Supplementary Information (ESI)

Enantiopure Imidazolinium-Dithiocarboxylates as Highly Selective Novel Organocatalysts

Oksana Sereda,[a] Amélie Blanrue[a] and René Wilhelm*[a]

[a]*Institute of Organic Chemistry, Clausthal University of Technology, Leibnizstr. 6, 38678 Clausthal-Zellerfeld, Germany*

rene.wilhelm@tu-clausthal.de

General Experimental.

All reactions, except otherwise indicated, were carried out in dried glassware under nitrogen. Toluene was dried over sodium. Tetrahydrofuran was dried over sodium/benzophenone. Dichloromethane was dried over CaH_2. Diamine for zwitterion **3**,[1] salts for the zwitterions **1**,[2] **2**,[3] and salt analogue of zwitterion **3** (4*S*,5*S*)-1,3-dimethyl-4,5-diphenyl-4,5-dihydro-3*H*-imidazol-1-ium tetrafluoroborate[4] were prepared according to the literature. Imines[5] and ketenes[6] (Table 2, Entries 1-10) were prepared according to the literature. All other chemicals were purchased and used without further purification. Flash column chromatography (FCC) was performed on Sorbisil C-60. The reactions were monitored by TLC with Merck Silica gel 60 F_{254} plates. Elemental analysis was carried out by the Microanalytical Laboratory of the Institut für Pharmazeutische Chemie der Technischen Universität Braunschweig. Infrared spectra were recorded on a Bruker Vector 22 FTIR instrument. NMR spectra were performed at ambient temperature on Bruker AMX 400 and Bruker AC 200F and, if not otherwise stated, measured in $CDCl_3$ with tetramethylsilan as an internal standard. Mass spectroscopy (EI) was conducted on Hewlett–Packard 5989B at 70 eV. Electron spray mass spectra (ESI) were recorded on MS LC/MSD 1100 MSD Hewlett–Packard (at 0 or 30 eV). HRMS were recorded on Bruker Daltonik Tesla-Fourier Transform-Ion Cyclotron Resonance Massspectrometer mit Electrospray-Ionisierung by Dr. Dräger at the Institute of Organic Chemistry, University of Hannover. Melting points were taken on a Dr. Tottoli apparatus from BÜCHI and are uncorrected. HPLC analysis was carried out using a Daicel CHIRALPACK AD-H column with a Waters 510 Pump system, an ISCO Model UA-5 UV/vis Detector (254 nm) and a Waters 410 Differential Refractometer. 1 mg of sample was completely dissolved in a mixture of 1.5 mL *i*PrOH/hexane. It is well known that pure enantiomers and racemates can have different solubility in one way or the other. In case of an 87% *ee* sample (Table 1, Entry 5), when not all compound was dissolved an *ee* of 69% *ee* was measured.

(4*S*,5*S*)-1,3-Dimethyl-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-3-ium-2-dithiocarboxylate (3)

(1*S*,2*S*)-*N*,*N*'-Dimethyl-1,2-diphenylethane-1,2-diamine[1] (1.19 g, 4.95 mmol) and *N*,*N*-dimethyl-formamide dimethylacetal (4.13 mL, 29.7 mmol, 6 eq.) were slowly distilled at 100 °C for 5 d until an oily solid was left in the flask. Dry xylene (3.5 mL) and CS_2 (2.8 mL, 46.3 mmol, 9 eq.) were added. After refluxing for 4 h at 140 °C the formed red precipitate was filtered, washed with diethyl ether and columned with CH_2Cl_2 to give a red solid (1.1 g, 3.37 mmol, 68%). mp = 205 °C. $[\alpha]_D^{20} = -200$ (*c* = 1.03, $CHCl_3$). ^{1}H-NMR (200 MHz): δ = 3.07 (s, 6 H), 4.74 (s, 2 H), 7.37-7.41 (m, 6 H), 7.49-7.55 (m, 4 H). ^{13}C-NMR (50 MHz): δ = 32.08, 73.90, 126.89, 129.93, 130.01, 136.29, 167.12, 225.82. IR (KBr) ν/cm^{-1}: 1592, 1576, 1454, 1072, 698. MS (EI): m/z = 326 $[M]^+$, 180, 165. Anal. Calcd for $C_{18}H_{18}N_2S_2$: C 66.22; H 5.56; N 8.58. Found: C 66.09; H 5.62; N 8.72.

General procedure for the formation of dithiocarboxylate zwitterions 1, 2 and 4

Procedure A. To the generated carbene from the imidazolinium salt and 1 eq. KO*t*Bu in THF after 30 min, an excess of CS_2 was added. The mixture was stirring at rt for 30 min or more. The crude product was purified on silica gel with CH_2Cl_2.

Procedure B. To the mixture of imidazolinium salt and 5-7 eq. CS_2 in THF, 1.5 eq. KHMDS (0.5 M in toluene) were quickly added at rt. After the completion of the reaction in 15-30 min, the reaction mixture was quenched with sat. $NH_4Cl_{(aq)}$. The aqueous phase was extracted with CH_2Cl_2. The organic phases were combined and dried (Na_2SO_4), and the solvent was evaporated under reduced pressure. The crude product was purified on silica gel with 30% ethyl acetate in petrol ether.

1,3-Bis((*R*)-1-phenylethyl)-4,5-dihydro-1*H*-imidazol-3-ium-2-dithiocarboxylate (1)

From 1,3-bis-(1(*R*)-phenyl-ethyl)-4,5-dihydro-3*H*imidazol-1-ium tetrafluoroborate[2] (1.1 g, 3 mmol), KO*t*Bu (337 mg, 3 mmol, 1.0 eq.) and CS_2 (0.9 ml, 15 mmol, 5 eq.) in THF (2 mL) according to procedure A. The product was purified by column chromatography with CH_2Cl_2 to give a red solid (371 mg, 1 mmol, 43%). mp = 201 °C. $[\alpha]_D^{20} = +172$ (*c* = 0.94, $CHCl_3$). ^{1}H-NMR (200 MHz): δ = 1.69 (d, *J* = 7 Hz, 6 H), 3.12-3.34 (m, 2 H), 3.45-3.7 (m, 2 H), 5.51 (q, *J* = 7 Hz, 2 H), 7.33-7.44 (m, 6 H), 7.46-7.52 (m, 4 H). ^{13}C-NMR (50 MHz): δ = 15.63, 41.42, 54.34, 127.84, 128.68, 129.0, 137.10, 165.70, 226.33. IR (KBr) ν/cm^{-1}: 2972, 1570, 1290, 1062, 698. MS (EI): m/z = 353 $[M]^+$, 249, 147, 105, 91, 77. Anal. Calcd for $C_{20}H_{22}N_2S_2$: C 67.76; H 6.25; N 7.90. Found: C 67.80; H 6.23; N 7.93.

1,3-Bis((1*R*,2*S*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)-4,5-dihydro-1*H*-imidazol-3-ium-2-dithiocarboxylate (2)

From 1,3-bis((1*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)-imidazolinium tetrafluoroborate[3] (300 mg, 0.70 mmol), CS_2 (0.216 mL, 3.5 mmol, 5 eq.) and KO*t*Bu (84 mg, 0.75 mmol, 1.1 eq) in THF (6 ml) according to procedure A to give a red solid (220 mg, 0.53 mmol, 74%). mp = 246 °C. $[\alpha]_D^{20} = -48$ (c = 0.48, $CHCl_3$). ^{1}H-NMR (200 MHz): δ = 0.87 (s, 6 H), 0.95 (s, 6 H), 1.03 (s, 6 H), 1.12-1.31 (m, 4 H), 1.42-1.57 (m, 4 H), 1.64-1.75 (m, 4 H), 1.85-1.99 (m, 2H), 3.67-3.91 (m, 4 H), 4.31 (t, J = 8.6 Hz, 2 H). ^{13}C-NMR (100 MHz): δ = 11.86, 21.36, 21.50, 26.05, 32.78, 38.65, 44.20, 45.99, 46.61, 49.72, 64.41, 170.59, 229.03. IR (KBr) ν/cm^{-1}: 2958, 2930, 1551, 1285, 1044. MS (EI): m/z = 418 $[M]^+$, 403, 385, 282, 167, 166, 137, 95. HRMS: found [M^+] 418.1649. $C_{24}H_{38}N_2S_2$ requires 418.2472.

(4*R*,5*R*)-1,3-Dimethyl-4,5-bis(3-(trifluoromethyl)phenyl)-4,5-dihydro-1*H*-imidazol-3-ium-2-dithiocarboxylate (4)

From (4*R*,5*R*)-1,3-dimethyl-4,5-bis(3-(trifluoromethyl)phenyl)-4,5-dihydro-1*H*-imidazol-3-ium tetrafluoroborate (115 mg, 0.24 mmol), CS_2 (0.073 mL, 1.2 mmol, 5 eq.) and KHMDS (0.728 ml, 0.36 mmol, 1.5 eq.) in THF (5 ml) according to procedure B to give a red solid (61 mg, 0.13 mmol, 54 %) yield. mp = 143 °C. $[\alpha]_D^{20} = +113$ (c = 0.7, $CHCl_3$). ^{1}H-NMR (400 MHz): δ = 3.04 (s, 6 H), 4.77 (s, 2 H), 7.55 (s, 2 H), 7.65-7.78 (m, 6 H). ^{13}C-NMR (100 MHz): δ = 29.68, 72.92, 123.37 (q, J = 271 Hz), 123.81 (q, J = 3.7 Hz), 127.07 (q, J = 3.6 Hz), 129.77, 131.04, 132.42 (q, J = 32.8 Hz), 136.81, 167.01, 224.34. IR (KBr) ν/cm^{-1}: 3449, 2925, 2854, 2361, 1735, 1571, 1451, 1320, 1270, 1159, 1122, 1061, 1013, 808, 709. MS (EI): m/z = 463 $[M+H]^+$, 316, 248, 180, 72. Anal. Calcd for $C_{20}H_{16}F_6N_2S_2$: C 51.94; H 3.49; N 6.06%. Found: C 52.32; H 3.76; N 6.14%.

(4*R*,5*R*)-1,3-Dimethyl-4,5-bis(3-(trifluoromethyl)phenyl)-4,5-dihydro-1*H*-imidazol-3-ium tetrafluoroborate was prepared from (1*R*,2*R*)-N^1,N^2-dimethyl-1,2-bis(3-(trifluoromethyl)phenyl)ethane-1,2-diamine (518 mg, 1.38 mmol), ammonium tetrafluoroborate (144 mg, 1.38 mmol, 1 eq.), and triethyl orthoformate (0.26 ml, 1.55 mmol, 1.13 eq.) after heating at 120°C for 5 h, resulting in a white solid (588 mg, 1.24 mmol, 90%). mp = 153 °C. $[\alpha]_D^{20} = +142$ (c = 0.68, CH_2Cl_2). ^{1}H-NMR (400 MHz): δ = 3.16 (s, 6 H), 5.02 (s, 2 H), 7.53 (s, 2 H), 7.66-7.76 (m, 6 H), 8.68 (s, 1 H). ^{13}C-NMR (100 MHz): δ = 35.52, 75.13, 123.39 (q, J = 270.9 Hz), 124.60 (q, J = 3.7 Hz), 127.24 (q, J = 3.6 Hz), 130.96,

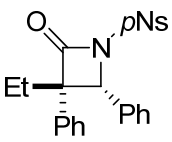
131.06, 132.20 (q, J = 32.8 Hz), 134.71, 160.80. IR (KBr) ν/cm^{-1}: 3423, 3097, 2957, 1658, 1456, 1419, 1331, 1273, 1224, 1172, 1126, 1076, 807, 705, 674, 602. MS (ESI): m/z = 387 $[M]^+$. Anal. Calcd for $C_{19}H_{17}BF_{10}N_2$: C 48.13; H 3.61; N 5.91. Found: C 48.32; H 3.70; N 5.91.

(4*S*,5*S*)-1,3-dimethyl-4,5-bis(3-(trifluoromethyl)phenyl)-4,5-dihydro-1*H*-imidazol-3-ium-2-carbodithioate (*ent*-4)

Synthesized from (4*S*,5*S*)-1,3-dimethyl-4,5-bis(3-(trifluoromethyl)phenyl)-4,5-dihydro-1*H*-imidazol-3-ium tetrafluoroborate in analogy to **4**. Analytical data were consistent with **4**.

General Experimental for the Staudinger reaction. An imine (0.1 mmol), a ketene (0.25 mmol) and a zwitterion (10 mol%) were dissolved in dry toluene (1.5 ml) and left to stir for 16 h. After total conversion the reaction mixture was applied to column chromatography on silica gel (eluent 1:8 diethyl ether/petrol ether) and the two diastereomers were isolated, if not otherwise stated, as white solids (yields: 96-99%).

(*R*)-3-ethyl-1-*p*-nitrobenzenesulfonyl-3,4-diphenylazetidin-2-one (Table 1, Entry 5)

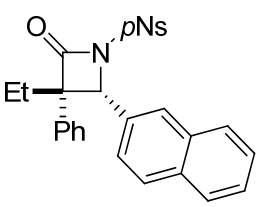


From ketene (40 µL, 0.27 mmol) and imine (29 mg, 0.1 mmol) in toluene (1.5 ml) with 10 mol% catalyst (0.01mmol) after stirring at rt for 16 h as a white solid (43.3 mg, 99 %, *trans : cis* 1 : 5.4). Analytical data are consistent with the literature.[7]

trans-Isomer: $[\alpha]_D^{20}$ = +116 (c = 0.37, CH_2Cl_2). HPLC (Chiralpack AD-H, 10% iPrOH/hexane, 1 ml/min.): 65% *ee*, R_t 19.53 min. (major), 31.18 min. (minor).

cis-Isomer: $[\alpha]_D^{20}$ = –75.4 (c = 0.41, CH_2Cl_2). HPLC (Chiralpack AD-H, 10% iPrOH/hexane, 1 ml/min.): 87% *ee*, R_t 18.78 min. (minor), 21.04 min. (major).

(*R*)-3-ethyl-4-(naphthalen-2-yl)-1-*p*-nitrobenzenesulfonyl-3-phenylazetidin-2-one (Table 2. Entry 1.)



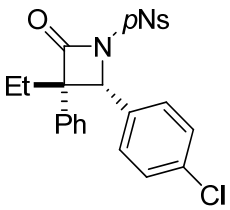
From ketene (40 µL, 0.27 mmol) and imine (34 mg, 0.1 mmol) in toluene (1.5 ml) with 10 mol% catalyst (0.01mmol) after stirring at rt for 16 h as a white solid (47.4 g, 97 %, *trans : cis* 1 : 6).

trans-Isomer: white crystals, mp = 155-157 °C. $[\alpha]_D^{20}$ = +145.45 (c = 0.11, CH_2Cl_2). HPLC (Chiralpack AD-H, 30% iPrOH/hexane, 1 ml/min.): 62% *ee*, R_t 13.43

min. (major), 55.40 min. (minor). ^{1}H-NMR (400 MHz): δ = 0.56 (t, J = 7.2 Hz, 3 H), 1.31-1.40 (m, 1 H), 1.74-1.83 (m, 1 H), 5.42 (s, 1 H), 7.30-7.41 (m, 6 H), 7.54-7.58 (m, 2 H), 7.73-7.77 (m, 2 H), 7.87-7.91 (m, 2 H), 8.13 (d, J = 8.8 Hz, 2 H), 8.34 (d, J = 8.8 Hz, 2 H). ^{13}C-NMR (100 MHz): δ = 8.60, 27.03, 29.69, 68.21, 69.98, 124.21, 124.44, 126.15, 126.70, 126.94, 127.00, 127.88, 127.90, 128.04, 128.67, 129.08, 129.10, 130.85, 132.86, 133.40, 137.27, 143.86, 150.85, 168.41. IR (KBr) ν/cm^{-1}: 1783 (C=O). MS (ESI): m/z = 508.8 [M + Na]$^{+\cdot}$. Anal. Calcd for $C_{27}H_{22}N_2O_5S$: C 66.65; H 4.56; N 5.76%. Found: C 66.71; H 4.43; N 5.70%.

cis-Isomer: white crystals, mp = 179 °C. $[\alpha]_D^{20}$ = –124.36 (c = 0.5, CH_2Cl_2). HPLC (Chiralpack AD-H, 10% iPrOH/hexane, 1 ml/min.): 92% *ee*, R_t 25.43 min. (major), 29.01 min. (minor). ^{1}H-NMR (200 MHz): δ = 0.99 (t, J = 7.4 Hz, 3 H), 2.17-2.36 (m, 2 H), 5.33 (s, 1 H), 6.51 (d, J = 8.6 Hz, 1 H), 6.89-7.01 (m, 5 H), 7.29 (d, J = 8.6 Hz, 1 H), 7.41-7.50 (m, 3 H), 7.57-7.69 (m, 2 H), 7.86 (d, J = 9.2 Hz, 2 H), 8.12 (d, J = 9.0 Hz, 2 H). ^{13}C-NMR (50 MHz): δ = 9.19, 32.84, 69.28, 69.96, 124.15, 124.47, 126.60, 126.87, 127.06, 127.32, 127.66, 127.72, 128.22, 128.59, 128.80, 130.92, 132.46, 132.98, 134.31, 144.17, 150.59, 167.61. IR (KBr) ν/cm^{-1}: 1788 (C=O). MS (ESI): m/z = 995.0 [2M + Na]$^{+}$. Anal. Calcd for $C_{27}H_{22}N_2O_5S$: C 66.65; H 4.56; N 5.76%. Found: C 66.78; H 4.55; N 5.83%.

(*R*)-4-(4-chlorophenyl)-3-ethyl-1-*p*-nitrobenzenesulfonyl-3-phenylazetidin-2-one (Table 2, Entry 2)



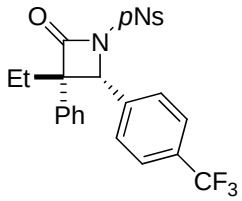
From ketene (40 µL, 0.27 mmol) and imine (32.5 mg, 0.1 mmol) in toluene (1.5 ml) with 10 mol% catalyst (0.01mmol) after stirring at rt for 16 h as a white solid (45.5 mg, 97 %, *trans : cis* 1 : 3).

trans-Isomer (columned with 5% diethyl ether in petrol ether): white crystals, mp = 163 °C. $[\alpha]_D^{20}$ = +4.8 (c = 0.5, CH_2Cl_2). HPLC (Chiralpack AD-H, 10% iPrOH/hexane, 1 ml/min.): 48% *ee*, R_t 18.78 min. (major), 52.77 min. (minor). ^{1}H-NMR (200 MHz): δ = 0.59 (t, J = 7.4 Hz, 3 H), 1.25-1.43 (m, 1 H), 1.62-1.80 (m, 1 H), 5.17 (s, 1 H), 7.16-7.21 (m, 2 H), 7.29-7.35 (m, 5 H), 7.42 (d, J = 8.6 Hz, 2 H), 8.14 (d, J = 9.0 Hz, 2 H), 8.36 (d, J = 9.0 Hz, 2 H). ^{13}C-NMR (50 MHz): δ = 8.55, 27.01, 68.00, 69.11, 124.51, 125.95, 128.12, 128.35, 129.01, 129.10, 129.14, 132.16, 135.13, 136.91, 143.52, 150.96, 168.19. IR (KBr) ν/cm^{-1}: 1789 (C=O). MS (ESI): m/z = 493.0 [M + Na]$^{+}$. Anal. Calcd for $C_{23}H_{19}ClN_2O_5S$: C 58.66; H 4.07; N 5.93%. Found: C 58.79; H 3.95; N 5.92%.

cis-Isomer: white crystals, mp = 134 °C. $[\alpha]_D^{20}$ = –69.2 (c = 0.5, CH_2Cl_2). HPLC (Chiralpack AD-H, 10% iPrOH/hexane, 1 ml/min.): 90% *ee*, R_t 18.78 min. (minor), 21.47

min. (major). ^{1}H-NMR (200 MHz): δ = 0.90 (t, J = 7.4 Hz, 3 H), 2.16 (q, J = 7.4 Hz, 2 H), 5.11 (s, 1 H), 6.72 (d, J = 8.4 Hz, 2 H), 6.83-6.87 (m, 2 H), 7.01 (d, J = 8.6 Hz, 2 H), 7.05-7.12 (m, 2 H), 8.02 (d, J = 9.2 Hz, 2 H), 8.33 (d, J = 9.2 Hz, 2 H). ^{13}C-NMR (50 MHz): δ = 9.13, 32.15, 68.20, 70.31, 124.43, 127.04, 127.59, 128.39, 128.87, 129.17, 132.41, 133.94, 134.78, 144.06, 150.86, 167.49. IR (KBr) ν/cm^{-1}: 1792 (C=O). MS (ESI): m/z = 493.1 [M + Na]$^{+}$. Anal. Calcd for $C_{23}H_{19}ClN_2O_5S$: C 58.66; H 4.07; N 5.93%. Found: C 58.80; H 4.09; N 6.05%.

(*R*)-3-ethyl-1-*p*-nitrobenzenesulfonyl-3-phenyl-4-(4-(trifluoromethyl)phenyl)azetidin-2-one (Table 2, Entry 3)

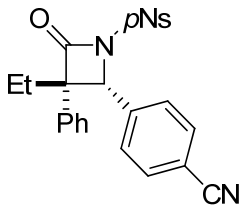


From ketene (40 µL, 0.27 mmol) and imine (35.8 mg, 0.1 mmol) in toluene (1.5 ml) with 10 mol% catalyst (0.01mmol) after stirring at rt for 16 h as a white solid (48 mg, 96 %, *trans : cis* 1 : 6.5).

trans-Isomer: white crystals, mp = 158-159 °C. $[\alpha]_D^{20}$ = +56.1 (c = 0.76, CH_2Cl_2). HPLC (Chiralpack AD-H, 10% iPrOH/hexane, 1 ml/min.): 83% *ee*, R_t 14.65 min. (major), 34.42 min. (minor). ^{1}H-NMR (200 MHz): δ = 0.61 (t, J = 7.2 Hz, 3 H), 1.23-1.42 (m, 1 H), 1.60-1.78 (m, 1 H), 5.22 (s, 1 H), 7.16-7.20 (m, 2 H), 7.31-7.37 (m, 3 H), 7.53 (d, J = 8.0 Hz, 2 H), 7.72 (d, J = 8.2 Hz, 2 H), 8.16 (d, J = 9.0 Hz, 2 H), 8.38 (d, J = 9.0 Hz, 2 H). ^{13}C-NMR (50 MHz): δ = 8.57, 27.02, 68.17, 69.09, 124.57, 125.89, 125.98, 127.40, 128.25, 129.04, 129.23, 136.68, 137.79, 143.33, 151.02, 168.02. IR (KBr) ν/cm^{-1}: 1783 (C=O). MS (ESI): m/z = 527.0 [M + Na]$^{+}$. Anal. Calcd for $C_{24}H_{19}N_2O_5S$: C 57.14; H 3.80; N 5.55%. Found: C 56.98; H 3.85; N 5.41%.

cis-Isomer: white crystals, mp = 131 °C. $[\alpha]_D^{20}$ = –76.6 (c = 0.5 g/100 ml; CH_2Cl_2). HPLC (Chiralpack AD-H, 11.5% iPrOH/hexane, 0.4 ml/min.): 95% *ee*, R_t 34.64 min. (minor), 36.50 min. (major). ^{1}H-NMR (200 MHz): δ = 0.91 (t, J = 7.4 Hz, 3 H), 2.17 (q, J = 7.0 Hz, 2 H), 5.16 (s, 1 H), 6.81-6.81 (m, 2 H), 6.94 (d, J = 8.0 Hz, 2 H), 7.10-7.30 (m, 3 H), 7.30 (d, J = 8.0 Hz, 2 H), 8.37 (d, J = 9.0 Hz, 2 H), 8.35 (d, J = 9.0 Hz, 2 H). ^{13}C-NMR (50 MHz): δ = 9.13, 31.91, 68.01, 70.72, 124.50, 125.03, 125.11, 125.18, 126.96, 127.73, 128.13, 128.43, 128.89, 133.62, 138.01, 143.87, 150.93, 167.35. IR (KBr) ν/cm^{-1}: 1796 (C=O). MS (ESI): m/z = 526.8 [M + Na]$^{+}$. Anal. Calcd for $C_{24}H_{19}N_2O_5S$: C 57.14; H 3.80; N 5.55%. Found: C 56.87; H 3.85; N 5.39%.

(*R*)-4-(3-ethyl-1-*p*-nitrobenzenesulfonyl-4-oxo-3-phenylazetidin-2-yl)benzonitrile (Table 2, Entry 4)

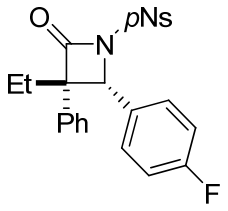


From ketene (40 µL, 0.27 mmol) and imine (31.5 mg, 0.1 mmol) in toluene (1.5 ml) with 10 mol% catalyst (0.01mmol) after stirring at rt for 16 h as a white solid (46 g, 99.9 %; *trans : cis* 1 : 2.7).

trans-Isomer (columned with 10% ethyl acetate in petrol ether): white crystals, mp = 168 °C. $[\alpha]_D^{20}$ = +60.0 (*c* = 0.5, CH_2Cl_2). HPLC (Chiralpack AD-H, 10% iPrOH/hexane, 1 ml/min.): 74% *ee*, R_t 28.64 min. (major), 62.88 min. (minor). ^{1}H-NMR (200 MHz): δ = 0.61 (t, *J* = 7.4 Hz, 3 H), 1.22-1.42 (m, 1 H), 1.56-1.76 (m, 1 H), 5.18 (s, 1 H), 7.12-7.17 (m, 2 H), 7.31-7.37 (m, 3 H), 7.55 (d, *J* = 8.2 Hz, 2 H), 7.78 (d, *J* = 8.4 Hz, 2 H), 8.16 (d, *J* = 9.0 Hz, 2 H), 8.38 (d, *J* = 9.0 Hz, 2 H). ^{13}C-NMR (50 MHz): δ = 8.57, 27.00, 68.40, 68.97, 113.18, 118.01, 124.61, 125.82, 127.73, 128.37, 129.04, 129.29, 132.63, 136.41, 139.11, 143.14, 151.09, 167.75. IR (KBr) ν/cm^{-1}: 1797 (C=O). MS (ESI): m/z = 381.3, 484.09 $[M + Na]^+$, 945.1 $[2M + Na]^+$. HRMS Calcd for $C_{24}H_{19}N_3O_5SNa$: 484.0943. Found: 484.0941. Anal. Calcd for $C_{24}H_{19}N_3O_5S$: C 62.46; H 4.15; N 9.11%. Found: C 62.61; H 4.19; N 9.15%.

cis-Isomer (columned with 15% ethyl acetate in petrol ether): white crystals, mp = 103-104 °C. $[\alpha]_D^{20}$ = –98.6 (*c* = 0.5, CH_2Cl_2). HPLC (Chiralpack AD-H, 10% iPrOH/hexane, 1 ml/min.): 93% *ee*, R_t 28.08 min. (minor), 34.66 min. (major). ^{1}H-NMR (200 MHz): δ = 0.87 (t, *J* = 7.4 Hz, 3 H), 2.05-2.25 (m, 2 H), 5.13 (s, 1 H), 6.80-6.86 (m, 2 H), 6.99 (d, *J* = 8.4 Hz, 2 H), 7.04-7.09 (m, 3 H), 7.37 (d, *J* = 8.4 Hz, 2 H), 8.13 (d, *J* = 9.0 Hz, 2 H), 8.41 (d, *J* = 9.0 Hz, 2 H). ^{13}C-NMR (50 MHz): δ = 9.11, 31.54, 67.87, 71.12, 112.29, 112.65, 117.99, 124.65, 126.92, 127.94, 128.22, 128.58, 128.95, 131.91, 133.33, 139.52, 143.72, 151.10, 167.20. IR (KBr) ν/cm^{-1}: 1786 (C=O). MS (ESI): m/z = 381.3, 413.2, 441.3, 484.09 $[M + Na]^+$. HRMS Calcd for $C_{24}H_{19}N_3O_5SNa$: 484.0943. Found: 484.0941. Anal. Calcd for $C_{24}H_{19}N_3O_5S$: C 62.46; H 4.15; N 9.11%. Found: C 62.45; H 4.19; N 9.36%.

(*R*)-3-ethyl-4-(4-fluorophenyl)-1-*p*-nitrobenzenesulfonyl-3-phenylazetidin-2-one (Table 2, Entry 5)



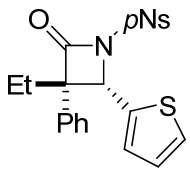
From ketene (40 µL, 0.27 mmol) and imine (30.8 mg, 0.1 mmol) in toluene (1.5 ml) with 10 mol% catalyst (0.01mmol) after stirring at rt for 16 h as a white solid (45.3 mg, 99.9 %; *trans : cis* 1 : 4.4).

trans-Isomer: white crystals, mp = 79 °C. HPLC (Chiralpack AD-H, 10%

iPrOH/hexane, 1 ml/min.): 64% *ee*, R_t 18.78 min. (major), 37.98 min. (minor). ^{1}H-NMR (200 MHz): δ = 0.59 (t, J = 7.4 Hz, 3 H), 1.25-1.43 (m, 1 H), 1.63-1.81 (m, 1 H), 5.19 (s, 1 H), 7.09-7.21 (m, 4 H), 7.29-7.39 (m, 5 H), 8.13 (d, J = 9.2 Hz, 2 H), 8.36 (d, J = 9.0 Hz, 2 H). ^{13}C-NMR (50 MHz): δ = 8.53, 27.01, 67.95, 69.13, 115.74, 116.17, 124.49, 125.98, 128.08, 128.72, 128.89, 129.01, 129.12, 129.36, 129.43, 137.02, 143.59, 168.30. IR (KBr) ν/cm^{-1}: 1786 (C=O). MS (ESI): m/z = 477.0 $[M + Na]^+$.

cis-Isomer: white crystals, mp = 124 °C. $[\alpha]_D^{20}$ = –71.7 (c = 0.52, CH_2Cl_2). HPLC (Chiralpack AD-H, 10% iPrOH/hexane, 1 ml/min.): 96% *ee*, R_t 17.37 min. (minor), 20.07 min. (major). ^{1}H-NMR (200 MHz): δ = 0.91 (t, J = 7.4 Hz, 3 H), 2.16 (q, J = 7.4 Hz, 2 H), 5.13 (s, 1 H), 6.72-6.76 (m, 4 H), 6.82-6.87 (m, 2 H), 7.04-7.11 (m, 3 H), 8.01 (d, J = 9.0 Hz, 2 H), 8.33 (d, J = 9.0 Hz, 2 H). ^{13}C-NMR (50 MHz): δ = 9.15, 32.18, 68.24, 70.25, 115.01, 115.44, 124.40, 127.08, 127.50, 128.34, 128.86, 129.56, 129.64, 129.73, 134.09, 144.15, 150.84, 160.19, 165.14, 167.57. IR (KBr) ν/cm^{-1}: 1784 (C=O). MS (ESI): m/z = 477.0 $[M + Na]^+$.

(*R*)-3-ethyl-1-*p*-nitrobenzenesulfonyl-3-phenyl-4-(thiophen-2-yl)azetidin-2-one (Table 2, Entry 6)

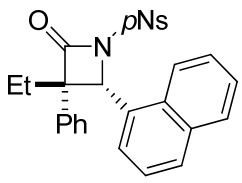


From ketene (40 µL, 0.27 mmol) and imine (29.6 mg, 0.1 mmol) in toluene (1.5 ml) with 10 mol% catalyst (0.01mmol) after stirring at rt for 16 h as a white solid (43.7 mg, 99 %; *trans : cis* 1 : 3). Analytical data are consistent with the literature.[7]

trans-Isomer: $[\alpha]_D^{20}$ = +115 (c = 0.5, CH_2Cl_2). HPLC (Chiralpack AD-H, 10% iPrOH/hexane, 1 ml/min.): 65% *ee*, R_t 24.93 min. (major), 34.10 min. (minor).

cis-Isomer: $[\alpha]_D^{20}$ = –74 (c = 0.5, CH_2Cl_2). HPLC (Chiralpack AD-H, 10% iPrOH/hexane, 1 ml/min.): 84% *ee*, R_t 26.10 min. (minor), 29.95 min. (major).

