Discovery of the Aggregation Pheromone of the Brown Marmorated Stink Bug (*Halyomorpha halys*) through the Creation of Stereoisomeric Libraries of 1-Bisabolen-3-ols

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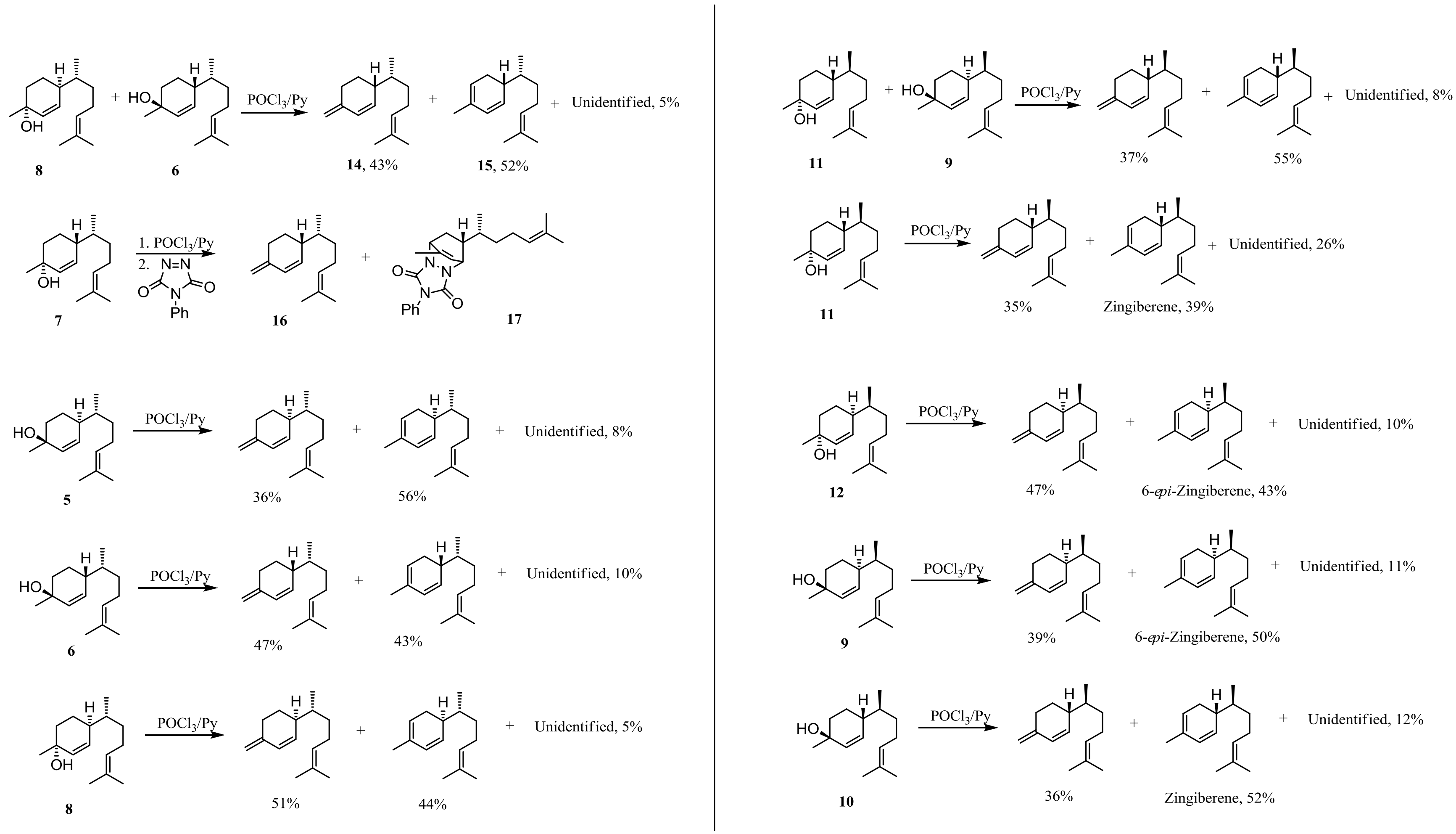
Supporting Information



Scheme S1. Dehydrations of bisaboladienols with 7*R* configurations (left) and 7*S* configurations (right) with phosphorus(V) oxychloride in pyridine at 0 to 25 ^{o}C.

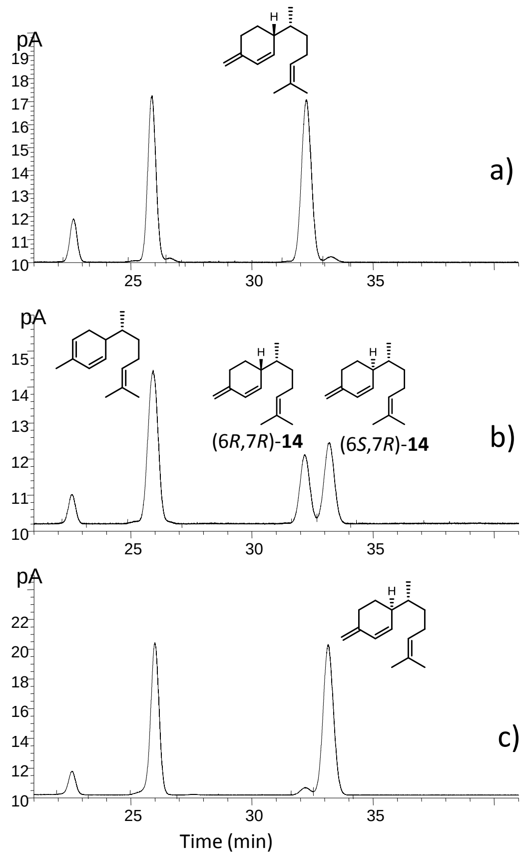


Figure. S1. Gas chromatograms of bisabolatriene dehydration products on Hydrodex-β-6TBDM at 110 °C, isothermal; H_2 2.0 ml/min.: a) from alcohol **6**; b) from **6** + **8**; c) from **8**.

