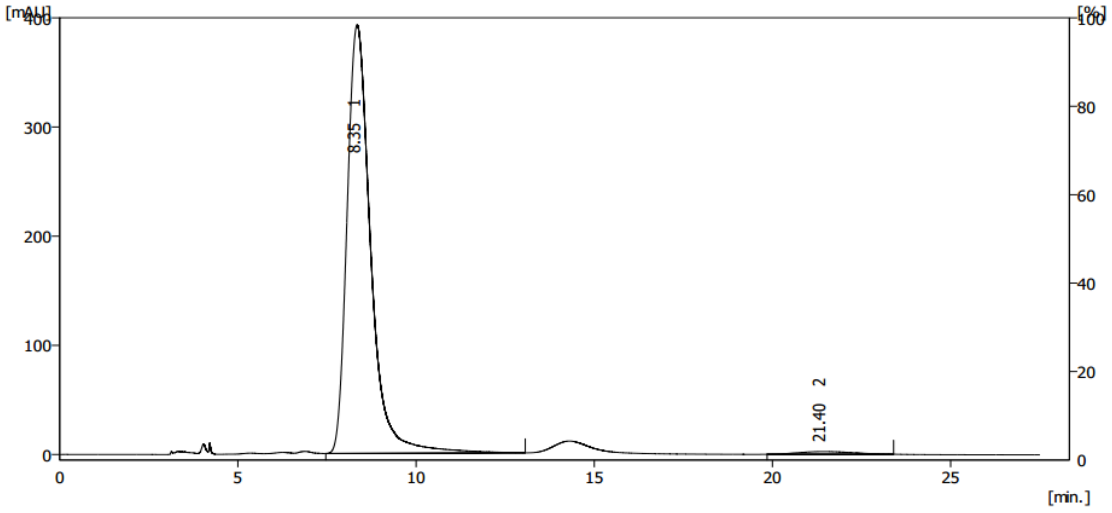
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	5.381	227.417	99.8	6673.644	99.6379
2	11.068	0.476	0.2	24.252	0.3621

3i:



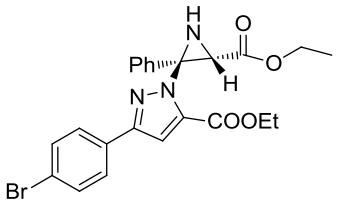


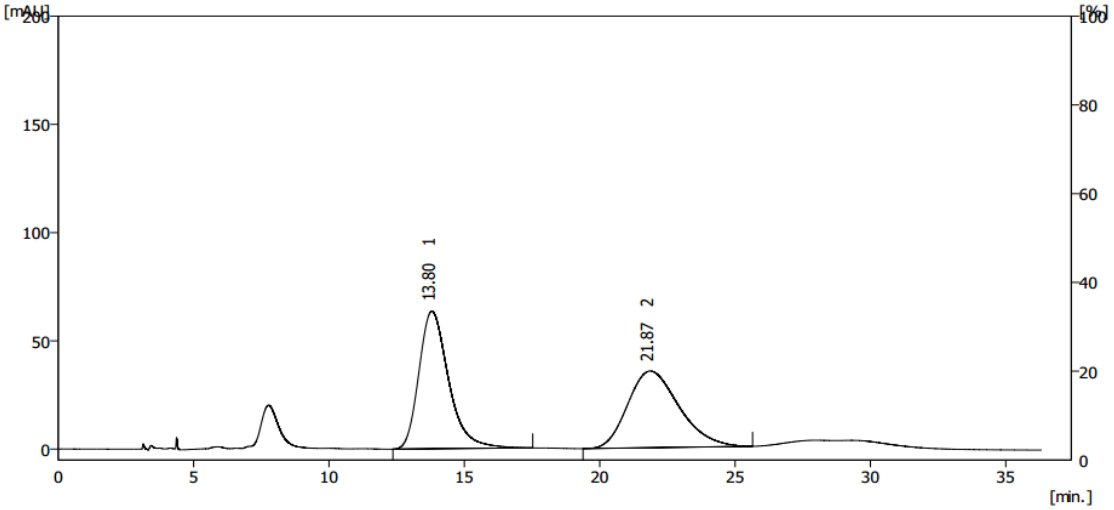
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	8.457	38.106	72.9	1667.094	48.5885
2	21.975	14.175	27.1	1763.954	51.4115



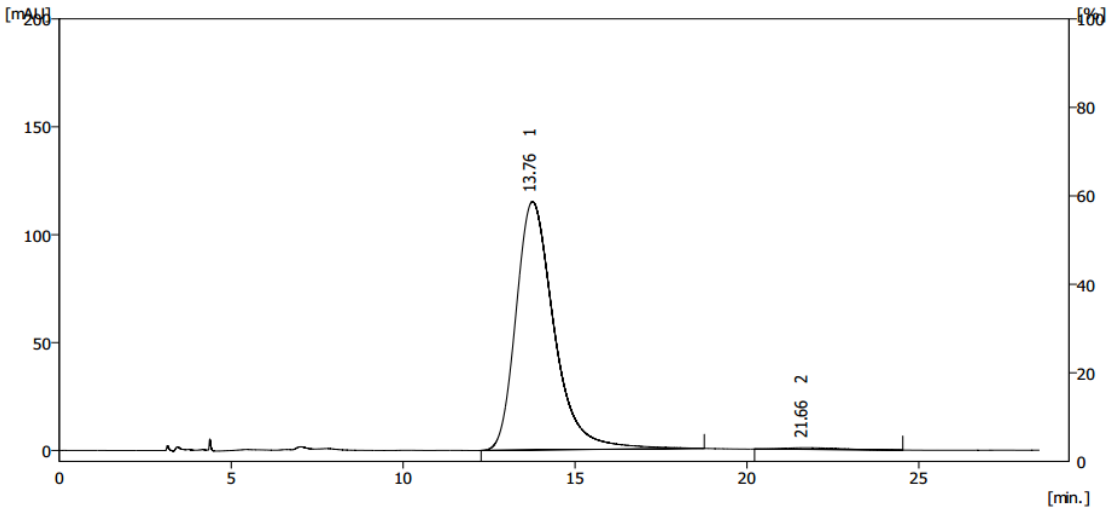
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	8.346	392.499	99.4	18033.560	98.5635
2	21.402	2.482	0.6	262.821	1.4365

3j:



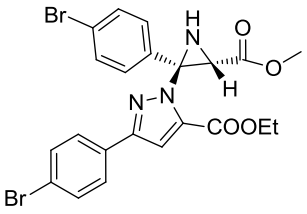


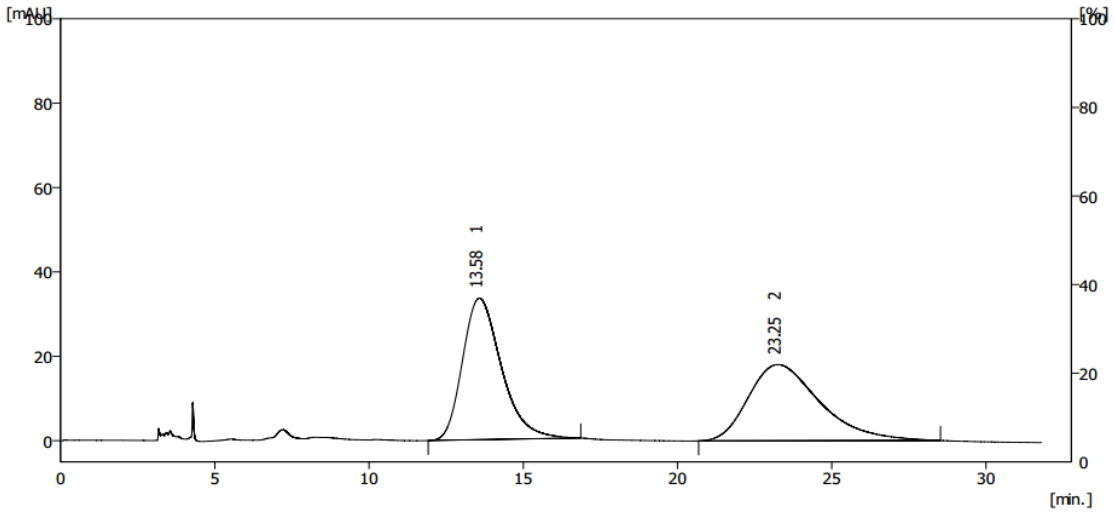
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	13.802	63.602	64.2	4845.514	50.9073
2	21.869	35.438	35.8	4672.788	49.0927