(*R*)-3-ethyl-4-(naphthalen-1-yl)-1-*p*-nitrobenzenesulfonyl-3-phenylazetidin-2-one (Table 2, Entry 7)

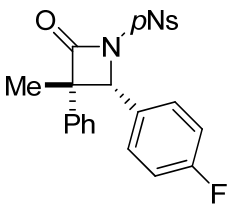


From ketene (40 µL, 0.27 mmol) and imine (34 mg, 0.1 mmol) in toluene (1.5 ml) with 10 mol% catalyst (0.01mmol) after stirring at rt for 16 h as a white solid (46.5 mg, 96%; *trans : cis* 1 : 8). Analytical data are consistent with the literature.[7]

trans-Isomer: $[\alpha]_D^{20}$ = +105 (c = 0.5, CH_2Cl_2). HPLC (Chiralpack AD-H, 10% iPrOH/hexane, 1 ml/min.): 70% *ee*, R_t 19.82 min. (major), 24.01 min. (minor).

cis-Isomer: $[\alpha]_D^{20} =$ –202 (*c* = 0.52, CH_2Cl_2). HPLC (Chiralpack AD-H, 10% iPrOH/hexane, 1 ml/min.): 83% *ee*, R_t 16.35 min. (major), 64.74 min. (minor).

(*R*)-4-(4-fluorophenyl)-3-methyl-1-*p*-nitrobenzenesulfonyl-3-phenylazetidin-2-one (Table 2, Entry 8)

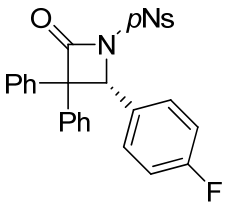


From ketene (36 µL, 0.27 mmol) and imine (30.8 mg, 0.1 mmol) in toluene (1.5 ml) with 10 mol% catalyst (0.01mmol) after stirring at rt for 16 h as a white solid (43.5 g, 99 %; *trans : cis* 1 : 3).

trans-Isomer: white crystals, mp = 59 °C. $[\alpha]_D^{20} =$ +72 (*c* = 0.4, CH_2Cl_2). HPLC (Chiralpack AD-H, 10% iPrOH/hexane, 1 ml/min.): 56% *ee*, R_t 29.60 min. (major), 48.48 min. (minor). ^{1}H-NMR (200 MHz): δ = 1.18 (s, 3 H), 5.23 (s, 1 H), 7.08-7.21 (m, 4 H), 7.27-7.36 (m, 5 H), 8.16 (d, *J* = 9.2 Hz, 2 H), 8.38 (d, *J* = 9.2 Hz, 2 H). ^{13}C-NMR (100 MHz): δ = 19.77, 29.70, 63.97, 69.26, 115.94, 116.16, 124.56, 125.19, 128.19, 128.57, 128.65, 129.03, 129.30, 139.11, 143.64, 150.96, 168.81. IR (KBr) ν/cm^{-1}: 1795 (C=O).). MS (ESI): m/z = 377, 463.08 $[M + Na]^+$, 487.06. HRMS Calcd for $C_{22}H_{17}FN_2O_5SNa$: 463.0740. Found: 463.0758.

cis-Isomer: white crystals, mp = 139 °C. $[\alpha]_D^{20} =$ –69 (*c* = 0.5, CH_2Cl_2). HPLC (Chiralpack AD-H, 11.5% iPrOH/hexane, 0.4 ml/min.): 86% *ee*, R_t 99.61 min. (minor), 103.00 min. (major). ^{1}H-NMR (200 MHz): δ = 1.77 (s, 3 H), 5.09 (s, 1 H), 6.68-6.79 (m, 4 H), 6.85-6.91 (m, 2 H), 7.04-7.11 (m, 3 H), 8.04 (d, *J* = 9.0 Hz, 2 H), 8.35 (d, *J* = 9.0 Hz, 2 H). ^{13}C-NMR (50 MHz): δ = 24.88, 69.91, 70.20, 115.03, 115.47, 124.46, 126.57, 127.62, 128.48, 128.89, 129.30, 129.47, 129.56, 129.62, 135.38, 143.84, 150.89, 160.19, 165.14, 168.22. IR (KBr) ν/cm^{-1}: 1794 (C=O). MS (ESI): m/z = 463.1 $[M + Na]^+$. HRMS Calcd for $C_{22}H_{17}FN_2O_5SNa$: 463.0740. Found: 463.0741.

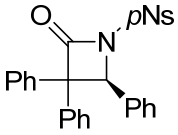
(*R*)-4-(4-fluorophenyl)-1-*p*-nitrobenzenesulfonyl-3,3-triphenylazetidin-2-one (Table 2, Entry 9)



From ketene (53 µL, 0.27 mmol) and imine (30.8 mg, 0.1 mmol) in toluene (1.5 ml) with 10 mol% catalyst (0.01mmol) after stirring at rt for 16 h as a white solid (47.7 mg, 96 %). White crystals, mp= 121°C. $[\alpha]_D^{20} =$ +24 (*c* = 0.53, CH_2Cl_2). HPLC (Chiralpack AD-H, 10% iPrOH/hexane, 1 ml/min.): 76% *ee*, R_t 27.11 min. (major), 35.46 min. (minor). ^{1}H-NMR (200 MHz): δ = 5.84 (s, 1 H), 6.75-6.96 (t, 6 H), 7.01-7.09. (m, 3 H), 7.28-7.44 (m, 5 H), 8.04 (d, *J* = 9.0 Hz, 2 H), 8.30 (d, *J* = 9.0 Hz, 2 H). ^{13}C-NMR (50 MHz): δ = 29.69, 68.76, 115.15,

115.59, 124.43, 126.78, 127.70, 128.28, 128.43, 128.92, 129.14, 129.51, 129.68, 135.24, 138.27, 143.63, 166.53. IR (KBr) ν/cm^{-1}: 1791 (C=O). MS (ESI): m/z = 524.8 $[M + Na]^+$. Anal. Calcd for $C_{27}H_{19}FN_2O_5S$: C 64.53; H 3.81; N 5.57%. Found: C 64.83; H 3.89; N 5.67%.

(*S*)-1-*p*-nitrobenzenesulfonyl-3,3,4-triphenylazetidin-2-one (Table 2, Entry 10)

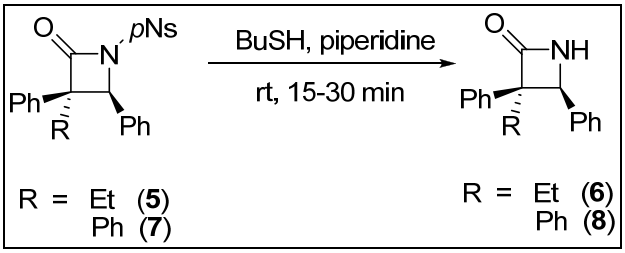


From ketene (53 µL, 0.27 mmol) and imine (29 mg, 0.1 mmol) in toluene (1.5 ml) with 10 mol% catalyst *ent*-**4** (0.01mmol) after stirring at rt for 24 h as a white solid (47.7 mg, 96 %). Analytical data are consistent with the literature.[7]

$[\alpha]_D^{20}$ = +19 (c = 0.5, CH_2Cl_2). HPLC (Chiralpack AD-H, 10% iPrOH/hexane, 1 ml/min.): 67% *ee*, R_t 28.70 min. (minor), 56.02 min. (major).

Establishment of the Absolute Configuration

General procedure for deprotection of the *β*-lactams *cis*-5 (from *ent*-4)and 7



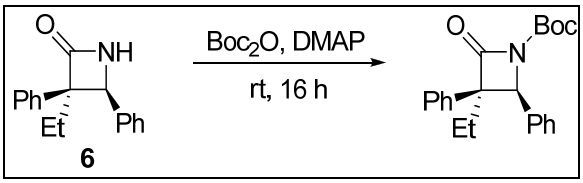
Ns-protected *β*-lactam (0.06 mmol) and piperidine (0.9 mmol) were dissolved in 0.4 ml *n*-BuSH. The mixture was stirring for 15-30 min to yield deprotected product in 99 % yield. The product was columned on silica gel with 5→12.5% ethyl acetate in petrol ether.

(3*R*,4*S*)-3-Ethyl-3,4-diphenylazetidin-2-one (6). From *β*-lactam **5** (26 mg, 0.06 mmol) and piperidine (0.09 ml, 0.9 mmol) in *n*-BuSH (0.4 ml) after stirring at rt for 30 min to give a colorless oil (11.9 mg, 0.059 mmol, 99%). $[\alpha]_D^{20}$ = +37.8 (c = 0.5, CH_2Cl_2). ^{1}H-NMR (200 MHz): δ = 1.05 (t, J = 7.4 Hz, 3 H), 2.24 (q, J = 7.4 Hz, 2 H), 4.76 (s, 1 H), 6.13 (s, 1 H), 6.98-7.06 (m, 7 H), 7.08-7.13 (m, 3 H). ^{13}C-NMR (50 MHz): δ = 9.05, 31.35, 63.14, 71.15, 126.43, 127.25, 127.56, 127.76, 127.81, 127.98, 136.77, 137.63, 171.94.

(*S*)-3,3,4-Triphenylazetidin-2-one (8). From *β*-lactam **7** (19 mg, 0.04 mmol) and piperidine (0.06 ml, 0.6 mmol) in *n*-BuSH (0.3 ml) after stirring at rt for 15 min to give a white solid (12 mg, 0.0396 mmol, 99 %). Analytical data were consistent with the literature[8]. $[\alpha]_D^{20}$ =

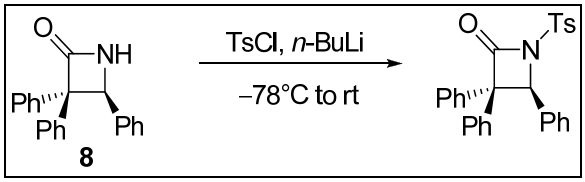
+149.3 (c = 0.345, CH_2Cl_2). ^{1}H-NMR (200 MHz): δ = 5.51 (s, 1 H), 6.37 (s, 1 H),6.98-7.06 (m, 5 H), 7.16 (s, 5 H), 7.29-7.44 (m, 3 H),7.60-7.66 (m, 2 H). ^{13}C-NMR (50 MHz): δ = 29.69, 63.61, 126.66, 127.25, 127.34, 127.85, 127.98, 128.12, 128.22, 128.69, 137.01, 137.50, 140.61, 170.31.

Procedure for Boc-protection of *β*-lactam 6 (from *ent*-4)



The solution of deprotected *β*-lactam **6 (**from *ent*-**4)** (13.4 mg, 0.052 mmol), DMAP (4.74 mg, 0,039 mmol) and Boc_2O (33.9 mg, 0.1554 mmol) in dry acetonitrile was stirring at rt for 16 h. The product (3*R*,4*S*)-*tert*-butyl 3-ethyl-2-oxo-3,4-diphenylazetidine-1-carboxylate was purified on silica gel with 12.5% ethyl acetate in petrol ether to give a white solid (9.6 mg, 0.028 mmol, 53%). Analytical data are consistent with the literature.[9] $[\alpha]_D^{20}$ = +69.6 (c = 0.425, CH_2Cl_2). HPLC (Chiralpack AD-H, 2% iPrOH/hexane, 1 ml/min.): 91% *ee*, R_t 9.28 min. (major), 10.68 min. (minor). ^{1}H-NMR (200 MHz): δ = 1.01 (t, J = 7.4 Hz, 3 H), 1.36 (s, 9 H), 2.25 (q, J = 7.4 Hz, 2 H), 4.95 (s, 1 H), 6.25-7.12 (m, 10 H). ^{13}C-NMR (50 MHz): δ = 9.41, 27.82, 32.27, 66.32, 68.90, 83.27, 126.74, 127.18, 127.57, 127.84, 127.95, 135.33, 135.85, 169.01.

Procedure for tosylation of *β*-lactam 8

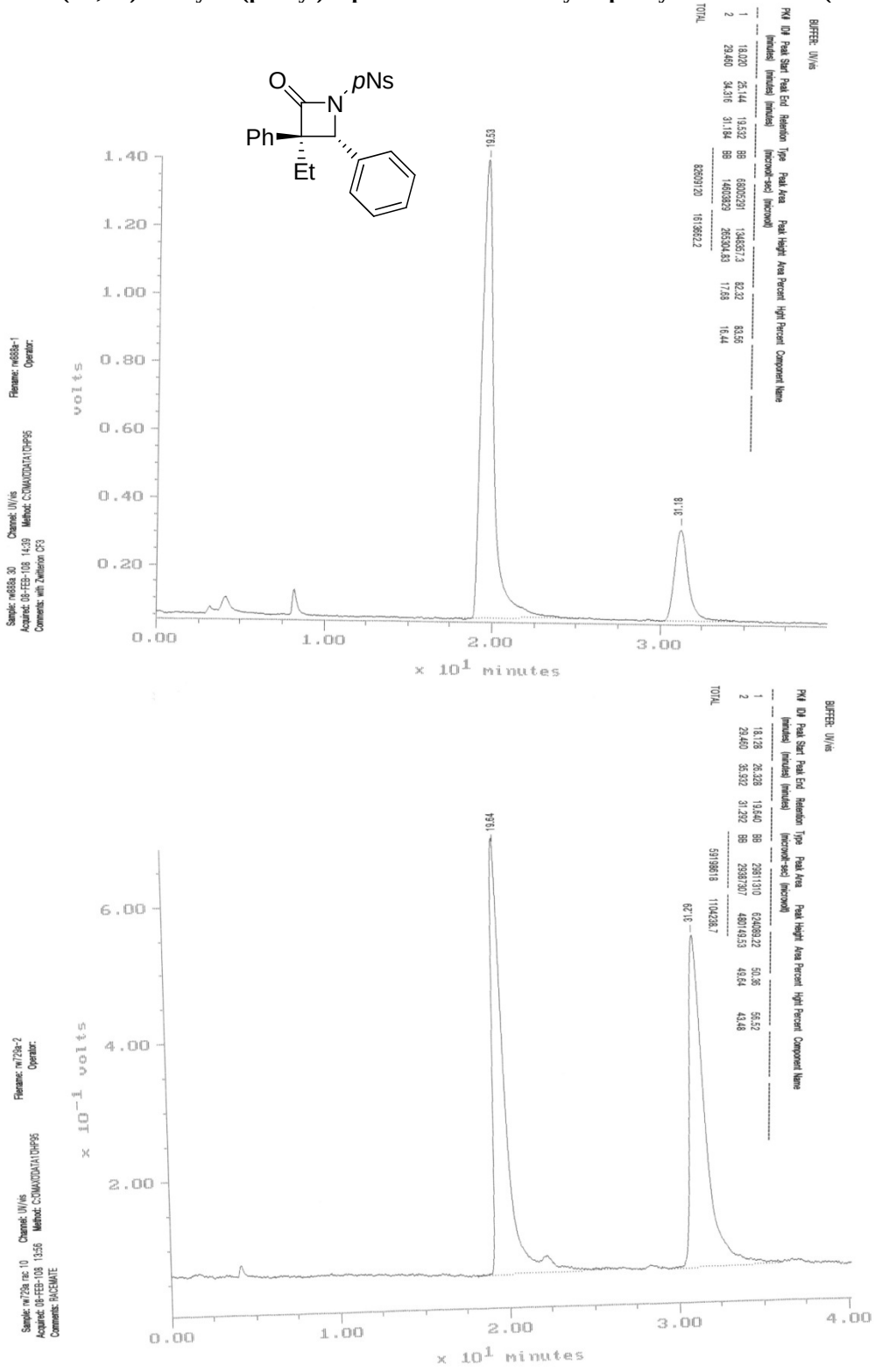


To the solution of deprotected *β*-lactam **8** (9.3 mg, 0.031 mmol) in THF (1.5 ml), *n*-BuLi (17 µL, 0.0341 mmol, 2M sol. in cyclohexane) was added at −78°C. In 15 min TsCl (7.1 mg, 0.0372 mmol) in dry THF (0.5 ml) followed. The mixture was warmed up to rt left to stir for 15 min. The product was purified on silica gel column with 10% diethyl ether in petrol ether to give (*S*)-3,3,4-triphenyl-1-tosylazetidin-2-one as a white solid (8.7 mg, 0.0303 mmol, 98%in 98%). Analytical data are consistent with the literature.[10] $[\alpha]_D^{20}$ = +24 (c = 0.35, CH_2Cl_2). HPLC (Chiralpack AD-H, 10% iPrOH/hexane, 1 ml/min.): 85% *ee*, R_t 8.63 min. (major), 15.43 min. (minor). ^{1}H-NMR (200 MHz): δ = 2.42 (s, 3 H), 5.78 (s, 1 H), 6.88-7.14 (m, 10 H), 7.22-7.42 (m, 7 H), 7.73 (d, J = 8.2 Hz, 2 H). ^{13}C-NMR (50 MHz): δ = 21.69,

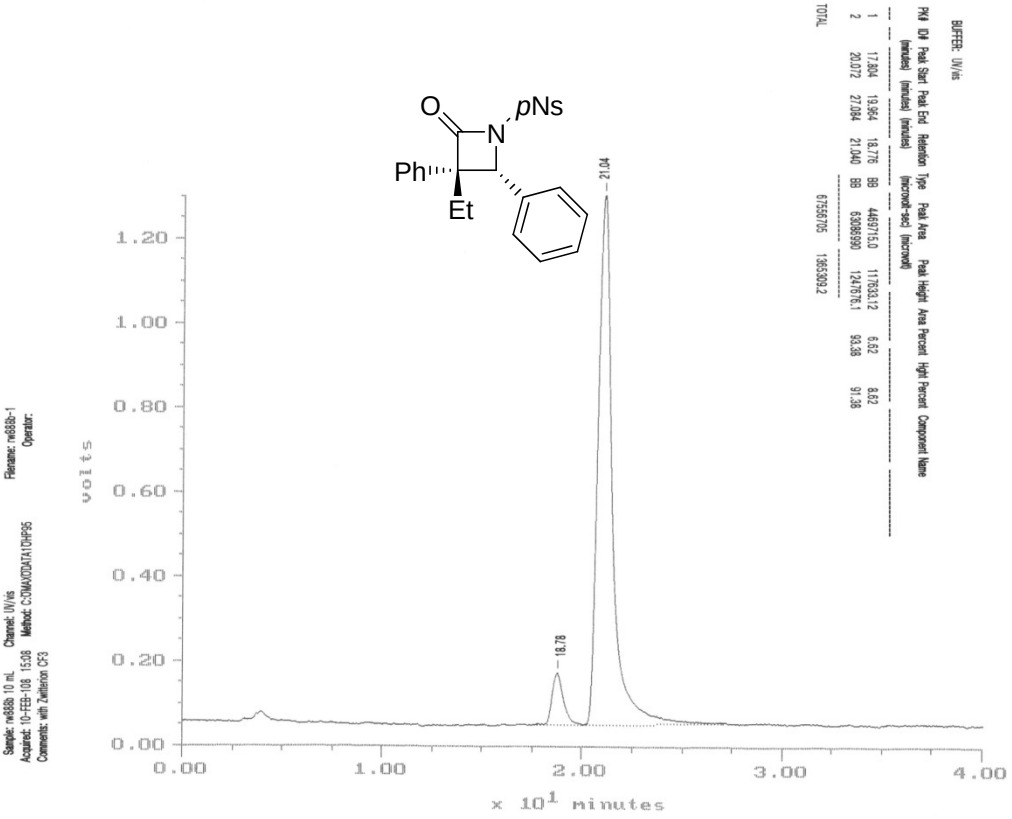
69.25, 72.82, 126.99, 127.19, 127.67, 127.87, 127.99, 128.04, 128.46,128.90, 129.77, 133.95, 135.41, 135.81, 139.01, 143.31, 166.79.

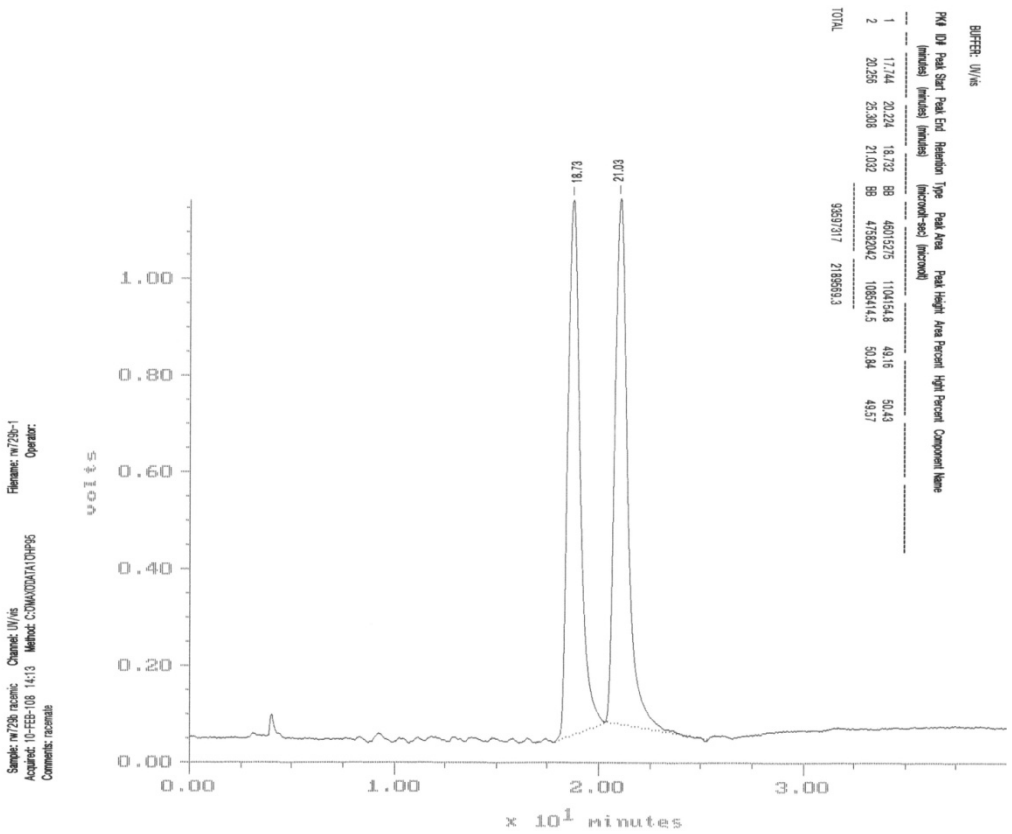
Spectral and HPLC Data of *ß*-lactams

***trans*-(3*R*,4*R*)-3-ethyl-4-(phenyl)-1-p-nitrobenzenesulfonyl-3-phenylazetidin-2-one (Table 1. Entry 5.)**[7]

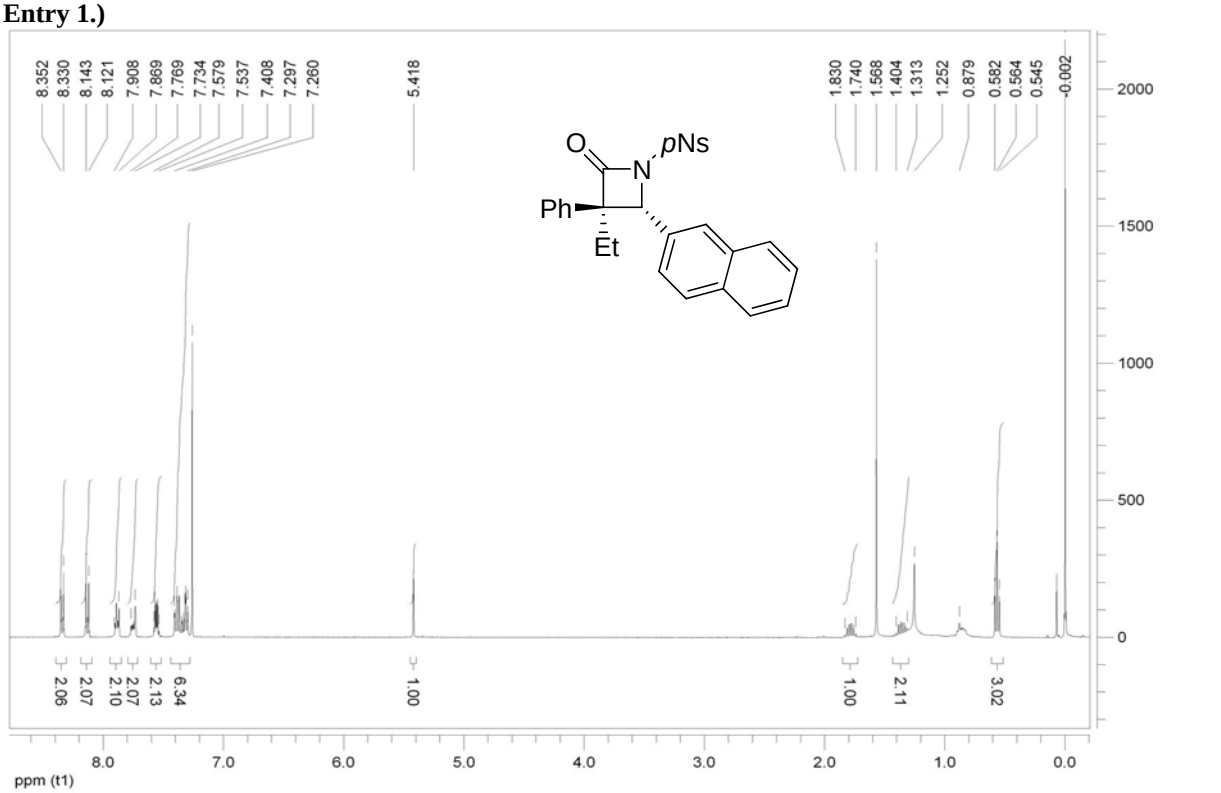


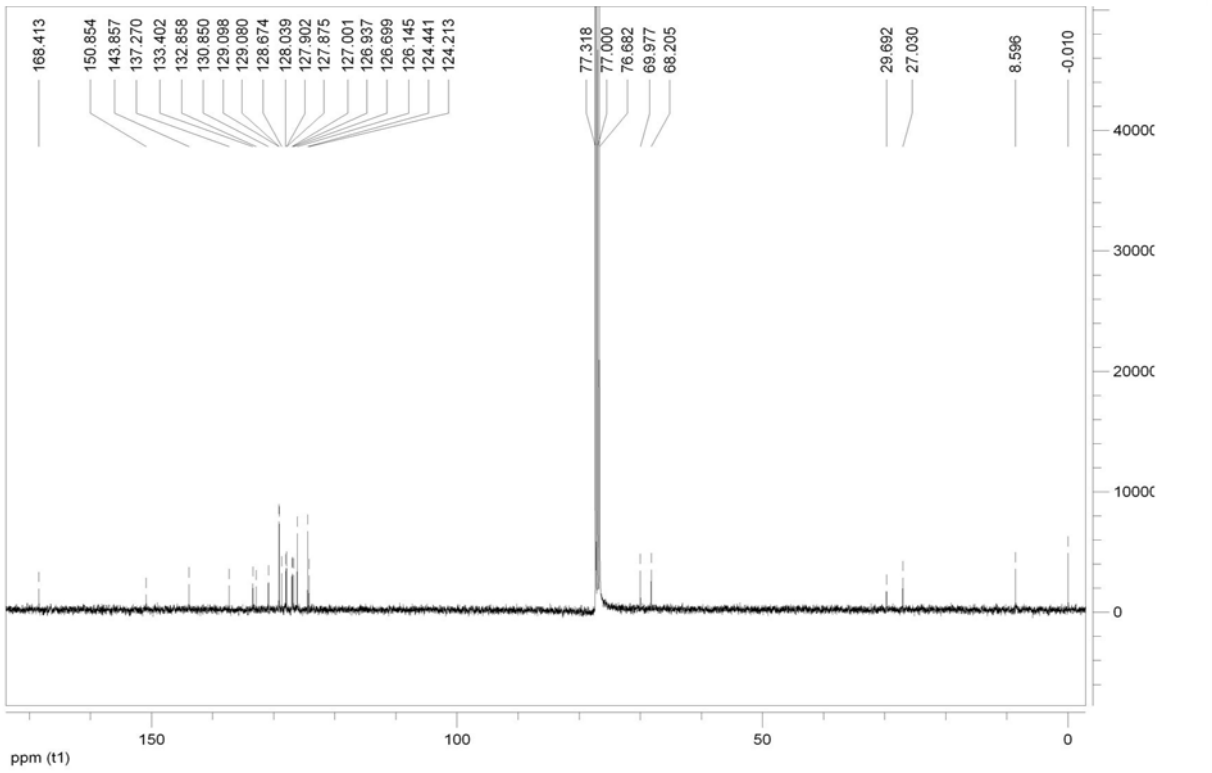
***cis*-(3*S*,4*R*)-3-ethyl-4-(phenyl)-1-p-nitrobenzenesulfonyl-3-phenylazetidin-2-one (Table 1. Entry 5.)[7]**

