Supplementary data

First Enantioselective Total Synthesis of Altersolanol A

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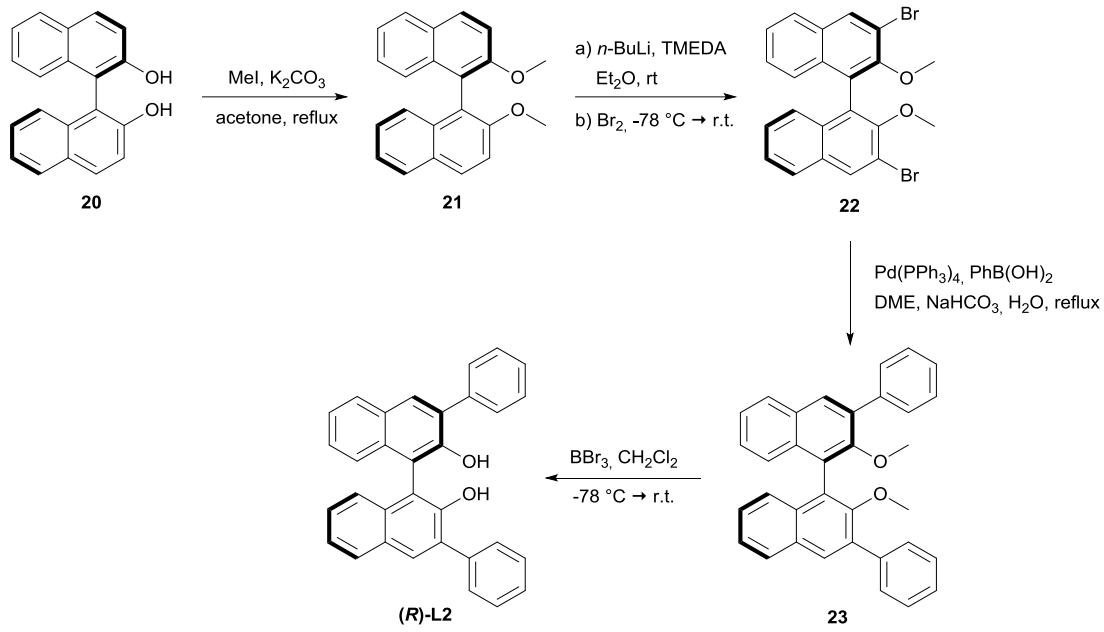
Table of Content

S1. General methods for chemical synthesis procedures

Unless specified, the reactions were carried out by standard *Schlenk*-technique under dry Ar/N_2 and magnetic stirring. All reagents were used as purchased from commercial suppliers without further purification. Glassware was oven-dried at 120 °C overnight. Solvents were dried and purified by conventional methods prior to use. THF and dichloromethane were used directly from a MB SPS-800 (M Braun). Solvents for chromatography (petroleum ether, ethyl acetate, dichloromethane and methanol) were distilled prior to use. Column chromatography was performed on silica gel 60, 0.040-0.063 nm (230-400 mesh). Thin layer chromatography (TLC) was performed on silica gel POLY-GRAM® SIL G/U254 plates (Macherey-Nagel) and was visualized by UV light (254/366 nm UV-lamp) and cerium-molybdate-solution [10 g $Ce(SO_4)_2 \cdot 4 H_2O$, 25 g phosphomolybdic acid, 60 mL conc. H_2SO_4, 940 mL H_2O]. Preparative TLC was performed on precoated TLC plates SIL G-100 UV_{254} (20 cm x 20 cm) (Macherey-Nagel). NMR spectra were recorded on a Bruker Advance DRX/600 spectrometer. ^{1}H-NMR analysis were admitted at 600 MHz and ^{13}C-NMR analysis were measured proton decoupled at 151 MHz. Chemical shifts are reported in ppm relative to residual solvent signals ($CDCl_3$: 7.26 ppm for ^{1}H-NMR and 77.16 ppm for ^{13}C-NMR, DMSO-d_6: 2.50 ppm for ^{1}H-NMR and 39.52 ppm for ^{13}C-NMR, MeOD-d_4: 3.31 ppm for 1H-NMR and 49.0 ppm for^{13}C-NMR). The multiplicity in NMR spectra is given in the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. The enantiomeric excess of the products were determined by HPLC (DIONEX GmbH, Chiralcel ODH, Chiralpak IA, Chiralpak IB, Chiralpak IC columns, flow 0.5 mL min^{-1}, 25°C). High resolution mass spectra were recorded on FT-IR-MS using electrospray ionization (ESI$^+$) at the Heinrich Heine University Dusseldorf (Applied Biosystems/ MDS SCIEXQ Model Trap 4000). GC-MS analysis was performed on a *HP* 6890 gas chromatograph (*Hewlett Packard Inc*) equipped with a HP 6890 series injector and a split injection system, fitted with a HP- ms column (30 m x 0.25 mm, 0.25 µm) and coupled with a mass selective detector 5973 mass spectrometer. Infrared data were recorded on a *Perkin-Elmer SpectrumOne* instrument and *Perkin-Elmer SpectrumTwo* instrument as neat samples. Melting points were measured on a *Büchi Melting Point B-540* instrument. Optical rotations were recorded on an *A. Krüss Optronic* P8000 polarimeter.

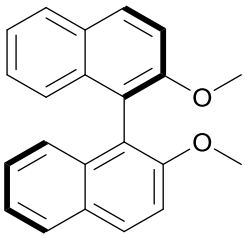
S2. Compound characterization

S2.1 Synthesis procedure of the catalyst (*S*)- and (*R*)-L2



Scheme 1: Synthetic route of 3,3'-Ph_2-BINOL (*S*)- and (*R*)-**L2**.[1-3]

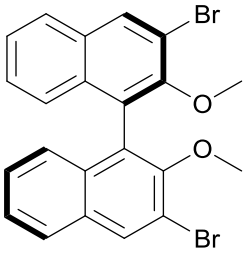
(*R*)-2,2'-Dimethoxy-1,1'-binaphthalene (21)



In a 500 mL flask a solution of (*R*)-BINOL (**20**) (9.00 g, 31.4 mmol), MeI (9.78 mL, 157 mmol) and K_2CO_3 (14.8 g, 107 mmol) in acetone (290 mL) was refluxed under nitrogen atmosphere for 20 h. After full conversion the reaction mixture was cooled to ambient temperature and volatile compounds were removed in vacuo. The resulting white solid was partitioned between water and dichloromethane (200 mL). The layers were then separated, and the aqueous layer was further extracted with dichloromethane (3 x 100 mL). The combined organic extracts were washed with brine (1 x 100 mL) and dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude solid was used without any further purification. The product **21** was isolated as a white crystalline solid (9.10 g, 100%). The spectroscopic data are in agreement with previously reported literature values.[1]

R_f = 0.5 (PE/EE, 80:20); mp 232 °C (in PE); $[\alpha]_D^{20}$ = +50.7 (c = 1.00, $CHCl_3$). δH (600 MHz, $CDCl_3$) 3.77 (s, 6H, OCH_3) 7.11 (d, *J* 8.4 Hz, 2H, arom. H), 7.19-7.25 (m, 2H, arom. H), 7.30-7.34 (m, 2H, arom. H), 7.47 (d, *J* 9.0 Hz, 2H, arom. H), 7.87 (d, *J* 8.2 Hz, 2H, arom. H), 7.98 (d, *J* 9.0 Hz, 2H, arom. H). δC (151 MHz, $CDCl_3$) 57.1 (OCH_3), 114.1 (arom. CH), 119.8 (arom. CH), 123.7 (arom. CH), 125.4 (arom. CH), 126.4 (arom. CH), 128.1 (arom. CH), 129.4 (arom. CH), 129.5 (arom. CH), 134.2 (arom. CH), 155.1 (arom. CH) ppm; ν_{max}/cm^{-1} 3075, 3048, 2958, 2931, 2838, 1615, 1590, 1505,1461, 1322, 1263, 1249, 1148, 1132, 1090, 1063, 1019, 896, 809, 781, 746, 679, 595, 519; GC-MS (EI, 70eV): *m/z* (%) = 314 (100) [M^+], 268 (64), 239 (26), 120 (31).

(*R*)-3,3'-Dibromo-2,2'-dimethoxy-1,1'-binaphthalene (**22**)

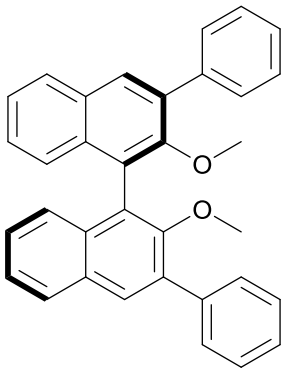


In a 1 L *Schlenk*-flask TMEDA (10.9 mL, 72.5 mmol) was dissolved in ether (540 mL) and *n*-BuLi (c = 1.6 M in hexane, 37.8 mL, 94.6 mmol) was added at room temperature. The solution was stirred for 15 min and (*R*)-2,2'-Dimethoxy-1,1'-binaphthalene (**21**) (9.91 g, 31.5 mmol) was then added in one portion and stirred overnight. The resulting brownish suspension was cooled to -78 °C and bromine (19.4 mL, 378 mmol) was added over a period of 15 min. The reaction mixture was warmed to room temperature and stirred for additional 4 h. A saturated Na_2SO_3 solution (500 mL) was added cautiously and the reaction was stirred for another 4 h. The reaction was diluted with ether (200 mL) then water (200 mL) and the organic layer was washed with brine (100 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The product **22** was purified *via* column chromatography (PE:EE = 90:10) and could be isolated as a light-yellow solid (8.94 g, 60%). The spectroscopic data are in agreement with previously reported literature values.[2]

R_f = 0.6 (PE/EE, 90:10); mp 173 °C (in PE); $[\alpha]_D^{25}$ +11.4 (c 1.01 in $CHCl_3$); δH (600 MHz, $CDCl_3$) 3.51 (s, 6H, OCH_3) 7.08 (d, *J* 8.6 Hz, 2H, arom. H), 7.26-7.29 (m, 2H, arom. H), 7.41-7.44 (m, 2H, arom. H), 7.82 (d, *J* 8.2 Hz, 2H, arom. H), 8.27 (s, 2H, arom. H) ppm; δC (151 MHz, $CDCl_3$) 61.2

(OCH_3), 117.7 (arom. CH), 125.9 (arom. CH), 126.0 (arom. CH), 126.7 (arom. CH), 127.0 (arom. CH), 127.3 (arom. CH), 131.6 (arom. CH), 133.2 (arom. CH), 133.3 (arom. CH), 152.7 (arom. CH) ppm; ν_{max}/cm^{-1} 2939, 1570, 1493, 1456, 1388, 1352,1233, 1138, 1045, 1021, 976, 900, 878, 850, 806, 751, 675, 605, 584, 516, 466; GC-MS (EI, 70eV): *m/z* (%) = 472 (100) [M^+], 426 (21), 361 (23), 239 (27), 156 (36), 118 (48), 112 (35).

(*R*)-2,2'-Dimethoxy-3,3'-diphenyl-1,1'-binaphthalene (**23**)

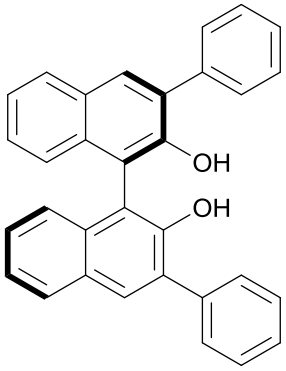


In a 250 mL *Schlenk*-flask (*R*)-3,3'-Dibromo-2,2'-dimethoxy-1,1'-binaphthalene (**22**) was dissolved in 1,2-dimethoxyethane (94 mL) and $Pd(PPh_3)_4$ (1.44 g, 1.24 mmol) was added in one portion thereafter. After the reaction mixture was stirred for 30 min phenylboronic acid (5.56 g, 45.5 mmol) and aqueous $NaHCO_3$ (10.4 g in 122 ml water) were added. The resulting suspension was then refluxed for 18 h. The conversion was measured *via* ^{1}H-NMR. The reaction mixture formed a colourless solution with a brownish residue and was cooled to room temperature. Once cool ethyl acetate (100 mL) was added and layers were partitioned. The organic layer was washed with brine (50 mL), dried with $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was then transferred to a silica column (PE:EE = 97:3) and product **23** could be isolated as a colourless solid (9.42 g, 97%). The spectroscopic data are in agreement with previously reported literature values.[3]

R_f = 0.4 (PE/EE, 97:3); mp 99 °C (in PE); $[\alpha]_D^{20}$ -0.3 (c 1.00 in $CHCl_3$); δH (600 MHz, $CDCl_3$) 3.19 (s, 6H, OCH_3), 7.23-7.28 (m, 6H, arom. H), 7.37-7.43 (m, 4H, arom. H), 7.44-7.47 (m, 4H, arom. H), 7.76-7.79 (m, 4H, arom. H), 7.92 (d, *J* 8.2 Hz, 2H, arom. H), 7.98 (s, 2H, arom. H) ppm; δC (151 MHz, $CDCl_3$) 60.7 (OCH_3), 125.1 (arom. CH), 126.0 (arom. CH), 126.1 (arom. CH), 126.4 (arom. CH), 127.4 (arom. CH), 128.2 (arom. CH), 128.5 (arom. CH), 129.5 (arom. CH), 130.7

(arom. CH), 131.0 (arom. CH), 133.8 (arom. CH), 135.2 (arom. CH), 139.1 (arom. CH), 154.3 (arom. CH) ppm; ν_{max}/cm^{-1} 3056, 2931, 1492, 1459, 1443, 1403, 1350, 1248, 1216, 1143, 1041, 1016, 890, 749, 697, 620, 541, 508; GC-MS (EI, 70eV): *m/z* (%) = 466 (100) [M$^+$], 420 (27).