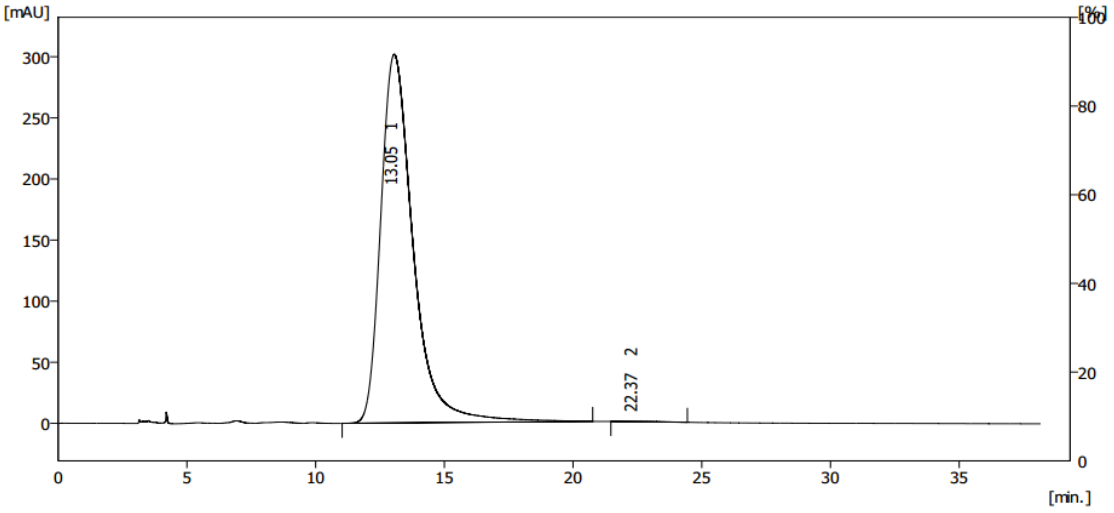
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	13.763	115.128	99.3	8852.730	99.0086
2	21.661	0.760	0.7	88.649	0.9914

3k:



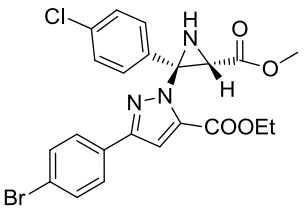


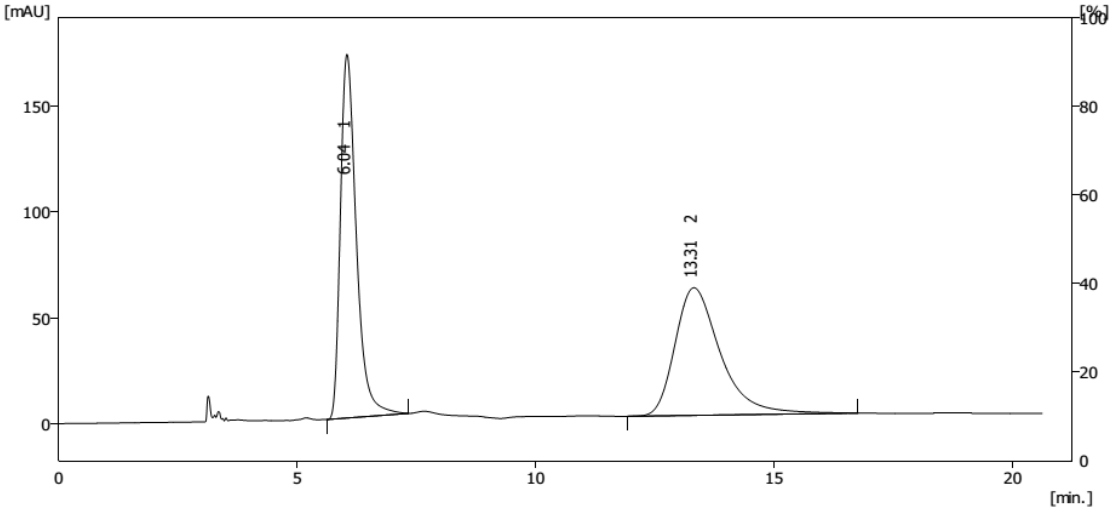
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	13.576	33.537	65.0	2931.443	50.2462
2	23.250	18.049	35.0	2902.710	49.7538



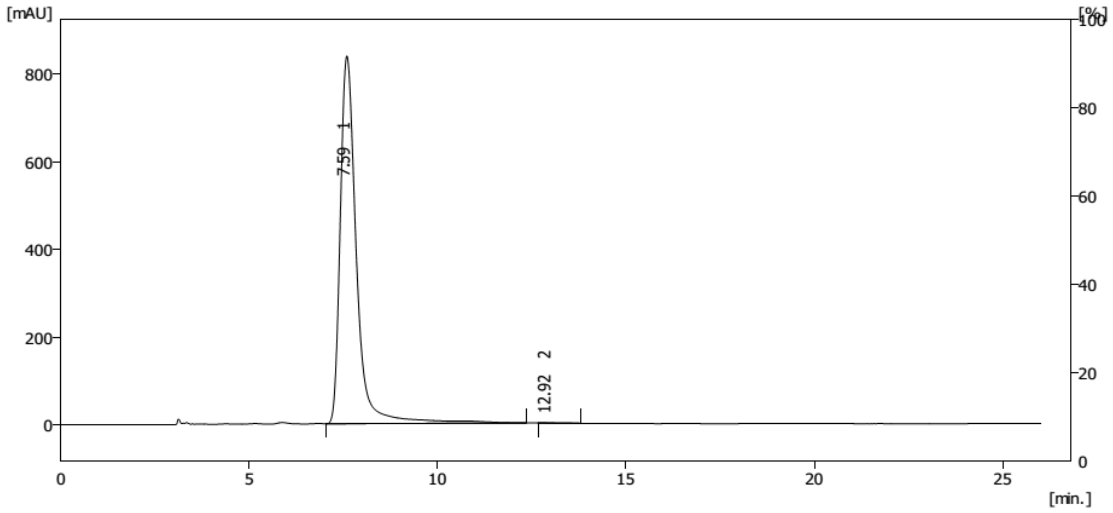
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	13.053	301.677	99.9	26432.245	99.8408
2	22.370	0.376	0.1	42.136	0.1592

3l:



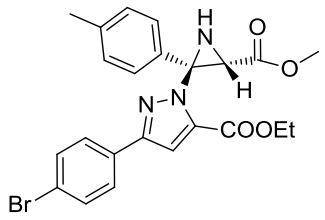


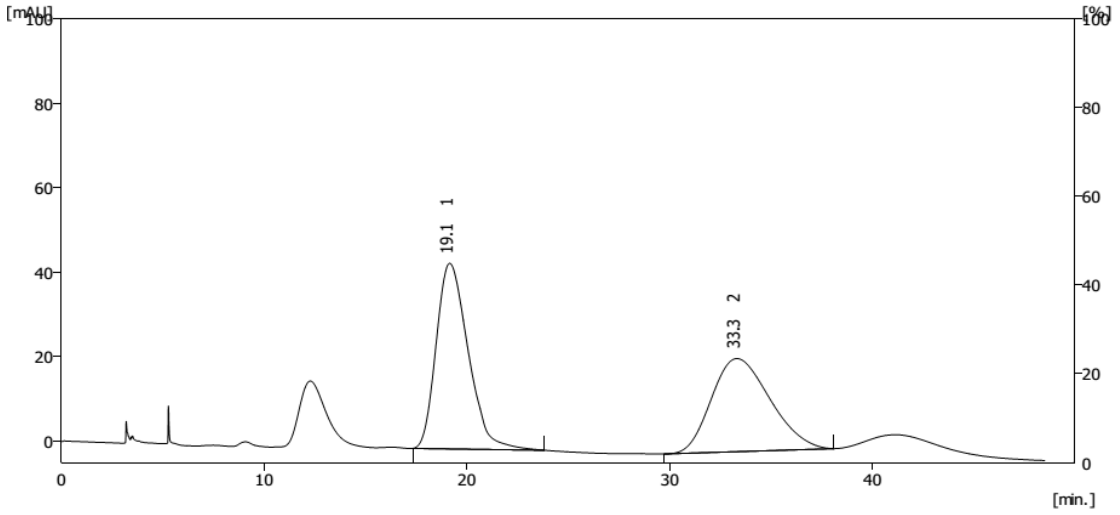
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	6.039	171.792	74.0	3985.619	49.9795
2	13.308	60.314	26.0	3988.888	50.0205



