CHEMISTRY
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Supporting Information

A Gold Catalyzed Entry into the Sesquisabinene and Sesquithujene Families of Terpenoids and Formal Total Syntheses of Cedrene and Cedrol

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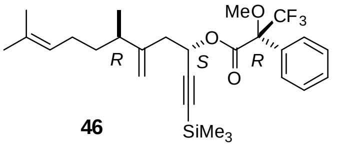
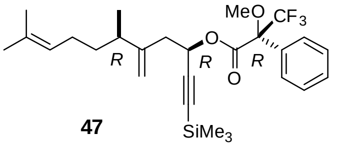
Mosher-Ester Analysis:

Compound 46: Pyridine (4.5 µl, 54 µmol) and (*S*)-Mosher-Cl (9.5 µl, 50 µmol) were added to a solution of *S*-**4** (10 mg, 36 µmol) in CH_2Cl_2 (0.5 mL) at 0 °C and the reaction allowed to warm to ambient temperature. After stirring for 1.5 h, the mixture was diluted with pH = 7 buffer (1 mL) and Et_2O (2 mL), the aqueous phase was extracted with Et_2O (3 x 1 mL), the combined organic layers were washed with brine, dried over Na_2SO_4, adsorbed on silica gel and purified by flash chromatography (10 % Et_2O in pentanes) to give Mosher ester **46** as a colorless oil (11.6 mg, 65 %); ^{1}H NMR (400 MHz, $CDCl_3$): *d* = 7.54-7.52 (m, 2H), 7.41-7.36 (m, 3H), 5.70-5.66 (m, 1H), 5.09-5.05 (m, 1H), 4.91 (s, 1H), 4.87 (s, 1H), 3.54 (d, *J* = 1.0 Hz, 3H), 2.56-2.54 (m, 2H), 2.17-2.09 (m, 1H), 1.92 (q, *J* = 7.5 Hz, 2H), 1.68 (s, 3H), 1.57 (s, 3H), 1.49-1.40 (m, 1H), 1.35-1.26 (m, 1H), 1.02 (d, *J* = 6.9 Hz, 3H), 0.15 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): *d* = 165.6, 148.1, 132.1, 131.5, 129.5, 128.3, 127.5, 124.3, 111.4, 101.0, 91.7, 65.4, 55.6, 39.3, 39.0, 35.5, 25.8, 25.7, 19.7, 17.7, –0.5; IR (film): 2961, 2916, 2850, 1752, 1645, 1452, 1250, 1185, 1168, 1019, 842, 761, 719, 695 cm^{-1}; MS (70 eV): *m/z* (%): 494 (1) [*M*$^+$], 260 (15), 217 (14), 189 (100), 136 (17), 119 (10), 105 (14), 82 (94), 73 (93), 69 (28), 59 (14), 41 (23); HRMS (ESI): calcd for $C_{27}H_{37}O_3SiF_3Na$ [*M*$^+$ +Na]: 517.2356, found: 517.2354.



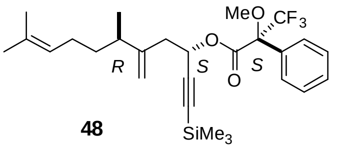
46

Compound 47: Colorless oil (11.8 mg, 66 %); ^{1}H NMR (400 MHz, $CDCl_3$): *d* = 7.56-7.54 (m, 2H), 7.40-7.35 (m, 3H), 5.73-5.69 (m, 1H), 5.09-5.05 (m, 1H), 4.82 (s, 1H), 4.77 (s, 1H), 3.59 (d, *J* = 0.9 Hz, 3H), 2.51-2.47 (m, 2H), 2.13-2.04 (m, 1H), 1.90 (q, *J* = 7.5 Hz, 2H), 1.68 (s, 3H), 1.58 (s, 3H), 1.46-1.37 (m, 1H), 1.30-1.19 (m, 1H), 0.95 (d, *J* = 6.9 Hz, 3H), 0.17 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): *d* = 165.7, 147.5, 132.4, 131.5, 129.5, 128.2, 127.4, 124.4, 111.7, 101.3, 91.9, 65.0, 55.4, 39.1, 38.9, 35.7, 25.7, 25.7, 19.4, 17.7, –0.4; IR (film): 2962, 2916, 2850, 1753, 1645, 1451, 1250, 1169, 1021, 842, 761, 718, 696 cm^{-1}; MS (70 eV): *m/z* (%): 494 (1) [*M*$^+$], 260 (13), 217 (13), 189 (100), 136 (16), 119 (10), 105 (14), 82 (93), 73 (90), 69 (27), 59 (13), 41 (22); HRMS (ESI): calcd for $C_{27}H_{37}O_3SiF_3Na$ [*M*$^+$ +Na]: 517.2356, found: 517.2355.



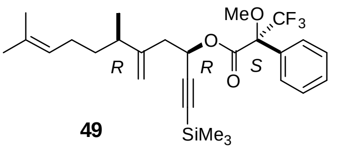
47

Compound 48: Colorless oil (11.5 mg, 65 %); ^{1}H NMR (400 MHz, $CDCl_3$): *d* = 7.57-7.55 (m, 2H), 7.42-7.35 (m, 3H), 5.72-5.69 (m, 1H), 5.09-5.05 (m, 1H), 4.82 (s, 1H), 4.76 (s, 1H), 3.59 (d, *J* = 0.9 Hz, 3H), 2.50-2.48 (m, 2H), 2.09-2.04 (m, 1H), 1.88 (q, *J* = 7.6 Hz, 2H), 1.68 (s, 3H), 1.58 (s, 3H), 1.45-1.36 (m, 1H), 1.30-1.21 (m, 1H), 0.97 (d, *J* = 6.9 Hz, 3H), 0.17 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): *d* = 165.6, 147.7, 132.4, 131.4, 129.5, 128.3, 127.4, 124.4, 111.6, 101.3, 91.9, 65.2, 55.4, 39.2, 39.0, 35.4, 25.8, 25.7, 19.6, 17.7, –0.4; IR (film): 2962, 2916, 2850, 1753, 1645, 1452, 1250, 1169, 1021, 839, 761, 717, 696 cm^{-1}; MS (70 eV): *m/z* (%): 494 (1) [*M*$^+$], 260 (15), 217 (14), 189 (100), 136 (17), 119 (10), 105 (14), 82 (99), 73 (92), 69 (27), 59 (14), 41 (23); HRMS (ESI): calcd for $C_{27}H_{37}O_3SiF_3Na$ [*M*$^+$ +Na]: 517.2356, found: 517.2356.



48

Compound 49: Colorless oil (11.0 mg, 62 %); ^{1}H NMR (400 MHz, $CDCl_3$): *d* = 7.55-7.53 (m, 2H), 7.42-7.35 (m, 3H), 5.69 (dd, *J* = 8.2, 6.1 Hz, 1H), 5.10-5.06 (m, 1H), 4.92 (s, 1H), 4.88 (s, 1H), 3.54 (d, *J* = 1.0 Hz, 3H), 2.59 (dd, *J* = 15.2, 8.3 Hz, 1H), 2.52 (dd, *J* = 15.2, 5.9 Hz, 1H), 2.19-2.11 (m, 1H), 1.93 (q, *J* = 7.4 Hz, 2H), 1.69 (s, 3H), 1.59 (s, 3H), 1.50-1.41 (m, 1H), 1.33-1.26 (m, 1H), 1.01 (d, *J* = 6.9 Hz, 3H), 0.15 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): *d* = 165.6, 148.0, 132.1, 131.6, 129.5, 128.3, 127.5,



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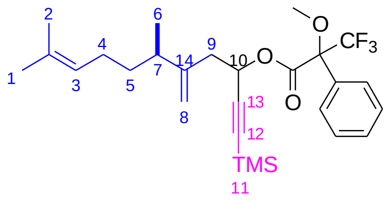
124.3, 111.6, 101.0, 91.7, 65.2, 55.6, 39.1, 38.9, 35.7, 25.7, 25.7, 19.5, 17.7, –0.4; IR (film): 2962, 2921, 2850, 1752, 1644, 1452, 1251, 1168, 1020, 839, 761, 720, 696 cm^{-1}; MS (70 eV): *m/z* (%): 494 (1) [M^+], 260 (13), 217 (12), 189 (100), 136 (15), 119 (10), 105 (14), 82 (87), 73 (89), 69 (26), 59 (13), 41 (22); HRMS (ESI): calcd for $C_{27}H_{37}O_3SiF_3Na$ [M^+ +Na]: 517.2356, found: 517.2354.



^{1}H NMR

position	Compound **48** (*S*)-Ester	Compound **46** (*R*)-Ester	? (*S*)-(*R*)	Compound **49** (*S*)-Ester	Compound 47 (*R*)-Ester	? (*S*)-(*R*)
	derived from *S*-**4**			derived from *R*-**4**		
1	1.680	1.678	+0.002	1.685	1.682	+0.003
2	1.577	1.574	+0.003	1.586	1.581	+0.005
3	5.706	5.683	+0.023	5.688	5.714	-0.026
4	1.888	1.918	-0.033	1.931	1.900	+0.031
5	1.264	1.308	-0.044	1.296	1.247	+0.049
5‘	1.394	1.440	-0.046	1.453	1.408	+0.045
6	0.965	1.017	-0.052	1.009	0.954	+0.055
7	2.065	2.121	-0.056	2.149	2.092	+0.057
8	4.762	4.865	-0.103	4.879	4.772	+0.107
8‘	4.821	4.913	-0.092	4.918	4.821	+0.097
9	2.496	2.550	-0.054	2.555	2.487	+0.068
10	5.067	5.072	-0.005	5.081	5.067	+0.014
11	0.167	0.145	+0.022	0.146	0.166	-0.020

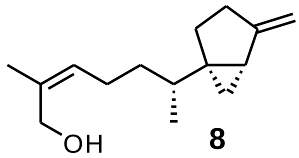
^{13}C NMR

position						
1	25.68	25.68	0	25.69	25.69	0
2	17.65	17.66	-0.01	17.70	17.70	0
3	124.43	124.34	+0.09	124.35	124.42	-0.07
4	25.79	25.81	-0.02	25.73	25.71	+0.02
5	34.43	35.45	-0.02	35.69	35.65	+0.04
6	19.65	19.73	-0.08	19.47	19.40	+0.07
7	39.24	39.28	-0.04	39.12	39.13	+0.01
8	111.57	111.41	+0.16	111.63	111.74	-0.11
9	39.00	38.96	+0.04	38.94	38.94	0
10	65.21	65.41	-0.2	65.25	64.99	+0.26
11	-0.37	-0.38	+0.01	-0.39	-0.37	-0.02
12	91.94	91.69	+0.25	91.68	91.91	-0.23
13	101.27	101.01	+0.26	101.01	101.30	-0.29
14	147.71	148.12	-0.41	148.02	147.66	-0.36

?$_{(S)\text{-}(R)}$/?$_{(S)\text{-}(R)}$: shifts consistent within the side chain; ?$_{(S)\text{-}(R)}$: shifts inconsistent within the side chain

?$_{(S)\text{-}(R)}$: R^1 negative and R^2 positive: (*S*)-configuration for *S*-**4;** ?$_{(S)\text{-}(R)}$: R^1 positive and R^2 negative: (*R*)–configuration for *R*-**4** (according to J. M. Seco, E. Quiñoá, R. Riguera, *Chem. Rev.* **2004**, *104*, 17-118).

Pheromone isolated from *Erysarcoris lewisi* (Distant)



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^{1}H-NMR (C_6D_6) literature[1]	^{1}H-NMR (C_6D_6) synthetic sample	^{13}C-NMR (C_6D_6) literature[1]	^{13}C-NMR (C_6D_6) synthetic sample
0.40 (1H, ddd, J = 1.2, 4.8, 7.8 Hz)	0.42 (ddd, *J* = 7.7, 4.6, 1.1 Hz, 1H)	16.2	16.3
0.53 (1H, t, J = 5.4 Hz)	[a]	18.3	18.3
0.57 (1H, dd, J = 3.6, 4.8 Hz)	0.58 (dd, *J* = 4.2, 3.5 Hz, 1H)	21.3	21.4
0.85 (3H, d, J = 6.6 Hz)	0.86 (d, *J* = 6.7 Hz, 3H)	25.8	25.9
1.01 (1H, q, J = 7.2 Hz)	1.08-1.01 (m, 2H) [a]	26.5	26.7
1.19-1.26 (1H, m)	1.29-1.17 (m, 1H)	29.0	29.1
1.40-1.47 (2H, m)	1.51-1.39 (m, 2H)	31.7	31.8
1.56 (1H,dd, J = 3.0,8.4 Hz)	1.67-1.55 (m, 2H)	35.2	35.3
1.57-1.62 (1H, m)		36.4	36.6
1.75 (3H, d, J = 1.2 Hz)	1.76 (d, *J* = 1.2 Hz, 3H)	38.0	38.1
1.84-1.92 (1H, m)	2.10-1.86 (m, 4H)	61.4	61.5
1.92-2.00 (2H, m)		102.5	102.5
2.05 (1H, dd, J = 9.0,16 Hz)		128.1	[b]
3.93-3.98 (2H, m)	3.97 (s, 2H)	135.0	135.1
4.79 (1H, s)	4.79 (bs, 1H)	153.8	153.8
5.00 (1H, s)	5.00 (bs, 1H)		
5.17 (1H, t, J = 7.2 Hz)	5.18 (t, *J* = 7.3 Hz, 1H)		

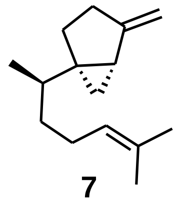
[a] The difference is caused by a different shift of the –OH group; [b] The signal is hided under the signal caused by residual C_6H_6 in C_6D_6.

$[\alpha]_D^{27}$ =–38.9 (c = 1.1 in hexanes); Lit.[2]: $[\alpha]_D^{27}$ =–37.9 (c = 1.19 in hexanes)

1) K. Mori, *Tetrahedron: Asymmetry* **2007**, *18*, 838-846.

2) K. Mori, T. Tashiro, T. Yoshimura, M. Takita, J. Tabata, S. Hiradate, H. Sugie, *Tetrahedron Lett*. **2008**, *49*, 354-357.

Sesquisabinene



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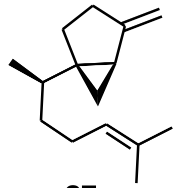
^{1}H-NMR (CDCl$_3$)		^{13}C-NMR (CDCl$_3$)	
literature[1],[a]	**synthetic sample**	**literature[1, 2]**	**synthetic sample**
5.08 (tq, 1H)	5.12-5.06 (m, 1H)	154.1	154.2
4.80 (bs, 1H)	4.80 (s, 1H)	131.1	131.1
4.63 (bs, 1H)	4.62 (s, 1H)	124.9	125.0
	2.14 (dd, *J* = 16.1, 7.3 Hz, 1H),	101.7	101.8
	2.06-1.92 (m, 3H)	37.7	37.8
	1.77-1.66 (m, 2H)	36.5	36.7
1.68 (bs, 3H)	1.68 (d, *J* = 1.1 Hz, 3H)	34.5	34.6
1.60 (bs, 3H)	1.60 (bs, 4H)	31.0	31.2
1.45 (dd, 1H)	1.51-1.42 (m, 1H)	28.6	28.8
1.21 (qt, 1H),	1.35-1.18 (m, 2H)	26.5	26.7
0.92 (d, 3H)	0.93 (d, *J* = 6.7 Hz, 3H),	25.9	26.1
0.67 (dd, 1H)	0.66 (dd, *J* = 4.3, 3.5 Hz, 1H)	25.6	25.7
0.57 (dd, 1H)	0.57 (ddd, *J* = 0.6, 4.6, 8.2 Hz, 1H)	17.9	18.0
[a]		17.6	17.7
		16.0	16.1

[a] The proton count in the published spectrum is incorrect (16H instead of the required 24H).

1) D. Joulain, W. A. König, *The Atlas of Spectral Data of Sesquiterpene Hydrocarbons*, EB-Verlag, Hamburg, **1998**. (ISBN 3-930826-48-8) ("Sequisabinene A")

2) P. Weyerstahl, H.-C. Wahlburg, U. Splittgerber, H. Marschall, *Flavour Fragrance J.* **1994**, 9, 179-186.

