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Combining Organocatalysis with PhotoOrganocatalysis: Photocatalytic Hydroacylation of Asymmetric Organocatalytic Michael Addition Products

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SUPPORTING INFORMATION

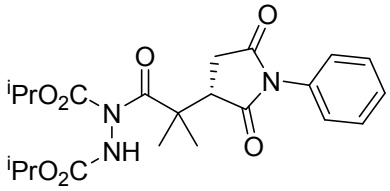
General Remarks

Chromatographic purification of products was accomplished using forced-flow chromatography on Merck® Kieselgel 60 F_{254} 230-400 mesh. Thin-layer chromatography (TLC) was performed on aluminum backed silica plates (0.2 mm, 60 F_{254}). Visualization of the developed chromatogram was performed by fluorescence quenching using ninhydrine or PMA. Mass spectra (ESI) were recorded on a Finningan® Surveyor MSQ LC-MS spectrometer. HRMS spectra were recorded on Bruker® Maxis Impact QTOF spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on Varian® Mercury (200 MHz and 50 MHz, respectively) and are internally referenced to residual solvent signals. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br s = broad singlet), coupling constant and assignment. Data for ^{13}C are reported in terms of chemical shift (δ ppm). High Performance Liquid Chromatography (HPLC) was used to determine enantiomeric excesses and was performed on an Agilent 1100 Series apparatus using Chiralpak AD-H and OD-H columns. Optical rotations were measured on a Perkin Elmer 343 polarometer. The *diastereomeric ratio* of the crude reaction mixture was determined by ^{1}H-NMR. The configuration of the products has been assigned by comparison to literature data. All new compounds were assigned by analogy.

General Procedure for the Combination of Organocatalysis with PhotoOrganocatalysis

In a dry flask, maleimide (1.00 mmol), *L*-*β*-phenylalanine (0.05 mmol, 8 mg), KOH (0.10 mmol, 6 mg) were dissolved in CH_2Cl_2 (2 mL) and aldehyde (1.50 mmol) was added. The mixture was stirred at room temperature for 24 h. After completion of the reaction, the reaction mixture was diluted with CH_2Cl_2 (5 mL) and washed with water (2 × 5 mL). The organic layer was dried over Na_2SO_4. Then, the solvent was removed *in vacuo*. The crude product was transferred to a vial, benzoin methyl ether (0.20 mmol, 45 mg), diisopropyl azodicarboxylate (1.50 mmol, 303 mg) and H_2O (1mL) were added. The reaction mixture was stirred vigorously under household bulb irradiation (2 × 80W household lamps) for 24 h. The mixture was diluted with CH_2Cl_2 (5 mL) and washed with water (2 × 5 mL). The organic layer was dried over Na_2SO_4. Then, the solvent was removed *in vacuo*. Purification was performed by silica gel chromatography with petroleum ether/ethyl acetate

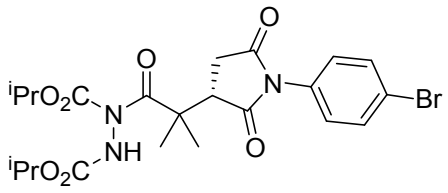
(*S*)-Diisopropyl 1-(2-(2,5-dioxo-1-phenylpyrrolidin-3-yl)-2-methyl propanoyl) hydrazine-1,2-dicarboxylate (4a)



The crude mixture of **4a** was purified by column chromatography (40% EtOAc in Pet ether). White solid; 84% yield; m.p. 68-72 °C; ^{1}H NMR (200MHz, $CDCl_3$): δ = 7.50-7.31 (3H, m, ArH), 7.29-7.19 (2H, m, ArH), 7.12 (1H, br s, NH), 5.08-4.81 (2H, m, 2 × OCH), 3.31-3.11 (1H, m, CH), 2.90 (1H, dd, *J* = 18.2 and 9.2 Hz, C*H*H), 2.67 (1H, dd, *J* = 18.2 and 5.5 Hz, C*H*H), 1.58 (3H, m, CH_3), 1.43 (3H, m, CH_3), 1.32-1.01 (12H, m, 4 × CH_3) ppm. ^{13}C (50MHz, $CDCl_3$): δ= 177.1, 177.0, 175.1, 156.5, 155.6, 154.8, 152.6,

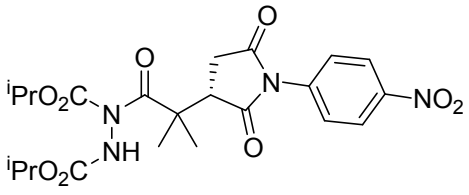
131.9, 129.9, 128.9 128.4, 128.2, 126.5, 126.3, 72.5, 70.6, 69.7, 69.4, 49.2, 48.6, 32.6, 31.7, 23.2, 22.6, 21.9, 21.7, 21.5, 21.4 ppm; $[\alpha]_D$ = -2.3 (c 1, $CHCl_3$); HPLC data analysis: OD-H column, hexane/2-propanol: 82/18, 0.9 mL/min, t_R = 54.13 min, >99% ee; HRMS (ESI) m/z calcd. for $C_{22}H_{29}N_3O_7$ $[M+H]^+$ 447.2006; found 447.2011.

(*S*)-Diisopropyl 1-(2-(1-(4-bromophenyl)-2,5-dioxopyrrolidin-3-yl)-2-methyl propanoyl)hydrazine-1,2-dicarboxylate (4b)



The crude mixture of **4b** was purified by column chromatography (40% EtOAc in Pet ether). White solid; 52% yield; m.p. 75-78 °C; ^{1}H NMR (200MHz, $CDCl_3$): δ = 7.55 (2H, d, *J* = 8.7 Hz, ArH), 7.16 (2H, d, *J* = 8.7 Hz, ArH), 6.85 (1H, br s, NH), 5.08-4.89 (2H, m, 2 × OCH), 3.14 (1H, dd, *J* = 9.1 and 5.3 Hz, CH), 2.92 (1H, dd, *J* = 18.3 and 9.1 Hz, C*H*H), 2.70 (1H, dd, *J* = 18.3 and 5.3 Hz, C*H*H), 1.63 (3H, s, CH_3), 1.45 (3H, s, CH_3), 1.35-1.16 (12H, m, 4 × CH_3) ppm. ^{13}C NMR (50MHz, $CDCl_3$): δ = 176.8, 175.8, 174.7, 155.6, 152.5, 132.2, 131.0, 128.2, 122.3, 72.7, 71.0, 49.7, 48.9, 32.8, 23.5, 22.9, 21.8 ppm; $[\alpha]_D$ = -6.7 (c 1, $CHCl_3$); HPLC data analysis: AD-H column, hexane/2-propanol: 80/20, 1.0 mL/min, t_R = 26.17 min (minor), t_R = 60.82 min (major), 99% ee; HRMS (ESI) m/z calcd. for $C_{22}H_{29}N_3O_7$ $[M+H]^+$ 525.1111; found 525.1114.

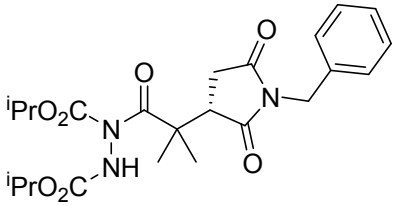
(*S*)-Diisopropyl 1-(2-methyl-2-(1-(4-nitrophenyl)-2,5-dioxopyrrolidin-3-yl)propanoyl)hydrazine-1,2-dicarboxylate (4c)



The crude mixture of **4c** was purified by column chromatography (40% EtOAc in Pet ether). White solid; 51% yield; m.p. 72-75 °C; ^{1}H NMR (200MHz, $CDCl_3$): δ = 8.28 (2H,

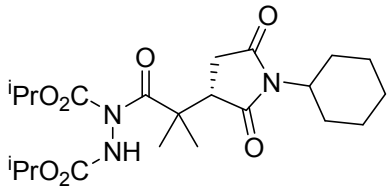
d, *J* = 9.0 Hz, ArH), 7.55 (2H, d, *J* = 9.0 Hz, ArH), 6.82 (1H, s, NH), 5.08-4.89 (2H, m, 2 × OCH), 3.16-3.01 (1H, m, CH), 2.98-2.67 (2H, m, 2 × C*H*H), 1.70 (3H, s, CH_3), 1.47 (3H, s, CH_3), 1.39-1.17 (12H, m, 4 × CH_3) ppm. ^{13}C NMR (50MHz, $CDCl_3$): δ = 176.3, 176.2, 174.2, 155.6, 152.3, 146.9, 137.8, 127.2, 124.2, 72.8, 71.1, 50.2, 49.3, 33.0, 23.8, 23.3, 21.8 ppm. $[\alpha]_D$ = -23.6 (c 1, $CHCl_3$); HPLC data analysis: AD-H column, hexane/2-propanol: 75/25, 1.0 mL/min, t_R = 33.98 min (minor), t_R = 55.14 min (major) 99% ee; HRMS (ESI) m/z calcd. for $C_{22}H_{28}N_4O_9$ $[M+H]^+$ 492.1856; found 492.1857.

(*S*)-Diisopropyl 1-(2-(1-benzyl-2,5-dioxopyrrolidin-3-yl)-2-methylpropanoyl) hydrazine-1,2-dicarboxylate (4d)



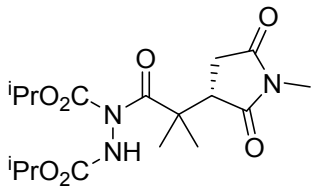
The crude mixture of **4d** was purified by column chromatography (30% EtOAc in Pet ether). Pale yellow oil; 66% yield; ^{1}H NMR (200MHz, $CDCl_3$): δ= 7.36-7.11 (6H, m, 5ArH and NH), 5.03-4.85 (2H, m, 2 × OCH), 4.62 (1H, d, *J* = 14.4 Hz, NC*H*H), 4.53 (1H, d, *J* = 14.4 Hz, NC*H*H), 3.20-3.06 (1H, m, CH), 2.73 (1H, dd, *J* = 18.3 and 9.1 Hz, C*H*H), 2.48 (1H, dd, *J* = 18.3 and 5.4 Hz, C*H*H), 1.40 (3H, s, CH_3), 1.36 (3H, s, CH_3), 1.28-1.16 (12H, m, 4 × CH_3) ppm. ^{13}C NMR (50MHz, $CDCl_3$): δ = 177.6, 176.7, 175.6, 155.6, 152.6, 135.6, 128.3, 127.5, 72.4, 70.6, 48.0, 42.1, 32.3, 22.6, 21.7, 21.5, 21.4 ppm; $[\alpha]_D$ = +3.4 (c 1, $CHCl_3$); HPLC data analysis: AD-H column, hexane/2-propanol: 80/20, 1.0 mL/min, t_R = 21.16 min (minor), t_R = 44.91 min (major), 99% ee; HRMS (ESI) m/z calcd. for $C_{23}H_{31}N_3O_7$ $[M+H]^+$ 461.2162; found 461.2163.

(*S*)-Diisopropyl 1-(2-(1-cyclohexyl-2,5-dioxopyrrolidin-3-yl)-2-methyl propanoyl) hydrazine-1,2-dicarboxylate (4e)



The crude mixture of **4e** was purified by column chromatography (15% EtOAc in Pet ether). Pale yellow oil; 54% yield; ^{1}H NMR (200MHz, $CDCl_3$) : δ= 6.74 (1H, br s, NH), 5.06-4.88 (2H, m, 2 × OCH), 4.01-3.83 (1H, m, NCH), 3.30-3.13 (1H, m, CH), 2.72 (1H, dd, *J* = 18.3 and J = 9.1 Hz, C*H*H), 2.44 (1H, dd, *J* = 18.3 and J = 5.5 Hz, C*H*H), 2.22-1.95 (2H, m, 2 × C*H*H), 1.84-1.68 (2H, m, 2 × C*H*H), 1.67-1.49 (2H, m, 2 × C*H*H), 1.45 (3H, s, CH_3), 1.38 (3H, s, CH_3), 1.31-1.09 (16H, m, 4 x CH_3 and 4 × C*H*H) ppm. ^{13}C NMR (50MHz, $CDCl_3$): δ= 178.2, 177.4, 176.2, 155.6, 152.9, 72.6, 70.8, 70.0, 51.6, 48.0, 32.0, 28.5, 25.8, 25.0, 22.7, 21.9, 21.7 ppm. $[\alpha]_D$ = +7.2 (c 1, $CHCl_3$); HPLC data analysis: AD-H column, hexane/2-propanol: 80/20, 1.0 mL/min, t_R = 13.25 min (minor), t_R = 31.71 min (major), 99% ee; HRMS (ESI) m/z calcd. for $C_{22}H_{35}N_3O_7$ $[M+H]^+$ 453.2475; found 453.2476.

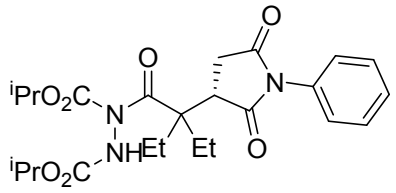
(*S*)-Diisopropyl 1-(2-methyl-2-(1-methyl-2,5-dioxopyrrolidin-3-yl) propanoyl) hydrazine-1,2-dicarboxylate (4f)



The crude mixture of **4f** was purified by column chromatography (30% EtOAc in Pet ether). Yellow oil; 72% yield; ^{1}H NMR (200MHz, $CDCl_3$): δ = 7.13 (1H, br s, NH), 5.03-4.83 (2H, m, 2 × OCH), 3.13 (1H, dd, *J* = 9.0 and 5.4 Hz, CH), 2.89 (3H, s, CH_3N), 2.73 (1H, dd, *J* = 18.1 and 9.0 Hz, C*H*H), 2.46 (1H, dd, *J* = 18.1 and 5.4 Hz, C*H*H), 1.45 (3H, s, CH_3), 1.38 (3H, s, CH_3), 1.31-1.10 (12H, m, 4 × CH_3) ppm. ^{13}C NMR (50MHz,

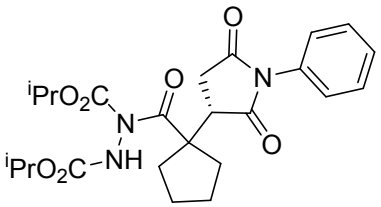
$CDCl_3$): δ = 178.0, 176.9, 176.1, 155.6, 152.5, 72.4, 70.6, 48.8, 48.0, 32.4, 24.6, 22.8, 22.6, 21.7, 21.5, 21.4 ppm. $[\alpha]_D$ = +12.9 (c 1, $CHCl_3$); HPLC data analysis: AD-H column, hexane/2-propanol: 85/15, 1.0 mL/min, t_R = 24.04 min (minor), t_R = 34.45 min (major), 99% ee; HRMS (ESI) m/z calcd. for $C_{17}H_{27}N_3O_7$ $[M+H]^+$ 385.1849; found 385.1852.

