Supporting Information

Unified Enantiospecific Synthesis of Drimane Meroterpenoids Enabled by Enzyme Catalysis and Transition Metal Catalysis

Yipeng You,‡[a] Xue-Jie Zhang,‡[b] Wen Xiao,[b] Thittaya Kunthic,[b] Zheng Xiang,*[b,c] and Chen Xu*[a]

[a]Shenzhen Grubbs Institute and Department of Chemistry, Guangdong Provincial Key Laboratory of Catalysis, Southern University of Science and Technology, 1088 Xueyuan Avenue, Shenzhen (P. R. China). E-mail: xuc@sustech.edu.cn

[b]State Key Laboratory of Chemical Oncogenomics, Shenzhen Key Laboratory of Chemical Genomics, AI for Science (AI4S) Preferred Program, School of Chemical Biology and Biotechnology, Peking University Shenzhen Graduate School, University Town of Shenzhen, Nanshan District, Shenzhen 518055 (P. R. China). E-mail: zxiang@pku.edu.cn

[c]Institute of Chemical Biology, Shenzhen Bay Laboratory, Gaoke Innovation Center, Guangqiao Road, Guangming District, Shenzhen 518132 (P.R. China).

‡ These authors contributed equally to this work.

Table of Contents

1. Supplementary figures and schemes

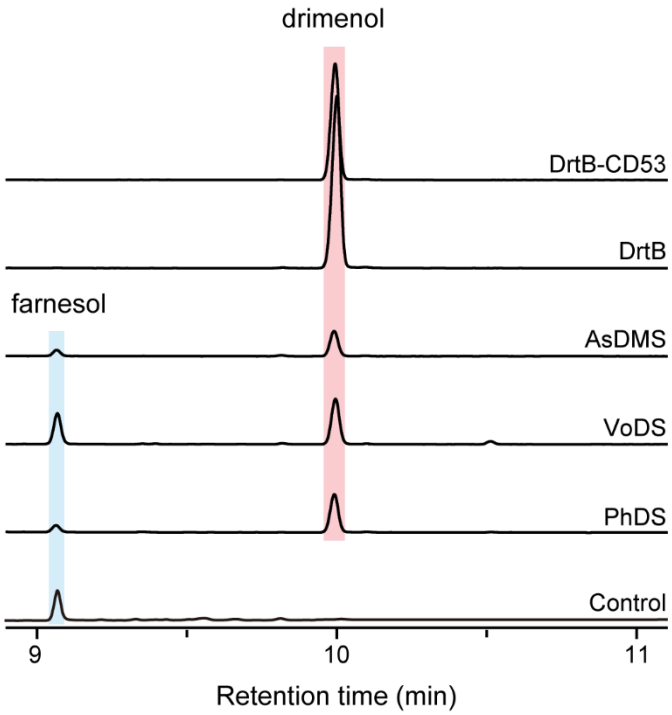


Figure S1. GC-MS analysis of product profile of drimenol synthases from four species in *E. coli*. The main product drimenol and side product farnesol were shaded with red and blue background, respectively. The *E. coli* strain harboring pACYCDuet-T1B1 and pETDuet-ERG20 as control.

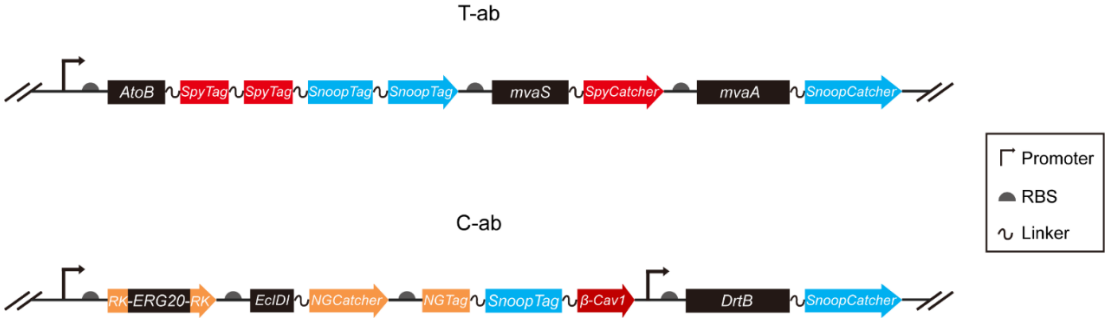


Figure S2. Schematic overview of the genetic design of multienzyme assembly for drimenol production.

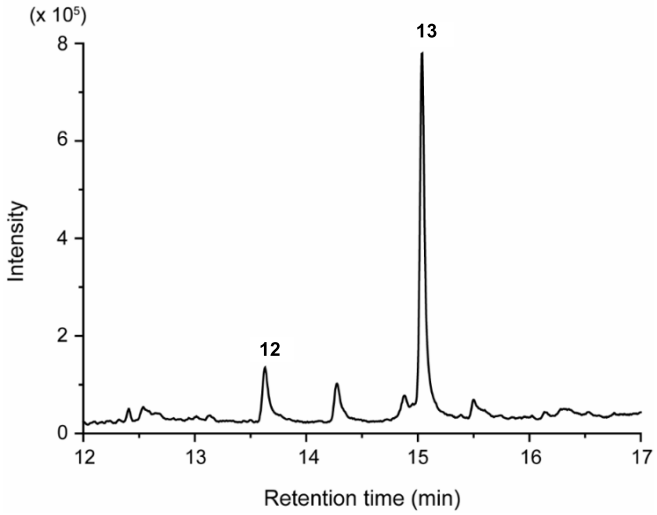


Figure S3. *In vitro* enzymatic assay of $P450_{BM3}$ (F87A) using 0.2 mM compound **12** (Rt. 13.63 min) as substrate. Compound **13** (Rt. 15.04 min) is observed after 16 h reaction.

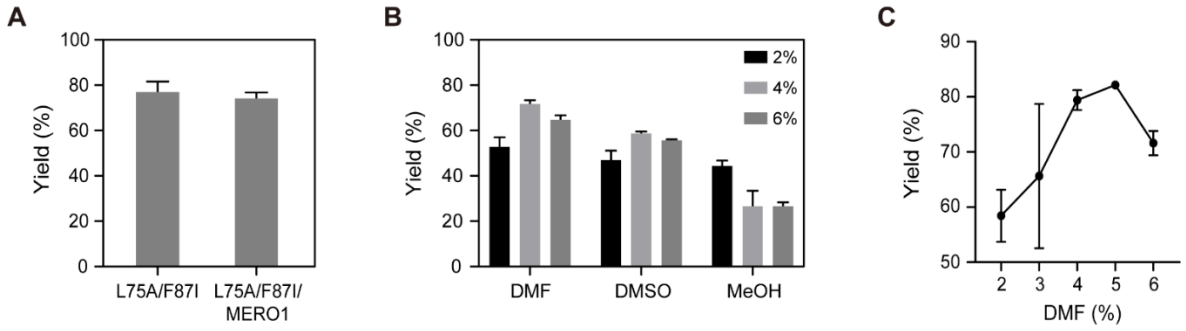


Figure S4. Optimization of C3-hydroxylation of drimenol (**11**). A) Comparison of the yield of **12** between $P450_{BM3}$ (L75A/F87I) and $P450_{BM3}$ (L75A/F87I/MERO1). B) Comparison of the yield of **12** catalyzed by optimal $P450_{BM3}$ (L75A/F87I) with various co-solvents in three different concentrations. C) Comparison of the yield of **12** in a range of concentrations of DMF.

2. Materials and methods

All reactions were carried out under an argon atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. Anhydrous THF was distilled from sodium-benzophenone, dichloroethane and dichloromethane were distilled from calcium hydride. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. The platinum catalysts were synthesized following the procedure outlined by our group recently.[1] Thin-layer chromatography (TLC) was conducted with 0.25 mm Tsingtao silica gel plates (60F-254) and visualized by exposure to UV light (254

nm). Flash column chromatography was performed using Tsingtao silica gel (60, particle size 0.040–0.063 mm). ^{1}H NMR (400 MHz and 600 MHz), ^{13}C NMR (101 MHz and 151 MHz) spectra were recorded on a Bruker AV III HD spectrometer, and were reported in terms of chemical shift relative to residual $CDCl_3$ (δ 7.26 and δ 77.16 ppm, respectively) and $(CD_3)_2CO$ (δ 2.05 and δ 29.84 ppm, respectively). Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). Abbreviations are used as follows: s = singlet, br = broad singlet, d = doublet, t = triplet, q = quartet, m = complex multiplet. Data for ^{13}C NMR spectra are reported in terms of chemical shift. High-resolution mass spectra (HRMS) data was obtained by using Thermo Scientific™ Q Exactive™ Quadrupole-Orbitrap Mass Spectrometer.

3. Heterologous biosynthesis of drimenol

3.1 Strains and plasmids

Escherichia coli DH5α cells were used for molecular cloning and site-directed mutagenesis. *E. coli* BL21(DE3) and MG1655(DE3) cells were used for protein expression and microbial production.

The previously reported plasmids pACYCDuet-T1B1 harboring the MVA pathway genes and pETDuet-ERG20 were used for producing C5 building blocks isopentenyl diphosphate (IPP) and dimethylallyl diphosphate (DMAPP) and linear C15 precursor farnesyl diphosphate (FPP), respectively.[2] Four genes encoding drimenol synthase (*PhDS*, *VoDS*, *AsDMS* and *DrtB*) were codon-optimized and synthesized by GenScript (Nanjing, China) and cloned into the multiple cloning site 2 (MCS2) of pETDuet-ERG20 with NdeI/BglII. Besides, the truncated form of DrtB with C' terminal 53 amino acid residues removal was constructed by using quick-change strategy to provide the plasmid pETDuet-ERG20-DrtB-CD53.

For metabolic engineering of drimenol production, a second copy of the *mvaA* and *idi* genes were cloned into pACYCDuet-T1B1 with EcoRI/SacI and pETDuet-ERG20-DrtB with BamHI/EcoRI restriction site, respectively. Briefly, the *mvaA* gene was amplified from pACYCDuet-T1B1 as template and cloned into pET28a(+) with NcoI/XhoI restriction site to provide pET28a-mvaA, from which the *mvaA* gene along with flanking T7 terminator was amplified and cloned into pACYCDuet-T1B1 with EcoRI/SacI restriction site to provide pACYCDuet-T1B1-mvaA. The *idi* gene from *E. coli* was codon-optimized and synthesized by GenScript (Nanjing, China) and cloned into the MCS1 of pETDuet-ERG20-DrtB with BamHI/EcoRI restriction site to provide pETDuet-ERG20-EcIDI-DrtB.

For multienzymes assembly, top MVA pathway enzymes (AtoB, mvaS and mvaA) were assembled by scaffold-free SpyTag/SpyCatcher and SnoopTag/SnoopCatcher pair with ratio of 1:2:2 assembly (namely T-ab). Cross-linking of MVA-drimenol pathway enzymes (ERG20, EcIDI and DrtB) were utilized an engineered caveolin-1 isoform beta (β-Cav1) as scaffold along with covalent conjugation via SnoopTag/SnoopCatcher pair and another covalent bonds and noncovalent interactions based on NGCatcher, NGTag and RK (Arginine/Lysine) tails (namely C-ab). The SpyTag-SpyTag-SnoopTag-SnoopTag, SpyCatcher, SnoopCatcher, NGCatcher-rbs-NGTag-SnoopTag-β-Cav1 fragments were codon-optimized and synthesized by GenScript (Nanjing, China). The atoB_tail-SpyTag-SpyTag-SnoopTag-SnoopTag-rbs-mvaS-SpyCatcher and rbs-mvaA-SnoopCatcher fragments were constructed by overlap-extension PCR and assembled with vector pACYCDuet-atoB-B1 by seamless joining to provide pACYCDuet-T-ab-B1. The

RK-ERG20-RK, rbs-EcIDI-NGCatcher, rbs-NGTag-SnoopTag-β-Cav1 and DrtB-SnoopCatcher fragments were constructed by overlap-extension PCR. The front three fragments were assembled by seamless joining and cloned into the MCS1 of pETDuet-1 with NcoI/SacI restriction site. The MCS2 of this resulting plasmid was inserted by the DrtB-SnoopCatcher fragment with NdeI/XhoI restriction site.

The sequence information of enzymes and multienzymes assembly modules used in this study are shown below. The primers used for heterologous biosynthesis of drimenol are listed in Table S1.

3.2 Protein and codon-optimized nucleotide sequences of enzymes and multienzymes assembly modules used in this study.

PhDS (559 aa, 1680 bp)

MSTAVNVPSAVRPADKRPIASFHPSPWGDYFLKYVPCDQVTQAKMEDEVKKVEEDVKKELRKLAKAVGKPLELLNFIDVVERL
GVGYRLEQEIEDLVQAIFDNDKFGVDEFDLYHTSLWFRLLRQHGFHVSCDVFGKFKGRNGRFKDSLASDVKGILGLYEASHVR
THGDDTLDEALVFTTTHLKAVVTNQPNHPLVPQVTHALMQPYHKGMPRLESRHFIAFYEKDPYHDKTLLKFGKLDFNLVQALH
KKELKDLSRWWKDLDMHAKMPFPSRDRVPEGYFWTLGPFYEPQFALCRKFFLQVFKVTSIVDDIYDAYGTIDELTAFTKAAER
WDRSCLDELPEYMKVSYASLIDTFEEFERDLAPQGRSWSVKYAREEMIQMCRVYYQEAKWCHEKYSPTCDEYLEKASIVSFGY
NLGTVVCFLGMGDVATKEAFEWARGNPKVVRAAGIIGRLMDDIGSHHFEQGRDHVPSAVECYIRQHGVDEVTAQRELGKRVES
SWKDINEMMLKPYMMPKPLLTRILNECRIVDVIYKGEDSYTFSNTTMKKNISHILTDPIPI

atgagcaccgcggtgaacgtgccgagcgcggtgcgtccggcggacaaacgtccgatcgcgagctttcacccgagcccgtgggg
tgactacttcctgaaatatgtgccgtgcgatcaggttacccaagcgaagatggaggacgaagtgaagaaagttgaggaagatg
tgaagaaagagctgcgtaagctggcgaaagcggttggtaaaccgctggagctgctgaacttcattgacgtggttgaacgtctg
ggtgttggctaccgtctggagcaggaaatcgaggatctggtgcaagcgattttcgacaacgataagtttggcgttgacgaatt
cgatctgtatcacaccagcctgtggtttcgtctgctgcgtcagcacggtttccacgtgagctgcgacgttttcggcaagtttta
aaggtcgtaacggccgttttaaagacagcctggcgagcgatgtgaagggtatcctgggcctgtacgaggcgagccacgttcgt
acccacggtgacgataccctggatgaagcgctggtgttcaccaccacccacctgaaagcggtggttaccaaccaaccgaacca
cccgctggtgccgcaggttacccacgcgctgatgcaaccgtaccacaagggtatgccgcgtctggagagccgtcacttcattg
cgttttacgaaaaggacccgtatcacgataaaaccctgctgaagtttggcaaactggacttcaacctggtgcaagcgctgcac
aagaaagagctgaaggatctgagccgttggtggaaagacctggatatgcacgcgaagatgccgtttccgagccgtgaccgtgt
tccggagggttacttctggaccctgggcccgttttatgaaccgcagttcgcgctgtgccgtaaattctttctgcaagtgttta
aggttaccagcatcgtggacgatatttacgacgcgtatggtaccatcgatgagctgaccgcgttcaccaaagcggcggaacgt
tgggaccgtagctgcctggatgaactgccggagtacatgaaagttagctatgcgagcctgatcgacaccttcgaggaatttga

acgtgatctggcgccgcagggccgtagctggagcgtgaaatacgcgcgtgaggaaatgattcagatgtgccgtgtttactatc

aagaagcgaagtggtgccacgagaaatacagcccgacctgcgacgaatatctggagaaggcgagcatcgtgagctttggttat

aacctgggcaccgtggtttgcttcctgggtatgggcgatgttgcgaccaaagaagcgtttgagtgggcgcgtggtaacccgaa

ggtggttcgtgcggcgggtatcattggccgtctgatggacgatatcggtagccaccactttgagcaaggtcgtgaccatgtgc

cgagcgcggttgaatgctacattcgtcagcacggtgtggatgaagttaccgcgcaacgtgagctgggcaaacgtgttgaaagc

agctggaaggacatcaacgaaatgatgctgaagccgtatatgatgccgaaaccgctgctgacccgtattctgaacgagtgccg

tatcgtggacgttatttacaagggcgaagatagctataccttcagcaacaccaccatgaagaaaaacatcagccacattctga

ccgatccgatcccgatttaa

VoDS (556 aa, 1671 bp)

MSTALNSEHETVRPLASFQPSTWGDLFISYSEDSQLKEVYGKEHECLKQQVKTMLLDVTNYRISEKIAFINTLERLGVSHEFE

NEIEGLLHQMFDAHSKFQDGIQHFDLFTLGIYFRILRQHGYRIYCDVFNKLKDSNNEFKKELKEDAIGLLSLYEATQVRAHAE

EILDEALIFTKAQLESIAATSSLSPFVEKQITHALVQALHKGIPRVESRHFISVYEEDPDKNDLLLRFSKIDYNIVQMLHKQE

LCHISKWWRDSELETKLTYARNRVAECFLWTLCVYHEPKYSPARLLLGKLINIISCTDDTYDAYGTLEEVQIFTDVIQRLDRS

SMEQLPDYMKILYKAVLDLFDEVEVQLSNQETNNTYRMAYAKEELKAIAKCYEKEHIWFRKCHVPPFEEYLENAVVSIGNRLA

VTFSFLGMDQVAAVEAFEWAKTDPKMVKSCGKVLRLVDDVMSHEEEDVRGHVATGVECYMKEHGVSREEAVVEFYKRVEYAWK

DVNEEFITPNHLHIDLLNRVLNLTRIADVVYKFEDGYTHPEKTLKHHIMALFVDPVPI

atgagcaccgcgctgaacagcgaacacgagaccgttcgtccgctggcgagcttccagccgagcacctggggcgacctgtttat

cagctacagcgaagatagccaactgaaagaggtgtatggtaaagaacacgagtgcctgaagcagcaagttaaaaccatgctgc

tggacgtgaccaactatcgtattagcgaaaagatcgcgttcattaacaccctggagcgtctgggcgttagccacgaatttgag

aacgaaatcgagggtctgctgcaccagatgttcgatgcgcacagcaaatttcaggacggtattcaacacttcgacctgttcac

cctgggcatctactttcgtattctgcgtcaacacggttaccgtatctattgcgacgttttcaacaagctgaaggatagcaaca

acgaattcaagaaagaactgaaagaggacgcgattggcctgctgagcctgtatgaagcgacccaagtgcgtgcgcatgcggag

gaaatcctggatgaagcgctgattttcaccaaagcgcaactggagagcattgcggcgaccagcagcctgagcccgtttgttga

aaagcagattacccacgcgctggtgcaagcgctgcacaaaggtatcccgcgtgttgagagccgtcacttcattagcgtgtacg

aggaagacccggataagaacgacctgctgctgcgtttcagcaagatcgattacaacatcgttcagatgctgcacaagcaagaa

ctgtgccacatcagcaaatggtggcgtgacagcgaactggagaccaagctgacctacgcgcgtaaccgtgttgcggaatgctt

cctgtggaccctgtgcgtgtaccacgagccgaagtatagcccggcgcgtctgctgctgggcaaactgatcaacatcattagct

gcaccgacgatacctacgacgcgtatggtaccctggaggaagttcagatcttcaccgacgtgattcaacgtctggatcgtagc

agcatggaacagctgccggattacatgaagattctgtataaagcggtgctggacctgtttgatgaagttgaggtgcagctgag

caaccaagagaccaacaacacctaccgtatggcgtatgcgaaagaggagctgaaagcgatcgcgaagtgctacgaaaaagagc

acatttggttccgtaaatgccacgttccgccgtttgaggaatatctggagaacgcggtggttagcatcggcaaccgtctggcg

gtgaccttcagctttctgggtatggaccaagtggcggcggttgaagcgttcgagtgggcgaagaccgatccgaagatggttaa

aagctgcggcaaagtgctgcgtctggtggacgatgttatgagccacgaggaagaggacgtgcgtggtcacgttgcgaccggcg

tggaatgctacatgaaggagcacggtgttagccgtgaagaggcggtggttgaattctacaagcgtgttgagtatgcgtggaaa

gacgtgaacgaagagtttatcaccccgaaccacctgcacattgatctgctgaaccgtgtgctgaacctgacccgtatcgcgga

cgtggtttacaaattcgaagatggctatacccacccggagaagaccctgaaacaccacatcatggcgctgtttgtggatccgg

ttccgatttaa

AsDMS (536 aa, 1611 bp)

MDFSSNVSPINQNNMKEVLTPELITSLQELSQILDRYDTIVFDLGDVLLHWDSVHFTSETKGIDDVRKMVKHPVWQDLEKGLI

NQEFALTALSCELETPCSKLKEMLELSIASLQVNPLMVEVLRVLHKKDKQIYCLSNVDLESFSYLYKQFDFWKYFDGIYVSAL

LQLRKPNPDIFQYLISSASINTKSTIFIDDKSENLQEAANFGISTLKYNKDNFEYTAIEGGWPIPLQNMTPEIHKKRTLGEDY

LNLRLRKFPFCKSFVSNNVELIGGEDFSKEIFSTAVILHSYTSLPDDIIASMCHEILNHDGQNKLRWCFYKNEARPDNFPDDL

DTTSMVLSFLLNHNKLTIEKIIPVAEQMIANRNEEGIIQVYFDDNRPRIDAIVAINVLYLMHQIGYGERKELKETEAFVFDFL

ISKEYLKGTRYYPAPDVFLFFLSRLVVDFPDQFEKFHKPLTEMLITRVNCSTFPLERALRIIALKKLGIVNRVDFLKLLDTQL

ADGGWPVYGLFIAPRSNTYFGSRELSTAFALEALHILS

atggatttttcaagtaatgtatctcccataaaccaaaacaacatgaaagaagtcctcacgccggaactgatcacgagcctgca

agagttgtcgcagatcctggatcgttatgataccatcgtattcgacctgggcgatgtgttgctgcattgggacagcgttcatt

ttacctctgagaccaaaggtattgacgacgtgcgtaagatggtgaaacacccggtgtggcaggatctggagaagggcctgatt

aaccaggagtttgccttgaccgcgttgagctgcgaactggaaaccccgtgtagcaaattgaaagagatgctggaactgtctat

tgcgagcctgcaagttaatccattaatggtcgaggtcctgcgcgtacttcacaaaaaggacaagcaaatttactgcctgtcca

acgtggacttggagagcttttcatatctgtacaaacaattcgatttctggaaatactttgacggcatttacgtgtcagctttg

ttacaactgcgcaagccgaatccggacatcttccagtatctgatcagcagcgcatccattaacacgaagtccacgatcttcat

cgatgacaaaagcgagaacctgcaagaagcagctaatttcggtatcagcaccctgaagtataacaaggataatttcgagtaca

ccgcgatcgagggtggctggccgatcccgctgcaaaacatgaccccggagatacataagaaacgtaccctgggtgaagattat

ctgaacctgagactgcgtaagttcccgttttgcaagagcttcgtttccaataacgttgaattgattggcggtgaagattttag

caaagagattttcagtactgcggttatcctccacagctacacgtctctgccggatgacatcatcgcgtctatgtgccatgaaa

tcctgaaccacgatggtcagaataaattgcgctggtgtttttataagaacgaagcgcgtccagataatttcccggacgacctg

gatactaccagcatggttttatcgttcctgctgaaccacaataaacttaccattgagaagatcatcccggttgcagaacagat

gattgcgaaccgtaatgaggagggcatcattcaggtgtacttcgacgacaaccgcccgcgtattgatgcaatcgtggccatca

acgtcctgtacttaatgcatcagattggttatggtgagcgcaaagagttgaaggagactgaagcgttcgtgttcgacttcctc

atctccaaagagtatctgaagggtacacgttactacccggcaccggacgttttcttgttttttctgagccgtctggttgttga

cttcccagatcagtttgaaaaattccacaagccgttgaccgagatgctgatcacccgtgtgaactgctctacgtttccgttgg

aacgtgctctccgtattatagcgctgaagaagctgggcattgttaaccgcgtggacttcttaaagctgctggacacccagctt

gccgatggcggttggcctgtttacggccttttattgctccgcgttccaatacctattttggtagcagagaactgagtaccgc

gtttgctttggaagcgctgcacatcttgtcgtaa

DrtB (528 aa, 1587 bp)

MVRALILDLGDVLFNWDAPASTPISRKTLGQMLHSEIWGEYERGHLTEDEAYNALAKRYSCEAKDVAHTFVLARESLRLDTKF

KTFLQTLKQNANGSLRVYGMSNISKPDFEVLLGKADDWTLFDKIFPSGHVGMRKPDLAFFRYVLKDISTPVEDVVFVDDNLDN

VTSARSLGMRSVLFHKKDEVQRQLTNIFGSPAERGLEYLSANKTNLQSATTTDIPIQDNFGQLLILEATEDPSLVRMEPGKRT

WNFFIGSPSLTTDTFPDDLDTTSLALSIVPTSPDVVNSVIDEIISRRDKDGIVPTYFDNTRPRVDPIVCVNVLSMFAKYGREH

DLPATVAWVRDVLYHRAYLGGTRYYGSAEAFLFFFTRFVRNLRPGTLKQDLHALLSERVRERLNTPVDALALSMRIQACHALG

FDAPADIATLITMQDEDGGWPAAVIYKYGAGGLGITNRGVSTAFAVKAITGSPVKTETNIGGDGARAVSAMSSLEARRLQPIS

SVGDWVRFIIASLHVHLAWLWNVLLLSKVV

atggtaagggctctaatattggacttaggagatgtcctcttcaactgggatgcgccggctagcaccccgatcagccgtaaaac

gctgggccagatgctgcactccgagatttggggtgaatatgaacgtggtcatctgaccgaagacgaggcctataacgcgctag

cgaagcgctacagctgcgaagcgaaggacgtcgcacataccttcgtgttggcgcgcgagagcttgcgcctggataccaaattt

aaaaccttcctgcaaaccttaaagcaaaacgcgaacggttcactgcgcgtgtatggcatgagcaatatttcgaagccggactt

tgaagttttgctgggcaaagctgatgactggaccttgttcgataaaatcttcccgagcggtcacgtgggcatgcgaaagccgg

acttggcgttctttcgttacgtcttgaaagacatctccacgccggtggaagacgttgttttcgtagacgataacttggacaac

gtgacgtcggcccgtagcctgggtatgagaagcgttctttttcacaagaaagatgaggttcagcgtcagttgacgaatatttt

tggtagcccggcagagcgcggtctggagtacctgtctgcgaataaaactaaccttcaaagcgcgaccacgactgacatcccga

tccaggacaatttcggccaactgctgatcctggaggctaccgaggacccgtctctggttcgtatggaaccgggtaaaagaaca

tggaatttttcattggctctccgagcctgaccaccgatacttttccggatgacttagataccaccagtcttgcgctgtccat

tgttccgacttcgccggacgtggtgaacagcgtgattgacgagatcatcagtcgtcgcgataaagacggcatcgtgccgacgt

acttcgacaacacccgtcctcgtgtagacccgattgtttgcgttaacgtgttgagcatgtttgcgaaatacgggcgtgagcac

gatctgccggcaacagttgcgtgggttcgtgatgtgctgtatcatcgtgcctacctgggcggtacccgctactatggttccgc

cgaagcatttctgttcttcttcacccgttttgttcgtaatctgcgtccaggtacgctgaagcaggatttgcacgccctcctgt

ccgaacgcgtgcgcgagcgcttaaataccccggttgatgcactggctttgtctatgcgtattcaggcatgtcatgcgctgggt

tttgacgcgccagcggatatcgcgaccctgattaccatgcaggatgaggatggcggttggccggcggcagtcatctataagta

cggcgcgggtggtctgggcatcaccaaccgtggtgtttctaccgcattcgcagttaaagcaattaccggttccccggtcaaga

ccgaaaccaatatcggtggcgacggcgctcgtgcggtgagcgctatgagcagccttgaagctcgtcgtcttcaaccaattagc

agcgtgggcgattgggtgcgcttcatcattgctagcctgcacgttcacctggcgtggctgtggaacgtgctgttgctgtccaa

ggtggtataa

EcIDI (182 aa, 549 bp)

MQTEHVILLNAQGVPTGTLEKYAAHTADTRLHLAFSSWLFNAKGQLLVTRRALSKKAWPGVWTNSVCGHPQLGESNEDAVIRR

CRYELGVEITPPESIYPDFRYRATDPSGIVENEVCPVFAARTTSALQINDDEVMDYQWCDLADVLHGIDATPWAFSPWMVMQA

TNREARKRLSAFTQLK

atgcagaccgagcacgtgatcctgctgaacgcgcaaggtgttccgaccggcaccctggaaaagtatgcggcgcacaccgcgga

cacccgtctgcacctggcgttcagcagctggctgtttaacgcgaagggtcagctgctggtgacccgtcgtgcgctgagcaaga

aagcgtggccgggcgtgtggaccaacagcgtttgcggtcacccgcaactgggcgagagcaacgaagatgcggtgatccgtcgt

tgccgttacgagctgggtgttgaaatcaccccgccggagagcatttacccggacttccgttatcgtgcgaccgatccgagcgg

catcgtggagaacgaagtgtgcccggtttttgcggcgcgtaccaccagcgcgctgcaaattaacgacgatgaggtgatggact

atcaatggtgcgacctggcggatgttctgcacggtattgatgcgaccccgtgggcgttcagcccgtggatggttatgcaggcg

accaaccgtgaagcgcgtaagcgtctgagcgcgtttacccaactgaaataa

RK-ERG20-RK (RKRKRK-CDS-RKRK)

MRKRKRKASEKEIRRERFLNVFPKLVEELNASLLAYGMPKEACDWYAHSLNYNTPGGKLNRGLSVVDTYAILSNKTVEQLGQE

EYEKVAILGWCIELLQAYFLVADDMMDKSITRRGQPCWYKVPEVGEIAINDAFMLEAAIYKLLKSHFRNEKYYIDITELFHEV

TFQTELGQLMDLITAPEDKVDLSKFSLKKHSFIVTFKTAYYSFYLPVALAMYVAGITDEKDLKQARDVLIPLGEYFQIQDDYL

DCFGTPEQIGKIGTDIQDNKCSWVINKALELASAEQRKTLDENYGKKDSVAEAKCKKIFNDLKIEQLYHEYEESIAKDLKAKI

SQVDESRGFKADVLTAFLNKVYKRSKRKRK

atgcgtaaacgtaaacgtaaagcgagcgagaaagaaatccgtcgtgagcgtttcctgaacgtgtttccgaagctggttgagga

actgaacgcgagcctgctggcgtacggtatgccgaaagaagcgtgcgactggtacgcgcacagcctgaactataacaccccgg

gtggcaagctgaaccgtggcctgagcgtggttgatacctacgcgattctgagcaacaaaaccgtggagcagctgggtcaagag

gaatatgaaaaggttgcgatcctgggctggtgcattgagctgctgcaagcgtacttcctggtggcggacgatatgatggacaa

aagcatcacccgtcgtggtcaaccgtgctggtataaggtgccggaagtgggcgaaatcgcgattaacgatgcgttcatgctgg

aggcggcgatttacaagctgctgaaaagccacttccgtaacgaaaagtactacatcgacattaccgagctgttccacgaagtt

acctttcagaccgagctgggtcaactgatggatctgatcaccgcgccggaagacaaagtggatctgagcaagttcagcctgaa

gaaacacagcttcattgttacctttaagaccgcgtactatagcttttacctgccggtggcgctggcgatgtatgttgcgggca

tcaccgacgagaaggatctgaaacaggcgcgtgacgtgctgatcccgctgggtgaatacttccagattcaagacgattatctg

gattgctttggcaccccggagcagatcggtaaaattggcaccgacatccaagataacaaatgcagctgggtgattaacaaggc

gctggagctggcgagcgcggaacagcgtaagaccctggacgagaactatggtaagaaagatagcgttgcggaagcgaaatgca

agaaaatctttaacgacctgaagattgagcagctgtaccacgaatatgaggaaagcatcgcgaaggacctgaaggcgaaaatt

agccaagttgacgaaagccgtggcttcaaggcggatgtgctgaccgcgtttctgaacaaggtttacaaacgtagcaagcgtaa

acgtaaataa

SpyTag

AHIVMVDAYKPTK

gcccatattgtcatggttgatgcatacaagccgacgaag

SpyCatcher

AMVDTLSGLSSEQGQSGDMTIEEDSATHIKFSKRDEDGKELAGATMELRDSSGKTISTWISDGQVKDFYLYPGKYTFVETAAP

DGYEVATAITFTVNEQGQVTVNGKATKGDAHI

gccatggttgataccttatcaggtttatcaagtgagcaaggtcagtccggtgatatgacaattgaagaagatagtgctaccca

tattaaattctcaaaacgtgatgaggacggcaaagagttagctggtgcaactatggagttgcgtgattcatctggtaaaacta

ttagtacatggatttcagatggacaagtgaaagatttctacctgtatccaggaaaatatacatttgtcgaaaccgcagcacca

gacggttatgaggtagcaactgctattacctttacagttaatgagcaaggtcaggttactgtaaatggcaaagcaactaaagg

tgacgctcatatt

NGTag

RGAHIVMVDAYKPTK

cgcggcgcgcacatcgttatggtcgatgcatataaacccaccaaa

NGCatcher

AMVDTLSGLSSEQGQSGDMTIEEDDATHIEFSKRDEDGKELPGATMELRDSSGKTISTWISDGQVKDFYLEPGEYTFVETEAP

DGYEVDDAITFTVNEDGQVTEEGKATKGDAHI

gcaatggtggatacactgagtggtctgagcagcgaacaggggcagagcggagatatgaccattgaagaagatgatgcaaccca

tattgaattcagcaaacgcgatgaggacggtaaagaactgccgggggcaaccatggaactgcgcgatagcagcggtaaaacaa

ttagcacctggattagcgatggacaggtgaaagatttttacctggaaccaggagaatacacatttgtggaaaccgaagcacca

gacggctatgaagttgatgatgcaattacctttaccgtaaacgaagatggacaggtgaccgaagaaggaaaagcaaccaaagg

agatgcacatatc

SnoopTag

ASKLGDIEFIKVNK

gctagcaaactgggcgatattgaatttattaaagtgaacaaa

SnoopCatcher

ASKPLRGAVFSLQKQHPDYPDIYGAIDQNGTYQNVRTGEDGKLTFKNLSDGKYRLFENSEPAGYKPVQNKPIVAFQIVNGEVR

DVTSIVPQDIPATYEFTNGKHYITNEPIPPK

gctagcaagccgctgcgtggtgccgtgtttagcctgcagaaacagcatcccgactatcccgatatctatggcgcgattgatca

gaatgggacctatcaaaatgtgcgtaccggcgaagatggtaaactgacctttaagaatctgagcgatggcaaatatcgcctgt

ttgaaaatagcgaacccgctggctataaaccggtgcagaataagccgattgtggcgtttcagattgtgaatggcgaagtgcgt

gatgtgaccagcattgtgccgcaggatattccggctacatatgaatttaccaacggtaaacattatatcaccaatgaaccgat

accgccgaaa

β-Cav1

MADELSEKQVYDAHTKEIDLVNRDPKHLNDDVVKIDFEDVIAEPEGTHSFDGIWKASFTTFTVTKYWFYRLLSALFGIPMALI

WGIYFAILSFLHIWAVVPCIKSFLIEIQCISRVYSIYVHTVCDPLFEAVGKIFSNVRINLQKEI

atggcggatgaactgagcgagaaacaggtttatgatgcccacaccaaggagatcgacttggttaaccgtgacccaaagcacct

gaatgatgacgtggtgaagatcgacttcgaggacgtcatcgccgaaccggaaggcactcatagcttcgacggcatttggaaag

cgagcttcaccaccttcaccgttaccaaatactggttttatcgtcttctgagtgcattgttcggcatcccgatggcgttaatc

tggggtatctattttgcaattctgtccttcctgcatatttgggcggtggttccgtgcatcaagtccttcttgatcgagatcca

gtgtattagccgcgtgtacagcatttacgtgcacacggtttgtgatccgctgtttgaagctgtgggtaaaatttttagcaatg

ttcgtattaacctgcaaaaagagatctaa

3.3 Multienzymes assembly modules of top MVA pathway (MCS1 of pACYCDuet-1 plasmid)

AtoB-SpyTag-SpyTag-SnoopTag-SnoopTag-rbs-mvaS-SpyCatcher-rbs-mvaA-SnoopCatcher (linker)

ATGAAGAACTGCGTGATTGTTAGCGCGGTTCGTACCGCGATTGGCAGCTTCAACGGTAGCCTGGCGAGCACCAGCGCGATCGA

TCTGGGTGCGACCGTGATCAAGGCGGCGATTGAGCGTGCGAAAATCGACAGCCAGCACGTGGATGAAGTTATTATGGGCAACG

TTCTGCAAGCGGGTCTGGGTCAAAACCCGGCGCGTCAGGCGCTGCTGAAGAGCGGTCTGGCGGAGACCGTGTGCGGCTTTACC

GTGAACAAGGTTTGCGGCAGCGGTCTGAAAAGCGTTGCGCTGGCGGCGCAGGCGATCCAAGCGGGTCAGGCGCAAAGCATTGT

GGCGGGTGGCATGGAAAACATGAGCCTGGCGCCGTACCTGCTGGATGCGAAAGCGCGTAGCGGTTACCGTCTGGGCGACGGTC

AAGTGTATGATGTTATTCTGCGTGATGGTCTGATGTGCGCGACCCACGGCTACCACATGGGTATCACCGCGGAGAACGTGGCG

AAGGAATATGGTATTACCCGTGAGATGCAAGATGAACTGGCGCTGCACAGCCAGCGTAAAGCTGCGGCGGCGATTGAGAGCGG

TGCGTTCACCGCGGAAATTGTGCCGGTTAACGTGGTTACCCGTAAGAAAACCTTCGTTTTTAGCCAGGACGAGTTCCCGAAAG

CGAACAGCACCGCGGAAGCGCTGGGTGCGCTGCGTCCGGCGTTTGATAAAGCGGGCACCGTTACCGCGGGCAACGCGAGCGGT

ATCAACGATGGTGCTGCGGCGCTGGTGATTATGGAGGAAAGCGCGGCGCTGGCGGCGGGTCTGACCCCGCTGGCGCGTATCAA

GAGCTATGCGAGCGGTGGCGTGCCGCCGGCGCTGATGGGCATGGGTCCGGTTCCGGCGACCCAGAAAGCGCTGCAACTGGCGG

GTCTGCAACTGGCGGACATCGATCTGATTGAGGCGAACGAAGCGTTCGCGGCGCAGTTTCTGGCGGTGGGCAAGAACCTGGGC

TTTGATAGCGAGAAAGTGAACGTTAACGGTGGCGCGATTGCGCTGGGTCACCCGATTGGTGCGAGCGGTGCGCGTATCCTGGT

GACCCTGCTGCACGCGATGCAAGCGCGTGACAAAACCCTGGGTCTGGCGACCCTGTGCATTGGTGGCGGTCAGGGCATCGCGA

TGGTTATTGAACGTCTGAACGGTGGTGGTGGTTCAGGTGGTGGTGGTTCAGGTGGTGGTGGTTGTGGTGCCCATATTGTCATG

GTTGATGCATACAAGCCGACGAAGGGTGGTGGTGGTTCAGGTGGTGGTGGTTCAGGTGGTGGTGGTTGTGGTGCCCATATTGT

CATGGTTGATGCATACAAGCCGACGAAGGGTGGTGGTGGTTCAGGTGGTGGTGGTTCAGGTGGTGGTGGTTGTGGTGCTAGCA

AACTGGGCGATATTGAATTTATTAAAGTGAACAAAGGTGGTGGTGGTTCAGGTGGTGGTGGTTCAGGTGGTGGTGGTTGTGGT

GCTAGCAAACTGGGCGATATTGAATTTATTAAAGTGAACAAATAAggatccaggaggaaagcaaaATGACCATCGGTATTGAC

AAAATCAACTTCTACGTGCCGAAGTACTATGTTGACATGGCGAAACTGGCGGAAGCGCGTCAGGTGGACCCGAACAAGTTTCT

GATCGGTATTGGCCAGACCGAGATGGCTGTGAGCCCGGTTAACCAAGACATTGTTAGCATGGGTGCGAACGCGGCGAAAGACA

TCATTACCGACGAAGATAAGAAAAAGATCGGCATGGTGATTGTGGCGACCGAGAGCGCGGTGGATGCGGCGAAGGCGGCGGCG

GTGCAGATCCACAACCTGCTGGGTATTCAACCGTTCGCGCGTTGCTTTGAGATGAAAGAAGCGTGCTATGCGGCGACCCCGGC

GATCCAGCTGGCGAAGGACTATCTGGCGACCCGTCCGAACGAAAAAGTGCTGGTTATTGCGACCGATACCGCGCGTTATGGTC

TGAACAGCGGTGGCGAGCCGACCCAGGGTGCGGGTGCGGTGGCGATGGTTATTGCGCACAACCCGAGCATTCTGGCGCTGAAC

GAAGACGCGGTGGCGTACACCGAGGACGTTTATGATTTCTGGCGTCCGACCGGTCACAAGTACCCGCTGGTTGACGGCGCGCT

GAGCAAAGATGCGTACATCCGTAGCTTCCAGCAAAGCTGGAACGAATATGCGAAACGTCAGGGCAAGAGCCTGGCGGATTTTG

CGAGCCTGTGCTTCCACGTTCCGTTTACCAAGATGGGCAAAAAGGCGCTGGAAAGCATCATTGACAACGCGGATGAGACCACC

CAAGAACGTCTGCGTAGCGGTTACGAGGACGCGGTGGATTACAACCGTTATGTTGGTAACATCTACACCGGCAGCCTGTATCT

GAGCCTGATTAGCCTGCTGGAAAACCGTGACCTGCAAGCGGGCGAGACCATCGGCCTGTTCAGCTACGGTAGCGGCAGCGTGG

TTGAGTTTTACAGCGCGACCCTGGTGGTTGGCTATAAGGACCACCTGGATCAAGCGGCGCACAAAGCGCTGCTGAACAACCGT

ACCGAAGTGAGCGTTGACGCGTATGAGACCTTCTTTAAACGTTTCGACGATGTGGAATTTGACGAGGAACAAGATGCGGTTCA

CGAGGATCGTCACATCTTTTACCTGAGCAACATTGAGAACAACGTGCGTGAATATCACCGTCCGGAGGGTGGTGGTGGTTCAG

GTGGTGGTGGTTCAGGTGGTGGTGGTTGTGGTGCCATGGTTGATACCTTATCAGGTTTATCAAGTGAGCAAGGTCAGTCCGGT

GATATGACAATTGAAGAAGATAGTGCTACCCATATTAAATTCTCAAAACGTGATGAGGACGGCAAAGAGTTAGCTGGTGCAAC

TATGGAGTTGCGTGATTCATCTGGTAAAACTATTAGTACATGGATTTCAGATGGACAAGTGAAAGATTTCTACCTGTATCCAG

GAAAATATACATTTGTCGAAACCGCAGCACCAGACGGTTATGAGGTAGCAACTGCTATTACCTTTACAGTTAATGAGCAAGGT

CAGGTTACTGTAAATGGCAAAGCAACTAAAGGTGACGCTCATATTTAAgaattcaggaggaaaacatcATGCAGAGCCTGGAC

AAAAACTTCCGTCACCTGAGCCGTCAGCAAAAGCTGCAACAACTGGTTGATAAGCAGTGGCTGAGCGAGGACCAATTTGACAT

CCTGCTGAACCACCCGCTGATTGACGAGGAAGTGGCGAACAGCCTGATCGAAAACGTTATTGCGCAAGGTGCGCTGCCGGTGG

GTCTGCTGCCGAACATCATTGTTGACGATAAGGCGTACGTGGTTCCGATGATGGTGGAGGAACCGAGCGTGGTTGCTGCGGCG

AGCTATGGTGCGAAACTGGTGAACCAGACCGGTGGCTTCAAGACCGTTAGCAGCGAGCGTATCATGATTGGTCAAATCGTGTT

TGACGGCGTTGACGATACCGAAAAACTGAGCGCGGATATTAAGGCGCTGGAGAAACAGATCCACAAGATTGCGGACGAAGCGT

ACCCGAGCATCAAGGCGCGTGGTGGCGGTTATCAACGTATCGCGATTGATACCTTCCCGGAGCAGCAACTGCTGAGCCTGAAA

GTGTTTGTTGACACCAAGGATGCGATGGGTGCGAACATGCTGAACACCATCCTGGAGGCGATTACCGCGTTCCTGAAAAACGA

AAGCCCGCAGAGCGACATCCTGATGAGCATTCTGAGCAACCACGCGACCGCGAGCGTGGTTAAAGTGCAAGGCGAGATCGACG

TTAAGGATCTGGCGCGTGGTGAACGTACCGGCGAGGAAGTTGCGAAACGTATGGAACGTGCGAGCGTGCTGGCGCAGGTTGAC

ATCCACCGTGCGGCGACCCACAACAAGGGTGTGATGAACGGCATTCACGCGGTGGTTCTGGCGACCGGTAACGATACCCGTGG

CGCGGAGGCGAGCGCGCATGCGTACGCGAGCCGTGACGGTCAATATCGTGGCATCGCGACCTGGCGTTACGATCAGAAACGTC

AACGTCTGATCGGCACCATTGAAGTTCCGATGACCCTGGCGATTGTGGGCGGTGGCACCAAAGTTCTGCCGATTGCGAAGGCG

AGCCTGGAGCTGCTGAACGTGGACAGCGCGCAGGAACTGGGTCATGTGGTTGCGGCGGTTGGTCTGGCGCAAAACTTTGCGGC

GTGCCGTGCGCTGGTTAGCGAGGGTATTCAGCAAGGCCACATGAGCCTGCAATATAAAAGCCTGGCGATCGTGGTTGGTGCGA

AGGGCGATGAAATTGCGCAGGTTGCGGAGGCGCTGAAGCAAGAGCCGCGTGCGAACACCCAGGTGGCGGAGCGTATCCTGCAA

GAAATTCGTCAGCAAactagtGGTGGTGGTGGTTCAGGTGGTGGTGGTTGTGGTGCTAGCAAGCCGCTGCGTGGTGCCGTGTT

TAGCCTGCAGAAACAGCATCCCGACTATCCCGATATCTATGGCGCGATTGATCAGAATGGGACCTATCAAAATGTGCGTACCG

GCGAAGATGGTAAACTGACCTTTAAGAATCTGAGCGATGGCAAATATCGCCTGTTTGAAAATAGCGAACCCGCTGGCTATAAA

CCGGTGCAGAATAAGCCGATTGTGGCGTTTCAGATTGTGAATGGCGAAGTGCGTGATGTGACCAGCATTGTGCCGCAGGATAT

TCCGGCTACATATGAATTTACCAACGGTAAACATTATATCACCAATGAACCGATACCGCCGAAATAA

3.4 Multienzymes assembly modules of cross-linking MVA-drimenol synthesis pathway (pETDuet-1)

MCS1: RK-ERG20-RK-rbs-EcIDI-NGCatcher-rbs-NGTag-SnoopTag-β-Cav1 (linker)

ATGCGTAAACGTAAACGTAAAGCGAGCGAGAAAGAAATCCGTCGTGAGCGTTTCCTGAACGTGTTTCCGAAGCTGGTTGAGGA

ACTGAACGCGAGCCTGCTGGCGTACGGTATGCCGAAAGAAGCGTGCGACTGGTACGCGCACAGCCTGAACTATAACACCCCGG

GTGGCAAGCTGAACCGTGGCCTGAGCGTGGTTGATACCTACGCGATTCTGAGCAACAAAACCGTGGAGCAGCTGGGTCAAGAG

GAATATGAAAAGGTTGCGATCCTGGGCTGGTGCATTGAGCTGCTGCAAGCGTACTTCCTGGTGGCGGACGATATGATGGACAA

AAGCATCACCCGTCGTGGTCAACCGTGCTGGTATAAGGTGCCGGAAGTGGGCGAAATCGCGATTAACGATGCGTTCATGCTGG

AGGCGGCGATTTACAAGCTGCTGAAAAGCCACTTCCGTAACGAAAAGTACTACATCGACATTACCGAGCTGTTCCACGAAGTT

ACCTTTCAGACCGAGCTGGGTCAACTGATGGATCTGATCACCGCGCCGGAAGACAAAGTGGATCTGAGCAAGTTCAGCCTGAA

GAAACACAGCTTCATTGTTACCTTTAAGACCGCGTACTATAGCTTTTACCTGCCGGTGGCGCTGGCGATGTATGTTGCGGGCA

TCACCGACGAGAAGGATCTGAAACAGGCGCGTGACGTGCTGATCCCGCTGGGTGAATACTTCCAGATTCAAGACGATTATCTG

GATTGCTTTGGCACCCCGGAGCAGATCGGTAAAATTGGCACCGACATCCAAGATAACAAATGCAGCTGGGTGATTAACAAGGC

GCTGGAGCTGGCGAGCGCGGAACAGCGTAAGACCCTGGACGAGAACTATGGTAAGAAAGATAGCGTTGCGGAAGCGAAATGCA

AGAAAATCTTTAACGACCTGAAGATTGAGCAGCTGTACCACGAATATGAGGAAAGCATCGCGAAGGACCTGAAGGCGAAAATT

AGCCAAGTTGACGAAAGCCGTGGCTTCAAGGCGGATGTGCTGACCGCGTTTCTGAACAAGGTTTACAAACGTAGCAAGCGTAA

ACGTAAATAAggatcggatctaggaggtaatcataATGCAGACCGAGCACGTGATCCTGCTGAACGCGCAAGGTGTTCCGACC

GGCACCCTGGAAAAGTATGCGGCGCACACCGCGGACACCCGTCTGCACCTGGCGTTCAGCAGCTGGCTGTTTAACGCGAAGGG

TCAGCTGCTGGTGACCCGTCGTGCGCTGAGCAAGAAAGCGTGGCCGGGCGTGTGGACCAACAGCGTTTGCGGTCACCCGCAAC

TGGGCGAGAGCAACGAAGATGCGGTGATCCGTCGTTGCCGTTACGAGCTGGGTGTTGAAATCACCCCGCCGGAGAGCATTTAC

CCGGACTTCCGTTATCGTGCGACCGATCCGAGCGGCATCGTGGAGAACGAAGTGTGCCCGGTTTTTGCGGCGCGTACCACCAG

CGCGCTGCAAATTAACGACGATGAGGTGATGGACTATCAATGGTGCGACCTGGCGGATGTTCTGCACGGTATTGATGCGACCC

CGTGGGCGTTCAGCCCGTGGATGGTTATGCAGGCGACCAACCGTGAAGCGCGTAAGCGTCTGAGCGCGTTTACCCAACTGAAA

GGTGGTGGTGGTTCAGGTGGTGGTGGTTGTGGTGCAATGGTGGATACACTGAGTGGTCTGAGCAGCGAACAGGGGCAGAGCGG

AGATATGACCATTGAAGAAGATGATGCAACCCATATTGAATTCAGCAAACGCGATGAGGACGGTAAAGAACTGCCGGGGGCAA

CCATGGAACTGCGCGATAGCAGCGGTAAAACAATTAGCACCTGGATTAGCGATGGACAGGTGAAAGATTTTTACCTGGAACCA

GGAGAATACACATTTGTGGAAACCGAAGCACCAGACGGCTATGAAGTTGATGATGCAATTACCTTTACCGTAAACGAAGATGG

ACAGGTGACCGAAGAAGGAAAAGCAACCAAAGGAGATGCACATATCTAAgaattcaggaggaaaacatcATGAGGGGGGCTCA

CATAGTAATGGTTGATGCGTACAAGCCGACGAAGGGTGGTGGCTCTGGTGGCGGGGGCTGCGGTGCTTCGAAACTGGGTGATA

TTGAATTTATTAAGGTCAACAAAGGCGGCGGTTCTGGCGGTGGTGGGTGCGGTATGGCGGATGAACTGAGCGAGAAACAGGTT

TATGATGCCCACACCAAGGAGATCGACTTGGTTAACCGTGACCCAAAGCACCTGAATGATGACGTGGTGAAGATCGACTTCGA

GGACGTCATCGCCGAACCGGAAGGCACTCATAGCTTCGACGGCATTTGGAAAGCGAGCTTCACCACCTTCACCGTTACCAAAT

ACTGGTTTTATCGTCTTCTGAGTGCATTGTTCGGCATCCCGATGGCGTTAATCTGGGGTATCTATTTTGCAATTCTGTCCTTC

CTGCATATTTGGGCGGTGGTTCCGTGCATCAAGTCCTTCTTGATCGAGATCCAGTGTATTAGCCGCGTGTACAGCATTTACGT

GCACACGGTTTGTGATCCGCTGTTTGAAGCTGTGGGTAAAATTTTTAGCAATGTTCGTATTAACCTGCAAAAAGAGATCTAA

MCS2: DrtB-SnoopCatcher (linker)

ATGGTAAGGGCTCTAATATTGGACTTAGGAGATGTCCTCTTCAACTGGGATGCGCCGGCTAGCACCCCGATCAGCCGTAAAAC

GCTGGGCCAGATGCTGCACTCCGAGATTTGGGGTGAATATGAACGTGGTCATCTGACCGAAGACGAGGCCTATAACGCGCTAG

CGAAGCGCTACAGCTGCGAAGCGAAGGACGTCGCACATACCTTCGTGTTGGCGCGCGAGAGCTTGCGCCTGGATACCAAATTT

AAAACCTTCCTGCAAACCTTAAAGCAAAACGCGAACGGTTCACTGCGCGTGTATGGCATGAGCAATATTTCGAAGCCGGACTT

TGAAGTTTTGCTGGGCAAAGCTGATGACTGGACCTTGTTCGATAAAATCTTCCCGAGCGGTCACGTGGGCATGCGAAAGCCGG

ACTTGGCGTTCTTTCGTTACGTCTTGAAAGACATCTCCACGCCGGTGGAAGACGTTGTTTTCGTAGACGATAACTTGGACAAC

GTGACGTCGGCCCGTAGCCTGGGTATGAGAAGCGTTCTTTTTCACAAGAAAGATGAGGTTCAGCGTCAGTTGACGAATATTTT

TGGTAGCCCGGCAGAGCGCGGTCTGGAGTACCTGTCTGCGAATAAAACTAACCTTCAAAGCGCGACCACGACTGACATCCCGA

TCCAGGACAATTTCGGCCAACTGCTGATCCTGGAGGCTACCGAGGACCCGTCTCTGGTTCGTATGGAACCGGGTAAAAGAACA

TGGAATTTTTTCATTGGCTCTCCGAGCCTGACCACCGATACTTTTCCGGATGACTTAGATACCACCAGTCTTGCGCTGTCCAT

TGTTCCGACTTCGCCGGACGTGGTGAACAGCGTGATTGACGAGATCATCAGTCGTCGCGATAAAGACGGCATCGTGCCGACGT

ACTTCGACAACACCCGTCCTCGTGTAGACCCGATTGTTTGCGTTAACGTGTTGAGCATGTTTGCGAAATACGGGCGTGAGCAC

GATCTGCCGGCAACAGTTGCGTGGGTTCGTGATGTGCTGTATCATCGTGCCTACCTGGGCGGTACCCGCTACTATGGTTCCGC

CGAAGCATTTCTGTTCTTCTTCACCCGTTTTGTTCGTAATCTGCGTCCAGGTACGCTGAAGCAGGATTTGCACGCCCTCCTGT

CCGAACGCGTGCGCGAGCGCTTAAATACCCCGGTTGATGCACTGGCTTTGTCTATGCGTATTCAGGCATGTCATGCGCTGGGT

TTTGACGCGCCAGCGGATATCGCGACCCTGATTACCATGCAGGATGAGGATGGCGGTTGGCCGGCGGCAGTCATCTATAAGTA

CGGCGCGGGTGGTCTGGGCATCACCAACCGTGGTGTTTCTACCGCATTCGCAGTTAAAGCAATTACCGGTTCCCCGGTCAAGA

CCGAAACCAATATCGGTGGCGACGGCGCTCGTGCGGTGAGCGCTATGAGCAGCCTTGAAGCTCGTCGTCTTCAACCAATTAGC

AGCGTGGGCGATTGGGTGCGCTTCATCATTGCTAGCCTGCACGTTCACCTGGCGTGGCTGTGGAACGTGCTGTTGCTGTCCAA

GGTGGTAGGGGGAGGCGGATCAGGTGGGGGAGGTTGTGGCGCCTCTAAGCCGTTACGTGGTGCTGTGTTCAGCCTGCAGAAGC

AGCACCCGGACTATCCGGACATCTATGGTGCGATTGATCAAAACGGCACGTACCAAAACGTTCGTACCGGTGAAGATGGCAAG

CTGACCTTTAAGAATTTGTCCGACGGCAAGTACCGCCTGTTCGAAAACAGCGAGCCGGCAGGTTATAAACCGGTCCAGAATAA

ACCGATTGTGGCGTTTCAGATCGTAAATGGCGAGGTTCGTGACGTTACCTCGATCGTGCCGCAAGATATTCCGGCGACCTACG

AGTTCACTAACGGTAAACATTACATTACCAACGAACCAATCCCGCCTAAATAA

3.5 Heterologous biosynthesis of drimenol in *E. coli*

Recombinant plasmids were transformed into *E. coli* BL21(DE3) or MG1655(DE3) strain for drimenol production. A single colony was inoculated into LB medium (1 mL) containing chloramphenicol (34 mg/L) and carbenicillin (50 mg/L) and incubated at 37 °C and 220 rpm overnight. 180 μL of seed culture was inoculated into 9 mL of AM mineral medium containing chloramphenicol (17 mg/L) and carbenicillin (100 mg/L) and incubated at 37 °C and 220 rpm until OD_{600} reach 0.5–0.6. The culture was precooled at 4 °C before it was induced with isopropyl β-D-1-thiogalactopyranoside (IPTG, 0.1 mM) and overlaid with 20% (v/v) dodecane. After shaking at 25 °C and 180 rpm for 72 h, the final OD_{600} of culture (50-fold dilution) was measured with ultraviolet-visible spectrophotometer and the culture was centrifuged at 48,000*g* for 10 min. 1 μL of organic layer was diluted to 400-fold with dodecane, and the resulting sample was analyzed by GC-MS. The quantification of product was determined by the external standard method. All assays were performed with three biological replicates.

For large-scale flask fermentation, the optimal recombinant strain (MG1655(DE3) harboring pACYCDuet-T1B1 and pETDuet-ERG20-DrtB) was cultured and enlarged to 1 L AM mineral medium, and the process was same as mentioned above. After 72 h fermentation, the culture was centrifuged at 9,000*g* for 30 min. The organic phase was separated, and the aqueous phase was extract with ethyl acetate for three times. The resulting samples were dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by flash chromatography (silica gel) and eluted with hexane/ethyl acetate (50:1) to afford 1.1 g drimenol as a white powder.

GC-MS analysis

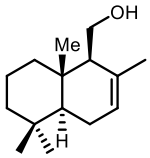
GC-MS was performed on a Shimadzu Nexis GC-2030 series GC system equipped with an SH-Rxi-5Sil column (30 m × 0.25 mm × 0.25 μm; Shimadzu) and coupled with a QP2020 NX mass spectrometer. For drimenol, the carrier gas was helium at a constant linear velocity of 40 cm/sec. Injection (1 μL) was in split-less mode with the injector temperature set at 250 °C and the oven temperature was programmed from 80 °C to 170 °C at 20 °C/min (2 min hold), followed by an 8 °C/min ramp to 210 °C, then a 15 °C/min ramp to 300 °C (2 min hold). The identity of the drimenol was confirmed based on the concordance of mass spectrum

with the National Institute of Standards and Technology (NIST) Standard Reference Database (version 2017). For oxidated product of drimenol by $P450_{BM3}$ enzyme, the oven temperature program was set from 65 °C to 160 °C at 25°C/min (1 min hold), followed by a 6 °C/min ramp to 230 °C (2 min hold), then a 50 °C/min ramp to 310 °C (2 min hold).

Table S1. The primers used for heterologous biosynthesis of drimenol.

Primer	**Sequence (5'-3')**	**Purpose**
DrtB-CD53-F	ACCGAAACCAATATCTAAAGATCTCAATTGG	A plasmid pETDuet-ERG20-DrtB-CD53 construction
DrtB-CD53-R	CTTTAGATATTGGTTTCGGTCTTGACCGGG	
flank-IDI-F	AAACGTAGCAAGTAAGGATCCGGATCTAGGAGGTAATC	One more copy of *EcIDI* gene insertion into pETDuet-ERG20-DrtB plasmid
flank-IDI-R	AGGCGCGCCGAGCTCGAATTC	
28a-rbs-mvaA-F	TAAGAAGGAGATATACCATGGAGGAGGAAAACATCATGCAG	*mvaA* gene insertion into pET28a(+)
28a-rbs-mvaA-R	GTGGTGGTGGTGGTGCTCGAGTTATTGCTGACGAATTTCTTG	
T1-mvaA-ter-F	ATTCGTCAGCAATAAGAATTCAGGAGGAAAACATCATGCAGAG	One more copy of *mvaA* gene with T7 terminator insertion into pACYCDuet-T1B1
T1-mvaA-ter-R	GACCTGCAGGCGCGCCGAGCTCCAGCAAAAAACCCCTCAAGACCC	
RK-ERG20-F	TAAGAAGGAGATATACCATGCGTAAACGTAAACGTAAAGCGAGCGAGAAAGAAATCCG	RK-ERG20-RK, EcIDI-NGCatcher and NGTag-SnoopTag-β-Cav1 fragments assembly
RK-ERG20-R	TTATTTACGTTTACGCTTGCTACGTTTGTAAACCTTG	
RK tail-IDI-F	CGTAAACGTAAATAAGGATCCGGATCTAGGAGGTAATC	
linker-IDI-R	CTGAACCACCACCACCTTTCAGTTGGGTAAACGCGCTC	
linker-NGCatcher-F	GGTGGTGGTGGTTCAGGTG	
β-Cav1-R	AAGCTTGTCGACCTGCAG	
DrtB-F	TAAGAAGGAGATATACATATGGTAAGGG	DrtB-SnoopCatcher fragment assembly
DrtB-R	TACCACCTTGGACAGCAACAG	
DrtB tail-F	CTGTTGCTGTCCAAGGTGGTA	
Duet-R	GGTTTCTTTACCAGACTCGAG	
rev-atoB-B1-F	GAGCTCGGCGCGCCTGCAGGTC	pACYCDuet-atoB-B1 vector linearization
rev-atoB-B1-R	GTTCAGACGTTCAATAACCATCGCGATGCCCTGAC	

AtoB tail-F	GCGATGGTTATTGAACGTC	AtoB_tail-SpyTag-SpyTag-SnoopTag-SnoopTag, mvaS-SpyCatcher and mvaA-SnoopCatcher fragments assembly
mvaS-head-R	GATTTTGTCAATACCGATGG	
mvaS-head-F	ACCATCGGTATTGACAAAATC	
mvaS-R	CTCCGGACGGTGATATTCAC	
mvaS-tail-F	GTGAATATCACCGTCCGGAG	
mvaA-head-R	GAAGTTTTTGTCCAGGCTCTG	
mvaA-head-F	AGAGCCTGGACAAAAACTTC	
mvaA-R	TTGCTGACGAATTTCTTGCAG	
mvaA-tail-F	ATCCTGCAAGAAATTCGTCAGC	
ACYC-R	ACCTGCAGGCGCGCCGAGC	



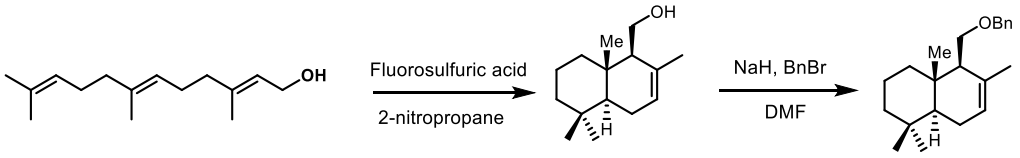
(-)-Drimenol
11

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.54 (m, 1H), 3.86 (dd, *J* = 11.3, 3.4 Hz, 1H), 3.74 (dd, *J* = 11.3, 4.9 Hz, 1H), 1.93 – 2.05 (m, 2H), 1.83 – 1.92 (m, 2H), 1.77 – 1.79 (m, 3H), 1.55 (m, 1H), 1.39 – 1.49 (m, 2H), 1.13 – 1.22 (m, 2H), 1.07 (td, *J* = 13.1, 3.9 Hz, 1H), 0.89 (s, 3H), 0.86 (s, 3H), 0.86 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 133.0, 124.2, 61.0, 57.4, 50.0, 42.3, 40.0, 36.2, 33.5, 33.0, 23.7, 22.2, 22.1, 18.9, 15.0.

$[\alpha]_D^{23}$ = −43.30 (c = 1.00, $CHCl_3$).

HRMS (ESI+): calculated for $C_{15}H_{25}O_2$ $[M+H-H_2O]^+$: 205.1951, found 205.1950.



