Supporting Information for

"Carbon Assimilation" Inspired Design and Divergent Synthesis of Drimane Meroterpenoids Mimics as Novel Fungicidal Leads

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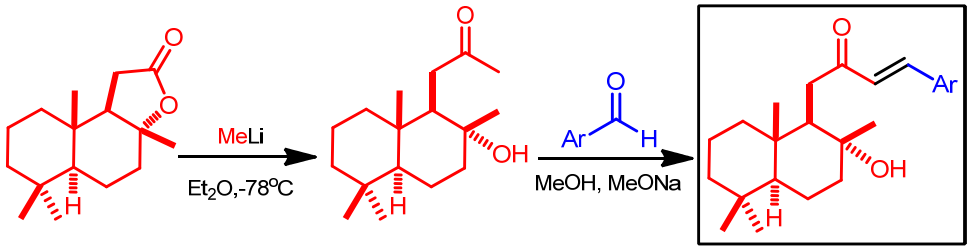
General Information

All solvents and reagents were purchased from commercial sources (Energy or Meryer Chemicals etc.), they were analytically pure and used as received. Anhydrous solvents were dried and distilled by standard techniques before use. Silica gel GF_{254} and column chromatography silica gel for isolation (200~300 mesh) were both purchased from Qingdao Broadchem Industrial Co., Ltd. Reaction progress was monitored by thin-layer chromatography (TLC) on silica gel GF_{254} with ultraviolet (UV_{254}nm) detection and phosphomolybdic acid. Yields of all the title compounds were not optimized. Melting points (m.p.) were recorded on Shenguang WRS-1B melting point apparatus and are uncorrected. ^{1}HNMR and ^{13}C NMR spectra were carried out utilizing a Bruker AV400 spectrometer with $CDCl_3$ as solvent and tetramethylsilane as the internal standard. Data for ^{1}H-NMR are reported as follows: chemical shift (δ: ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), integration and assignment (italic H). Data for ^{13}C NMR are reported in terms of chemical shift (δ: ppm). (*C*) stands for quaternary carbon, (*CH*) stands for tertiary carbon, (CH_2) stands for secondary carbon, (CH_3) stands for primary carbon. Electrospray ionization mass spectrometry (ESI-MS) data were obtained with Waters Xevo TQ-S Micro-Spectrometer. The single crystal diffraction was carried out on Bruker SMART APEX CCD diffractometer. The fungi were provided by the Department of Pesticide, College of Plant Protection, Nanjing Agricultural University (Nanjing, China).

General Procedure for the Synthesis of *α*, *β*-unsaturated Ketone Inserted Mimics.



(+)-Sclareolide HomoDrimane | **1** Drimanyl methyl ketone | **2** Mimics

To a solution of (+)-sclareolide (20.0 g, 79.8 mmol) in anhydrous Et_2O (250 mL), MeLi (1.5 M in Et_2O, 100 mL, 150 mmol) was added dropwise at -78°C. The reaction mixture was stirred at -78°C and the reaction progress was monitored by TLC until the reaction was complete (about 1 hour). The mixture was quenched by slow addition of 10% H_2SO_4 aqueous solution and was warmed gradually to room temperature. The layers were separated and the aqueous phase was extracted with Et_2O (2 x 150 mL). The combined organics were washed sequentially with saturated $NaHCO_3$ aqueous solution (2 x 150 mL), H_2O (150 mL) and brine (100 mL), dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo to yield drimanyl methyl ketone **1** with the yield > 90%, and it was used directly for next step without further purification.

Sodium methoxide (65mg, 1.2mmol, 1.2 equiv) was added to the cooled solution of drimanyl methyl ketone **1** (267mg, 1.0mmol, 1.0 equiv) in 10 mL MeOH with ice bath (0-5°C), after being stirred for 20min, 4-chlorobenzaldehyde (141mg, 1.0mmol, 1.0 equiv) was added and the mixture was moved to the pre-heated oil bath at 80°C. The complex was stirred and the reaction progress was monitored by TLC until the reaction was complete (~48h). The solvent was removed under reduced pressure and to the residue was added saturated aqueous solution of NH_4Cl (15mL) and ethyl acetate (15mL).The organic layer was separated and the aqueous phase was extracted

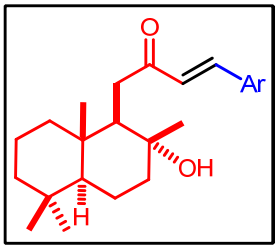
with ethyl acetate (2 x 15 mL). The combined organic layers were washed with brine (10mL), dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography (200-300m) with PE/EtOAc = 8:1 as eluent to give *α*, *β*-unsaturated ketone inserted merosesquiterpenoid mimic **2d** as white solid (263 mg, yield 67.6%). M.p.164.5-164.7(°C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.80 (s, 3H, *CH₃*) , 0.85 (s, 3H, *CH₃*), 0.88 (s, 3H, *CH₃*), 1.03 (dd, J_1 = 12.24 Hz, J_2 = 2.32 Hz, 1H, H in naphthane ring), 1.15 (td, J_1 = 13.64 Hz, J_2 = 3.92 Hz, 1H, H in naphthane ring), 1.16 (s, 3H, *CH₃*), 1.28(td, J_1 = 12.52 Hz, J_2 = 3.24 Hz, 1H, H in naphthane ring), 1.34~1.42(m, 3H, H in naphthane ring), 1.49(td, J_1 = 12.52 Hz, J_2 = 4.04 Hz, 1H, H in naphthane ring), 1.58(m, 1H, H in naphthane ring), 1.68~1.74(m, 2H, H in naphthane ring), 1.78(br, 1H, *OH*), 1.96 (dt, J_1 = 12.48, J_2 = 3.20 Hz, 1H, H in naphthane ring), 2.08 (dd, J_1 = J_2 = 4.92 Hz, 1H, *CH*-CH_2-CO), 2.72 (dd, J_1 = J_2 = 4.92 Hz, 2H, *CH₂*-CO), 6.79(d, *J* = 16.08 Hz, 1H, =*CH*-CO), 7.35 (d, *J* = 6.52 Hz, 2H, *aromatic H*), 7.49 (d, *J* = 6.52 Hz, 2H, *aromatic H*), 7.54(d, *J* = 16.08 Hz, 1H, *CH*=CH-CO).

^{13}C NMR (100 MHz, $CDCl_3$) δ 15.70 (CH_3), 18.41(CH_2), 20.62(CH_2), 21.43(CH_3), 23.35(CH_3), 33.24(C), 33.34(CH_3), 37.56(CH_2), 38.62(C), 39.54(CH_2), 41.75(CH_2), 44.63(CH_2), 55.91(CH), 56.12(CH), 73.16(C), 126.56(CH), 129.18(2×CH), 129.46(2×CH), 133.14(C), 136.24(C), 140.73(CH), 201.06(C).

ESI-MS calcd for $C_{24}H_{33}ClNaO_2$ [M+Na^+]: 411.21 and 413.20, found: 411.32 and 413.21; $C_{24}H_{32}ClO$ [M-H_2O+H^+]: 371.21 and 373.21, found: 371.30 and 373.21.

The *α*, *β*-unsaturated ketone inserted merosesquiterpenoid mimics in Table 2 were synthesized according to the similar procedure.



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Entry	Compd.	Original No.	Ar	Yield	Status and M.P.
1	**2a**	M-7	Ph	88.6%	White solid, 108.6-111.0℃
2	**2b**	ZSB-43	4-NO_2-Ph	62.3%	Yellow solid,154.4-157.2℃
3	**2c**	ZSB-17	4-F-Ph	74.1%	White solid,115.3-116.1℃
4	**2d**	ZSB-105	4-Cl-Ph	67.5%	White solid,164.5-164.7℃
5	**2e**	ZSB-62	4-Br-Ph	92.8%	White solid,163.6-165.0℃
6	**2f**	ZSB-49	4-CH_3-Ph	39.6%	White solid,167.6-168.3℃
7	**2g**	ZSB-99	4-CH_3O-Ph	50.3%	White solid,129.9-131.0℃
8	**2h**	ZSB-100	4-$(CH_3)_2N$-Ph	60.0%	Yellow solid,156.9-159.1℃
9	**2i**	ZSB-40	3-NO_2-Ph	65.6%	White solid, 91.3-94.8℃
10	**2j**	ZSB-85	3-CF_3-Ph	78.6%	Yellow Wax
11	**2k**	ZSB-53	3-Cl-Ph	59.3%	White solid, 102.1-104.0℃
12	**2l**	ZSB-64	3-Br-Ph	76.6%	White solid, 141.7-142.9℃
13	**2m**	ZSB-16	3-CH_3-Ph	79.6%	White solid, 109.5-111.2℃
14	**2n**	ZSB-113	3-OH-Ph	77.4%	White solid, 129.7-131.3℃
15	**2o**	ZSB-75	2-Br-Ph	93.8%	Pale Yellow Wax
16	**2p**	ZSB-41	2-CH_3O-Ph	60.2%	White solid, 122.3-125.1℃
17	**2q**	ZSB-96	2-Naphthyl	48.9%	White solid, 140.8-142.1℃
18	**2r**	ZSB-51	2,4-Cl-Ph	93.2%	White solid, 102.2-103.0℃
19	**2s**	ZSB-20	2,5-Cl-Ph	62.8%	White solid, 134.3-136.3℃
20	**2t**	ZSB-103	2,5-F-Ph	45.7%	White solid, 91.5-91.7℃
21	**2u**	ZSB-101	3,5-F-Ph	49.9%	White solid, 98.1-101.5℃
22	**2v**	ZSB-22	2,6-Cl-Ph	61.2%	White solid, 115.9-116.7℃
23	**2w**	ZSB-50	3,4-CH_3-Ph	44.6%	White solid, 139.2-140.2℃
24	**2x**	ZSB-93	2-Furyl	73.4%	Pale Yellow solid, 99.7-101.4℃
25	**2y**	ZSB-95	2-Thienyl	72.2%	White solid, 118.4-118.6℃
26	**2z**	ZSB-84	3-Pyridyl	59.5%	White solid, 127.9-127.9℃

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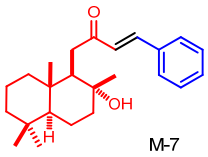
Structures of *α*, *β*-unsaturated Ketone Inserted Mimics



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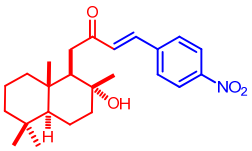

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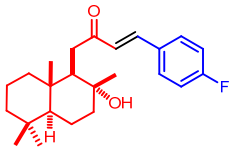

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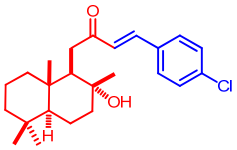

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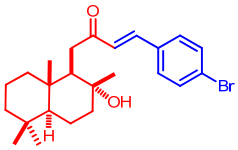

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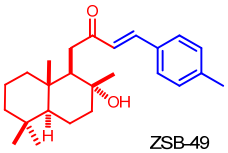

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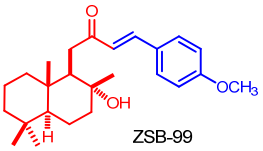

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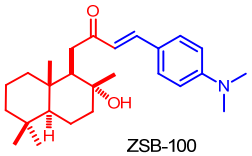

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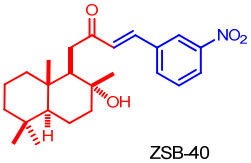

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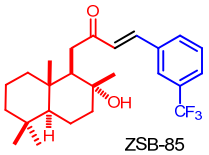

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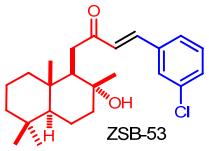

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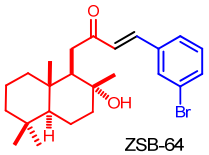

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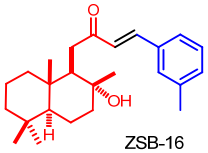

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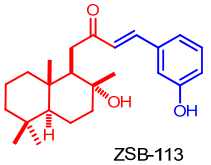

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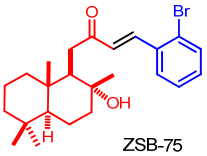

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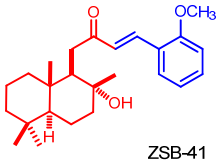

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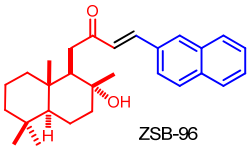

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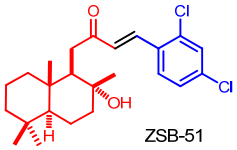

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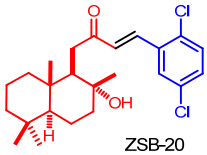

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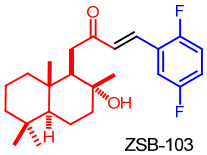

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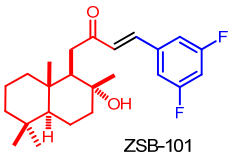

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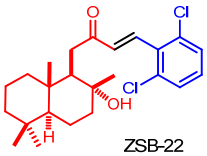

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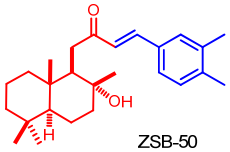

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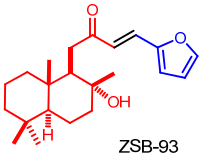

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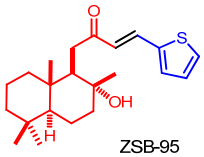

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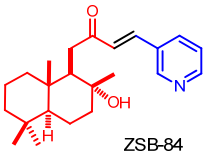
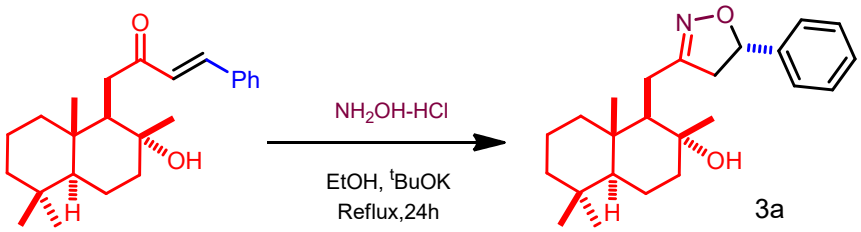


ZSB-84

General Procedure for the Synthesis of Heterocycles Mimics.

Synthesis of drimanyl heterocycles 3a, 3c and 3e.



3a
M-13

To the solution of α, β-unsaturated ketone inserted merosesquiterpenoid mimic **2a** (355mg, 1.0mmol, 1.0 equiv) in 10mL EtOH was added potassium tert-butoxide (449mg, 4.0mmol, 4.0 equiv) and hydroxylamine hydrochloride (139mg, 2.0mmol, 2.0 equiv) subsequently, the flask was immersed into the pre-heated oil bath at 90°C. The complex was stirred and the reaction progress was monitored by TLC until the reaction was complete (~24h). The solvent was removed under reduced pressure and to the residue was added saturated aqueous solution of NH_4Cl (15mL) and ethyl acetate (15mL). The organic layer was separated and the aqueous phase was extracted with ethyl acetate (2 x 15 mL). The combined organic layers were washed with brine (10mL), dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography (200-300m) with PE/EtOAc = 5:1 as eluent to give drimanyl isoxazoline **3a** as white solid (171mg, yield 46.3%). M.p.122.9~124.5 (°C);

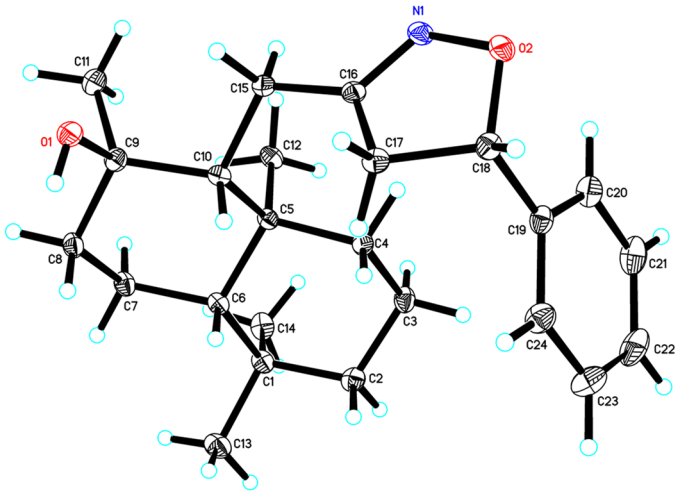
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.80 (s, 3H, *CH₃*) , 0.83 (s, 3H, *CH₃*), 0.88 (s, 3H, *CH₃*), 1.15 (dd, J_1 = 14.20 Hz, J_2 = 4.24 Hz, 1H, H in naphthane ring), 1.19 (td, J_1 = 9.02 Hz, J_2 = 4.08 Hz, 1H, H in naphthane ring), 1.21 (s, 3H, *CH₃*), 1.29(td, J_1 = 12.08 Hz, J_2 = 3.24 Hz, 1H, H in naphthane ring), 1.40~1.46(m, 3H, H in naphthane ring), 1.57(dt, J_1 = 12.72 Hz, J_2 = 3.60 Hz, 1H, H in naphthane ring), 1.58~1.64 (m,

3H, H in naphthane ring), 1.66(br, 1H, *OH*), 1.74 (dd, J_1 = J_2 = 4.80 Hz, 1H, H in naphthane ring), 1.91 (dt, J_1 = 12.40 Hz, J_2 = 3.32 Hz, 1H, H in naphthane ring), 2.47 (m, 2H, CH_2-CO), 3.02 (dd, J_1 =16.92 Hz, J_2 = 8.60 Hz, 1H, Ph-CH-*CH*2), 3.41(dd, J_1 =16.92 Hz, J_2 =10.64 Hz, 1H, Ph-CH-*CH*2), 5.52(dd, J_1 =10.64 Hz, J_2 =8.60 Hz, 1H, Ph-*CH*-CH2), 7.29~7.36 (m, 5H, *aromatic H*).

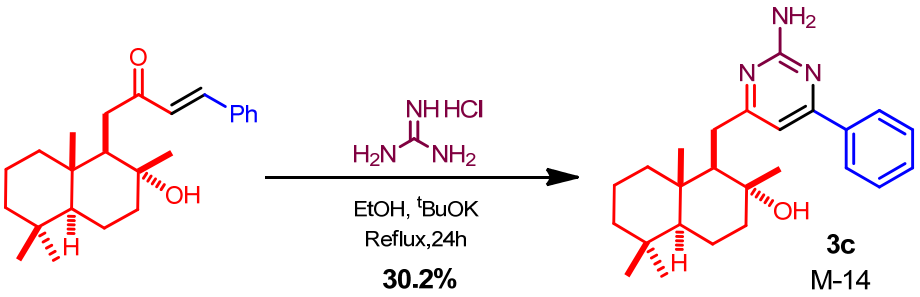
^{13}C NMR (100 MHz, CDCl3) δ 15.14 (CH_3), 18.42 (CH_2), 20.41(CH_2), 21.48(CH_3), 23.63(CH_3), 23.73(CH_2), 33.26(*C*), 33.40(CH_3), 38.90(*C*), 39.65(CH_2), 41.71(CH_2), 44.32(CH_2), 46.08(CH_2), 55.93(*CH*), 57.87(*CH*), 73.67(*C*), 81.51(*CH*), 125.92(2×CH), 127.96(CH), 128.61(2×CH), 141.21(*C*), 161.30(*C*).

ESI-MS calcd for $C_{24}H_{35}NNaO_2$ [M+Na^+]: 392.26, found: 392.30; $C_{24}H_{34}NO$ [M-H_2O+H^+]: 352.26, found: 352.31.

The white solid was dissolved in ethyl acetate to afford colorless square crystal easily. The molecular structure was further confirmed by X-ray single crystal diffraction (CCDC: 1555836), as shown below, two six-membered rings of the naphthane scaffold are *trans*-fused and adopt chair conformations. The isoxazoline is enantioselectively formed and the chiral carbon was assigned as *S* configuration.



Drimanyl pyrimidines **3c** and analogs and drimanyl pyrazoline **3e** were synthesized through similar manipulation.