(*S*)-Diisopropyl 1-(2-(2,5-dioxo-1-phenylpyrrolidin-3-yl)-2-ethyl butanoyl) hydrazine-1,2-dicarboxylate (4g)



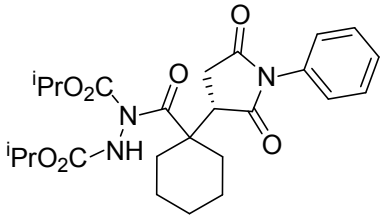
The crude mixture of **4g** was purified by column chromatography (20% EtOAc in Pet ether). Pale yellow oil; 55% yield; ^{1}H NMR (200MHz, $CDCl_3$): δ = 7.49-7.29 (3H, m, ArH), 7.25-7.15 (2H, m, ArH), 6.98 (1H, br s, NH), 5.05-4.88 (2H, m, 2 × OCH), 3.79-3.61 (1H, m, CH), 2.95 (1H, dd, *J* = 18.2 and 8.7 Hz, C*H*H), 2.75 (1H, dd, *J* = 18.2 and 5.9 Hz, C*H*H), 2.22-1.76 (4H, m, 2 × CH_2), 1.33-1.09 (12H, m, 4 × CH_3), 1.04-0.81 (6H, m, 2 × CH_3) ppm. ^{13}C (50MHz, $CDCl_3$): δ = 177.6, 175.2, 175.1, 155.6, 152.9, 131.8, 129.0, 128.4, 126.3, 72.4, 70.7, 69.8, 55.6, 44.7, 32.4, 28.3, 27.3, 21.7, 21.5, 21.4, 9.8, 9.4 ppm; $[\alpha]_D$ = +5.3 (c 1, $CHCl_3$); HPLC data analysis: AD-H column, hexane/2-propanol: 80/20, 1.0 mL/min, t_R = 17.17 min (minor), t_R = 32.02 min (major), 99% ee; HRMS (ESI) m/z calcd. for $C_{24}H_{33}N_3O_7$ $[M+H]^+$ 475.2319; found 475.2321.

(*S*)-Diisopropyl 1-(1-(2,5-dioxo-1-phenylpyrrolidin-3-yl)cyclopentane carbonyl) hydrazine-1,2-dicarboxylate (4h)



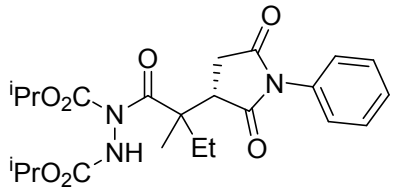
The crude mixture of **4h** was purified by column chromatography (30% EtOAc in Pet ether). Pale yellow oil; 44% yield; ^{1}H NMR (200MHz, $CDCl_3$): δ = 7.51-7.17 (5H, m, ArH), 6.66 (1H, s, NH), 5.09-4.90 (2H, m, 2 × OCH), 3.74-3.57 (1H, m, CH), 2.97 (1H, dd, *J* = 18.5 and 9.1 Hz, C*H*H), 2.67 (1H, dd, *J* = 18.5 and 5.6 Hz, C*H*H), 2.45-1.62 (8H, m, 4 × C*H*H), 1.38-0.99 (12H, m, 4 × CH_3) ppm. ^{13}C NMR (50MHz, $CDCl_3$): δ = 177.5, 175.8, 175.1, 155.5, 152.7, 132.0, 129.1, 128.6, 126.6, 72.6, 70.8, 70.1, 58.6, 45.3, 34.8, 34.1, 33.0, 26.5, 26.4, 21.9, 21.7 ppm. $[\alpha]_D$ = -17.5 (c 1, $CHCl_3$); HPLC data analysis: AD-H column, hexane/2-propanol: 80/20, 1.0 mL/min, t_R = 53.95 min, >99% ee; HRMS (ESI) m/z calcd. for $C_{24}H_{31}N_3O_7$ $[M+H]^+$ 473.2162; found 473.2165.

(*S*)-Diisopropyl 1-(1-(2,5-dioxo-1-phenylpyrrolidin-3-yl)cyclohexane carbonyl) hydrazine-1,2-dicarboxylate (4i)



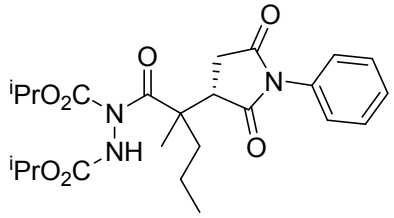
The crude mixture of **4i** was purified by column chromatography (15% EtOAc in Pet ether). Pale yellow oil; 65% yield; ^{1}H NMR (200MHz, $CDCl_3$): δ = 7.51-7.08 (6H, m, 5 × ArH and 1 × NH), 5.07-4.84 (2H, m, 2 × OCH), 3.78-3.59 (1H, m, CH), 2.92-2.60 (2H, m, 2 × C*H*H), 2.35-2.14 (2H, m , 2 × C*H*H), 1.99-1.78 (2H, m, 2 × C*H*H), 1.66-1.39 (6H, m, 6 × C*H*H), 1.35-1.07 (12H, m, 4 × CH_3) ppm. ^{13}C NMR (50MHz, $CDCl_3$): δ = 180.4, 176.8, 175.4, 175.0, 155.8, 153.2, 131.8, 128.9, 128.4, 126.4, 72.5, 70.7, 53.1, 52.0, 44.1, 42.6, 31.5, 31.3, 30.0, 28.7, 25.5, 25.0, 22.9, 22.3, 21.7, 21.5, 21.2, 21.0 ppm. $[\alpha]_D$ = -17.6 (*c* 1, $CHCl_3$); HPLC data analysis: AD-H column, hexane/2-propanol: 80/20, 1.0 mL/min, t_R = 20.36 min (minor), t_R = 26.76 min (major), 98% ee; HRMS (ESI) m/z calcd. for $C_{25}H_{33}N_3O_7$ $[M+H]^+$ 487.2319; found 487.2323.

Diisopropyl 1-(2-((*S*)-2,5-dioxo-1-phenylpyrrolidin-3-yl)-2-methyl butanoyl) hydrazine-1,2-dicarboxylate (4j)



The crude mixture of **4j** was purified by column chromatography (30% EtOAc in Pet ether). Pale yellow oil; 53% yield; dr: 62:38; Major diastereomer: ^{1}H NMR (200MHz, $CDCl_3$): δ = 7.49-7.32 (3H, m, ArH), 7.29-7.18 (2H, m, ArH), 6.80 (1H, br s, NH), 5.08-4.89 (2H, m, 2 × OCH), 3.69 (1H, dd, *J* = 5.6 and 9.3 Hz, CH), 2.90 (1H, dd, *J* = 18.4 and 9.3 Hz, C*H*H), 2.68 (1H, dd, *J* = 18.4 and 5.6 Hz, C*H*H), 2.13-1.84 (2H, m, 2 × C*H*H), 1.53-1.13 (15H, m, 5 × CH_3), 0.97 (3H, t, *J* = 7.3 Hz, CH_3). ^{13}C NMR (50MHz, $CDCl_3$): δ= 177.2, 177.1, 175.0, 155.5, 153.0, 131.8, 129.1, 128.6, 126.5, 72.5, 70.7, 52.1, 46.3, 31.7, 29.0, 21.8, 18.4, 8.6 ppm; $[\alpha]_D$ = -5.8 (*c* 1, $CHCl_3$); HPLC data analysis: OD-H column, hexane/2-propanol: 90/10, 1.0 mL/min, t_R = 33.41 min (major), t_R = 48.88 min (minor), 82% ee; HRMS (ESI) m/z calcd. for $C_{23}H_{31}N_3O_7$ $[M+H]^+$ 461.2162; found 461.2165.

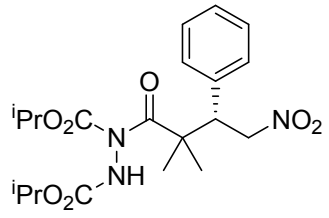
Diisopropyl 1-(2-((*S*)-2,5-dioxo-1-phenylpyrrolidin-3-yl)-2-methyl pentanoyl) hydrazine-1,2-dicarboxylate (4k)



The crude mixture of **4k** was purified by column chromatography (20% EtOAc in Pet ether). Pale yellow oil; 48% yield; dr: 60:40; Major diastereomer: ^{1}H NMR (200MHz, $CDCl_3$): δ= 7.50-7.29 (3H, m, ArH), 7.29-7.16 (2H, m, ArH), 6.81 (1H, br s, NH), 5.07-

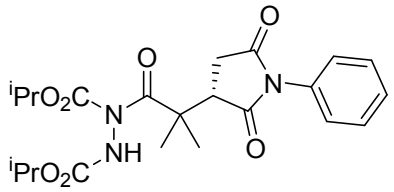
4.89 (2H, m, 2 × OCH), 3.66 (1H, dd, *J* = 9.1 and 5.8 Hz, CH), 2.89 (1H, dd, *J* = 18.4 and 9.1 Hz, C*H*H), 2.68 (1H, dd, *J* = 18.4 and 5.8 Hz, C*H*H), 2.02-1-66 (2H, m, 2 × C*H*H), 1.61-1.02 (17H, m, 5 × CH_3 and 2 x C*H*H), 0.91 (3H, t, *J* = 7.1 Hz, CH_3) ppm. ^{13}C NMR (50MHz, $CDCl_3$): δ= 177.2, 175.0, 155.5, 153.0, 131.8, 129.1, 128.6, 126.5, 72.5, 70.7, 51.9, 46.8, 38.4, 31.8, 21.9, 21.6, 18.9, 17.5, 14.4 ppm. $[\alpha]_D$ = -2.3 (*c* 1, CH_2Cl_2); HPLC data analysis: OD-H column, hexane/2-propanol: 90/10, 1.0 mL/min, t_R = 25.00 min, >99% ee; HRMS (ESI) m/z calcd. for $C_{24}H_{33}N_3O_7$ $[M+H]^+$ 475.2319; found 475.2321.

(*S*)-Diisopropyl 1-(2,2-dimethyl-4-nitro-3-phenylbutanoyl)hydrazine-1,2-dicarboxylate (7a)



In a dry flask, nitrostyrene (1.00 mmol, 149 mg), L-β-phenylalanine (0.10 mmol, 17 mg), KOH (0.10 mmol, 6 mg) were dissolved in CH_2Cl_2 (2 mL) and isobutyraldehyde (1.50 mmol, 115 mg) was added. The reaction mixture was stirred at room temperature for 48 h. After completion of the reaction, the mixture was diluted with CH_2Cl_2 (5 mL) and washed with water (2 × 5 mL). The organic layer was dried over Na_2SO_4. Then, the solvent was removed *in vacuo*. The crude product was transferred to a vial, benzoin methyl ether (0.20 mmol, 45 mg), diisopropyl azodicarboxylate (1.50 mmol, 303 mg) and H_2O (1 mL) were added. The reaction mixture was stirred vigorously under household bulb irradiation (2 × 80W household lamps) for 24 h. The reaction mixture was diluted with CH_2Cl_2 (5 mL) and washed with water (2 × 5 mL). The organic layer was dried over Na_2SO_4. Then, the solvent was removed *in vacuo*. The crude mixture of **7a** was purified by column chromatography (10% EtOAc in Pet ether). Pale yellow oil; 67% yield; ^{1}H NMR (200MHz, $CDCl_3$): δ = 7.51-7.10 (5H, m, ArH), 6.80-6.64 (1H, br s, NH), 5.14-4.68 (4H, m, 2 × OCH and 2 × C*H*HNO_2), 4.38-4.18 (1H, m, C*H*HPh), 1.38-0.81 (18H, m, 6 × CH_3) ppm. ^{13}C NMR (50MHz, $CDCl_3$): δ = 178.8, 178.4, 156.9, 155.7, 154.8, 153.1, 135.4, 131.9, 129.5, 128.3, 128.1, 128.0, 72.7, 72.2, 71.0, 70.3, 49.3, 48.6, 24.5,

21.8, 21.6, 21.3 ppm. $[\alpha]_D$ = -10.4 (*c* 0.5, $CHCl_3$); HPLC data analysis: OD-H column, hexane/2-propanol: 82/18, 0.9 mL/min, t_R = 37.67 min, >99% ee; **HRMS** (ESI) m/z calcd. for $C_{22}H_{29}N_3O_7$ $[M+H]^+$ 423.2006; found 423.2009.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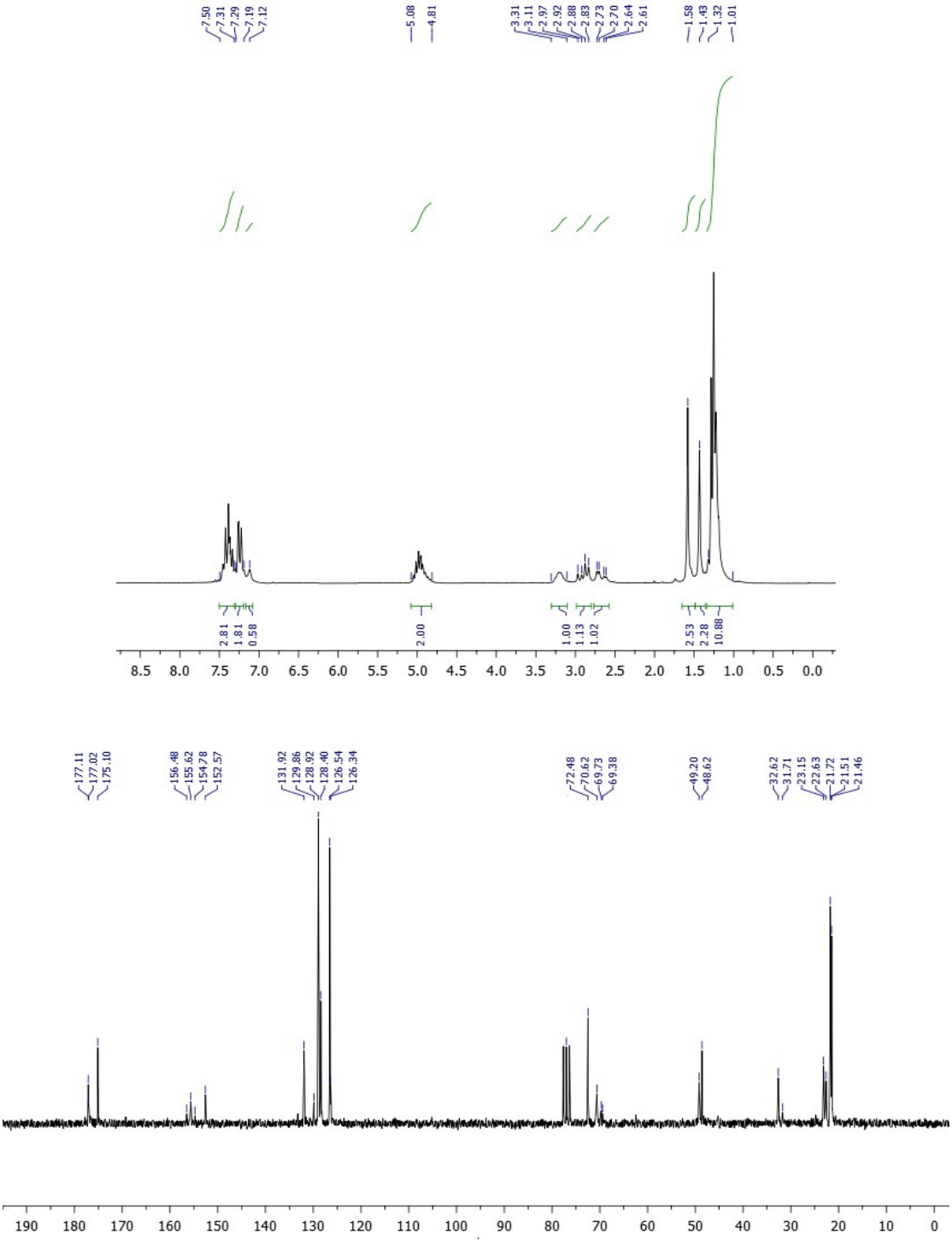
N
NH
$^{i}PrO_2C$
O
O

