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SUPPORTING INFORMATION

Peptidomimetic Organocatalysts: Efficient Michael Addition of Ketones onto Nitroolefins with Very Low Catalyst Loading

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1. General information

Melting points were recorded after column chromatography of compound on Polmon Melting point apparatus and were uncorrected. ^{1}H NMR (300 MHz or 500 MHz and ^{13}C NMR (75 MHz or 125 MHz) spectra were recorded in $CDCl_3$, CD_3COCD_3 and D_2O solvents on Bruker Avance 300 or INOVA 500 MHz spectrometer at ambient temperature. The chemical shifts are reported in ppm relative to $CDCl_3$ (δ = 7.26), to DMSO δ = 2.50) and toD_2O (δ = 4.79) for ^{1}H NMR and relative to the central resonances of $CDCl_3$ (δ = 77.0) and to DMSO (δ = 39.5) for ^{13}C NMR. HRMS of the compounds were recorded on high resolution QSTAR XL hybrid MS/MS system, applied bio systems under electron spray ionization method conditions preparing samples in methanol. The optical rotations were recorded on ANTON PAAR MCP-200 digital polarimeter. IR spectra were recorded on Perkin-Elmer Infrared spectrometer and samples were scanned either in neat KBr wafers or in chloroform as a thin film. Routine monitoring of reaction was performed by TLC, using precoated silica gel TLC plates obtained from E-Merck. IUPAC names of catalysts and Michael products were taken from Chem. ultra 12. All the column chromatographic separations were done by using silica gel (Acme's, 60-120 mesh). Evaporation of solvents was performed at reduced pressure. Analytical high performance liquid chromatography (HPLC) was performed using Daicel Chiralpak IA and IC columns.

2. Materials

All reactions were performed under an atmosphere of nitrogen or argon in flame-dried or oven-dried glassware with magnetic stirring. All solvents were dried prior to use. For HPLC commercially available HPLC grade isopropanol and hexane were used. Nitroolefines were prepared following the known procedure in the literature[1].

3. Experimental procedures, analytical and spectroscopic data

3.1 Preparation procedure of compounds 2 and 2a

(*S*)-Ethyl 1-((1-(*tert*-butoxycarbonyl)pyrrolidin-2-yl)methyl)-*1H*-1,2,3-triazole-5-carboxylate (2) and (*S*)-ethyl 1-((1-(*tert*-butoxycarbonyl)pyrrolidin-2-yl)methyl)-*1H*-1,2,3-triazole-4-carboxylate (2a):

Triazole catalysts **7** and **7a** were synthesized from Boc-protected proline azide.[2]

1. For aromatic nitroalkenes J. Bourguignon, G. Le Nard, G. Queguiner, *Can. J. Chem*., 1985, **63**, 2354-2361;

2. For synthesis of Proline azide from *L*-proline a) A. Paul, H. Bittermann and P. Gmeiner, *Tetrahedron,* 2006, **62**,8919-8927. b) A**.** Esther , C. Xacobe, Cambeiro, J. Ciril and M. A. Perica`s, *Org.Lett.,* 2007, **9,** 3717-3720. To a solution of **1** (3.5 g, 15.4 mmol) in toluene (60 mL) was added ethyl propiolate (4.5 g, 46.4 mmol). The mixture was heated to reflux for 19 h, after cooling to room temperature, the solvent was removed and the two isomers were separated by silica gel column chromatography, furnishing 3.31 g (66%) of **2a** and 1.25 g (25%) of **2** as waxy solid and viscous oil respectively yield 91%.

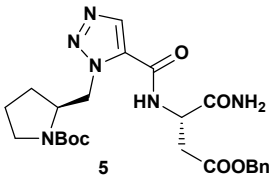
Ru-catalyzed click reaction

To the azide **1** (4.0 g, 17.6 mmol) and ethyl propiolate (5.2 g, 53.0 mmol) in dry benzene (30 mL) was added catalytic amount[3a] (0.281 g, 2 mol %) of Cp*RuCl(PPh_3)$_2$ in argon atmosphere and resulting mixture was stirred at 80 ^oC. After completion of the starting materials, mixture was filtered, solvent was removed *in vacuo* and residue was purified on silica gel column chromatography to yield triazole **2** (4.0 g, 70%).

Cu- catalyzed click reaction

Compound **1** (4.0 g, 17.6 mmol) upon Cu-catalysed [3+2] cycloaddition reaction[3b] with ethyl propiolate (5.2 g, 53.0 mmol) gave **2a** as white solid (4.87g, 85 % yield). Analytical data of **2** and **2a** matched with the data reported in literature.[3b]

3.2 Synthetic procedure of 1,5-substituted triazole catalyst 7
(*S*)-*tert*-Butyl-2-((5-(((*S*)-1-amino-4-(benzyloxy)-1,4-dioxobutan-2-yl)carbamoyl)-*1H*-1,2,3-triazol-1-yl)methyl)pyrrolidine-1-carboxylate (5)



5

Ester hydrolysis of **2** (3.0 g, 9.2 mmol) carried out using LiOH.H_2O (1.1 g, 27 mmol) in 7:3 ratio of THF: H_2O (20 mL) gave acid **3** (2.19 g, 80% crude), which was used as such for the next step. To the acid **3** (2.0 g, 6.17 mmol) in dry CH_2Cl_2 (15 mL) was added HOBt (0.91 g, 6.79 mmol) and stirred for 10 min. EDCI (1.29 g, 6.79 mmol) was added to the reaction mixture at 0 ^oC and allowed to stir for another 10 min. Then was added amine **4**[4] (1.37 g, 6.17 mmol) (pre basified with DIPEA, (2.68 mL, 15.43 mmol)) and the resultant mixture was allowed to stir at ambient temperature for 24 h. After consumption of the starting materials reaction was quenched with saturated aqueous NH_4Cl and extracted with CH_2Cl_2. Organic layer was sequentially washed with saturated aqueous $NaHCO_3$, brine solution, dried over anhydrous Na_2SO_4, concentrated *in vacuo* and residue was purified by silica gel column chromatography to yield **5** as a white solid.

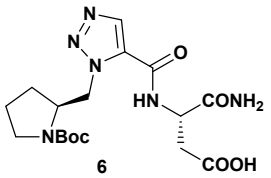
Yield 80% (3.6 g); mp 80-82 ^oC; $[\alpha]_D^{25}$ = -4.8 (*c* 1, MeOH); IR (υ_{max}): 3402, 2973, 2926, 1733, 1681, 1570, 1396, 1170, 771 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ: 8.16 (d, *J* = 7.6 Hz, 1H), 7.37 (rotamer, 1H), 6.64 (s, 1H), 6.54-6.39 (rotamer, 6H), 4.26 (s, 2H), 4.04-3.76 (rotamer, 3H),

3.49-3.34 (rotamer, 1H), 2.43-2.25 (rotamer, 2H), 2.18-2.06 (rotamer, 1H), 1.95-1.81 (rotamer, 1H), 1.05-0.64 (rotamer, 4H), 0.52-0.43 (rotamer, 9H). ^{13}C NMR (75 MHz, DMSO-d_6) δ: 171.0, 169.7, 157.0, 153.0, 135.6, 133.9, 130.5, 127.9, 127.4, 127.5, 78.2, 65.3, 56.2, 55.4, 50.6, 48.9, 45.4, 35.6, 27.5, 22.5, 21.6; HRMS (ESI): *m/z* calculated for $[C_{24}H_{33}O_6N_6]$ 501.2456 $[M+H]^+$, found 523.2457.

3. a) For Ruthenium catalysed azide alkyne cycloaddition reactions (RuAAC) see: L. Zhang, X. Chen, P. Xue, H. H. Y. Sun, I. D. Williams, K. B. Sharpless, V. V. Fokin, G.Jia, *J. Am. Chem. Soc.* **2005**, *127,* 15998-15999; b) For the synthetic procedure and Characterisation data of compound **2a** see: A. Paul, H. Bittermann, P. Gmeiner, *Tetrahedron 62*, **2006**, 8919-8927;

4. For synthesis of *β*-Benzyl *L*-Isoasparaginate see: J. Eldo, J. P. Cardia, E. M. O'Day, J. Xia, H. Tsuruta, E. R. Kantrowitz, *J. Med. Chem.* **2006,** *49,* 5932-5938.

(*S*)-4-Amino-3-(1-(((*S*)-1-(*tert*-butoxycarbonyl)pyrrolidin-2-yl)methyl)-*1H*-1,2,3-triazole-5-carboxamido)-4-oxobutanoic acid (6)

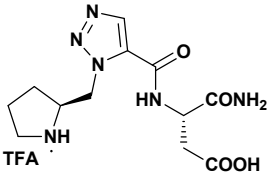


6

To compound **5** (2.5 g, 5.0 mmol) in methanol (6 mL) was added 10% Pd/C (53 mg 0.5 mmol) under inert atmosphere. This was allowed to react under H_2 atmosphere for about 5-6 h. After completion of the reaction, the mixture was filtered through a pad of celite bed using methanol, concentrated *in vacuo*, resultant solid was purified through silica gel column chromatography ($CHCl_3$: MeOH; 9:1) to get **6** as fine white colored solid.

Yield 95% (1.94 g); mp 98-101 ^{o}C; $[\alpha]_D^{25}$ = -11.7 (*c* 1, MeOH); IR (υ_{max}): 3181, 2967, 2928, 1691, 1569, 1396, 772 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ: 8.12 (rotamer, 1H), 7.39 (rotamer d, 1H), 6.59 (s, 1H), 6.35 (s, 1H), 4.00-3.78 (rotamer, 3H), 3.50-3.35 (rotamer, 1H), 2.40-2.22 (rotamer, 2H), 2.04-1.89 (rotamer, 1H), 1.84-1.63 (rotamer, 1H), 1.05-0.64 (rotamer , 4H), 0.60-0.40 (rotamer, 9H). ^{13}C NMR (75 MHz, DMSO-d_6) δ: 171.6, 157.3, 153.3, 134.1, 130.9, 78.5, 56.4, 55.7, 50.9, 49.4, 45.6, 35.8, 27.8, 22.7, 21.8 HRMS (ESI): *m/z* calculated for $[C_{17}H_{26}O_6N_6Na]$ 433.1806 $[M+Na]^+$, found 433.1800.

(*S*)-4-Amino-4-oxo-3-(1-((*S*)-pyrrolidin-2-ylmethyl)-*1H*-1,2,3-triazole-5-carboxamido)butanoic acid (7)



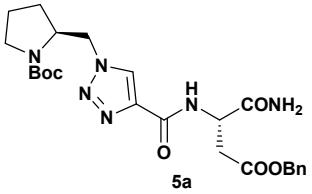
7

To a suspension of compound **6** (1.50 g, 3.6 mmol) in CH_2Cl_2 (5 mL) was added trifluoroacetic acid (5 mL) (CH_2Cl_2: TFA; 1:1) at 0 ^{o}C and stirred at room temperature. Reaction was monitored by thin layer chromatography. After completion of the reaction, CH_2Cl_2 was removed *in vacuo*. Excess

trifluoroacetic acid was co-distilled with 5 mL of CH_2Cl_2, this process was repeated several times and residue was finally washed with *n*- pentane, dried under vacuum to get compound **7** as white solid. Yield 88% (0.99 g); mp 80-82 ^oC; $[\alpha]_D^{25}$ = +9.0 (*c* 1, CH_3OH); IR (υ_{max}): 3415, 1672, 1561, 1200, 1137 cm^{-1}; ^1H NMR (300 MHz, D_2O) δ: 8.22 (d, *J* = 8.3 Hz, 1H), 5.09 (dd, *J* = 14.9, 3.6 Hz, 1H), -4.91 (m, 1H), 4.19-4.04 (m, 1H), 3.46-3.24 (m, 2H), 2.90-2.55 (m, 2H), 2.39-2.24 (m, 1H), 2.24-1.77 (m, 4H); ^{13}C NMR (75 MHz, D_2O) δ: 175.9, 174.7, 158.3, 134.1, 130.4, 58.9, 50.7, 49.2, 45.1, 37.2, 26.7, 21.9; HRMS (ESI): *m/z* calculated for $[C_{12}H_{19}O_4N_6]$ 311.1462 $[M + H]^+$, found 311.1460.

3.3 Synthetic procedure of 1,4-substitutedtriazole catalyst 7a

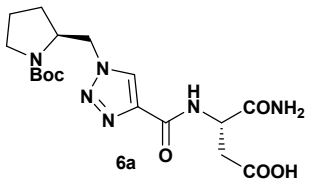
(*S*)-*tert*-Butyl-2-((4-(((*S*)-1-amino-4-(benzyloxy)-1,4-dioxobutan-2-yl)carbamoyl)-*1H*-1,2,3-triazol-1-yl)methyl)pyrrolidine-1- carboxylate (5a)



5a

Compound **2a** (4.0 g, 12.3 mmol) was treated with $LiOH.H_2O$ (1.59 g, 37 mmol) in 30 mL of THF: H_2O (7:3). After completion of the reaction THF was removed in *vacuo* and diluted with 50 mL of water. To this aqueous layer, 5 mL of ethyl acetate was added and layers separated to remove impurities, aqueous layer was acidified (p^H = 2-3) with solid $KHSO_4$, extracted with ethyl acetate, organic layer was dried over anhydrous Na_2SO_4 and concentrated to obtain (2.99 g, 82% crude) a fine white colored solid **3a**. To this acid (2.93 g, 9.89 mmol) in dry CH_2Cl_2 (20 mL) was added HOBt (1.46 g, 10.88 mmol) at room temperature and stirred for 10 min under nitrogen gas. Then, to the reaction mixture was added EDCI (2.07 g, 10.88 mmol) at 0 ^oC, allowed to stir at ice cold temperature for another 10 min. To this, *β*-benzyl *L*-isoasparaginate (**4)** (2.19 g, 9.89 mmol) (Pre basified with DIPEA; 3.83 g, 29.69 mmol) was added and stirred for 24 h. Reaction was monitored by TLC, after total consumption of the starting materials, reaction was quenched with super saturated aqueous NH_4Cl and extracted with CH_2Cl_2. Organic layer was given washings with saturated aqueous $NaHCO_3$ and brine solutions, dried over anhydrous Na_2SO_4, concentrated in *vacuo* and the residue was purified by column chromatography using hexane and EtOAc (2:8) to obtain **5a** as a white solid. Yield 85% (4.19 g); mp 70-73 ^oC; $[\alpha]_D^{25}$ = -25.8 (*c* 1, MeOH); IR (υ_{max}): 3348, 2976, 2885, 1733, 1683, 1569, 1396, 1170, 771 cm^{-1};^1H NMR (300 MHz, $CDCl_3$) δ: 8.21 (d, *J* = 7.6 Hz, 1H), 8.06 (s, 1H), 7.40-7.29 (m, 5H), 6.62 (s, 1H), 5.84 (s, 1H), 5.16 (s, 2H), 5.11-5.03 (m, 1H), 4.76-4.36 (m, 2H), 4.19-4.08 (br, 1H), 3.48-3.21 (m, 2H), 3.22 (dd, *J* = 17.4, 4.5 Hz, 1H), 2.88 (dd, *J* = 16.6, 6.0 Hz, 1H), 2.12-1.66 (m, 4H), 1.49 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$+ DMSO-d_6) δ: 171.6, 170.1, 159.2, 141.9, 134.8, 127.7, 127.3, 125.9, 79.4, 65.8, 56.2, 52.6, 51.1, 48.3, 46.2, 46.0, 35.6, 27.7, 22.6, 21.9; HRMS (ESI): *m/z* calculated for $[C_{24}H_{33}O_6N_6]$ 501.2456 $[M+H]^+$, found 501.2455.

(*S*)-4-Amino-3-(1-(((S)-1-(*tert*-butoxycarbonyl)pyrrolidin-2-yl)methyl)-*1H*-1,2,3-triazole-4-carboxamido)-4-oxobutanoic acid (6a)

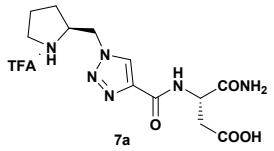


6a

To **5a** (2.0 g, 4.0 mmol) in methanol (8 mL) was added 10% Pd/C (42 mg 0.4 mmol) under nitrogen atmosphere and was reacted under hydrogen atmosphere for about 4-5 h. After consumption of the starting material, mixture was filtered through a short bed of celite using methanol, solvent was removed on rotary evaporator to attain the solid which was column purified to obtain **6a** as white coloured solid.

Yield 96% (1.58 g); mp 85-87 ^{o}C; $[\alpha]_D^{25}$ = -28.3 (*c* 1, MeOH); IR (υ_{max}): 3701, 3082, 2908, 1676, 1586, 773cm^{-1} ; ^{1}H NMR (300 MHz, D_2O) δ: 8.44 (s, 1H), 4.99-4.89 (rotamer, 1H), 4.70-4.55 (rotamer, 1H), 4.37-4.30 (rotamer, 2H), 3.45-3.27 (rotamer, 2H), 3.45-3.28 (rotamer, 2H), 3.09-2.88 (rotamer, 2H), 2.12-1.78 (rotamer, 4H), 1.41- 1.07 (rotamer, 9H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO-d_6) δ: 171.5, 158.6, 153.2, 141.2, 125.6, 78.6, 55.6, 51.4, 50.5, 47.9, 45.6, 35.1, 27.1, 21.9, 21.2; HRMS (ESI): *m/z* calculated for [$C_{17}H_{27}O_6N_6$] 411.1986 [M+H]$^{+}$, found 411.1982.

(*S*)-4-Amino-4-oxo-3-(1-((*S*)-pyrrolidin-2-ylmethyl)-*1H*-1,2,3-triazole-4-carboxamido) butanoic acid (7a)



7a

To a suspension of **6a** (1.50 g, 3.6 mmol) in CH_2Cl_2 (5 mL) was added trifluoroacetic acid (5 mL) CH_2Cl_2: TFA (1:1) at 0 ^{o}C and stirred at room temperature. Reaction was monitored by thin layer chromatography. After completion of the reaction dichloromethane was removed *in vacuo*. Excess trifluoroacetic acid was co-distilled with 5 mL of CH_2Cl_2, this process was repeated several times, and residue was finally washed with *n*- pentane and dried under vacuum to get compound **7a** as solid.

Yield 88% (1.0 g); mp 179-181 ^{o}C; $[\alpha]_D^{25}$ = +28.8 (*c* 1, MeOH); IR (υ_{max}): 3391, 1676, 1571, 1200, 1134 cm^{-1}; ^{1}H NMR (300 MHz, D_2O) δ: 8.52 (s, 1H), 4.94-4.87 (m, 2H), 4.20-4.04 (m, 1H), 3.49-3.27 (m, 2H), 3.11-2.88 (m, 2H), 2.31-2.12 (m, 1H), 2.21-1.76 (m, 4H); ^{13}C NMR (75 MHz, D_2O) δ: 174.1, 173.9, 160.7, 140.7, 126.9, 58.4, 49.5, 49.1, 45.0, 35.2, 26.6, 21.8 HRMS (ESI): *m/z* calculated for [$C_{12}H_{19}O_4N_6$] 311.1462 [M+H]$^{+}$, found 311.1460.

4. Substrate scope

4.1. General procedure for Michael addition reaction with 0.5 mol % catalyst loading

To the catalyst **7** (0.005 equiv/ 0.5 mol %) or **7a** (0.005 equiv/ 0.5 mol %) (10 mg of Catalyst was dissolved in 2 mL of methanol and from this required quantity of catalyst was taken) in MeOH (0.3

mL) was added ketone (5.0 equiv) followed by nitro olefin (1.0 equiv) at room temperature. Reaction was typically monitored by TLC, after completion of the reaction compound was directly adsorbed on silica gel and product was isolated using EtOAc and hexane.

4.2. General procedure for racemic Michael addition reaction with *DL*-Proline

To *DL*-Proline (0.3 equiv, 30 mol %) in MeOH (0.3 mL) was sequentially added ketone (5.0 equiv) and nitro olefin (1.0 equiv) at room temperature. After completion of the reaction crude material was column purified on silica gel using hexane and EtOAc.

4.3. Analytical data of the compounds 10a-10n

(*S*)- 2-((*R*)-2-Nitro-1-(3-nitrophenyl)ethyl)cyclohexanone (10a)[5]

Reaction was performed with 30 mg (0.15 mmol) of nitroolefin **9a**, 80 µL (0.78 mmol) of cyclohexanone and 40 µL of catalyst solution **7** or **7a** following the general procedure.

White solid; ^{1}H NMR (300 MHz, CDCl3) δ 8.16-8.09 (m, 2H), 7.60-7.50 (m, 2H), 5.02 (dd, *J* = 13.0 4.4, Hz, 1H), 4.71 (dd, *J* = 12.9, 10.1 Hz, 1H), 3.96 (dt, *J* = 9.8, 4.4 Hz, 1H), 2.78-2.70 (m, 1H), 2.55-2.36 (m, 2H), 2.17-2.13 (m, 1H), 1.87-1.58 (m, 4H), 1.36-1.16 (m, 1H).

HPLC: chiral pak-IA column, 210 nm, isopropanol/hexane = 8:92, 1.0 mL/min; with catalyst **7** Rt = 23.81 (major), 20.65 (minor), 94:6 *er*, *syn/anti* = 96:4; Yield: 52% (23 mg); $[\alpha]_D^{25}$ = -18.04 (*c* 2.6, $CHCl_3$); with catalyst **7a** Rt = 23.46 (major), 20.47 (minor), 94:6 *er*, *syn/anti* = 95:5; Yield: 50% (22 mg); $[\alpha]_D^{25}$ = -16.08 (*c* 2.8, $CHCl_3$).

(*S*)- 2-((*S*)-1-(3-Methylthiophen-2-yl)-2-nitroethyl)cyclohexanone (10b)

Reaction was performed with 30 mg (0.21 mmol) of nitroolefin **9b**, 112 µL (1.0 mmol) of cyclohexanone and 66 µL of catalyst solution **7** or **7a** following the general procedure.

Solid; m.p 87-89 ^{o}C; IR (υ_{max}) : 2932, 1707, 1552, 1378, 1128, 756, 716 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 7.14 (d, *J* = 5.0 Hz, 1H), 6.75 (d, *J* = 5.0 Hz, 1H), 4.98 (dd, *J* = 12.5, 4.1 Hz, 1H), 4.49 (dd, *J* = 12.6, 10.3 Hz, 1H), 4.18 (td, *J* = 3.8, 9.8, 14.4 Hz, 1H), 2.62-2.55 (m, 1H), 2.50-2.44 (m, 1H), 2.42-2.34 (m, 1H), 2.18 (s, 3H), 2.15-2.08 (m, 1H), 1.88-1.78 (m, 2H), 1.74-1.55 (m, 2H), 1.31-122 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ*: 211.6, 136.5, 134.4, 130.0, 123.2, 79.5, 54.0, 42.7, 37.3, 32.9, 28.6, 25.1, 13.8; HRMS (ESI): *m/z* calculated for $[C_{13}H_{17}NNa\ O_3S]$ 290.0821$[M+Na]^+$, found 290.0826.

HPLC: chiral pak-IA column, 210 nm, isopropanol/hexane = 5:95, 1.0 mL/min, with catalyst **7** Rt = 16.42 (major), 18.93 (minor), 93:7 *er*, *syn/anti* = 90:10; Yield: 72% (41 mg); $[\alpha]_D^{25}$ = -28.0 (*c* 1, $CHCl_3$); with catalyst **7a** Rt = 15.44 (major), 17.91(minor), 89:11 *er*, *syn/anti* = 88:12; Yield: 69% (39 mg); $[\alpha]_D^{25}$ = -30.0 (*c* 1, $CHCl_3$).