Structural analysis for the drimanyl pyrimidine **3c** was as follows:

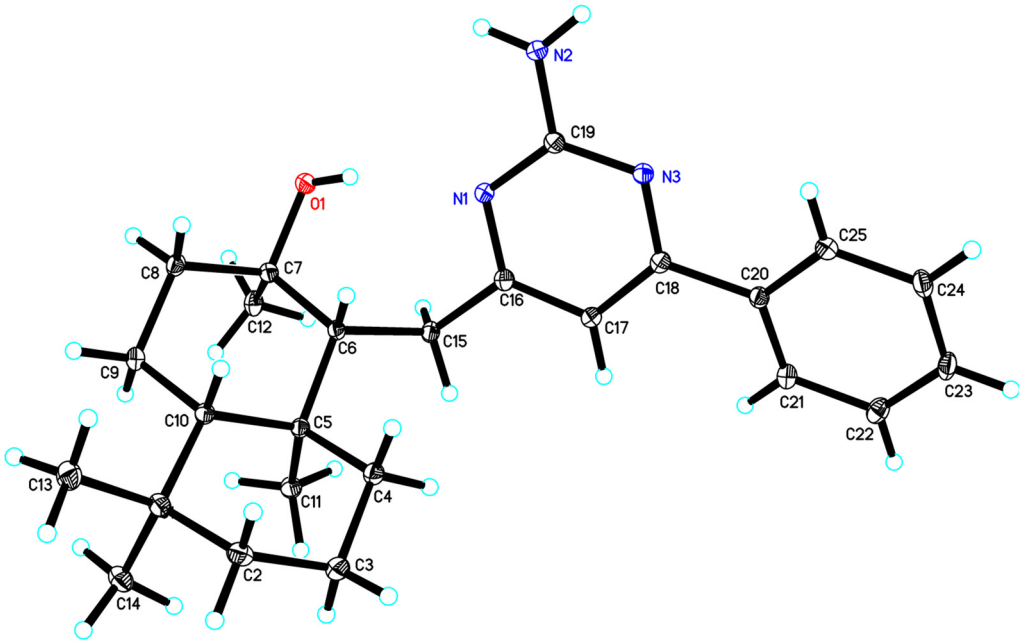
Yield 30.2%, M.p. 205.5~206.3 (°C);

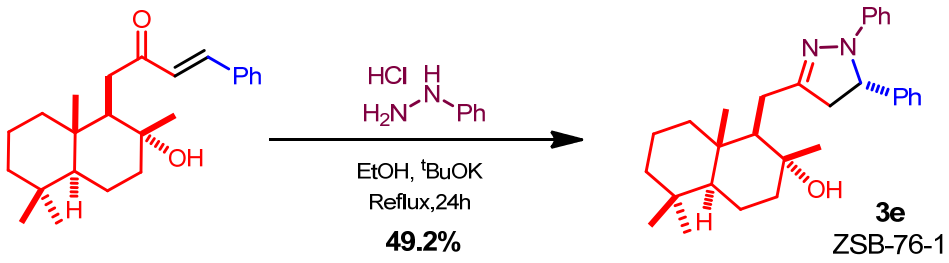
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.81 (s, 3H, *CH₃*) , 0.86 (s, 3H, *CH₃*), 0.90 (s, 3H, *CH₃*), 0.95 (dd, J_1 = 12.20 Hz, J_2 = 2.28 Hz, 1H, H in naphthane ring), 1.09 (td, J_1 = 13.12 Hz, J_2 = 3.88 Hz, 1H, H in naphthane ring), 1.25 (s, 3H, *CH₃*), 1.29(m, 1H, H in naphthane ring), 1.32~1.42(m, 3H, H in naphthane ring), 1.52(td, J_1 = 12.76 Hz, J_2 = 3.88 Hz, 1H, H in naphthane ring), 1.61(dt, J_1 = 13.32 Hz, J_2 = 3.52 Hz, 1H, H in naphthane ring), 1.66~1.76 (m, 3H, H in naphthane ring), 2.01 (dt, J_1 = 12.60 Hz, J_2 = 3.28 Hz, 1H, H in naphthane ring), 2.66(dd, J_1 =15.20 Hz, J_2 = 3.16 Hz, 1H, pyrimidyl-CH2), 2.82(dd, J_1 =15.20 Hz, J_2 = 4.96 Hz, 1H, pyrimidyl-CH2), 5.13(s, br, 2H, NH2), 6.93 (s, 1H, H in pyrimidyl ring), 7.46~7.49(m, 3H, *aromatic H*), 7.96~7.99(m, 2H, *aromatic H*).

^{13}C NMR (100 MHz, $CDCl_3$) δ 15.64(*CH₃*), 18.40(*CH₂*), 20.51(*CH₂*), 21.43(*CH₃*), 24.68(*CH₃*), 33.29(*C*), 33.35(*CH₃*), 33.50(*CH₂*), 39.55(*CH₂*), 39.61(*C*), 41.81(*CH₂*), 44.17(*CH₂*), 56.17(*CH*), 60.47(*CH*), 72.40(*C*), 106.90(*CH*), 127.17(2×*CH*), 128.74(2×*CH*), 130.57(*CH*), 137.35(*C*), 162.47(*C*), 165.99(*C*), 173.72(*C*). ESI-MS calcd for $C_{25}H_{34}N_3$ [M-H_2O+H^+]: 376.28, found 376.32; $C_{25}H_{36}N_3O$ [M+H^+]:394.29, found

394.38.

The molecular structure of **3c** was also confirmed by X-ray single crystal diffraction as shown below, the naphthane scaffold is also *trans* fused, and adopt chair conformations, keeping the original stereocenters untouched.





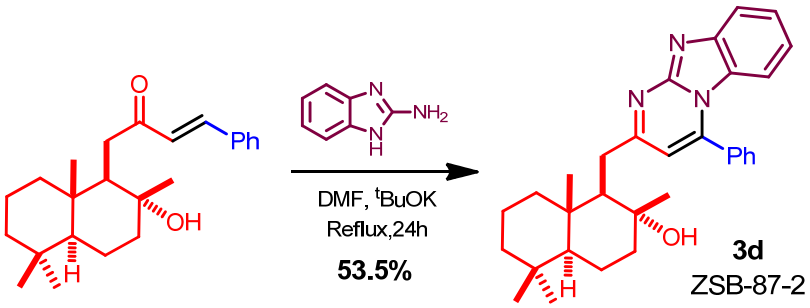
Structural analysis for the drimanyl pyrimidine **3e** was as follows:

Yield 51%, Yellow wax.

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.80 (s, 3H, *CH₃*) ,0.84 (s, 3H, *CH₃*), 0.89 (s, 3H, *CH₃*), 1.15 (dd, J_1 = 13.64 Hz, J_2 = 4.36 Hz, 1H, H in naphthane ring), 1.24(s, 3H, *CH₃*), 1.32~1.44 (m, 4H, H in naphthane ring), 1.47~1.60 (m, 3H, H in naphthane ring), 1.64~1.71 (m, 2H, H in naphthane ring), 1.67(s, br, 1H, OH), 1.81(dd, J_1 = 6.36 Hz, J_2 = 3.80 Hz, 1H, H in naphthane ring), 1.94 (dt, J_1 = 12.64 Hz, J_2 = 3.24 Hz, 1H, H in naphthane ring), 2.37 (dd, J_1 = 16.52 Hz, J_2 = 3.76 Hz, 1H, dihydropyrazole- *CH₂*), 2.56 (dd, J_1 = 16.52 Hz, J_2 = 6.28 Hz, 1H, dihydropyrazole- *CH₂*), 2.79 (dd, J_1 = 17.48 Hz, J_2 = 8.28 Hz, 1H, Ph-CH*CH₂*), 3.45 (dd, J_1 = 17.48 Hz, J_2 = 11.92 Hz, 1H, Ph-CH*CH₂*), 4.97 (dd, J_1 = 11.92 Hz, J_2 = 8.28 Hz, 1H, Ph-*CH*), 6.72 (ddd, J_1 = 7.92 Hz, J_2 = 6.76 Hz, J_3 = 1.16 Hz, 1H, *aromatic H*), 6.89 (d, J = 8.12 Hz, 2H, *aromatic H*), 7.12(dd, J_1 = J_2 =7.80 Hz, 2H, *aromatic H*), 7.27~7.35 (m, 5H, *aromatic H*).

ESI-MS calcd for $C_{30}H_{41}N_2O$ [M+H$^+$]: 445.32, found 445.41; $C_{30}H_{39}N_2$[M-H_2O+H$^+$]: 427.31, found 427.38.

Synthesis of drimanyl heterocycles 3b and 3d



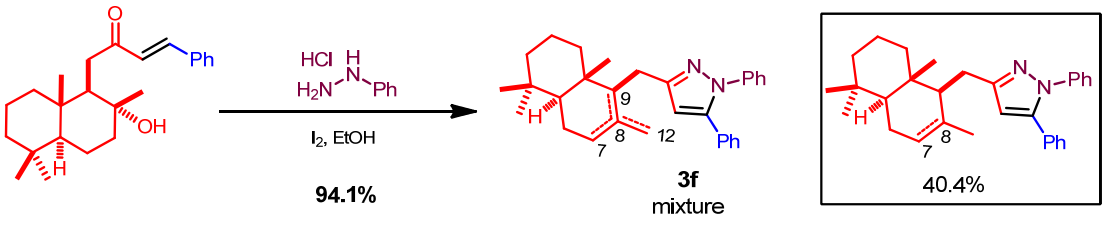
To the stirred solution of *α,β-unsaturated ketone inserted merosesquiterpenoid mimic* **2a** (355mg, 1.0mmol, 1.0 equiv) in 5mL DMF was added potassium tert-butoxide (449mg, 4.0mmol, 4.0 equiv) and 1H-benzo[d]imidazol-2-amine (266mg, 2.0mmol, 2.0 equiv) successively, the mixture was stirred at reflux with an oil bath and the reaction progress was monitored by TLC until the reaction was complete (~24h). The reaction was quenched by the addition of saturated aqueous solution of NH_4Cl (20mL). The resulting mixture was extracted by ethyl acetate (3 X 20mL). The organic layers were combined and washed sequentially with H_2O (3 X 10mL), brine (10mL), dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography (200-300m) with PE/EtOAc = 4:1 as eluent to give ***3d*** as yellow solid (250 mg, yield 53.5%). M.p.199.1~201.7 (°C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.81 (s, 3H, *CH₃*), 0.88 (s, 3H, *CH₃*), 0.93 (s, 3H, *CH₃*), 1.09 (m, 2H, H in naphthane ring), 1.26 (s, 3H, *CH₃*), 1.28 (m, 1H, H in naphthane ring), 1.31~1.35(m, 3H, H in naphthane ring), 1.56~1.59(m, 3H, H in naphthane ring), 1.72 (dm, J_1 = 13.68 Hz, 1H, H in naphthane ring), 1.92 (s, br, 1H, OH), 1.99 (dt, J_1 = 12.72 Hz, J_2 = 3.20 Hz, 1H, H in naphthane ring), 2.41(dd, J_1 = 4.64 Hz, J_2 = 4.60 Hz, 1H, H in naphthane ring), 2.93(dd, J_1 =16.32 Hz, J_2 = 4.60 Hz, 1H, pyrimidyl-CH_2), 3.19 (dd, J_1 =16.32 Hz, J_2 = 4.48 Hz, 1H, pyrimidyl-CH2), 6.64(d, J_1 = 8.44 Hz, 1H, *aromatic H*), 6.70(s, 1H, H in pyrimidyl ring), 6.99(m, 1H, *aromatic H*), 7.42(ddd, J_1 =7.16 Hz, J_2 = 7.16 Hz, J_3 = 1.08 Hz, 1H, *aromatic H*), 7.57~7.71(m, 5H, *aromatic H*), 7.91(d, *J*

=8.16 Hz, 1H, *aromatic H*).

ESI-MS calcd for $C_{31}H_{38}N_3O$ [M+H$^+$]: 468.30, found 468.43; $C_{31}H_{37}N_3NaO$ [M+ Na$^+$]: 490.28, found 490.41;

The drimanyl isoxazole **3b** was prepared according to the similar procedure.

Synthesis of drimanyl pyrazole 3f



To the stirred solution of α,β-unsaturated ketone inserted merosesquiterpenoid mimic **2a** (355mg, 1.0mmol, 1.0 equiv.) in 10mL EtOH was added iodine (507mg, 2.0mmol, 2.0 equiv) and phenylhydrazine hydrochloride (289mg, 2.0mmol, 2.0 equiv) successively. The mixture was stirred at reflux with an oil bath and the reaction progress was monitored by TLC until the reaction was complete (~5h). The reaction was quenched by the addition of a saturated aqueous solution of $Na_2S_2O_3$ (10mL), 10mL of saturated aqueous solution of $NaHCO_3$ was added and the EtOH was removed under reduced pressure. The inorganic mixture was extracted with ethyl acetate (3 X 15mL). The organic layers were combined and washed sequentially with H_2O (3 X 10mL), brine (10mL), dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography (200-300m) with PE/EtOAc = 5:1 as eluent to produce an isomeric mixture ($\triangle^{7,8}$, $\triangle^{8,9}$ and $\triangle^{8,12}$) of drimanyl pyrazole **3f** with high yield (~94.1%). Careful gradient elution furnished the successful isolation of $\triangle^{7,8}$ isomer as a pure product with the yield of 40.4%, M.p. 86.1-87.2 (°C);

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (s, 3H, *CH*$_3$), 0.88 (s, 3H, *CH*$_3$), 0.92 (s, 3H,

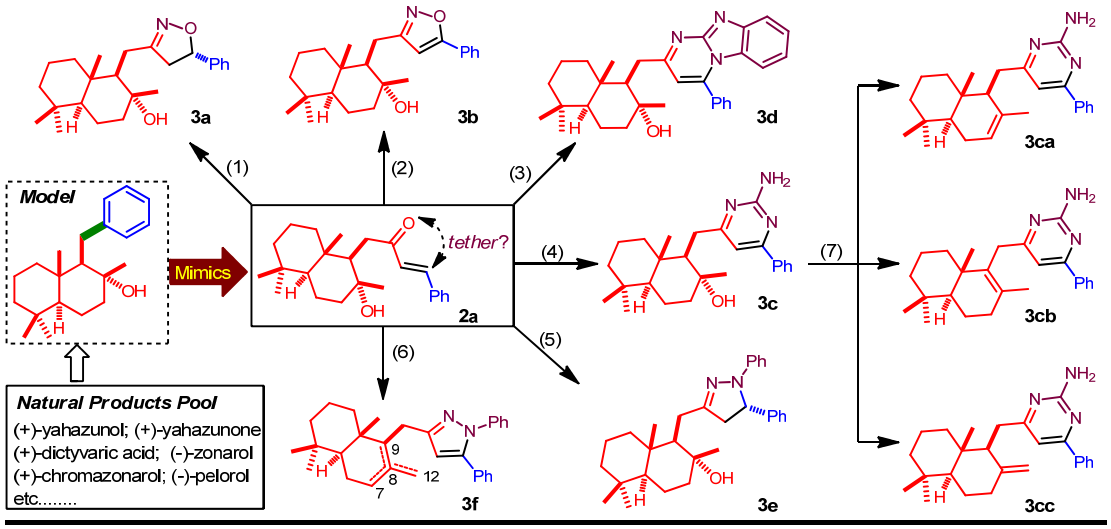
CH₃), 1.18(dt, J_1 = 13.12 Hz, J_2 = 3.84 Hz, 1H), 1.23~1.26(m, 2H), 1.28~1.33(m, 2H), 1.42~1.49(m, 2H), 1.62 (s, 3H, =C*CH₃*), 1.94~2.04(m, 2H), 2.47(m, 1H), 2.65(dd, J_1 = 15.64 Hz, J_2 = 9.36 Hz, 1H, pyrazole-CH2), 2.89(dd, J_1 = 15.64 Hz, J_2 = 2.12 Hz, 1H, pyrazole-CH2), 5.42(s, 1H, =*CH*), 6.35(s, 1H, H in pyrazole ring), 7.21~7.24(m, 2H, *aromatic H*), 7.27~7.33(m, 8H, *aromatic H*).

^{13}C NMR (100 MHz, CDCl3) δ 13.75 (*CH₃*), 18.92 (*CH₂*), 21.90 (*CH₃*), 22.73 (*CH₃*), 23.82 (*CH₂*), 26.21 (*CH₂*), 33.04 (*C*), 33.24 (*CH₃*), 36.66 (*C*), 39.45(*CH₂*), 42.27(*CH₂*), 50.13(*CH*), 53.92(*CH*), 106.82(*CH*), 122.23(*CH*), 125.16(2 × CH), 126.95(*CH*), 127.96(*CH*), 128.33(2×CH), 128.62(2×CH), 128.79(2×CH), 130.90 (*C*), 135.49 (*C*), 140.22 (*C*), 143.29 (*C*), 155.60 (*C*).

ESI-MS calcd for $C_{30}H_{37}N_2$ [$M+H^+$]: 425.30, found 425.34; $C_{30}H_{36}N_2Na$ [$M+Na^+$]: 447.28, found 447.34.

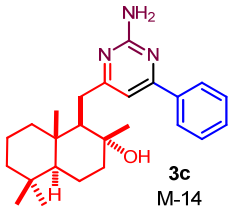
All the drimanyl pyrazole mimics were prepared and isolated accordingly.

Overview of Synthesized Drimanyl Heterocycles Mimics

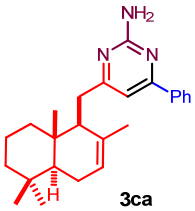


(1) NH_2OH-HCl, EtOH, ^tBuOK,reflux,24h,46.3%; (2) NH_2OH-HCl, DMF, ^tBuOK, reflux, 48h, 11%; (3) 1*H*-benzo[*d*]imidazol-2-amine,DMF, ^tBuOK, reflux,24h, 53.5%; (4) Guanidine Hydrochloride, EtOH, ^tBuOK, reflux,24h,30.2%; (5) Phenylhydrazine hydrochloride, EtOH, ^tBuOK,Reflux, 49.2%; (6) Phenylhydrazine hydrochloride, I_2, EtOH,Reflux, 40.4% (total yield 94.1%, three isomers); (7) TFA, DCM, R.T. total yield 84.4%.

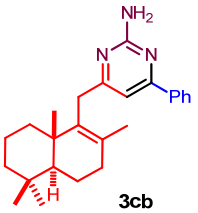
Drimanyl Pyrimidine Mimics



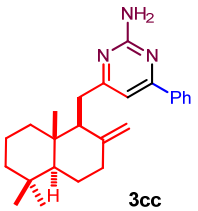
3c
M-14



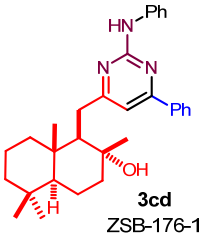
3ca
ZSB-184-3



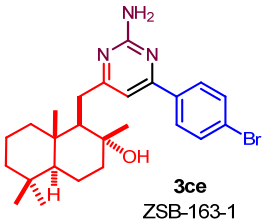
3cb
ZSB-184-3



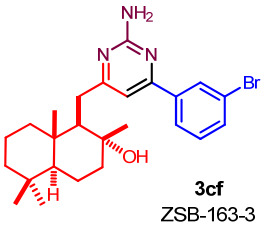
3cc
ZSB-184-5



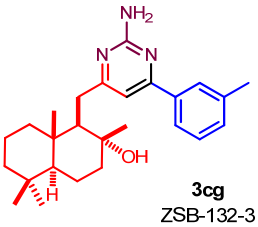
3cd
ZSB-176-1



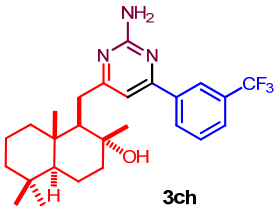
3ce
ZSB-163-1



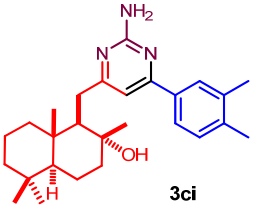
3cf
ZSB-163-3



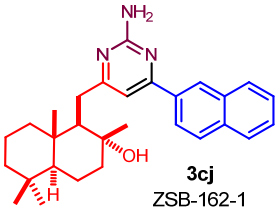
3cg
ZSB-132-3



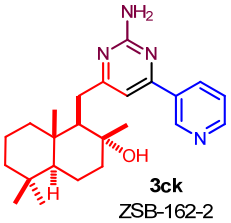
3ch
ZSB-160-2



3ci
ZSB-132-1

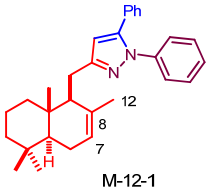


3cj
ZSB-162-1

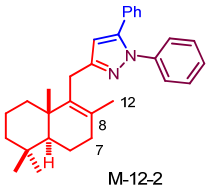


3ck
ZSB-162-2

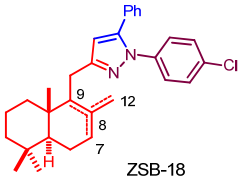
Drimanyl Pyrazole Mimics



M-12-1

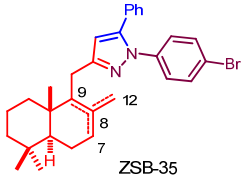


M-12-2



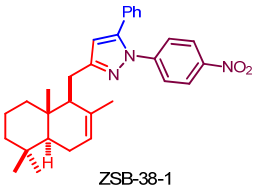
ZSB-18

$\Delta^{8,9}$: $\Delta^{8,12}$ = 5.1:1

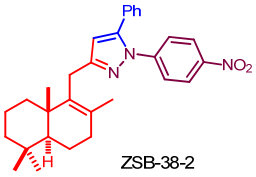


ZSB-35

$\Delta^{7,8}$: $\Delta^{8,9}$: $\Delta^{8,12}$ = 3.5: 17.1 :1

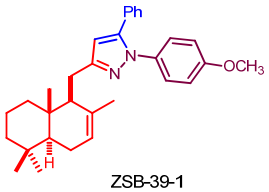


ZSB-38-1

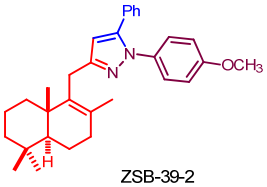


ZSB-38-2

$\Delta^{8,9}$: $\Delta^{8,12}$ = 24.1 :1

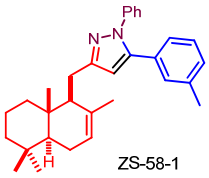


ZSB-39-1

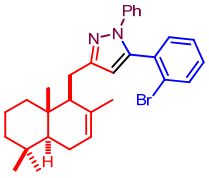


ZSB-39-2

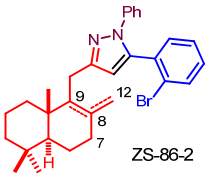
$\Delta^{8,9}$: $\Delta^{8,12}$ = 1.1 :1



ZS-58-1

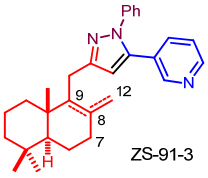


ZS-86-1



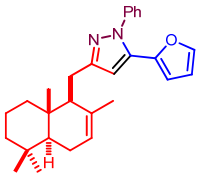
ZS-86-2

$\Delta^{8,9}$: $\Delta^{8,12}$ = 2.2:1



ZS-91-3

$\Delta^{7,8}$: $\Delta^{8,9}$ = 1:2.9



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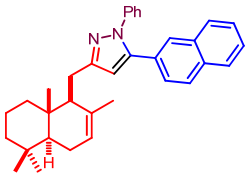

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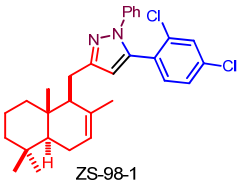

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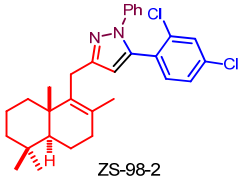

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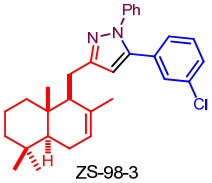

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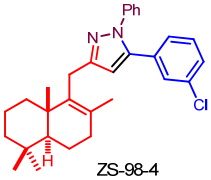

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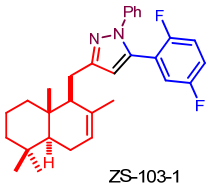

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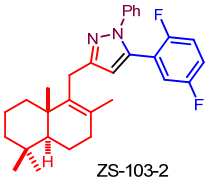

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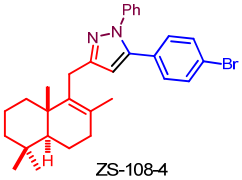

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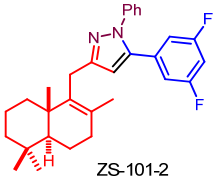
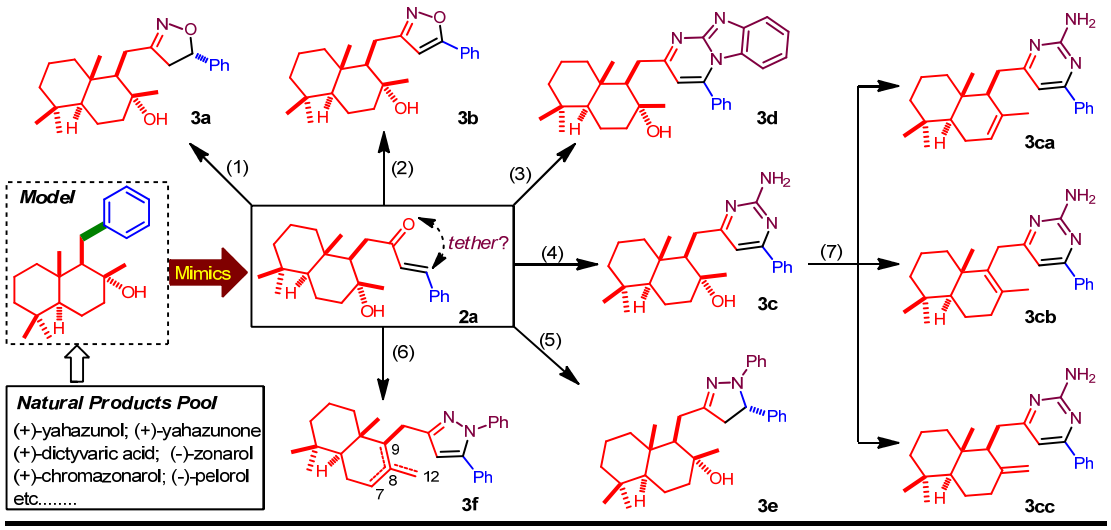


ZS-101-2

General Procedure for Biological Assay

The fungicidal activity of the target compounds was tested in vitro against the aforementioned plant pathogenic fungi using the mycelium growth rate test according to our previous report[1]. All the tested compounds were dissolved in DMSO at a concentration of 20 mg/mL. The media containing compounds at a concentration of 100 μg/mL were then poured into Petri dishes for initial screening. In the precision antifungal test of a specific compound, the 20 mg/mL solutions were diluted to 50, 25, 12.5, 6.25, 3.125 $\mu g \cdot mL^{-1}$ and the above experiments were repeated three times, the inhibition rates were calculated separately. The statistical analyses were performed by SPSS software version 20.0.

