Evaluation of 3,3'-Triazolyl Biisoquinoline N,N'-dioxide Catalysts for Asymmetric Transfer Hydrogenation of Hydrazones with Trichlorosilane

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1. General Information.

All reactions were carried out in oven- or flame-dried glassware under an atmosphere of dry argon or nitrogen unless otherwise noted. Except as otherwise indicated, all reactions were magnetically stirred and monitored by analytical thin-layer chromatography using SiliCycle® Inc. and EMD Millipore pre-coated silica gel plates with F_{254} indicator. Visualization was accomplished by UV light (254 nm) with combination of potassium permanganate. Flash column chromatography was performed according to the method of Still [1] using silica gel 60 (mesh 230-400) supplied by SiliCycle® Inc. Yields refer to chromatographically and spectroscopically pure compounds, unless otherwise stated.

Commercial grade reagents and solvents were purchased from Sigma-Aldrich, Alfa-Aesar, Acros, Fisher, TCI, and VWR, and were used as received without further purification except as indicated below. Trichlorosilane was distilled over calcium hydride under an atmosphere of dry nitrogen prior to use. Dichloromethane, chloroform, and acetonitrile were freshly distilled over calcium hydride under an atmosphere of dry nitrogen prior to use. Tetrahydrofuran was freshly distilled over sodium and benzophenone under an atmosphere of dry nitrogen prior to use.

All racemic hydrazine samples were prepared by sodium cyanoborohydride reduction of corresponding hydrazones.

All ^{1}H NMR and ^{13}C NMR spectra were obtained using a Bruker 400 Ultrashield or an Oxford AS400 Spectrometer (^{1}H 400 MHz, ^{13}C 100 MHz) at ambient temperature in $CDCl_3$ purchased from Cambridge Isotope Laboratories, Inc. Chemical shifts in ^{1}H NMR spectra are reported in parts per million (ppm) respective to tetramethylsilane (δ

0.00 ppm) unless otherwise noted. The proton spectra are reported as follows δ (multiplicity, coupling constant *J*, number of protons). Multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad). Chemical shifts in ^{13}C NMR spectra are reported in ppm respective to $CDCl_3$ (δ 77.0 ppm). All ^{13}C NMR spectra were recorded with complete proton decoupling. Infrared (IR) spectra were recorded using a Nicolet iS5 FT-IR instrument. MS data were obtained using an Agilent 6100 Quadrupole LC/MS. HRMS data were obtained at USF Mass Spec and Peptide Core Facility in Department of Chemistry at University of South Florida. Optical rotations were measured using a Jasco P2000 Polarimeter at 589 nm and were reported as $[\alpha]_D^{T\,^\circ C}$, where C is reported in g/mL.

2. Experimental Procedures.

Preparation of Hydrazones.

All hydrazones were prepared accordingly to the reported procedure. [2]

Preparation of Catalysts.

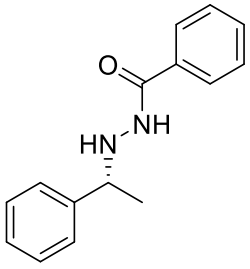
Catalysts **2a**-**d** were prepared accordingly to our published procedure. [3]

Catalysts **2e**,**f** were prepared accordingly to our published procedure. [4]

Catalytic Asymmetric Transfer Hydrogenation with Trichlorosilane.

Representative Procedure:

(*R*)-*N*'-(1-Phenylethyl)benzohydrazide (3a):



A flame-dried test tube with a magnetic stir bar was charged with hydrazone **1a** (60 mg, 0.25 mmol), catalyst **2a** (15 mg, 0.025 mmol) and CH_2Cl_2 (1.0 mL), cooled to –50 °C, and then treated slowly with a solution of $HSiCl_3$ in CH_2Cl_2 (250 µL, 1.5 M). The reaction mixture was stirred at –40 °C for 20 hours, and then quenched by pouring it into 30 mL of saturated aqueous $NaHCO_3$ solution cooled to 0 °C. The resulting mixture was vigorously stirred for 30 min at room temperature and extracted twice with 15 mL of CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, filtered, and condensed *in vacuo*. A ^1H NMR spectrum of the crude reaction mixture was taken with 1,1,2,2-tetracholoroethane as an internal standard (48% NMR yield). A fraction of the crude mixture was purified by prep TLC using 20% EtOAc in CH_2Cl_2 as an eluent for characterization purposes.

All spectral data were consistent with the literature values.[2]

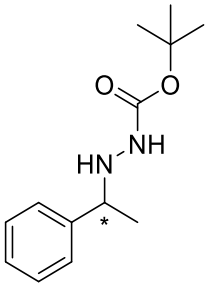
^1H NMR (400 MHz, $CDCl_3$) δ 7.63-7.60 (m, 2H), 7.50-7.46 (m, 1H), 7.42-7.34 (m, 7H), 7.32-7.27 (m, 1H), 5.10 (br d, *J* = 4.8 Hz, 1H), 4.26 (q, *J* = 6.8 Hz, 1H), 1.44 (d, *J* = 6.8 Hz, 3H).

ee = 53 %; $[\alpha]^{22}_{D}$ = +7.4 (c = 0.00067, CH_2Cl_2); The enantiomeric excess and the absolute stereochemistry were determined by HPLC analysis:[2] t_R (major) = 19.95 min; t_R (minor) = 29.01 min (Daicel Chiralcel® OJ-H with an OJ-H guard column, hexane/2-propanol = 90:10, 0.5mL/min).

The 1.0 mmol scale reaction:

A flame-dried Schlenck tube with a magnetic stir bar was charged with hydrazone **1a** (238 mg, 1.00 mmol), catalyst **2a** (60 mg, 0.10 mmol) and CH_2Cl_2 (4.0 mL), cooled to –50 °C, and then treated slowly with a solution of $HSiCl_3$ in CH_2Cl_2 (1.0 mL, 1.5 M). The reaction mixture was stirred at –40 °C for 20 hours, and then quenched by pouring it into 120 mL of saturated aqueous $NaHCO_3$ solution cooled to 0 °C. The resulting mixture was vigorously stirred for 30 min. at room temperature and extracted twice with 60 mL of CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, filtered, and condensed *in vacuo*. A ^1H NMR spectrum of the crude reaction mixture was taken with 1,1,2,2-tetracholoroethane as an internal standard (40% NMR yield). The crude material was purified by flash column chromatography on silica gel with 2% Et_2O in CH_2Cl_2 to afford the title compound as a white solid (90 mg, 37%), followed by 50% EtOAc in CH_2Cl_2 to recover catalyst **2a** (60 mg, >99%).

(+)-*tert*-Butyl 2-(1-phenylethyl)hydrazinecarboxylate (3b):



A ^1H NMR spectrum of the crude reaction mixture was taken with 1,1,2,2-tetracholoroethane as an internal standard (36% NMR yield). A fraction of the crude

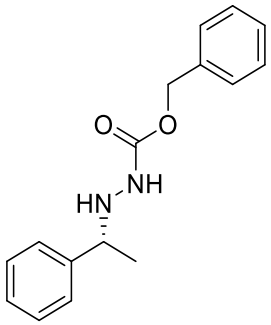
mixture was purified by prep TLC using 5% EtOAc in CH_2Cl_2 as an eluent for characterization purposes.

All spectral data were consistent with the literature values.[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.26 (m, 5H), 5.97 (br s, 1H), 4.18 (br s, 2H), 1.44 (s, 9H), 1.33 (d, *J* = 6.8 Hz, 3H).

ee = approximately 71 %; $[\alpha]^{23}_{D}$ = +39.3 (c = 0.00067, CH_2Cl_2); The enantiomeric excess was estimated by HPLC analysis as both enantiomers were not fully separated at the base line: t_R (major) = 20.63 min; t_R (minor) = 17.25 min (Daicel Chiralcel® OJ-H with an OJ-H guard column, hexane/2-propanol = 99:1, 0.5mL/min).

(*R*)-Benzyl-2-(1-phenylethyl)hydrazine-1-carboxylate (3c):



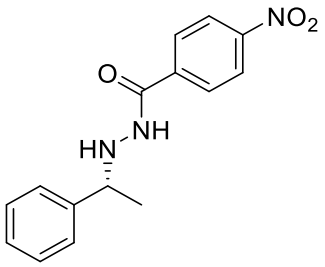
A ^{1}H NMR spectrum of the crude reaction mixture was taken with 1,1,2,2-tetracholoroethane as an internal standard (21% NMR yield). A fraction of the crude mixture was purified by prep TLC using 5% EtOAc in CH_2Cl_2 as an eluent for characterization purposes.

All spectral data were consistent with the literature values.[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.27 (m, 10H), 6.13 (br s, 1H), 5.12 (s, 2H), 4.21 (br s, 2H), 1.34 (d, *J* = 6.4 Hz, 3H).

ee = 64 %; $[\alpha]^{23}_{D}$ = +60.4 (c = 0.00067, CH_2Cl_2); The enantiomeric excess and the absolute stereochemistry were determined by HPLC analysis:[6] t_R (major) = 43.57 min; t_R (minor) = 33.45 min (Daicel Chiralcel® OJ-H with an OJ-H guard column, hexane/2-propanol = 90:10, 0.5mL/min).

(*R*)-1-Phenyl-1-(2-*p*-nitrobenzoylhydrazino)ethane (3d):



A ^{1}H NMR spectrum of the crude reaction mixture was taken with 1,1,2,2-tetracholoroethane as an internal standard (14% NMR yield). A fraction of the crude mixture was purified by prep TLC using 20% EtOAc in CH_2Cl_2 as an eluent for characterization purposes.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.8 Hz, 2H), 7.77 (d, *J* = 8.8 Hz, 2H), 7.54 (d, *J* = 5.6 Hz, 1H), 7.41-7.29 (m, 5H), 5.11 (br d, *J* = 4.8 Hz, 1H), 4.26 (q, *J* = 6.4 Hz, 1H), 1.45 (d, *J* = 6.4 Hz, 3H).

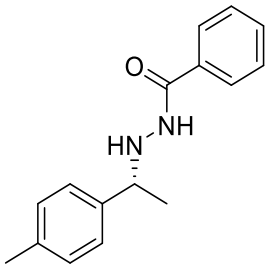
^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 149.8, 142.7, 138.5, 128.7, 128.1, 127.8, 127.2, 123.9, 60.1, 21.3.

IR (thin film): 3276, 2973, 1642, 1522, 1343, 867, 848, 760, 715, 699 cm^{-1}

HRMS (ESI): Exact mass calculated for $C_{15}H_{16}N_3O_3^+$ $[M+H]^+$ expected: 286.1186, found: 286.1188.

ee = 69 %; [α] $^{23}_{D}$ = +84.9 (c = 0.00067, CH_2Cl_2); The enantiomeric excess and the absolute stereochemistry were determined by HPLC analysis:[7] t_R (major) = 57.56 min; t_R (minor) = 51.44 min (Daicel Chiralcel® OJ-H with an OJ-H guard column, hexane/2-propanol = 90:10, 0.5mL/min).

(*R*)-*N*'-(1-(*p*-Tolyl)ethyl)benzohydrazide (3e):



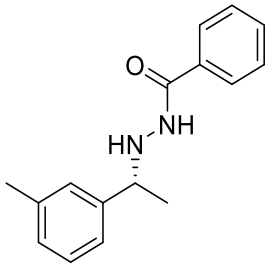
A ^{1}H NMR spectrum of the crude reaction mixture was taken with 1,1,2,2-tetracholoroethane as an internal standard (27% NMR yield). A fraction of the crude mixture was purified by prep TLC using 20% EtOAc in CH_2Cl_2 as an eluent for characterization purposes.

All spectral data were consistent with the literature values.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.61 (m, 2H), 7.51-7.47 (m, 1H), 7.41-7.38 (m, 3H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 5.09 (b rs, 1H), 4.23 (q, *J* = 6.8 Hz, 1H), 2.36 (s, 3H), 1.42 (d, *J* = 6.8 Hz, 3H).

ee = 57 %; [α] $^{23}_{D}$ = +8.5 (c = 0.00067, CH_2Cl_2); The enantiomeric excess and the absolute stereochemistry were determined by HPLC analysis:[2] t_R (major) = 17.27 min; t_R (minor) = 31.13 min (Daicel Chiralcel® OJ-H with an OJ-H guard column, hexane/2-propanol = 90:10, 0.5mL/min).

(*R*)-*N*'-(1-(m-Tolyl)ethyl)benzohydrazide (3f):



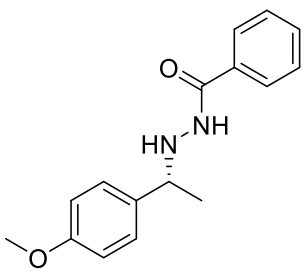
A ^{1}H NMR spectrum of the crude reaction mixture was taken with 1,1,2,2-tetracholoroethane as an internal standard (49% NMR yield). A fraction of the crude mixture was purified by prep TLC using 20% EtOAc in CH_2Cl_2 as an eluent for characterization purposes.

All spectral data were consistent with the literature values.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.2 Hz, 2H), 7.51-7.38 (m, 4H), 7.26-7.19 (m, 3H), 7.11 (d, *J* = 7.2 Hz, 1H), 5.10 (br s, 1H), 4.22 (q, *J* = 6.8 Hz, 1H), 2.36 (s, 3H), 1.43 (d, *J* = 6.8 Hz, 3H).

ee = 41 %; $[\alpha]^{22}_{D}$ = +29.0 (c = 0.0013, CH_2Cl_2); The enantiomeric excess and the absolute stereochemistry were determined by HPLC analysis:[2] t_R (major) = 25.65 min; t_R (minor) = 29.36 min (Daicel Chiralcel® OJ-H with an OJ-H guard column, hexane/2-propanol = 95:5, 0.5mL/min).

(*R*)-*N*'-(1-(4-Methoxyphenyl)ethyl)benzohydrazide (3h):



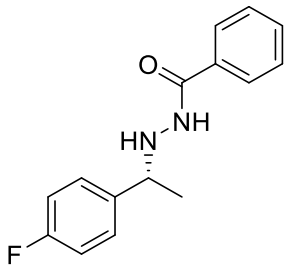
A ^{1}H NMR spectrum of the crude reaction mixture was taken with 1,1,2,2-tetracholoroethane as an internal standard (12% NMR yield). A fraction of the crude mixture was purified by prep TLC using 20% EtOAc in CH_2Cl_2 as an eluent for characterization purposes.

All spectral data were consistent with the literature values.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.61 (m, 2H), 7.51-7.47 (m, 1H), 7.42-7.38 (m, 3H), 7.34-7.31 (m , 2H), 6.91-6.88 (m, 2H), 5.08 (b rs, 1H), 4.22 (q, *J* = 6.8 Hz, 1H), 3.82 (s, 3H), 1.42 (d, *J* = 6.8 Hz, 3H).

ee = 58 %; $[\alpha]^{22}_{D}$ = +23.8 (c = 0.0013, CH_2Cl_2); The enantiomeric excess and the absolute stereochemistry were determined by HPLC analysis:[2] t_R (major) = 35.59 min; t_R (minor) = 59.24 min (Daicel Chiralcel® OJ-H with an OJ-H guard column, hexane/2-propanol = 90:10, 0.5mL/min).

(*R*)-*N*'-(1-(4-Fluorophenyl)ethyl)benzohydrazide (3i):



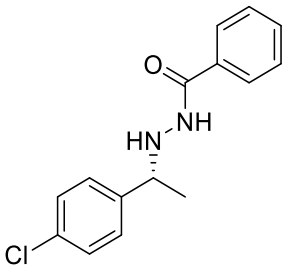
A ^{1}H NMR spectrum of the crude reaction mixture was taken with 1,1,2,2-tetracholoroethane as an internal standard (28% NMR yield). A fraction of the crude mixture was purified by prep TLC using 20% EtOAc in CH_2Cl_2 as an eluent for characterization purposes.

All spectral data were consistent with the literature values.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.61 (m, 2H), 7.52-7.35 (m, 6H), 7.04 (dd, J= 8.4, 8.4 Hz, 2H), 5.06 (br s, 1H), 4.26 (q, *J* = 6.8 Hz, 1H), 1.41 (d, *J* = 6.8 Hz, 3H).

ee = 37 %; $[\alpha]^{23}_{D}$ = +3.4 (c = 0.00067, CH_2Cl_2); The enantiomeric excess and the absolute stereochemistry were determined by HPLC analysis:[2] t_R (major) = 21.37 min; t_R (minor) = 27.53 min (Daicel Chiralcel® OJ-H with an OJ-H guard column, hexane/2-propanol = 90:10, 0.5mL/min).

(*R*)-*N*'-(1-(4-Chlorophenyl)ethyl)benzohydrazide (3j):



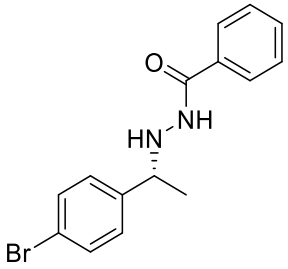
A ^{1}H NMR spectrum of the crude reaction mixture was taken with 1,1,2,2-tetracholoroethane as an internal standard (22% NMR yield). A fraction of the crude mixture was purified by prep TLC using 20% EtOAc in CH_2Cl_2 as an eluent for characterization purposes.

All spectral data were consistent with the literature values.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.2 Hz, 2H), 7.52-7.48 (m, 1H), 7.42-7.29 (m, 7H), 5.05 (br d, *J* = 4.8 Hz, 1H), 4.27-4.23 (m, 1H), 1.41 (d, *J* = 6.4 Hz, 3H).

ee = 43 %; $[\alpha]^{23}_{D}$ = +50.4 (c = 0.00067, CH_2Cl_2); The enantiomeric excess and the absolute stereochemistry were determined by HPLC analysis:[2] t_R (major) = 20.97 min; t_R (minor) = 26.49 min (Daicel Chiralcel® OJ-H with an OJ-H guard column, hexane/2-propanol = 90:10, 0.5mL/min).

(*R*)-*N*'-(1-(4-Bromophenyl)ethyl)benzohydrazide (3k):



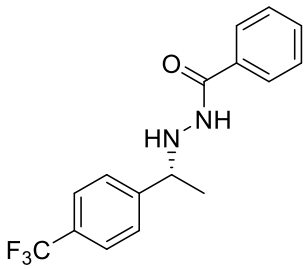
A ^{1}H NMR spectrum of the crude reaction mixture was taken with 1,1,2,2-tetracholoroethane as an internal standard (27% NMR yield). A fraction of the crude mixture was purified by prep TLC using 20% EtOAc in CH_2Cl_2 as an eluent for characterization purposes.

All spectral data were consistent with the literature values.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.6 Hz, 2H), 7.52-7.39 (m, 6H), 7.29 (d, *J* = 8.4 Hz, 2H), 5.06 (br s, 1H), 4.24 (q, *J* = 6.4 Hz, 1H), 1.40 (d, *J* = 6.4 Hz, 3H).

ee = 44 %; $[\alpha]^{23}_{D}$ = +50.7 (c = 0.002, CH_2Cl_2); The enantiomeric excess and the absolute stereochemistry were determined by HPLC analysis:[2] t_R (major) = 23.36 min; t_R (minor) = 29.21 min (Daicel Chiralcel® OJ-H with an OJ-H guard column, hexane/2-propanol = 90:10, 0.5mL/min).

(*R*)-*N*'-(1-(4-(Trifluoromethyl)phenyl)ethyl)benzohydrazide (3l):



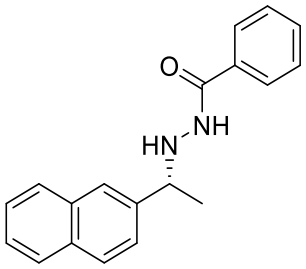
A ^{1}H NMR spectrum of the crude reaction mixture was taken with 1,1,2,2-tetracholoroethane as an internal standard (37% NMR yield). A fraction of the crude mixture was purified by prep TLC using 20% EtOAc in CH_2Cl_2 as an eluent for characterization purposes.

All spectral data were consistent with the literature values.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.61 (m, 4H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.51-7.48 (m, 1H), 7.42-7.38 (m, 3H), 5.07 (br d, *J* = 6.8 Hz, 1H), 4.37-4.32 (m, 1H), 1.44 (d, *J* = 6.8 Hz, 3H).

ee = 35 %; $[\alpha]^{23}_{D}$ = +56.1 (c = 0.00067, CH_2Cl_2); The enantiomeric excess and the absolute stereochemistry were determined by HPLC analysis:[6]: t_R (major) = 28.48 min; t_R (minor) = 25.77 min (Daicel Chiralpak® AS-H with an AS-H guard column, hexane/2-propanol = 80:20, 0.5mL/min).

(*R*)-*N*'-(1-(Naphthalen-2-yl)ethyl)benzohydrazide (3m):



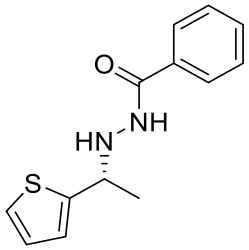
A ^{1}H NMR spectrum of the crude reaction mixture was taken with 1,1,2,2-tetracholoroethane as an internal standard (38% NMR yield). A fraction of the crude mixture was purified by prep TLC using 20% EtOAc in CH_2Cl_2 as an eluent for characterization purposes.

All spectral data were consistent with the literature values.[8]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.81 (m, 4H), 7.61-7.56 (m, 3H), 7.50-7.44 (m, 4H), 7.37-7.34 (m, 2H), 5.19 (br d, *J* = 5.2 Hz, 1H), 4.43 (q, *J* = 6.8 Hz, 1H), 1.51 (d, *J* = 6.8 Hz, 3H).

ee = 43 %; $[\alpha]^{23}_{D}$ = +82.4 (c = 0.00067, CH_2Cl_2); The enantiomeric excess and the absolute stereochemistry were determined by HPLC analysis:[8] t_R (major) = 36.05 min; t_R (minor) = 43.91 min (Daicel Chiralcel® OJ-H with an OJ-H guard column, hexane/2-propanol = 85:15, 0.5mL/min).

(*R*)-*N*'-(1-(Thiophen-2-yl)ethyl)benzohydrazide (3n):



A ^{1}H NMR spectrum of the crude reaction mixture was taken with 1,1,2,2-tetracholoroethane as an internal standard (33% NMR yield). A fraction of the crude mixture was purified by prep TLC using 20% EtOAc in CH_2Cl_2 as an eluent for characterization purposes.

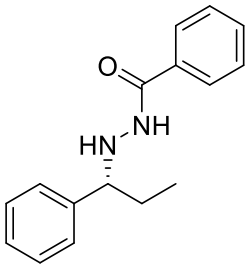
All spectral data were consistent with the literature values.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.2 Hz, 2H), 7.53-7.49 (m, 2H), 7.44-7.40 (m, 2H), 7.28-7.26 (m, 1H), 7.00-6.97 (m, 2H), 5.14 (br d, *J* = 4.8 Hz, 1H), 4.60-4.56 (m, 1H), 1.53 (d, *J* = 6.8 Hz, 3H).

ee = 38 %; $[\alpha]^{23}_{D}$ = +32.5 (c = 0.001, CH_2Cl_2); The enantiomeric excess and the absolute stereochemistry were determined by HPLC analysis:[2] t_R (major) = 26.72 min;

t_R (minor) = 32.39 min (Daicel Chiralcel® OJ-H with an OJ-H guard column, hexane/2-propanol = 90:10, 0.5mL/min).

(*R*)-*N'*-(1-Phenylpropyl)benzohydrazide (3o):



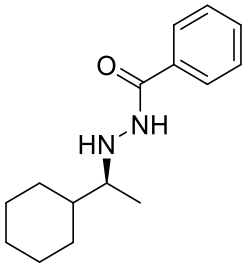
A ^{1}H NMR spectrum of the crude reaction mixture was taken with 1,1,2,2-tetracholoroethane as an internal standard (44% NMR yield). A fraction of the crude mixture was purified by prep TLC using 20% EtOAc in CH_2Cl_2 as an eluent for characterization purposes, which provided 2.5 mg of the title compound. The remaining crude mixture was purified by flash column chromatography on silica gel with 2% Et_2O in CH_2Cl_2 to afford 23 mg of the title compound (total 25.5 mg, 40%).

All spectral data were consistent with the literature values.[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.58 (m, 2H), 7.49-7.46 (m, 1H), 7.40-7.33 (m, 7H), 7.32-7.27 (m, 1H), 5.18 (br d, *J* = 5.6 Hz, 1H), 4.00 (br dd, *J* = 6.8, 7.2 Hz, 1H), 1.94-1.83 (m, 1H), 1.77-1.66 (m, 1H), 0.87 (t, *J* = 7.6 Hz, 3H).

ee = 36 %; $[\alpha]^{23}_{D}$ = +37.2 (c = 0.0013, CH_2Cl_2); The enantiomeric excess and the absolute stereochemistry were determined by HPLC analysis:[6] t_R (major) = 16.49 min; t_R (minor) = 19.55 min (Daicel Chiralcel® OJ-H with an OJ-H guard column, hexane/2-propanol = 90:10, 0.5mL/min).

(*S*)-*N*'-(1-Cyclohexylethyl)benzohydrazide (3p):



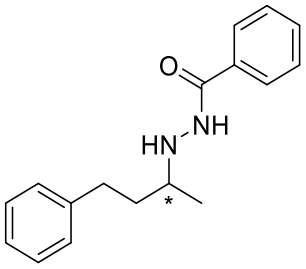
A ^{1}H NMR spectrum of the crude reaction mixture was taken with 1,1,2,2-tetracholoroethane as an internal standard (33% NMR yield). A fraction of the crude mixture was purified by prep TLC using 20% EtOAc in CH_2Cl_2 as an eluent for characterization purposes.

All spectral data were consistent with the literature values.[9]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.74 (m, 2H), 7.54-7.43 (m, 4H), 4.89 (br s, 1H), 2.94-2.88 (m, 1H), 1.78-1.67 (m, 6H), 1.47-1.40 (m, 1H), 1.31-1.09 (m, 4H), 1.06 (d, *J* = 6.4 Hz, 3H).

ee = 46 %; $[\alpha]^{21}_{D}$ = +4.1 (c = 0.001, CH_2Cl_2); The enantiomeric excess and the absolute stereochemistry were determined by HPLC analysis:[9] t_R (major) = 36.08 min; t_R (minor) = 41.83 min (Daicel Chiralcel® OJ-H with an OJ-H guard column, hexane/2-propanol = 99:1, 0.5mL/min).

(+)-*N*'-(4-Phenylbutan-2-yl)benzohydrazide (3q):



A ^{1}H NMR spectrum of the crude reaction mixture was taken with 1,1,2,2-tetracholoroethane as an internal standard (48% NMR yield). A fraction of the crude mixture was purified by prep TLC using 20% EtOAc in CH_2Cl_2 as an eluent for characterization purposes, which provided 3 mg of the title compound. The remaining crude mixture was purified by flash column chromatography on silica gel with 2% Et_2O in CH_2Cl_2 and then with 5% Et_2O in CH_2Cl_2 to afford 26 mg of the title compound (total 29 mg, 43%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.72 (m, 2H), 7.55-7.43 (m, 4H), 7.31-7.17 (m, 5H), 4.91 (br s, 1H), 3.17-3.12 (m, 1H), 2.80-2.65 (m, 2H), 1.94-1.85 (m, 1H), 1.73-1.61 (m, 1H), 1.18 (d, *J* = 6.4 Hz, 3H).

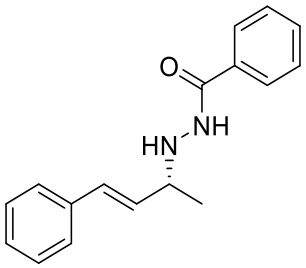
^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 142.1, 132.9, 131.8, 128.7, 128.4, 128.3, 126.8, 125.8, 55.6, 36.7, 32.1, 18.6.

IR (thin film): 3315, 1640, 1539, 1472, 1456, 1377, 905, 894, 854, 729, 696 cm^{-1}

HRMS (ESI): Exact mass calculated for $C_{17}H_{21}N_2O^+$ $[M+H]^+$ expected: 269.1648, found: 269.1652.

ee = 14 %; $[\alpha]^{21}_{D}$ = +4.7 (c = 0.002, CH_2Cl_2); The enantiomeric excess was determined by HPLC analysis: t_R (major) = 37.17 min; t_R (minor) = 30.40 min (Daicel Chiralcel® OD-H with an OD-H guard column, hexane/2-propanol = 90:10, 0.5mL/min).

(*R*)-*N*'-(4-Phenyl-3-buten-2-yl)benzohydrazide (3r):



A ^{1}H NMR spectrum of the crude reaction mixture was taken with 1,1,2,2-tetracholoroethane as an internal standard (**3r:** 4% NMR yield; **3q**: 19% NMR yield). A fraction of the crude mixture was purified by prep TLC using 20% EtOAc in CH_2Cl_2 as an eluent for characterization purposes. Compounds **3r** and **3q** were isolated as an inseparable mixture.

The mixture of **3r** and **3q** was analyzed by LC/MS (ES-APCI): t_R (**3r**) = 31.567 min, calculated for $C_{17}H_{19}N_2O^+$ $[M+H]^+$ expected: 267.1, found: 267.2; t_R (**3q**) = 31.344 min, calculated for $C_{17}H_{21}N_2O^+$ $[M+H]^+$ expected: 269.2, found: 269.2 (LC column: Poroshell120-EC-C18 43.0*50 mm, 2.7 um; 24 °C; H_2O/Methanol=90:10; 0.5 ml/min). Racemic **3r** was prepared by sodium cyanoborohydride reduction of the corresponding hydrazone, which also produced **3q** (**3r**:**3q** = *ca.* 4:1). While enantiomers of **3q** were fully separated on Daicel Chiralcel® OD-H (*vide supra*), enantiomers of **3r** were not separable from those of **3q**. We found out that enantiomers of **3r** were separable from those of **3q** under following HPLC condition: Daicel Chiralpak® AD-H with an AD-H guard column, hexane/2-propanol = 92:8,0.5mL/min. The first peak (t_R = 36.56) and second peak (t_R = 40.21) were the corresponding enantiomers of **3r**, and the third peak (t_R = 45.41) and fourth peak (t_R = 48.85) were the corresponding enantiomers of **3q**. Therefore, we were able to determine the ee of **3r**, as its enantiomers were fully

separated at the base line on the Daicel Chiralpak® AD-H column. However, the enantiomeric excess of **3q** was provided as an estimated value, for the enantiomers of **3q** were not fully separated at the base line by chiral HPLC on the Daicel Chiralpak® AD-H column.

3r : ee = 15 %; The enantiomeric excess and the absolute stereochemistry were determined by HPLC analysis:[10] t_R (major) = 40.47 min; t_R (minor) = 36.56 min (Daicel Chiralcel® AD-H with an AD-H guard column, hexane/2-propanol = 92:8, 0.5mL/min)

3q : ee = approximately 7 %; The enantiomeric excess was estimated by HPLC analysis as both enantiomers were not fully separated at the base line: t_R (major) = 45.25 min; t_R (minor) = 48.99 min (Daicel Chiralpak® AD-H with an AD-H guard column, hexane/2-propanol = 92:8, 0.5mL/min).

3. Computational Procedures.

All calculations have been performed with the Q-Chem 4 quantum chemistry code,[11] using the PBEh-3c density functional theory composite procedure.[12] Solvent effects have been included using the C-PCM method with the dielectric constant of DCM (ε = 9.08). Minima are converged within a threshold of 10^{-8} E_h, and have been confirmed minima using frequency calculations. Molecular symmetry was not used because of the necessity of the C-PCM method. The C_2 symmetry expected for the two main minima (complex 1 and complex 2) is respected in an approximate manner. The initial structures for the geometry optimizations have been obtained via a molecular mechanics based conformational search algorithm, developed in-house. Given the fact that the molecules in this project and the nature of their interaction are well within the

limits of recent validation studies of the method that we used, we expect geometries to be converged within 0.05 Å accuracy,[14] and energies to be converged within 2 kcal/mol accuracy.[15] The structures of the minima for the complex and the free Lewis bases are also provided in cartesian coordinates (xyz) as additional supplementary text files.