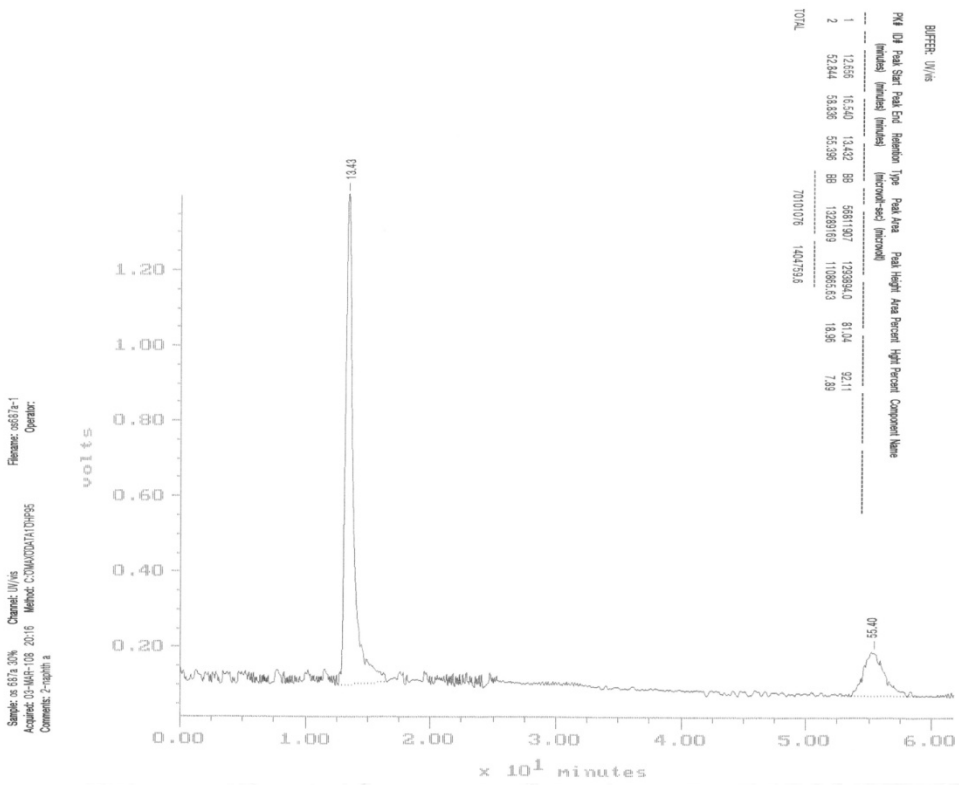


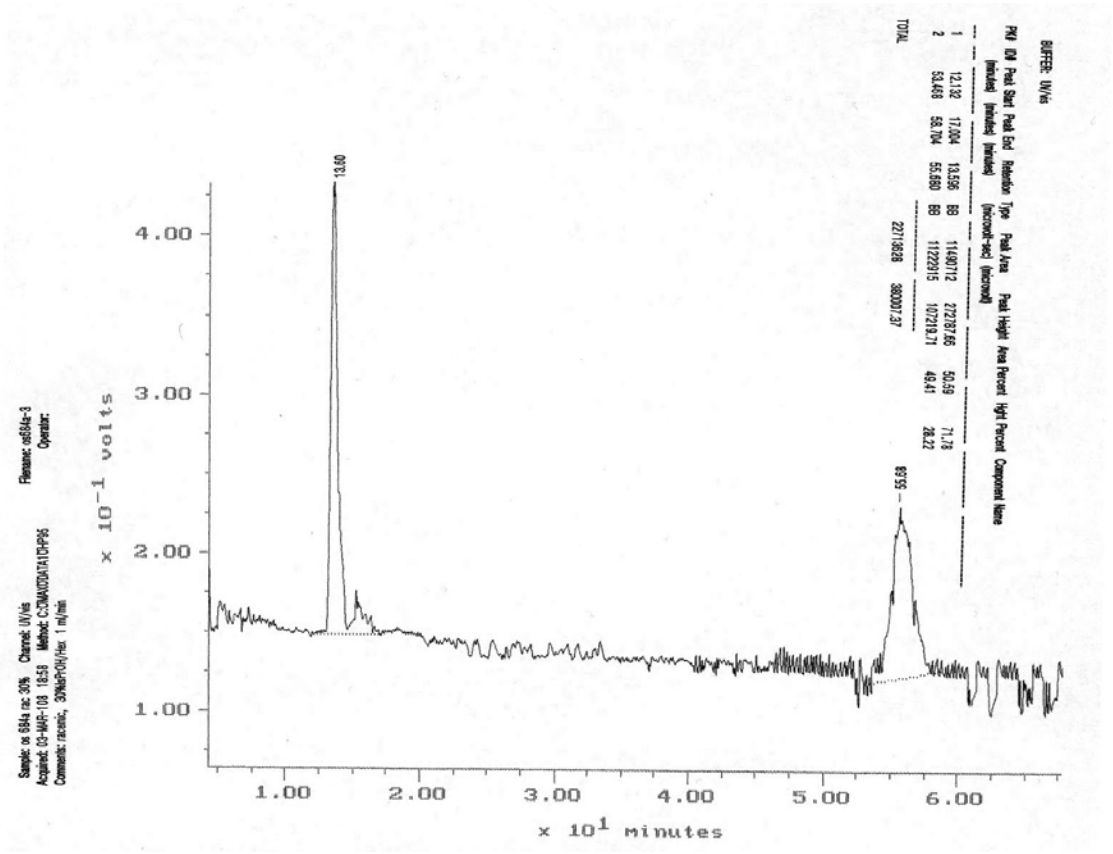


***trans*-(3*R*,4*R*)-3-ethyl-4-(naphthalen-2-yl)-1-p-nitrobenzenesulfonyl-3-phenylazetidin-2-one (Table 2. Entry 1.)**

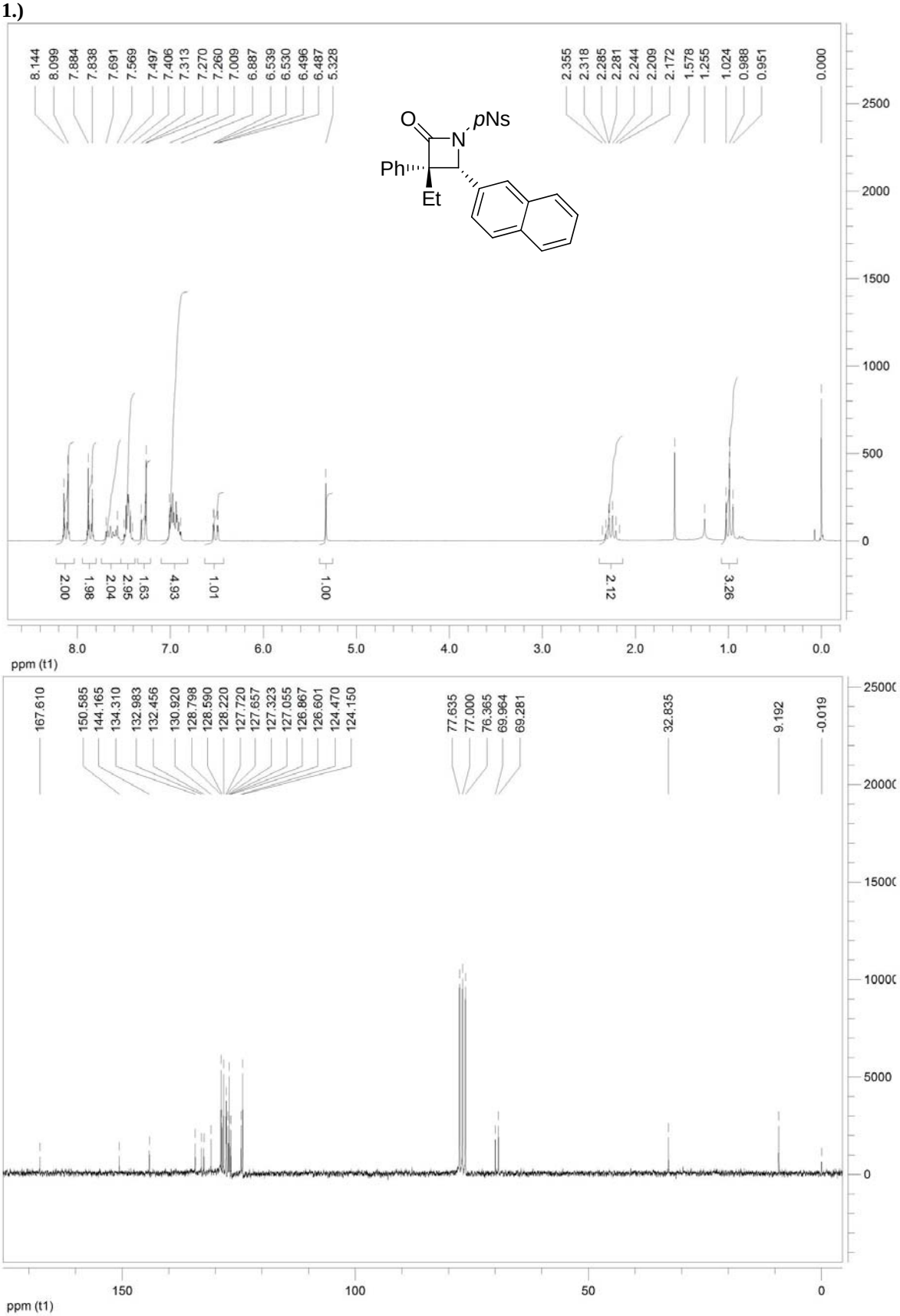


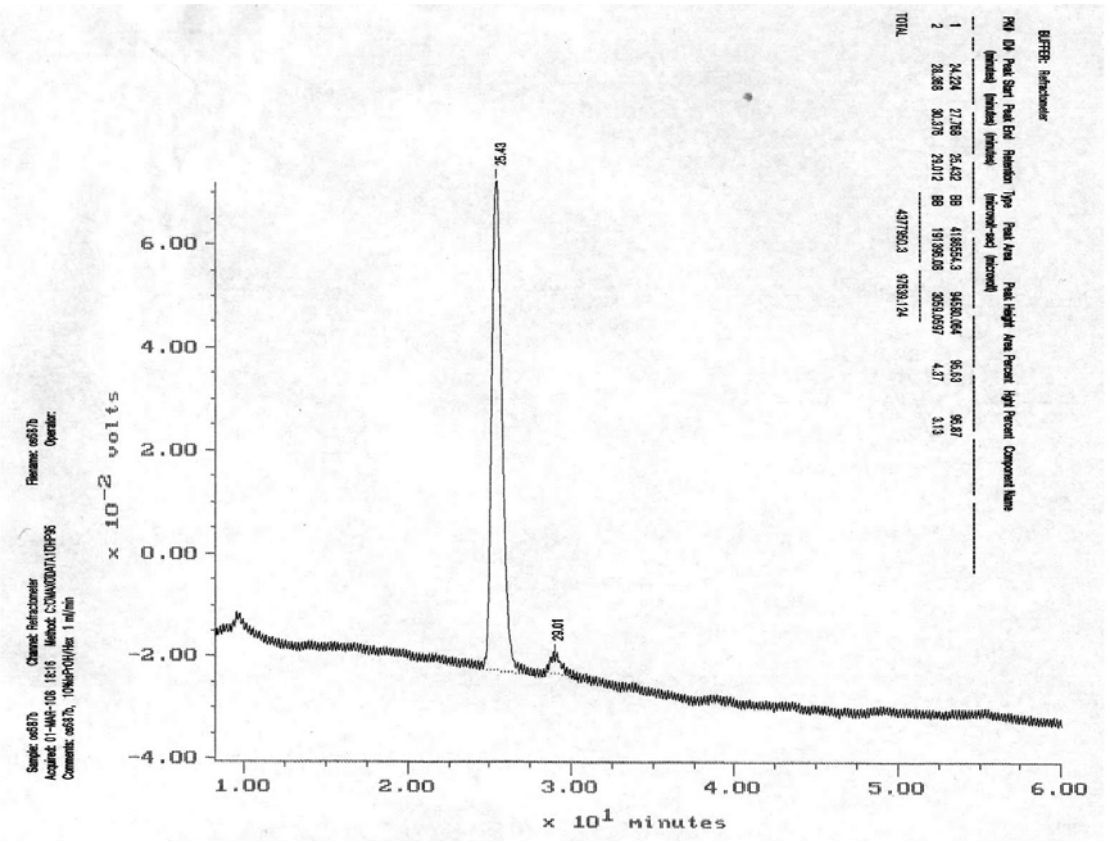


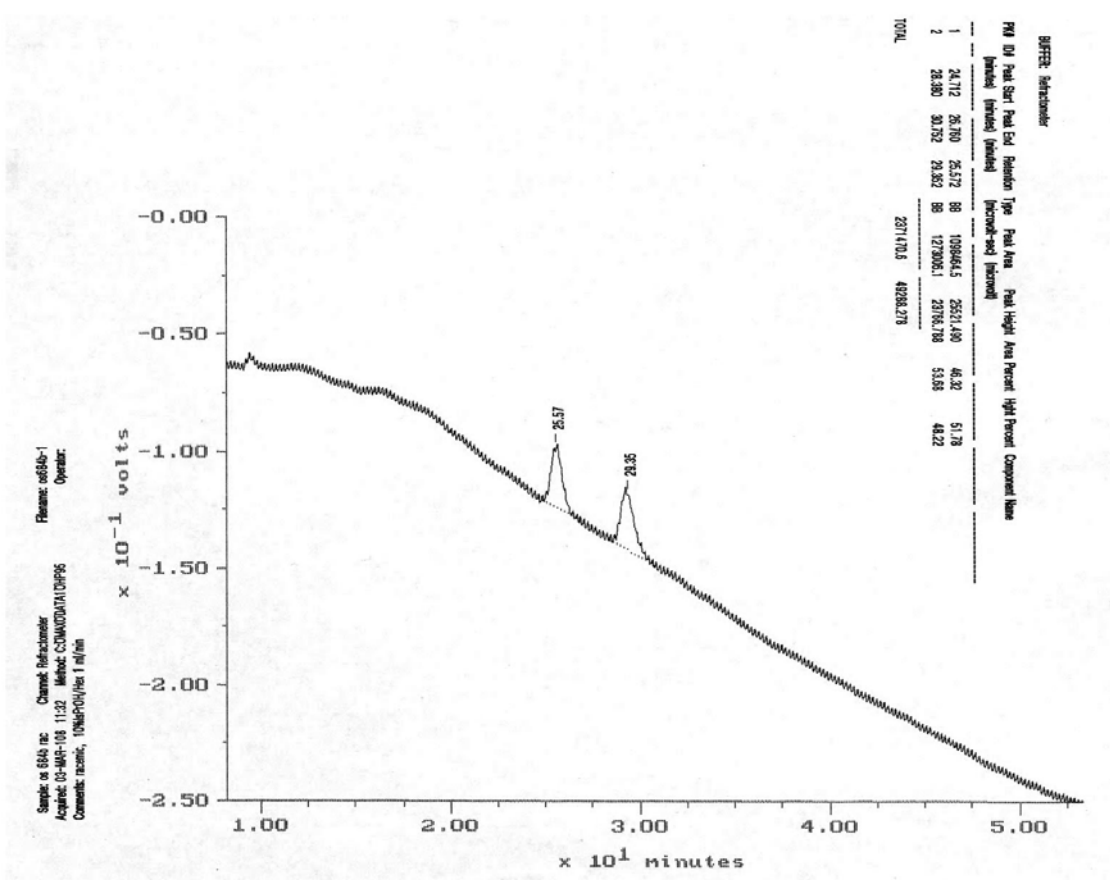

Sample: os 667a 30%
Acquired: 03-MAR-108 20:16
Comments: 2-naphth a
Channel: UV/vis
Method: C:\DMA\ODA1A1CHP95
Filename: os667a-1
Operator:
BUFFER: UV/vis
PK# EM Peak Start (minutes) Peak End (minutes) Retention Time (minutes) Type Peak Area (microvolt-sec) Peak Height (microvolt) Area Percent Hght Percent Component Name
1 12.656 16.540 13.432 BB 56811907 1233894.0 81.04 92.11
2 52.844 58.836 55.396 BB 13289169 1109865.63 18.96 7.89
TOTAL 70101076 1404759.6
13.43
55.40
volts
1.20
1.00
0.80
0.60
0.40
0.20
0.00
1.00
2.00
3.00
4.00
5.00
6.00
x 10^1 minutes


Sample: os 664a rac 30%
Acquired: 03-MAR-108 18:58
Comments: racemic, 30%IsoPrOH/Hex 1 ml/min
Channel: UV/vis
Method: C:\DMA\ODA1A1CHP95
Filename: os664a-3
Operator:
BUFFER: UV/vis
PK# EM Peak Start (minutes) Peak End (minutes) Retention Time (minutes) Type Peak Area (microvolt-sec) Peak Height (microvolt) Area Percent Hght Percent Component Name
1 12.132 17.004 13.456 BB 11490712 2272787.66 50.59 71.78
2 53.468 58.704 55.680 BB 11222915 1072219.71 49.41 28.22
TOTAL 22713628 3800007.37
13.46
55.68
x 10^-1 volts
4.00
3.00
2.00
1.00
1.00
2.00
3.00
4.00
5.00
6.00
x 10^1 minutes

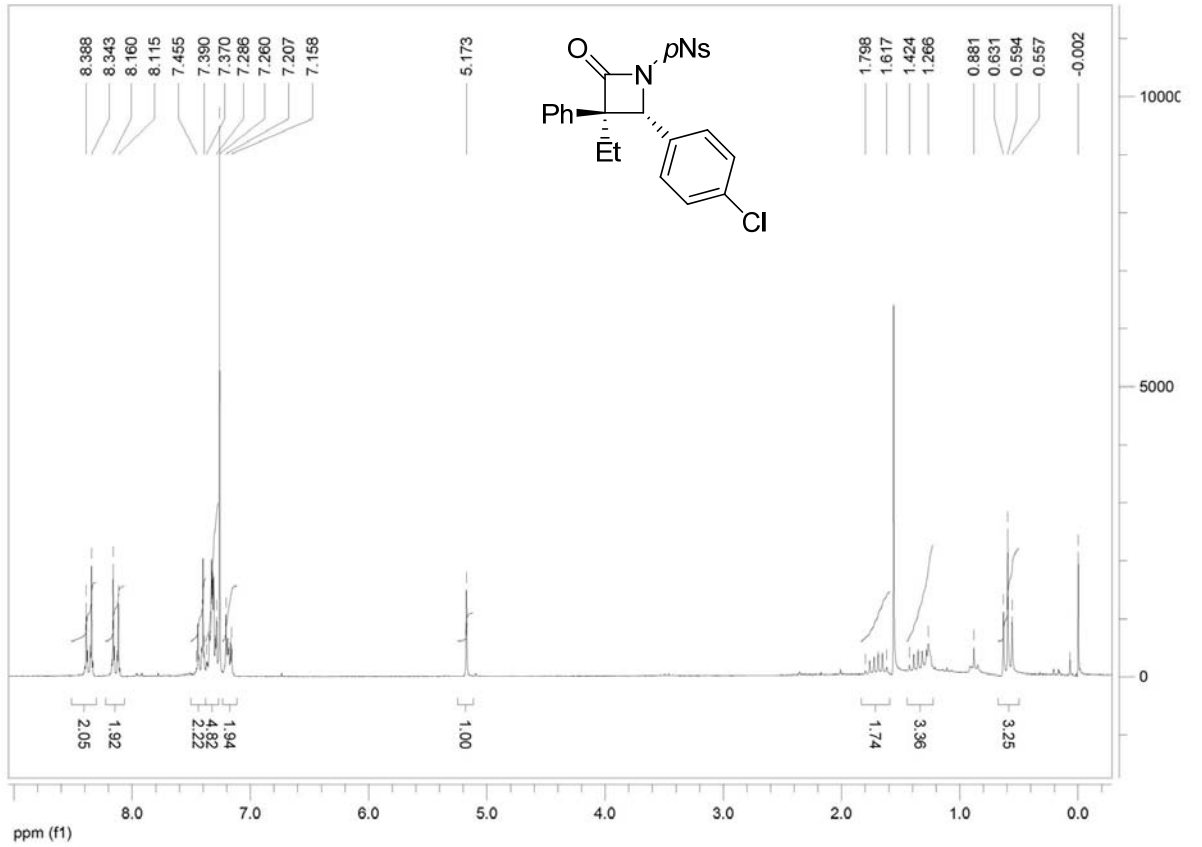
***cis*-(3*S*,4*R*)-3-ethyl-4-(naphthalen-2-yl)-1-p-nitrobenzenesulfonyl-3-phenylazetidin-2-one (Table 2. Entry 1.)**

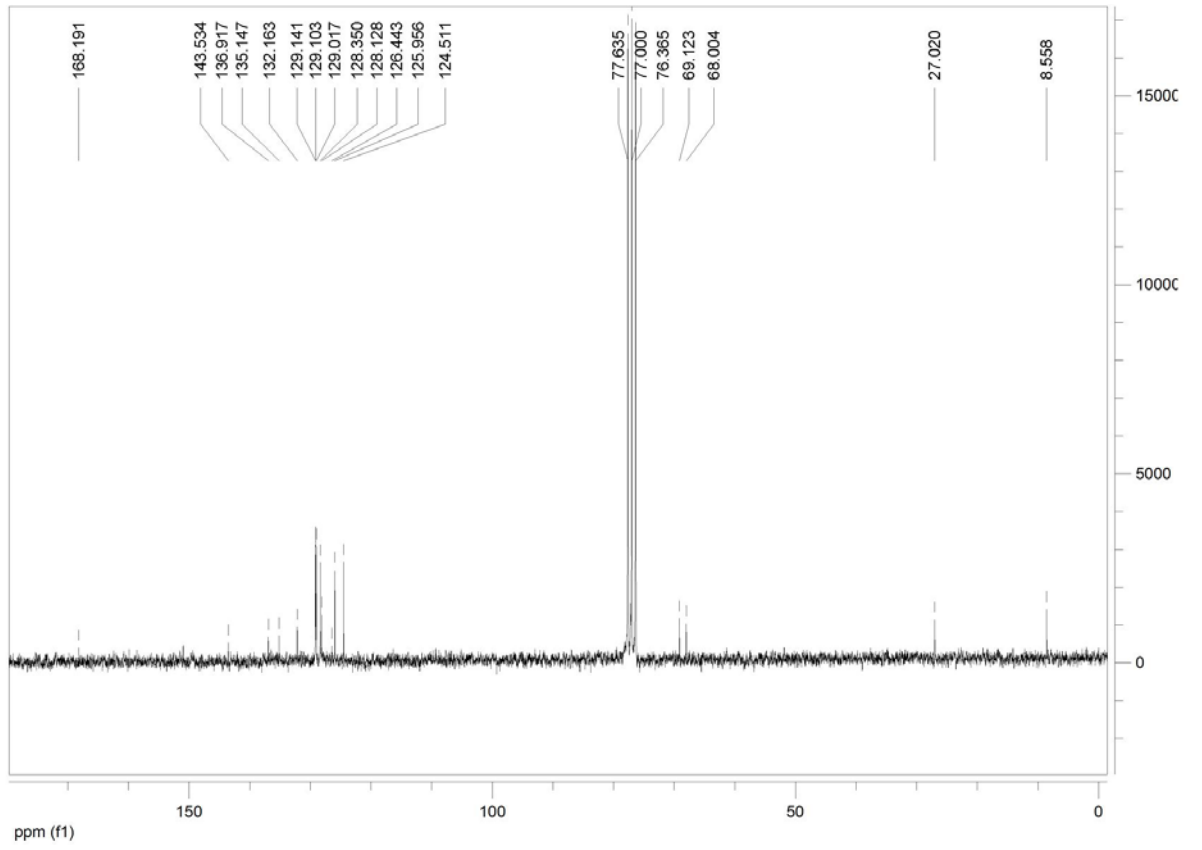


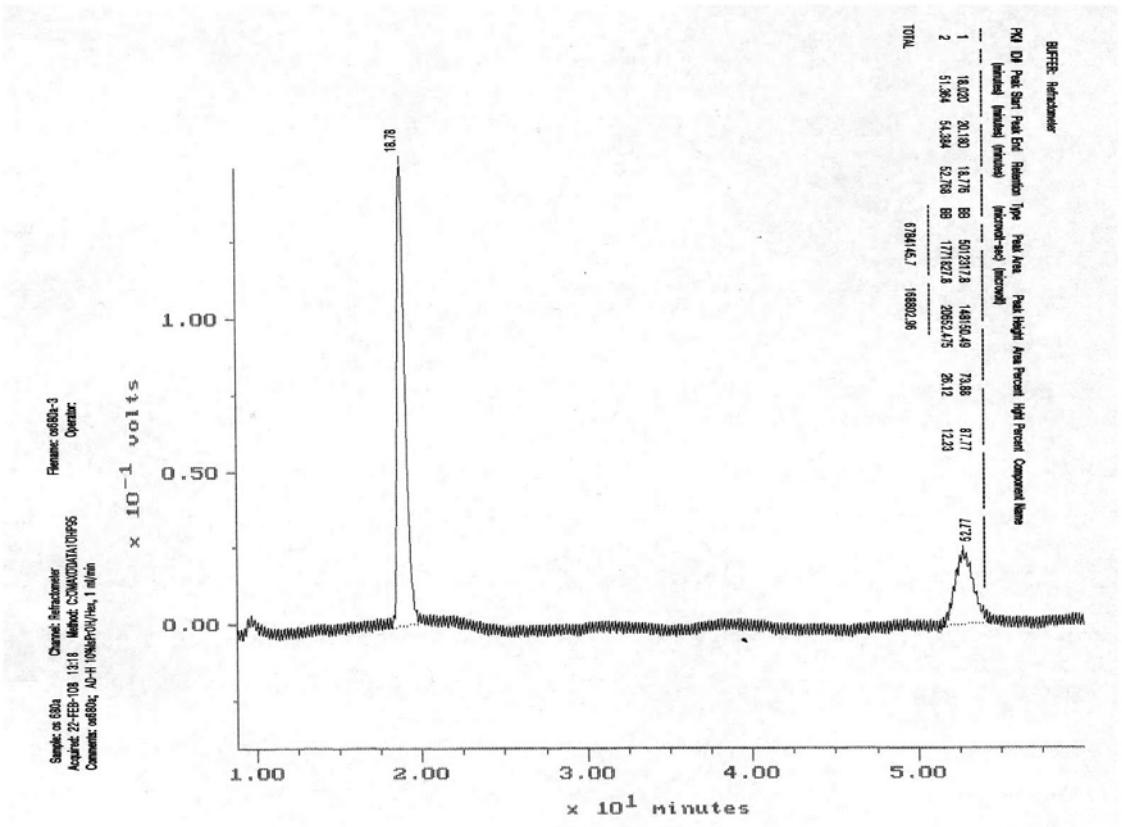

BUFFER: Refractometer
PK# ID# Peak Start Peak End Retention Type Peak Area Peak Height Area Percent Hght Percent Component Name
1 24.224 27.768 25.432 BB 4185554.3 94580.064 95.63 96.87
2 28.368 30.376 29.012 BB 191366.08 3059.0697 4.37 3.13
TOTAL 4377920.3 97639.134
Sample: os617b Channel: Refractometer Filename: os617b
Acquired: 01-MAR-108 18:16 Method: C:\DMA\TODAY\A1TOHP96 Operator:
Comments: os617b, 10%isPrOH/Hex 1 ml/min
25.43
28.01
x 10-2 volts
6.00
4.00
2.00
0.00
-2.00
-4.00
1.00
2.00
3.00
4.00
5.00
6.00
x 101 minutes

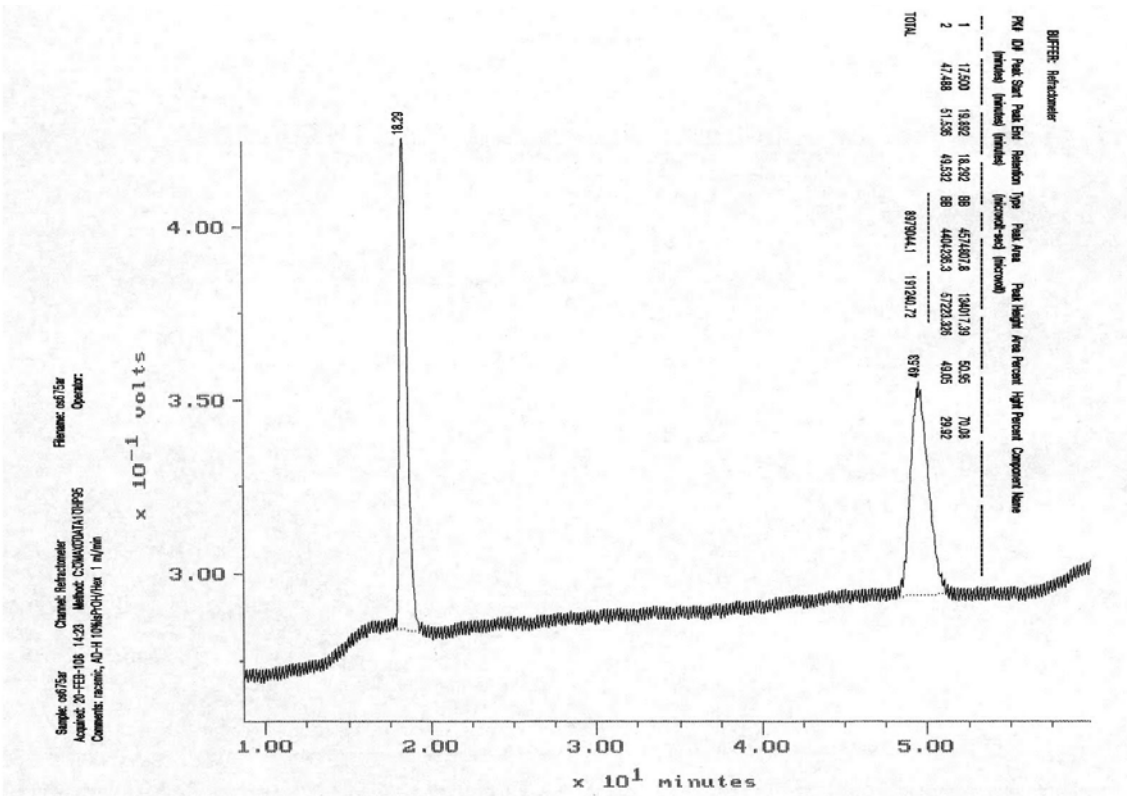

BUFFER: Refractometer
PK# ID# Peak Start Peak End Retention Type Peak Area Peak Height Area Percent Hght Percent Component Name
1 24.712 26.760 25.572 BB 1098464.5 25531.490 46.32 51.78
2 28.380 30.752 29.362 BB 1273006.1 23766.708 53.68 48.22
TOTAL 2371470.6 49298.278
Sample: os 604b rac Channel: Refractometer Filename: os604b-1
Acquired: 03-MAR-108 11:32 Method: C:\DMA\TODAY\A1TOHP96 Operator:
Comments: racemic, 10%isPrOH/Hex 1 ml/min
25.57
28.36
x 10-1 volts
-0.00
-0.50
-1.00
-1.50
-2.00
-2.50
1.00
2.00
3.00
4.00
5.00
x 101 minutes

