Design, Synthesis and Evaluation of a Helicenoidal DMAP Lewis Base Catalyst

Supporting Information

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Contents

I. General

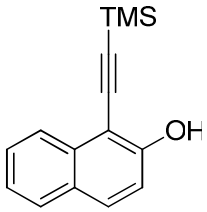
All reactions were performed under an inert atmosphere of nitrogen. Reaction solvents were purified by passing through anhydrous alumina columns using an Innovative Technology Inc PS-400-7 solvent purification system. Reagents were purchased from commercial suppliers: Acros Organics, Alfa Aesar, Sigma Aldrich and used without purification. Acetic anhydride and isobutyric anhydride were purified by passing through a short pad of potassium carbonate. Reactions were magnetically stirred and monitored by thin layer chromatography (TLC) using pre-coated MN Alugram Sil G/UV_{254} silica gel 60 aluminium backed plates. Plates were developed using UV light and $KMnO_4$. Silica gel flash chromatography was performed on chromatography grade silica 60 Å particle size 35-70 micron from Fisher Scientific using the solvent system as stated.

Analytical chiral HPLC was performed on either a Daicel CHIRALCEL OD-H, 4.6 mm × 25 cm column, a Daicel CHIRALCEL OB, 4.6 mm × 25 cm column, a Daicel CHIRALCEL OJ 4.6 mm × 25 cm column or a Daicel CHIRALCEL AD 4.6 mm × 25 cm column.

NMR spectra were recorded on a Brüker Avance 250 at 250 MHz (^{1}H) or Brüker Avance 300 at 300 MHz (^{1}H) and 75 MHz (^{13}C) or on a Brüker Avance 500 at 500 MHz (^{1}H) and 125 MHz (^{13}C) using the residual solvent as internal standard. Chemical shifts were reported in parts per million (ppm) and coupling constants (*J*) in Hertz (Hz). Signal multiplicity is denoted as singlet (s), doublet (d), doublet of doublets (dd), triplet (t), triplet of doublets (td), quartet (q), quartet of triplets (qt), septet (sept) and multiplet (m). High resolution mass spectrometry electrospray (ESI) was performed on a Brüker μTOF using electrospray ionisation in either positive or negative ionisation.

II. Preparation of [6]helicenoid DMAP analogue 4.

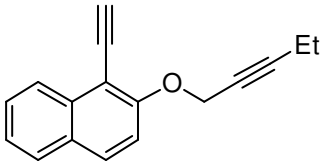
1-((trimethylsilyl)ethynyl)naphthalen-2-ol (5a)



5a

A solution of 1-iodonaphthalen-2-ol (**5**) (1 g, 3.70 mmol) in di*iso*propyl amine (15 mL) was heated to 60 ^{o}C. To this solution was added $PdCl_2(PPh_3)_2$ (130 mg, 0.185 mmol), copper (I) iodide (112 mg, 0.556 mmol) and trimethylsilylacetylene (1.5 mL, 10.83 mnmol) dropwise. The resulting mixture was stirred at this temperature for 1 h. The solvent was then evaporated to yield the crude product which was purified by column chromatography using 90:10 petroleum ether/ethyl acetate as eluent. The desired product was isolated as a brown oil (0.84 g, 94 %); υ_{max} (film)/cm^{-1}: 3500, 3061, 2959, 2899, 2135; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 8.30 (d, 1H, *J* = 8.5 Hz), 7.90 (d, 1H, *J* = 7.8 Hz), 7.87 (d, 1H, *J* = 9.0 Hz), 7.71 (t, 1H, *J* = 8.5 Hz), 7.52 (t, 1H, *J* = 7.8 Hz), 7.37 (d, 1H, *J* = 9.0 Hz), 0.55 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 156.6, 133.4, 130.7, 128.2, 128.1, 127.3, 124.6, 123.9, 116.1, 107.1, 102.7, 97.5, 0.0; (ESI HRMS) *m*/*z* calcd. for $C_{15}H_{15}OSi$ 239.0898 $(M-H)^-$, found 239.0886.

1-ethynyl-2-(pent-2-yn-1-yloxy)naphthalene (6)

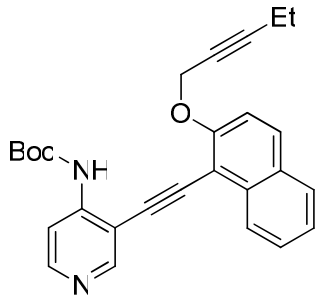


6

To a solution of 1-((trimethylsilyl)ethynyl)naphthalen-2-ol **5a** (0.56 g, 2.33 mmol) in DMF (9.3 mL) was added K_2CO_3 (0.52 g, 3.73 mmol), then 1-bromo-2-pentyne (381 µl, 3.73 mmol) and the mixture left to stir for 1 h at room temperature. On consumption of the starting material, K_2CO_3 was added (0.52 g, 3.73 mmol) followed by methanol (9.3 mL) and the reaction left to stir for 15 min at room temperature. The reaction was quenched via addition of water (9 mL) and the organics extracted with ethyl acetate (4 × 5 mL). The organics were combined, washed with LiCl (satd.) (4 × 5 mL), brine (satd.) (1 × 5 mL) and dried over $MgSO_4$ before being concentrated under reduced pressure. The crude mixture was subjected

to column chromatography using 90:10 petroleum ether/ethyl acetate as the eluent to afford the desired product as an orange oil (0.54 g, 99 %). υ_{max} (film)/cm^{-1}: 3283, 3059, 2976, 2936, 2877, 2233, 2098; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 8.30 (d, 1H, *J* = 8.5 Hz), 7.84 (d, 1H, *J* = 9.1 Hz), 7.80 (d, 1H, *J* = 8.2 Hz), 7.56 (t, 1H, *J* = 8.5 Hz), 7.41 (t, 1H, *J* = 8.2 Hz), 7.40 (d, 1H, *J* = 9.1 Hz), 4.92 (t, 2H, *J* = 2.2 Hz), 3.75 (s, 1H), 2.22 (qt, 2H, *J* = 7.5, 2.2 Hz), 1.12, (t, 3H, *J* = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 158.7, 135.1, 130.6, 129.1, 128.4, 127.7, 125.6, 124.8, 115.0, 106.6, 90.5, 87.0, 78.4, 74.6, 58.3, 13.9, 12.8; (ESI HRMS) *m/z* calcd. for $C_{17}H_{14}ONa$ 257.0937 $(M+Na)^+$, found 257.0922.

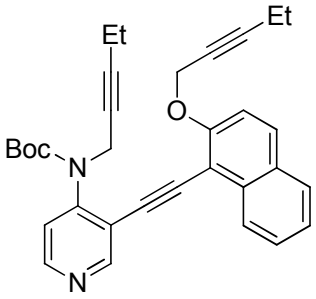
***tert*-butyl (3-((2-(pent-2-yn-1-yloxy)naphthalen-1-yl)ethynyl)pyridin-4-yl)carbamate (8)**



8

To a solution of *tert*-butyl (3-iodopyridin-4-yl)carbamate **7** (2 g, 6.25 mmol) in di*iso*propyl amine (6.5 mL) and toluene (26 mL) was added $Pd(PPh_3)_4$ (301 mg, 0.26 mmol) and CuI (0.78 mmol). The mixture was degassed by passing nitrogen through the solution and stirred for 15 min at room temperature. To this was added a degassed solution of **6** (1.22 g, 5.20 mmol) in diisopropyl amine (26 mL) and toluene (52 mL) *via* syringe pump over a period of 30 min. The resultant mixture was left to stir at room temperature for 24 h. Evaporation of solvents and subsequent purification of the residue by flash chromatography on silica gel using petroleum ether/ethyl acetate (80:20) afforded the title product as an orange oil (1.82 g, 82 %). υ_{max} (film)/cm^{-1}: 3356. 2978, 2937, 2206, 2008, 1736; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 8.73 (s, 1H), 8.43 (d, 1H, *J* = 7.2 Hz), 8.28 (d, 1H, *J* = 8.4 Hz), 8.19 (d, 1H, *J* = 7.2 Hz), 7.99 (s, 1H), 7.88 (d, 1H, *J* = 9.2 Hz), 7.82 (d, 1H, *J* = 8.2 Hz), 7.60 (t, 1H, *J* = 8.4 Hz), 7.49 (d, 1H, *J* = 9.2 Hz), 7.43 (t, 1H, *J* = 8.2 Hz), 5.01(t, 2H, *J* = 2.1 Hz), 2.21 (qt, 2H, *J* = 7.6, 2.1 Hz), 1.61 (s, 9H), 1.10 (t, 3H, *J* = 7.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 157.9, 152.2, 151.7, 149.9, 146.2, 133.6, 130.8, 128.9, 128.4, 127.8, 125.2, 124.9, 114.2, 111.4, 108.8, 106.5, 94.3, 91.3, 91.0, 82.3, 74.5, 58.0, 28.5, 13.7, 12.7; (ESI HRMS) *m/z* calcd. for $C_{27}H_{26}N_2O_3Na$ 449.1836 $(M+Na)^+$, found 449.1844.

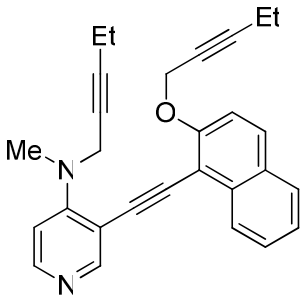
***Tert*-butyl pent-2-yn-1-yl(3-((2-(pent-2-yn-1-yloxy)naphthalen-1-yl)ethynyl)pyridin-4-yl)carbamate (8a)**



8a

To a solution of **8** (1.82 g, 4.27 mmol) in DMF (85 mL) was added NaH (0.5 g, 21.3 mmol) and 1-bromo-2-pentyne (1.09 mL, 10.67 mmol) dropwise. The resultant mixture was left to stir for 1 h at room temperature. The reaction was quenched via the addition of water (50 mL) and the organics extracted with ethyl acetate (4 × 30 mL). The organics were combined, washed with LiCl (satd.) (4 × 30 mL), brine (1 × 30 mL) and dried over $MgSO_4$ before being concentrated under reduced pressure. The crude mixture was purified by column chromatography using petroleum ether/ethyl acetate (80:20) to afford the desired product as an orange oil (1.90 g, 90 %). υ_{max} (film)/cm^{-1}: 2976, 2936, 2202, 2160, 2011, 1978, 1704; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 8.92 (s, 1H), 8.55 (d, 1H, *J* = 5.3 Hz), 8.29 (d, 1H, *J* = 8.2 Hz), 7.84 (d, 1H, *J* = 9.2 Hz), 7.79 (d, 1H, *J* = 8.5 Hz), 7.58 (t, 1H, *J* = 8.2 Hz), 7.40 (t, 1H, *J* = 8.5 Hz), 7.39 (d, 1H, *J* = 9.2 Hz), 7.33 (d, 1H, *J* = 5.3 Hz), 4.93 (t, 2H, *J* = 1.9 Hz), 4.63 (t, 2H, *J* = 1.9 Hz), 2.22 (qt, 2H, *J* = 7.6, 1.9 Hz), 2.08 (qt, 2H, *J* = 7.6, 1.9 Hz), 1.38 (s, 9H), 1.11 (t, 3H, *J* = 7.6 Hz), 1.01 (t, *J* = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 158.3, 154.0, 153.5, 150.1, 149.2, 134.4, 130.8, 129.0, 128.4, 127.9, 125.6, 124.9, 124.0, 120.3, 114.9, 107.0, 93.0, 92.2, 90.5, 86.7 81.7, 74.9, 75.6, 58.1, 38.9, 28.4, 14.0, 13.9, 12.8, 12.6; (ESI HRMS) *m/z* calcd. for $C_{32}H_{33}N_2O_3$ 493.2491 $(M+H)^+$, found 493.2483.

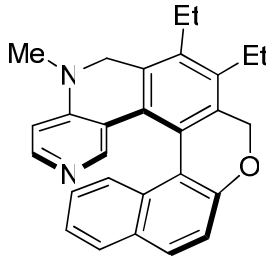
***N*-methyl-*N*-(pent-2-yn-1-yl)-3-((2-(pent-2-yn-1-yloxy)naphthalen-1-yl)ethynyl)pyridin-4-amine (9)**



9

To a solution of **8a** (1.74 g, 3.54 mmol) in CH_2Cl_2 (97 mL) was added triethylamine (0.74 mL, 5.30 mmol) followed by TMSOTf (1.28 mL, 7.07 mmol) dropwise. The reaction was left to stir at room temperature for 1 h. The reaction was quenched *via* addition of NH_4Cl (satd.) (1 × 50 mL) and the organics extracted with CH_2Cl_2 (3 × 10 mL). The organics were combined, washed with brine (satd.) (1 × 50 mL) and dried over $MgSO_4$ before being concentrated under reduced pressure. The residue was re-dissolved in DMF (155 mL) before NaH (0.43 g, 17.73 mmol) and iodomethane (331 µl, 5.32 mmol) were subsequently added. The reaction was left to stir at room temperature for 1 h before quenching by the addition of water (100 mL) and the organics extracted with ethyl acetate (4 × 40 mL). The organics were combined, washed with LiCl (satd.) (4 × 40 mL), brine (satd.) (1 × 40 mL) and dried over $MgSO_4$ before being concentrated under reduced pressure. The resultant residue was purified *via* flash chromatography on silica gel using petroleum ether/ethyl acetate (60:40) to give the title product as an orange oil (1.15 g, 80 %). υ_{max} (film)/cm^{-1}: 2976, 2937, 2877, 2232; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 8.68 (s, 1H), 8.33 (d, 1H, *J* = 8.5 Hz), 8.27 (d, 1H, *J* = 5.9 Hz), 7.82 (d, 1H, *J* = 9.2 Hz), 7.80 (d, 1H, *J* = 7.9 Hz), 7.56 (t, 1H, *J* = 8.5 Hz), 7.41 (t, 1H, *J* = 7.9 Hz), 7.38 (d, 1H, *J* = 9.2 Hz), 6.79 (d, 1H, *J* = 5.9 Hz), 4.90 (t, 2H, *J* = 1.9 Hz), 4.48 (t, 2H, *J* = 1.9 Hz), 3.27 (s, 3H), 2.24 (qt, 2H, *J* = 7.6, 1.9 Hz), 2.16 (qt, 2H, *J* = 7.5, 1.9 Hz), 1.13 (t, 3H, *J* = 7.6 H), 1.08 (t, 3H, *J* = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) : δ_C 157.9, 156.5, 155.6, 149.3, 134.5, 130.2, 129.2, 128.4, 127.7, 125.7, 124.9, 114.8, 111.2, 109.5, 108.0, 96.3, 91.9, 90.4, 87.2, 74.6, 74.4, 58.3, 43.8, 39.4, 14.3, 13.9, 12.8, 12.7; (ESI HRMS) *m/z* calcd. for $C_{28}H_{26}N_2ONa$ 429.1937 $(M+Na)^+$, found 429.1946.

[6]-helicenoid DMAP analogue (4)

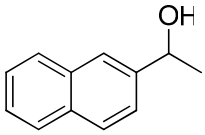
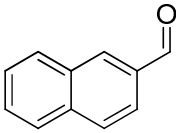
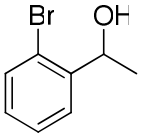
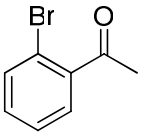
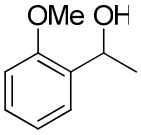
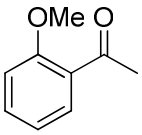
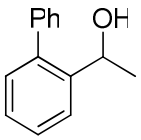
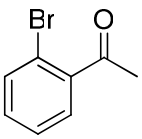


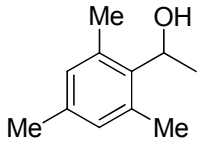
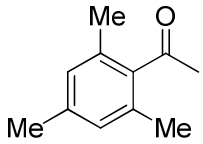
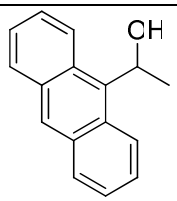
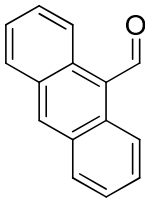
4

A solution of **9** (43 mg, 0.11 mmol) and tris(triphenylphosphine)rhodium(I) chloride (4.8 mg, 0.005 mmol) in dioxane (2.5 mL) was transferred to an ampule under an argon atmosphere and degassed for 20 min. The ampule was sealed and the reaction mixture heated to 130 ^oC for 16 h. Following completion of the reaction, solvent was removed under reduced pressure and the resultant crude mixture subjected to flash column chromatography using acetonitrile/ethanol (80:20) followed by ethyl acetate (1% NEt_3) to yield the title product as a yellow solid (32 mg, 74 %). υ_{max} (film)/cm^{-1}: 2965, 2872, 1619, 1591; ^{1}H NMR (500 MHz,

$CDCl_3$): δ_H 7.84 (d, 1H, *J* = 5.3 Hz), 7.71 (d, 1H, *J* = 8.4 Hz,, 7.68 (d, 1H, *J* = 8.4 Hz), 7.37–7.30 (m, 3H), 7.13 (t, 1H, *J* = 7.9 Hz), 6.93 (t, 1H, *J* = 7.9 Hz), 6.55 (d, 1H, *J* = 5.3 Hz), 5.45 (d, 1H, *J* = 13.1 Hz), 4.66 (d, 1H, *J* = 13.1 Hz), 4.38 (d, 1H, *J* = 14.1 Hz), 4.06 (d, 1H, *J* = 14.1 Hz), 3.01 (s, 3H), 2.80–2.65 (m, 4H), 1.27–1.20 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) : δ_C 155.8, 153.2, 148.2, 148.1, 136.6, 136.6, 136.3, 136.1, 130.6, 130.3, 129.2, 128.6, 125.7, 125.5, 124.4, 123.8, 120.6, 119.2, 118.3, 107.1, 77.6, 67.7, 52.8, 38.3, 22.1, 21.9, 15.7, 15.1; (ESI HRMS) *m/z* calcd. for $C_{28}H_{26}N_2ONa$ 429.1937 $(M+Na)^+$, found 429.1925. The enantiomers of the product were separated using preparative HPLC (Chiralpak IC (250 x 4.6 mm, 5 micron, hexane/ethanol/isopropylamine 90:10:0.4 15 mL/min). Enantiomer (*P*)-**4** ($[\alpha]^{20}_D$ = +540 (c = 0.10, CH_3CN); >99 % ee by analytical chiral HPLC) was collected from 25 minutes to 30 minutes, while enantiomer (*M*)-**4** ($[\alpha]^{20}_D$ = -560 (c = 0.10, CH_3CN); >99 % ee by analytical chiral HPLC) was collected from 34 minutes to 40 minutes.

Table 1. Synthesis of starting known racemic alcohols **10f**, **10h**-**10l**

Alcohol	Synthesised from	Conditions	Reference
 **10f**		MeLi (2 equiv), Et_2O, 0 °C, 2 h	**1**
 **10g**		$NaBH_4$ (2 equiv), MeOH, 0 °C to rt, 2h	**2**
 **10i**		$NaBH_4$ (2equiv), MeOH, 0 °C to rt, 2h	**2**
 **10j**		1) $PhB(OH)_2$ (1 equiv), $Pd(OAc)_2$ (5 mol%), PPh_3 (10 mol%), Na_2CO_3 aq, (1 equiv), propan-1-ol, reflux, o/n 2) $NaBH_4$ (2 equiv), MeOH 0 °C to rt, 2h	**2**

 **10k**		$LiAlH_4$ (5 equiv), THF, reflux, 24 h	**3**
 **10l**		MeLi (2 equiv), Et_2O, 0 ^oC, 2 h	**2**

Spectral data for previously unreported isobutyric esters

1-(4-fluorophenyl)ethyl isobutyrate (11b)

υ_{max} (film)/cm^{-1}: 2978, 2938, 1731, 1606; ^1H NMR (500 MHz, $CDCl_3$): δ_H 7.35–7.29 (m, 2H), 7.05–6.98 (m, 2H), 5.85 (q, 1H, *J* = 6.6 Hz), 2.55 (sept, 1H, *J* = 6.9 Hz), 1.51 (d, 3H, *J* = 6.6 Hz), 1.2 (d, 3H, *J* = 6.9 Hz), 1.1 (d, 3H, *J* = 6.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) : δ_C 176.5, 162.6 (d, *J* = 247 Hz), 138.1 (d, *J* = 3.6 Hz), 128.0 (d, 7.6 Hz), 115.6 (d, *J* = 22.0 Hz), 71.5, 34.4, 22.5, 19.1; (ESI HRMS) *m/z* calcd. for $C_{12}H_{15}FO_2Na$ 233.1160 $(M+Na)^+$, found 233.1147.

1-([1,1'-biphenyl]-2-yl)ethyl isobutyrate (11j)

υ_{max} (film)/cm^{-1}: 2977, 2932, 2875, 1733; ^1H NMR (500 MHz, $CDCl_3$): δ_H 7.52 (dd, 1H, *J* = 7.6, 1.5 Hz), 7.46–7.29 (m, 6H), 7.32 (td, 1H, *J* = 7.6, 1.5 Hz), 7.21 (dd, 1H, *J* = 7.6, 1.5 Hz), 5.91 (q, 1H, *J* = 6.6 Hz), 2.54 (sept, 1H, *J* = 7.0 Hz), 1.37 (d, 3H, *J* = 6.6 Hz), 1.16 (d, 3H, *J* = 7.0 Hz), 1.15 (d, 3H, *J* = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) : δ_C 176.3, 141.0, 140.9, 140.4, 130.4, 129.5, 128.6, 128.1, 127.6, 127.5, 125.4, 69.7, 34.4, 22.9, 19.2; (ESI HRMS) *m/z* calcd. for $C_{18}H_{20}O_2Na$ 291.1361 $(M+Na)^+$, found 291.1358.

1-(anthracen-9-yl)ethyl isobutyrate (11l)

υ_{max} (film)/cm^{-1} : 2972, 2933, 2873, 1727, 1624; ^1H NMR (500 MHz, $CDCl_3$): δ_H 8.65 (d, 2H, *J* = 8.5 Hz), 8.43 (s, 1H), 8.02 (d, 2H, *J* = 8.5 Hz), 7.58-7.52 (m, 2H), 7.50–7.41 (m, 3H), 2.64 (sept, 1H, *J* = 6.9 Hz), 1.96 (d, 3H, *J* = 7.0 Hz), 1.21 (d, 3H, *J* = 6.9 Hz), 1.11 (d, 3H, *J* = 6.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) : δ_C 176.8, 132.7, 132.0, 129.7, 129.3, 128.7, 126.1, 125.1, 69.0, 34.5, 30.7, 21.9, 19.2, 19.2; (ESI HRMS) *m/z* calcd. for $C_{20}H_{20}O_2Na$ 315.1361 $(M+Na)^+$, found 315.1350.

1-(2-bromophenyl)ethyl isobutyrate (11g)

υ_{max} (film)/cm^{-1} :2981, 2883, 1735, 1569; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.53 (dd, 1H, *J* = 8.0, 1.0 Hz), 7.44 (dd, 1H, *J* = 7.8, 1.9 Hz), 7.32 (td, 1H, *J* = 8.0, 1.0 Hz), 7.13 (td, 1H, *J* = 7.8, 1.9 Hz), 6.15 (q, 1H, *J* = 6.6 Hz), 2.60 (sept, 1H, *J* = 6.9 Hz), 1.51 (d, 3H, *J* = 6.6 Hz), 1.20 (d, 3H, *J* = 6.9 Hz), 1.19 (d, 3H, *J* = 6.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) : δ_C 176.2, 141.8, 133.2, 129.3, 128.0, 126.9, 122.2, 71.5, 34.4, 21.5, 19.2, 19.2; (ESI HRMS) *m/z* calcd. for $C_{12}H_{15}BrO_2Na$ 293.0153 $(M+Na)^+$, found 293.0144.

III. Kinetic Resolutions

Determination of enantiomeric excesses, conversions and selectivities.

All unreacted alcohols recovered from kinetic resolutions employing catalyst (*P*)-**4** were found to be enriched in the (*S*)-enantiomer, as inferred by the negative sign of optical rotation.[4] Conversely, esters were deemed to be enriched in the (*R*)-enantiomer. Enantiomeric excesses of the alcohols were determined by analytical HPLC. In all but two cases (1-(4-fluorophenyl)ethanol, **10b** and 1-naphthyl ethanol **10e** preparative scale reaction), enantiomeric excesses of the ester products were determined by HPLC analysis after saponification (see General procedure). See **Table 2** for full HPLC assay conditions. Selectivity was calculated according to:

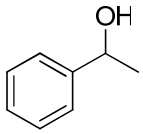
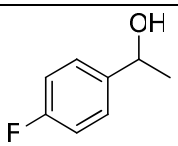
$$s = In((1 - C_{HPLC})(1 - ee_A))/In((1 - C_{HPLC})(1 + ee_A))$$

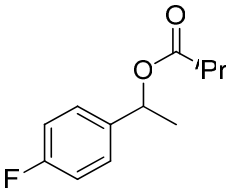
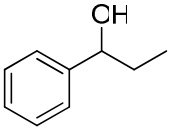
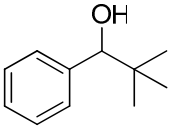
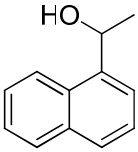
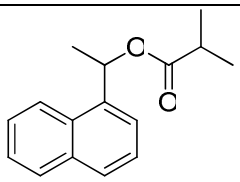
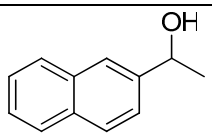
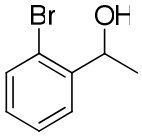
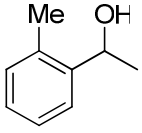
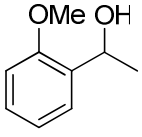
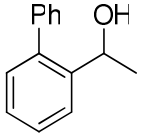
C_{HPLC} was calculated according to:

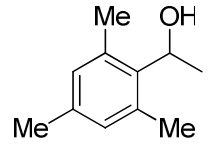
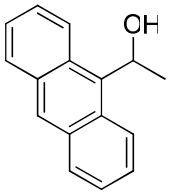
$$C_{HPLC} = ee_A/(ee_A + ee_E)$$

Whereby ee_A is the enantiomeric excess of the unreacted alcohol and ee_E is the enantiomeric excess of the ester. The conversion values obtained were found to be generally within 1-2 % of the values obtained by ^{1}H NMR integration of the crude reaction mixtures.

Table 2. HPLC conditions used to assay enantiomeric excess

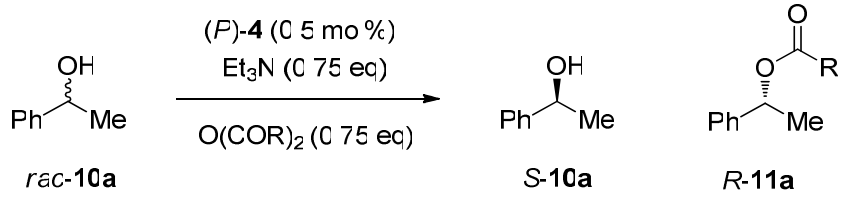
Substrate	ee Assay	Conditions	Retention Time of (*R*) Isomer (min)	Retention Time of (*S*) Isomer (min)
 10a	HPLC CHIRACEL OD-H	5% ^{i}PrOH/hexane 1.0 mL/min	7.72	9.24
 10b	HPLC CHIRACEL OB	1% ^{i}PrOH/hexane 0.3 mL/min	49.60	45.23

 **11b**	HPLC CHIRACEL OB	2% ^{i}PrOH/hexane 1.0 mL/min	4.73	6.34
 **10c**	HPLC CHIRACEL OD-H	2% ^{i}PrOH/hexane 1.0 mL/min	13.03	15.32
 **10d**	HPLC CHIRACEL OD-H	2% ^{i}PrOH/hexane 1.0 mL/min	11.98	9.39
 **10e**	HPLC CHIRACEL OD-H	10% ^{i}PrOH/hexane 1.0 mL/min	12.57	9.39
 **11e**	HPLC CHIRACEL OD-H	2% ^{i}PrOH/hexane 1.0 mL/min	6.05	4.92
 **10f**	HPLC CHIRACEL OJ	5% ^{i}PrOH/hexane 1.0 mL/min	30.58	23.44
 **10g**	HPLC CHIRACEL OB	2% ^{i}PrOH/hexane 1 mL/min	10.09	8.07
 **10h**	HPLC CHIRACEL OB	10% ^{i}PrOH/hexane 0.5 mL/min	10.50	9.10
 **10i**	HPLC CHIRACEL OB	5% ^{i}PrOH/hexane 1 mL/min	10.69	7.53
 **10j**	HPLC CHIRACEL OJ	2% ^{i}PrOH/hexane 1 mL/min	16.41	21.11

 10k	HPLC CHIRACEL AD	1% ^{i}PrOH/hexane 0.8 mL/min	18.10	21.36
 10l	HPLC CHIRACEL AD	4% ^{i}PrOH/hexane 0.8 mL/min	25.21	33.32

General procedure for the analytical-scale Catalytic Kinetic Resolution of alcohols by reaction with isobutyric anhydride and catalyst (*P*)-4. CKR of alcohol (±)-10a. A solution of catalyst (*P*)-**4** (1 mg, 2.4×10^{-3} mmol), (±)-1-phenylethanol (60 mg, 0.492 mmol) and triethylamine (37 mg, 0.369 mmol) in ^{t}amyl alcohol (1 mL) was cooled to 0 ^{o}C. With vigorous stirring, isobutyric anhydride (58 mg, 0.369 mmol) was added dropwise. After 3.5 h the reaction was quenched by dropwise addition of MeOH (8 mL) and the mixture left to stir at 0 ^{o}C for 15 min followed by 15 min at room temperature. The solvents were removed *in vacuo* and alcohol and ester separated via flash column chromatography using petroleum ether/ethyl acetate (90:10). The ester was saponified by heating to reflux in 2M KOH/MeOH (1 mL) for 15 min, followed by removal of the solvent *in vacuo*. The resultant residue was then passed through a short flash silica column using ethyl acetate. The enantiomeric excess for the unreacted alcohol and the alcohol obtained from ester saponification was determined by analytical HPLC. The results for (±)-1-phenylethanol are given in **Table 3.** For results pertaining to other substrates, see **Table 4.**

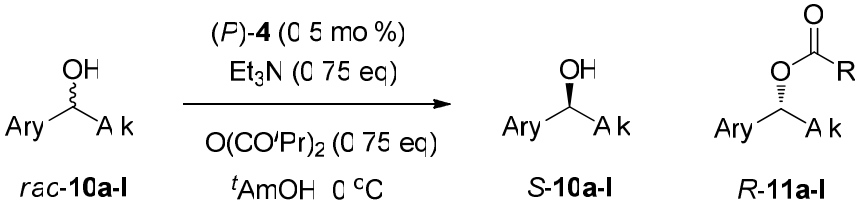
Table 3. Optimization of Kinetic Resolution using **(±)-10a**

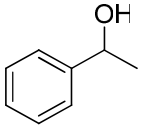
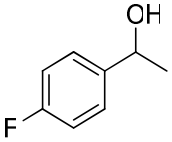
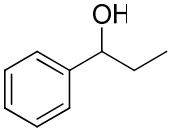


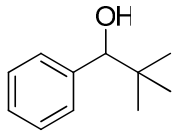
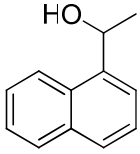
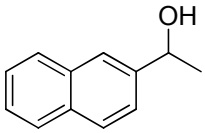
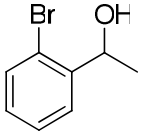
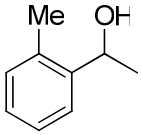
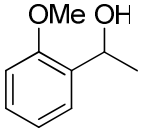
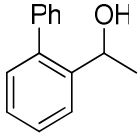
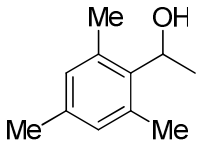
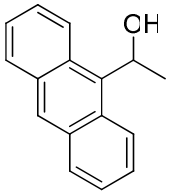
entry	solvent	base	R	T (°C)	t (h)	ee_A (%)	ee_E (%)	c (%)	S
1	THF	Et_3N	Me	0	2	7.1	48.2	14.1[a]	2.7
2	PhMe	Et_3N	Me	0	2	37.0	56.0	41.6[a]	4.4
3	Et_2O	Et_3N	Me	0	2	24.6	51.1	30.4[a]	4.5
4	PhMe	Et_3N	Me	-40	5.5	68.1	47.0	58.4[a]	5.6
5	PhMe	Et_3N	Me	-78	17	37.7	74.0	32.5[a]	11.8
6	^{t}AmOH	Et_3N	Me	0	2	48.0	46.0	45.3[a]	6
7	^{t}AmOH	Pyridine	^{i}Pr	0	4	88.0	63.1	58.2	12.4
8	^{t}AmOH	$EtN(^iPr)_2$	^{i}Pr	0	3	21.7	84.6	20.4	14.8
9	^{t}AmOH	-	^{i}Pr	0	4	66.2	78.3	45.8	16.2
10	^{t}AmOH	Et_3N	^{i}Pr	0	3	41.0	84.7	32.6	18.0
11	^{t}AmOH	Et_3N	^{i}Pr	0	4	67.4	79.9	45.8	
12	^{t}AmOH	Et_3N	^{i}Pr	-7	22.5	78.2	77.7	50.1	18.3
13	^{t}AmOH	Et_3N	^{i}Pr	-7	24	82.6	75.3	52.3	
14	^{t}AmOH/PhMe (2:3)	Et_3N	^{i}Pr	-50	24	22.3	87.2	20.4	18.1
15	^{t}AmOH/PhMe (2:3)	Et_3N	^{i}Pr	-50	25	32.0	85.9	27.1	

