Supporting Information for:

Catalytic enantioselective 1,3-dipolar cycloadditions of alkyl diazoacetates with α,β-disubstituted acroleins

Lizhu Gao[a], Geum-Sook Hwang[b], Mi Young Lee[a] and Do Hyun Ryu*[a]

[a] *Department of Chemistry, Sungkyunkwan University, Suwon 440-746, Korea.*

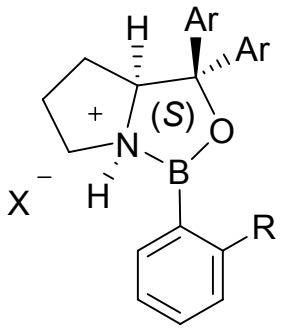
[b] *Korea Basic Science Institute and Graduate School of Analytical Science and Technology Chungnam National University, 5St, Anam-Dong, Seongbuk-Gu, Seoul, 136-713, Korea.*

Supporting Information

General Information

Unless stated otherwise, reactions were carried out under a dry argon atmosphere in vacuum-flame dried glassware. Thin-layer chromatography (TLC) was performed on Merck silica gel 60 F254. Flash chromatography was performed using E. Merck silica gel (40-60 μm partical size). ^{1}H and ^{13}C NMR spectra were recorded on a Varian at 300 and 75 MHz. Chemical shift values are reported in ppm from tetramethylsilanewith as the internal standard ($CHCl_3$: δ 7.26 for ^{1}H and δ 77.16 for ^{13}C). Data are reported as follows: chemical shifts, multiplicity(s = singlet, d = doublet, t = triplet, q = quartet, dd = doublets of doublets, dq = doublets of quartets, m = multiplet, br = broad, app = apparent), coupling constants (Hz), and integration. Infrared spectra were recorded on a Bruker Vertex 70. HRMS were recorded on JEOL JMS-SX102A mass spectrometer with EI resource. Analytical high performance liquid chromatography (HPLC) was performed on FUTECS NS 4000 at 256 nm using the indicated chiral column (4.6 mm × 25 cm). Optical rotations were determined on a Perkin-Elmer polarimeter Model 343 plus at 589 nm. Commercial grade reagents and solvents were used without further purification except as indicated below. Ethyl diazoacetate was purchased from Aldrich. Trifluoromethanesulfonic (triflic) acid[1] was distilled from phosphorus pentoxide. The chiral α, α-diaryl-2-pyrrolidinemethanol ligands[2] were prepared according to literature procedures. Dichloromethane, propionitrile, 2-methacrolien, 2-ethylacrolein,[3a] 2-isopropylacrolein,[3b] 2-cyclohexylacrolein,[3c] 2-benzylacrolein,[3d] (*E*)-2-Methyl-2-butenal, 1-cyclopentene-1-carboxaldehyde,[3e] 1-cyclohexene-1-carboxaldehyde, (*E*)-2-phenyl-2-pentenal, and (*E*)-2-phenylcrotonaldehyde,[3f] 1-cycloheptene-1-carboxaldehyde,[3g] (*E*)-2-methyl-2-pentenal were distilled from calcium hydride. Toluene was distilled from sodium.

General Procedure for Preparation of Oxazaborolidinium Catalyst



1a: Ar = phenyl, R = Me
1b: Ar = phenyl, R = H
1c: Ar = 3,5-dimethylphenyl(mexyl), R = H

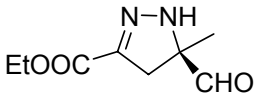
A 25-mL, two-necked, round-bottomed flask equipped with stir bar, a glass stopper and a 10-mL pressure-equalizing addition funnel (containing a cotton plug and *ca*. 2 g of 4A molecular sieves,[4] and functioning as a Soxhlet extractor) fitted on top with a reflux condenser and a nitrogen inlet adaptor was charged with (*S*)-(-)-α,α-diphenyl-2-pyrrolidinemethanol (0.166 mmol, 42 mg, from Aldrich), triphenylboroxine[5] (0.055 mmol, 17.3 mg) and 20 mL of toluene. The resulting mixture was heated to reflux (bath temperature ~ 145 ^{o}C). After 3 h, the reaction mixture was cooled to *ca*. 60 ^{o}C and the addition funnel and condenser were quickly replaced with a short-path distillation head. The mixture was concentrated by distillation (air-cooling) to a volume *ca*. 5 mL. This distillation protocol was repeated three times by re-charging with 3 × 5 mL of toluene. The solution was then allowed to cool room temperature and the distillation head was quickly replaced with a vacuum adaptor. Concentration in vacuo (ca. 0.1 mmHg, 1 h) afforded the corresponding oxazaborolidine as clear oil. The oxazaborolidine from (*S*)-(-)-α,α-*bis*(3,5-dimethylphenyl)-2-pyrrolidinemethanol[6] ligands was prepared in a similar manner.

To an aliquot oxazaborolidine precursor (0.166 mmol, theoretical) at -40 ^{o}C was added trifluoromethanesulfonimide or trifluoromethanesulfonic acid (0.200 M solution in solvent,[7] freshly prepared, 0.127 mmol, 0.635 mL) dropwise under N_2. After 15-20 min at -40 ^{o}C, a slight yellow homogeneous catalyst solution was ready for use in Dies-Alder experiments.

General Procedure for Preparation of Pyrazolines

To a catalyst solution prepared as described above was added the corresponding substitued acrolein (0.635 mmol, 1 equiv) at -78 ^{o}C, followed by alkyl diazoacetate (0.953 mmol, 1.5 equiv). The resulting mixture was stirred at the same temperature until complete consumption of the acrolein. The reaction mixture was quenched with 30.0 μL of Et_3N and was allowed to warm to room temperature after 30 min. Solvent was removed under reduced pressure and the residue was purified by silica gel chromatography quickly to afford Diels-Alder cycloadduct.

Synthesis and Characterization of Pyrazolines

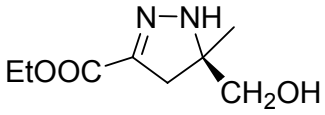


(*R*)-Ethyl 5-formyl-5-methyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (Table 2, entry 1).

The compound was prepared according to the general procedure with 2-methylacrolein (0.635 mmol, 44.5 mg) and ethyl diazoacetate (0.953 mmol, 108.7 mg) catalyzed by **1c** over a course of 2 h. The crude material was purified by column chromatography on silica gel (eluting with dichloromethane/ethyl acetate = 3:1) to give the title cycloadduct as a pale yellow oil [86% yield (100.7 mg)].

^{1}H NMR (300MHz, $CDCl_3$) δ 9.54 (1H, s, C**H**O), 6.45 (1H, s, N**H**), 4.12 (2H, q, *J* = 7.2 Hz, OC**H**$_2$), 3.30 (1H, d, *J* = 17.7 Hz, C**H**H), 2.83 (1H, d, *J* = 17.7 Hz, CH**H**), 1.42 (3H, s, CCH_3), 1.35 (3H, t, *J* = 7.2 Hz, OCH_2C**H**$_3$) ppm; HRMS (EI) exact mass calcd. for $C_8H_{12}N_2O_3$: m/z 184.0848 ($[M]^+$), found: m/z 184.0845 ($[M]^+$).

The physical and spectral data were identical to the previously reported for this compound.[8]



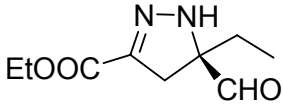
(*R*)-Ethyl 5-formyl-5-(hydroxymethyl)-4,5-dihydro-1*H*-pyrazole-3-carboxylate

Reduction of the pyrazoline according to the method[7] afforded the desired product as colorless oil, in 71% yield and 95% ee.

The enantiomeric purity was determined by HPLC analysis (Daicel Chiralcel OJ-H, hexane/2-propanol = 9:1, 0.5 mL/min, t_R = 39.6 min (minor) and t_R = 46.9 min (major)).

^{1}H NMR (300MHz, $CDCl_3$) δ 6.31 (1H, s, N**H**), 4.30 (2H, q, *J* = 7.2 Hz, OC**H**$_2$), 3.51 (1H, s, O**H**), 2.99 (1H, d, *J* = 17.4 Hz, C**H**H), 2.66 (1H, d, *J* = 17.4 Hz, CH**H**), 1.34 (3H, t, *J* = 7.1 Hz, OCH_2C**H**$_3$), 1.26 (3H, s, CCH_3) ppm; $[\alpha]_D^{20}$ = -38.9 (*c* = 1.0, C_6H_6; 95% ee).

The physical and spectral data were identical to those previously reported for this compound.[8]

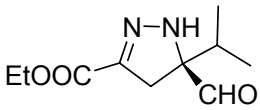


(*R*)-Ethyl 5-formyl-5-ethyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (Table 2, entry 2).

The compound was prepared according to the general procedure with 2-ethylacrolein (0.635 mmol, 53.4 mg) and ethyl diazoacetate (0.953 mmol, 108.7 mg) catalyzed by **1b** over a course of 1 h. The crude material was purified by column chromatography on silica gel (eluting with dichloromethane/ethyl acetate = 8:1) to give the title cycloadduct as a pale yellow oil [91% yield (114.7 mg)].

The enantiomeric purity was determined by HPLC analysis (Daicel Chiralcel OJ-H, hexane/2-propanol = 19:1, 1.0 mL/min, t_R = 34.5 min (major) and t_R = 41.2 min (minor)).

^{1}H NMR (300MHz, $CDCl_3$) δ 9.52 (1H, s, C**H**O), 6.87 (1H, s, N**H**), 4.29 (2H, q, *J* = 7.2 Hz, OC**H**$_2$), 3.28 (1H, d, *J* = 17.7 Hz, C**H**H), 2.86 (1H, d, *J* = 18 Hz, CH**H**), 1.85 (2H, dq, *J* = 4.1, 7.5 HZ, CC**H**$_2$CH$_3$), 1.34 (3H, t, *J* = 7.1 Hz, OCH$_2$C**H**$_3$), 0.93 (3H, t, *J* = 7.7 Hz, CH$_2$C**H**$_3$) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.3, 162.0, 141.9, 76.8, 61.3, 36.4, 26.3, 14.1, 7.9 ppm; IR (neat) 3333, 2975, 1726, 1569, 1337, 1256, 1174, 1123, 781, 731cm^{-1}; HRMS (EI) exact mass calcd. for $C_9H_{14}N_2O_3$: m/z 198.1004 ([M]$^+$), found: m/z 198.1004 ([M]$^+$); $[\alpha]_D^{20}$ = -220.5 (*c* = 1.0, C_6H_6; 91% ee).



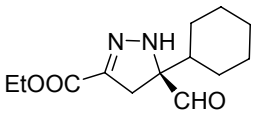
(*R*)-Ethyl 5-formyl-5-isopropyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (Table 2, entry 3).

The compound was prepared according to the general procedure with 2-isopropylacrolein (0.635 mmol, 62.3 mg) and ethyl diazoacetate (0.953 mmol, 108.7 mg) catalyzed by **1b** over a course of 1 h. The crude material was purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 2:1) to give the title cycloadduct as a pale yellow oil [97% yield (130.7 mg)].

The enantiomeric purity was determined by HPLC analysis (Daicel Chiralcel OJ-H, hexane/2-propanol = 19:1, 1.0 mL/min, t_R = 21.2min (major) and t_R =25.5 min (minor)).

^{1}H NMR (300MHz, $CDCl_3$) δ 9.55 (1H, s, C**H**O), 6.75 (1H, s, N**H**), 4.29 (2H, q, *J* = 7.1 Hz, OC**H**$_2$), 3.27 (1H, d, *J* = 18.0 Hz, CH**H**), 2.91 (1H, d, *J* = 18.0 Hz, C**H**H), 2.17 (1H, m, C**H**), 1.34 (3H, t, *J* = 7.1 Hz, OCH$_2$C**H**$_3$), 0.98 (6H, app dd, *J* = 6.8, 10.1 Hz, CH(C**H**$_3$)$_2$) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.0, 162.1, 142.2, 79.8, 61.4, 34.3, 31.9, 17.5, 17.0, 14.3 ppm; IR (neat) 3327, 2970, 2877, 1725, 1569, 1467, 1373, 1261, 1113, 913, 747 cm^{-1}; HRMS (EI) exact mass calcd. for

$C_{10}H_{16}N_2O_3$: m/z 213.1234 ($[M + H]^+$), found: m/z 213.1239 ($[M + H]^+$); $[\alpha]_D^{20}$ = -287.8 (*c* = 1.0, C_6H_6; 92% ee).

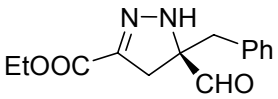


(*R*)-Ethyl 5-formyl-5-cyclohexyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (Table 2, entry 5).

The compound was prepared according to the general procedure with 2-cyclohexylacrolein (0.635 mmol, 87.8 mg) and ethyl diazoacetate (0.953 mmol, 108.7 mg) catalyzed by **1c** over a course of 1 h. The crude material was purified by column chromatography on silica gel (eluting with dichloromethane/ ethyl acetate = 5:1) to give the title cycloadduct as a pale yellow oil [94% yield (151.1 mg)].

The enantiomeric purity was determined by HPLC analysis (Daicel Chiralcel OJ-H, hexane/2-propanol = 97:3, 1.0 mL/min, t_R = 32.5 min (major) and t_R = 48.3 min (minor)).

^{1}H NMR (300MHz, $CDCl_3$) δ 9.53 (1H, s, C**H**O), 6.65 (1H, s, N**H**), 4.29 (2H, q, *J* = 7.1 Hz, OC**H**$_2$), 3.24 (1H, d, *J* = 17.7 Hz, C**H**H), 2.94 (1H, d, *J* = 18.0 Hz, CH**H**), 1.68-1.86 (6H, m, Cy), 1.34 (3H, t, *J* = 7.1 Hz, $OCH_2C\mathbf{H}_3$), 1.00-1.27 (5H, m, Cy) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.5, 162.3, 142.5, 79.7, 61.6, 42.3, 34.7, 28.0, 27.5, 26.4, 26.2, 26.1, 14.5 ppm; IR(neat) 3323, 2929, 2853, 1724, 1449, 1261, 1120, 913, 749 cm^{-1}; HRMS (EI) exact mass calcd. for $C_{13}H_{20}N_2O_3$: m/z 252.1474 ($[M + H]^+$), found: m/z 253.1552 ($[M + H]^+$); $[\alpha]_D^{20}$ = -203.9 (*c* = 1.0, C_6H_6; 92% ee).

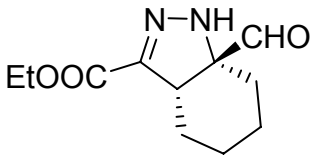


(*R*)-Ethyl 5-formyl-5-benzyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (Table 2, entry 7).

The compound was prepared according to the general procedure with 2-benzylacrolein (0.635 mmol, 92.8 mg) and ethyl diazoacetate (0.953 mmol, 108.7 mg) catalyzed by **1b** over a course of 0.5 h. The crude material was purified by column chromatography on silica gel (eluting with dichloromethane/ethyl acetate = 8:1) to give the title cycloadduct as a slight pale yellow oil [72% yield (118.7 mg)].

The enantiomeric purity was determined by HPLC analysis (Daicel Chiralcel OJ-H, hexane/2-propanol = 9:1, 1.0 mL/min, t_R = 39.1 min (major) and t_R = 50.4 min (minor)).

^{1}H NMR (300MHz, $CDCl_3$) δ 9.56 (1H, s, C**H**O), 7.27-7.34 (3H, m, Ar**H**), 7.15-7.18 (2H, m, Ar**H**), 6.56 (1H, s, N**H**), 4.28 (2H, q, *J* = 7.1 Hz, OC**H**$_2$), 3.24 (1H, d, *J* = 13.8 Hz, PhCH**H**), 3.22 (1H, d, *J* = 17.4 Hz, CH**H**), 3.01 (1H, d, *J* = 13.8 Hz, PhC**H**H), 2.95 (1H, d, *J* = 17.4 Hz, C**H**H), 1.33 (3H, t, *J* = 7.1 Hz, OCH_2C**H**$_3$) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.3, 161.9, 142.6, 134.1, 130.2, 129.0, 127.7, 77.0, 61.6, 39.5, 38.0, 14.3 ppm; IR (neat) 3334, 2985, 1727, 1705, 1571, 1421, 1262, 1121, 760, 747, 703 cm^{-1}; HRMS (EI) exact mass calcd. for $C_{14}H_{16}N_2O_3$: m/z 260.1161 ($[M]^+$), found: m/z 260.1151 ($[M]^+$); $[\alpha]_D^{20}$ = -138.9 (*c* = 1.0, C_6H_6; 91% ee).



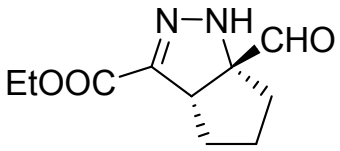
(*3aS*, *7aR*)-Ethyl 7a-formyl-3a,4,5,6,7,7a-hexahydro-*1H*-indazole-3-carboxylate (Table 3, entry 2).

The compound was prepared according to the general procedure with 1-cyclohexene-1-carboxaldehyde (0.635 mmol, 69.9 mg) and ethyl diazoacetate (0.953 mmol, 108.7 mg) catalyzed by **1b** in over a course of 1 h. The crude material was purified by column chromatography on silica gel (eluting with dichloromethane/ethyl acetate = 20:1) to give the title cycloadduct as a pale yellow oil [75% yield (106.9 mg)].

The enantiomeric purity was determined by HPLC analysis (Daicel Chiralcel OJ-H, hexane/2-propanol = 19:1, 1.0 mL/min, t_R = 31.7 min (major) and t_R = 36.2 min (minor)).

The *cis* geometry assigned is consistent with nOe data (*vide infra*).

^{1}H NMR (300MHz, $CDCl_3$) δ 9.38 (1H, s, C**H**O, positive nOe with δ 3.20 (CC**H**(C)CH_2)), 6.73 (1H, s, N**H**), 4.29 (2H, dq, *J* = 1.8, 7.2 Hz, OC**H**$_2$), 3.20 (1H, app dd, *J* = 6.8, 9.8Hz, CC**H**(C)CH_2, positive nOe with δ 9.38), 2.08-2.15 (1H, m, Cy), 1.62-1.77 (4H, m, Cy), 1.48-1.55 (1H, m, Cy), 1.34 (3H, t, *J* = 7.2 Hz, OCH_2C**H**$_3$), 1.20-1.29 (2H, m, Cy) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.4, 161.9, 147.7, 75.5, 61.4, 41.5, 25.3, 24.0, 21.4, 20.3, 14.3 ppm; IR (neat) 3325, 2938, 2859, 1726, 1706, 1402, 1238, 1175, 1132, 1099, 734, 713 cm^{-1}; HRMS (EI) exact mass calcd. for $C_{11}H_{16}N_2O_3$: m/z 225.1234 ($[M + H]^+$), found: m/z 225.1239 ($[M + H]^+$); $[\alpha]_D^{20}$ = -228.2 (*c* = 1.0, C_6H_6; 92% ee).

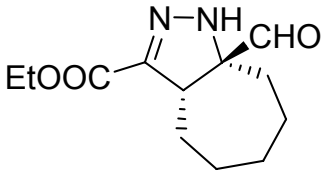


(*3aS*, *6aR*)-Ethyl 6a-formyl-1,3a,4,5,6,6a-hexahydrocyclopenta[c]pyrazole-3-carboxylate (Table 3, entry 3).

The compound was prepared according to the general procedure with 1-cyclopentene-1-carboxaldehyde (0.635 mmol, 61.0 mg,) and ethyl diazoacetate (0.953 mmol, 108.7 mg) catalyzed by **1b** over a course of 0.5 h. The crude material was purified by column chromatography on silica gel (eluting with dichloromethane/ethyl acetate = 4:1) to give the title cycloadduct as a pale yellow oil [73% yield (97.2 mg)].

The enantiomeric purity was determined by HPLC analysis (Daicel Chiralcel OJ-H, hexane/2-propanol = 19:1, 1.0 mL/min, t_R = 40.2 min (major) and t_R = 48.1 min (minor)).

^{1}H NMR (300MHz, $CDCl_3$) δ 9.60 (1H, s, C**H**O), 6.81 (1H, s, N**H**), 4.29 (2H, dq, *J* = 2.8, 7.1 Hz, OC**H**$_2$), 3.86 (1H, app dd, *J* = 2.9, 8.6 Hz, CC**H**(C)CH$_2$), 1.83-2.19 (4H, m, Cy), 1.62-1.70 (1H, m, Cy), 1.35 (3H, t, *J* = 7.1 Hz, OCH$_2$C**H**$_3$), 1.22-1.30 (1H, m, Cy) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.1, 162.0, 144.5, 84.4, 61.3, 52.8, 36.5, 33.1, 25.8, 14.3 ppm; IR (neat) 3324, 2962, 2871, 1721, 1704, 1563, 1179, 1124, 1083, 780, 731 cm^{-1}; HRMS (EI) exact mass calcd. for $C_{10}H_{14}N_2O_3$: m/z 211.1077 ([M + H]$^+$), found: m/z 211.1083 ([M + H]$^+$); $[\alpha]_D^{20}$ = -407.7 (*c* = 1.0, C_6H_6; 97% ee).