The antifungal bioactivity of different drimanyl merosesquiterepnoids mimics



(1) NH_2OH-HCl, EtOH, ^tBuOK,reflux,24h,46.3%; (2) NH_2OH-HCl, DMF, ^tBuOK, reflux, 48h, 11%; (3) 1*H*-benzo[*d*]imidazol-2-amine,DMF, ^tBuOK, reflux,24h, 53.5%; (4) Guanidine Hydrochloride, EtOH, ^tBuOK, reflux,24h,30.2%; (5) Phenylhydrazine hydrochloride, EtOH, ^tBuOK,Reflux, 49.2%; (6) Phenylhydrazine hydrochloride, I_2, EtOH,Reflux, 40.4% (total yield 94.1%, three isomers); (7) TFA, DCM, R.T. total yield 84.4%.

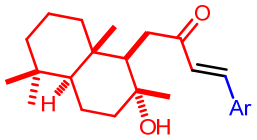
Table 1, The Antifungal Bioactivity of Different Drimanyl Merosesquiterepnoids Mimics

Entry	Compd.	Antifungal Bioactivity (%, 50mg/L)									ClogP
		R. S.	*S.S*	*B.C.*	*F.G.*	*P.C.*	*G.G.*	*A.S.*	*F.S.*	*C.L.*	*F.F.*	
1	**2a**	48.46± 0.04 d	37.12± 0.50 e	34.25± 1.30 d	34.30± 0.54 d	21.30± 0.48 c	38.00 ±0.37 d	32.40± 0.28 b	17.50± 0.09 c	24.91± 0.19 c	29.00± 0.12 d	5.037
2	**3a**	**58.15**± 1.14 c	**57.05**± 1.80 c	**73.76**± 0.84 b	36.43± 0.43 c	38.48± 0.31 a	14.34± 0.21 g	25.29± 0.56 d	30.20± 0.71 a	20.00± 0.82 d	38.42± 0.55 b	4.6985
3	**3c**	**57.45**± 1.10 c	**69.50**± 1.29 b	**78.85**± 2.11 a	**73.81**± 1.03 b	27.92± 0.36 b	32.02± 0.11 f	28.07± 0.63 c	18.20± 0.12 b	35.90± 0.58 b	46.48± 0.48 a	4.5810
4	**3d**	35.17± 0.28 e	**54.73**± 0.21 d	39.58± 0.11 c	27.97± 0.10 e	17.13± 0.09 d	35.38± 0.12 e	23.72± 0.17 e	16.00± 0.08 d	42.29± 0.21 a	21.29± 0.11 e	6.7962
5	**3e**	34.00± 0.12 f	1.85± 0.02 h	32.86± 0.15 d	17.01± 0.11 f	9.58± 0.09 f	42.00± 0.28 b	11.58± 0.18 f	4.98± 0.16 f	6.51± 0.11 f	6.87± 0.10 f	7.3190
6	**3f**	18.36± 0.39 g	18.82± 0.12 f	5.68± 0.29 g	10.00± 0.01 g	15.87± 0.33 e	38.43± 0.17 c	7.01± 0.02 g	12.00± 0.10 e	11.00± 0.41 e	5.92± 0.19 f	8.474
7	**DM**	62.89± 0.02 b	9.82± 0.01 g	18.07± 0.11 f	34.98± 0.31 d	20.98± 0.11 c	55.75± 0.61 a	39.30± 0.56 a	N.T.	N.T.-	35.08± 0.32 c	4.949
	DMSO	—	—	—	—	—	—	—	—	—	—	
	Carbendazim	100± 0.01a	100± 0.01a	20.39± 0.38e	100± 0.01a	N.T.	N.T.	N.T.	N.T.	N.T.	N.T.	

Note: *R. S.: Rhizoctonia solani, S.S.: Sclerotinia scleotiorum, B.C.: Botrytis cinerea, F.G.: Fusarium graminearum, P.C.: Phytophthora capsici, G.G.: Gaeumanomyces graminis, A.S.: Alternaria solani, F.S.: Fusarium sulphureum, C.L.:Colletotrichum lagenarium, F.F.: Fusarium fujikuroi,* Inhibitory rates are mean values of triplicate experiments.

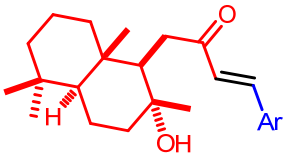
N.T.: *Not test.*, "—": no inhibitory effect. Different small letters in the same column showed significant difference at $P < 0.05$ level, through Duncan's multiple range test in SPSS statistics 22.0. The alphabetical order is consistent with the high to low order of the antifungal activity.

The antifungal bioactivity of michael acceptors inserted merosesquiterpenoids



Entry	Compd.	Ar	Antifungal Bioactivity (%)			
			R.S. (100mg/L)	*R.S.* (50mg/L)	*G.G.* (100mg/L)	*G.G.* (50mg/L)
	1	-	61.54±0.41 f	49.65±0.29 g	19.00±0.11 r	6.00±0.12 q
1	**2a**	Ph	57.01±0.31 g	48.46±0.04 g	49.16±0.21 gh	38.00±0.37 e
2	**2b**	4-NO_2-Ph	40.00±0.23 l	25.00±0.11 no	22.00±0.12 q	17.00±0.09 o
3	**2c**	4-F-Ph	60.59±0.29 f	56.77±0.23 f	39.92±0.13 m	28.00±0.15 k
4	**2d**	4-Cl-Ph	68.50±0.35 d	61.42±0.28 e	47.00±0.23 i	35.00±0.16 fg
5	**2e**	4-Br-Ph	36.81±0.17 n	35.52±0.12 j	41.05±0.19 m	30.00±0.13 ij
6	**2f**	4-CH_3-Ph	23.60±0.09 p	9.92±0.07 r	31.09±0.13 p	12.00±0.11 p
7	**2g**	4-CH_3O-Ph	38.24±0.13 mn	33.33±0.14 k	49.21±0.21 gh	27.34±0.15 kl
8	**2h**	4-$(CH_3)_2N$-Ph	42.42±0.19 k	30.74±0.11 l	42.80±0.18 k	30.00±0.12 ij
9	**2i**	3-NO_2-Ph	49.33±0.31 j	45.71±0.30 h	40.00±0.19 m	33.00±0.10 h
10	**2j**	3-CF_3-Ph	54.11±0.30 h	48.05±0.26 g	53.78±0.17 d	43.00±0.15 cd
11	**2k**	3-Cl-Ph	68.55±0.41 d	64.98±0.39 d	62.00±0.34 b	49.00±0.32 b
12	**2l**	3-Br-Ph	38.21±0.16 mn	32.38±0.18 kl	55.00±0.23 d	42.00±0.20 d
13	**2m**	3-CH_3-Ph	32.44±0.12 o	23.37±0.14 op	36.00±0.18 n	26.00±0.05 lm
14	**2n**	3-OH-Ph	77.43±0.51 bc	67.44±0.48 c	33.00±0.21 o	25.00±0.13 m
15	**2o**	2-Br-Ph	23.68±0.09 p	22.63±0.11 p	41.18±0.21 lm	31.00±0.20 i
16	**2p**	2-CH_3O-Ph	51.64±0.31 i	39.10±0.19 i	48.10±0.21 hi	22.63±0.13 n
17	**2q**	2-Naphthyl	36.43±0.20 n	29.00±0.17 m	52.11±0.36 e	28.95±0.20 jk
18	**2r**	2,4-Cl-Ph	38.10±0.12 mn	26.41±0.07 n	50.00±0.19 fg	42.00±0.12 d
19	**2s**	2,5-Cl-Ph	39.05±0.17 lm	14.92±0.06 q	55.26±0.23 d	44.21±0.18 c
20	**2t**	2,5-F-Ph	78.35±0.45 b	44.59±0.29 h	59.46±0.24 c	36.00±0.19 f
21	**2u**	3,5-F-Ph	61.69±0.38 f	61.59±0.49 e	54.83±0.23 d	28.00±0.11 k
22	**2v**	2,6-Cl-Ph	37.31±0.15 mn	24.77±0.09 no	45.00±0.16 j	34.00±0.14 gh
23	**2w**	3,4-CH_3-Ph	37.22±0.12 mn	31.20±0.16 l	51.35±0.33 ef	21.00±0.15 n
24	**2x**	2-Furyl	66.53±0.26 e	64.96±0.39 d	50.00±0.18 fg	43.00±0.21 cd
25	**2y**	2-Thienyl	75.82±0.42 c	61.94±0.30 e	64.63±0.28 a	52.83±0.24 a
26	**2z**	3-Pyridyl	76.27±0.56 c	73.58±0.39 b	33.19±0.16 o	29.00±0.11 jk
27	**DMSO**		—	—	—	—
28	**Carbendazim**		100± 0.01a	100± 0.01a	N.T.	N.T.

401 EC_{50} values of drimanyl merosesquiterpenoids **2** against *Rhizoctonia solani*



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Entry	Compd.	Ar	EC_{50} (mg/L)	regression equation	correlation coefficient
1	**2c**	4-F-Ph	16.00±0.78	y = 0.4207x + 4.5488	0.9628
2	**2d**	4-Cl-Ph	8.70±0.31	y = 0.6834x + 4.3502	0.9760
3	**2k**	3-Cl-Ph	14.63±0.12	y = 0.3582x + 4.5913	0.9709
4	**2u**	3,5-F-Ph	18.74±0.99	y = 0.4792x + 4.3991	0.9613
5	**2x**	2-Furyl	10.60±0.59	y = 0.4156x + 4.5807	0.9909
6	**2y**	2-Thienyl	12.53±0.89	y = 0.3318x + 4.6258	0.9999
7	**2z**	3-Pyridyl	4.47±0.42	y = 0.8035x + 4.5113	0.9918

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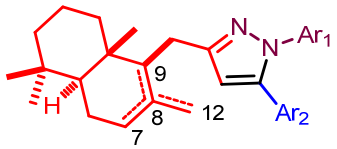
The antifungal bioactivity of different drimanyl pyrazole mimics at 50mg/L



For Specific Structures see "Drimanyl Pyrazole Mimics"

Entry	Original No	Structures		*G. graminis*	*R. solani*	*P. capsici*	*S. scleotiorum*
		Ar_1	Ar_2				
1	M-12-1	Ph	Ph	38.43%	18.36%	15.87%	14.28%
2	ZSB-18	4-Cl-Ph	Ph	31.21%	15.45%	16.54%	20.00%
3	ZSB-**35**	4-Br-Ph	Ph	25.99%	9.84%	15.87%	9.54%
4	ZSB-38-1	4-NO_2-Ph	Ph	21.51%	8.00%	11.64%	18.11%
5	ZSB-38-2	4-NO_2-Ph	Ph	33.72%	6.54%	14.81%	22.65%
6	ZSB-39-1	4-MeO-Ph	Ph	44.18%	21.50%	15.34%	22.64%
7	ZSB-39-2	4-MeO-Ph	Ph	49.41%	29.43%	15.34%	35.47%
8	ZSB-44	3-Cl-Ph	Ph	26.16%	22.42%	8.99%	9.06%
9	ZSB-86-1	Ph	2-Br-Ph	18.33%	3.4%	8.33%	7.6%
10	ZSB-91-3	Ph	2-Pyridyl	35.48%	44.89%	9.44%	24.09%
11	ZSB-93-1	Ph	2-Furyl	34.63%	25.00%	16.73%	12.72%
12	ZSB-96-1	Ph	2-Naphthyl	33.11%	40.30%	9.87%	13.18%
13	ZSB-98-1	Ph	2,4-Cl-Ph	28.36%	20.95%	16.73%	16.73%
14	ZSB-98-2	Ph	2,4-Cl-Ph	23.51%	20.91%	7.72%	19.09%
15	ZSB-98-3	Ph	3-Cl-Ph	28.84%	41.32%	15.87%	18.18%
16	ZSB-98-4	Ph	3-Cl-Ph	19.87%	14.07%	10.19%	9.75%
17	ZSB-101-2	Ph	3,5-F- Ph	29.63%	28.52%	10.65%	15.68%
18	ZSB-103-1	Ph	2,5-F- Ph	14.73%	20.53%	8.34%	14.41%
19	ZSB-103-2	Ph	2,5-F- Ph	21.41%	8.4%	5.10%	8.05%
20	ZSB-108-4	Ph	4-Br- Ph	28.84%	8.33%	12.44%	12.72%

Note: *G. graminis*: *Gaeumanomyces graminis*, *R. solani: Rhizoctonia solani, P. capsici*: *Phytophthora capsici*
S. scleotiorum: Sclerotinia scleotiorum

The antifungal bioactivity of drimanyl pyrimidine mimics at 50mg/L

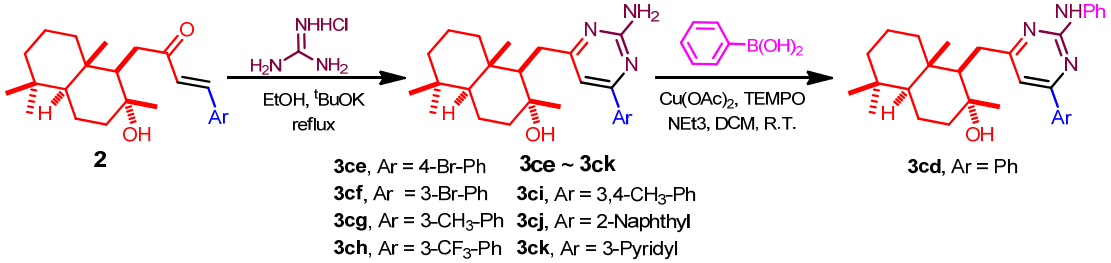
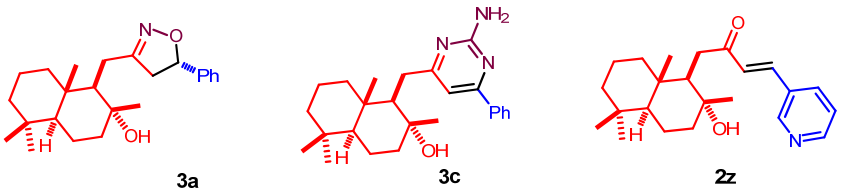


Table 3, Fungicidal bioactivity of Drimanyl Pyrimidine mimics

Entry	Compd.	Antifungal Bioactivity (%, 50mg/L)			
		S. scleotiorum	*R. solani*	*B. cinerea*	*F. graminearum*
1	**3c**	69.50± 2.29 d	57.45±1.10 c	78.85±2.11 a	73.81±1.03 b
2	**3ca**	33.39± 0.22 g	35.20± 0.29 gh	24.60± 0.19 e	14.50± 0.09 f
3	**3cb**	27.64± 0.08 h	30.10± 0.11 i	20.31± 0.10 g	18.00± 0.10 e
4	**3cc**	20.73± 0.10 i	36.22± 0.14 g	27.73± 0.12 d	19.50± 0.11 e
5	**3cd**	36.40± 0.24 f	23.21± 0.11 j	10.63± 0.06 i	50.00± 0.24 c
6	**3ce**	82.40± 0.41 b	48.18±0.23 e	15.60±0.13 h	8.10±0.09 ij
7	**3cf**	17.23±0.06 j	33.58±0.11 h	28.00±0.13 d	9.70±0.10 hi
8	**3cg**	81.27±0.41 b	47.81±0.21 e	38.07±0.12 c	19.50±0.06 e
9	**3ch**	10.86±0.05 k	40.15±0.21 f	5.00±0.02 j	6.80±0.04 j
10	**3ci**	41.98±0.18 e	51.82±0.20 d	22.48±0.11 f	11.86±0.05 g
11	**3cj**	71.91±0.50 c	7.04±0.04 k	5.00±0.06 j	10.17±0.09 h
12	**3ck**	68.54±0.31 d	74.45±0.38 b	56.42±0.29 b	41.53±0.39 d
13	**DMSO**	—	—	—	—
14	**Carbendazim**	100±0.02 a	100±0.15 a	20.39±0.38 g	100±0.01 a

Note: *S. scleotiorum: Sclerotinia scleotiorum; R. solani*: *Rhizoctonia solani*; *B. cinerea*: *Botrytis cinerea; F. graminearum*: *Fusarium graminearum.*

Discovery of promising antifungal leads

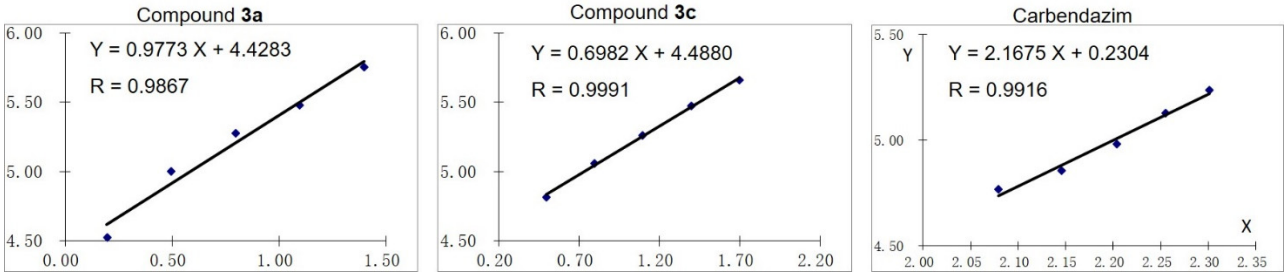


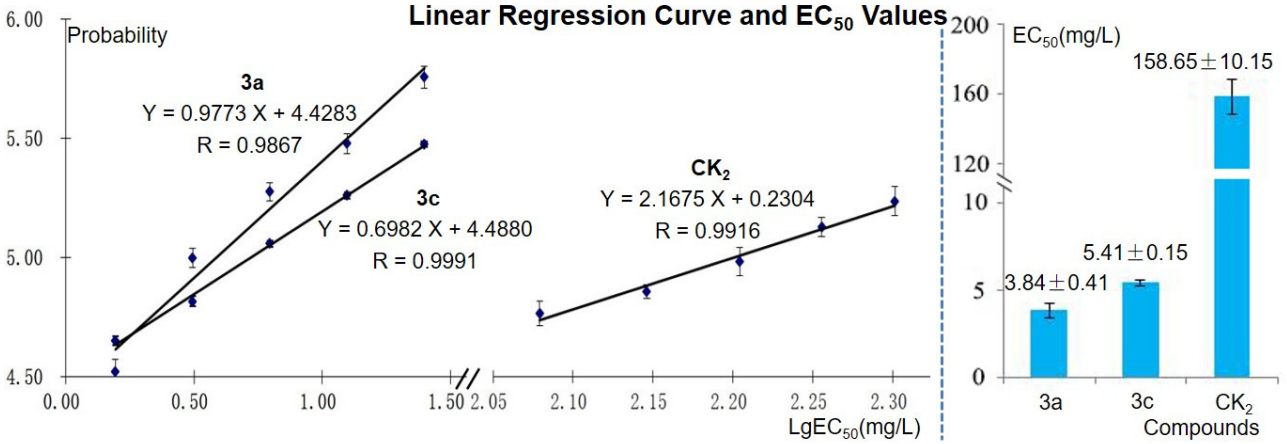
, Bioactivity and structural analysis of fungicidal drimanyl meroterpenoids mimics