(*R*)-3,3'-Diphenyl-[1,1'-binaphthalene]-2,2'-diol ((*R*)-L2)

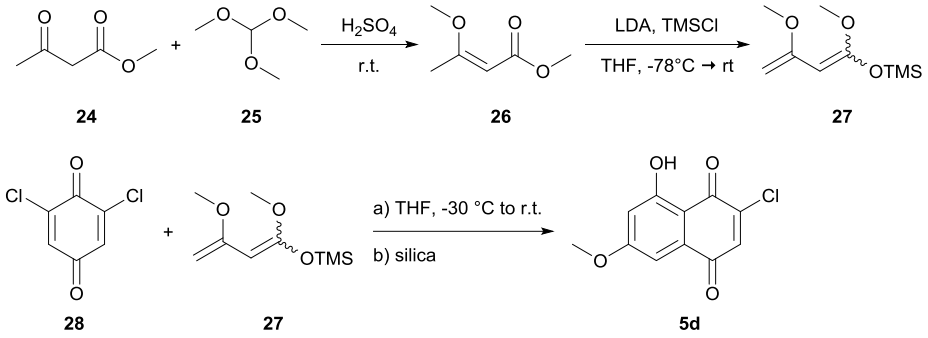


In a 500 mL *Schlenk*-flask **23** (9.42 g, 20.2 mmol) was dissolved in CH_2Cl_2 (280 mL) and BBr_3 (1M solution in CH_2Cl_2, 72.7 mL, 72.7 mmol) at -78 °C was added. The reaction mixture was warmed to room temperature, stirred for 16h and quenched with water (170 mL) with external ice bath cooling. The organic phase was separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 100 mL). The combined organic layers were washed with brine (100 mL), dried with $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by column chromatography (PE:EE = 90:10) and product (*R*)-**L2** could be isolated as a colourless solid (8.08 g, 91%, 99.5:0.5 er). The spectroscopic data are in agreement with previously reported literature values.[3]

R_f = 0.3 (PE/EE, 90:10). mp 196 °C (in PE); $[\alpha]_D^{24}$ +73.1 (c 1.00 in $CHCl_3$, 99:1 er), δH (600 MHz, $CDCl_3$) 5.35 (s, 2H, 2-OH), 7.24 (d, *J* 8.6 Hz, 2H, arom. H), 7.31-7.35 (m, 4H, arom. H), 7.38-7.43 (m, 4H, arom. H), 7.48-7.52 (m, 4H, arom. H), 7.74 (d, *J* 7.5 Hz, 2H, arom. H), 7.93 (d, *J* 8.0 Hz, 2H, arom. H), 8.03 (s, 2H, arom. H) ppm; δC (151 MHz, $CDCl_3$) 112.6 (arom. CH), 124.1 (arom. CH), 124.5 (arom. CH), 127.5 (arom. CH), 127.9 (arom. CH), 128.6 (arom. CH), 128.6 (arom. CH), 129.6 (arom. CH), 129.8 (arom. CH), 130.9 (arom. CH), 131.5 (arom. CH), 133.1 (arom. CH), 137.7 (arom. CH), 150.3 (arom. CH) ppm; ν_{max}/cm^{-1} 3484, 3392, 3056, 1624, 1495, 1426, 1382, 1367, 1318, 1235, 1128, 1077, 894, 786, 766, 748, 702, 684, 617, 552, 492; GC-MS (EI, 70eV): *m/z* (%) = 472 (100) [M$^+$], 426 (21), 361 (23), 239 (27), 156 (36), 118 (48), 112 (35). HRMS (ESI, positive-ion): calc.: 439.1698 ($C_{32}H_{23}O_2$) [(M+H)$^+$], found: 439.1688; HPLC column:

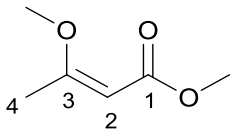
Chiralpak IC (250 mm· 46 mm, Fa. Daicel); solvent: heptane/2-propanol = 90:10; flowrate: 0.5 mL/min, detection: 249 nm; t_R [(*R*)-**2**] 16.3 min; t_R [(*S*)-**2**] 10.5 min.

S2.2 Synthesis of dienophile 5d



Scheme 2: Synthesis of dienophile **5d**.

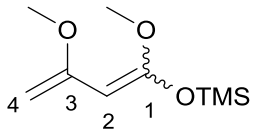
Methyl (*Z*/*E*)-3-methoxybut-2-enoate (26)



In a 250 mL *Schlenk*-flask methyl acetoacetate (**24**) (55.6 mL, 517 mmol), trimethyl orthoformate (**25**) (56.6 mL, 517 mmol) and a catalytic amount (18 drops) of conc. H_2SO_4 were added and the reaction mixture was stirred for 18 h at room temperature. GC-MS was used for reaction monitoring and after full conversion, 12 drops of quinoline were added and stirred for 30 min. Afterwards the crude liquid was purified by vacuum distillation and product **26** was isolated as a colourless liquid (61.6 g, 92%). The spectroscopic data are in agreement with previously reported literature values.[4]

bp 87-90 °C (69 mbar); δH (600 MHz, $CDCl_3$) 2.28 (s, 3H, 4-H), 3.62 (s, 3H, 3-OCH_3), 3.67 (s, 3H, 1-OCH_3), 5.01 (s, 1H, 2-H) ppm; δC (151 MHz, $CDCl_3$) 19.0 (C-1), 50.9 (1-OCH_3), 55.5 (3-OCH_3), 90.6 (C-2), 168.4 (C-1), 173.4 (C-3) ppm; ν_{max}/cm^{-1} 2950, 2844, 1711, 1623, 1436, 1393, 1349, 1276, 1228, 1193, 1136, 1049, 927, 815, 741; GC-MS (EI, 70 eV): t_R = 8.3 min, m/z (%) 130 (26) [$M+H^+$], 99 (100) [$(M-CH_3)^+$], 69 (13), 59 (29) [$(M-C_4H_7O)^+$].

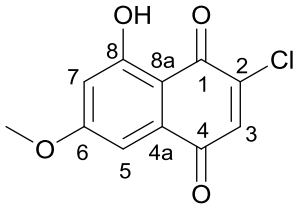
((1,3-Dimethoxybuta-1,3-dien-1-yl)oxy)trimethylsilane 27



In a 50 mL *Schlenk*-tube diisopropylamine (3.24 mL, 23.0 mmol) was dissolved in THF (13 mL), cooled to -78 °C and *n*-BuLi (c = 2.5 M in hexane, 9.20 mL, 23.1 mmol) was added. After 15 min methyl (*Z*/*E*)-3-methoxybut-2-enoate (**26**) (2.50 g, 19.2 mmol) was added and stirred for an additional hour. Afterwards at -78 °C, TMSCl (3.00 mL, 23.5 mmol) was added and the reaction mixture was warmed to room temperature and stirred for 1 h. Then THF was evaporated under reduced pressure and the residue was resolved in *n*-pentane (50 ml), extracted with a water:$NaHCO_3$-solution (1:1,1 x 50 mL) and the organic layer was dried with $MgSO_4$, filtered and the solvent was evaporated. The product **27** was obtained as a yellow oil (3.73 g, 95%) and was used without further purification. The product can be stored at -20 °C without decomposition. The spectroscopic data are in agreement with previously reported literature values.[4]

δH (600 MHz, $CDCl_3$) 0.25 (s, 9H, $OSi(CH_3)_3$), 3.56 (s, 3H, OCH_3), 3.57 (s, 3H, OCH_3), 3.98 (dd, $^2J_{4Hb,4Ha}$ 1.8 Hz, $^4J_{4Hb,2}$ 1.5 Hz, 1H, 4-Hb), 4.31 (d, $^4J_{2,4Hb}$ 1.5 Hz, 1H, 2-H), 4.35 (d, $^2J_{4Ha,4Hb}$ 1.3 Hz, 1H, 4-Ha) ppm; δC (151 MHz, $CDCl_3$) 0.5 ($Si(CH_3)_3$), 54.3 (OCH_3), 55.2 (OCH_3), 75.7 (C-2), 78.8 (C-4), 158.9 (C-1), 158.9 (C-1) ppm, ν_{max}/cm^{-1} 2996, 2960, 2903, 2841, 1656, 1630, 1442, 1389, 1351, 1266, 1252, 1200, 1167, 1095, 965, 841, 778, 759, 698, 634, 575, 464; GC-MS (EI, 70 eV): t_R = 7.7 min, m/z (%) = 187 (89) [$(M\text{-}CH_3)^+$], 171 (86) [$(M\text{-}OCH_3)^+$], 98 (72) [$C_5H_6O_2^{2+}$], 89 (75) [$OTMS^+$], 73 (100), 67 (52).

2-Chloro-8-hydroxy-6-methoxynaphthalene-1,4-dione 5d



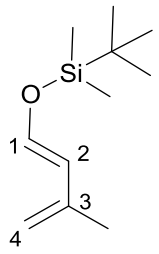
In a *Schlenk*-tube 2,6-dichloro-1,4-benzoquinone (**28**) (796 mg, 4.50 mmol) was dissolved in THF (41 mL) and cooled to -30 °C. A solution of diene **27** (1.00 g, 4.95 mmol) in THF (10 mL)

was added over a period of 30 min and stirred for 1 h. The reaction solution was then warmed to room temperature and stirred overnight. The reaction mixture was transferred to a 500 mL round bottom flask and 100 g of silica was added. The THF was evaporated under reduced pressure and a yellow residue was let stand overnight. The silica was then washed with acetone, concentrated and the residue was purified by column chromatography (CH_2Cl_2:*n*-pentane = 50:50). The product **5d** was obtained as an orange solid (507 mg, 47%). The spectroscopic data are in agreement with previously reported literature values.[5]

R_f = 0.3 (CH_2Cl_2:*n*-pentane = 50:50); mp 177 °C (in CH_2Cl_2); δH (600 MHz, $CDCl_3$) 3.92 (s, 3H, OCH_3), 6.66 (d, $^4J_{7,5}$ 2.5 Hz, 1H, 7-H), 7.13 (s, 1H, 3-H), 7.18 (d, $^4J_{5,7}$ 2.5 Hz, 1H, 3-H), 11.91 (s, 1H, 8-OH) ppm; δC (151 MHz, $CDCl_3$) 56.4 (OCH_3), 106.3 (C-7), 109.5 (C-8a), 109.1 (C-5), 133.5 (C-2), 136.3 (C-3), 146.8 (C-4a), 165.2 (C-8), 168.9 (C-6), 181.0 (C-4), 181.9 (C-1) ppm; ν_{max}/cm^{-1} 3051, 1659, 1629,1574, 1593, 1504, 1430, 1390, 1309, 1286, 1257, 1239, 1202, 1181, 1136, 1081, 1003, 891, 860, 847, 808, 761, 689. HRMS (ESI, positive-ion): calc.: 236.9960 ($C_{11}H_6O_4Cl$) [$(M+H)^+$], found: 236.9961.

S2.3 Synthesis of diene 6d

(*E*)-1-(*tert*-Butyldimethylsilyl)oxy-3-methyl-buta-1,3-butadiene 6d



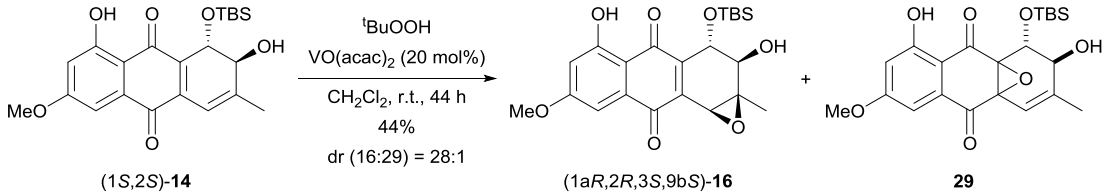
In a 100 mL *Schlenk*-flask 3-methylbut-2-enal (5.00 ml, 51.8 mmol) and TBSCl (11.7 g, 77.8 mmol) were dissolved in acetonitrile (50 mL) and NaI (12.4 g, 82.9 mmol) and Et_3N (11.6 mL, 82.9 mmol) were added. The reaction was stirred at room temperature under a nitrogen atmosphere and ^{1}H-NMR was used to monitor the reaction (18 h). The reaction mixture was extracted with *n*-pentane (3 x 100 mL), the combined organic layers were washed with saturated $NaCO_3$ (2 x 50 mL), dried over $MgSO_4$ and filtered. The filtrates volume was then evaporated. The residue was distilled under reduced pressure and product **6d** was isolated as a clear colourless oil (8.25 g, 80 %). The spectroscopic data are in agreement with previously reported literature values.[6]

bp 83 °C (15 mbar); δH (600 MHz, $CDCl_3$) 0.16 (s, 6H, $Si(CH_3)_2$), 0.93 (s, 9H, $SiC(CH_3)_3$), 1.80 (s, 3H, 3-CH_3), 4.67 (m_c, 1H, 4-H_a), 4.74 (m_c, 1H, 4-H_b), 5.82 (d, $^3J_{2,1}$ 12.4 Hz, 1H, 2-H), 6.53 (d, $^3J_{1,2}$ 12.4 Hz, 1H, 1-H) ppm; δC (151 MHz, $CDCl_3$) -5.1 ($Si(CH_3)_2$), 18.5 (SiC), 19.2 (3-CH_3), 25.8 (($SiC(CH_3)_3$), 111.9 (C-4), 116.3 (C-2), 140.0 (C-3), 142.4 (C-1) ppm; ν_{max}/cm^{-1} 2955, 2930, 2887, 2859, 1644, 1606, 1472, 1463, 1390, 1362, 1253, 1168, 1071, 1006, 922, 870, 828, 779, 670. GC-MS (EI, 70 eV): t_R = 6.4 min, m/z (%) = 198 (26) [M^+], 141 (M-C_4H_9) (100), 127 (22), 113 (17), 101 (34), 75 (52), 59 (24).

S2.4 Further Epoxidation experiments

To improve the diastereomeric ratio in the epoxidation procedure, we first tested the classical Sharpless reaction.[7] Under the reported reaction conditions (1*S*,2*S*)-**14** led to decomposition and no products could be observed.

Next, we used the vanadium-catalysed epoxidation reaction ($VO(acac)_2$/^{t}BuOOH-system), which is known as a selective *cis*-epoxidation reagent for pseudo-axial allylic alcohols (Scheme 3).[8]



Scheme 3: Epoxidation of (1*S*,2*S*)-**14** *via* $VO(acac)_2$/^{t}BuOOH-system.

In a 20 mL *Schlenk*-flask allyl alcohol (1*S*,2*S*)-**14** (40.0 mg, 96.0 µmol, 1.00 equiv.) was dissolved in CH_2Cl_2 (2 mL) and vanadyl acetylacetonate (5.01 mg, 19.2 µmol, 0.20 equiv.) and ^{t}BuOOH (5.5 M in dodecane, 17.5 µL, 10.7 µmol, 1.00 equiv.) was added and the reaction mixture was stirred at room temperature for 44 h. After full conversion 10-(w/w)-% $NaHSO_3$ (20 mL) and sat. $NaHCO_3$ was added and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL) and the combined organic layer were dried over $MgSO_4$, filtered and the crude product was purified *via* column chromatography (PE:EE = 80:20) and the product was isolated as yellow solid (18.2 mg, 42.1 µmol, 44%).

The analytical data were in agreement with (1a*R*,2*R*,3*S*,9b*S*)-**16** reported in the article. The yield is the same as reported with the *m*CPBA procedure that there is no advantage for the

vanadium-catalysed reaction procedure. Also, ^{t}BuOOH is that reactive that an attack of the benzoquinone double bond takes place and epoxide **29** can be observed without known absolute configuration of the epoxide.

S3. Notes and References

1. P. Wipf and J.-K. Jung, *J. Org. Chem.*, 2000, **65**, 6319-6337.
2. D. S. Lingenfelter, R. C. Helgeson and D. J. Cram, *J. Org. Chem.*, 1981, **46**, 393-406.
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5. J. P. Gesson, J. C. Jacquesy and B. Renoux, *Tetrahedron Lett.*, 1983, **24**, 2761-2764.
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8. K. Kaneda, Y. Kawanishi, K. Jitsukawa and S. Teranishi, *Tetrahedron Lett.*, 1983, **24**, 5009-5010.