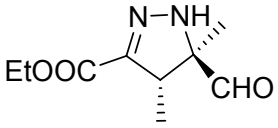
(*3aS*, *8aR*)-Ethyl 8a-formyl-1,3a,4,5,6,7,8,8a-octahydrocyclohepta[c]pyrazole-3-carboxylate (Table 3, entry 4).

The compound was prepared according to the general procedure with 1-cycloheptene-1-carboxaldehyde (0.635 mmol, 78.9 mg) and ethyl diazoacetate (0.953 mmol, 108.7 mg) catalyzed by **1b** over a course of 0.5 h. The crude material was purified by column chromatography on silica gel (eluting with dichloromethane/ethyl acetate = 20:1) to give the title cycloadduct as a pale yellow oil [70% yield (105.2 mg)].

The enantiomeric purity was determined by HPLC analysis (Daicel Chiralcel AS-H,

hexane/2-propanol = 9:1, 0.5 mL/min, t_R = 16.9 min (major) and t_R = 19.9 min (minor)).

^{1}H NMR (300MHz, $CDCl_3$) δ 9.45 (1H, s, C**H**O), 6.55 (1H, s, N**H**), 4.29 (2H, dq, *J* = 2.1, 7.2 Hz, OC**H**$_2$), 3.60 (1H, app dd, *J* = 3.3, 7.5 Hz, CC**H**(C)CH$_2$), 1.75-2.11 (4H, m, Cy), 1.35 (3H, t, *J* = 7.1 Hz, OCH$_2$C**H**$_3$), 1.40-1.68 (6H, m, Cy); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.0, 162.2, 144.8, 78.5, 61.4, 48.2, 31.1, 30.3, 27.6, 27.4, 23.9, 14.4 ppm; IR (neat) 3310, 2929, 2852, 1723, 1707, 1563, 1445, 1246, 1126, 1098, 972, 742, 638 cm^{-1}; HRMS (EI) exact mass calcd. for $C_{12}H_{18}N_2O_3$: m/z 210.1390 ([M + H]$^+$), found: m/z 239.1396 ([M + H]$^+$). $[\alpha]_D^{20}$ = -267.7 (*c* = 1.0, C_6H_6; 85% ee).

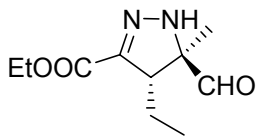


(*4S*, *5R*)-Ethyl 5-formyl-4,5-dimethyl-4,5-dihydro-*1H*-pyrazole-3-carboxylate (Table 3, entry 5).

The compound was prepared according to the general procedure with (*E*)-2-Methyl-2-butenal (0.635 mmol, 53.4 mg) and ethyl diazoacetate (0.953 mmol, 108.7 mg) catalyzed by **1b** over a course of 1 h. The crude material was purified by column chromatography on silica gel (eluting with dichloromethane/ethyl acetate = 6:1) to give the title cycloadduct as a pale yellow oil [93% yield (116.8 mg)].

The enantiomeric purity was determined by HPLC analysis (Daicel Chiralcel AS-H, hexane/2-propanol = 19:1, 1.0 mL/min, t_R = 22.9 min (major) and t_R = 26.6 min (minor)).

^{1}H NMR (300MHz, $CDCl_3$) δ 9.48 (1H, s, C**H**O), 6.57 (1H, s, N**H**), 4.30 (2H, dq, *J* = 1.2, 7.2 Hz, OC**H**$_2$), 3.40 (1H, q, *J* = 7.3 Hz, C**H**), 1.35 (3H, t, *J* = 7.2 Hz, OCH$_2$C**H**$_3$), 1.30 (3H, s, CC**H**$_3$), 1.24 (3H, d, *J* = 7.2 Hz, CHC**H**$_3$) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.9, 161.9, 146.7, 75.9, 61.4, 41.8, 14.3, 13.4, 11.1 ppm; IR (neat) 3334, 2981, 2940, 1726, 1706, 1560, 1420, 1251, 1097, 1047,769, 698 cm^{-1}; HRMS (EI) exact mass calcd. for $C_9H_{14}N_2O_3$: m/z 199.1077 ([M + H]$^+$), found: m/z 199.1083 ([M + H]$^+$); $[\alpha]_D^{20}$ = -299.6 (*c* = 1.0, C_6H_6; 90% ee).



(*4S*, *5R*)-Ethyl 4-ethyl-5-formyl-5-methyl-4,5-dihydro-*1H*-pyrazole-3-carboxylate (Table 3,

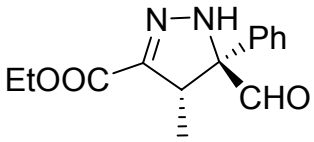
entry 6).

The compound was prepared according to the general procedure with (*E*)-2-Phenylcrotonaldehyde (0.635 mmol, 62.3 mg) and ethyl diazoacetate (0.953 mmol, 108.7 mg) catalyzed by **1b** over a course of 1h. The crude material was purified by column chromatography on silica gel (eluting with dichloromethane/ethyl acetate = 15:1) to give the title cycloadduct as a pale colorless oil [90% yield (121.3 mg)].

The enantiomeric purity was determined by HPLC analysis (Daicel Chiralcel AD-H, hexane/2-propanol = 19:1, 1.0 mL/min, t_R = 18.8 min (major) and t_R = 25.2 min (minor)).

The *cis* geometry assigned is consistent with nOe data (*vide infra*).

^{1}H NMR (300MHz, $CDCl_3$) δ 9.45 (1H, s, C**H**O, positive nOe with δ 3.29 (C**H**CH_2CH_3) and 1.34 (CC**H**$_3$)), 6.45 (1H, br s, N**H**), 4.30 (2H, q, *J* = 7.1 Hz, OC**H**$_2$), 3.29 (1H, app dd, *J* = 4.4, 7.7 Hz, C**H**CH_2CH_3, positive nOe with δ 9.45 (C**H**O)), 1.76 (2H, m, CHC**H**$_2CH_3$), 1.35 (3H, t, *J* = 7.2 Hz, OCH_2C**H**$_3$), 1.34(3H, s, CC**H**$_3$), 0.95 (3H, t, *J* = 7.5 Hz, $CHCH_2$C**H**$_3$) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.8, 162.1, 146.0, 76.2, 61.4, 47.9, 19.4, 14.3, 13.2, 11.8 ppm; IR (neat) 3327, 2984, 1727, 1707, 1420, 1377, 1101, 1038, 1028, 1016, 707 cm^{-1}; HRMS (EI) exact mass calcd. for $C_{10}H_{16}N_2O_3$: m/z 213.1234 ($[M + H]^+$), found: m/z 213.1239 ($[M + H]^+$); $[\alpha]_D^{20}$ = -286.0 (*c* = 1.0, C_6H_6; 85% ee).



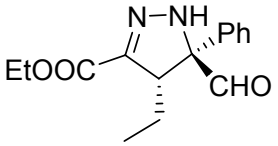
(*4S*, *5R*)-Ethyl 5-formyl-4-methyl-5-phenyl-4,5-dihydro-*1H*-pyrazole-3-carboxylate (Table 3, entry 7).

The compound was prepared according to the general procedure with (E)-2-Phenylcrotonaldehyde (0.635 mmol, 92.8 mg) and ethyl diazoacetate (0.953 mmol, 108.7 mg) catalyzed by **1b** over a course of 1h. The crude material was purified by column chromatography on silica gel (eluting with dichloromethane/ethyl acetate = 20:1) to give the title cycloadduct as a pale yellow oil [70% yield (116.2 mg)].

The enantiomeric purity was determined by HPLC analysis (Daicel Chiralcel OD-H, hexane/2-propanol = 19:1, 1.0 mL/min, t_R = 25.1 min (major) and t_R = 33.5 min (minor)).

The *cis* geometry assigned is consistent with nOe data (*vide infra*).

^{1}H NMR (300MHz, $CDCl_3$) δ 9.54 (1H, s, C**H**O, positive nOe with δ 3.84 (C**H**CH_3)), 7.32-7.48 (5H, m, **Ph**), 7.05 (1H, s, N**H**), 4.31 (2H, dq, *J* = 1.6, 7.1 Hz, OC**H**$_2$), 3.84 (1H, q, *J* = 7.3 Hz, C**H**CH_3, positive nOe with δ 9.54 (C**H**O) and 0.83 (CHC**H**$_3$)), 1.36 (3H, t, *J* = 7.2 Hz, OCH_2C**H**$_3$), 0.83 (2H, d, *J* = 7.2 Hz, CHC**H**$_3$) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.0, 161.7, 148.3, 131.8, 129.3, 128.7, 127.2, 82.3, 61.5, 42.3, 14.3, 12.8 ppm; IR (neat) 3327, 2987, 2931, 2890, 1724, 1570, 1494, 1252, 1231,1136, 1096, 1038, 702 cm^{-1}; HRMS (EI) exact mass calcd. for $C_{14}H_{16}N_2O_3$: m/z 261.1234 ($[M + H]^+$), fo*u*nd: m/z 260.1239 ($[M + H]^+$). $[\alpha]_D^{20}$ = -464.2 (*c* = 1.0, C_6H_6; 92% ee).



(*4S*, *5R*)-Ethyl 4-ethyl-5-formyl-5-phenyl-4,5-dihydro-*1H*-pyrazole-3-carboxylate (Table 3, entry 8).

The compound was prepared according to the general procedure with (*E*)-2-Phenylcrotonaldehyde (0.635 mmol, 101.7 mg) and ethyl diazoacetate (0.953 mmol, 108.7 mg) catalyzed by **1b** over a course of 1h. The crude material was purified by column chromatography on silica gel (eluting with dichloromethane/ethyl acetate = 20:1) to give the title cycloadduct as a pale colorless oil [81% yield (140.6 mg)].

The enantiomeric purity was determined by HPLC analysis (Daicel Chiralcel OD-H, hexane/2-propanol = 19:1, 1.0 mL/min, t_R = 22.7 min (major) and t_R = 33.0 min (minor)).

^{1}H NMR (300MHz, $CDCl_3$) δ 9.48 (1H, s, C**H**O), 7.35-7.48 (5H, m, ArH), 7.04 (1H, s, N**H**), 4.31 (2H, q, *J* = 7.2 Hz, OC**H**$_2$), 3.79 (1H, t, *J* = 5.4 Hz, C**H**CH_2CH_3), 1.50-1.64 (2H, m, CHC**H**$_2CH_3$), 1.36 (3H, t, *J* = 7.2 Hz, OCH_2C**H**$_3$), 0.58 (3H, t, *J* = 7.5 Hz, $CHCH_2$C**H**$_3$) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.8, 161.9, 147.5, 131.4, 129.3, 128.7, 127.4, 82.2, 61.5, 47.9, 20.7, 14.3, 10.2 ppm; IR (neat) 3324, 2889, 2851, 1724, 1571, 1427, 1223, 1103, 1039, 703 cm^{-1}; HRMS (EI) exact mass calcd. for $C_{15}H_{18}N_2O_3$: m/z 275.1390 ($[M + H]^+$), found: m/z 275.1396 ($[M + H]^+$); $[\alpha]_D^{20}$ = -457.4 (*c* = 1.0, C_6H_6; 99% ee).

Notes and references

1. Triflic acid reacts with P_2O_5 to form triflic anhydride. Therefore, only a small amount of P_2O_5

was used and the forerun containing triflic anhydride was discarded.

2. (a) E. J. Corey, B. B. Snider, *J. Am.Chem. Soc.* **1972**, *94*, 2549. (b) E. J. Corey, T. P. Loh, *J. Am.Chem. Soc.* **1991**, *113*, 8966.

3. (a) C. S. Marvel, R. L. Myers, J. H. Saunders, *J. Am. Chem, Soc.* **1948**, *70,*1694. (b) G. Riehs, E. Urban, *Tetrahedron*. **1996**, *52*, 1221. (c) N. T. Reynolds, T. Rovis, *Tetrahedron.* **2005**, *61*, 6368. (d) A. Erkkilä, P. M. Pihko, *J. Org. Chem.* **2006**, *71*, 2538. (e) D. H. Ryu, T. W. Lee, E. J. Corey, *J. Am. Chem, Soc.* **2002**, *124*, 9992. (f) K**.** Clinch, C. J. Marquez, M. J. Parrott, R. Ramage, *Tetrahedron*. **1989**, *45*, 239. (g) A. Naya, M. Ishikawa, K. Matsuda, K. Ohwaki, T. Saeki, K. Noguchi, N. Ohtake, *Bioorg. Med. Chem.* **2003**, *11*, 875.

4. Molecular sieves (pellets) were dried in *vacuo* at *ca.* 200 ^{o}C with a gas burner for 20 min prior to use.

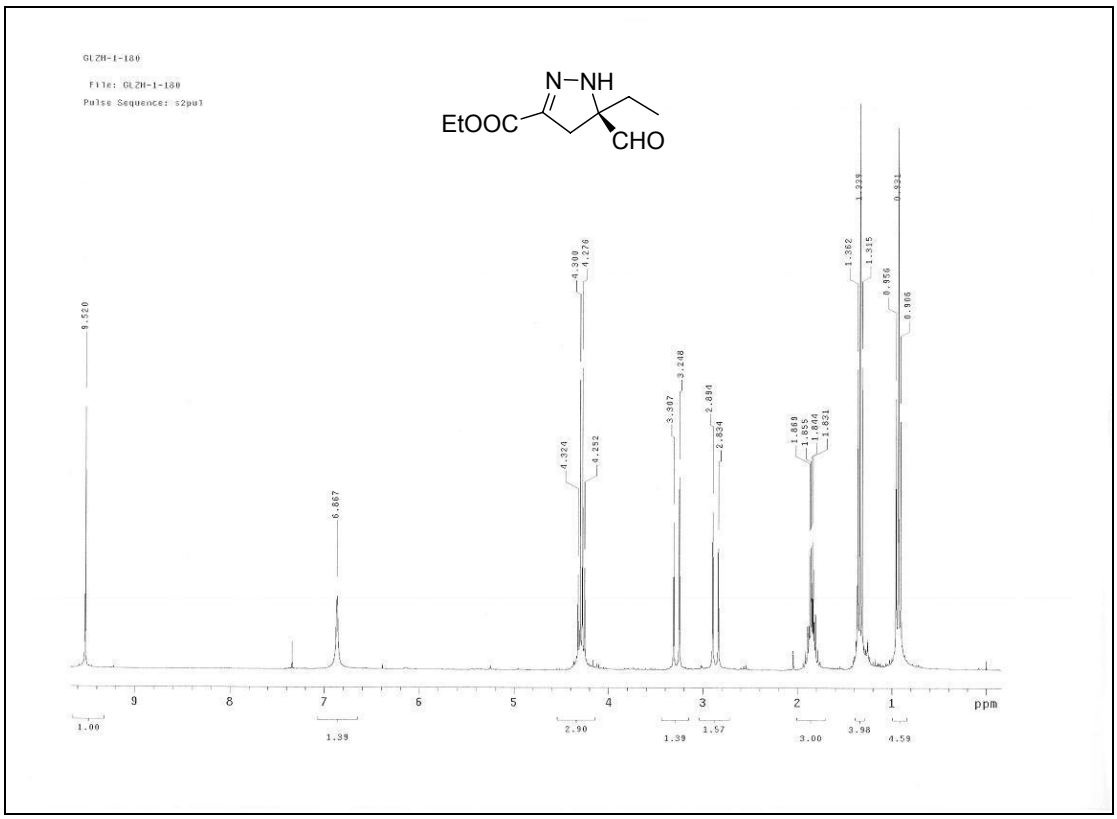
5. D. J. Mathre, T. K. Jones, L. C. Xavier, T. J. Blacklock, T. A. Reamer, J. J. Mohan, E. T. T. Jones, K. Hoogsteen, M. W. Baum, E. J. J. Grabowski, J. *Org. Chem.* **1991**, *56*, 751.

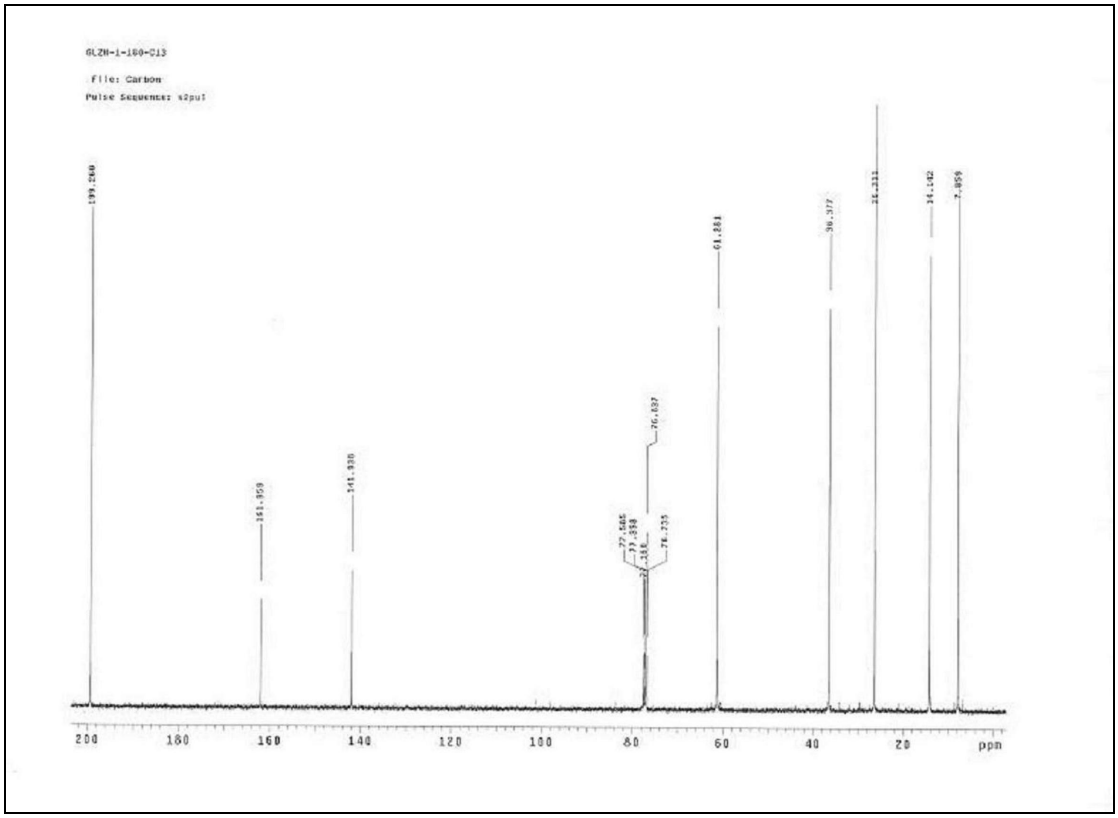
6. D. H. Ryu, E. J. Corey, *J. Am. Chem. Soc*. **2004**, *126*, 8106.

7. Dichloromethane was used in the cycloaddition of α-substituted acrolein with alkyl diazoacetate and propionitrile was used in the cycloaddition of α,β-disubstituted acrolein with ethyl diazoacetate.