Sesquisabinene B



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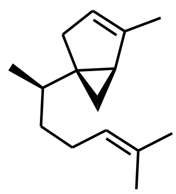
^{1}H-NMR ($CDCl_3$)[a]		^{13}C-NMR ($CDCl_3$)[a]	
literature[1, 2]	**synthetic sample**	**literature[1, 2]**	**synthetic sample**
5.12 (ddqq, 1H)	5.13-5.07 (m, 1H)	154.9	154.5
4.82 (bs, 1H)	4.80 (s, 1H)	131.6	131.2
4.64 (bs, 1H)	4.62 (s, 1H)	125.3	124.9
2.17 (dd, 1H)	2.15 (dd, *J* = 15.8, 9.2, 1H)	102.0	101.6
1.98-2.10 (m, 3H)	2.08-1.94 (m, 3H)	38.4	38.0
1.78 (dddd, 1H)	1.82-1.71 (m, 1H)	37.2	36.8
1.71 (d, 3H)	1.68 (s, 3H)	35.6	35.2
1.64 (m, 1H)	1.65-1.59 (m, 1H)	30.1	29.7
1.57 (s, 3H),	1.61 (s, 3H)	29.3	29.0
1.55 (dd, 1H)	1.52 (dd, *J* = 8.2, 3.4 Hz, 1H)	26.7	26.3
1.38-1.48 (m, 1H)	1.47-1.35 (m, 1H)	26.6	26.2
1.18-1.30 (m, 2H)	1.30-1.16 (m, 2H)	26.1	25.7
0.97 (d, 3H)	0.94 (d, *J* = 6.5 Hz, 3H),	18.7	18.3
0.77 (dd, 1H)	0.74 (dd, *J* = 4.4, 3.5 Hz, 1H),	18.1	17.7
0.68 (ddd, 1H)	0.66 (ddd, *J* = 8.2, 4.6, 1.2 Hz, 1H)	17.9	17.4

[a] As the shift differences are systematic (ca. 0.03 ppm in the ^{1}H NMR and ca. 0.4 ppm in the ^{13}C NMR), they are likely an issue of calibration.

1) D. Joulain, W. A. König, *The Atlas of Spectral Data of Sesquiterpene Hydrocarbons*, EB-Verlag, Hamburg, **1998**. (ISBN 3-930826-48-8).

2) R. P. Adams, T. A. Zanoni, T. A. van Beek, M. A Posthumus, C. van de Haar, *J. Essent. Oil Res.* **1998**, *10*, 175-178.

Sesquithujene



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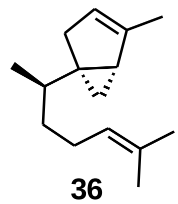
^{1}H-NMR (CDCl$_3$)		^{13}C-NMR (CDCl$_3$)	
literature[1]	**synthetic sample**	**literature[2]**	**synthetic sample**
5.12 (t, J = 7Hz, 1H)	5.15-5.08 (m, 1H)		145.2
4.95 (s, 1H)	4.94 (bs, 1H)		131.0
2.38 (dm, 1H)	2.43-2.35 (m, 1H)		125.1
2.11 (dm, 1H),	2.15-2.00 (m, 3H)		120.9
2.04 (dt, 2H)			
1.76 (dt, 3H)	1.77-1.75 (m, 3H)		38.1
1.68 (s, 3H)	1.69 (d, *J* = 1.0 Hz, 3H)		35.5
1.61 (s, 3H)	1.60 (s, 3H)		35.3
1.4 (m, 1H)	1.49-1.38 (m, 1H)		33.1
1.31 (md, 1H)	1.34-1.23 (m, 2H)		30.9
1.1 (m, 2H)	1.19-1.11 (m, 1H)		26.2
0.93 (d, 3H)	0.93 (d, *J* = 6.6 Hz, 3H)		25.7
0.76 (dd, 1H)	0.76 (dd, *J* = 7.5, 3.5 Hz, 1H)		23.7
0.10 (t, 1H)	0.10 (t, *J* = 3.3 Hz, 1H)		17.9
			17.6
			16.3

1) S. J. Terhune, J. W. Hogg, A. C. Bromstein, B. M. Lawrence, *Can. J. Chem.* **1975**, *53*, 3285-3293.

2) The spectral data reported in: D. Joulain, W. A. König, *The Atlas of Spectral Data of Sesquiterpene Hydrocarbons*, EB-Verlag, Hamburg, **1998** (ISBN 3-930826-48-8) are wrong and must not be used for comparison.

7-*epi*-Sesquithujene



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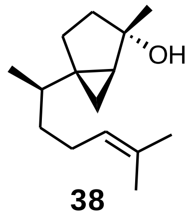
^{1}H-NMR (CDCl$_3$)		^{13}C-NMR (CDCl$_3$)	
literature[2]	**synthetic sample**	**literature[2]**	**synthetic sample**
5.09 (tq, 1H)	5.13-5.06 (m, 1H)	144.9	145.0
4.95 (m, 1H)	4.95 (bs, 1H)	131.0	131.0
2.36 (dq, 1H)	2.40-2.33 (m, 1H)	125.1	125.2
2.14 (dq, 1H)	2.18-2.10 (m, 1H)	120.9	120.9
1.95 (m, 2H)	2.00-1.93 (m, 2H)	38.0	38.0
1.75 (ddd, 3H)	1.75 (q, *J* = 1.9 Hz, 3H)	36.0	36.1
1.67 (d, 3H)	1.68 (d, *J* = 1.1 Hz, 3H)	35.1	35.2
1.59 (bs, 3H)	1.59 (s, 3H)	33.2	33.2
1.46 (qt (1H)	1.51-1.38 (m, 2H)	32.5	32.5
1.40 (dd, 1H)		26.1	26.1
1.30 (m, 1H)	1.35-1.13 (m, 2H)	25.7	25.7
1.17 (m, 1H)		21.5	21.5
0.93 (d, 3H)	0.93 (d, *J* = 6.7 Hz, 3H)	18.2	18.1
0.68 (dd, 1H)	0.68 (dd, *J* = 7.5, 3.5 Hz, 1H)	17.6	17.6
0.01 (dd, 1H)	0.01 (t, *J* = 3.2 Hz, 1H)	16.4	16.3

1) D. Joulain, W. A. König, *The Atlas of Spectral Data of Sesquiterpene Hydrocarbons*, EB-Verlag, Hamburg, **1998**. (ISBN 3-930826-48-8)

2) P. Weyerstahl, H.-C. Wahlburg, U. Splittgerber, H. Marschall, *Flavour Fragrance J.* **1994**, 9, 179-186.

7-*epi*-*trans*-Sesquisabinene hydrate



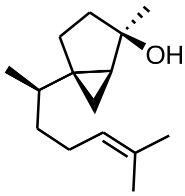
38

^{1}H-NMR ($CDCl_3$)		^{13}C-NMR ($CDCl_3$)	
literature[1],[a]	**synthetic sample**	**literature[1]**	**synthetic sample**
5.09 (tq, 1H)	5.11-5.07 (m, 1H),	131.1	131.2
	2.01 (q, *J* = 7.5 Hz, 2H)	124.9	124.9
	1.90-1.82 (m, 1H)	80.5	80.5
1.69 (s, 3H)	1.68 (s, 3H)	37.5	37.5
1.60 (d, 3H)	1.60 (s, 3H)	36.6	36.6
	1.56-1.50 (m, 2H)	35.4	35.4
	1.47-1.39 (m, 2H)	33.9	34.0
	1.31-1.19 (m, 2H)	33.8	33.8
1.29 (s, 3H)	1.29 (s, 3H)	26.2	26.2
	1.16-1.08 (m, 1H)	25.7	25.7
0.99 (d, 3H)	1.01-0.98 (m, 4H)	24.9	24.9
0.99 (dd, 1H)		24.8	24.8
0.41 (dd, 1H)	0.41 (dd, *J* = 7.7, 5.3 Hz, 1H	17.8	17.8
0.31 (dd, 1H)	0.31 (dd, *J* = 5.1, 3.7 Hz, 1H)	17.7	17.7
[a]		15.5	15.5

[a] The proton count in the published spectrum is incorrect (16H instead of the required 26H)

1) P. Weyerstahl, H. Marschall, K. Thefeld, G. C. Subba, *Flavour Fragrance J.* **1998**, *13*, 377-388.

7-*epi*-*cis*-Sesquisabinene hydrate



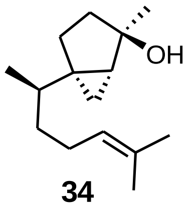
39

^{1}H-NMR ($CDCl_3$)		^{13}C-NMR ($CDCl_3$)	
literature[1],[a]	**synthetic sample**	**literature[1]**	**synthetic sample**
5.09 (tq, 1H)	5.10-5.07 (m, 1H)	131.1	131.2
	2.00 (q, J = 7.6 Hz, 2H)	124.8	124.9
1.69 (s, 3H)	1.68 (s, 3H)	79.3	79.4
	1.64-1.53 (m, 3H)	37.8	37.8
1.61 (d, 3H)	1.60 (s, 3H)	35.9	36.1
	1.45-1.36 (m, 2H)	34.8	34.9
1.34 (s, 3H)	1.34 (s, 3H)	32.9	33.1
	1.30-1.17 (m, 2H)	32.3	32.4
	1.05 (q, J = 6.9 Hz, 1H)	27.9	27.9
1.00 (dd, 1H)	1.00 (dd, J = 7.5, 3.7 Hz, 1H)	26.1	26.2
0.93 (d, 3H)	0.93 (d, J = 6.7 Hz, 3H)	25.6	25.7
0.73 (dd, 1H)	0.73 (dd, J = 4.7, 4.0 Hz, 1H)	24.5	24.6
0.35 (dd, 1H)	0.34 (dd, J = 7.9, 5.1 Hz, 1H)	17.6	17.7
[a]		17.3	17.4
		13.2	13.1

[a] The proton count in the published spectrum is incorrect (16H instead of the required 26H)

1) P. Weyerstahl, H. Marschall, K. Thefeld, G. C. Subba, *Flavour Fragrance J.* **1998**, *13*, 377-388.

trans-Sesquisabinene hydrate



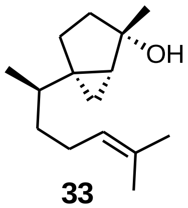
34

^{1}H-NMR ($CDCl_3$)		**^{13}C-NMR ($CDCl_3$)**	
literature[1, 2),[a]	**synthetic sample**	**literature[1, 2]**	**synthetic sample**
5.10 (ddt, *J* = 7, 7, 1 Hz, 1H)	5.12-5.06 (m, 1H)	131.2	131.2
2.03 (mc(?), 2H)	2.10-1.94 (m, 2H)	124.9	124.9
1.84 (ddd, *J* = 12, 11, 9 Hz, 1H)	1.89-1.78 (m, 1H)	80.6	80.6
1.69 (bs, 3H)	1.67 (d, *J* = 1.0 Hz, 3H)	37.3	37.3
	1.62 (d, *J* = 8.1 Hz, 1H)	36.5	36.5
1.61 (d, *J* = 1.5, 3H)	1.60 (s, 3H)	34.8	34.9
	1.57-1.43 (m, 2H)	34.8	
	1.39 (bs, 1H)	34.3	34.3
	1.35-1.23 (m, 2H)	26.1	26.1
1.31 (s, 3H)	1.30 (s, 3H),	25.8	25.8
	1.21-1.14 (m, 1H),	25.7	25.7
1.10 (ddd, *J* = 8, 3.5, 1 Hz, 1H)	1.09 (ddd, *J* = 8.3, 4.8, 3.5 Hz, 1H)	25.2	25.2
0.93 (d, *J* = 7 Hz, 3H)	0.91 (d, *J* = 6.7 Hz, 3H)	17.7	17.7
0.35 (ddd, *J* = 8, 5, 1 Hz, 1H)	0.34 (ddd, *J* = 8.4, 5.2, 0.7 Hz, 1H)	17.7	
0.23 (dd, *J* = 5, 3.5 Hz, 1H)	0.22 (dd, *J* = 5.1, 3.5 Hz, 1H)	13.6	13.6
[a]			

[a] The proton count in the published spectrum is incorrect (19H instead of the required 26H).

1) P. Weyerstahl, H. Marschall-Weyerstahl, C. Christiansen, *Flavour Fragrance J.* **1989**, *4*, 93-98.
2) P. Weyerstahl, H. Marschall, K. Thefeld, G. C. Subba, *Flavour Fragrance J.* **1998**, *13*, 377-388.

cis-Sesquisabinene hydrate



33

^{1}H-NMR ($CDCl_3$)		**^{13}C-NMR ($CDCl_3$)**	
literature[2, 3]	**synthetic sample**	**literature[2, 3]**	**synthetic sample**
5.08 (bt, *J* = 7 Hz, 1H)	5.10-5.06 (m, 1H)	131.4	131.3
2.00 (mc, 1H)	2.07-1.98 (m, 1H)	124.9	124.9
1.90 (mc, 1H)	1.95-1.85 (m, 1H)	79.5	79.4
1.69 (s, 3H)	1.68 (s, 3H)	37.7	37.6
1.67 (mc, 2H)		36.2	36.1
1.57 (mc, 3H)	1.64-1.52 (m, 3H)	34.4	34.3
1.60 (d, *J* = 1.5 Hz, 3H)	1.60 (s, 3H)	34.0	33.9
1.44 (mc, 1H)	1.49-1.38 (m, 2H)	33.3	33.2
1.35 (s, 3H)	1.35 (s, 3H)	28.1	28.1
1.25 (mc, 1H)	1.30-1.22 (m, 2H)	26.2	26.1
1.10 (dd, *J* = 8, 3.5 Hz, 1H)	1.10 (dd, *J* = 7.6, 3.4 Hz, 2H)	25.9	25.8
0.90 (d, *J* = 7 Hz, 3H)	0.89 (d, *J* = 6.8 Hz, 3H)	25.8	25.7
0.65 (dd, *J* = 5, 3.5 Hz, 1H)	0.65 (dd, *J* = 4.8, 3.7 Hz, 1H)	17.8	17.7
0.29 (dd, *J* = 8, 5 Hz, 1H)	0.29 (dd, *J* = 7.6, 5.1 Hz, 1H)	17.2	17.1
[a]		11.4	11.3

[a] The reported spectrum lacks the signal of the –OH proton

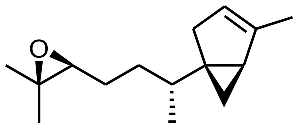
$[\alpha]_D^{20}$ = –10.3 (c = 1.2 in $CHCl_3$); $[\alpha]_D^{22}$ –10.4 (c = 0.4 in $CHCl_3$); Lit.[1]: $[\alpha]_D^{20}$ =–12 (c = 1.3 in $CHCl_3$)

1) P. Weyerstahl, H. Marschall-Weyerstahl, C. Christiansen, *Flavour Fragrance J.* **1989**, *4*, 93-98.

2) P. Weyerstahl, H. Marschall, K. Thefeld, G. C. Subba, *Flavour Fragrance J.* **1998**, *13*, 377-388.

3) P. Weyerstahl, H. Marschall-Weyerstahl, V. K. Kaul, E. Manteuffel, L. Glasow, *Liebigs Ann. Chem.* **1987**, 21-28.