(*E,E*)-farnesol (±)-Drimenol (±)-**S8**

The racemic drimenol was synthesized according to the literature.[3]

Synthesis of racemic benzyl-substituted drimenol derivative (±)-**S8**:

A solution of (*E,E*)-farnesol (44.4 mg, 0.20 mmol, 1.0 equiv.) was treated with fluorosulfonic acid (400 mg, 4.0 mmol, 20 equiv.) in 2-nitropropane (2 mL) at –78 °C for 2 hours. The reaction mixture was neutralized with Et_3N, washed with H_2O (10 mL) and extracted with Et_2O (10 mL × 3). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/ethyl acetate = 30:1) to give (±)-Drimenol (26.6 mg, 60%

yield) as white solid.

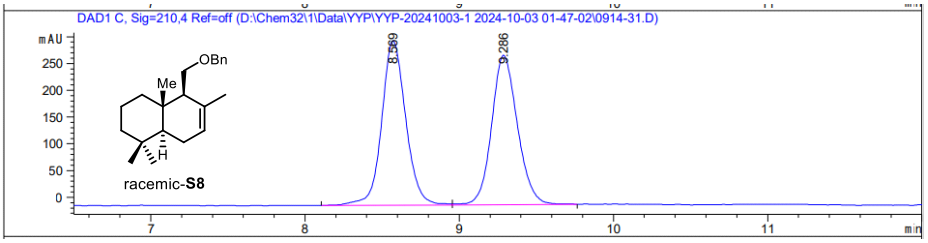
A solution of (±)-Drimenol (22.2 mg, 0.10 mmol, 1.0 equiv.) in DMF (1 mL) was treated with NaH (60% dispersion in mineral oil, 6 mg, 0.15 mmol, 1.5 equiv.) and BnBr (25.7 mg, 0.15 mmol, 1.5 equiv.). The reaction mixture was stirred at 23 °C for 10 hours before it was quenched with H_2O (10 mL) and extracted with EtOAc (10 mL × 3). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/ethyl acetate = 70:1) to give (±)-**S8** (29.6 mg, 95% yield) as colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.33 (d, *J* = 4.4 Hz, 4H), 7.29 – 7.23 (m, 1H), 5.41 – 5.51 (m, 1H), 4.46 (dd, *J* = 12.0, 2.8 Hz, 2H), 3.61 (dd, *J* = 9.7, 2.9 Hz, 1H), 3.42 (dd, *J* = 9.7, 6.2 Hz, 1H), 1.95 – 2.02 (m, 2H), 1.81 – 1.94 (m, 2H), 1.74 (s, 3H), 1.48 – 1.56 (m, 1H), 1.35 – 1.46 (m, 2H), 1.19 (dd, *J* = 12.3, 4.5 Hz, 1H), 1.15 (dd, *J* = 13.3, 3.7 Hz, 1H), 1.08 (td, *J* = 13.1, 3.7 Hz, 1H), 0.88 (s, 3H), 0.86 (s, 3H), 0.80 (s, 3H)..

^{13}C NMR (151 MHz, $CDCl_3$): δ 138.7, 134.1, 128.4, 127.8, 127.5, 122.9, 73.1, 69.3, 54.8, 50.1, 42.4, 39.7, 36.0, 33.5, 33.1, 23.8, 22.1, 22.1, 19.0, 14.7.

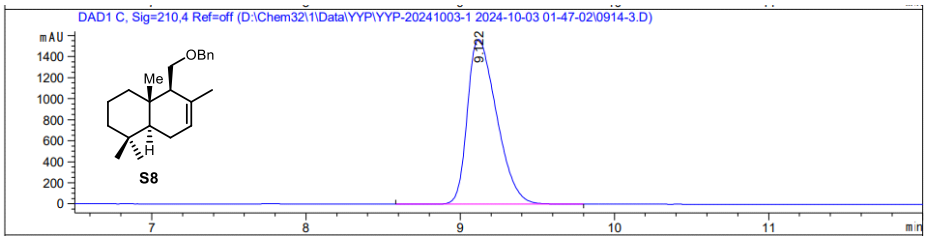
(-)-Drimenol was derivated with benzyl group to determine the *ee* value (>99% *ee*).

HPLC (OD-H, 0.46*25 cm, 5μm, hexane / 2-propanol = 99.5/0.5, flow 1 mL/min, detection at 210 nm) retention time = 9.122 min (>99% *ee*).



Signal 2: DAD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.569	BV	0.1647	3340.55859	307.69394	50.5954
2	9.286	VB	0.1801	3261.93384	279.60977	49.4046



Signal 2: DAD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.122	VV R	0.2029	2.05207e4	1564.71045	100.0000

4. Biocatalytic oxidation of drimenol catalyzed by $P450_{BM3}$ mutants

4.1 Expression and purification of cytochrome $P450_{BM3}$ (F87A) and BmGDH

$P450_{BM3}$ (F87A) was codon-optimized and synthesized by GenScript (Nanjing, China) and cloned into the multiple cloning site of pET28a(+) with NdeI/XhoI restriction site. Recombinant plasmid was transformed into *E. coli* BL21(DE3) strain for $P450_{BM3}$ (F87A) expression. A single colony was inoculated into LB medium (20 mL) containing kanamycin (50 μg/mL) and incubated at 37 °C and 220 rpm overnight as the seed culture. Then the seed culture was inoculated into 1 L modified P450 expression medium, of which the saturated glutamate was removed in power mix.[4] The culture was incubated at 37 °C and 220 rpm until OD_{600} arrived ~0.8. After cooling on ice for 30 min, the culture was induced with 0.1 mM IPTG and incubated at 30 °C, 200 rpm for 20 h. After expression, the cells were harvested by centrifugation at 4 °C and 9,000*g* for 15 min. The pellets were stored at −80 °C until further processing. For cell lysis, the pellet was thawed by adding 50 mL of lysis buffer (50 mM Kpi buffer, pH 7.4, 0.1 M KCl, 5 mM $MgCl_2$, 5 mM imidazole, 2 mM PMSF, 5% glycerol, 0.05% Triton X-100, and 20 mg/L DNAse I, 1 mg/mL lysozyme, room temperature) per liter of initial culture and resuspended by vortexing. Cells were lysed by high pressure homogenizer. The collected lysate was centrifuged at 4 °C and 48,000*g* for 30 min. The resulted brownish-red supernatant was combined with 15 mL of Ni-NTA Beads pre-equilibrated with wash buffer (50 mM Kpi buffer, pH 7.4, 0.1 M KCl, 5 mM imidazole, 5% glycerol) at 4 °C for 30 min. After washing with 3 column volumes of wash buffer, $P450_{BM3}$ (F87A) was eluted with 3 column volumes of the elution buffer A (50 mM Kpi buffer, pH 7.4, 0.1 M KCl, 100 mM imidazole, 5% glycerol) and 1 column volume of the elution buffer B (50 mM Kpi buffer, pH 7.4, 0.1 M KCl, 250 mM imidazole, 5% glycerol). The purified protein was exchanged with stock buffer (50 mM Kpi buffer, pH 7.4, 0.1 M KCl, 5% glycerol) and concentrated by ultrafiltration. The concentration of $P450_{BM3}$ (F87A) was measured by A_{280} of $P450_{BM3}$. The purified $P450_{BM3}$ (F87A) was frozen in stock buffer at −80 ºC until further usage.

The plasmid pET22b-BmGDH was kindly provided by Pingkai Ouyang lab from Nanjing Tech University and utilized as template to construct a BmGDH C' terminal 6xhis tag fused plasmid pET22b-BmGDH-His by Gibson Assembly with primers GDH-F (5'-GTGGTGGTGGTGGTGCTCGAGGCCTCTTCCTGCTTGGAAAGAAG-3') and GDH-R 5'-CTTTAAGAAGGAGATATACATATGTATACAGATTTAAAAGATAAAGTAG-3') and NdeI/XhoI restriction site. The plasmid pET22b-BmGDH-His was transformed into *E. coli* BL21(DE3) cells. A single

colony was inoculated in 20 mL of LB medium containing ampicillin (100 μg/mL). After shaking at 37 ºC and 220 rpm overnight, the culture was added to 1 L of LB medium containing ampicillin (100 μg/mL). The cultures were incubated at 37 ºC and 220 rpm until OD_{600} reached 0.8–0.9. The culture was pre-cooled to 4 ºC, and induced with IPTG (0.1 mM). After shaking at 25 ºC and 180 rpm for 16h, the cells were harvested by centrifugation at 20 °C and 9,000*g* for 15 min. The pellets were stored at −80 °C until further processing. The purification of BmGDH was the same as $P450_{BM3}$ (F87A).

$P450_{BM3}$ (F87A) (1049 aa, 3150 bp)

MTIKEMPQPKTFGELKNLPLLNTDKPVQALMKIADELGEIFKFEAPGRVTRYLSSQRLIKEACDESRFDKNLSQALKFVRDFA
GDGLATSWTHEKNWKKAHNILLPSFSQQAMKGYHAMMVDIAVQLVQKWERLNADEHIEVPEDMTRLTLDTIGLCGFNYRFNSF
YRDQPHPFITSMVRALDEAMNKLQRANPDDPAYDENKRQFQEDIKVMNDLVDKIIADRKASGEQSDDLLTHMLNGKDPETGEP
LDDENIRYQIITFLIAGHETTSGLLSFALYFLVKNPHVLQKAAEEAARVLVDPVPSYKQVKQLKYVGMVLNEALRLWPTAPAF
SLYAKEDTVLGGEYPLEKGDELMVLIPQLHRDKTIWGDDVEEFRPERFENPSAIPQHAFKPFGNGQRACIGQQFALHEATLVL
GMMLKHFDFEDHTNYELDIKETLTLKPEGFVVKAKSKKIPLGGIPSPSTEQSAKKVRKKAENAHNTPLLVLYGSNMGTAEGTA
RDLADIAMSKGFAPQVATLDSHAGNLPREGAVLIVTASYNGHPPDNAKQFVDWLDQASADEVKGVRYSVFGCGDKNWATTYQK
VPAFIDETLAAKGAENIADRGEADASDDFEGTYEEWREHMWSDVAAYFNLDIENSEDNKSTLSLQFVDSAADMPLAKMHGAFS
TNVVASKELQQPGSARSTRHLEIELPKEASYQEGDHLGVIPRNYEGIVNRVTARFGLDASQQIRLEAEEEKLAHLPLAKTVSV
EELLQYVELQDPVTRTQLRAMAAKTVCPPHKVELEALLEKQAYKEQVLAKRLTMLELLEKYPACEMKFSEFIALLPSIRPRYY
SISSSPRVDEKQASITVSVVSGEAWSGYGEYKGIASNYLAELQEGDTITCFISTPQSEFTLPKDPETPLIMVGPGTGVAPFRG
FVQARKQLKEQGQSLGEAHLYFGCRSPHEDYLYQEELENAQSEGIITLHTAFSRMPNQPKTYVQHVMEQDGKKLIELLDQGAH
FYICGDGSQMAPAVEATLMKSYADVHQVSEADARLWLQQLEEKGRYAKDVWAG

atgaccatcaaagaaatgccgcagccgaagaccttcggcgagctgaaaaacctgccgctgctgaacaccgacaagccggtgca
agcgctgatgaaaatcgcggatgaactgggcgagattttcaagtttgaggcgccgggccgtgttacccgttacctgagcagcc
agcgtctgatcaaagaggcgtgcgacgaaagccgtttcgataagaacctgagccaagcgctgaaattcgtgcgtgactttgcg
ggtgatggtctggcgaccagctggacccacgaaaagaactggaagaaagcgcacaacatcctgctgccaagctttagccagca
agcgatgaagggttatcacgcgatgatggtggacattgcggtgcagctggttcaaaaatgggagcgtctgaacgcggatgaac
acatcgaggttccggaagacatgacccgtctgaccctggataccattggcctgtgcggtttcaactaccgtttcaacagcttt
tatcgtgaccagccgcacccgtttatcaccagcatggttcgtgcgctggatgaagcgatgaacaagctgcaacgtgcgaaccc
ggacgatccggcgtacgacgaaaacaagcgtcagttccaagaggatattaaagtgatgaacgacctggttgataagatcattg

cggaccgtaaagcgagcggcgagcagagcgacgatctgctgacccacatgctgaacggtaaagatccggagaccggcgaaccg

ctggacgatgaaaacatccgttaccaaatcattacctttctgattgcgggtcatgagaccaccagcggcctgctgagcttcgc

gctgtattttctggtgaagaacccgcacgttctgcaaaaggcggcggaggaagcggcgcgtgtgctggtcgacccggtgccga

gctacaagcaggttaaacaactgaagtatgtgggtatggttctgaacgaagcgctgcgtctgtggccgaccgcgccggcgttc

agcctgtacgcgaaagaggacaccgtgctgggtggcgagtatccgctggaaaaaggtgacgagctgatggttctgatcccgca

gctgcaccgtgataagaccatttggggcgacgatgtggaggagttccgtccggagcgttttgaaaacccgagcgcgatcccgc

agcacgcgttcaaaccgtttggtaacggccaacgtgcgtgcattggtcagcaattcgcgctgcacgaagcgaccctggttctg

ggcatgatgctgaagcacttcgactttgaggatcacaccaactacgaactggacatcaaggagaccctgaccctgaaaccgga

gggttttgtggttaaggcgaaaagcaagaaaatcccgctgggtggcattccgagcccgagcaccgaacagagcgcgaagaaag

tgcgtaagaaagcggagaacgcgcacaacaccccgctgctggttctgtacggcagcaacatgggcaccgcggagggcaccgcg

cgtgacctggcggacatcgcgatgagcaaaggttttgcgccgcaagtggcgaccctggacagccatgcgggtaacctgccgcg

tgagggtgcggtgctgattgttaccgcgagctataacggtcacccgccggataacgcgaagcagtttgttgactggctggatc

aagcgagcgcggacgaagtgaaaggcgttcgttacagcgtgttcggttgcggcgataagaactgggcgaccacctatcagaaa

gttccggcgtttattgatgagaccctggcggcgaagggtgcggaaaacattgcggaccgtggcgaggcggatgcgagcgacga

tttcgaaggcacctacgaggaatggcgtgagcacatgtggagcgatgtggcggcgtattttaacctggacatcgagaacagcg

aagataacaaaagcaccctgagcctgcaattcgttgacagcgcggcggatatgccgctggcgaagatgcacggtgcgtttagc

accaacgtggttgcgagcaaagagctgcaacaaccgggcagcgcgcgtagcacccgtcacctggaaatcgagctgccgaaaga

agcgagctaccaagagggtgaccacctgggcgtgatcccgcgtaactatgaaggtattgtgaaccgtgttaccgcgcgttttg

gtctggatgcgagccagcaaattcgtctggaggcggaggaagagaagctggcgcacctgccgctggcgaaaaccgtgagcgtt

gaagagctgctgcaatacgtggagctgcaagacccggttacccgtacccaactgcgtgcgatggcggcgaagaccgtgtgccc

gccgcacaaagttgaactggaggcgctgctggaaaaacaggcgtacaaggagcaagttctggcgaagcgtctgaccatgctgg

agctgctggaaaagtatccggcgtgcgaaatgaaattcagcgagtttatcgcgctgctgccgagcattcgtccgcgttactat

agcatcagcagcagcccgcgtgtggacgaaaagcaggcgagcattaccgttagcgtggttagcggtgaagcgtggagcggtta

cggcgagtataaaggcatcgcgagcaactatctggcggagctgcaagagggtgacaccatcacctgcttcattagcaccccgc

aaagcgaatttaccctgccgaaagatccggagaccccgctgattatggttggtccgggcaccggtgttgcgccgttccgtggc

tttgtgcaggcgcgtaaacaactgaaggaacagggtcaaagcctgggcgaggcgcacctgtacttcggttgccgtagcccgca

cgaggactacctgtatcaggaagagctggaaaacgcgcaaagcgagggcatcattaccctgcacaccgcgtttagccgtatgc

cgaaccagccgaagacctatgtgcagcacgttatggaacaagacggtaagaaactgatcgagctgctggatcagggcgcgcac

ttctacatttgcggtgatggtagccagatggcgccggcggtggaagcgaccctgatgaaaagctatgcggacgtgcaccaagt

tagcgaggcggatgcgcgtctgtggctgcaacaactggaagagaaaggtcgttacgcgaaggatgtttgggcgggctaa

BmGDH (261 aa, 789 bp)

MYTDLKDKVVVITGGSTGLGRAMAVRFGQEEAKVVINYYNNEEEALDAKKEVEEAGGQAIIVQGDVTKEEDVVNLVQTATKEF

GTLDVMINNAGVENPVPSHELSLDNWNKVIDTNLTGAFLGSREAIKYFVENDIKGNVINMSSVHEMIPWPLFVHYAASKGGMK

LMTETLALEYAPKGIRVNNIGPGAMNTPINAEKFADPEQRADVESMIPMGYIGKPEEVAAVAAFLASSQASYVTGITLFADGG

MTKYPSFQAGRG

atgtatacagatttaaaagataaagtagttgtaattacaggtggatcaacaggtttaggacgcgcaatggctgttcgtttcgg

tcaagaagaagcaaaagttgttattaactattacaacaatgaagaagaagctttagatgcgaaaaaagaagtagaagaagcag

gcggacaagcaatcatcgttcaaggcgacgtaacaaaagaagaagacgttgtaaatcttgttcagacagctactaaagaattc

ggtacattagacgttatgattaacaacgctggtgttgaaaatccagttccttctcatgagttatctctagataactggaacaa

agttattgatacaaacttaacaggtgcattcttaggaagccgtgaagcaattaaatatttcgttgaaaacgatattaaaggaa

atgttatcaacatgtctagcgttcacgaaatgattccttggccattatttgttcactatgcagcaagtaaaggcggcatgaaa

ctaatgacggaaacattggctcttgaatatgcgccaaaaggtatccgcgtaaataacattggaccaggtgcgatgaacacacc

aattaacgcagagaaatttgcagatccagaacaacgtgcagacgtagaaagcatgattccaatgggctacatcggtaaaccag

aagaagtagcagcagttgcagcattcttagcatcatcacaagcaagctatgtaacaggtattacattatttgctgatggtggt

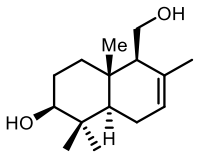
atgacgaaataccttctttccaagcaggaagaggctaa

4.2 *In vitro* enzymatic assay of $P450_{BM3}$ (F87A)

The 100 µL reaction mixture contained 100 mM Kpi buffer, pH 7.4, 100 mM glucose (1 M stock solution in 100 mM Kpi buffer, pH 7.4), 1 mM $NADP^+$ (100 mM stock solution in 100 mM Kpi buffer, pH 7.4), 10 µM $P450_{BM3}$ (F87A), 45 µM BmGDH in 2 mL tube. And the reaction was started by addition of 2 µL drimenol stock solution (50 mM, 100 mM in DMF, respectively). Then the tubes were shaken at 25 °C, 200 rpm for 16 h. The reaction was quenched by adding 200 µL ethyl acetate and extracted twice by vortexing. The mixture was centrifuged at 21,000g for 1 min. The collected organic phase was transferred into a new tube and concentrated with N_2 stream. The residual sample was dissolved with 100 µL ethyl acetate for the following GC-MS analysis. To verify that **11** was produced through selective epoxidation of **10**, 2 µL **10** stock solution (10 mM) was added to start the reaction instead of drimenol. The reaction condition and extraction method were the same as mentioned above. The sample was analyzed by GC-MS (Figure S3).

4.3 Product identification

In vitro enzymatic assay indicated that purified $P450_{BM3}$ (F87A) enzyme catalyzed the oxidation from drimenol to **12** with higher drimenol concentration and to **13** with lower drimenol concentration. To identify the structure of **12**, 100 mg drimenol dissolved in 4.5 mL DMF was added into the reaction mixture (100 mM Kpi buffer, pH 7.4, 100 mM glucose, 1 mM $NADP^+$, 10 μM $P450_{BM3}$ (F87A), 45 μM BmGDH). The total reaction volume was 225 mL and the final concentration of drimenol was 2 mM. The reaction was incubated at 25 °C, 200 rpm. During the reaction process, 100 μL reaction mixture was sampled and monitored by GC-MS analysis. After 32 h, the reaction mixture was extracted with equal volume ethyl acetate in three times. The organic phase was dried over Na_2SO_4 and removed at the rotary evaporator. After purification by column chromatography on silica gel, 65.4 mg **12** was obtained. **12** was confirmed by ^1H, ^{13}C, and X-ray crystallography (Table S2). To identify the structure of **13**, 20 mg drimenol dissolved in 4.5 mL DMF was added into the reaction mixture (100 mM Kpi buffer, pH 7.4, 200 mM glucose, 2 mM $NADP^+$, 20 μM $P450_{BM3}$ (F87A), 90 μM BmGDH). The total reaction volume was 225 mL and the final concentration of drimenol was 0.4 mM. The reaction was incubated for 22 h before extraction and the post-treatment was similar to mentioned above. Compound **13** was confirmed by ^1H, ^{13}C according to the previous report.[5]



12

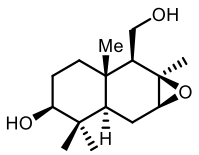
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.32 – 5.65 (m, 1H), 3.84 (dd, *J* = 11.3, 3.5 Hz, 1H), 3.73 (dd, *J* = 11.3, 5.1 Hz, 1H), 3.17 – 3.29 (m, 1H), 1.93 – 2.10 (m, 3H), 1.84 (bs, 1H), 1.74 – 1.80 (m, 3H), 1.54 – 1.69 (m, 2H), 1.27 – 1.29 (m, 1H), 1.23 – 1.26 (m, 1H), 1.19 (dd, *J* = 11.0, 5.7 Hz, 1H), 0.98 (s, 3H), 0.86 (s, 3H), 0.85 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 132.9, 124.0, 79.1, 60.9, 57.2, 49.5, 38.8, 38.0, 36.0, 28.2, 27.4, 23.4, 21.9, 15.5, 15.0.

$[\alpha]_D^{22} = -20.00$ (c = 0.50, $CHCl_3$).

Melting Point: 135-136 ºC.

HRMS (ESI+): calculated for $C_{15}H_{26}O_2Na$ $[M+Na]^+$: 261.1825, found 261.1824.



13

^{1}H NMR (400 MHz, $CDCl_3$) : δ 3.99 (dd, *J* = 11.4, 4.0 Hz, 1H), 3.95 (dd, *J* = 11.3, 4.0 Hz, 1H), 3.15 – 3.24 (m, 1H), 3.04 (d, *J* = 6.4 Hz, 1H), 1.91 – 2.06 (m, 2H), 1.76 – 1.88 (m, 2H), 1.63 – 1.55 (m, 2H), 1.43 (t, *J* = 4.0 Hz, 1H), 1.39 (s, 3H), 1.04 – 1.13 (m, 1H), 1.00 (s, 3H), 0.97 (dd, *J* = 13.3, 4.8 Hz, 1H), 0.92 (s, 3H), 0.80 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 78.9, 60.7, 60.6, 59.4, 55.1, 49.2, 39.0, 38.7, 36.1, 28.2, 27.0, 22.9, 21.7, 16.0, 15.3.

HRMS (ESI+): calculated for $C_{15}H_{26}O_3Na$ $[M+Na]^+$: 277.1780, found 277.1773.

Table S2. Crystal data and structure refinement for 3-(OH)-drimenol (**12**).

CCDC Number	2307775
Empirical formula	$C_{15}H_{26}O_2$
Formula weight	238.36
Temperature/K	100.0(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	9.9809(8)
b/Å	12.4367(11)
c/Å	21.6963(18)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2693.1(4)
Z	8
ρ_{calc}g/cm^3	1.176
μ/mm^{-1}	0.374
F(000)	1056.0
Crystal size/mm^3	0.21 × 0.19 × 0.16
Radiation	GaKα (λ = 1.34138)
2Θ range for data collection/°	7.09 to 147.078
Index ranges	-14 ⩽ h ⩽ 13, -17 ⩽ k ⩽ 17, -31 ⩽ l ⩽ 31
Reflections collected	126855

Independent reflections	8233 [Rint = 0.0637, Rsigma = 0.0234]
Data/restraints/parameters	8233/0/319
Goodness-of-fit on F^2	1.060
Final R indexes [I>=2σ (I)]	R1 = 0.0282, wR2 = 0.0760
Final R indexes [all data]	R1 = 0.0289, wR2 = 0.0767
Largest diff. peak/hole / e $Å^{-3}$	0.29/-0.16
Flack parameter	-0.03(4)

4.4 Docking drimenol into $P450_{BM3}$ (F87A)

The haem domain of $P450_{BM3}$ (F87A) was used as receptor structure for docking study, which was performed in Autodock Vina. Mutation of F87A was added to the wild-type $P450_{BM3}$ crystal structure (PDB code, 6K24) via Pymol. Simultaneously, the ligand, N-Abietoyl-L-Tryptophan, and all water molecules were removed from the structure prior to the docking calculation, and both receptor and substrate **9**, were treated as rigid entities. In Vina, the docking site was defined as a 22.5 Å × 22.5 Å × 22.5 Å box centered on the 87A, and poses were ranked using the Autodock Vina scoring function. The best pose of nine poses was selected according to the closest distance between C-3 of **11** and haem iron.

4.5 Construction of the focus library of $P450_{BM3}$

The $P450_{BM3}$ L75/F87 library was created by Quik-change PCR for site mutation. The annealing temperature was 72 ºC. The sequences of primers are shown in Table S3. The L75 mutagenetic primers were firstly applied to obtained nine L75 mutants with $P450_{BM3}$ (F87A) as template. Subsequently, those mutants were utilized as templates for generating remaining 72 mutants with F87 mutagenetic primers.

Table S3. The primers used for L75/F87 mutant library.

Primer	Sequence (5'-3')
L75A-F	CGATAAGAACCTGAGCCAAGCGgcgAAATTCGTG
L75A-R	GCAAAGTCACGCACGAATTTcgcCGCTTGGCTC
L75F-F	AAGAACCTGAGCCAAGCGtttAAATTCGTG
L75F-R	aaaCGCTTGGCTCAGGTTCTTATCGAAACGG
L75I-F	AAGAACCTGAGCCAAGCGattAAATTCGTG
L75I-R	aatCGCTTGGCTCAGGTTCTTATCGAAACGG
L75M-F	AAGAACCTGAGCCAAGCGatgAAATTCGTG
L75M-R	catCGCTTGGCTCAGGTTCTTATCGAAACGG

L75V-F	AAGAACCTGAGCCAAGCGgtgAAATTCGTG
L75V-R	cacCGCTTGGCTCAGGTTCTTATCGAAACGG
L75T-F	AAGAACCTGAGCCAAGCGaccAAATTCGTG
L75T-R	ggtCGCTTGGCTCAGGTTCTTATCGAAACGG
L75S-F	AAGAACCTGAGCCAAGCGagcAAATTCGTG
L75S-R	gctCGCTTGGCTCAGGTTCTTATCGAAACGG
L75G-F	AAGAACCTGAGCCAAGCGggcAAATTCGTG
L75G-R	gccCGCTTGGCTCAGGTTCTTATCGAAACGG
A87F-F	CTTTGCGGGTGATGGTCTGtttACCAGCTGGA
A87F-R	aaaCAGACCATCACCCGCAAAGTCACGCACG
F87L-F	CTTTGCGGGTGATGGTCTGctgACCAGCTGGA
F87L-R	cagCAGACCATCACCCGCAAAGTCACGCACG
F87I-F	CTTTGCGGGTGATGGTCTGattACCAGCTGGA
F87I-R	aatCAGACCATCACCCGCAAAGTCACGCACG
F87M-F	CTTTGCGGGTGATGGTCTGatgACCAGCTGGA
F87M-R	catCAGACCATCACCCGCAAAGTCACGCACG
F87V-F	CTTTGCGGGTGATGGTCTGgtgACCAGCTGGA
F87V-R	cacCAGACCATCACCCGCAAAGTCACGCACG
F87T-F	CTTTGCGGGTGATGGTCTGaccACCAGCTGGA
F87T-R	ggtCAGACCATCACCCGCAAAGTCACGCACG
F87S-F	CTTTGCGGGTGATGGTCTGagcACCAGCTGGA
F87S-R	gctCAGACCATCACCCGCAAAGTCACGCACG
F87G-F	CTTTGCGGGTGATGGTCTGggcACCAGCTGGA
F87G-R	gccCAGACCATCACCCGCAAAGTCACGCACG

4.6 Screening of the $P450_{BM3}$ library

Each pET28a-$P450_{BM3}$ mutant was co-transformed with pET22b-BmGDH into *E. coli* BL21(DE3). Three colonies or glycerol stocks were inoculated into a 96 deep wells plate, which was filled with 500 μL LB medium contained 50 μg/mL kanamycin and 100 μg/mL ampicillin. The cultures were grown at 37 °C, 500 rpm for 16 h. The expression and cell harvest methods were according to the previous report.[4] Briefly, 100 μL of seed culture was inoculated into 800 μL modified P450 expression medium (containing appropriate antibiotics and 0.1 mM IPTG) in another 96 deep wells plate and incubated at 25 °C, 200 rpm for 8 h. The cell pellets were harvested and washed with 600 μL 100 mM Kpi buffer, pH 7.4. After

centrifugation at 3,000*g* for 5 min, the cell pellets were frozen in liquid nitrogen for 15 min and thawed at room temperature. The 100 μL reaction mixture containing 100 mM Kpi buffer, pH 7.4, 100 mM glucose, 1 mM $NADP^+$, and 1 mM drimenol (50 mM stock solution in DMF) was added in each well. Then the deep wells plate was shaken at 25 °C, 200 rpm for 16 h. The reaction was stopped by adding 200 μL ethyl acetate. Then the extraction was completed by mixing with pipette. The mixture was centrifuged at 3,000*g* for 10 min. The 100 μL organic phase was transferred into the interior tube of GC vial followed by GC-MS analysis.

$P450_{BM3}$ (L75A/F87I) and $P450_{BM3}$ (L75G/F87I) were re-cultured in 96 deep wells plate for whole cell and cell lysate catalysis in triplicate. The concentration of cells was around 14 OD/mL measured by UV spectrophotometer. The whole cell catalysis experiments were the same as above. For the cell lysate catalysis, the cells were removed from wells and resuspended with 87 μL 100 mM Kpi buffer, pH 7.4 in new tubes, followed by ultrasonication (30% power, 1 s on, 3 s off). The lysate was centrifuged at 4 °C and 21,000*g* for 2 min. The brownish-red supernatant was transferred into a new 2 mL tube. The reaction was started by adding 100 mM glucose, 1 mM $NADP^+$, and 1 mM drimenol (50 mM stock solution in DMF) in the lysate solution and incubated at 25 °C, 200 rpm for 16 h. The reaction was stopped by adding 200 μL ethyl acetate and extracted by vortexing. The mixture was centrifuged at 21,000*g* for 1 min. The organic phase was used for GC-MS analysis.

4.7 Optimization of the reaction conditions for drimenol oxidation

To screen the appropriate co-solvent and its concentration, 3 mM drimenol was added with the concentration of DMF, DMSO, MeOH ranging from 2% to 6%. Besides, the reaction mixture contained 28 OD/mL cell lysate (in 100 mM Kpi buffer, pH 7.4), 100 mM glucose and 1 mM $NADP^+$. Then, the reaction was incubated at 25 °C, 200 rpm for 16 h. The post-treatment was same as library screening procedure (Figure S4B, S4C).

4.8 Gram-scale oxidation of drimenol with $P450_{BM3}$ (L75A/F87I)

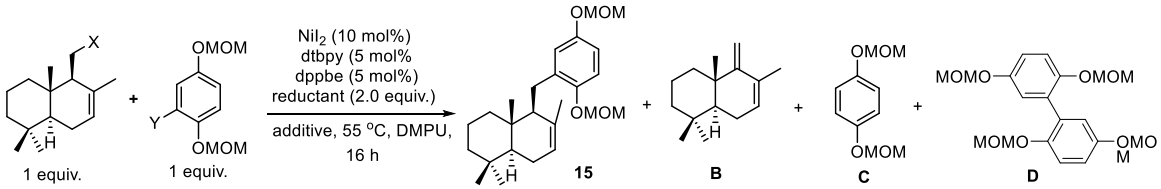
E. coli BL21(DE3) harboring pET28a-$P450_{BM3}$ (L75A/F87I) and pET22b-BmGDH was cultured in 13 L modified P450 expression medium at 37 °C, 220 rpm until OD_{600} reached 0.8–0.9. The culture was pre-cooled on ice, and induced with 0.1 mM IPTG. After expression at 25 ºC, 180 rpm for 16 h, the concentration of cells is about 8300 OD/L measured by UV spectrophotometer. The cells were harvested by centrifugation at 20 °C and 9,000*g* for 15 min. The cell pellets were collected in 50 mL tube per 0.76 L initial medium and

stored at −80 °C until further processing. For cell lysis, the cell pellet was thawed and resuspended by 200 mL Kpi buffer (100 mM, pH 7.4) per 0.76 L of initial culture. Cells were broken by high pressure homogenizer. The collected lysate was centrifuged at 4 °C and 36,000*g* for 30 min. Then the obtained brownish-red supernatant was added into the 2.8 L flask which contained freshly pre-dissolved 335 mg $NADP^+$ and 7.6 g glucose in 200 mL Kpi buffer (100 mM, pH 7.4). The reaction was started by addition of 140 mg drimenol dissolved in 21 mL DMF. Then seventeen flasks contained 2.38 g drimenol in total were shaken at 25 °C, 200 rpm for 16 h. The reaction mixtures were extracted with 1/2 volume ethyl acetate in three times. The resulting sample was dried over Na_2SO_4 and concentrated by the rotary evaporator under reduced pressure. After purification by column chromatography on silica gel, 1.55 g of compound **12** was obtained.

5. Synthetic procedures

5.1 Optimization for the Ni-catalzyed reductive coupling reaction

Table S4. Optimization for the Ni-catalzyed reductive coupling reaction



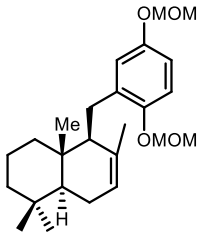
Entries	X	Y	reductant	additive	yield of 15[b]	yield of B[b]	yield of C[c]	yield of D[c]
1	I	I	Mn	pyridine (12 mol%)	6%	71%	32%	12%
2	Br	I	Mn	pyridine (12 mol%)	40%	38%	16%	18%
3	I	Br	Mn	pyridine (12 mol%)	3%	75%	30%	10%
4	Br	Br	Mn	pyridine (12 mol%)	49%	35%	5%	13%
5	Br	Br	Mn	pyridine (12 mol%) + $Co^{II}Pc$ (5 mo%)	57%	25%	5%	8%
6	Br	I	Mn	pyridine (12 mol%) + $Co^{II}Pc$ (5 mo%)	62%	20%	8%	7%
7	Br	I	Zn	pyridine (12 mol%) + $Co^{II}Pc$ (5 mo%)	26%	46%	15%	12%
8	Br	I	TDAE	pyridine (12 mol%) + $Co^{II}Pc$ (5 mo%)	35%	40%	12%	-

[a] dtbpy = 4,4-Di-tert-butyl bipyridine, dppbe = 1,2-bis(diphenylphosphino)benzene, DMPU = 1,3-Dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone, TDAE = Tetrakis(dimethylamino)ethylene, $Co^{II}Pc$ = Cobalt phthalocyanin. The yields of isolated products were given. [b] Yield of **15** and yield of **B** were calculated based on the drimane moiety. [c] Yield of C and D were calculated based on the aryl halide moiety.

General Procedure for the Ni-catalyzed reductive coupling reaction:

A solution of drimane halide (0.10 mmol, 1.0 equiv.) and aryl halide (0.10 mmol, 1.0 equiv.) in DMPU (0.3

mL) was treated with NiI_2 (3.1 mg, 0.01 mmol, 10 mol%), 1,2-bis(diphenylphosphino)benzene (2.2 mg, 0.005 mmol, 5 mol%), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (if needed, 1.3 mg, 0.005 mmol, 5 mol%), cobalt phthalocyanin (if needed, 2.9 mg, 0.005mmol, 5 mol%), reductant (0.20 mmol, 2.0 equiv.), and pyridine (if need, 1 μL, 0.012 mmol, 12 mol%). The reaction mixture was heated to 55 °C and stirred at the same temperature for 16 hours. The reaction was quenched with saturated aq. $Na_2S_2O_3$ solution (5 mL), and extracted with EtOAc (10 mL × 3). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography to yield elimination product **B** (hexane), desired product **13** (hexane/ethyl acetate = 20:1), reduced aryl compound **C** (hexane/ethyl acetate = 20:1) and homocoupling product **D** (hexane/ethyl acetate = 10:1).



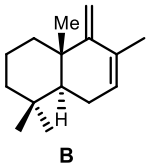
15

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.92 – 7.01 (m, 2H), 6.80 (dd, *J* = 8.9, 3.0 Hz, 1H), 5.38 (m, 1H), 5.13 (s, 2H), 5.11 (s, 2H), 3.48 (s, 3H), 3.47 (s, 3H), 2.73 (dd, *J* = 15.4, 9.3 Hz, 1H), 2.59 (dd, *J* = 15.3, 2.6 Hz, 1H), 2.31 – 2.41 (m, 1H), 1.83 – 2.04 (m, 3H), 1.49 – 1.56 (m, 1H), 1.46 (s, 3H), 1.39 – 1.46 (m, 2H), 1.29 (dd, *J* = 11.9, 4.9 Hz, 1H), 1.16 – 1.25 (m, 1H), 1.05 – 1.15 (m, 1H), 0.91 (s, 3H), 0.90 (s, 3H), 0.88 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 152.0, 150.3, 135.9, 134.6, 122.3, 118.4, 115.4, 113.7, 95.4, 95.3, 56.1, 56.0, 54.5, 50.5, 42.4, 39.7, 37.0, 33.4, 33.2, 26.5, 23.9, 22.5, 22.1, 19.1, 14.1.

$[\alpha]_D^{23}$ = -16.09 (c = 1.10, $CHCl_3$).

HRMS (ESI+): calculated for $C_{25}H_{39}O_4$ $[M+H]^+$: 403.2843, found 403.2840.



B

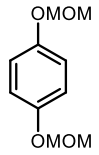
^{1}H NMR (600 MHz, $CDCl_3$): δ 5.63 – 5.69 (m, 1H), 4.83 (s, 1H), 4.79 (s, 1H), 2.11 – 2.18 (m, 1H), 1.98 – 2.06 (m, 1H), 1.84 – 1.90 (m, 1H), 1.78 – 1.81 (m, 3H), 1.63 (dt, *J* = 13.7, 3.2 Hz, 1H), 1.59 – 1.61 (m, 1H),

1.52 – 1.57 (m, 1H), 1.39 – 1.42 (m, 1H), 1.29 (dd, *J* = 11.8, 4.6 Hz, 1H), 1.14 – 1.21 (m, 1H), 0.97 (s, 3H), 0.93 (s, 3H), 0.86 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 158.3, 131.3, 126.7, 103.9, 48.8, 42.3, 37.9, 37.8, 33.5, 33.1, 24.4, 22.3, 21.2, 20.7, 19.2.

$[\alpha]_D^{24}$ = -9.40 (c = 1.00, $CHCl_3$).

The NMR data was consistent with literature report.[6]



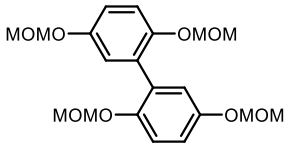
C

^{1}H NMR (600 MHz, $CDCl_3$): δ 6.97 (s, 4H), 5.12 (s, 4H), 3.48 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 152.4, 117.6, 95.3, 56.0.

HRMS (ESI+): calculated for $C_{10}H_{15}O_4$ $[M+H]^+$: 199.0965, found 199.0966.

The NMR data was consistent with literature report.[7]



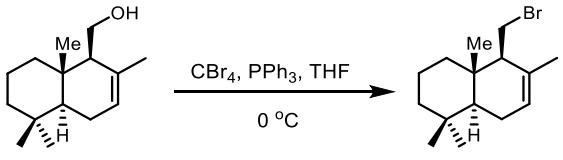
D

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.13 (d, *J* = 8.6 Hz, 1H), 6.95 – 7.00 (m, 2H), 5.13 (s, 2H), 4.99 (s, 2H), 3.48 (s, 3H), 3.33 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 152.2, 150.0, 130.2, 119.8, 117.4, 116.6, 96.2, 95.3, 56.0, 56.0.

HRMS (ESI+): calculated for $C_{20}H_{27}O_8$ $[M+H]^+$: 395.1700, found 395.1705.

5.2 Synthesis of drimane halides and aryl halides



11 **9**

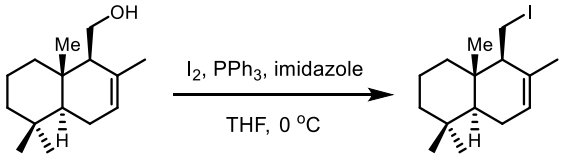
A solution of **11** (222 mg, 1.0 mmol, 1.0 equiv.) and carbon tetrabromide (830 mg, 2.5 mmol, 2.5 equiv.) in dry THF (4 mL) was treated with PPh_3 (655 mg, 2.5 mmol, 2.5 equiv.) in THF (4 mL) dropwise at 0 °C. The reaction mixture was stirred at 0 °C for 2 hours then quenched with MeOH (5 mL). The solution was

concentrated in vacuo. The crude product was purified by flash column chromatography (hexane) to yield **9** (228 mg, 80% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.48 (m, 1H), 3.65 (dd, *J* = 10.8, 2.2 Hz, 1H), 3.28 (dd, *J* = 10.8, 6.7 Hz, 1H), 2.34 – 2.40 (m, 1H), 1.90 – 2.04 (m, 2H), 1.86 (s, 1H), 1.78 – 1.84 (m, 1H), 1.52 – 1.55 (m, 1H), 1.47 – 1.52 (m, 1H), 1.15 – 1.24 (m, 2H), 1.12 (dd, *J* = 13.1, 4.4 Hz, 1H), 0.88 (s, 3H), 0.86 (s, 3H), 0.81 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 132.7, 124.1, 57.8, 50.1, 42.1, 39.4, 37.9, 33.3, 33.2, 31.6, 23.7, 22.0, 21.9, 18.8, 14.1.

$[\alpha]_D^{24}$ = -10.40 (c = 0.50, $CHCl_3$).



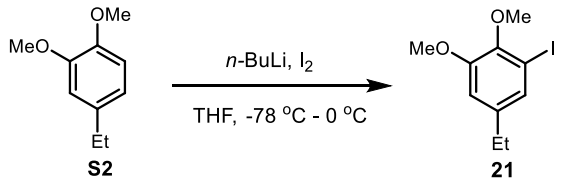
11 **S1**

A solution of **11** (222 mg, 1.0 mmol, 1.0 equiv.), imidazole (170 mg, 2.5 mmol, 2.5 equiv.) and iodine (635 mg, 2.5 mmol, 2.5 equiv.) in dry THF (4 mL) was treated with PPh_3 (655 mg, 2.5 mmol, 2.5 equiv.) in THF (4 mL) dropwise at 0 °C. After stirring at 0 °C for 2 hours, the reaction was quenched with saturated aq. $Na_2S_2O_3$ solution (10 mL) and extracted with EtOAc (10 mL × 3). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (hexane) to yield **S1** (199 mg, 60% yield) as faint yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 5.37 – 5.47 (m, 1H), 3.50 (dd, *J* = 10.6, 2.0 Hz, 1H), 2.96 (dd, *J* = 10.6, 7.0 Hz, 1H), 2.44 – 2.51 (m, 1H), 1.90 – 2.01 (m, 5H), 1.77 – 1.87 (m, 1H), 1.52 – 1.56 (m, 1H), 1.45 – 1.52 (m, 1H), 1.38 – 1.44 (m, 1H), 1.11 – 1.21 (m, 4H), 0.87 (s, 3H), 0.85 (s, 3H), 0.79 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 133.1, 123.9, 58.5, 50.2, 42.1, 39.2, 38.7, 33.2, 33.2, 23.7, 22.0, 21.9, 18.9, 13.4.

$[\alpha]_D^{24}$ = -45.80 (c = 0.50, $CHCl_3$).



S2 **21**

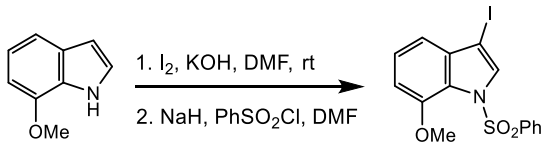
A solution of **S2** (1.66 g, 10 mmol, 1.0 equiv.) in dry THF (10 mL) was treated with *n*-BuLi (2.0 M in n-

hexane, 5.5 mL, 1.1 equiv.) in dropwise at -78 °C. The resulting mixture was warm to room temperature and stir for 2 hours. Add a solution of iodine (2.79 g, 11 mmol, 1.1 equiv.) in THF (10 mL) to the mixture at -78°C. The resulting mixture was stirred for 2 hours at room temperature. The solvents were evaporated and CH_2Cl_2 (30 mL) was added. The organic layer was washed with aqueous $NaHSO_3$ (20%), aqueous saturated $NaHCO_3$ and aqueous saturated brine, and the layer was dried with Na_2SO_4 and concentrated. The residue was purified by flash column chromatography (hexane / dichloromethane = 10:1) to afford **21** (2.57 g, 88% yield) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 (d, *J* = 1.9 Hz, 1H), 6.71 (d, *J* = 1.9 Hz, 1H), 3.84 (s, 3H), 3.80 (s, 3H), 2.56 (q, *J* = 7.6 Hz, 2H), 1.21 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 152.4, 146.9, 142.4, 129.5, 112.7, 92.3, 60.4, 56.0, 28.3, 15.6.

HRMS (ESI+): calculated for $C_{10}H_{13}IO_2Na$ $[M+Na]^+$: 314.9852, found 314.9852.



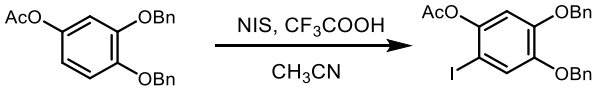
S3 **24**

A solution of **S3** (1.47 g, 10 mmol, 1.0 equiv.) in dry DMF (10 mL) was treated with KOH (1.40 g, 25 mmol, 2.5 equiv.) and iodine (2.79 g, 11 mmol,1.1 equiv.), The mixture was stirred for 2 hours at room temperature and was quenched by a saturated aqueous solution of $Na_2S_2O_3$ (20 mL), the aqueous phase was extracted with EtOAc (20 mL× 3). The organic layer was washed with water and aqueous saturated brine, and the layer was dried with Na_2SO_4 and concentrated. The 3-iodo-indole derivative was not isolated and directly engaged in the protection step without any purification. The flask containing the crude product was flushed with Ar, then DMF (15 mL) was introduced and the mixture was stirred and cool to 0 °C using an ice bath. NaH (60% in oil, 1.2 equiv.) in added by portions and the mixture was stirred for an additional 20 minutes. Then, $PhSO_2Cl$ was introduced dropwise, the reaction was stirred at 0 °C for 30 minutes then the ice bath was removed and allowed to heat up to room temperature. The mixture was stirred for 3 hours at room temperature and was quenched by distillated water and a same volume of EtOAc. The layers were separated and the aqueous phase is extracted with two additional volumes of EtOAc. The organic phase was washed with water and brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography (hexane / dichloromethane = 10:1) to afford **24** (3.10 g, 75% yield) as beige powder.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (s, 1H), 7.81 – 7.89 (m, 2H), 7.53 – 7.62 (m, 1H), 7.45 – 7.51 (m, 2H), 7.21 (t, *J* = 7.9 Hz, 1H), 7.03 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.74 (dd, *J* = 7.9, 0.9 Hz, 1H), 3.66 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 147.1, 140.0, 135.3, 133.6, 132.1, 129.0, 127.5, 124.8, 124.3, 114.7, 107.8, 64.8, 55.7.

HRMS (ESI+): calculated for $C_{15}H_{12}INO_3SNa$ $[M+Na]^+$: 435.9475, found 435.9475.



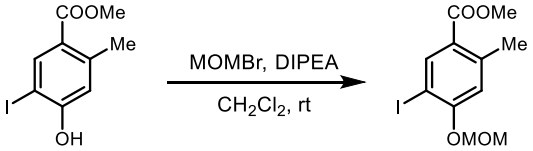
S4 **17**

A solution of **S4** (2.0 g, 5.74 mmol, 1.0 equiv.) in CH_3CN (30 mL) was treated with CF_3COOH (196 mg, 1.72 mmol, 0.3 equiv.) and *N*-iodosuccinimide (1.42 g, 6.31 mmol, 1.1 equiv.) in CH_3CN (10 mL) dropwise at room temperature. The reaction mixture was stirred at 40 °C for 2 hours and quenched with H_2O (20 mL). The mixture was extracted with EtOAc (20 mL × 3). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/ dichloromethane = 1:1) to give **17** (2.2 g, 81% yield) as white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 – 7.50 (m, 11H), 6.74 (s, 1H), 5.10 (d, *J* = 3.4 Hz, 1H), 2.33 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 169.0, 150.1, 147.8, 145.7, 136.7, 136.5, 128.7, 128.7, 128.7, 128.2, 128.2, 127.5, 127.5, 127.4, 124.4, 109.6, 78.7, 72.1, 71.5, 21.3.

HRMS (ESI+): calculated for $C_{22}H_{19}IO_4Na$ $[M+Na]^+$: 497.0220, found 497.0219.



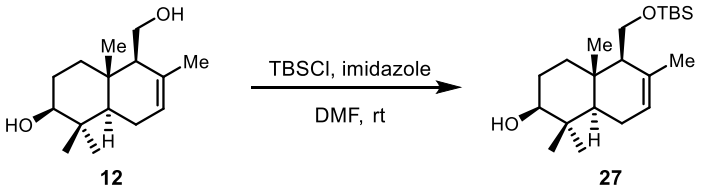
S5 **30**

A solution of **S5** (1.69 g, 5.80 mmol, 1.0 equiv.) in dichloromethane (30 mL) was treated with DIPEA (897 mg, 6.95 mmol, 1.2 equiv.). Methoxybromomethane (868 g, 6.95 mmol, 1.2 equiv.) was added to the reaction mixture at room temperature. The reaction mixture was stirred at room temperature for 5 hours before it was quenched with H_2O (20 mL). The mixture was extracted with EtOAc (20 mL × 3). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/ EtOAc = 10:1) to give **30** (1.83 g, 94% yield) as white solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.34 (s, 1H), 6.87 (s, 1H), 5.26 (s, 2H), 3.84 (s, 3H), 3.49 (s, 3H), 2.55 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 166.1, 158.6, 143.3, 142.1, 124.5, 116.9, 94.7, 82.6, 56.6, 51.9, 22.2.

HRMS (ESI+): calculated for $C_{11}H_{14}IO_4$ $[M+H]^+$: 336.9931, found 336.9931.



12 **27**

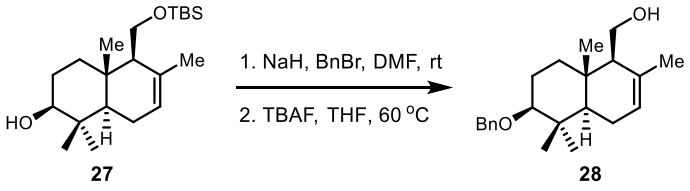
A solution of **12** (23.8 mg, 0.10 mmol, 1.0 equiv.) in DMF (2 mL) was treated with imidazole (6.8 mg, 0.10 mmol, 1.0 equiv.) and TBSCl (15.1 mg, 0.10 mmol, 1.0 equiv.). After stirring at 23 °C for 5 hours. The reaction was quenched with H_2O (10 mL) and extracted with EtOAc (10 mL × 3). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/ethyl acetate = 10:1) to give **27** (31.8 mg, 90% yield) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.33 – 5.52 (m, 1H), 3.75 (dd, *J* = 10.5, 3.5 Hz, 1H), 3.62 (dd, *J* = 10.5, 5.8 Hz, 1H), 3.19 – 3.30 (m, 1H), 1.92 – 2.04 (m, 3H), 1.78 – 1.83 (m, 1H), 1.72 (s, 3H), 1.59 – 1.66 (m, 2H), 1.23 – 1.29 (m, 1H), 1.14 – 1.21 (m, 1H), 0.97 (s, 3H), 0.86 – 0.90 (m, 10H), 0.85 (s, 3H), 0.81 (s, 3H), 0.03 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 134.3, 122.5, 79.2, 61.0, 56.9, 49.7, 38.8, 38.0, 35.9, 28.2, 27.6, 26.0, 26.0, 23.4, 22.0, 18.2, 15.4, 14.9, -5.3, -5.4.

$[\alpha]_D^{22}$ = +2.20 (c = 0.50, $CHCl_3$).

HRMS (ESI+): calculated for $C_{21}H_{41}O_2Si$ $[M+H]^+$: 353.2870, found 353.2870.



27 **28**

A solution of **27** (35.3 mg, 0.10 mmol, 1.0 equiv.) in DMF (2 mL) was treated with NaH (60% dispersion in mineral oil, 6 mg, 0.15 mmol, 1.5 equiv.) and BnBr (25.7 mg, 0.15 mmol, 1.5 equiv.). The reaction mixture was stirred at 23 °C for 10 hours before it was quenched with H_2O (10 mL) and extracted with EtOAc (10

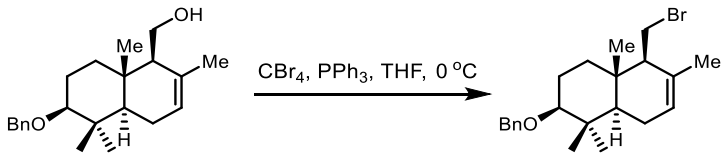
mL × 3). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was dissolved in THF (4 mL) and was treated with tetrabutylammonium fluoride xhydrate (85%, 65.8 mg, 0.20 mmol, 0.2 equiv.). The reaction mixture was stirred at 60 °C for 12 hours then quenched with H_2O (10 mL) and extracted with EtOAc (10 mL × 3). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/ethyl acetate = 10:1) to give **28** (30.2 mg, 92% yield) as white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 – 7.39 (m, 4H), 7.27 (m, 1H), 5.50 – 5.59 (m, 1H), 4.68 (d, *J* = 11.9 Hz, 1H), 4.44 (d, *J* = 11.9 Hz, 1H), 3.86 (dd, *J* = 11.3, 3.5 Hz, 1H), 3.74 (dd, *J* = 11.3, 5.2 Hz, 1H), 2.96 (dd, *J* = 11.7, 3.9 Hz, 1H), 2.05 (dt, *J* = 13.3, 3.5 Hz, 1H), 1.93 – 2.02 (m, 2H), 1.81 – 1.89 (m, 2H), 1.78 (s, 3H), 1.49 – 1.63 (m, 2H), 1.16 – 1.22 (m, 2H), 0.99 (s, 3H), 0.92 (s, 3H), 0.87 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 139.5, 132.9, 128.3, 127.5, 127.4, 124.2, 86.7, 71.6, 61.0, 57.2, 50.0, 38.9, 38.0, 36.0, 28.5, 23.3, 23.0, 21.9, 16.5, 15.1.

$[\alpha]_D^{22}$ = +29.80 (c = 0.50, $CHCl_3$).

HRMS (ESI+): calculated for $C_{22}H_{32}O_2Na$ $[M+Na]^+$: 351.2295, found 351.2294.



28 **10**

A solution of **28** (32.8 mg, 0.1 mmol, 1.0 equiv.) and carbon tetrabromide (83 mg, 0.25 mmol, 2.5 equiv.) in dry THF (2 mL) was treated with PPh_3 (65.5 mg, 0.25 mmol, 2.5 equiv.) in THF (2 mL) dropwise at 0 °C. The reaction mixture was stirred at 0 °C for 2 hours before it was quenched with MeOH (5 mL). The solution was concentrated in vacuo. The residue was purified by flash column chromatography (hexane/ethyl acetate = 100:1) to yield **10** (24.2 mg, 62% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 – 7.39 (m, 4H), 7.24 – 7.30 (m, 1H), 5.36 – 5.64 (m, 1H), 4.68 (d, *J* = 11.8 Hz, 1H), 4.45 (d, *J* = 11.9 Hz, 1H), 3.65 (dd, *J* = 10.8, 2.2 Hz, 1H), 3.29 (dd, *J* = 10.8, 6.7 Hz, 1H), 2.96 (dd, *J* = 11.7, 3.8 Hz, 1H), 2.30 – 2.39 (m, 1H), 2.07 – 1.93 (m, 3H), 1.89 – 1.92 (m, 1H), 1.87 (s, 3H), 1.49 – 1.61 (m, 1H), 1.16 – 1.31 (m, 2H), 0.99 (s, 3H), 0.92 (s, 3H), 0.84 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 139.4, 132.5, 128.3, 127.6, 127.4, 124.0, 86.4, 71.6, 57.8, 50.0, 39.0, 37.6, 37.4, 31.2, 28.3, 23.3, 22.9, 21.7, 16.4, 14.1.

$[\alpha]_D^{25}$ = +32.71 (c = 1.33, $CHCl_3$).

HRMS (ESI+): calculated for $C_{22}H_{32}BrO$ $[M+H]^+$: 391.1631, found 391.1633.

5.3 Synthesis of (+)-*ent*-chromazonarol

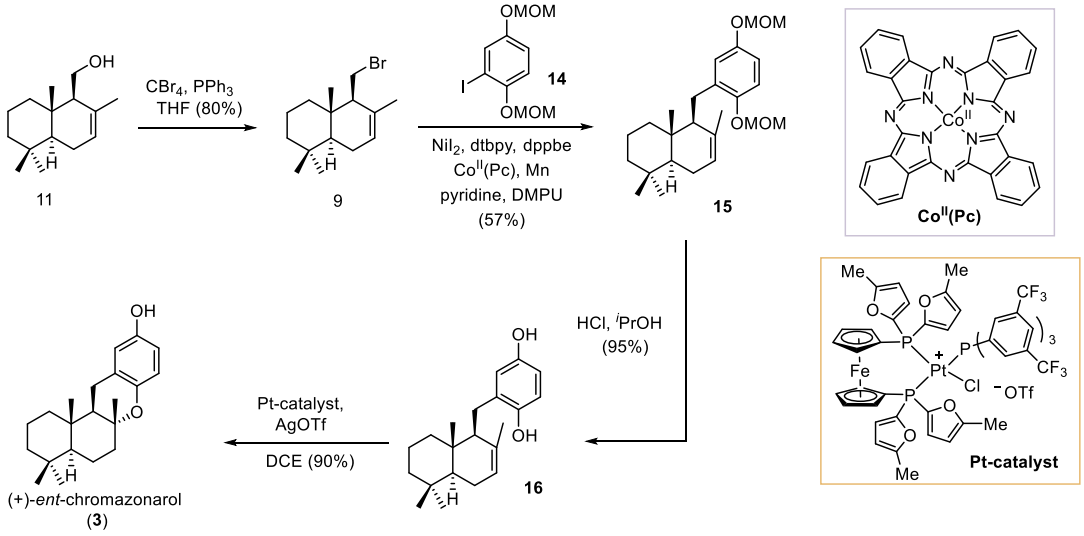
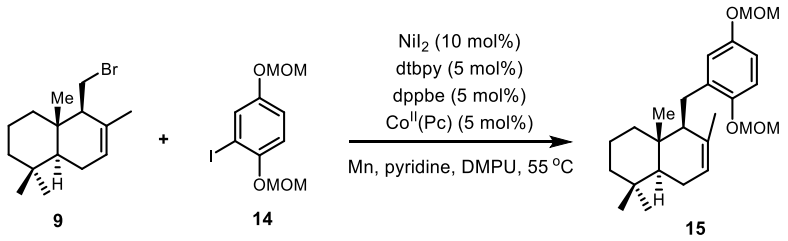


Figure S5. Synthetic route of (+)-*ent*-chromazonarol



A solution of **9** (28.5 mg, 0.10 mmol, 1.0 equiv.) and **14** (27.7 mg, 0.10 mmol, 1.0 equiv.) in DMPU (0.3 mL) was treated with NiI_2 (3.1 mg, 0.01 mmol, 10 mol%), 1,2-bis(diphenylphosphino)benzene (2.2 mg, 0.005 mmol, 5 mol%), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (1.3 mg, 0.005 mmol, 5 mol%), Co^{II}(Pc) (2.9 mg, 0.005mmol, 5 mol%), manganese powder (11.0 mg, 0.20 mmol, 2.0 equiv.), and pyridine (1 μL, 0.012 mmol, 12 mol%). The reaction mixture was heated to 55 °C and stirred at the same temperature for 16 hours. The reaction was quenched with saturated aq. $Na_2S_2O_3$ solution (5 mL) and extracted with EtOAc (10 mL × 3). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/ethyl acetate = 20:1) to yield **15** (22.9 mg, 57% yield) as colorless oil.

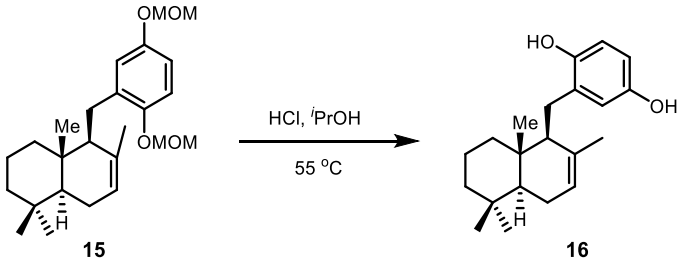
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.92 – 7.01 (m, 2H), 6.80 (dd, *J* = 8.9, 3.0 Hz, 1H), 5.38 (m, 1H), 5.13 (s,

2H), 5.11 (s, 2H), 3.48 (s, 3H), 3.47 (s, 3H), 2.73 (dd, *J* = 15.4, 9.3 Hz, 1H), 2.59 (dd, *J* = 15.3, 2.6 Hz, 1H), 2.31 – 2.41 (m, 1H), 1.83 – 2.04 (m, 3H), 1.49 – 1.56 (m, 1H), 1.46 (s, 3H), 1.39 – 1.46 (m, 2H), 1.29 (dd, *J* = 11.9, 4.9 Hz, 1H), 1.16 – 1.25 (m, 1H), 1.05 – 1.15 (m, 1H), 0.91 (s, 3H), 0.90 (s, 3H), 0.88 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 152.0, 150.3, 135.9, 134.6, 122.3, 118.4, 115.4, 113.7, 95.4, 95.3, 56.1, 56.0, 54.5, 50.5, 42.4, 39.7, 37.0, 33.4, 33.2, 26.5, 23.9, 22.5, 22.1, 19.1, 14.1.

$[\alpha]_D^{23}$ = -16.09 (c = 1.10, $CHCl_3$).

HRMS (ESI+): calculated for $C_{25}H_{39}O_4$ $[M+H]^+$: 403.2843, found 403.2840.



15 **16**

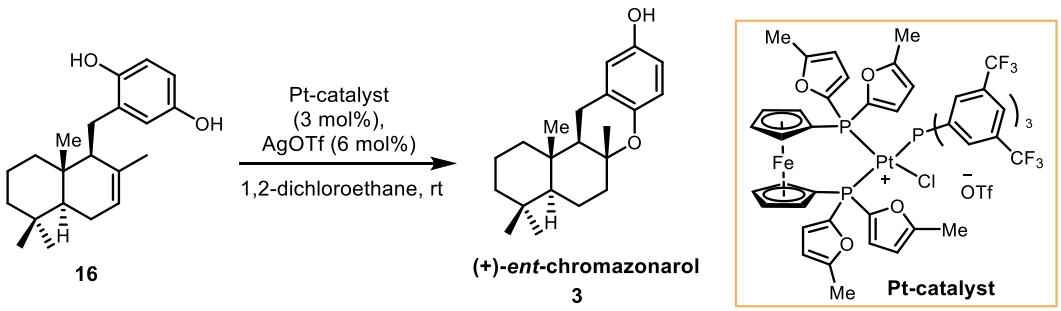
A solution of **15** (40.2 mg, 0.10 mmol, 1.0 equiv.) in ^{i}PrOH (2 mL) was treated with two drops of concentrated hydrochloric acid. The reaction mixture was stirred at 55 °C for 1 hour before it was quenched with H_2O (10 mL) and extracted with EtOAc (10 mL × 3). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/ethyl acetate = 5:1) to give **16** (29.8 mg, 95% yield) as white solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 6.74 (d, *J* = 2.9 Hz, 1H), 6.60 (d, *J* = 8.5 Hz, 1H), 6.51 (dd, *J* = 8.5, 3.0 Hz, 1H), 5.38 (m, 1H), 4.63 (br, 2H), 2.55 – 2.63 (m, 2H), 2.31 – 2.37 (m, 1H), 1.96 – 2.04 (m, 1H), 1.84 – 1.94 (m, 2H), 1.51 – 1.60 (m, 1H), 1.47 (s, 3H), 1.40 – 1.46 (m, 2H), 1.28 (dd, *J* = 12.1, 4.8 Hz, 1H), 1.16 – 1.23 (m, 1H), 1.07 – 1.13 (m, 1H), 0.91 (s, 3H), 0.89 (s, 3H), 0.88 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 149.4, 147.2, 135.5, 131.5, 122.5, 116.7, 116.2, 112.95, 54.4, 50.5, 42.4, 39.7, 37.0, 33.4, 33.2, 26.3, 23.9, 22.4, 22.1, 19.1, 14.1.

$[\alpha]_D^{23}$ = -17.25 (c = 0.80, $CHCl_3$).

HRMS (ESI+): calculated for $C_{21}H_{29}O_2$ $[M-H]^-$: 313.2162, found 313.2170.