[a] Determined by ^{1}H NMR of crude reaction mixture

Table 4. Kinetic resolution of alcohols **10a-l**



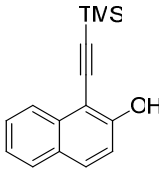
entry	substrate	#	t (h)	ee_A (%)	ee_E (%)	c (%)	s	s_{AVG}
1	 **10a**	1	3	41.0	84.7	32.6	18.0	17.2
		2	5	65.4	78.6	45.8	16.3	
2	 **10b**	1	5	57.1	81.7	41.1	17.6	18.0
		2	6	71.4	79.3	47.4	18.3	
3	 **10c**	1	5.5	56.4	85.5	39.8	22.5	23.0
		2	6.5	65.8	84.5	43.8	23.4	

4	 **10d**	1	14	67.0	86.1	43.8	26.8	26.3
		2	14.5	77.3	83.4	48.1	25.7	
5	 **10e**	1	3	68.3	88.2	43.6	32.5	32.9
		2	4	80.3	86.3	48.2	33.3	
6	 **10f**	1	6	87.1	84.3	50.8	33.1	33.1[a]
		2	7	89.5	83.4	51.8	33.1	
7	 **10g**	1	20	61.5	85.6	41.8	24.2	23.3[a]
		2	20	61.9	84.4	42.3	22.3	
8	 **10h**	1	5	58.6	89.2	39.6	31.7	32.0
		2	6	62.6	88.9	41.3	32.3	
9	 **10i**	1	24	85.6	87.7	49.4	42.1	42.9[a]
		2	24	74.5	90.2	45.2	43.6	
10	 **10j**	1	48	95.5	76.1	55.7	27.5	27.2[a]
		2	48	93.8	77.3	54.8	26.9	
11	 **10k**	1	6	52	94	35.6	54.4	53[a]
		2	7	60.7	93.2	39.4	52.8	
		3	12	74.9	91.7	45.0	51.8	
12	 **10l**	1	6	83.6	95.7	46.6	119.2	116.7[a]
		2	7	98.4	91.9	51.7	114.2	

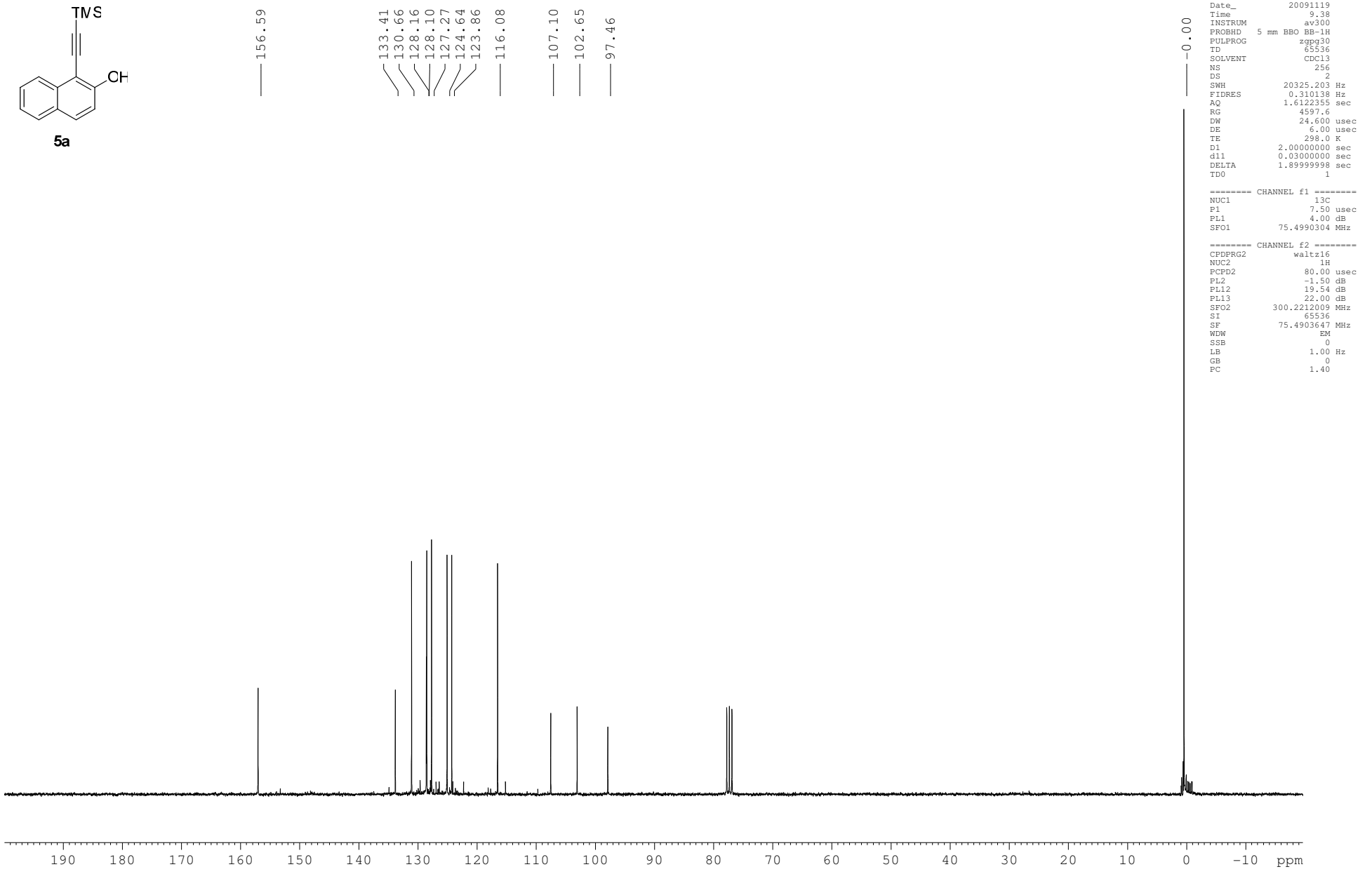
[a] Catalyst (*M*)-**4** used; *S*-**11f**, **11i-j** formed.

Preparative-scale Catalytic Kinetic Resolution of 1-(1-naphthyl) ethanol (±)-10e. A solution of catalyst (*M*)-**4** (1mg, 2.4 x 10^{-3} mmol), (±)-1-naphthyl ethanol (0.85 g, 4.936 mmol) and triethylamine (0.37 g, 3.702 mmol) in ^{t}amyl alcohol (10 mL) was cooled to 0 ^{o}C. During vigorous stirring, isobutyric anhydride (1.56 g, 9.871 mmol) was added dropwise. After 48 h the reaction was quenched by slow addition of MeOH (20 mL) and the mixture left to stir at 0 ^{o}C for 15 min followed by 15 min at room temperature. The solvents were removed *in vacuo* and alcohol and ester separated via flash column chromatography using petroleum ether/ethyl acetate (95:5) to give ester (*S*)-**11e** (715 mg) as a pale yellow oil and alcohol (*R*)-**10e** (339 mg) as a colourless oil. HPLC analysis revealed the unreacted alcohol to possess a 99.9 % ee and the ester a 65.6 % ee. This corresponded to a selectivity factor (s) of 33.7 at 60.3 % conversion.

V. NMR spectra and HPLC chromatograms



5a


TMS
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124.64
123.86
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107.10
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97.46
0.00
NAME Nov19-2009-drc
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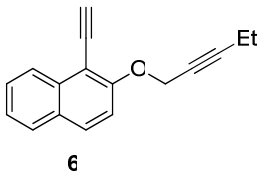
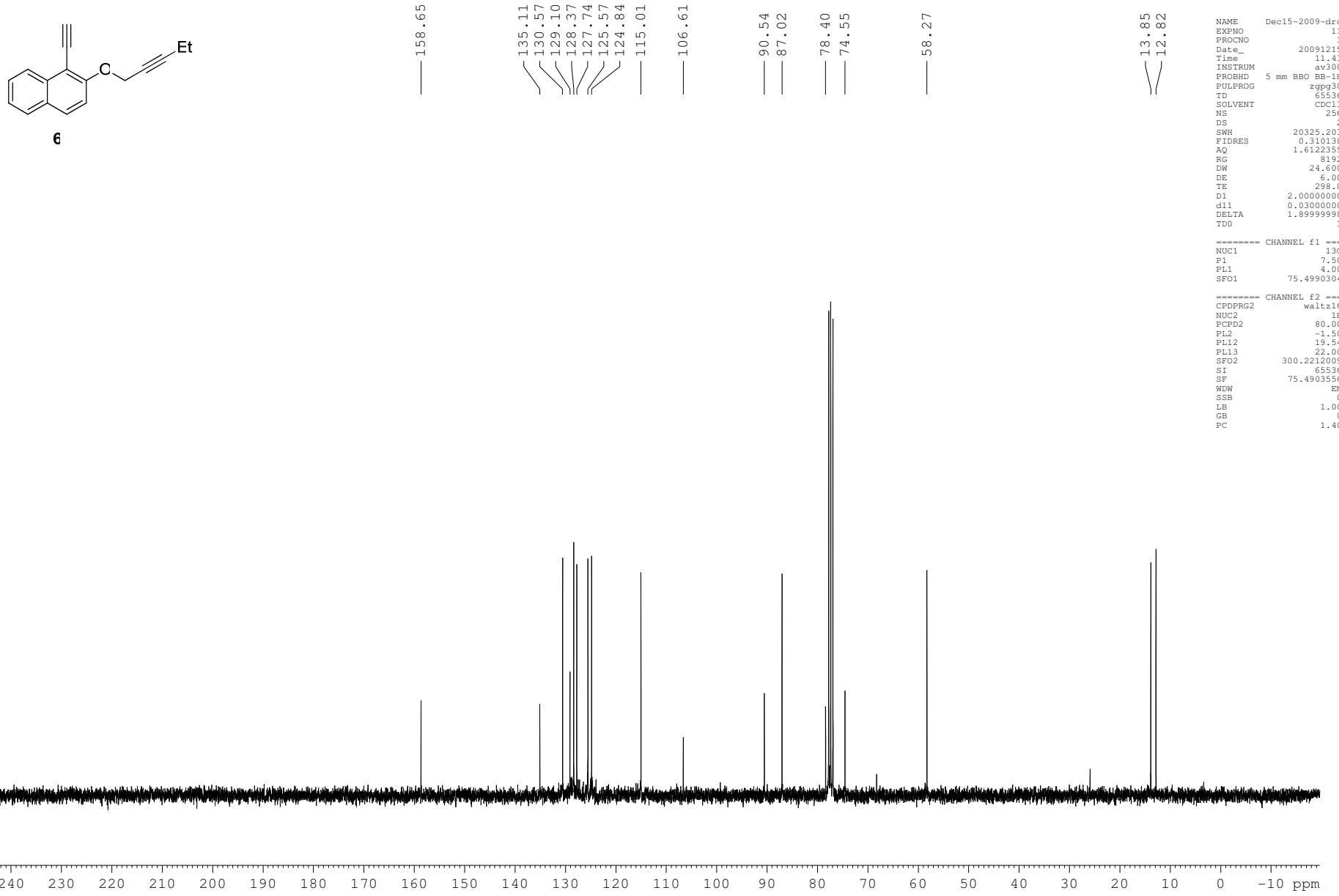
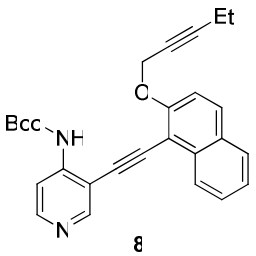
PROCNO 1
Date_ 20091119
Time 9.38
INSTRUM av300
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 2
SWH 20325.203 Hz
FIDRES 0.310138 Hz
AQ 1.6122355 sec
RG 4597.6
DW 24.600 usec
DE 6.00 usec
TE 298.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.50 usec
PL1 4.00 dB
SFO1 75.4990304 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.50 dB
PL12 19.54 dB
PL13 22.00 dB
SFO2 300.2212009 MHz
SI 65536
SF 75.4903647 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm


Et
C

6

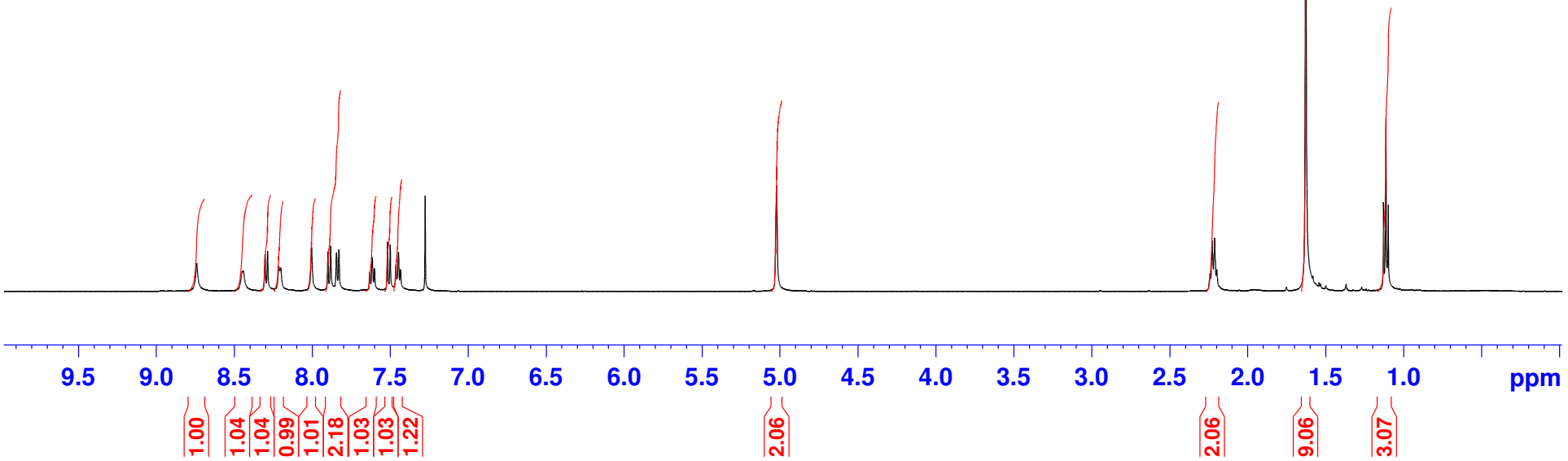
NAME Dec15-2009-drc
EXPNO 10
PROCNO 1
Date_ 20091215
Time 11.25
INSTRUM av300
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 181
DW 81.000 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.10 usec
PL1 -1.50 dB
SFO1 300.2218540 MHz
SI 32768
SF 300.2200025 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 ppm
1.00
2.03
1.00
2.01
1.98
1.05
2.08
2.98

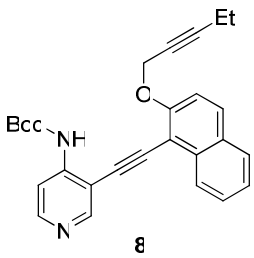

Et
O
6
158.65
135.11
130.57
129.10
128.37
127.74
125.57
124.84
115.01
106.61
90.54
87.02
78.40
74.55
58.27
13.85
12.82
NAME Dec15-2009-drc
EXPNO 11
PROCNO 1
Date_ 20091215
Time 11.43
INSTRUM av300
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 256
DS 2
SWH 20325.203 Hz
FIDRES 0.310138 Hz
AQ 1.6122355 sec
RG 8192
DW 24.600 usec
DE 6.00 usec
TE 298.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.50 usec
PL1 4.00 dB
SFO1 75.4990304 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.50 dB
PL12 19.54 dB
PL13 22.00 dB
SFO2 300.2212009 MHz
SI 65536
SF 75.4903556 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm



8

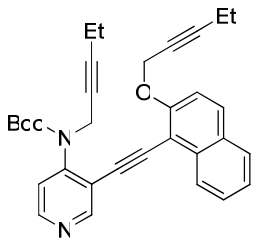
```
NAME            mrc_444
EXPNO                 1
PROCNO                1
Date_          20100611
Time              13.08
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    0
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ            3.1719923 sec
RG                 90.5
DW               48.400 usec
DE                6.00 usec
TE               298.0 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                9.50 usec
PL1              -1.00 dB
SFO1        500.1330885 MHz
SI                32768
SF          500.1300000 MHz
WDW                  no
SSB                   0
LB                0.00 Hz
GB                    0
PC                 1.00
```





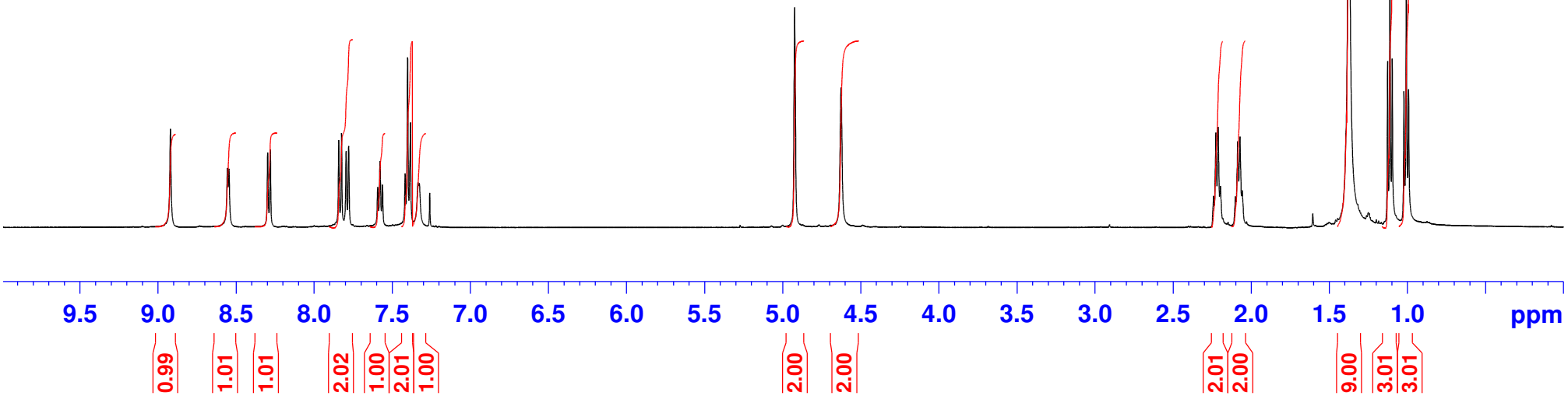
8

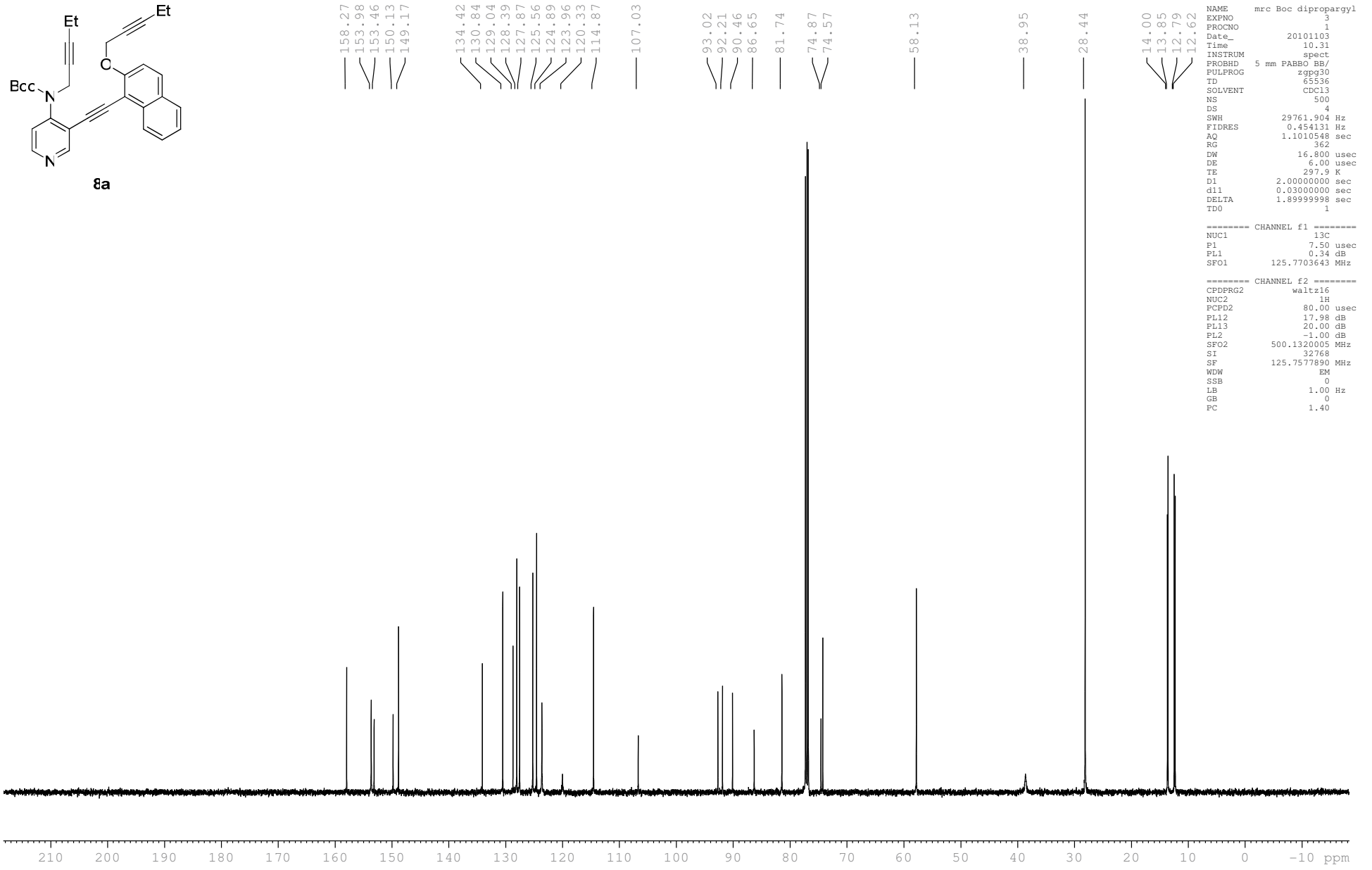

```
NAME      Jun10-2010-drc
EXPNO                 31
PROCNO                 1
Date_           20100611
Time                1.01
INSTRUM          av300
PROBHD   5 mm BBO BB-1H
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                  256
DS                    2
SWH           20325.203 Hz
FIDRES        0.310138 Hz
AQ            1.6122355 sec
RG              18390.4
DW               24.600 usec
DE                6.00 usec
TE               298.0 K
D1          2.00000000 sec
d11         0.03000000 sec
DELTA       1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 7.50 usec
PL1                4.00 dB
SFO1        75.4990304 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2             80.00 usec
PL2               -1.50 dB
PL12              19.54 dB
PL13              22.00 dB
SFO2       300.2212009 MHz
SI                65536
SF          75.4903623 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

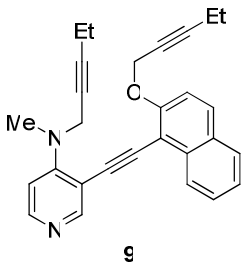


8a

```
NAME        mrc Boc dipropargyl
EXPNO                         2
PROCNO                        1
Date_                  20101103
Time                       9.58
INSTRUM                   spect
PROBHD    5 mm PABBO BB/
PULPROG                    zg30
TD                        65536
SOLVENT                   CDCl3
NS                           16
DS                            0
SWH                   10330.578 Hz
FIDRES                0.157632 Hz
AQ                    3.1719923 sec
RG                           64
DW                       48.400 usec
DE                        6.00 usec
TE                       298.0 K
D1                  1.00000000 sec
TD0                           1

======== CHANNEL f1 ========
NUC1                         1H
P1                        9.50 usec
PL1                      -1.00 dB
SFO1               500.1330885 MHz
SI                        32768
SF                 500.1300085 MHz
WDW                          no
SSB                           0
LB                        0.00 Hz
GB                            0
PC                         1.00
```

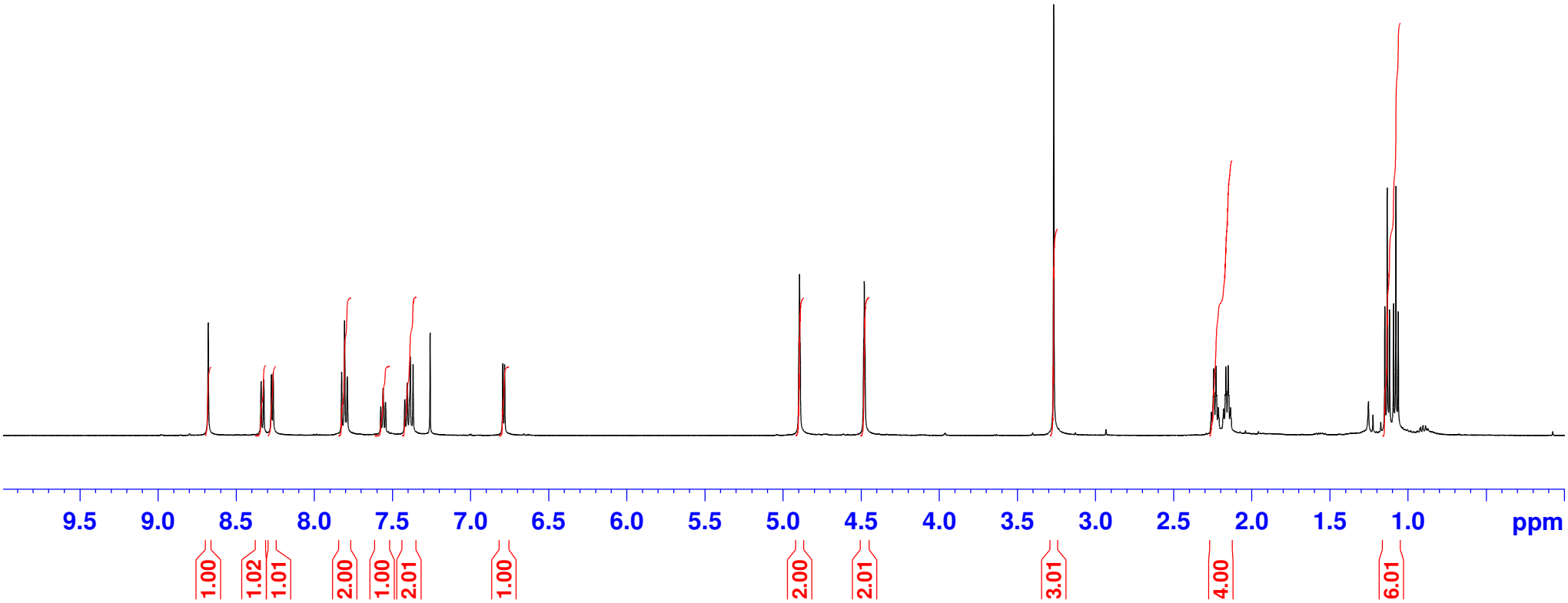


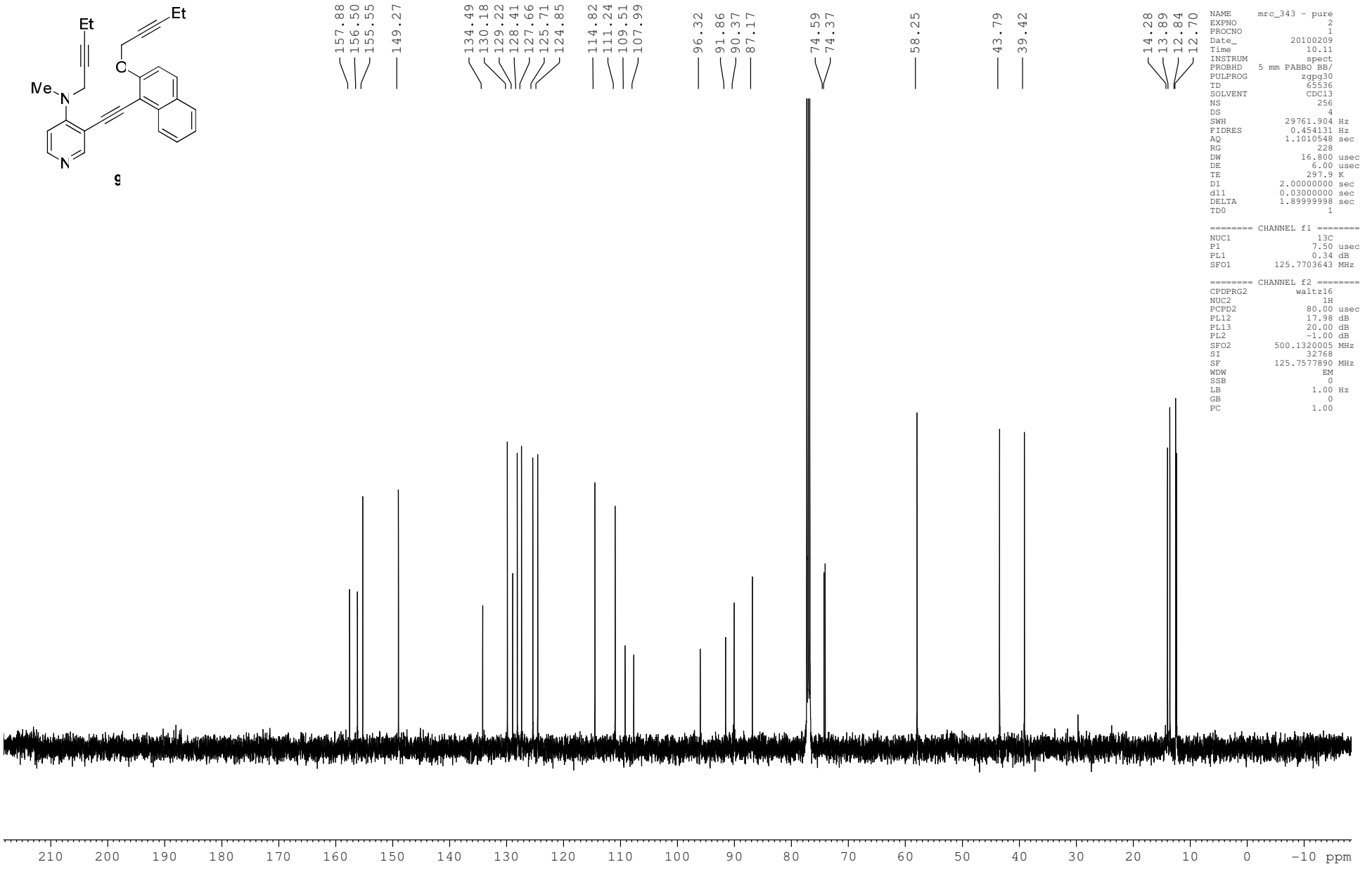

Et
Et
O
Bcc
N
N
8a
158.27
153.98
153.46
150.13
149.17
134.42
130.84
129.04
128.39
127.87
125.56
124.89
123.96
120.33
114.87
107.03
93.02
92.21
90.46
86.65
81.74
74.87
74.57
58.13
38.95
28.44
14.00
13.85
12.79
12.62
NAME mrc Boc dipropargyl
EXPNO 3
PROCNO 1
Date_ 20101103
Time 10.31
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 500
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 362
DW 16.800 usec
DE 6.00 usec
TE 297.9 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.50 usec
PL1 0.34 dB
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL12 17.98 dB
PL13 20.00 dB
PL2 -1.00 dB
SFO2 500.1320005 MHz
SI 32768
SF 125.7577890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

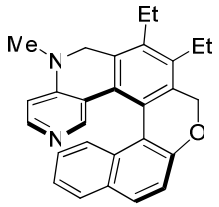


9