4. References:

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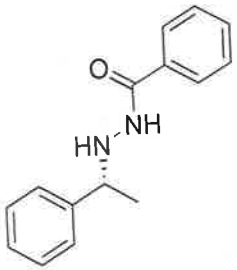
Ph

7.484 7.480 7.469 7.466 7.463 7.422 7.418 7.408 7.401 7.389 7.377 7.371 7.359 7.340 7.315 7.311 7.307 7.300 7.293 7.287 7.279 7.276 7.272 7.260 5.101 5.089 4.286 4.270 4.253 4.238

1.607 1.445 1.428

-0.000



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FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	322.5
DW	60.400 usec
DE	6.50 usec
TE	296.6 K
D1	1.00000000 sec
TD0	1
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P1	11.60 usec
PL1	3.00 dB
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SI	32768
SF	400.1300098 MHz
WDW	EM
SSB	0
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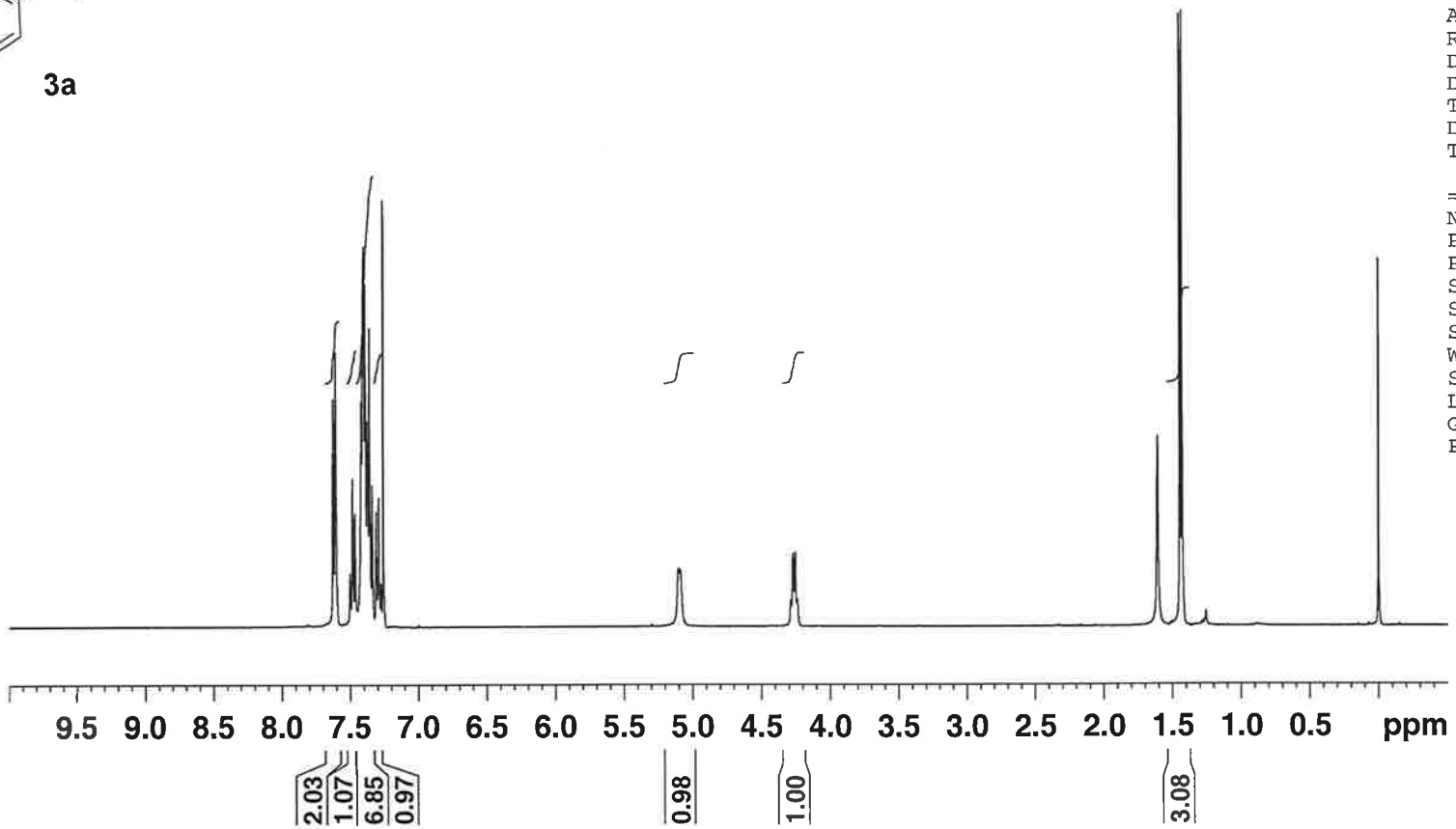

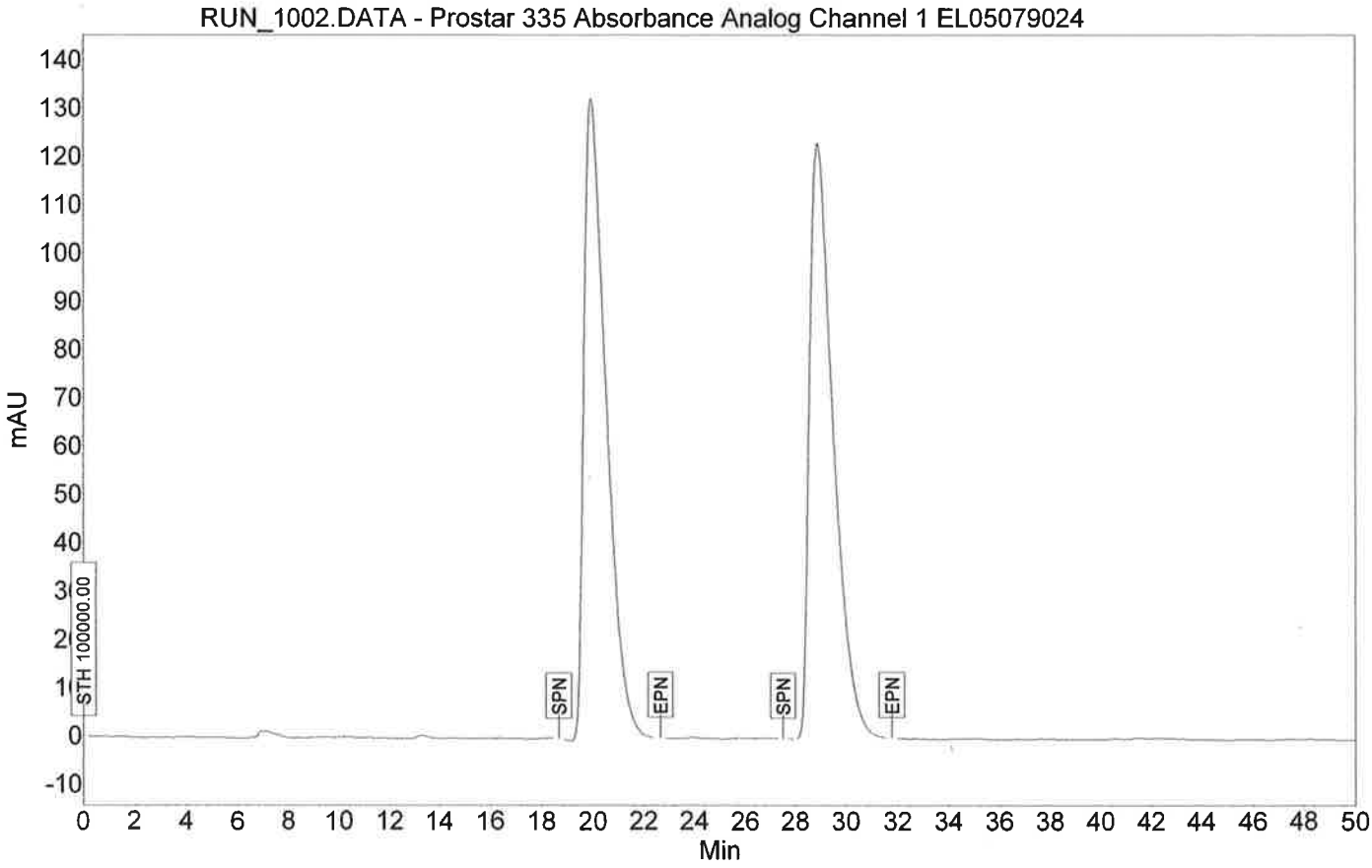

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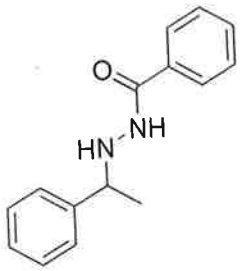

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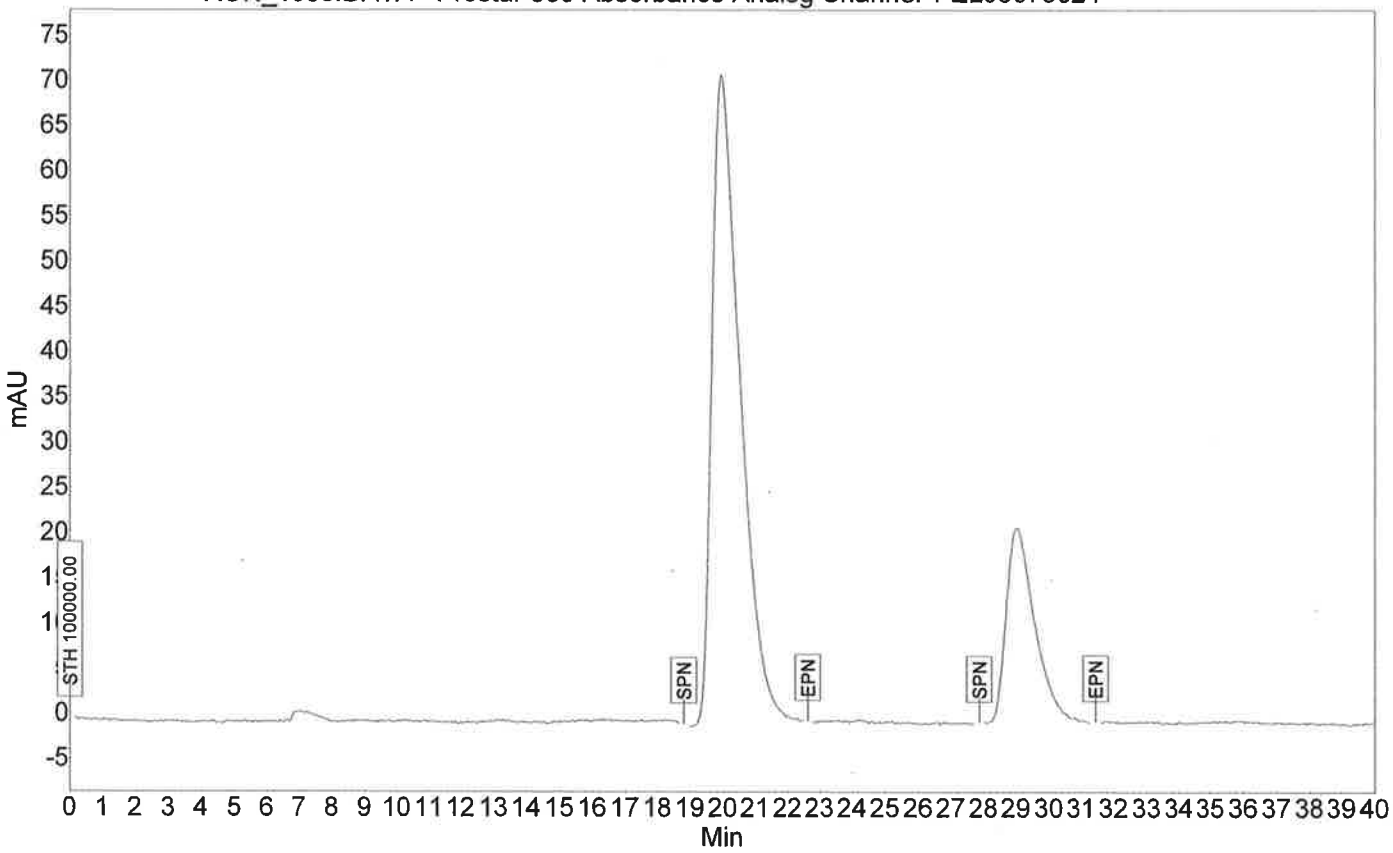
RUN_1003.DATA - Prostar 335 Absorbance Analog Channel 1 EL05079024



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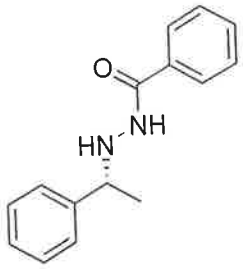
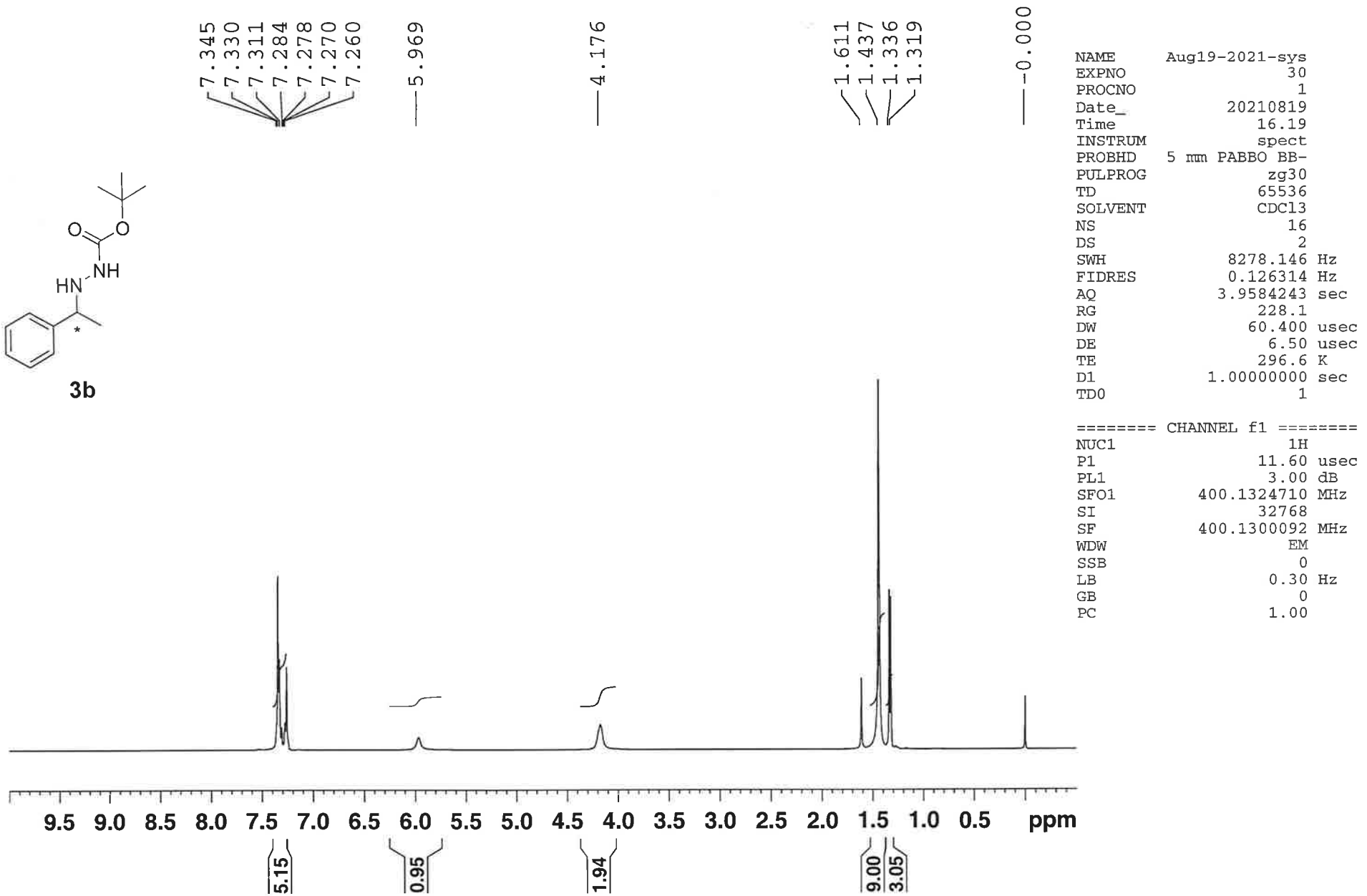


3a

boc



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Date_	20210819
Time	16.19
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SOLVENT	CDCl3
NS	16
DS	2
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FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	228.1
DW	60.400 usec
DE	6.50 usec
TE	296.6 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	11.60 usec
PL1	3.00 dB
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SI	32768
SF	400.1300092 MHz
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SSB	0
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GB	0
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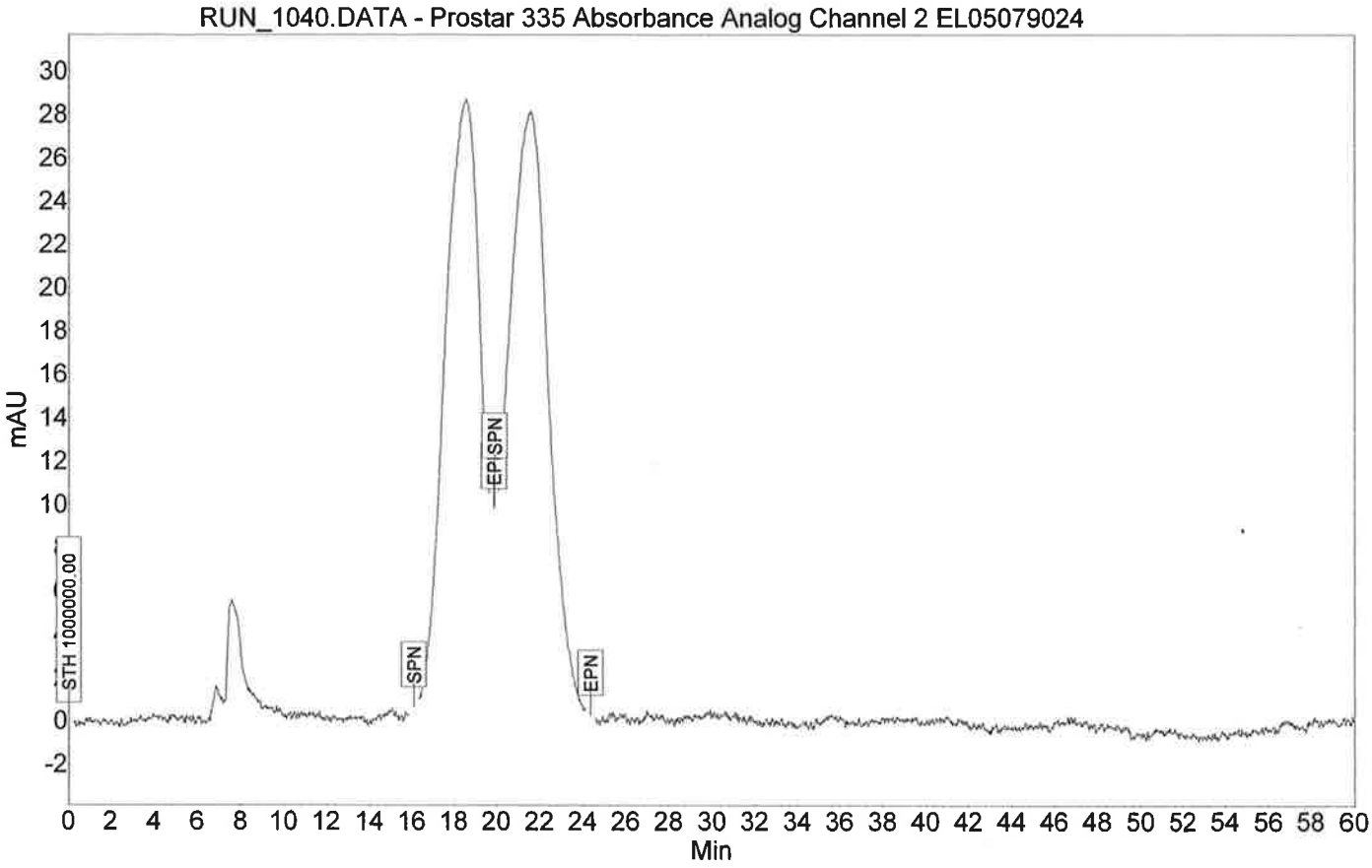

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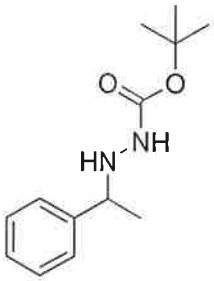

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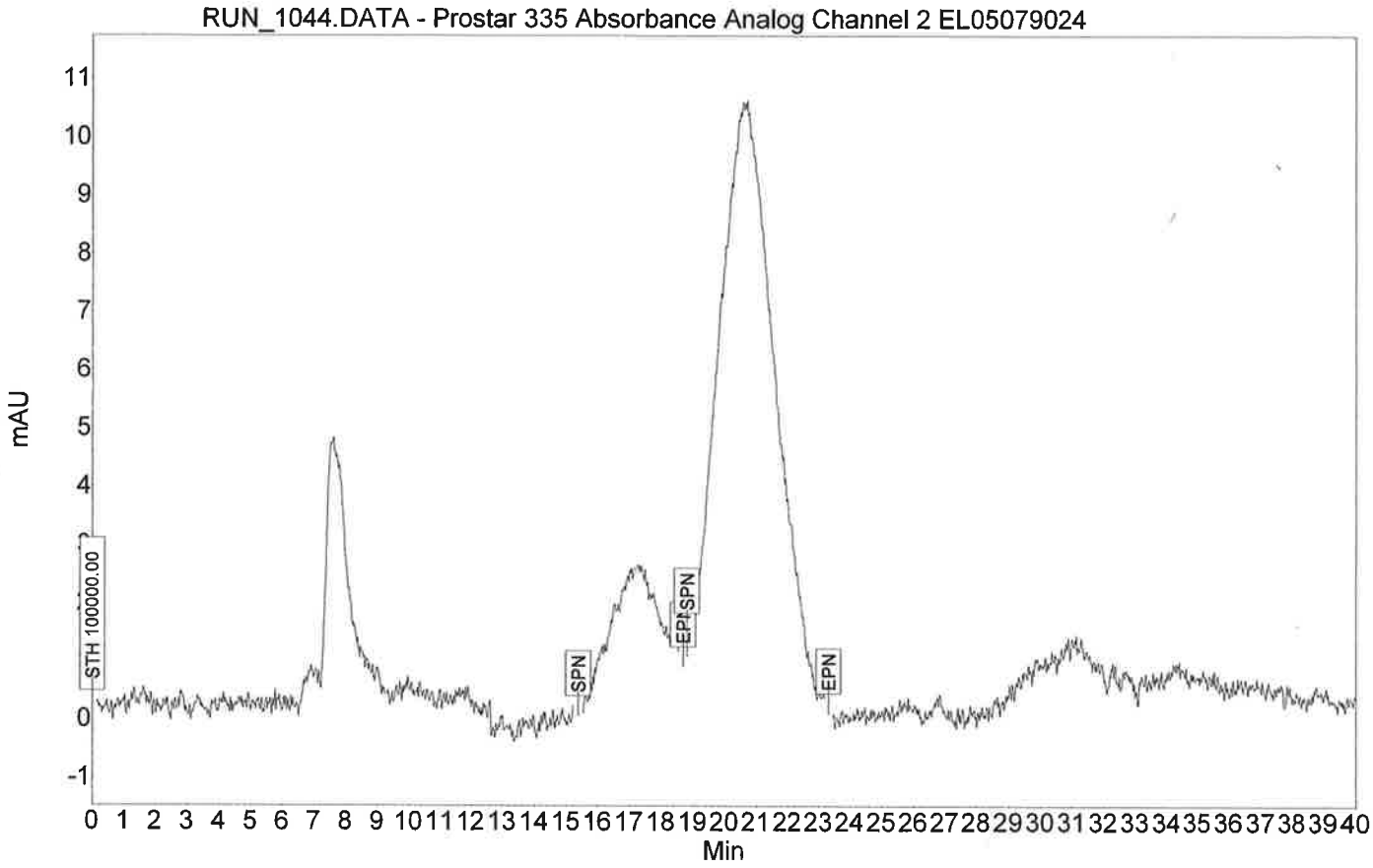

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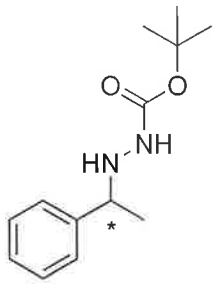
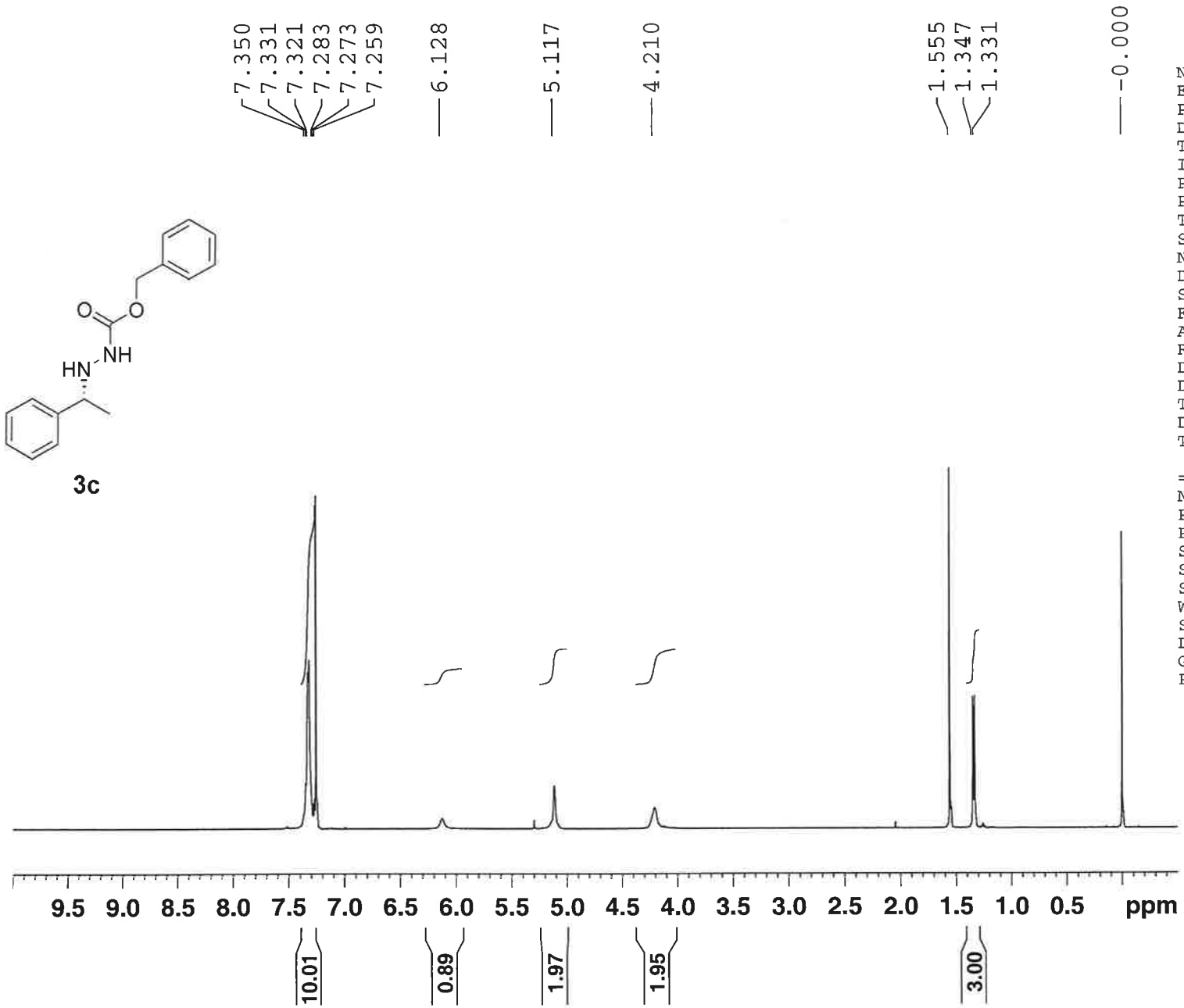


3b

cbz



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PROCNO	1
Date_	20210820
Time	15.59
INSTRUM	spect
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DS	2
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FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	362
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DE	6.50 usec
TE	297.6 K
D1	1.00000000 sec
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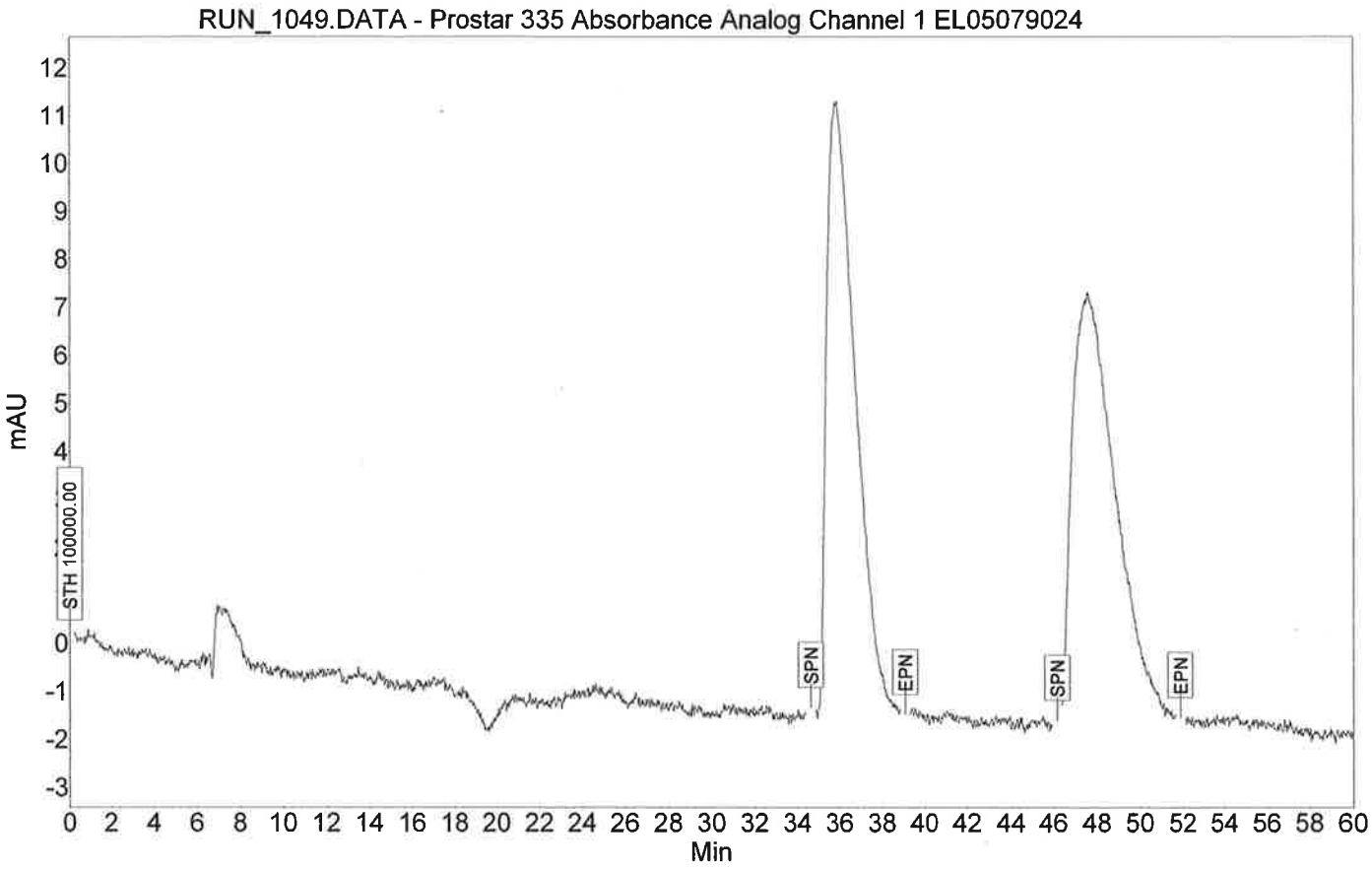