Table 4, Bioactivity and structural analysis of fungicidal drimanyl meroterpenoids mimics

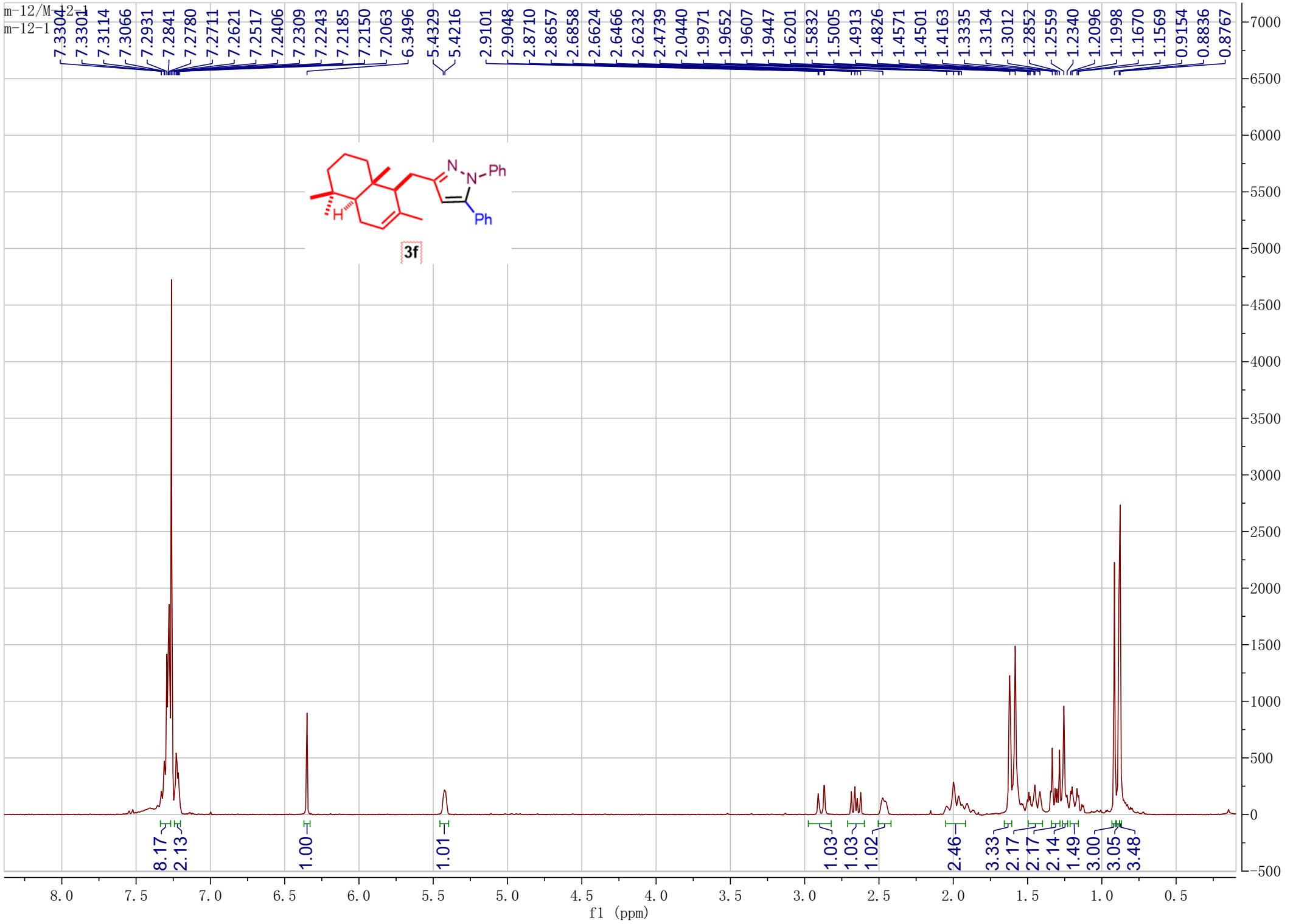
Compd.	Antifungal Bioactivity (EC_{50}, mg/L)				Properties			
	S.S.	***R.S.***	***B.C.***	***F.G.***	Fsp3	ClogP	TPSA	LE
3a	27.01 ± 0.25 B	32.31±1.11 D	**3.84**±0.41 A	>25	0.7083	4.6985	41.82	-0.0258[a]
3c	14.06 ± 0.19 C	22.81±2.91 C	**5.41**±0.15 B	9.51±0.37	0.60	4.581	70.97	-0.0364[a] -0.0462[b]
2z	>25	**4.47**±0.42 B	>25	>25	0.6522	3.54	49.66	-0.0343[c]
2a	>50	>50	>50	>50	0.625	5.037	37.3	<-0.0895
CK1	—	—	—	—	—	—	—	—
CK2	0.18±0.01 A	0.48±0.04 A	158.65±10.15 C	0.59±0.12	—	—	—	—

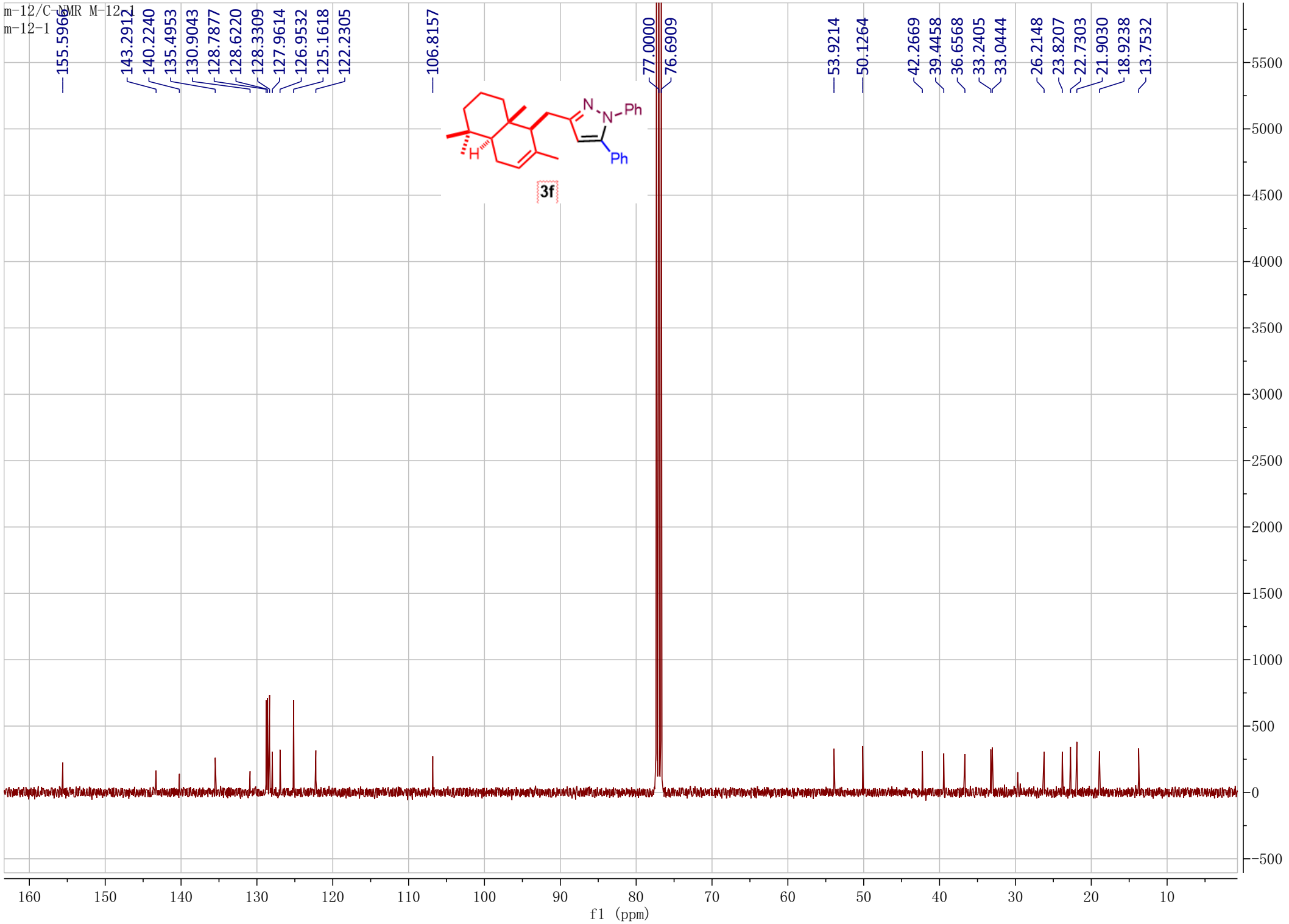
Note: LE=-1.37 Log(EC_{50})/number of heavy atoms. a: based on EC_{50} against *Botrytis cinerea*, b: based on EC_{50} against *Fusarium graminearum*, c: based on EC_{50} against *Rhizoctonia solani*. Different capital letters in the same column showed significant difference at $P < 0.01$ level, through Duncan's multiple range test in SPSS statistics 22.0. The alphabetical order is consistent with the high to low order of the antifungal activity.





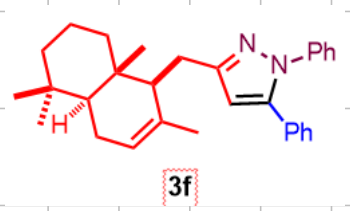
Typical Spectra of NMR and X-ray single crystal diffraction


m-12/M-12-1
m-12-1
7.3304
7.3301
7.3114
7.3066
7.2931
7.2841
7.2780
7.2711
7.2621
7.2517
7.2406
7.2309
7.2243
7.2185
7.2150
7.2063
6.3496
5.4329
5.4216
2.9101
2.9048
2.8710
2.8657
2.6858
2.6624
2.6466
2.6232
2.4739
2.0440
1.9971
1.9652
1.9607
1.9447
1.6201
1.5832
1.5005
1.4913
1.4826
1.4571
1.4501
1.4163
1.3335
1.3134
1.3012
1.2852
1.2559
1.2340
1.2096
1.1998
1.1670
1.1569
0.9154
0.8836
0.8767
N
N
Ph
Ph
H
3f
8.17
2.13
1.00
1.01
1.03
1.03
1.02
2.46
3.33
2.17
2.17
2.14
1.49
3.00
3.05
3.48
f1 (ppm)


m-12/C-NMR M-12-1
m-12-1
155.5966
143.2912
140.2240
135.4953
130.9043
128.7877
128.6220
128.3309
127.9614
126.9532
125.1618
122.2305
106.8157
77.0000
76.6909
53.9214
50.1264
42.2669
39.4458
36.6568
33.2405
33.0444
26.2148
23.8207
22.7303
21.9030
18.9238
13.7532
N
N
Ph
Ph
H
3f
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

m-12/DEPT135_M-12-1
m-12-1
DEPT135

128.7902
128.6189
128.3322
127.9624
126.9561
125.1599
122.2293
106.8113
53.9125
50.1187
42.2598
39.4382
33.2396
26.2116
23.8156
22.7343
21.9025
18.9198
13.7508

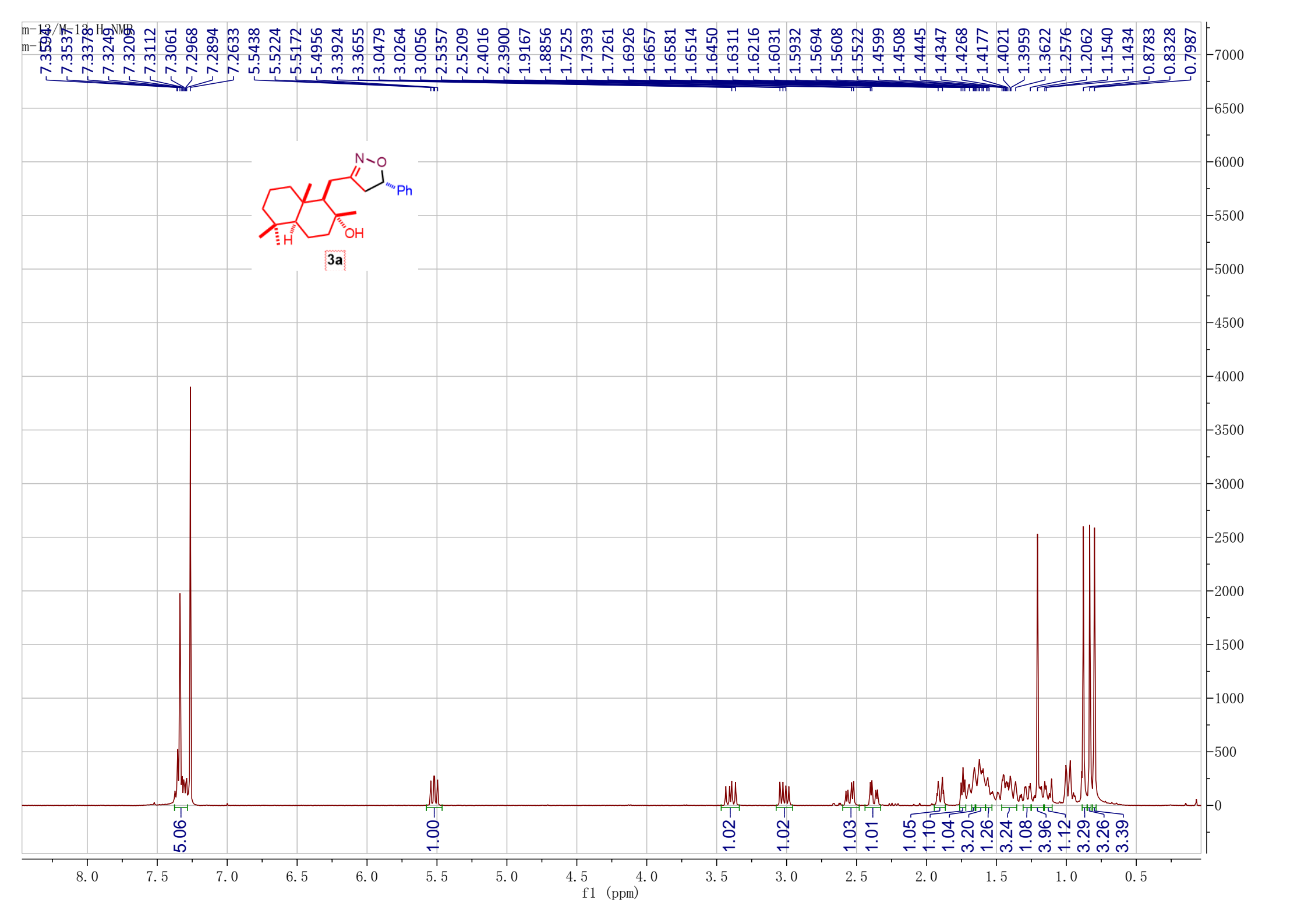


3f

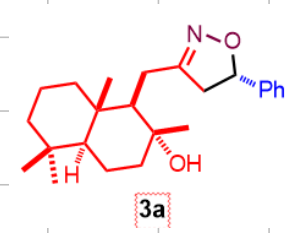
1000
900
800
700
600
500
400
300
200
100
0
−100
−200
−300
−400

140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5

f1 (ppm)


m-15/M-13 H NMR
7.3594
7.3537
7.3378
7.3249
7.3209
7.3112
7.3061
7.2968
7.2894
7.2633
5.5438
5.5224
5.5172
5.4956
3.3924
3.3655
3.0479
3.0264
3.0056
2.5357
2.5209
2.4016
2.3900
1.9167
1.8856
1.7525
1.7393
1.7261
1.6926
1.6657
1.6581
1.6514
1.6450
1.6311
1.6216
1.6031
1.5932
1.5694
1.5608
1.5522
1.4599
1.4508
1.4445
1.4347
1.4268
1.4177
1.4021
1.3959
1.3622
1.2576
1.2062
1.1540
1.1434
0.8783
0.8328
0.7987
N
O
Ph
H
OH
3a
5.06
1.00
1.02
1.02
1.03
1.01
1.05
1.10
1.04
3.20
1.26
3.24
1.08
3.96
1.12
3.29
3.26
3.39
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)

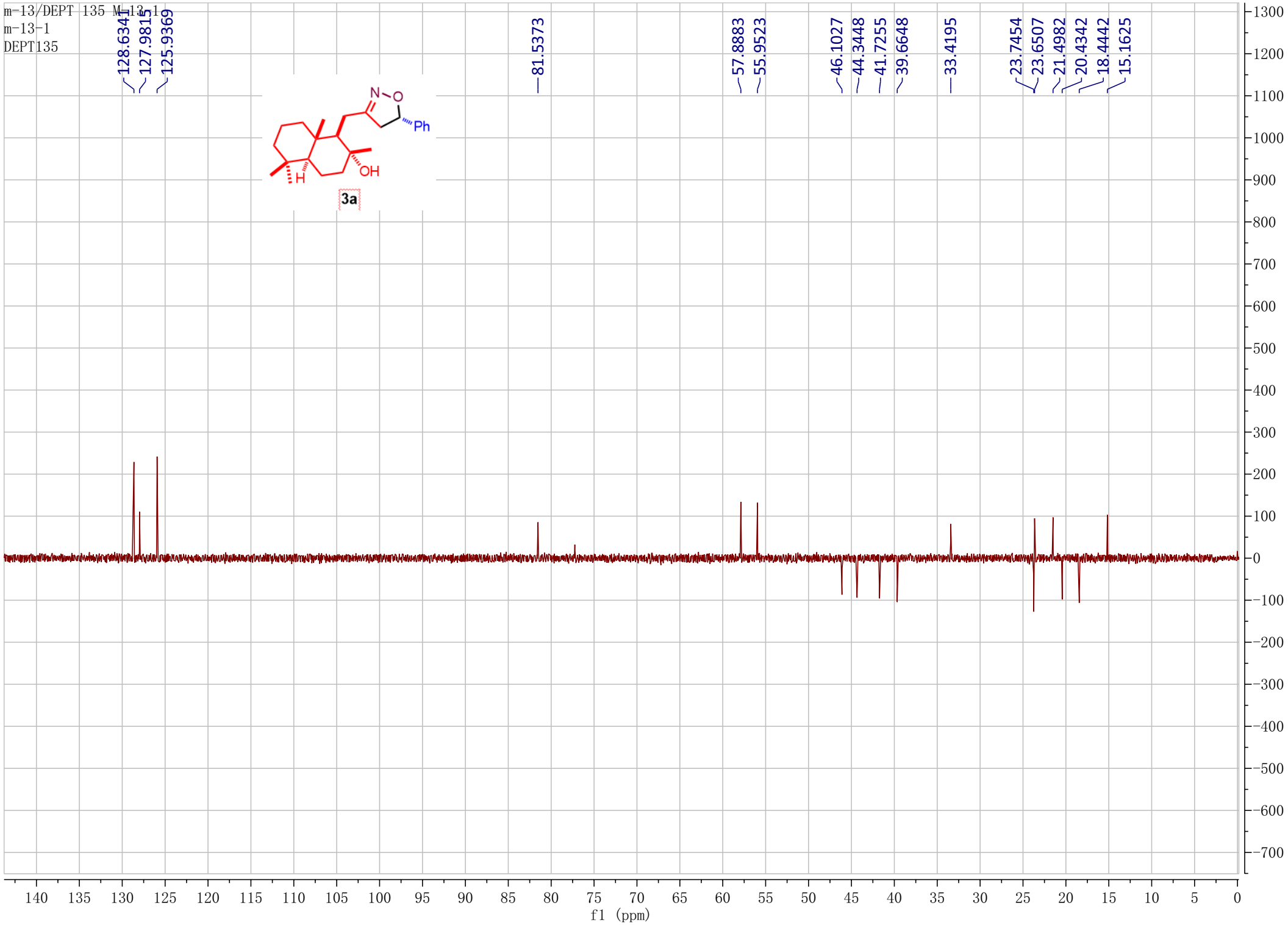
m-13/C-NMR M-13-1
m-13-1



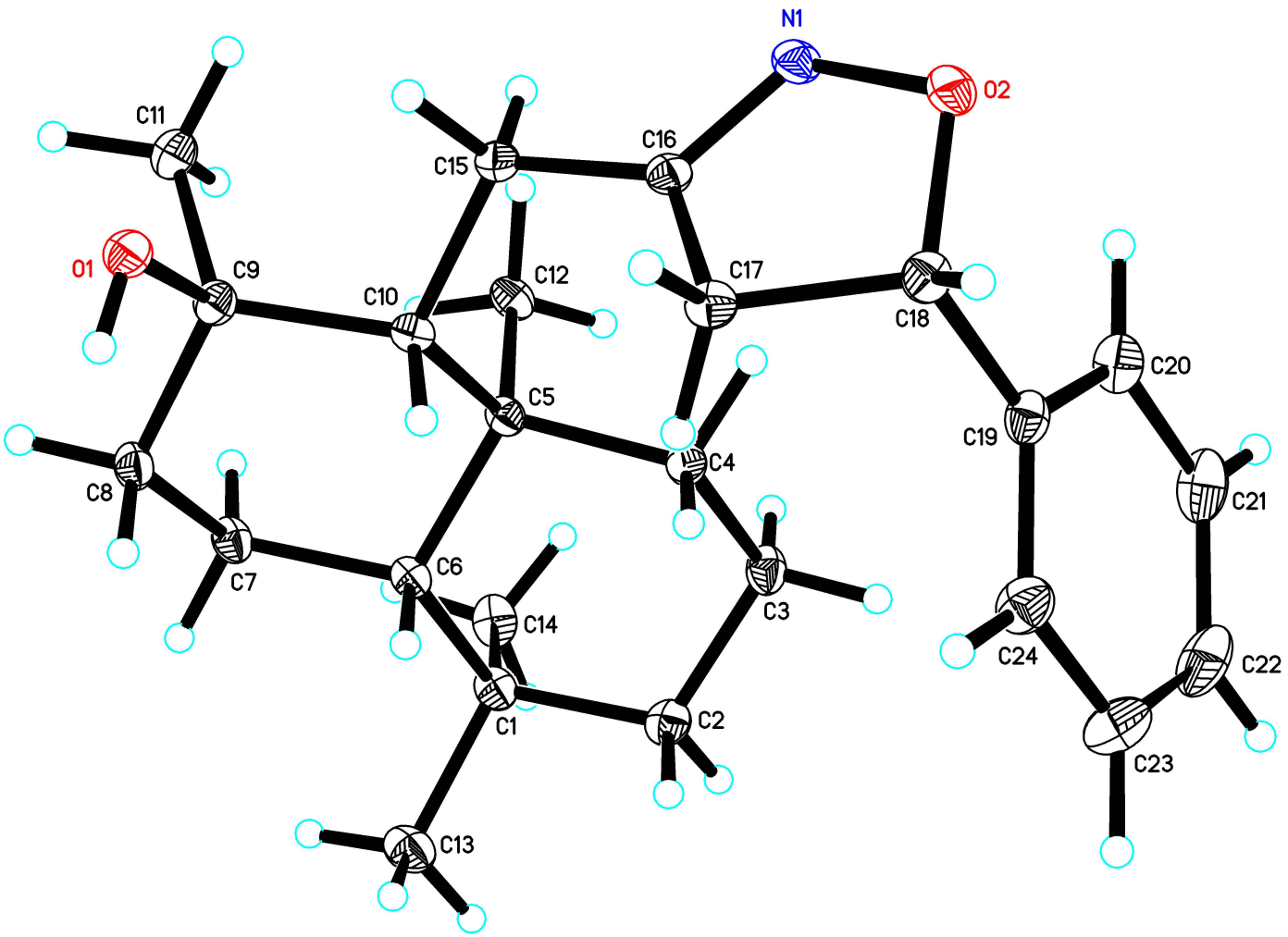
3a

161.3034
141.2088
128.6095
127.9573
125.9123
81.5127
77.3336
77.0149
76.6978
73.6726
57.8760
55.9339
46.0817
44.3242
41.7078
39.6515
38.8973
33.3959
33.2643
23.7213
23.6286
21.4770
20.4141
18.4241
15.1383

f1 (ppm)


m-13/DEPT 135 M-13-1
m-13-1
DEPT135
128.6341
127.9815
125.9369
81.5373
57.8883
55.9523
46.1027
44.3448
41.7255
39.6648
33.4195
23.7454
23.6507
21.4982
20.4342
18.4442
15.1625
N
O
Ph
OH
H
3a
f1 (ppm)