(*S*)-2-((*R*)-1-(3-(Benzyloxy)phenyl)-2-nitroethyl)cyclohexanone (10c)

Reaction was performed with 30 mg (0.11 mmol) of nitroolefin **9c**, 60 µL (0.58 mmol) of cyclohexanone and 36 µL catalyst solution **7** or **7a** following the general procedure.

Solid; m.p 126-128 ^{o}C; IR (υ_{max}) : 2935, 2360, 1706, 1507, 825 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.45-7.31 (m, 6H), 7.25-7.21 (m, 1H), 6.89-6.85 (m, 1H), 6.78-6.75 (m, 1H), 5.03 (s, 2H), 4.91 (dd, *J* = 12.5, 4.4 Hz, 1H), 4.60 (dd, *J* = 12.6, 10.0 Hz, 1H), 3.72 (td, *J* = 4.4, 9.9, 14.3 Hz, 1H), 2.66-2.59 (m, 1H), 2.49-2.43 (m, 1H), 2.40-2.32 (m, 1H), 2.11-2.04 (m, 1H), 1.80-1.48 (m, 4H), 1.23-1.16 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 211.8, 158.9, 139.3, 136.6, 129.9, 128.5, 127.9, 127.5, 120.6, 115.2, 113.6, 78.7, 70.0, 52.4, 43.8, 42.7, 33.1, 29.6, 28.4, 25.0; HRMS (ESI): *m/z* calculated for $[C_{21}H_{23}NNaO_4]$ 376.1519 $[M+Na]^+$, found 376.1542.

HPLC: chiral pak-IA column, 210 nm, isopropanol/hexane = 5:95, 1.0 mL/min, with catalyst **7** Rt = 21.85 (major), 17.29 (minor), 87:13 *er*, *syn/anti* = 97:3; Yield: 72% (29 mg); $[\alpha]_D^{25}$ = -24.0 (*c* 1, $CHCl_3$); with catalyst **7a** Rt = 21.84 (major), 17.26 (minor), 84:16 *er*, *syn/anti* = 93:7; Yield: 68% (28 mg); $[\alpha]_D^{25}$ = -13.0 (*c* 1, $CHCl_3$).

(*S*)-2-((*S*)-1-(Furan-2-yl)-2-nitroethyl)cyclohexanone (10d)[5]

Reaction was performed with 30 mg (0.21 mmol) of nitroolefin **9d**, 110µL (1.0 mmol) of cyclohexanone and 66 µL of catalyst solution **7** or **7a** following the general procedure. Yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1H NMR (CDCl3, 400 MHz): δ 7.37 (s, 1H), 6.30-6.27 (m, 1H), 6.18 (d, *J* = 3.2 Hz, 1H), 4.83-4.75 (m, 1H), 4.70-4.63 (m, 1H), 4.01-3.93 (m, 1H), 2.80-2.71 (m, 1H), 2.50- 2.32 (m, 2H), 2.15-2.08 (m, 1H), 1.87-1.56 (m, 3H), 1.32-1.24 (m, 1H).

HPLC: chiral pak-IA column, 210 nm, isopropanol/hexane = 7:93, 1.0 mL/min, with catalyst **7** Rt = 11.45 (major), 14.42 (minor), 79:21*er*, *syn/anti* = 97:3; Yield: 68% (34 mg); $[\alpha]_D^{25}$ = -4.31 (*c* 0.85, $CHCl_3$); with catalyst **7a** Rt = 11.56 (major), 14.48 (minor), 75:25 *er*, *syn/anti* = 94:6; Yield: 65% (33 mg); $[\alpha]_D^{25}$ = -4.00 (*c* 0.8, $CHCl_3$).

(*S*)-2-((*R*)-2-Nitro-1-(*p*-tolyl)ethyl)cyclohexanone (10e)[5]

Reaction was performed with 30 mg (0.18 mmol) of nitroolefin **9e**, 90 µL (0.92 mmol) of cyclohexanone and 57 µL catalyst solution **7** or **7a** following the general procedure.

^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.12 (d, *J* = 7.5 Hz, 2H), 7.04 (d, *J* = 8.3 Hz, 2H), 4.91(dd, *J* = 12.0, 4.5 Hz, 1H), 4.60 (dd, *J* = 12.0, 9.8 Hz, 1H), 3.72 (dt, *J* = 9.8, 4.5 Hz, 1H), 2.66 (dt, *J* = 11.3, 5.2 Hz, 1H), 2.52-2.34 (m, 1H), 2.31 (s, 3H), 2.13-2.02 (m, 1H), 1.82-1.50 (m, 1H), 1.31-1.15 (m, 1H).

HPLC: chiral pak-IA column, 210 nm, isopropanol/hexane = 5:95, 1.0 mL/min, with catalyst **7** Rt = 12.47 (major), 10.31 (minor), 96:4 *er*, *syn/anti* = 94:6; Solid; Yield: 64% (30 mg); $[\alpha]_D^{25}$ = -22.0 (*c* 0.5, $CHCl_3$); with catalyst **7a** Rt = 12.50 (major), 10.31 (minor), 91:9 *er*, *syn/anti* = 93:7; Yield: 60% (28 mg); $[\alpha]_D^{25}$ = -20.4 (*c* 0.54, $CHCl_3$).

(*S*)-2-((*R*)-1-(4-Fluorophenyl)-2-nitroethyl)cyclohexanone (10f)[5]

Reaction was performed with 30 mg (0.17 mmol) of nitroolefin **9f**, 92 µL (0.89 mmol) of cyclohexanone and 55 µL catalyst solution **7** or **7a** following the general procedure.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.35-7.24 (m, 2H), 7.03-6.86 (m, 2H), 4.95 (dd, J = 12.6, 4.3 Hz, 1H), 4.61 (dd, J = 12.6, 10.0 Hz, 1H), 3.78 (dt, J = 9.8, 4.3 Hz, 1H), 2.65 (dt, J = 12.4, 4.9 Hz, 1H), 2.54-2.31 (m, 2H), 2.16-2.01 (m, 1H), 1.86-1.50 (m, 4H), 1.36-1.17 (m,1H).

HPLC: chiral pak-IA column, 210 nm, isopropanol/hexane = 5:95, 1.0 mL/min, with catalyst **7** Rt = 16.20 (major), 14.19 (minor), 96:4 *er*, *syn/anti* = 93:7; Solid; Yield: 65% (30 mg); $[\alpha]_D^{25}$ = -12.6 (*c* 1.2, $CHCl_3$); with catalyst **7a** Rt = 16.02 (major), 14.04 (minor), 95:5 *er*, *syn/anti* = 95:5; Yield: 60% (28 mg); $[\alpha]_D^{25}$ = -12.0 (*c* 1.2, $CHCl_3$).

(*S*)-2-((*R*)-1-(4-Methoxyphenyl)-2-nitroethyl)cyclohexanone (10g)[7,8]

Reaction was performed with 30 mg (0.16 mmol) of nitroolefin **9g**, 86 µL (0.83 mmol) of cyclohexanone and 51 µL catalyst solution **7** or **7a** following the general procedure.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.08 (d, J = 8.6 Hz, 2H), 6.85 (d, J = 8.4 Hz, 2H), 4.91 (dd, J = 12.2, 4.5 Hz, 1H), 4.58 (dd, J = 12.2, 10.0 Hz, 1H), 3.87 (s, 3H), 3.77-3.66 (m,1H), 2.64 (dt, J = 11.1, 4.7 Hz, 1H), 2.54-2.31 (m, 1H), 2.14-2.01 (m, 1H), 1.83-1.50 (m, 4H), 1.31-1.15 (m, 1H).

HPLC: chiral pak-IA column, 210 nm, isopropanol/hexane = 5:95, 1.0 mL/min, with catalyst **7** Rt = 18.49 (major), 15.29 (minor), 91:9 *er*, *syn/anti* = 95:5; White solid; Yield: 71% (32 mg); $[\alpha]_D^{25}$ = -18.2 (*c* 0.4, $CHCl_3$); with catalyst **7a** Rt = 18.52(major), 15.28 (minor), 88:12 *er*, *syn/anti* = 94:6; Yield: 65% (30 mg); $[\alpha]_D^{25}$ = -16.1 (*c* 0.41, $CHCl_3$).

(*S*)-2-((*R*)-2-Nitro-1-(4-(trifluoromethyl)phenyl)ethyl)cyclohexanone (10h)[6]

Reaction was performed with 30 mg (0.13 mmol) of nitroolefin **9h**, 71 µL (0.69 mmol) of cyclohexanone and 42 µL of catalyst solution **7** or **7a** following the general procedure.

^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.59 (d, J = 7.5 Hz, 2H), 7.32 (d, J = 8.3 Hz, 2H), 4.98 (dd, J = 12.0, 3.7 Hz, 1H), 4.75-4.64 (m, 1H), 3.86 (dt, J = 9.8, 4.5 Hz, 1H), 2.77-2.64 (m, 1H), 2.55-2.31 (m, 2H), 2.18-2.00 (m, 1H), 1.87-1.50 (m, 4H), 1.36-1.16- (m, 1H).

HPLC: chiral pak-IA column, 210 nm, isopropanol/hexane = 6:94, 1.0 mL/min, with catalyst **7** Rt = 28.53 (major), 13.54 (minor), 99:1 *er*, *syn/anti* = 95:5; White Solid; Yield: 70% (30 mg); $[\alpha]_D^{25}$ = -27.4 (*c* 0.4, $CHCl_3$); with catalyst **7a** Rt = 28.40 (major), 13.54 (minor), 97:3 *er*, *syn/anti* = 93:7; Yield: 67% (29 mg); $[\alpha]_D^{25}$ = -26.2 (*c* 0.41, $CHCl_3$).

(*S*)-2-((*R*)-1-(3-Bromophenyl)-2-nitroethyl)cyclohexanone (10i)[7]

Reaction was performed with 30 mg (0.13 mmol) of nitroolefin **9i**, 68 µL (0.66 mmol) of cyclohexanone and 41 µL of catalyst solution **7** or **7a** following the general procedure.

^{1}HNMR (500 MHz,CDCl3) δ: 7.42-7.39 (m,1H),7.33 (t, J = 1.8 Hz, 1H), 7.21-7.18 (m, 1H), 7.14-7.11 (m,1H), 4.94 (dd, J = 12.8, 4.4 Hz, 1H), 4.61 (dd, J = 12.8, 9.9 Hz, 1H), 3.74 (dt, J = 9.7, 4.4 Hz, 1H), 2.69-2.62 (m, 1H), 2.51-2.45 (m, 1H), 2.42-2.34 (m,1H), 2.14- 2.07 (m, 1H), 1.84-1.78 (m, 1H), 1.76-1.57 (m, 3H), 1.30-1.20 (m, 1);

HPLC: chiral pak-IA column, 210 nm, isopropanol/hexane = 5:95, 1.0 mL/min, with catalyst **7** Rt = 14.49 (major), 13.63 (minor), 82:18 *er*, *syn/anti* = 90:10; Solid; Yield: 66% (28 mg); $[\alpha]_D^{25}$ = -28.0 (*c*

1, $CHCl_3$); with catalyst **7a** Rt = 14.45 (major), 13.59 (minor), 68:32 *er*, *syn/anti* = 81:19; Yield: 60% (25 mg); $[\alpha]_D^{25}$ = -25.0 (*c* 0.98, $CHCl_3$).

(*S*)-2-((*R*)-1-(Anthracen-9-yl)-2-nitroethyl)cyclohexanone (10j)

Reaction was performed with 30 mg (0.12 mmol) of nitroolefin **9j**, 62 µL (0.60 mmol) of cyclohexanone and 37 µL of catalyst solution **7** or **7a** following the general procedure.

Solid; m.p 199-201 ^oC; IR (υ_{max}): 2934, 1707, 1554, 1215, 758 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 8.55 (d, *J* = 9.0 Hz, 1H), 8.43 (s, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 8.4 Hz,1H), 7.91 (d, *J* = 8.9, Hz, 1H), 7.61-7.46 (m, 4H), 5.76-5.70 (m, 1H), 5.20 (dd, *J* = 13.4, 4.6 Hz, 1H), 5.11 (dd, *J* = 13.1, 7.3 Hz, 1H), 3.49 (td, *J* = 5.3, 11.6, 16.9 Hz, 1H), 2.63-2.57 (m, 1H), 2.48 (td, *J* = 6.1, 13.3, 19.4 Hz, 1H), 2.10-2.01 (m, 1H), 1.72-1.52 (m, 3H), 1.52-1.49 (m, 1H), 1.38-1.23 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 212.0, 131.9, 131.6, 131.6, 130.3, 129.3, 129.2, 128.5, 126.9, 126.2, 125.1, 124.6, 124.0, 123.5, 79.7, 53.3, 42.6, 36.3, 32.9, 29.6, 28.2, 25.2; HRMS (ESI): *m/z* calculated for $[C_{22}H_{21}NNaO_3]$ 370.1414 $[M+Na]^+$, found 370.1420.

HPLC: chiral pak-IA column, 210 nm, isopropanol/hexane = 8:92, 1.0 mL/min, with catalyst **7** Rt = 22.02 (major), 15.33 (minor), 95:5 *er*, *syn/anti* = 94:6; Yield: 73% (30 mg); $[\alpha]_D^{25}$ = -34.2 (*c* 1, $CHCl_3$); with catalyst **7a** Rt = 22.00 (major), 15.33 (minor), 95:5 *er*, *syn/anti* = 97:3; Yield: 69% (28 mg); $[\alpha]_D^{25}$ = -32.0 (*c* 1.09, $CHCl_3$).

(*S*)-3-((*R*)-2-Nitro-1-phenylethyl)dihydro-*2H*-thiopyran-4(*3H*)-one (10k)[7]

Reaction was performed with 30 mg (0.20 mmol) of nitroolefin **9k**, 70 mg (0.60 mmol) of dihydro-2H-thiopyran-4-one and 62 µL of catalyst solution **7** or **7a** following the general procedure.

Solid; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.38-7.28 (m, 3H), 7.22-7.19 (m, 2H), 4.74 (dd, *J* = 12.6 4.5 Hz, 1H), 4.63 (dd, *J* = 12.5, 9.6 Hz, 1H), 3.98 (dt, *J* = 10.2, 4.5 Hz, 1H), 3.05 (dt, *J* = 9.7, 4.2 Hz, 1H), 3.01-2.96 (m, 2H), 2.88-2.77 (m, 2H), 2.62 (ddd, *J* = 13. 8, 4.2, 1.8 Hz, 1H), 2.46 (dd, *J* = 9.3, 13.7 Hz, 1H).

HPLC: chiral pak-IC column, 210 nm, isopropanol/hexane = 10:90, 1.0 mL/min. with catalyst **7** Rt = 26.38 (major), 35.45 (minor), 93:7 *er*, *syn/anti* = 96:4; Yield: 70% (37 mg); $[\alpha]_D^{25}$ = -24.6 (*c* 1, $CHCl_3$); with catalyst **7a** Rt = 26.41 (major), 35.43 (minor), 89:11 *er*, *syn/anti* = 95/5; Yield: 66% (35 mg); $[\alpha]_D^{25}$ = -26.2 (*c* 0.91, $CHCl_3$).

(*S*)-4-(3-Methylthiophen-2-yl)-5-nitropentan-2-one (10l)

Reaction was performed with 30 mg (0.17 mmol) of nitroolefin **9l**, 130 µL (1.77 mmol) of acetone and 55 µL of catalyst solution **7** or **7a** following the general procedure.

Viscous oil; IR (υ_{max}): 2926, 1717, 1554, 1378, 758 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.11 (d, *J* = 5.1 Hz, 1H), 6.77 (d, *J* = 4.9 Hz, 1H), 4.69-4.60 (m, 1H), 4.55-4.37 (m, 2H), 2.96-2.86 (m, 2H), 2.25 (s, 3H), 2.13 (s, 3H); C^{13} NMR (125 MHz, $CDCl_3$) δ: 204.9, 135.3, 134.9, 130.3, 122.9, 79.5, 47.1, 32.7, 30.3, 13.6 ; HRMS (ESI): m/*z* calculated for $[C_{10}H_{13}NNaO_3S]$ 250.0508 $[M+Na]^+$, found 250.0537.

HPLC: chiral pak-IC column, 210 nm, isopropanol/hexane = 10:90, 1.0 mL/min, with catalyst **7** Rt = 16.96 (major), 15.58 (minor), 68:32 *er*; Yield: 50% (20 mg); $[\alpha]_D^{25}$ = -8.5 (*c* 1., $CHCl_3$); with catalyst **7a** Rt = 17.01 (major), 15.64 (minor), 65:35 *er*; Yield: 45% (18 mg); $[\alpha]_D^{25}$ = -11.0 (*c* 0.94, $CHCl_3$).

(*R*)-5-Nitro-4-phenylpentan-2-one (10m)[5, 7]

Reaction was performed with 30 mg (0.20 mmol) of nitroolefin **9m**, 147 µL (2.01 mmol) of acetone and 62 µL of catalyst solution **7** or **7a** following the general procedure.

Solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.35–7.22 (m, 5H), 4.75–4.51 (m, 2H), 4.05–4.00 (m, 1H), 2.94 (d, *J* = 6.6 Hz, 2H), 2.14 (s, 3H).

HPLC: chiral pak-IA column, 210 nm, hexane/isopropanol = 94:6, 1.0 mL/min, with catalyst **7** Rt = 12.19 (major), 11.33 (minor), 68:32 *er*; Yield: 56% (23 mg); $[\alpha]_D^{25}$ = -5.7 (*c* 0.7, $CHCl_3$); with catalyst **7a** Rt = 12.21 (major), 11.34 (minor), 63:37 *er*; Yield: 50% (20 mg); $[\alpha]_D^{25}$ = -3.8 (*c* 0.71, $CHCl_3$).

(*R*)-4-(3-(Benzyloxy)phenyl)-5-nitropentan-2-one (10n)

Reaction was performed with 30 mg (0.11 mmol) of nitroolefin **9n**, 86 µL (1.17 mmol) of acetone and 36 µL of catalyst solution **7** or **7a** following the general procedure.

Viscous oil; IR (υ_{max}): 2925, 1716, 1553, 1379, 1258, 756 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.47-7.19 (m, 6H), 6.91-6.71 (m, 3H), 5.02 (s, 2H), 4.69-4.50 (m, 2H), 4.01-3.90 (m, 1H), 2.86 (d, *J* = 7.0 Hz, 2H), 2.09 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 205.2, 159.0, 140.3, 136.6, 130.0, 128.5, 127.9, 127.4, 119.7, 114.3, 113.7, 79.2, 69.9, 45.9, 38.9, 30.2; HRMS (ESI): *m/z* calculated for $[C_{18}H_{19}NNaO_4]$ 336.1206 $[M+Na]^+$, found 336.1234.

HPLC: chiral pak-IC column, 210 nm, hexane/isopropanol = 75:15, 1.0 mL/min, with catalyst **7** Rt = 19.04 (major), 20.23 (minor), 69:31 *er*; Yield: 53% (19 mg); $[\alpha]_D^{25}$ = -9.07 (*c* 0.86, $CHCl_3$); with catalyst **7a** Rt = 19.09 (major), 20.30 (minor), 67:33 *er*; Yield: 50% (18 mg); $[\alpha]_D^{25}$ = -7.06 (*c* 0.7, $CHCl_3$).

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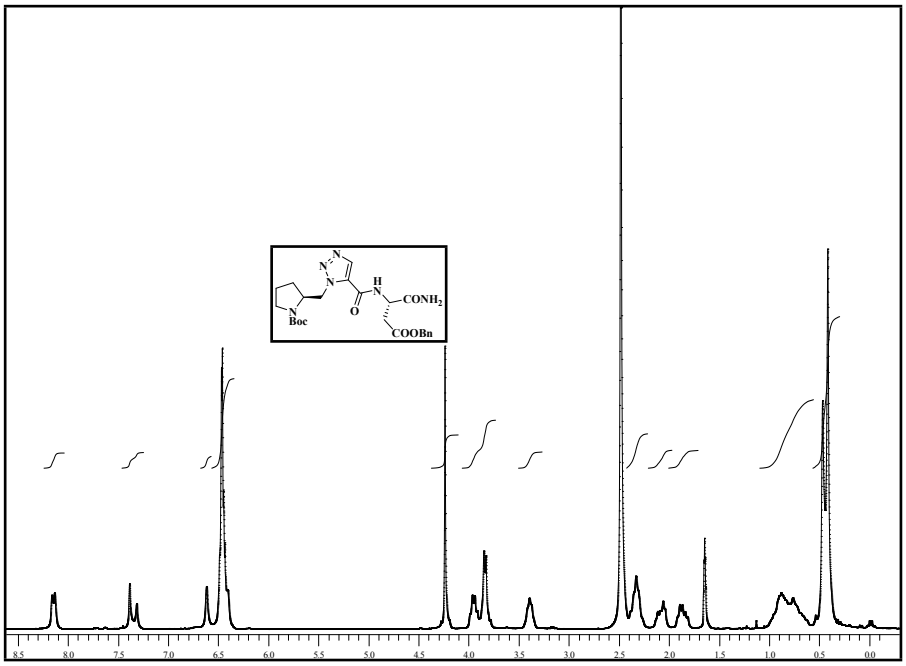
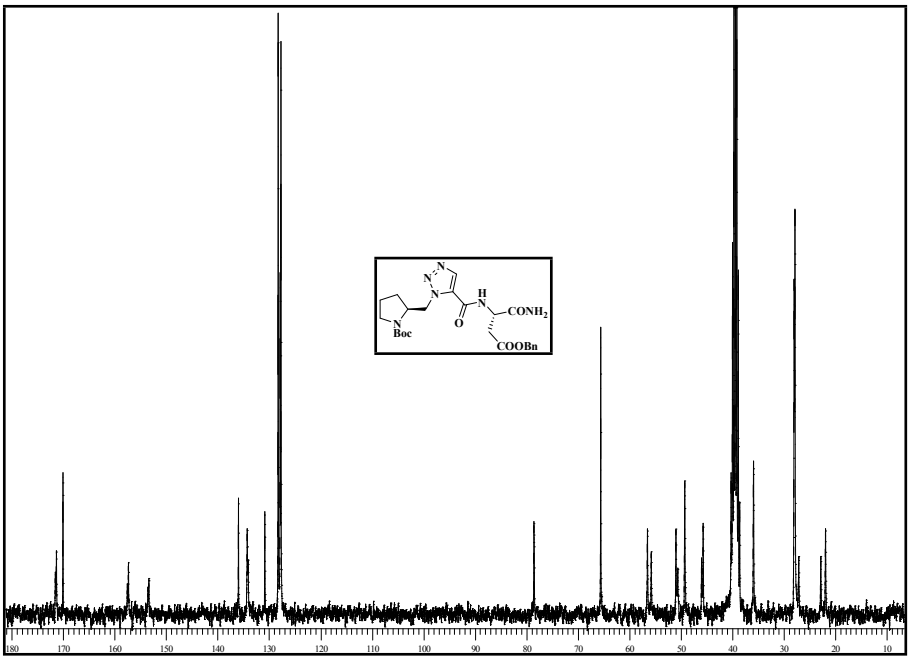
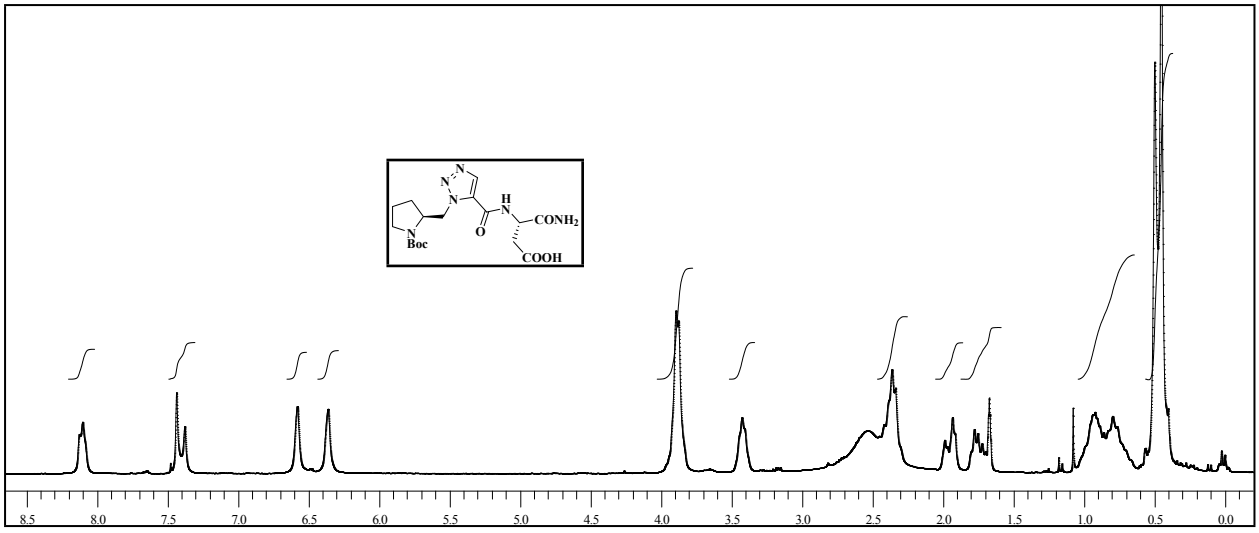
5. ^{1}H and ^{13}C NMR SPECTRA