***trans*-(3*R*,4*R*)-4-(4-chlorophenyl)-3-ethyl-1-p-nitrobenzenesulfonyl-3-phenylazetidin-2-one (Table 2. Entry 2.)**

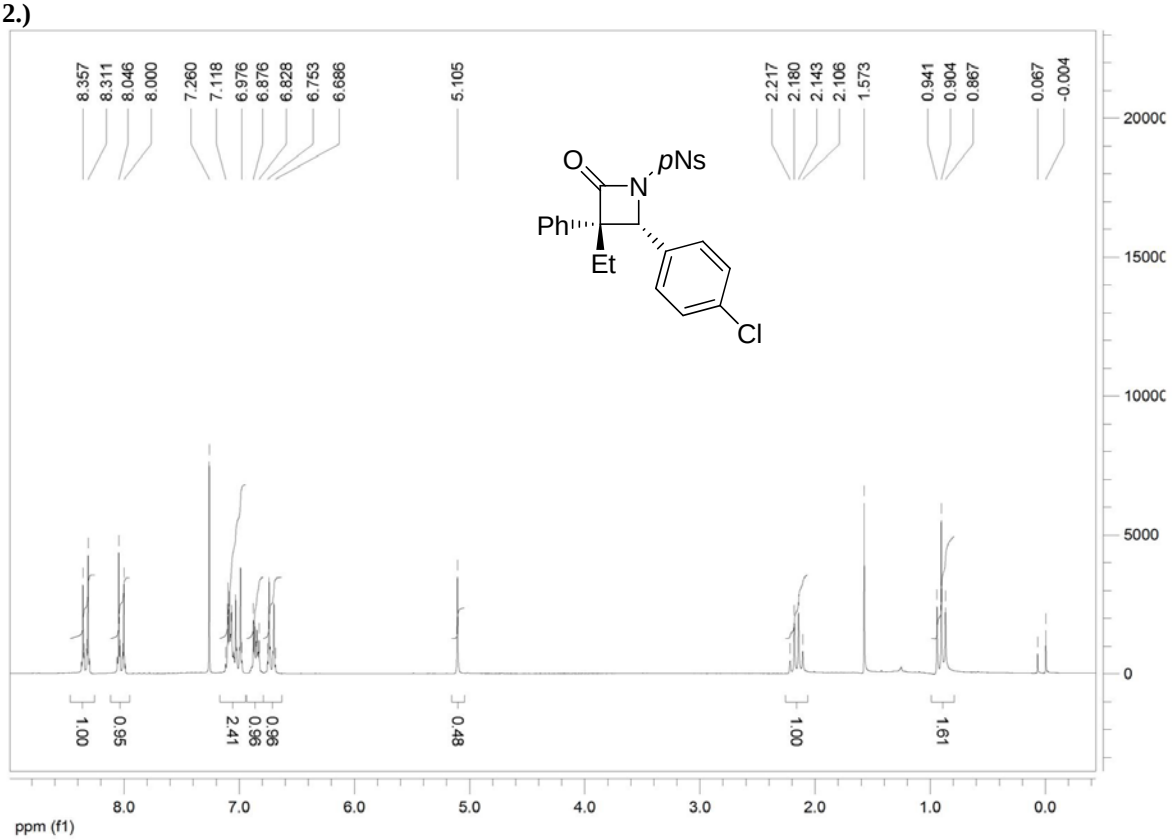


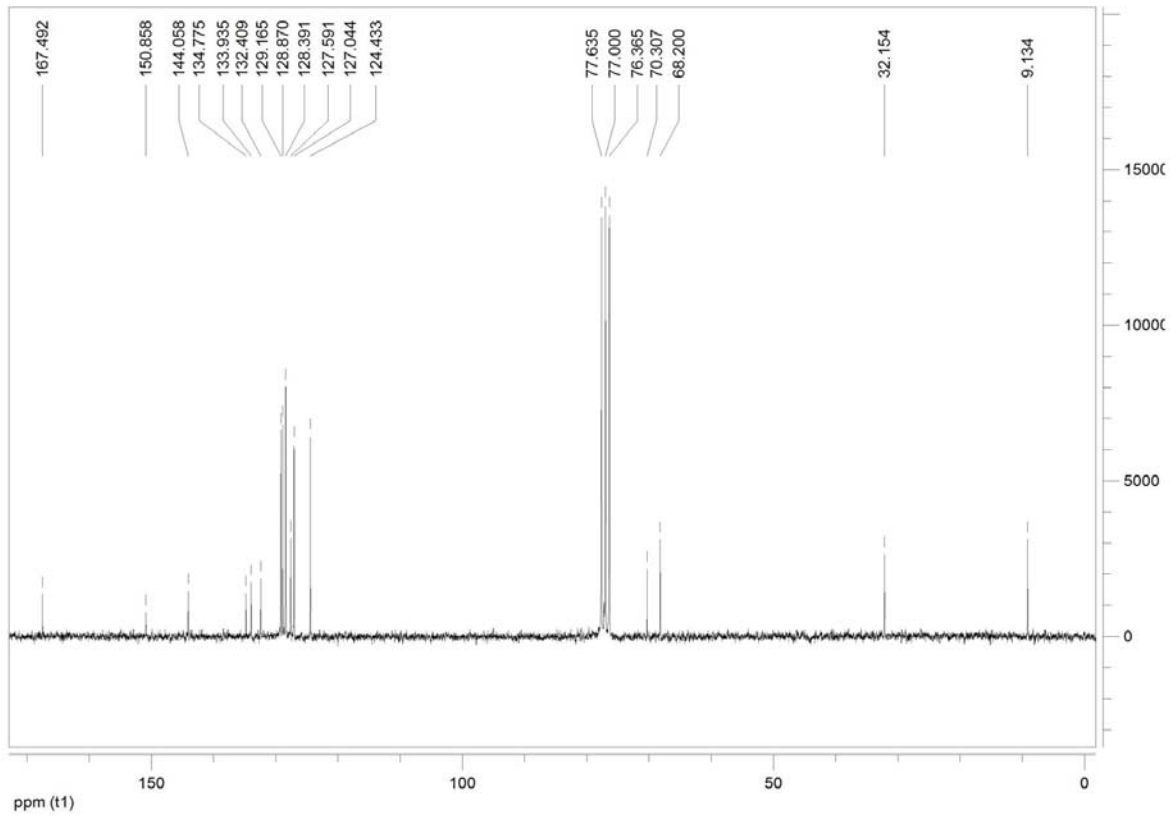


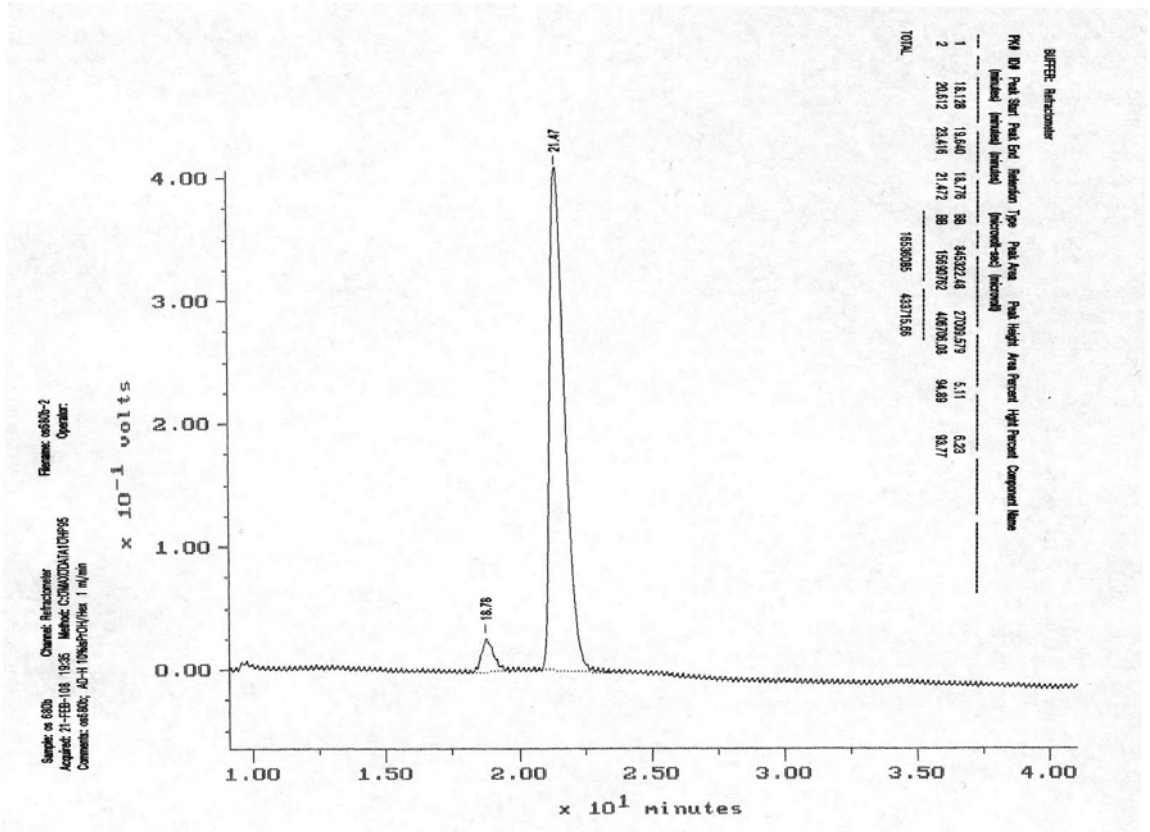

BUFFER: Refractometer
PK# ID# Peak Start (minutes) Peak End (minutes) Retention (minutes) Type Peak Area (microvolt-sec) Peak Height (microvolt) Area Percent Hight Percent Component Name
1 18.020 20.190 18.776 BB 501231.8 148150.49 73.88 81.77
2 51.364 54.334 52.768 BB 177162.8 20652.475 26.12 11.23
TOTAL 678414.5 168802.96
18.78
51.77
1.00
0.50
0.00
x 10⁻¹ volts
1.00 2.00 3.00 4.00 5.00
x 10¹ minutes
Sample: os 680a Channel: Refractometer Filename: os680a-3
Acquired: 22-FEB-108 13:18 Method: C:\DWAX\DATA\10HP95 Operator:
Comments: os680a; AD-H 10%IsPrOH/Hex, 1 ml/min

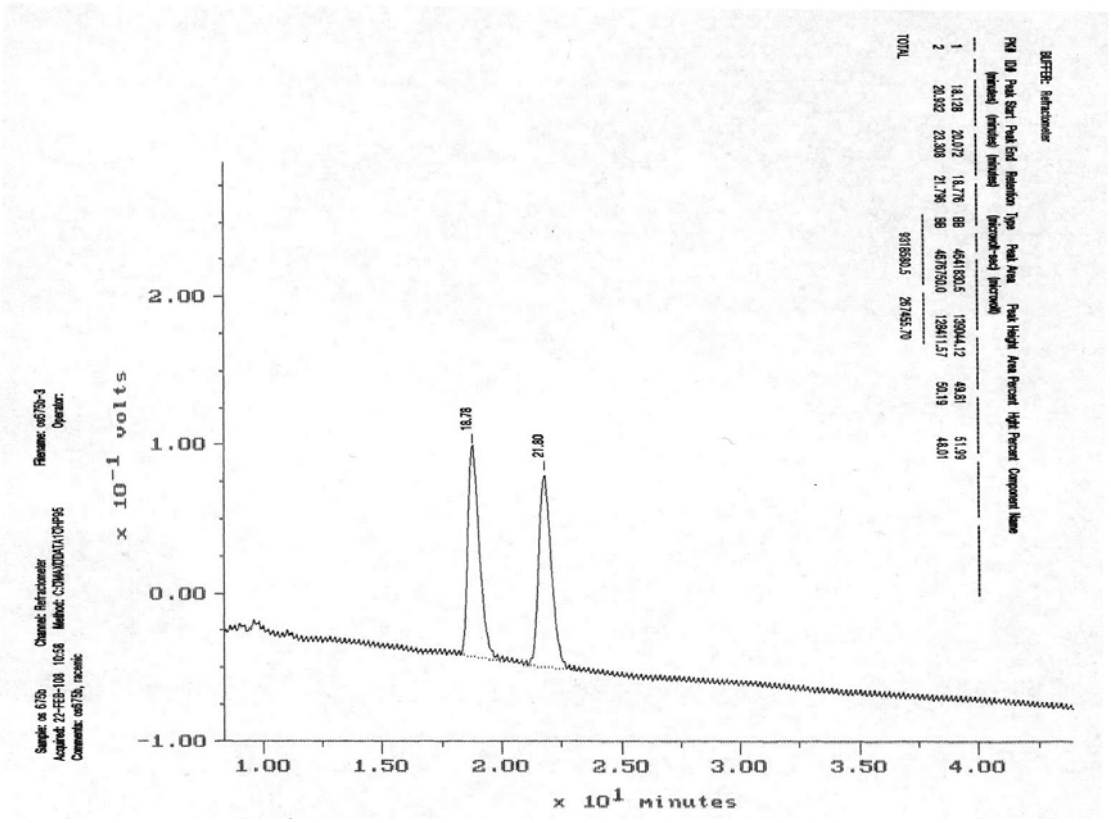

BUFFER: Refractometer
PK# ID# Peak Start (minutes) Peak End (minutes) Retention (minutes) Type Peak Area (microvolt-sec) Peak Height (microvolt) Area Percent Hight Percent Component Name
1 17.509 19.892 18.292 BB 457480.8 134017.39 50.95 70.08
2 47.488 51.536 49.532 BB 440436.3 57223.328 49.05 29.92
TOTAL 897844.1 191240.72
18.29
49.53
4.00
3.50
3.00
x 10⁻¹ volts
1.00 2.00 3.00 4.00 5.00
x 10¹ minutes
Sample: os75ar Channel: Refractometer Filename: os75ar
Acquired: 26-FEB-108 14:29 Method: C:\DWAX\DATA\10HP95 Operator:
Comments: racemic, AD-H 10%IsPrOH/Hex 1 ml/min

***cis*-(3*S*,4*R*)-4-(4-chlorophenyl)-3-ethyl-1-p-nitrobenzenesulfonyl-3-phenylazetidin-2-one (Table 2. Entry 2.)**

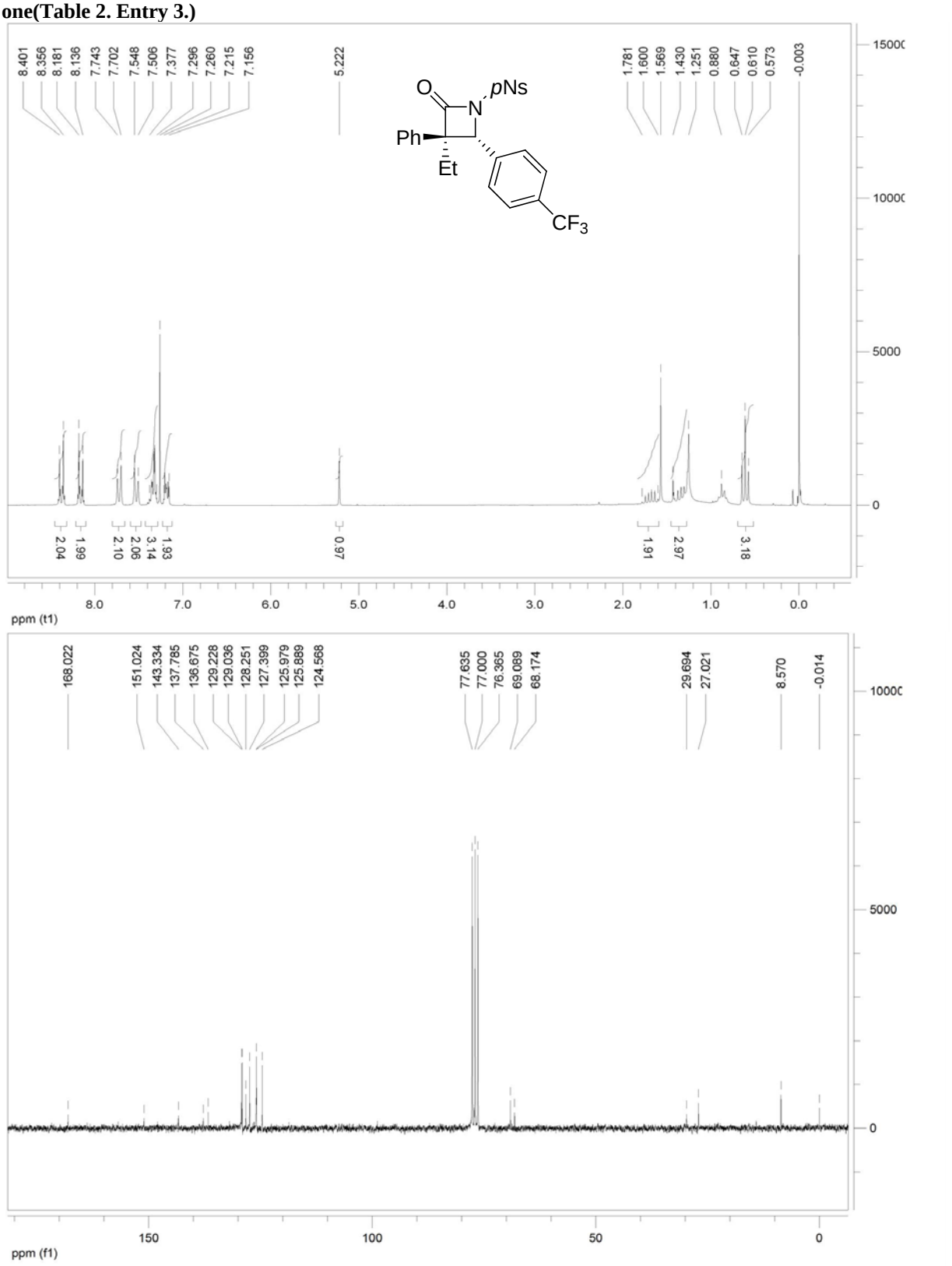


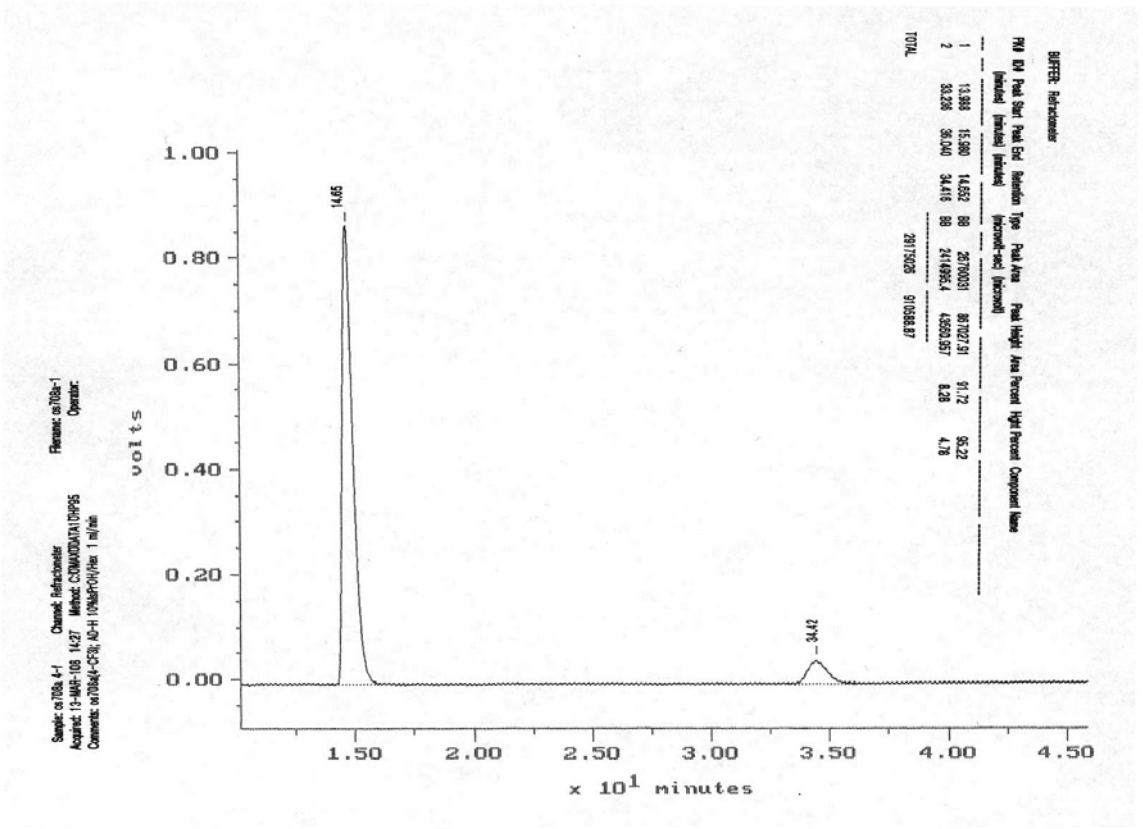


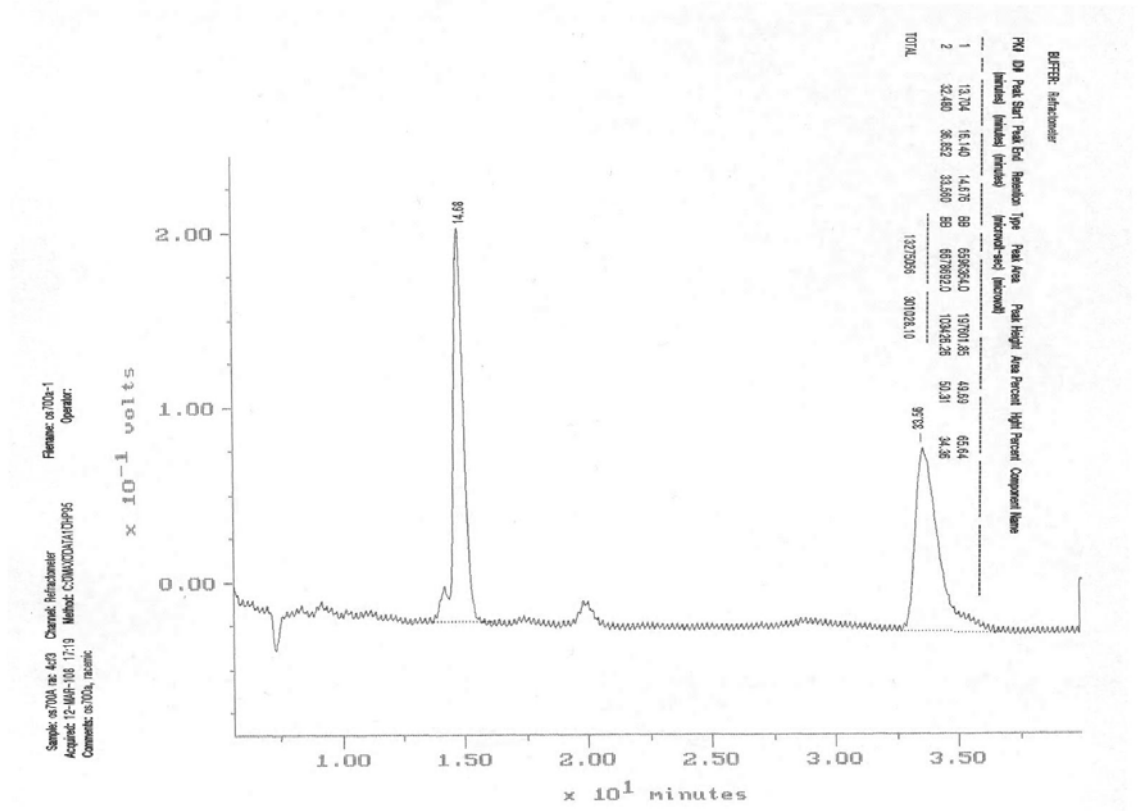

BUFFER: Refractometer
PK# RM Peak Start Peak End Retention Type Peak Area Peak Height Area Percent Hght Percent Component Name
(minutes) (minutes) (minutes) (microvolt-sec) (microvolt)
1 18.128 19.640 18.776 BB 945922.48 27009.579 5.11 6.23
2 20.512 23.416 21.472 BB 15580762 406706.09 94.89 93.77
TOTAL 16526685 433715.66
Sample: os 680b Channel: Refractometer Filename: os680b-2
Acquired: 21-FEB-108 19:05 Method: C:\DMA\DATA1\CHP95 Operator:
Comments: os680b; AD-H 10%IsPrOH/Hex 1 ml/min
18.78
21.47
x 10⁻¹ volts
4.00
3.00
2.00
1.00
0.00
1.00
1.50
2.00
2.50
3.00
3.50
4.00
x 10¹ minutes


BUFFER: Refractometer
PK# RM Peak Start Peak End Retention Type Peak Area Peak Height Area Percent Hght Percent Component Name
(minutes) (minutes) (minutes) (microvolt-sec) (microvolt)
1 18.128 20.072 18.776 BB 4641930.5 139044.12 49.81 51.99
2 20.992 23.308 21.796 BB 4676750.0 128411.57 50.19 48.01
TOTAL 9318680.5 267455.70
Sample: os 675b Channel: Refractometer Filename: os675b-3
Acquired: 22-FEB-108 10:58 Method: C:\DMA\DATA1\CHP95 Operator:
Comments: os675b, racemic
18.78
21.81
x 10⁻¹ volts
2.00
1.00
0.00
-1.00
1.00
1.50
2.00
2.50
3.00
3.50
4.00
x 10¹ minutes

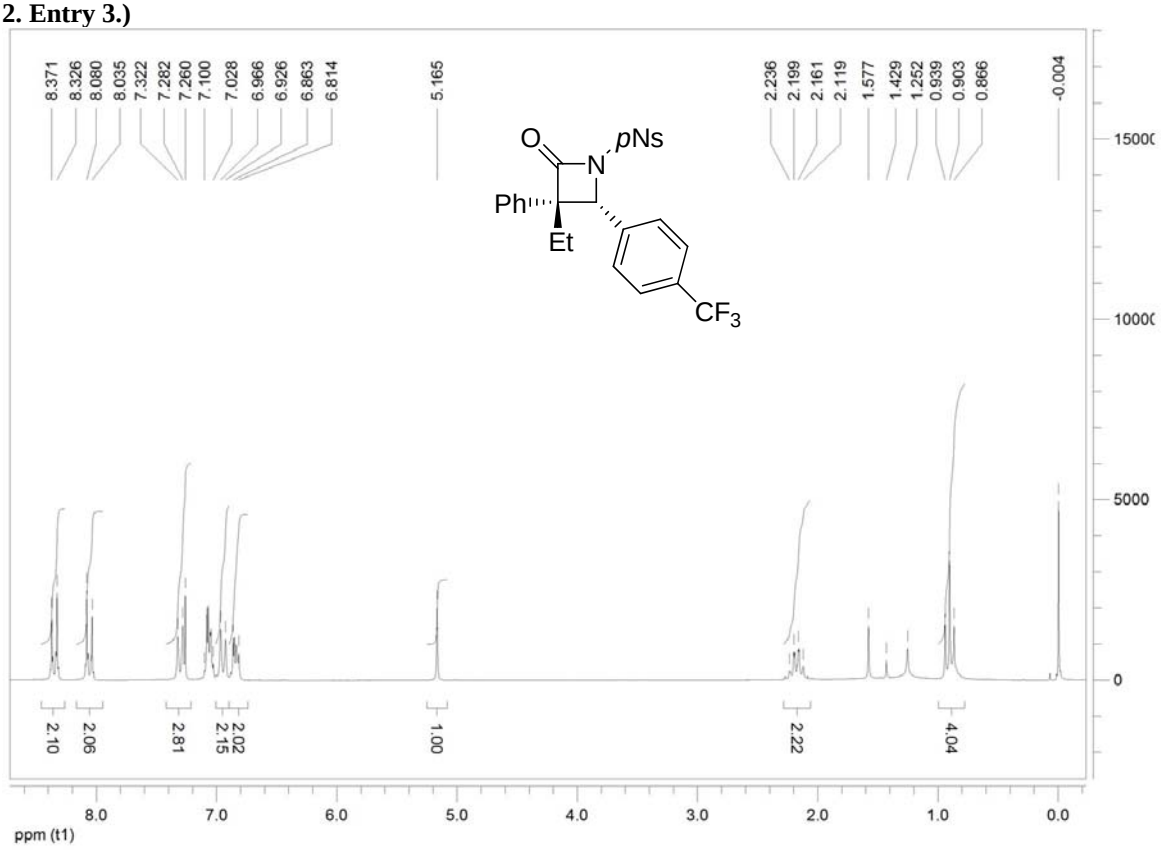
***trans*-(3*R*,4*R*)-3-ethyl-1-p-nitrobenzenesulfonyl-3-phenyl-4-(4-(trifluoromethyl)phenyl)azetidin-2-one(Table 2. Entry 3.)**

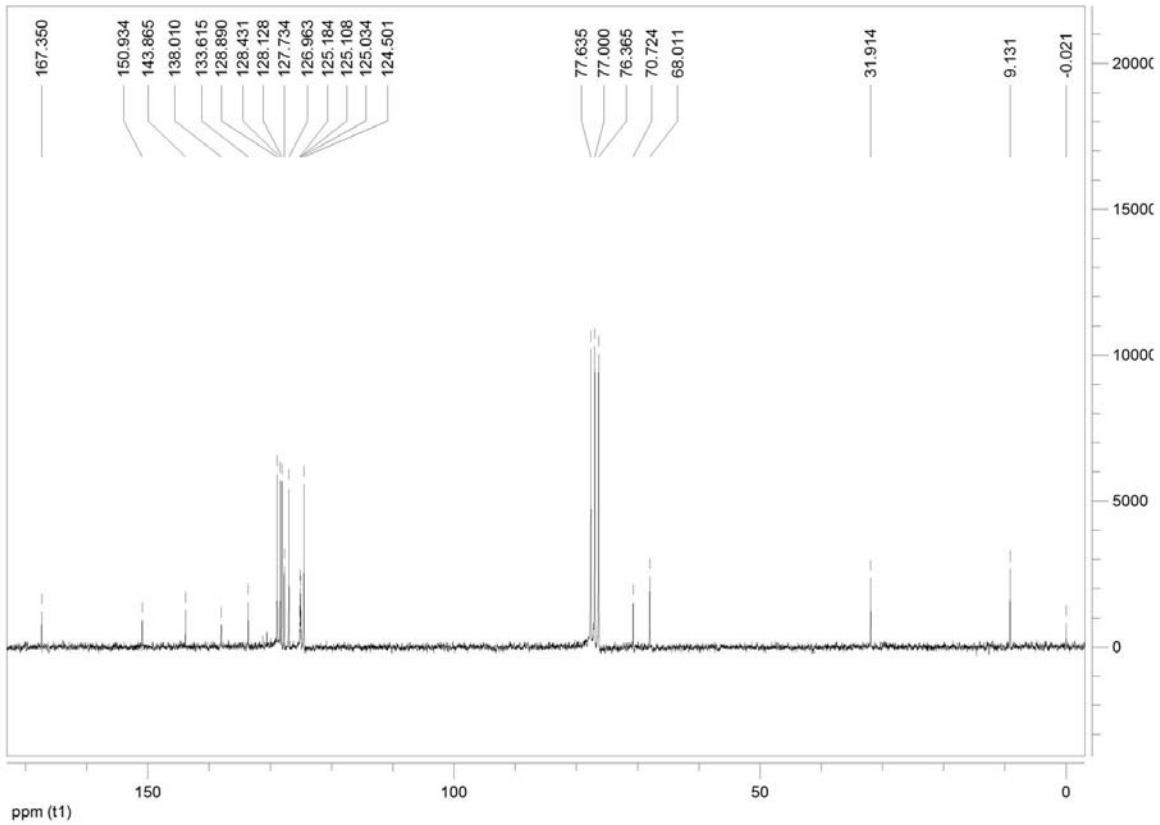


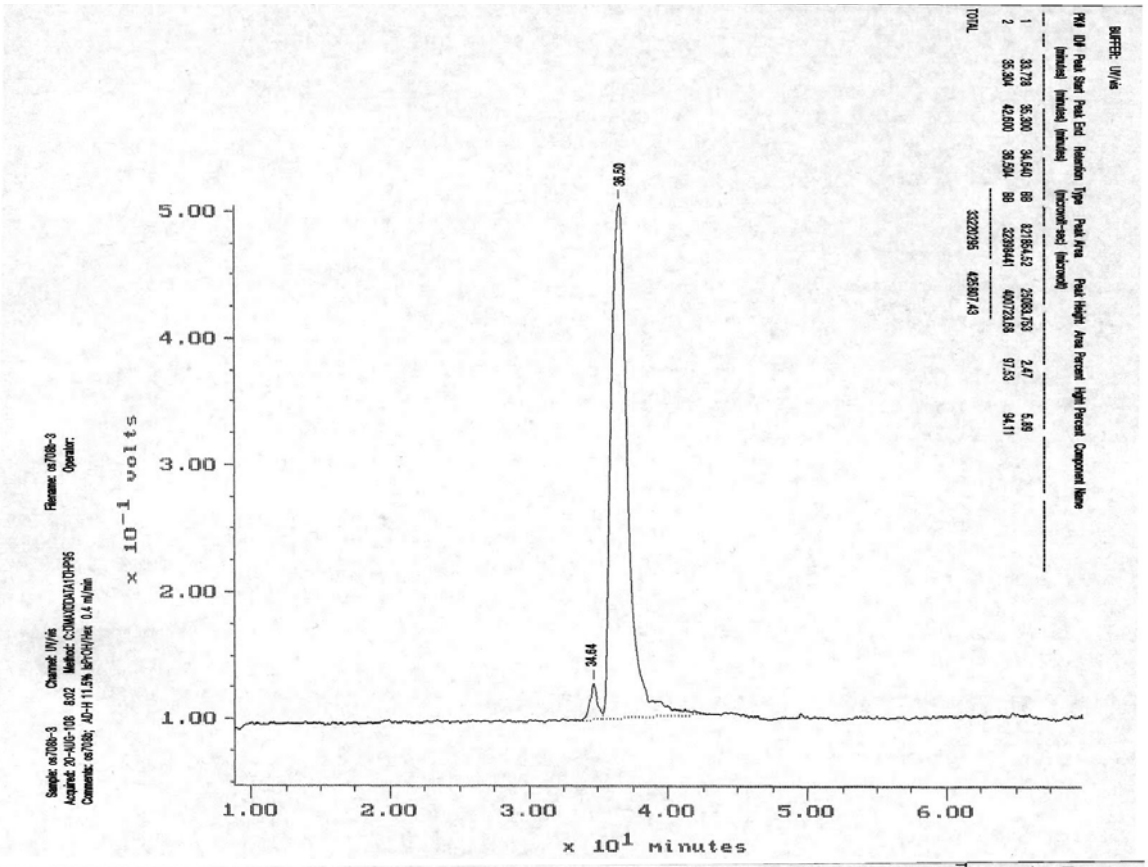

BUFFER: Refractometer
Sample: os703a 4-1 Channel: Refractometer Filename: os703a-1
Acquired: 19-MAR-108 14:27 Method: C:\DAVIDDATA1\DHP95 Operator:
Comments: os703a(4-CF3); AD-H 10%IsoProOH/Hex 1 ml/min
PkV EM Peak Start Peak End Retention Type Peak Area Peak Height Area Percent Hght Percent Component Name
(minutes) (minutes) (minutes) (microvolt-sec) (microvolt)
1 13.988 15.980 14.652 BB 25780031 867027.91 91.72 95.22
2 33.206 36.040 34.416 BB 2414065.4 43650.957 8.28 4.78
TOTAL 29179026 910588.87
volts
1.00
0.80
0.60
0.40
0.20
0.00
14.65
34.42
1.50 2.00 2.50 3.00 3.50 4.00 4.50
x 10^1 minutes

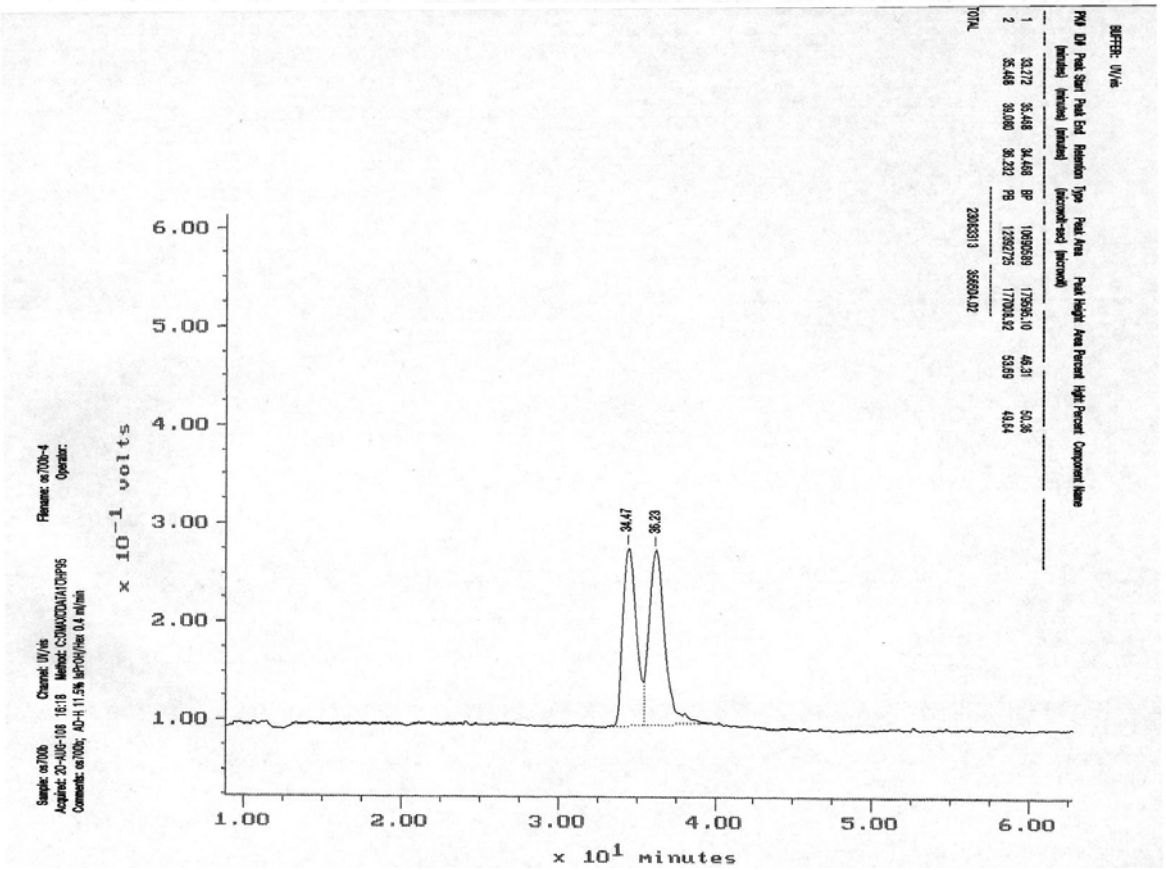

BUFFER: Refractometer
Sample: os700A rac 4cl3 Channel: Refractometer Filename: os700a-1
Acquired: 12-MAR-108 17:19 Method: C:\DAVIDDATA1\DHP95 Operator:
Comments: os700a, racemic
PkV EM Peak Start Peak End Retention Type Peak Area Peak Height Area Percent Hght Percent Component Name
(minutes) (minutes) (minutes) (microvolt-sec) (microvolt)
1 13.704 16.140 14.676 BB 65365964.0 197601.85 49.69 65.64
2 32.480 36.852 33.560 BB 66178932.0 103428.26 50.31 34.36
TOTAL 131735896 301028.10
x 10^-1 volts
2.00
1.00
0.00
14.68
33.56
1.00 1.50 2.00 2.50 3.00 3.50
x 10^1 minutes

cis-(3_S_,4_R_)-3-ethyl-1-p-nitrobenzenesulfonyl-3-phenyl-4-(4-(trifluoromethyl)phenyl)azetidin-2-one (Table 2. Entry 3.)

