Supplementary Materials for

# The chemical metamorphosis of taxane diterpenes by synthetic design

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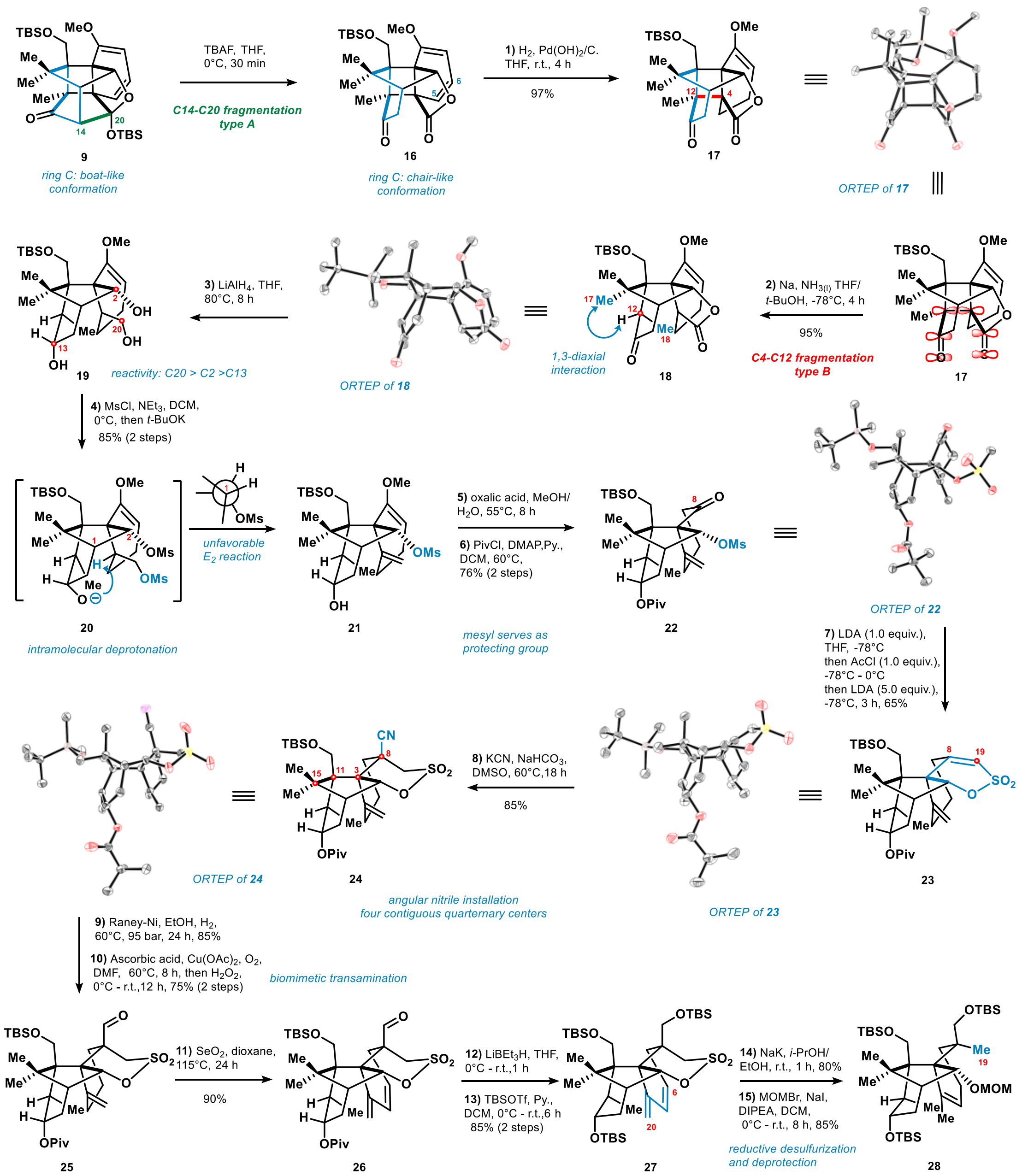
# Part-I General Information

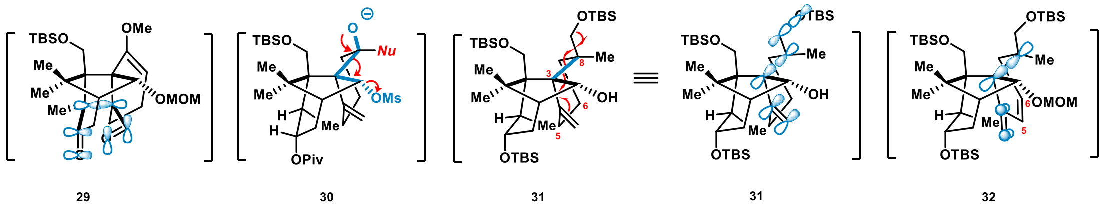
All moisture- and oxygen-sensitive reactions were performed in flame-dried glassware under a slight nitrogen overpressure. All reactions were stirred magnetically. Sensitive solutions, solvents, or reagents were transferred *via* cannula or syringe. Reactions were monitored by thin-layer chromatography (TLC) or NMR or GC-MS of the crude mixture. Evaporations were conducted under reduced pressure at temperatures less than 40 °C, unless otherwise noted. Further dryings of the residues were accomplished using a high vacuum pump. All solvents were purchased as the highest available grade from Sigma-Aldrich, Acros-Organics or Fisher-Chemicals. Ethyl acetate, hexane, and dichloromethane for column chromatography were distilled and used without further purification. All other reagents were used as received from Sigma-Aldrich, Acros-Organics, TCI, or Fisher-Chemicals unless otherwise noted. Thin-layer chromatography was carried out on pre-coated Merck silica gel 60 F254 to monitor all reactions. The detection of spots was first performed by using a UV (254 nm) lamp followed by visualization by a ceric ammonium molybdate-based TLC stain. Preparative column chromatography was performed with silica gel 60 from Merck (0.040-0.063 µm, 240-400 mesh). All NMR spectra were measured on a Bruker Avance III 400 or Avance III 600 or Bruker Avance Neo 800. Chemical shifts are given in ppm and referenced to the solvent residual peaks (Chloroform-*d* $^{1}$H, = 7.26 ppm, $^{13}$C, = 77.00 ppm; DMSO-$d_6$ $^{1}$H, = 2.50 ppm, $^{13}$C, = 39.52 ppm; Benzene-$d_6$ $^{1}$H, = 7.16 ppm, $^{13}$C, = 128.06 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant *J*, and integration. Infrared spectra were recorded as thin films of pure products on an ATR-unit on a Perkin Elmer Spectrum 100 ATR spectrometer. High-resolution mass spectra were measured on a Fischer Scientific Orbitrap Velos Pro.

# Part-II Overview of The Synthetic Route

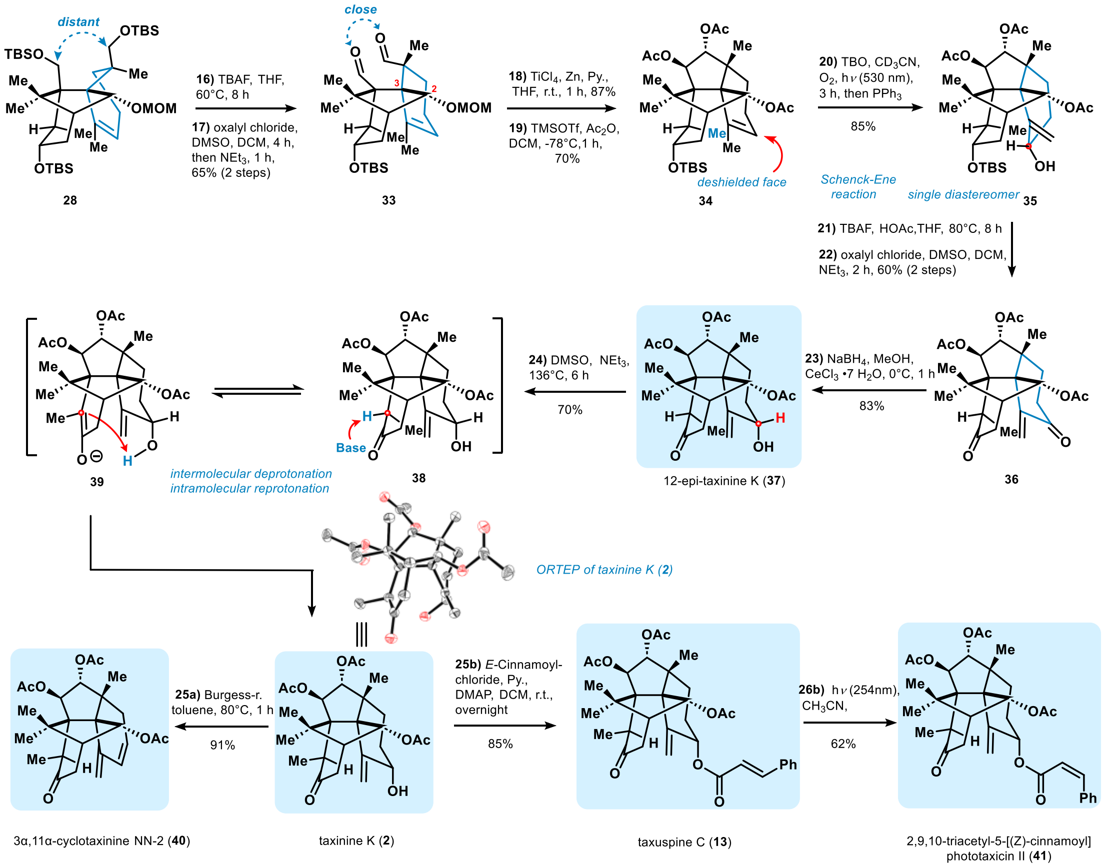
***A.*** *Metamorphosis stage : synthesis part* ***I***



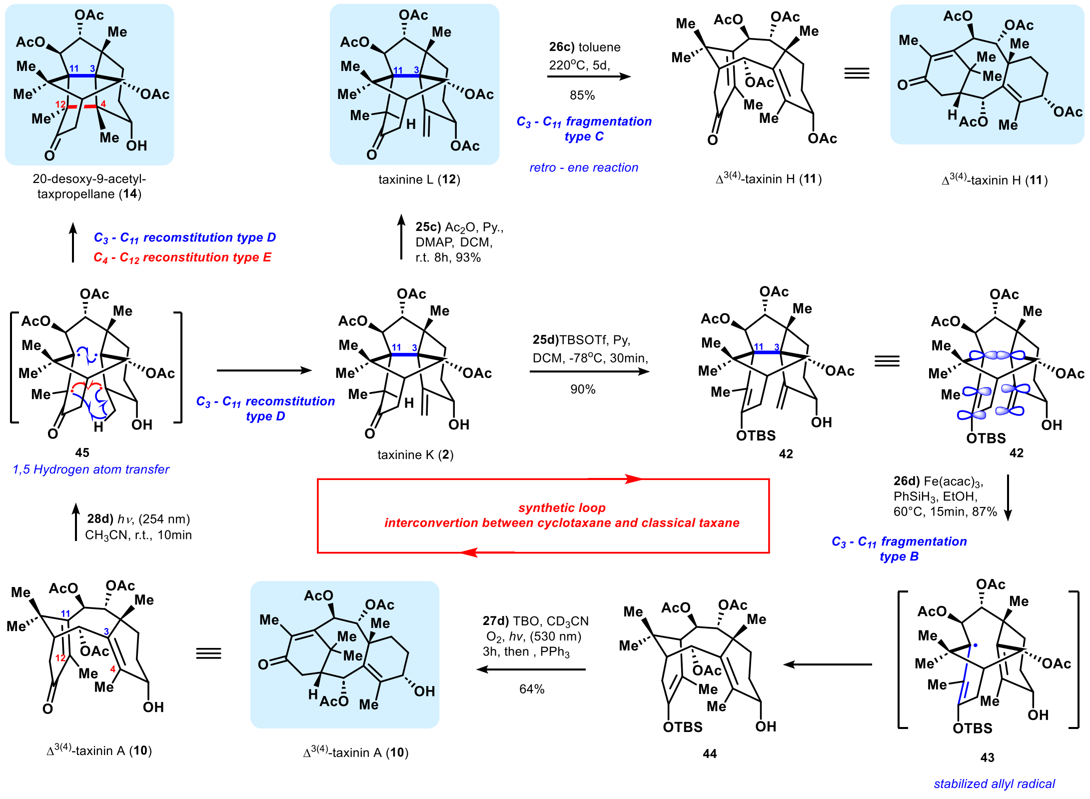
***B.*** *Conformational relevant intermediates in the metamorphosis stage*



*Metamorphosis stage : synthesis part* ***II***



*Metamorphosis stage synthesis part -* ***III***



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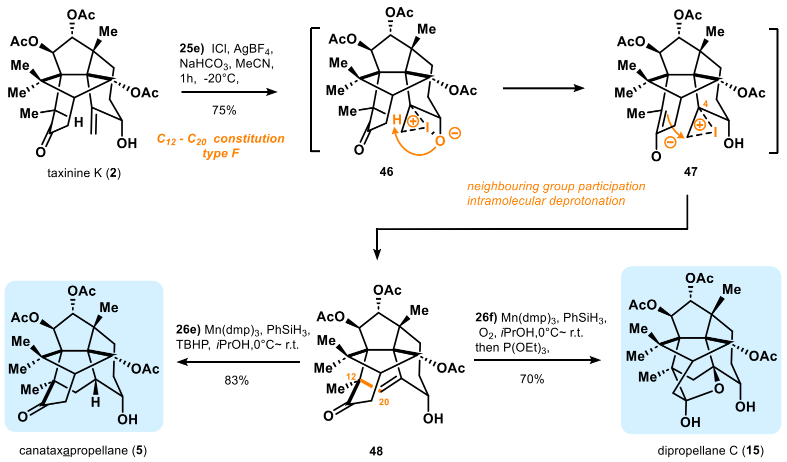
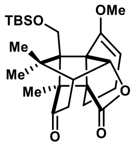


Reagents and Conditions: 1) palladium hydroxide on charcoal ($Pd(OH)_2/C$. 20 wt%) (0.05 mol%), tetrahydrofuran (THF), room temperature (r.t.), hydrogen ($H_2$), 97%; 2) sodium (Na), ammonia ($NH_{3\,(l)}$), THF/*tert*-butanol (*t*-BuOH) = 1:1, -78ºC, 4 h, 95%; 3) lithium aluminium hydride ($LiAlH_4$, 1 M in THF, 10.0 equiv.), THF, 80ºC, 8 h; 4) methanesulfonyl chloride (MsCl, 2.1 equiv. 0.5 M in dichloromethane (DCM)), triethylamine ($NEt_3$, 3.0 equiv.) then potassium *tert*-butoxide (*t*-BuOK, 1.0 M in THF, 5.0 equiv.), 85% over 2 steps; 5) oxalic acid (10.0 equiv.) methanol (MeOH) / water ($H_2O$) = 1:1, 55ºC, 6 h; 6) pivaloyl chloride (PivCl 1.2 equiv.) , 4-dimethylaminopyridine (DMAP, 0.05 mol%), pyridine (Py., 1.5 equiv.), DCM, 60ºC, 6 h, 76% over 2 steps; 7) lithium diisopropylamide (LDA, 0.5 M in THF, 1.0 equiv.), THF, -78ºC, 1 h, then acetyl chloride (AcCl, 1.0 equiv.), -78ºC to 0ºC, 1 h, then LDA (0.5 M in THF, 5.0 equiv.), -78ºC, 3 h, 65%; 8) potassium cyanide (KCN, 3.0 equiv.), ($NaHCO_3$, 6.0 equiv.), dimethylsulfoxide (DMSO), 60ºC, 18 h; 9) Raney nickel (Raney-Ni, 5 mol%), ethanol (EtOH), 60ºC, 24 h, 95 bar, 85%; 10) ascorbic acid (5.0 equiv.), copper(II) acetate ($Cu(OAc)_2$, 0.05 mol%), oxygen ($O_2$), dimethylformamide (DMF), 60ºC, 8 h, then hydrogen peroxide ($H_2O_2$, 35% in $H_2O$, 5.0 equiv.), 0ºC to r.t., 12 h, 75%; 11) selenium dioxide ($SeO_2$, 5.0 equiv.), dioxane, 115ºC, 24 h, 90%; 12) lithium triethylborohydride ($LiBEt_3H$, 1.0 M in THF), THF, 0°C to r.t., 1h; 13 ) *tert*-butyldimethylsilyl trifluoromethanesulfonate (TBSOTf, 2.1 equiv.), py. (4.1 equiv.), DCM, 0ºC to r.t., 6 h, 85% over 2 steps; 14) sodium-potassium alloy (NaK, 0.5 mL) , *iso*-propanol (*i*-PrOH) / MeOH = 20:1, r.t., 1 h, 80%; 15) bromomethyl methyl ether (MOMBr, 1.5 equiv.), sodium iodide (NaI, 0.5 equiv.), *N*,*N* -diisopropylethylamine (DIPEA, 2.0 equiv.), DCM, 0°C to r.t., 8 h, 85%.16) tetra-*n*-butylammonium fluoride (TBAF 1.0 M in THF, 10.0 equiv.), THF, 60°C, 8 h; 17) oxalyl chloride (8.0 equiv.), DMSO (16.0 equiv.), $NEt_3$ (24.0 equiv.), DCM, -78°C, 4 h, 65% over 2 steps; 18) titanium (IV) chloride ($TiCl_4$, 1.0 M in DCM, 20.0 equiv.), zinc dust (40.0 equiv.), py. (20.0 equiv.), THF, r.t., 1 h, 87%; 19) trimethylsilyl triflate (TMSOTf, 0.05 mol%), acetic anhydride ($Ac_2O$, 1.5 equiv.), DCM, -78°C, 1 h, 70%; 20) toluidine blue O (TBO, 0.03 mol%), $O_2$, acetonitrile-d3 ($CD_3CN$), triphenylphosphine ($PPh_3$, 1.0 equiv.), hv, (530 nm), 85%; 21) TBAF (1 M in THF, 10.0 equiv.), acetic acid (HOAc, 0.2 equiv.), THF, 80°C, 8 h; 22) oxalyl chloride (8.0 equiv.), DMSO (16.0 equiv.), $NEt_3$ (24.0 equiv.), DCM, -78°C, 4 h, 60% over 2 steps; 23) sodium borohydride ($NaBH_4$, 1.0 equiv.), MeOH, 0°C, 1 h, 55%; 24) $NEt_3$ (5.0 equiv.), DMSO, 136°C, 70%; 25a) methyl *N*-(triethylammoniumsulfonyl)carbamate (Burgess-r., 3.0 equiv.), toluene, 80°C, 1 h, 91%; 25b) *E*-cinnamoyl chloride (5.0 equiv.), py. (10.0 equiv.), DMAP (0.05 mol%), DCM, r.t., overnight, 90%; 26b) hv (254 nm), r.t., acetonitrile ($CH_3CN$), 62%. 25c) $Ac_2O$ (1.5 equiv.), py. (1.5 equiv.), DMAP (0.05 mol%), DCM, r.t., 8 h, 93%; 26c) toluene, 220°C, 5 days, 85%; 25d) TBSOTf (5.0 equiv.), py. (10.0 equiv.), DCM, -78°C, 30 min, 90%; 26d) phenylsilane ($PhSiH_3$, 15.0 equiv.), tris(acetylacetonato) iron (III) ($Fe(acac)_3$, 5.0 equiv.), EtOH, 60°C, 15 min, 87%; 27d) TBO (0.03 mol%), $O_2$ (dry), hv (530 nm), $CD_3CN$, $PPh_3$ (1.0 equiv.), 64%; 28d) hv (250 nm), $CH_3CN$, r.t., 10 min, 50% (20-desoxy-9-acetyl-taxpropellane), 25% (taxinine K). 25e) chloroiodide (ICl, 0.1 M in $CH_3CN$, 1.1 equiv.), silver tetrafluoroborate ($AgBF_4$, 1.1 equiv.), $NaHCO_3$ (1.5 equiv.), $CH_3CN$, 1 h, 0°C, 75%; 26e) $PhSiH_3$ (15.0 equiv.), tris(2,2,6,6-tetramethyl-3,5-heptanedionato) manganese (III) ($Mn(dpm)_3$, 0.5 equiv.), *tert*-butylhydro-peroxide (TBHP, 15.0 equiv.), *i*-PrOH, r.t., 8 h, 83%; 26f) $PhSiH_3$, (15.0 equiv.), ($Mn(dpm)_3$, 0.5 equiv.), *i*-PrOH, $O_2$ (dry), r.t., 8 h, then, triethyl phosphite ($P(OEt)_3$, 2.0 equiv.), 70%.

# Part-III Overview of X-ray Crystallography

*In this part, the overview includes X-ray crystallography of both the compounds in our final synthetic approach and the side products, which will be discussed later in part-**IV** and part-**V**.*



**17**

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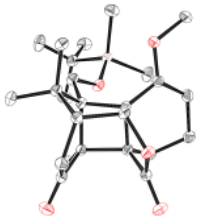

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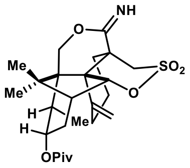

**S49**

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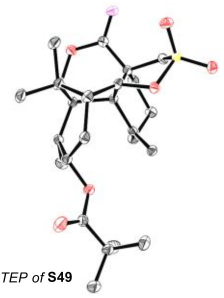

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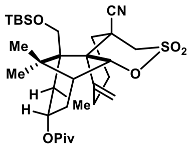

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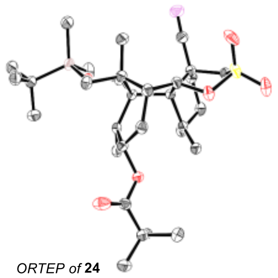

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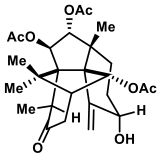

**taxinine (2)**

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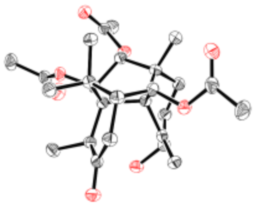

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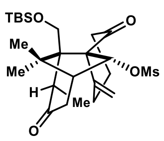

**S50**

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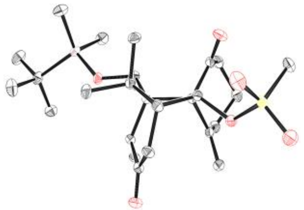

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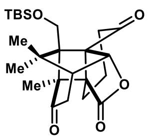

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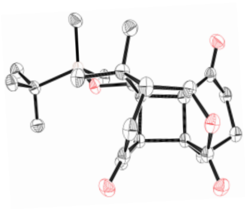

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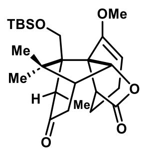

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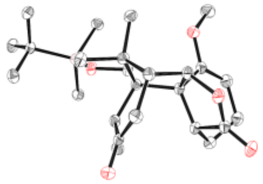

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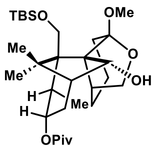

**S52**

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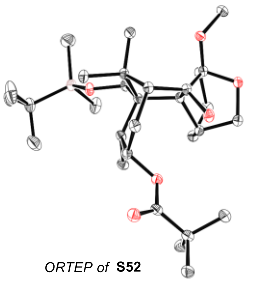

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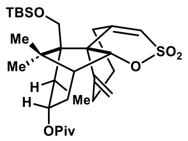

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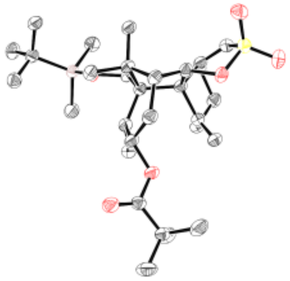

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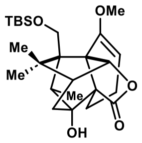

**S53**

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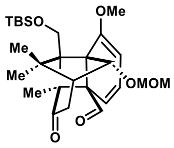
*ORTEP of* **S53**



**S54**

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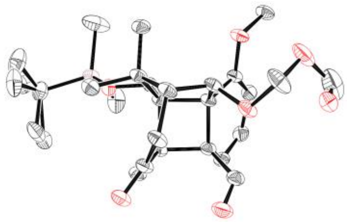

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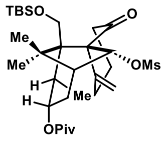

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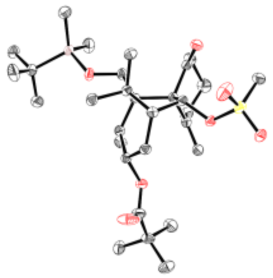

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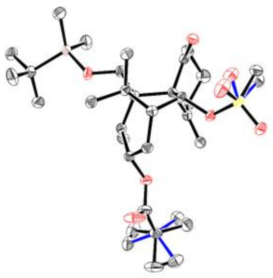


*ORTEP of* **22**

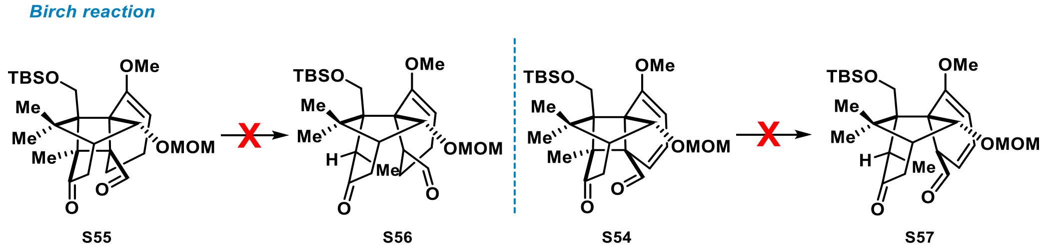
*Notes:*

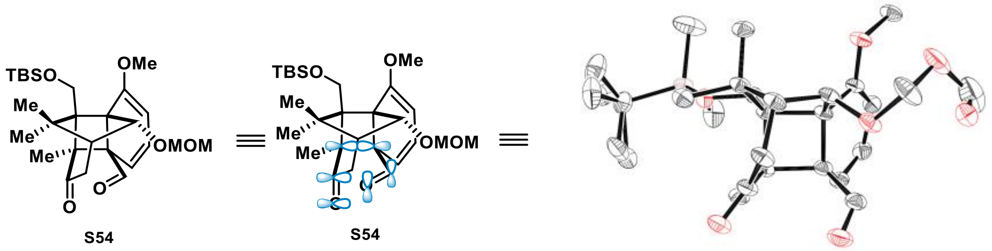
*X-ray of Compound **22** reveals partial disorder at Piv and Ms positions due to rotations of single bonds. To enhance structural clarity, one of the rotamers is omitted in the right figure. Both rotamers are highlighted in blue and black in the lower figure.*

# Part-IV Discussion of Key Steps

*In the following part, we will discuss the details of the key steps in our reaction sequence, including the successfully established conditions, undesired products that were obtained upon the examination of alternative conditions, and plausible mechanisms leading to their formation. This discussion will exclusively focus on the successful approach, excluding all other failed approaches and strategies.*

## Step-2 Attempts to the fragmentation of C4-C12 bond





*ORTEP of* **S54**

The initial attempts to fragment the C4-12 bond with compound **S55** were unsuccessful, presumably due to the misalignment of the aldehyde's $\pi$-orbital and the C12-4 bond's $\sigma$-orbital (highlighted in blue).

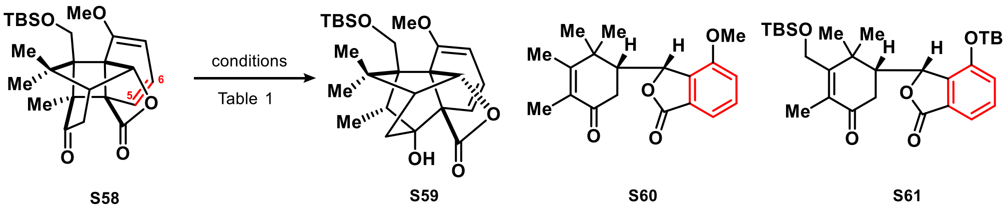
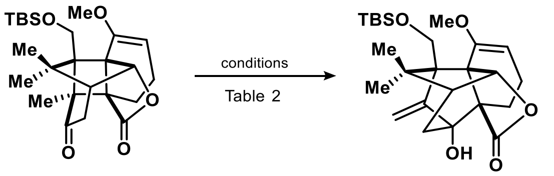


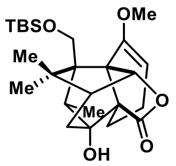
Table 1 **Initial studies to fragment the C4-12 bond with compound S58**

| Entry | Conditions | Results |
|---|---|---|
| 1 | Li, $NH_3$(l), THF, -78°C, then $NH_4Cl$ (s) | S59 |
| 2 | hν (254 nm), $CH_3CN$, $Et_3N$, r.t. | S60 : S61 = 2.5 : 1 |
| 3 | hν (254 nm), $CH_3CN$, $Et_3N$, HAc, r.t. | S60 : S61 = 2.5 : 1 |

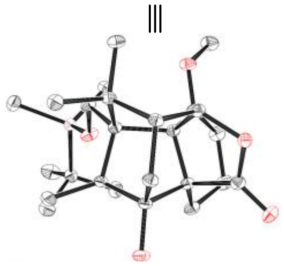
In the presence of an olefine at the C5 and C6 positions (highlighted in red), the B ring exhibited a significant propensity for aromatization under reductive SET conditions, resulting in the formation of a mixture of undesired products **S60** and **S61**.



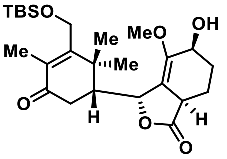
**17** **S62**



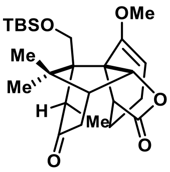
**S53**



*ORTEP of* **S53**



**S63**



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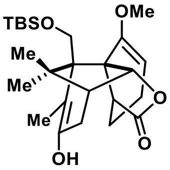


**S64** *(unstable)*

Table 2 **Optimization of Birch reaction**

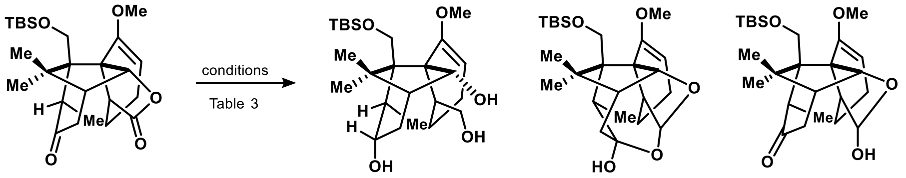
| Entry | Notes | Conditions | Results |
|---|---|---|---|
| 1 | | hν (254 nm), CH$_3$CN, Et$_3$N, r.t. | S62 |
| 2 | | Li, NH$_3$(l), THF, EtOH, -78$^{o}$C, then NH$_4$Cl (s) | 18 : S53 : S63 : S64 = 1 : 3 : 1 : 0.1 |
| 3 | | Li, NH$_3$(l), THF,i-PrOH, -78$^{o}$C, then NH$_4$Cl (s) | 18 : S53 : S63 : S64 = 1 : 0.5 : 0.5 : 0.3 |
| 4 | | Li, NH$_3$(l), THF,t-BuOH, -78$^{o}$C, then NH$_4$Cl (s) | 18 : S53 : S63 : S64 = 1 : 0.3 : 0.8 : 0.1 |
| 5 | | Li, NH$_3$(l), THF, -78$^{o}$C, then NH$_4$Cl (s) | 18 : S53 : S63 : S64 = 1 : 0.6 : 2.8 : 0.4 |
| 6 | | Li, NH$_3$(l), THF,t-BuOH, -78$^{o}$C, then NH$_4$Cl (s), 15min | 18 : S53 : S63 : S64 = 1 : 0.3 : 0.8 : 0.1 |
| 7 | | Li, NH$_3$(l), THF,t-BuOH, -33$^{o}$C, then NH$_4$Cl (s) | 18 : S53 : S63 : S64 = 1 : 1.5 : 2.1 : 1.5 |
| 8 | | Li, NH$_3$(l), Et$_2$O,t-BuOH, -78$^{o}$C, then NH$_4$Cl (s) | 18 : S53 : S63 : S64 = 1 : 0.6 : 1.6 : 0.0 |
| 9 | | Li, NH$_3$(l),t-BuOH, -78$^{o}$C, then NH$_4$Cl (s) | 18 : S53 : S63 : S64 = 1 : 0.3 : 0.5 : 1.3 |
| 10 | | Na, NH$_3$(l), THF,t-BuOH, -78$^{o}$C, then NH$_4$Cl (s) | 18 : S53 : S63 : S64 = 1 : 0.0 : 1.1 : 2.1 |
| 11 | | Na, NH$_3$(l), THF, -78$^{o}$C, then NH$_4$Cl (s) | 18 : S53 : S63 : S64 = 1 : 0.0 : 0.7 : 2.0 |
| 12 | | K, NH$_3$(l), THF,t-BuOH, -78$^{o}$C, then NH$_4$Cl (s) | 18 : S53 : S63 : S64 = 1 : 0.0 : 0.3 : 1.1 |
| 13 | | K, NH$_3$(l), THF, -78$^{o}$C, then NH$_4$Cl (s) | 18 : S53 : S63 : S64 = 1 : 0.0 : 2.5 : 1.6 |
| 14 | | K, NH$_3$(l) ,t-BuOH, -78$^{o}$C, then NH$_4$Cl (s) | 18 : S53 : S63 : S64 = 1 : 0.0 : 0.6 : 0.4 |
| 15 | | K, NH$_3$(l), i-PrOH, -78$^{o}$C, then NH$_4$Cl (s) | 18 : S53 : S63 : S64 = 1 : 0.3 : 0.4 : 0.0 |

|  |  |  |  |
|---|---|---|---|
| 16 |  | K, $NH_3$(l), EtOH, -78$^o$C, then $NH_4Cl$ (s) | 18 : S53 : S63 : S64 = 1 : 1.4 : 1.2 : 0.0 |
| 17 |  | Ca, $NH_3$(l), THF,t-BuOH, -78$^o$C, then $NH_4Cl$ (s) | 18 : S53 : S63 : S64 = 1 : 0.9 : 1.8 : 0.0 |
| 18 |  | Li, $NH_3$(l), THF,t-BuOH, -78$^o$C, then $NH_4Cl$ (s), then overnight | S53 |
| 19 |  | Na, $NH_3$(l), THF,t-BuOH, -78$^o$C, then $NH_4Cl$ (s), then $P(OEt)_3$ | 18 |
| 20 | 5g | Na, $NH_3$(l) (50ml), THF:t-BuOH(1;1 10ml), -78$^o$C, (1h) then $NH_4Cl$ (s), $P(OEt)_3$ | 18 20~ 30% |
| 21 | 5g | Na, $NH_3$(l) (100ml), THF:t-BuOH(1;1 10ml), -78$^o$C, (1h) then $NH_4Cl$ (s), $P(OEt)_3$ | 18 20~ 30% |
| 22 | 5g | Na, $NH_3$(l) (100ml), THF:t-BuOH(1;1 10ml), -78$^o$C, (2h) then $NH_4Cl$ (s), $P(OEt)_3$ | 18 30% |
| 23 | 5g | Na, $NH_3$(l) (100ml), THF:t-BuOH(1;1 10ml), -78$^o$C, (4h) then $NH_4Cl$ (s), $P(OEt)_3$ | 18 30% |
| 24 | 5g | Na, $NH_3$(l) (200ml), THF:t-BuOH(1;1 10ml), -78$^o$C, (6h) then $NH_4Cl$ (s), $P(OEt)_3$ | 18 30~ 40% |
| 25 | 5g | Na, $NH_3$(l) (200ml), THF:t-BuOH(1;1 10ml), -78$^o$C, (6h) then $NH_4Cl$ (s), $P(OEt)_3$, rpm 300 | 18 70% |
| 26 | 5g | Na, $NH_3$(l) (300ml), THF:t-BuOH(1;1 20ml), -78$^o$C, (6h) then $NH_4Cl$ (s), $P(OEt)_3$, rpm 300 | 18 ~ 70% |
| 27 | 5g | Na, $NH_3$(l) (300ml), THF:t-BuOH(1;1 20ml), -78$^o$C, (6h) then $NH_4Cl$ (s), $P(OEt)_3$, rpm 800 | 18 95 % |
| 28 | 10g | Na, $NH_3$(l) (300ml), THF:t-BuOH(1;1 20ml), -78$^o$C, (12h) then $NH_4Cl$ (s), $P(OEt)_3$, rpm 800 | 18 93 % |

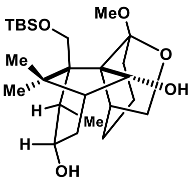
After extensive optimization, it was found that condition 28 yielded the best results (highlighted in red). Furthermore, the addition of triethyl phosphite was proven to effectively prevent the formation of side product **S63**.

The plausible mechanism for the formation of side product **S63** is provided in the experimental part.

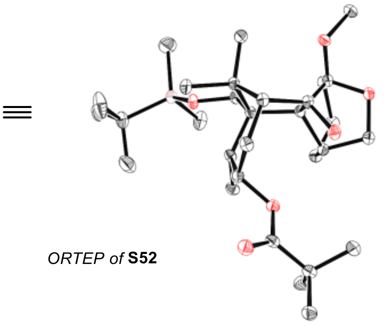
## Step- 3 Attempts to the elaboration of lactone moiety in compound 18



**18** **19** **S65** **S66**



**S52**



*ORTEP of* **S52**

Table 3 **Optimization of reduction**

| Entry | Conditions | Results |
|---|---|---|
| 1 | $NaBH_4$, MeOH, 0$^o$C | no/slow conversion |
| 2 | $Ca(BH_4)_2$·2THF, $CH_2Cl_2$, 0$^o$C | ketal S65, slow isomerozation to S66 in the NMR tube |
| 3 | $LiAlH_4$ (2.5M in THF), THF, r.t. | lactone S66 |
| 4 | $LiAlH_4$ (2.5M in THF), THF, 75$^o$C (sealed tube), then Rochelles | 19 |
| 5 | $LiAlH_4$ (2.5M in THF), THF, 75$^o$C (sealed tube) then $NH_4Cl$ | S52 |
| 6 | NHMe(OMe)HCl, i-PrMgBr, THF, 0$^o$C to 80$^o$C | undefined |
| 7 | NHMe(OMe)HCl, $Me_2AlCl$, DCM, 0$^o$C | undefined |

All attempts to chemoselectively reduce or nucleophilically attack the lactone were unsuccessful.

Under acidic conditions, triol **19** was unstable and its conversion to compound **S52** was observed then.

### Step-7 Attempts to the C1-enlongation of compound S67 at C8 position

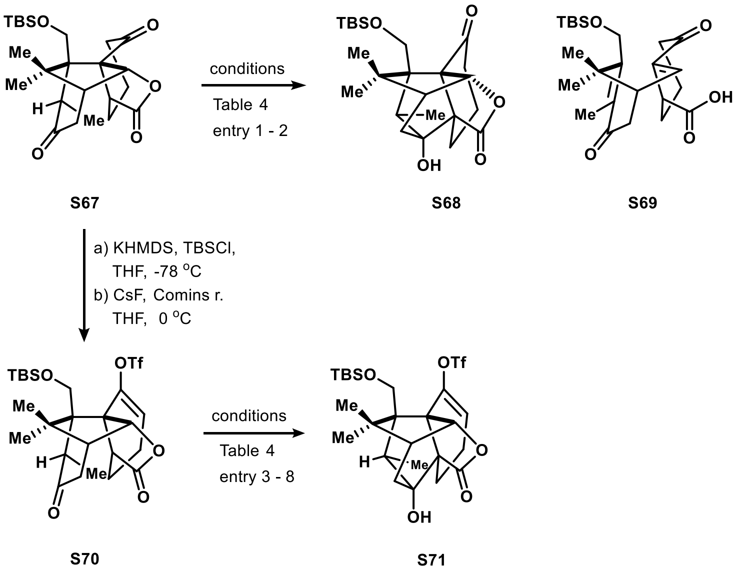
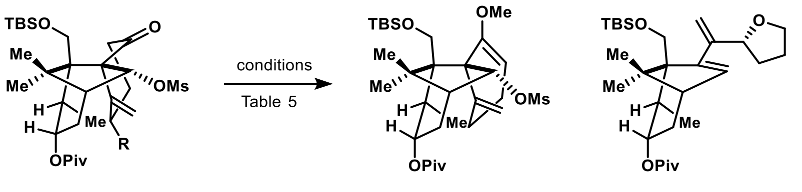


Table 4 Initial attempts to the C1-enlongation of compound S67

| Entry | Conditions | Results |
|---|---|---|
| 1 | $Ph_3PCH_2OMeCl$, KOtBu, THF, r.t. | S68 |
| 2 | $(EtO)_2P(O)CH_2OMe$, KOtBu, THF, r.t. | S69 |
| 3 | $Pd(PPh_3)_4$, CO, *n*-$Bu_3SnH$, DMF, LiCl, TEA, 60°C | trace amount of aldehyde |
| 4 | $Pd(OAc)_2$, dppp, CO, TESiH, DMF, TEA, 60°C , 2 h | no reaction |
| 5 | $Pd(PPh_3)_4$, CO, TESiH, DMF, $Na_2CO_3$, 60°C, 24 h | S71 |
| 6 | $Pd(OAc)_2$, dppp, CO, $H_2$ (40 bar 1:1) , DMF, Py, 60°C, 72 h | S71 |
| 7 | $Pd(PPh_3)_4$, KCN, 18-C-6, DMF, 60°C, overnight | decomposed |
| 8 | TBAF, THF, 0°C to r.t. | S71 |

Beyond our expectation, subjecting compound **S67** to Wittig reaction conditions predominantly resulted in the formation of an intramolecular aldol-type product **S68** or a C3-C11 fragmentation product **S69**.

Multiple Pd-catalyzed CO or CN insertion conditions were tested, but they solely yielded compound **S71** as the undesired product.



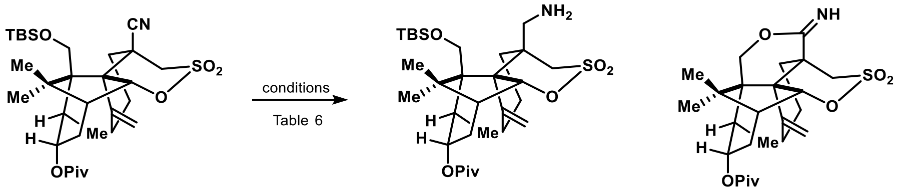
**22** **S72** **S73**

Table 5 Initial attempts to the C1-enlongation of compound 22

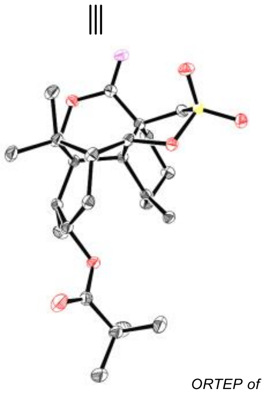
| Entry | R | Conditions | Results |
|---|---|---|---|
| 1 | H | $Me_3SI$, NaH, DMSO, THF, r.t. | S72 |
| 2 | H | $Me_3SI$, KHMDS, THF, -78°C to r.t. | S72 |
| 3 | H | $Me_3S(O)I$, KHMDS, THF, -78°C to r.t. | fragmentation |
| 4 | H | TosMIC, KOtBu, EtOH, $Et_2O$, THF, 0°C to r.t. | fragmentation |
| 5 | OH | $Ph_3PCH_2OMeCl$, KOtBu, THF, r.t. | S73 |
| 6 | H | $Ph_3PCH_2OMeCl$, KOtBu, THF, r.t. to 50°C | no conversion |
| 7 | H | $Ph_2P(O)CH_2OMe$, KHMDS, THF, -78°C to r.t. | S72 |
| 8 | H | $(EtO)_2P(O)CH_2OMe$, KHMDS, THF, -78°C to 50°C | no conversion |
| 9 | H | $Ph_3PCH_2OMeCl$, KHMDS, THF, -78°C to r.t. | S72 |

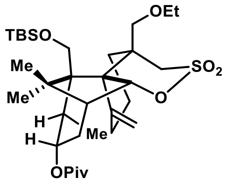
Attempts to C1-enlongation at C8 ketone in compound **22** via Corey-Chaykovsky, Van-Leusen reaction, Wittig reaction, and Horner-Wadsworth-Emmons reaction either resulted in the formation of methyl enol ether **S72** or Grob-type fragmentation product **S73**.

## Step-10 Attempts to the conversion of nitrile group

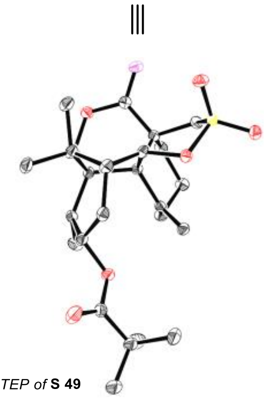


**24** **S74** **S49**





**S75**



*ORTEP of* **24** *ORTEP of* **S 49**

Table 6 Attempts to the conversion of nitrile group

| Entry | Conditions | Results |
|---|---|---|
| 1 | KOH, $H_2O$, 120°C, overnight | no conversion |
| 2 | KOH, $H_2O$, $H_2O_2$, reflux, overnight | no conversion |
| 3 | HCl (2M.), THF, 80°C, overnight | no conversion |
| 4 | HCl (6M.), THF, 80°C, overnight | S49 |
| 5 | | |
| 6 | $Rh/Al_2O_3$, $H_2$ (75bar) THF, 8h | no conversion |
| 7 | Raney-Ni, EtOH, $H_2$ (75 bar), 60°C, 72h | S74 (80%) : S75 (20%) |
| 8 | Raney-Ni, EtOH, $H_2$ (95 bar), 60°C, 24h | S74 |
| 9 | Raney-Ni, $NaH_2PO_4$, Py., $H_2O$, HAc, (2:1:1) $H_2$ (75bar), 80°C | no conversion |
| 10 | Raney-Ni, $NaH_2PO_4$, Py., $H_2O$, HAc, (2:1:1) EtOH $H_2$ (75bar), 80°C | no conversion |
| 11 | Raney-Ni, EtOH, $H_2O$, HAc, $H_2$ (75bar), 60°C, 24h | S74 (50%) conversion |

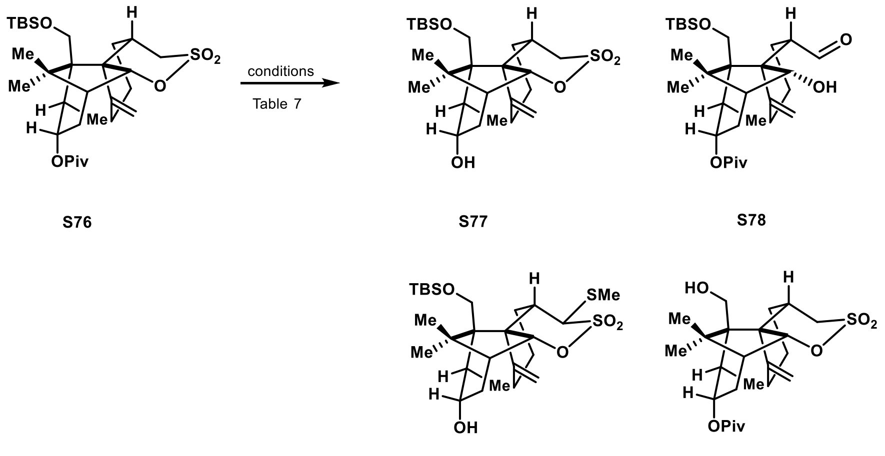
The hydrolysis of the angular nitrile group under basic or acidic conditions (entries 1-3) did not yield the corresponding carboxylic acid. Increasing the concentration of HCl (entry 4) resulted in the deprotection of the TBS-protected alcohol at C10, which subsequently underwent spontaneous ring closure to lactam **S49**.

Furthermore, all attempts to partially reduce the nitrile to the aldehyde (entries 8-10) were unsuccessful.

## Step-14 Attempts to the desulfurization

A comprehensive investigation involving more than 90 conditions has been performed to address the challenging task of desulfurization. Generally, these conditions can be classified into two distinct categories: oxidative desulfurization and reductive desulfurization.

The oxidative conditions are listed in the first two tables and the reductive conditions are depicted in the third and fourth table of this subsection.



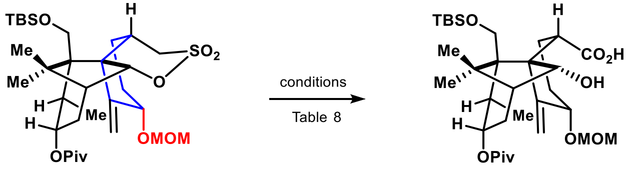
**S76** **S77** **S78**

**S79** **S80**

**Table 7 Optimization of oxidative desulfurization with compound S76**

| Entry | Conditions | Results |
|---|---|---|
| 1 | *t*-BuOK, THF, $O_2$, r.t. | no conversion |
| 2 | *t*-BuOK, THF, *t*-BuOH, $O_2$, r.t. | no conversion |
| 3 | LDA, THF, then $O_2$ -78°C to r.t. | no conversion |
| 4 | tBuLi, THF, then $O_2$ -78°C to r.t. | no conversion |
| 5 | tBuLi, DMPU, THF, then dryed $O_2$ -78°C to r.t. | S77 |
| 6 | LDA, DMPU, THF, then dryed $O_2$ -78°C to r.t. | no conversion |
| 7 | LDA, DMPU, THF, then $TMS_2O_2$, -78°C to r.t. | no conversion |
| 8 | LDA, DMPU, THF, then Davis-Oxaz. -78°C to r.t. | S78 (30 %) |
| 9 | KHMDS, THF, then Davis-Oxaz -78°C to r.t. | S78 (30 %) |
| 10 | LDA, THF, then tBuOOLi, -78°C to r.t. | no conversion |
| 11 | tBuLi, THF, then MeOB(pin), -78°C to r.t. | no conversion |
| 12 | LDA, THF, then $B(OMe)_3$ -78°C to r.t. | no conversion |
| 13 | LDA, THF, then $ClB(OMe)_2$ -78°C to r.t. | no conversion |
| 14 | tBuLi, THF, then $ClB(OMe)_2$ -78°C to r.t.. | no conversion |
| 15 | KHMDS, THF, then MeOB(pin) -78°C to r.t. | no conversion |
| 16 | KHMDS, THF, then MoOPH -78°C to r.t. | no conversion |
| 17 | LDA, THF, then MoOPH, -78°C to r.t. | S78 (30-50 %) |
| 18 | KHMDS, THF, $Ph_2(CO_2)_2$ -78°C to r.t. | no conversion |
| 19 | NaHMDS, THF, then DMDO -78°C to r.t.DMDO dryed ($MgSO_4$) | no conversion |
| 20 | LDA, THF, then DMDO -78°C DMDO dryed (mole sieves) | overoxidation |
| 21 | KHMDS, DMF, PhNO, -78°C to r.t. | no conversion |
| 22 | KOtBu, THF/tBuOH, $O_2$ -78°C to r.t. | no conversion |
| 23 | $Pb(OAc)_4$, benzene,100°C | no conversion |
| 24 | LDA, HMPA; THF, then $S_2Me_2$ -78°C to r.t. | S79 |
| 25 | LDA, HMPA; THF, then MoOPH -78°C to r.t. | very low conversion |
| 26 | allylic alcohol xx, KOtBu/THF, $O_2$ -78°C to r.t. | no conversion |
| 27 | KOtBu, THF/ DMSO, $O_2$ -78°C to r.t. | S80 |
| 28 | LDA, HMPA, THF, then TEMPO, | S77 |
| 29 | ferrocinium hexafluorophosphate -78°C to r.t. | no conversion |
| 30 | KHMDS, THF,-78°C, then $O_2$ -78°C to r.t. dry $O_2$ | S78, low conv. |
| 31 | KHMDS, 18-crown-6, THF, -78°C, then $O_2$ -78°C to r.t.. | S78, 70 % |

To our delight, after extensive experimentation, compound **S76** was readily converted to the desired aldehyde **S78** in 70% yield using conditions 31.

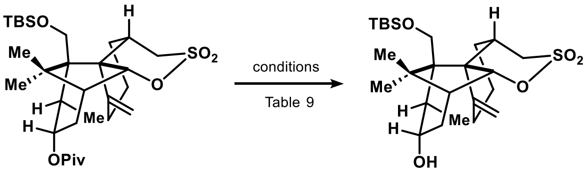


**S81** **S82**

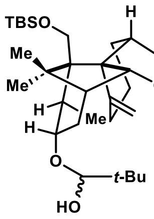
**Table 8 Optimization of oxidative desulfurization with compound S81**

| Entry | Conditions | Results |
|---|---|---|
| 32 | KHMDS, THF, -78$^o$C (30 min) 0$^o$C (2 min) to -78$^o$C, then,18-crown-6 (10 min), then, $O_2$ (30 min), then, P(OEt)$_3$ (-78$^o$C), then, $NH_4Cl$ | no conversion |
| 33 | KHMDS, THF (BHT free),-78$^o$C (30 min)to 0$^o$C (2 min)to -78$^o$C,then,18-crown-6 (10 min), then, $O_2$ (30 min), then, P(OEt)$_3$ (-78$^o$C), then, $NH_4Cl$ | no conversion |
| 34 | KHMDS, THF (BHT free),-78$^o$C (30 min)to 0$^o$C (2 min)to -78$^o$C,then,18-crown-6 (10 min),then,$O_2$ (30 min), then,$N_2$,then,P(OEt)$_3$,(10 min, -78$^o$C),then,$NH_4Cl$ | no conversion |
| 35 | KHMDS, THF (BHT free),-78$^o$C (30 min)to 0$^o$C (2 min)to -78$^o$C,then,18-crown-6 (10 min), then, $O_2$ (30 min),then,$N_2$,then,P(OEt)$_3$,(30 min, -78$^o$C),then,$NH_4Cl$ | no conversion |
| 36 | P(OEt)$_3$, then, KHMDS, THF (BHT free),-78$^o$C (30 min)to 0$^o$C (2 min)to -78$^o$C,then,18-crown-6 (10 min), then, $O_2$ (30 min), then, $NH_4Cl$ | no conversion |
| 37 | P(OEt)$_3$, then, KHMDS, THF (BHT free), -78$^o$C (30 min)to 0$^o$C (2 min)to -78$^o$C,then, $O_2$ (30 min), then, $NH_4Cl$ | no conversion |
| 38 | P(OEt)$_3$, then, KHMDS (1.5 eq ), THF (BHT free), -78$^o$C (30 min)to 0$^o$C (2 min)to -78$^o$C,then, $O_2$ (30 min), then, $NH_4Cl$ | no conversion |
| 39 | KHMDS, THF (BHT free), -78$^o$C (30 min)to 0$^o$C (2 min)to -78$^o$C,then,18-crown-6 (10 min), then, $O_2$ (30 min), then,$N_2$,then, PPh$_3$ (-78$^o$C), then, $NH_4Cl$ | S82 (30%) |
| 40 | KHMDS, THF (BHT free), -78$^o$C (30 min)to 0$^o$C (2 min)to -78$^o$C, then, 18-crown-6 (10 min), then, $O_2$ (30 min), then, $NH_4Cl$ | S82 (90%) |
| 41 | KHMDS, THF (BHT free), -78$^o$C (30 min)to 0$^o$C (2 min)to -78$^o$C, then,18-crown-6 (10 min), then, $O_2$ (30 min), then,MeOH, then, $NH_4Cl$ | S82 |
| 42 | KHMDS, THF (BHT free), -78$^o$C (30 min)to 0$^o$C (2 min)to -78$^o$C, then,18-crown-6 (10 min), then, $O_2$ (30 min), then,MeOH/ $NH_4Cl$ ( solid) | S82 |
| 43 | KHMDS, THF (BHT free), -78$^o$C (30 min)to 0$^o$C (2 min)to -78$^o$C, then, 18-crown-6 (10 min), then, $O_2$ (30 min), then,MeOH/HOAc | S82 |

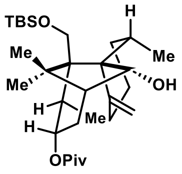
In order to further explore the oxidative desulfurization approach, compound **S81** bearing a MOM-group at C5 (highlighted in red) was subjected to conditions 31. Even though these conditions have been successfully tested on a similar substrate, no conversion was observed. As a result of extensive optimization of the reaction conditions, carboxylic acid **S82** was obtained as the single product. Presumably, this outcome was attributed to a conformational change in the B ring, transitioning from a chair-like conformation to a boat-like conformation (highlighted in blue).



**S76** **S77**



**S83**

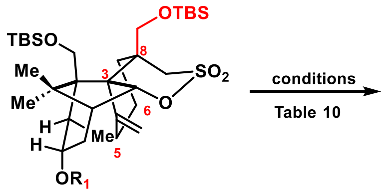


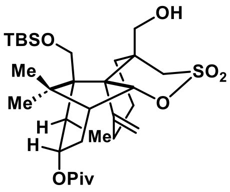
**S84**

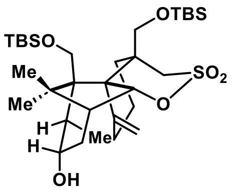
**Table 9 Investigations of reductive desulfurization with compound S76**

| Entry | Conditions | Results |
|---|---|---|
| 44 | E-Birch condition | S83 |
| 45 | Na, NH$_3$(l), THF, -33°C | S83 |
| 46 | Raney-Ni (commercial), EtOH, r.t. to 200°C | no reaction |
| 47 | Raney-Ni (self prepared), EtOH, r.t. to 220°C | no reaction |
| 48 | LiAlH$_4$, TiCl$_4$, THF, -78°C to r.t. | S83, S77 |
| 49 | S$_8$(l), neat, 200°C | decomposed |
| 50 | t-AmOH, *N*aH, Ni(OAc)$_2$,DME, 130°C | very slow at 100$^{o}$C and decomposed at 130$^{o}$C |
| 51 | Na, t-BuOH, re*fl*ux | S84 |

Preliminary investigation of reductive desulfurization was conducted using compound **S76**, and we are pleased to observe that the desired product **S84** was obtained under Bouveault–Blanc reduction conditions while preserving the C13 pivaloyl protection.



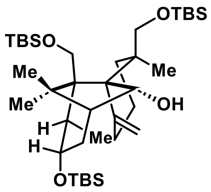


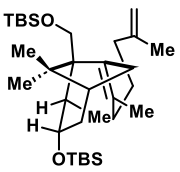


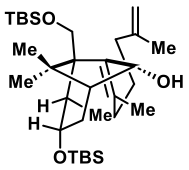
**S85**

**S86**

**S87**



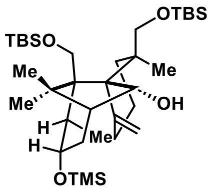


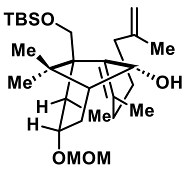


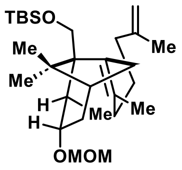
**S88**

**S89**

**S90**



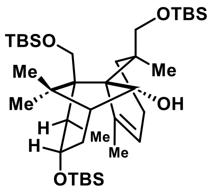


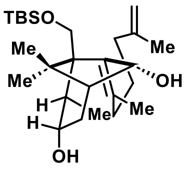


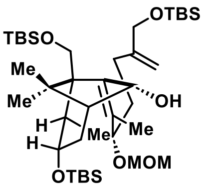
**S91**

**S92**

**S93**



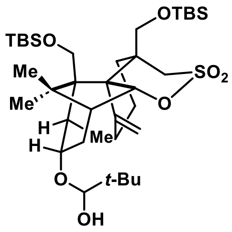


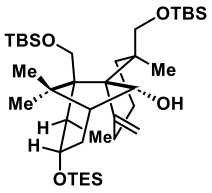


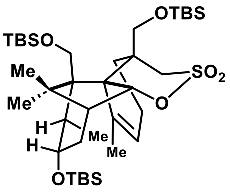
**S94**

**S95**

**S96**







**S97**

**S98**

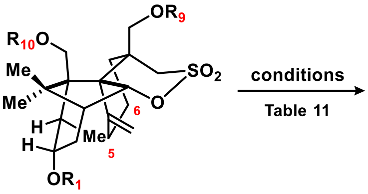
**S99**

**Table 10 Investigations of reductive desulfurization with compound S85**

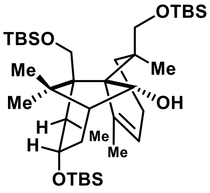
| Entry | $R_1$ | Others | Conditions | Results |
|---|---|---|---|---|
| 51 | OPiv | | Na, t-BuOH, 120~130$^{o}$C, 1 hour | no reaction |
| 52 | OPiv | | Na toluene Methyl glycol, 120$^{o}$C | S86 |
| 53 | OPiv | | Li, Naphthalene, THF, i-$Pr_2$NH, -78$^{o}$C to -40$^{o}$C | decomposed |
| 54 | OPiv | | Na, Naphthalene, THF, i-$Pr_2$NH, -78$^{o}$ to -40$^{o}$C | decomposed |
| 55 | OPiv | | LAH, $AlCl_3$, THF, 100$^{o}$C | S87 |
| 56 | OPiv | | Li, $NH_3$, , - 78$^{o}$C to - 40$^{o}$C, THF, t-BuOH | S97 |
| 57 | OPiv | | $Mo(CO)_6$, acetone, r.t. to 120$^{o}$C | no reaction |
| 58 | OPiv | | Na-K, THF, dimethylurea, r.t. | trace amount of S95 |
| 59 | OPiv | | Na-K, THF, r.t. | decomposed |
| 60 | OPiv | | Na-K, t-BuOH, r.t. | S95 |
| 61 | OPiv | | Na-K, THF, t-BuOH (5:1), r.t. | trace amount of S95 |
| 62 | OPiv | | Na-K, THF, tBuOH, r.t, 1,4-cyclodiene | S95 |
| 63 | OPiv | | Na-K, THF, tBuOH, r.t, $HSnBu_3$ (exc.) | S95 |
| 64 | OPiv | | $Fe(acac)_3$, $PhSiH_3$, EtOH, 60°C | no reaction |
| 65 | OPiv | | NaK, 18-crown-6, THF, tBuOH, r.t. | decomposed |
| 66 | OPiv | | K, 18-crown-6, THF, *t*BuOH, -20°C | mostly decomposed |
| 67 | OPiv | | K (exc.), 18-crown-6 , (very small load), THF, *t*BuOH, -78°C | S87, S97 |
| 68 | OTBS | | Na-K, t-BuOH, r.t. | S95, S89, S90 |
| 69 | OTES | | Na-K, t-BuOH, r.t. | S98 |
| 70 | OTMS | | Na-K, t-BuOH, r.t. | S91 |
| 71 | OMOM | | Na-K, t-BuOH, r.t. | S92, S93 |
| 72 | OTBS | $C_5$-OMOM, | Na-K, t-BuOH, r.t. | S94, S96 |
| 73 | OPiv | $\Delta(C_5$-$C_6)$ | Na-K, t-BuOH, r.t. | decomposed |
| 74 | OTBS | $\Delta(C_5$-$C_6)$ | Na-K, t-BuOH, r.t. | S94 |

In an effort to broaden the substrate scope of the reductive desulfurization approach, compound **S85** (featuring a C8-$CH_2$OTBS protective group indicated in red) was subjected to the Bouveault–Blanc reduction conditions that have previously been tested successfully. However, no conversion was observed, likely due to the escalating steric hindrance around the sultone moiety.

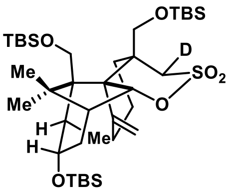
As illustrated in the scheme above, C3, C8 fragmentation products were predominantly observed under various reductive conditions. Notably, it was observed that the introduction of an olefin at the C5 and C6 positions effectively suppressed the C3, C8 fragmentation phenomenon.



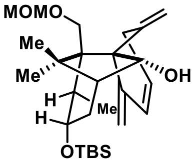
S100



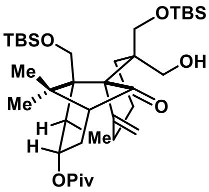
S94



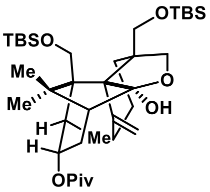
S101



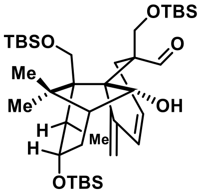
S102



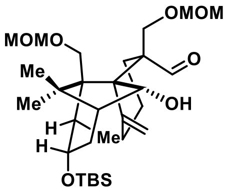
S103



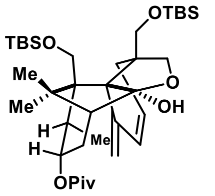
S104



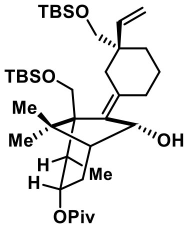
S105



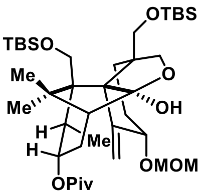
S106



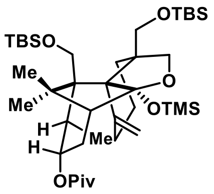
S107



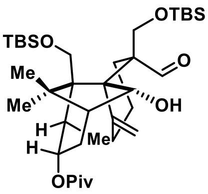
S108



S109



S110



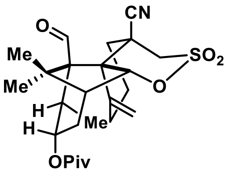
S111

**Table 11 Investigations of desulfurization with compound S100 bearing different protecting group at C9,10,13**

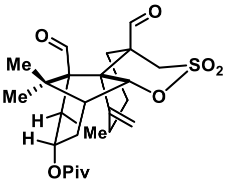
| Entry | $R_1$ | Others | Conditions | Results |
|---|---|---|---|---|
| 76 | OPiv | $C_5$-OMOM | Na-K, t-BuOH, r.t. | decomposed |
| 77 | OMOM | $C_5$-OMOM, | Na-K, t-BuOH, r.t. | decomposed |
| 78 | OTBS | $C_5$-OMOM | Na-K, t-BuOH/ i-PrOH, r.t. | S94 |
| 79 | OTBS | $\Delta(C_5\text{-}C_6)$ | Na-K, THF/t-BuOH, r.t. | very sluggish |
| 80 | OTBS | $\Delta(C_5\text{-}C_6)$ | Na-K, THF, r.t. | no reaction |
| 81 | OTBS | $\Delta(C_5\text{-}C_6)$ | Na-K, i-PrOH, r.t. | S94 |
| 82 | OPiv | | KHMDS, 18-C-6, THF, -78°C, $D_2O$ quench | S101 |
| 83 | OPiv | | KHMDS, $O_2$, 18-C-6, THF, without $P(OEt)_3$ quench | S111, S103, S104 |
| 84 | OPiv | | KHMDS, $O_2$, 18-C-6, THF, $P(OEt)_3$ quench | S111, S103, S104 |
| 85 | OPiv | | KHMDS, 18-C-6, THF, Davis oxaziridine, -78°C | S103, S104 |
| 86 | OPiv | | KHMDS, 18-C-6, THF, $TMS_2O_2$, -78°C | S110 |
| 87 | OPiv | | KHMDS, 18-C-6, $CH_2I_2$, i-$Pr_2MgBr$, , THF, -78°C | S108 |
| 88 | OPiv | $C_5$-OMOM | KHMDS, 18-C-6, THF, Davis oxaziridine, -78°C | S109 |
| 89 | OPiv | $\Delta(C_5\text{-}C_6)$, $C_9,C_{10}$=OMOM | KHMDS, 18-C-6, THF, Davis oxaziridine, -78°C | S105, S107 |
| 90 | OPiv | $\Delta(C_5\text{-}C_6)$, $C_9,C_{10}$=OMOM | KHMDS, 18-C-6, THF, Davis oxaziridine, -78°C | S102 |
| 91 | OPiv | $\Delta(C_5\text{-}C_6)$, $C_9,C_{10}$=OMOM | KHMDS, 18-C-6, THF, $O_2$, -78°C | S106 |

Significant influence on the outcome was observed when subtle changes were made to the protective pattern at the C9, C10, C13, and C5, C6 positions. To systematically explore the impact of different protective groups and substitutions at the C5, C6 position, we conducted a comprehensive screening of reductive desulfurization and oxidative desulfurization using compound **S100**. The results of these investigations are presented in the scheme provided above.

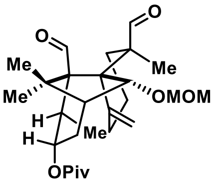
## Step-18 Attempts to The Pinacol Coupling



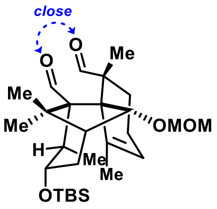
**24**



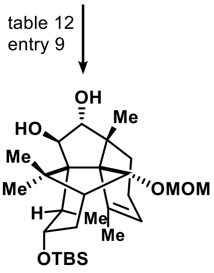
**25**



**S112**



**33**



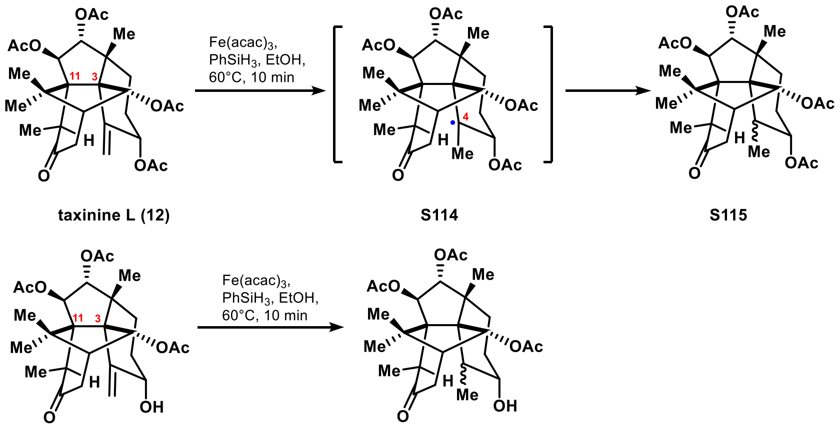
**S113**

**Table 12 Investigations of pinacol coupling with compound 24, 25, S112, 33**

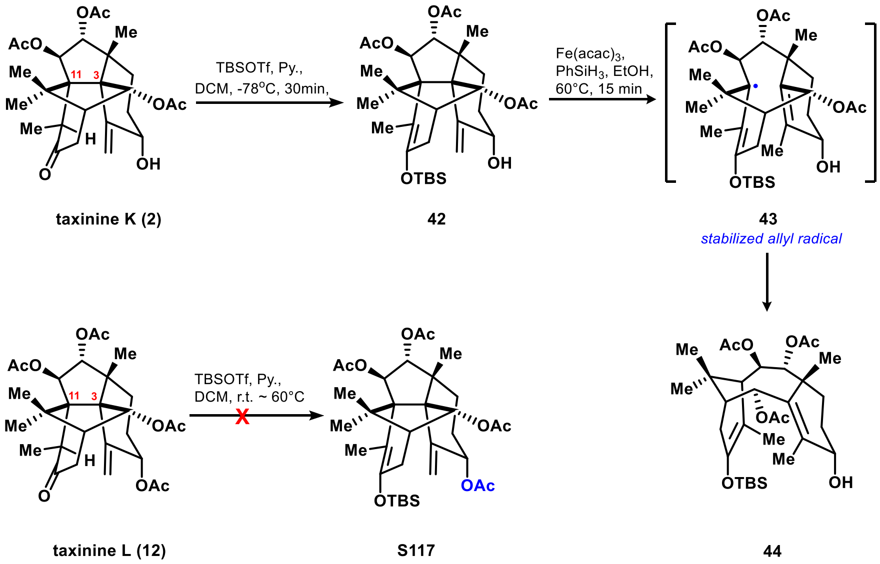
| Entry | Substrate | Conditions | Results |
|---|---|---|---|
| 1 | 24 | $TiCl_4$ (20 equiv.), Zn (40 equiv.) , Py, THF, r.t. overnignt | no conversion |
| 2 | 24 | $TiCl_4$, Zn, Py, THF, r.t. overnignt double concentration | no conversion |
| 3 | 24 | $SmI_2$, THF, *t*-BuOH, 0°C to r.t. 5h | no conversion |
| 4 | 24 | $SmI_2$ (excess) , THF, *t*-BuOH, r.t. 1h | decomposition |
| 5 | 24 | $Cp_2TiCl_2$, *i*-PrMgCl, PhMgBr, Ether, 30min | decomposition |
| 6 | 25 | $TiCl_4$ (20 equiv.), Zn (40 equiv.) , Py, THF, r.t. 1h | decomposition |
| 7 | 25 | $SmI_2$ (excess) , THF, *t*-BuOH, r.t. 1h | decomposition |
| 8 | S112 | $TiCl_4$ (20 equiv.), Zn (40 equiv.) , Py, THF, r.t. 1h | decomposition |
| 9 | 33 | $TiCl_4$ (20 equiv.), Zn (40 equiv.) , Py, THF, r.t. 1h | S113 |

It was observed that only compound **33**, featuring an olefin moiety at the C4-C5 position, yielded the desired trans-diol product. Other attempts utilizing the sultone **24**, **25** and compound **S112** failed to give the desired result. Presumably, this was attributed to the unfavorable conformation of the B ring and the spatial distance between the two aldehyde moieties.

## Step- 26d Attempts to the C3, C11 bond fragmentation via MHAT reaction



Initial investigations focusing on the fragmentation of the C3-C11 bond of taxinine L (**12**) under MHAT conditions, resulted in the formation of an undesired product **S115** that originated from a trivial reduction of the *exo*-methylene group. Mechanistically, we surmise the generation of a tertiary radical at the C4-position; however, further fragmentation was suppressed due to the misalignment of the p-radical orbital and the C3-C11 σ-orbital. Notably, a similar result was observed with taxinine K.



To overcome this challenge, taxinine K was converted into the corresponding silyl enol ether **42**. Encouragingly, compound **42** underwent a smooth C3-C11 fragmentation that resulted in the formation of **44** under MHAT conditions. It is important to highlight that the presence of a C5 alcohol group seems to play a crucial role in the generation of the silyl enol ether. Taxinine L, for example, that bears a C5-acetate did not undergo the conversion into the corresponding silyl enol ether **S117**.

## Step- 25e Attempts to the C12, C20 bond formation

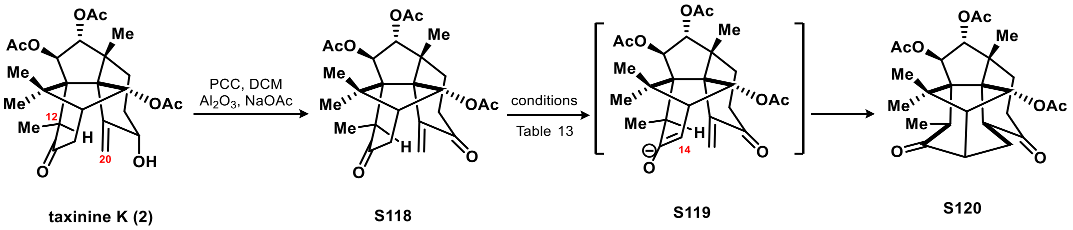
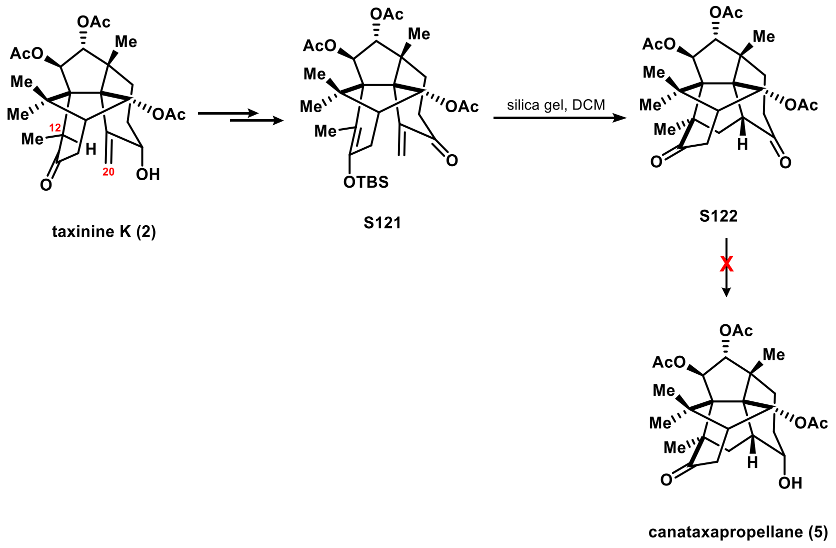


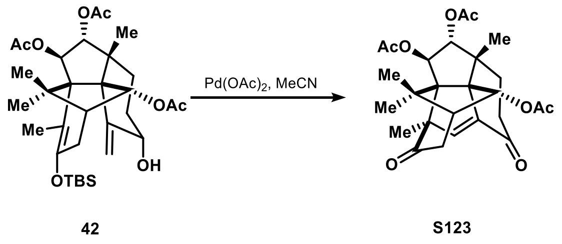
**Table 13 Investigations of pinacol coupling with compound 24, 25, S112, 33**

| Entry | Conditions | Results |
|---|---|---|
| 1 | $Mn(OAc)_3$, HAc, MeOH, 50°C | decomposition |
| 2 | *t*-BuOK, *t*-BuOH, THF, 0°C | decomposition |
| 3 | *t*-BuOK, *t*-BuOH, toluene, 0°C | decomposition |
| 4 | $Cs_2CO_3$, TBAB, DCM, r.t. | no conversion |
| 5 | TMSOTf, DCM, 0°C | no conversion |
| 6 | $BF_3Et_2O$, DCM, 0°C | decomposition |
| 7 | PTSA, DCM, 40°C | S120 |

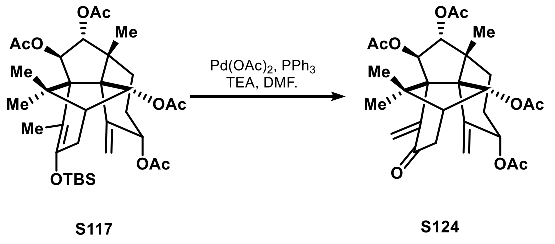
Initial investigations concerning the C12-C20 bond formation with compound **S118** via an intramolecular Michael reaction did not yield the desired product. Instead, compound **S120** was obtained as a major product under Brønsted acidic conditions (entry 7). This result indicated that the corresponding enol **S119** was formed at the C14-position.



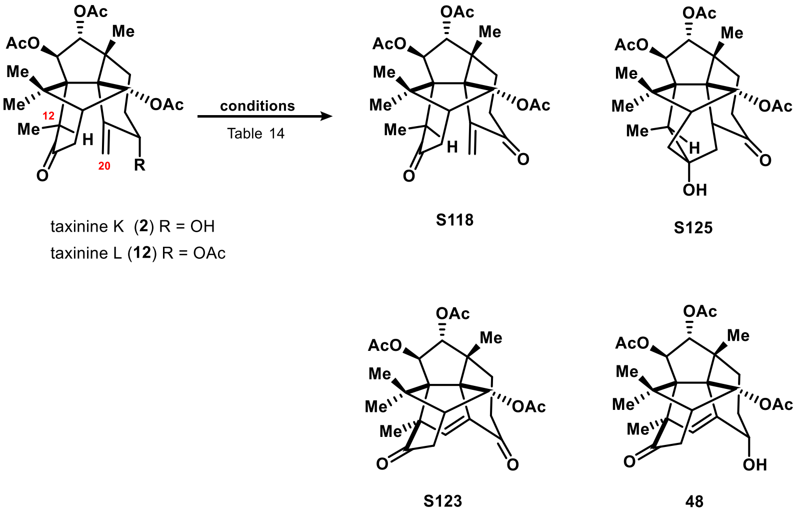
To circumvent this problem, compound **S121** was prepared from taxinine K in 2 steps. To our delight, the desired cyclization product **S122** was obtained in quantitative yield by treating compound **S121** with silica gel. Unfortunately, further reduction of the C5-ketone was not feasible.



Compound **42** underwent a Saegusa-type cyclization reaction that was accompanied by the oxidation of the C5-alcohol, resulting in the formation of compound **S123** as the major product. However, the reduction of the C5-ketone was not successful as it was already observed for previous attempts on related substrates.



The intramolecular Tsuji-Trost reaction was also investigated with compound **S117** and afforded compound **S124** as a single product.



taxinine K (**2**) R = OH
taxinine L (**12**) R = OAc

**S118**

**S125**

**S123**

**48**

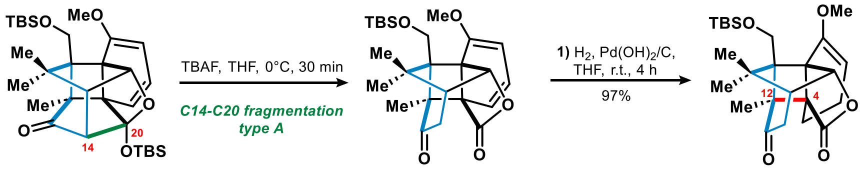
**Table 14 Investigations of C12-C20 coupling with compound 2, 12**

| Entry | R | Conditions | Results |
|---|---|---|---|
| 1 | OH | $Pd(OAc)_2$, $CH_3CN$ | S118 |
| 2 | OAc | $Pd(OAc)_2$, $CH_3CN$ | no conversion |
| 3 | OH | PhSeCl, DCM, -78°C to r.t, | S123, 48, S125 |
| 4 | OH | PhSeCl, DCM, 2,6-lutidine, -78°C to r.t, | S118 |
| 5 | OH | PhSeCl, silica gel, DCM, -78°C to r.t, | S125 |
| 6 | OH | $(PhSe)_2$, NBS, DCM, r.t. | S118 |
| 7 | OAc | PhSeCl, DCM, -78°C to r.t, | no conversion |
| 8 | OH | PhSCl, DCM, -78°C to r.t, | no conversion |
| 9 | OH | $I_2$, $NaHCO_3$, DCM, 80°C | S125 |
| 10 | OH | HCl, DCM, r.t. | S125 |
| 11 | OH | NBS, DCM | S118 |
| 12 | OH | NIS, DCM | S118 |
| 13 | OH | ICl, $NaHCO_3$, DCM | S123, S118 |
| 14 | OH | $I_2$, $AgBF_4$, DCM, $NaHCO_3$ | S118 |
| 15 | OH | $I_2$, AgOTf, DCM, $NaHCO_3$ | S118 |
| 16 | OH | $I_2$, $NaHCO_3$, MeCN, 70°C, | S118, 48 |
| 17 | OH | $I_2$, AgOTf, $CH_3CN$, $NaHCO_3$, 70°C | S123 (75%) |
| 18 | OH | ICl, AgOTf, $CH_3CN$, $NaHCO_3$, -78°C to r.t. | 48 (83%) |

After extensive experimentation and screening of various electrophiles, solvents, and temperatures, we were pleased to find that the desired cyclization could be achieved under conditions 18 providing the desired product in 83% yield.

# Part-V Experimental Procedures

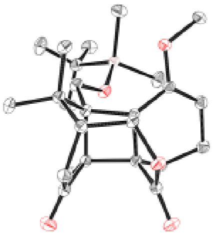
## *Step-1*



**9** *boat-like conformation*

**16** *chair-like conformation*

**17**



*ORTEP of* **17**

Compound **9** (12.5 g, 22.5 mmol, 1 equiv.) was dissolved in THF (200 mL, ~0.1 M) under nitrogen and cooled to 0 °C. TBAF (1 M in THF, 23.6 mL, 23.6 mmol, 1.05 equiv.) was added and the mixture was stirred at 0 °C for 30 min. Upon completion of the reaction, as determined by TLC, the reaction was quenched upon addition of saturated $NH_4Cl$ aq. (150 mL) and extracted with ethyl acetate (3 x 100 mL), washed with brine (100 mL) and dried over $MgSO_4$. The crude product was used in the following steps without further purification. An analytically pure sample was obtained by column chromatography on silica gel (PE: EtOAc 10: 1~5: 1).

**$^1$H NMR** (400 MHz, Chloroform-d) δ [ppm] = 5.95 (dd, J = 9.4, 6.6 Hz, 1H), 5.55 (d, J = 7.3 Hz, 1H), 5.38 (d, J = 9.4 Hz, 1H), 5.04 (d, J = 6.6 Hz, 1H), 4.11 (d, J = 11.4 Hz, 1H), 3.66 (d, J = 11.4 Hz, 1H), 3.62 (s, 3H), 2.78 (dd, J = 20.2, 2.0 Hz, 1H), 2.66 (dd, J = 20.2, 5.2 Hz, 1H), 2.47 (ddd, J = 7.3, 5.2, 2.0 Hz, 1H), 1.44 (s, 3H), 1.13 (s, 3H), 0.93 (s, 3H), 0.85 (s, 9H), 0.03 (s, 6H).

**HRMS** Calculated for $C_{25}H_{37}O_5Si^+$ $[M+H]^+$: 445.2405, found: 445.2403

The crude product **16** (10.0 g, 22.5 mmol, 1.0 equiv.) was dissolved in THF (250.0 mL, 0.09 - 0.1 M) under nitrogen in a flame-dried Schlenk flask. Palladium hydroxide on carbon (1.5 g, 2.3 mmol, 0.1 equiv. 20 wt %) was added and the solution was degassed (freeze-pump-thaw, 3 cycles). The Schlenk flask and the solution were purged with $H_2$ (through septum via needle/double-walled balloon) the mixture was stirred under positive $H_2$ pressure at room temperature for 4-6 h. Upon completion of the reaction, as determined by TLC, the reaction was flushed with $N_2$ briefly to remove the remaining $H_2$ and the reaction mixture was filtered through a Celite pad and concentrated in vacuo. The product was purified by column chromatography on silica gel (PE: EtOAc 20: 1 ~ 5: 1) to give the product as a colorless solid (9.7 g, 21.8 mmol, 97%).

**$^1$H NMR** (400 MHz, Chloroform-d) δ [ppm] = 5.16 (d, J = 7.3 Hz, 1H), 4.88 (dd, J = 6.9, 1.8 Hz, 1H), 3.86 (q, J = 11.4 Hz, 2H), 3.52 (s, 3H), 2.72 (dd, J = 20.2, 2.1 Hz, 1H), 2.60 (dd, J = 20.2, 5.1 Hz, 1H), 2.40-2.36 (m, 1H), 2.17-2.09 (m, 1H), 2.01-1.97 (m, 1H), 1.93-1.85 (m, 1H), 1.83-1.76 (m, 1H), 1.36 (s, 3H), 1.19 (s, 3H), 0.93 (s, 3H), 0.85 (s, 9H), 0.04 (s, 3H), 0.03 (s, 3H).

**$^{13}$C NMR** (101 MHz, Chloroform-d) δ [ppm] = 209.4, 179.2, 151.2, 98.3, 85.9, 61.2, 60.5, 58.9, 54.3, 54.1, 48.9, 48.1, 45.5, 37.5, 25.9, 23.9, 22.6, 21.9, 19.9, 18.1, 14.3, -5.8.

**HRMS** Calculated for $C_{25}H_{39}O_5Si^+$ [M+H]$^+$: 447.2561, found: 447.2569.

*Notes:*

*For the TBS deprotection:*

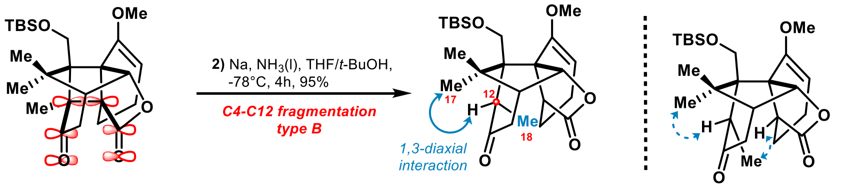
*--The reaction time should not be elongated more than necessary to prevent lowered yields by deprotection of the primary alcohol functionality.*

*For the hydrogenation*

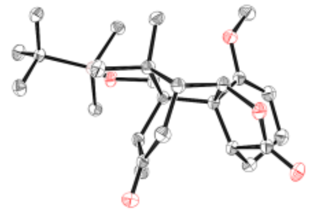
*--Due to the similar polarity of the starting material **16** and product **17**, the TLC was required to be performed two times to get a better separation. The starting material could be identified by UV absorption (254 nm) and the product could be stained with CAM.*

*--The reaction time should not be elongated more than necessary to prevent the over-reduction of the methyl enol ether.*

***Step-2***



**17** **18** **18**



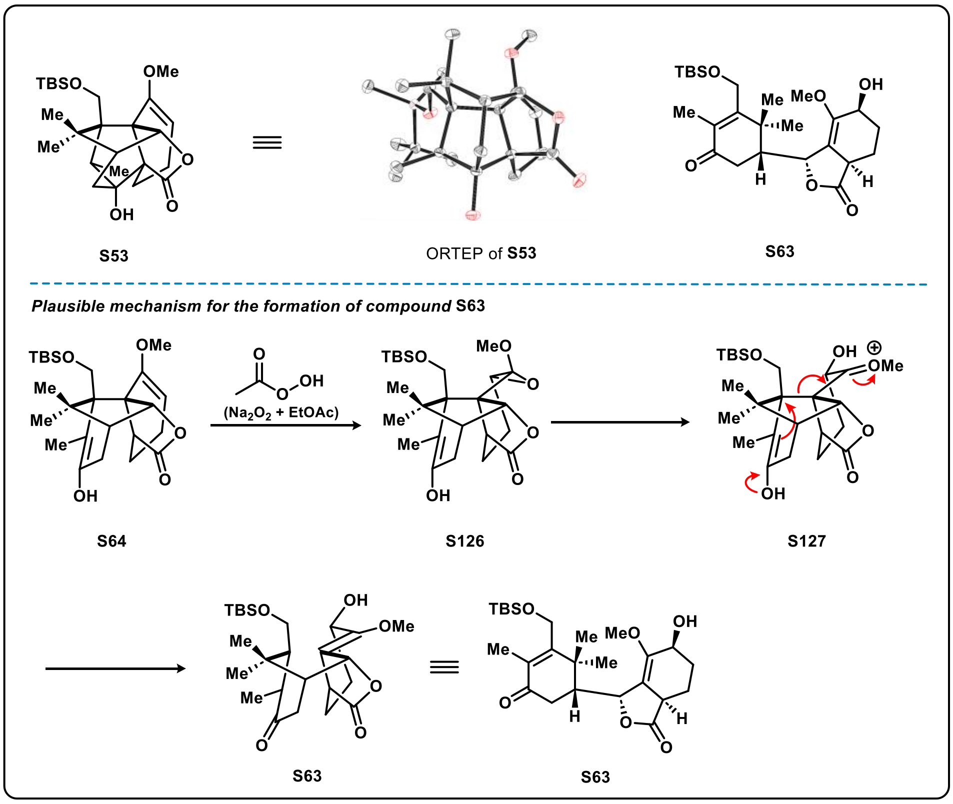
*ORTEP of* **18**

300.0 mL of ammonia was condensed into a flame-dried round Schlenk flask at -78 °C. 7-8 pieces of freshly cut sodium (~500.0 mg per piece) were added to the solution. The solution was stirred at -78 °C for 15 min until the sodium was dissolved completely and the solution turned dark blue. A solution of compound **17** (5.0 g, 11.2 mmol 1.0 equiv.) in THF/*t*-BuOH (1: 1 20 mL, ~0.5 M) was added dropwise to the reaction. The mixture was vigorously stirred at -78 °C for 6 hours. The solution must remain dark blue during this time. Upon completion, the reaction was quenched with solid $NH_4Cl$ and $P(OEt)_3$ (0.1 mL). The cooling bath was removed and the mixture was allowed to warm to room temperature slowly and the ammonia was allowed to evaporate. 150 mL of $H_2O$ were added and the mixture was neutralized with sodium phosphate buffer (pH = 7.0, 1 M), followed by extraction with diethyl ether, (3 x 150 mL). The organic phase was further washed with brine (150 mL) and dried over $MgSO_4$. The solvent was removed in vacuo and the residue was purified by column chromatography on silica gel (PE: EtOAc 20:1 ~ 5:1) to obtain the product as a colorless solid (4.7 g, 10.6 mmol, 95%).

**$^1$H NMR** (500 MHz, Chloroform-d) δ [ppm] = 5.11 (dd, J = 5.8, 1.1 Hz, 1H), 4.98 (t, J = 4.4 Hz, 1H), 3.98 (d, J = 10.6 Hz, 1H), 3.51 (s, 3H), 3.44 (d, J = 10.6 Hz, 1H), 3.31 (q, J = 6.8 Hz, 1H), 2.67 – 2.60 (m, 1H), 2.52 – 2.46 (m, 2H), 2.17 (t, J = 6.2 Hz, 1H), 2.13 – 2.08 (m, 1H), 2.03 – 1.94 (m, 2H), 1.81 – 1.72 (m, 1H), 1.43 (s, 3H), 1.27 (s, 3H), 1.22 (d, J = 6.8 Hz, 3H), 0.87 (s, 9H), 0.06 (s, 3H), 0.04 (s, 3H).

**$^{13}$C NMR** (126 MHz, Chloroform-d) δ [ppm] = 215.2, 178.3, 152.3, 100.8, 85.5, 61.8, 56.6, 55.2, 53.8, 49.2, 46.8, 46.3, 44.3, 38.1, 25.9, 24.8, 22.0, 19.8, 18.1, 11.9, -5.5, -5.7.

**HRMS** Calculated for $C_{25}H_{41}O_5Si^+$ $[M+H]^+$: 449.2718, found: 449.2710.



*Notes:*

*--For best results, t-BuOH was dried over $CaH_2$ (refluxing for 6 hours followed by distillation) before use.*

*--The BHT in commercial THF (99.5%, Extra Dry over Molecular Sieve, Stabilized, AcroSeal™), was removed by distilling with benzophenone-sodium.*

*--The reaction time was optimized and should be kept as stated by the procedure. Shorter reaction times lead to incomplete conversion.*

*--The starting material **17** and product **18** were found to be inseparable by TLC. Alternatively, the reaction can only be monitored by NMR.*

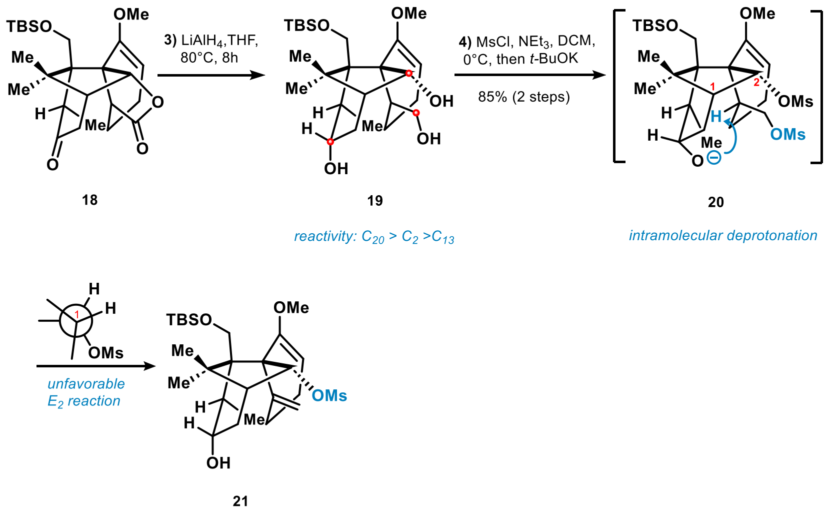
*--The mixture should be really vigorously stirred to prevent the t-BuOH/THF/starting material **17** solution from solidifying in the Schlenk flask.*

*--To prevent the cyclization side product **S53**, the extraction and neutralization should be conducted as soon as the ammonia is evaporated. Storage of the unquenched product led to increased by-product formation.*

*--Triethyl phosphite was added to avoid an oxidative side reaction, presumably a consequence of contamination with sodium peroxide, during the quenching process which led to the fragmentation side product **S63**.*

*--The C12 stereocenter was unambiguously confirmed by the NOESY and X-ray structure analysis.*

### *Step-3,4*



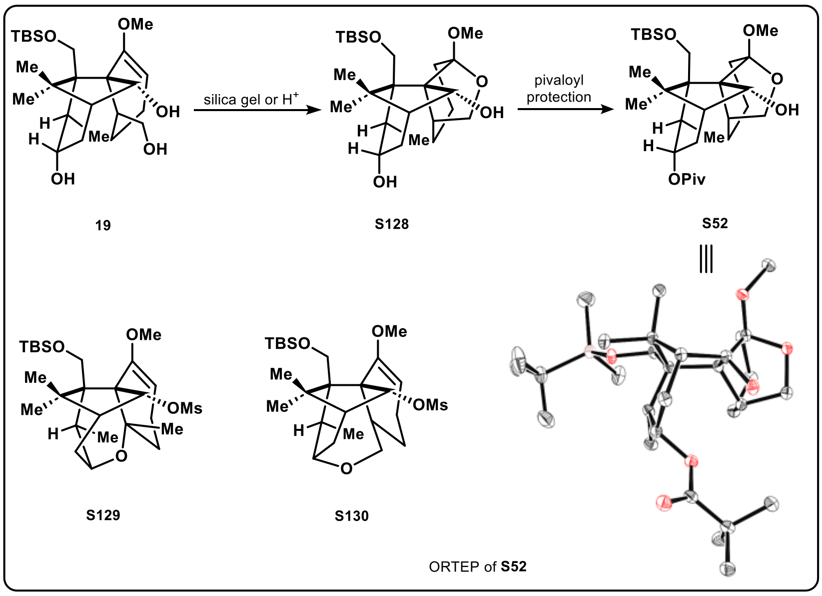
In a 500 mL flame-dried sealed tube, compound **18** (9.2 g 20.7 mmol, 1.0 equiv.) was dissolved in dry THF (200 mL) and cooled to 0 °C. $LiAlH_4$ (41.5 mL 2.5 M in THF, 5.0 equiv.) was added and the mixture was heated to 75 °C for 8 hours. Upon complete conversion of the starting material, the reaction was quenched with saturated $NH_4Cl$ aq. (50 mL) at 0 °C followed by the addition of aqueous saturated Rochelle salt solution (150 mL) and stirring at room temperature for another 2 hours. The mixture was extracted with diethyl ether (3 x 150 mL). The organic phase was further neutralized with sodium phosphate buffer (pH = 7.0, 1 M) and washed with brine (150 mL) and dried over $MgSO_4$. The solvent was concentrated in vacuo and provided triol **19** as a colorless solid. The crude product was directly used for the following steps without further purification.

Triol **19** (2.0 g, 4.4 mmol, 1.0 equiv.) was dissolved in dry dichloromethane (50 mL) under nitrogen in a flame-dried Schlenk flask. The mixture was cooled to 0 °C. Triethylamine (1.6 mL, 1.2 g 12.3 mmol, 2.8 equiv.) was added, followed by a solution of methane sulfonyl chloride (5.5 g, 3.7 mL in dichloromethane (44 mL), 4.8 mmol, 2.1 equiv., 0.1 M) that was added dropwise to the reaction over 30 min. The reaction was stirred at 0 °C for another 30 min. Upon complete conversion as indicated by TLC (PE: EtOAc 2:1), a solution of potassium tert-butoxide (2.0 g in THF (20 mL), 17.6 mmol, 4.0 equiv. 0.8 M) was added. The mixture was warmed to room temperature and stirred for 1 hour. The reaction was quenched upon addition of a saturated aqueous solution of $NH_4Cl$ (100 mL) and the aqueous phase was extracted with diethyl ether (3 x 150 mL). The organic phase was further neutralized with sodium phosphate buffer (pH = 7.0, 1 M), then washed with brine (150 mL) and dried over $MgSO_4$. The solvent was removed in vacuo. The crude product was purified by column chromatography on silica gel (PE: EtOAc 10: 1~ 5: 1) and gave the product as a bright yellow oil (9.0 g, 17.5 mmol, 85%).

**$^1$H NMR** (400 MHz, Chloroform-d) δ [ppm] = 5.92 (d, J = 5.6 Hz, 1H), 5.63 (d, J = 1.8 Hz, 1H), 5.24 (d, J = 1.8 Hz, 1H), 5.05 – 4.99 (m, 1H), 4.13 (td, J = 10.7, 3.9 Hz, 1H), 3.78 (d, J = 10.3 Hz, 1H), 3.60 (d, J = 10.3 Hz, 1H), 3.56 (s, 3H), 3.08 – 2.97 (m, 1H), 2.85 (s, 3H), 2.69 – 2.57 (m, 1H), 2.40 (td, J = 12.1, 5.8 Hz, 1H), 2.26-2.19 (2H), 2.10 – 2.02 (m, 2H), 1.99-1.95 (m, 1H), 1.37 (s, 3H), 1.14 (s, 3H), 1.04 (d, J = 7.8 Hz, 3H), 0.89 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H).

**$^{13}$C NMR** (101 MHz, Chloroform-d) δ [ppm] = 153.5, 151.5, 114.4, 101.8, 84.1, 66.7, 63.5, 62.8, 58.4, 54.6, 49.7, 42.7, 38.8, 38.5, 38.3, 34.0, 27.4, 26.5, 26.0, 25.0, 18.3, 13.3, -5.5, -5.7.

**HRMS** Calculated for $C_{26}H_{46}O_6SSi^+$ $[M+H]^+$:515.2857, found: 515.2863.



ORTEP of **S52**

*Notes:*

*For $LiAlH_4$ reduction reaction*

*--The $LiAlH_4$ reduction reaction could only be monitored by either NMR or triethylamine-neutralized silica gel TLC (DCM: MeOH: TEA 10: 1: 0.1).*

*--The triol **19** was found to be very sensitive to acid. Undesired product **S128** was predominantly formed during the evaporation of the solvent, if the organic phase was not neutralized with sodium phosphate buffer (pH = 7.0, 1 M). the structure was unambiguously confirmed by a X-ray structure of its derivative **S52**.*

*For mesylation/elimination reaction*

*--Triethylamine was distilled from $CaH_2$ prior to use.*

*--For best results, methane sulfonyl chloride was also freshly distilled to give a colorless oil before use and it was noticed that the quality of methane sulfonyl chloride had a great impact on the resulting yield.*

*--Di-mesylated intermediate **20** is unstable and will slowly decompose to an apolar side product **S130** on TLC or silica gel column.*

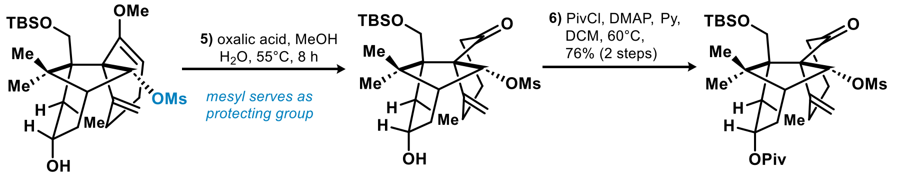
*-- Potassium tert-butoxide in this reaction was purified by sublimation at 220 °C under vacuum before use.*

*--To increase the solubility of potassium tert-butoxide in THF, ultrasonication was utilized before adding it to the reaction.*

*--Adding potassium tert-butoxide (solid) directly to the reaction did not yield any conversion.*

*--Undesired product **S129** was predominantly formed during the concentration of the crude mixture, if the organic phase was not neutralized with sodium phosphate buffer (pH = 7.0, 1 M).*

***Step-5,6***



21 S131 22

Compound **21** (4.5 g, 8.8 mmol, 1.0 equiv.) was dissolved in MeOH (100 mL) and a solution of oxalic acid (15.8 g, 175 mmol, 20.0 equiv.) in water (50 mL) was added to the reaction. The mixture was heated to 55 °C and vigorously stirred for 12 hours. Upon complete conversion of the starting material as indicated by TLC, the reaction was cooled down to 0 °C and saturated aqueous $NaHCO_3$ solution was slowly added to the mixture until pH = 7.5-8.0 was reached. The majority of the organic solvent (MeOH) was removed in vacuo and the remaining aqueous phase was extracted with diethyl ether (3 x 150 mL). The organic phase was further washed with brine (100 mL) and dried over $MgSO_4$. The crude mixture was concentrated in vacuo. The product was purified by column chromatography on neutralized silica gel (PE: EtOAc 10: 1~ 1:1 and 10% of TEA) and the product **S131** was obtained as a white solid. (3.5 g, 7.0 mmol, 80 %).

**$^1$H NMR** (400 MHz, Chloroform-d) δ [ppm] = 6.46 (d, J = 6.3 Hz, 1H), 5.82 (s, 1H), 5.30 (s, 1H), 4.23 (d, J = 9.5 Hz, 1H), 4.02 (s, 1H), 3.58 (d, J = 9.4 Hz, 1H), 2.95 (s, 4H), 2.84 – 2.75 (m, 2H), 2.51 – 2.40 (m, 3H), 2.10 – 2.03 (m, 3H), 1.63 – 1.52 (m, 1H), 1.18 (d, J = 7.6 Hz, 3H), 1.11 (s, 3H), 0.96 (s, 3H), 0.89 (s, 9H), 0.09 (s,3H), 0.07 (s,3H).

**$^{13}$C NMR** (101 MHz, Chloroform-d) δ [ppm] = 209.7, 150.0, 119.6, 82.7, 70.4, 66.6, 66.1, 63.6, 49.3, 44.1, 43.3, 40.8, 37.9, 37.9, 32.2, 26.9, 26.0, 25.9, 24.4, 18.2, 13.2, -5.4, -5.7.

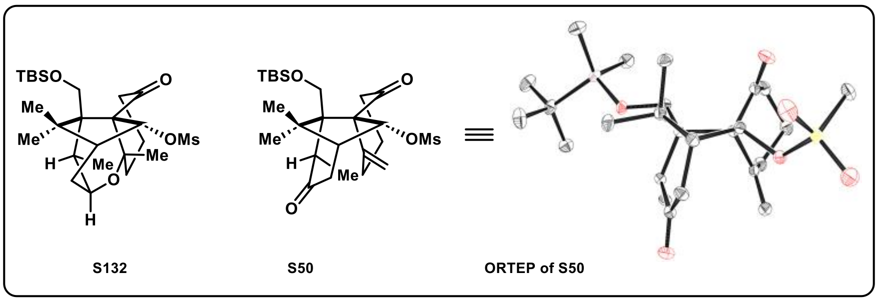
**HRMS** Calculated for $C_{25}H_{44}NaO_6SSi^+$ $[M+Na]^+$: 523.2520, found: 523. 2517

Pyridine (1.0 mL, 1.0 g, 12.6 mmol, 1.8 equiv.), DMAP (85.4 mg, 0.7 mmol, 0.1 equiv.), and pivaloyl chloride (1.3 mL, 1.2 g, 10.5 mmol, 1.5 equiv.) were added to a solution of compound **S131** (3.5 g, 7.0 mmol, 1.0 equiv.) in dry dichloromethane (70 mL). The mixture was heated to 40 °C for 8 hours. The reaction was cooled down to room temperature and quenched upon addition of a saturated aqueous solution of $NaHCO_3$ (150 mL) and the aqueous phase was extracted with ethyl acetate (3 x 150 mL). The organic phase was further washed with brine (150 mL) and dried over $MgSO_4$. The solvent was removed in vacuo. The residue was purified by column chromatography on silica gel (PE: EtOAc 10: 1~ 1:1) to give the product as an amorphous solid (3.9 g, 6.7 mmol, 95 %).

**$^1$H NMR** (400 MHz, Chloroform-d) δ [ppm] = 6.37 (d, J = 5.2 Hz, 1H), 5.60 (s, 1H), 5.44 (td, J = 10.9, 4.0 Hz, 1H), 5.34 (s, 1H), 4.17 (d, J = 9.5 Hz, 1H), 3.47 (d, J = 9.5 Hz, 1H), 3.18 – 3.06 (m, 1H), 2.90 (s, 3H), 2.83-2.78 (m, 1H), 2.67 (td, J = 13.7, 3.8 Hz, 1H), 2.54 – 2.37 (m, 3H), 2.13 – 2.07 (m, 1H), 2.01 (dd, J = 6.3, 3.3 Hz, 1H), 1.96 (dd, J = 16.4, 4.0 Hz, 1H), 1.64-1.56 (m, 2H), 1.17 (s, 9H), 1.16 (s, 3H), 1.09 (d, J = 7.7 Hz, 3H), 1.03 (s, 3H), 0.87 (s, 9H), 0.07 (s, 3H), 0.05 (s, 3H).

**$^{13}$C NMR** (101 MHz, Chloroform-d) δ [ppm] = 210.6, 178.5, 141.4, 122.9, 82.1, 69.3, 66.6, 65.7, 62.1, 49.0, 44.5, 43.6, 40.4, 38.9, 37.8, 36.5, 29.0, 27.3, 26.5, 26.1, 25.9, 24.1, 18.2, 12.0, -5.4, -5.7.