In an argon filled glovebox, to a 4 mL vial with a magnetic stir bar were added the Pt-catalyst[1] (4.9 mg, 3 mol%), silver trifluoromethanesulfonate (1.5 mg, 6 mol%), the substrate **16** (31.4 mg, 0.1 mmol, 1.0 equiv.), and $ClCH_2CH_2Cl$ (1 mL). The resulting mixture was stirred at room temperature (23 °C) for 15 h. The reaction mixture was diluted with CH_2Cl_2, filtered through a pad of celite and concentrated. The residue was purified with flash column chromatography (hexane/ethyl acetate = 10:1, silica gel) to yield **3** (28.3 mg, 90% yield) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.63 (d, *J* = 8.4 Hz, 1H), 6.52 – 6.59 (m, 2H), 4.43 (br, 1H, OH), 2.54 – 2.60 (m, 2H), 2.04 (dt, *J* = 12.5, 3.2 Hz, 1H), 1.72 - 1.78 (m, 1H), 1.61 – 1.71 (m, 4H), 1.36 – 1.50 (m, 3H), 1.15 – 1.21 (m, 4H), 1.02 (dd, *J* = 12.2, 2.3 Hz, 1H), 0.94 – 0.98 (m, 1H), 0.90 (s, 3H), 0.88 (s, 3H), 0.84 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 148.6, 147.3, 123.4, 117.7, 115.9, 114.4, 76.8, 56.3, 52.2, 42.0, 41.3, 39.4, 36.9, 33.6, 33.3, 22.6, 21.8, 20.8, 19.9, 18.7, 15.0.

$[\alpha]_D^{22}$ = +42.00 (c = 0.35, $CHCl_3$).

HRMS (ESI+): calculated for $C_{21}H_{29}O_2$ $[M\text{-}H]^-$: 313.2162, found 313.2169.

5.4 Synthesis of (+)-8-*epi*-puupehenol

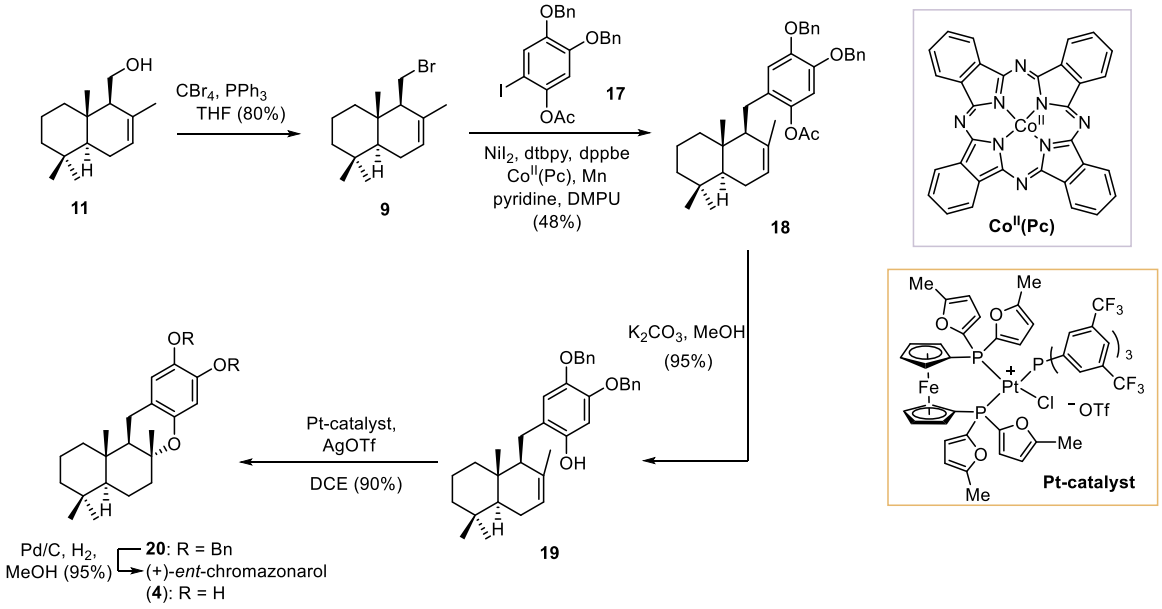
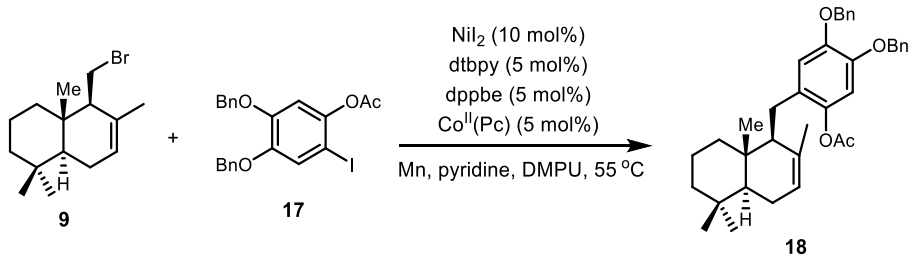


Figure S6. Synthetic route of (+)-8-*epi*-puupehenol



A solution of **9** (28.5 mg, 0.10 mmol, 1.0 equiv.) and **17** (47.4 mg, 0.10 mmol, 1.0 equiv.) in DMPU (0.3 mL) was treated with NiI_2 (3.1 mg, 0.01 mmol, 10 mol%), 1,2-bis(diphenylphosphino)benzene (2.2 mg, 0.005 mmol, 5 mol%), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (1.3 mg, 0.005 mmol, 5 mol%), Co^{II}(Pc) (2.9 mg, 0.005mmol, 5 mol%), manganese powder (11.0 mg, 0.20 mmol, 2.0 equiv.) and pyridine (1 μL, 0.012 mmol, 12 mol%). The reaction mixture was heated to 55 °C for 16 hours then quenched with saturated aq. $Na_2S_2O_3$ solution (5 mL). The mixture was extracted with EtOAc (10 mL × 3). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/ethyl acetate = 10:1) to yield **18** (26.5 mg, 48% yield) as colorless oil.

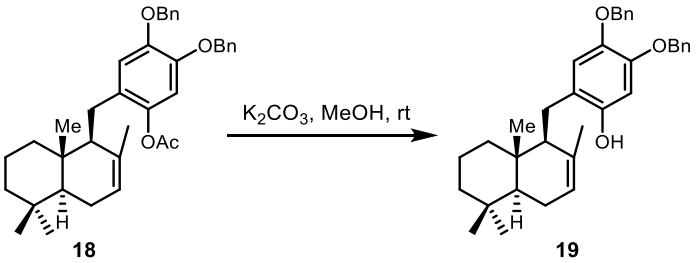
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 – 7.49 (m, 10H), 6.83 (s, 1H), 6.62 (s, 1H), 5.31 – 5.42 (m, 1H), 5.13 (s, 2H), 5.09 (s, 2H), 2.45 (dd, *J* = 15.5, 3.1 Hz, 1H), 2.28 (m, 4H), 2.08 – 2.17 (m, 1H), 1.92 – 2.04 (m, 1H), 1.79 – 1.91 (m, 1H), 1.74 (d, *J* = 12.9 Hz, 1H), 1.40 – 1.53 (m, 3H), 1.37 (s, 3H), 1.13 – 1.24 (m, 2H), 0.86

– 0.96 (m, 7H), 0.81 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 169.8, 147.5, 146.6, 142.4, 137.5, 137.0, 135.2, 128.6, 128.0, 127.9, 127.6, 122.6, 117.0, 109.2, 72.3, 71.5, 54.6, 50.4, 42.3, 39.7, 36.9, 33.4, 33.2, 26.4, 23.8, 22.5, 22.1, 21.1, 19.0, 14.0.

$[\alpha]_D^{23}$ = -14.67 (c = 0.90, $CHCl_3$).

HRMS (ESI+): calculated for $C_{37}H_{44}O_4Na$ $[M+Na]^+$: 575.3132, found 575.3128.



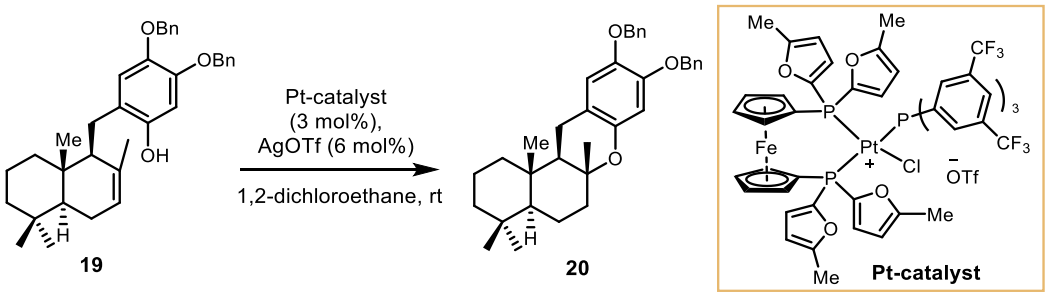
A solution of **18** (55.3 mg, 0.10 mmol, 1.0 equiv.) in MeOH (2 mL) was treated with K_2CO_3 (27.6 mg, 0.2 mmol, 2.0 equiv.). The reaction mixture was stirred at 23 °C for 5 hours before it was quenched with H_2O (10 mL) and extracted with EtOAc (10 mL × 3). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/ethyl acetate = 5:1) to give **19** (48.5 mg, 95% yield) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 – 7.48 (m,4H), 7.27 – 7.38 (m,6H), 6.76 (s, 1H), 6.39 (s, 1H), 5.34 – 5.39 (m, 1H), 5.07 (s, 4H), 4.67 (s, 1H), 2.51 (dd, *J* = 15.3, 3.2 Hz, 1H), 2.44 (dd, *J* = 15.2, 8.7 Hz, 1H), 2.13 – 2.22 (m, 1H), 1.93 – 2.06 (m, 1H), 1.79 – 1.93 (m, 2H), 1.48 – 1.57 (m, 1H), 1.37 – 1.48 (m, 5H), 1.19 – 1.26 (m, 2H), 0.94 – 1.03 (m, 1H), 0.91 (s, 3H), 0.90 (s, 3H), 0.85 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 148.0, 147.9, 142.5, 137.8, 137.3, 135.5, 128.6, 128.5, 127.9, 127.9, 127.9, 127.5, 122.4, 121.8, 119.4, 103.8, 73.3, 71.5, 54.4, 50.4, 42.4, 39.7, 37.0, 33.4, 33.2, 25.9, 23.9, 22.4, 22.1, 19.1, 14.0.

$[\alpha]_D^{22}$ = -16.91 (c = 0.55, $CHCl_3$).

HRMS (ESI+): calculated for $C_{35}H_{41}O_3$ $[M-H]^-$: 509.3050, found 509.3053.



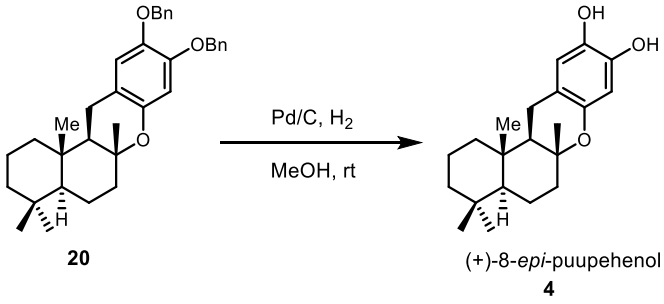
In an argon filled glovebox, to a 4 mL vial with a magnetic stir bar were added the Pt-catalyst (4.9 mg, 3 mol%), silver trifluoromethanesulfonate (1.5 mg, 6 mol%), **19** (51.1 mg, 0.1 mmol, 1.0 equiv.), and $ClCH_2CH_2Cl$ (1 mL). After stirring at room temperature (23 °C) for 12 h, the reaction mixture was diluted with CH_2Cl_2, filtered through a pad of celite and concentrated. The residue was purified by flash column chromatography (hexane/ethyl acetate = 10:1) to yield **20** (48.0 mg, 94% yield) as colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.44 (d, *J* = 7.5 Hz, 4H), 7.35 (q, *J* = 6.9 Hz, 4H),7.27 – 7.32 (m, 2H), 6.67 (s, 1H), 6.44 (s, 1H), 5.02 – 5.09 (m, 4H), 2.50 (d, *J* = 9.1 Hz, 2H), 2.00 – 2.07 (m, 1H), 1.73 – 1.79 (m, 1H), 1.64 – 1.71 (m, 2H), 1.58 – 1.63 (m, 2H), 1.44 – 1.51 (m, 1H), 1.30 – 1.42 (m, 2H), 1.18 (s, 3H), 1.10 – 1.15 (m, 1H), 0.94 – 1.06 (m, 2H), 0.91 (s, 3H), 0.88 (s, 3H), 0.85 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 148.9, 148.0, 142.5, 138.1, 137.5, 128.5, 128.5, 127.8, 127.7, 127.7, 127.5, 117.9, 114.0, 103.8, 77.0, 73.0, 71.1, 56.3, 52.4, 42.0, 41.2, 39.4, 37.0, 33.6, 33.3, 22.0, 21.7, 20.9, 19.9, 18.7, 15.0.

$[\alpha]_D^{21}$ = +27.20 (c = 1.00, $CHCl_3$).

HRMS (ESI+): calculated for $C_{35}H_{43}O_3$ $[M+H]^+$: 511.3207, found 511.3206.



A solution of **20** (51.1 mg, 0.10 mmol, 1.0 equiv.) in MeOH (2 mL) was treated with Pd (10% on carbon, 32 mg, 0.03 mmol, 0.3 equiv.). The reaction mixture was stirred at 23 °C under hydrogen atmosphere (1 atm) for 3 hours then filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/ethyl acetate = 3:1) to give **4** (31.3 mg, 95% yield) as colorless oil.

^{1}H NMR (600 MHz, Acetone-d_6): δ 7.61 (s, 1H), 7.20 (s, 1H), 6.50 (s, 1H), 6.19 (s, 1H), 2.40 – 2.51 (m, 2H), 1.96 (dt, *J* = 12.5, 3.2 Hz, 1H), 1.64 – 1.76 (m, 3H), 1.59 (dd, *J* = 13.0, 4.4 Hz, 1H), 1.53 (dd, *J* = 11.4, 7.0 Hz, 1H), 1.43 – 1.47 (m, 1H), 1.38 – 1.42 (m, 2H), 1.18 – 1.23 (m, 1H), 1.13 (s, 3H), 1.06 (dd, *J* = 12.4, 2.5 Hz, 1H), 0.98 – 1.02 (m, 1H), 0.90 (s, 6H), 0.86 (s, 3H).

^{13}C NMR (151 MHz, Acetone-d_6): δ 147.1, 144.9, 139.3, 116.3, 113.3, 104.5, 76.6, 56.9, 53.5, 42.6, 42.0, 39.9, 37.5, 33.8, 33.8, 22.3, 21.9, 21.0, 20.4, 19.2, 15.2.

$[\alpha]_D^{25}$ = +43.83 (c = 0.60, $CHCl_3$).

HRMS (ESI+): calculated for $C_{21}H_{29}O_3$ [M-H]$^-$: 329.2111, found 329.2115.

5.5 Synthesis of (-)-pelorol

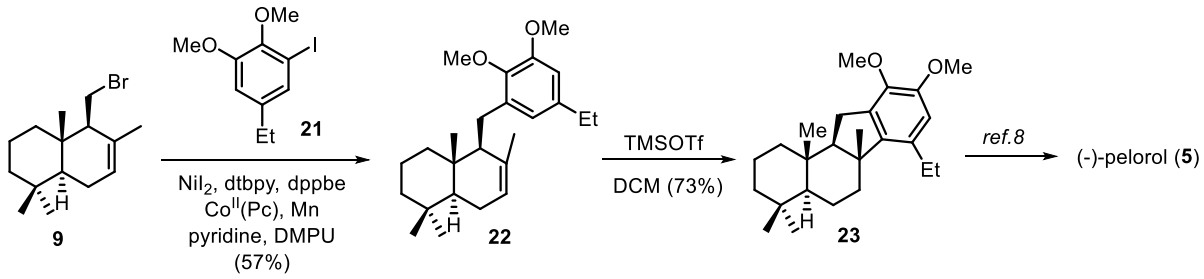
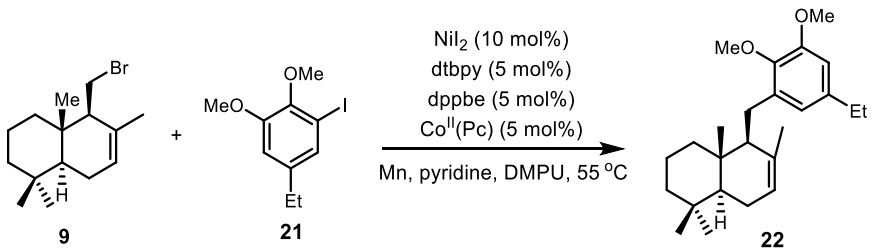


Figure S7. Synthetic route of (-)-pelorol[8]



A solution of **9** (28.5 mg, 0.10 mmol, 1.0 equiv.) and **21** (29.2 mg, 0.10 mmol, 1.0 equiv.) in DMPU (0.3 mL) was treated with NiI_2 (3.1 mg, 0.01 mmol, 10 mol%), 1,2-bis(diphenylphosphino)benzene (2.2 mg, 0.005 mmol, 5 mol%), 4,4'-di-tert-butyl-2,2'-dipyridyl (1.3 mg, 0.005 mmol, 5 mol%), Co^{II}(Pc) (2.9 mg, 0.005mmol, 5 mol%), manganese powder (11.0 mg, 0.20 mmol, 2.0 equiv.) and pyridine (1 μL, 0.012 mmol, 12 mol%). The reaction mixture was heated to 55 °C for 16 hours then quenched with saturated aq. $Na_2S_2O_3$ solution (5 mL) and extracted with EtOAc (10 mL × 3). The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/ethyl acetate = 10:1) to yield **22** (21.1 mg, 57% yield) as colorless oil.

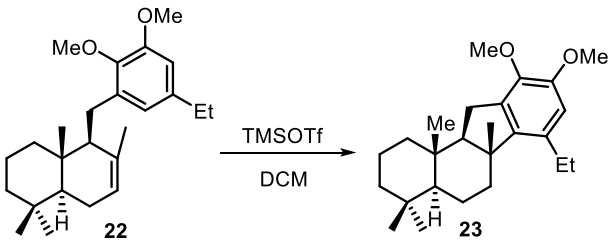
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.69 (d, *J* = 2.0 Hz, 1H), 6.57 (d, *J* = 1.9 Hz, 1H), 5.29 – 5.48 (m, 1H), 3.85

(s, 3H), 3.77 (s, 3H), 2.71 (dd, *J* = 15.1, 9.2 Hz, 1H), 2.64 (d, *J* = 2.8 Hz, 1H), 2.59 (q, *J* = 7.5 Hz, 2H), 2.31 – 2.43 (m, 1H), 1.83 – 2.06 (m, 3H), 1.52 – 1.59 (m, 1H), 1.40 – 1.51 (m, 5H), 1.30 (dd, *J* = 11.9, 4.9 Hz, 1H), 1.23 (t, *J* = 7.6 Hz, 3H), 1.18 (dd, *J* = 8.1, 3.7 Hz, 1H), 1.12 (dd, *J* = 13.1, 3.8 Hz, 1H), 0.92 (s, 3H), 0.91 (s, 3H), 0.89 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 152.5, 144.9, 139.6, 137.4, 136.1, 122.0, 120.6, 109.1, 60.5, 55.7, 54.6, 50.4, 42.4, 39.6, 37.0, 33.4, 33.2, 29.1, 26.3, 23.9, 22.6, 22.2, 19.1, 16.0, 14.1.

$[\alpha]_D^{24}$ = -10.87 (c = 3.10, $CHCl_3$).

HRMS (ESI+): calculated for $C_{25}H_{38}O_2Na$ $[M+Na]^+$: 393.2764, found 393.2761.



A solution of **22** (37.1 mg, 0.10 mmol, 1.0 equiv.) in CH_2Cl_2 (2 mL) was stirred at 0 °C for 0.5 hours, trimethylsilyl triflate (44.4 mg, 0.2 mmol, 2.0 equiv.) was added. Then the reaction mixture was stirred at 25 °C for 2.5 h. After completion of the reaction, the reaction mixture was quenched with sat. $NaHCO_3$ solution (10 ml). Then it was extracted with CH_2Cl_2 (15 ml x 3). The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/ethyl acetate = 10:1) to yield **23** (27.1 mg, 73% yield) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.51 (s, 1H), 3.83 (s, 3H), 3.82 (s, 3H), 2.73 (dd, *J* = 6.8, 4.6 Hz, 1H), 2.69 (dd, *J* = 6.8, 4.4 Hz, 1H), 2.56 – 2.63 (m, 1H), 2.51 (dd, *J* = 14.8, 12.8 Hz, 1H), 2.38 (dt, *J* = 12.0, 3.2 Hz, 1H), 1.80 (dd, *J* = 12.6, 3.9 Hz, 1H), 1.68 – 1.76 (m, 3H), 1.54 – 1.60 (m, 2H), 1.37 – 1.46 (m, 2H), 1.24 (t, *J* = 7.6 Hz, 3H), 1.17 (dd, *J* = 13.1, 4.2 Hz, 1H), 1.11 (s, 3H), 1.04 (s, 3H), 0.95 – 1.02 (m, 2H), 0.88 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 150.5, 145.0, 143.7, 136.0, 133.9, 111.2, 64.4, 60.5, 57.2, 56.1, 48.0, 42.7, 40.3, 39.4, 37.2, 33.5, 33.2, 25.4, 24.8, 21.5, 21.3, 19.8, 18.5, 16.3, 16.2.

$[\alpha]_D^{24}$ = +8.50 (c = 1.60, $CHCl_3$).

HRMS (ESI+): calculated for $C_{25}H_{38}O_2Na$ $[M+Na]^+$: 393.2764, found 393.2760.

5.6 Synthesis of (-)-mycoleptodiscin A

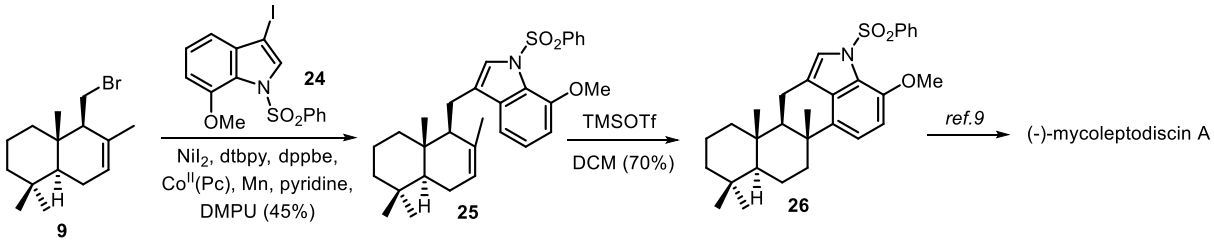
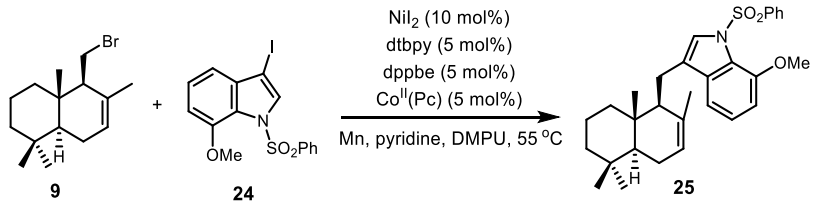


Figure S8. Synthetic route of (-)-mycoleptodiscin A[9]



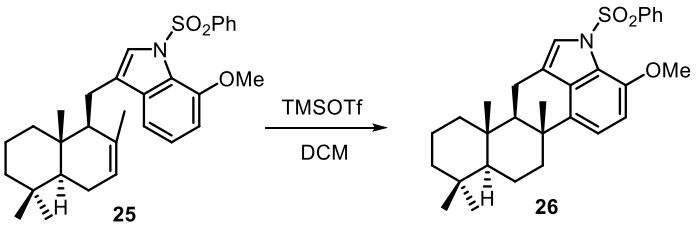
A solution of **9** (28.5 mg, 0.10 mmol, 1.0 equiv.) and **24** (41.3 mg, 0.10 mmol, 1.0 equiv.) in DMPU (0.3 mL) was treated with NiI_2 (3.1 mg, 0.01 mmol, 10 mol%), 1,2-bis(diphenylphosphino)benzene (2.2 mg, 0.005 mmol, 5 mol%), 4,4'-di-tert-butyl-2,2'-dipyridyl (1.3 mg, 0.005 mmol, 5 mol%), Co^{II}(Pc) (2.9 mg, 0.005mmol, 5 mol%), manganese powder (11.0 mg, 0.20 mmol, 2.0 equiv.) and pyridine (1 μL, 0.012 mmol, 12 mol%). The reaction mixture was heated to 55 °C for 16 hours then quenched with saturated aq. $Na_2S_2O_3$ solution (5 mL) and extracted with EtOAc (10 mL × 3). The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/ethyl acetate = 10:1) to yield **25** (22.1 mg, 45% yield) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (s, 1H), 7.81 (s, 1H), 7.64 (s, 1H), 7.50 – 7.56 (m, 1H), 7.46 (t, J = 7.8 Hz, 2H), 7.10 – 7.20 (m, 2H), 6.68 (d, J = 7.6 Hz, 1H), 5.39 – 5.57 (m, 1H), 3.65 (s, 3H), 2.82 (dt, J = 16.1, 2.0 Hz, 1H), 2.57 (dd, J = 16.1, 9.4 Hz, 1H), 2.44 – 2.50 (m, 1H), 2.02 – 2.09 (m, 1H), 1.89 – 2.00 (m, 2H), 1.60 – 1.64 (m, 1H), 1.54 (s, 3H), 1.43 – 1.52 (m, 2H), 1.35 (dd, J = 12.2, 4.7 Hz, 1H), 1.21 – 1.28 (m, 1H), 1.18 (td, J = 13.0, 3.6 Hz, 1H), 0.94 (s, 3H), 0.93 (s, 3H), 0.92 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 147.5, 140.7, 134.9, 134.2, 133.1, 128.8, 127.2, 125.6, 124.9, 123.9, 123.1, 123.0, 112.2, 107.1, 55.5, 53.6, 50.3, 42.4, 39.7, 37.0, 33.4, 33.2, 24.0, 22.8, 22.1, 19.0, 13.8.

$[\alpha]_D^{24}$ = +3.63 (c = 2.40, $CHCl_3$).

HRMS (ESI+): calculated for $C_{30}H_{37}NO_3SNa$ $[M+Na]^+$: 514.2386, found 514.2388.



A solution of **25** (49.2 mg, 0.10 mmol, 1.0 equiv.) in CH_2Cl_2 (2 mL) was stirred at 0 °C for 0.5 hours, trimethylsilyl triflate (44.4 mg, 0.2 mmol, 2.0 equiv.) was added. Then the reaction mixture was stirred at 25 °C for 2.5 h. After completion of the reaction, the reaction mixture was quenched with sat. $NaHCO_3$ solution (10 ml). Then it was extracted with CH_2Cl_2 (15 ml x 3). The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/ethyl acetate = 10:1) to yield **26** (34.4 mg, 70% yield) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 – 7.94 (m, 2H), 7.48 – 7.57 (m, 1H), 7.40 – 7.48 (m, 3H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.62 (d, *J* = 8.0 Hz, 1H), 3.68 (s, 3H), 2.91 (dd, *J* = 15.7, 3.4 Hz, 1H), 2.61 (ddd, *J* = 15.5, 12.9, 2.1 Hz, 1H), 2.32 – 2.49 (m, 1H), 1.81 – 1.90 (m, 1H), 1.66 – 1.77 (m, 2H), 1.62 – 1.66 (m, 2H), 1.49 – 1.54 (m, 2H), 1.43 – 1.49 (m, 2H), 1.35 – 1.40 (m, 1H), 1.12 (s, 3H), 1.04 (s, 3H), 0.88 – 0.93 (m, 1H), 0.88 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 145.2, 140.4, 138.7, 133.1, 130.8, 128.8, 127.7, 122.4, 121.5, 118.7, 116.6, 108.0, 56.7, 56.5, 56.0, 42.0, 40.3, 39.0, 38.2, 37.3, 33.6, 33.5, 25.1, 21.7, 18.9, 18.8, 18.1, 16.4.

$[\alpha]_D^{24}$ = +26.0 (c = 0.50, $CHCl_3$).

HRMS (ESI+): calculated for $C_{30}H_{37}NO_3SNa$ $[M+Na]^+$: 514.2386, found 514.2386.

5.7 Synthesis of (+)-hongoquercin A

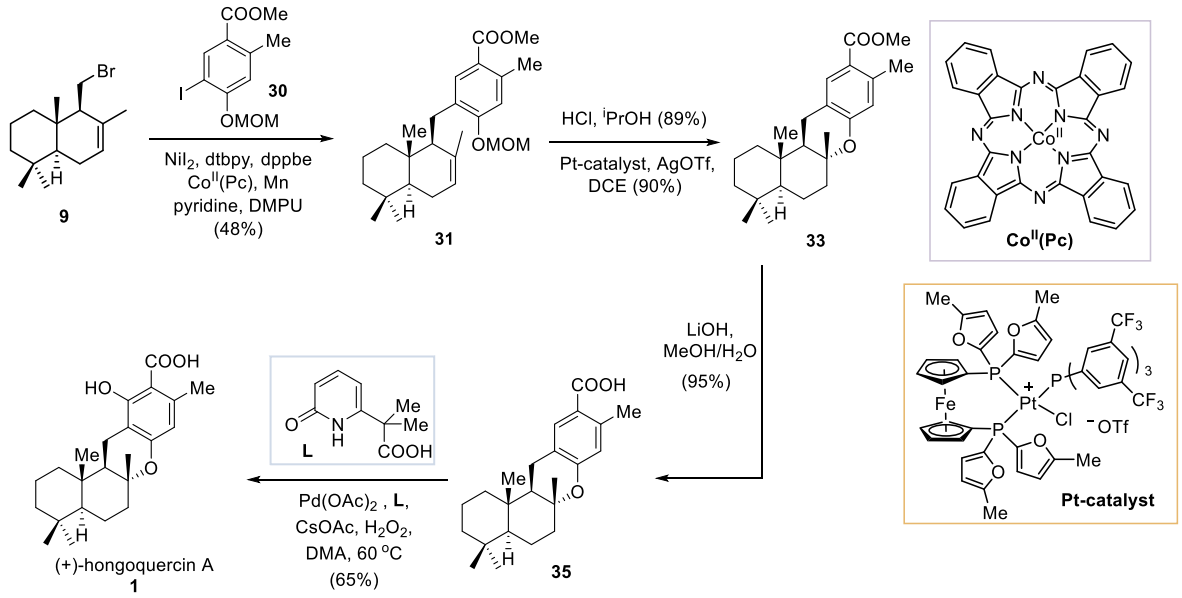
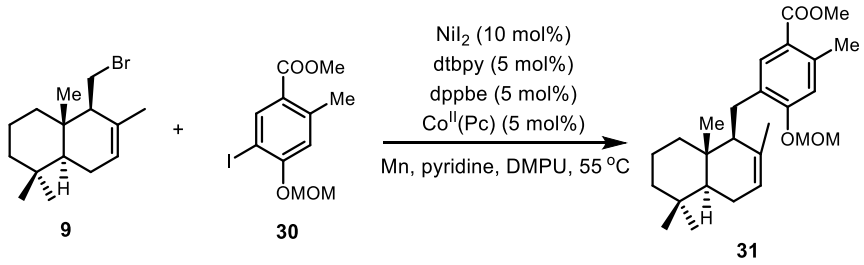


Figure S9. Synthetic route of (+)-hongoquercin A



A solution of **9** (28.5 mg, 0.10 mmol, 1.0 equiv.) and **30** (33.6 mg, 0.10 mmol, 1.0 equiv.) in DMPU (0.3 mL) was treated with NiI_2 (3.1 mg, 0.01 mmol, 10 mol%), 1,2-bis(diphenylphosphino)benzene (2.2 mg, 0.005 mmol, 5 mol%), 4,4'-di-tert-butyl-2,2'-dipyridyl (1.3 mg, 0.005 mmol, 5 mol%), Co^{II}(Pc) (2.9 mg, 0.005mmol, 5 mol%), manganese powder (11.0 mg, 0.20 mmol, 2.0 equiv.) and pyridine (1 μL, 0.012 mmol, 12 mol%). The reaction mixture was heated to 55 °C for 16 hours then quenched with saturated aq. $Na_2S_2O_3$ solution (5 mL) and extracted with EtOAc (10 mL × 3). The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/ethyl acetate = 10:1) to yield **31** (19.9 mg, 48% yield) as colorless oil.

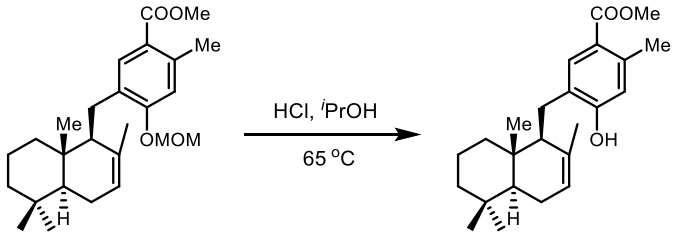
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.85 (s, 1H), 6.88 (s, 1H), 5.36 – 5.40 (m, 1H), 5.23 5.23 (d, *J* = 1.5 Hz, 2H), 3.86 (s, 3H), 3.48 (s, 3H), 2.69 (dd, *J* = 15.4, 9.3 Hz, 1H), 2.61 (d, *J* = 2.7 Hz, 1H), 2.56 (s, 3H), 2.41 (d, *J* = 9.2 Hz, 1H), 1.96 – 2.03 (m, 1H), 1.86 – 1.93 (m, 2H), 1.50 – 1.58 (m, 1H), 1.41 – 1.48 (m, 5H), 1.31

(dd, *J* = 12.2, 4.7 Hz, 1H), 1.21 (td, *J* = 13.6, 13.0, 4.0 Hz, 1H), 1.12 (td, *J* = 13.2, 3.7 Hz, 1H), 0.91 (s, 3H), 0.90 (s, 3H), 0.88 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 168.0, 157.7, 139.9, 135.7, 132.6, 130.1, 122.5, 122.4, 116.4, 94.2, 56.4, 54.1, 51.7, 50.4, 42.4, 39.7, 37.1, 33.4, 33.2, 26.0, 23.9, 22.7, 22.2, 22.1, 19.1, 14.1.

$[\alpha]_D^{24}$ = -26.13 (c = 1.60, $CHCl_3$).

HRMS (ESI+): calculated for $C_{26}H_{39}O_4$ $[M+H]^+$: 415.2843, found 415.2841.



31 **S6**

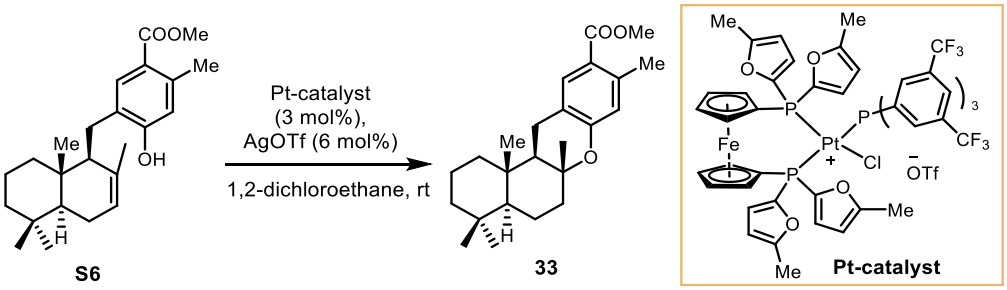
A solution of **31** (41.5 mg, 0.10 mmol, 1.0 equiv.) in ^{i}PrOH (2 mL) was treated with two drops of concentrated hydrochloric acid. The reaction mixture was stirred at 65 °C for 3 hours then quenched with H_2O (10 mL) and extracted with EtOAc (10 mL × 3). The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/ethyl acetate = 5:1) to give **S6** (33.0 mg, 89% yield) as white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (s, 1H), 6.62 (s, 1H), 5.38 (m, 1H), 3.88 (s, 3H), 2.58 – 2.65 (m, 2H), 2.50 (s, 3H), 2.48 – 2.44 (m, 1H), 1.93 – 2.05 (m, 1H), 1.85 – 1.94 (m, 2H), 1.47 – 1.60 (m, 2H), 1.37 – 1.48 (m, 5H), 1.30 (dd, *J* = 12.0, 4.8 Hz, 1H), 1.21 (dd, *J* = 13.6, 4.0 Hz, 1H), 1.10 (dd, *J* = 13.2, 3.9 Hz, 1H), 0.90 (s, 3H), 0.88 (s, 3H), 0.88 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 168.6, 157.0, 140.0, 135.5, 133.2, 127.5, 122.5, 121.1, 118.4, 53.8, 51.9, 50.2, 42.3, 39.6, 37.0, 33.4, 33.2, 25.8, 23.9, 22.6, 22.1, 21.8, 19.1, 14.0.

$[\alpha]_D^{23}$ = +26.91 (c = 1.60, $CHCl_3$).

HRMS (ESI+): calculated for $C_{24}H_{33}O_3$ $[M-H]^-$: 369.2424, found 369.2428.



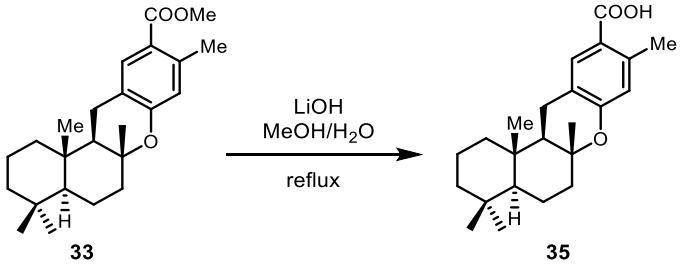
In an argon filled glovebox, to a 4 mL vial with a magnetic stir bar were added the Pt-catalyst[1] (4.9 mg, 3 mol%), silver trifluoromethanesulfonate (1.5 mg, 6 mol%), **S6** (37.1 mg, 0.1 mmol, 1.0 equiv.), and dichloroethane (1 mL). The resulting mixture was stirred at room temperature (23 °C) for 24 h. The reaction mixture was diluted with CH_2Cl_2, filtered through a pad of celite and concentrated. The residue was purified with silica gel chromatography (hexane/ethyl acetate = 10:1) to yield **33** (29.7 mg, 80% yield) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (s, 1H), 6.60 (s, 1H), 3.84 (s, 3H), 2.55 – 2.63 (m, 2H), 2.51 (s, 3H), 2.02 – 2.12 (m, 1H), 1.58 – 1.80 (m, 4H), 1.58 (s, 3H), 1.31 – 1.52 (m, 3H), 1.23 – 1.28 (m, 1H), 1.19 (s, 3H), 1.11 – 1.18 (m, 1H), 1.02 (dd, J = 12.3, 2.2 Hz, 1H), 0.96 (dd, J = 12.9, 3.8 Hz, 1H), 0.90 (s, 3H), 0.89 (s, 3H), 0.84 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 167.9, 156.6, 140.5, 133.4, 120.7, 119.8, 119.7, 78.2, 56.2, 52.2, 51.6, 41.9, 41.2, 39.3, 37.0, 33.5, 33.3, 21.9, 21.8, 21.7, 21.1, 19.9, 18.7, 15.1.

$[\alpha]_D^{22}$ = +77.92 (c = 1.25, $CHCl_3$).

HRMS (ESI+): calculated for $C_{24}H_{35}O_3$ $[M+H]^+$: 371.2581, found 371.2581.



A solution of **33** (37.1 mg, 0.10 mmol, 1.0 equiv.) in MeOH/H_2O (3 mL:0.6 mL) was treated with LiOH (24 mg, 1.00 mmol, 10 equiv.). The reaction mixture was stirred at 100 °C for 10 hours then quenched with 3 M HCl (10 mL) and extracted with EtOAc (10 mL × 3). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column

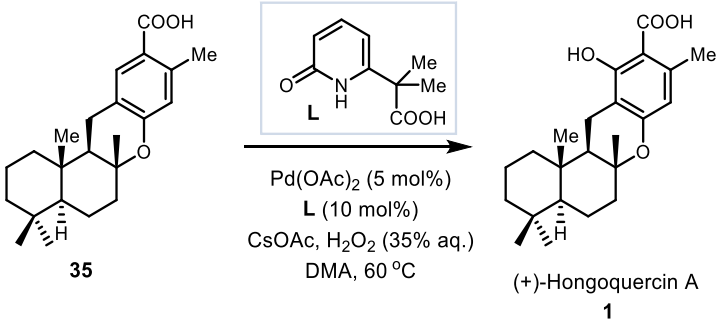
chromatography (hexane/ethyl acetate = 5:1, with 1% AcOH, v/v) to give **35** (33.1 mg, 93% yield) as white solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.85 (s, 1H), 6.62 (s, 1H), 2.65 (dd, *J* = 16.2, 5.3 Hz, 1H), 2.59 (dd, *J* = 16.4, 13.0 Hz, 1H), 2.55 (s, 3H), 2.08 (dt, *J* = 12.5, 3.2 Hz, 1H), 1.77 (dt, *J* = 13.7, 3.3 Hz, 1H), 1.67 – 1.73 (m, 1H), 1.57 – 1.63 (m, 2H), 1.45 – 1.51 (m, 1H), 1.40– 1.43 (m, 2H), 1.31 – 1.38 (m, 1H), 1.21 (s, 3H), 1.16 (dd, *J* = 13.6, 4.2 Hz, 1H), 1.03 (dd, *J* = 12.3, 2.2 Hz, 1H), 0.96 (td, *J* = 12.8, 3.9 Hz, 1H), 0.91 (s, 3H), 0.90 (s, 4H), 0.85 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 172.9, 157.5, 141.6, 134.5, 120.0, 119.9, 119.5, 78.4, 56.2, 52.2, 41.9, 41.1, 39.3, 37.1, 33.5, 33.3, 22.3, 21.8, 21.7, 21.1, 19.9, 18.6, 15.1.

$[\alpha]_D^{22}$ = +79.60 (c = 1.00, $CHCl_3$).

HRMS (ESI+): calculated for $C_{23}H_{33}O_3$ $[M+H]^+$: 357.2424, found 357.2422.



L was prepared according to literature procedure.[10]

$Pd(OAc)_2$ (1.1 mg, 0.005 mmol, 5 mol%), L (1.8 mg, 0.01 mmol, 10 mol%), **35** (35.7 mg, 0.1 mmol, 1.0 equiv.), and CsOAc (28.8 mg, 0.15 mmol, 1.5 equiv.) were weighed and placed in a reaction tube. Then, DMA (0.3 mL) was added and stirred for 10 min, followed by the addition of H_2O_2 (35% aq., 30 uL, 3.0 equiv.). The vial was sealed with a screw cap and stirred at 60 ºC for 24 h. Upon completion, the reaction was quenched with saturated solution of Na_2SO_3 in water until H_2O_2 was completely decomposed. (Tested by the potassium iodide starch test paper). The mixture was diluted with methanol and acidified with formic acid. The solution was filtered through a pad of Celite, and the aqueous layer was extracted with EtOAc (10 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude mixture was purified by flash chromatography (Hexane/EtOAc = 5:1, with 1% AcOH, v/v) to give **1** (24.2 mg, 65% yield) as white solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 11.83 (s, 1H), 6.21 (s, 1H), 2.68 (dd, *J* = 16.8, 4.9 Hz, 1H), 2.52 (s, 3H), 2.29 (dd, *J* = 16.8, 13.2 Hz, 1H), 2.03 – 2.11 (m, 1H), 1.79 – 1.84 (m, 1H), 1.74 – 1.79 (m, 1H), 1.67 – 1.71

(m, 1H), 1.62 – 1.66 (m, 1H), 1.55 (dd, J = 13.1, 5.0 Hz, 1H), 1.45 – 1.50 (m, 1H), 1.39 – 1.43 (m, 1H), 1.35 – 1.39 (m, 1H), 1.20 (s, 3H), 1.13 – 1.20 (m, 1H), 1.03 (dd, J = 12.2, 2.2 Hz, 1H), 0.95 – 1.01 (m, 1H), 0.92 (s, 3H), 0.91 (s, 3H), 0.85 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 176.1, 164.0, 159.0, 141.6, 112.8, 108.2, 102.7, 78.6, 56.3, 51.7, 42.0, 41.0, 39.3, 37.1, 33.6, 33.4, 24.3, 21.7, 20.9, 19.9, 18.6, 16.8, 15.1.

$[\alpha]_D^{22}$ = +86.20 (c = 0.50, $CHCl_3$).

HRMS (ESI+): calculated for $C_{23}H_{31}O_4$ $[M\text{-}H]^-$: 371.2217, found 371.2218.

5.8 Synthesis of (+)-hongoquercin B

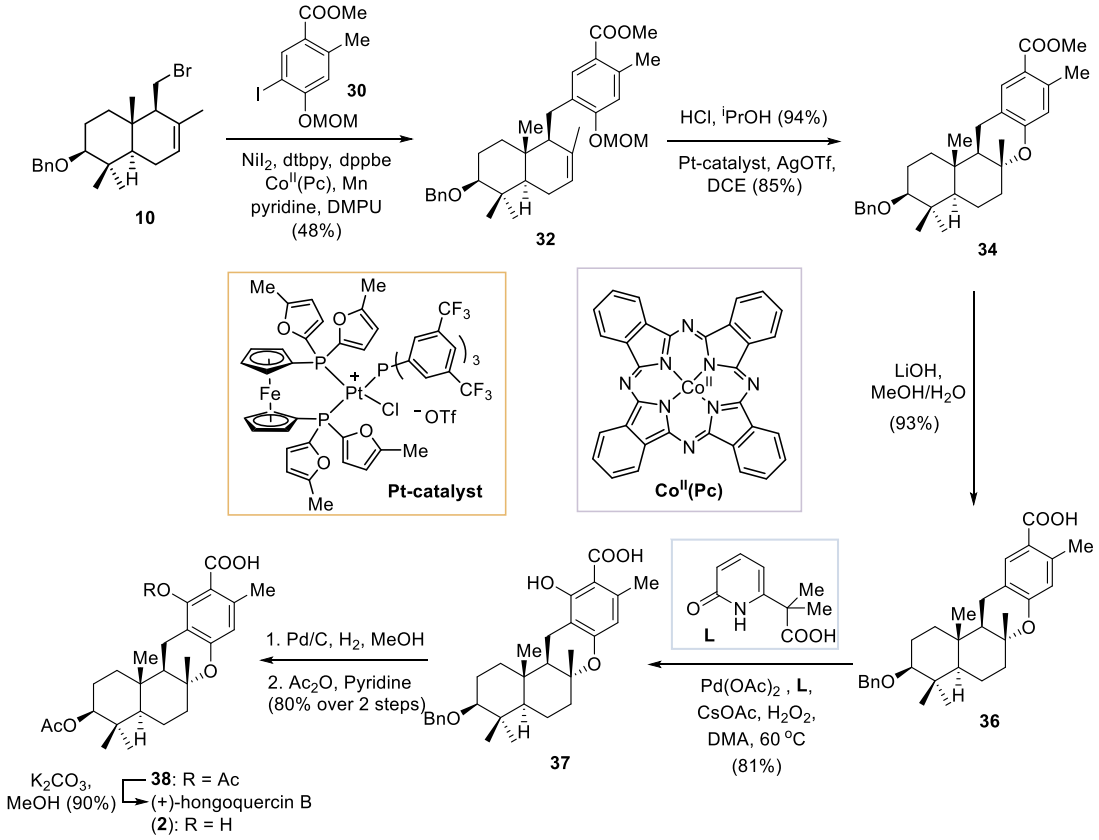
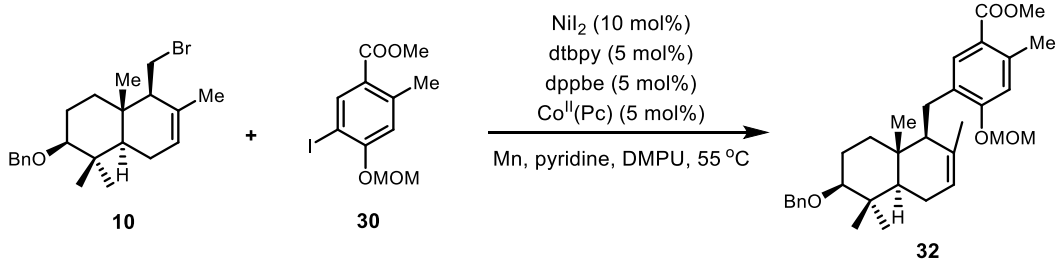


Figure S10. Synthetic route of (+)-hongoquercin B



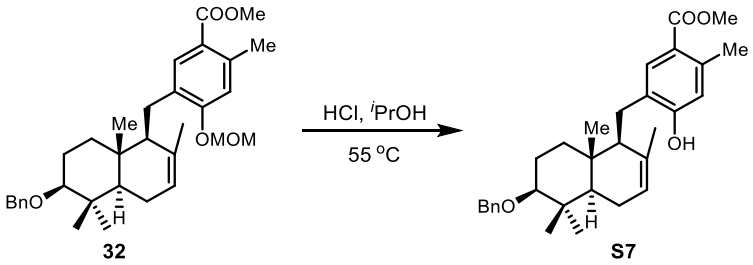
A solution of **10** (39.1 mg, 0.10 mmol, 1.0 equiv.) and **30** (33.6 mg, 0.10 mmol, 1.0 equiv.) in DMPU (0.3 mL) was treated with NiI_2 (3.1 mg, 0.01 mmol, 10 mol%), 1,2-bis(diphenylphosphino)benzene (2.2 mg, 0.005 mmol, 5 mol%), 4,4'-di-tert-butyl-2,2'-dipyridyl (1.3 mg, 0.005 mmol, 5 mol%), Co^{II}(Pc) (2.9 mg, 0.005mmol, 5 mol%), manganese powder (11.0 mg, 0.20 mmol, 2.0 equiv.), and pyridine (1 μL, 0.012 mmol, 12 mol%). The reaction mixture was heated to 55 °C for 16 hours then quenched with saturated aq. $Na_2S_2O_3$ solution (5 mL) and extracted with EtOAc (10 mL × 3). The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/ethyl acetate = 10:1) to yield **32** (25.5 mg, 49% yield) as colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.84 (s, 1H), 7.30 – 7.38 (m, 4H), 7.24 – 7.28 (m, 1H), 6.89 (s, 1H), 5.36 – 5.42 (m, 1H), 5.24 (s, 2H), 4.68 (d, *J* = 11.8 Hz, 1H), 4.45 (d, *J* = 11.8 Hz, 1H), 3.88 (s, 3H), 3.49 (s, 3H), 3.00 (dd, *J* = 11.7, 3.8 Hz, 1H), 2.73 (dd, *J* = 15.4, 9.1 Hz, 1H), 2.57 – 2.64 (m, 1H), 2.57 (s, 3H), 2.39 (d, *J* = 8.9 Hz, 1H), 1.98 – 2.01 (m, 2H), 1.95 (dt, *J* = 13.4, 3.5 Hz, 1H), 1.84 (dd, *J* = 13.2, 3.8 Hz, 1H), 1.55 (dd, *J* = 11.6, 2.8 Hz, 1H), 1.45 (s, 3H), 1.32 (dd, *J* = 9.5, 7.2 Hz, 1H), 1.20 (td, *J* = 13.6, 3.6 Hz, 1H), 1.01 (s, 3H), 0.95 (s, 3H), 0.93 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 168.0, 157.7, 140.0, 139.6, 135.5, 132.5, 129.9, 128.3, 127.5, 127.4, 122.5, 122.4, 116.5, 94.3, 86.8, 71.5, 56.5, 53.9, 51.7, 50.3, 39.0, 37.7, 36.9, 28.4, 26.0, 23.5, 23.2, 22.5, 22.2, 16.4, 14.1.

$[\alpha]_D^{21}$ = -8.51 (c = 1.75, $CHCl_3$).

HRMS (ESI+): calculated for $C_{33}H_{44}O_5Na$ $[M+Na]^+$: 543.3081, found 543.3080.



32 **S7**

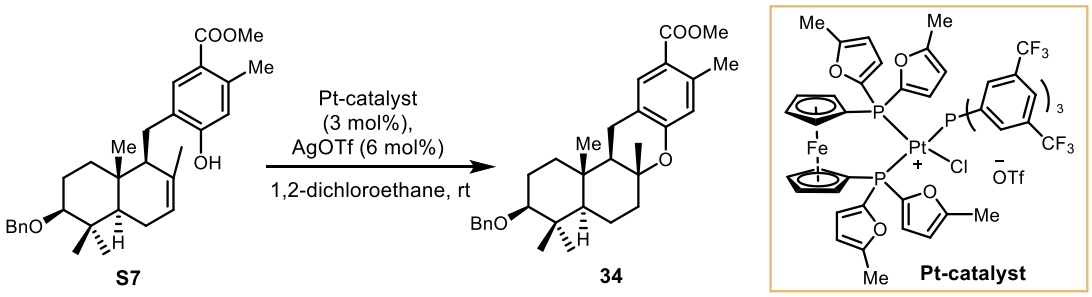
A solution of **32** (52.1 mg, 0.10 mmol, 1.0 equiv.) in ^{i}PrOH (2 mL) was treated with two drops of concentrated hydrochloric acid. The reaction mixture was stirred at 55 °C for 3 hours then quenched with H_2O (10 mL) and extracted with EtOAc (10 mL × 3). The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/ethyl acetate = 5:1) to give **S7** (44.8 mg, 94% yield) as white solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.85 (s, 1H), 7.30 – 7.39 (m, 4H), 7.20 – 7.29 (m, 1H), 6.56 (s, 1H), 5.38 – 5.42 (m, 1H), 5.36 (s, 1H), 4.68 (d, *J* = 11.8 Hz, 1H), 4.45 (d, *J* = 11.9 Hz, 1H), 3.87 (s, 3H), 3.00 (dd, *J* = 11.8, 3.8 Hz, 1H), 2.63 (d, *J* = 6.3 Hz, 3H), 2.52 (s, 3H), 2.36 – 2.43 (m, 1H), 1.91 – 2.03 (m, 3H), 1.84 (dd, *J* = 13.2, 3.7 Hz, 1H), 1.53 – 1.59 (m, 1H), 1.46 (s, 3H), 1.32 (dd, *J* = 9.7, 7.0 Hz, 2H), 1.21 (td, *J* = 13.6, 3.5 Hz, 1H), 1.01 (s, 3H), 0.95 (s, 3H), 0.92 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 168.1, 156.4, 140.1, 139.6, 135.2, 133.3, 128.4, 127.6, 127.4, 127.1, 122.7, 121.8, 118.4, 86.8, 71.6, 53.7, 51.8, 50.3, 39.0, 37.7, 36.9, 28.4, 25.9, 23.5, 23.2, 22.5, 21.8, 16.4, 14.1.

$[\alpha]_D^{22}$ = -12.24 (c = 1.25, $CHCl_3$).

HRMS (ESI+): calculated for $C_{31}H_{40}O_4Na$ $[M+Na]^+$: 499.2819, found 499.2819.



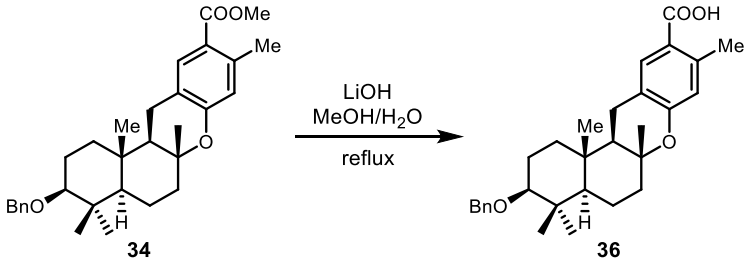
In an argon filled glovebox, to a 4 mL vial with a magnetic stir bar were added the Pt-catalyst[1] (4.9 mg, 3 mol%), silver trifluoromethanesulfonate (1.5 mg, 6 mol%), **S7** (47.7 mg, 0.1 mmol, 1.0 equiv.), and $ClCH_2CH_2Cl$ (1 mL). Then the vial was taken outside of the glovebox and the resulting mixture was stirred at room temperature (23 °C) for 12 h. The reaction mixture was diluted with CH_2Cl_2, filtered through a pad of celite and concentrated. The residue was purified with silica gel chromatography (hexane/ethyl acetate = 10:1) to yield **34** (40.5 mg, 85% yield) as colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.73 (s, 1H), 7.30 – 7.40 (m, 4H), 7.24 – 7.30 (m, 1H), 6.61 (s, 1H), 4.68 (d, *J* = 11.8 Hz, 1H), 4.44 (d, *J* = 11.8 Hz, 1H), 3.84 (s, 3H), 2.95 (dd, *J* = 11.8, 4.3 Hz, 1H), 2.58 – 2.63 (m, 2H), 2.52 (s, 3H), 2.09 (dt, *J* = 12.5, 3.2 Hz, 1H), 1.89 (dd, *J* = 13.5, 4.0 Hz, 1H), 1.78 (t, *J* = 3.6 Hz, 1H), 1.76 (t, *J* = 3.5 Hz, 1H), 1.64 – 1.69 (m, 1H), 1.59 – 1.61 (m, 1H), 1.53 – 1.57 (m, 1H), 1.38 – 1.47 (m, 1H), 1.20 (s, 3H), 1.03 (s, 3H), 1.00 – 1.02 (m, 1H), 0.92 (s, 3H), 0.87 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 167.9, 156.6, 140.5, 139.4, 133.4, 128.4, 127.6, 127.4, 120.8, 119.9, 119.4, 86.3, 78.0, 71.7, 55.7, 52.1, 51.6, 41.1, 39.1, 37.5, 36.8, 28.5, 22.9, 21.9, 21.0, 19.5, 16.7, 15.2.

$[\alpha]_D^{22}$ = +101.22 (c = 0.90, $CHCl_3$).

HRMS (ESI+): calculated for $C_{31}H_{41}O_4$ $[M+H]^+$: 477.2999, found 477.2998.



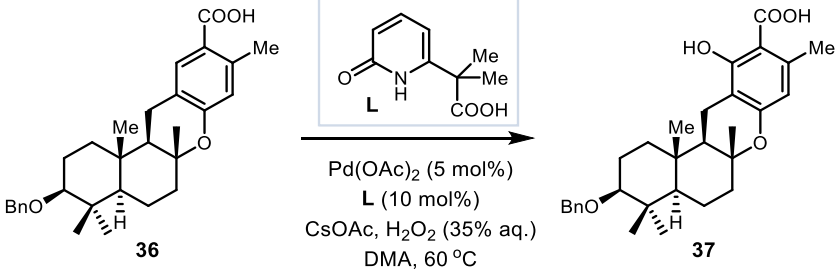
A solution of **34** (47.7 mg, 0.10 mmol, 1.0 equiv.) in MeOH/H_2O (3 mL:0.6 mL) was treated with LiOH (24 mg, 1.00 mmol, 10 equiv.). The reaction mixture was stirred at 100 °C for 10 hours then quenched with 3 M HCl (10 mL) and extracted with EtOAc (10 mL × 3). The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/ethyl acetate = 5:1, with 1% AcOH, v/v)) to give **36** (43.1 mg, 93% yield) as white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (s, 1H), 7.29 – 7.40 (m, 4H), 7.23 – 7.31 (m, 1H), 6.63 (s, 1H), 4.68 (d, *J* = 11.8 Hz, 1H), 4.44 (d, *J* = 11.8 Hz, 1H), 2.96 (dd, *J* = 11.7, 4.3 Hz, 1H), 2.58 – 2.67 (m, 2H), 2.56 (s, 3H), 2.05 – 2.14 (m, 1H), 1.90 (dd, *J* = 13.5, 3.9 Hz, 1H), 1.78 (dd, *J* = 13.1, 3.5 Hz, 2H), 1.59 – 1.74 (m, 2H), 1.51 – 1.61 (m, 1H), 1.39 – 1.48 (m, 1H), 1.21 (s, 3H), 1.04 (s, 3H), 0.98 – 1.03 (m, 2H), 0.92 (s, 3H), 0.88 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.8, 157.4, 141.7, 139.4, 134.5, 128.4, 127.6, 127.4, 120.0, 119.6, 119.6, 86.2, 78.2, 71.7, 55.6, 52.0, 41.1, 39.1, 37.5, 36.8, 28.4, 22.9, 22.3, 21.9, 21.1, 19.5, 16.7, 15.2.

$[\alpha]_D^{23}$ = +122.80 (c = 0.75, $CHCl_3$).

HRMS (ESI+): calculated for $C_{30}H_{38}O_4Na$ $[M+Na]^+$: 485.2662, found 485.2664.



L was prepared according to literature procedure.[8]

$Pd(OAc)_2$ (1.1 mg, 0.005 mmol, 5 mol%), L (1.8 mg, 0.01 mmol, 10 mol%), **36** (46.3 mg, 0.1 mmol, 1.0 equiv.), and CsOAc (28.8 mg, 0.15 mmol, 1.5 equiv.) were weighed and placed in a reaction tube. Then, DMA (0.3 mL) was added and stirred for 10 min, followed by the addition of H_2O_2 (35% aq., 30 uL, 3.0

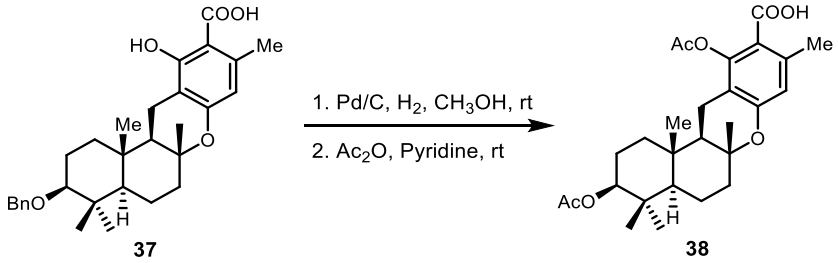
equiv.). The vial was sealed with a screw cap and stirred at 60 ºC for 24 h. Upon completion, the reaction was quenched with saturated solution of Na_2SO_3 in water until H_2O_2 was completely decomposed. (Tested by the potassium iodide starch test paper). The mixture was diluted with methanol and acidified with formic acid. The solution was filtered through a pad of Celite, and the aqueous layer was extracted with EtOAc (10 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude mixture was purified by flash chromatography (Hexane/EtOAc = 5:1, with 1% AcOH, v/v) to give **37** (38.8 mg, 81% yield) as white solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 11.85 (s, 1H), 7.31 – 7.40 (m, 4H), 7.24 – 7.30 (m, 1H), 6.21 (s, 1H), 4.69 (d, *J* = 11.8 Hz, 1H), 4.44 (d, *J* = 11.9 Hz, 1H), 2.96 (dd, *J* = 11.7, 4.1 Hz, 1H), 2.67 (dd, *J* = 16.7, 4.9 Hz, 1H), 2.52 (s, 3H), 2.31 (dd, *J* = 16.7, 13.2 Hz, 1H), 2.09 (dt, *J* = 12.3, 3.2 Hz, 1H), 1.85 – 1.93 (m, 2H), 1.74 – 1.82 (m, 1H), 1.62 – 1.71 (m, 1H), 1.55 – 1.64 (m, 1H), 1.51 (dd, *J* = 13.1, 4.9 Hz, 1H), 1.39 – 1.49 (m, 1H), 1.21 (s, 3H), 0.99 – 1.08 (m, 5H), 0.95 (s, 3H), 0.88 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 176.4, 164.0, 158.9, 141.7, 139.4, 128.4, 127.6, 127.4, 112.8, 108.0, 102.8, 86.3, 78.4, 71.6, 55.8, 51.5, 41.0, 39.1, 37.5, 36.9, 28.5, 24.3, 22.9, 20.8, 19.5, 16.9, 16.7, 15.1.

$[\alpha]_D^{25}$ = +143.20 (c = 1.00, $CHCl_3$).

HRMS (ESI+): calculated for $C_{30}H_{37}O_5$ [M-H]$^-$: 477.2636, found 477.2634.



A solution of **37** (47.9 mg, 0.10 mmol, 1.0 equiv.) in MeOH (2 mL) was treated with Pd (10% on carbon, 32 mg, 0.03 mmol, 0.3 equiv.). The reaction mixture was stirred at 23 ºC in hydrogen (1 atm) for 5 hours then filtered, and concentrated in vacuo. Acetic anhydride (47 μL, 0.50 mmol, 5.0 equiv.) was added to a magnetically stirred solution of the crude residue in pyridine (0.5 mL) at room temperature. The mixture was stirred for 24 h, then the resulting solution was diluted with water (5 mL), and the mixture was extracted with CH_2Cl_2 (5 mL × 3). The organic phase was washed with HCl (1 N aq.), sat. $CuSO_4$ solution, water, and brine, dried with Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography (Hexane/EtOAc = 5:1, with 1% AcOH, v/v) to give **38** (38.3 mg, 80% yield) as

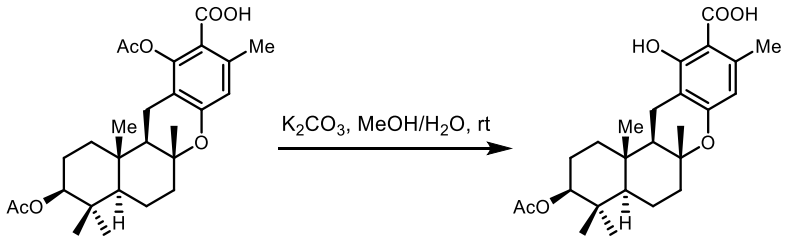
colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ. 6.57 (s, 1H), 4.50 (dd, *J* = 11.6, 4.5 Hz, 1H), 2.45 – 2.52 (m, 1H), 2.43 (s, 3H), 2.30 (s, 3H), 2.21 – 2.29 (m, 1H), 2.06 (s, 3H), 1.95 – 2.04 (m, 1H), 1.69 – 1.80 (m, 3H), 1.60 – 1.68 (m, 2H), 1.54 (dd, *J* = 13.1, 5.0 Hz, 1H), 1.38 – 1.47 (m, 1H), 1.18 (s, 3H), 1.13 – 1.17 (m, 1H), 1.09 (dd, *J* = 12.1, 2.2 Hz, 1H), 0.91 (s, 3H), 0.91 (s, 3H), 0.89 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 171.2, 171.1, 169.2, 156.4, 149.8, 139.2, 117.4, 115.6, 114.2, 80.4, 77.8, 55.2, 51.2, 40.7, 37.9, 37.2, 36.7, 28.2, 23.6, 21.5, 21.4, 21.0, 20.8, 19.4, 17.3, 16.8, 15.1.