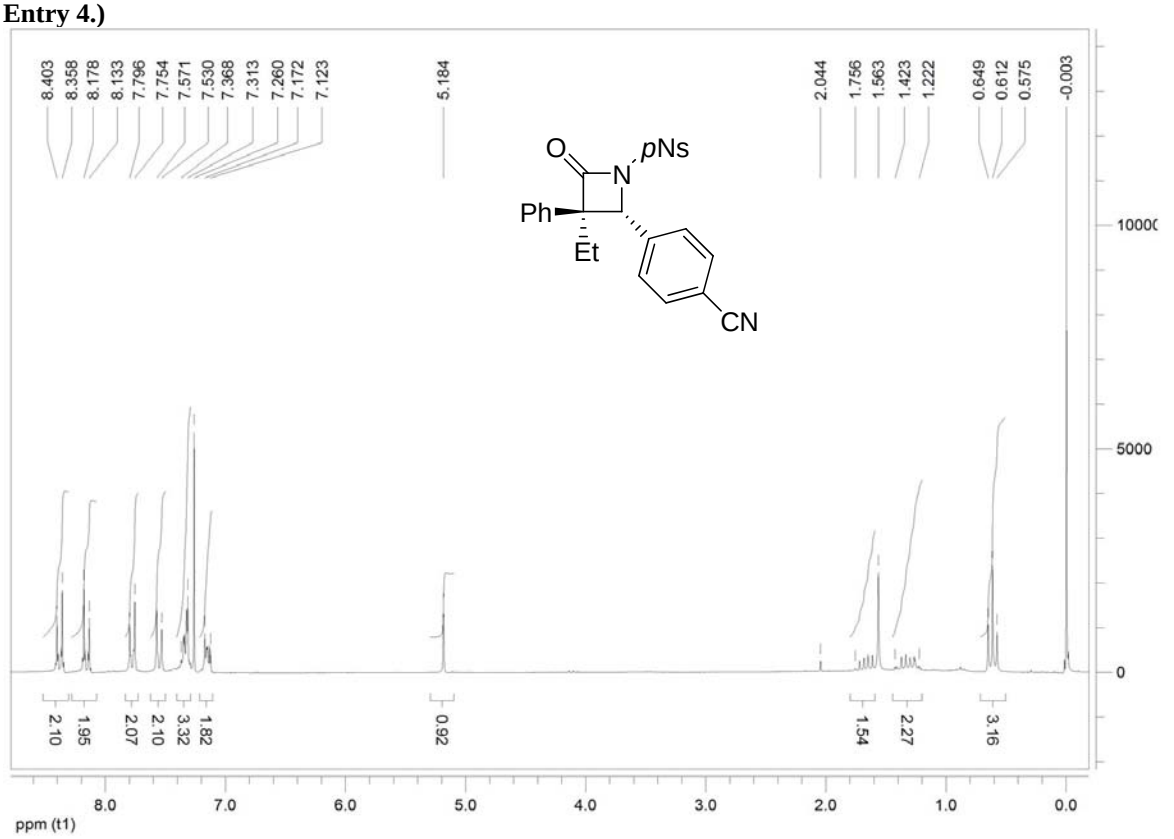


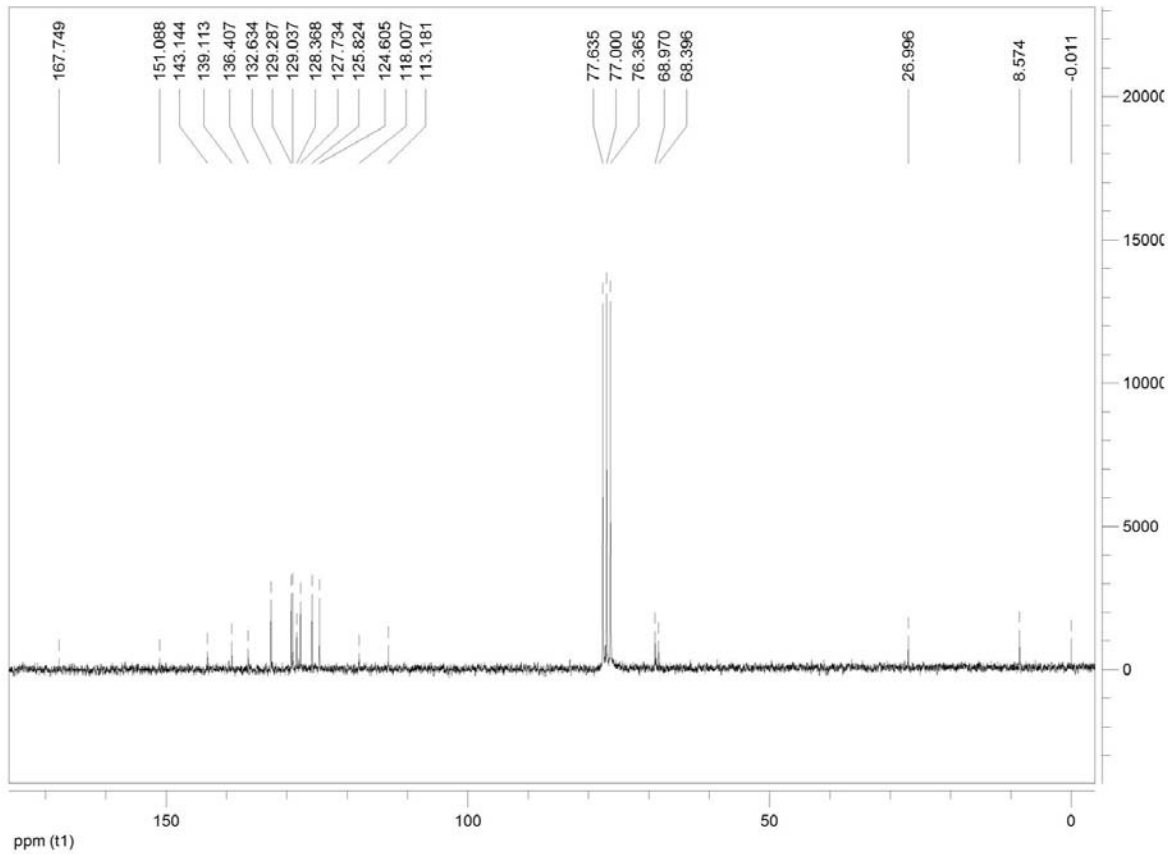


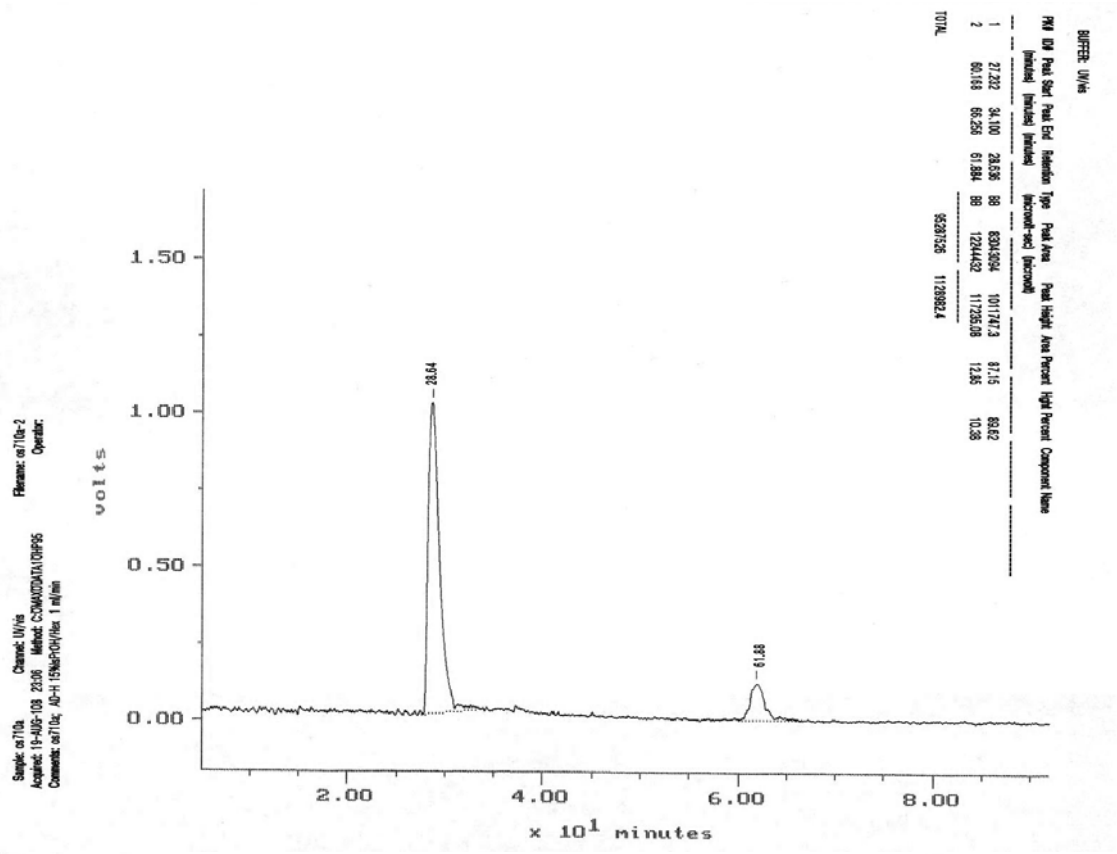

BUFFER: UV/vis
PK# RT Peak Start Peak End Retention Type Peak Area Peak Height Area Percent Hght Percent Component Name
(minutes) (minutes) (minutes) (microvolt-sec) (microvolt)
1 33.728 35.300 34.640 BB 821854.52 26583.753 2.47 5.89
2 35.304 42.500 38.504 BB 32398441 400728.68 97.53 94.11
TOTAL 33220295 425967.43
Sample: os708b-3 Channel: UV/vis Filename: os708b-3
Acquired: 20-AUG-108 8:02 Method: C:\DMA\CDA\ATOHP95 Operator:
Comments: os708b; AD-H 11.5% IsPrOH/Hex 0.4 ml/min
x 10⁻¹ volts
34.64
36.50
1.00
2.00
3.00
4.00
5.00
1.00
2.00
3.00
4.00
5.00
6.00
x 10¹ minutes

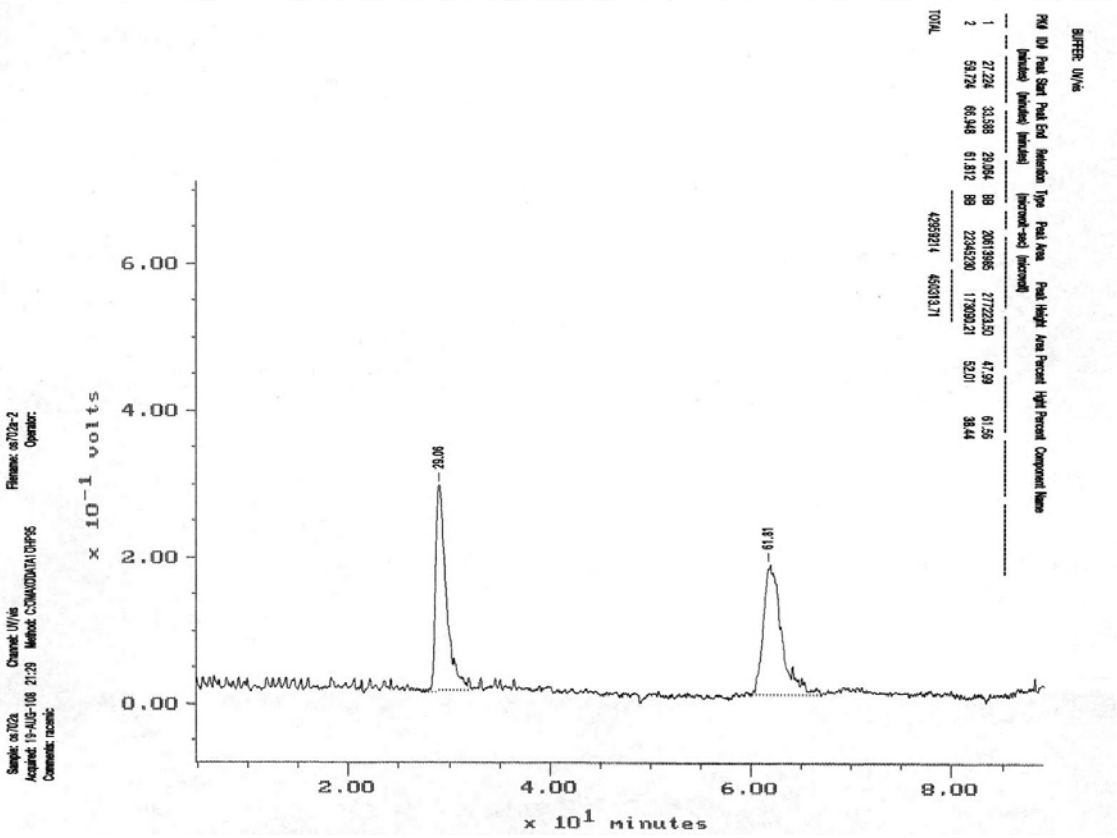

BUFFER: UV/vis
PK# RT Peak Start Peak End Retention Type Peak Area Peak Height Area Percent Hght Percent Component Name
(minutes) (minutes) (minutes) (microvolt-sec) (microvolt)
1 33.272 35.448 34.468 BP 10930589 175686.10 46.31 50.36
2 35.448 39.080 36.232 PB 12662725 177018.92 53.69 49.64
TOTAL 23593313 352634.02
Sample: os700b Channel: UV/vis Filename: os700b-4
Acquired: 20-AUG-108 16:18 Method: C:\DMA\CDA\ATOHP95 Operator:
Comments: os700b; AD-H 11.5% IsPrOH/Hex 0.4 ml/min
x 10⁻¹ volts
34.47
36.23
1.00
2.00
3.00
4.00
5.00
6.00
1.00
2.00
3.00
4.00
5.00
6.00
x 10¹ minutes

***trans*-(3*R*,4*R*)-4-(3-ethyl-1-p-nitrobenzenesulfonyl-4-oxo-3-phenylazetidin-2-yl)benzonitrile (Table 2. Entry 4.)**

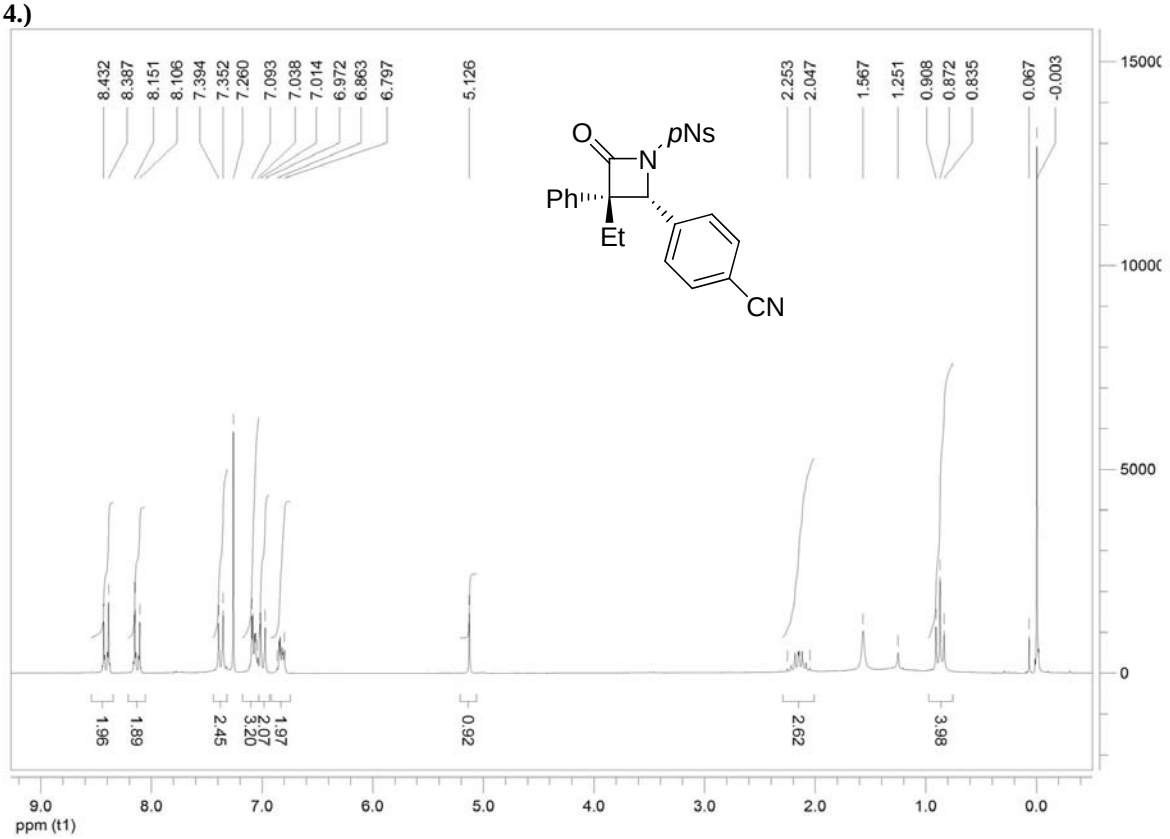


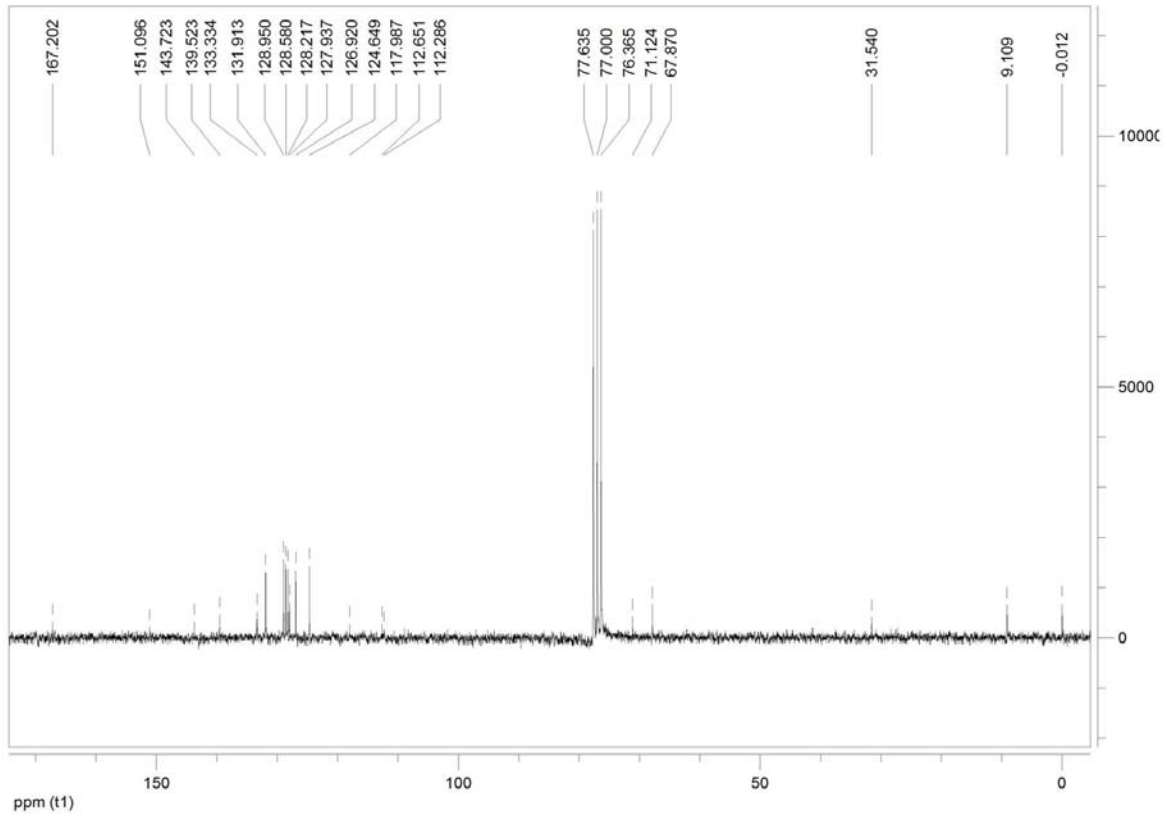


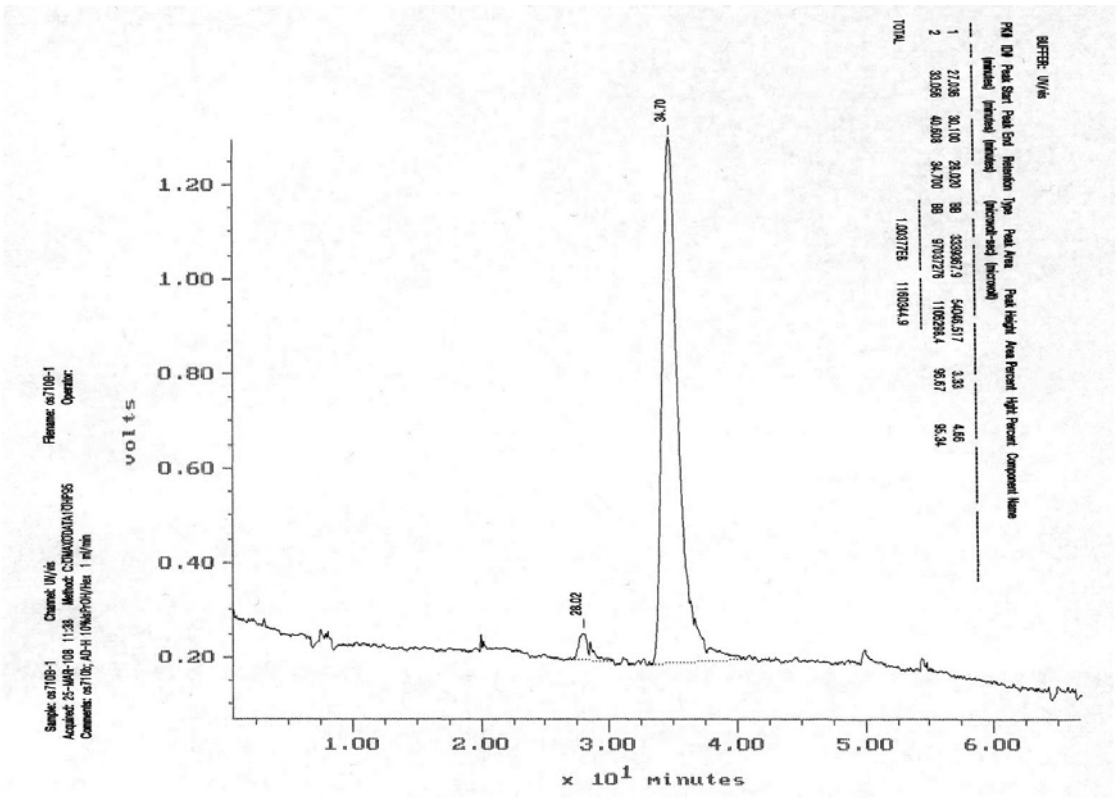

BUFFER: UV/vis
PKI RM Peak Start Peak End Retention Type Peak Area Peak Height Area Percent Hght Percent Component Name
(minutes) (minutes) (minutes) (microvolt-sec) (microvolt)
1 27.222 34.100 28.536 BB 8304.9694 1011747.3 87.15 89.62
2 60.168 66.256 61.884 BB 1224.4432 117235.08 12.85 10.38
TOTAL 9529.726 1128982.4
Filename: os710a-2
Operator:
Sample: os710a
Channel: UV/vis
Acquired: 19-AUG-108 23:06
Method: C:\DMA\DDATA\CHP95
Comments: os710a; AD-H 15%NaOH/Hex 1 ml/min
volts
1.50
1.00
0.50
0.00
28.84
61.88
2.00
4.00
6.00
8.00
x 10^1 minutes

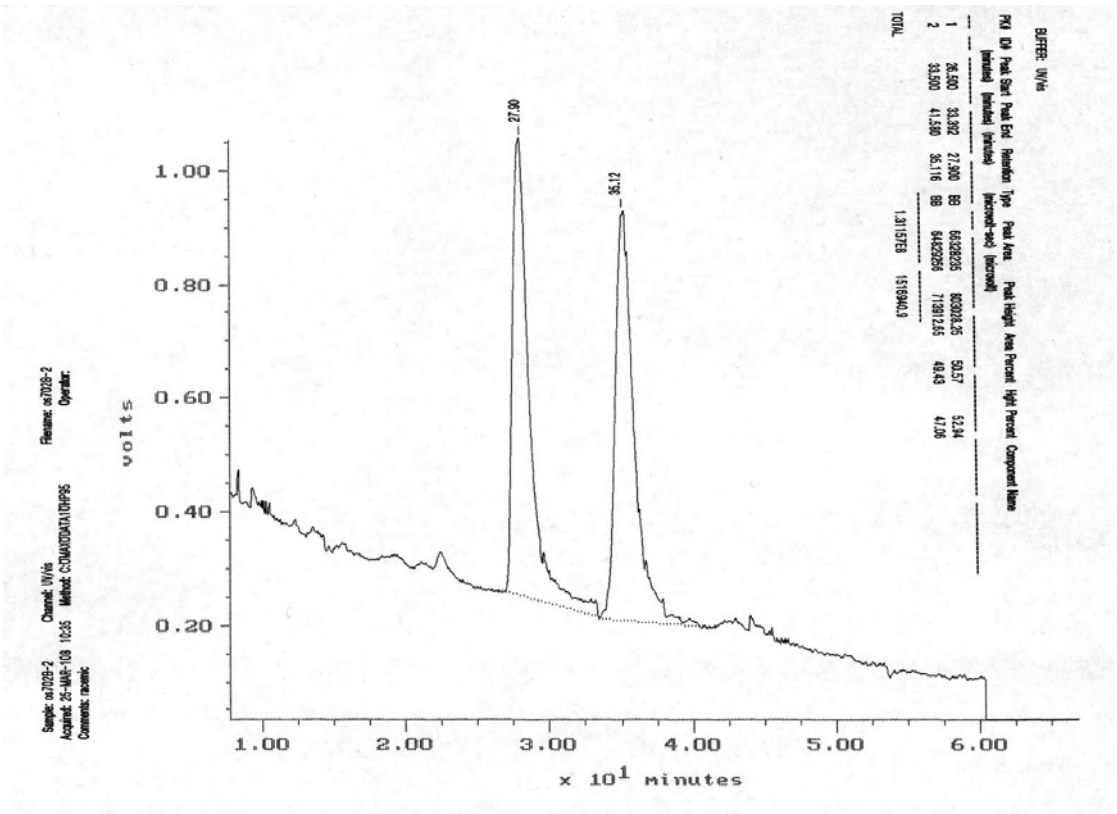

BUFFER: UV/vis
PKI RM Peak Start Peak End Retention Type Peak Area Peak Height Area Percent Hght Percent Component Name
(minutes) (minutes) (minutes) (microvolt-sec) (microvolt)
1 27.224 33.588 29.064 BB 2061.9985 277223.50 47.99 61.56
2 53.724 66.948 61.812 BB 2234.9230 173089.21 52.01 38.44
TOTAL 4295.9214 450319.71
Filename: os702a-2
Operator:
Sample: os702a
Channel: UV/vis
Acquired: 19-AUG-108 21:29
Method: C:\DMA\DDATA\CHP95
Comments: racemic
x 10^-1 volts
6.00
4.00
2.00
0.00
29.06
61.81
2.00
4.00
6.00
8.00
x 10^1 minutes

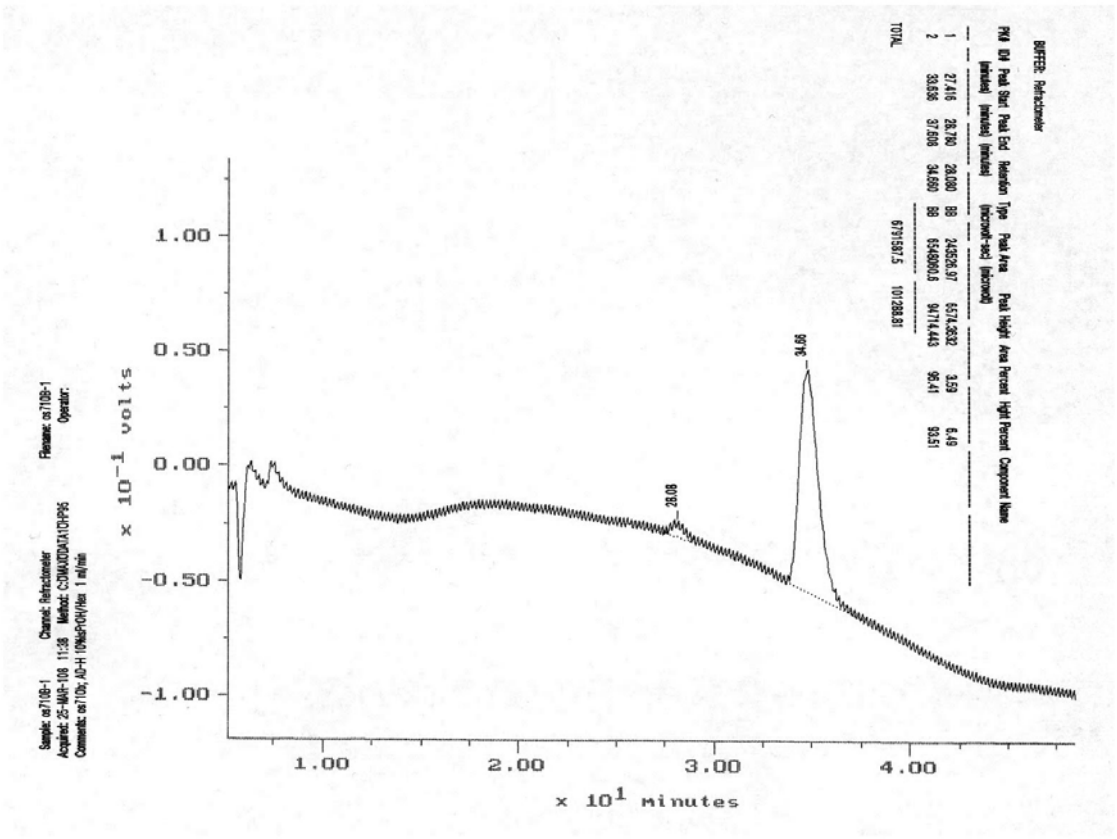
cis-(3_S_,4_R_)-4-(3-ethyl-1-p-nitrobenzenesulfonyl-4-oxo-3-phenylazetidin-2-yl)benzonitrile (Table 2. Entry 4.)