**HRMS** Calculated for $C_{30}H_{52}NaO_7SSi^+$ $[M+Na]^+$: 607.3095, found: 607.3092



S132

S50

ORTEP of S50

*Notes:*

*--The solubility of the compound* ***21*** *and oxalic acid in MeOH/$H_2O$ is limited, ultrasonication might be utilized at elevated temperatures (55 °C – 60 °C) until the solution became completely transparent.*

*--The reaction time should not be elongated more than necessary to prevent the deprotection of the TBS group.*

*--Especially upon scale-up, additional ultrasonication might be necessary, if the starting material starts to accumulate on the stirring bar as a yellow viscous oil or if the mixture becomes an emulsion.*

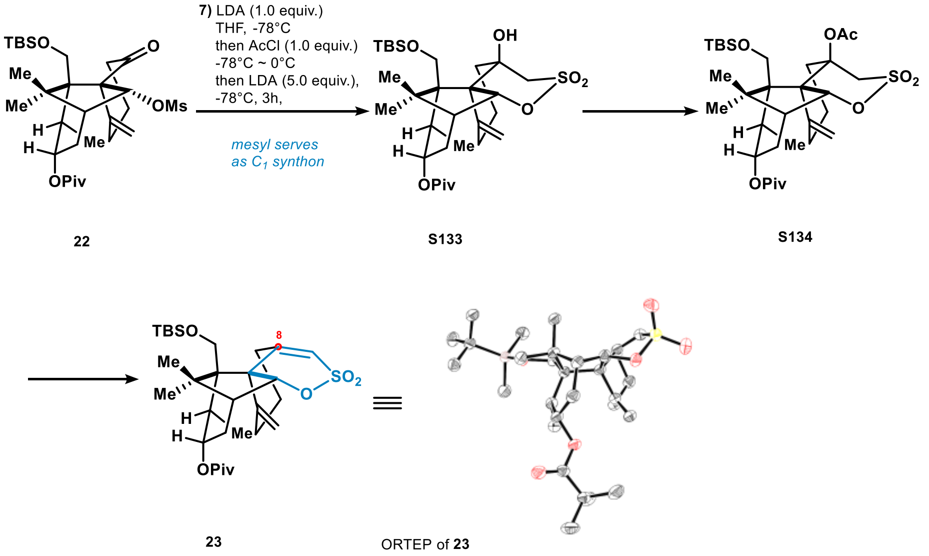
*--The product is unstable under acidic conditions and the undesired product* ***S132*** *was predominantly formed during the evaporation of MeOH, in case that the solution was not neutralized to pH = 7.5 - 8.0 with aqueous $NaHCO_3$ solution.*

*--It might be necessary in some cases to extract the aqueous phase more than 3 times with diethyl ether. The extraction of remaining product was monitored by TLC of the diethyl ether phase and only ended when there was no product detectable anymore to guarantee full extraction of the product.*

*--To prevent the formation of the side product* ***S132****, the silica gel for column chromatography was neutralized with triethylamine prior to addition of the crude product.*

*--The structure of compound* ***S132*** *was also indirectly confirmed by an X-ray crystallographic analysis of its C13 ketone derivate* ***S50****.*

## ***Step-7***

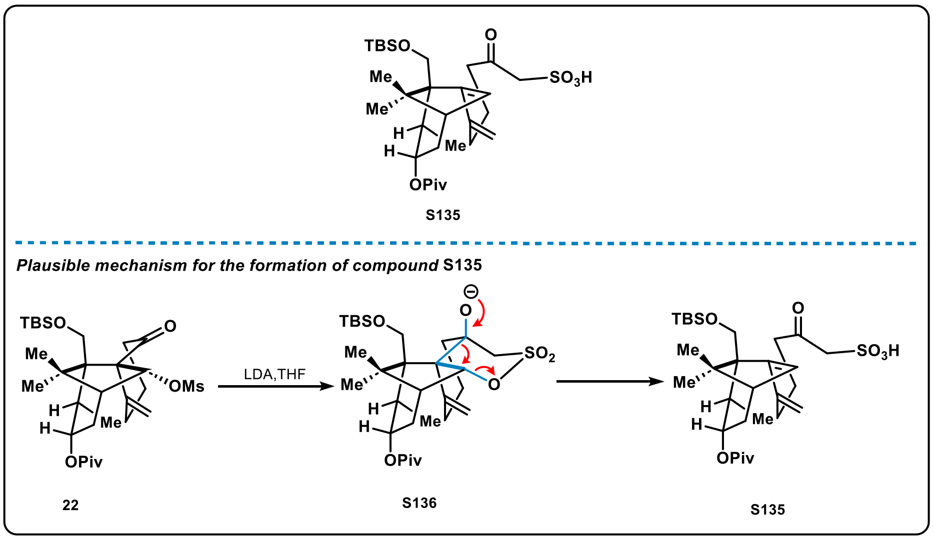


Compound **22** (3.9 g, 6.7 mmol, 1.0 equiv.) was dissolved in dry THF under nitrogen in a flame-dried Schlenk tube. The mixture was cooled to -78 °C and freshly prepared LDA (7.4 mmol, 14.8 mL, 0.5 M in THF, 1.1 equiv.) was added dropwise over 30 min via syringe pump. The mixture was then stirred for another hour at -78 °C upon which the solution turned slightly yellow. Upon TLC showed consumption of the starting material, a solution of acetyl chloride (0.53 mL, 0.6 g, 7.4 mmol 1.1 equiv.) in THF (15.0 mL) was added dropwise to the mixture at -78 °C over 30 min. The cooling bath was removed and the reaction was allowed to warm to 0 °C slowly. The complete conversion of intermediate **S133** to intermediate **S134** was monitored by TLC. Then, the mixture was cooled down to -78 °C again and an excess of freshly prepared LDA (33.5 mmol, 33.5 mL, 1.0 M in THF, 5.0 equiv.) was added to the reaction. The reaction was then stirred at -78 °C for 4 hours. The reaction was quenched upon addition of a saturated aqueous solution of $NH_4Cl$ (100 mL) and the aqueous phase was extracted with ethyl acetate (3 x 150 mL). The organic phase was further washed with brine (100 mL) and dried over $MgSO_4$. The solvent was removed in vacuo and the product **23** was purified by column chromatography on silica gel (PE: EtOAc 10: 1~ 2:1) as a crystalline solid. (2.5 g, 4.4 mmol, 65 %).

**$^1$H NMR** (400 MHz, Chloroform-d) δ [ppm] = 6.00 (s, 1H), 5.49 – 5.40 (m, 2H), 5.25 (s, 1H), 5.09 (s, 1H), 4.26 (d, J = 9.9 Hz, 1H), 3.89 (d, J = 9.9 Hz, 1H), 3.21 – 3.10 (m, 1H), 2.63 – 2.54 (m, 1H), 2.52 – 2.42 (m, 2H), 2.34 (dd, J = 12.0, 5.3 Hz, 1H), 2.27 – 2.21 (m, 1H), 2.16 – 2.10 (m, 1H), 2.07 (dd, J = 8.1, 5.2 Hz, 1H), 1.88 (dd, J = 16.3, 4.6 Hz, 1H), 1.63 – 1.55 (m, 1H), 1.27 (s, 3H), 1.16 (s, 9H), 1.16 (s, 3H), 1.04 (d, J = 7.7 Hz, 3H), 0.90 (s, 9H), 0.10 (s, 6H).

**$^{13}$C NMR** (101 MHz, Chloroform-d) δ [ppm] = 178.4, 167.5, 143.6, 121.3, 115.8, 86.5, 66.3, 65.5, 61.4, 57.1, 46.4, 44.6, 38.9, 38.8, 36.9, 35.9, 34.5, 29.2, 27.3, 26.9, 25.9, 25.6, 18.3, 13.2, -5.4, -5.6.

**HRMS** Calculated for $C_{30}H_{50}NaO_7SSi^+$ $[M+Na]^+$: 589.2990, found: 589.2986



*Plausible mechanism for the formation of compound* S135

*Notes:*

*For the cyclization reaction*

*--LDA preparation: n-BuLi (4.0 mL, 10.0 mmol, 2.5 M in THF) was added to a solution of i-Pr$_2$NH (1.6 mL, 1.1 g, 11 mmol) in THF (15.5 mL) at -78 °C. The mixture was allowed*

*to warm to 0 °C and stirred for 30 min at this temperature. The resulting LDA stock solution was then directly used for the described reaction within a few hours.*

*--The BHT in commercial THF (99.5%, Extra Dry over Molecular Sieve, Stabilized, AcroSeal™), was removed by distillation with benzophenone-sodium.*

*--For the best results, the Schlenk tube was tilted at a 45° angle to the bench and submerged in the dry ice bath as far as possible. LDA was then added by syringe pump via a bended needle to the glass wall of the flask at the top end of the Schlenk tube and allowed to slowly run over the cooled glass surface into the reaction mixture to achieve cooling of the reagent before encountering the reaction mixture.*

*--Occasionally, it was necessary to add additional portions of LDA (0.5 ~1 mL each time) until TLC indicated full conversion.*

*--It was observed that the side product* ***S135*** *started to form upon addition of an excess of LDA or at elevated temperature (~ -40 °C.) Application of the pre-cooled LDA solution as described above, thus helped to reduce the formation of side product* ***S135****.*

*For the acetylation reaction*

*--Acetyl chloride was freshly distilled under* $N_2$ *atmosphere prior to use. The reaction would be quenched and conversion stopped at the cyclization stage, if the acetyl chloride was contaminated by HCl.*

*--In case that there were residual amounts of cyclization intermediate* ***S133*** *left, the reaction could be brought to completion by cooling the reaction to -78 °C and adding an additional portion of acetyl chloride and LDA dropwise to the mixture. The reaction was slowly warmed to 0 °C and stirred for another 30 min. The above operation could be repeated until the cyclization intermediate* ***S133*** *was converted completely.*

*--On TLC, the spot of the acetylated product* ***S134*** *appeared to be slightly less polar than the cyclization compound's spot (****S133****) (PE:* EtOAc *4:1).*

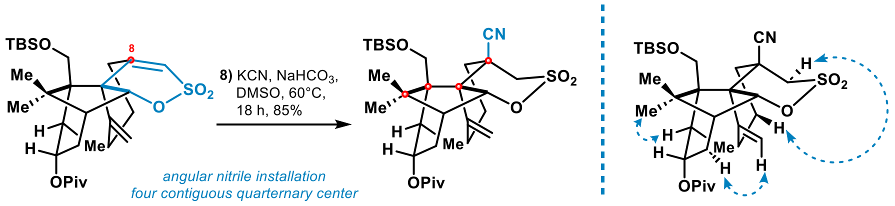
*For the elimination reaction*

*--LDA preparation: n-BuLi (4.0 mL, 10.0 mmol, 2.5 M in THF) was added to a solution of* $i$-$Pr_2NH$ *(1.6 mL, 1.1 g, 11 mmol) in THF (5.5 mL) at -78 °C. The mixture was allowed to warm to 0 °C and stirred for 30 min at this temperature. The resulting LDA stock solution was then directly used for the described reaction within a few hours.*

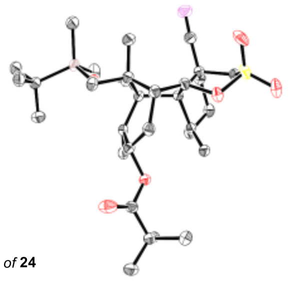
*--Vinyl sultone* ***23*** *and intermediate* ***S134*** *have exactly the same polarity and could not be distinguished on TLC and the reaction can only be monitored by NMR.*

*--In case of remaining acetylated intermediate* ***S134*** *after quenching, the crude mixture could be resubjected to the elimination conditions.*

## *Step-8*



23 24 24



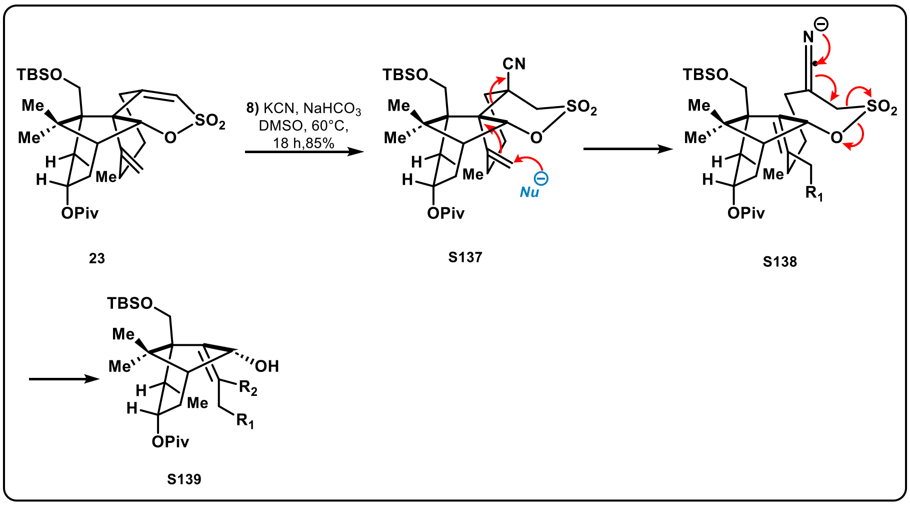
*ORTEP of* **24**

Compound **23** (2.5 g, 4.4 mmol, 1.0 equiv.) was dissolved in dry DMSO (50 mL) in a Schlenk flask under nitrogen protection. $NaHCO_3$ (0.7 mg, 8.8 mmol, 2.0 equiv.), and potassium cyanide (1.4 g, 22.0 mmol, 5.0 equiv.) were added to the mixture, and the reaction was stirred at 55 °C for 18 hours. Upon completion, the reaction was quenched by the addition of a saturated aqueous solution of $NaHCO_3$ (100 mL), and the aqueous phase was extracted with ethyl acetate (3 x 150mL). The organic phase was further washed with brine (150 mL) and dried over $MgSO_4$. The solvent was removed in vacuo. The product **24** was obtained by column chromatography on silica gel (PE: EtOAc 8: 1~ 2: 1) as a crystalline solid. (2.2 g, 3.7 mmol 85%).

**$^1$H NMR** (600 MHz, Chloroform-d) δ [ppm] = 5.63 (s, 1H), 5.52 – 5.45 (m, 2H), 5.36 (d, J = 5.6 Hz, 1H), 4.28 (d, J = 9.8 Hz, 1H), 4.23 (d, J = 10.3 Hz, 1H), 4.00 (d, J = 14.1 Hz, 1H), 3.28 – 3.20 (m, 1H), 3.12 (d, J = 14.1 Hz, 1H), 2.60-2.54 (m, 1H), 2.46 (td, J = 13.6, 5.0 Hz, 1H), 2.34 – 2.24 (m, 2H), 2.07 (dd, J = 8.3, 5.1 Hz, 1H), 1.91 (d, J = 10.0 Hz, 1H), 1.86 (dd, J = 16.4, 4.6 Hz, 1H), 1.81 (d, J = 14.2 Hz, 1H), 1.63 (s, 3H), 1.59 (dt, J = 14.3, 4.8 Hz, 1H), 1.32 (s, 3H), 1.17 (s, 9H), 1.01 (d, J = 7.7 Hz, 3H), 0.92 (s, 9H), 0.14 (s, 3H), 0.12 (s, 3H).

**$^{13}$C NMR** (101 MHz, Chloroform-d) δ [ppm] = 178.3, 137.2, 123.0, 122.8, 87.3, 66.8, 62.9, 55.5, 54.3, 46.6, 46.3, 45.0, 39.4, 38.9, 38.5, 36.7, 30.0, 29.5, 28.5, 27.3, 26.9, 26.0, 22.1, 18.3, 14.2, -5.4, -5.6.

**HRMS** Calculated for $C_{31}H_{51}NNaO_6SSi^+$ $[M+Na]^+$:616.3099, found: 616.3043



23, S137, S138, S139

*Notes:*

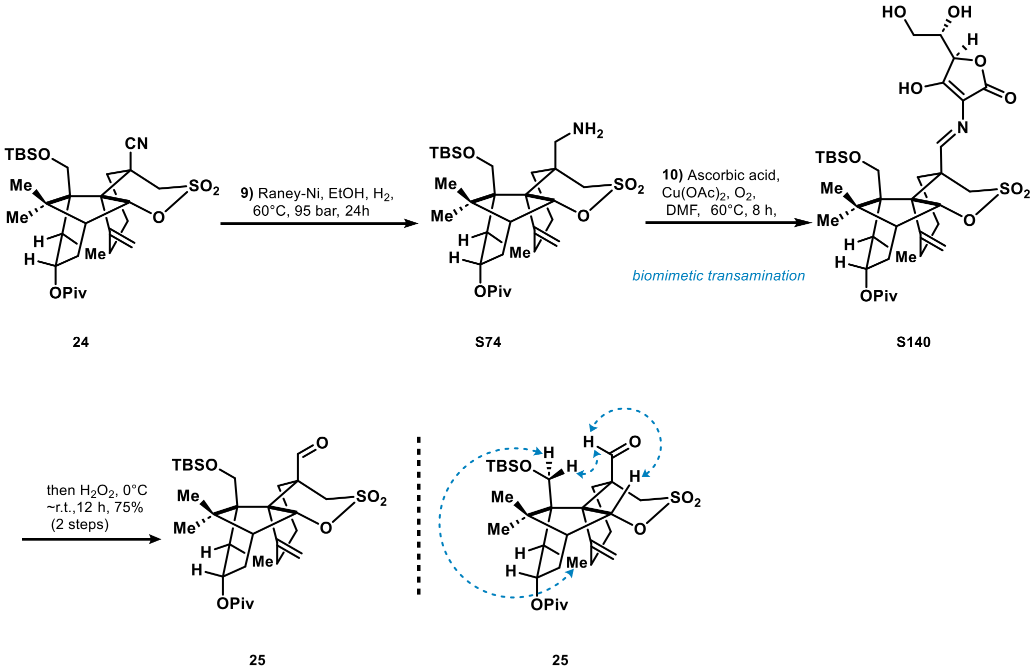
*--Potassium cyanide utilized in this reaction was purified in crystalline form following the procedure of Theodore J. Neubert. Purification and Single‐Crystal Growth of Potassium Cyanide. J. Chem. Phys.* ***41****, 722 (1964). It was observed that impurities in the KCN will trigger the formation of side product* ***S139****.*

*--Occasionally, it was necessary to add additional portions of KCN and elongate the reaction time until TLC indicated full conversion of the starting material.*

*--The KCN containing aqueous phase was mixed with an excess of sodium hypochlorite solution in NaOH solution (pH 10) for a period of 24 hours before disposal.*

*--The conformation of the product was unambiguously assigned by NOESY and X-ray structure analysis.*

## *Step-9, 10*



24, S74, S140, 25, 25

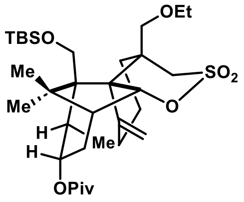
Compound **24** (1.1 g, 1.9 mmol, 1.0 equiv.). was dissolved in EtOH (20 mL) in an autoclave and freshly prepared Raney-Ni was added to the reaction. The mixture was stirred vigorously at 60 °C under 95 bar of hydrogen for 24 hours. After TLC indicated complete conversion, the reaction mixture was flushed with $N_2$ briefly to remove the remaining $H_2$ in the solution. The Raney-Ni was removed by filtration through a Celite pad with pure EtOAc ~ EtOAc: EtOH 10:1 and the filtrate were concentrated in vacuo. The crude product was directly utilized for the next step without further purification.

Ascorbic acids (0.8 g, 4.8 mmol, 2.5 equiv.) and $Cu(OAc)_2$ (90.5 mg 0.5 mmol, 0.1 equiv.) were dissolved in dry DMF (25 mL) and heated to 50 °C for 2 hours under a flow of dry $O_2$. This solution was then added to compound **S74** in DMF (15 mL) and heated to 70 °C for 12 hours. Upon complete conversion of the starting material as indicated by TLC, the purple reaction mixture was cooled to 0 °C and $H_2O_2$ (2.2 mL, 2.2 g, 19 mmol, 10.0 equiv. 30wt%) was added dropwise at this temperature. The mixture was warmed to room temperature and stirred for 12 hours. Upon full consumption of intermediate **S140** as indicated by TLC, the remaining $H_2O_2$ was quenched upon addition of saturated aqueous $Na_2S_2O_3$ solution at 0 °C and the aqueous phase was extracted with ethyl acetate (3 x 150 mL). The organic phase was further washed with brine (150 mL), dried over $MgSO_4$ and the solvent was removed in vacuo. The product **25** was purified by column chromatography on silica gel (PE: EtOAc 8: 1~ 2: 1) resulting in an amorphous solid. (0.8 g, 1.4 mmol 75%).

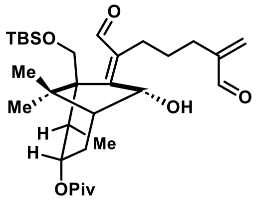
**$^1$H NMR** (400 MHz, Chloroform-d) δ [ppm] = 10.35 (s, 1H), 5.65 (s, 1H), 5.49 – 5.39 (m, 2H), 5.18 (d, J = 5.4 Hz, 1H), 4.22 (d, J = 10.2 Hz, 1H), 4.03 (d, J = 10.2 Hz, 1H), 3.80 (d, J = 14.3 Hz, 1H), 3.23 (dd, J = 10.7, 7.5 Hz, 1H), 3.15 (dd, J = 14.4, 0.9 Hz, 1H), 2.53 (dt, J = 16.3, 10.2 Hz, 1H), 2.47 – 2.36 (m, 1H), 2.26 (d, J = 8.9 Hz, 1H), 2.13 (td, J = 14.1, 5.1 Hz, 1H), 1.99 (dd, J = 8.3, 5.3 Hz, 1H), 1.88 (dd, J = 16.5, 4.7 Hz, 1H), 1.86 – 1.80 (m, 1H), 1.48 (m, 1H), 1.26 (s, 3H), 1.19 – 1.16 (m, 1H), 1.17 (s, 9H), 1.11 (s, 3H), 1.01 (d, J = 7.6 Hz, 3H), 0.90 (s, 9H), 0.10 (s, 6H).

**$^{13}$C NMR** (201 MHz, Chloroform-d) δ [ppm] = 201.4, 178.3, 139.2, 121.5, 85.4, 66.7, 63.4, 62.7, 62.2, 55.5, 52.0, 46.0, 44.6, 39.7, 38.8, 38.2, 30.3, 29.7, 29.5, 27.7, 27.2, 26.7, 25.8, 22.0, 18.2, 14.1, 13.9, -5.5, -5.7.

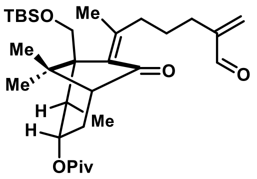
**HRMS** Calculated for $C_{31}H_{53}O_7SSi^+$ $[M+H]^+$: 597.3276, found: 597.3282



S75

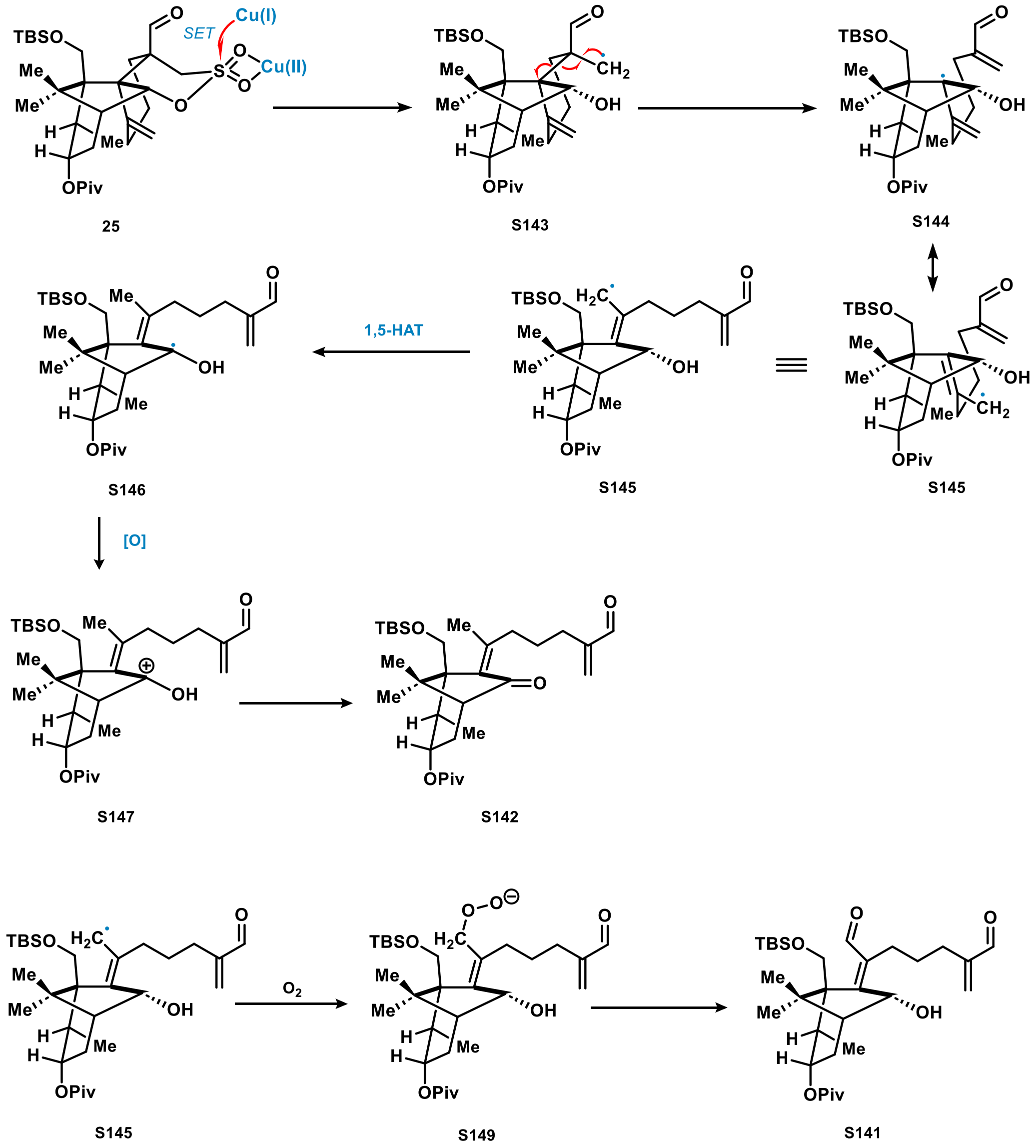


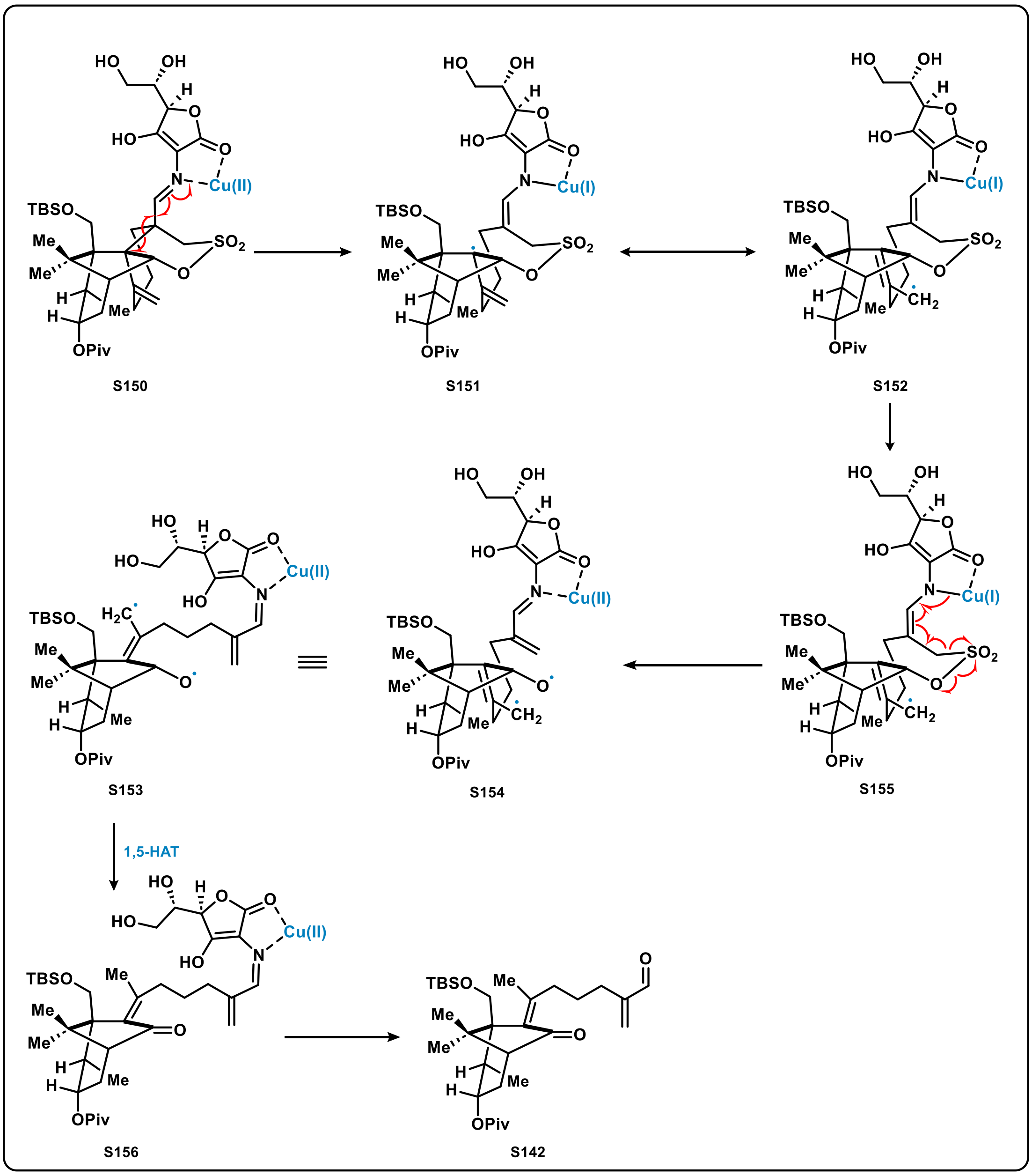
S141



S142

*Two different versions of plausible mechanism for compound S141 and compound S142*





*Notes*

*For the Raney-Nickel reduction*

*--The Raney-Nickel used in this reaction was freshly prepared following the procedure of* A. A. Pavlic; Homer Adkins. Preparation of a Raney Nickel Catalyst. *J. Am. Chem. Soc.* 1946, ***68,*** *8, 1471. It was noticed that some of the commercially available Raney Nickel Catalysts did not yield any conversion.*

*--The reaction was monitored by TLC (PE: EtOAc 2:1 Rf (starting material) = 0.3, DCM: MeOH 10: 1 Rf (amine) = 0.4).*

*--The reaction time should not be elongated more than necessary to prevent the formation of the side product **S75** which had the same polarity and Rf value as the starting material on TLC.*

*--The solubility of the starting material in EtOH was limited. Sonication (45 min, 30 °C) might be used to dissolve the material completely and obtain a transparent solution*

*before adding the Raney-Nickel catalyst.*

*For the ascorbic acid-induced transamination reaction*

*--The reaction time for the formation of dehydroascorbic acid should not be shortened. Side-product **S141** and **S142** were predominately observed, if there was remaining ascorbic acid introduced into the reaction mixture.*

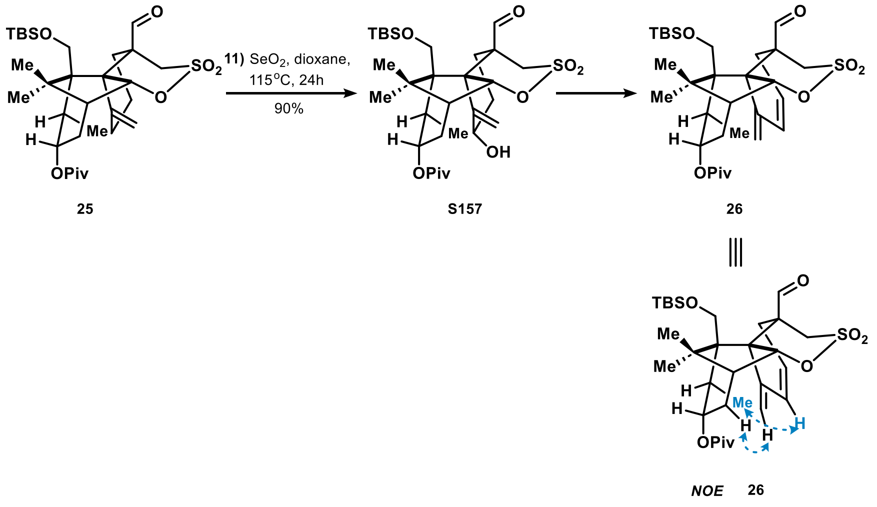
*--$O_2$ was dried by passing through a sequence of $CaCl_2$ and allochronic silica gel columns.*

*--The intermediate **S140** could be detected by silica gel TLC on silica gel (EtOAc: EtOH 10: 1 $R_f$ (amine **S74**) = 0.8, $R_f$ (intermediate **S140**) = 0.3).*

*--The reaction turned from dark violet to colorless after the addition of $H_2O_2$.*

*--For the best results, the saturated aqueous $Na_2S_2O_3$ solution was added dropwise to the mixture at 0 °C to avoid decomposition originating from warming the reaction mixture by the exothermic reaction. The mixture was checked for remaining oxidant by potassium iodide-starch test paper before the extraction.*

***Step-11***



In a 50 mL sealed tube, compound **25** (0.8 g, 1.4 mmol, 1.0 equiv.) was dissolved in dry dioxane under nitrogen and $SeO_2$ (1.5 g, 14.0 mmol 10.0 equiv.) was added. The mixture was heated to 115 °C for 24 hours. Upon completion, the reaction was quenched by the addition of a saturated aqueous solution of $NH_4Cl$ (150 mL), and the aqueous phase was extracted with ethyl acetate (3 x 100mL). The organic phase was further washed with brine (100 mL) and dried over $MgSO_4$. The solvent was removed in vacuo. The product **26** was purified by column chromatography on silica gel (PE: EtOAc 10: 1~ 2:1) to provide a colorless solid (772.0 mg, 1.3 mmol, 90 %).

**$^1$H NMR** (400 MHz, Chloroform-d) δ [ppm] = 10.57 (s, 1H), 6.16 (d, J = 10.3 Hz, 1H), 5.92 (s, 1H), 5.67 (s, 1H), 5.55 – 5.42 (m, 2H), 5.41 (d, J = 5.3 Hz, 1H), 3.91 – 3.85 (m, 2H), 3.54 (d, J = 14.3 Hz, 1H), 3.15 (t, J = 13.5 Hz, 2H), 2.97 (d, J = 20.3 Hz, 1H), 2.59 (dd, J = 16.6, 8.2 Hz, 1H), 2.11 – 2.06 (m, 1H), 2.04 – 1.97 (m, 1H), 1.53 – 1.49 (m, 1H), 1.24 (s, 3H), 1.19 (s, 9H), 1.10 (s, 3H), 0.91 (d, J = 7.5 Hz, 3H), 0.87 (s, 9H), 0.05 (s, 3H). 0.03 (s, 3H).

**$^{13}$C NMR** (201 MHz, Chloroform-d) δ [ppm] = 201.7, 178.2, 135.2, 134.8, 126.4, 118.8, 83.5, 66.4, 61.8, 61.2, 57.2, 55.3, 52.7, 46.4, 44.9, 38.8, 37.4, 31.5, 30.4, 27.3, 27.2, 26.8, 25.8, 18.1, 12.4, -5.6, -5.8.

**HRMS** Calculated for $C_{31}H_{50}NaO_7SSi^+$ $[M+Na]^+$: 617.2939, found: 617.2934

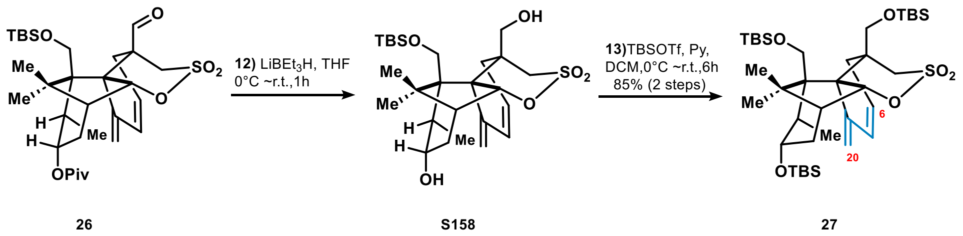
*Notes:*

*--A significant excess of $SeO_2$ was necessary. With a reduced amount (10.0 equiv. of $SeO_2$) incomplete conversion was observed, resulting in a mixture of product and intermediate **S157**. Resubjecting the mixture to the identical reaction conditions allowed to convert intermediate **S157** to the desired product smoothly.*

*--Occasionally, the commercial $SeO_2$ appeared slightly reddish or yellow. Purification by sublimation was conducted in this case.*

*--It was observed that temperature control is essential for the success of the reaction. Below 110 °C, hardly any conversion was observed. The internal temperature should be precisely adjusted and kept between 115-120 °C.*

### *Step-12,13*



Compound **26** (500 mg, 0.8 mmol, 1.0 equiv.) was dissolved with dry THF (15 mL) under nitrogen in a flame-dried Schlenk tube and cooled to 0 °C. Super-hydride (2.0 mmol, 2.0 mL 2.0 M in THF, 5.0 equiv.) was added dropwise by syringe pump over a period of 5 min. The mixture was allowed to warm to room temperature and stirred for another 45 min. As soon as TLC confirmed complete conversion of the starting material, the mixture was quenched upon addition of a saturated aqueous solution of $NH_4Cl$ (100 mL) at 0 °C and extracted with ethyl acetate (3 x 150mL). The organic phase was further neutralized with sodium phosphate buffer (pH = 7.0, 1 M), washed with brine (150 mL) and dried over $MgSO_4$. The solvent was removed in vacuo to give the diol **S158** as a light-yellow oil. The crude product was directly used for the following steps without further purification.

Dry pyridine (190.0 mg, 0.2 mL, 2.4 mmol 3.0 equiv.) was added to a solution of diol **S158** in dry dichloromethane (10.0 mL) under nitrogen and the mixture was cooled to 0 °C. TBSOTf (444.4 mg, 0.4 mL, 2.0 mmol, 2.5 equiv.) was added dropwise over 5 min and the mixture was allowed to warm to room temperature and was further stirred at this temperature for 6 hours. Upon complete conversion of the starting material as indicated by TLC, the mixture was quenched by the addition of a saturated aqueous solution of $NaHCO_3$ (100 mL) and extracted with dichloromethane (3 x 100mL). The organic phase was washed with brine (150 mL), dried over $MgSO_4$ and the solvent was removed in vacuo. The product **27** was purified by column chromatography on silica gel (PE: EtOAc 100: 1~ 50:1) to obtain a colorless oil (518 mg, 0.7 mmol, 85 %).

**$^1$H NMR** (400 MHz, Chloroform-d) δ [ppm] = 6.09 (d, J = 9.8 Hz, 1H), 5.78 (s, 1H), 5.40 (s, 1H), 5.37 (m, 1H), 5.21 (d, J = 5.3 Hz, 1H), 4.62 (d, J = 8.2 Hz, 1H), 4.23 (td, J = 10.5, 3.9 Hz, 1H), 3.98 (d, J = 9.7 Hz, 1H), 3.83 (d, J = 9.8 Hz, 1H), 3.77 (d, J = 6.6 Hz, 1H), 3.44 (d, J = 13.6 Hz, 1H), 3.17 (d, J = 13.6 Hz, 1H), 2.92 (dq, J = 10.3, 7.5 Hz, 1H), 2.49-2.40 (m, 1H), 2.18 – 2.09 (m, 2H), 2.09 – 1.95 (m, 2H), 1.16 (s, 3H), 1.13 (s, 3H), 0.95 (d, J = 7.5 Hz, 3H), 0.91 (s, 9H), 0.88 (s, 18H), 0.11 (s, 3H), 0.09 (s, 3H), 0.03 (s, 3H), 0.02 (s, 6H), 0.01 (s, 3H).

**$^{13}$C NMR** (201 MHz, Chloroform-d) δ [ppm] = 135.9, 134.6, 126.1, 119.1, 81.8, 67.6, 66.2, 63.6, 62.9, 53.4, 51.9, 48.2, 47.1, 44.4, 39.3, 35.0, 34.7, 27.7, 26.0, 26.0, 25.7, 18.4, 18.4, 18.2, 13.6, -4.2, -5.0, -5.4, -5.6, -5.7.

**HRMS** Calculated for $C_{38}H_{72}NaO_6SSi_3^+$ [M+Na]$^+$: 763.4250, found: 763.4256

*Notes:*

*For the super-hydride reduction*

*--It was noticed that the aldehyde was reduced first at 0 °C leading to the formation of a more polar spot on the TLC (PE: EtOAc 2:1 $R_f$ = 0.3). The pivaloyl ester was only reduced when the reaction was warmed to room temperature (PE: EtOAc 2:1 $R_f$ = 0.2).*

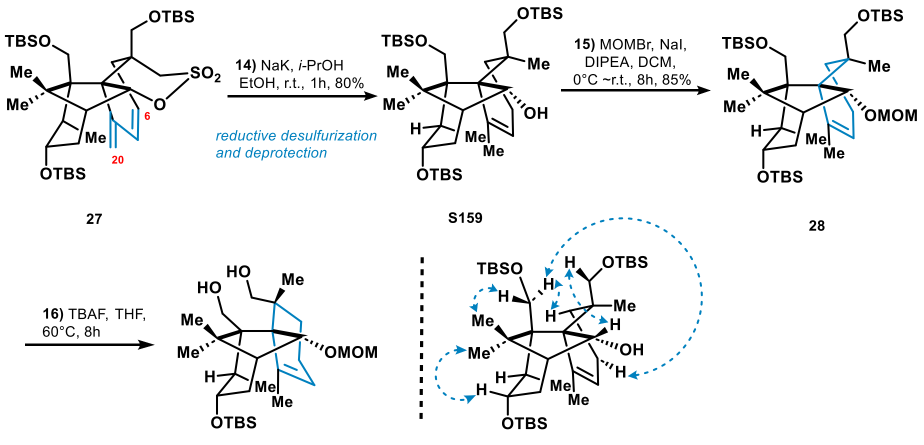
*For the TBS protection*

*--Owing to the steric hindrance, the TBS protection, especially at the C13 position, was rather slow. It was observed that the addition of catalytic amounts of DMAP accelerated the reaction.*

*--Additional portions of TBSOTf and pyridine might be added, if remaining starting material or mono-silylated intermediate was observed after stirring for 6 hours.*

*--The apolar silyl impurities should be carefully separated upon column chromatography to prevent side reactions in the following step. For this purpose, it proved to be beneficial to flash the column with pure PE (100 mL). Gradient-elution column chromatography is highly recommended to purify the product (PE: EtOAc 50: 1 $R_f$ = 0.5)*

## Step-14,15,16



27

S159

28

S160

28

(The following procedure was used in case there remained no more sodium-potassium alloy after completion of the reaction. An alternative quenching procedure has to be followed in case of remaining sodium-potassium alloy in the reaction mixture which will be provided in the notes below.)

In a 100 mL flame-dried Schlenk flask, compound **27** (100 mg, 0.1 mmol, 1.0 equiv.) was dissolved in dry *i*-PrOH/EtOH (6.0 mL/0.2 mL, v/v 30:1) under nitrogen. Freshly prepared sodium-potassium alloy (0.5 - 0.6 mL, excess) was added dropwise via syringe to the mixture. The mixture was stirred at room temperature for 1 hour. Upon completion of the reaction as indicated by TLC, a saturated aqueous $NH_4Cl$ solution was carefully added to neutralize the mixture until pH = 7 was reached and the aqueous phase was extracted with diethyl ether (3 x 100 mL). The organic phase was further washed with brine (100 mL) and dried over $MgSO_4$. The solvent was removed in vacuo. The product XX was purified by column chromatography on silica gel (PE: EtOAc 100: 1~ 50:1) to give a light-yellow foam (54.4 mg, 0.08 mmol, 80 %). (PE: EtOAc 50: 1 $R_f$ (starting material) = 0.5, $R_f$ (product) = 0.8)

**$^1$H NMR** (400 MHz, Chloroform-d) δ [ppm] = 5.32 (s, 1H), 5.09 (t, J = 6.5 Hz, 1H), 4.32 (td, J = 10.6, 4.5 Hz, 1H), 4.05 (d, J = 9.6 Hz, 1H), 3.97 (d, J = 10.3 Hz, 1H), 3.85 (d, J = 9.6 Hz, 1H), 3.40 (d, J = 10.4 Hz, 1H), 3.14 (dd, J = 10.9, 7.7 Hz, 1H), 2.35-2.28 (m, 1H), 2.28 (s, 3H), 2.13 – 2.08 (m, 3H), 1.67-1.57 (m, 1H), 1.51-1.47 (m, 1H), 1.24 (m, 1H), 1.23 (s, 3H), 1.15 (s, 3H), 1.14 (s, 3H), 0.97 (d, J = 7.7 Hz, 3H), 0.89 (s, 9H), 0.88 (s, 18H), 0.04 (s, 3H), 0.04 (s, 3H), 0.03 (s, 3H), 0.03 (s, 3H), 0.02 (s, 3H), 0.01 (s, 3H).

**$^{13}$C NMR** (201 MHz, Chloroform-d) δ [ppm] = 139.9, 127.1, 72.0, 66.4, 65.3, 63.7, 59.9, 50.5, 47.7, 43.9, 38.5, 33.2, 31.6, 31.4, 30.3, 30.2, 29.0, 26.9, 26.0, 25.9, 25.9, 25.8, 22.0, 18.3, 18.2, 12.7, -4.3, -5.2, -5.5, -5.7, -5.7, -5.8.

**HRMS** Calculated for $C_{38}H_{77}O_4Si_3^+$ $[M+H]^+$: 681.5124, found: 681.5131

Compound **S159** (54.4 mg, 0.08 mmol, 1.0 equiv.), NaI (13.2 mg, 0.09 mmol, 1.1 equiv.) DIPEA (32.4 mg, 46.2 µl (8-10 drops), 0.32 mmol, 4.0 equiv.) were dissolved in dry dichloromethane (5.0 mL) under nitrogen in a flame-dried Schlenk tube. The mixture was cooled to 0 °C and a solution of MOMBr (24 mg, 1.6 mL, 0.16 mmol, 0.1 M in DCM, 2.0 equiv.) was added dropwise over 30 min via syringe pump. The reaction was slowly allowed to warm to room temperature and stirred overnight. Upon completion of the reaction as indicated by TLC, the reaction was quenched by the addition of a saturated aqueous $NaHCO_3$ solution (100 mL). The aqueous phase was extracted with dichloromethane (3 x 100mL). The organic phase was further washed with brine (150 mL) and dried over $MgSO_4$. The solvent was removed in vacuo. The crude product was directly used for the next step without further purification.

To a stirred solution of compound **28** in THF (2.0 mL), TBAF (1.2 mL, 1.2 mmol, 1.0 M in THF, 15.0 equiv.) was added. The mixture was heated to 60 °C and stirred for 8 hours. Upon completion, as determined by TLC, the reaction was quenched upon addition of $NH_4Cl$ aq. (100 mL) and the aqueous phase was extracted with ethyl acetate (3 x 100 mL). The organic phase was further washed with brine (150 mL) and dried over $MgSO_4$. The solvent was removed in vacuo. The product **S160** was purified by column chromatography on silica gel (PE: EtOAc 8: 1~ 2:1) to give the product as a colorless oil (19.8 mg, 0.04 mmol, 61% (85% for MOM protection and 72% for TBS deprotection).

**$^1$H NMR** (400 MHz, Chloroform-d) δ [ppm] = 5.31 (t, J = 4.7 Hz, 1H), 4.70 (d, J = 5.9 Hz, 1H), 4.66 – 4.56 (m, 2H), 4.35 (td, J = 10.3, 5.7 Hz, 1H), 4.20 (d, J = 10.8 Hz, 1H), 4.06 (d, J = 11.6 Hz, 1H), 4.01 (d, J = 10.8 Hz, 1H), 3.56 (d, J = 11.6 Hz, 1H), 3.36 (s, 3H), 3.13 – 2.97 (m, 1H), 2.33 – 2.27 (m, 1H), 2.26 (s, 3H), 2.17 – 2.06 (m, 2H), 1.67 – 1.58 (m, 2H), 1.53-1.45 (m, 1H), 1.29 (s, 3H), 1.20 (s, 3H), 1.21 – 1.18 (m, 1H), 1.11 (s, 3H), 1.07 (d, J = 7.8 Hz, 3H), 0.90 (s, 9H), 0.04 (s, 3H), 0.02 (s, 3H).

**$^{13}$C NMR** (101 MHz, Chloroform-d) δ [ppm] = 140.6, 126.6, 97.6, 85.1, 72.1, 66.3, 64.4, 64.1, 60.3, 56.4, 48.4, 47.6, 44.2, 38.7, 33.5, 31.5, 30.4, 29.5, 26.1, 26.0, 25.8, 21.8, 18.3, 12.7, -4.3, -5.1.

**HRMS** Calculated for $C_{28}H_{53}O_5Si^+$ $[M+H]^+$: 497.3657, found: 497.3650

*Notes*

*For the reductive desulfurization*

*--EtOH and i-PrOH were dried over CaO (refluxing for 4 hours) and distilled prior to use.*

*--Sodium-potassium alloy was freshly prepared following the procedure of J, F. Birmingham, Jr. Making Glean Liquid Sodium Potassium Alloy, Ind. Eng. Chem. Anal. Ed.* ***1935,*** *7, 1, 53. Gilman, H.; Young, R. V., J. Org. Chem.* ***1936****, 1, 315.*

*--Two sodium-potassium alloy compositions (56% K, 44% Na and 78% K, 22% Na) were tested and it was observed that 78% K, 22% Na worked substantially better.*

*--It was observed that BHT had a similar polarity as the product and was difficult to separate by column chromatography. Thus, diethyl ether that was used for the extraction was distilled to remove BHT.*

*--The quenching procedure in case of remaining sodium-potassium alloy:*

*The reaction solution was carefully separated and transferred by syringe to a beaker equipped with a stirring bar.*

*The remaining sodium-potassium alloy was washed three times with dry i-PrOH. All the solution phases were combined in the beaker and 0.5 mL of dry EtOH was added to the mixture dropwise to ensure that there were no sodium-potassium alloy particles left. A saturated aqueous* $NH_4Cl$ *solution was added to neutralize the mixture until pH = 7 was reached and the aqueous phase was extracted with diethyl ether (3 x 100 mL).*

*--The reaction time should not be elongated more than necessary to prevent the TBS deprotection which could be identified by a spot appearing on the baseline of the TLC (PE: EA 50:1).*

*--For the best result, the stirring rate should be precisely adjusted. It was observed that it was favorable, if the sodium-potassium alloy could float in the middle of the solution. Rapid stirring resulted in a finely dispersed sodium-potassium alloy which quickly reacted with the solvent. Slow stirring rates resulted in a substancial part of the sodium-potassium alloy floating on top of the solution without sufficient contact with the substrate.*

*--Other solvents such as t-BuOH, THF, or a mixture of protic and aprotic solvents (i-PrOH/THF, t-BuOH/THF) were also tested and resulted in either very slow or no conversion.*

*For MOM protection*

*--NaI was dried by heating to 70* °C under vacuum prior to use.

*--DIPEA was dried over* $CaH_2$ *(refluxing for 6 hours) and distilled before use.*

*--If necessary, the commercial MOMBr (light reddish) was purified by a simple distillation under nitrogen that provided a colorless oil that can be stored in a storage Schlenk tube with vacuum valve.*

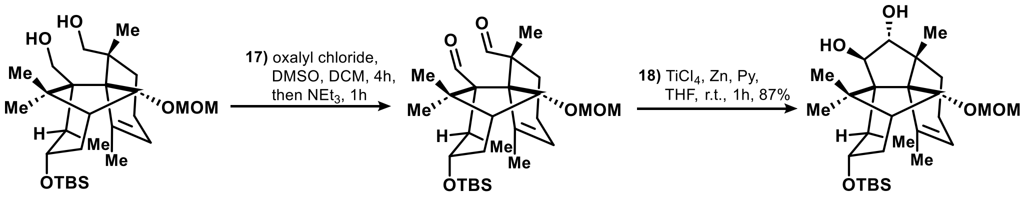
*--Other conditions such as MOMCl, DIPEA, DCM, 60 °C, 8 hours were observed to give the desired product, however, the reaction was less defined and cannot be directly submitted to the next step without purification.*

*For the TBAF deprotection reaction.*

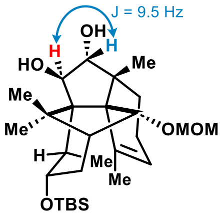
*--Excess of TBAF proved to be necessary for the reaction. With less equivalents, the C9-mono TBS deprotection product was predominantly observed.*

*--It was observed that the TBS group at the C13 position was not susceptible to deprotection in this intermediate and could not even be removed under harsher conditions.*

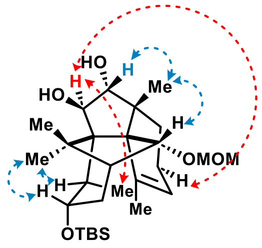
### Step-17,18



**S160** **33** **S161**



**S161**



**NOE** **S161**

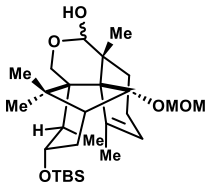
Oxalyl chloride (72.0 mg, 37.9 µl, 0.8 mmol, 20.0 equiv.) was dissolved in dichloromethane (1.0 mL) in a flame dried Schlenk tube under nitrogen and cooled to -78 °C. After 10 min, dry DMSO (124.8 mg, 0.1mL, 1.6 mmol, 40.0 equiv.) was added dropwise and the mixture was stirred for 15 min at-78 °C. A solution of the diol intermediate **S160** (19.8 mg, 0.04 mmol, 1.0 equiv.) in dichloromethane (1.0 mL) was added over 10 min via syringe pump and stirred for 2 hours. Then $NEt_3$ (242.4 mg, 0.35 mL, 2.4 mmol, 60.0 equiv.) was added and stirred at -78 °C. After 15 minutes, the cooling bath was removed and the reaction was allowed to warm to 0 °C. The reaction mixture was stirred at 0 °C for another hour before quenching with saturated aqueous $NaHCO_3$ solution (100 mL). The aqueous phase was extracted with dichloromethane (3 x 100 mL). The organic phase was further washed with brine (150 mL) and dried over $MgSO_4$. The solvent was removed in vacuo. The crude product was passed through a short silica gel column (PE: EtOAc 10:1 ~5:1) and was directly utilized for the next step without further purification.

Following a procedure by Swindell and coworkers, THF (1.0 mL) was cooled to 0 °C in a flame-dried Schlenk flask under nitrogen. After 15 min, a solution of $TiCl_4$ (0.8 mL, 0.8 mmol, 20.0 equiv. 1 M in DCM) was added and the ice bath was removed. After stirring at room temperature for 10 min, zinc dust (104 mg, 1.6 mmol, 40.0 equiv.) was added and stirred for another 10 min, resulting in a color change from bright yellow to green and later to a bright blue solution. Upon addition of pyridine (64.0 mg, 81.0 µl, 0.8 mmol, 20.0 equiv.), the color immediately changed to green again. A solution of dialdehyde **33** in THF (1.0 mL) was added dropwise via a syringe pump over 30 min and the reaction was stirred for another 30 min at room temperature. Then, the reaction was quenched upon addition of a saturated aqueous $NaHCO_3$ solution (100 mL). The aqueous phase was extracted with ethyl acetate (3 x 100 mL). The organic phase was further washed with brine (150 mL) and dried over $MgSO_4$. The solvent was removed in vacuo. The product **S161** was purified by column chromatography on neutralized silica gel (PE: EtOAc 8: 1~ 2:1 10% TEA) to provide the product as a colorless oil (17.1 mg, 0.03 mmol, 87%).

**$^{1}$H NMR** (800 MHz, Chloroform-d) δ [ppm] = 5.86 (t, J = 4.7 Hz, 1H), 4.61 (s, 2H), 4.50 (d, J = 5.4 Hz, 1H), 4.46 (d, J = 5.4 Hz, 1H), 4.37 (d, J = 9.4 Hz, 1H), 4.14 (d, J = 9.5 Hz, 1H), 3.36 (s, 3H), 2.87 (dq, J = 10.8, 7.7 Hz, 1H), 2.36 (dd, J = 15.7, 6.3 Hz, 1H), 2.30 (s, 3H), 2.27 (dd, J = 15.9, 9.9 Hz, 1H), 1.91 – 1.87 (m, 1H), 1.85 – 1.81 (m, 2H), 1.77 (dd, J = 9.0, 5.3 Hz, 1H), 1.36 (s, 3H), 1.36 – 1.33 (m, 1H), 1.31 (s, 3H), 1.28 (s, 3H), 1.28 (m, 1,H), 1.09 (d, J = 7.8 Hz, 3H), 0.93 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H).

**$^{13}$C NMR** (201 MHz, Chloroform-d) δ [ppm] = 137.6, 132.4, 96.0, 83.8, 82.1, 66.2, 64.6, 60.9, 55.4, 50.6, 44.2, 39.7, 34.4, 33.7, 32.1, 28.9, 27.8, 25.9, 25.3, 22.7, 18.1, 11.5, -4.4, -5.1.

**HRMS** Calculated for $C_{28}H_{51}O_5Si^+$ $[M+H]^+$:495.3500, found: 495.3508



**S162**

*Notes*:

*For the Swern oxidation*

*--Triethylamine was dried over $CaH_2$ (refluxing for 6 hours) and distilled before use*.

*--The product obtained after purification over a short column is not analytically pure. The column served to remove potential sulfur-containing contaminants from the Swern procedure that might interfere with the subsequent pinacol coupling.*

*--The reaction time should not be shortened to less than 2 hours before adding triethylamine to prevent the formation of the hemiacetal **S162** as a side product.*

*--The dialdehyde **33** was observed to be unstable under acidic conditions and the quality of oxalyl chloride had a great impact on the results of the reaction. With commercial oxalyl chloride, an additional distillation was required and the reagent should be stored in an ampoule under nitrogen and should resemble a colorless oil.*

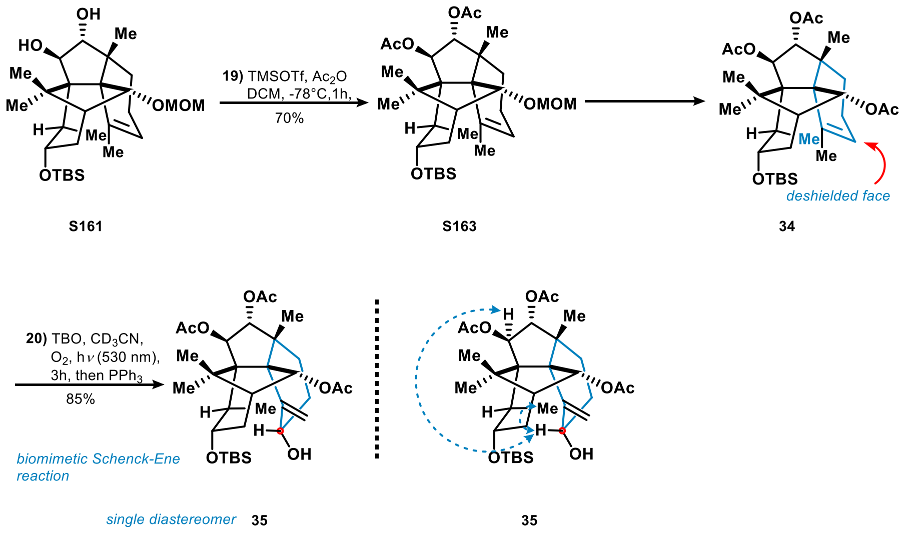
*--The Hamilton syringes used in the procedure were dried in the oven for 6 hours prior to use and cooled down under nitrogen atmosphere before use.*

*For the Pinacol coupling reaction*

*--During the reaction, 1,2-reduction that resulted in the recovery of diol **S160** was observed (less than 10%) which was inseparable from the pinacol product by column chromatography.*

*--The rate of addition of the dialdehyde **33** should be strictly controlled, otherwise, the ratio of the undesired diol will increase.*

## *Step-19,20*



S161 S163 34 35 35

Following a procedure by Procopiou and coworkers, acetic anhydride (65.4 mg, 60.5 µl, 0.6 mmol, 20.0 equiv.) was added to a solution of compound **S161** (17.0 mg, 0.03 mmol, 1.0 equiv.) in dichloromethane (1.0 mL) under nitrogen in a flame-dried Schlenk flask. The mixture was cooled down to -78 °C and stirred for 10 min. A solution of TMSOTf in dichloromethane (0.3 mL, 0.015 mmol, 0.05 M in DCM, 0.5 equiv.) was added dropwise via syringe pump and stirred for 1 hour. Upon complete conversion as indicated by TLC, the reaction was quenched by the addition of a saturated aqueous NaHCO$_3$ solution (10 mL). The aqueous phase was extracted with dichloromethane (3 x 10 mL). The organic phase was further washed with brine (10 mL) and dried over MgSO$_4$. The solvent was removed in vacuo. The product **34** was purified by column chromatography on silica gel (PE: EtOAc 8:1~ 2:1) to give a light-yellow foam (11.1 mg, 0.02 mmol, 70%).

$^1$**H NMR** (800 MHz, Chloroform-d) δ [ppm] = 5.90 (d, J = 5.4 Hz, 1H), 5.80 (d, J 9.7 Hz, 1H), 5.77 (d, J = 5.7 Hz, 1H), 5.65 (d, J = 9.6 Hz, 1H), 4.40 (dt, J = 10.0, 5.1 Hz, 1H), 2.48 (dd, J = 10.6, 7.7 Hz, 1H), 2.27 (s, 3H), 2.23-2.19 (m, 1H), 2.16-2.10 (m, 1H), 2.04 (s, 3H), 2.03 (s, 6H), 1.90 (dd, J = 9.0, 5.5 Hz, 2H), 1.70 (dd, J = 12.5, 4.9 Hz, 1H), 1.55 (s, 3H), 1.29-1.26 (m, 2H), 1.24 (s, 3H), 1.19 (s, 3H), 1.10 (d, J = 7.7 Hz, 3H), 0.89 (s, 9H) 0.03 (s, 3H), 0.02 (s, 3H).

**$^{13}$C NMR** (201 MHz, Chloroform-d) δ [ppm] = 171.1, 170.4, 170.0, 135.4, 133.8, 81.1, 78.3, 65.7, 64.1, 60.8, 49.2, 44.7, 39.9, 35.4, 33.9, 31.6, 31.4, 29.7, 28.9, 27.2, 25.9, 24.5, 22.7, 22.3, 21.6, 21.1, 21.1, 21.0, 18.1, 11.6, -4.4, -5.1.

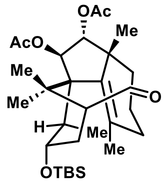
**HRMS** Calculated for $C_{32}H_{53}O_7Si^+$ $[M+H]^+$:577.3555, found: 577.3568

In a 10 mL Schlenk-tube, toluidine blue O (0.54 mg, 0.002 mmol, 0.1 equiv.) was added to a solution of compound **34** (11.1 mg, 0.02 mmol, 1.0 equiv.) in CD$_3$CN (3 mL). Dry O$_2$ was bubbled through the solution continuously through septum via needle/double-walled balloon. The reaction was irradiated at 530 nm (24W LED) for 3 hours at room temperature. Upon complete conversion of the starting material, as determined by TLC, the $O_2$ balloon was removed and the reaction was flushed with $N_2$ briefly to remove the remaining $O_2$. $Ph_3P$ (5.24 mg, 0.02 mmol, 1.1 equiv.) was added to the mixture and stirred for another 30 min to quench the peroxide intermediate. The mixture was filtered through a very short silica gel column with pure ethyl acetate (20 mL) and concentrated in vacuo. The product was obtained by column chromatography on silica gel (PE: EtOAc 10: 1~ 2:1) as an amorphous solid (9.5 mg, 0.016 mmol, 85 %).

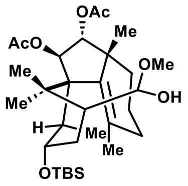
**$^1$H NMR** (400 MHz, Chloroform-d) δ [ppm] = 5.99 (d, J = 1.0 Hz, 1H), 5.81 (d, J = 8.5 Hz, 1H), 5.77 (d, J = 5.4 Hz, 1H), 5.65 (d, J = 1.5 Hz, 1H), 5.58 (d, J = 8.4 Hz, 1H), 4.38 (s, 1H), 4.17 (td, J = 10.1, 4.1 Hz, 1H), 2.49 – 2.38 (m, 1H), 2.36 – 2.26 (m, 1H), 2.12 – 2.09 (m, 1H), 2.06 (s, 6H), 2.03 (s, 3H), 1.99 (dd, J = 15.4, 4.1 Hz, 1H), 1.91 (dd, J = 8.3, 5.3 Hz, 1H), 1.58 – 1.56 (m, 2H), 1.53 (s, 3H), 1.45 – 1.43 (m, 1H), 1.41 (s, 3H), 1.10 (s, 3H), 1.07 (d, J = 7.6 Hz, 3H), 0.89 (s, 9H), 0.02 (s, 3H), 0.00 (s, 3H).

**$^{13}$C NMR** (151 MHz, Chloroform-d) δ [ppm] = 170.9, 170.3, 169.9, 143.7, 121.1, 83.9, 79.1, 78.0, 71.2, 66.5, 65.7, 62.5, 49.6, 46.3, 43.5, 40.5, 34.3, 32.9, 30.1, 29.4, 28.1, 27.6, 25.9, 25.9, 21.6, 21.1, 21.0, 18.1, 13.4, -4.4, -5.1.

**HRMS** Calculated for $C_{32}H_{53}O_8Si^+$ $[M+H]^+$: 593.3504, found: 593.3510

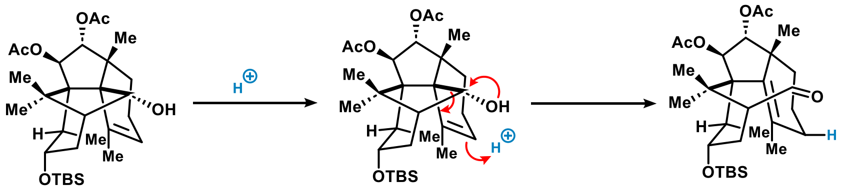


**S164**



**S165**

***Plausible mechanism for the formation of compound S 164***



**S166** **S167** **S164**

*Notes:*

*For the acetylation:*

*--It was noticed that an apolar spot could be observed 15 minutes after the addition of TMSOTf, which was confirmed to be diacetate **S163**. (PE: EtOAc 3: 1 Rf = 0.4) Upon elongation of the reaction time, diacetate **S163** was smoothly converted to the desired triacetate **34** which was slightly more polar than the diacetate **S163** on TLC (PE: EtOAc 3: 1 $R_f$ = 0.3-0.4).*

*--Due to the similar polarity of diacetate* ***S163*** *and triacetate* ***34****, the TLC was required to be performed two times to obtain a better separation.*

*--If there was remaining diacetate* ***S163*** *after stirring at -78 °C for one hour, the cooling bath was removed and the reaction was stirred for 1 min (without the cooling bath, but not fully warmed to room temperature). The reaction was then transferred back into the cooling bath before monitoring the progress of the reaction via TLC. Repeating the above procedure allowed to convert remaining diacetate* ***S163*** *completely.*

*--It is worth mentioning that extensive experimentation has been performed on the deprotection of the C2-MOM group on diacetate* ***S163****. Finally, it was realized that the intermediate with the free C2-alcohol was unstable under acidic conditions and would spontaneously fragment to intermediate* ***S164*** *and* ***S165,*** *if it was not masked* in situ *with another protecting group.*

*--The reaction time should not be elongated more than necessary. Usually, less than 5% of residual diacetate* ***S163*** *was detected in the NMR spectrum of the triacetate* ***34*** *after purification.*

*For the Schenck-ene reaction:*

*--The lamp was placed in a distance of 10 cm from the Schlenk tube.*

*--The temperature in the reaction vessel stayed close to room temperature. A 10 min cool-down cycle was conducted after each hour of irradiation or a small fan was positioned next to the reaction if necessary.*

*--The* $O_2$ *was dried by passing through a sequence of a* $CaCl_2$ *and an allochronic silica gel column.*

*--The peroxide was observed to be quite stable. It was the only newly formed spot that could be observed on TLC before quenching with* $PPh_3$*. A much more polar spot was detected on TLC after adding* $PPh_3$*.*

*--For the best results, the reaction time should not be elongated more than necessary. Testing an overnight irradiation resulted in a dramatically lowered yield.*

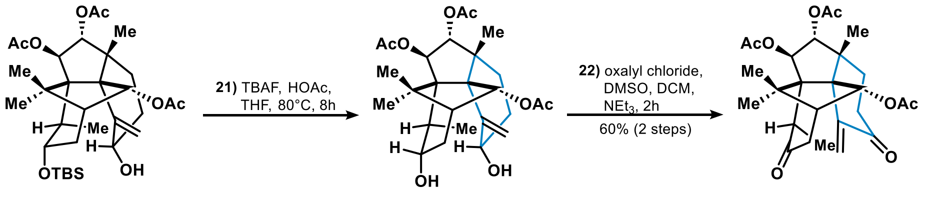
*--The purpose of the short silica gel filtration with pure ethyl acetate was to remove TBO.*

*--The purpose of first flushing the reaction with* $N_2$ *rather than directly quenching with* $PPh_3$ *was to minimize the generation of the* $OPPh_3$ *which was very difficult to separate from the product during column chromatography due to their similar polarities.*

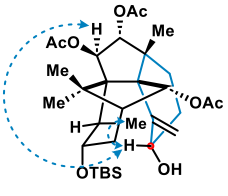
*--Other reducing reagents such as thiourea, BHT,* $P(OEt)_3$ *were also examined and resulted in a lower yield.*

*--*$CD_3CN$ *was used to elongate the lifetime of singlet oxygen in solution as opposed to decay by energy transfer to CH vibrational energies.*

### *Step-21, 22*

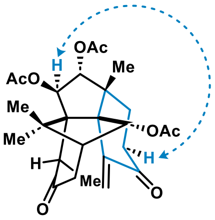


**35** **S168** **36**



**35**

*boat-like conformation*



**36**

*chair-like conformation*

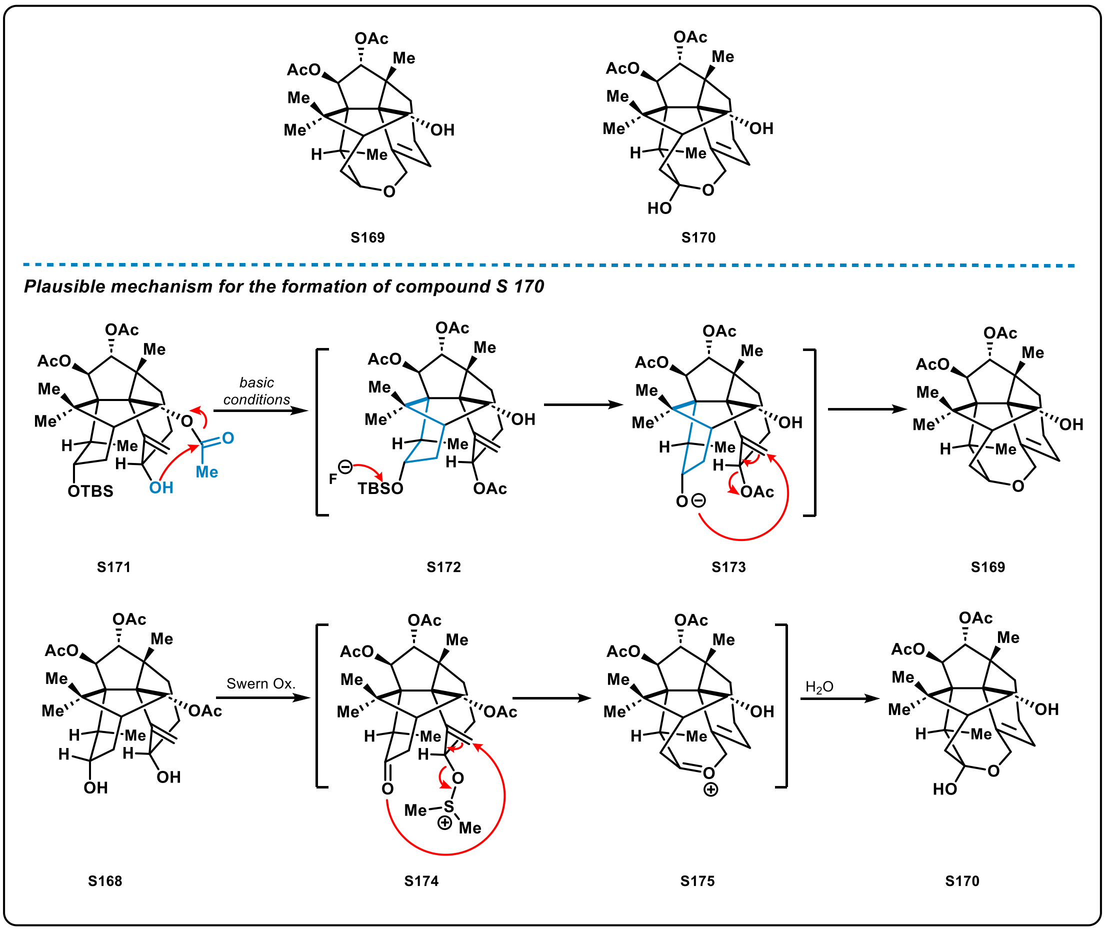
To a stirred solution of compound **35** (9.5 mg, 0.016 mmol, 1.0 equiv.) in THF, TBAF (0.16 mL, 0.16 mmol, 1.0 M in THF, 10.0 equiv.) and a drop of acetic acid were added. The mixture was heated to 80 °C and stirred for 8 hours. After completion of the reaction, as determined by TLC, it was quenched upon addition of a saturated aqueous solution of $NH_4Cl$ (10 mL) and the aqueous phase was extracted with ethyl acetate (3 x 10 mL), The organic phase was further washed with $NaHCO_3$ aq. (10 mL) and brine (10 mL) and dried over $MgSO_4$.The solvent was removed in vacuo. The crude product was passed through a short silica gel column (PE: EtOAc 1: 1) and directly utilized for the next step without further purification.

Oxalyl chloride (28.8 mg, 15.2 μl, 0.32 mmol, 20.0 equiv.) was dissolved in dichloromethane (1.0 mL) in a flame-dried Schlenk tube under nitrogen and cooled to -78 °C. After 10 min, dry DMSO (46.5 μl, 0.64 mmol, 40.0 equiv.) was added dropwise and the mixture was stirred for 15 min at -78 °C. A solution of the diol intermediate **S168** in dichloromethane (1.0 mL) was added over 15 min via a syringe pump and stirred for 30 min. Then, $NEt_3$ (96.9 mg, 138.5 μl, 0.96 mmol, 60.0 equiv.) was added and stirred at -78 °C. After 15 minutes, the cooling bath was removed and the reaction was allowed to warm to 0 °C. The reaction mixture was stirred at 0 °C for another 30 min before quenching with saturated $NaHCO_3$ aq. (10 mL). The aqueous phase was extracted with dichloromethane (3 x 10 mL). The organic phase was further washed with brine (15 mL) and dried over $MgSO_4$. The solvent was removed in vacuo. The product **36** was purified by column chromatography on silica gel (PE: EtOAc 8:1~ 2:1) was obtained as an amorphous solid (4.5 mg, 0.01 mmol, 60%).

**$^1$H NMR** (400 MHz, Chloroform-d) δ [ppm] = 6.57 (s, 1H), 6.14 (d, J = 5.3 Hz, 1H), 6.01 (s, 1H), 5.75 (d, J = 9.5 Hz, 1H), 5.67 (d, J = 9.5 Hz, 1H), 2.85 (d, J = 6.9 Hz, 1H), 2.65 – 2.61 (m, 3H), 2.49 – 2.40 (m, 1H), 2.20 (d, J = 6.1 Hz, 1H), 2.08 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 1.99-1.95 (m, 1H), 1.72 (s, 3H), 1.51-1.43 (m, 1H), 1.41 (s, 3H), 1.26 (s, 3H), 1.04 (d, J = 6.8 Hz, 3H).

**$^{13}$C NMR** (151 MHz, Chloroform-d) δ [ppm] = 210.6, 201.2, 170.8, 169.9, 169.3, 81.9, 78.4, 77.3, 61.5, 60.8, 49.7, 47.4, 45.0, 43.7, 39.5, 36.1, 32.1, 28.9, 27.5, 25.7, 21.4, 21.0, 20.8, 12.3.

**HRMS** Calculated for $C_{26}H_{35}O_8^+$ [M+H]$^+$: 475.2326, found:475.2329.



S169 S170

*Plausible mechanism for the formation of compound S 170*

S171 S172 S173 S169

S168 S174 S175 S170

*Notes:*

*For the TBS deprotection reaction*

*--The BHT in commercial THF (99.5%, Extra Dry over Molecular Sieve, Stabilized, AcroSeal™), was removed by distillation with benzophenone-sodium to avoid purification problems later upon column chromatography.*

*--It was observed that the reaction was highly temperature-dependent. Hardly any conversion was observed when the internal temperature was below 70 °C. A mixture of C9/10 partially deacetylated products was obtained, when the internal temperature was higher than 90°C.*

*--The quality and the amount of TBAF also had a great influence on the result of this reaction. Side product **S169** was observed, if TBAF was used in excess.*

*--The purpose of adding acetic acid was to neutralize the basicity of TBAF and avoid deacetylation.*

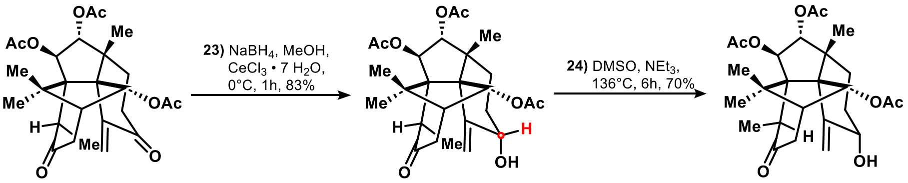
*For the Swern oxidation reaction*

*--Triethylamine was dried over $CaH_2$ (refluxing for 6 hours) and distilled before use.*

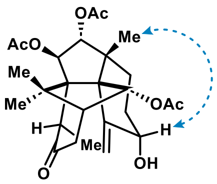
*--A number of other oxidation conditions led to the formation of the hemiacetal side product **S170**.*

*--The Hamilton syringes used for this procedure were dried in the oven for 6 hours and cooled down under nitrogen atmosphere before use.*

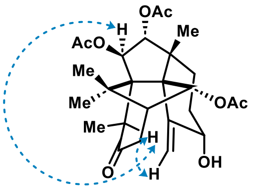
### *Step-23, 24*



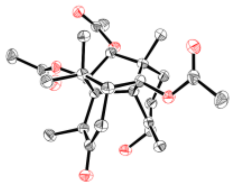
**36** *12-epi-taxinine K* **(37)** *taxinine K* **(2)**



***12-epi-taxinine K* (37)**



***taxinine K* (2)**



*ORTEP of* ***taxinine K* (2)**

Compound **36** (4.5 mg, 0.01 mmol, 1.0 equiv.) was dissolved in MeOH (1.0 mL) in a flame-dried Schlenk tube under nitrogen and cooled to 0 °C. A solution of $CeCl_3$•$7H_2O$ in MeOH (0.02 mmol, 40 µl (~8 drops) 0.5 M in MeOH, 2.0 equiv.) was added and the mixture was then stirred at 0 °C for 5 min. $NaBH_4$ (3.8 mg, 0.1 mmol, 10.0 equiv.) was added in two portions. The mixture was stirred for 5-10min at 0 °C. Upon completion of the reaction as indicated by TLC (EtOAc: PE 2: 1 $R_f$ (*starting material*) = 0.5, $R_f$ (*product*) = 0.3), a saturated aqueous $NaHCO_3$ solution (3 mL) was added carefully and the aqueous phase was extracted with ethyl acetate (3 x 5 mL). The organic phase was further washed with brine (5 mL) and dried over $MgSO_4$. The solvent was removed in vacuo. The crude product was passed through a short silica gel column using pure EtOAc as the eluant and directly utilized for the next steps without further purification.

**$^1$H NMR** (400 MHz, Chloroform-d) δ [ppm] = 5.85 (d, J = 5.6 Hz, 1H), 5.69 (d, J = 6.0 Hz 1H), 5.58 (s, 1H), 5.54 (d, J = 6.0 Hz 1H), 4.76 (s, 1H), 4.03 (m, 1H), 2.96 (m, 1H), 2.75 (d, J = 20.8 Hz, 1H), 2.48 (d, J = 20.8 Hz, 1H), 2.20 (m, 1H), 2.13 (m, 1H), 2.09 (m, 1H), 2.03 (s, 3H), 2.02 (s, 3H),2.02 (s, 3H), 1.63 (s, 3H), 1.47 (d, J = 5.7 Hz, 3H), 1.34 (m, 1H), 1.32 (m, 1H), 1.24 (s, 3H), 1.21 (s, 3H).

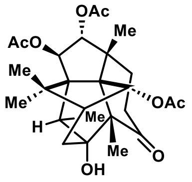
**$^{13}$C NMR** (151 MHz, Chloroform-d) δ [ppm] = 216.0, 171.0, 170.2, 170.1, 150.1, 110.9, 84.1, 78.0, 77.0, 69.9, 64.5, 61.7, 48.9, 48.9, 45.5, 44.5, 39.0, 31.3, 30.4, 28.5, 26.3, 23.0, 21.0, 20.9, 20.8, 15.7.

The crude product **37** was dissolved in dry DMSO (1.0 mL) in a flame-dried sealed tube under nitrogen and $NEt_3$ (14 µl (3-4 drops), 0.1 mmol, 10.0 equiv.) was added to the solution. The mixture was heated gradually to 136 °C in a sand bath. Upon complete conversion as indicated by TLC, the reaction was quenched with a saturated aqueous solution of $NH_4Cl$ (3 mL) and the aqueous phase was extracted with ethyl acetate (3 x 3 mL). The organic phase was further washed with brine (3 mL) and dried over $MgSO_4$. The solvent was removed in vacuo. The product **2** was purified by column chromatography on silica gel (PE: EtOAc 8:1~ 2:1) to give a crystalline solid (2.6 mg, 5.8 µmol, 58% (83% yield for the reduction step and 70% yield for the epimerization step)).

**$^1$H NMR** (600 MHz, Chloroform-d) δ [ppm] = 6.11 (d, J = 4.2 Hz, 1H), 5.76 (s, 1H), 5.69 (d, J = 9.6 Hz, 1H), 5.66 (d, J = 9.6 Hz, 1H), 5.59 (s, 1H), 4.45 (t, J = 9.0 Hz, 1H), 3.81 (m, 1H), 2.62 (d, J = 20.4 Hz, 1H), 2.50 (ddt, J = 20.4, 7.2, 1.4 Hz, 1H), 2.18 – 2.15 (m, 1H), 2.09 (s, 3H), 2.07 (s, 3H), 2.05 (s, 3H), 2.05 – 2.00 (m, 1H), 1.76 – 1.70 (m, 2H), 1.69 (s, 3H), 1.29 (s, 3H), 1.24 (d, J = 5.7 Hz, 3H), 1.23 (s, 3H), 1.14 – 1.08 (m, 1H).

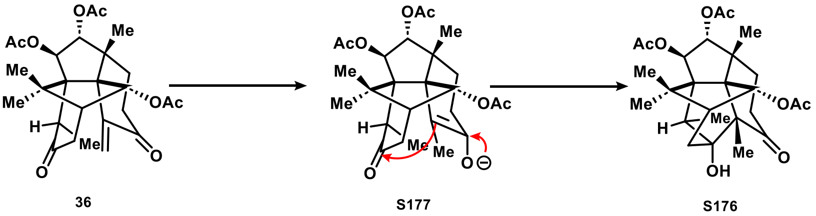
**$^{13}$C NMR** (151 MHz, Chloroform-d) δ [ppm] = 215.8, 171.1, 169.9, 169.6, 147.4, 125.8, 82.5, 79.7, 76.8, 74.9, 66.0, 57.7, 52.6, 47.9, 44.6, 42.5, 38.8, 31.3, 28.7, 27.9, 26.7, 26.3, 21.4, 21.1, 21.0, 15.6.

**HRMS** Calculated for $C_{26}H_{37}O_8^+$ $[M+H]^+$: 477.2483, found:477.2479.



S176

*Plausible mechanism for the formation of compound S176*



*Notes:*

*For the Luche reduction:*

*--Other reducing agents, such as $NaBH_4$/MeOH/-78°C, $LiBH_4$ and $ZnBH_4$/THF/-78 °C, were tested and predominantly gave compound **S176**.*

*--It was observed that the reduction was highly temperature-dependent. Compound **S176** was still observed as the major product when the reaction was conducted at -78 °C under Luche conditions.*

*--The yield was dramatically reduced, if saturated $NH_4Cl$ was used for the extraction.*

*--It was observed that the product was acid-sensitive and would decompose in the NMR tube. The $CCl_3D$ should be neutralized with dry $NaHCO_3$ and passed through a short aluminum oxide (basic) column before preparing an NMR sample.*

*--The TLC and silica gel used in this reaction were neutralized with $Et_3N$ before use.*

*--The purpose of the short silica gel filtration with pure ethyl acetate was to remove the solids generated from $NaBH_4$ upon quenching.*

*For the epimerization.*

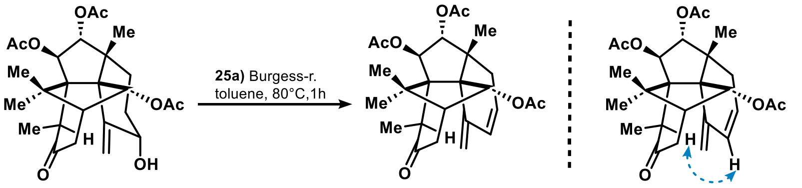
*--Hardly any conversion was observed at temperatures below 100 °C.*

*--Since the reaction was performed in a sealed tube, the temperature here was measured from the sand bath. Besides the digital thermometer of the stirrer, it is strongly recommended to add another separate (classic glass tube) thermometer to the sand bath.*

*--Triethylamine was dried over $CaH_2$ (refluxing for 6 hours) and distilled before use.*

*-- The molecular sieve powder in commercial DMSO (99.5%, Extra Dry over Molecular Sieve, Stabilized, AcroSeal™), was removed by distilling with $CaH_2$ under reduced pressure. Otherwise, a more polar spot was detected on TLC (something not related to the structure). This may either be impurities from DMSO or generated from decomposition, if DMSO was used directly without further distillation in this reaction.*

***Step-25a***



**taxinine K (2)**  **3α,11α-cyclotaxinine NN-2 (40)**  **3α,11α-cyclotaxinine NN-2 (40) NOE**

Taxinine K (**2**) (0.5 mg, 1.0 µmol, 1.0 equiv.) was dissolved in toluene (1.0 mL) under nitrogen in a flame-dried Schlenk flask. Burgess reagent (0.8 mg, 3.0 µmol, 3.0 equiv.) was added and the mixture was heated to 80 °C for 1 hour. Upon completion, as determined by TLC, the reaction was quenched upon addition of a saturated aqueous solution of $NH_4Cl$ (10 mL) and the aqueous phase was extracted with ethyl acetate (3 x 10 mL). The organic phase was further washed with brine (10 mL) and dried over $MgSO_4$. The solvent was removed in vacuo. The product **40** was obtained by column chromatography on silica gel (PE: EtOAc 10:1 ~ 2:1) as a colorless foam (0.4 mg, 0.9 µmol, 91 %).

**$^1$H NMR** (600 MHz, Chloroform-d) δ [ppm] = 6.28 (d, J = 8.9 Hz, 1H), 6.16 (d, J = 5.4 Hz, 1H), 6.12 (t, J = 6.8 Hz, 1H), 5.68 (s, 1H), 5.56 (d, J = 9.0 Hz, 1H), 5.25 (d, J = 9.0 Hz, 1H), 5.12 (s, 1H), 2.73 – 2.67 (m, 2H), 2.51 (dd, J = 20.4, 7.4 Hz, 1H), 2.23 (dd, J = 14.7, 6.9 Hz, 1H), 2.20 – 2.17 (m, 1H), 2.12 (s, 3H), 2.08 (s, 3H), 2.02 (s, 3H), 1.70 – 1.67 (m, 1H), 1.65 (s, 3H), 1.39 (d, J = 7.4 Hz, 3H), 1.21 (s, 3H), 1.21 (s, 3H).

**$^{13}$C NMR** (151 MHz, Chloroform-d) δ [ppm] = 214.1, 170.9, 169.9, 169.7, 143.3, 134.4, 131.5, 117.0, 83.3, 80.3, 76.3, 66.9, 57.8, 52.2, 49.3, 48.1, 42.1, 38.7, 34.5, 28.1, 26.9, 26.7, 21.4, 21.1, 21.0, 15.8.

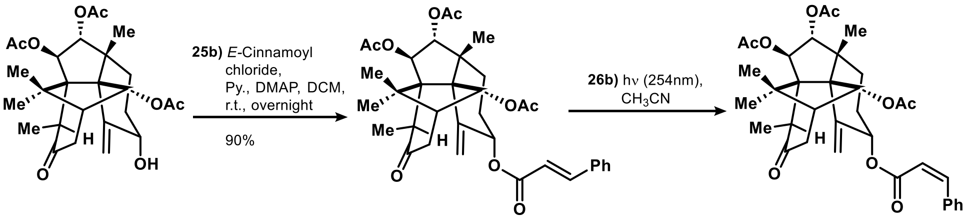
**HRMS** Calculated for $C_{26}H_{35}O_7^+$ [M+H]$^+$: 459.2377, found:459.2370.

*Notes:*

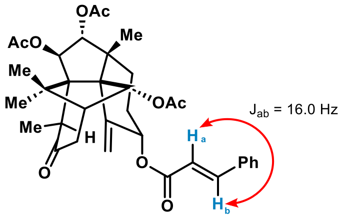
*--For the best results, the reaction time should not be elongated more than necessary.*

*--The conformation of the product **40** was unambiguously assigned by the NOESY spectrum.*

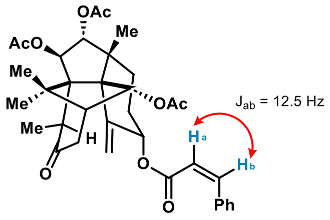
### *Step-25b,26b*



*taxinine K* (2) *taxuspine C* (13) *2,9,10-triacetyl-5-[(Z)-cinnamoyl] phototaxicin II* (41)



*taxuspine C* (13)



*2,9,10-triacetyl-5-[(Z)-cinnamoyl] phototaxicin II* (41)

Pyridine (1.2 mg, 1.22 µl (~1 drop), 16.0 µmol, 10.0 equiv.), DMAP (0.2 mg, 1.6 µmol, 1.0 equiv.), and *E*-cinnamoyl chloride (1.2 mg, 8.0 µmol, 5.0 equiv.) were added to a solution of taxinine K (**2**) (0.8 mg, 1.6 µmol, 1.0 equiv.) in dry dichloromethane (1.0 mL) at 0 °C. The mixture was allowed to warm to room temperature and stirred for 12 hours. The progress of the reaction was monitored by TLC and upon complete conversion of the starting material, the reaction was quenched upon addition of a saturated aqueous solution of $NaHCO_3$ (3 mL) and the aqueous phase was extracted with dichloromethane (3 x 3 mL). The organic phase was further washed with brine (5 mL) and dried over $MgSO_4$. The solvent was removed in vacuo. Taxuspine C (**13**) was purified by column chromatography on silica gel (PE: EtOAc 10: 1~ 1:1) to give an amorphous solid. (0.8 mg, 1.4 µmol, 85 %).

**$^1$H NMR** (600 MHz, Chloroform-d) δ [ppm] = 7.67 (d, J = 16.0 Hz, 1H), 7.55 (m, 2H), 7.37 (m, 3H), 6.38 (d, J = 16.0 Hz, 1H), 6.13 (d, J = 5.3 Hz, 1H), 5.84 (s, 1H), 5.72 (s, 1H), 5.70 (m, 1H), 5.68 (m, 1H), 5.65 (t, J = 8.9 Hz, 1H), 3.54 (d, J = 7.1 Hz, 1H), 2.59 (d, J = 20.4 Hz, 1H), 2.52 (dd, J = 20.4, 7.1 Hz, 1H), 2.18 (m, 2H), 2.07 (s, 3H), 2.04 (s, 3H), 2.04 (s, 3H), 1.78 (m, 2H), 1.69 (s, 3H), 1.31 (s, 3H), 1.28 (d, J = 7.3 Hz, 3H), 1.27 (m, 1H), 1.22 (s, 3H).

**$^{13}$C NMR** (201 MHz, Chloroform-d) δ [ppm] = 214.3, 171.0, 170.0, 169.6, 165.8, 145.4, 142.2, 134.3, 130.4, 129.5, 128.8, 128.3, 117.8, 82.3, 79.5, 76.6, 76.5, 65.9, 57.8, 52.3, 47.8, 44.5, 42.7, 38.8, 31.2, 28.8, 26.7, 26.5, 25.9, 21.5, 21.1, 21.0, 15.7.

**HRMS** Calculated for $C_{35}H_{43}O_9^+$ [M+H]$^+$: 607.2902, found:607.2900.

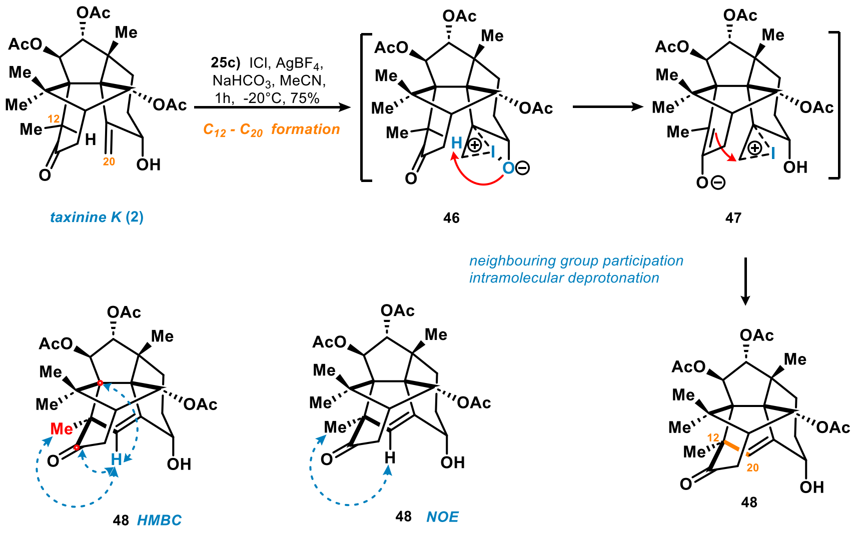
Taxuspine C (**13**) (0.8 mg, 1.4 μmol, 1.0 equiv.) was dissolved in $CH_3CN$ (200 mL) in a 10 mL quartz tube under nitrogen and degassed by nitrogen bubbling and sonication for 30 min. Then, the solution was irradiated at 254 nm (6 x OSRAM PURITEC HNS L 18W (5.5 W emission around 254 nm) for 3 min, followed by a 5 min cool-down phase. This procedure was repeated over 3 cycles. Taxuspine C (**13**) and 2,9,10-triacetyl-5-[(Z)-cinnamoyl] phototaxicin II (**41**) were observed to have the same polarity and could not be distinguished via TLC. The solvent was removed in vacuo. The crude product was purified by column chromatography on silica gel (PE: EtOAc 10: 1~ 1:1) and provided a mixture of Z/E-isomers in a ratio of 1:0.7 (Z-isomer 0.5mg, 0.8 μmol, E-isomer 0.3mg, 0.6μmol).

**$^1$H NMR** (600 MHz, Chloroform-d) δ [ppm] = 7.65 (m, 2H), 7.35 (m, 3H), 7.03 (d, J = 12.5 Hz, 1H), 6.11 (d, J = 5.3 Hz, 1H), 5.94 (d, J = 12.6 Hz, 1H), 5.78 (s, 1H), 5.70 (m, 1H), 5.64 (s, 1H), 5.60 (m, 1H), 5.58 (t, J = 8.6 Hz, 1H), 3.47 (q, J = 7.1 Hz, 1H), 2.57 (dd, J = 20.5, 7.3 Hz, 1H), 2.49 (d, J = 20.5 Hz, 1H), 2.18 (m, 1H), 2.14 (m, 1H), 2.05 (s, 3H), 2.05 (s, 3H), 2.05 (s, 3H), 2.05 (s, 3H), 1.75 (m, 1H), 1.74 (m, 1H), 1.69 (s, 3H), 1.27 (d, J = 7.1 Hz, 3H), 1.21 (s, 3H), 1.20 (m, 1H), 1.20 (s, 3H).

**$^{13}$C NMR** (201 MHz, Chloroform-d) δ [ppm] = 214.2, 171.0, 170.0, 169.6, 145.1, 142.3, 134.6, 130.4, 129.2, 128.9, 128.0, 119.2, 82.2, 79.4, 77.0, 76.8, 65.8, 57.9, 52.3, 47.8, 44.5, 42.8, 38.7, 29.7, 29.0, 26.7, 26.4, 21.2, 21.0, 20.9, 15.5.

*Notes:*
*For the photo reaction:*
*--The lamp was placed at a distance of 10 cm from the Schlenk tube.*
*--The temperature in the reaction vessel stayed close to room temperature.*
*--The isomerization reached a state of equilibrium. The ratio of the Z/E-isomers represented the photostationary state of the reaction.*

### *Step-25e*

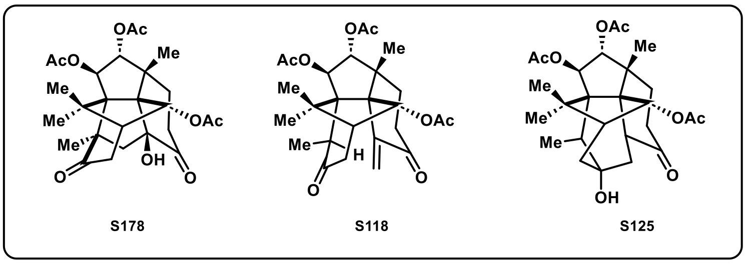


Taxinine K (**2**) (5.0 mg, 10.9 µmol, 1.0 equiv.) was dissolved in dry MeCN under nitrogen in a flame-dried Schlenk tube. The mixture was cooled to -20 °C and $NaHCO_3$ (13.6 mg, 16.3 µmol, 1.5 equiv.) and $AgBF_4$ (2.1 mg, 11.0 mmol, 1.1 equiv.) were added. A solution of ICl in MeCN (11.0 µmol, 0.1mL, 0.1M in MeCN, 1.1 equiv.) was added dropwise and the resulting mixture was stirred at -20 °C for 1 hour. The ice bath was then removed and the mixture was allowed to warm to room temperature slowly and stirred for another hour. The progress of the reaction was monitored via TLC and upon complete conversion of the starting material, the reaction was quenched upon addition of a saturated aqueous solution of $NaHCO_3$ (5 mL) and the aqueous phase was extracted with ethyl acetate (3 x 5 mL). The organic phase was further washed with brine (10 mL) and dried over $MgSO_4$. The solvent was removed in vacuo. The crude product **48** was purified by column chromatography on silica gel (PE: EtOAc 10: 1~ 2: 1) to give a bright yellow foam (3.8 mg, 8.2µmol 75%).

**$^1$H NMR** (400 MHz, Chloroform-d) δ [ppm] = 5.61 – 5.51 (m, 2H), 5.45 (d, J = 9.3 Hz, 1H), 5.14 (d, J = 2.2 Hz, 1H), 4.55 (t, J = 6.6 Hz, 1H), 2.69 (d, J = 18.3 Hz, 1H), 2.41 – 2.25 (m, 2H), 2.07 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H), 1.94 – 1.67 (m, 1H), 1.67 – 1.57 (m, 3H), 1.43 (s, 3H), 1.34 (s, 3H), 1.26 (s, 3H), 1.15 (s, 3H).

**$^{13}$C NMR** (151 MHz, Chloroform-d) δ [ppm] = 209.0, 171.0, 169.8, 169.7, 151.1, 128.4, 83.4, 78.3, 77.7, 69.1, 68.5, 66.8, 66.6, 49.0, 43.3, 42.3, 34.1, 29.1, 29.0, 27.6, 23.8, 22.3, 21.2, 21.0, 20.9, 16.2.

**HRMS** Calculated for $C_{26}H_{35}O_8^+$ [M+H]$^+$: 475.2326, found: 475.2332.



*Notes:*

*--For the -20 °C ice bath, 100g ice were supplemented with 30 g NaCl.*

*--$NaHCO_3$ was dried by heating to 50 °C under vacuum overnight prior to use.*

*--For the best results, the Schlenk tube was tilted at a 45° angle to the bench and submerged in the ice bath. ICl was then added by the syringe pump via a bended needle to the glass wall of the flask at the top end of the Schlenk tube and allowed to slowly run over the cooled glass surface into the reaction mixture to achieve cooling of the reagent before encountering the reaction mixture.*

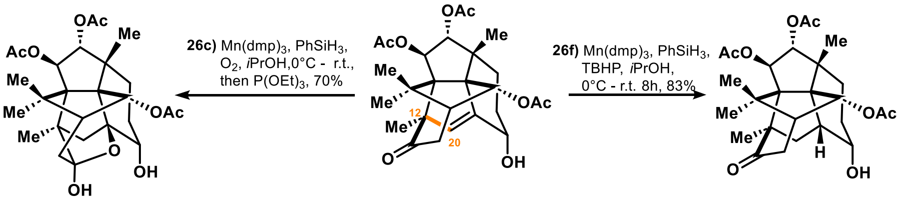
*--To prevent the decomposition of ICl, the light in the fume hood was switched off and the Schlenk tube was wrapped with aluminum foil before the addition of ICl.*

*--The quality of ICl had a great impact on the success of the reaction. The side-product* ***S178*** *was predominantly formed, if the reagent was contaminated by HCl and IOH.*

*--The rate of addition of ICl should be strictly controlled, since side-product* ***S118*** *was observed, if ICl was added too fast.*

*--Other electrophiles for activation of the olefin, such as PhSeCl, PhSCl, and $Pd(OAc)_2$, were also tested and resulted in either no conversion or the formation of side-product* ***S118*** *and side-product* ***S125***

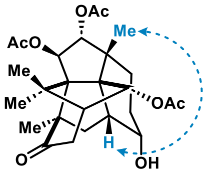
### *Step-26e, 26f*



***dipropellane C*** **(15)**

**48**

***canataxapropellane*** **(5)**



***canataxapropellane*** **(5)**

Compound **48** (0.5 mg, 1.1 μmol, 1.0 equiv.) was dissolved in dry *i*-PrOH (1.0 mL) in a flame-dried Schlenk flask. Phenyl silane (2.2μl (1-2 drops), 1.8 mg, 16.5 μmol, 15.0 equiv.)

was added and the solution was degassed (freeze-pump-thaw, 3 cycles with oxygen). Mn(dpm)$_3$ (0.3 mg, 0.6 µmol, 0.5 equiv.) was added and the solution was again degassed (freeze-pump-thaw, 3 cycles with oxygen). The Schlenk flask and the solution were purged with $O_2$ (through septum via needle/double-walled balloon) and the mixture was stirred under positive $O_2$ pressure at room temperature for 8 hours. Upon completion of the reaction, as determined by TLC, the reaction was flushed with $N_2$ briefly to remove the remaining $O_2$. P(OEt)$_3$ (0.5 µl (half drop, 0.4 mg, 2.2 µmol, 2.0 equiv.) was added to the mixture and it was stirred for another 10 min to quench the peroxide intermediate. A saturated aqueous solution of $NH_4Cl$ (5 mL) was added and the aqueous phase was extracted with ethyl acetate (3 X 3 mL). The organic phase was further washed with brine (5 mL) and dried over $MgSO_4$. The solvent was removed in vacuo. The crude product was purified by column chromatography on silica gel (PE: EtOAc 1: 1~ EtOAc: EtOH 10: 1) to provide a bright yellow oil (0.4 mg, 0.9 µmol, 79%).

**$^1$H NMR** (400 MHz, Chloroform-d) δ [ppm] = 5.65 (d, J = 5.3 Hz, 1H), 5.60 (d, J = 9.2 Hz, 1H), 5.44 (d, J = 9.2 Hz, 1H), 4.33 – 4.27 (m, 1H), 2.14 (m, 2H), 2.07 (s, 3H), 2.04 (s, 3H), 2.03 (m, 1H), 2.00 (s, 3H), 1.98 (m, 2H), 1.92 (m, 2H), 1.63 (m, 1H), 1.46 (s, 3H), 1.25 (s, 3H), 1.24 (m, 1H), 1.22 (s, 3H), 1.16 (s, 3H).

**$^{13}$C NMR** (201 MHz, Chloroform-d) δ [ppm] = 170.8, 170.6, 170.1, 101.0, 87.7, 85.2, 78.0, 78.0, 65.3, 64.8, 63.5, 55.6, 47.5, 47.0, 41.3, 39.5, 33.6, 29.2, 29.2, 28.0, 23.9, 22.5, 21.3, 21.1, 20.8, 14.4.

**HRMS** Calculated for $C_{26}H_{37}O_9^+$ [M+H]$^+$: 493.2438, found: 493.2445.

Compound **48** (0.5 mg, 1.1 µmol, 1.0 equiv.) was dissolved in dry *i*-PrOH (0.8 ~1 mL) under nitrogen in a flame-dried Schlenk flask. Phenyl silane (2.2µl (1~2 drops), 1.8mg, 16.5 µmol, 15.0 equiv.) and *tert*-butyl hydroperoxide (3.3µl (2-2.5 drops), 16.5 µmol, 15.0 equiv., 5 M in decane) was added and the solution was degassed (freeze-pump-thaw, 3 cycles). Mn(dpm)$_3$ (0.3 mg, 0.6 µmol, 0.5 equiv.) was added and the solution was again degassed (freeze-pump-thaw, 3 cycles). The mixture was allowed to warm to room temperature and stirred for 8 hours. The reaction turned from a brown suspension to a bright transparent yellow solution. Upon completion of the reaction, as determined by TLC, the reaction was quenched upon addition of a saturated aqueous solution of $Na_2S_2O_3$ (3 mL) and the aqueous phase was extracted with ethyl acetate (3 x 3 mL). The organic phase was further washed with brine (5 mL) and dried over $MgSO_4$. The solvent was removed in vacuo. The crude product was purified by column chromatography on silica gel (PE: EtOAc 10: 1~ EtOAc: PE 2: 1) to give a bright yellow oil (0.34 mg, 0.7 µmol, 65%).

**$^1$H NMR** (400 MHz, Chloroform-d) δ [ppm] = 5.71 (d, J = 5.5 Hz, 1H), 5.57 (d, J = 9.9 Hz, 1H), 5.45 (d, J = 9.8 Hz, 1H), 4.12 (m, 1H), 2.62 (d, J = 20.2 Hz, 1H), 2.56 (m, 1H), 2.52 (m, 1H), 2.21 (t, J = 6.3 Hz, 1H), 2.08 (s, 3H), 2.02 (s, 3H), 2.02 (m, 1H), 2.01 (s, 3H), 1.98 (s, 1H), 1.99 – 1.93 (m, 1H), 1.78 – 1.70 (m, 1H), 1.58 (s, 3H), 1.52 (m, 1H), 1.45 (m, 1H), 1.22 (s, 3H), 1.12 (s, 3H), 1.08 (s, 3H).

**$^{13}$C NMR** (201 MHz, Chloroform-d) δ [ppm] = 216.9, 171.0, 170.0, 169.9, 82.2, 77.0, 76.5, 65.3, 63.6, 62.7, 60.8, 47.1, 43.9, 42.7, 42.2, 38.6, 38.6, 28.4, 28.0, 24.5, 24.5, 21.2, 21.0, 20.9, 20.8, 18.8.

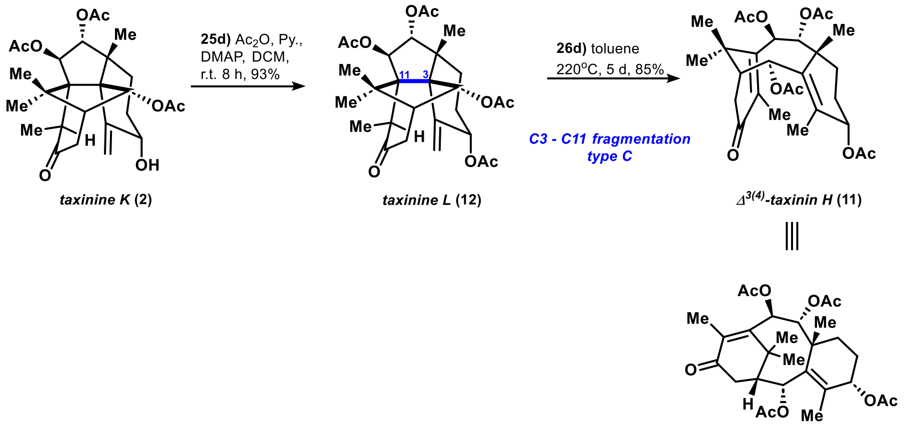
**HRMS** Calculated for $C_{26}H_{37}O_8^+$ $[M+H]^+$: 477.2488, found: 477.2483.

*Notes:*

*For Mukaiyama hydration:*

- *--Mn(dpm)$_3$ was freshly prepared following the procedure of Jérôme Waser and Erick M. Carreira, Catalytic Hydrohydrazination of a Wide Range of Alkenes with a Simple Mn-Complex, Angew. Chem. Int. Ed.* ***2004,*** *43, 4099.*
- *--i-PrOH was dried over CaO (refluxing for 6 hours) and distilled prior to use.*
- *--To remove the remaining phenyl silane, the crude product was either subjected to reduced pressure (line vacuum) or treated with a steady stream of nitrogen overnight.*
- *--Various other reduction conditions, such as Pd/C H$_2$ under high pressure, and hydroboration-reduction, did not yield the desired product.*
- *--The stereocenter at the C-4 position was unambiguously assigned by the NOESY spectrum.*
- *--It was observed that the reaction was very sensitive to oxygen and a slightly more polar spot was observed if the reaction mixture was contaminated by residual oxygen. The species was identified as dipropellane C.*
- *--Other reducing reagents, such as PPh$_3$, were screened for the peroxide quench, but it was observed that POPh$_3$ was difficult to separate from the product.*

***Step-25c, 26c***



*taxinine K* (2) *taxinine L* (12) *Δ$^{3(4)}$-taxinin H* (11)

*Δ$^{3(4)}$-taxinin H* (11)

Ac$_2$O (2.0 µl (1-2 drops), 2.4 mg, 20.0 µmol, 10.0 equiv.), DMAP (1.2 mg, 10.0 µmol, 5.0 equiv.), and pyridine (3.3 µl (2-3 drops), 3.2 mg, 40.0 µmol, 20.0 equiv.) were added to a solution of taxinine K (**2**) (1.0 mg, 2.0 µmol, 1.0 equiv.) in dry dichloromethane (1.0 mL). The mixture was stirred at room temperature for 8 hours. The progress of the reaction was monitored via TLC and upon complete conversion of the starting material, the reaction was quenched with $NaHCO_3$ aq. (3.0 mL) and the aqueous phase was extracted with dichloromethane (3 x 3.0 mL). The organic phase was further washed with brine (3.0 mL) and dried over $MgSO_4$. The solvent was removed in vacuo. taxinine L (**12**) was purified by column chromatography on silica gel (PE: EtOAc 10: 1~ 1:1) to provide an amorphous solid. (1.0 mg, 1.8 μmol, 93%).

**$^1$H NMR** (400 MHz, Chloroform-d) δ [ppm] = 6.14 (d, J = 5.4 Hz, 1H), 5.83 (s, 1H), 5.72 (d, J = 9.6 Hz, 1H), 5.68 – 5.64 (m, 2H), 5.57 (t, J = 8.8 Hz, 1H), 3.48 (q, J = 7.2 Hz, 1H), 2.57 (d, J = 20.4 Hz, 1H), 2.52 (dd, J = 20.4, 7.2 Hz, 1H), 2.21 – 2.11 (m, 1H), 2.10 (s, 3H), 2.09 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H), 1.79 – 1.72 (m, 2H), 1.70 (s, 3H), 1.33 (s, 4H ), 1.27 (d, J = 7.2 Hz, 3H), 1.23 (s, 3H), 1.16 (m, 1H).

**$^{13}$C NMR** (201 MHz, Chloroform-d) δ [ppm] = 214.3, 171.0, 170.1, 169.7, 169.5, 142.2, 129.3, 82.3, 79.4, 79.4, 76.7, 65.9, 57.7, 52.3, 47.7, 44.4, 42.7, 31.3, 28.7, 26.7, 26.7, 25.9, 21.5, 21.4, 21.1, 21.0, 15.4.

**HRMS** Calculated for $C_{28}H_{39}O_9^+$ [M+H]$^+$: 519.2589, found: 519.2585

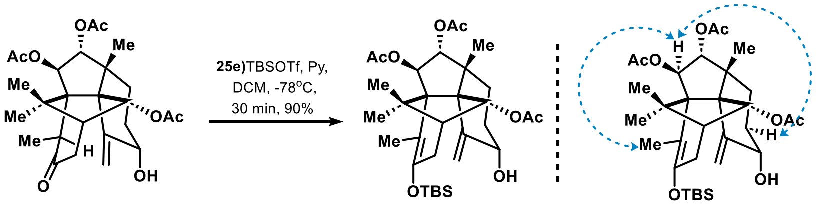
taxinine L (**12**) (1.0 mg, 1.8 μmol, 1.0 equiv.) was dissolved in dry toluene (1.0 mL) in a flame-dried sealed tube under nitrogen. The mixture was heated gradually to 220 °C in a sand bath. Since the starting material and product had exactly the same polarity and were inseparable on TLC, the reaction could only be monitored by NMR. Upon complete conversion of the starting material, the solvent was removed in vacuo $\Delta^{3(4)}$-taxinin H (**11**) was purified by column chromatography on silica gel (PE: EtOAc 10: 1~ 1:1) to give a crystalline solid (0.8 mg, 1.5 μmol, 85%).

