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Supporting Information

for

Enantioselective regiospecific addition of propargyltrichlorosilane to aldehydes catalyzed by biisoquinoline *N*,*N'*-dioxide

Noble Brako, Sreerag Moorkkannur Narayanan, Amber Burns, Layla Auter, Valentino Cesiliano, Rajeev Prabhakar and Norito Takenaka

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Experimental details, characterization data, spectra, and HPLC traces

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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 EMD Millipore pre-coated silica gel plates with F_{254} indicator. Visualization was accomplished by UV light (254 nm), with a combination of potassium permanganate, *p*-anisaldehyde, and/or cerium molybdate solution as an indicator. Chiral HPLC analysis was performed on Varian Polaris HPLC system with a diode array detector using analytical chiral columns (250 × 4.6 mm, L × I.D.) purchased from CHIRAL TECHNOLOGIES, INC. (CHIRALCEL® OD-H, CHIRALPAK® AD-H, and CHIRALPAK® AS-H). Flash column chromatography was performed according to the method of Still [1] using silica gel 60 (mesh 230–400) supplied by SiliCycle® Inc. Isolated 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. Aldehydes were freshly distilled over CaH_2 in vacuo prior to use. Et_2O was freshly distilled over sodium/benzophenone under an atmosphere of dry nitrogen prior to use. CH_2Cl_2 was freshly distilled over CaH_2 under an atmosphere of dry nitrogen prior to use. *N*,*N*-Diisopropylethylamine was distilled over KOH under an atmosphere of dry nitrogen, stored over NaOH in a Schlenk flask, and used from there.

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. 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/100 mL.

2. Experimental procedures

2.1. Synthesis and distillation of propargyltrichlorosilane

A 500 mL Schlenk round-bottomed flask equipped with a 60 mL addition funnel was charged with CuF_2 (254 mg, 2.5 mmol), freshly distilled Et_2O (80 mL), propargyl bromide (3.8 mL, 50.0 mmol), and *N*,*N*-diisopropylethylamine (17.5 mL, 100.0 mmol). The resulting mixture was cooled to 0 °C in an ice bath, and then treated dropwise with a solution of $HSiCl_3$ (11.1 mL, 110.0 mmol) in freshly distilled Et_2O (20 mL) through the addition funnel. The reaction mixture was stirred at room temperature for 12 h.

To this stirring mixture was added freshly distilled CH_2Cl_2 (3.2 mL, 50.0 mmol) as an internal standard for ^{1}H NMR analysis. Magnetic stirring was stopped to allow all solids to settle down at the bottom of the reaction flask. A small aliquot of the supernatant was transferred to a flame-dried NMR tube with a septum by a gas-tight syringe and diluted with anhydrous $CDCl_3$ (ca. 0.7 mL) that was dried over activated 4 Å molecular sieves. The ^{1}H NMR analysis of the reaction mixture indicated that 21.5 mmol of propargyltrichlorosilane (43% yield) formed and 4.8 mmol of *N*,*N*-diisopropylethylamine remained in the solution. There were no signs of allenyltrichlorosilane and propargyl bromide observable by ^{1}H NMR in the reaction mixture.

The reaction mixture was treated with a solution of HCl in Et_2O (1.0 M, 4.8 mL) and stirred for 5 min at room temperature. Magnetic stirring was stopped to allow all solids to settle down at the bottom of the reaction flask, and a small aliquot of the supernatant was analyzed by ^{1}H NMR in the same manner as above. The analysis confirmed that there was no *N*,*N*-diisopropylethylamine present in the reaction mixture, and no loss of propargyltrichlorosilane. The reaction mixture was filtered into another 500 mL Schlenk round-bottomed flask through a filter tube containing a short pad of oven-dried Celite®. The resulting clear solution was fractionally distilled as following. A short path distillation head with a 500 mL receiving flask was attached to the Schlenk flask containing the filtrate. Then, the Schlenk flask was immersed in an oil bath at 28 °C and the receiving flask was immersed in liquid nitrogen. Et_2O and other volatiles were distilled by gradually increasing the vacuum from 150 to 10 mmHg till bubbling was no longer seen at the bottom of the Schlenk flask. Then, the vacuum was released by dry nitrogen gas. The 500 mL receiving flask containing volatile distillates was replaced with a 50 mL receiving flask under an atmosphere of dry nitrogen. Propargyltrichlorosilane was then distilled into the 50 mL receiving flask immersed in liquid nitrogen in vacuo (0.5 mmHg) to give clear liquid (0.93 g, 25%). Propargyltrichlorosilane:allenyltrichlorosilane = 200:1 by ^{1}H NMR. Propargyltrichlorosilane (0.93 g, 5.4 mmol) was diluted with freshly distilled CH_2Cl_2 up to the total volume of 3.6 mL (1.5 M solution), transferred to a 10 mL Schlenk flask, and used from there. For storage, we put the 10 mL Schlenk flask in a Mason jar containing a small amount of indicating Drierite and stored the jar in the regular freezer (ca. −20 °C) to minimize the evaporation of CH_2Cl_2. So far, we have used the propargyltrichlorosilane solution in allenylation reactions up to four months without any noticeable changes. All spectral data were identical to literature values [2]. ^{1}H NMR ($CDCl_3$): δ 2.42 (d, J = 2.8 Hz, 2H), 2.11 (t, J = 2.8 Hz, 1H).

2.2. Synthesis of catalysts 3–8

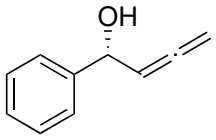
(*S*)-3,3'-Dimethyl-2,2'-biquinoline *N*,*N'*-dioxide (**3**) and (*S*)-1,1'-biisoquinoline *N*,*N'*-dioxide (**8**) were prepared by following the procedures reported by Nakajima [3]. (*S*)-3,3'-Bis(4-methylphenyl)-1,1'-biisoquinoline *N*,*N'*-dioxide (**4**), (*S*)-3,3'-bis(3,5-dimethylphenyl)-1,1'-biisoquinoline *N*,*N'*-dioxide (**5**), and (*S*)-3,3'-dibromo-1,1'-

biisoquinoline *N*, *N'*-dioxide (**7**) were prepared as we previously reported [4]. (*S*)-3,3'-Bis-(1-benzyl-1*H*-1,2,3-triazole-4-yl)-1,1'-biisoquinoline *N,N'*-dioxide (**6**) was prepared as we previously reported [5].

2.3. General procedure for allenylation of aldehydes

A small test tube containing a magnetic stirring bar was charged with activated 4 Å molecular sieves powder (100 mg), (*S*)-biisoquinoline *N*,*N'*-dioxide (2.9 mg, 0.01 mmol), a solution of aldehyde in CH_2Cl_2 (1.0 M, 100 μL), and CH_2Cl_2 (200 μL). The resulting mixture was cooled to −78 °C, and then treated with a solution of propargyltrichlorosilane in CH_2Cl_2 (1.5 M, 100 μL). The reaction mixture was stirred at −78 °C for 12 h, poured into saturated aqueous $NaHCO_3$ solution (20 mL) cooled to 0 °C, and stirred at room temperature for 30 min. The resulting heterogenous mixture was filtered through a short pad of Celite® and extracted three times with CH_2Cl_2 (5 mL × 3). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and condensed in vacuo. The resulting crude mixture was purified by flash chromatography on silica gel using EtOAc and hexanes as eluents.

(*R*)-1-Phenylbuta-2,3-dien-1-ol (**2a**)



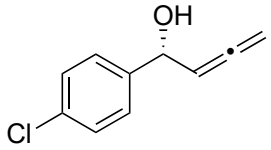
Prepared as described in general procedure using aldehyde **1a** (10.6 mg, 0.1 mmol) to give the title compound in 99% NMR yield. The crude mixture was purified by flash chromatography on silica using 15% EtOAc in hexanes as eluent to afford a pale yellow oil (14.6mg, 99%). All spectra data were identical to literature values [6,7].

^{1}H NMR ($CDCl_3$): *δ* 7.42-7.35 (m, 4H), 7.32-7.28 (m, 1H), 5.46 (q, *J* = 6.4 Hz, 1H), 5.30-5.28 (m, 1H), 4.96-4.93 (m, 2H), 2.13 (d, *J* = 4.0 Hz, 1H).

The (*R*)-absolute stereochemistry was assigned by HPLC analysis [9]. er = 88:12; t_R (R) 18.6 min; (S) 25.3 min, (Daicel Chiralcel® OD-H with an OD-H guard column, hexanes/2-propanol = 95/5, 0.5 mL/min, 214 nm).

$[\alpha]_D^{21}$ = +6.20 (c = 0.67, CH_2Cl_2).

(*R*)-1-(4-Chlorophenyl)buta-2,3-dien-1-ol (**2b**)



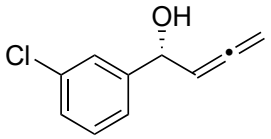
Prepared as described in general procedure using aldehyde **1b** (14.1 mg, 0.1 mmol) to give the title compound in 99% NMR yield. The crude mixture was purified by flash chromatography on silica using 15% EtOAc in hexanes as eluent to afford a viscous oil (17.1 mg, 95%). All spectra data were identical to literature values [6].

^{1}H NMR ($CDCl_3$): δ 7.36-7.33 (m, 4H), 5.41 (q, J = 6.4 Hz, 1H), 5.28-5.23 (m, 1H), 4.95-4.93 (m, 2H), 2.17(br, 1H).

The (*R*)-absolute stereochemistry was assigned by HPLC analysis [9]. er = 90:10; t_R (R) 55.7 min; (S) 59.5 min, (Daicel Chiralcel® OD-H with an OD-H guard column, hexanes/2-propanol = 99/1, 0.5 mL/min, 214 nm).

$[\alpha]_D^{20}$ = -14.60 (c = 0.76, CH_2Cl_2).

***(R)*-1-(3-Chlorophenyl)buta-2,3-dien-1-ol** (**2c**)



Prepared as described in general procedure using aldehyde **1c** (14.1 mg, 0.1 mmol) to give the title compound in 99% NMR yield. The crude mixture was purified by flash chromatography on silica using 15% EtOAc in hexanes as eluent to afford a viscous oil (17.9 mg, 99%). All spectra data were identical to literature values [7].

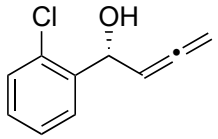
^{1}H NMR ($CDCl_3$): δ 7.41 (s, 1H), 7.30-7.26 (m, 3H), 5.42 (q, J = 6.4 Hz, 1H), 5.27-5.25 (m, 1H), 4.98-4.96 (m, 2H), 2.13 (d, J = 4.0 Hz, 1H).

The (*R*)-absolute stereochemistry was assigned by HPLC analysis [9]. er = 92:8;

t_R (R) 18.0 min; (S) 19.2 min, (Daicel Chiralcel® OD-H with an OD-H guard column, hexanes/2-propanol = 95/5, 0.5 mL/min, 214 nm).

$[\alpha]_D^{21}$ = -17.51 (c = 0.80, CH_2Cl_2).

(*R*)-1-(2-Chlorophenyl)buta-2,3-dien-1-ol (**2d**)



Prepared as described in general procedure using aldehyde **1d** (14.1 mg, 0.1 mmol) to give the title compound in 99% NMR yield. The crude mixture was purified by flash chromatography on silica using 15% EtOAc in hexanes as eluent to afford a viscous oil (18 mg, 99%). All spectra data were identical to literature values [8].

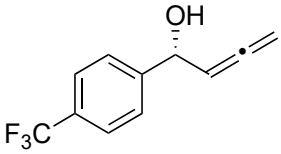
^{1}H NMR ($CDCl_3$): δ 7.58 (dd, J = 7.6, 1.2 Hz, 1H), 7.36-7.28 (m, 2H) 7.25-7.22 (m, 1H), 5.70-5.64 (m, 1H), 5.48 (q, J = 6.4 Hz, 1H), 4.94 (dd, J = 6.4, 2.8 Hz, 2H), 2.32 (d, J = 4.4 Hz, 1H).

The (*R*)-absolute stereochemistry was assigned by HPLC analysis [8]. er = 88:12;

t_R (R) 47.2 min; (S) 54.9 min, (Daicel Chiralcel® OD-H with an OD-H guard column, hexanes/2-propanol = 99/1, 0.5 mL/min, 214 nm).

$[\alpha]_D^{21}$ = +14.56 (c = 0.85, CH_2Cl_2).

(*R*)-1-(4-(Trifluoromethyl)phenyl)buta-2,3-dien-1-ol (**2e**)



Prepared as described in general procedure using aldehyde **1e** (17.4 mg, 0.1 mmol) to give the title compound in 97% NMR yield. The crude mixture was purified by flash chromatography on silica using 15% EtOAc in hexanes as eluent to afford a viscous oil (19 mg, 89%). All spectra data were identical to literature values [8].

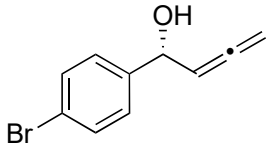
^{1}H NMR ($CDCl_3$): δ 7.62 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H), 5.41 (q, J = 6.4 Hz, 1H), 5.37-5.32 (m, 1H), 4.97-4.95 (m, 2H), 2.24 (d, J = 3.6 Hz, 1H).

The (*R*)-absolute stereochemistry was assigned by HPLC analysis [8]. er = 86.5:13.5;

t_R (R) 32.5 min; (S) 36.5 min, (Daicel Chiralpak® AD-H with an AD-H guard column, hexanes/2-propanol = 98/2, 0.5 mL/min, 214 nm).

$[\alpha]_D^{21}$ = -7.53 (c = 0.6, CH_2Cl_2).

(*R*)-1-(4-Bromophenyl)buta-2,3-dien-1-ol (**2f**)



Prepared as described in general procedure using aldehyde **1f** (18.5 mg, 0.1 mmol) to give the title compound in 99% NMR yield. The crude mixture was purified by flash chromatography on silica using 15% EtOAc in hexanes as eluent to afford a viscous oil (21.3 mg, 95%). All spectra data were identical to literature values [6].

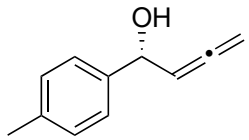
^{1}H NMR ($CDCl_3$): δ 7.49 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 5.39 (q, J = 6.4 Hz, 1H), 5.27-5.22 (m, 1H), 4.96-4.93 (m, 2H), 2.15 (d, J = 3.6 Hz, 1H).

The (*R*)-absolute stereochemistry was assigned by HPLC analysis [8]. er = 89.5:10.5;

t_R (R) 79.5 min; (S) 88.9 min, (Daicel Chiralpak® AD-H with an AD-H guard column, hexanes/2-propanol = 99/1, 0.5 mL/min, 214 nm).

$[\alpha]_D^{21}$ = +6.16 (c = 0.64, CH_2Cl_2).

***(R)*-1-(*p*-Tolyl)buta-2,3-dien-1-ol** (**2g**)



Prepared as described in general procedure using aldehyde **1g** (12.0 mg, 0.1 mmol) to give the title compound in 77% NMR yield. The crude mixture was purified by flash chromatography on silica using 20% EtOAc in hexanes as eluent to afford a viscous oil (11.4 mg, 71%). All spectra data were identical to literature values [6].

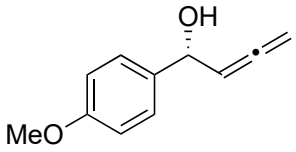
^{1}H NMR ($CDCl_3$): δ 7.30 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 5.43 (q, J = 6.4 Hz, 1H), 5.27-5.22 (m, 1H), 4.95-4.92 (m, 2H), 2.35 (s, 3H), 2.10 (d, J = 4 Hz, 1H).

The (*R*)-absolute stereochemistry was assigned by HPLC analysis [9]. er = 88:12;

t_R (R) 21.4 min; (S) 24.2 min, (Daicel Chiralpak® AD-H with an AD-H guard column, hexanes/2-propanol = 95/5, 0.5 mL/min, 214 nm).

$[\alpha]_D^{20}$ = -1.25 (c = 0.50, CH_2Cl_2).

(*R*)-1-(4-Methoxyphenyl)buta-2,3-dien-1-ol (**2h**)



Prepared as described in general procedure using aldehyde **1h** (13.6 mg, 0.1 mmol) to give the title compound in 45% NMR yield. The crude mixture was purified by flash chromatography on silica using 20% EtOAc in hexanes as eluent to afford a pale yellow oil (7.3 mg, 41%). All spectra data were identical to literature values [6].

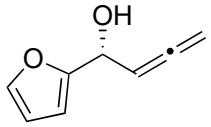
^{1}H NMR ($CDCl_3$): δ 7.33 (d, J = 8.8, 2H), 6.90 (d, J = 8.8, 2H), 5.44 (q, J = 6.4, 1H), 5.27-5.21 (m, 1H), 4.95-4.92 (m, 2H), 3.81 (s, 3H), 2.06 (d, J = 4 Hz, 1H).

The (*R*)-absolute stereochemistry was assigned by HPLC analysis [9]. er = 91:9;

t_R (R) 26.0 min; (S) 33.9 min, (Daicel Chiralpak® OD-H with an OD-H guard column, hexanes/2-propanol = 95/5, 0.5 mL/min, 214 nm).

$[\alpha]_D^{20}$ = +20.44 (c = 0.32, CH_2Cl_2).

***(R)*-1-(Furan-2-yl)buta-2,3-dien-1-ol** (**2i**)



Prepared as described in general procedure using aldehyde **1i** (9.6 mg, 0.1 mmol) to give the title compound in 34% NMR yield. The crude mixture was purified by flash chromatography on silica using 20% EtOAc in hexanes as eluent to afford a viscous oil (3 mg, 22%). All spectra data were identical to literature values [9].

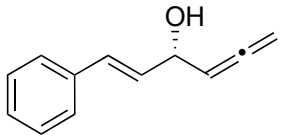
^{1}H NMR ($CDCl_3$) δ 7.41 (br s, 1H), 6.35-6.34 (m, 1H), 6.31 (d, J = 3.2 Hz, 2H), 5.54 (q, J = 6.4 Hz, 1H), 5.30-5.25 (m, 1H), 4.99-4.97 (m, 2H), 2.16 (d, J = 5.6 Hz, 1H).

The (*R*)-absolute stereochemistry was assigned by HPLC analysis [9]. er = 67.5:32.5;

t_R (S) 32.5 min; (R) 27.0 min, (Daicel Chiralcel® OD-H with an OD-H guard column, hexanes/2-propanol = 95/5, 0.5 mL/min, 214 nm).

$[\alpha]_D^{21}$ = +17.3 (c = 0.10, CH_2Cl_2).

(*S,E*)-1-Phenylhexa-1,4,5-trien-3-ol (**2j**)



Prepared as described in general procedure using aldehyde **1j** (13.2 mg, 0.1 mmol) to give the title compound in 43% NMR yield. The crude mixture was purified by flash chromatography on silica using 20% EtOAc in hexanes as eluent to afford a viscous oil (7.5 mg, 44%). All spectra data were identical to literature values [6].

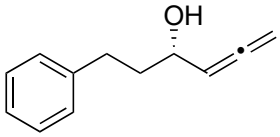
^{1}H NMR ($CDCl_3$) δ 7.40 (d, J = 7.2 Hz, 2H), 7.32 (t, J = 7.2 Hz, 2H), 7.26 (t, J = 5.2 Hz, 1H), 6.65 (d, J = 16.0 Hz, 1H), 6.28 (dd, J = 16.0, 6.4 Hz, 1H), 5.38 (q, J = 6.4 Hz, 1H), 4.94 (dd, J = 6.4, 2.4 Hz, 2H), 4.90-4.84 (m,1H), 1.89 (d, J = 4.4 Hz, 1H).