$[\alpha]_D^{24}$ = +136.83 (c = 0.60, $CHCl_3$).

HRMS (ESI+): calculated for $C_{27}H_{36}O_7Na$ $[M+Na]^+$: 495.2353, found 495.2353.



38 (+)-Hongoquercin B **2**

38 (20 mg, 0.042 mmol, 1.0 equiv.) was dissolved in methanol (1 mL) and water (0.1 mL), and then K_2CO_3 (17.5 mg, 0.127 mmol, 3.0 equiv.) was added at room temperature. The mixture was stirred for 5 h at room temperature, then the resulting mixture was acidified by 2 N HCl to pH 2–3, and extracted with EtOAc (10 mL × 3). The extract was washed with water and brine, and dried with sodium sulfate. The solvent was evaporated, and the residue was purified by silica gel column chromatography (Hexane/Et_2O = 5:1, with 1% AcOH, v/v) to give **2** (16.3mg, 90 % yield) as a white solid.

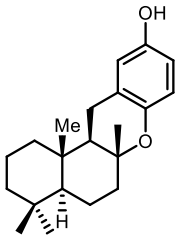
^{1}H NMR (400 MHz, $CDCl_3$): δ 11.88 (s, 1H), 6.21 (s, 1H), 4.52 (dd, *J* = 11.5, 4.9 Hz, 1H), 2.66 (dd, *J* = 16.8, 5.0 Hz, 1H), 2.51 (s, 3H), 2.30 (dd, *J* = 17.0, 13.2 Hz, 1H), 2.05 – 2.14 (m, 1H), 2.07 (s, 3H), 1.86 (dt, *J* = 13.1, 3.6 Hz, 1H), 1.60 – 1.80 (m, 4H), 1.53 (dd, *J* = 13.1, 5.0 Hz, 1H), 1.43 – 1.49 (m, 1H), 1.20 (s, 3H), 1.12 – 1.21 (m, 1H), 1.10 (dd, *J* = 12.0, 2.1 Hz, 1H), 0.95 (s, 3H), 0.91 (s, 3H), 0.89 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 175.7, 171.2, 164.0, 158.8, 141.7, 112.7, 107.9, 102.8, 80.6, 78.1, 55.3, 51.4, 40.8, 37.9, 37.3, 36.8, 28.3, 27.1, 24.3, 23.7, 21.4, 20.8, 19.5, 16.9, 16.8, 15.2.

$[\alpha]_D^{24}$ = +89.00 (c = 0.30, $CHCl_3$).

HRMS (ESI+): calculated for $C_{25}H_{33}O_6$ $[M-H]^-$: 429.2272, found 429.2276.

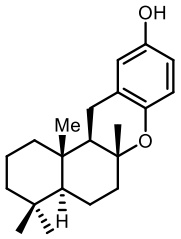
6. NMR comparisons



(+)-*ent*-chromazonarol

^{1}H NMR[11]

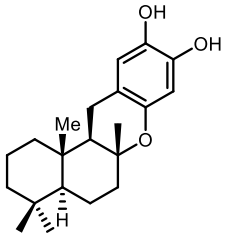
Literature (500 MHz in $CDCl_3$)	Synthetic (400 MHz in $CDCl_3$)
6.63 (d, *J* = 8.3 Hz, 1 H)	6.63 (d, *J* = 8.4 Hz, 1 H)
6.53 – 6.59 (m, 2 H)	6.52 – 6.59 (m, 2 H)
4.72 (s, 1H, OH)	4.33 (br, 1H, OH)
2.54 – 2.58 (m, 2 H)	2.54 – 2.60 (m, 2 H)
2.04 (dt, *J* = 12.5, 3.2 Hz, 1 H)	2.04 (dt, *J* = 12.5, 3.2 Hz, 1 H)
1.78 (m, 1 H)	1.72 - 1.78 (m, 1 H)
1.71 – 1.58 (m, 4 H)	1.61 – 1.71 (m, 4 H)
1.31 – 1.51 (m, 3 H)	1.36 – 1.50 (m, 3 H)
1.13 – 1.22 (m, 4 H)	1.15 – 1.21 (m, 4 H)
1.02 (dd, *J* = 12.3, 2.3 Hz, 1 H)	1.02 (dd, *J* = 12.2, 2.3 Hz, 1 H)
0.92 –0.99 (m, 1 H)	0.94 – 0.98 (m, 1 H)
0.90 (s, 3 H)	0.90 (s, 3 H)
0.88 (s, 3 H)	0.88 (s, 3 H)
0.84 (s, 3 H)	0.84 (s, 3 H)



(+)-*ent*-chromazonarol

^{13}C NMR[11]

Literature (125 MHz in $CDCl_3$)	Synthetic (151 MHz in $CDCl_3$)
148.7	148.6
147.2	147.3
123.4	123.4
117.6	117.7
115.9	115.9
114.4	114.4
76.9	76.8
56.2	56.3
52.2	52.2
42.0	42.0
41.2	41.3
39.3	39.4
36.9	36.9
33.6	33.6
33.3	33.3
22.6	22.6
21.7	21.8
20.8	20.8
19.9	19.9
18.7	18.7
14.9	15.0

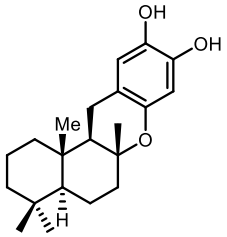


(+)-8-*epi*-puupehenol

^{1}H NMR[12]

Literature (300 MHz in Acetone-d_6)	Synthetic (400 MHz in Acetone-d_6)
7.60 (bs, 1 H)	7.61 (s, 1 H)
7.20 (bs, 1 H)	7.20 (s, 1 H)
6.49 (s, 1 H)	6.50 (s, 1 H)
6.18 (s, 1 H)	6.19 (s, 1 H)
2.47 (d, *J* = 2.0 Hz, 1 H)	2.40 – 2.51 (m, 2 H)
2.44 (s, 1 H)	
1.95 (dt, *J* = 12.2, 2.9 Hz, 1 H)	1.96 (dt, *J* = 12.5, 3.2 Hz, 1 H),
1.25 (s, 3 H)	1.64 – 1.76 (m, 3 H)
0.89 (s, 3 H)	1.59 (dd, *J* = 13.0, 4.4 Hz, 1 H)
0.89 (s, 6 H)	1.53 (dd, *J* = 11.4, 7.0 Hz, 1 H)
	1.43 – 1.47 (m, 1 H)
	1.38 – 1.42 (m, 2 H)
	1.18 – 1.23 (m, 1 H)
	1.13 (s, 3 H)
	1.06 (dd, *J* = 12.4, 2.5 Hz, 1 H)
	0.98 – 1.02 (m, 1 H)
	0.90 (s, 6 H)
	0.86 (s, 3 H)

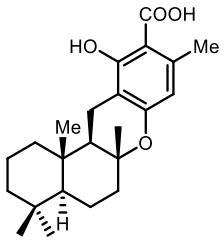
Note: References for solvent peaks were not listed in all literature reports, which could be responsible for slight variations in chemical shifts. Also, complete peak listings were not always reported.



(+)-8-*epi*-puupehenol

^{13}C NMR[12]

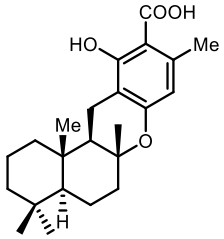
Literature (75 MHz in Acetone-d_6)	Synthetic (151 MHz in Acetone-d_6)
147.0	146.2
144.8	144.0
139.2	138.4
116.2	115.2
115.2	112.4
104.5	103.7
76.5	75.7
56.8	56.1
53.4	52.6
42.5	41.7
41.9	41.2
39.8	39.0
37.4	36.6
34.0	32.9
33.7	32.9
22.3	21.5
21.9	21.1
21.3	20.1
21.0	19.5
19.2	18.3
15.2	14.3



(+)-Hongoquercin A

^{1}H NMR[13]

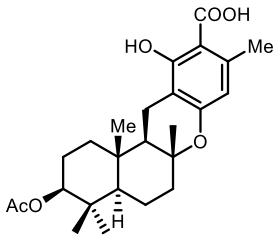
Literature (500 MHz in $CDCl_3$)	Synthetic (600 MHz in $CDCl_3$)
11.81 (s, 1 H)	11.83 (s, 1 H)
6.21 (s, 1 H)	6.21 (s, 1 H)
2.69 (dd, *J* = 16.8, 4.8 Hz, 1 H)	2.68 (dd, *J* = 16.8, 4.9 Hz, 1 H)
2.52 (s, 3 H)	2.52 (s, 3 H)
2.28 (dd, *J* = 16.6, 13.3 Hz, 1 H)	2.29 (dd, *J* = 16.8, 13.2 Hz, 1 H)
2.07 (ddd, *J* = 12.5, 3.0, 3.0 Hz, 1 H)	2.03 – 2.11 (m, 1 H)
1.78 (m, 1 H)	1.79 – 1.84 (m, 1 H)
1.81 (m, 1 H)	1.74 – 1.79 (m, 1 H)
1.67 (ddd, *J* = 13.2, 13.2, 4.1 Hz, 1 H)	1.67 – 1.71 (m, 1 H)
1.62 (m, 1 H)	1.62 – 1.66 (m, 1 H)
1.55 (dd, *J* = 13.2, 4.9 Hz, 1 H)	1.55 (dd, *J* = 13.1, 5.0 Hz, 1 H)
1.49 (m, 1 H)	1.45 – 1.50 (m, 1 H)
1.42 (d, *J* = 12.4, 1 H)	1.39 – 1.43 (m, 1 H)
1.36 (ddd, *J* = 13.7, 13.7, 3.2 Hz, 1 H)	1.35 – 1.39 (m, 1 H)
1.20 (s, 3 H)	1.20 (s, 3 H)
1.17 (ddd, *J* = 13.5, 13.5, 3.7 Hz, 1 H)	1.13 – 1.20 (m, 1 H)
1.03 (dd, *J* = 12.2, 1.4 Hz, 1 H)	1.03 (dd, *J* = 12.2, 2.2 Hz, 1 H)
0.97 (ddd, J = 13.5, 3.1 Hz, 1 H)	0.95 – 1.01 (m, 1 H)
0.92 (s, 3 H)	0.92 (s, 3 H)
0.91 (s, 3 H)	0.91 (s, 3 H)
0.85 (s, 3 H)	0.85 (s, 3 H)



(+)-Hongoquercin A

^{13}C NMR[13]

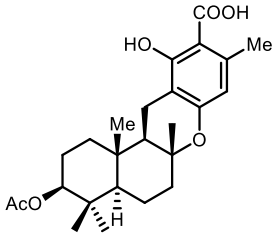
Literature (100 MHz in $CDCl_3$)	Synthetic (151 MHz in $CDCl_3$)
176.3	176.1
164.1	164.0
159.1	159.0
141.7	141.6
112.9	112.8
108.3	108.2
102.7	102.7
78.7	78.6
56.4	56.3
51.8	51.7
42.1	42.0
41.1	41.0
39.4	39.3
37.2	37.1
33.7	33.6
33.4	33.4
24.4	24.3
21.8	21.7
21.0	20.9
20.0	19.9
18.7	18.6
16.9	16.8
15.2	15.1



(+)-Hongoquercin B

^{1}H NMR[14]

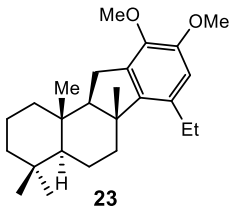
Literature (500 MHz in $CDCl_3$)	Synthetic (400 MHz in $CDCl_3$)
11.85 (s, 1 H)	11.88 (s, 1 H)
6.21 (s, 1 H)	6.21 (s, 1 H)
4.52 (dd, *J* = 11.6, 4.9 Hz,1 H)	4.52 (dd, *J* = 11.5, 4.9 Hz,1 H)
2.67 (dd, *J* = 16.8, 4.9 Hz, 1 H)	2.66 (dd, *J* = 16.8, 5.0 Hz, 1 H)
2.52 (s, 3 H)	2.51 (s, 3 H)
2.31 (dd, *J* = 16.8, 13.1 Hz, 1 H)	2.30 (dd, *J* = 17.0, 13.2 Hz, 1 H)
2.08 (ddd, *J* = 12.5, 3.1, 1 H)	2.05 – 2.14 (m, 1 H)
2.07 (s,3 H)	2.07 (s,3 H)
1.86 (ddd, *J* = 13.2, 3.4, 3.4 Hz, 1 H)	1.86 (dt, *J* = 13.1, 3.6 Hz, 1 H)
1.64 – 1.80 (m, 4 H)	1.60 – 1.80 (m, 4 H)
1.53 (dd, *J* = 13.1, 4.9 Hz, 1 H)	1.53 (dd, *J* = 13.1, 5.0 Hz, 1 H)
1.44 (m, 1 H)	1.43 – 1.49 (m, 1 H)
1.20 (s, 3 H)	1.20 (s, 3 H)
1.19 (ddd, *J* = 13.2, 13.2, 3.7 Hz, 1 H)	1.12 – 1.21 (m, 1 H)
1.10 (dd, *J* = 12.2, 1.8 Hz, 1 H)	1.10 (dd, *J* = 12.0, 2.1 Hz, 1 H)
0.96 (s, 3 H)	0.95 (s, 3 H)
0.91 (s, 3 H)	0.91 (s, 3 H)
0.90 (s, 3 H)	0.89 (s, 3 H)



(+)-Hongoquercin B

^{13}C NMR[14]

Literature (75 MHz in $CDCl_3$)	Synthetic (151 MHz in $CDCl_3$)
176.1	175.7
171.1	171.2
163.8	164.0
158.5	158.8
141.5	141.7
112.6	112.7
107.7	107.9
102.9	102.8
80.6	80.6
77.9	78.1
55.1	55.3
51.2	51.4
40.6	40.8
37.7	37.9
37.1	37.3
36.6	36.8
28.0	28.3
24.1	24.3
23.5	23.7
21.3	21.4
20.6	20.8
19.3	19.5
16.8	16.9
16.6	16.8
15.0	15.2

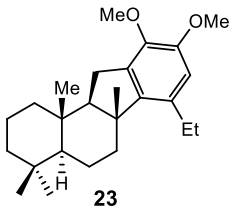


23

^{1}H NMR[8]

Literature (400 MHz in $CDCl_3$)	Synthetic (400 MHz in $CDCl_3$)
6.49 (s, 1H)	6.51 (s, 1H)
3.81 (s, 3H)	3.83 (s, 3H)
3.80 (s, 3H)	3.82 (s, 3H)
2.69 (m, 2H)	2.73 (dd, *J* = 6.8, 4.6 Hz, 1H)
	2.69 (dd, *J* = 6.8, 4.4 Hz, 1H)
2.56 (dd, *J* = 14.5, 7.5 Hz, 1H)	2.56 – 2.63 (m, 1H)
2.49 (dd, *J* = 14.5, 13.0 Hz, 1H)	2.51 (dd, *J* = 14.8, 12.8 Hz, 1H)
2.36 (dt, *J* = 12.0, 3.4 Hz, 1H)	2.38 (dt, *J* = 12.0, 3.2 Hz, 1H)
	1.80 (dd, *J* = 12.6, 3.9 Hz, 1H)
	1.68 – 1.76 (m, 3H)
	1.54 – 1.60 (m, 2H)
	1.37 – 1.46 (m, 2H)
1.22 (t, *J* = 7.6 Hz, 3H)	1.24 (t, *J* = 7.6 Hz, 3H)
	1.17 (dd, *J* = 13.1, 4.2 Hz, 1H)
1.08 (s, 3H)	1.11 (s, 3H)
1.02 (s, 3 H)	1.04 (s, 3H)
	0.95 – 1.02 (m, 2H)
0.85 (s, 6 H)	0.88 (s, 6H)

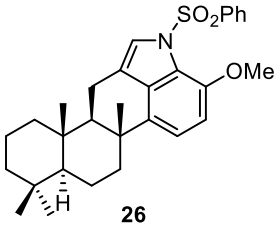
Note: References for solvent peaks were not listed in all literature reports, which could be responsible for slight variations in chemical shifts. Also, complete peak listings were not always reported



23

^{13}C NMR[8]

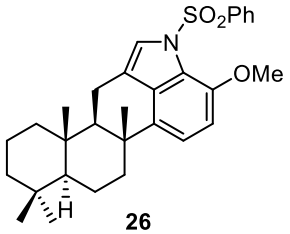
Literature (75 MHz in $CDCl_3$)	Synthetic (101 MHz in $CDCl_3$)
150.3	150.5
144.8	145.0
143.6	143.7
135.8	136.0
133.7	133.9
111.1	111.2
64.3	64.4
60.4	60.5
57.1	57.2
55.9	56.1
47.9	48.0
42.5	42.7
40.2	40.3
39.3	39.4
37.1	37.2
33.4	33.5
33.1	33.2
25.2	25.4
24.7	24.8
21.3	21.5
21.1	21.3
19.7	19.8
18.3	18.5
16.1	16.3
16.0	16.2



26

^{1}H NMR[9]

Literature (400 MHz in $CDCl_3$)	Synthetic (400 MHz in $CDCl_3$)
7.93 (d, *J* = 8.2 Hz 2H)	7.87 – 7.94 (m, 2H)
7.51 - 7.58 (m, 1H)	7.48 – 7.57 (m, 1H)
7.42 - 7.49 (m, 3H)	7.40 - 7.48 (m, 3 H)
6.88 (d, *J* = 8.15 Hz, 1H)	6.87 (d, *J* = 8.0 Hz, 1H)
6.65 (d, *J* = 8.15 Hz, 1H)	6.62 (d, *J* = 8.0 Hz, 1H)
3.70 (s, 3H)	3.68 (s, 3H)
2.94 (dd, *J* = 15.8, 2.8 Hz, 1H)	2.91 (dd, *J* = 15.7, 3.4 Hz, 1H)
2.66 (dd, *J* = 16, 11.8 Hz, 1H)	2.61 (ddd, *J* = 15.5, 12.9, 2.1 Hz, 1H)
2.44 (d, *J* = 12.2 Hz, 1H)	2.32 – 2.49 (m, 1H)
1.85-1.88 (m, 1H)	1.81 – 1.90 (m, 1H)
1.71-1.76 (m, 2H)	1.66 – 1.77 (m, 2H)
1.66-1.70 (m, 2H)	1.62 – 1.66 (m, 2H)
1.50-1.58 (m, 2H)	1.49 – 1.54 (m, 2H)
1.46-1.48 (m, 2H)	1.43 – 1.49 (m, 2H)
1.36-1.39 (m, 1H)	1.35 – 1.40 (m, 1H)
1.13 (s, 3H)	1.12 (s, 3H)
1.05 (s, 3H)	1.04 (s, 3H)
0.81 – 0.92 (m, 1H)	0.88 – 0.93 (m, 1H)
0.89 (s, 6H)	0.88 (s, 6H)



26

^{13}C NMR[9]

Literature (75 MHz in $CDCl_3$)	Synthetic (101 MHz in $CDCl_3$)
145.3	145.2
140.6	140.4
138.8	138.7
133.2	133.1
130.9	130.8
128.9	128.8
127.8	127.7
122.5	122.4
121.6	121.5
118.8	118.7
116.7	116.6
108.2	108.0
56.8	56.7
56.6	56.5
56.1	56.0
42.1	42.0
40.4	40.3
39.1	39.0
38.3	38.2
37.4	37.3
33.7	33.6
33.6	33.5
25.2	25.1
21.8	21.7
19.0	18.9
18.9	18.8
18.2	18.1
16.5	16.4

7. References

1 Y. Zhou, X. Xu, H. Sun, G. Tao, X.-Y. Chang, X. Xing, B. Chen and C. Xu, *Nat. Commun.*, 2021, **12**, 1953.

2 S.-B. Mou, W. Xiao, H.-Q. Wang, S.-J. Wang and Z. Xiang, *Org. Lett.*, 2020, **22**, 1976–1979.

3 M. P. Polovinka, D. V. Korchagina, Y. V. Gatilov, I. Y. Bagrianskaya, V. A. Barkhash, V. B. Perutskii, N. D. Ungur, P. F. Vlad, V. V. Shcherbukhin and N. S. Zefirov, *J. Org. Chem.*, 1994, **59**, 1509–1517.

4 S. Kille, F. E. Zilly, J. P. Acevedo and M. T. Reetz, *Nat. Chem.*, 2011, **3**, 738–743.

5 S. W. Pelletier, S. Lajsic, Y. Ohtsuka and Z. Djarmati, *J. Org. Chem.*, 1975, **40**, 1607–1609.

6 P. F. Vlad, A. G. Ciocarlan, M. N. Coltsa, A. V. Baranovsky and N. B. Khripach, *Synth. Commun.*, 2008, **38**, 3960–3972.

7 Z.-F. Shi, L.-J. Wang, H. Wang, X.-P. Cao and H.-L. Zhang, *Org. Lett.*, 2007, **9**, 595–598.

8 L. Yang, D. E. Williams, A. Mui, C. Ong, G. Krystal, R. van Soest and R. J. Andersen, *Org. Lett.*, 2005, **7**, 1073–1076.

9 D. H. Dethe, S. K. Sau and S. Mahapatra, *Org. Lett.*, 2016, **18**, 6392–6395.

10 Z. Li, H. S. Park, J. X. Qiao, K.-S. Yeung and J.-Q. Yu, *J. Am. Chem. Soc.*, 2022, **144**, 18109–18116.

11 D. D. Dixon, J. W. Lockner, Q. Zhou and P. S. Baran, *J. Am. Chem. Soc.*, 2012, **134**, 8432–8435.

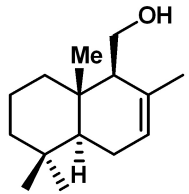
12 A. F. Barrero, E. J. Alvarez-Manzaneda, R. Chahboun, M. Cortés and V. Armstrong, *Tetrahedron*, 1999, **55**, 15181–15208.

13 D. H. Dethe, G. M. Murhade, B. D. Dherange and S. K. Sau, *Eur. J. Org. Chem.*, 2017, **2017**, 1143–1150.

14 H. TSUJIMORI and K. MORI, *Biosci. Biotechnol., Biochem.*, 2000, **64**, 1410–1415.

8. NMR spectra

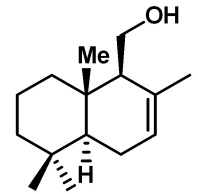
Parameter	Value
1 Title	Drimenol-220808.1.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDCl3
9 Temperature	298.1
10 Pulse Sequence	zg30
11 Experiment	1D
12 Probe	Z116098_0723 (PA BBO 400S1 BBF-H-D-05 Z SP)
13 Number of Scans	8
14 Receiver Gain	101.0
15 Relaxation Delay	1.0000
16 Pulse Width	8.5800
17 Presaturation Frequency	
18 Acquisition Time	3.9977
19 Acquisition Date	2022-08-08T18:44:36
20 Modification Date	2023-11-17T10:24:31
21 Class	
22 Spectrometer Frequency	400.13
23 Spectral Width	8196.7
24 Lowest Frequency	-1636.9
25 Nucleus	1H
26 Acquired Size	32768
27 Spectral Size	65536



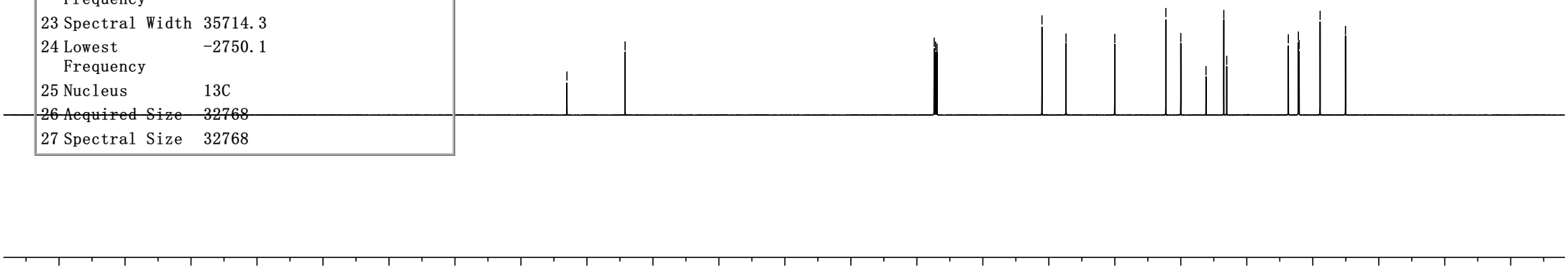
(-)-Drimenol
11

Parameter	Value
1 Title	YYP-drimenol-20210920.11.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	Avance NEO 600
7 Author	
8 Solvent	CDCl3
9 Temperature	298.2
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Probe	Z168773_0027 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
13 Number of Scans	128
14 Receiver Gain	101.0
15 Relaxation Delay	2.0000
16 Pulse Width	9.9100
17 Presaturation Frequency	
18 Acquisition Time	0.9175
19 Acquisition Date	2021-09-21T06:12:14
20 Modification Date	2023-04-26T14:43:59
21 Class	
22 Spectrometer Frequency	150.91
23 Spectral Width	35714.3
24 Lowest Frequency	-2750.1
25 Nucleus	13C
26 Acquired Size	32768
27 Spectral Size	32768

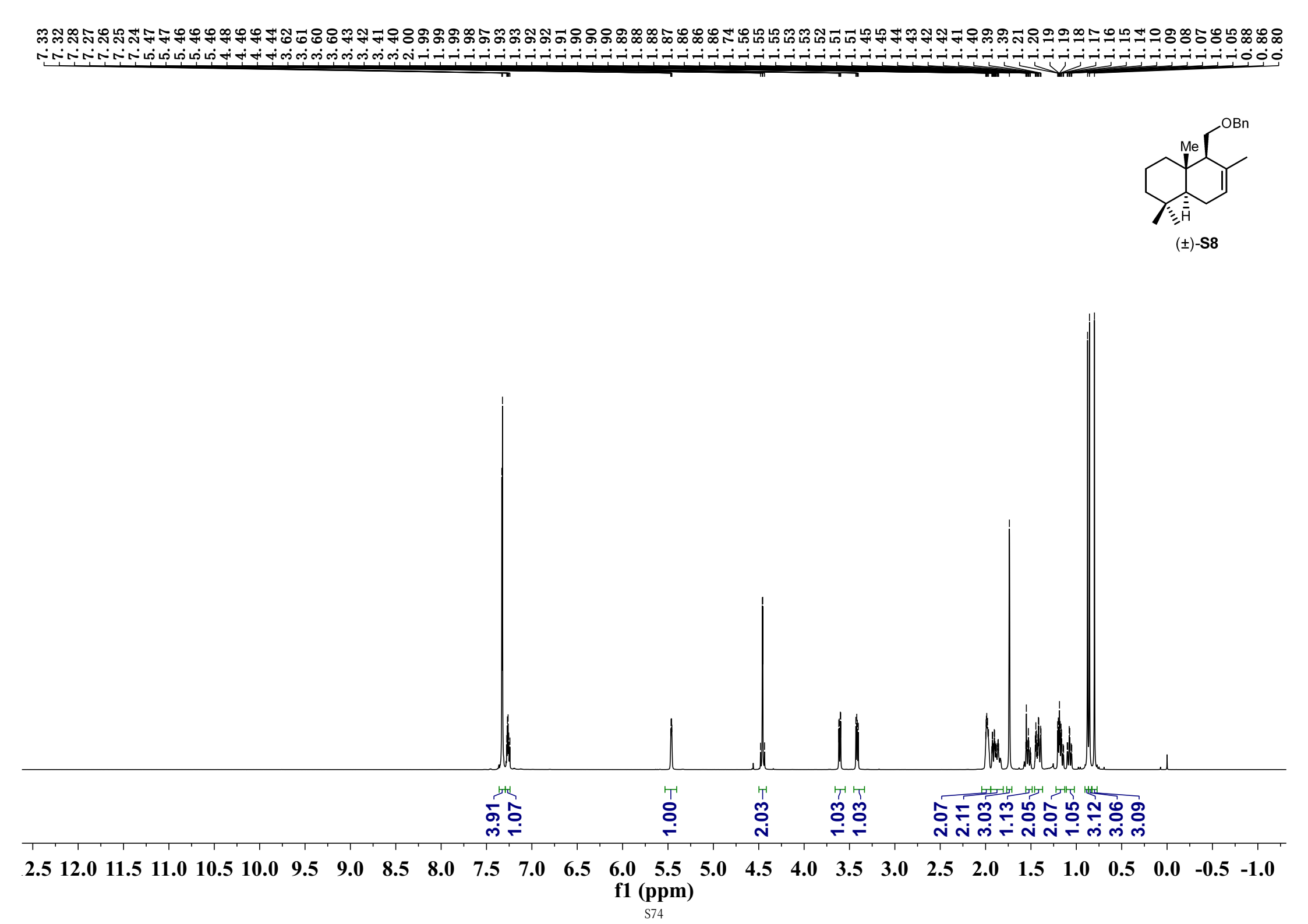
133.0 124.2 77.4 77.2 76.9 61.0 57.4 50.0 42.3 40.0 36.2 33.5 33.0 23.7 22.2 22.1 18.9 15.0

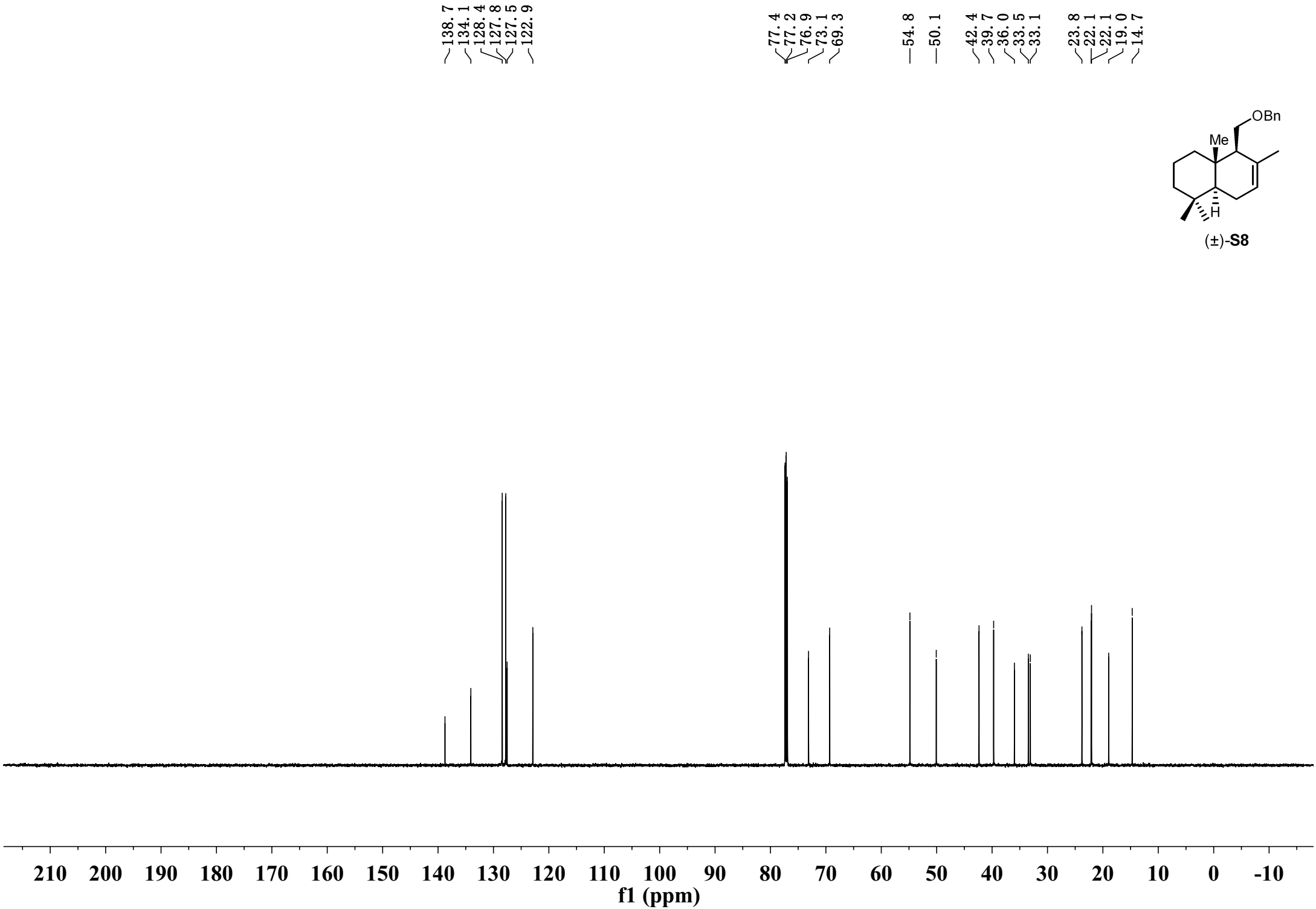


(-)-Drimenol
11

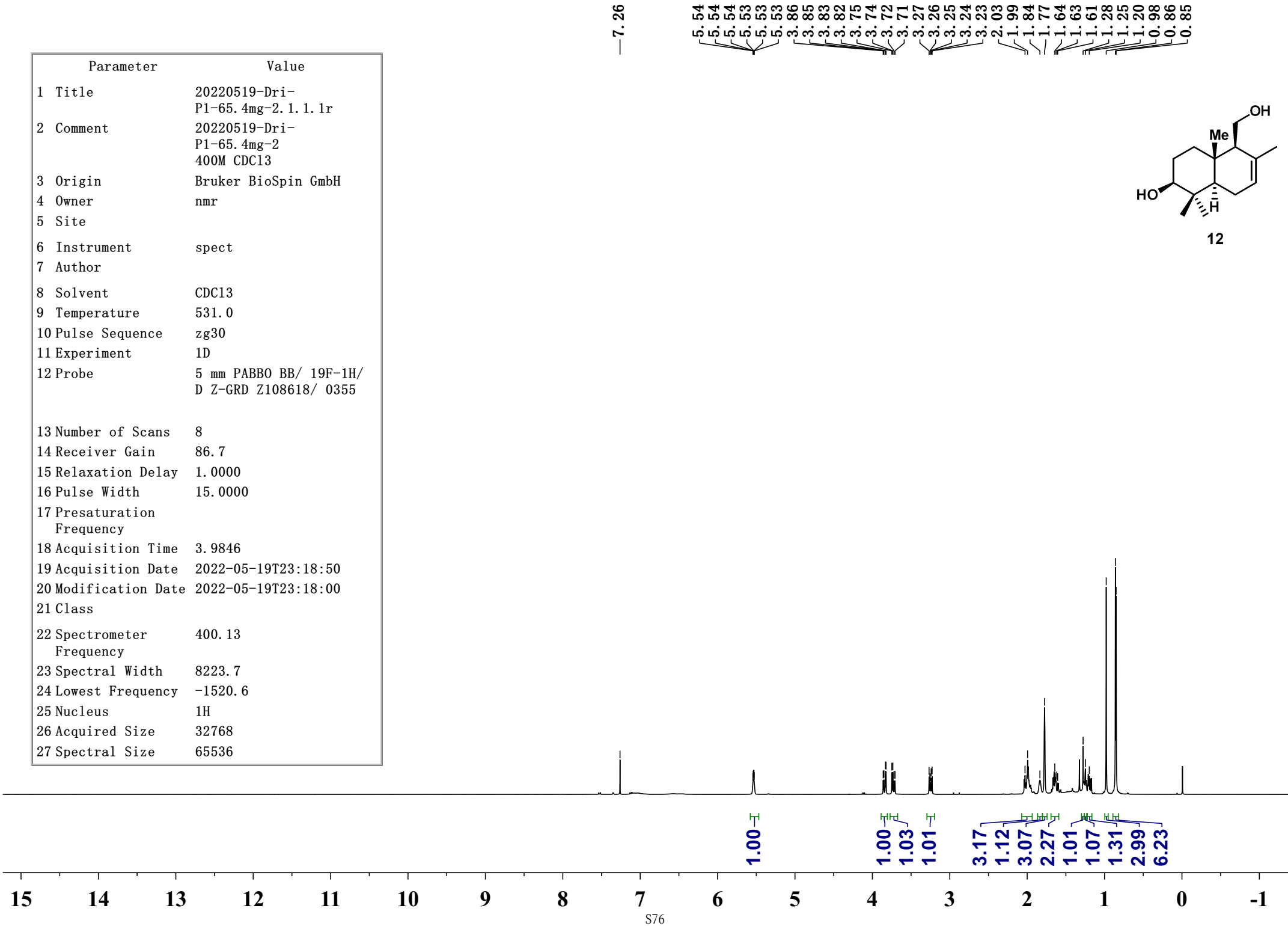


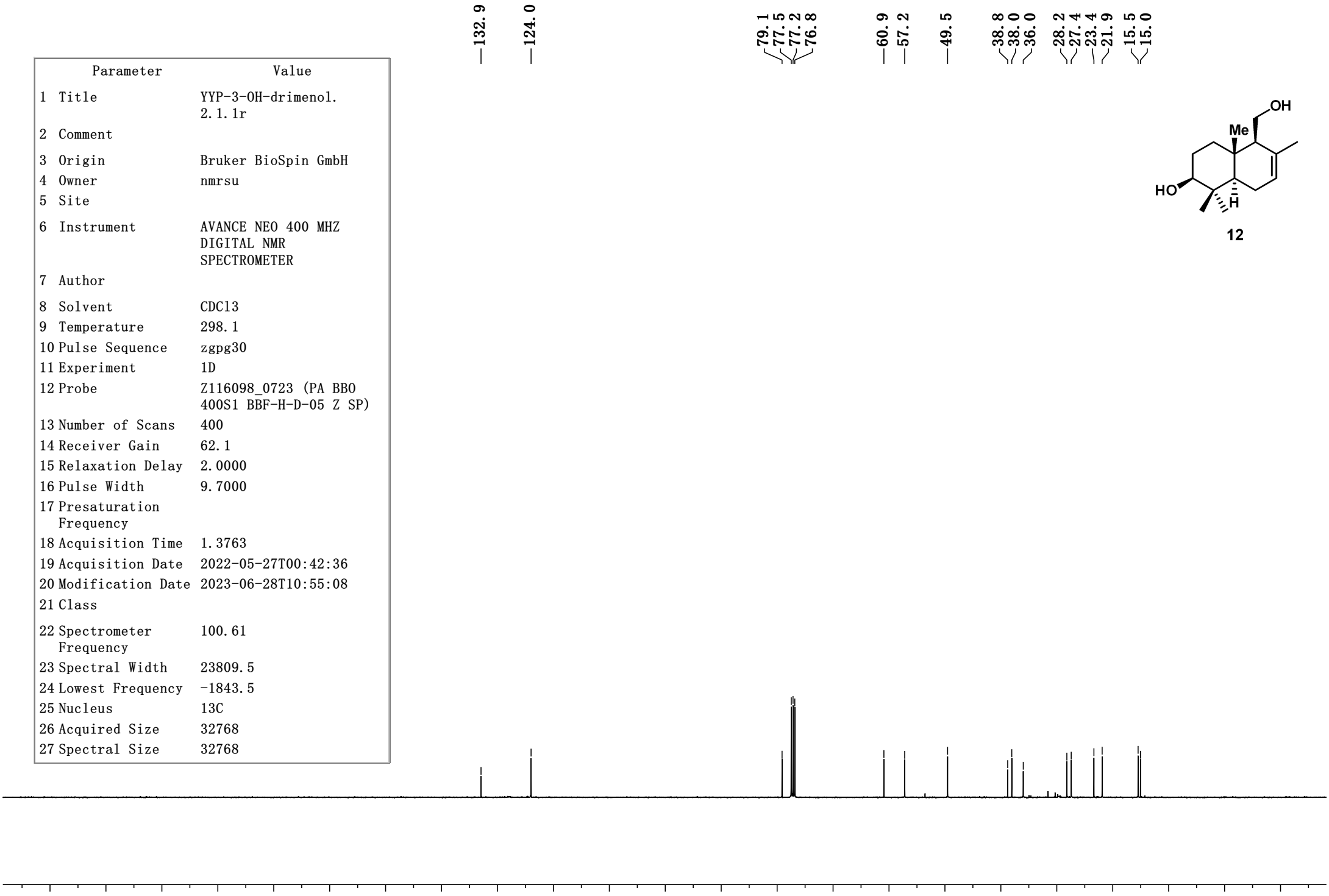
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


7.33 7.32 7.28 7.27 7.26 7.25 7.24 5.47 5.46 5.46 5.46 4.48 4.46 4.46 4.44 3.62 3.61 3.60 3.60 3.43 3.42 3.41 3.40 2.00 1.99 1.99 1.99 1.98 1.97 1.93 1.93 1.92 1.92 1.91 1.90 1.90 1.90 1.89 1.88 1.88 1.87 1.86 1.86 1.86 1.74 1.56 1.55 1.55 1.53 1.53 1.52 1.51 1.51 1.45 1.45 1.44 1.43 1.42 1.42 1.41 1.40 1.39 1.39 1.21 1.20 1.19 1.19 1.18 1.17 1.16 1.15 1.14 1.10 1.09 1.08 1.07 1.06 1.05 0.88 0.86 0.80
OBn
Me
H
(±)-S8
3.91 1.07 1.00 2.03 1.03 1.03 2.07 2.11 3.03 1.13 2.05 2.07 1.05 3.12 3.06 3.09
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


138.7
134.1
128.4
127.8
127.5
122.9
77.4
77.2
76.9
73.1
69.3
54.8
50.1
42.4
39.7
36.0
33.5
33.1
23.8
22.1
22.1
19.0
14.7
OBn
Me
H
(±)-S8
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

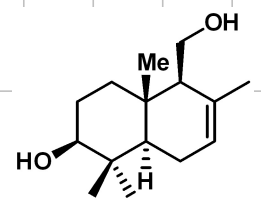
Parameter	Value
1 Title	20220519-Dri-P1-65.4mg-2.1.1.1r
2 Comment	20220519-Dri-P1-65.4mg-2 400M CDCl3
3 Origin	Bruker BioSpin GmbH
4 Owner	nmr
5 Site	
6 Instrument	spect
7 Author	
8 Solvent	CDCl3
9 Temperature	531.0
10 Pulse Sequence	zg30
11 Experiment	1D
12 Probe	5 mm PABBO BB/ 19F-1H/D Z-GRD Z108618/ 0355
13 Number of Scans	8
14 Receiver Gain	86.7
15 Relaxation Delay	1.0000
16 Pulse Width	15.0000
17 Presaturation Frequency	
18 Acquisition Time	3.9846
19 Acquisition Date	2022-05-19T23:18:50
20 Modification Date	2022-05-19T23:18:00
21 Class	
22 Spectrometer Frequency	400.13
23 Spectral Width	8223.7
24 Lowest Frequency	-1520.6
25 Nucleus	1H
26 Acquired Size	32768
27 Spectral Size	65536





Parameter	Value
1 Title	YYP-3-OH-drimenol. 2.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDCl3
9 Temperature	298.1
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Probe	Z116098_0723 (PA BBO 400S1 BBF-H-D-05 Z SP)
13 Number of Scans	400
14 Receiver Gain	62.1
15 Relaxation Delay	2.0000
16 Pulse Width	9.7000
17 Presaturation Frequency	
18 Acquisition Time	1.3763
19 Acquisition Date	2022-05-27T00:42:36
20 Modification Date	2023-06-28T10:55:08
21 Class	
22 Spectrometer Frequency	100.61
23 Spectral Width	23809.5
24 Lowest Frequency	-1843.5
25 Nucleus	13C
26 Acquired Size	32768
27 Spectral Size	32768

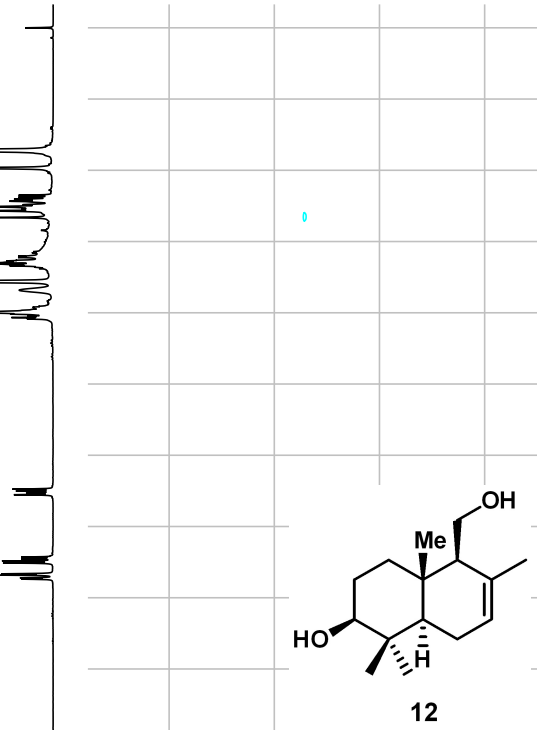
Cosy



12

f1 (ppm)

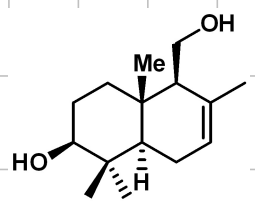
Noesy



12

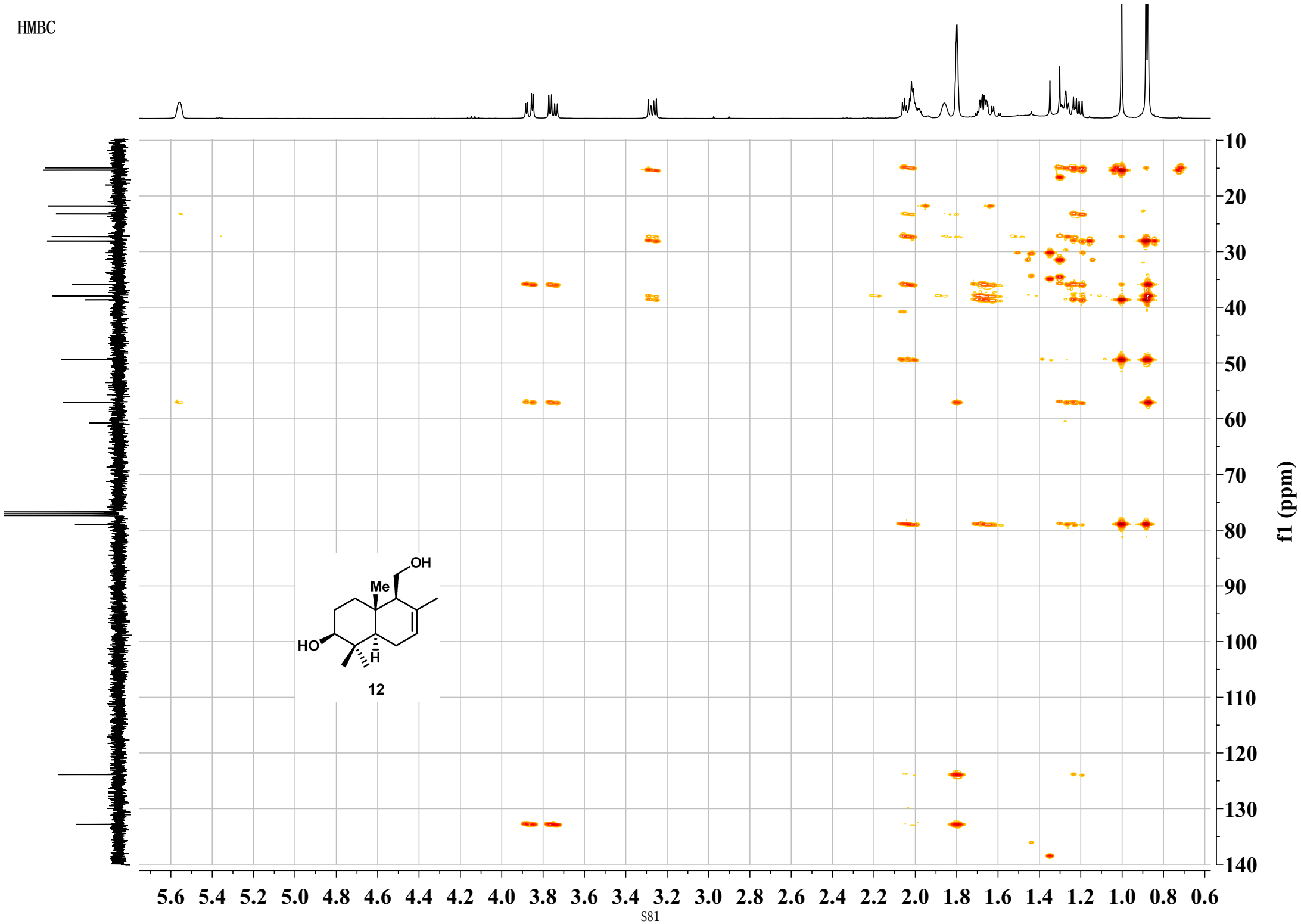
f1 (ppm)

HSQC

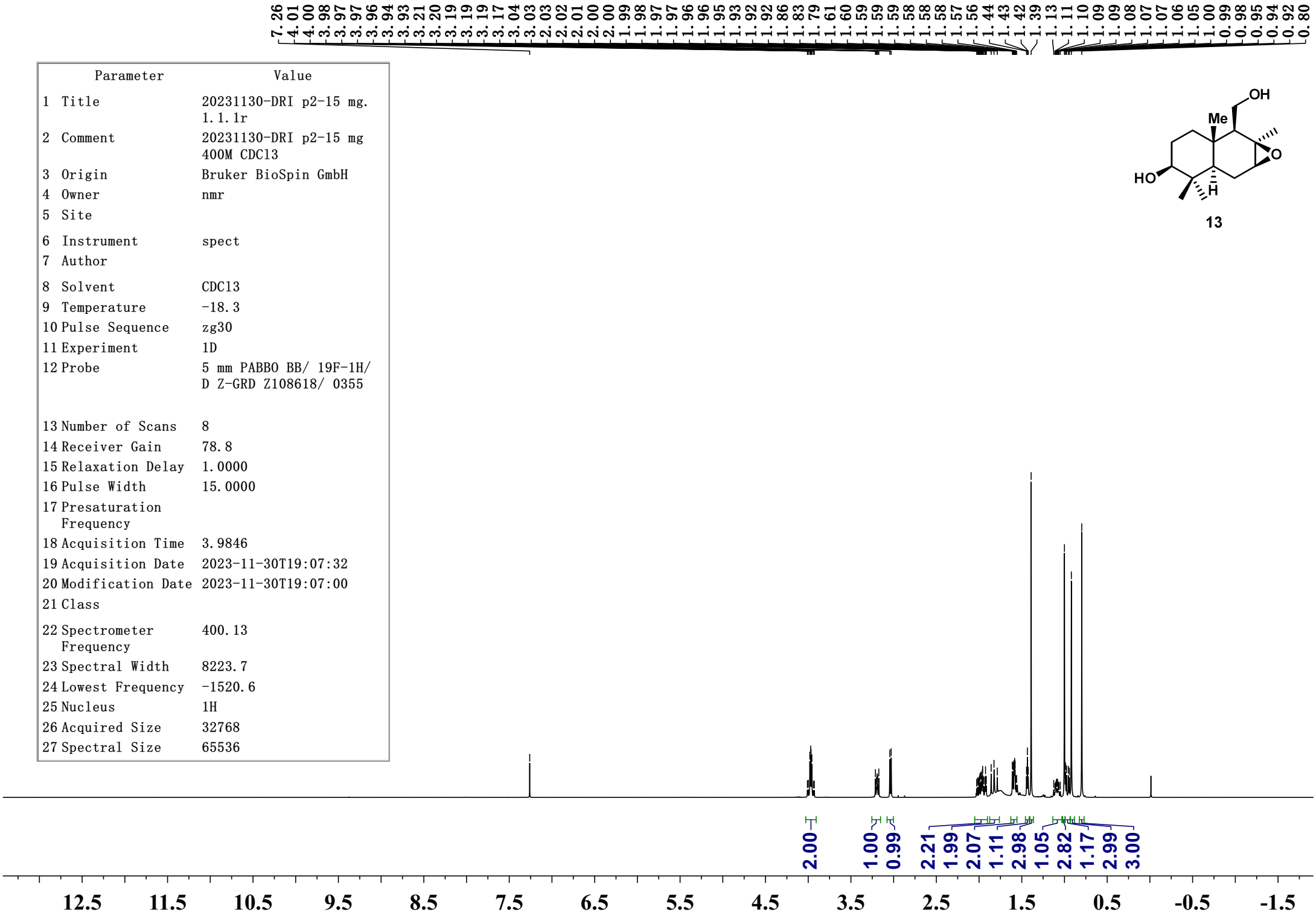

OH
Me
HO
H

12

f1 (ppm)
10
20
30
40
50
60
70
80
90
100
110
120
130
140
5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6

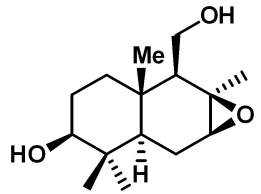

HMBC
OH
Me
HO
H
12
5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6
10 20 30 40 50 60 70 80 90 100 110 120 130 140
f1 (ppm)

Parameter	Value
1 Title	20231130-DRI p2-15 mg. 1.1.1r
2 Comment	20231130-DRI p2-15 mg 400M CDCl3
3 Origin	Bruker BioSpin GmbH
4 Owner	nmr
5 Site	
6 Instrument	spect
7 Author	
8 Solvent	CDCl3
9 Temperature	-18.3
10 Pulse Sequence	zg30
11 Experiment	1D
12 Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z108618/ 0355
13 Number of Scans	8
14 Receiver Gain	78.8
15 Relaxation Delay	1.0000
16 Pulse Width	15.0000
17 Presaturation Frequency	
18 Acquisition Time	3.9846
19 Acquisition Date	2023-11-30T19:07:32
20 Modification Date	2023-11-30T19:07:00
21 Class	
22 Spectrometer Frequency	400.13
23 Spectral Width	8223.7
24 Lowest Frequency	-1520.6
25 Nucleus	1H
26 Acquired Size	32768
27 Spectral Size	65536



Parameter	Value
1 Title	20231130-DRI p2-15 mg. 2.1.1r
2 Comment	20231130-DRI p2-15 mg 400M CDCl3
3 Origin	Bruker BioSpin GmbH
4 Owner	nmr
5 Site	
6 Instrument	spect
7 Author	
8 Solvent	CDCl3
9 Temperature	-18.3
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z108618/ 0355
13 Number of Scans	31
14 Receiver Gain	195.8
15 Relaxation Delay	2.0000
16 Pulse Width	10.5800
17 Presaturation Frequency	
18 Acquisition Time	1.2583
19 Acquisition Date	2023-11-30T19:09:22
20 Modification Date	2023-11-30T19:10:00
21 Class	
22 Spectrometer Frequency	100.61
23 Spectral Width	26041.7
24 Lowest Frequency	-2444.1
25 Nucleus	13C
26 Acquired Size	32768
27 Spectral Size	32768

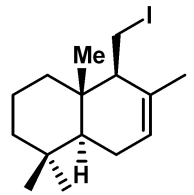
78.9 77.5 77.2 76.8 60.7 60.6 59.4 55.1 49.2 39.0 38.7 36.1 28.2 27.0 22.9 21.7 16.0 15.3



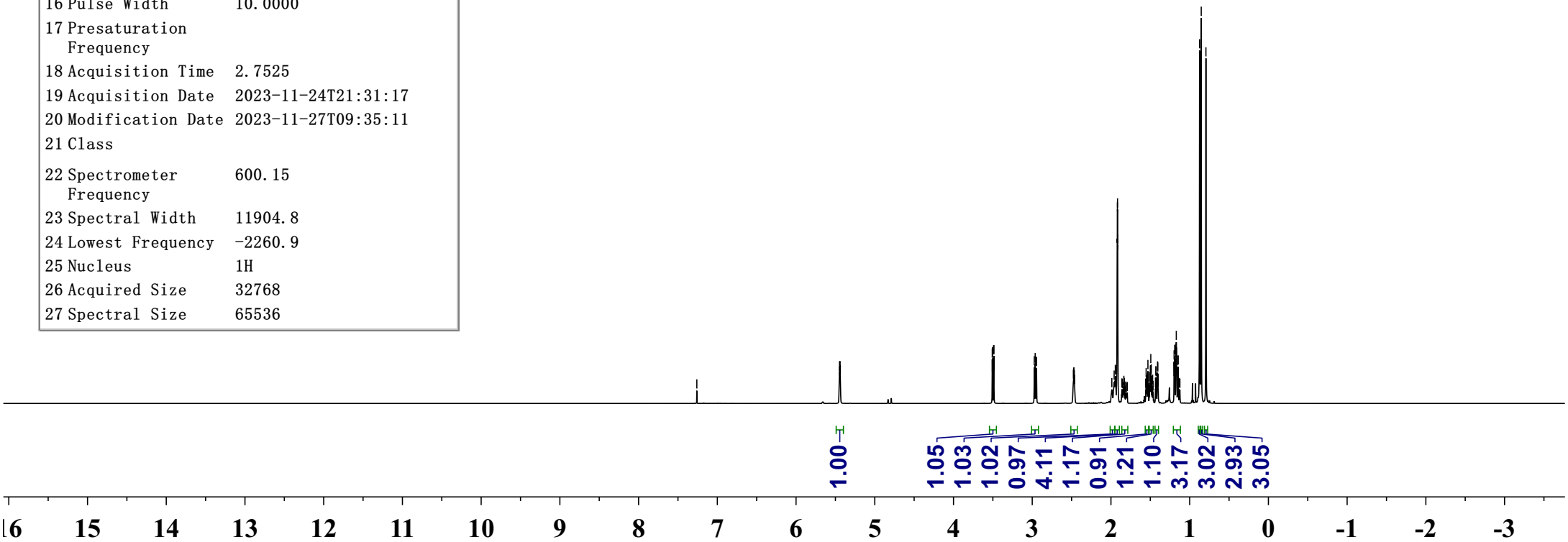
13

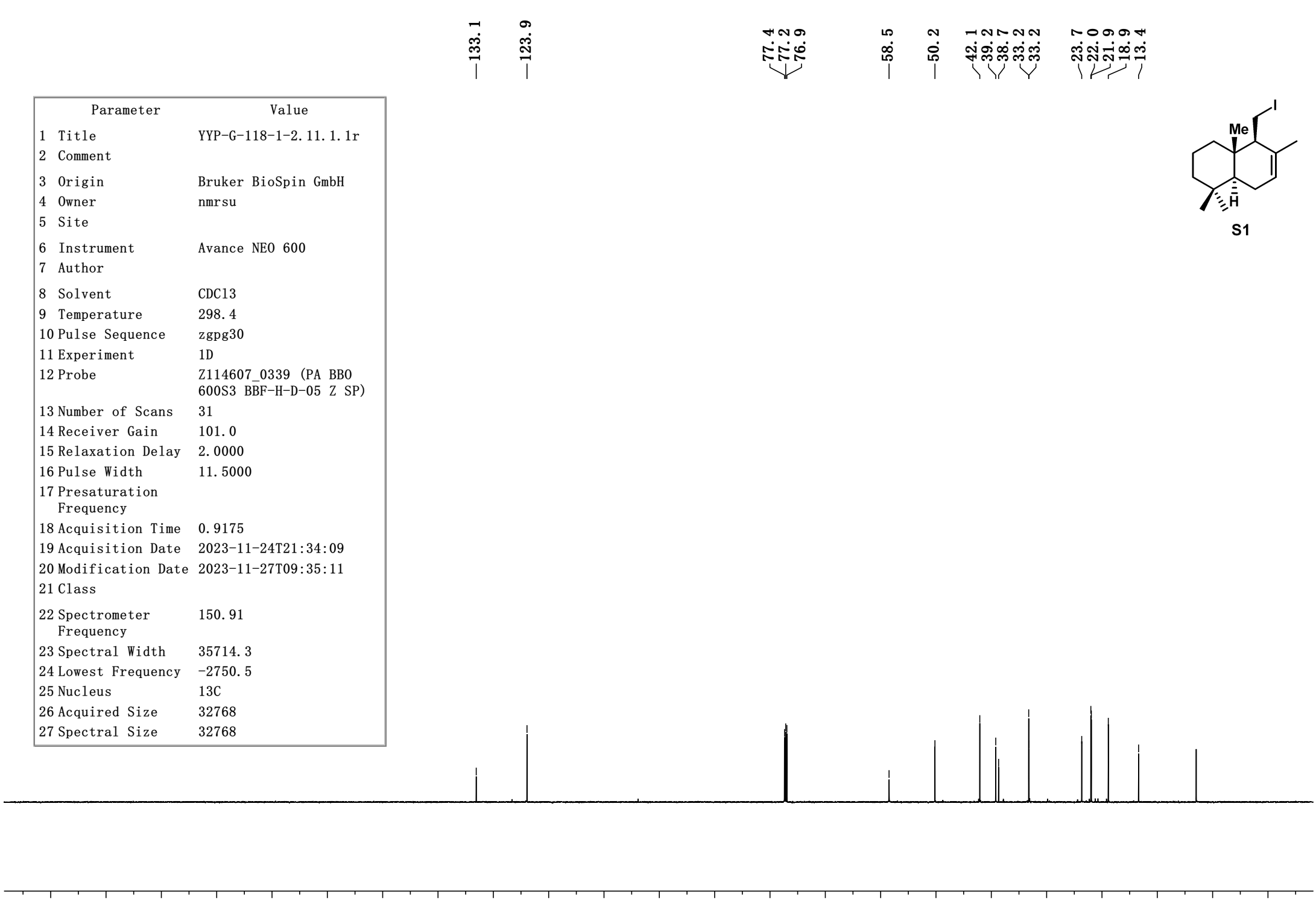
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20

	Parameter	Value
1	Title	YYP-G-118-1-2.10.1.1r
2	Comment	
3	Origin	Bruker BioSpin GmbH
4	Owner	nmrsu
5	Site	
6	Instrument	Avance NEO 600
7	Author	
8	Solvent	CDCl3
9	Temperature	298.1
10	Pulse Sequence	zg30
11	Experiment	1D
12	Probe	Z114607_0339 (PA BBO 600S3 BBF-H-D-05 Z SP)
13	Number of Scans	6
14	Receiver Gain	22.6
15	Relaxation Delay	1.0000
16	Pulse Width	10.0000
17	Presaturation Frequency	
18	Acquisition Time	2.7525
19	Acquisition Date	2023-11-24T21:31:17
20	Modification Date	2023-11-27T09:35:11
21	Class	
22	Spectrometer Frequency	600.15
23	Spectral Width	11904.8
24	Lowest Frequency	-2260.9
25	Nucleus	1H
26	Acquired Size	32768
27	Spectral Size	65536



S1

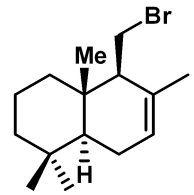




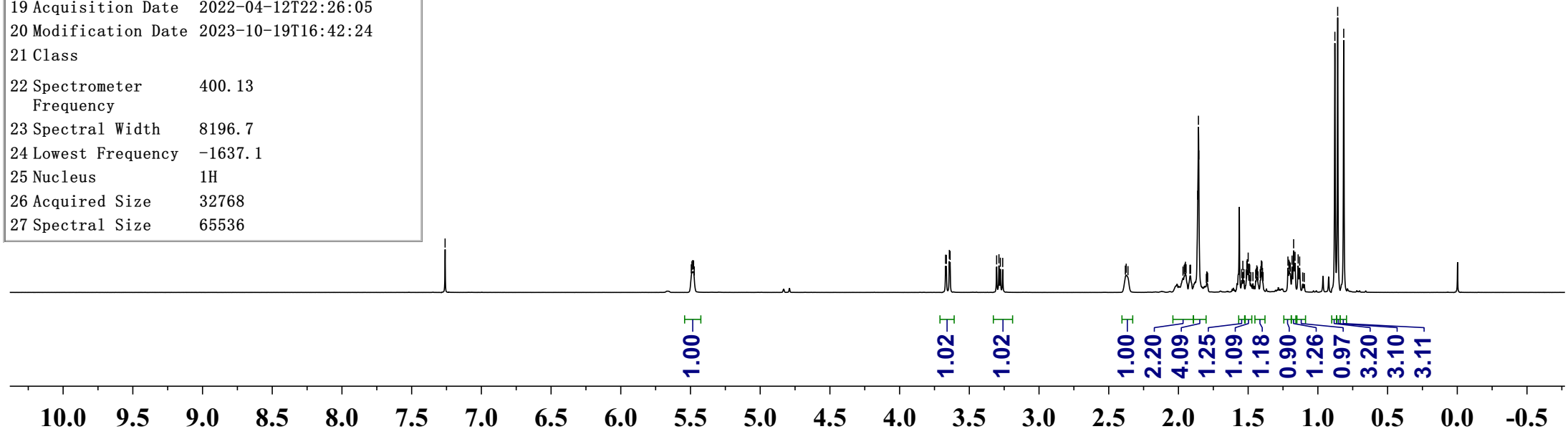
Parameter	Value
1 Title	YYP-G-118-1-2.11.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	Avance NEO 600
7 Author	
8 Solvent	CDCl3
9 Temperature	298.4
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Probe	Z114607_0339 (PA BBO 600S3 BBF-H-D-05 Z SP)
13 Number of Scans	31
14 Receiver Gain	101.0
15 Relaxation Delay	2.0000
16 Pulse Width	11.5000
17 Presaturation Frequency	
18 Acquisition Time	0.9175
19 Acquisition Date	2023-11-24T21:34:09
20 Modification Date	2023-11-27T09:35:11
21 Class	
22 Spectrometer Frequency	150.91
23 Spectral Width	35714.3
24 Lowest Frequency	-2750.5
25 Nucleus	13C
26 Acquired Size	32768
27 Spectral Size	32768