**$^1$H NMR** (400 MHz, Chloroform-d) δ [ppm] = 6.09 (d, J = 10.5 Hz, 1H), 5.97 (d, J = 10.5 Hz, 1H), 5.92 (d, J = 2.4 Hz, 1H), 4.98 (d, J = 4.2 Hz, 1H), 2.96 (d, J = 20.0 Hz, 1H), 2.82 (dd, J = 20.1, 5.4 Hz, 1H), 2.34 (s, 1H), 2.12 (s, 3H), 2.08 (s, 6H), 2.06 (s, 3H), 2.04 (s, 3H), 1.87 (s, 3H), 1.81 (s, 4H), 1.75 – 1.69 (m, 3H), 1.20 (s, 3H), 1.04 (s, 3H).

**$^{13}$C NMR** (201 MHz, Chloroform-d) δ [ppm] = 197.9, 170.7, 170.1, 169.9, 169.0, 150.6, 140.3, 137.4, 130.6, 75.1, 73.3, 71.8, 71.5, 53.0, 43.4, 37.9, 36.8, 36.1, 25.9, 25.6, 23.7, 24.2, 22.4, 21.5, 21.3, 20.9, 20.7, 13.5.

**HRMS** Calculated for $C_{28}H_{39}O_9^+$ [M+H]$^+$: 519.2589, found: 519.2590

## *Step-25d*



*taxinine K* (2) **42** *NOE* **42**

Taxinine K (**2**) (2.4 mg, 4.8 µmol, 1.0 equiv.) was dissolved in dry dichloromethane (0.8 - 1.0 mL) under nitrogen in a flame-dried Schlenk tube. The mixture was cooled to -78 °C and stirred for 10 min. Then, 2,6-lutidine (5.1 mg, 5.5 µl, 48.0 µmol, 10.0 equiv.) was added to the solution followed by a solution of TBSOTf (24 µmol, 0.2mL in 0.1M in dichloromethane, 24µmol, 5.0 equiv.) that was added dropwise to the reaction. The obtained reaction mixture was stirred at -78 °C for another 15 min. Upon complete conversion of the starting material as indicated by TLC (PE: EA 2:1), the reaction was quenched upon addition of saturated aqueous solution of $NaHCO_3$ (3 mL) and the aqueous phase was extracted with dichloromethane (3 x 3mL). The organic phase was further neutralized with sodium phosphate buffer (pH = 7.0, 1 M), then washed with brine (5 mL) and dried over $MgSO_4$. The solvent was removed in vacuo. The crude product **42** was obtained upon column chromatography on silica gel (PE: EtOAc 10: 1~ 5: 1) as a bright yellow oil (2.5 mg, 4.3 µmol, 89%).

**$^1$H NMR** (600 MHz, Chloroform-d) δ [ppm] = 5.77 – 5.72 (m, 1H), 5.68 (s, 2H), 5.43 (d, J = 1.1 Hz, 1H), 5.33 (d, J = 8.8 Hz, 1H), 3.98 (s, 1H), 2.17-2.12 (m, 1H), 2.09 (s, 3H), 2.07-2.04 (m, 1H), 2.03 (s, 6H), 1.75-1.70 (m, 1H), 1.63 (t, J = 1.9 Hz, 3H), 1.53 (s, 3H), 1.51-1.47 (m, 1H), 1.38 – 1.34 (m, 3H), 1.33 -1.30 (m, 2H), 1.29 – 1.24 (m, 4H), 0.97 (s, 9H), 0.15 (d, J = 3.1 Hz, 6H).

**$^{13}$C NMR** (151 MHz, Chloroform-d) δ [ppm] = 171.1, 170.0, 169.9, 152.5, 145.3, 114.2, 107.8, 81.1, 78.1, 68.9, 66.6, 60.2, 49.6, 45.7, 44.3, 30.2, 29.7, 29.7, 29.2, 25.8, 23.6, 21.6, 21.2, 21.0, 21.0, 18.1, 14.0, -2.7, -3.0.

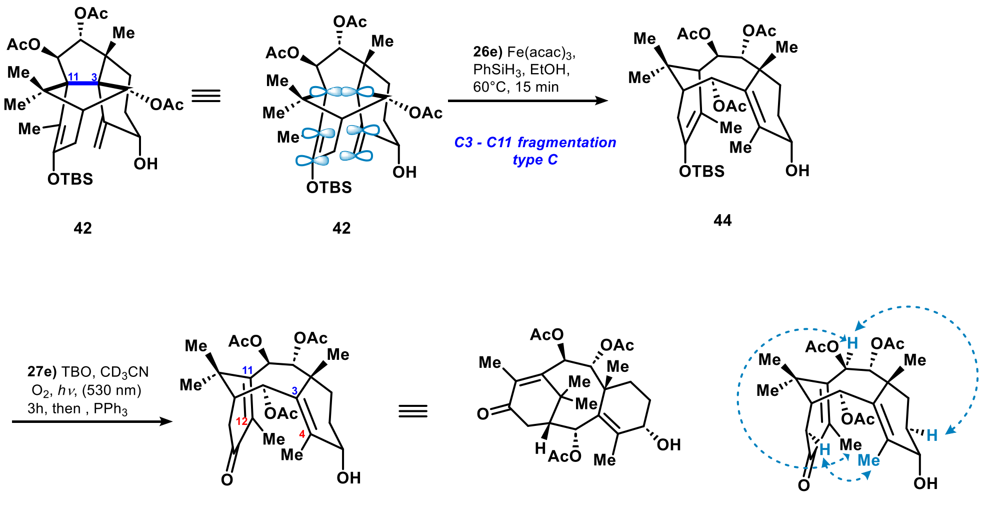
**HRMS** Calculated for $C_{32}H_{51}O_8Si^+$ [M+H]$^+$: 591.3348, found:591.3354.

Notes:

*--2,6-lutidine was dried over $CaH_2$ (refluxing for 6 hours) and distilled before use.*

*--For the best results, the reaction time should not be elongated more than necessary.*

## *Step-26d, 27d*



*Δ$^{3(4)}$-taxinin A (10)*   *Δ$^{3(4)}$-taxinin A (10)*   *NOE Δ$^{3(4)}$-taxinin A (10)*

Compound **42** (2.5 mg, 4.3 µmol, 1.0 equiv.) was dissolved in dry EtOH (1.0 mL) under nitrogen in a flame-dried Schlenk flask. Phenyl silane (8.8 µl (2-3 drops), 6.9 mg, 64.5 µmol, 15 equiv.) was added and the solution was degassed (freeze-pump-thaw, 3 cycles). Fe(acac)$_3$ (3.0 mg, 8.6 µmol, 5.0 equiv.) was added and the solution was again degassed (freeze-pump-thaw, 3 cycles). The mixture was heated to 60 °C for 5 – 10 min. Upon complete conversion of the starting material, as determined by TLC, the reaction was quenched with upon addition of a saturated aqueous solution of NaHCO$_3$ (5 mL) and the aqueous phase was extracted with ethyl acetate (3 x 3mL). The organic phase was further washed with brine (5 mL) and dried over MgSO$_4$. The solvent was removed in vacuo. The crude product **44** was passed through a short silica gel column (pure PE (10mL), then PE: EtOAc 2 : 1(10 mL)) and was directly used for the next step without further purification.

In a 10mL Schlenk tube, toluidine blue O (1.2 mg, 4.3 µmol, 1.0 equiv.) was added to a solution of compound **44** in CD$_3$CN (1.2 mL). O$_2$ was bubbled through the solution continuously (through a septum via needle/double-walled balloon). The reaction was irradiated at 530 nm (24W, LED). Upon complete conversion of the starting material, as determined by TLC, the O$_2$ balloon was removed and the reaction was flushed with N$_2$ briefly to remove the remaining O$_2$ dissolving in the solution. Ph$_3$P (1.1 mg, 4.3 µmol, 1,0 equiv.) was added to the reaction mixture and stirred for another 30 min to quench the peroxide intermediate. The mixture was filtered through a very short silica gel column with pure ethyl acetate (10mL) and concentrated in vacuo. Δ$^{3(4)}$-taxinin A (**10**) was purified by column chromatography on silica gel (PE: EtOAc 5: 1~ EtOAc: PE 2:1) to give a colorless solid (1.1mg, 2.4 µmol, 56 % (87% for the MHAT fragmentation) and (64% for the Schenck-ene reaction)).

**$^1$H NMR** (400 MHz, Chloroform-d) δ [ppm] = 6.07 (d, J = 10.5 Hz, 1H), 5.96 (d, J = 10.5 Hz, 1H), 5.91 (d, J = 5.1 Hz, 1H), 3.76 (s, 1H), 2.99 (d, J = 20.0 Hz, 1H), 2.84 (d, J = 19.9 Hz, 1H), 2.33 (d, J = 4.9 Hz, 1H), 2.11 (s, 3H), 2.08 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 1.83-1.67 (m, 4H), 1.81 (s, 3H), 1.22 (s, 3H), 1.02 (s, 3H).

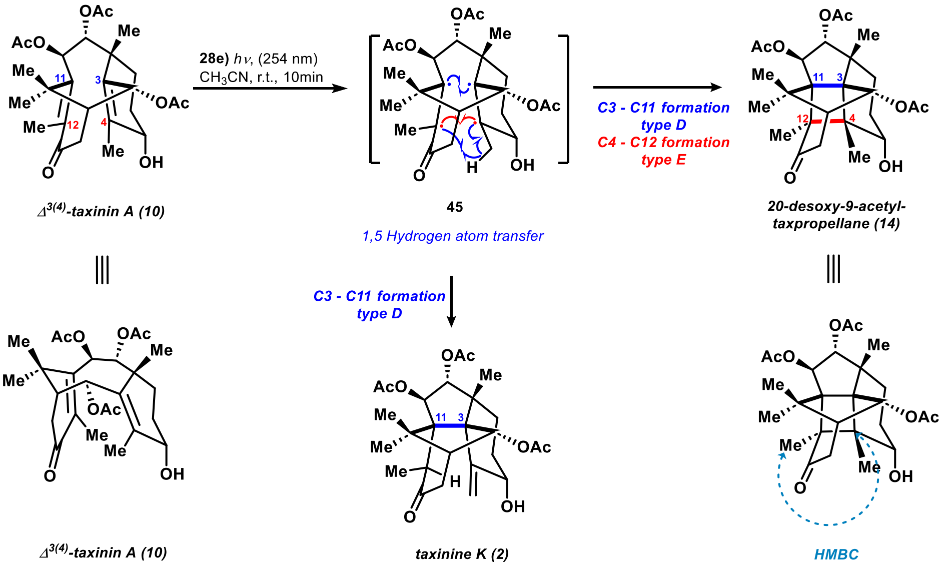
**$^{13}$C NMR** (151 MHz, Chloroform-d) δ [ppm] = 198.8, 170.2, 169.9, 169.0, 151.4, 137.7, 137.5, 133.5, 75.2, 73.5, 71.7, 70.1, 53.4, 43.7, 37.9, 36.9, 36.3, 25.9, 25.9, 25.6, 23.6, 22.8, 21.3, 20.9, 20.8, 13.7.

**HRMS** Calculated for $C_{26}H_{37}O_8^+$ $[M+H]^+$: 477.2483, found: 477.2480.

*Notes:*
*For the MHAT reaction:*
*--The $Fe(acac)_3$ (bordeaux red crystal) in this reaction was purified by recrystallization from ethanol before application.*
*--To remove the majority of the remaining phenyl silane, the crude product was either subjected to reduced pressure (line vacuum) or treated with a steady stream of nitrogen overnight.*
*--The product obtained after the short column is not analytically pure. The column rather serves to remove the remaining phenyl silane.*
*--The newly generated C11 stereocenter was unambiguously assigned by the NOESY spectrum.*
*--It is worth mentioning that the substrate without TBS silyl enol ether moiety (bearing the C12 ketone instead) only yielded the trivial exo-methylene reduction product.*
*--Hardly any conversion was observed when the internal temperature was < 60 °C.*

*For the Schenck-ene reaction*
*--The lamp was placed at a distance of 10 cm from the Schlenk tube.*
*--The temperature in the reaction vessel stayed close to room temperature. The 10 min cool-down cycle was conducted after each hour of irradiation or a small fan was placed next to the reaction, if necessary.*
*--For the best results, the reaction should be quenched as soon as all the starting material was converted. The reaction time should not be elongated more than necessary.*
*--The purpose of first flushing the reaction with $N_2$ rather than directly quenching with $PPh_3$ is to minimize the generation of the $OPPh_3$ which was very difficult to separate from the product by column chromatography due to their similar polarities.*
*--After quenching with $PPh_3$, the product could be detected on TLC via UV absorption (250 nm).*
*--Other dehydrogenation conditions, such as $SeO_2$ and the Saegusa protocol, have been examined, but only resulted in oxidation of the C5-OH group.*

### *Step-28d*



Δ$^{3(4)}$-taxinin A (**10**) (1.1 mg, 2.4 µmol, 1.0 equiv.) was dissolved in $CH_3CN$ (1.0mL) in a 10 mL quartz tube under nitrogen and degassed by nitrogen bubbling and sonication for 30 min. Then, the solution was irradiated at 254 nm (6 x OSRAM PURITEC HNS L 18W (5.5 W emission around 254 nm) for 3 min, followed by a 5 min cool-down break. This procedure was repeated over 3 cycles. The solvent was removed in *vacuo*. The crude product was purified by column chromatography on silica gel (PE: EtOAc 10: 1~ EtOAc: PE 2:1) and provided a mixture of 20-deoxy-9acetyl taxpropellane (**14**) and taxinine K (**2**) in a ratio of 2:1 (20-deoxy-9acetyl taxpropellane (**14**) 0.6 mg, 1.2 µmol, 50% and taxine K (**2**) 0.3 mg, 0.6µmol, 25%).

*Notes:*

*--The reaction time should not be elongated more than necessary, since the product will decompose to a slightly apolar species (observed on TLC) upon irradiation over an elongated time.*

**$^1$H NMR** (400 MHz, Chloroform-d) δ [ppm] = 6.17 (d, J = 6.0 Hz, 1H), 5.71- 5.69 (m, 1H), 5.51 (d, J = 6.0 Hz, 1H), 4.68 (d, J = 7.9 Hz, 1H), 2.28 (t, J = 14.1 Hz, 1H), 2.12 (s, 3H), 2.11 (s, 3H), 2.08 (s, 3H), 2.01 (d, J = 12.9 Hz, 1H), 1.93 - 1.90 (m, 2H), 1.64 (m, 1H), 1.62 (s, 3H), 1.61 -1.59 (m, 2H), 1.60 (s, 3H), 1.58 (s, 3H), 1.56 (s, 3H), 1.17 (s, 3H).

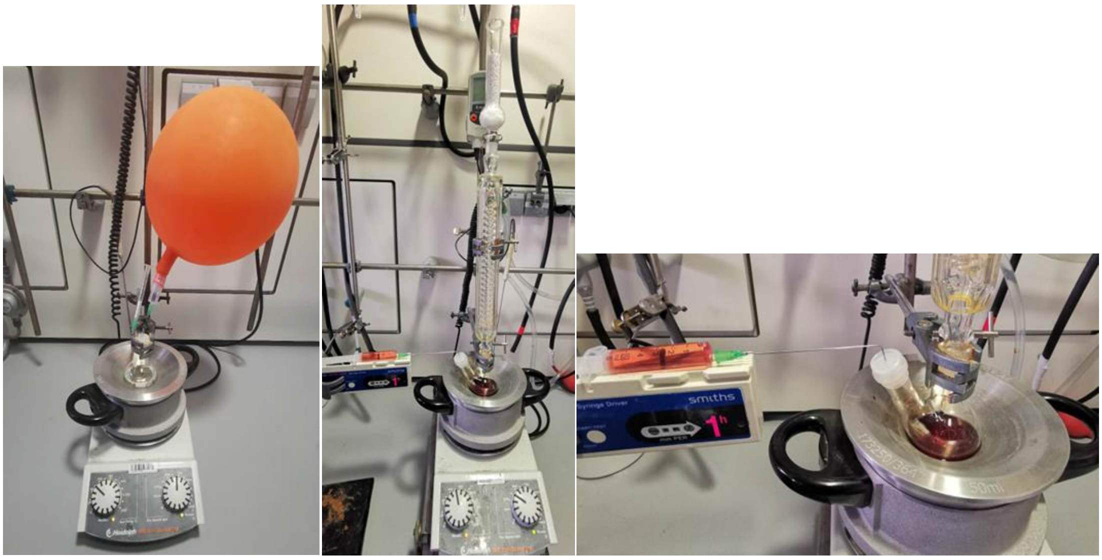
**$^{13}$C NMR** (201 MHz, Chloroform-d) δ [ppm] = 217.3, 170.3, 170.0, 169.7, 91.0, 78.5, 78.2, 70.2, 64.8, 64.2, 58.8, 58.6, 51.3, 47.3, 44.7, 38.9, 30.8, 27.8, 26.3, 25.5, 23.6, 21.4, 21.1, 20.8, 19.3.
**HRMS** Calculated for $C_{26}H_{37}O_8^+$ [M+H]$^+$: 477.2488, found: 477.2484.

## Part-VI Pictures of Experimental Apparatus

### Step- 2 Birch reaction

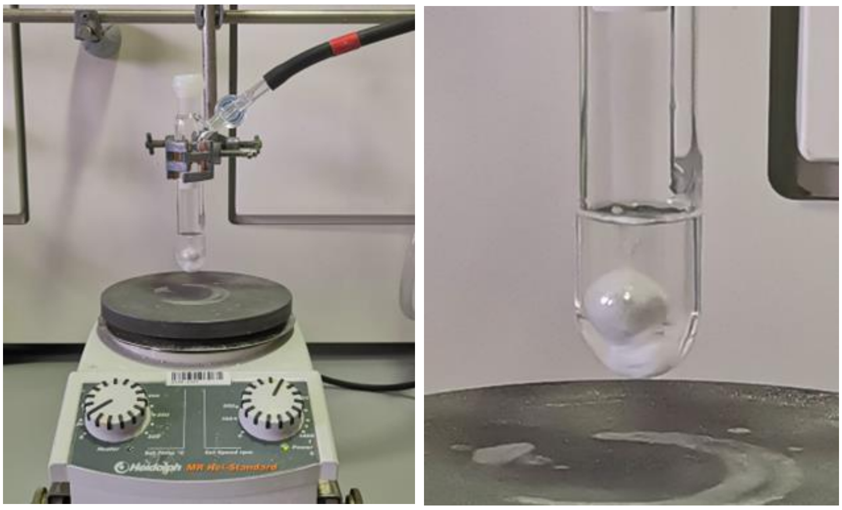
To achieve optimal results, it is crucial to ensure that the $NH_{3(l)}$ level in the system is maintained at a similar or slightly higher level than the cooling bath. Additionally, it is important to vigorously stir the mixture to prevent the t-BuOH/THF/starting material solution from solidifying in the Schlenk flask. The starting material solution is added by using a syringe pump at a controlled speed of 50 mL/h.

### Step-10 Biomimetic transamination



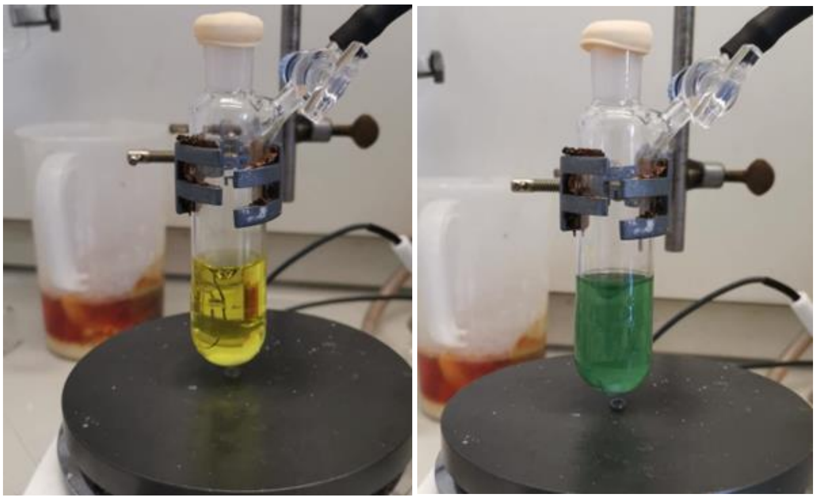
After heating the ascorbic acid solution for 2 hours under oxygen flow, it was observed a change in color to Bordeaux red before adding it to the reaction.

## Step-14 NaK (sodium-potassium alloy) desulfurization

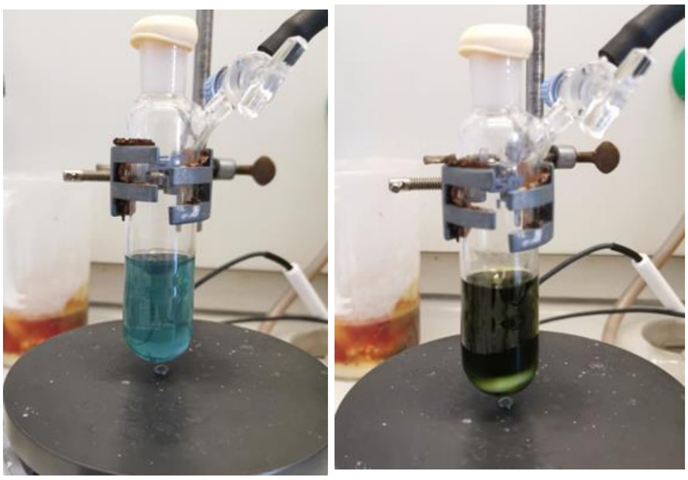


The stirring rate should be precisely adjusted. It was observed that it was favorable, if the sodium-potassium alloy could float in the middle of the solution and have a sufficient contact with the substrate.

## Step-18 Pinacol coupling reaction



The color of $TiCl_4$/DCM solution immediately changes to green upon adding the Zn dust. The green color likely arises from the formation of Ti(III) species.

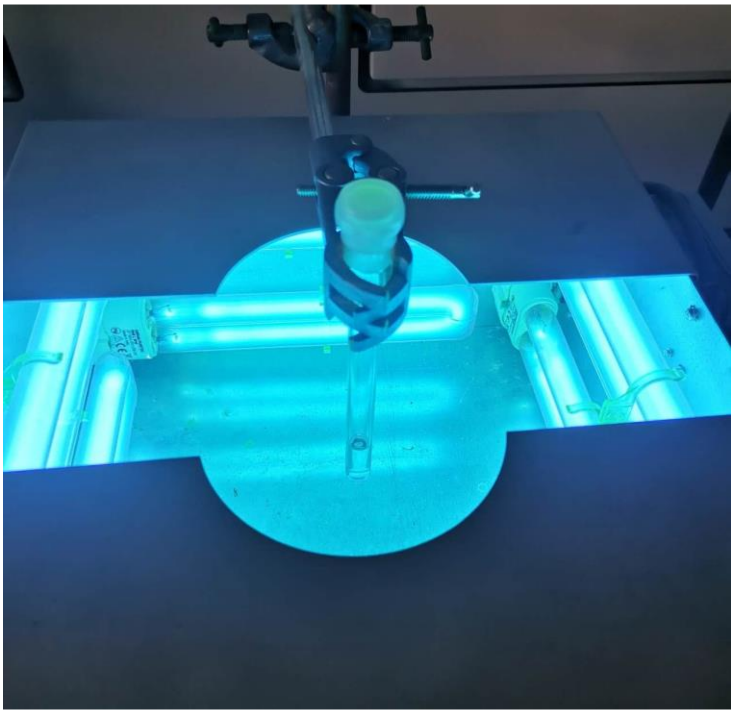


The change in color of the solution from green to light blue after 10 minutes of stirring, followed by a return to dark green upon adding pyridine.

## Step-20 Schenck-ene reaction

The lamp was placed in a distance of 10 cm from the Schlenk tube (left). The $O_2$ was dried by passing through a sequence of a $CaCl_2$ and an allochronic silica gel column (right).

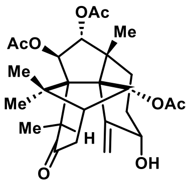
## Step-28d [2+2] photoirradiation



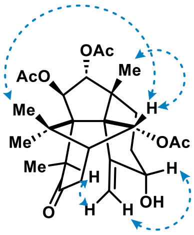
The lamp was placed in a distance of 10 cm from the quartz tube. The reaction time shouldn’t be elongated to more than necessary to avoid the decomposition.

# Part-VII Comparison of Synthetic Complex Taxanes with Isolated

*In the following part, we provide a comparison of the data obtained for our synthetic complex taxanes and the isolated natural products. In addition to that, data for analogues of the natural products are included.*

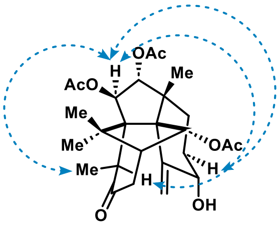


**taxinine K (2)**



**taxinine K (2)**

***NOE***



**taxinine K (2)**

***NOE***

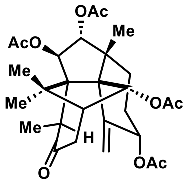
| Position | δ = $^{1}$H [ppm], mult, *J* = [Hz] (synthetic) in $CCl_3D$ | | | |
|---|---|---|---|---|
| 1 | 2.16 | m | | 1H |
| 2 | 6.11 | d | *J* = 4.2 Hz | 1H |
| 5 | 4.45 | t | *J* = 9.0 Hz | 1H |
| 6a | 2.05 | m | | 1H |
| 6b | 1.73 | o.m | | 1H |
| 7a | 1.73 | o.m | | 1H |
| 7b | 1.12 | m | | 1H |
| 9 | 5.69 | d | *J* = 9.6 Hz | 1H |
| 10 | 5.66 | d | *J* = 9.6 Hz | 1H |
| 12 | 3.81 | m | | 1H |
| 14a | 2.62 | d | *J* = 20.4 Hz | 1H |
| 14b | 2.50 | ddt | *J* = 20.4, 7.2, 1.4 Hz | 1H |
| 16 | 1.23 | s | | 3H |
| 17 | 1.29 | s | | 3H |
| 18 | 1.23 | d | *J* = 5.7 Hz | 3H |
| 19 | 1.69 | s | | 3H |
| 20a | 5.76 | s | | 1H |
| 20b | 5.59 | s | | 1H |
| $CH_3CO$ | 2.09 | s | | 3H |
| $CH_3CO$ | 2.07 | s | | 3H |
| $CH_3CO$ | 2.05 | s | | 3H |

| Position | δ = $^{13}$C [ppm] (synthetic) in $CCl_3D$ |
|---|---|
| 1 | 47.9 |
| 2 | 76.8 |
| 3 | 66.0 |
| 4 | 147.4 |
| 5 | 74.9 |
| 6 | 27.9 |
| 7 | 31.3 |
| 8 | 42.5 |
| 9 | 82.5 |
| 10 | 79.7 |
| 11 | 57.7 |
| 12 | 52.6 |
| 13 | 215.8 |
| 14 | 38.8 |
| 15 | 44.6 |
| 16 | 26.3 |
| 17 | 26.7 |
| 18 | 15.6 |
| 19 | 28.7 |
| 20 | 125.8 |
| $\underline{CH_3}CO$ | 21.4 |
| $\underline{CH_3}CO$ | 21.1 |
| $\underline{CH_3}CO$ | 21.0 |
| $CH_3\underline{CO}$ | 171.1 |
| $CH_3\underline{CO}$ | 169.9 |
| $CH_3\underline{CO}$ | 169.6 |

| Position | NOESY (synthetic) in CCl$_3$D | Position | NOESY (synthetic) in CCl$_3$D |
|---|---|---|---|
| 1 | 14b, 2 | 12 | 10, 18 |
| 2 | 16, 19, 2 | 14a | 20a |
| 5 | 20b, 6a | 14b | |
| 6a | | 16 | 2, 17 |
| 6b | | 17 | 16 |
| 7a | | 18 | 10 |
| 7b | | 19 | 2, 9 |
| 9 | 16, 19 | 20a | 14a, 12 |
| 10 | 18 | 20b | 5 |

*Notes:*

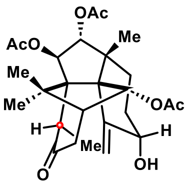
*--Due to the absence of $^1$H NMR and $^{13}$C NMR data of taxinine K in the original isolation paper, we have exclusively listed our synthetic data here. (Chiang, H. C.; Woods, M. C.; Nakadaira, Y.; Nakanishi, K. Chem. Commun.* ***1967****, 23, 1201.)*



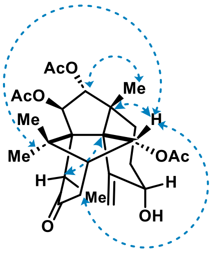
**taxinine L (12)**

| Position | $\delta$ = $^1$H [ppm], mult, $J$ = [Hz] (synthetic) in CCl$_3$D | | | | $\delta$ = $^1$H [ppm], mult, $J$ = [Hz] (isolation) in CCl$_3$D | | | |
|---|---|---|---|---|---|---|---|---|
| 1 | 2.18 | m | | 1H | 2.14 | m | | 1H |
| 2 | 6.14 | d | *J* = 5.4 Hz | 1H | 6.12 | d | *J* = 5.4 Hz | 1H |
| 5 | 5.57 | t | *J* = 8.8 Hz | 1H | 5.56 | t | *J* = 8.5 Hz | 1H |
| 6a | 1.75 | m | | 1H | 2.3 - 1.2 | m | | 1H |
| 6b | 1.33 | m | | 1H | 2.3 - 1.2 | m | | 1H |
| 7a | 1.16 | m | *J* = 14.7, 6.9 Hz | 1H | 2.3 - 1.2 | m | | 1H |
| 7b | 1.75 | m | | 1H | 2.3 - 1.2 | m | | 1H |
| 9 | 5.72 | d | *J* = 9.6 Hz | 1H | 5.71 | d | *J* = 10 Hz | 1H |
| 10 | 5.66 | d | *J* = 9.6 Hz | 1H | 5.65 | d | *J* = 10 Hz | 1H |
| 12 | 3.48 | q | *J* = 7.2 Hz | 1H | 3.45 | q | *J* = 7.3 Hz | 1H |
| 14a | 2.57 | d | *J* = 20.4 Hz | 1H | 2.60 | dd | *J* = 20, 2.5 Hz | 1H |
| 14b | 2.52 | dd | *J* = 20.4, 7.2 Hz | 1H | 2.44 | dd | *J* = 20, 2.5 Hz | 1H |
| 16 | 1.70 | s | | 3H | 1.68 | s | | 3H |
| 17 | 1.23 | s | | 3H | 1.21 | s | | 3H |
| 18 | 1.27 | d | *J* = 7.2 Hz | 3H | 1.24 | d | *J* = 7 Hz | 3H |
| 19 | 1.33 | s | | 3H | 1.31 | s | | 3H |
| 20a | 5.83 | s | | 1H | 5.81 | s | | 1H |
| 20b | 5.66 | s | | 1H | 5.64 | s | | 1H |
| CH$_3$CO | 2.10 | s | | 3H | | | | |
| CH$_3$CO | 2.09 | s | | 3H | | | | |
| CH$_3$CO | 2.07 | s | | 3H | | | | |
| CH$_3$CO | 2.06 | s | | 3H | | | | |

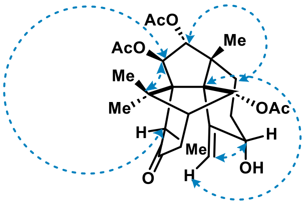
| Position | δ = $^{13}$C [ppm] (synthetic) in CCl$_3$D | Position | δ = $^{13}$C [ppm] (synthetic) in CCl$_3$D |
|---|---|---|---|
| 1 | 47.7 | 15 | 44.4 |
| 2 | 76.7 | 16 | 25.9 |
| 3 | 65.8 | 17 | 26.7 |
| 4 | 142.2 | 18 | 15.4 |
| 5 | 79.4 | 19 | 28.7 |
| 6 | 26.7 | 20 | 129.3 |
| 7 | 31.3 | $\underline{CH_3}CO$ | 21.5 |
| 8 | 42.7 | $\underline{CH_3}CO$ | 21.4 |
| 9 | 82.3 | $\underline{CH_3}CO$ | 21.1 |
| 10 | 79.4 | $\underline{CH_3}CO$ | 21.0 |
| 11 | 57.7 | $CH_3\underline{CO}$ | 171.0 |
| 12 | 52.3 | $CH_3\underline{CO}$ | 170.1 |
| 13 | 214.3 | $CH_3\underline{CO}$ | 169.7 |
| 14 | 38.7 | $CH_3\underline{CO}$ | 169.5 |



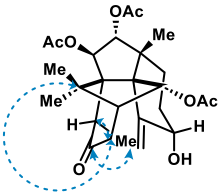
**12-epi-taxinine K (37)**



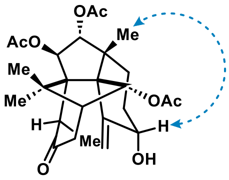
**12-epi-taxinine K (37)**
**HMBC**



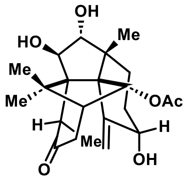
**12-epi-taxinine K (37)**
**HMBC**



**12-epi-taxinine K (37)**
**HMBC**

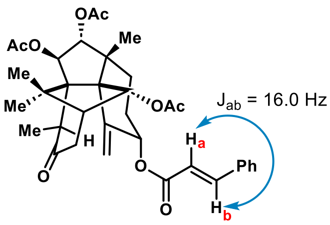


**12-epi-taxinine K (37)**
**NOE**

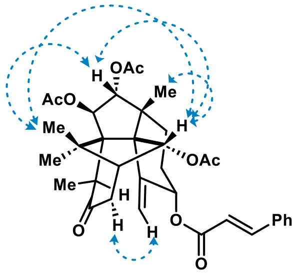


**isolated**
**nature product (179)**

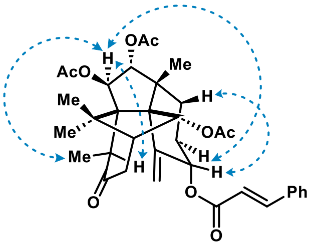
| Position | $\delta$ = $^{1}$H [ppm], mult, $J$ = [Hz] (synthetic) in $CCl_3D$ | | | | Position | $\delta$ = $^{13}$C [ppm] (synthetic) in $CCl_3D$ |
|---|---|---|---|---|---|---|
| 1 | 2.09 | m | | 1H | 1 | 48.9 |
| 2 | 5.85 | d | $J$ = 5.6 Hz | 1H | 2 | 77.0 |
| 5 | 4.03 | m | | 1H | 3 | 64.5 |
| 6a | 1.32 | m | | 1H | 4 | 150.1 |
| 6b | 2.13 | o.m | | 1H | 5 | 69.9 |
| 7a | 1.34 | o.m | | 1H | 6 | 28.5 |
| 7b | 2.20 | m | | 1H | 7 | 31.3 |
| 9 | 5.69 | d | $J$ = 6.0 Hz | 1H | 8 | 45.5 |
| 10 | 5.54 | d | $J$ = 6.0 Hz | 1H | 9 | 84.1 |
| 12 | 2.96 | m | | 1H | 10 | 78.0 |
| 14a | 2.75 | d | $J$ = 20.8 Hz | 1H | 11 | 61.7 |
| 14b | 2.48 | d | $J$ = 20.8 Hz | 1H | 12 | 48.9 |
| 16 | 1.63 | s | | 3H | 13 | 216.0 |
| 17 | 1.24 | s | | 3H | 14 | 39.0 |
| 18 | 1.47 | d | $J$ = 5.7 Hz | 3H | 15 | 44.5 |
| 19 | 1.21 | s | | 3H | 16 | 30.4 |
| 20a | 5.58 | s | | 1H | 17 | 26.3 |
| 20b | 4.76 | s | | 1H | 18 | 15.7 |
| $CH_3CO$ | 2.03 | s | | 3H | 19 | 23.0 |
| $CH_3CO$ | 2.02 | s | | 3H | 20 | 110.9 |
| $CH_3CO$ | 2.02 | s | | 3H | $\underline{CH_3}CO$ | 21.0 |
| | | | | | $\underline{CH_3}CO$ | 20.9 |
| | | | | | $\underline{CH_3}CO$ | 20.8 |
| | | | | | $CH_3\underline{CO}$ | 171.0 |
| | | | | | $CH_3\underline{CO}$ | 170.2 |
| | | | | | $CH_3\underline{CO}$ | 170.1 |



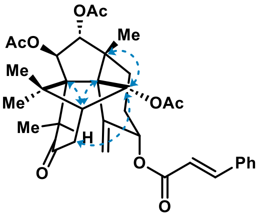
**taxuspine C (13)**



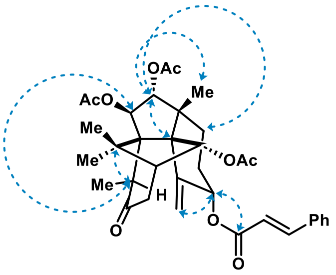
**taxuspine C (13)**
**NOE**



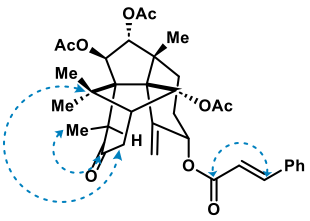
**taxuspine C (13)**
**NOE**



**taxuspine C (13)**
**HMBC**



**taxuspine C (13)**
**HMBC**

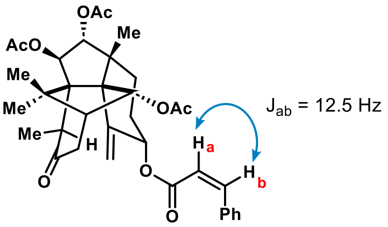


**taxuspine C (13)**
**HMBC**

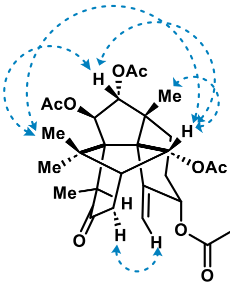
| Position | δ = $^1$H [ppm], mult, *J* = [Hz] (synthetic) in $CCl_3D$ | | | | δ = $^1$H [ppm], mult, *J* = [Hz] (isolation) in $CCl_3D$ | | | |
|---|---|---|---|---|---|---|---|---|
| 1 | 2.18 | m | | 1H | 2.18 | m | | 1H |
| 2 | 6.13 | d | *J* = 5.3 Hz | 1H | 6.14 | d | *J* = 5.3 Hz | 1H |
| 5 | 5.65 | t | *J* = 8.9 Hz | 1H | 5.64 | m | | 1H |
| 6a | 1.78 | m | | 1H | 1.78 | m | | 2H |
| 6b | 2.18 | o.m | | 1H | | | | |
| 7a | 1.78 | o.m | | 1H | 1.80 | m | | 2H |
| 7b | 1.27 | o.m | | 1H | | | | |
| 9 | 5.70 | o.d | | 1H | 5.70 | d | *J* = 8.8 Hz | 1H |
| 10 | 5.68 | o.d | | 1H | 5.68 | d | *J* = 8.8 Hz | 1H |
| 12 | 3.54 | d | *J* = 7.1 Hz | 1H | 3.55 | q | *J* = 6.8 Hz | 1H |
| 14a | 2.59 | d | *J* = 20.4 Hz | 1H | 2.59 | d | *J* = 20.5 Hz | 1H |
| 14b | 2.52 | dt | *J* = 20.4, 7.1 Hz | 1H | 2.50 | dt | *J* = 20.5, 6.8 Hz | 1H |
| 16 | 1.69 | s | | 3H | 1.70 | s | | 3H |
| 17 | 1.22 | s | | 3H | 1.22 | s | | 3H |
| 18 | 1.28 | d | *J* = 7.3 Hz | 3H | 1.29 | d | *J* = 6.8 Hz | 3H |
| 19 | 1.31 | s | | 3H | 1.32 | s | | 3H |
| 20a | 5.84 | s | | 1H | 5.85 | s | | 1H |
| 20b | 5.72 | o.s | | 1H | 5.71 | s | | 1H |
| 22 | 6.38 | d | *J* = 16.0 Hz | 1H | 6.39 | d | *J* = 16.1 Hz | 1H |
| 23 | 7.67 | d | *J* = 16.0 Hz | 1H | 7.67 | d | *J* = 16.1 Hz | 1H |
| 25 | 7.55 | m | | 2H | 7.56 | m | | 2H |
| 26 | 7.37 | m | | 2H | 7.38 | m | | 2H |
| 27 | 7.37 | m | | 1H | 7.38 | m | | 1H |
| $CH_3CO$ | 2.07 | s | | 3H | 2.07 | s | | 3H |
| $CH_3CO$ | 2.04 | s | | 3H | 2.05 | s | | 3H |
| $CH_3CO$ | 2.04 | s | | 3H | 2.05 | s | | 3H |

| Position | HMBC (synthetic) in CCl$_3$D | HMBC (isolation) in CCl$_3$D | NOESY (synthetic) in CCl$_3$D | NOESY (isolation) in CCl$_3$D |
|---|---|---|---|---|
| 1 | 2, 3, 11, 13, 15 | 2, 13, 15 | 2 | 2, 14, 16, 17 |
| 2 | 3, 4, 8, 14, Ac | 1, 3, 4, 8, 14, Ac | 1, 16, 19 | 16, 19 |
| 5 | 3, 4, 6, 20, 21 | 3, 4, 6, 20, 21 | 7 | 7, 20 |
| 6a | 5 |  | 10 | 7 |
| 6b |  |  | 7 |  |
| 7a | 3, 8 | 3, 8 |  | 19 |
| 7b |  |  |  |  |
| 9 | 3, 7, 8, 10, 19, Ac | 3, 7, 10, 19, Ac | 16, 19 | 16, 19 |
| 10 | 9, 11, 12, 15, Ac | 9, 11, 12, 15, Ac | 7, 12, 18 | 12, 18 |
| 12 | 3, 11, 13, 15, 18 | 3, 11, 13, 15, 18 | 10, 18 | 18, 20, 22, 23 |
| 14a | 1, 2, 13, 15 | 1, 2, 13, 15 | 20 | 17, 20 |
| 14b | 1, 2, 13 | 1, 2, 13 |  |  |
| 16 | 1, 11, 15, 17 | 1, 11, 15, 17 | 2, 9 |  |
| 17 | 1, 11, 15, 16 | 1, 11, 16 |  |  |
| 18 | 11, 12, 13 | 13 | 12 | 22, 23, 25 |
| 19 | 3, 7, 8, 9 | 3, 7, 8, 9 | 2 |  |
| 20a | 3, 4, 5 | 4, 5 | 14a, 20b | 23 |
| 20b | 3, 4, 5 | 4, 5 | 20a |  |
| 22 | 21, 24 | 21, 24 | 25 | 25 |
| 23 | 21, 22 | 21, 22 | 24 | 25 |
| 25 | 26, 27 | 26, 27 |  |  |
| 26 | 24, 25 | 24, 25 |  |  |
| 27 |  |  |  |  |

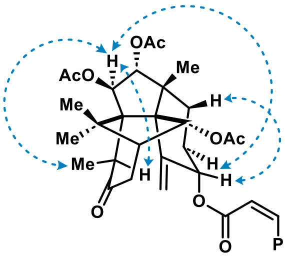
| Position | $\delta$ = $^{13}$C [ppm] (synthetic) in $CCl_3D$ | $\delta$ = $^{13}$C [ppm] (isolation) in $CCl_3D$ | $\Delta\delta$ [ppm] |
|---|---|---|---|
| 1 | 47.8 | 47.8 | |
| 2 | 76.5 | 76.5 | |
| 3 | 65.9 | 65.9 | |
| 4 | 142.2 | 142.2 | |
| 5 | 76.6 | 77.2 | 0.6 |
| 6 | 25.9 | 25.8 | 0.1 |
| 7 | 31.2 | 31.2 | |
| 8 | 44.5 | 44.5 | |
| 9 | 82.3 | 79.5 | |
| 10 | 79.5 | 82.3 | |
| 11 | 57.8 | 57.8 | |
| 12 | 52.3 | 52.3 | |
| 13 | 214.3 | 214.8 | 0.5 |
| 14 | 38.8 | 38.8 | |
| 15 | 42.7 | 42.6 | 0.1 |
| 16 | 28.8 | 28.8 | |
| 17 | 26.5 | 26.5 | |
| 18 | 15.7 | 15.7 | |
| 19 | 26.7 | 26.7 | |
| 20 | 129.5 | 129.4 | 0.1 |
| 21 | 165.8 | 165.7 | 0.1 |
| 22 | 117.8 | 117.8 | 0.1 |
| 23 | 145.4 | 145.3 | 0.1 |
| 24 | 134.3 | 134.3 | |
| 25 | 128.3 | 128.2 | 0.1 |
| 26 | 128.8 | 128.8 | |
| 27 | 130.4 | 130.3 | 0.1 |
| $\underline{CH_3}CO$ | 21.5 | 21.4 | 0.1 |
| $\underline{CH_3}CO$ | 21.1 | 21.1 | |
| $\underline{CH_3}CO$ | 21.0 | 20.9 | 0.1 |
| $CH_3\underline{CO}$ | 171.0 | 170.9 | 0.1 |
| $CH_3\underline{CO}$ | 170.0 | 170.0 | |
| $CH_3\underline{CO}$ | 169.6 | 169.5 | 0.1 |



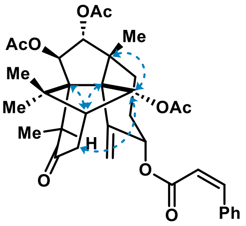
**2,9,10-triacetyl-5-[(Z)-cinnamoyl] phototaxicin II (41)**



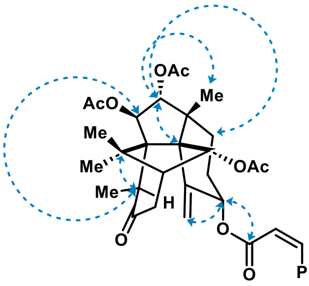
**2,9,10-triacetyl-5-[(Z)-cinnamoyl] phototaxicin II (41)**
**NOE**



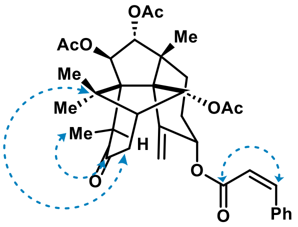
**2,9,10-triacetyl-5-[(Z)-cinnamoyl] phototaxicin II (41)**
**NOE**



**2,9,10-triacetyl-5-[(Z)-cinnamoyl] phototaxicin II (41)**
**HMBC**

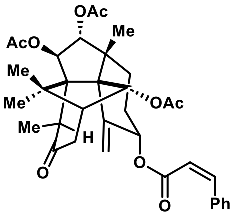


**2,9,10-triacetyl-5-[(Z)-cinnamoyl] phototaxicin II (41)**
**HMBC**

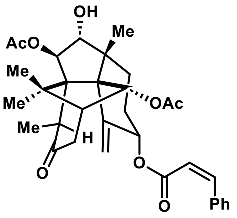


**2,9,10-triacetyl-5-[(Z)-cinnamoyl] phototaxicin II (41)**
**HMBC**

| Position | $\delta$ = $^1$H [ppm], mult, $J$ = [Hz] (synthetic) in $CCl_3D$ | | | | $\delta$ = $^1$H [ppm], mult, $J$ = [Hz] (isolation) in $CCl_3D$ | | | |
|---|---|---|---|---|---|---|---|---|
| 1 | 2.18 | m | | 1H | 2.16 | m | | 1H |
| 2 | 6.11 | d | $J$ = 5.3 Hz | 1H | 6.10 | d | $J$ = 5.1 Hz | 1H |
| 5 | 5.58 | t | $J$ = 8.6 Hz | 1H | 5.63 | m | | 1H |
| 6a | 1.74 | m | | 1H | 1.77 | m | | 2H |
| 6b | 2.14 | m | | 1H | | | | |
| 7a | 1.75 | m | | 1H | 1.80 | m | | 2H |
| 7b | 1.20 | m | | 1H | | | | |
| 9 | 5.60 | m | | 1H | 5.59 | d | $J$ = 8.4 Hz | 1H |
| 10 | 5.70 | m | | 1H | 5.70 | d | $J$ = 8.4 Hz | 1H |
| 12 | 3.47 | q | $J$ = 7.1 Hz | 1H | 3.46 | q | $J$ = 6.9 Hz | 1H |
| 14a | 2.57 | d | $J$ = 20.5 Hz | 1H | 2.57 | d | $J$ = 20.5 Hz | 1H |
| 14b | 2.49 | dd | $J$ = 20.5, 7.3 Hz | 1H | 2.50 | dd | $J$ = 20.5, 6.8 Hz | 1H |
| 16 | 1.69 | s | | 3H | 1.68 | s | | 3H |
| 17 | 1.21 | s | | 3H | 1.30 | s | | 3H |
| 18 | 1.27 | d | $J$ = 7.3 Hz | 3H | 1.25 | d | $J$ = 6.9 Hz | 3H |
| 19 | 1.20 | s | | 3H | 1.20 | s | | 3H |
| 20a | 5.78 | s | | 1H | 5.77 | s | | 1H |
| 20b | 5.64 | s | | 1H | 5.64 | s | | 1H |
| 22 | 5.94 | d | $J$ = 12.6 Hz | 1H | 5.91 | d | $J$ = 12.4 Hz | 1H |
| 23 | 7.03 | d | $J$ = 12.5 Hz | 1H | 7.00 | d | $J$ = 12.4 Hz | 1H |
| 25 | 7.65 | m | | 2H | 7.62 | m | | 1H |
| 26 | 7.35 | m | | 2H | 7.35 | m | | 2H |
| 27 | 7.35 | m | | 1H | 7.35 | m | | 1H |
| $CH_3CO$ | 2.05 | s | | 3H | 2.05 | s | | 3H |
| $CH_3CO$ | 2.05 | s | | 3H | 2.05 | s | | 3H |
| $CH_3CO$ | 2.05 | s | | 3H | 2.05 | s | | 3H |



**2,9,10-triacetyl-5-[(Z)-cinnamoyl] phototaxicin II (41)**



**isolated nature product S180**

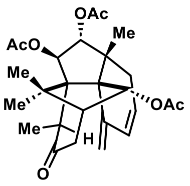
| | $\delta$ = $^{13}$C [ppm] (synthetic) in $CCl_3D$ | $\delta$ = $^{13}$C [ppm] (isolation) in $CCl_3D$ |
|---|---|---|
| 1 | 47.8 | 47.9 |
| 2 | 76.8 | 76.2 |
| 3 | 65.8 | 66.0 |
| 4 | 142.3 | 142.7 |
| 5 | 77.0 | 76.2 |
| 6 | 26.4 | 26.0 |
| 7 | 29.7 | 29.7 |
| 8 | 44.5 | 45.2 |
| 9 | 79.4 | 82.7 |
| 10 | 82.2 | 84.5 |
| 11 | 57.9 | 58.0 |
| 12 | 52.3 | 52.2 |
| 13 | 214.2 | 214.3 |
| 14 | 38.7 | 38.8 |
| 15 | 42.8 | 42.7 |
| 16 | 26.7 | 26.7 |
| 17 | 29.0 | 29.2 |
| 18 | 15.5 | 15.6 |
| 19 | 26.7 | 26.2 |
| 20 | 128.9 | 128.7 |
| 21 | 164.5 | 167.2 |
| 22 | 119.2 | 119.4 |
| 23 | 145.1 | 144.3 |
| 24 | 134.6 | 135.2 |
| 25 | 130.4 | 129.8 |
| 26 | 128.0 | 128.0 |
| 27 | 129.2 | 129.2 |
| $\underline{CH_3}CO$ | 21.2 | 21.4 |
| $\underline{CH_3}CO$ | 21.0 | 21.3 |
| $\underline{CH_3}CO$ | 20.9 | |
| $CH_3\underline{CO}$ | 171.0 | 172.5 |
| $CH_3\underline{CO}$ | 170.0 | 169.4 |
| $CH_3\underline{CO}$ | 169.6 | |

*Notes*:

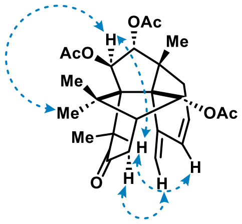
*--Since the original paper solely presented the $^1$H NMR data and did not include $^{13}$C NMR information, we compared the $^{13}$C NMR data of the synthetic product and natural product **S180** which exhibits a high similarity.*

*--Yang, C.; Wang, J. S.; Luo, J. G.; Kong, L. Y. J. Asian Nat. Prod. Res. **2009**, 11, 534.*

*--Kobayashi, J.; Ogiwara, A.; Hosoyama, H.; Shigemori, H.; Yoshida, N.; Sasaki, T.; Li, Y.; Iwasaki, S.; Naito, M.; Tsuruo, T. Tetrahedron **1994**, 50, 7401.*



**3α,11α-cyclotaxinine NN-2 (40)**

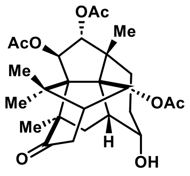


**3α,11α-cyclotaxinine NN-2 (40)**
**NOE**

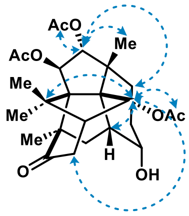
| Position | δ = $^1$H [ppm], mult, $J$ = [Hz] (synthetic) in $CCl_3D$ | | | | δ = $^1$H [ppm], mult, $J$ = [Hz] (isolation) in $CCl_3D$ | | | |
|---|---|---|---|---|---|---|---|---|
| 1 | 2.18 | m | | 1H | 2.17 | m | | 1H |
| 2 | 6.16 | d | $J$ = 5.4 Hz | 1H | 6.14 | d | $J$ = 5.1 Hz | 1H |
| 5 | 6.28 | d | $J$ = 8.9 Hz | 1H | 6.26 | dd | $J$ = 9.0, 2.0 Hz | 1H |
| 6 | 6.12 | t | $J$ = 6.8 Hz | 1H | 6.10 | ddd | $J$ = 9.2, 6.6, 2.7 Hz | 1H |
| 7a | 2.23 | dd | $J$ = 14.7, 6.9 Hz | 1H | 2.20 | dd | $J$ = 14.7, 7.1 Hz | 1H |
| 7b | 1.68 | m | | 1H | 1.66 | ddd | $J$ = 14.7, 2.7, 2.0 Hz | 1H |
| 9 | 5.56 | d | $J$ = 9.0 Hz | 1H | 5.54 | d | $J$ = 9.0 Hz | 1H |
| 10 | 5.25 | d | $J$ = 9.0 Hz | 1H | 5.23 | d | $J$ = 9.0 Hz | 1H |
| 12 | 2.70 | m | | 1H | 2.68 | d | $J$ = 7.3 Hz | 1H |
| 14a | 2.70 | o.d | $J$ = 20.4 Hz | 1H | 2.68 | dd | $J$ = 20.3, 7.3 Hz | 1H |
| 14b | 2.51 | dd | $J$ = 20.4, 7.4 Hz | 1H | 2.49 | d | $J$ = 20.3 Hz | 1H |
| 16 | 1.65 | s | | 1H | 1.63 | s | | 1H |
| 17 | 1.21 | s | | 3H | 1.19 | s | | 3H |
| 18 | 1.21 | d | $J$ = 7.4 Hz | 3H | 1.19 | d | $J$ = 7.3 Hz | 3H |
| 19 | 1.39 | s | | 3H | 1.37 | s | | 3H |
| 20a | 5.68 | s | | 3H | 5.56 | d | $J$ = 1.0 Hz | 3H |
| 20b | 5.12 | s | | 1H | 5.10 | br.s | | 1H |
| $CH_3CO$ | 2.12 | s | | 1H | 2.10 | s | | 1H |
| $CH_3CO$ | 2.08 | s | | 3H | 2.06 | s | | 3H |
| $CH_3CO$ | 2.02 | s | | 3H | 2.00 | s | | 3H |
| | | | | 3H | | | | 3H |

| Position | NOESY (synthetic) in $CCl_3D$ | Position | NOESY (synthetic) in $CCl_3D$ |
|---|---|---|---|
| 1 | 2 | 14a | 20 |
| 2 | 19, 16, 1 | 14b | |
| 5 | 20b, 12 | 16 | 2, 9 |
| 6 | 5, 7 | 17 | 16 |
| 7a | 7b | 18 | 10, 12 |
| 7b | 7a | 19 | 2, 9 |
| 9 | 19, 16 | 20a | 14a, 20b |
| 10 | 18, 12 | 20b | 20a, 5 |
| 12 | 6 | | |

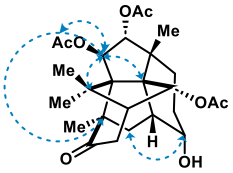
| Position | δ = $^{13}$C [ppm] (synthetic) in CCl$_3$D | δ = $^{13}$C [ppm] (isolation) in CCl$_3$D | Δ δ [ppm] |
|---|---|---|---|
| 1 | 48.1 | 48.1 | |
| 2 | 76.3 | 76.3 | |
| 3 | 66.9 | 66.9 | |
| 4 | 143.3 | 143.2 | 0.1 |
| 5 | 134.4 | 134.4 | |
| 6 | 131.5 | 131.5 | |
| 7 | 34.5 | 34.5 | |
| 8 | 49.3 | 49.3 | |
| 9 | 80.3 | 80.3 | |
| 10 | 83.3 | 83.3 | |
| 11 | 57.8 | 57.8 | |
| 12 | 52.2 | 52.2 | |
| 13 | 214.1 | 214.1 | |
| 14 | 38.7 | 38.7 | |
| 15 | 42.1 | 42.1 | |
| 16 | 28.1 | 28.1 | |
| 17 | 26.7 | 26.7 | |
| 18 | 15.8 | 15.8 | |
| 19 | 26.9 | 26.9 | |
| 20 | 117.0 | 117.0 | |
| $\underline{CH_3}$CO | 21.4 | 21.4 | |
| $\underline{CH_3}$CO | 21.1 | 21.1 | |
| $\underline{CH_3}$CO | 21.0 | 21.0 | |
| CH$_3$$\underline{CO}$ | 170.9 | 170.9 | |
| CH$_3$$\underline{CO}$ | 169.9 | 169.8 | 0.1 |
| CH$_3$$\underline{CO}$ | 169.7 | 169.6 | 0.1 |



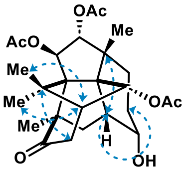
**canataxapropellane (5)**



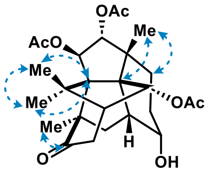
**canataxapropellane (5)**
**HMBC**



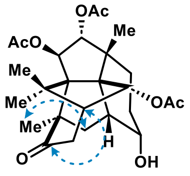
**canataxapropellane (5)**
**HMBC**



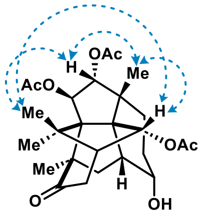
**canataxapropellane (5)**
**HMBC**



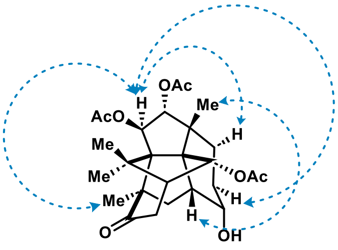
**canataxapropellane (5)**
**HMBC**



**canataxapropellane (5)**
**HMBC**



**canataxapropellane (5)**
**NOE**



**canataxapropellane (5)**
**NOE**

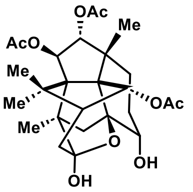
| Position | $\delta$ = $^{1}$H [ppm], mult, $J$ = [Hz] (synthetic) in $CCl_3D$ | | | | $\delta$ = $^{1}$H [ppm], mult, $J$ = [Hz] (isolation) in $CCl_3D$ | | | |
|---|---|---|---|---|---|---|---|---|
| 1 | 2.21 | t | $J$ = 6.3 Hz | 1H | 2.21 | br | $J$ = 6.1 Hz | 1H |
| 2 | 5.71 | d | $J$ = 5.5 Hz | 1H | 5.71 | d | $J$ = 5.2 Hz | 1H |
| 4 | 2.56 | o.m | | 1H | 2.55 | o.m | | 1H |
| 5 | 4.12 | m | | 1H | 4.12 | m | | 1H |
| 6a | 2.02 | o.m | | 1H | 2.00 | o.m | | 1H |
| 6b | 1.45 | m | | 1H | 1.46 | m | | 1H |
| 7a | 1.98 | o.m | | 1H | 2.00 | o.m | | 1H |
| 7b | 1.52 | o.m | | 1H | 1.54 | o.m | | 1H |
| 9 | 5.57 | d | $J$ = 9.9 Hz | 1H | 5.57 | d | $J$ = 9.8 Hz | 1H |
| 10 | 5.45 | d | $J$ = 9.8 Hz | 1H | 5.46 | d | $J$ = 9.8 Hz | 1H |
| 14a | 2.62 | d | $J$ = 20.2 Hz | 1H | 2.61 | d | $J$ = 20.2 Hz | 1H |
| 14b | 2.52 | m | | 1H | 2.53 | dd | $J$ = 20.2, 7.2 Hz | 1H |
| 16 | 1.58 | s | | 3H | 1.12 | s | | 3H |
| 17 | 1.12 | s | | 3H | 1.58 | s | | 3H |
| 18 | 1.22 | s | | 3H | 1.22 | s | | 3H |
| 19 | 1.08 | s | | 3H | 1.09 | s | | 3H |
| 20a | 1.98 | o.m | | 1H | 1.97 | o.m | | 1H |
| 20b | 1.74 | m | | 1H | 1.74 | o.m | | 1H |
| $CH_3CO$ | 2.08 | s | | 3H | 2.08 | s | | 3H |
| $CH_3CO$ | 2.02 | s | | 3H | 2.02 | s | | 3H |
| $CH_3CO$ | 2.01 | s | | 3H | 2.01 | s | | 3H |

| Position | $\delta$ = $^{13}$C [ppm] (synthetic) in $CCl_3D$ | $\delta$ = $^{13}$C [ppm] (isolation) in $CCl_3D$ | $\Delta$ $\delta$ [ppm] |
|---|---|---|---|
| 1 | 47.1 | 47.0 | 0.1 |
| 2 | 77.0 (from HSQC) | 76.9 | 0.1 |
| 3 | 62.7 | 62.7 | |
| 4 | 43.9 | 43.8 | 0.1 |
| 5 | 65.3 | 65.1 | 0.2 |
| 6 | 24.5 | 24.4 | 0.1 |
| 7 | 28.0 | 28.0 | |
| 8 | 38.6 | 38.6 | |
| 9 | 82.2 | 82.0 | 0.2 |
| 10 | 76.5 | 76.3 | 0.2 |
| 11 | 63.6 | 63.6 | |
| 12 | 60.8 | 60.8 | |
| 13 | 216.9 | 216.9 | |
| 14 | 38.6 | 38.9 | 0.3 |
| 15 | 42.2 | 42.2 | |
| 16 | 28.4 | 24.3 | |
| 17 | 24.5 | 28.3 | |
| 18 | 18.8 | 18.7 | 0.1 |
| 19 | 20.8 | 20.6 | 0.2 |
| 20 | 42.7 | 42.6 | 0.1 |
| $\underline{CH_3}CO$ | 21.2 | 20-21 | |
| $\underline{CH_3}CO$ | 21.0 | 20-21 | |
| $\underline{CH_3}CO$ | 20.9 | 20-21 | |
| $CH_3\underline{CO}$ | 171.0 | 170.7 | 0.3 |
| $CH_3\underline{CO}$ | 170.0 | 169.7 | 0.3 |
| $CH_3\underline{CO}$ | 169.9 | 169.7 | 0.2 |

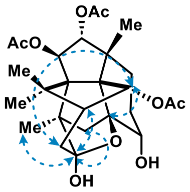
*Notes:*

*--Upon comparison of our proton and carbon NMR data with the isolation paper by L. Zamir, we noticed that C16 and C17 have been switched.*

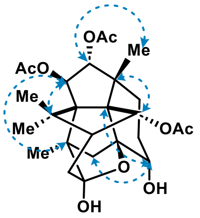
| Position | HMBC<br>(synthetic) in $CCl_3D$ | HMBC<br>(isolation) in $CCl_3D$ | NOESY<br>(synthetic) in $CCl_3D$ | NOESY<br>(isolation) in $CCl_3D$ |
|---|---|---|---|---|
| 1 | 2, 3, 13, 15, 16 | 2, 11, 13, 15 | 2, 16 | 2, 14b, 16, 17, 20a |
| 2 | 1, 3, 4, 8, 14, 15, Ac | 1, 3, 4, 8, 14, Ac | 1, 16, 19 | 1, 17, 19 |
| 4 | 2, 3, 5, 6, 8, 20 | 2, 3, 5, 6, 8, 20 | 5 | 1, 5, 18 |
| 5 | 4, 6, 20 |  | 4, 6a | 4 |
| 6a | 4, 8 |  | 5 | 5, 19 |
| 6b | 5, 7, 8 |  | 10 |  |
| 7a | 8, 9, 19 |  |  | 5, 19 |
| 7b | 3, 5, 6, 8, 9, 19 |  | 10 | 7a, 19 |
| 9 | 7, 8, 10, 19, Ac | 7, 8, 10, 19, Ac | 16, 19 | 2, 17, 19 |
| 10 | 3, 9, 11, 12, 15, Ac | 9, 11, 12, 15, Ac | 6a, 7a, 18 | 6a, 7a, 18, 20a |
| 14a | 1, 2, 13, 15 | 1, 2, 14 |  | 14b |
| 14b | 1, 2, 13, 15 | 2, 13 |  | 1, 5, 14a, 18 |
| 16 | 1, 11, 15, 17 | 1, 11, 15, 17 | 2, 9, 17 |  |
| 17 | 1, 11, 15, 16 | 1, 11, 15, 16 | 16 |  |
| 18 | 11, 12, 13, 20 | 11, 12, 13, 20 | 10 |  |
| 19 | 3, 7, 8, 9 | 3, 7, 8, 9 | 2, 9 |  |
| 20a | 4, 11, 12, 13 | 13 |  |  |
| 20b | 4, 5, 12, 13, 18 | 13 |  | 18, 20a |



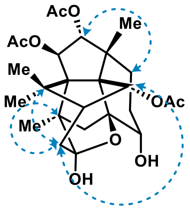
**dipropellane C (15)**



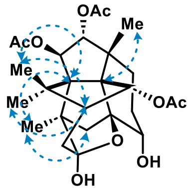
**dipropellane C (15)**
**HMBC**



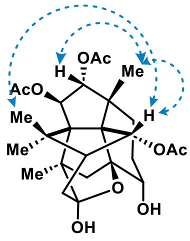
**dipropellane C (15)**
**HMBC**



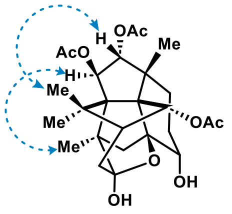
**dipropellane C (15)**
**HMBC**



**dipropellane C (15)**
**HMBC**



**dipropellane C (15)**
**NOE**

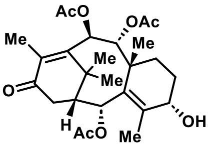


**dipropellane C (15)**
**NOE**

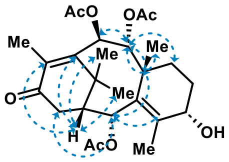
| Position | $\delta$ = $^{1}$H [ppm], mult, $J$ = [Hz] (synthetic) in $CCl_3D$ | | | | $\delta$ = $^{1}$H [ppm], mult, $J$ = [Hz] (isolation) in acetone-$d_6$ | | | |
|---|---|---|---|---|---|---|---|---|
| 1 | 1.98 | m | | 1H | 1.96 | m | | 1H |
| 2 | 5.65 | d | $J$ = 5.3 Hz | 1H | 5.63 | d | $J$ = 5.0 Hz | 1H |
| 5 | 4.30 | m | | 1H | 4.23 | m | | 1H |
| OH | - | | | 1H | 3.50 | br | | 1H |
| 6a | 1.98 | m | | 1H | 1.95 | m | | 1H |
| 6b | 1.63 | m | | 1H | 1.54 | m | | 1H |
| 7a | 2.03 | m | | 1H | 1.95 | m | | 1H |
| 7b | 1.24 | m | | 1H | 1.18 | m | | 1H |
| 9 | 5.44 | d | $J$ = 9.2 Hz | 1H | 5.43 | d | $J$ = 9.2 Hz | 1H |
| 10 | 5.60 | d | $J$ = 9.2 Hz | 1H | 5.63 | d | $J$ = 9.2 Hz | 1H |
| OH | - | | | 1H | 4.77 | -OH | | 1H |
| 14a | 2.14 | m | | 1H | 2.07 | m | | 1H |
| 14b | 1.92 | m | | 1H | 1.87 | o.m | | 1H |
| 16 | 1.25 | s | | 3H | 1.26 | s | | 3H |
| 17 | 1.46 | s | | 3H | 1.43 | s | | 3H |
| 18 | 1.22 | s | | 3H | 1.19 | s | | 3H |
| 19 | 1.16 | s | | 3H | 1.15 | s | | 3H |
| 20a | 2.14 | d | $J$ = 11.7 Hz | 1H | 2.15 | d | $J$ = 11.7 Hz | 1H |
| 20b | 1.92 | dd | $J$ = 11.7, 3.4 Hz | 1H | 1.99 | d | $J$ = 11.7 Hz | 1H |
| $CH_3CO$ | 2.07 | s | | 3H | 2.04 | s | | 3H |
| $CH_3CO$ | 2.04 | s | | 3H | 2.01 | s | | 3H |
| $CH_3CO$ | 2.00 | s | | 3H | 2.03 | s | | 3H |

| Position | $\delta$ = $^{13}$C [ppm] (synthetic) in $CCl_3D$ | $\delta$ = $^{13}$C [ppm] (isolation) in acetone-$d_6$ |
|---|---|---|
| 1 | 47.5 | 48.5 |
| 2 | 78.0 | 78.3 |
| 3 | 63.5 | 66.3 |
| 4 | 87.7 | 88.2 |
| 5 | 65.3 | 65.6 |
| 6 | 28.0 | 27.2 |
| 7 | 29.2 | 28.4 |
| 8 | 41.3 | 42.2 |
| 9 | 85.2 | 86.0 |
| 10 | 78.0 | 78.3 |
| 11 | 64.8 | 64.7 |
| 12 | 55.6 | 56.4 |
| 13 | 101.0 | 101.3 |
| 14 | 33.6 | 34.1 |
| 15 | 39.5 | 40.6 |
| 16 | 23.9 | 24.1 |
| 17 | 29.2 | 29.3 |
| 18 | 14.4 | 14.8 |
| 19 | 22.5 | 23.0 |
| 20 | 47.0 | 47.0 |
| $\underline{CH_3}CO$ | 21.3 | 21.0 |
| $\underline{CH_3}CO$ | 21.1 | 20.7 |
| $\underline{CH_3}CO$ | 20.8 | 20.4 |
| $CH_3\underline{CO}$ | 170.8 | 171.0 |
| $CH_3\underline{CO}$ | 107.6 | 171.0 |
| $CH_3\underline{CO}$ | 170.1 | 170.4 |

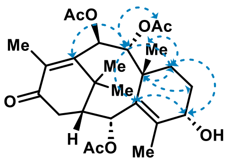
| Position | HMBC (synthetic) in $CCl_3D$ | NOESY (synthetic) in $CCl_3D$ |
|---|---|---|
| 1 | 13 | |
| 2 | 1, 4, 8, 14, Ac | 1, 16, 19 |
| 5 | 2, 4, Ac | 6a, 6b |
| 6a | | |
| 6b | | |
| 7a | | |
| 7b | | |
| 9 | 7, 8, 10, 19, Ac | 16, 19 |
| 10 | 9, 11, 12, 15, Ac | 18, 20a |
| 14a | 1, 12, 13, 15 | |
| 14b | 1, 2, 12, 13, 15 | |
| 16 | 1, 11, 15 | 2, 9 |
| 17 | 1, 11, 15 | |
| 18 | 11, 13, 20 | 10 |
| 19 | 3, 7, 8, 9 | 9 |
| 20a | 5, 13 | |
| 20b | 5, 13 | |



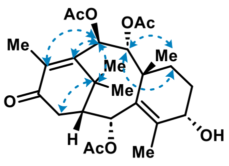
**$\Delta^{3(4)}$-taxinin A (10)**



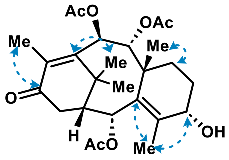
**$\Delta^{3(4)}$-taxinin A (10)**
**HMBC**



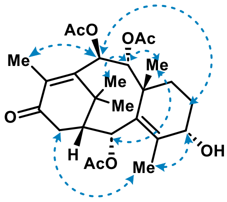
**$\Delta^{3(4)}$-taxinin A (10)**
**HMBC**



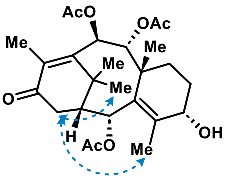
**$\Delta^{3(4)}$-taxinin A (10)**
**HMBC**



**$\Delta^{3(4)}$-taxinin A (10)**
**HMBC**



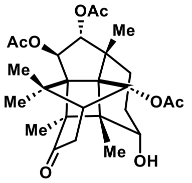
**$\Delta^{3(4)}$-taxinin A (10)**
**NOE**



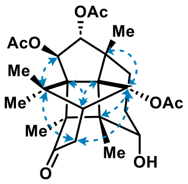
**$\Delta^{3(4)}$-taxinin A (10)**
**NOE**

| Position | δ = $^1$H [ppm], mult, *J* = [Hz] (synthetic) in $CCl_3D$ | | | | Position | δ = $^{13}$C [ppm] (synthetic) in $CCl_3D$ |
|---|---|---|---|---|---|---|
| 1 | 2.33 | d | *J* = 4.9 Hz | 1H | 1 | 53.4 |
| 2 | 5.91 | d | *J* = 5.1 Hz | 1H | 2 | 71.7 |
| 5 | 3.76 | br | | 1H | 3 | 137.7 |
| 6a | 1.72 | m | | 1H | 4 | 133.5 |
| 6b | 1.77 | m | | 1H | 5 | 70.1 |
| 7a | 1.67 | m | | 1H | 6 | 25.9 |
| 7b | 1.83 | o.m | | 1H | 7 | 23.6 |
| 9 | 6.07 | d | *J* = 10.5 Hz | 1H | 8 | 43.7 |
| 10 | 5.96 | d | *J* = 10.5 Hz | 1H | 9 | 75.2 |
| 14a | 2.99 | d | *J* = 20.0 Hz | 1H | 10 | 53.5 |
| 14b | 2.84 | dd | *J* = 19.9 Hz | 1H | 11 | 151.4 |
| 16 | 1.81 | s | | 3H | 12 | 137.5 |
| 17 | 1.22 | s | | 3H | 13 | 198.8 |
| 18 | 2.11 | s | | 3H | 14 | 36.3 |
| 19 | 1.02 | s | | 3H | 15 | 37.9 |
| 20 | 2.03 | s | | 3H | 16 | 25.9 |
| $CH_3CO$ | 2.08 | s | | 3H | 17 | 36.9 |
| $CH_3CO$ | 2.05 | s | | 3H | 18 | 13.7 |
| $CH_3CO$ | 2.04 | s | | 3H | 19 | 25.6 |
| | | | | | 20 | 22.8 |
| | | | | | $\underline{CH_3}CO$ | 21.3 |
| | | | | | $\underline{CH_3}CO$ | 20.9 |
| | | | | | $\underline{CH_3}CO$ | 20.8 |
| | | | | | $CH_3\underline{CO}$ | 170.2 |
| | | | | | $CH_3\underline{CO}$ | 169.8 |
| | | | | | $CH_3\underline{CO}$ | 169.0 |

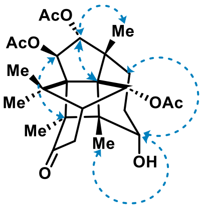
| Position | HMBC (synthetic) in $CCl_3D$ | NOESY (synthetic) in $CCl_3D$ |
|---|---|---|
| 1 | 2, 3, 11, 13, 14, 15, 16, 17 | 2, 14b |
| 2 | 1, 3, 4, 8, 14, Ac | 1, 16, 19 |
| 5 | 3, 7 | 6a, 20 |
| 6a | 8 | |
| 6b | | |
| 7a | 3, 5, 8, 19 | |
| 7b | 8 | |
| 9 | 7, 8, 10, 11, 19, Ac | 16, 19 |
| 10 | 8, 9, 11, 12, 15, Ac | 6, 18 |
| 14a | 1, 2, 13, 15 | 1, 14b, 20 |
| 14b | 1, 2, 13, 15 | 1, 14a, 17 |
| 16 | 1, 11, 15, 17 | 1, 2, 9, 17 |
| 17 | 1, 11, 15, 16 | 14b, 16 |
| 18 | 11, 12, 13 | 10 |
| 19 | 3, 7, 8, 9 | 2, 9 |
| 20 | 3, 4, 5 | 5, 14a |



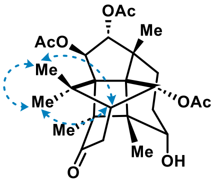
20-desoxy-9-acetyl-
taxpropellane(14)



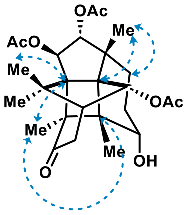
20-desoxy-9-acetyl-
taxpropellane(14)
HMBC



20-desoxy-9-acetyl-
taxpropellane(14)
HMBC



20-desoxy-9-acetyl-
taxpropellane(14)
HMBC

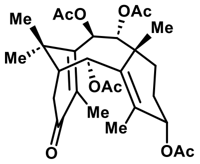


20-desoxy-9-acetyl-
taxpropellane(14)
HMBC

| Position | δ = $^1$H [ppm], mult, $J$ = [Hz] (synthetic) in CCl$_3$D | | | |
|---|---|---|---|---|
| 1 | 1.92 | m | | 1H |
| 2 | 5.71 - 5.69 | m | | 1H |
| 5 | 4.68 | d | $J$ = 7.9 Hz | 1H |
| 6a | 1.61 - 1.59 | m | | 1H |
| 6b | 1.61 - 1.59 | m | | 1H |
| 7a | 2.28 | t | $J$ = 14.1 Hz | 1H |
| 7b | 1.64 | m | | 1H |
| 9 | 5.51 | d | $J$ = 6.0 Hz | 1H |
| 10 | 6.17 | d | $J$ = 6.0 Hz | 1H |
| 14a | 2.01 | d | $J$ = 12.9 Hz | 1H |
| 14b | 1.93 - 1.90 | m | | 1H |
| 16 | 1.56 | s | | 3H |
| 17 | 1.17 | s | | 3H |
| 18 | 1.58 | s | | 3H |
| 19 | 1.62 | s | | 3H |
| 20 | 1.60 | s | | 3H |
| $\mathrm{CH_3CO}$ | 2.12 | s | | 3H |
| $\mathrm{CH_3CO}$ | 2.11 | s | | 3H |
| $\mathrm{CH_3CO}$ | 2.08 | s | | 3H |

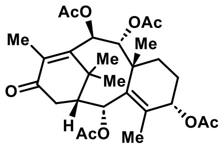
| Position | δ = $^{13}$C [ppm] (synthetic) in CCl$_3$D |
|---|---|
| 1 | 51.3 |
| 2 | 78.5 |
| 3 | 64.8 |
| 4 | 58.6 |
| 5 | 64.2 |
| 6 | 28.5 |
| 7 | 30.8 |
| 8 | 44.7 |
| 9 | 91.0 |
| 10 | 78.2 |
| 11 | 70.2 |
| 12 | 58.8 |
| 13 | 217.3 |
| 14 | 38.9 |
| 15 | 47.3 |
| 16 | 26.3 |
| 17 | 25.5 |
| 18 | 23.6 |
| 19 | 27.8 |
| 20 | 19.3 |
| $\underline{\mathrm{CH_3}}\mathrm{CO}$ | 21.4 |
| $\underline{\mathrm{CH_3}}\mathrm{CO}$ | 21.1 |
| $\underline{\mathrm{CH_3}}\mathrm{CO}$ | 20.8 |
| $\mathrm{CH_3}\underline{\mathrm{CO}}$ | 170.3 |
| $\mathrm{CH_3}\underline{\mathrm{CO}}$ | 170.0 |
| $\mathrm{CH_3}\underline{\mathrm{CO}}$ | 169.7 |

| Position | HMBC (synthetic) in CCl$_3$D | Position | HMBC (synthetic) in CCl$_3$D |
|---|---|---|---|
| 1 | 2, 3, 11 | 10 | 9, 11, 12, 15, Ac |
| 2 | 1, 3, 4, 8, 14 | 14 | 1, 2, 15 |
| 5 | 6, 7, 20 | 16 | 1, 11, 15, 17 |
| 6a | | 17 | 1, 11, 15, 17 |
| 6b | | 18 | 4, 11, 14 |
| 7a | | 19 | 3, 7, 8, 9 |
| 7b | | 20 | 4, 5 |
| 9 | 3, 7, 8, 9, 10, 19, Ac | | |

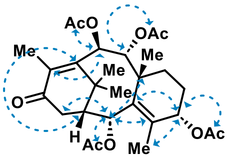


**$\Delta^{3(4)}$-taxinin H (11)**

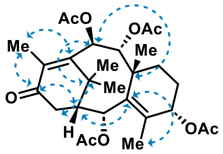
≡



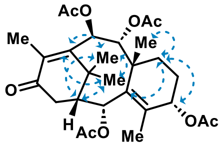
**$\Delta^{3(4)}$-taxinin H (11)**



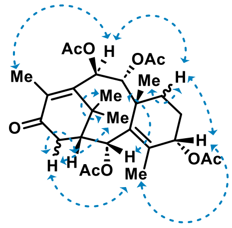
**$\Delta^{3(4)}$-taxinin H (11)**
**HMBC**



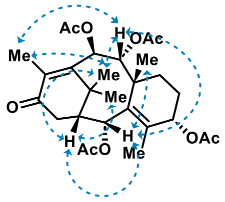
**$\Delta^{3(4)}$-taxinin H (11)**
**HMBC**



**$\Delta^{3(4)}$-taxinin H (11)**
**HMBC**



**$\Delta^{3(4)}$-taxinin H (11)**
**NOE**

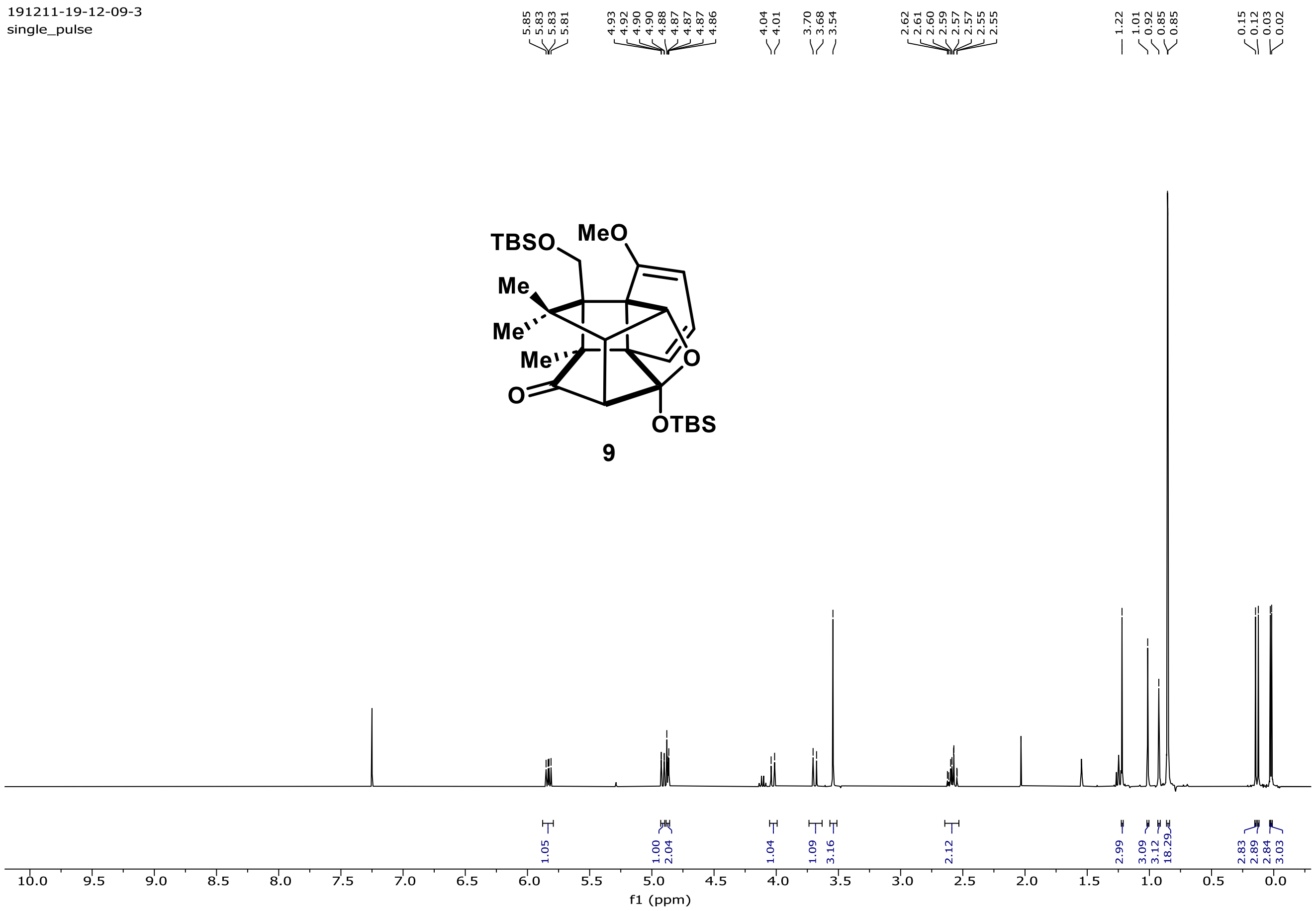


**$\Delta^{3(4)}$-taxinin H (11)**
**NOE**

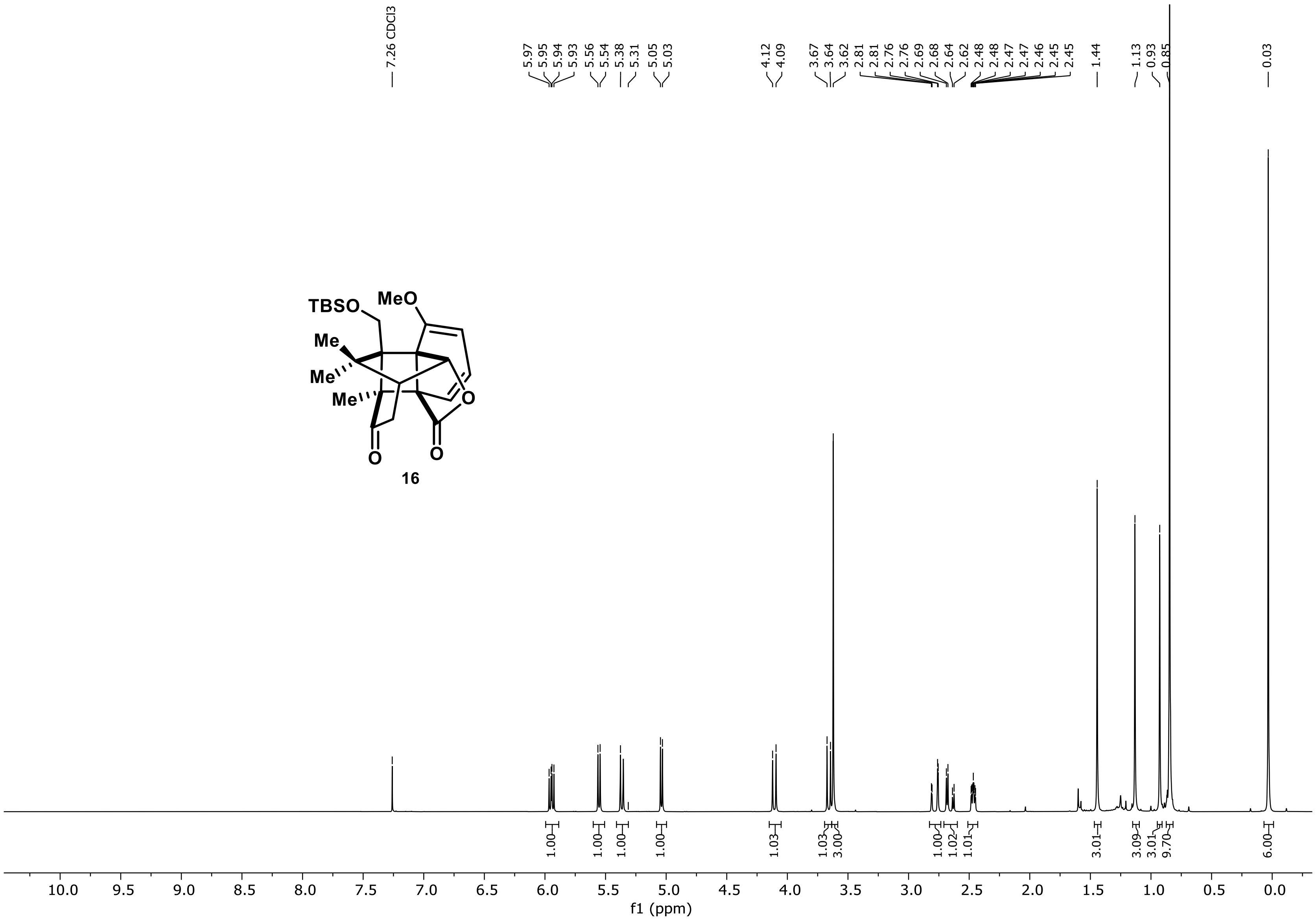
| Position | δ = $^{1}$H [ppm], mult, $J$ = [Hz] (synthetic) in $CCl_3D$ | | | | Position | δ = $^{13}$C [ppm] (synthetic) in $CCl_3D$ |
|---|---|---|---|---|---|---|
| 1 | 2.34 | s | | 1H | 1 | 53.0 |
| 2 | 5.92 | d | $J$ = 2.4 Hz | 1H | 2 | 71.5 |
| 5 | 4.98 | d | $J$ = 4.3 Hz | 1H | 3 | 140.3 |
| 6a | 1.84 | m | | 1H | 4 | 130.6 |
| 6b | 1.73 | m | | 1H | 5 | 71.8 |
| 7a | 1.75 | m | | 1H | 6 | 23.7 |
| 7b | 1.75 | m | | 1H | 7 | 24.2 |
| 9 | 6.09 | d | $J$ = 10.5 Hz | 1H | 8 | 43.4 |
| 10 | 5.97 | d | $J$ = 10.5 Hz | 1H | 9 | 75.1 |
| 14a | 2.96 | d | $J$ = 20.0 Hz | 1H | 10 | 73.3 |
| 14b | 2.82 | dd | $J$ = 20.1, 5.4 Hz | 1H | 11 | 150.6 |
| 16 | 1.81 | s | | 3H | 12 | 137.4 |
| 17 | 1.20 | s | | 3H | 13 | 197.9 |
| 18 | 2.12 | s | | 3H | 14 | 36.1 |
| 19 | 1.04 | s | | 3H | 15 | 37.9 |
| 20 | 1.87 | s | | 3H | 16 | 25.9 |
| $CH_3CO$ | 2.08 | s | | 3H | 17 | 36.8 |
| $CH_3CO$ | 2.08 | s | | 3H | 18 | 13.5 |
| $CH_3CO$ | 2.06 | s | | 3H | 19 | 25.6 |
| $CH_3CO$ | 2.04 | s | | 3H | 20 | 22.4 |
| | | | | | $\underline{CH_3}CO$ | 21.5 |
| | | | | | $\underline{CH_3}CO$ | 21.3 |
| | | | | | $\underline{CH_3}CO$ | 20.9 |
| | | | | | $\underline{CH_3}CO$ | 20.7 |
| | | | | | $CH_3\underline{CO}$ | 170.7 |
| | | | | | $CH_3\underline{CO}$ | 170.1 |
| | | | | | $CH_3\underline{CO}$ | 169.9 |
| | | | | | $CH_3\underline{CO}$ | 169.0 |

| Position | HMBC (synthetic) in $CCl_3D$ | NOESY (synthetic) in $CCl_3D$ |
|---|---|---|
| 1 | 2, 3, 11, 13, 15 | 2, 14b, 16, 17 |
| 2 | 1, 3, 4, 8, 14, Ac | 1, 9, 16, 19 |
| 5 | 3, 4, 20, Ac | 20 |
| 6 | | |
| 7 | 3, 5, 8, 19 | 5, 9, 10, 19 |
| 9 | 8, 10, Ac | 2, 16, 19 |
| 10 | 8, 9, 11, 12, 15, Ac | 7, 18 |
| 14a | 1, 2, 13, 15 | 14b, 20 |
| 14b | 1, 2, 13 | 1, 14a, 17 |
| 16 | 1, 11, 15, 17 | 1, 2, 9, 17 |
| 17 | 1, 11, 15, 16 | 14b |
| 18 | 11, 12, 13 | 10 |
| 19 | 3, 7, 8, 9 | 2, 9, 16 |
| 20 | 3, 4, 5 | 5, 14a |

# Part-VIII NMR Spectra

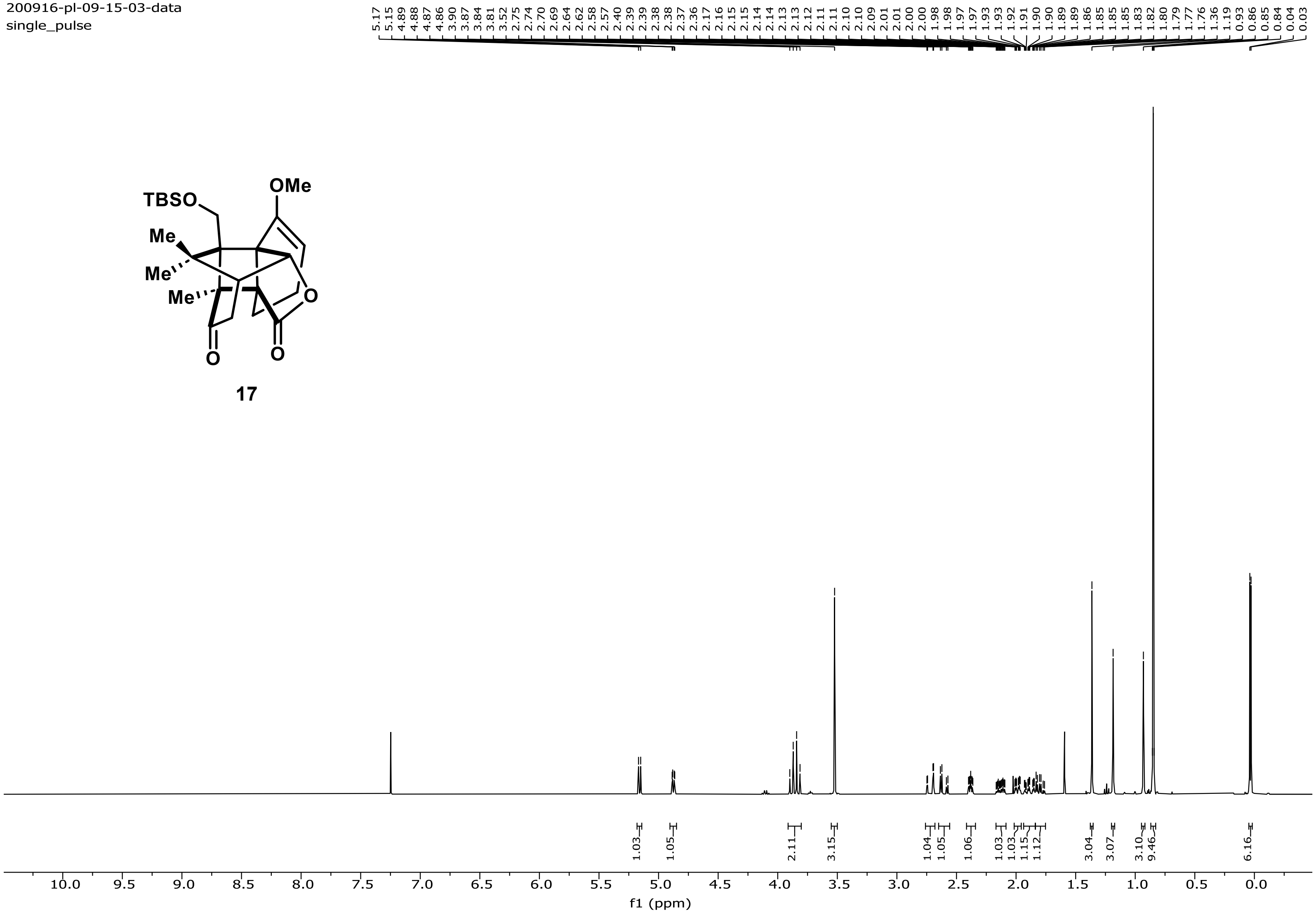


9

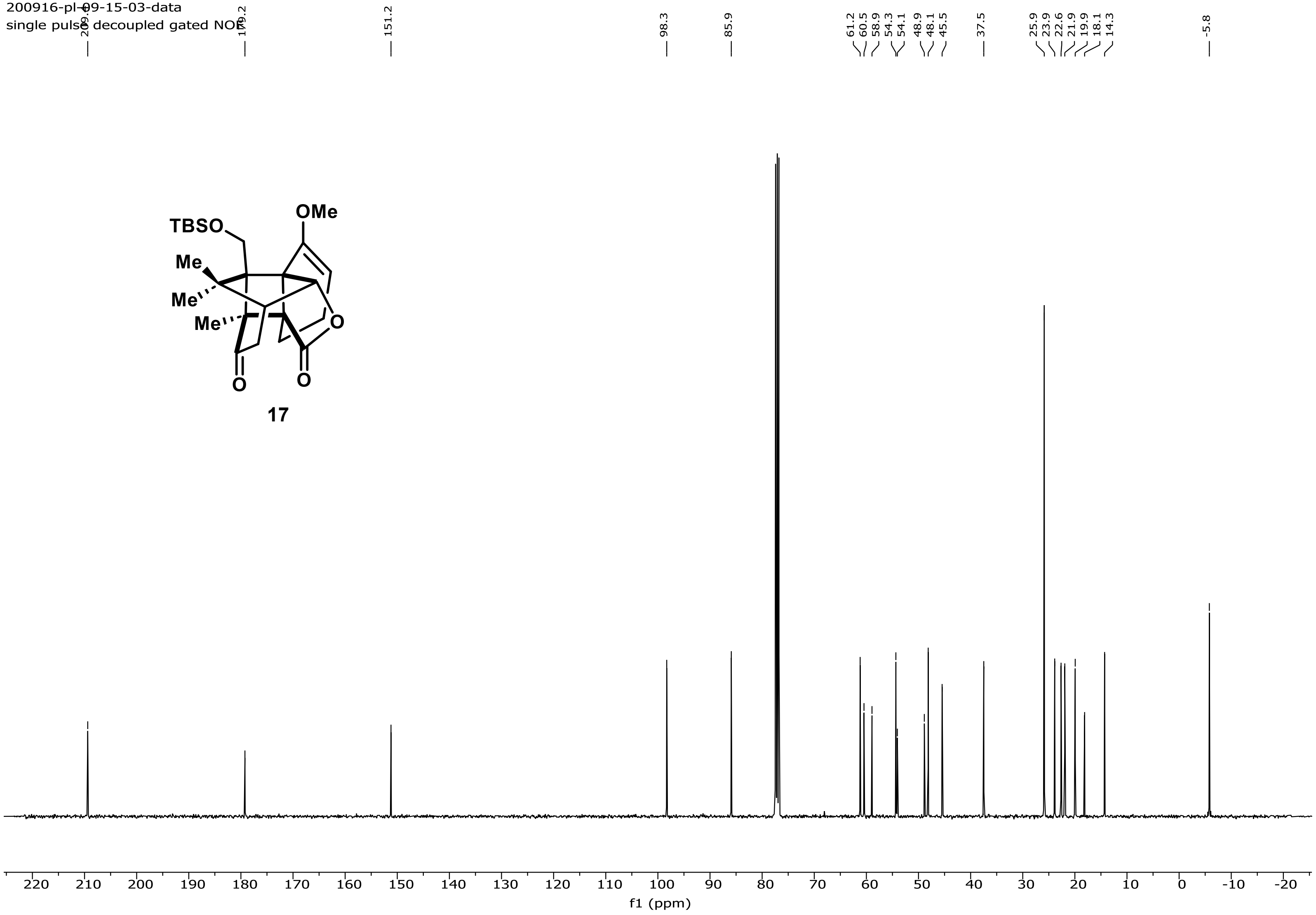

7.26 CDCl3
5.97
5.95
5.94
5.93
5.56
5.54
5.38
5.31
5.05
5.03
4.12
4.09
3.67
3.64
3.62
2.81
2.81
2.76
2.76
2.69
2.68
2.64
2.62
2.48
2.48
2.47
2.46
2.45
2.45
1.44
1.13
0.93
0.85
0.03
TBSO
MeO
Me
Me
Me
O
O
O
1.00
1.00
1.00
1.00
1.03
1.03
3.00
1.00
1.02
1.01
3.01
3.09
3.01
9.70
6.00
10.0
9.5
9.0
8.5
8.0
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
f1 (ppm)

**16**

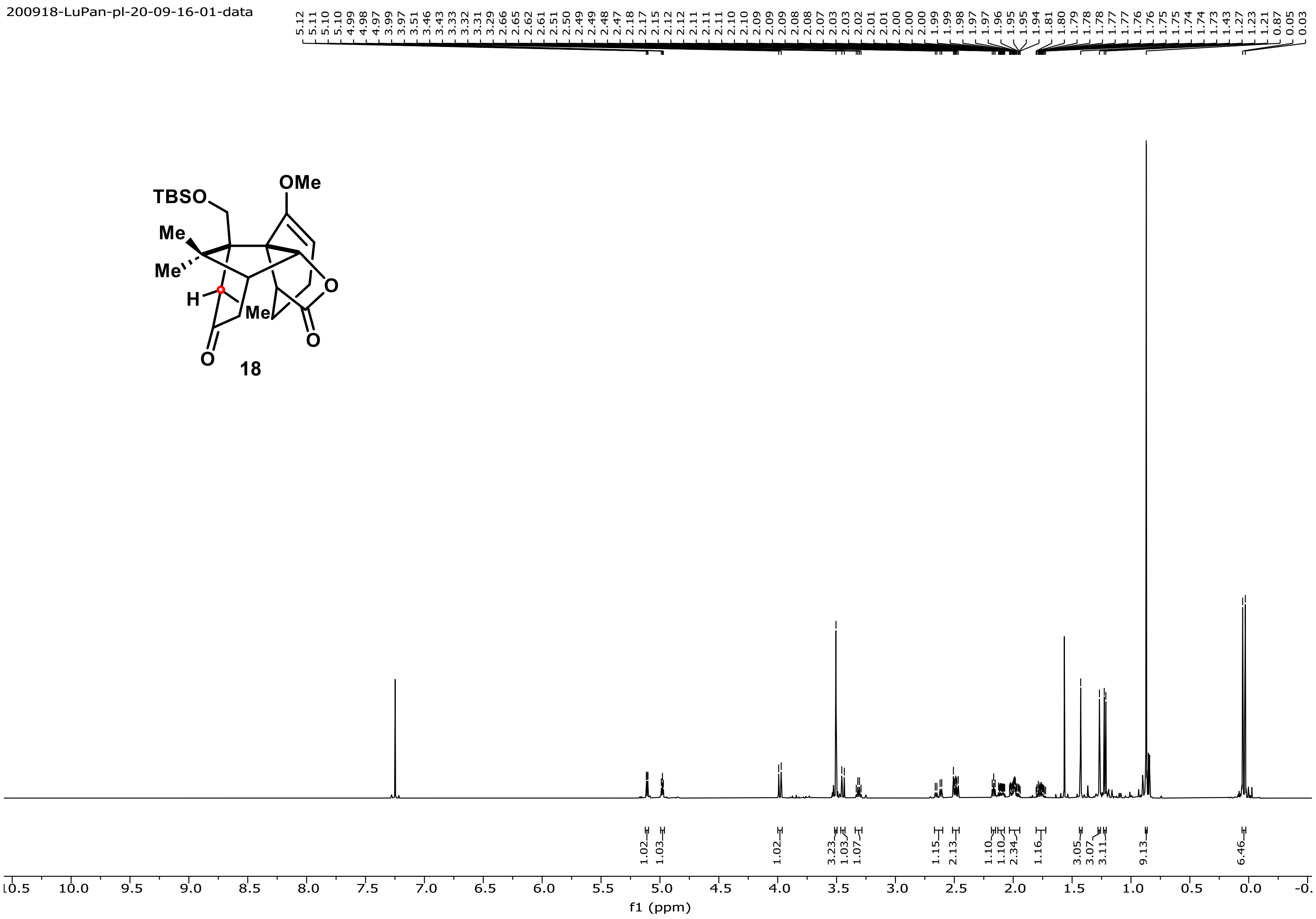
200916-pl-09-15-03-data
single_pulse

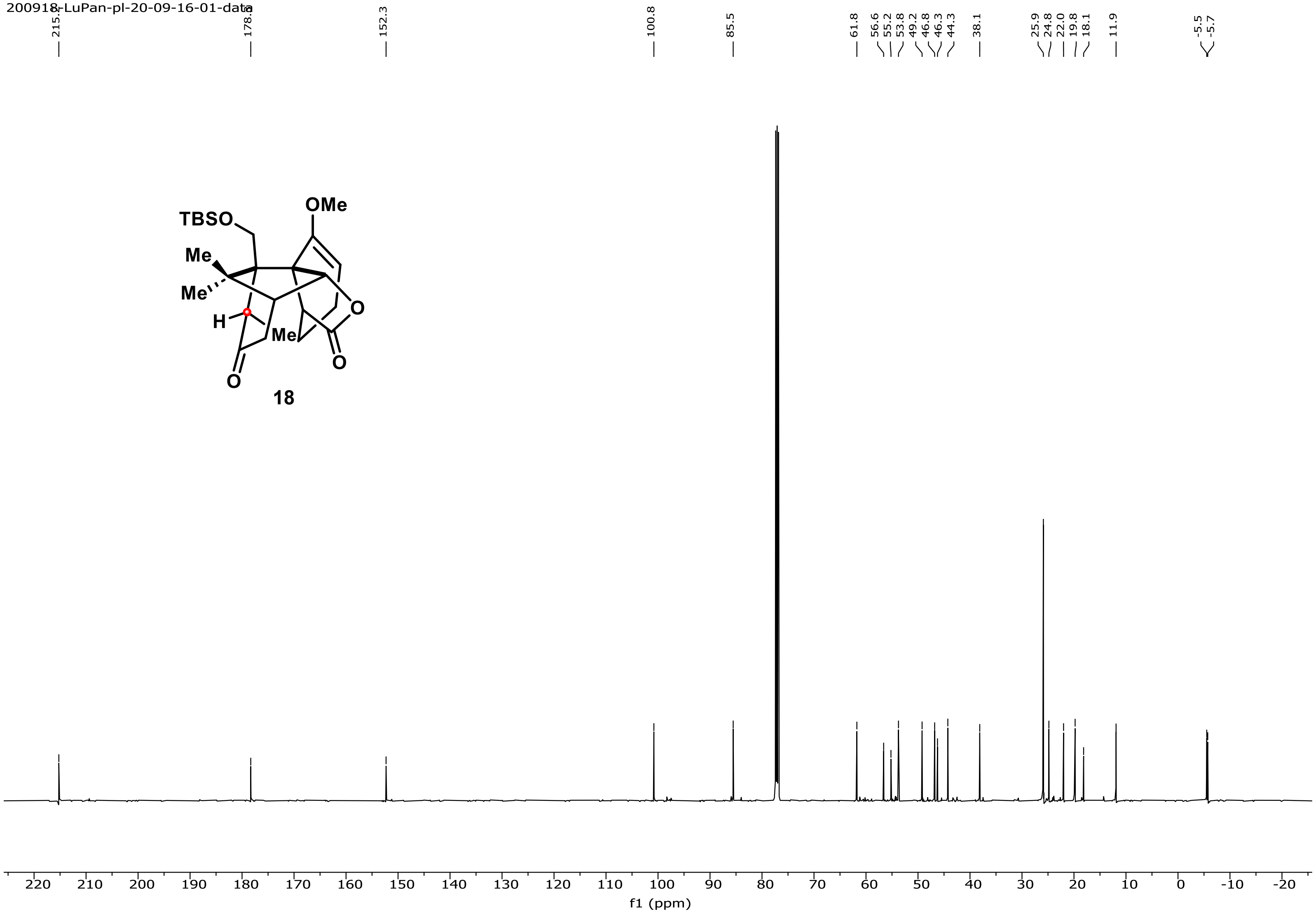


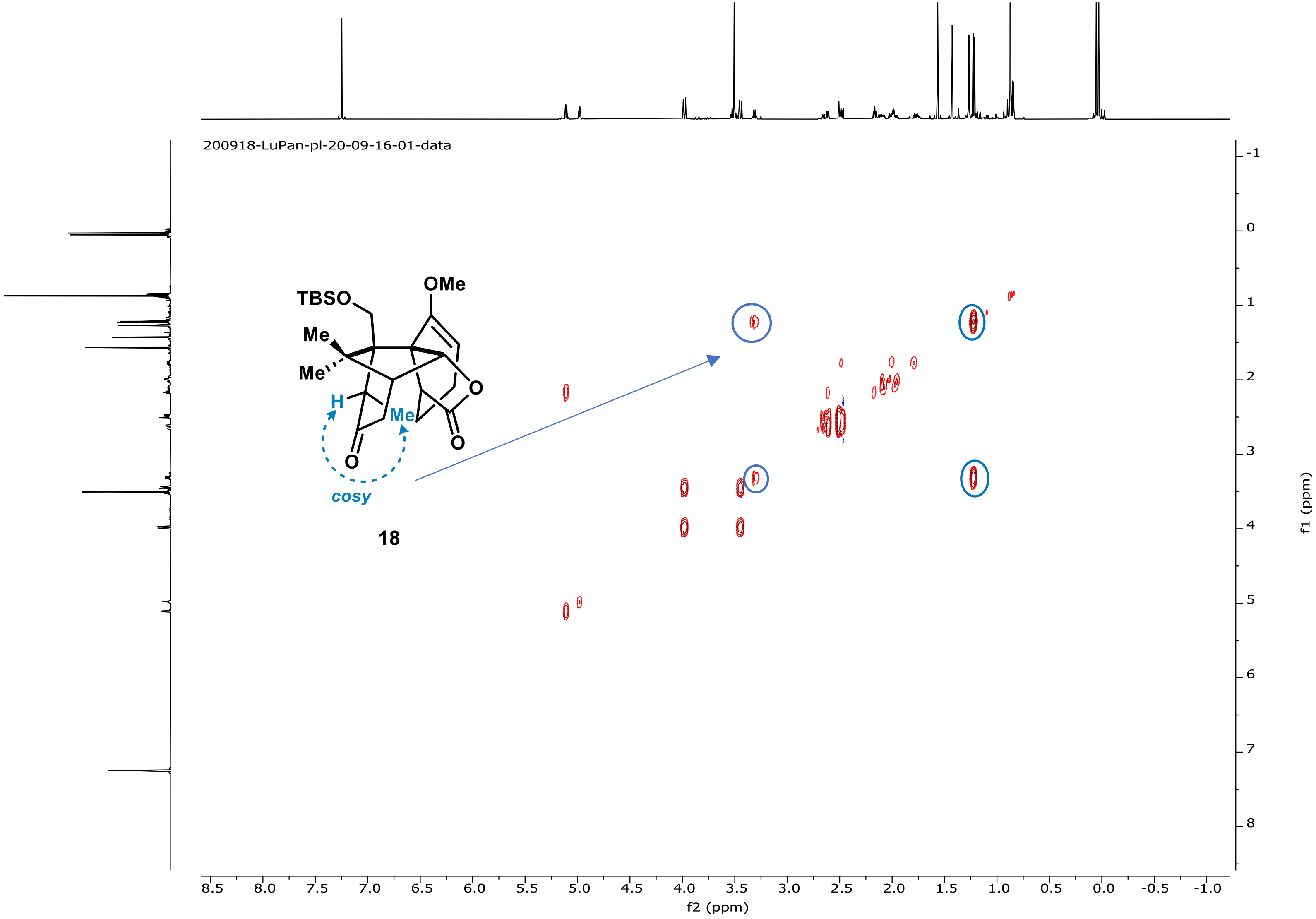
200916-pl-09-15-03-data
single pulse decoupled gated NOE