The (*S*)-absolute stereochemistry was assigned by HPLC analysis [9]. er = 61:39;

t_R (S) 13.0 min; (R) 14.5 min, (Daicel Chiralpak® AS-H with an AS-H guard column, hexanes/2-propanol = 90/10, 0.5 mL/min, 214 nm).

$[\alpha]_D^{21}$ = +13.29 (c = 0.23, CH_2Cl_2).

(*S*)-1-Phenylhexa-4,5-dien-3-ol (**2k**)



Prepared as described in general procedure using aldehyde **1k** (13.4 mg, 0.1 mmol) to give the title compound in 38% NMR yield. The crude mixture was purified by flash chromatography on silica using 15% EtOAc in hexanes as eluent to afford a viscous oil (8.6 mg, 49%). All spectra data were identical to literature values [6].

^{1}H NMR ($CDCl_3$) δ 7.27-7.17 (m, 5H), 5.28 (q, J = 6.4 Hz, 1H), 4.89 (dd, J = 6.4, 2.4 Hz, 2H), 4.25-4.16 (m,1H), 2.78-2.7 (m, 2H), 1.93-1.87 (m, 2H), 1.67 (d, J = 4.4 Hz, 1H).

The (*S*)-absolute stereochemistry was assigned by HPLC analysis [9]. er = 74:26;

t_R (S) 23.4 min; (R) 34.8 min, (Daicel Chiralcel® OD-H with an OD-H guard column, hexanes/2-propanol = 95/5, 0.5 mL/min, 214 nm).

$[\alpha]_D^{21}$ = +5.97 (c = 0.33, CH_2Cl_2).

3. Computations

All calculations were performed using the Gaussian 16 software package [10]. All structures were optimized using the M06-2X [11] functional and 6-311G(d) [12] basis set as implemented in Gaussian 16. Hessians were calculated with the same level of theory as the optimizations. The final energies were further improved by performing single point calculations with 6-311++g(d,p) [12,13] basis set on optimized structures. To simulate experimentally used *N*,*N*-diisopropylethylamine solvent, diethylamine was used in self-consistent reaction field-SMD implicit solvent model (SCRF-SMD) [14]. The dispersion corrections were included by performing single point calculations using Grimme D3 function [15]. Zero-point vibrational (unscaled), thermal (at 298.15 K and 1 atm), solvent, dispersion, and entropy corrections (at 298.15 K) were added to the final energies of the optimized structures.

4. References

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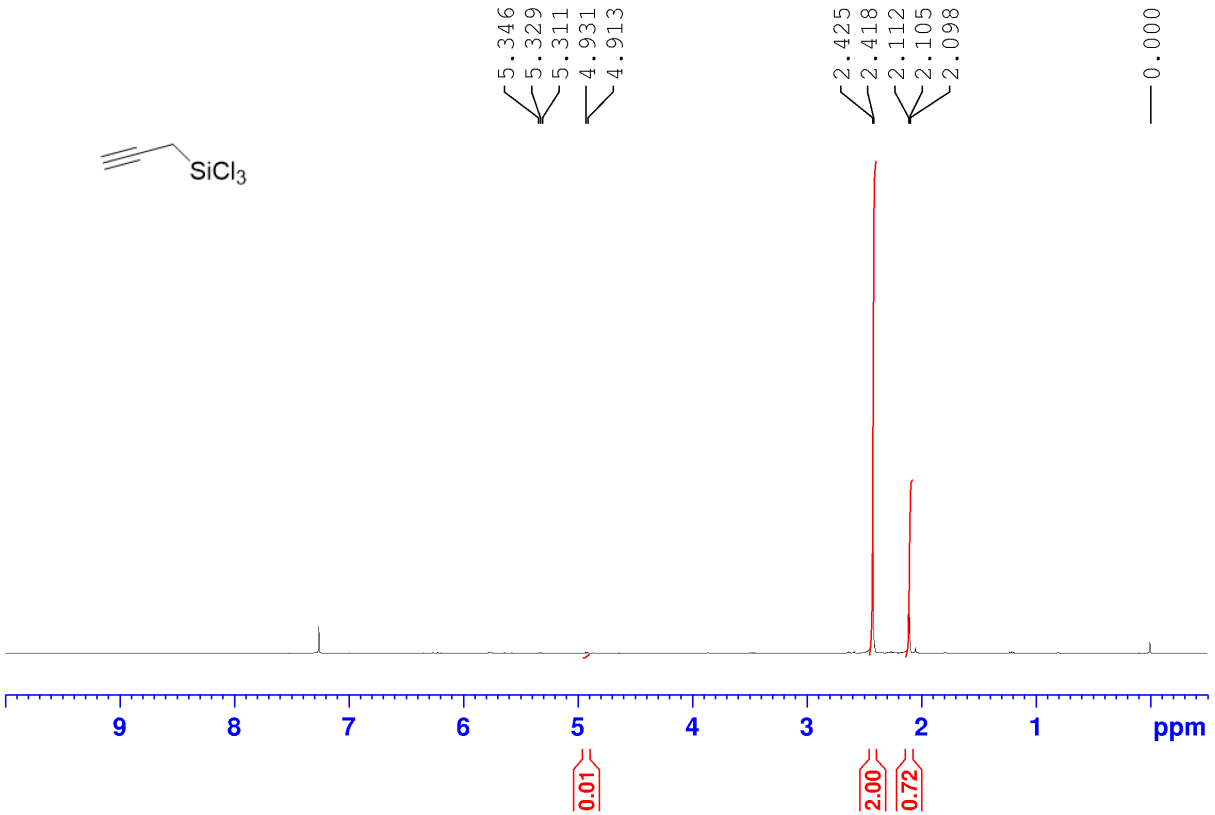
03-27-2024_propargyltrichlorosilane



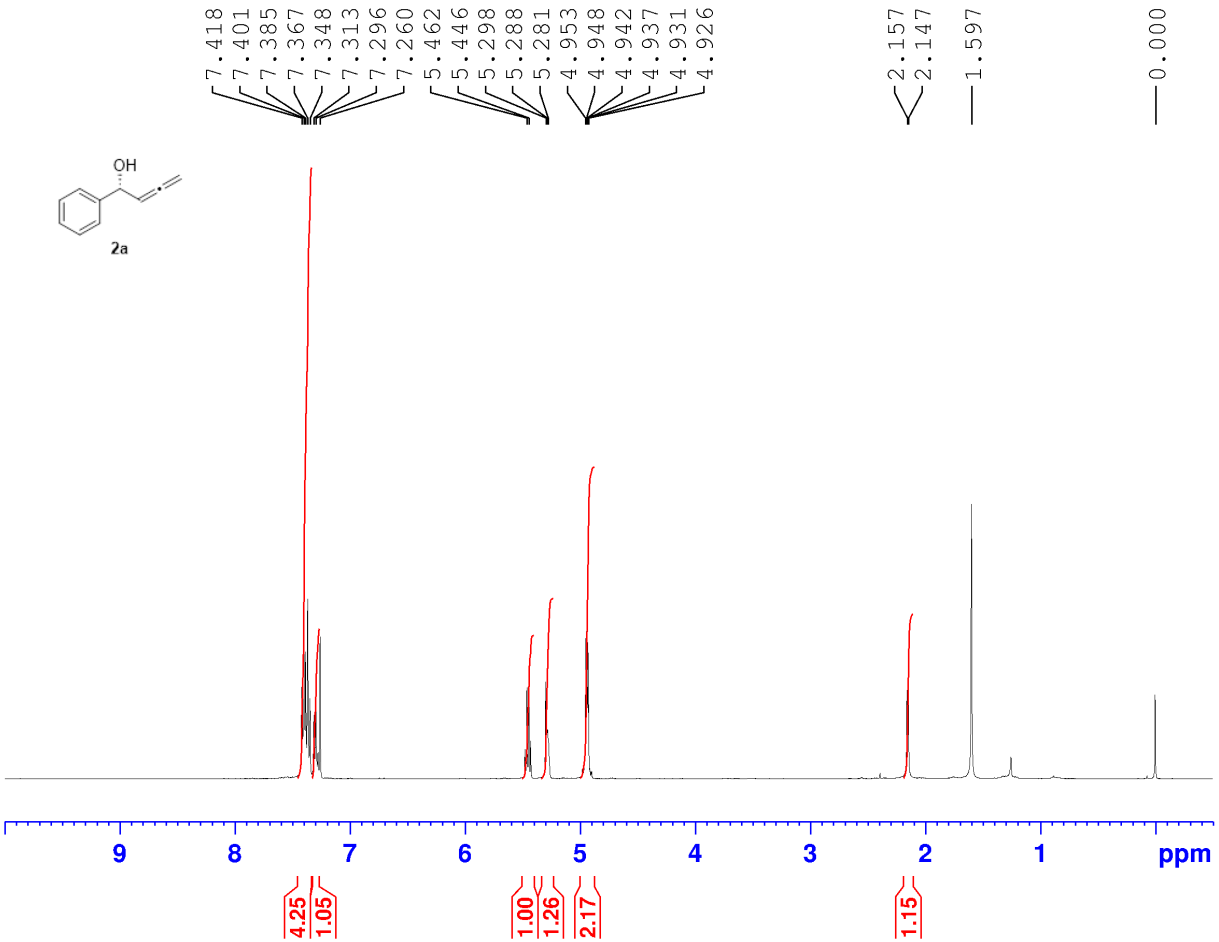
Current Data Parameters
NAME Mar27-2024
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20240327
Time 18.50
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9583745 sec
RG 256
DW 60.400 usec
DE 6.50 usec
TE 297.1 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 11.60 usec
PL1 0 dB
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300103 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

NB-I 172 isolated



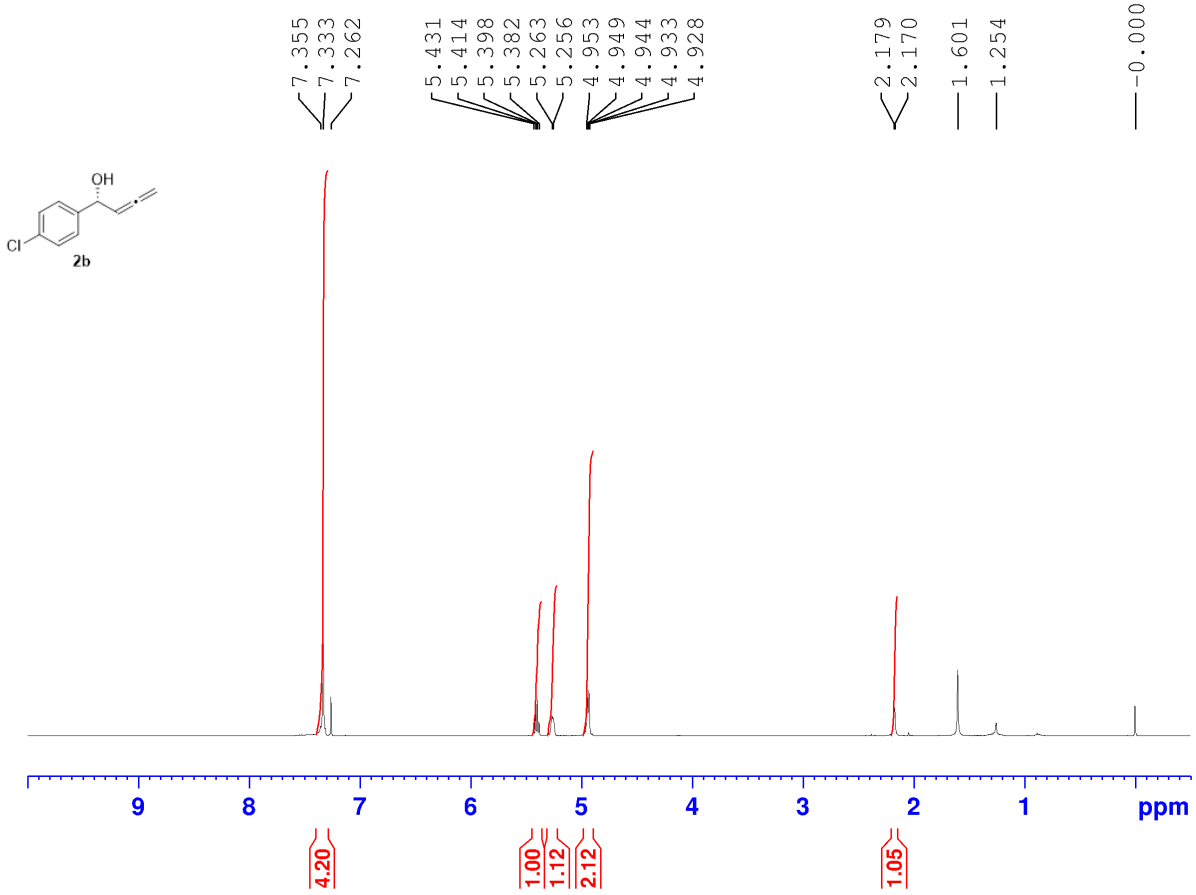

```
Current Data Parameters
NAME          May07-2024
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20240507
Time               16.32
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            3.9583745 sec
RG                  512
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

F2 - Processing parameters
SI                32768
SF          400.1300098 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

NB-I 174 isolated



Current Data Parameters

NAME	May08-2024
EXPNO	3
PROCNO	1

F2 - Acquisition Parameters

Date_	20240508
Time	16.12
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	3.9583745 sec
RG	512
DW	60.400 usec
DE	6.50 usec
TE	300.0 K
D1	1.00000000 sec
TD0	1

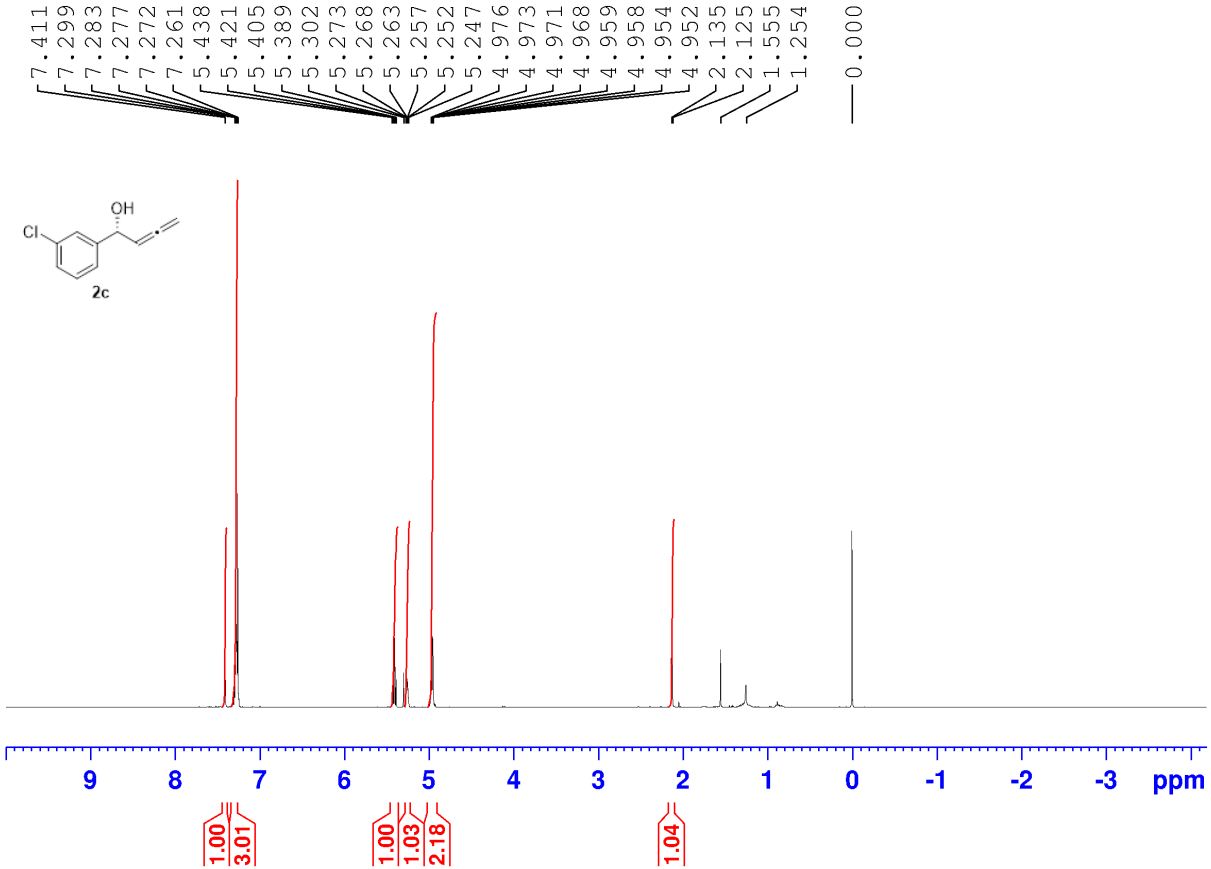
======== CHANNEL f1 ========

NUC1	1H
P1	18.75 usec
PL1	0.50 dB
SFO1	400.1324710 MHz

F2 - Processing parameters

SI	32768
SF	400.1300093 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

NB-I 182 isolated



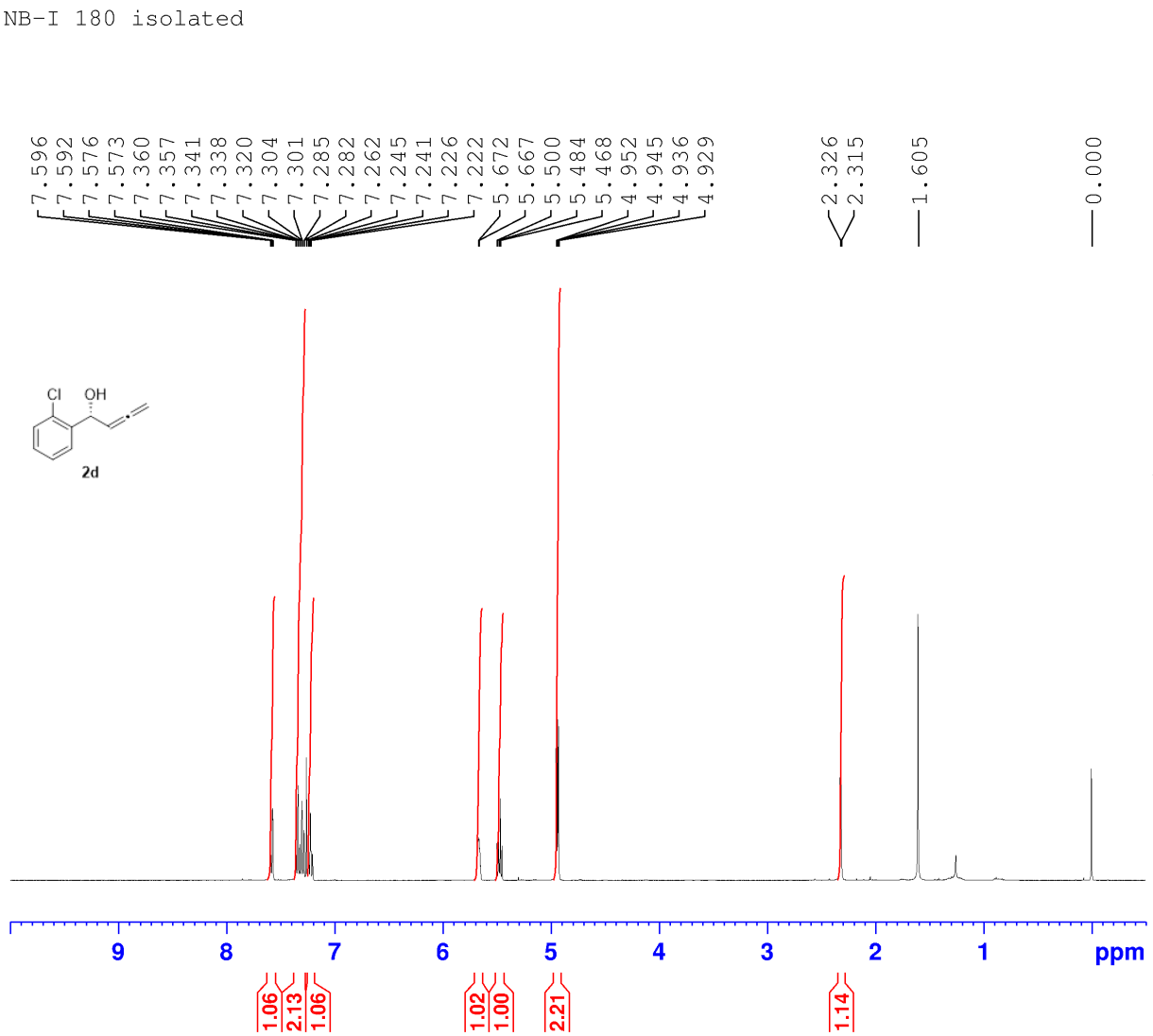
Current Data Parameters
NAME May11-2024
EXPNO 4
PROCNO 1

F2 - Acquisition Parameters
Date_ 20240511
Time 14.21
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 3.9583745 sec
RG 812.7
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

F2 - Processing parameters
SI 32768
SF 400.1300092 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

NB-I 180 isolated



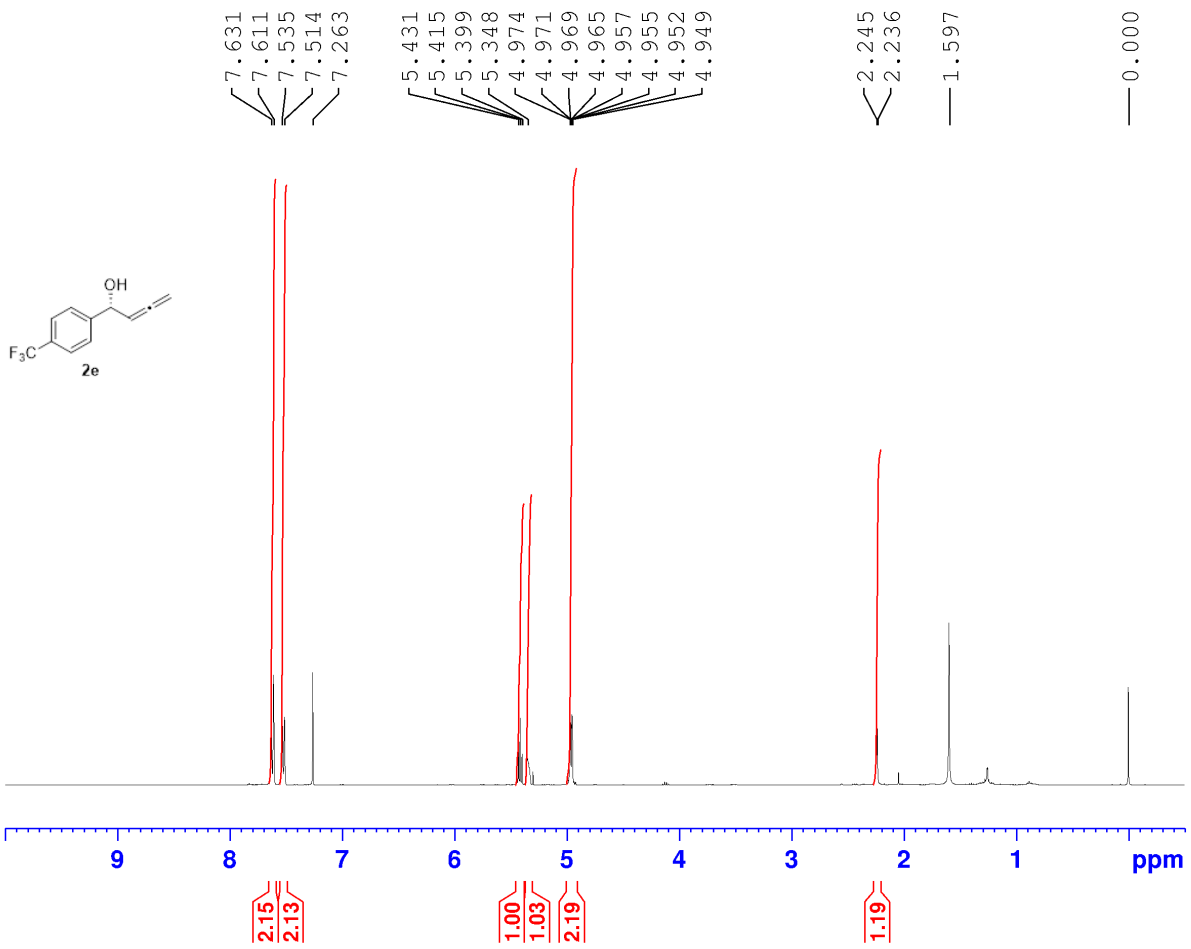