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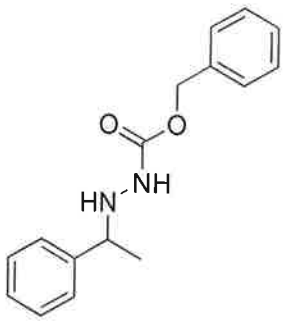

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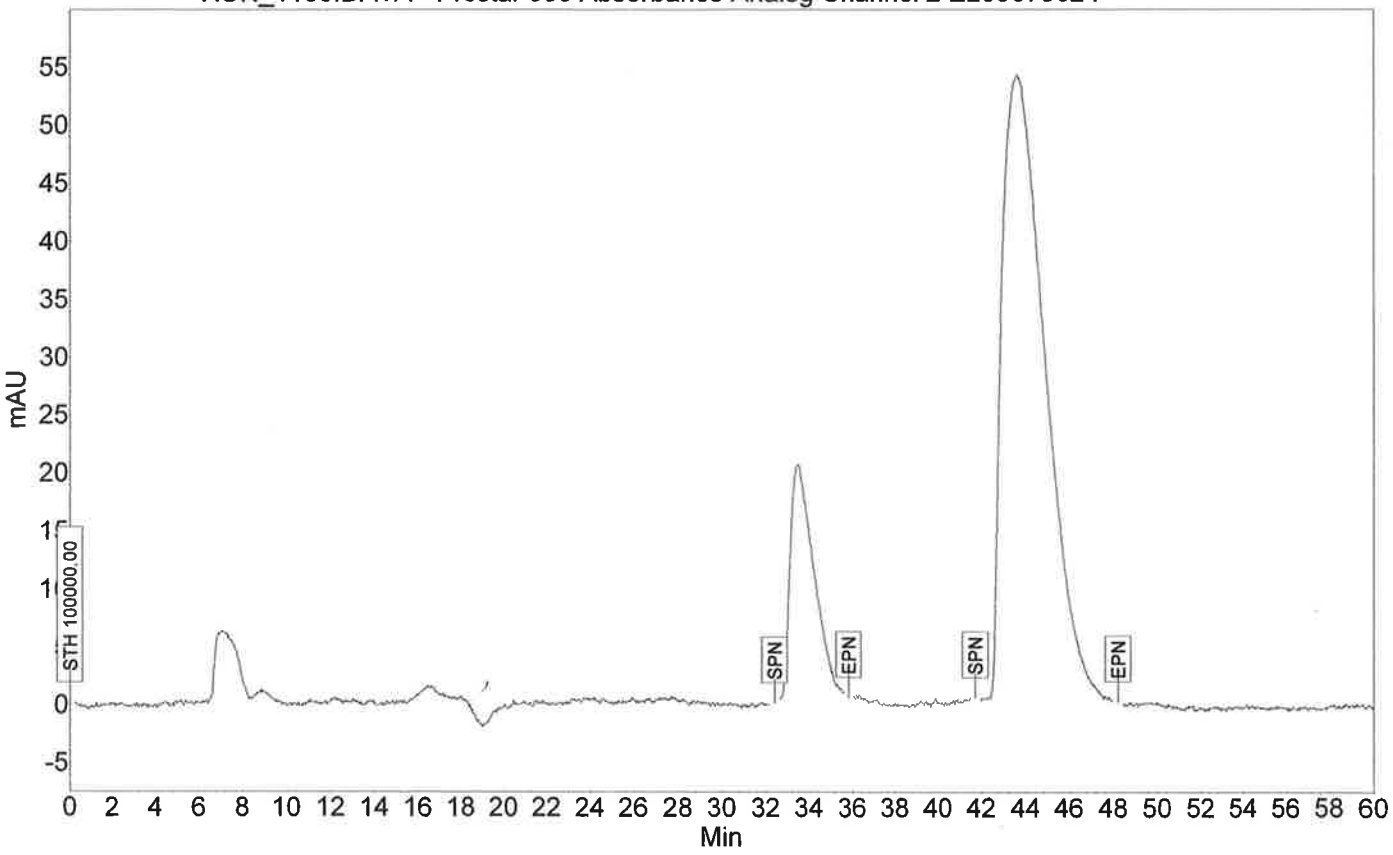
RUN_1160.DATA - Prostar 335 Absorbance Analog Channel 2 EL05079024



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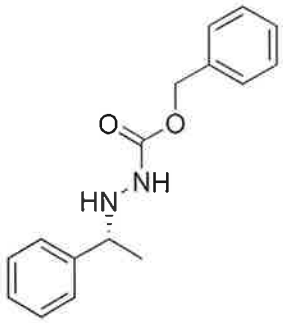
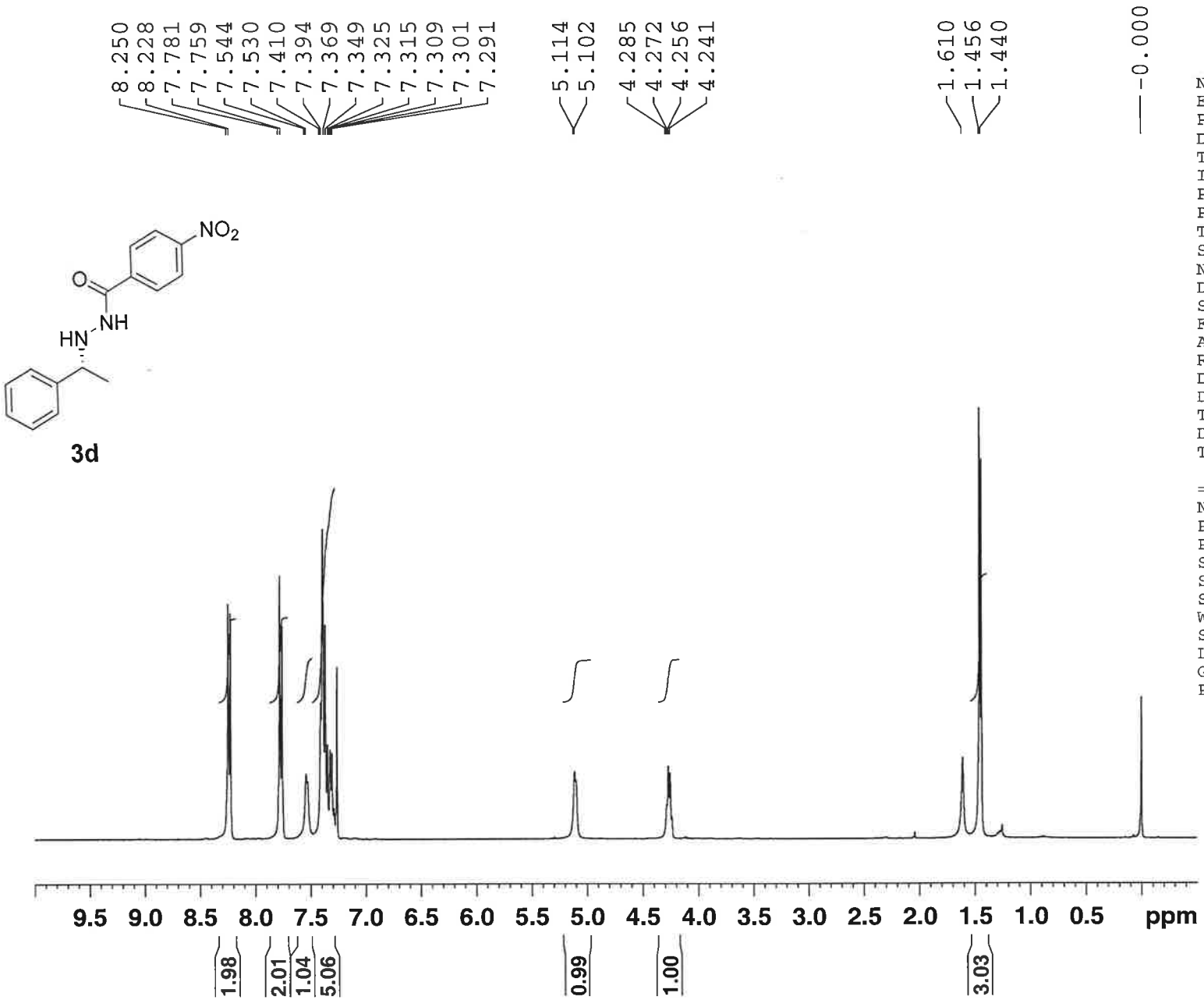


3c

NO2



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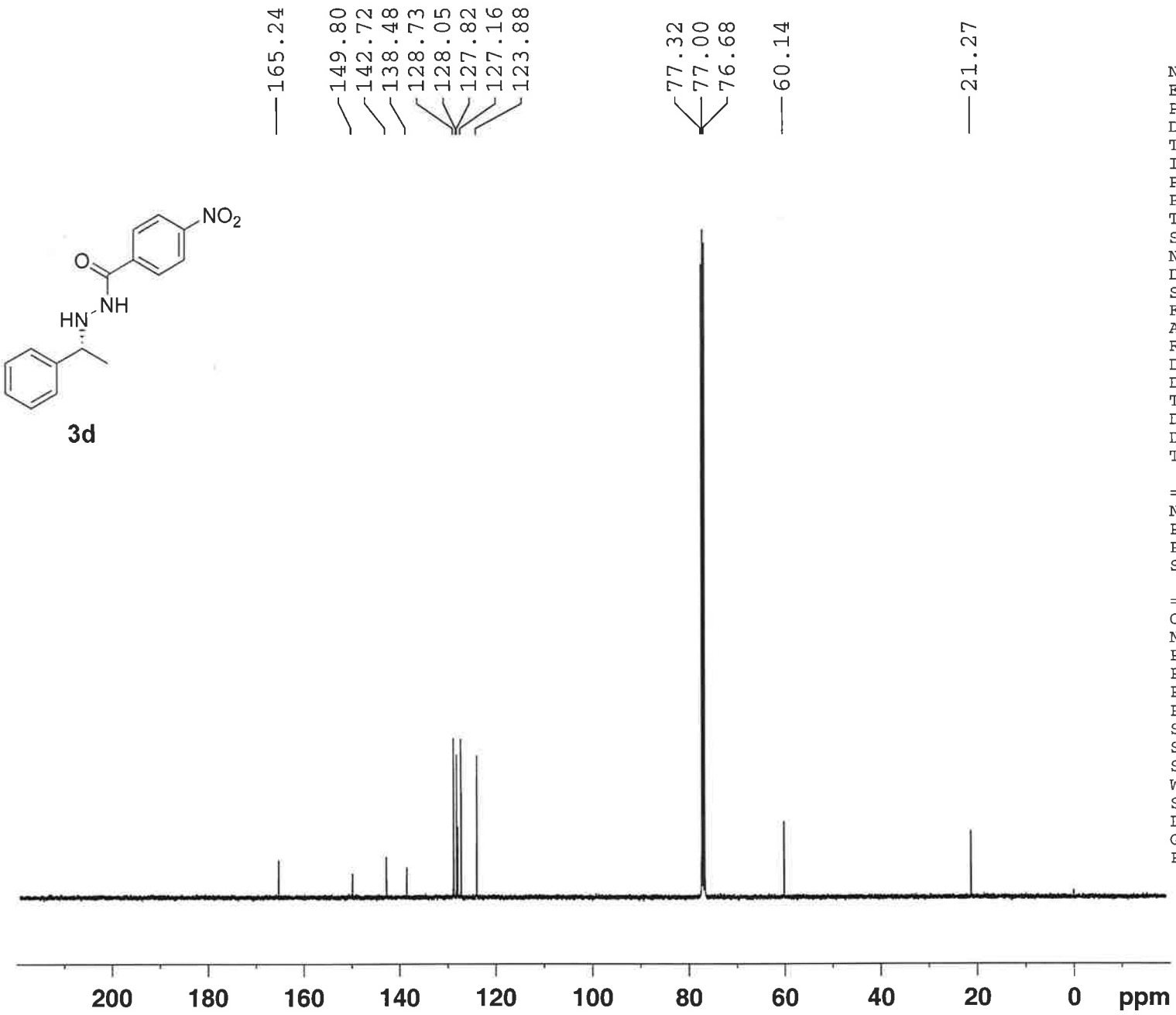
NO2



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PL13	15.00 dB
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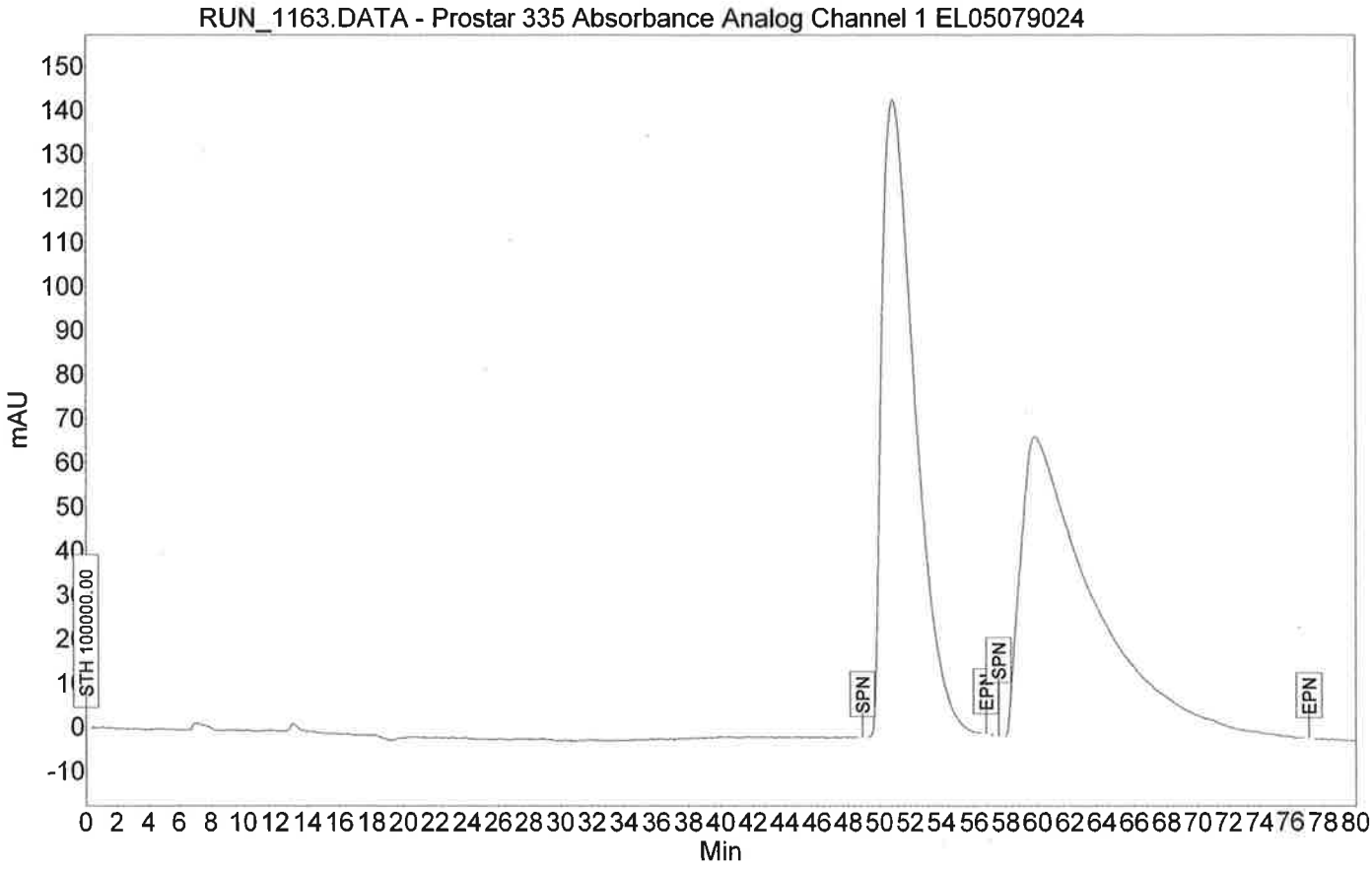
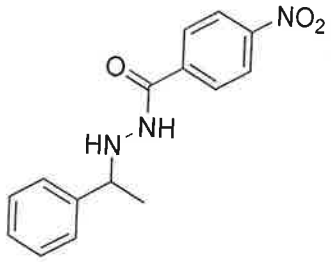
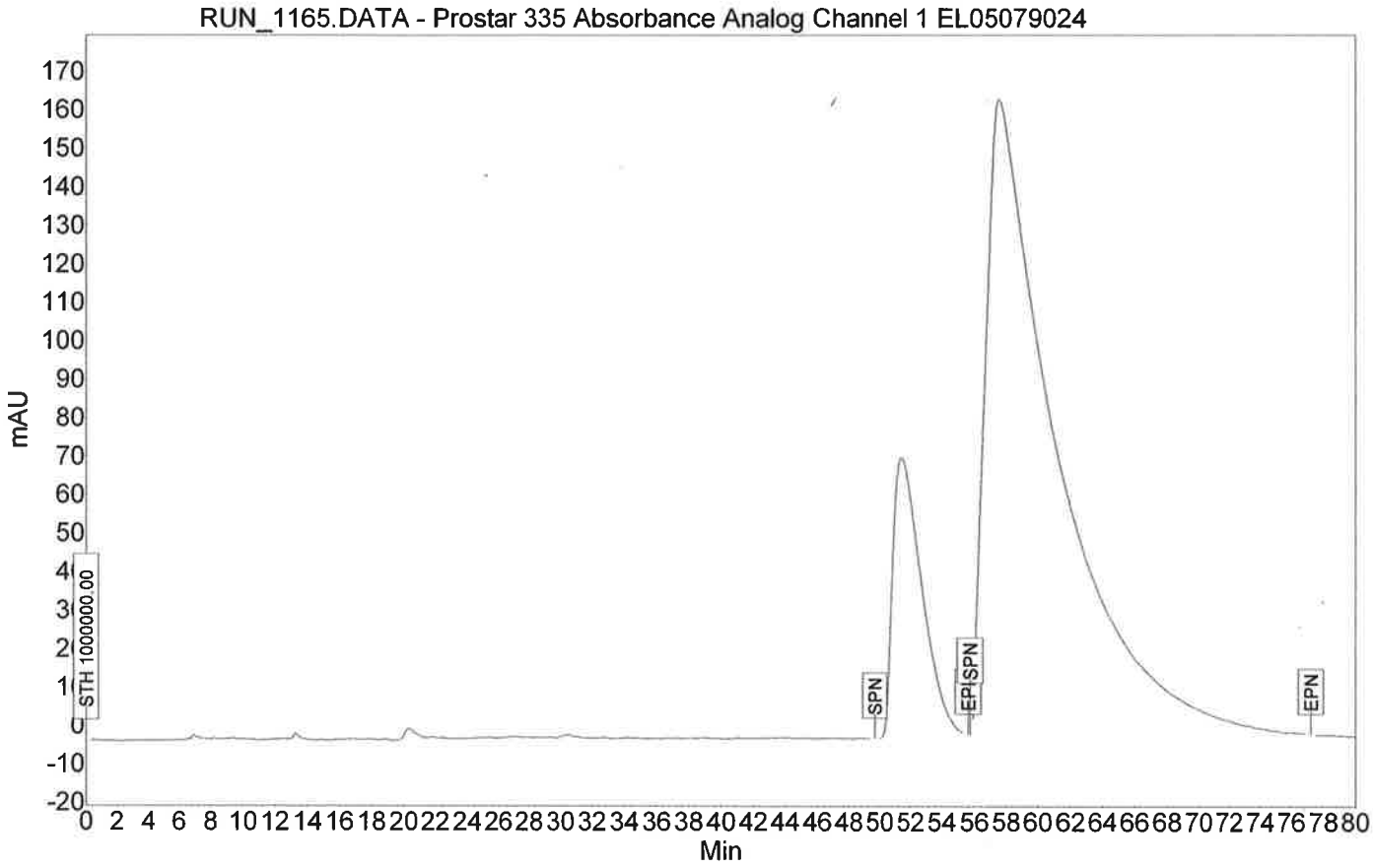
PC	1.40



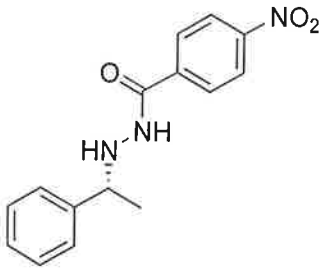
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	50.85	50.34	144.5	361.9	50.341
2	UNKNOWN	59.80	49.66	68.0	357.0	49.659
Total			100.00	212.6	718.9	100.000



(±)



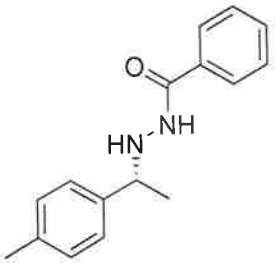
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	51.44	15.72	72.6	159.7	15.720
2	UNKNOWN	57.56	84.28	165.1	856.2	84.280
Total			100.00	237.6	1015.8	100.000



3d

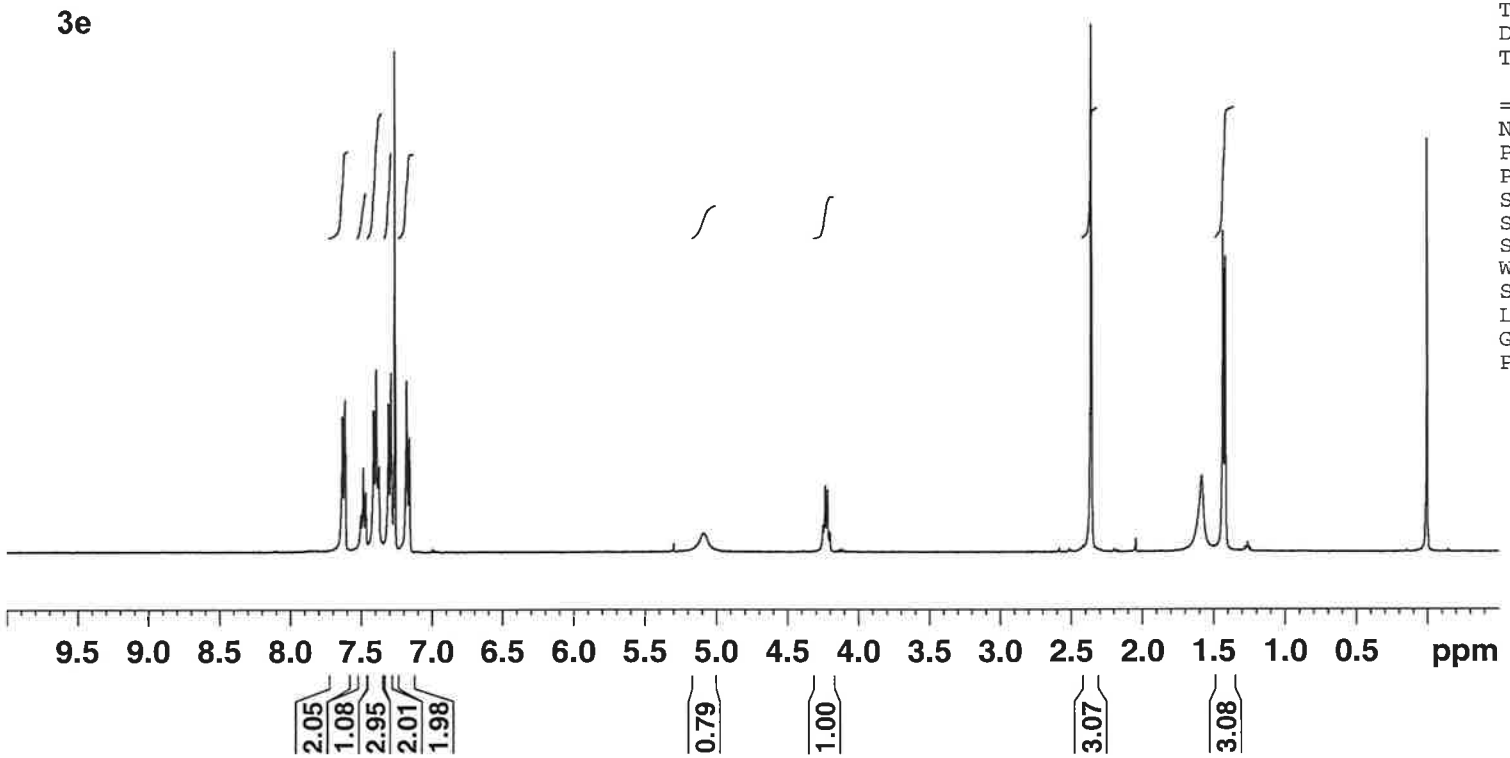
Me

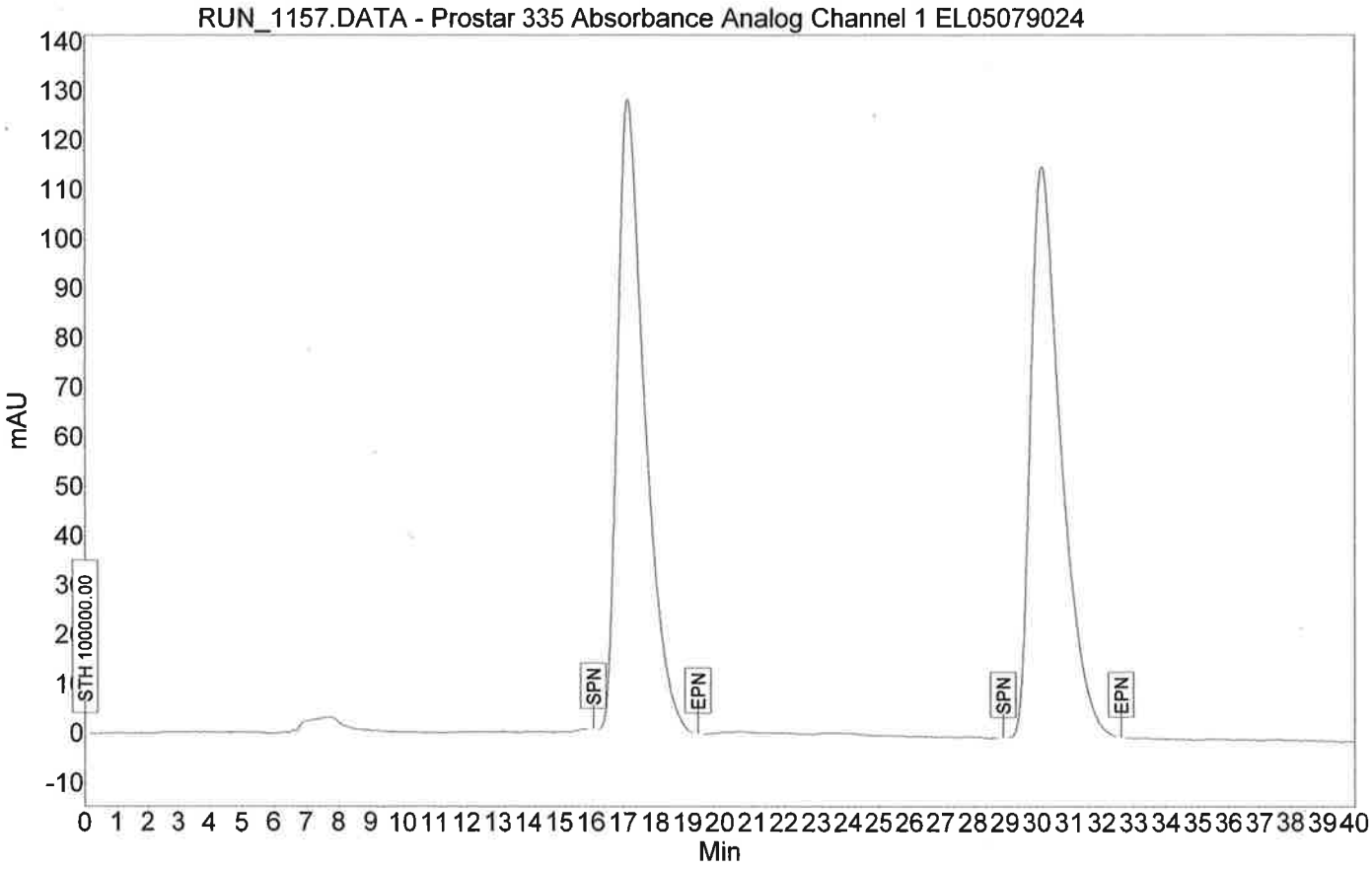
7.635
7.615
7.612
7.505
7.501
7.487
7.481
7.471
7.468
7.414
7.394
7.379
7.376
7.309
7.289
7.260
7.180
7.160
5.088
4.250
4.233
4.217
4.200
2.355
1.430
1.413
0.000



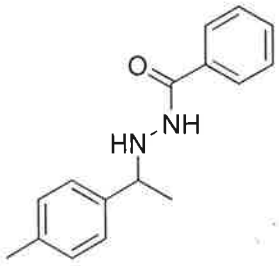
3e

NAME	Aug14-2021-sys
EXPNO	60
PROCNO	1
Date_	20210814
Time	16.31
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	362
DW	60.400 usec
DE	6.50 usec
TE	296.2 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	11.60 usec
PL1	3.00 dB
SFO1	400.1324710 MHz
SI	32768
SF	400.1300089 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00





Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	17.15	49.95	127.7	126.4	49.947
2	UNKNOWN	30.15	50.05	115.5	126.7	50.053
Total			100.00	243.2	253.1	100.000



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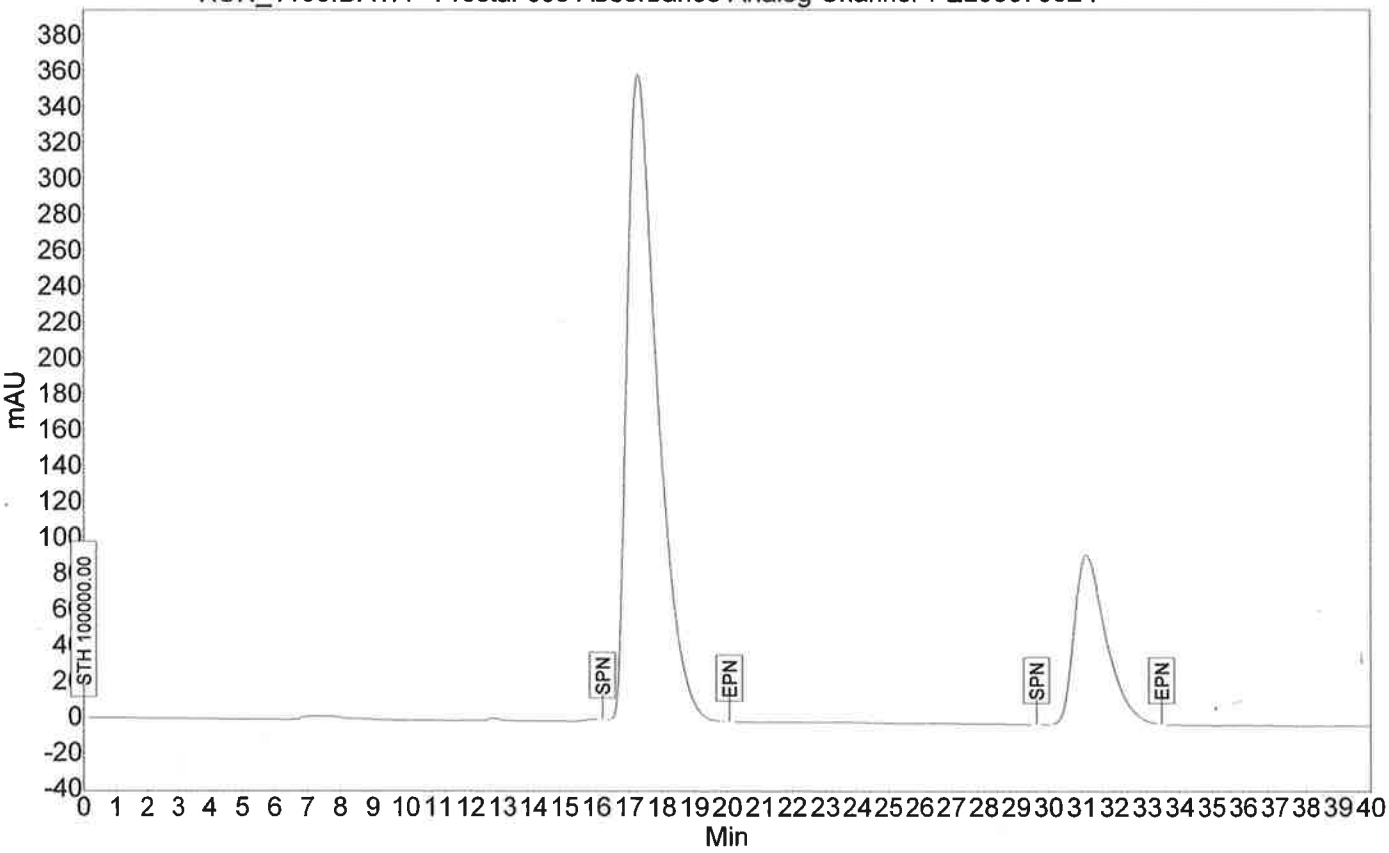
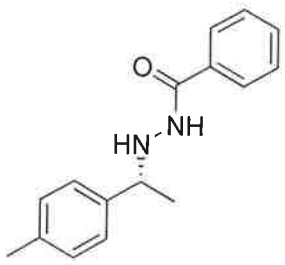
RUN_1156.DATA - Prostar 335 Absorbance Analog Channel 1 EL05079024