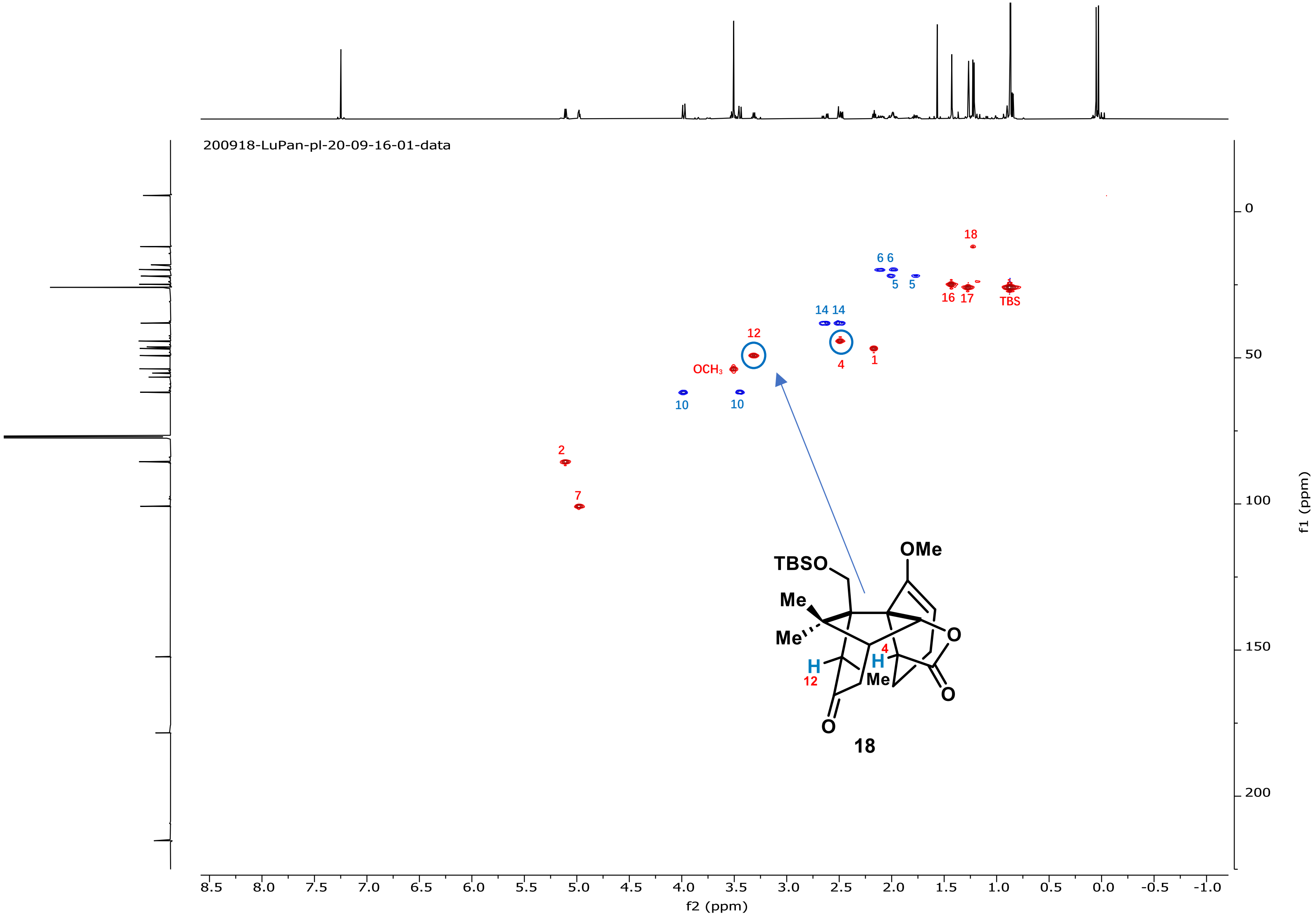


**17**

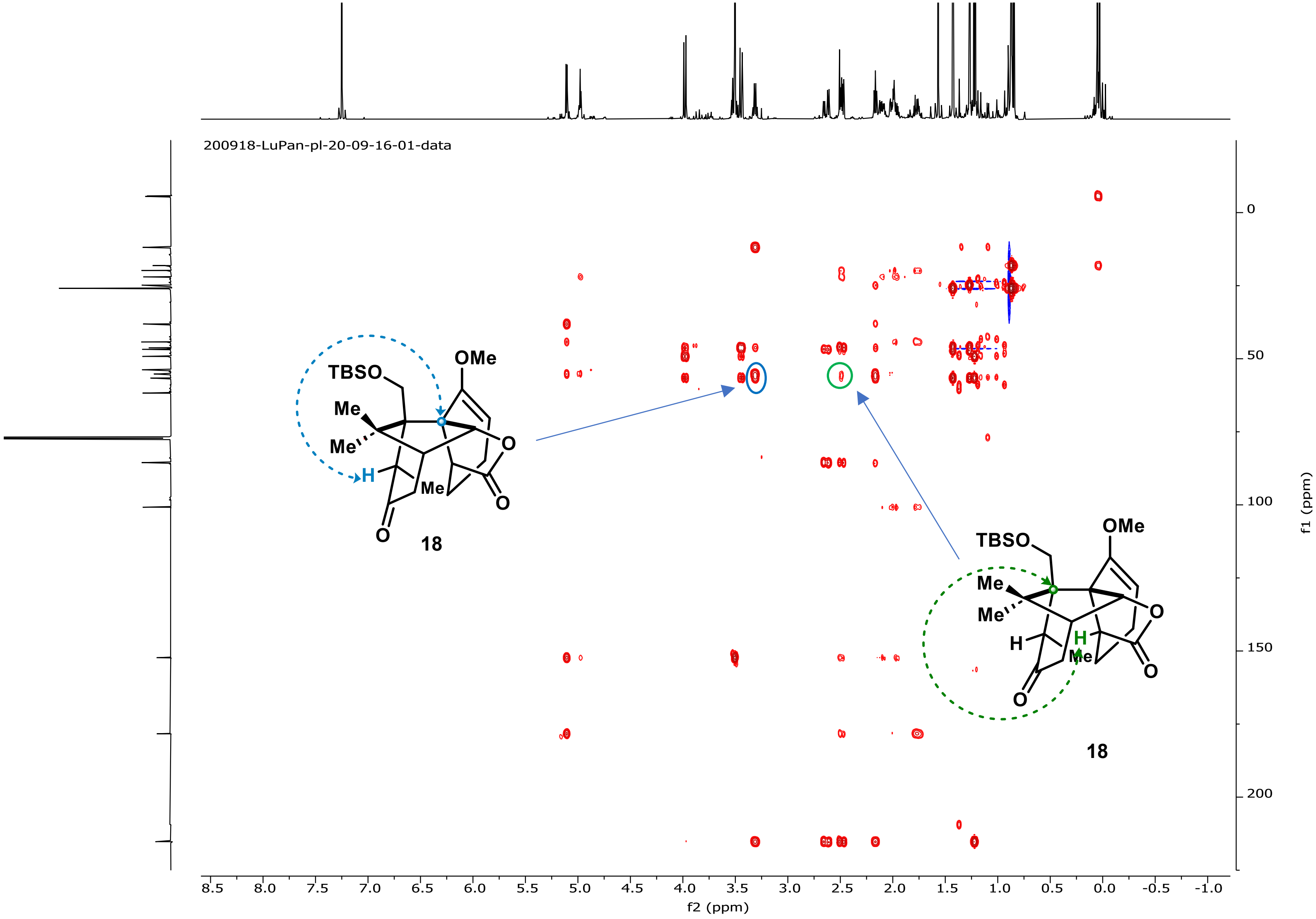

200918-LuPan-pl-20-09-16-01-data
5.12 5.11 5.10 5.10 4.99 4.98 4.97 3.99 3.97 3.51 3.46 3.43 3.33 3.32 3.31 3.29 2.66 2.65 2.62 2.61 2.51 2.50 2.49 2.49 2.48 2.47 2.18 2.17 2.15 2.12 2.12 2.11 2.11 2.11 2.10 2.10 2.09 2.09 2.09 2.08 2.08 2.07 2.03 2.03 2.02 2.01 2.01 2.00 2.00 2.00 1.99 1.99 1.98 1.97 1.97 1.96 1.95 1.95 1.94 1.81 1.80 1.79 1.78 1.78 1.77 1.77 1.76 1.76 1.75 1.75 1.74 1.74 1.73 1.43 1.27 1.23 1.21 0.87 0.05 0.03
TBSO
OMe
Me
Me
H
Me
O
O
O
18
1.02
1.03
1.02
3.23
1.03
1.07
1.15
2.13
1.10
1.10
2.34
1.16
3.05
3.07
3.11
9.13
6.46
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.
f1 (ppm)

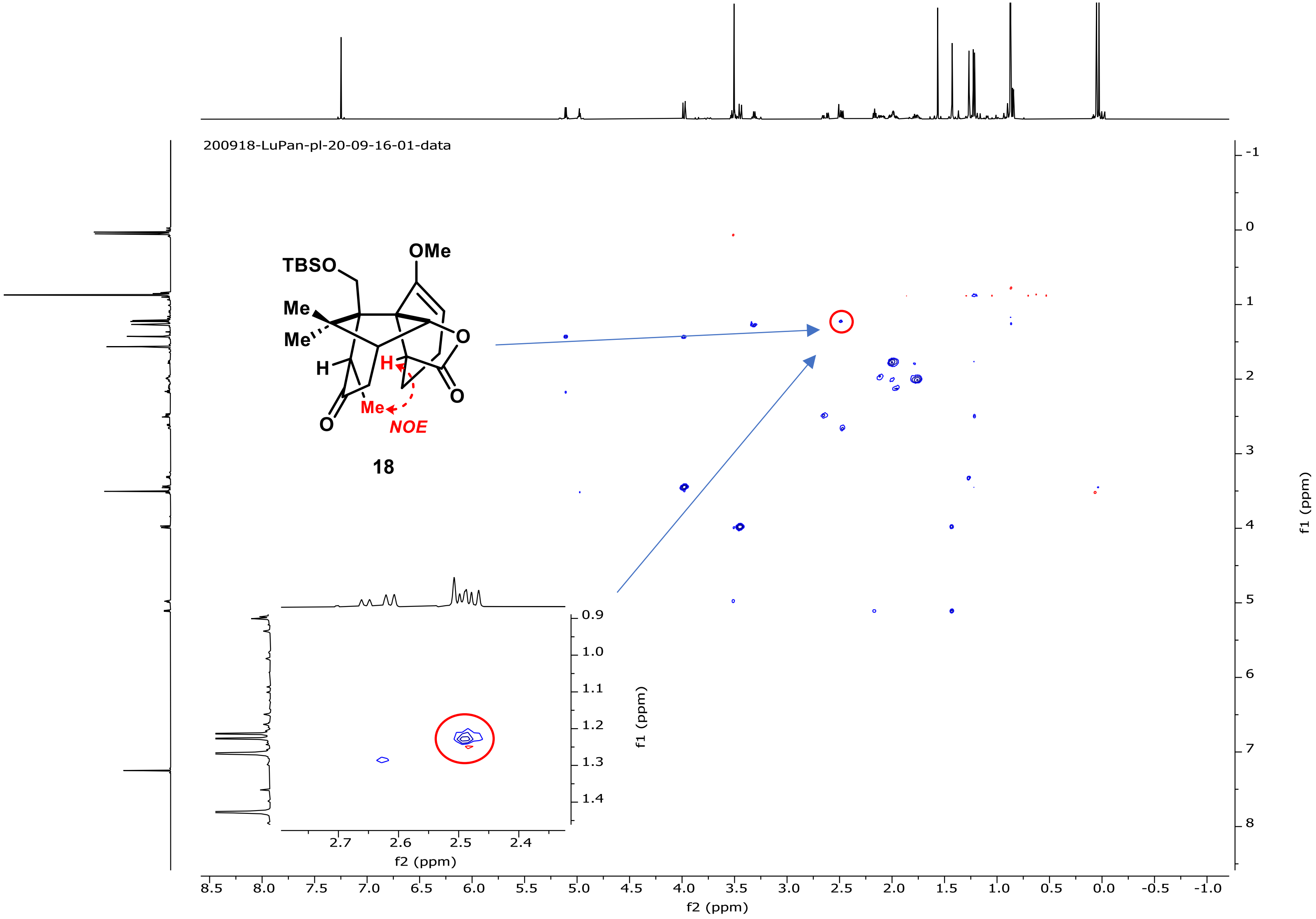

200918-LuPan-pl-20-09-16-01-data
215.
178.
152.3
100.8
85.5
61.8
56.6
55.2
53.8
49.2
46.8
46.3
44.3
38.1
25.9
24.8
22.0
19.8
18.1
11.9
-5.5
-5.7
TBSO
OMe
Me
Me
H
Me
O
O
O
18
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

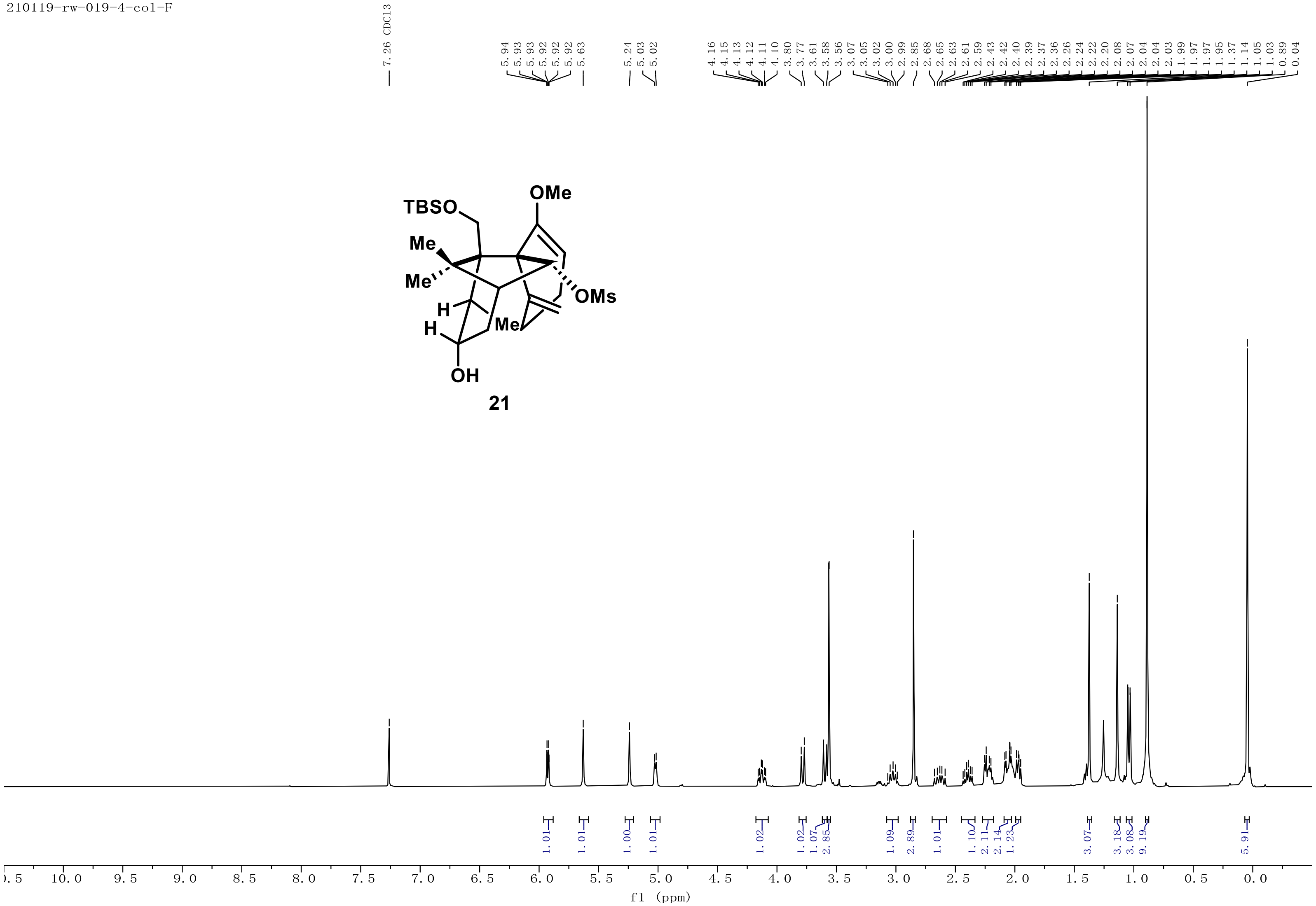

200918-LuPan-pl-20-09-16-01-data
TBSO
OMe
Me
Me
H
Me
O
O
O
cosy
18
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f2 (ppm)
-1
0
1
2
3
4
5
6
7
8
f1 (ppm)



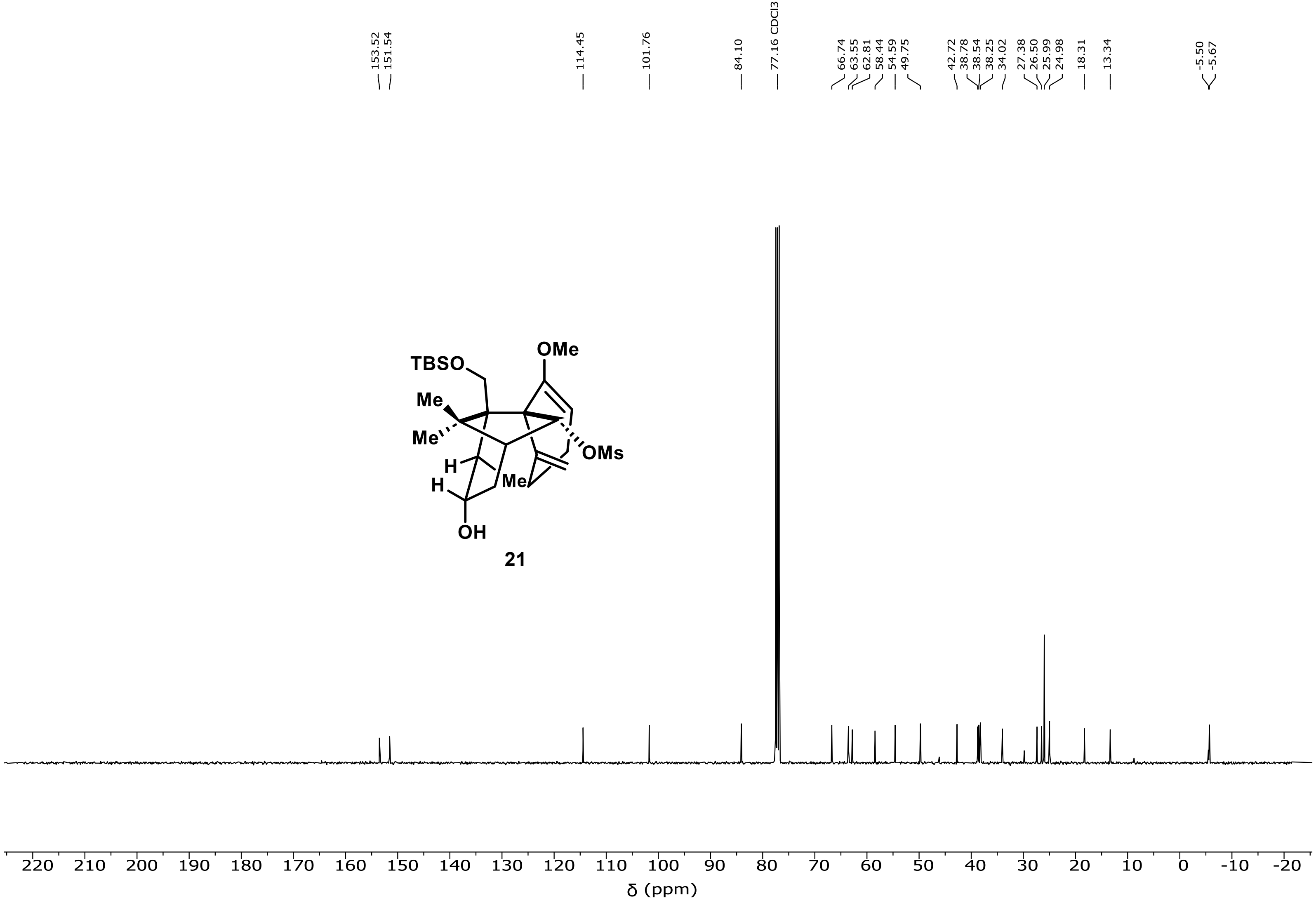
200918-LuPan-pl-20-09-16-01-data
18
6 6
5 5
16 17
TBS
14 14
12
4
1
OCH₃
10 10
2
7
TBSO
OMe
Me
Me
O
O
H
H
12
4
Me
O
18
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f2 (ppm)
0 50 100 150 200
f1 (ppm)

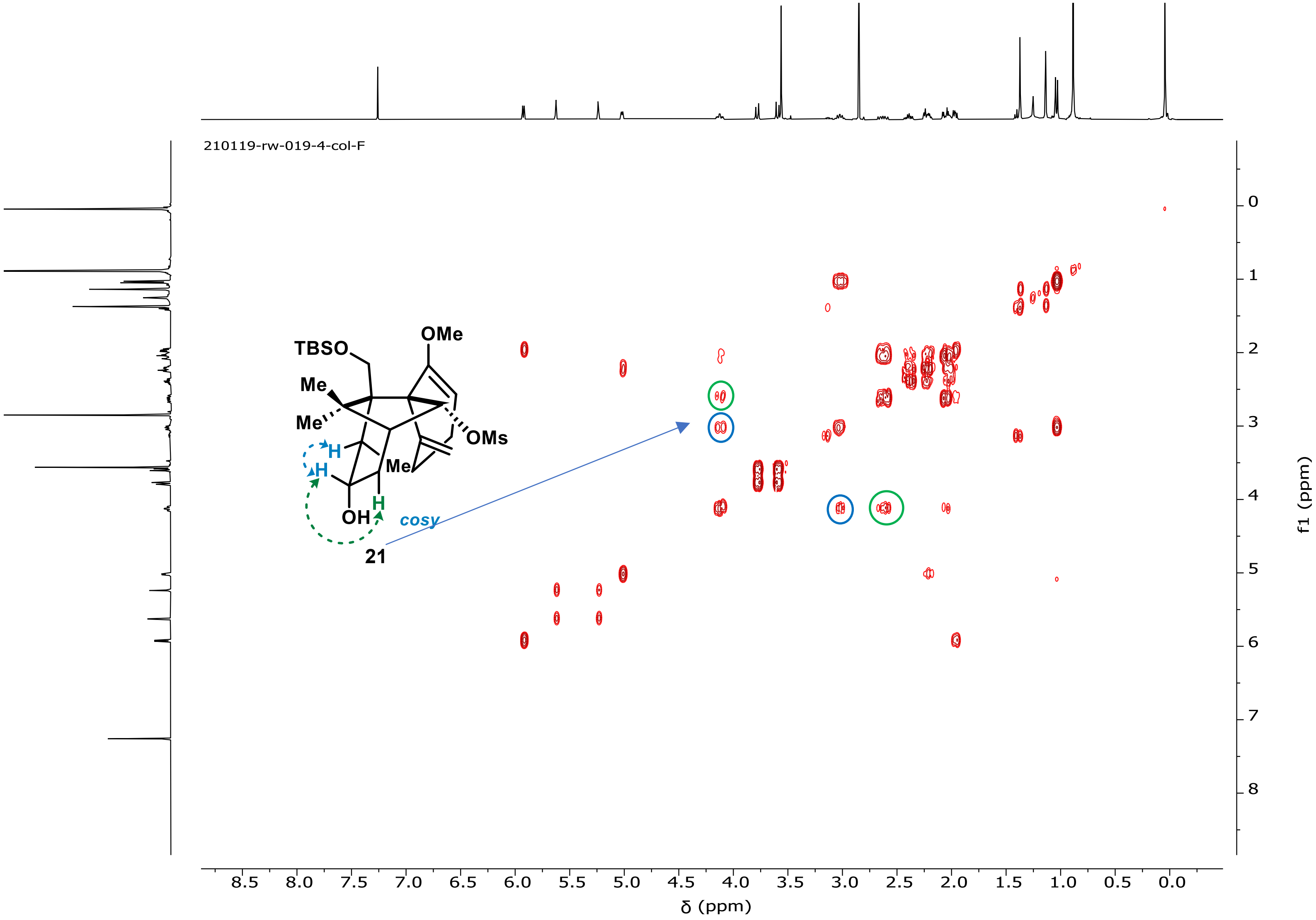

200918-LuPan-pl-20-09-16-01-data
TBSO
OMe
Me
Me
H
Me
O
O
O
18
TBSO
OMe
Me
Me
H
H
Me
O
O
O
18
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f2 (ppm)
0
50
100
150
200
f1 (ppm)

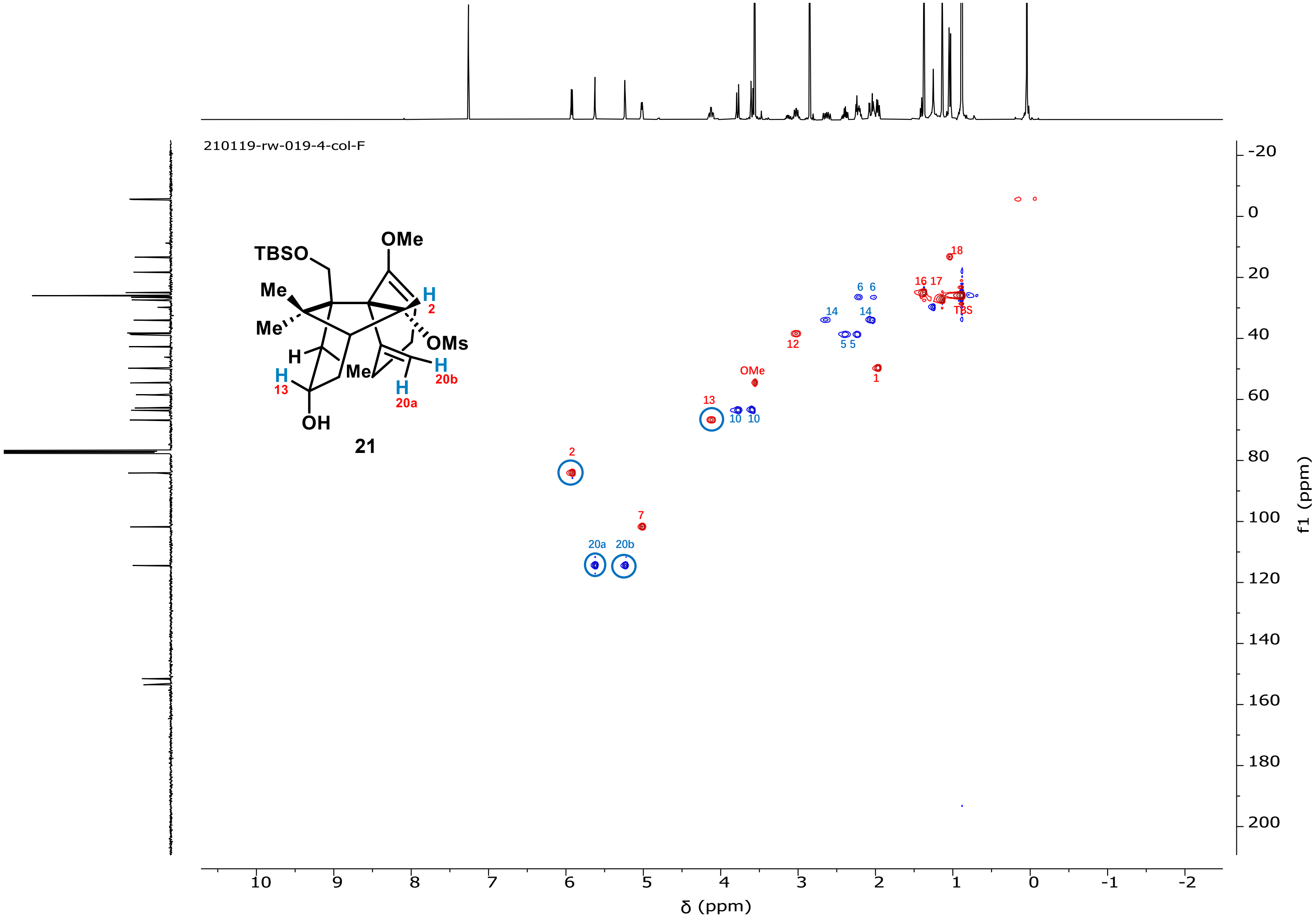

200918-LuPan-pl-20-09-16-01-data
TBSO
OMe
Me
Me
H
O
H
Me
O
O
NOE
18
0.9
1.0
1.1
1.2
1.3
1.4
2.7
2.6
2.5
2.4
f2 (ppm)
f1 (ppm)
-1
0
1
2
3
4
5
6
7
8
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f2 (ppm)
f1 (ppm)

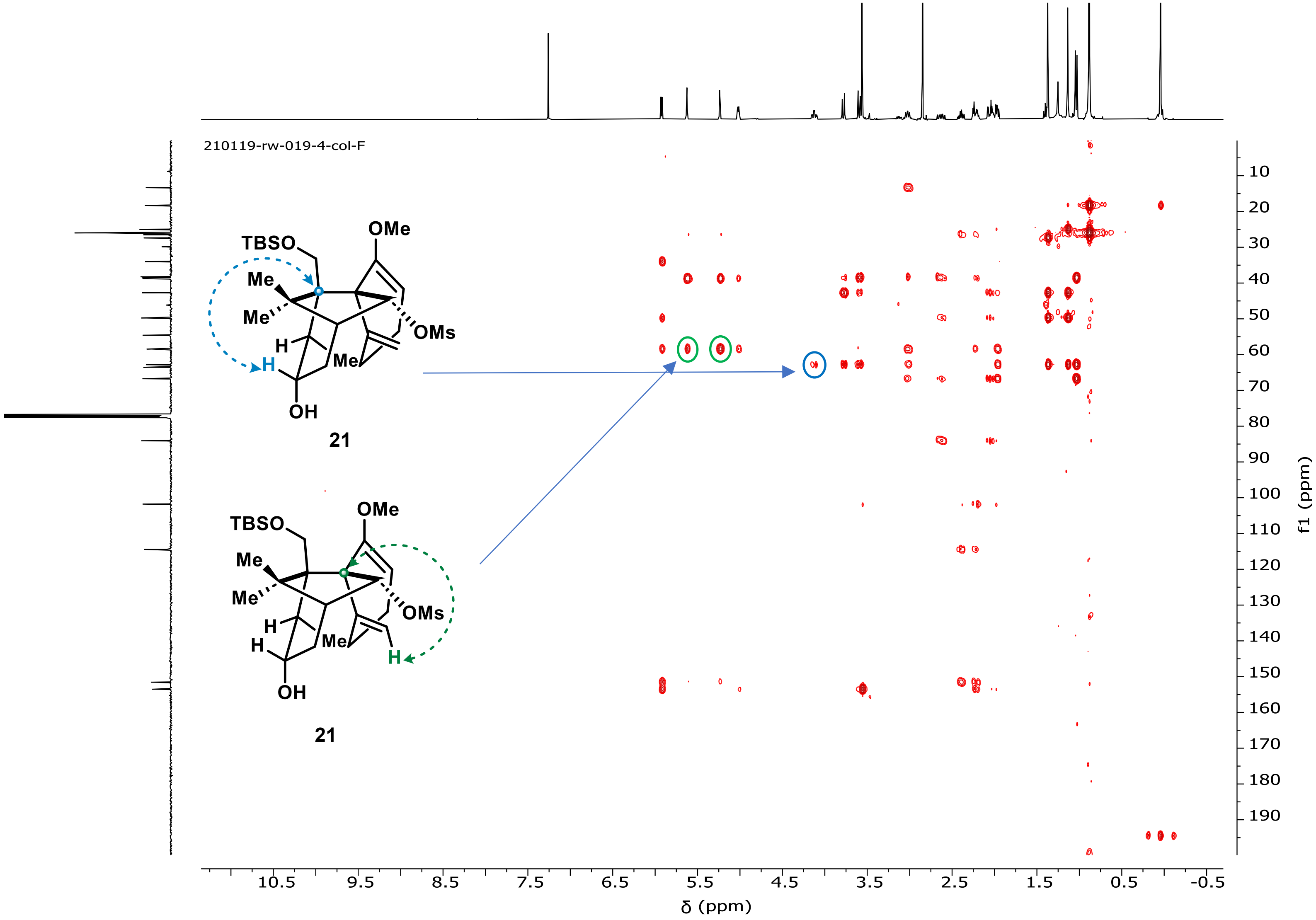

210119-rw-019-4-col-F
7.26 CDCl3
5.94
5.93
5.93
5.92
5.92
5.92
5.63
5.24
5.03
5.02
4.16
4.15
4.13
4.12
4.11
4.10
3.80
3.77
3.61
3.58
3.56
3.07
3.05
3.02
3.00
2.99
2.85
2.68
2.65
2.63
2.61
2.59
2.43
2.42
2.40
2.39
2.37
2.36
2.26
2.24
2.22
2.20
2.08
2.07
2.04
2.04
2.03
1.99
1.97
1.95
1.37
1.14
1.05
1.03
0.89
0.04
TBSO
OMe
Me
Me
H
H
OMs
Me
OH
21
1.01
1.01
1.00
1.01
1.02
1.02
1.07
2.85
1.09
2.89
1.01
1.10
2.11
2.14
1.23
3.07
3.18
3.08
9.19
5.91
).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
f1 (ppm)

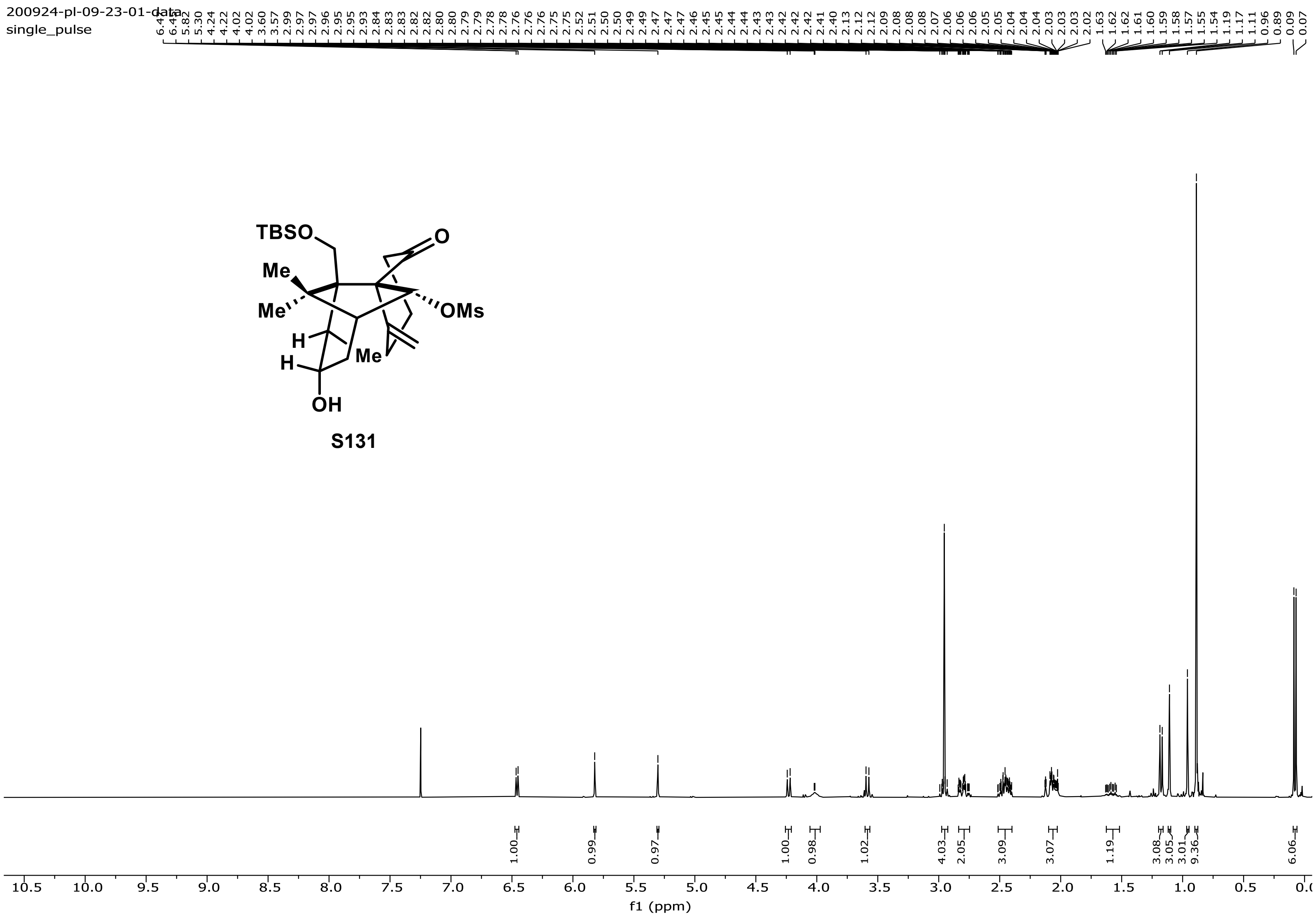
210119-rw-019-4-col-F



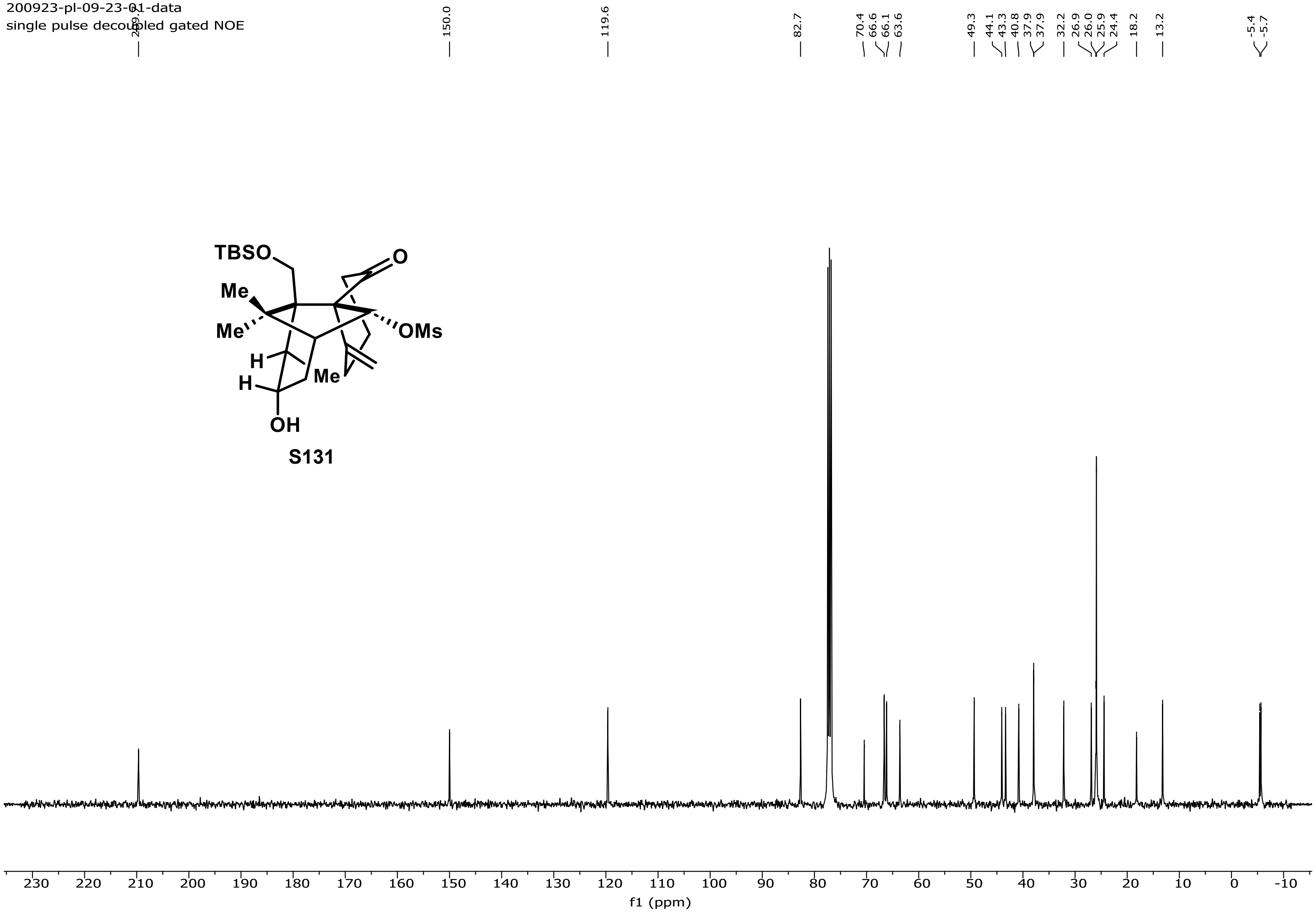

210119-rw-019-4-col-F
TBSO
OMe
Me
Me
OMs
H
H
Me
OH
H
cosy
21
δ (ppm)
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
1
2
3
4
5
6
7
8


210119-rw-019-4-col-F
TBSO
OMe
Me
Me
H
2
OMs
H
H
13
OH
Me
H
20b
H
20a
21
18
16 17
TBS
6 6
14
14
12
5 5
OMe
1
13
10 10
2
7
20a 20b
δ (ppm)
f1 (ppm)
10 9 8 7 6 5 4 3 2 1 0 -1 -2
-20 0 20 40 60 80 100 120 140 160 180 200

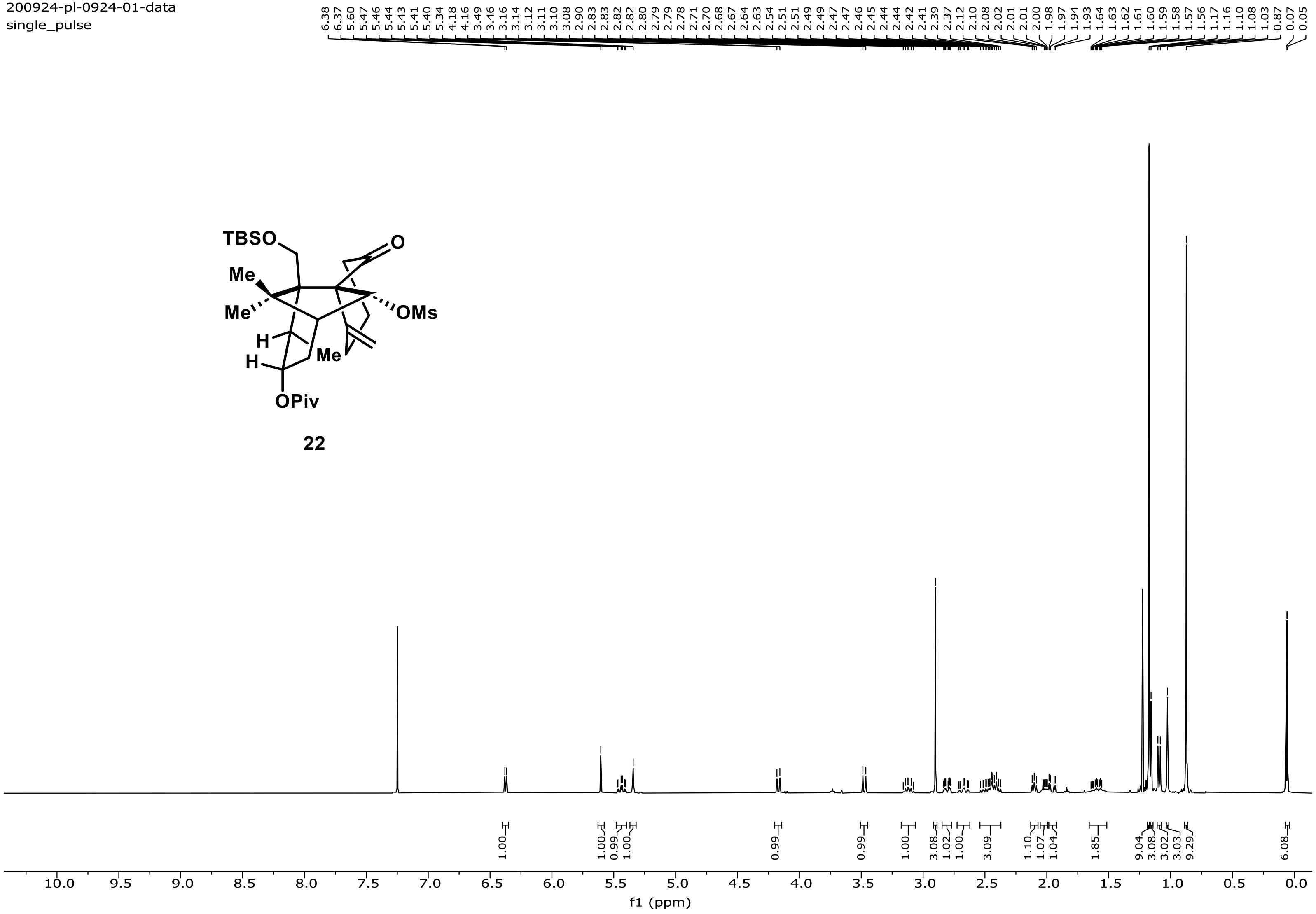

210119-rw-019-4-col-F
TBSO
OMe
Me
Me
OMs
H
H
Me
OH
21
TBSO
OMe
Me
Me
OMs
H
H
Me
H
OH
21
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
δ (ppm)
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
f1 (ppm)


200924-pl-09-23-01-data
single_pulse
6.4 6.45 5.82 5.30 4.24 4.22 4.02 4.02 3.60 3.57 2.99 2.97 2.97 2.96 2.95 2.95 2.93 2.84 2.83 2.83 2.82 2.82 2.80 2.80 2.79 2.79 2.78 2.78 2.76 2.76 2.76 2.75 2.75 2.52 2.51 2.50 2.50 2.49 2.49 2.47 2.47 2.47 2.46 2.45 2.45 2.44 2.44 2.43 2.43 2.42 2.42 2.42 2.41 2.40 2.13 2.12 2.12 2.09 2.08 2.08 2.08 2.07 2.06 2.06 2.06 2.05 2.05 2.04 2.04 2.04 2.03 2.03 2.03 2.02 1.63 1.62 1.62 1.61 1.60 1.59 1.58 1.57 1.55 1.54 1.19 1.17 1.11 0.96 0.89 0.09 0.07
TBSO
O
Me
Me
OMs
H
H
Me
OH
1.00
0.99
0.97
1.00
0.98
1.02
4.03
2.05
3.09
3.07
1.19
3.08
3.05
3.01
9.36
6.06
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
f1 (ppm)

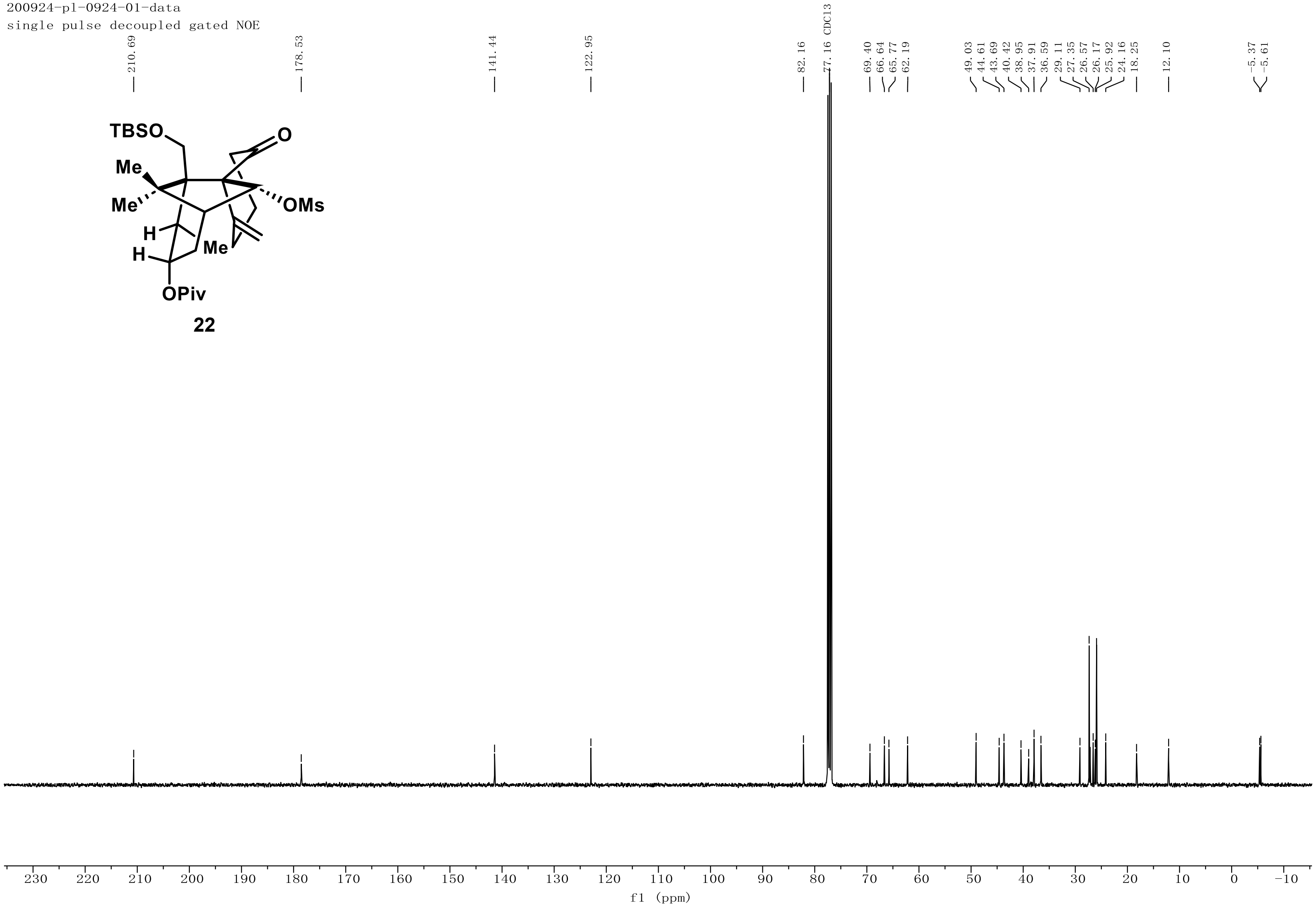
**S131**

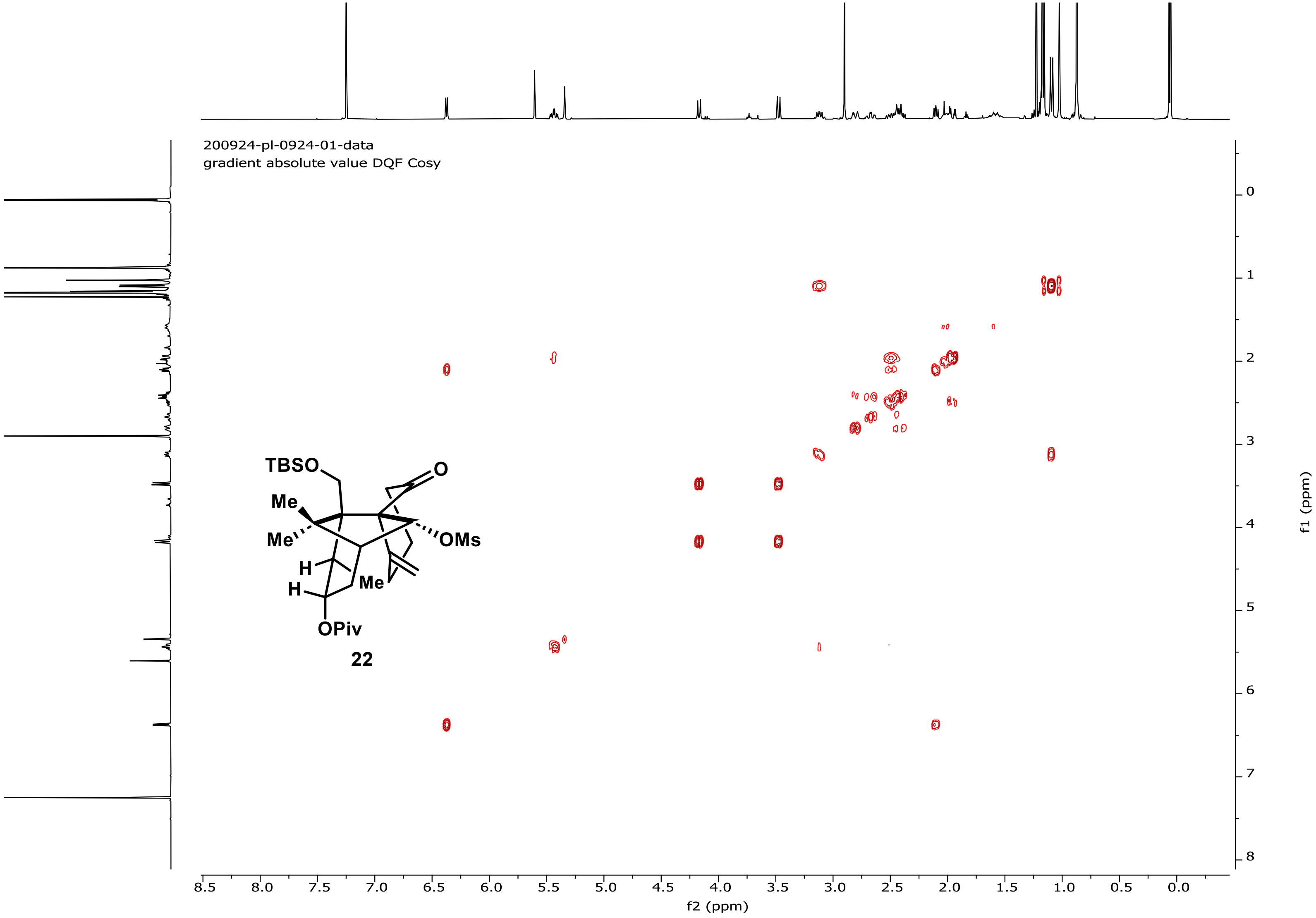

200923-pl-09-23-01-data
single pulse decoupled gated NOE
209.7
150.0
119.6
82.7
70.4
66.6
66.1
63.6
49.3
44.1
43.3
40.8
37.9
37.9
32.2
26.9
26.0
25.9
24.4
18.2
13.2
-5.4
-5.7
TBSO
O
Me
Me
OMs
H
H
Me
OH
S131
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

200924-pl-0924-01-data
single_pulse



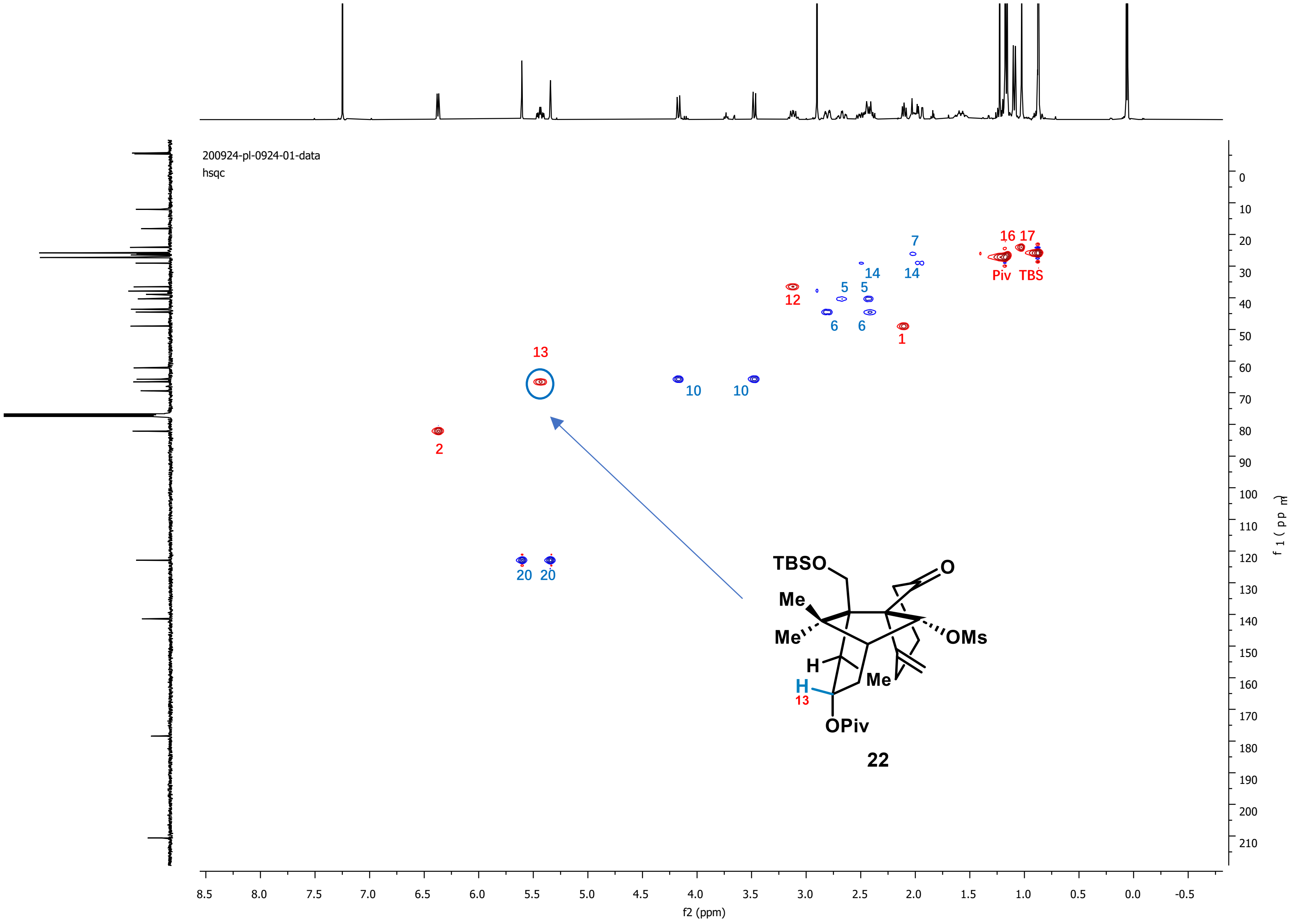
**22**

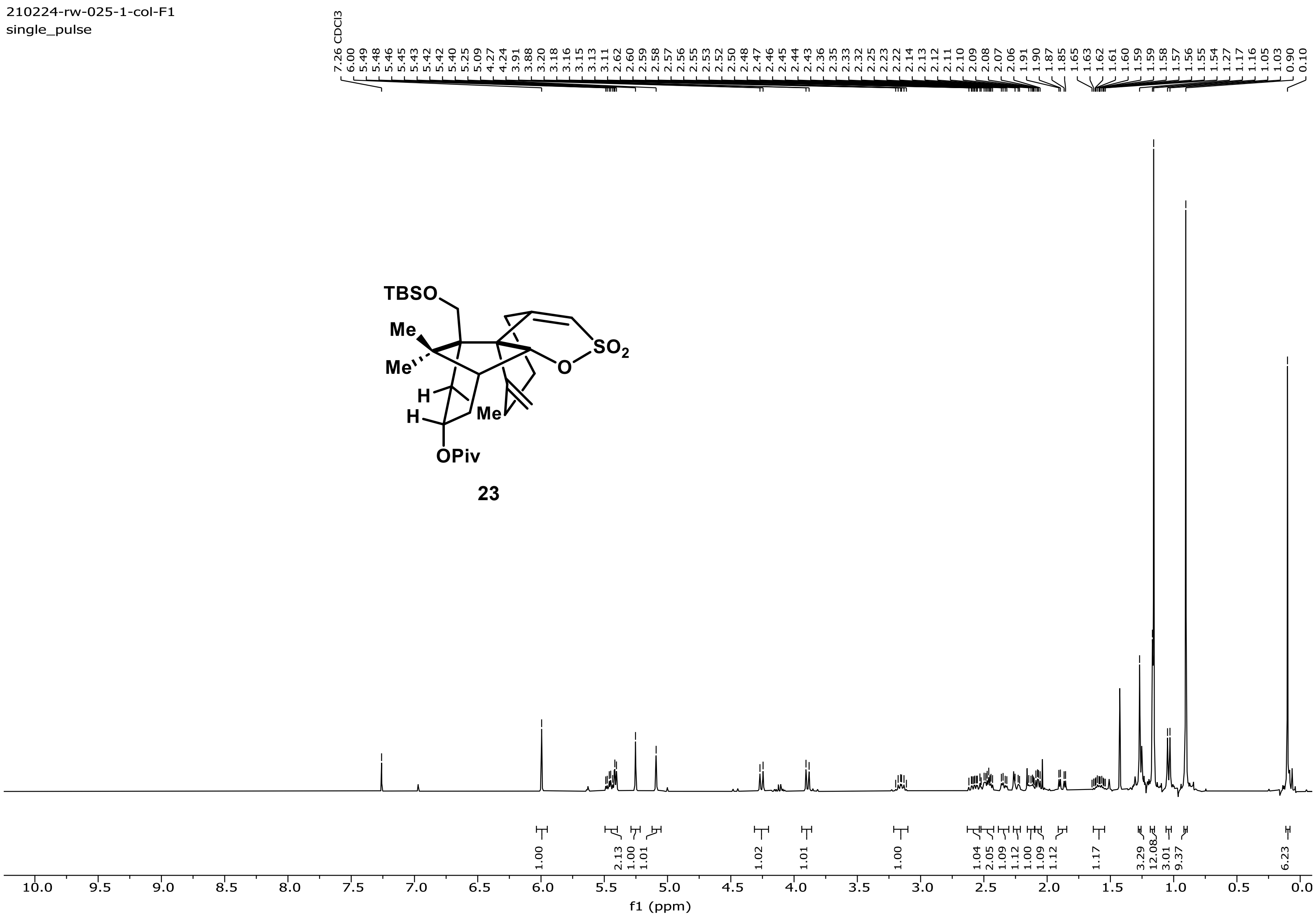

200924-p1-0924-01-data
single pulse decoupled gated NOE
210.69
178.53
141.44
122.95
82.16
77.16 CDCl3
69.40
66.64
65.77
62.19
49.03
44.61
43.69
40.42
38.95
37.91
36.59
29.11
27.35
26.57
26.17
25.92
24.16
18.25
12.10
-5.37
-5.61
TBSO
O
Me
Me
OMs
H
H
Me
OPiv
22
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



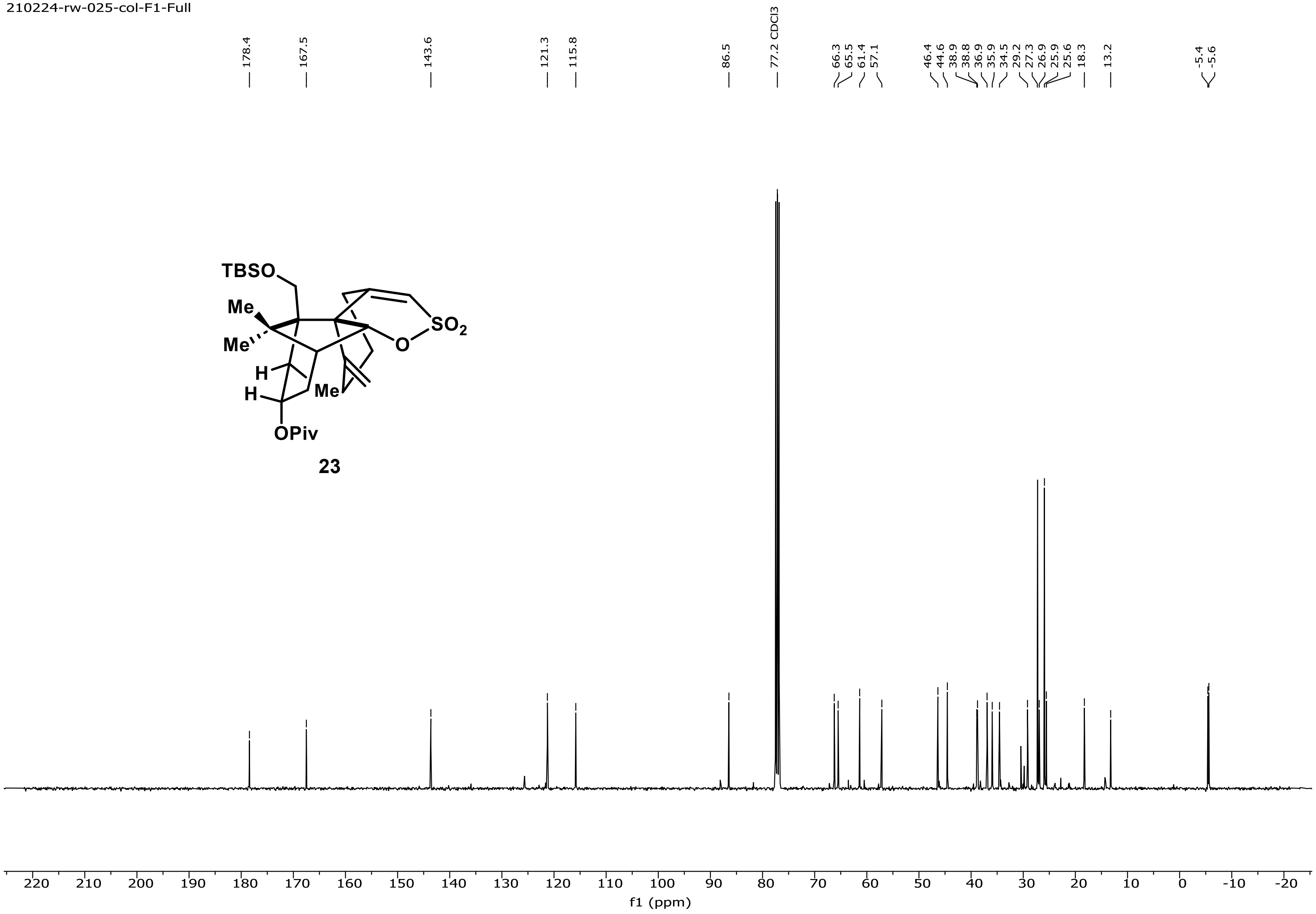
200924-pl-0924-01-data
gradient absolute value DQF Cosy
TBSO
O
Me
Me
OMs
H
H
Me
OPiv
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0
1
2
3
4
5
6
7
8
f1 (ppm)

**22**

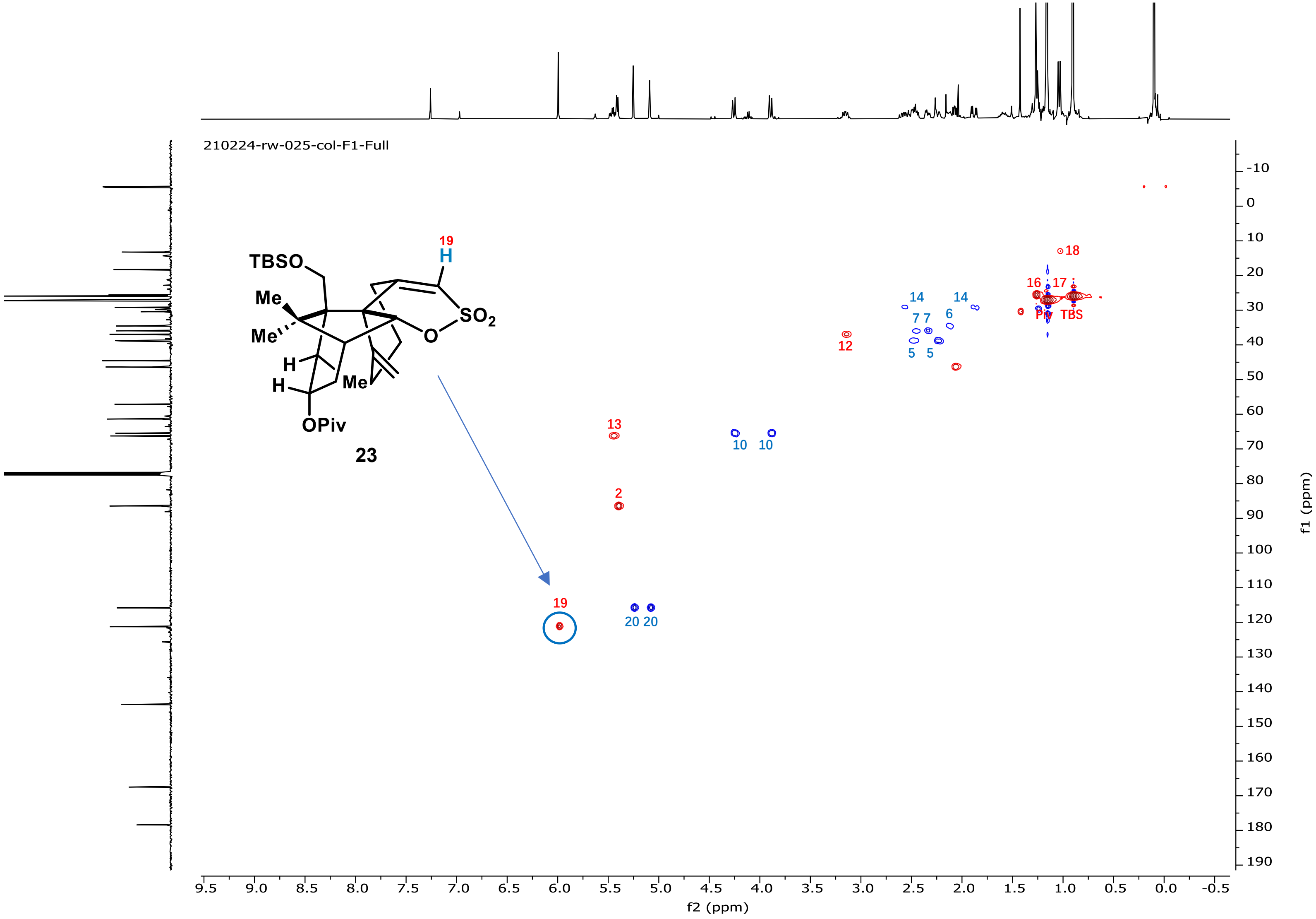

200924-pl-0924-01-data
hsqc
13
10
10
2
12
5
5
6
6
1
7
14
14
16
17
Piv
TBS
20
20
f2 (ppm)
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
TBSO
O
Me
Me
OMs
H
H
13
Me
OPiv
22

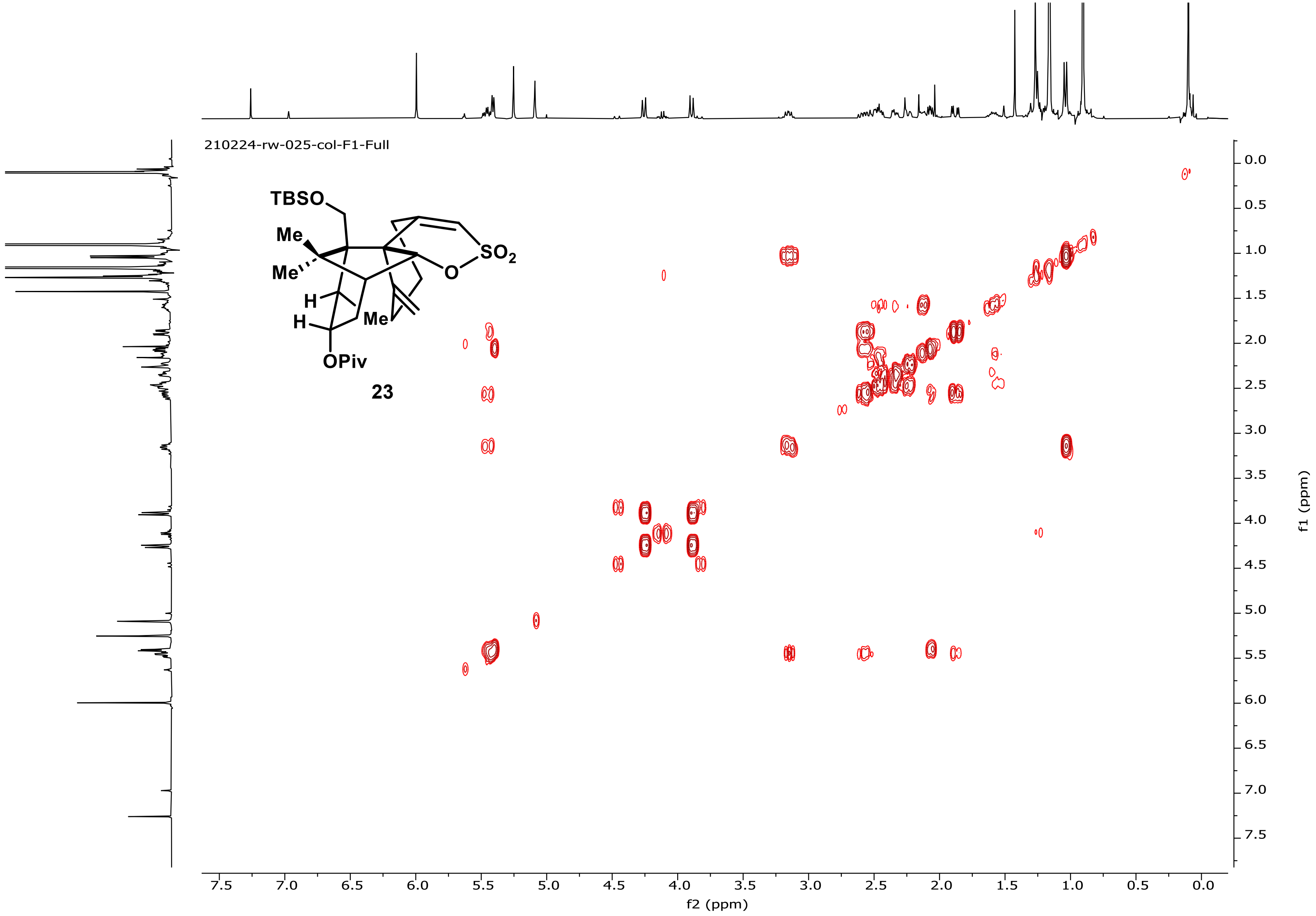

210224-rw-025-1-col-F1
single_pulse
7.26 CDCl3
6.00
5.49
5.48
5.46
5.45
5.43
5.42
5.42
5.40
5.25
5.09
4.27
4.24
3.91
3.88
3.20
3.18
3.16
3.15
3.13
3.11
2.62
2.60
2.59
2.58
2.57
2.56
2.55
2.53
2.52
2.50
2.48
2.47
2.46
2.45
2.44
2.43
2.36
2.35
2.33
2.32
2.25
2.23
2.22
2.14
2.13
2.12
2.11
2.10
2.09
2.08
2.07
2.06
1.91
1.90
1.87
1.85
1.65
1.63
1.62
1.61
1.60
1.59
1.59
1.58
1.57
1.56
1.55
1.54
1.27
1.17
1.16
1.05
1.03
0.90
0.10
TBSO
Me
Me
H
H
Me
SO2
O
OPiv
23
1.00
2.13
1.00
1.01
1.02
1.01
1.00
1.04
2.05
1.09
1.12
1.00
1.09
1.12
1.17
3.29
12.08
3.01
9.37
6.23
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
f1 (ppm)

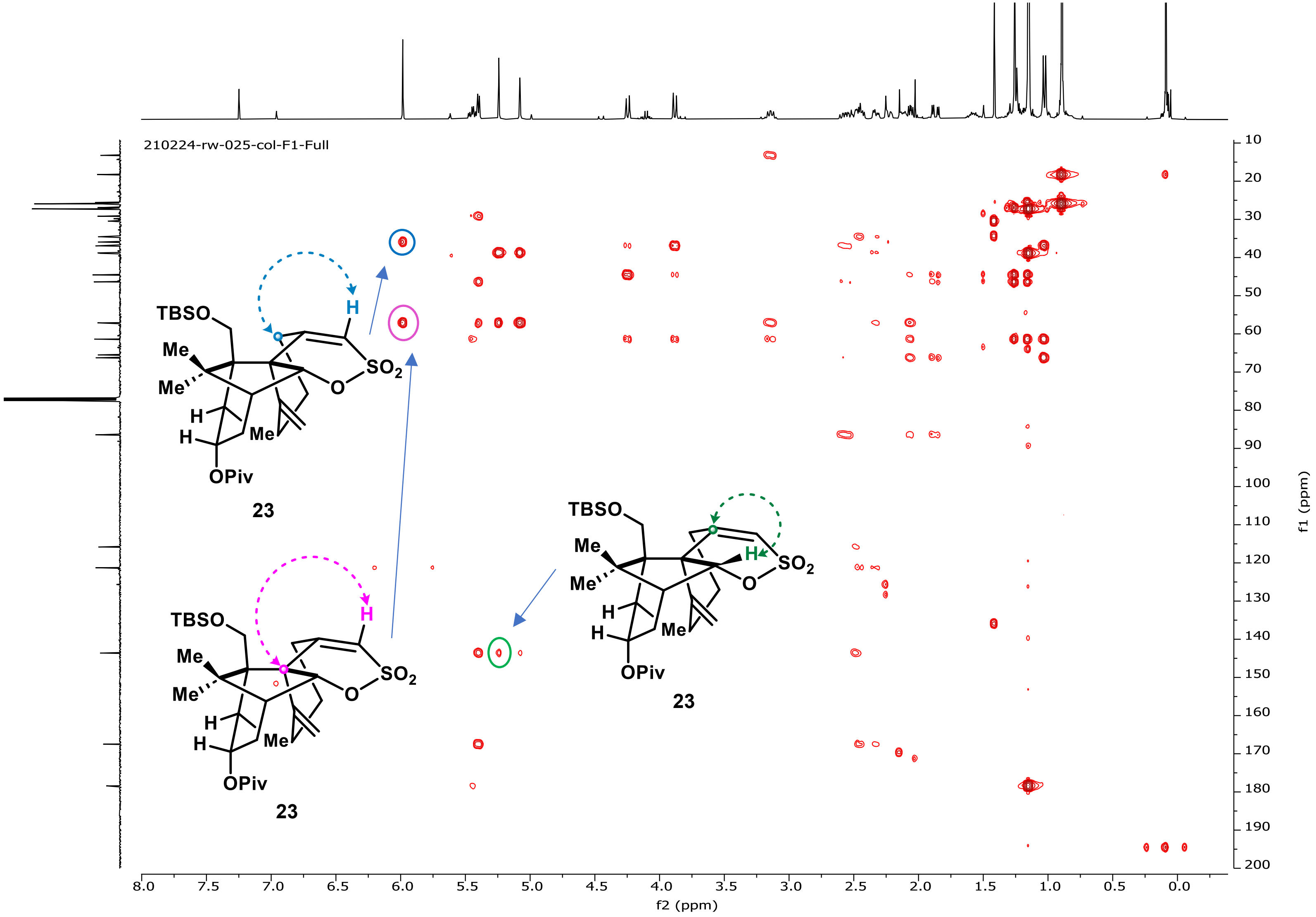
210224-rw-025-col-F1-Full



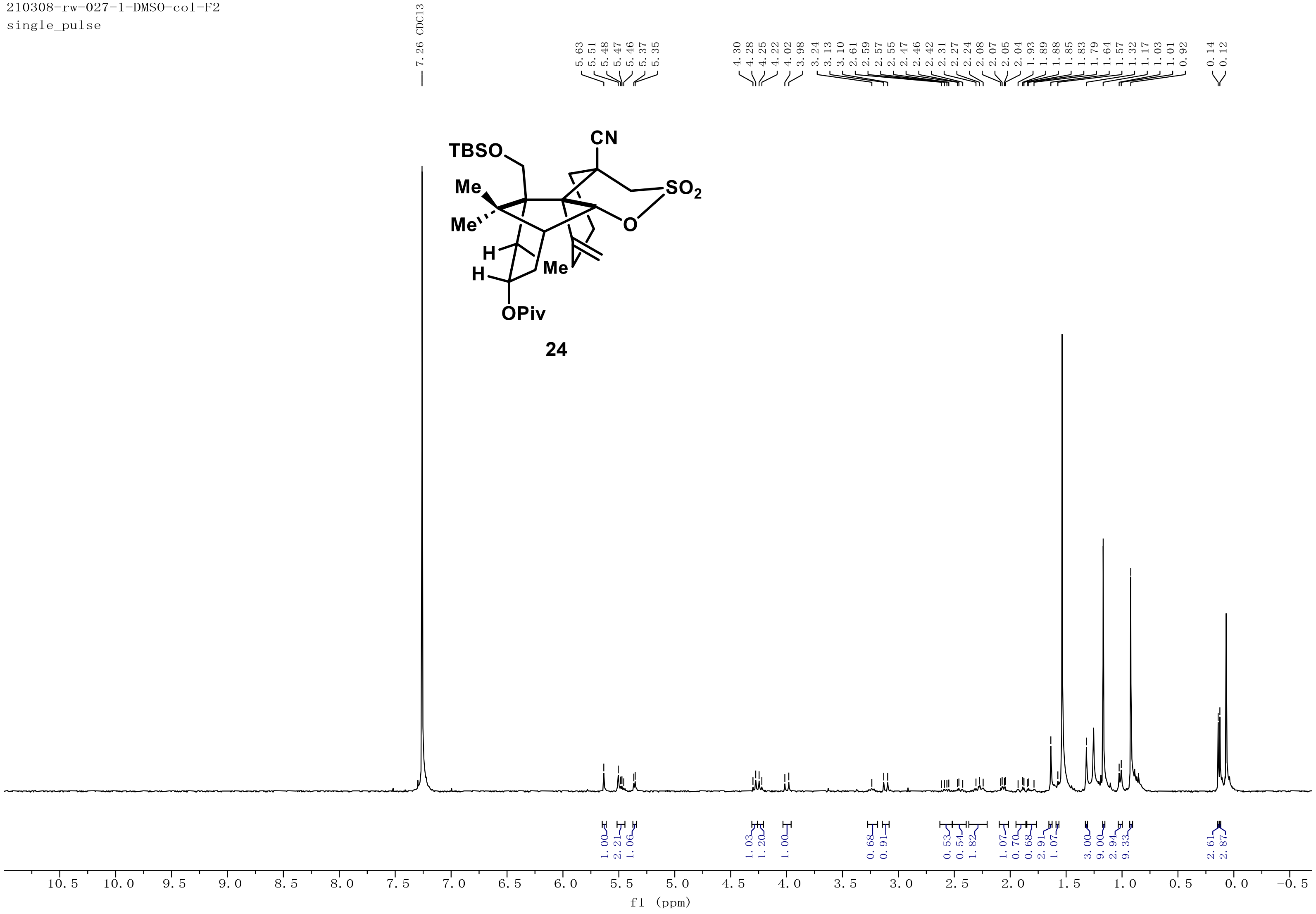
**23**


210224-rw-025-col-F1-Full
TBSO
Me
Me
H
H
OPiv
Me
19
H
SO2
O
23
13
2
19
10 10
20 20
12
14 14
7 7
6
5 5
18
16 17
Piv TBS
f2 (ppm)
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
f1 (ppm)
-10 0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190

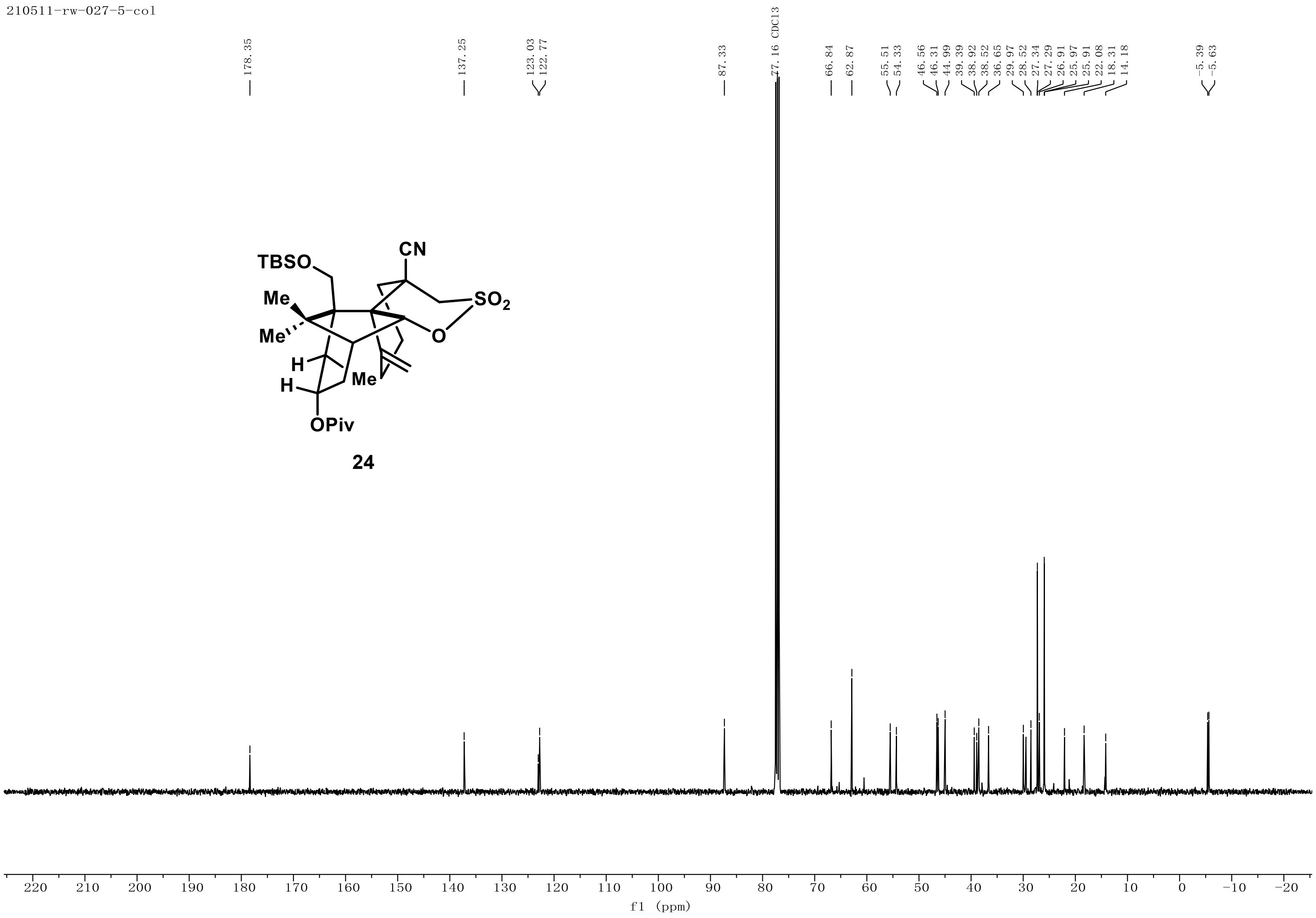

210224-rw-025-col-F1-Full
TBSO
Me
Me
SO2
O
H
H
Me
OPiv
23
f2 (ppm)
f1 (ppm)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

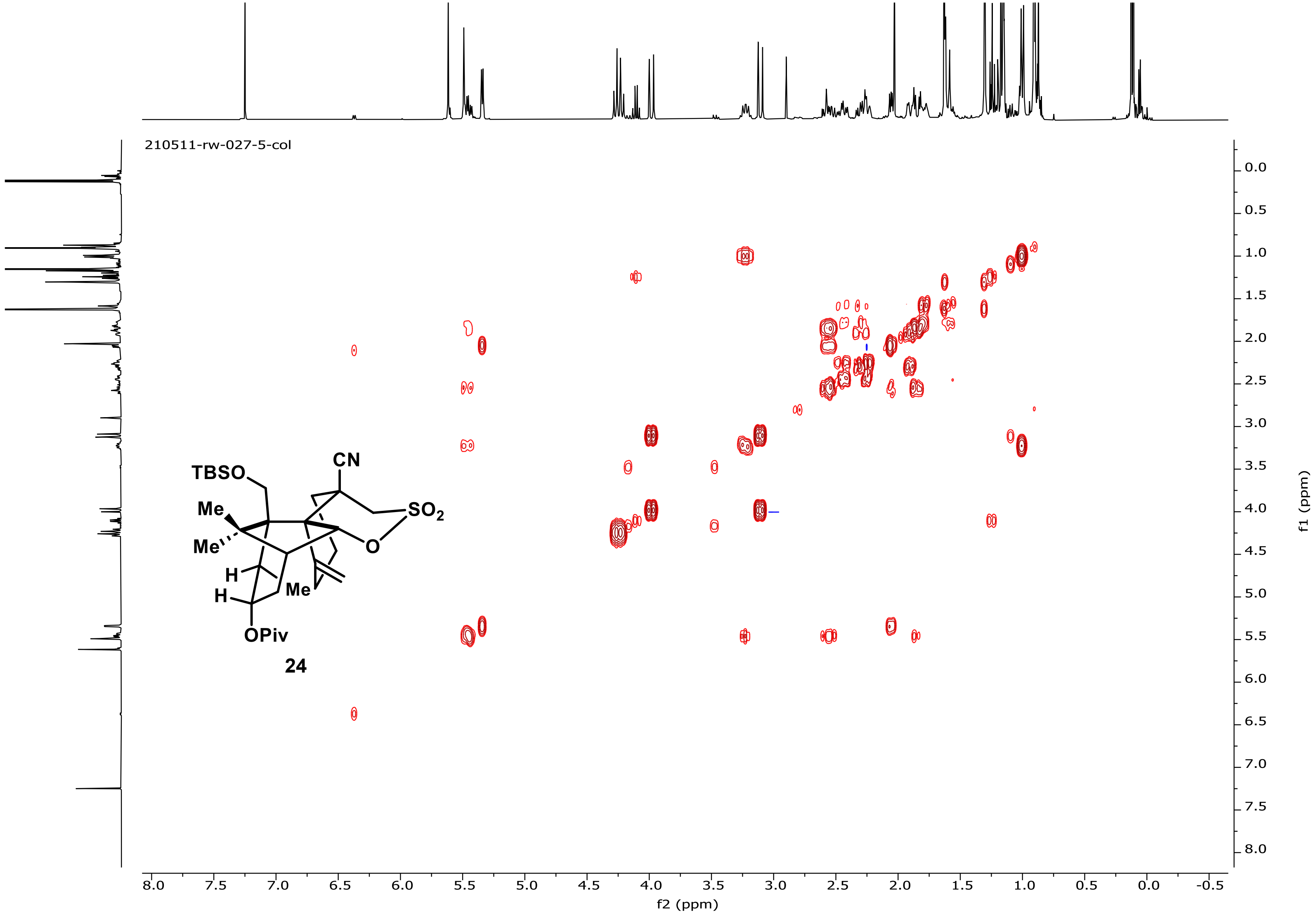

210224-rw-025-col-F1-Full
TBSO
Me
Me
H
H
SO2
O
Me
OPiv
23
TBSO
Me
Me
H
H
SO2
O
Me
OPiv
23
TBSO
Me
Me
H
H
SO2
O
Me
OPiv
23
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
f1 (ppm)

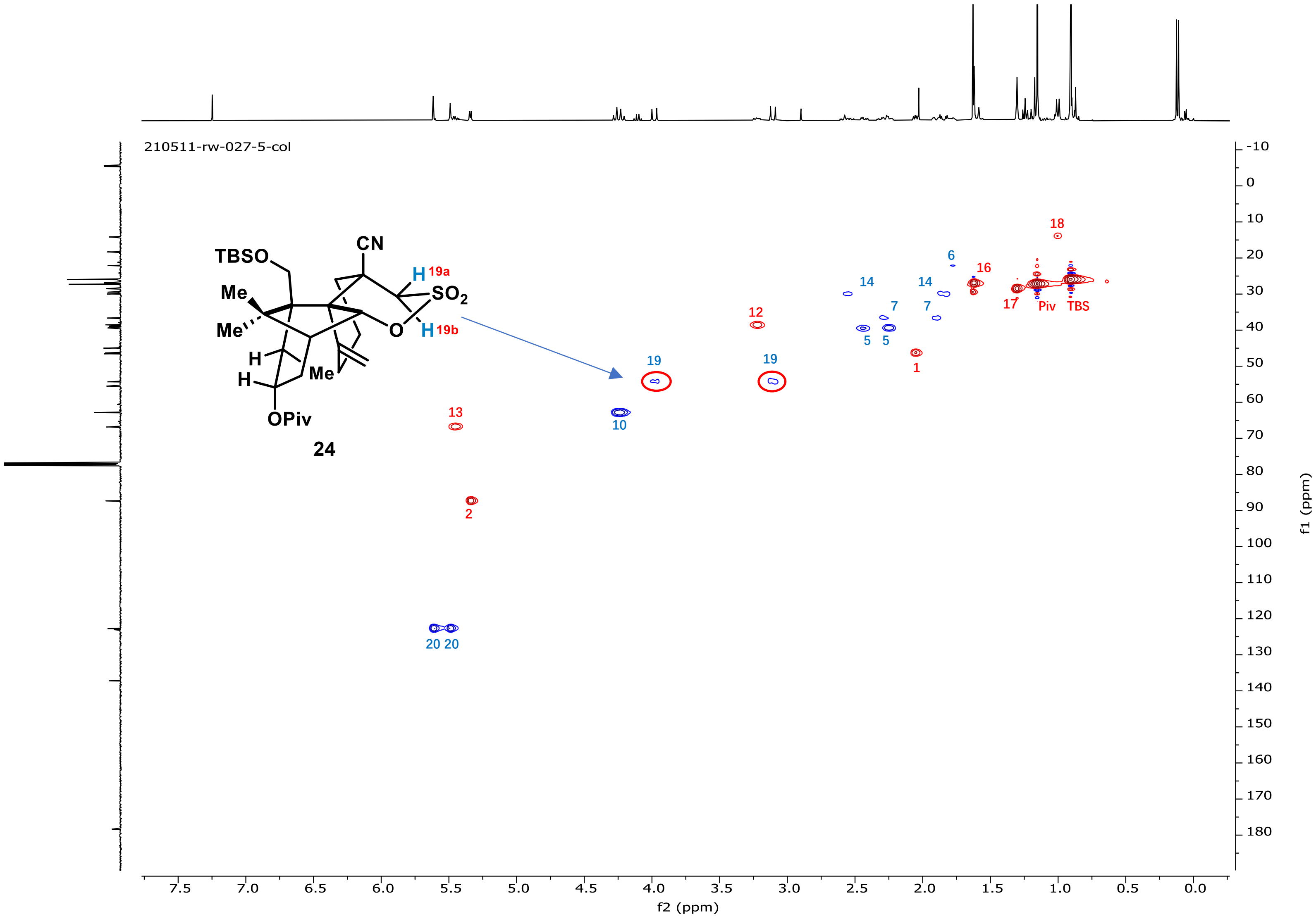
210308-rw-027-1-DMSO-col-F2
single_pulse

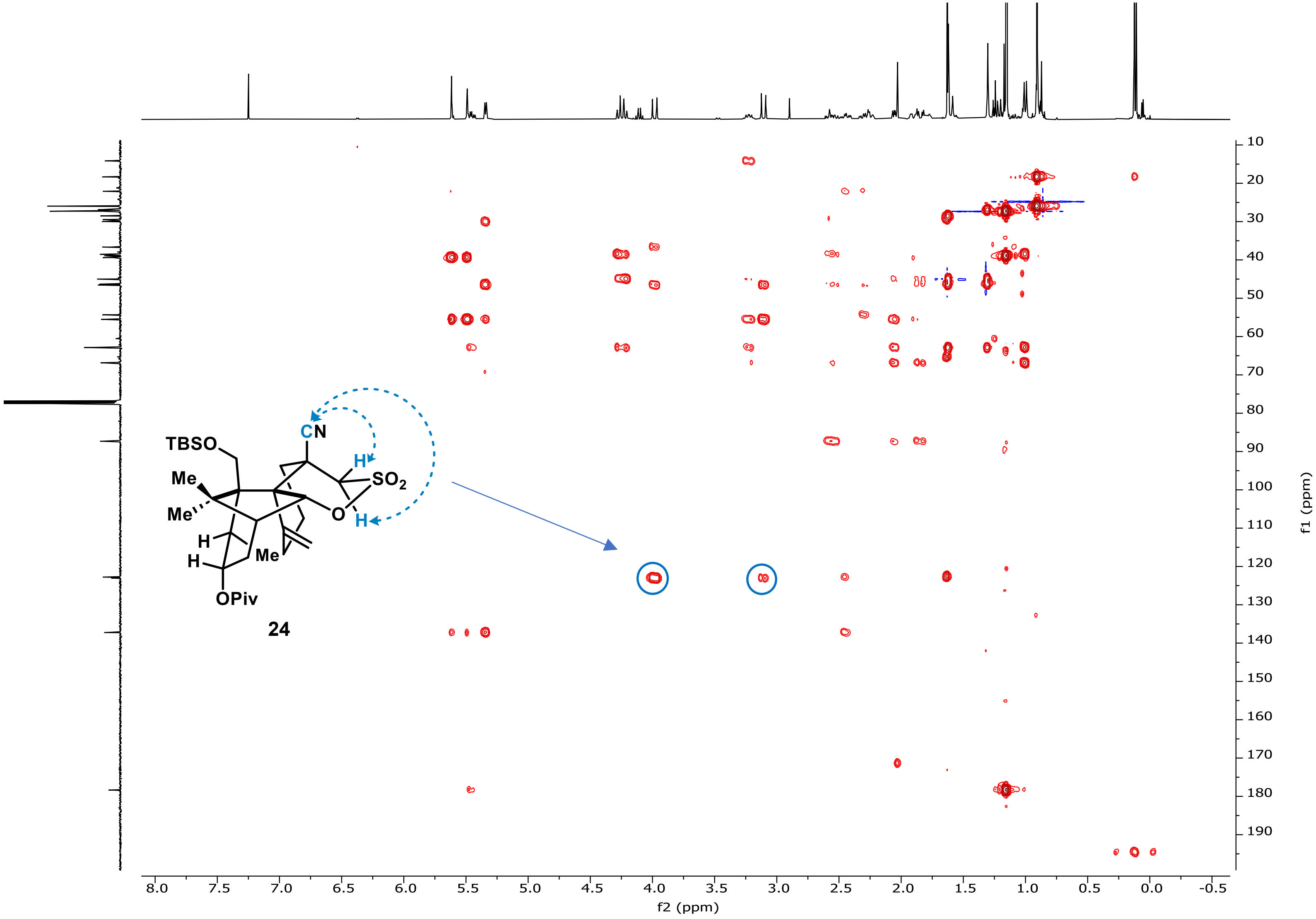


**24**

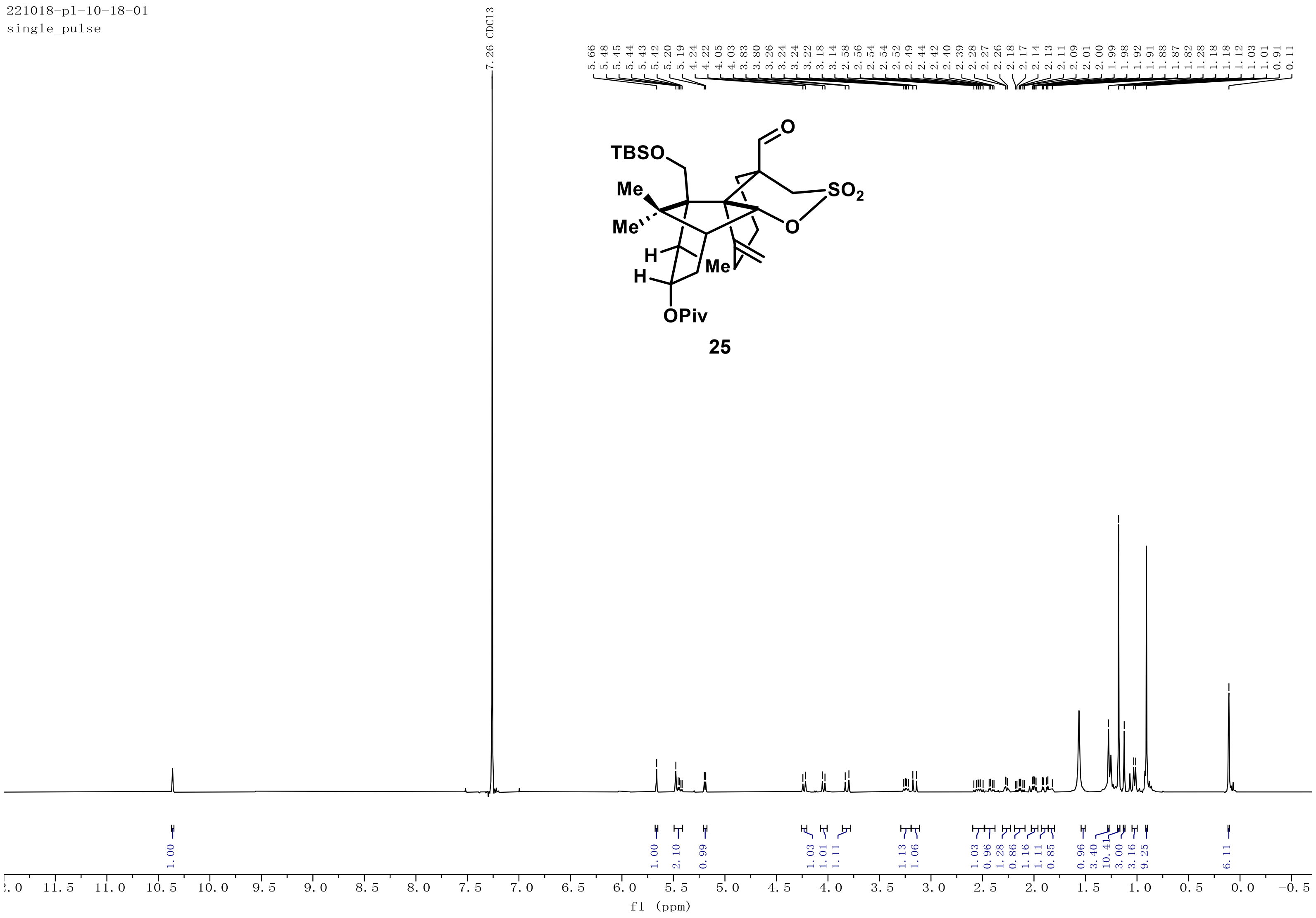

210511-rw-027-5-col
178.35
137.25
123.03
122.77
87.33
77.16 CDCl3
66.84
62.87
55.51
54.33
46.56
46.31
44.99
39.39
38.92
38.52
36.65
29.97
28.52
27.34
27.29
26.91
25.97
25.91
22.08
18.31
14.18
-5.39
-5.63
TBSO
CN
Me
Me
SO2
O
H
H
Me
OPiv
24
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

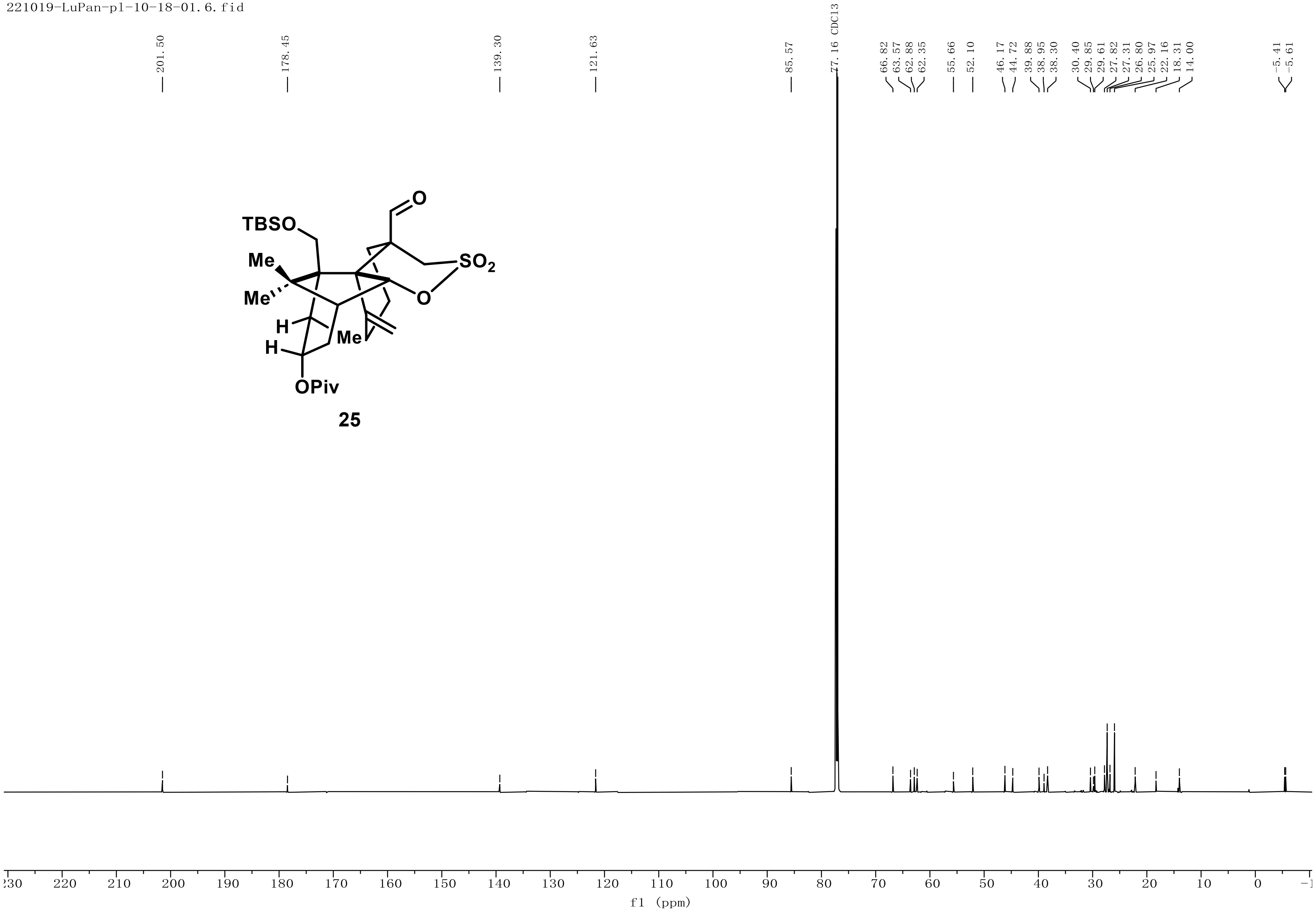

210511-rw-027-5-col
TBSO
CN
Me
Me
SO2
O
H
H
Me
OPiv
24
f2 (ppm)
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


210511-rw-027-5-col
TBSO
CN
H 19a
SO2
Me
Me
O
H 19b
H
H
Me
OPiv
24
19
19
12
14
14
6
16
18
7
7
5
5
1
17
Piv
TBS
13
10
2
20 20
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
f2 (ppm)
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
f1 (ppm)

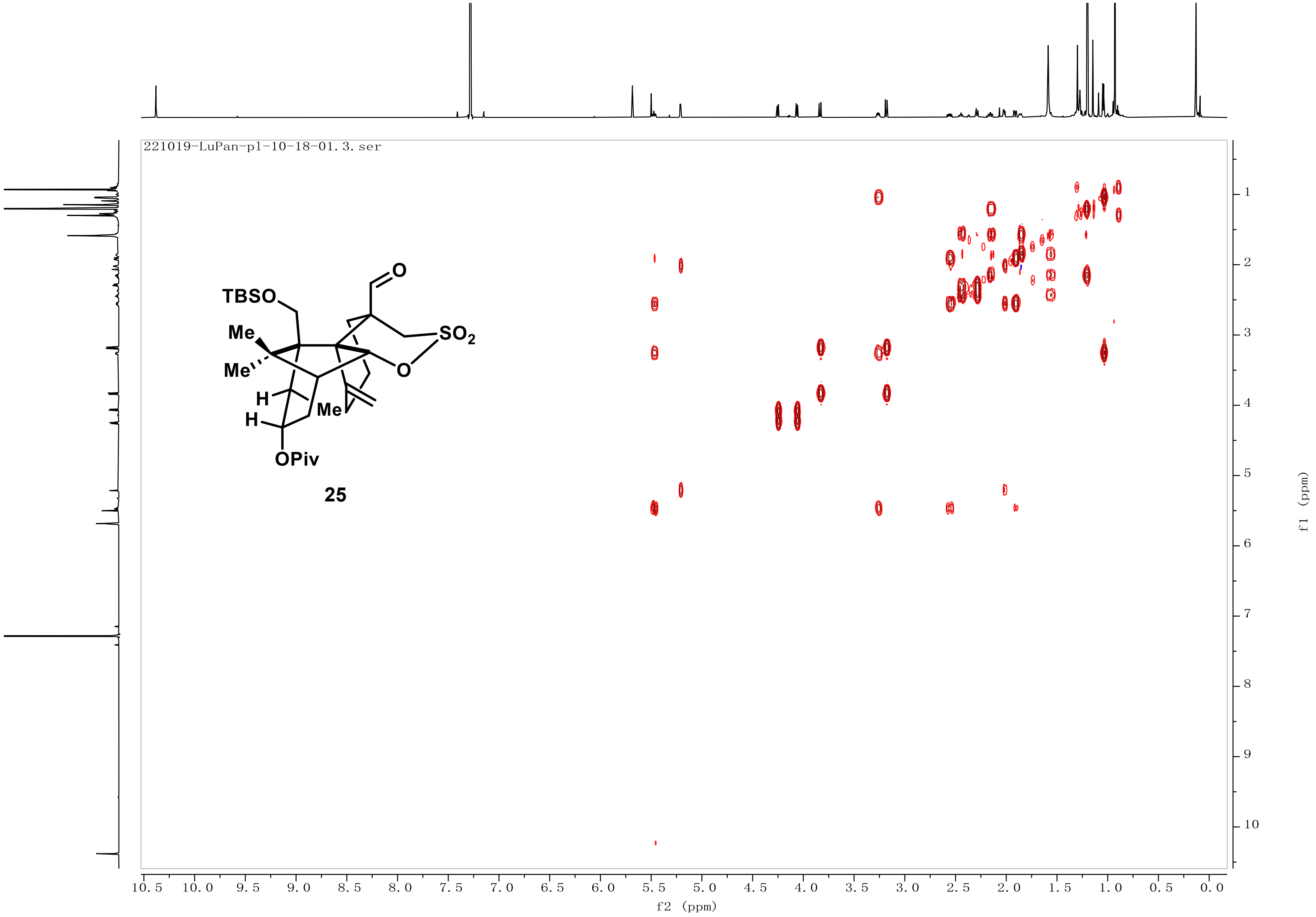

TBSO
Me
Me
H
H
Me
OPiv
CN
H
SO$_2$
O
H
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f2 (ppm)
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
f1 (ppm)