8. T. Kano, T. Hashimoto, K. Maruoka, *J. Am. Chem. Soc*. **2006**, *128*, 2174.

^{1}H NMR and ^{13}C NMR Spectra of Pyrazolines

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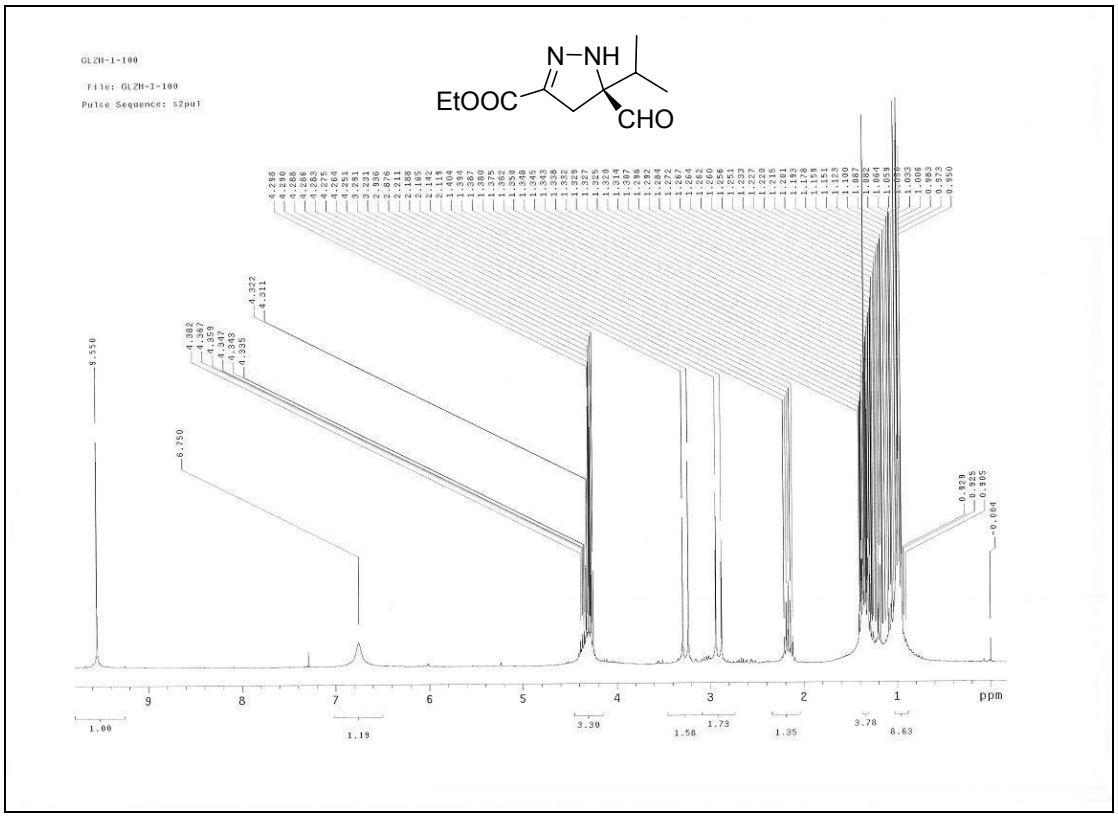
80
60
40
20
ppm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4.343
4.335
0.929
0.925
0.905
0.064
9
8
7
6
5
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ppm
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1.35
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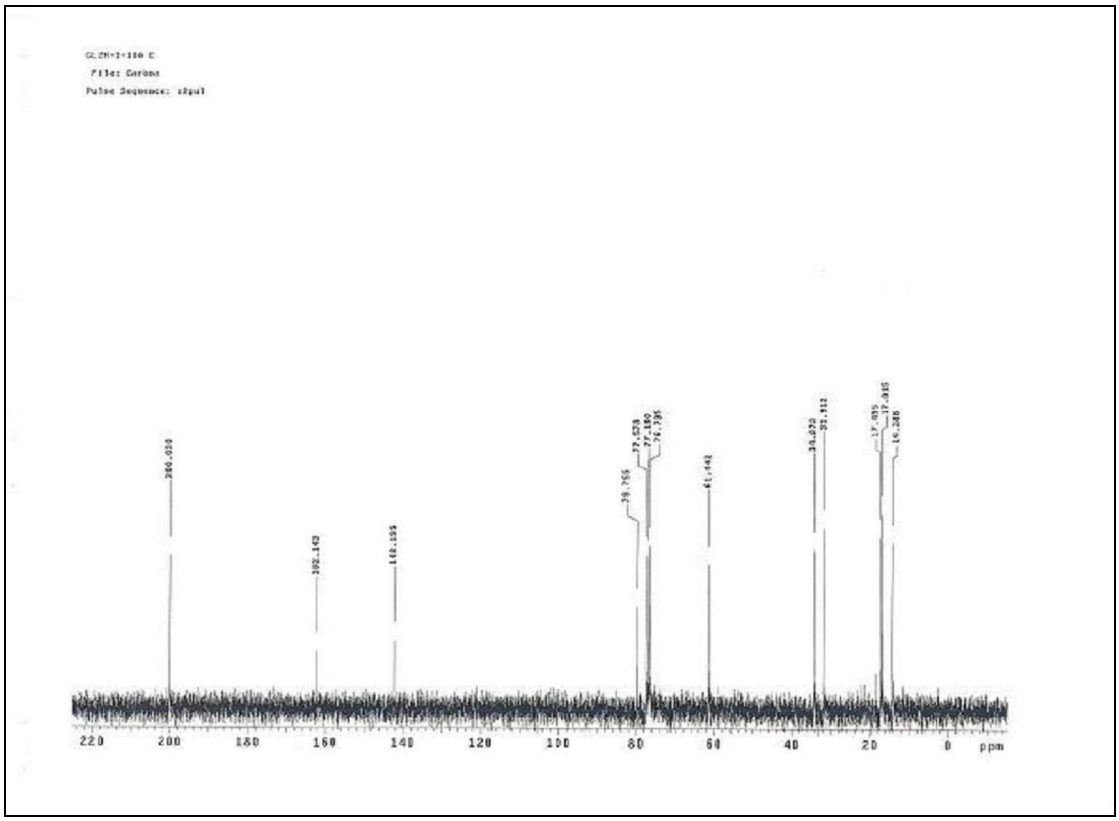
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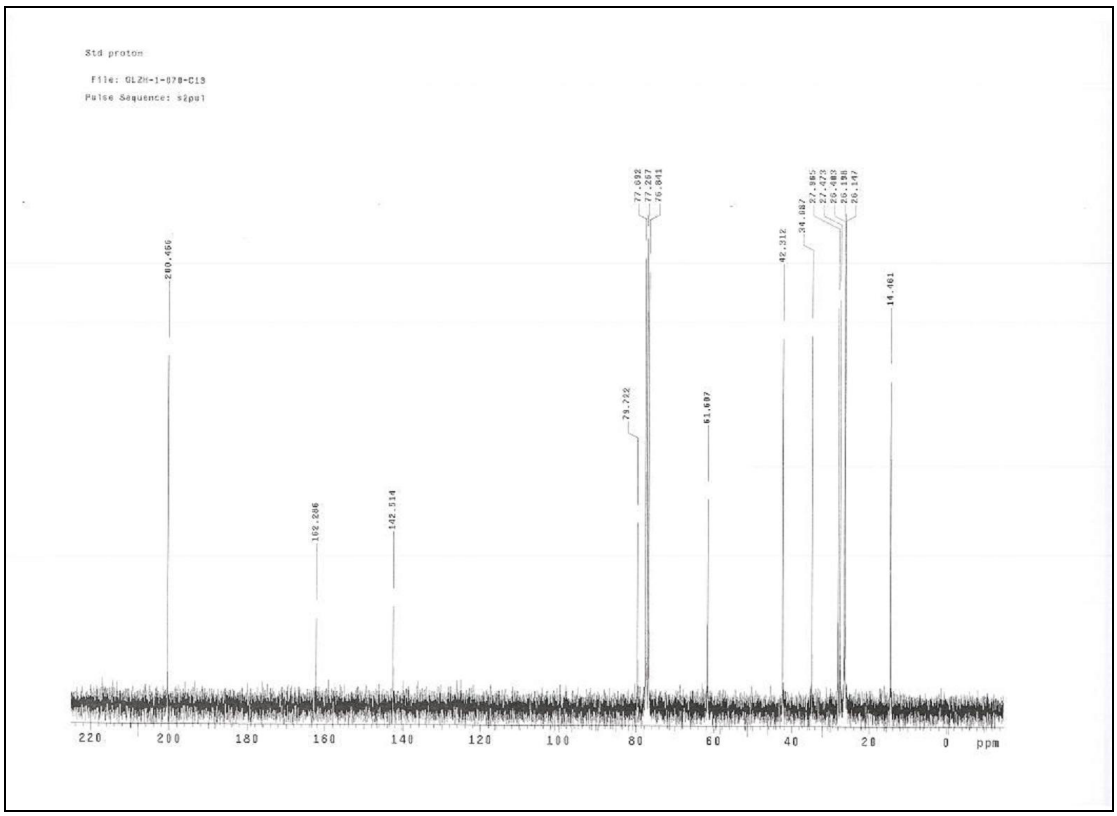
CHO
ppm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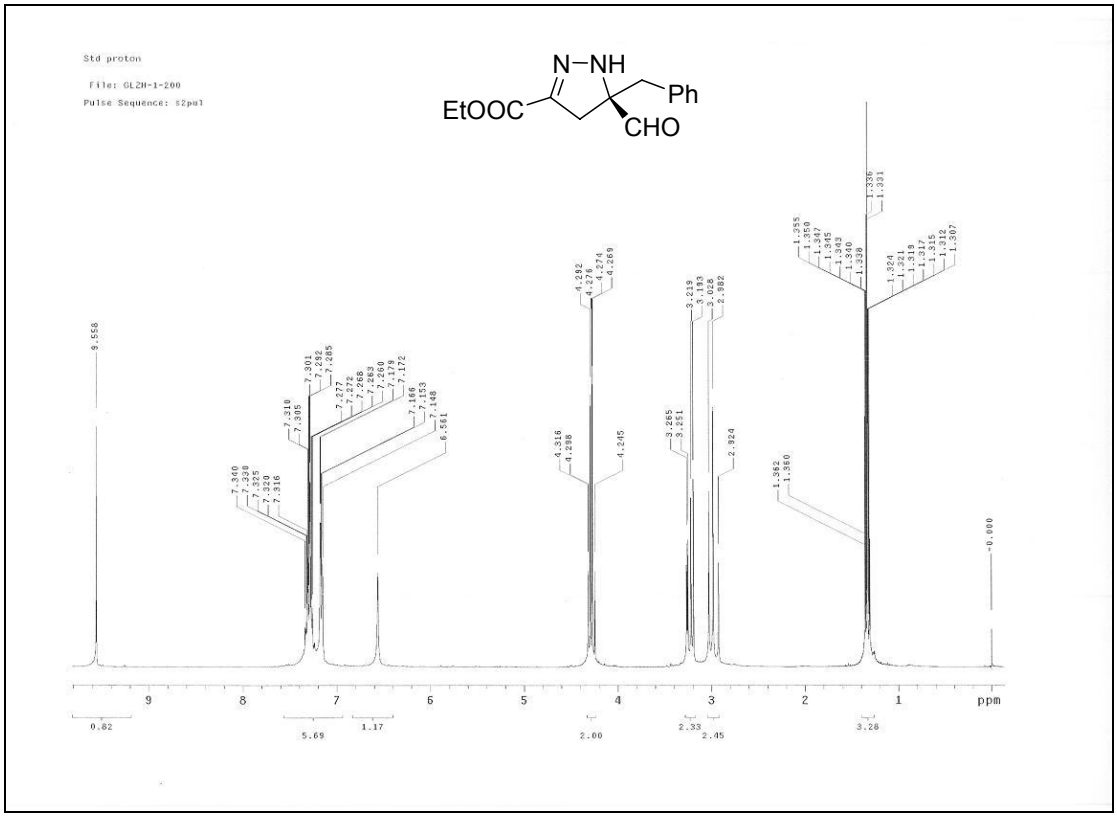
ppm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Ph
CHO
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5
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3
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2.33
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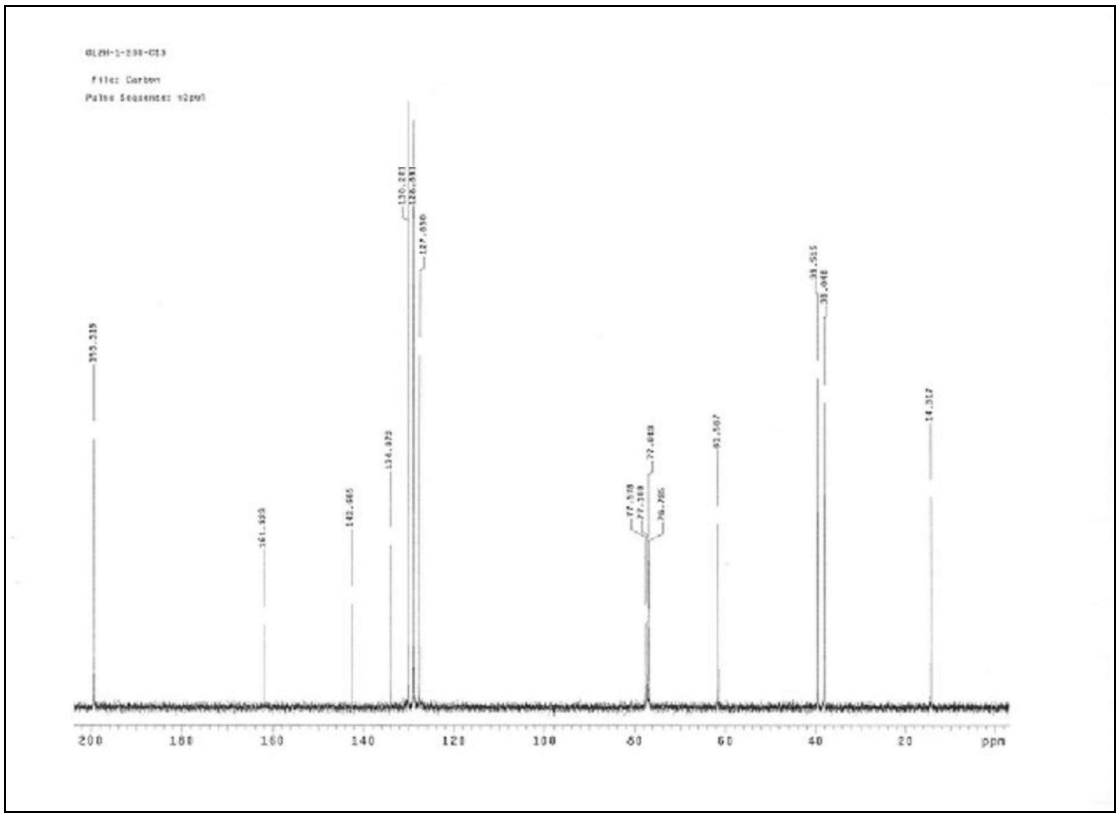
3.28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80
60
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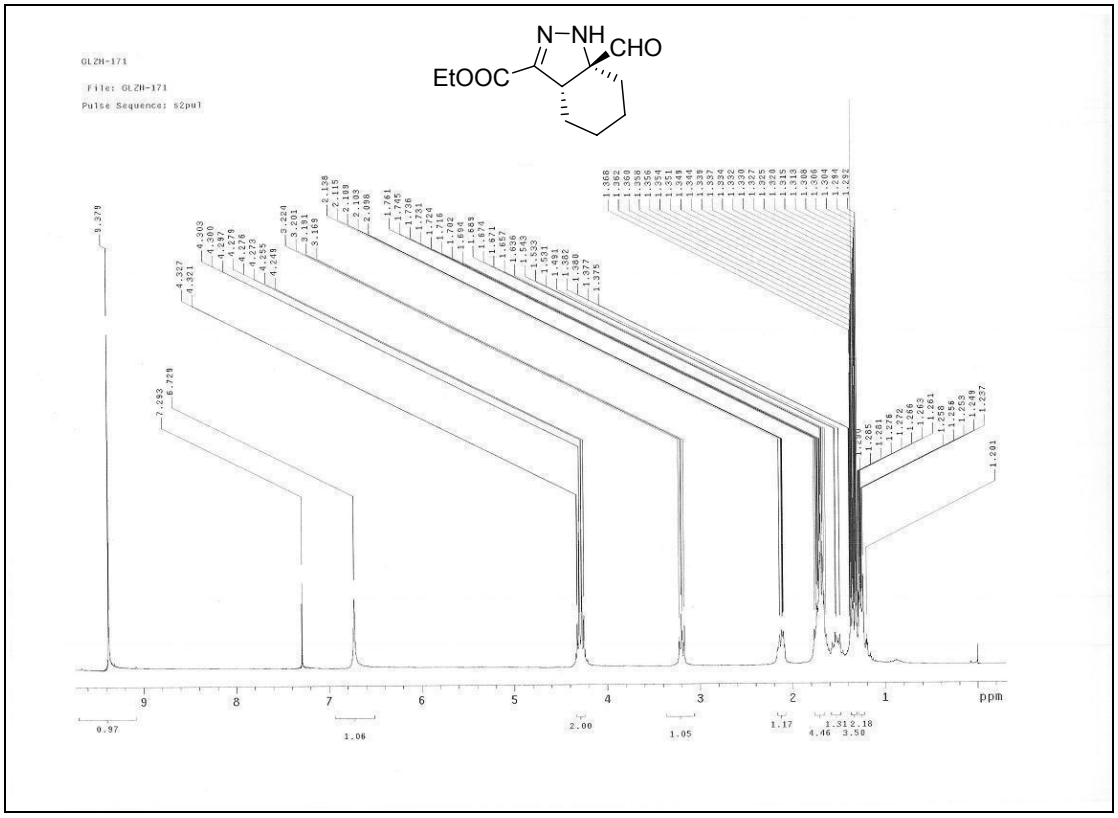