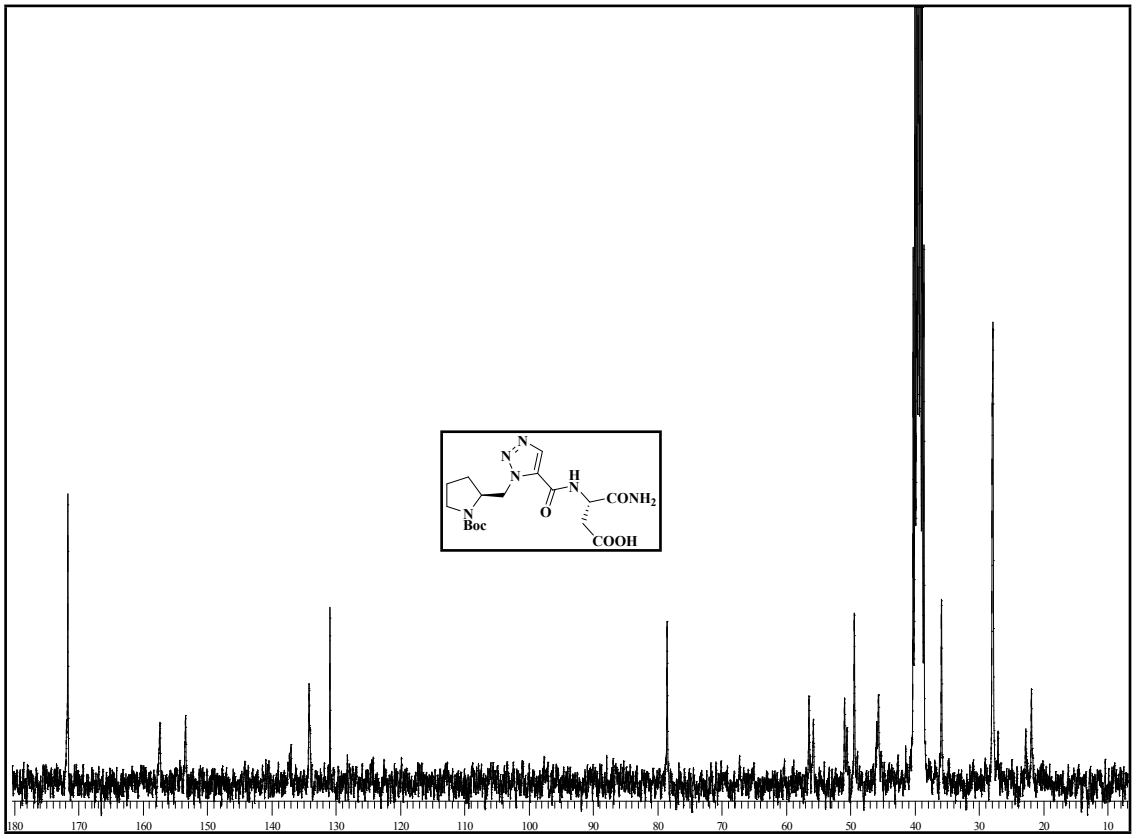
^{1}H NMR OF COMPOUND **5** (DMSO-d_6, 300 MHz)



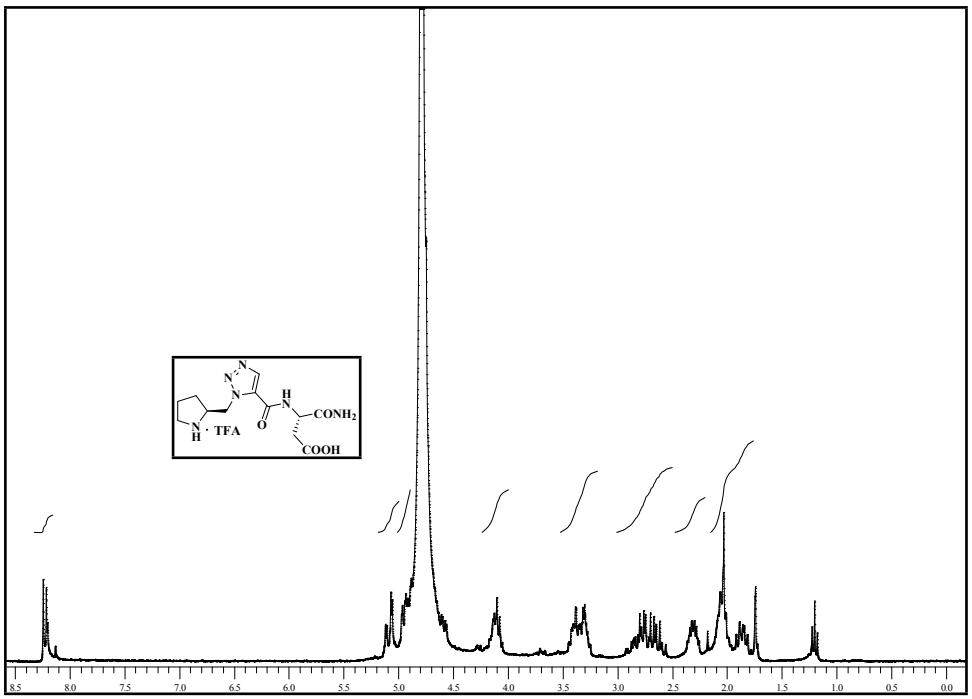
^{13}C NMR OF COMPOUND **5** (DMSO-d_6, 75 MHz)



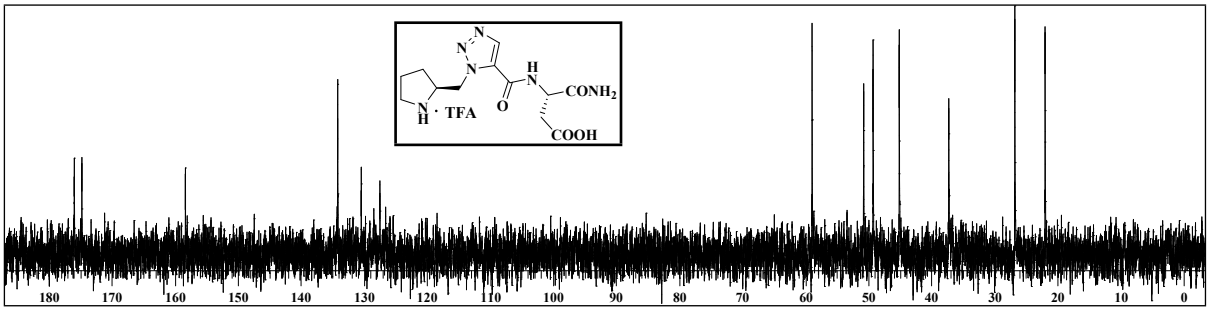
^{1}H NMR OF COMPOUND **6** (DMSO-d_6, 300 MHz)



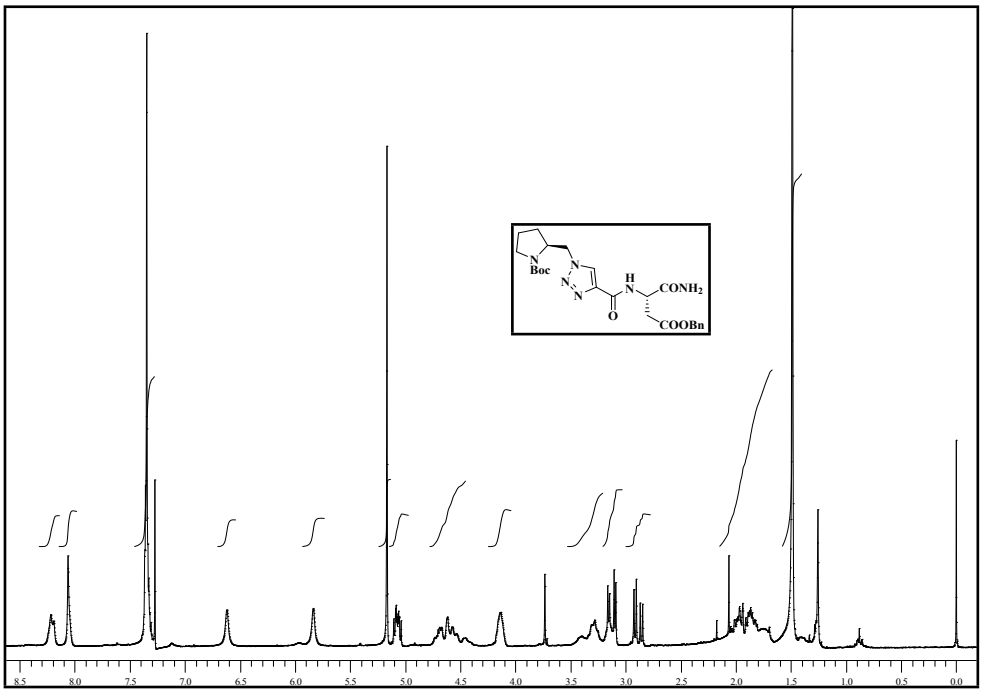
^{13}C NMR OF COMPOUND **6** (DMSO-d_6, 75 MHz)



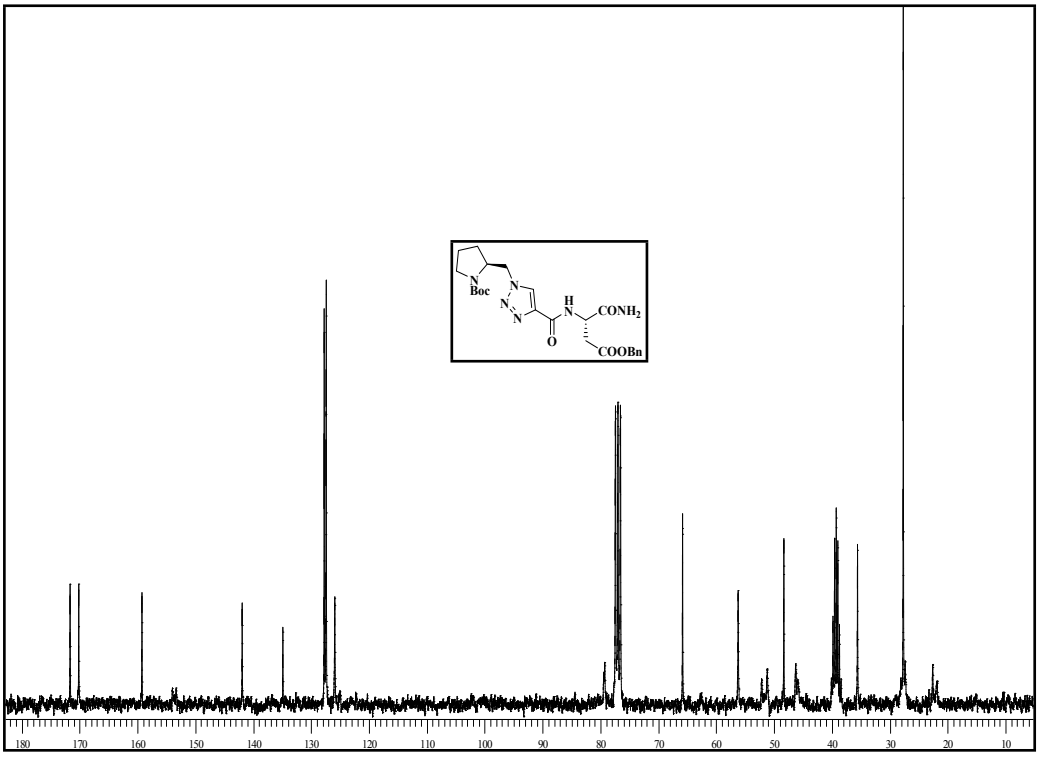
^{1}H NMR OF COMPOUND **7** (D_2O, 300 MHz)



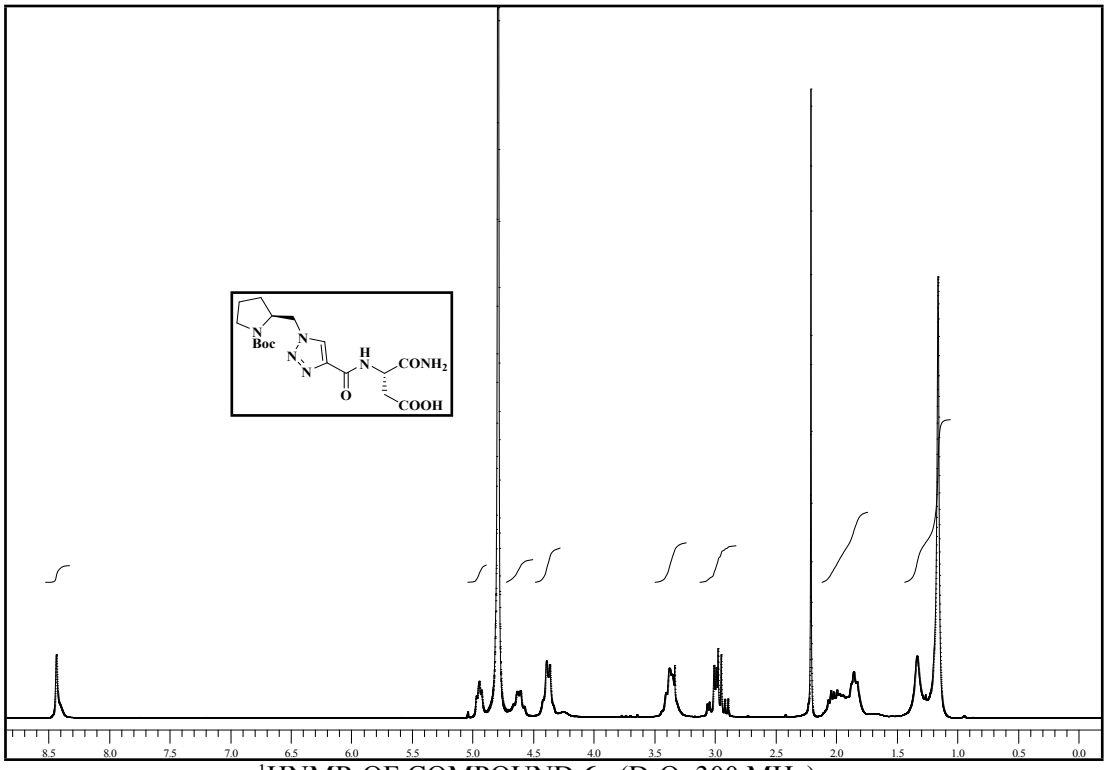
^{13}C NMR OF COMPOUND **7** (D_2O, 75 MHz)



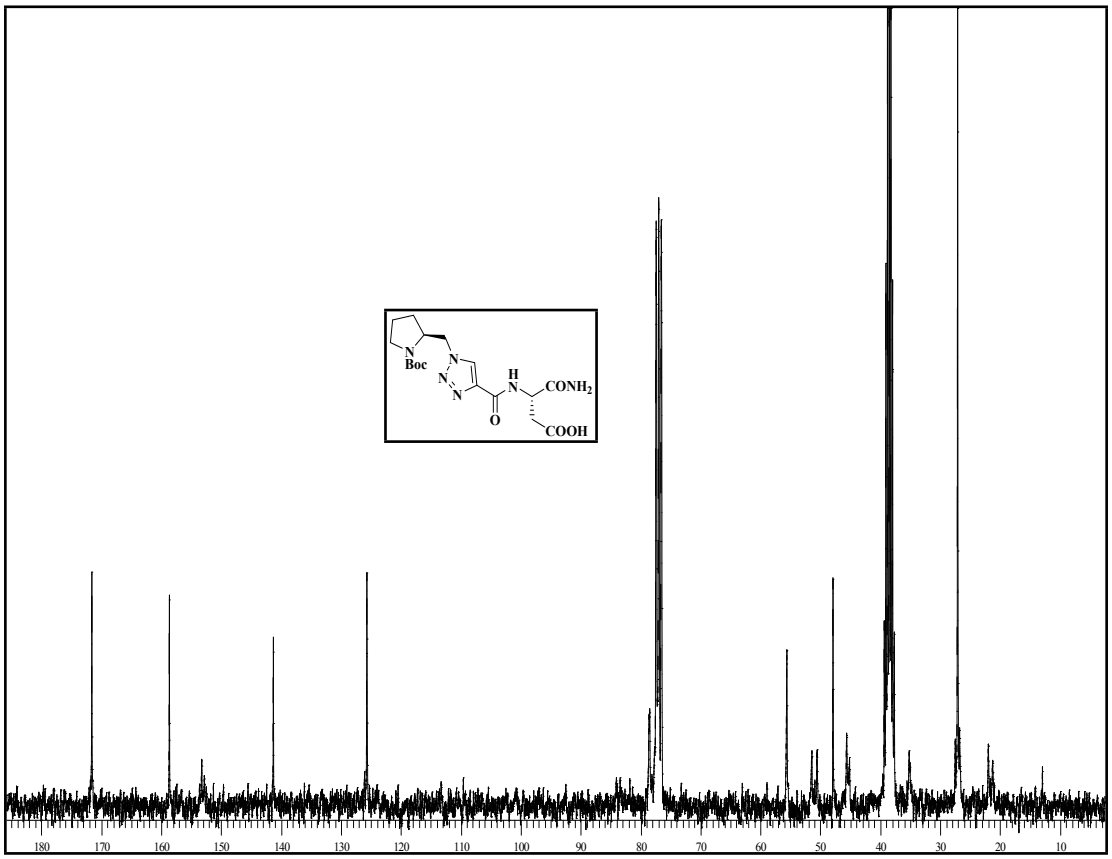
^{1}H NMR OF COMPOUND **5a** ($CDCl_3$, 300 MHz)



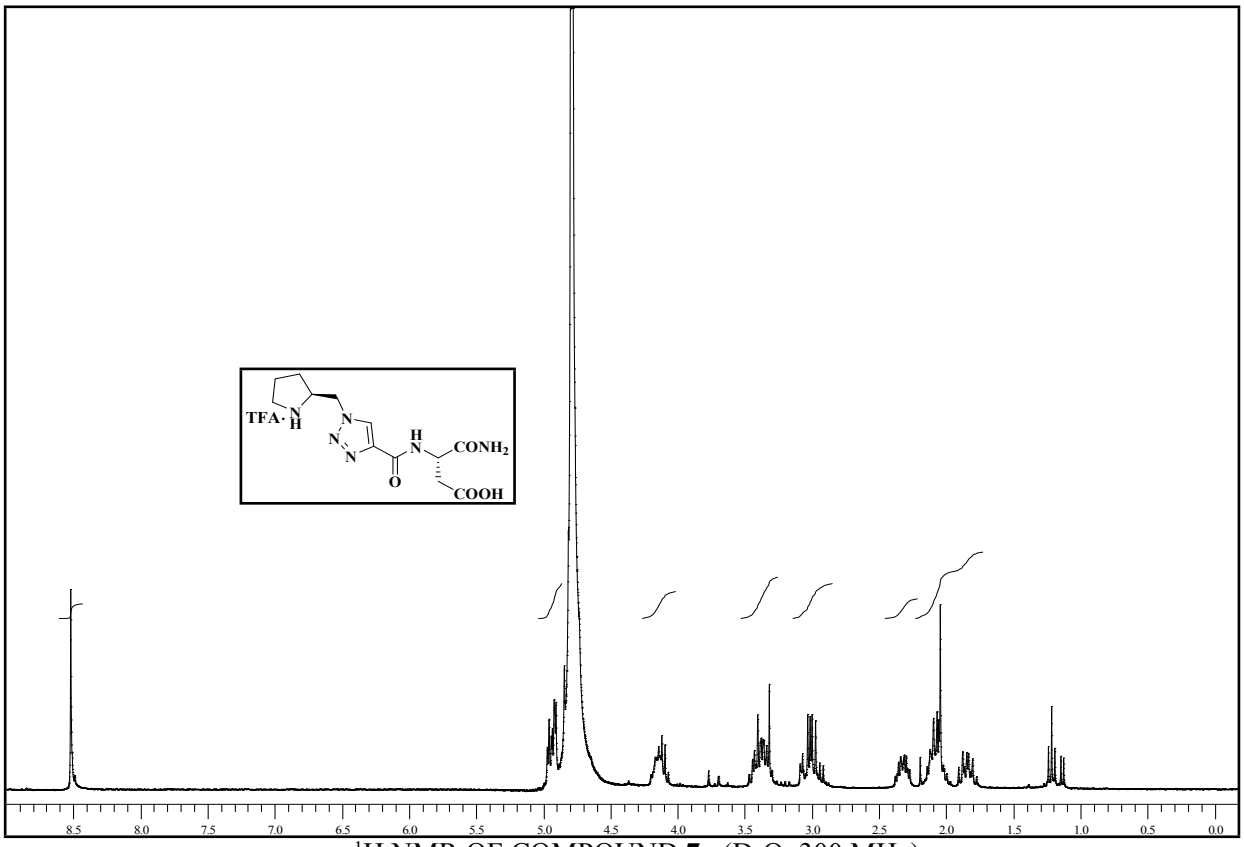
^{13}C NMR OF COMPOUND **5a** ($CDCl_3$+DMSO-d_6, 75MHz)