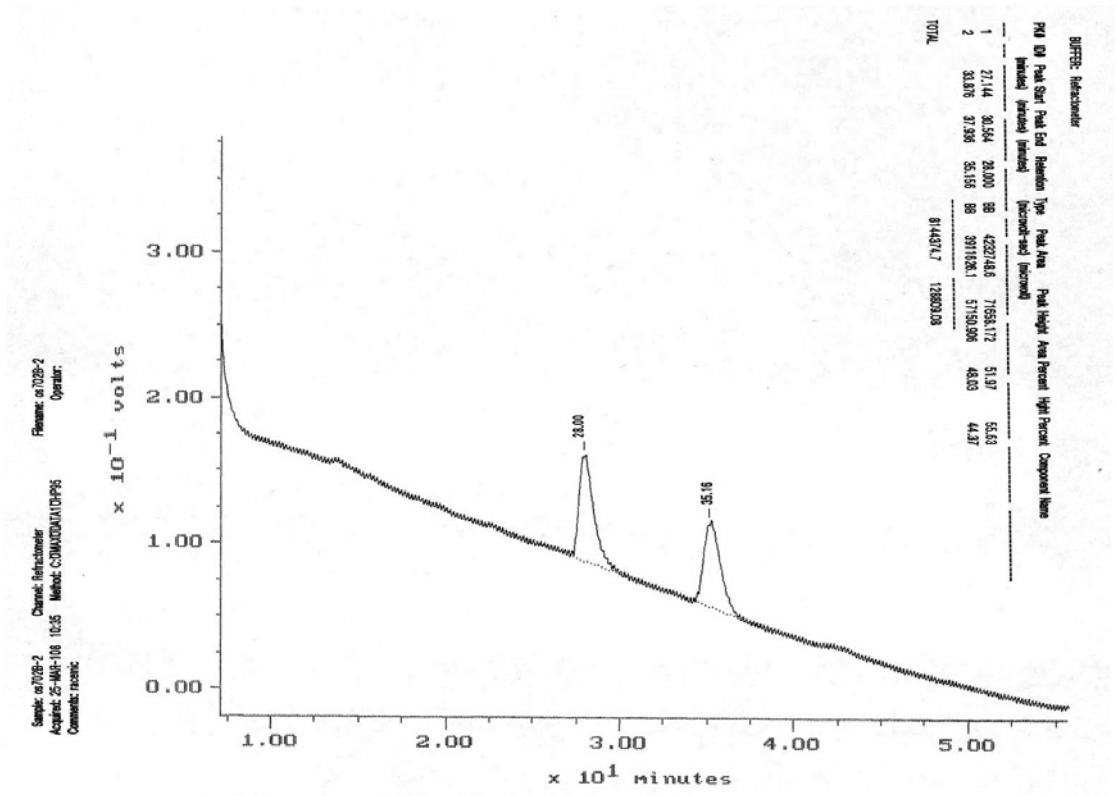




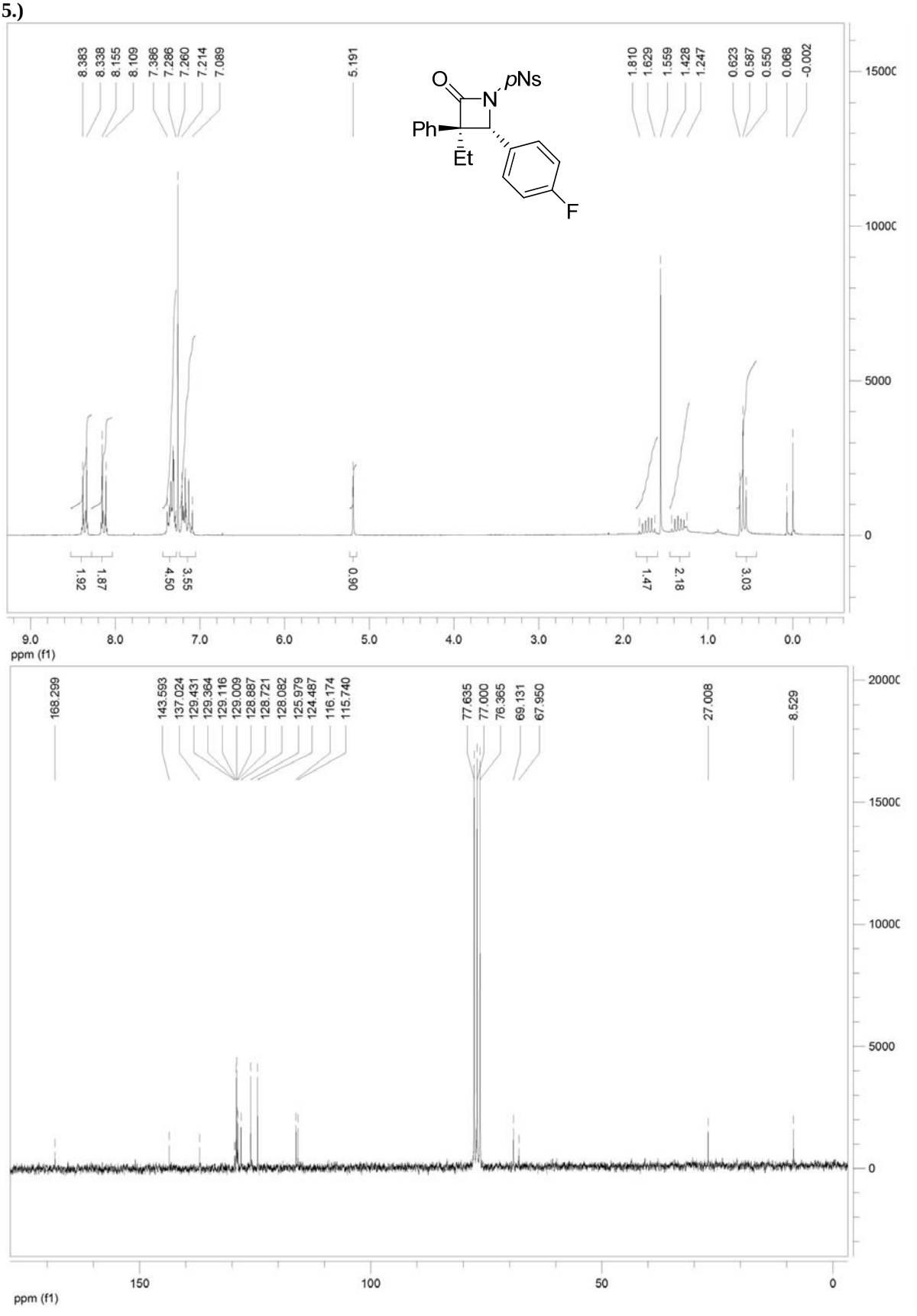

volts
x 10^1 minutes
1.00
2.00
3.00
4.00
5.00
6.00
0.20
0.40
0.60
0.80
1.00
1.20
34.70
28.02

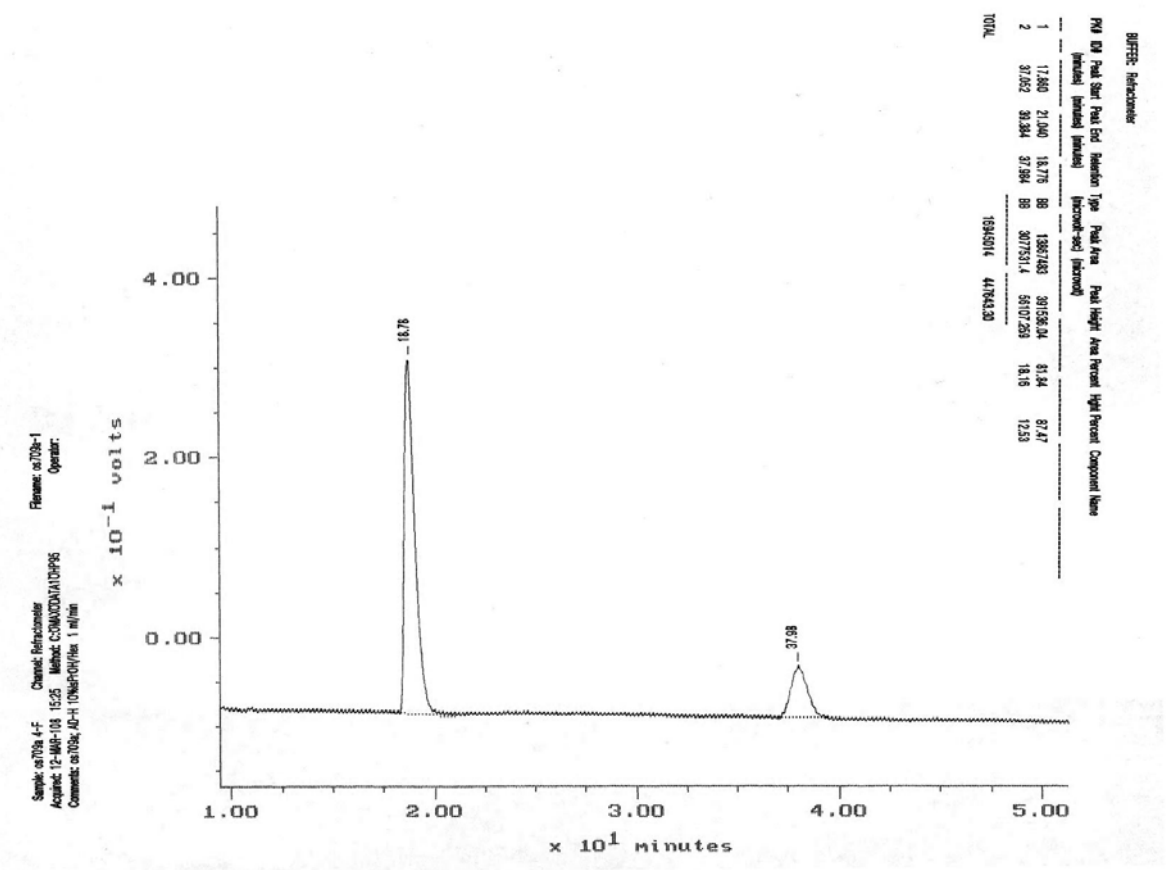

volts
x 10^1 minutes
1.00
2.00
3.00
4.00
5.00
6.00
0.20
0.40
0.60
0.80
1.00
27.90
35.12

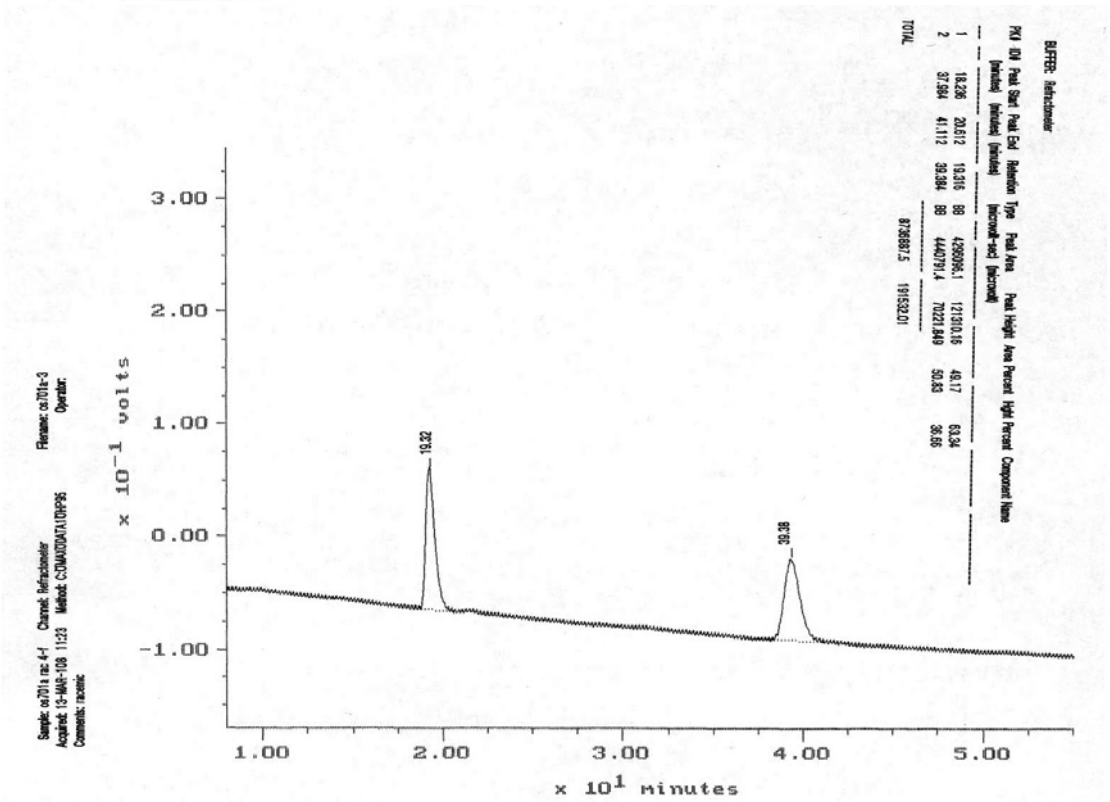

BUFFER: Refractometer
PKN BN Peak Start Peak End Retention Type Peak Area Peak Height Area Percent Hght Percent Component Name
(minutes) (minutes) (minutes) (microvolt-sec) (microvolt)
1 27.416 28.760 28.000 BB 243526.97 6574.3632 3.59 6.49
2 33.638 37.609 34.660 BB 6548060.8 94714.443 96.41 93.51
TOTAL 6791587.5 101288.81
Sample: os7108-1 Channel: Refractometer Filename: os7108-1
Acquired: 25-MAR-108 11:38 Method: C:\DMA\DDA\X10\HP95 Operator:
Comments: os7108; AD-H 10%IsPrOH/Hex 1 ml/min
28.08
99.16
x 10-1 volts
1.00
0.50
0.00
-0.50
-1.00
1.00
2.00
3.00
4.00
x 10¹ minutes


BUFFER: Refractometer
PKN BN Peak Start Peak End Retention Type Peak Area Peak Height Area Percent Hght Percent Component Name
(minutes) (minutes) (minutes) (microvolt-sec) (microvolt)
1 27.144 30.584 28.000 BB 4232748.6 71658.172 51.97 55.63
2 33.876 37.936 35.158 BB 3911926.1 57150.906 48.03 44.37
TOTAL 8144374.7 128809.08
Sample: os7028-2 Channel: Refractometer Filename: os7028-2
Acquired: 25-MAR-108 10:35 Method: C:\DMA\DDA\X10\HP95 Operator:
Comments: racemic
24.00
35.16
x 10-1 volts
3.00
2.00
1.00
0.00
1.00
2.00
3.00
4.00
5.00
x 10¹ minutes

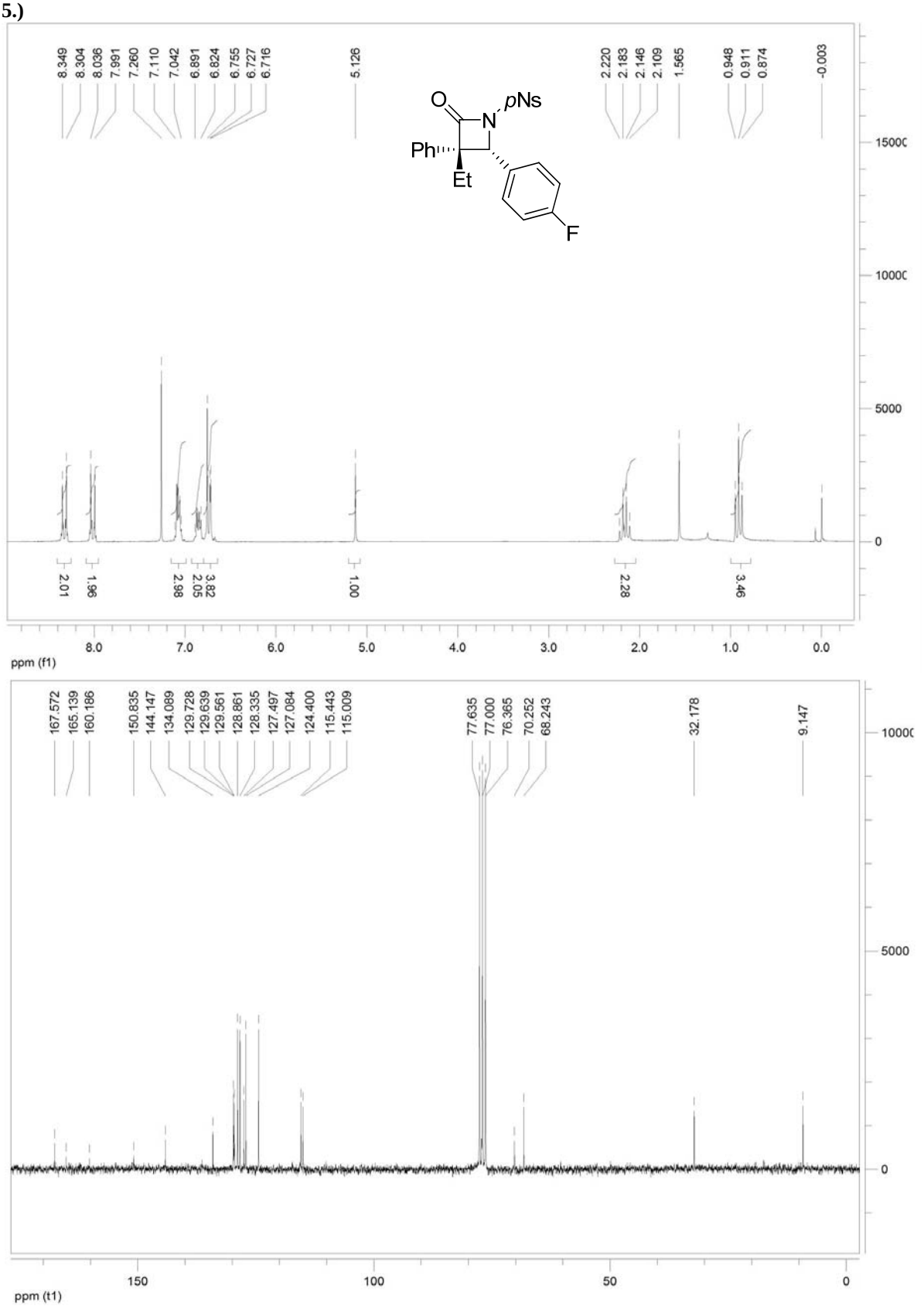
***trans*-(3*R*,4*R*)-3-ethyl-4-(4-fluorophenyl)-1-p-nitrobenzenesulfonyl-3-phenylazetidin-2-one (Table 2. Entry 5.)**

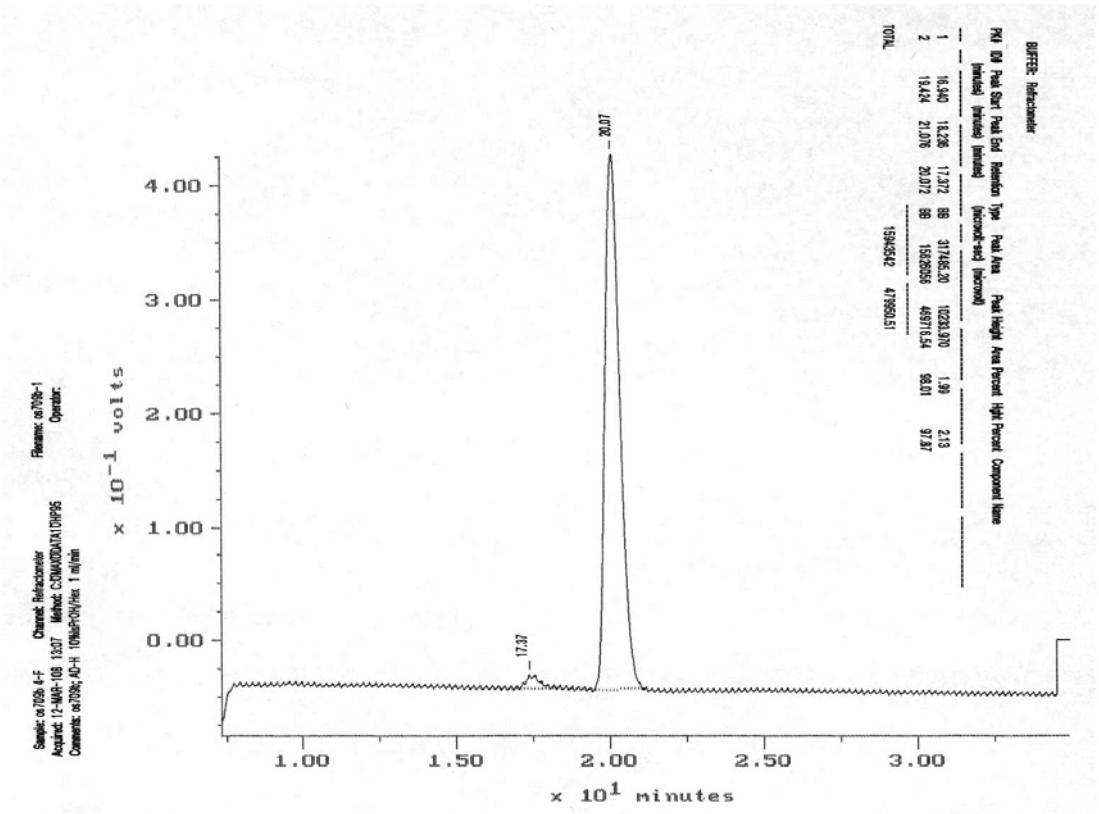


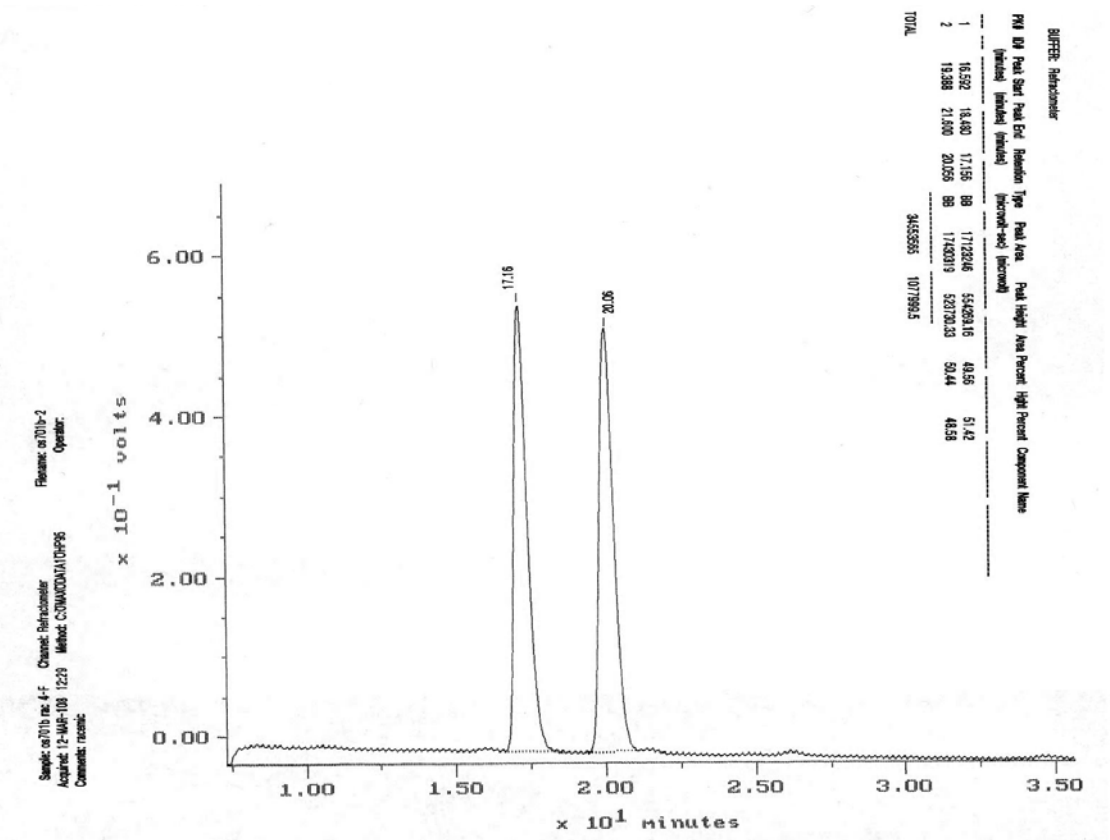

BUFFER: Refractometer
PK# RM Peak Start Peak End Retention Type Peak Area Peak Height Area Percent Hght Percent Component Name
(minutes) (minutes) (minutes) (microRIU-sec) (microRIU)
1 17.840 21.040 18.776 BB 13867483 391536.04 81.84 87.47
2 37.052 39.384 37.984 BB 3077531.4 56107.259 18.16 12.53
TOTAL 16945014 447643.30
Filename: os1709r-1
Operator:
Sample: os1709 4-F
Acquired: 12-MAR-108 15:25
Comments: os1709r; AD-H 10%IsPrOH/Hex 1 ml/min
Channel: Refractometer
Method: C:\DIANA\DATA1\DHP95
4.00
2.00
0.00
x 10-1 volts
18.78
37.98
1.00
2.00
3.00
4.00
5.00
x 10^1 minutes


BUFFER: Refractometer
PK# RM Peak Start Peak End Retention Type Peak Area Peak Height Area Percent Hght Percent Component Name
(minutes) (minutes) (minutes) (microRIU-sec) (microRIU)
1 18.236 20.612 19.316 BB 4398996.1 121310.16 49.17 63.34
2 37.984 41.112 39.384 BB 4440791.4 70221.849 50.83 36.66
TOTAL 8839887.5 191532.01
Filename: os1701r-3
Operator:
Sample: os1701r rac 4-F
Acquired: 13-MAR-108 11:23
Comments: racemic
Channel: Refractometer
Method: C:\DIANA\DATA1\DHP95
3.00
2.00
1.00
0.00
-1.00
x 10-1 volts
19.32
39.18
1.00
2.00
3.00
4.00
5.00
x 10^1 minutes

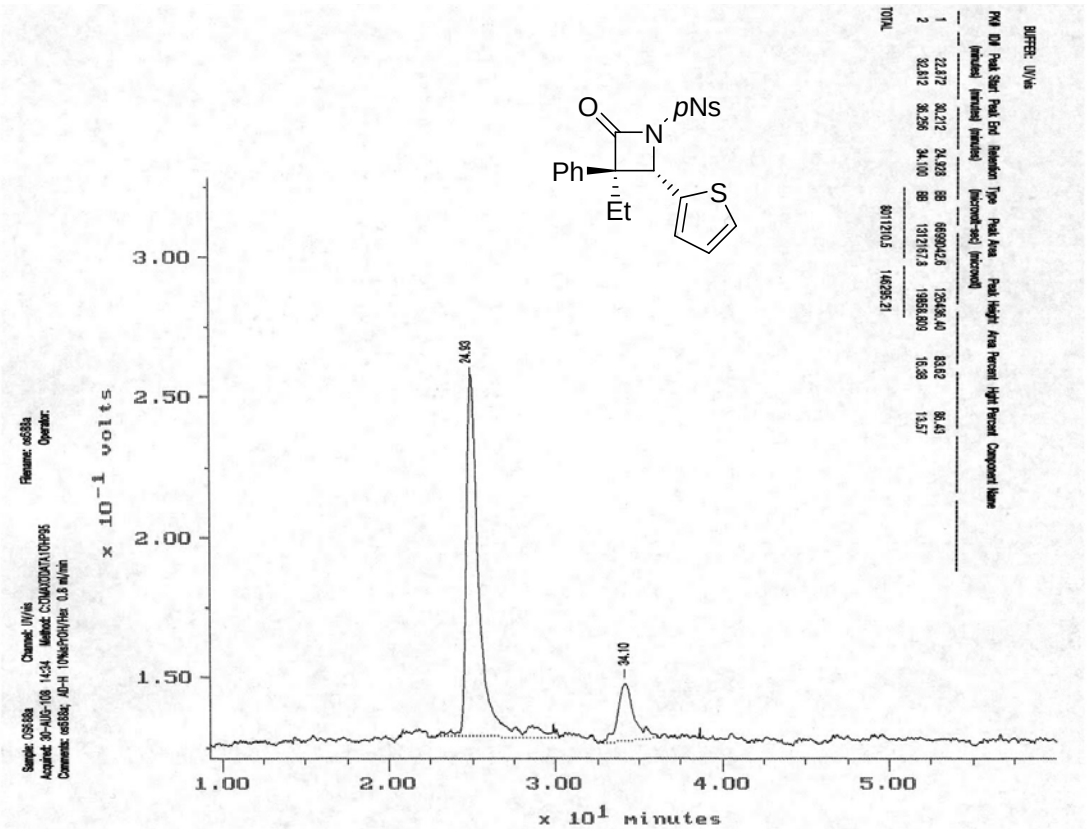
***cis*-(3*S*,4*R*)-3-ethyl-4-(4-fluorophenyl)-1-p-nitrobenzenesulfonyl-3-phenylazetidin-2-one (Table 2. Entry 5.)**