```
NAME      mrc_343 - pure
EXPNO                  1
PROCNO                 1
Date_           20100209
Time                9.51
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ            3.1719923 sec
RG                   144
DW                48.400 usec
DE                 6.00 usec
TE                298.0 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                  9.50 usec
PL1                -1.00 dB
SFO1        500.1330885 MHz
SI                 32768
SF          500.1300079 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.40
```

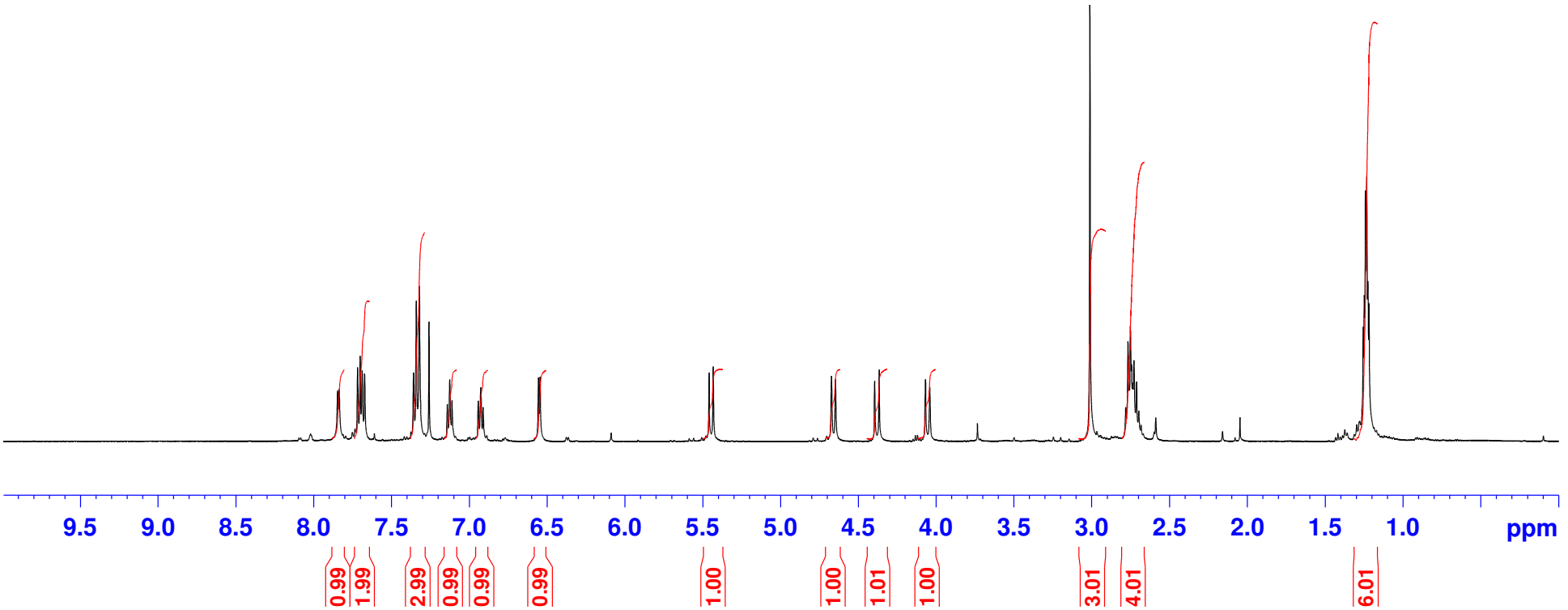


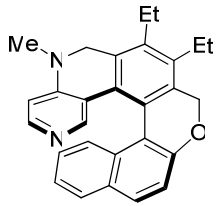

Et
Et
Me
N
O
N
9
157.88
156.50
155.55
149.27
134.49
130.18
129.22
128.41
127.66
125.71
124.85
114.82
111.24
109.51
107.99
96.32
91.86
90.37
87.17
74.59
74.37
58.25
43.79
39.42
14.28
13.89
12.84
12.70
NAME mrc_343 - pure
EXPNO 2
PROCNO 1
Date_ 20100209
Time 10.11
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 228
DW 16.800 usec
DE 6.00 usec
TE 297.9 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.50 usec
PL1 0.34 dB
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL12 17.98 dB
PL13 20.00 dB
PL2 -1.00 dB
SFO2 500.1320005 MHz
SI 32768
SF 125.7577890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm



4