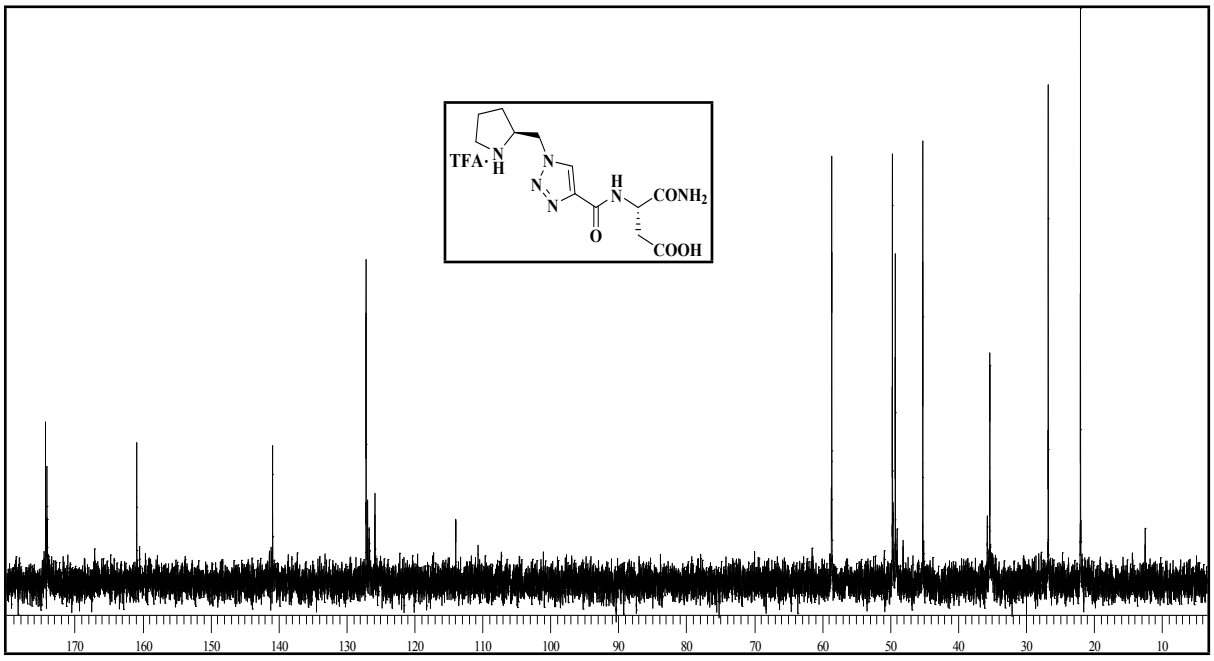
^{1}HNMR OF COMPOUND **6a** (D_2O, 300 MHz)



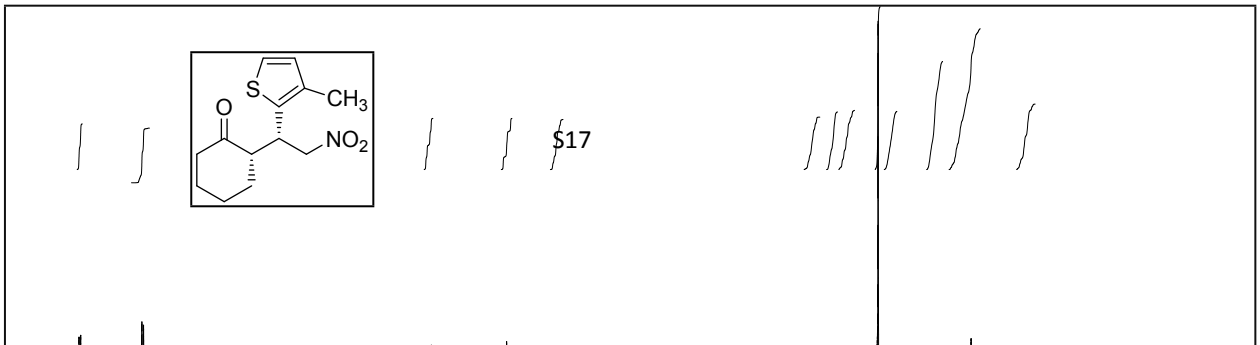
^{13}C NMR OF COMPOUND **6a** ($CDCl_3$+DMSO-d_6, 75 MHz)



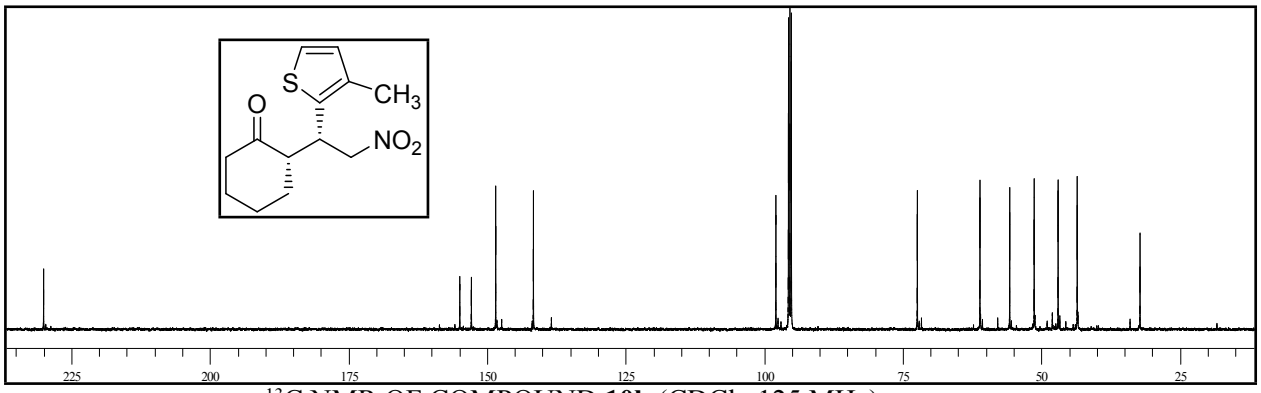
^{1}H NMR OF COMPOUND **7a** (D_2O, 300 MHz)



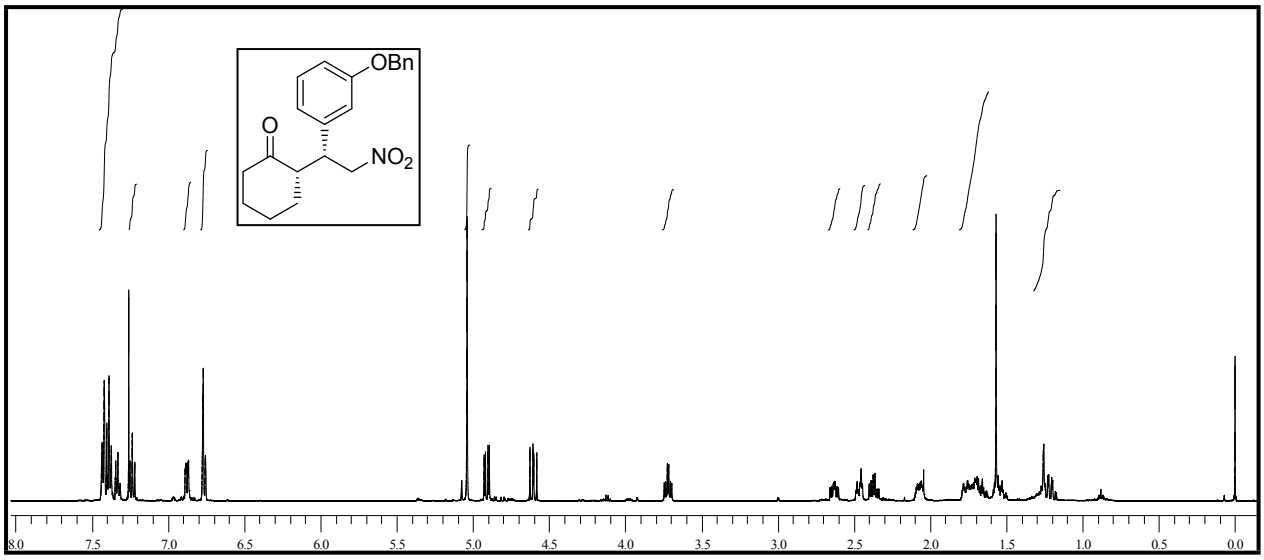
^{13}C NMR OF COMPOUND **7a** (D_2O, 75 MHz)



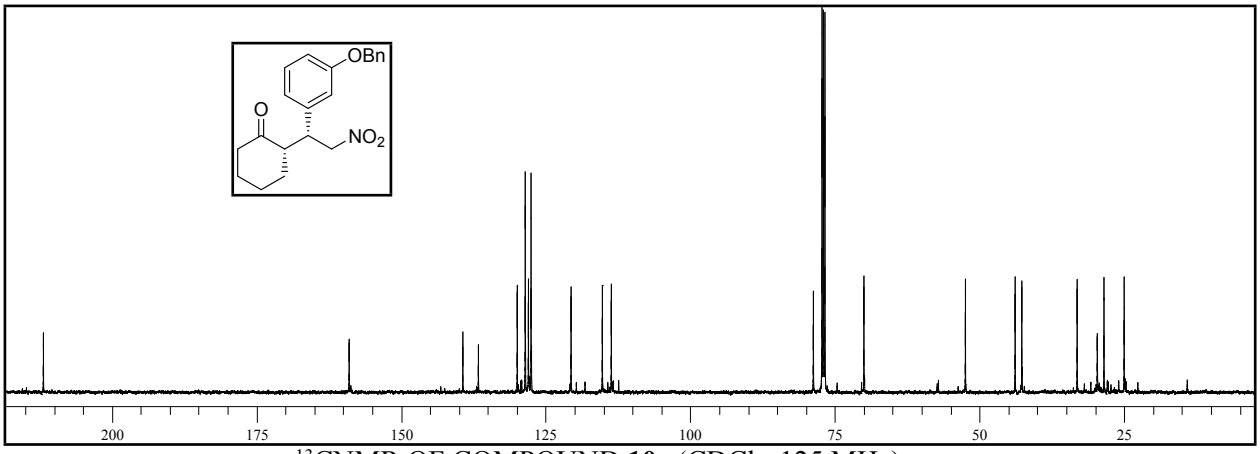
^{1}H NMR OF COMPOUND **10b** ($CDCl_3$, 500 MHz)



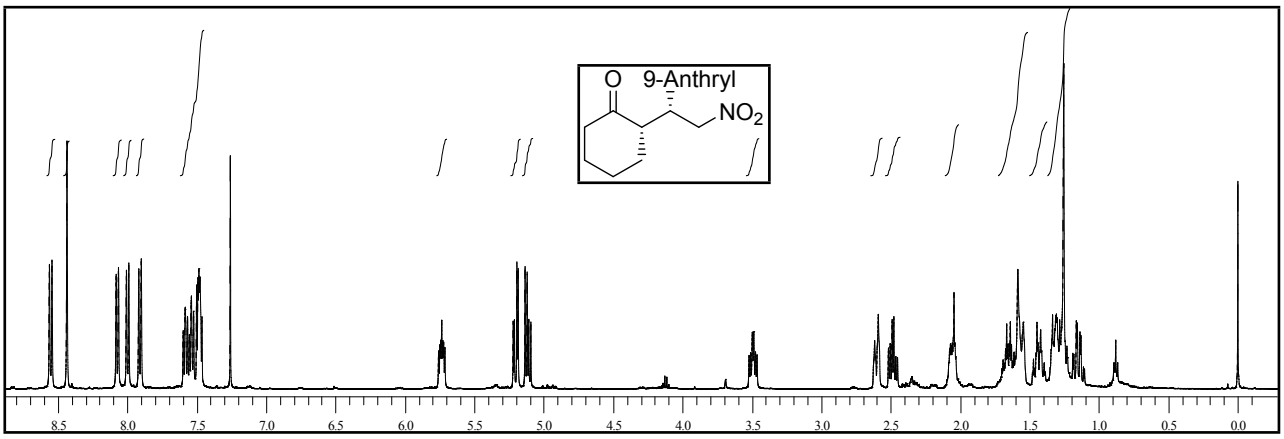
^{13}C NMR OF COMPOUND **10b** ($CDCl_3$, 125 MHz)



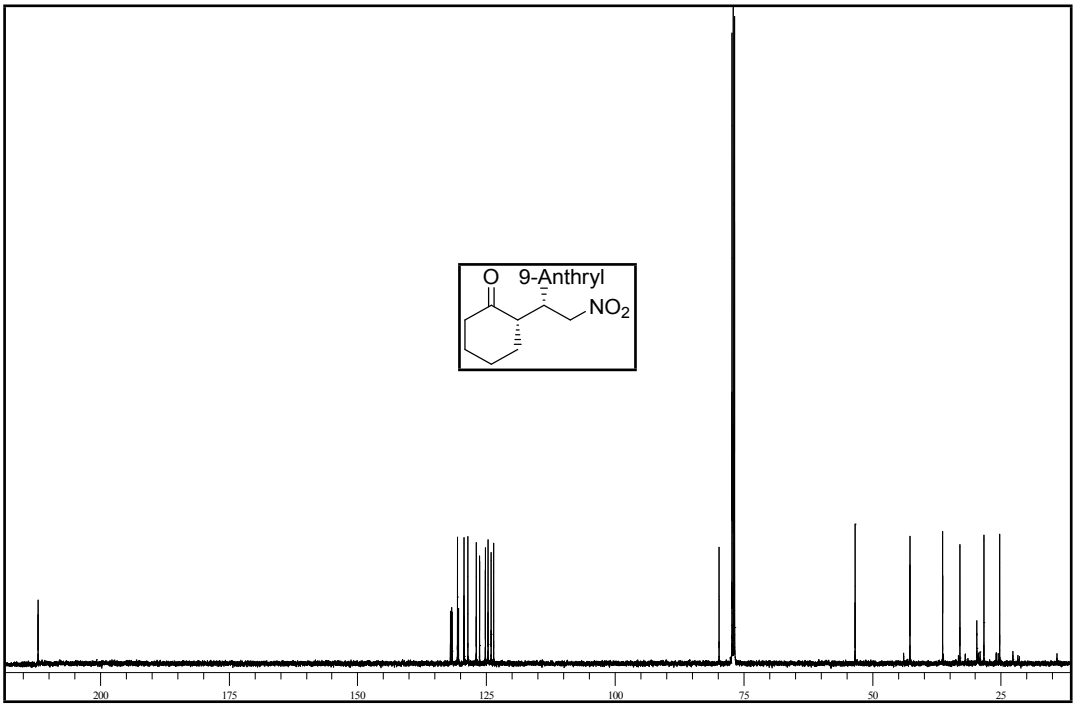
^{1}H NMR OF COMPOUND **10c** ($CDCl_3$, 500 MHz)



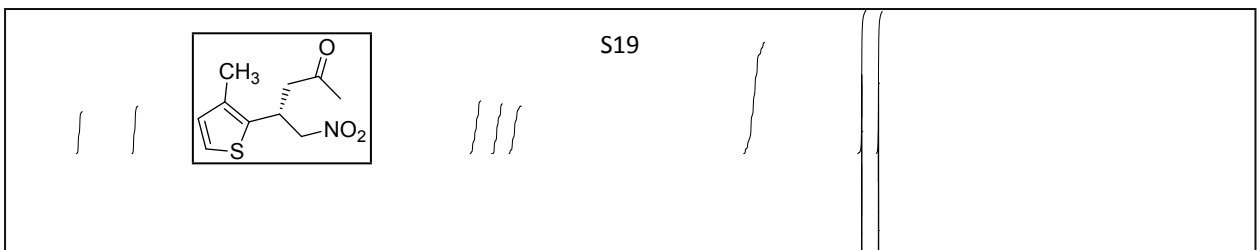
^{13}CNMR OF COMPOUND **10c** ($CDCl_3$, 125 MHz)



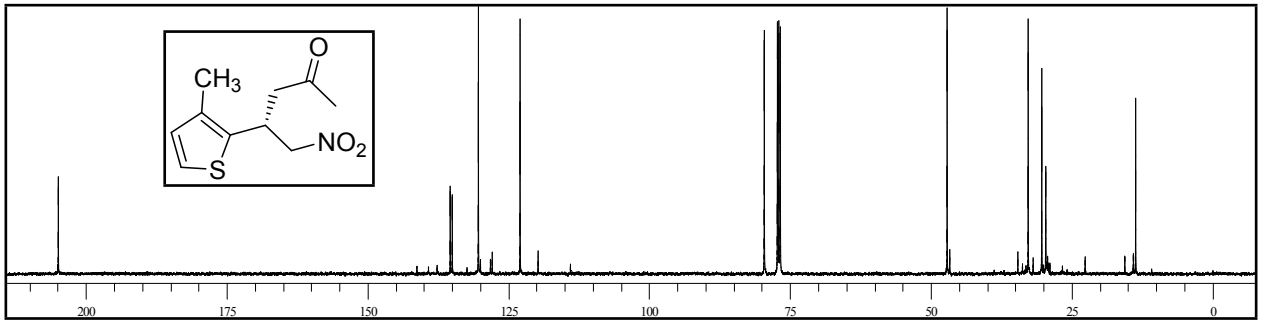
^{1}H NMR OF COMPOUND **10j** ($CDCl_3$, 500 MHz)



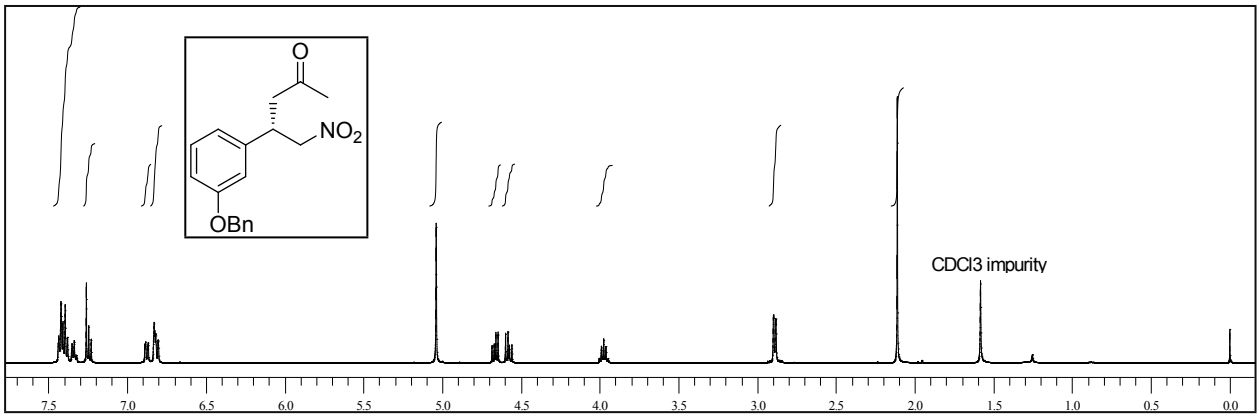
^{13}C NMR OF COMPOUND **10j** ($CDCl_3$, 125 MHz)



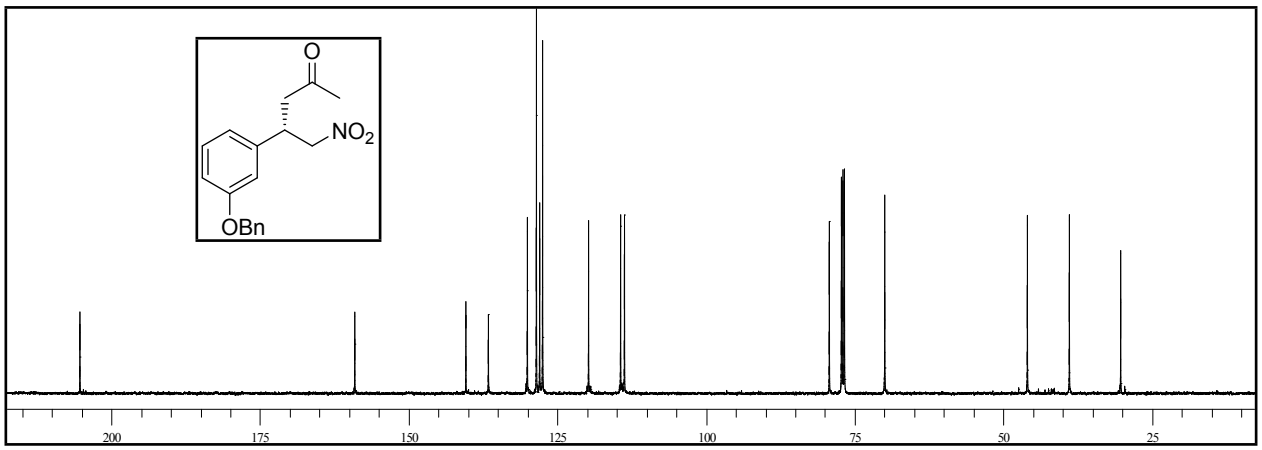
^{1}H NMR OF COMPOUND **10l** ($CDCl_3$, 300 MHz)



^{13}C NMR OF COMPOUND **10l** ($CDCl_3$, 125 MHz)

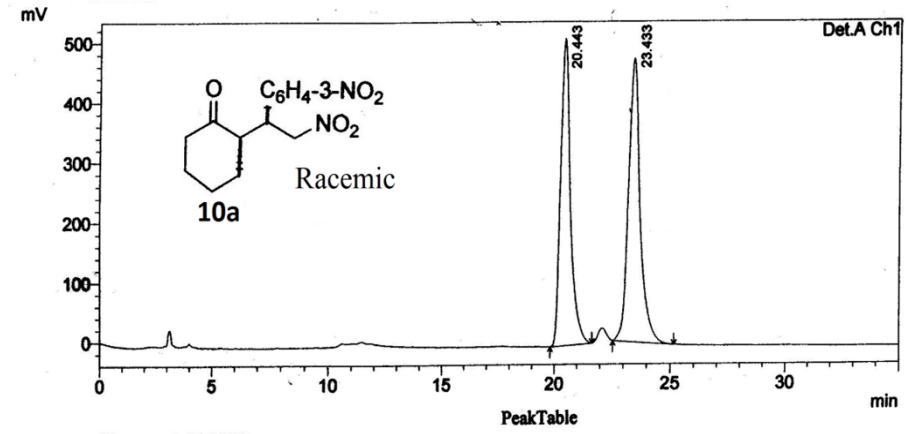


^{1}H NMR OF COMPOUND **10n** ($CDCl_3$, 300 MHz)



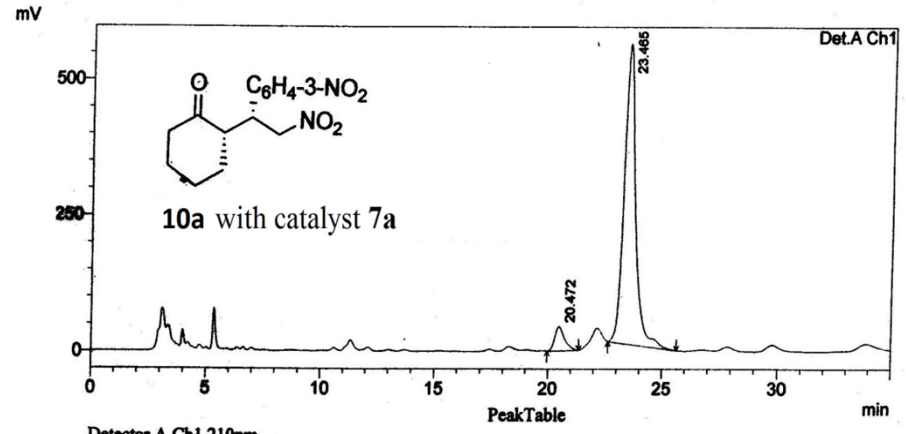
^{13}C NMR OF COMPOUND **10n** ($CDCl_3$, 125MHz)