4a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7.19
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5.08
4.81
3.31
3.11
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2.92
2.88
2.83
2.73
2.70
2.64
2.61
1.58
1.43
1.32
1.01
2.81
1.81
0.58
2.00
1.00
1.13
1.02
2.53
2.28
10.88
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
177.11
177.02
175.10
156.48
155.62
154.78
152.57
131.92
129.86
128.92
128.40
126.54
126.34
72.48
70.62
69.73
69.38
49.20
48.62
32.62
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23.15
22.63
21.72
21.51
21.46
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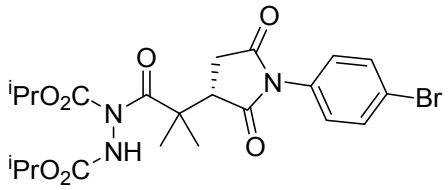
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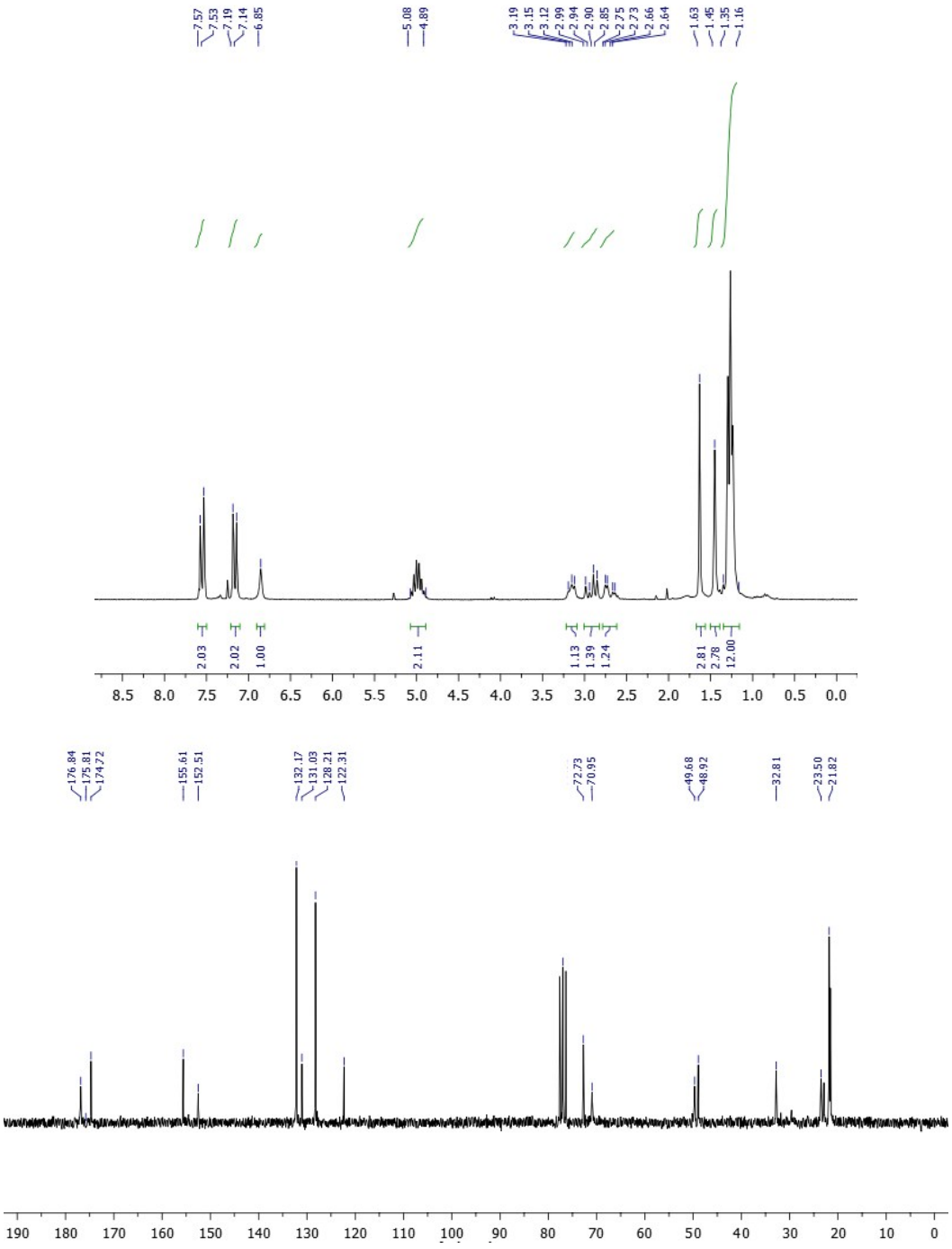
N
NH
$^{i}PrO_2C$
O
O

4b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2.94
2.90
2.85
2.75
2.73
2.66
2.64
1.63
1.45
1.35
1.16
2.03
2.02
1.00
2.11
1.13
1.39
1.24
2.81
2.78
12.00
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
176.84
175.81
174.72
155.61
152.51
132.17
131.03
128.21
122.31
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49.68
48.92
32.81
23.50
21.82
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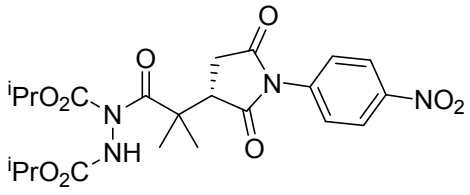
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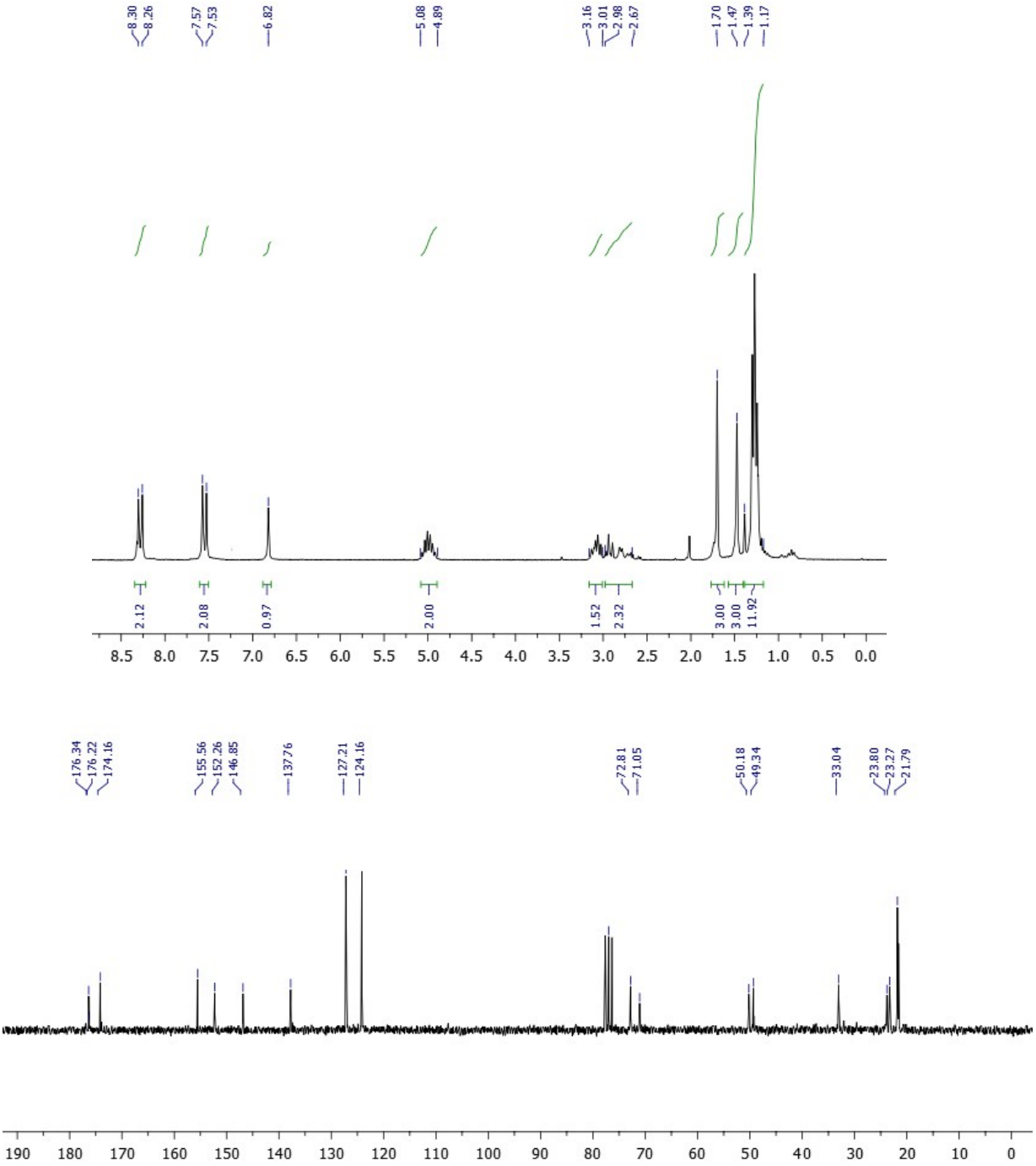
NH
$^{i}PrO_2C$
O
O
NO_2

4c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2.67
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1.47
1.39
1.17
2.12
2.08
0.97
2.00
1.52
2.32
3.00
3.00
11.92
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
176.34
176.22
174.16
155.56
152.26
146.85
137.76
127.21
124.16
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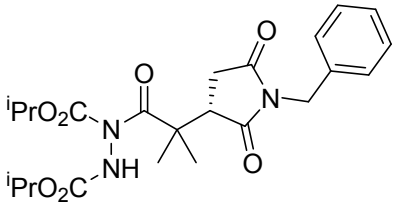
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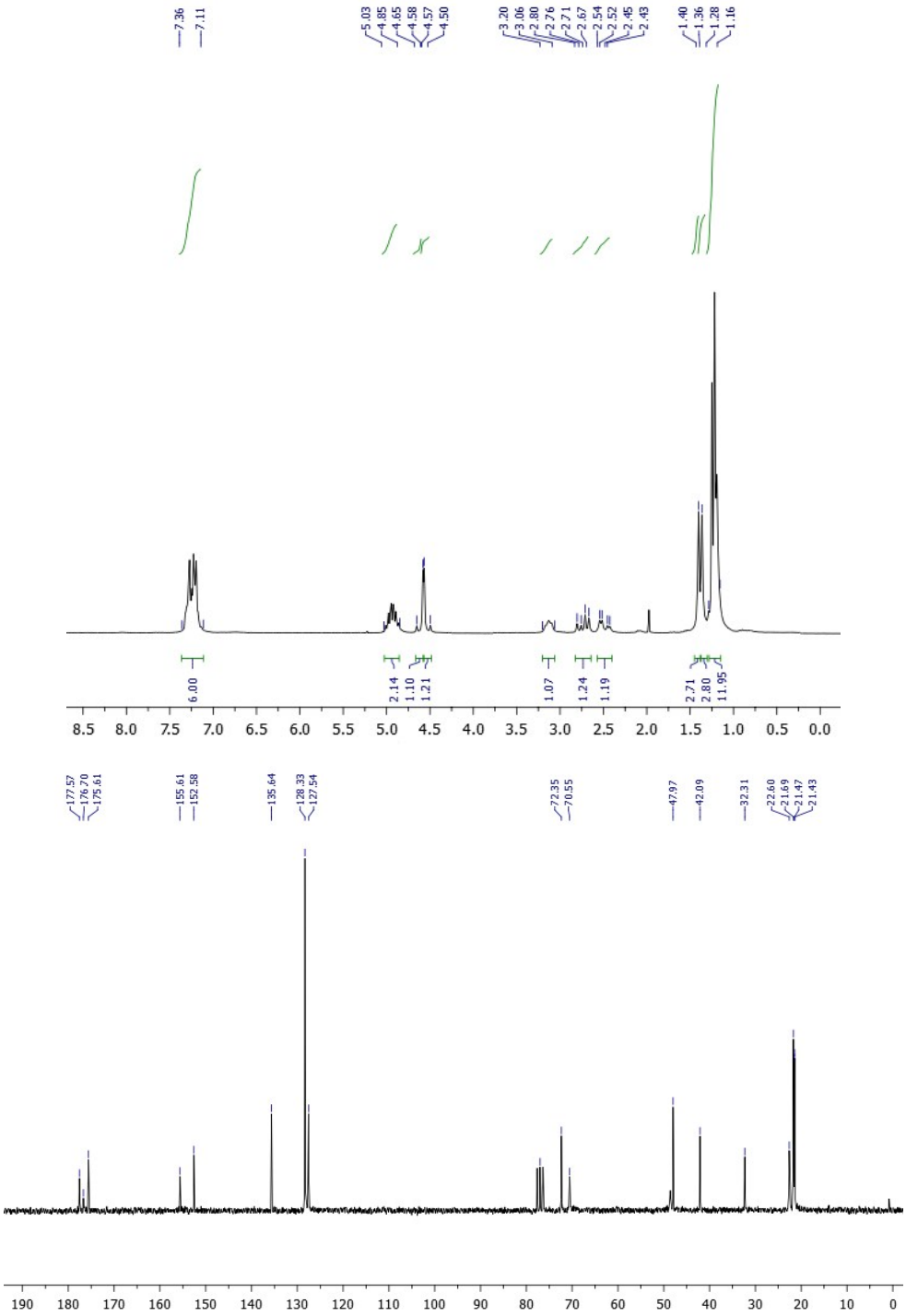
N
NH
$^{i}PrO_2C$
O

4d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2.71
2.67
2.54
2.52
2.45
2.43
1.40
1.36
1.28
1.16
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1.10
1.21
1.07
1.24
1.19
2.71
2.80
11.95
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
177.57
176.70
175.61
155.61
152.58
135.64
128.33
127.54
72.35
70.55
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32.31
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21.47
21.43
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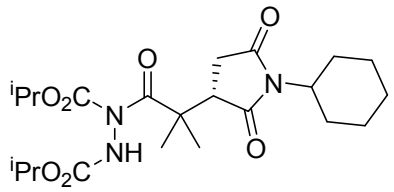