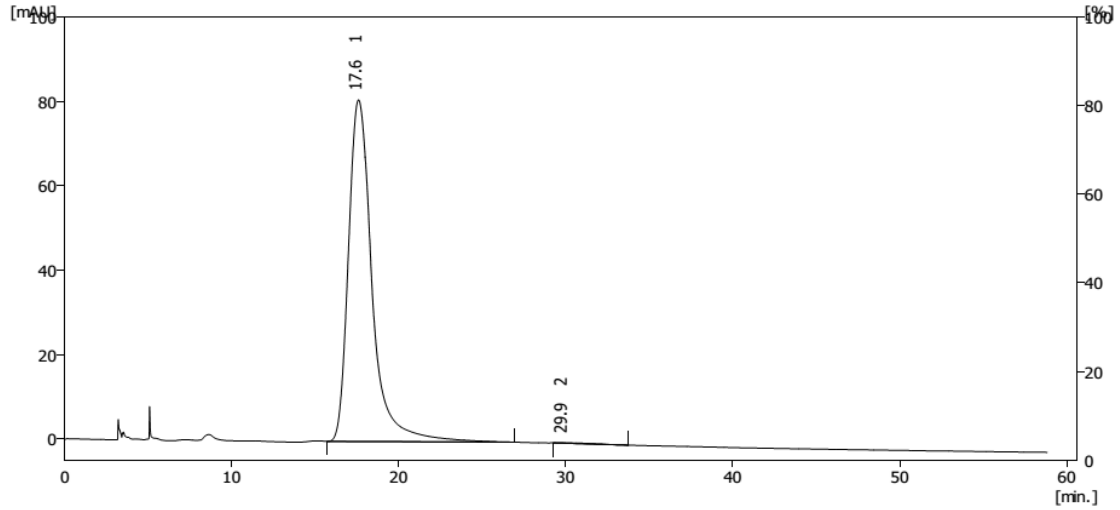
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	7.589	840.004	100.0	25126.172	99.9590
2	12.916	0.191	0.0	10.305	0.0410

3m:



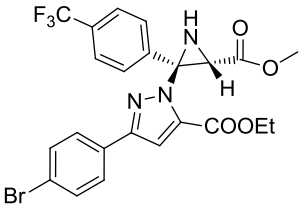


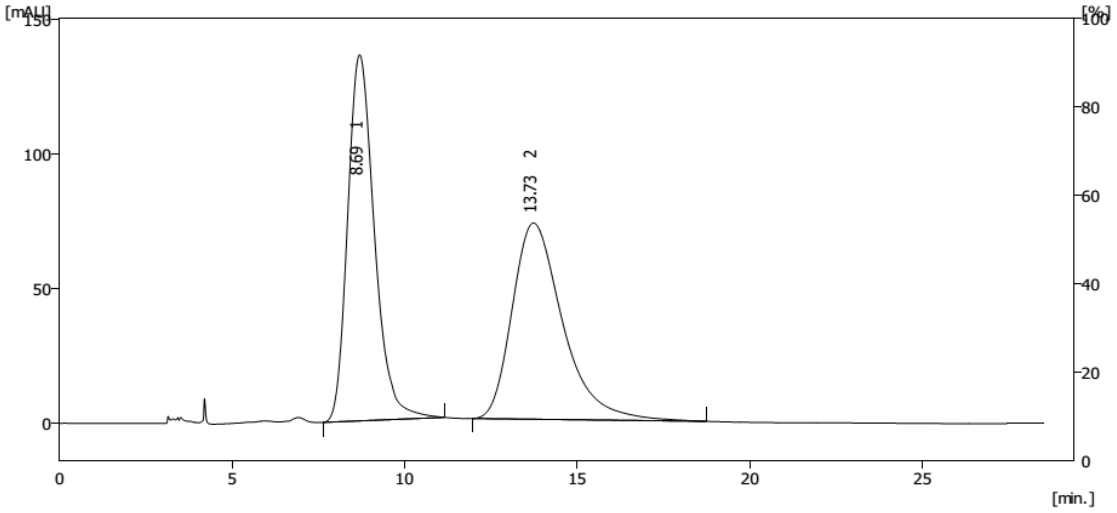
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	19.146	43.904	66.6	4812.438	52.1712
2	33.288	22.029	33.4	4411.882	47.8288



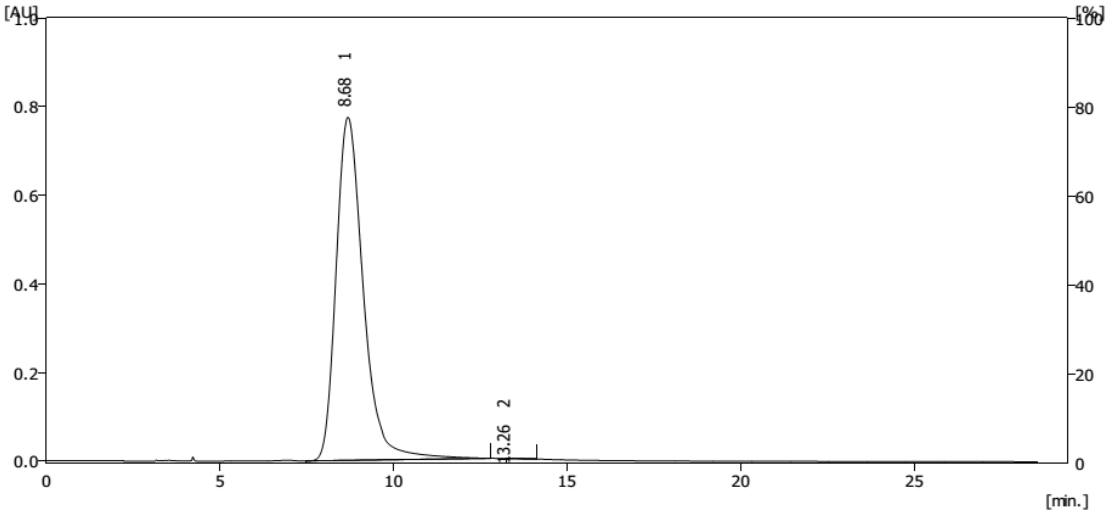
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	17.583	80.989	99.9	7973.814	99.7685
2	29.890	0.094	0.1	18.499	0.2315

3n:



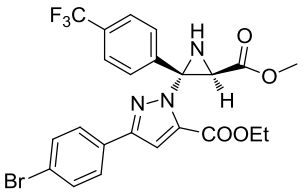


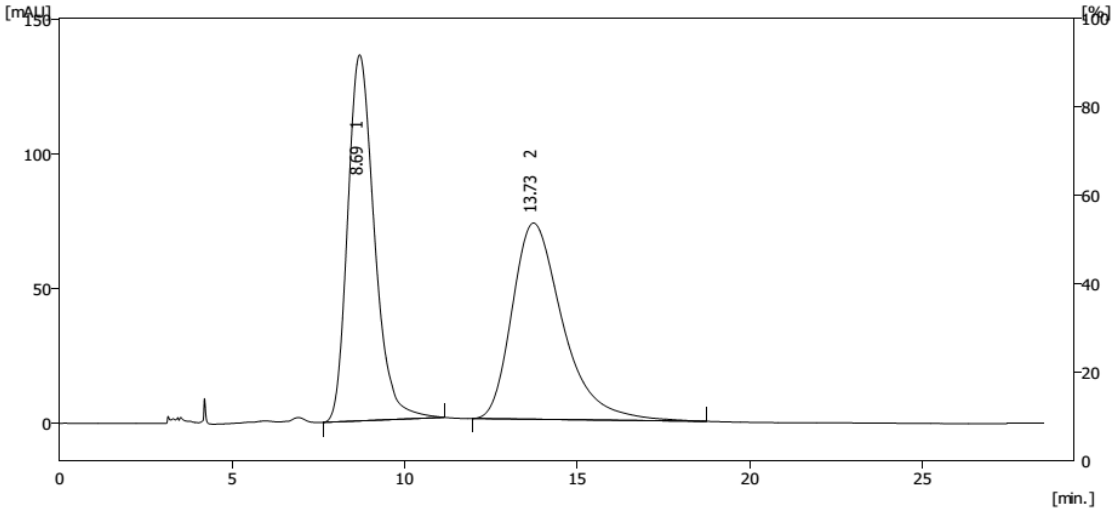
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	8.689	135.892	65.1	7316.537	49.6600
2	13.726	72.863	34.9	7416.720	50.3400