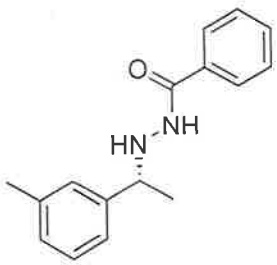


Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	17.27	78.64	359.4	388.6	78.642
2	UNKNOWN	31.13	21.36	94.1	105.5	21.358
Total			100.00	453.5	494.2	100.000

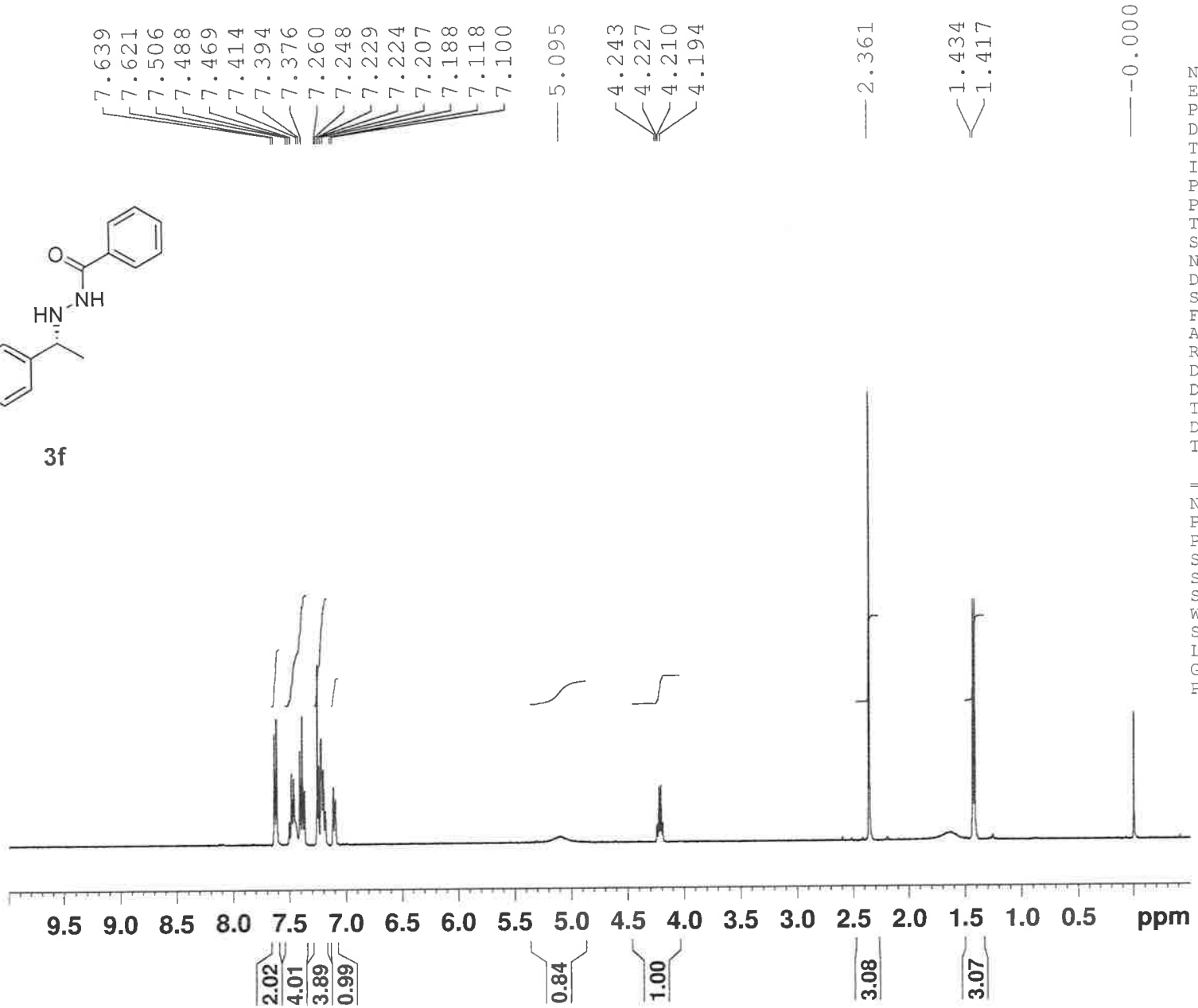


3e

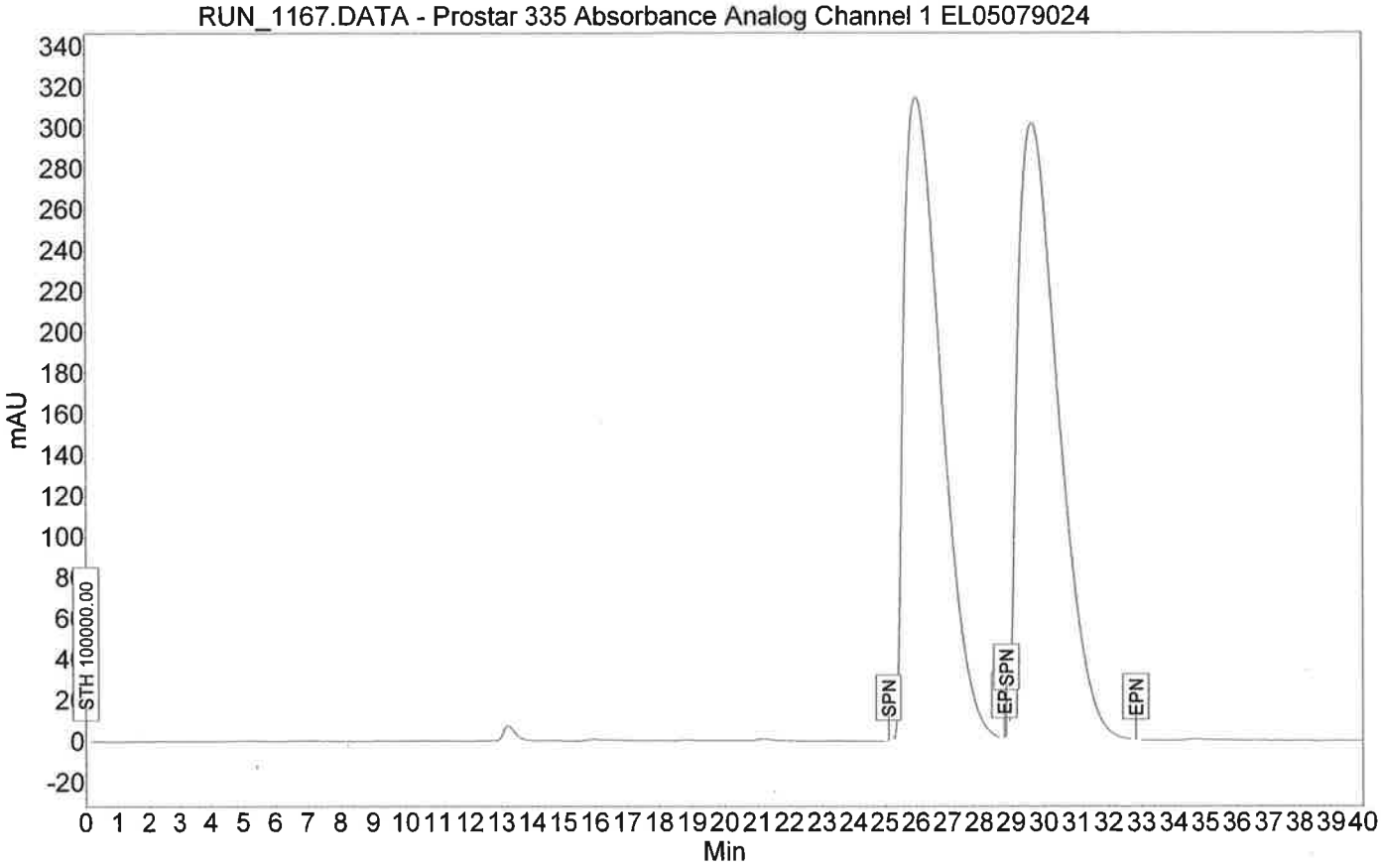
3Me



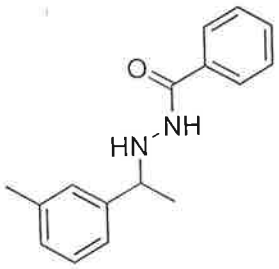
3f



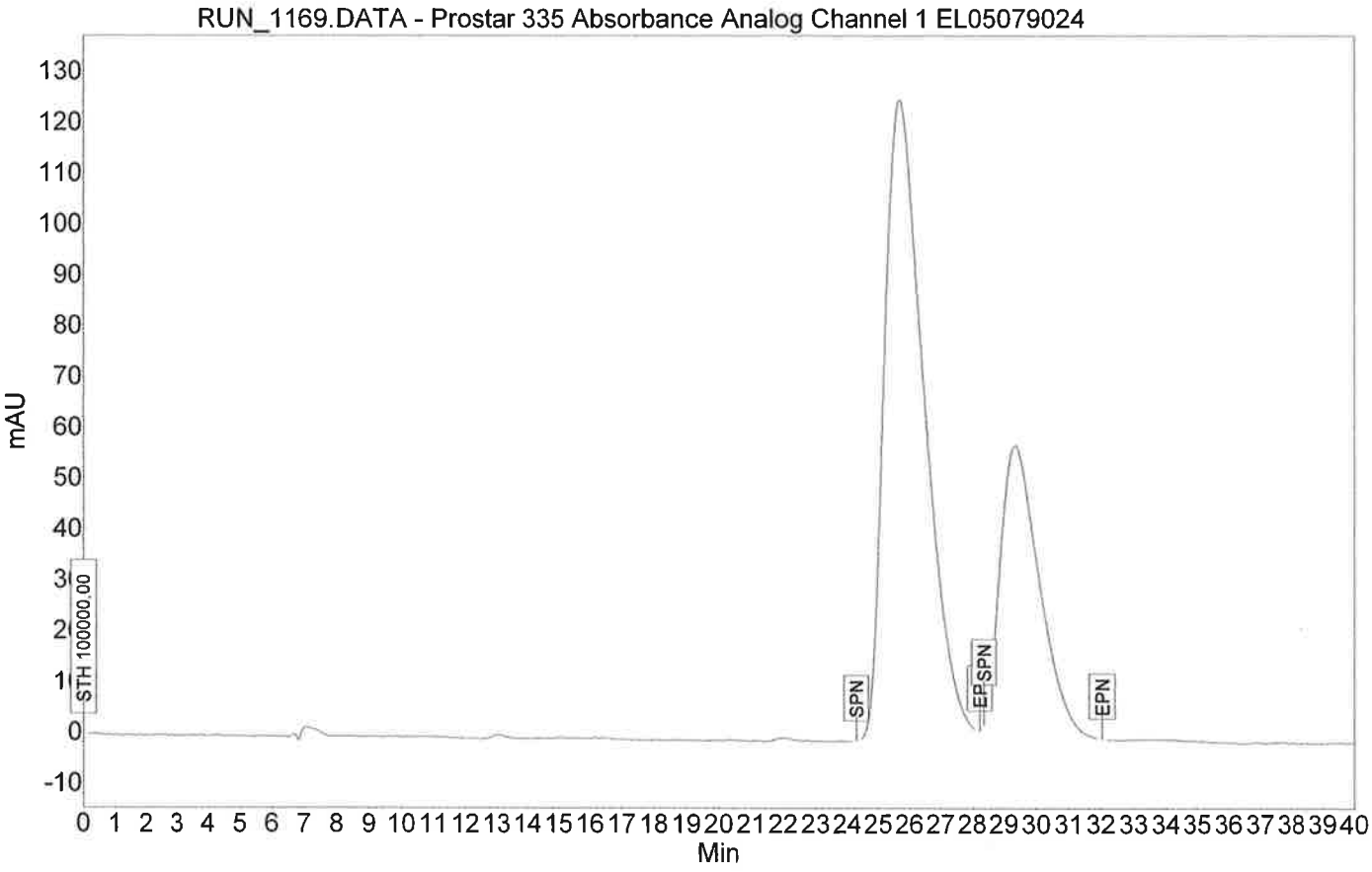
NAME	Aug13-2021-cxu
EXPNO	1
PROCNO	1
Date_	20210813
Time	12.26
INSTRUM	spect
PROBHD	5 mm TBI 1H/31
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	13004
DW	60.400 usec
DE	6.50 usec
TE	300.0 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	18.75 usec
PL1	0.50 dB
SFO1	400.1324710 MHz
SI	32768
SF	400.1300095 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



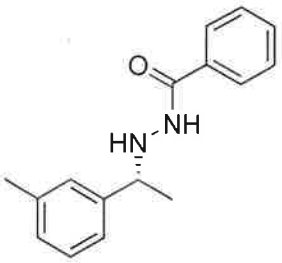
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	26.03	49.93	314.4	432.1	49.932
2	UNKNOWN	29.65	50.07	300.9	433.3	50.068
Total			100.00	615.3	865.5	100.000



(±)

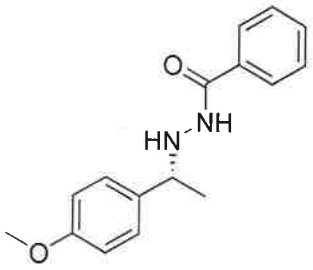


Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	25.65	70.37	125.4	184.4	70.373
2	UNKNOWN	29.36	29.63	56.2	77.6	29.627
Total			100.00	181.6	262.0	100.000

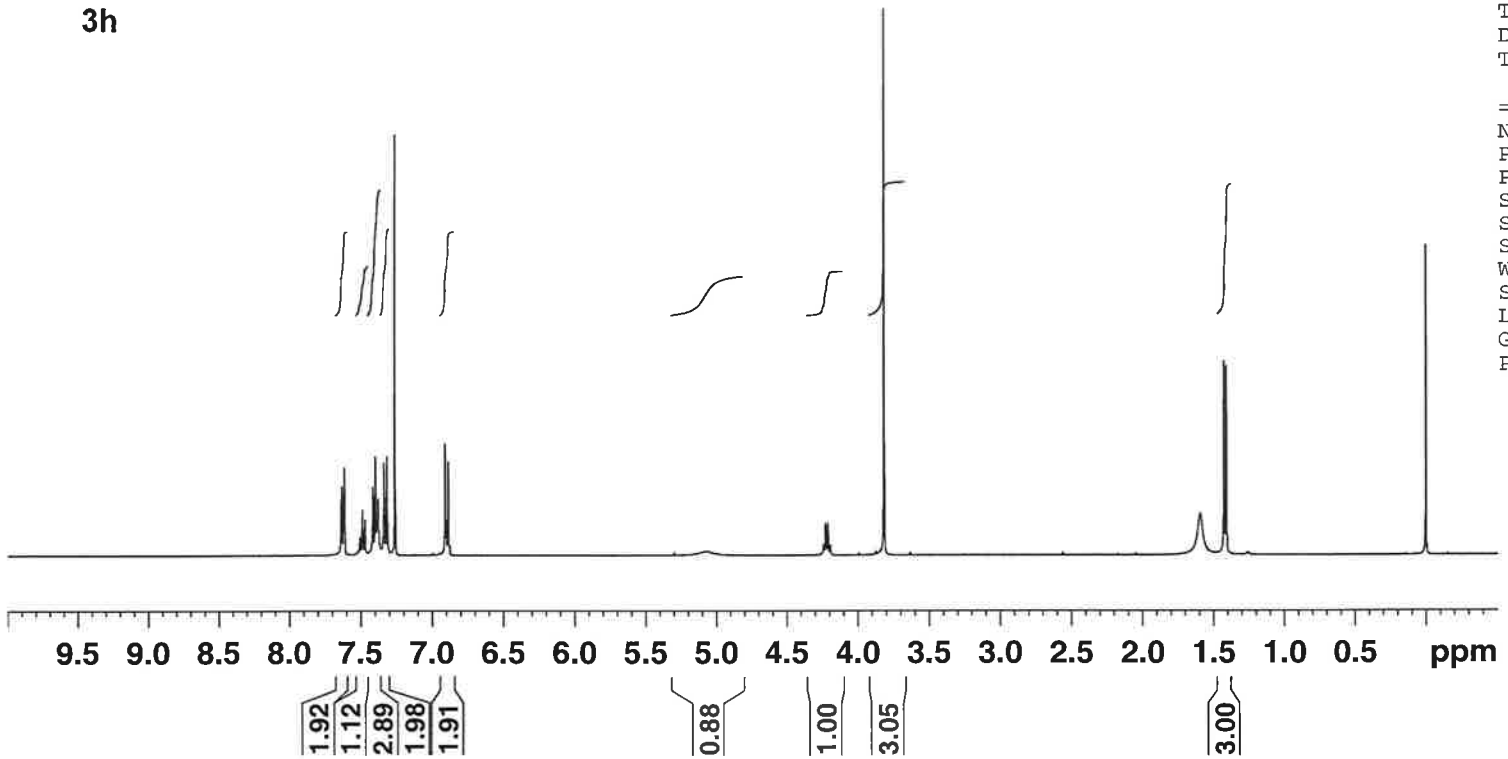


3f

MeO

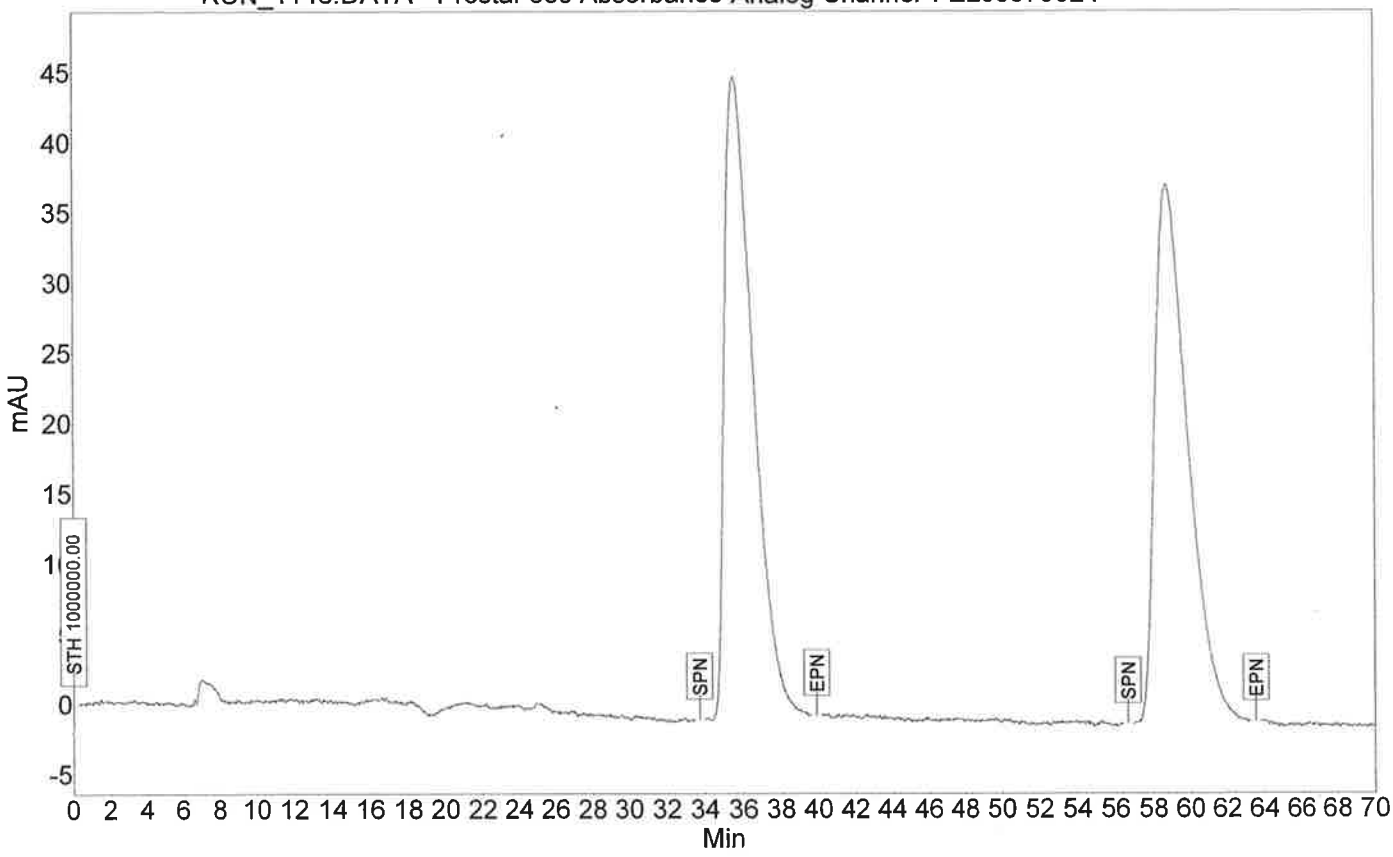


3h

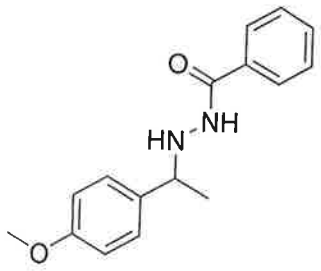


NAME	Aug14-2021-sys
EXPNO	50
PROCNO	1
Date_	20210814
Time	16.21
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	362
DW	60.400 usec
DE	6.50 usec
TE	296.2 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	11.60 usec
PL1	3.00 dB
SFO1	400.1324710 MHz
SI	32768
SF	400.1300089 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

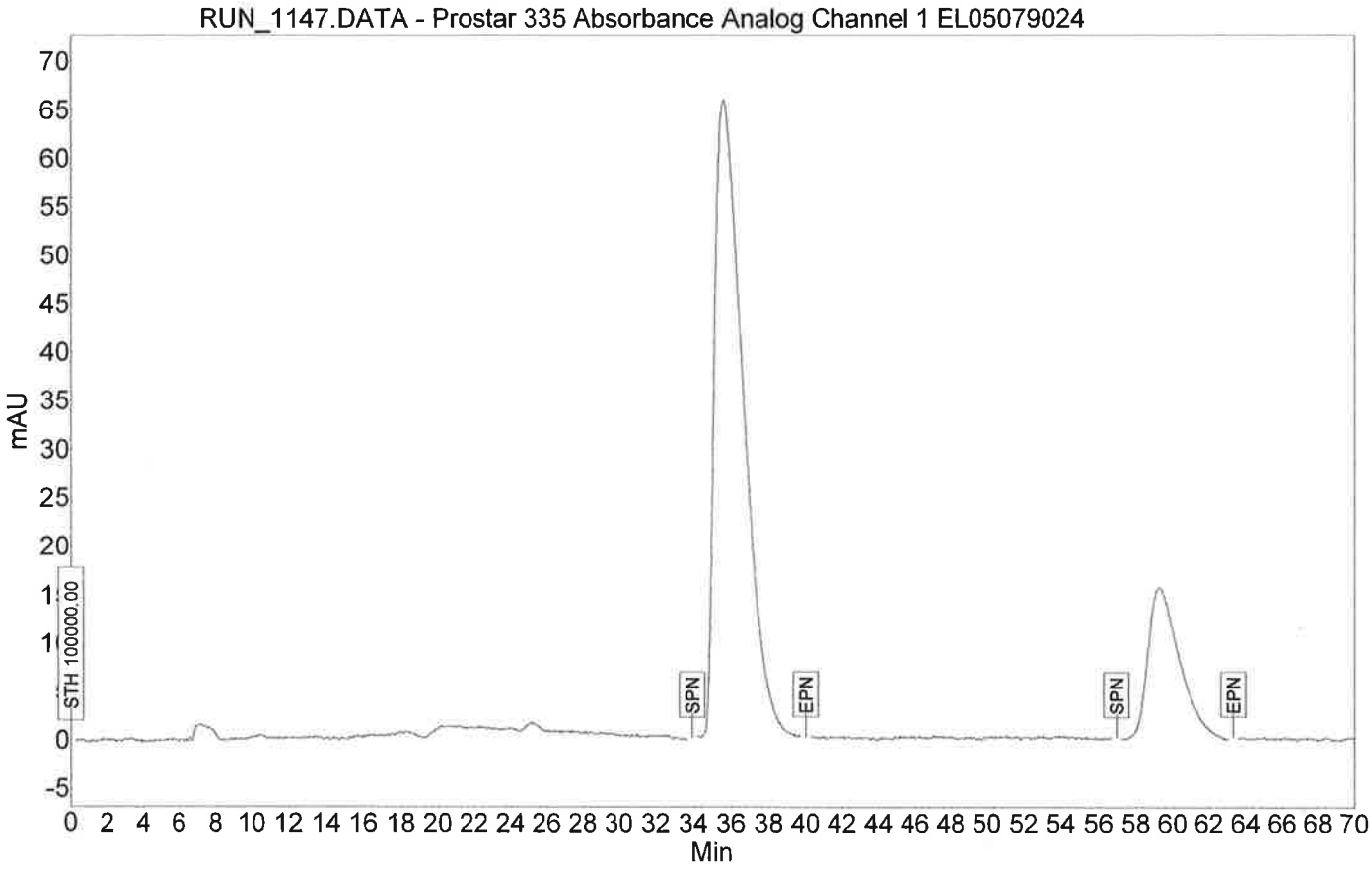
RUN_1146.DATA - Prostar 335 Absorbance Analog Channel 1 EL05079024



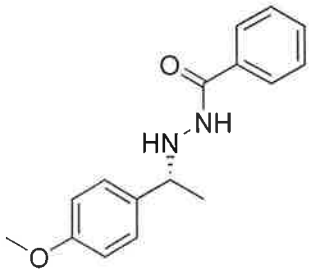
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	35.53	50.13	45.7	79.2	50.135
2	UNKNOWN	58.68	49.87	38.4	78.7	49.865
Total			100.00	84.2	157.9	100.000



(±)

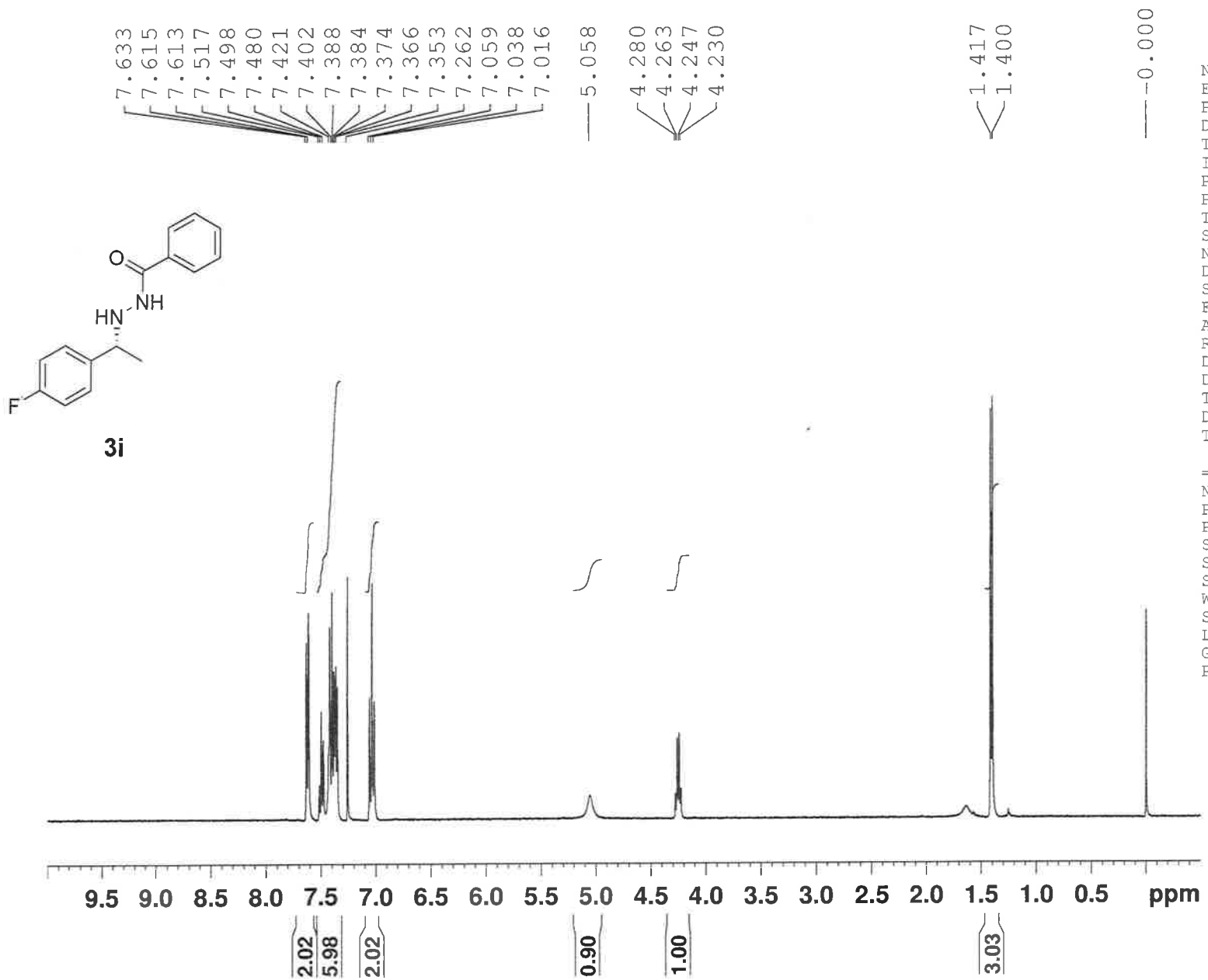


Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	35.59	79.13	65.8	115.7	79.133
2	UNKNOWN	59.24	20.87	15.4	30.5	20.867
Total			100.00	81.2	146.2	100.000