S4. NMR spectra of compounds

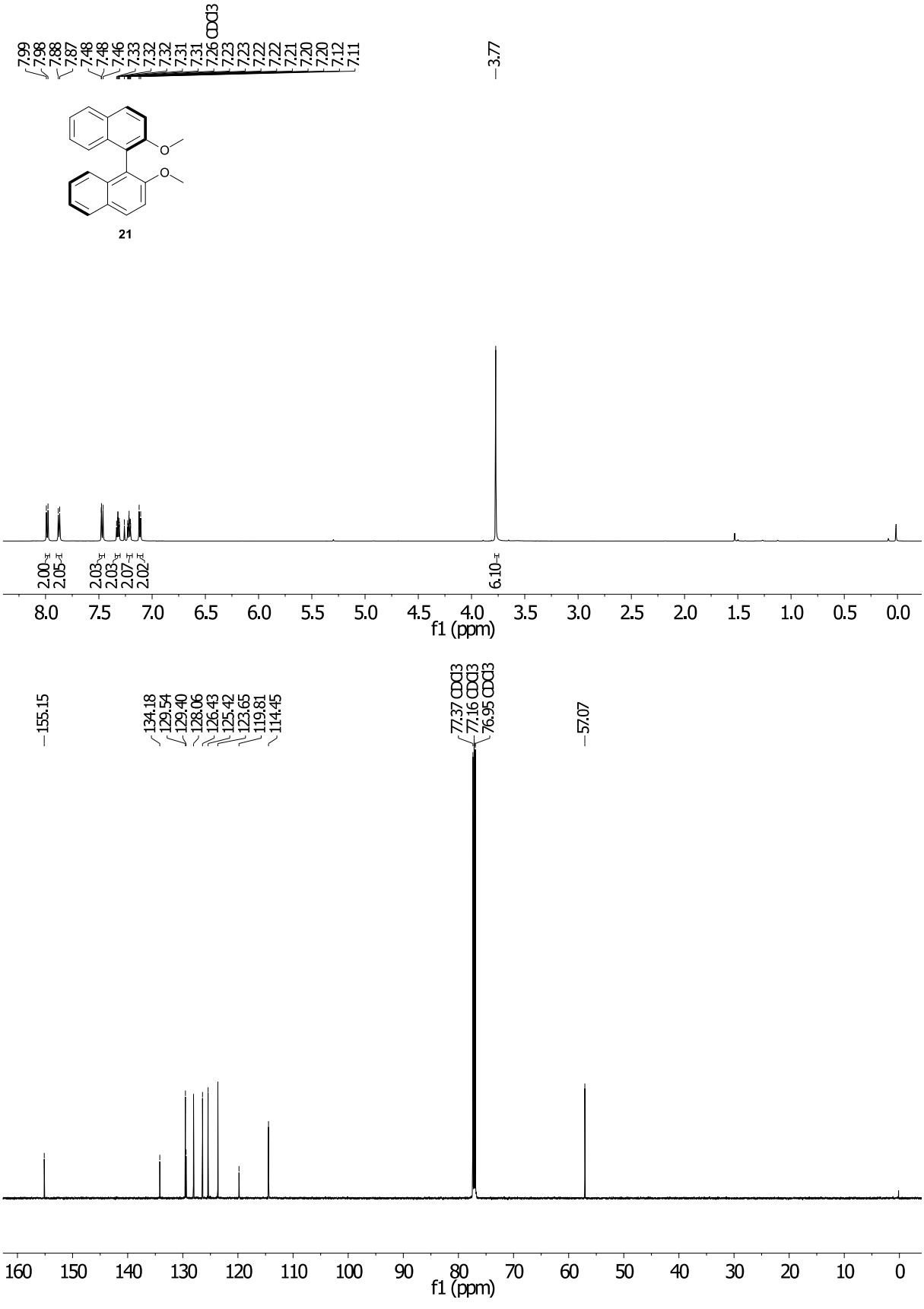


Figure 1: ^{1}H and ^{13}C-NMR-Spectra of **21** in $CDCl_3$ (600 MHz/151 MHz).

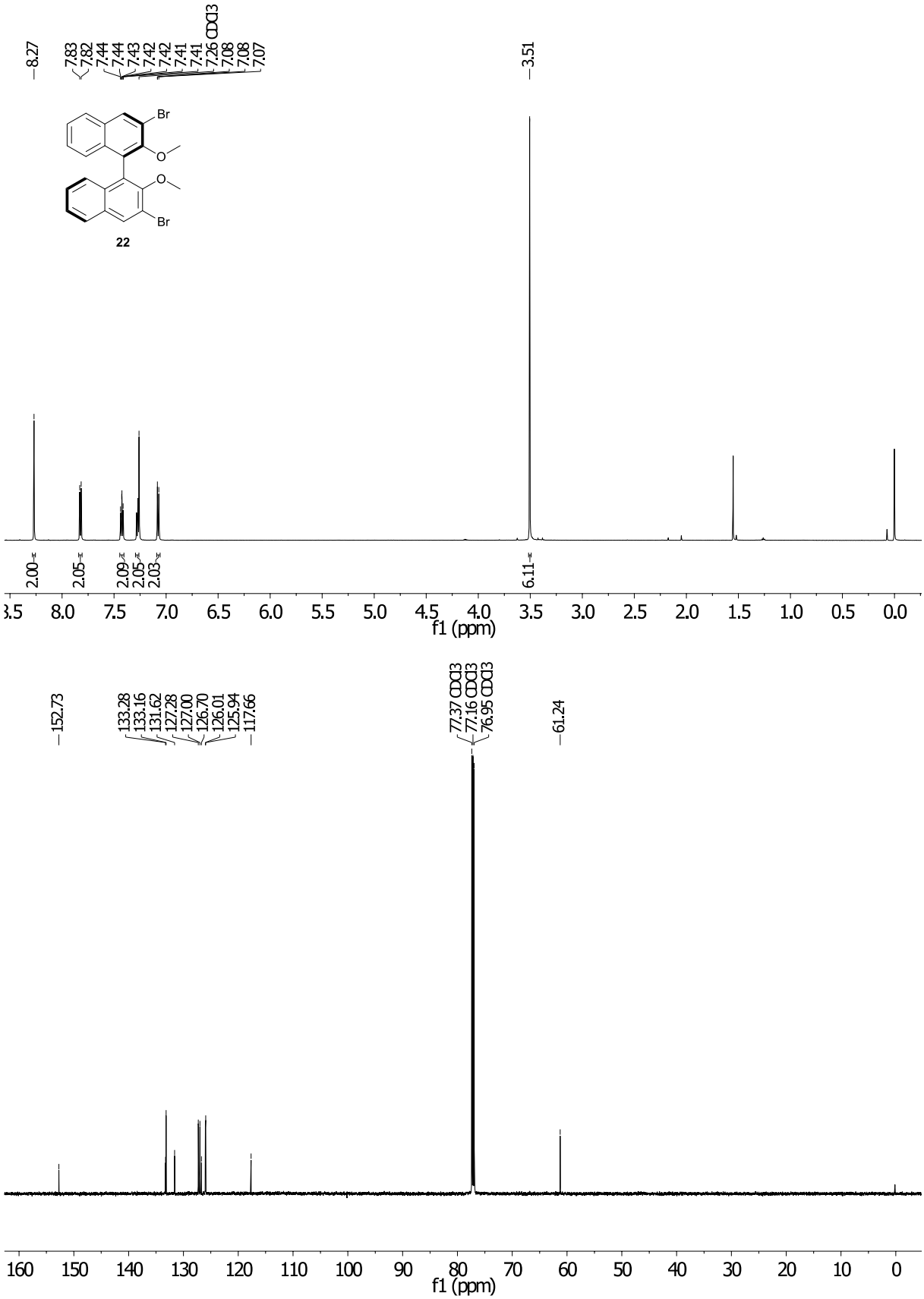


Figure 2: ^{1}H and ^{13}C-NMR-Spectra of **22** in $CDCl_3$ (600 MHz/151 MHz).

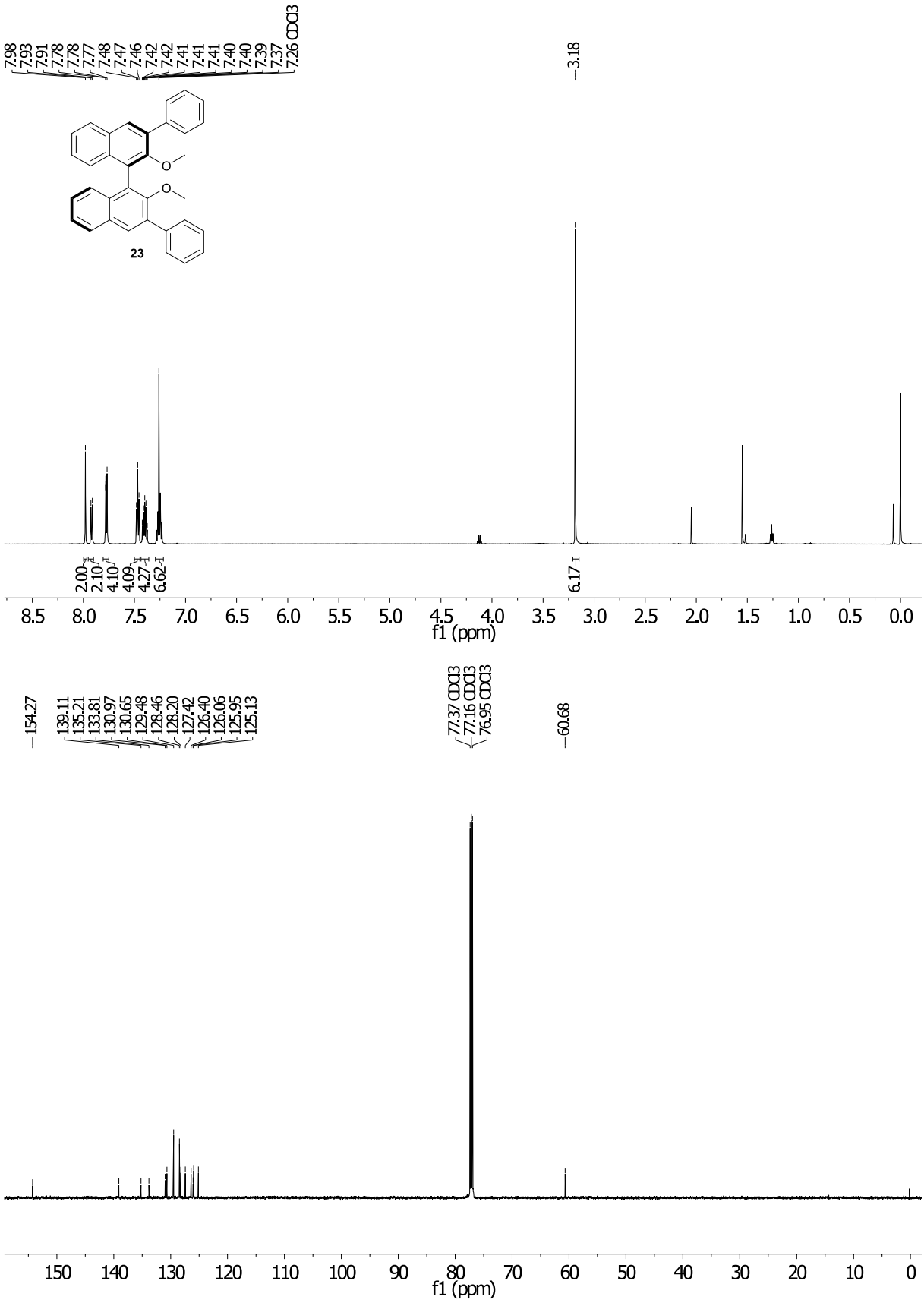


Figure 3: ^{1}H and ^{13}C-NMR-Spectra of **23** in $CDCl_3$ (600 MHz/151 MHz).

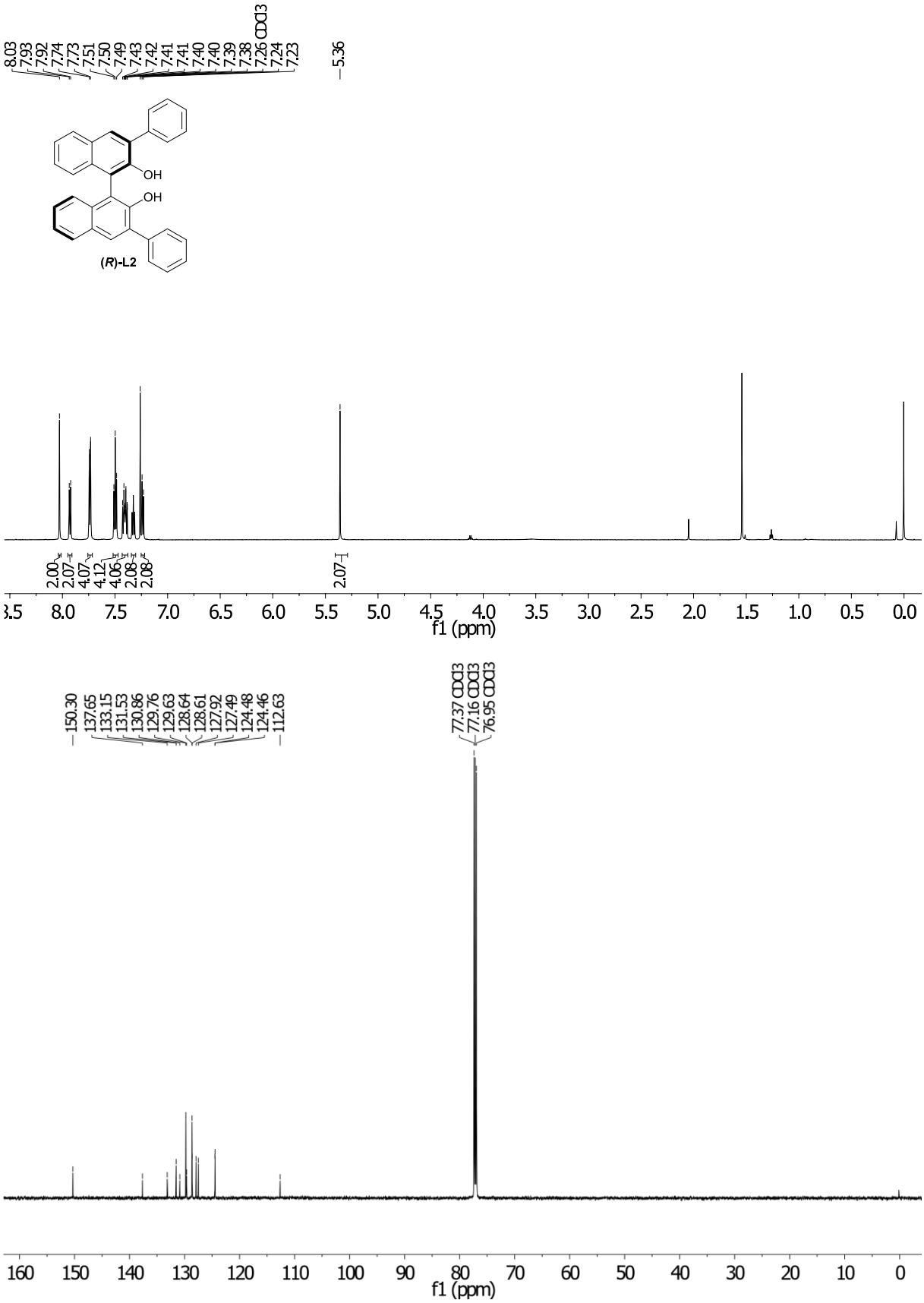


Figure 4: ^{1}H and ^{13}C-NMR-Spectra of ***(R)*-L2** in $CDCl_3$ (600 MHz/151 MHz).