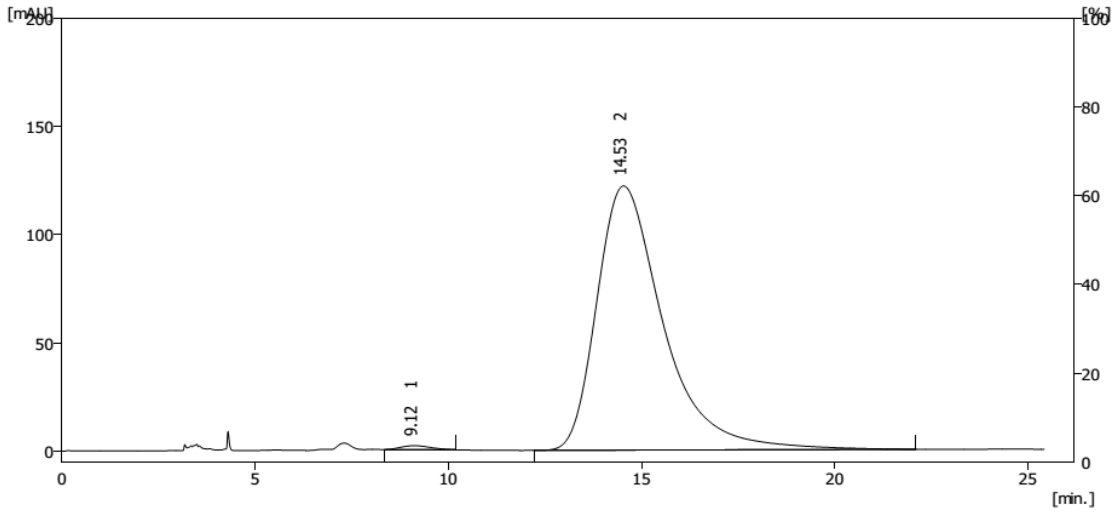
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	8.681	774.137	100.0	42260.187	99.9753
2	13.256	0.003	0.0	10.434	0.0247

(-)-3n:



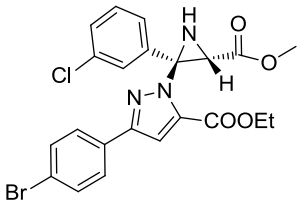


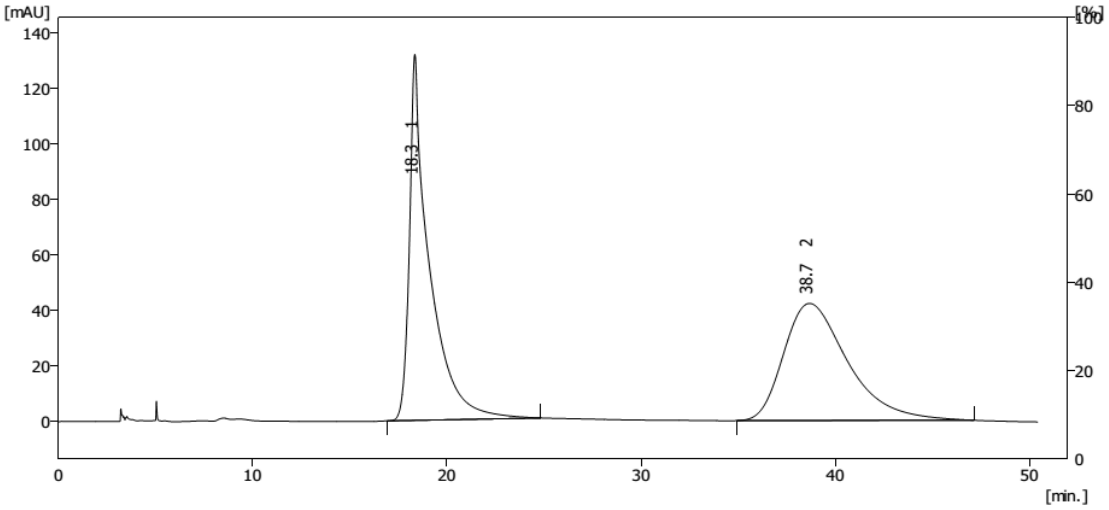
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	8.689	135.892	65.1	7316.537	49.6600
2	13.726	72.863	34.9	7416.720	50.3400



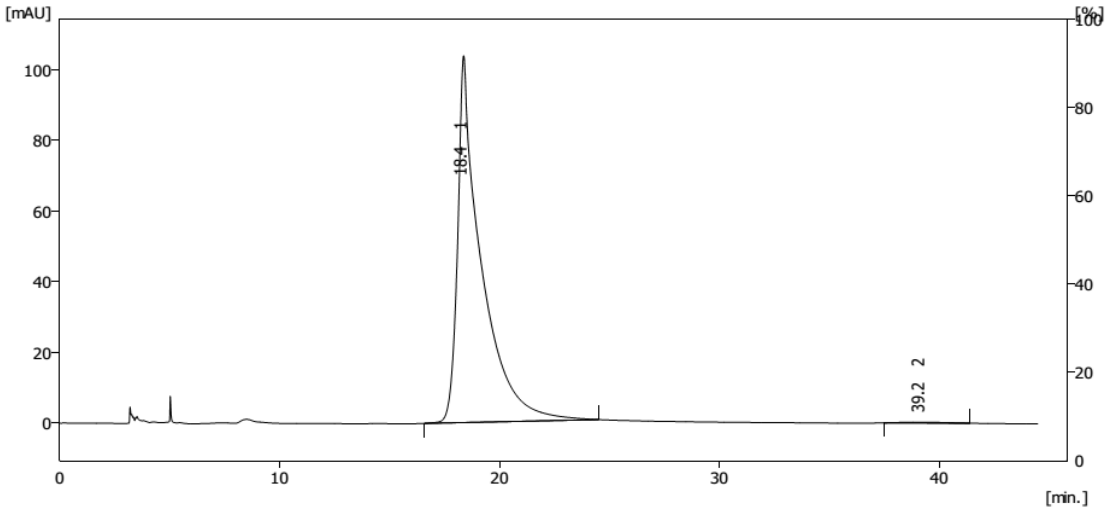
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	9.116	1.848	1.5	98.934	0.6724
2	14.532	122.168	98.5	14614.466	99.3276

3o:



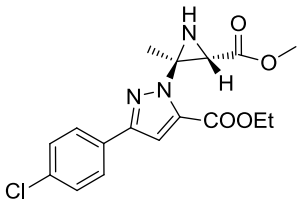


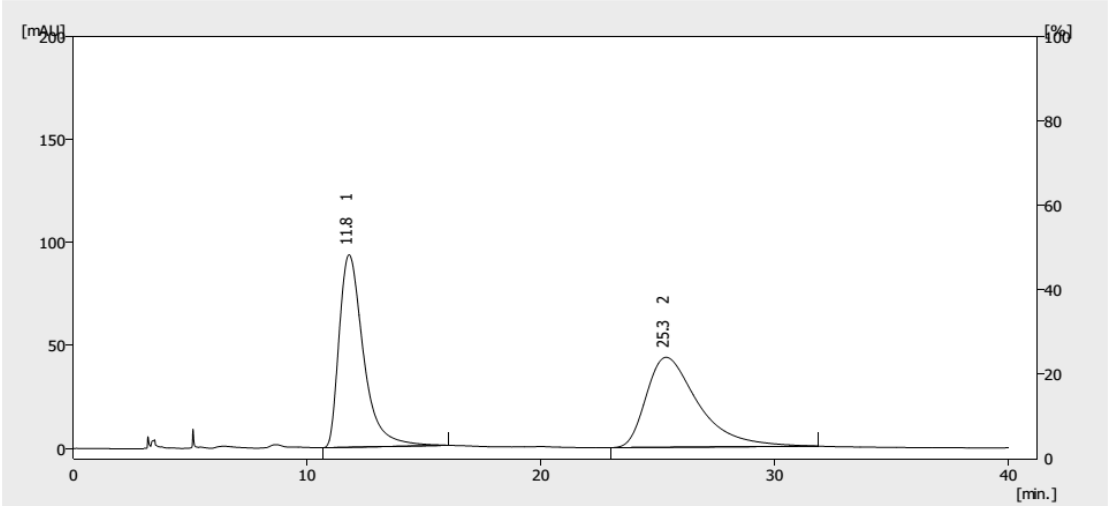
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	18.348	131.676	75.8	9333.174	49.1371
2	38.657	42.138	24.2	9660.976	50.8629



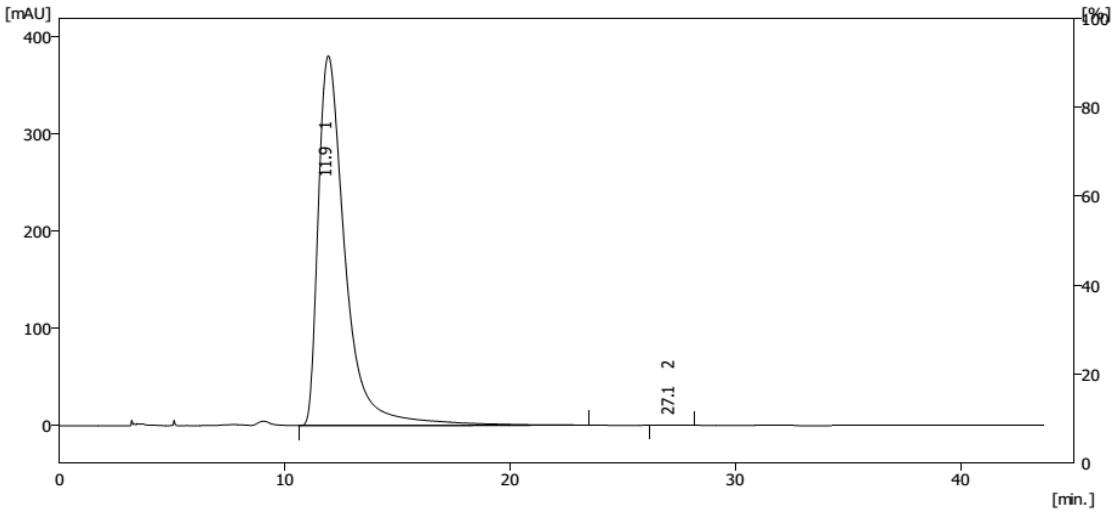
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	18.370	103.643	99.8	7697.860	99.5641
2	39.180	0.240	0.2	33.699	0.4359