6. HPLC CHROMATOGRAMS OF THE COMPOUNDS 10a-10n



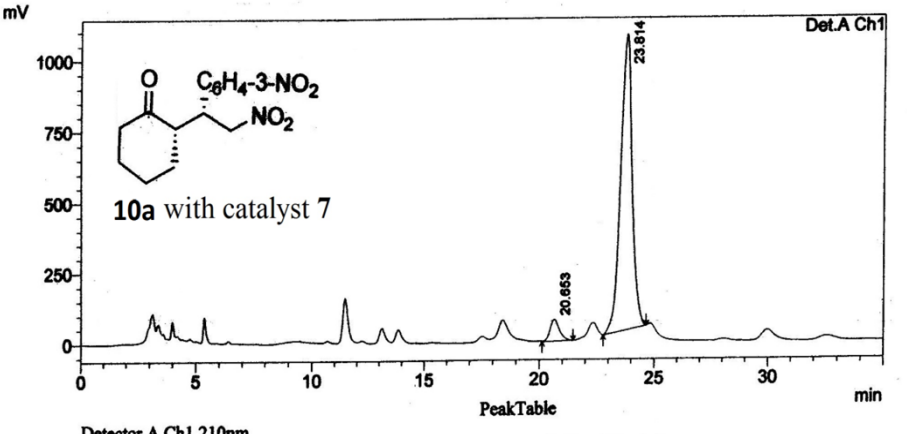
Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %
1	20.443	15450248	512996	48.460
2	23.433	16431972	474309	51.540
Total		31882220	987305	100.000



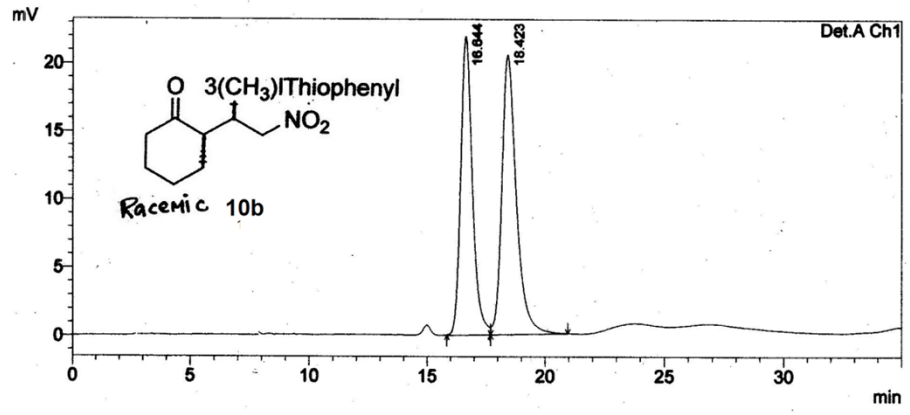
Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %
1	20.472	1311013	43868	6.347
2	23.465	19343946	553398	93.653
Total		20654958	597266	100.000



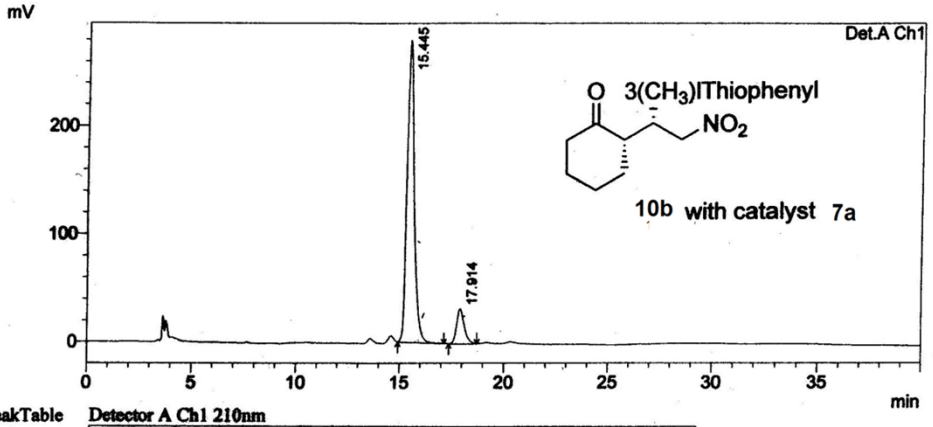
Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %
1	20.653	2112212	76048	5.515
2	23.814	36188964	1041373	94.485
Total		38301176	1117421	100.000



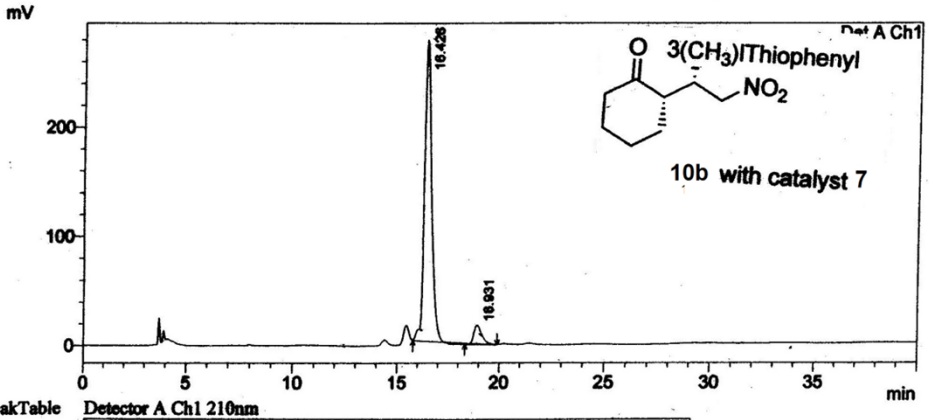
PeakTable Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %
1	16.644	757441	21953	46.387
2	18.423	875441	20540	53.613
Total		1632882	42493	100.000



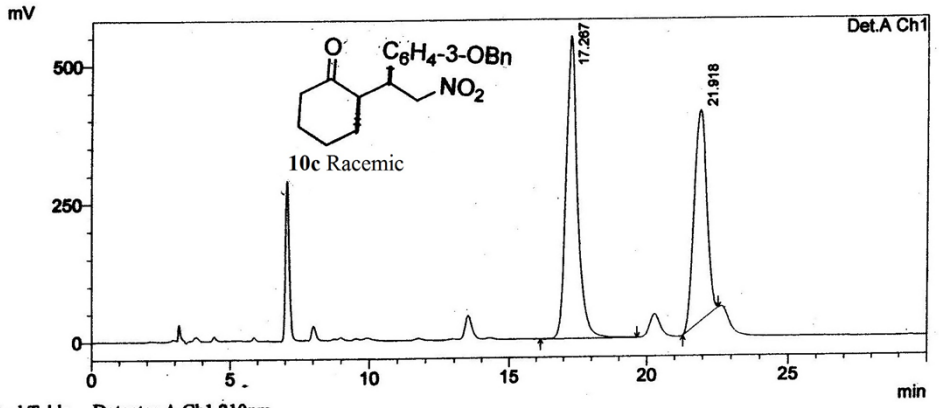
PeakTable Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %
1	15.445	6714386	279879	88.952
2	17.914	833966	32621	11.048
Total		7548351	312500	100.000



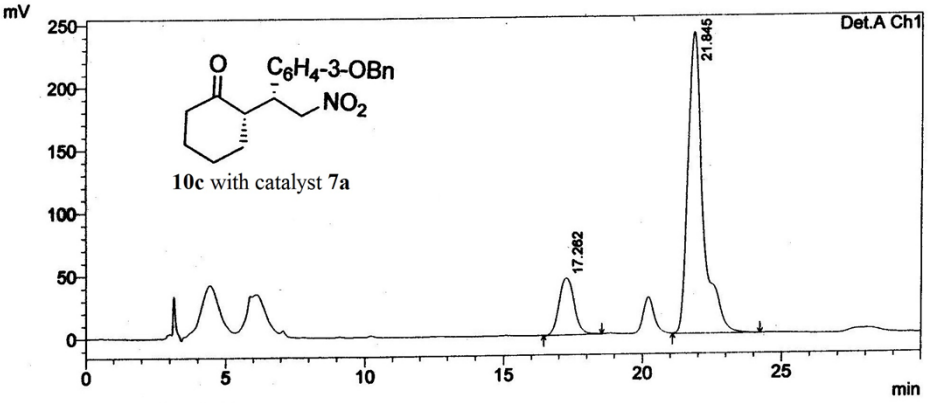
PeakTable Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %
1	16.426	6535153	275259	93.222
2	18.931	475171	17754	6.778
Total		7010324	293013	100.000



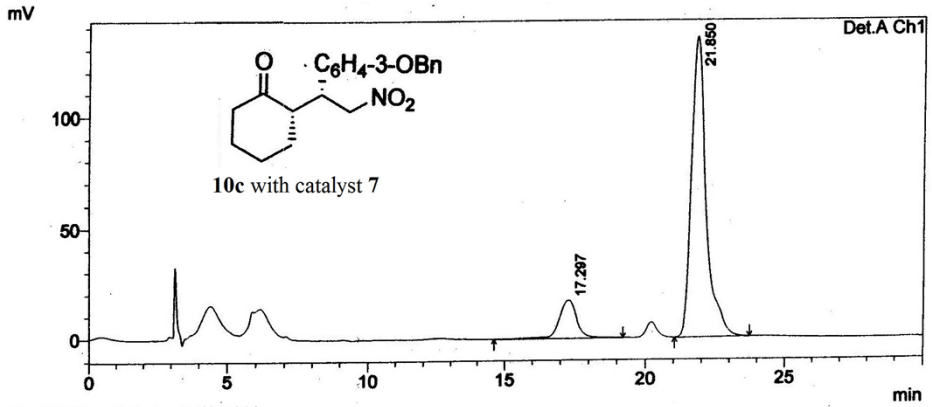
PeakTable Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %
1	17.267	15576899	549147	56.796
2	21.918	11849326	383010	43.204
Total		27426225	932156	100.000



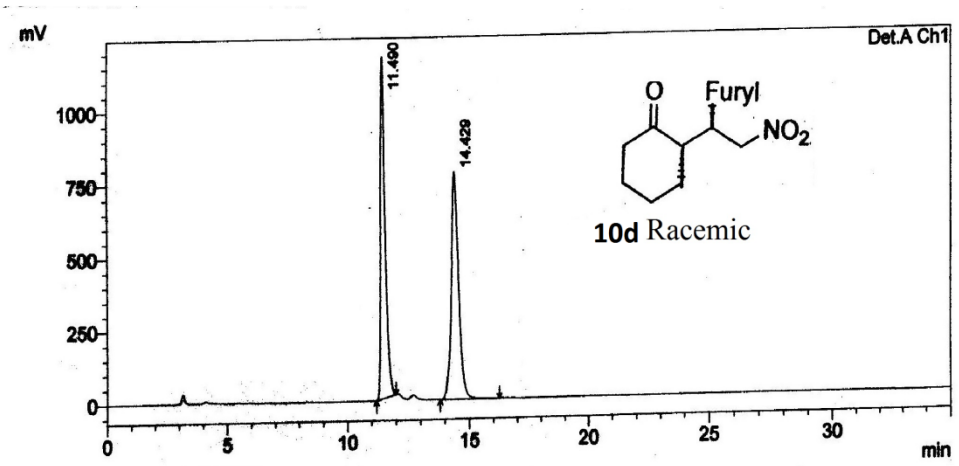
PeakTable Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %
1	17.262	1709310	45199	15.863
2	21.845	9066326	240297	84.137
Total		10775636	285495	100.000



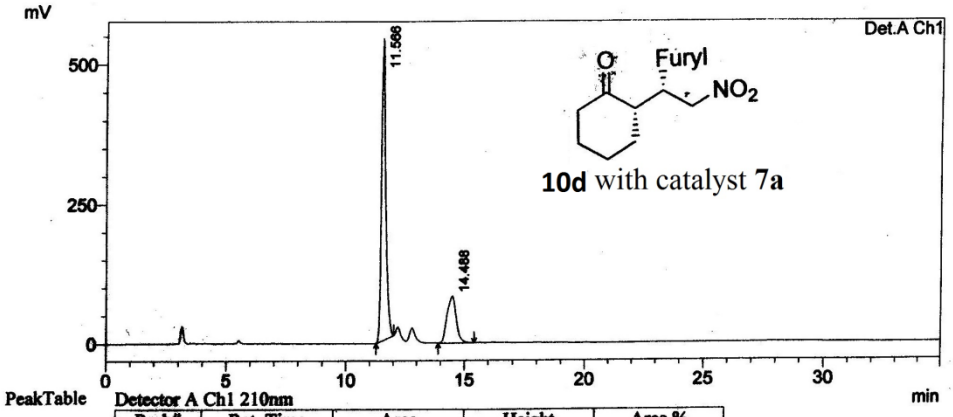
PeakTable Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %
1	17.297	746356	17168	13.210
2	21.850	4903631	135770	86.790
Total		5649988	152938	100.000



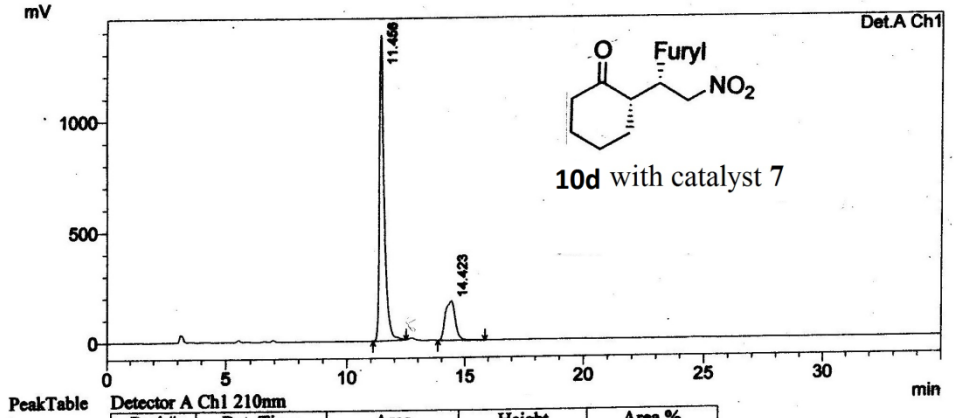
PeakTable Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %
1	11.490	15448318	1172595	48.503
2	14.429	16402166	781060	51.497
Total		31850484	1953654	100.000



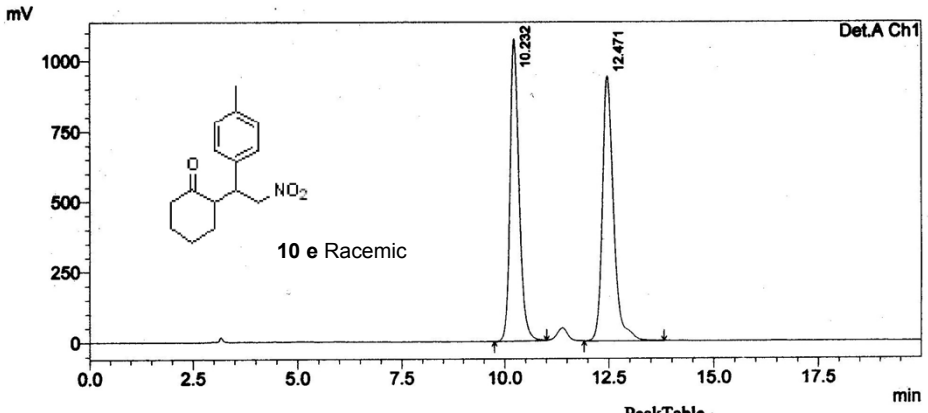
PeakTable Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %
1	11.566	6755595	540755	75.463
2	14.488	2196565	83319	24.537
Total		8952160	624075	100.000



PeakTable Detector A Ch1 210nm

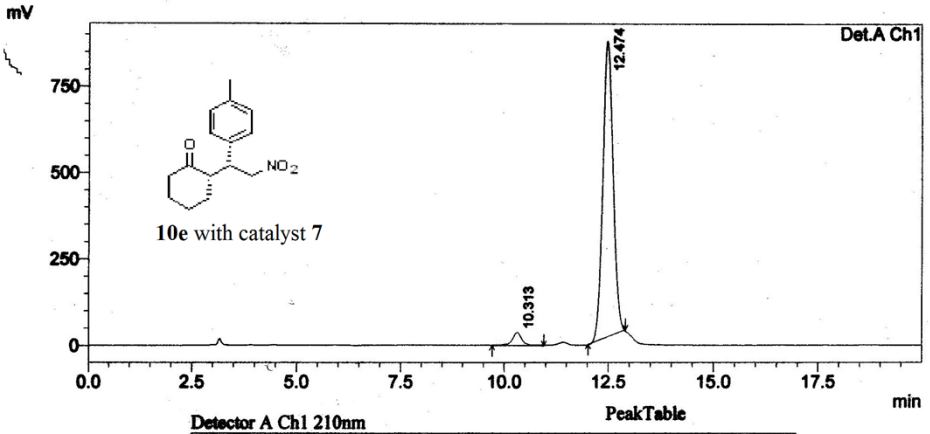
Peak#	Ret. Time	Area	Height	Area %
1	11.456	19397675	1382960	79.088
2	14.423	5129006	177092	20.912
Total		24526681	1560052	100.000



PeakTable

Detector A Ch1 210nm

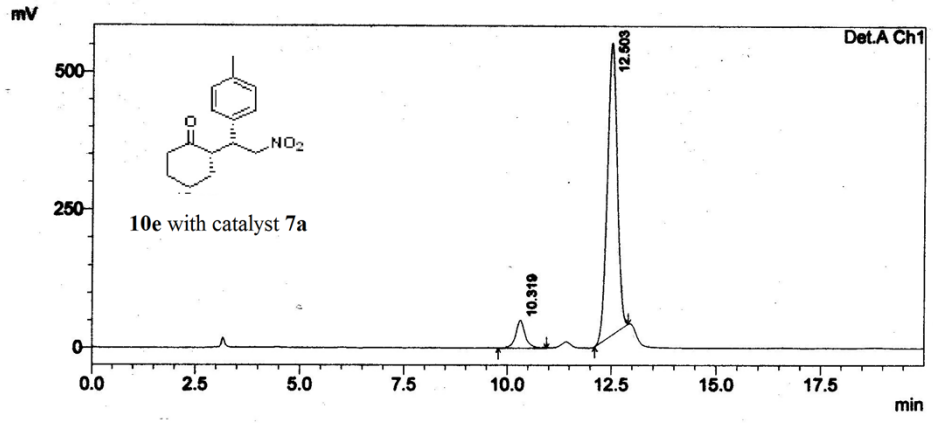
Peak#	Ret. Time	Area	Height	Area %
1	10.232	16270668	1074869	48.254
2	12.471	17448404	941704	51.746
Total		33719071	2016573	100.000



PeakTable

Detector A Ch1 210nm

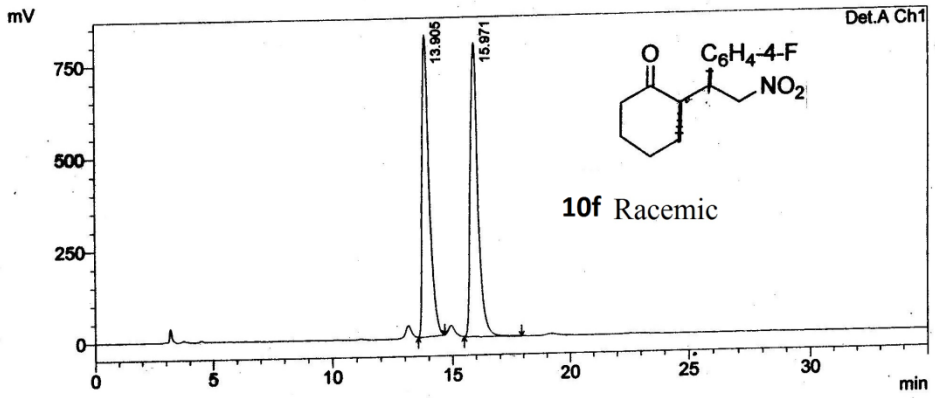
Peak#	Ret. Time	Area	Height	Area %
1	10.313	564201	37137	3.738
2	12.474	14527571	856493	96.262
Total		15091772	893631	100.000



PeakTable

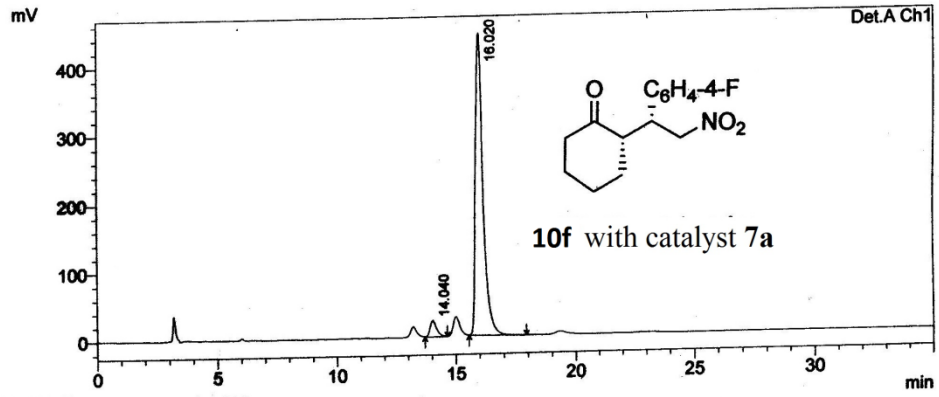
Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %
1	10.319	795857	50577	8.374
2	12.503	8708218	531293	91.626
Total		9504076	581869	100.000



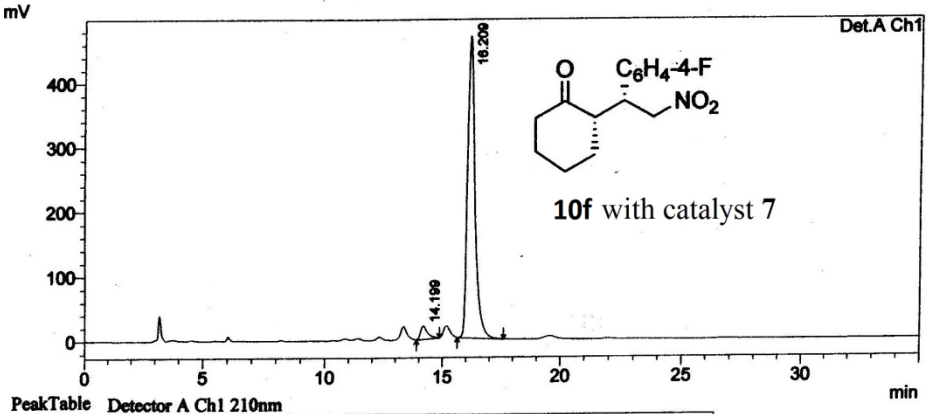
PeakTable Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %
1	13.905	16778050	818384	48.778
2	15.971	17618436	796714	51.222
Total		34396487	1615098	100.000



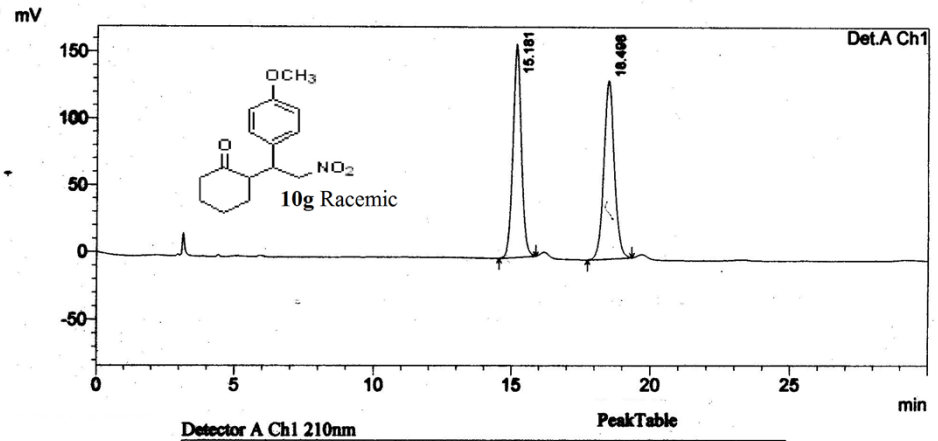
PeakTable Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %
1	14.040	453330	23959	4.536
2	16.020	9540441	442974	95.464
Total		9993771	466933	100.000