7.26 5.49 5.49 5.48 5.48 5.47 3.67 3.66 3.64 3.64 3.30 3.29 3.28 3.26 2.38 2.37 2.36 1.97 1.96 1.95 1.95 1.92 1.91 1.86 1.86 1.85 1.80 1.80 1.79 1.79 1.55 1.54 1.53 1.51 1.51 1.51 1.50 1.49 1.49 1.48 1.47 1.45 1.44 1.44 1.43 1.43 1.41 1.41 1.41 1.40 1.40 1.39 1.21 1.21 1.20 1.20 1.19 1.17 1.16 1.14 1.13 1.11 1.10 0.88 0.86 0.81

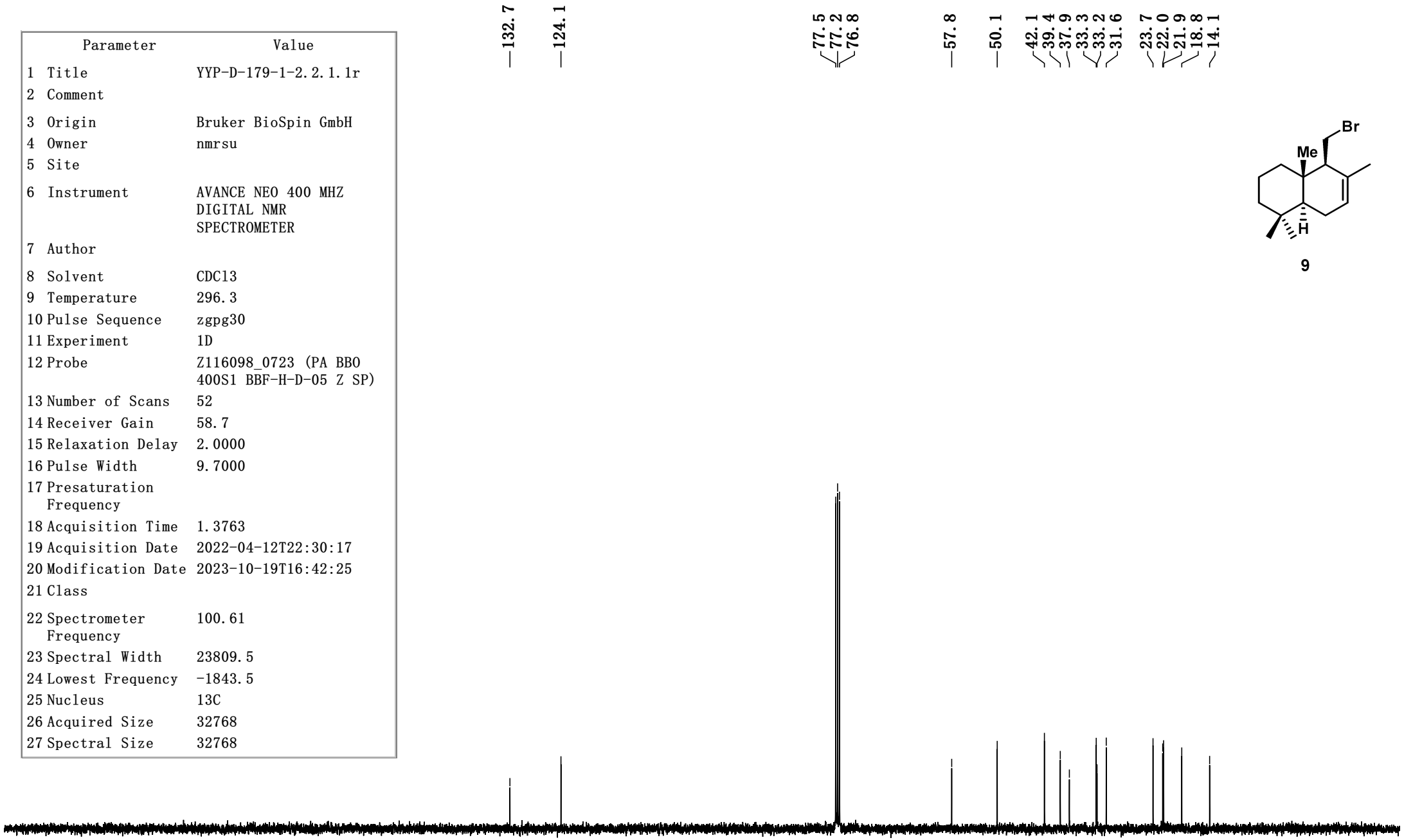
	Parameter	Value
1	Title	YYP-D-179-1-2.1.1.1r
2	Comment	
3	Origin	Bruker BioSpin GmbH
4	Owner	nmrsu
5	Site	
6	Instrument	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7	Author	
8	Solvent	CDCl3
9	Temperature	295.9
10	Pulse Sequence	zg30
11	Experiment	1D
12	Probe	Z116098_0723 (PA BBO 400S1 BBF-H-D-05 Z SP)
13	Number of Scans	3
14	Receiver Gain	101.0
15	Relaxation Delay	1.0000
16	Pulse Width	8.5800
17	Presaturation Frequency	
18	Acquisition Time	3.9977
19	Acquisition Date	2022-04-12T22:26:05
20	Modification Date	2023-10-19T16:42:24
21	Class	
22	Spectrometer Frequency	400.13
23	Spectral Width	8196.7
24	Lowest Frequency	-1637.1
25	Nucleus	1H
26	Acquired Size	32768
27	Spectral Size	65536



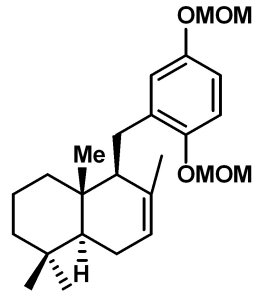
9



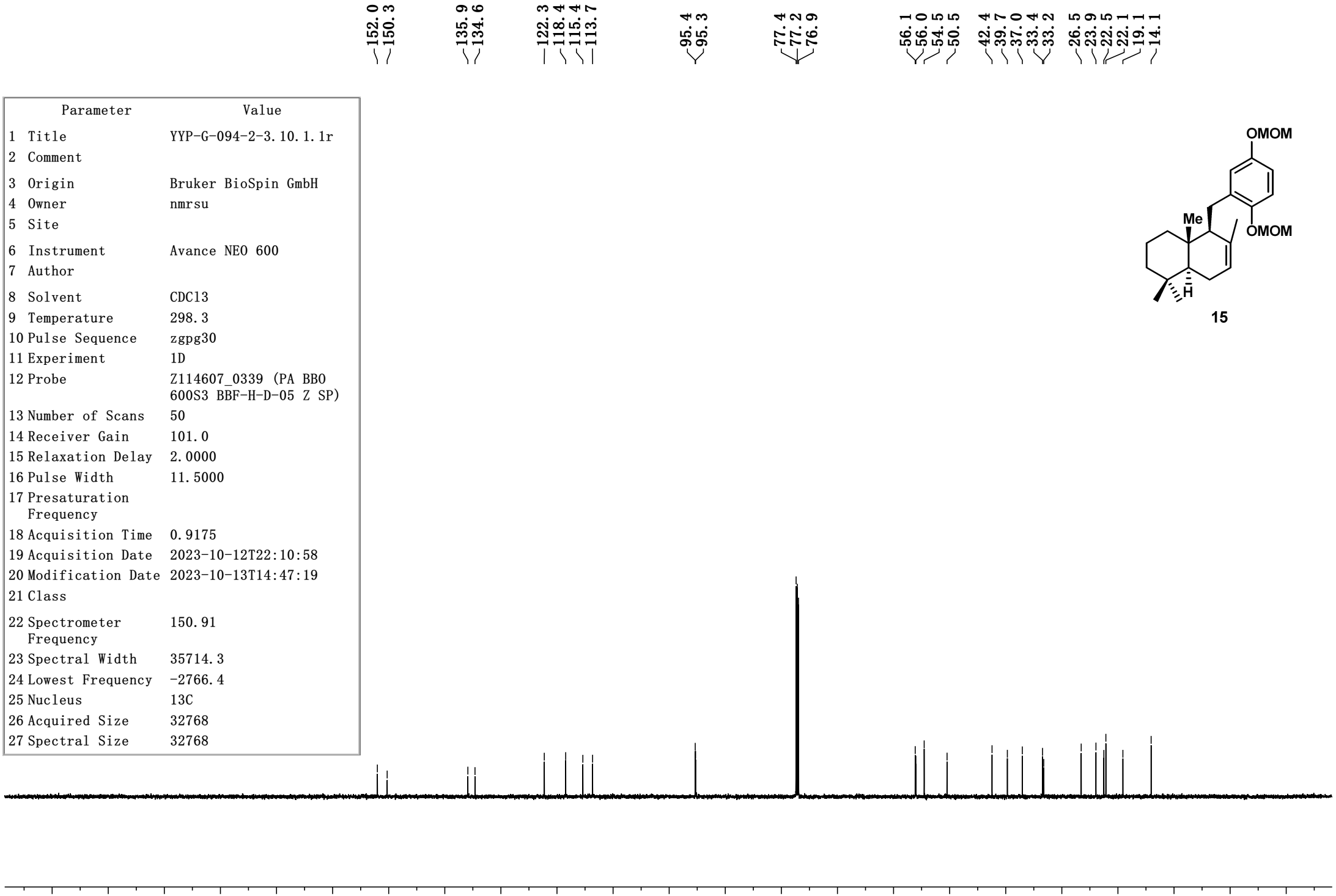
Parameter	Value
1 Title	YYP-D-179-1-2.2.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDCl3
9 Temperature	296.3
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Probe	Z116098_0723 (PA BBO 400S1 BBF-H-D-05 Z SP)
13 Number of Scans	52
14 Receiver Gain	58.7
15 Relaxation Delay	2.0000
16 Pulse Width	9.7000
17 Presaturation Frequency	
18 Acquisition Time	1.3763
19 Acquisition Date	2022-04-12T22:30:17
20 Modification Date	2023-10-19T16:42:25
21 Class	
22 Spectrometer Frequency	100.61
23 Spectral Width	23809.5
24 Lowest Frequency	-1843.5
25 Nucleus	13C
26 Acquired Size	32768
27 Spectral Size	32768



Parameter	Value
1 Title	YYP-G-094-2-3.3.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDCl3
9 Temperature	298.1
10 Pulse Sequence	zg30
11 Experiment	1D
12 Probe	Z116098_0723 (PA BBO 400S1 BBF-H-D-05 Z SP)
13 Number of Scans	7
14 Receiver Gain	101.0
15 Relaxation Delay	1.0000
16 Pulse Width	8.8100
17 Presaturation Frequency	
18 Acquisition Time	3.9977
19 Acquisition Date	2023-10-12T21:58:16
20 Modification Date	2023-10-13T14:47:19
21 Class	
22 Spectrometer Frequency	400.13
23 Spectral Width	8196.7
24 Lowest Frequency	-1637.2
25 Nucleus	1H
26 Acquired Size	32768
27 Spectral Size	65536

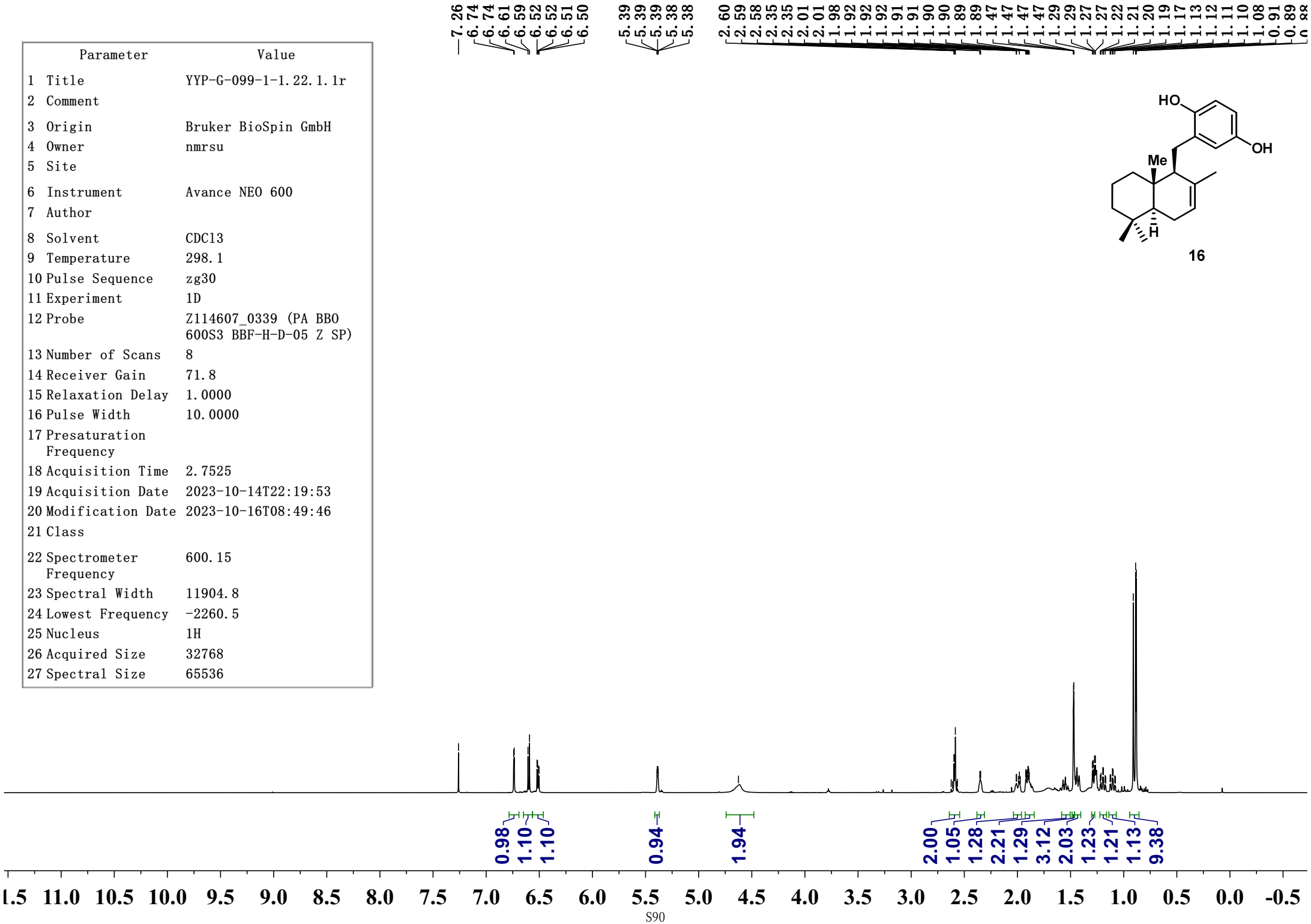


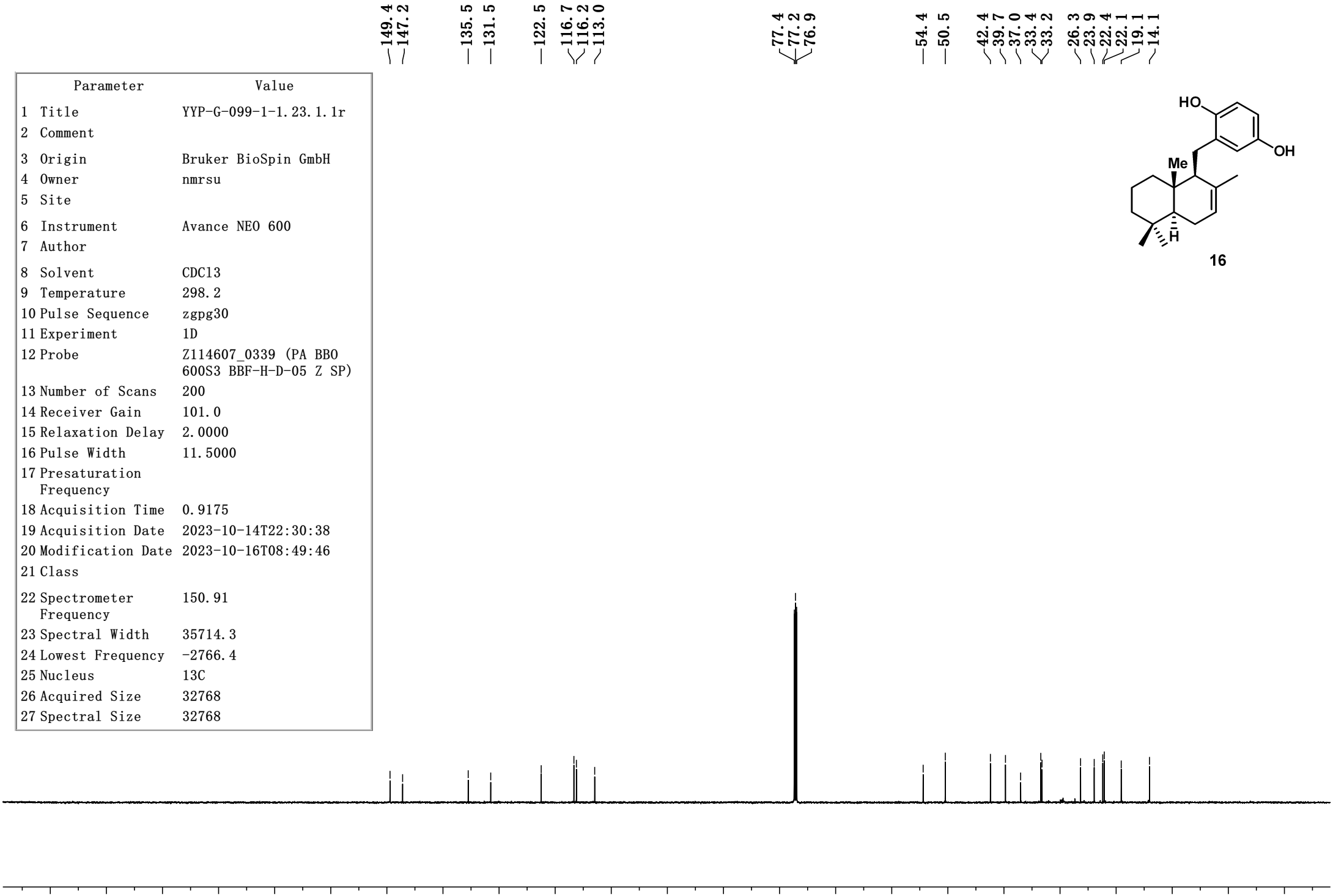
15



Parameter	Value
1 Title	YYP-G-094-2-3.10.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	Avance NEO 600
7 Author	
8 Solvent	CDCl3
9 Temperature	298.3
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Probe	Z114607_0339 (PA BBO 600S3 BBF-H-D-05 Z SP)
13 Number of Scans	50
14 Receiver Gain	101.0
15 Relaxation Delay	2.0000
16 Pulse Width	11.5000
17 Presaturation Frequency	
18 Acquisition Time	0.9175
19 Acquisition Date	2023-10-12T22:10:58
20 Modification Date	2023-10-13T14:47:19
21 Class	
22 Spectrometer Frequency	150.91
23 Spectral Width	35714.3
24 Lowest Frequency	-2766.4
25 Nucleus	13C
26 Acquired Size	32768
27 Spectral Size	32768

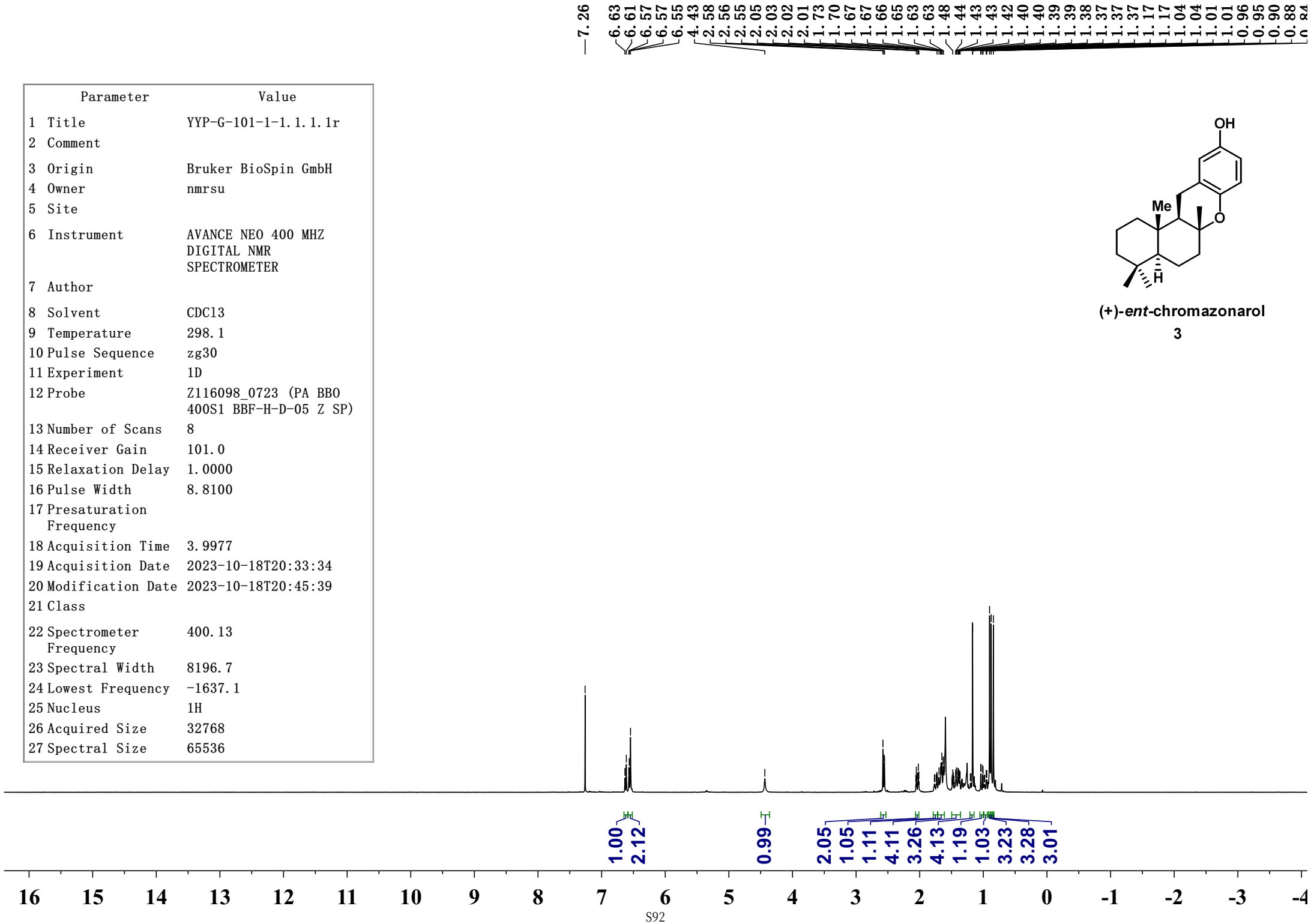
Parameter	Value
1 Title	YYP-G-099-1-1.22.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	Avance NEO 600
7 Author	
8 Solvent	CDCl3
9 Temperature	298.1
10 Pulse Sequence	zg30
11 Experiment	1D
12 Probe	Z114607_0339 (PA BBO 600S3 BBF-H-D-05 Z SP)
13 Number of Scans	8
14 Receiver Gain	71.8
15 Relaxation Delay	1.0000
16 Pulse Width	10.0000
17 Presaturation Frequency	
18 Acquisition Time	2.7525
19 Acquisition Date	2023-10-14T22:19:53
20 Modification Date	2023-10-16T08:49:46
21 Class	
22 Spectrometer Frequency	600.15
23 Spectral Width	11904.8
24 Lowest Frequency	-2260.5
25 Nucleus	1H
26 Acquired Size	32768
27 Spectral Size	65536





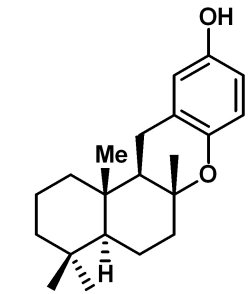
Parameter	Value
1 Title	YYP-G-099-1-1.23.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	Avance NEO 600
7 Author	
8 Solvent	CDCl3
9 Temperature	298.2
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Probe	Z114607_0339 (PA BBO 600S3 BBF-H-D-05 Z SP)
13 Number of Scans	200
14 Receiver Gain	101.0
15 Relaxation Delay	2.0000
16 Pulse Width	11.5000
17 Presaturation Frequency	
18 Acquisition Time	0.9175
19 Acquisition Date	2023-10-14T22:30:38
20 Modification Date	2023-10-16T08:49:46
21 Class	
22 Spectrometer Frequency	150.91
23 Spectral Width	35714.3
24 Lowest Frequency	-2766.4
25 Nucleus	13C
26 Acquired Size	32768
27 Spectral Size	32768

Parameter	Value
1 Title	YYP-G-101-1-1.1.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDCl3
9 Temperature	298.1
10 Pulse Sequence	zg30
11 Experiment	1D
12 Probe	Z116098_0723 (PA BBO 400S1 BBF-H-D-05 Z SP)
13 Number of Scans	8
14 Receiver Gain	101.0
15 Relaxation Delay	1.0000
16 Pulse Width	8.8100
17 Presaturation Frequency	
18 Acquisition Time	3.9977
19 Acquisition Date	2023-10-18T20:33:34
20 Modification Date	2023-10-18T20:45:39
21 Class	
22 Spectrometer Frequency	400.13
23 Spectral Width	8196.7
24 Lowest Frequency	-1637.1
25 Nucleus	1H
26 Acquired Size	32768
27 Spectral Size	65536



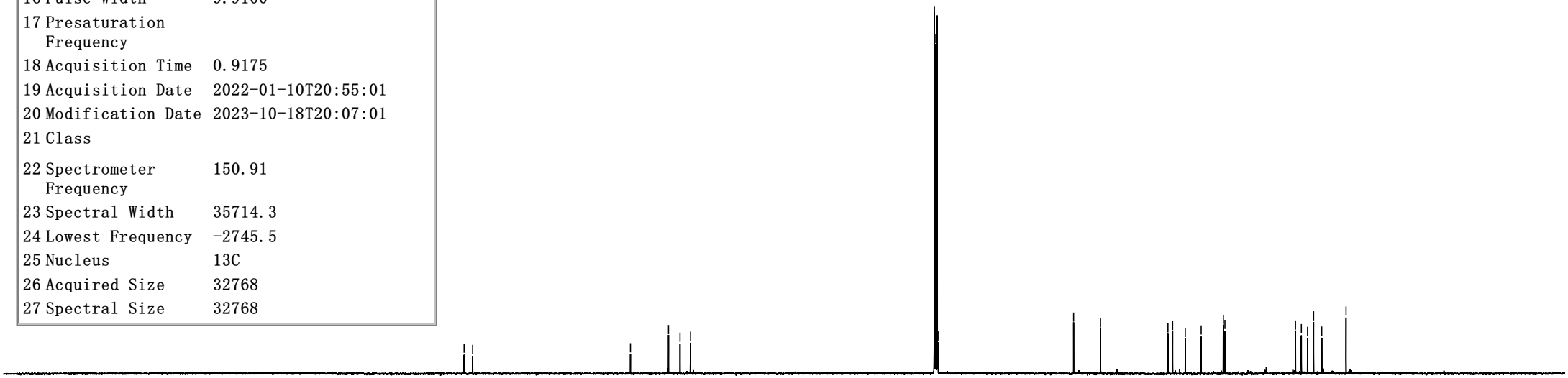
148.6
147.4
123.4
117.7
115.9
114.4
77.4
77.2
76.9
76.8
56.3
52.2
42.0
41.3
39.4
36.9
33.6
33.3
22.6
21.8
20.8
19.9
18.7
15.0

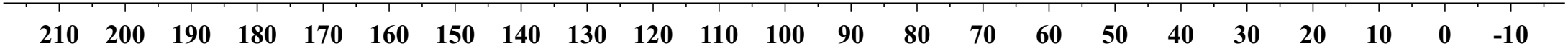
Parameter	Value
1 Title	YYP-D-112-1-1.11.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	Avance NEO 600
7 Author	
8 Solvent	CDCl3
9 Temperature	298.1
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Probe	Z168773_0027 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
13 Number of Scans	102
14 Receiver Gain	101.0
15 Relaxation Delay	2.0000
16 Pulse Width	9.9100
17 Presaturation Frequency	
18 Acquisition Time	0.9175
19 Acquisition Date	2022-01-10T20:55:01
20 Modification Date	2023-10-18T20:07:01
21 Class	
22 Spectrometer Frequency	150.91
23 Spectral Width	35714.3
24 Lowest Frequency	-2745.5
25 Nucleus	13C
26 Acquired Size	32768
27 Spectral Size	32768

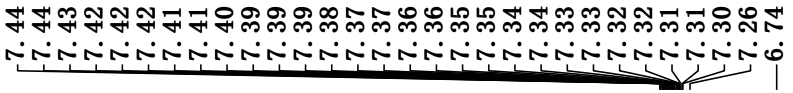


(+)-*ent*-chromazonarol

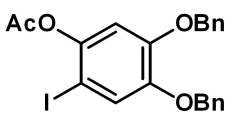
3



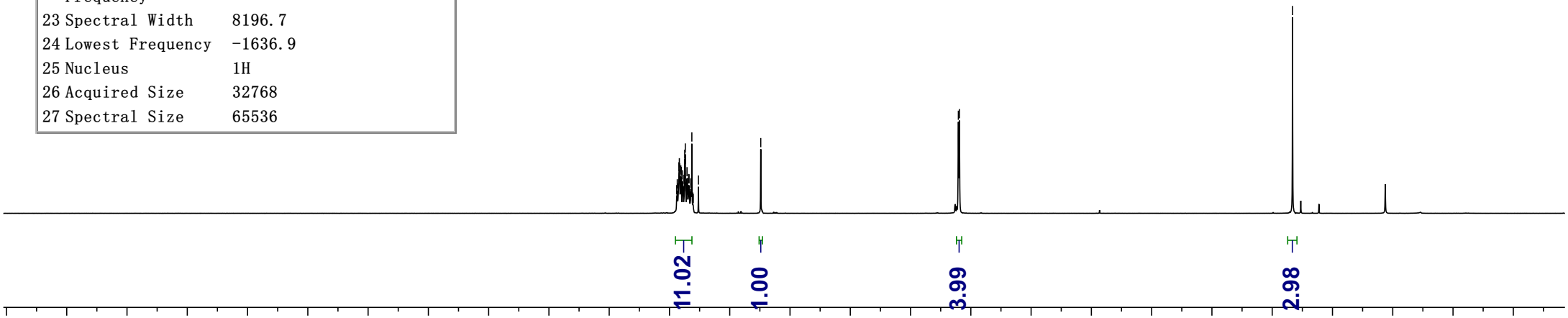


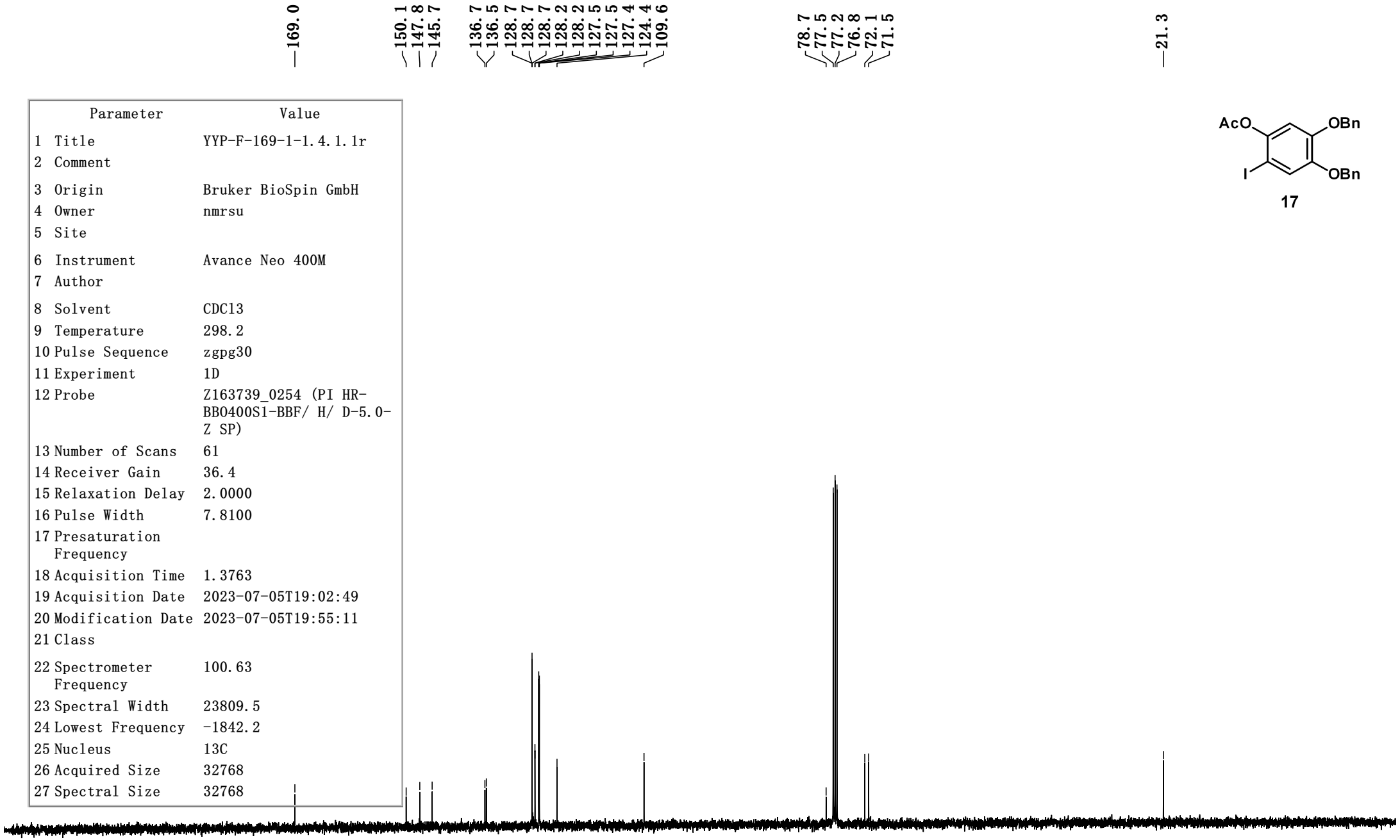


Parameter	Value
1 Title	YYP-F-169-1-1.3.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	Avance Neo 400M
7 Author	
8 Solvent	CDCl3
9 Temperature	298.1
10 Pulse Sequence	zg30
11 Experiment	1D
12 Probe	Z163739_0254 (PI HR-BBO400S1-BBF/ H/ D-5.0-Z SP)
13 Number of Scans	4
14 Receiver Gain	101.0
15 Relaxation Delay	1.0000
16 Pulse Width	8.0000
17 Presaturation Frequency	
18 Acquisition Time	3.9977
19 Acquisition Date	2023-07-05T18:57:34
20 Modification Date	2023-07-05T19:55:11
21 Class	
22 Spectrometer Frequency	400.18
23 Spectral Width	8196.7
24 Lowest Frequency	-1636.9
25 Nucleus	1H
26 Acquired Size	32768
27 Spectral Size	65536



17

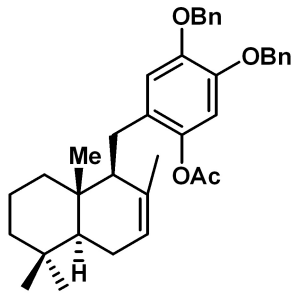




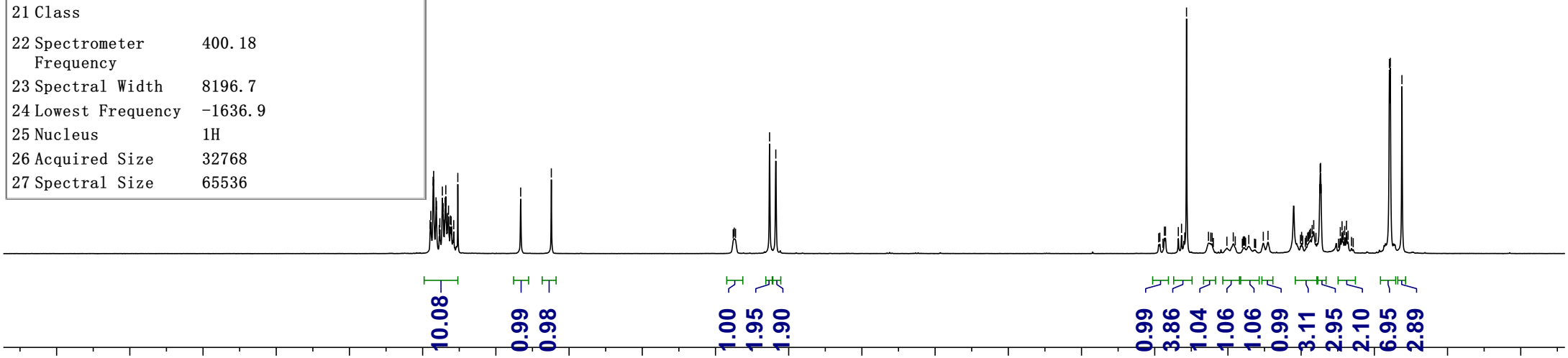
Parameter	Value
1 Title	YYP-F-169-1-1.4.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	Avance Neo 400M
7 Author	
8 Solvent	CDCl3
9 Temperature	298.2
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Probe	Z163739_0254 (PI HR-BBO400S1-BBF/ H/ D-5.0-Z SP)
13 Number of Scans	61
14 Receiver Gain	36.4
15 Relaxation Delay	2.0000
16 Pulse Width	7.8100
17 Presaturation Frequency	
18 Acquisition Time	1.3763
19 Acquisition Date	2023-07-05T19:02:49
20 Modification Date	2023-07-05T19:55:11
21 Class	
22 Spectrometer Frequency	100.63
23 Spectral Width	23809.5
24 Lowest Frequency	-1842.2
25 Nucleus	13C
26 Acquired Size	32768
27 Spectral Size	32768

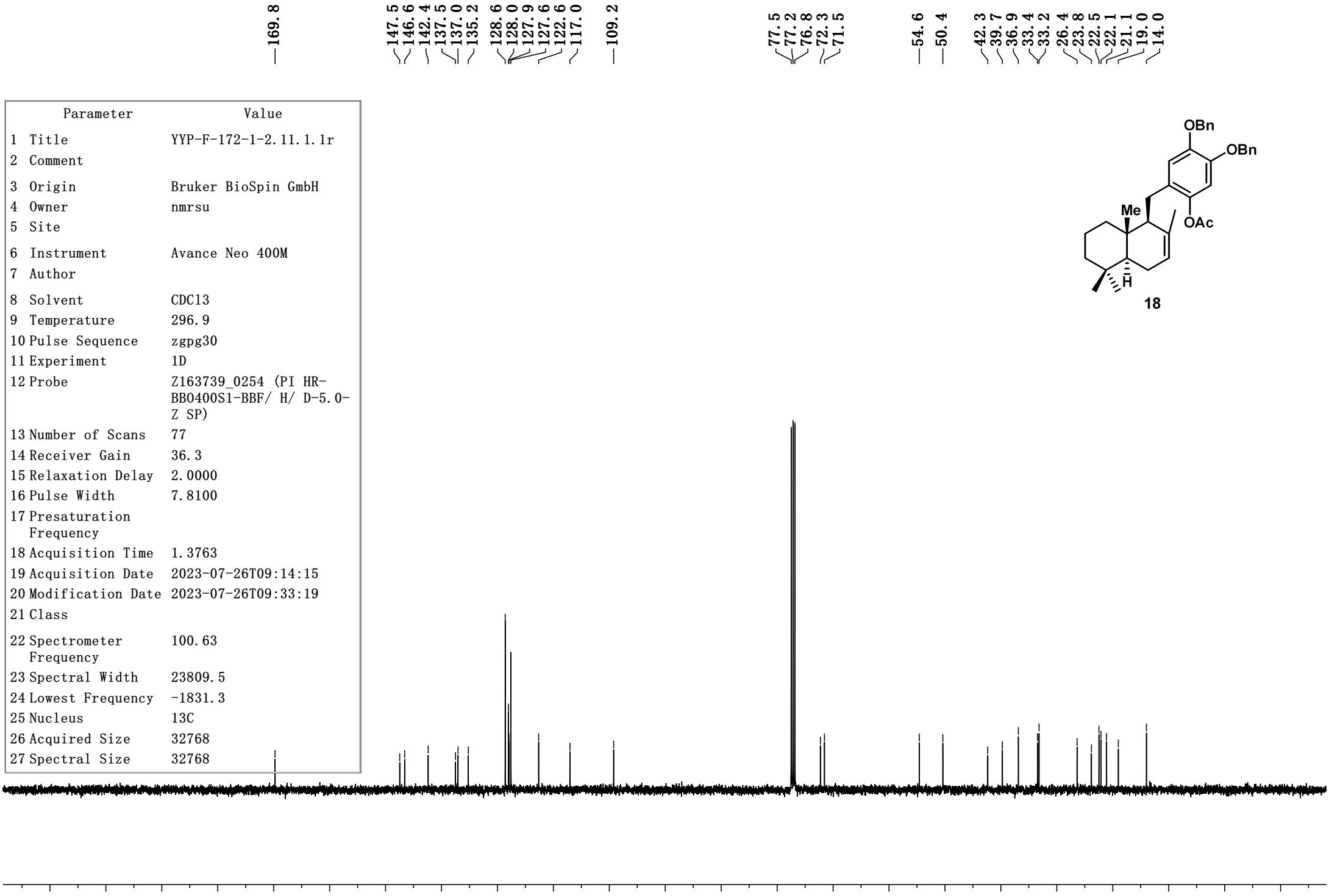
7.45 7.44 7.43 7.42 7.41 7.41 7.39 7.38 7.37 7.36 7.35 7.35 7.35 7.34 7.34 7.33 7.33 7.32 7.32 7.31 7.31 7.30 7.29 7.26 6.83 6.62 5.38 5.37 5.36 5.13 5.09 2.47 2.47 2.43 2.43 2.34 2.32 2.29 2.28 2.13 2.12 2.11 2.10 2.01 1.96 1.95 1.90 1.90 1.89 1.89 1.88 1.86 1.76 1.73 1.50 1.50 1.49 1.47 1.46 1.46 1.45 1.44 1.44 1.42 1.41 1.40 1.37 1.37 1.36 1.24 1.23 1.22 1.21 1.20 1.19 1.18 1.16 1.14 0.90 0.89 0.81

Parameter	Value
1 Title	YYP-F-172-1-2.3.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	Avance Neo 400M
7 Author	
8 Solvent	CDCl3
9 Temperature	298.2
10 Pulse Sequence	zg30
11 Experiment	1D
12 Probe	Z163739_0254 (PI HR-BBO400S1-BBF/ H/ D-5.0-Z SP)
13 Number of Scans	9
14 Receiver Gain	101.0
15 Relaxation Delay	1.0000
16 Pulse Width	8.0000
17 Presaturation Frequency	
18 Acquisition Time	3.9977
19 Acquisition Date	2023-07-06T15:58:03
20 Modification Date	2023-07-06T16:04:00
21 Class	
22 Spectrometer Frequency	400.18
23 Spectral Width	8196.7
24 Lowest Frequency	-1636.9
25 Nucleus	1H
26 Acquired Size	32768
27 Spectral Size	65536



18

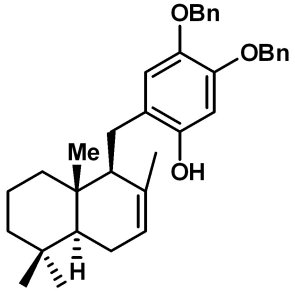




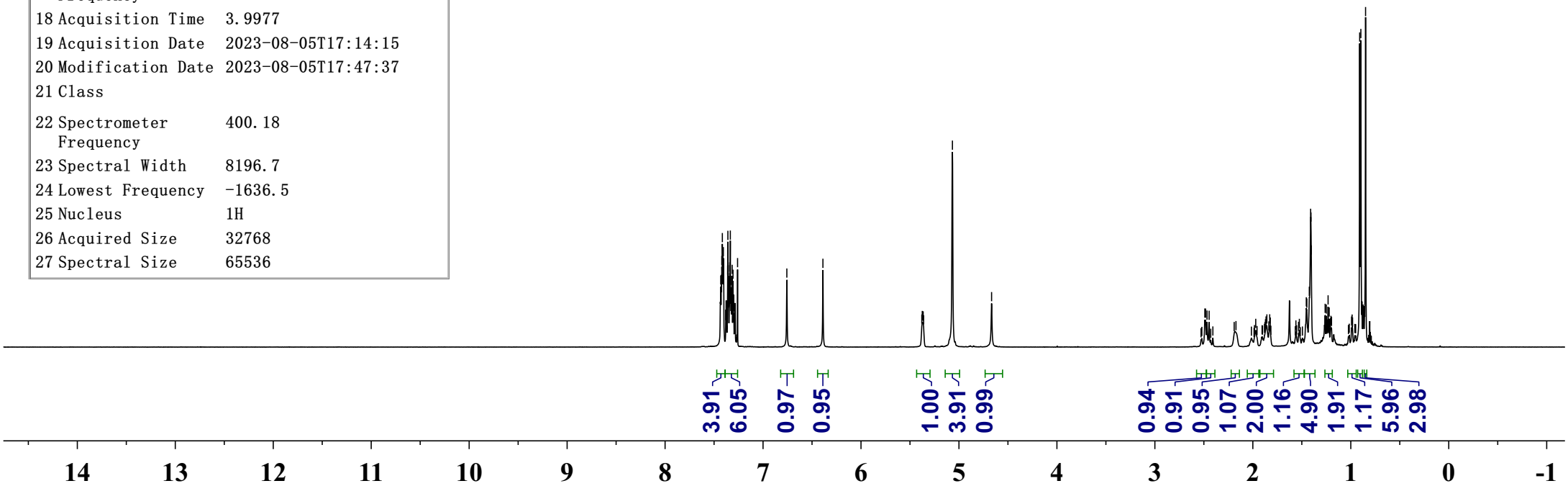
Parameter	Value
1 Title	YYP-F-172-1-2.11.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	Avance Neo 400M
7 Author	
8 Solvent	CDCl3
9 Temperature	296.9
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Probe	Z163739_0254 (PI HR-BBO400S1-BBF/ H/ D-5.0-Z SP)
13 Number of Scans	77
14 Receiver Gain	36.3
15 Relaxation Delay	2.0000
16 Pulse Width	7.8100
17 Presaturation Frequency	
18 Acquisition Time	1.3763
19 Acquisition Date	2023-07-26T09:14:15
20 Modification Date	2023-07-26T09:33:19
21 Class	
22 Spectrometer Frequency	100.63
23 Spectral Width	23809.5
24 Lowest Frequency	-1831.3
25 Nucleus	13C
26 Acquired Size	32768
27 Spectral Size	32768

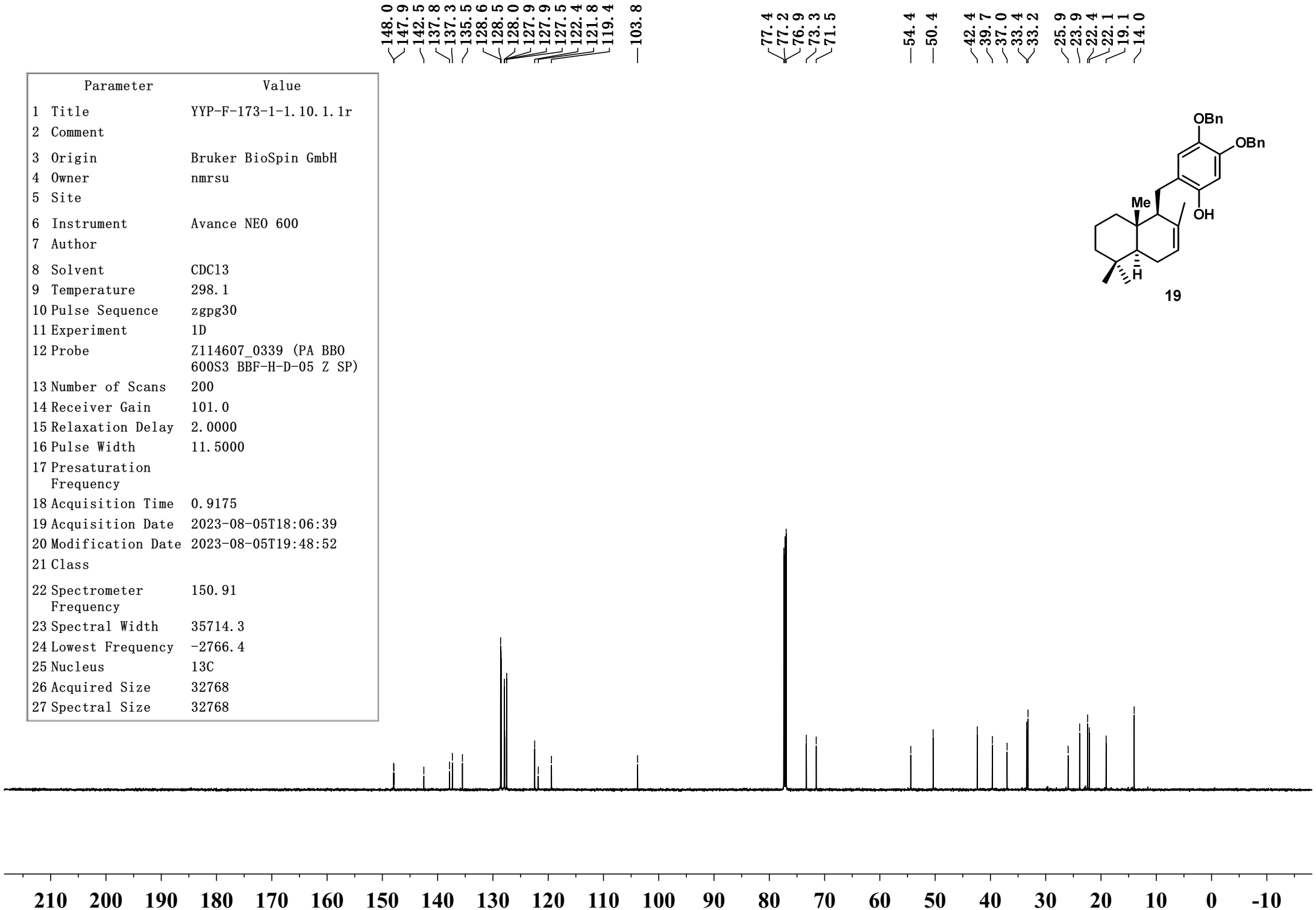
7.43 7.43 7.42 7.42 7.41 7.41 7.40 7.40 7.36 7.36 7.35 7.34 7.33 7.33 7.32 7.31 7.26 6.76 6.39 5.38 5.37 5.37 5.36 5.07 4.67 2.53 2.52 2.49 2.48 2.47 2.45 2.43 2.41 2.19 2.17 2.01 1.99 1.98 1.97 1.96 1.91 1.90 1.88 1.88 1.87 1.87 1.86 1.84 1.83 1.82 1.82 1.57 1.56 1.55 1.53 1.53 1.52 1.49 1.45 1.45 1.42 1.41 1.41 1.40 1.26 1.25 1.24 1.23 1.22 1.21 1.20 1.20 1.02 1.02 0.99 0.99 0.98 0.96 0.95 0.91 0.90 0.85

Parameter	Value
1 Title	YYP-F-173-1-1.3.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	Avance Neo 400M
7 Author	
8 Solvent	CDCl3
9 Temperature	297.1
10 Pulse Sequence	zg30
11 Experiment	1D
12 Probe	Z163739_0254 (PI HR-BBO400S1-BBF/ H/ D-5.0-Z SP)
13 Number of Scans	4
14 Receiver Gain	93.9
15 Relaxation Delay	1.0000
16 Pulse Width	8.0000
17 Presaturation Frequency	
18 Acquisition Time	3.9977
19 Acquisition Date	2023-08-05T17:14:15
20 Modification Date	2023-08-05T17:47:37
21 Class	
22 Spectrometer Frequency	400.18
23 Spectral Width	8196.7
24 Lowest Frequency	-1636.5
25 Nucleus	1H
26 Acquired Size	32768
27 Spectral Size	65536



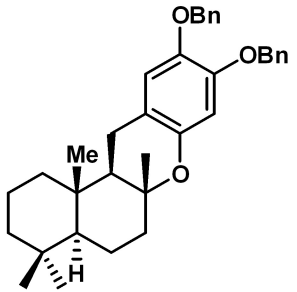
19



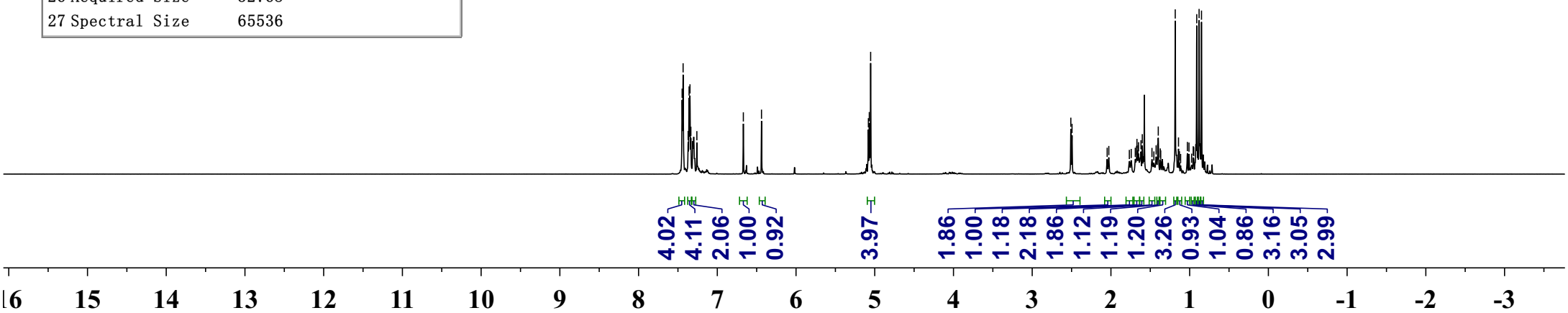


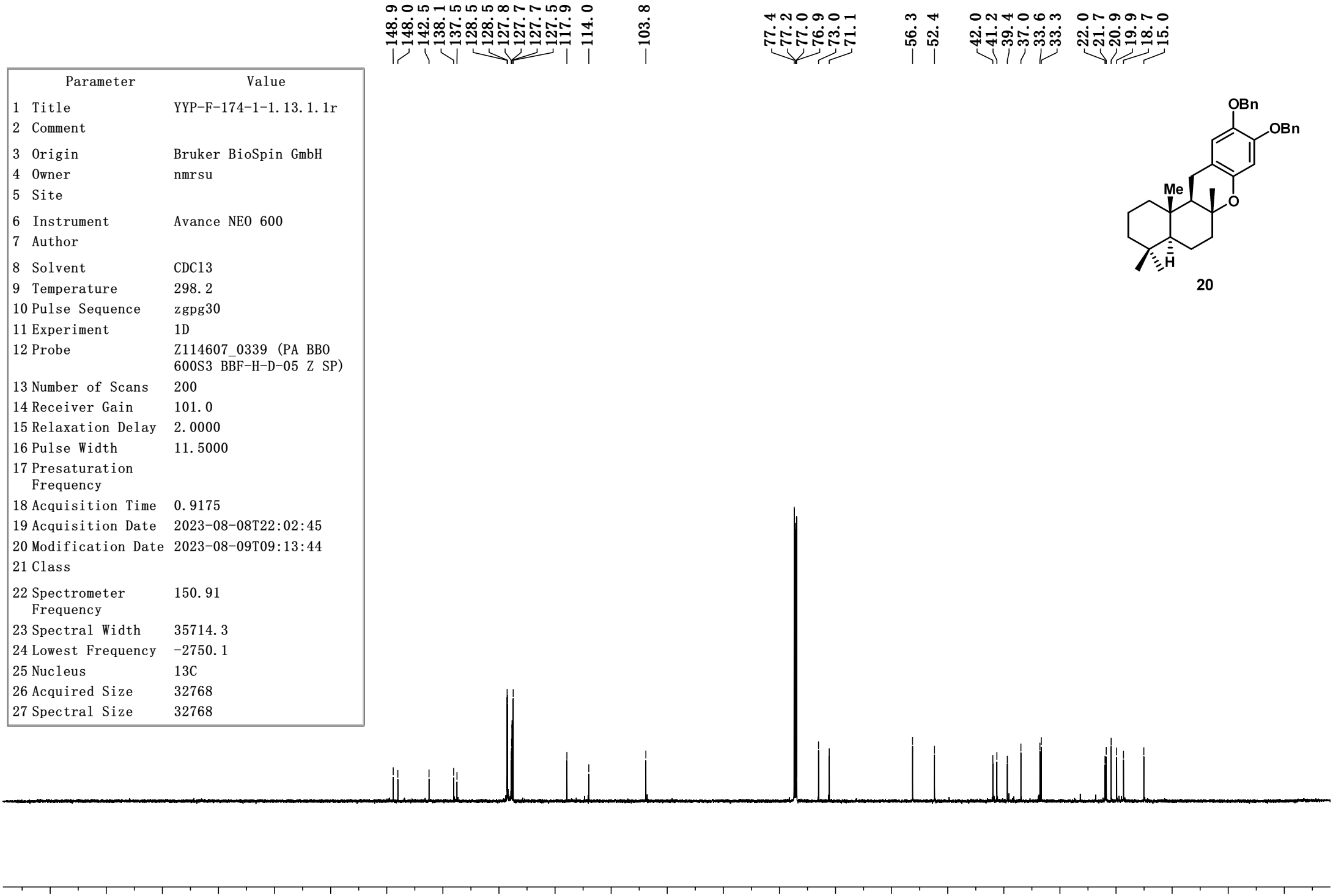
Parameter	Value
1 Title	YYP-F-173-1-1.10.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	Avance NEO 600
7 Author	
8 Solvent	CDCl3
9 Temperature	298.1
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Probe	Z114607_0339 (PA BBO 600S3 BBF-H-D-05 Z SP)
13 Number of Scans	200
14 Receiver Gain	101.0
15 Relaxation Delay	2.0000
16 Pulse Width	11.5000
17 Presaturation Frequency	
18 Acquisition Time	0.9175
19 Acquisition Date	2023-08-05T18:06:39
20 Modification Date	2023-08-05T19:48:52
21 Class	
22 Spectrometer Frequency	150.91
23 Spectral Width	35714.3
24 Lowest Frequency	-2766.4
25 Nucleus	13C
26 Acquired Size	32768
27 Spectral Size	32768

	Parameter	Value
1	Title	YYP-F-174-1-1.12.1.1r
2	Comment	
3	Origin	Bruker BioSpin GmbH
4	Owner	nmrsu
5	Site	
6	Instrument	Avance NEO 600
7	Author	
8	Solvent	CDCl3
9	Temperature	298.1
10	Pulse Sequence	zg30
11	Experiment	1D
12	Probe	Z114607_0339 (PA BBO 600S3 BBF-H-D-05 Z SP)
13	Number of Scans	5
14	Receiver Gain	64.0
15	Relaxation Delay	1.0000
16	Pulse Width	10.0000
17	Presaturation Frequency	
18	Acquisition Time	2.7525
19	Acquisition Date	2023-08-08T21:51:24
20	Modification Date	2023-08-09T09:13:43
21	Class	
22	Spectrometer Frequency	600.15
23	Spectral Width	11904.8
24	Lowest Frequency	-2261.0
25	Nucleus	1H
26	Acquired Size	32768
27	Spectral Size	65536



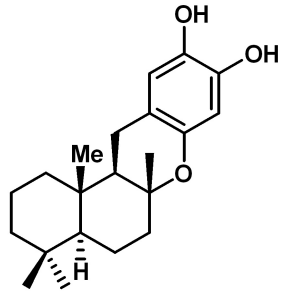
20





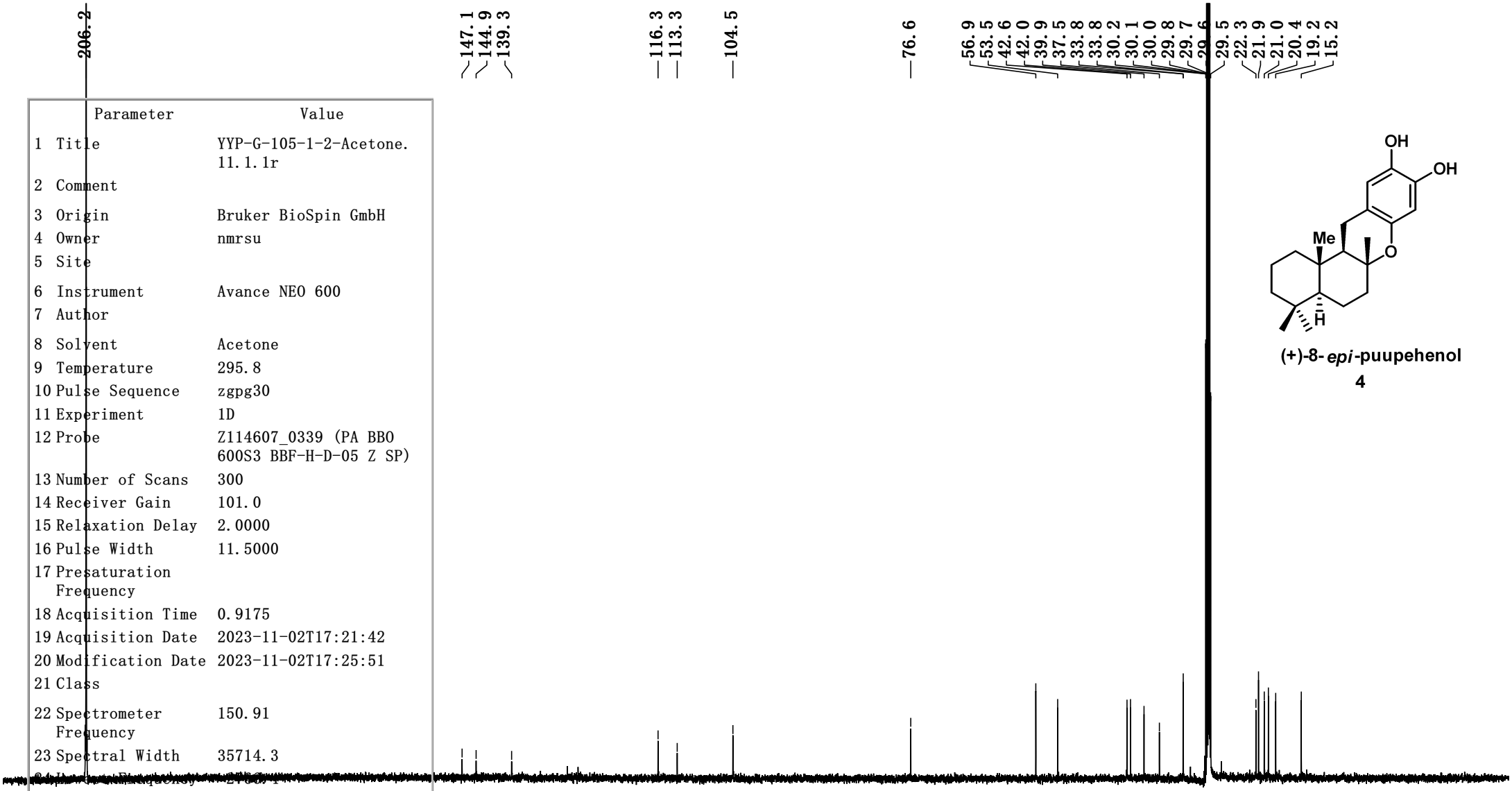
Parameter	Value
1 Title	YYP-F-174-1-1.13.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	Avance NEO 600
7 Author	
8 Solvent	CDCl3
9 Temperature	298.2
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Probe	Z114607_0339 (PA BBO 600S3 BBF-H-D-05 Z SP)
13 Number of Scans	200
14 Receiver Gain	101.0
15 Relaxation Delay	2.0000
16 Pulse Width	11.5000
17 Presaturation Frequency	
18 Acquisition Time	0.9175
19 Acquisition Date	2023-08-08T22:02:45
20 Modification Date	2023-08-09T09:13:44
21 Class	
22 Spectrometer Frequency	150.91
23 Spectral Width	35714.3
24 Lowest Frequency	-2750.1
25 Nucleus	13C
26 Acquired Size	32768
27 Spectral Size	32768