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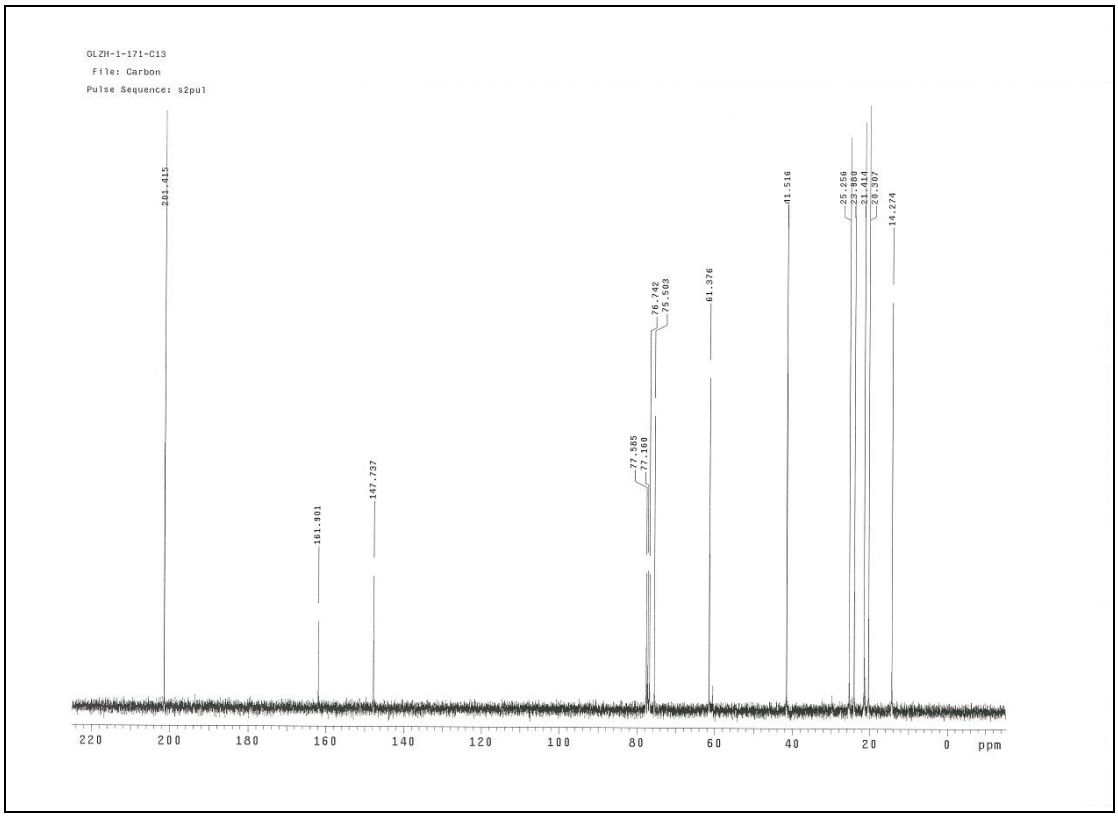
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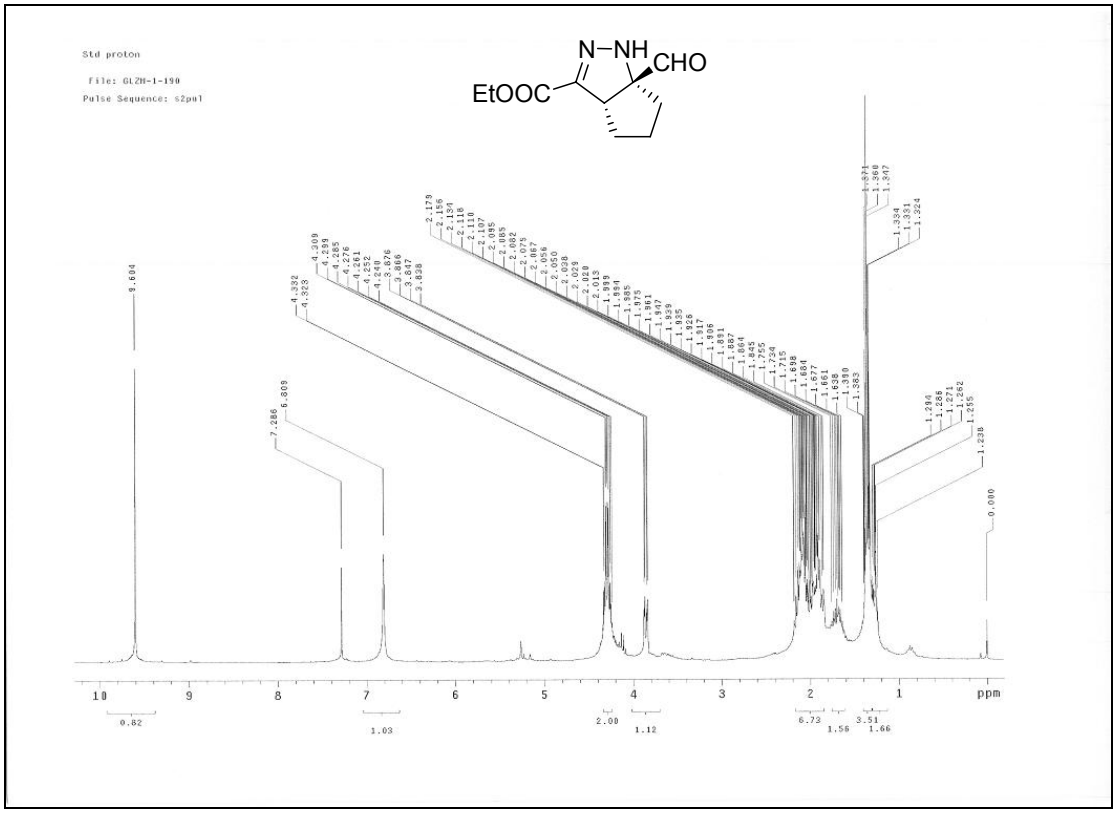
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7
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2
1
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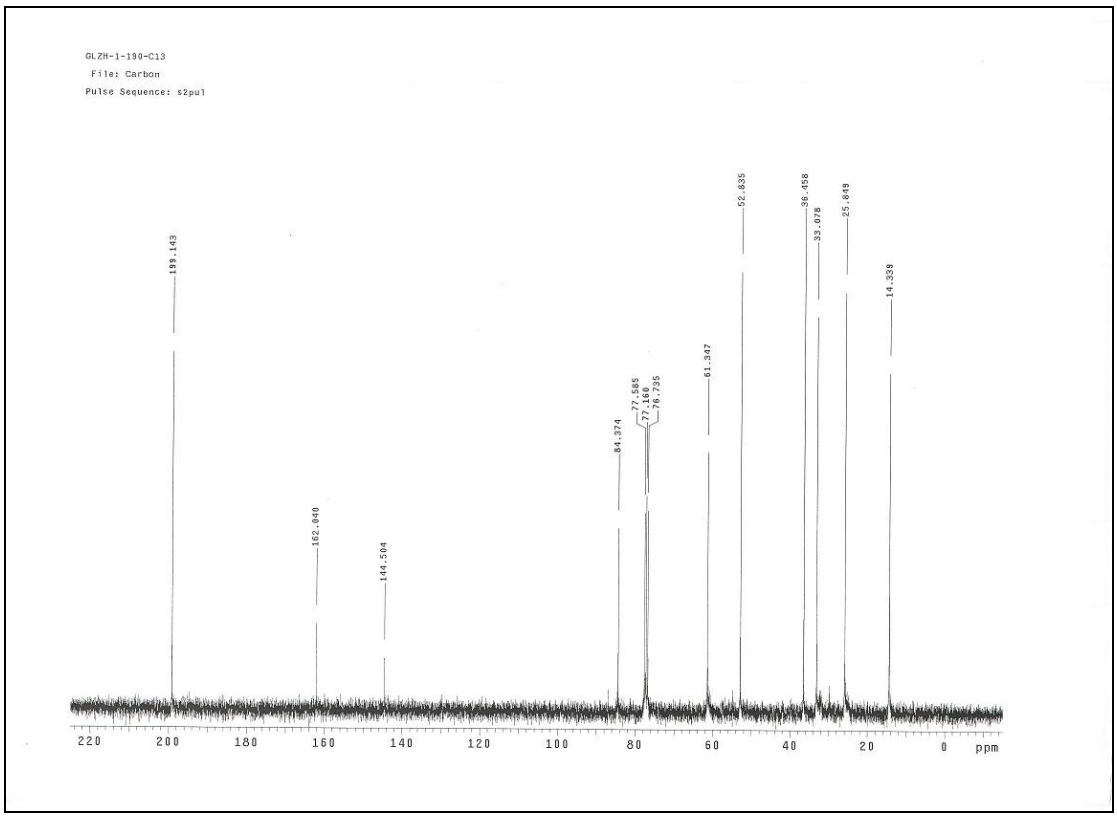
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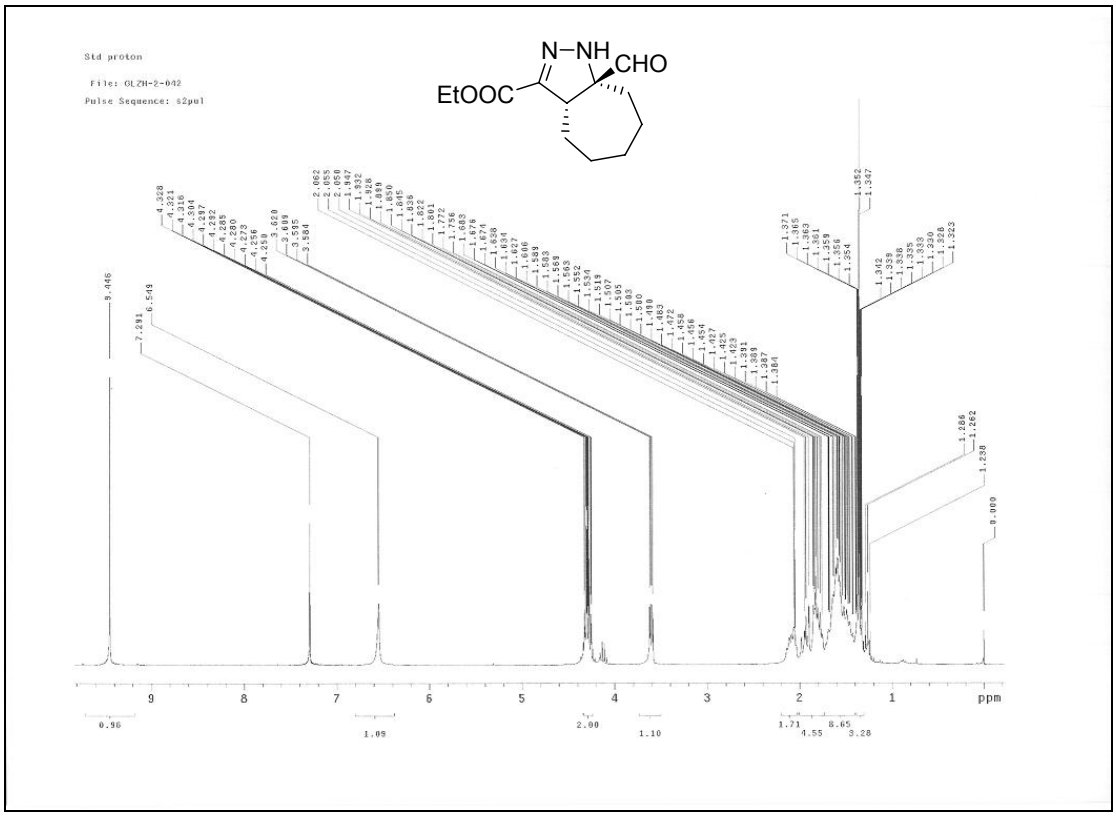
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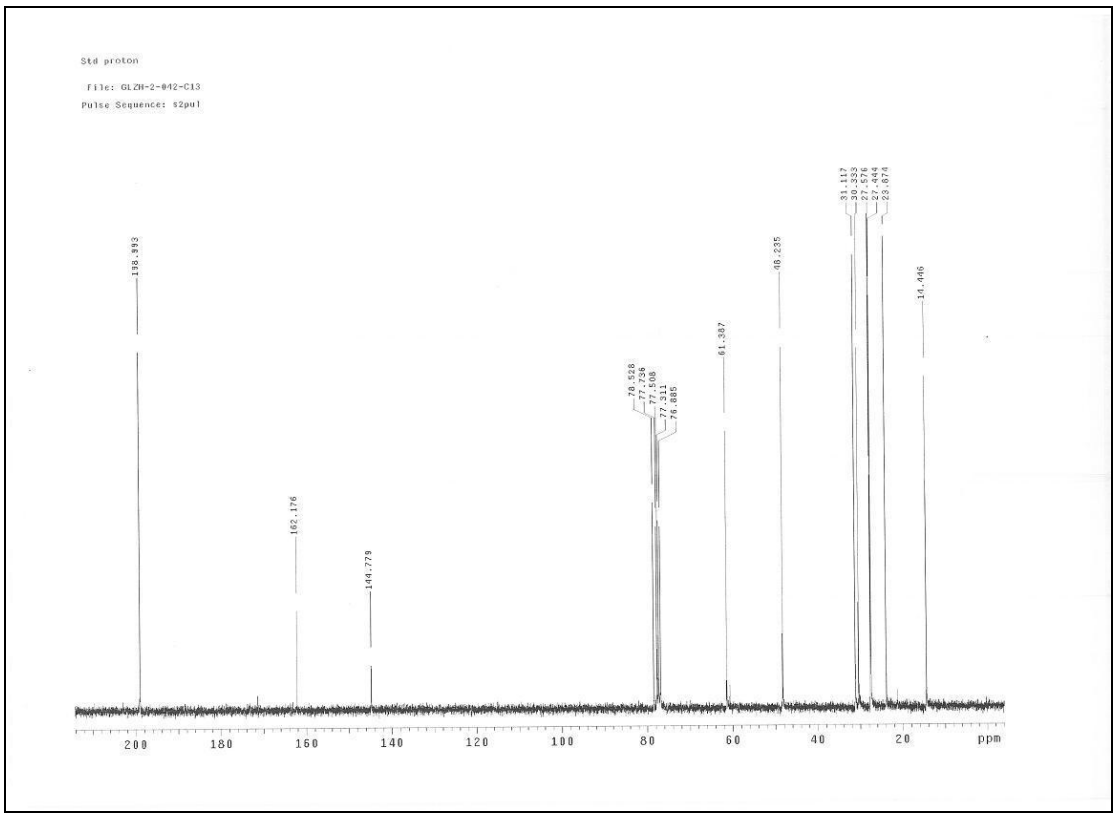
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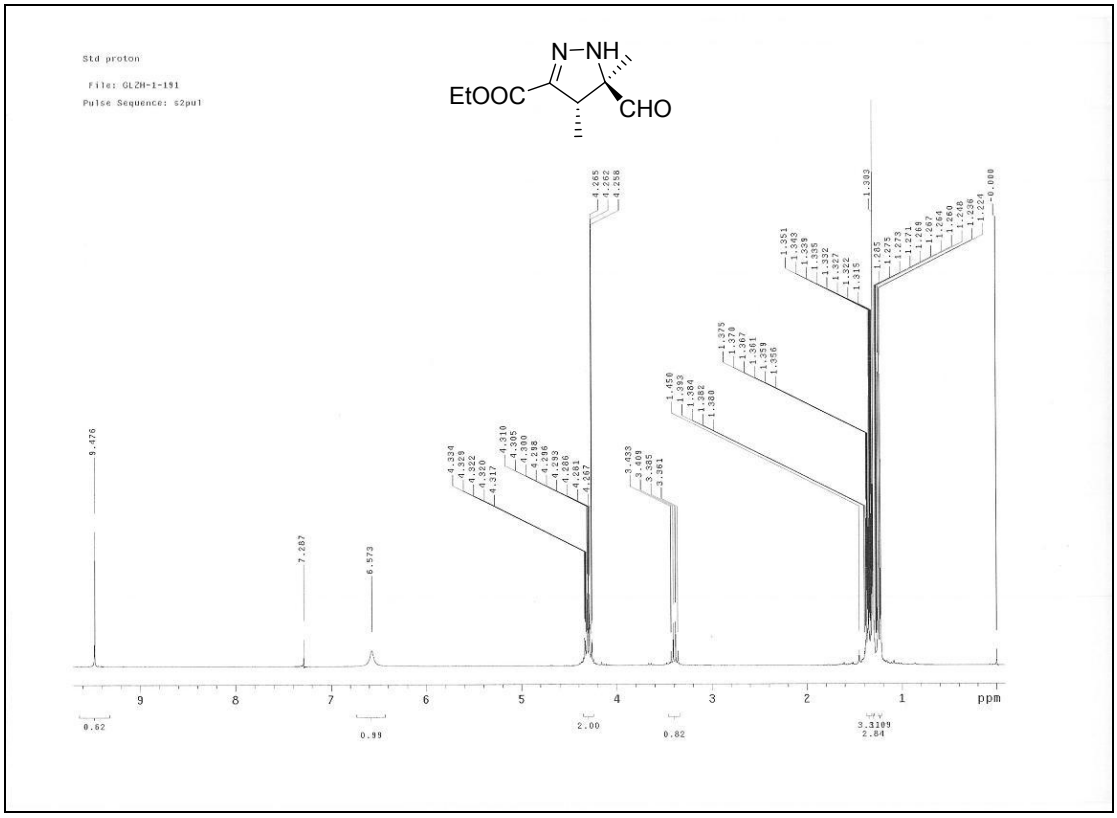
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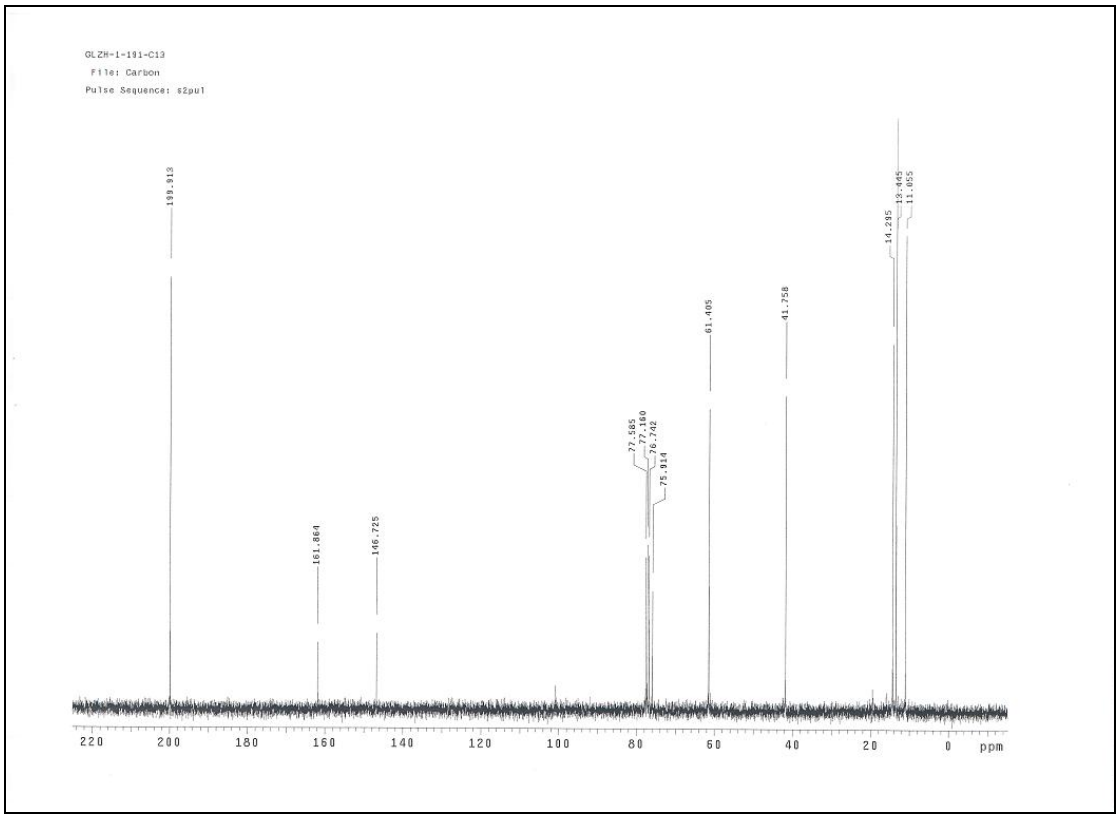
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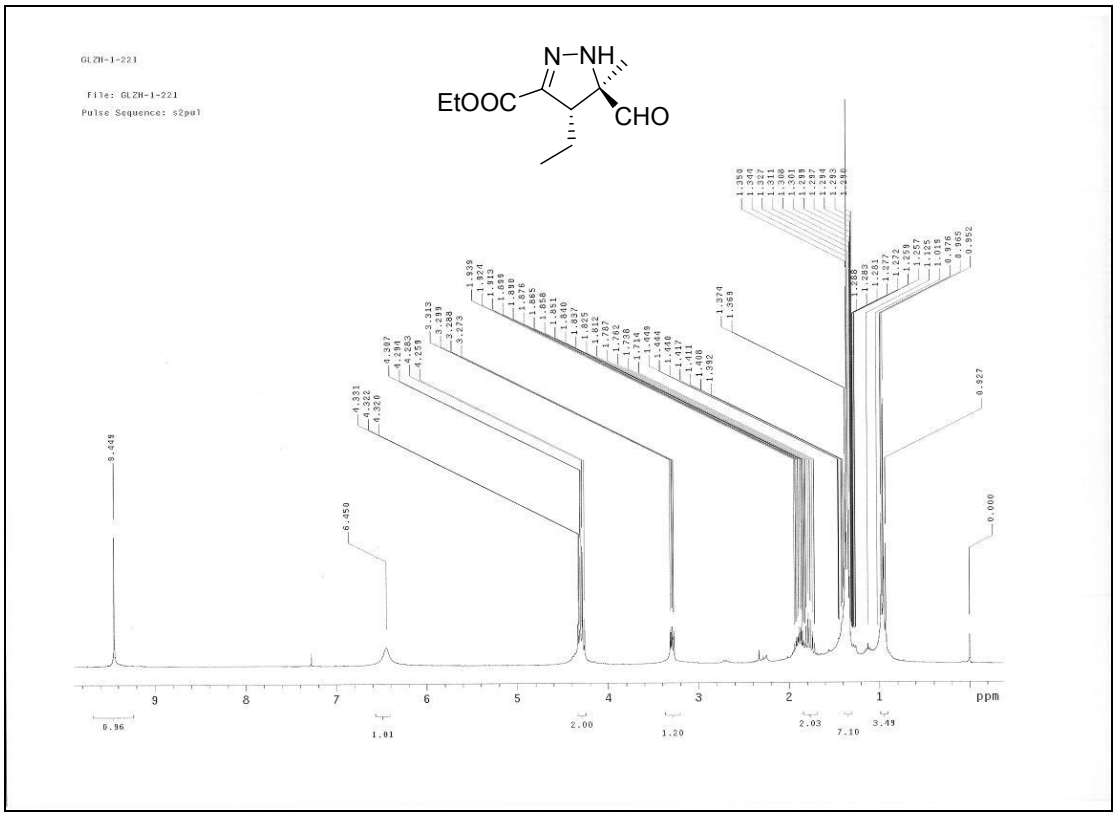
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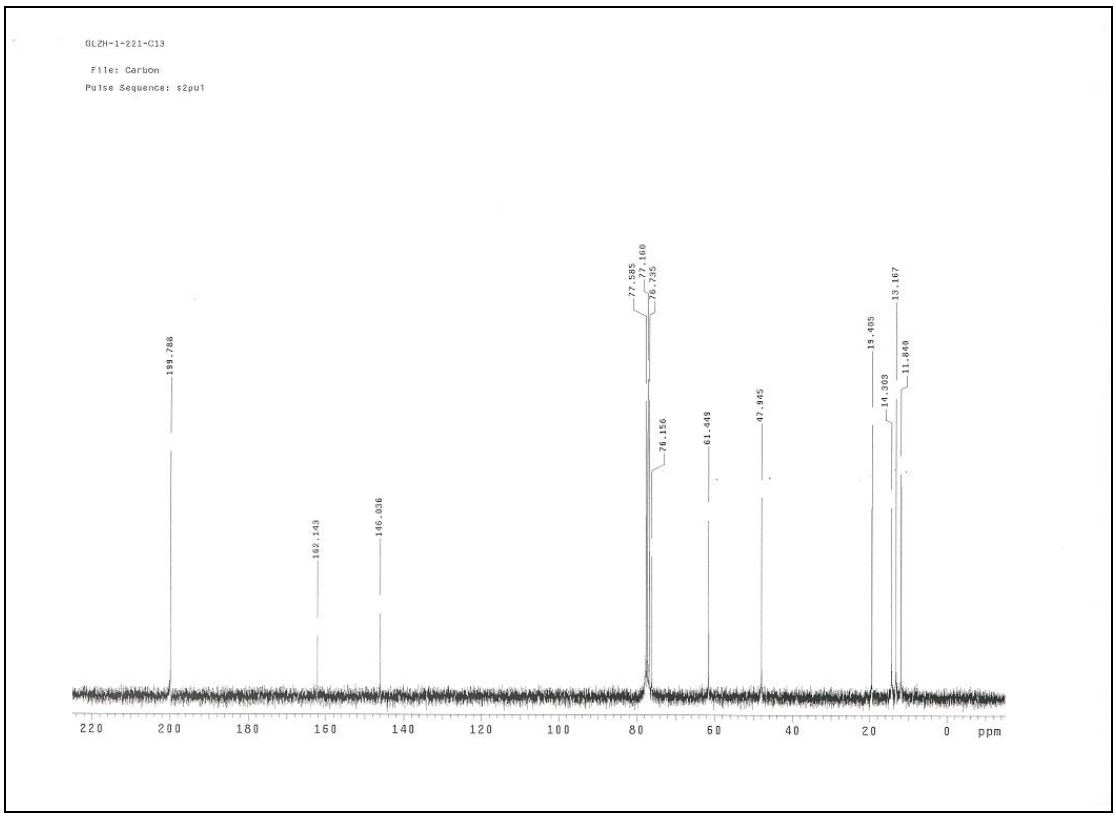
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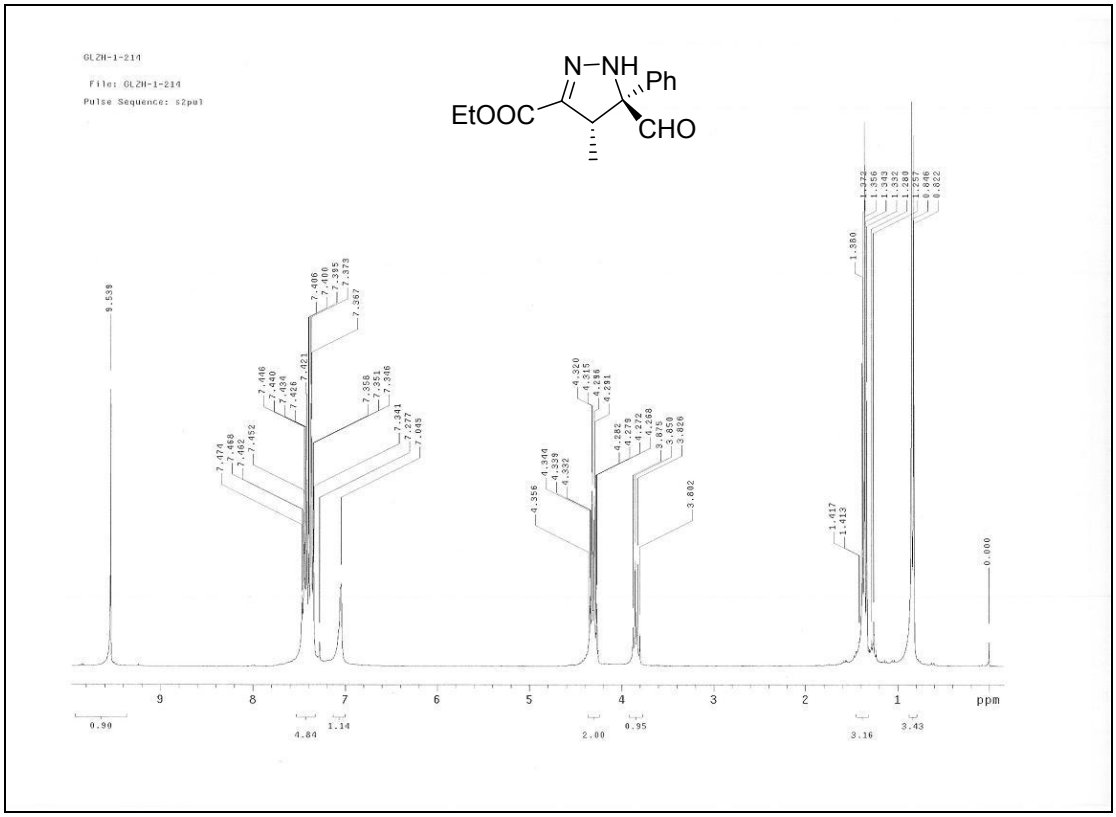
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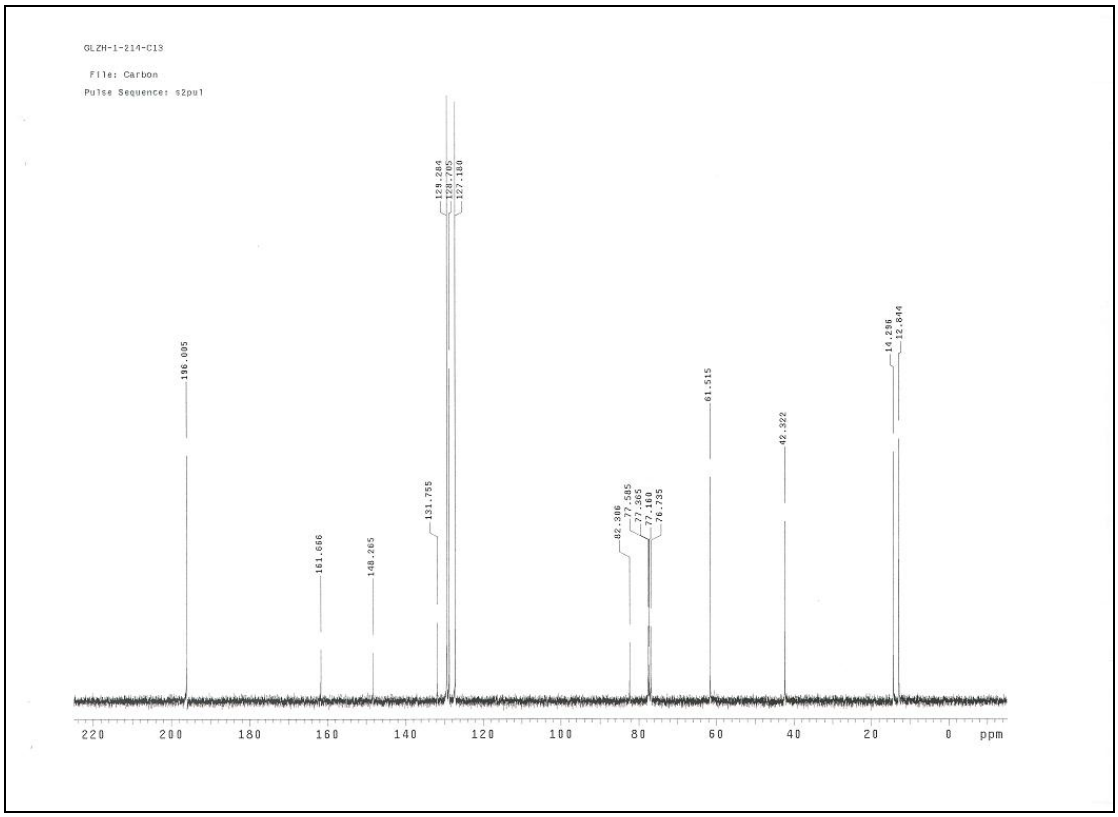
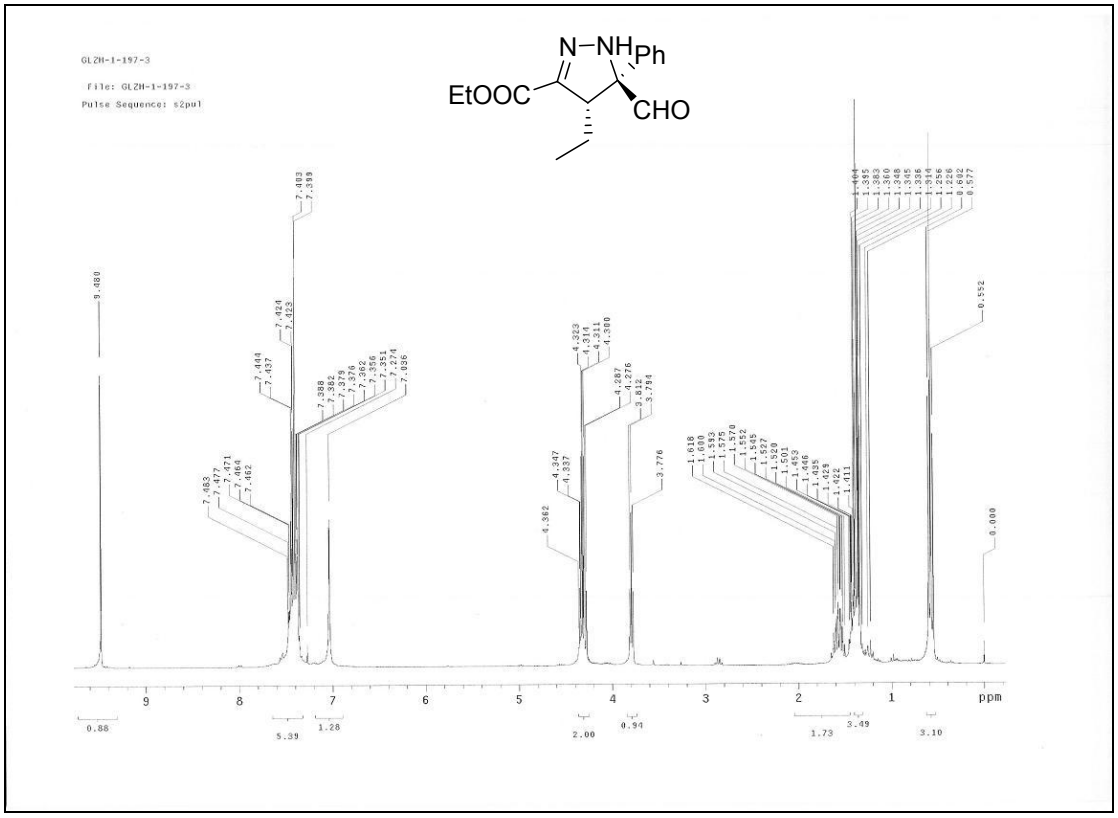
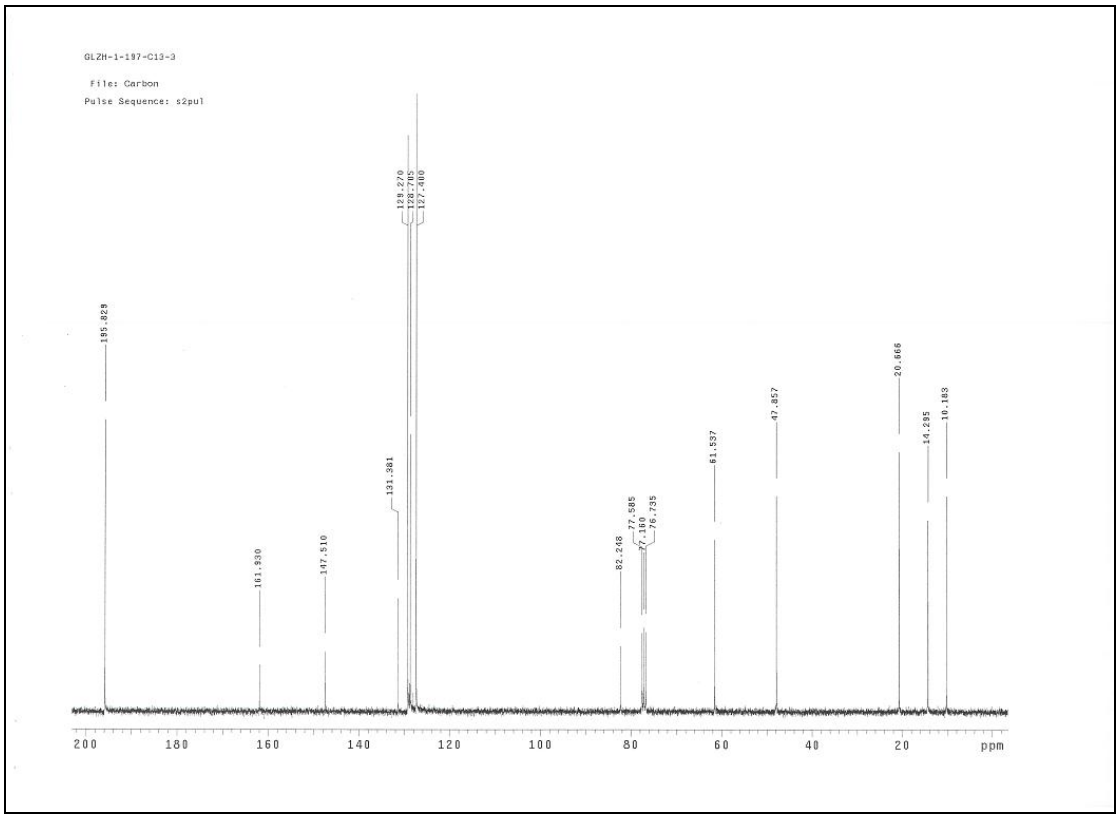
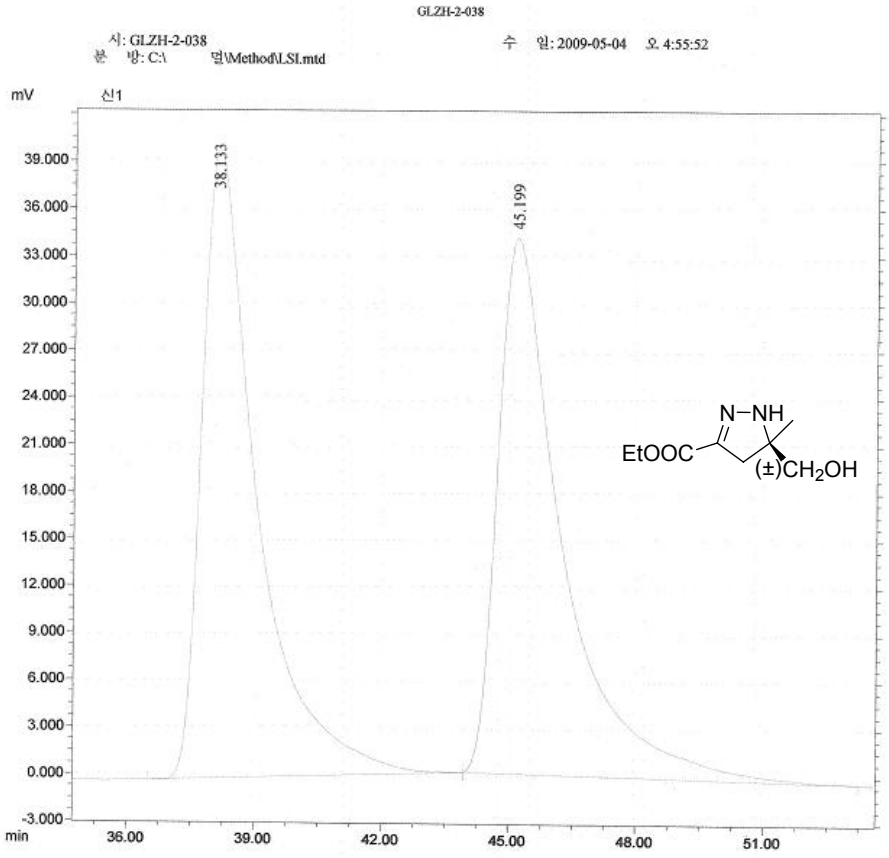
3.16
3.43