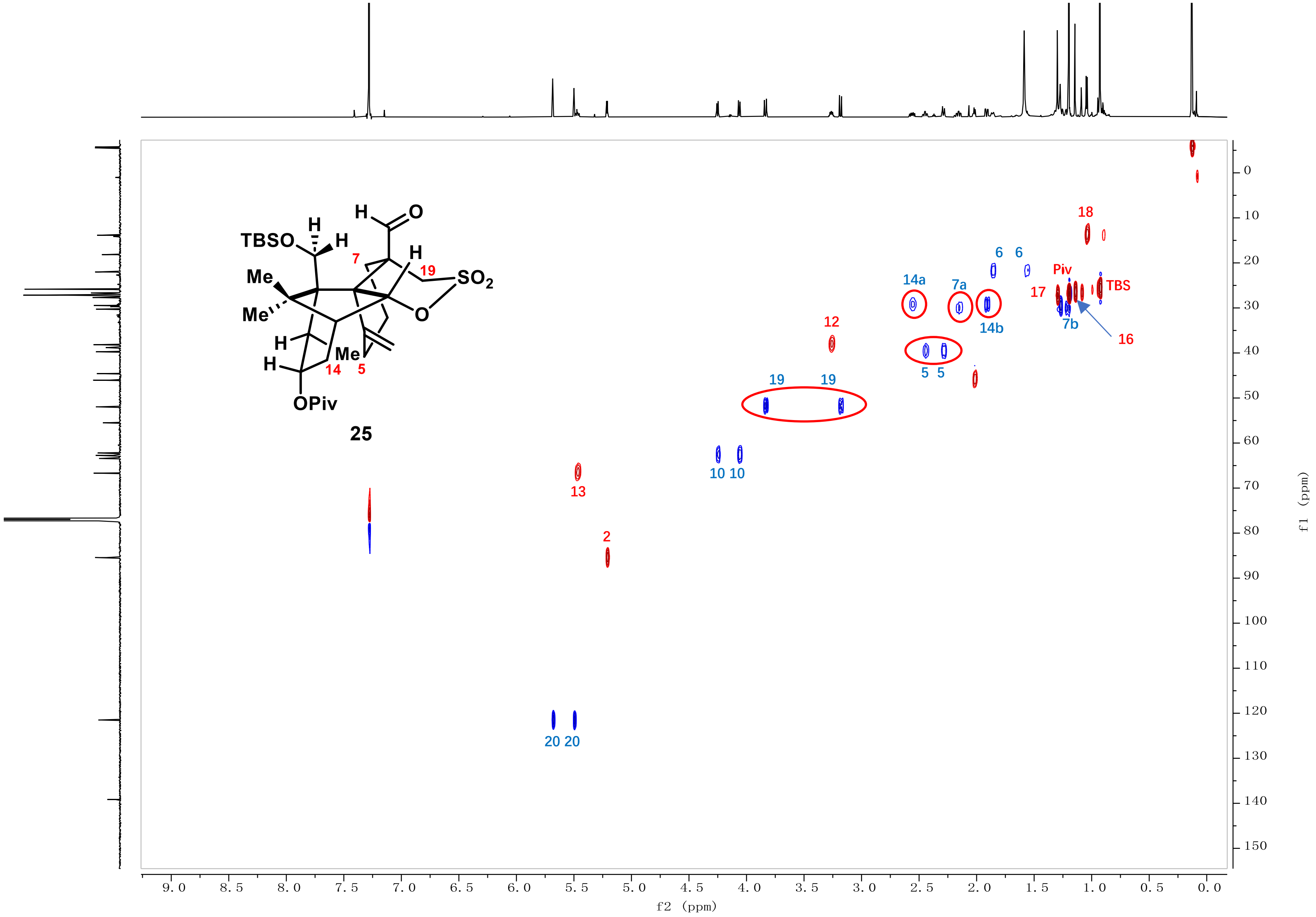
**24**

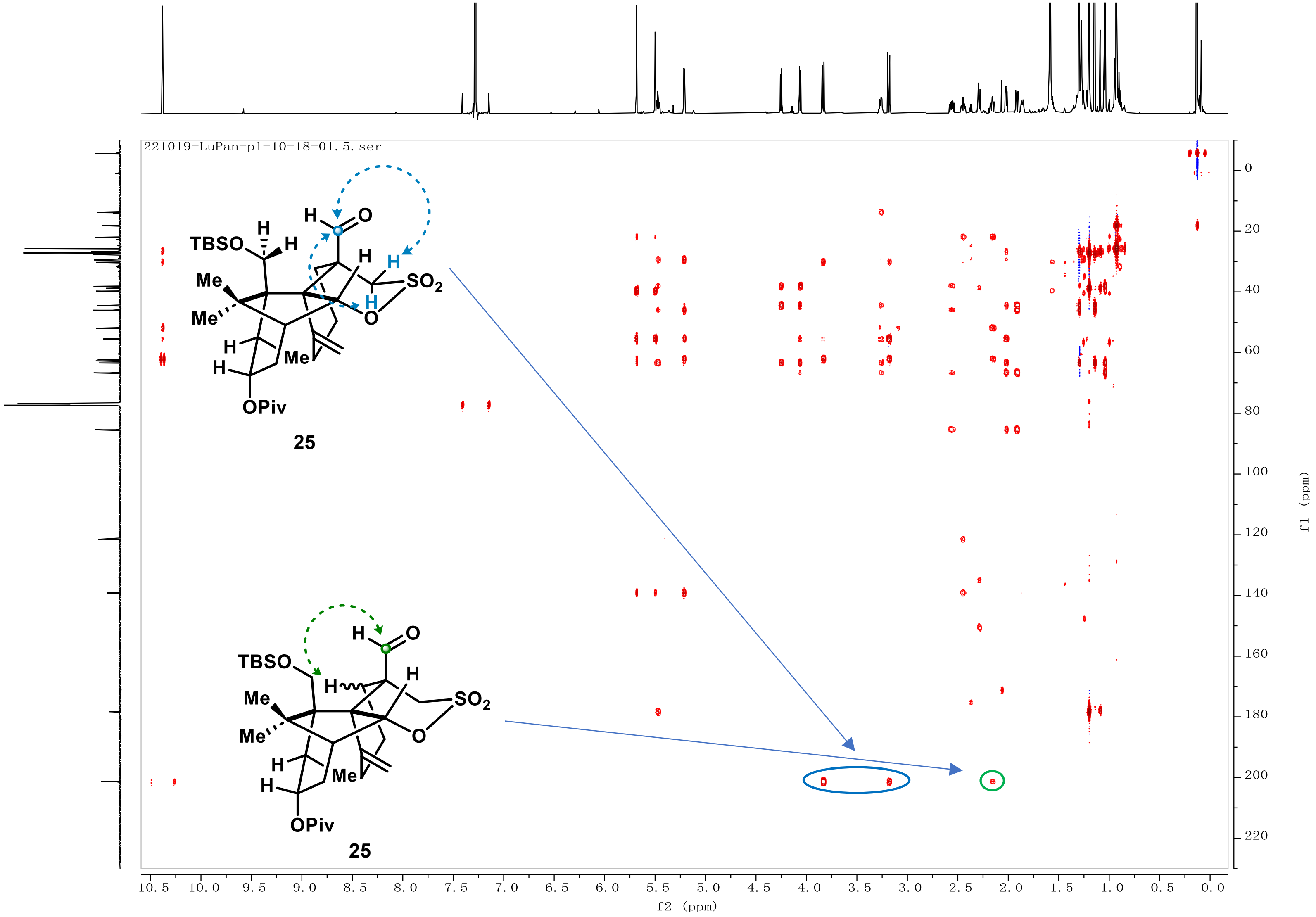

221018-pl-10-18-01
single_pulse
7.26 CDCl3
5.66 5.48 5.45 5.44 5.43 5.42 5.20 5.19 4.24 4.22 4.05 4.03 3.83 3.80 3.26 3.24 3.22 3.18 3.14 2.58 2.56 2.54 2.54 2.52 2.49 2.44 2.42 2.40 2.39 2.28 2.27 2.26 2.18 2.17 2.14 2.13 2.11 2.09 2.01 2.00 1.99 1.98 1.92 1.91 1.88 1.87 1.82 1.28 1.18 1.18 1.12 1.03 1.01 0.91 0.11
TBSO
Me
Me
H
H
OPiv
Me
O
SO2
O
25
1.00
1.00
2.10
0.99
1.03
1.01
1.11
1.13
1.06
1.03
0.96
1.28
0.86
1.16
1.11
0.85
0.96
3.40
10.41
3.00
3.16
9.25
6.11
2.0
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
f1 (ppm)

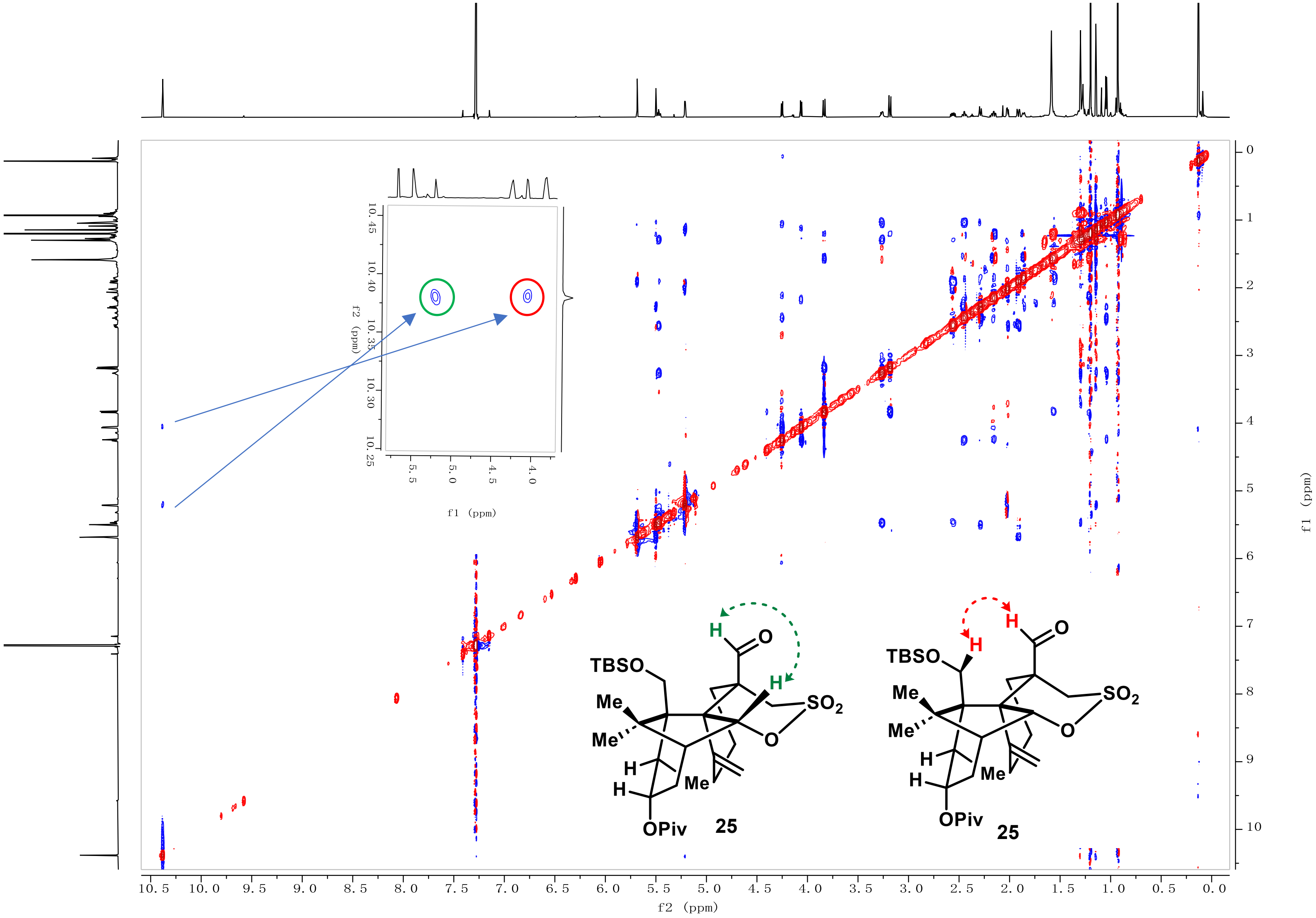

221019-LuPan-pl-10-18-01.6.fid
201.50
178.45
139.30
121.63
85.57
77.16 CDCl3
66.82
63.57
62.88
62.35
55.66
52.10
46.17
44.72
39.88
38.95
38.30
30.40
29.85
29.61
27.82
27.31
26.80
25.97
22.16
18.31
14.00
-5.41
-5.61
TBSO
Me
Me
H
H
OPiv
Me
O
SO2
O
30
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

25


221019-LuPan-pl-10-18-01.3.ser
TBSO
Me
Me
H
H
Me
O
SO2
O
OPiv
25
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
f2 (ppm)
1
2
3
4
5
6
7
8
9
10
f1 (ppm)

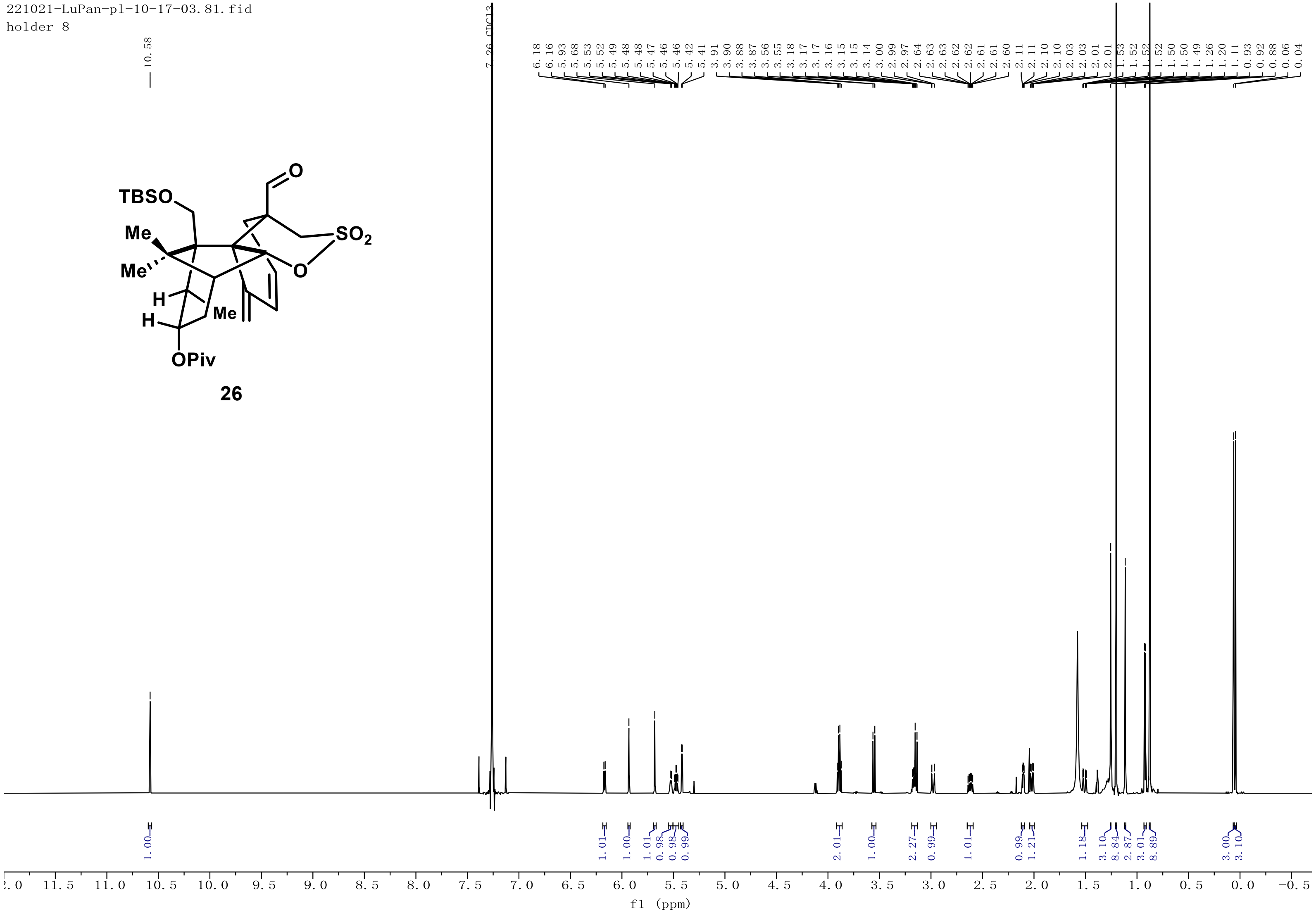

TBSO
H
H
H
O
Me
Me
H
SO2
O
H
H
Me
OPiv
7
19
14
5
25
18
6
6
Piv
TBS
14a
7a
17
14b
7b
16
12
5
5
19
19
10
10
13
2
20
20
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)


221019-LuPan-pl-10-18-01.5.ser
TBSO
H
H
Me
Me
H
H
OPiv
H
O
H
H
SO2
H
O
Me
25
TBSO
Me
Me
H
H
OPiv
H
O
H
H
SO2
O
Me
25
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
f2 (ppm)
0
20
40
60
80
100
120
140
160
180
200
220
f1 (ppm)



TBSO
Me
Me
H
H
OPiv
Me
H
O
H
SO2
O
25
TBSO
H
Me
Me
H
H
OPiv
Me
H
O
SO2
O
25
10.45
10.40
10.35
10.30
10.25
f2 (ppm)
5.5
5.0
4.5
4.0
f1 (ppm)
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
f2 (ppm)
0
1
2
3
4
5
6
7
8
9
10
f1 (ppm)

221021-LuPan-pl-10-17-03.81.fid
holder 8



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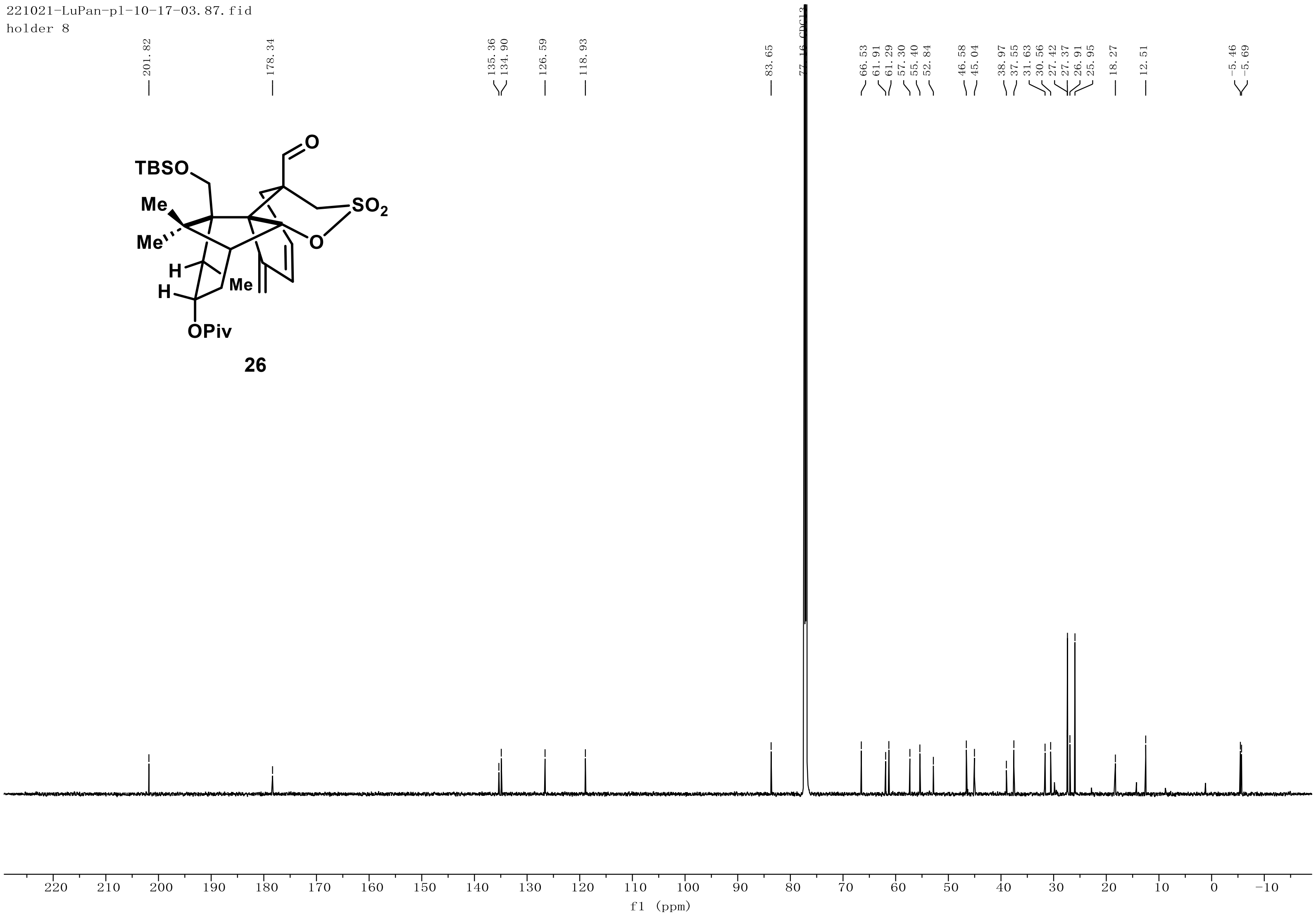
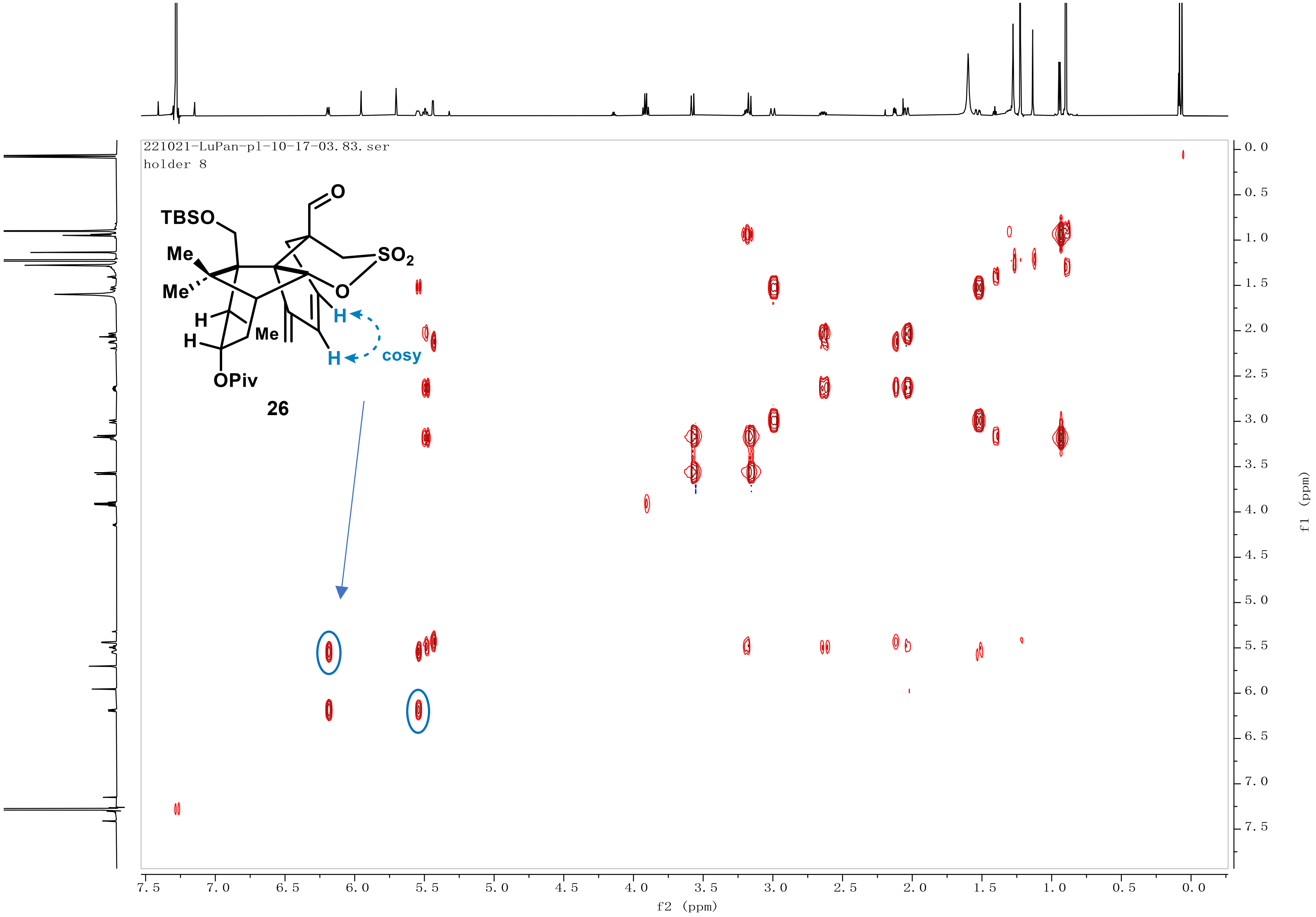
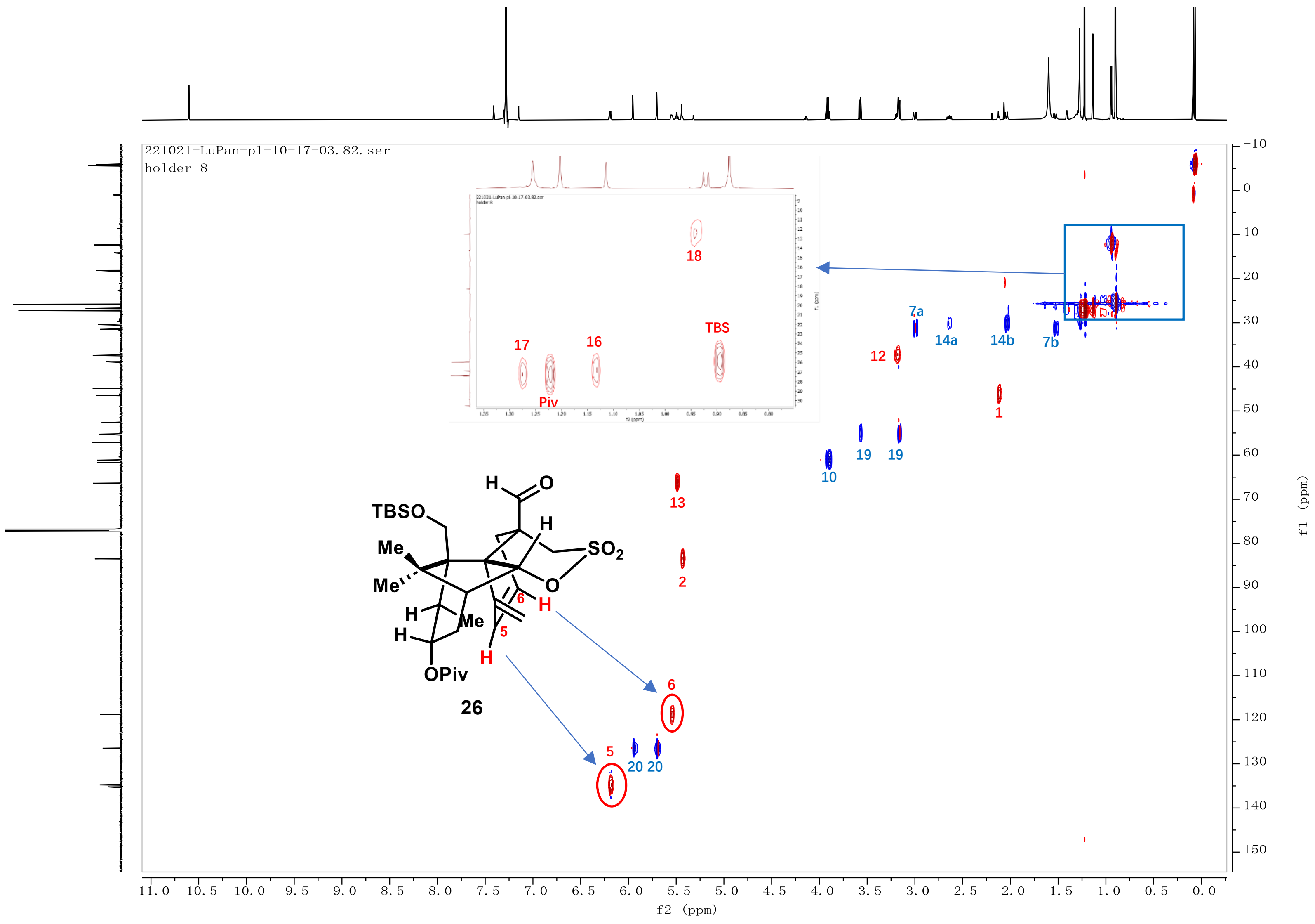
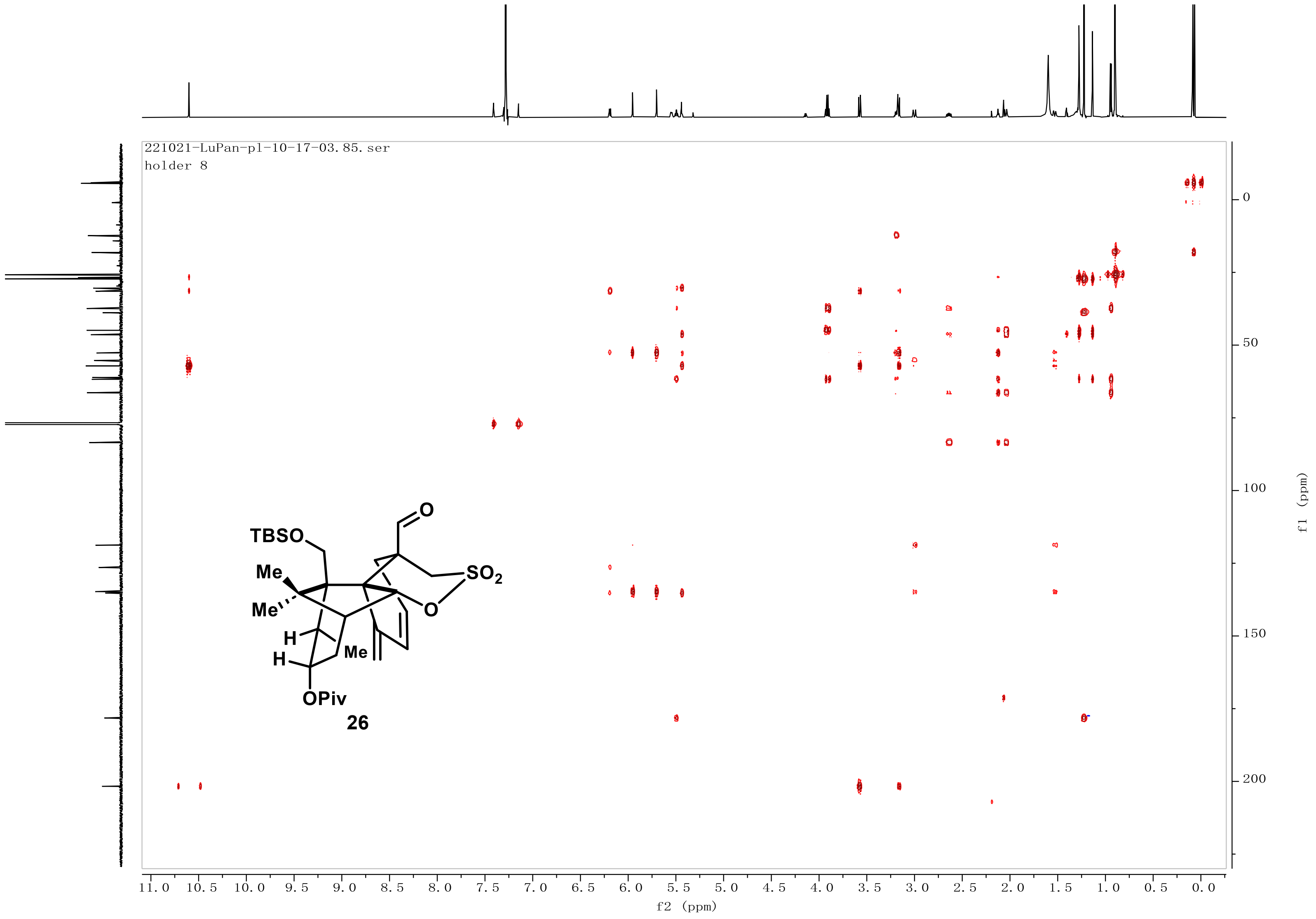
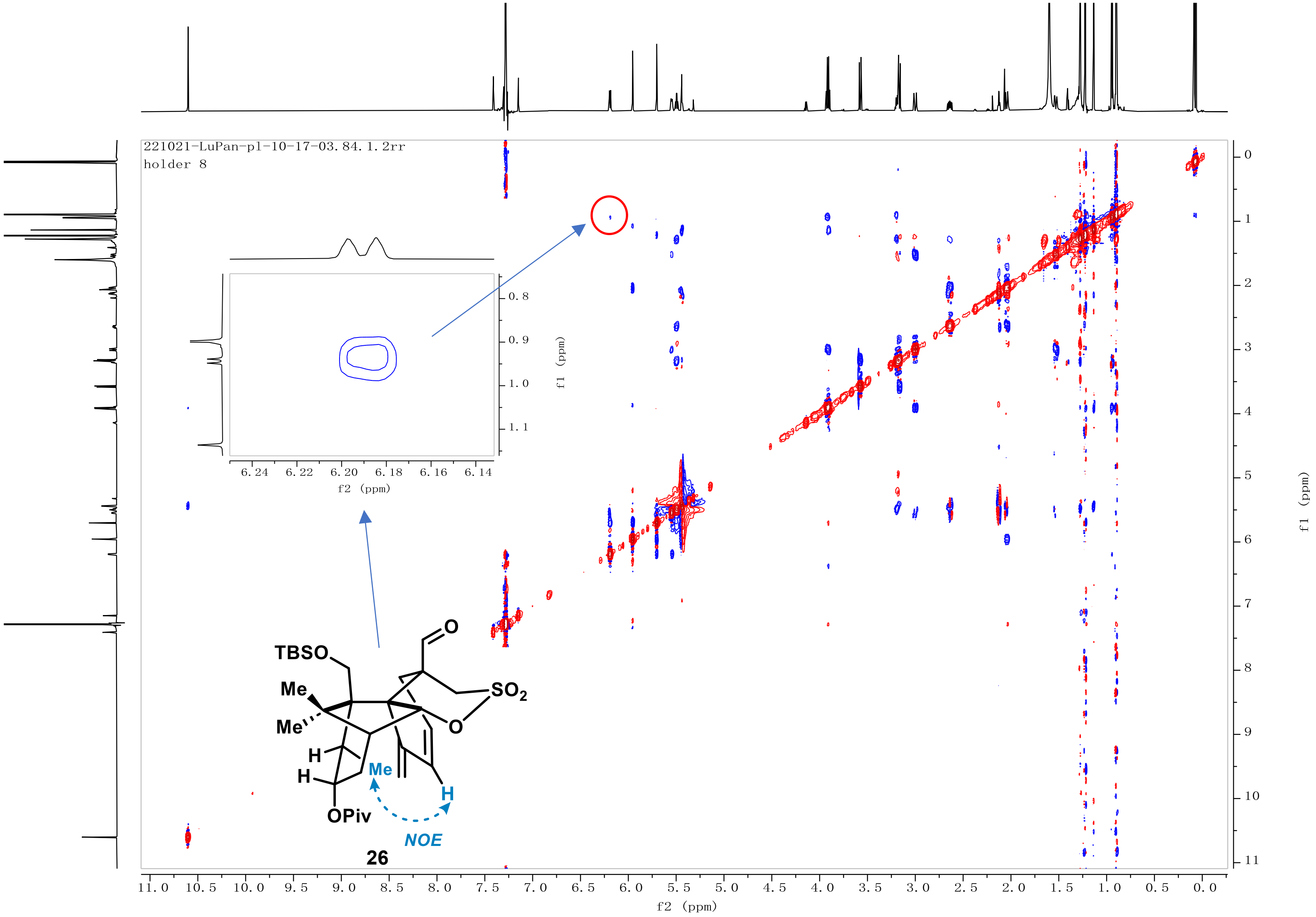

221021-LuPan-pl-10-17-03.87.fid
holder 8
201.82
178.34
135.36
134.90
126.59
118.93
83.65
77.16 CDCl3
66.53
61.91
61.29
57.30
55.40
52.84
46.58
45.04
38.97
37.55
31.63
30.56
27.42
27.37
26.91
25.95
18.27
12.51
-5.46
-5.69
TBSO
Me
Me
H
H
Me
OPiv
O
SO2
O
26
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

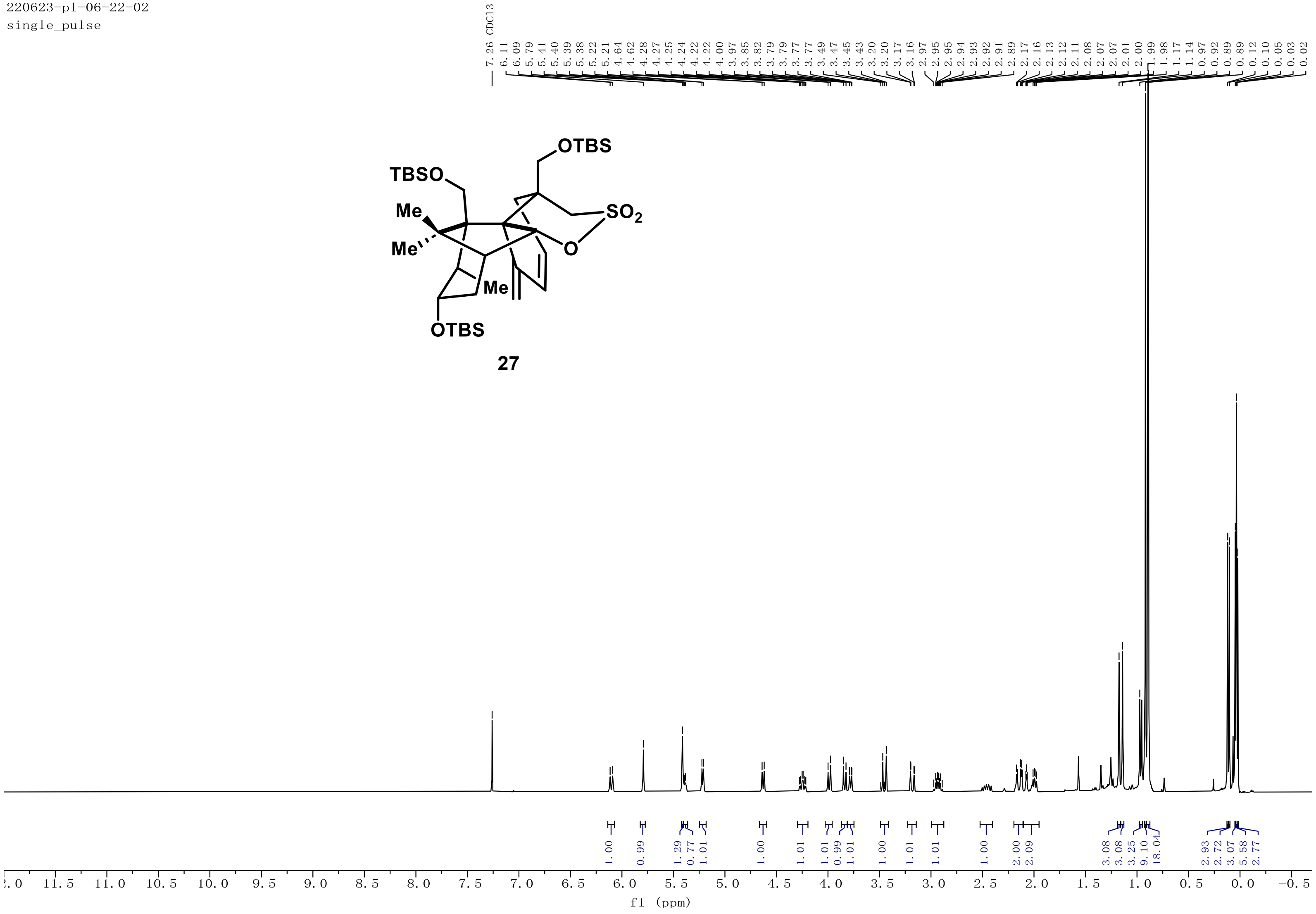

221021-LuPan-pl-10-17-03.83.ser
holder 8
TBSO
O
SO2
Me
Me
O
H
H
H
Me
H
cosy
OPiv
26
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
f1 (ppm)


221021-LuPan-pl-10-17-03.82.ser
holder 8
18
17
16
TBS
Piv
7a
14a
14b
7b
12
1
19
19
10
13
2
6
5
20
20
TBSO
H
O
H
SO2
O
Me
Me
H
H
Me
6
H
5
H
OPiv
26
f2 (ppm)
f1 (ppm)
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
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150


221021-LuPan-pl-10-17-03.85.ser
holder 8
TBSO
Me
Me
H
H
Me
OPiv
O
SO2
O
26
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
f2 (ppm)
0
50
100
150
200
f1 (ppm)

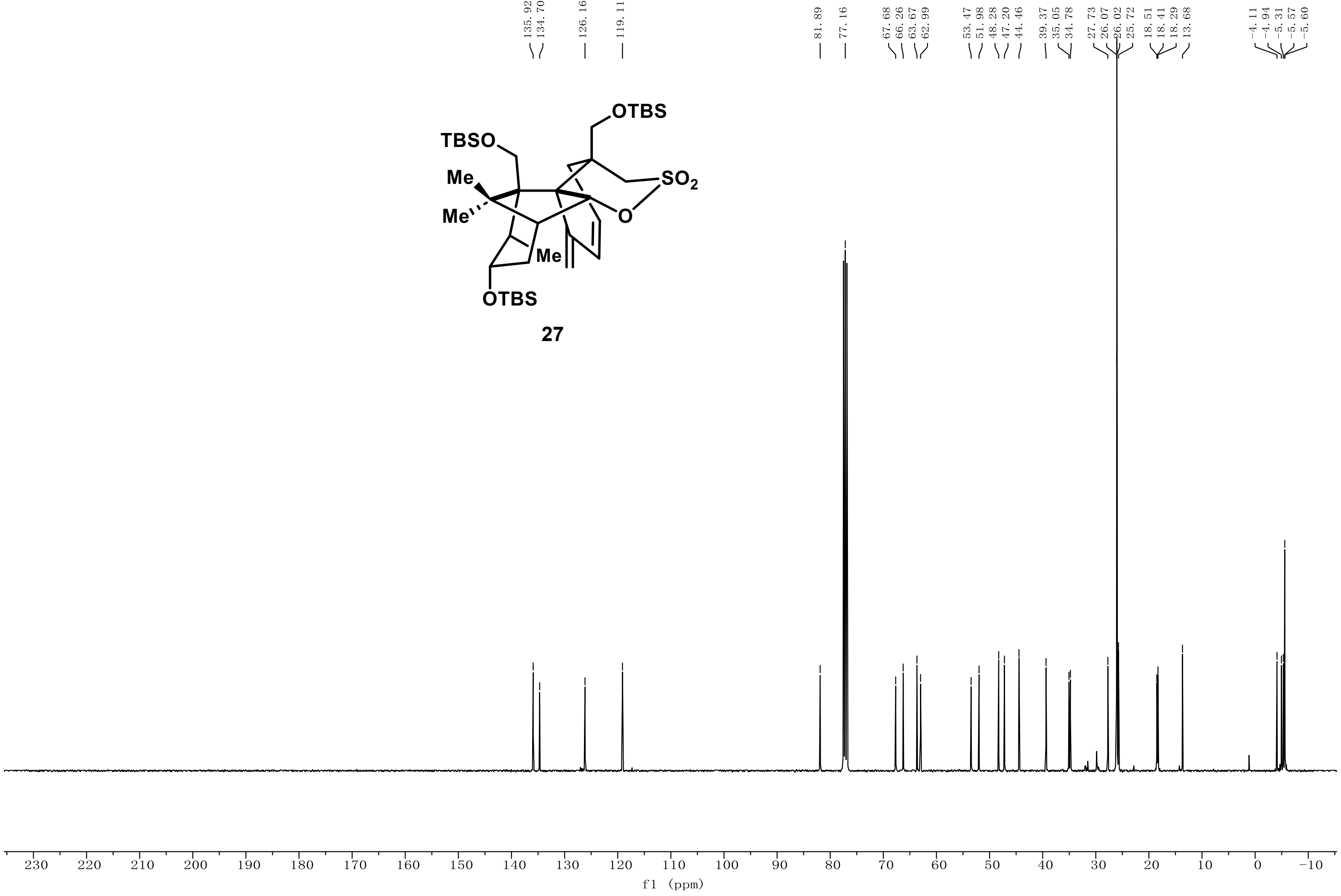

221021-LuPan-p1-10-17-03.84.1.2rr
holder 8
f2 (ppm)
f1 (ppm)
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
0 1 2 3 4 5 6 7 8 9 10 11
6.24 6.22 6.20 6.18 6.16 6.14
0.8 0.9 1.0 1.1
TBSO
Me
Me
H
H
OPiv
O
SO2
O
Me
H
NOE
26

220623-pl-06-22-02
single_pulse



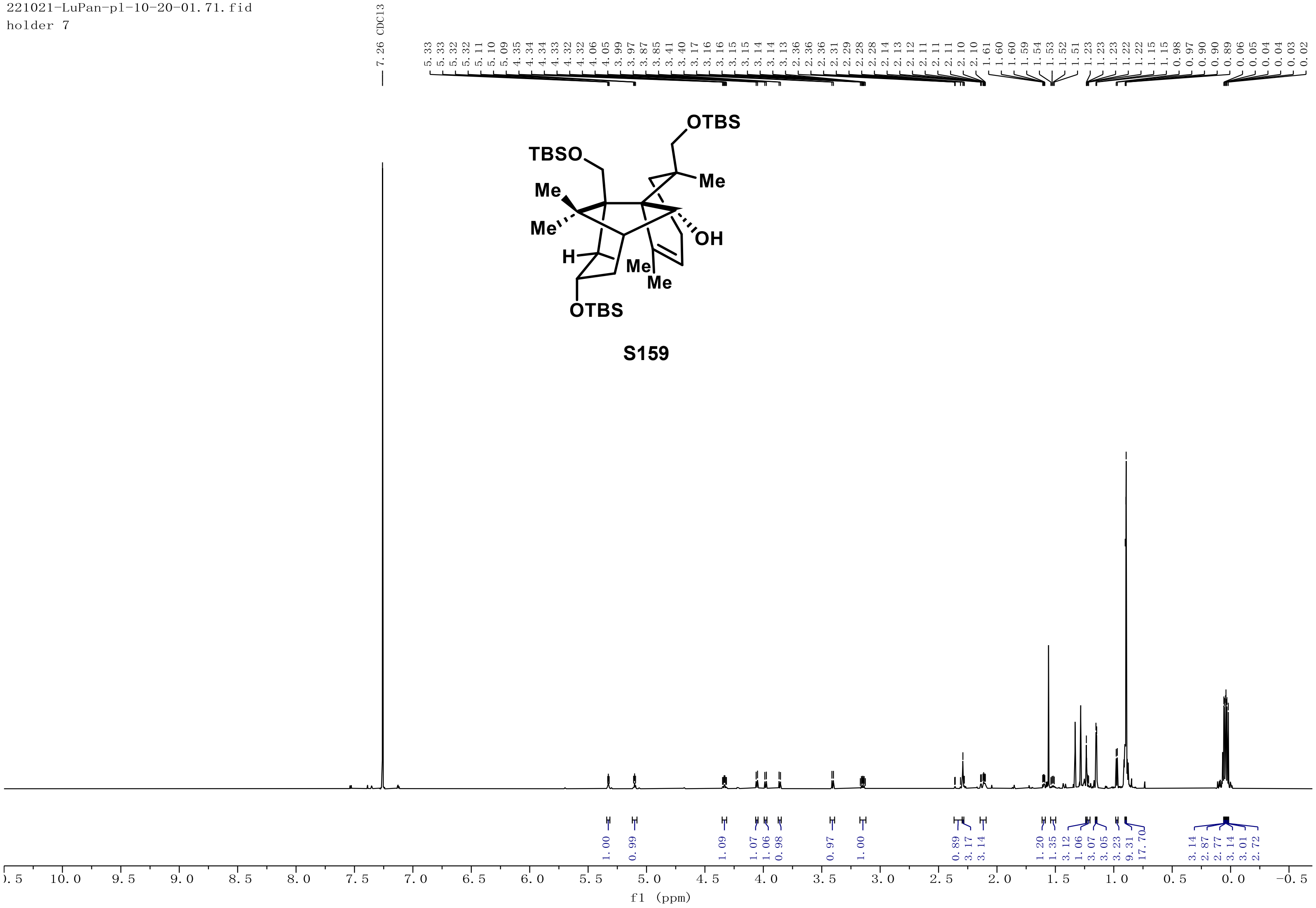
27

220623-p1-06-22-02
single pulse decoupled gated NOE

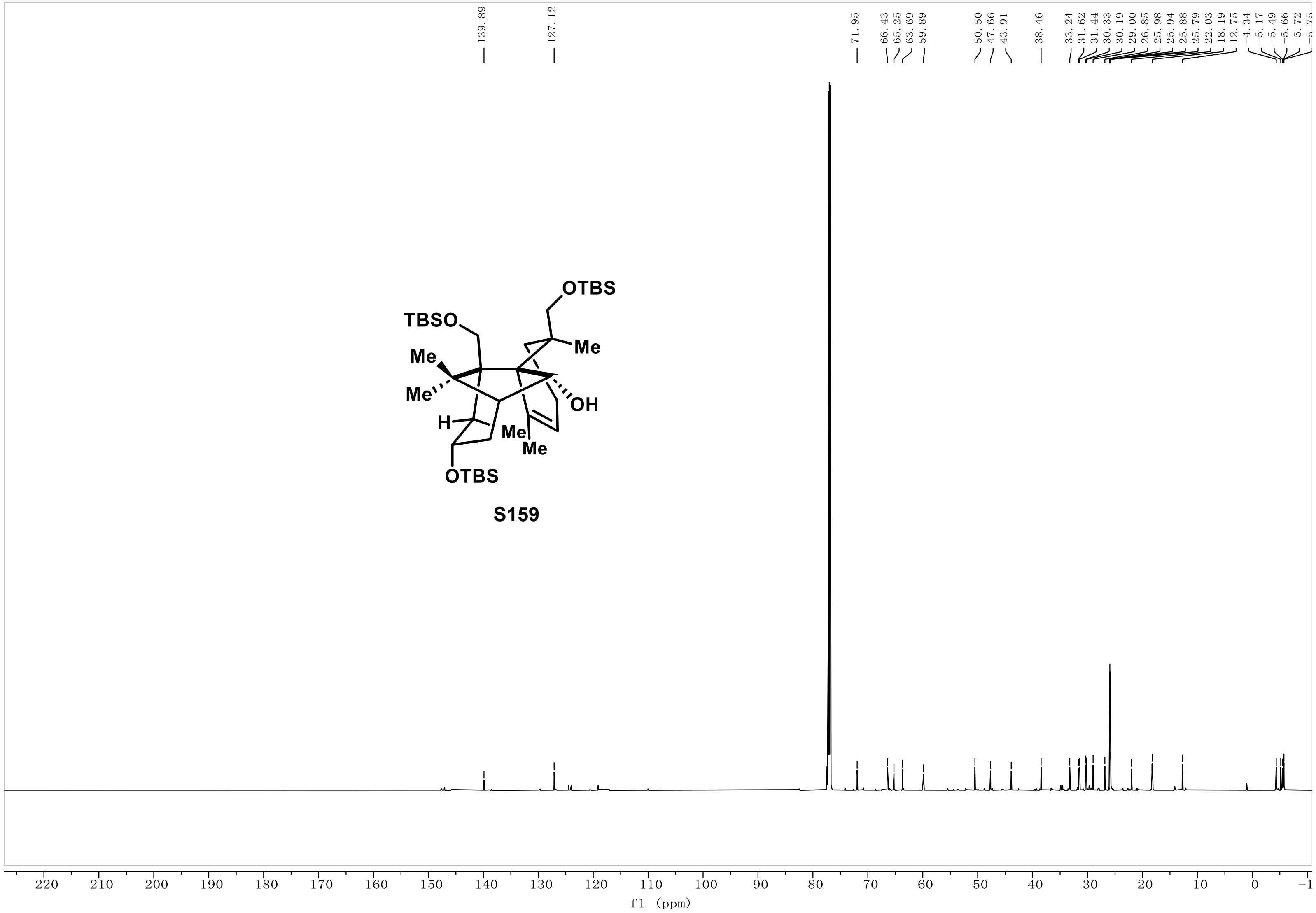


**27**

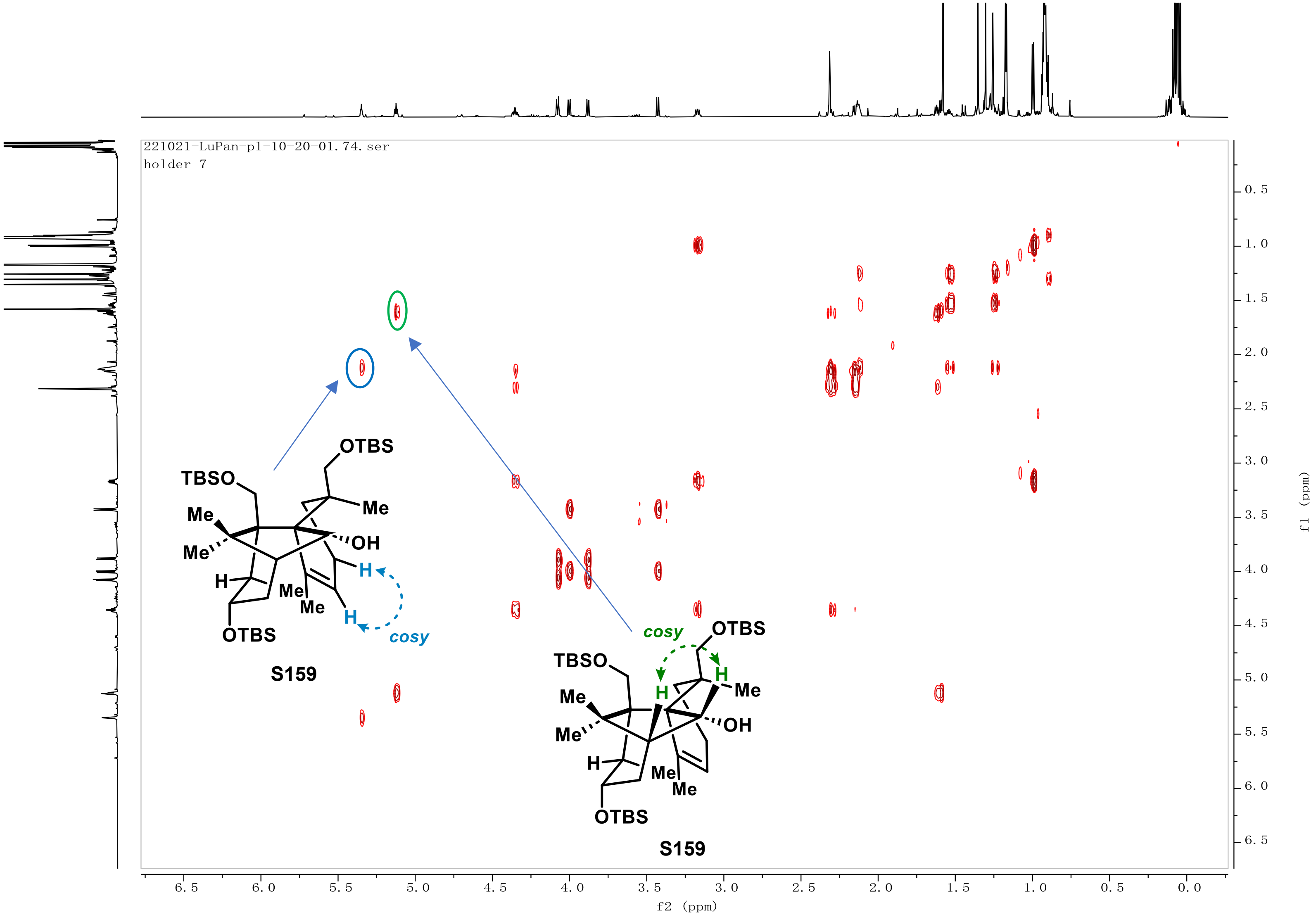
221021-LuPan-pl-10-20-01.71.fid
holder 7

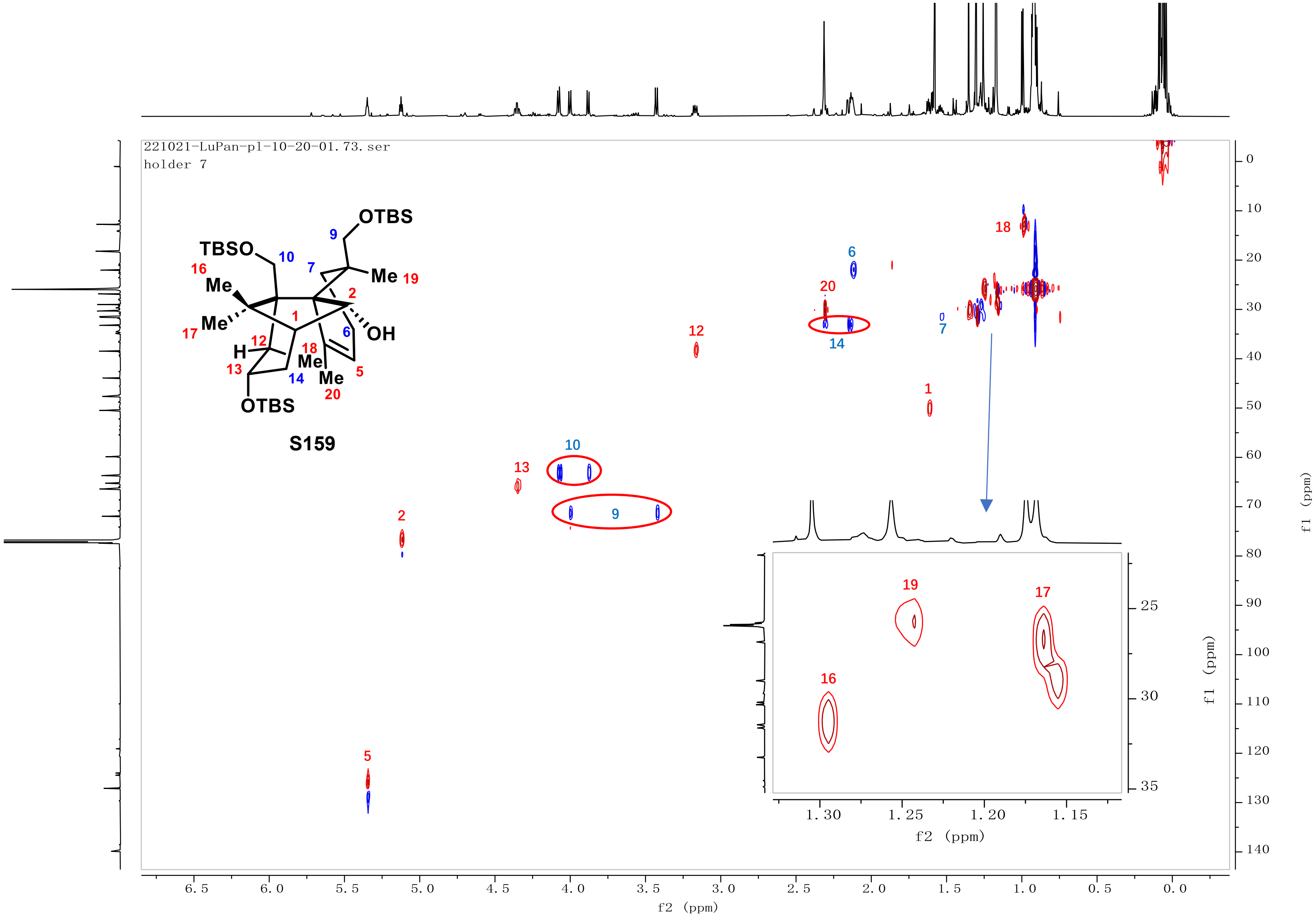


**S159**

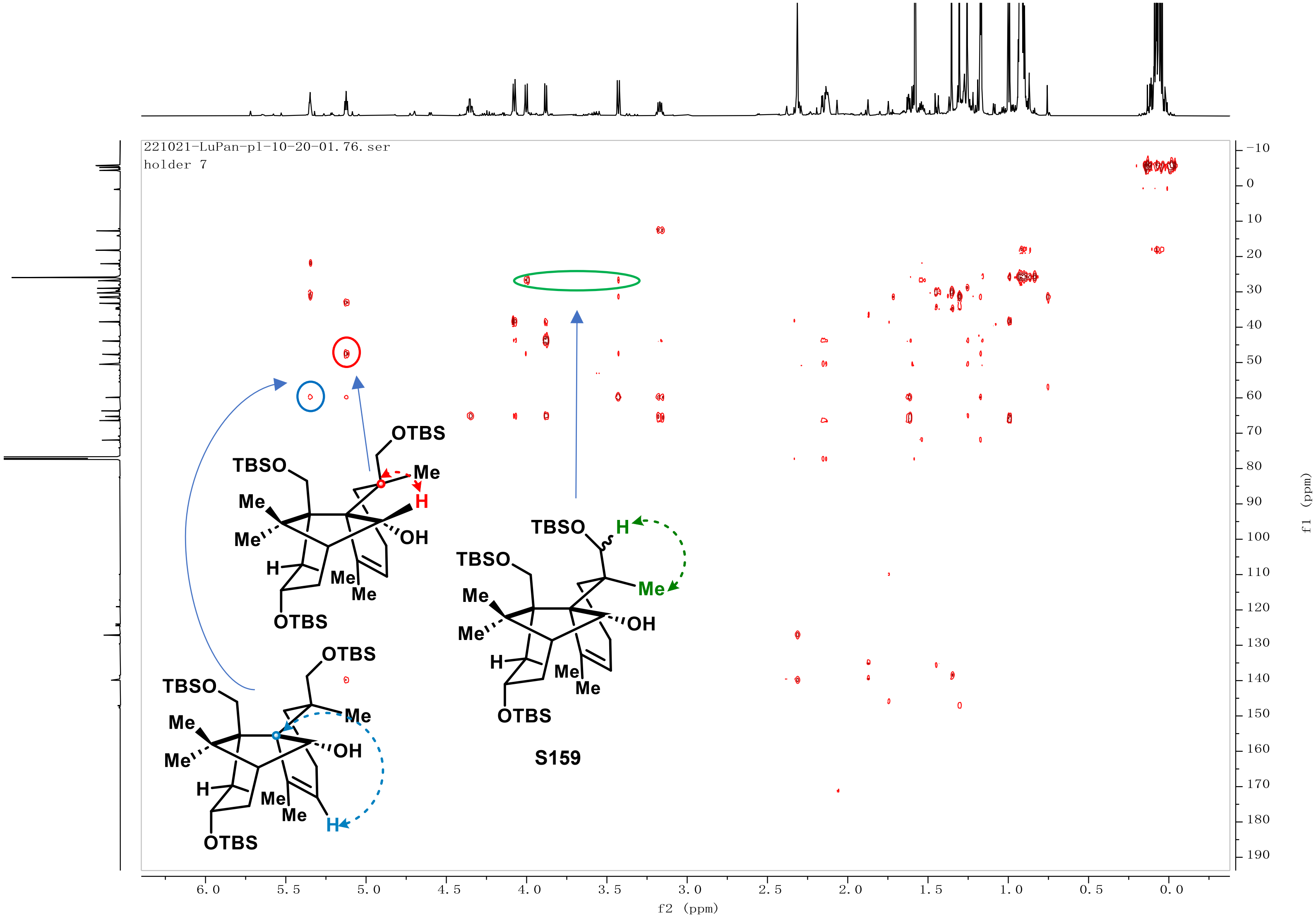

S159

139.89
127.12
71.95
66.43
65.25
63.69
59.89
50.50
47.66
43.91
38.46
33.24
31.62
31.44
30.33
30.19
29.00
26.85
25.98
25.94
25.88
25.79
22.03
18.19
12.75
-4.34
-5.17
-5.49
-5.66
-5.72
-5.75
TBSO
OTBS
Me
Me
Me
OH
H
Me
Me
OTBS
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


221021-LuPan-pl-10-20-01.74.ser
holder 7
TBSO
OTBS
Me
Me
Me
OH
H
H
H
Me
Me
OTBS
cosy
S159
cosy
OTBS
TBSO
Me
H
H
Me
Me
OH
H
Me
Me
OTBS
S159
f2 (ppm)
f1 (ppm)
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

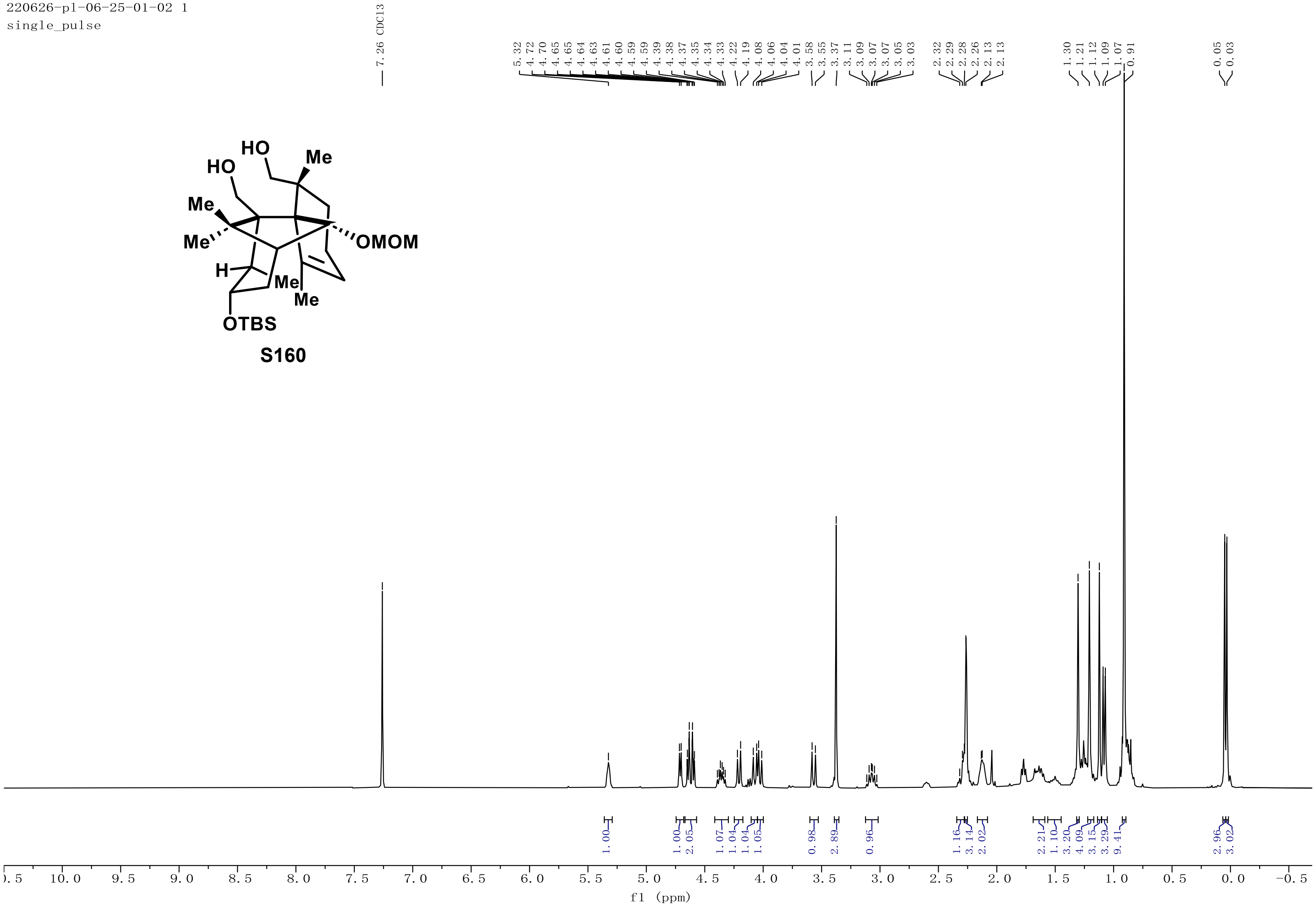

221021-LuPan-pl-10-20-01.73.ser
holder 7
OTBS
TBSO
OTBS
Me
Me
Me
Me
Me
H
OH
1
2
5
6
7
9
10
12
13
14
16
17
18
19
20
f2 (ppm)
f1 (ppm)
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
1.30
1.25
1.20
1.15
25
30
35

S159



S159

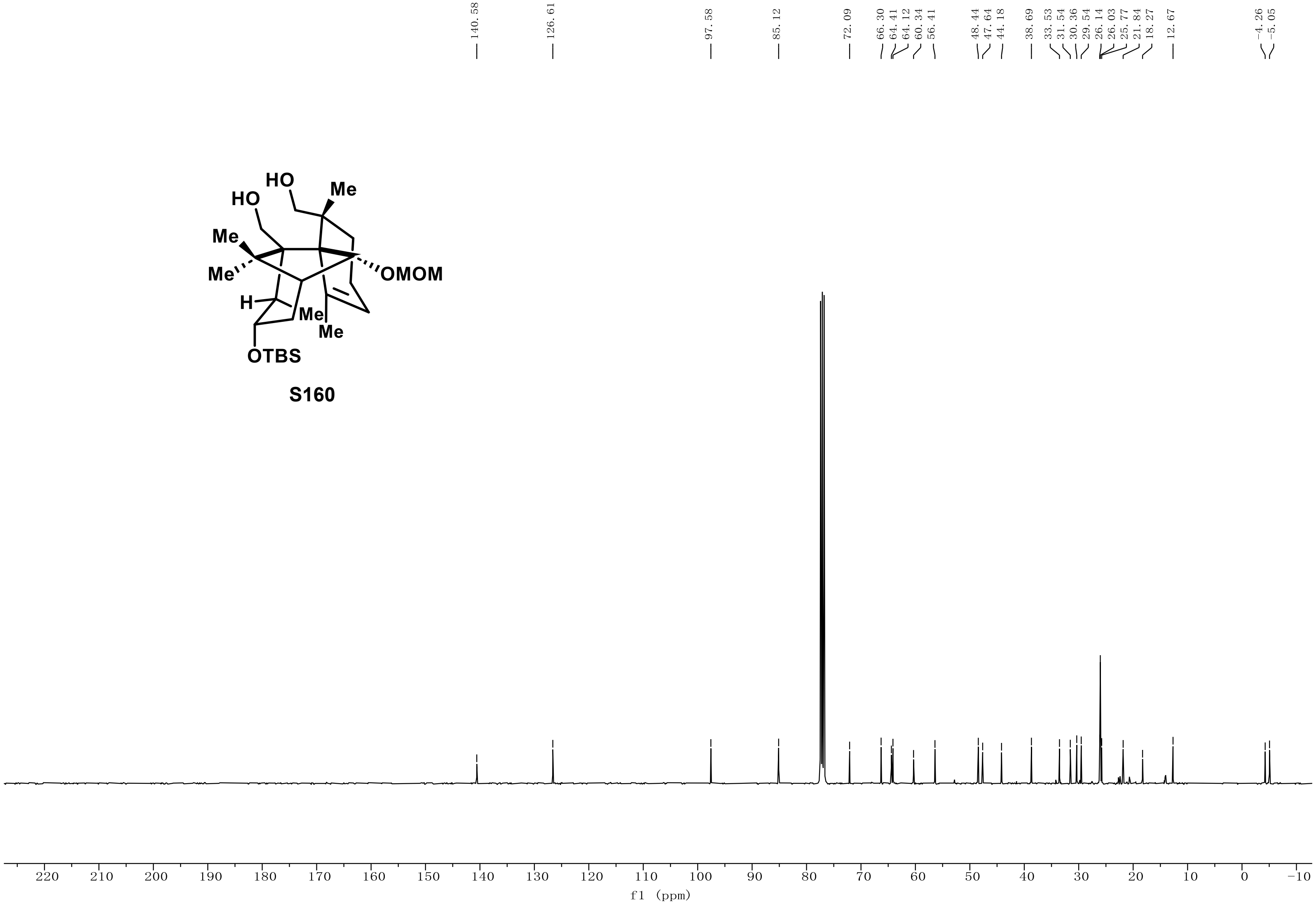
221021-LuPan-pl-10-20-01.76.ser
holder 7
TBSO
OTBS
Me
H
OH
f2 (ppm)
f1 (ppm)
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190

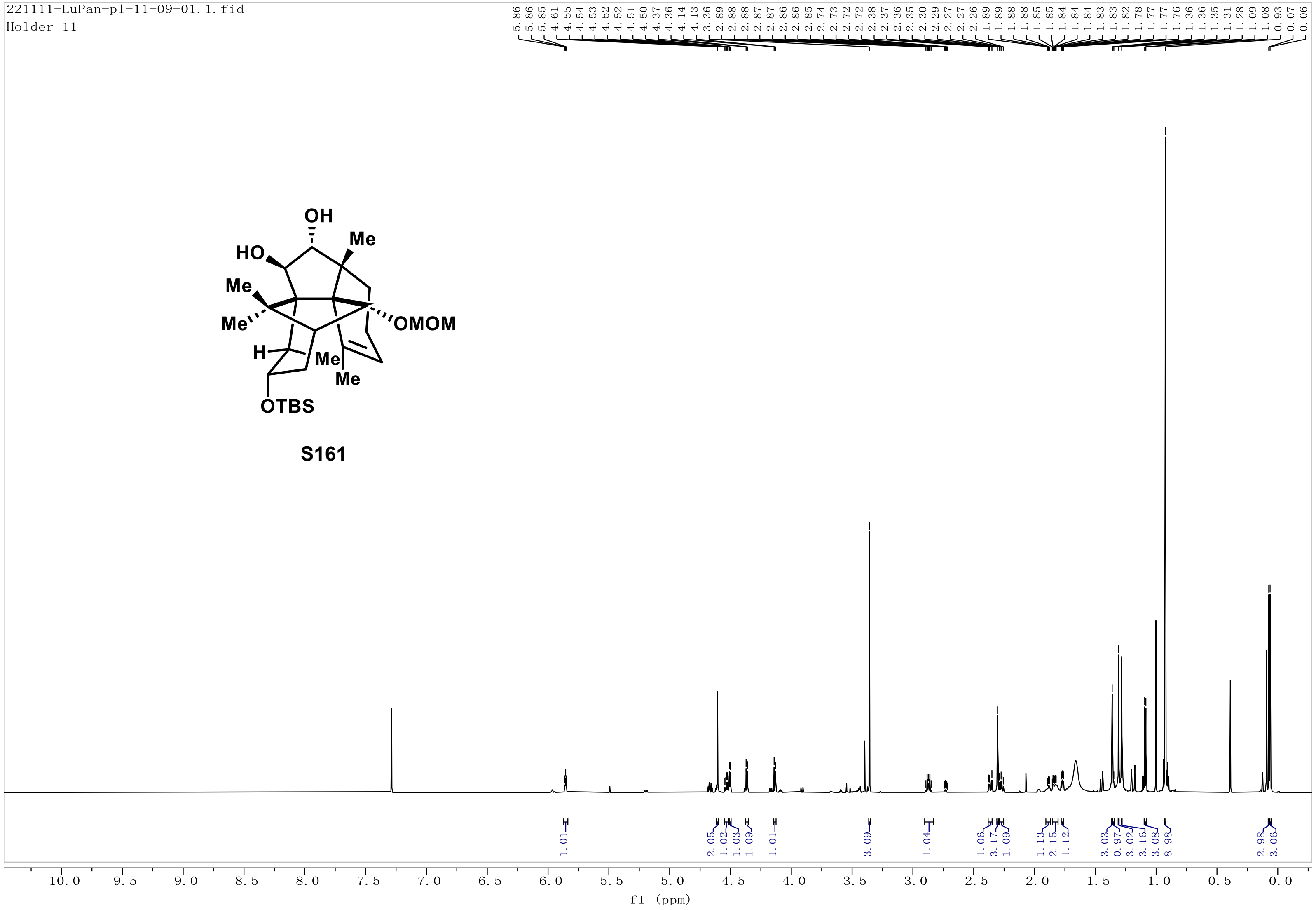

220626-p1-06-25-01-02 1
single_pulse
7.26 CDCl3
5.32
4.72
4.70
4.65
4.65
4.64
4.63
4.61
4.60
4.59
4.59
4.59
4.39
4.38
4.37
4.35
4.34
4.33
4.22
4.19
4.08
4.06
4.04
4.01
3.58
3.55
3.37
3.11
3.09
3.07
3.07
3.05
3.03
2.32
2.29
2.28
2.26
2.13
2.13
1.30
1.21
1.12
1.09
1.07
0.91
0.05
0.03
HO
HO
Me
Me
Me
OMOM
H
Me
Me
OTBS
1.00
1.00
2.05
1.07
1.04
1.04
1.05
0.98
2.89
0.96
1.16
3.14
2.02
2.21
1.10
3.20
4.09
3.15
3.29
9.41
2.96
3.02
0.5
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
f1 (ppm)

S160

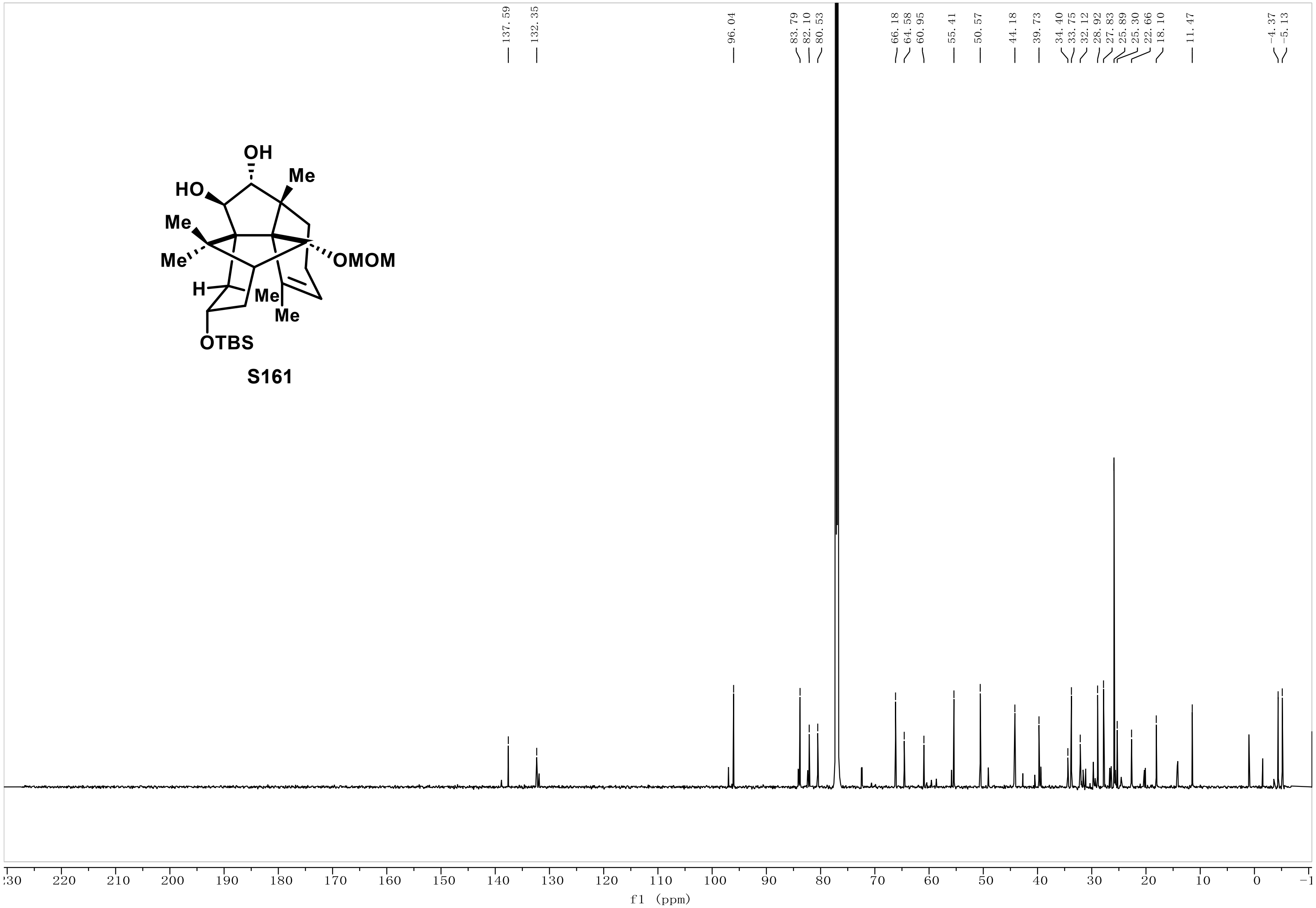
HO
HO
Me
Me
Me
OMOM
H
Me
Me
OTBS

**S160**

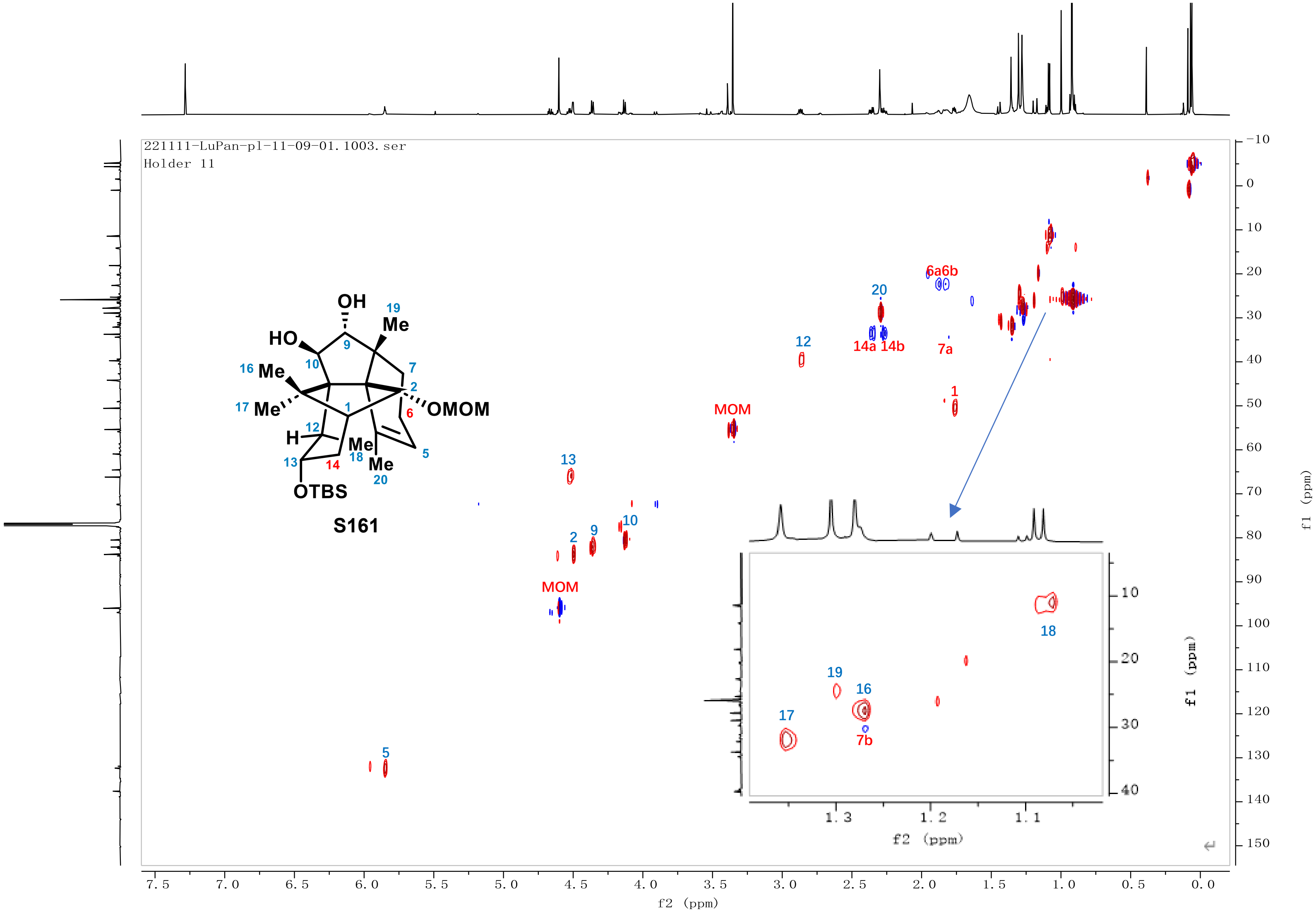

140.58
126.61
97.58
85.12
72.09
66.30
64.41
64.12
60.34
56.41
48.44
47.64
44.18
38.69
33.53
31.54
30.36
29.54
26.14
26.03
25.77
21.84
18.27
12.67
-4.26
-5.05
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

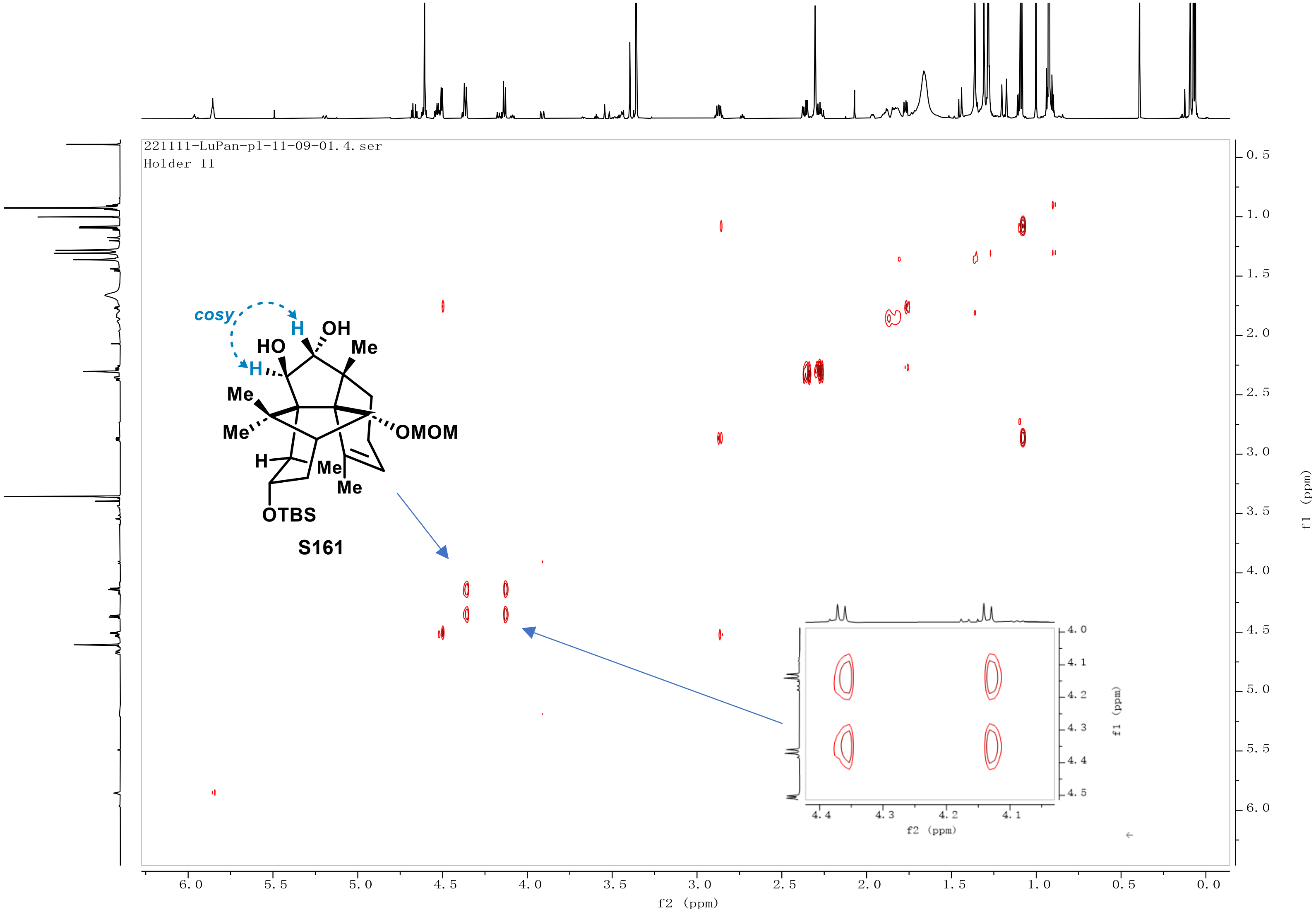

221111-LuPan-pl-11-09-01.1.fid
Holder 11
5.86
5.86
5.85
4.61
4.55
4.54
4.53
4.52
4.51
4.50
4.37
4.36
4.14
4.13
3.36
2.89
2.88
2.88
2.87
2.87
2.86
2.85
2.74
2.73
2.72
2.72
2.38
2.37
2.36
2.35
2.30
2.29
2.27
2.27
2.26
1.89
1.89
1.88
1.88
1.85
1.84
1.84
1.84
1.83
1.83
1.82
1.78
1.77
1.77
1.76
1.36
1.36
1.35
1.31
1.28
1.09
1.08
0.93
0.07
0.06
OH
HO
Me
Me
Me
OMOM
H
Me
Me
OTBS
1.01
2.05
1.02
1.03
1.09
1.01
3.09
1.04
1.06
3.17
1.09
1.13
2.15
1.12
3.03
0.97
3.02
3.16
3.08
8.98
2.98
3.06
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
f1 (ppm)

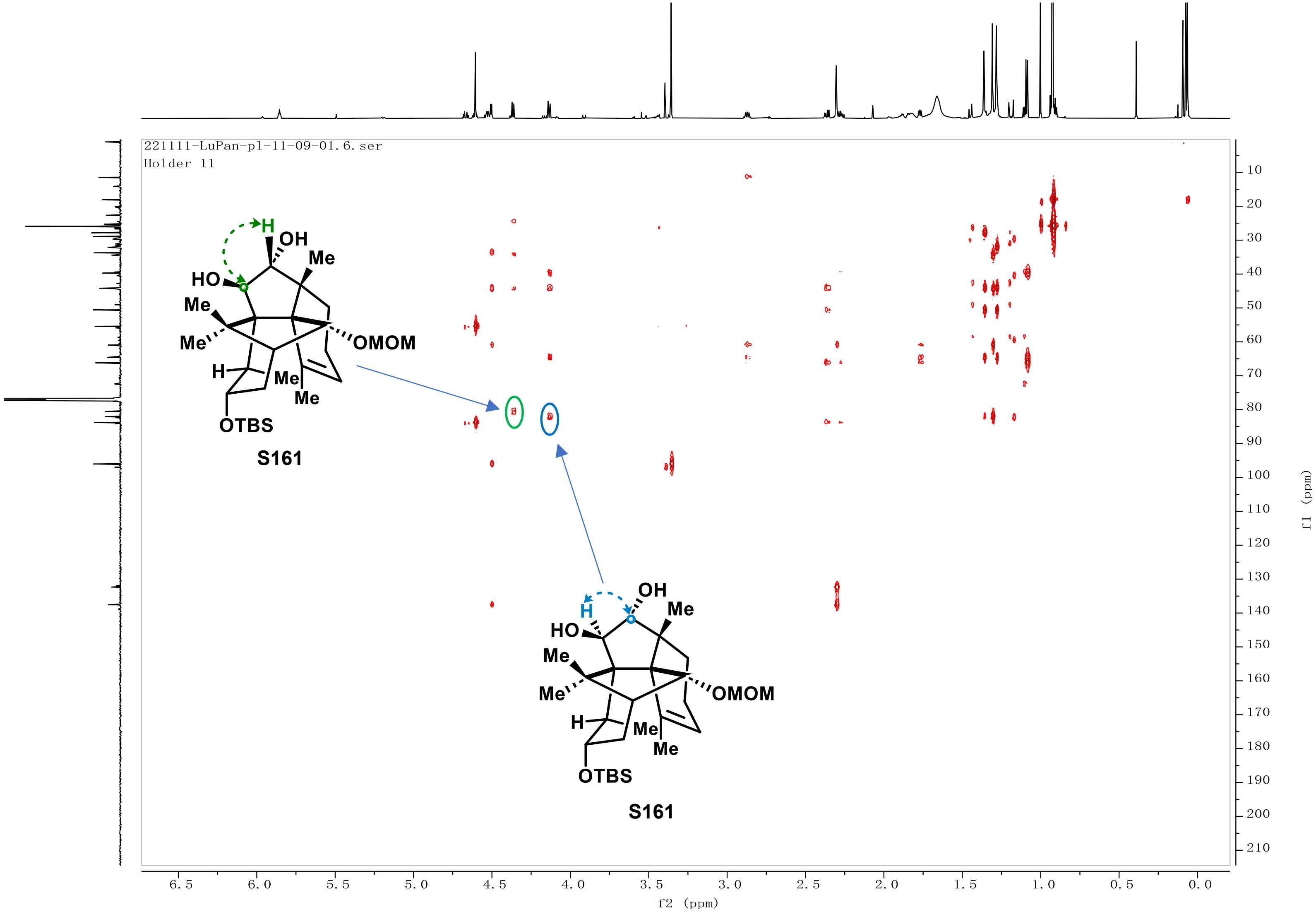
**S161**

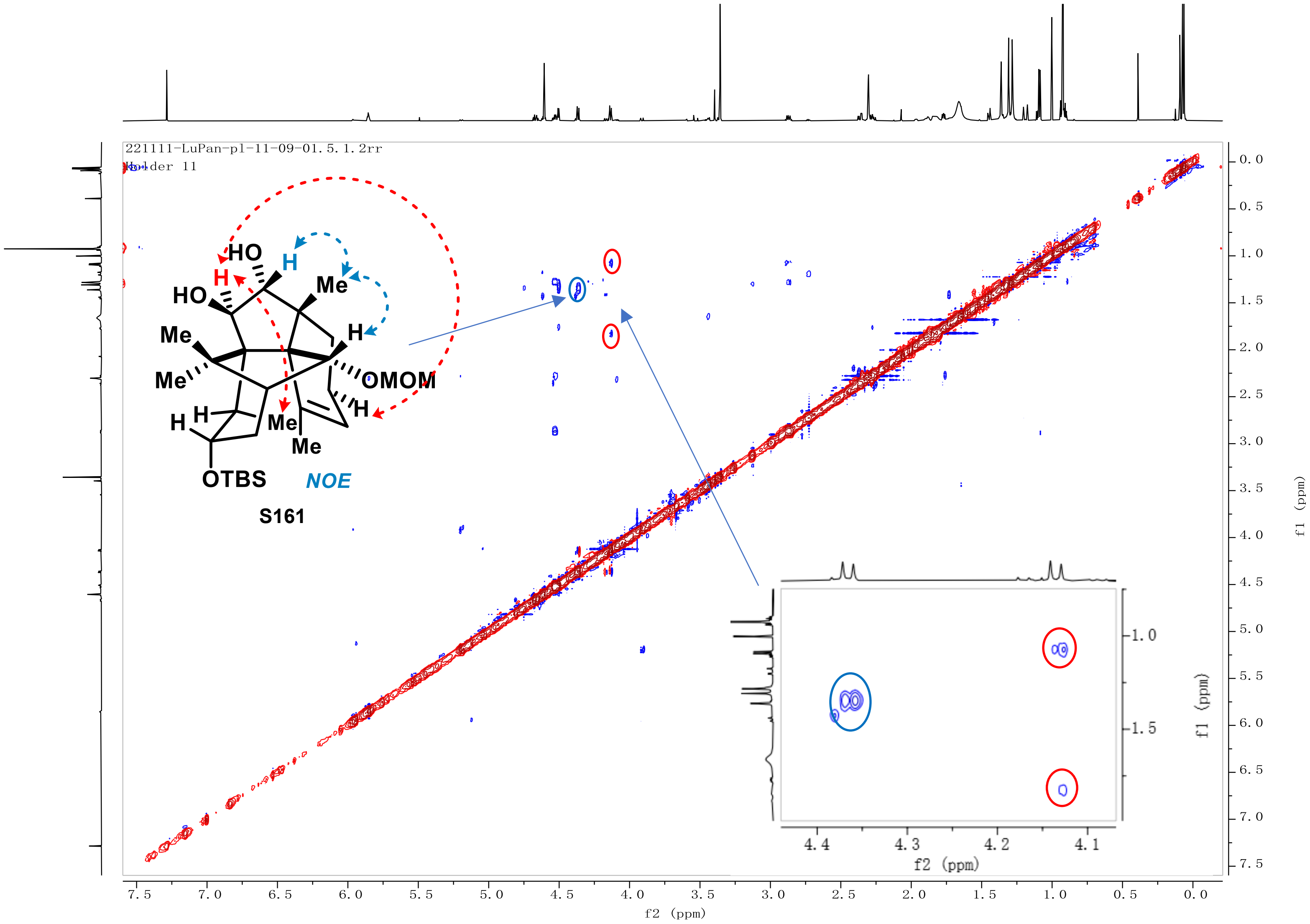

137.59
132.35
96.04
83.79
82.10
80.53
66.18
64.58
60.95
55.41
50.57
44.18
39.73
34.40
33.75
32.12
28.92
27.83
25.89
25.30
22.66
18.10
11.47
-4.37
-5.13
OH
HO
Me
Me
Me
OMOM
H
Me
Me
OTBS
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

**S161**

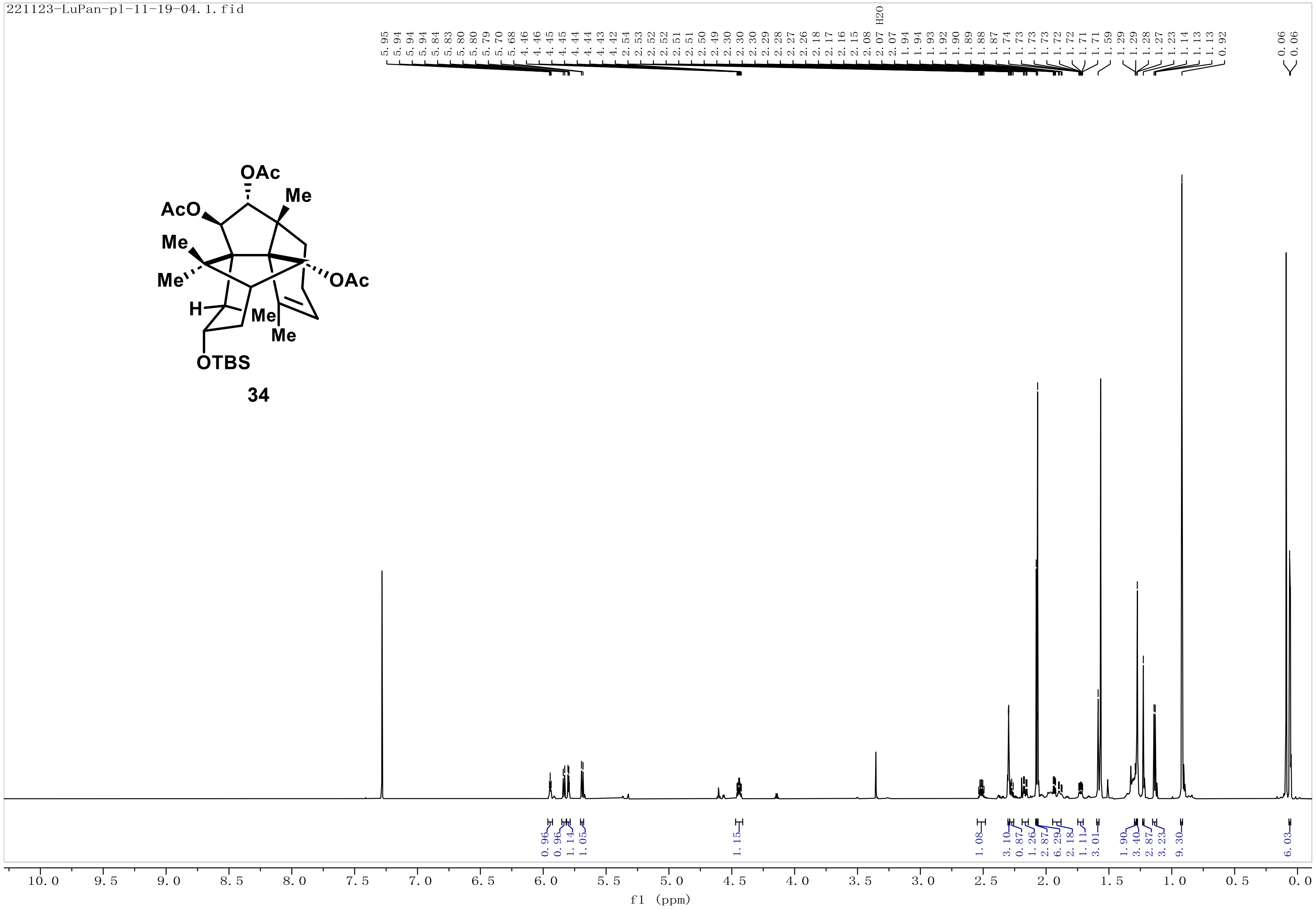

221111-LuPan-pl-11-09-01.1003.ser
Holder 11
OH
HO
19
Me
9
10
7
16 Me
2
1
OMOM
17 Me
6
12
H
Me
18
5
13
14
Me
20
OTBS
S161
20
6a6b
12
14a 14b
7a
1
MOM
13
2
9
10
MOM
5
18
19
16
17
7b
1.3
1.2
1.1
f2 (ppm)
10
20
30
40
f1 (ppm)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)

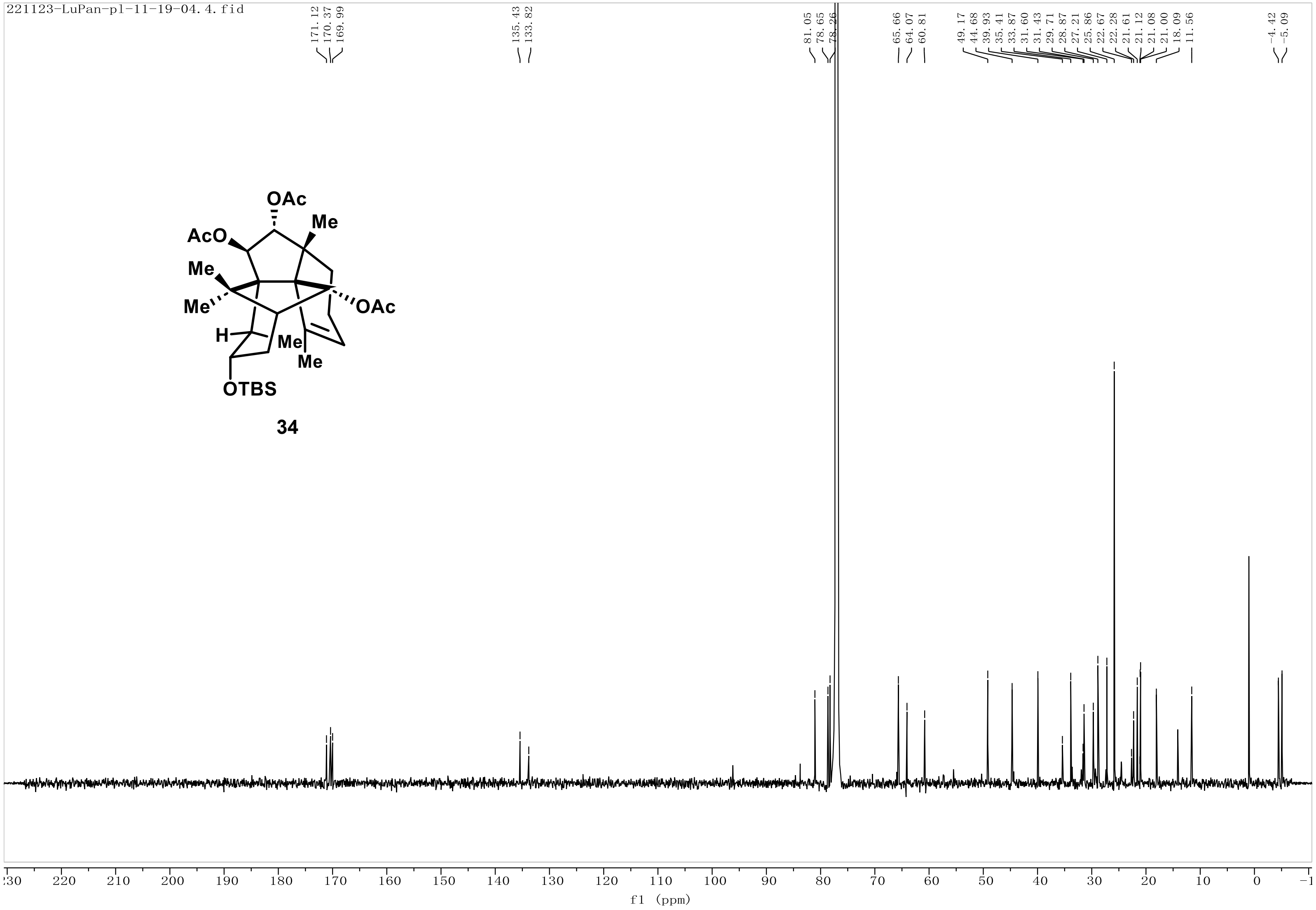

221111-LuPan-pl-11-09-01.4.ser
Holder 11
cosy
H
OH
HO
H
Me
Me
Me
OMOM
H
Me
Me
OTBS
S161
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
f1 (ppm)
4.4
4.3
4.2
4.1
f2 (ppm)
4.0
4.1
4.2
4.3
4.4
4.5
f1 (ppm)


221111-LuPan-pl-11-09-01.6.ser
Holder 11
HO
OH
H
Me
Me
Me
OMOM
H
Me
Me
OTBS
S161
S161
f2 (ppm)
f1 (ppm)
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
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210

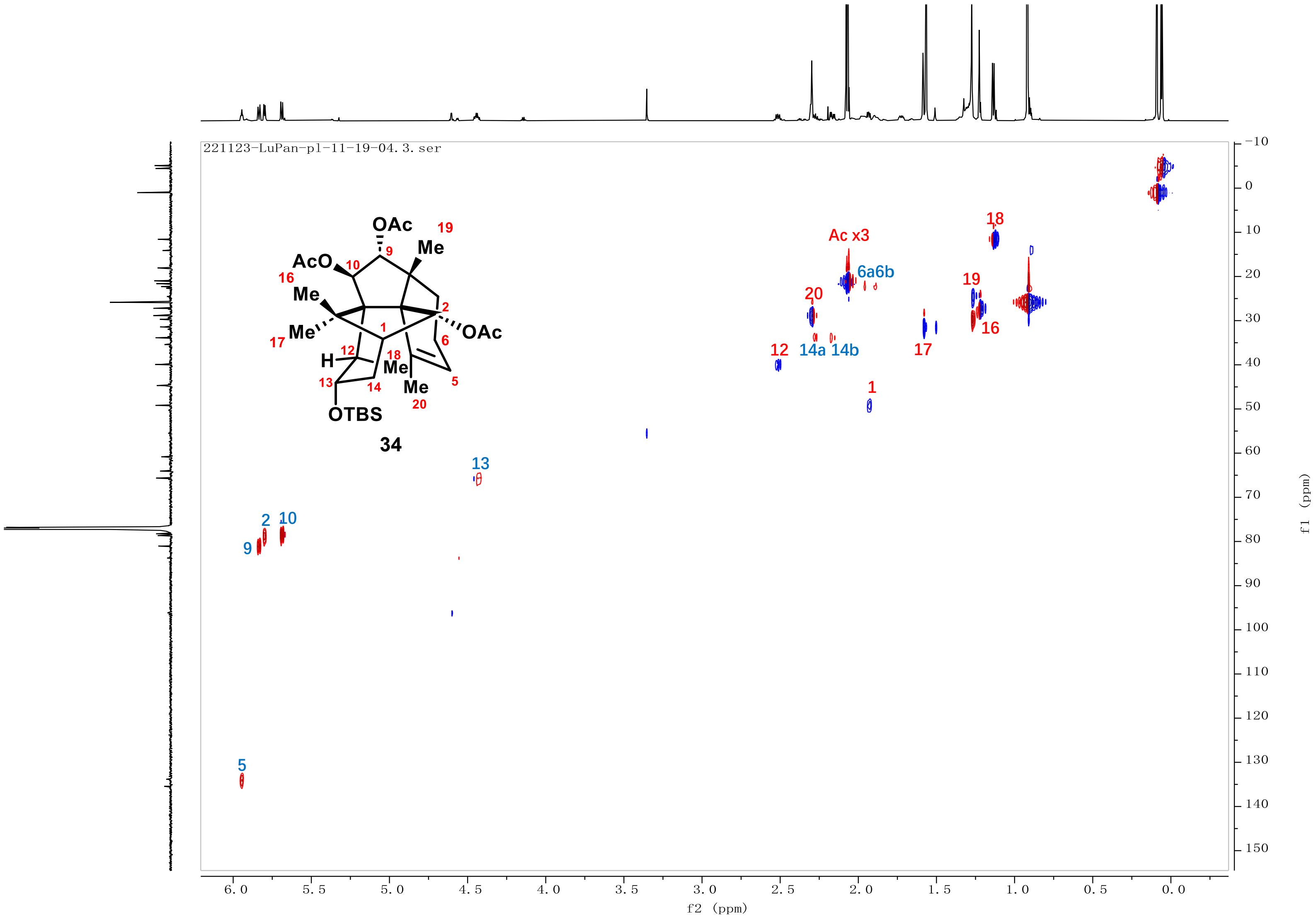


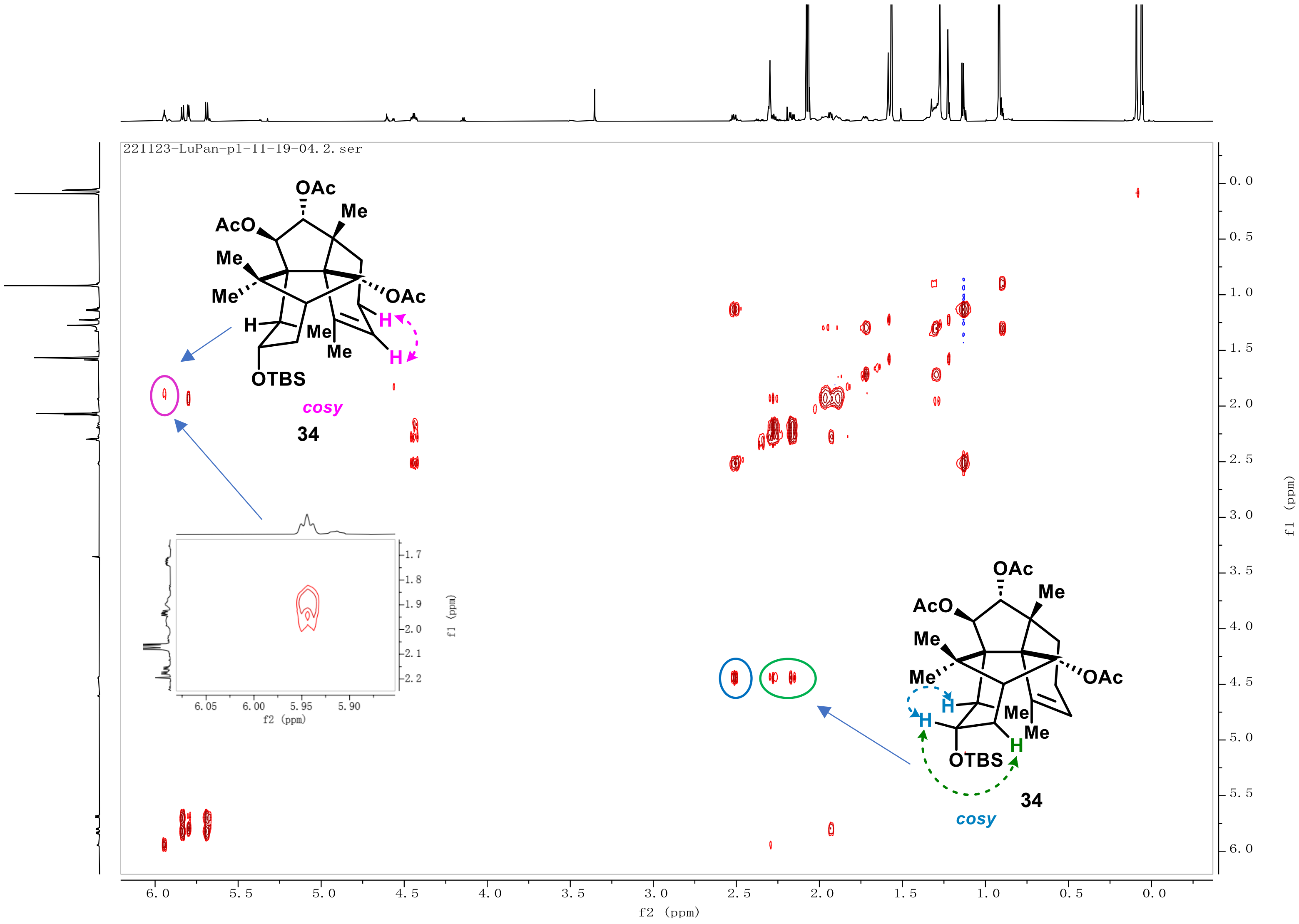
221111-LuPan-p1-11-09-01.5.1.2rr
folder 11
HO
H
H
Me
HO
Me
H
Me
OMOM
H
H H
Me
Me
OTBS
NOE
S161
4.4
4.3
4.2
4.1
f2 (ppm)
1.0
1.5
f1 (ppm)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
f1 (ppm)