```
NAME            MRC 444
EXPNO                 1
PROCNO                1
Date_          20100615
Time              12.08
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    0
SWH           10330.578 Hz
FIDRES        0.157632 Hz
AQ            3.1719923 sec
RG                 50.8
DW               48.400 usec
DE                6.00 usec
TE               298.0 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.50 usec
PL1               -1.00 dB
SFO1        500.1330885 MHz
SI                32768
SF          500.1300088 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00
```





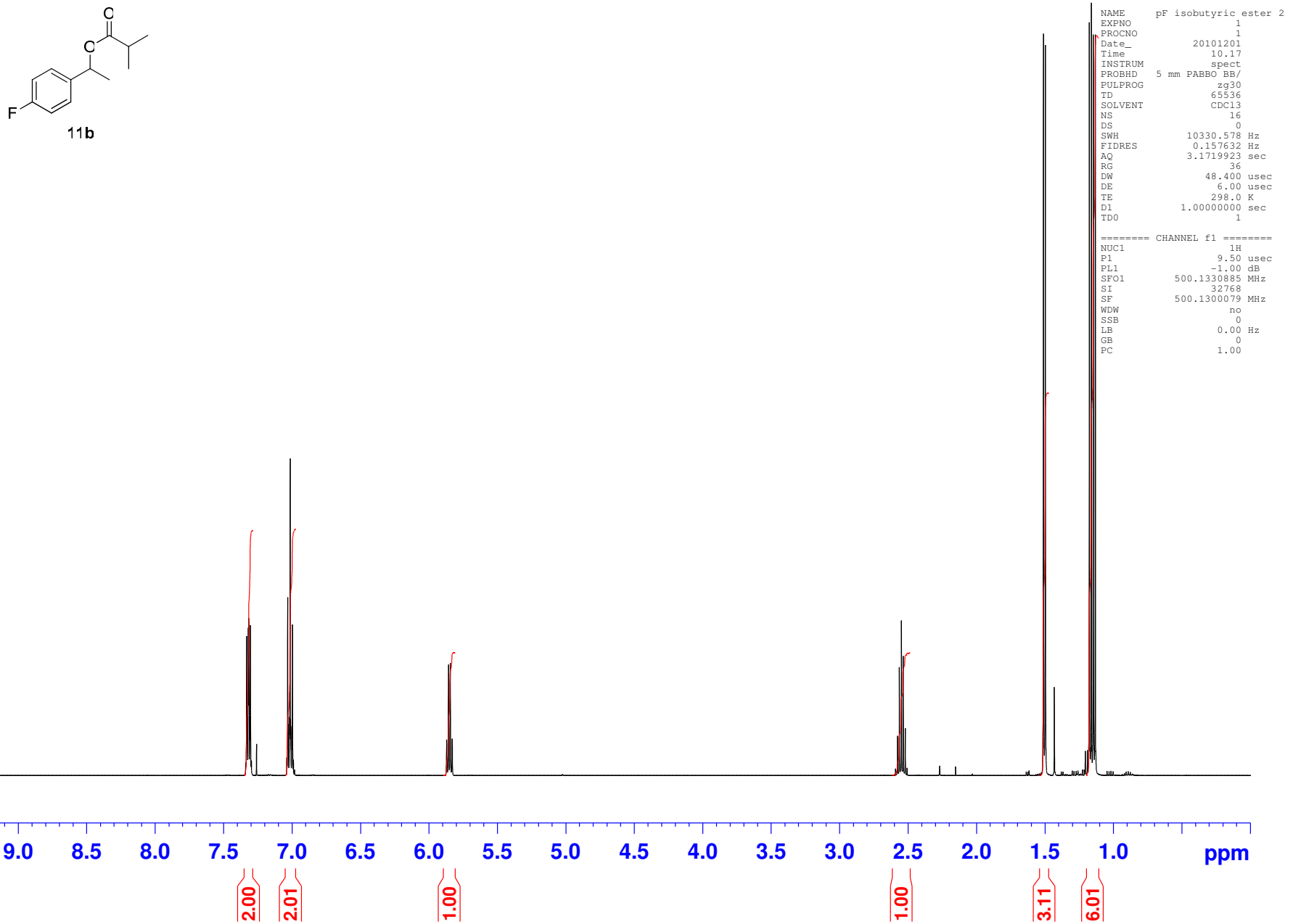
4

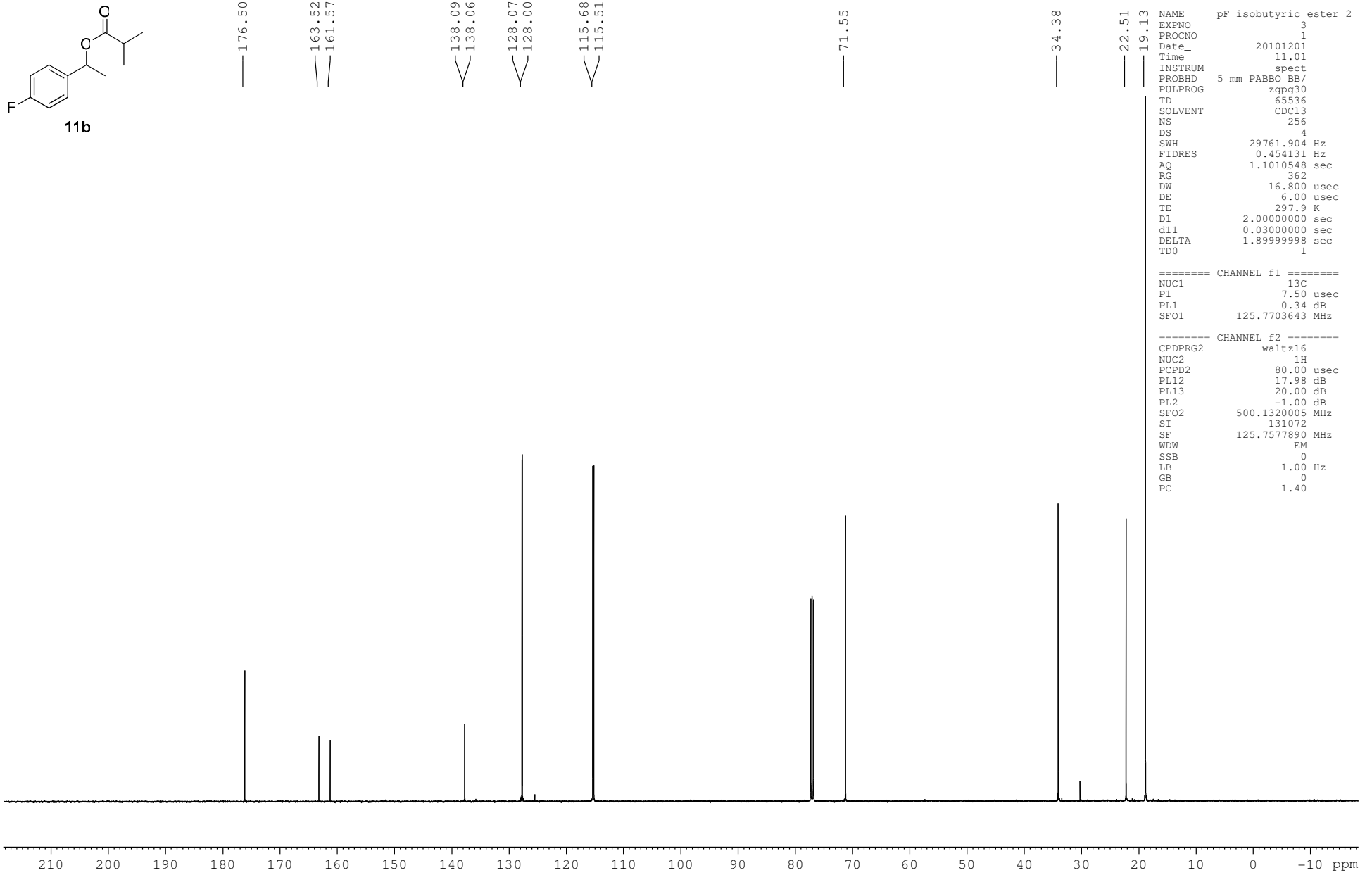
155.84
153.17
148.17
148.06
136.64
136.56
136.27
136.05
130.56
130.34
129.21
128.57
125.70
125.47
124.38
123.84
120.56
119.23
118.32
107.06

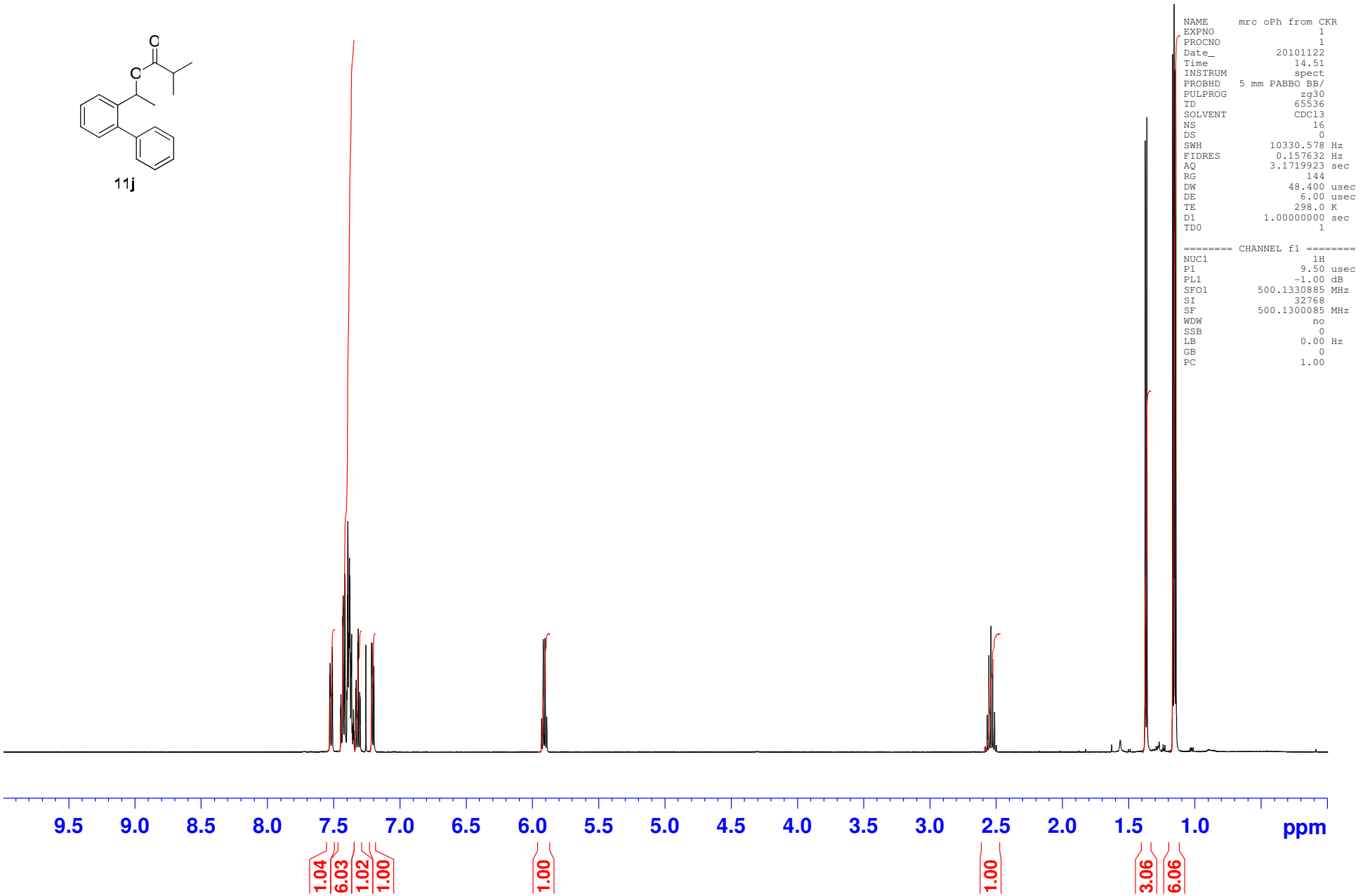
77.56
67.70
52.81
38.34
22.12
21.94
15.70
15.05

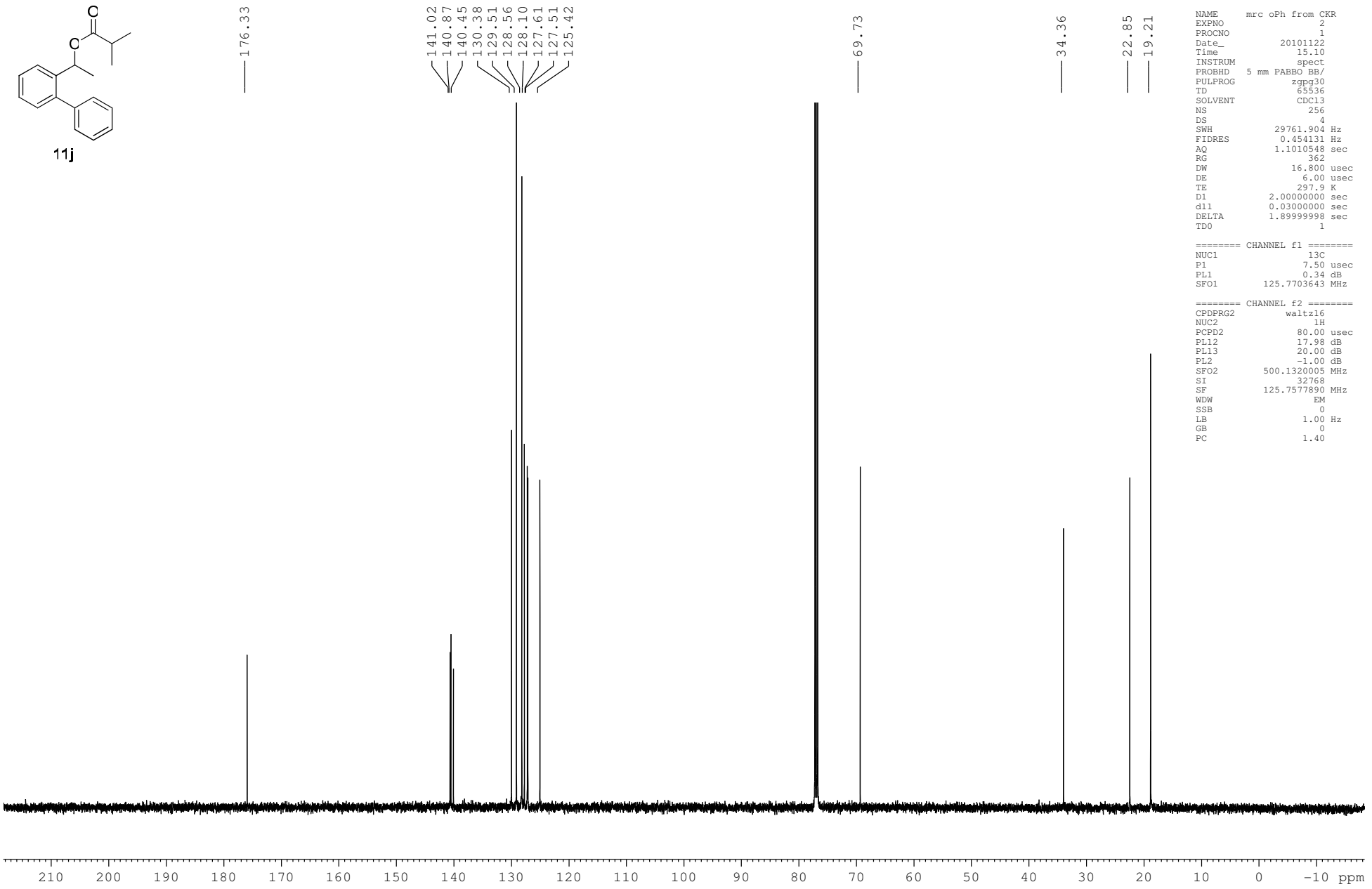
NAME	MRC 444
EXPNO	4
PROCNO	1
Date_	20100615
Time	13.12
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	300
DS	4
SWH	29761.904 Hz
FIDRES	0.454131 Hz
AQ	1.1010548 sec
RG	645
DW	16.800 usec
DE	6.00 usec
TE	297.9 K
D1	2.00000000 sec
d11	0.03000000 sec
DELTA	1.89999998 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	7.50 usec
PL1	0.34 dB
SFO1	125.7703643 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL12	17.98 dB
PL13	20.00 dB
PL2	-1.00 dB
SFO2	500.1320005 MHz
SI	32768
SF	125.7577890 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.40

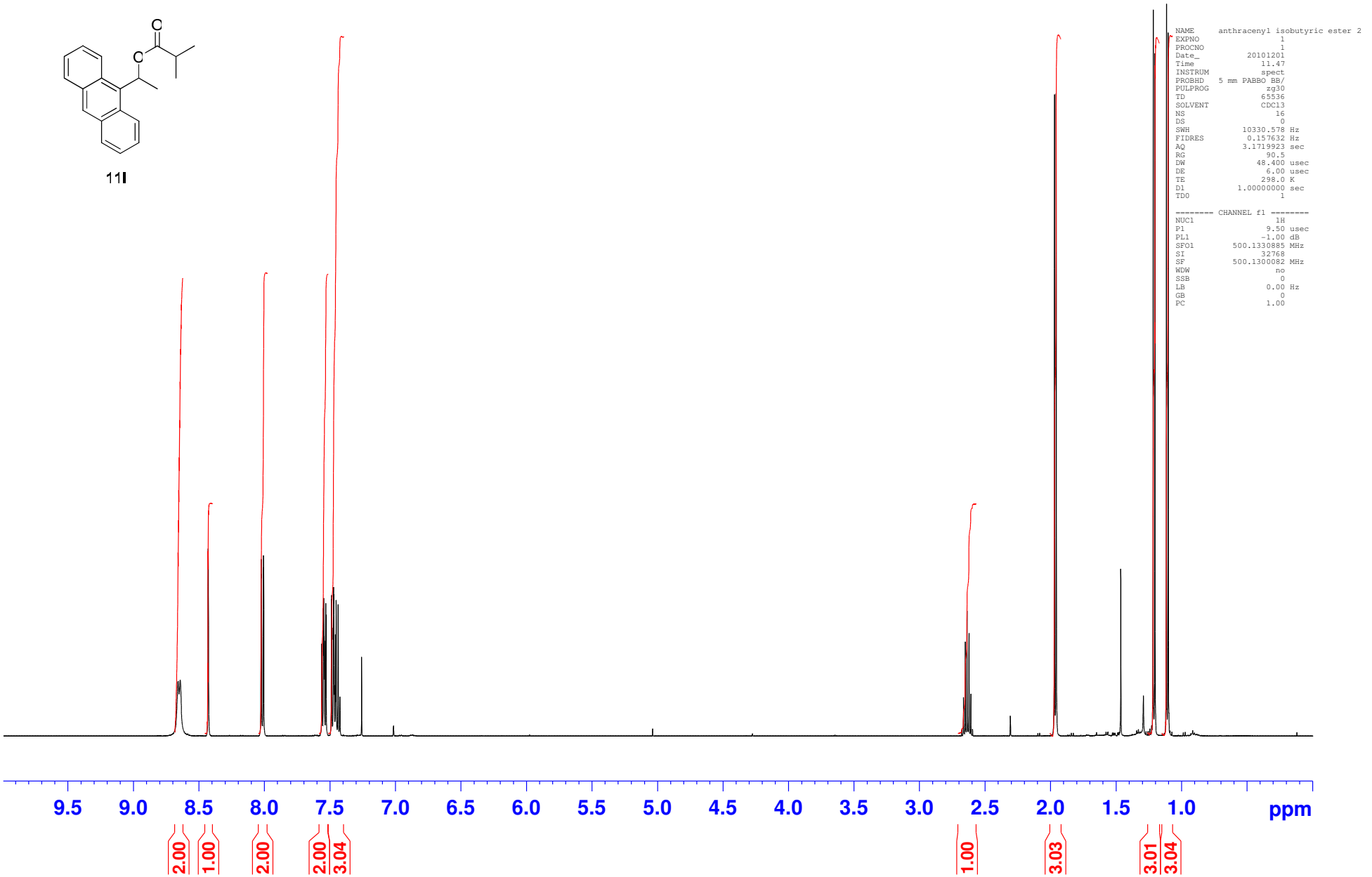
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

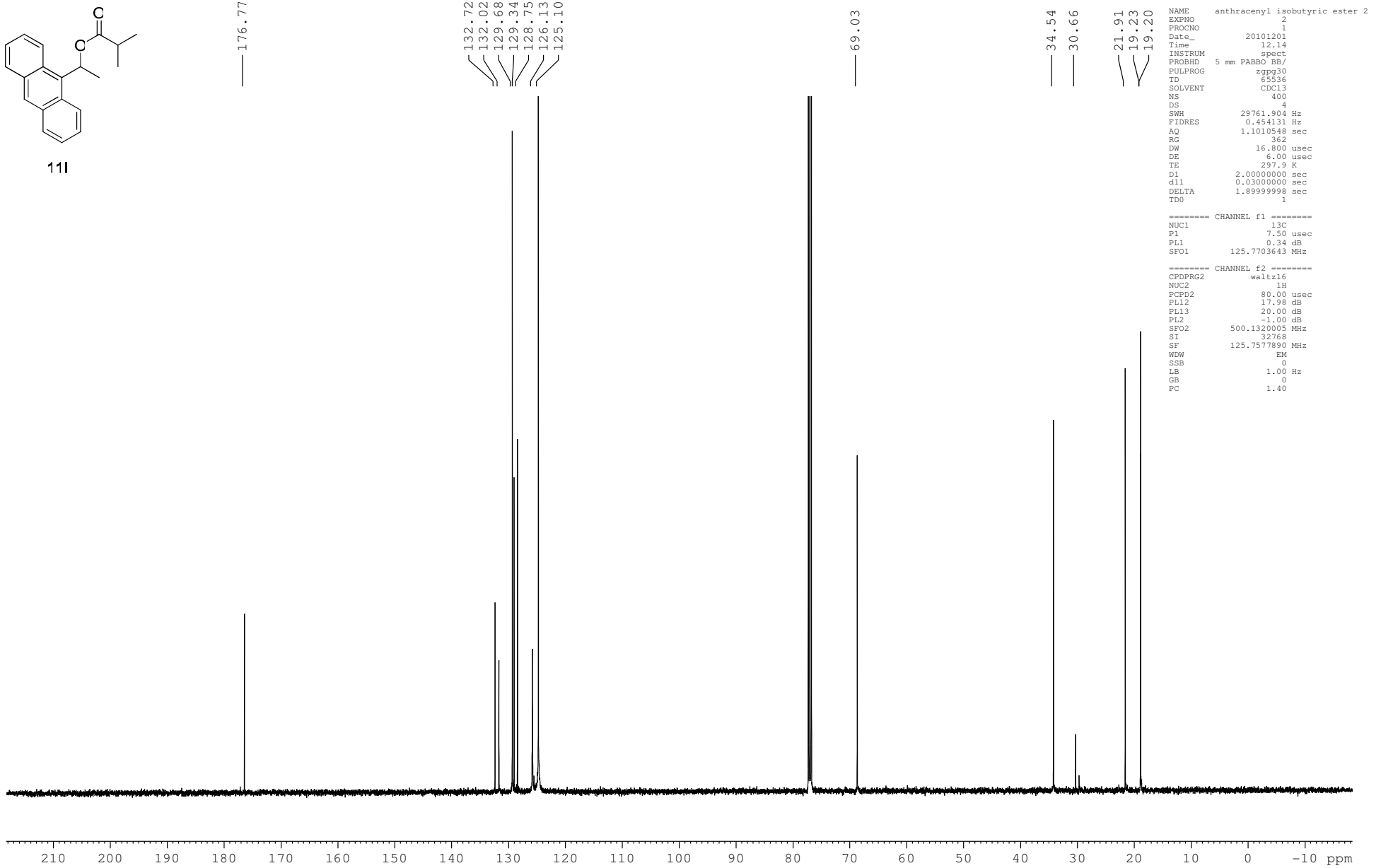

11b
NAME pF isobutyric ester 2
EXPNO 1
PROCNO 1
Date_ 20101201
Time 10.17
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 36
DW 48.400 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PL1 -1.00 dB
SFO1 500.1330885 MHz
SI 32768
SF 500.1300079 MHz
WDW no
SSB 0
LB 0.00 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 ppm
2.00
2.01
1.00
1.00
3.11
6.01

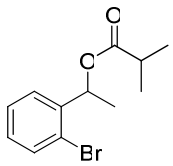

11b
176.50
163.52
161.57
138.09
138.06
128.07
128.00
115.68
115.51
71.55
34.38
22.51
19.13
NAME pF isobutyric ester 2
EXPNO 3
PROCNO 1
Date_ 20101201
Time 11.01
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 256
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 362
DW 16.800 usec
DE 6.00 usec
TE 297.9 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.50 usec
PL1 0.34 dB
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL12 17.98 dB
PL13 20.00 dB
PL2 -1.00 dB
SFO2 500.1320005 MHz
SI 131072
SF 125.7577890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm


11j
NAME mrc oPh from CKR
EXPNO 1
PROCNO 1
Date_ 20101122
Time 14.51
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 144
DW 48.400 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PL1 -1.00 dB
SFO1 500.1330885 MHz
SI 32768
SF 500.1300085 MHz
WDW no
SSB 0
LB 0.00 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 ppm
1.04 6.03 1.02 1.00 1.00 1.00 3.06 6.06


11j
176.33
141.02
140.87
140.45
130.38
129.51