GLZH-1-214-C13
File: Carbon
Pulse Sequence: s2pul
196.095
161.666
148.265
131.755
129.284
128.805
127.180
82.306
77.585
77.365
77.160
76.735
61.515
42.322
14.286
12.644
220
200
180
160
140
120
100
80
60
40
20
0
ppm


GLZH-1-197-3
File: GLZH-1-197-3
Pulse Sequence: s2pul
N–NHPh
EtOOC
CHO
9.480
7.493
7.489
7.483
7.477
7.471
7.466
7.462
7.424
7.423
7.414
7.407
7.388
7.382
7.379
7.376
7.362
7.356
7.351
7.274
7.036
4.362
4.347
4.337
4.323
4.314
4.311
4.300
4.287
4.276
3.812
3.794
3.776
1.618
1.600
1.593
1.575
1.570
1.552
1.545
1.527
1.520
1.503
1.453
1.446
1.435
1.428
1.422
1.411
1.404
1.395
1.383
1.360
1.345
1.336
1.314
1.295
1.226
0.692
0.577
0.552
0.000
9
8
7
6
5
4
3
2
1
ppm
0.88
5.39
1.28
2.00
0.94
1.73
3.49
3.10



HPLC Spectra

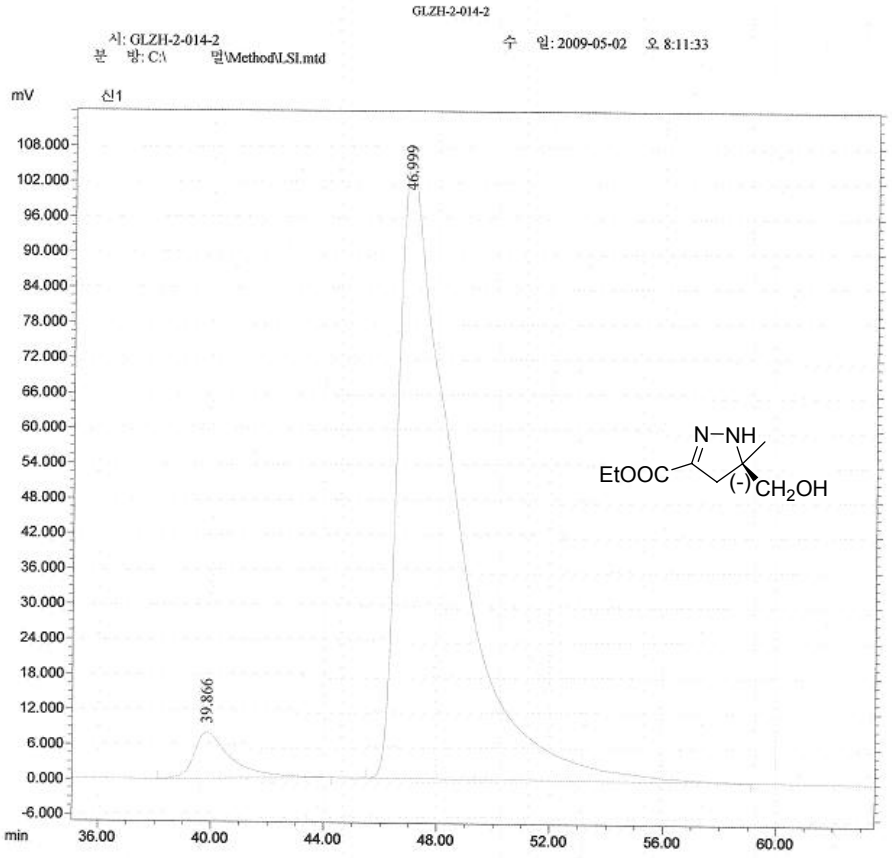


	머 시 [min]	면 [uV*sec]	면% [%]	표
	38.133	3624341.29	50.058	BMB
	45.199	3615932.42	49.942	BMB
Σ		7240273.72	100.000	