N
O
Ph
OH
H


N1
O2
C11
C15
C16
O1
C9
C10
C12
C17
C18
C20
C5
C19
C4
C8
C21
C7
C6
C3
C14
C24
C22
C1
C2
C23
C13

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: exp_177

```
Bond precision:  C-C = 0.0030 A          Wavelength=1.54184

Cell:           a=9.67127(7)    b=7.05127(7)       c=15.44464(12)
                alpha=90        beta=93.4847(6)    gamma=90
Temperature:    100 K

                Calculated                Reported
Volume          1051.296(15)              1051.296(15)
Space group     P 21                      P 1 21 1
Hall group      P 2yb                     P 2yb
Moiety formula  C24 H35 N O2              C24 H35 N O2
Sum formula     C24 H35 N O2              C24 H35 N O2
Mr              369.53                    369.53
Dx,g cm-3       1.167                     1.167
Z               2                         2
Mu (mm-1)       0.563                     0.563
F000            404.0                     404.0
F000'           405.07
h,k,lmax        12,8,19                   12,8,18
Nref            4231[ 2296]               3930
Tmin,Tmax       0.850,0.894               0.408,1.000
Tmin'           0.835

Correction method= # Reported T Limits: Tmin=0.408 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.71/0.93      Theta(max)= 73.619

R(reflections)= 0.0386( 3897)     wR2(reflections)= 0.1025( 3930)

S = 1.042                 Npar= 249
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level G

```
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms .............          1 Report
PLAT012_ALERT_1_G No     _shelx_res_checksum found in CIF ........     Please Check
PLAT142_ALERT_4_G s.u. on b - Axis Small or Missing ..............    0.00007 Ang.
PLAT143_ALERT_4_G s.u. on c - Axis Small or Missing ..............    0.00012 Ang.
PLAT395_ALERT_2_G Deviating  X-O-Y  Angle from 120 Deg for  O2          106.9 Degree
PLAT791_ALERT_4_G The Model has Chirality at C5      (Chiral SPGR)          S Verify
PLAT791_ALERT_4_G The Model has Chirality at C6      (Chiral SPGR)          S Verify
PLAT791_ALERT_4_G The Model has Chirality at C9      (Chiral SPGR)          R Verify
PLAT791_ALERT_4_G The Model has Chirality at C10     (Chiral SPGR)          R Verify
PLAT791_ALERT_4_G The Model has Chirality at C18     (Chiral SPGR)          S Verify
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   0 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  10 ALERT level G = General information/check it is not something unexpected

   1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   1 ALERT type 2 Indicator that the structure model may be wrong or deficient
   0 ALERT type 3 Indicator that the structure quality may be low
   7 ALERT type 4 Improvement, methodology, query or suggestion
   1 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

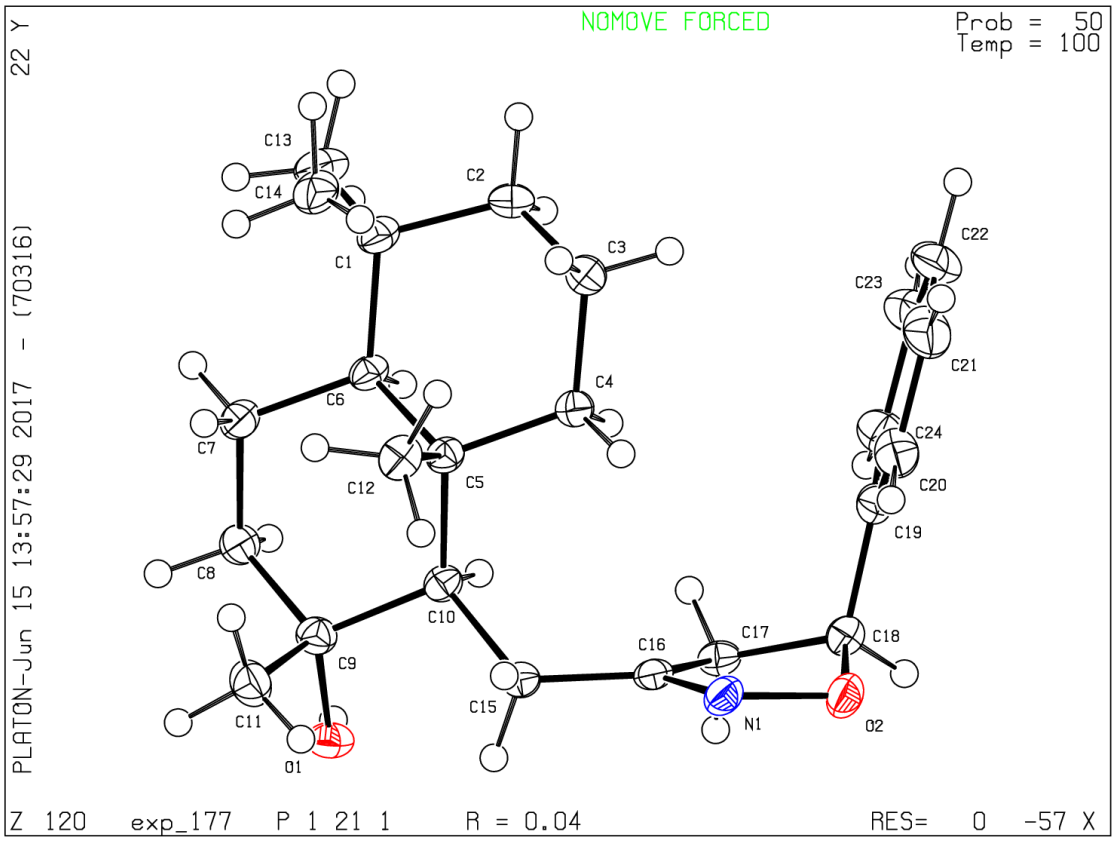
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica, Journal of Applied Crystallography, Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

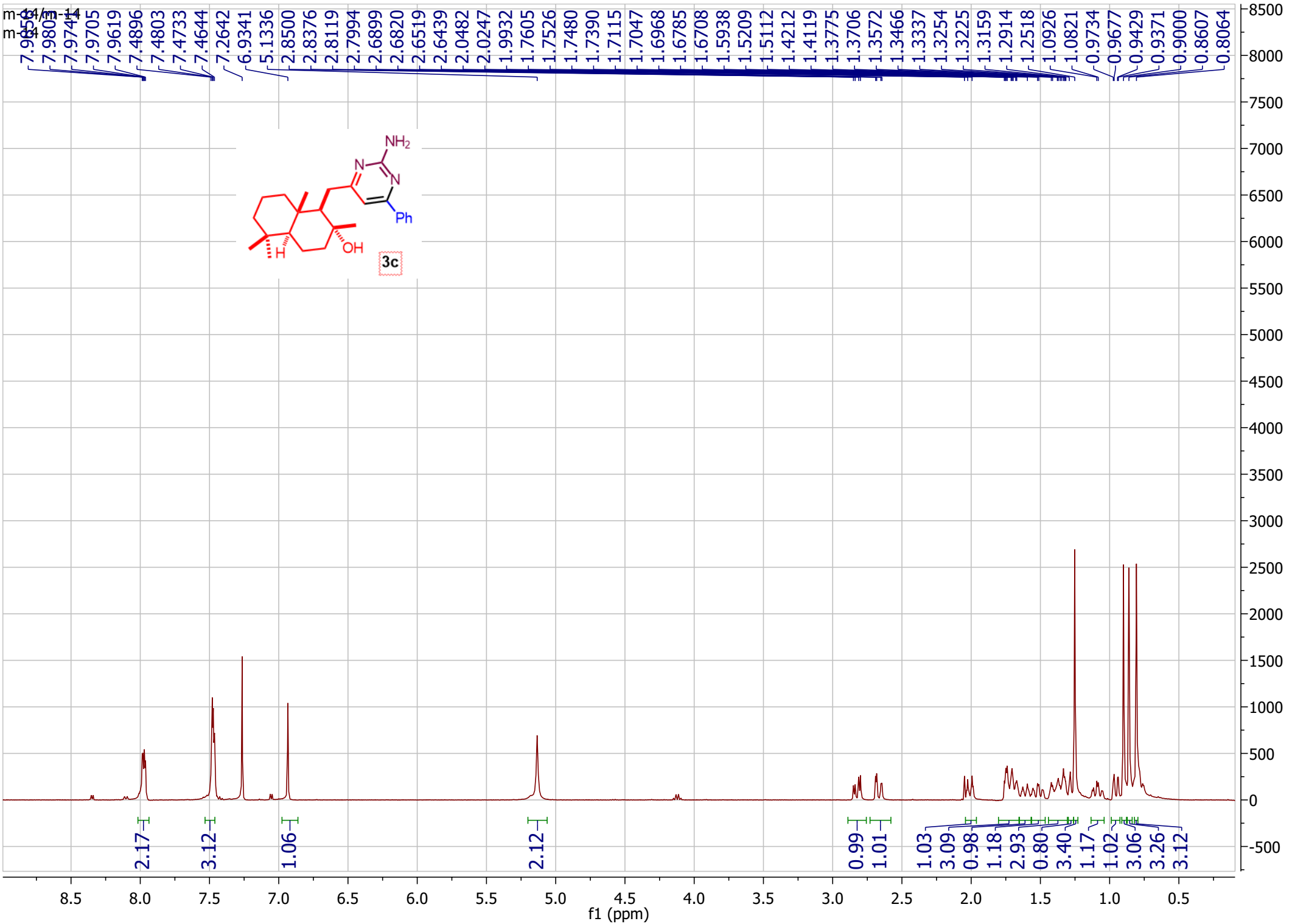
Publication of your CIF in other journals

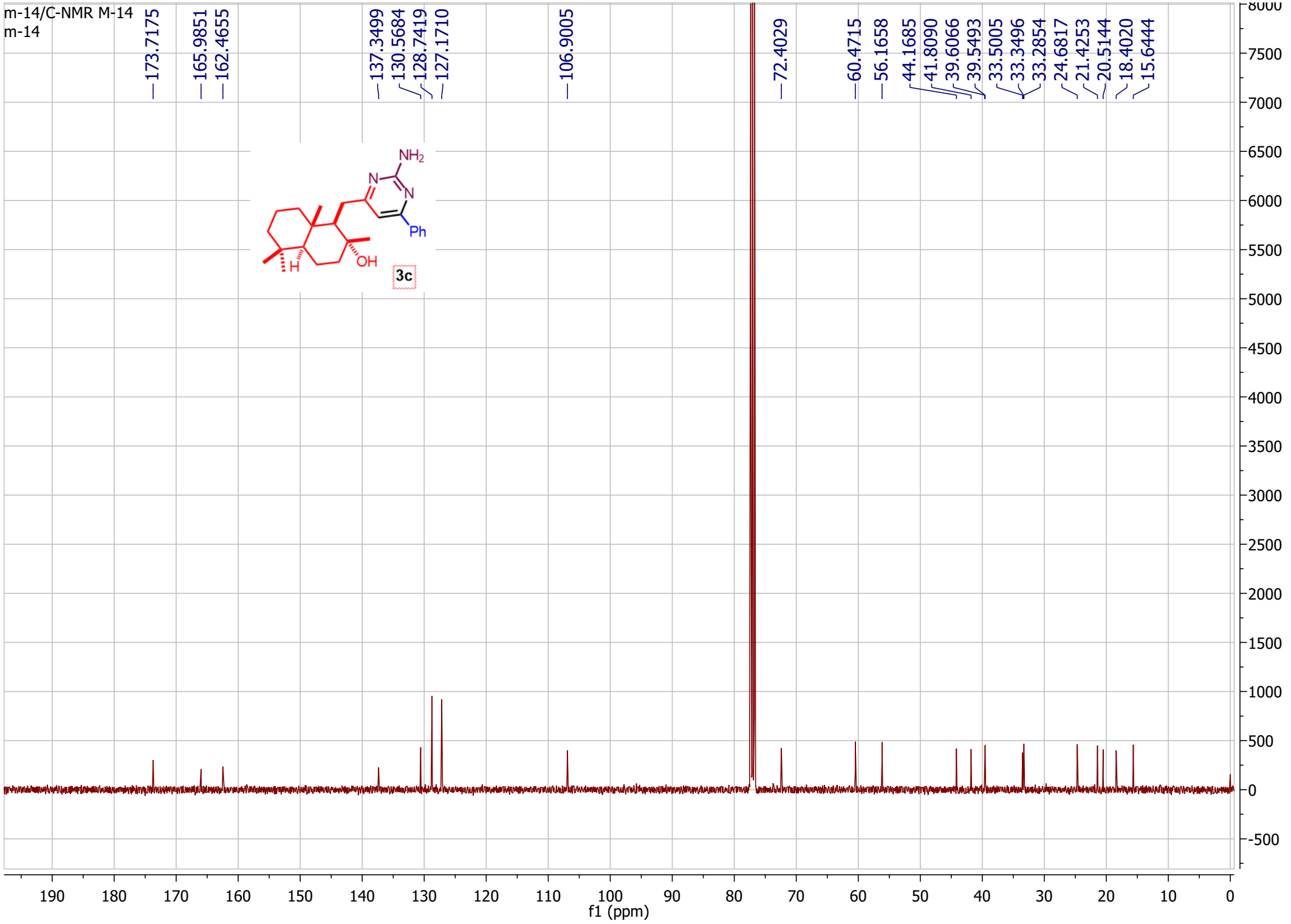
Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

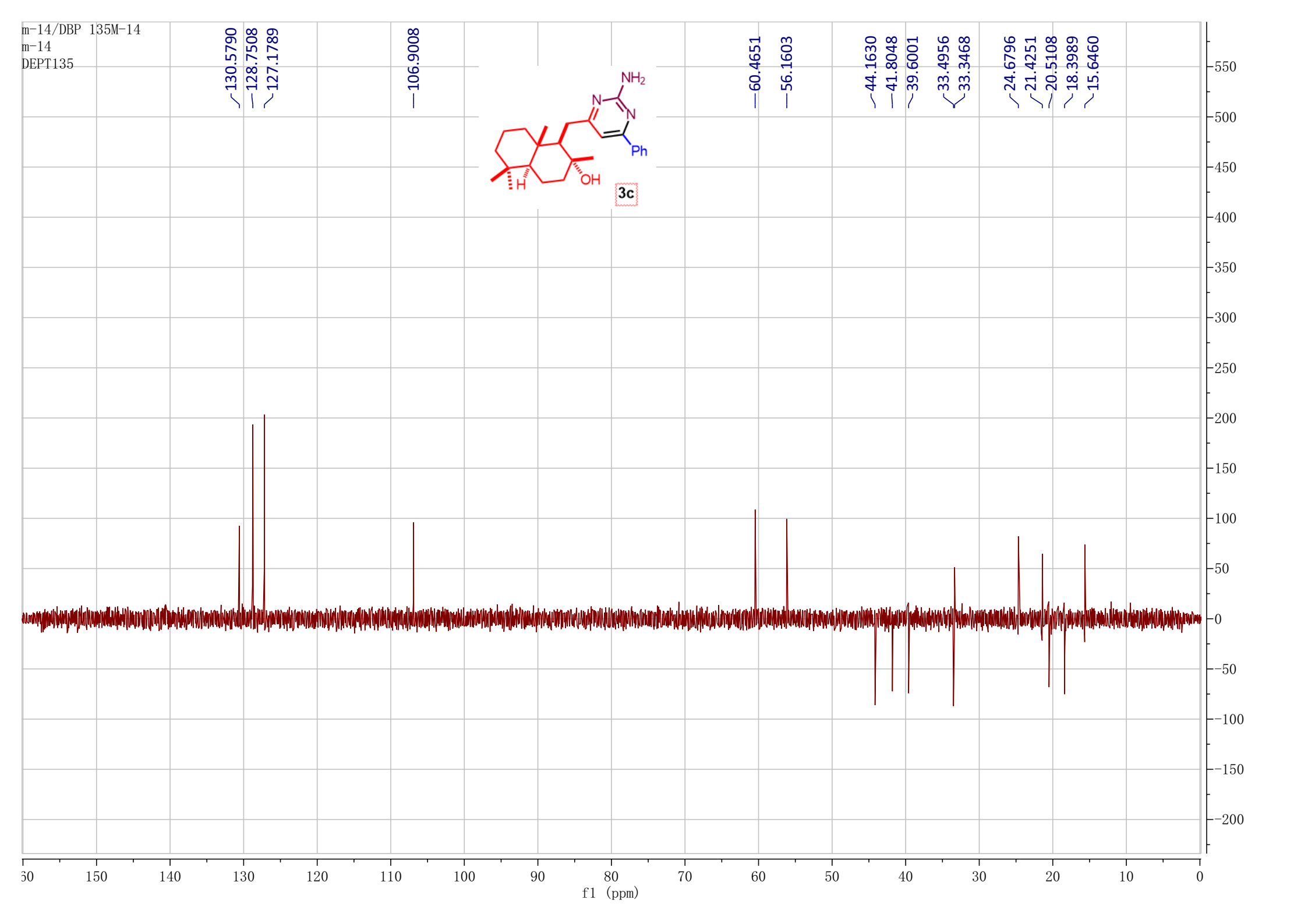
PLATON version of 27/03/2017; check.def file version of 24/03/2017