128.56
128.10
127.61
127.51
125.42
69.73
34.36
22.85
19.21
NAME mrc oPh from CKR
EXPNO 2
PROCNO 1
Date_ 20101122
Time 15.10
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 362
DW 16.800 usec
DE 6.00 usec
TE 297.9 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.50 usec
PL1 0.34 dB
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL12 17.98 dB
PL13 20.00 dB
PL2 -1.00 dB
SFO2 500.1320005 MHz
SI 32768
SF 125.7577890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

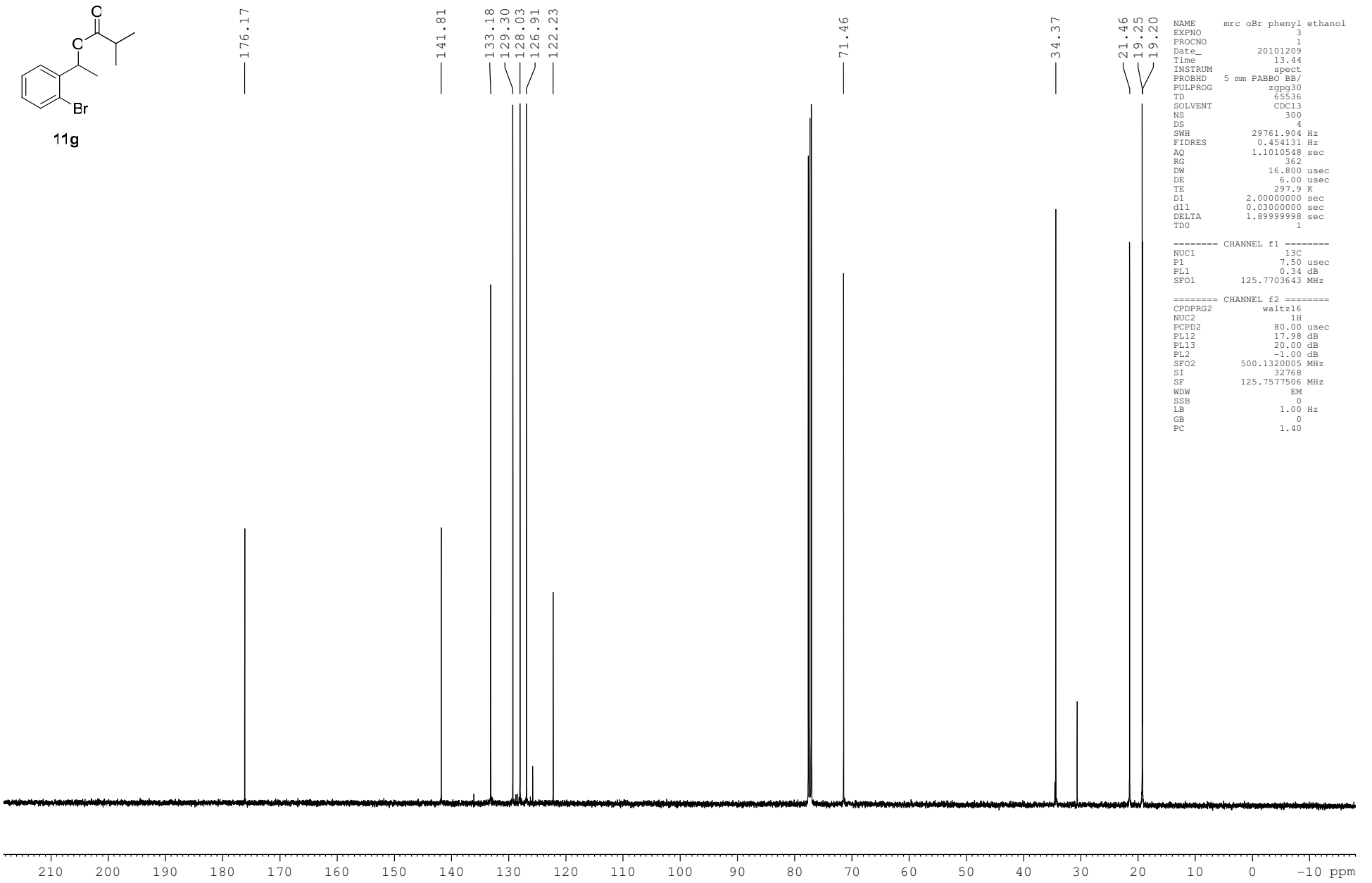

11l
NAME anthracenyl isobutyric ester 2
EXPNO 1
PROCNO 1
Date_ 20101201
Time 11.47
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 90.5
DW 48.400 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PL1 -1.00 dB
SFO1 500.1330885 MHz
SI 32768
SF 500.1300082 MHz
WDW no
SSB 0
LB 0.00 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 ppm
2.00 1.00 2.00 2.00 3.04 1.00 3.03 3.01 3.04


11l
176.77
132.72
132.02
129.68
129.34
128.75
126.13
125.10
69.03
34.54
30.66
21.91
19.23
19.20
NAME anthracenyl isobutyric ester 2
EXPNO 2
PROCNO 1
Date_ 20101201
Time 12.14
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 400
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 362
DW 16.800 usec
DE 6.00 usec
TE 297.9 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.50 usec
PL1 0.34 dB
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL12 17.98 dB
PL13 20.00 dB
PL2 -1.00 dB
SFO2 500.1320005 MHz
SI 32768
SF 125.7577890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

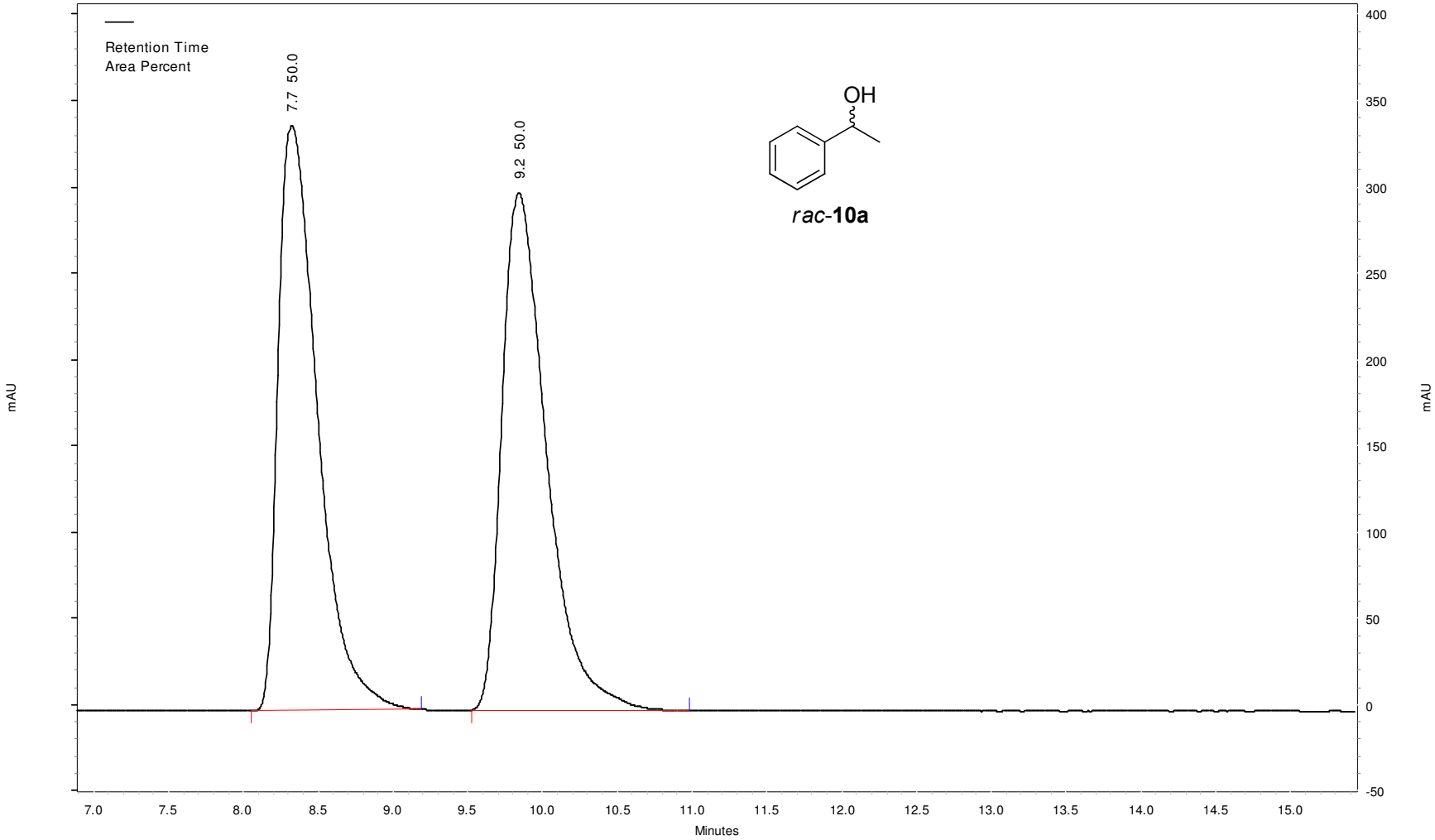

O
O
Br

11g

NAME mrc oBr phenyl ethanol
EXPNO 2
PROCNO 1
Date_ 20101209
Time 13.22
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 50.8
DW 48.400 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PL1 -1.00 dB
SFO1 500.1330885 MHz
SI 32768
SF 500.1300082 MHz
WDW no
SSB 0
LB 0.00 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 ppm
0.99
1.02
1.06
1.02
1.00
1.01
3.02
6.02


O
O
Br
11g
176.17
141.81
133.18
129.30
128.03
126.91
122.23
71.46
34.37
21.46
19.25
19.20
NAME mrc oBr phenyl ethanol
EXPNO 3
PROCNO 1
Date_ 20101209
Time 13.44
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 300
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 362
DW 16.800 usec
DE 6.00 usec
TE 297.9 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.50 usec
PL1 0.34 dB
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL12 17.98 dB
PL13 20.00 dB
PL2 -1.00 dB
SFO2 500.1320005 MHz
SI 32768
SF 125.7577506 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

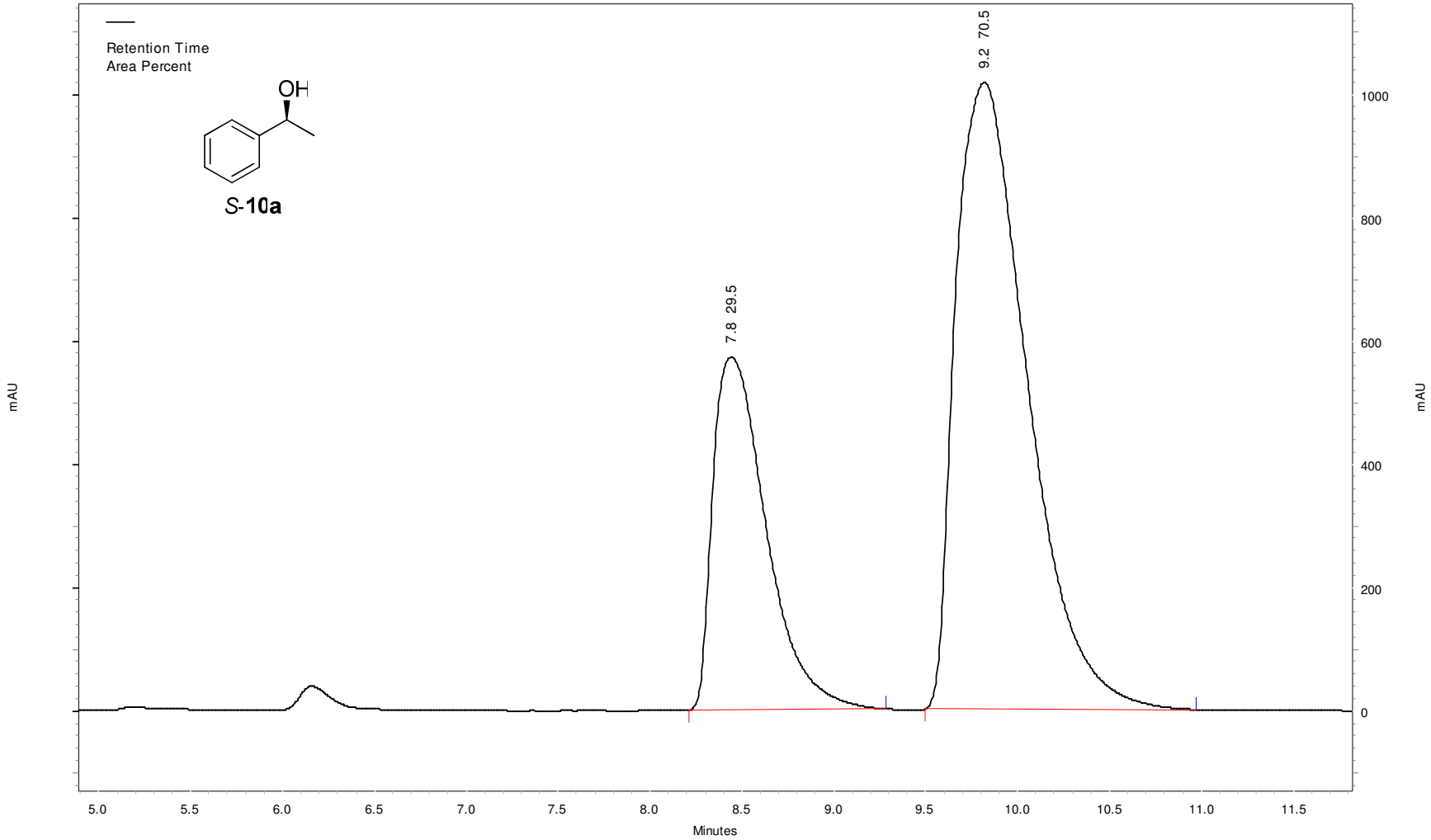
1-phenyl ethanol (±) 10a entry 1, # 1



VWD 1 Results

Retention Time	Area	Area %	Height	Height %
7.721	6208400	50.00	338987	53.08
9.242	6208749	50.00	299634	46.92

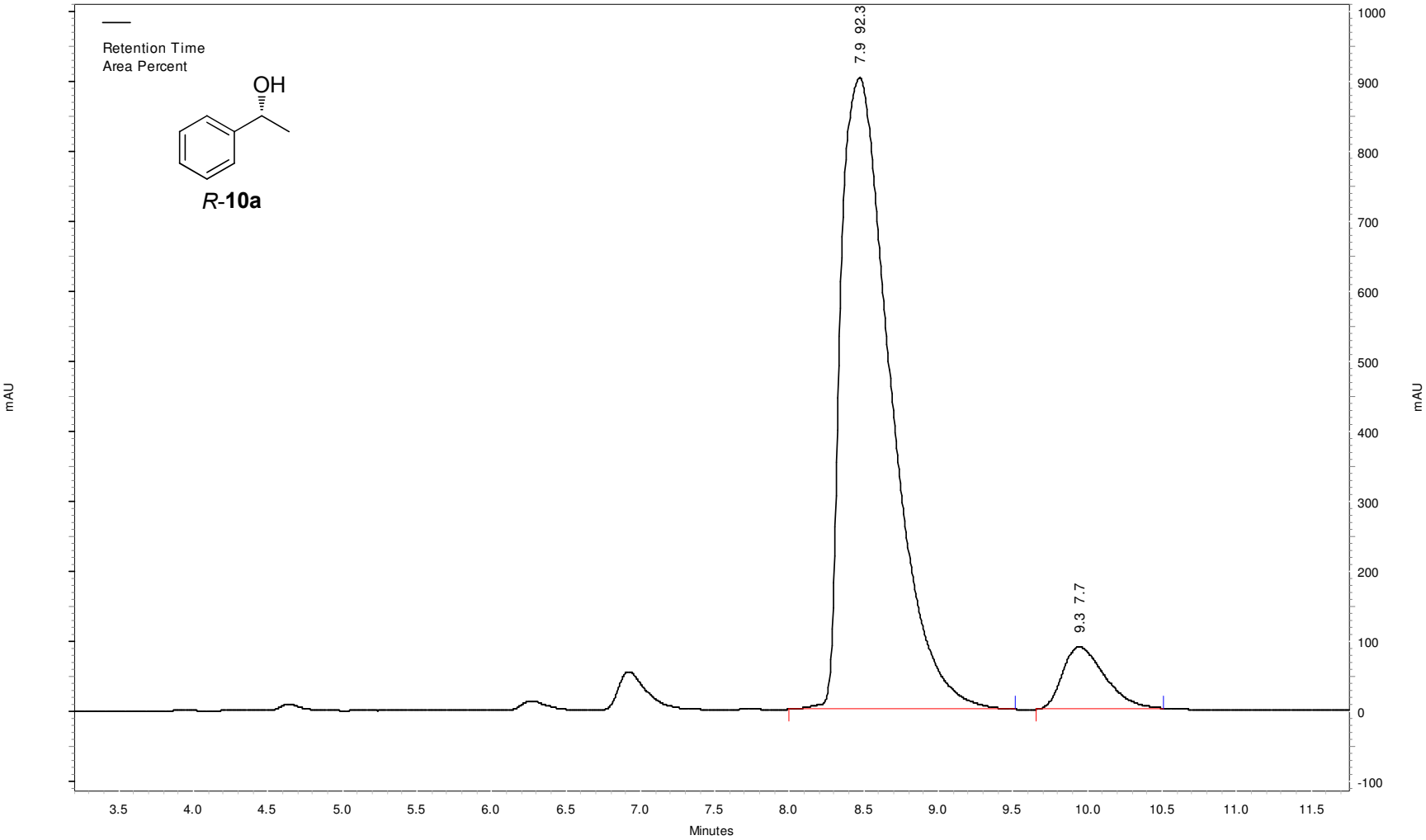
Totals	12417149	100.00	638621	100.00



VWD 1 Results

Retention Time	Area	Area %	Height	Height %
7.843	11587770	29.52	571938	36.00
9.218	27662696	70.48	1016939	64.00

Totals	39250466	100.00	1588877	100.00

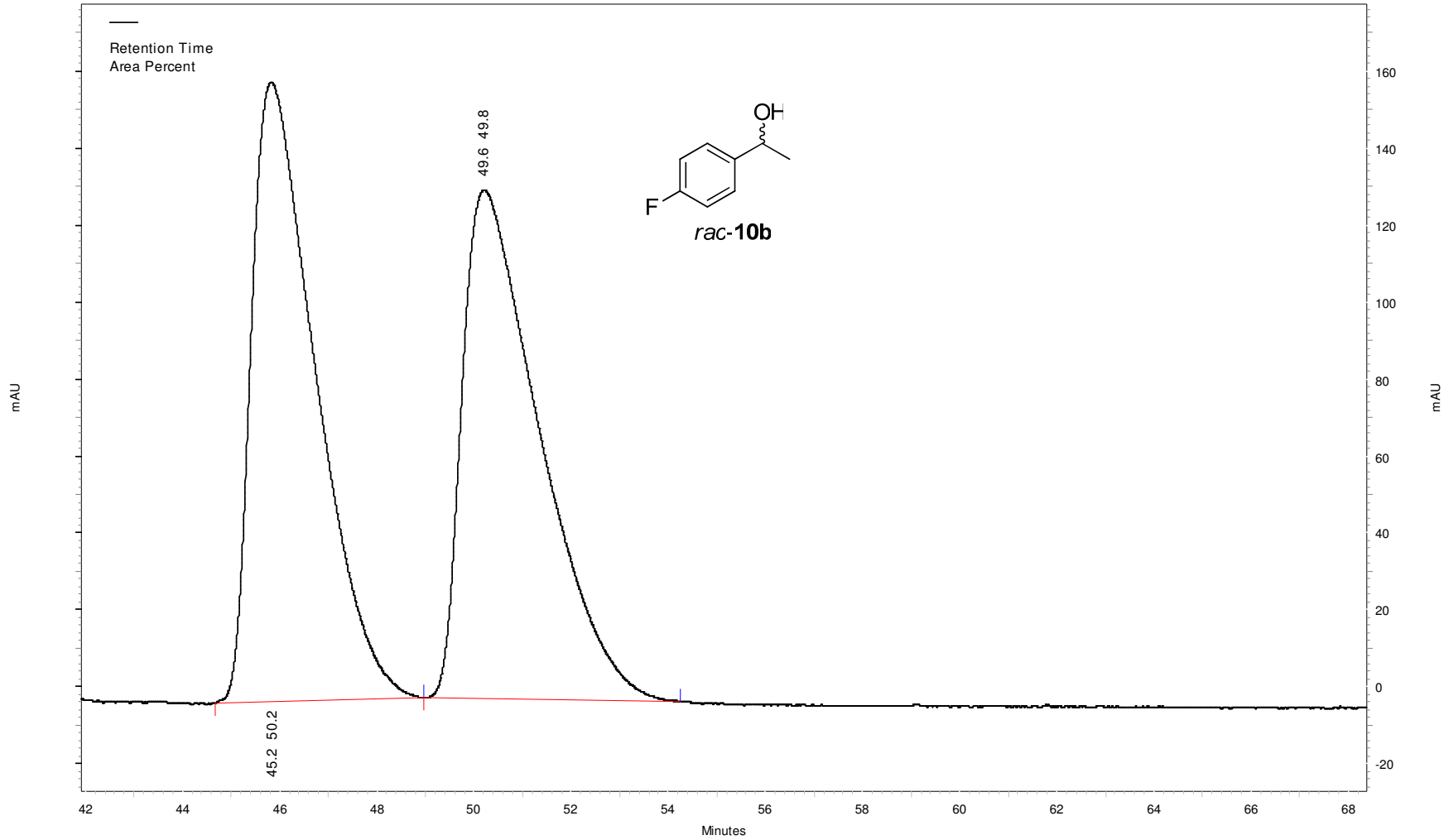


VWD 1 Results

Retention Time	Area	Area %	Height	Height %