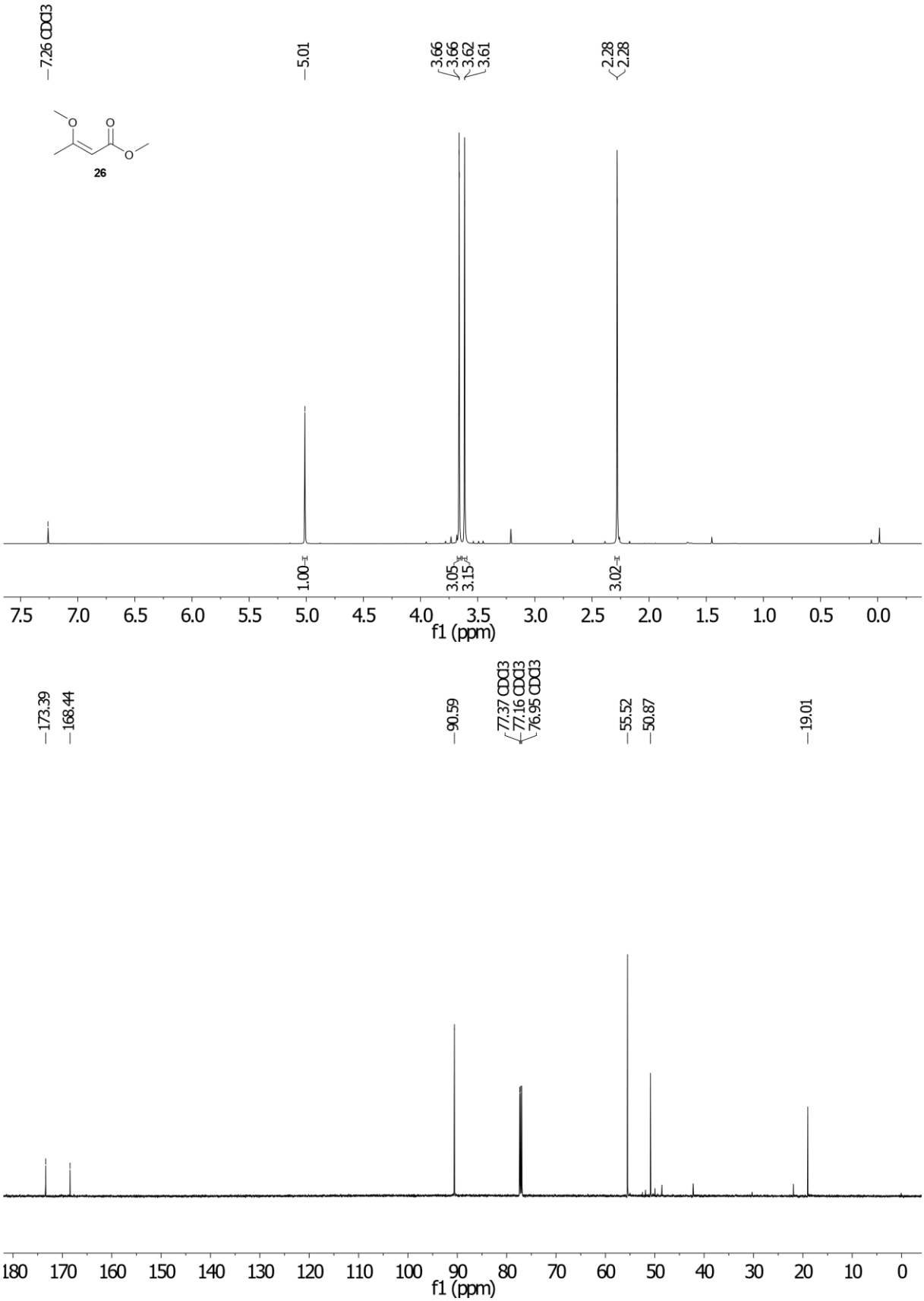


Figure 5: ^{1}H and ^{13}C-NMR-Spectra of **26** in $CDCl_3$ (600 MHz/151 MHz).

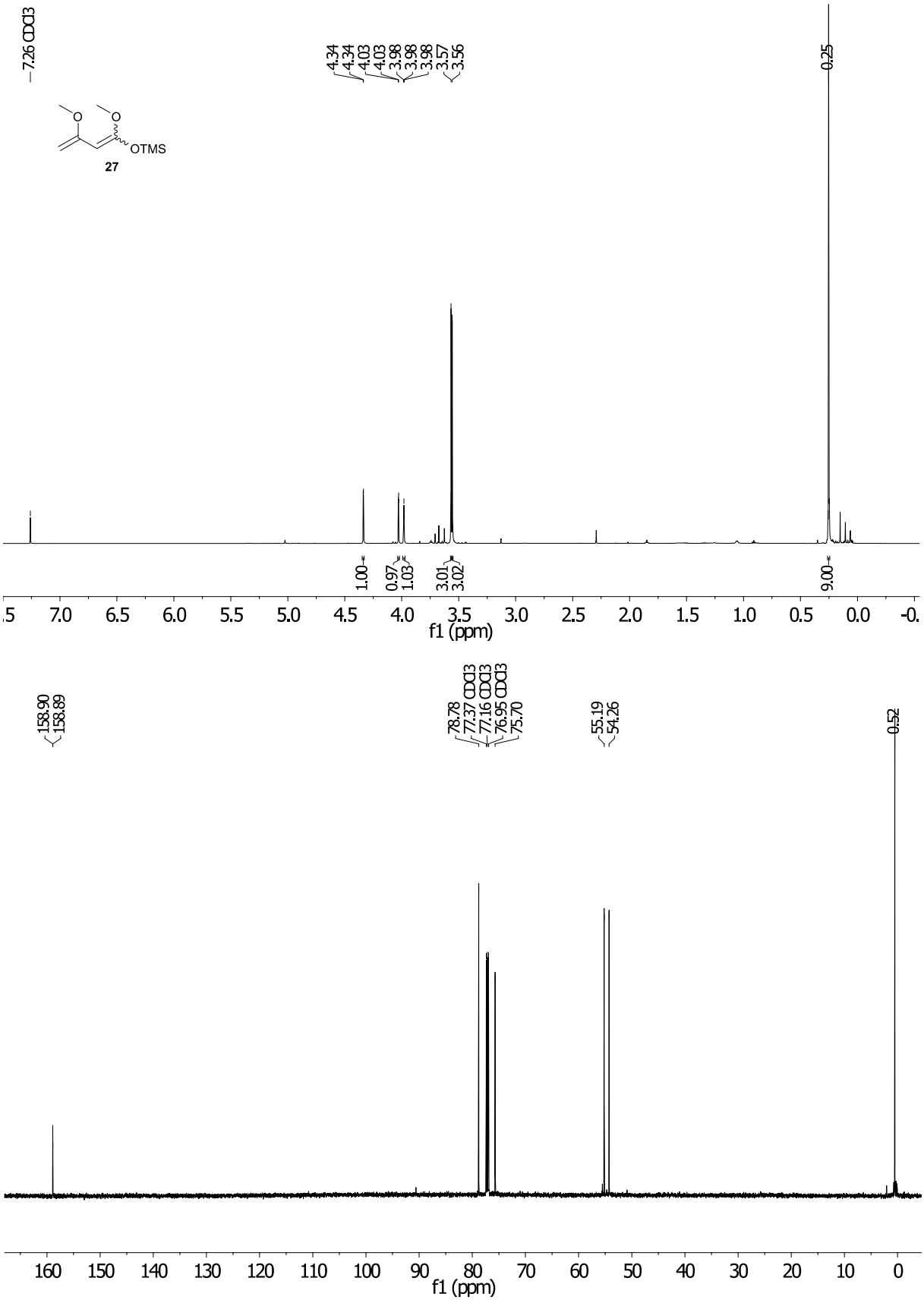


Figure 6: ^{1}H and ^{13}C-NMR-Spectra of **27** in $CDCl_3$ (600 MHz/151 MHz).

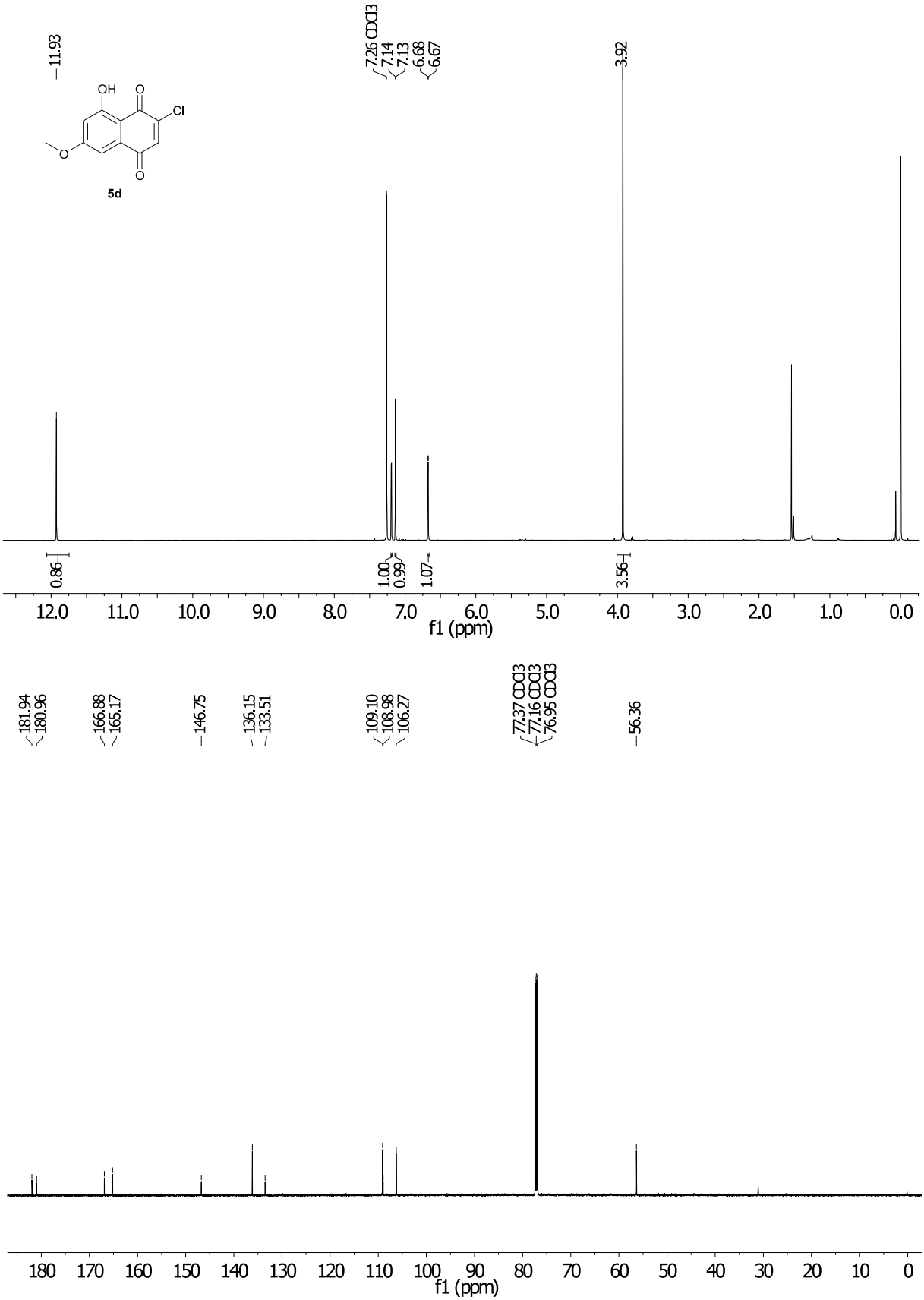


Figure 7: ^{1}H and ^{13}C-NMR-Spectra of **5d** in $CDCl_3$ (600 MHz/151 MHz).

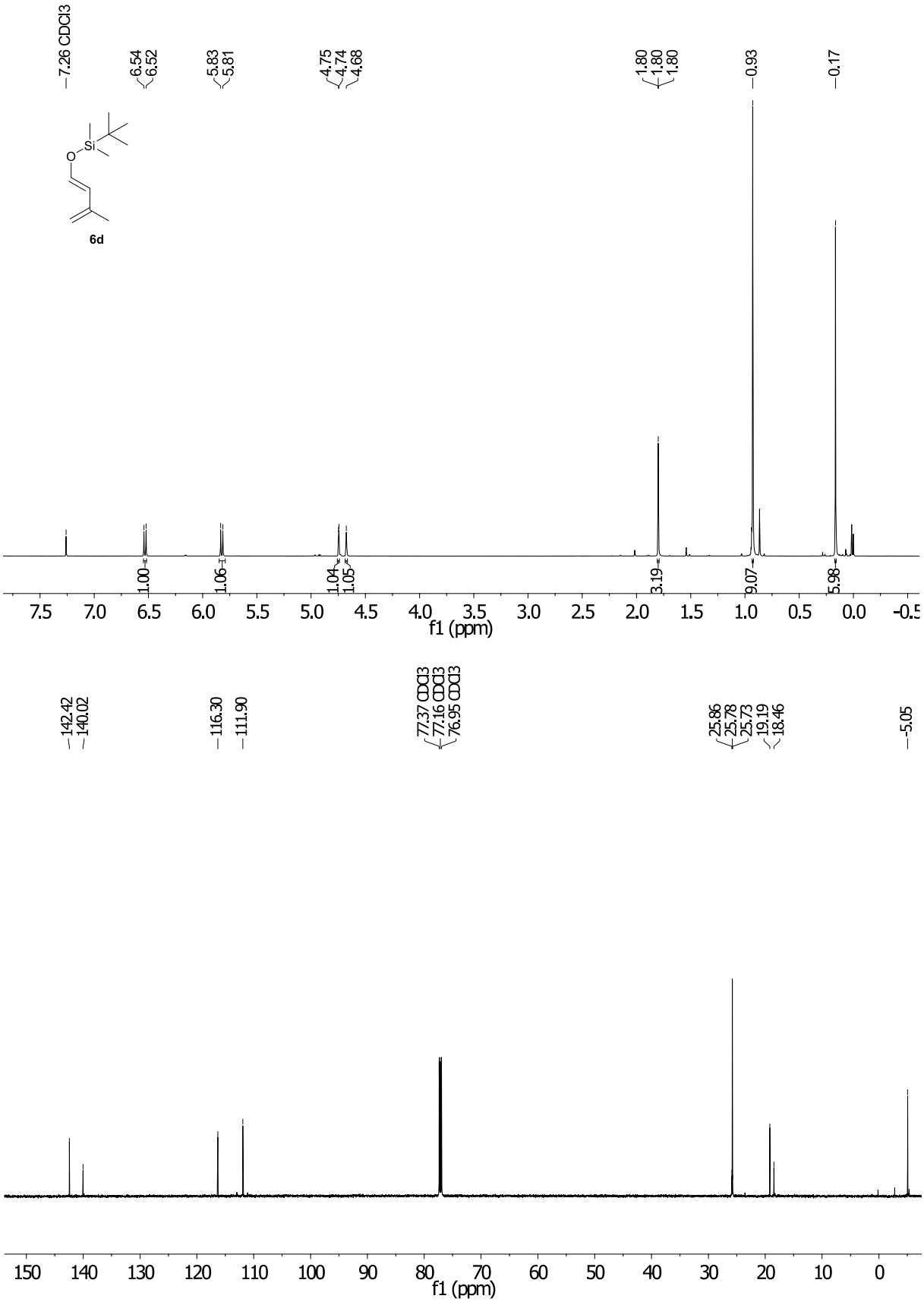


Figure 8: ^{1}H and ^{13}C-NMR-Spectra of **6d** in $CDCl_3$ (600 MHz/151 MHz).