```
Current Data Parameters
NAME          May10-2024
EXPNO                  7
PROCNO                 1

F2 - Acquisition Parameters
Date_           20240510
Time               21.38
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              3.9583745 sec
RG                   512
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

F2 - Processing parameters
SI                 32768
SF          400.1300089 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

NB-I 181 isolated



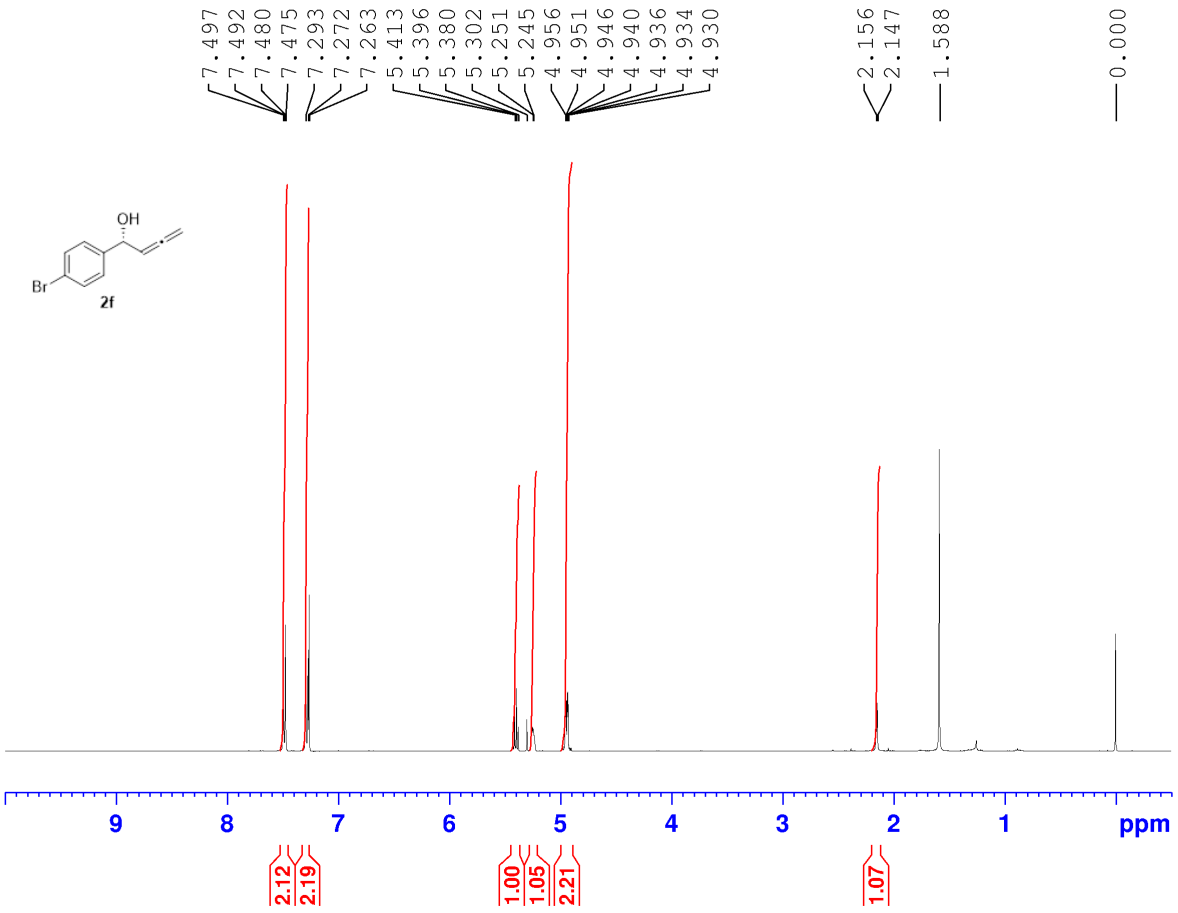
Current Data Parameters
NAME May11-2024
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20240511
Time 11.50
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 3.9583745 sec
RG 574.7
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

F2 - Processing parameters
SI 32768
SF 400.1300087 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

NB-I 179



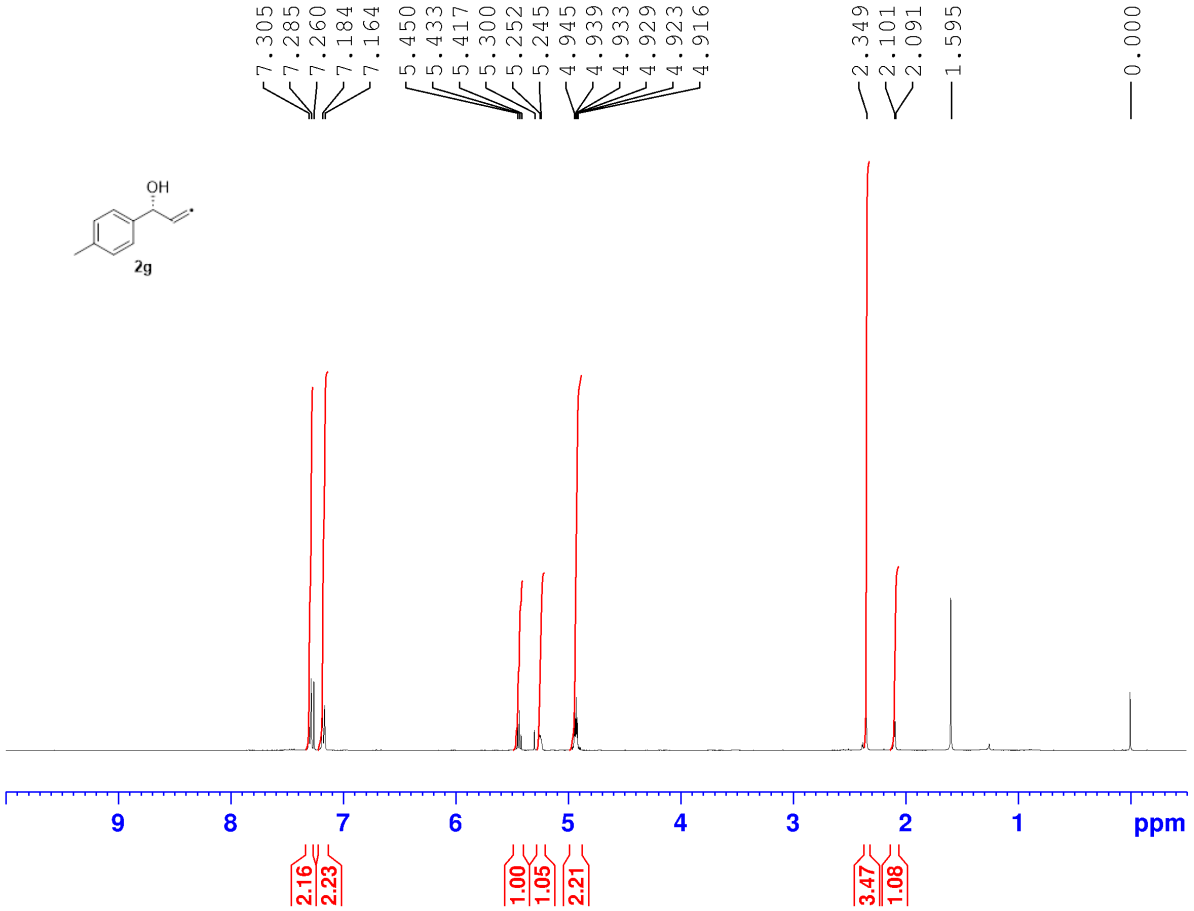

```
Current Data Parameters
NAME          May10-2024
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20240510
Time               15.27
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              3.9583745 sec
RG                 645.1
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

F2 - Processing parameters
SI                 32768
SF          400.1300085 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

NB-I 176 isolated



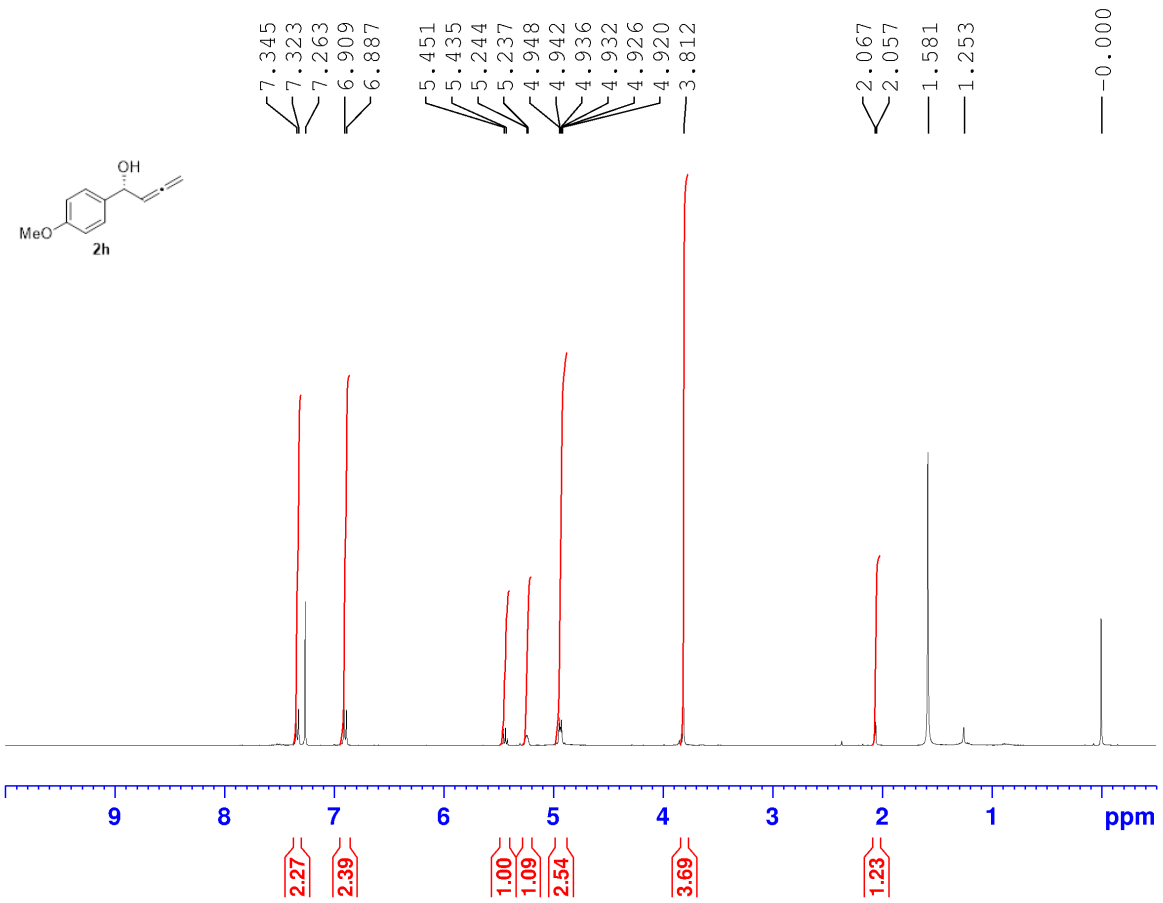

```
Current Data Parameters
NAME          May09-2024
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20240509
Time               12.36
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              3.9583745 sec
RG                 574.7
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

F2 - Processing parameters
SI                 32768
SF          400.1300095 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