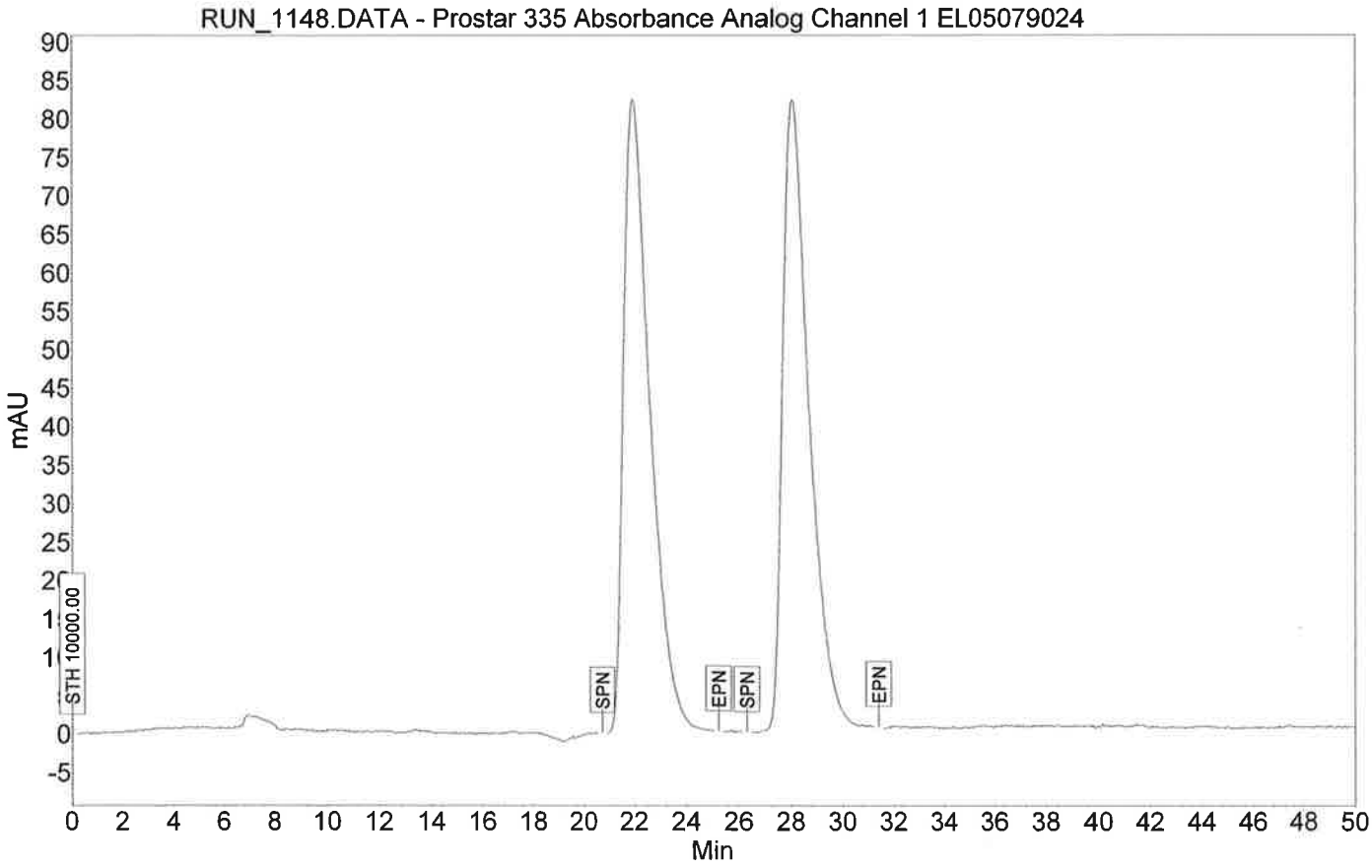


3h

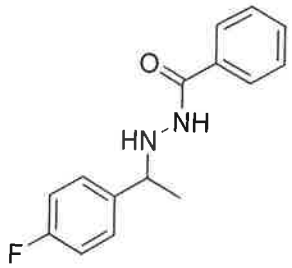
F



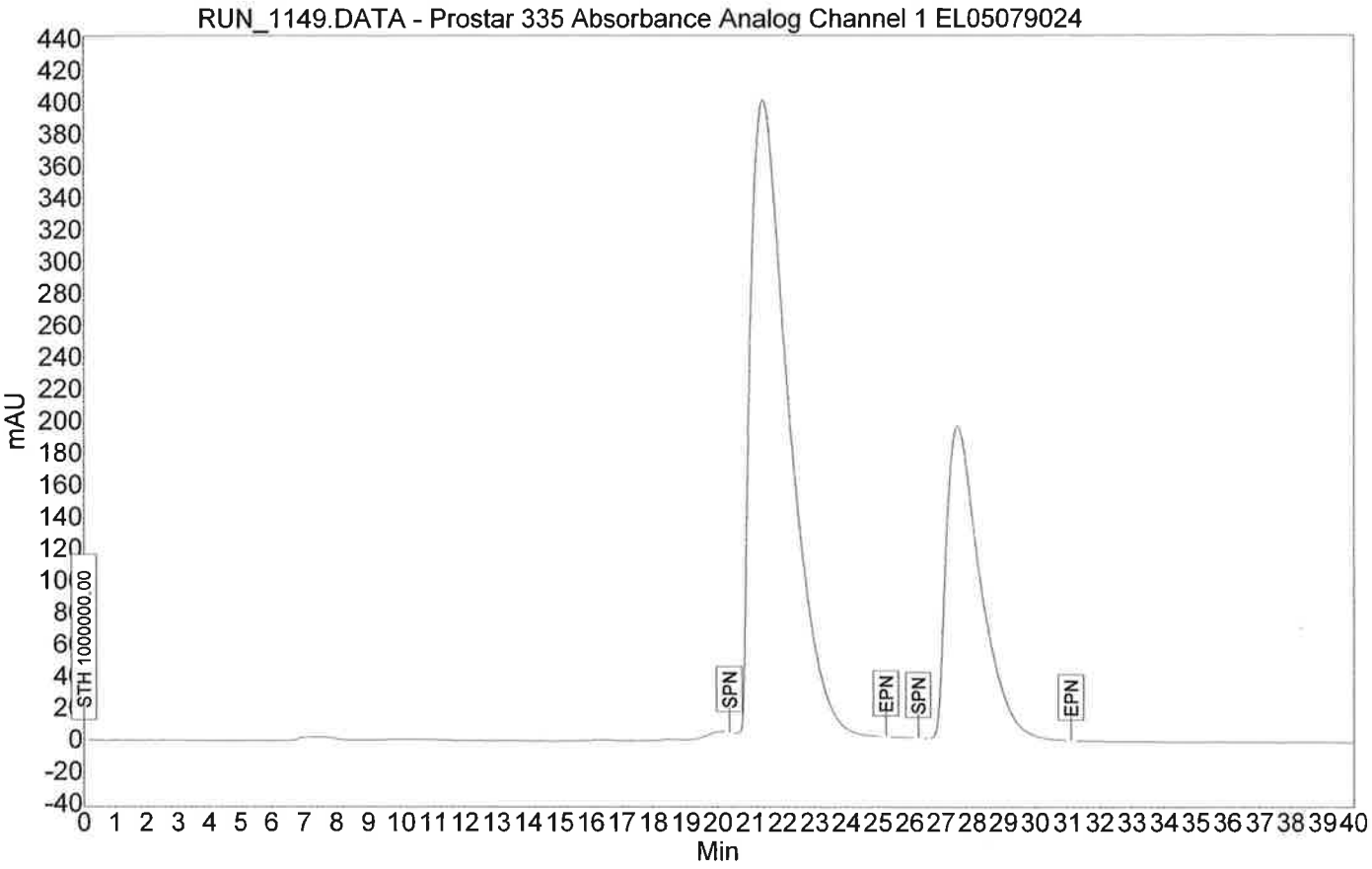
NAME	Aug11-2021
EXPNO	10
PROCNO	1
Date_	20210811
Time	17.23
INSTRUM	spect
PROBHD	5 mm TBI 1H/31
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	13004
DW	60.400 usec
DE	6.50 usec
TE	300.0 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	18.75 usec
PL1	0.50 dB
SFO1	400.1324710 MHz
SI	32768
SF	400.1300088 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



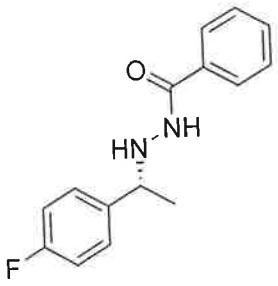
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	21.93	49.98	82.2	97.8	49.982
2	UNKNOWN	28.03	50.02	81.9	97.9	50.018
Total			100.00	164.1	195.7	100.000



(±)

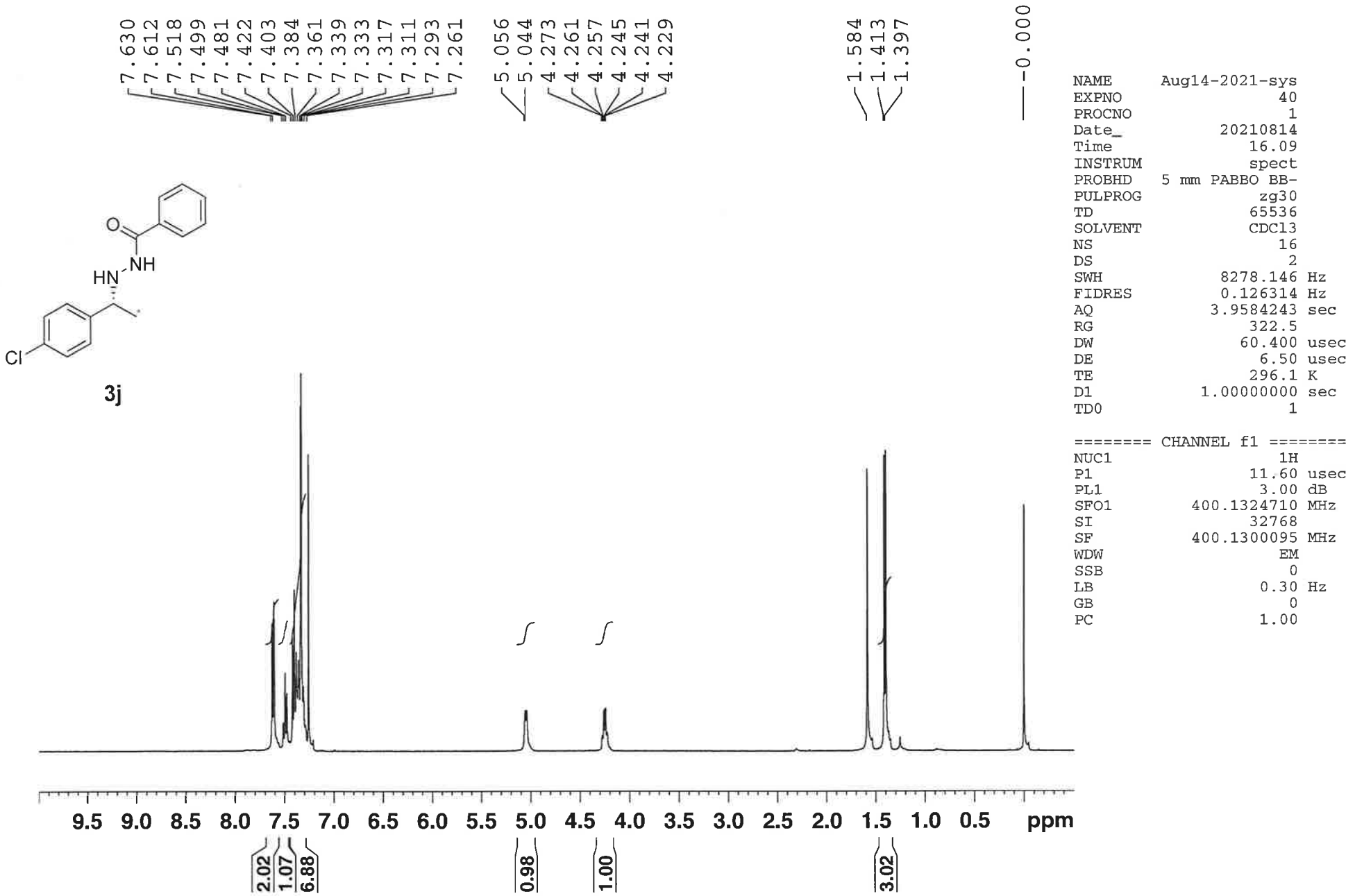


Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	21.37	68.67	397.3	545.0	68.674
2	UNKNOWN	27.53	31.33	196.0	248.6	31.326
Total			100.00	593.4	793.6	100.000

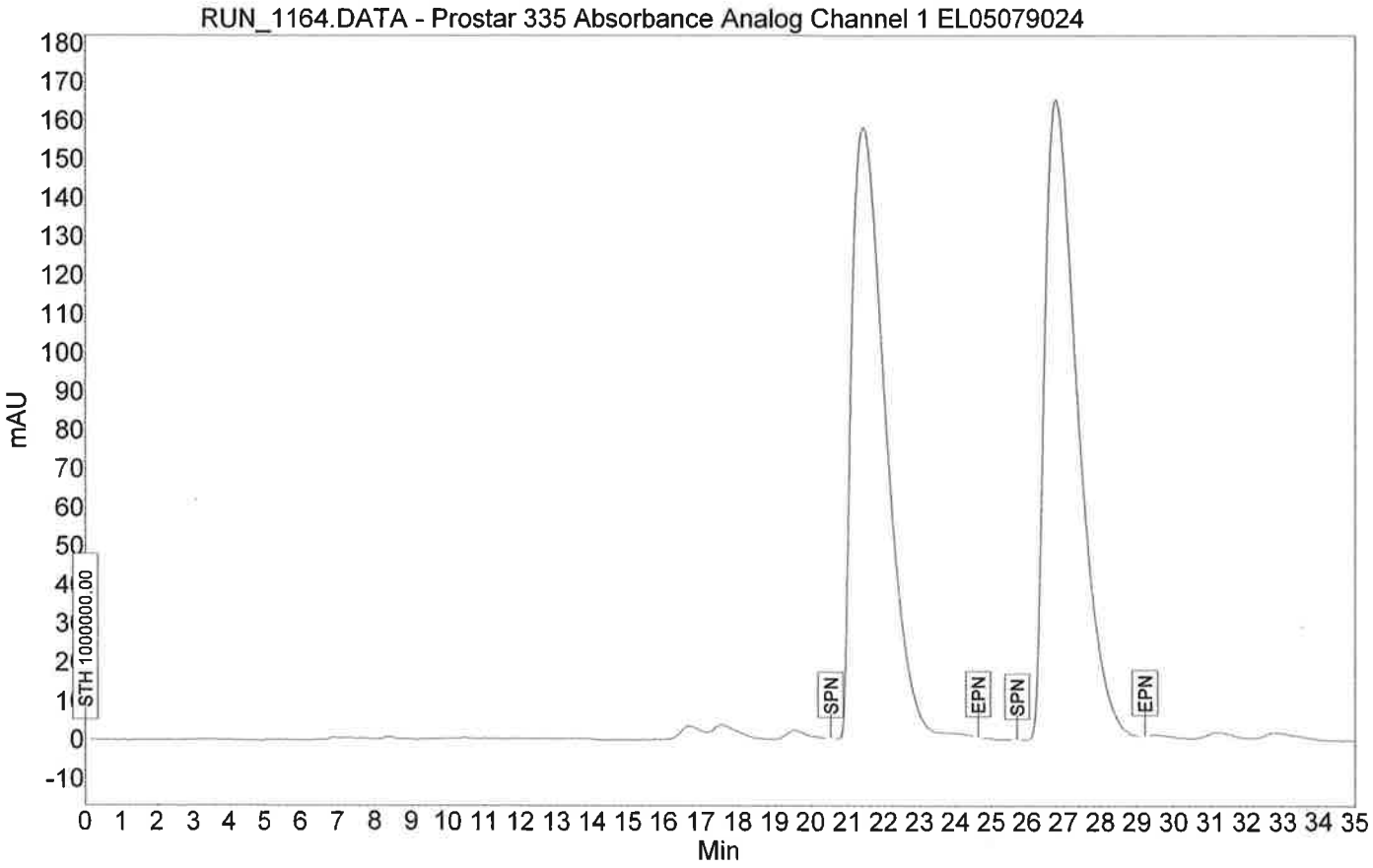


3i

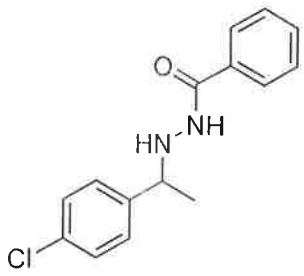
Cl



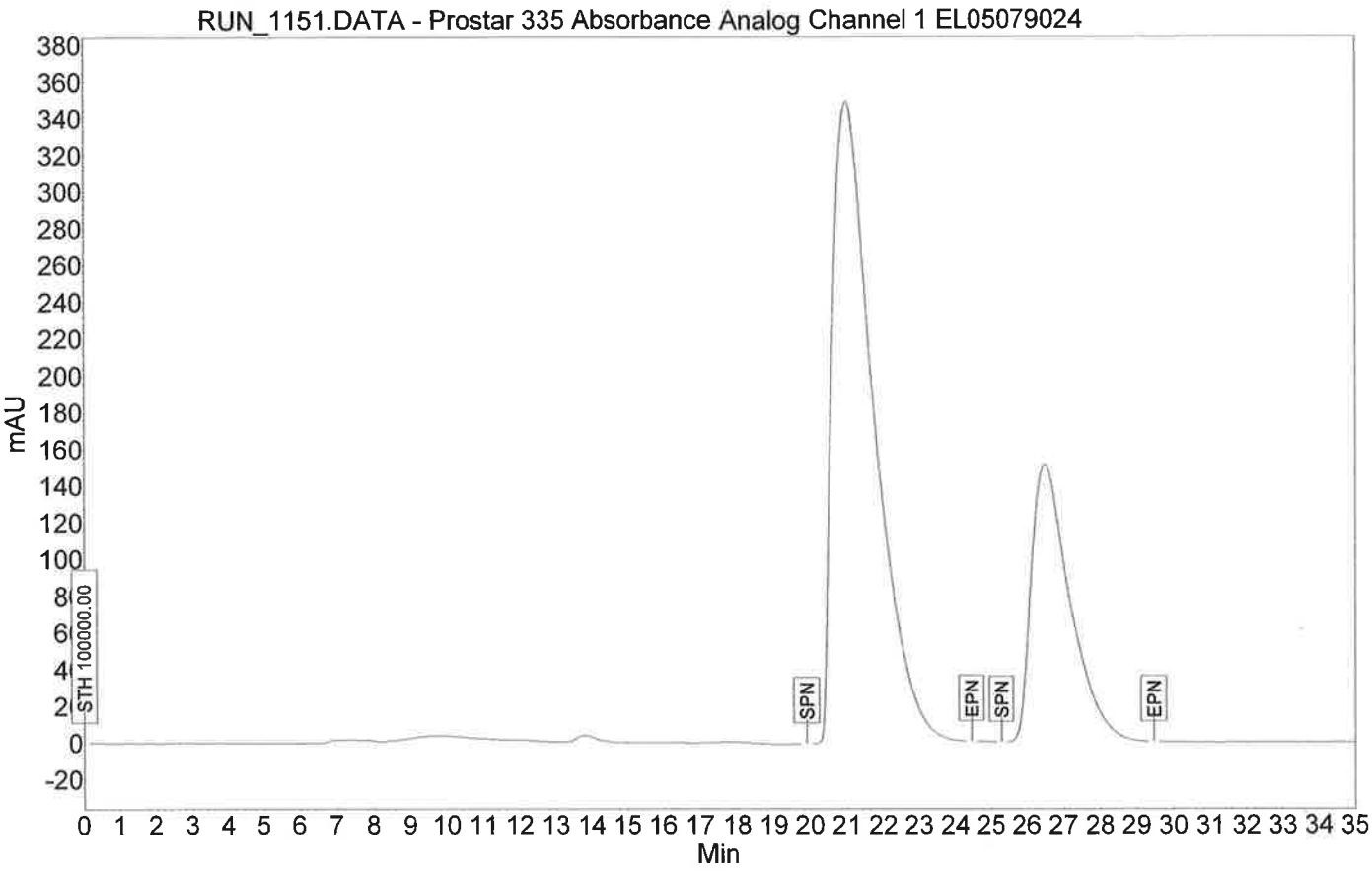
NAME	Aug14-2021-sys
EXPNO	40
PROCNO	1
Date_	20210814
Time	16.09
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	322.5
DW	60.400 usec
DE	6.50 usec
TE	296.1 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	11.60 usec
PL1	3.00 dB
SFO1	400.1324710 MHz
SI	32768
SF	400.1300095 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



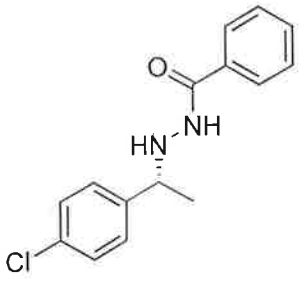
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	21.43	49.98	157.6	169.2	49.977
2	UNKNOWN	26.77	50.02	165.0	169.3	50.023
Total			100.00	322.6	338.5	100.000



(±)

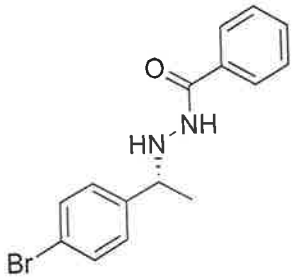


Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	20.97	71.50	349.3	459.2	71.503
2	UNKNOWN	26.49	28.50	151.1	183.0	28.497
Total			100.00	500.4	642.2	100.000

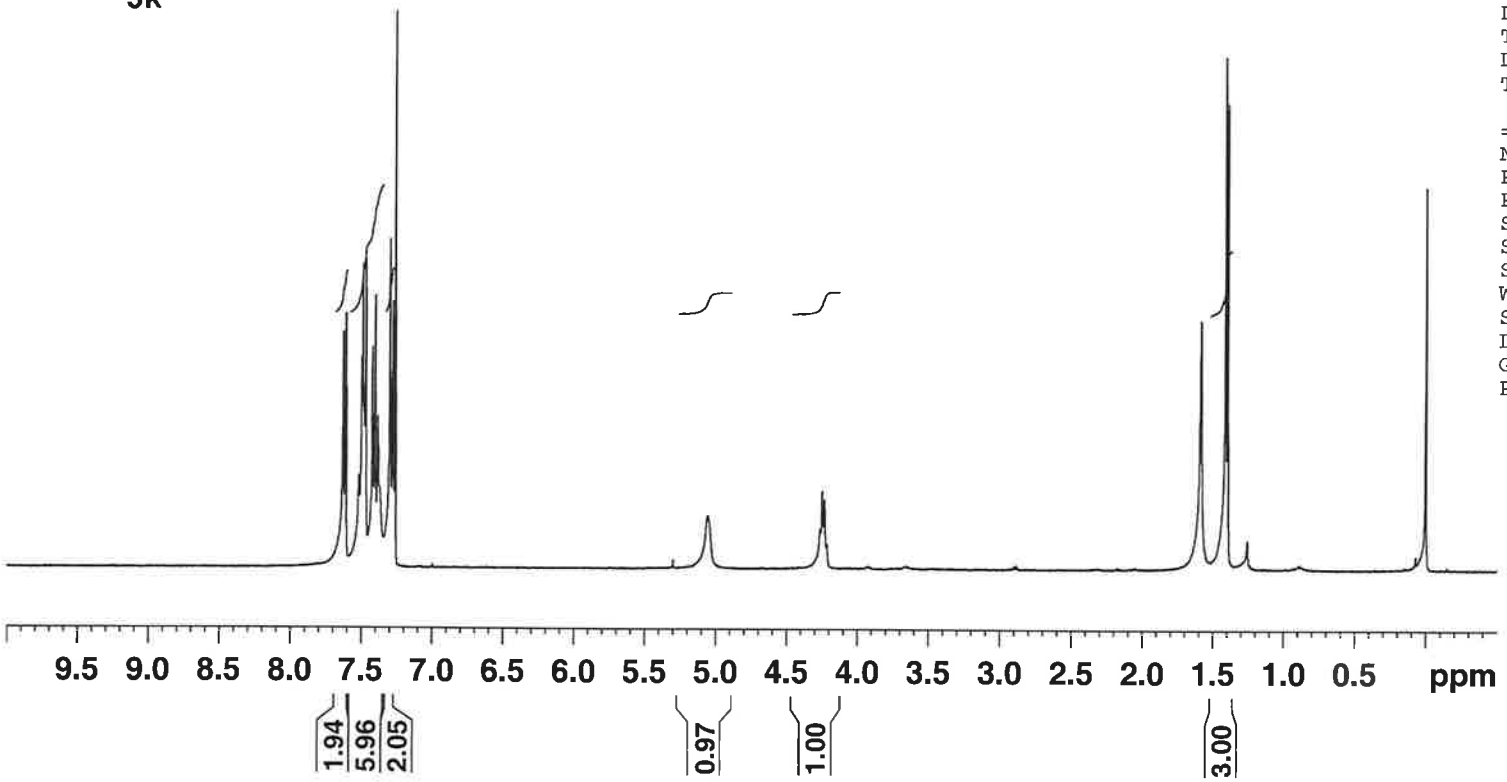


3j

Br

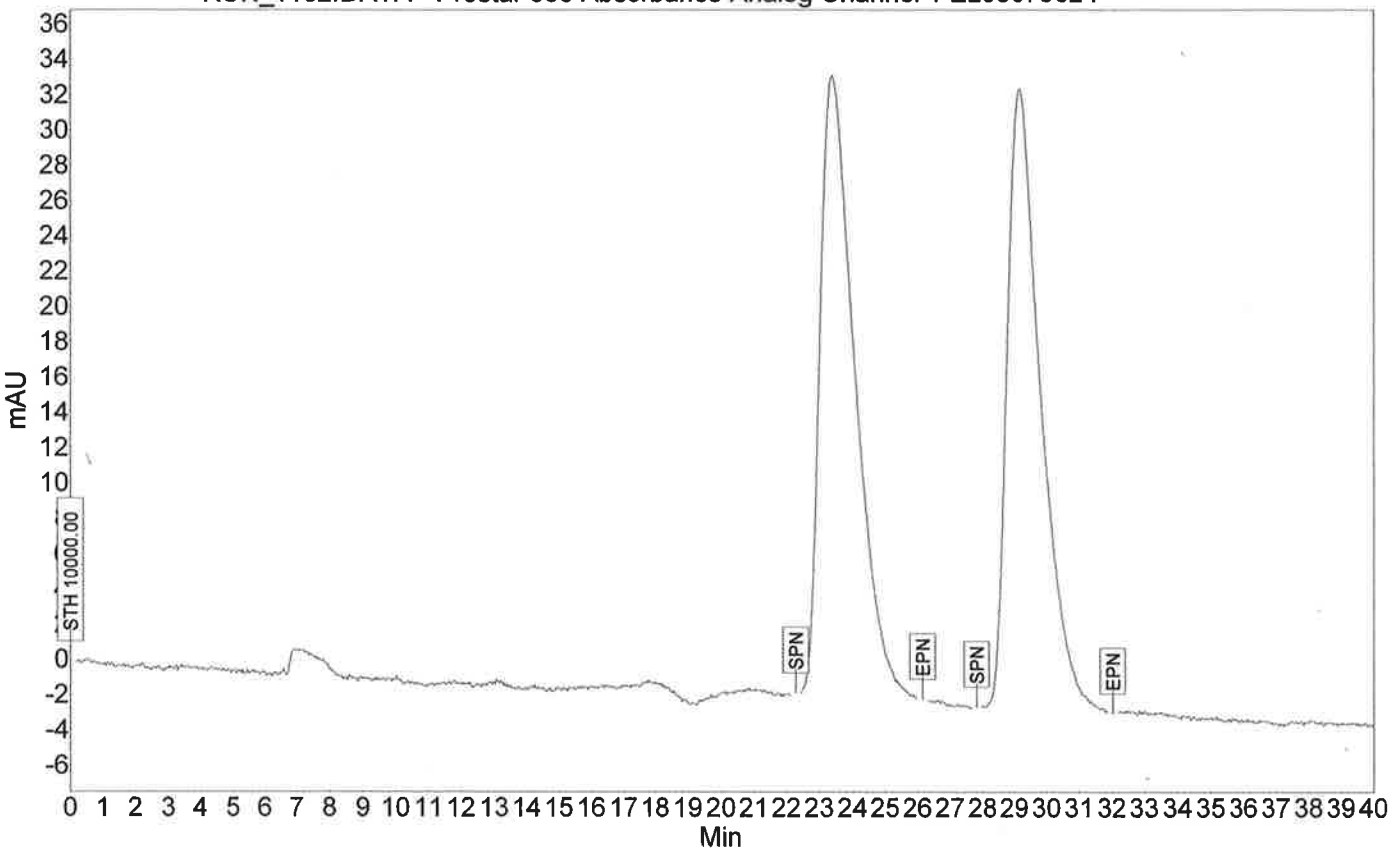


3k

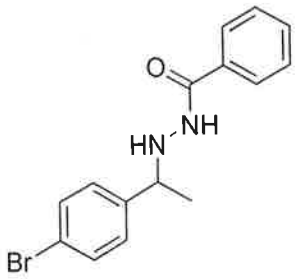


NAME	Aug16-2021-sys
EXPNO	30
PROCNO	1
Date_	20210816
Time	16.55
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	362
DW	60.400 usec
DE	6.50 usec
TE	296.3 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	11.60 usec
PL1	3.00 dB
SFO1	400.1324710 MHz
SI	32768
SF	400.1300086 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

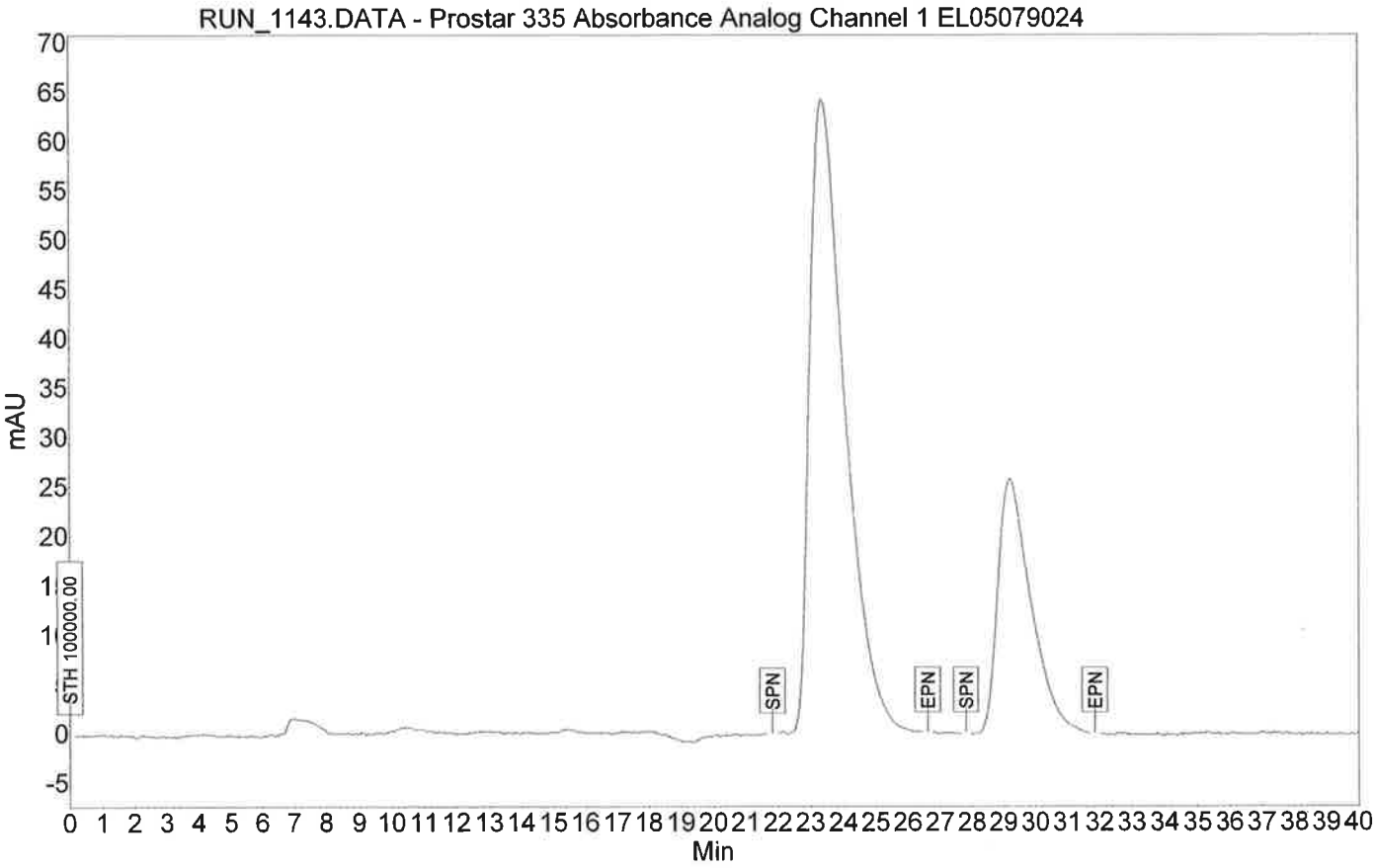
RUN_1162.DATA - Prostar 335 Absorbance Analog Channel 1 EL05079024



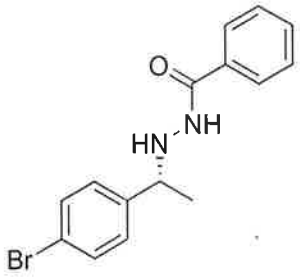
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	23.39	49.80	35.1	42.9	49.801
2	UNKNOWN	29.15	50.20	35.1	43.2	50.199
Total			100.00	70.2	86.1	100.000