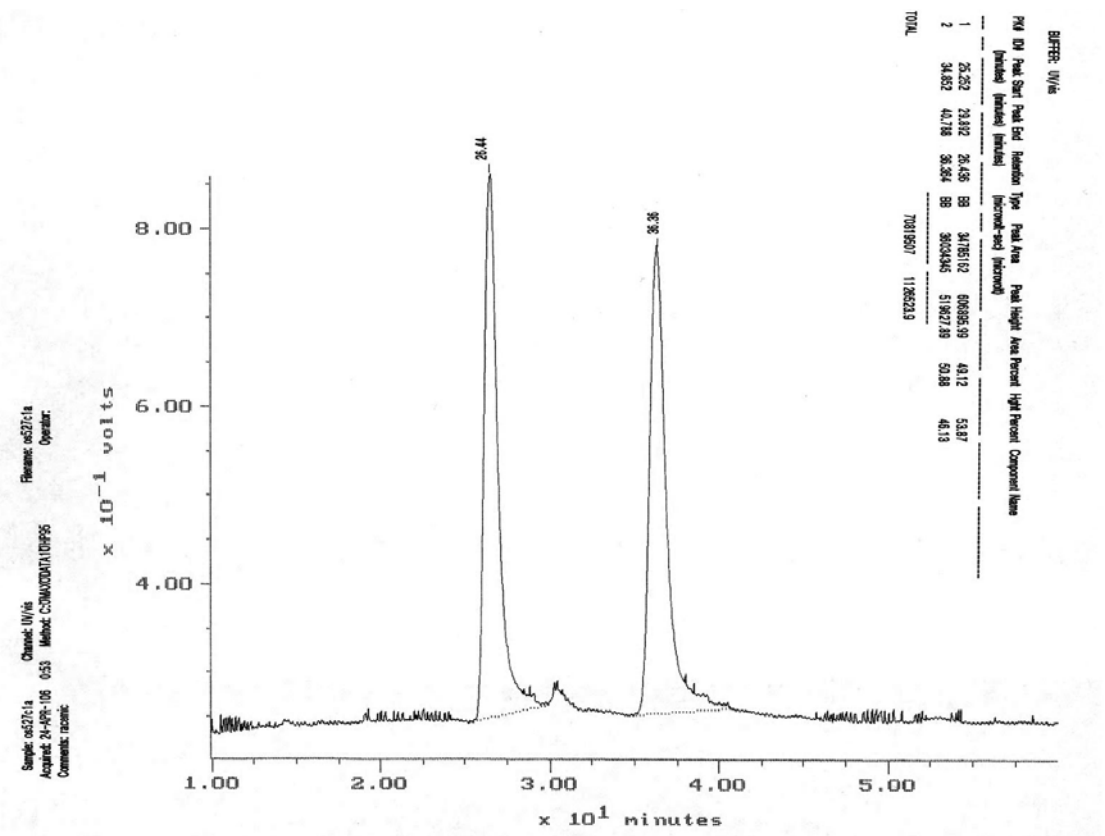



BUFFER: Refractometer
Sample: os709b 4+F Channel: Refractometer Filename: os709b-1
Acquired: 12-MAR-108 13:07 Method: C:\DAVID\DATA1\OHP95 Operator:
Comments: os709a; AD-H 10%isPrOH/Hex 1 ml/min
PK# BM Peak Start Peak End Retention Type Peak Area Peak Height Area Percent Hght Percent Component Name
(minutes) (minutes) (minutes) (microRI-sec) (microRI)
1 16.340 18.286 17.372 BB 317485.20 10228.970 1.99 2.13
2 19.424 21.076 20.072 BB 15626056 469716.54 98.01 97.87
TOTAL 15943542 479950.51
x 10⁻¹ volts
x 10¹ minutes
17.37
20.07

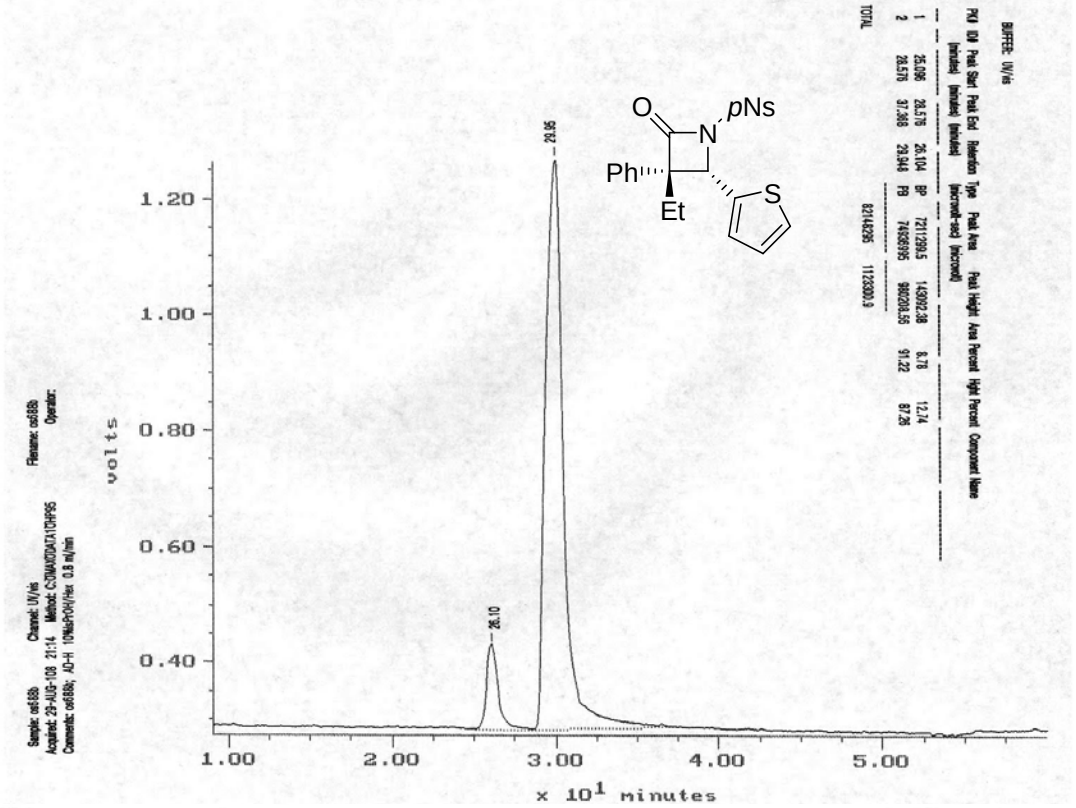

BUFFER: Refractometer
Sample: os701b rac 4+F Channel: Refractometer Filename: os701b-2
Acquired: 12-MAR-108 12:29 Method: C:\DAVID\DATA1\OHP95 Operator:
Comments: racemic
PK# BM Peak Start Peak End Retention Type Peak Area Peak Height Area Percent Hght Percent Component Name
(minutes) (minutes) (minutes) (microRI-sec) (microRI)
1 16.592 18.493 17.156 BB 17128246 554269.16 49.56 51.42
2 19.388 21.500 20.056 BB 17430319 523730.33 50.44 48.58
TOTAL 34558565 1077999.5
x 10⁻¹ volts
x 10¹ minutes
17.16
20.06

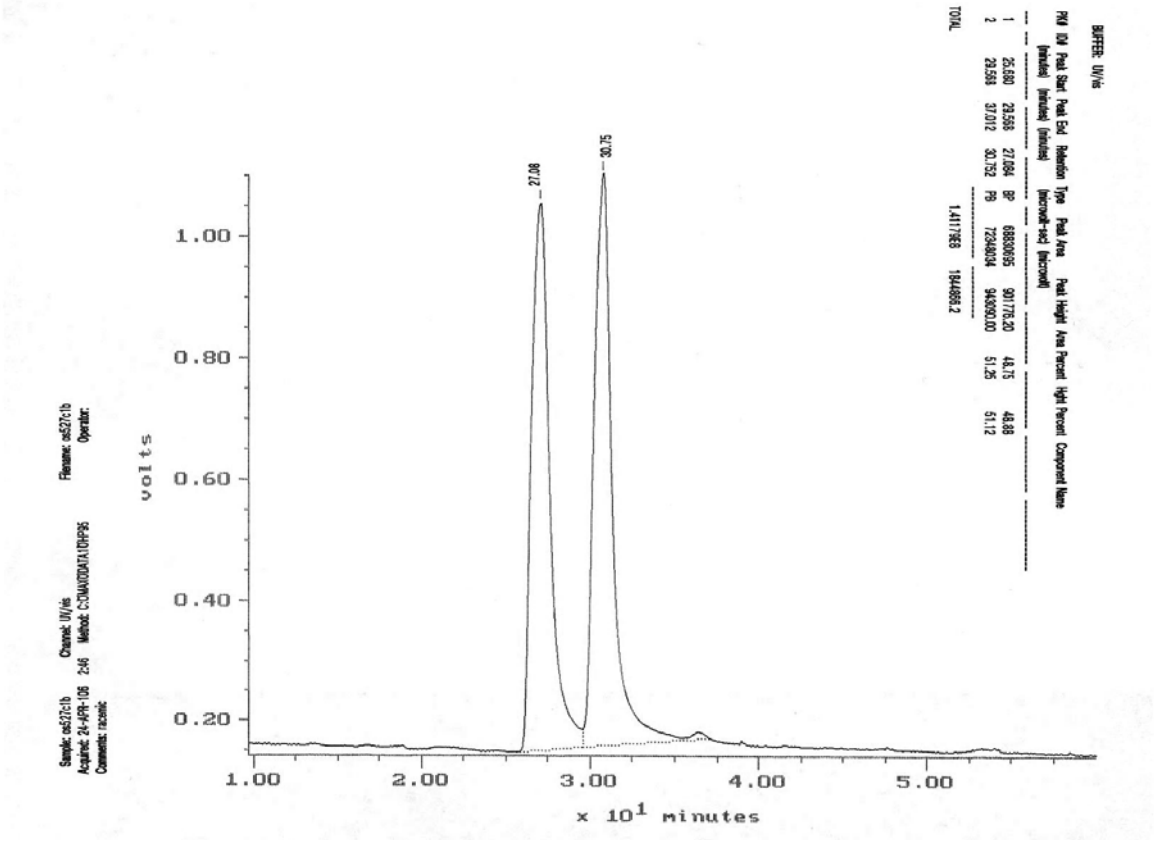
***trans*-(3*R*,4*R*)-3-ethyl-1-p-nitrobenzenesulfonyl-3-phenyl-4-(thiophen-2-yl)azetidin-2-one (Table 2. Entry 6.)**[7]



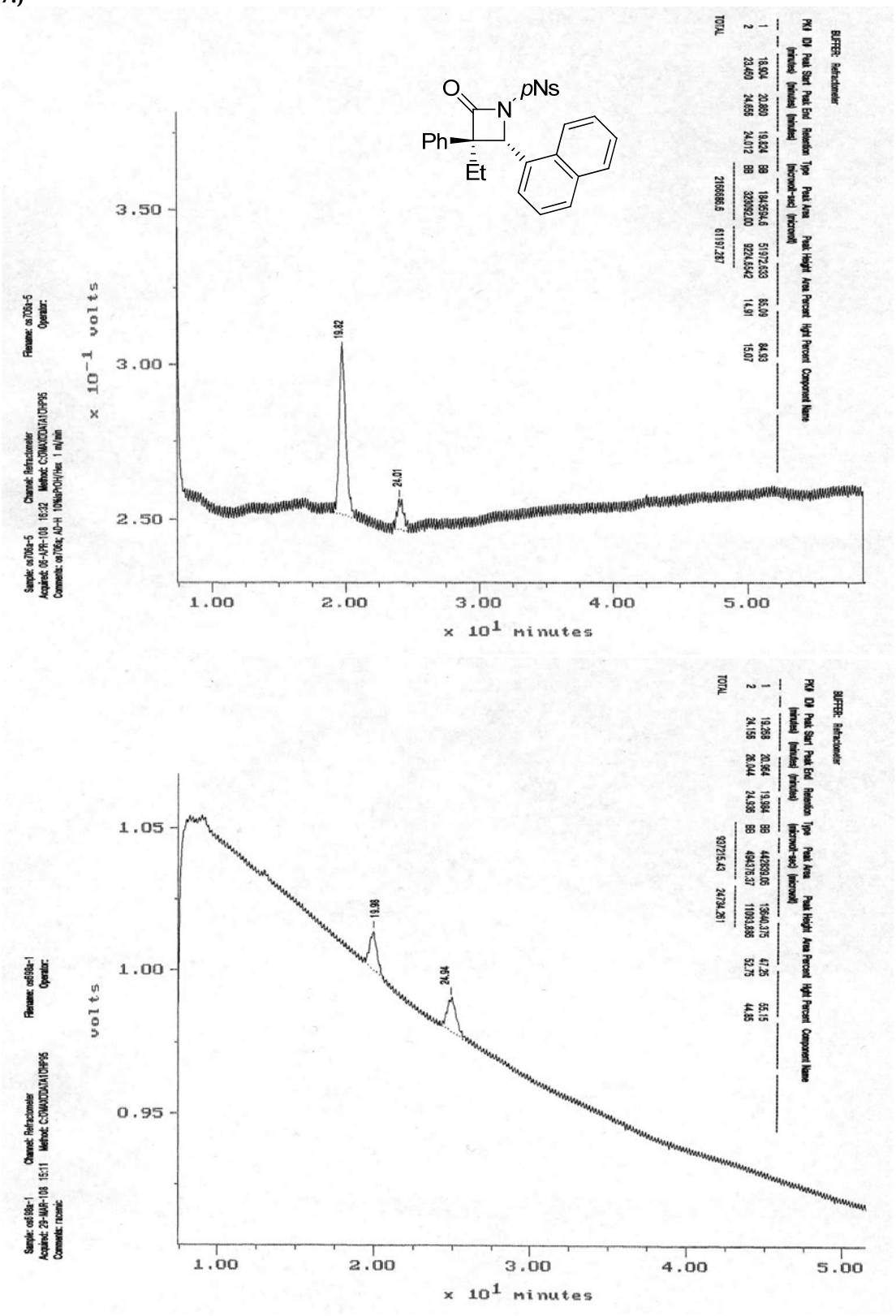


***cis*-(3*S*,4*R*)-3-ethyl-1-p-nitrobenzenesulfonyl-3-phenyl-4-(thiophen-2-yl)azetidin-2-one (Table 2. Entry 6.)**[7]

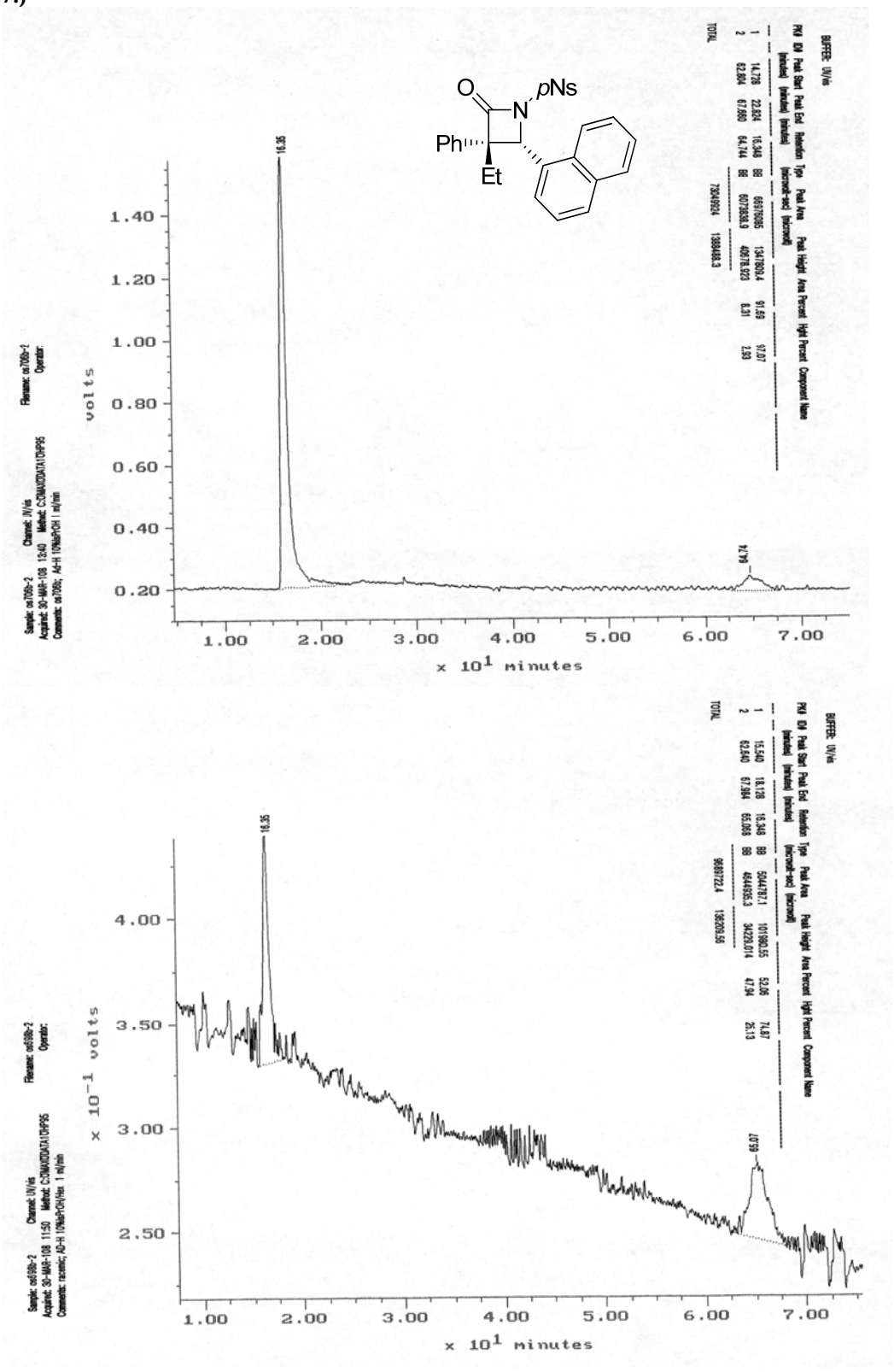




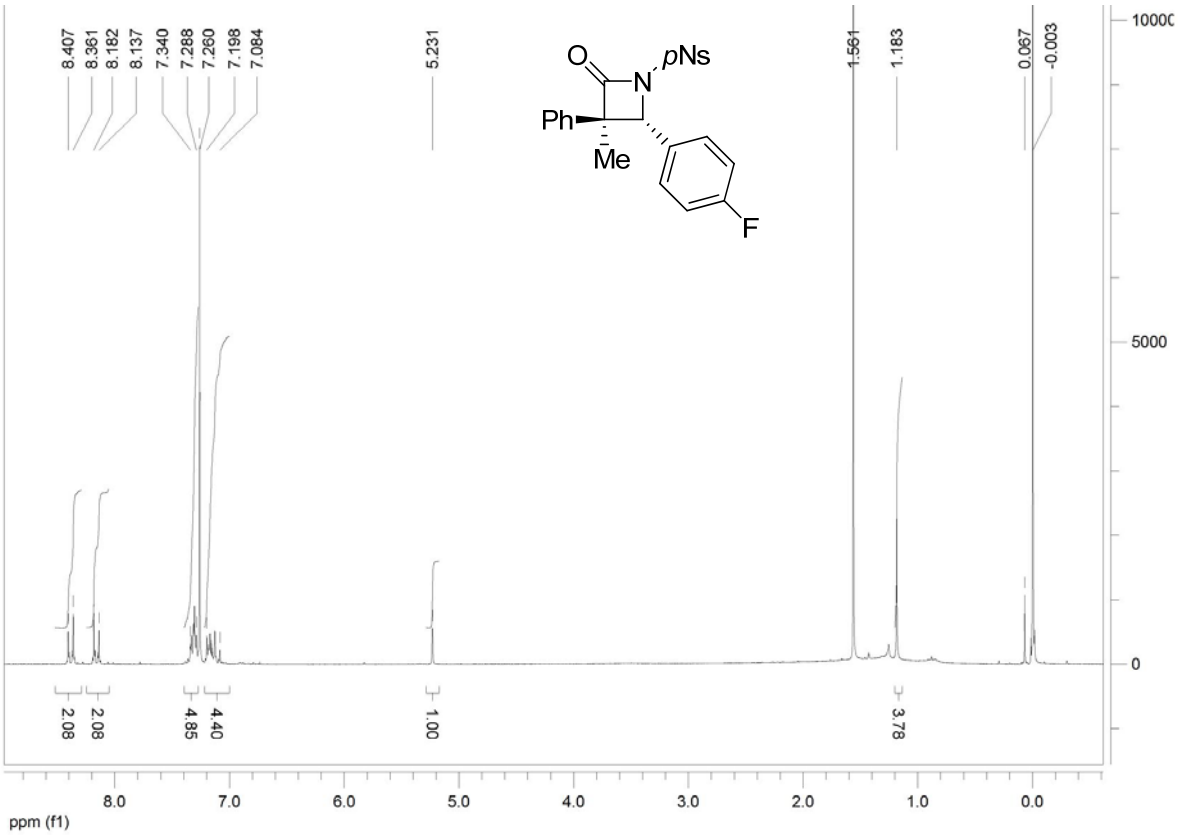
***trans*-(3*R*,4*R*)-3-ethyl-4-(naphthalen-1-yl)-1-p-nitrobenzenesulfonyl-3-phenylazetidin-2-one (Table 2. Entry 7.)**[7]

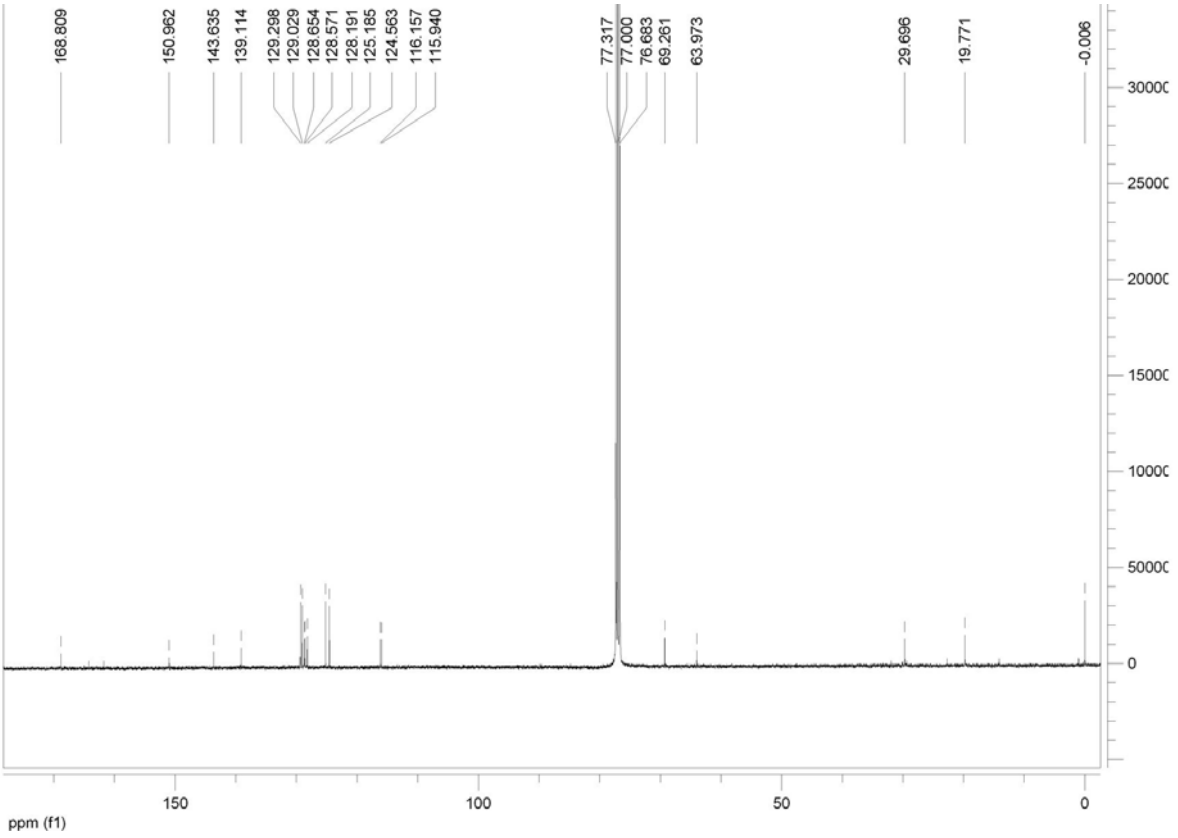


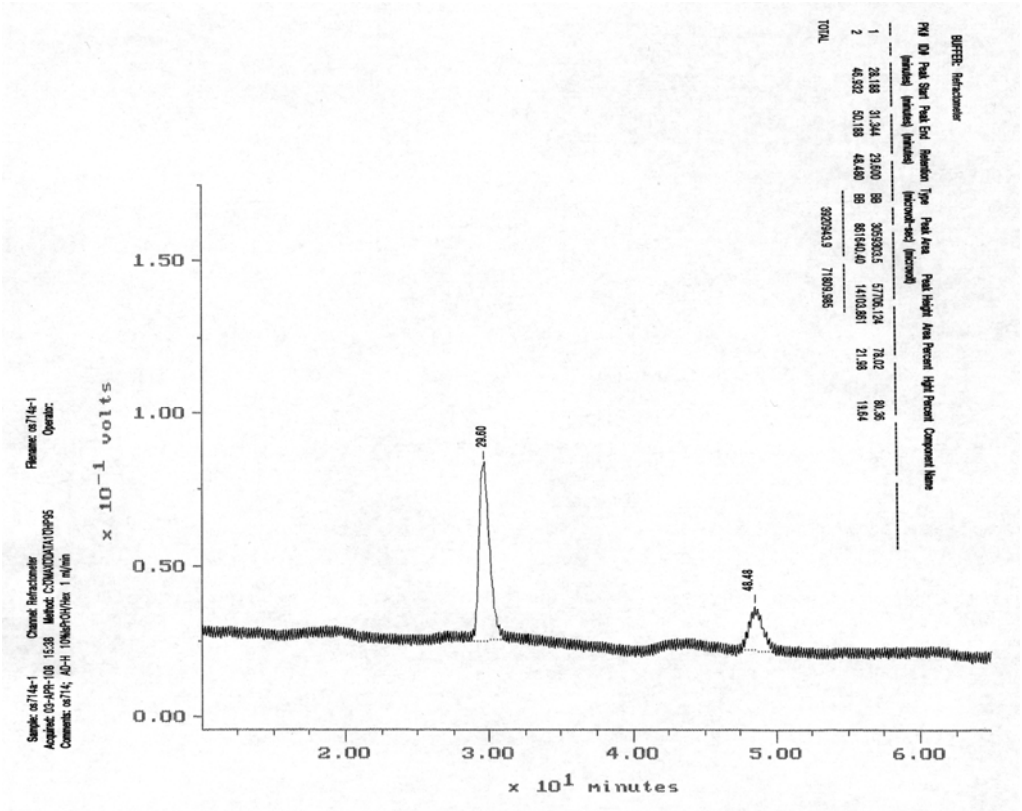
***cis*-(3*S*,4*R*)-3-ethyl-4-(naphthalen-1-yl)-1-p-nitrobenzenesulfonyl-3-phenylazetidin-2-one (Table 2. Entry 7.)**[7]