Epoxysesquithujene



45

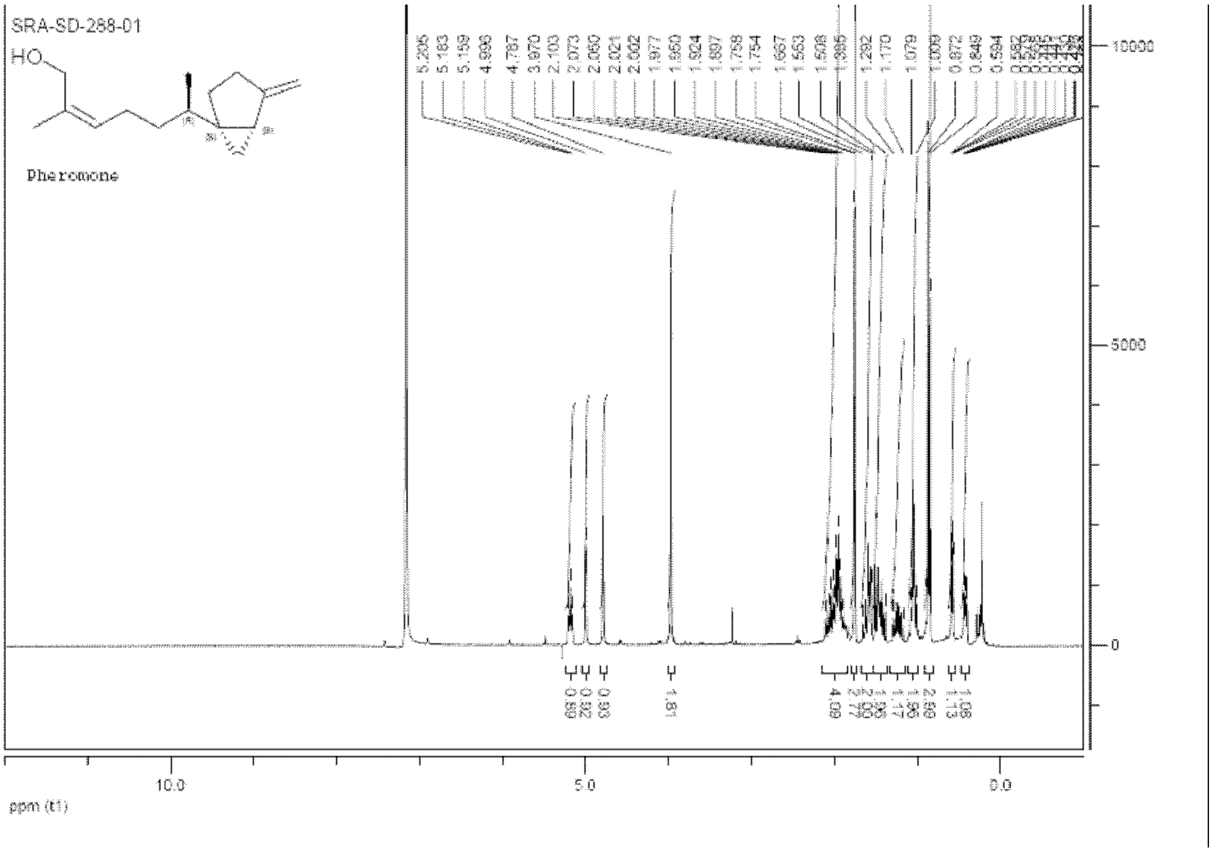
^{1}H-NMR ($CDCl_3$)		^{13}C-NMR ($CDCl_3$)	
literature[1],[a]	**synthetic sample**	**literature[1]**	**synthetic sample**
4.90 (1H, dt)	4.94 (bs, 1H)	145.0	145.1
2.71 (1H, t)	2.73-2.70 (m, 1H)	120.8	120.9
2.39 (1H, dt)	2.40 (dt, *J* = 17.0, 2.2 Hz, 1H)	64.6	64.7
2.10 (1H, dm)	2.14-2.09 (m, 1H)	58.0	58.1
1.75 (3H, bs)	1.76 (d, *J* = 1.7 Hz, 3H)	38.3	38.4
2*1.59 (1H, m)	1.65-1.57 (m, 3H)	35.3	35.4
1.32 (1H, m)	1.36-1.30 (m, 2H)	33.0	33.1
1.31 (3H, s)	1.31 (s, 3H)	31.8	31.9
1.26 (3H, s)	1.27 (s, 3H)	30.9	31.0
1.17 (1H, m)	1.20-1.16 (m, 1H)	27.0	27.1
0.95 (3H, d)	0.95 (d, *J* = 6.8 Hz, 3H)	24.9	24.9
0.76 (1H, m)	0.76 (dd, *J* = 7.5, 3.5 Hz, 1H)	23.6	23.7
0.11 (1H, m)	0.11 (t, *J* = 3.2 Hz, 1H)	18.6	18.7
[a]		17.8	17.8
		16.2	16.3

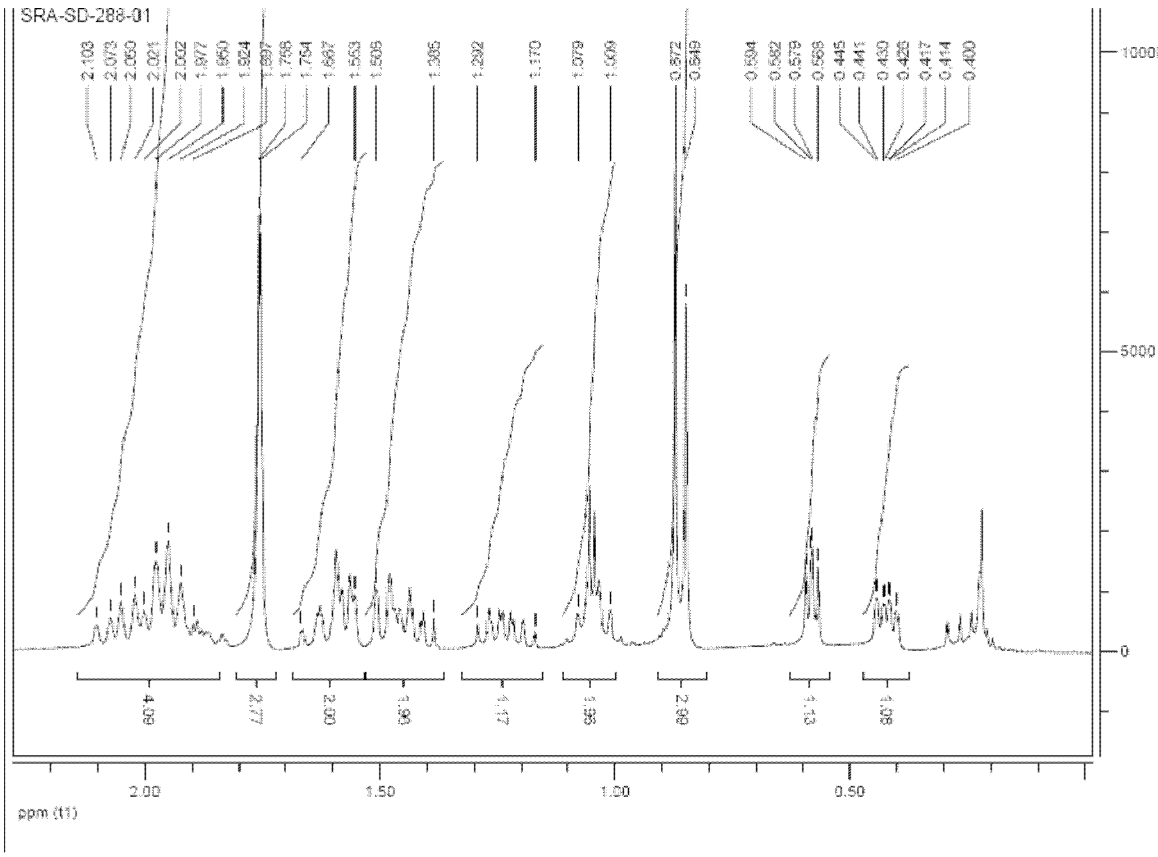
[a] The proton count in the published spectrum is incorrect (22H instead of the required 24H).

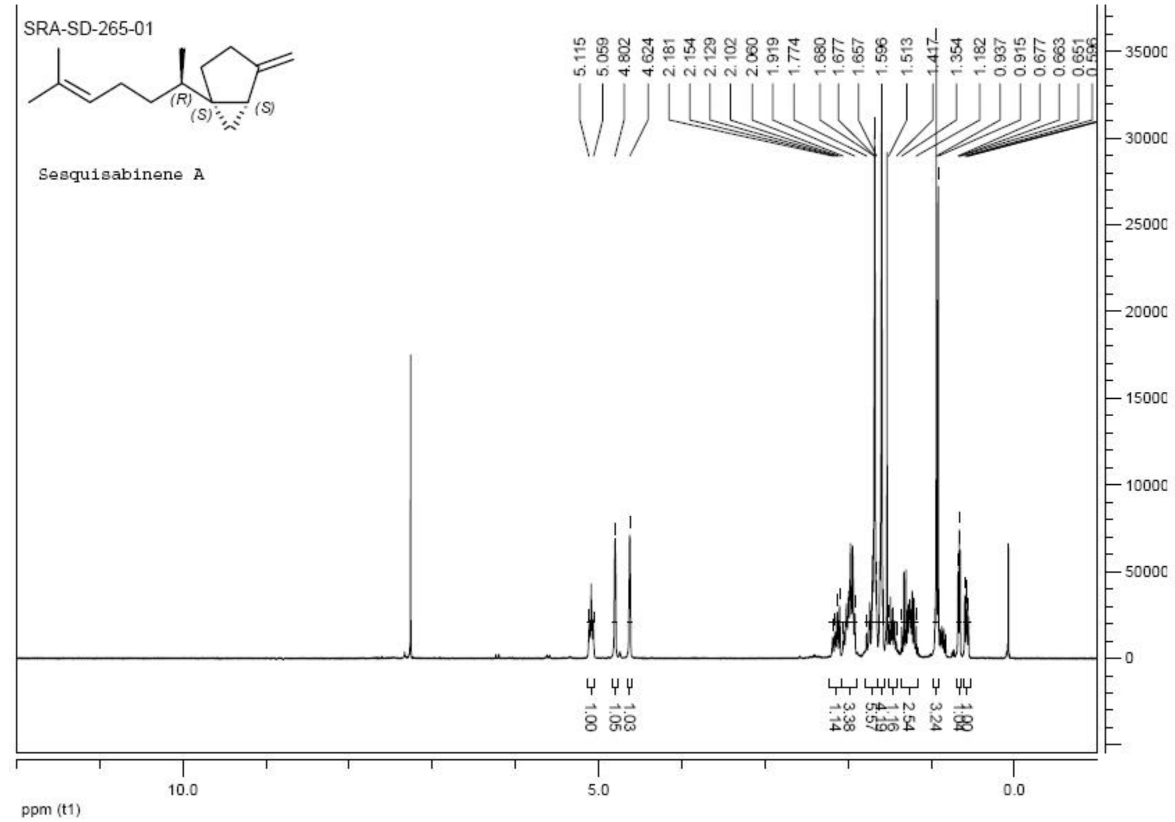
$[\alpha]_D^{20}$ = –17.9 (c = 0.48 in $CHCl_3$) [Note that the synthetic sample consists of a mixture of diastereomers, dr = 8:1)]; Lit.[1)]: $[\alpha]_D^{20}$ = –38.04 (c = 0.34 in $CHCl_3$)

1) C. S. Mathela, C. S. Chanotiya, S. Sati, S. S. Sammal, V. Wray, *Fitoterapia* **2007**, *78*, 279-282.

[1]H NMR SPECTRA



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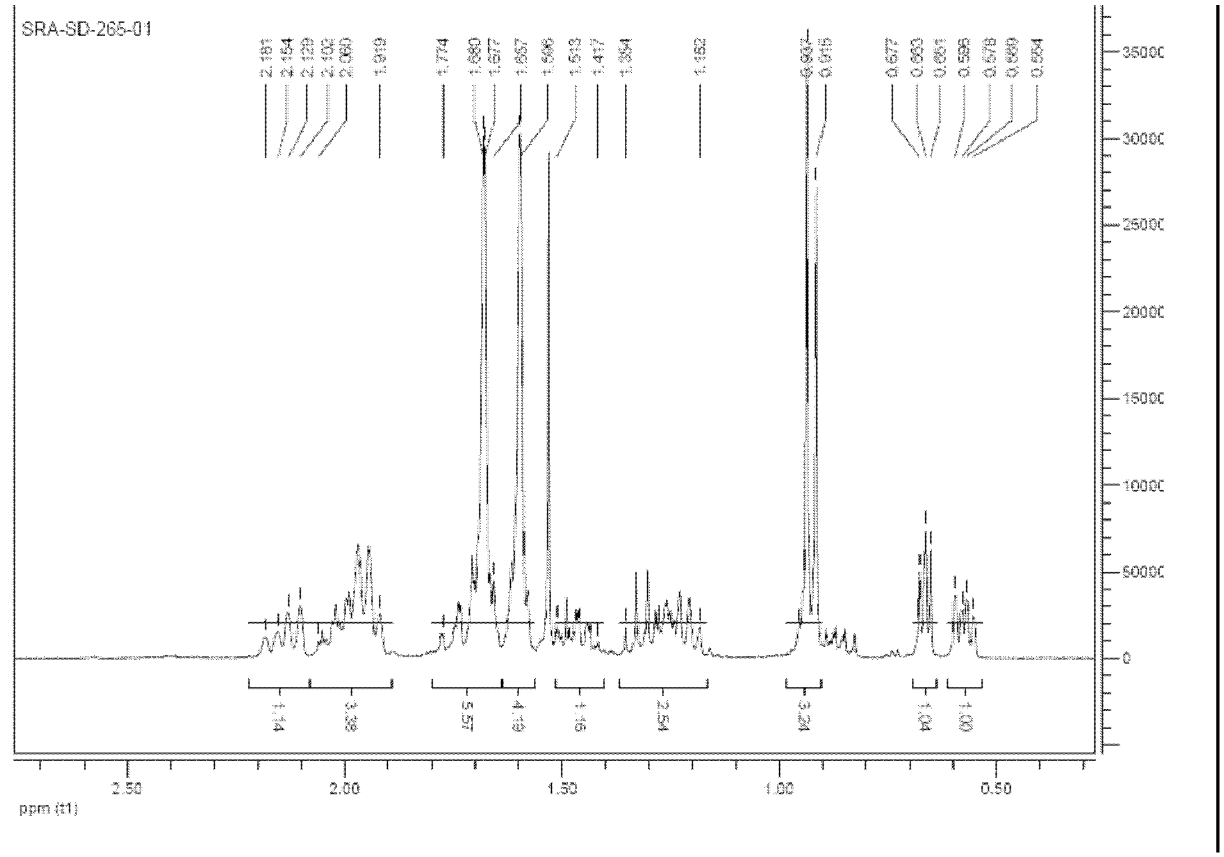
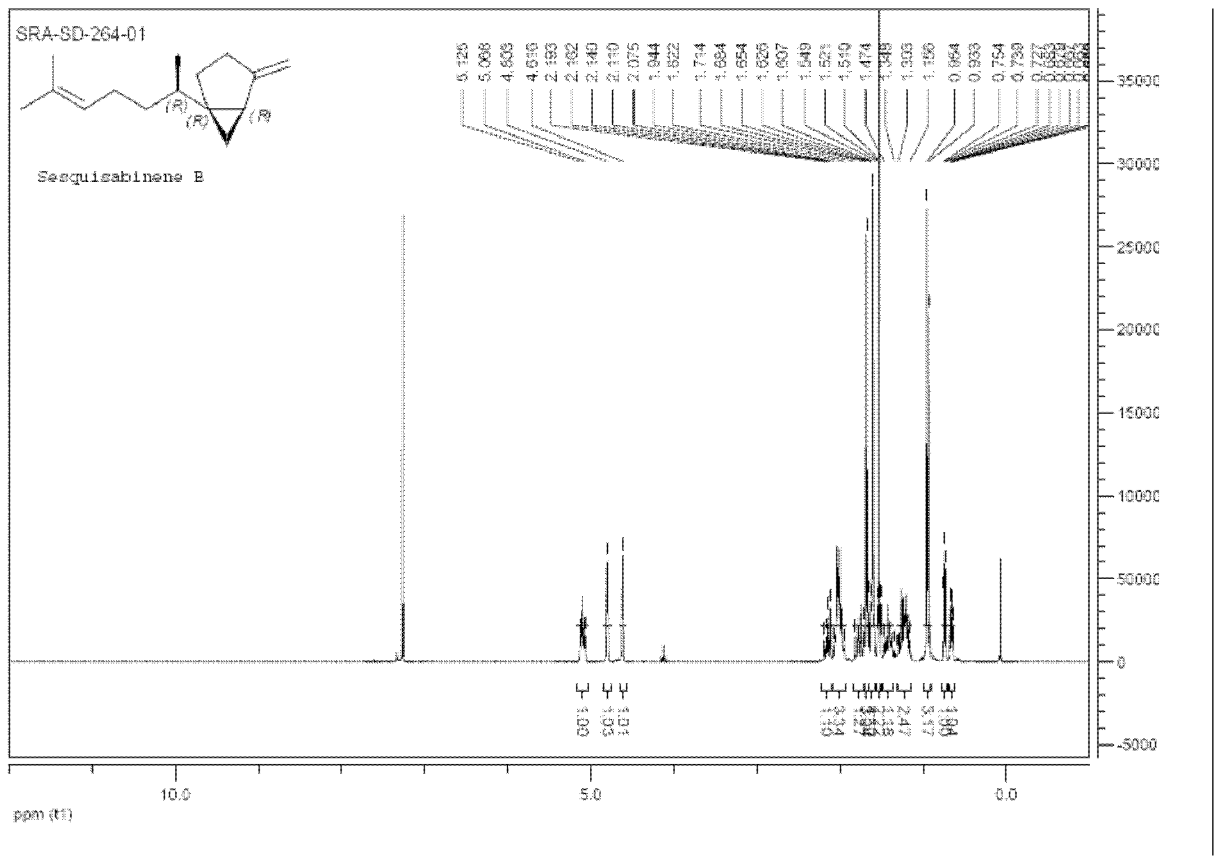
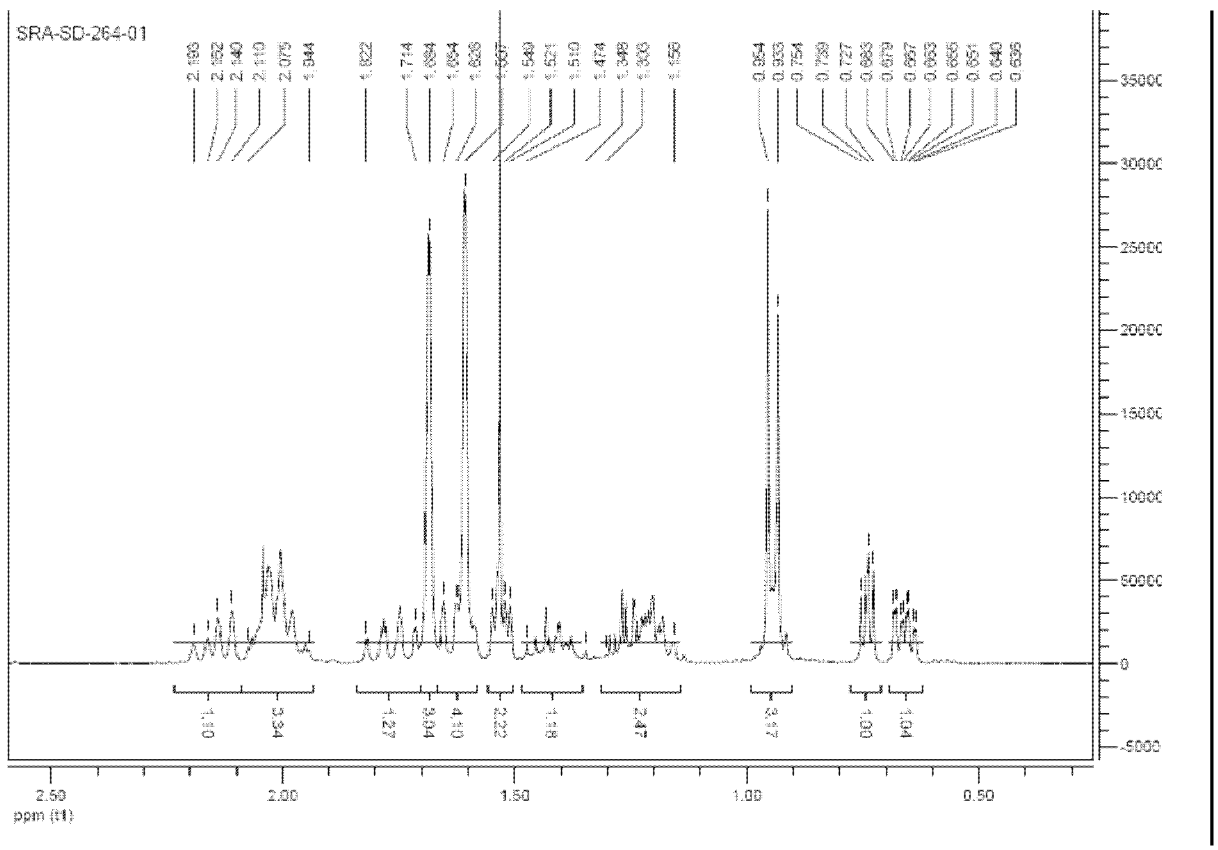
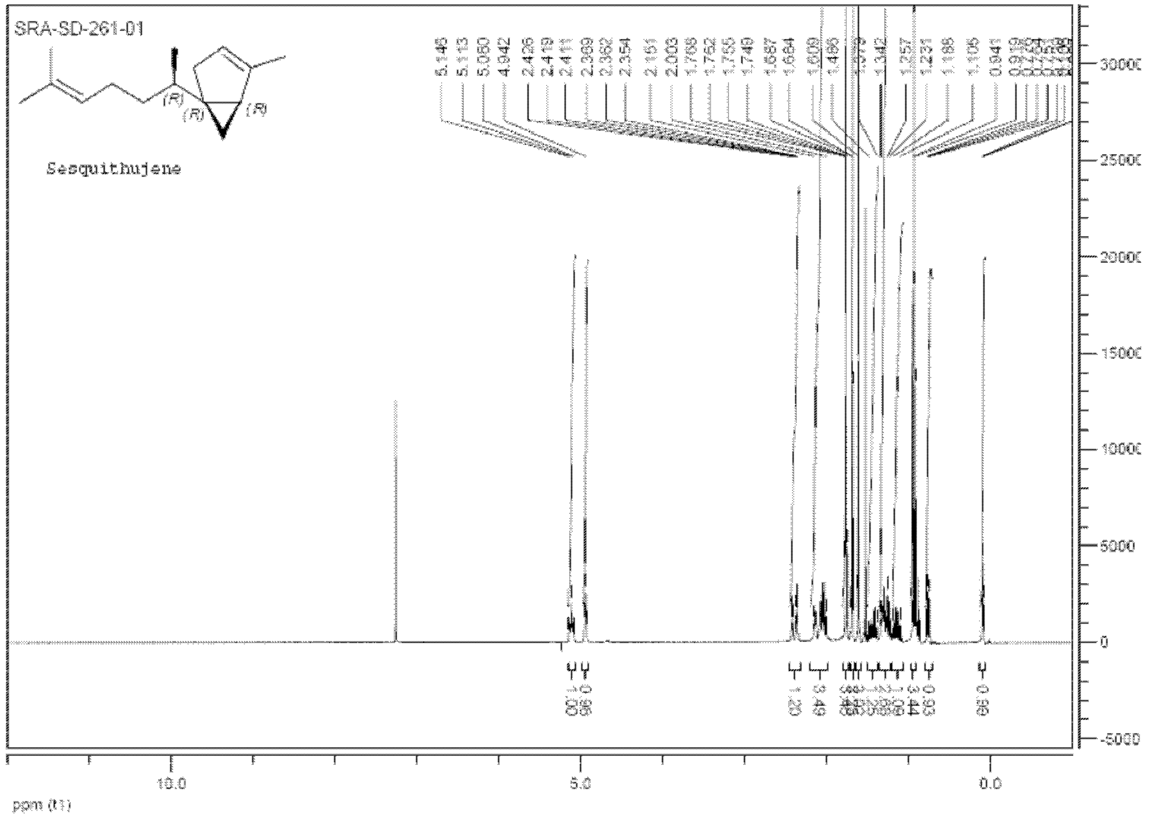
Sesquisabinene A
(R)
(S)
(S)
ppm (t1)