NB-I 173 isolated



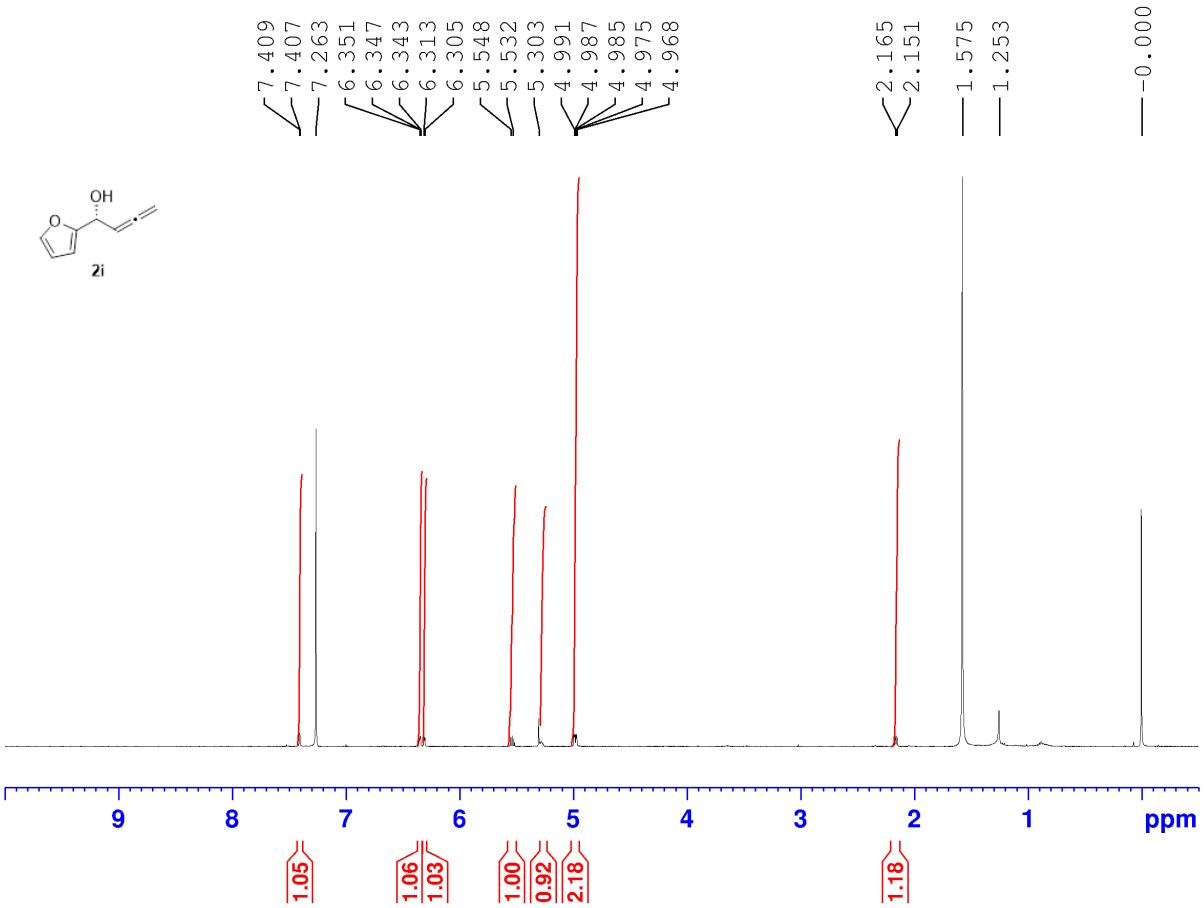

```
Current Data Parameters
NAME          May09-2024
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20240509
Time                9.56
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              3.9583745 sec
RG                  1024
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

F2 - Processing parameters
SI                 32768
SF          400.1300085 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

NB-I 178 isolated



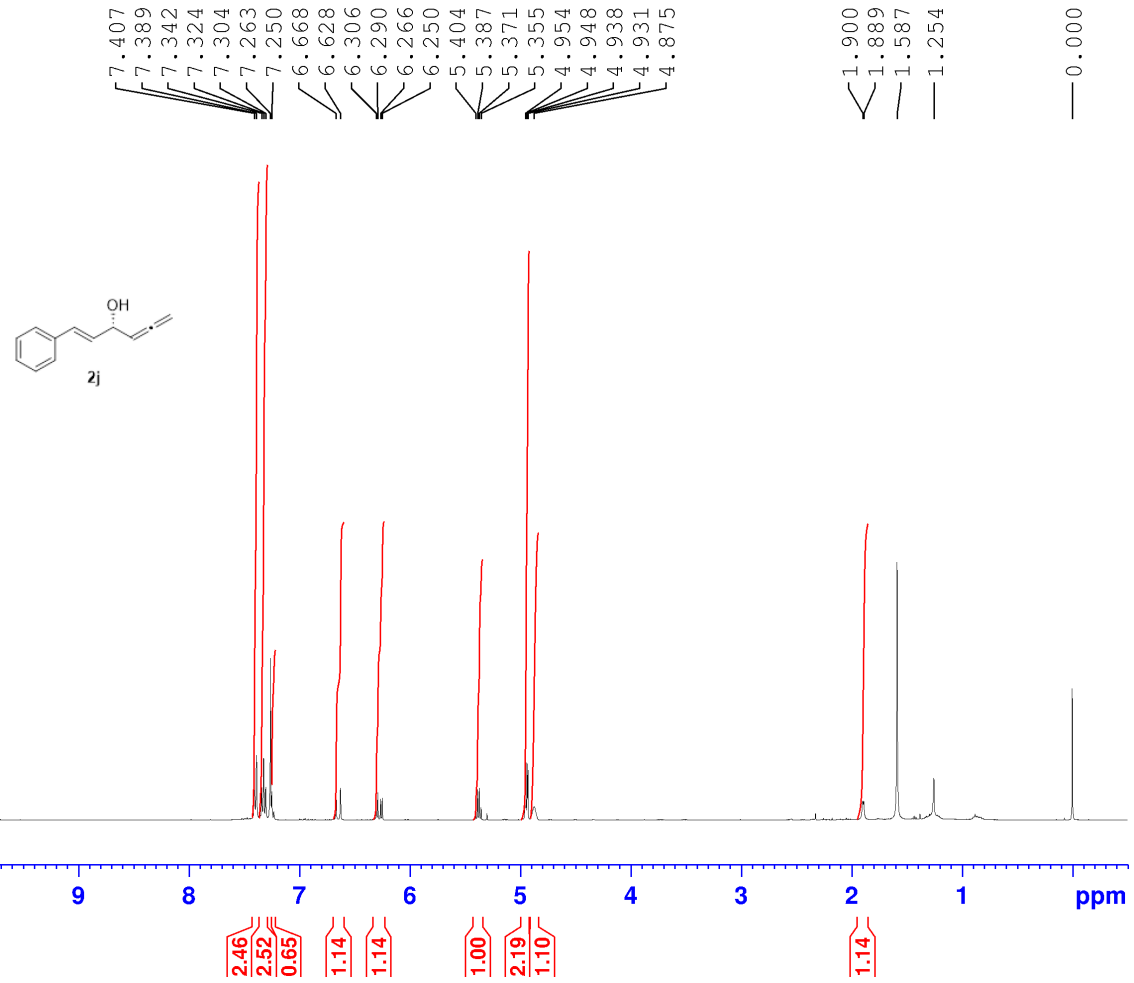

```
Current Data Parameters
NAME                  May11-2024
EXPNO                          2
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20240511
Time                       14.07
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                      3.9583745 sec
RG                         1290.2
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

F2 - Processing parameters
SI                         32768
SF                  400.1300085 MHz
WDW                           EM
SSB                            0
LB                          0.30 Hz
GB                             0
PC                          1.00
```

NB-I 177 isolated



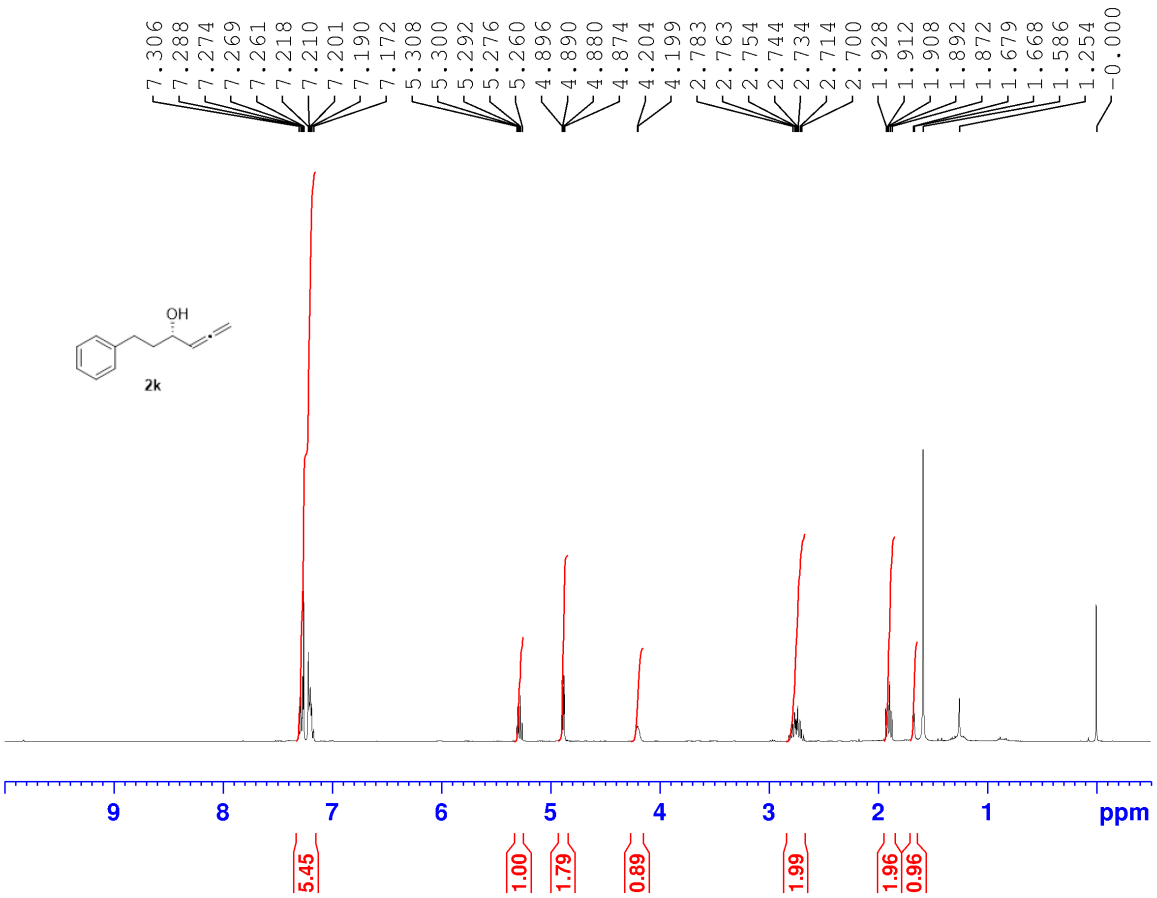

```
Current Data Parameters
NAME          May09-2024
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20240509
Time               15.52
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              3.9583745 sec
RG                 812.7
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

F2 - Processing parameters
SI                 32768
SF           400.1300087 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                  1.00
```

NB-I 175 isolated




```
Current Data Parameters
NAME                  May08-2024
EXPNO                          4
PROCNO                         1

F2 - Acquisition Parameters
Date_                  20240508
Time                      20.51
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                     3.9583745 sec
RG                        574.7
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

F2 - Processing parameters
SI                         32768
SF                  400.1300092 MHz
WDW                           EM
SSB                            0
LB                        0.30 Hz
GB                             0
PC                        1.00
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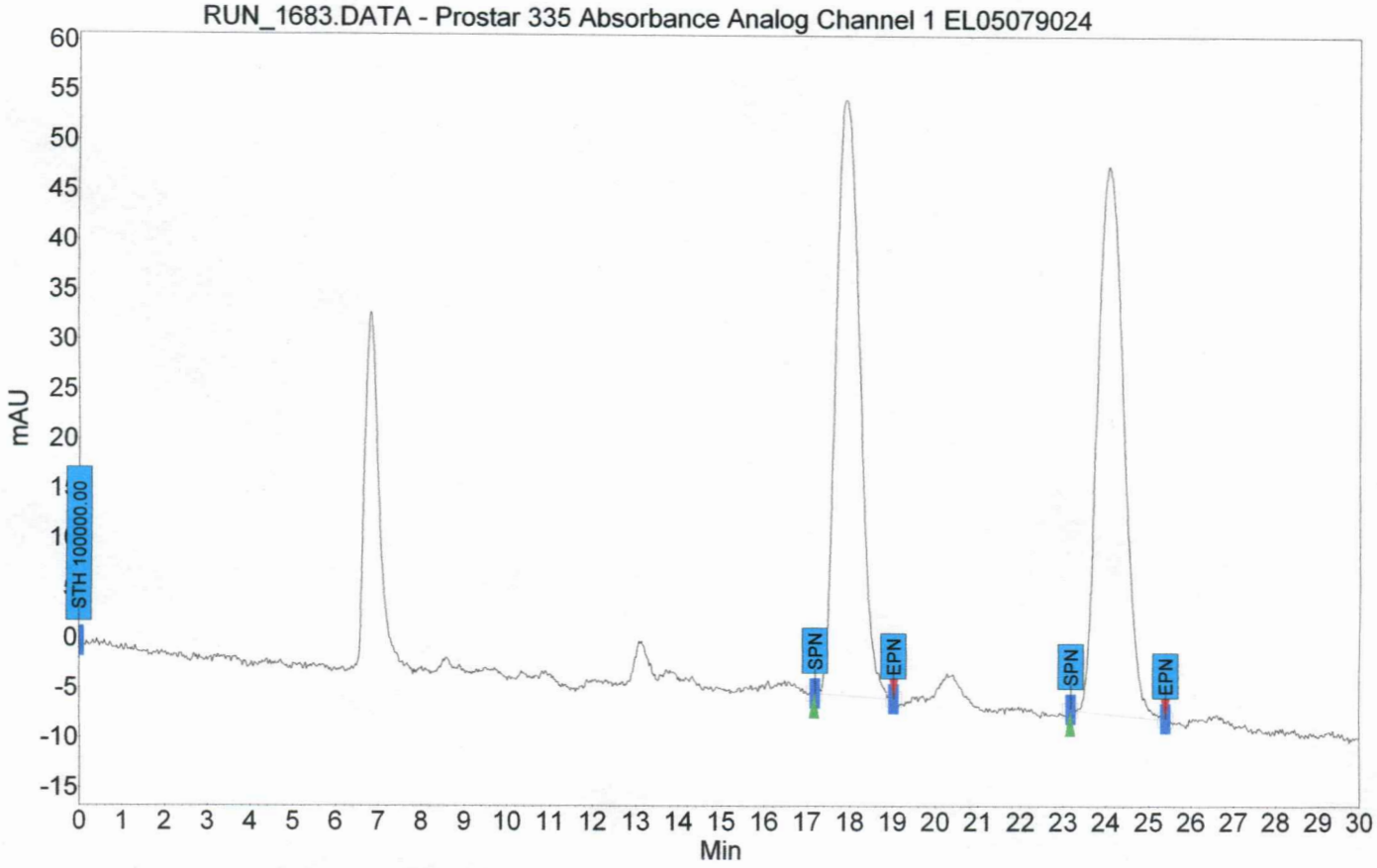
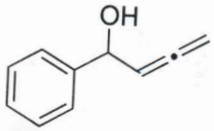
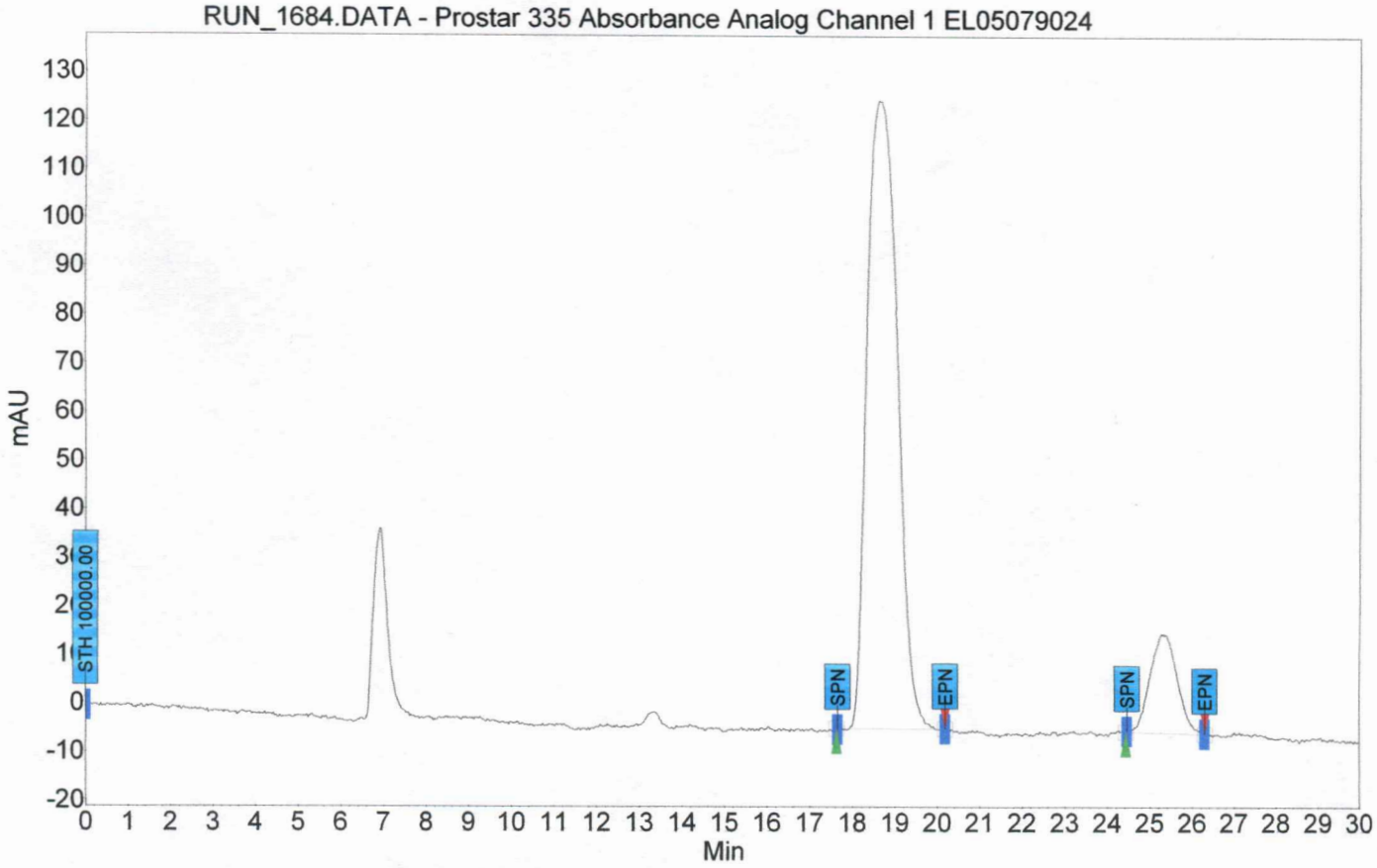


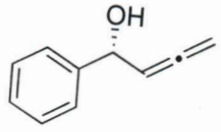
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	17.92	49.68	59.9	38.7	49.681
2	UNKNOWN	24.08	50.32	55.1	39.2	50.319
Total			100.00	115.0	77.9	100.000



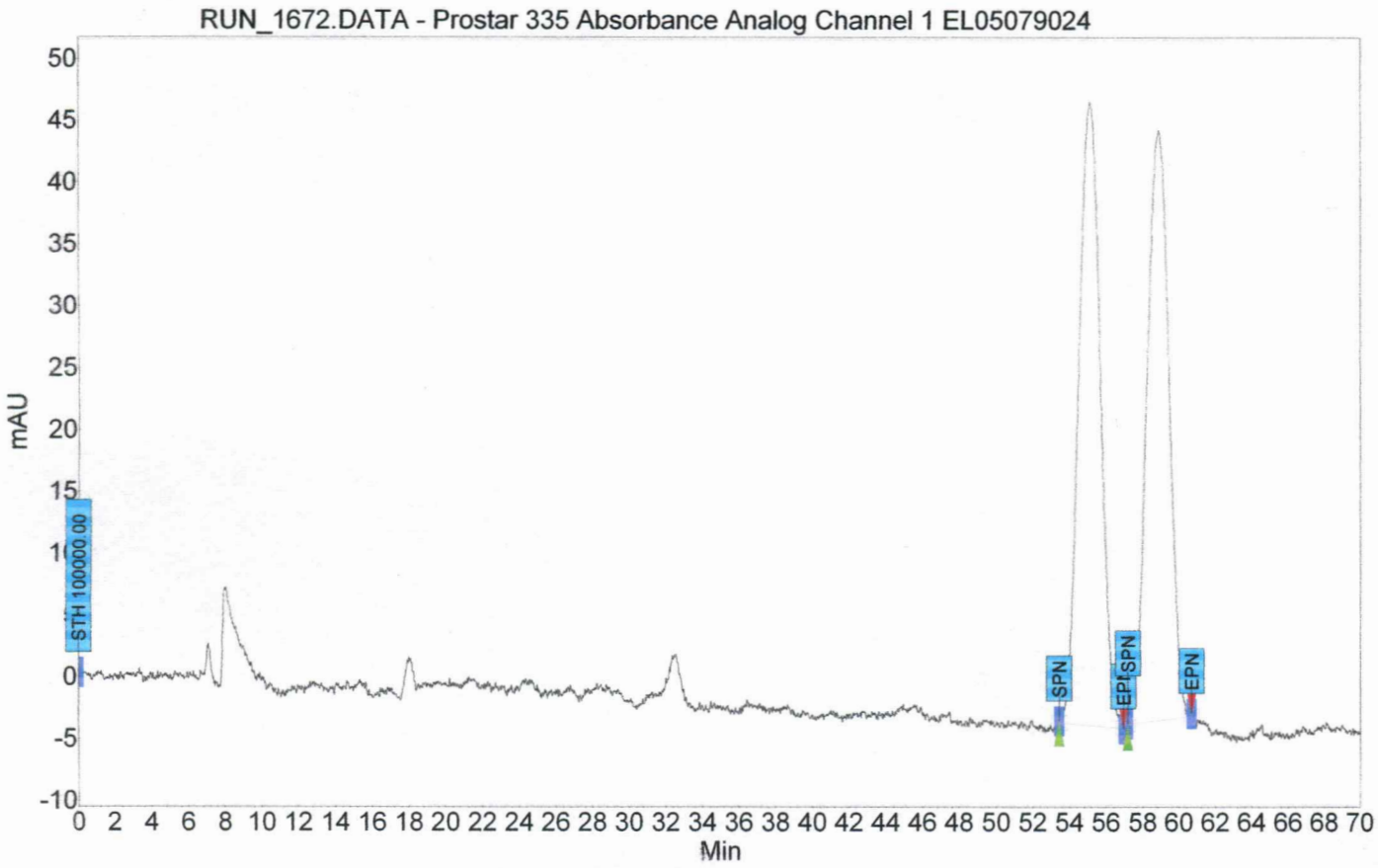
(±)-**2a**



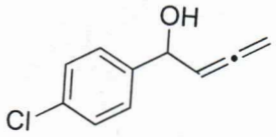
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	18.63	87.57	129.6	106.9	87.570
2	UNKNOWN	25.29	12.43	20.2	15.2	12.430
Total			100.00	149.8	122.1	100.000