(±)

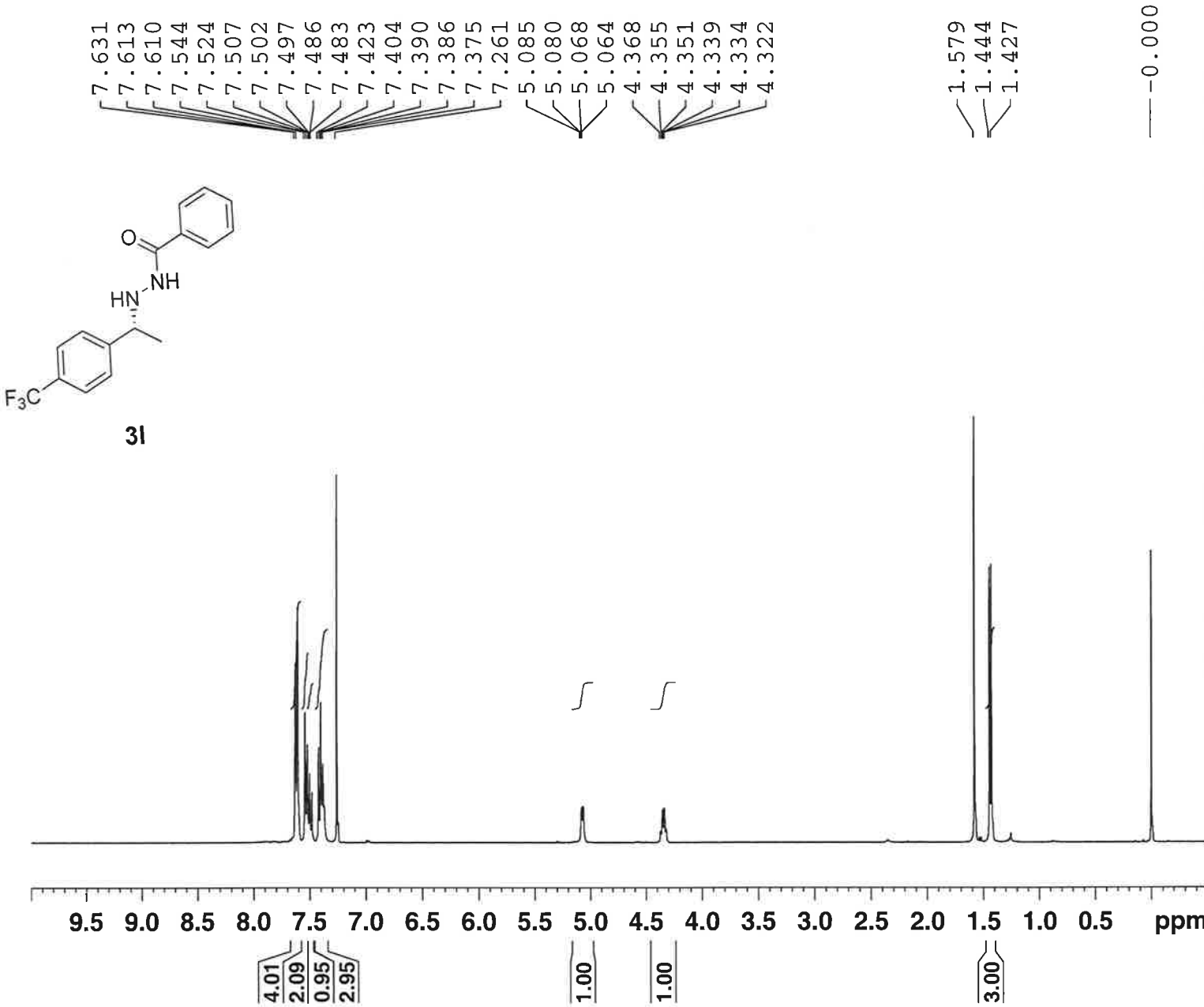


Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	23.36	71.91	64.2	79.6	71.906
2	UNKNOWN	29.21	28.09	25.8	31.1	28.094
Total			100.00	90.0	110.7	100.000

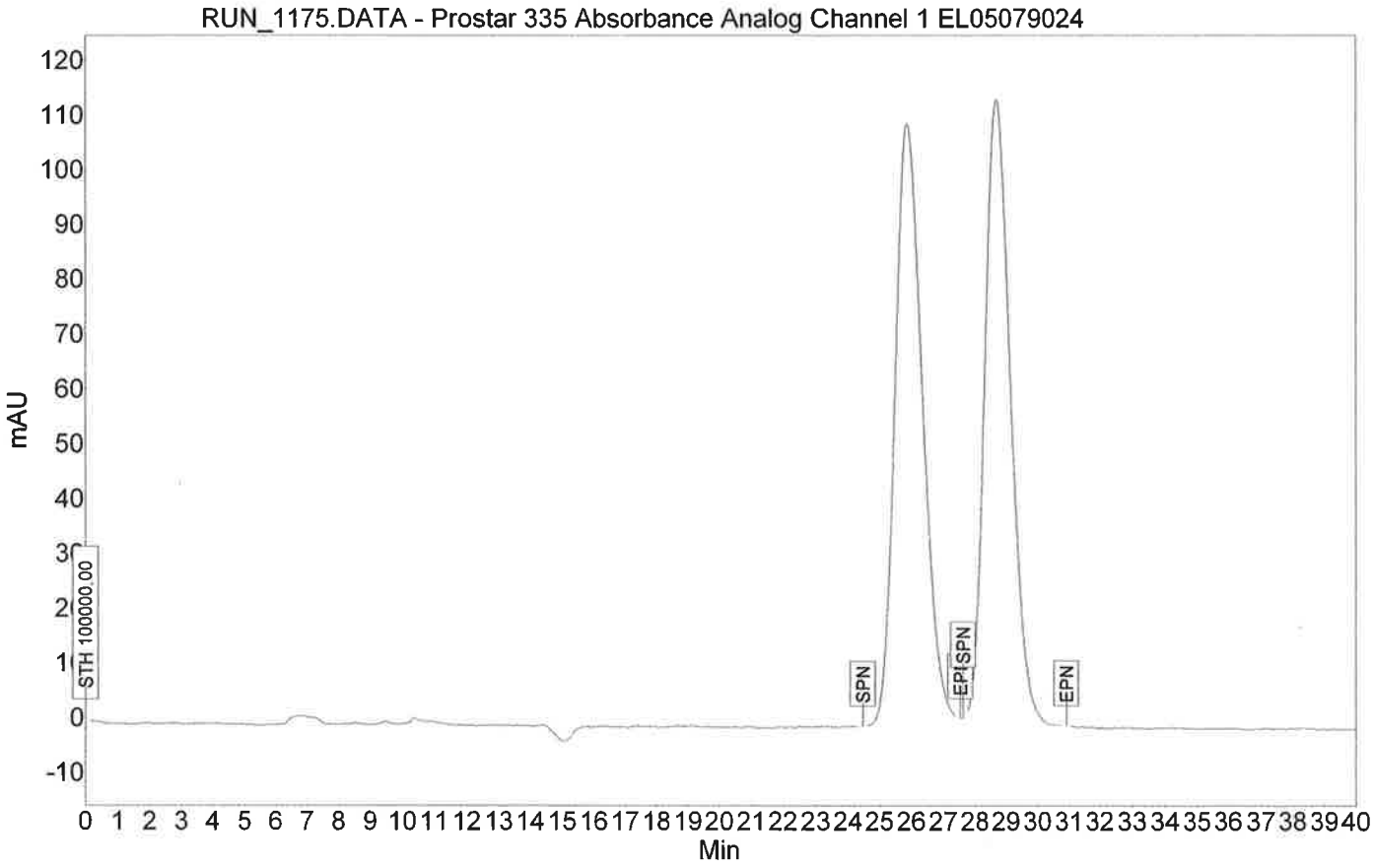


3k

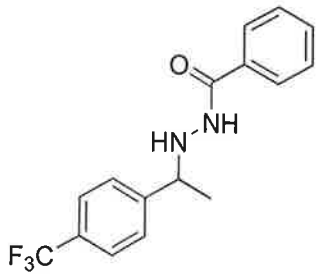
CF3



NAME	Aug16-2021-cxu
EXPNO	30
PROCNO	1
Date_	20210816
Time	17.18
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	362
DW	60.400 usec
DE	6.50 usec
TE	296.2 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	11.60 usec
PL1	3.00 dB
SFO1	400.1324710 MHz
SI	32768
SF	400.1300089 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	25.87	50.00	109.4	109.0	49.996
2	UNKNOWN	28.68	50.00	113.5	109.0	50.004
Total			100.00	222.9	218.0	100.000



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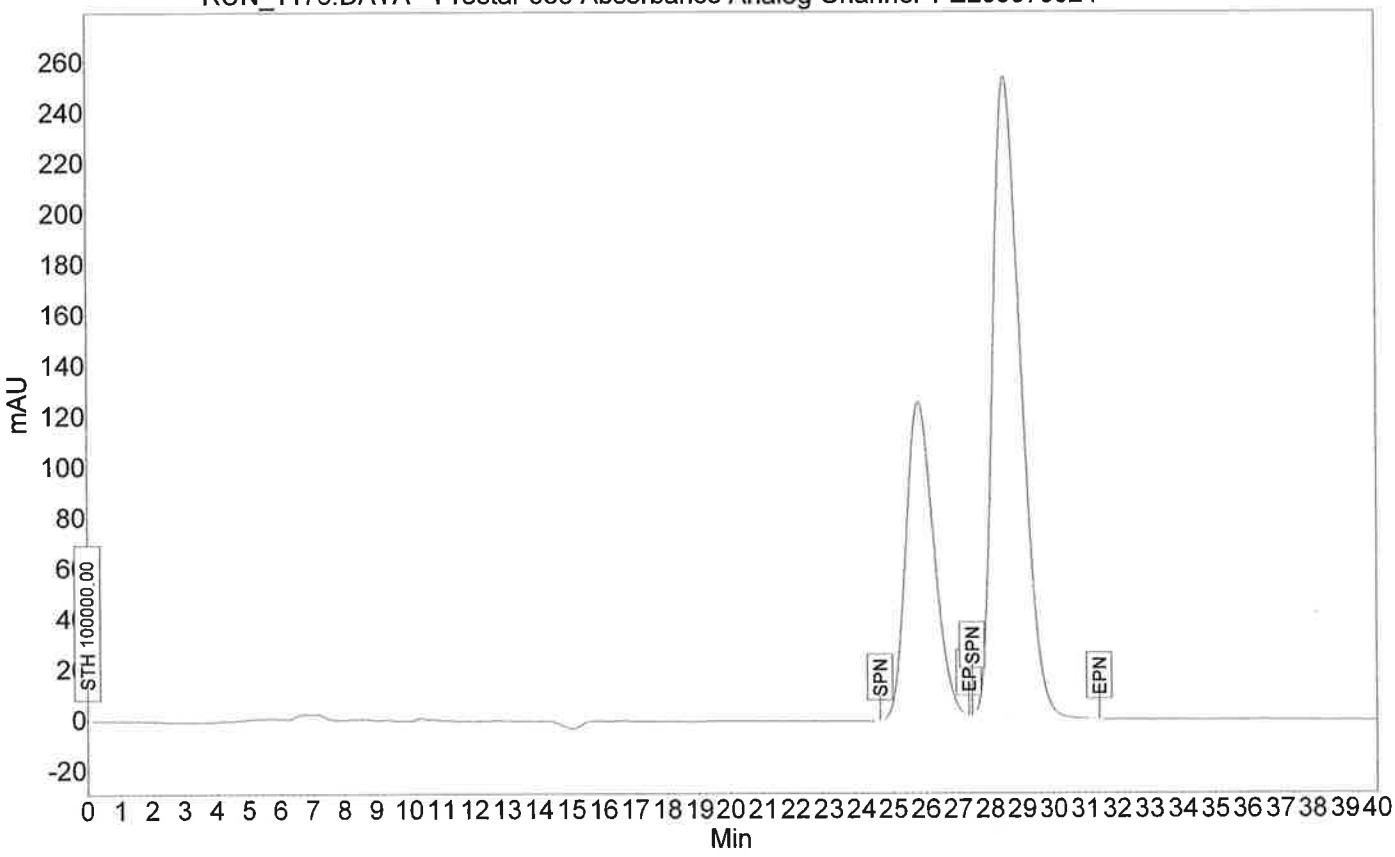
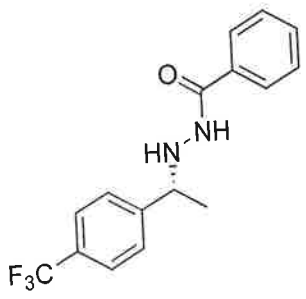
RUN_1176.DATA - Prostar 335 Absorbance Analog Channel 1 EL05079024

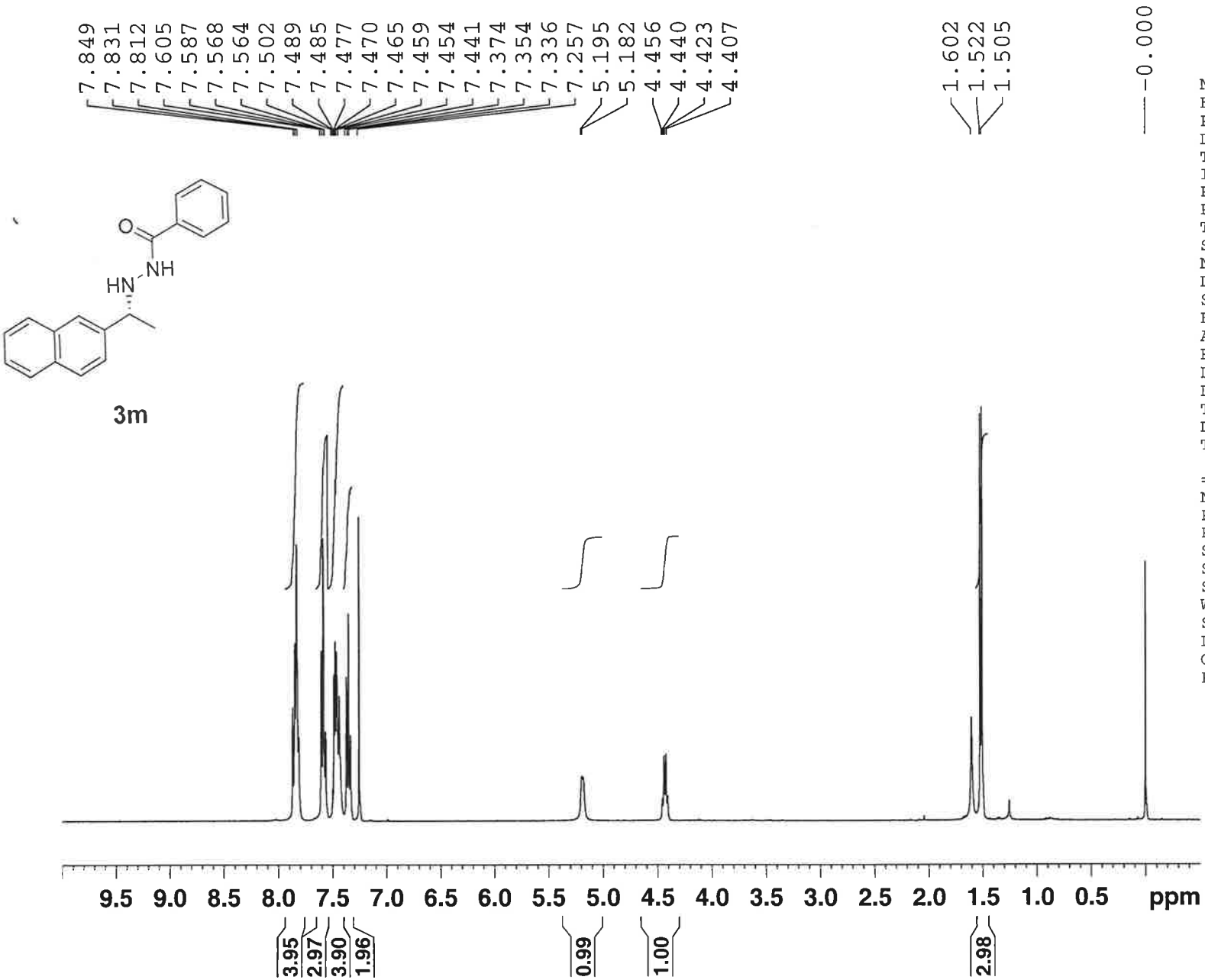


Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	25.77	32.27	125.3	124.2	32.271
2	UNKNOWN	28.48	67.73	253.1	260.6	67.729
Total			100.00	378.4	384.8	100.000



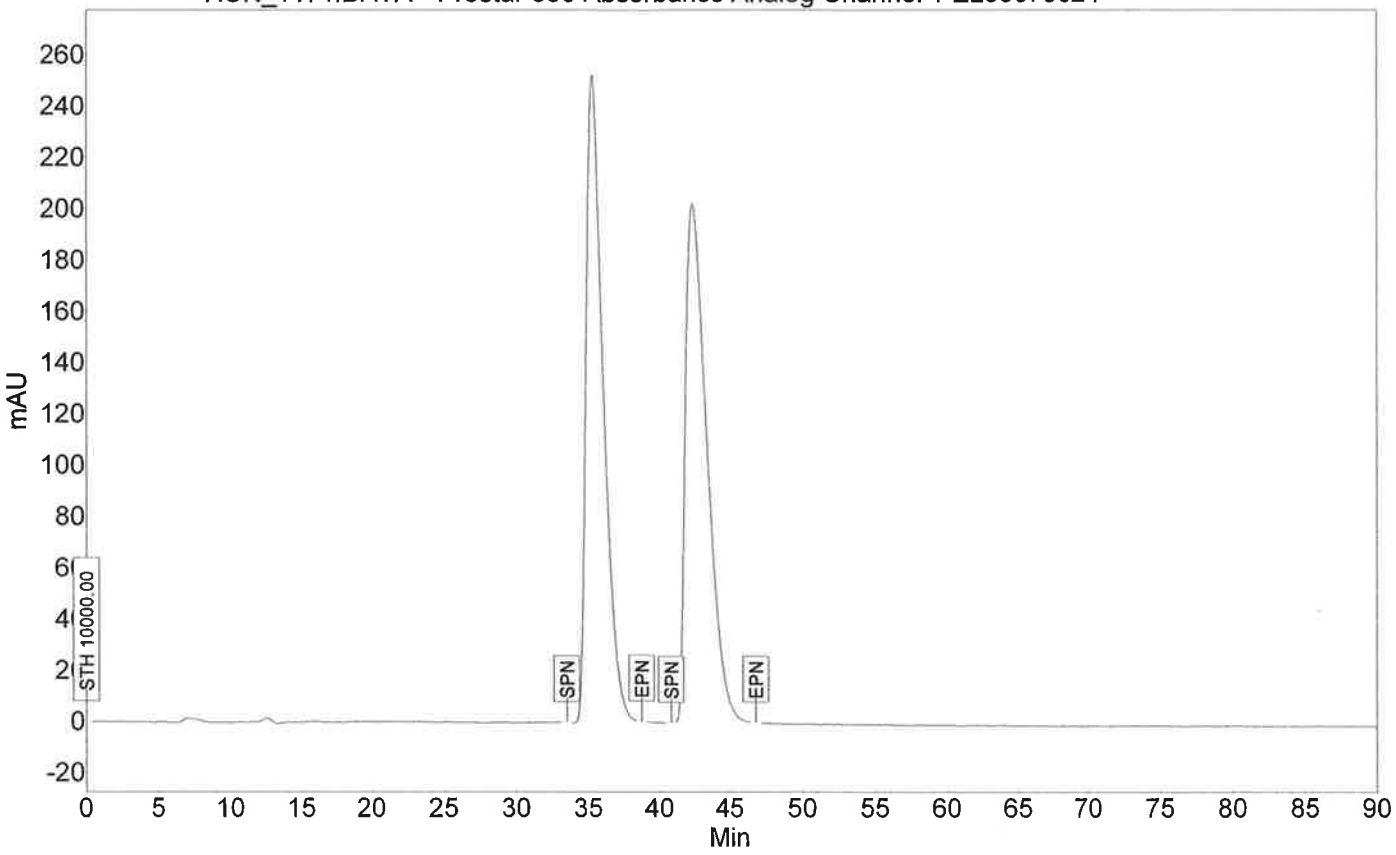
3l

nap

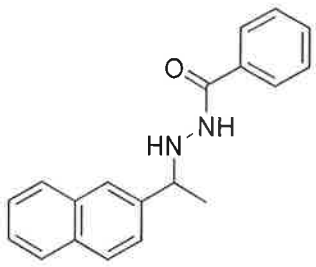


NAME	Aug15-2021-sys
EXPNO	40
PROCNO	1
Date_	20210815
Time	16.38
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	256
DW	60.400 usec
DE	6.50 usec
TE	296.3 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	11.60 usec
PL1	3.00 dB
SFO1	400.1324710 MHz
SI	32768
SF	400.1300108 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

RUN_1171.DATA - Prostar 335 Absorbance Analog Channel 1 EL05079024



Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	35.23	49.53	252.4	352.2	49.530
2	UNKNOWN	42.29	50.47	202.4	358.9	50.470
Total			100.00	454.8	711.1	100.000



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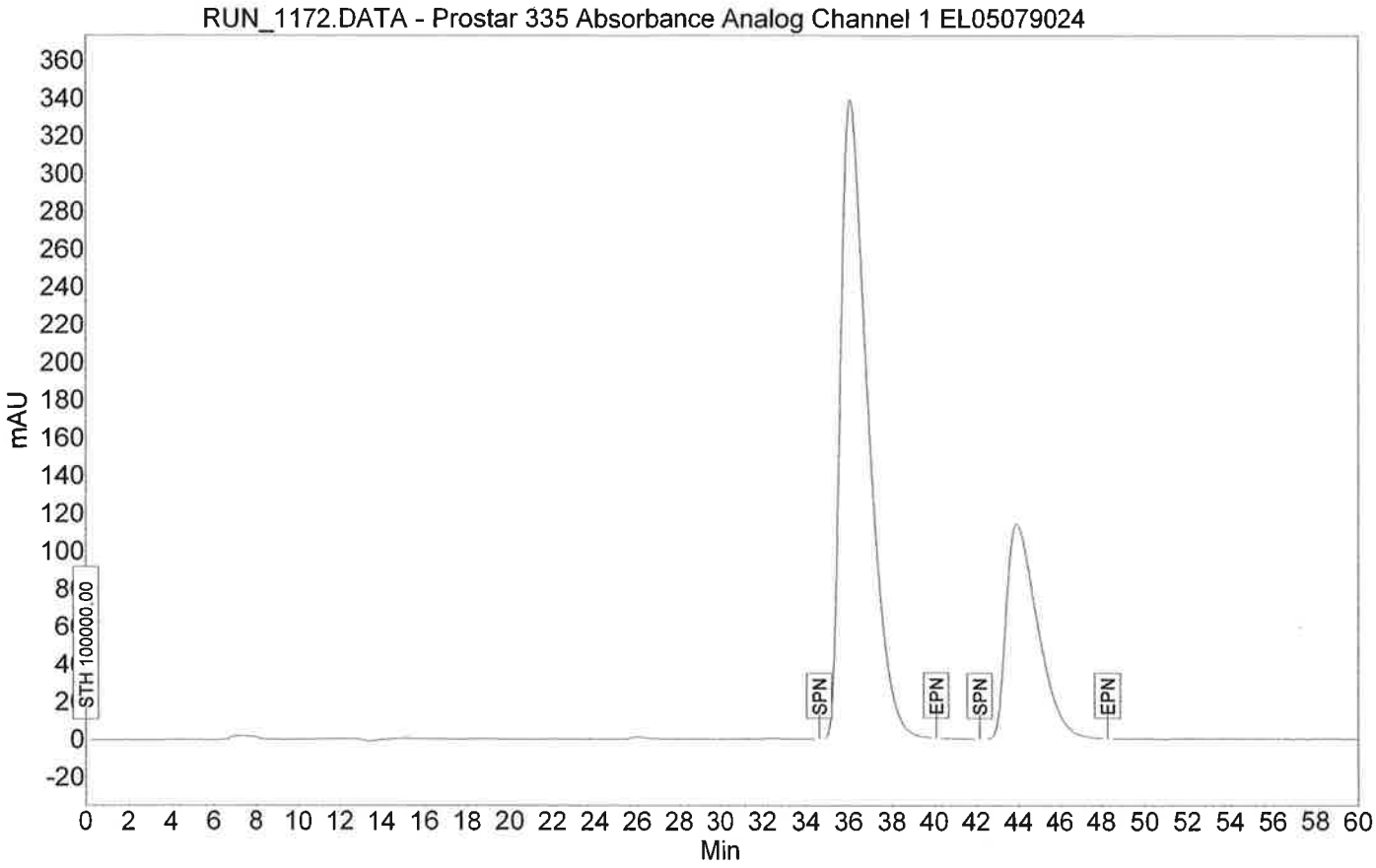
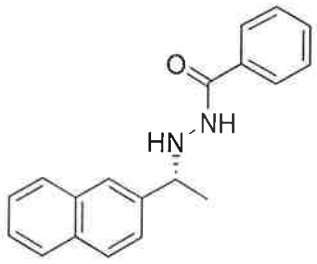


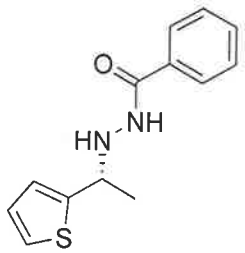
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	36.05	71.55	338.6	498.8	71.547
2	UNKNOWN	43.91	28.45	114.0	198.4	28.453
Total			100.00	452.5	697.2	100.000



3m

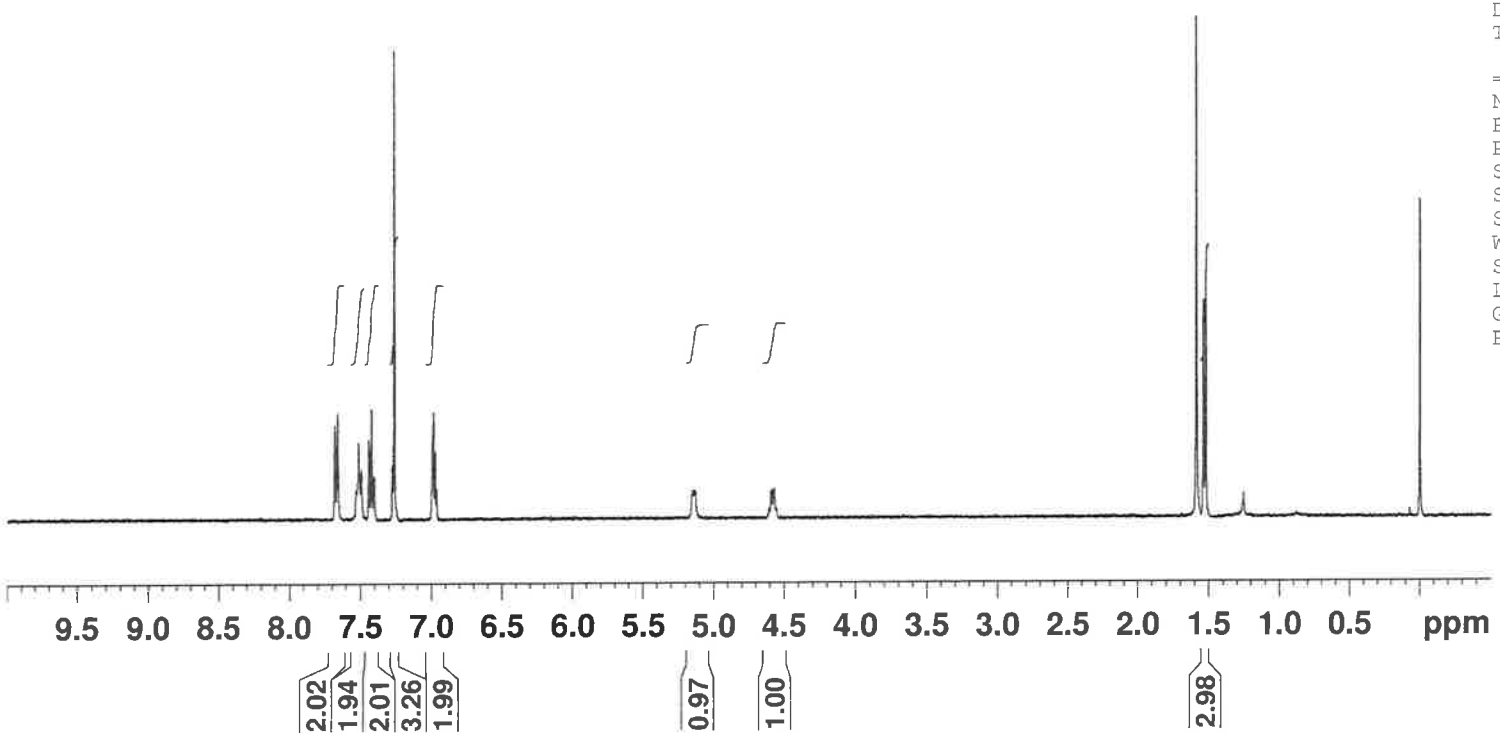
Thio

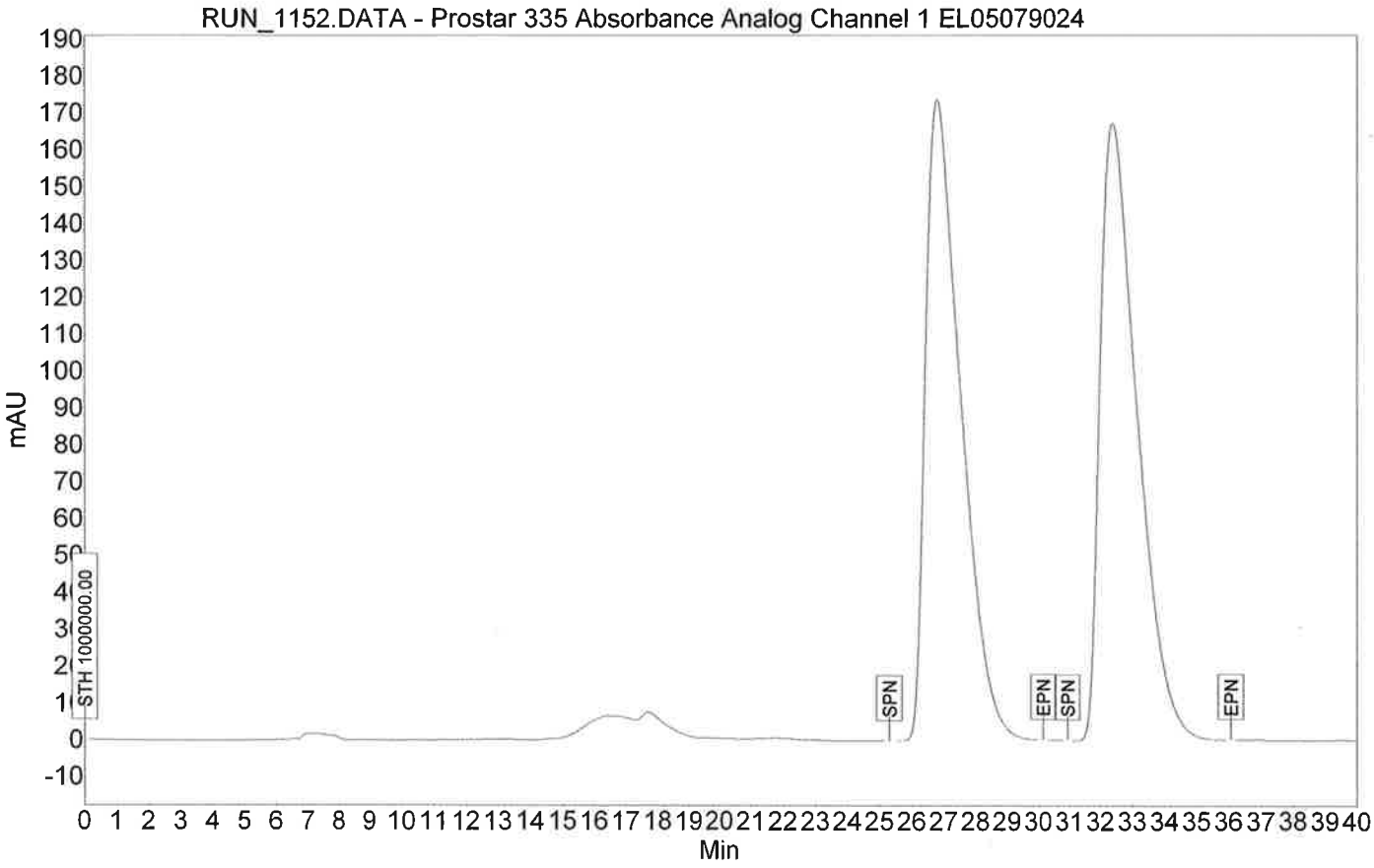
7.681
7.663
7.530
7.512
7.494
7.441
7.422
7.403
7.274
7.263
6.987
6.974
6.966
5.148
5.136
4.603
4.592
4.588
4.576
4.561
1.588
1.538
1.521
0.000