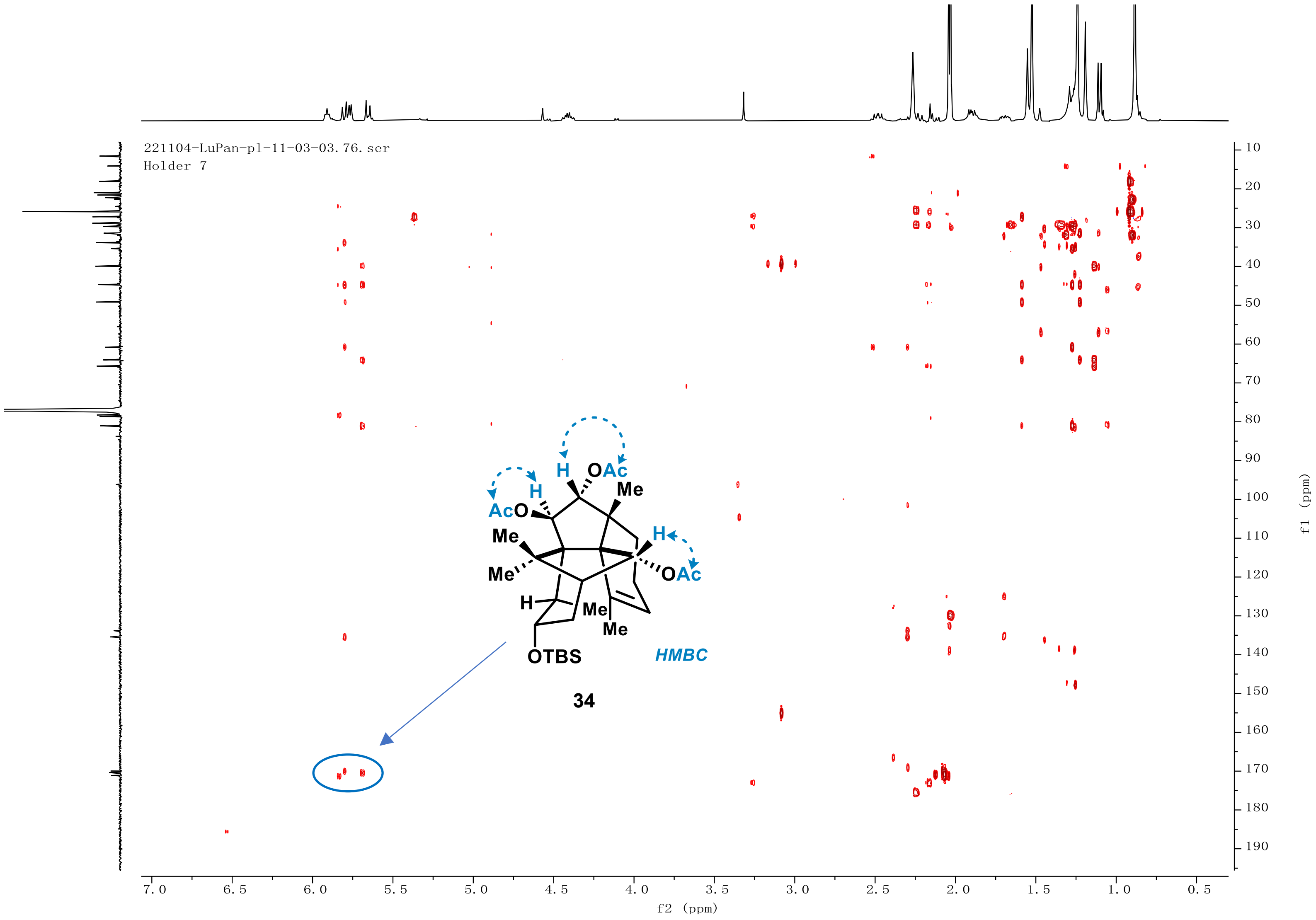

221123-LuPan-pl-11-19-04.1.fid
H2O
5.95 5.94 5.94 5.94 5.84 5.83 5.80 5.80 5.79 5.70 5.68 4.46 4.45 4.45 4.44 4.44 4.43 4.42 2.54 2.53 2.52 2.52 2.51 2.50 2.49 2.30 2.30 2.30 2.29 2.28 2.27 2.26 2.18 2.17 2.16 2.15 2.08 2.07 2.07 1.94 1.94 1.93 1.92 1.90 1.89 1.88 1.87 1.74 1.73 1.73 1.73 1.72 1.72 1.71 1.71 1.59 1.29 1.29 1.28 1.27 1.23 1.14 1.13 1.13 0.92 0.06 0.06
OAc
Me
AcO
Me
Me
OAc
H
Me
Me
OTBS
34
0.96 0.96 1.14 1.05 1.15 1.08 3.10 0.87 1.26 2.87 6.29 2.18 1.11 3.01 1.90 3.40 2.87 3.23 9.30 6.03
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
f1 (ppm)


221123-LuPan-pl-11-19-04.4.fid
171.12
170.37
169.99
135.43
133.82
81.05
78.65
78.26
65.66
64.07
60.81
49.17
44.68
39.93
35.41
33.87
31.60
31.43
29.71
28.87
27.21
25.86
22.67
22.28
21.61
21.12
21.08
21.00
18.09
11.56
-4.42
-5.09
OAc
AcO
Me
Me
Me
OAc
H
Me
Me
OTBS
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1
f1 (ppm)

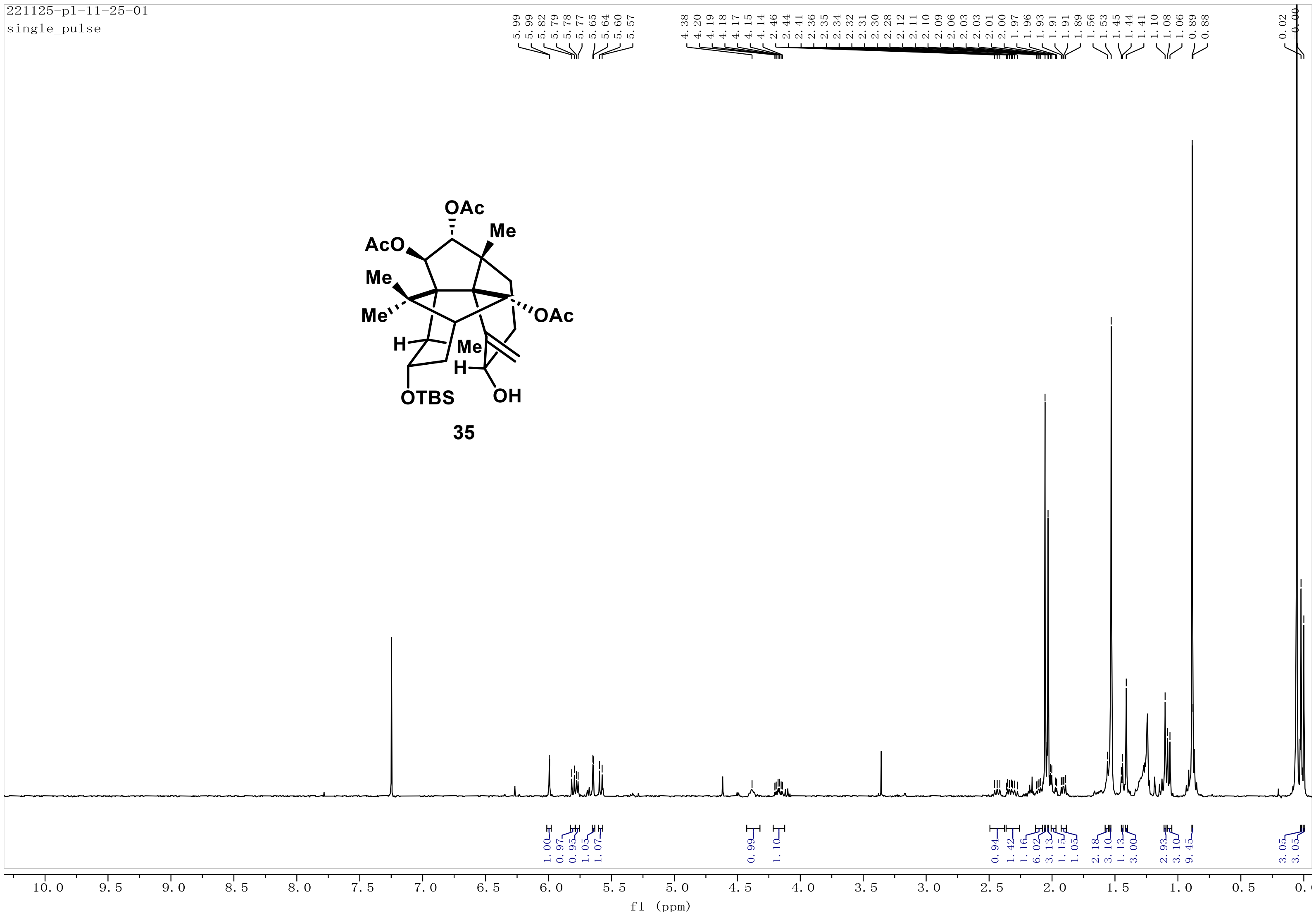
**34**


221123-LuPan-pl-11-19-04.3.ser
OAc
AcO
OAc
Me
Me
Me
Me
Me
H
OTBS
34
1
2
5
6
9
10
12
13
14
16
17
18
19
20
Ac x3
6a6b
20
19
18
12
14a
14b
17
16
1
13
2
10
9
5
f2 (ppm)
f1 (ppm)
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
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150

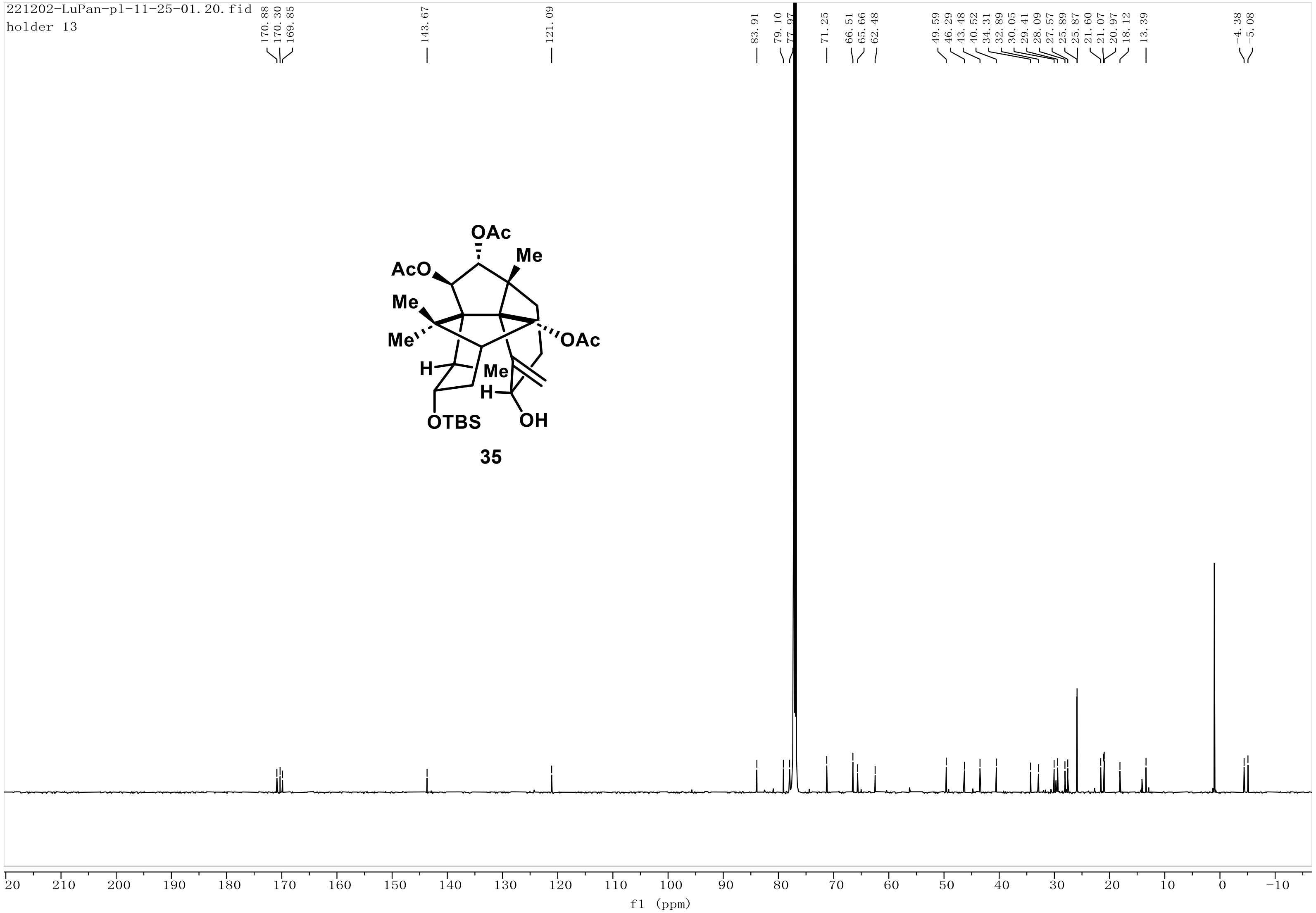

221123-LuPan-pl-11-19-04.2.ser
OAc
AcO
Me
Me
Me
OAc
H
H
H
Me
Me
OTBS
cosy
34
OAc
AcO
Me
Me
Me
OAc
H
H
H
Me
Me
OTBS
cosy
34
6.05
6.00
5.95
5.90
f2 (ppm)
1.7
1.8
1.9
2.0
2.1
2.2
f1 (ppm)
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
f1 (ppm)

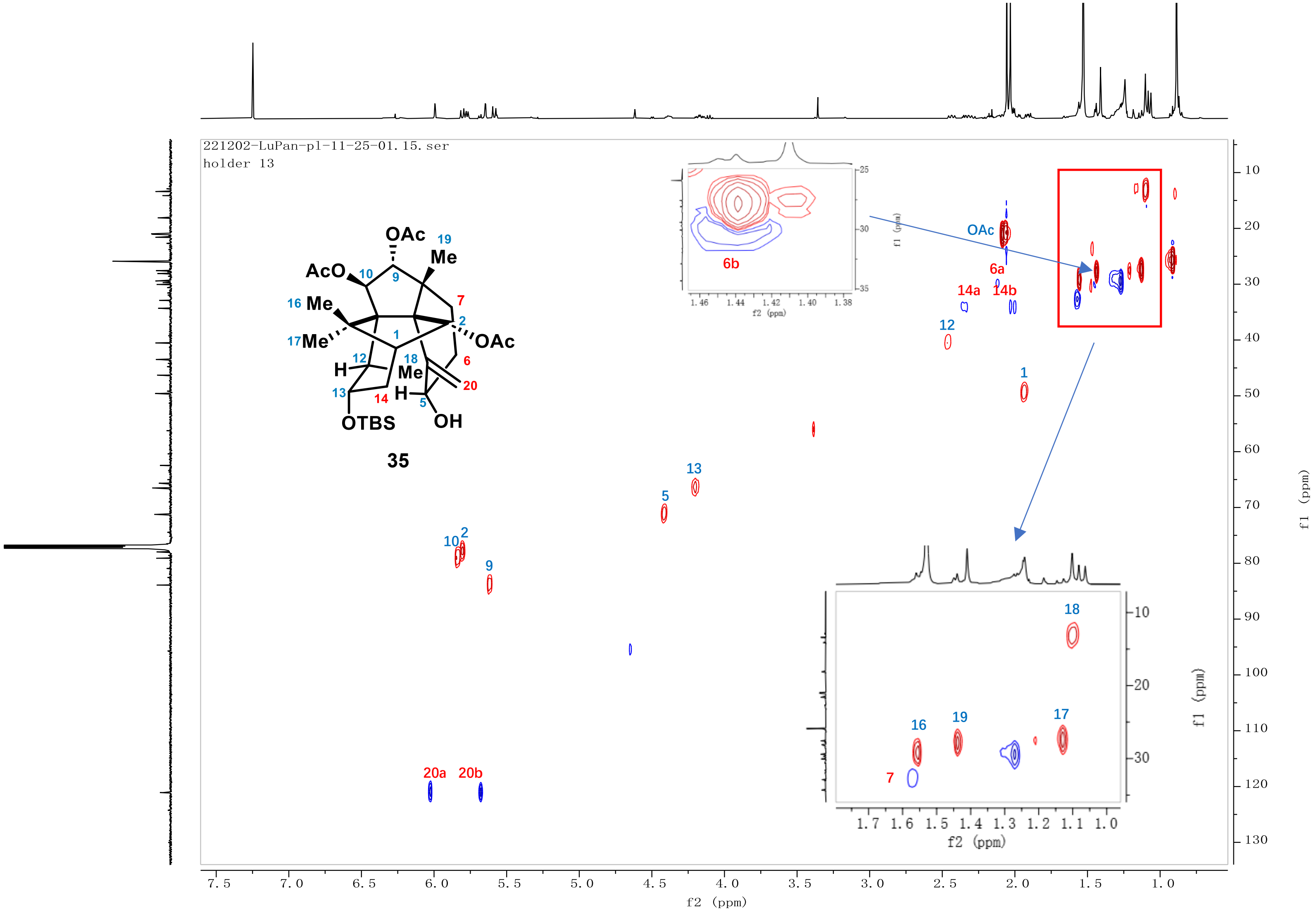

221104-LuPan-pl-11-03-03.76.ser
Holder 7
H
OAc
H
AcO
Me
Me
Me
H
OAc
H
Me
Me
OTBS
HMBC
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
f1 (ppm)

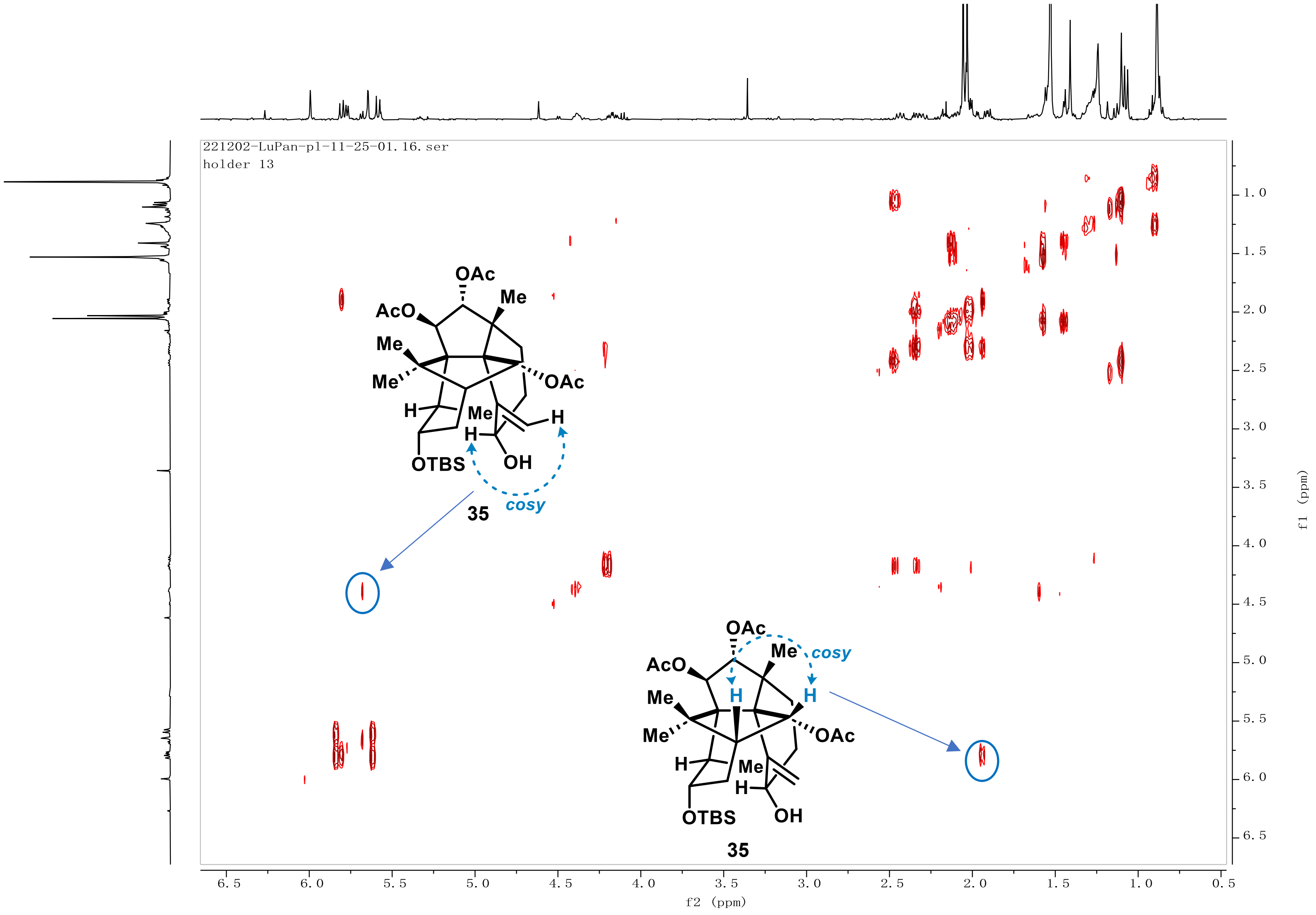
34

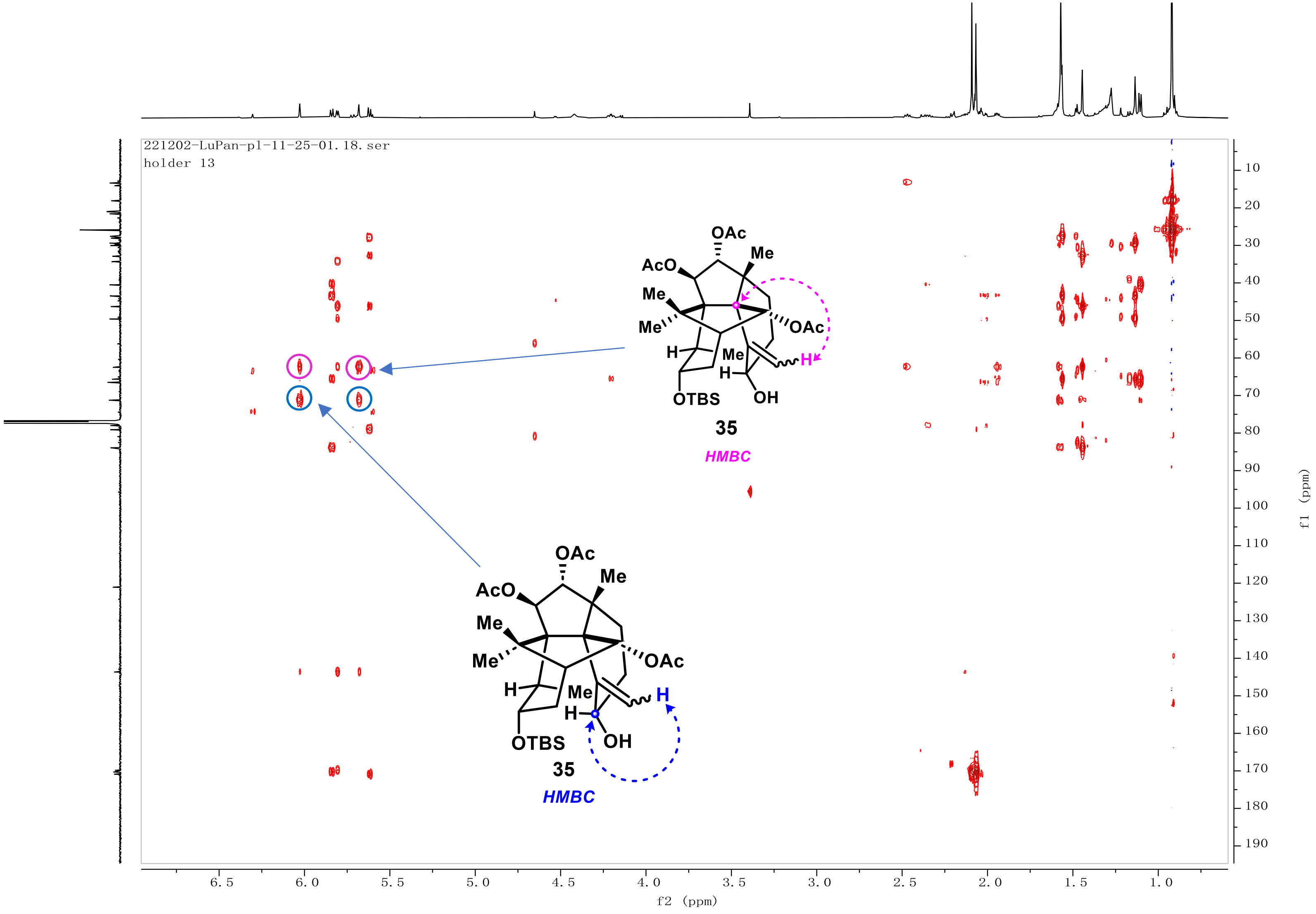

35

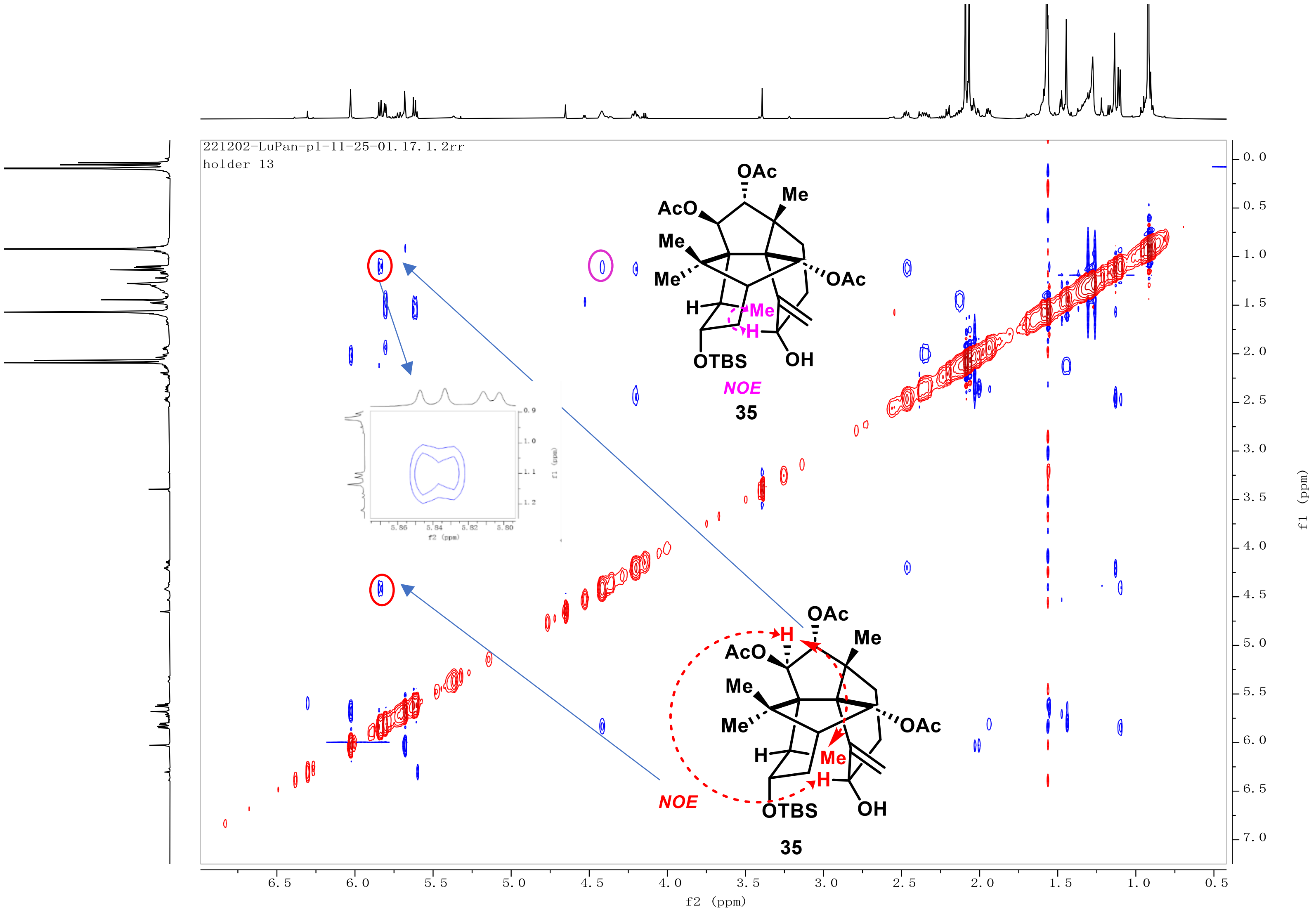
221125-pl-11-25-01
single_pulse
5.99
5.99
5.82
5.79
5.78
5.77
5.65
5.64
5.60
5.57
4.38
4.20
4.19
4.18
4.17
4.15
4.14
2.46
2.44
2.41
2.36
2.35
2.34
2.32
2.31
2.30
2.28
2.12
2.11
2.10
2.09
2.06
2.03
2.03
2.01
2.00
1.97
1.96
1.93
1.91
1.91
1.89
1.56
1.53
1.45
1.44
1.41
1.10
1.08
1.06
0.89
0.88
0.02
0.00
OAc
AcO
Me
Me
Me
OAc
H
Me
H
OTBS
OH
1.00
0.97
0.95
1.05
1.07
0.99
1.10
0.94
1.42
1.16
6.02
3.13
1.15
1.05
2.18
3.10
1.13
3.00
2.93
3.10
9.45
3.05
3.05
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
f1 (ppm)


221202-LuPan-pl-11-25-01.20.fid
holder 13
170.88
170.30
169.85
143.67
121.09
83.91
79.10
77.97
71.25
66.51
65.66
62.48
49.59
46.29
43.48
40.52
34.31
32.89
30.05
29.41
28.09
27.57
25.89
25.87
21.60
21.07
20.97
18.12
13.39
-4.38
-5.08
OAc
AcO
Me
Me
Me
OAc
H
Me
H
OTBS
OH
35
20
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)

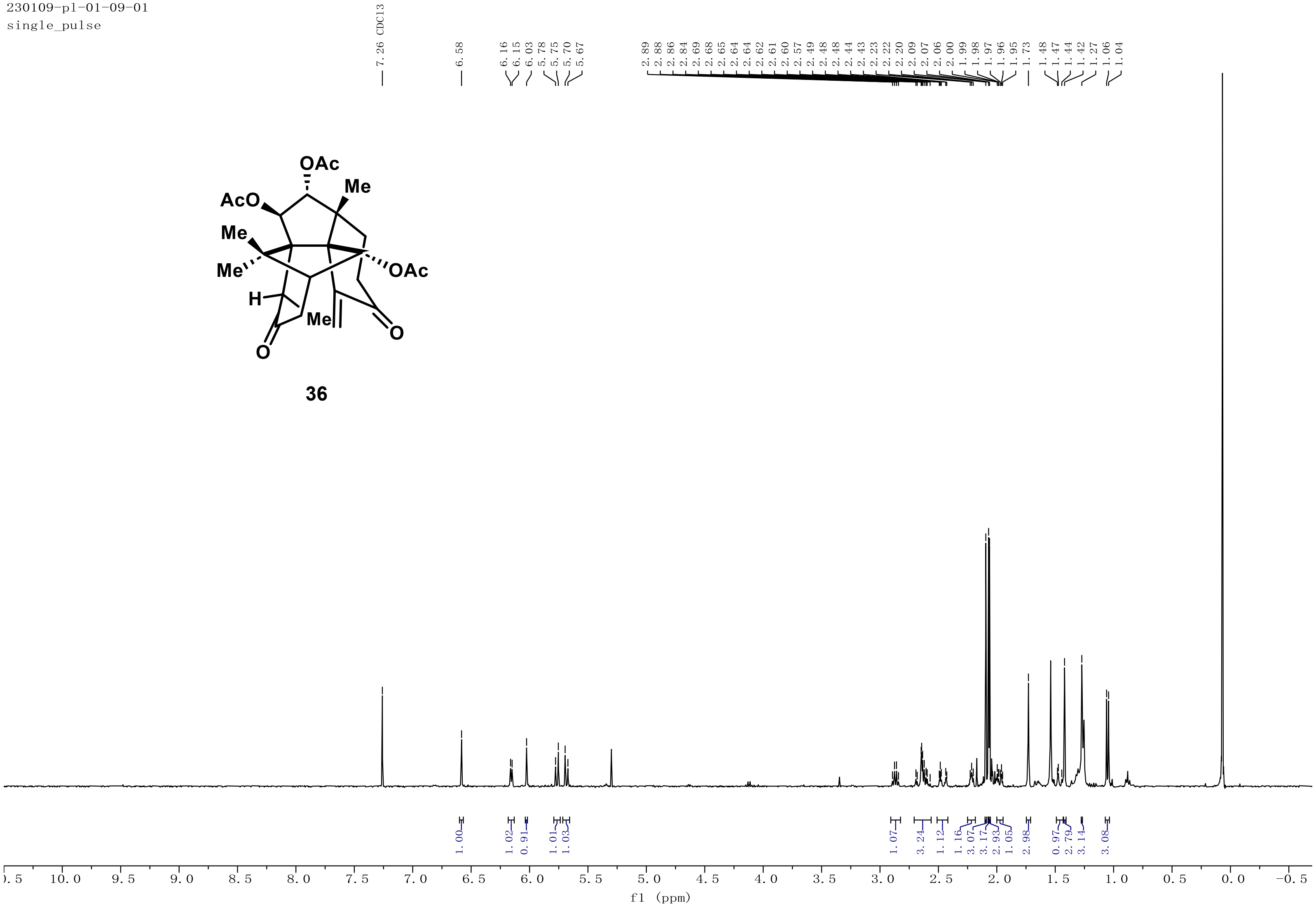

221202-LuPan-pl-11-25-01.15.ser
holder 13
OAc
AcO
Me
OTBS
OH
H
1
2
5
6
7
9
10
12
13
14
16
17
18
19
20
35
OAc
6a
6b
14a
14b
12
1
13
5
10
2
9
20a
20b
18
16
19
17
7
f2 (ppm)
f1 (ppm)


221202-LuPan-pl-11-25-01.16.ser
holder 13
OAc
AcO
Me
Me
Me
OAc
H
Me
H
H
OTBS
OH
cosy
35
OAc
Me
cosy
AcO
Me
H
H
Me
OAc
H
Me
H
OTBS
OH
35
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
f2 (ppm)
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
f1 (ppm)


221202-LuPan-p1-11-25-01.18.ser
holder 13
OAc
AcO
Me
Me
Me
OAc
H
Me
H
OTBS
OH
H
35
HMBC
OAc
AcO
Me
Me
Me
OAc
H
Me
H
OTBS
OH
H
35
HMBC
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
f1 (ppm)


221202-LuPan-pl-11-25-01. 17. 1. 2rr
holder 13
OAc
Me
AcO
Me
Me
OAc
H
Me
H
OTBS
OH
NOE
35
OAc
H
Me
AcO
Me
Me
OAc
H
Me
H
OTBS
OH
NOE
35
f2 (ppm)
f1 (ppm)
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
7.0
5.86
5.84
5.82
5.80
0.9
1.0
1.1
1.2

230109-p1-01-09-01
single_pulse



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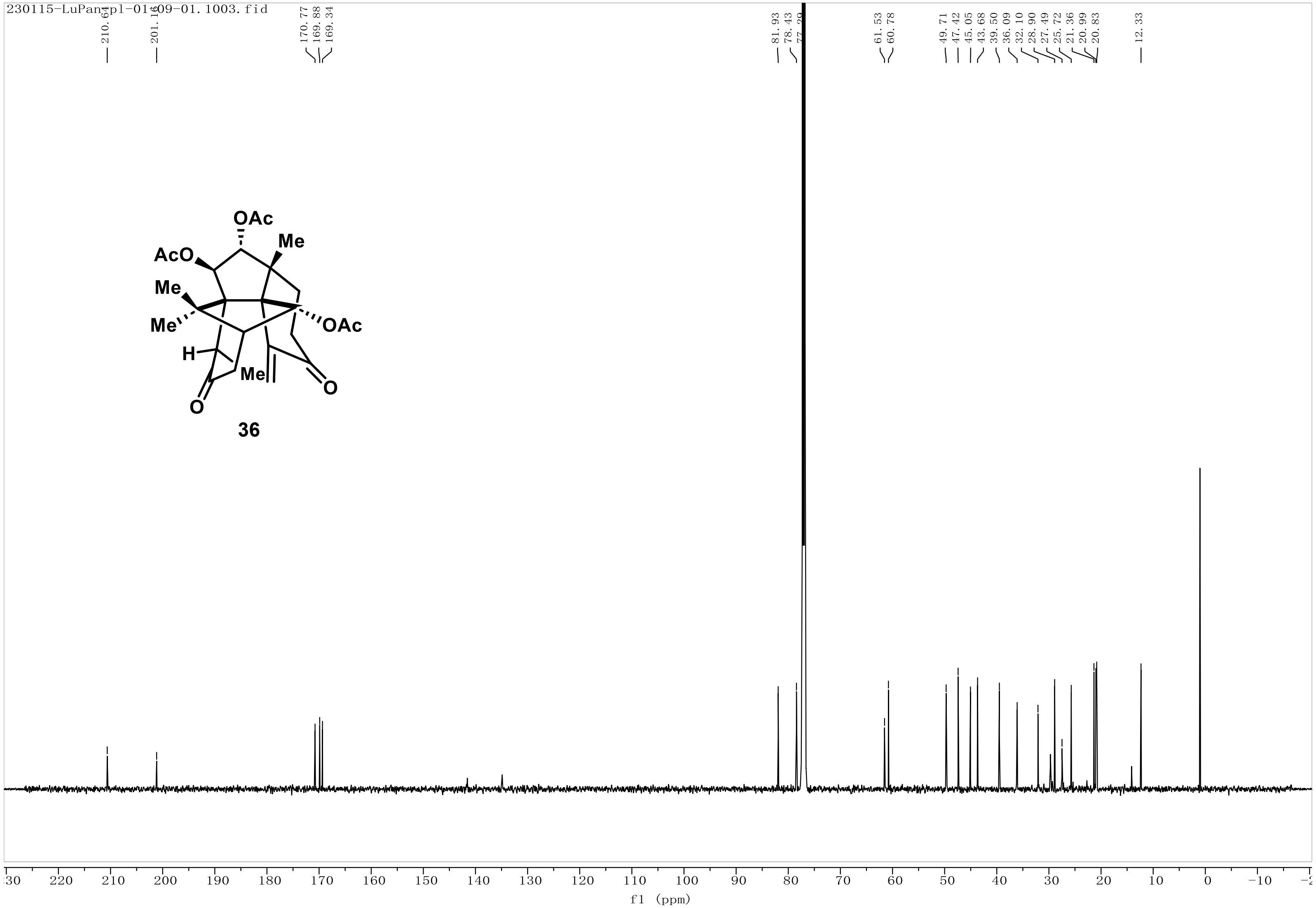
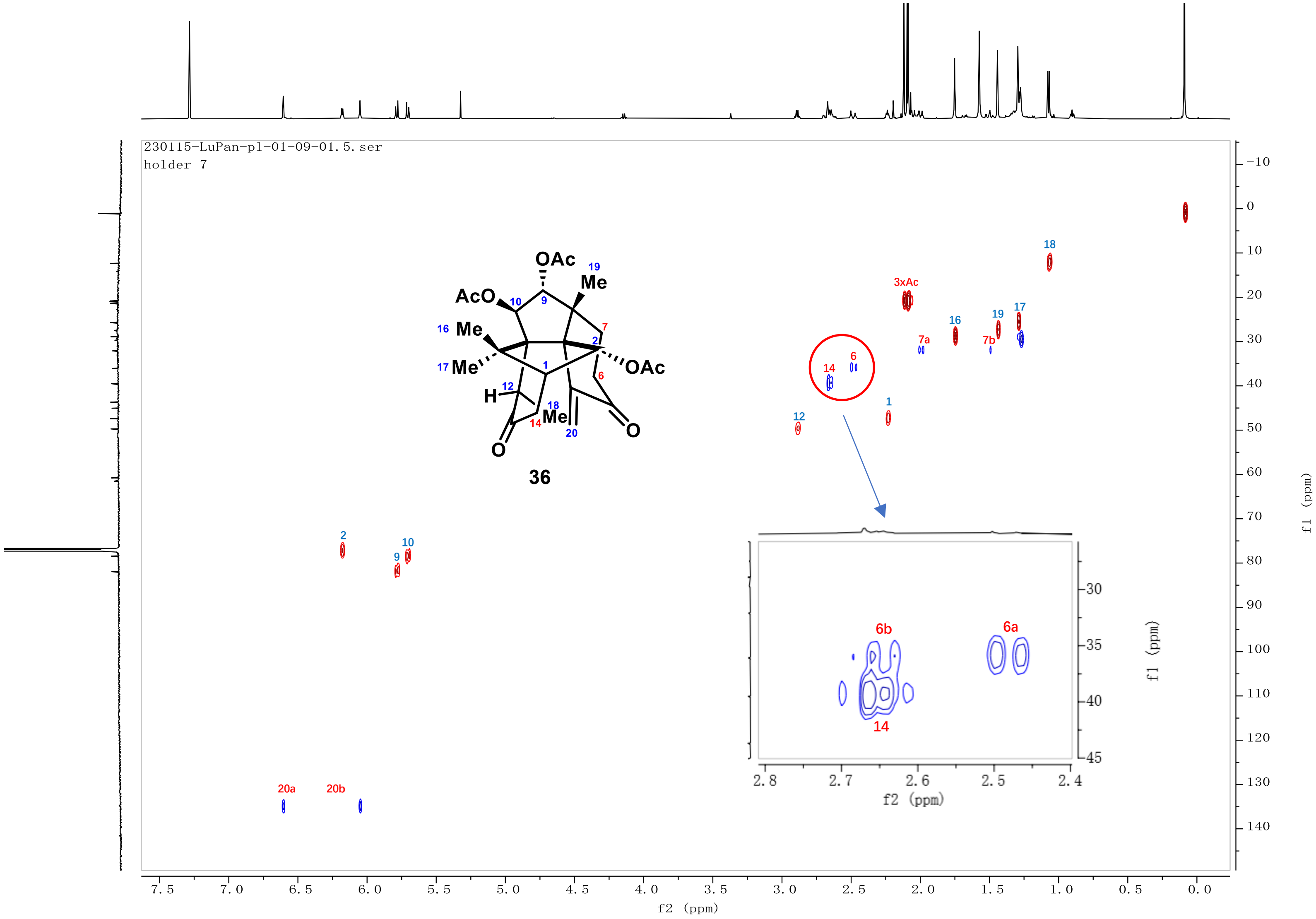
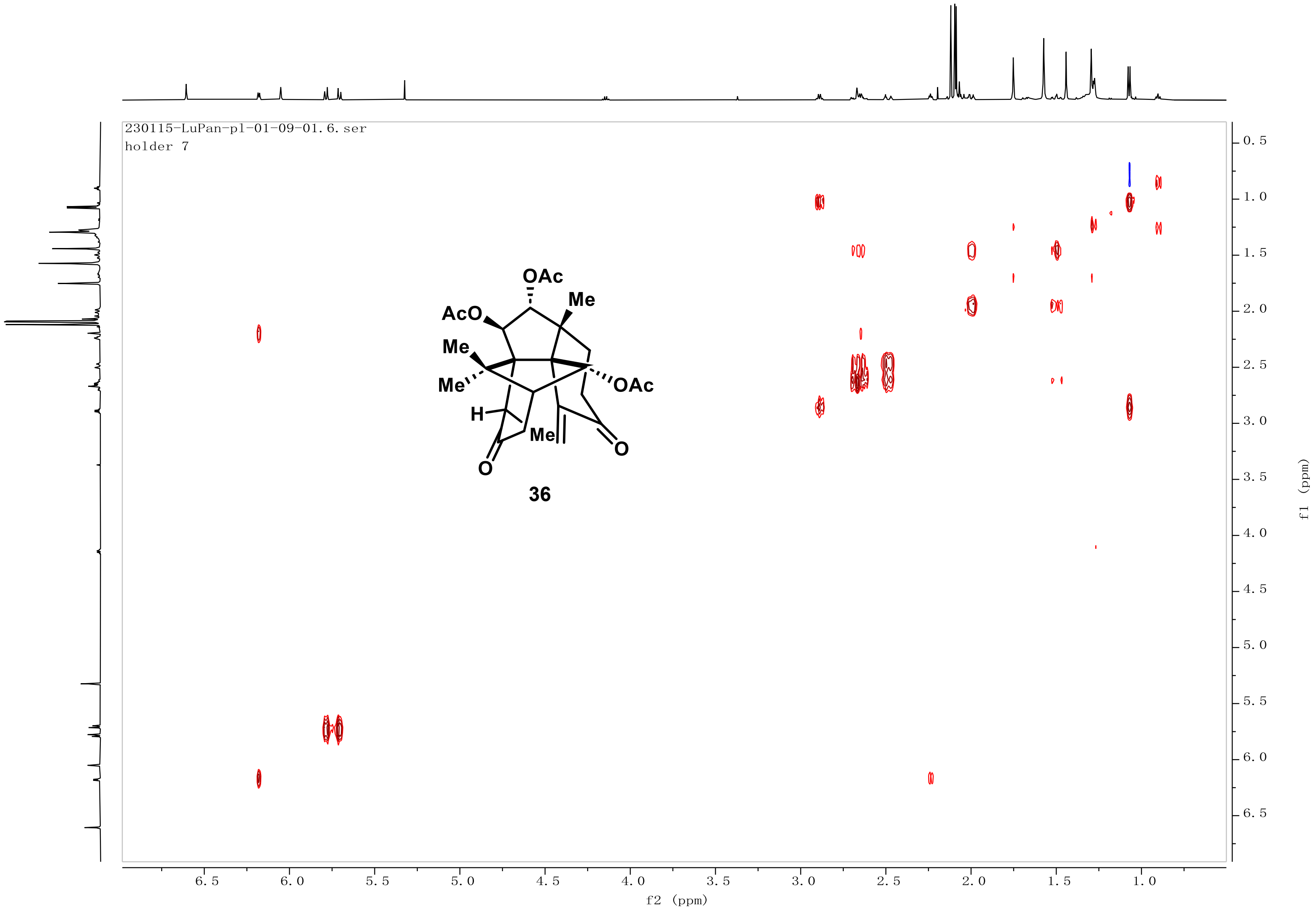
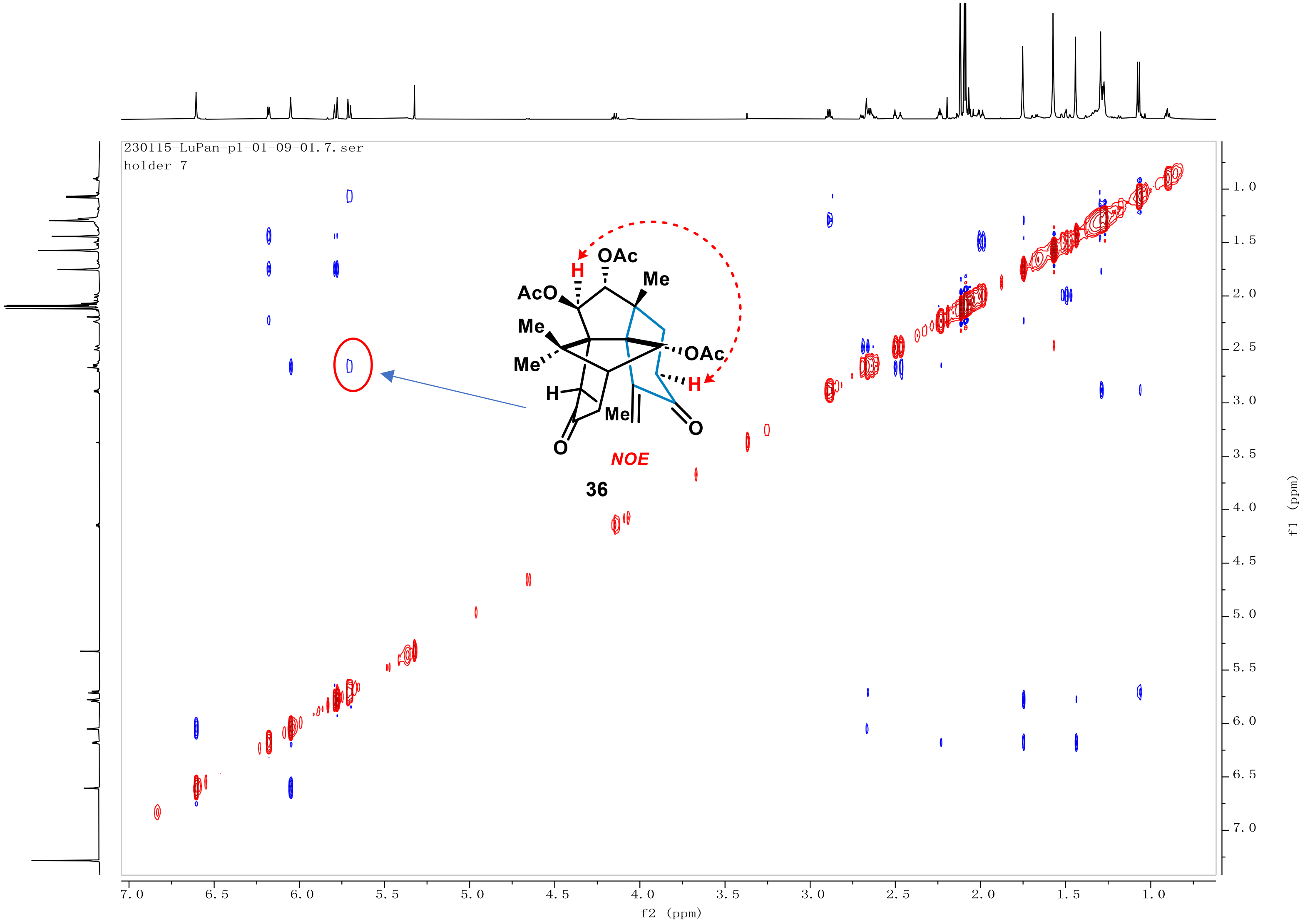

230115-LuPan-pl-01-09-01.1003.fid
210.64
201.16
170.77
169.88
169.34
81.93
78.43
77.29
61.53
60.78
49.71
47.42
45.05
43.68
39.50
36.09
32.10
28.90
27.49
25.72
21.36
20.99
20.83
12.33
OAc
Me
AcO
Me
Me
OAc
H
Me
O
O
36
30
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−2
f1 (ppm)

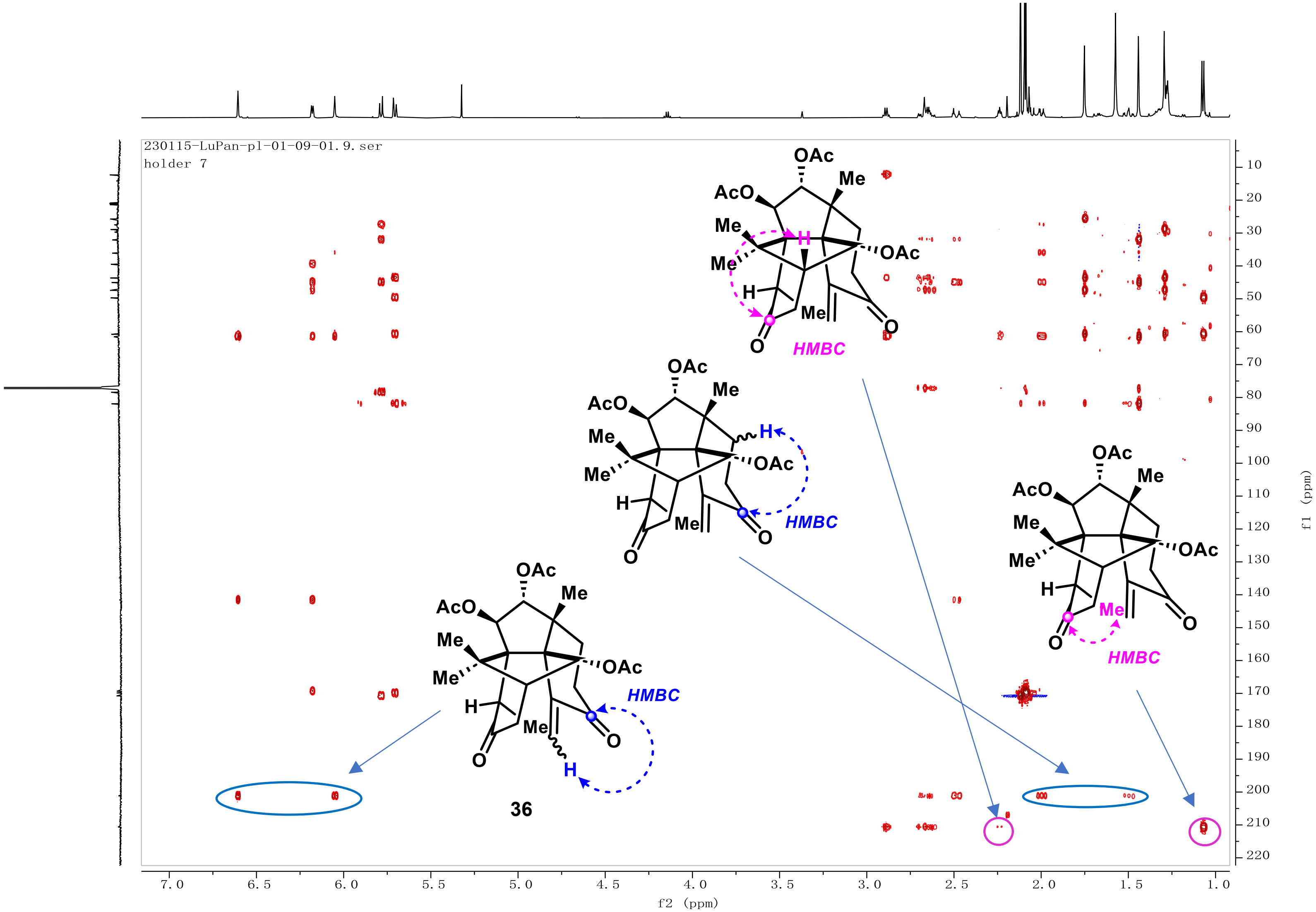

230115-LuPan-pl-01-09-01.5.ser
holder 7
OAc
19
Me
AcO
10
9
16
Me
7
2
17
Me
OAc
12
1
6
H
18
Me
14
20
O
O
36
18
3xAc
16
19
17
7a
7b
14
6
1
12
2
10
9
20a
20b
6b
6a
14
2.8
2.7
2.6
2.5
2.4
f2 (ppm)
30
35
40
45
f1 (ppm)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
f1 (ppm)


230115-LuPan-p1-01-09-01.6.ser
holder 7
OAc
AcO
Me
Me
Me
OAc
H
Me
O
O
f2 (ppm)
f1 (ppm)
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

36


230115-LuPan-p1-01-09-01.7.ser
holder 7
OAc
H
Me
AcO
Me
Me
OAc
H
H
Me
O
O
NOE
f2 (ppm)
f1 (ppm)
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

36



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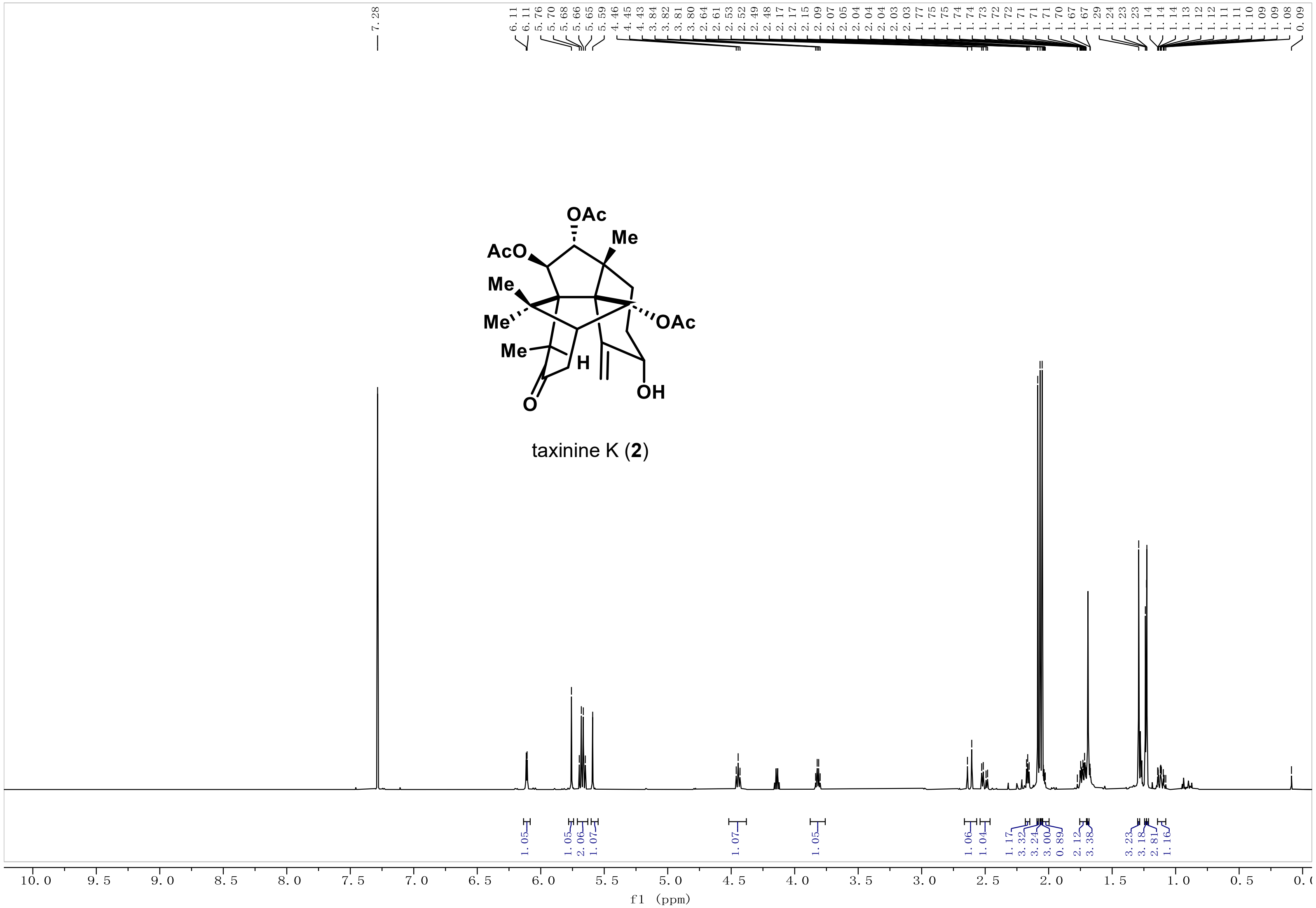
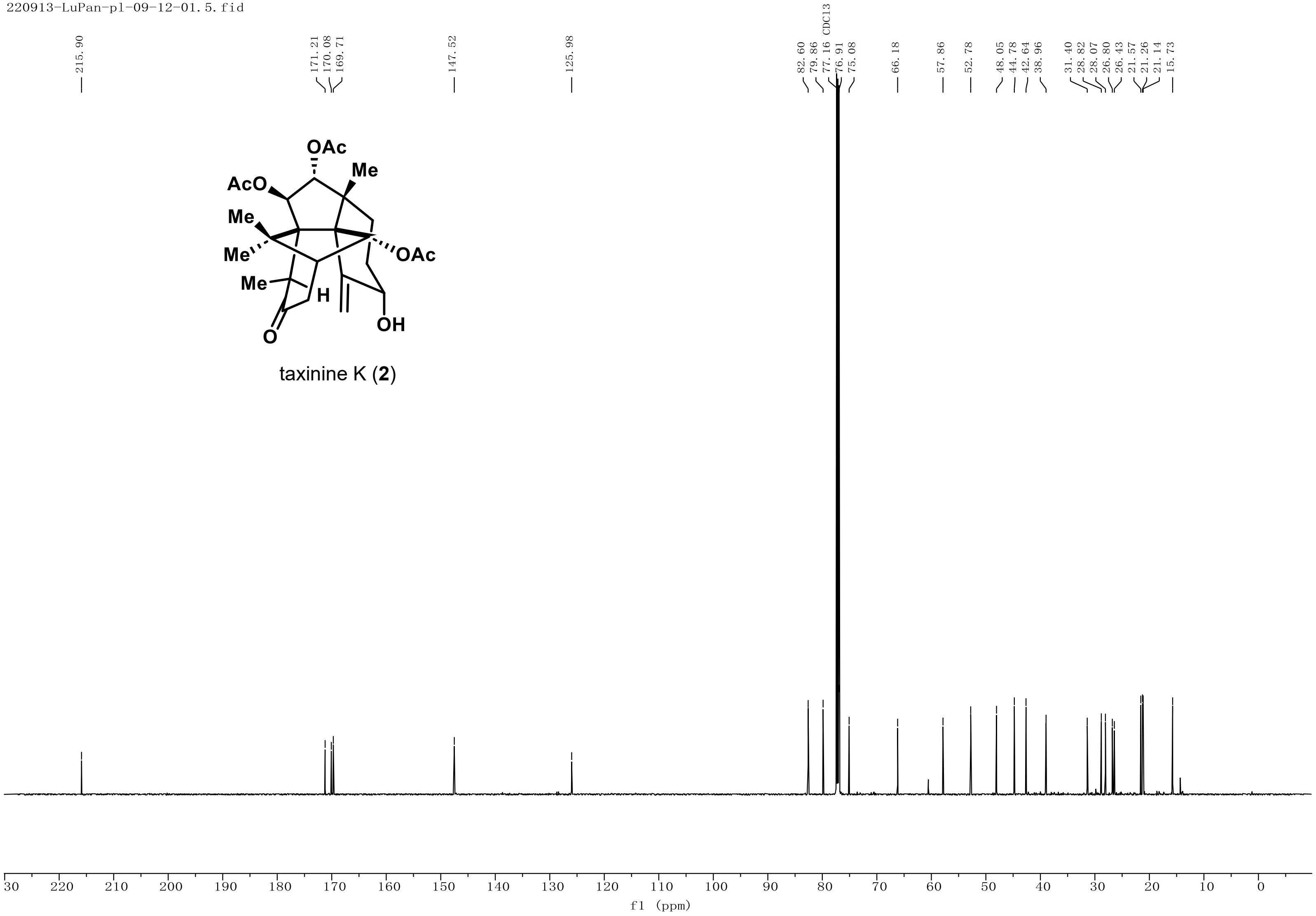
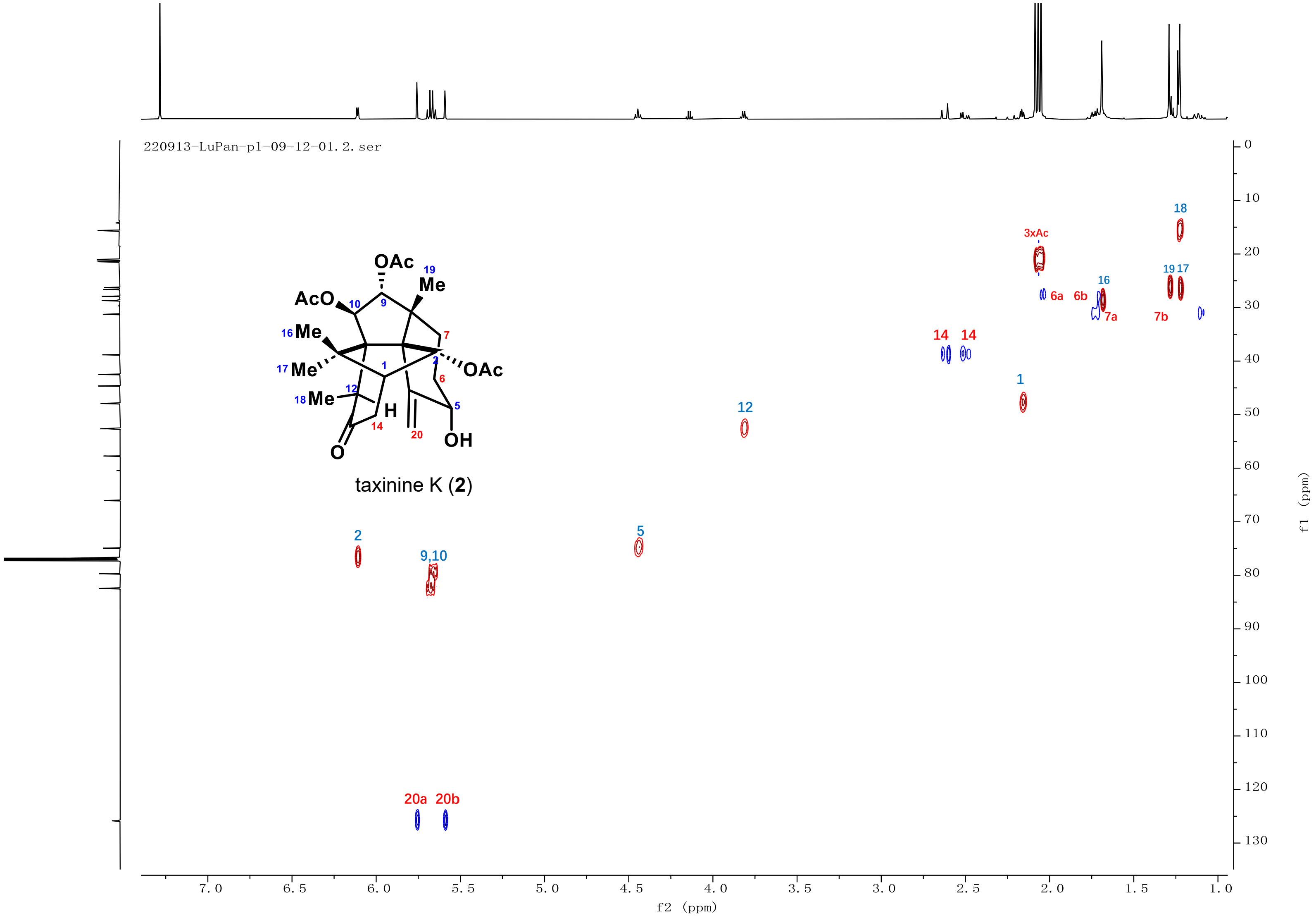
230115-LuPan-p1-01-09-01.9.ser
holder 7
OAc
AcO
Me
H
O
HMBC
f2 (ppm)
f1 (ppm)
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220

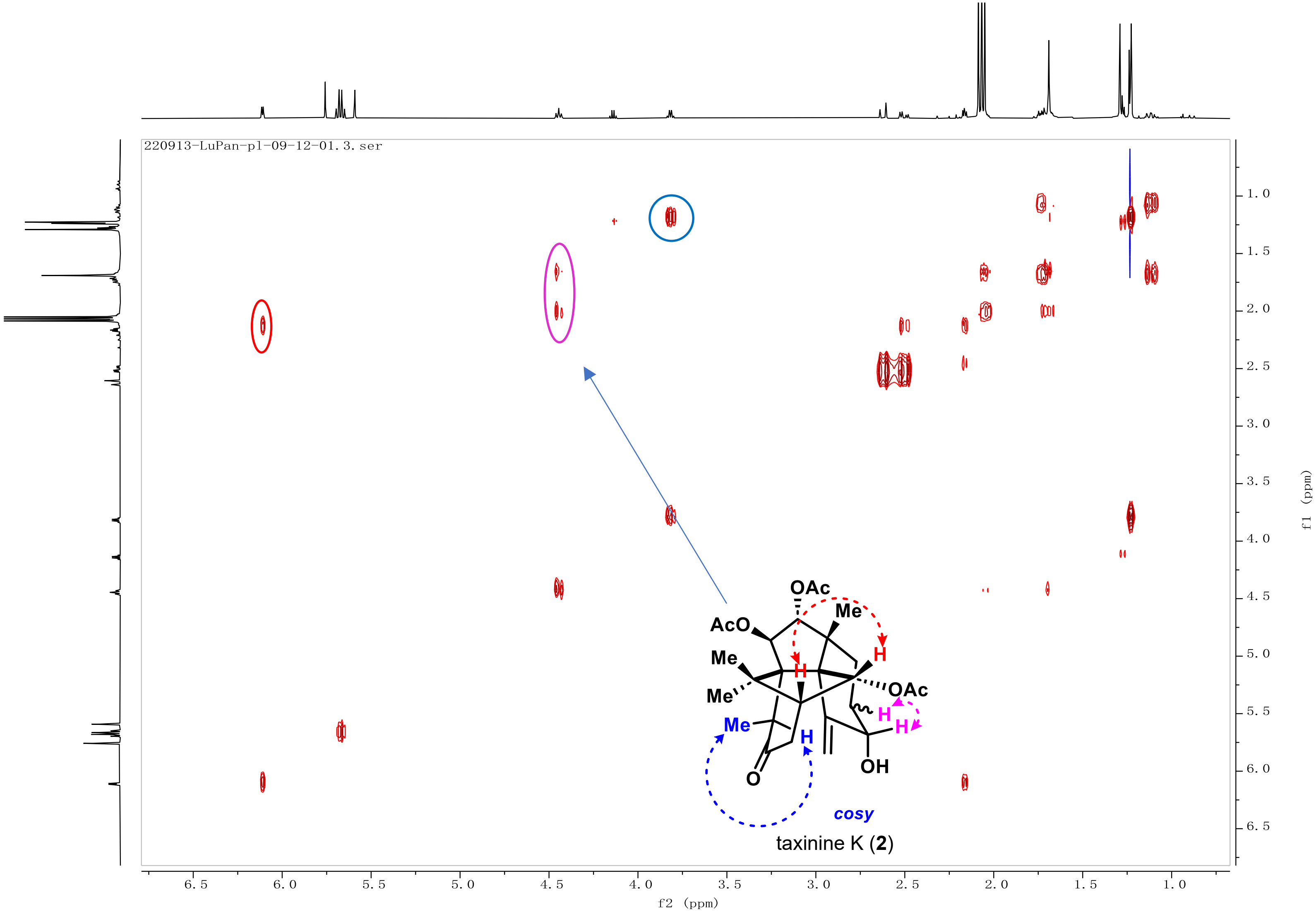

7.28
6.11
6.11
5.76
5.70
5.68
5.66
5.65
5.59
4.46
4.45
4.43
3.84
3.82
3.81
3.80
2.64
2.61
2.53
2.52
2.49
2.48
2.17
2.17
2.15
2.09
2.07
2.05
2.04
2.04
2.04
2.03
2.03
1.77
1.75
1.75
1.74
1.74
1.73
1.73
1.72
1.72
1.71
1.71
1.71
1.71
1.70
1.67
1.29
1.24
1.23
1.23
1.14
1.14
1.14
1.13
1.12
1.12
1.11
1.11
1.10
1.09
1.09
1.08
0.09
OAc
Me
AcO
Me
Me
OAc
Me
H
O
OH
1.05
1.05
2.06
1.07
1.07
1.05
1.06
1.04
1.17
3.32
3.24
3.00
0.89
2.12
3.38
3.23
3.18
2.81
1.16
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
f1 (ppm)

taxinine K (**2**)

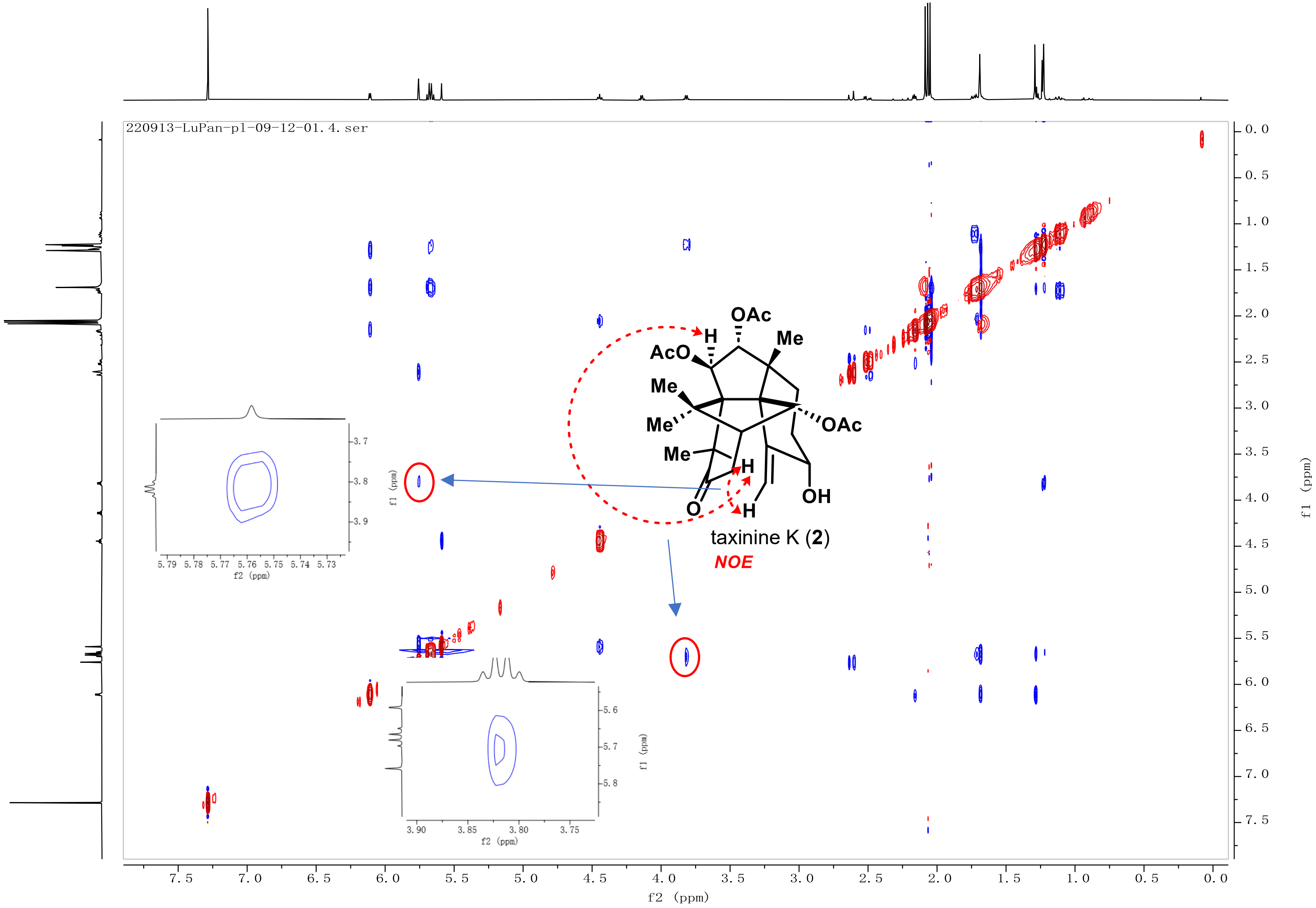

220913-LuPan-pl-09-12-01.5.fid
215.90
171.21
170.08
169.71
147.52
125.98
82.60
79.86
77.16 CDCl3
76.91
75.08
66.18
57.86
52.78
48.05
44.78
42.64
38.96
31.40
28.82
28.07
26.80
26.43
21.57
21.26
21.14
15.73
OAc
Me
AcO
Me
Me
OAc
Me
H
O
OH
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

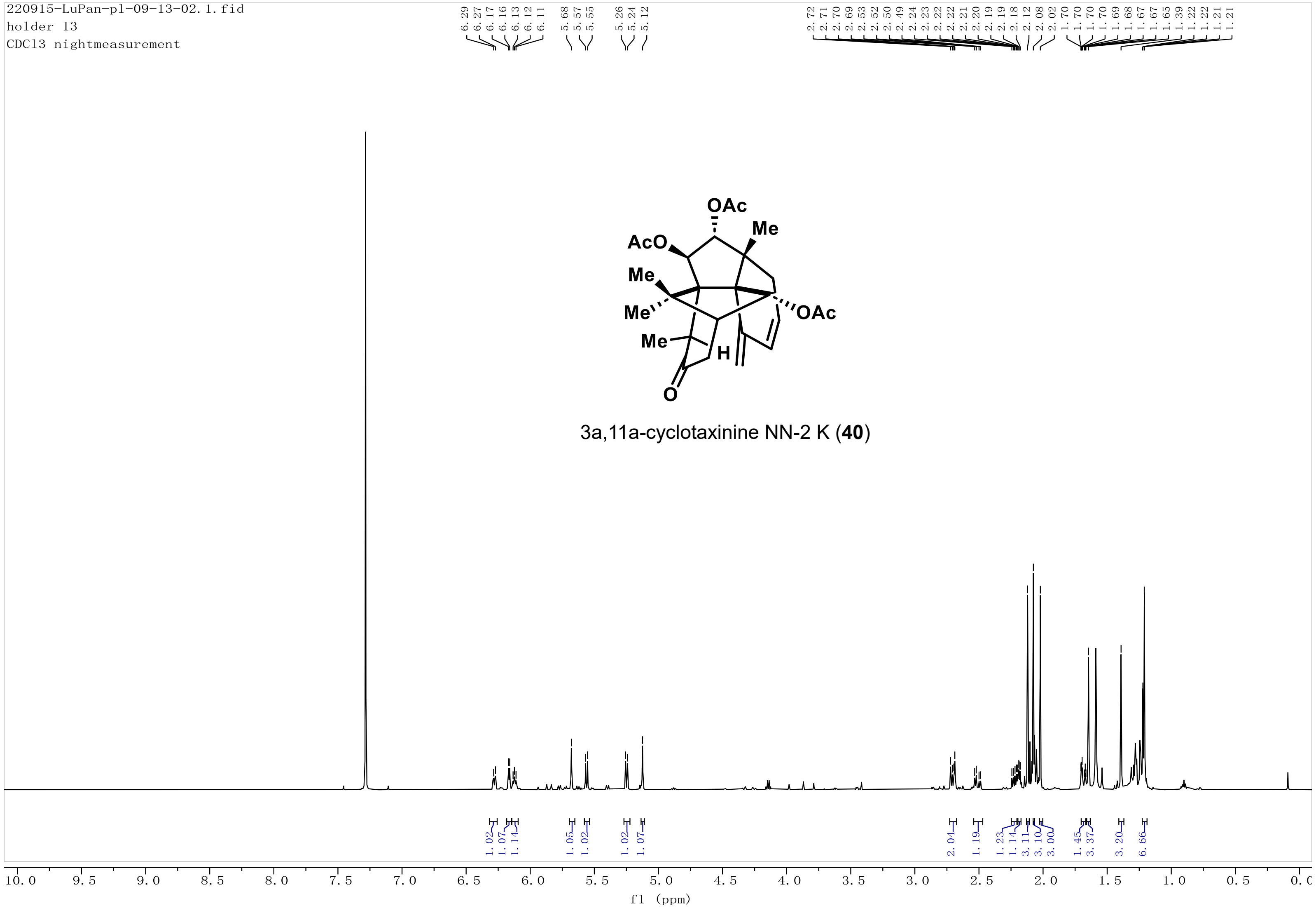
taxinine K (**2**)


220913-LuPan-p1-09-12-01.2.ser
taxinine K (2)
OAc
19
Me
AcO
10
9
16 Me
17 Me
18 Me
12
1
7
OAc
6
5
H
14
20
OH
O
18
3xAc
16
19 17
6a 6b
7a 7b
14 14
1
12
2
5
9,10
20a 20b
f2 (ppm)
f1 (ppm)
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 10 20 30 40 50 60 70 80 90 100 110 120 130

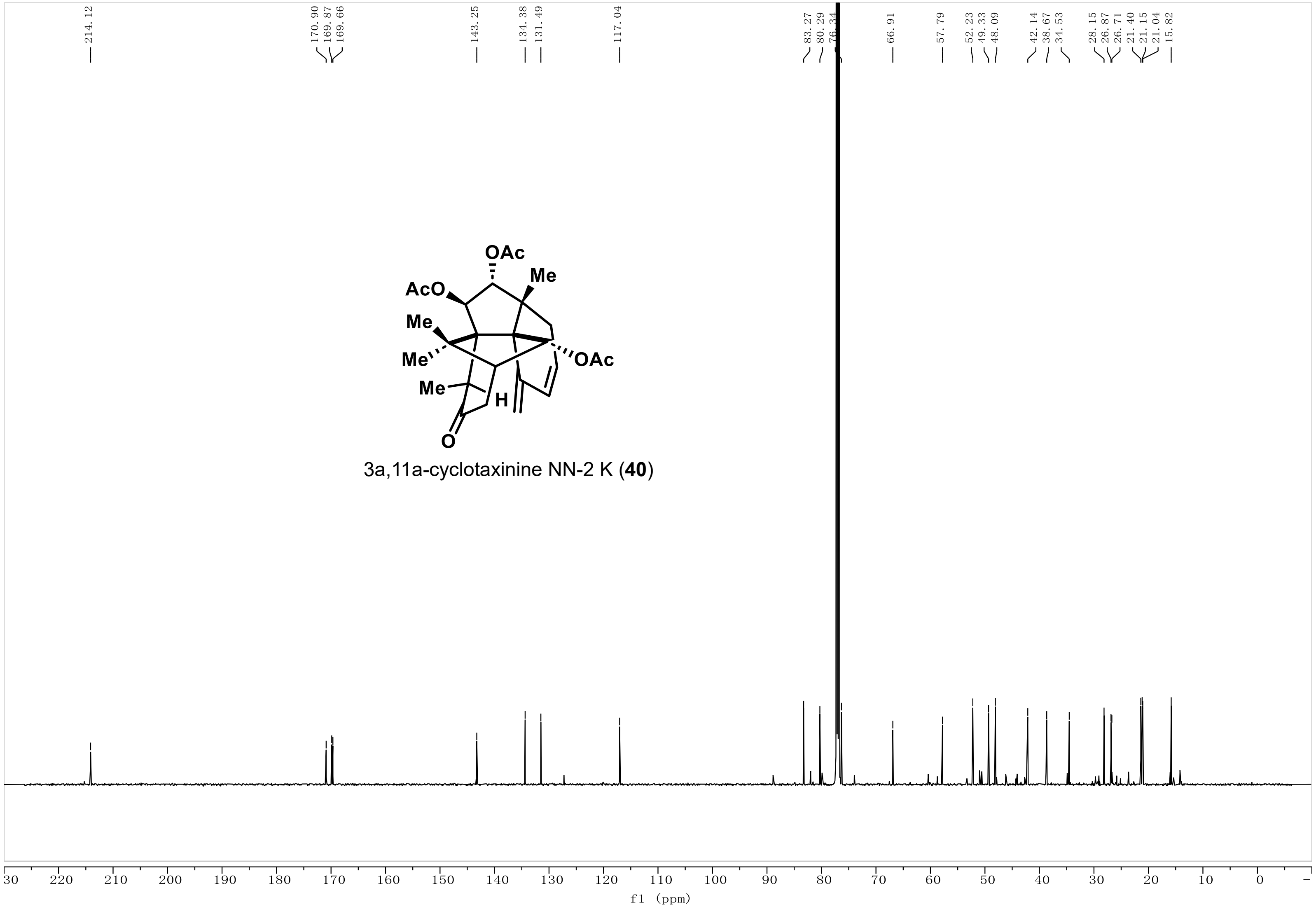


220913-LuPan-p1-09-12-01.3.ser
f2 (ppm)
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
OAc
AcO
Me
H
Me
H
Me
OAc
Me
H
H
H
O
OH
cosy
taxinine K (2)

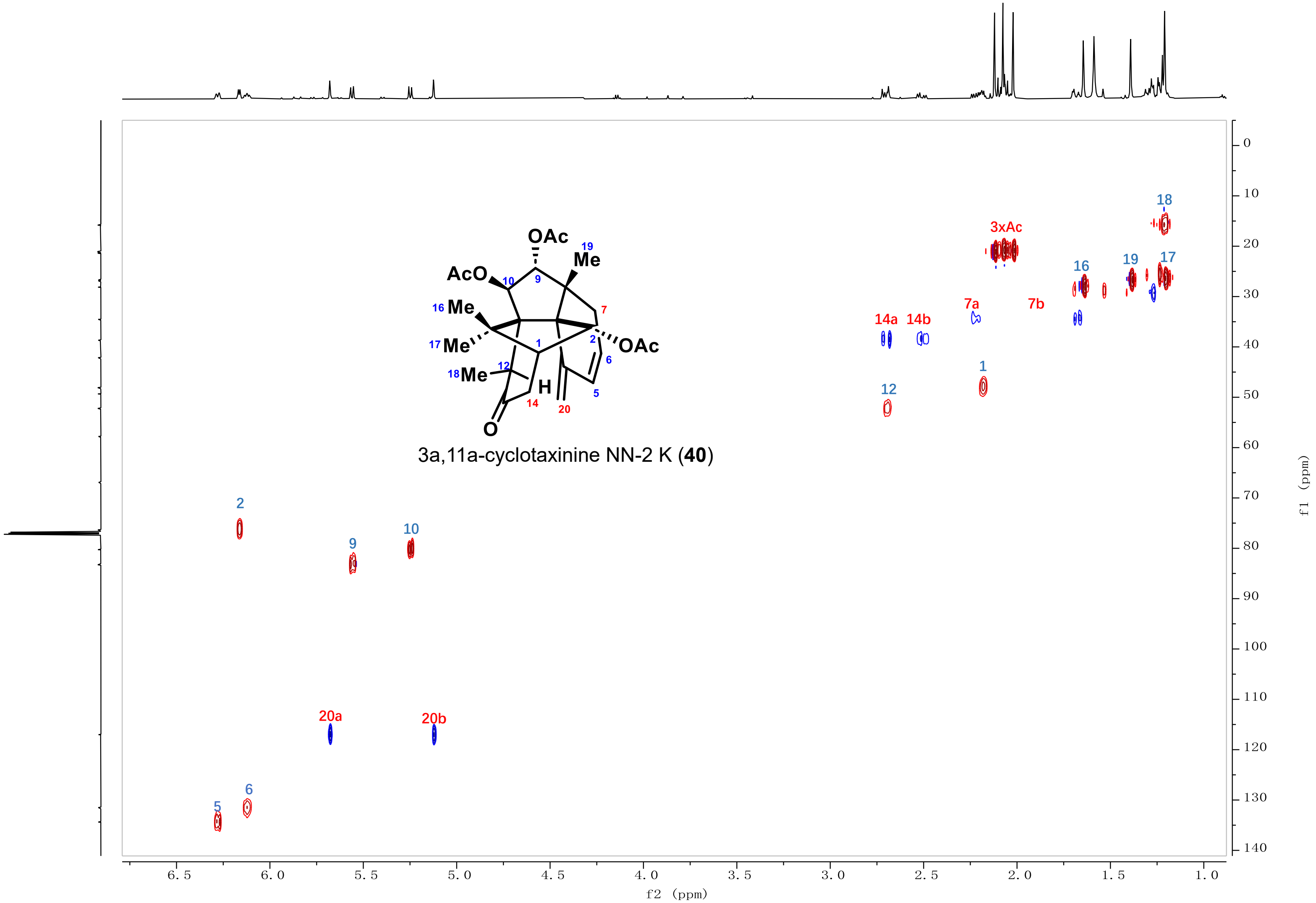

220913-LuPan-p1-09-12-01.4.ser
OAc
H
Me
AcO
Me
Me
OAc
Me
H
OH
O
H
taxinine K (2)
NOE
5.79 5.78 5.77 5.76 5.75 5.74 5.73
f2 (ppm)
3.7
3.8
3.9
f1 (ppm)
3.90 3.85 3.80 3.75
f2 (ppm)
5.6
5.7
5.8
f1 (ppm)
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f2 (ppm)
0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5
f1 (ppm)



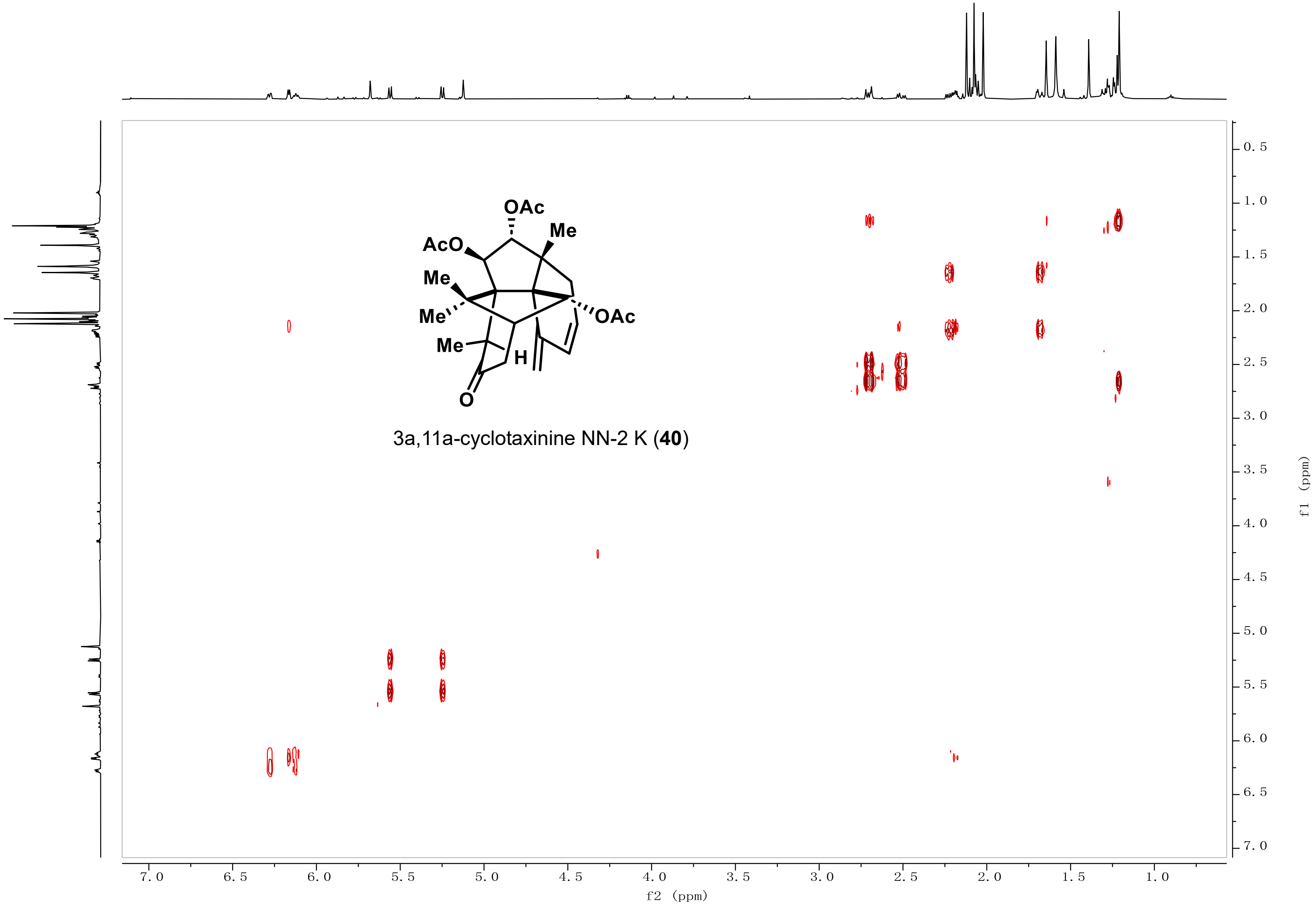
3a,11a-cyclotaxinine NN-2 K (**40**)



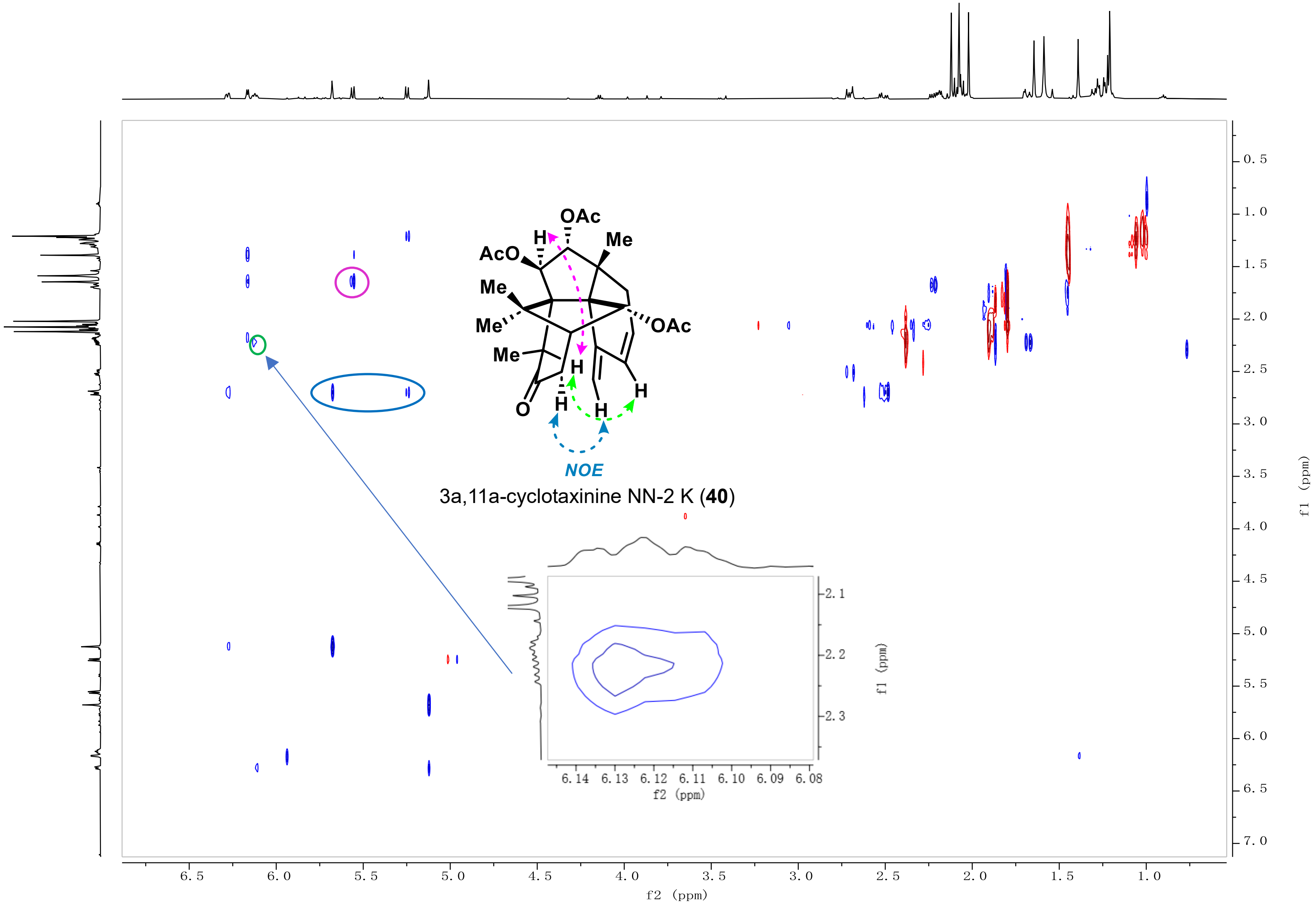
3a,11a-cyclotaxinine NN-2 K (**40**)



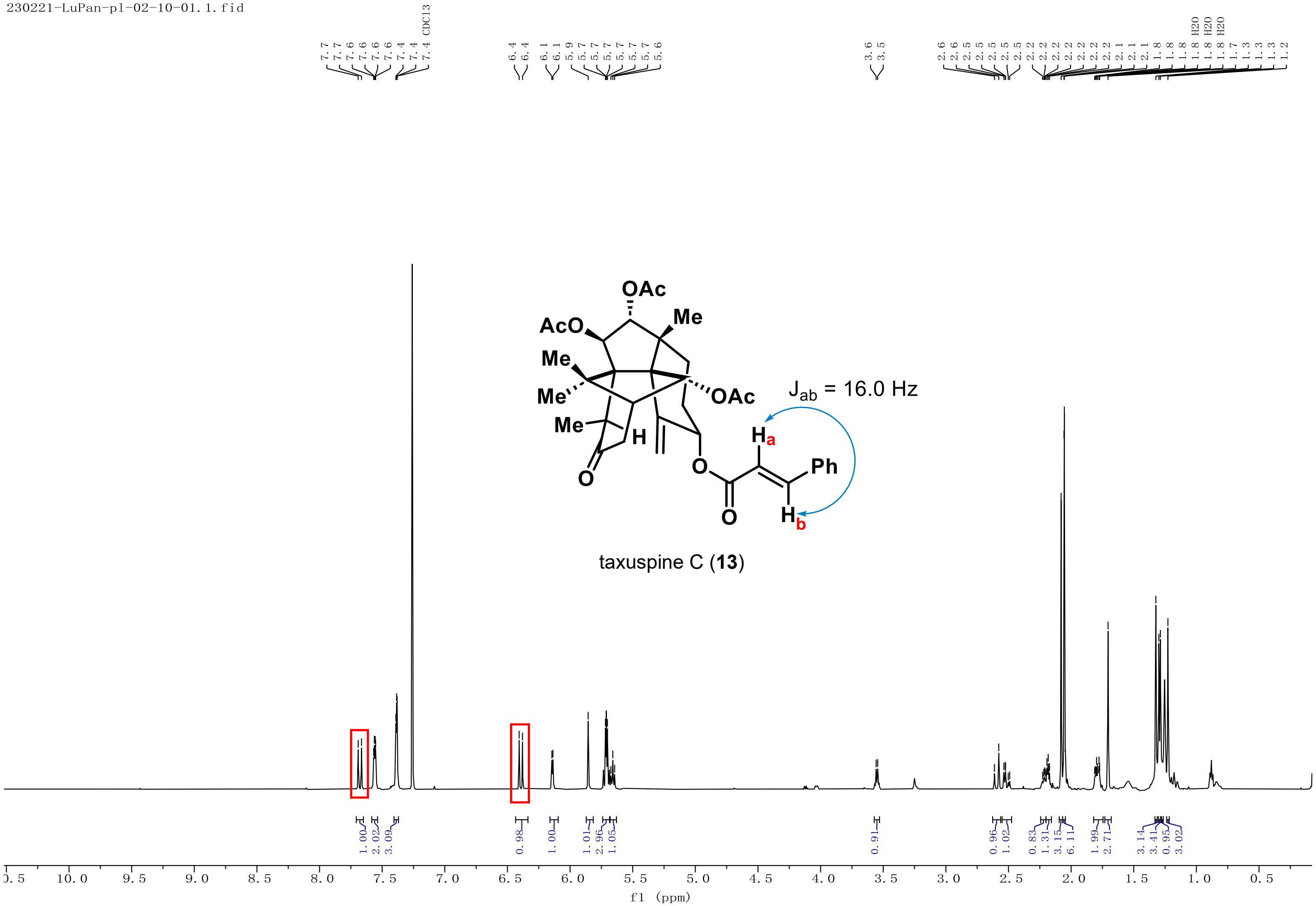
3a,11a-cyclotaxinine NN-2 K (**40**)



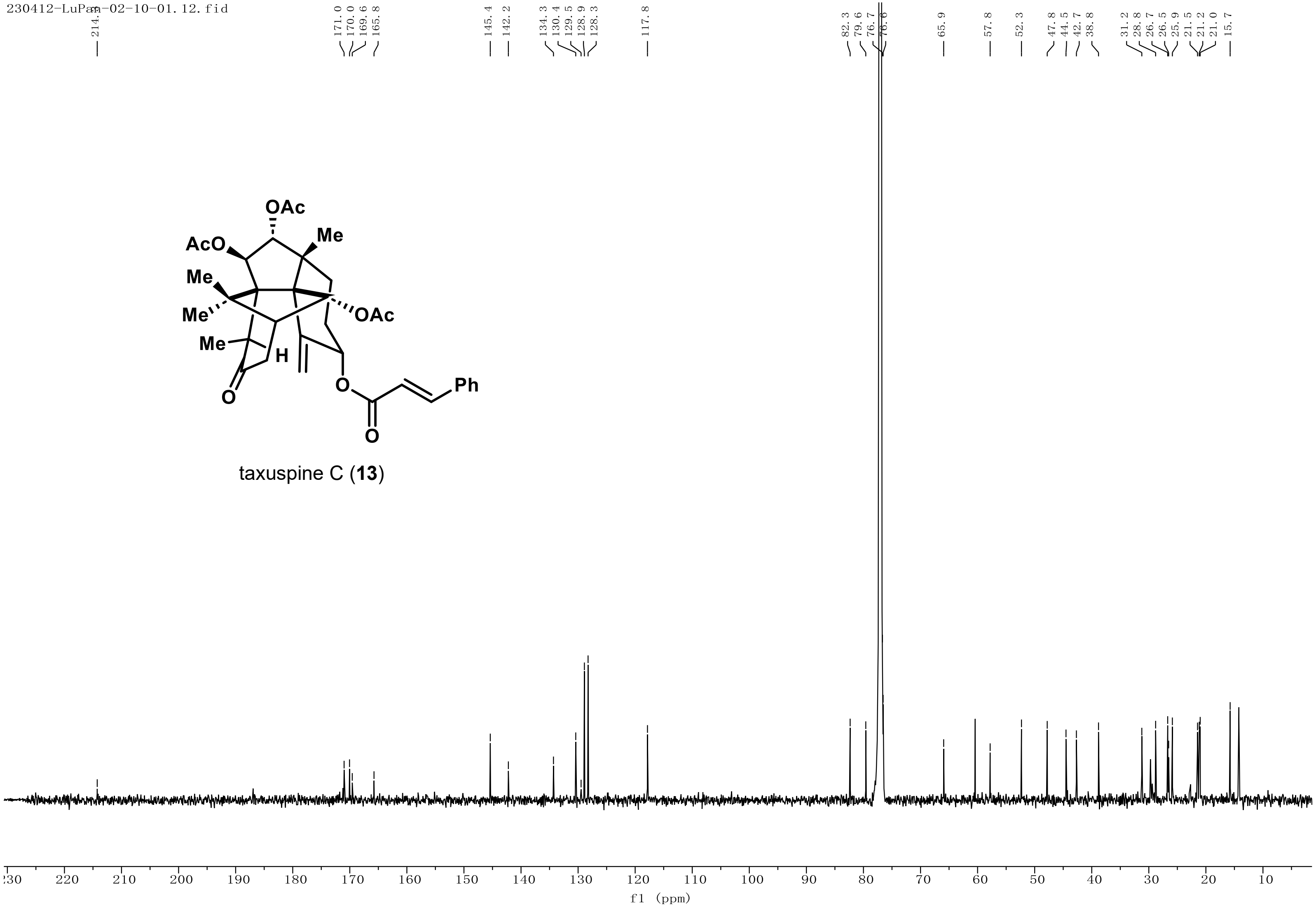
3a,11a-cyclotaxinine NN-2 K (**40**)



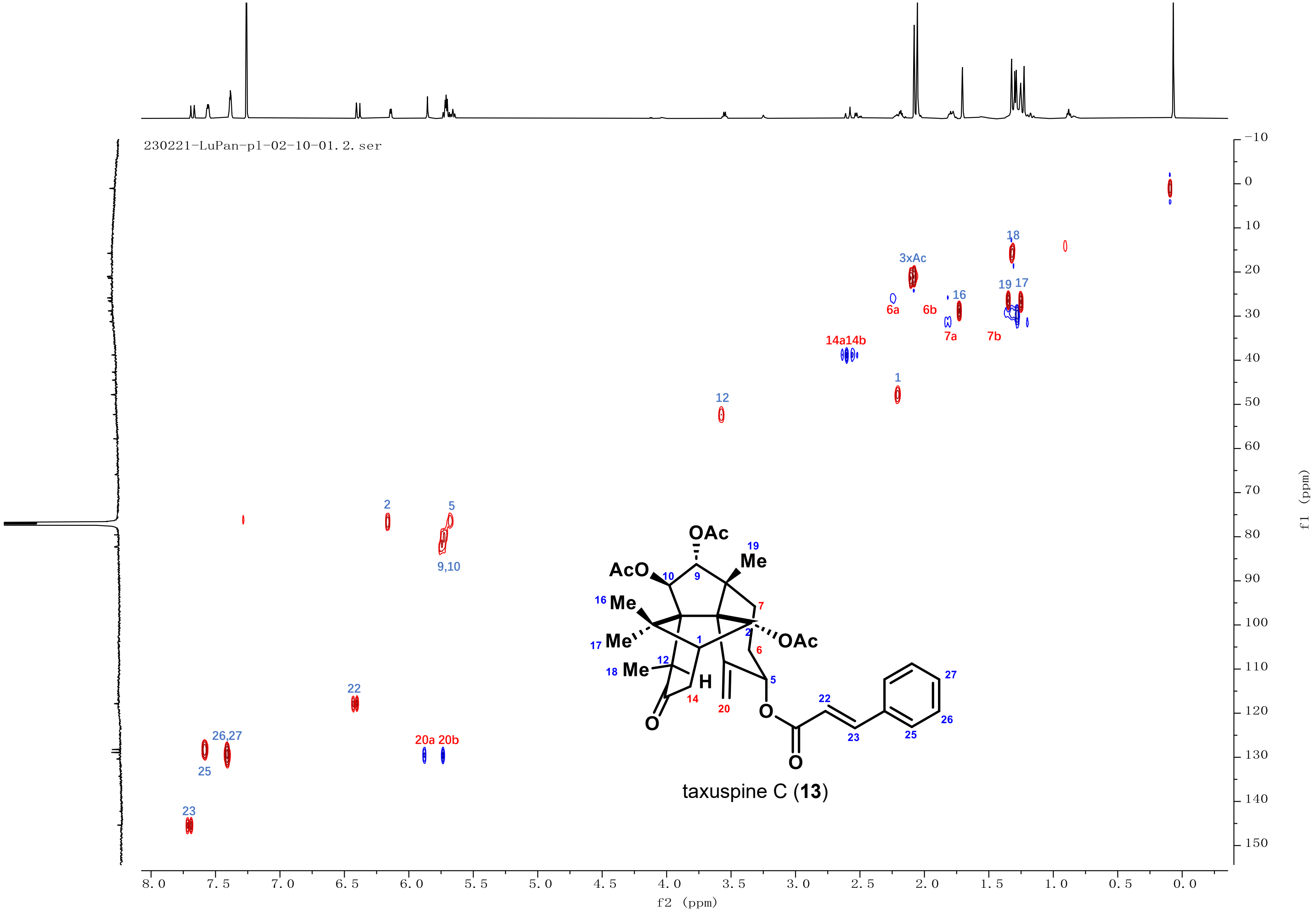
3a,11a-cyclotaxinine NN-2 K (**40**)