7.872	20936446	92.34	902154	91.04
9.344	1736518	7.66	88818	8.96

Totals	22672964	100.00	990972	100.00

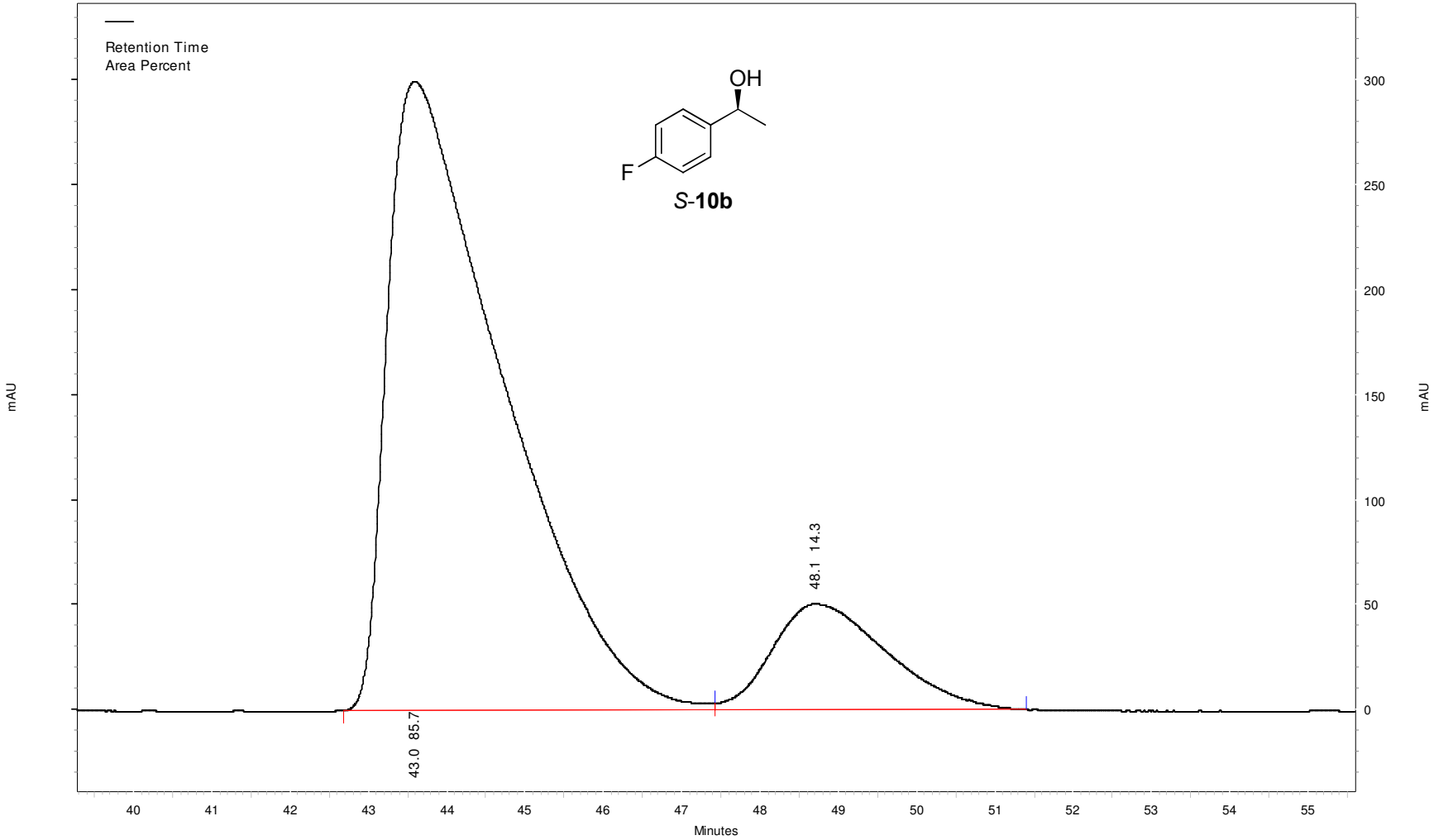
1-(4-Fluorophenyl)ethanol (±) 10b entry 2, # 2



VWD 1 Results

Retention Time	Area	Area %	Height	Height %
45.228	14738921	50.21	161016	54.90
49.597	14615407	49.79	132255	45.10

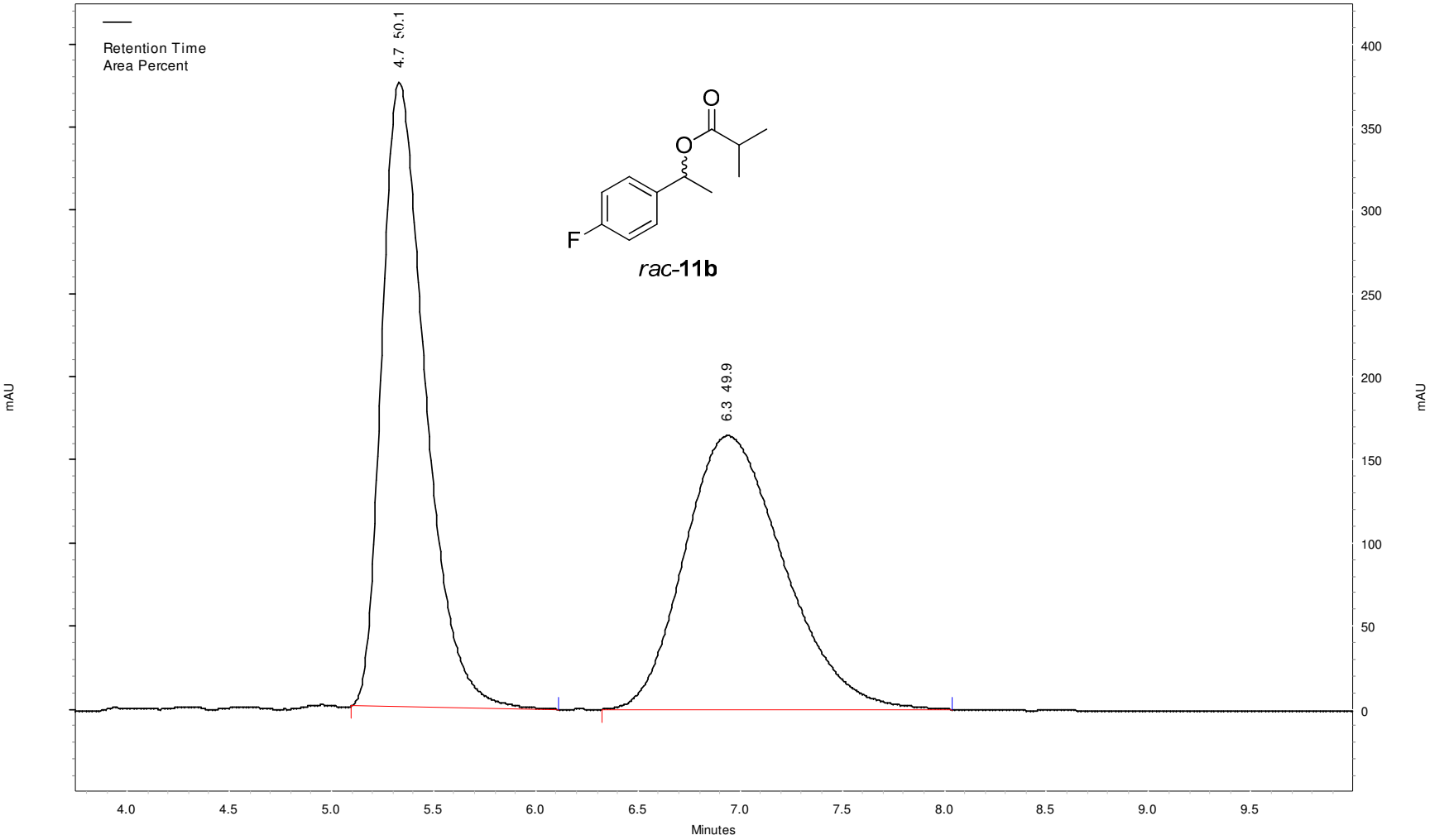
Totals	29354328	100.00	293271	100.00



VWD 1 Results

Retention Time	Area	Area %	Height	Height %
42.983	30788538	85.71	299714	85.60
48.105	5132335	14.29	50417	14.40

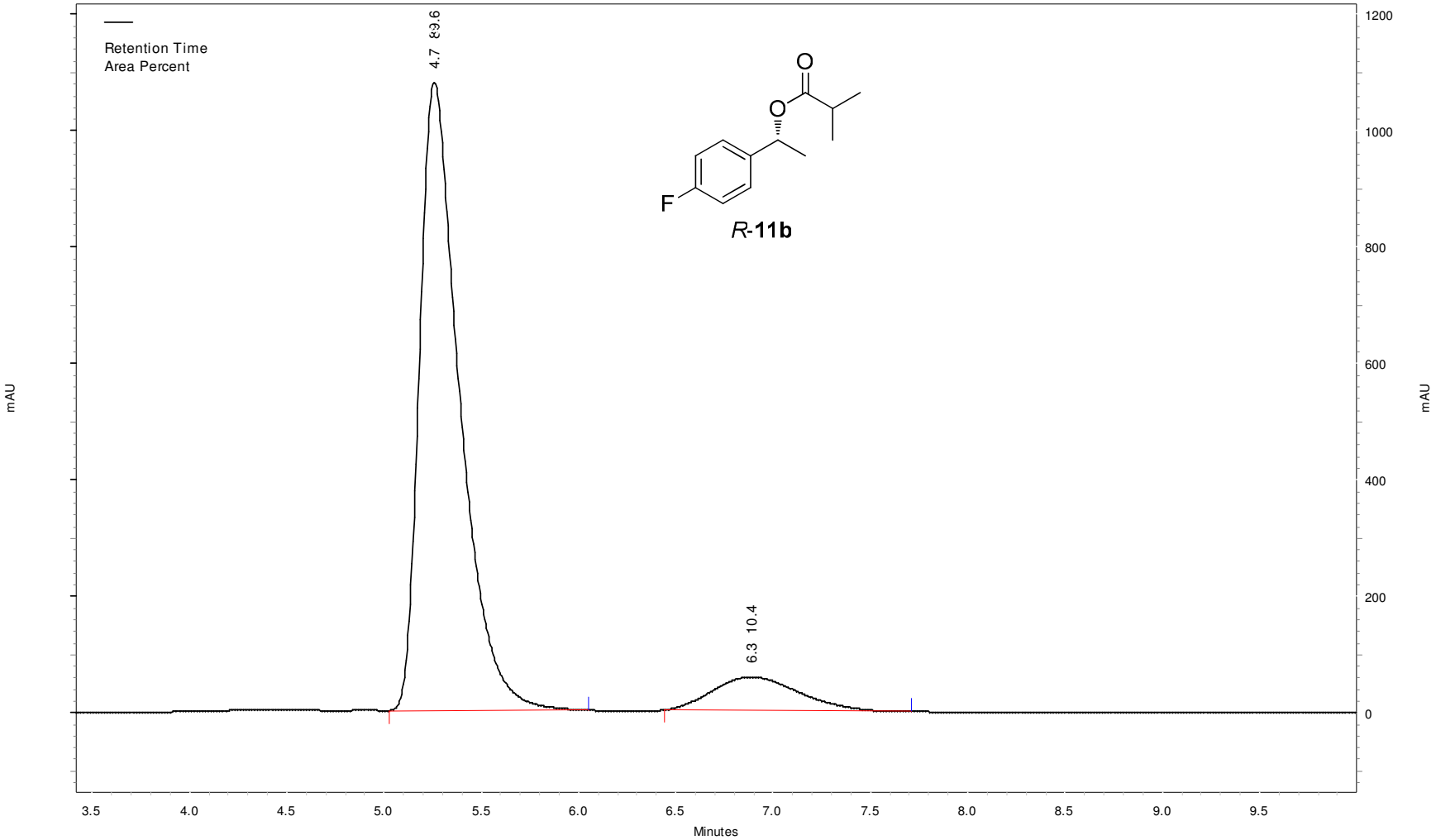
Totals	35920873	100.00	350131	100.00



VWD 1 Results

Retention Time	Area	Area %	Height	Height %
4.733	5577771	50.08	375679	69.56
6.336	5559937	49.92	164390	30.44

Totals	11137708	100.00	540069	100.00

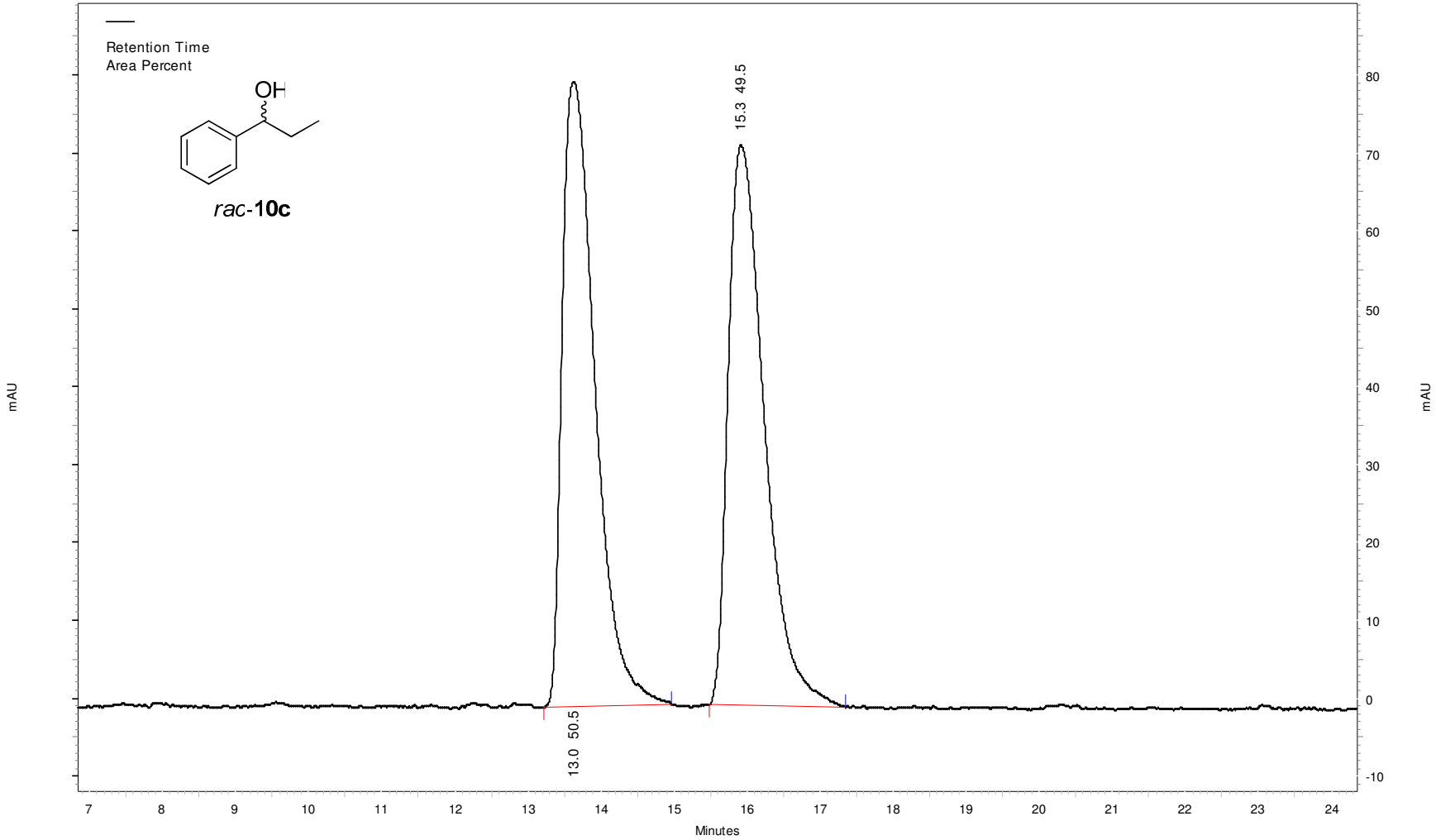


VWD 1 Results

Retention Time	Area	Area %	Height	Height %
4.660	15486522	89.63	1079487	94.90
6.288	1790929	10.37	57980	5.10

Totals	17277451	100.00	1137467	100.00

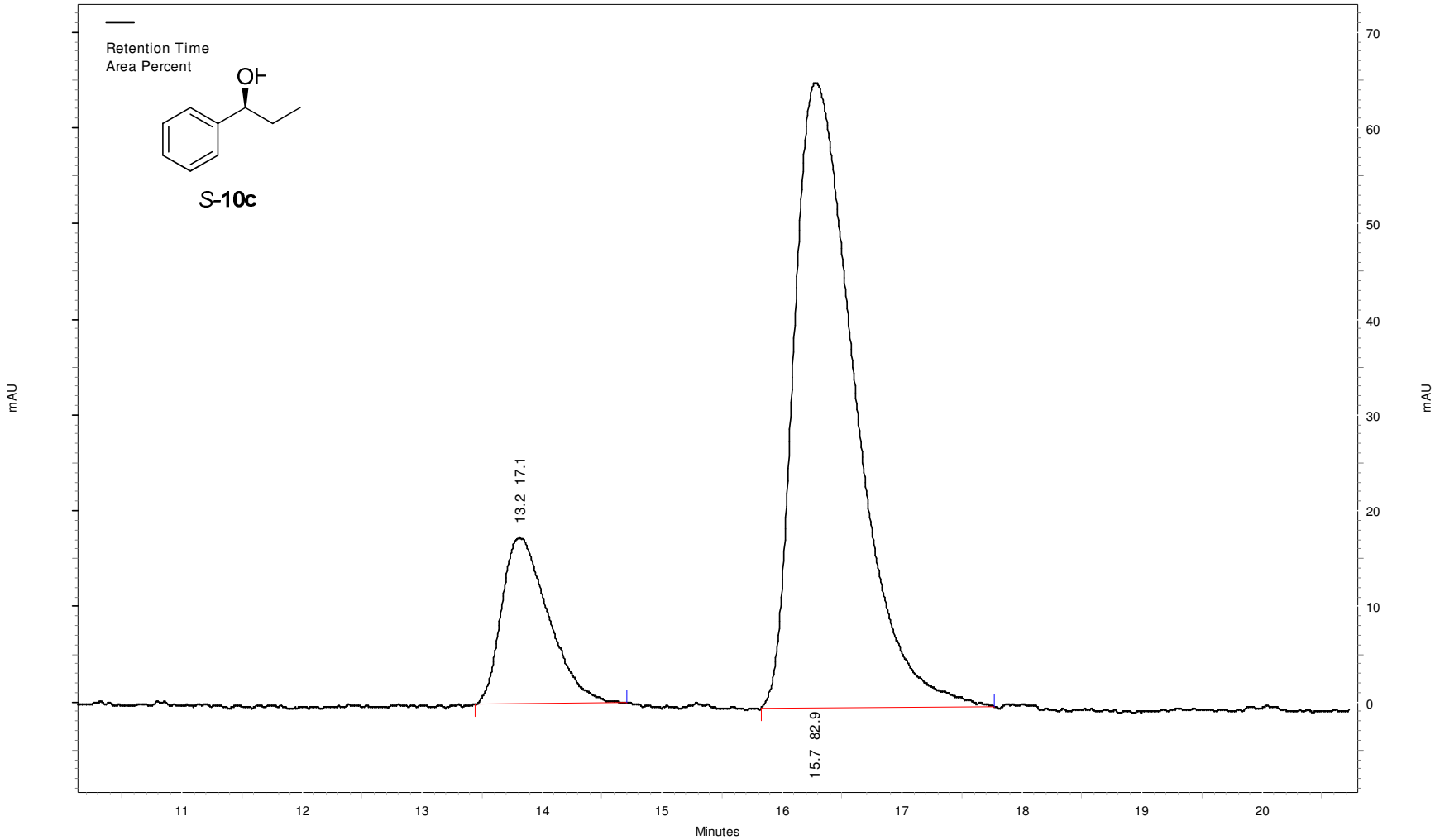
1-phenyl-1-propanol (±) 10c entry 3 # 2



VWD 1 Results

Retention Time	Area	Area %	Height	Height %
13.027	2513887	50.45	80265	52.75
15.316	2468702	49.55	71897	47.25

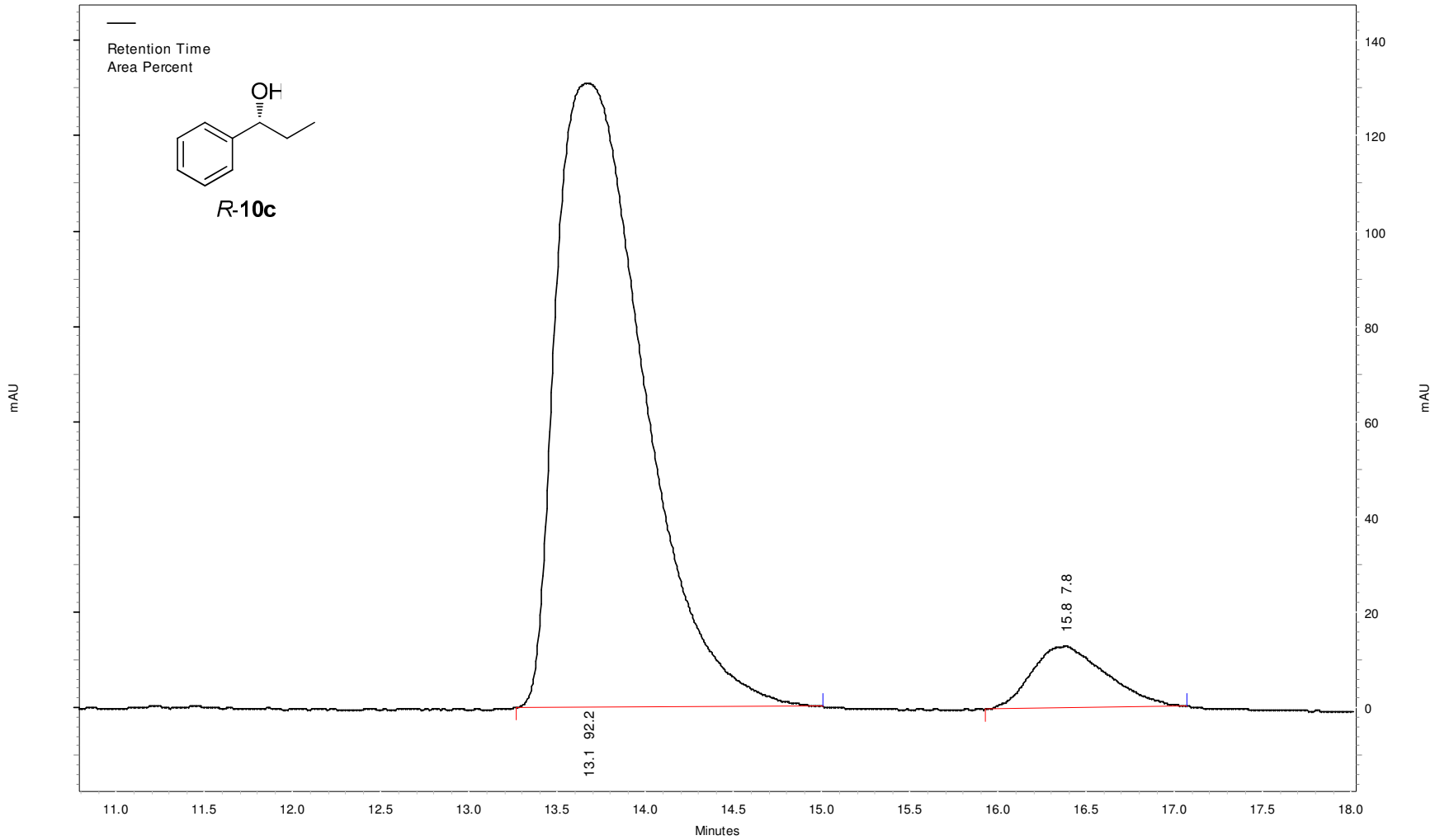
Totals	4982589	100.00	152162	100.00



VWD 1 Results

Retention Time	Area	Area %	Height	Height %
13.212	472426	17.08	17391	21.02
15.675	2293367	82.92	65360	78.98

Totals	2765793	100.00	82751	100.00

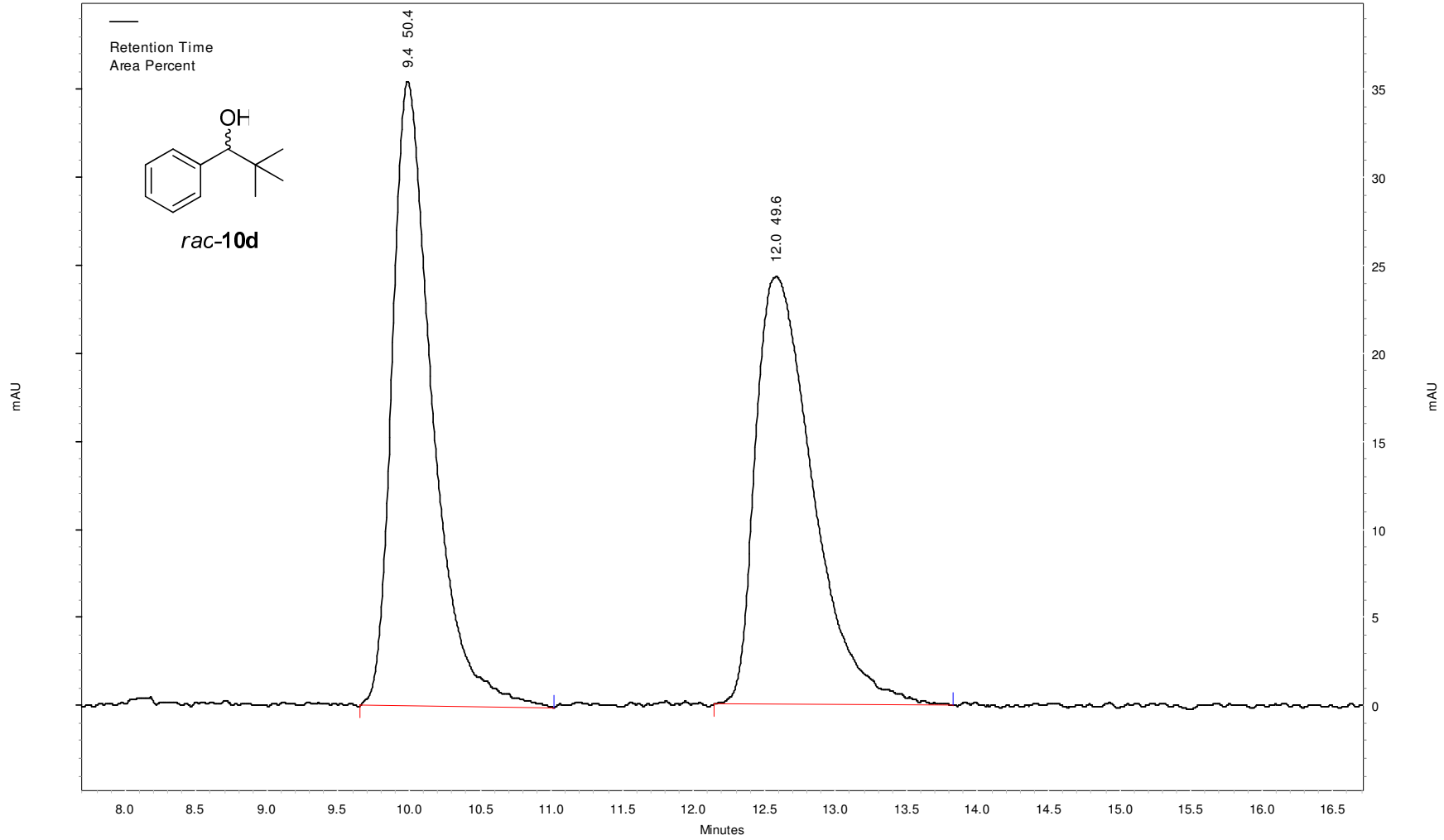


VWD 1 Results

Retention Time	Area	Area %	Height	Height %
13.076	4527053	92.23	131017	90.99
15.787	381545	7.77	12969	9.01

Totals	4908598	100.00	143986	100.00

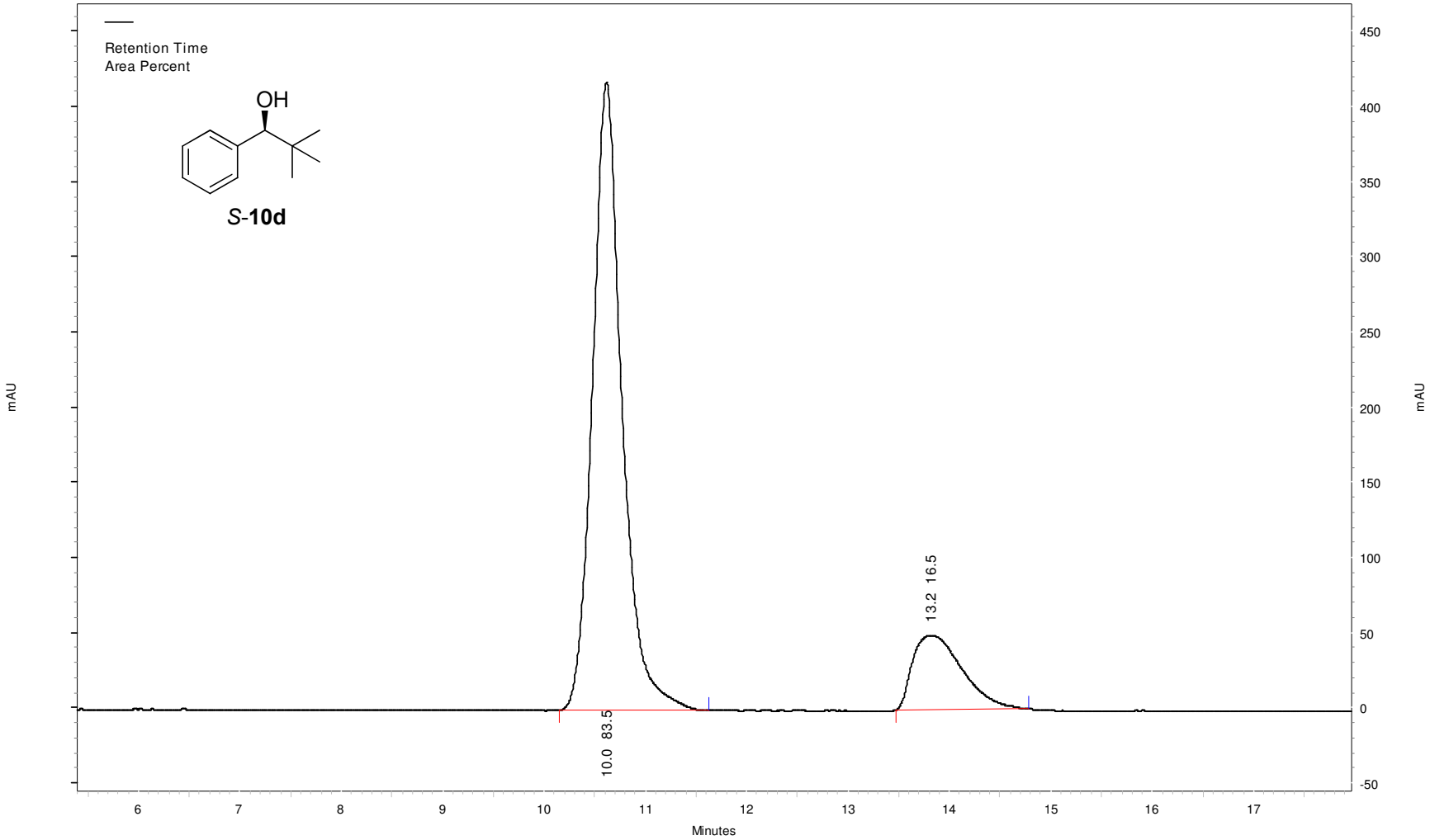
2,2'-Dimethyl-1-phenyl-1-propanol (±) 10d entry 4 # 1



VWD 1 Results

Retention Time	Area	Area %	Height	Height %
9.388	695685	50.41	35478	59.36
11.983	684496	49.59	24294	40.64

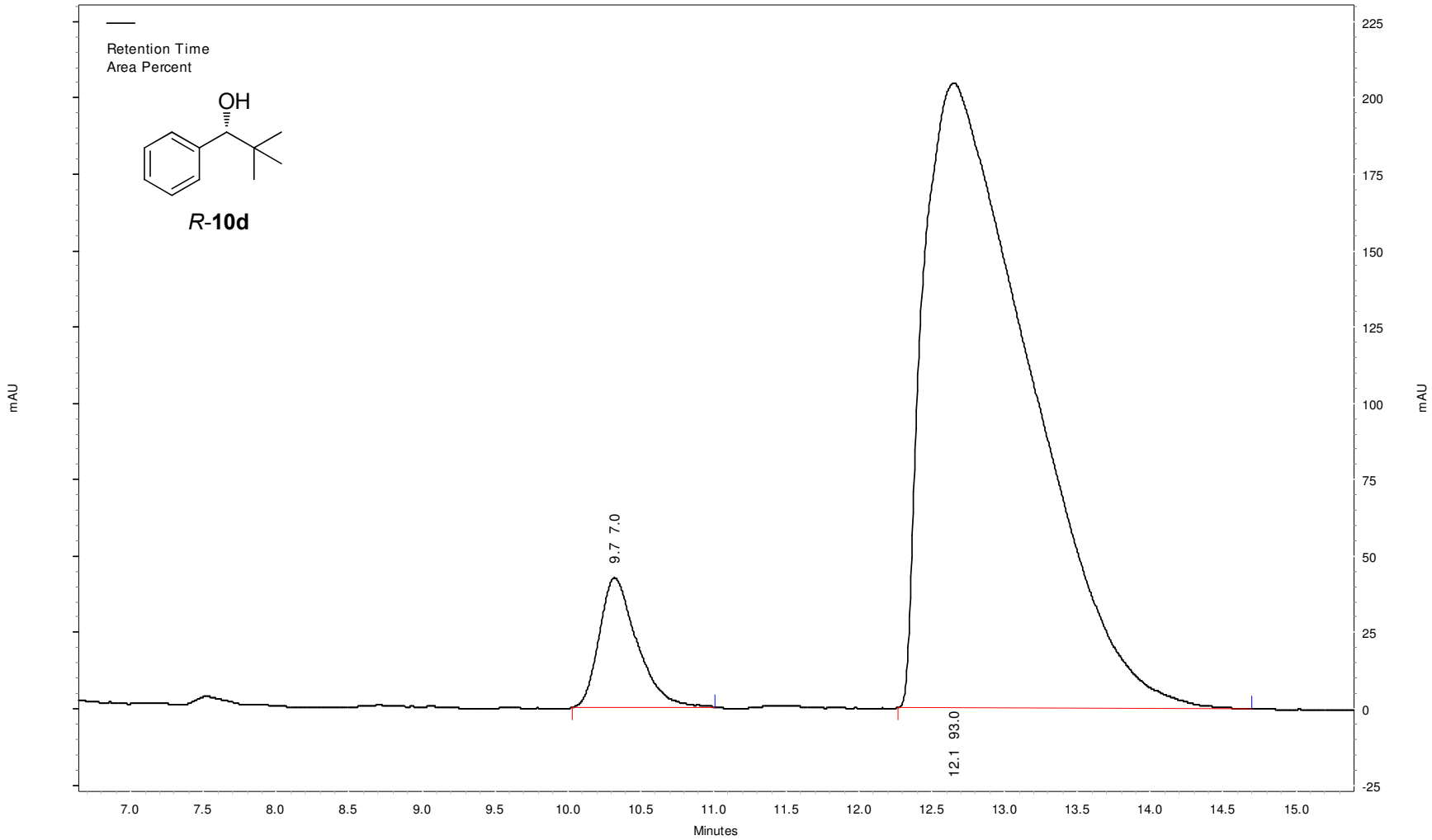
Totals	1380181	100.00	59772	100.00



VWD 1 Results

Retention Time	Area	Area %	Height	Height %
10.019	8434933	83.49	418035	89.42
13.222	1668177	16.51	49479	10.58

Totals	10103110	100.00	467514	100.00

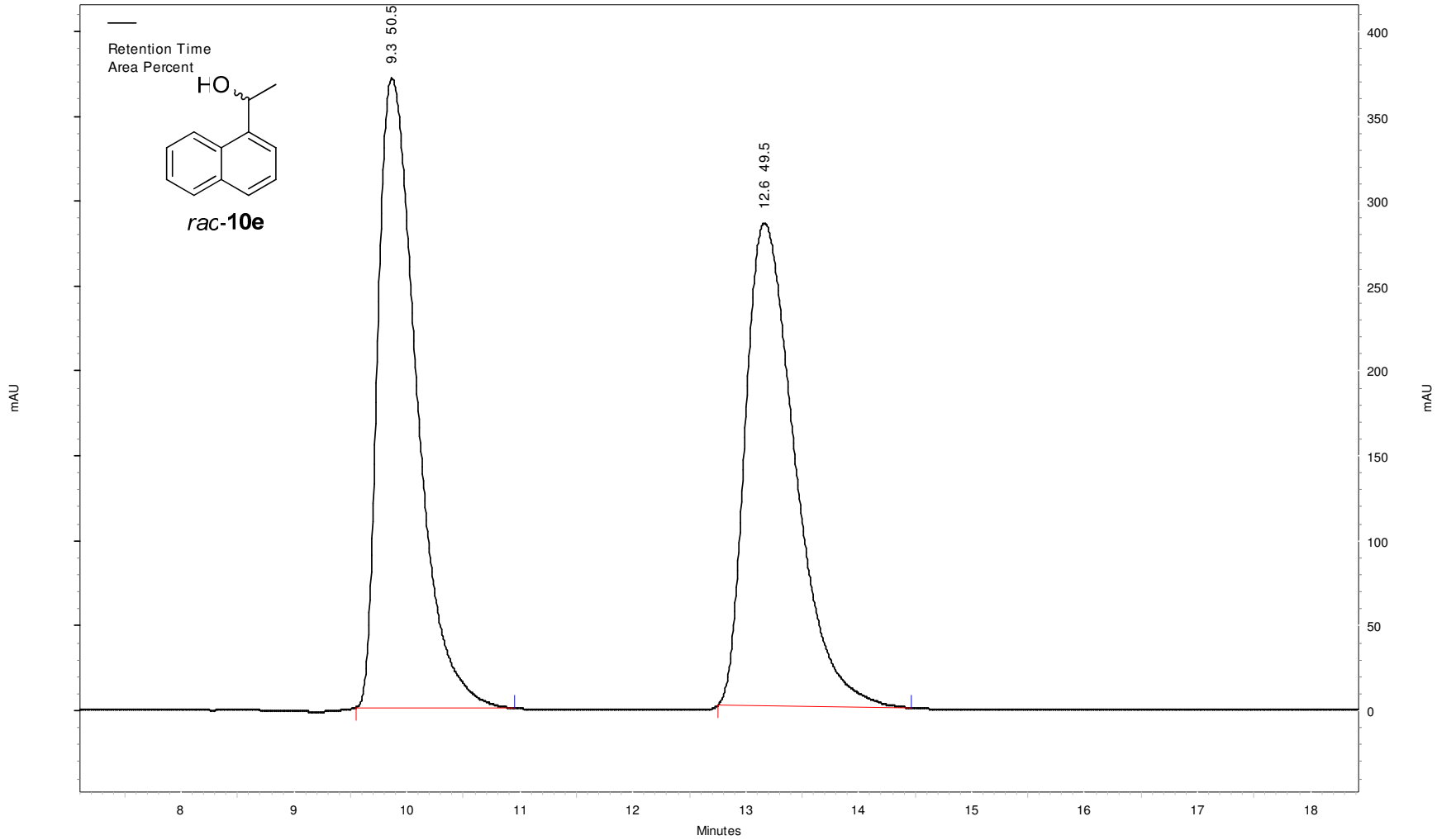


VWD 1 Results

Retention Time	Area	Area %	Height	Height %
9.723	769285	6.96	42449	17.18
12.051	10289290	93.04	204618	82.82

Totals	11058575	100.00	247067	100.00

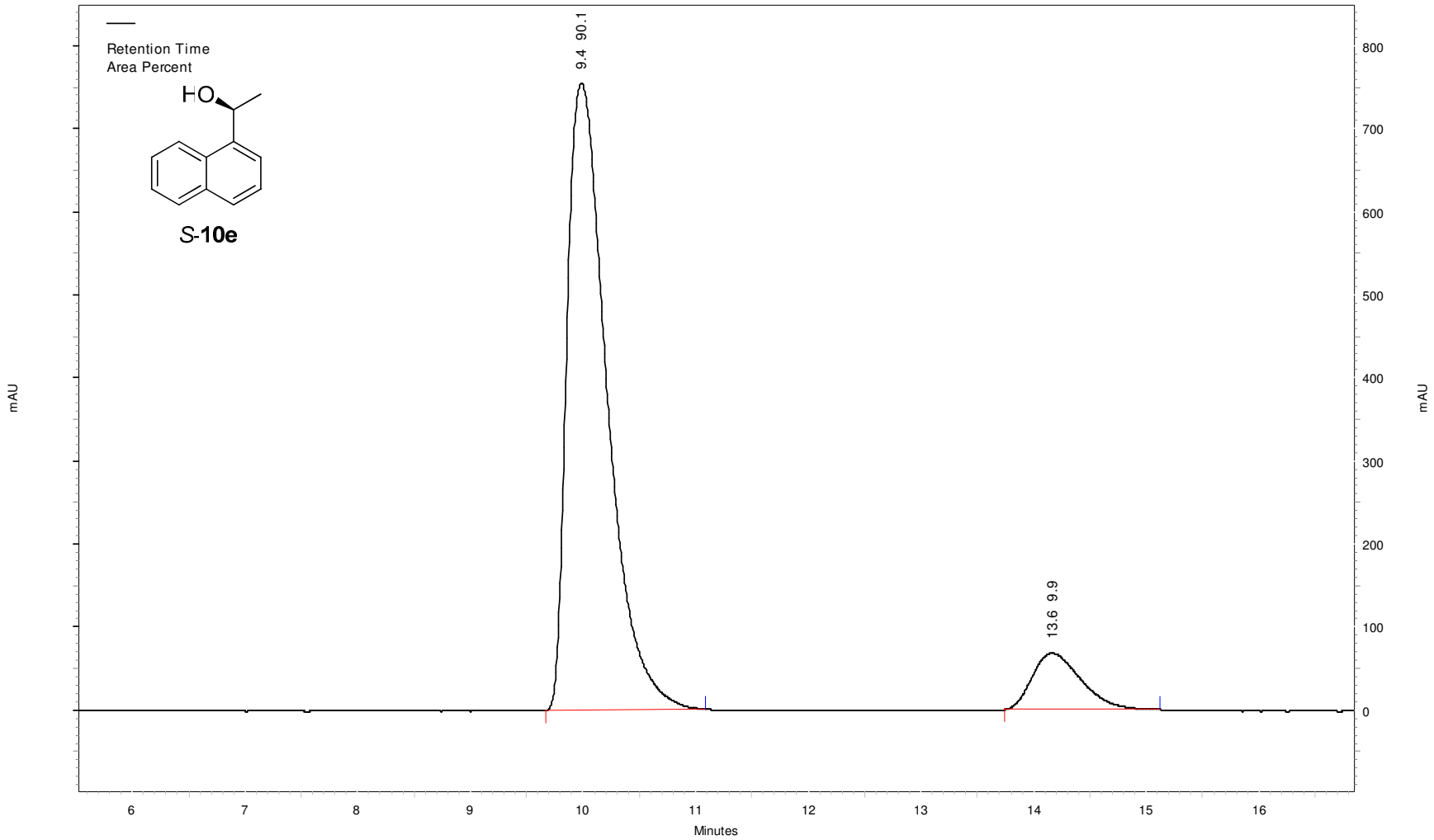
1-naphthyl ethanol (±) 10e entry 5 # 2



VWD 1 Results

Retention Time	Area	Area %	Height	Height %
9.266	8818117	50.48	370596	56.60
12.566	8651167	49.52	284143	43.40

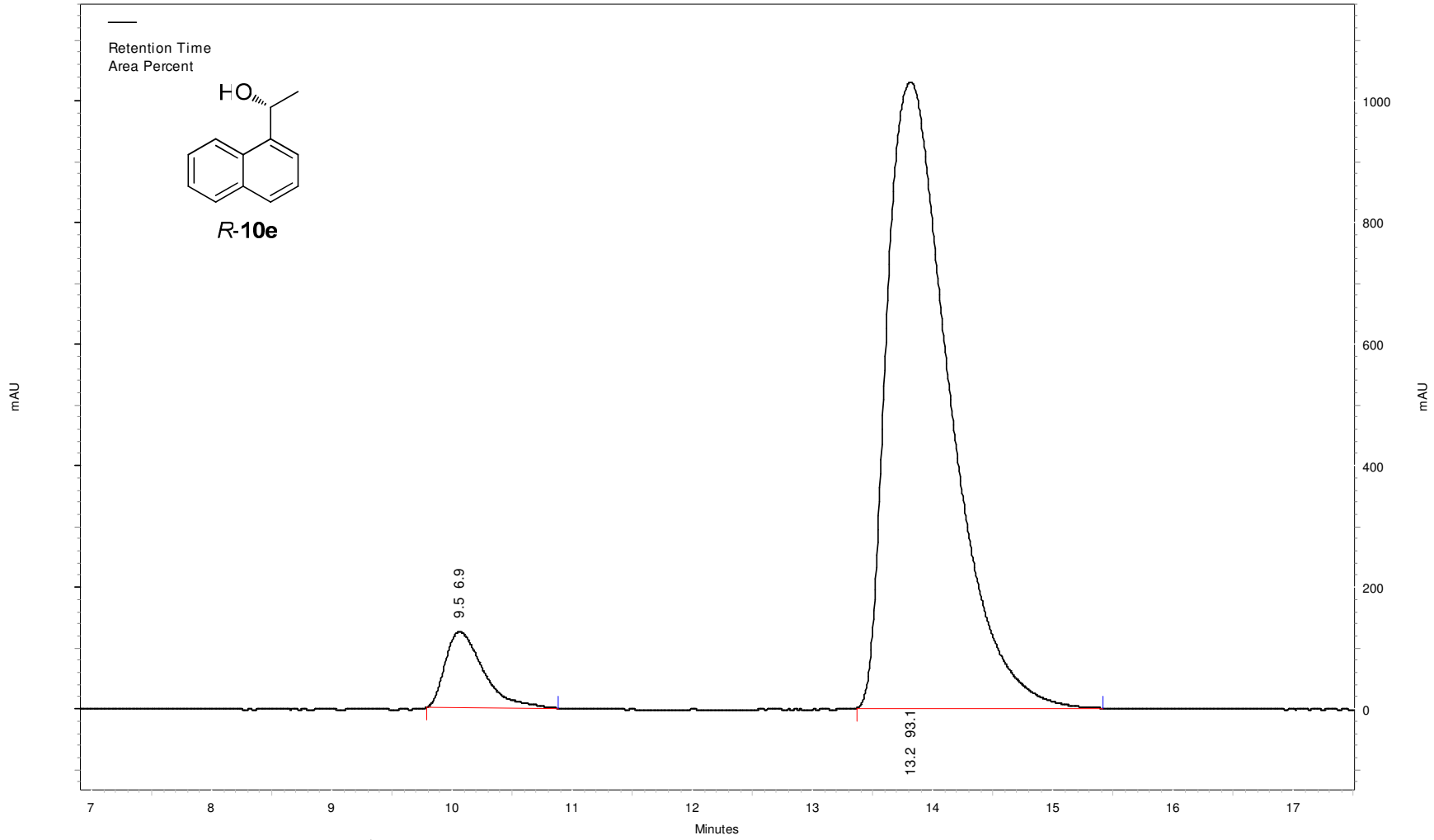
Totals	17469284	100.00	654739	100.00



VWD 1 Results

Retention Time	Area	Area %	Height	Height %
9.388	18608949	90.14	755157	91.77
13.562	2036181	9.86	67716	8.23

Totals	20645130	100.00	822873	100.00

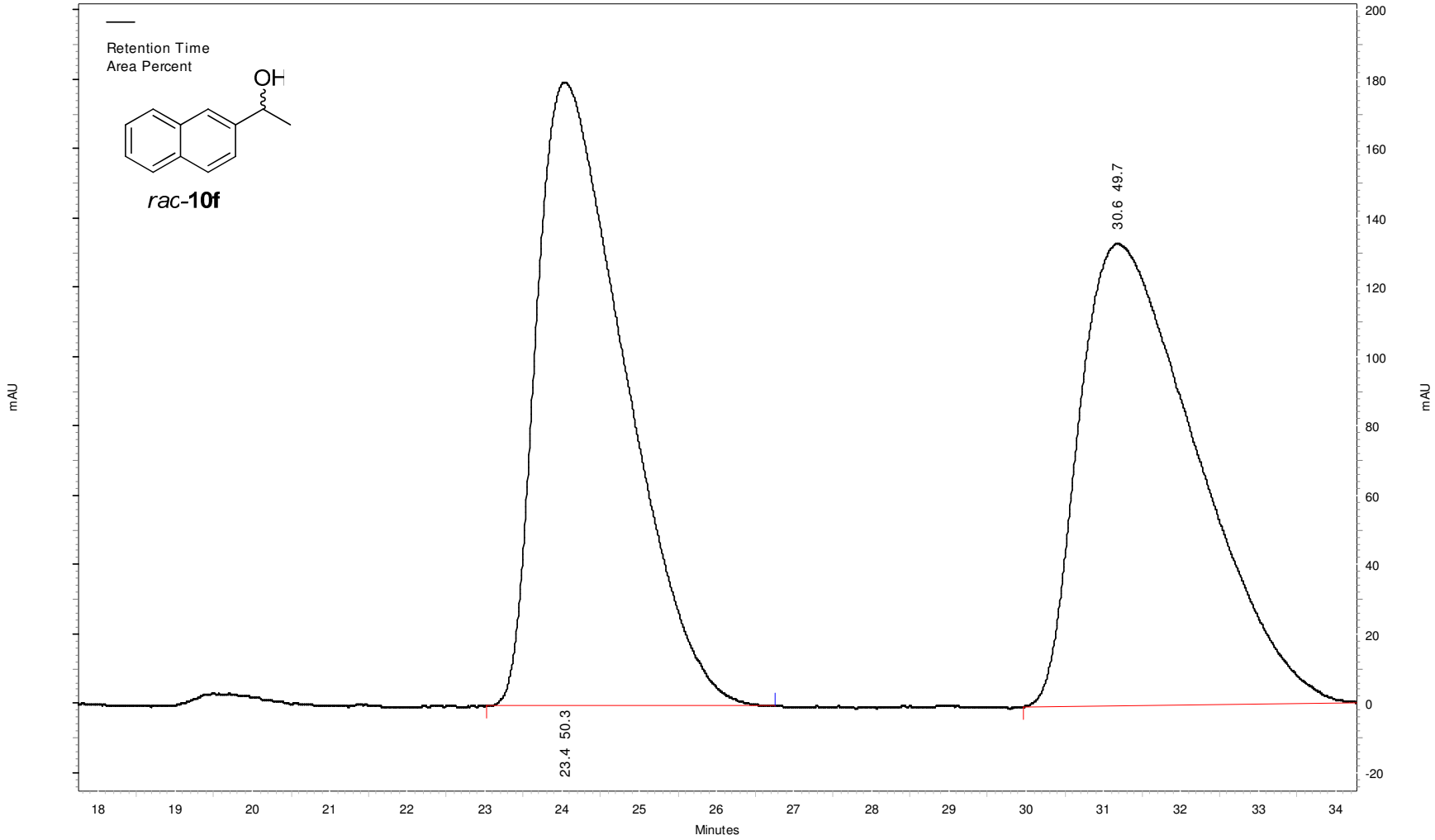


VWD 1 Results

Retention Time	Area	Area %	Height	Height %
9.461	2739899	6.87	124509	10.79
13.212	37138910	93.13	1029574	89.21

Totals	39878809	100.00	1154083	100.00

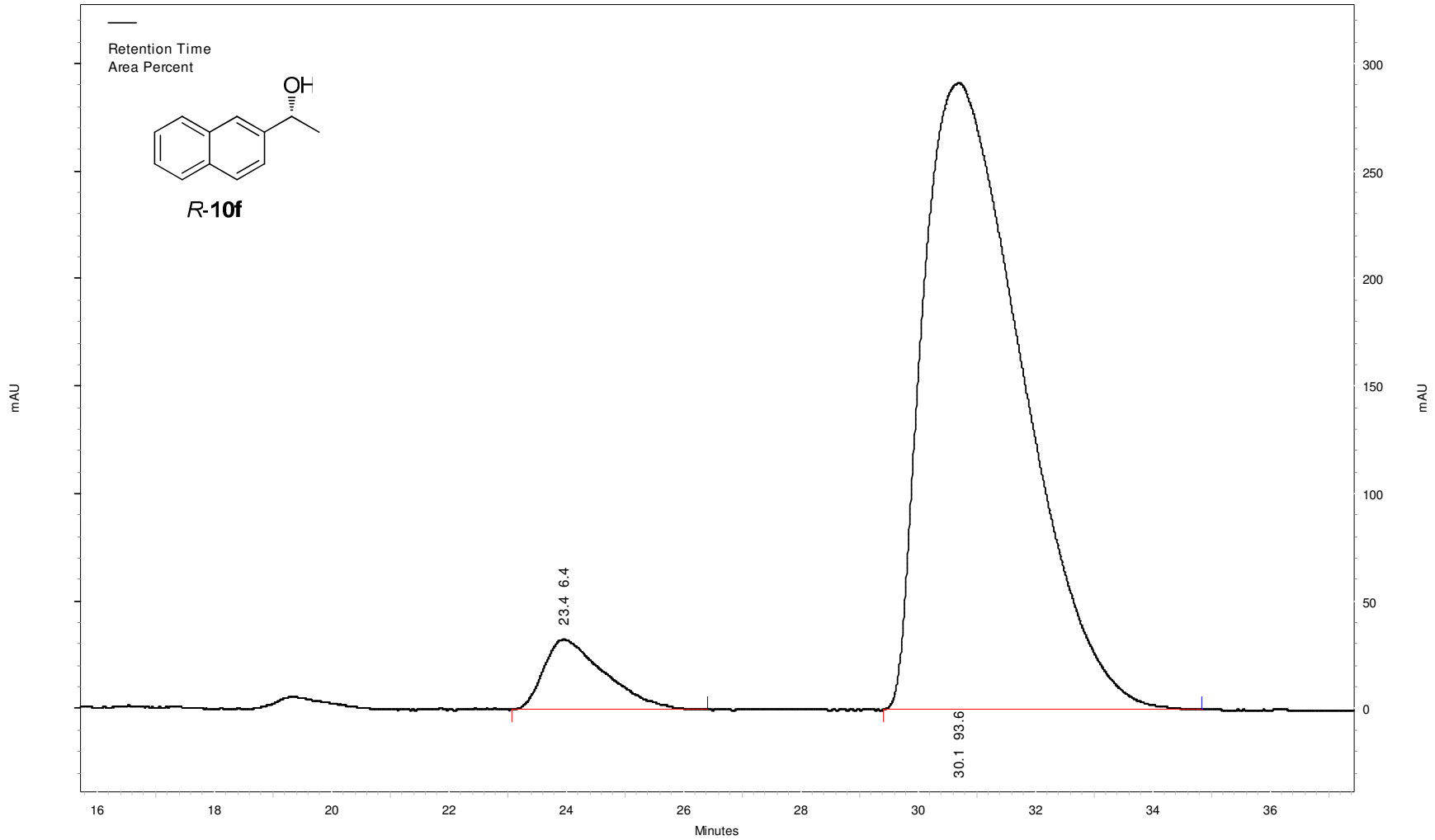
2-naphthyl ethanol (±) 10f entry 6 # 1



VWD 1 Results