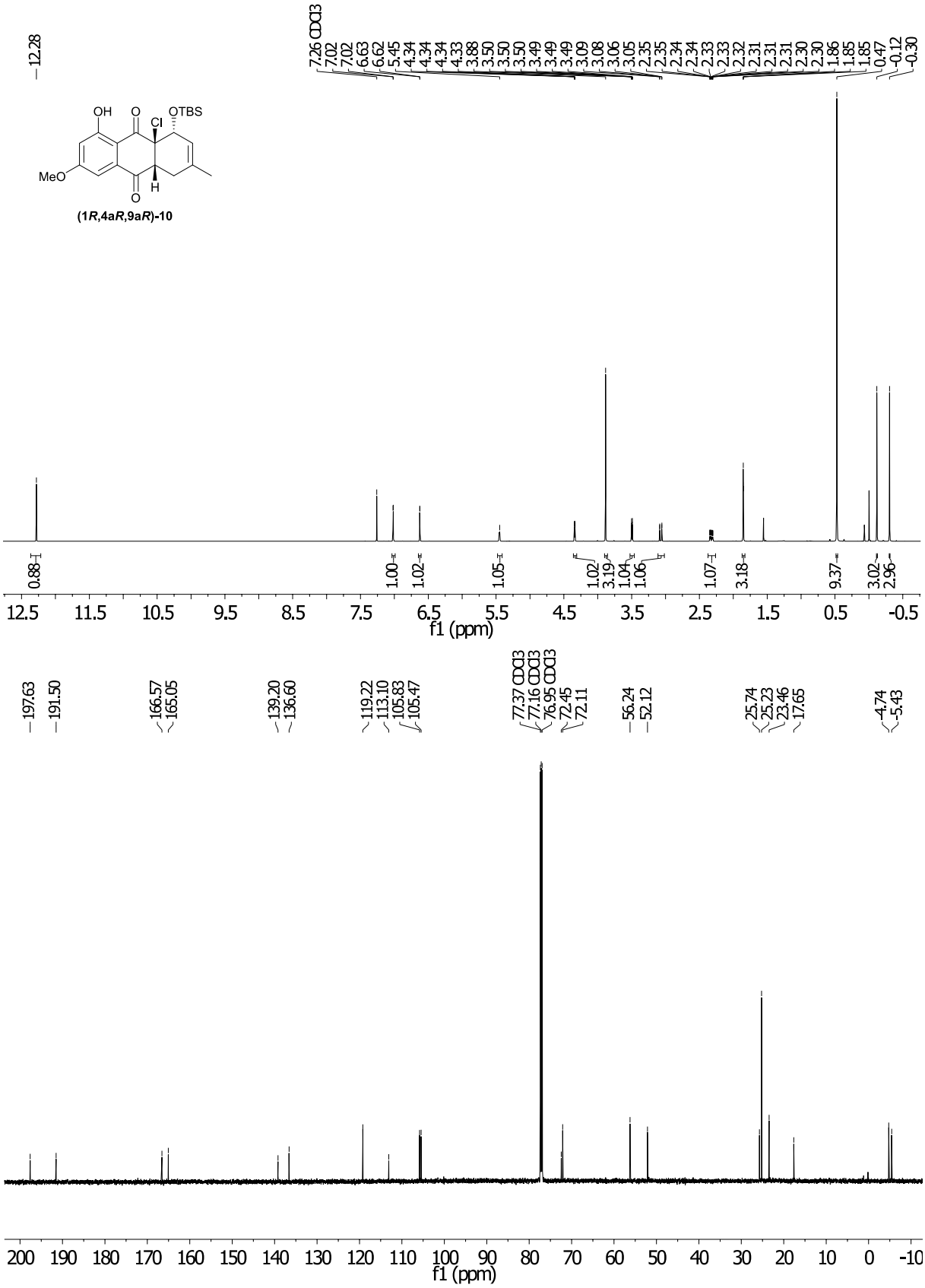


Figure 9: ^{1}H and ^{13}C-NMR-Spectra of **(1*R*,4a*R*,9a*R*)-10** in $CDCl_3$ (600 MHz/151 MHz).

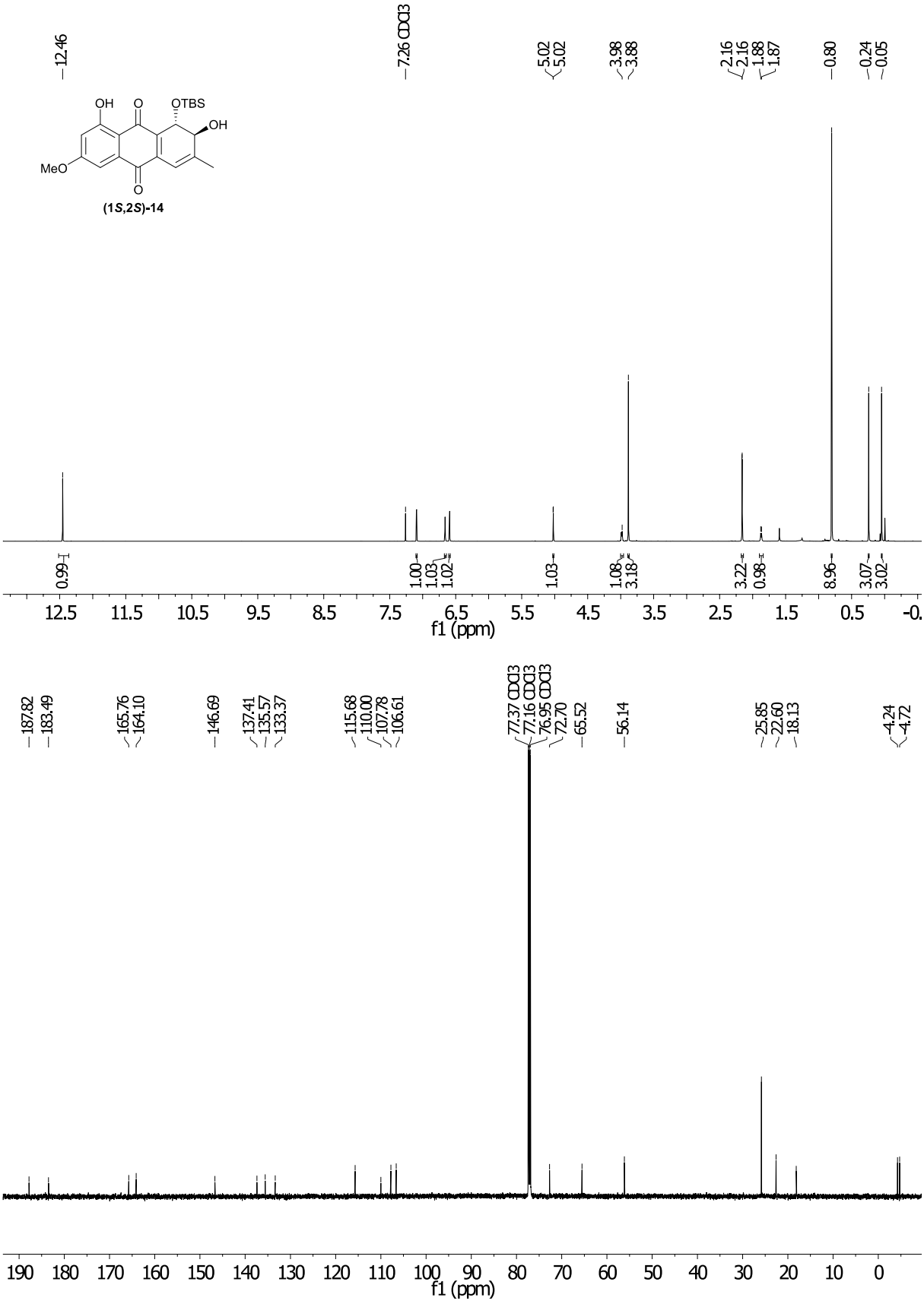


Figure 10: ^{1}H and ^{13}C-NMR-Spectra of **(1*S*,2*S*)-14** in $CDCl_3$ (600 MHz/151 MHz).

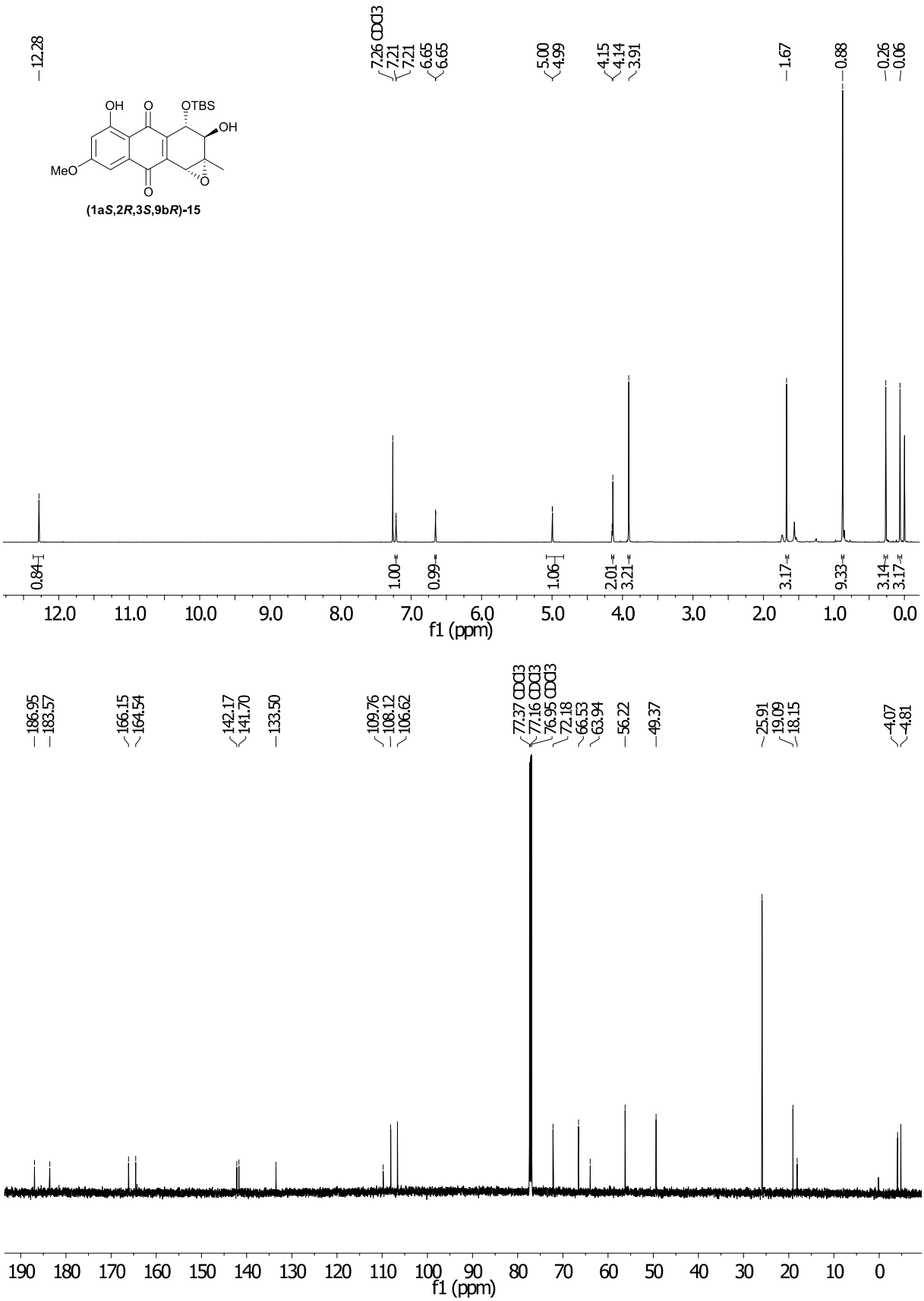


Figure 11: ^{1}H and ^{13}C-NMR-Spectra of **(1a*S*,2*R*,3*S*,9b*R*)-15** in $CDCl_3$ (600 MHz/151 MHz).

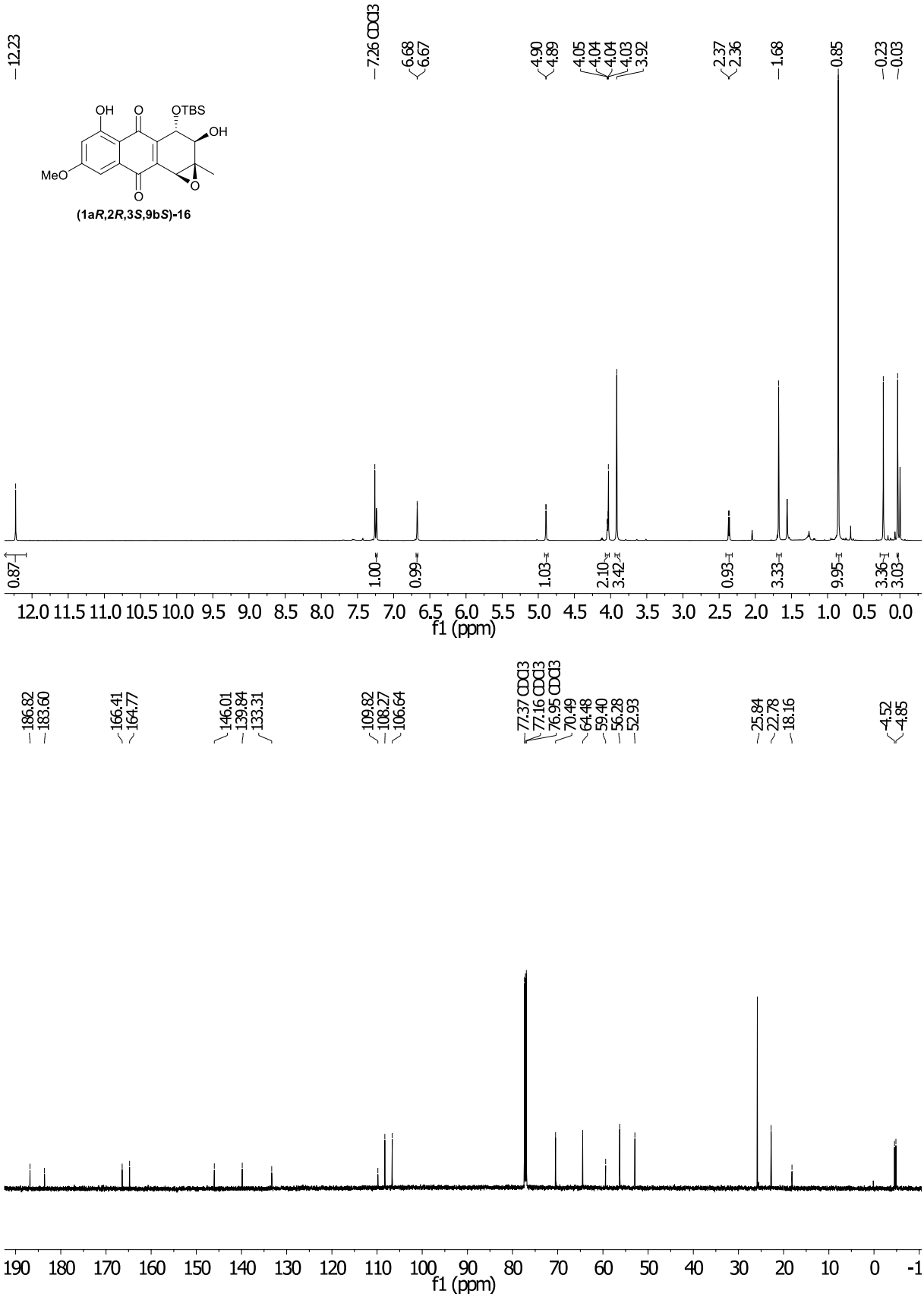


Figure 12: ^{1}H and ^{13}C-NMR-Spectra of **(1a*R*,2*R*,3*S*,9b*S*)-16** in $CDCl_3$ (600 MHz/151 MHz).