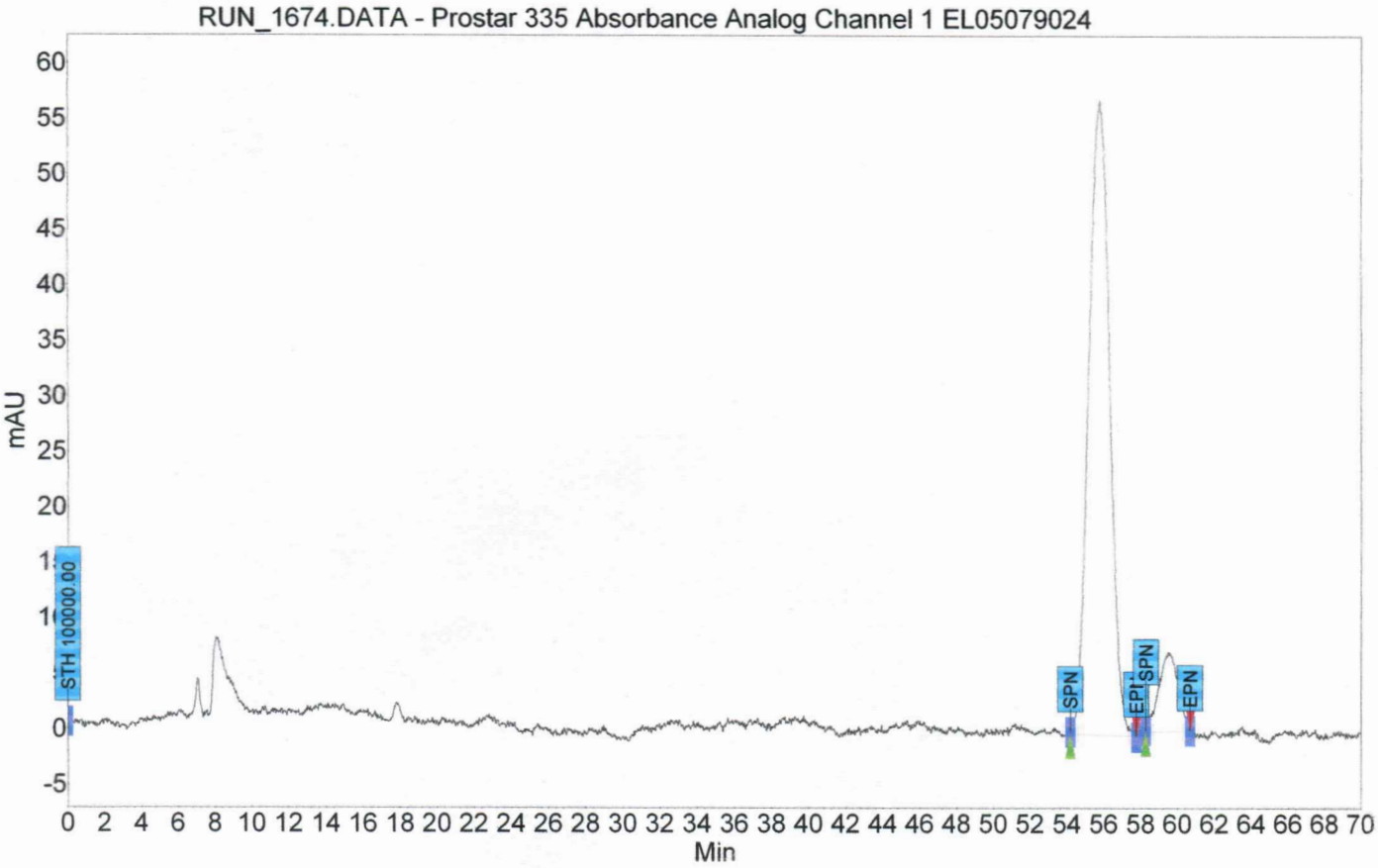
2a



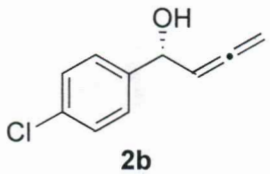
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	55.11	50.80	50.5	68.9	50.799
2	UNKNOWN	58.84	49.20	47.8	66.7	49.201
Total			100.00	98.3	135.6	100.000



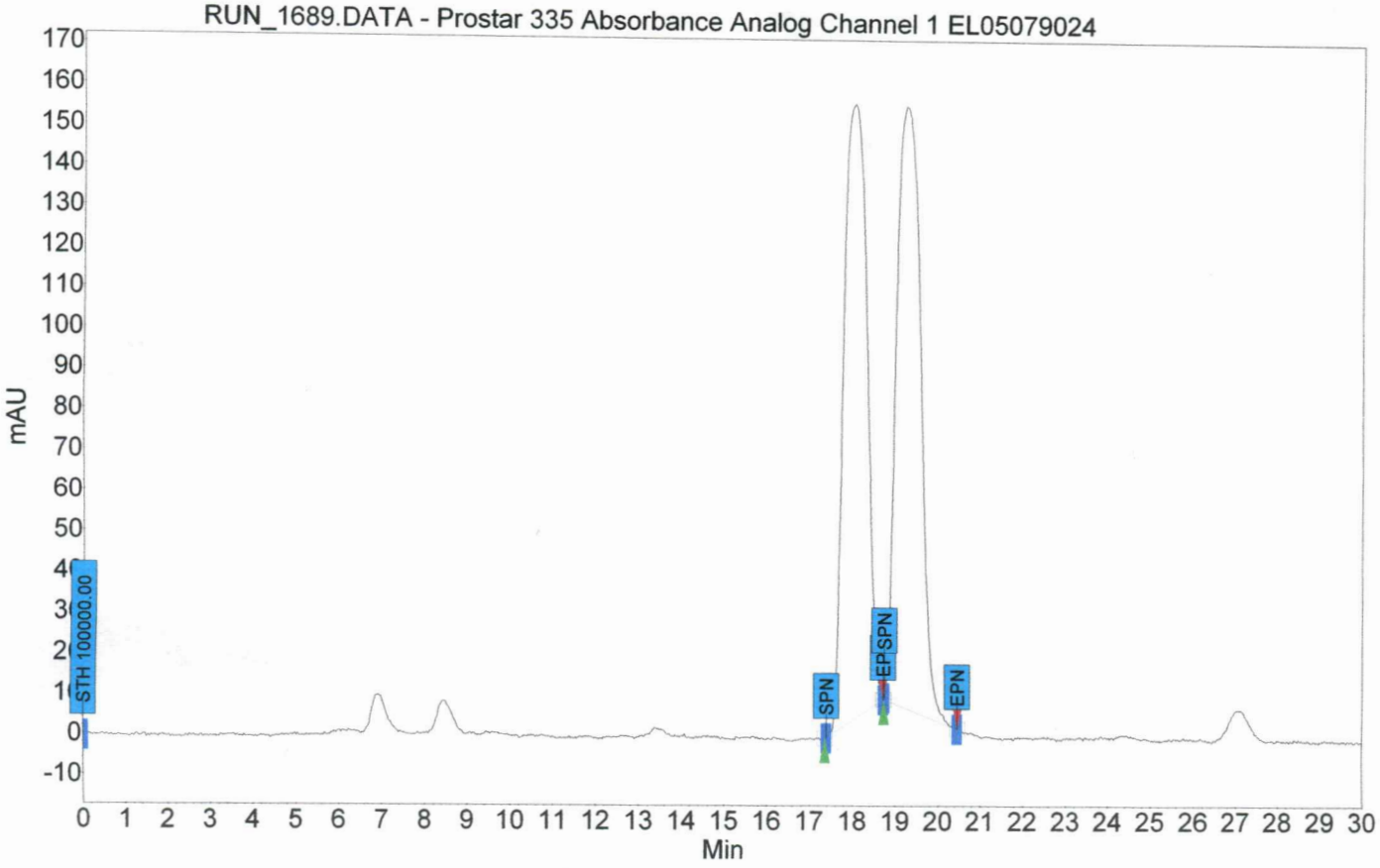
(±)-**2b**



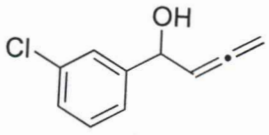
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	55.71	89.85	57.2	74.9	89.852
2	UNKNOWN	59.51	10.15	7.2	8.5	10.148
Total			100.00	64.4	83.3	100.000



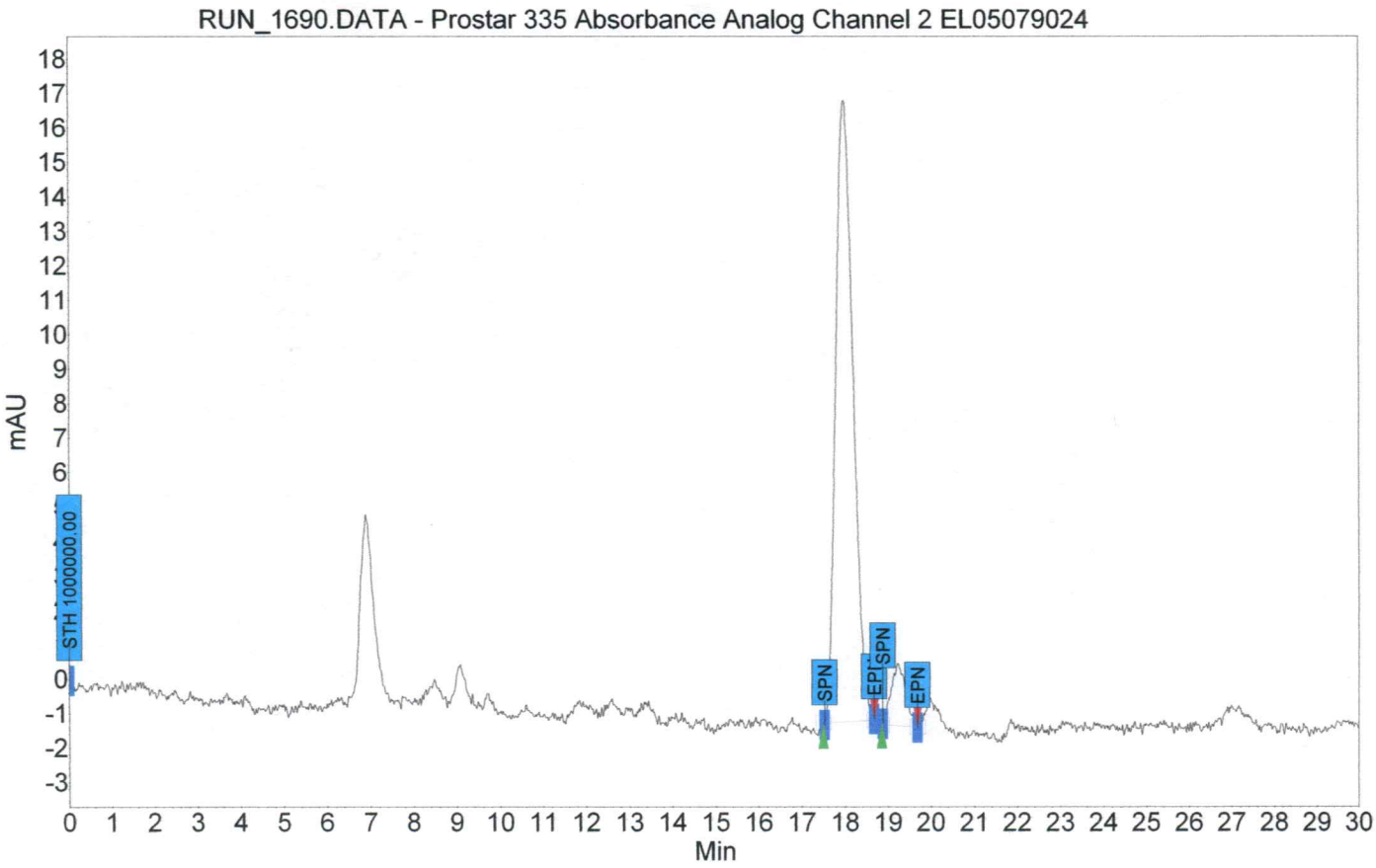
2b



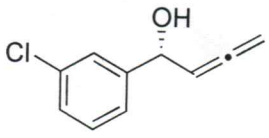
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	18.01	49.44	152.3	95.0	49.437
2	UNKNOWN	19.23	50.56	148.8	97.2	50.563
Total			100.00	301.1	192.2	100.000



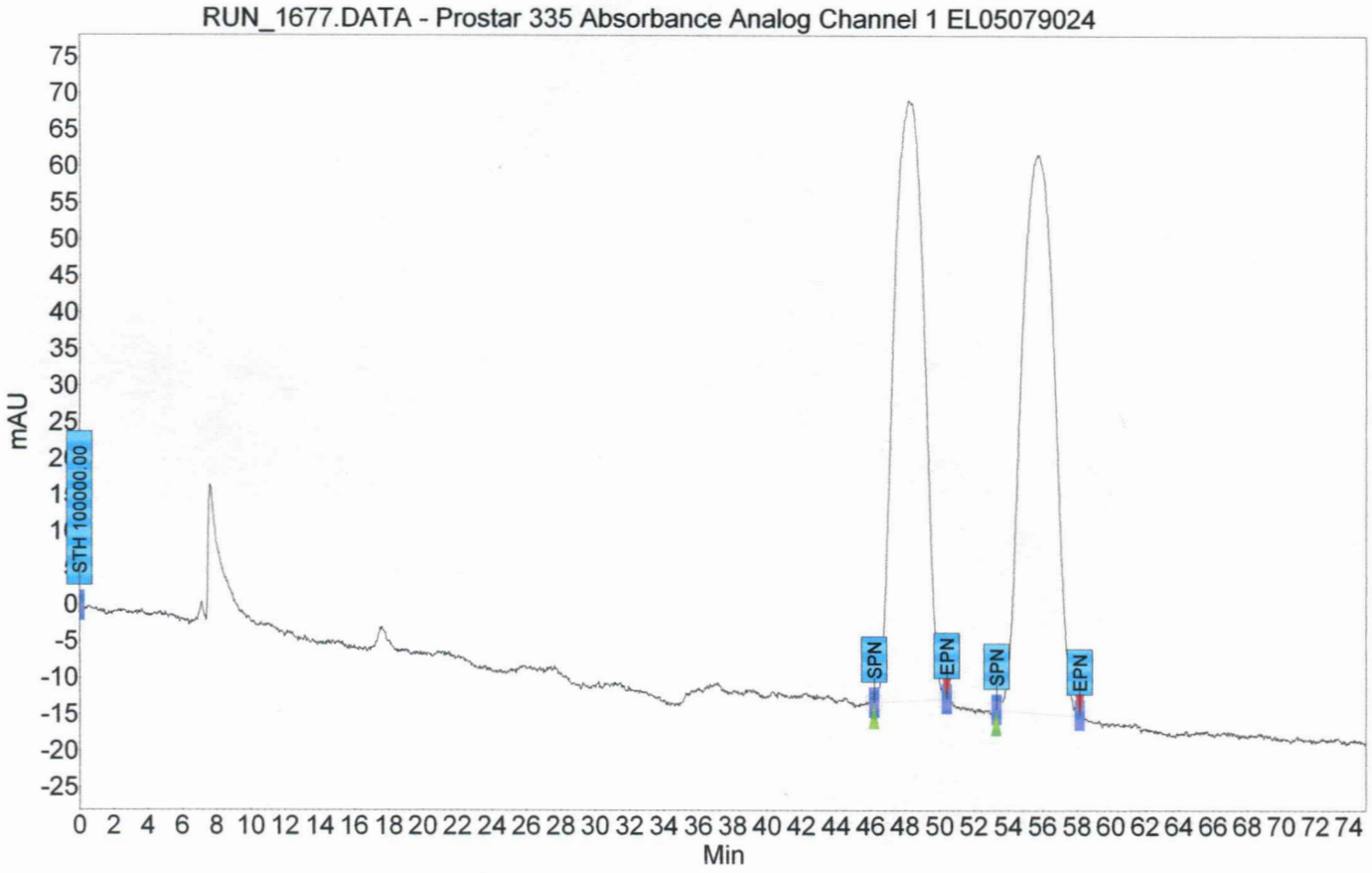
(±)-**2c**



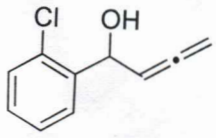
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	17.97	92.40	18.1	8.4	92.402
2	UNKNOWN	19.24	7.60	1.8	0.7	7.598
Total			100.00	19.9	9.1	100.000



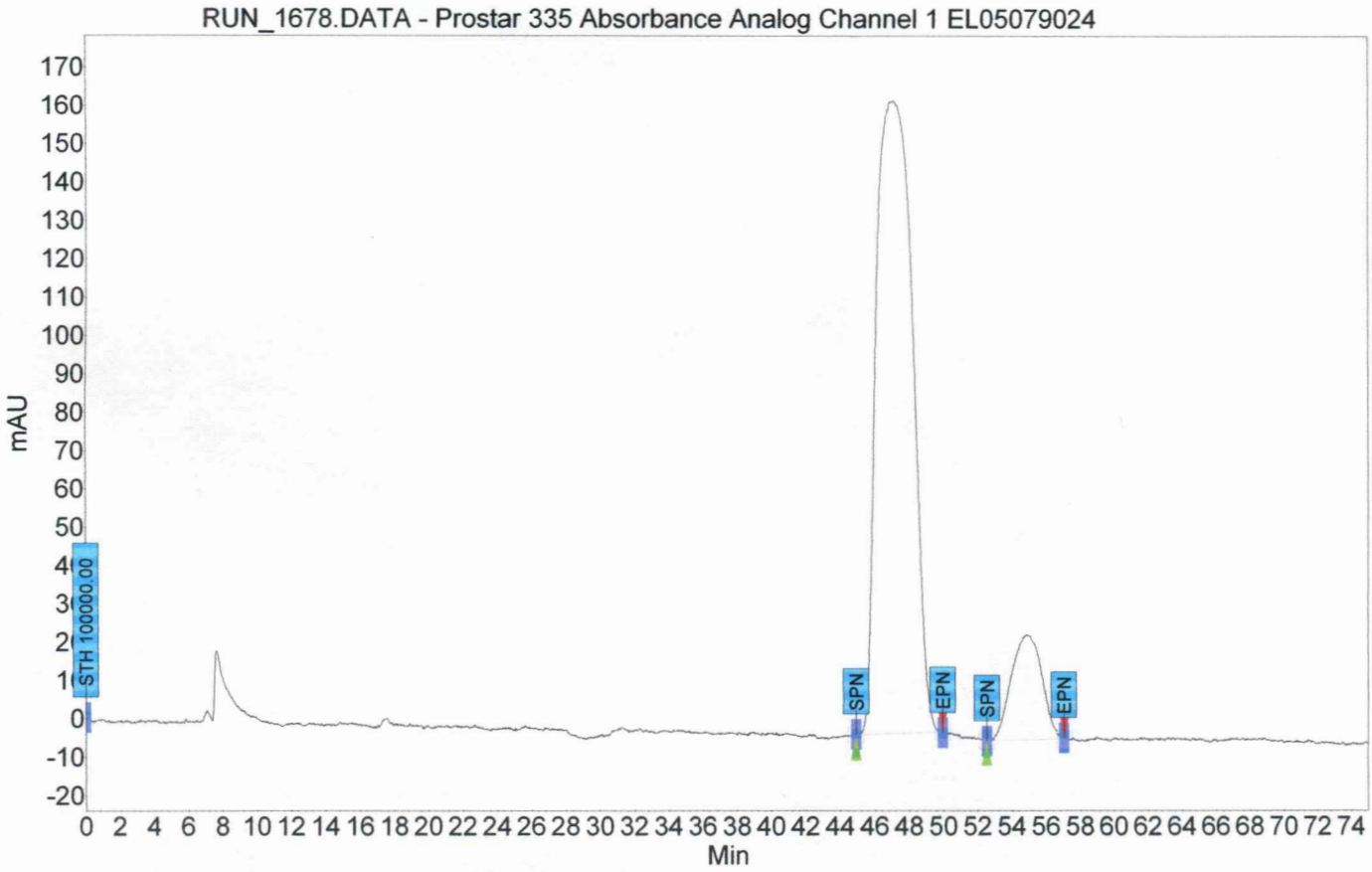
2c



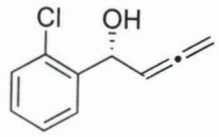
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	48.25	49.68	82.1	167.0	49.681
2	UNKNOWN	55.76	50.32	76.6	169.2	50.319
Total			100.00	158.7	336.2	100.000