데:
flow= 0.5
IPA:Hex= 1:9
256nm
OJ-H
6 μℓ

- 1 -

Table 1, Entry 5

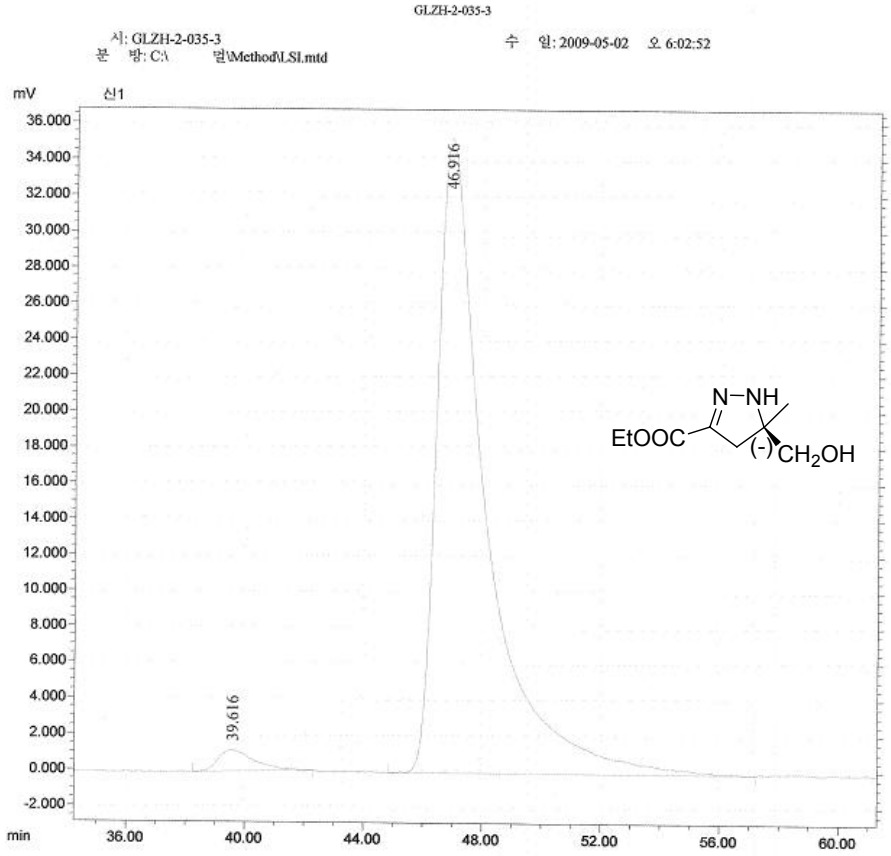


	머 시 [min]	면 [uV*sec]	면% [%]	표
A?	39.866	716821.87	4.681	BMB
A?	46.999	14595168.55	95.319	BMB
Σ		15311990.42	100.000	

데:
flow= 0.5
IPA:Hex= 1:9
256nm
OJ-H
6 μℓ

- 1 -

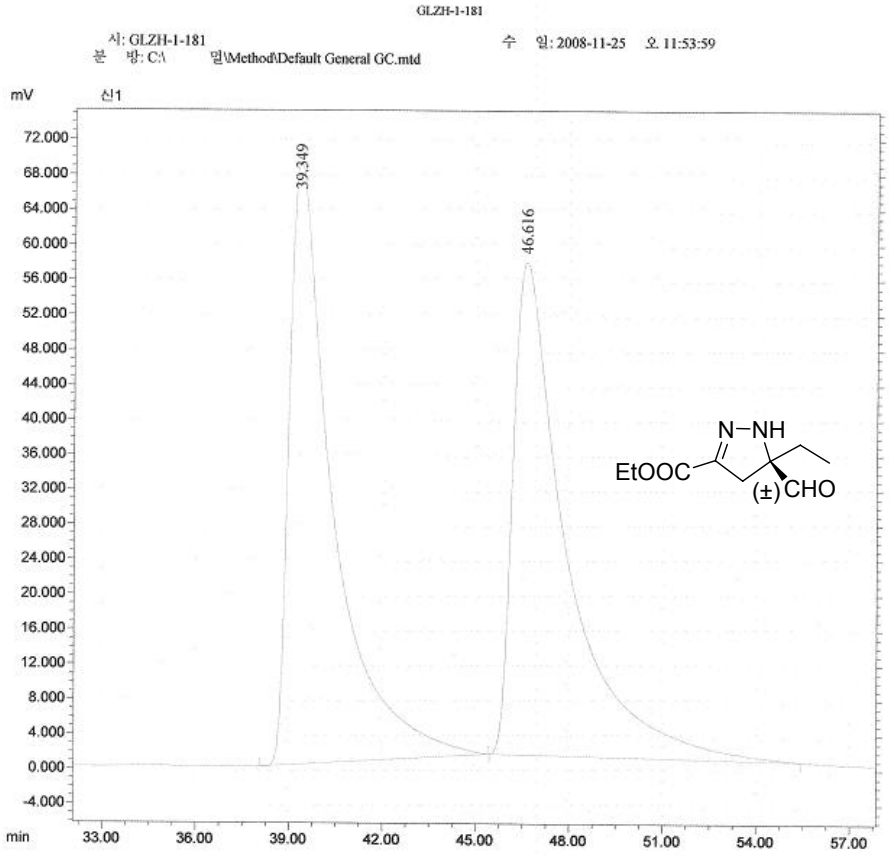
Table 2, Entry 1



	머 시 [min]	면 [uV*sec]	면% [%]	표
A?	39.616	98736.22	2.369	BMB
A?	46.916	4069822.29	97.631	BMB
Σ		4168558.50	100.000	

테:
flow= 0.5
IPA:Hex= 1:9
256nm
OJ-H
6 μℓ

- 1 -



	머 시 [min]	면 [uV*sec]	면% [%]	표
A?	39.349	6751276.70	50.007	BMB
A?	46.616	6749409.50	49.993	BMB
Σ		13500686.20	100.000	

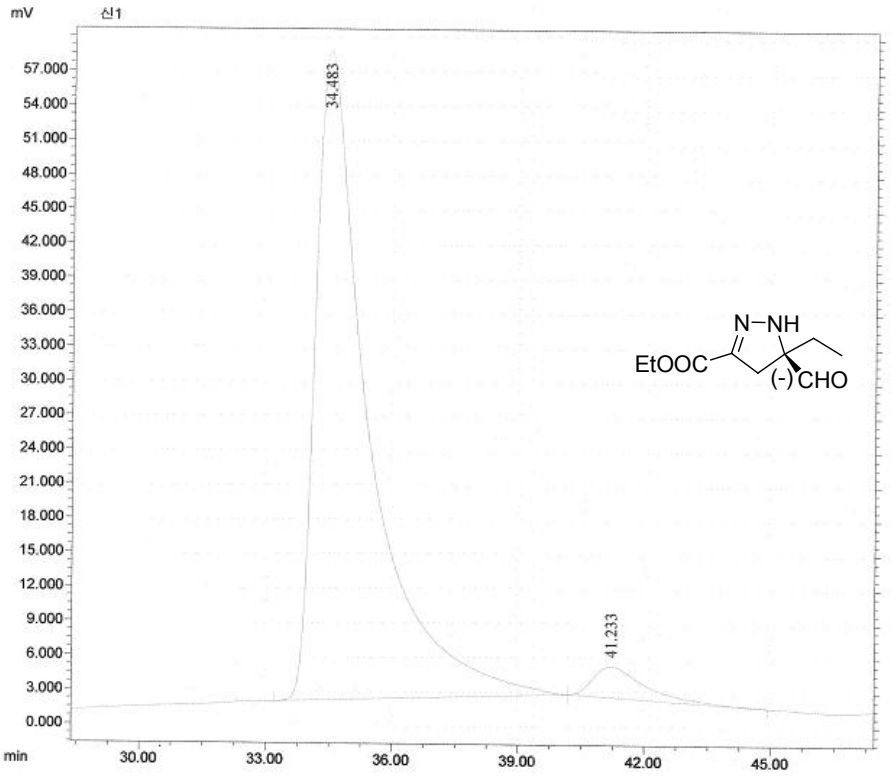
테:
OJ-H
flow=1
IPA:Hex=5:95
256nm
5㎕

- 1 -

Table 2, Entry 2

GLZH-1-180-3

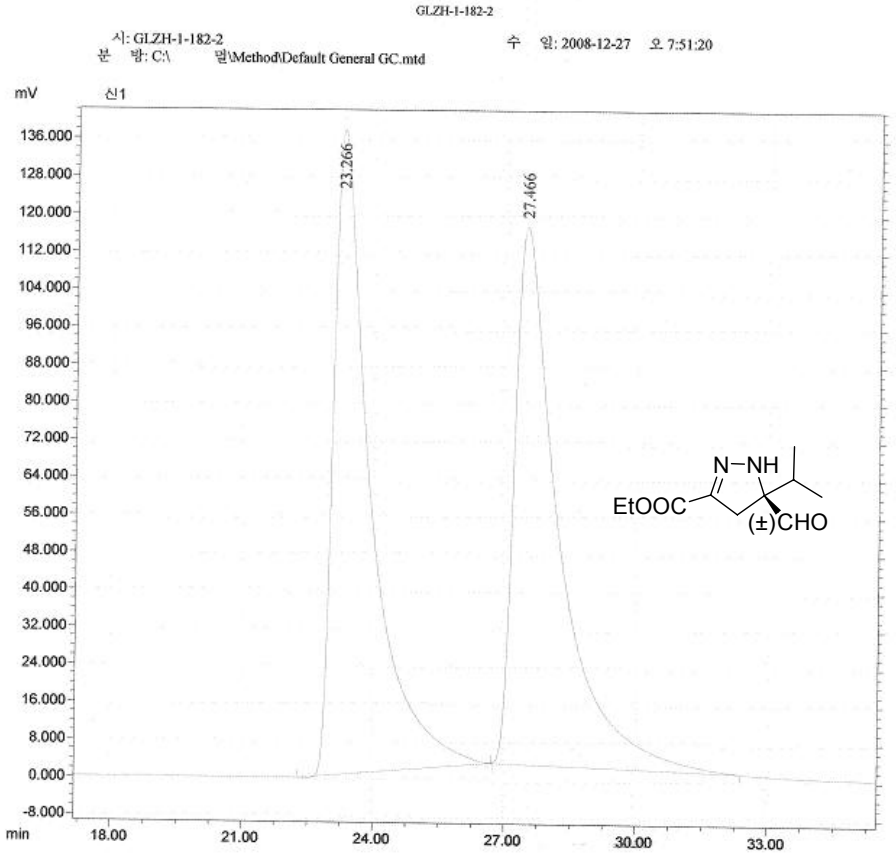
시: GLZH-1-180-3 수 일: 2008-11-26 오 2:36:46
분 방: C:\ 널\Method\Default General GC.mtd



	머 시 [min]	면 [uV*sec]	면% [%]	표
BA?	34.483	5017729.48	95.585	BMB
BA?	41.233	231751.14	4.415	BMB
Σ		5249480.62	100.000	

테:
OJ-H
flow=1.0
IPA:Hex=5:95
256nm
5㎕

- 1 -



	머 시 [min]	면 [uV*sec]	면% [%]	표
1	23.266	8078214.32	49.955	BMB
2	27.466	8092760.41	50.045	BMB
Σ		16170974.73	100.000	

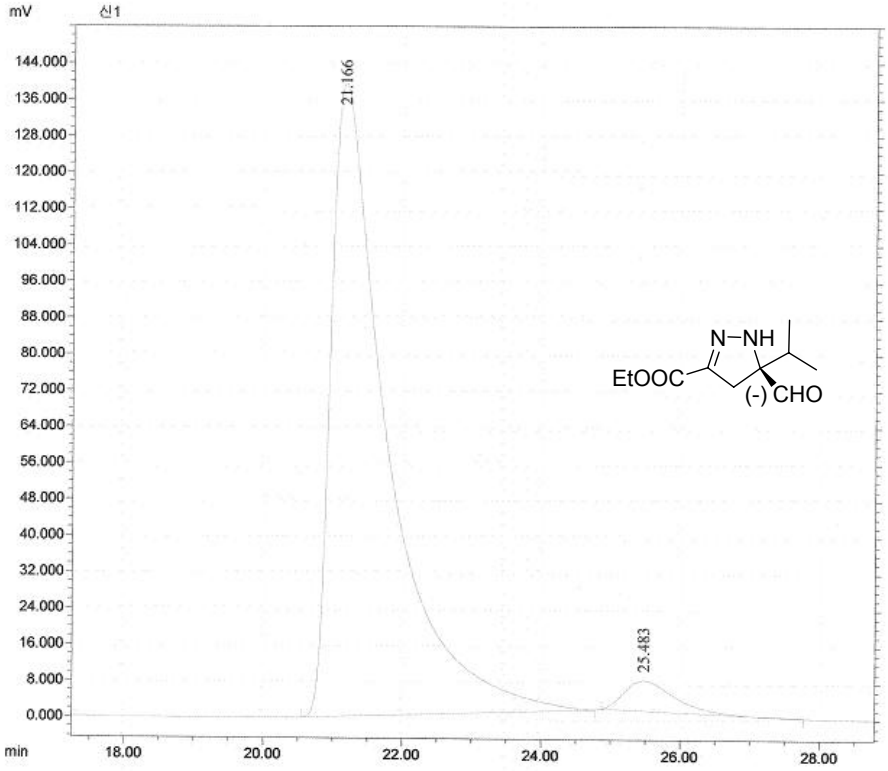
데:
flow=1.0
IPA:Hex=5:95
256nm
OJ-H
6 μℓ

- 1 -

Table 2, Entry 3

GLZH-1-199-2

시: GLZH-1-199-2 수 일: 2008-12-30 오 12:01:57
분 방: C:\ 델\Method\Default General GC.mtd



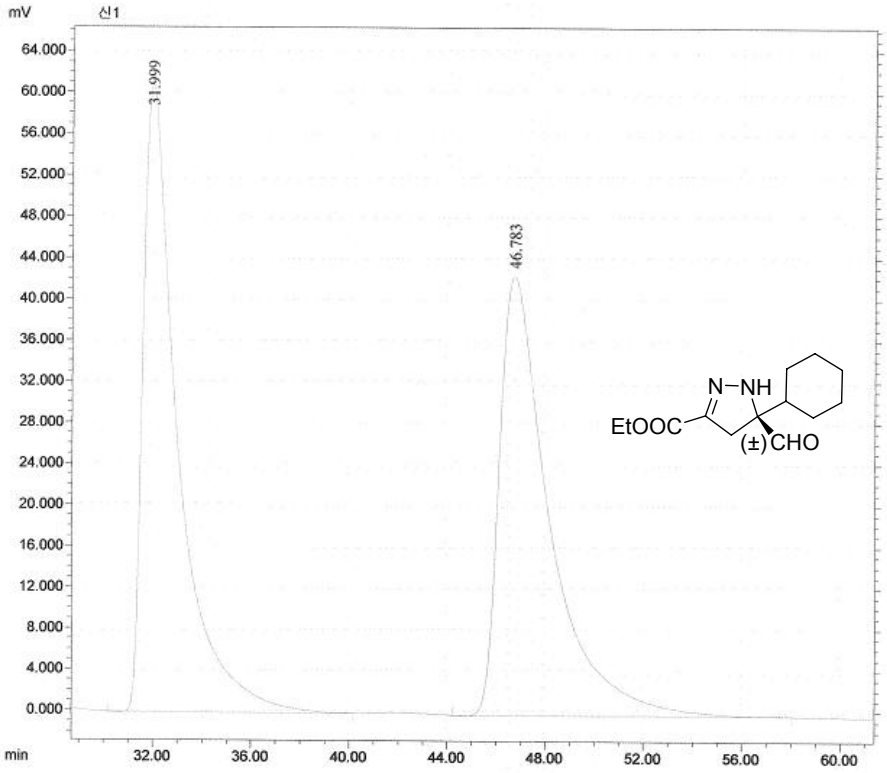
	머 시 [min]	면 [uV*sec]	면% [%]	표
	21.166	7864631.62	95.929	BMB
	25.483	333762.29	4.071	BMB
Σ		8198393.91	100.000	

데:
flow=1.0
IPA:Hex=5:95
256nm
OJ-H
6 μℓ

- 1 -

GLZH-1-178-5

시: GLZH-1-178-5 수 일: 2009-03-27 오 8:51:28
분 방: C:\ 털\Method\LSI.mtd



	머 시 [min]	면 [uV*sec]	면% [%]	표
A?	31.999	6028159.64	49.793	BMB
A?	46.783	6078184.86	50.207	BMB
Σ		12106344.50	100.000	

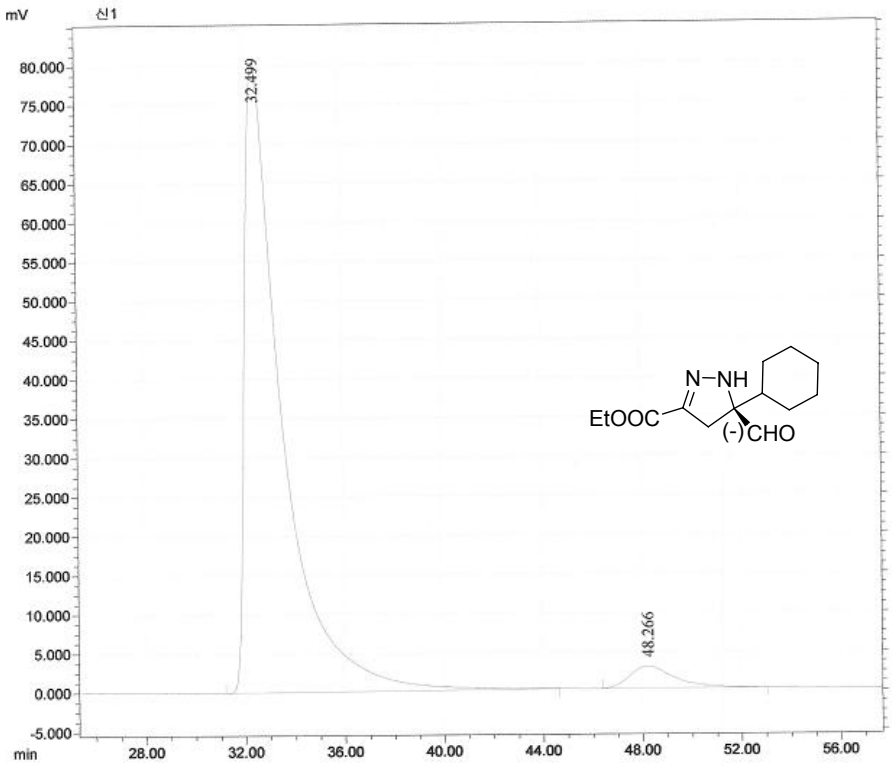
데:
flow= 1.0
IPA:Hex= 3:97
256nm
OJ-H
5 μℓ

- 1 -

Table 2, Entry 4

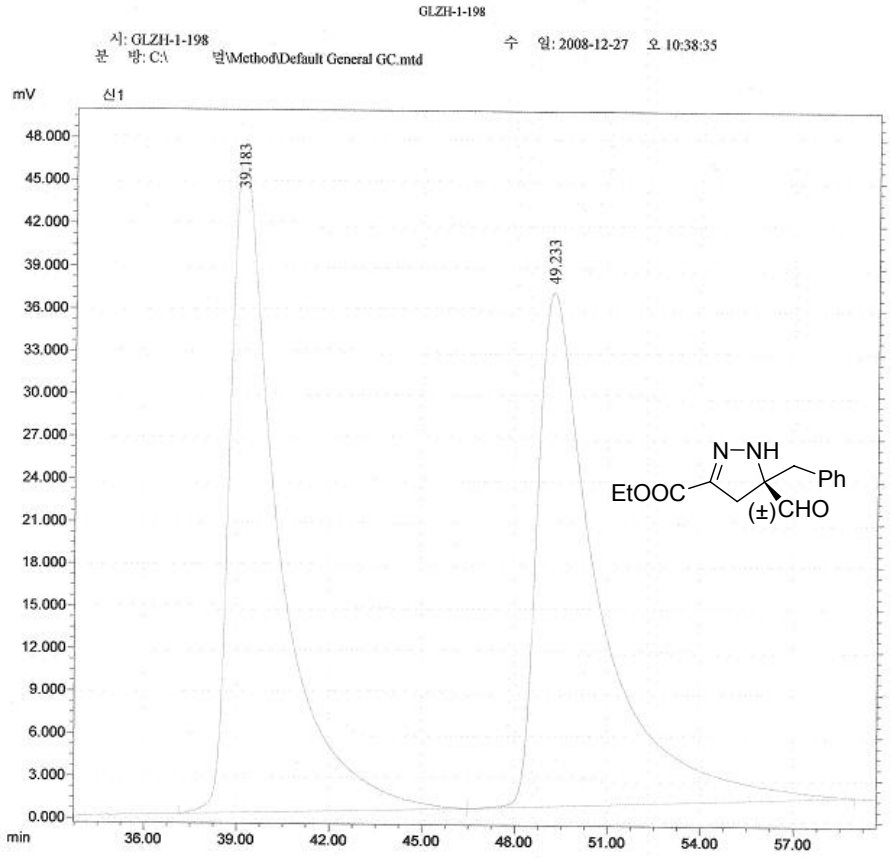
GLZH-1-218-2

시: GLZH-1-218-2 수 일: 2009-03-28 오 12:01:57
분 방: C:\ 릴\Method\LSI.mtd



	머 시 [min]	면 [uV*sec]	면% [%]	표
A?	32.499	8348565.40	95.970	BMB
A?	48.266	350607.98	4.030	BMB
Σ		8699173.38	100.000	