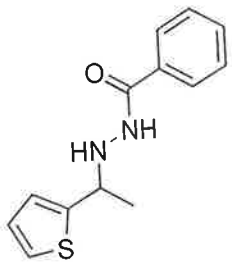
3n

NAME	Aug14-2021-cxu
EXPNO	6
PROCNO	1
Date_	20210814
Time	16.13
INSTRUM	spect
PROBHD	5 mm TBI 1H/31
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	29193
DW	60.400 usec
DE	6.50 usec
TE	300.0 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	18.75 usec
PL1	0.50 dB
SFO1	400.1324710 MHz
SI	32768
SF	400.1300085 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

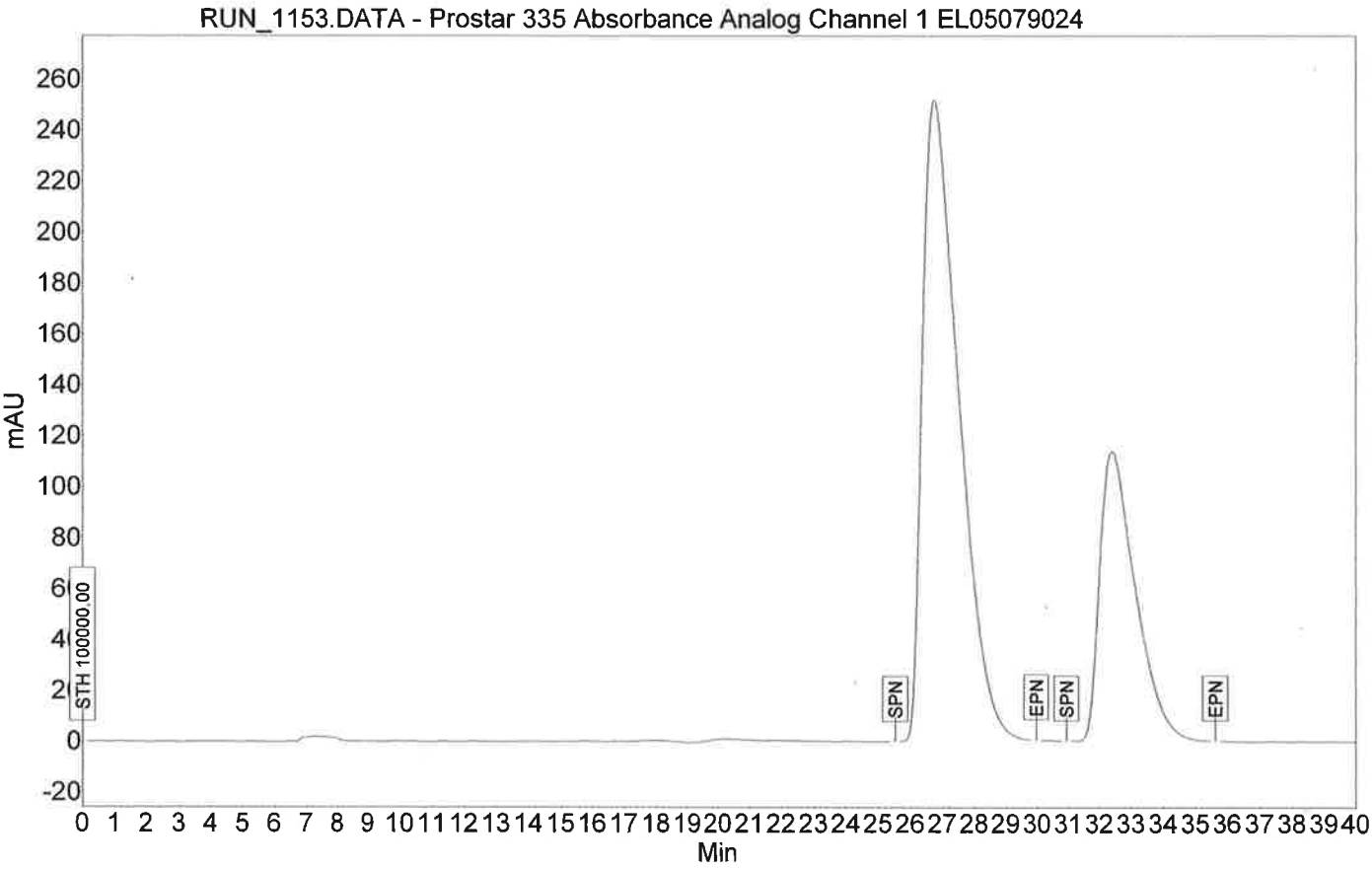




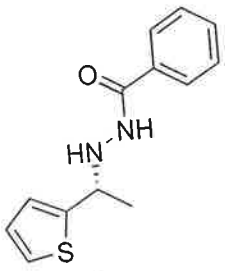
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	26.77	49.94	173.7	224.1	49.941
2	UNKNOWN	32.36	50.06	167.0	224.6	50.059
Total			100.00	340.7	448.6	100.000



(±)

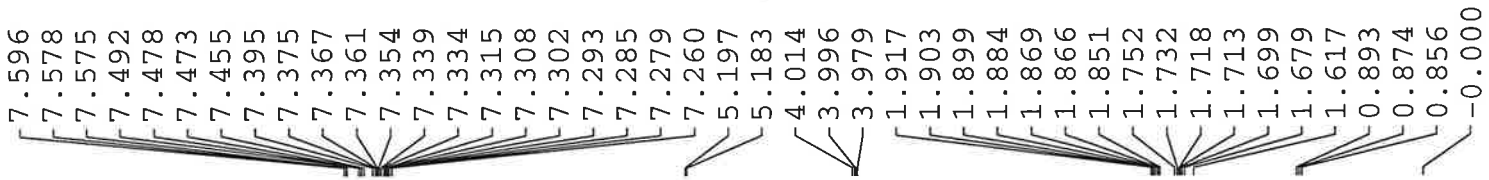


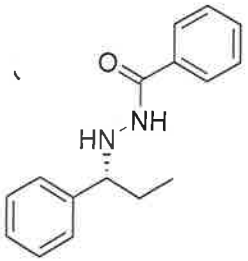
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	26.72	69.16	251.6	333.2	69.159
2	UNKNOWN	32.39	30.84	113.8	148.6	30.841
Total			100.00	365.4	481.7	100.000



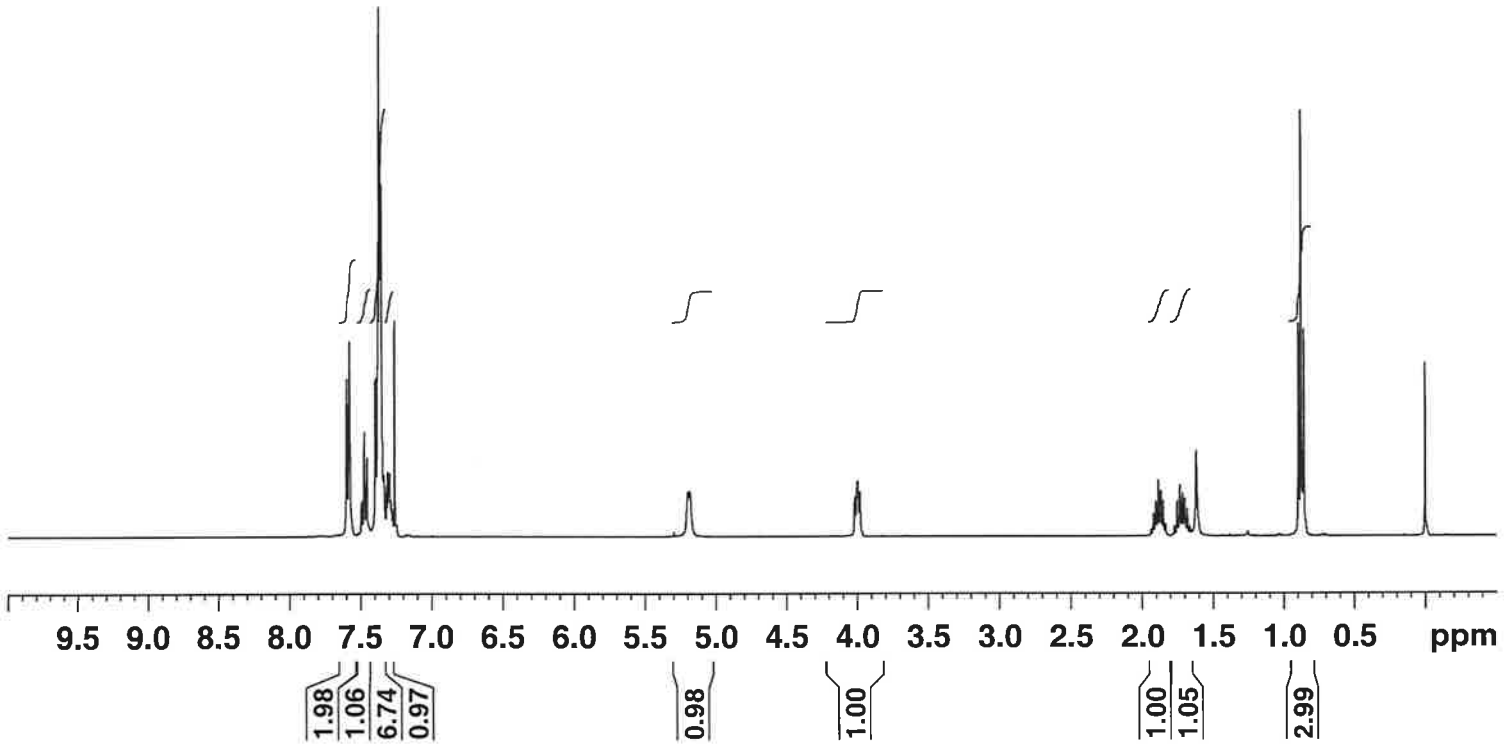
3n

Et

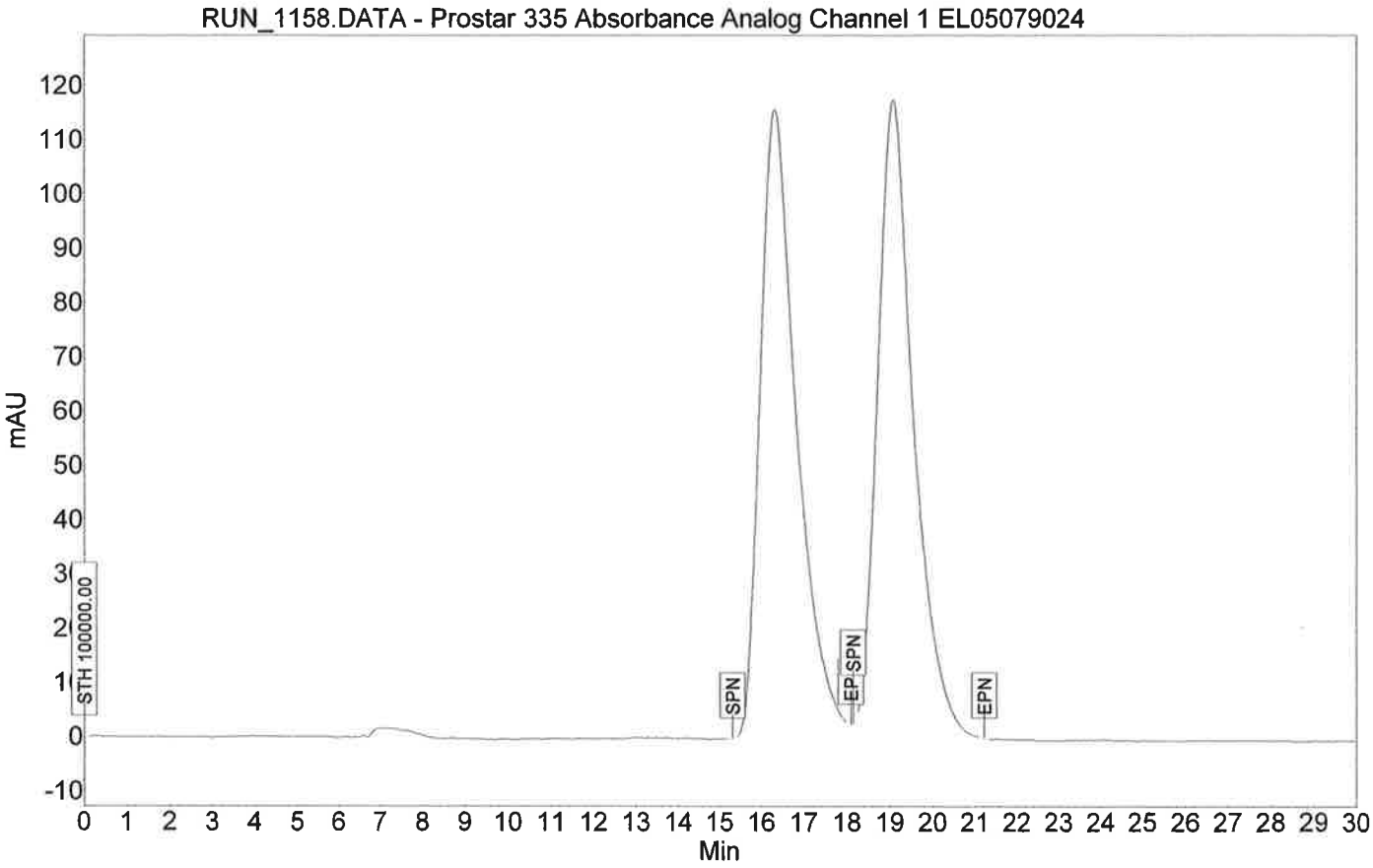




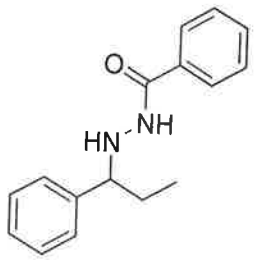
3o



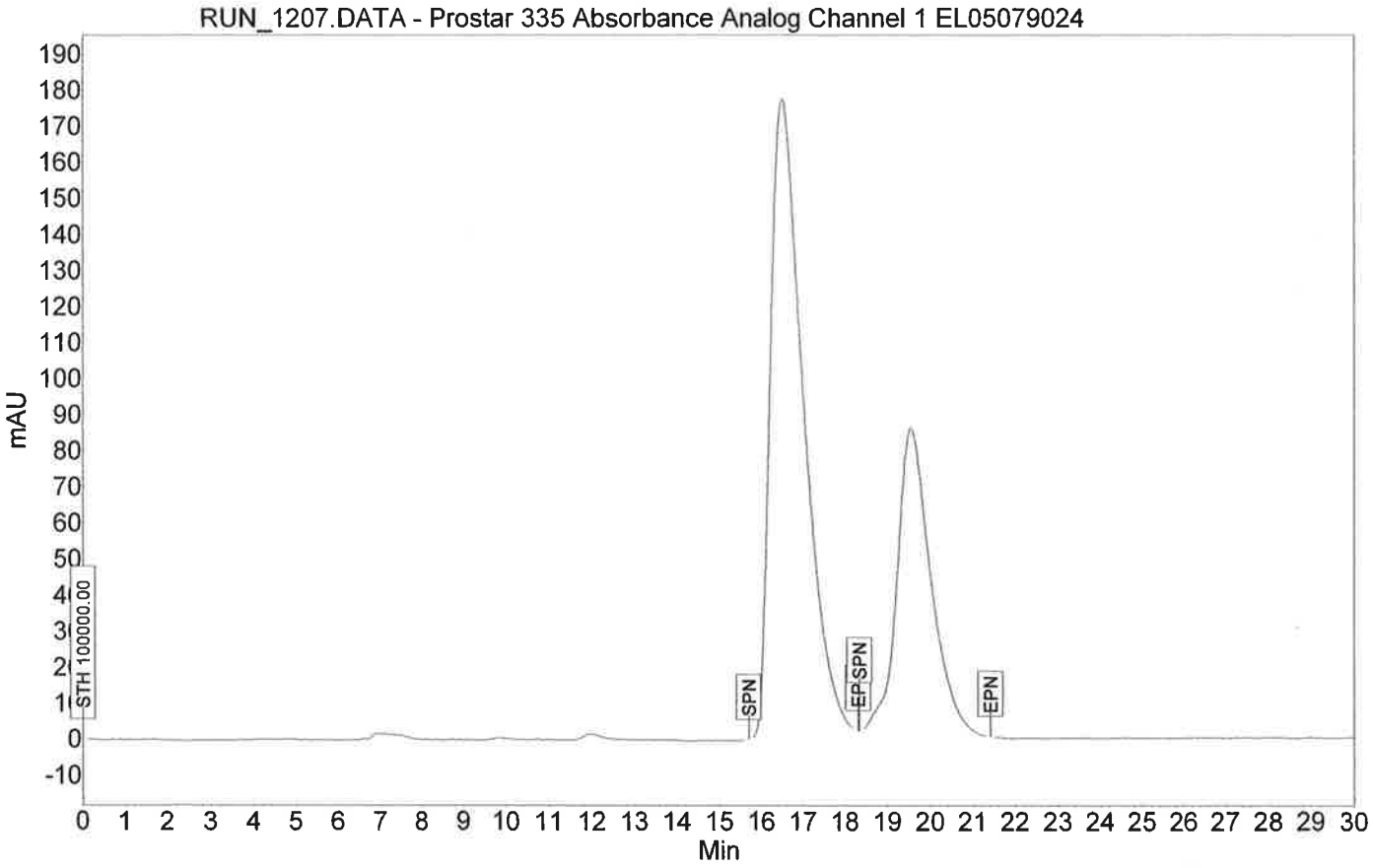
NAME	Aug19-2021-sys
EXPNO	20
PROCNO	1
Date_	20210819
Time	15.56
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	256
DW	60.400 usec
DE	6.50 usec
TE	296.6 K
D1	1.00000000 sec
TD0	1
========	CHANNEL f1 ========
NUC1	1H
P1	11.60 usec
PL1	3.00 dB
SFO1	400.1324710 MHz
SI	32768
SF	400.1300097 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



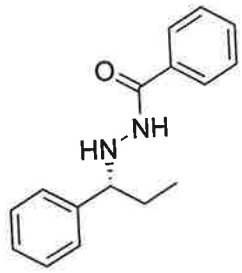
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	16.31	50.19	115.0	112.6	50.194
2	UNKNOWN	19.08	49.81	115.9	111.8	49.806
Total			100.00	230.9	224.4	100.000



(±)



Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	16.49	67.80	176.9	163.0	67.802
2	UNKNOWN	19.55	32.20	84.6	77.4	32.198
Total			100.00	261.5	240.4	100.000



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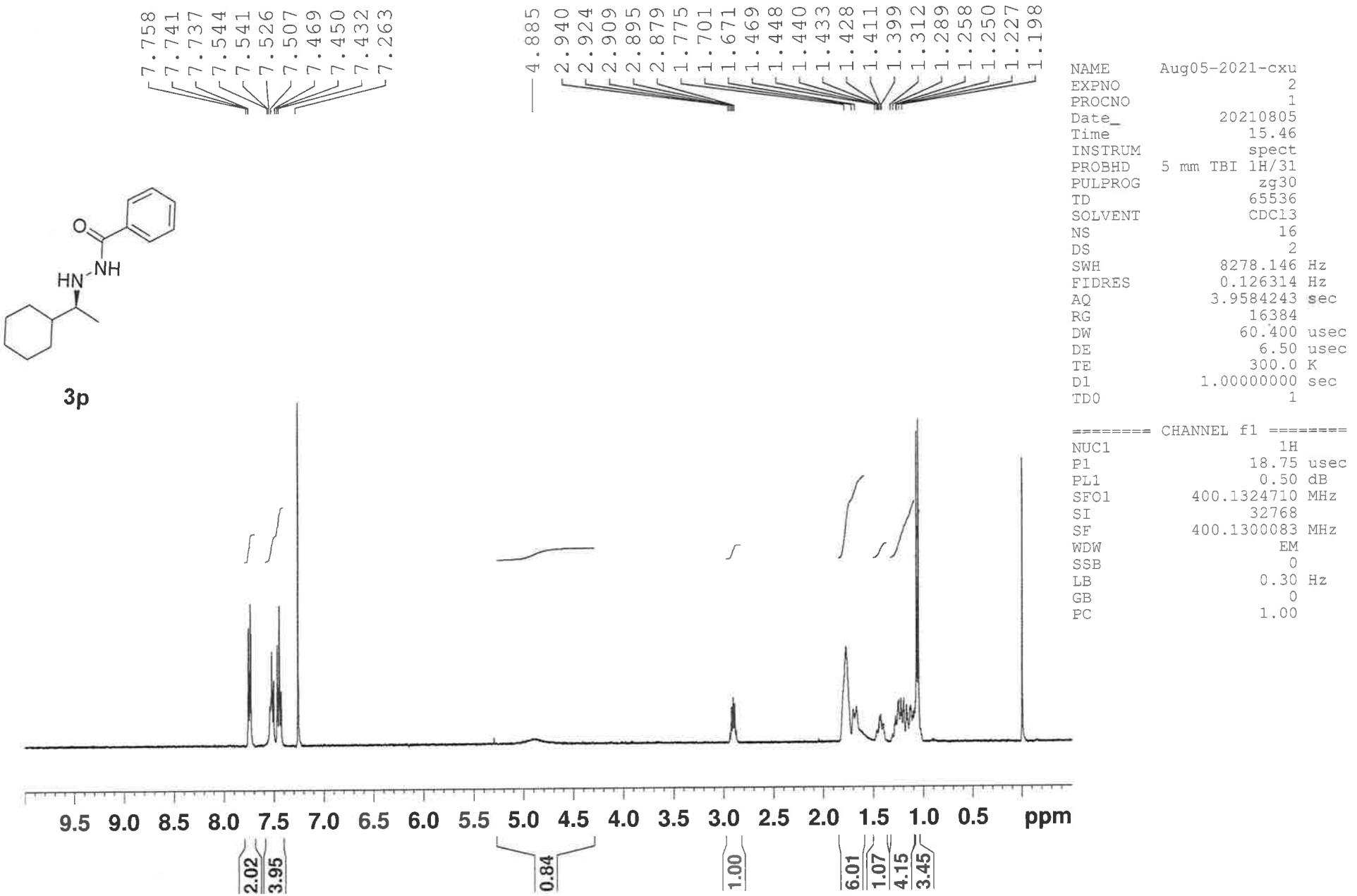
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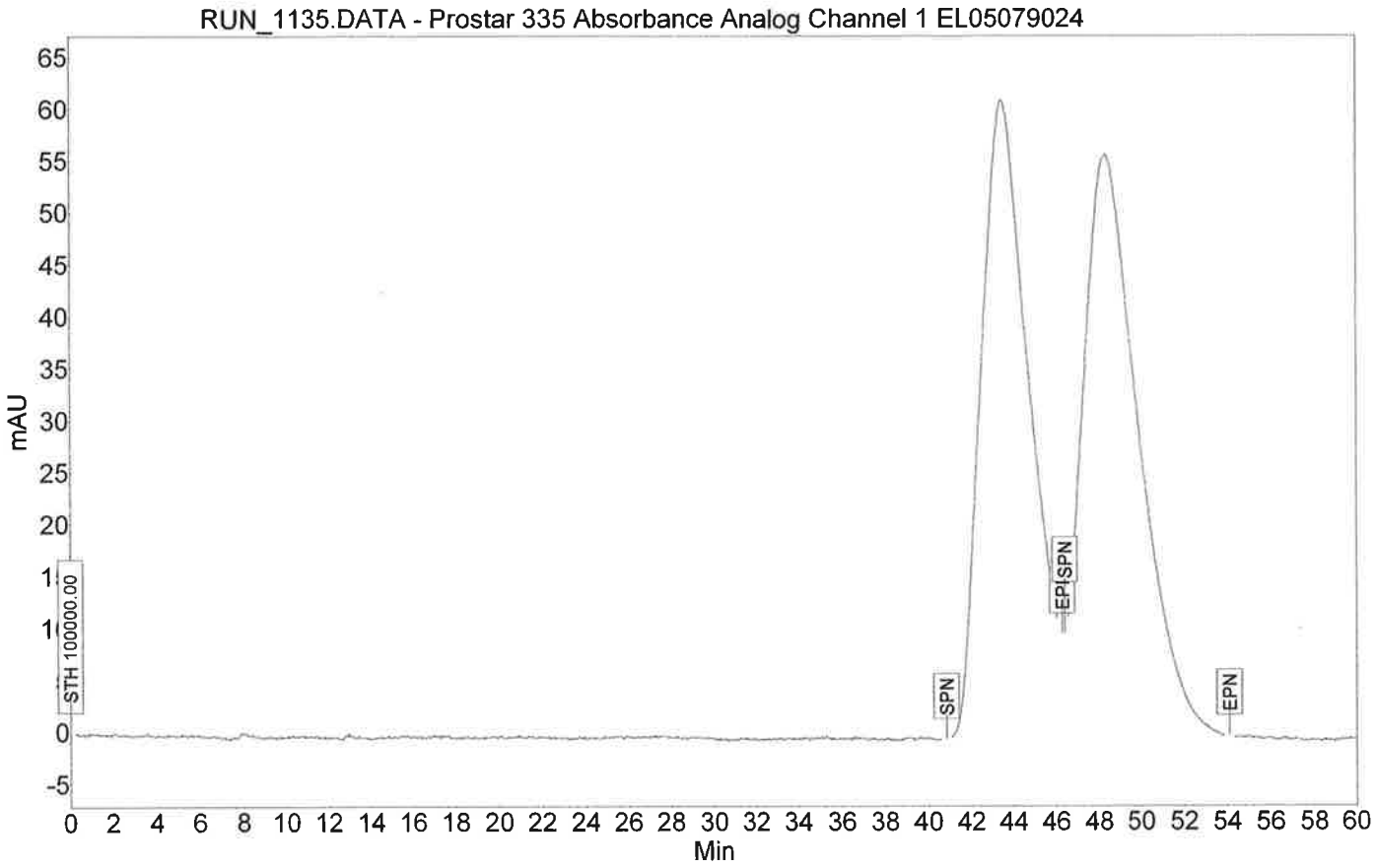
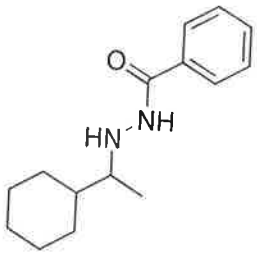
7.737
7.544
7.541
7.526
7.507
7.469
7.450
7.432
7.263
4.885
2.940
2.924
2.909
2.895
2.879
1.775
1.701
1.671
1.469
1.448
1.440
1.433
1.428
1.411
1.399
1.312
1.289
1.258
1.250
1.227
1.198
O
NH
HN
3p
NAME Aug05-2021-cxu
EXPNO 2
PROCNO 1
Date_ 20210805
Time 15.46
INSTRUM spect
PROBHD 5 mm TBI 1H/31
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 16384
DW 60.400 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 18.75 usec
PL1 0.50 dB
SFO1 400.1324710 MHz
SI 32768
SF 400.1300083 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.02
3.95
0.84
1.00
6.01
1.07
4.15
3.45



Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	43.41	50.49	56.8	135.1	50.486
2	UNKNOWN	48.35	49.51	48.6	132.5	49.514
Total			100.00	105.4	267.7	100.000



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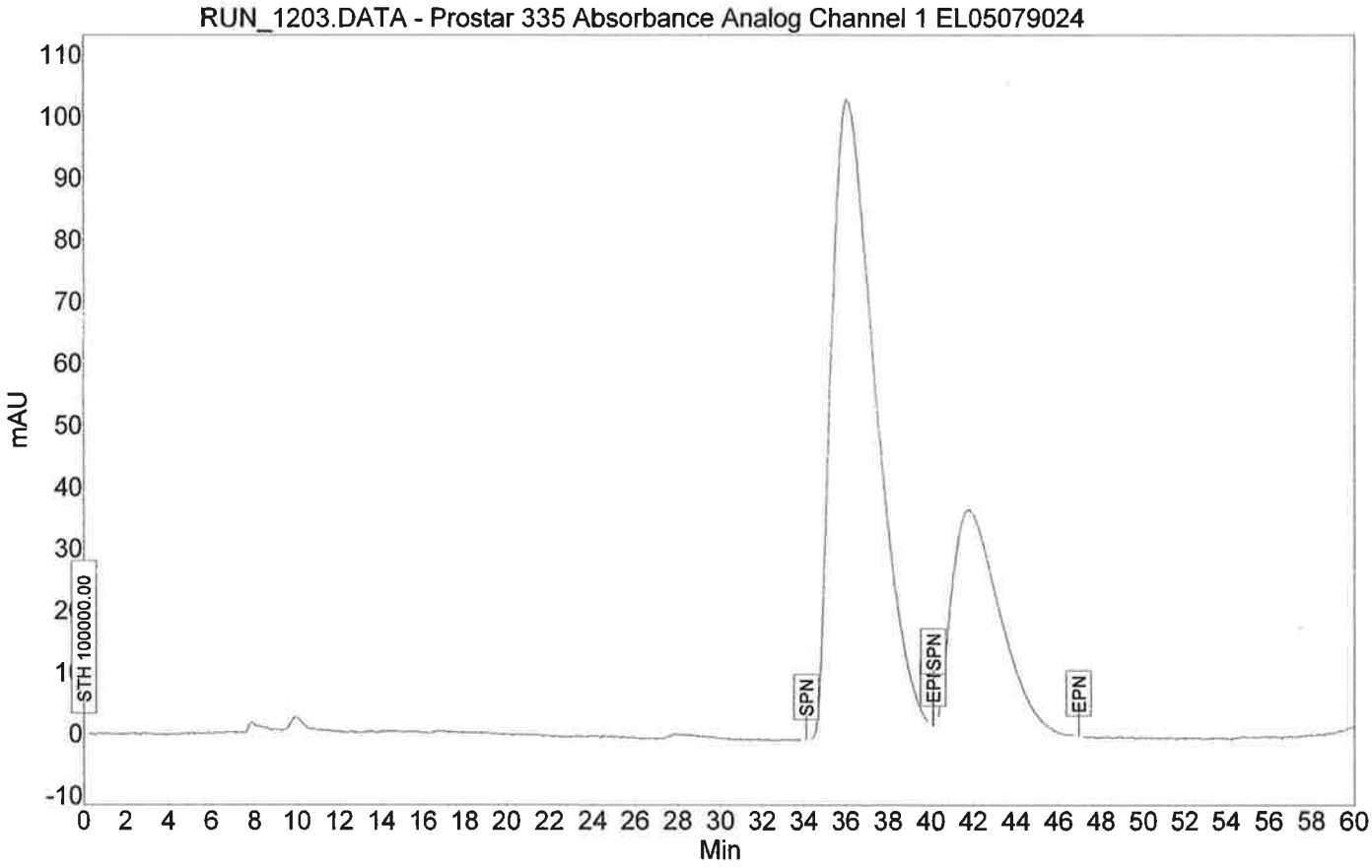
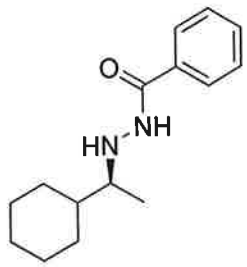


Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	36.08	72.91	103.0	248.6	72.907
2	UNKNOWN	41.83	27.09	35.5	92.4	27.093
Total			100.00	138.5	341.0	100.000