(±)-**2d**



Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	47.17	87.56	165.3	400.8	87.560
2	UNKNOWN	54.93	12.44	27.3	56.9	12.440
Total			100.00	192.6	457.8	100.000



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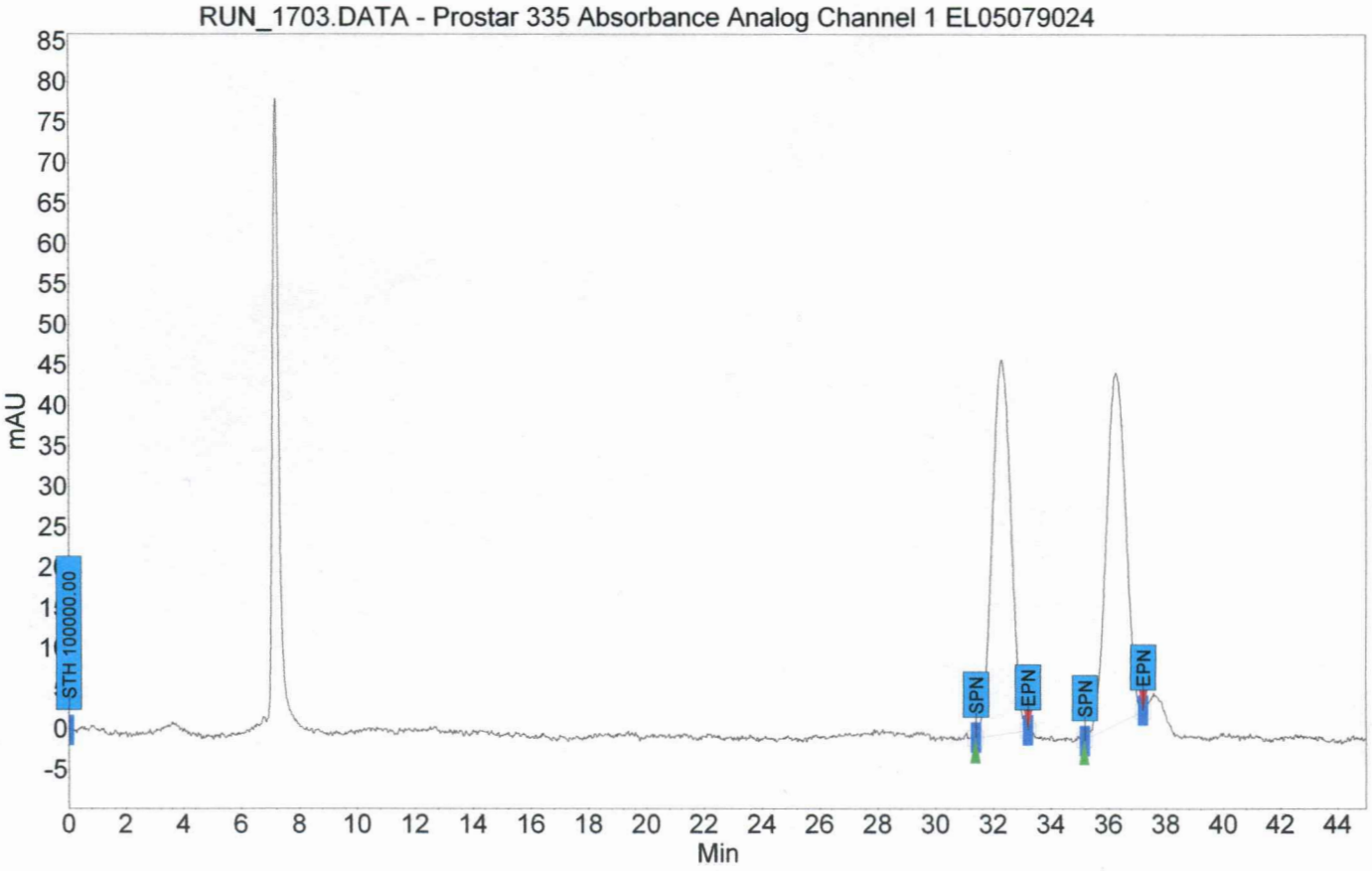
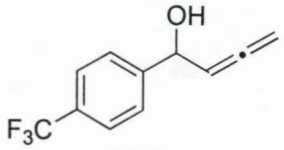
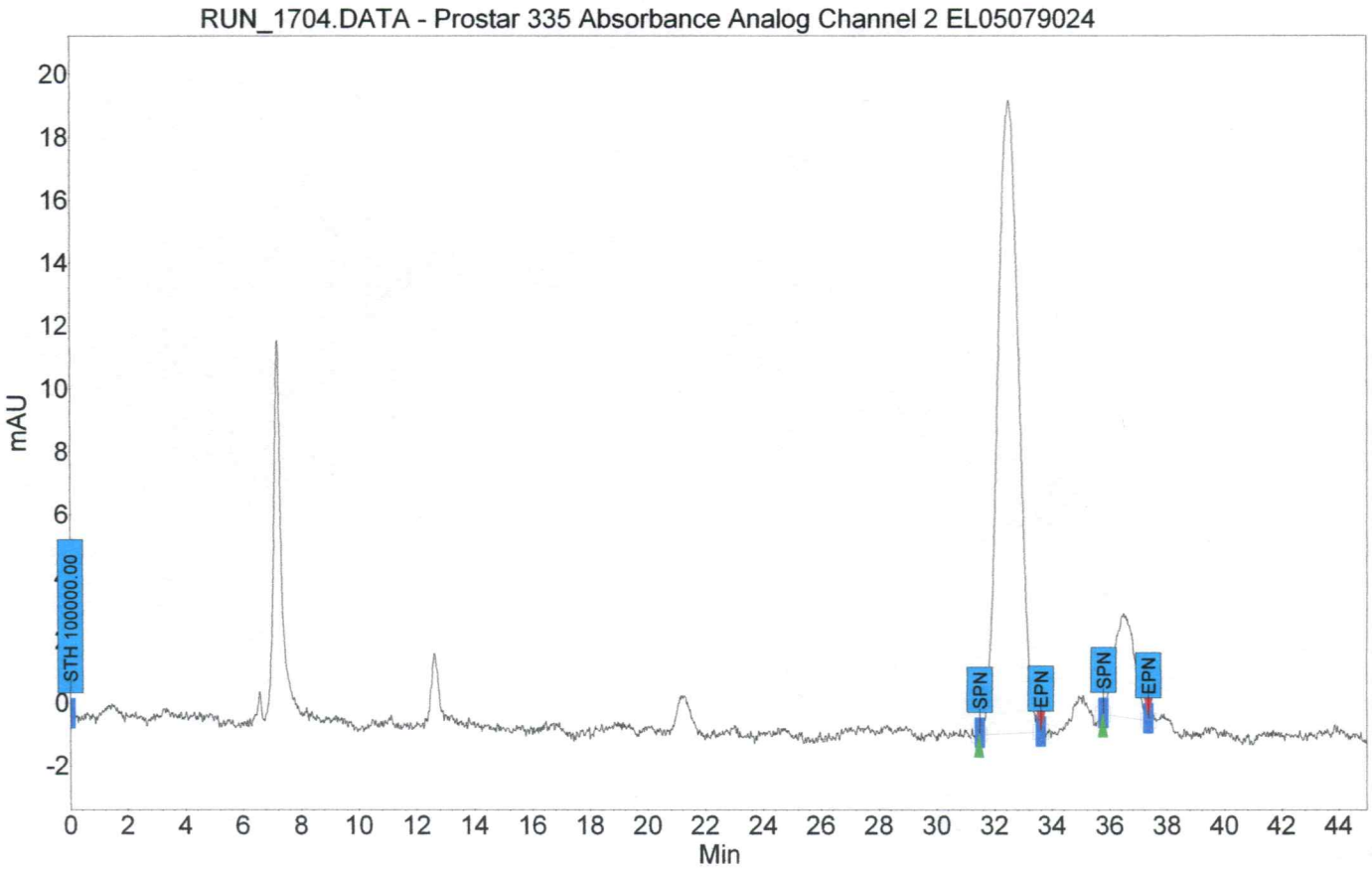


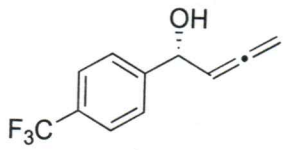
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	32.28	50.24	46.3	34.4	50.237
2	UNKNOWN	36.23	49.76	43.4	34.1	49.763
Total			100.00	89.6	68.4	100.000



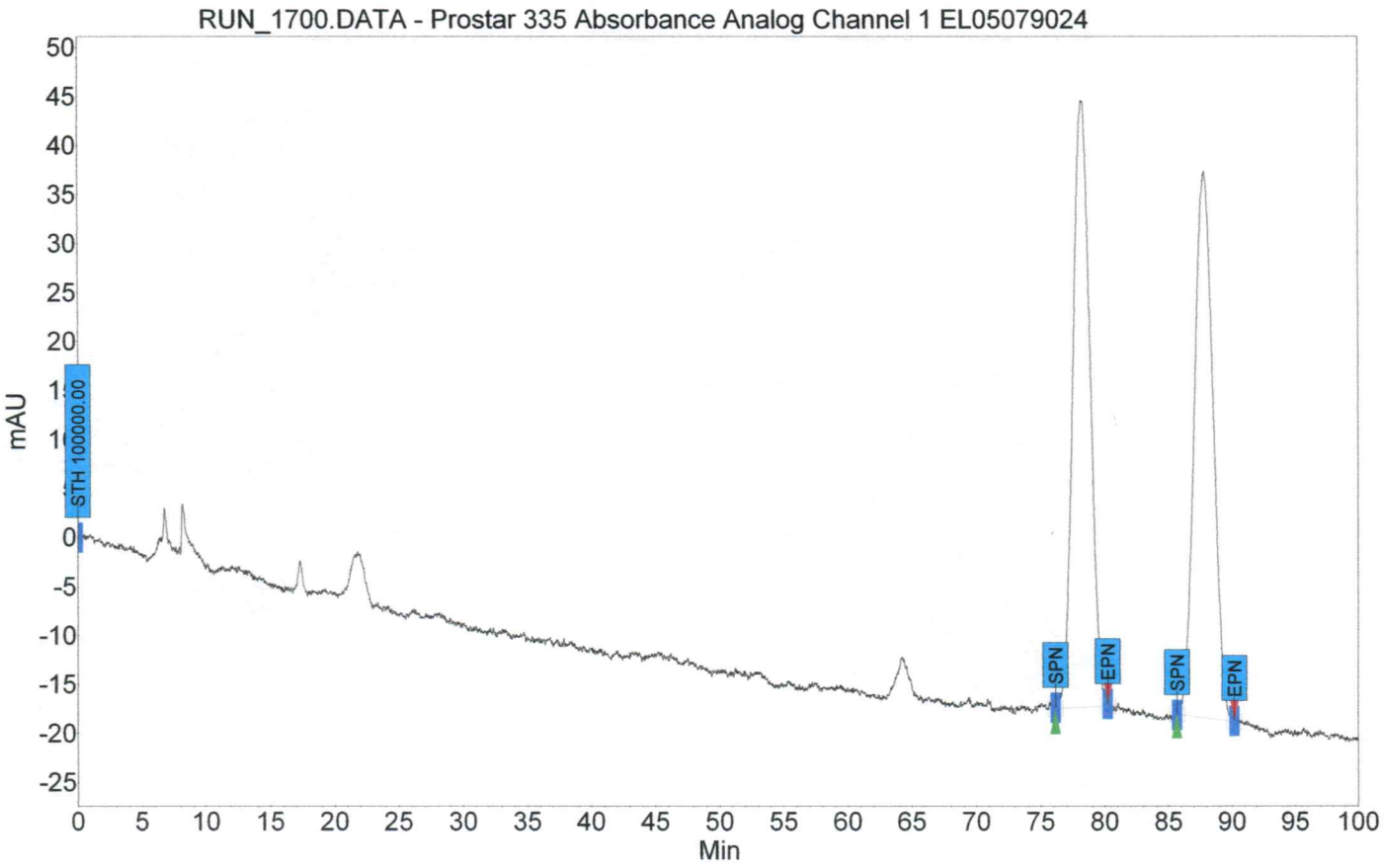
(±)-**2e**



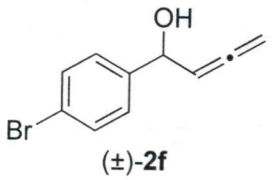
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	32.49	86.54	20.1	16.9	86.540
2	UNKNOWN	36.47	13.46	3.3	2.6	13.460
Total			100.00	23.4	19.6	100.000



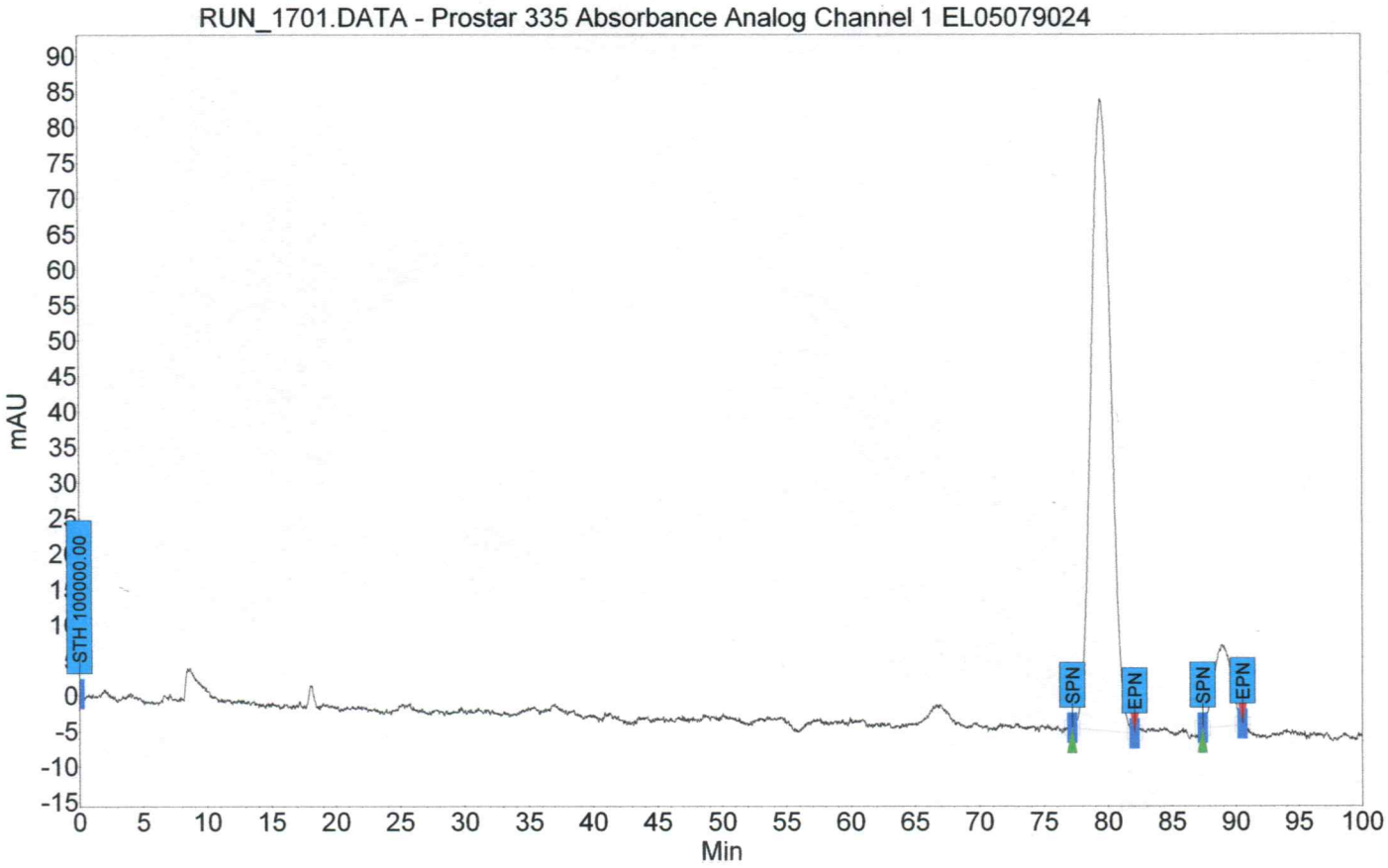
2e



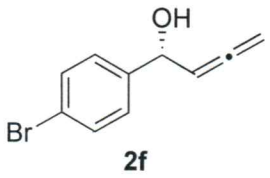
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	78.16	50.15	61.9	96.2	50.155
2	UNKNOWN	87.80	49.85	55.6	95.6	49.845
Total			100.00	117.5	191.9	100.000



(±)-**2f**



Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	79.45	89.49	88.9	157.9	89.492
2	UNKNOWN	88.88	10.51	11.4	18.5	10.508
Total			100.00	100.3	176.5	100.000