메:
flow= 1.0
IPA:Hex= 3:97
256nm
OJ-H
5 μℓ



	머 시 [min]	면 [uV*sec]	면% [%]	표
A?	39.183	5001334.94	50.073	BMB
A?	49.233	4986660.23	49.927	BMB
Σ		9987995.17	100.000	

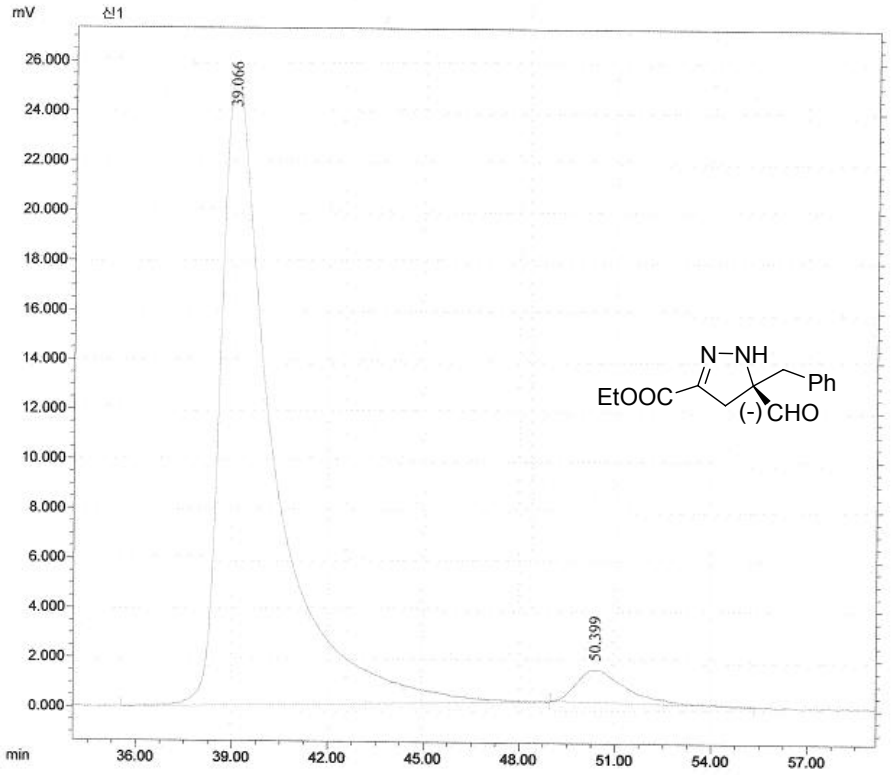
데:
flow=1.0
IPA:Hex=1:9
256nm
OJ-H
4 μℓ

- 1 -

Table 2, Entry 7

GLZH-1-219

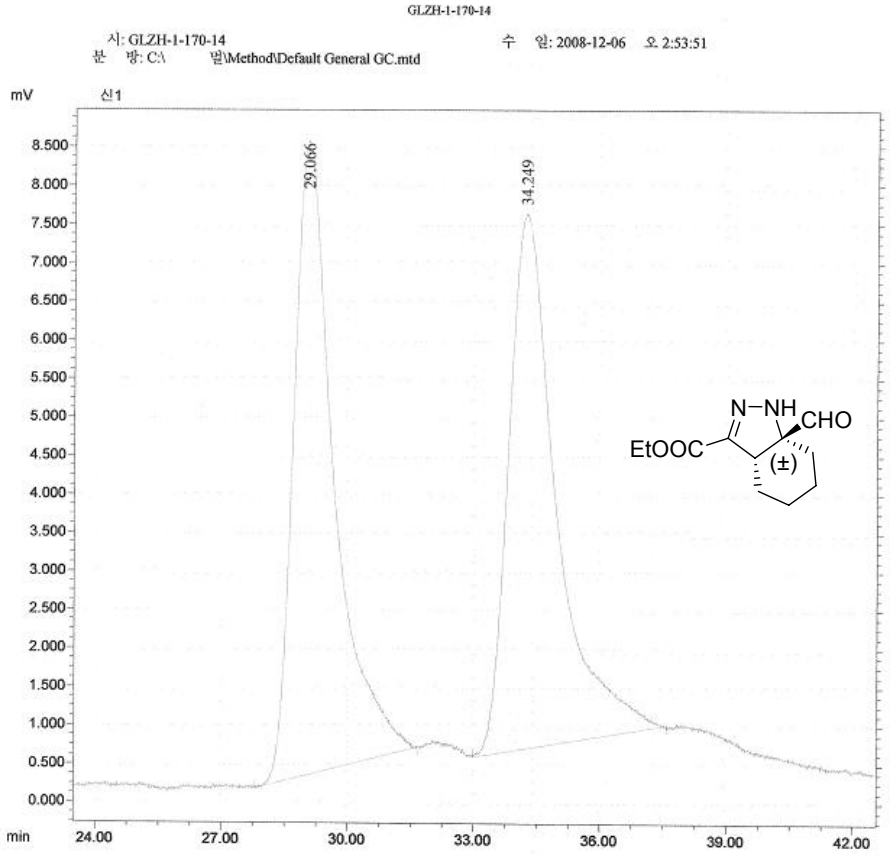
시: GLZH-1-219 수 일: 2009-01-21 오 3:19:20
분 방: C:\ 멀\Method\Default General GC.mtd



	머 시 [min]	면 [uV*sec]	면% [%]	표
A?	39.066	2899186.23	95.413	BMB
A?	50.399	139384.94	4.587	BMB
Σ		3038571.17	100.000	

데:
flow=1.0
IPA:Hex=1:9
256nm
OJ-H
8 μℓ

- 1 -



	머 시 [min]	면 [uV*sec]	면% [%]	표
A?	29.066	549363.77	50.149	BMB
A?	34.249	546104.54	49.851	BMB
Σ		1095468.31	100.000	

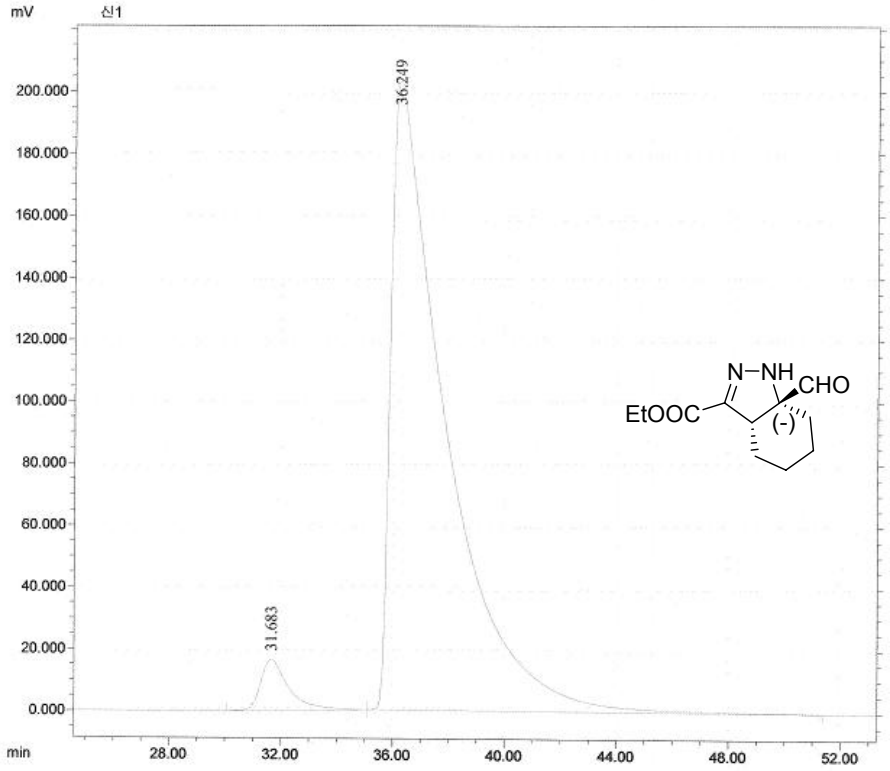
데:
flow=1.0
IPA:Hex=5:95
256nm
OJ-H
6㎕

- 1 -

Table 3, Entry 1, 2

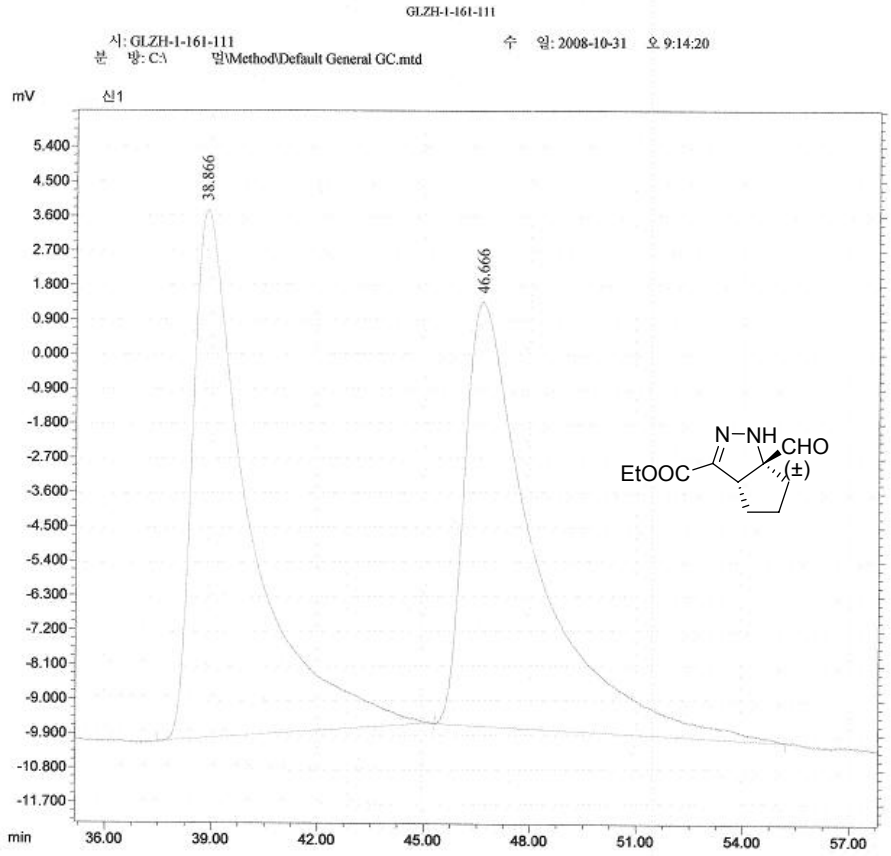
GLZH-1-187-3

시: GLZH-1-187-3 수 일: 2008-12-06 오 2:28:11
분 방: C:\ 밀\Method\Default General GC.mtd



	머 시 [min]	면 [uV*sec]	면% [%]	표
A?	31.683	1139046.97	3.968	BMB
A?	36.249	27563542.84	96.032	BMB
Σ		28702589.80	100.000	

데:
flow=1.0
IPA:Hex=5:95
256nm
OJ-H
6㎕



	머 시 [min]	면 [uV*sec]	면% [%]	표
A?	38.866	1531926.07	49.983	BMB
A?	46.666	1532970.26	50.017	BMB
Σ		3064896.33	100.000	

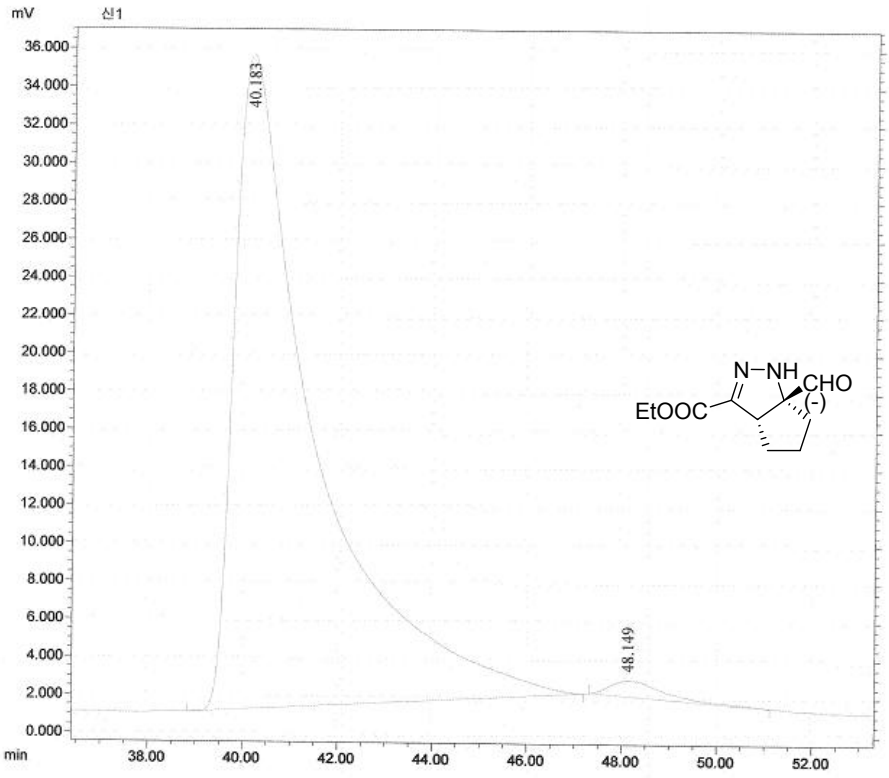
데:
flow=1.0
IPA:Hex=5:95
256nm
OJ-H
10 μℓ

- 1 -

Table 3, Entry 3

GLZH-1-190

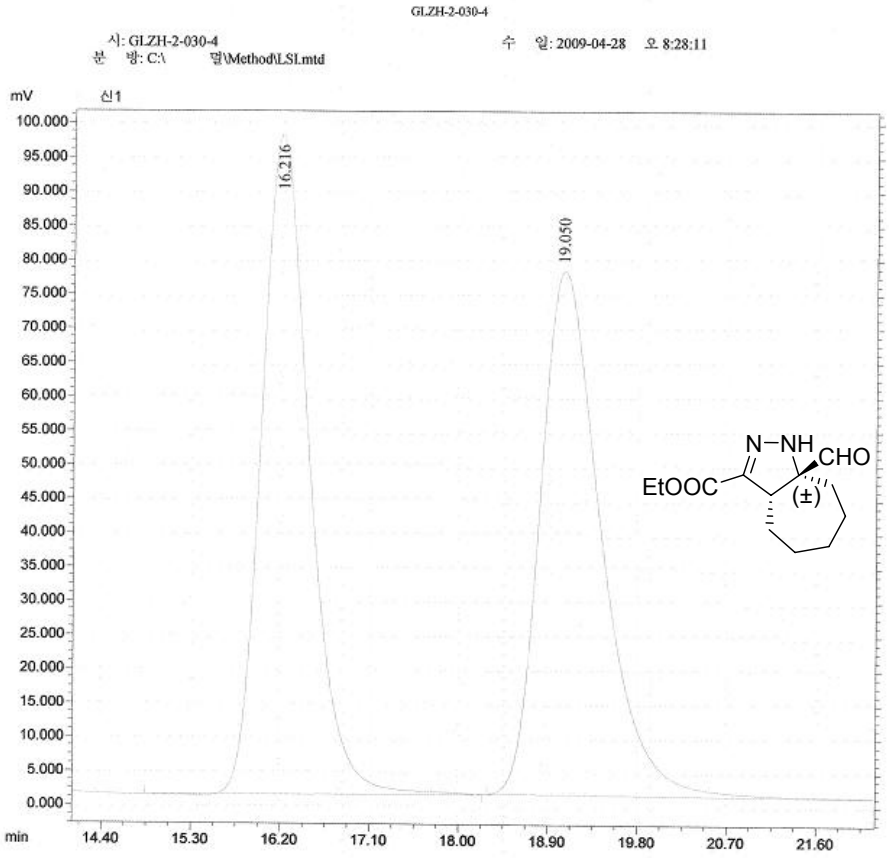
시: GLZH-1-190 수 입: 2008-12-12 오 2:57:56
분 방: C:\ 명\Method\Default General GC.mtd



	머 시 [min]	면 [uV*sec]	면% [%]	표
A?	40.183	4084401.04	98.362	BMB
A?	48.149	68013.75	1.638	BMB
Σ		4152414.79	100.000	

배:
flow=1.0
IPA:Hex=5:95
256nm
OJ-H
8 μℓ

- 1 -



	머 시 [min]	면 [uV*sec]	면% [%]	표
	16.216	3256933.12	49.855	BMB
	19.050	3275903.26	50.145	BMB
Σ		6532836.38	100.000	

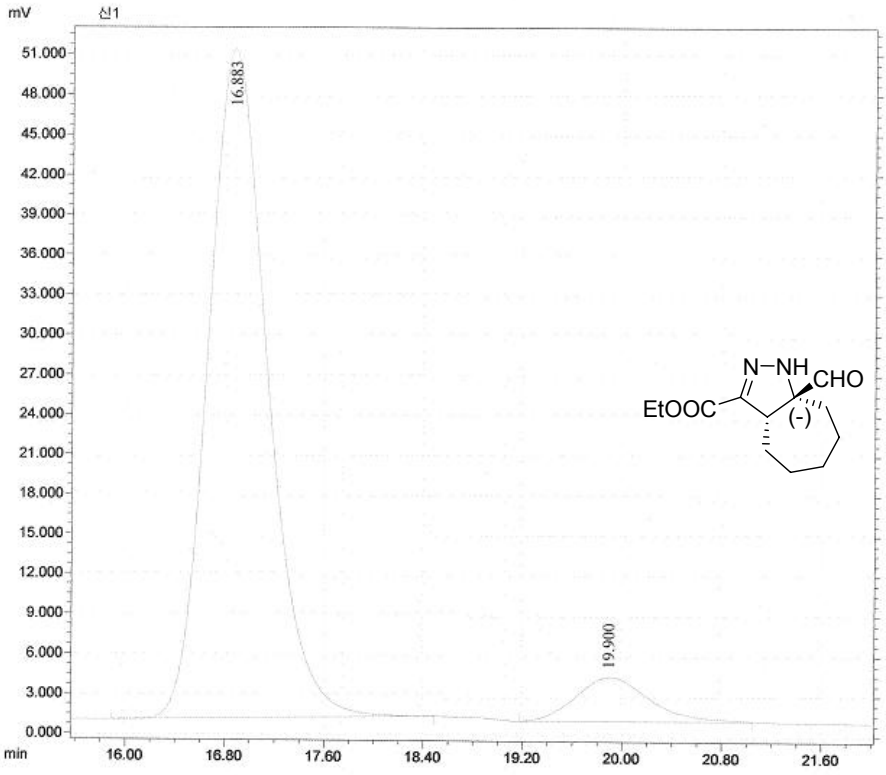
테:
flow= 1.0
IPA:Hex= 1:9
256nm
AS-H
6 μℓ

- 1 -

Table 3, Entry 4

GLZH-2-032

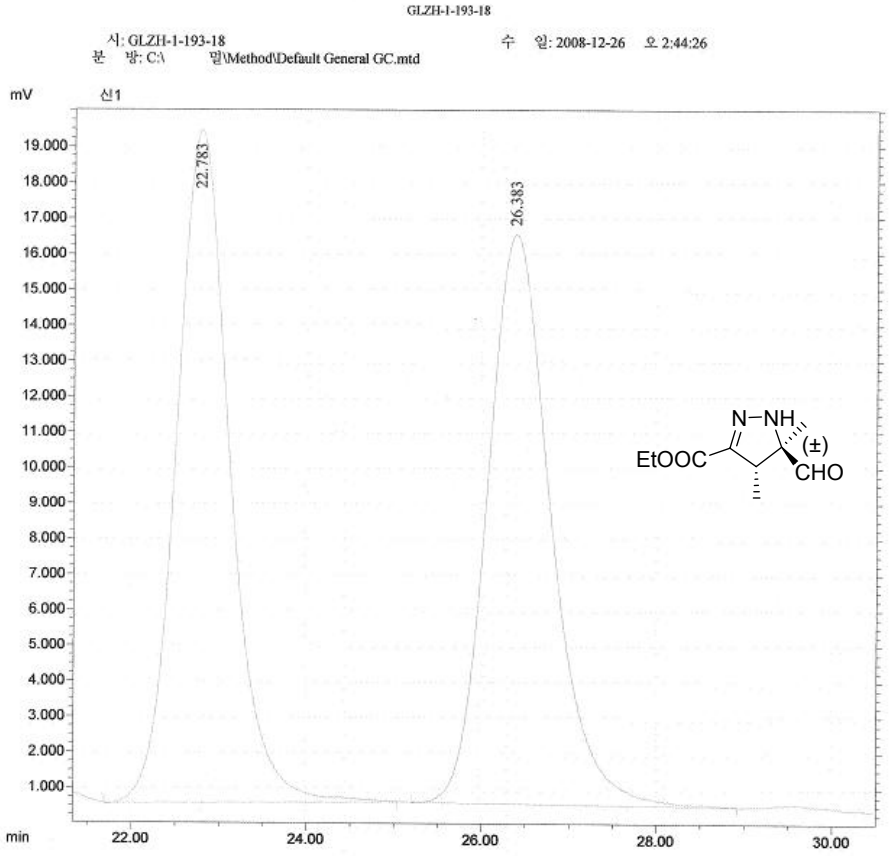
시: GLZH-2-032 수 일: 2009-04-28 오 10:49:10
분 방: C:\ 멀\Method\LSI.mtd