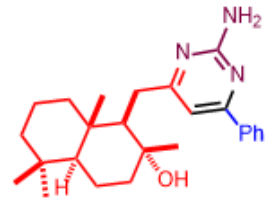
Datablock exp_177 - ellipsoid plot

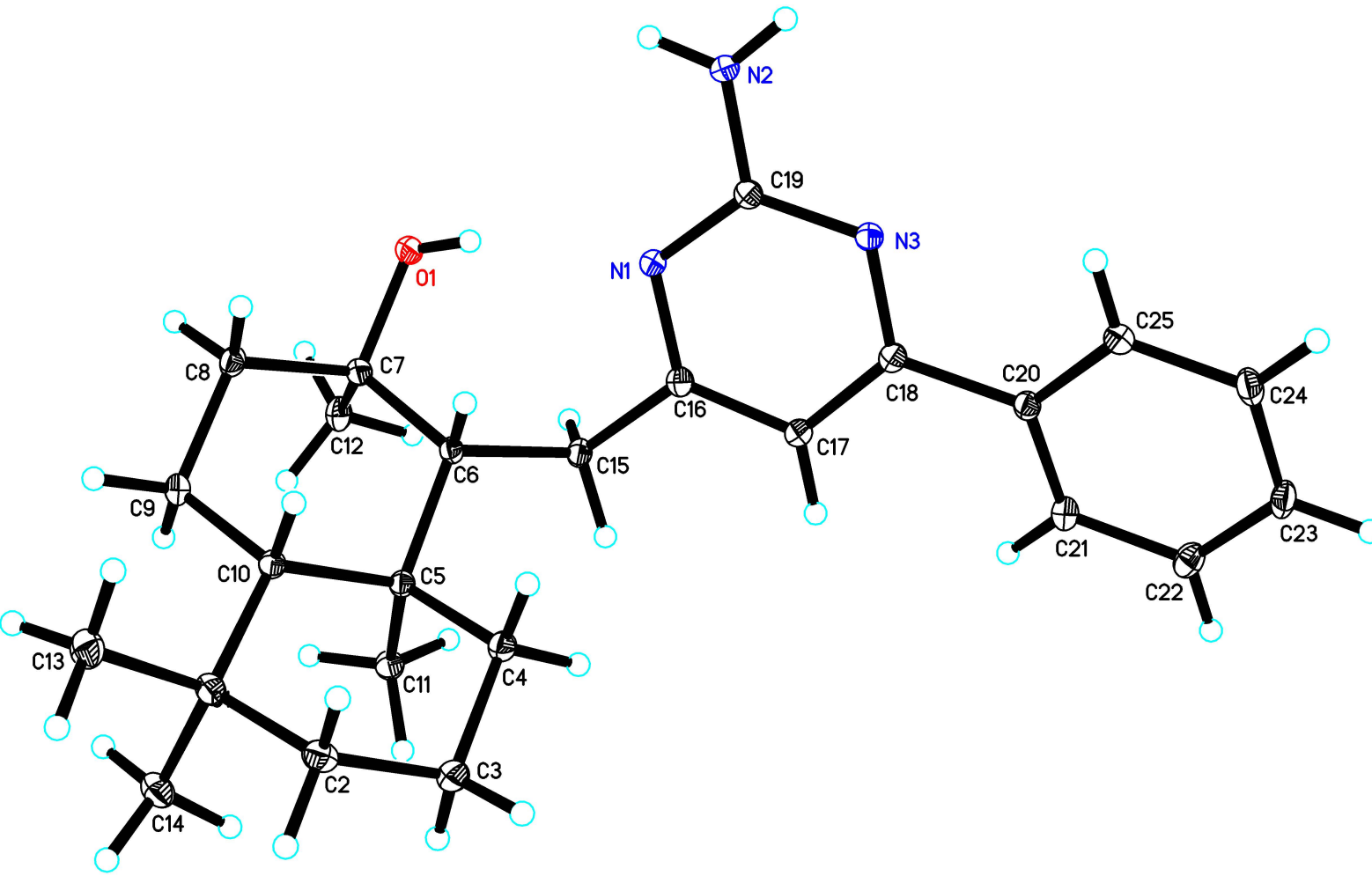



m-14/m-14
m-64
7.9852
7.9803
7.9741
7.9705
7.9619
7.4896
7.4803
7.4733
7.4644
7.2642
6.9341
5.1336
2.8500
2.8376
2.8119
2.7994
2.6899
2.6820
2.6519
2.6439
2.0482
2.0247
1.9932
1.7605
1.7526
1.7480
1.7390
1.7115
1.7047
1.6968
1.6785
1.6708
1.5938
1.5209
1.5112
1.4212
1.4119
1.3775
1.3706
1.3572
1.3466
1.3337
1.3254
1.3225
1.3159
1.2914
1.2518
1.0926
1.0821
0.9734
0.9677
0.9429
0.9371
0.9000
0.8607
0.8064
NH2
N
N
Ph
OH
H
3c
2.17
3.12
1.06
2.12
0.99
1.01
1.03
3.09
0.98
1.18
2.93
0.80
3.40
1.17
1.02
3.06
3.26
3.12
f1 (ppm)


m-14/C-NMR M-14
m-14
173.7175
165.9851
162.4655
137.3499
130.5684
128.7419
127.1710
106.9005
72.4029
60.4715
56.1658
44.1685
41.8090
39.6066
39.5493
33.5005
33.3496
33.2854
24.6817
21.4253
20.5144
18.4020
15.6444
NH2
N
N
Ph
OH
H
3c
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


m-14/DBP 135M-14
m-14
DEPT135
130.5790
128.7508
127.1789
106.9008
60.4651
56.1603
44.1630
41.8048
39.6001
33.4956
33.3468
24.6796
21.4251
20.5108
18.3989
15.6460
NH2
N
N
Ph
OH
H
3c
f1 (ppm)


NH2
N
N
Ph
H
OH


N2
C19
N3
N1
O1
C25
C8
C7
C20
C24
C18
C16
C12
C17
C6
C15
C9
C23
C21
C10
C5
C22
C13
C11
C4
C2
C3
C14

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: exp_176

```
Bond precision:  C-C = 0.0030 A          Wavelength=1.54184

Cell:            a=6.04476(8)    b=13.48040(17)     c=26.4744(3)
                 alpha=90        beta=90            gamma=90
Temperature:     100 K

                 Calculated                Reported
Volume           2157.29(5)                2157.28(5)
Space group      P 21 21 21                P 21 21 21
Hall group       P 2ac 2ab                 P 2ac 2ab
Moiety formula   C25 H35 N3 O              C25 H35 N3 O
Sum formula      C25 H35 N3 O              C25 H35 N3 O
Mr               393.56                    393.56
Dx,g cm-3        1.212                     1.212
Z                4                         4
Mu (mm-1)        0.574                     0.574
F000             856.0                     856.0
F000'            858.23
h,k,lmax         7,16,32                   7,16,32
Nref             4358[ 2527]               4187
Tmin,Tmax        0.871,0.944               0.749,1.000
Tmin'            0.842

Correction method= # Reported T Limits: Tmin=0.749 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.66/0.96      Theta(max)= 73.480

R(reflections)= 0.0378( 4075)     wR2(reflections)= 0.0969( 4187)

S = 1.045                 Npar= 267
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT420_ALERT_2_C D-H Without Acceptor       N2     --  H2B    ...     Please Check
```

Alert level G

```
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms .............          3 Report
PLAT012_ALERT_1_G No     _shelx_res_checksum found in CIF ........     Please Check
PLAT791_ALERT_4_G The Model has Chirality at C5      (Chiral SPGR)          S Verify
PLAT791_ALERT_4_G The Model has Chirality at C6      (Chiral SPGR)          R Verify
PLAT791_ALERT_4_G The Model has Chirality at C7      (Chiral SPGR)          R Verify
PLAT791_ALERT_4_G The Model has Chirality at C10     (Chiral SPGR)          S Verify
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   1 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   6 ALERT level G = General information/check it is not something unexpected

   1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   1 ALERT type 2 Indicator that the structure model may be wrong or deficient
   0 ALERT type 3 Indicator that the structure quality may be low
   4 ALERT type 4 Improvement, methodology, query or suggestion
   1 ALERT type 5 Informative message, check
```

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Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

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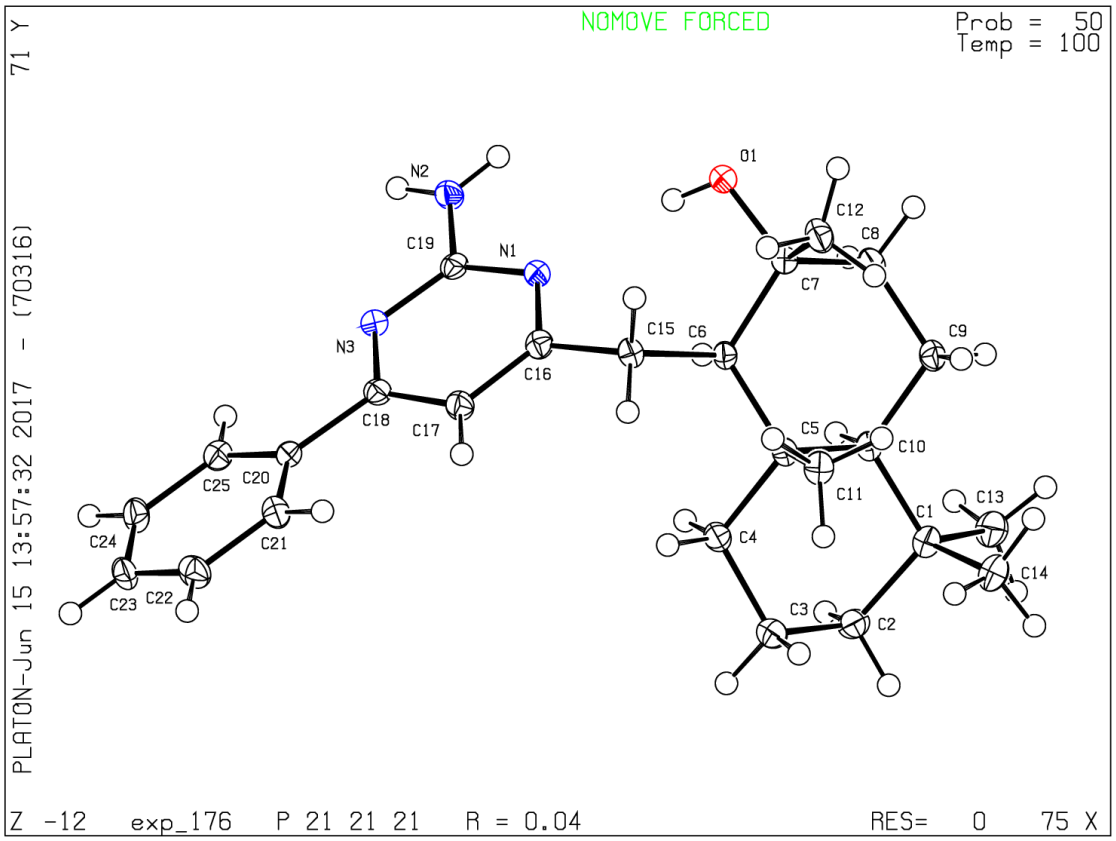
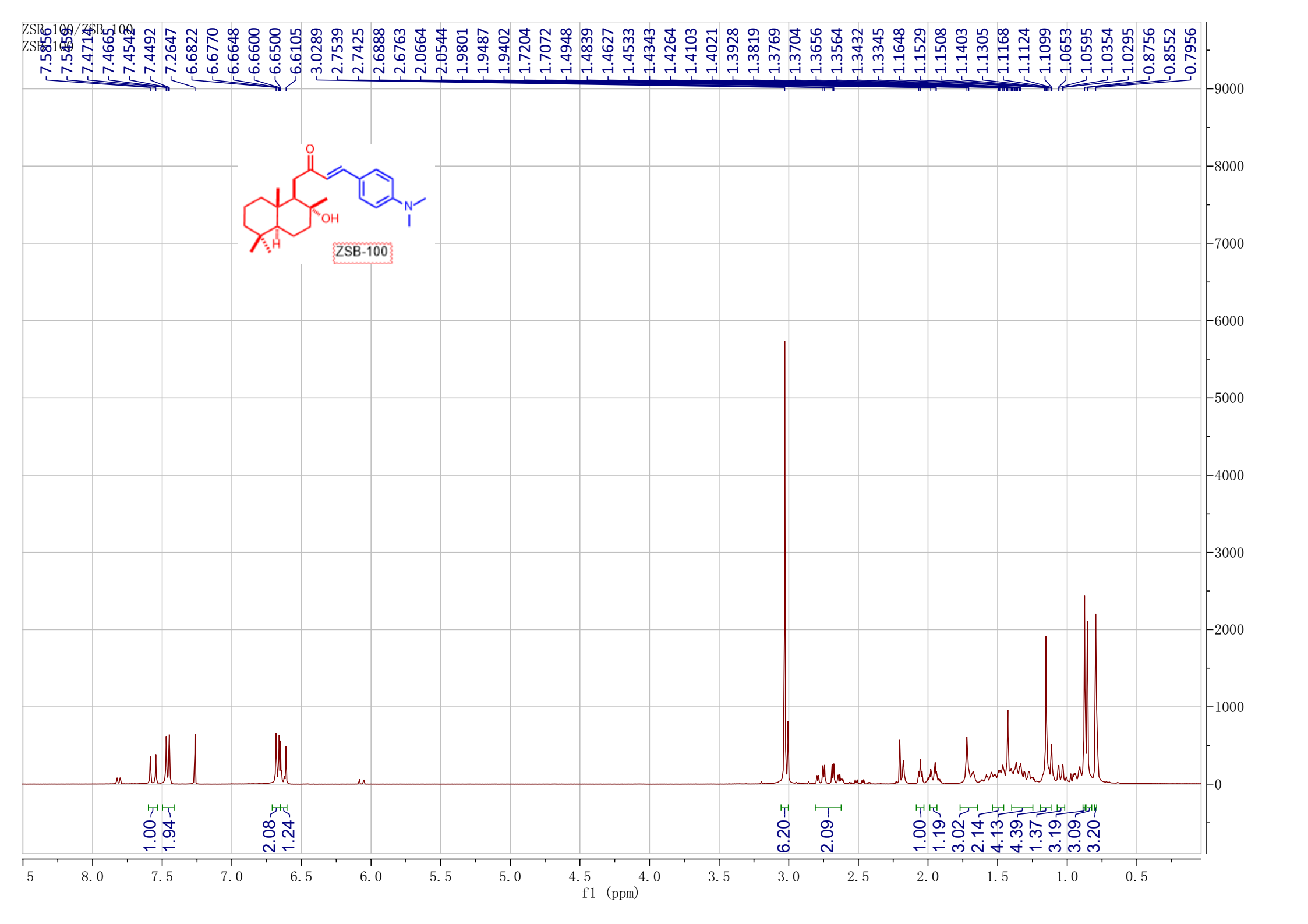
PLATON version of 27/03/2017; check.def file version of 24/03/2017

Datablock exp_176 - ellipsoid plot



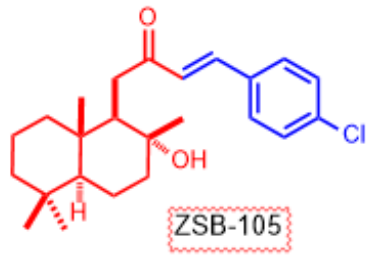

ZSB-100/ZSB-100
ZSB-100
7.5855
7.5456
7.4715
7.4665
7.4542
7.4492
7.2647
6.6822
6.6770
6.6648
6.6600
6.6500
6.6105
3.0289
2.7539
2.7425
2.6888
2.6763
2.0664
2.0544
1.9801
1.9487
1.9402
1.7204
1.7072
1.4948
1.4839
1.4627
1.4533
1.4343
1.4264
1.4103
1.4021
1.3928
1.3819
1.3769
1.3704
1.3656
1.3564
1.3432
1.3345
1.1648
1.1529
1.1508
1.1403
1.1305
1.1168
1.1124
1.1099
1.0653
1.0595
1.0354
1.0295
0.8756
0.8552
0.7956
O
OH
N
H
ZSB-100
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
1.00
1.94
2.08
1.24
6.20
2.09
1.00
1.19
3.02
2.14
4.13
4.39
1.37
3.19
3.09
3.20
.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)

ZSB-100/ZSB-100 C-NMR
ZSB-100

201.6366
151.9205
143.4335
130.1966
122.1534
121.1814
111.8272
77.3651
77.0476
76.7298
72.9851
56.0504
55.9032
44.5766
41.7893
40.1506
39.4351
38.6845
36.8105
33.3673
33.2574
23.3950
21.4529
20.6500
18.4271
15.7435

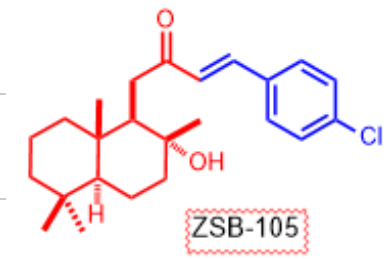
f1 (ppm)

ZSB-105/ZSB-105 H-NMR
ZSB-105



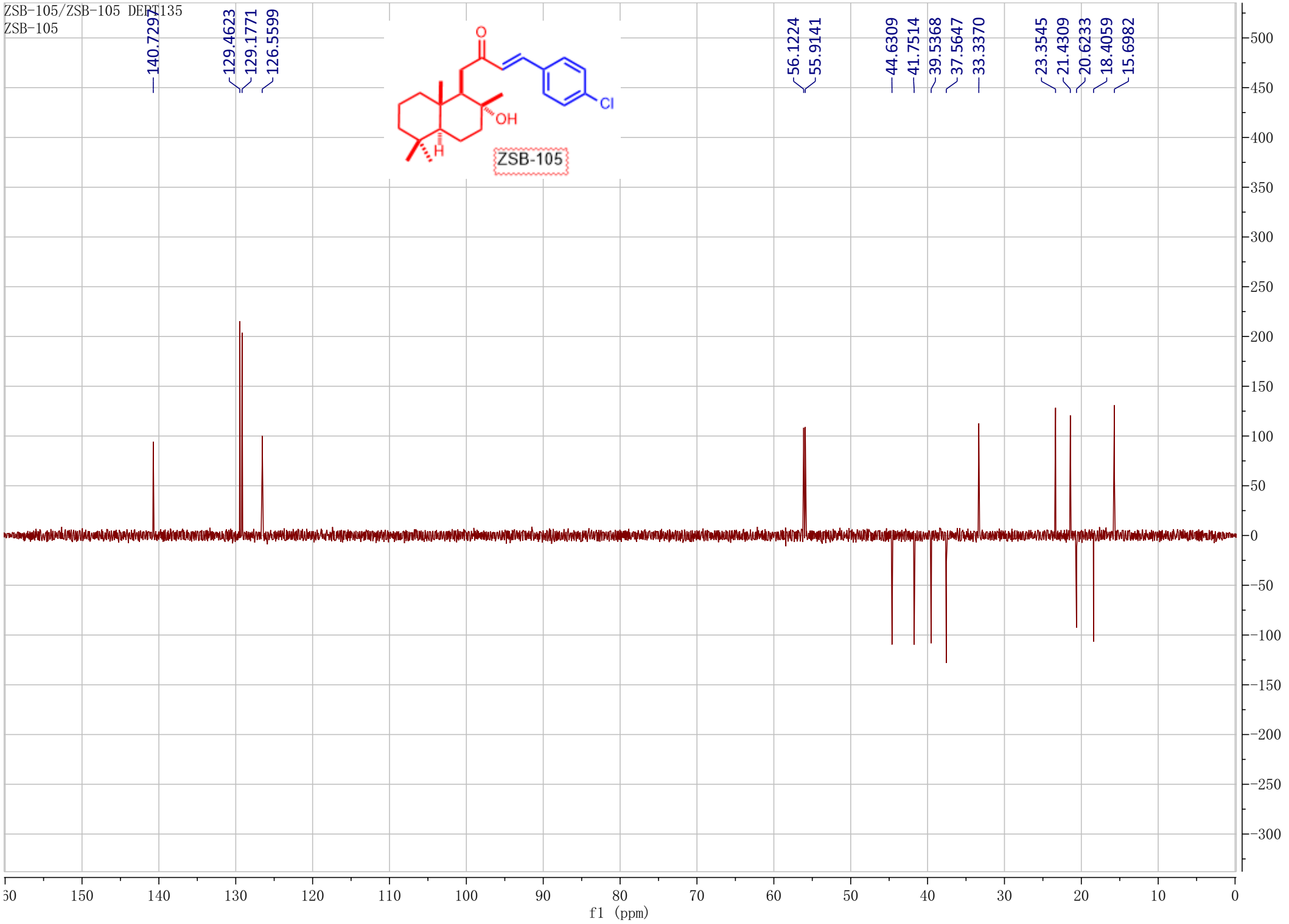
f1 (ppm)

ZSB-105/ZSB-105 C-NMR
ZSB-105

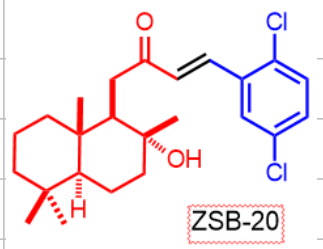


201.0622
140.7235
136.2394
133.1452
129.4587
129.1748
126.5625
77.3388
77.0211
76.7029
73.1628
56.1265
55.9154
44.6328
41.7524
39.5385
38.6191
37.5649
33.3350
33.2492
23.3562
21.4299
20.6225
18.4057
15.6965

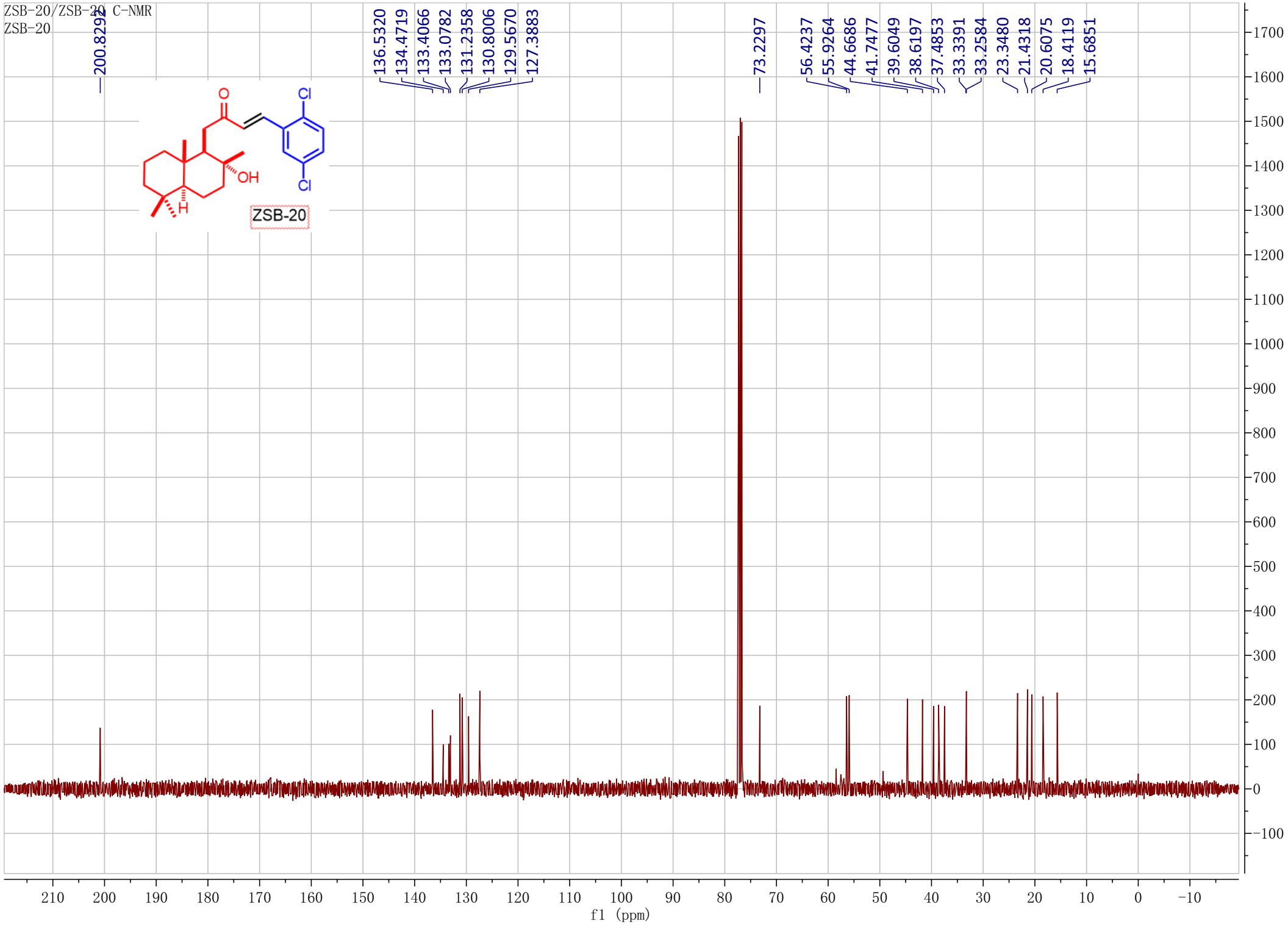
f1 (ppm)