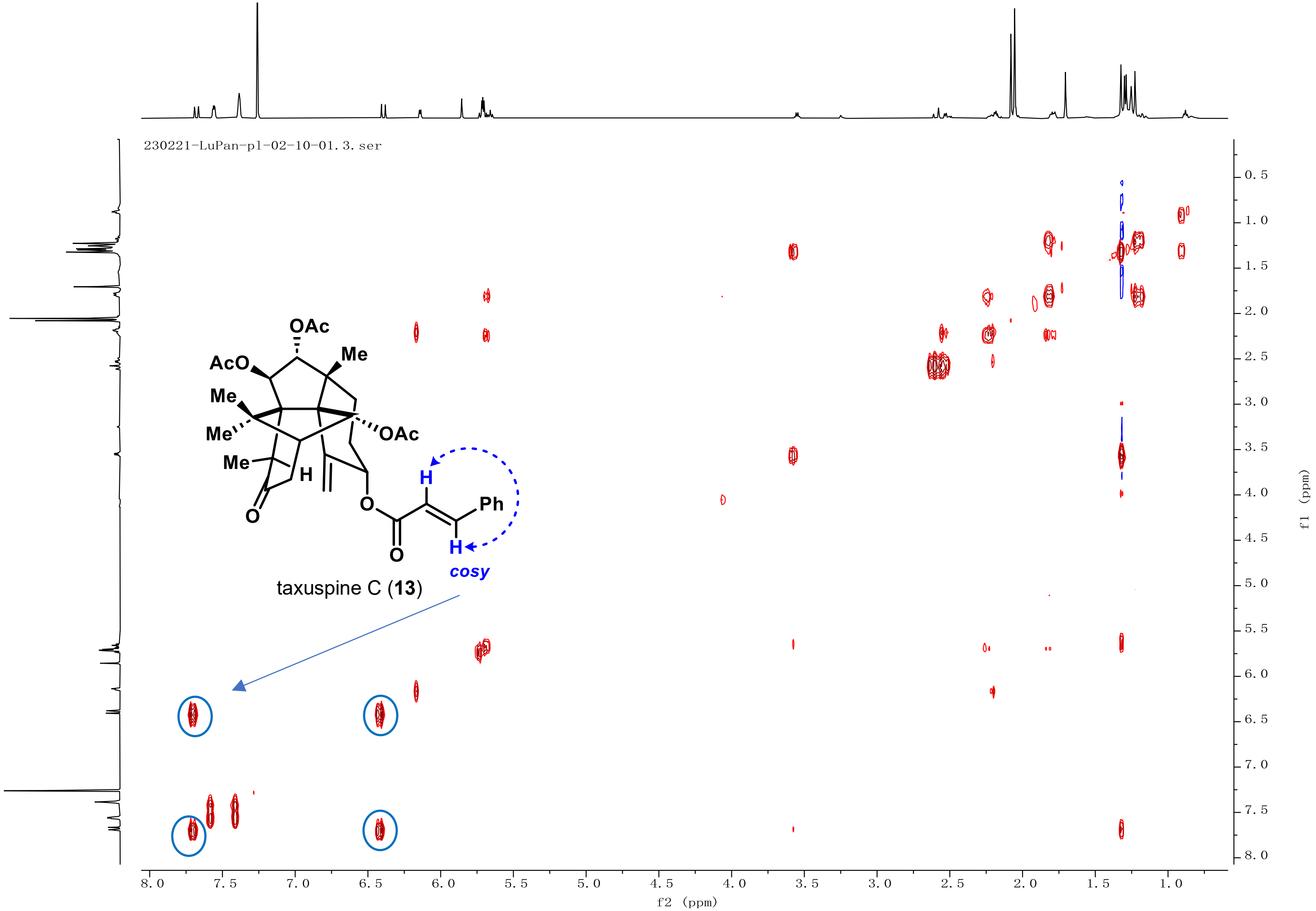
taxuspine C (**13**)

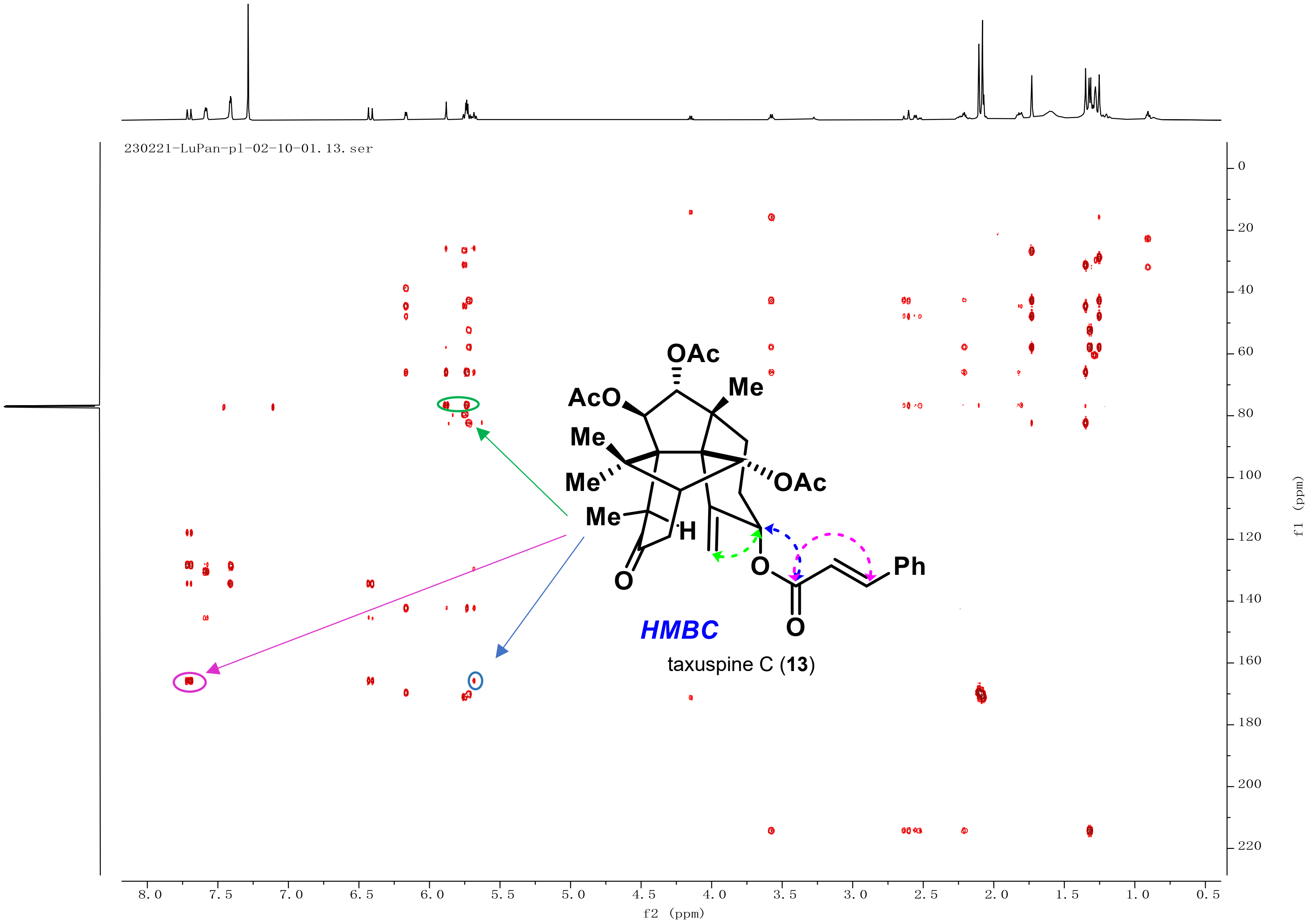


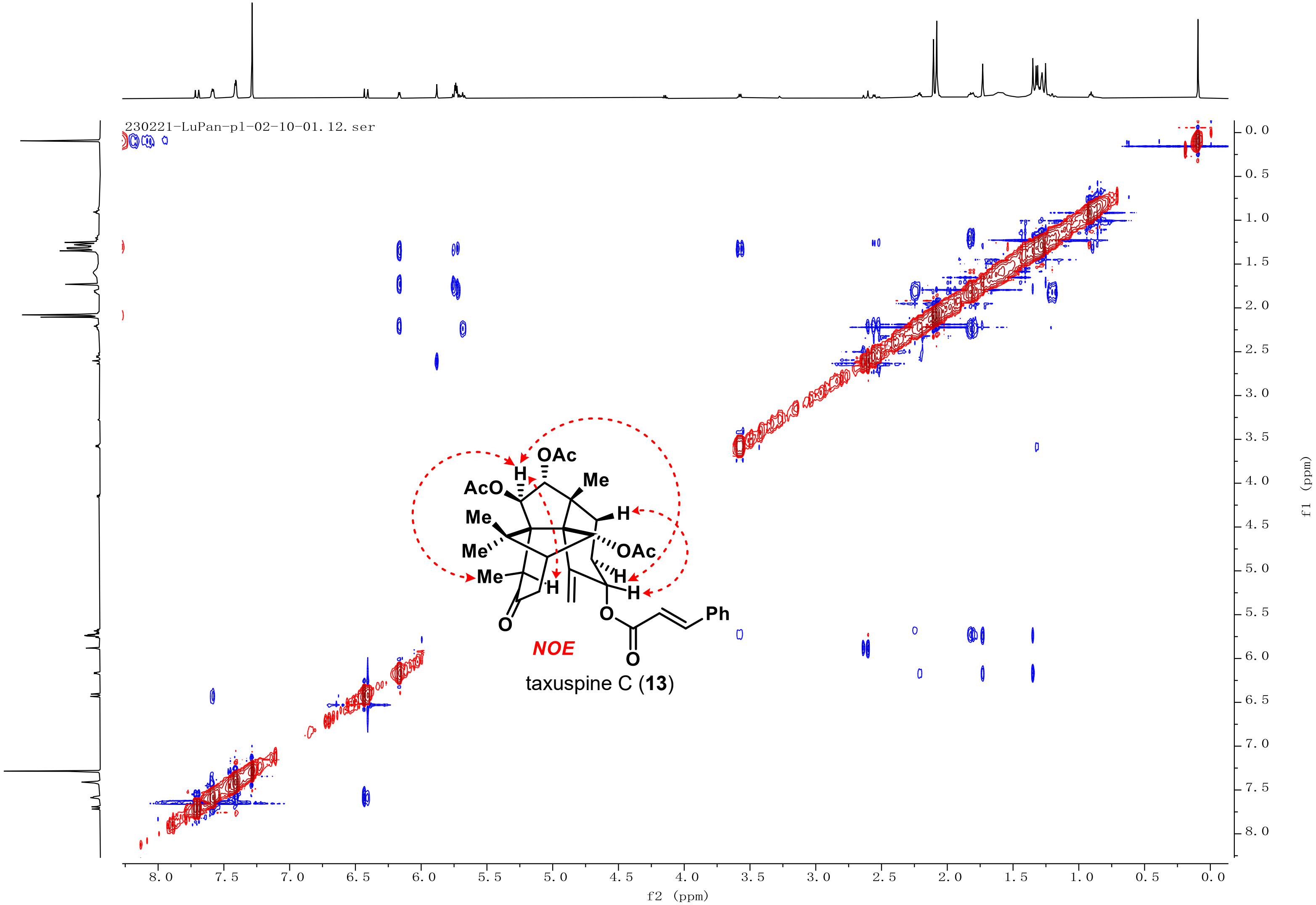
taxuspine C (**13**)



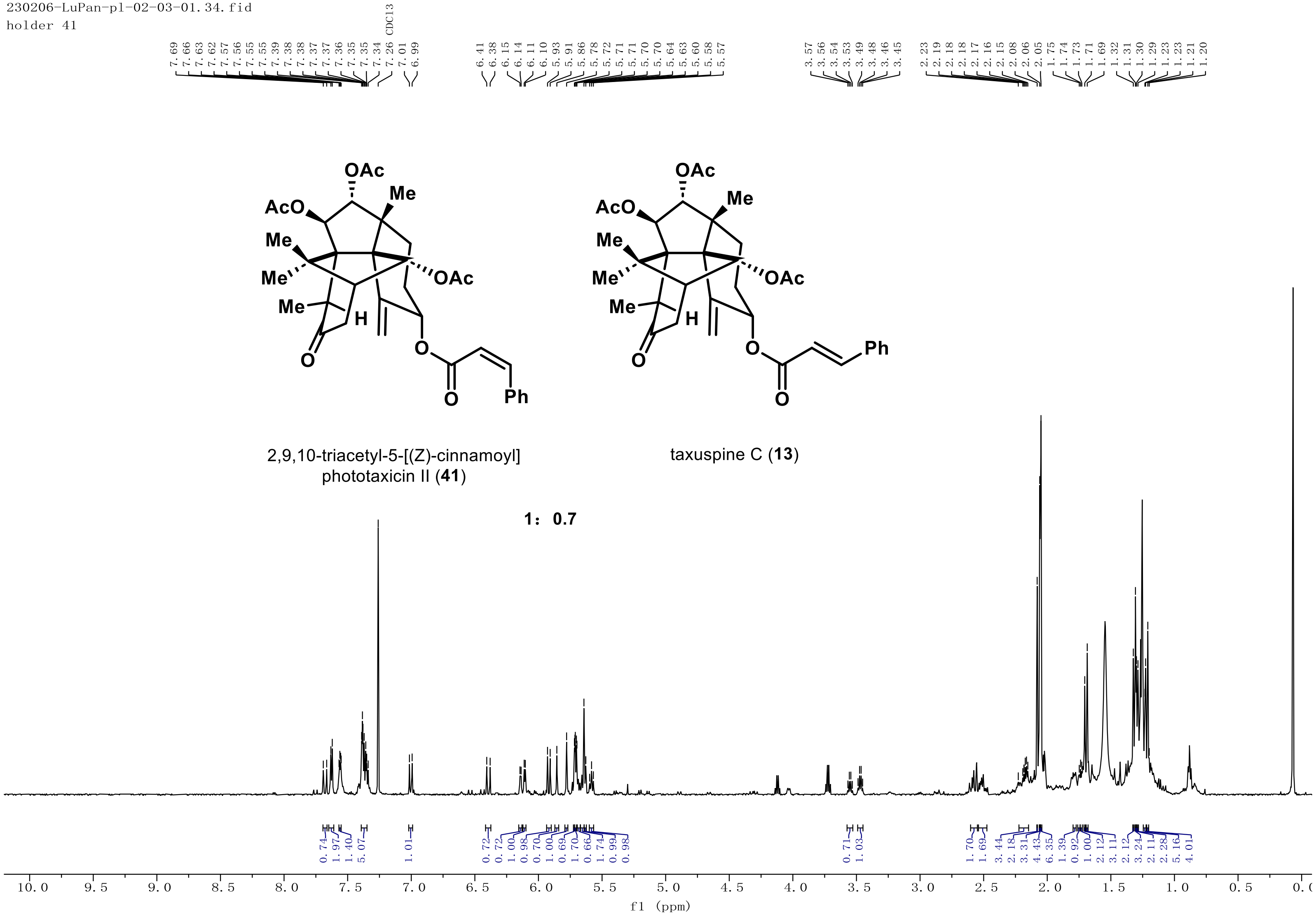
taxuspine C (**13**)


230221-LuPan-p1-02-10-01.3.ser
OAc
AcO
Me
Me
Me
Me
OAc
H
O
O
H
Ph
O
H
cosy
taxuspine C (13)
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
f2 (ppm)
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
f1 (ppm)


230221-LuPan-p1-02-10-01.13.ser
OAc
AcO
Me
Me
Me
Me
H
OAc
O
O
Ph
O
HMBC
taxuspine C (13)
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
f2 (ppm)
0
20
40
60
80
100
120
140
160
180
200
220
f1 (ppm)



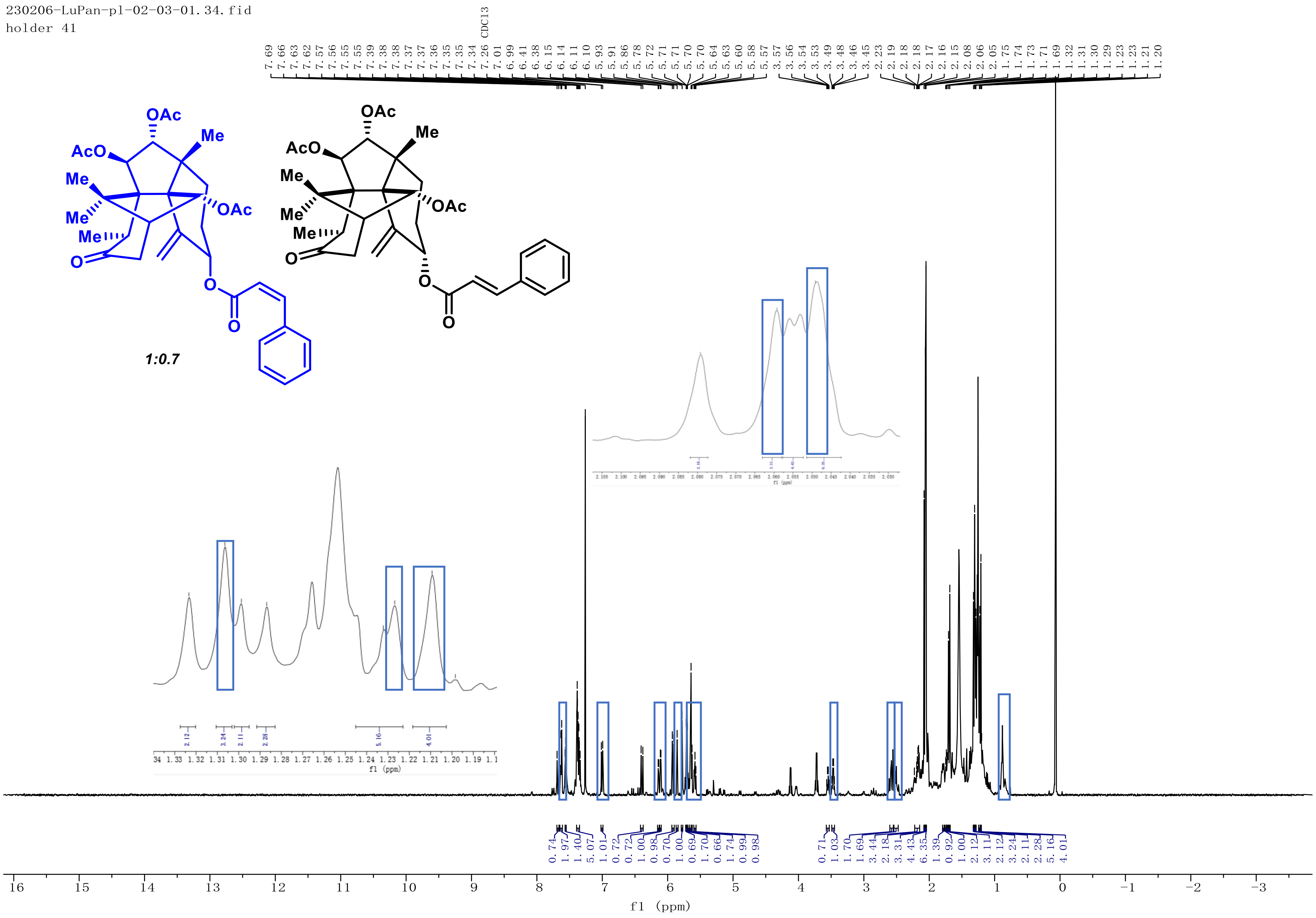
taxuspine C (**13**)

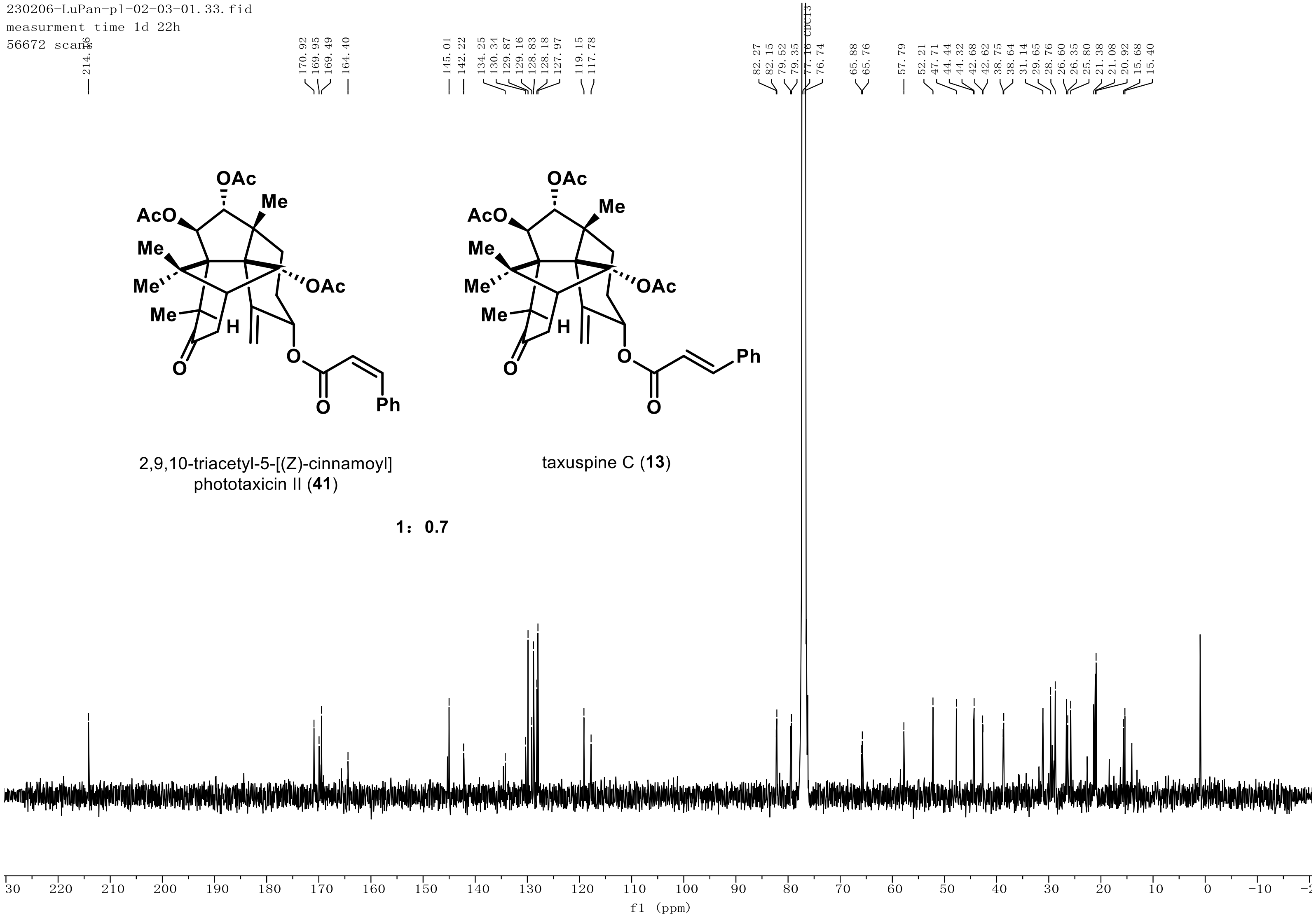


2,9,10-triacetyl-5-[(Z)-cinnamoyl]
phototaxicin II (**41**)

taxuspine C (**13**)

**1：0.7**

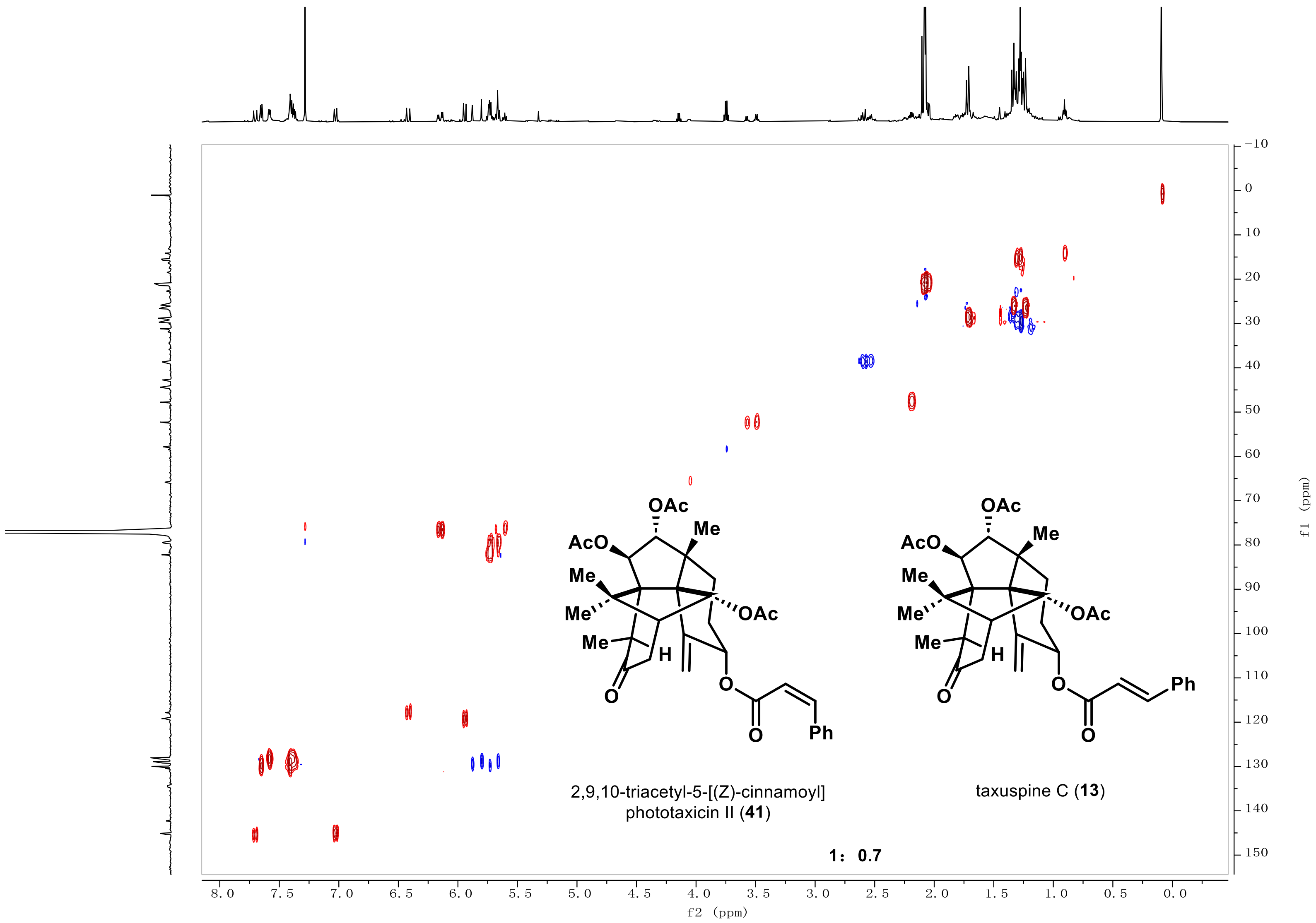

230206-LuPan-p1-02-03-01.34.fid
holder 41
CDCl3
7.69 7.66 7.63 7.62 7.57 7.56 7.55 7.55 7.39 7.38 7.38 7.37 7.37 7.36 7.35 7.35 7.34 7.26 7.01 6.99 6.41 6.38 6.15 6.14 6.11 6.10 5.93 5.91 5.86 5.78 5.72 5.71 5.71 5.70 5.70 5.64 5.63 5.60 5.58 5.57 3.57 3.56 3.54 3.53 3.49 3.48 3.46 3.45 2.23 2.19 2.18 2.18 2.17 2.16 2.15 2.08 2.06 2.05 1.75 1.74 1.73 1.71 1.69 1.32 1.31 1.30 1.29 1.23 1.23 1.21 1.20
OAc
AcO
Me
Me
Me
Me
OAc
O
O
O
1:0.7
0.74 1.97 1.40 5.07 1.01 0.72 0.72 1.00 0.98 0.70 1.00 0.69 1.70 0.66 1.74 0.99 0.98
0.71 1.03 1.70 1.69 3.44 2.18 3.31 4.43 6.35 1.39 0.92 1.00 2.12 3.11 2.12 3.24 2.11 2.28 5.16 4.01
2.12 3.24 2.11 2.28 5.16 4.01
1.34 1.33 1.32 1.31 1.30 1.29 1.28 1.27 1.26 1.25 1.24 1.23 1.22 1.21 1.20 1.19 1.1
f1 (ppm)
2.105 2.100 2.095 2.090 2.085 2.080 2.075 2.070 2.065 2.060 2.055 2.050 2.045 2.040 2.035 2.030
f1 (ppm)
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3
f1 (ppm)



2,9,10-triacetyl-5-[(Z)-cinnamoyl]
phototaxicin II (**41**)

taxuspine C (**13**)

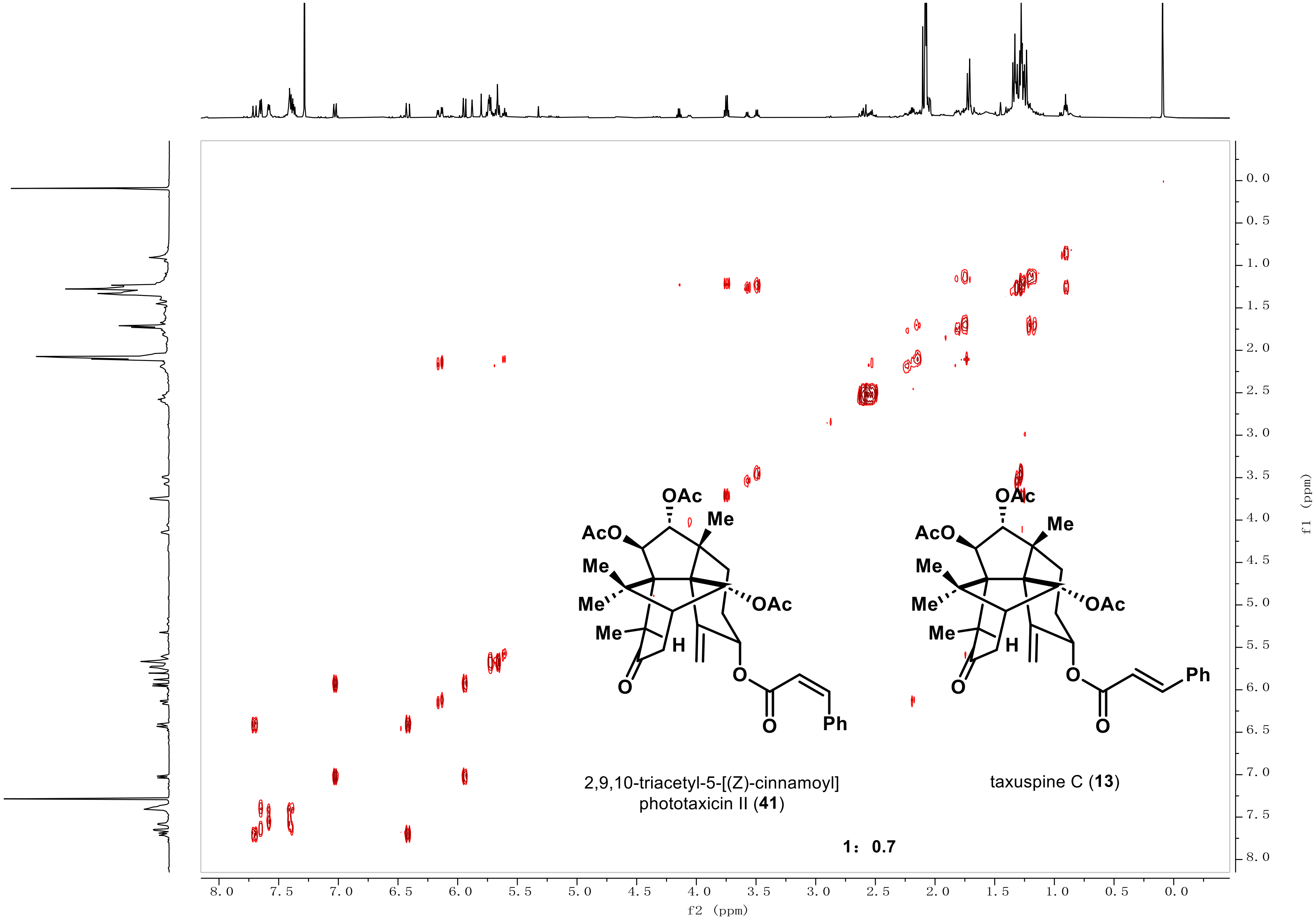
**1：0.7**



2,9,10-triacetyl-5-[(Z)-cinnamoyl] phototaxicin II (**41**)

taxuspine C (**13**)

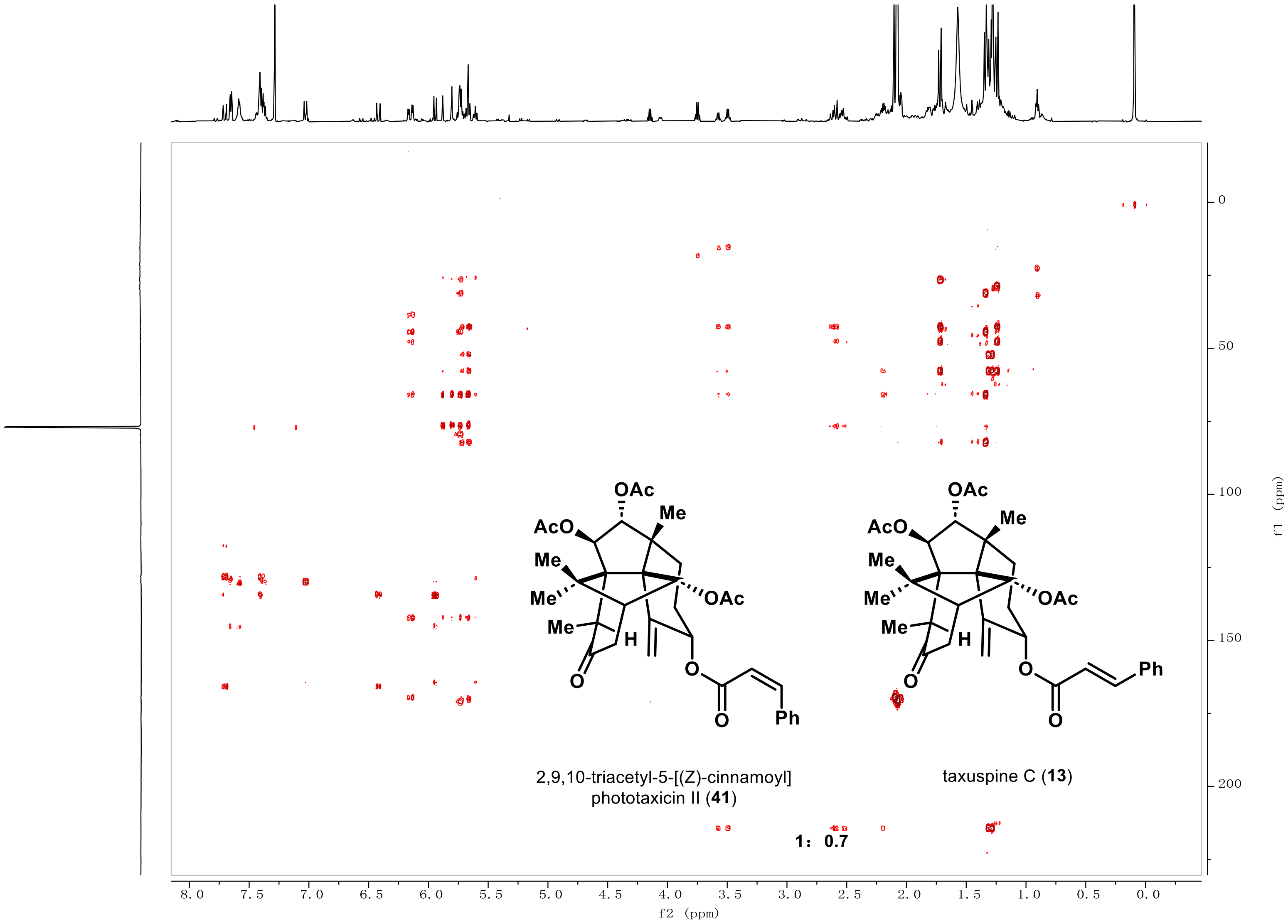
**1: 0.7**



2,9,10-triacetyl-5-[(Z)-cinnamoyl] phototaxicin II (**41**)

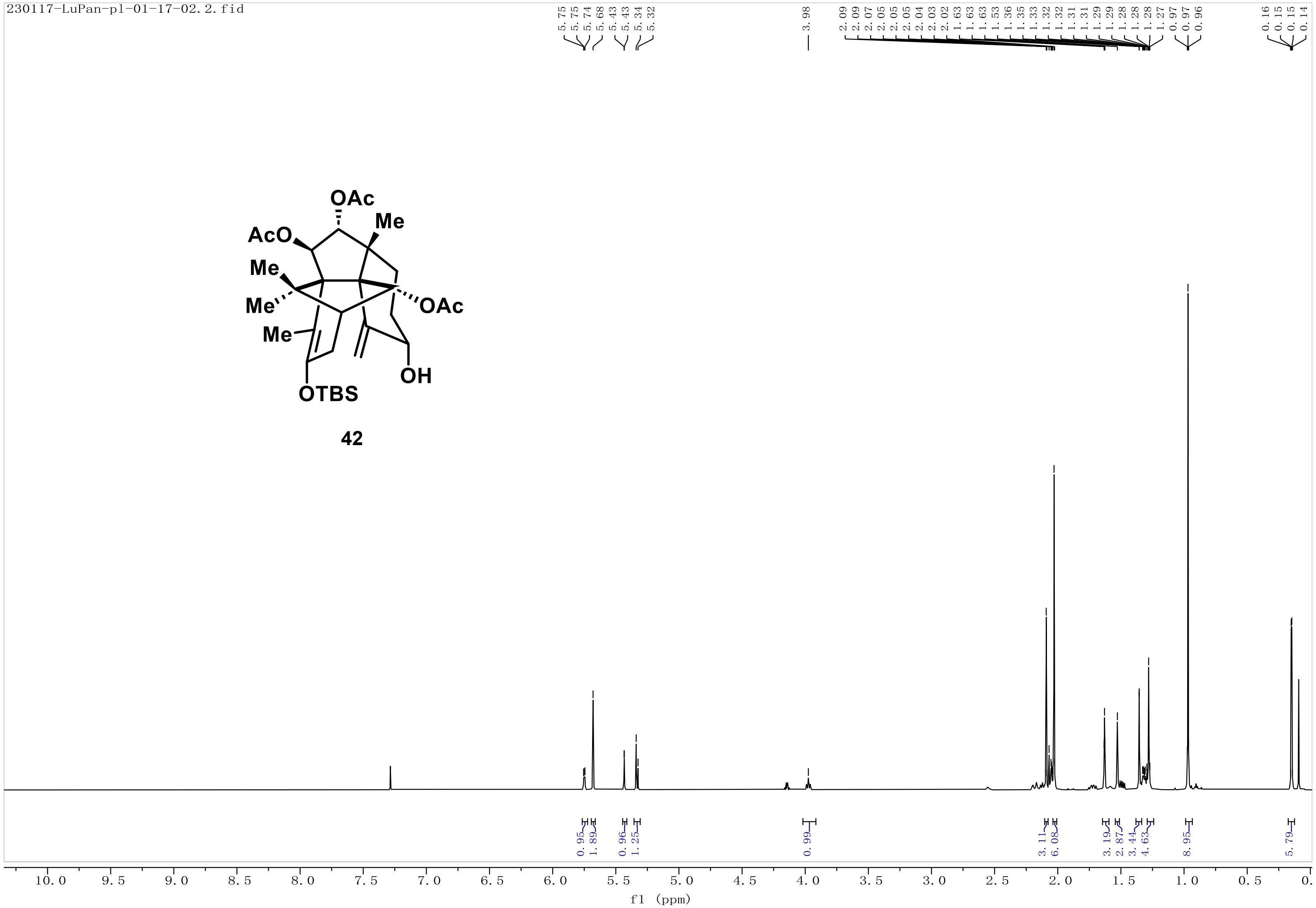
taxuspine C (**13**)

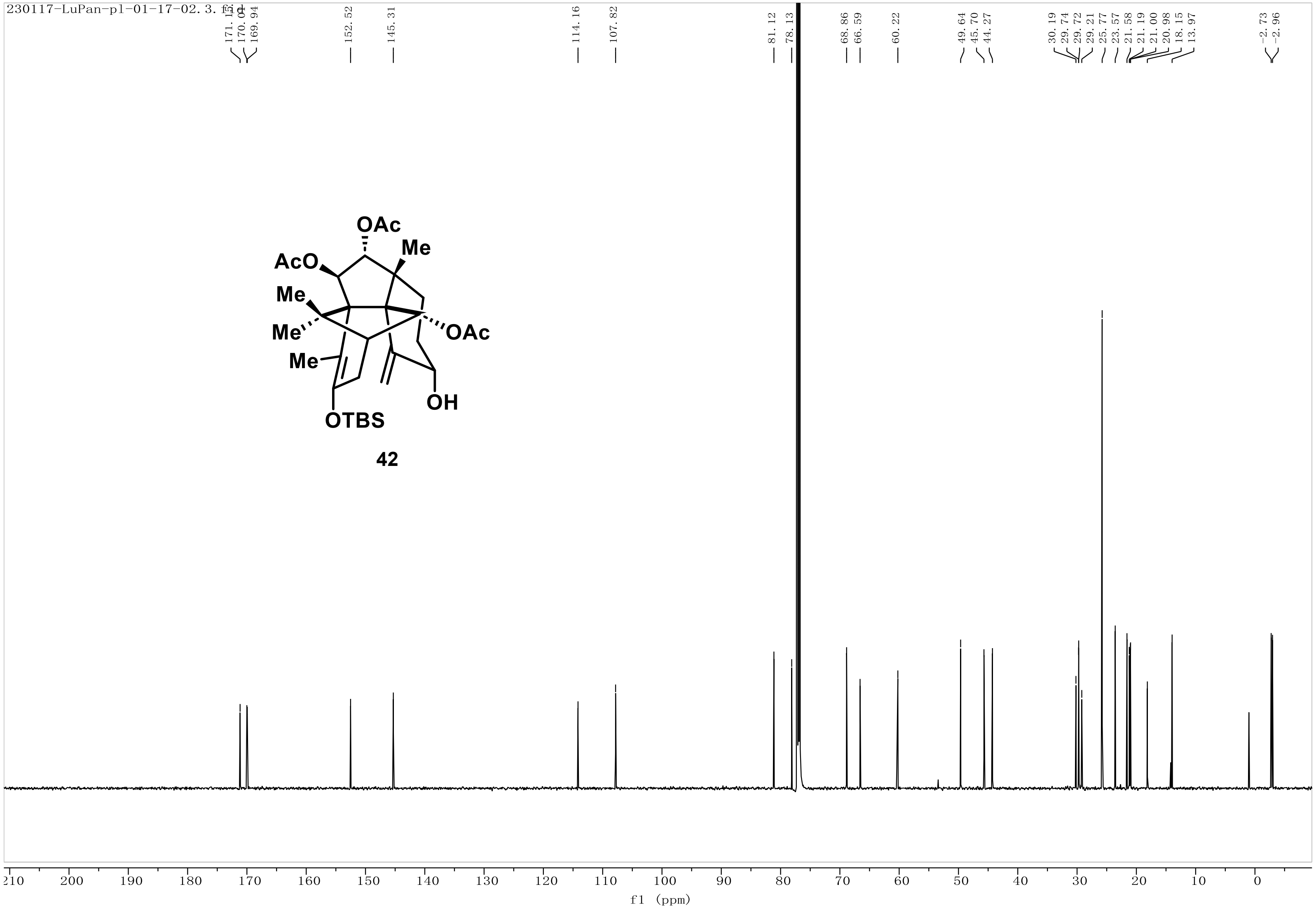
**1：0.7**

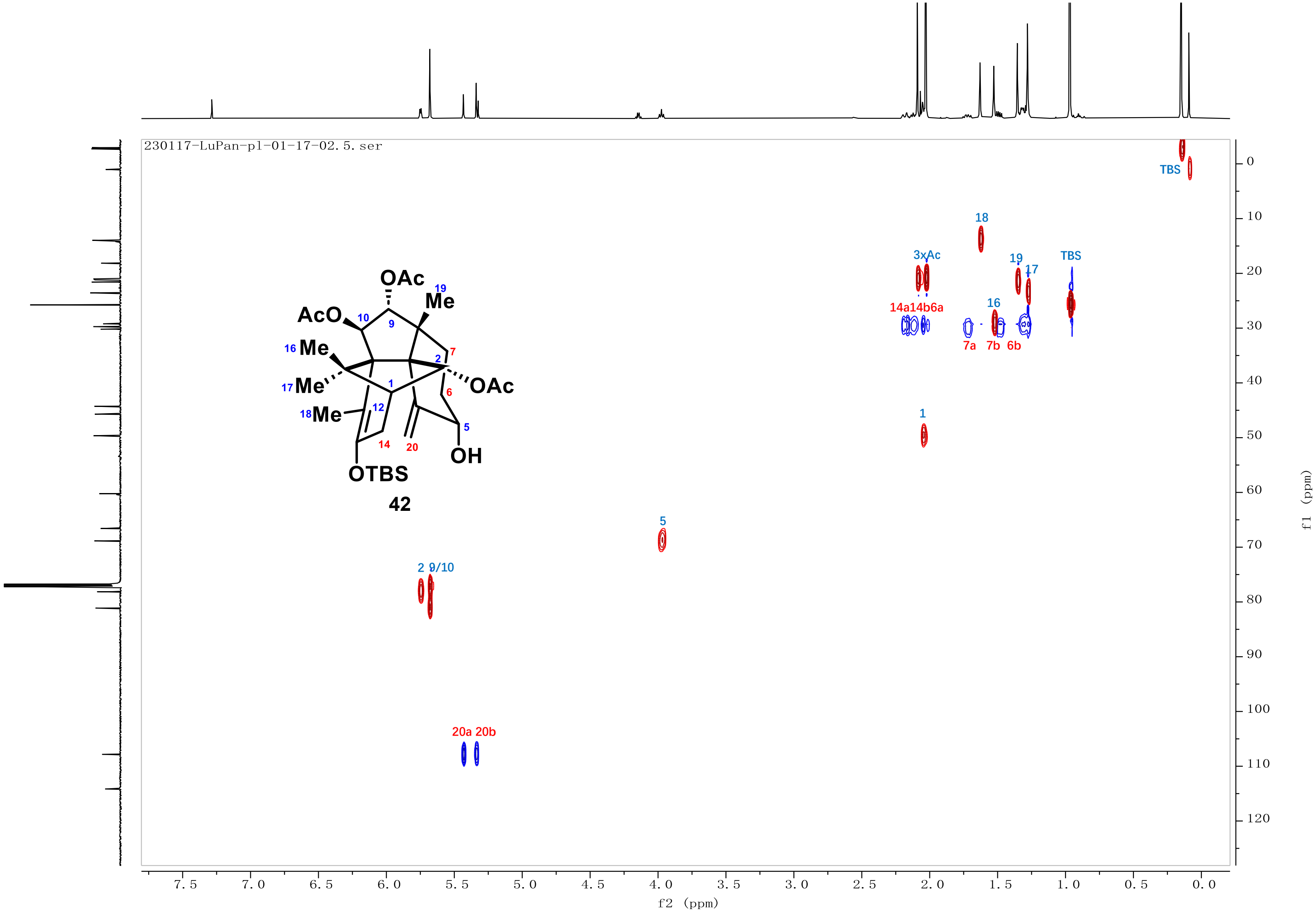


2,9,10-triacetyl-5-[(Z)-cinnamoyl] phototaxicin II (**41**)

taxuspine C (**13**)

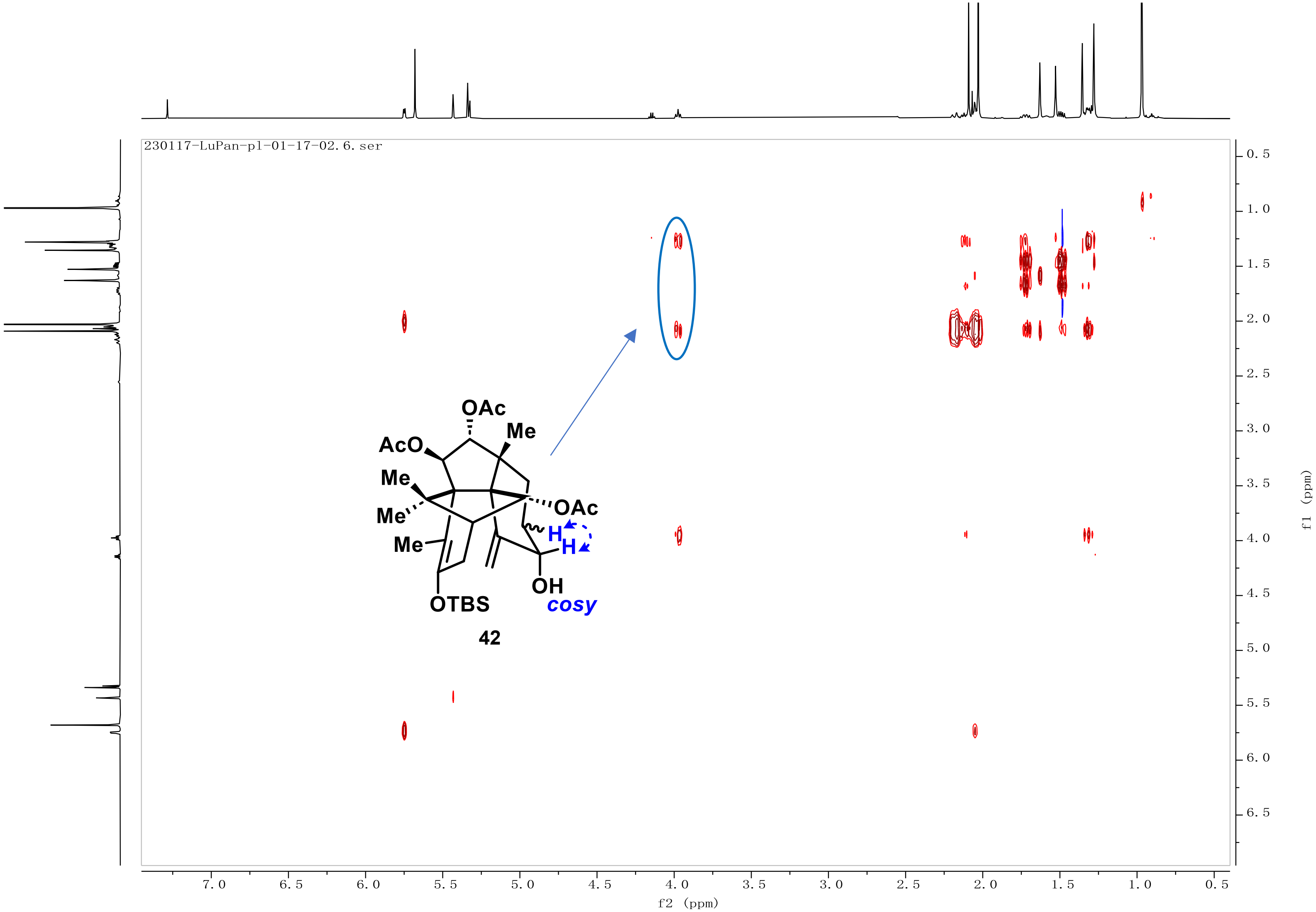

230117-LuPan-p1-01-17-02.2.fid
5.75
5.75
5.74
5.68
5.43
5.43
5.34
5.32
3.98
2.09
2.09
2.07
2.05
2.05
2.05
2.04
2.03
2.02
1.63
1.63
1.63
1.53
1.36
1.35
1.33
1.32
1.32
1.31
1.31
1.29
1.29
1.28
1.28
1.28
1.27
0.97
0.97
0.96
0.16
0.15
0.15
0.14
OAc
Me
AcO
Me
Me
OAc
Me
OH
OTBS
42
0.95
1.89
0.96
1.25
0.99
3.11
6.08
3.19
2.87
3.44
4.63
8.95
5.79
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.
f1 (ppm)

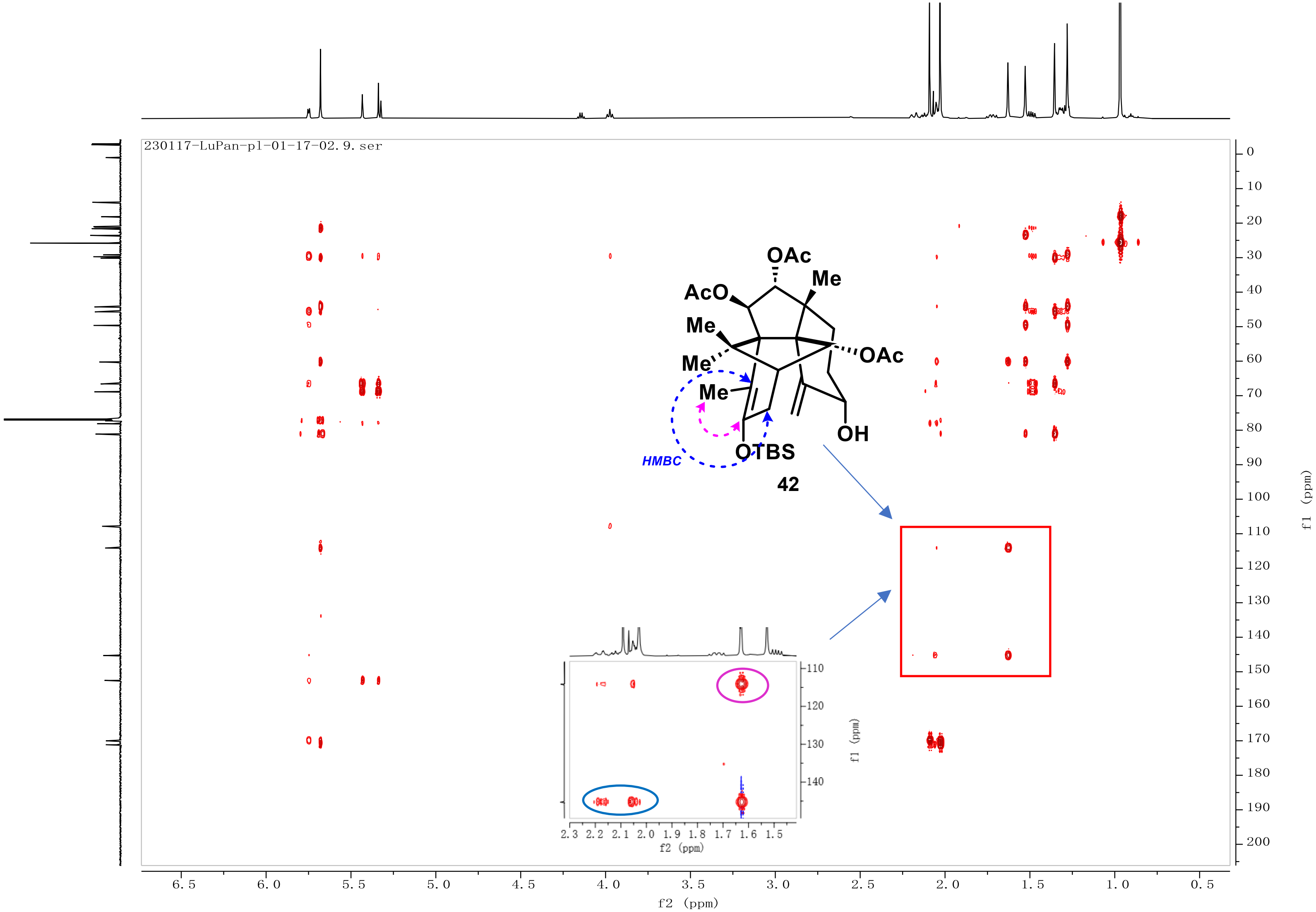

230117-LuPan-pl-01-17-02.3.fid
171.15
170.04
169.94
152.52
145.31
114.16
107.82
81.12
78.13
68.86
66.59
60.22
49.64
45.70
44.27
30.19
29.74
29.72
29.21
25.77
23.57
21.58
21.19
21.00
20.98
18.15
13.97
-2.73
-2.96
OAc
AcO
Me
Me
Me
OAc
Me
OTBS
OH
42
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

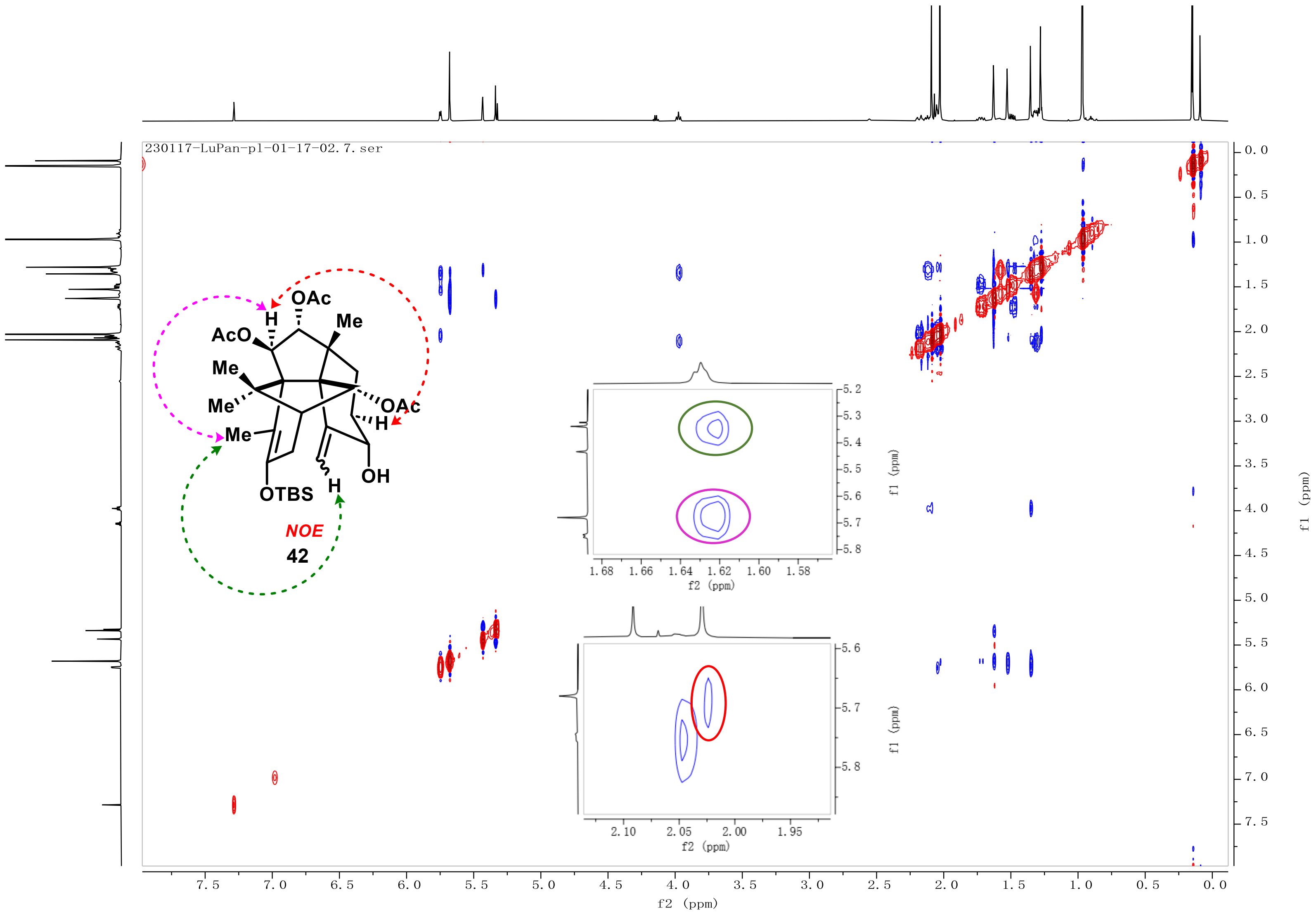


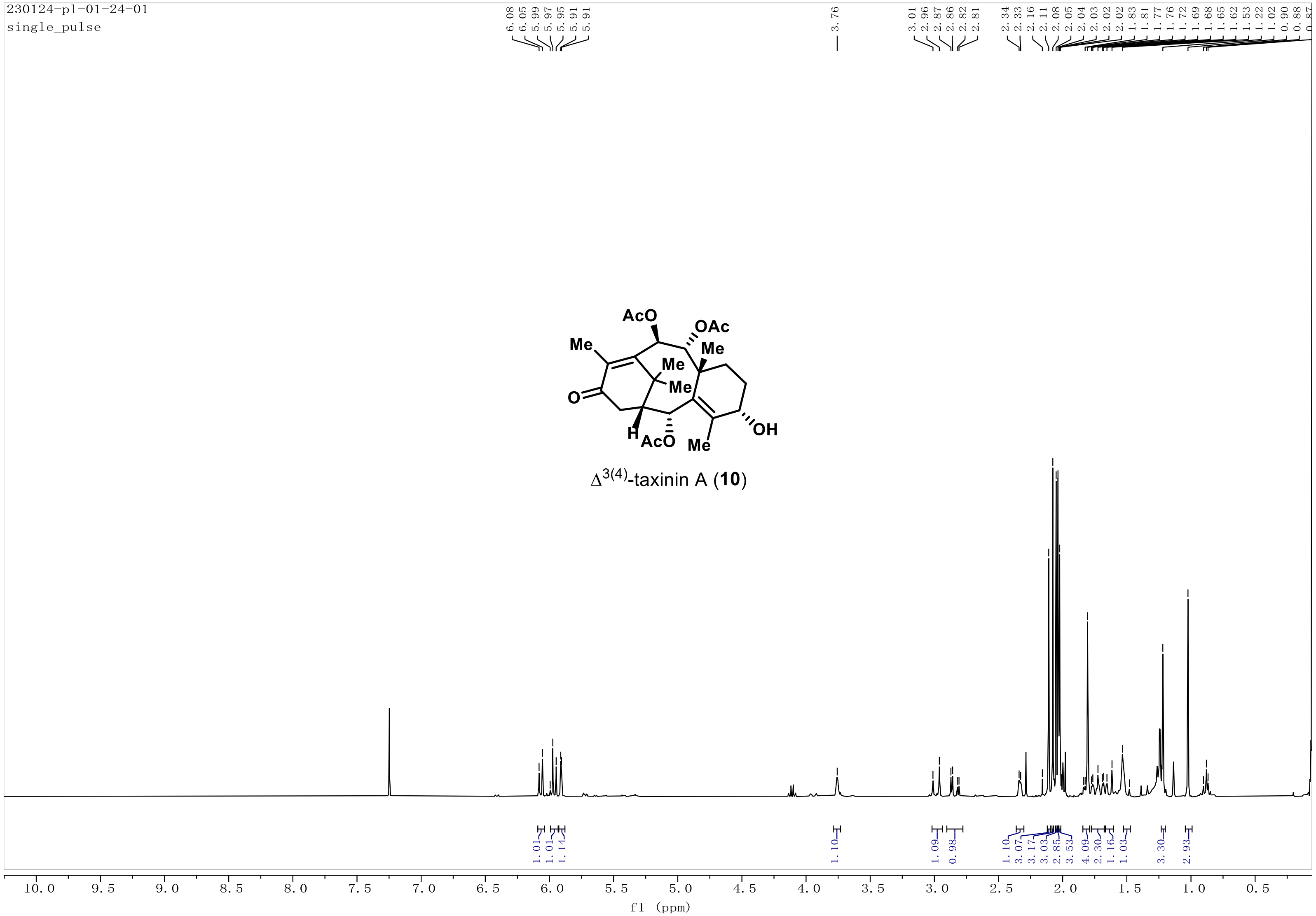
230117-LuPan-p1-01-17-02.5.ser
TBS
18
3xAc
19
17
TBS
14a14b6a
16
7a
7b
6b
1
5
2
9/10
20a
20b
OAc
19
Me
AcO
10
9
16 Me
2
7
17 Me
1
OAc
18 Me
12
6
5
14
20
OH
OTBS
f2 (ppm)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120

42

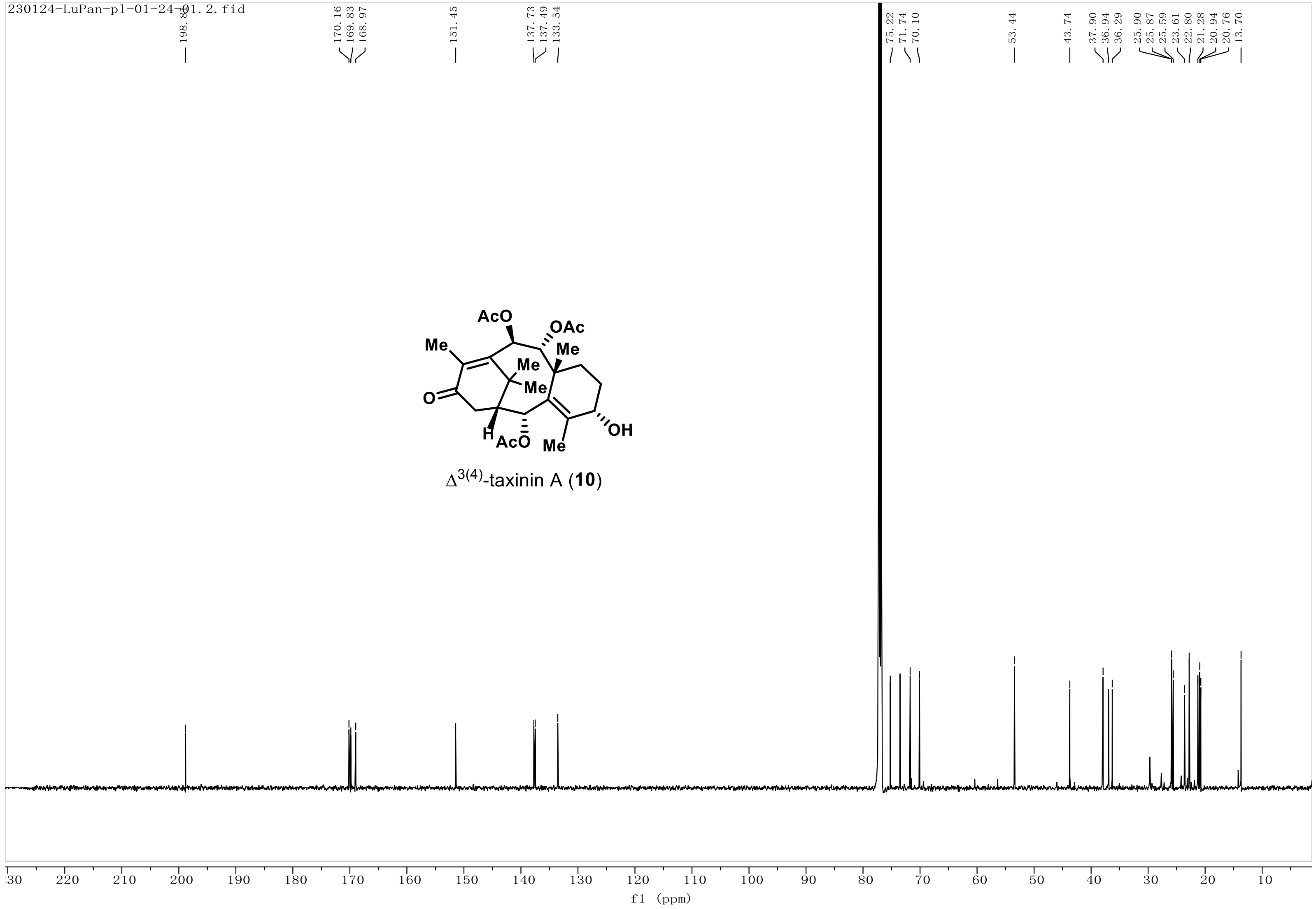

230117-LuPan-p1-01-17-02.6.ser
OAc
AcO
Me
Me
Me
Me
OAc
H
H
OH
OTBS
cosy
42
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
f1 (ppm)


230117-LuPan-p1-01-17-02.9.ser
OAc
Me
AcO
Me
Me
OAc
Me
OH
OTBS
HMBC
42
f2 (ppm)
f1 (ppm)
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
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
110
120
130
140

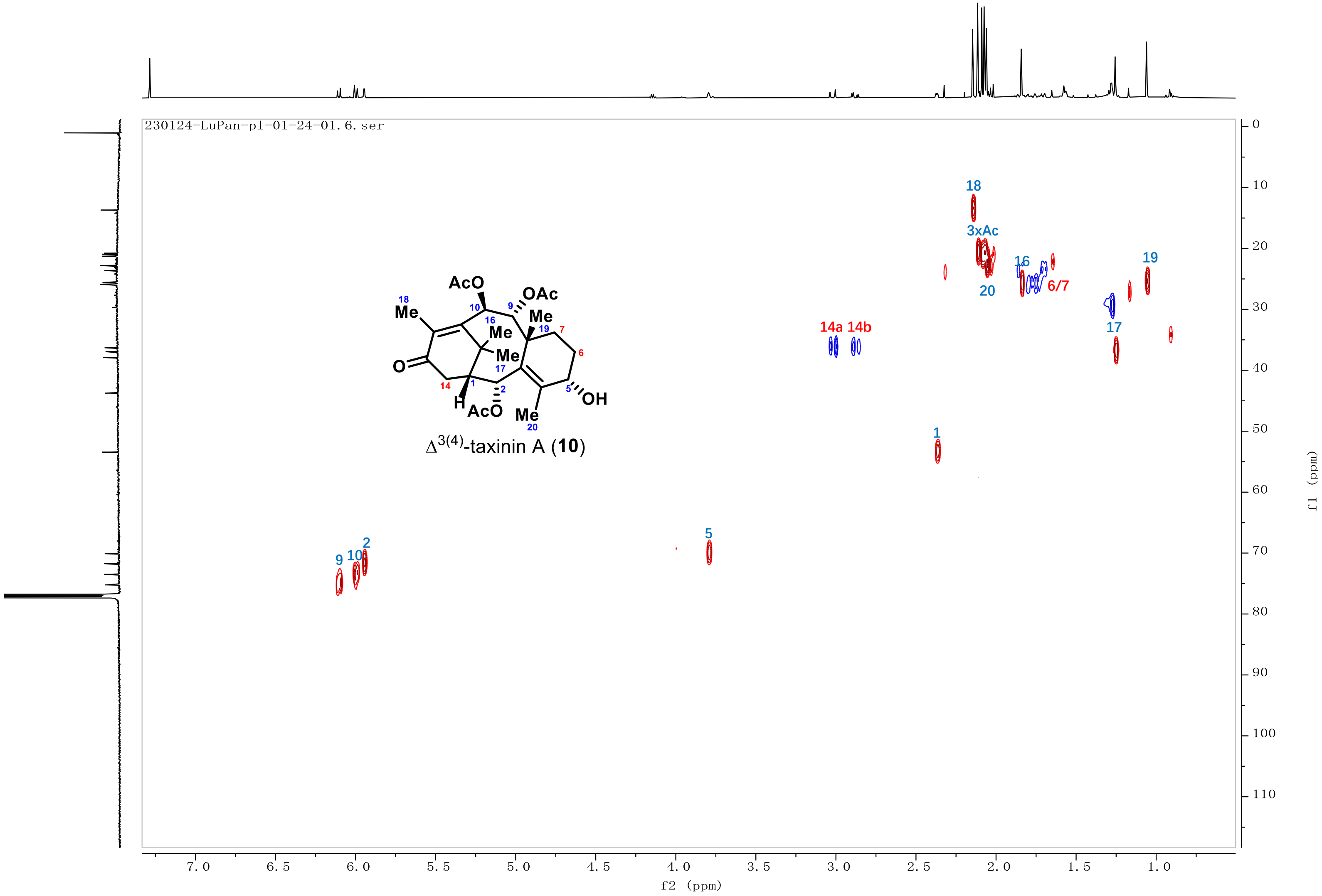

230117-LuPan-p1-01-17-02.7.ser
AcO
OAc
H
Me
Me
Me
Me
OAc
H
OTBS
H
OH
NOE
42
1.68 1.66 1.64 1.62 1.60 1.58
f2 (ppm)
5.2 5.3 5.4 5.5 5.6 5.7 5.8
f1 (ppm)
2.10 2.05 2.00 1.95
f2 (ppm)
5.6 5.7 5.8
f1 (ppm)
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f2 (ppm)
0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5
f1 (ppm)



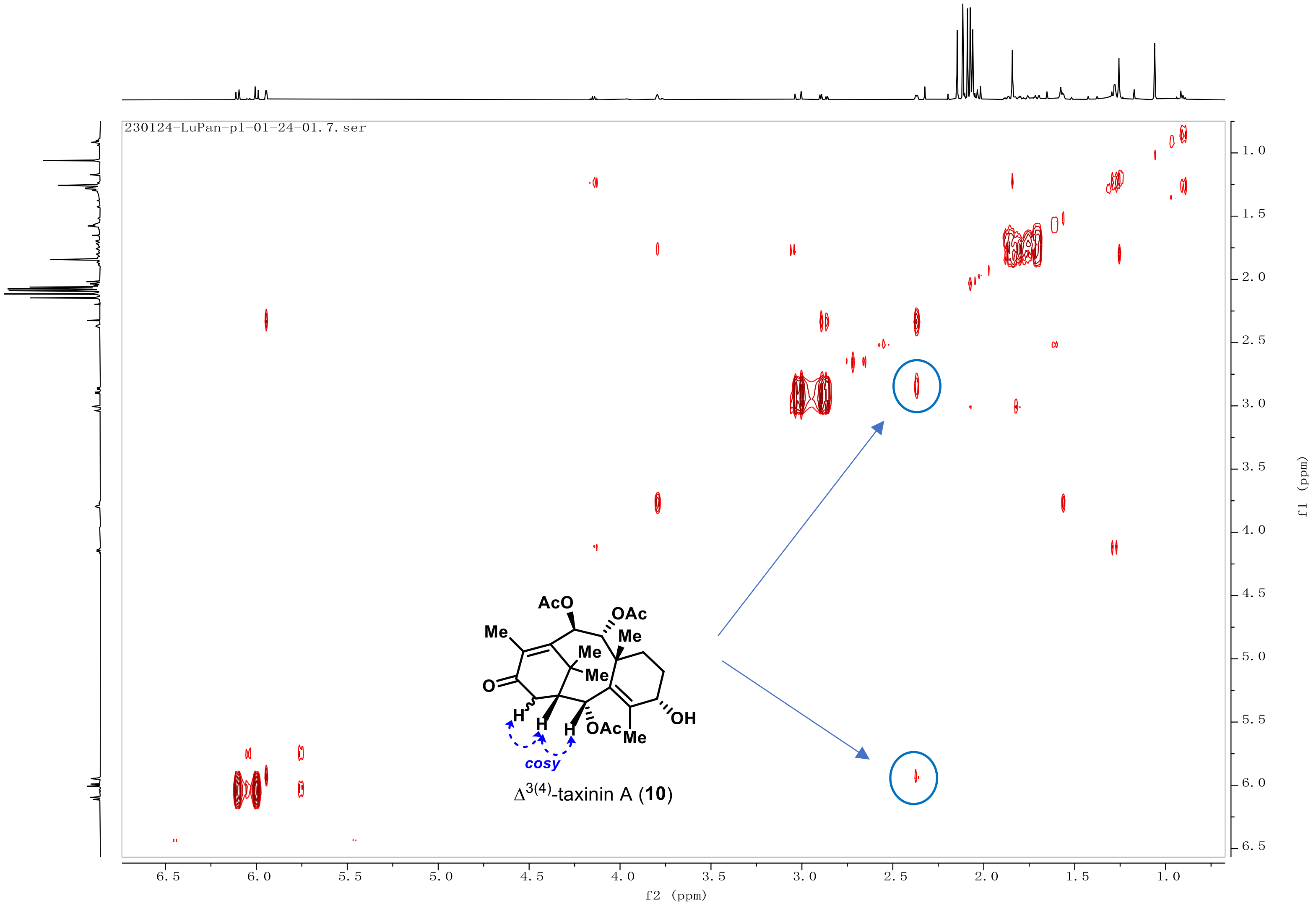
$\Delta^{3(4)}$-taxinin A (**10**)



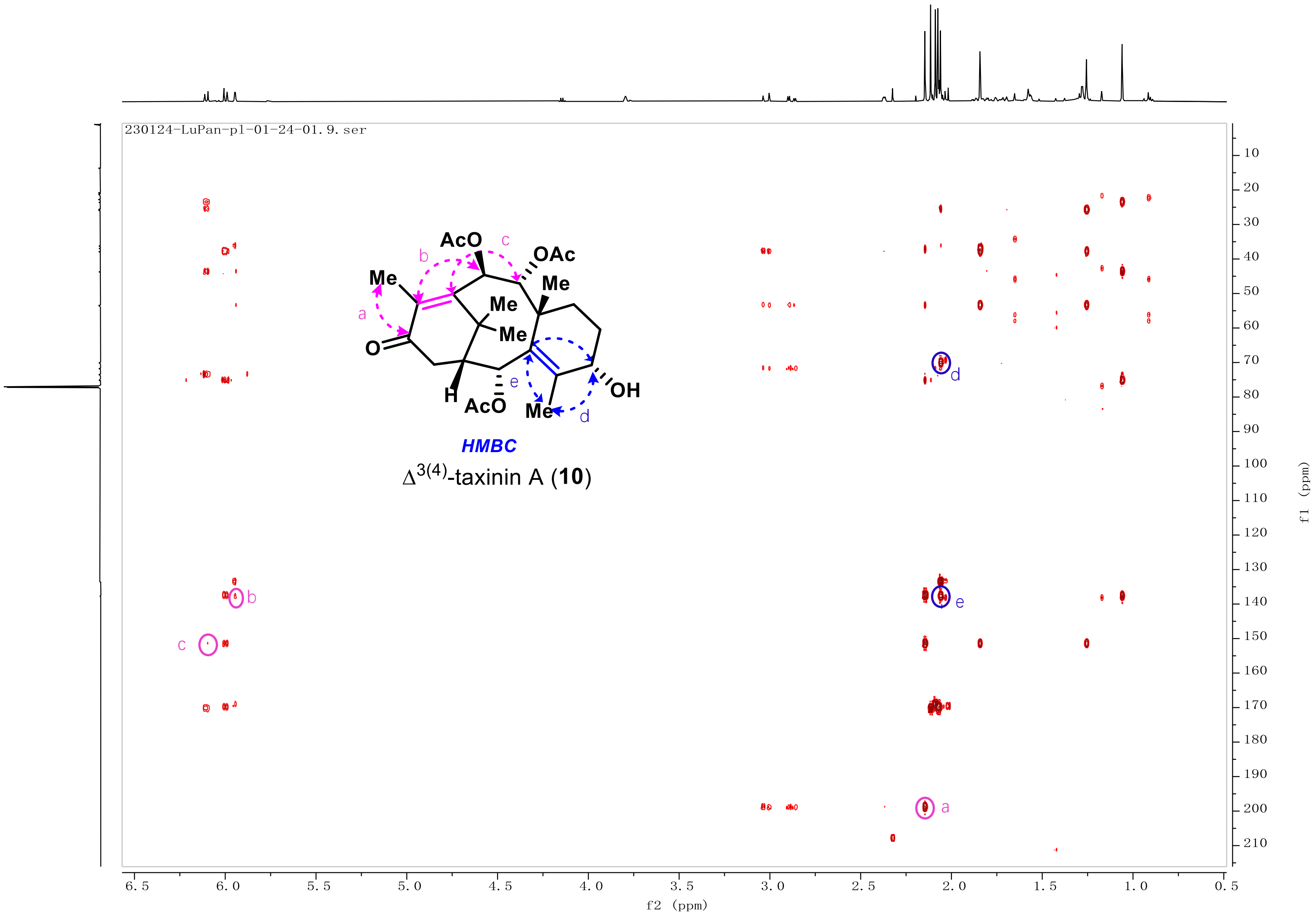
$\Delta^{3(4)}$-taxinin A (**10**)



Δ$^{3(4)}$-taxinin A (**10**)

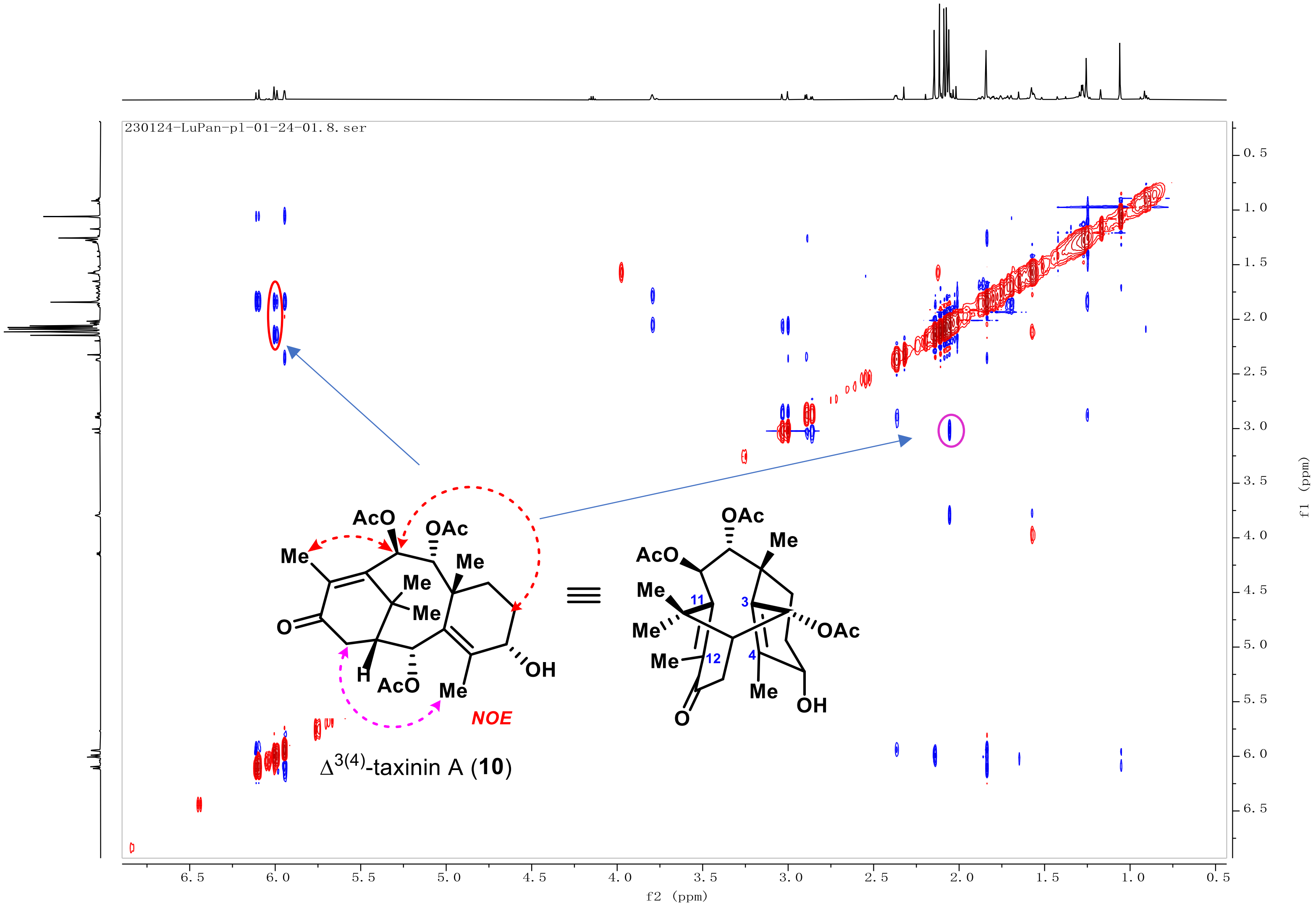


$\Delta^{3(4)}$-taxinin A (**10**)

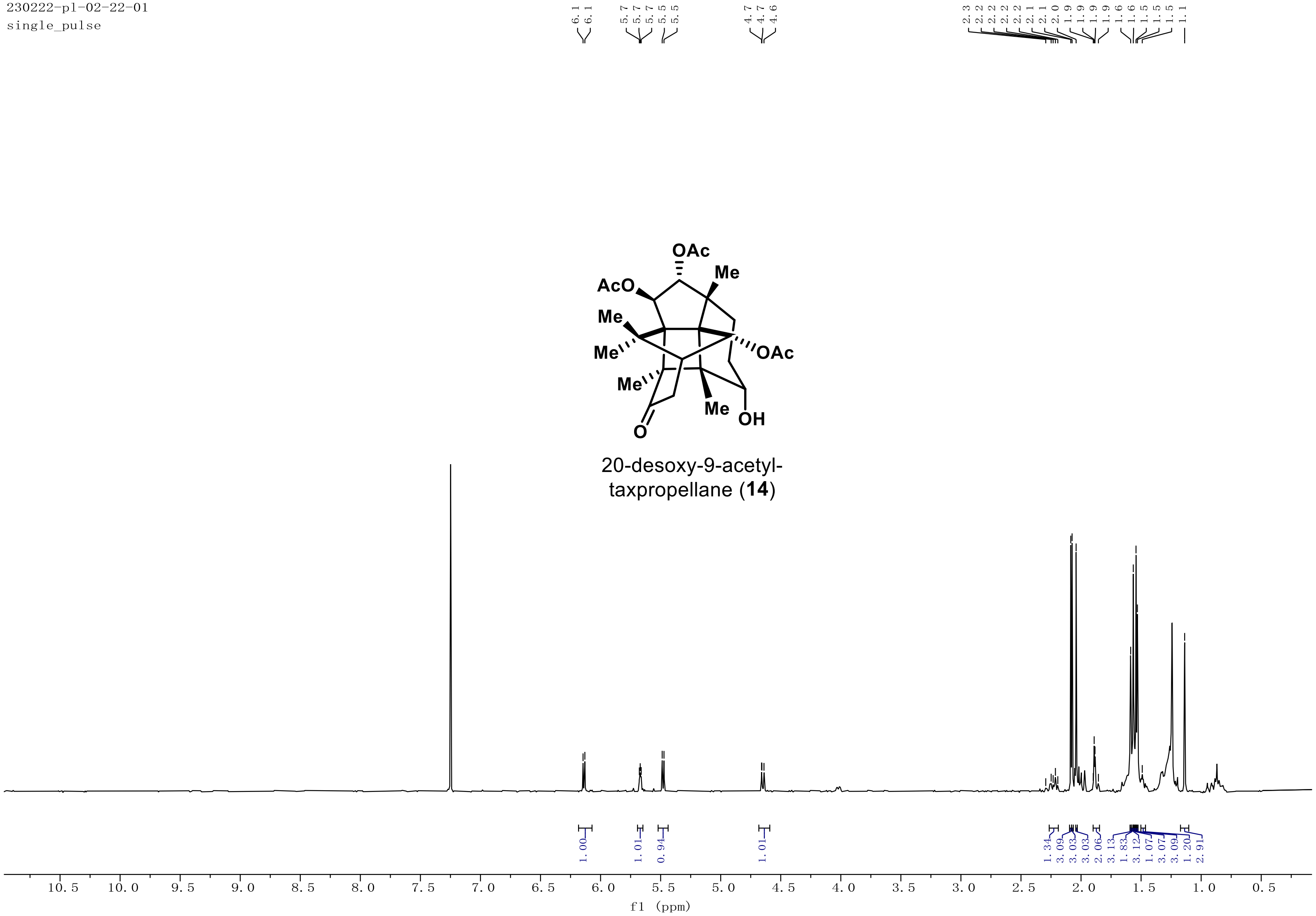


***HMBC***

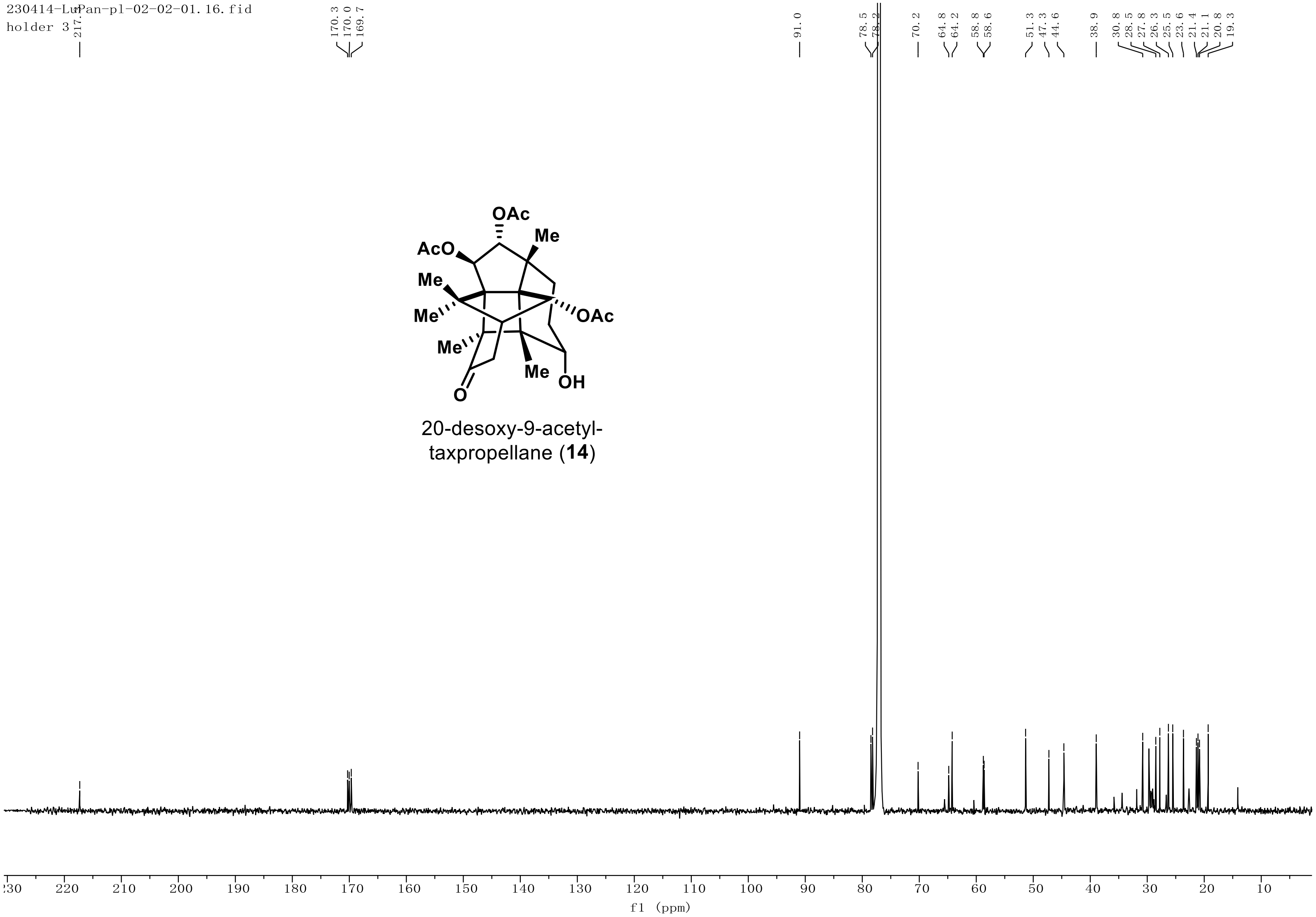
Δ$^{3(4)}$-taxinin A (**10**)


$\Delta^{3(4)}$-taxinin A (**10**)

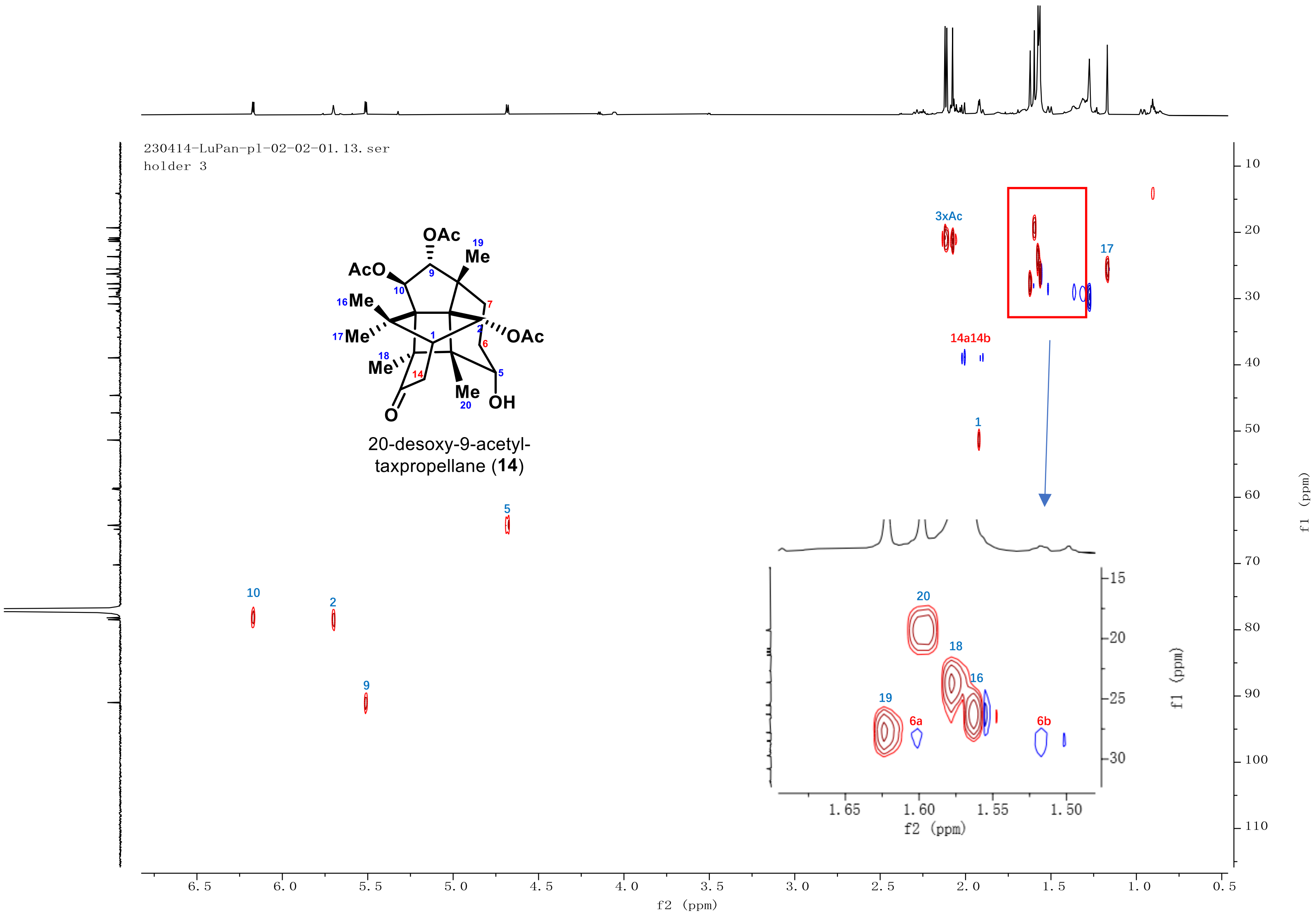
230222-pl-02-22-01
single_pulse

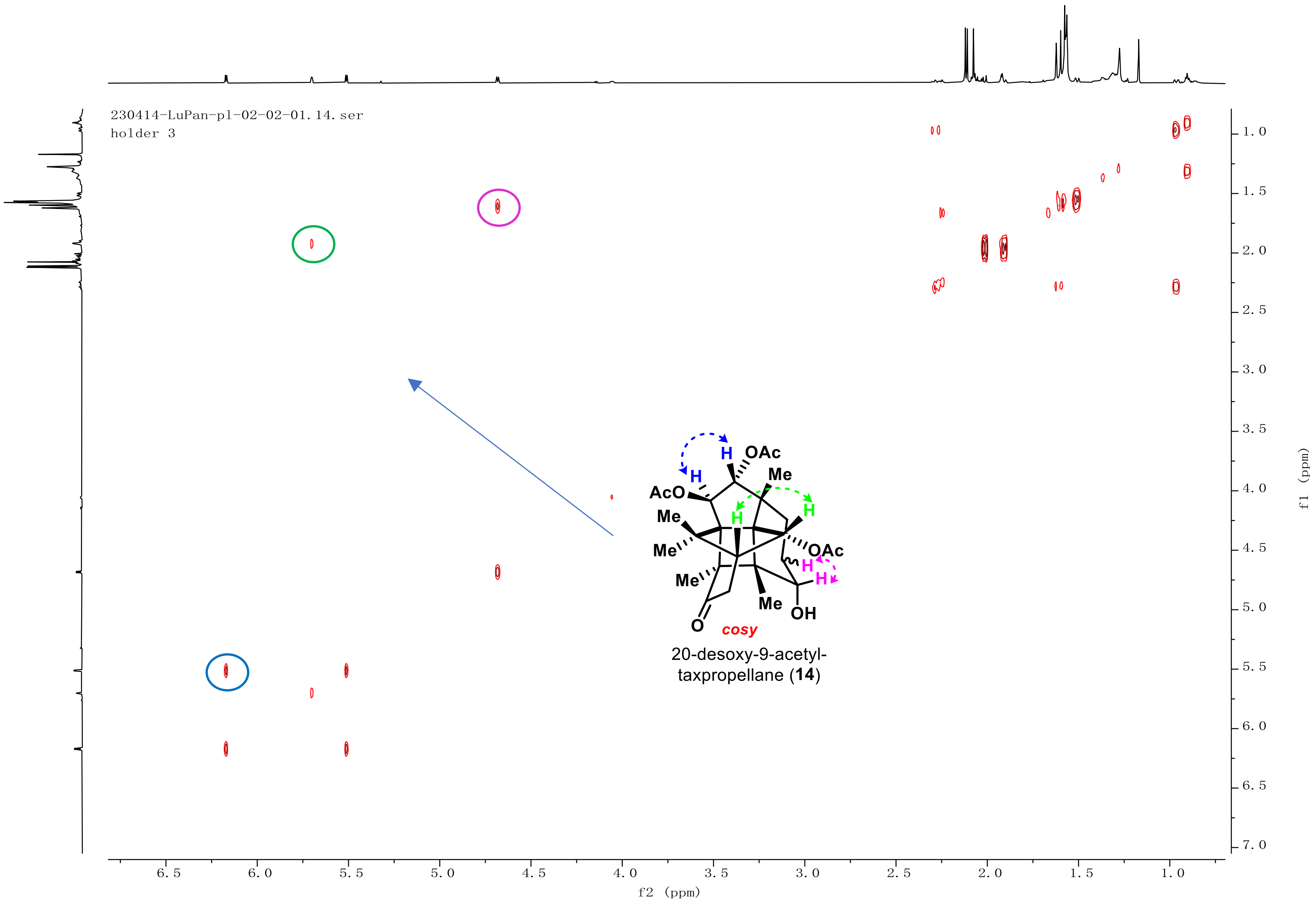


20-desoxy-9-acetyl-taxpropellane (**14**)

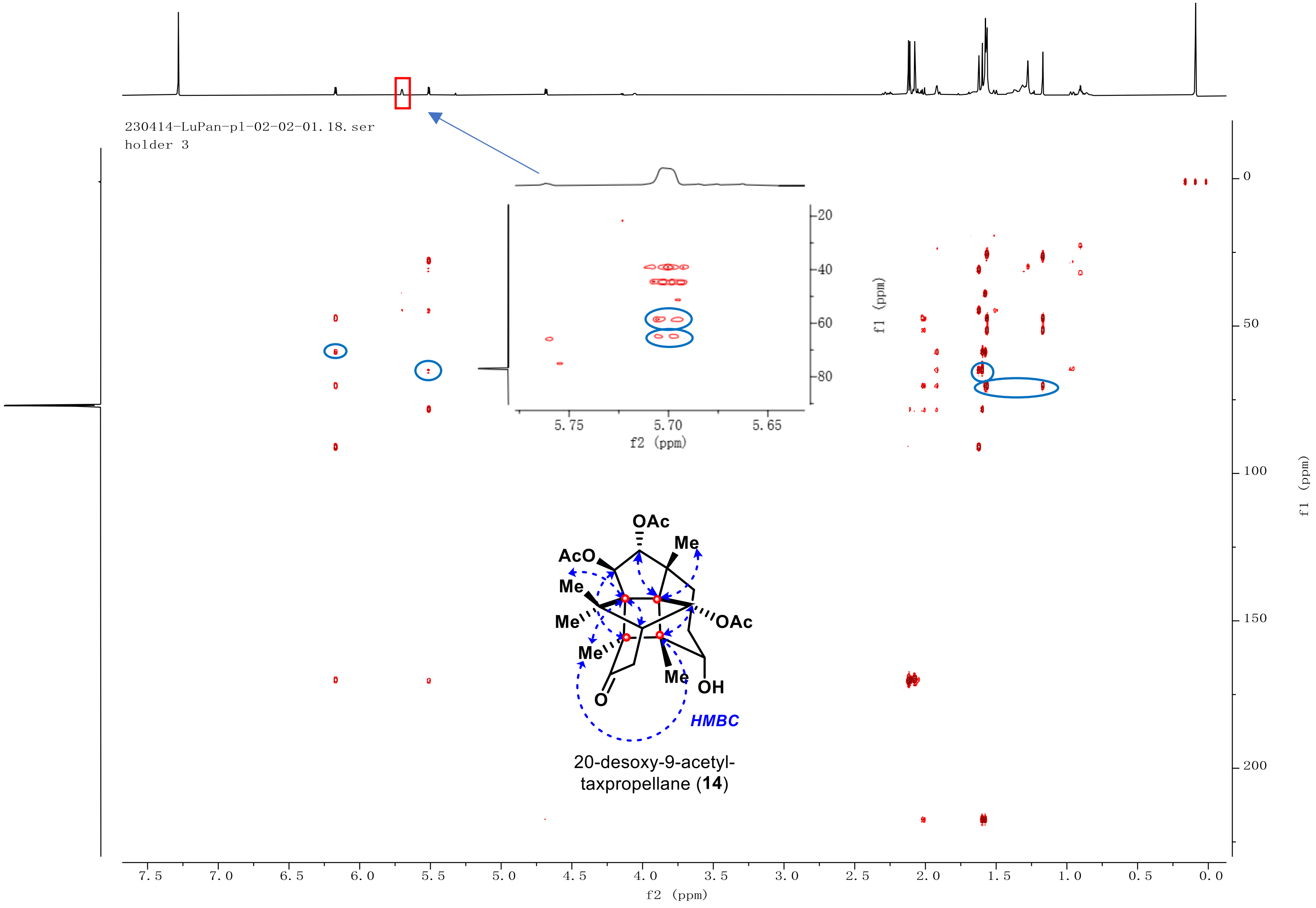


20-desoxy-9-acetyl-taxpropellane (**14**)

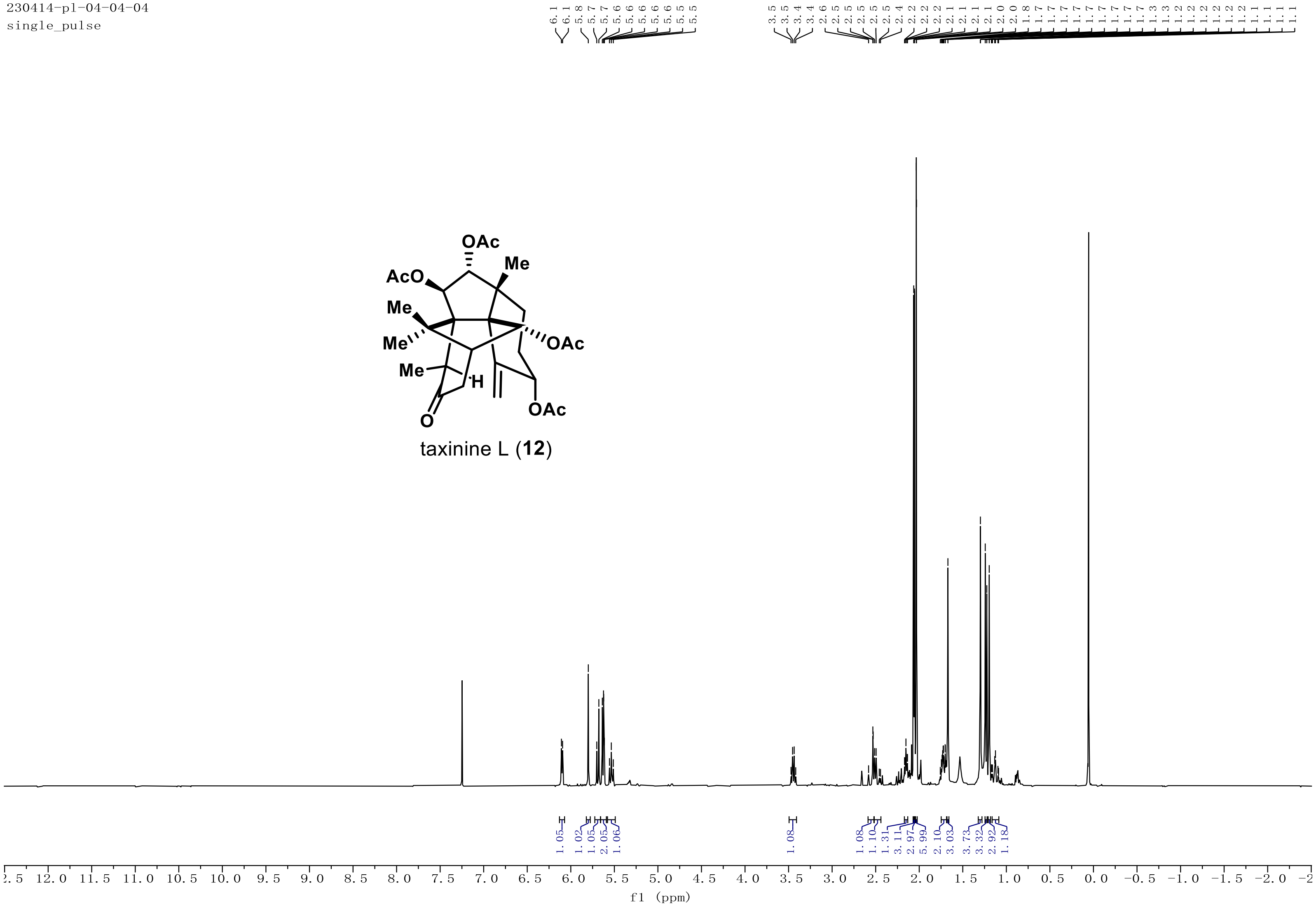

230414-LuPan-p1-02-02-01.13.ser
holder 3
OAc
19
Me
AcO
9
10
16Me
7
17Me
1
2
OAc
18
Me
6
14
5
Me
20
OH
O
20-desoxy-9-acetyl-taxpropellane (14)
3xAc
17
14a14b
1
5
10
2
9
20
18
16
19
6a
6b
15
20
25
30
1.65
1.60
1.55
1.50
f2 (ppm)
f1 (ppm)
10
20
30
40
50
60
70
80
90
100
110
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
f1 (ppm)



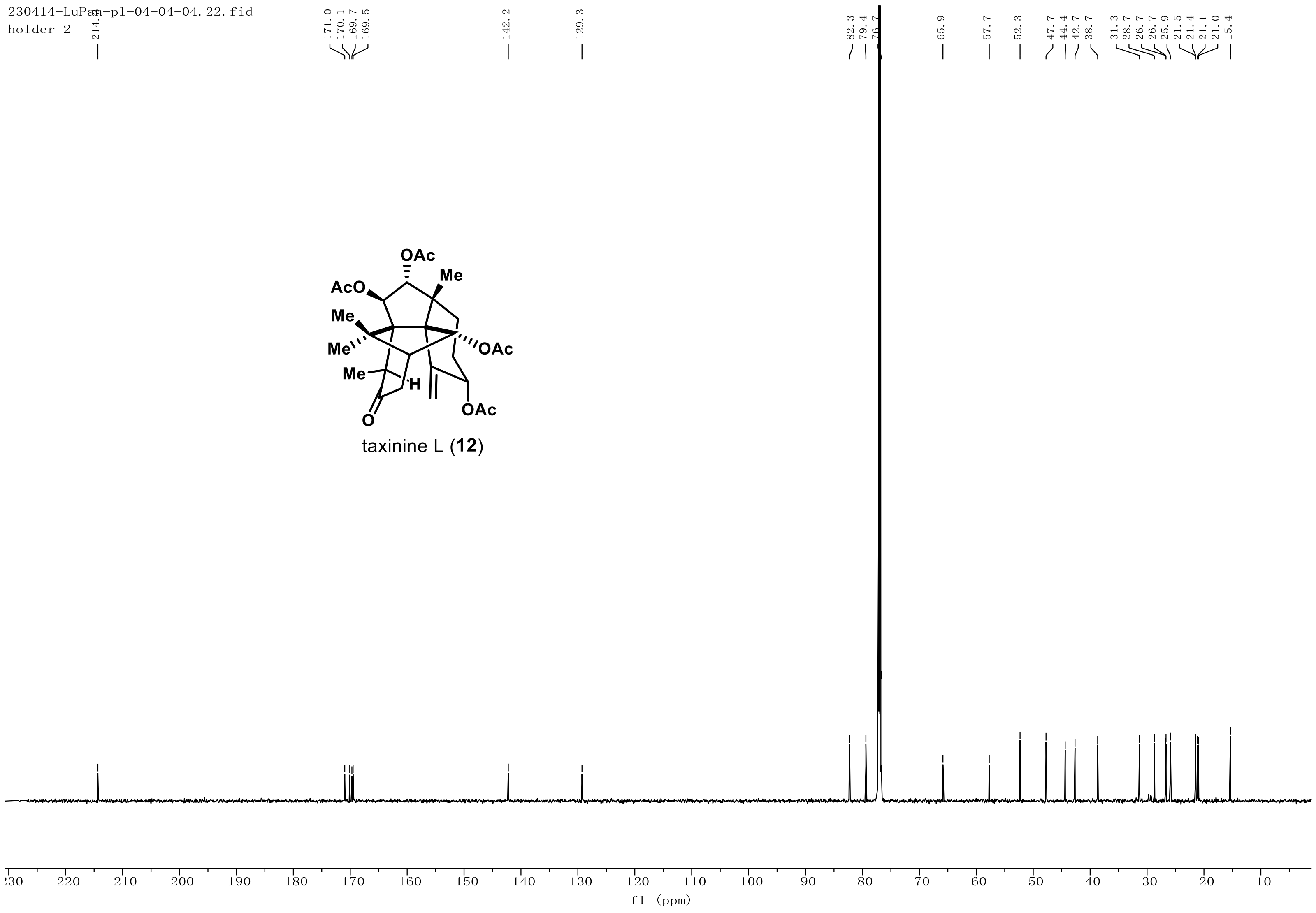
20-desoxy-9-acetyl-taxpropellane (**14**)



20-desoxy-9-acetyl-taxpropellane (**14**)

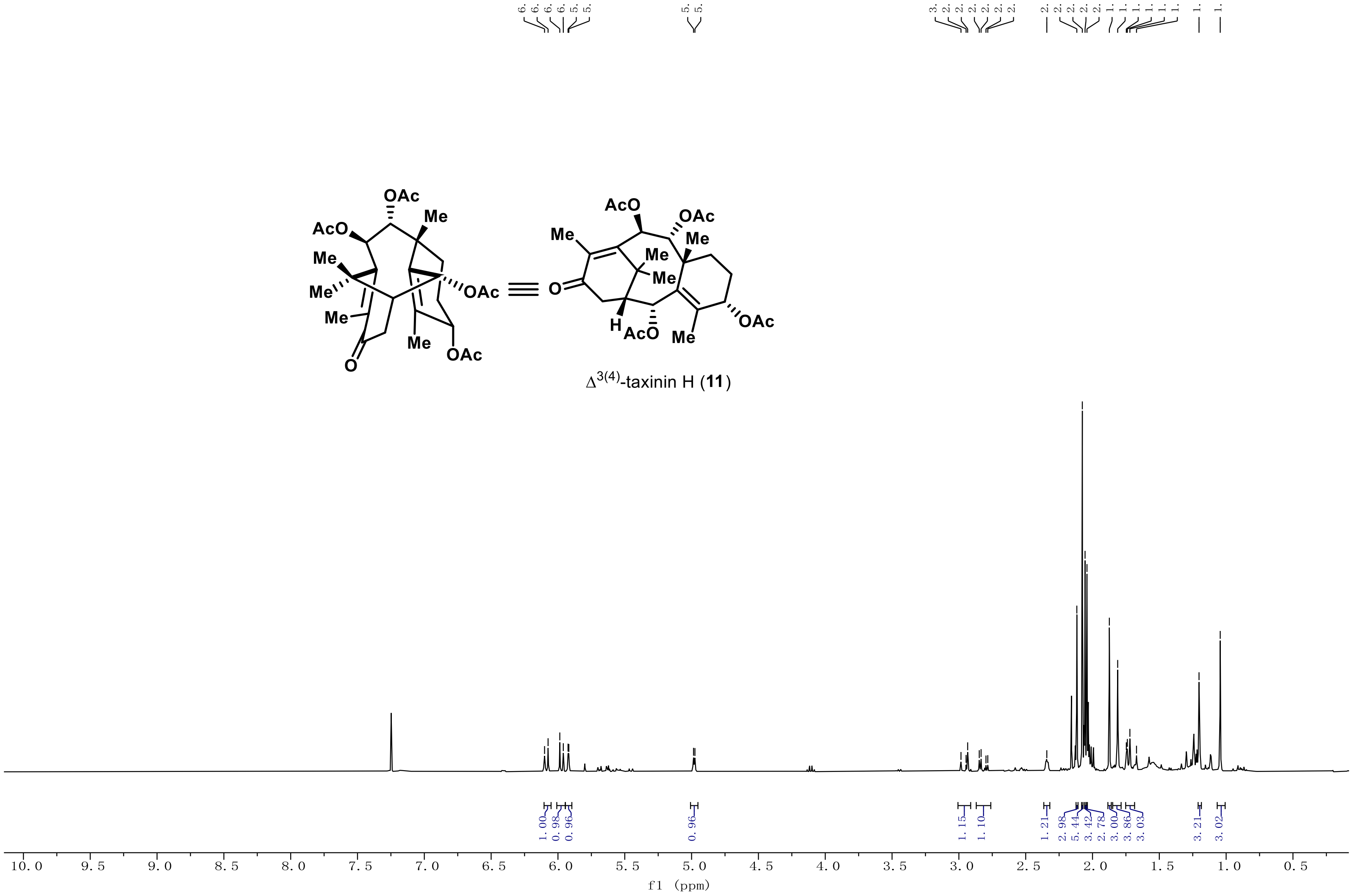


taxinine L (**12**)