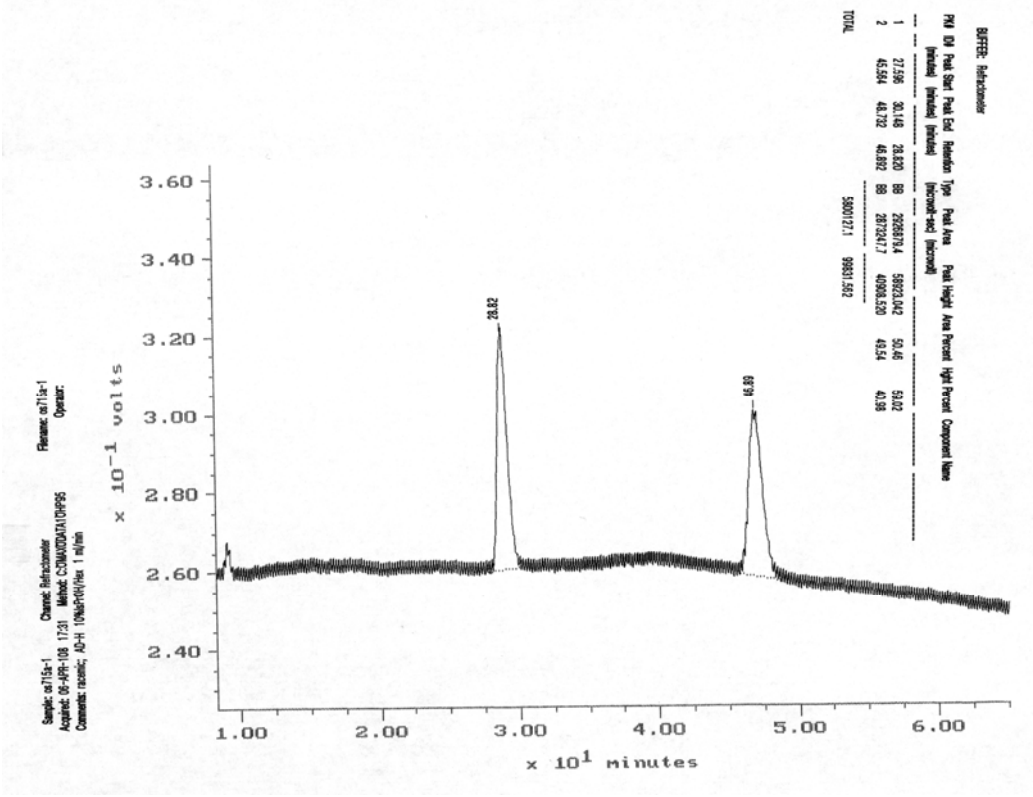


***trans*-(3*R*,4*R*)-4-(4-fluorophenyl)-3-methyl-1-p-nitrobenzenesulfonyl-3-phenylazetidin-2-one (Table 2. Entry 8.)**

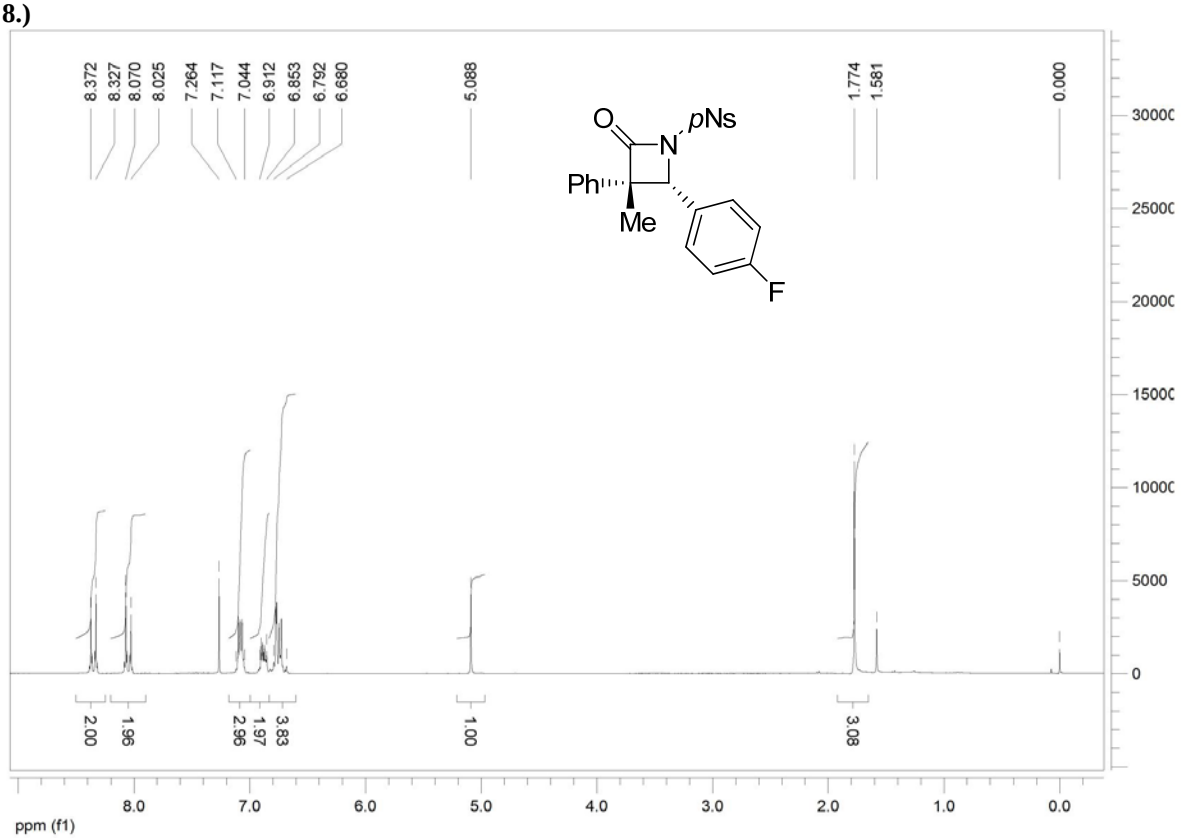


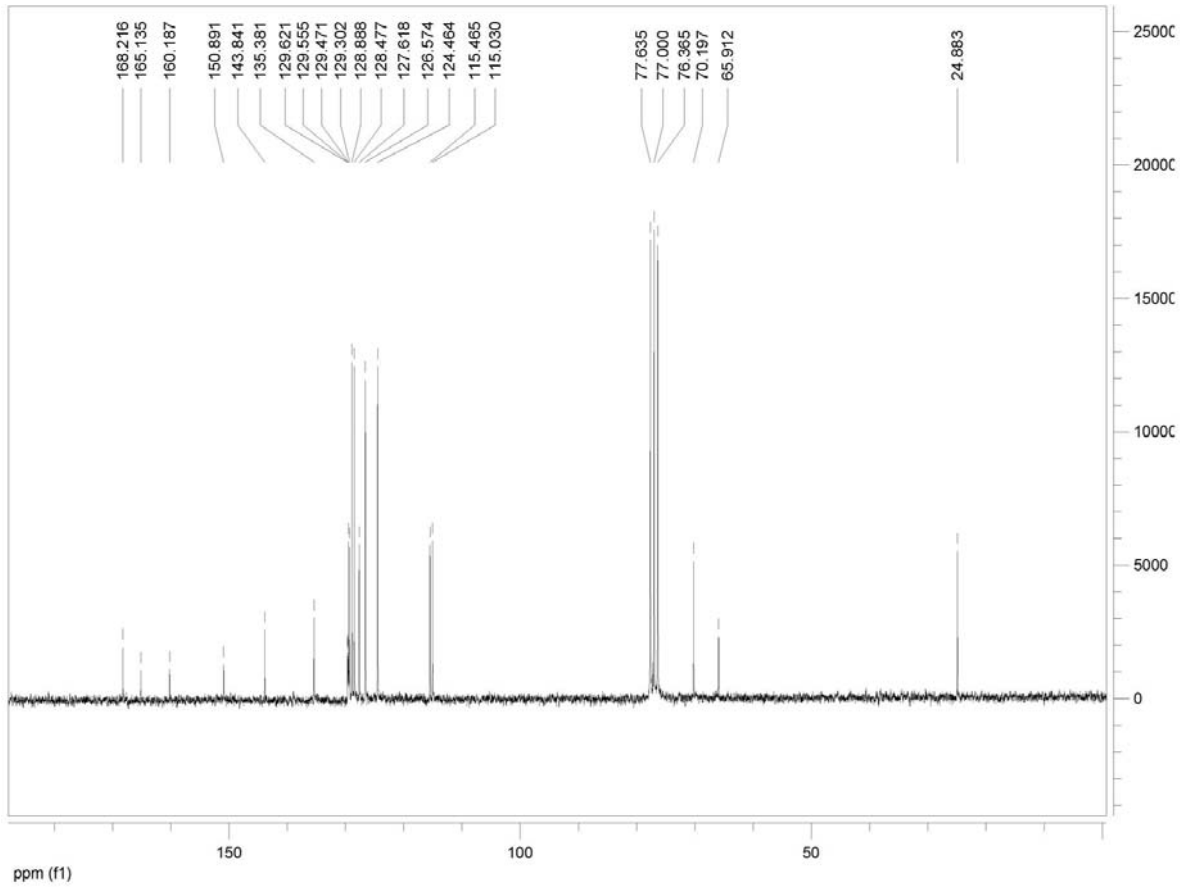


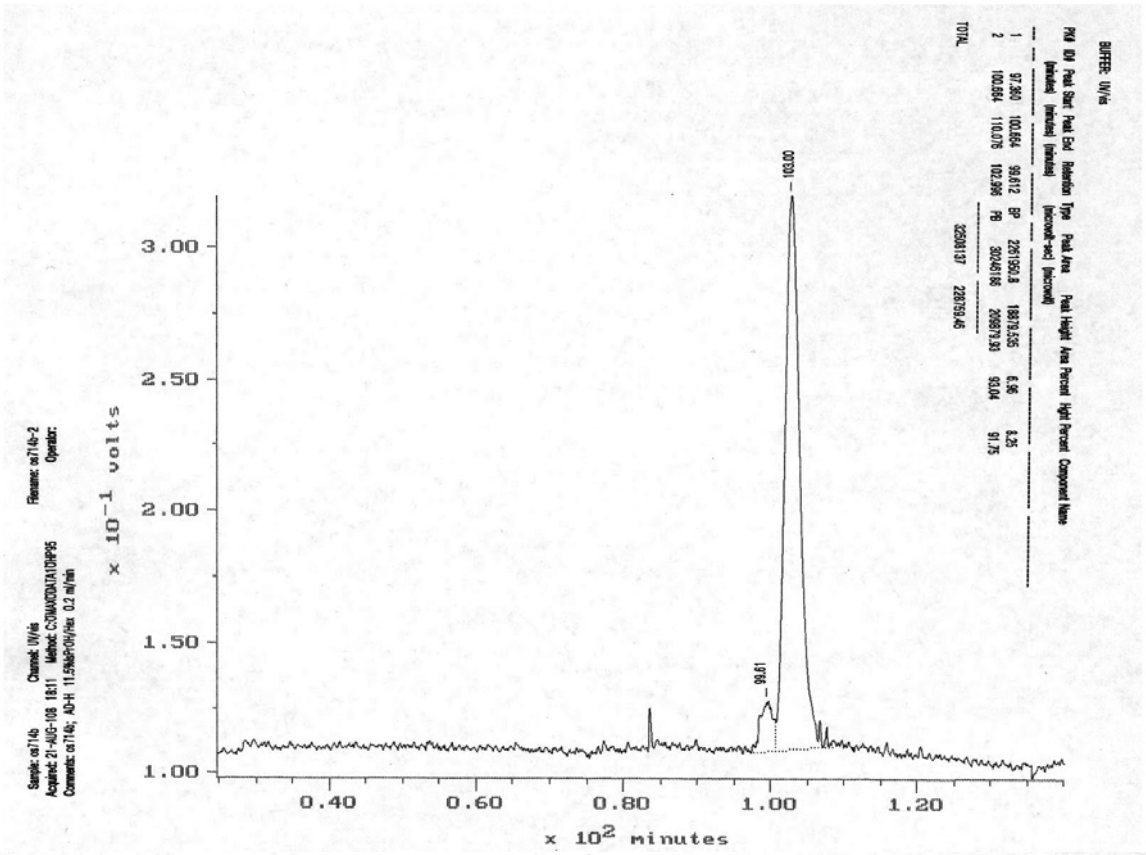

BUFFER: Refractometer
PK# RM Peak Start Peak End Retention Type Peak Area Peak Height Area Percent Hght Percent Component Name
(minutes) (minutes) (minutes) (microvolt-sec) (microvolt)
1 28.188 31.944 29.600 BB 3059303.5 57706.124 78.02 80.36
2 48.932 50.108 48.480 BB 861640.40 14103.861 21.98 19.64
TOTAL 3920943.9 71809.985
Sample: os714a-1 Channel: Refractometer Filename: os714a-1
Acquired: 03-APR-108 15:38 Method: C:\DAVIDDATA\1\DVP95 Operator:
Comment: os714; AD-H 10%IsPrOH/Hex 1 ml/min
x 10⁻¹ volts
1.50
1.00
0.50
0.00
28.60
48.79
2.00
3.00
4.00
5.00
6.00
x 10¹ minutes

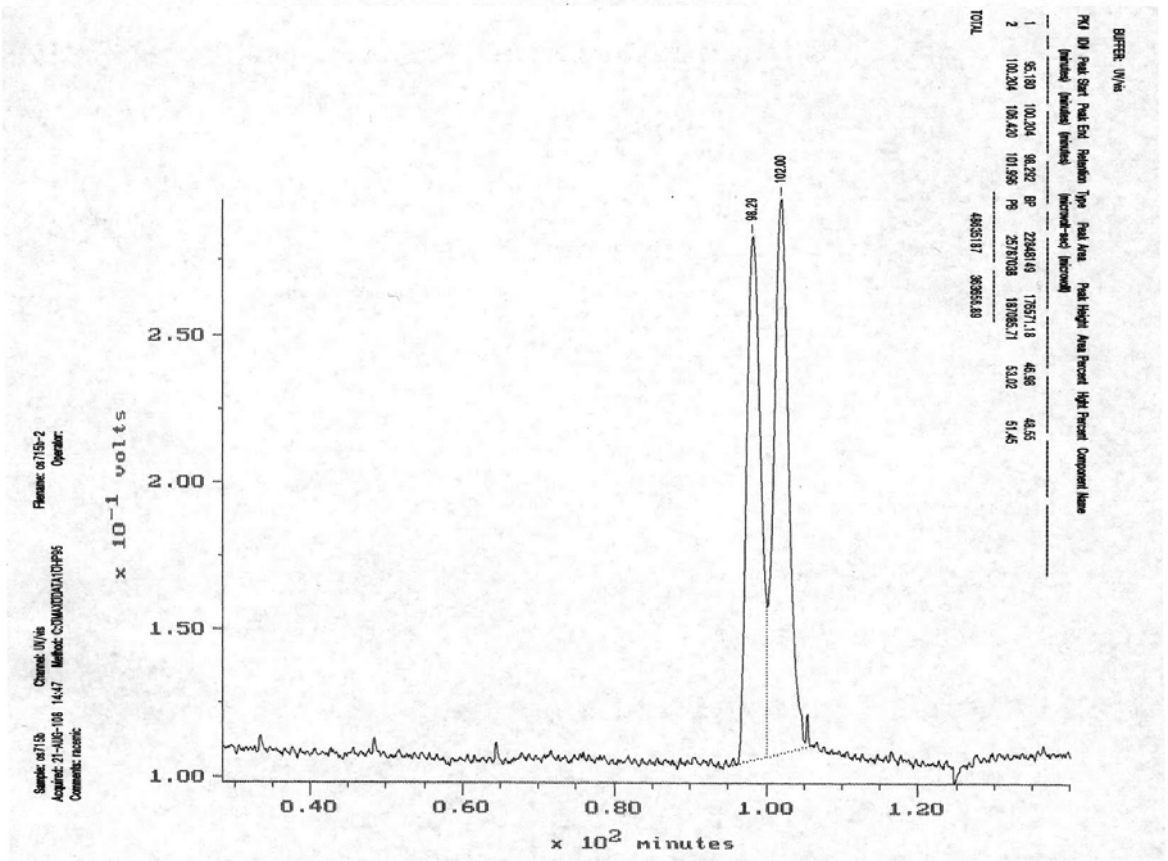

BUFFER: Refractometer
PK# RM Peak Start Peak End Retention Type Peak Area Peak Height Area Percent Hght Percent Component Name
(minutes) (minutes) (minutes) (microvolt-sec) (microvolt)
1 27.596 30.148 28.820 BB 2926878.4 58923.042 50.46 59.02
2 45.564 48.732 46.892 BB 2872241.7 40906.520 49.54 40.98
TOTAL 5800127.1 99831.562
Sample: os715a-1 Channel: Refractometer Filename: os715a-1
Acquired: 06-APR-108 17:31 Method: C:\DAVIDDATA\1\DVP95 Operator:
Comment: racemic; AD-H 10%IsPrOH/Hex 1 ml/min
x 10⁻¹ volts
3.60
3.40
3.20
3.00
2.80
2.60
2.40
28.82
46.96
1.00
2.00
3.00
4.00
5.00
6.00
x 10¹ minutes

***cis*-(3*S*,4*R*)-4-(4-fluorophenyl)-3-methyl-1-p-nitrobenzenesulfonyl-3-phenylazetidin-2-one (Table 2. Entry 8.)**

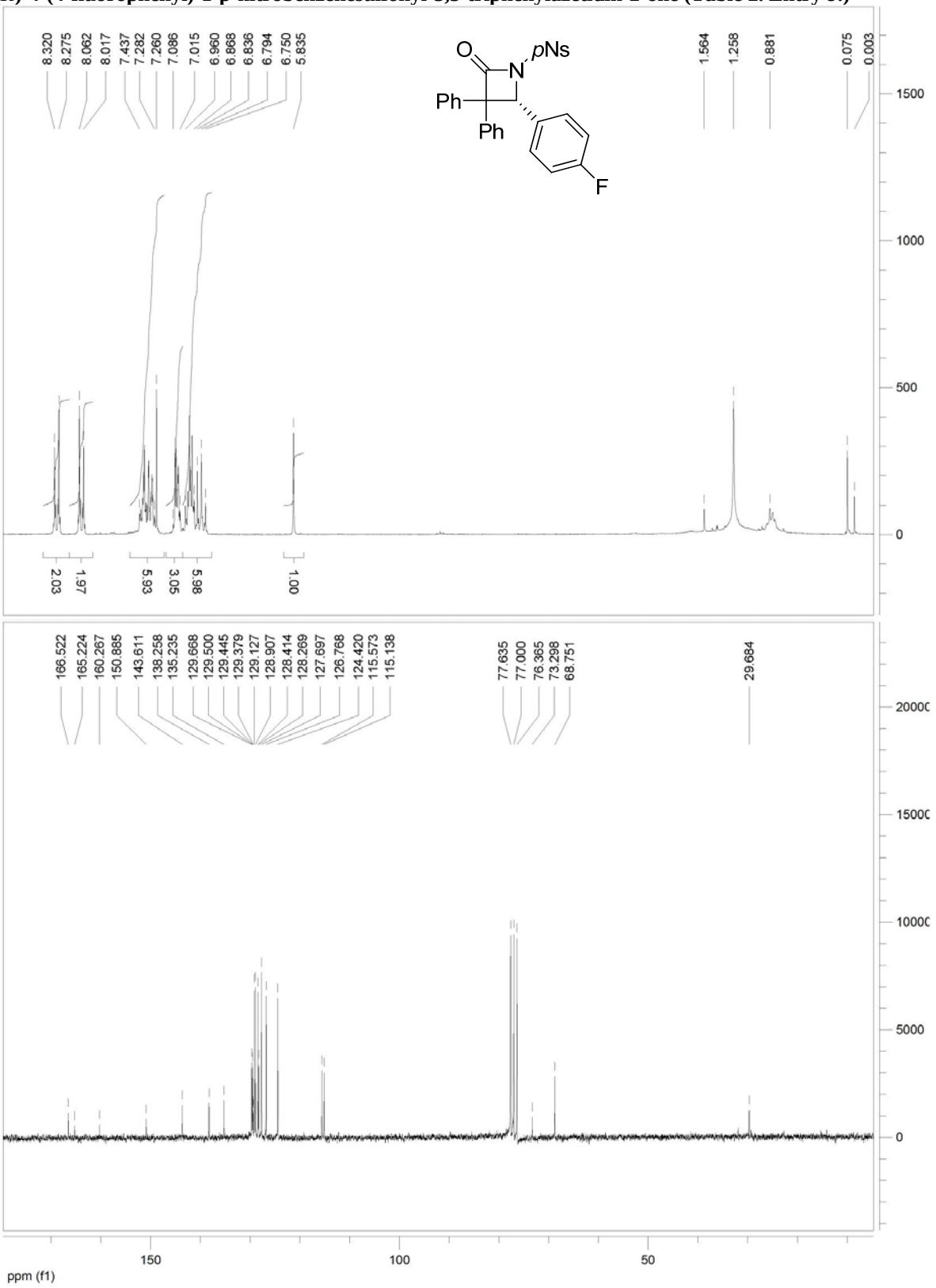


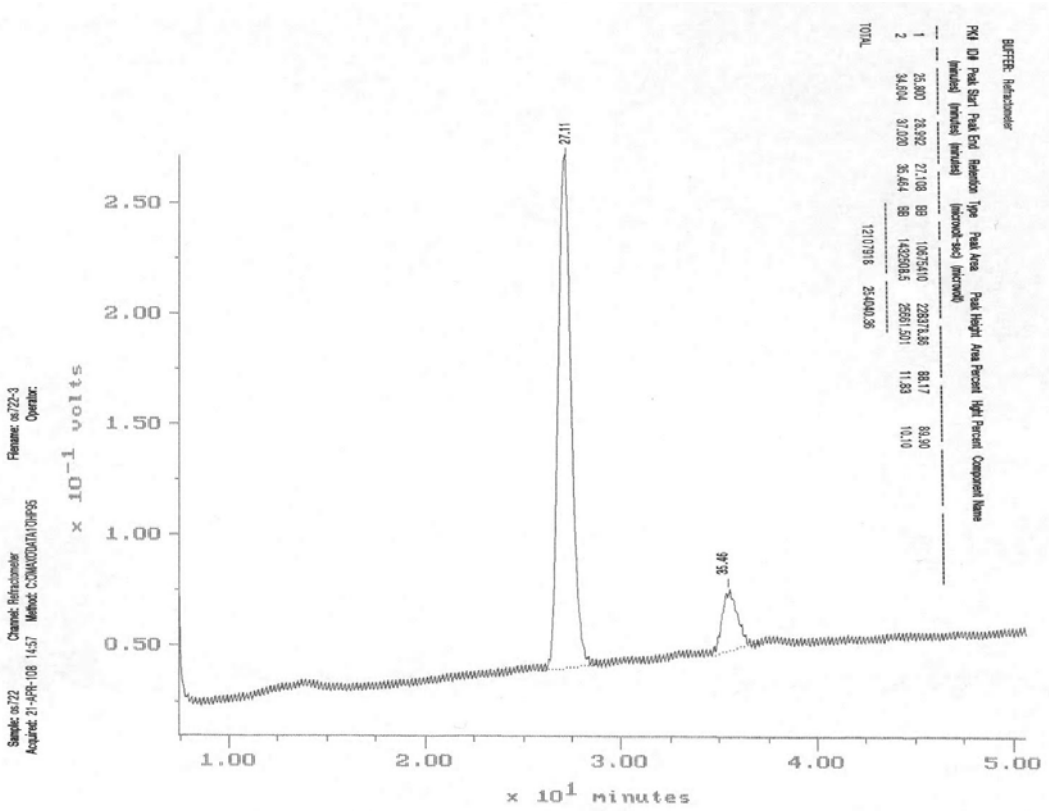


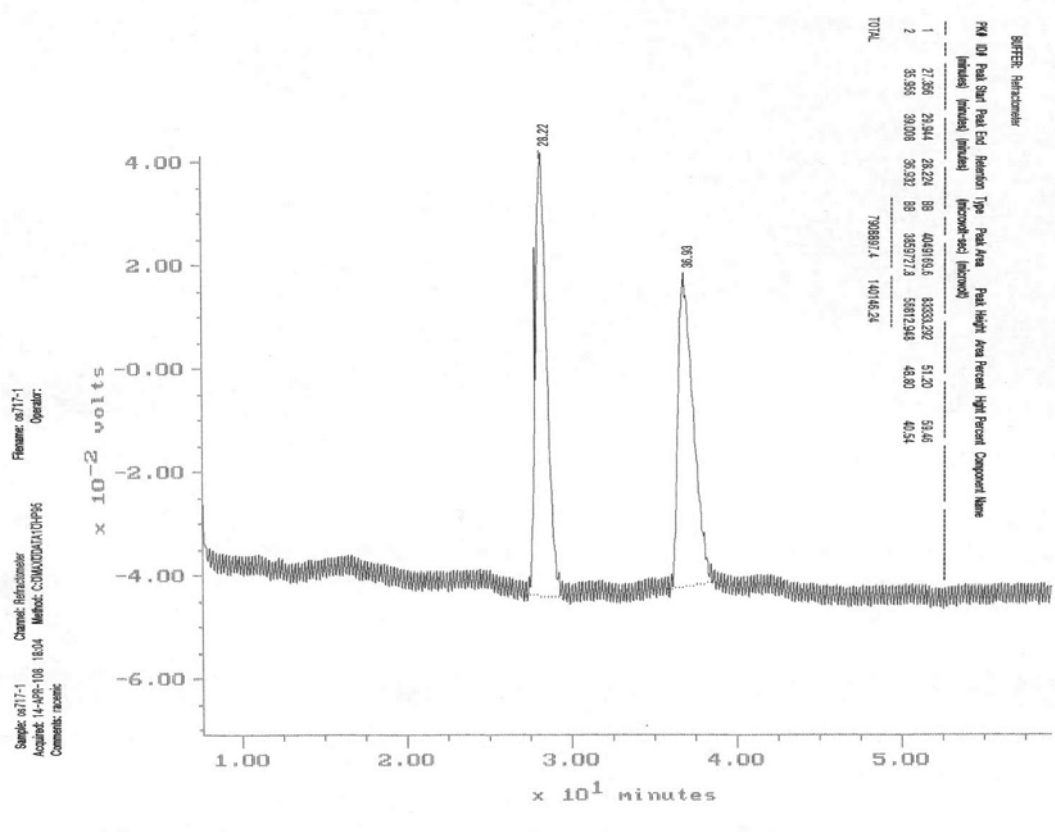

BUFFER: UV/vis
PK# RT# Peak Start Peak End Retention Type Peak Area Peak Height Area Percent Hght Percent Component Name
(minutes) (minutes) (minutes) (microvolt-sec) (microvolt)
1 97.360 100.884 99.612 BP 2261950.8 18879.535 6.96 8.25
2 100.884 110.076 102.996 PB 30249168 209979.93 93.04 91.75
TOTAL 32509137 228769.46
Sample: os714b Channel: UV/vis Filename: os714b-2
Acquired: 21-AUG-108 18:11 Method: C:\DMAX\DATA1\DHP95 Operator:
Comments: os714b; AD-H 11.5%isPrOH/Hex 0.2 ml/min
99.61
100.00
x 10-1 volts
3.00
2.50
2.00
1.50
1.00
0.40
0.60
0.80
1.00
1.20
x 10^2 minutes


BUFFER: UV/vis
PK# RT# Peak Start Peak End Retention Type Peak Area Peak Height Area Percent Hght Percent Component Name
(minutes) (minutes) (minutes) (microvolt-sec) (microvolt)
1 95.180 100.204 98.292 BP 2284814.9 176571.18 46.98 48.55
2 100.204 109.420 101.996 PB 25781038 187085.71 53.02 51.45
TOTAL 48835187 363656.89
Sample: os715b Channel: UV/vis Filename: os715b-2
Acquired: 21-AUG-108 14:47 Method: C:\DMAX\DATA1\DHP95 Operator:
Comments: racemic
98.29
100.00
x 10-1 volts
2.50
2.00
1.50
1.00
0.40
0.60
0.80
1.00
1.20
x 10^2 minutes

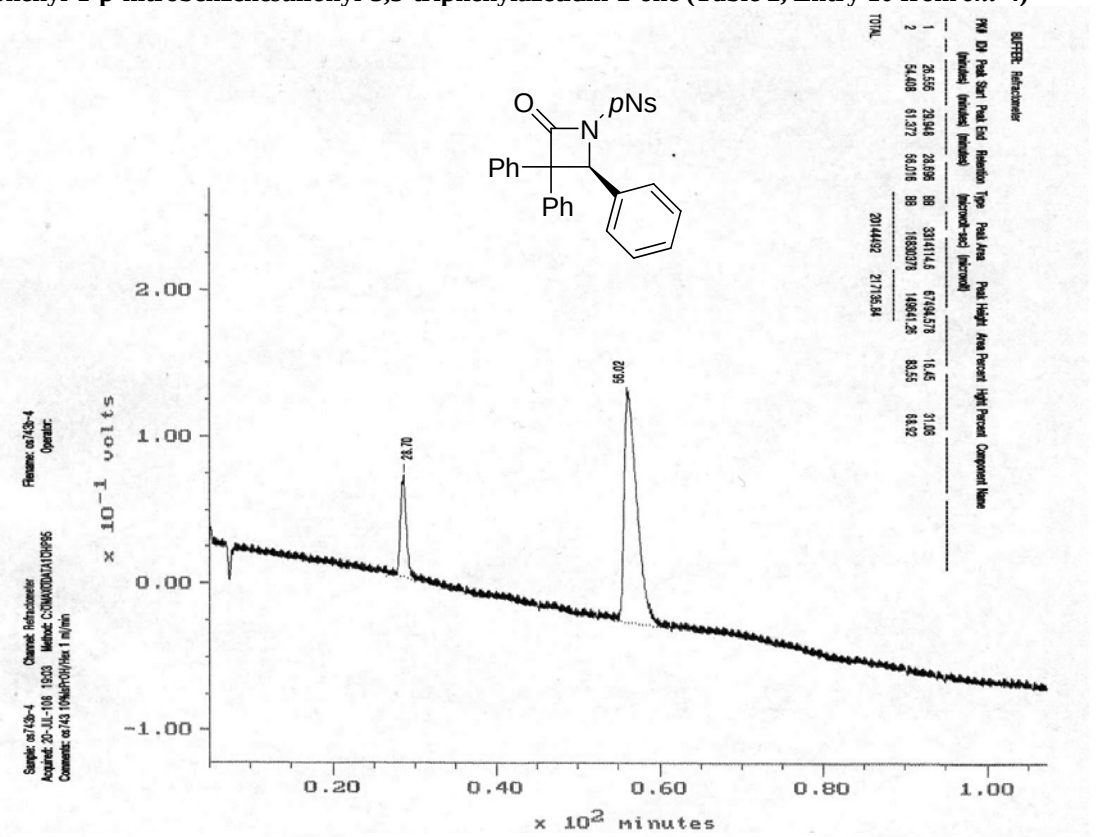
(*R*)-4-(4-fluorophenyl)-1-p-nitrobenzenesulfonyl-3,3-triphenylazetidin-2-one (Table 2. Entry 9.)

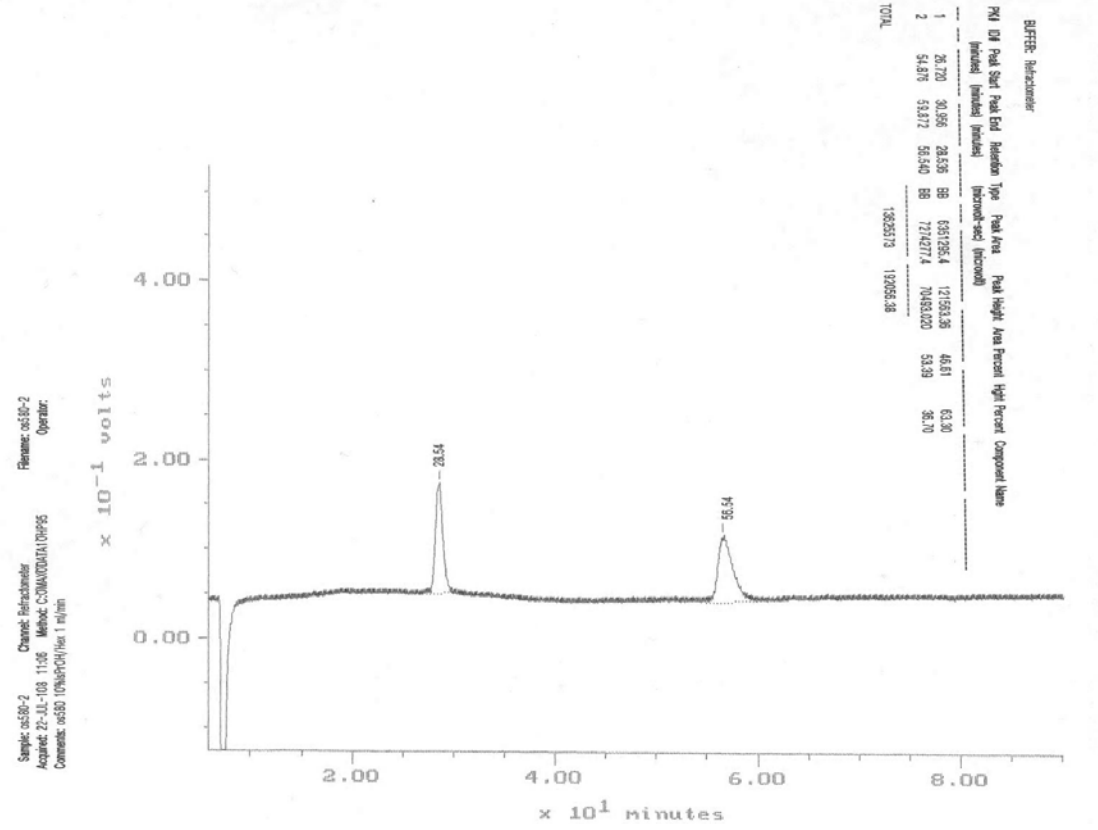



BUFFER: Refractometer
PK# ID# Peak Start Peak End Retention Type Peak Area Peak Height Area Percent Hight Percent Component Name
(minutes) (minutes) (minutes) (microvolt-sec) (microvolt)
1 25.900 28.992 27.108 BB 10675410 2283716.86 88.17 89.90
2 34.604 37.020 36.464 BB 1429508.5 256561.501 11.83 10.10
TOTAL 12107918 2540040.36
2711
36.49
Sample: os722 Channel: Refractometer Filename: os722-3
Acquired: 21-APR-108 14:57 Method: C:\DMAX\DATA\10HP95 Operator:
x 10-1 volts
2.50
2.00
1.50
1.00
0.50
1.00
2.00
3.00
4.00
5.00
x 10^1 minutes


BUFFER: Refractometer
PK# ID# Peak Start Peak End Retention Type Peak Area Peak Height Area Percent Hight Percent Component Name
(minutes) (minutes) (minutes) (microvolt-sec) (microvolt)
1 27.366 29.944 28.224 BB 4049169.6 833533.292 51.20 53.46
2 35.955 39.008 36.592 BB 3859727.8 58812.948 48.80 40.54
TOTAL 7909897.4 1401146.24
2827
36.36
Sample: os717-1 Channel: Refractometer Filename: os717-1
Acquired: 14-APR-108 18:04 Method: C:\DMAX\DATA\10HP95 Operator:
Comments: racemic
x 10-2 volts
4.00
2.00
-0.00
-2.00
-4.00
-6.00
1.00
2.00
3.00
4.00
5.00
x 10^1 minutes

(*S*)-4-phenyl-1-p-nitrobenzenesulfonyl-3,3-triphenylazetidin-2-one (Table 2, Entry 10 from *ent*-4)[7]





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