SRA-SD-265-01
ppm (t1)


SRA-SD-264-01
Sesquisabinene B
(R)
(R)
(R)
ppm (t1)
10.0
5.0
0.0


SRA-SD-264-01
1.10
3.34
1.27
3.04
4.10
2.22
1.18
2.47
3.17
1.00
1.04
2.50
2.00
1.50
1.00
0.50
ppm (t1)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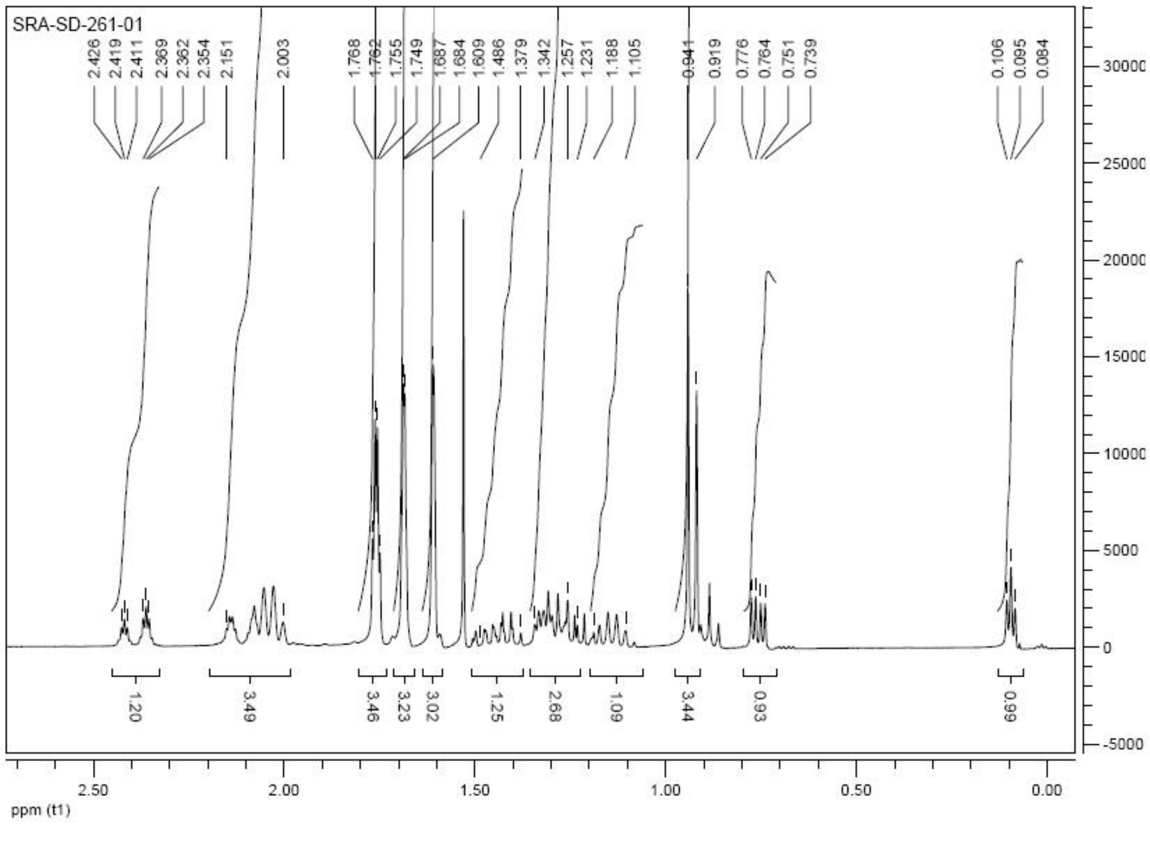
Sesquithujene
ppm (t1)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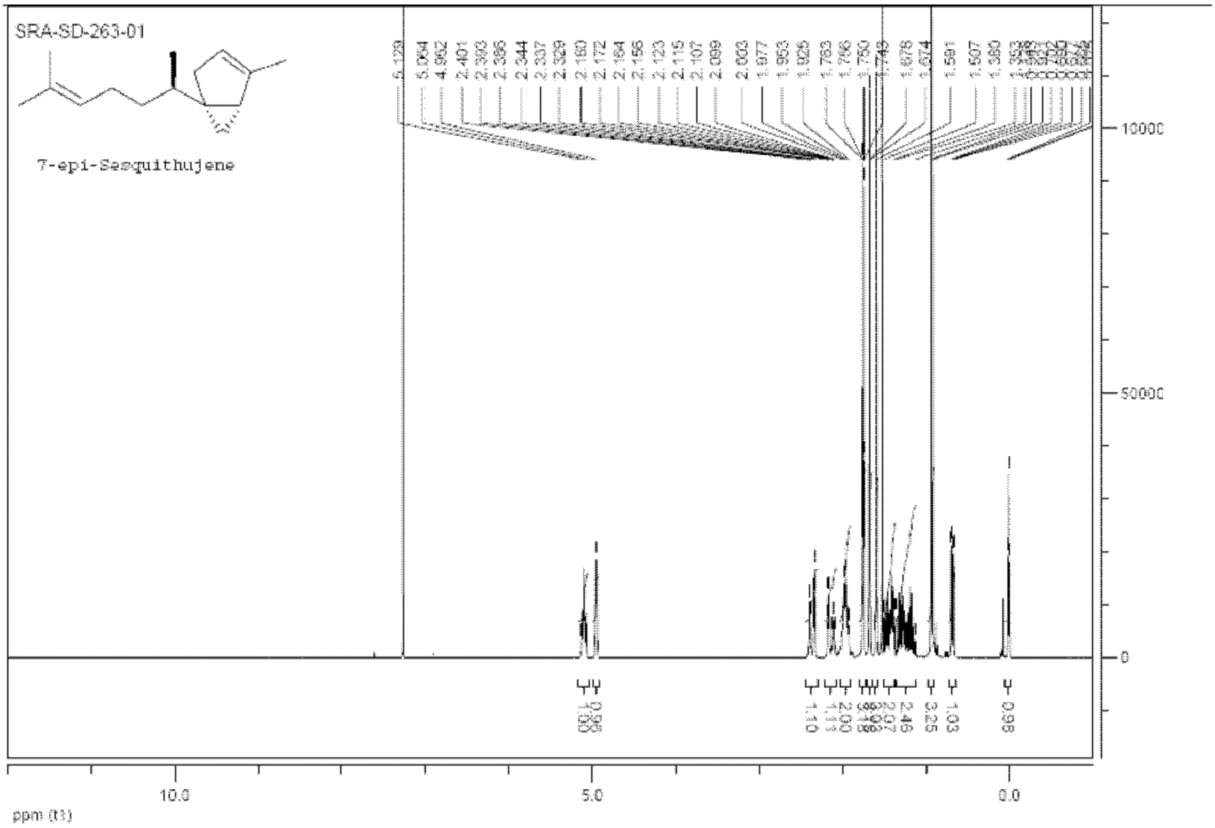
ppm (t1)