Retention Time	Area	Area %	Height	Height %
23.440	14235789	50.30	180008	57.43
30.583	14068631	49.70	133413	42.57

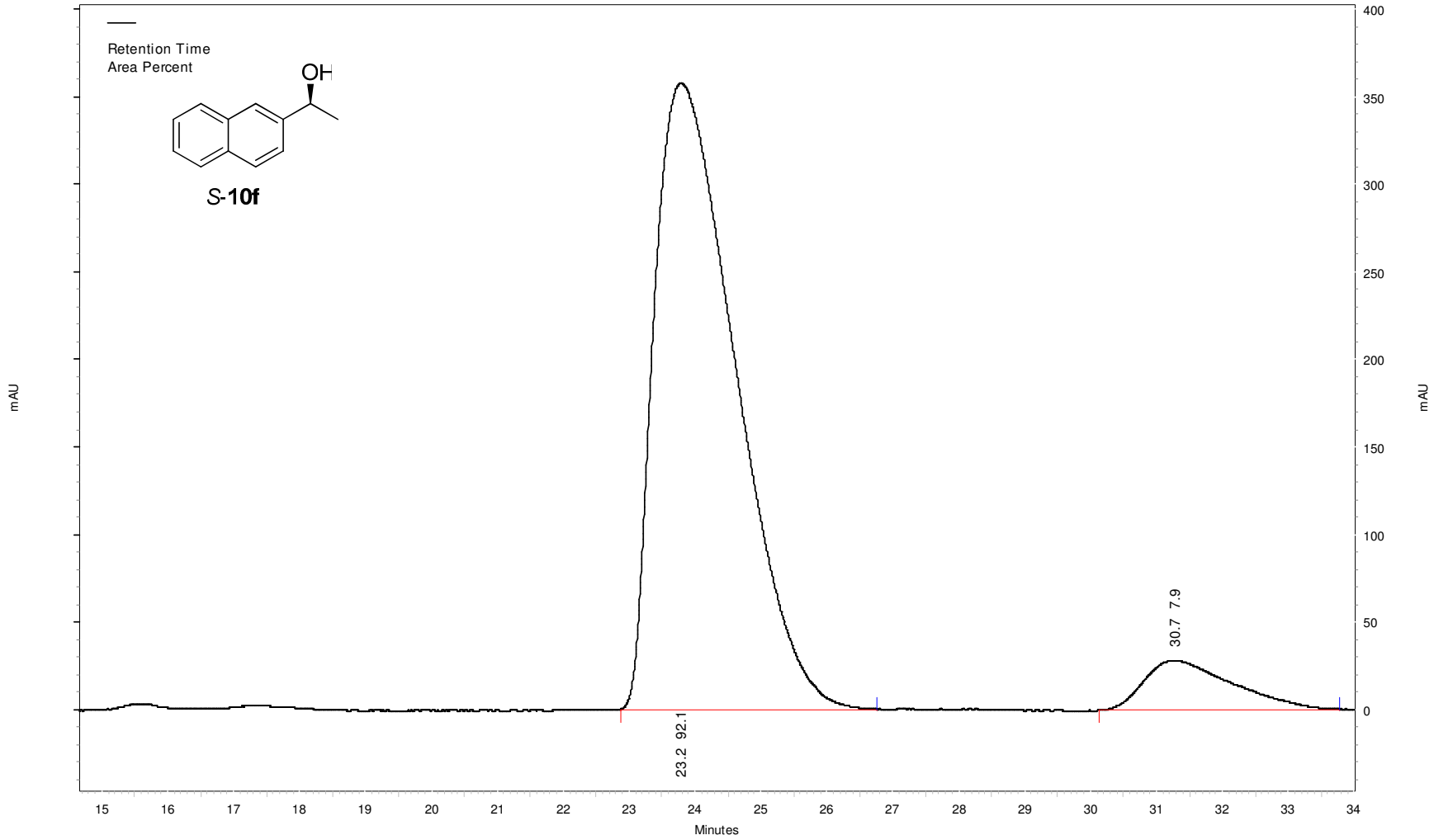
Totals	28304420	100.00	313421	100.00



VWD 1 Results

Retention Time	Area	Area %	Height	Height %
23.362	2344897	6.44	32539	10.04
30.102	34082850	93.56	291500	89.96

Totals	36427747	100.00	324039	100.00

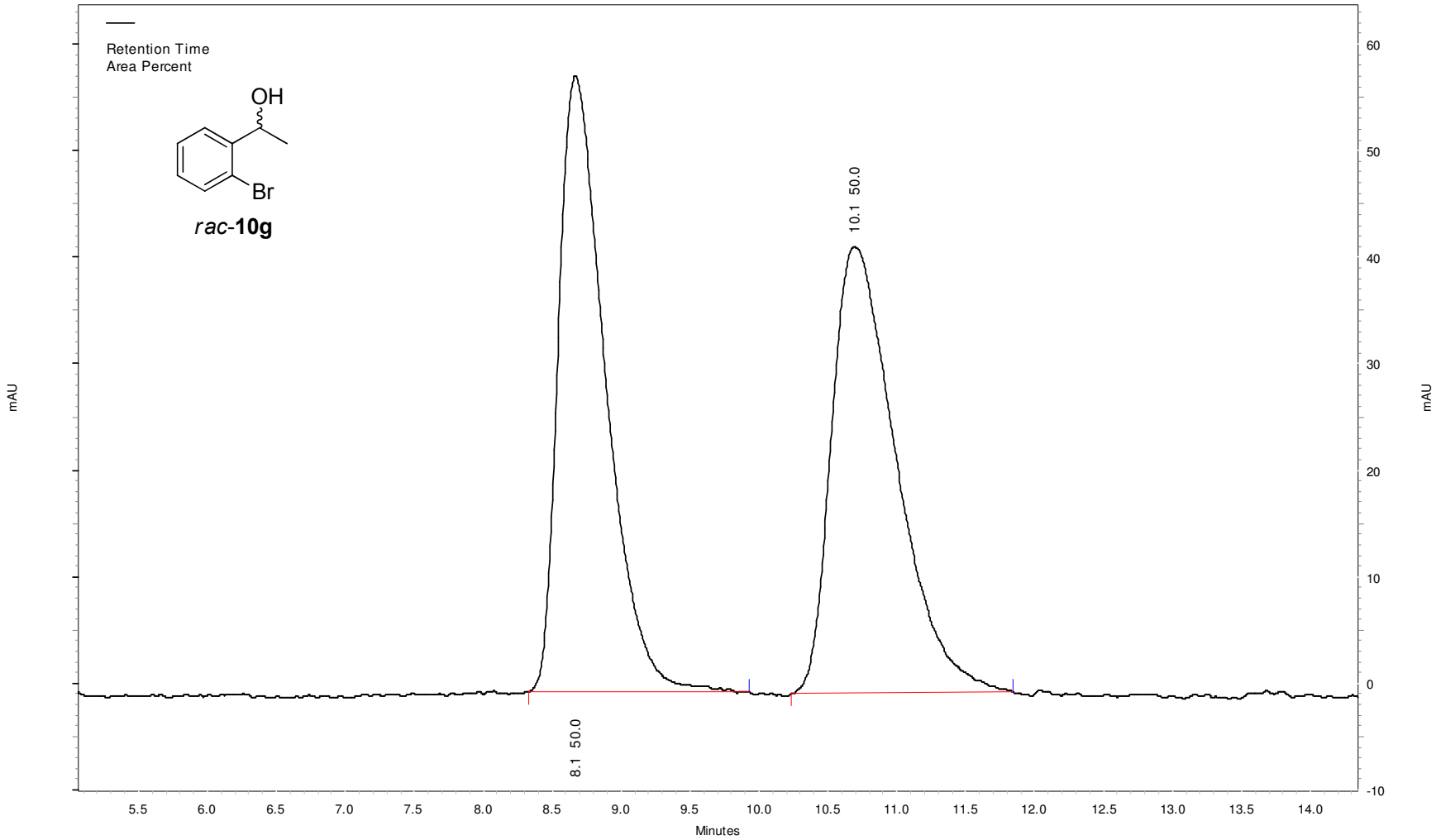


VWD 1 Results

Retention Time	Area	Area %	Height	Height %
23.183	30561542	92.13	358065	92.69
30.680	2611727	7.87	28245	7.31

Totals	33173269	100.00	386310	100.00

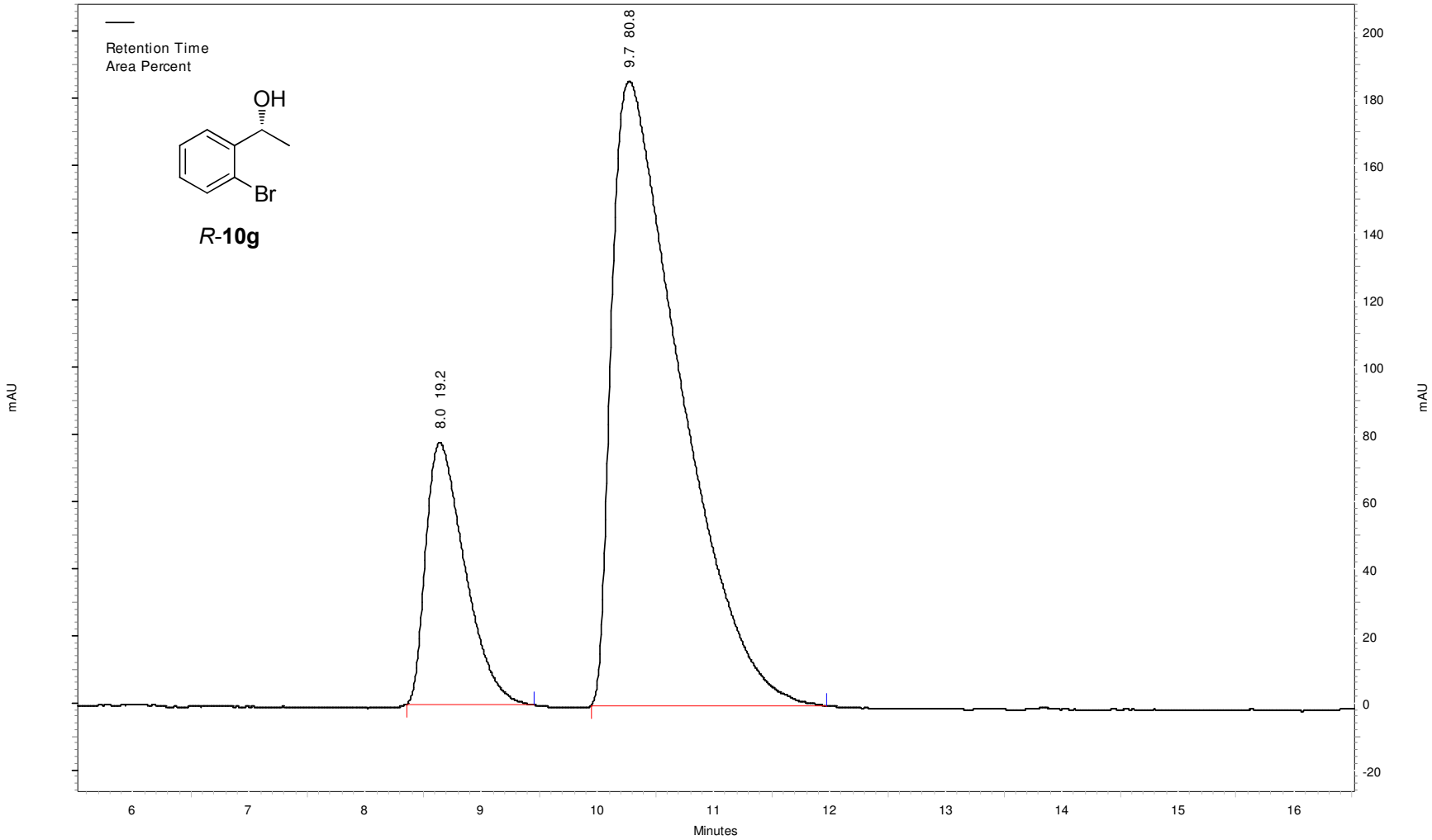
2'-bromo1-phenyl ethanol (±) 10g entry 7 # 1



VWD 1 Results

Retention Time	Area	Area %	Height	Height %
8.066	1370256	50.03	57886	57.99
10.092	1368828	49.97	41929	42.01

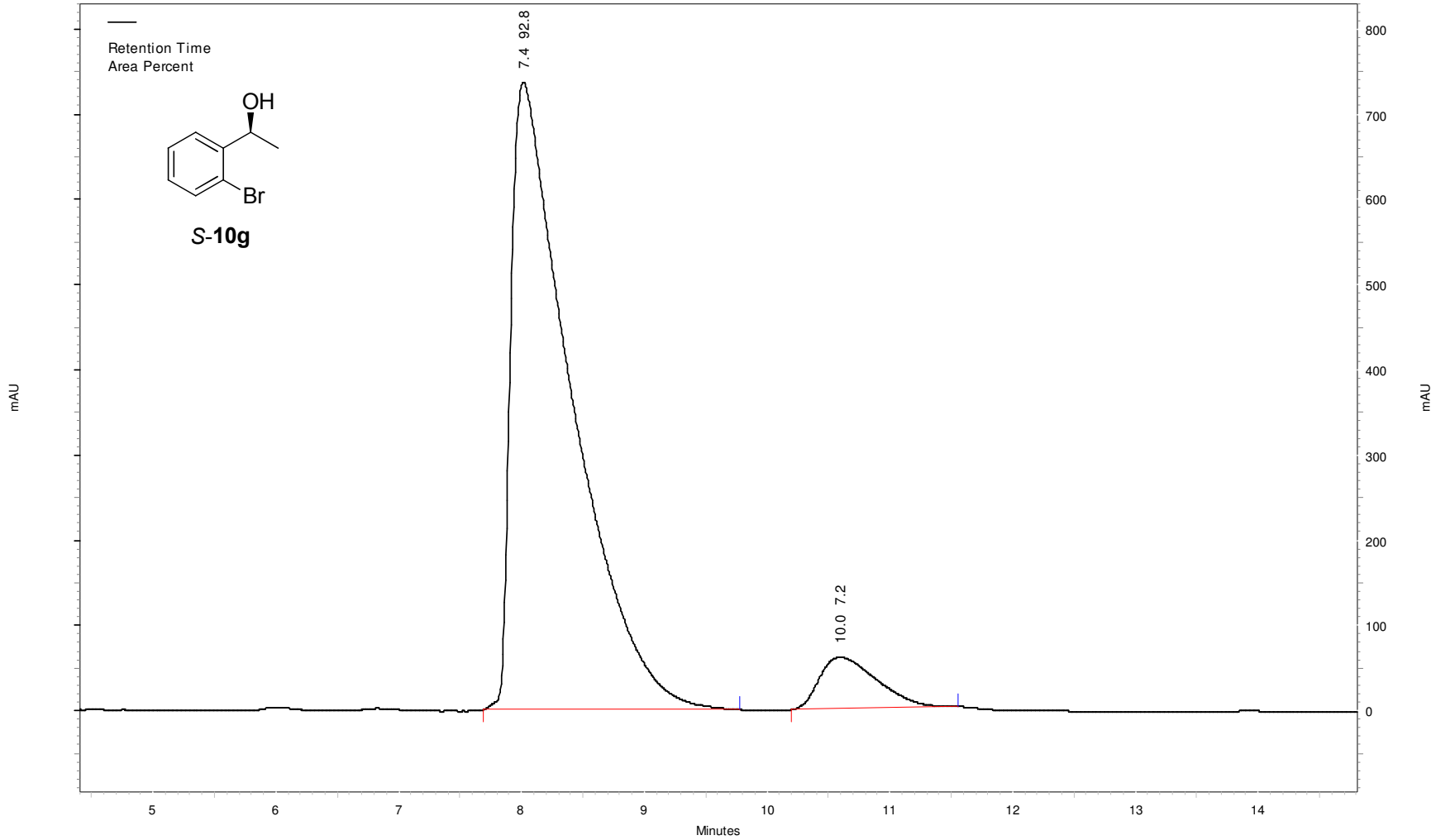
Totals	2739084	100.00	99815	100.00



VWD 1 Results

Retention Time	Area	Area %	Height	Height %
8.042	1818332	19.23	77897	29.52
9.674	7638959	80.77	185982	70.48

Totals	9457291	100.00	263879	100.00

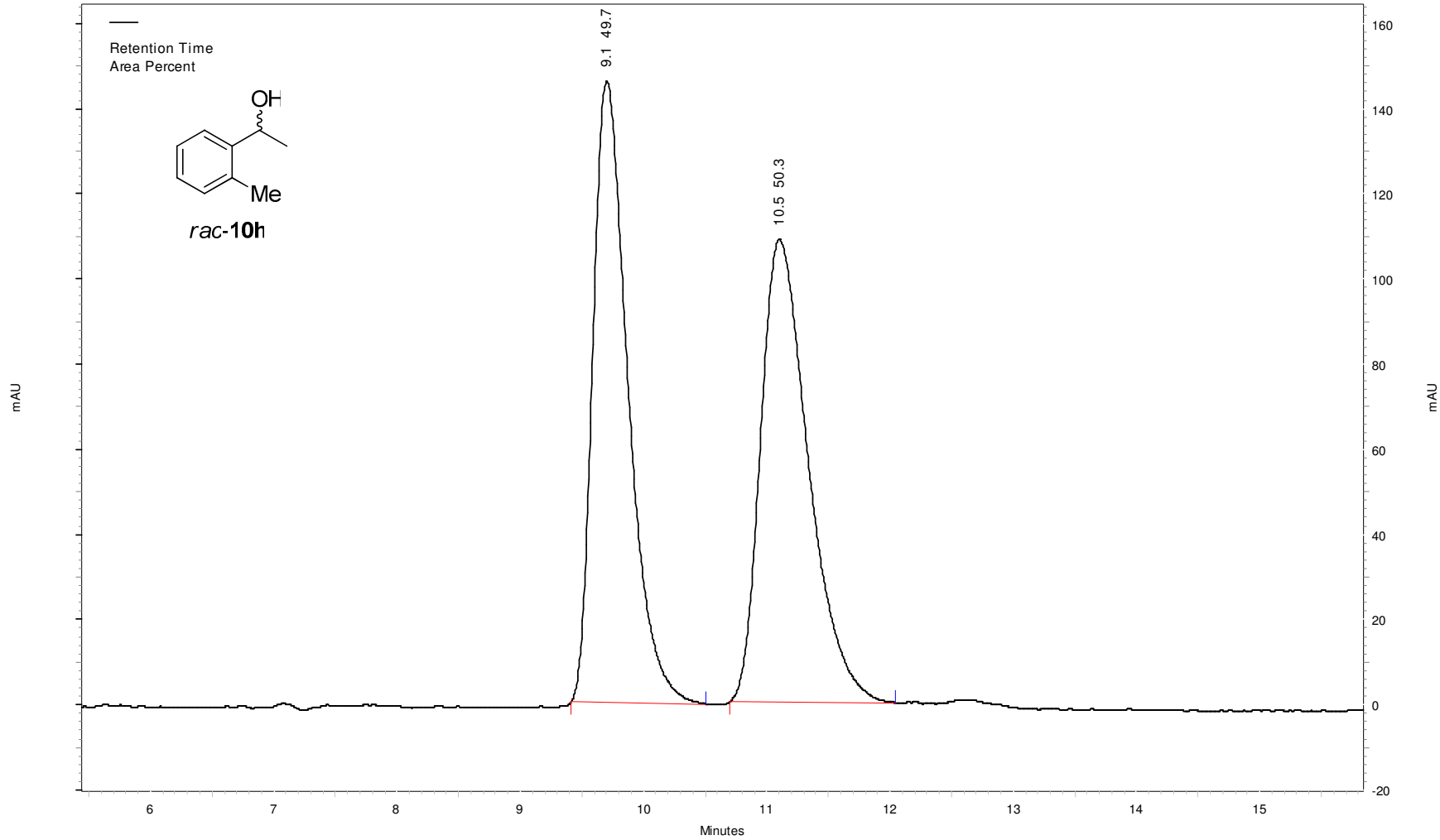


VWD 1 Results

Retention Time	Area	Area %	Height	Height %
7.415	25327316	92.82	736250	92.44
10.000	1959555	7.18	60247	7.56

Totals	27286871	100.00	796497	100.00

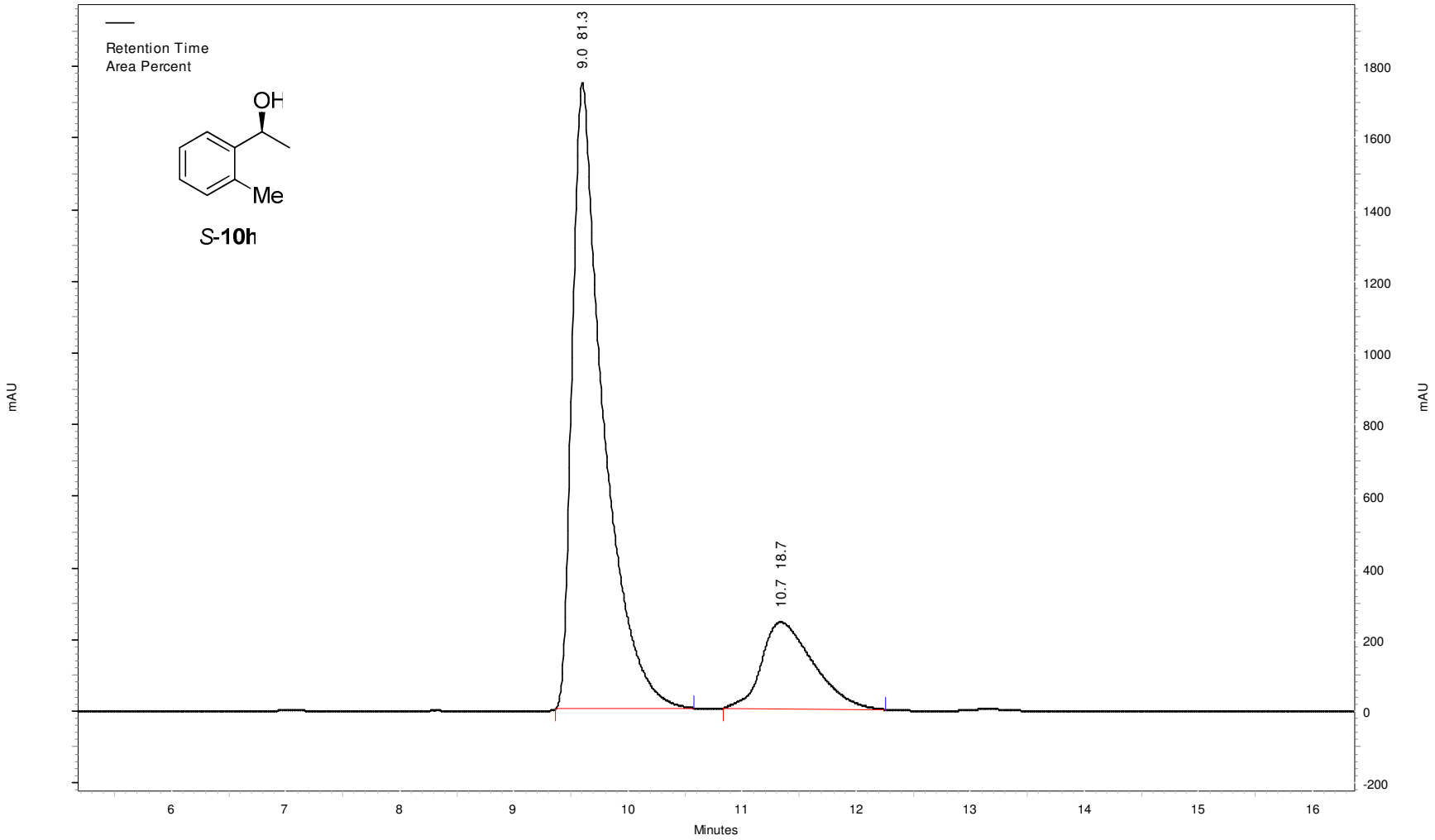
2'-methyl1-phenyl ethanol (±) 10h entry 8 # 2



VWD 1 Results

Retention Time	Area	Area %	Height	Height %
9.101	2889452	49.68	145896	57.30
10.500	2926095	50.32	108717	42.70

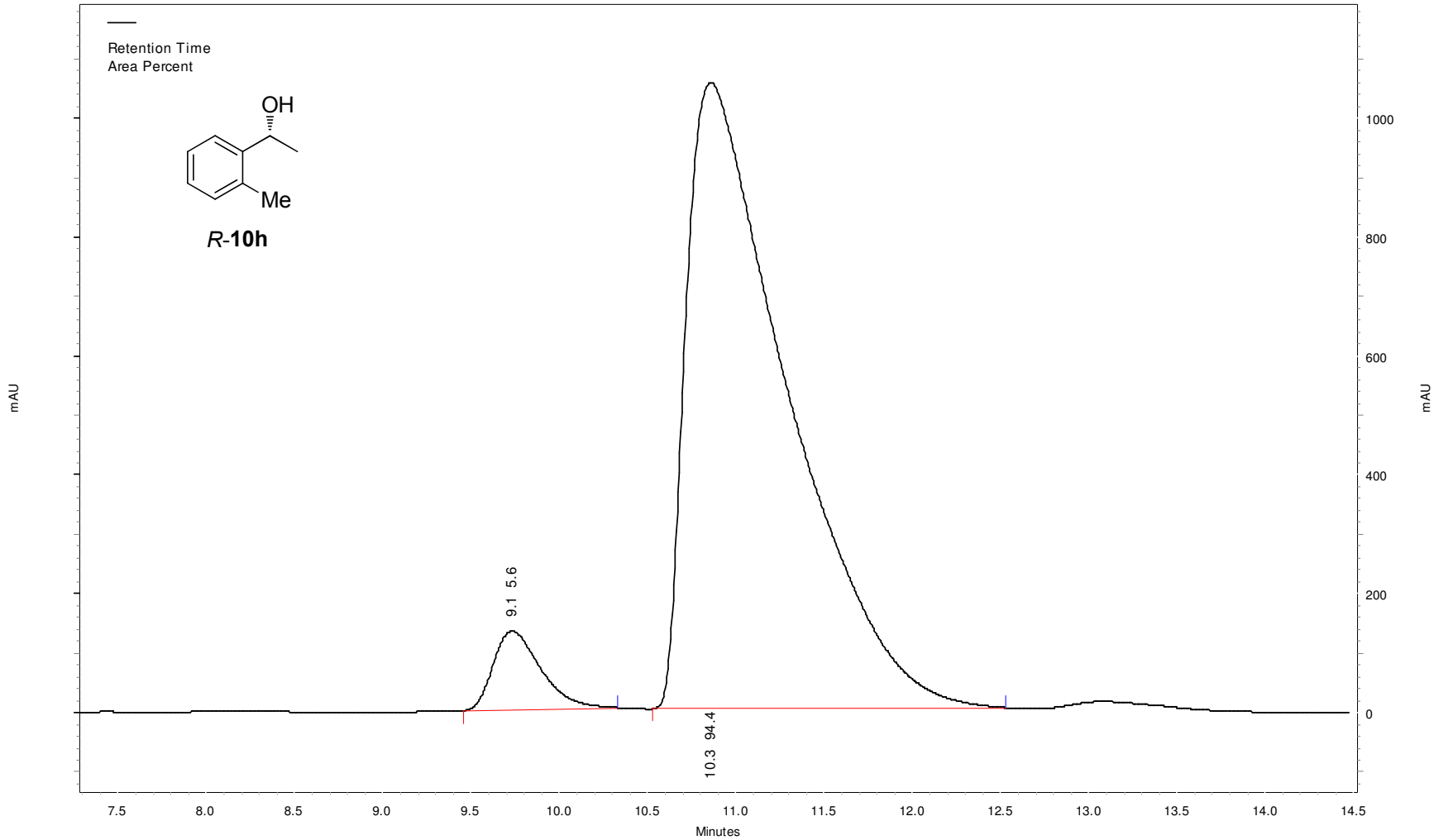
Totals	5815547	100.00	254613	100.00



VWD 1 Results

Retention Time	Area	Area %	Height	Height %
8.999	32949896	81.32	1748670	87.88
10.739	7570560	18.68	241280	12.12

Totals	40520456	100.00	1989950	100.00

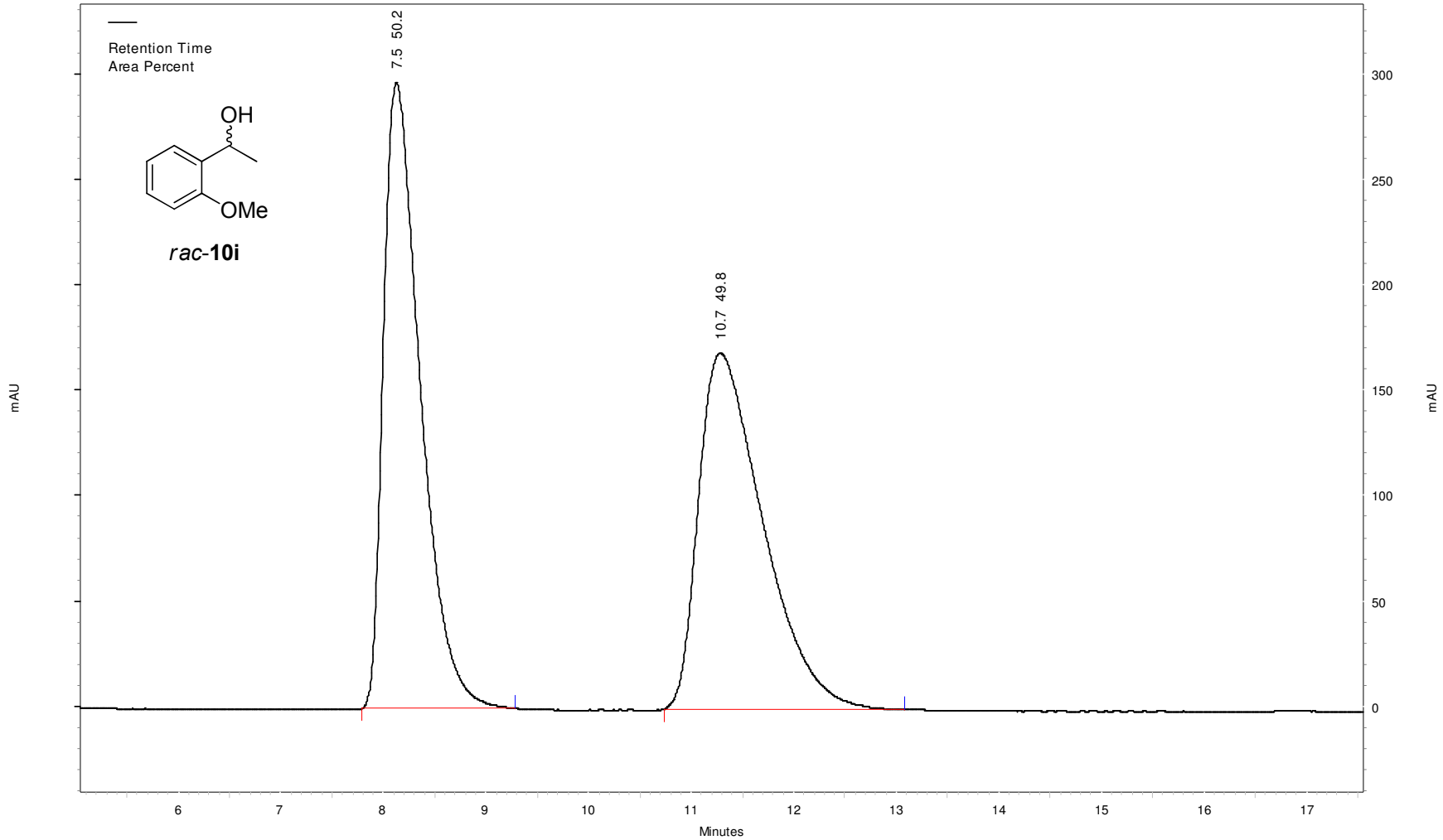


VWD 1 Results

Retention Time	Area	Area %	Height	Height %
9.130	2473021	5.56	132146	11.15
10.258	41995247	94.44	1053392	88.85

Totals	44468268	100.00	1185538	100.00

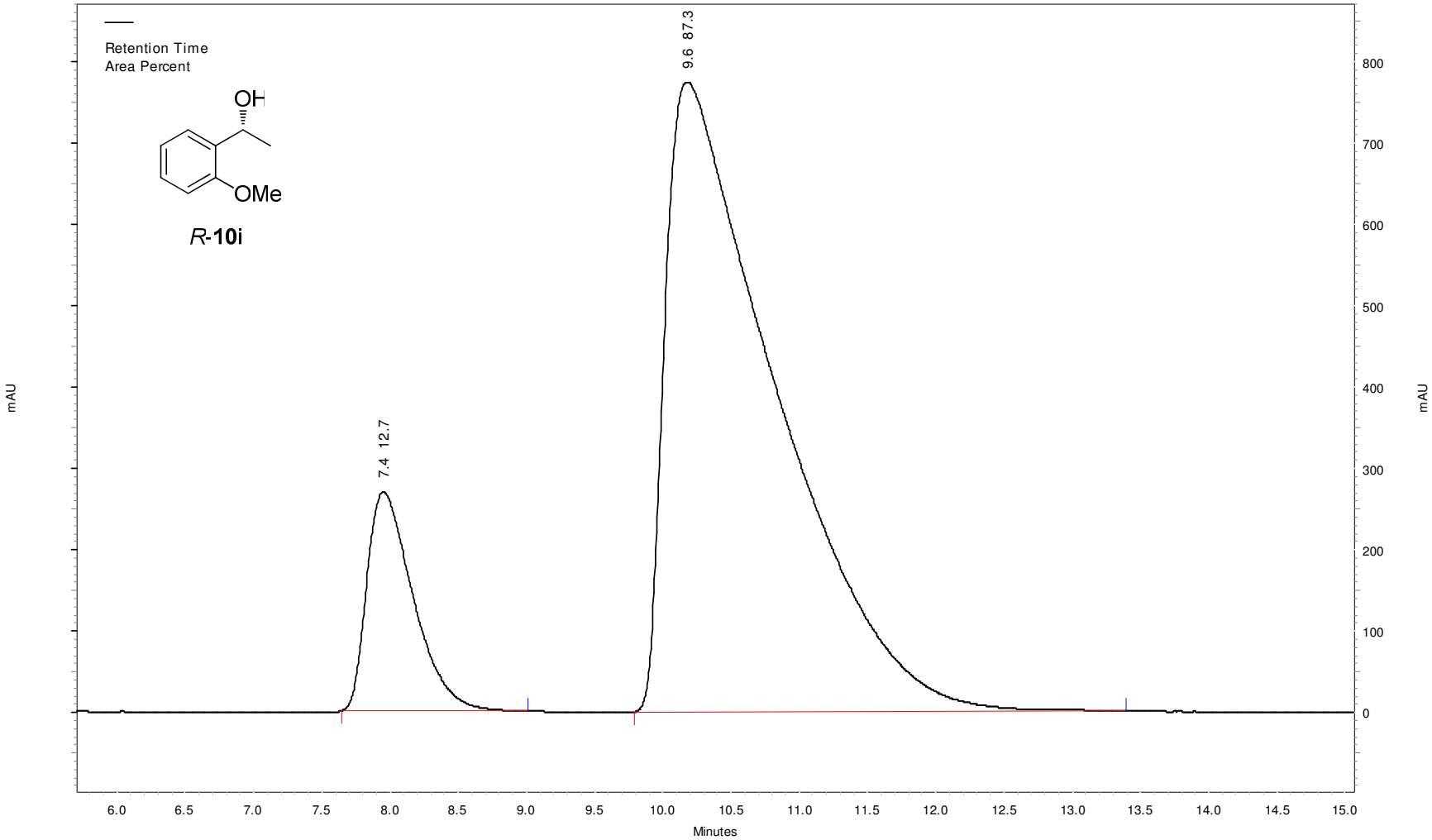
2'-methoxy1-phenyl ethanol (±) 10i entry 9 # 1



VWD 1 Results

Retention Time	Area	Area %	Height	Height %
7.527	7426260	50.21	296925	63.77
10.685	7364010	49.79	168679	36.23

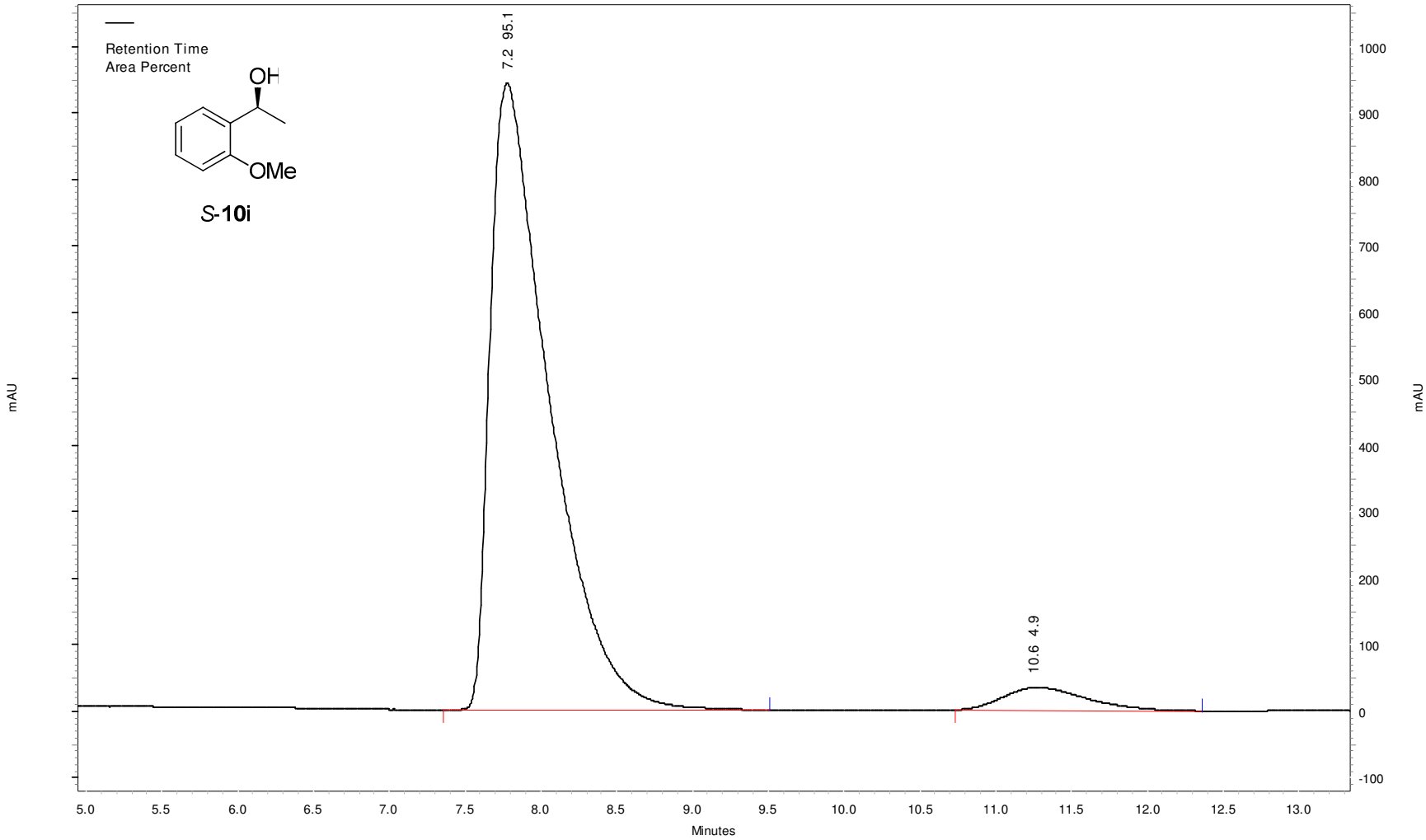
Totals	14790270	100.00	465604	100.00



VWD 1 Results

Retention Time	Area	Area %	Height	Height %
7.352	6373886	12.74	269326	25.82
9.582	43649706	87.26	773567	74.18

Totals	50023592	100.00	1042893	100.00

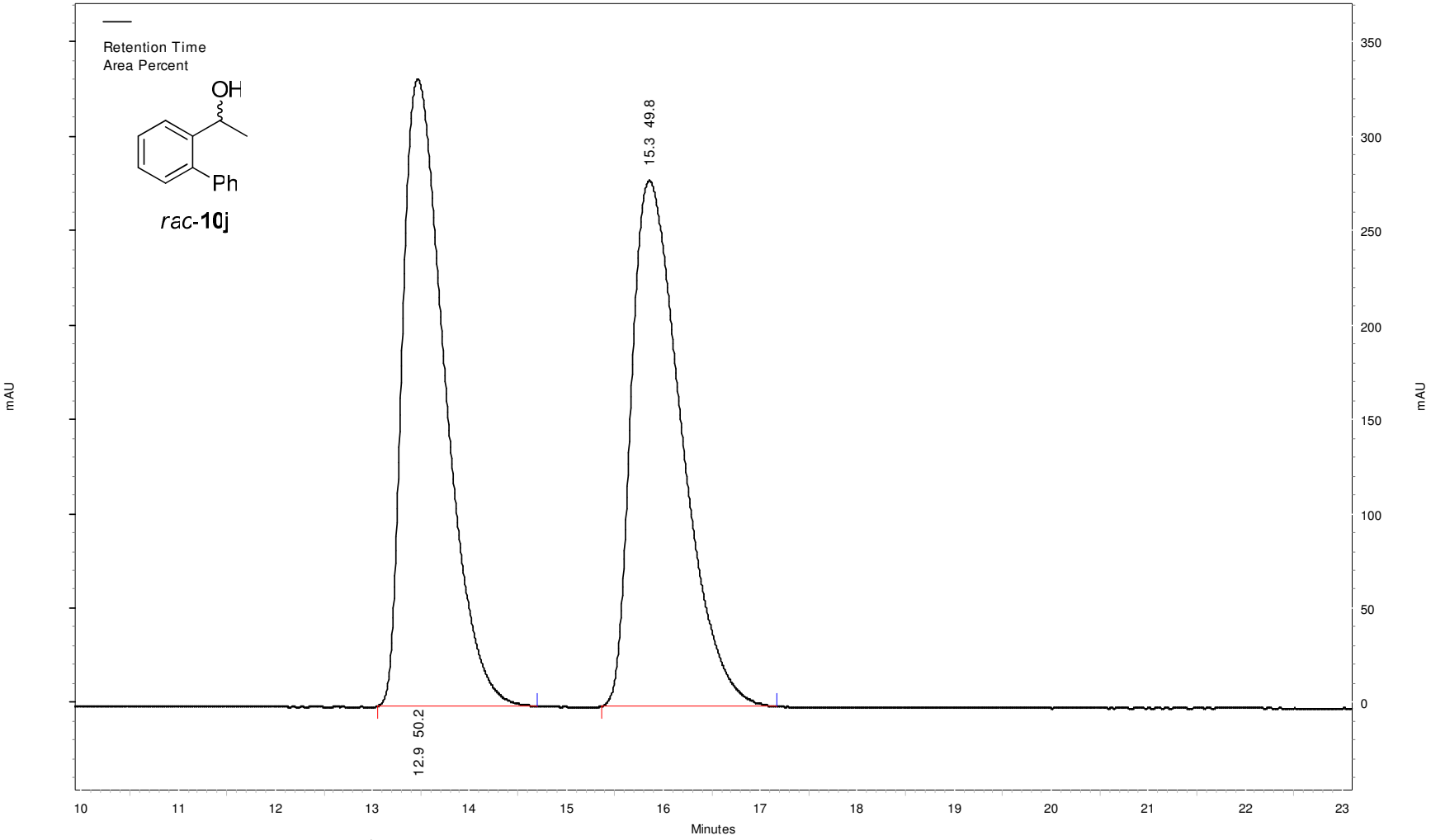


VWD 1 Results

Retention Time	Area	Area %	Height	Height %
7.177	25454426	95.12	943134	96.53
10.646	1307254	4.88	33908	3.47

Totals	26761680	100.00	977042	100.00

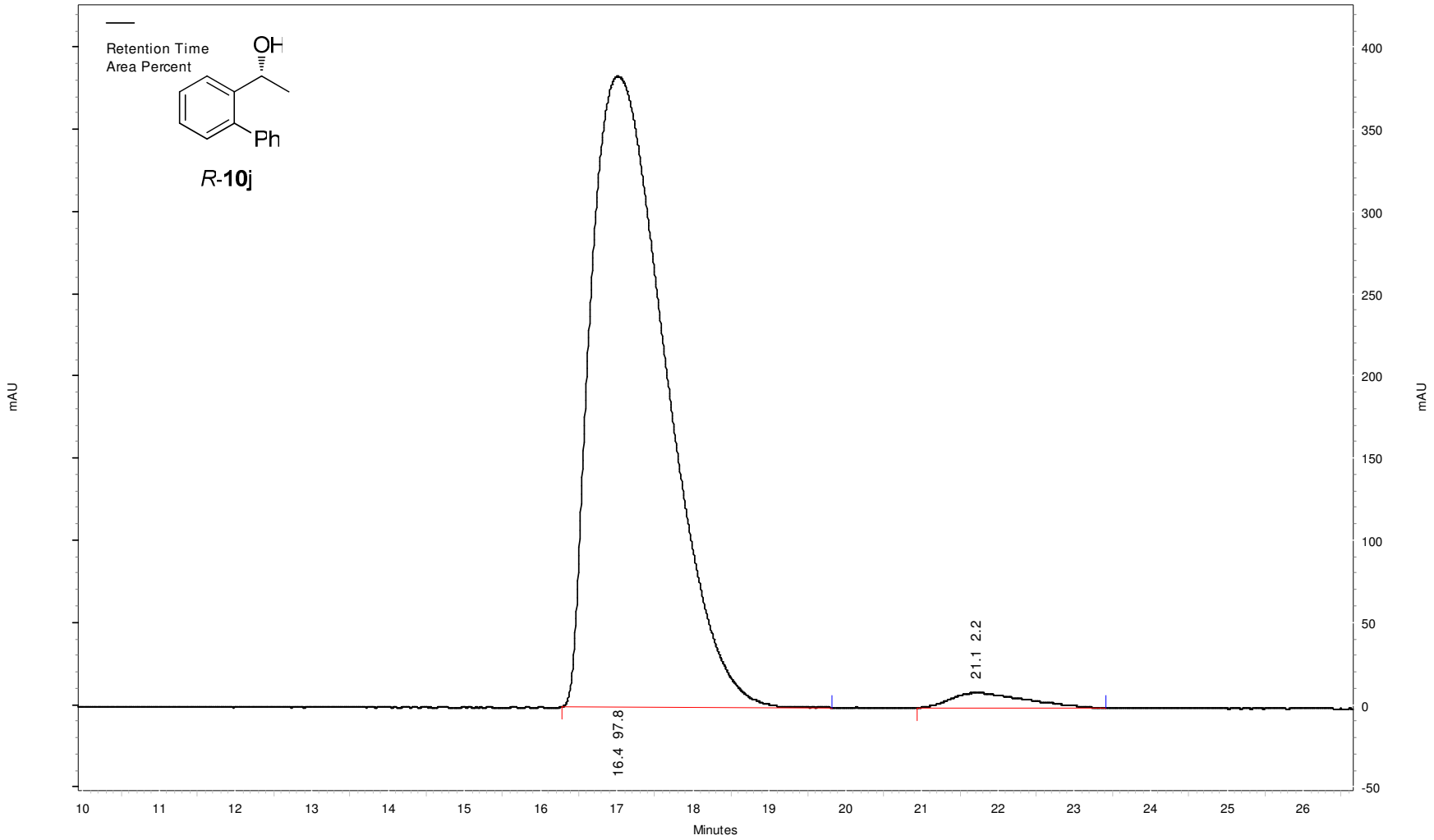
2'-phenyl1-phenyl ethanol (±) 10j entry 10 # 1



VWD 1 Results

Retention Time	Area	Area %	Height	Height %
12.872	10051911	50.16	332273	54.40
15.258	9988209	49.84	278540	45.60

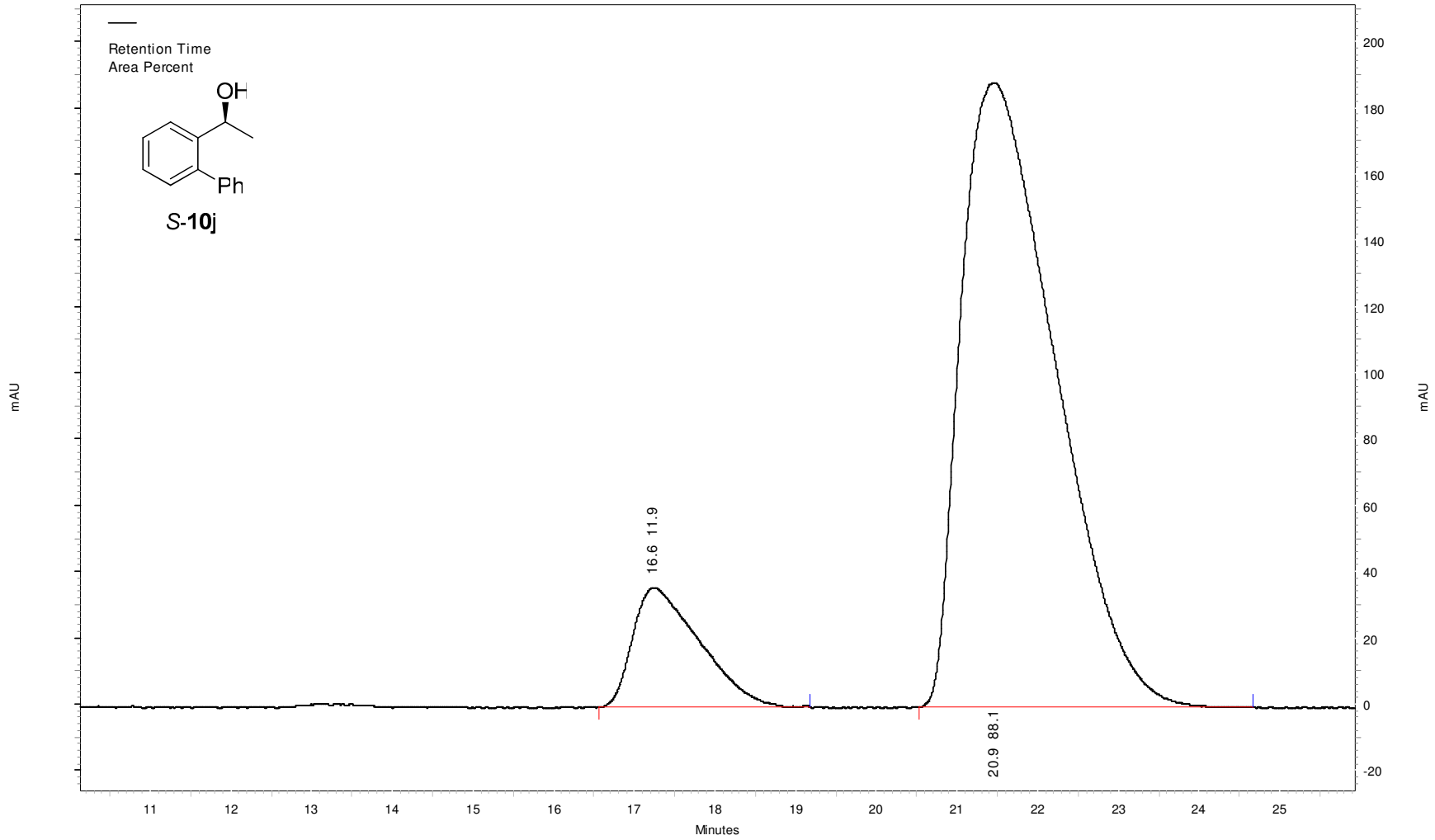
Totals	20040120	100.00	610813	100.00



VWD 1 Results

Retention Time	Area	Area %	Height	Height %
16.414	26026788	97.77	383395	97.69
21.108	594802	2.23	9074	2.31

Totals	26621590	100.00	392469	100.00

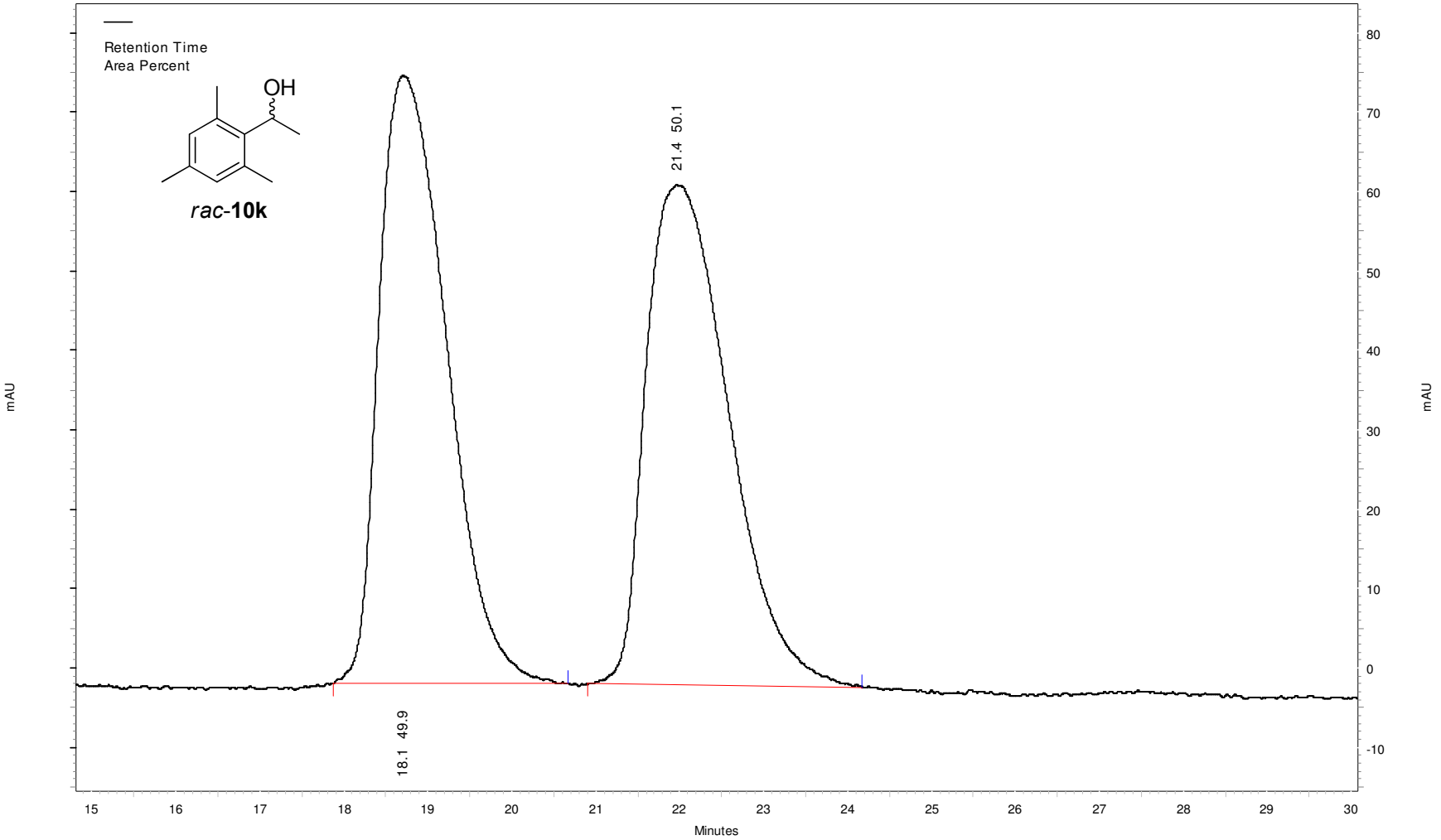