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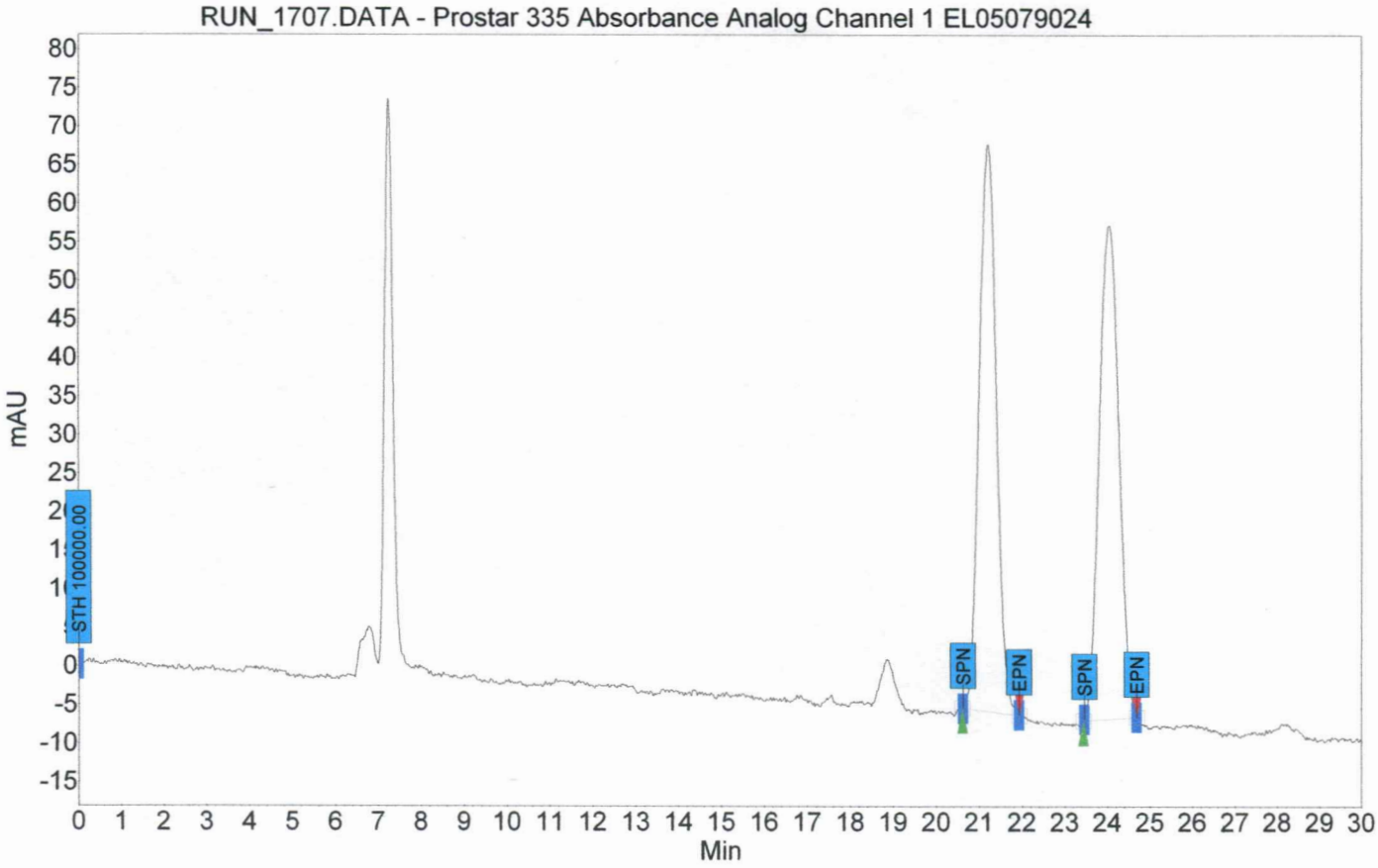
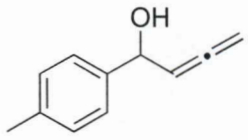
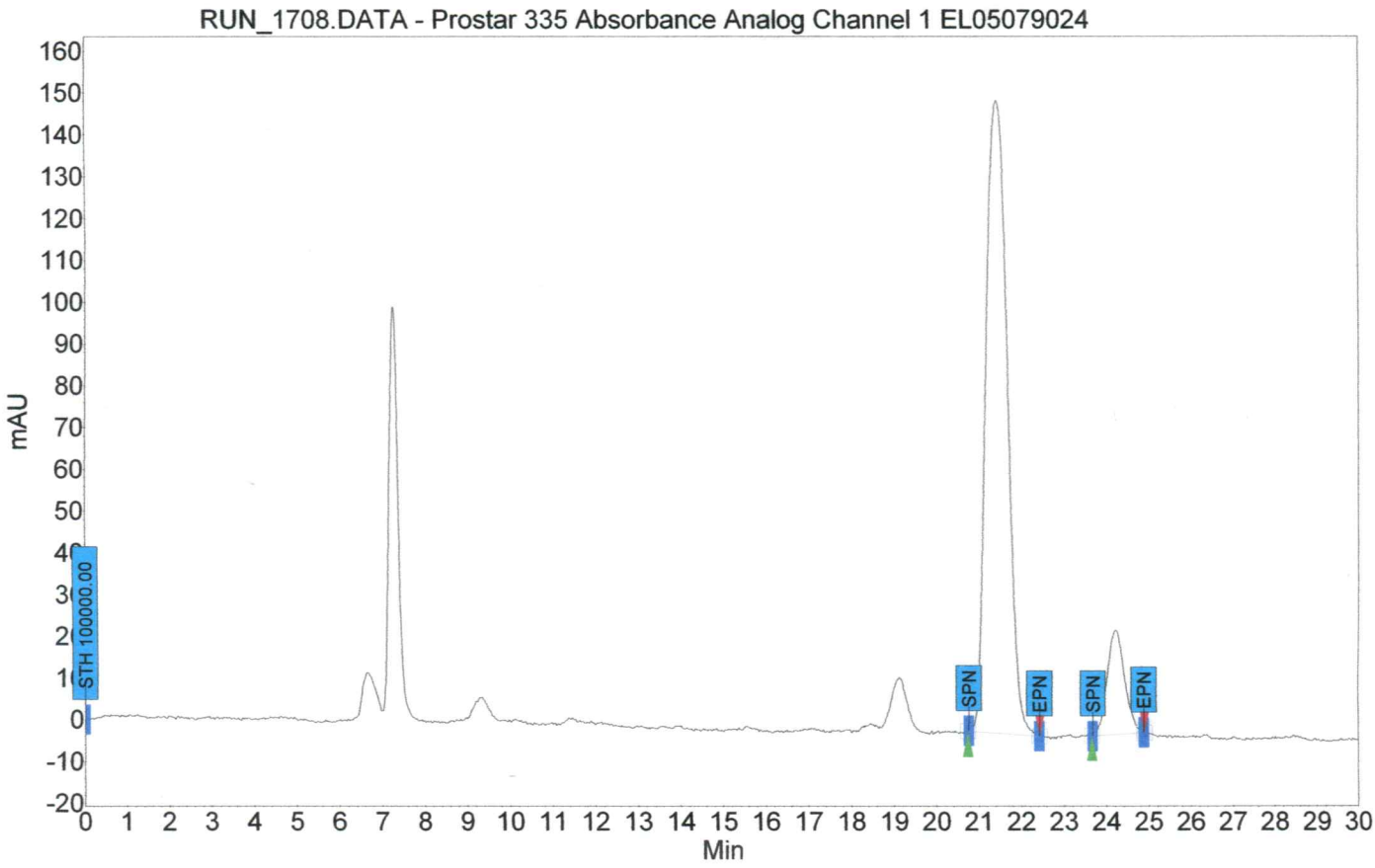


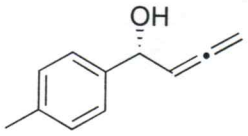
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	21.20	49.89	73.5	34.2	49.888
2	UNKNOWN	24.03	50.11	64.0	34.3	50.112
Total			100.00	137.5	68.5	100.000



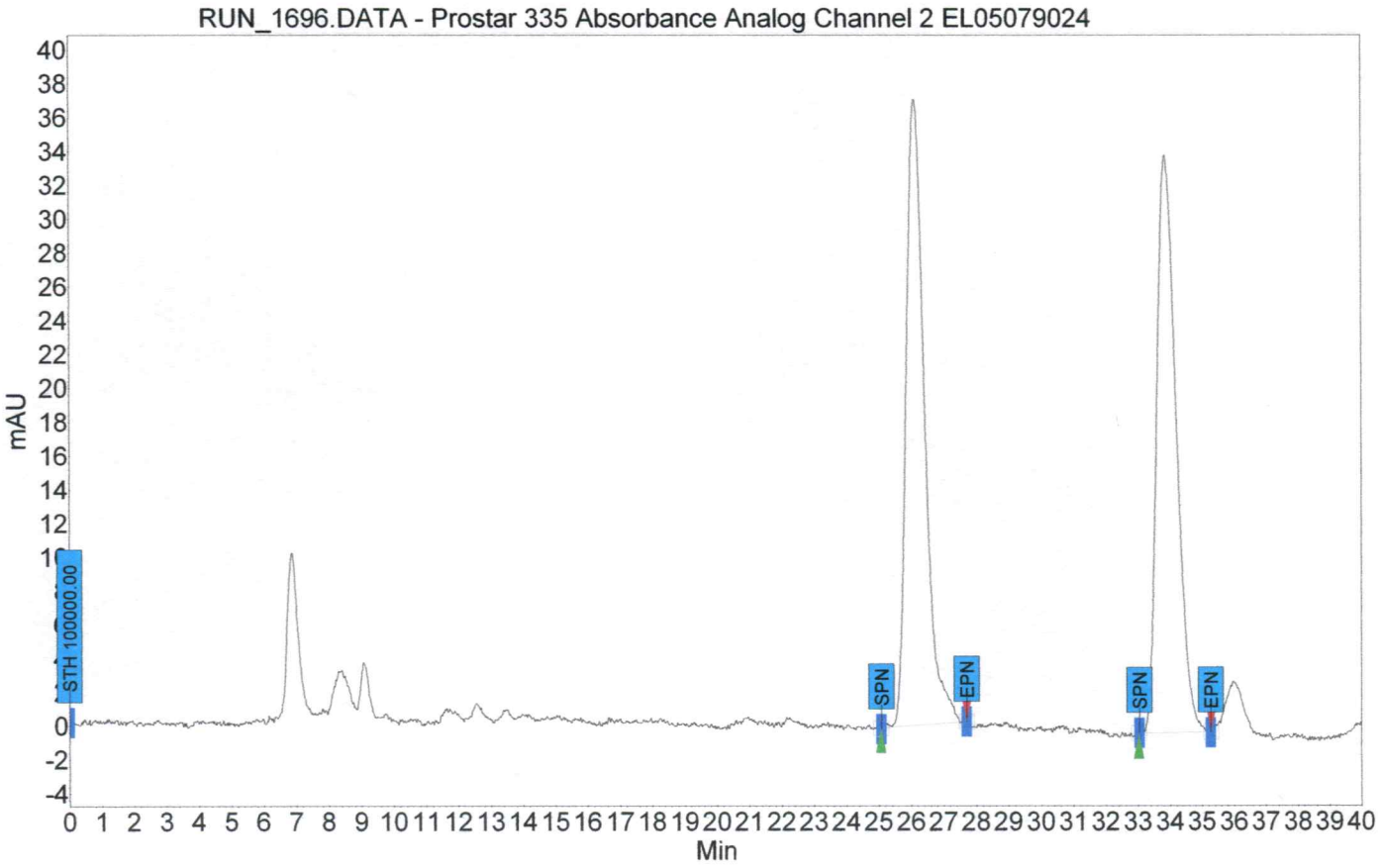
(±)-**2g**



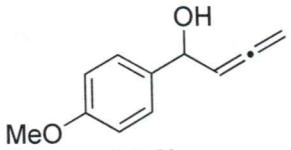
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	21.41	87.94	151.5	87.8	87.937
2	UNKNOWN	24.21	12.06	25.1	12.0	12.063
Total			100.00	176.6	99.8	100.000



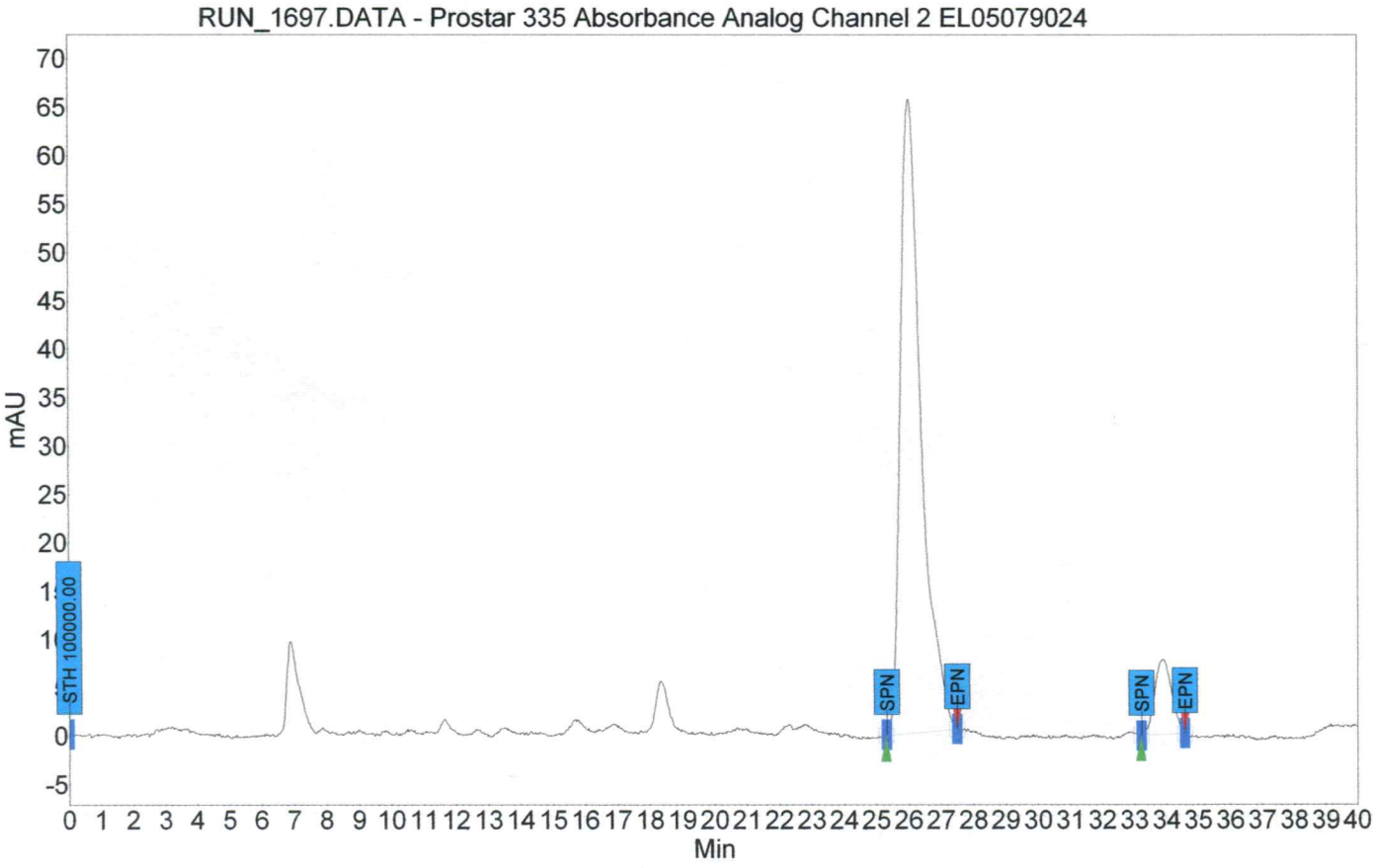
2g



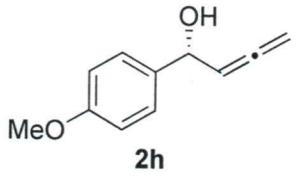
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	26.08	50.32	37.1	24.2	50.322
2	UNKNOWN	33.85	49.68	34.2	23.9	49.678
Total			100.00	71.2	48.2	100.000



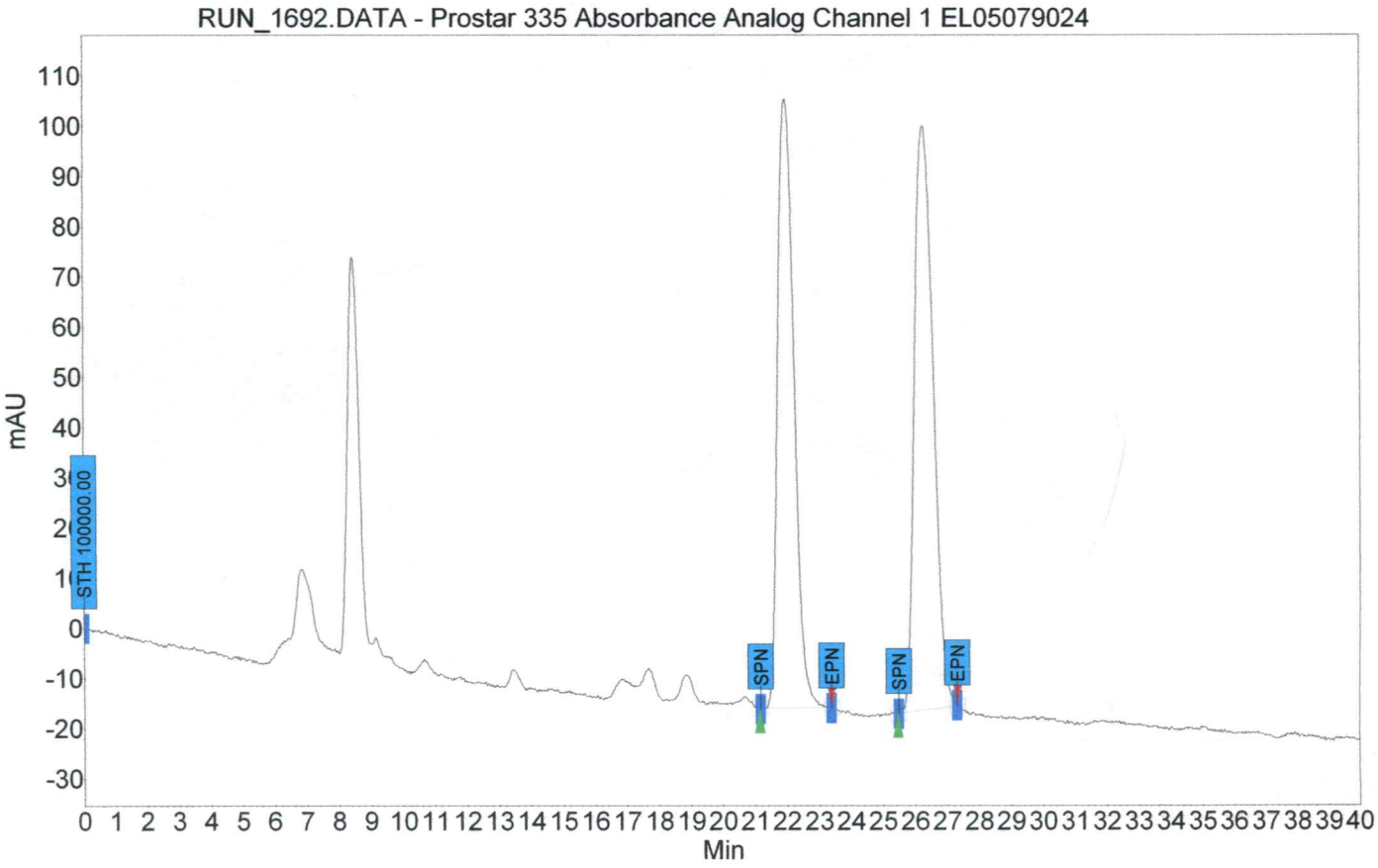
(±)-**2h**



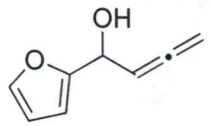
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	26.00	91.09	65.7	49.0	91.093
2	UNKNOWN	33.88	8.91	7.8	4.8	8.907
Total			100.00	73.4	53.7	100.000