SRA-SD-263-01
7-epi-Sesquithujene
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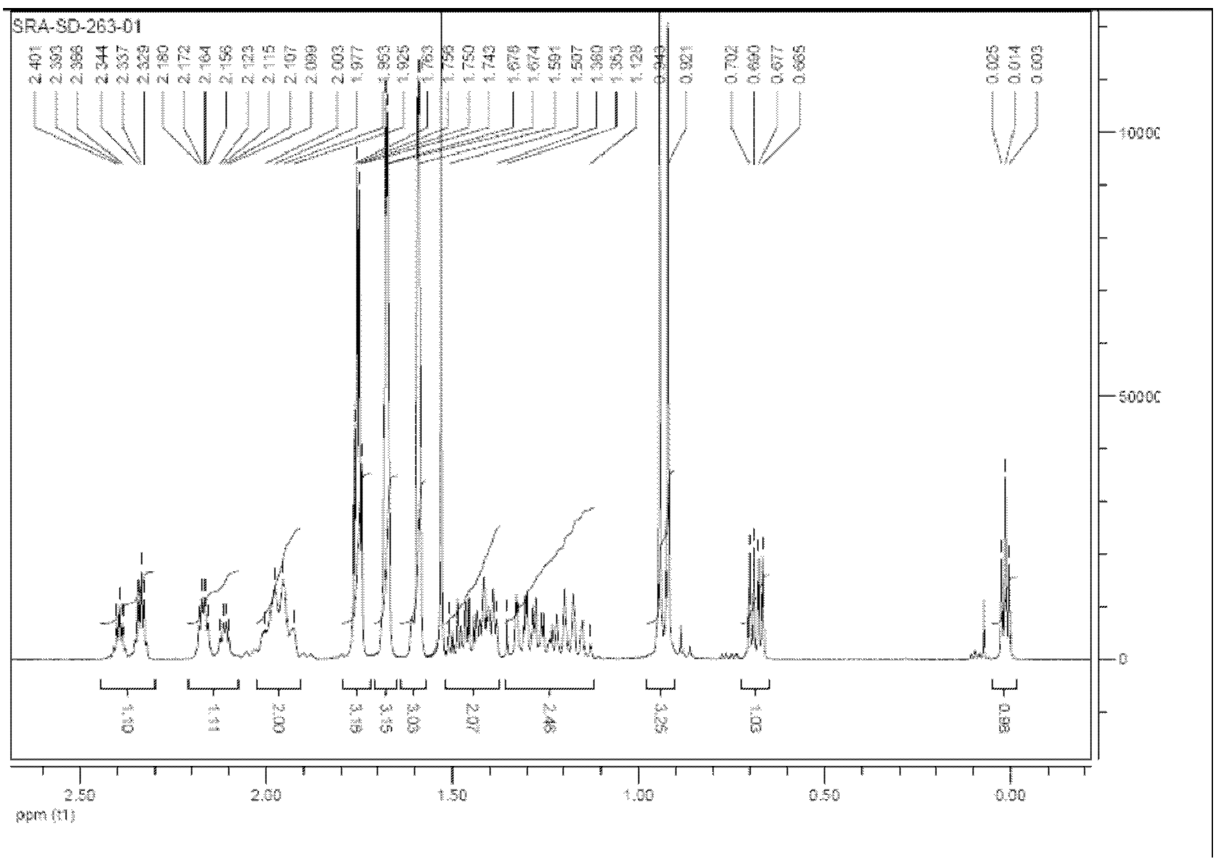
5.0
0.0
ppm (t1)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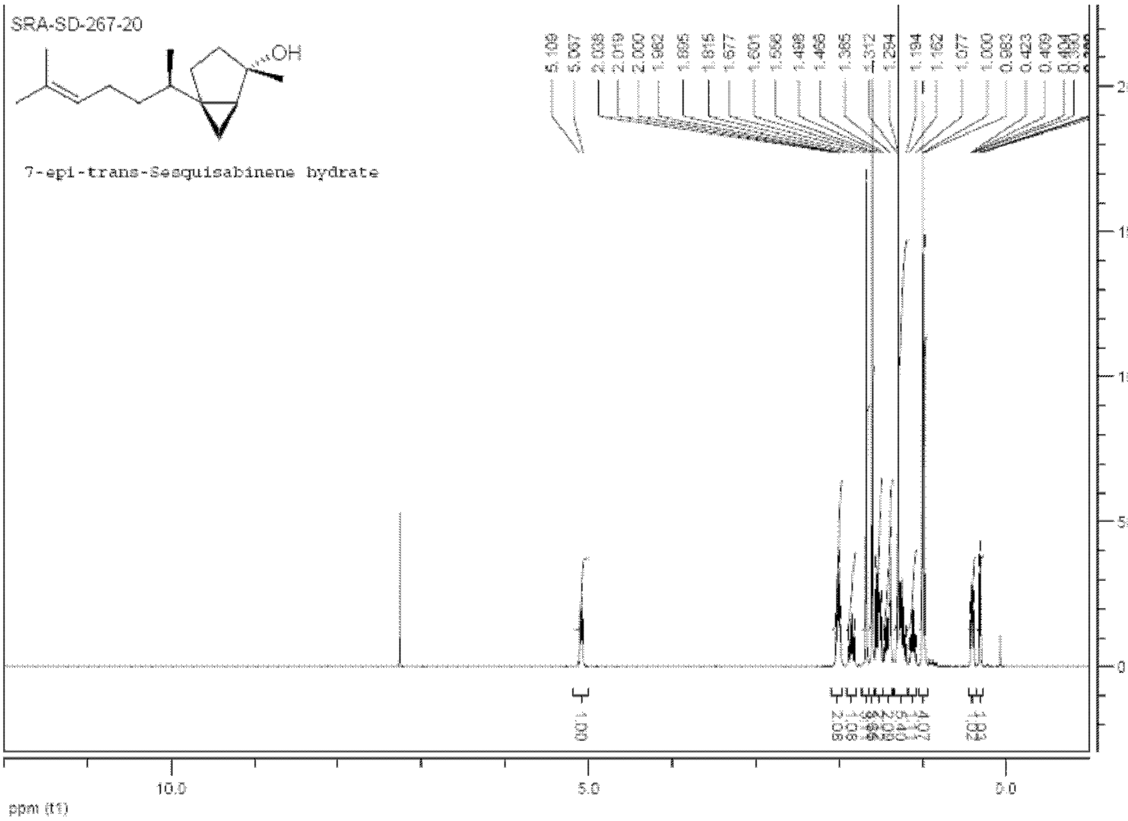
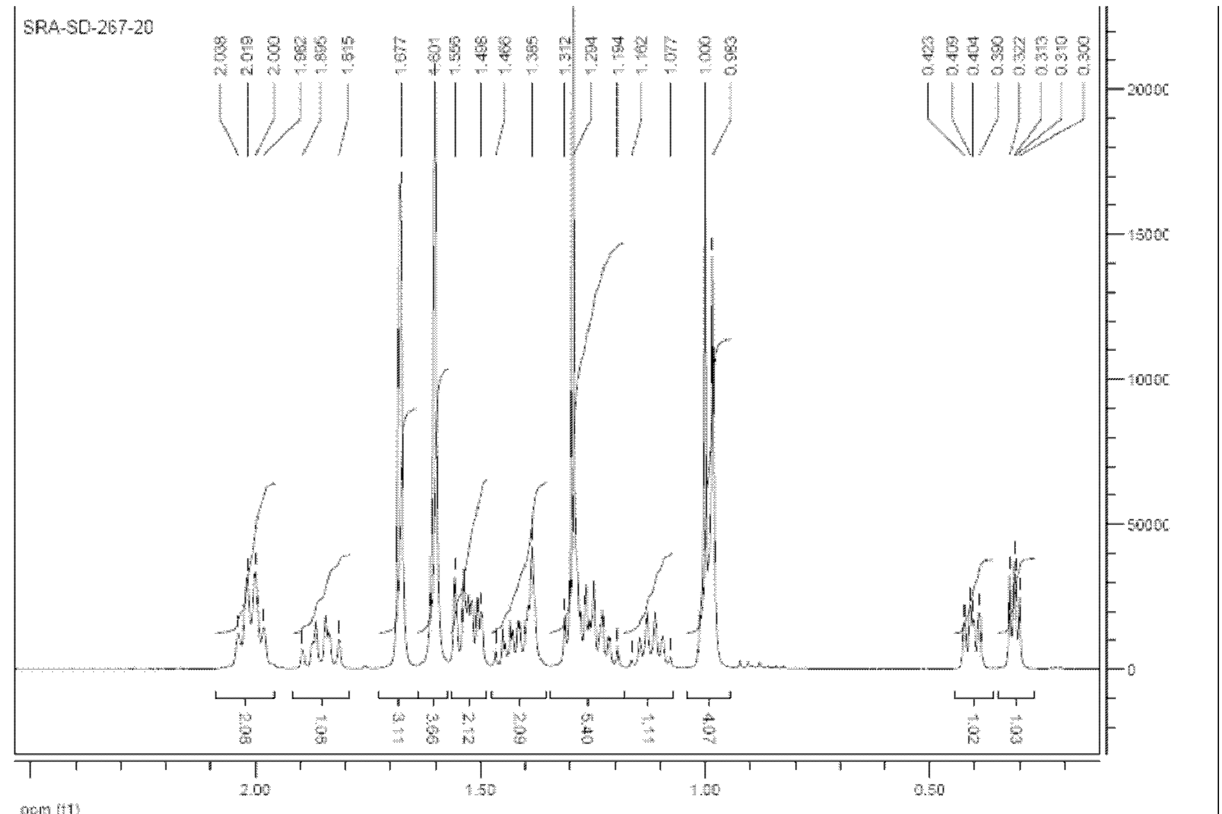
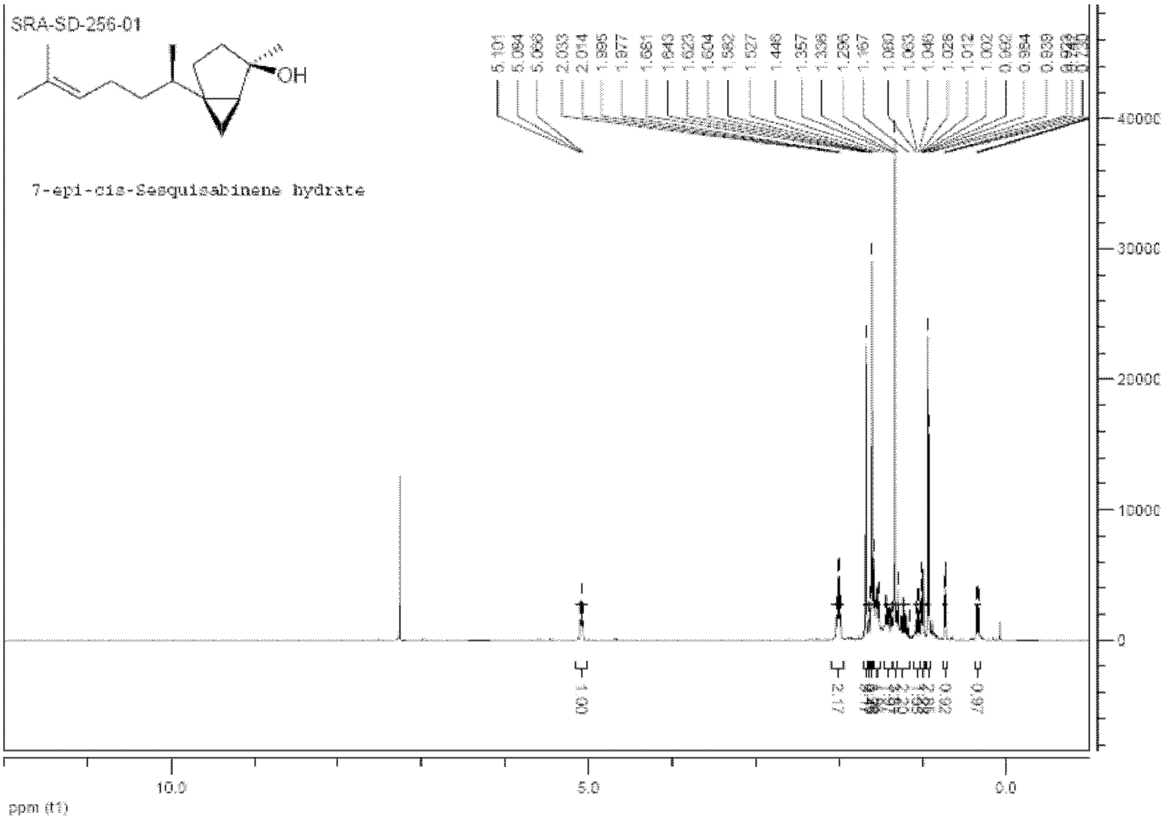
2.00
1.50
1.00
0.50
0.00
ppm (t1)


SRA-SD-267-20
OH
7-epi-trans-Sesquisabinene hydrate
ppm (t1)