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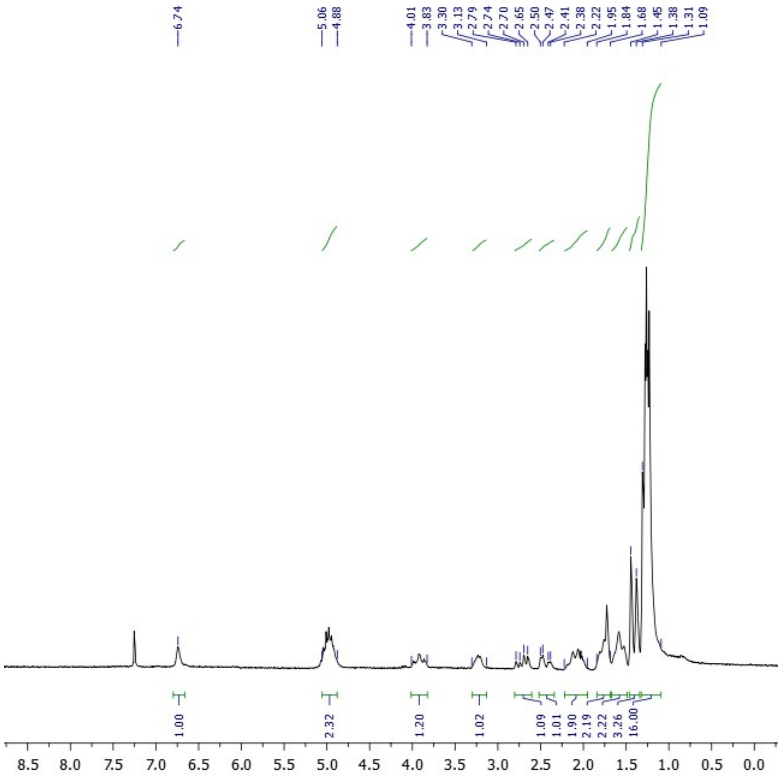
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1.38
1.31
1.09
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2.32
1.20
1.02
1.09
1.01
1.90
2.19
2.22
3.26
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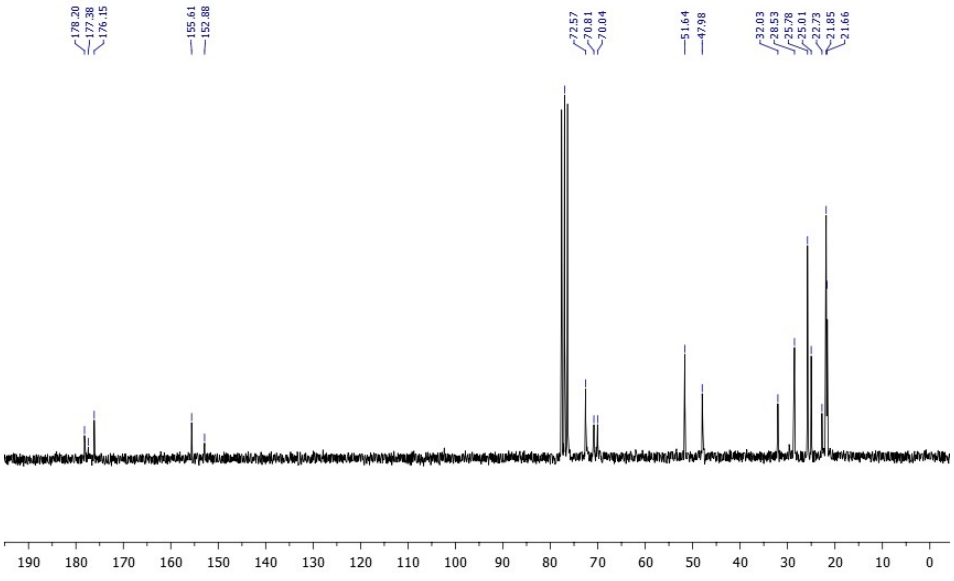
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72.57
70.81
70.04
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25.01
22.73
21.85
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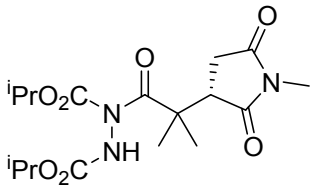

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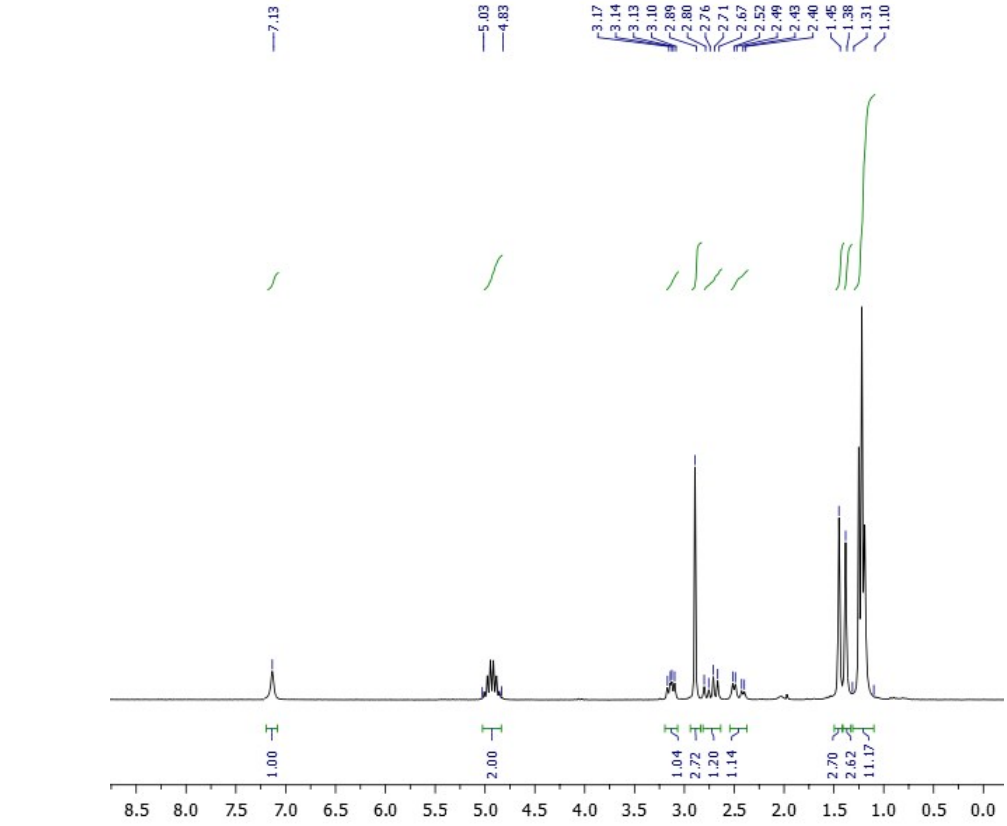
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3.17
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3.13
3.10
2.89
2.80
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2.71
2.67
2.52
2.49
2.43
2.40
1.45
1.38
1.31
1.10
1.00
2.00
1.04
2.72
1.20
1.14
2.70
2.62
11.17
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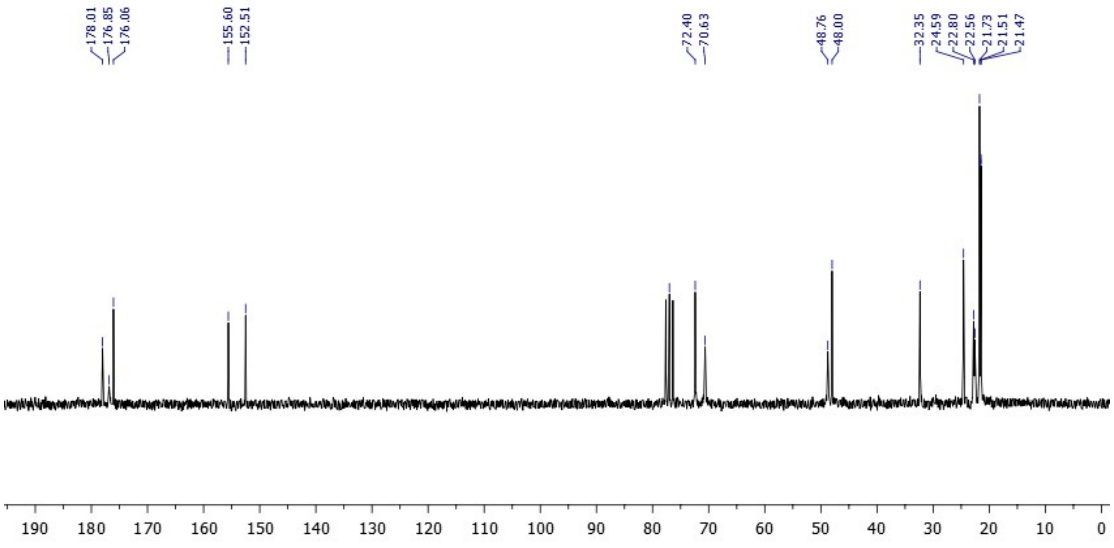
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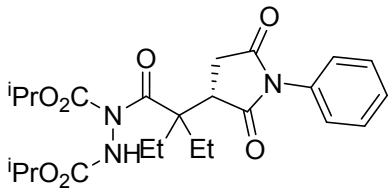
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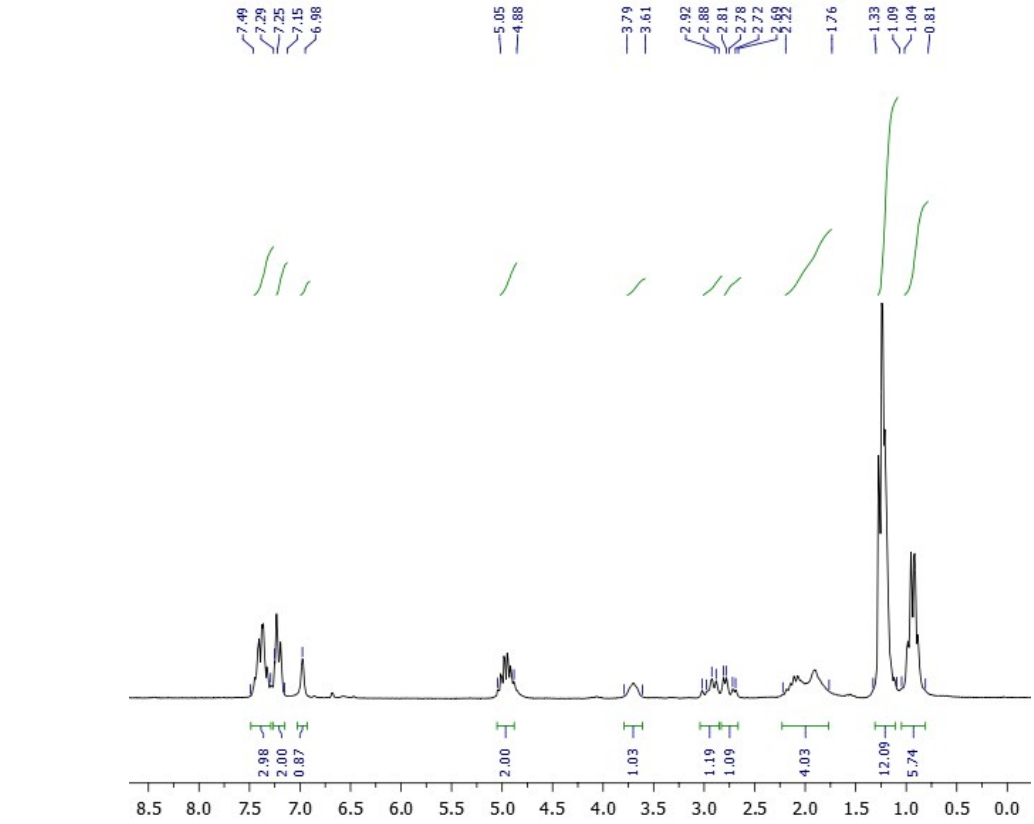
NH
Et
Et
O
$^{i}PrO_2C$
O

4g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2.92
2.88
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2.78
2.72
2.22
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1.33
1.09
1.04
0.81
2.98
2.00
0.87
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1.19
1.09
4.03
12.09
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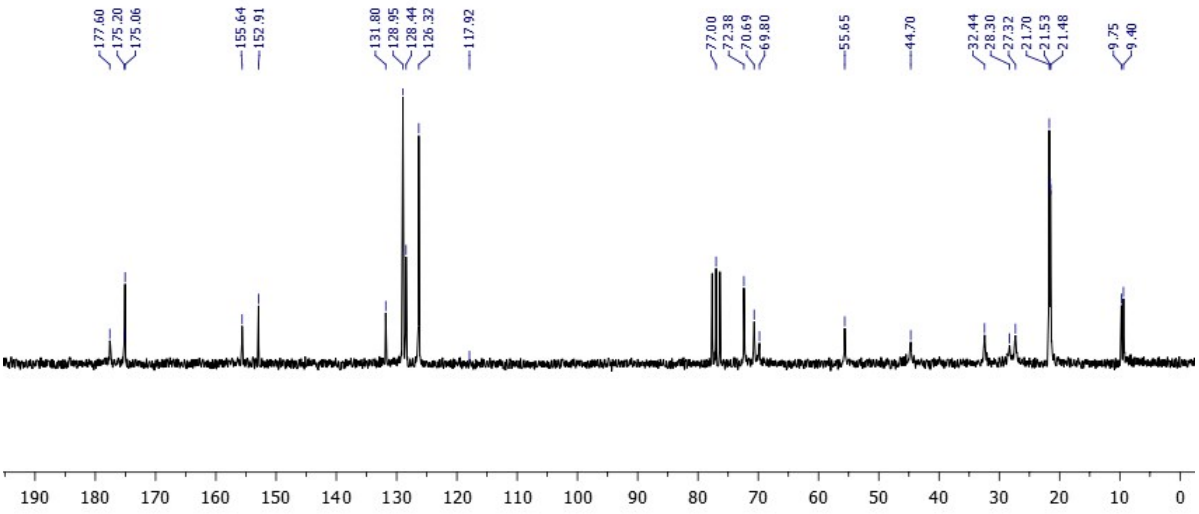
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69.80
55.65
44.70
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21.48
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9.40
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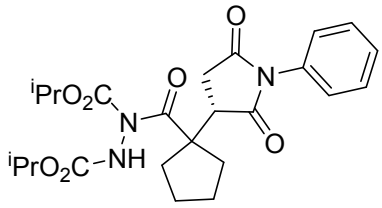
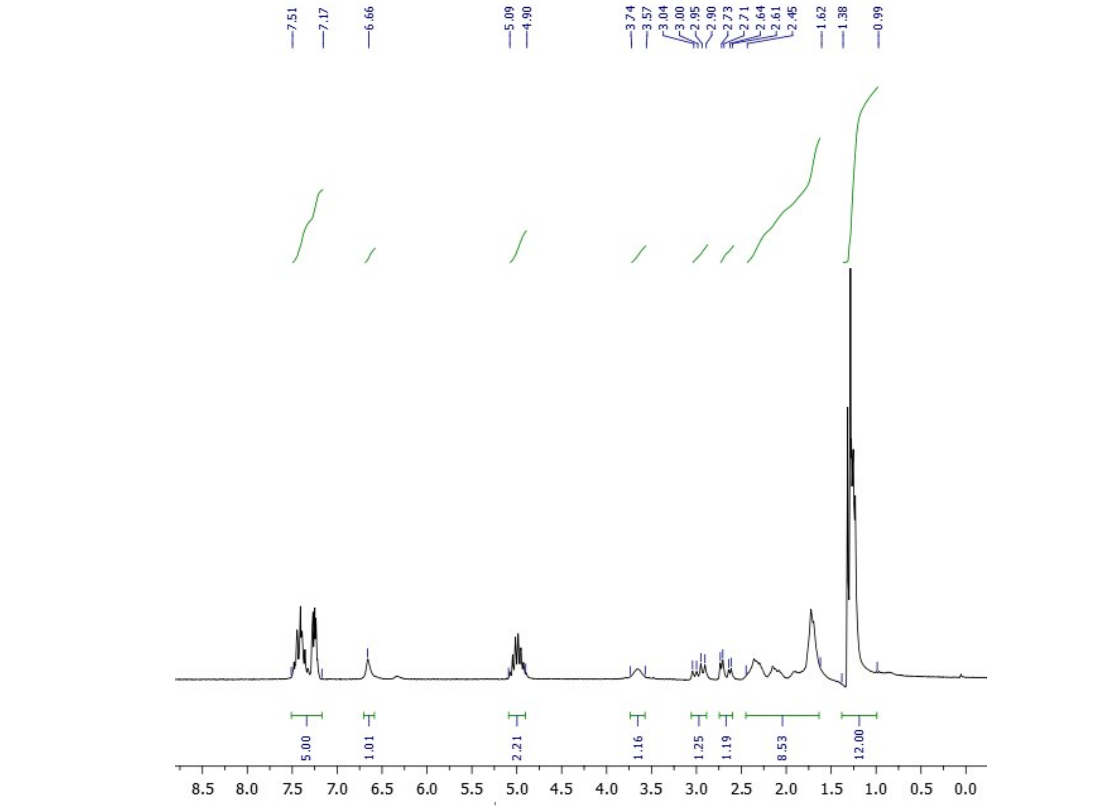