	머 시 [min]	면 [uV*sec]	면% [%]	표
BA?	16.883	1668916.61	92.430	BMB
BA?	19.900	136682.55	7.570	BMB
Σ		1805599.16	100.000	

테:
flow= 1.0
IPA:Hex= 1:9
256nm
AS-H
6 μℓ

- 1 -



	머 시 [min]	면 [uV*sec]	면% [%]	표
	22.783	805616.77	50.006	BMB
	26.383	805407.56	49.994	BMB
Σ		1611024.33	100.000	

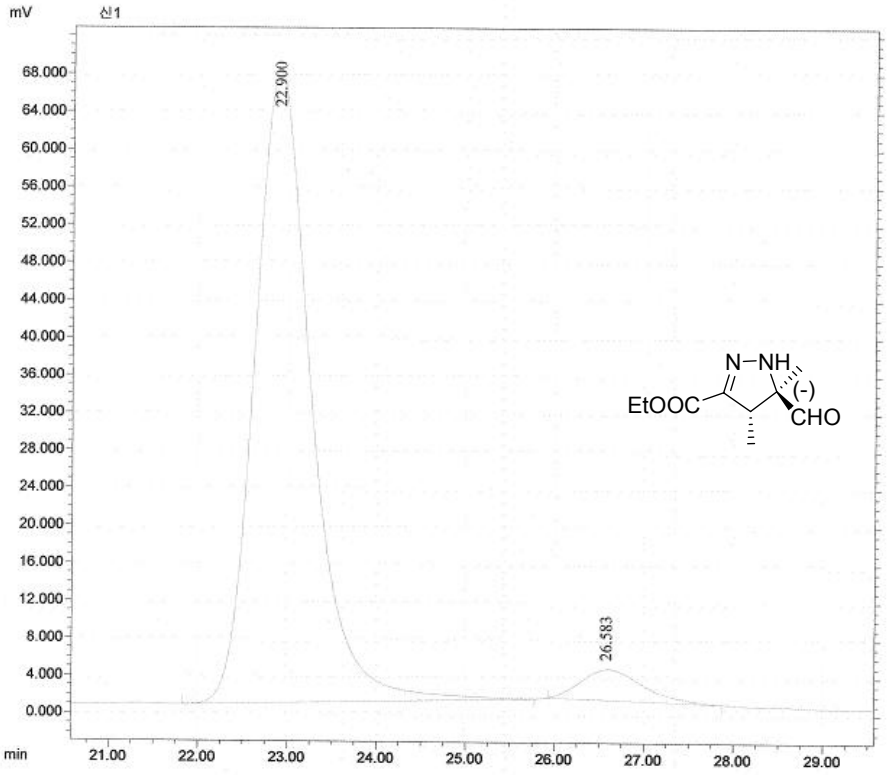
태:
flow=1.0
IPA:Hex=5:95
256nm
AS-H
7 μℓ

- 1 -

Table 3, Entry 5

GLZH-1-191-8

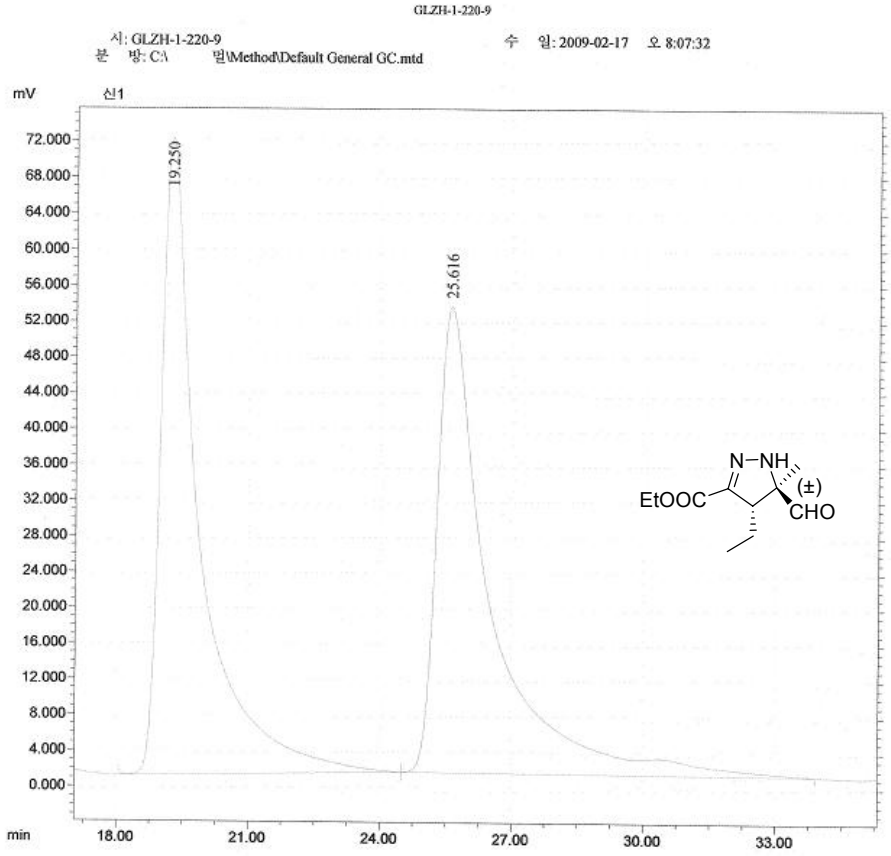
시: GLZH-1-191-8 수 일: 2008-12-26 오 1:34:26
분 방: C:\ 명\Method\Default General GC.mtd



	머 시 [min]	면 [uV*sec]	면% [%]	표
	22.900	2968240.39	94.945	BMB
	26.583	158033.40	5.055	BMB
Σ		3126273.79	100.000	

비:
flow=1.0
IPA:Hex=5:95
256nm
AS-H
7 μℓ

- 1 -



	머 시 [min]	면 [uV*sec]	면% [%]	표
A?	19.250	4365961.41	49.696	BMB
A?	25.616	4419325.86	50.304	BMB
Σ		8785287.27	100.000	

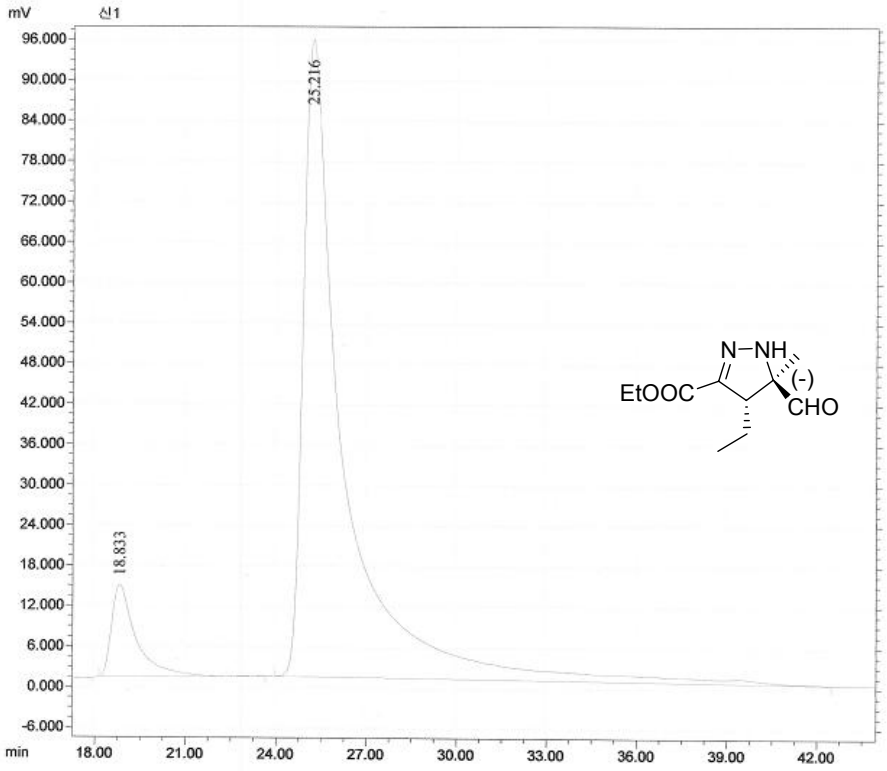
데:
flow=1.0
IPA:Hex=5:95
256nm
AD-H
5 μl
256 nm

- 1 -

Table 3, Entry 6

GLZH-1-229

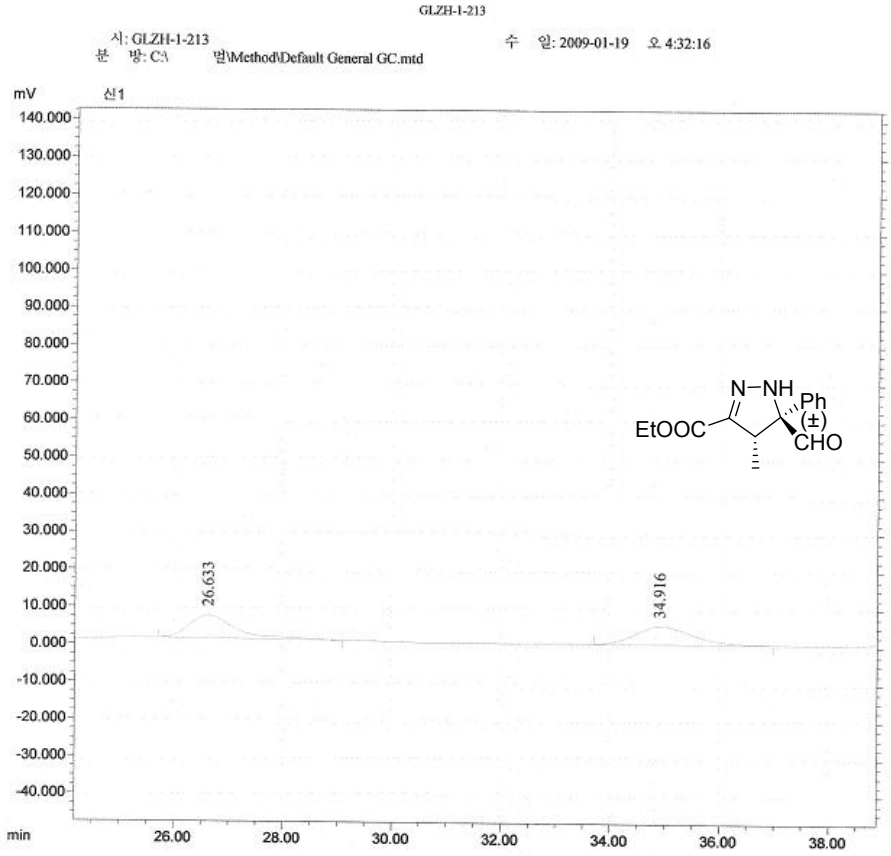
시: GLZH-1-229 수 일: 2009-03-03 오 11:23:54
분 방: C:\ 멜\Method\Default General GC.mtd



	머 시 [min]	면 [uV*sec]	면% [%]	표
	18.833	751777.28	7.706	BMB
	25.216	9004140.49	92.294	BMB
Σ		9755917.77	100.000	

데:
flow=1.0
IPA:Hex=5:95
256 nm
AD-H
8 μℓ

- 1 -



	머 시 [min]	면 [uV*sec]	면% [%]	표
A?	26.633	356231.36	50.484	BMB
A?	34.916	349394.44	49.516	BMB
Σ		705625.81	100.000	

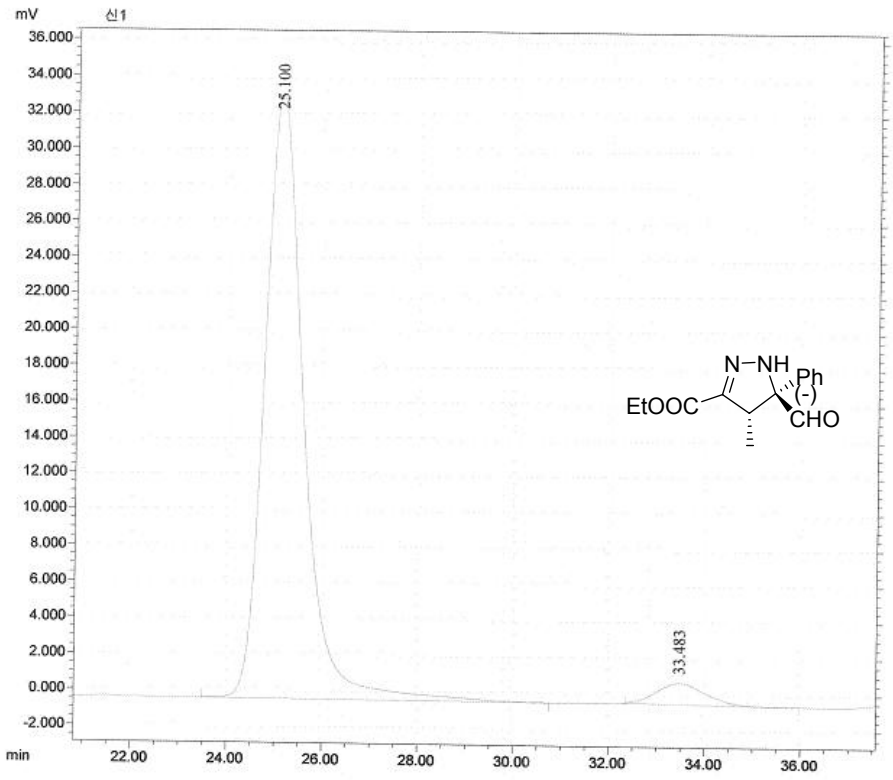
데:
flow=1.0
IPA:Hex=5:95
256nm
OD-H
6 μℓ

- 1 -

Table 3, Entry 7

GLZH-1-214

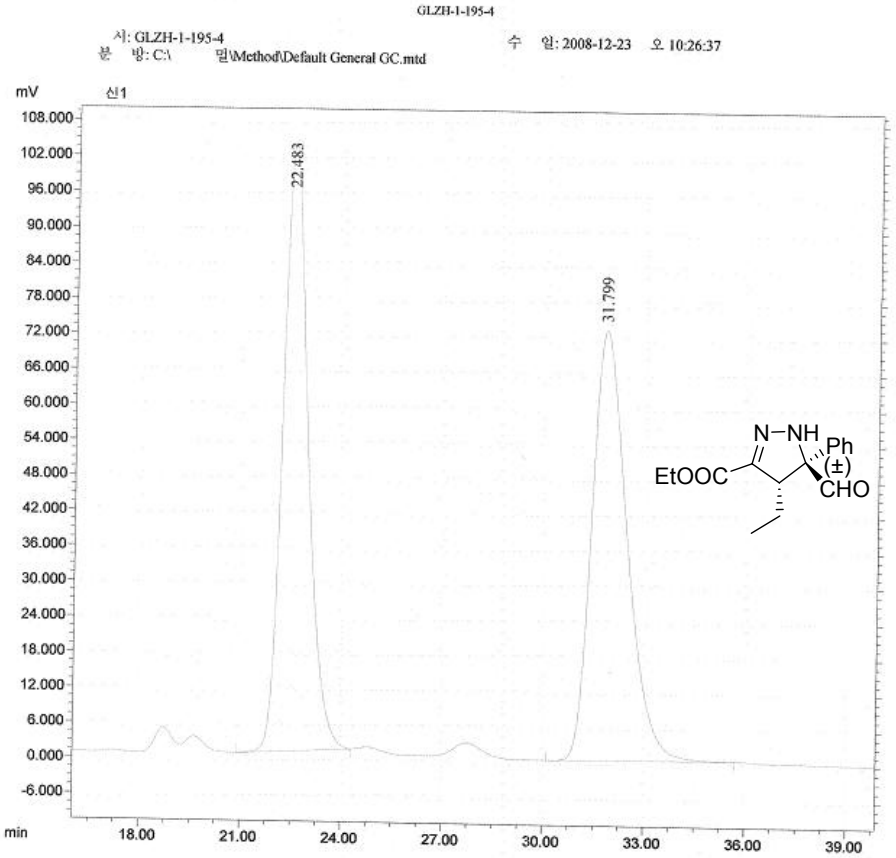
시: GLZH-1-214 수 일: 2009-01-19 오 5:37:42
분 방: C:\ 말\Method\Default General GC.mtd



	머 시 [min]	면 [uV*sec]	면% [%]	표
	25.100	1912391.15	95.769	BMB
	33.483	84485.00	4.231	BMB
Σ		1996876.15	100.000	

메:
flow=1.0
IPA:Hex=5:95
256nm
OD-H
6 μℓ

- 1 -



	머 시 [min]	면 [uV*sec]	면% [%]	표
	22.483	5342726.25	50.203	BMB
	31.799	5299500.47	49.797	BMB
Σ		10642226.72	100.000	

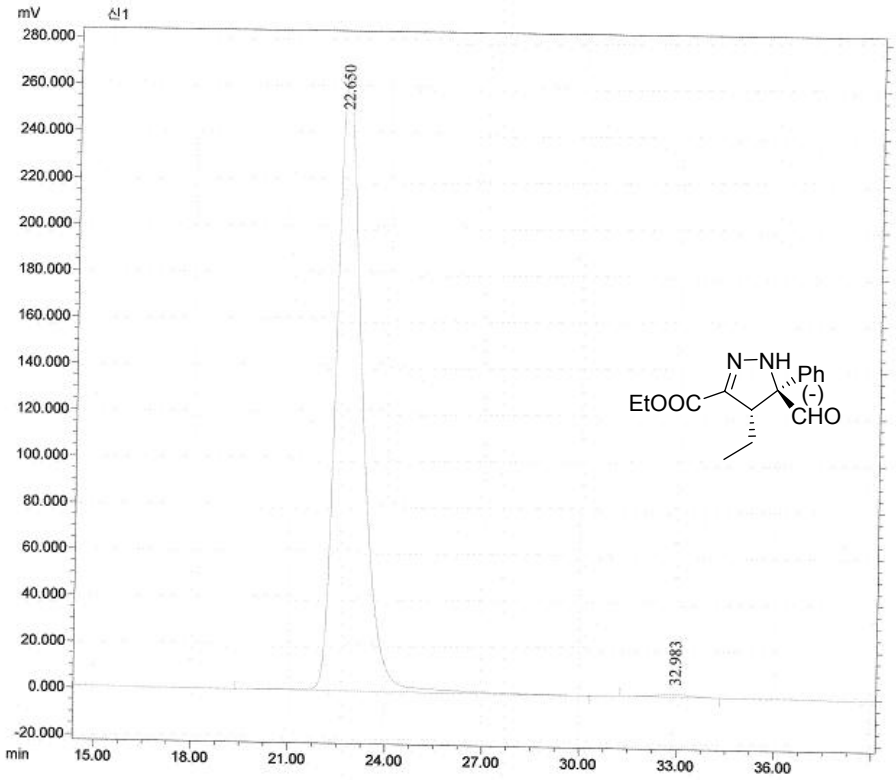
데:
flow=1.0
IPA:Hex=5:95
256nm
OD-H
5㎕

- 1 -

Table 3, Entry 8

GLZH-1-197

시: GLZH-1-197 수 일: 2008-12-20 오 2:26:45
분 방: C:\ 말\Method\Default General GC.mtd



	머 시 [min]	면 [uV*sec]	면% [%]	표
Â?	22.650	14705730.83	99.464	BMB
Â?	32.983	79248.86	0.536	BMB
Σ		14784979.68	100.000	

데:
flow=1.0
IPA:Hex=5:95
256nm
OD-H
10 μl

- 1 -