Parameter	Value
1 Title	YYP-G-105-1-2-Acetone. 10.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	Avance NEO 600
7 Author	
8 Solvent	Acetone
9 Temperature	294.2
10 Pulse Sequence	zg30
11 Experiment	1D
12 Probe	Z114607_0339 (PA BBO 600S3 BBF-H-D-05 Z SP)
13 Number of Scans	5
14 Receiver Gain	90.5
15 Relaxation Delay	1.0000
16 Pulse Width	10.0000
17 Presaturation Frequency	
18 Acquisition Time	2.7525
19 Acquisition Date	2023-11-02T16:32:12
20 Modification Date	2023-11-02T16:33:36
21 Class	
22 Spectrometer Frequency	600.15
23 Spectral Width	11904.8
24 Lowest Frequency	-2256.9
25 Nucleus	1H
26 Acquired Size	32768
27 Spectral Size	65536



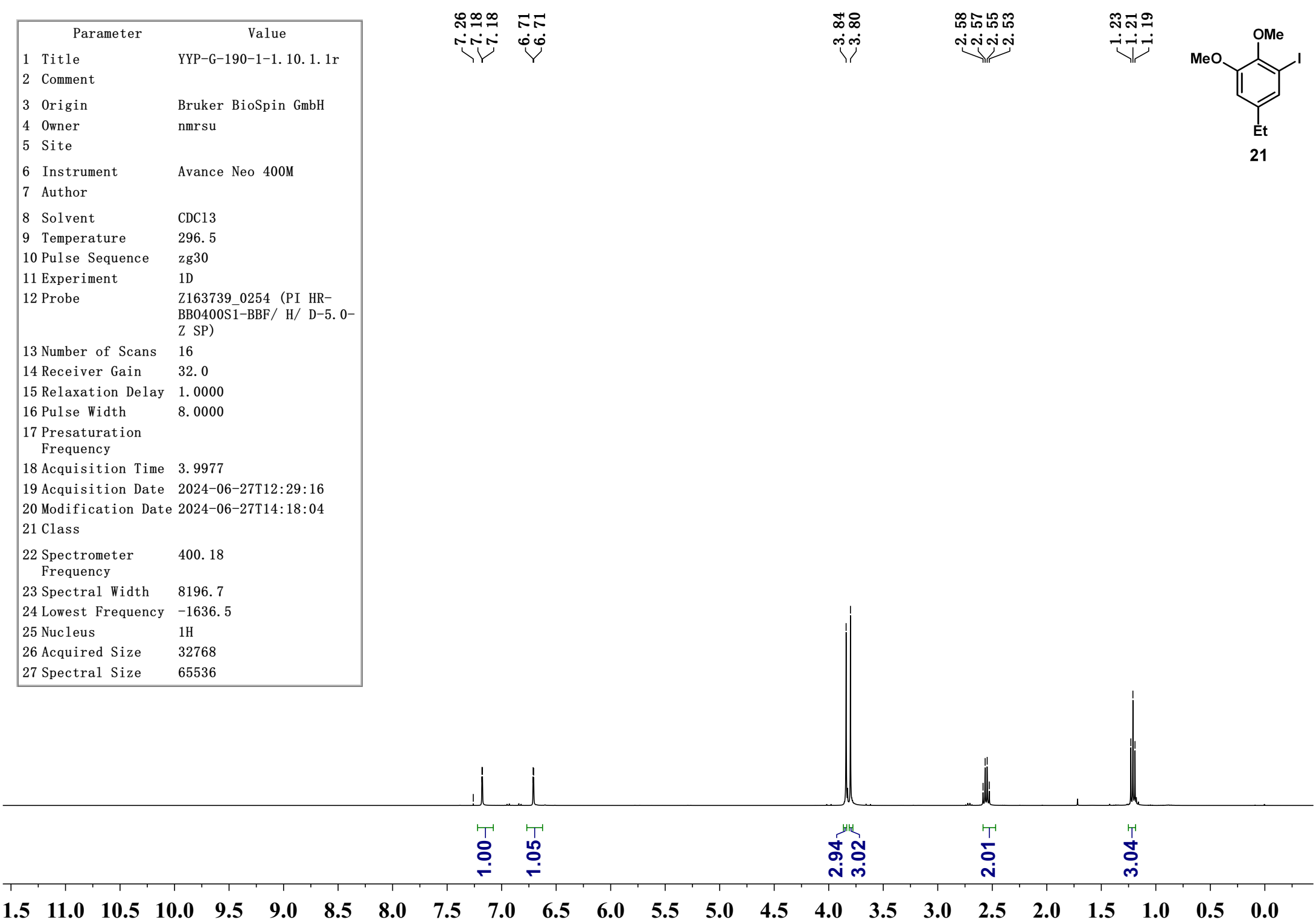
(+)-8-*epi*-puupehenol

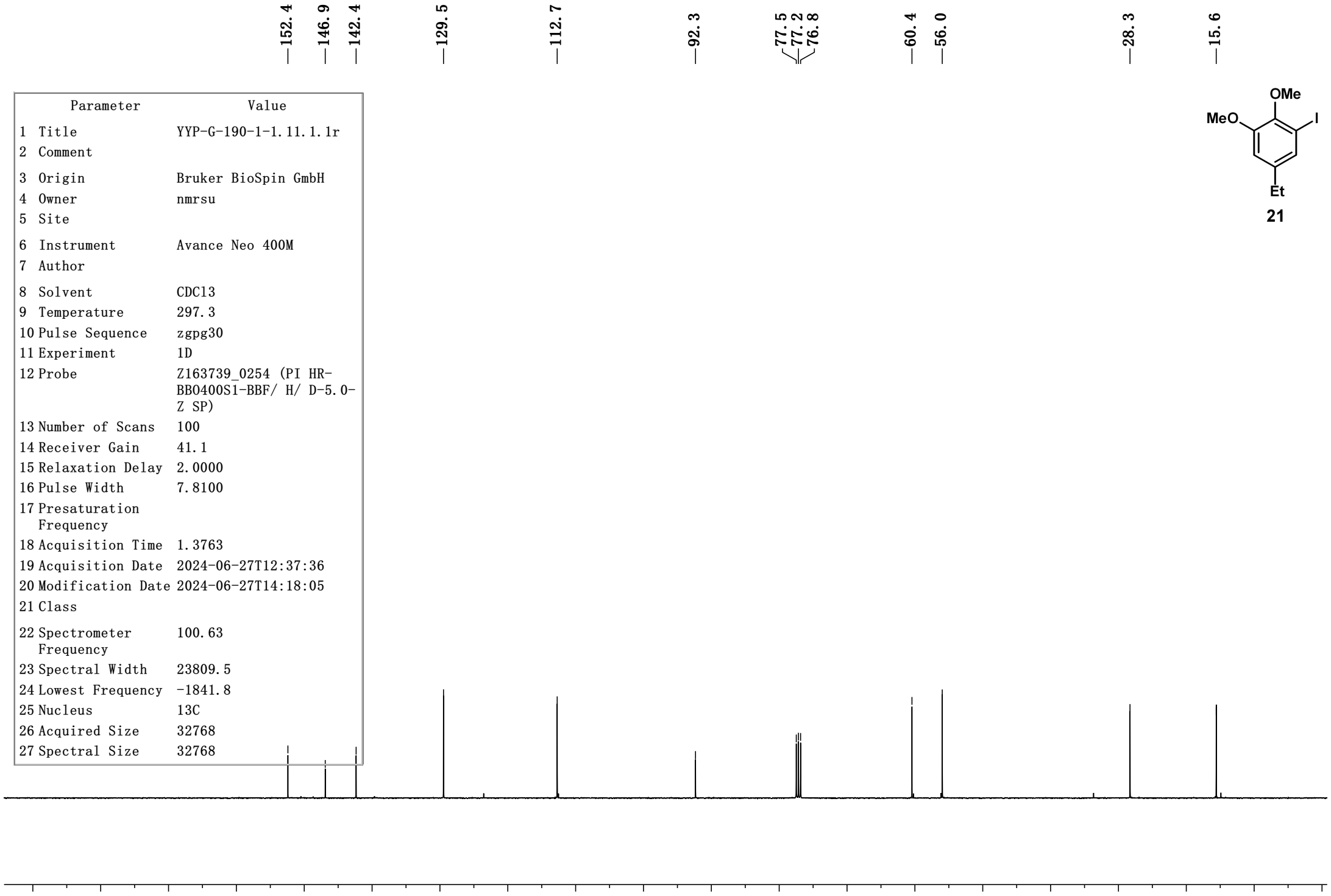
4



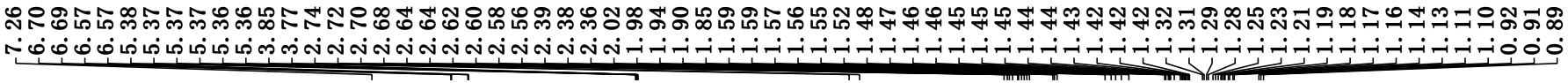
	Parameter	Value
1	Title	YYP-G-105-1-2-Acetone. 11.1.1r
2	Comment	
3	Origin	Bruker BioSpin GmbH
4	Owner	nmrsu
5	Site	
6	Instrument	Avance NEO 600
7	Author	
8	Solvent	Acetone
9	Temperature	295.8
10	Pulse Sequence	zgpg30
11	Experiment	1D
12	Probe	Z114607_0339 (PA BBO 600S3 BBF-H-D-05 Z SP)
13	Number of Scans	300
14	Receiver Gain	101.0
15	Relaxation Delay	2.0000
16	Pulse Width	11.5000
17	Presaturation Frequency	
18	Acquisition Time	0.9175
19	Acquisition Date	2023-11-02T17:21:42
20	Modification Date	2023-11-02T17:25:51
21	Class	
22	Spectrometer Frequency	150.91
23	Spectral Width	35714.3
24	[illegible]	[illegible]
25	Nucleus	13C
26	Acquired Size	32768
27	Spectral Size	32768

	Parameter	Value
1	Title	YYP-G-190-1-1.10.1.1r
2	Comment	
3	Origin	Bruker BioSpin GmbH
4	Owner	nmrsu
5	Site	
6	Instrument	Avance Neo 400M
7	Author	
8	Solvent	CDCl3
9	Temperature	296.5
10	Pulse Sequence	zg30
11	Experiment	1D
12	Probe	Z163739_0254 (PI HR-BBO400S1-BBF/ H/ D-5.0-Z SP)
13	Number of Scans	16
14	Receiver Gain	32.0
15	Relaxation Delay	1.0000
16	Pulse Width	8.0000
17	Presaturation Frequency	
18	Acquisition Time	3.9977
19	Acquisition Date	2024-06-27T12:29:16
20	Modification Date	2024-06-27T14:18:04
21	Class	
22	Spectrometer Frequency	400.18
23	Spectral Width	8196.7
24	Lowest Frequency	-1636.5
25	Nucleus	1H
26	Acquired Size	32768
27	Spectral Size	65536

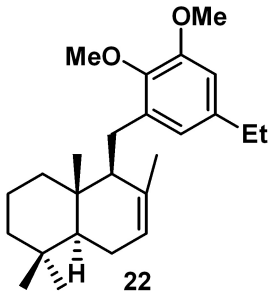


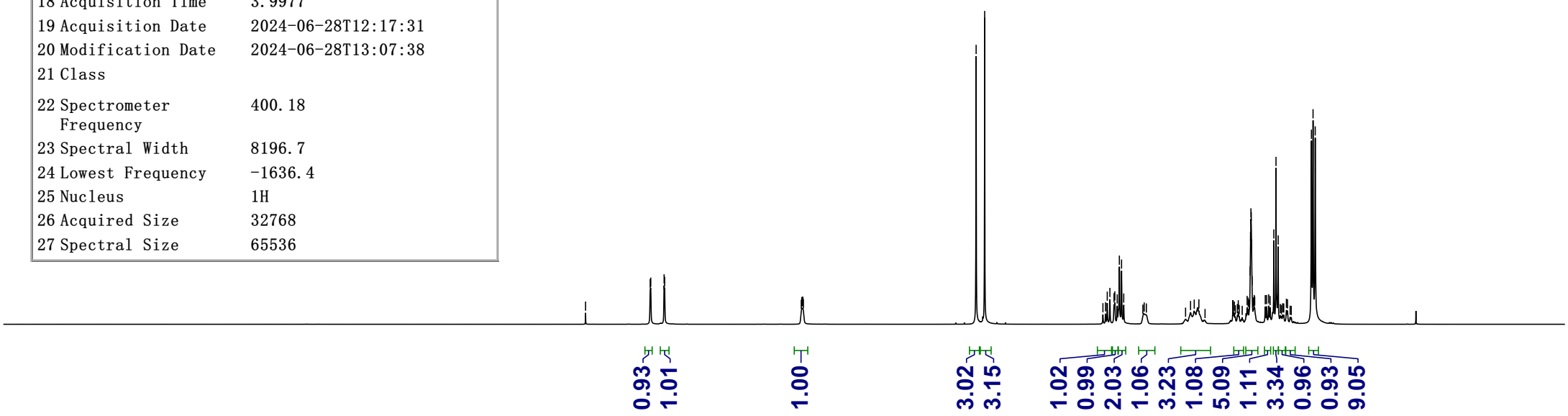


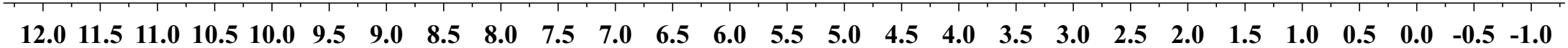
Parameter	Value
1 Title	YYP-G-190-1-1.11.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	Avance Neo 400M
7 Author	
8 Solvent	CDCl3
9 Temperature	297.3
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Probe	Z163739_0254 (PI HR-BBO400S1-BBF/ H/ D-5.0-Z SP)
13 Number of Scans	100
14 Receiver Gain	41.1
15 Relaxation Delay	2.0000
16 Pulse Width	7.8100
17 Presaturation Frequency	
18 Acquisition Time	1.3763
19 Acquisition Date	2024-06-27T12:37:36
20 Modification Date	2024-06-27T14:18:05
21 Class	
22 Spectrometer Frequency	100.63
23 Spectral Width	23809.5
24 Lowest Frequency	-1841.8
25 Nucleus	13C
26 Acquired Size	32768
27 Spectral Size	32768



Parameter	Value
1 Title	YYP-G-193-2-2.10.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	Avance Neo 400M
7 Author	
8 Solvent	CDCl3
9 Temperature	296.5
10 Pulse Sequence	zg30
11 Experiment	1D
12 Probe	Z163739_0254 (PI HR-BBO400S1-BBF/ H/ D-5.0-Z SP)
13 Number of Scans	16
14 Receiver Gain	46.2
15 Relaxation Delay	1.0000
16 Pulse Width	8.0000
17 Presaturation Frequency	
18 Acquisition Time	3.9977
19 Acquisition Date	2024-06-28T12:17:31
20 Modification Date	2024-06-28T13:07:38
21 Class	
22 Spectrometer Frequency	400.18
23 Spectral Width	8196.7
24 Lowest Frequency	-1636.4
25 Nucleus	1H
26 Acquired Size	32768
27 Spectral Size	65536

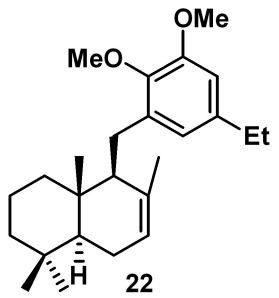




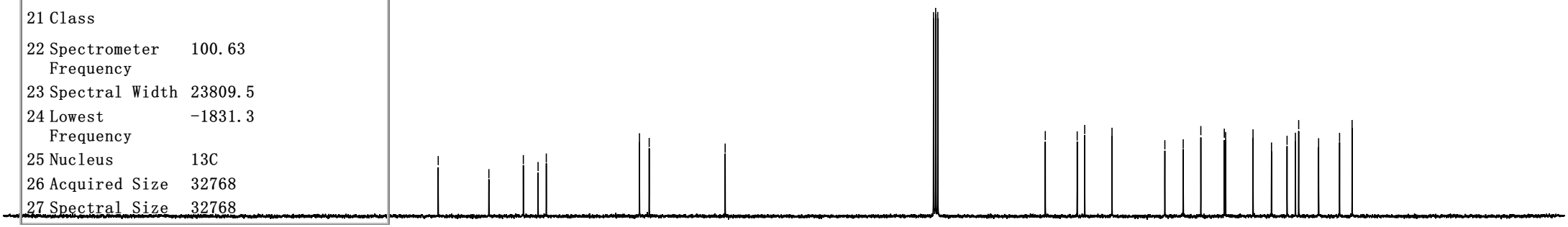


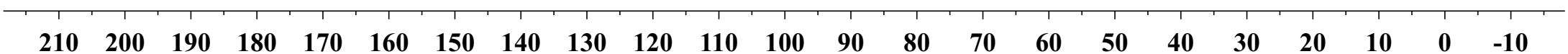
Parameter	Value
1 Title	YYP-G-193-2-2.11.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	Avance Neo 400M
7 Author	
8 Solvent	CDCl3
9 Temperature	297.2
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Probe	Z163739_0254 (PI HR-BBO400S1-BBF/ H/ D-5.0-Z SP)
13 Number of Scans	150
14 Receiver Gain	40.1
15 Relaxation Delay	2.0000
16 Pulse Width	7.8100
17 Presaturation Frequency	
18 Acquisition Time	1.3763
19 Acquisition Date	2024-06-28T12:28:22
20 Modification Date	2024-06-28T13:07:38
21 Class	
22 Spectrometer Frequency	100.63
23 Spectral Width	23809.5
24 Lowest Frequency	-1831.3
25 Nucleus	13C
26 Acquired Size	32768
27 Spectral Size	32768

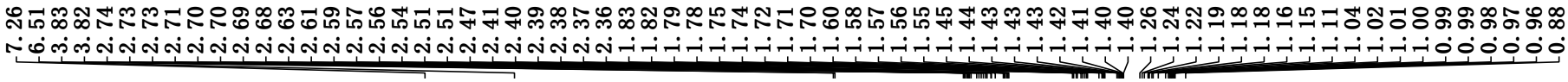
152.5 144.9 139.6 137.4 136.1 122.0 120.6 109.1 77.5 77.2 76.8 60.5 55.7 54.6 50.4 42.4 39.6 37.0 33.4 33.2 29.1 26.3 23.9 22.6 22.2 19.1 16.0 14.1



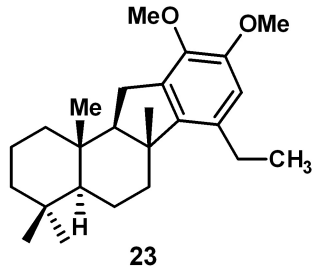
22



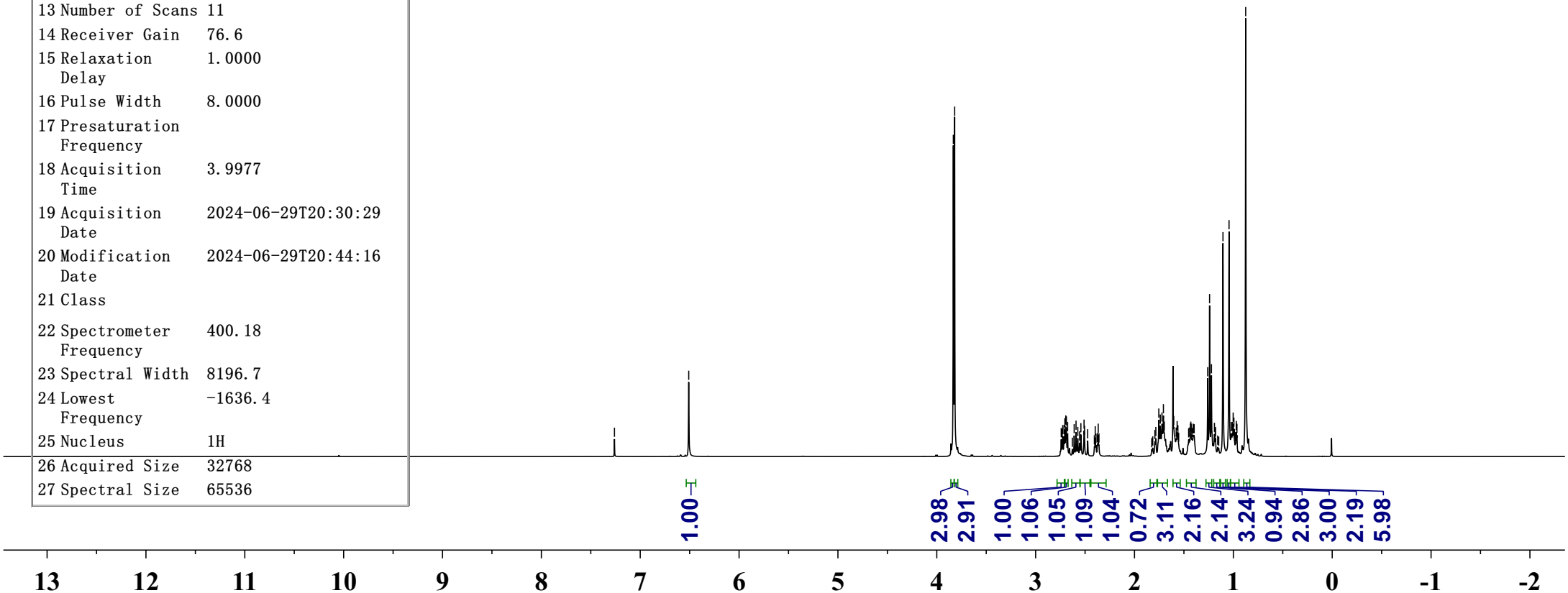




Parameter		Value
1	Title	YYP-G-194-1-3.22.1.1r
2	Comment	
3	Origin	Bruker BioSpin GmbH
4	Owner	nmrsu
5	Site	
6	Instrument	Avance Neo 400M
7	Author	
8	Solvent	CDCl3
9	Temperature	297.5
10	Pulse Sequence	zg30
11	Experiment	1D
12	Probe	Z163739_0254 (PI HR-BBO400S1-BBF/ H/ D-5.0-Z SP)
13	Number of Scans	11
14	Receiver Gain	76.6
15	Relaxation Delay	1.0000
16	Pulse Width	8.0000
17	Presaturation Frequency	
18	Acquisition Time	3.9977
19	Acquisition Date	2024-06-29T20:30:29
20	Modification Date	2024-06-29T20:44:16
21	Class	
22	Spectrometer Frequency	400.18
23	Spectral Width	8196.7
24	Lowest Frequency	-1636.4
25	Nucleus	1H
26	Acquired Size	32768
27	Spectral Size	65536

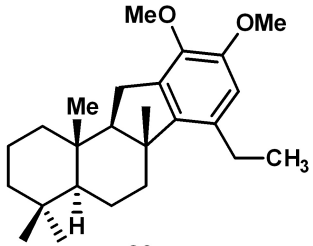


23

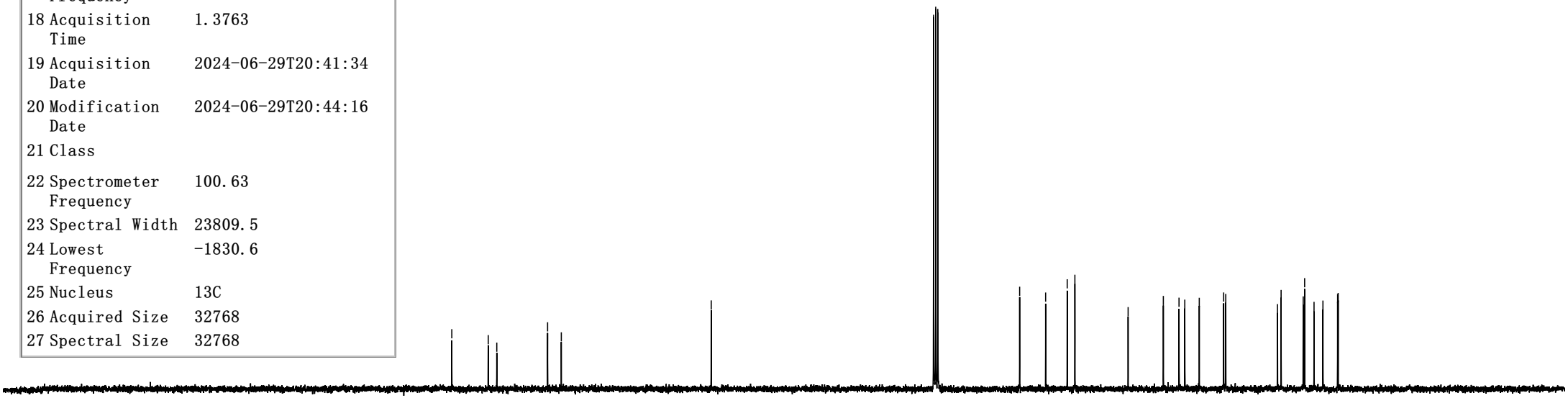


Parameter	Value
1 Title	YYP-G-194-1-3.23.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	Avance Neo 400M
7 Author	
8 Solvent	CDCl3
9 Temperature	298.1
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Probe	Z163739_0254 (PI HR-BBO400S1-BBF/ H/ D-5.0-Z SP)
13 Number of Scans	162
14 Receiver Gain	42.0
15 Relaxation Delay	2.0000
16 Pulse Width	7.8100
17 Presaturation Frequency	
18 Acquisition Time	1.3763
19 Acquisition Date	2024-06-29T20:41:34
20 Modification Date	2024-06-29T20:44:16
21 Class	
22 Spectrometer Frequency	100.63
23 Spectral Width	23809.5
24 Lowest Frequency	-1830.6
25 Nucleus	13C
26 Acquired Size	32768
27 Spectral Size	32768

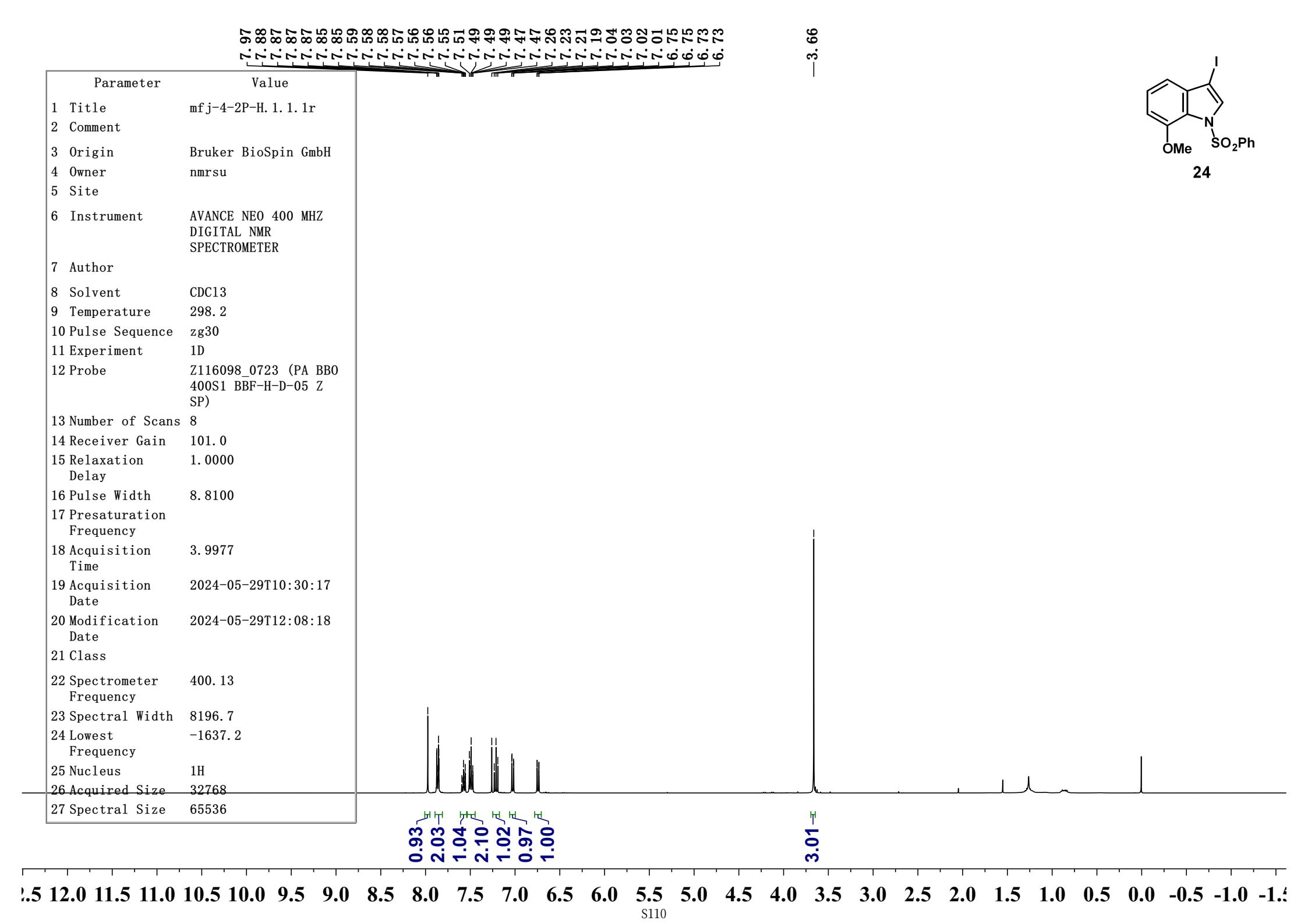
150.5 145.0 143.7 136.0 133.9 111.2 77.5 77.2 76.8 64.4 60.5 57.2 56.1 48.0 42.7 40.3 39.4 37.2 33.5 33.2 25.4 24.8 21.5 21.3 19.8 18.5 16.3 16.2



23

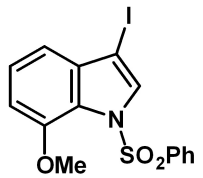


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

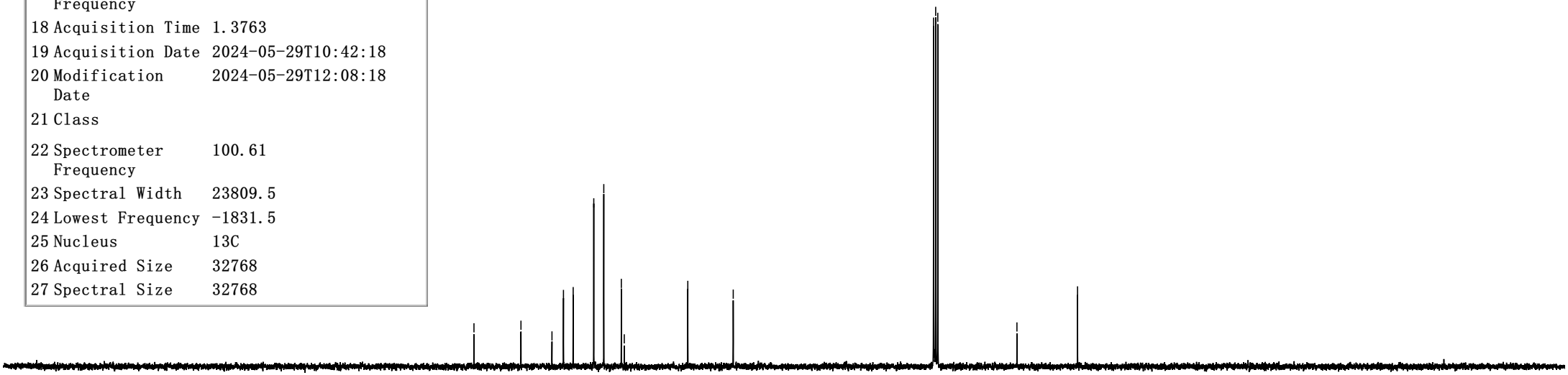

7.97
7.88
7.87
7.87
7.87
7.85
7.85
7.59
7.58
7.58
7.57
7.56
7.56
7.55
7.51
7.49
7.49
7.49
7.47
7.47
7.26
7.23
7.21
7.19
7.04
7.03
7.02
7.01
6.75
6.75
6.73
6.73
3.66
I
N
SO2Ph
OMe
24
Parameter Value
1 Title mfj-4-2P-H.1.1.1r
2 Comment
3 Origin Bruker BioSpin GmbH
4 Owner nmrsu
5 Site
6 Instrument AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author
8 Solvent CDCl3
9 Temperature 298.2
10 Pulse Sequence zg30
11 Experiment 1D
12 Probe Z116098_0723 (PA BBO 400S1 BBF-H-D-05 Z SP)
13 Number of Scans 8
14 Receiver Gain 101.0
15 Relaxation Delay 1.0000
16 Pulse Width 8.8100
17 Presaturation Frequency
18 Acquisition Time 3.9977
19 Acquisition Date 2024-05-29T10:30:17
20 Modification Date 2024-05-29T12:08:18
21 Class
22 Spectrometer Frequency 400.13
23 Spectral Width 8196.7
24 Lowest Frequency -1637.2
25 Nucleus 1H
26 Acquired Size 32768
27 Spectral Size 65536
0.93
2.03
1.04
2.10
1.02
0.97
1.00
3.01
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0

Parameter	Value
1 Title	mfj-4-2P-H.2.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDCl3
9 Temperature	298.2
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Probe	Z116098_0723 (PA BBO 400S1 BBF-H-D-05 Z SP)
13 Number of Scans	189
14 Receiver Gain	57.0
15 Relaxation Delay	2.0000
16 Pulse Width	10.0000
17 Presaturation Frequency	
18 Acquisition Time	1.3763
19 Acquisition Date	2024-05-29T10:42:18
20 Modification Date	2024-05-29T12:08:18
21 Class	
22 Spectrometer Frequency	100.61
23 Spectral Width	23809.5
24 Lowest Frequency	-1831.5
25 Nucleus	13C
26 Acquired Size	32768
27 Spectral Size	32768

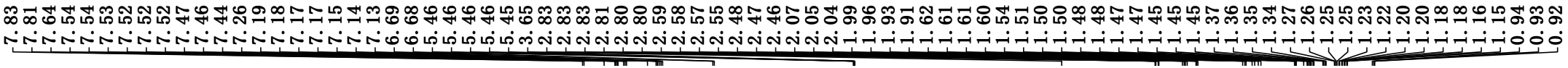
147.1
140.0
135.3
133.6
132.1
129.0
127.5
124.8
124.3
114.7
107.8
77.5
77.2
76.8
64.8
55.7



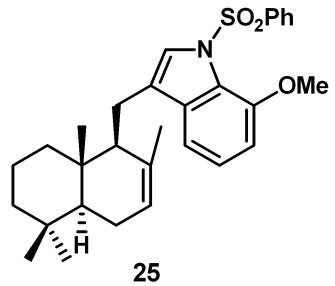
24



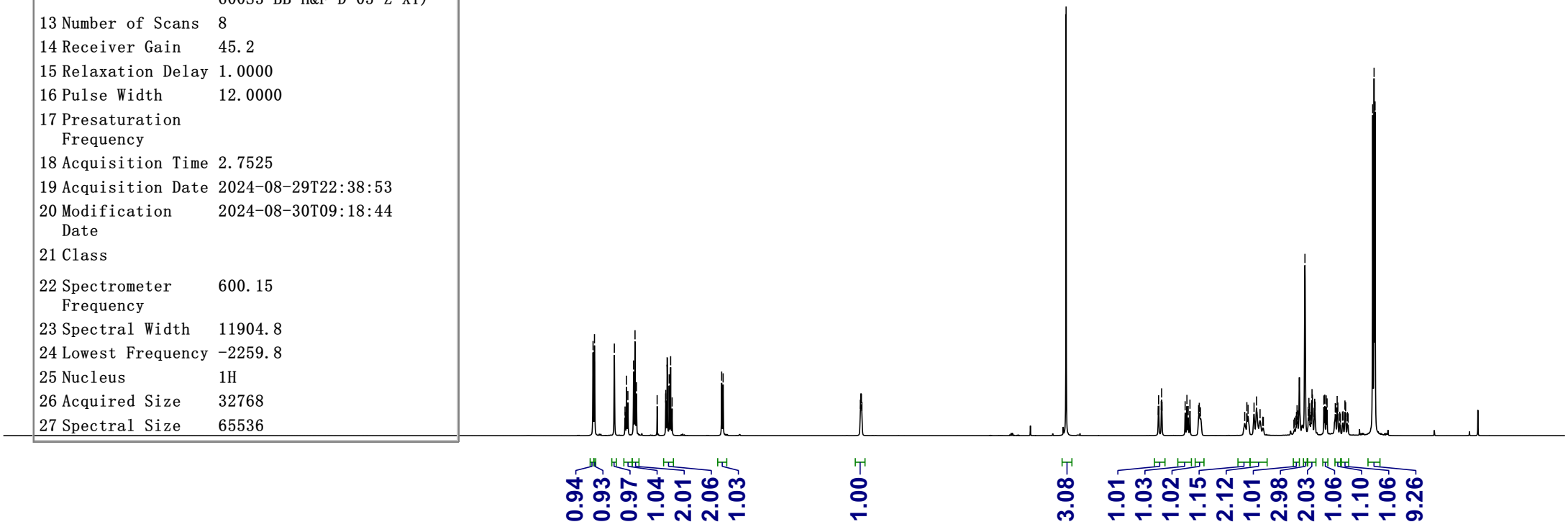
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

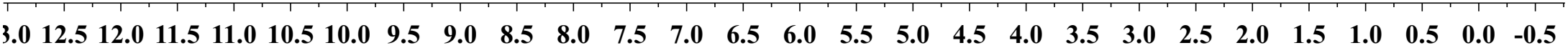


Parameter	Value
1 Title	YYP-G-174-4-4-0829.10.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	Avance NEO 600
7 Author	
8 Solvent	CDC13
9 Temperature	298.1
10 Pulse Sequence	zg30
11 Experiment	1D
12 Probe	Z168773_0001 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
13 Number of Scans	8
14 Receiver Gain	45.2
15 Relaxation Delay	1.0000
16 Pulse Width	12.0000
17 Presaturation Frequency	
18 Acquisition Time	2.7525
19 Acquisition Date	2024-08-29T22:38:53
20 Modification Date	2024-08-30T09:18:44
21 Class	
22 Spectrometer Frequency	600.15
23 Spectral Width	11904.8
24 Lowest Frequency	-2259.8
25 Nucleus	1H
26 Acquired Size	32768
27 Spectral Size	65536



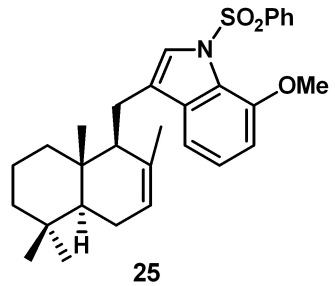
25



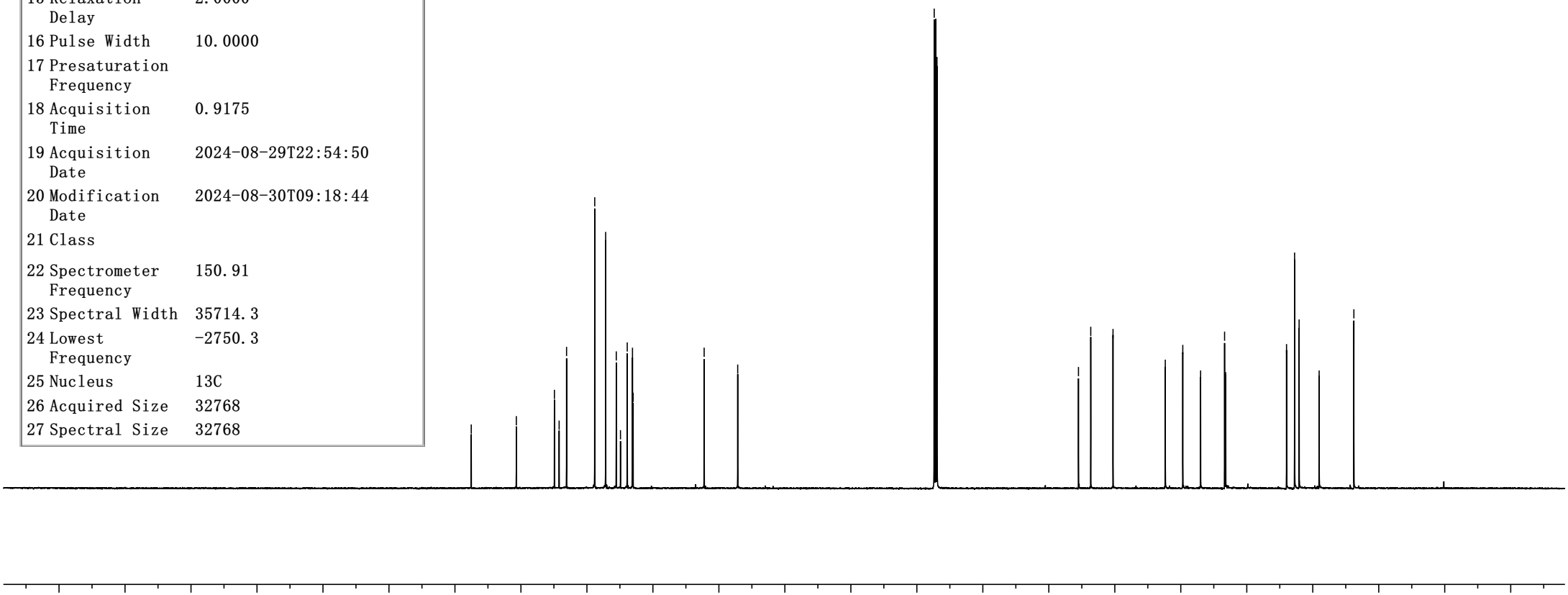


Parameter	Value
1 Title	YYP-G-174-4-4-0829.11.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	Avance NEO 600
7 Author	
8 Solvent	CDCl3
9 Temperature	298.2
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Probe	Z168773_0001 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
13 Number of Scans	300
14 Receiver Gain	101.0
15 Relaxation Delay	2.0000
16 Pulse Width	10.0000
17 Presaturation Frequency	
18 Acquisition Time	0.9175
19 Acquisition Date	2024-08-29T22:54:50
20 Modification Date	2024-08-30T09:18:44
21 Class	
22 Spectrometer Frequency	150.91
23 Spectral Width	35714.3
24 Lowest Frequency	-2750.3
25 Nucleus	13C
26 Acquired Size	32768
27 Spectral Size	32768

147.5 140.7 134.9 134.2 133.1 128.8 127.2 125.6 124.9 123.9 123.1 123.0 112.2 107.1 77.4 77.2 76.9 55.5 53.6 50.3 42.4 39.7 37.0 33.4 33.2 24.0 22.8 22.1 19.0 13.8



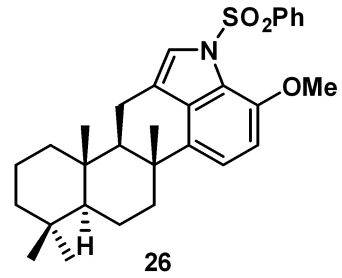
25



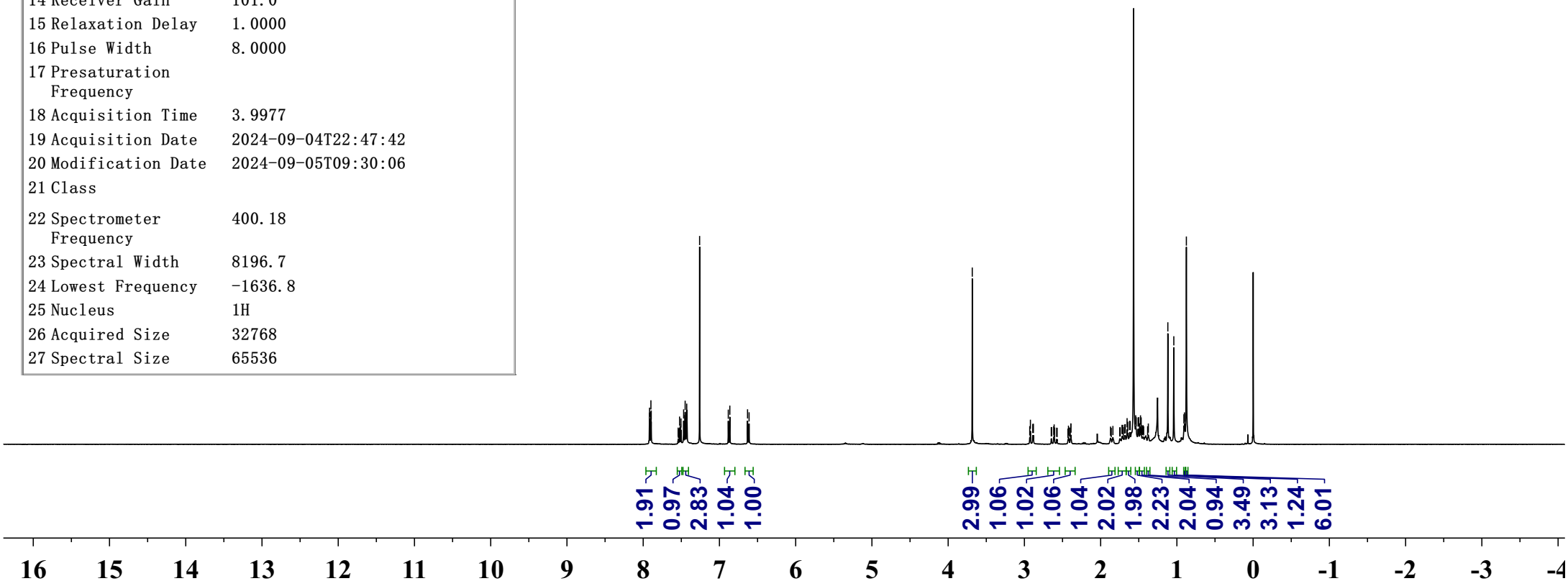
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

7.92 7.92 7.91 7.90 7.89 7.54 7.54 7.53 7.52 7.52 7.51 7.50 7.47 7.47 7.45 7.45 7.45 7.43 7.43 7.42 7.26 6.88 6.86 6.63 6.61 3.68 2.93 2.92 2.89 2.88 2.65 2.64 2.62 2.61 2.60 2.58 2.57 2.43 2.42 2.41 2.40 2.39 2.39 1.87 1.86 1.84 1.75 1.74 1.72 1.71 1.70 1.69 1.68 1.65 1.64 1.62 1.61 1.54 1.53 1.51 1.50 1.49 1.49 1.48 1.47 1.46 1.45 1.44 1.44 1.38 1.37 1.12 1.04 0.91 0.90 0.90 0.88

Parameter	Value
1 Title	YYP-G-175-2-1-0904-1.10.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	Avance Neo 400M
7 Author	
8 Solvent	CDCl3
9 Temperature	298.1
10 Pulse Sequence	zg30
11 Experiment	1D
12 Probe	Z163739_0254 (PI HR-BB0400S1-BBF/ H/ D-5.0-Z SP)
13 Number of Scans	16
14 Receiver Gain	101.0
15 Relaxation Delay	1.0000
16 Pulse Width	8.0000
17 Presaturation Frequency	
18 Acquisition Time	3.9977
19 Acquisition Date	2024-09-04T22:47:42
20 Modification Date	2024-09-05T09:30:06
21 Class	
22 Spectrometer Frequency	400.18
23 Spectral Width	8196.7
24 Lowest Frequency	-1636.8
25 Nucleus	1H
26 Acquired Size	32768
27 Spectral Size	65536

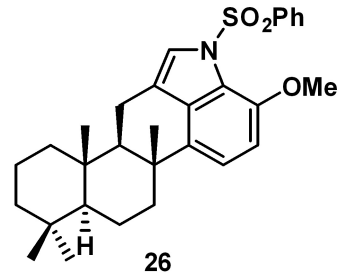


26



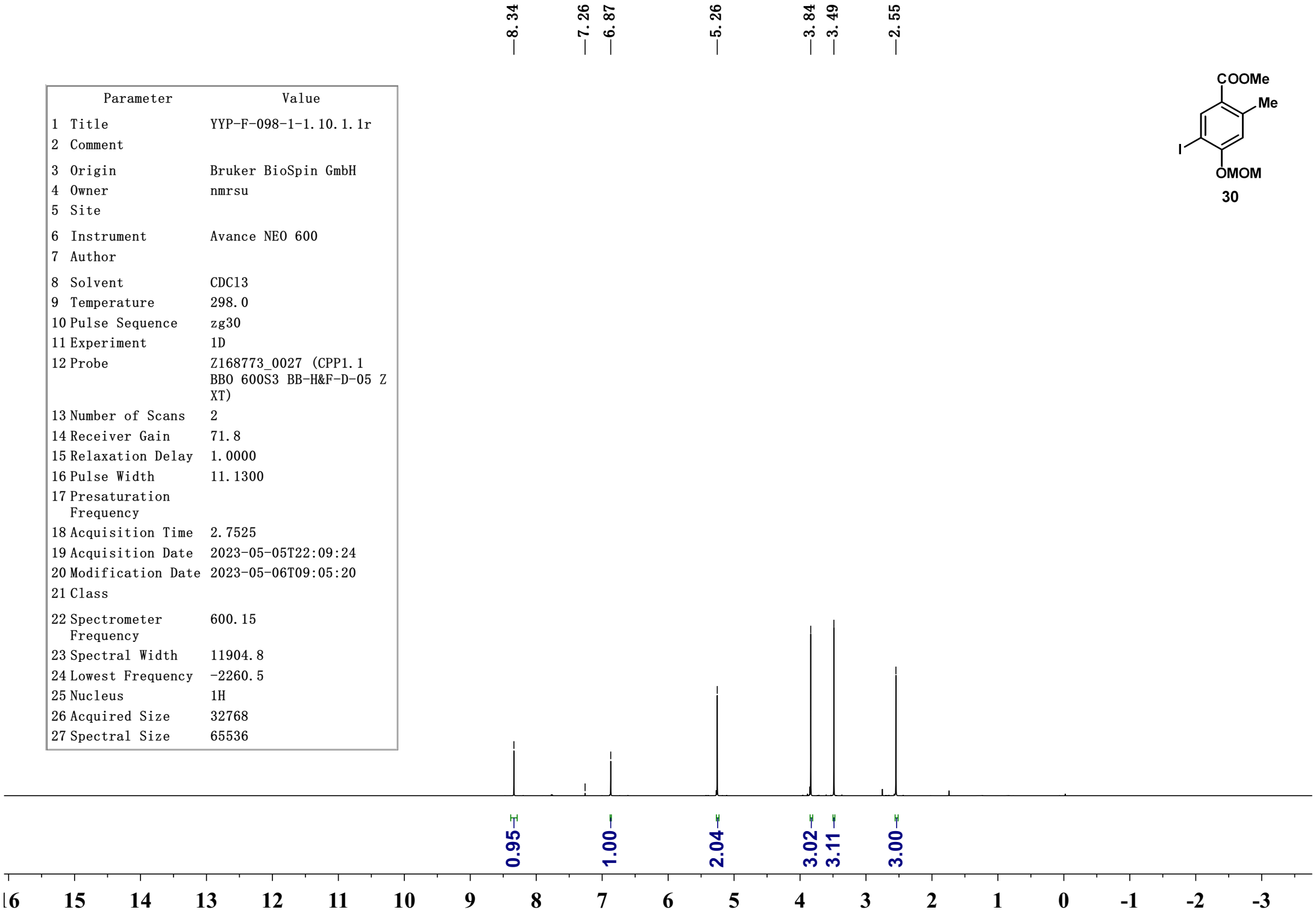
Parameter	Value
1 Title	YYP-G-175-2-1-0904.11.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	Avance NEO 600
7 Author	
8 Solvent	CDCl3
9 Temperature	298.2
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Probe	Z168773_0001 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
13 Number of Scans	251
14 Receiver Gain	101.0
15 Relaxation Delay	2.0000
16 Pulse Width	10.0000
17 Presaturation Frequency	
18 Acquisition Time	0.9175
19 Acquisition Date	2024-09-04T14:47:13
20 Modification Date	2024-09-04T14:56:02
21 Class	
22 Spectrometer Frequency	150.91
23 Spectral Width	35714.3
24 Lowest Frequency	-2746.1
25 Nucleus	13C
26 Acquired Size	32768
27 Spectral Size	32768

145.2 140.4 138.7 133.1 130.8 128.8 127.7 122.4 121.5 118.7 116.6 108.0 77.4 77.2 76.9 56.7 56.5 56.0 42.0 40.3 39.0 38.2 37.3 33.6 33.5 25.1 21.7 18.9 18.8 18.1 16.4



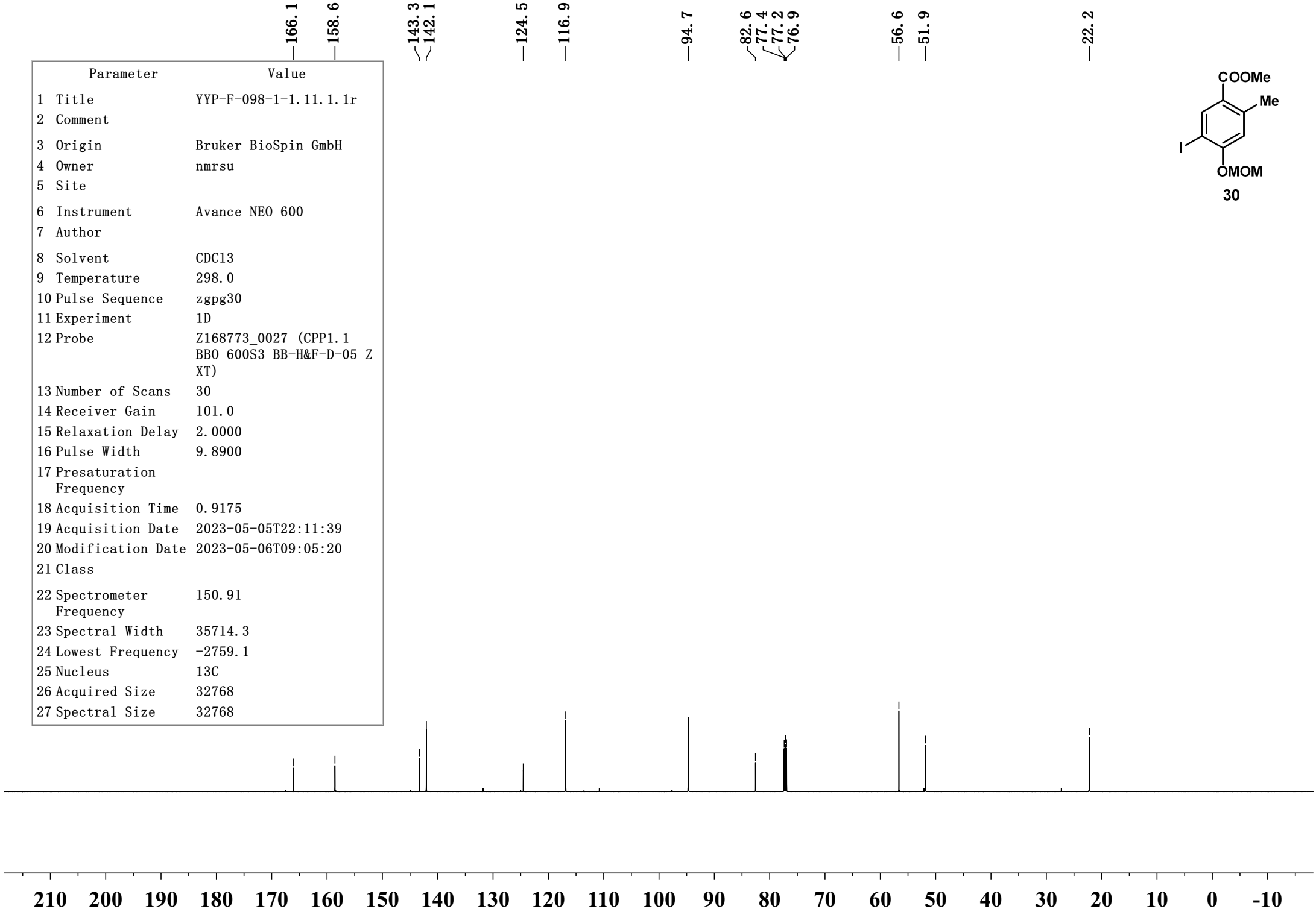
26

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



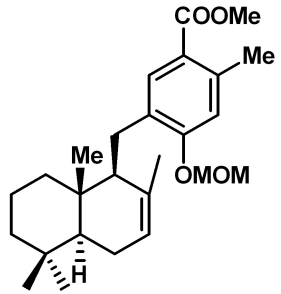
Parameter	Value
1 Title	YYP-F-098-1-1.10.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	Avance NEO 600
7 Author	
8 Solvent	CDCl3
9 Temperature	298.0
10 Pulse Sequence	zg30
11 Experiment	1D
12 Probe	Z168773_0027 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
13 Number of Scans	2
14 Receiver Gain	71.8
15 Relaxation Delay	1.0000
16 Pulse Width	11.1300
17 Presaturation Frequency	
18 Acquisition Time	2.7525
19 Acquisition Date	2023-05-05T22:09:24
20 Modification Date	2023-05-06T09:05:20
21 Class	
22 Spectrometer Frequency	600.15
23 Spectral Width	11904.8
24 Lowest Frequency	-2260.5
25 Nucleus	1H
26 Acquired Size	32768
27 Spectral Size	65536

30

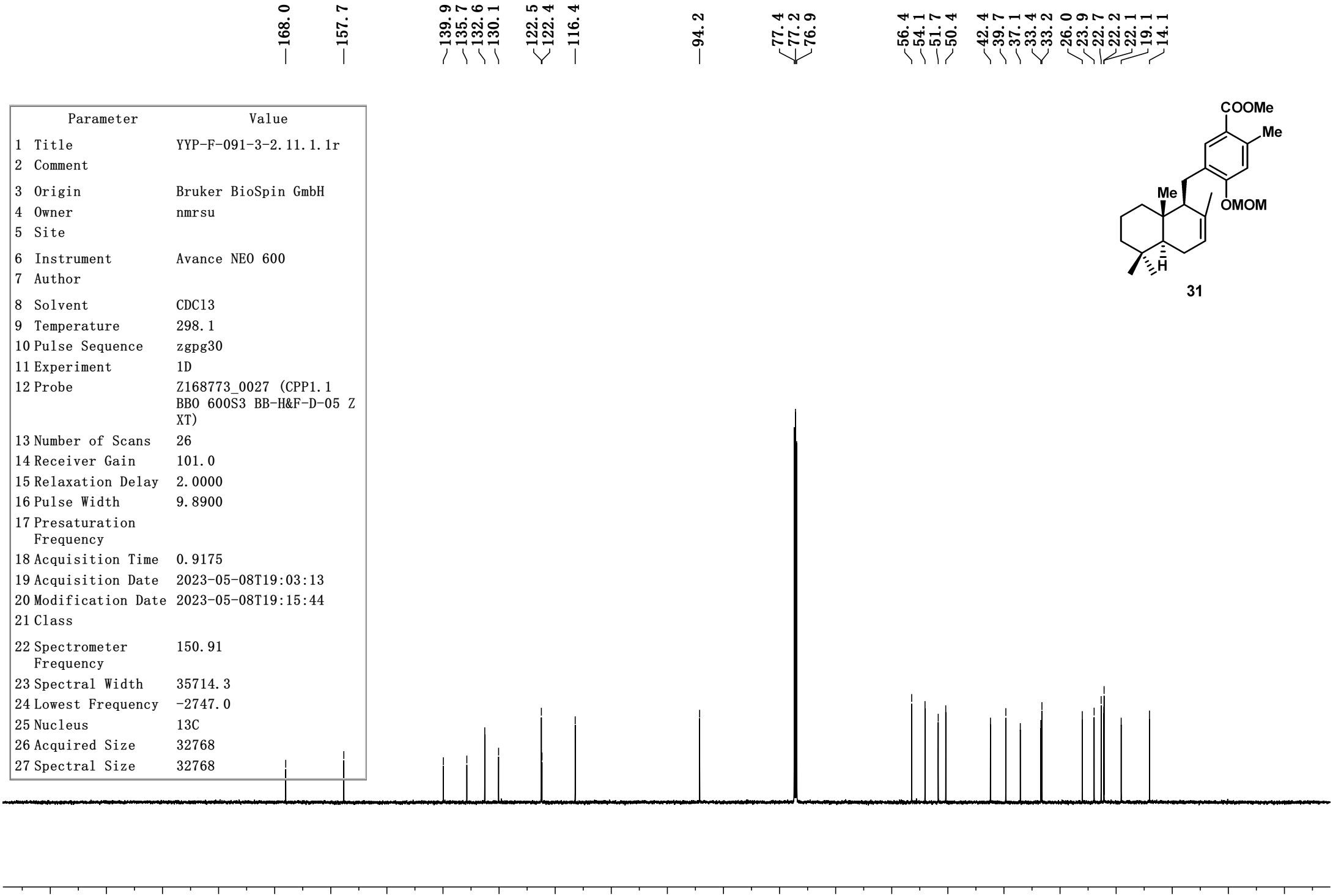


Parameter	Value
1 Title	YYP-F-098-1-1.11.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	Avance NEO 600
7 Author	
8 Solvent	CDCl3
9 Temperature	298.0
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Probe	Z168773_0027 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
13 Number of Scans	30
14 Receiver Gain	101.0
15 Relaxation Delay	2.0000
16 Pulse Width	9.8900
17 Presaturation Frequency	
18 Acquisition Time	0.9175
19 Acquisition Date	2023-05-05T22:11:39
20 Modification Date	2023-05-06T09:05:20
21 Class	
22 Spectrometer Frequency	150.91
23 Spectral Width	35714.3
24 Lowest Frequency	-2759.1
25 Nucleus	13C
26 Acquired Size	32768
27 Spectral Size	32768

Parameter	Value
1 Title	YYP-F-091-3-2.10.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	Avance NEO 600
7 Author	
8 Solvent	CDC13
9 Temperature	298.1
10 Pulse Sequence	zg30
11 Experiment	1D
12 Probe	Z168773_0027 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
13 Number of Scans	2
14 Receiver Gain	101.0
15 Relaxation Delay	1.0000
16 Pulse Width	11.1300
17 Presaturation Frequency	
18 Acquisition Time	2.7525
19 Acquisition Date	2023-05-08T19:01:10
20 Modification Date	2023-05-08T19:15:43
21 Class	
22 Spectrometer Frequency	600.15
23 Spectral Width	11904.8
24 Lowest Frequency	-2260.8
25 Nucleus	1H
26 Acquired Size	32768
27 Spectral Size	65536



31

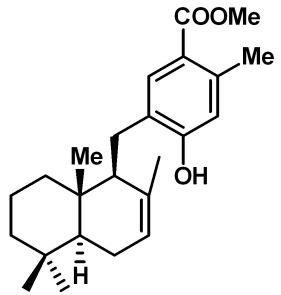


Parameter	Value
1 Title	YYP-F-091-3-2.11.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	Avance NEO 600
7 Author	
8 Solvent	CDC13
9 Temperature	298.1
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Probe	Z168773_0027 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
13 Number of Scans	26
14 Receiver Gain	101.0
15 Relaxation Delay	2.0000
16 Pulse Width	9.8900
17 Presaturation Frequency	
18 Acquisition Time	0.9175
19 Acquisition Date	2023-05-08T19:03:13
20 Modification Date	2023-05-08T19:15:44
21 Class	
22 Spectrometer Frequency	150.91
23 Spectral Width	35714.3
24 Lowest Frequency	-2747.0
25 Nucleus	13C
26 Acquired Size	32768
27 Spectral Size	32768