4h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2.61
2.45
1.62
1.38
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5.00
1.01
2.21
1.16
1.25
1.19
8.53
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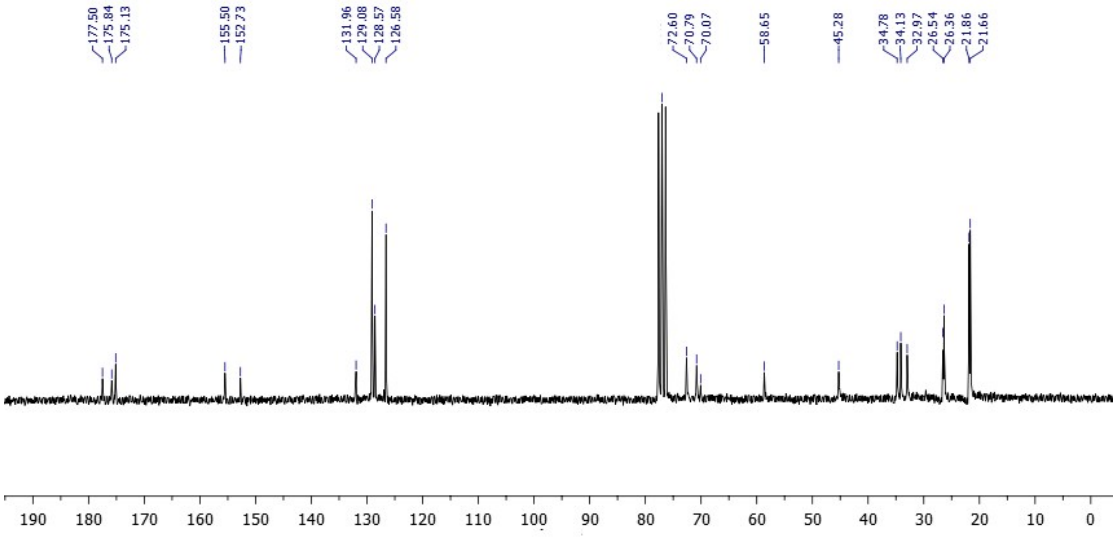
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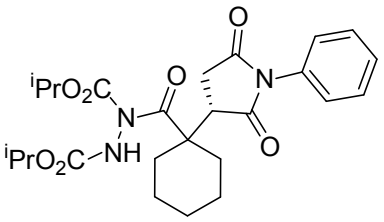
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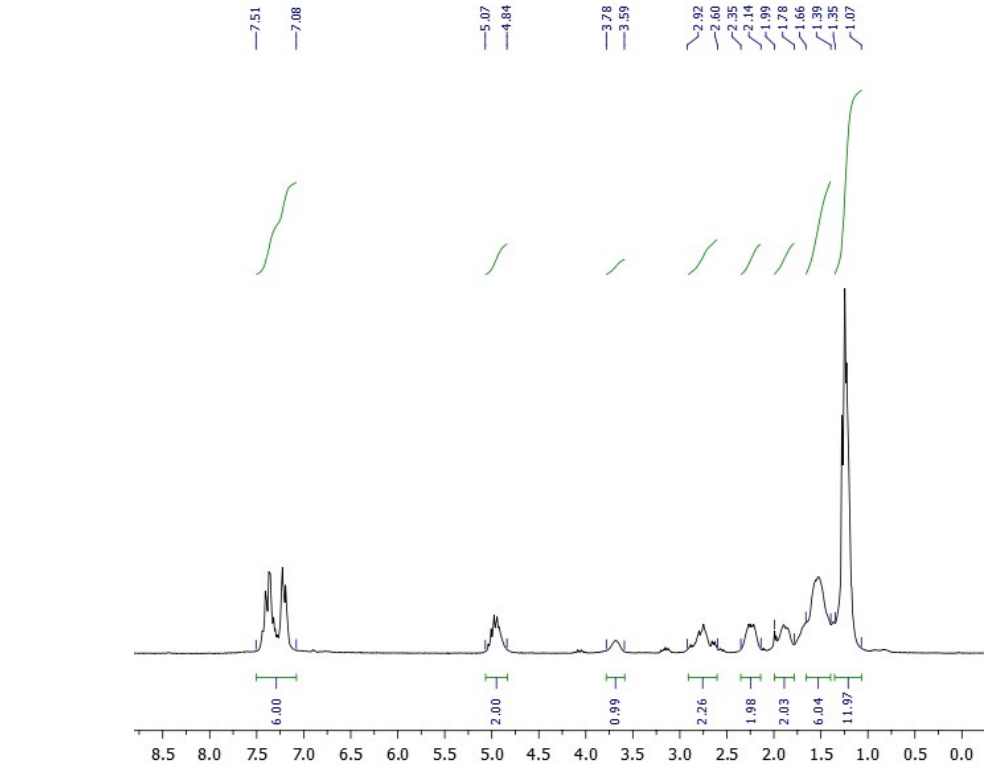
N
O
$^{i}PrO_2C$
NH
O

4i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1.66
1.39
1.35
1.07
6.00
2.00
0.99
2.26
1.98
2.03
6.04
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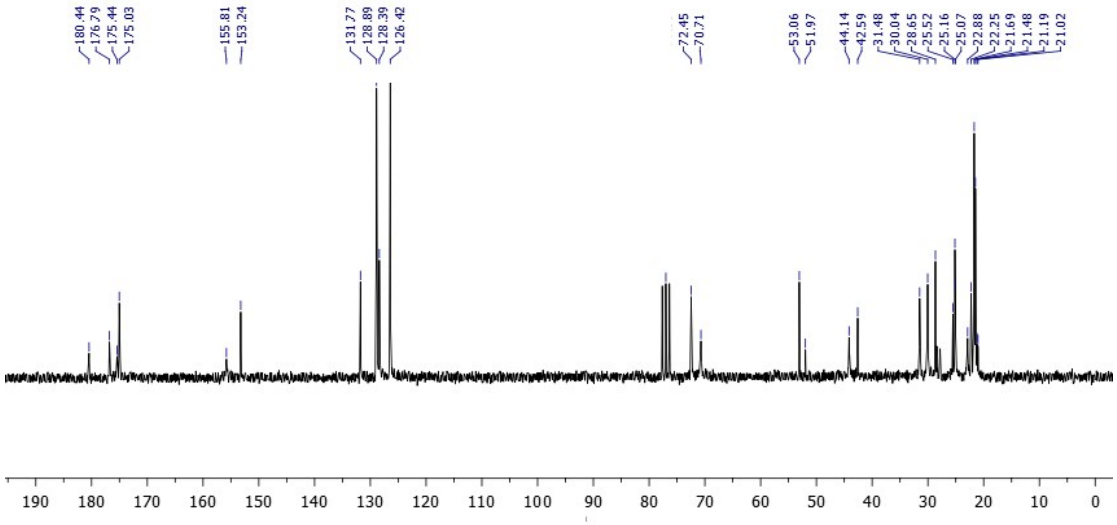
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42.59
31.48
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25.52
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21.19
21.02
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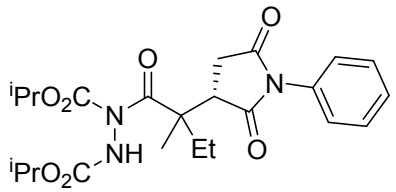
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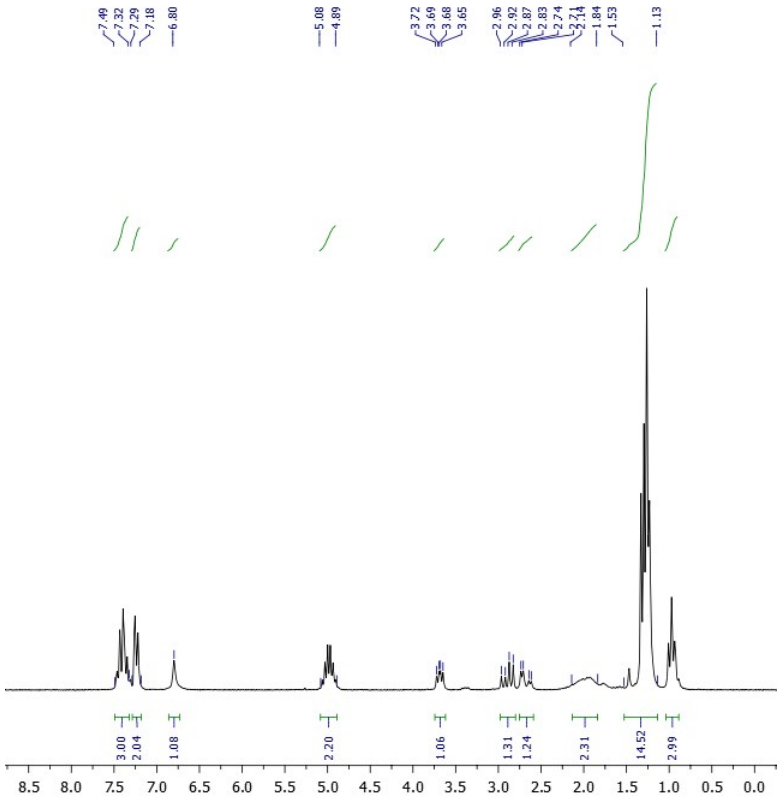
$^{i}PrO_2C$
N
NH
Et
O
$^{i}PrO_2C$

4j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2.83
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2.14
1.84
1.53
1.13
3.00
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1.08
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1.06
1.31
1.24
2.31
14.52
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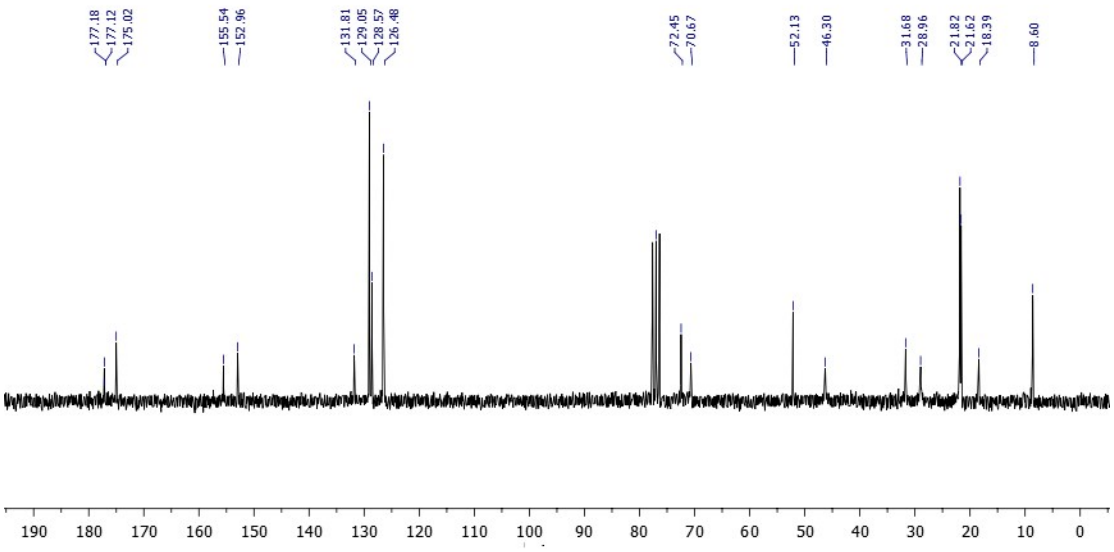
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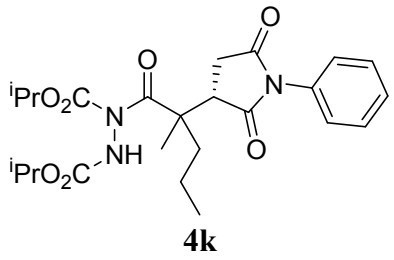
128.57
126.48
72.45
70.67
52.13
46.30
31.68
28.96
21.82
21.62
18.39
8.60
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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O
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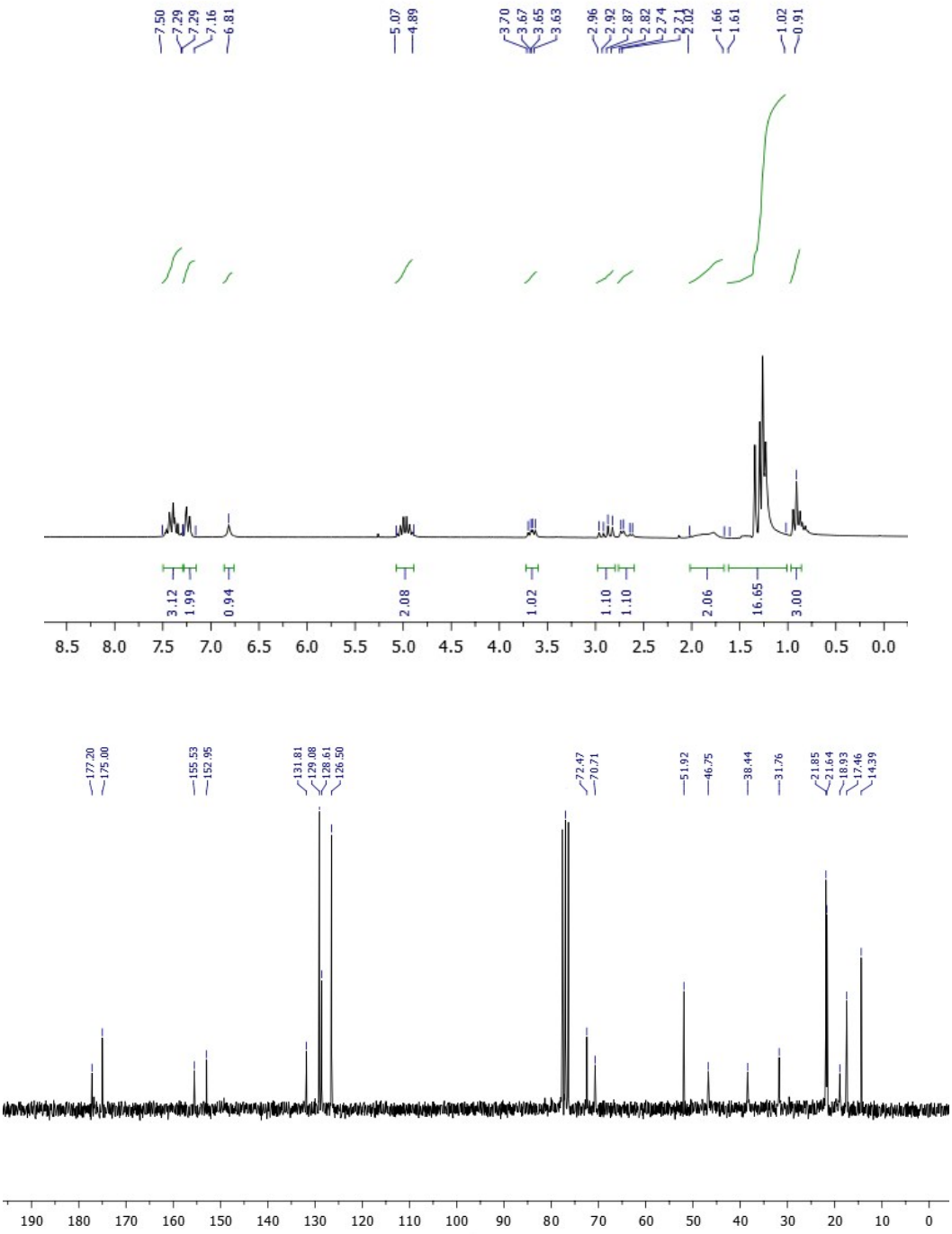
$^{i}PrO_2C$
N
NH
$^{i}PrO_2C$
O
O