PeakTable Detector A Ch1 210nm

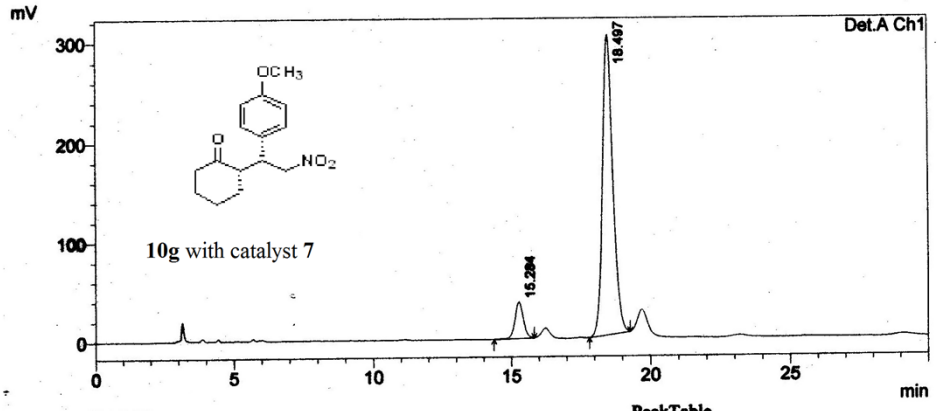
Peak#	Ret. Time	Area	Height	Area %
1	14.199	420905	20261	3.925
2	16.209	10302939	468975	96.075
Total		10723845	489236	100.000



PeakTable

Detector A Ch1 210nm

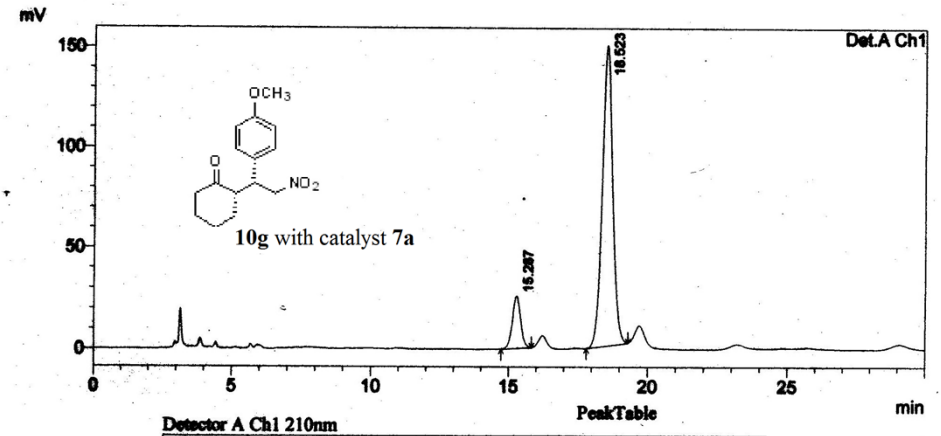
Peak#	Ret. Time	Area	Height	Area %
1	15.181	3371893	159662	49.155
2	18.498	3487866	133602	50.845
Total		6859759	293264	100.000



PeakTable

Detector A Ch1 210nm

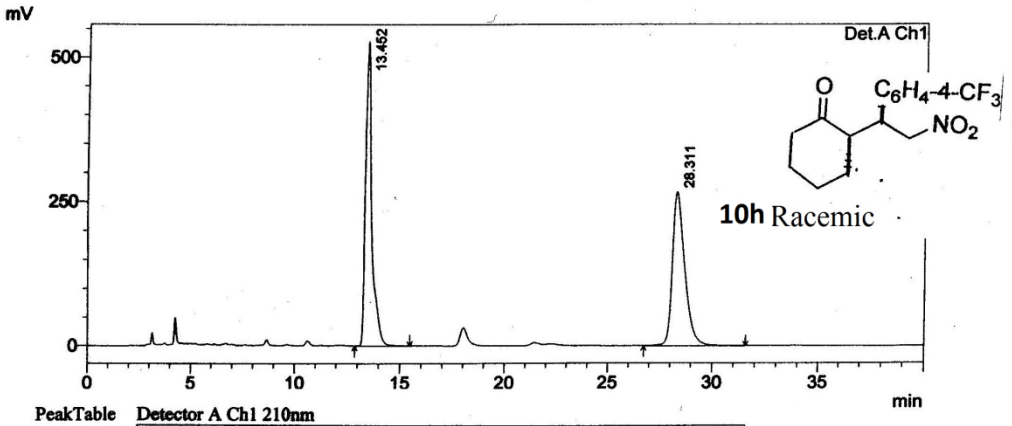
Peak#	Ret. Time	Area	Height	Area %
1	15.284	771657	36812	9.000
2	18.497	7802209	302111	91.000
Total		8573866	338922	100.000



PeakTable

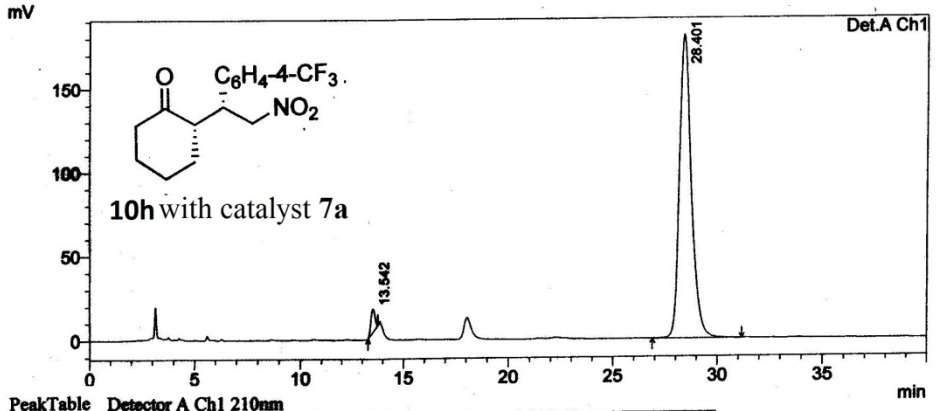
Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %
1	15.287	536091	25774	12.210
2	18.523	3854523	149554	87.790
Total		4390614	175329	100.000



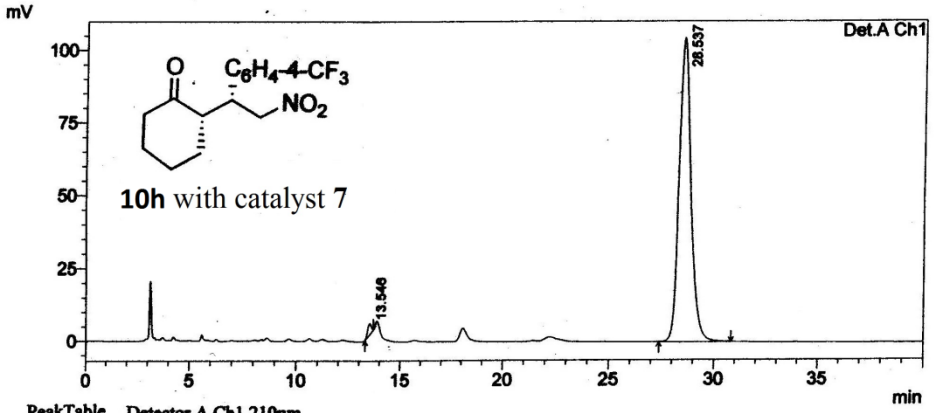
PeakTable Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %
1	13.452	11127003	528082	50.418
2	28.311	10942339	266782	49.582
Total		22069342	794864	100.000



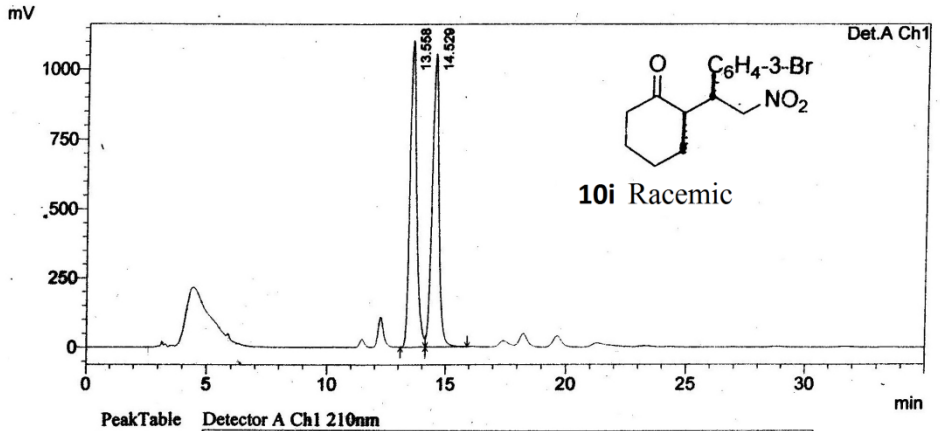
PeakTable Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %
1	13.542	185383	13685	2.525
2	28.401	7157694	181350	97.475
Total		7343077	195034	100.000



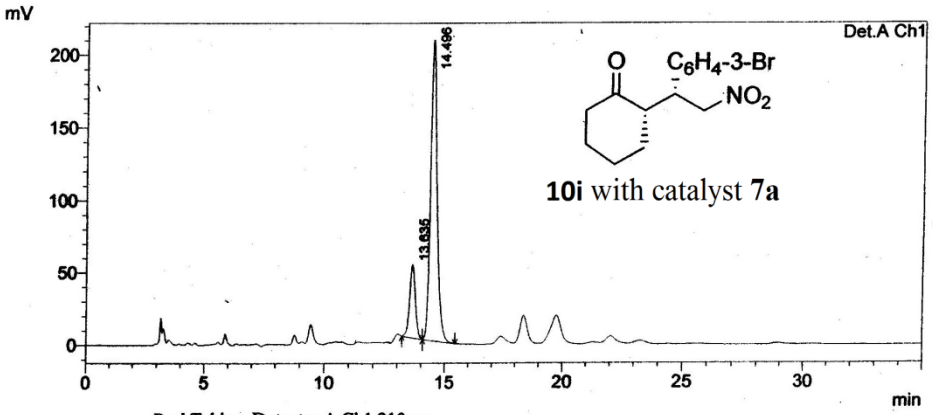
PeakTable Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %
1	13.546	46212	3728	1.128
2	28.537	4050008	104735	98.872
Total		4096220	108463	100.000



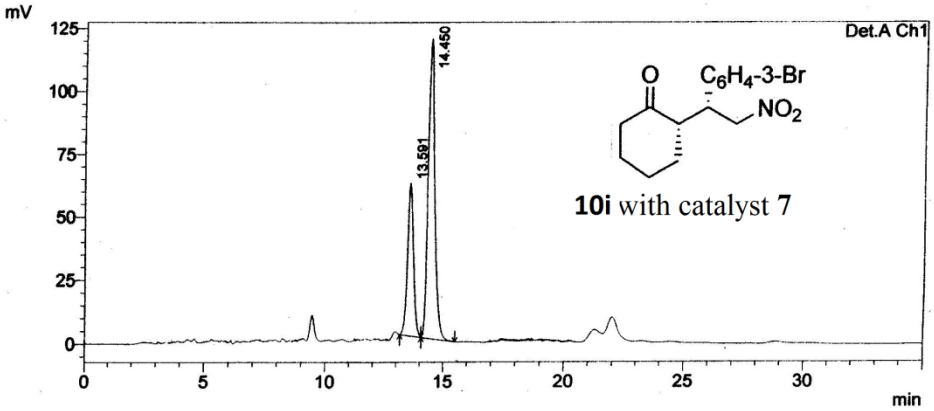
PeakTable Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %
1	13.558	21621886	1100718	50.465
2	14.529	21223677	1054513	49.535
Total		42845562	2155231	100.000



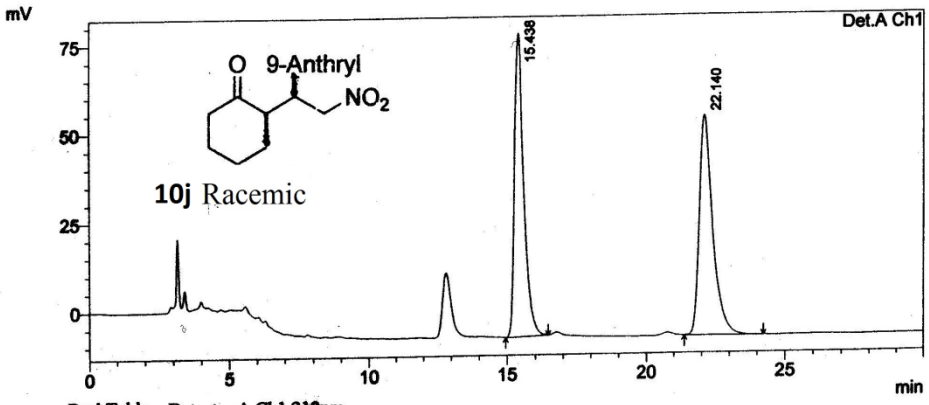
PeakTable Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %
1	13.635	855872	50528	17.675
2	14.496	3986433	207360	82.325
Total		4842305	257887	100.000



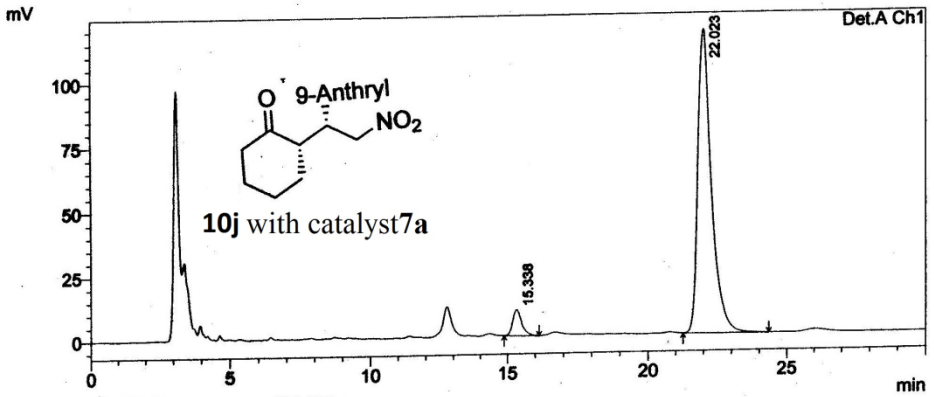
PeakTable Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %
1	13.591	1071624	60419	32.037
2	14.450	2273297	118689	67.963
Total		3344921	179109	100.000



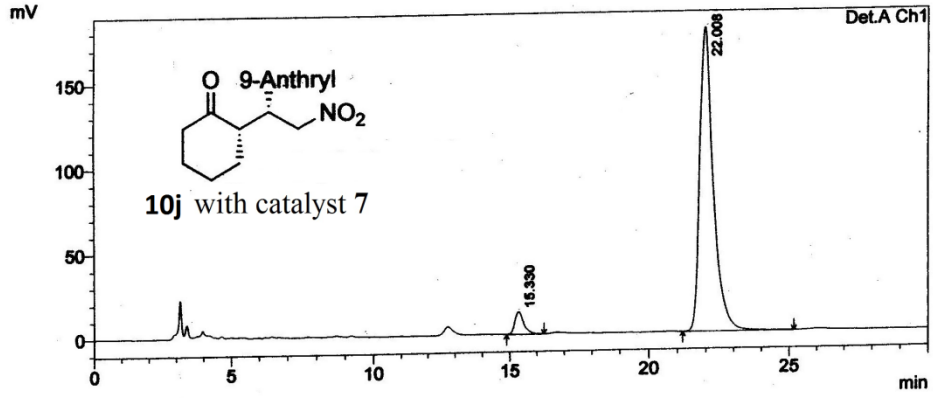
PeakTable Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %
1	15.438	1938079	85556	48.192
2	22.140	2083515	61966	51.808
Total		4021594	147522	100.000



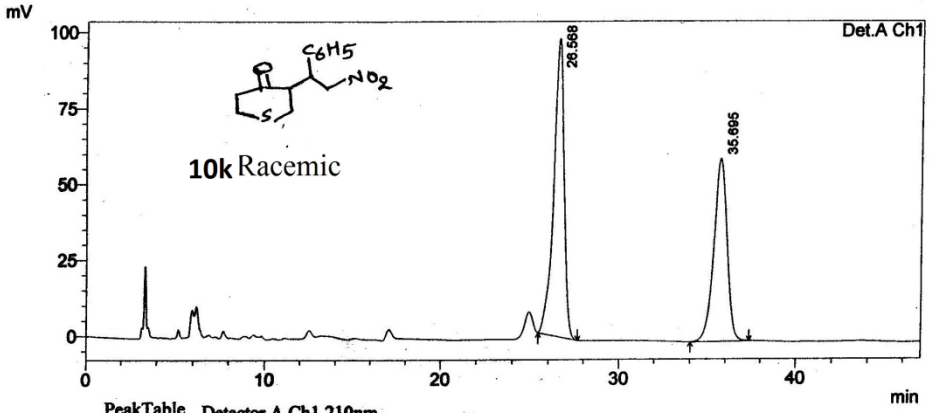
PeakTable Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %
1	15.338	223389	9984	5.316
2	22.023	3978566	118166	94.684
Total		4201955	128150	100.000



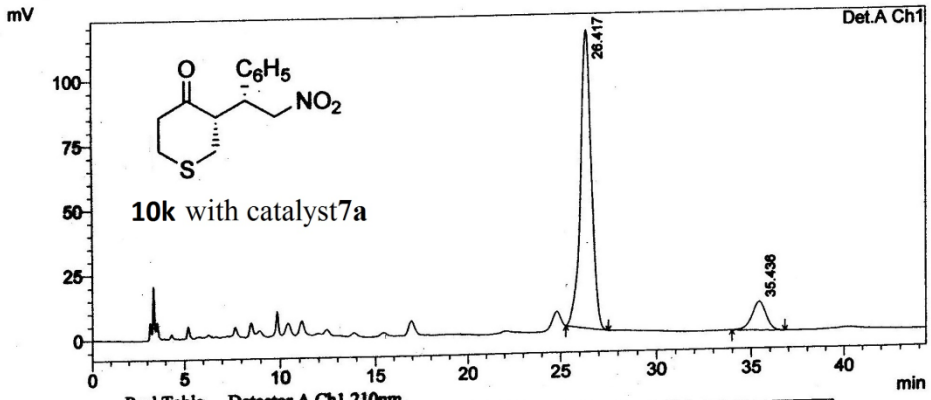
PeakTable Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %
1	15.330	300335	13313	4.731
2	22.008	6048367	179696	95.269
Total		6348703	193008	100.000



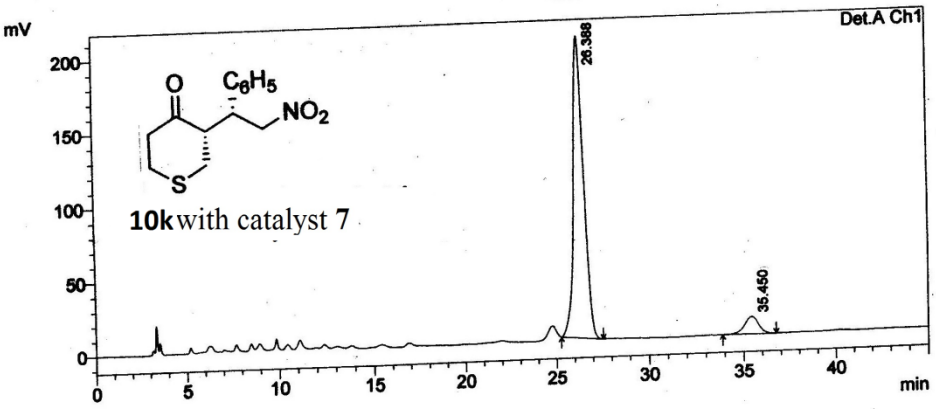
PeakTable Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %
1	26.568	3980059	98281	56.109
2	35.695	3113357	60227	43.891
Total		7093416	158509	100.000



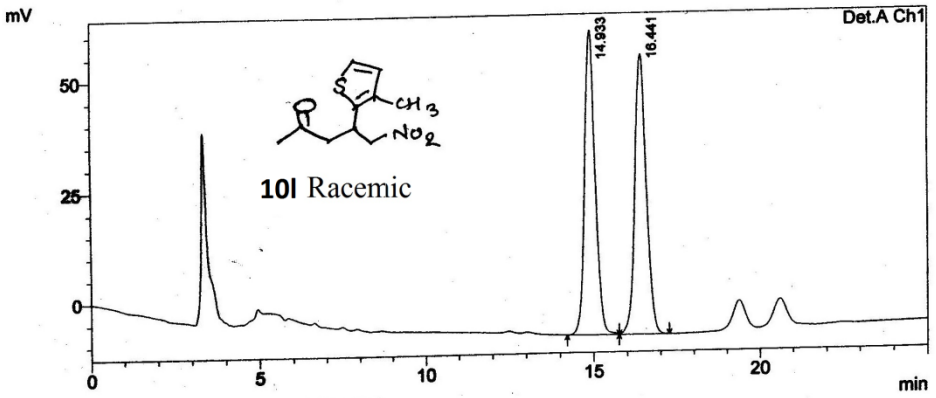
PeakTable Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %
1	26.417	4529008	115257	88.704
2	35.436	576740	11108	11.296
Total		5105748	126365	100.000



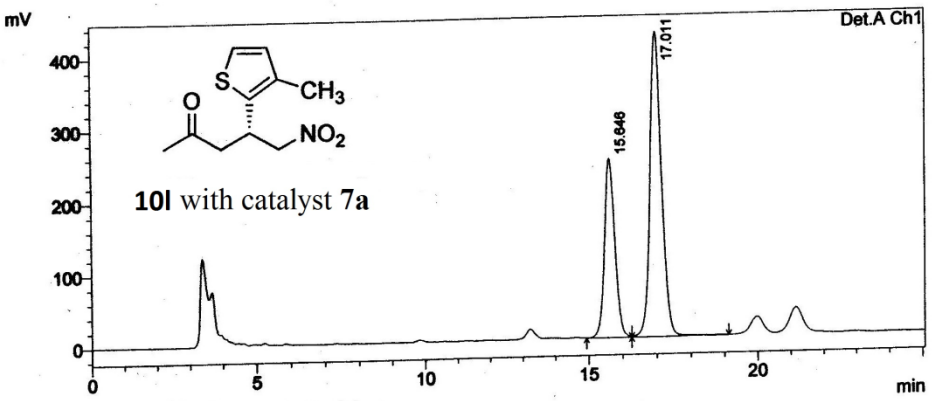
PeakTable Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %
1	26.388	8013903	204581	93.038
2	35.450	599653	11630	6.962
Total		8613557	216211	100.000