3p:



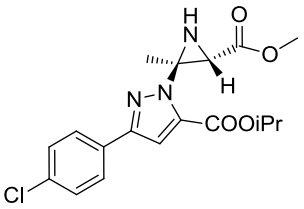


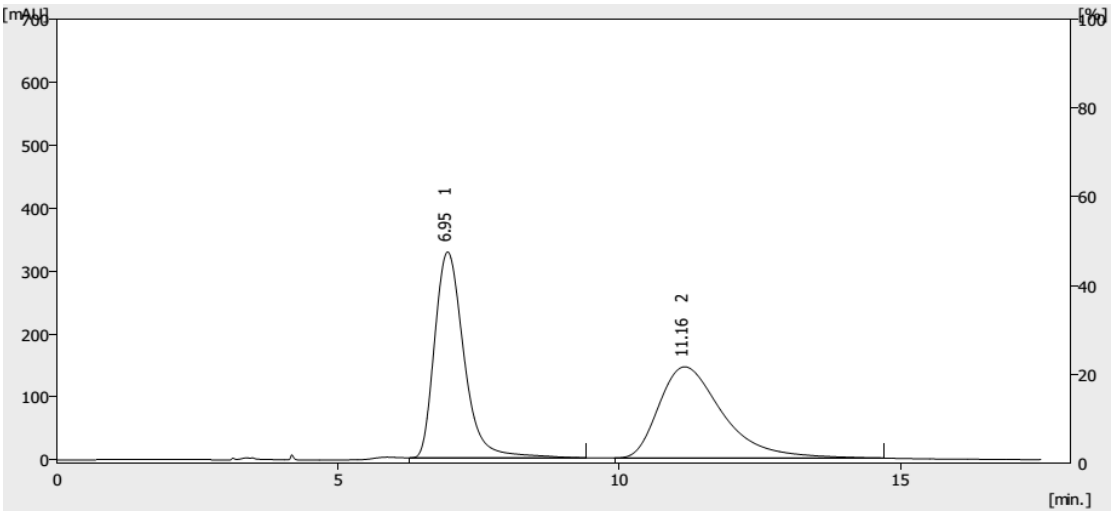
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	11.789	93.479	68.2	6769.246	50.0547
2	25.347	43.681	31.8	6754.457	49.9453



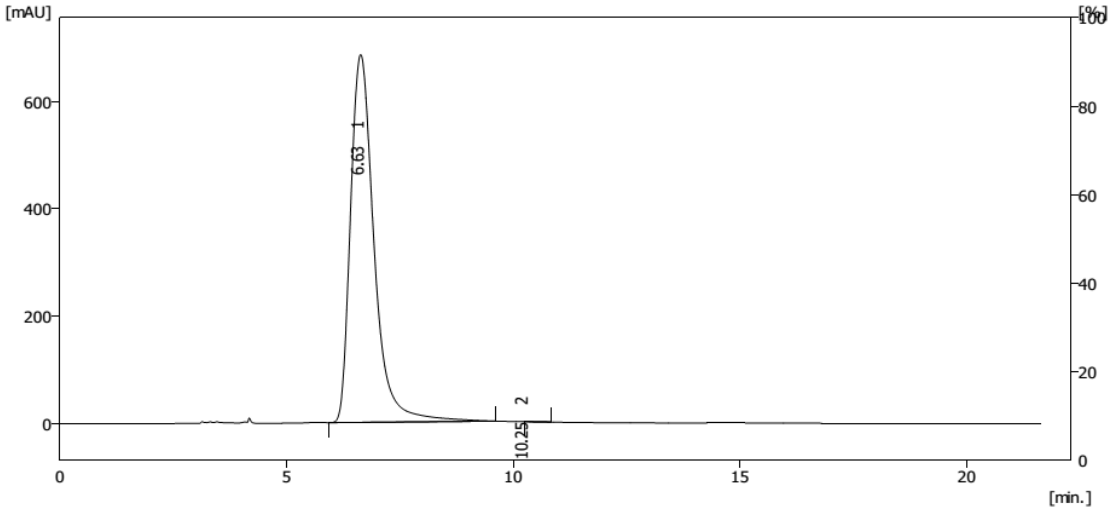
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	11.928	380.676	100.0	31723.309	99.9771
2	27.150	0.096	0.0	7.266	0.0229

3q:



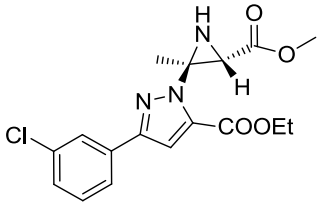


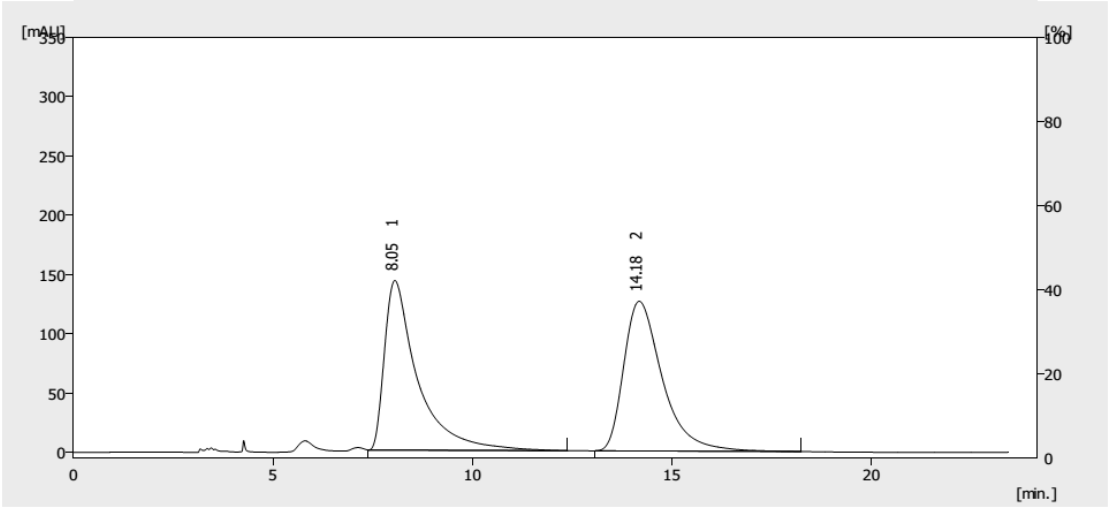
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	6.945	327.465	69.3	11892.252	50.9722
2	11.163	145.044	30.7	11438.607	49.0278



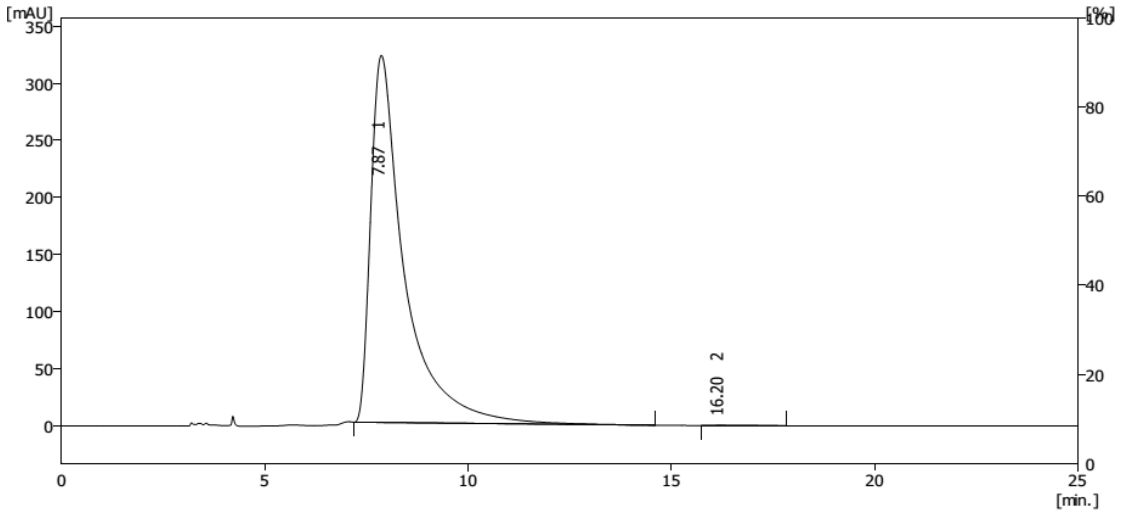
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	6.633	685.697	100.0	24765.362	99.9952
2	10.251	0.001	0.0	1.179	0.0048