VWD 1 Results

Retention Time	Area	Area %	Height	Height %
16.623	2068991	11.94	35927	16.02
20.855	15253433	88.06	188350	83.98

Totals	17322424	100.00	224277	100.00

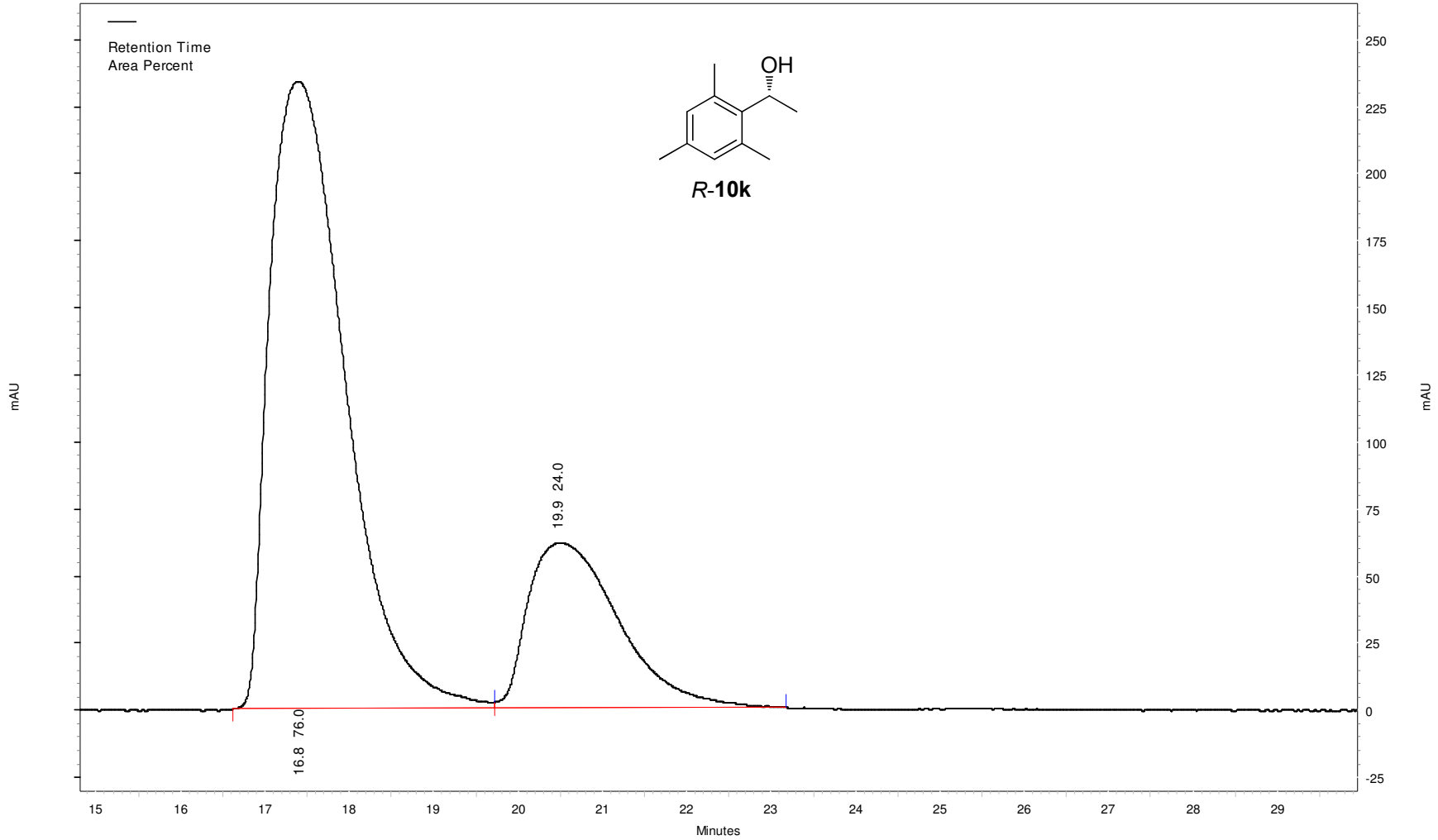
2,4,6-trimethyl1-phenyl ethanol (±) 10k entry 11 # 1



VWD 1 Results

Retention Time	Area	Area %	Height	Height %
18.100	4286003	49.88	76466	54.84
21.361	4306996	50.12	62961	45.16

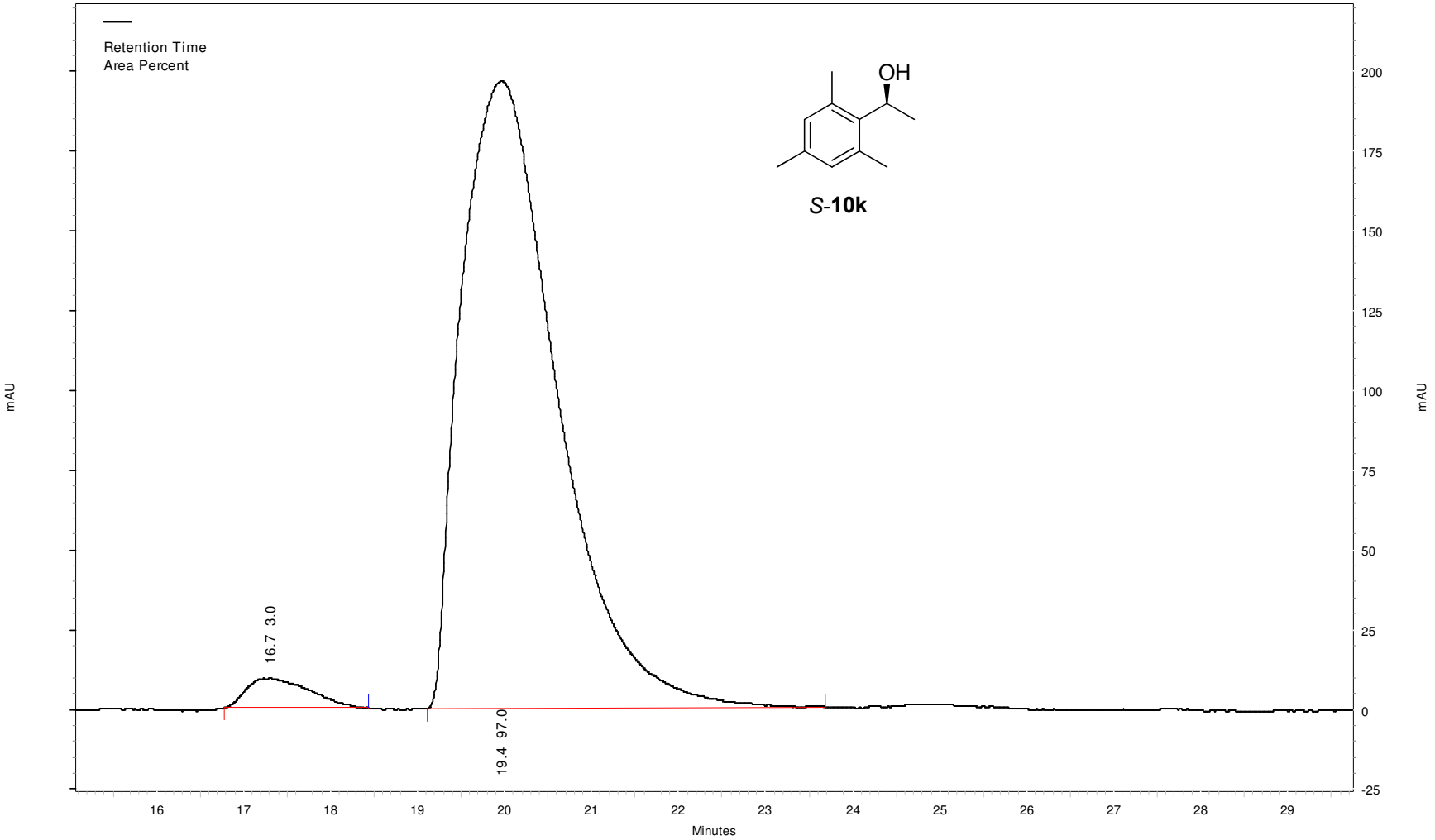
Totals	8592999	100.00	139427	100.00



VWD 1 Results

Retention Time	Area	Area %	Height	Height %
16.798	14615534	76.00	233897	79.15
19.874	4615880	24.00	61624	20.85

Totals	19231414	100.00	295521	100.00

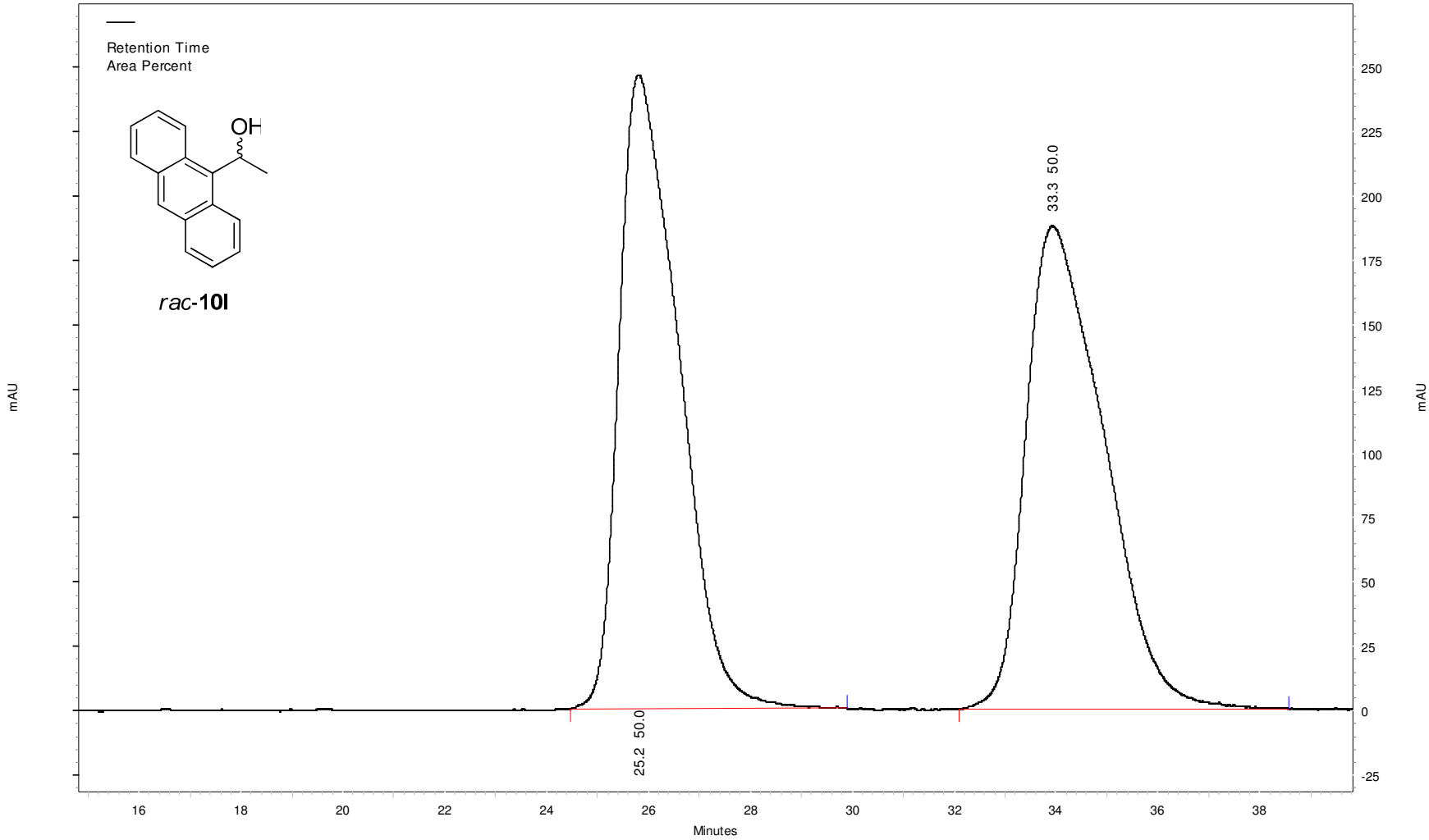


VWD 1 Results

Retention Time	Area	Area %	Height	Height %
16.710	463739	3.00	9274	4.50
19.363	14998412	97.00	196605	95.50

Totals	15462151	100.00	205879	100.00

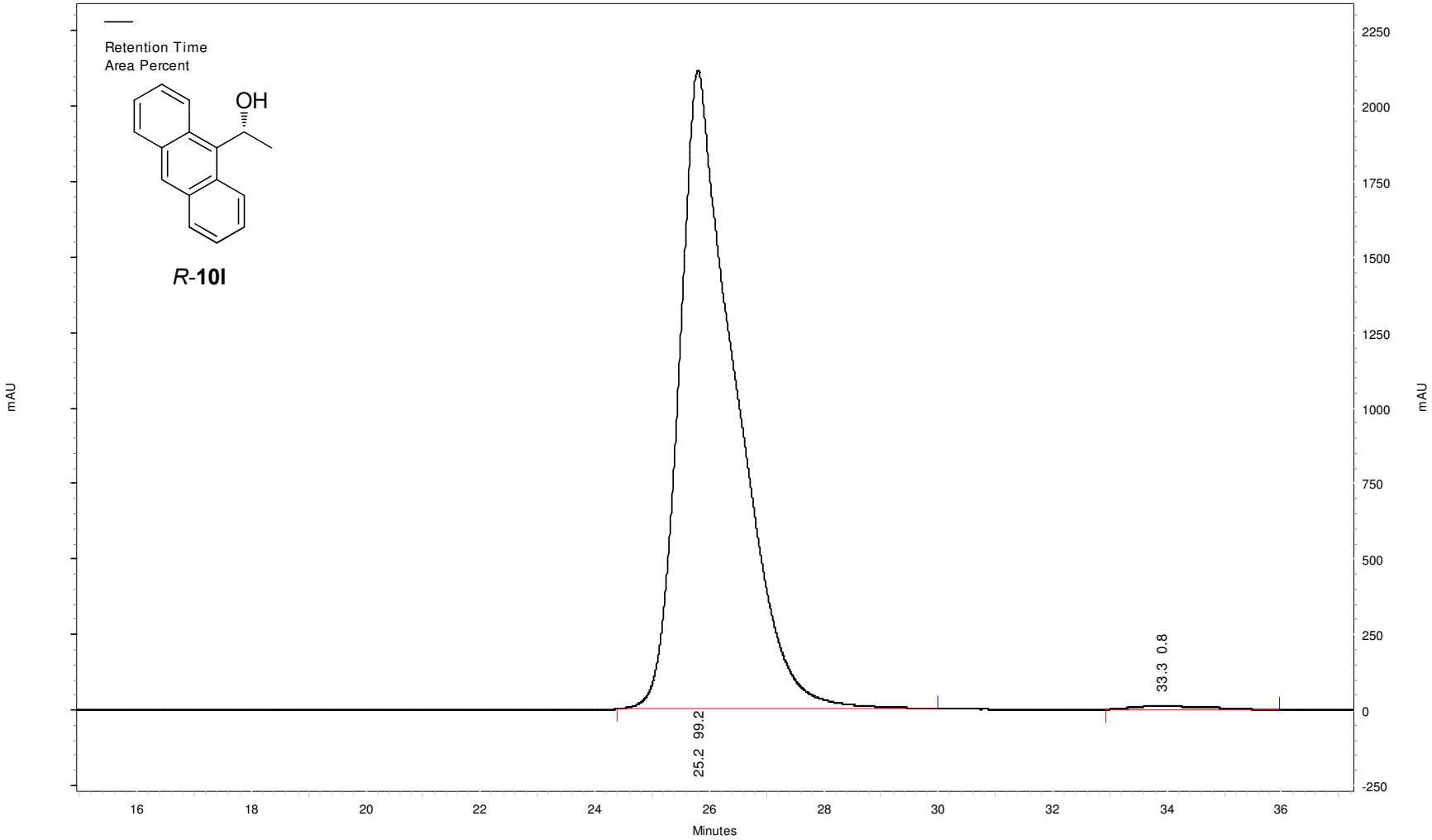
α-Methyl-9-anthracenemethanol (±) 10l entry 12 # 2



VWD 1 Results

Retention Time	Area	Area %	Height	Height %
25.214	19945906	50.03	246240	56.76
33.319	19923132	49.97	187608	43.24

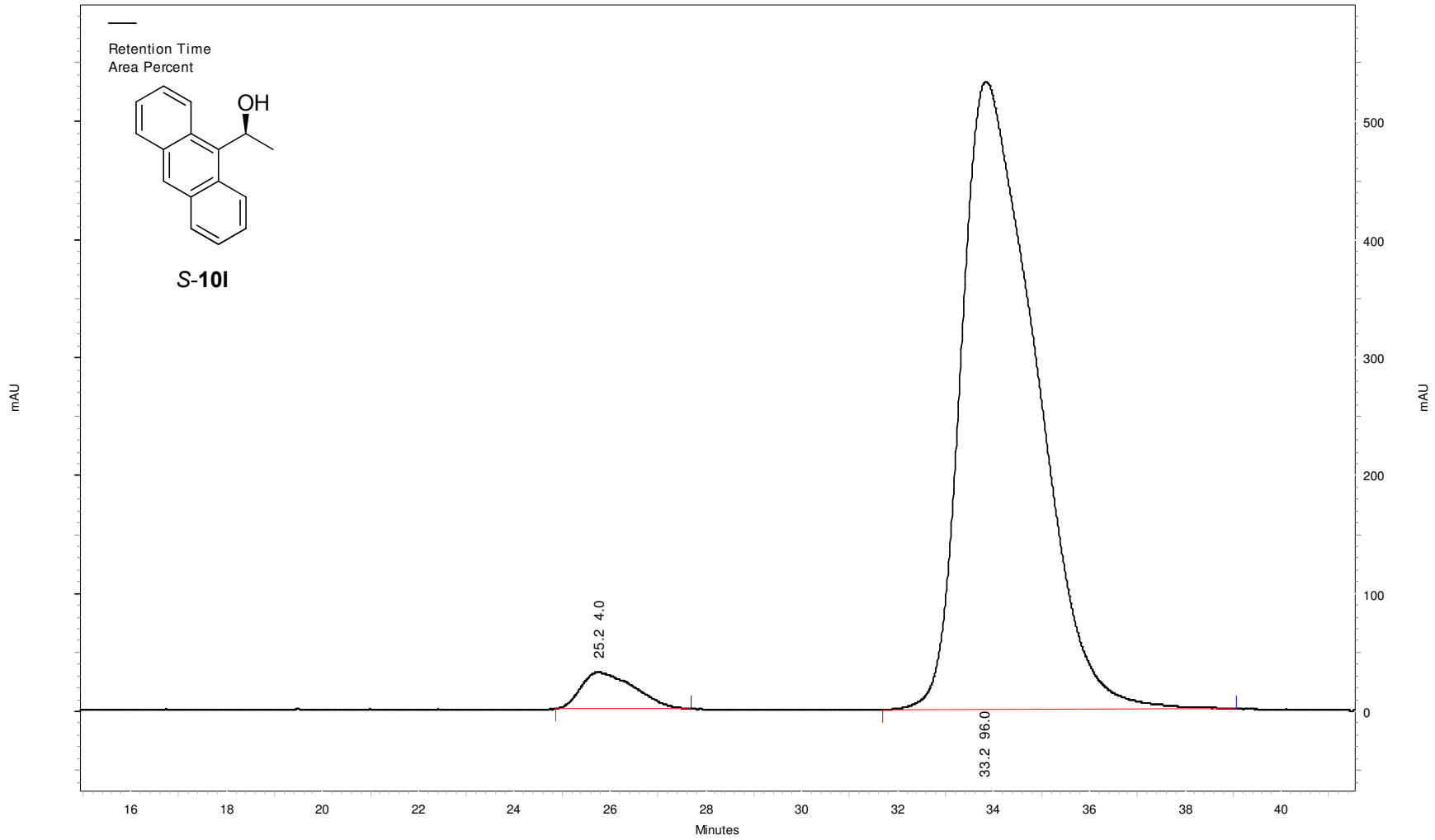
Totals	39869038	100.00	433848	100.00



VWD 1 Results

Retention Time	Area	Area %	Height	Height %
25.199	142914503	99.21	2114242	99.44
33.304	1136334	0.79	12011	0.56

Totals	144050837	100.00	2126253	100.00

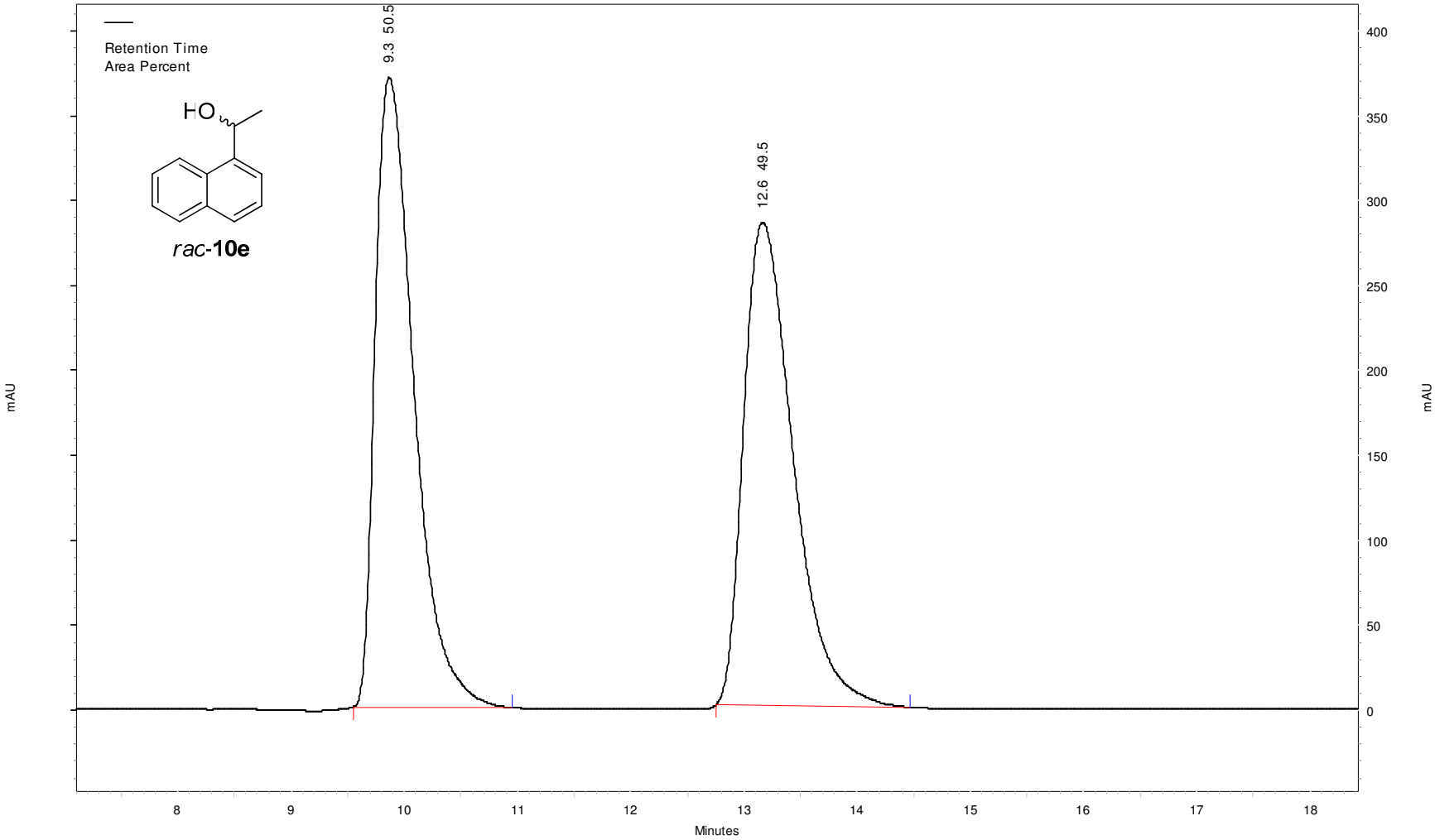


VWD 1 Results

Retention Time	Area	Area %	Height	Height %
25.165	2390133	4.04	31113	5.52
33.222	56712000	95.96	532340	94.48

Totals	59102133	100.00	563453	100.00

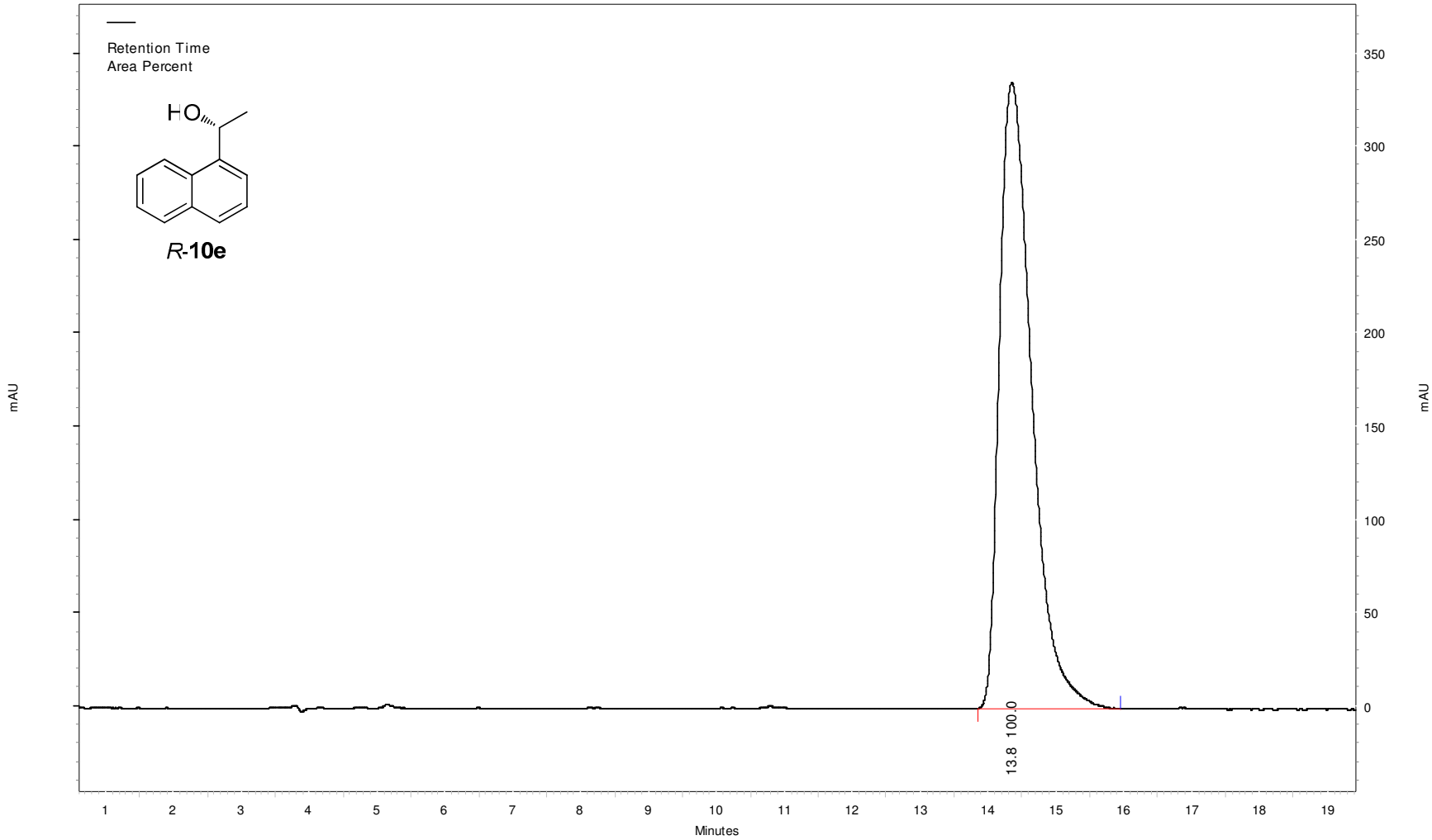
Preparative-scale Catalytic Kinetic Resolution of 1-(1-naphthyl) ethanol (±)-10e



VWD 1 Results

Retention Time	Area	Area %	Height	Height %
9.266	8818117	50.48	370596	56.60
12.566	8651167	49.52	284143	43.40

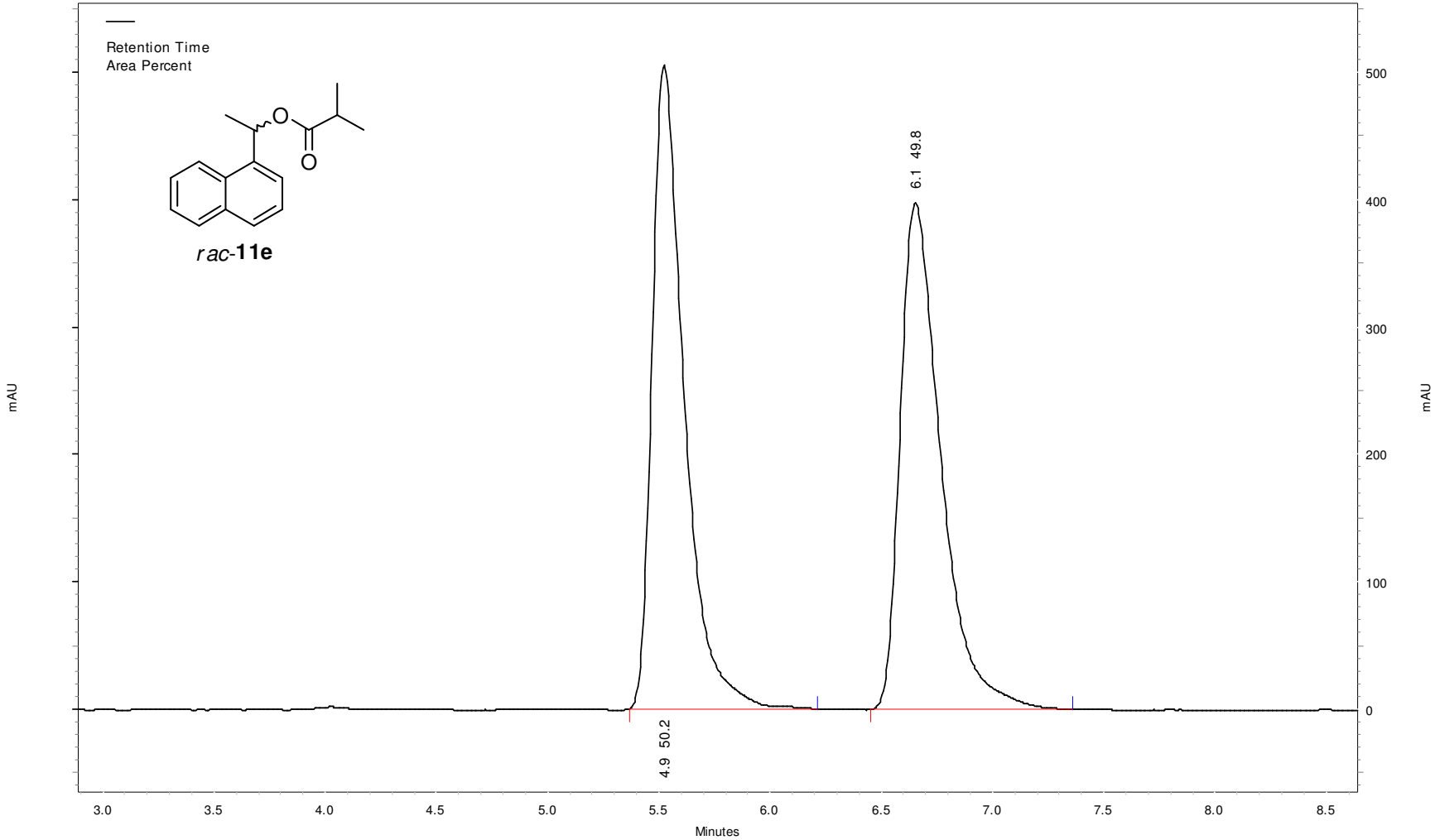
Totals	17469284	100.00	654739	100.00



VWD 1 Results

Retention Time	Area	Area %	Height	Height %
13.751	11072837	100.00	335667	100.00

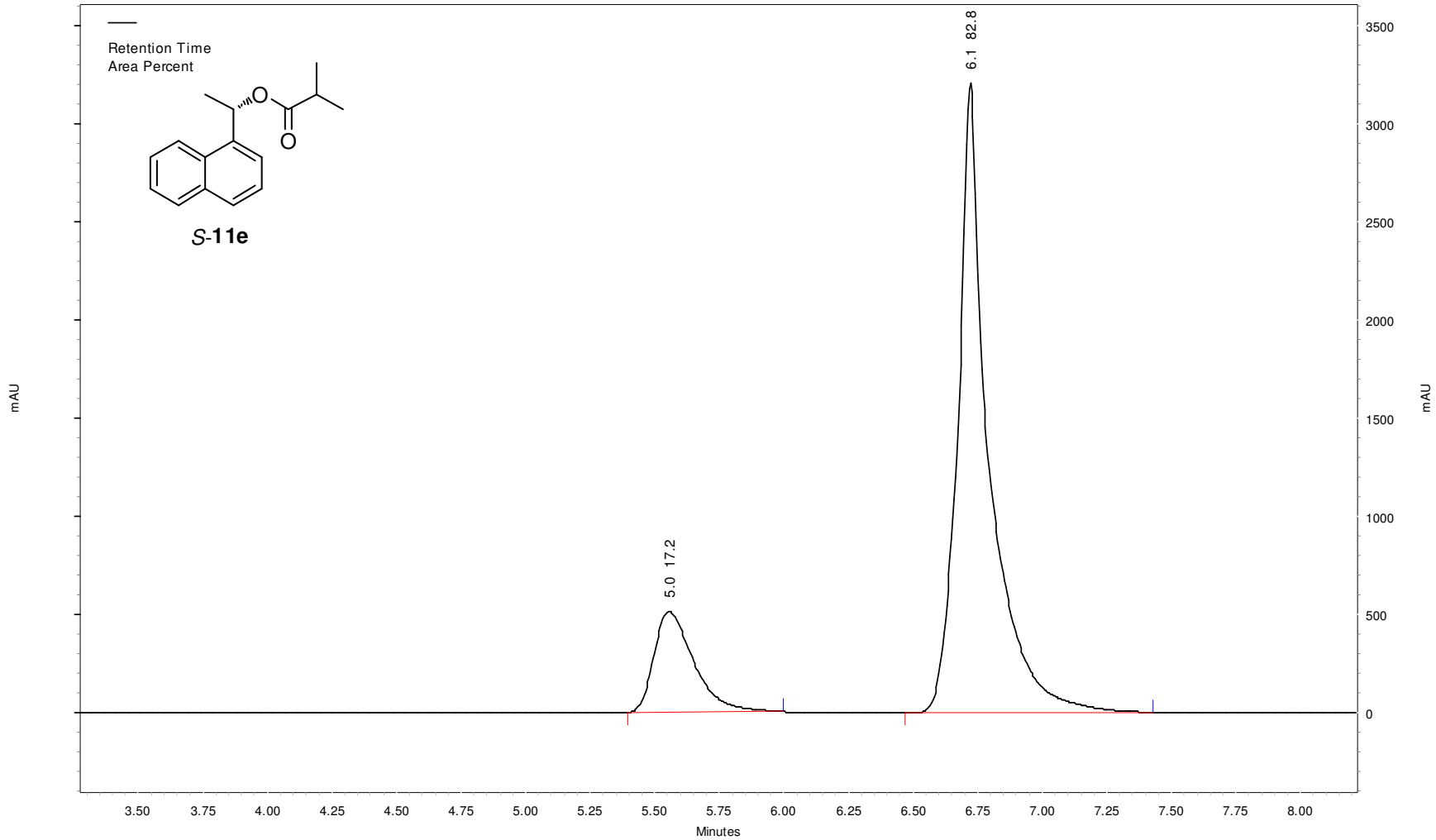
Totals	11072837	100.00	335667	100.00



VWD 1 Results

Retention Time	Area	Area %	Height	Height %
4.922	5084939	50.20	505337	55.97
6.054	5043533	49.80	397472	44.03

Totals	10128472	100.00	902809	100.00



VWD 1 Results

Retention Time	Area	Area %	Height	Height %
4.956	5512107	17.18	514917	13.83
6.122	26568531	82.82	3207583	86.17

Totals	32080638	100.00	3722500	100.00

REFERENCES

(1) Sanyal, A.; Snyder, J. K. *Org. Lett.* **2000**, *16*, 2527.
(2) Kourist, R.; González-Sabín, J.; Liz, R.; Rebolledo, F. *Adv. Synth. Catal.* **2005**, *347*, 695.
(3) Moss, J.; Thomas, J.; Ashley, A.; Cowley, A. R.; O'Hare, D. *Organometallics*, **2006**, *25*, 4279.
(4) (a) Birman, V. B.; Jiang, H. *Org. Lett.* **2005**, 7, 3445 (and references therein). (b) The absolute configuration was assigned by comparison to the commercially available alcohol (Aldrich) (c) The absolute configuration was assigned by comparison to the commercially available alcohol (Ryan Scientific). (d) Yli-Kauhalouma, J.; Finel, M.; Siiskonen, A. *J. Med. Chem.* **2006**, *49*, 1818 (and references therein).