4k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7.29
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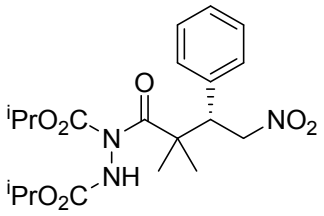
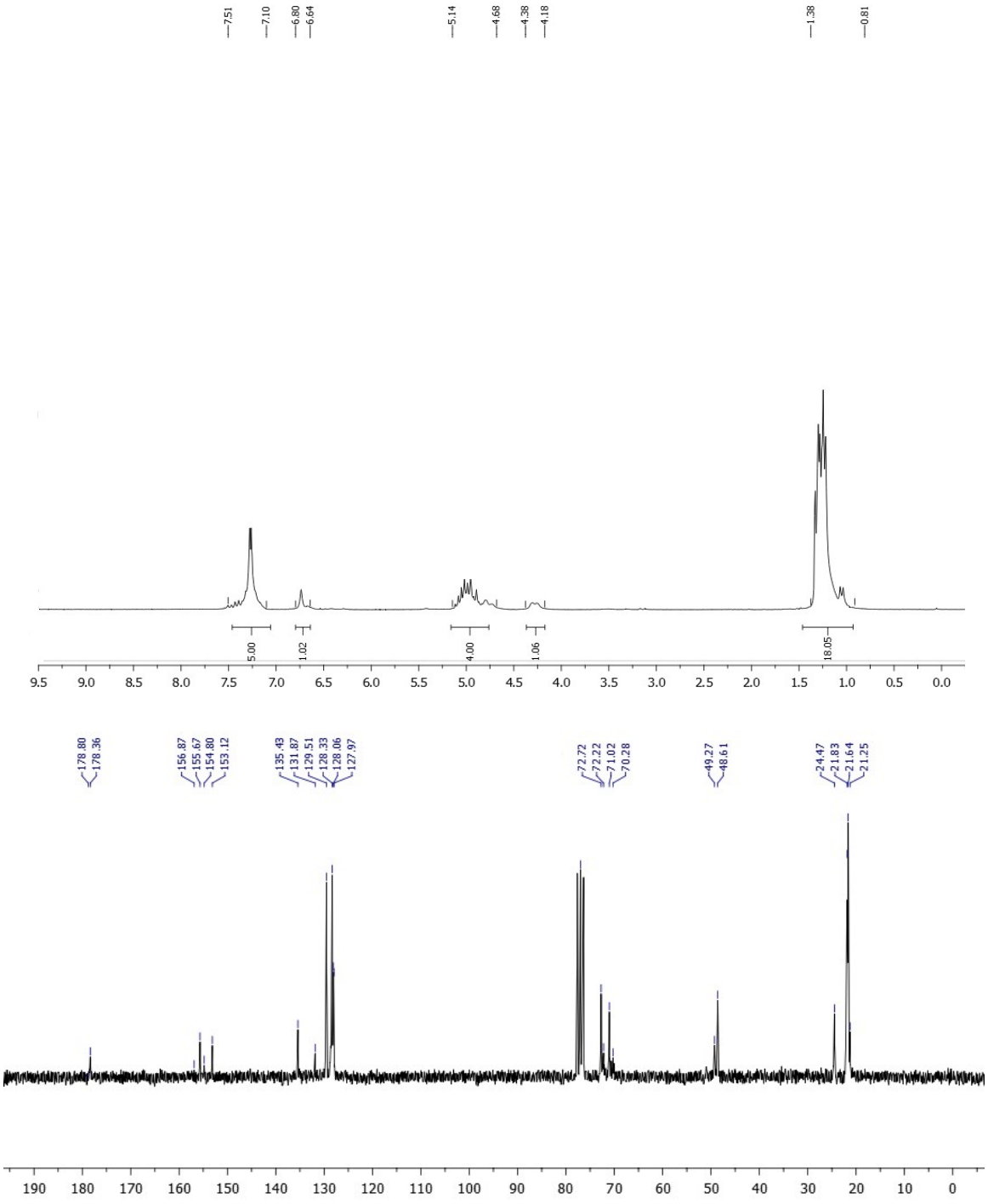
6.81
5.07
4.89
3.70
3.67
3.65
3.63
2.96
2.92
2.87
2.82
2.74
2.71
2.02
1.66
1.61
1.02
0.91
3.12
1.99
0.94
2.08
1.02
1.10
1.10
2.06
16.65
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
177.20
175.00
155.53
152.95
131.81
129.08
128.61
126.50
72.47
70.71
51.92
46.75
38.44
31.76
21.85
21.64
18.93
17.46
14.39
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


O
$^{i}PrO_2C$
N
NH
$^{i}PrO_2C$
NO_2

7a


7.51
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4.38
4.18
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0.81
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1.06
18.05
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155.67
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153.12
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129.51
128.33
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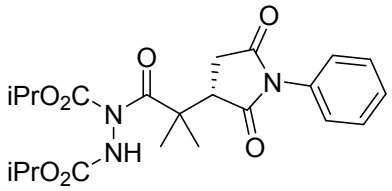
21.25



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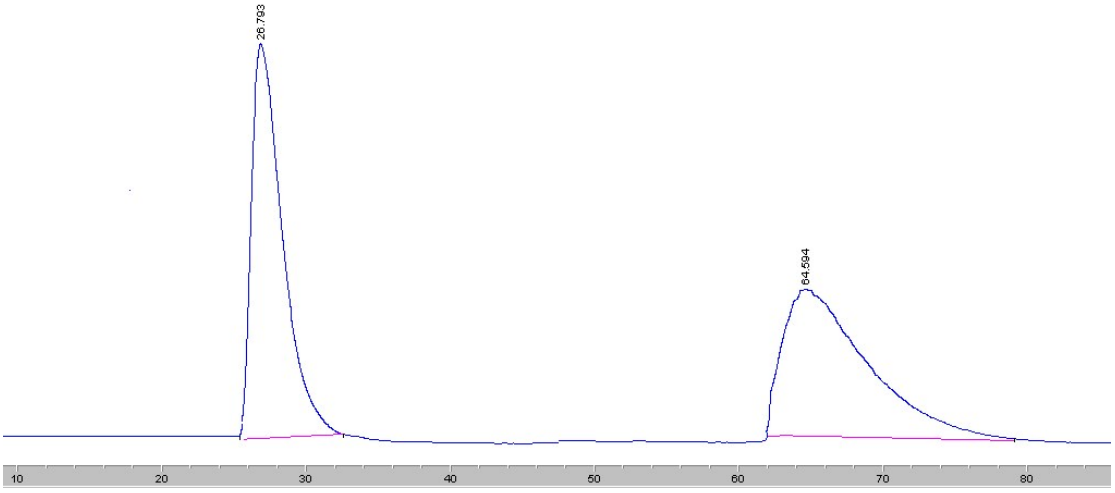
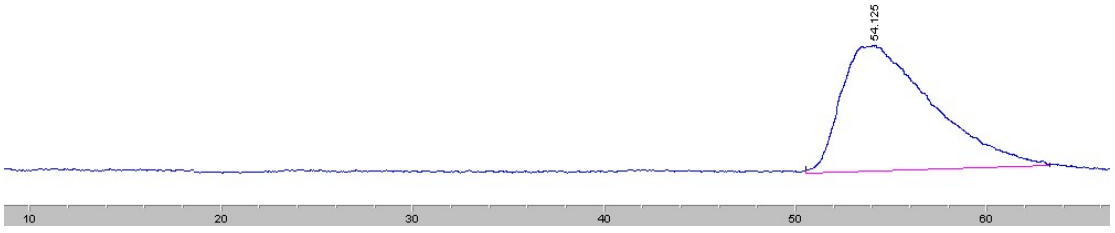
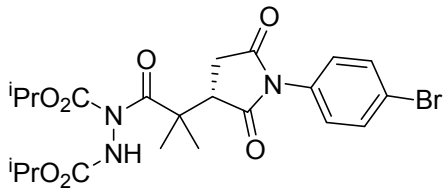


#	Time	Area	Height	Width	Area%	Symmetry
1	26.793	85240.2	561.7	1.8405	49.989	0.424
2	64.594	85278.7	208.7	6.8113	50.011	0.372



#	Time	Area	Height	Width	Area%	Symmetry
1	54.125	48125.7	144.3	5.5587	100.000	0.571



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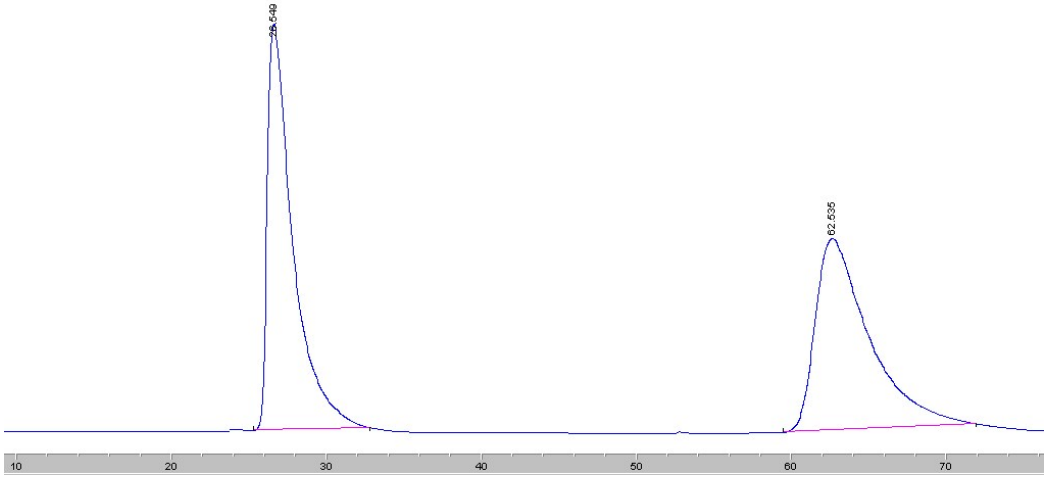
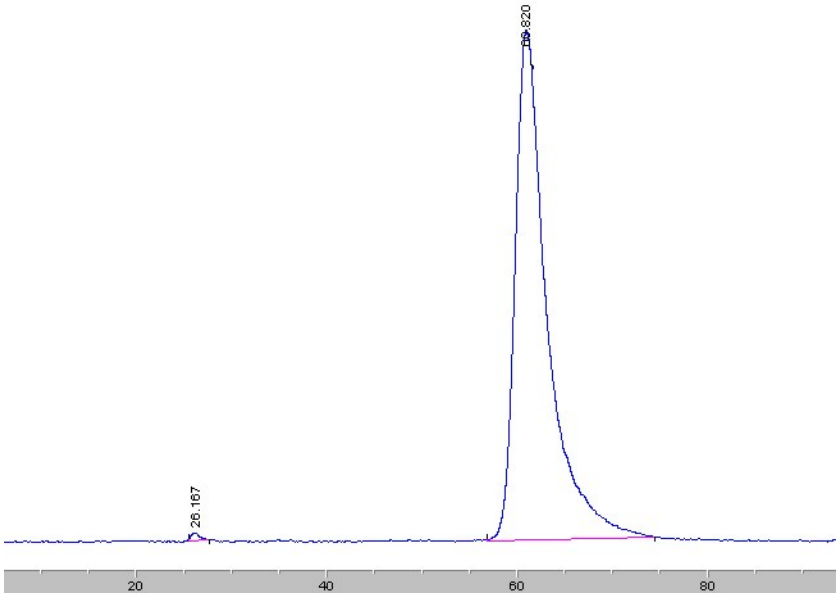
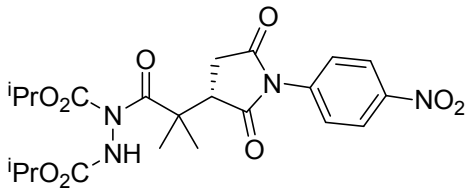


#	Time	Area	Height	Width	Area%	Symmetry
1	26.549	126394.6	1098.8	1.378	50.172	0.327
2	62.535	125527.1	518.3	2.8397	49.828	0.426



#	Time	Area	Height	Width	Area%	Symmetry
1	26.167	239.8	3.6	0.7758	0.443	1.178
2	60.82	53943.2	230.1	3.9079	99.557	0.499



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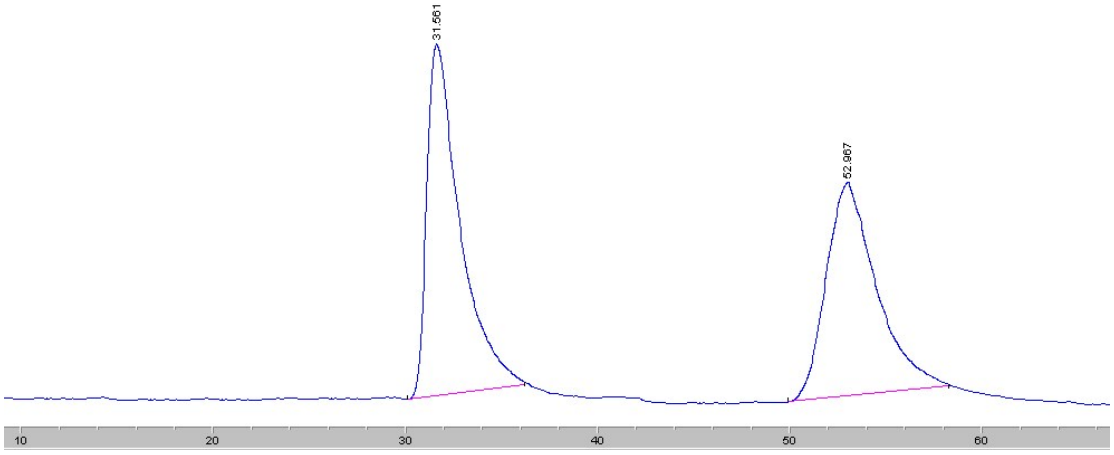
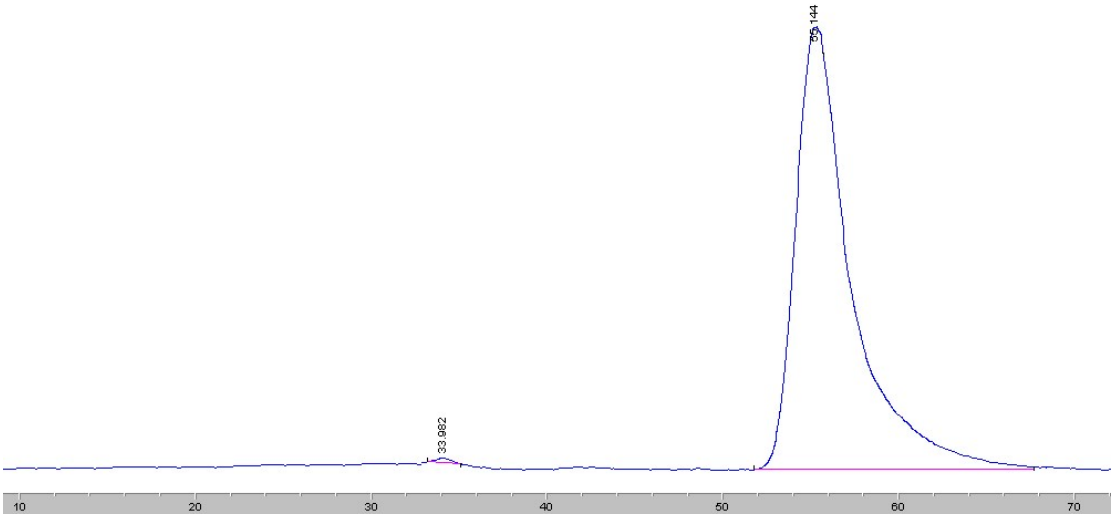
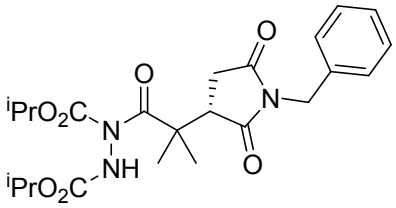