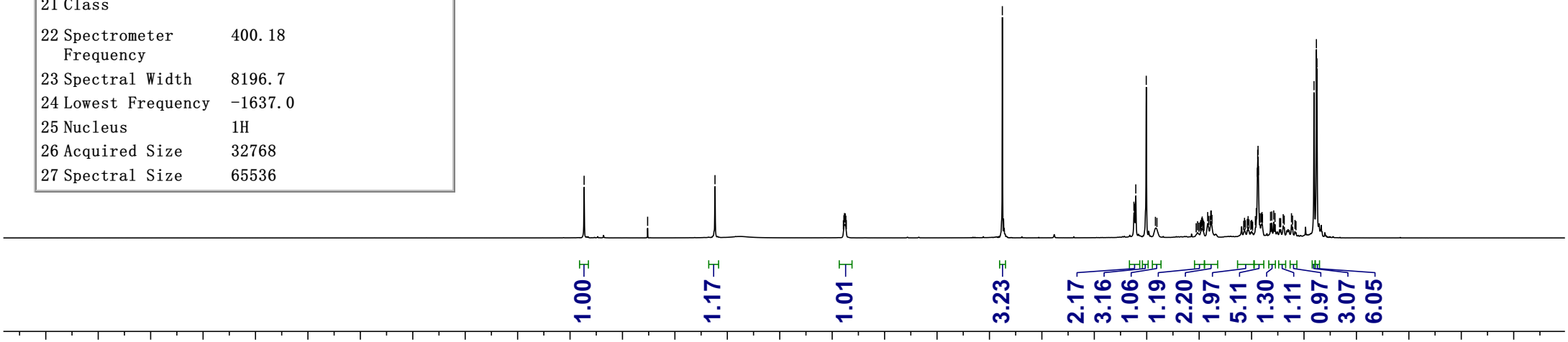
31

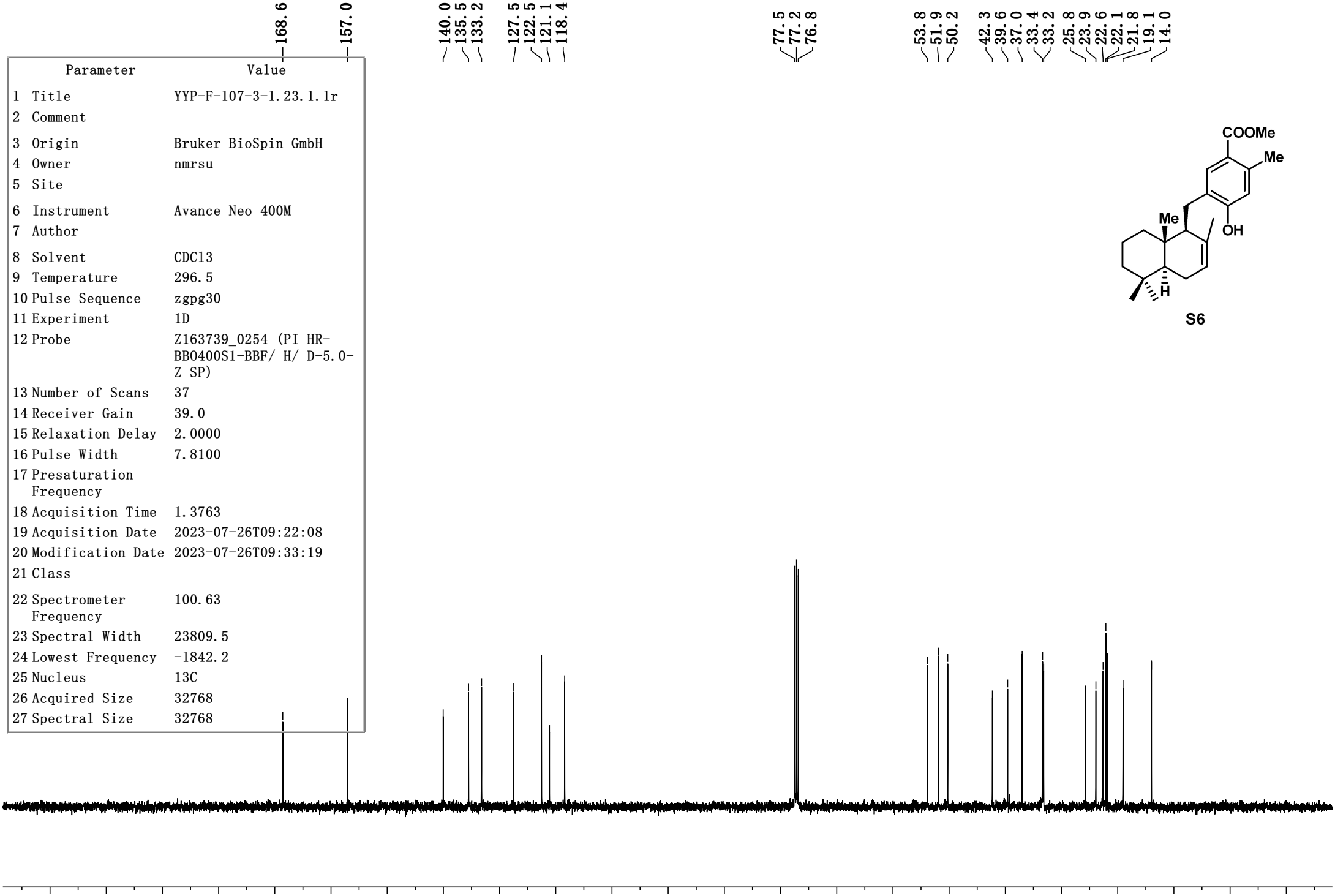
7.87 7.26 6.62 5.39 5.39 5.38 5.38 5.37 5.37 3.88 2.62 2.62 2.60 2.50 2.42 2.40 2.03 2.01 2.00 1.99 1.98 1.98 1.97 1.96 1.96 1.95 1.92 1.91 1.90 1.89 1.88 1.88 1.57 1.57 1.56 1.54 1.53 1.52 1.51 1.50 1.49 1.46 1.46 1.45 1.44 1.44 1.43 1.42 1.41 1.40 1.40 1.40 1.32 1.31 1.29 1.28 1.23 1.22 1.20 1.19 1.12 1.11 1.09 1.08 0.90 0.88 0.88

Parameter		Value
1	Title	YYP-F-107-3-1.22.1.1r
2	Comment	
3	Origin	Bruker BioSpin GmbH
4	Owner	nmrsu
5	Site	
6	Instrument	Avance Neo 400M
7	Author	
8	Solvent	CDCl3
9	Temperature	296.1
10	Pulse Sequence	zg30
11	Experiment	1D
12	Probe	Z163739_0254 (PI HR-BBO400S1-BBF/ H/ D-5.0-Z SP)
13	Number of Scans	3
14	Receiver Gain	32.0
15	Relaxation Delay	1.0000
16	Pulse Width	8.0000
17	Presaturation Frequency	
18	Acquisition Time	3.9977
19	Acquisition Date	2023-07-26T09:18:32
20	Modification Date	2023-07-26T09:33:19
21	Class	
22	Spectrometer Frequency	400.18
23	Spectral Width	8196.7
24	Lowest Frequency	-1637.0
25	Nucleus	1H
26	Acquired Size	32768
27	Spectral Size	65536



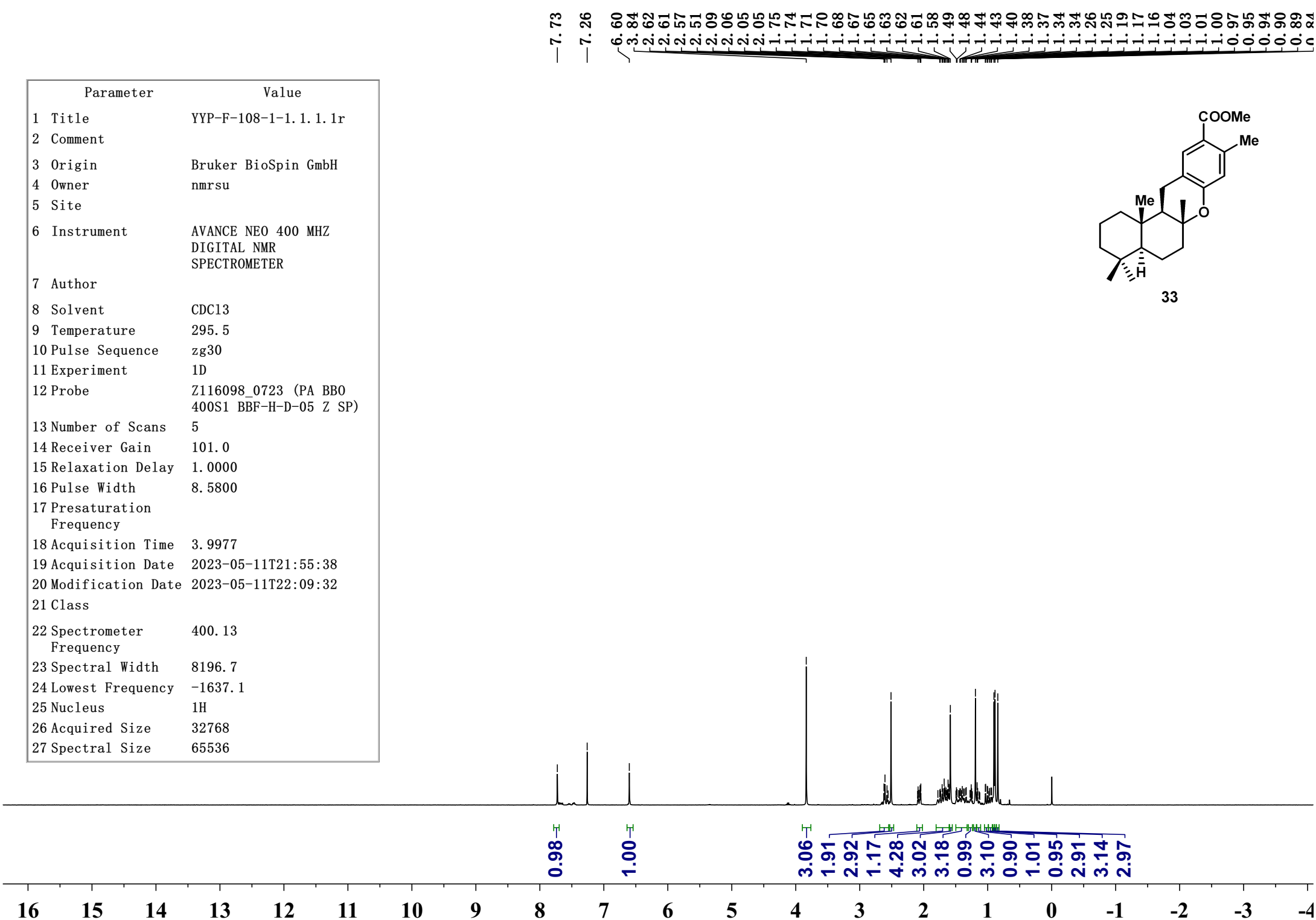
S6



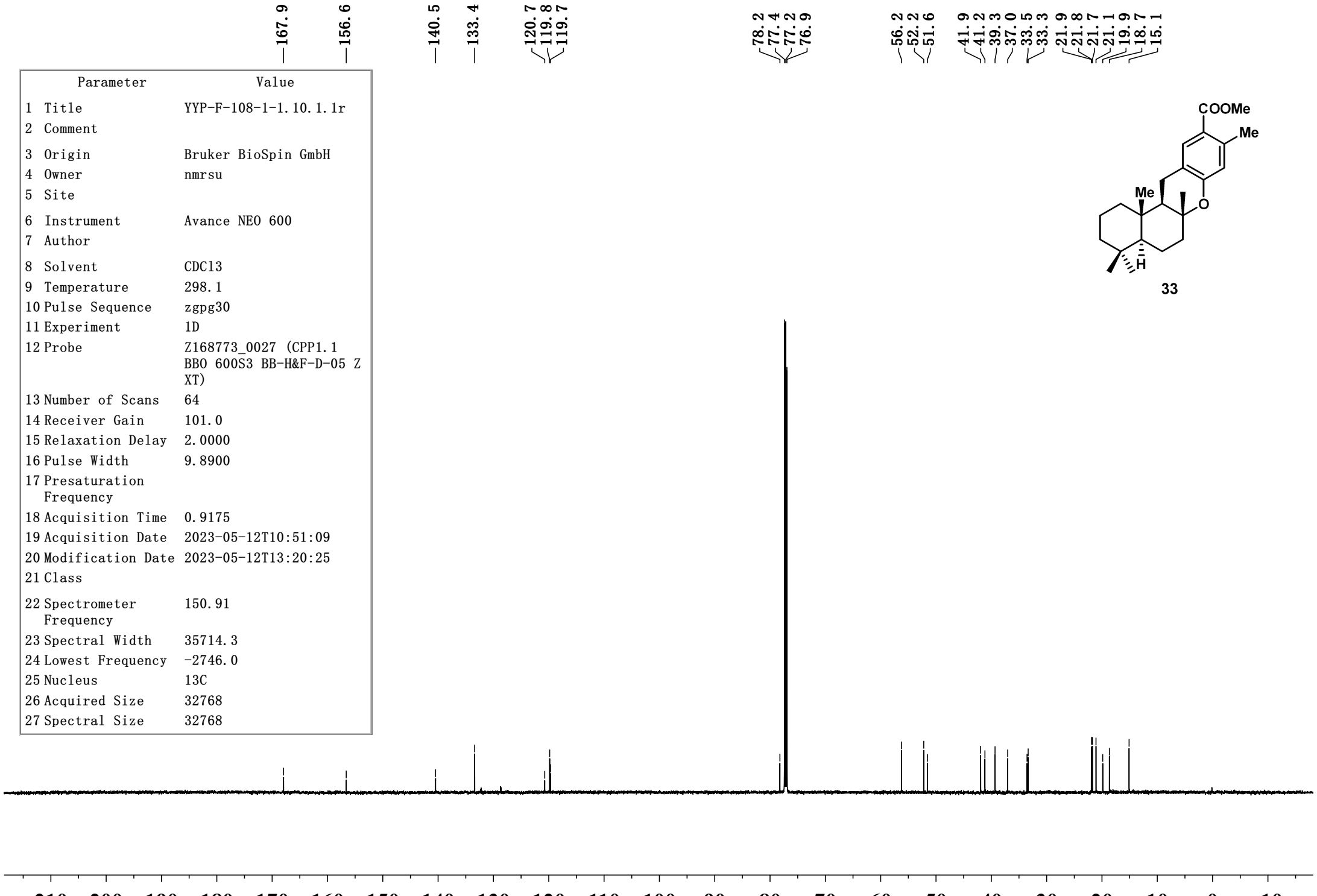


Parameter	Value
1 Title	YYP-F-107-3-1.23.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	Avance Neo 400M
7 Author	
8 Solvent	CDCl3
9 Temperature	296.5
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Probe	Z163739_0254 (PI HR-BBO400S1-BBF/ H/ D-5.0-Z SP)
13 Number of Scans	37
14 Receiver Gain	39.0
15 Relaxation Delay	2.0000
16 Pulse Width	7.8100
17 Presaturation Frequency	
18 Acquisition Time	1.3763
19 Acquisition Date	2023-07-26T09:22:08
20 Modification Date	2023-07-26T09:33:19
21 Class	
22 Spectrometer Frequency	100.63
23 Spectral Width	23809.5
24 Lowest Frequency	-1842.2
25 Nucleus	13C
26 Acquired Size	32768
27 Spectral Size	32768

Parameter	Value
1 Title	YYP-F-108-1-1.1.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	295.5
10 Pulse Sequence	zg30
11 Experiment	1D
12 Probe	Z116098_0723 (PA BBO 400S1 BBF-H-D-05 Z SP)
13 Number of Scans	5
14 Receiver Gain	101.0
15 Relaxation Delay	1.0000
16 Pulse Width	8.5800
17 Presaturation Frequency	
18 Acquisition Time	3.9977
19 Acquisition Date	2023-05-11T21:55:38
20 Modification Date	2023-05-11T22:09:32
21 Class	
22 Spectrometer Frequency	400.13
23 Spectral Width	8196.7
24 Lowest Frequency	-1637.1
25 Nucleus	1H
26 Acquired Size	32768
27 Spectral Size	65536



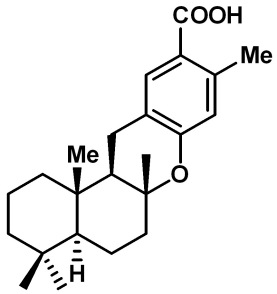
33



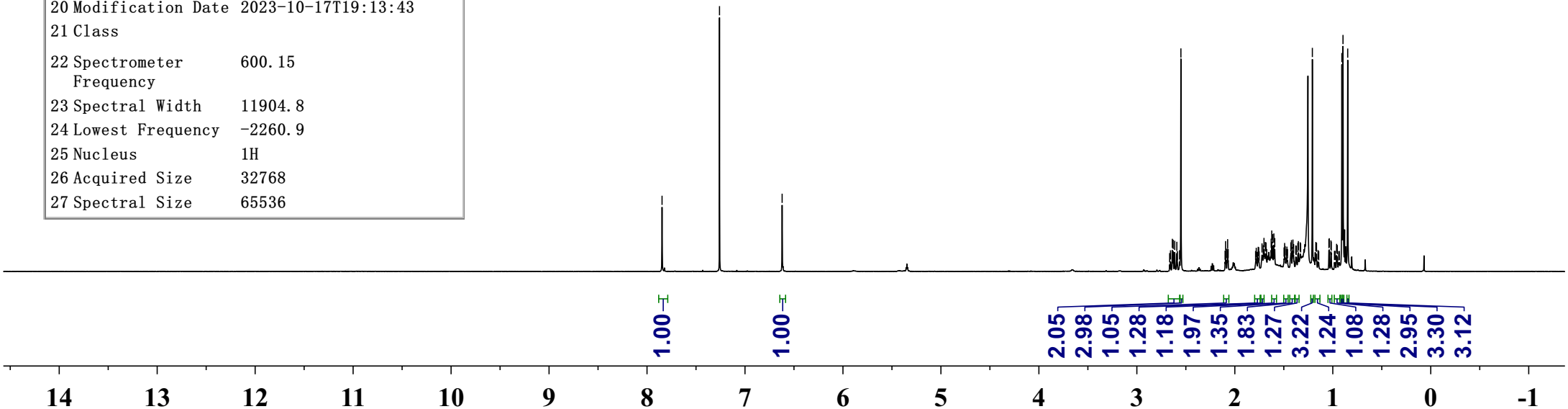
Parameter	Value
1 Title	YYP-F-108-1-1.10.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	Avance NEO 600
7 Author	
8 Solvent	CDCl3
9 Temperature	298.1
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Probe	Z168773_0027 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
13 Number of Scans	64
14 Receiver Gain	101.0
15 Relaxation Delay	2.0000
16 Pulse Width	9.8900
17 Presaturation Frequency	
18 Acquisition Time	0.9175
19 Acquisition Date	2023-05-12T10:51:09
20 Modification Date	2023-05-12T13:20:25
21 Class	
22 Spectrometer Frequency	150.91
23 Spectral Width	35714.3
24 Lowest Frequency	-2746.0
25 Nucleus	13C
26 Acquired Size	32768
27 Spectral Size	32768

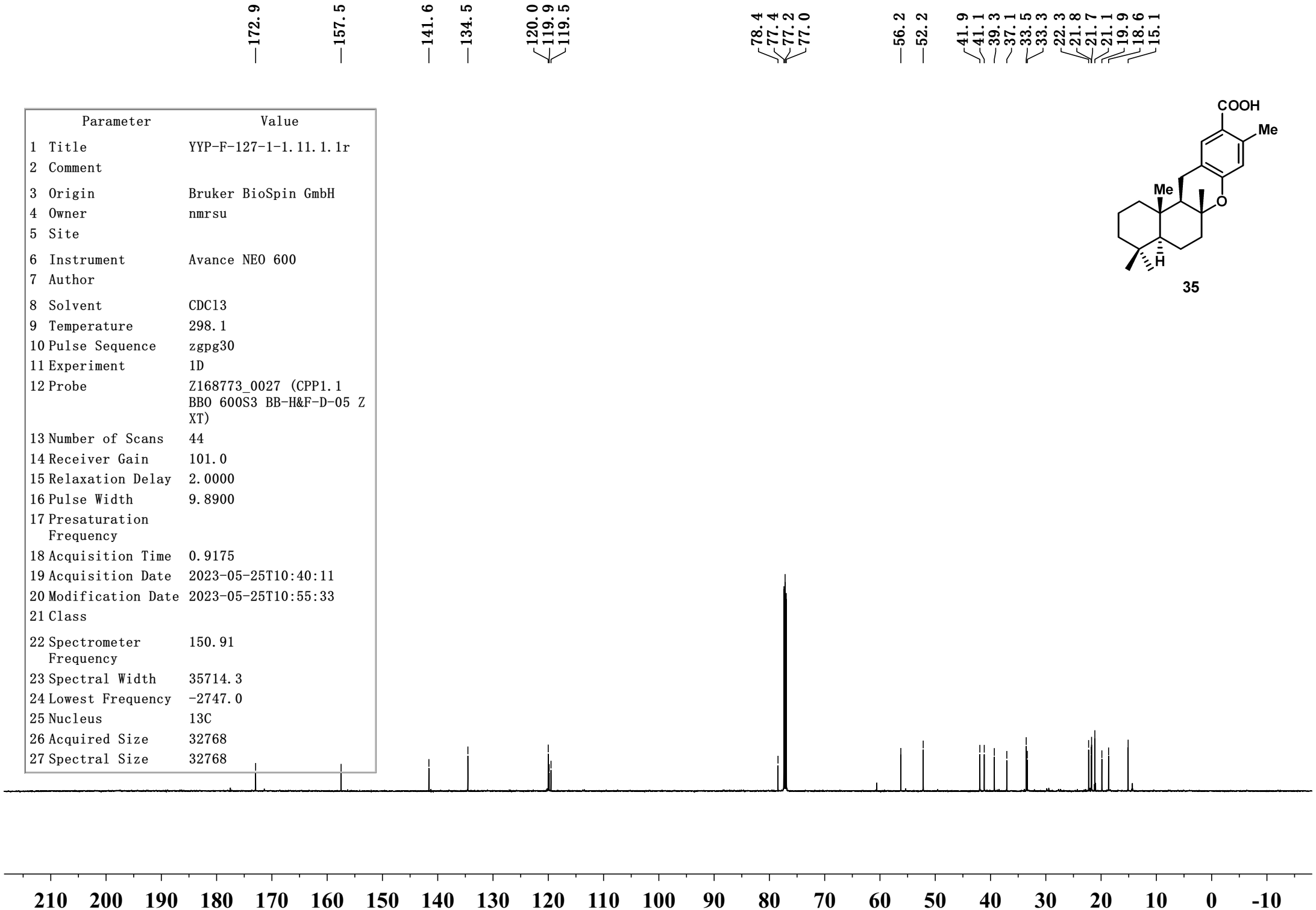
7.85 7.26 6.62 2.67 2.66 2.64 2.63 2.61 2.59 2.59 2.56 2.55 2.10 2.09 2.09 2.08 2.07 2.07 1.79 1.78 1.77 1.77 1.76 1.76 1.75 1.72 1.71 1.70 1.69 1.68 1.67 1.63 1.62 1.61 1.60 1.59 1.50 1.49 1.49 1.47 1.47 1.46 1.43 1.42 1.41 1.41 1.40 1.38 1.37 1.36 1.35 1.33 1.33 1.21 1.17 1.17 1.15 1.14 1.04 1.04 1.02 1.02 0.98 0.98 0.96 0.95 0.94 0.93 0.91 0.90 0.85

Parameter	Value
1 Title	YYP-G-100-1-1.10.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	Avance NEO 600
7 Author	
8 Solvent	CDCl3
9 Temperature	298.2
10 Pulse Sequence	zg30
11 Experiment	1D
12 Probe	Z114607_0339 (PA BBO 600S3 BBF-H-D-05 Z SP)
13 Number of Scans	3
14 Receiver Gain	101.0
15 Relaxation Delay	1.0000
16 Pulse Width	10.0000
17 Presaturation Frequency	
18 Acquisition Time	2.7525
19 Acquisition Date	2023-10-17T19:07:47
20 Modification Date	2023-10-17T19:13:43
21 Class	
22 Spectrometer Frequency	600.15
23 Spectral Width	11904.8
24 Lowest Frequency	-2260.9
25 Nucleus	1H
26 Acquired Size	32768
27 Spectral Size	65536



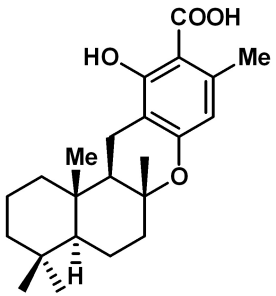
35





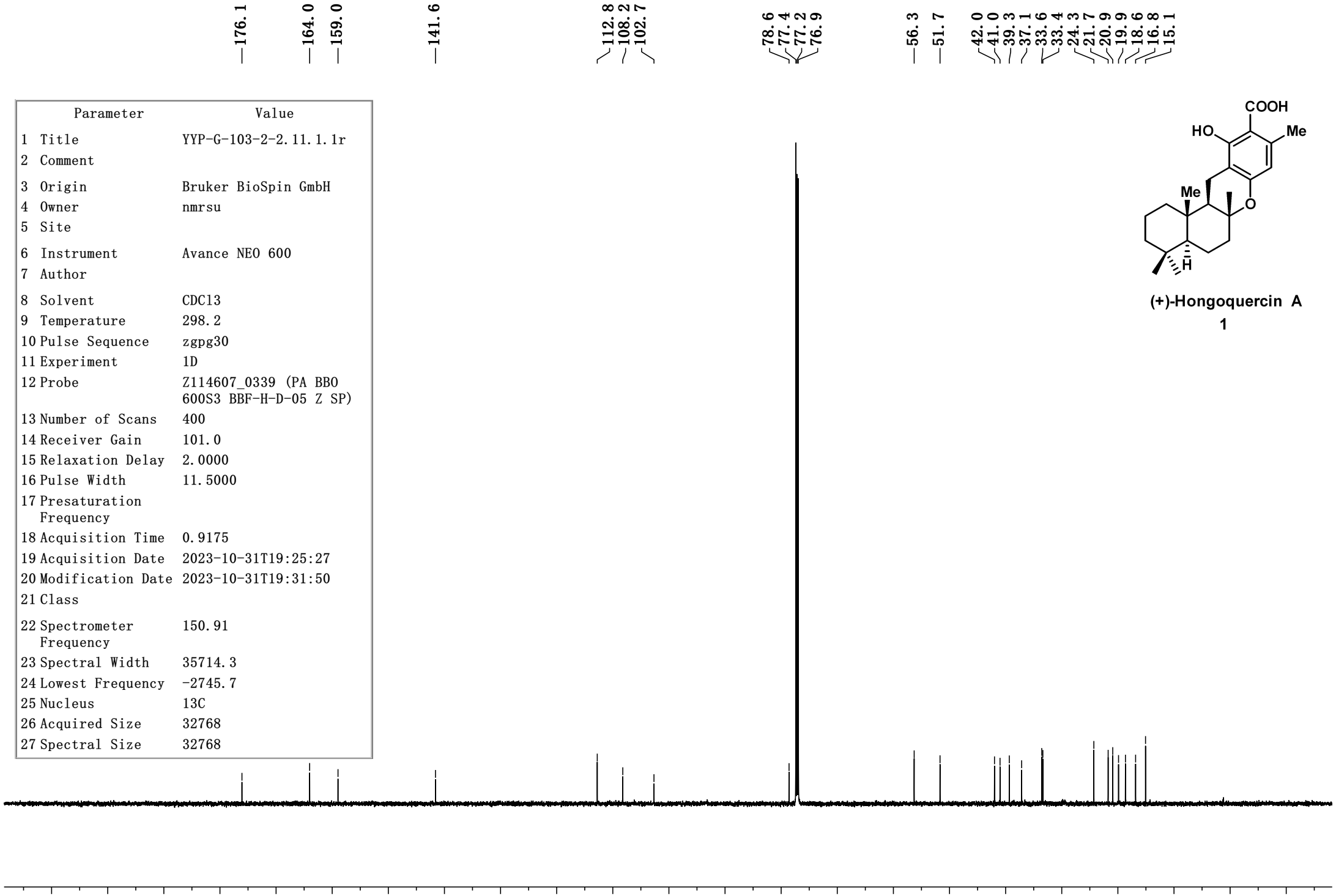
Parameter	Value
1 Title	YYP-F-127-1-1.11.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	Avance NEO 600
7 Author	
8 Solvent	CDCl3
9 Temperature	298.1
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Probe	Z168773_0027 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
13 Number of Scans	44
14 Receiver Gain	101.0
15 Relaxation Delay	2.0000
16 Pulse Width	9.8900
17 Presaturation Frequency	
18 Acquisition Time	0.9175
19 Acquisition Date	2023-05-25T10:40:11
20 Modification Date	2023-05-25T10:55:33
21 Class	
22 Spectrometer Frequency	150.91
23 Spectral Width	35714.3
24 Lowest Frequency	-2747.0
25 Nucleus	13C
26 Acquired Size	32768
27 Spectral Size	32768

Parameter	Value
1 Title	YYP-G-103-2-2.10.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	Avance NEO 600
7 Author	
8 Solvent	CDCl3
9 Temperature	298.2
10 Pulse Sequence	zg30
11 Experiment	1D
12 Probe	Z114607_0339 (PA BBO 600S3 BBF-H-D-05 Z SP)
13 Number of Scans	8
14 Receiver Gain	101.0
15 Relaxation Delay	1.0000
16 Pulse Width	10.0000
17 Presaturation Frequency	
18 Acquisition Time	2.7525
19 Acquisition Date	2023-10-31T19:04:29
20 Modification Date	2023-10-31T19:31:50
21 Class	
22 Spectrometer Frequency	600.15
23 Spectral Width	11904.8
24 Lowest Frequency	-2261.0
25 Nucleus	1H
26 Acquired Size	32768
27 Spectral Size	65536



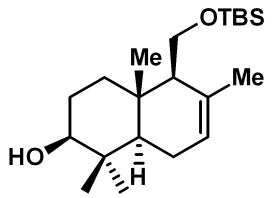
(+)-Hongoquercin A

1

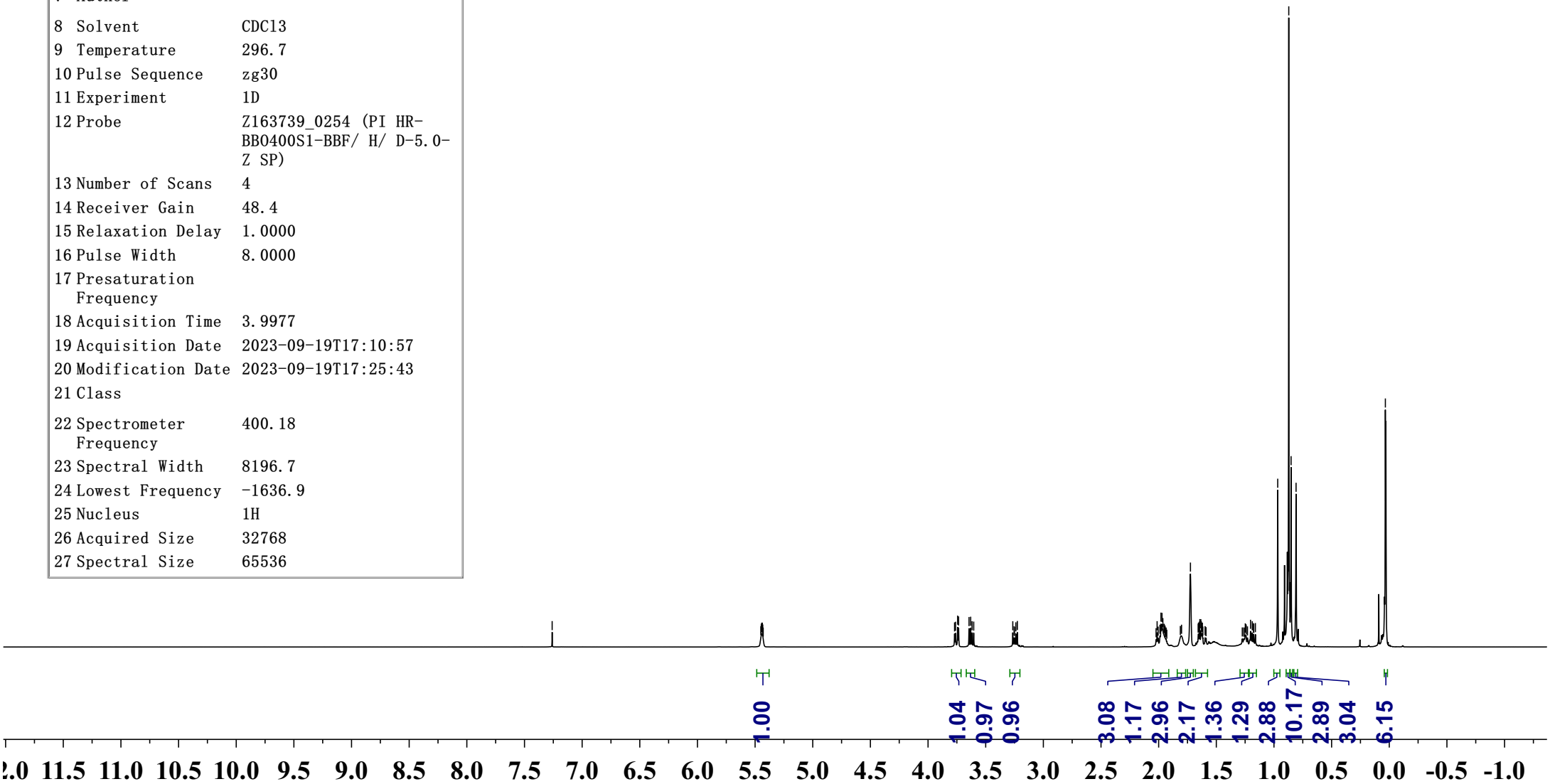


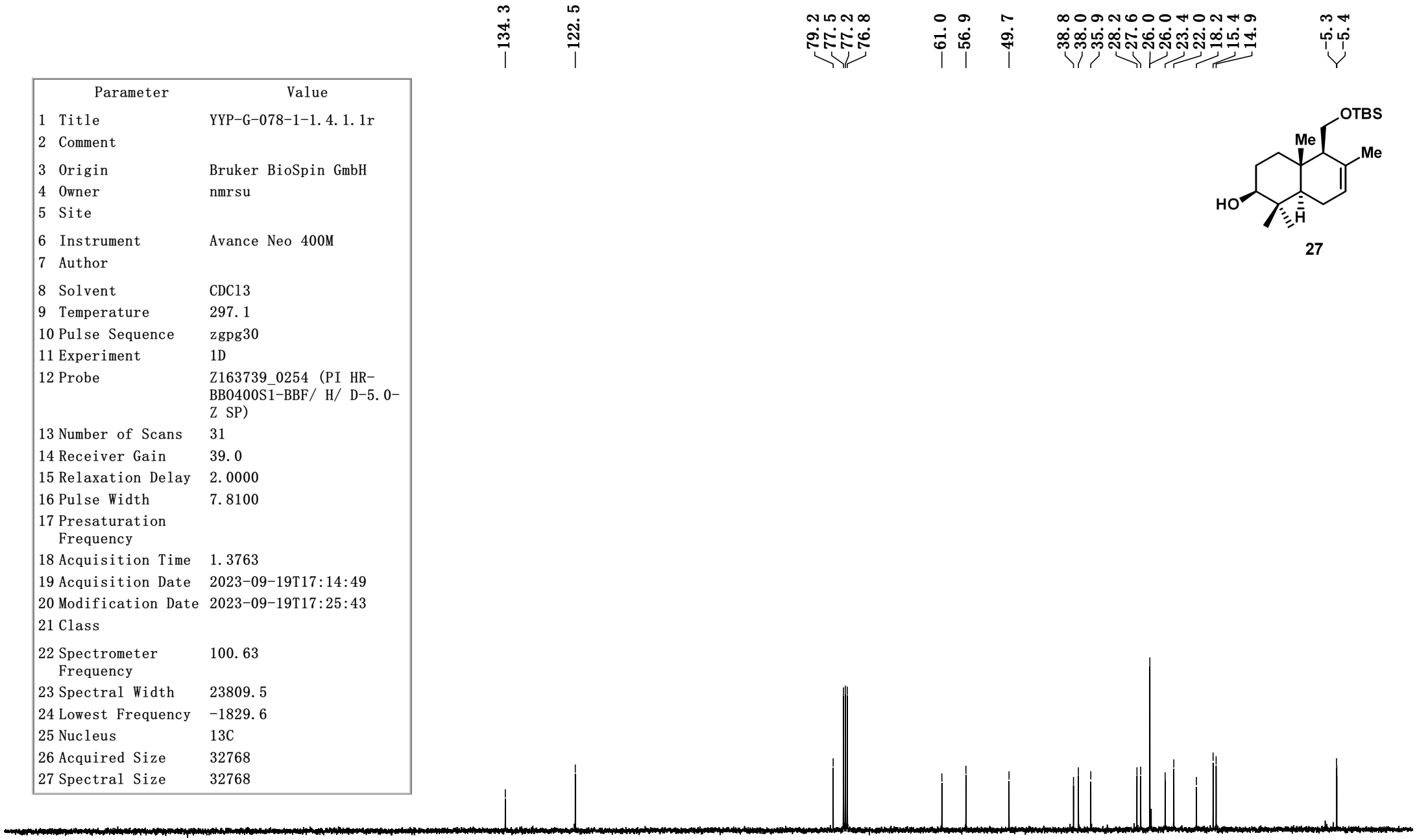
Parameter	Value
1 Title	YYP-G-103-2-2.11.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	Avance NEO 600
7 Author	
8 Solvent	CDCl3
9 Temperature	298.2
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Probe	Z114607_0339 (PA BBO 600S3 BBF-H-D-05 Z SP)
13 Number of Scans	400
14 Receiver Gain	101.0
15 Relaxation Delay	2.0000
16 Pulse Width	11.5000
17 Presaturation Frequency	
18 Acquisition Time	0.9175
19 Acquisition Date	2023-10-31T19:25:27
20 Modification Date	2023-10-31T19:31:50
21 Class	
22 Spectrometer Frequency	150.91
23 Spectral Width	35714.3
24 Lowest Frequency	-2745.7
25 Nucleus	13C
26 Acquired Size	32768
27 Spectral Size	32768

Parameter	Value
1 Title	YYP-G-078-1-1.3.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	Avance Neo 400M
7 Author	
8 Solvent	CDCl3
9 Temperature	296.7
10 Pulse Sequence	zg30
11 Experiment	1D
12 Probe	Z163739_0254 (PI HR-BBO400S1-BBF/ H/ D-5.0-Z SP)
13 Number of Scans	4
14 Receiver Gain	48.4
15 Relaxation Delay	1.0000
16 Pulse Width	8.0000
17 Presaturation Frequency	
18 Acquisition Time	3.9977
19 Acquisition Date	2023-09-19T17:10:57
20 Modification Date	2023-09-19T17:25:43
21 Class	
22 Spectrometer Frequency	400.18
23 Spectral Width	8196.7
24 Lowest Frequency	-1636.9
25 Nucleus	1H
26 Acquired Size	32768
27 Spectral Size	65536



27

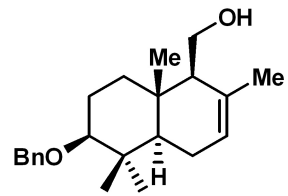




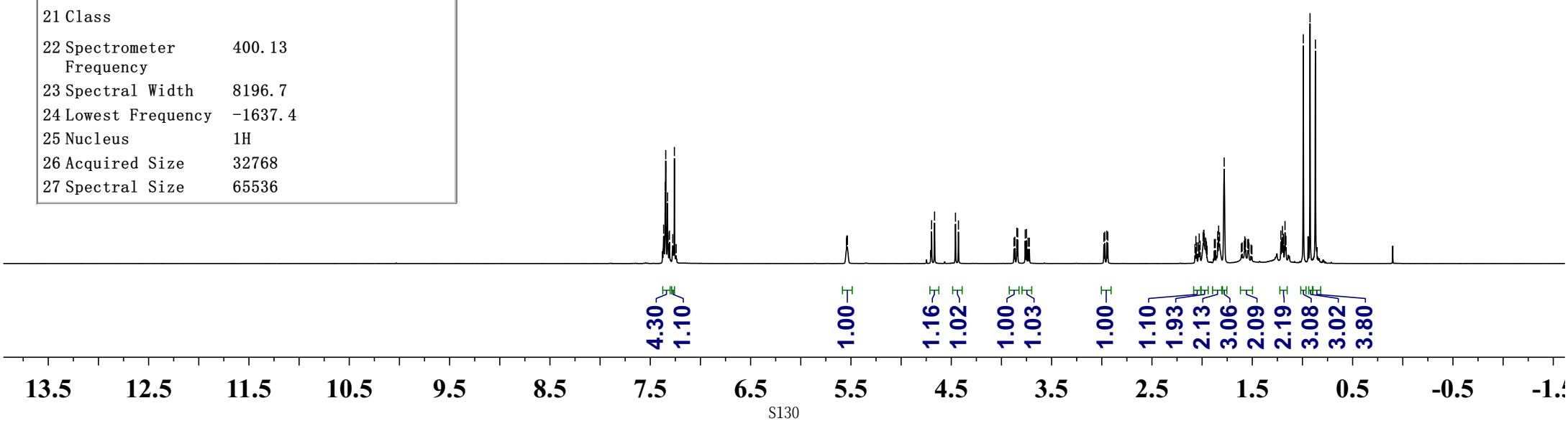
Parameter	Value
1 Title	YYP-G-078-1-1.4.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	Avance Neo 400M
7 Author	
8 Solvent	CDCl3
9 Temperature	297.1
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Probe	Z163739_0254 (PI HR-BBO400S1-BBF/ H/ D-5.0-Z SP)
13 Number of Scans	31
14 Receiver Gain	39.0
15 Relaxation Delay	2.0000
16 Pulse Width	7.8100
17 Presaturation Frequency	
18 Acquisition Time	1.3763
19 Acquisition Date	2023-09-19T17:14:49
20 Modification Date	2023-09-19T17:25:43
21 Class	
22 Spectrometer Frequency	100.63
23 Spectral Width	23809.5
24 Lowest Frequency	-1829.6
25 Nucleus	13C
26 Acquired Size	32768
27 Spectral Size	32768

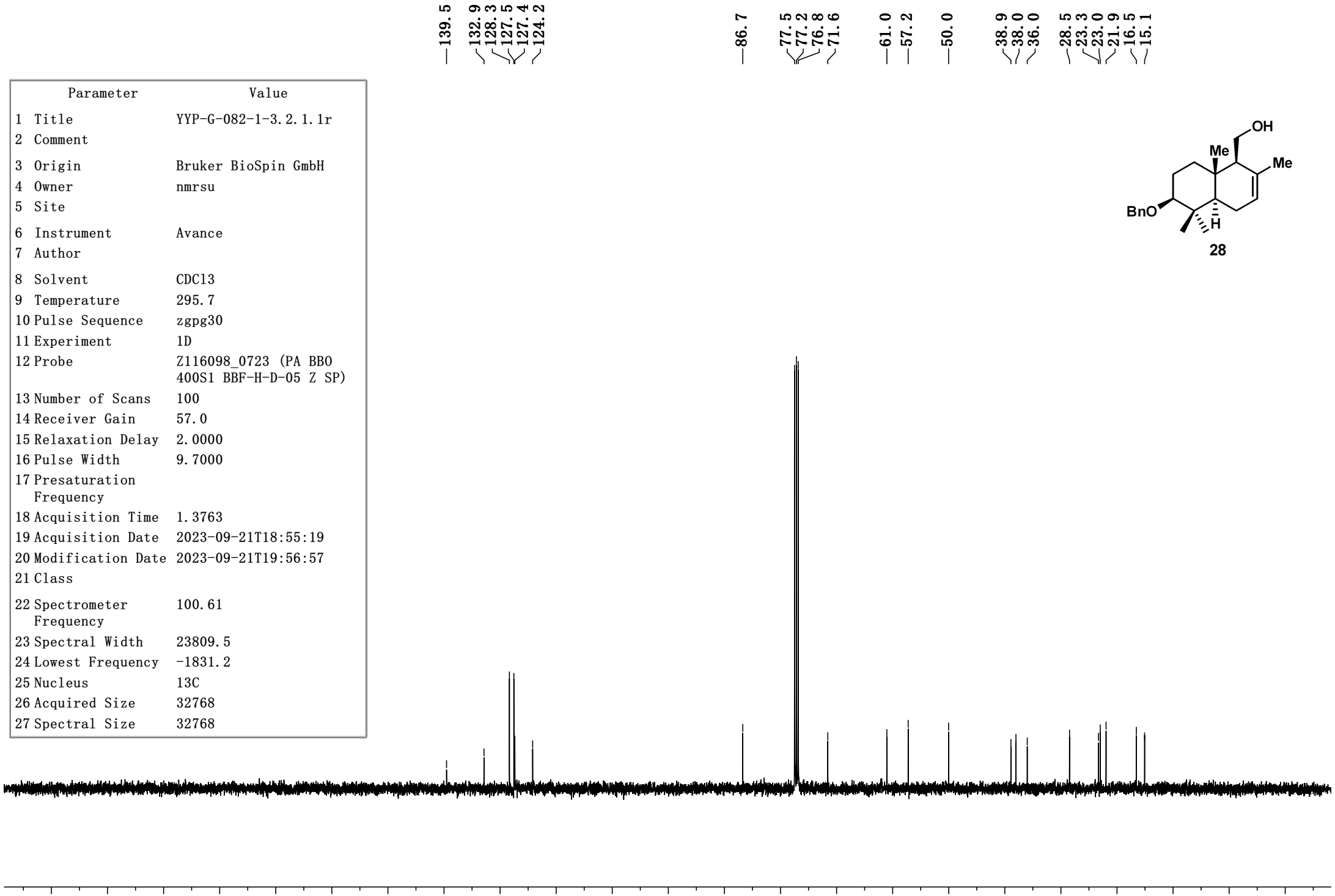
7.37 7.35 7.35 7.33 7.33 7.32 7.31 7.28 7.26 7.24 5.55 5.54 5.54 5.54 4.70 4.67 4.46 4.43 3.87 3.87 3.85 3.84 3.76 3.75 3.73 3.72 2.98 2.97 2.95 2.94 2.07 2.06 2.05 2.04 2.03 2.02 1.99 1.98 1.98 1.98 1.97 1.96 1.96 1.96 1.95 1.88 1.87 1.84 1.84 1.83 1.78 1.61 1.60 1.58 1.57 1.57 1.57 1.55 1.54 1.54 1.53 1.51 1.50 1.22 1.21 1.20 1.19 1.19 1.17 1.16 0.99 0.92 0.87

Parameter	Value
1 Title	YYP-G-082-1-3.1.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	Avance
7 Author	
8 Solvent	CDCl3
9 Temperature	295.3
10 Pulse Sequence	zg30
11 Experiment	1D
12 Probe	Z116098_0723 (PA BBO 400S1 BBF-H-D-05 Z SP)
13 Number of Scans	8
14 Receiver Gain	101.0
15 Relaxation Delay	1.0000
16 Pulse Width	8.5800
17 Presaturation Frequency	
18 Acquisition Time	3.9977
19 Acquisition Date	2023-09-21T18:48:10
20 Modification Date	2023-09-21T19:56:53
21 Class	
22 Spectrometer Frequency	400.13
23 Spectral Width	8196.7
24 Lowest Frequency	-1637.4
25 Nucleus	1H
26 Acquired Size	32768
27 Spectral Size	65536



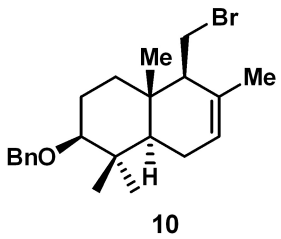
28





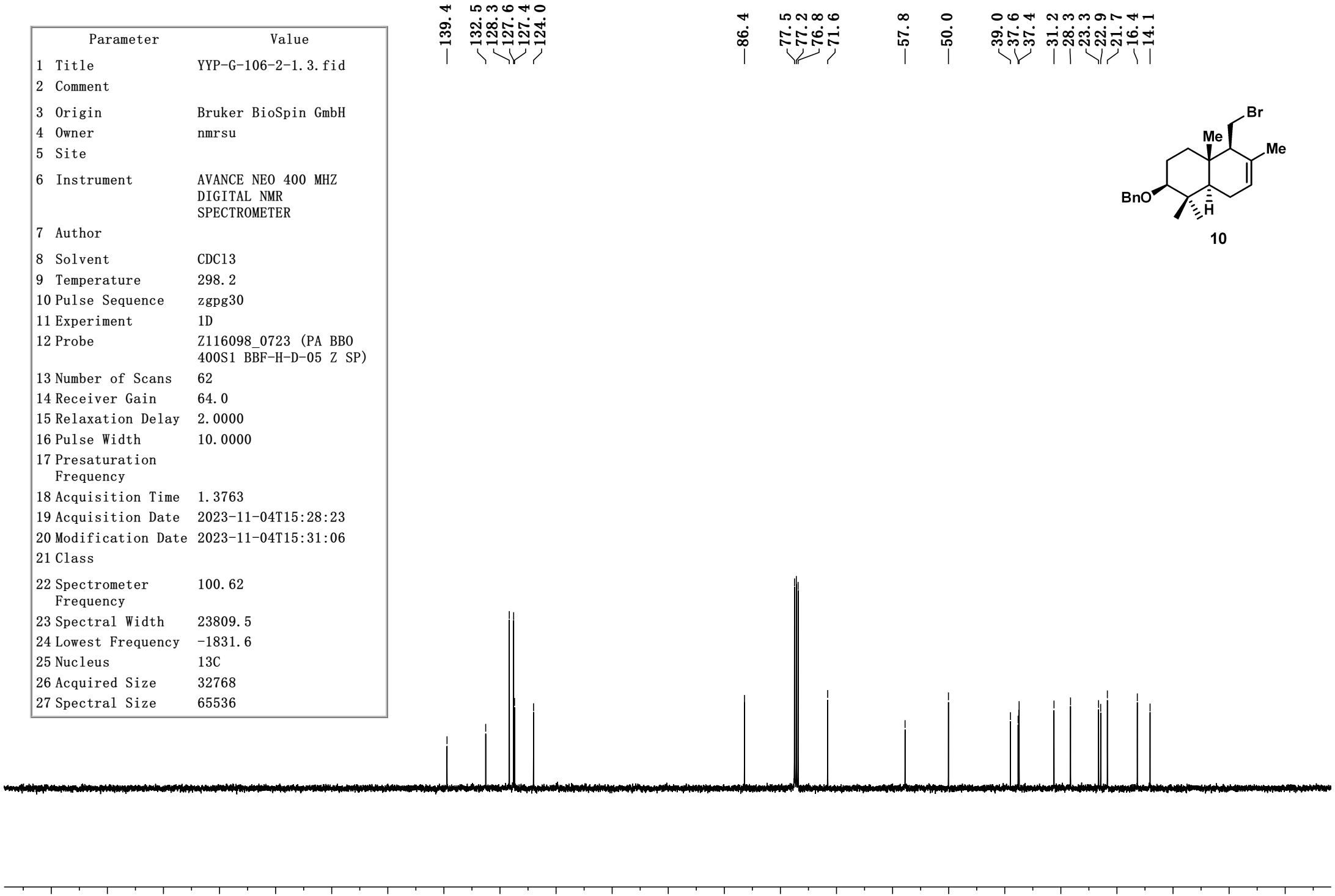
Parameter	Value
1 Title	YYP-G-082-1-3.2.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	Avance
7 Author	
8 Solvent	CDCl3
9 Temperature	295.7
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Probe	Z116098_0723 (PA BBO 400S1 BBF-H-D-05 Z SP)
13 Number of Scans	100
14 Receiver Gain	57.0
15 Relaxation Delay	2.0000
16 Pulse Width	9.7000
17 Presaturation Frequency	
18 Acquisition Time	1.3763
19 Acquisition Date	2023-09-21T18:55:19
20 Modification Date	2023-09-21T19:56:57
21 Class	
22 Spectrometer Frequency	100.61
23 Spectral Width	23809.5
24 Lowest Frequency	-1831.2
25 Nucleus	13C
26 Acquired Size	32768
27 Spectral Size	32768

Parameter	Value
1 Title	YYP-G-106-2-1.2.fid
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	298.1
10 Pulse Sequence	zg30
11 Experiment	1D
12 Probe	Z116098_0723 (PA BBO 400S1 BBF-H-D-05 Z SP)
13 Number of Scans	4
14 Receiver Gain	101.0
15 Relaxation Delay	1.0000
16 Pulse Width	8.8100
17 Presaturation Frequency	
18 Acquisition Time	3.9977
19 Acquisition Date	2023-11-04T15:23:52
20 Modification Date	2023-11-04T15:31:06
21 Class	
22 Spectrometer Frequency	400.13
23 Spectral Width	8196.7
24 Lowest Frequency	-1637.0
25 Nucleus	1H
26 Acquired Size	32768
27 Spectral Size	65536

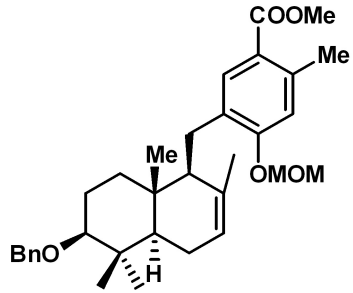


10

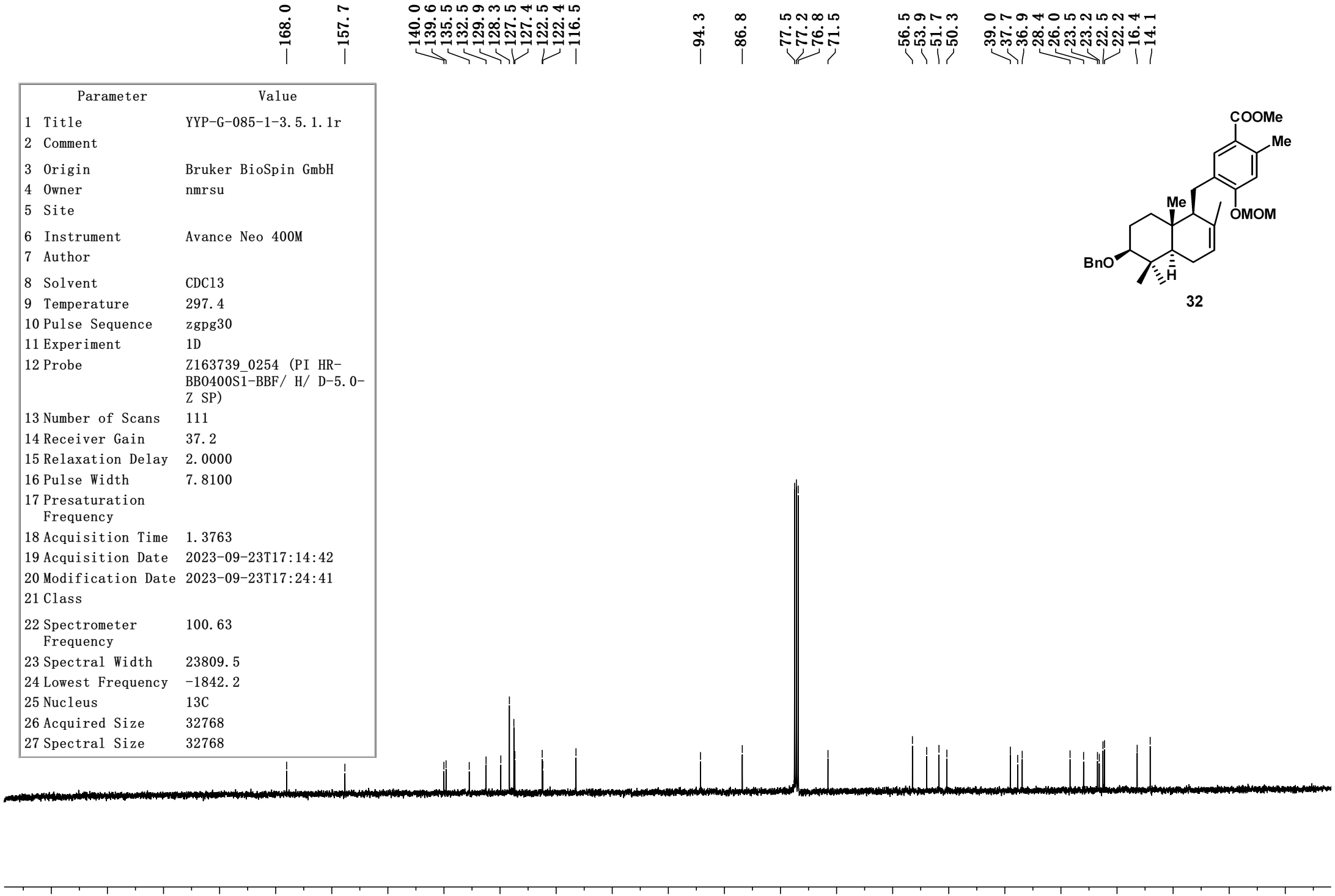
Parameter	Value
1 Title	YYP-G-106-2-1.3.fid
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDCl3
9 Temperature	298.2
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Probe	Z116098_0723 (PA BBO 400S1 BBF-H-D-05 Z SP)
13 Number of Scans	62
14 Receiver Gain	64.0
15 Relaxation Delay	2.0000
16 Pulse Width	10.0000
17 Presaturation Frequency	
18 Acquisition Time	1.3763
19 Acquisition Date	2023-11-04T15:28:23
20 Modification Date	2023-11-04T15:31:06
21 Class	
22 Spectrometer Frequency	100.62
23 Spectral Width	23809.5
24 Lowest Frequency	-1831.6
25 Nucleus	13C
26 Acquired Size	32768
27 Spectral Size	65536



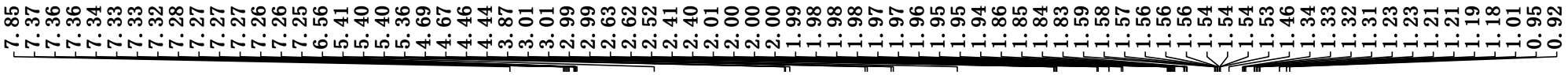
	Parameter	Value
1	Title	YYP-G-085-1-3.3.1.1r
2	Comment	
3	Origin	Bruker BioSpin GmbH
4	Owner	nmrsu
5	Site	
6	Instrument	Avance NEO 600
7	Author	
8	Solvent	CDCl3
9	Temperature	298.1
10	Pulse Sequence	zg30
11	Experiment	1D
12	Probe	Z114607_0339 (PA BBO 600S3 BBF-H-D-05 Z SP)
13	Number of Scans	2
14	Receiver Gain	71.8
15	Relaxation Delay	1.0000
16	Pulse Width	10.0000
17	Presaturation Frequency	
18	Acquisition Time	2.7525
19	Acquisition Date	2023-09-23T17:00:01
20	Modification Date	2023-09-23T17:24:40
21	Class	
22	Spectrometer Frequency	600.15
23	Spectral Width	11904.8
24	Lowest Frequency	-2260.9
25	Nucleus	1H
26	Acquired Size	32768
27	Spectral Size	65536



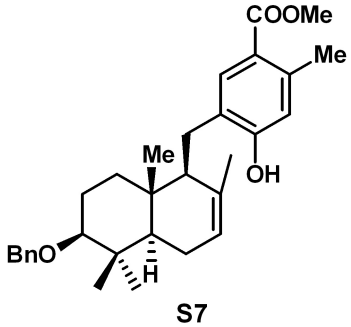
32



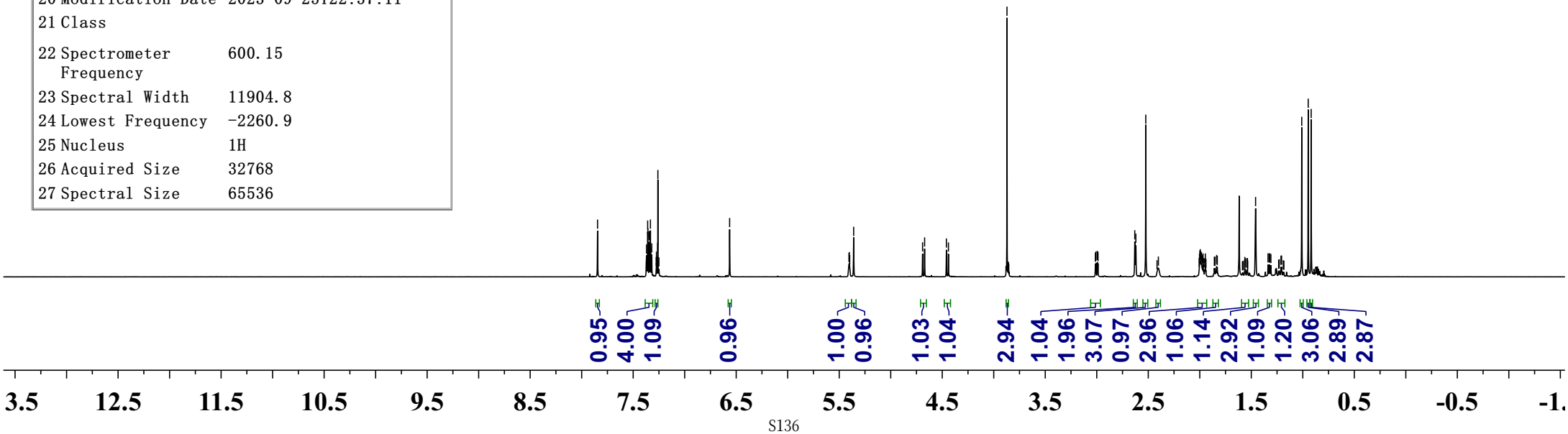
Parameter	Value
1 Title	YYP-G-085-1-3.5.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	Avance Neo 400M
7 Author	
8 Solvent	CDC13
9 Temperature	297.4
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Probe	Z163739_0254 (PI HR-BBO400S1-BBF/ H/ D-5.0-Z SP)
13 Number of Scans	111
14 Receiver Gain	37.2
15 Relaxation Delay	2.0000
16 Pulse Width	7.8100
17 Presaturation Frequency	
18 Acquisition Time	1.3763
19 Acquisition Date	2023-09-23T17:14:42
20 Modification Date	2023-09-23T17:24:41
21 Class	
22 Spectrometer Frequency	100.63
23 Spectral Width	23809.5
24 Lowest Frequency	-1842.2
25 Nucleus	13C
26 Acquired Size	32768
27 Spectral Size	32768

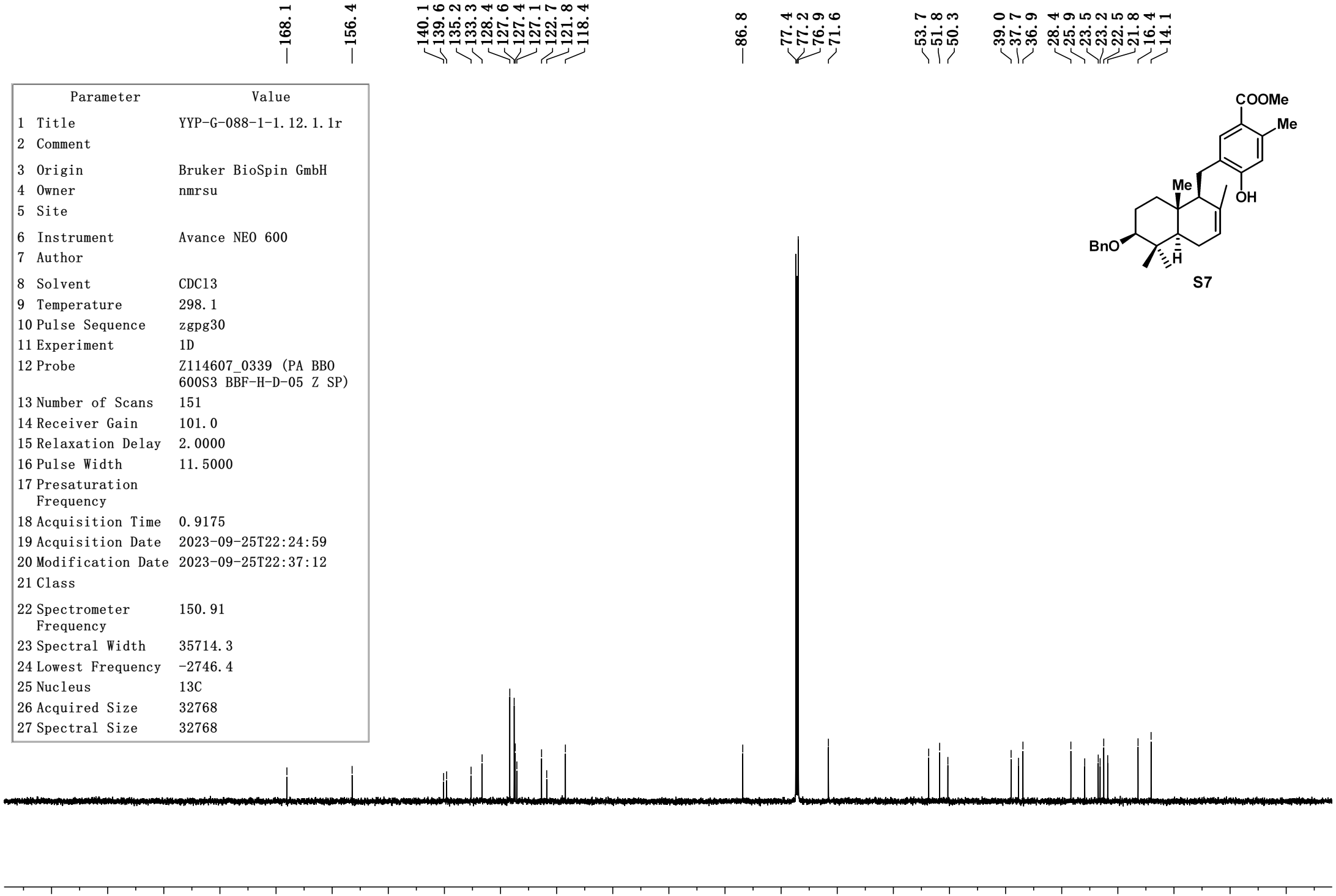


Parameter	Value
1 Title	YYP-G-088-1-1.11.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	Avance NEO 600
7 Author	
8 Solvent	CDCl3
9 Temperature	298.2
10 Pulse Sequence	zg30
11 Experiment	1D
12 Probe	Z114607_0339 (PA BBO 600S3 BBF-H-D-05 Z SP)
13 Number of Scans	6
14 Receiver Gain	101.0
15 Relaxation Delay	1.0000
16 Pulse Width	10.0000
17 Presaturation Frequency	
18 Acquisition Time	2.7525
19 Acquisition Date	2023-09-25T22:16:11
20 Modification Date	2023-09-25T22:37:11
21 Class	
22 Spectrometer Frequency	600.15
23 Spectral Width	11904.8
24 Lowest Frequency	-2260.9
25 Nucleus	1H
26 Acquired Size	32768
27 Spectral Size	65536