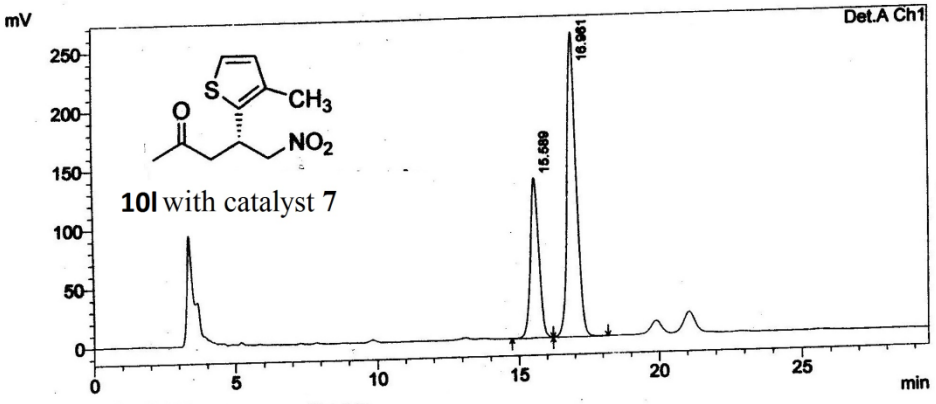
PeakTable Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %
1	14.933	1493067	68812	50.036
2	16.441	1490902	63299	49.964
Total		2983969	132111	100.000



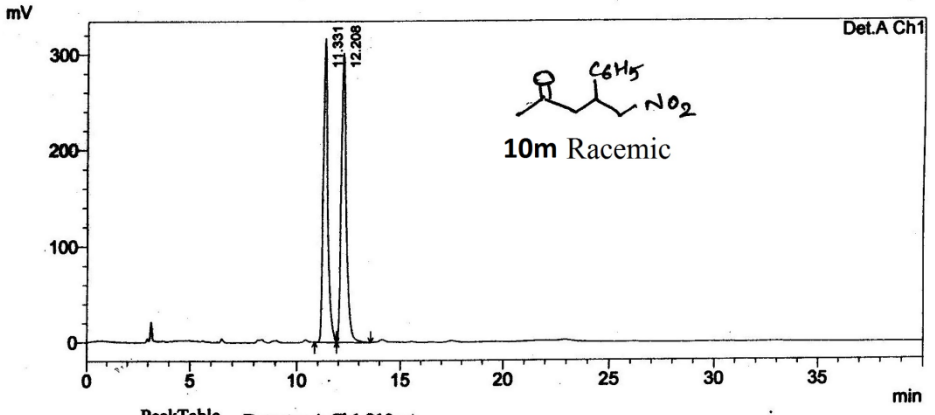
PeakTable Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %
1	15.646	5235522	248129	34.687
2	17.011	9858026	422698	65.313
Total		15093549	670827	100.000



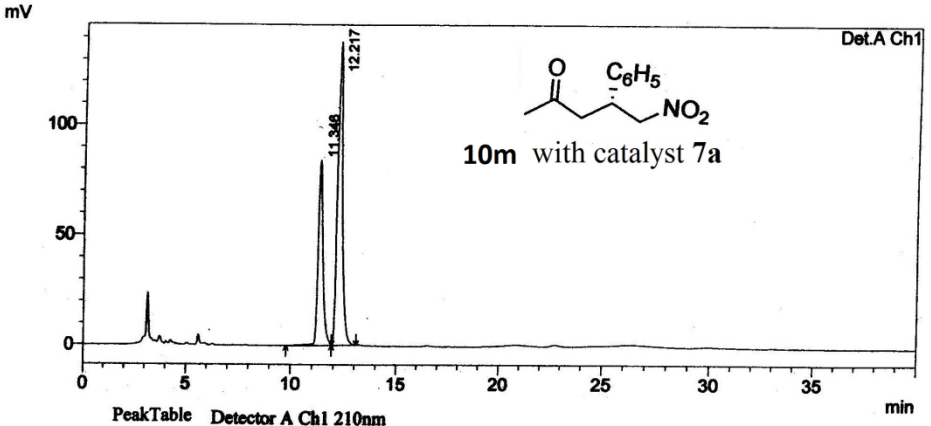
PeakTable Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %
1	15.589	2841222	135960	32.396
2	16.961	5929130	258457	67.604
Total		8770352	394417	100.000



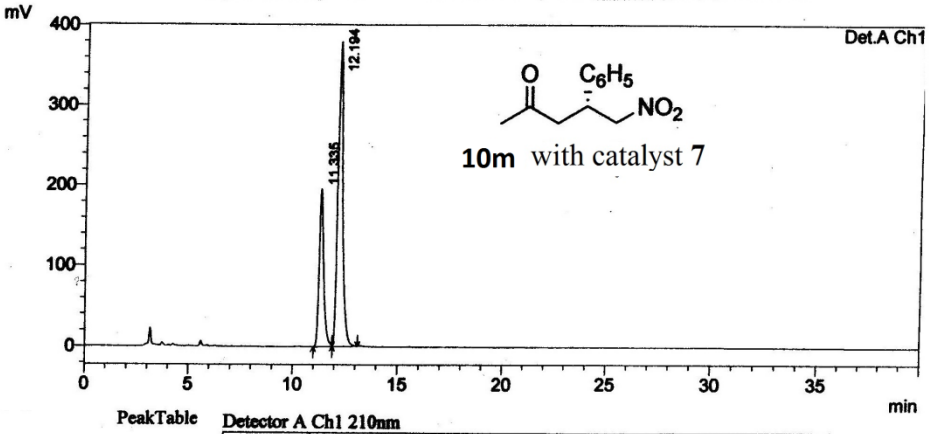
PeakTable Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %
1	11.331	4885023	316642	49.004
2	12.208	5083613	301574	50.996
Total		9968636	618217	100.000



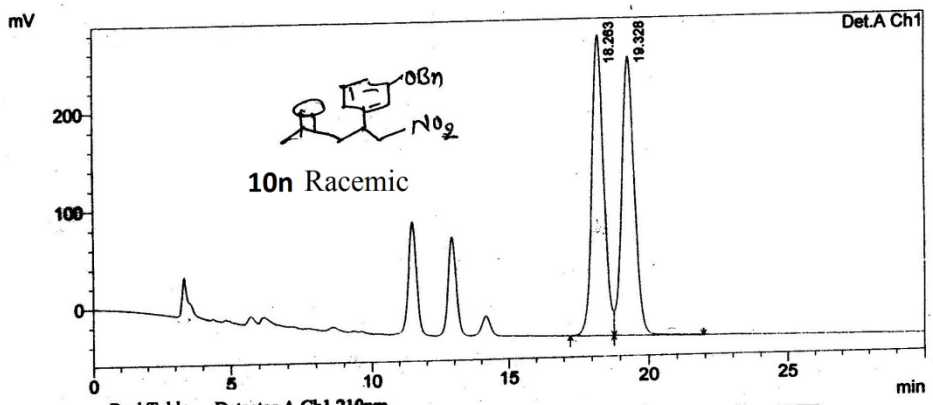
PeakTable Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %
1	11.346	1313099	84166	36.581
2	12.217	2276462	138049	63.419
Total		3589561	222216	100.000



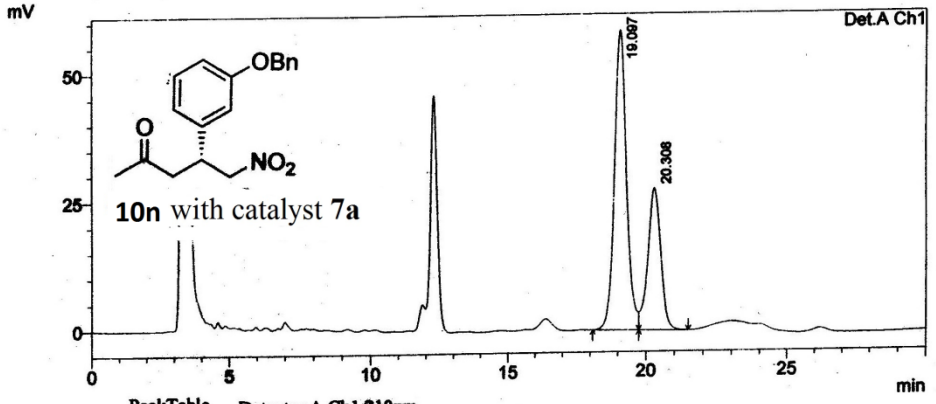
PeakTable Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %
1	11.335	2982269	196275	32.071
2	12.194	6316756	379378	67.929
Total		9299025	575654	100.000



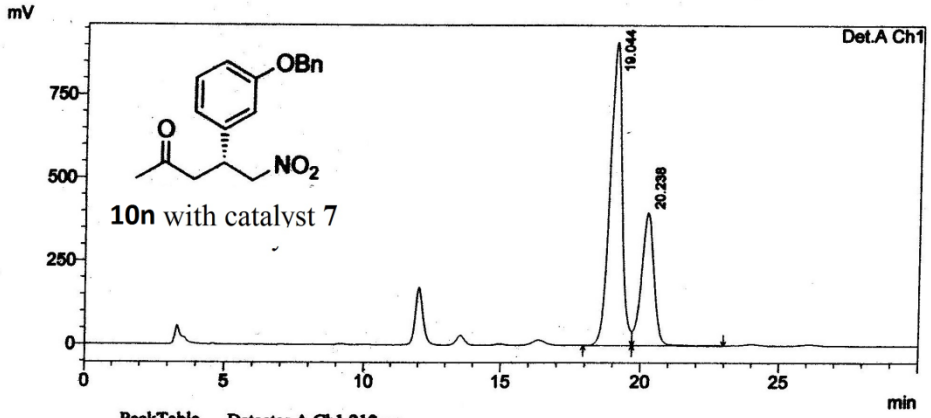
PeakTable Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %
1	18.263	8900988	309222	50.168
2	19.328	8841267	286433	49.832
Total		17742255	595656	100.000



PeakTable Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %
1	19.097	1749999	58556	66.858
2	20.308	867482	27534	33.142
Total		2617481	86090	100.000



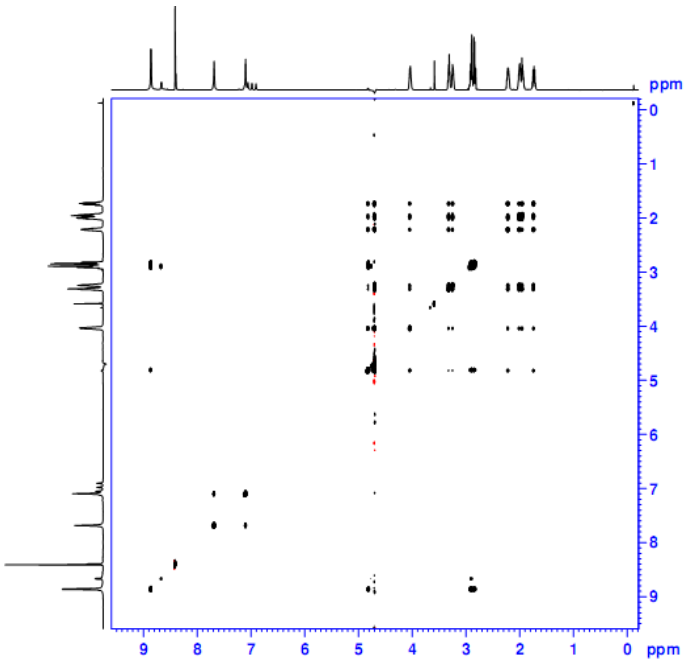
PeakTable Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %
1	19.044	27648836	912865	68.748
2	20.238	12568804	399114	31.252
Total		40217640	1311980	100.000

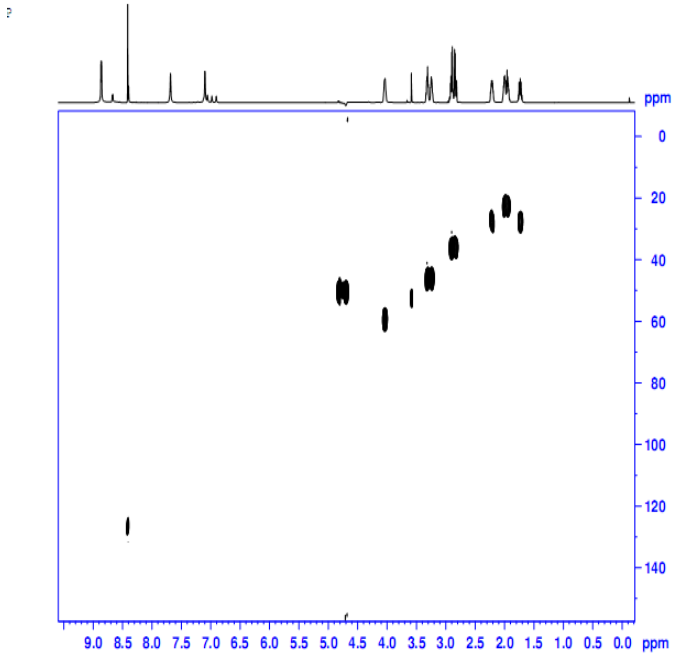
7. NMR-Experiments

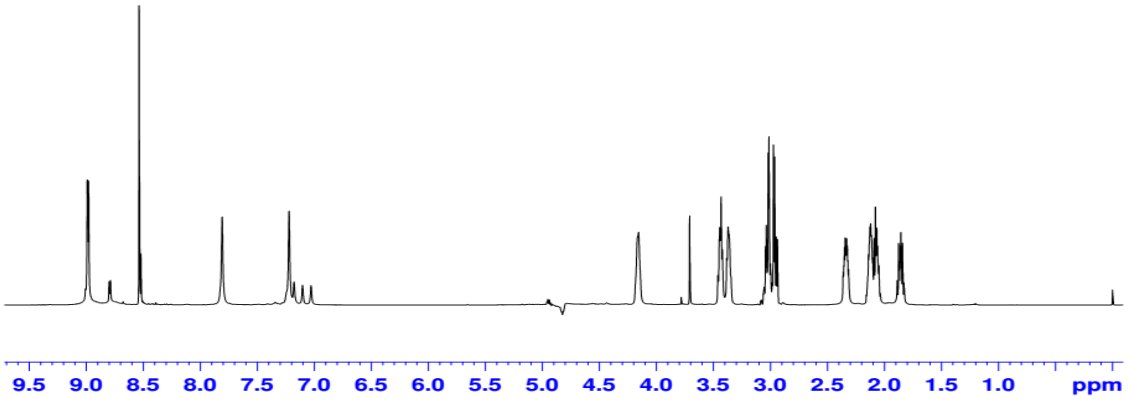
TOCSY, HSQC and proton Spectrums of **7a** in 500 µl of 90% D_2O and 10% H_2O (700MHz, 298K)

TOCSY



HSQC

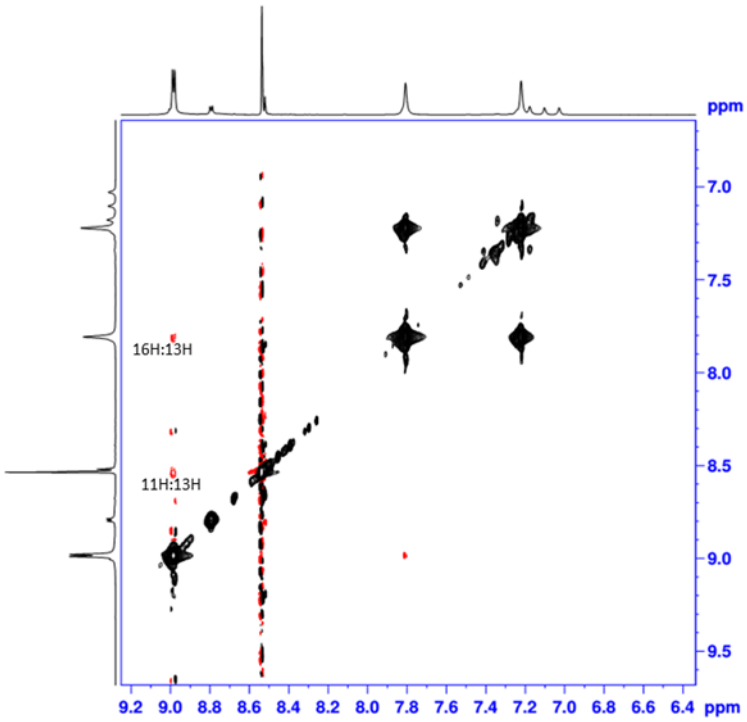




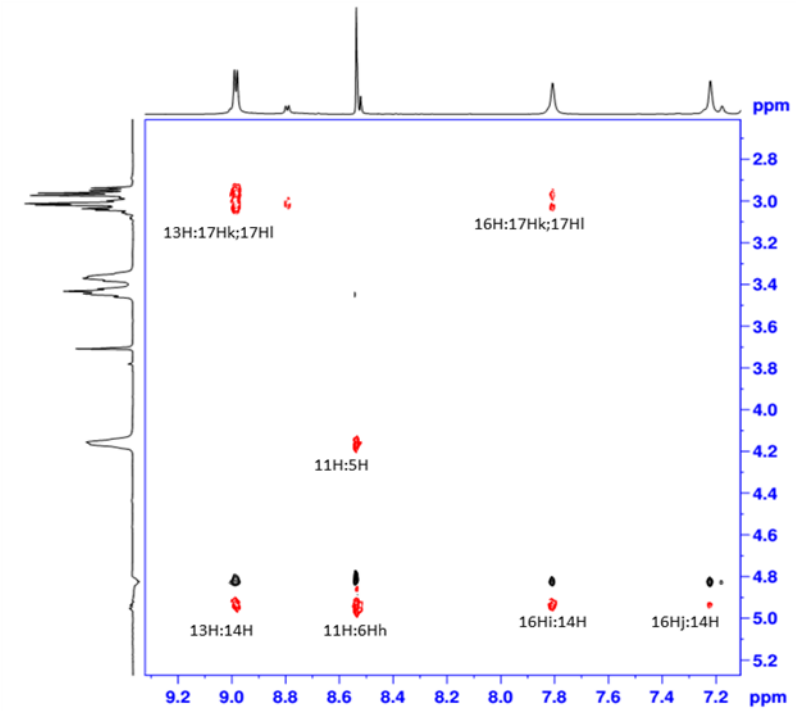
^{1}H NMR Spectrum of **7a**500 µl of 90% D_2O and 10% H_2O (700MHz, 298K)

Figures 1a and 1b ROESY Spectrum of **7a** in 500 µl of 90% D_2O and 10% H_2O (700MHz, 298K)

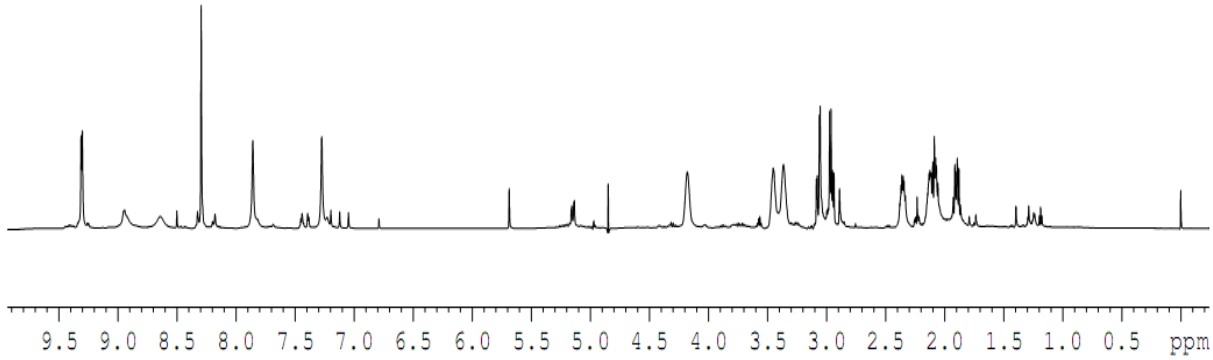
1a



1b

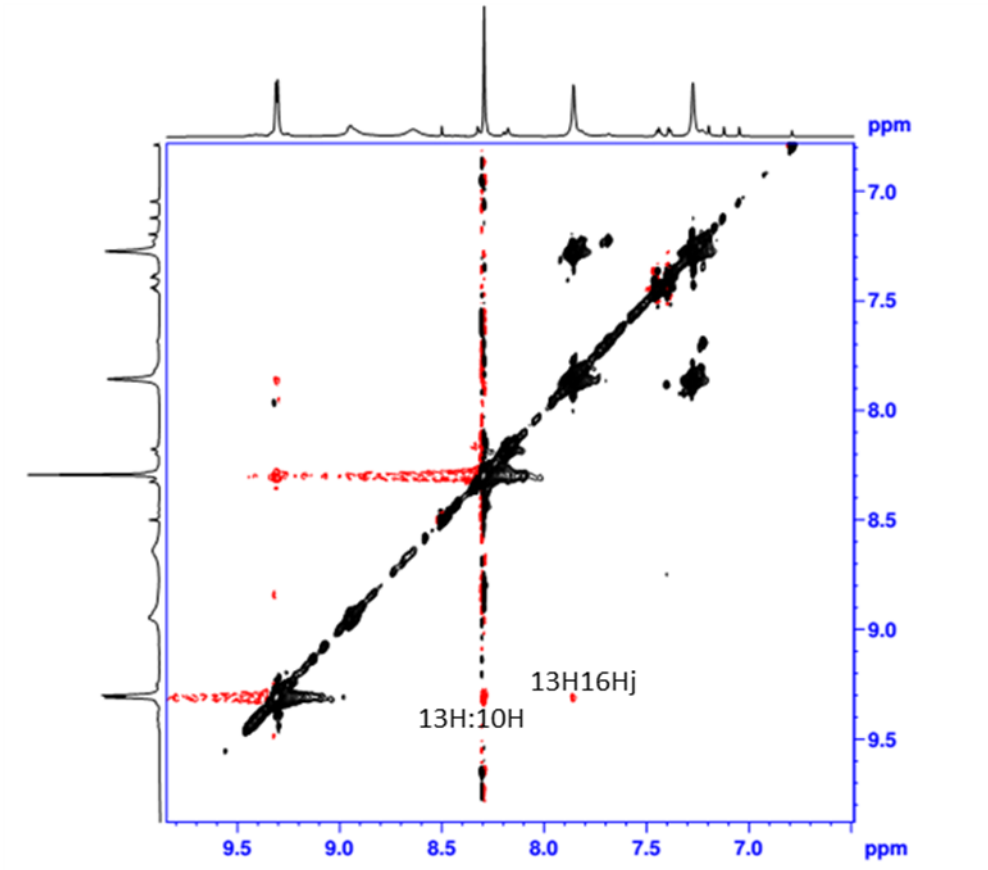


^{1}H NMR Spectrum of **7** in 500 µl of 90% D_2O and 10% H_2O (700 MHz, 298K)