#	Time	Area	Height	Width	Area%	Symmetry
1	31.561	38337.3	318.7	1.5636	52.091	0.379
2	52.967	35259.8	193.3	2.1842	47.909	0.717



#	Time	Area	Height	Width	Area%	Symmetry
1	33.982	272.8	4.5	1.0185	0.332	0.793
2	55.144	81937.7	368.9	3.7019	99.668	0.494



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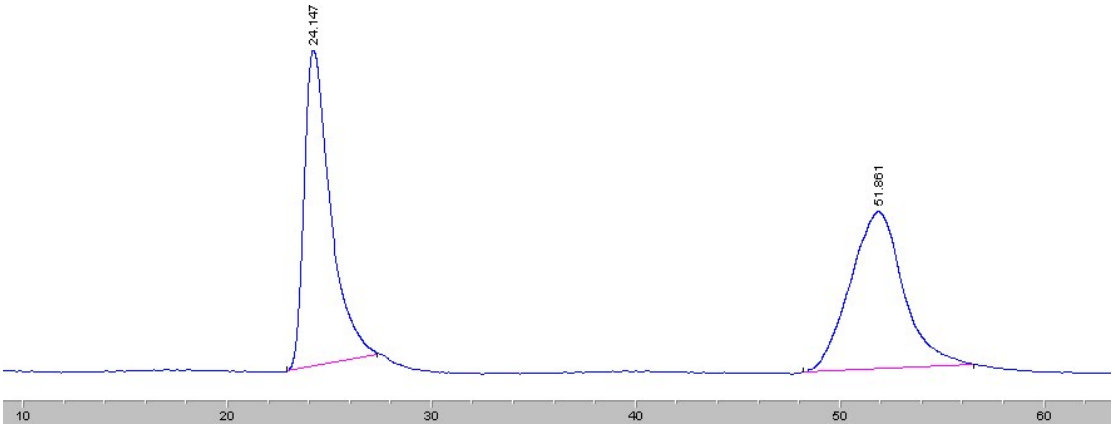
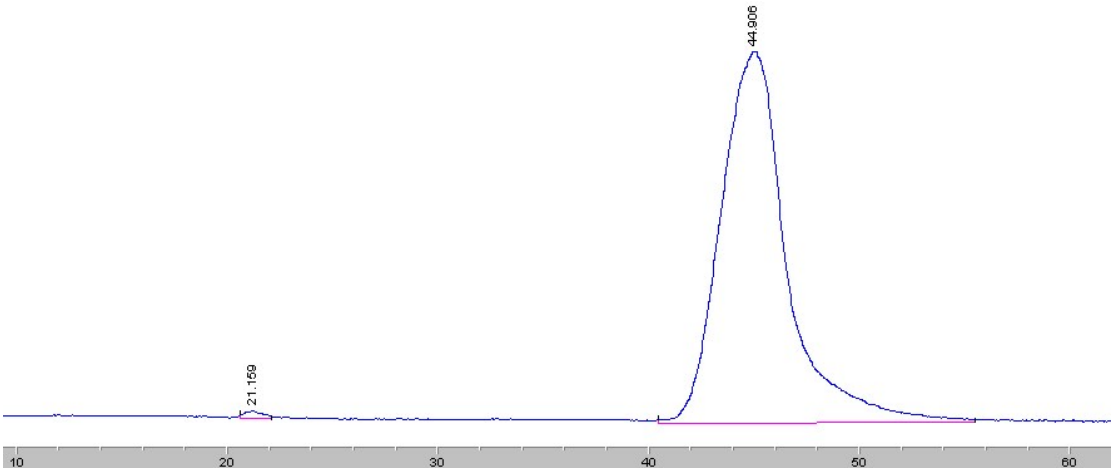
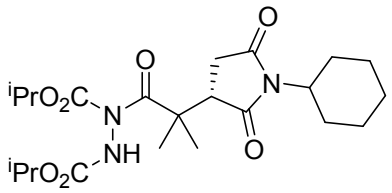


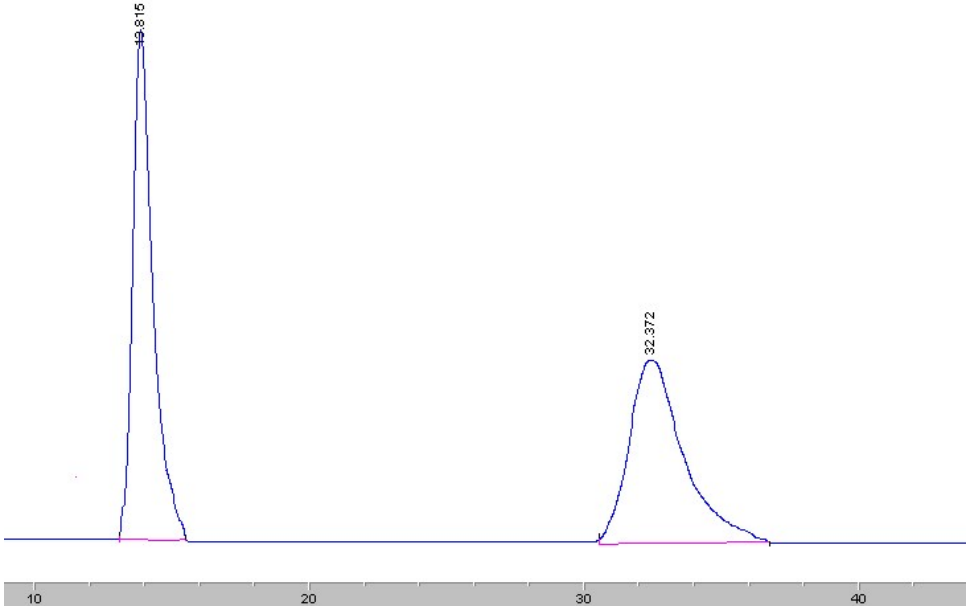
#	Time	Area	Height	Width	Area%	Symmetry
1	24.147	13859.6	155.6	1.1691	49.340	0.499
2	51.861	14230.3	77.9	2.1388	50.660	1.127



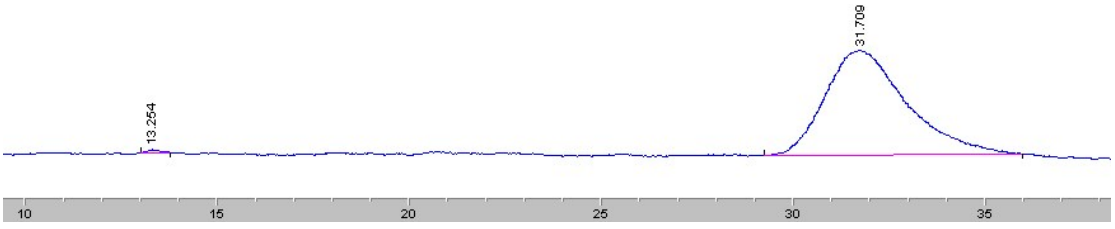
#	Time	Area	Height	Width	Area%	Symmetry
1	21.159	690.6	11.6	0.99	0.551	0.792
2	44.906	124564	570.6	3.6386	99.449	0.906



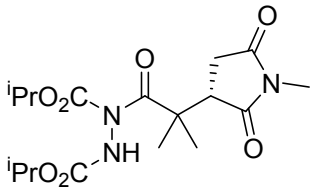
4e



#	Time	Area	Height	Width	Area%	Symmetry
1	13.815	3780.5	76.5	0.7002	49.114	0.609
2	32.372	3916.9	28	2.3316	50.886	0.629



#	Time	Area	Height	Width	Area%	Symmetry
1	13.254	84.7	3.3	0.4342	0.623	0.485
2	31.709	13511.7	90.7	2.4831	99.377	0.728



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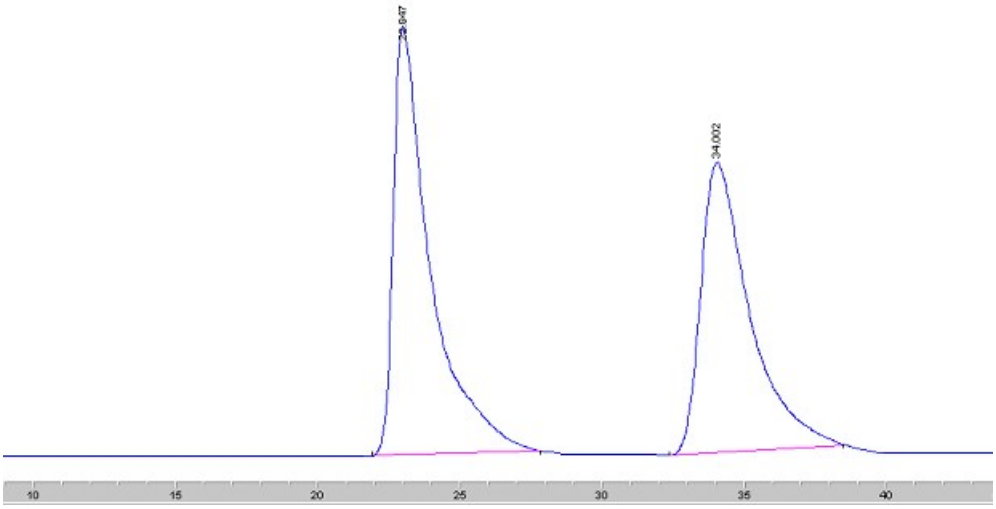
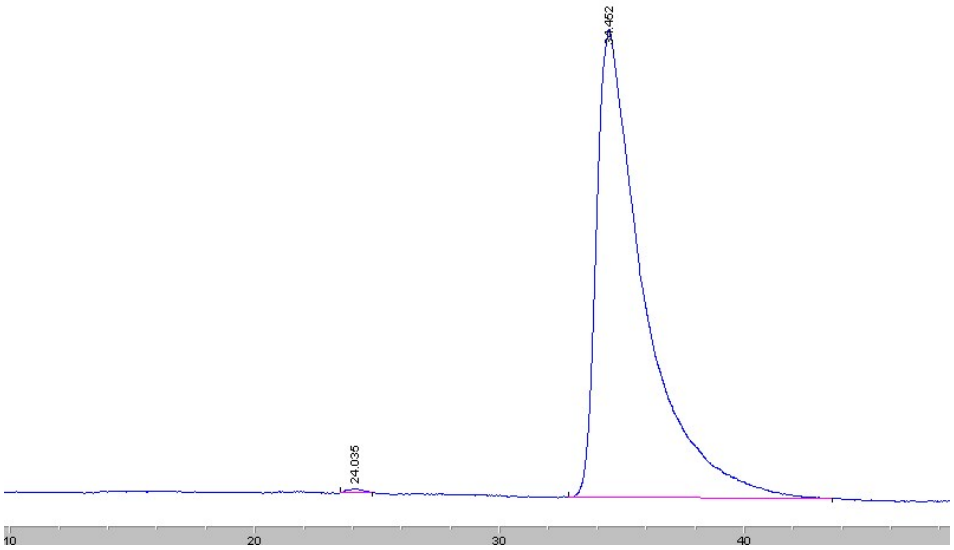
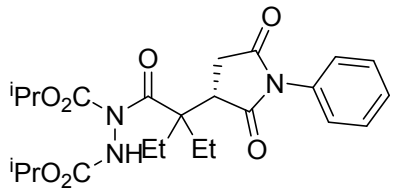


#	Time	Area	Height	Width	Area%	Symmetry
1	22.947	35708.3	392.2	1.1942	52.822	0.317
2	34.002	31892.4	265.8	1.4397	47.178	0.472



#	Time	Area	Height	Width	Area%	Symmetry
1	24.035	55	1.2	0.7575	0.330	0.818
2	34.452	16578	121.7	2.2697	99.670	0.368



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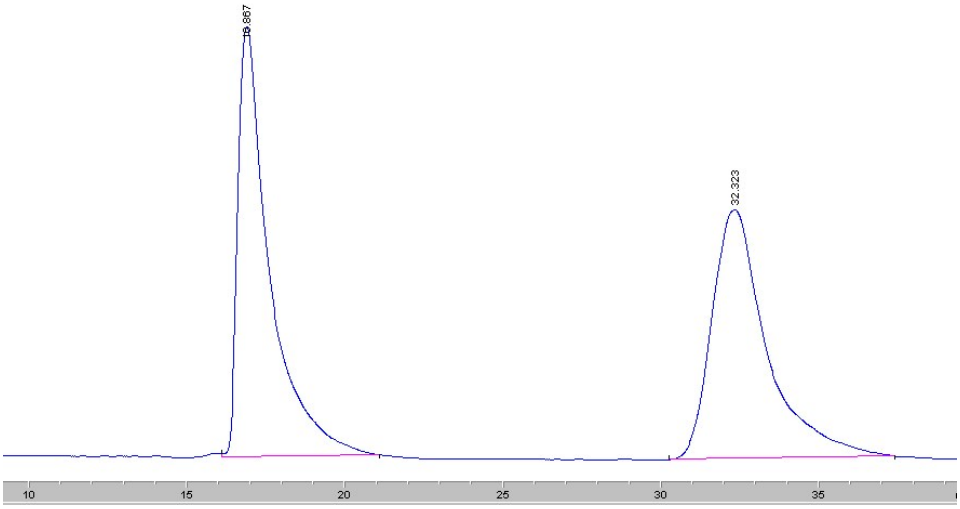
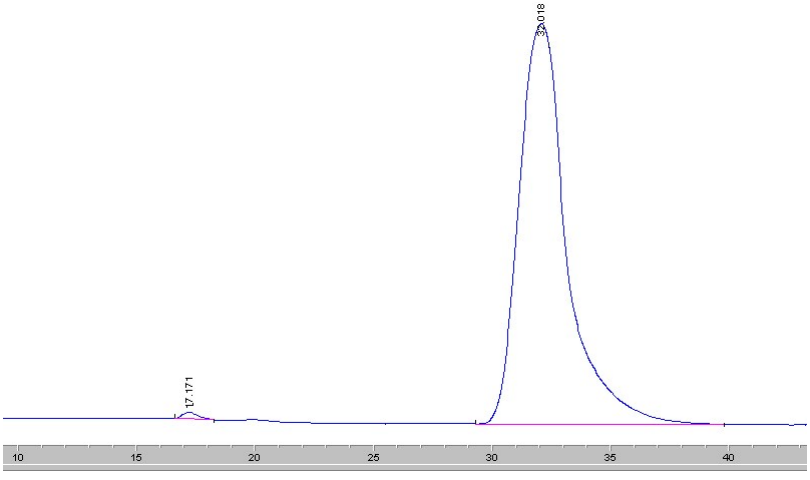
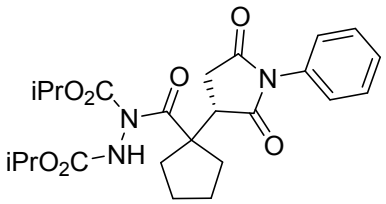


#	Time	Area	Height	Width	Area%	Symmetry
1	16.867	39023.1	560.7	0.982	49.788	0.356
2	32.323	39355.4	324.5	1.5351	50.212	0.704



#	Time	Area	Height	Width	Area%	Symmetry
1	17.171	907.6	19.4	0.7813	0.563	0.613
2	32.018	160309.6	1148.9	2.3255	99.437	0.8