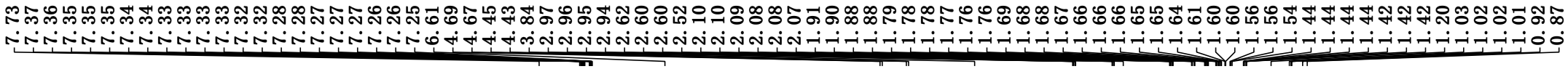


S7

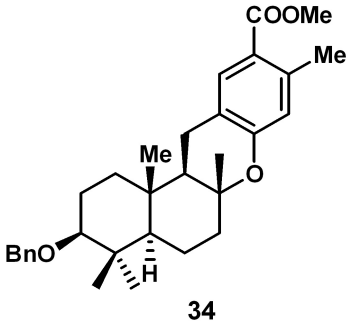




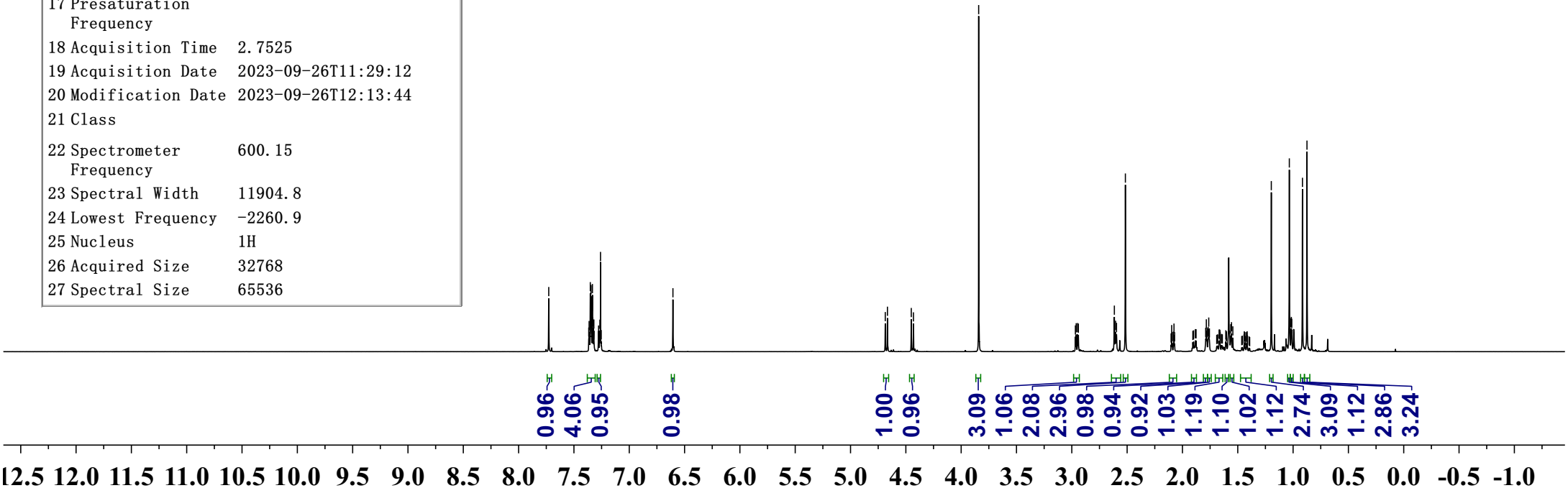
Parameter	Value
1 Title	YYP-G-088-1-1.12.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	Avance NEO 600
7 Author	
8 Solvent	CDCl3
9 Temperature	298.1
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Probe	Z114607_0339 (PA BBO 600S3 BBF-H-D-05 Z SP)
13 Number of Scans	151
14 Receiver Gain	101.0
15 Relaxation Delay	2.0000
16 Pulse Width	11.5000
17 Presaturation Frequency	
18 Acquisition Time	0.9175
19 Acquisition Date	2023-09-25T22:24:59
20 Modification Date	2023-09-25T22:37:12
21 Class	
22 Spectrometer Frequency	150.91
23 Spectral Width	35714.3
24 Lowest Frequency	-2746.4
25 Nucleus	13C
26 Acquired Size	32768
27 Spectral Size	32768

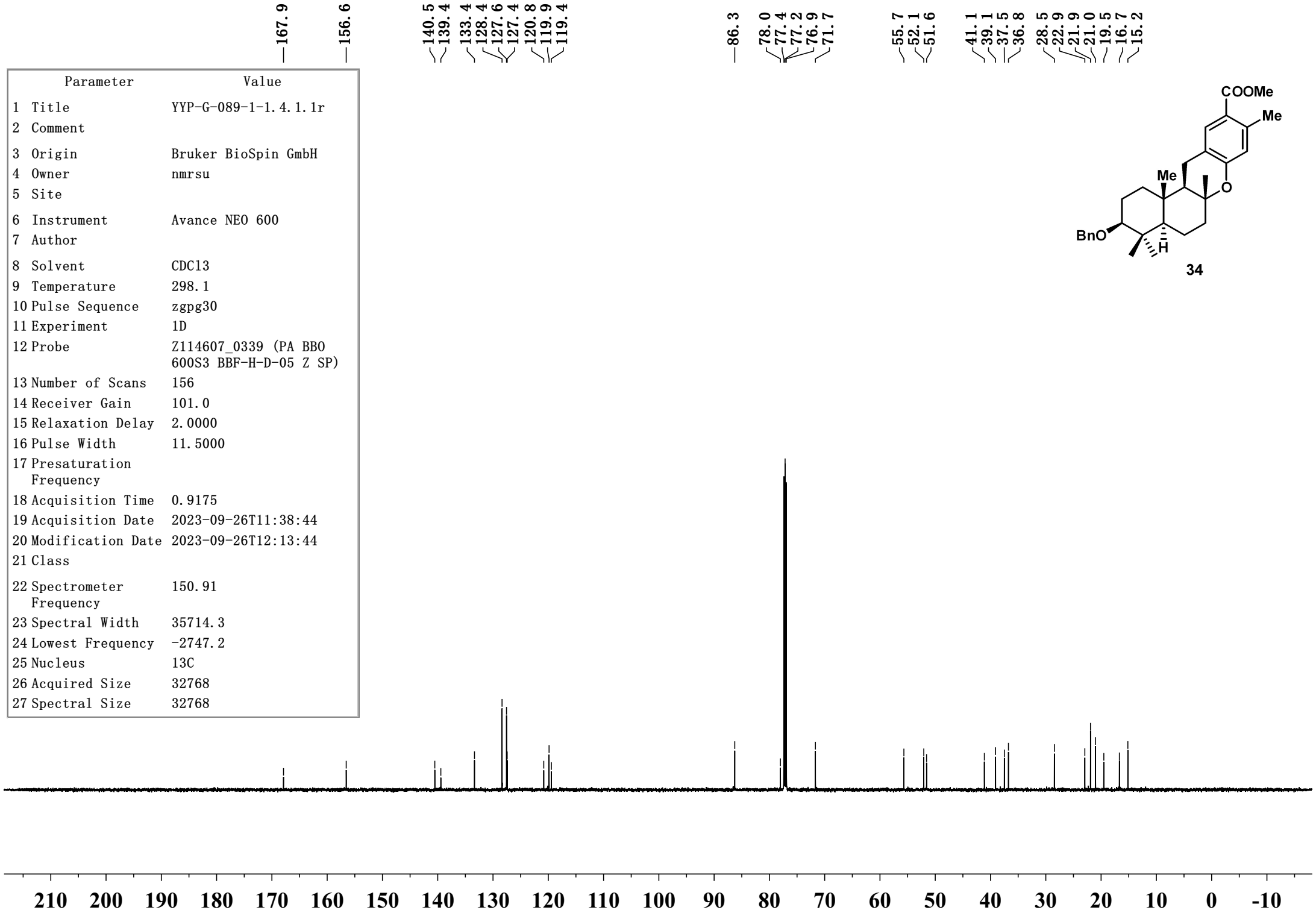


Parameter	Value
1 Title	YYP-G-089-1-1.3.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	Avance NEO 600
7 Author	
8 Solvent	CDCl3
9 Temperature	298.2
10 Pulse Sequence	zg30
11 Experiment	1D
12 Probe	Z114607_0339 (PA BBO 600S3 BBF-H-D-05 Z SP)
13 Number of Scans	6
14 Receiver Gain	101.0
15 Relaxation Delay	1.0000
16 Pulse Width	10.0000
17 Presaturation Frequency	
18 Acquisition Time	2.7525
19 Acquisition Date	2023-09-26T11:29:12
20 Modification Date	2023-09-26T12:13:44
21 Class	
22 Spectrometer Frequency	600.15
23 Spectral Width	11904.8
24 Lowest Frequency	-2260.9
25 Nucleus	1H
26 Acquired Size	32768
27 Spectral Size	65536

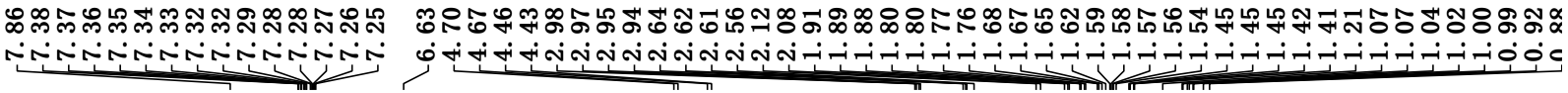


34

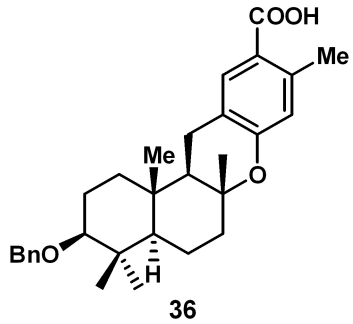




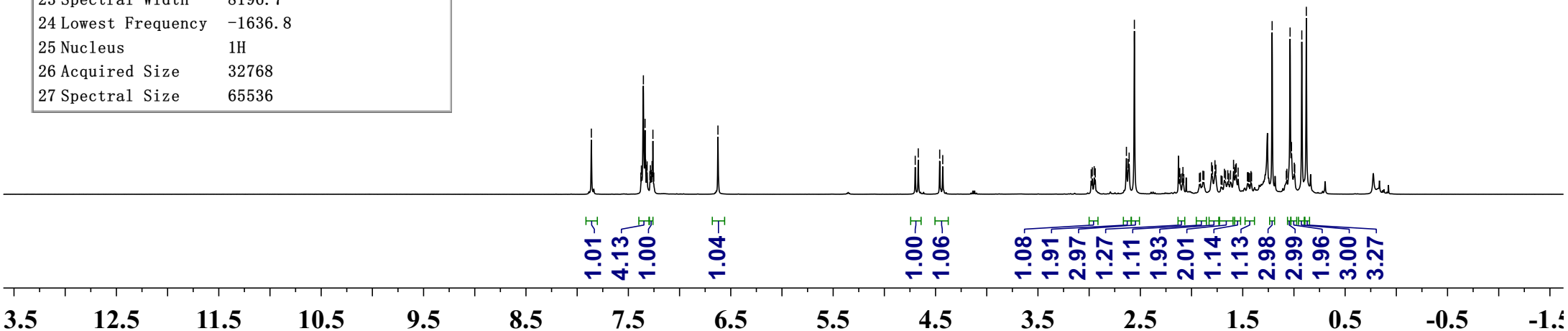
Parameter	Value
1 Title	YYP-G-089-1-1.4.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	Avance NEO 600
7 Author	
8 Solvent	CDCl3
9 Temperature	298.1
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Probe	Z114607_0339 (PA BBO 600S3 BBF-H-D-05 Z SP)
13 Number of Scans	156
14 Receiver Gain	101.0
15 Relaxation Delay	2.0000
16 Pulse Width	11.5000
17 Presaturation Frequency	
18 Acquisition Time	0.9175
19 Acquisition Date	2023-09-26T11:38:44
20 Modification Date	2023-09-26T12:13:44
21 Class	
22 Spectrometer Frequency	150.91
23 Spectral Width	35714.3
24 Lowest Frequency	-2747.2
25 Nucleus	13C
26 Acquired Size	32768
27 Spectral Size	32768

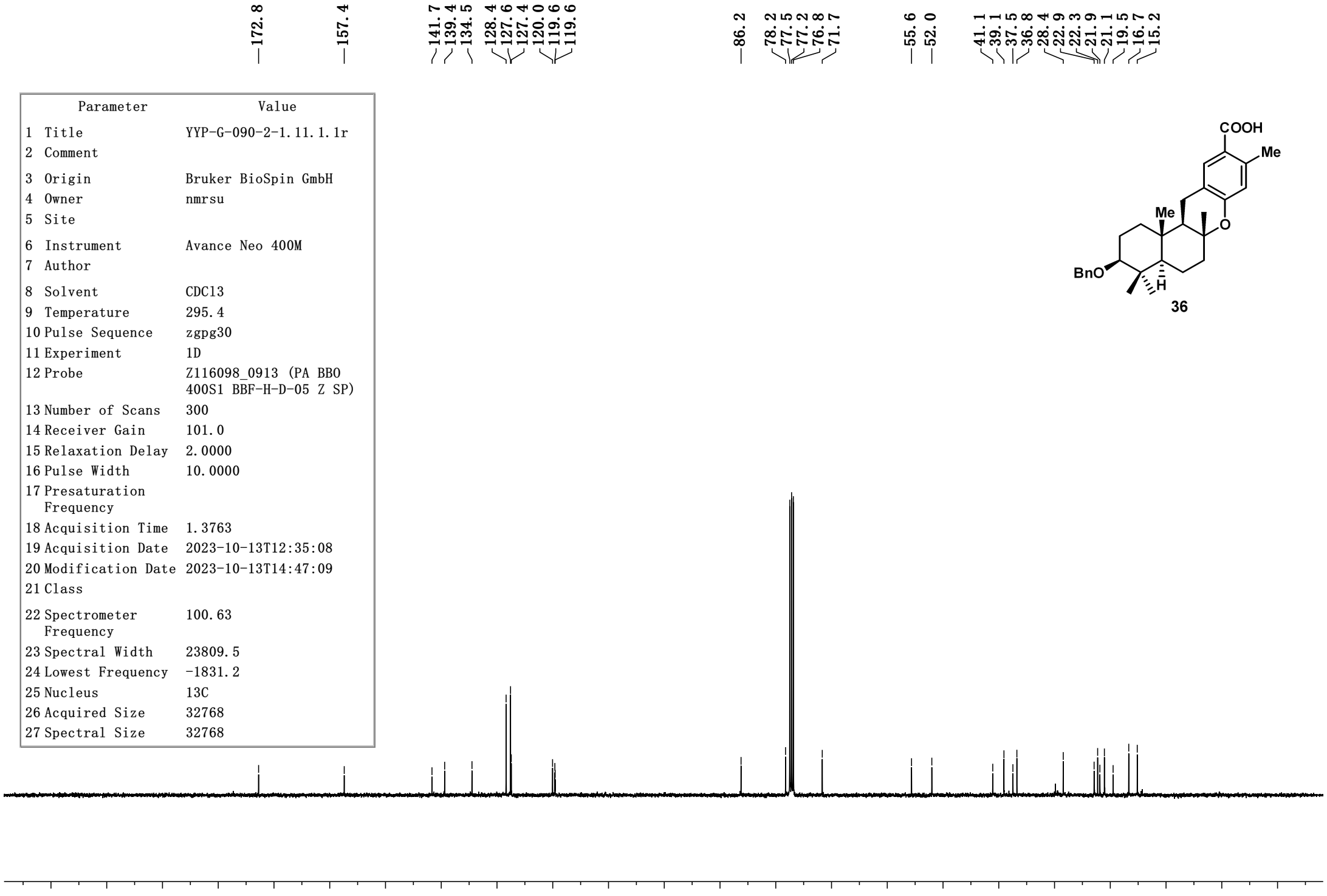


Parameter	Value
1 Title	YYP-G-090-2-1.10.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	Avance Neo 400M
7 Author	
8 Solvent	CDC13
9 Temperature	295.2
10 Pulse Sequence	zg30
11 Experiment	1D
12 Probe	Z116098_0913 (PA BBO 400S1 BBF-H-D-05 Z SP)
13 Number of Scans	16
14 Receiver Gain	101.0
15 Relaxation Delay	1.0000
16 Pulse Width	10.0000
17 Presaturation Frequency	
18 Acquisition Time	3.9977
19 Acquisition Date	2023-10-13T12:16:23
20 Modification Date	2023-10-13T14:47:08
21 Class	
22 Spectrometer Frequency	400.18
23 Spectral Width	8196.7
24 Lowest Frequency	-1636.8
25 Nucleus	1H
26 Acquired Size	32768
27 Spectral Size	65536



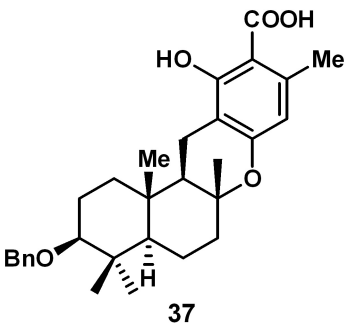
36



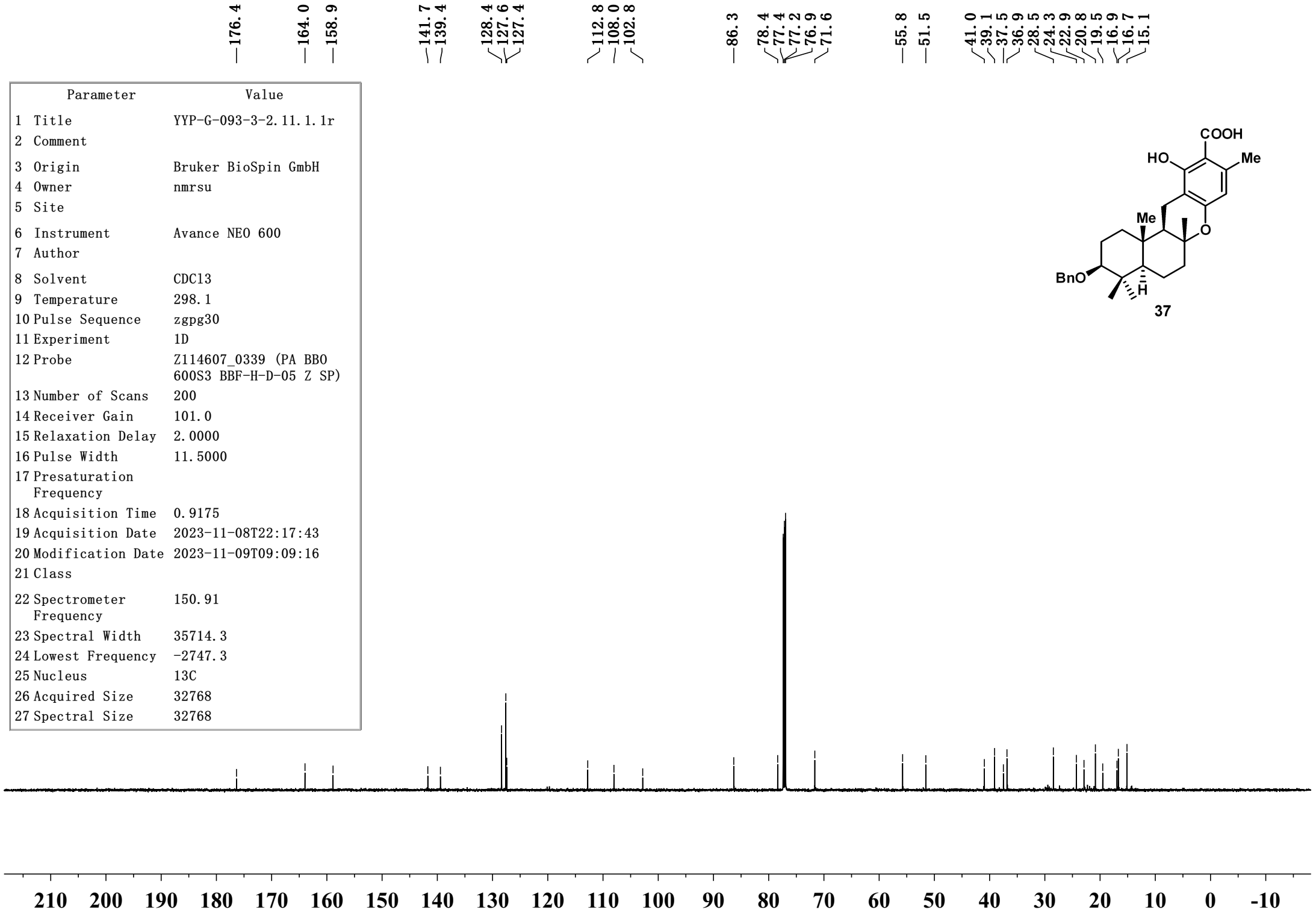


Parameter	Value
1 Title	YYP-G-090-2-1.11.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	Avance Neo 400M
7 Author	
8 Solvent	CDCl3
9 Temperature	295.4
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Probe	Z116098_0913 (PA BBO 400S1 BBF-H-D-05 Z SP)
13 Number of Scans	300
14 Receiver Gain	101.0
15 Relaxation Delay	2.0000
16 Pulse Width	10.0000
17 Presaturation Frequency	
18 Acquisition Time	1.3763
19 Acquisition Date	2023-10-13T12:35:08
20 Modification Date	2023-10-13T14:47:09
21 Class	
22 Spectrometer Frequency	100.63
23 Spectral Width	23809.5
24 Lowest Frequency	-1831.2
25 Nucleus	13C
26 Acquired Size	32768
27 Spectral Size	32768

	Parameter	Value
1	Title	YYP-G-093-3-2.10.1.1r
2	Comment	
3	Origin	Bruker BioSpin GmbH
4	Owner	nmrsu
5	Site	
6	Instrument	Avance NEO 600
7	Author	
8	Solvent	CDCl3
9	Temperature	298.1
10	Pulse Sequence	zg30
11	Experiment	1D
12	Probe	Z114607_0339 (PA BBO 600S3 BBF-H-D-05 Z SP)
13	Number of Scans	8
14	Receiver Gain	71.8
15	Relaxation Delay	1.0000
16	Pulse Width	10.0000
17	Presaturation Frequency	
18	Acquisition Time	2.7525
19	Acquisition Date	2023-11-08T22:07:04
20	Modification Date	2023-11-09T09:09:16
21	Class	
22	Spectrometer Frequency	600.15
23	Spectral Width	11904.8
24	Lowest Frequency	-2260.8
25	Nucleus	1H
26	Acquired Size	32768
27	Spectral Size	65536

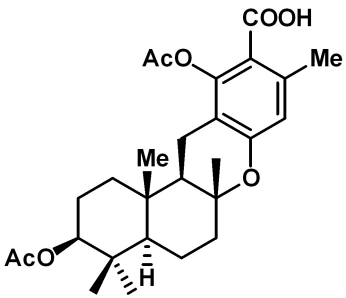


37

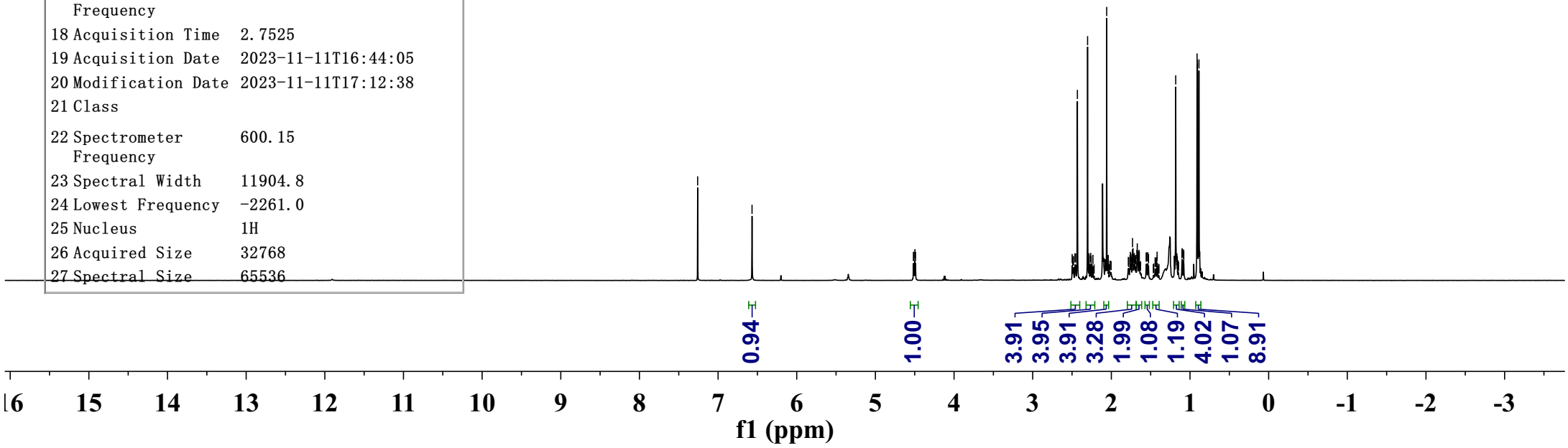


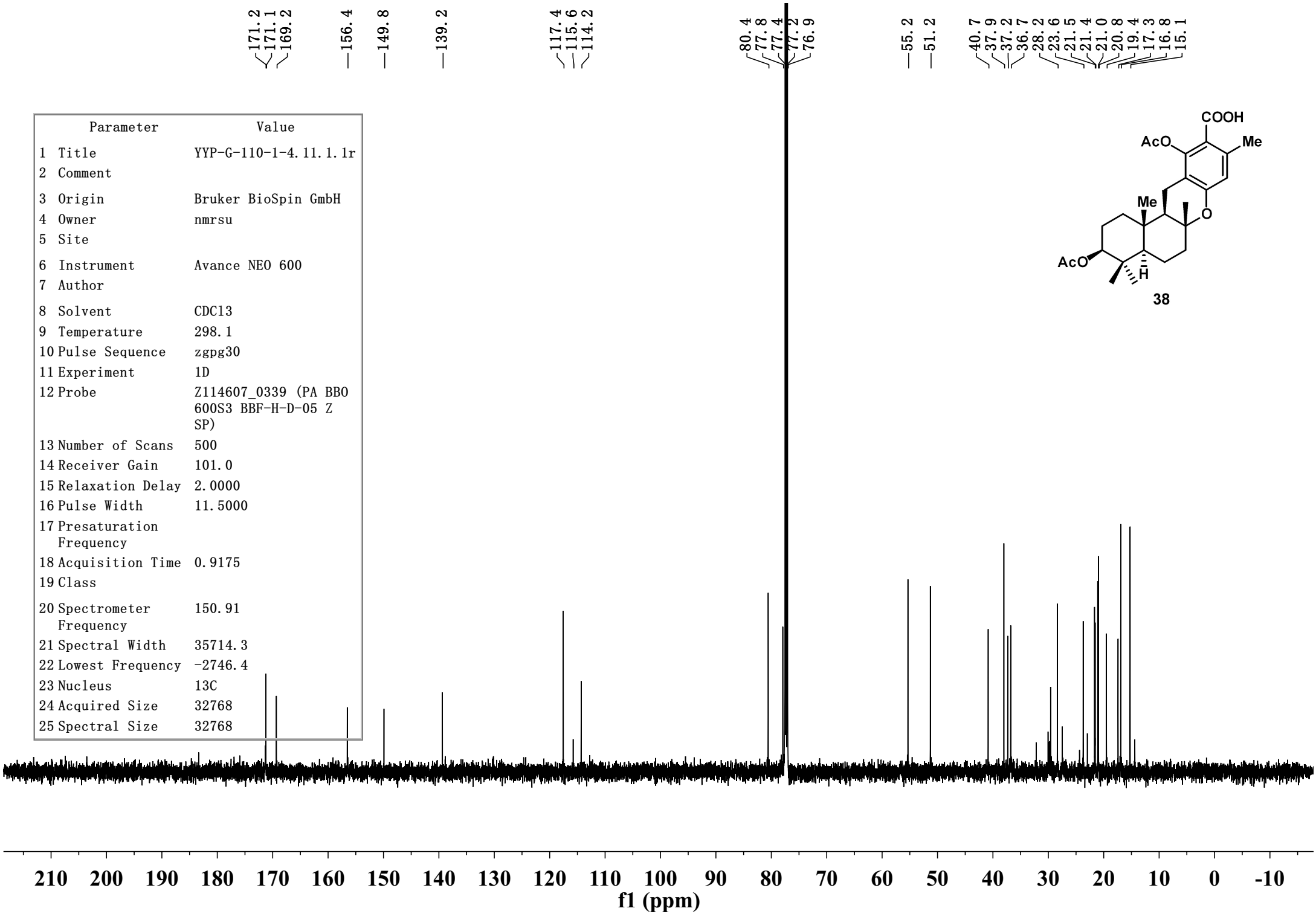
Parameter	Value
1 Title	YYP-G-093-3-2.11.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	Avance NEO 600
7 Author	
8 Solvent	CDCl3
9 Temperature	298.1
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Probe	Z114607_0339 (PA BBO 600S3 BBF-H-D-05 Z SP)
13 Number of Scans	200
14 Receiver Gain	101.0
15 Relaxation Delay	2.0000
16 Pulse Width	11.5000
17 Presaturation Frequency	
18 Acquisition Time	0.9175
19 Acquisition Date	2023-11-08T22:17:43
20 Modification Date	2023-11-09T09:09:16
21 Class	
22 Spectrometer Frequency	150.91
23 Spectral Width	35714.3
24 Lowest Frequency	-2747.3
25 Nucleus	13C
26 Acquired Size	32768
27 Spectral Size	32768

	Parameter	Value
1	Title	YYP-G-110-1-4.10.1.1r
2	Comment	
3	Origin	Bruker BioSpin GmbH
4	Owner	nmrsu
5	Site	
6	Instrument	Avance NEO 600
7	Author	
8	Solvent	CDCl3
9	Temperature	298.1
10	Pulse Sequence	zg30
11	Experiment	1D
12	Probe	Z114607_0339 (PA BBO 600S3 BBF-H-D-05 Z SP)
13	Number of Scans	8
14	Receiver Gain	101.0
15	Relaxation Delay	1.0000
16	Pulse Width	10.0000
17	Presaturation Frequency	
18	Acquisition Time	2.7525
19	Acquisition Date	2023-11-11T16:44:05
20	Modification Date	2023-11-11T17:12:38
21	Class	
22	Spectrometer Frequency	600.15
23	Spectral Width	11904.8
24	Lowest Frequency	-2261.0
25	Nucleus	1H
26	Acquired Size	32768
27	Spectral Size	65536

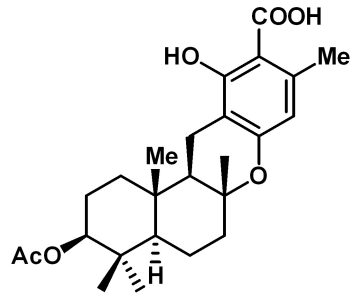


38



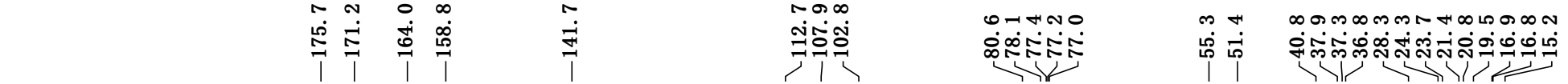

171.2
171.1
169.2
156.4
149.8
139.2
117.4
115.6
114.2
80.4
77.8
77.4
77.2
76.9
55.2
51.2
40.7
37.9
37.2
36.7
28.2
23.6
21.5
21.4
21.0
20.8
19.4
17.3
16.8
15.1
Parameter Value
1 Title YYP-G-110-1-4.11.1.1r
2 Comment
3 Origin Bruker BioSpin GmbH
4 Owner nmrsu
5 Site
6 Instrument Avance NEO 600
7 Author
8 Solvent CDCl3
9 Temperature 298.1
10 Pulse Sequence zgpg30
11 Experiment 1D
12 Probe Z114607_0339 (PA BBO 600S3 BBF-H-D-05 Z SP)
13 Number of Scans 500
14 Receiver Gain 101.0
15 Relaxation Delay 2.0000
16 Pulse Width 11.5000
17 Presaturation Frequency
18 Acquisition Time 0.9175
19 Class
20 Spectrometer Frequency 150.91
21 Spectral Width 35714.3
22 Lowest Frequency -2746.4
23 Nucleus 13C
24 Acquired Size 32768
25 Spectral Size 32768
COOH
AcO
Me
Me
O
AcO
H
38
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Parameter	Value
1 Title	YYP-G-112-1-1.1.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDCl3
9 Temperature	293.7
10 Pulse Sequence	zg30
11 Experiment	1D
12 Probe	Z116098_0723 (PA BBO 400S1 BBF-H-D-05 Z SP)
13 Number of Scans	8
14 Receiver Gain	101.0
15 Relaxation Delay	1.0000
16 Pulse Width	8.8100
17 Presaturation Frequency	
18 Acquisition Time	3.9977
19 Acquisition Date	2023-11-14T18:20:19
20 Modification Date	2023-11-14T18:39:02
21 Class	
22 Spectrometer Frequency	400.13
23 Spectral Width	8196.7
24 Lowest Frequency	-1637.2
25 Nucleus	1H
26 Acquired Size	32768
27 Spectral Size	65536

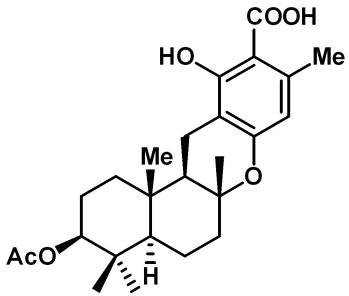


(+)-Hongoquercin B

2

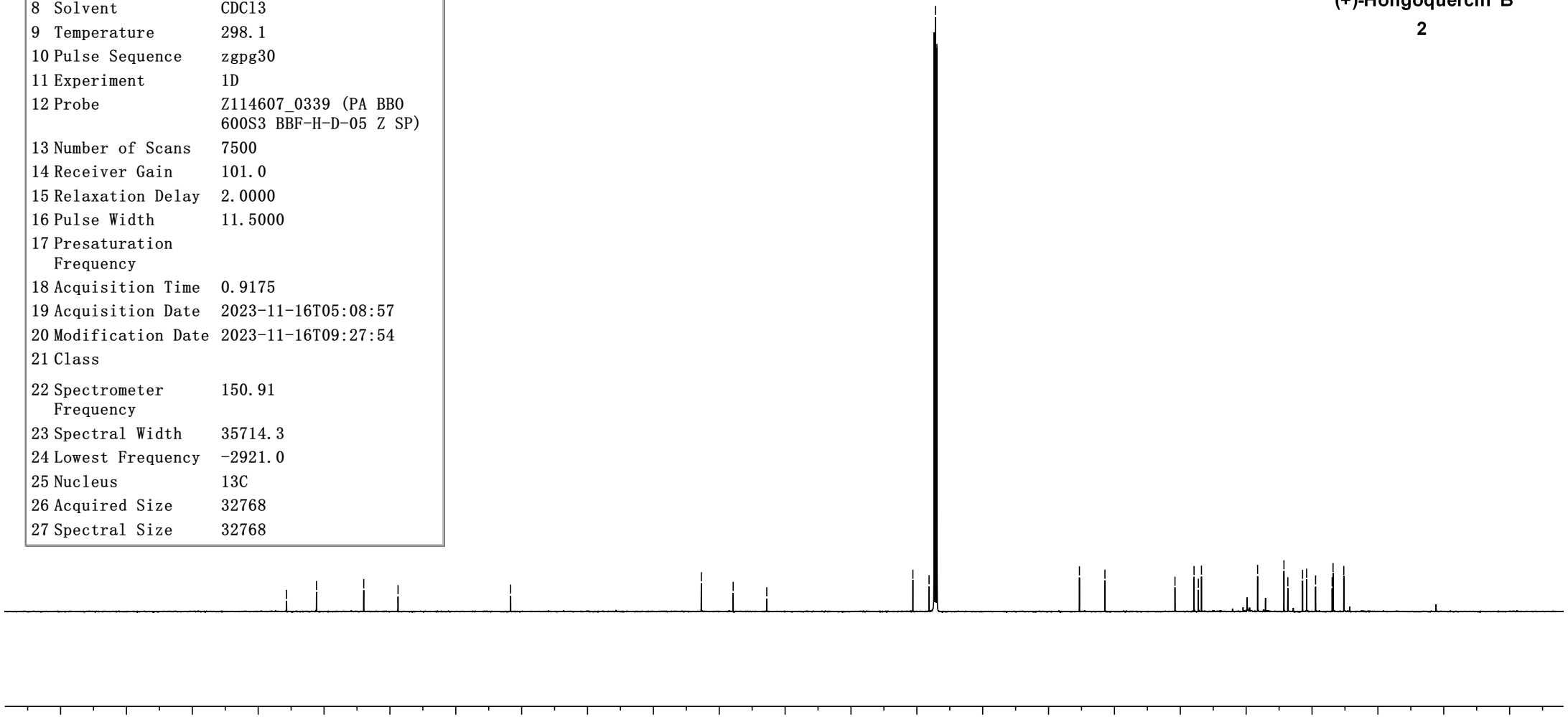


Parameter	Value
1 Title	YYP-G-112-1-1.23.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	Avance NEO 600
7 Author	
8 Solvent	CDCl3
9 Temperature	298.1
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Probe	Z114607_0339 (PA BBO 600S3 BBF-H-D-05 Z SP)
13 Number of Scans	7500
14 Receiver Gain	101.0
15 Relaxation Delay	2.0000
16 Pulse Width	11.5000
17 Presaturation Frequency	
18 Acquisition Time	0.9175
19 Acquisition Date	2023-11-16T05:08:57
20 Modification Date	2023-11-16T09:27:54
21 Class	
22 Spectrometer Frequency	150.91
23 Spectral Width	35714.3
24 Lowest Frequency	-2921.0
25 Nucleus	13C
26 Acquired Size	32768
27 Spectral Size	32768

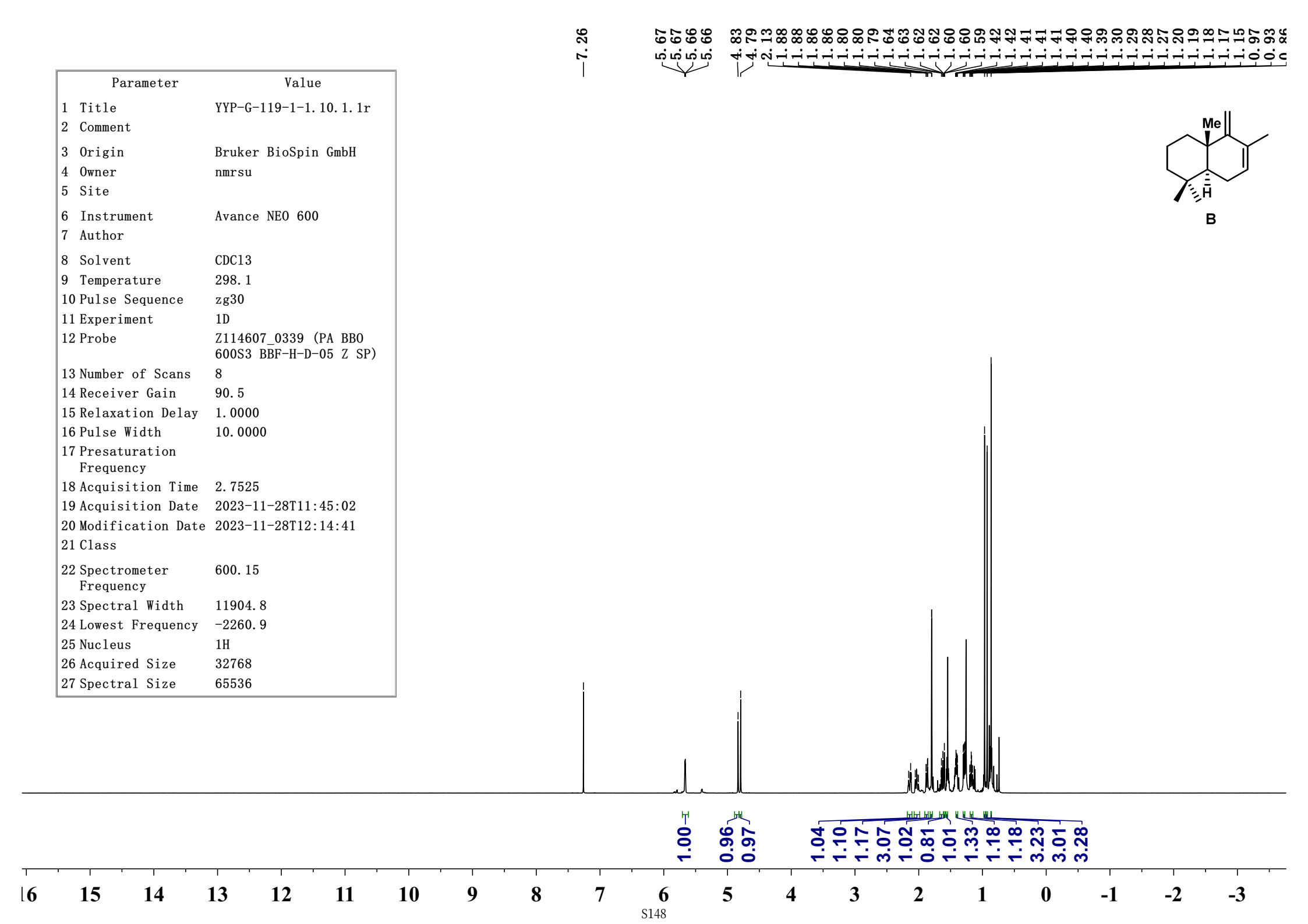


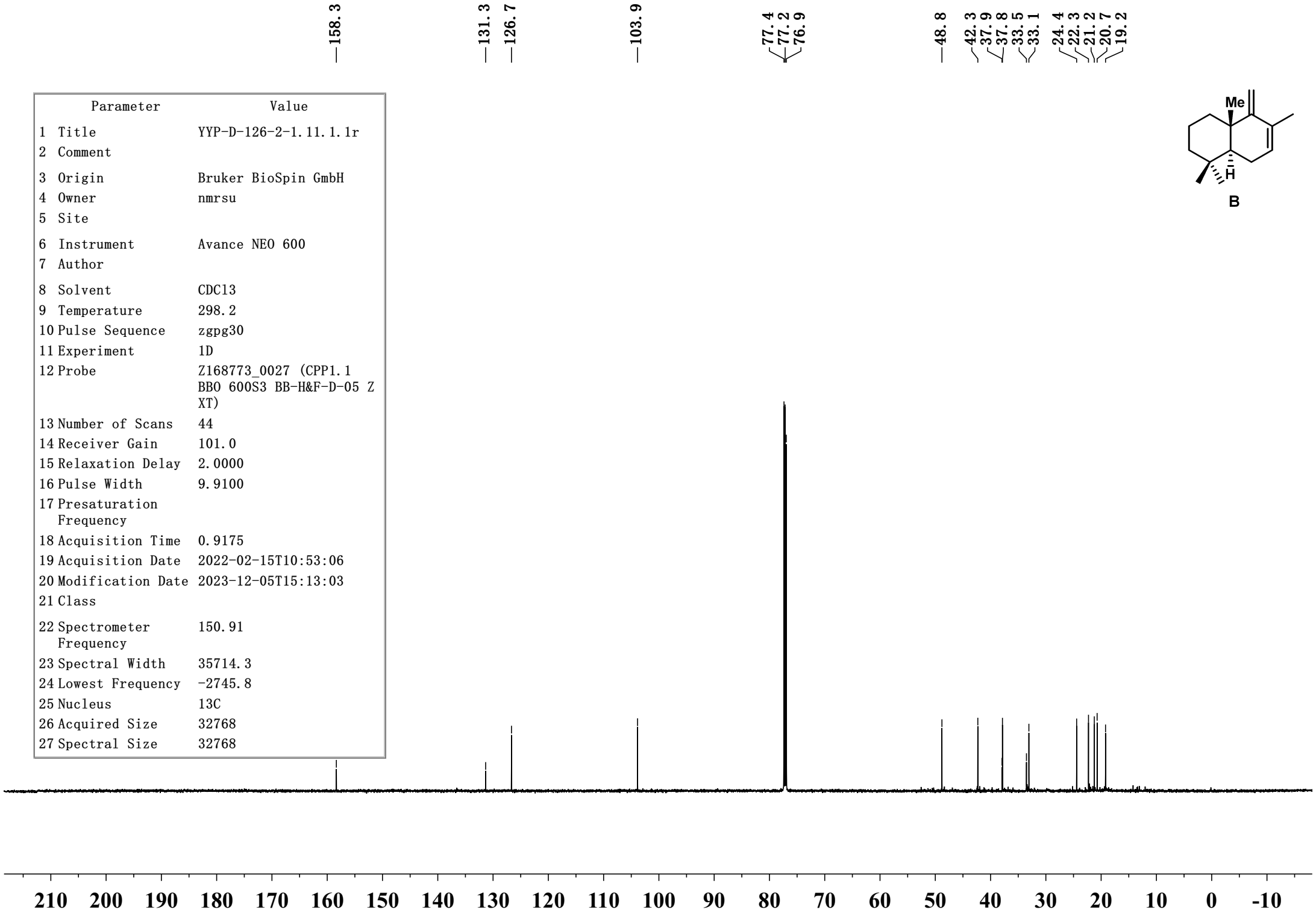
(+)-Hongoquercin B

2



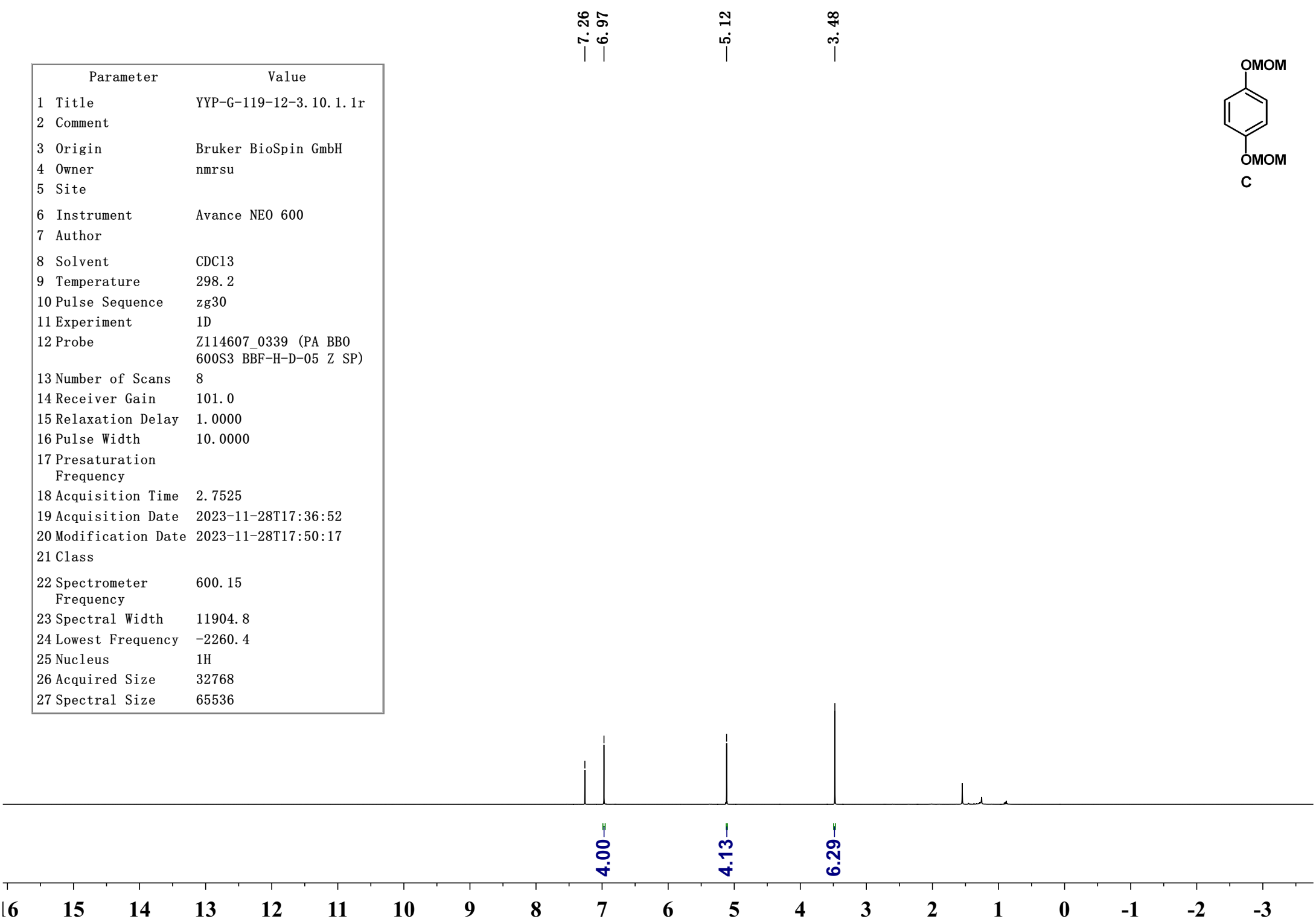
	Parameter	Value
1	Title	YYP-G-119-1-1.10.1.1r
2	Comment	
3	Origin	Bruker BioSpin GmbH
4	Owner	nmrsu
5	Site	
6	Instrument	Avance NEO 600
7	Author	
8	Solvent	CDCl3
9	Temperature	298.1
10	Pulse Sequence	zg30
11	Experiment	1D
12	Probe	Z114607_0339 (PA BBO 600S3 BBF-H-D-05 Z SP)
13	Number of Scans	8
14	Receiver Gain	90.5
15	Relaxation Delay	1.0000
16	Pulse Width	10.0000
17	Presaturation Frequency	
18	Acquisition Time	2.7525
19	Acquisition Date	2023-11-28T11:45:02
20	Modification Date	2023-11-28T12:14:41
21	Class	
22	Spectrometer Frequency	600.15
23	Spectral Width	11904.8
24	Lowest Frequency	-2260.9
25	Nucleus	1H
26	Acquired Size	32768
27	Spectral Size	65536



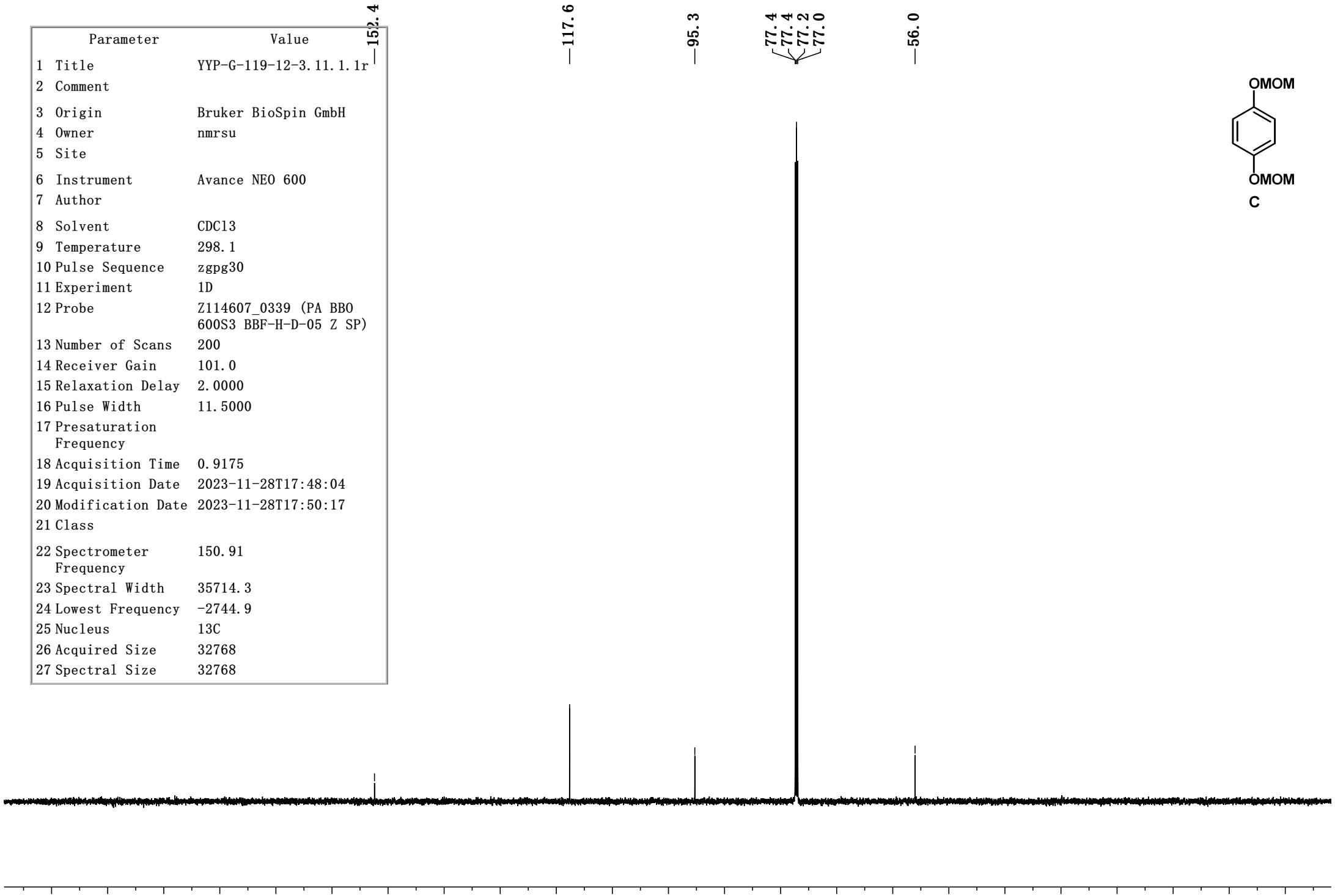


Parameter	Value
1 Title	YYP-D-126-2-1.11.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	Avance NEO 600
7 Author	
8 Solvent	CDCl3
9 Temperature	298.2
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Probe	Z168773_0027 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
13 Number of Scans	44
14 Receiver Gain	101.0
15 Relaxation Delay	2.0000
16 Pulse Width	9.9100
17 Presaturation Frequency	
18 Acquisition Time	0.9175
19 Acquisition Date	2022-02-15T10:53:06
20 Modification Date	2023-12-05T15:13:03
21 Class	
22 Spectrometer Frequency	150.91
23 Spectral Width	35714.3
24 Lowest Frequency	-2745.8
25 Nucleus	13C
26 Acquired Size	32768
27 Spectral Size	32768

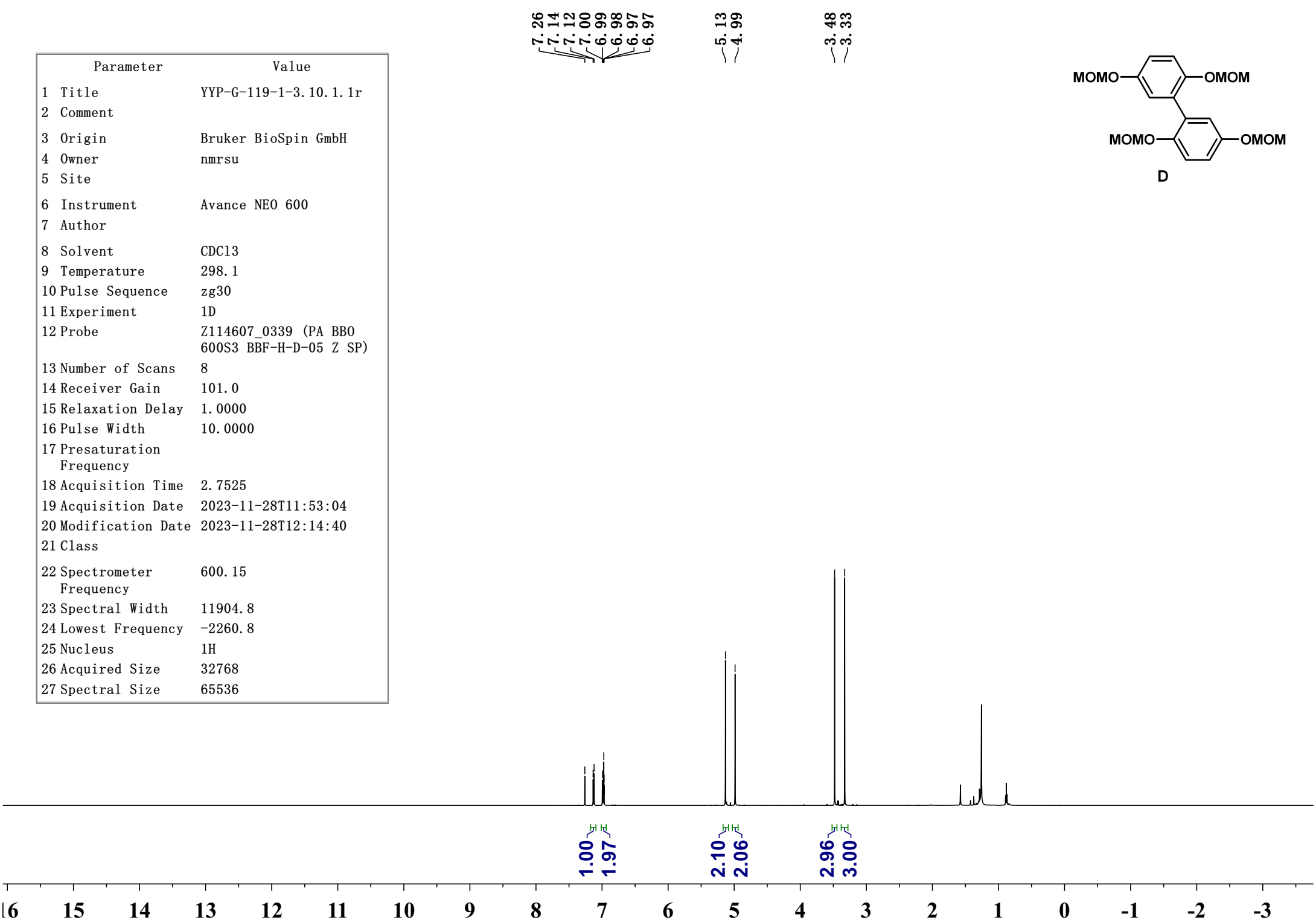
	Parameter	Value
1	Title	YYP-G-119-12-3.10.1.1r
2	Comment	
3	Origin	Bruker BioSpin GmbH
4	Owner	nmrsu
5	Site	
6	Instrument	Avance NEO 600
7	Author	
8	Solvent	CDCl3
9	Temperature	298.2
10	Pulse Sequence	zg30
11	Experiment	1D
12	Probe	Z114607_0339 (PA BBO 600S3 BBF-H-D-05 Z SP)
13	Number of Scans	8
14	Receiver Gain	101.0
15	Relaxation Delay	1.0000
16	Pulse Width	10.0000
17	Presaturation Frequency	
18	Acquisition Time	2.7525
19	Acquisition Date	2023-11-28T17:36:52
20	Modification Date	2023-11-28T17:50:17
21	Class	
22	Spectrometer Frequency	600.15
23	Spectral Width	11904.8
24	Lowest Frequency	-2260.4
25	Nucleus	1H
26	Acquired Size	32768
27	Spectral Size	65536

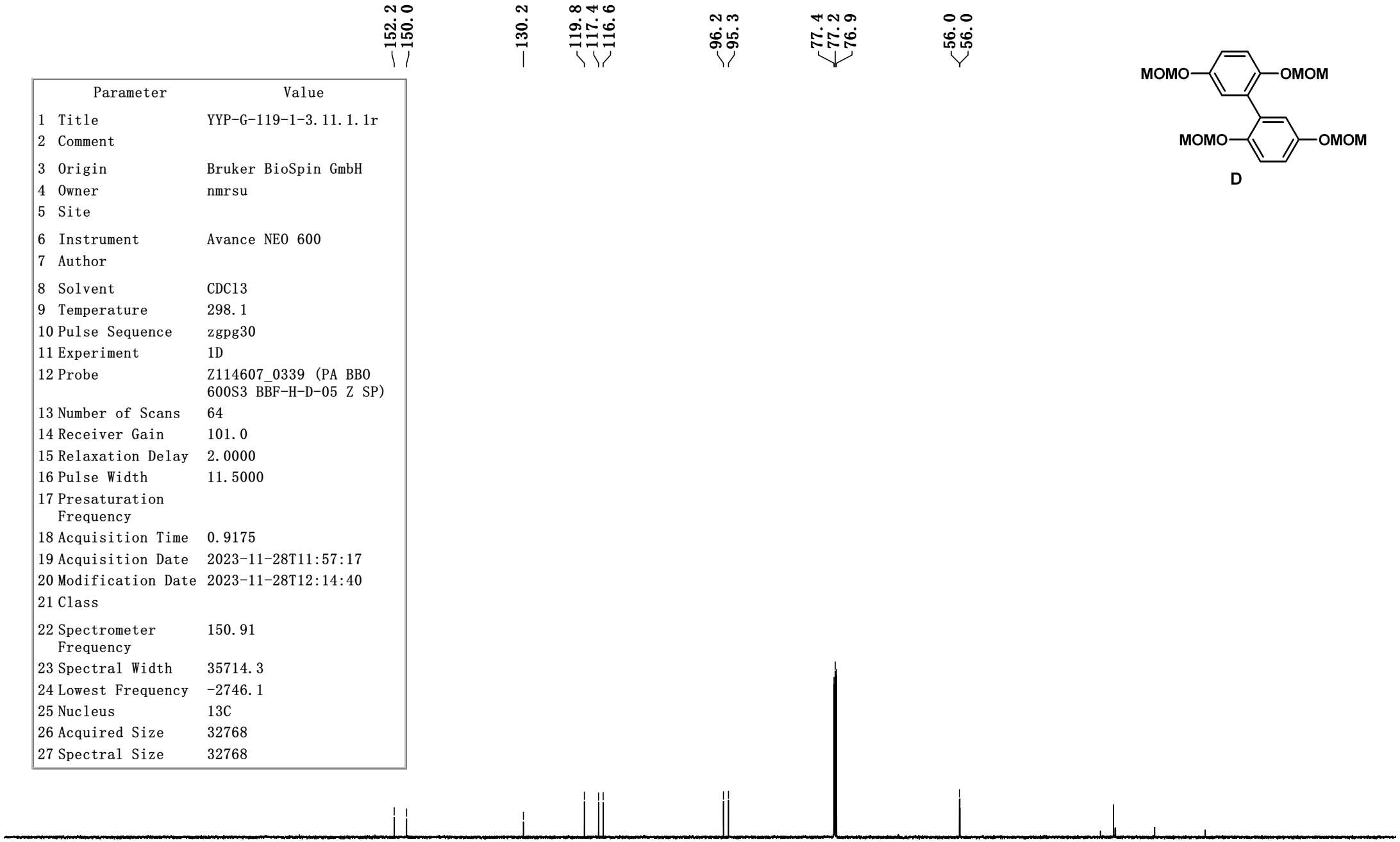


Parameter	Value
1 Title	YYP-G-119-12-3.11.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	Avance NEO 600
7 Author	
8 Solvent	CDCl3
9 Temperature	298.1
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Probe	Z114607_0339 (PA BBO 600S3 BBF-H-D-05 Z SP)
13 Number of Scans	200
14 Receiver Gain	101.0
15 Relaxation Delay	2.0000
16 Pulse Width	11.5000
17 Presaturation Frequency	
18 Acquisition Time	0.9175
19 Acquisition Date	2023-11-28T17:48:04
20 Modification Date	2023-11-28T17:50:17
21 Class	
22 Spectrometer Frequency	150.91
23 Spectral Width	35714.3
24 Lowest Frequency	-2744.9
25 Nucleus	13C
26 Acquired Size	32768
27 Spectral Size	32768



	Parameter	Value
1	Title	YYP-G-119-1-3.10.1.1r
2	Comment	
3	Origin	Bruker BioSpin GmbH
4	Owner	nmrsu
5	Site	
6	Instrument	Avance NEO 600
7	Author	
8	Solvent	CDCl3
9	Temperature	298.1
10	Pulse Sequence	zg30
11	Experiment	1D
12	Probe	Z114607_0339 (PA BBO 600S3 BBF-H-D-05 Z SP)
13	Number of Scans	8
14	Receiver Gain	101.0
15	Relaxation Delay	1.0000
16	Pulse Width	10.0000
17	Presaturation Frequency	
18	Acquisition Time	2.7525
19	Acquisition Date	2023-11-28T11:53:04
20	Modification Date	2023-11-28T12:14:40
21	Class	
22	Spectrometer Frequency	600.15
23	Spectral Width	11904.8
24	Lowest Frequency	-2260.8
25	Nucleus	1H
26	Acquired Size	32768
27	Spectral Size	65536





Parameter	Value
1 Title	YYP-G-119-1-3.11.1.1r
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Instrument	Avance NEO 600
7 Author	
8 Solvent	CDCl3
9 Temperature	298.1
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Probe	Z114607_0339 (PA BBO 600S3 BBF-H-D-05 Z SP)
13 Number of Scans	64
14 Receiver Gain	101.0
15 Relaxation Delay	2.0000
16 Pulse Width	11.5000
17 Presaturation Frequency	
18 Acquisition Time	0.9175
19 Acquisition Date	2023-11-28T11:57:17
20 Modification Date	2023-11-28T12:14:40
21 Class	
22 Spectrometer Frequency	150.91
23 Spectral Width	35714.3
24 Lowest Frequency	-2746.1
25 Nucleus	13C
26 Acquired Size	32768
27 Spectral Size	32768