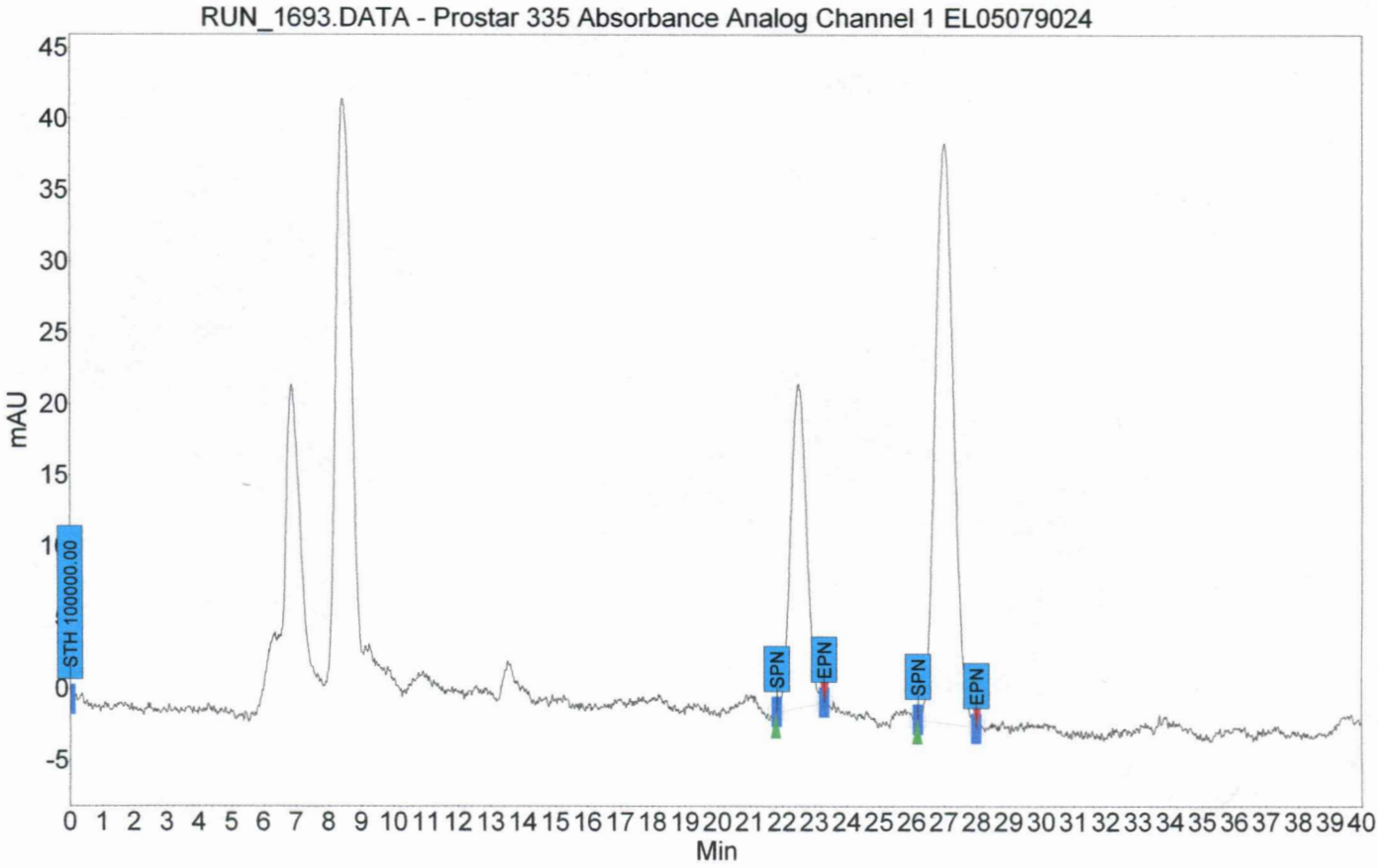
2h



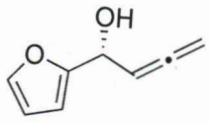
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	21.92	47.55	121.3	71.7	47.546
2	UNKNOWN	26.23	52.45	116.4	79.1	52.454
Total			100.00	237.7	150.8	100.000



(±)-**2i**



Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	22.49	32.47	22.8	12.9	32.468
2	UNKNOWN	27.00	67.53	40.7	26.8	67.532
Total			100.00	63.4	39.6	100.000



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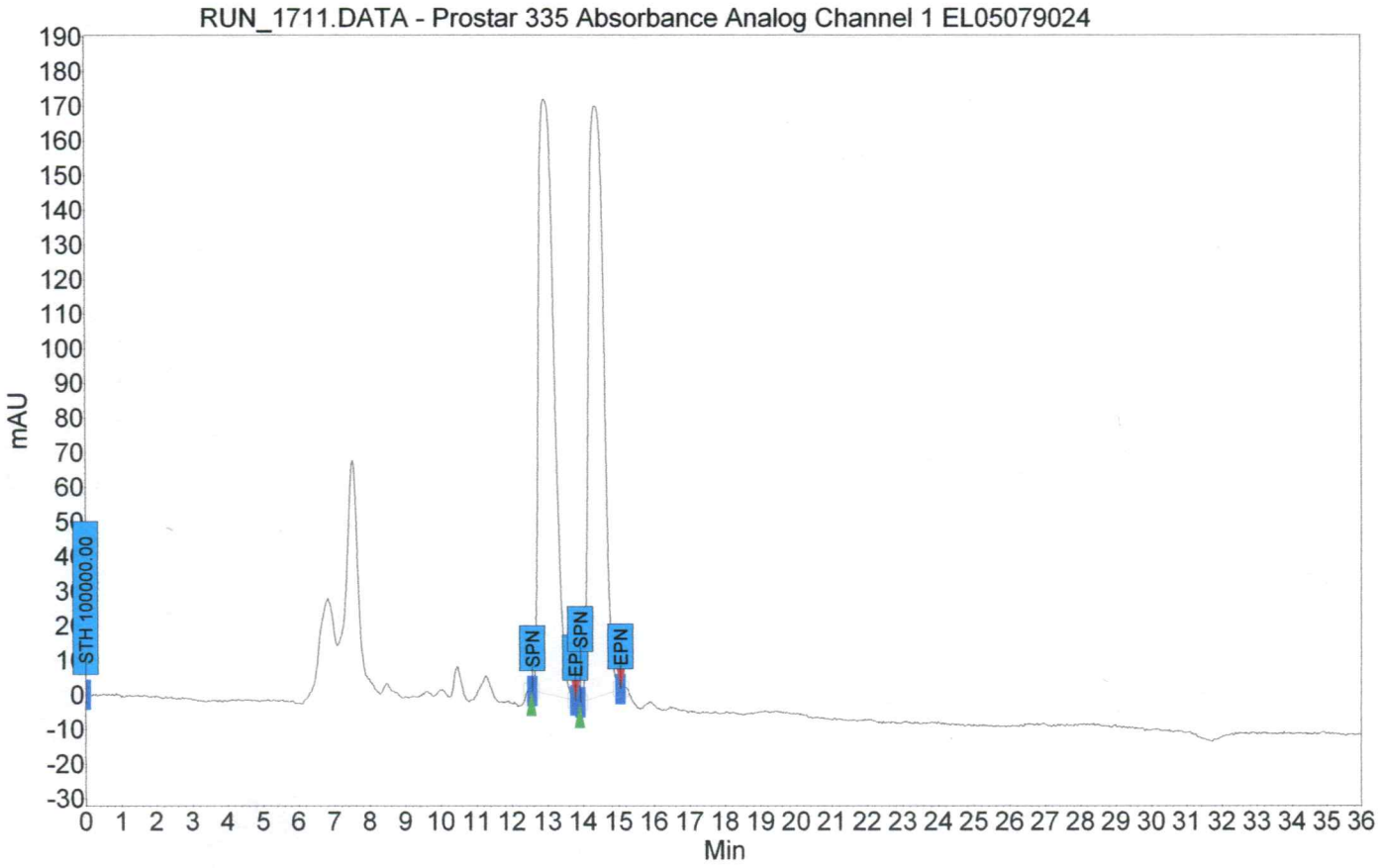
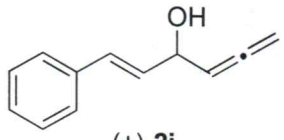


Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	12.93	50.86	171.7	86.4	50.861
2	UNKNOWN	14.33	49.14	170.9	83.5	49.139
Total			100.00	342.5	169.9	100.000



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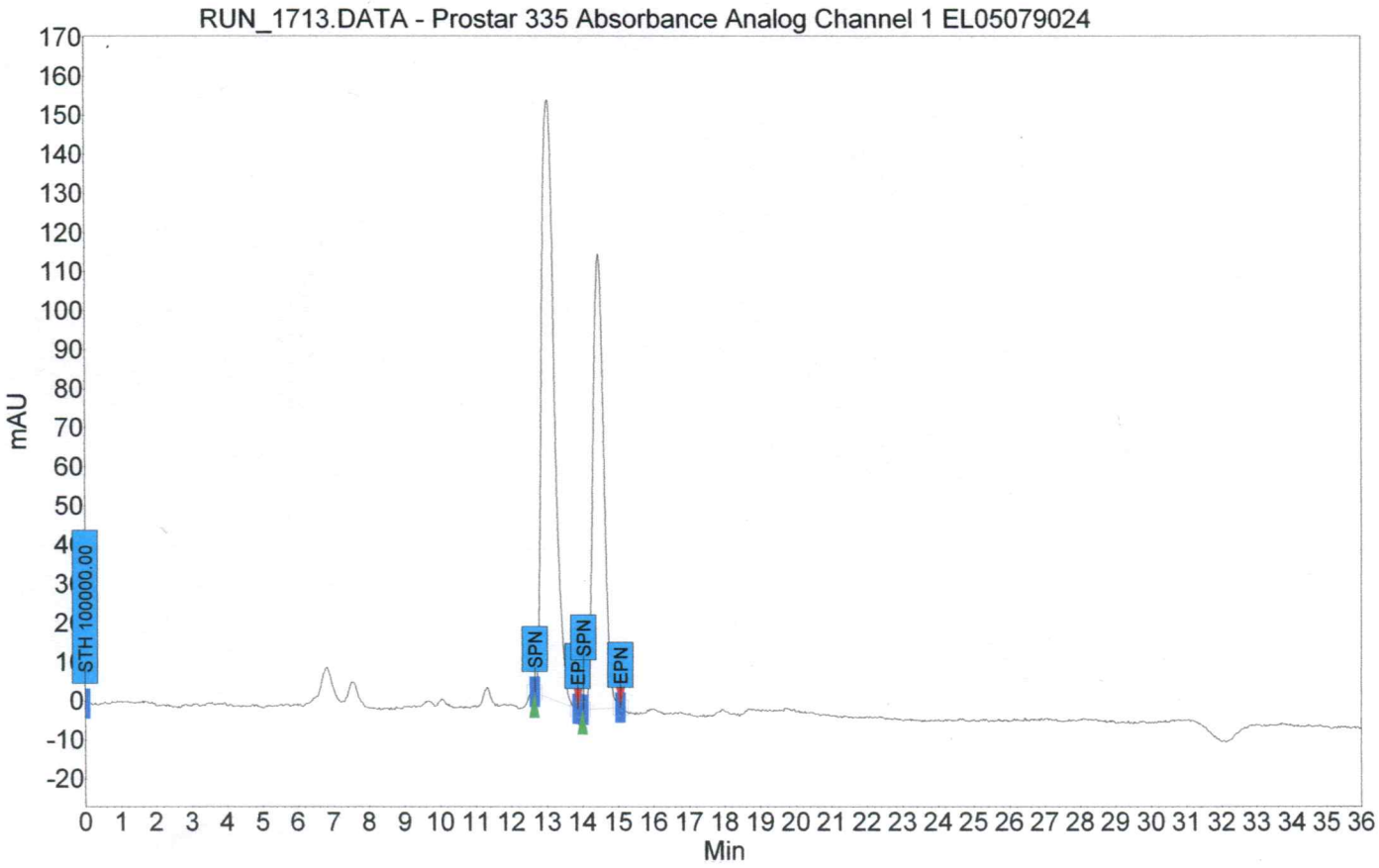
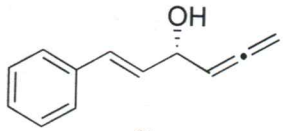


Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	13.03	60.65	153.1	62.9	60.653
2	UNKNOWN	14.45	39.35	116.6	40.8	39.347
Total			100.00	269.7	103.7	100.000



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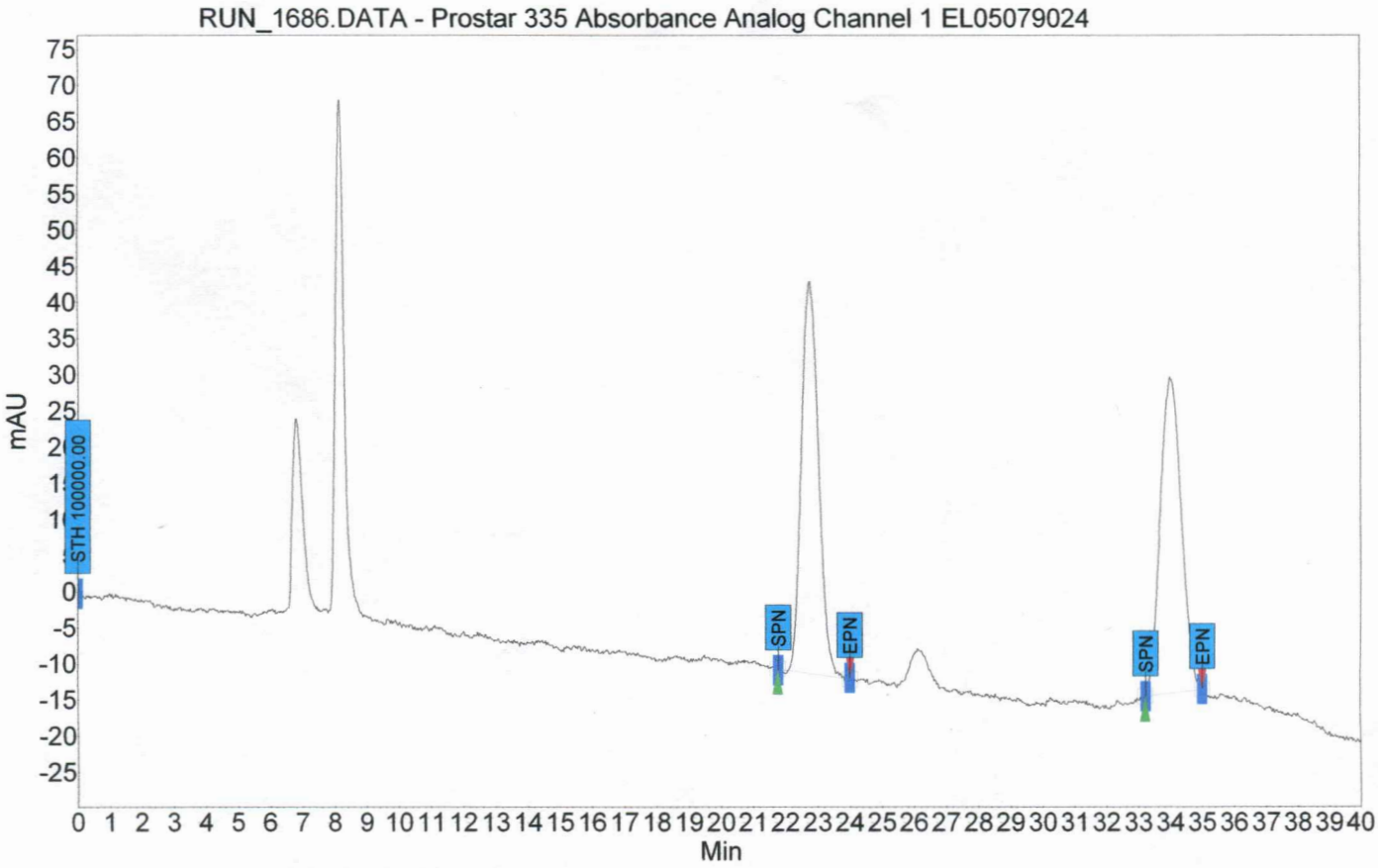
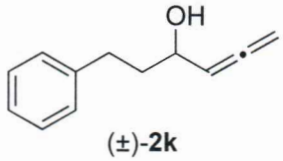


Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	22.76	50.04	54.3	33.4	50.041
2	UNKNOWN	33.99	49.96	43.7	33.3	49.959
Total			100.00	98.0	66.7	100.000



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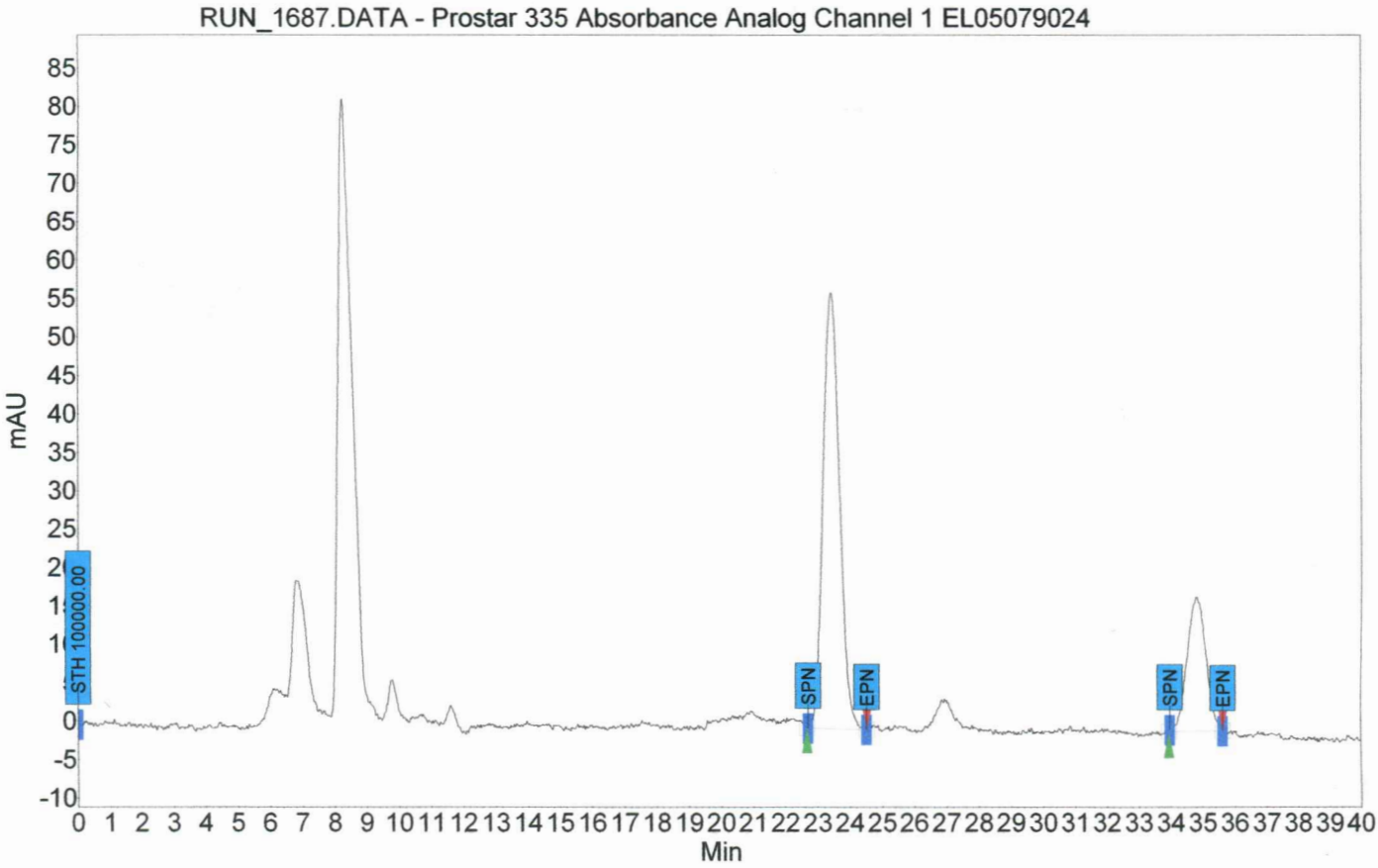
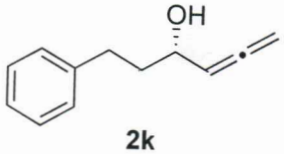


Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	23.40	73.88	56.7	33.7	73.875
2	UNKNOWN	34.79	26.12	17.3	11.9	26.125
Total			100.00	74.1	45.7	100.000



2k