3r:



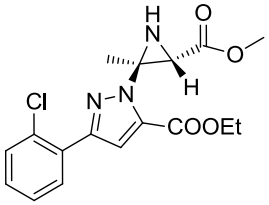


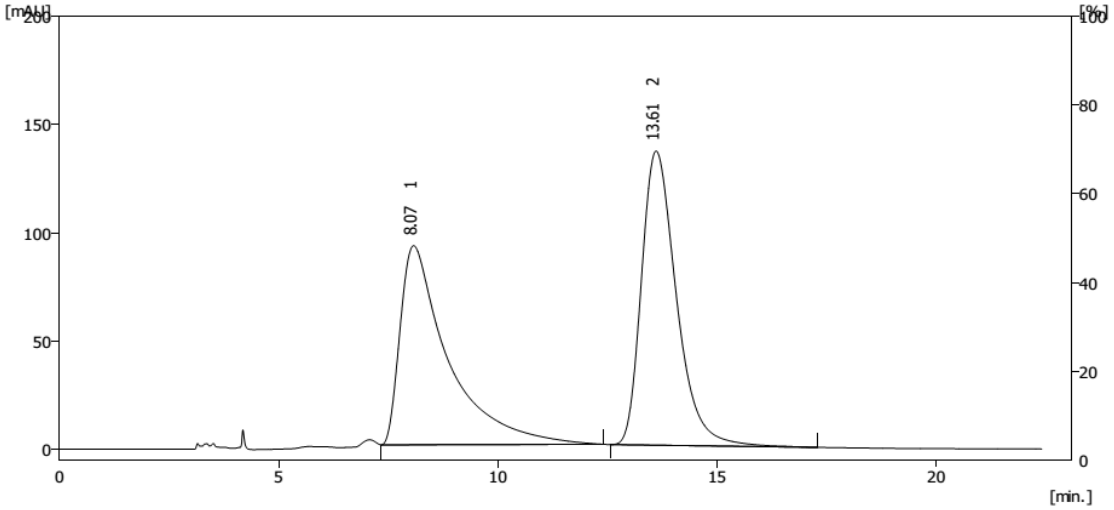
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	8.054	142.924	53.1	8247.937	49.3048
2	14.177	126.186	46.9	8480.517	50.6952



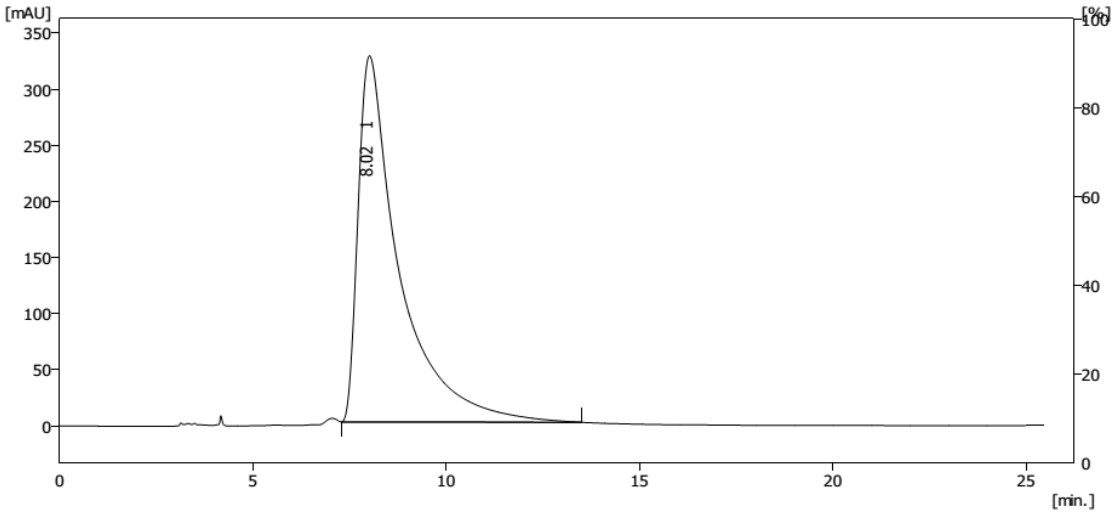
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	7.869	321.436	100.0	18499.239	99.9615
2	16.205	0.153	0.0	7.132	0.0385

3s:



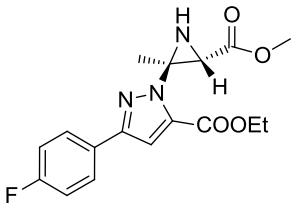


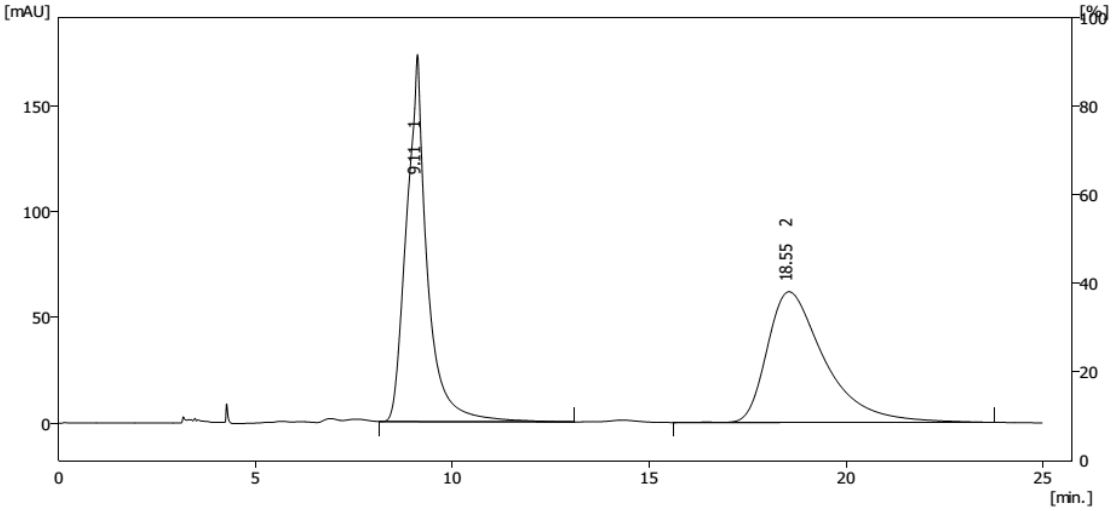
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	8.075	92.038	40.4	7004.399	48.1779
2	13.605	135.993	59.6	7534.228	51.8221



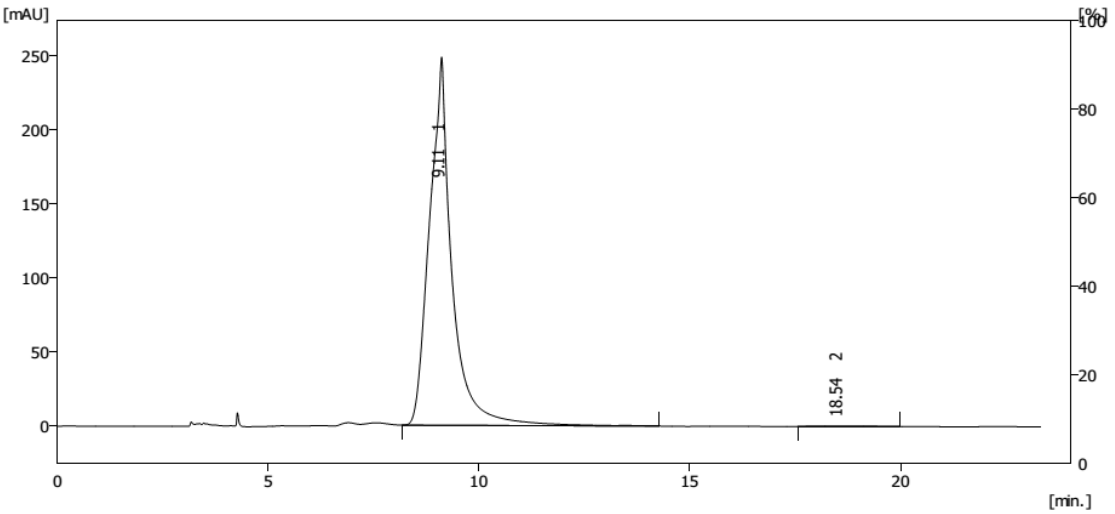
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	8.015	326.410	100.0	24100.117	100.0000