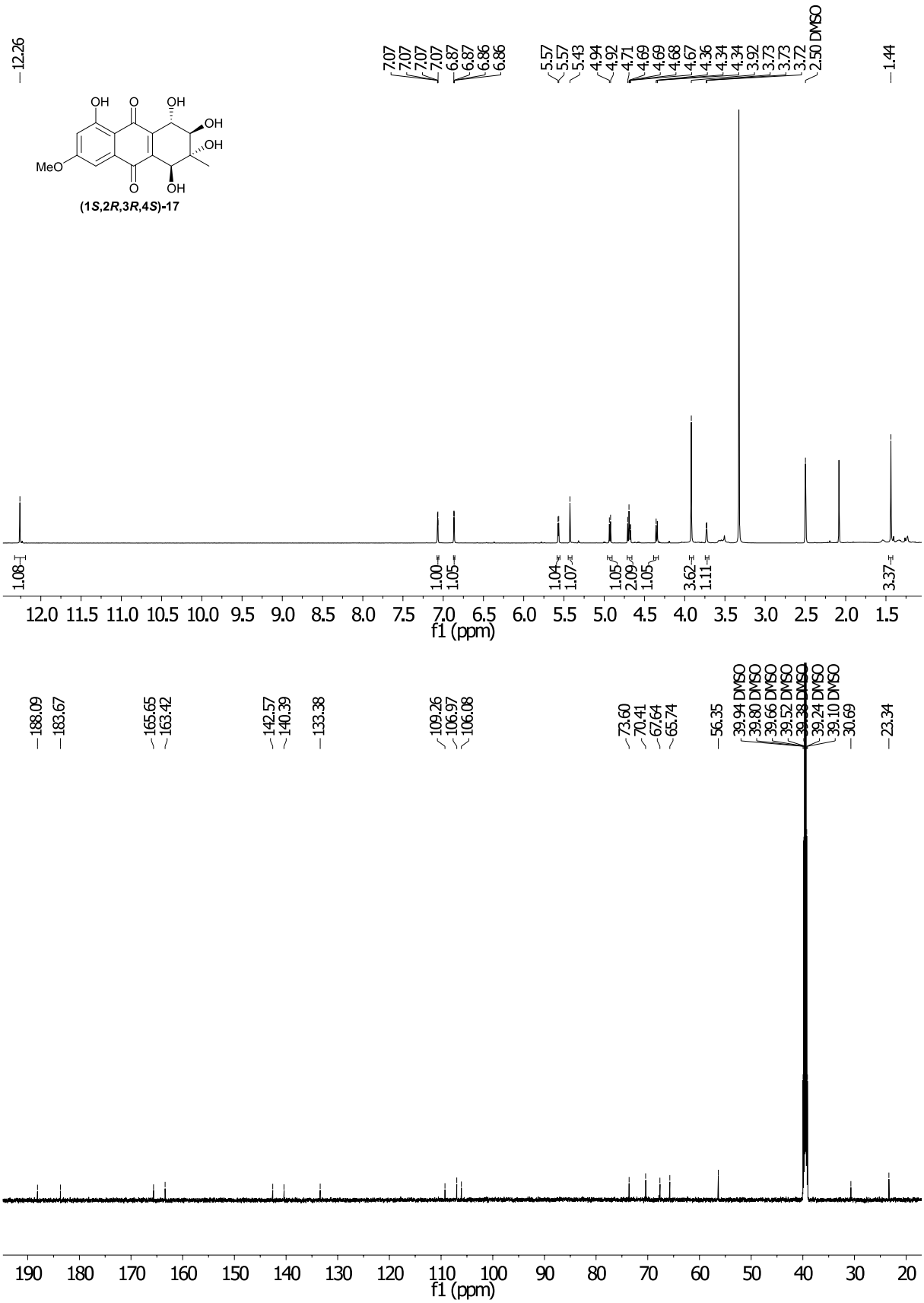


Figure 13: ^{1}H and ^{13}C-NMR-Spectra of **(1*S*,2*R*,3*R*,4*S*)-17** in DMSO (600 MHz/151 MHz).

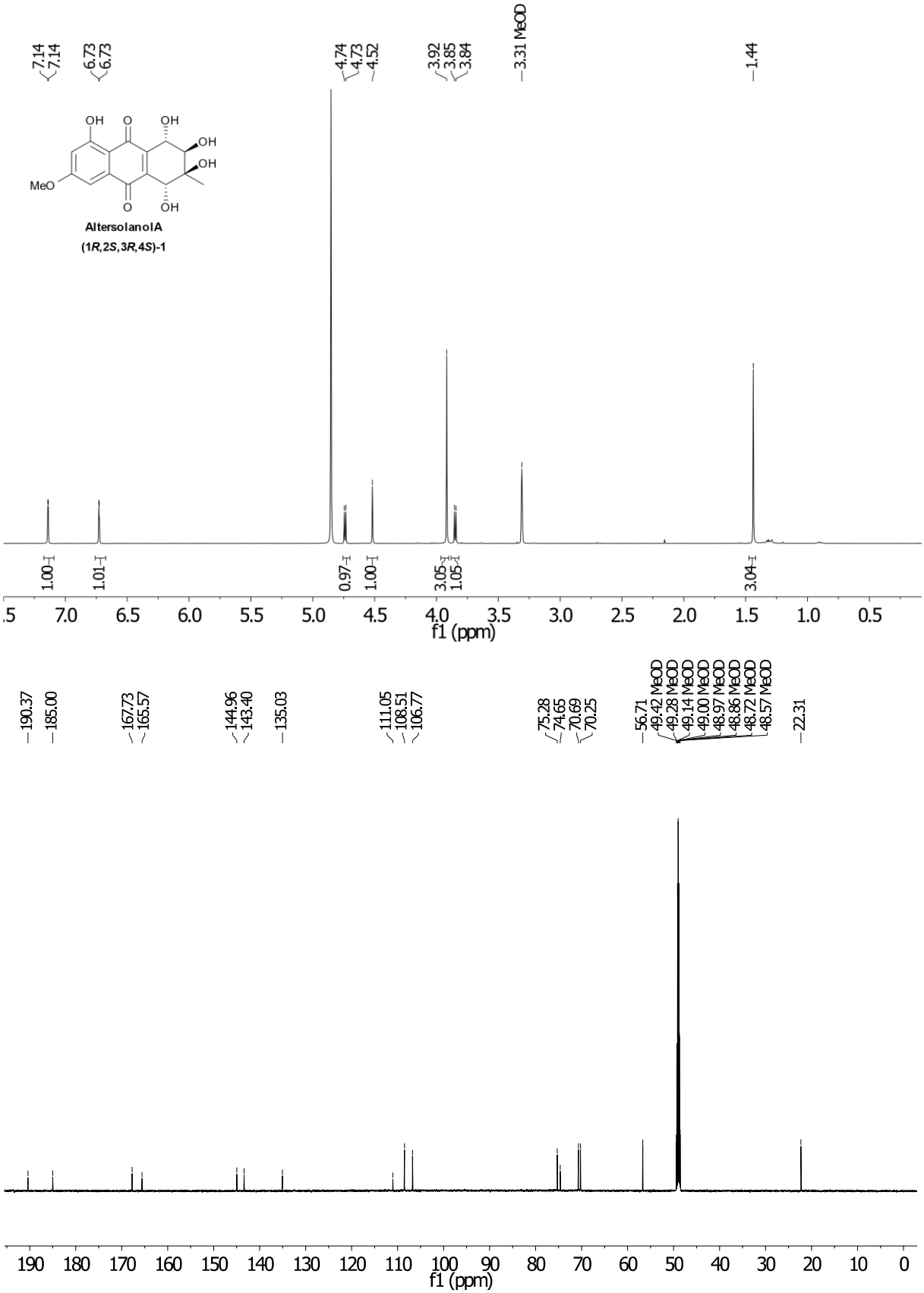
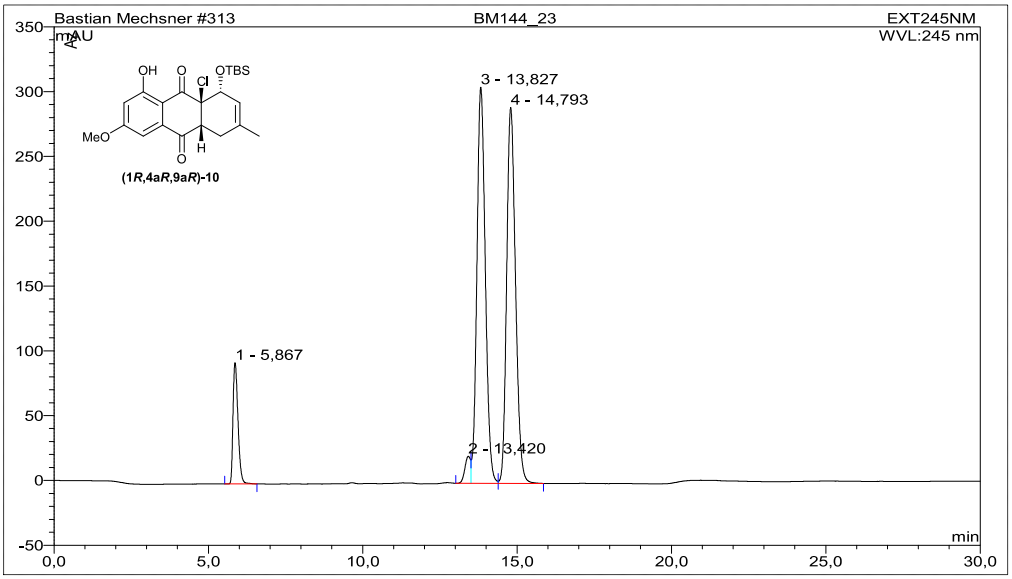
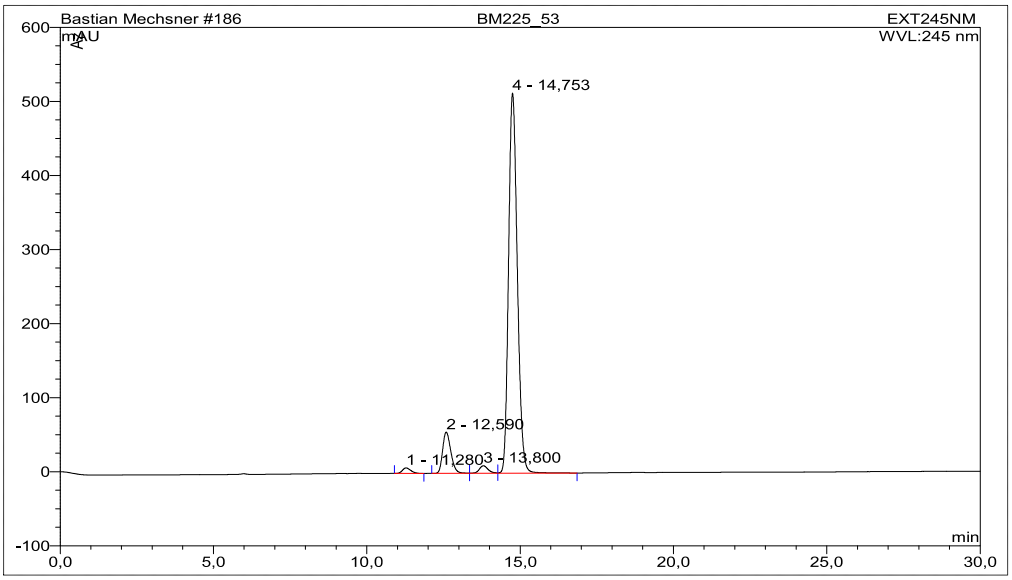


Figure 14: ^{1}H and ^{13}C-NMR-Spectra of **(1*R*,2*S*,3*R*,4*S*)-1** (**altersolanol A**) in MeOD (600 MHz/151 MHz).

S5. HPLC traces

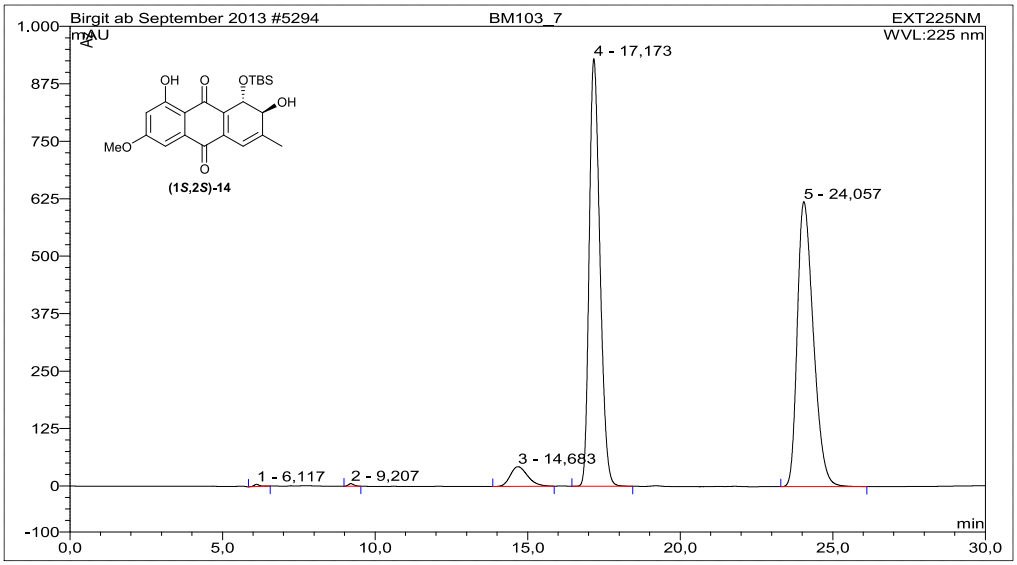


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	5,87	n.a.	93,566	17,479	8,13	n.a.	BMB
2	13,42	n.a.	20,877	4,374	2,04	n.a.	BM
3	13,83	n.a.	305,623	96,735	45,02	n.a.	M
4	14,79	n.a.	290,016	96,272	44,81	n.a.	MB
Total:			710,084	214,860	100,00	0,000	

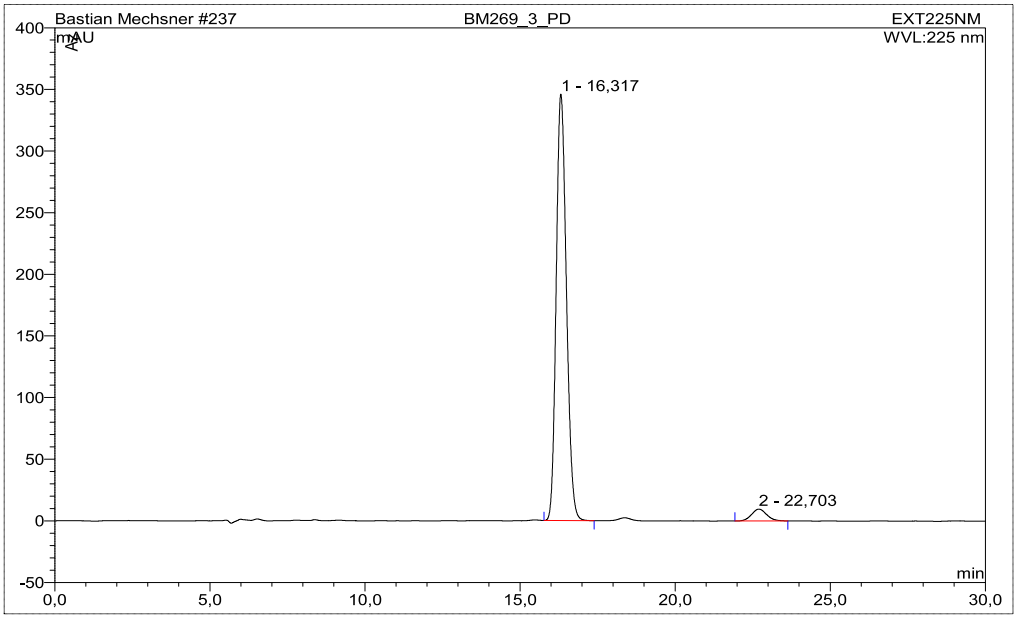


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11,28	n.a.	7,393	2,295	1,19	n.a.	BMB
2	12,59	n.a.	55,738	17,347	8,99	n.a.	BM
3	13,80	n.a.	10,216	3,423	1,78	n.a.	M
4	14,75	n.a.	513,358	169,796	88,04	n.a.	MB
Total:			586,705	192,862	100,00	0,000	

Figure 15: HPLC chromatograms of racemic **10** (above) and **(1*R*,4a*R*,9a*R*)-10** (Table 1, entry 6 and 8) (below).