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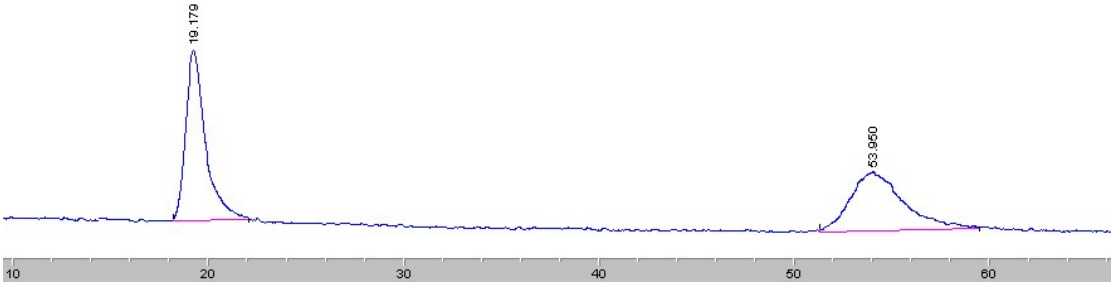
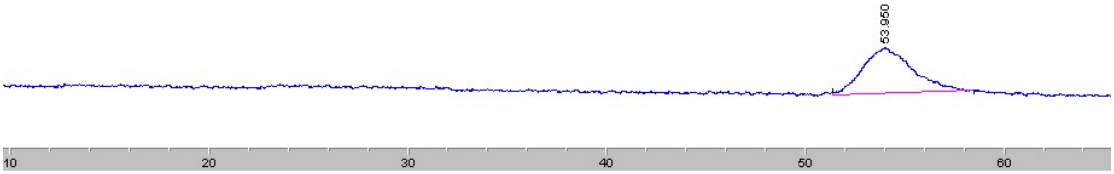
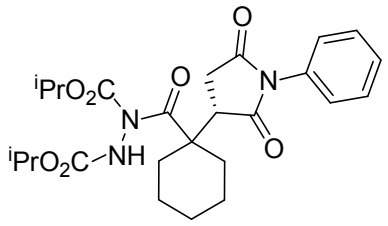


#	Time	Area	Height	Width	Area%	Symmetry
1	19.179	2233.1	31.8	1.1706	51.111	0.668
2	53.95	2136	11.2	3.1655	48.889	0.727



#	Time	Area	Height	Width	Area%	Symmetry
1	53.95	5167.7	30	2.8728	100.000	0.799



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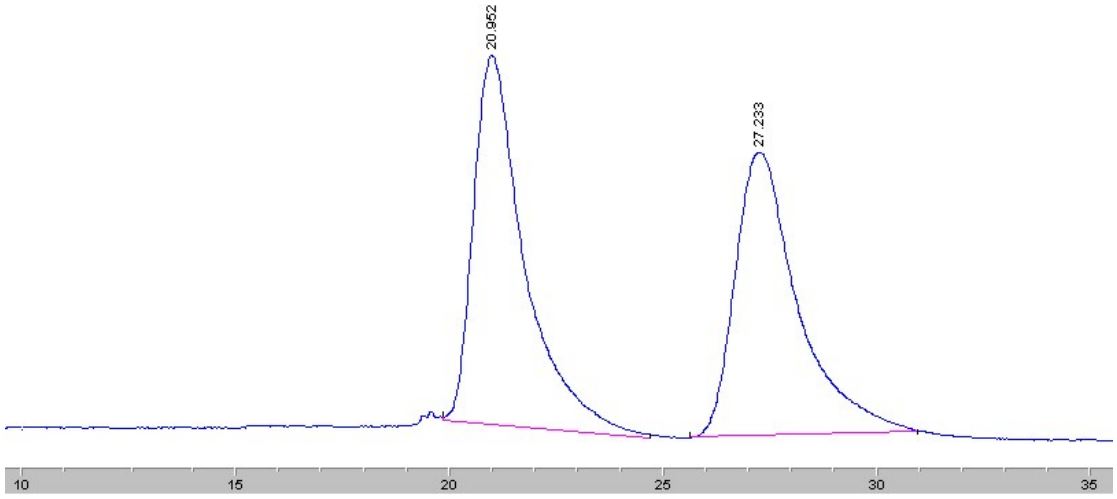
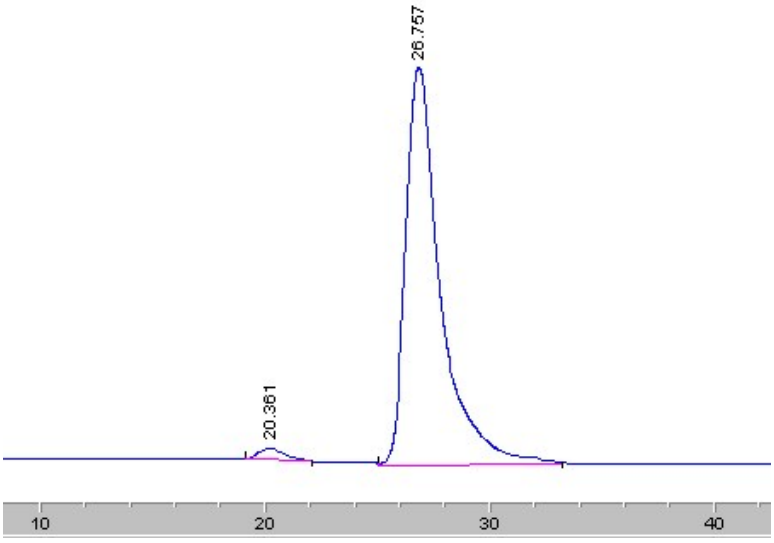
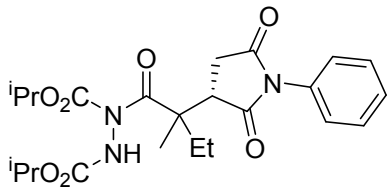


#	Time	Area	Height	Width	Area%	Symmetry
1	20.952	39755.5	477.7	1.387	51.468	0.524
2	27.233	37487.1	366.5	1.1992	48.532	0.625



#	Time	Area	Height	Width	Area%	Symmetry
1	20.361	339.6	4.9	1.1642	0.787	0.477
2	26.757	42803.4	397	1.7971	99.213	0.557



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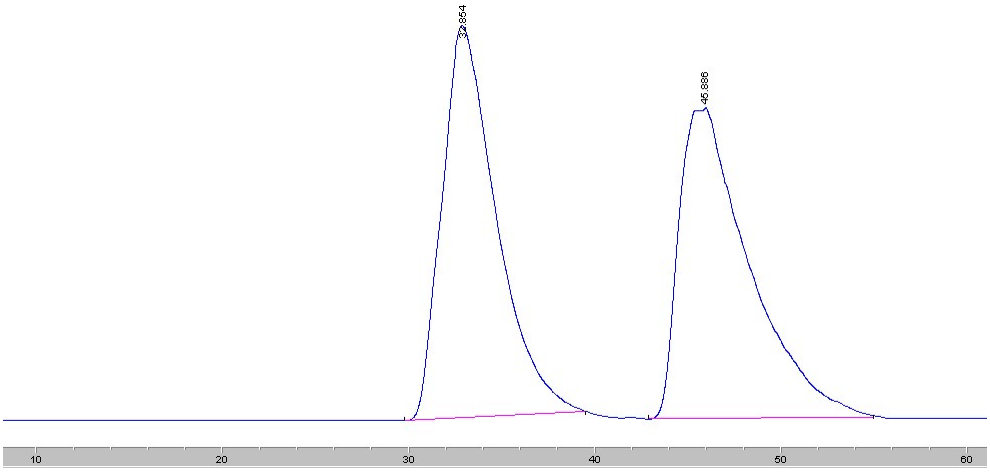
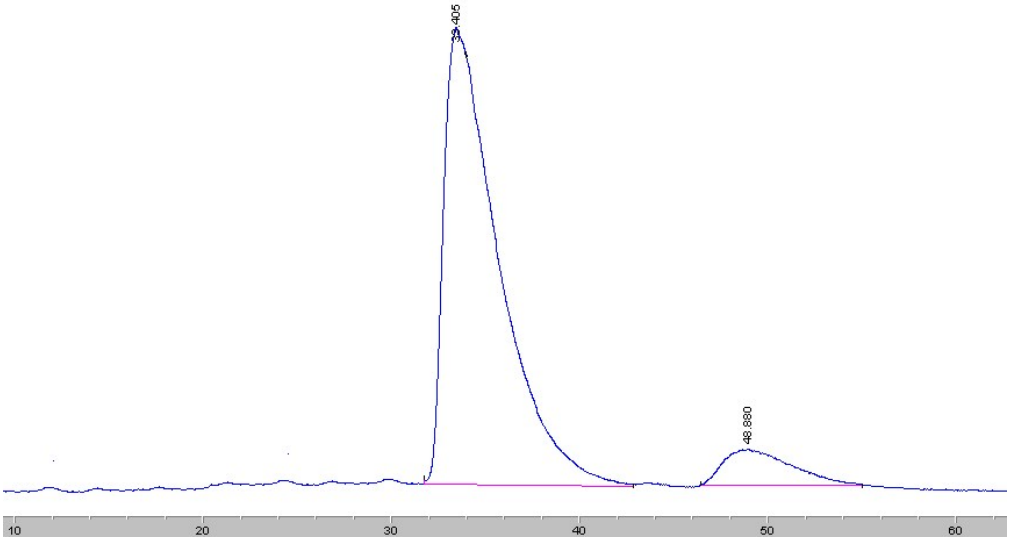
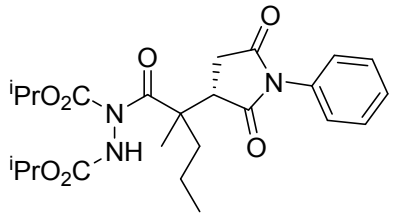


#	Time	Area	Height	Width	Area%	Symmetry
1	32.854	111917.2	546.7	2.4024	49.534	0.604
2	45.886	114025.2	433.3	4.3863	50.466	0.563



#	Time	Area	Height	Width	Area%	Symmetry
1	33.405	23589.6	115.2	3.4119	90.712	0.284
2	48.88	2415.4	9.4	4.283	9.288	0.552



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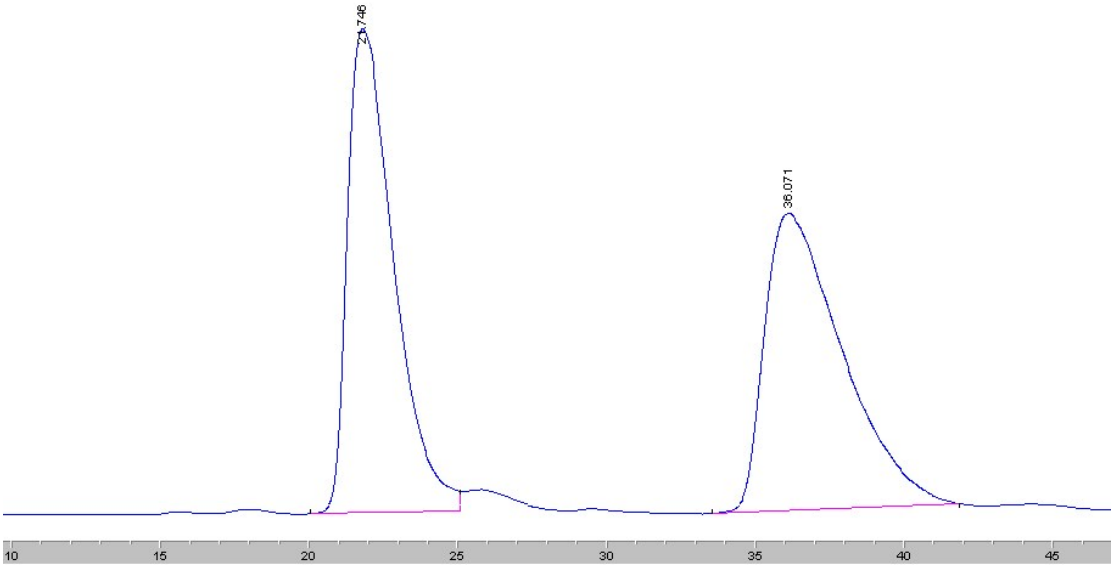
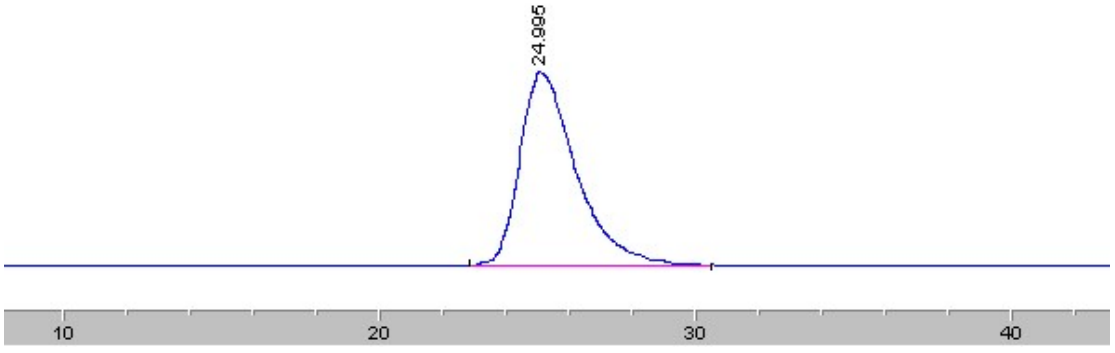
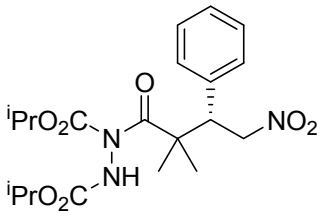


#	Time	Area	Height	Width	Area%	Symmetry
1	21.746	83671.3	772.9	1.3549	49.125	0.427
2	36.071	86651.9	476.5	2.1336	50.875	0.426



#	Time	Area	Height	Width	Area%	Symmetry
1	24.995	21837.1	174.2	2.089	100.000	0.549



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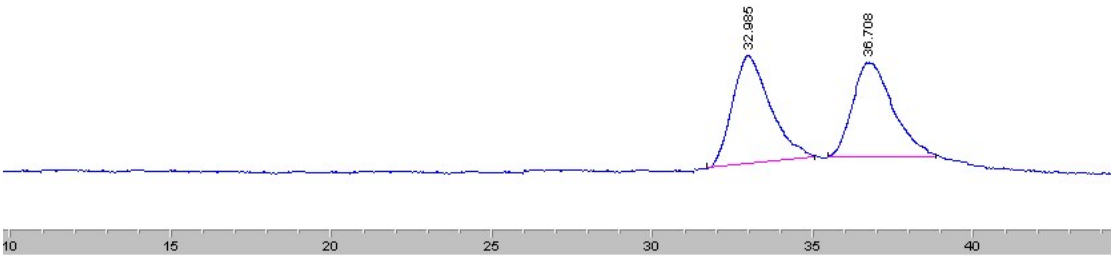
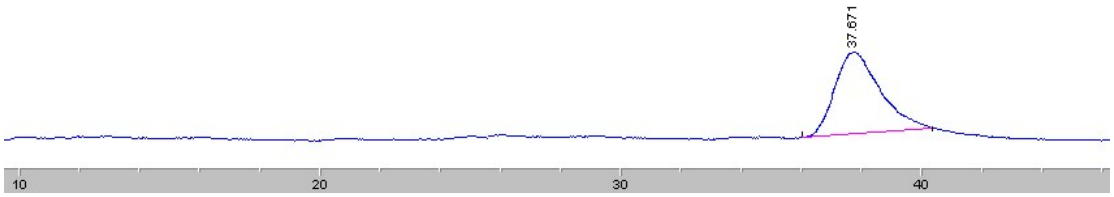


#	Time	Area	Height	Width	Area%	Symmetry
1	32.985	1254.7	15.3	0.971	51.639	0.768
2	36.708	1175.1	13.4	1.0327	48.361	0.663



#	Time	Area	Height	Width	Area%	Symmetry
1	37.671	2171.6	20.5	1.2514	100.000	0.638