3t:



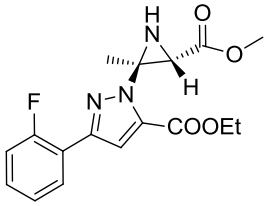


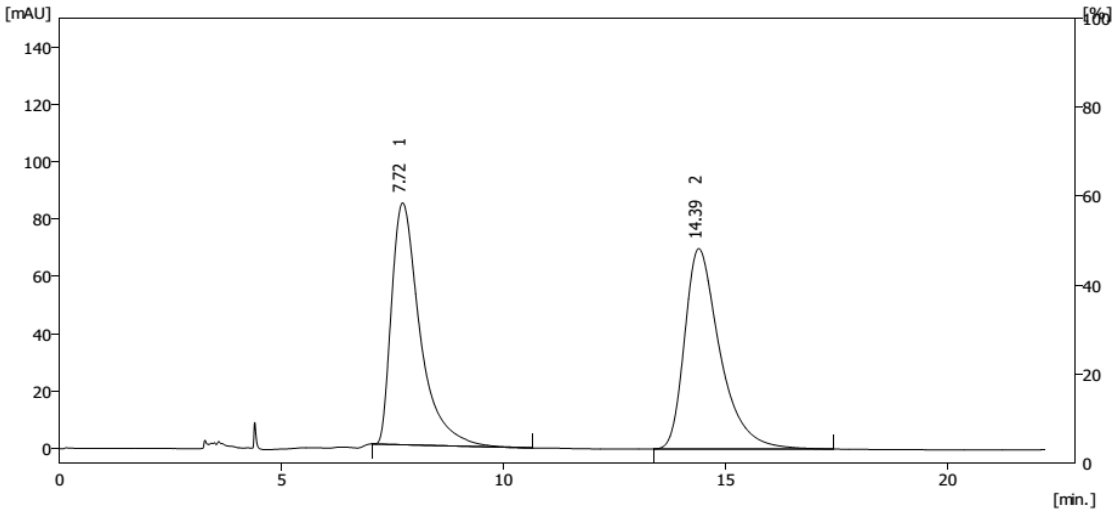
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	9.111	173.826	73.7	6319.381	50.1590
2	18.550	61.871	26.3	6279.320	49.8410



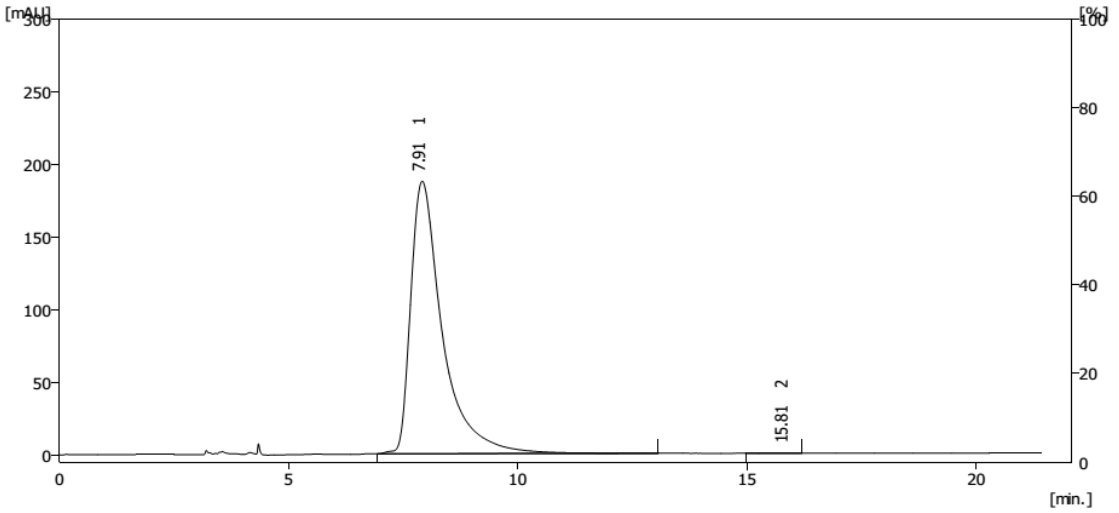
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	9.111	248.581	99.9	9162.784	99.8188
2	18.540	0.211	0.1	16.633	0.1812

3u:



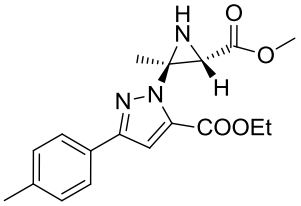


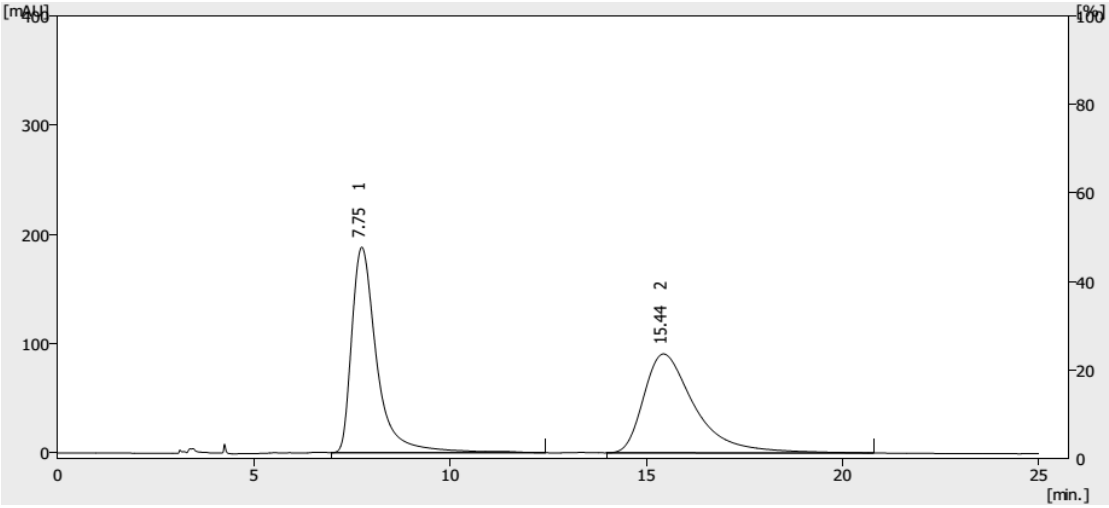
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	7.720	84.364	54.7	3745.538	49.2495
2	14.386	69.891	45.3	3859.698	50.7505



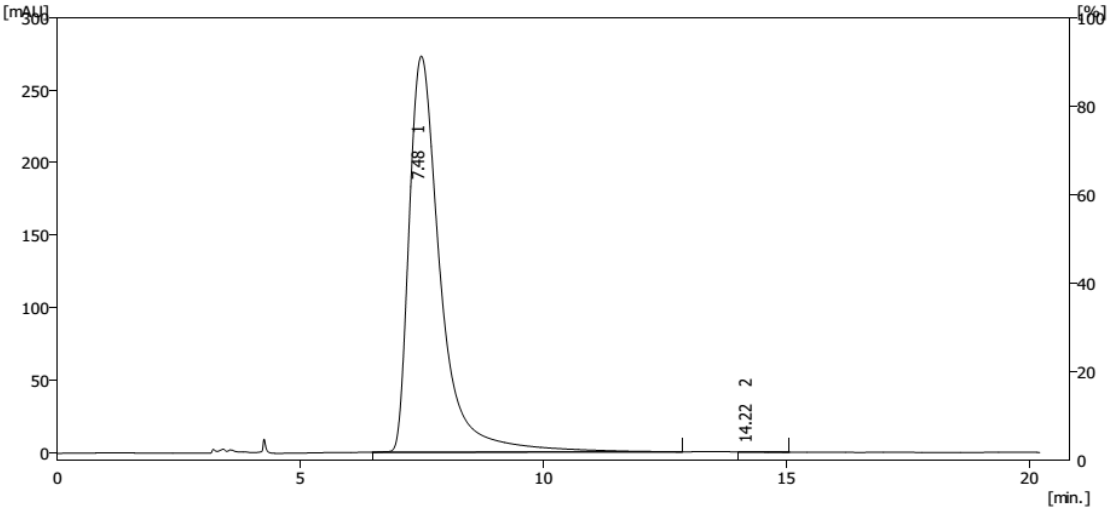
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	7.911	187.612	100.0	9016.181	99.9771
2	15.812	0.054	0.0	2.068	0.0229

3v:



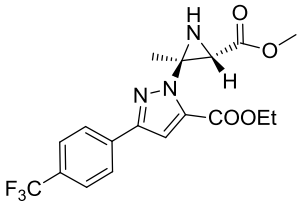


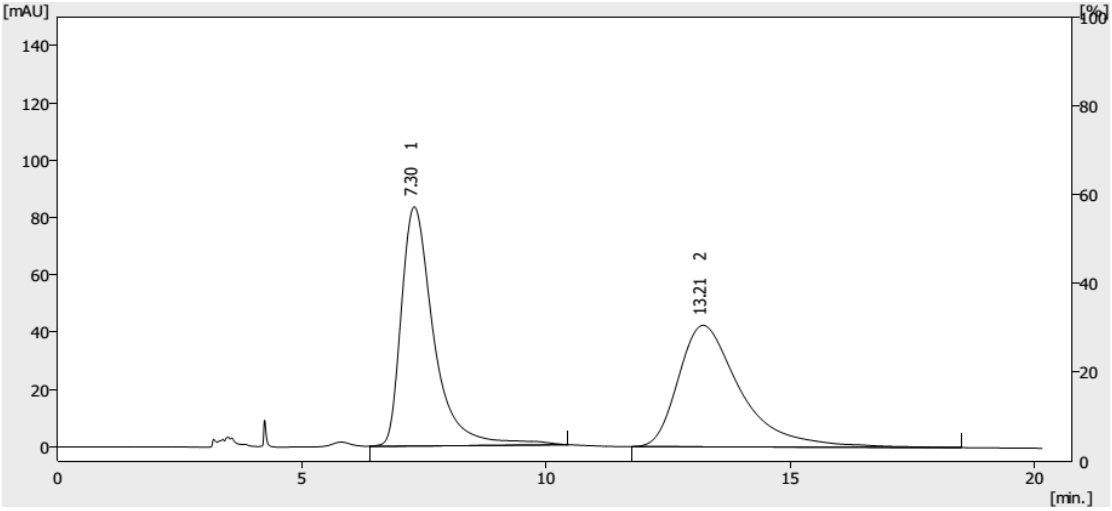
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	7.748	188.311	67.5	8428.868	50.7236
2	15.435	90.625	32.5	8188.373	49.2764



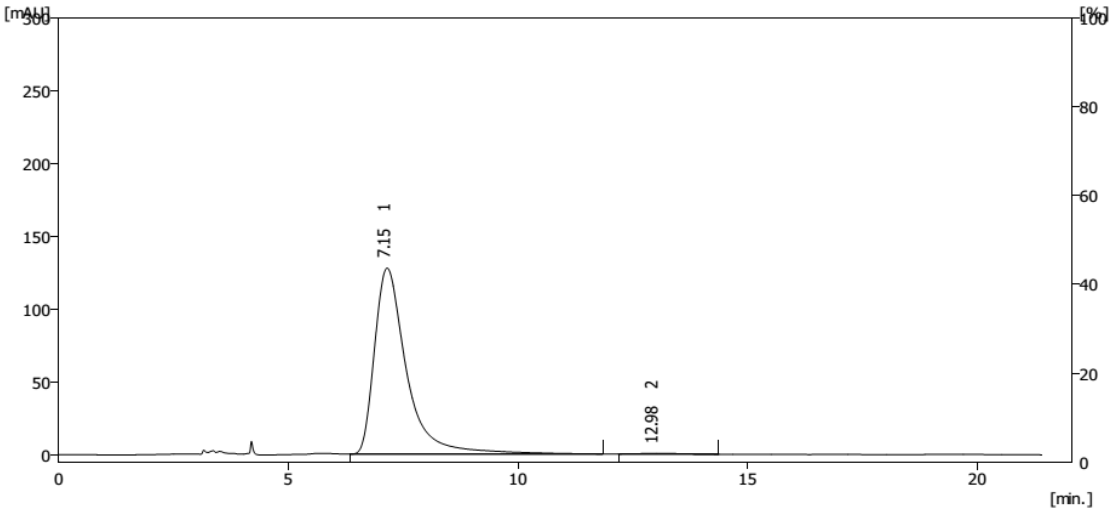
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	7.484	272.667	100.0	12191.731	99.9818
2	14.217	0.041	0.0	2.221	0.0182

3w:



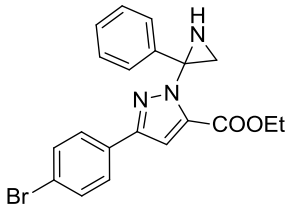


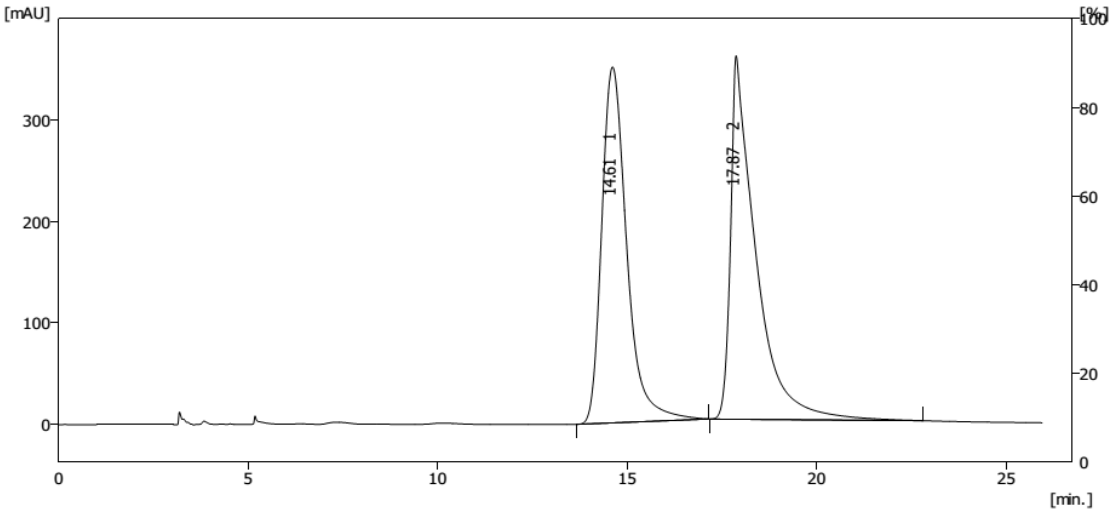
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	7.301	83.549	66.3	3871.573	50.8486
2	13.209	42.406	33.7	3742.355	49.1514



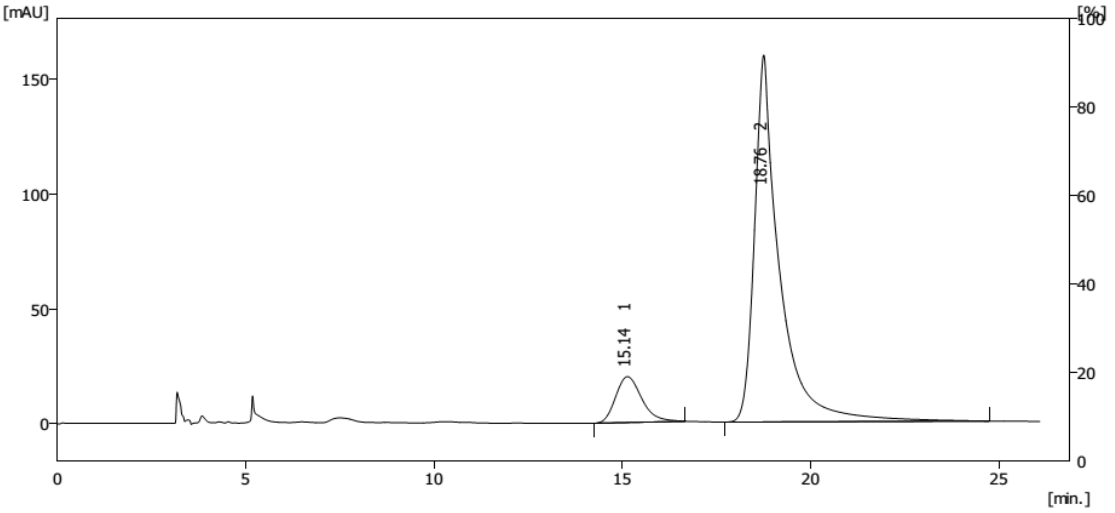
Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	7.150	127.776	99.7	6214.459	99.5590
2	12.975	0.382	0.3	27.530	0.4410

6:





Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	14.610	349.861	49.5	16051.429	49.4209
2	17.869	357.322	50.5	16427.582	50.5791



Peak	RT [min]	Height [mV]	Height %	Area[mV*s]	Area%
1	15.136	19.967	11.1	961.549	11.5226
2	18.757	159.726	88.9	7383.365	88.4774