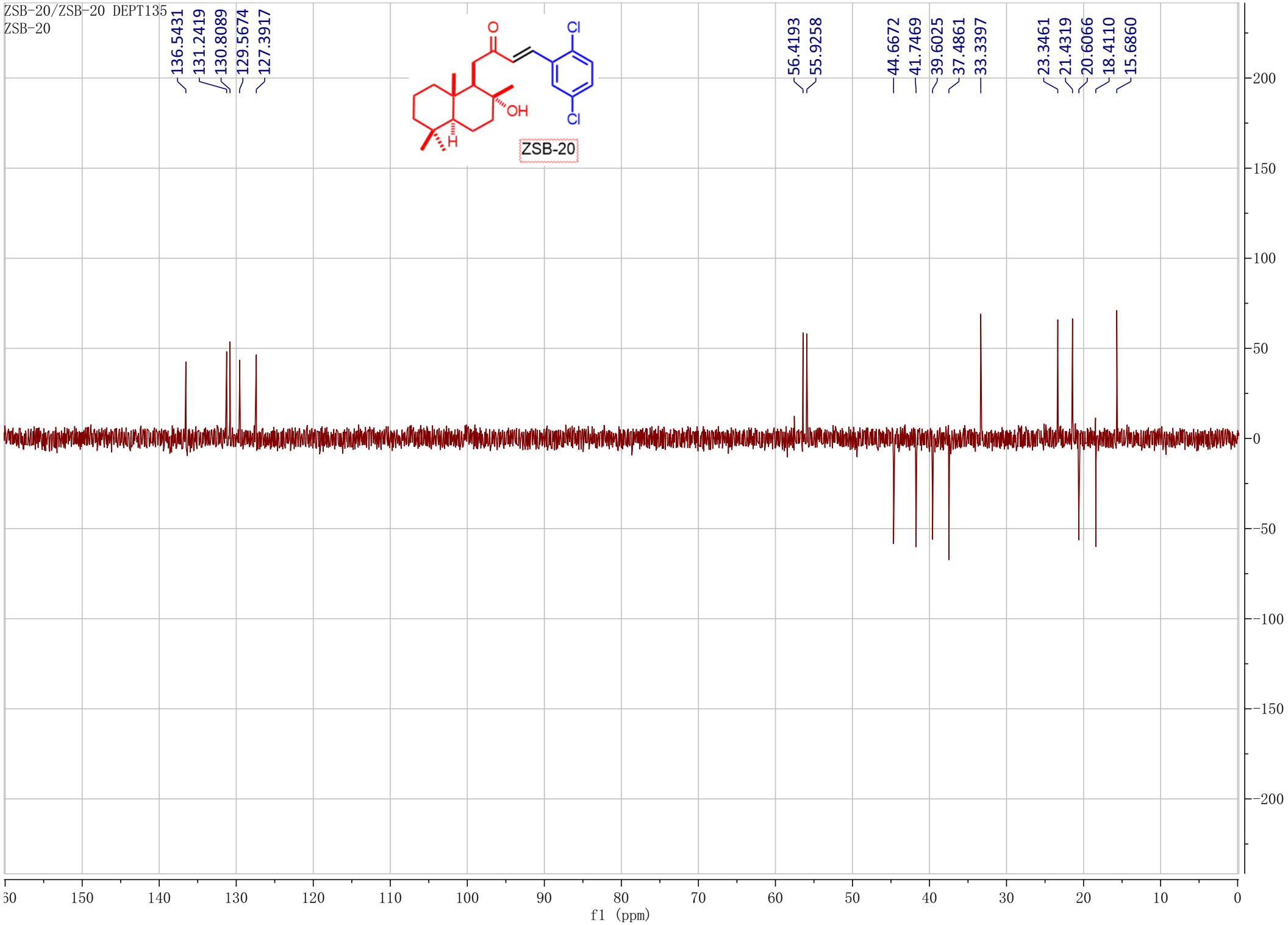

ZSB-105/ZSB-105 DEPT135
ZSB-105
140.7297
129.4623
129.1771
126.5599
56.1224
55.9141
44.6309
41.7514
39.5368
37.5647
33.3370
23.3545
21.4309
20.6233
18.4059
15.6982
O
OH
H
Cl
ZSB-105
f1 (ppm)

ZSB-20/ZSB-20HNMR
ZSB-20

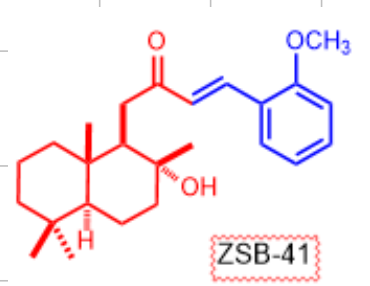


f1 (ppm)


ZSB-20/ZSB-20 C-NMR
ZSB-20
200.8292
136.5320
134.4719
133.4066
133.0782
131.2358
130.8006
129.5670
127.3883
73.2297
56.4237
55.9264
44.6686
41.7477
39.6049
38.6197
37.4853
33.3391
33.2584
23.3480
21.4318
20.6075
18.4119
15.6851
O
Cl
OH
Cl
H
ZSB-20
f1 (ppm)

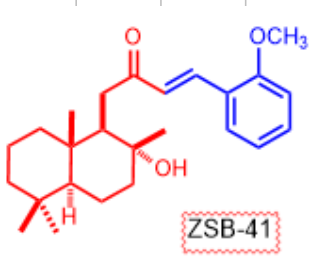

ZSB-20/ZSB-20 DEPT135
ZSB-20
136.5431
131.2419
130.8089
129.5674
127.3917
56.4193
55.9258
44.6672
41.7469
39.6025
37.4861
33.3397
23.3461
21.4319
20.6066
18.4110
15.6860
O
Cl
Cl
OH
H
ZSB-20
200
150
100
50
0
−50
−100
−150
−200
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

ZSB-41/ZSB-41 1H-NMR
ZSB-41



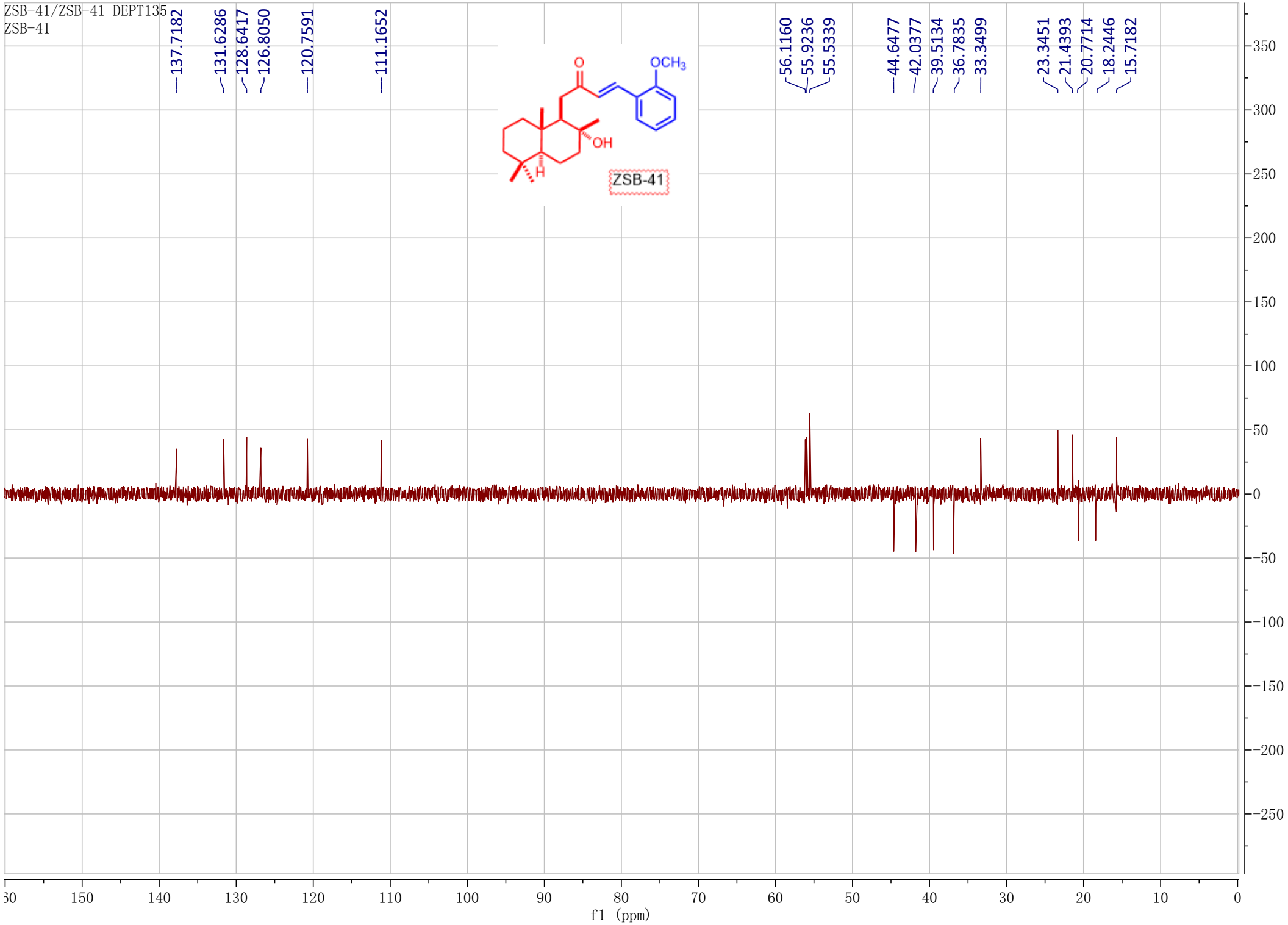
f1 (ppm)

ZSB-41/ZSB-41 C-NMR
ZSB-41

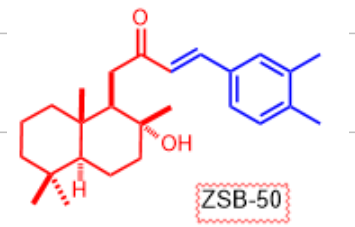


202.0596
158.4962
137.7093
131.6202
128.6383
126.8069
123.5795
120.7574
111.1674
73.1062
56.1253
55.9288
55.5353
44.6540
41.8015
39.4810
38.6788
36.9139
33.3519
33.2612
23.3516
21.4412
20.6434
18.4380
15.7190

f1 (ppm)

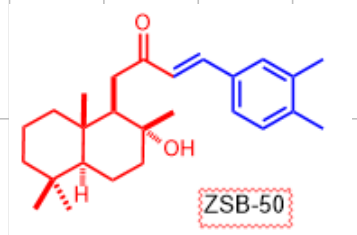

ZSB-41/ZSB-41 DEPT135
ZSB-41
137.7182
131.6286
128.6417
126.8050
120.7591
111.1652
56.1160
55.9236
55.5339
44.6477
42.0377
39.5134
36.7835
33.3499
23.3451
21.4393
20.7714
18.2446
15.7182
O
OCH3
OH
H
ZSB-41
350
300
250
200
150
100
50
0
−50
−100
−150
−200
−250
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

ZSB-50/ZSB-50 H-NMR
ZSB-50



f1 (ppm)

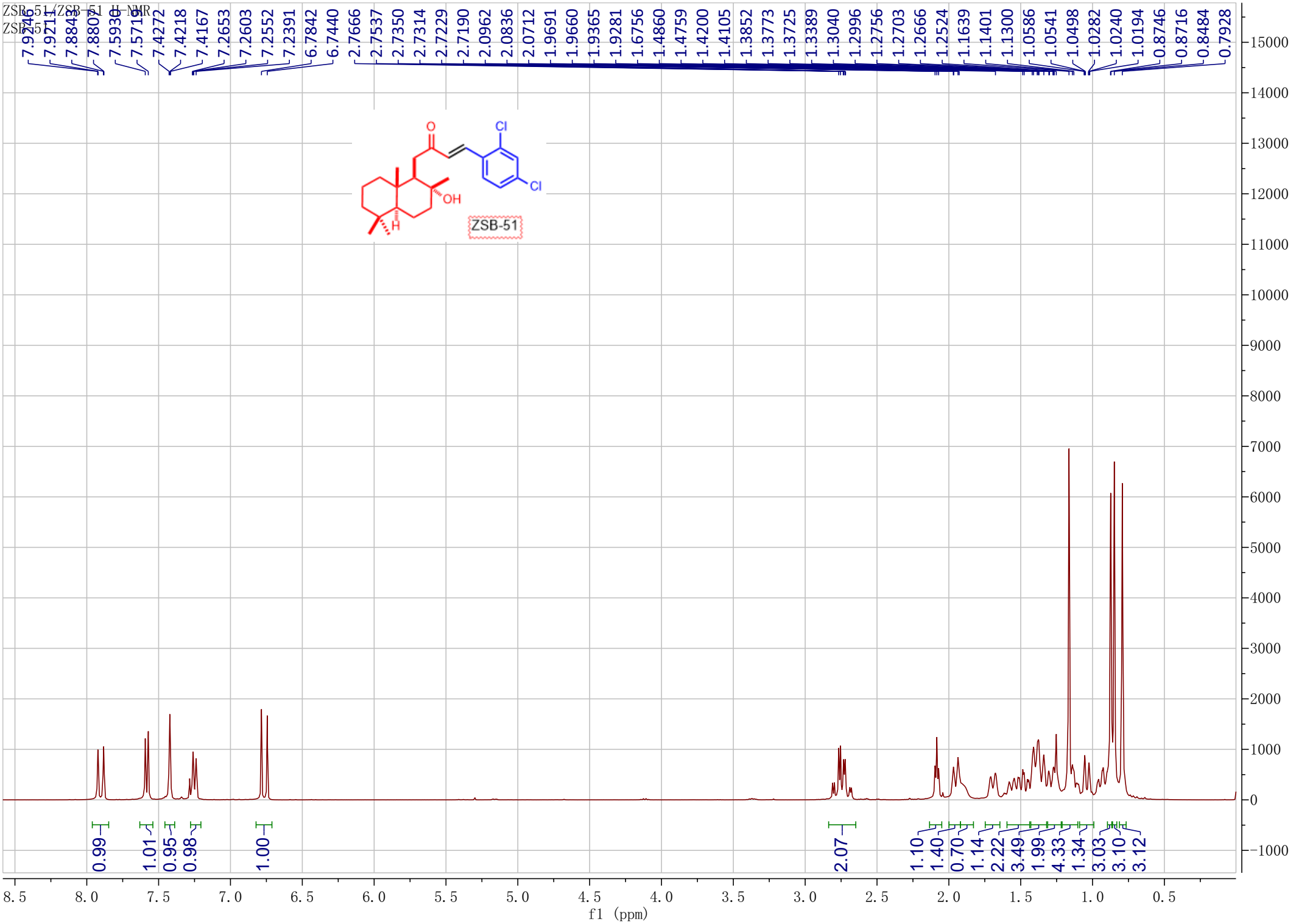
ZSB-50/ZSB-50 C-NMR
ZSB-50

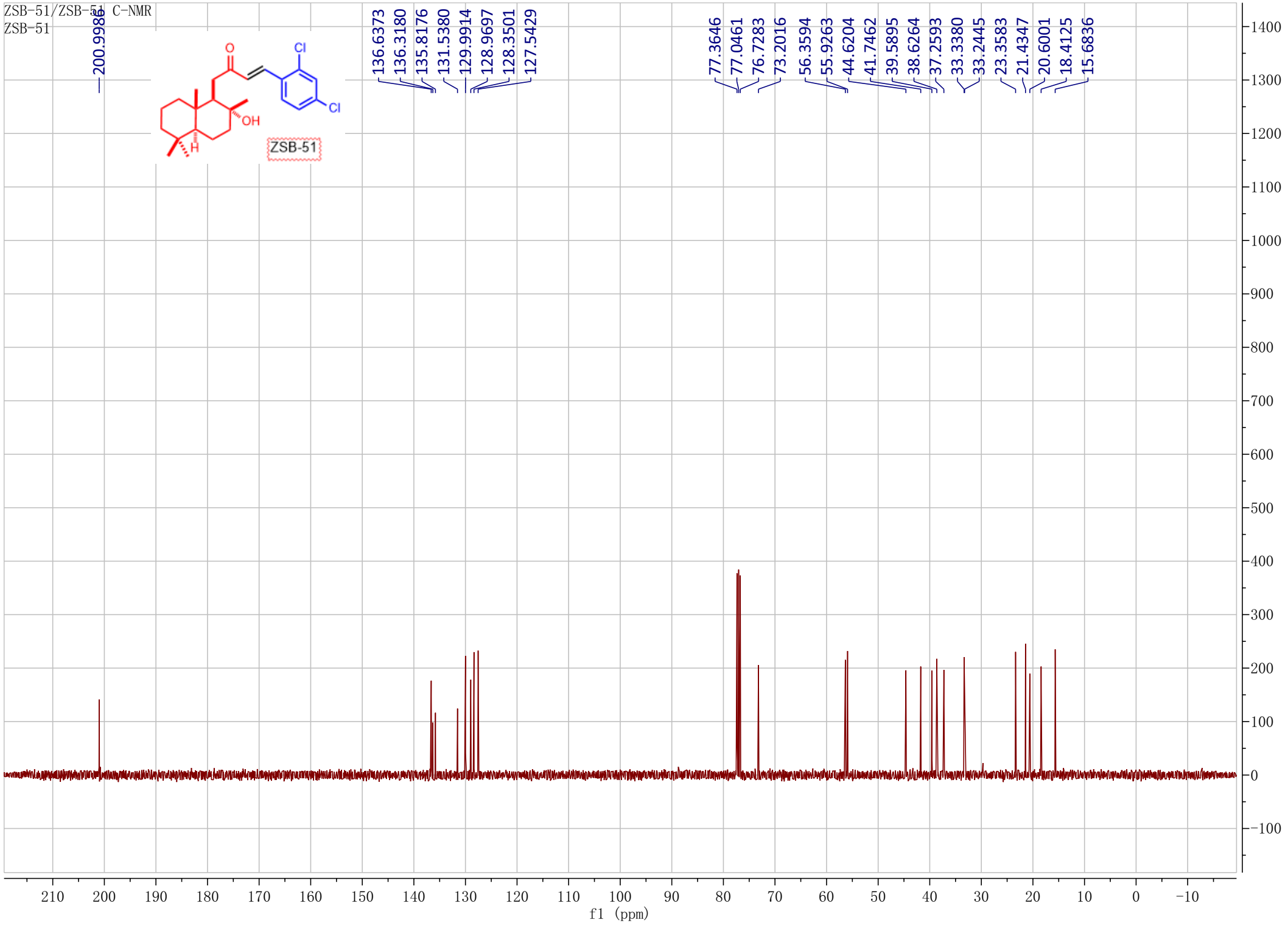


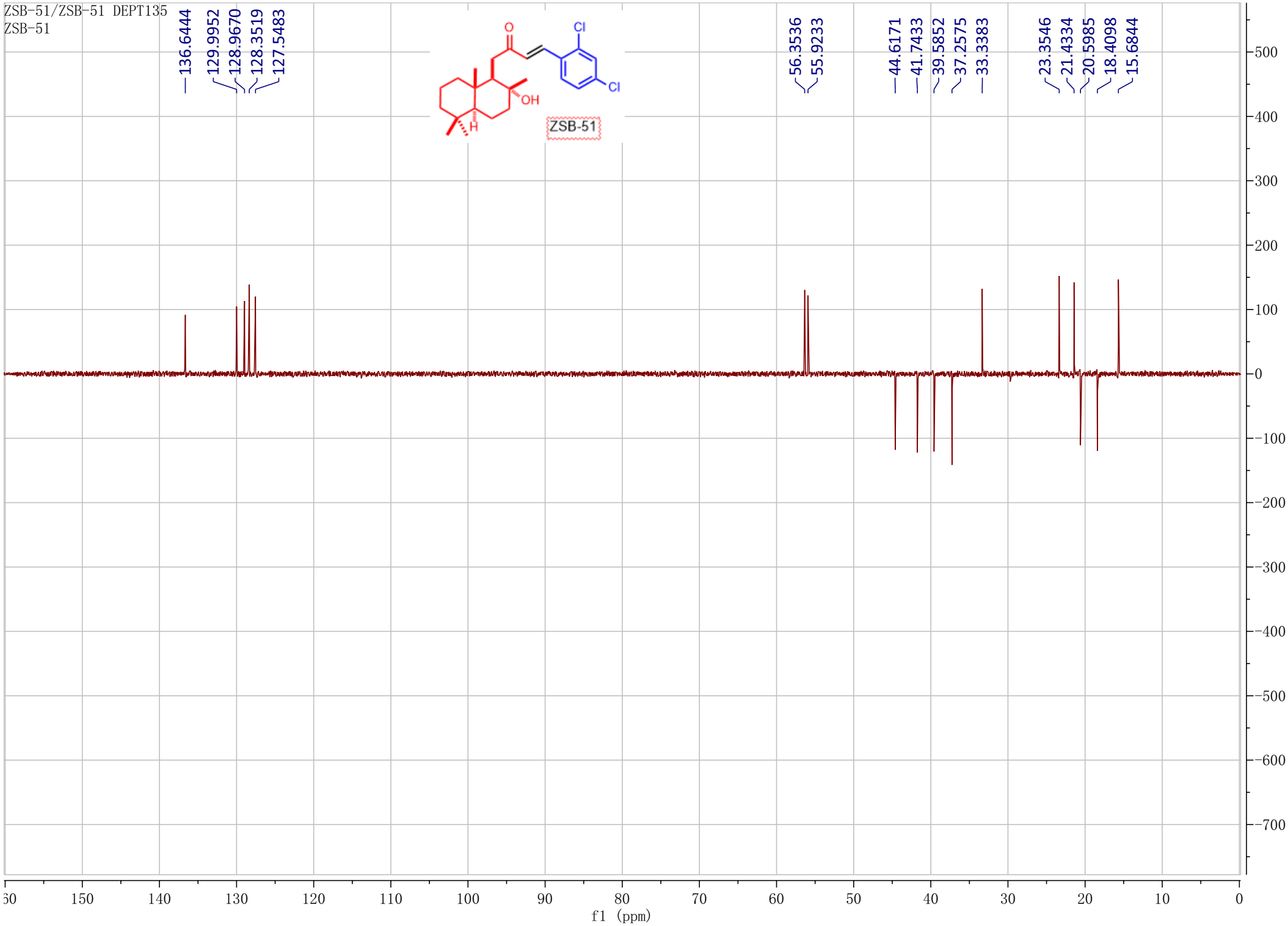
201.5609
142.6779
139.6781
137.1642
132.2095
130.2072
129.5576
126.0284
125.0845
77.3665
77.0481
76.7306
73.0892
56.0247
55.8935
44.6138
41.7614
39.4650
38.6383
37.1513
33.3586
33.2535
23.3379
21.4477
20.6439
19.8770
19.7756
18.4120
15.7202