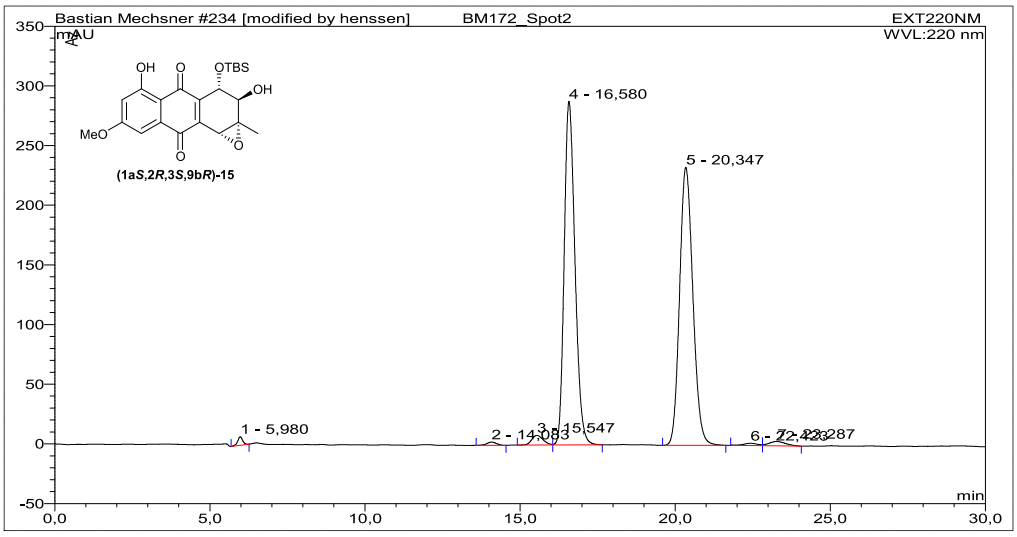


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	6,12	n.a.	4,985	1,053	0,13	n.a.	BMB
2	9,21	n.a.	5,351	1,091	0,14	n.a.	BMB
3	14,68	n.a.	42,729	28,003	3,55	n.a.	BMB
4	17,17	n.a.	930,260	379,359	48,15	n.a.	BMB
5	24,06	n.a.	620,078	378,315	48,02	n.a.	BMB
Total:			1603,403	787,820	100,00	0,000	

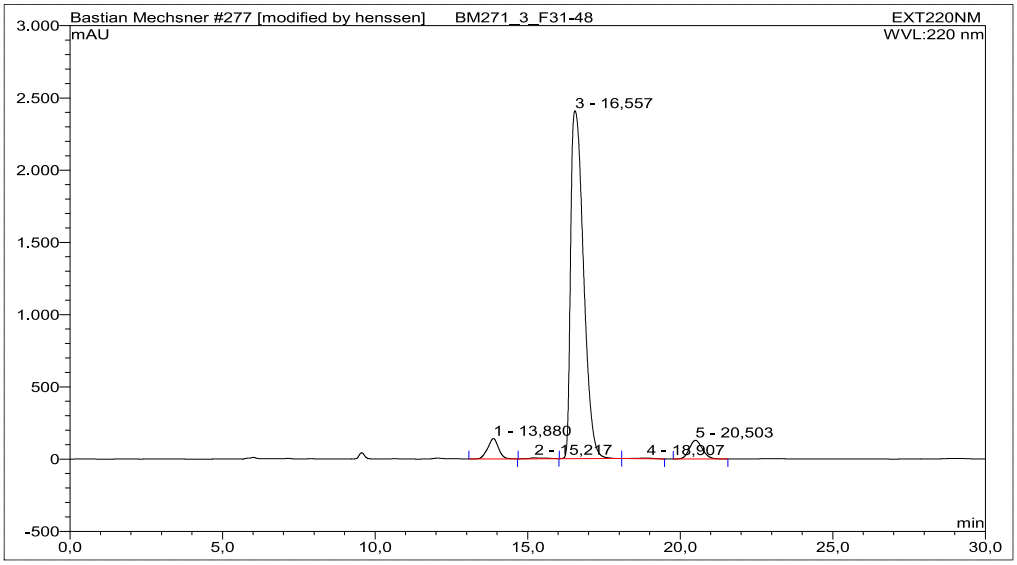


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	16,32	n.a.	345,968	131,975	96,05	n.a.	BMB
2	22,70	n.a.	9,570	5,421	3,95	n.a.	BMB
Total:			355,538	137,396	100,00	0,000	

Figure 16: HPLC chromatograms of racemic **14** (above) and **(1*S*,2*S*)-14** (below).

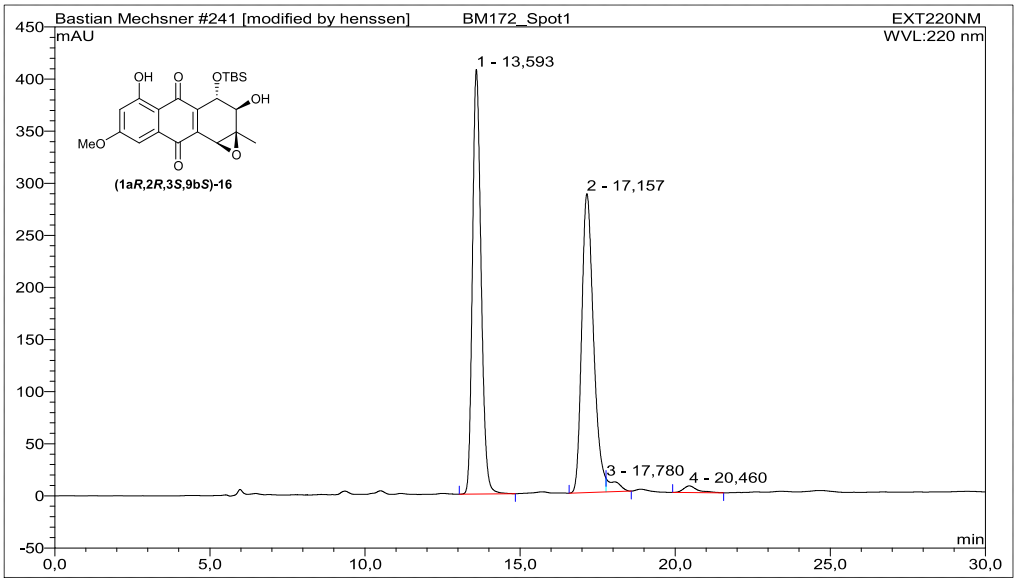


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	5,98	n.a.	7,228	1,356	0,56	n.a.	BMB
2	14,08	n.a.	2,673	0,944	0,39	n.a.	BMB*
3	15,55	n.a.	8,075	3,434	1,43	n.a.	BM
4	16,58	n.a.	287,890	115,803	48,20	n.a.	MB
5	20,35	n.a.	233,003	115,588	48,11	n.a.	BMB
6	22,42	n.a.	1,808	0,917	0,38	n.a.	BM *
7	23,29	n.a.	3,540	2,193	0,91	n.a.	MB*
Total:			544,217	240,235	100,00	0,000	

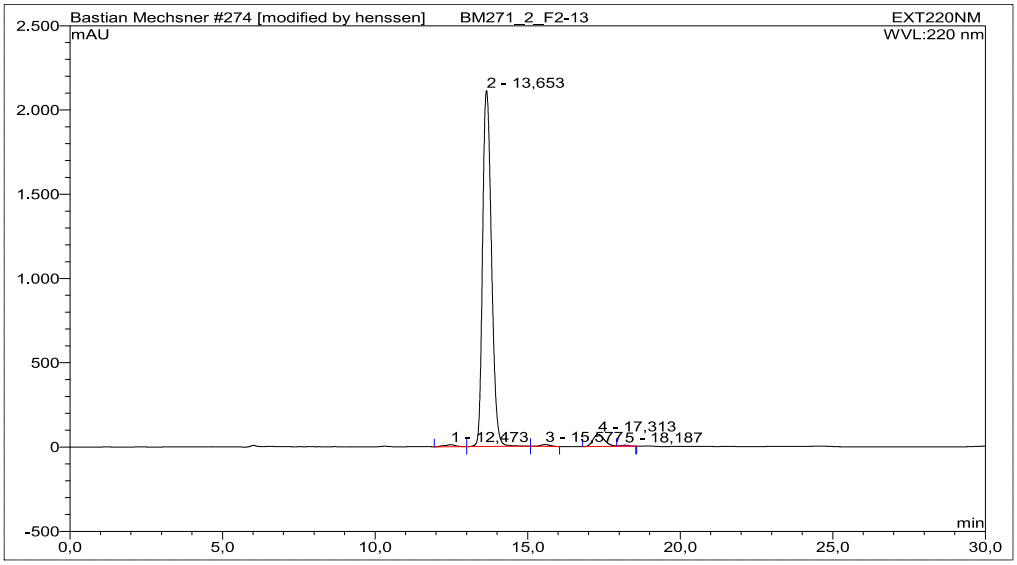


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	13,88	n.a.	140,979	57,545	4,41	n.a.	BMB*
2	15,22	n.a.	6,463	3,715	0,28	n.a.	BMB
3	16,56	n.a.	2407,564	1176,830	90,18	n.a.	BMb*
4	18,91	n.a.	5,607	3,441	0,26	n.a.	bMB
5	20,50	n.a.	128,826	63,391	4,86	n.a.	BMB
Total:			2689,439	1304,921	100,00	0,000	

Figure 17: HPLC chromatograms of racemic **15** (above) and **(1a*S*,2*R*,3*S*,9b*R*)-15** (below).

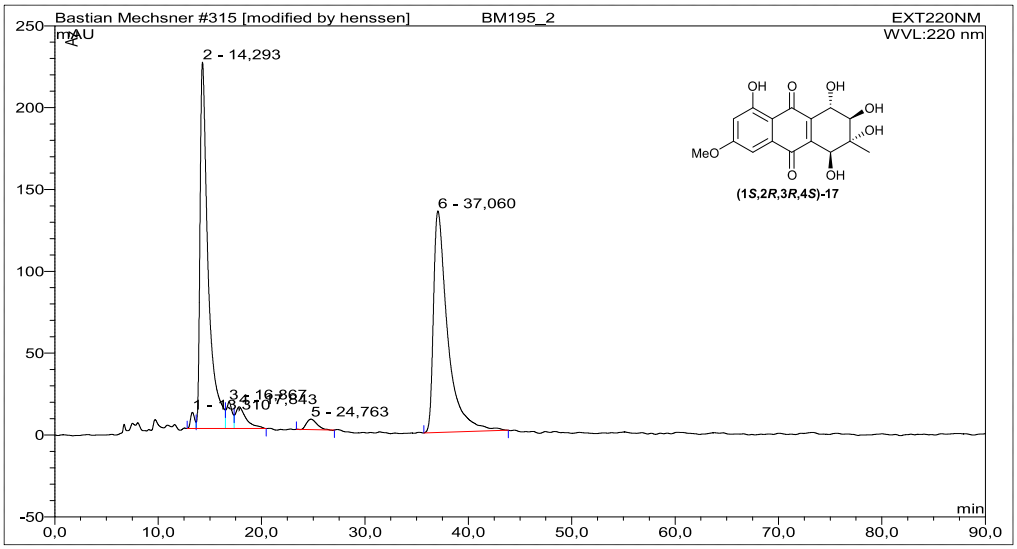


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	13,59	n.a.	407,416	131,145	49,35	n.a.	BMB
2	17,16	n.a.	286,937	126,445	47,58	n.a.	BM *
3	17,78	n.a.	12,825	4,875	1,83	n.a.	MB*
4	20,46	n.a.	6,346	3,296	1,24	n.a.	BMB
Total:			713,524	265,761	100,00	0,000	

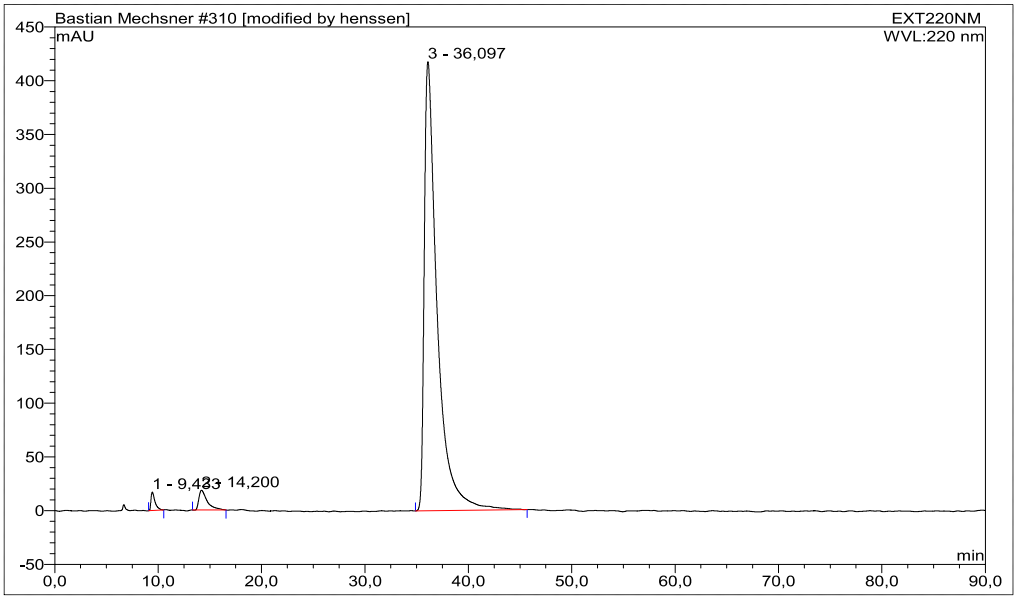


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12,47	n.a.	12,121	5,091	0,67	n.a.	BMB*
2	13,65	n.a.	2112,433	713,968	94,22	n.a.	BMb
3	15,58	n.a.	11,000	3,976	0,52	n.a.	bMB
4	17,31	n.a.	73,481	33,220	4,38	n.a.	BMB*
5	18,19	n.a.	4,950	1,494	0,20	n.a.	Rd
Total:			2213,984	757,748	100,00	0,000	

Figure 18: HPLC chromatograms of racemic **16** (above) and **(1a*R*,2*R*,3*S*,9b*S*)-15** (below).