SRA-SD-267-20
ppm (t1)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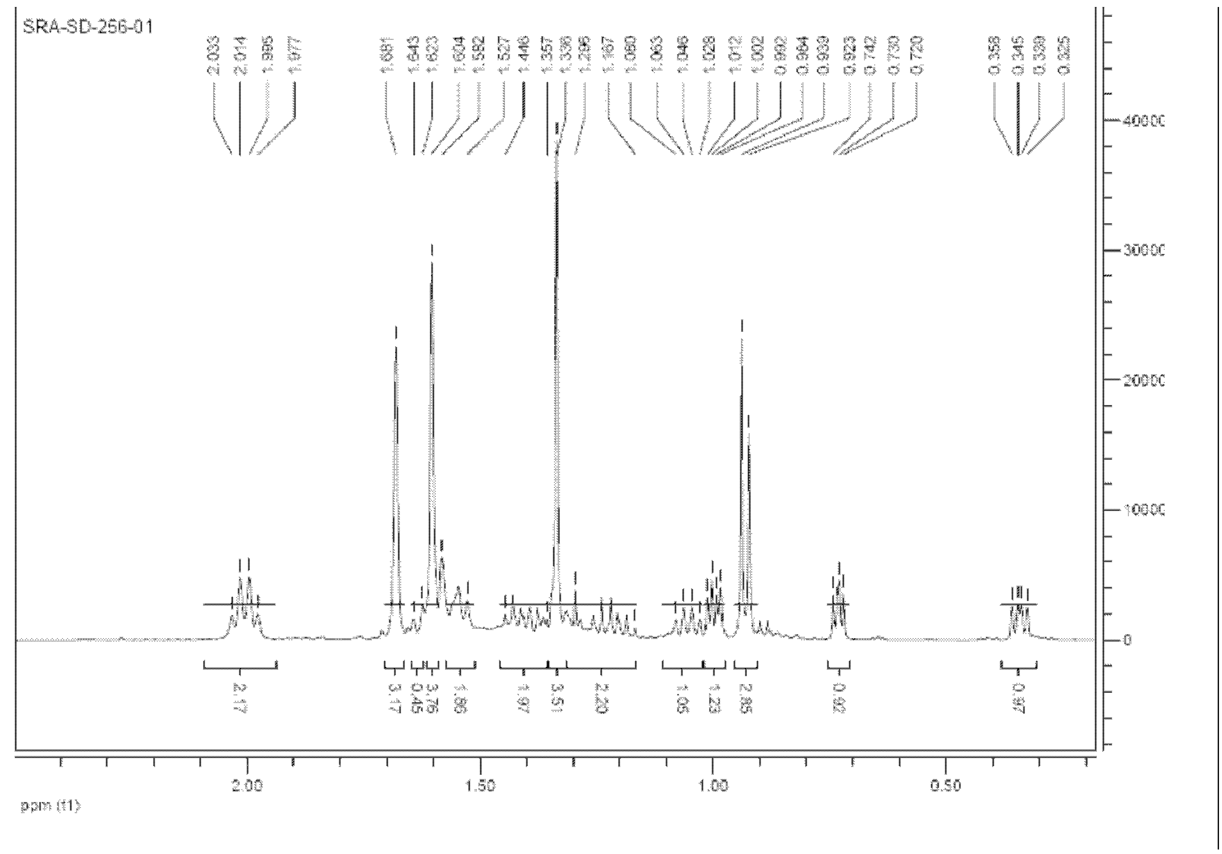
7-epi-cis-Sesquisabinene hydrate
ppm (t1)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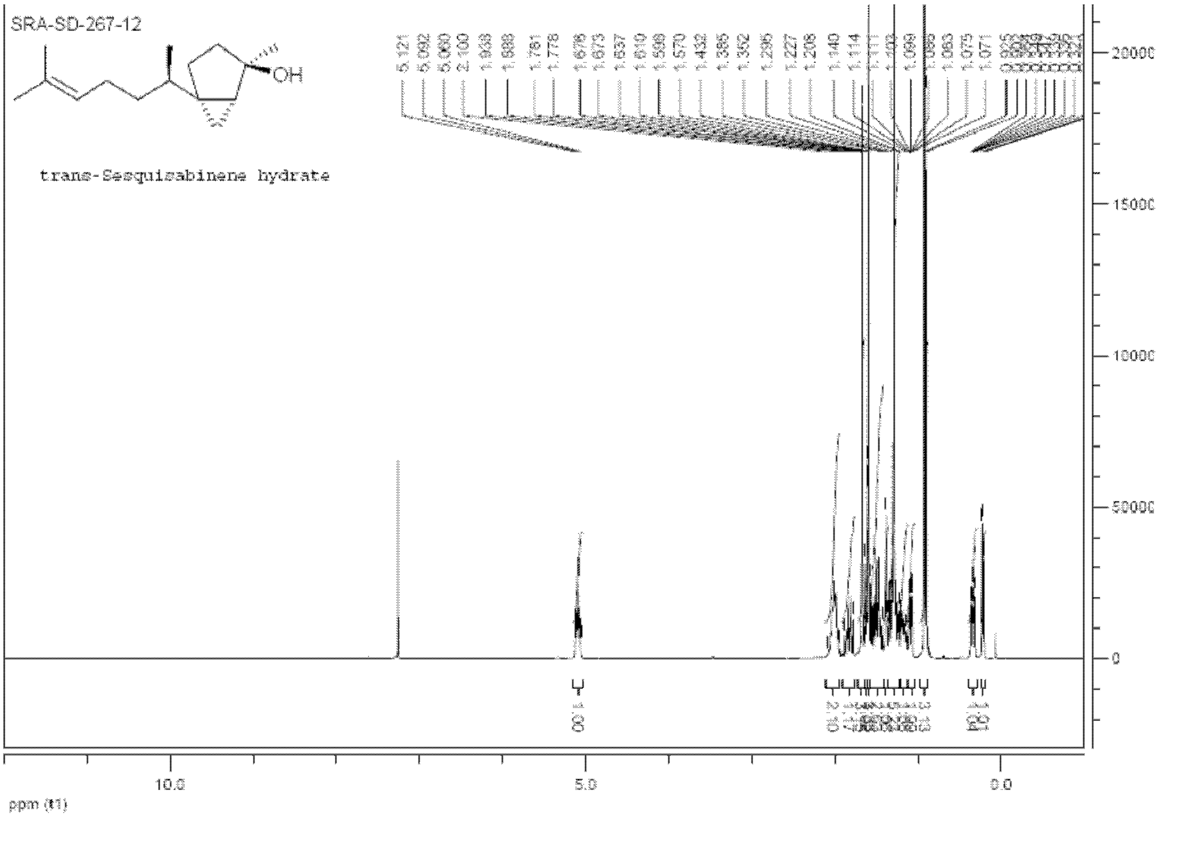
ppm (t1)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trans-Sesquisabinene hydrate
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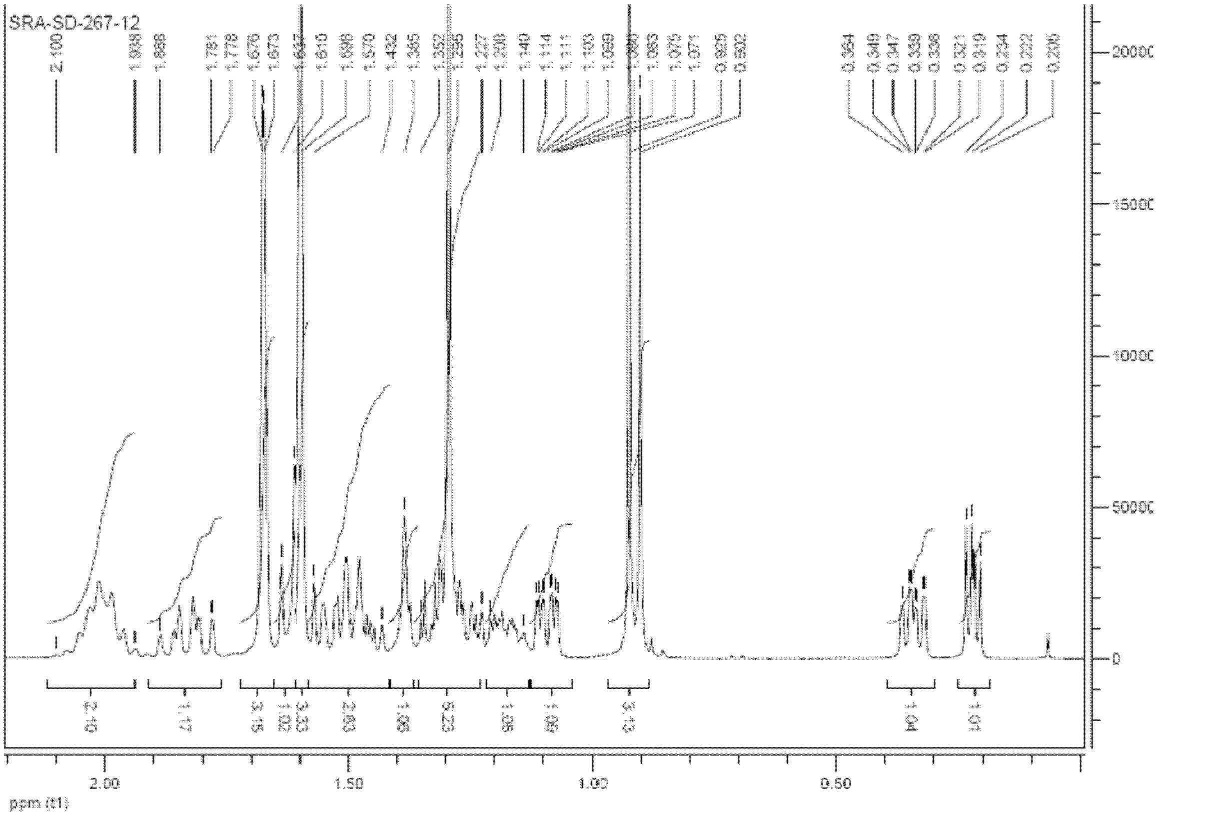
5.092
5.060
2.100
1.938
1.888
1.781
1.778
1.676
1.673
1.637
1.610
1.598
1.570
1.432
1.385
1.352
1.295
1.227
1.208
1.140
1.114
1.111
1.103
1.099
1.085
1.083
1.075
1.071
20000
15000
10000
50000
0
1.00
2.10
1.04
1.01
10.0
5.0
0.0
ppm (t1)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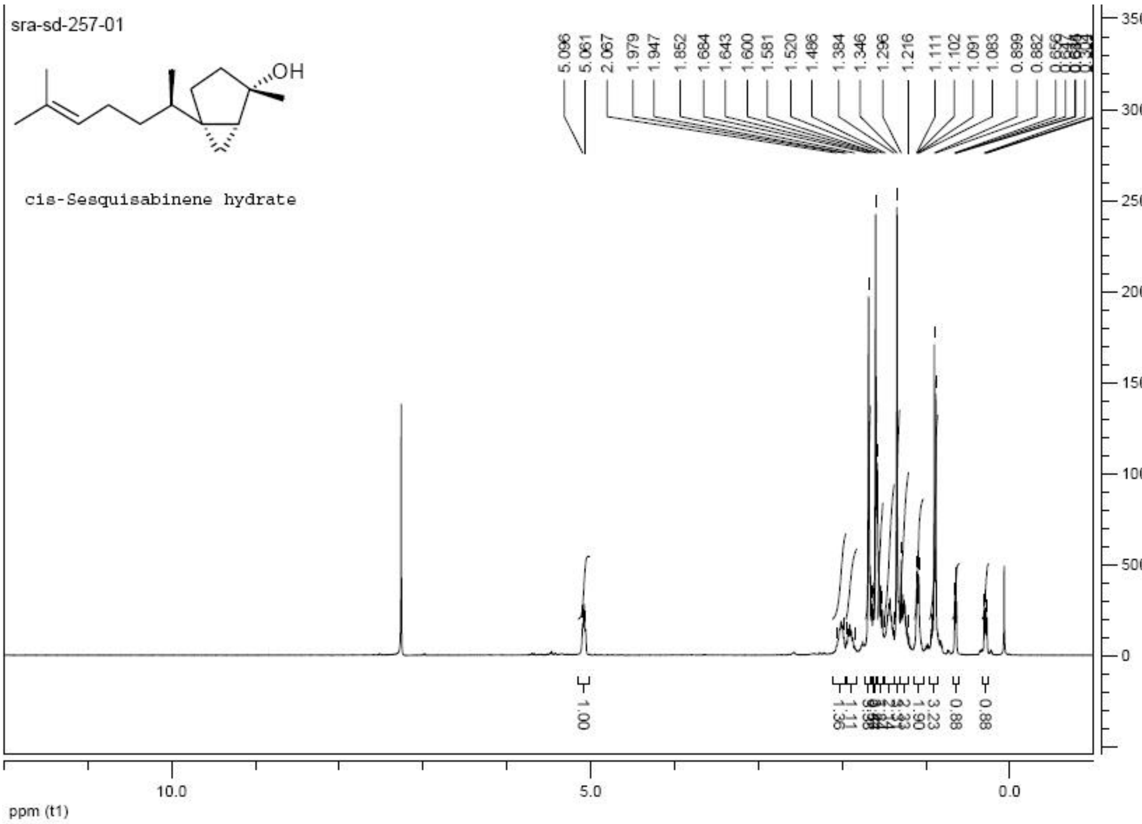
1.938
1.888
1.781
1.778
1.676
1.673
1.647
1.610
1.598
1.570
1.432
1.385
1.352
1.295
1.227
1.208
1.140
1.114
1.111
1.103
1.099
1.090
1.083
1.075
1.071
0.925
0.902
0.364
0.349
0.347
0.339
0.336
0.321
0.319
0.234
0.222
0.205
20000
15000
10000
50000
0
2.10
1.17
3.15
1.02
3.33
2.63
1.06
5.23
1.08
1.09
3.13
1.04
1.01
2.00
1.50
1.00
0.50
ppm (t1)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OH
cis-Sesquisabinene hydrate
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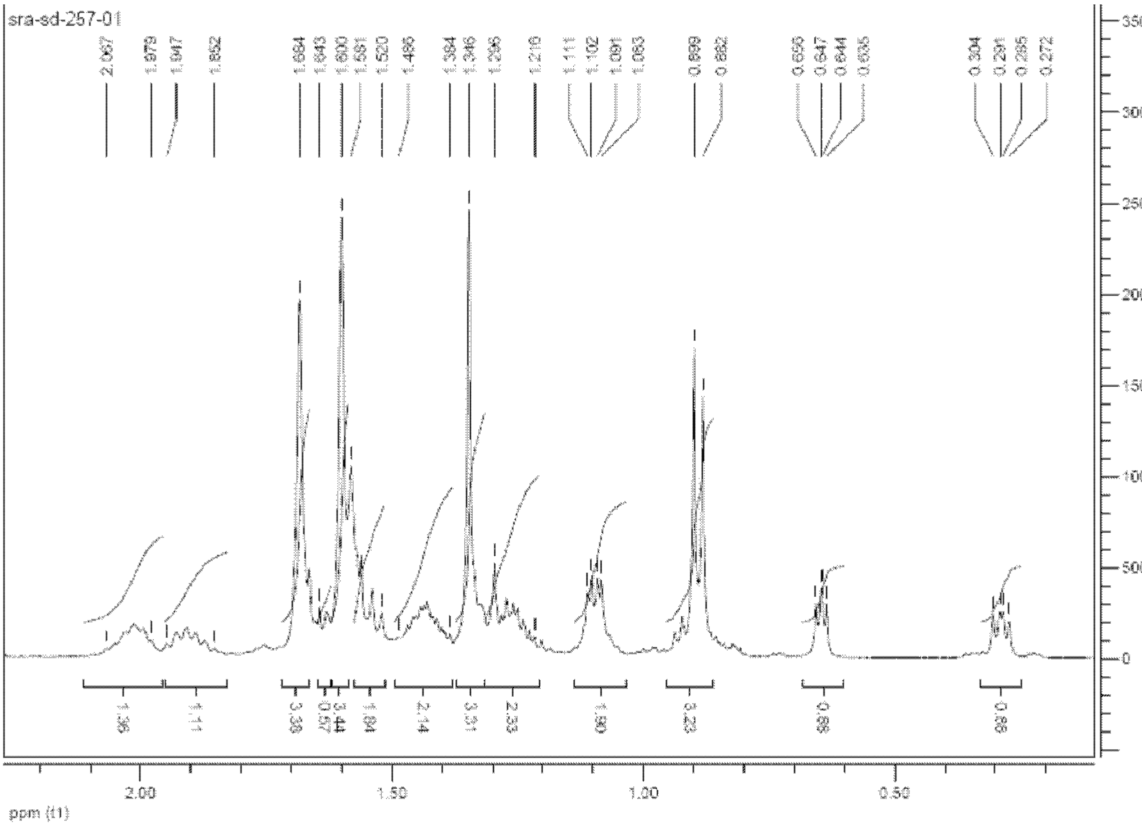
5.061
2.067
1.979
1.947
1.852
1.684
1.643
1.600
1.581
1.520
1.486
1.384
1.346
1.296
1.216
1.111
1.102
1.091
1.083
0.899
0.882
1.00
1.36
1.11
3.23
0.88
0.88
10.0
5.0
0.0
ppm (t1)
3500
3000
2500
2000
1500
1000
500
0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1.947
1.852
1.684
1.643
1.600
1.581
1.520
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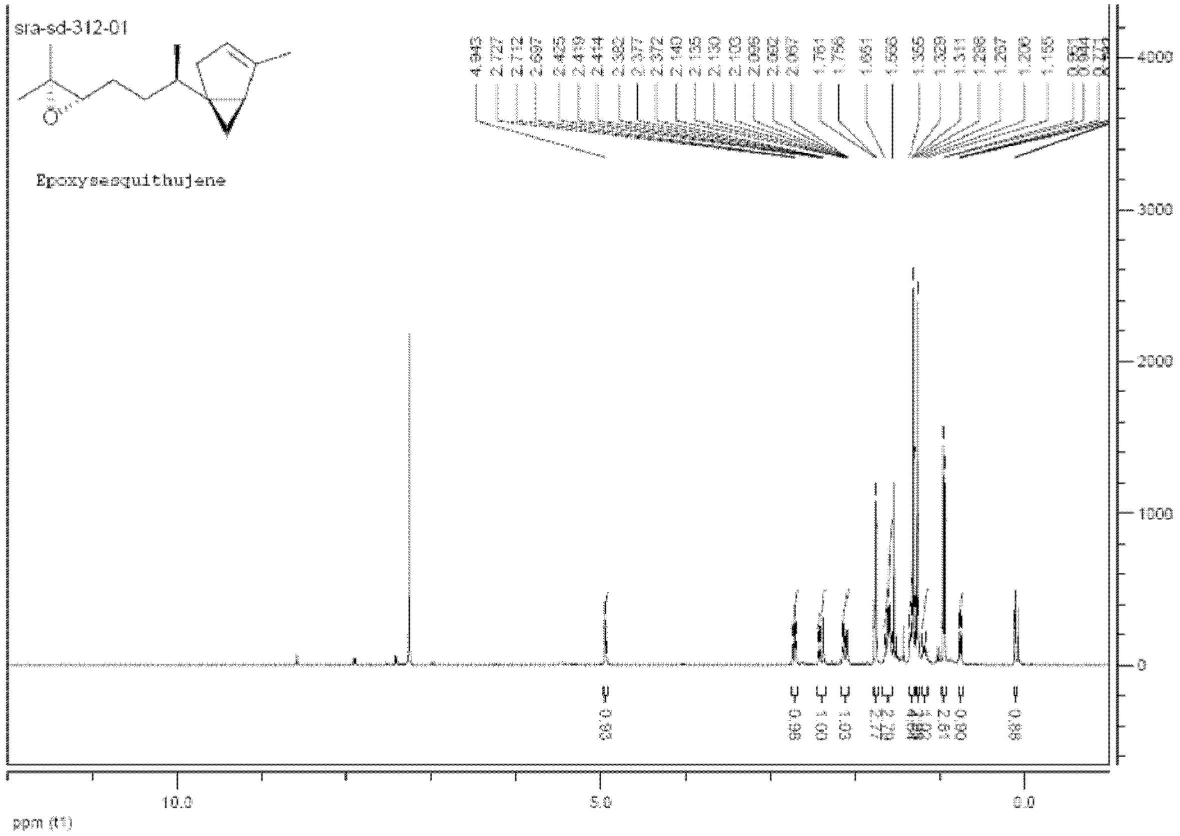
1.384
1.346
1.296
1.216
1.111
1.102
1.091
1.083
0.899
0.882
0.656
0.647
0.644
0.635
0.304
0.291
0.285
0.272
1.36
1.11
3.38
0.57
3.44
1.84
2.14
3.31
2.33
1.90
3.23
0.88
0.88
2.00
1.50
1.00
0.50
ppm (t1)
3500
3000
2500
2000
1500
1000
500
0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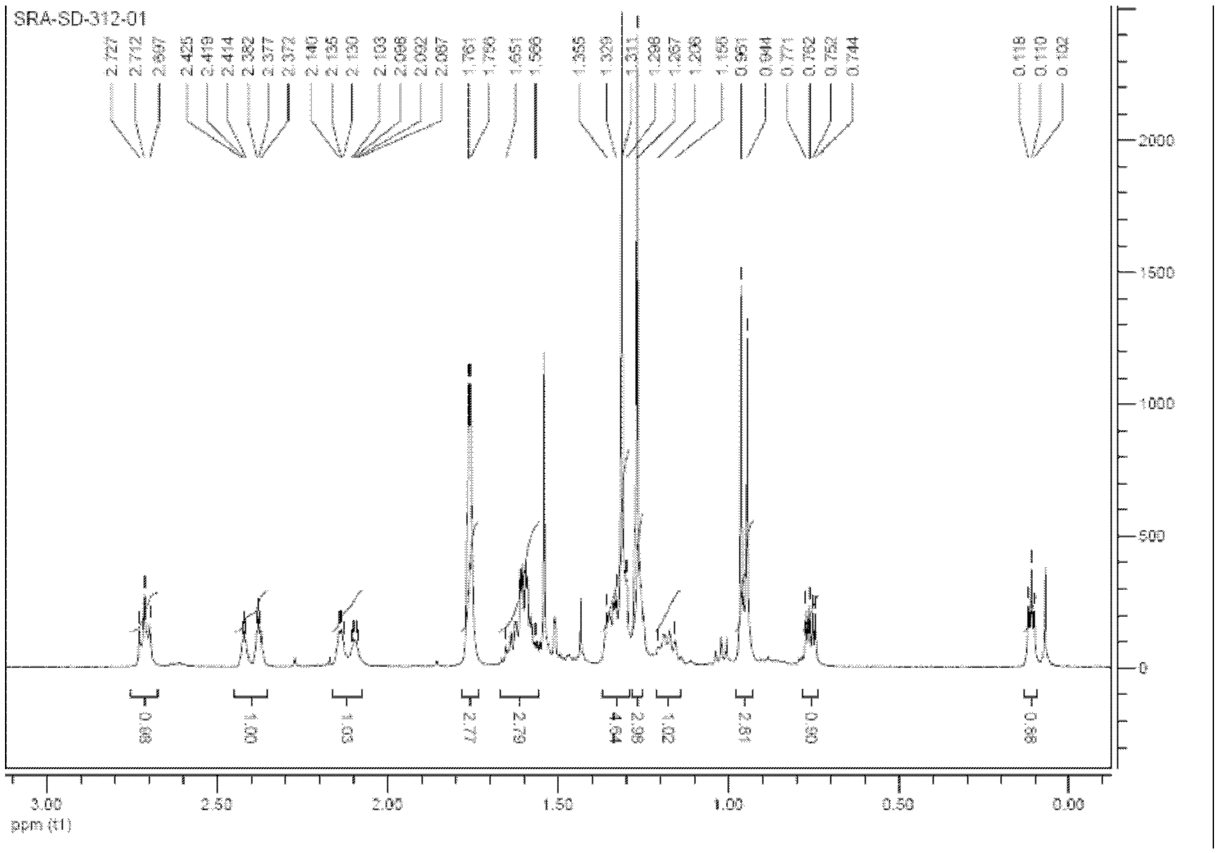
Epoxysesquithujene
ppm (t1)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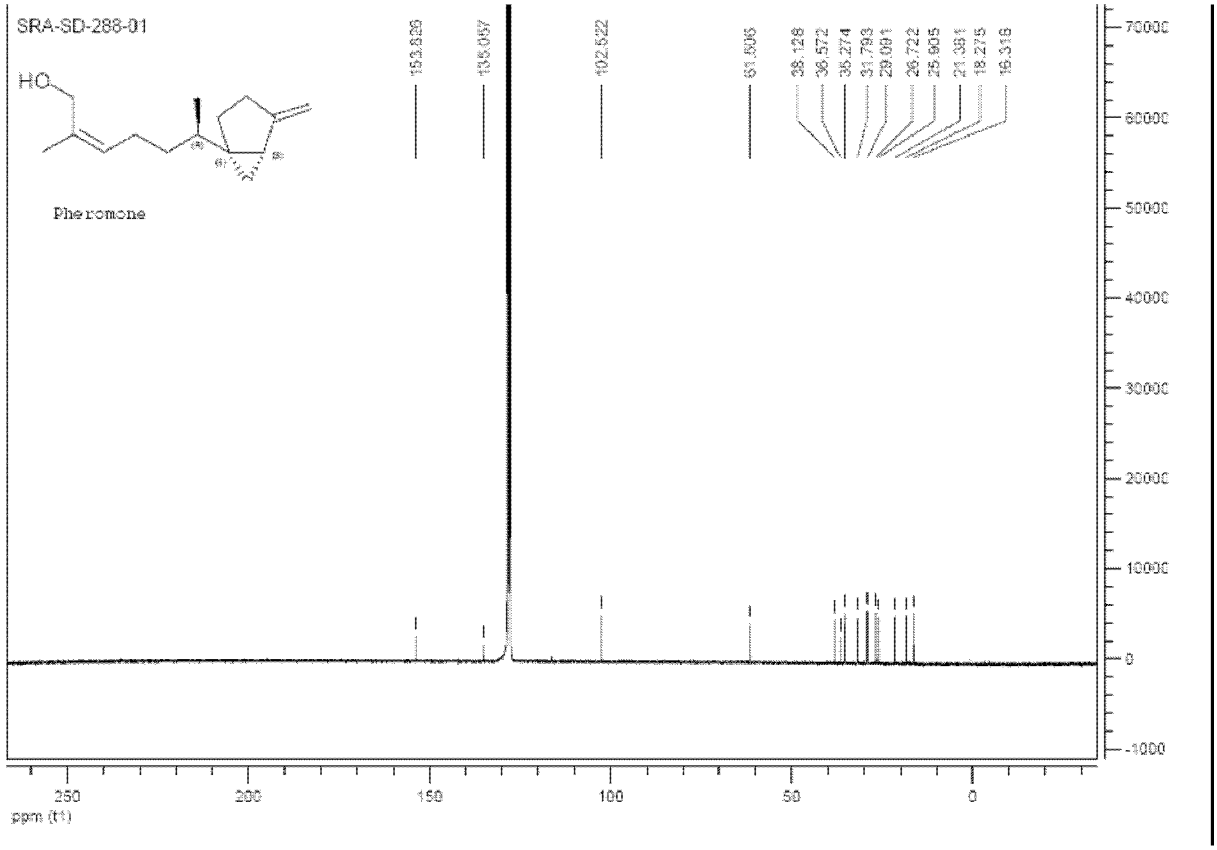
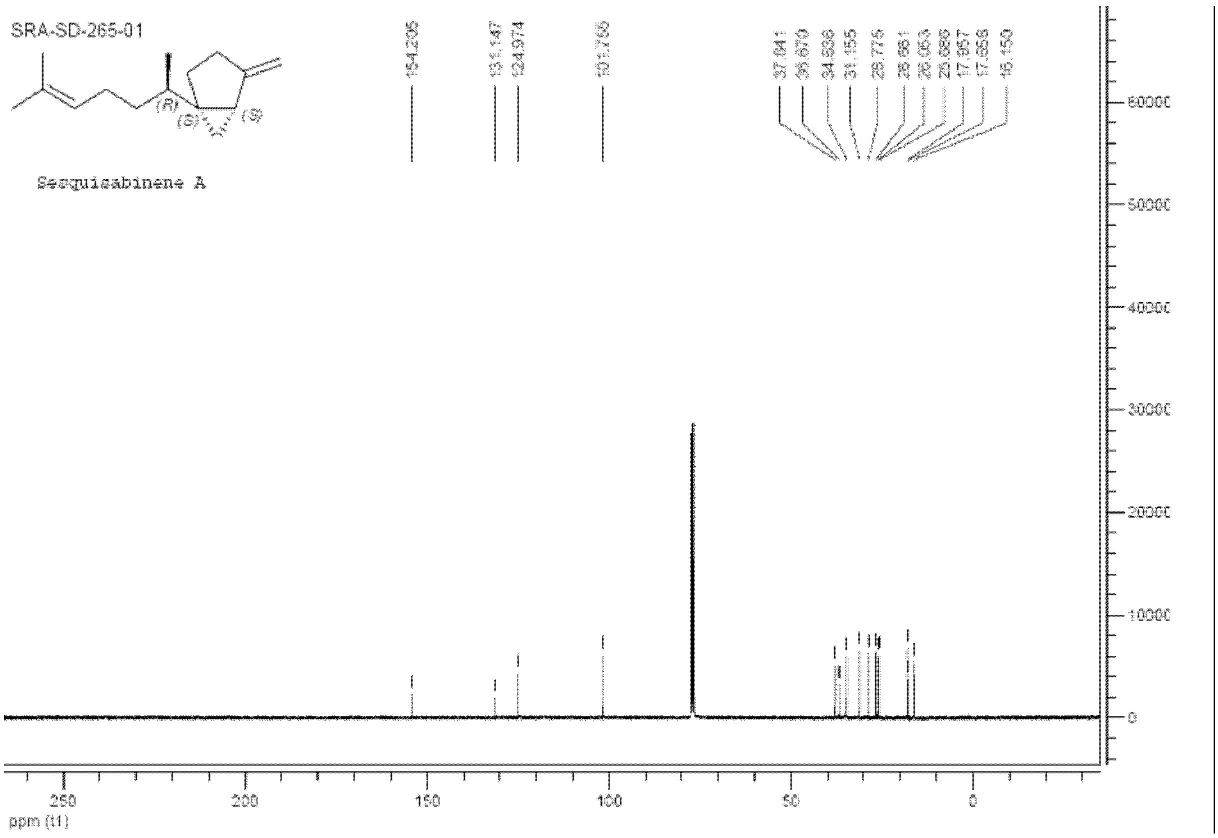
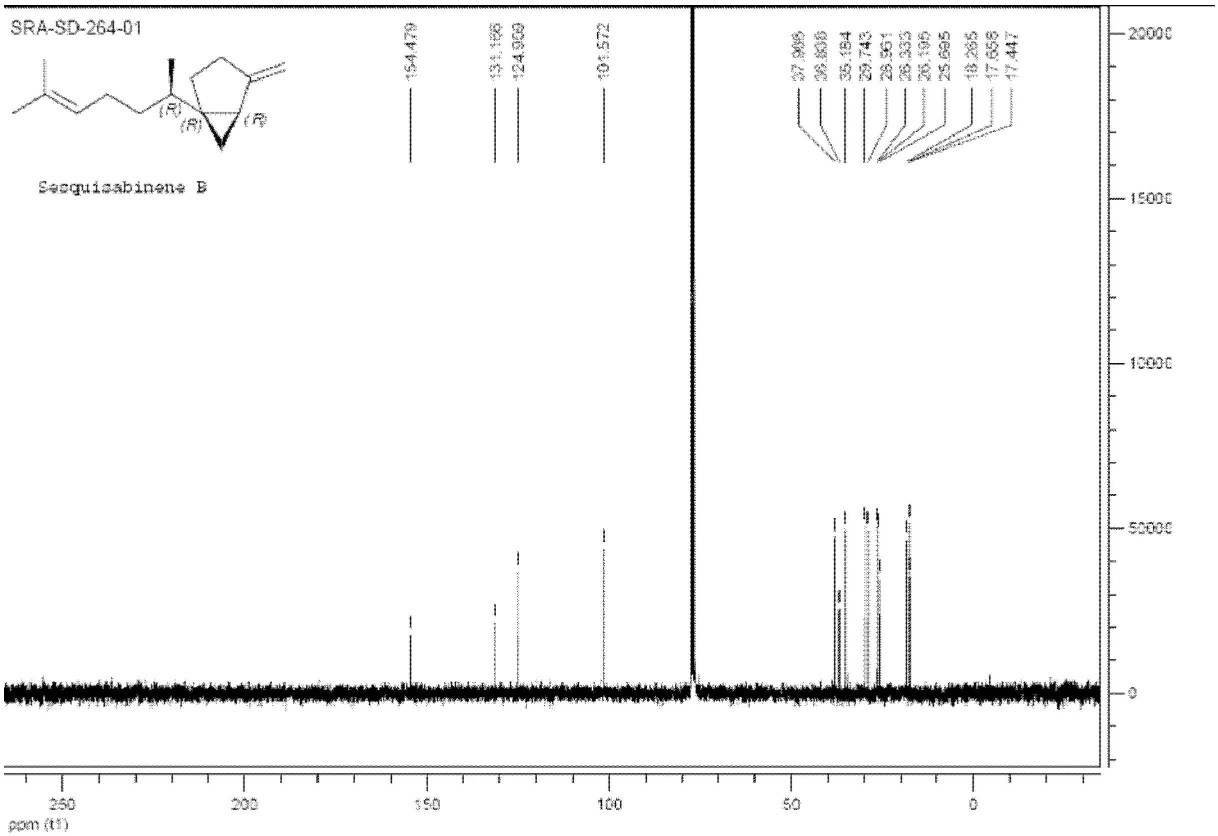
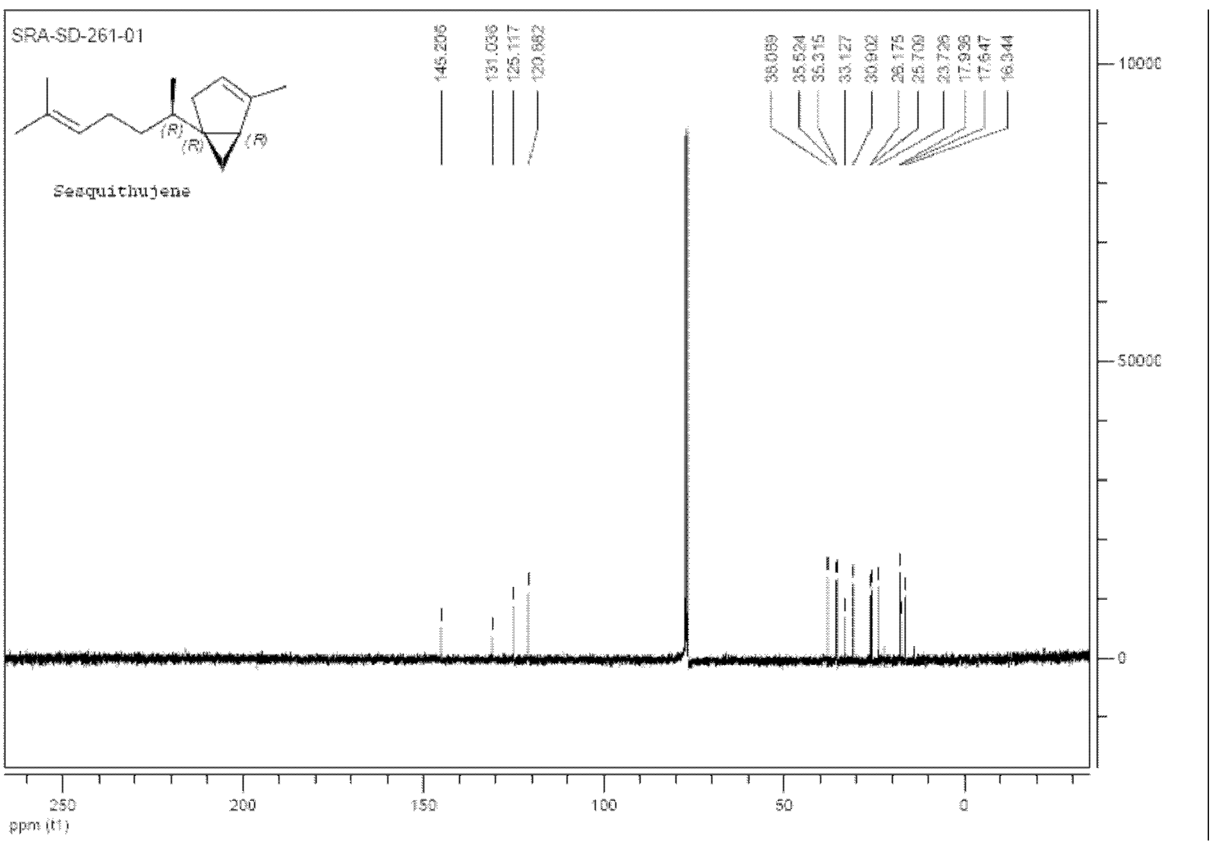
ppm (t1)