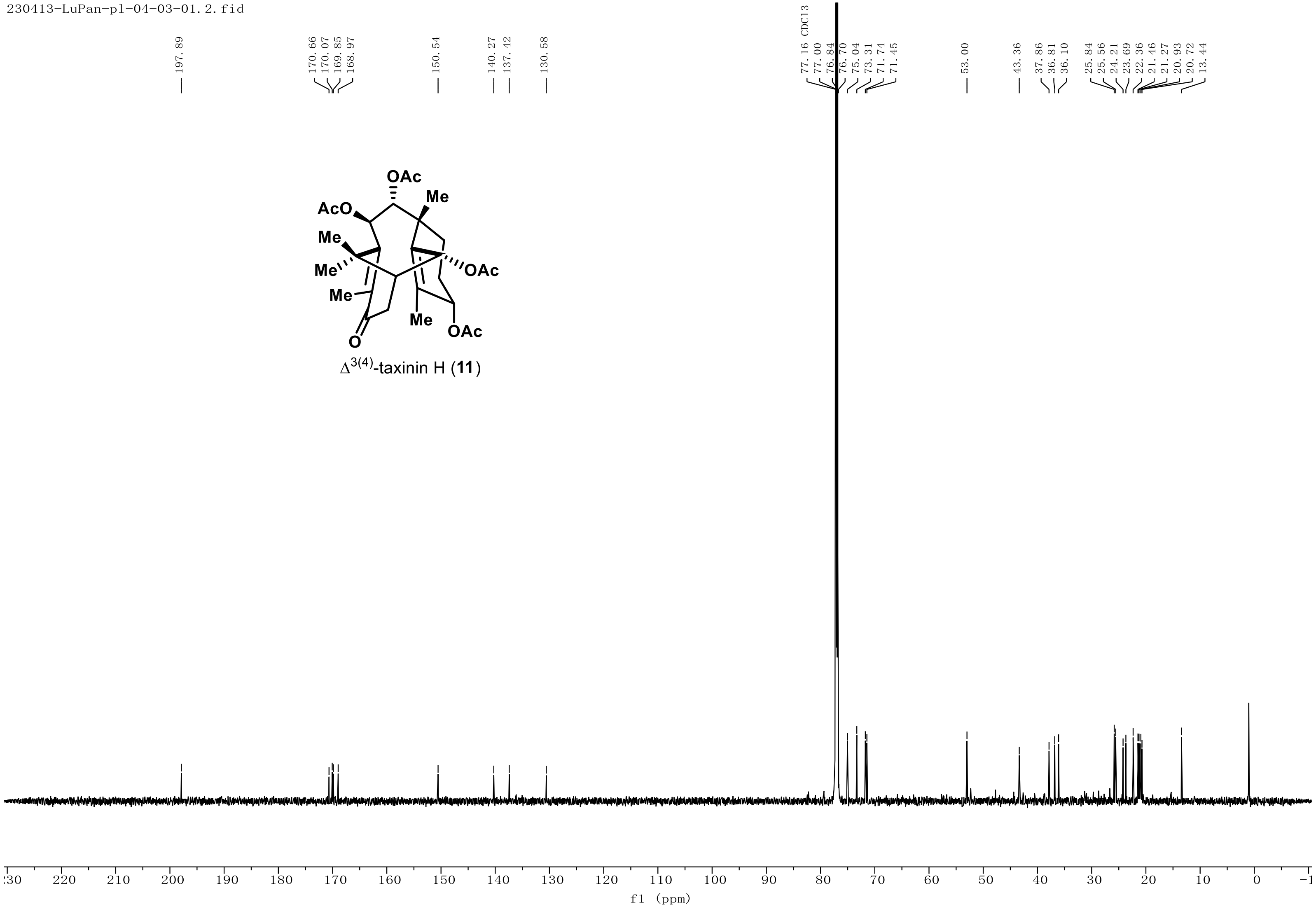


taxinine L (**12**)

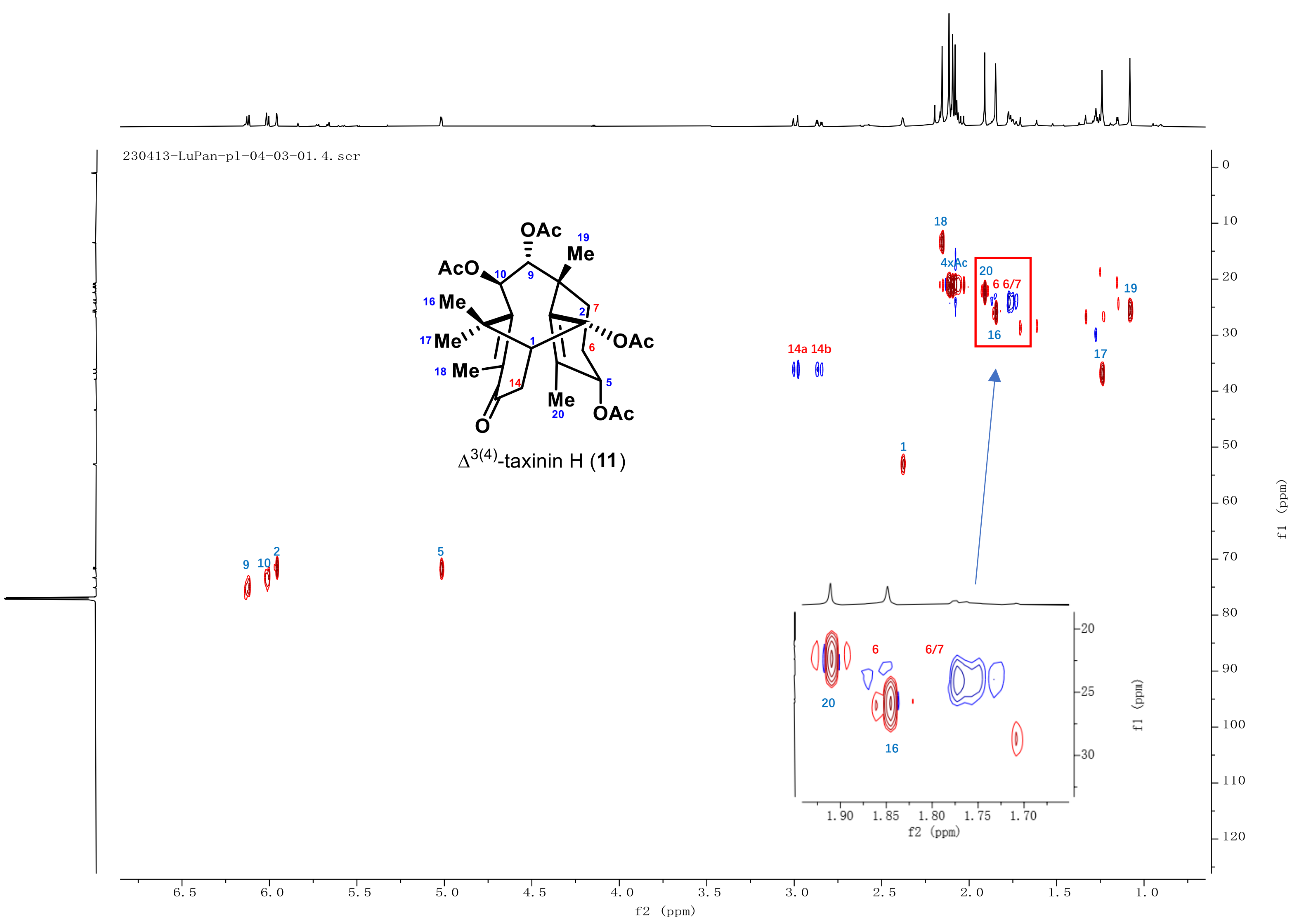
230413-pl-04-03-01
single_pulse



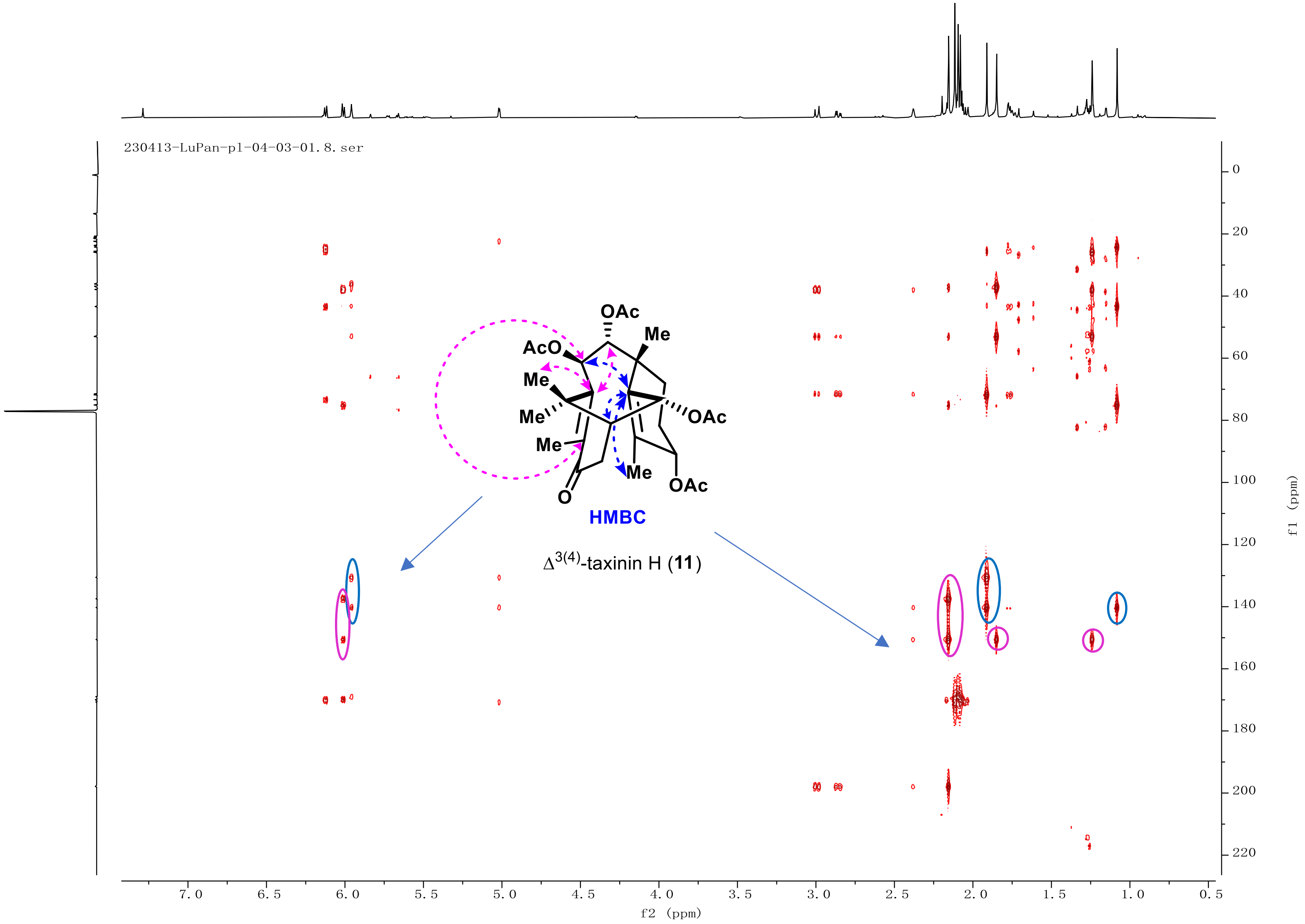
Δ$^{3(4)}$-taxinin H (**11**)



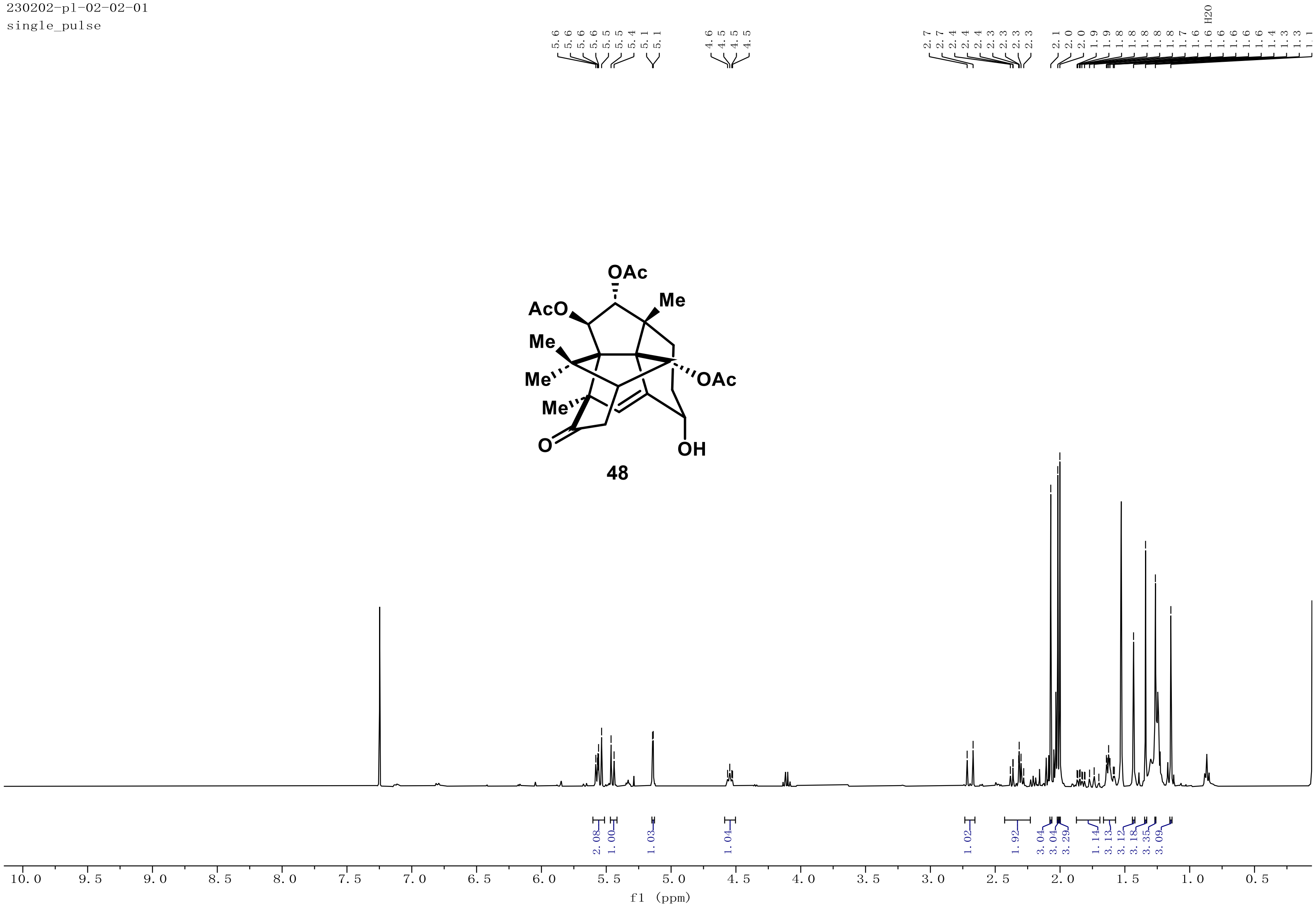
$\Delta^{3(4)}$-taxinin H (**11**)



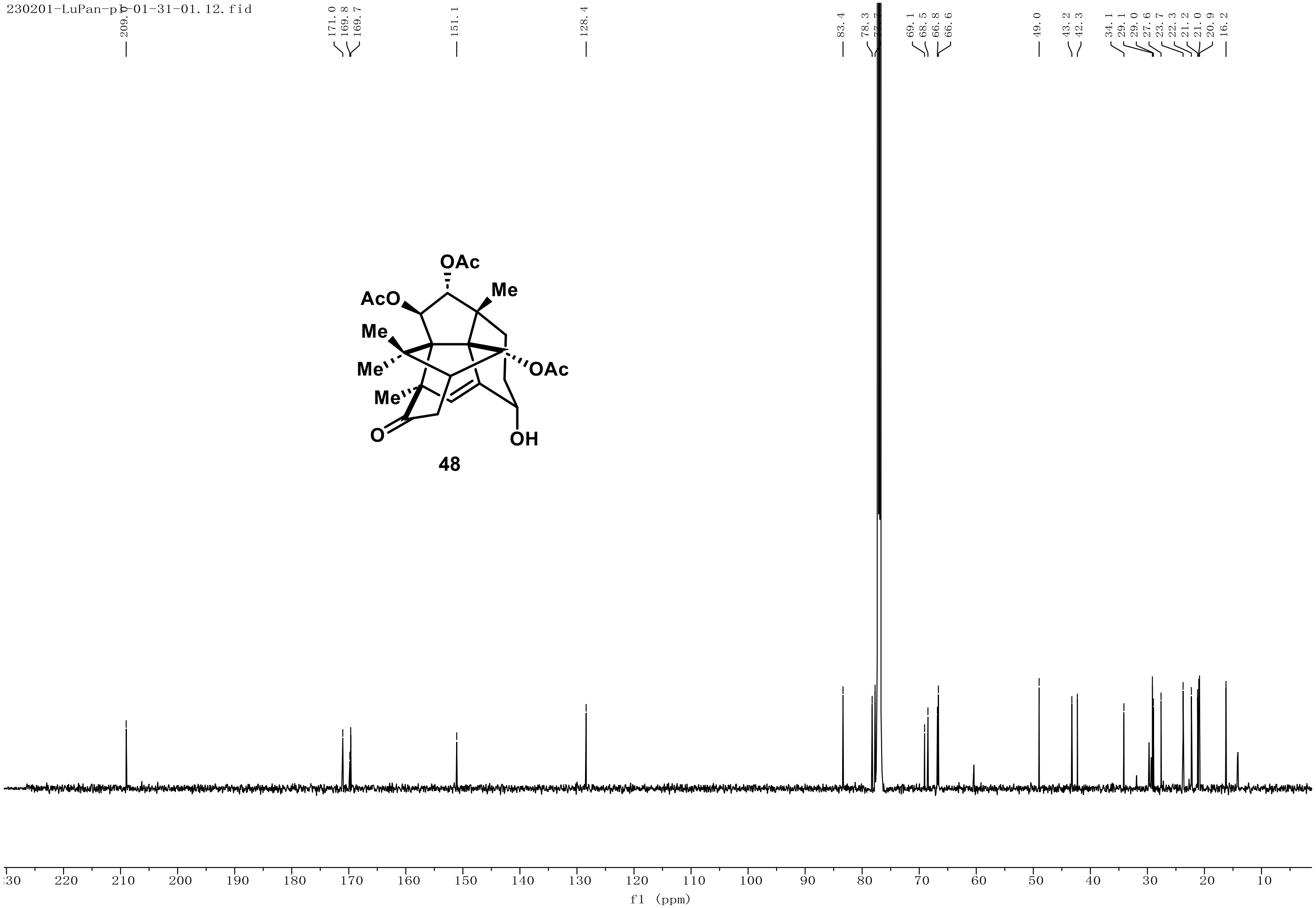
$\Delta^{3(4)}$-taxinin H (**11**)


230413-LuPan-p1-04-03-01.8.ser
OAc
Me
AcO
Me
Me
OAc
Me
Me
O
OAc
HMBC
Δ3(4)-taxinin H (11)
f2 (ppm)
f1 (ppm)
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
20
40
60
80
100
120
140
160
180
200
220

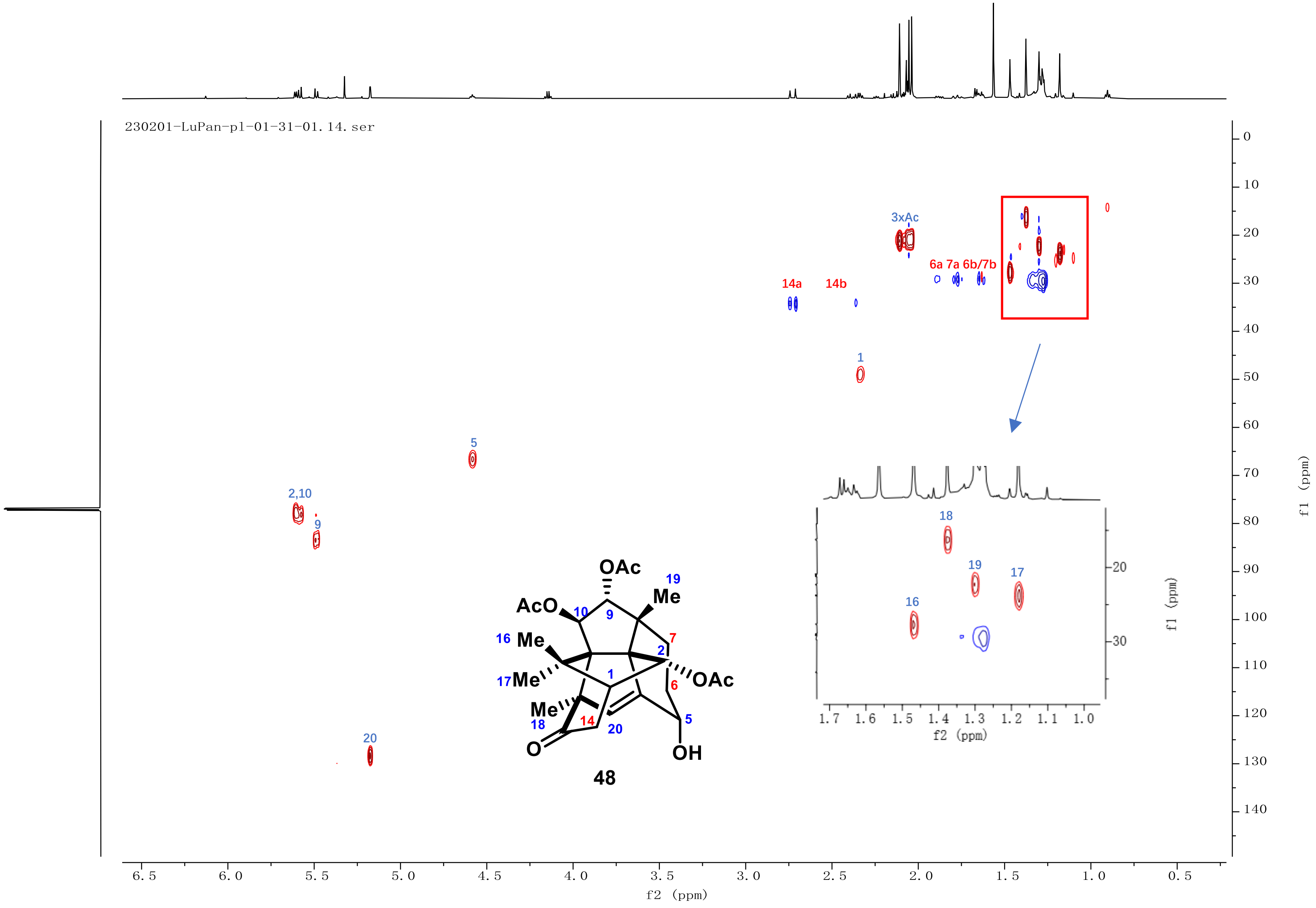
230202-pl-02-02-01
single_pulse

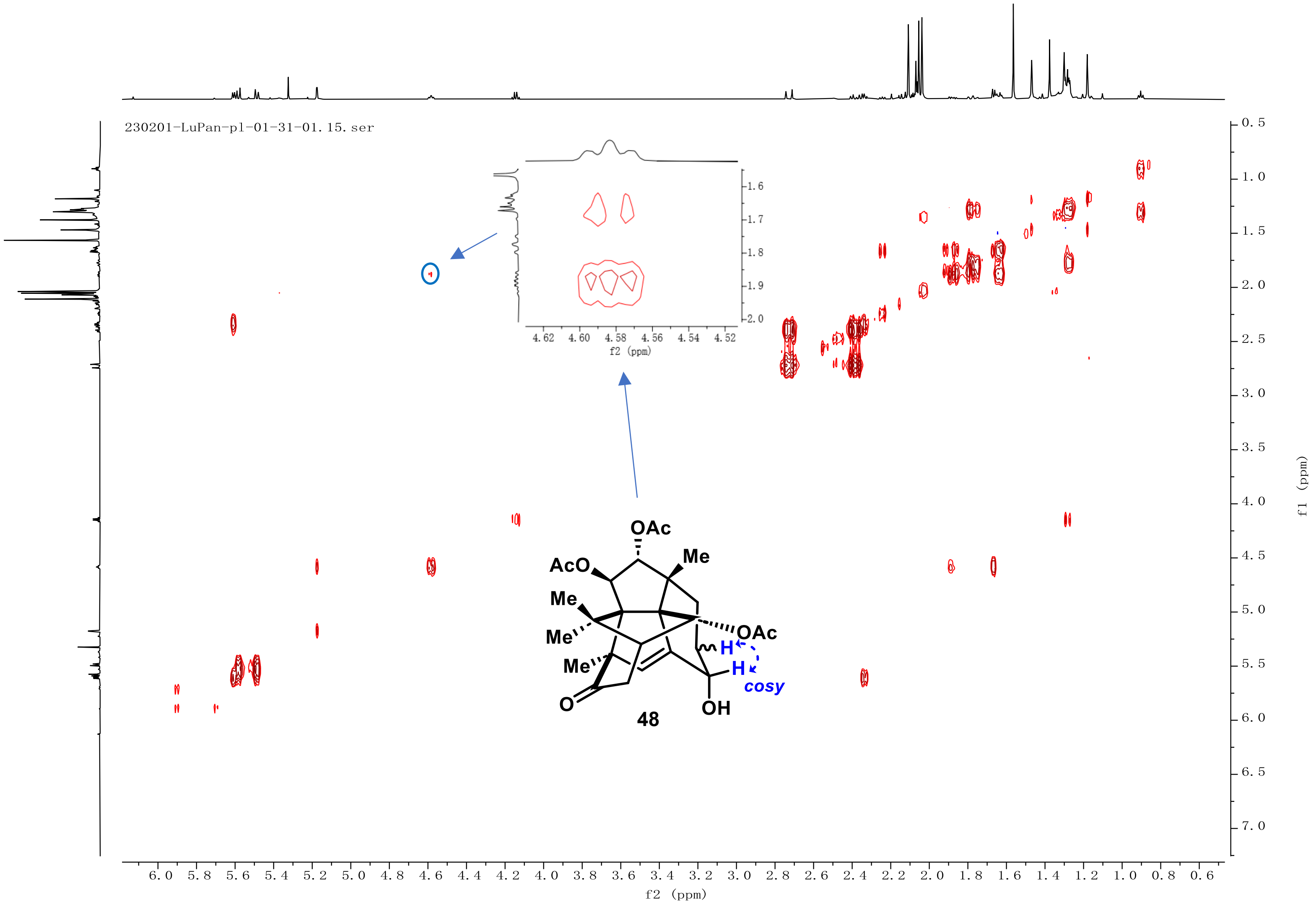


48

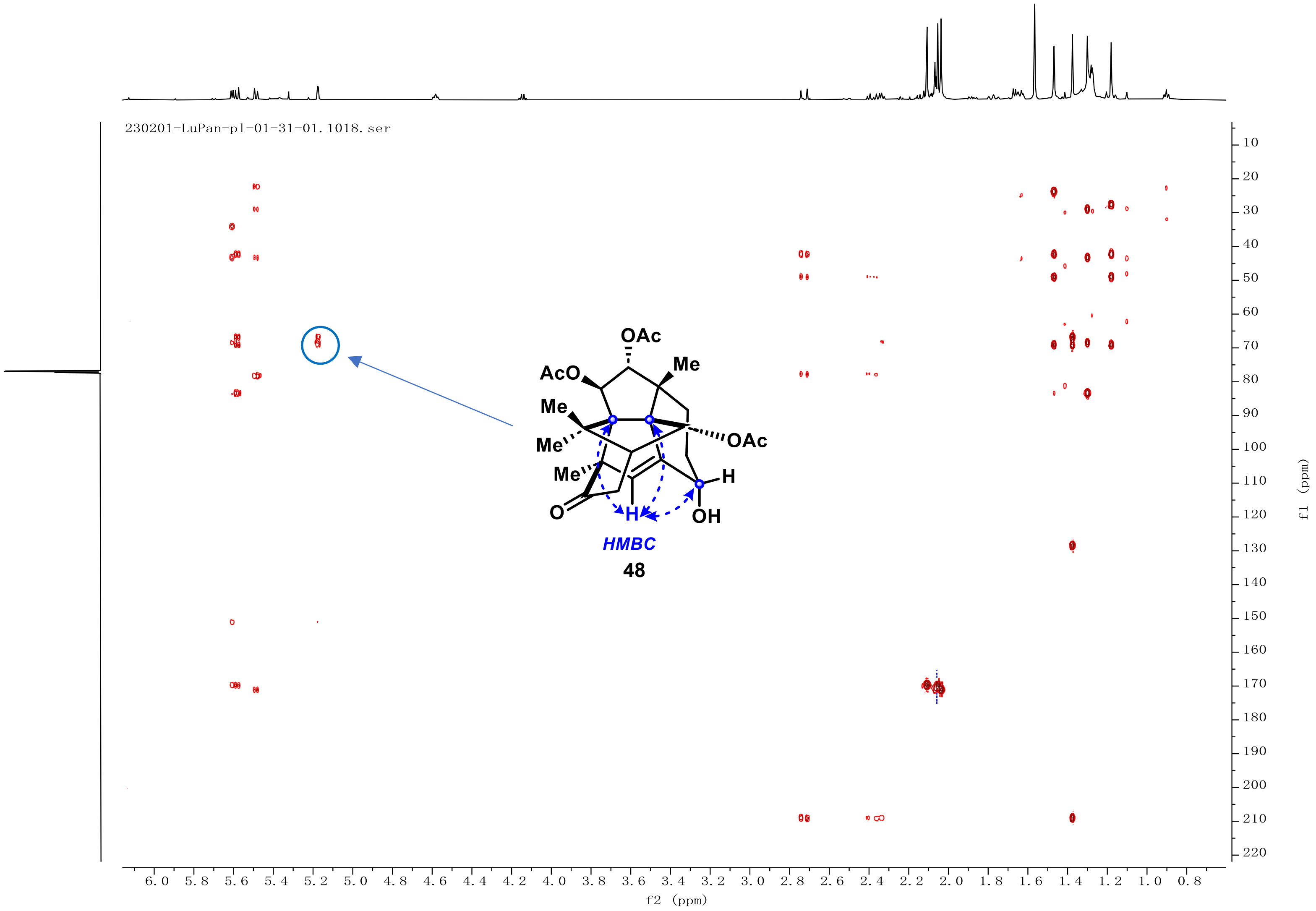

230201-LuPan-p1-01-31-01.12.fid
209.0
171.0
169.8
169.7
151.1
128.4
83.4
78.3
77.7
69.1
68.5
66.8
66.6
49.0
43.2
42.3
34.1
29.1
29.0
27.6
23.7
22.3
21.2
21.0
20.9
16.2
OAc
AcO
Me
Me
Me
OAc
Me
O
OH
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

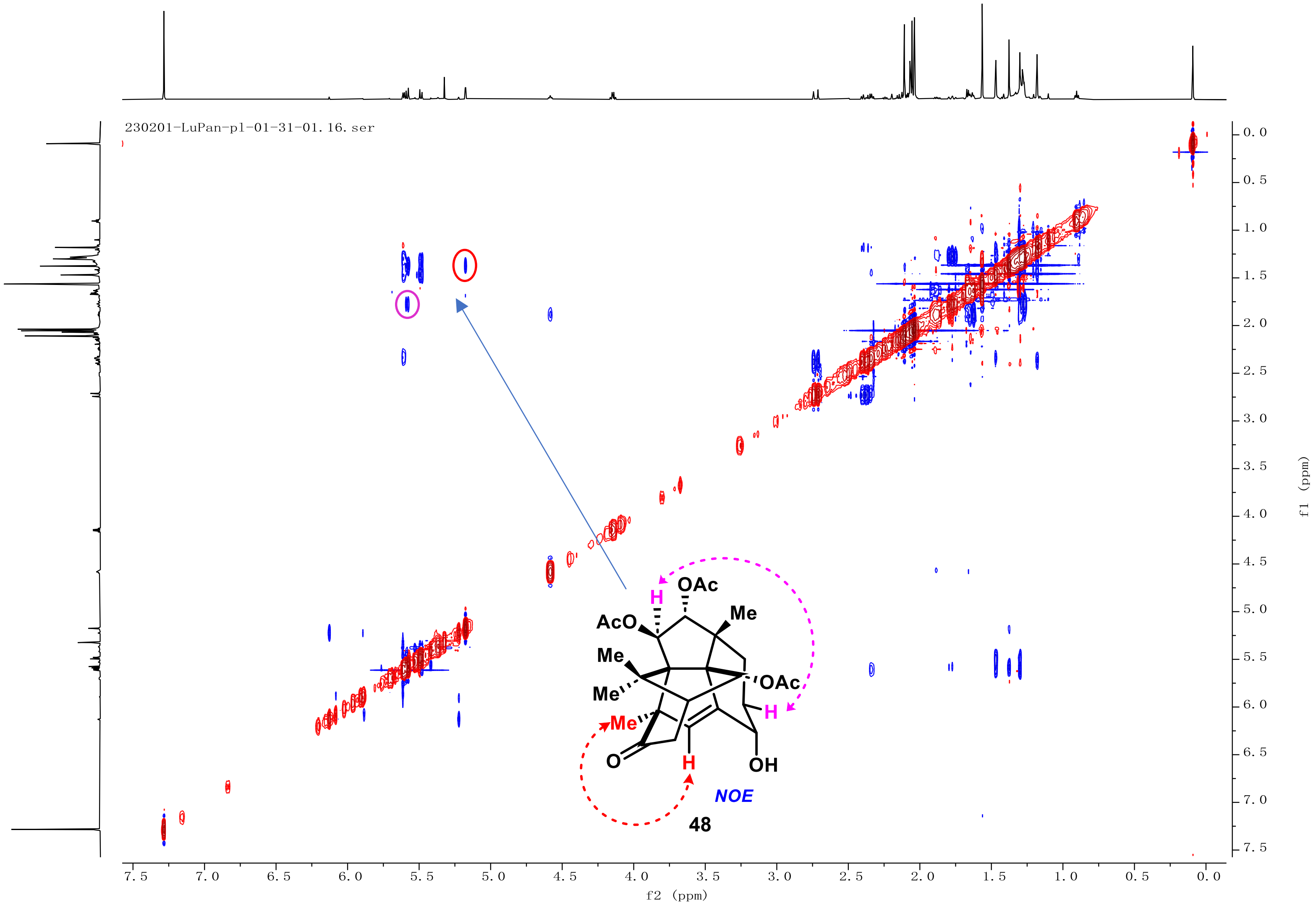
48


230201-LuPan-p1-01-31-01.14.ser
3xAc
14a
14b
6a 7a 6b/7b
1
5
2,10
9
20
18
19
17
16
OAc
AcO
Me
19
10
9
16 Me
7
2
17Me
1
6
OAc
Me
18
14
20
5
O
OH
48
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
f2 (ppm)
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140
f1 (ppm)
1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0
-20
-30

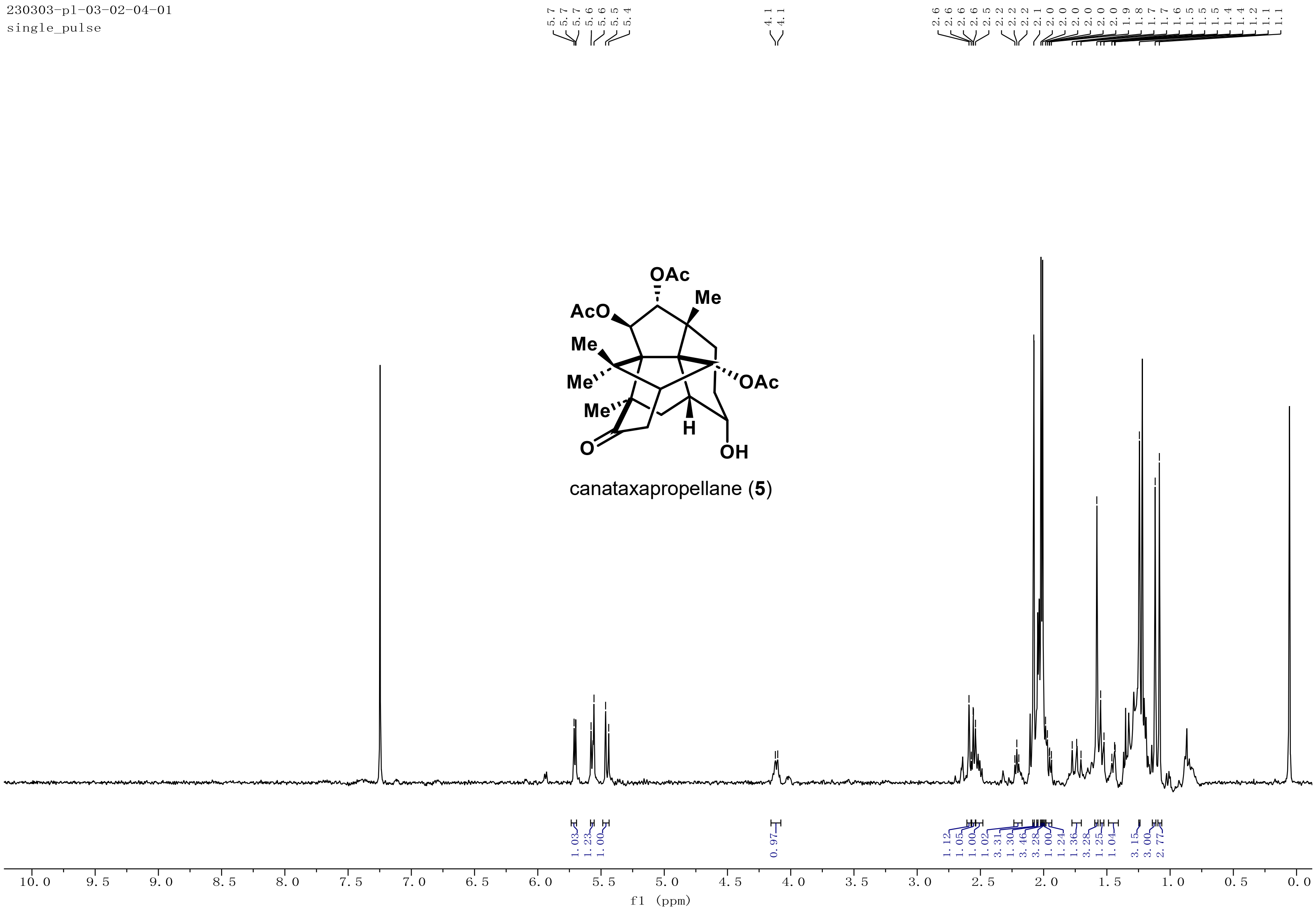

230201-LuPan-p1-01-31-01.15.ser
4.62
4.60
4.58
4.56
4.54
4.52
f2 (ppm)
1.6
1.7
1.8
1.9
2.0
OAc
Me
AcO
Me
Me
OAc
H
H
cosy
Me
O
OH
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
f2 (ppm)
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
f1 (ppm)

**48**

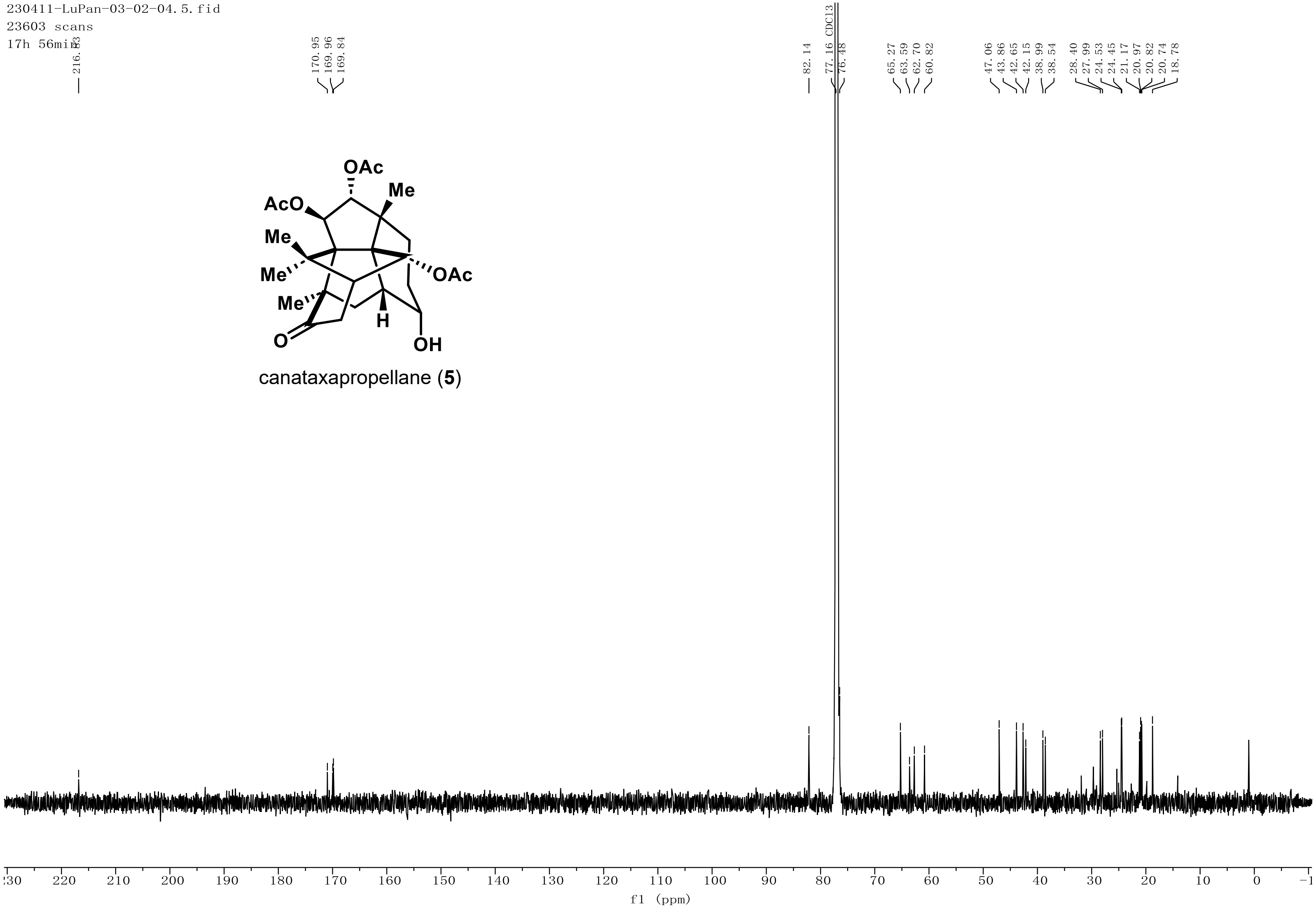

230201-LuPan-pl-01-31-01.1018.ser
OAc
AcO
Me
Me
Me
Me
OAc
H
O
H
OH
HMBC
48
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
f2 (ppm)
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
f1 (ppm)


230201-LuPan-p1-01-31-01.16.ser
AcO
OAc
H
Me
Me
Me
Me
OAc
H
O
H
OH
NOE
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
f2 (ppm)
f1 (ppm)

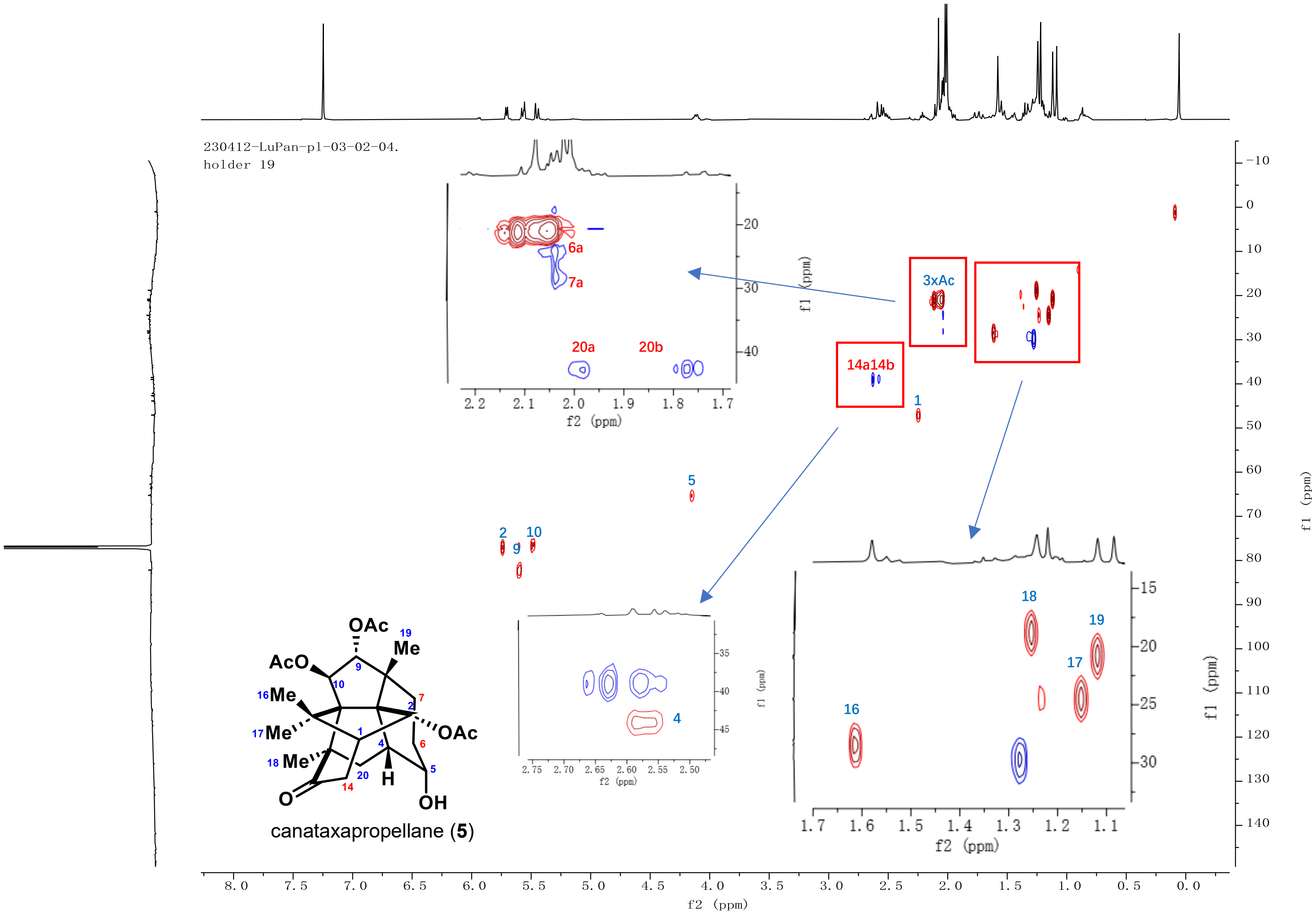
48

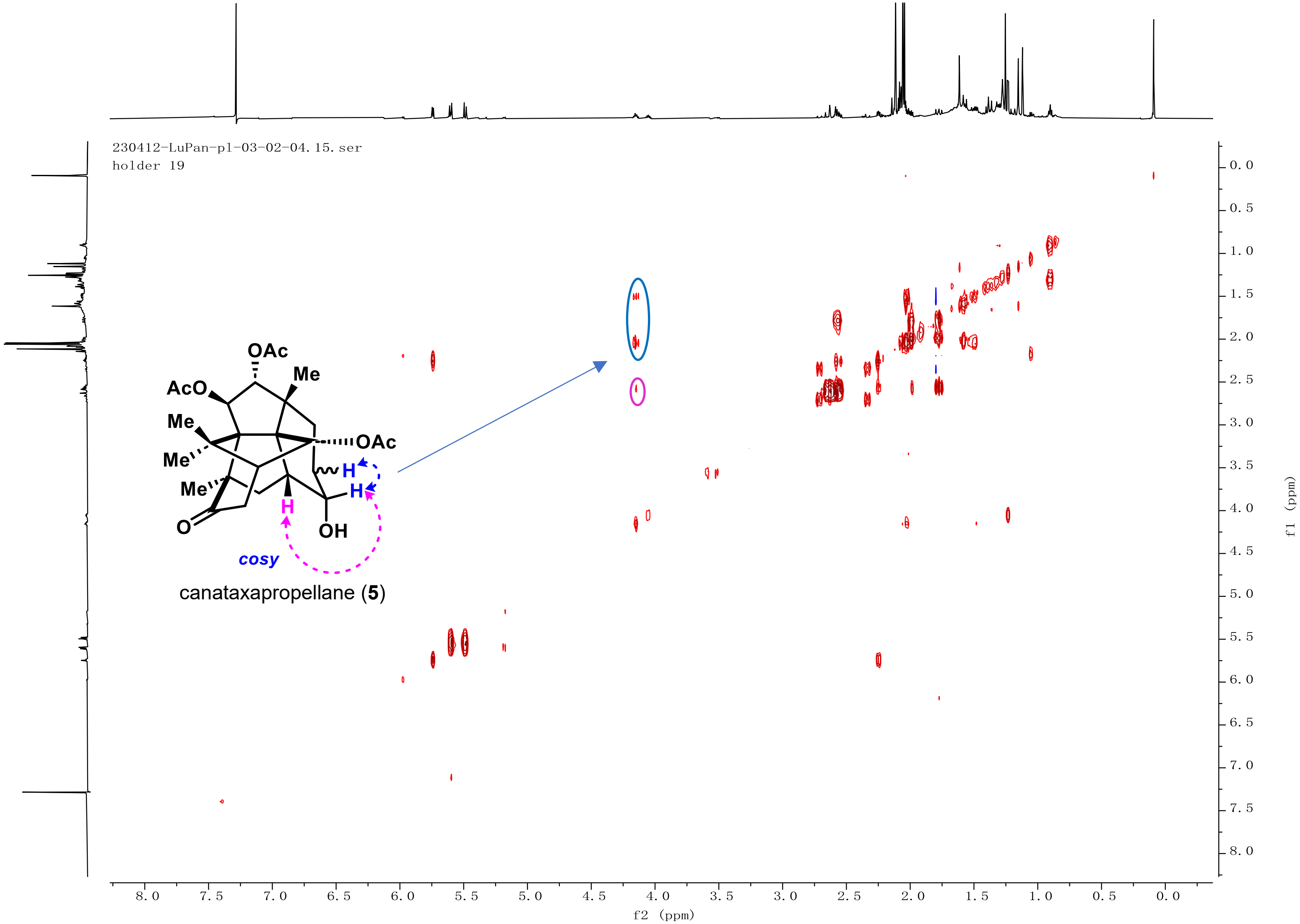


canataxapropellane (**5**)

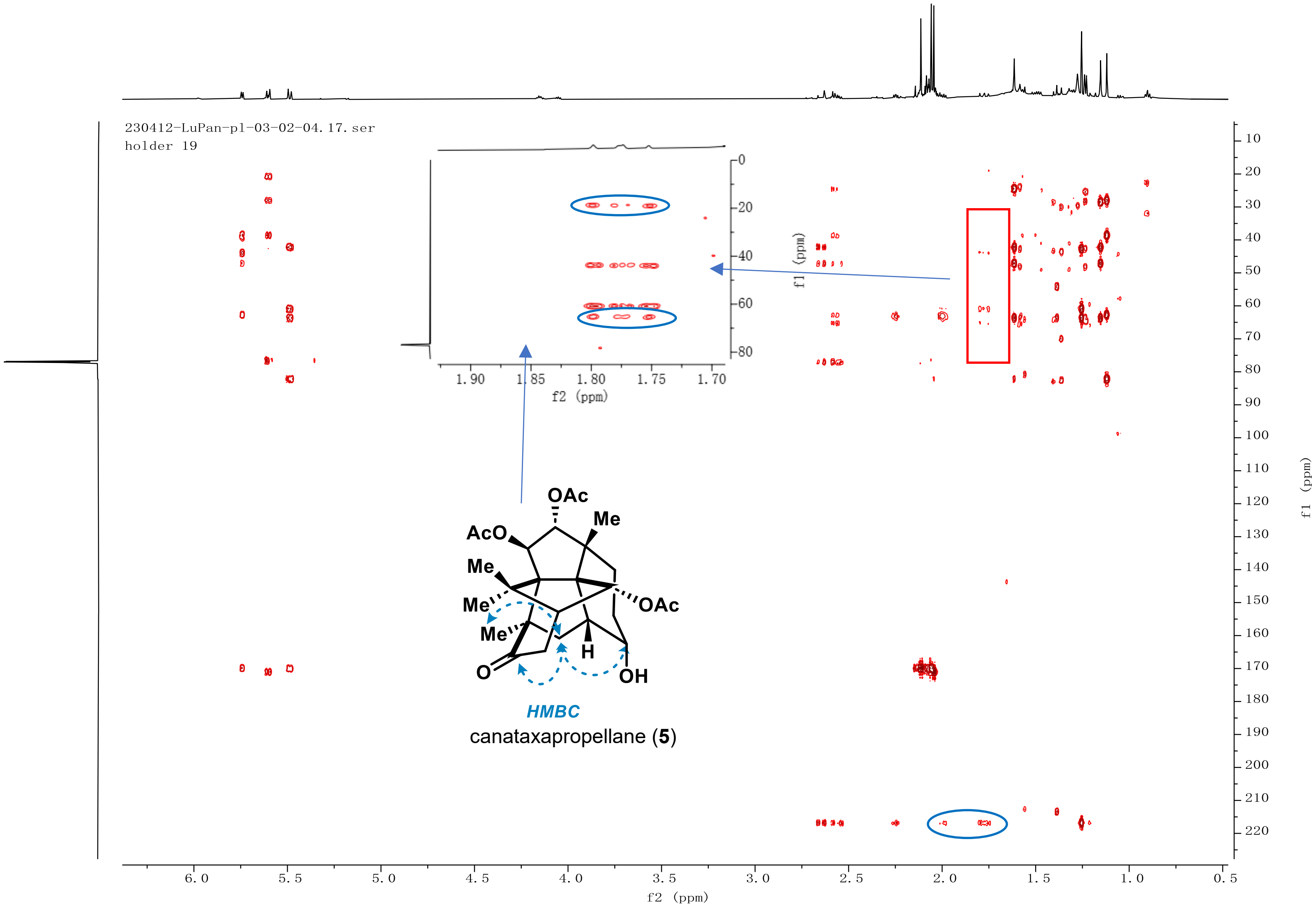


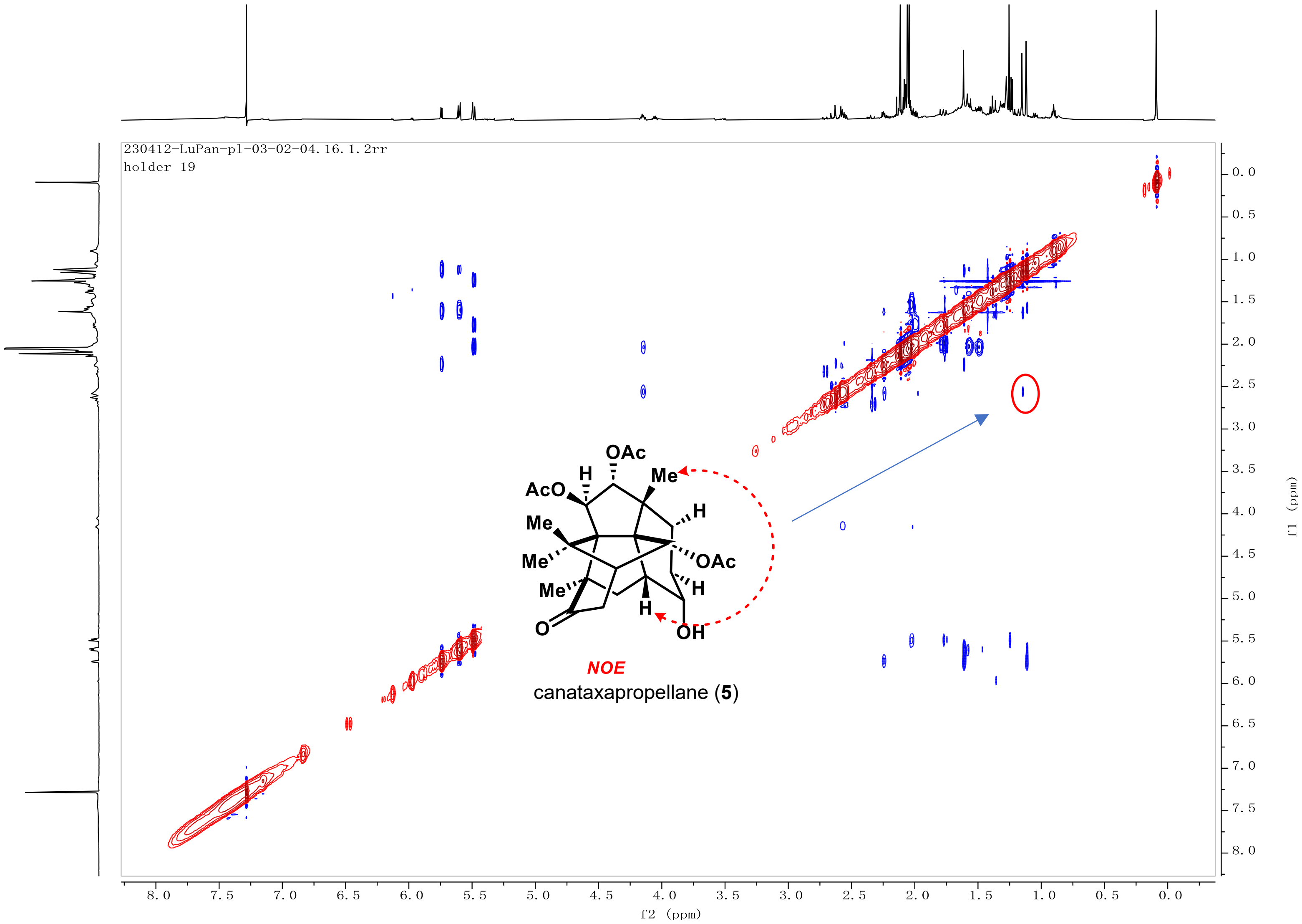
canataxapropellane (**5**)


230412-LuPan-p1-03-02-04.
holder 19
6a
7a
20a
20b
3xAc
14a14b
1
5
2
9
10
4
16
17
18
19
f1 (ppm)
f2 (ppm)
OAc
Me
AcO
Me
Me
Me
OAc
O
H
OH
canataxapropellane (5)

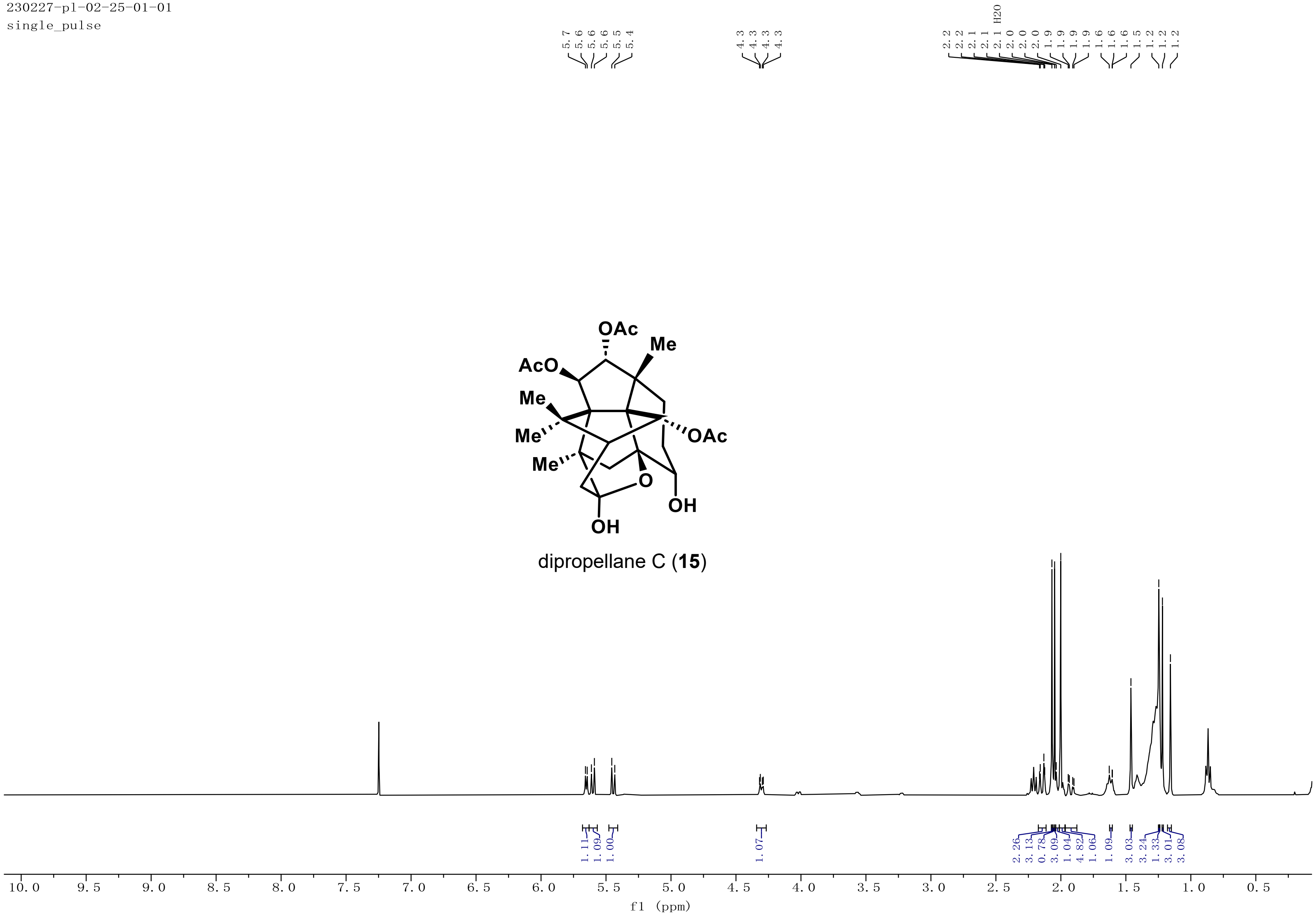


canataxapropellane (**5**)

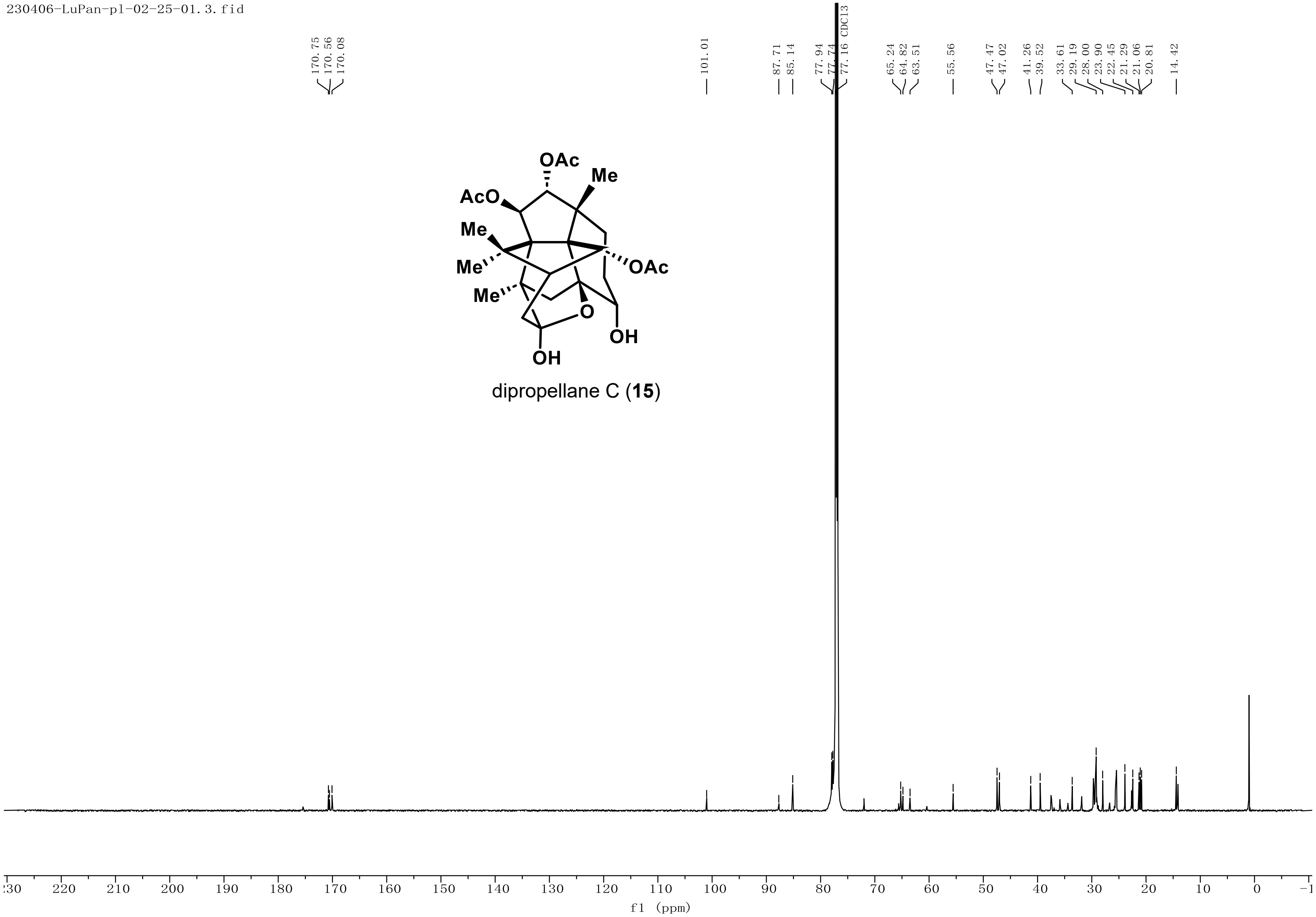

230412-LuPan-p1-03-02-04.17.ser
holder 19
f2 (ppm)
f1 (ppm)
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
1.90
1.85
1.80
1.75
1.70
0
20
40
60
80
OAc
Me
AcO
Me
Me
OAc
Me
H
O
OH
HMBC
canataxapropellane (5)



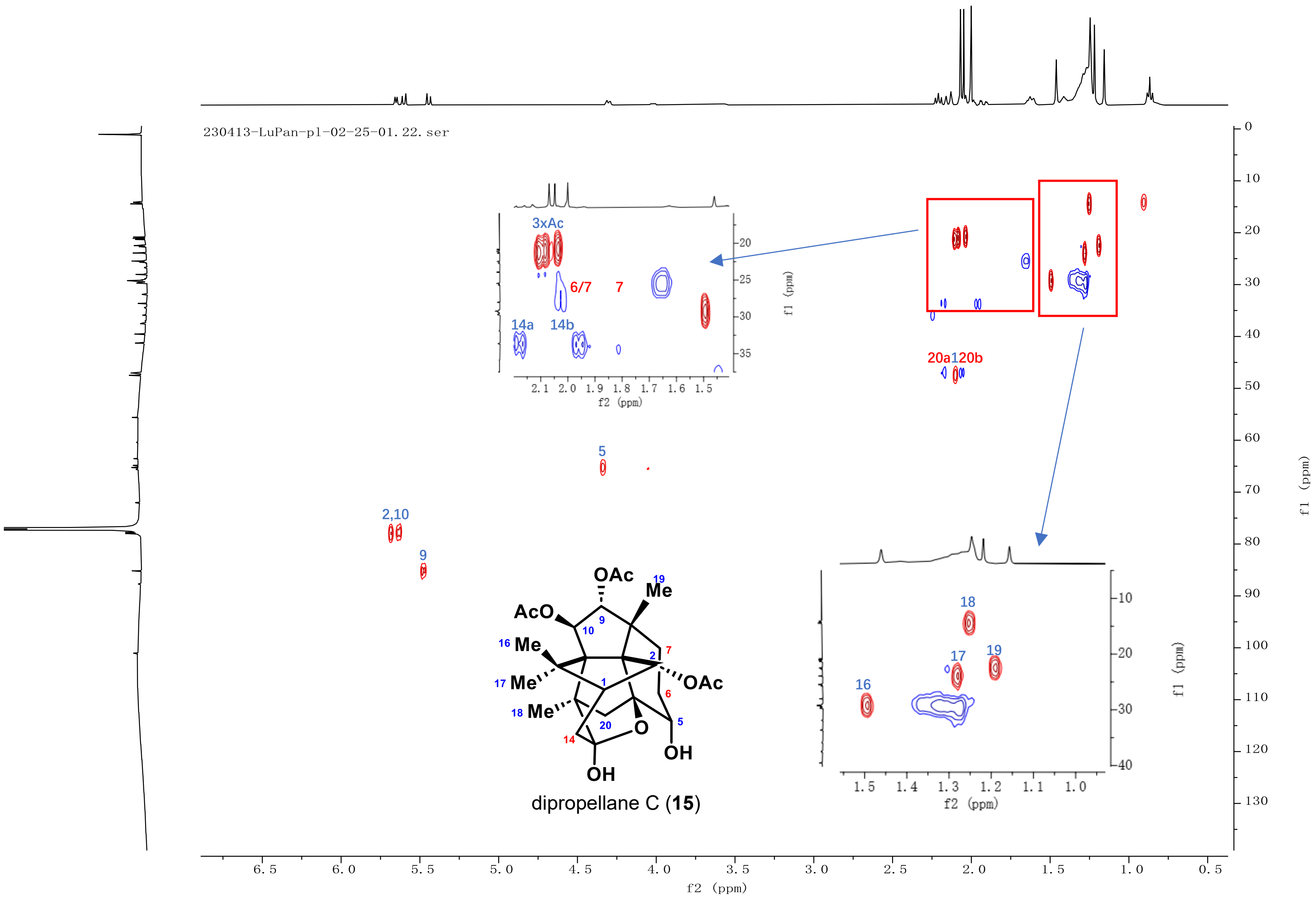
canataxapropellane (**5**)



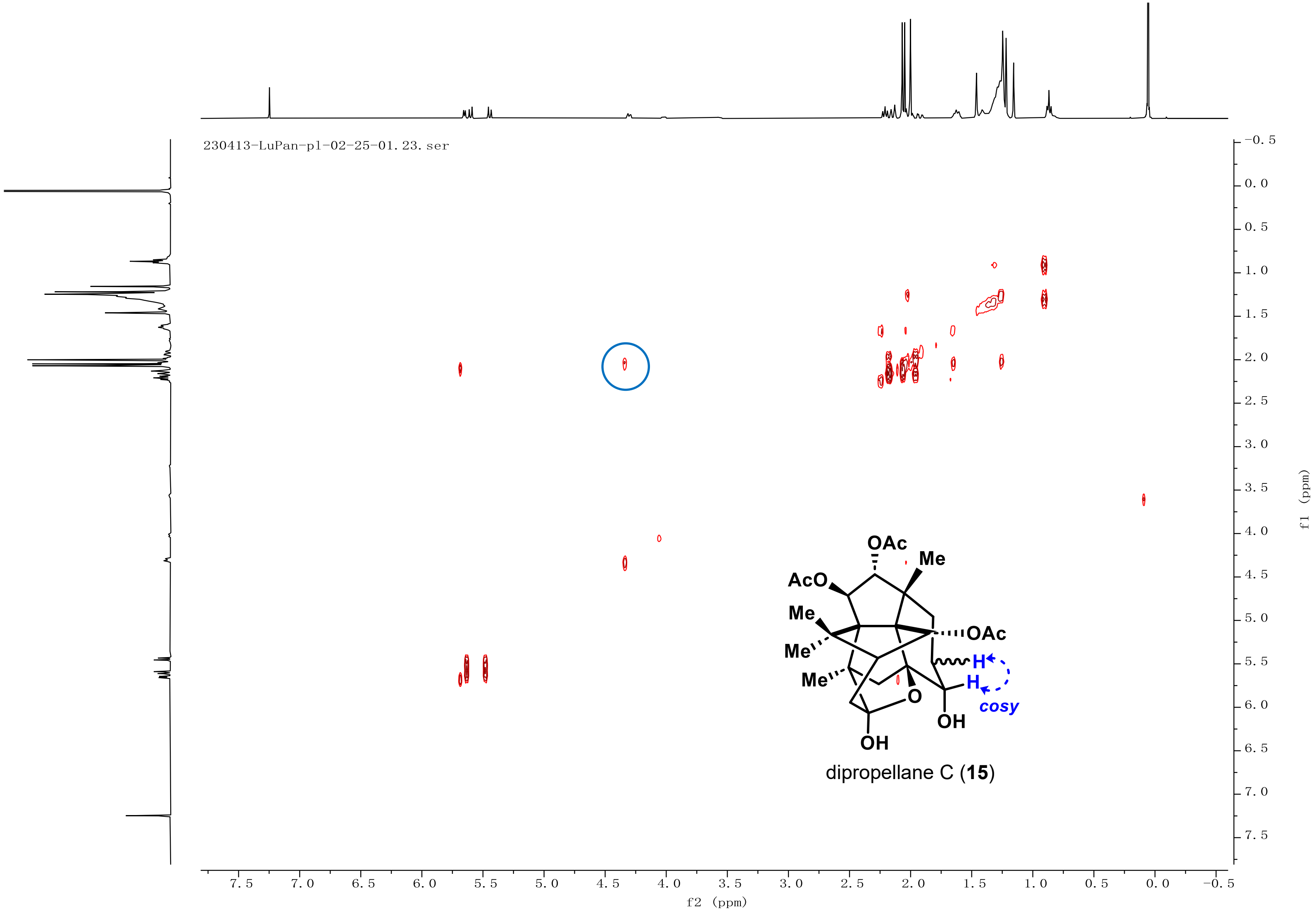
dipropellane C (**15**)



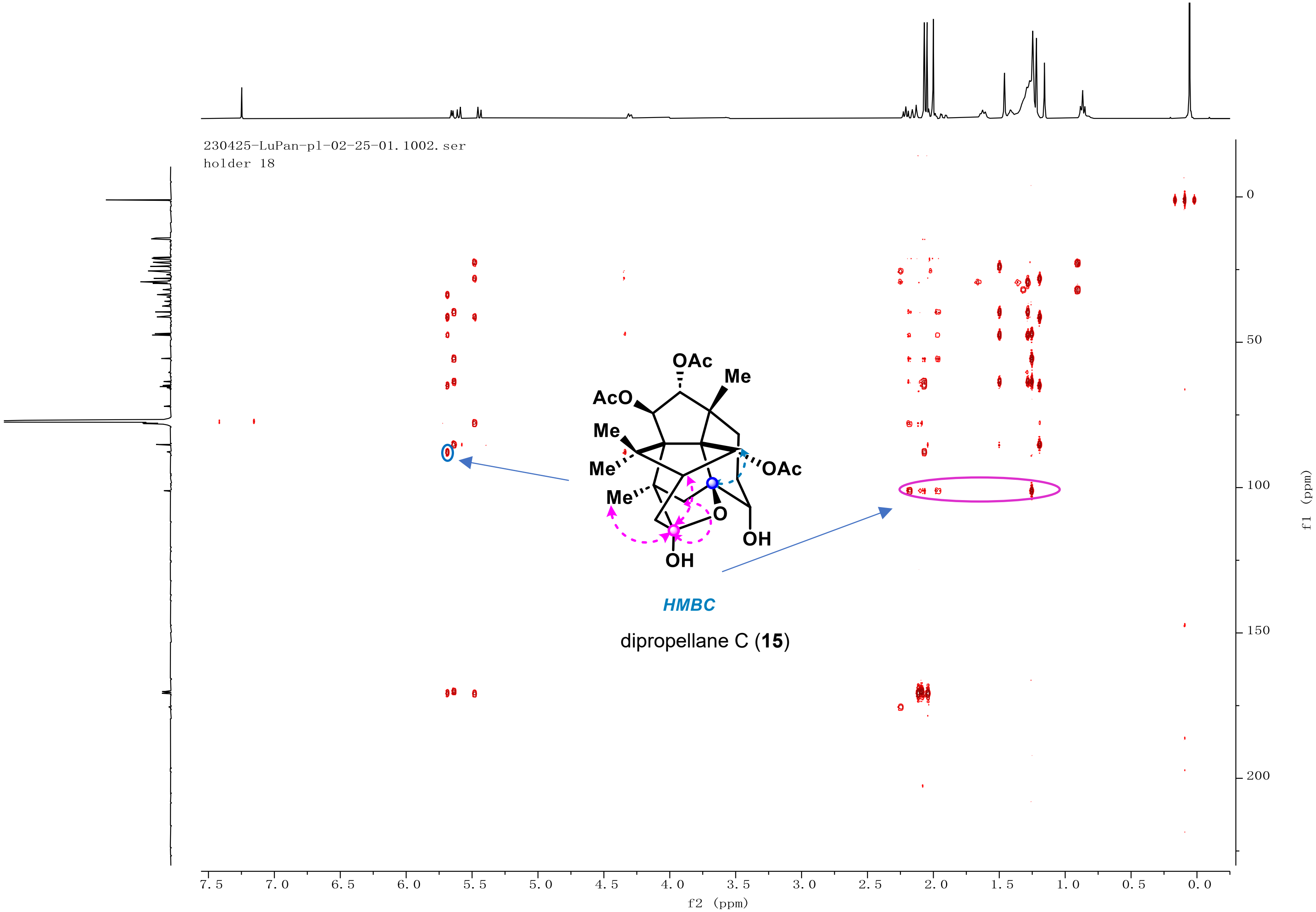
dipropellane C (**15**)



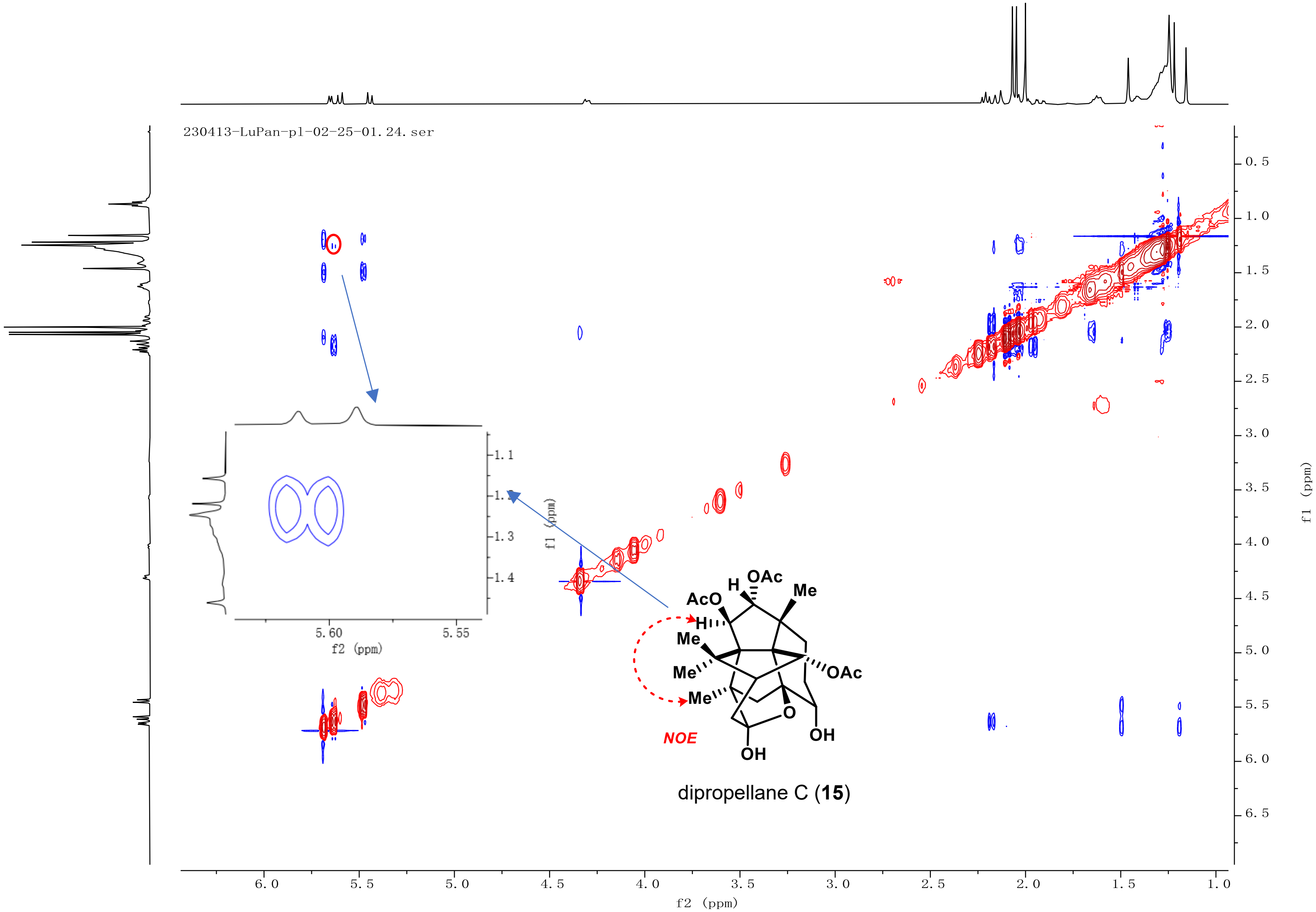
dipropellane C (**15**)



dipropellane C (**15**)

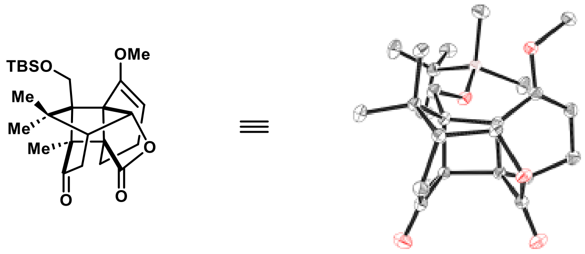


dipropellane C (**15**)



dipropellane C (**15**)

# Part-IX X-Ray Crystallography Data

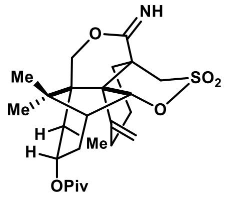


**17**

*ORTEP of* **17**

**Table 1. Crystal data and structure refinement for 2-pl-09-15-03**

| | |
|---|---|
| CCDC number | |
| Empirical formula | $C_{25}H_{38}O_5Si$ |
| Formula weight | 446.64 |
| Temperature [K] | 100 |
| Crystal system | monoclinic |
| Space group (number) | $C2/c$ (15) |
| $a$ [Å] | 34.5843(16) |
| $b$ [Å] | 10.2087(3) |
| $c$ [Å] | 14.0112(6) |
| α [°] | 90 |
| β [°] | 107.685(4) |
| γ [°] | 90 |
| Volume [Å$^3$] | 4713.0(3) |
| $Z$ | 1 |
| $\rho_{calc}$ [g/cm$^3$] | 0.157 |
| μ [mm $^{1}$] | 0.017 |
| $F$(000) | 242 |
| Crystal size [mm$^3$] | 0.4×0.2×0.1 |
| Crystal colour | clear |
| Crystal shape | cubic |
| Radiation | Mo$K_\alpha$ (λ=0.71073 Å) |
| 2θ range [°] | 4.18 to 53.72 (0.79 Å) |
| Index ranges | -43 ≤ h ≤ 41, -12 ≤ k ≤ 12, -17 ≤ l ≤ 17 |
| Reflections collected | 14400 |
| Independent reflections | 4975 ($R_{int}$ = 0.0532, $R_{sigma}$ = 0.0338) |
| Completeness to θ = 25.242° | 99.6 % |
| Data / Restraints / Parameters | 4975/0/289 |
| Goodness-of-fit on $F^2$ | 1.123 |
| Final $R$ indexes [$I$≥2σ($I$)] | $R_1$ = 0.0439<br>w$R_2$ = 0.1271 |
| Final $R$ indexes [all data] | $R_1$ = 0.0521<br>w$R_2$ = 0.1432 |
| Largest peak/hole [e Å$^{-3}$] | 0.54/-0.67 |



**S49**

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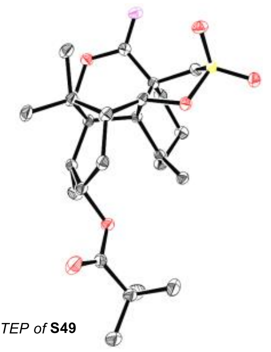
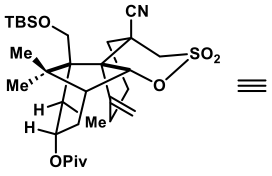


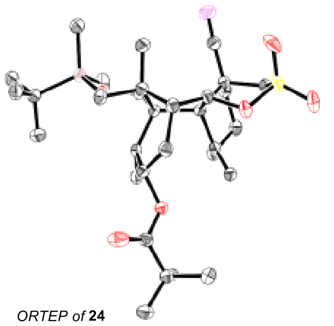
*ORTEP of* **S49**

## Table 1. Crystal data and structure refinement for rw01

| | |
|---|---|
| CCDC number | 2281573 |
| Empirical formula | $C_{25}H_{37}NO_6S$ |
| Formula weight | 479.61 |
| Temperature [K] | 100(2) |
| Crystal system | monoclinic |
| Space group (number) | $P2_1/c$ (14) |
| *a* [Å] | 8.190 |
| *b* [Å] | 13.054 |
| *c* [Å] | 22.604 |
| α [°] | 90 |
| β [°] | 94.37 |
| γ [°] | 90 |
| Volume [Å$^3$] | 2409.5 |
| *Z* | 4 |
| $\rho_{calc}$ [g/cm$^3$] | 1.322 |
| μ [mm $^1$] | 0.176 |
| *F*(000) | 1032 |
| Crystal size [mm$^3$] | 0.4×0.2×0.1 |
| Crystal colour | colourless |
| Crystal shape | needle |
| Radiation | Mo$K_\alpha$ (λ=0.71073 Å) |
| 2θ range [°] | 4.78 to 55.05 (0.77 Å) |
| Index ranges | -9≤ h ≤ 10, -15 ≤ k ≤ 16, -29 ≤ l ≤ 29 |
| Reflections collected | 15826 |
| Completeness to θ = 25.242° | 99.9 % |
| Data / Restraints / Parameters | 5502/0/308 |
| Goodness-of-fit on $F^2$ | 1.020 |
| Final *R* indexes [$I \geq 2\sigma(I)$] | $R_1$ = 0.0382<br>w$R_2$ = 0.0896 |
| Final *R* indexes [all data] | $R_1$ = 0.0530<br>w$R_2$ = 0.0981 |
| Largest peak/hole [eÅ$^3$] | 0.46/-0.35 |



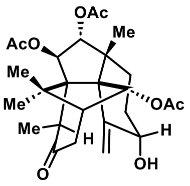
24



*ORTEP of* **24**

**Table 1. Crystal data and structure refinement for rw02**

| | |
|---|---|
| CCDC number | 2281574 |
| Empirical formula | $C_{31}H_{51}NO_6SSi$ |
| Formula weight | 593.88 |
| Temperature [K] | 100(2) |
| Crystal system | triclinic |
| Space group (number) | $P\bar{1}$ (2) |
| *a* [Å] | 8.829 |
| *b* [Å] | 12.892 |
| *c* [Å] | 15.967 |
| α [°] | 98.72 |
| β [°] | 100.97 |
| γ [°] | 109.68 |
| Volume [Å$^3$] | 1633.7 |
| *Z* | 2 |
| $\rho_{calc}$ [g/cm$^3$] | 1.207 |
| μ [mm$^{1}$] | 0.177 |
| *F*(000) | 644 |
| Crystal size [mm$^3$] | 0.4×0.3×0.2 |
| Crystal colour | colourless |
| Crystal shape | block |
| Radiation | Mo$K_\alpha$ (λ=0.71073 Å) |
| 2θ range [°] | 4.83 to 60.95 (0.70 Å) |
| Index ranges | -12≤ h ≤ 12, -18 ≤ k ≤ 18, -22≤ l ≤ 22 |
| Reflections collected | 25338 |
| Independent reflections | 9819 [ $R_{int}$ = 0.0681, $R_{sigma}$ = 0.0677] |
| Completeness to θ = 25.242° | 99.9 % |
| Data / Restraints / Parameters | 9819/0/373 |
| Goodness-of-fit on $F^2$ | 1.052 |
| Final *R* indexes [$I$≥2σ($I$)] | $R_1$ = 0.0566<br>w$R_2$ = 0.1490 |
| Final *R* indexes [all data] | $R_1$ = 0.0842<br>w$R_2$ = 0.1637 |
| Largest peak/hole [e Å$^{-3}$] | 0.41/-0.60 |
| Extinction coefficient | 0.014(3) |



**taxinine K (2)**

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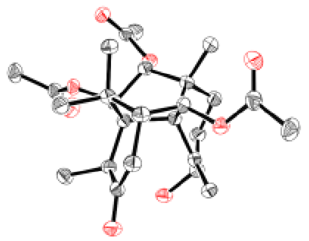
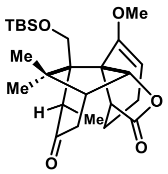


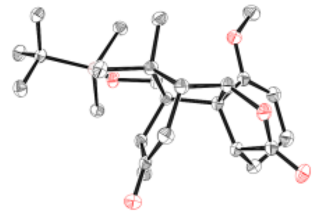
*ORTEP of* **taxinine K (2)**

## Table 1. Crystal data and structure refinement for pl-taxinine k

| | |
|---|---|
| CCDC number | 2281575 |
| Empirical formula | $C_{26}H_{36}O_8$ |
| Formula weight | 476.55 |
| Temperature [K] | 293(2) |
| Crystal system | orthorhombic |
| Space group (number) | $P2_12_12_1$ (19) |
| *a* [Å] | 8.6269(4) |
| *b* [Å] | 14.4154(6) |
| *c* [Å] | 19.8574(11) |
| α [°] | 90 |
| β [°] | 90 |
| γ [°] | 90 |
| Volume [Å$^3$] | 2469.5(2) |
| *Z* | 4 |
| $\rho_{calc}$ [g/cm$^3$] | 1.282 |
| μ [mm $^{1}$] | 0.094 |
| *F*(000) | 1024 |
| Crystal size [mm$^3$] | 0.3×0.2×0.1 |
| Crystal colour | colorless |
| Crystal shape | platelette |
| Radiation | Mo$K_\alpha$ (λ=0.71073 Å) |
| 2θ range [°] | 5.50 to 53.55 (0.79 Å) |
| Index ranges | -10≤ h ≤ 9, -18 ≤ k ≤ 15, -25≤ l ≤ 24 |
| Reflections collected | 10087 |
| Independent reflections | 5089 [ $R_{int}$ = 0.0380, $R_{sigma}$ = 0.0432] |
| Completeness to θ = 25.242° | 99.5 % |
| Data / Restraints / Parameters | 5089/0/323 |
| Goodness-of-fit on $F^2$ | 1.065 |
| Final *R* indexes [$I$≥2σ($I$)] | $R_1$ = 0.0466<br>w$R_2$ = 0.0988 |
| Final *R* indexes [all data] | $R_1$ = 0.0710<br>w$R_2$ = 0.1117 |
| Largest peak/hole [e Å$^{-3}$] | 0.20/-0.23 |
| Flack X parameter | -0.7(7) |



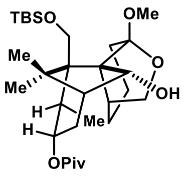
**18**



*ORTEP of* **18**

## Table 1. Crystal data and structure refinement for lupan05-08-01

| | |
|---|---|
| CCDC number | 2281567 |
| Empirical formula | $C_{25}H_{40}O_5Si$ |
| Formula weight | 448.66 |
| Temperature [K] | 100 |
| Crystal system | triclinic |
| Space group (number) | $P\bar{1}$ (2) |
| $a$ [Å] | 12.1439(9) |
| $b$ [Å] | 13.0507(11) |
| $c$ [Å] | 15.9365(13) |
| $\alpha$ [°] | 90.530(7) |
| $\beta$ [°] | 101.782(6) |
| $\gamma$ [°] | 90.017(7) |
| Volume [Å$^3$] | 2472.4(3) |
| $Z$ | 4 |
| $\rho_{calc}$ [g/cm$^3$] | 1.205 |
| $\mu$ [mm $^{1}$] | 0.127 |
| $F$(000) | 976 |
| Crystal size [mm$^3$] | 0.35×0.267×0.2 |
| Crystal colour | colourless |
| Crystal shape | block |
| Radiation | Mo $K_\alpha$ ($\lambda$=0.71073 Å) |
| 2θ range [°] | 4.95 to 62.44 (0.69 Å) |
| Index ranges | $-17 \leq h \leq 17$, $-18 \leq k \leq 18$, $-23 \leq l \leq 23$ |
| Reflections collected | 37468 |
| Independent reflections | 31839 [ $R_{int}$ = 0.1517, $R_{sigma}$ = 0.1139 ] |
| Completeness to θ = 25.242° | 99.9 % |
| Data / Restraints / Parameters | 15907/0/577 |
| Goodness-of-fit on $F^2$ | 1.049 |
| Final $R$ indexes [$I \geq 2\sigma(I)$] | $R_1$ = 0.0992<br>w$R_2$ = 0.2642 |
| Final $R$ indexes [all data] | $R_1$ = 0.1391<br>w$R_2$ = 0.3051 |
| Largest peak/hole [e Å$^{-3}$] | 1.57/-1.19 |



**S52**

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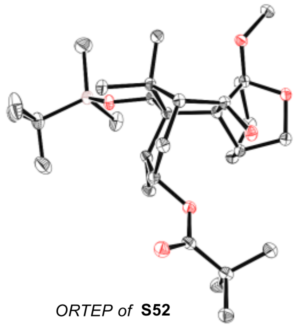
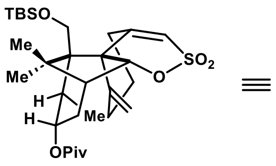


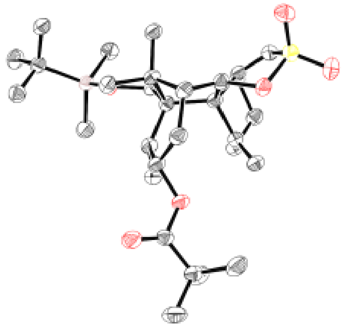
*ORTEP of* **S52**

### Table 1. Crystal data and structure refinement for lupan05-115-02

| | |
|---|---|
| CCDC number | 2281572 |
| Empirical formula | $C_{60}H_{108}O_{12}Si_2$ |
| Formula weight | 1077.64 |
| Temperature [K] | 100 |
| Crystal system | triclinic |
| Space group (number) | $P\bar{1}$ (2) |
| *a* [Å] | 9.2037(6) |
| *b* [Å] | 11.0970(8) |
| *c* [Å] | 15.5789(11) |
| α [°] | 88.055(6) |
| β [°] | 76.495(5) |
| γ [°] | 80.917(6) |
| Volume [Å$^3$] | 1527.72(19) |
| *Z* | 1 |
| $\rho_{calc}$ [g/cm$^3$] | 1.171 |
| μ [mm$^{-1}$] | 0.116 |
| *F*(000) | 592 |
| Crystal size [mm$^3$] | 0.5×0.45×0.4 |
| Crystal colour | colourless |
| Crystal shape | block |
| Radiation | Mo $K_\alpha$ (λ=0.71073 Å) |
| 2θ range [°] | 5.38 to 62.41 (0.69 Å) |
| Index ranges | -13≤ h ≤ 13, -16 ≤ k ≤ 16, -19≤ l ≤ 22 |
| Reflections collected | 21551 |
| Independent reflections | 21551 [$R_{int}$ = 0.0435, $R_{sigma}$ = 0.0364] |
| Completeness to θ = 25.242° | 99.8 % |
| Data / Restraints / Parameters | 9822/0/347 |
| Goodness-of-fit on $F^2$ | 1.042 |
| Final *R* indexes [$I$≥2σ($I$)] | $R_1$ = 0.0521<br>w$R_2$ = 0.1437 |
| Final *R* indexes [all data] | $R_1$ = 0.0634<br>w$R_2$ = 0.1692 |
| Largest peak/hole [e Å$^{-3}$] | 0.44/-0.94 |



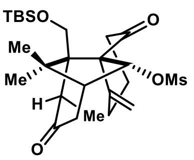
**23**



*ORTEP of* **23**

### Table 1. Crystal data and structure refinement for pl-04

| | |
|---|---|
| CCDC number | 2281465 |
| Empirical formula | $C_{240}H_{400}O_{48}S_8Si_8$ |
| Formula weight | 4534.78 |
| Temperature [K] | 100 |
| Crystal system | monoclinic |
| Space group (number) | $C2/c$ (15) |
| $a$ [Å] | 23.2084(7) |
| $b$ [Å] | 12.7026(2) |
| $c$ [Å] | 24.6744(7) |
| α [°] | 90 |
| β [°] | 120.025(2) |
| γ [°] | 90 |
| Volume [Å$^3$] | 6298.0(3) |
| $Z$ | 1 |
| $\rho_{calc}$ [g/cm$^3$] | 1.196 |
| μ [mm $^{1}$] | 0.180 |
| $F$(000) | 2464 |
| Crystal size [mm$^3$] | 0.5×0.5×0.5 |
| Crystal colour | colorless |
| Crystal shape | cubic |
| Radiation | Mo$K_\alpha$ (λ=0.71073 Å) |
| 2θ range [°] | 4.60 to 53.56 (0.79 Å) |
| Index ranges | -29≤ h ≤ 29, -16 ≤ k ≤ 14, -31≤ l ≤ 31 |
| Reflections collected | 15708 |
| Independent reflections | 6606 [$R_{int}$ = 0.0225, $R_{sigma}$ = 0.0202] |
| Completeness to θ = 25.242° | 99.3 % |
| Data / Restraints / Parameters | 6606/0/362 |
| Goodness-of-fit on $F^2$ | 1.087 |
| Final $R$ indexes [$I$≥2σ($I$)] | $R_1$ = 0.0509<br>w$R_2$ = 0.1320 |
| Final $R$ indexes [all data] | $R_1$ = 0.0626<br>w$R_2$ = 0.1469 |
| Largest peak/hole [e Å$^{-3}$] | 0.52/-0.64 |



**S50**

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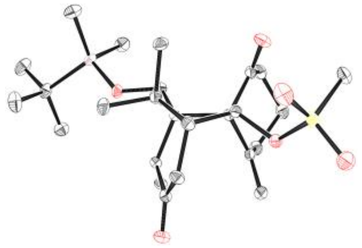
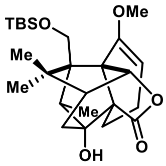


*ORTEP of* **S50**

### Table 1. Crystal data and structure refinement for pl-05-30-01-d

| | |
|---|---|
| CCDC number | 2281568 |
| Empirical formula | $C_{25}H_{42}O_6SSi$ |
| Formula weight | 498.73 |
| Temperature [K] | 100 |
| Crystal system | monoclinic |
| Space group (number) | $P2_1/n$ (14) |
| *a* [Å] | 11.9073(9) |
| *b* [Å] | 8.5115(5) |
| *c* [Å] | 26.557(2) |
| α [°] | 90 |
| β [°] | 101.092(6) |
| γ [°] | 90 |
| Volume [Å$^3$] | 2641.2(3) |
| *Z* | 4 |
| $\rho_{calc}$ [g/cm$^3$] | 1.254 |
| μ [mm$^{1}$] | 0.205 |
| *F*(000) | 1080 |
| Crystal size [mm$^3$] | 0.6×0.533×0.4 |
| Crystal colour | colorless |
| Crystal shape | block |
| Radiation | Mo $K_\alpha$ (λ=0.71073 Å) |
| 2θ range [°] | 5.03 to 58.61 (0.73 Å) |
| Index ranges | -16≤ h ≤ 16, -11 ≤ k ≤ 10, -26≤ l ≤ 36 |
| Reflections collected | 16804 |
| Independent reflections | 17462 [$R_{int}$ = 0.0217, $R_{sigma}$ = 0.0216] |
| Completeness to θ = 25.242° | 98.9 % |
| Data / Restraints / Parameters | 7128/0/307 |
| Goodness-of-fit on $F^2$ | 1.033 |
| Final *R* indexes [$I$≥2σ($I$)] | $R_1$ = 0.0340<br>w$R_2$ = 0.0852 |
| Final *R* indexes [all data] | $R_1$ = 0.0431<br>w$R_2$ = 0.0909 |
| Largest peak/hole [e Å$^{-3}$] | 0.36/-0.43 |

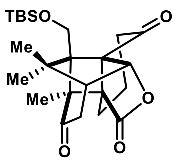


**S53**

*ORTEP of* **S53**

## Table 1. Crystal data and structure refinement for pl-07-27-01_hr

| | |
|---|---|
| CCDC number | 2281570 |
| Empirical formula | $C_{25}H_{40}O_5Si$ |
| Formula weight | 448.66 |
| Temperature [K] | 293(2) |
| Crystal system | monoclinic |
| Space group (number) | $I2/a$ (15) |
| $a$ [Å] | 35.560(3) |
| $b$ [Å] | 10.0147(8) |
| $c$ [Å] | 13.8884(12) |
| $\alpha$ [°] | 90 |
| $\beta$ [°] | 95.674(7) |
| $\gamma$ [°] | 90 |
| Volume [Å$^3$] | 4921.7(7) |
| $Z$ | 8 |
| $\rho_{calc}$ [g/cm$^3$] | 1.211 |
| $\mu$ [mm$^{-1}$] | 0.128 |
| $F$(000) | 1952 |
| Crystal size [mm$^3$] | 0.5×0.3×0.2 |
| Crystal colour | colorless |
| Crystal shape | plate |
| Radiation | Mo$K_\alpha$ ($\lambda$=0.71073 Å) |
| 2θ range [°] | 4.60 to 58.78 (0.72 Å) |
| Index ranges | $-48 \leq h \leq 48$ $-13 \leq k \leq 13$, $-19 \leq l \leq 14$ |
| Reflections collected | 17491 |
| Independent reflections | 6668 [$R_{int}$ = 0.0331, $R_{sigma}$ = 0.0327] |
| Completeness to θ = 25.242° | 99.7 % |
| Data / Restraints / Parameters | 6668/0/290 |
| Goodness-of-fit on $F^2$ | 1.131 |
| Final $R$ indexes [$I \geq 2\sigma(I)$] | $R_1$ = 0.0456<br>w$R_2$ = 0.0928 |
| Final $R$ indexes [all data] | $R_1$ = 0.0712<br>w$R_2$ = 0.1152 |
| Largest peak/hole [e Å$^{-3}$] | 0.41/-0.48 |



**S51**

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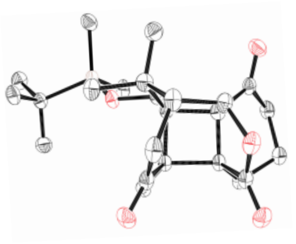
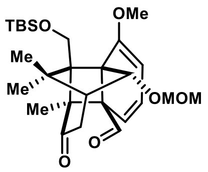


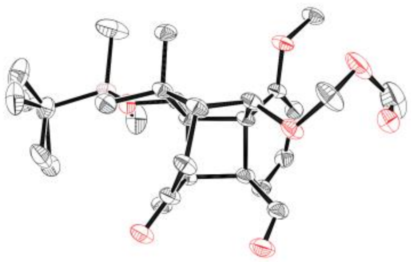
*ORTEP of* **S51**

## Table 1. Crystal data and structure refinement for pl-10-08-01_hr

| | |
|---|---|
| CCDC number | 2281571 |
| Empirical formula | $C_{24}H_{36}O_5Si$ |
| Formula weight | 432.62 |
| Temperature [K] | 293(2) |
| Crystal system | monoclinic |
| Space group (number) | $P2_1/c$ (14) |
| *a* [Å] | 13.966(3) |
| *b* [Å] | 12.001(2) |
| *c* [Å] | 14.280(3) |
| α [°] | 90 |
| β [°] | 91.350(15) |
| γ [°] | 90 |
| Volume [Å$^3$] | 2392.8(8) |
| *Z* | 4 |
| $\rho_{calc}$ [g/cm$^3$] | 1.201 |
| μ [mm $^1$] | 0.129 |
| *F*(000) | 936 |
| Crystal size [mm$^3$] | 0.6×0.433×0.1 |
| Crystal colour | colorless |
| Crystal shape | plate |
| Radiation | Mo$K_\alpha$ (λ=0.71073 Å) |
| 2θ range [°] | 4.43 to 58.79 (0.72 Å) |
| Index ranges | -19≤ h ≤ 15 -16 ≤ k ≤ 15, -19≤ l ≤19 |
| Reflections collected | 15313 |
| Independent reflections | 6471[$R_{int}$ = 0.0634, $R_{sigma}$ = 0.0656] |
| Completeness to θ = 25.242° | 99.2 % |
| Data / Restraints / Parameters | 6471/0/279 |
| Goodness-of-fit on $F^2$ | 1.022 |
| Final *R* indexes [$I≥2σ(I)$] | $R_1$ = 0.0688<br>w$R_2$ = 0.1542 |
| Final *R* indexes [all data] | $R_1$ = 0.1216<br>w$R_2$ = 0.1983 |
| Largest peak/hole [e Å$^{-3}$] | 0.49/-0.60 |



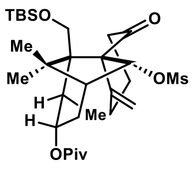
**S54**



*ORTEP of* **S54**

## Table 1. Crystal data and structure refinement for lupanmL2023-01

| | |
|---|---|
| CCDC number | 2281461 |
| Empirical formula | $C_{27}H_{42}O_6Si$ |
| Formula weight | 490.69 |
| Temperature [K] | 100 |
| Crystal system | monoclinic |
| Space group (number) | $P2_1/c$ (14) |
| *a* [Å] | 11.6831(6) |
| *b* [Å] | 13.9796(6) |
| *c* [Å] | 16.7730(9) |
| α [°] | 90 |
| β [°] | 104.715(4) |
| γ [°] | 90 |
| Volume [Å$^3$] | 2649.6(2) |
| *Z* | 4 |
| $\rho_{calc}$ [g/cm$^3$] | 1.230 |
| μ [mm $^{1}$] | 0.127 |
| *F*(000) | 1064 |
| Crystal size [mm$^3$] | 0.5×0.333×0.15 |
| Crystal colour | colourless |
| Crystal shape | plate |
| Radiation | Mo $K_\alpha$ (λ=0.71073 Å) |
| 2θ range [°] | 4.82 to 51.94 (0.81 Å) |
| Index ranges | -12≤ h ≤ 14 -16 ≤ k ≤ 17, -20≤ l ≤20 |
| Reflections collected | 11789 |
| Independent reflections | 5127[$R_{int}$ = 0.0333, $R_{sigma}$ = 0.0386] |
| Completeness to θ = 25.242° | 99.8 % |
| Data / Restraints / Parameters | 5127/14/349 |
| Goodness-of-fit on $F^2$ | 1.031 |
| Final *R* indexes [*I*≥2σ(*I*)] | $R_1$ = 0.0531<br>w$R_2$ = 0.1253 |
| Final *R* indexes [all data] | $R_1$ = 0.0770<br>w$R_2$ = 0.1409 |
| Largest peak/hole [e Å$^{-3}$] | 0.33/-0.34 |
| Extinction coefficient | 0.0096(11) |



22

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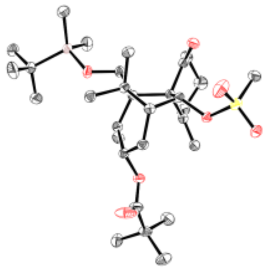

*ORTEP of **22***

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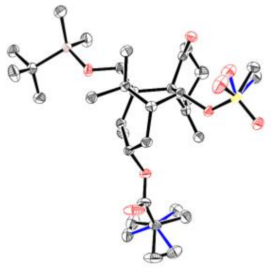

*ORTEP of **22***

*Notes:*

*X-ray of Compound **22** reveals partial disorder at Piv and Ms positions due to rotations of single bonds (Fig. right). To enhance structural clarity, one of the rotamers is omitted in the left figure. Both rotamers are highlighted in blue and black in the right figure.*

## Table 1. Crystal data and structure refinement for lupanml2023-04

| | |
|---|---|
| CCDC number | 2281576 |
| Empirical formula | $C_{30}H_{52}O_7SSi$ |
| Formula weight | 584.86 |
| Temperature [K] | 100 |
| Crystal system | monoclinic |
| Space group (number) | $P2_1/c$ (14) |
| $a$ [Å] | 11.5025(11) |
| $b$ [Å] | 11.6836(10) |
| $c$ [Å] | 23.741(3) |
| α [°] | 90 |
| β [°] | 91.920(9) |
| γ [°] | 90 |
| Volume [Å$^3$] | 3188.8(5) |
| $Z$ | 4 |
| $\rho_{calc}$ [gcm$^{-3}$] | 1.218 |
| $\mu$ [mm$^{-1}$] | 0.182 |
| $F$(000) | 1272 |
| Crystal size [mm$^3$] | 0.4×0.3×0.2 |
| Crystal colour | colourless |
| Crystal shape | fragment |
| Radiation | Mo $K_\alpha$ (λ=0.71073 Å) |
| 2θ range [°] | 4.85 to 57.22 (0.74 Å) |
| Index ranges | -15≤ h ≤ 13 -13 ≤ k ≤ 15, -31≤ l ≤31 |
| Reflections collected | 18011 |
| Independent reflections | 8087[$R_{int}$ = 0.0292, $R_{sigma}$ = 0.0434] |
| Completeness to θ = 25.242° | 99.6 % |
| Data / Restraints / Parameters | 8087/19/415 |
| Goodness-of-fit on $F^2$ | 1.087 |
| Final $R$ indexes [$I$≥2σ($I$)] | $R_1$ = 0.0456<br>w$R_2$ = 0.1118 |
| Final $R$ indexes [all data] | $R_1$ = 0.0790<br>w$R_2$ = 0.1305 |
| Largest peak/hole [e Å$^{-3}$] | 0.73/-0.48 |

# Part-X References

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