3000
2500
2000
1500
1000
500
0

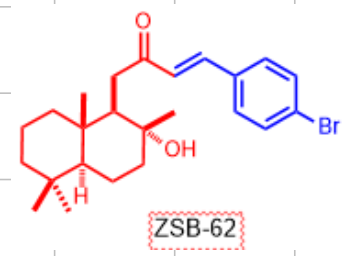
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


ZSB-51-1/ZSB-51 1H NMR
ZSB-51
7.9244
7.9211
7.8843
7.8807
7.5936
7.5719
7.4272
7.4218
7.4167
7.2653
7.2603
7.2552
7.2391
6.7842
6.7440
2.7666
2.7537
2.7350
2.7314
2.7229
2.7190
2.0962
2.0836
2.0712
1.9691
1.9660
1.9365
1.9281
1.6756
1.4860
1.4759
1.4200
1.4105
1.3852
1.3773
1.3725
1.3389
1.3040
1.2996
1.2756
1.2703
1.2666
1.2524
1.1639
1.1401
1.1300
1.0586
1.0541
1.0498
1.0282
1.0240
1.0194
0.8746
0.8716
0.8484
0.7928
O
Cl
Cl
OH
H
ZSB-51
0.99
1.01
0.95
0.98
1.00
2.07
1.10
1.40
0.70
1.14
2.22
3.49
1.99
4.33
1.34
3.03
3.10
3.12
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)
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000


ZSB-51/ZSB-51 C-NMR
ZSB-51
200.9986
136.6373
136.3180
135.8176
131.5380
129.9914
128.9697
128.3501
127.5429
77.3646
77.0461
76.7283
73.2016
56.3594
55.9263
44.6204
41.7462
39.5895
38.6264
37.2593
33.3380
33.2445
23.3583
21.4347
20.6001
18.4125
15.6836
O
Cl
Cl
OH
H
ZSB-51
f1 (ppm)


ZSB-51/ZSB-51 DEPT135
ZSB-51
136.6444
129.9952
128.9670
128.3519
127.5483
56.3536
55.9233
44.6171
41.7433
39.5852
37.2575
33.3383
23.3546
21.4334
20.5985
18.4098
15.6844
O
Cl
Cl
OH
H
ZSB-51
500
400
300
200
100
0
-100
-200
-300
-400
-500
-600
-700
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

ZSB-62/ZSB-62 H NMR
ZSB-62



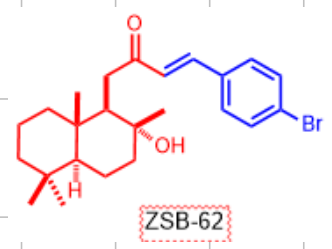
ZSB-62

7.5404 7.5311 7.5263 7.5148 7.5098 7.5005 7.4352 7.4291 7.4239 7.4128 7.4079 7.2683 6.8243 6.7842 2.7348 2.7222 2.7102 2.0896 2.0773 2.0650 1.9842 1.9762 1.9682 1.9530 1.9450 1.9372 1.7396 1.7240 1.7167 1.6903 1.6826 1.5819 1.5464 1.5164 1.5113 1.5063 1.4843 1.4743 1.4522 1.4188 1.4107 1.4037 1.3849 1.3787 1.3747 1.3675 1.3538 1.1575 1.1555 1.0677 1.0619 1.0371 1.0316 0.8802 0.8493 0.7968

0.52 1.90 0.59 2.00 1.00 2.07 1.04 1.04 2.99 1.08 1.04 3.27 1.11 4.26 1.06 3.34 3.14 2.97

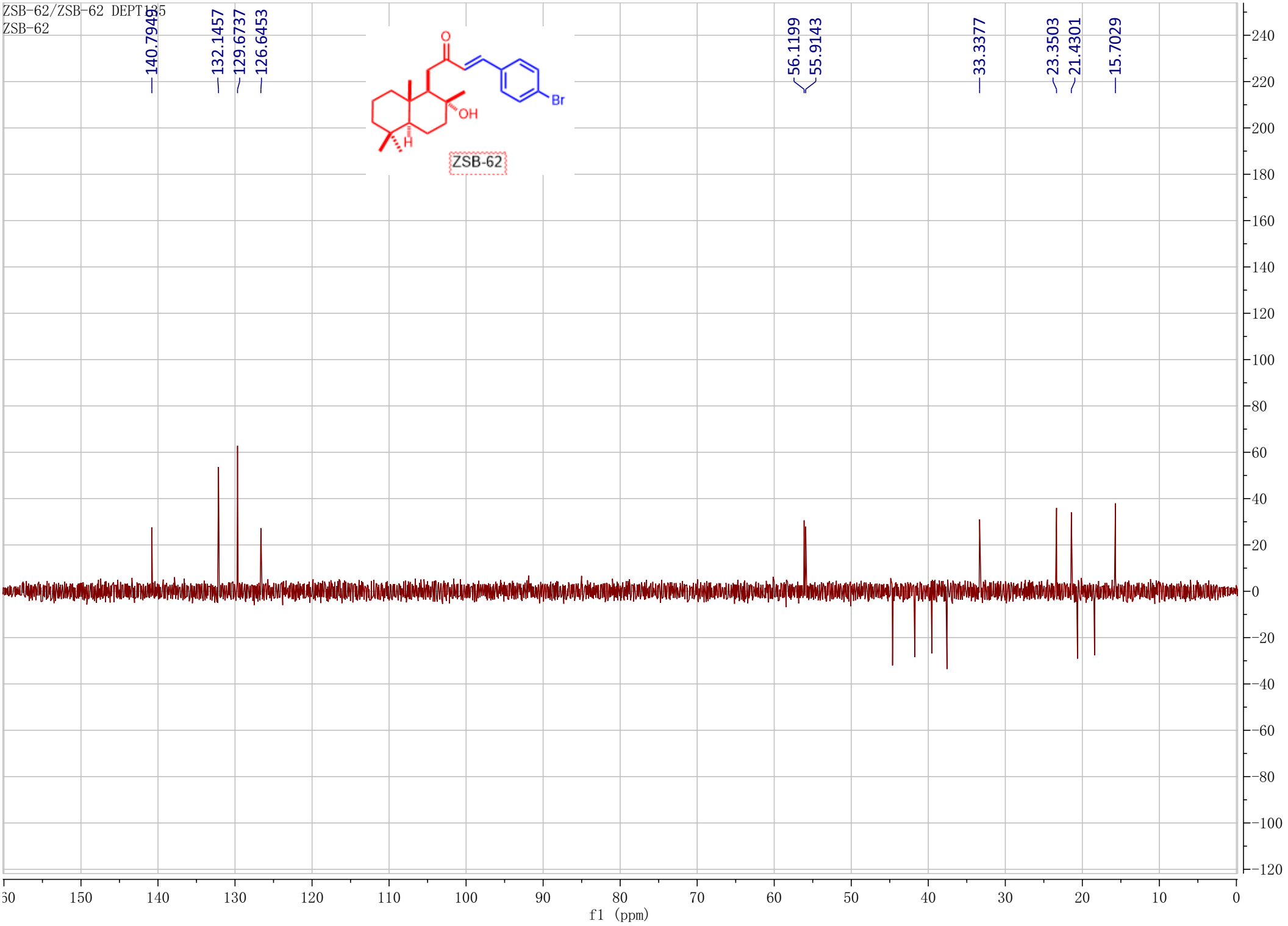
f1 (ppm)

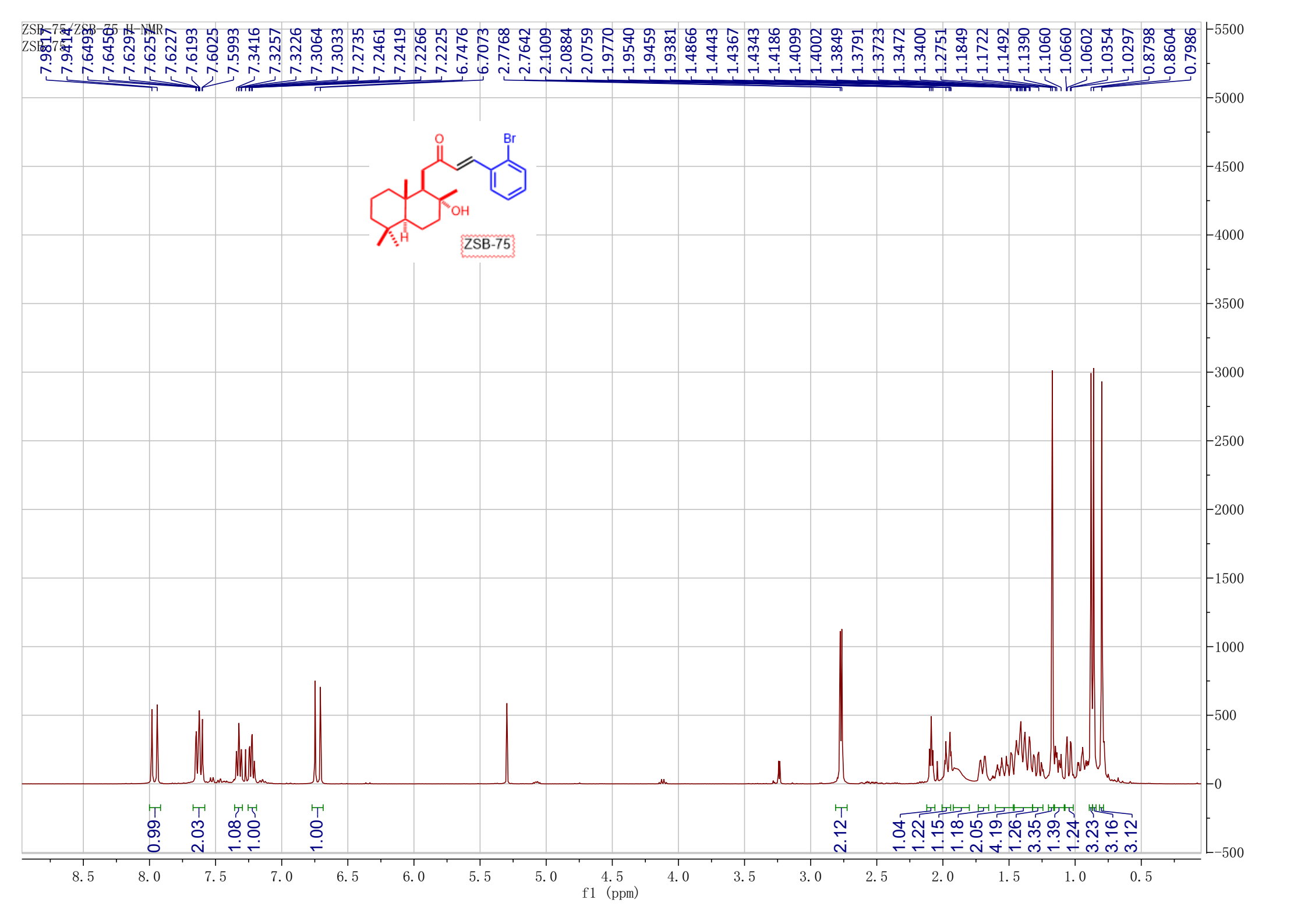
ZSB-62/ZSB-62 C-NMR
ZSB-62



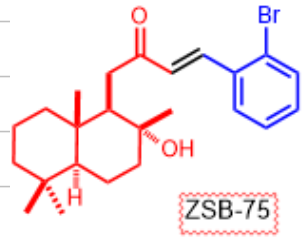
201.0617
140.7890
133.5781
132.1450
129.6708
126.6492
124.5892
77.3302
77.2170
77.0120
76.6943
73.1721
56.1227
55.9143
44.6392
41.7508
39.5379
38.6131
37.5735
33.3326
33.2492
23.3488
21.4252
20.6206
18.4022
15.6960

f1 (ppm)


ZSB-62/ZSB-62 DEPT135
ZSB-62
140.7945
132.1457
129.6737
126.6453
56.1199
55.9143
33.3377
23.3503
21.4301
15.7029
O
OH
H
Br
ZSB-62
f1 (ppm)


ZSB-75/ZSB-75 1H NMR
ZSB-75
O
Br
OH
H
ZSB-75
f1 (ppm)

ZSB-75/ZSB-75 C-NMR
ZSB-75



201.3898
140.6528
134.6367
133.4406
131.2598
128.9710
127.7828
127.7307
125.7706
77.3980
77.0803
76.7632
73.1905
56.3594
55.9076
44.6021
41.7444
39.5676
38.6431
36.8882
33.3632
33.2529
23.3461
21.4567
20.6108
18.4215
15.7002

f1 (ppm)

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: exp_177

```
Bond precision:  C-C = 0.0030 A          Wavelength=1.54184

Cell:           a=9.67127(7)    b=7.05127(7)       c=15.44464(12)
                alpha=90        beta=93.4847(6)    gamma=90
Temperature:    100 K

                Calculated                Reported
Volume          1051.296(15)              1051.296(15)
Space group     P 21                      P 1 21 1
Hall group      P 2yb                     P 2yb
Moiety formula  C24 H35 N O2              C24 H35 N O2
Sum formula     C24 H35 N O2              C24 H35 N O2
Mr              369.53                    369.53
Dx,g cm-3       1.167                     1.167
Z               2                         2
Mu (mm-1)       0.563                     0.563
F000            404.0                     404.0
F000'           405.07
h,k,lmax        12,8,19                   12,8,18
Nref            4231[ 2296]               3930
Tmin,Tmax       0.850,0.894               0.408,1.000
Tmin'           0.835

Correction method= # Reported T Limits: Tmin=0.408 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.71/0.93      Theta(max)= 73.619

R(reflections)= 0.0386( 3897)     wR2(reflections)= 0.1025( 3930)

S = 1.042                 Npar= 249
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level G

```
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms .............          1 Report
PLAT012_ALERT_1_G No     _shelx_res_checksum found in CIF ........     Please Check
PLAT142_ALERT_4_G s.u. on b - Axis Small or Missing ..............    0.00007 Ang.
PLAT143_ALERT_4_G s.u. on c - Axis Small or Missing ..............    0.00012 Ang.
PLAT395_ALERT_2_G Deviating  X-O-Y  Angle from 120 Deg for  O2          106.9 Degree
PLAT791_ALERT_4_G The Model has Chirality at C5      (Chiral SPGR)          S Verify
PLAT791_ALERT_4_G The Model has Chirality at C6      (Chiral SPGR)          S Verify
PLAT791_ALERT_4_G The Model has Chirality at C9      (Chiral SPGR)          R Verify
PLAT791_ALERT_4_G The Model has Chirality at C10     (Chiral SPGR)          R Verify
PLAT791_ALERT_4_G The Model has Chirality at C18     (Chiral SPGR)          S Verify
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   0 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  10 ALERT level G = General information/check it is not something unexpected

   1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   1 ALERT type 2 Indicator that the structure model may be wrong or deficient
   0 ALERT type 3 Indicator that the structure quality may be low
   7 ALERT type 4 Improvement, methodology, query or suggestion
   1 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

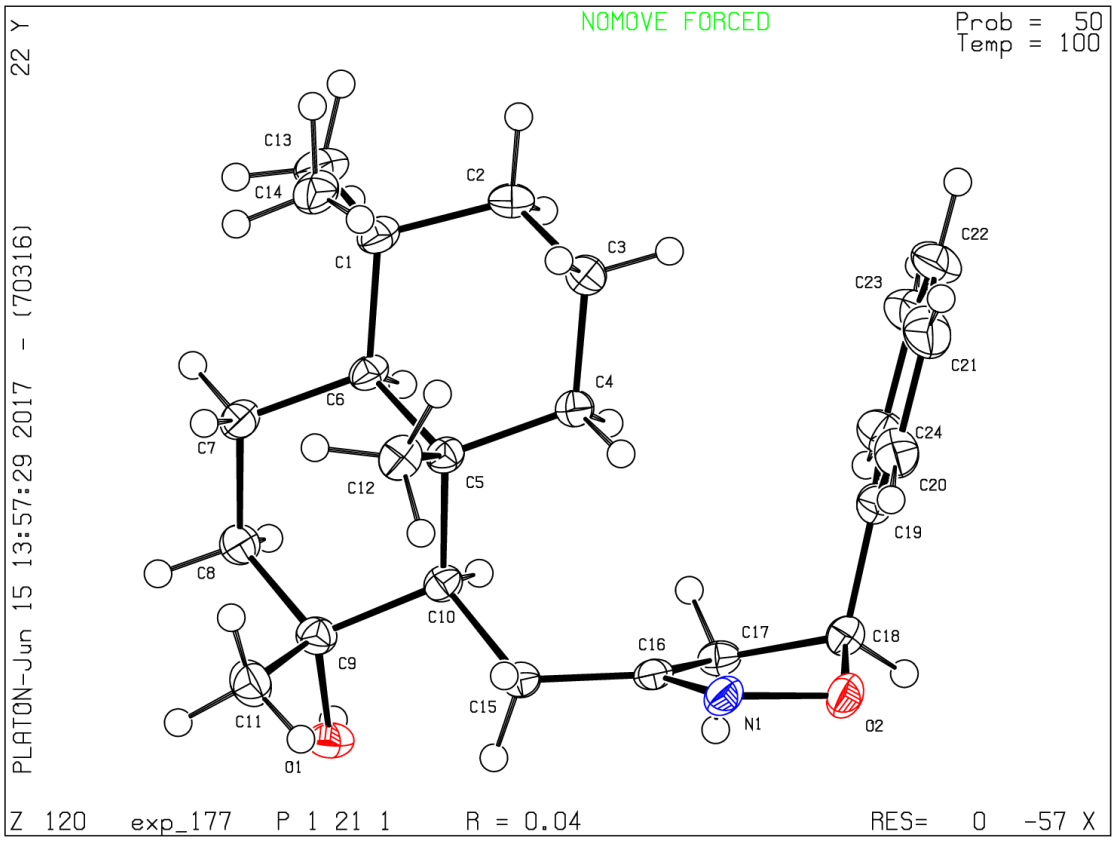
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica, Journal of Applied Crystallography, Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 27/03/2017; check.def file version of 24/03/2017

Datablock exp_177 - ellipsoid plot



checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: exp_176

```
Bond precision:  C-C = 0.0030 A          Wavelength=1.54184

Cell:            a=6.04476(8)    b=13.48040(17)     c=26.4744(3)
                 alpha=90        beta=90            gamma=90
Temperature:     100 K

                 Calculated                Reported
Volume           2157.29(5)                2157.28(5)
Space group      P 21 21 21                P 21 21 21
Hall group       P 2ac 2ab                 P 2ac 2ab
Moiety formula   C25 H35 N3 O              C25 H35 N3 O
Sum formula      C25 H35 N3 O              C25 H35 N3 O
Mr               393.56                    393.56
Dx,g cm-3        1.212                     1.212
Z                4                         4
Mu (mm-1)        0.574                     0.574
F000             856.0                     856.0
F000'            858.23
h,k,lmax         7,16,32                   7,16,32
Nref             4358[ 2527]               4187
Tmin,Tmax        0.871,0.944               0.749,1.000
Tmin'            0.842

Correction method= # Reported T Limits: Tmin=0.749 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.66/0.96      Theta(max)= 73.480

R(reflections)= 0.0378( 4075)     wR2(reflections)= 0.0969( 4187)

S = 1.045                 Npar= 267
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT420_ALERT_2_C D-H Without Acceptor       N2     --  H2B    ...     Please Check
```

Alert level G

```
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms .............          3 Report
PLAT012_ALERT_1_G No     _shelx_res_checksum found in CIF ........     Please Check
PLAT791_ALERT_4_G The Model has Chirality at C5      (Chiral SPGR)          S Verify
PLAT791_ALERT_4_G The Model has Chirality at C6      (Chiral SPGR)          R Verify
PLAT791_ALERT_4_G The Model has Chirality at C7      (Chiral SPGR)          R Verify
PLAT791_ALERT_4_G The Model has Chirality at C10     (Chiral SPGR)          S Verify
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   1 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   6 ALERT level G = General information/check it is not something unexpected

   1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   1 ALERT type 2 Indicator that the structure model may be wrong or deficient
   0 ALERT type 3 Indicator that the structure quality may be low
   4 ALERT type 4 Improvement, methodology, query or suggestion
   1 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 27/03/2017; check.def file version of 24/03/2017

Datablock exp_176 - ellipsoid plot