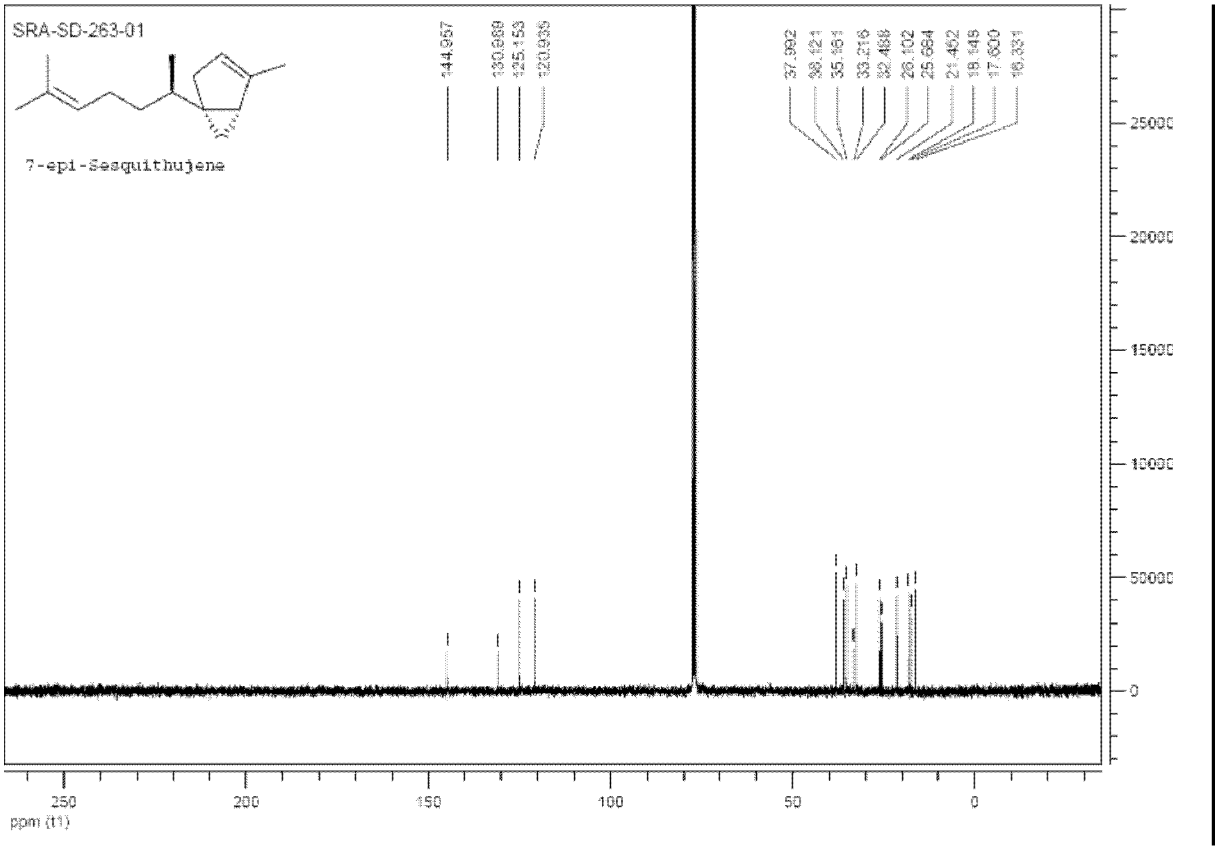
^{13}C NMR SPECTRA



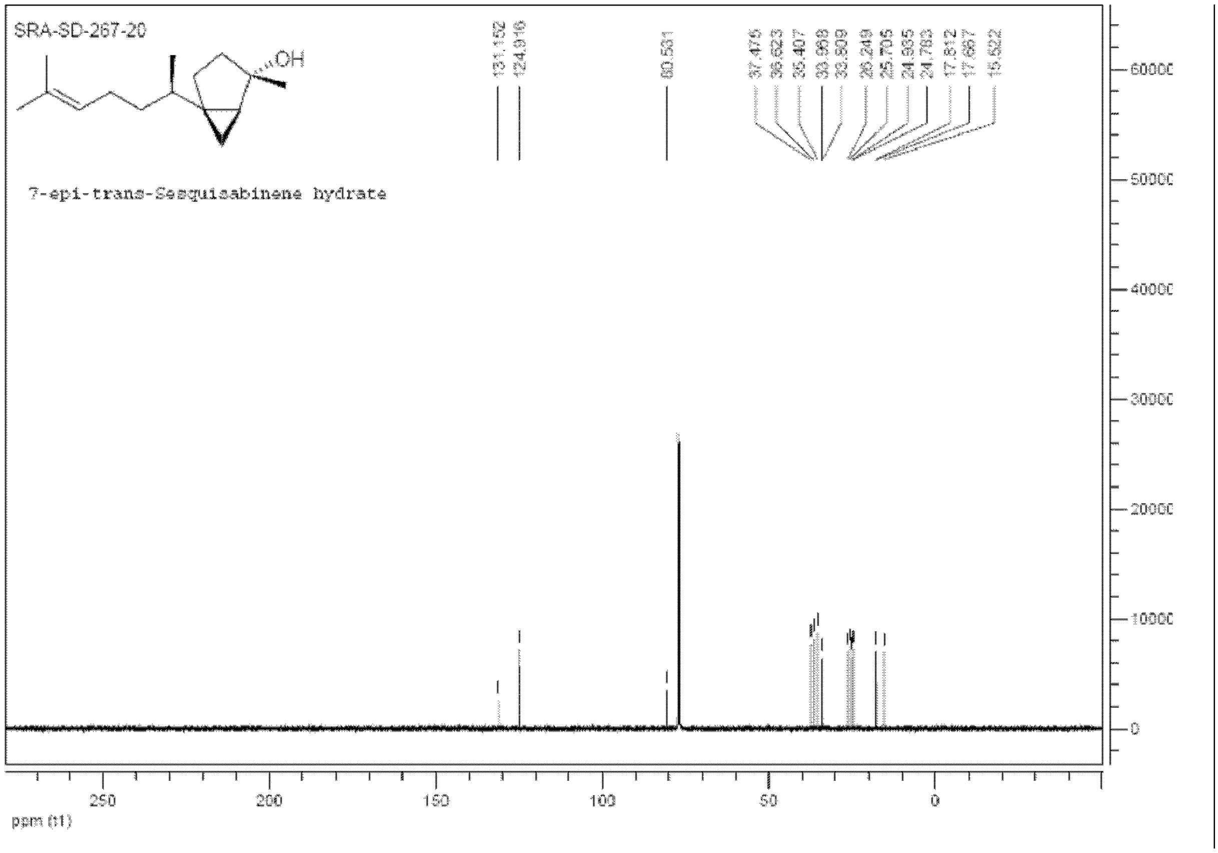



SRA-SD-264-01
Sesquisabinene B
ppm (t1)