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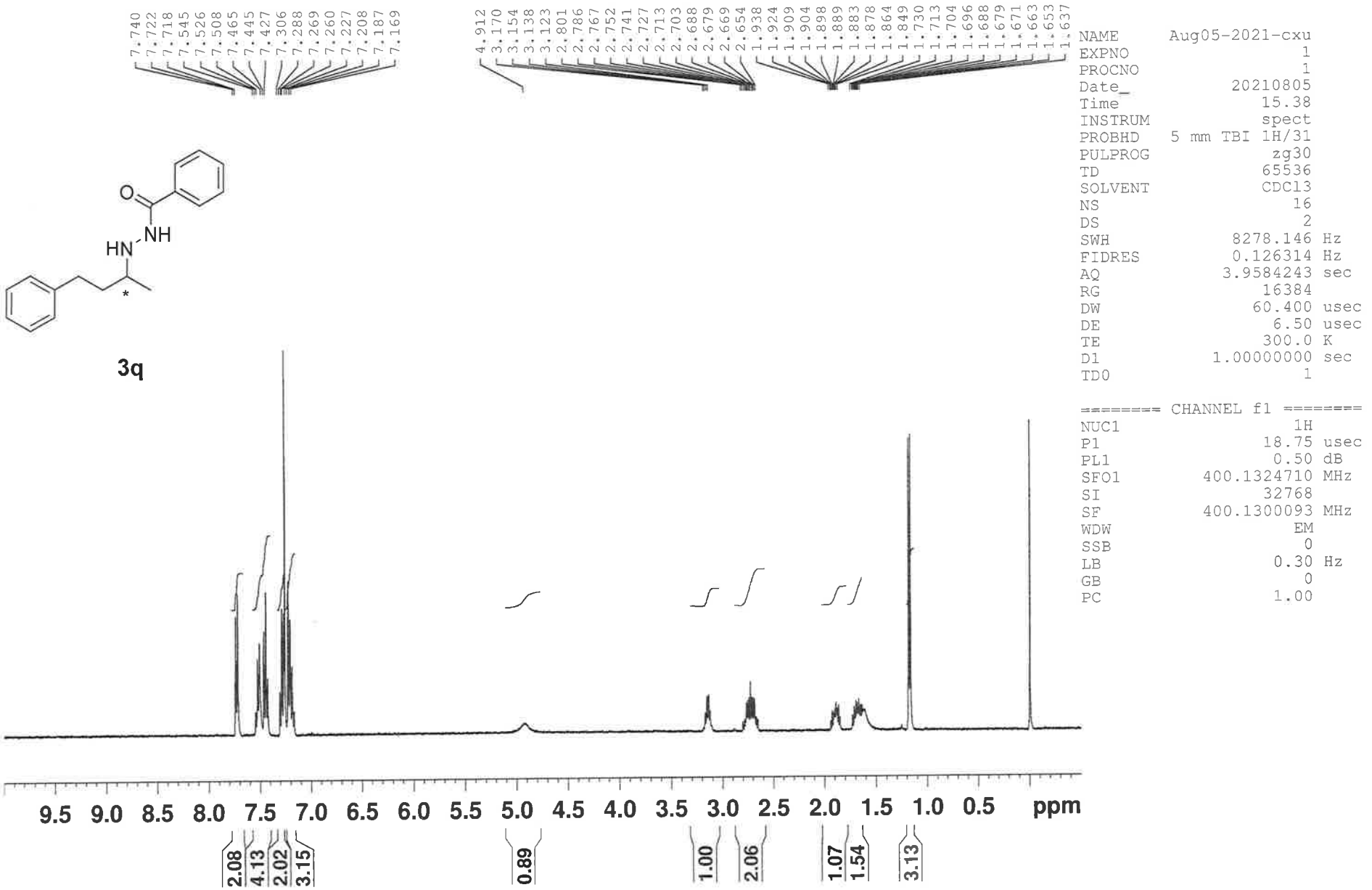
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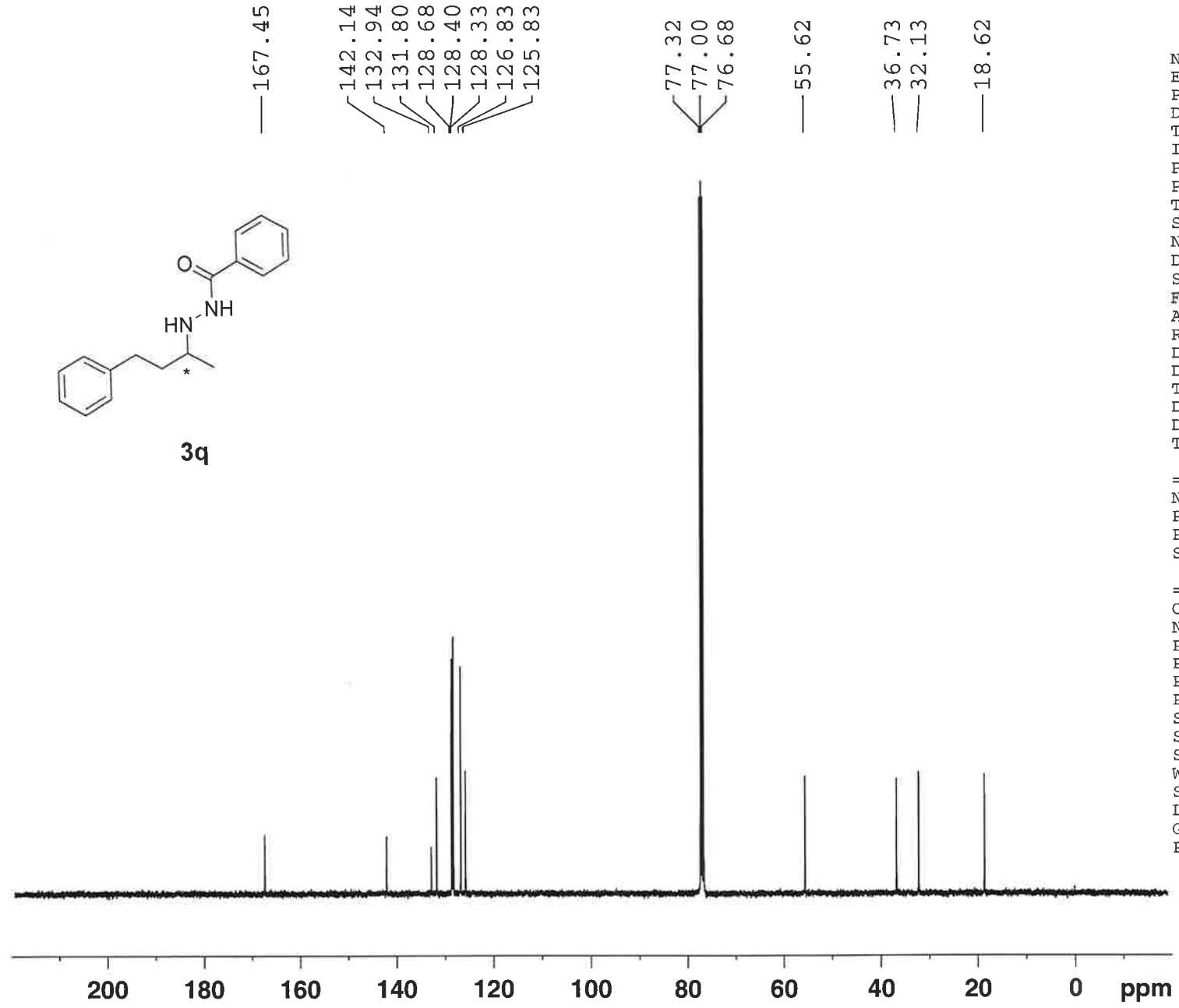
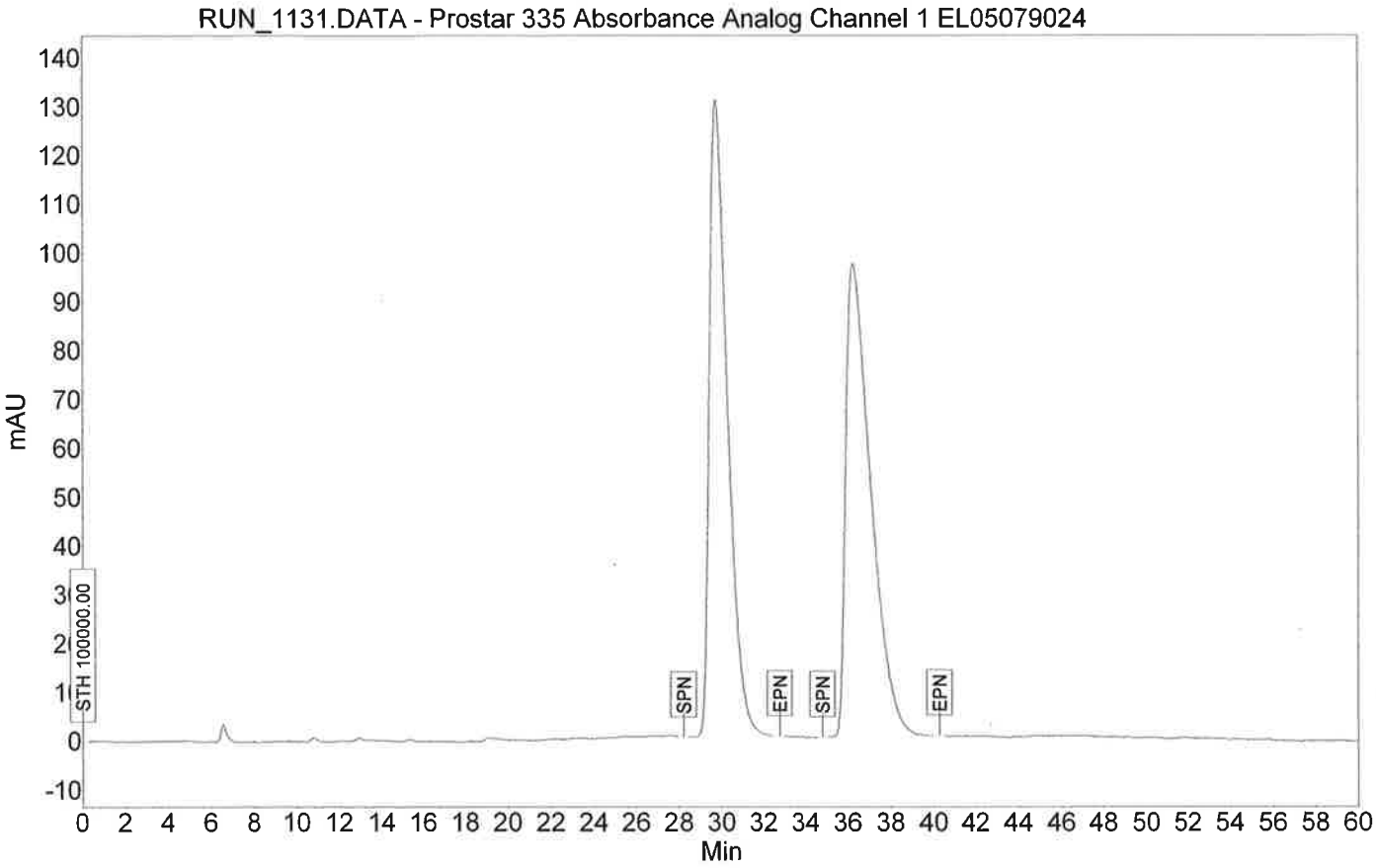
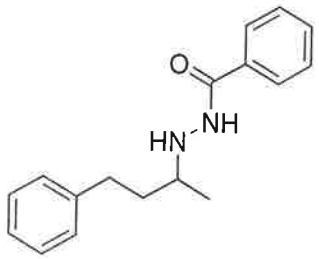
7.465
7.445
7.427
7.306
7.288
7.269
7.260
7.227
7.208
7.187
7.169
4.912
3.170
3.154
3.138
3.123
2.801
2.786
2.767
2.752
2.741
2.727
2.713
2.703
2.688
2.679
2.669
2.654
1.938
1.924
1.909
1.904
1.898
1.889
1.883
1.878
1.864
1.849
1.730
1.713
1.704
1.696
1.688
1.679
1.671
1.663
1.653
1.637
O
NH
HN
*
3q
NAME Aug05-2021-cxu
EXPNO 1
PROCNO 1
Date_ 20210805
Time 15.38
INSTRUM spect
PROBHD 5 mm TBI 1H/31
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 16384
DW 60.400 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 18.75 usec
PL1 0.50 dB
SFO1 400.1324710 MHz
SI 32768
SF 400.1300093 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.08
4.13
2.02
3.15
0.89
1.00
2.06
1.07
1.54
3.13



NAME	Aug09-2021-cxu
EXPNO	10
PROCNO	1
Date_	20210810
Time	6.29
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	10240
DS	4
SWH	23980.814 Hz
FIDRES	0.365918 Hz
AQ	1.3664756 sec
RG	32768
DW	20.850 usec
DE	6.50 usec
TE	301.9 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	14.75 usec
PL1	0.00 dB
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-2.00 dB
PL12	12.54 dB
PL13	15.00 dB
SFO2	400.1316005 MHz
SI	32768
SF	100.6127704 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	29.72	49.68	130.5	128.8	49.681
2	UNKNOWN	36.25	50.32	97.0	130.5	50.319
Total			100.00	227.6	259.3	100.000



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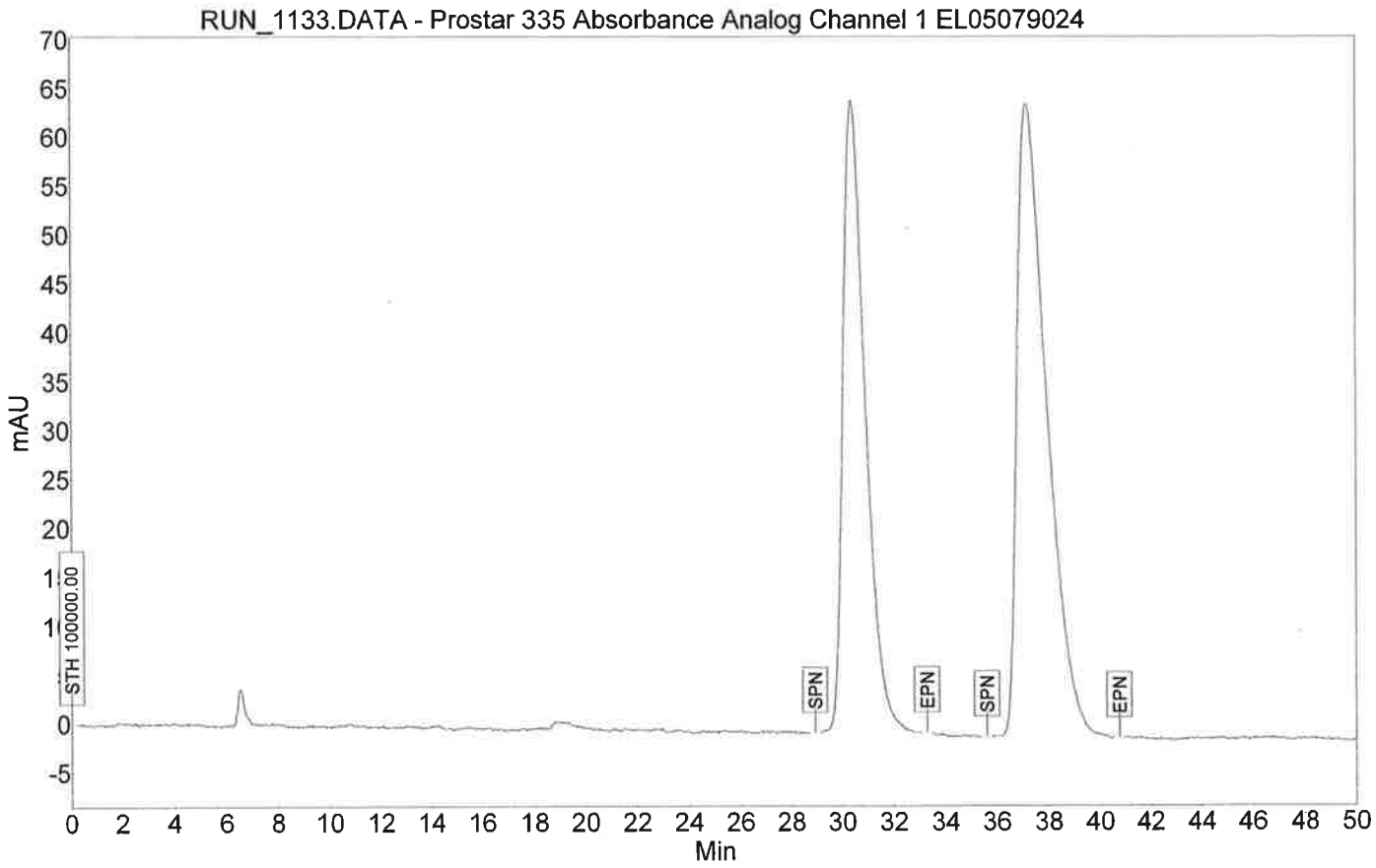
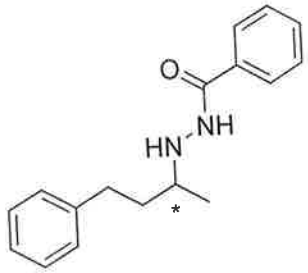


Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	30.40	42.98	64.8	64.8	42.983
2	UNKNOWN	37.17	57.02	64.9	85.9	57.017
Total			100.00	129.7	150.7	100.000



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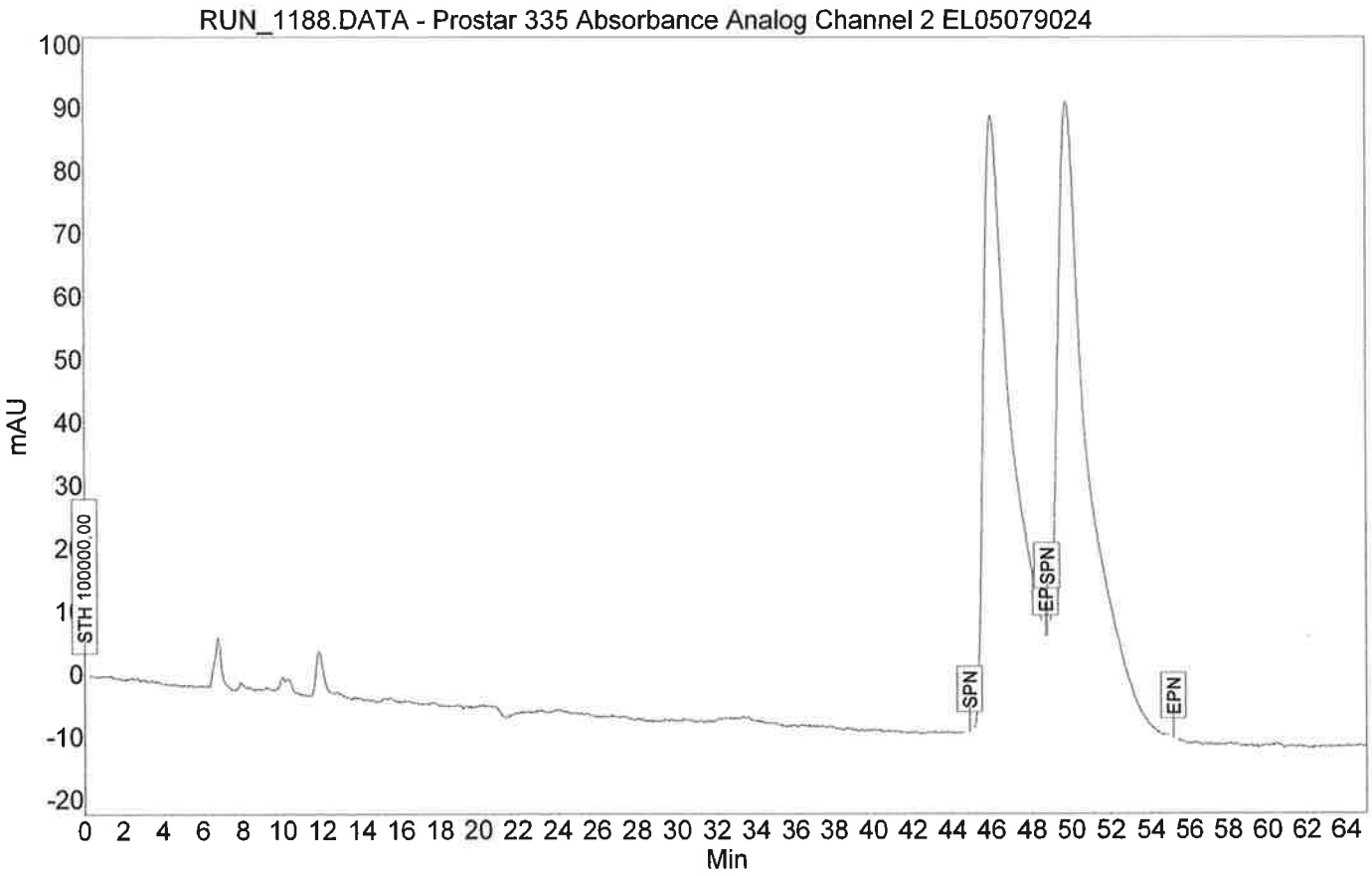
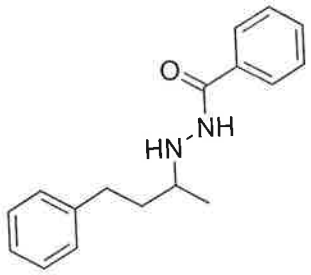


Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	45.99	49.70	93.6	135.3	49.697
2	UNKNOWN	49.79	50.30	87.6	136.9	50.303
Total			100.00	181.2	272.2	100.000



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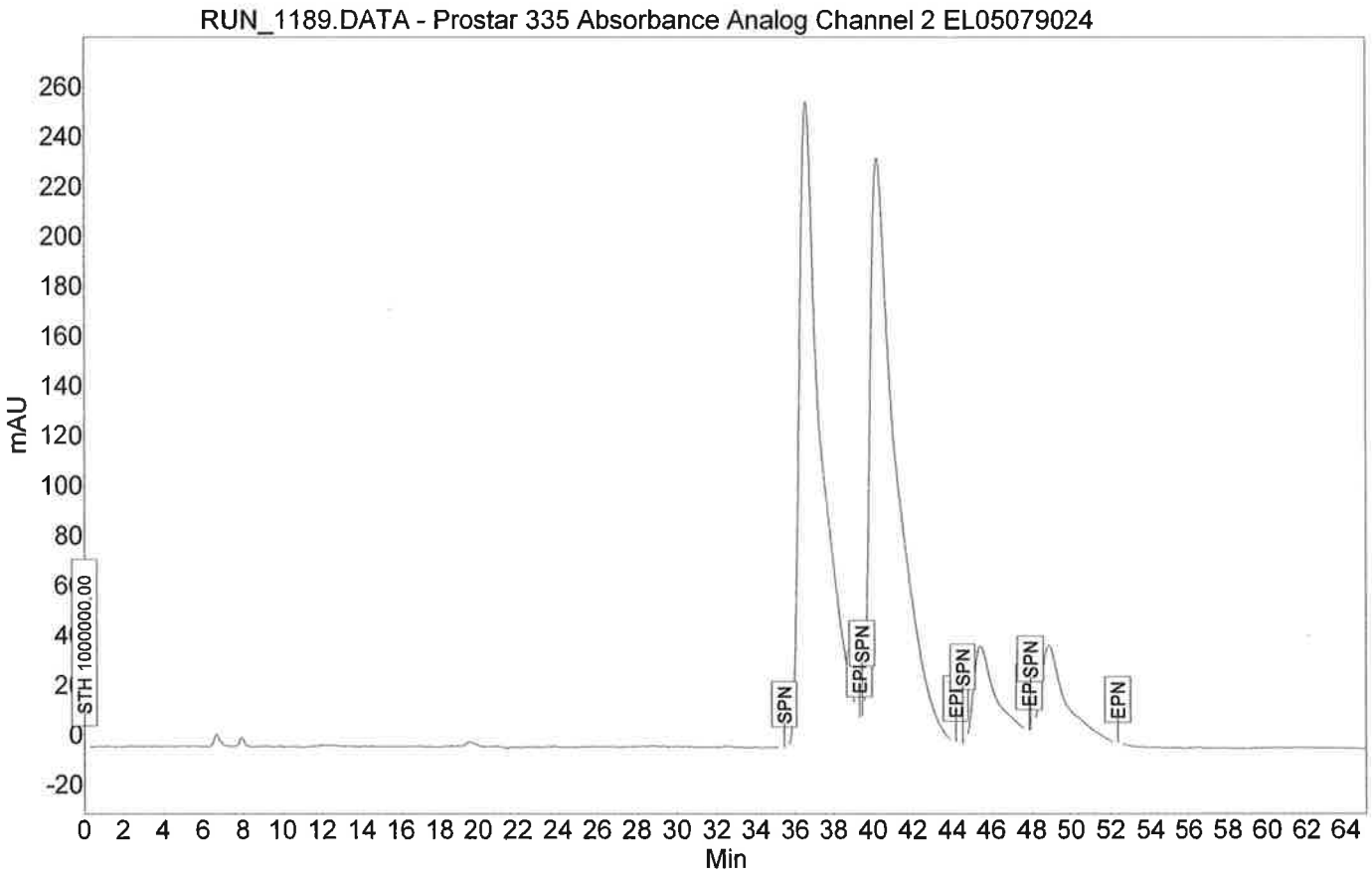
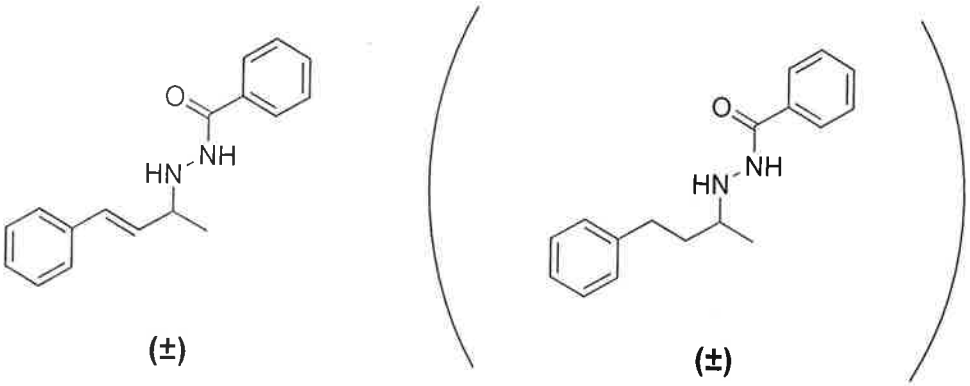
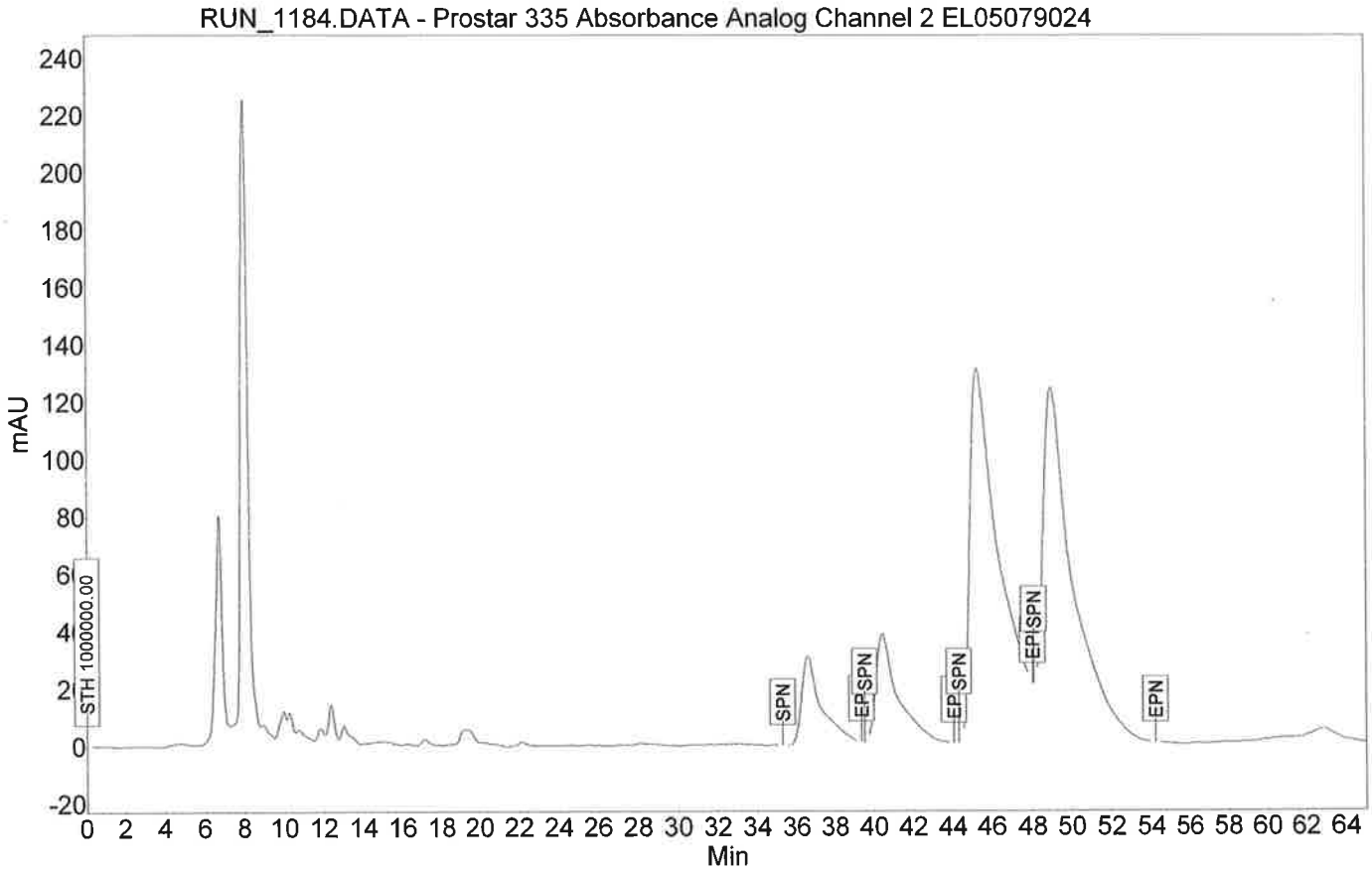
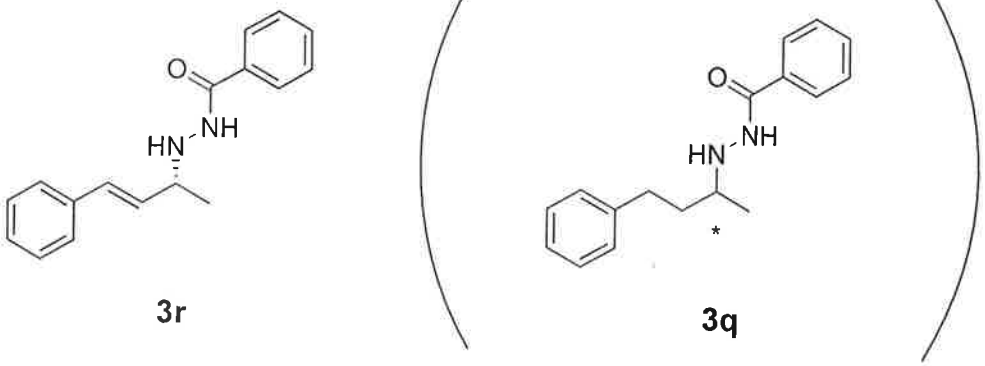


Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	36.56	43.45	255.5	332.7	43.446
2	UNKNOWN	40.21	44.01	226.0	337.1	44.014
3	UNKNOWN	45.41	6.12	37.6	46.8	6.115
4	UNKNOWN	48.85	6.43	35.1	49.2	6.426
Total			100.00	554.3	765.8	100.000





Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	36.56	8.30	30.7	36.0	8.301
2	UNKNOWN	40.47	11.28	37.9	48.9	11.282
3	UNKNOWN	45.25	43.01	125.4	186.3	43.008
4	UNKNOWN	48.99	37.41	106.8	162.1	37.409
Total			100.00	300.7	433.2	100.000



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