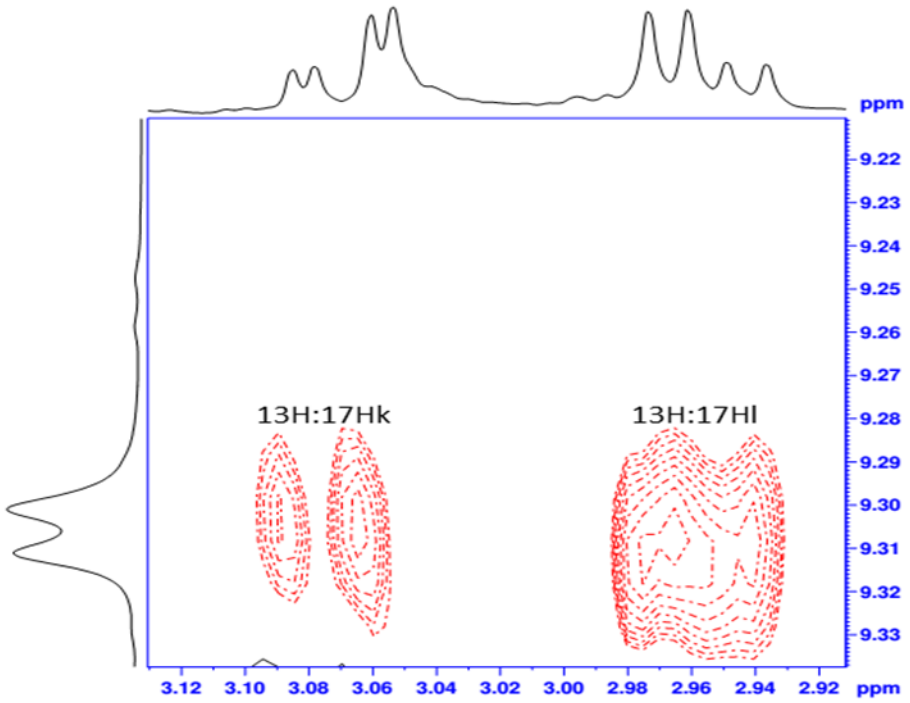


Figures 2a and 2b) ROESY Spectrum of **7** in 500 µl of 90% D_2O and 10% H_2O (700MHz, 298K)

2a

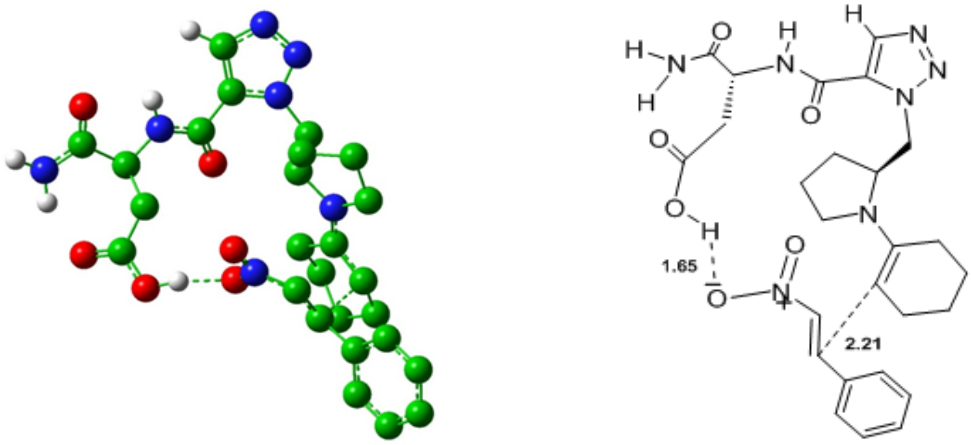


2b

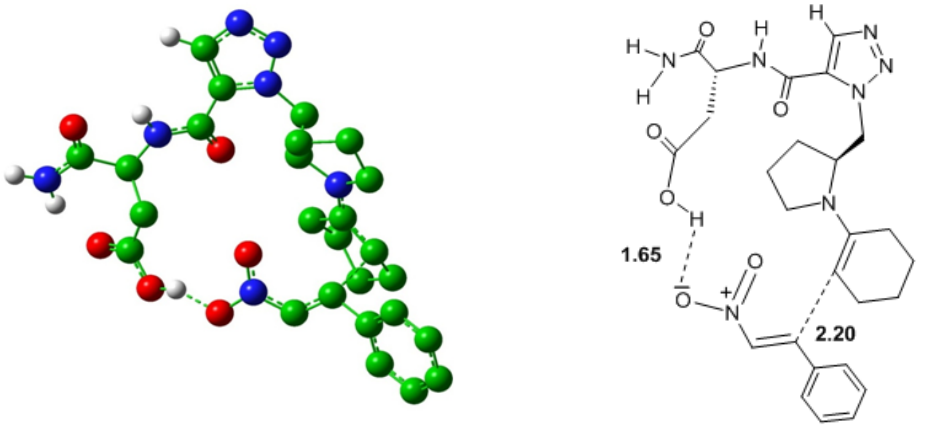


8. DFT Studies- Computational Methods of Transition States

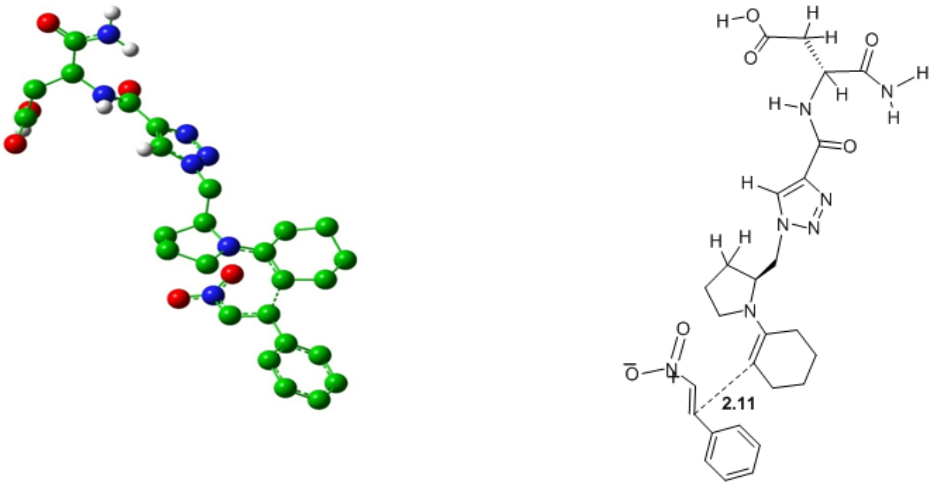
Standard protocols for observing transition states are followed, by using Gaussian 09 software. Initially, the fully relaxed minimum energy structures of 1,5-triazole catalyst (**7),** 1,4-triazole catalyst (**7a)** and nitrostyrene obtained from simulated annealing are subjected to optimization at B3LYP/6-31* level DFT calculations. The optimization was initially carried out in vacuum and then in MeOD solvent, by adopting PCM (Polarisable Continuum Model). These structures served as inputs (reactants) for computing transition state structures. The transition states for the addition of *anti* and *syn* enamine to the *si* and *re* faces of nitrostyrene were first located in the gas phase. These transition states are labelled *a-re*, *a-si, s-re*, and *s-si*. The noticeable charge separation in the transition state is expected upon addition of enamine to nitrostyrene. To obtain improved estimates of the reaction energetic continuum solvent effects are incorporated by computing the zero-point energies by using the PCM with methanol as the medium. Distances are in the angstrom units (Å).



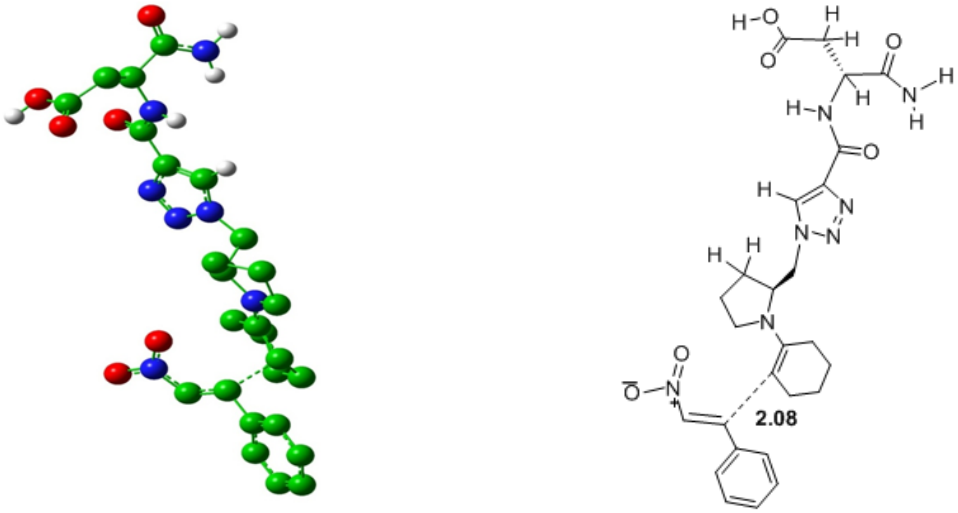
7-*anti* enamine + *re* nitrostyrene



7-*anti* enamine + *si* nitrostyrene



7a-*anti* enamine + *re* nitrostyrene



7a-*anti* enamine +*si* nitrostyrene

Quantum mechanical calculations of the transition states for the addition of *Anti* and *Syn* enamines to the *si* and *re* faces of nitrostyrene. Absolute Energies (HARTREE and Kcal/Mol) of all the Transition States calculated at DFT B3LYP/6-31G* level of theory.

ENAMINE+ NITRO STYRENE	TRANSITION STATE ENERGY (HARTREE)	TRANSITION STATE NERGY (Kcal/Mol)
anti- re	-1844.551983	12.75
anti-si	-1844. 548347	15.07
syn-re	-1844.548473	15.29
syn-si	-1844.548767	15.17

ENAMINE+ NITRO STYRENE	TRANSITION STATE ENERGY (HARTREE)	TRANSITION STATE NERGY (Kcal/Mol)
anti- re	-1844.567544	2.43
anti-si	-1844.565963	3.42
syn-re	-1844.562234	5.83
syn-si	-1844.562155	5.88

Cartesian Coordinates of Transition State Structures

The B3LYP/6-31G (d) optimized geometries (Cartesian coordinates in (A^0)), total electronic energies (in hartree/particle), of transition states of different stereochemical modes of addition of **7** enamine to nitrostyrene. The values in the parenthesis implies zero-point corrected energies evaluated at the PCM-B3LYP/6-31G (d) level of theory.

7-*anti* enamine + *re* nitrostyrene

Et = -1845.1601392 (-1844.567544)

C	-0.658388	2.065377	0.899325
C	0.431445	3.146661	0.920702
C	1.608733	2.48284	0.196215
N	0.985216	1.441204	-0.665242
C	-0.486796	1.410955	-0.481867
C	-1.205937	2.186357	-1.617355
N	-2.641222	2.343604	-1.371048
N	-3.146068	3.588549	-1.254060
N	-4.430867	3.485851	-1.016588
C	-4.759612	2.170504	-0.958889
C	-3.623320	1.414094	-1.185128
C	-3.380048	-0.053760	-1.233746
O	-2.510569	-0.544664	-1.964659
N	-4.149905	-0.775541	-0.394907
C	-4.003205	-2.208006	-0.199170
C	-5.236773	-2.638541	0.632511
N	-5.408720	-3.965257	0.753115
C	-2.653064	-2.517193	0.499783
C	-2.134588	-3.936043	0.322595
O	-0.836420	-4.110259	0.536434
O	-2.838743	-4.892795	0.022734
O	-5.988491	-1.790610	1.121662
H	-1.663252	2.466154	1.051577
H	-0.473501	1.309467	1.669585
H	0.102107	4.042058	0.383986
H	0.704214	3.450992	1.933983
H	2.290367	2.007480	0.903693
H	2.185941	3.175968	-0.423482
H	-0.815136	0.372487	-0.489797
H	-1.076110	1.686075	-2.576525
H	-0.818159	3.202652	-1.701117
H	-5.774373	1.841689	-0.785453
H	-4.839485	-0.341261	0.213115
H	-6.136484	-4.303487	1.369099
H	-4.665919	-4.594942	0.450037
H	-1.896472	-1.837902	0.101846
H	-2.715280	-2.307574	1.575166
H	-4.024181	-2.715787	-1.169128
C	1.702894	0.613028	-1.441047
C	3.105866	0.542476	-1.305457
C	3.958053	-0.01776	-2.429642
C	3.243721	-1.061696	-3.296604
C	1.836988	-0.584291	-3.663958

C	1.004035	-0.337261	-2.395823
H	3.585320	1.344136	-0.754830
H	4.268585	0.825449	-3.066184
H	4.887295	-0.429102	-2.018166
H	3.835249	-1.255489	-4.199009
H	3.171165	-2.016595	-2.758068
H	1.899114	0.339594	-4.254930
H	1.322247	-1.326178	-4.284865
H	0.007283	0.017837	-2.656595
H	0.860258	-1.285217	-1.867220
H	-0.330356	-3.242688	0.619818
C	5.127484	0.353361	1.520899
C	6.476680	0.480678	1.840928
C	7.409455	-0.437936	1.347064
C	6.980578	-1.483789	0.528744
C	5.628671	-1.609964	0.204654
C	4.679086	-0.697921	0.699335
H	4.420255	1.082345	1.906685
H	6.803001	1.300067	2.475177
H	8.461327	-0.335408	1.598021
H	7.695642	-2.204132	0.141618
H	5.299764	-2.434985	-0.421490
C	3.249684	-0.900664	0.368656
H	3.044188	-1.736540	-0.291424
C	2.280141	-0.688604	1.371942
H	2.448879	-0.103438	2.264046
N	1.052357	-1.276460	1.335208
O	0.244778	-1.131613	2.290727
O	0.724783	-2.002767	0.320349

7-*anti* enamine + *si* nitrostyrene

Et = -1845.1580996 (-1844.565963)

C	-1.476346	-2.742149	-1.759722
C	-0.962423	-3.755722	-2.791742
C	-0.104213	-2.894315	-3.722326
N	0.369416	-1.775552	-2.867776
C	-0.267564	-1.819176	-1.529250
C	0.712817	-2.376492	-0.465711
N	0.058593	-2.557668	0.830662
N	-0.128381	-3.806448	1.301483
N	-0.783924	-3.720012	2.434040
C	-1.041112	-2.412619	2.689048
C	-0.510548	-1.643290	1.667831
C	-0.451824	-0.172679	1.449034
O	0.493307	0.360294	0.854225

N	-1.504114	0.508142	1.945632
C	-1.586923	1.956939	1.954205
C	-2.702423	2.299899	2.972879
N	-2.797177	3.598849	3.297951
C	-1.862241	2.528768	0.537062
C	-1.381338	3.962304	0.359622
O	-1.255413	4.409418	-0.880035
O	-1.122216	4.705788	1.299660
O	-3.426517	1.411991	3.432539
H	-1.830072	-3.208818	-0.837614
H	-2.298729	-2.153041	-2.178876
H	-0.357301	-4.531242	-2.310622
H	-1.768517	-4.254300	-3.335192
H	-0.708007	-2.499998	-4.545474
H	0.750646	-3.424807	-4.151977
H	-0.571735	-0.807330	-1.257668
H	1.567191	-1.714818	-0.330230
H	1.075390	-3.365304	-0.750101
H	-1.557933	-2.095966	3.583819
H	-2.269682	0.043182	2.427097
H	-3.551518	3.899987	3.900444
H	-2.216663	4.283325	2.816590
H	-1.367067	1.897718	-0.206445
H	-2.933855	2.492875	0.301828
H	-0.636876	2.369443	2.309816
C	1.071627	-0.737854	-3.356371
C	1.303346	-0.593663	-4.742804
C	2.504913	0.190101	-5.241753
C	2.975373	1.302456	-4.296061
C	2.994022	0.812862	-2.846683
C	1.588994	0.340562	-2.432226
H	1.060784	-1.447295	-5.366765
H	3.326164	-0.529383	-5.385749
H	2.294915	0.594207	-6.239386
H	3.969860	1.647458	-4.602453
H	2.302959	2.166519	-4.371294
H	3.713063	-0.009351	-2.731783
H	3.312180	1.613258	-2.169082
H	1.572689	0.029012	-1.388602
H	0.907873	1.196738	-2.502490
C	0.177840	1.305350	-7.598815
C	0.240925	1.120557	-8.979941
C	-0.283586	-0.035661	-9.562311
C	-0.873141	-1.009688	-8.751606
C	-0.931031	-0.827964	-7.371613

C	-0.411148	0.332604	-6.769319
H	0.586915	2.214916	-7.170420
H	0.699304	1.884375	-9.601679
H	-0.234755	-0.176181	-10.638311
H	-1.289450	-1.910271	-9.194004
H	-1.395978	-1.589861	-6.750446
C	-0.529552	0.492723	-5.301373
H	-1.149708	-0.248576	-4.808741
C	-0.631514	1.783566	-4.745377
H	-0.331512	2.691455	-5.245025
N	-1.212741	1.998052	-3.529985
O	-1.391941	3.218742	-3.175574
O	-1.582062	1.047773	-2.783279
H	-1.407283	3.731822	-1.609703

The B3LYP/6-31G (d) optimized geometries (Cartesian coordinates in (A^0)), total electronic energies (in hartree/particle), of transition states of different stereo chemical modes of addition of **7a** enamine to nitro styrene. The values in the parenthesis implies zero-point corrected energies evaluated at the PCM-B3LYP/6-31G (d) level of theory

7a-*anti* enamine + *re* nitrostyrene

Et = -1845.1434395 (-1844.551983)

C	3.035325	-5.412734	-2.973328
C	3.132865	-5.403444	-1.439778
C	1.744605	-4.924013	-0.985617
C	1.365582	-3.880307	-2.047152
N	1.927342	-4.465005	-3.284348
C	1.987470	-2.488452	-1.763073
N	1.261865	-1.789778	-0.704584
C	1.629250	-1.532348	0.568114
C	0.547720	-0.859033	1.112778
N	-0.412444	-0.749230	0.144327
N	0.017531	-1.308103	-0.948912
C	0.313114	-0.292852	2.467135
O	-0.774595	0.178990	2.789515
N	1.392410	-0.318001	3.314307
C	1.300182	0.094118	4.706582
C	2.066534	1.396565	5.034273
N	2.492653	2.118064	3.977387
H	2.252838	-0.754788	3.008799
H	2.959686	3.000047	4.138267
H	2.334307	1.816184	3.027478
O	2.232470	1.736185	6.205226
C	1.752421	-1.020084	5.667296

C	0.883241	-2.257404	5.627258
O	-0.428089	-1.962665	5.758982
O	1.293794	-3.394357	5.515796
H	2.785911	-6.404748	-3.349133
H	3.953707	-5.076758	-3.465690
H	3.915495	-4.713162	-1.108397
H	3.382458	-6.392630	-1.048634
H	1.019527	-5.743151	-1.022667
H	1.740716	-4.508850	0.026266
H	0.283216	-3.786829	-2.158013
H	3.02767	-2.577636	-1.444938
H	1.965025	-1.852682	-2.649257
H	2.588737	-1.837030	0.957823
H	0.243329	0.315338	4.880751
H	1.729753	-0.607555	6.681288
H	2.779695	-1.329133	5.455739
H	-0.919901	-2.806281	5.734610
C	1.485225	-4.214038	-4.524510
C	1.893419	-5.021242	-5.615604
C	1.852645	-4.440319	-7.023048
C	0.710896	-3.443812	-7.252421
C	0.649476	-2.425139	-6.112285
C	0.446749	-3.133520	-4.762742
H	2.759767	-5.651915	-5.442358
H	2.811787	-3.931199	-7.203682
H	1.805752	-5.252421	-7.756255
H	0.852821	-2.937699	-8.214522
H	-0.24919	-3.974232	-7.315716
H	1.577587	-1.838035	-6.087126
H	-0.171861	-1.715719	-6.264601
H	0.434283	-2.402493	-3.953346
H	-0.534088	-3.622997	-4.748296
C	2.080464	-8.301695	-6.432576
C	2.499023	-9.146805	-7.458514
C	1.819054	-9.162960	-8.680599
C	0.719685	-8.323551	-8.867879
C	0.302804	-7.474491	-7.840775
C	0.970719	-7.455448	-6.604843
H	2.625133	-8.294343	-5.492313
H	3.359528	-9.792308	-7.305560
H	2.147234	-9.821698	-9.479677
H	0.184228	-8.326736	-9.813286
H	-0.558118	-6.828474	-7.992604
C	0.469354	-6.573611	-5.515032
H	-0.363112	-5.935497	-5.797350

C	0.357458	-7.139765	-4.224349
H	0.884242	-8.029553	-3.911692
N	-0.459753	-6.614617	-3.261088
O	-0.554454	-7.214940	-2.146711
O	-1.126325	-5.555705	-3.482409

7a-*anti* enamine + *si* nitrostyrene

Et = -1845.1395547 (-1844.548347)

C	3.439905	-4.545805	-3.121808
C	3.621987	-4.359378	-1.611820
C	2.214998	-3.965248	-1.138102
C	1.703080	-3.051430	-2.262346
N	2.320585	-3.636556	-3.473366
C	2.149839	-1.578100	-2.085084
N	1.327497	-0.888483	-1.093456
C	1.636401	-0.490972	0.158759
C	0.475369	0.098386	0.631750
N	-0.468269	0.028199	-0.356183
N	0.043517	-0.570452	-1.392185
C	0.167118	0.761302	1.926407
O	-0.804155	1.501165	2.059624
N	1.056049	0.504461	2.941915
C	0.863608	1.018896	4.290150
C	1.919726	2.060444	4.727274
N	2.723018	2.537230	3.754862
H	1.737229	-0.234019	2.815833
H	3.402560	3.250554	3.981150
H	2.652434	2.213357	2.801630
O	1.971565	2.428953	5.900133
C	0.800102	-0.110963	5.334091
C	-0.375854	-1.044558	5.151297
O	-1.548354	-0.376974	5.095971
O	-0.302823	-2.254176	5.080120
H	3.161777	-5.578556	-3.354082
H	4.329545	-4.290448	-3.704837
H	4.343388	-3.561173	-1.406671
H	3.991145	-5.269983	-1.134299
H	1.570627	-4.848062	-1.076423
H	2.206439	-3.471875	-0.162243
H	0.616250	-3.100037	-2.356546
H	3.187872	-1.518109	-1.753159
H	2.065614	-1.025151	-3.021833
H	2.621599	-0.628225	0.577615
H	-0.093265	1.548456	4.272584

H	0.729283	0.357887	6.320716
H	1.711595	-0.714640	5.314026
H	-2.256472	-1.040254	4.982798
C	1.792637	-3.562302	-4.703505
C	2.226875	-4.408606	-5.759651
C	2.151406	-3.886530	-7.191430
C	0.966133	-2.952409	-7.465171
C	0.821730	-1.914671	-6.350735
C	0.650547	-2.621342	-4.993016
H	3.144154	-4.959062	-5.569436
H	3.087317	-3.342614	-7.391612
H	2.143843	-4.729461	-7.891057
H	1.103314	-2.460864	-8.435595
H	0.037884	-3.533931	-7.532202
H	1.703557	-1.260806	-6.321176
H	-0.048149	-1.271744	-6.526259
H	0.494775	-1.894349	-4.196022
H	-0.261500	-3.233239	-5.045286
C	1.019418	-7.080583	-7.872602
C	1.583116	-7.962905	-8.794814
C	2.689255	-8.740349	-8.443067
C	3.229580	-8.627067	-7.159588
C	2.667334	-7.742518	-6.240111
C	1.550286	-6.957714	-6.575993
H	0.157687	-6.489341	-8.166830
H	1.154589	-8.043459	-9.790007
H	3.125288	-9.428262	-9.161991
H	4.087124	-9.229361	-6.872517
H	3.092207	-7.665010	-5.241941
C	0.966225	-6.057910	-5.543016
H	1.328681	-6.256821	-4.539550
C	-0.422573	-5.783615	-5.571501
H	-1.054736	-5.871978	-6.441787
N	-1.096924	-5.442295	-4.426931
O	-2.356086	-5.320563	-4.467516
O	-0.460242	-5.255218	-3.340881