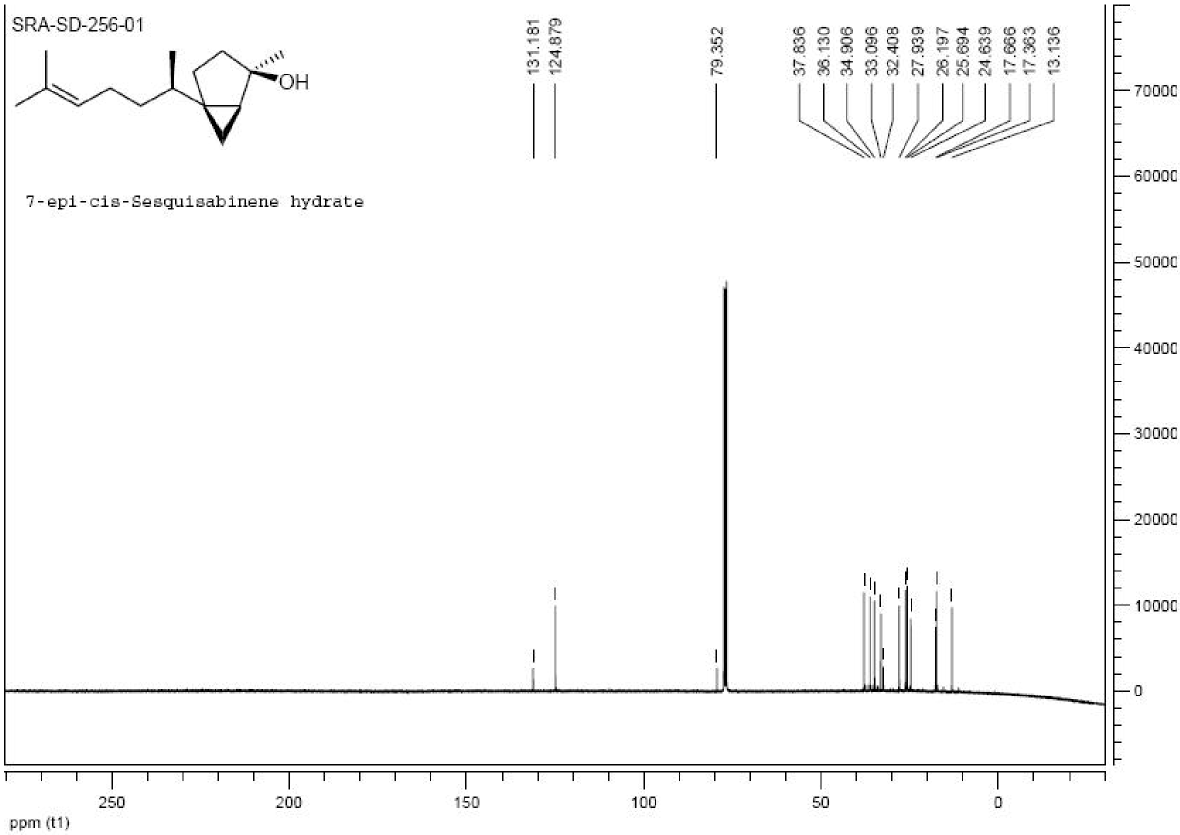

SRA-SD-261-01
Sesquithujene
ppm (t1)

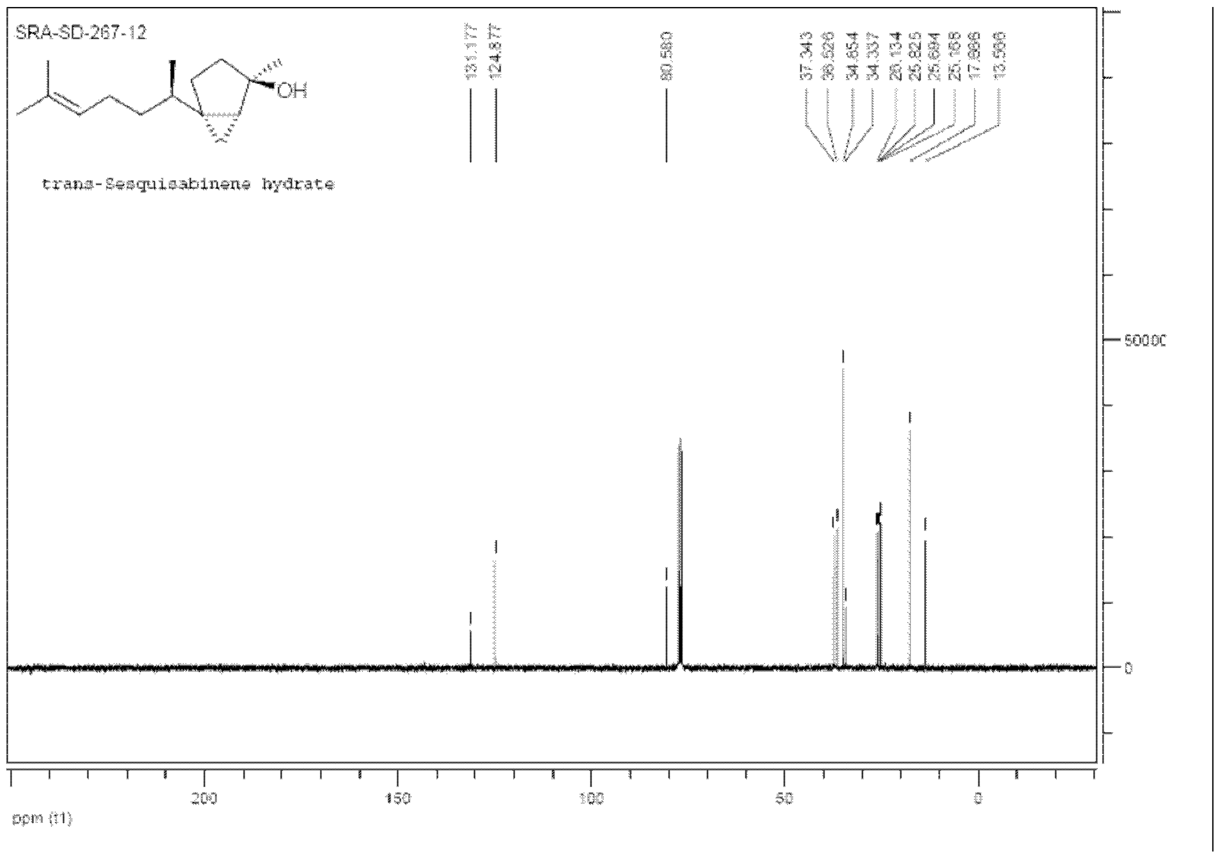


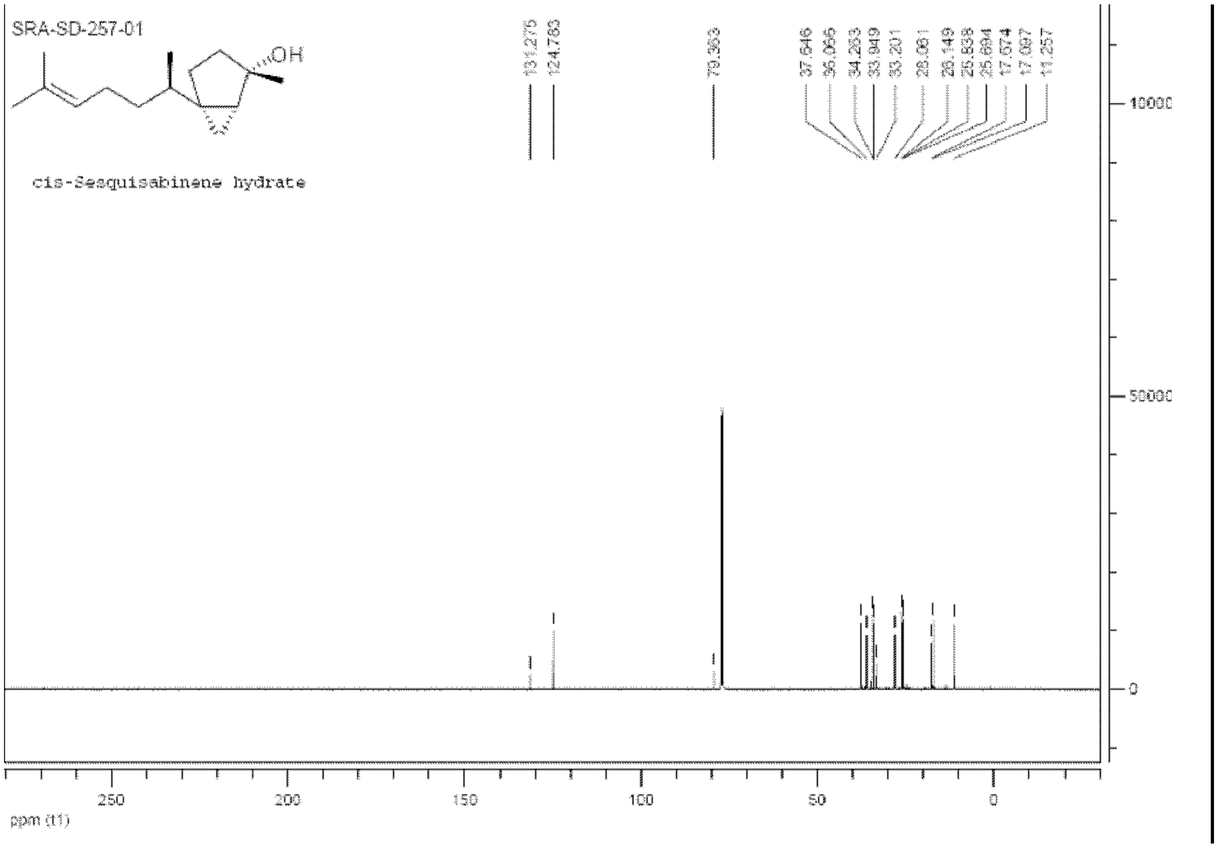
SRA-SD-263-01
7-epi-Sesquithujene
144.957
130.969
125.153
120.935
37.992
36.121
35.161
33.216
32.488
26.102
25.684
21.452
18.148
17.600
16.331
ppm (t1)

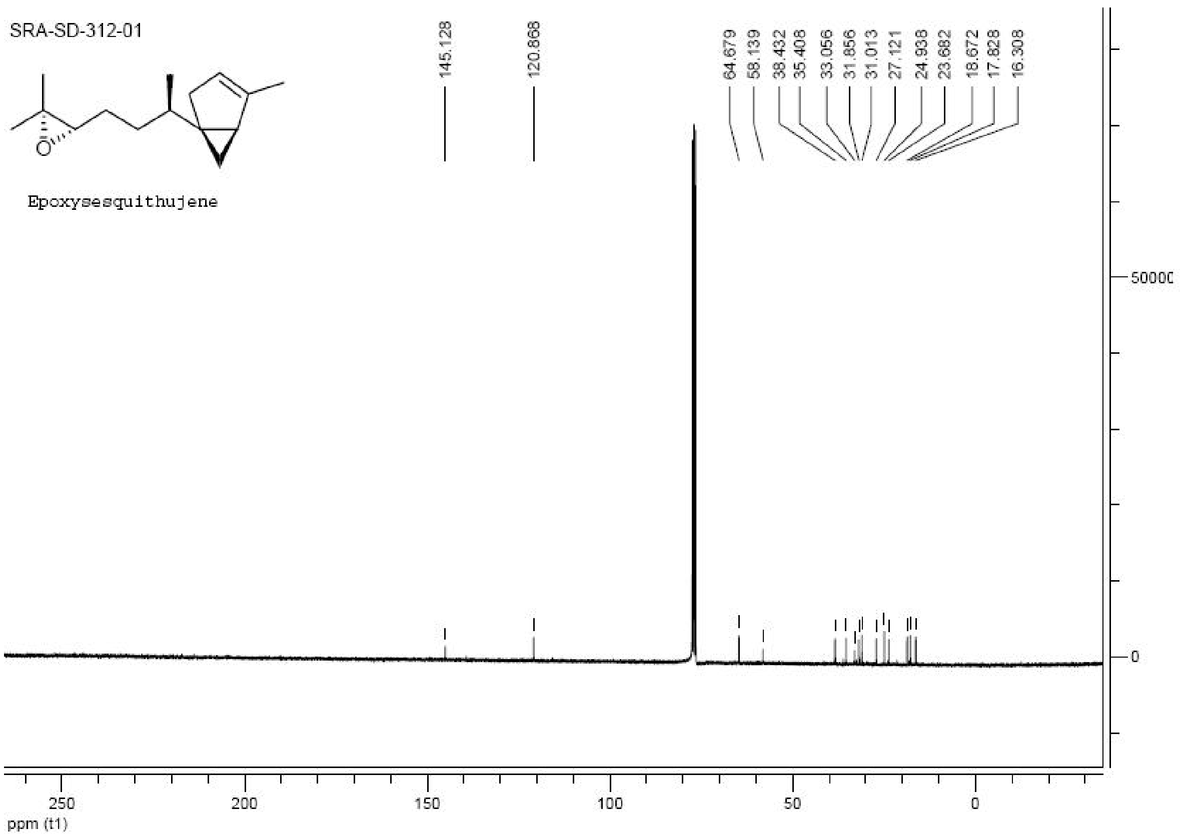


SRA-SD-267-20
OH
7-epi-trans-Sesquisabinene hydrate
131.152
124.916
80.531
37.475
36.623
35.407
33.968
33.809
26.249
25.705
24.935
24.783
17.812
17.667
15.522
ppm (t1)


SRA-SD-256-01
OH
7-epi-cis-Sesquisabinene hydrate
131.181
124.879
79.352
37.836
36.130
34.906
33.096
32.408
27.939
26.197
25.694
24.639
17.666
17.363
13.136
70000
60000
50000
40000
30000
20000
10000
0
250
200
150
100
50
0
ppm (t1)


SRA-SD-267-12
OH
trans-Sesquisabinene hydrate
131.177
124.877
80.580
37.343
36.526
34.854
34.337
26.134
25.825
25.694
25.168
17.886
13.566
50000
0
200
150
100
50
0
ppm (t1)


SRA-SD-257-01
OH
cis-Sesquisabinene hydrate
131.275
124.783
79.363
37.646
36.066
34.263
33.949
33.201
28.061
26.149
25.638
25.694
17.674
17.097
11.257
100000
50000
0
250
200
150
100
50
0
ppm (t1)


SRA-SD-312-01
O
Epoxysesquithujene
145.128
120.868
64.679
58.139
38.432
35.408
33.056
31.856
31.013
27.121
24.938
23.682
18.672
17.828
16.308
50000
0
250
200
150
100
50
0
ppm (t1)