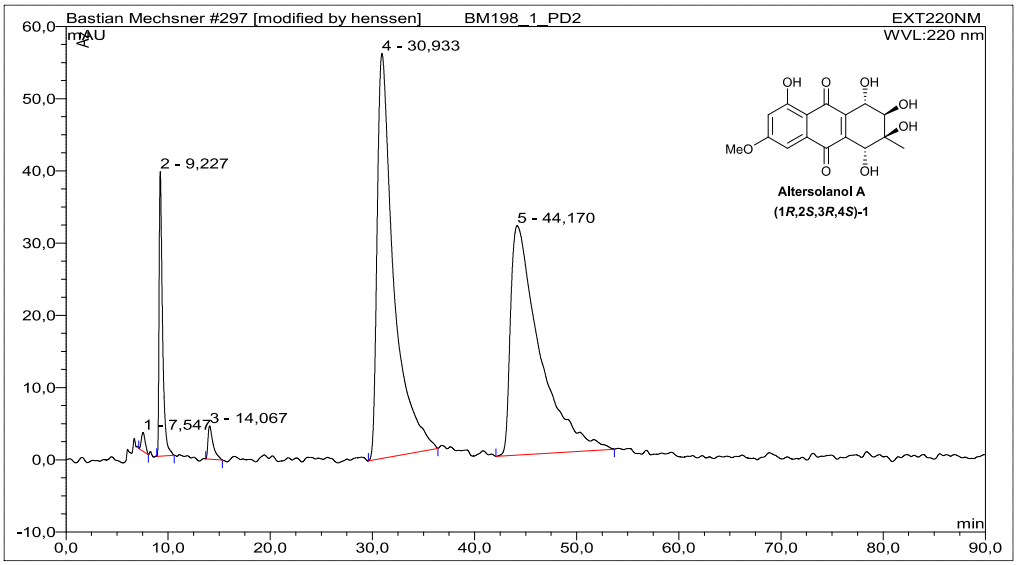


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	13,31	n.a.	9,980	4,567	0,99	n.a.	BM
2	14,29	n.a.	223,842	204,974	44,56	n.a.	M
3	16,87	n.a.	16,147	10,421	2,27	n.a.	M
4	17,84	n.a.	13,294	16,176	3,52	n.a.	MB
5	24,76	n.a.	6,394	7,434	1,62	n.a.	BMB*
6	37,06	n.a.	135,332	216,400	47,05	n.a.	BMB*
Total:			404,989	459,973	100,00	0,000	

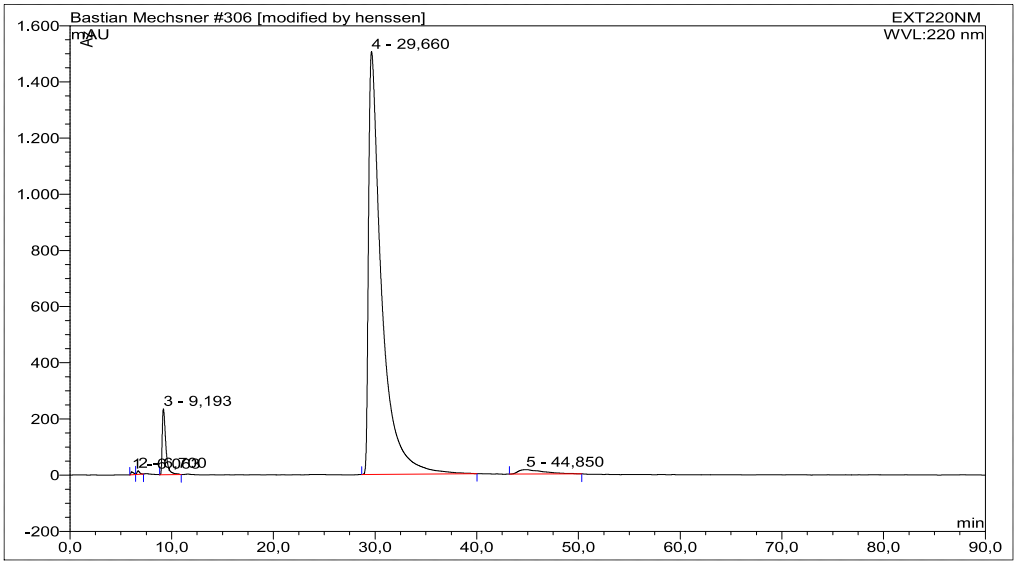


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9,43	n.a.	17,175	7,728	1,23	n.a.	BMB
2	14,20	n.a.	18,435	17,332	2,75	n.a.	BMB*
3	36,10	n.a.	418,044	604,181	96,02	n.a.	BMB*
Total:			453,654	629,242	100,00	0,000	

Figure 19: HPLC chromatograms of racemic **17** (above) and **(1*S*,2*R*,3*R*,4*S*)-17** (below).



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7,55	n.a.	2,604	1,127	0,49	n.a.	BMB
2	9,23	n.a.	39,410	15,366	6,69	n.a.	BMB
3	14,07	n.a.	4,631	2,698	1,17	n.a.	BMB
4	30,93	n.a.	56,075	105,933	46,13	n.a.	BMB
5	44,17	n.a.	31,767	104,520	45,51	n.a.	BMB*
Total:			134,486	229,644	100,00	0,000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	6,06	n.a.	11,432	3,478	0,14	n.a.	BM
2	6,70	n.a.	12,988	3,863	0,16	n.a.	MB
3	9,19	n.a.	234,749	95,930	3,99	n.a.	BMB
4	29,66	n.a.	1505,238	2254,475	93,79	n.a.	BMB
5	44,85	n.a.	15,751	46,083	1,92	n.a.	BMB*
Total:			1780,158	2403,831	100,00	0,000	

Figure 20: HPLC chromatograms of racemic altersolanol A (**1**) (above) and altersolanol A **(1*R*,2*S*,3*R*,4*S*)-1** (below).

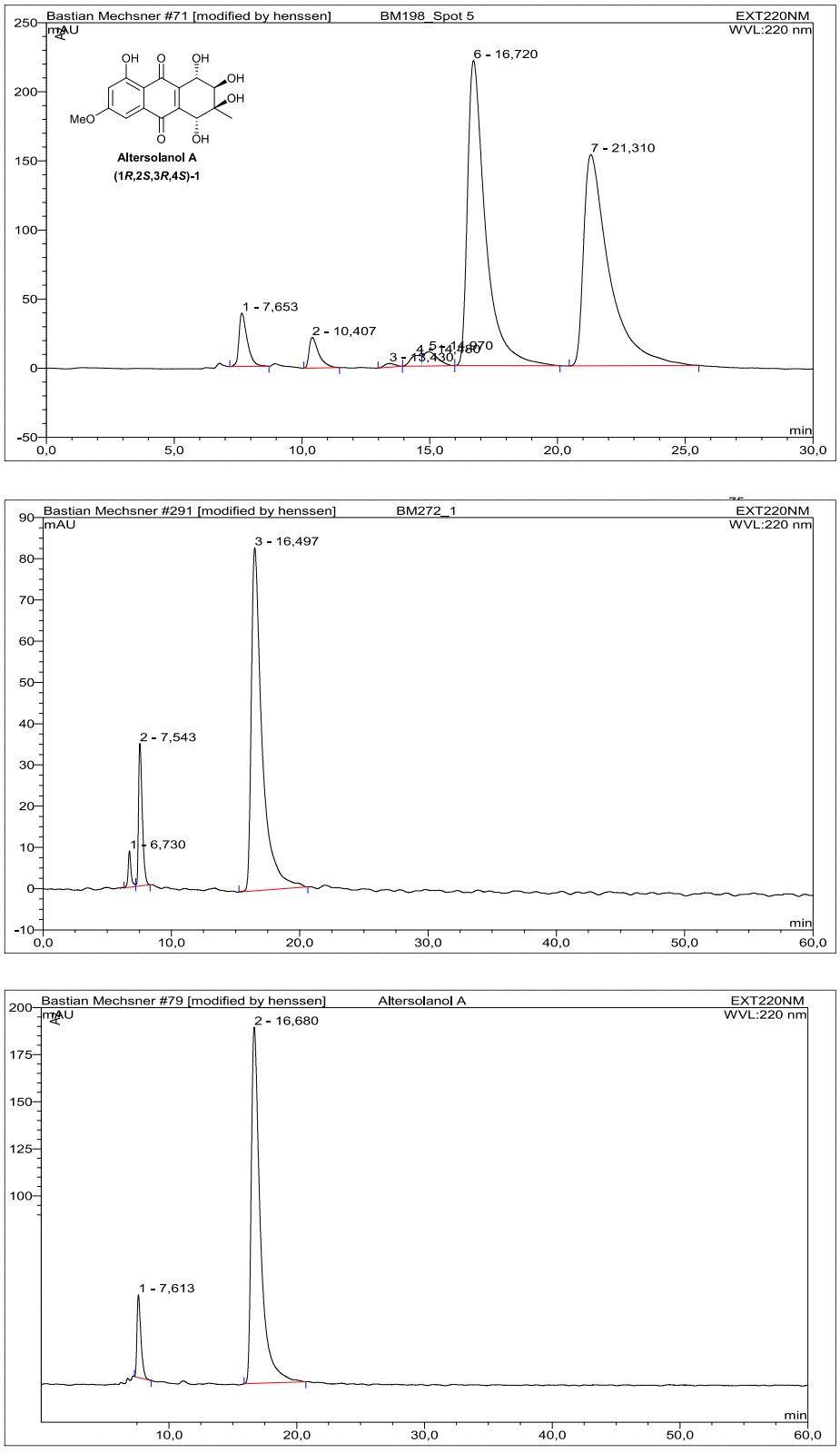


Figure 21: HPLC chromatograms of racemic altersolanol A (**1**) (above), synthesised altersolanol A **(1*R*,2*S*,3*R*,4*S*)-1** (middle) and the authentic sample of natural product by Prof. Proksch (below).

S6. Reversed-phase HPLC chromatograms

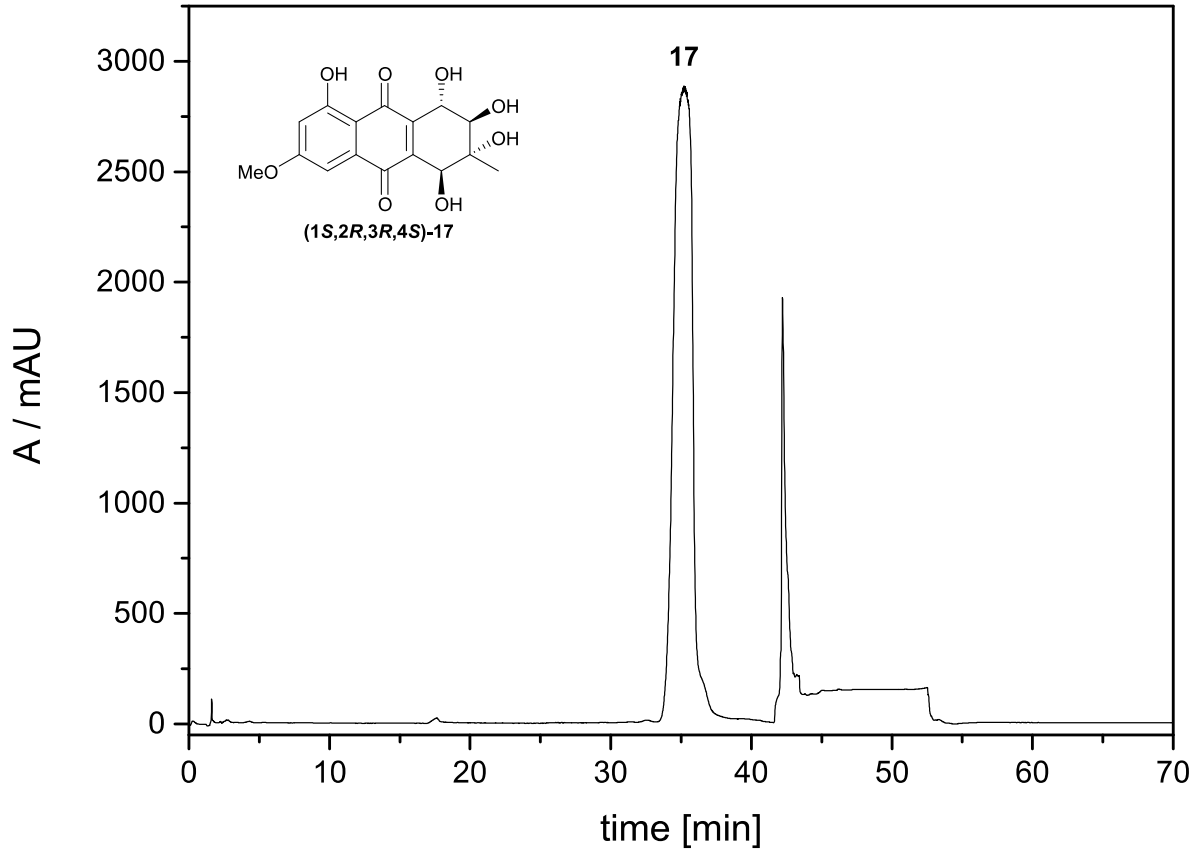


Figure 22: Achiral reversed-phase HPLC chromatogram of racemic **17** and **(1*S*,2*R*,3*R*,4*S*)-17**.

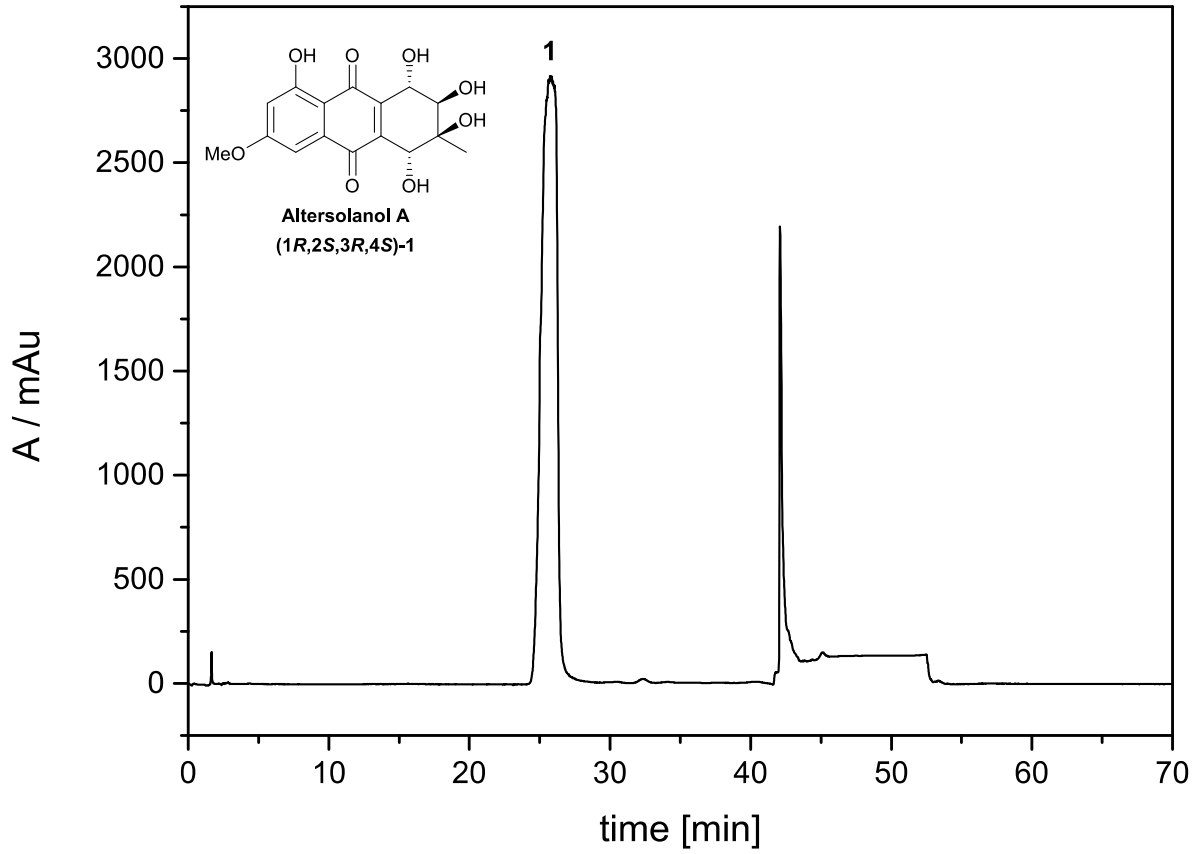


Figure 23: Achiral reversed-phase HPLC chromatogram of racemic altersolanol A **1** and **(1*S*,2*R*,3*R*,4*S*)-1**.