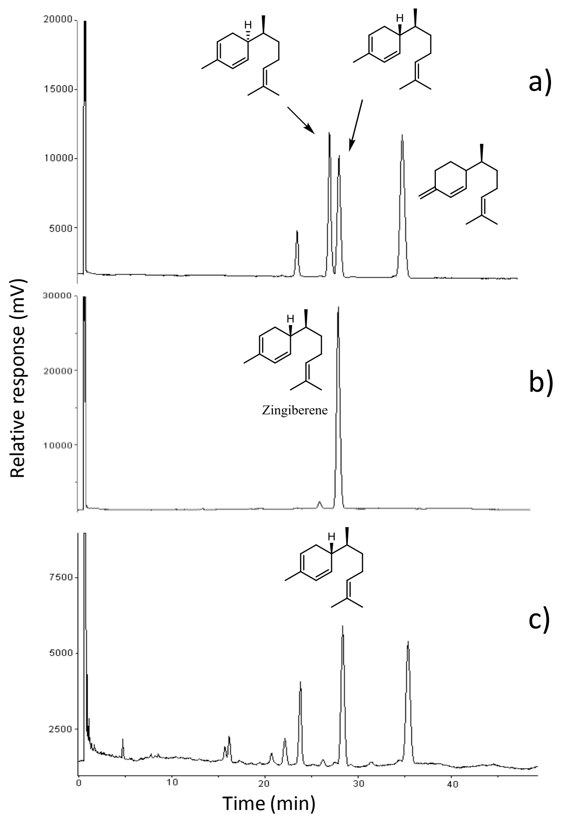


Figure S2. Gas chromatograms of bisabolatrienes on Hydrodex-β-6TBDM at 110 ºC; H_2 1.5 ml/min: a) from alcohols **9 + 11**; b) zingiberene; c) from alcohol **11**.

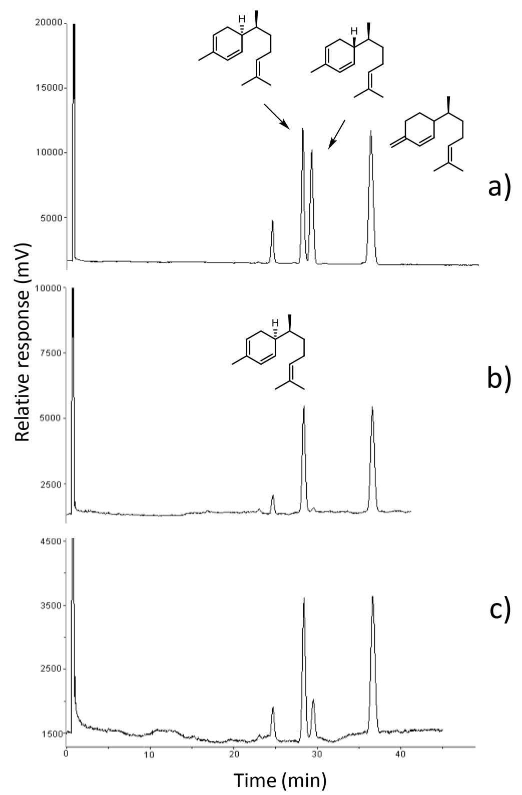


Figure S3. Gas chromatograms of bisabolatrienes on Hydrodex-β-6TBDM at 110 ºC; H_2 1.5 ml/min: a) from alcohols **9 + 11**; b) from alcohol **12**; c) co-injection of a) and b).

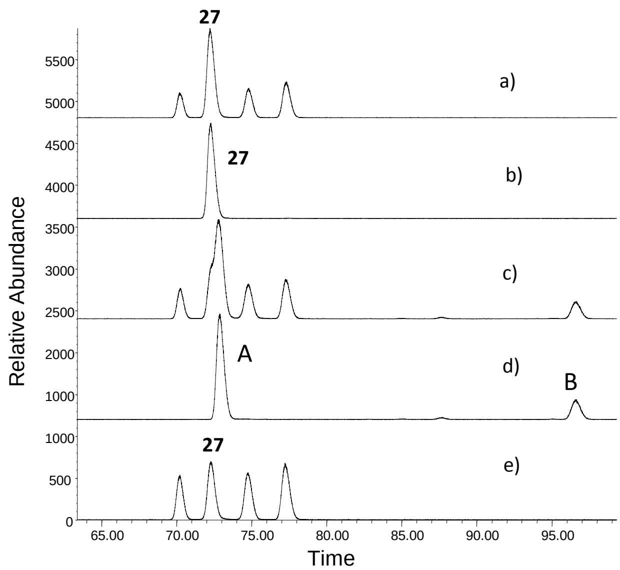


Figure S4. Segments of GC-MS total ion chromatograms on Hydrodex-β-6TBDM column, He 1.0 ml/min, 140 ^{o}C isothermal: a) Co-injection of **27** and *cis*-(7*S*)-10,11-epoxy-1-bisabolen-3-ols; b) 3*R*,6*R*,7*S*,10*S* stereoisomer **27**; c) Co-injection of *H. halys* male aeration and *cis*-(7*S*)-10,11-epoxy-1-bisabolen-3-ols; d) *Halyomorpha halys* male aeration; e) *cis*-(7*S*)-10,11-epoxy-1-bisabolen-3-ols

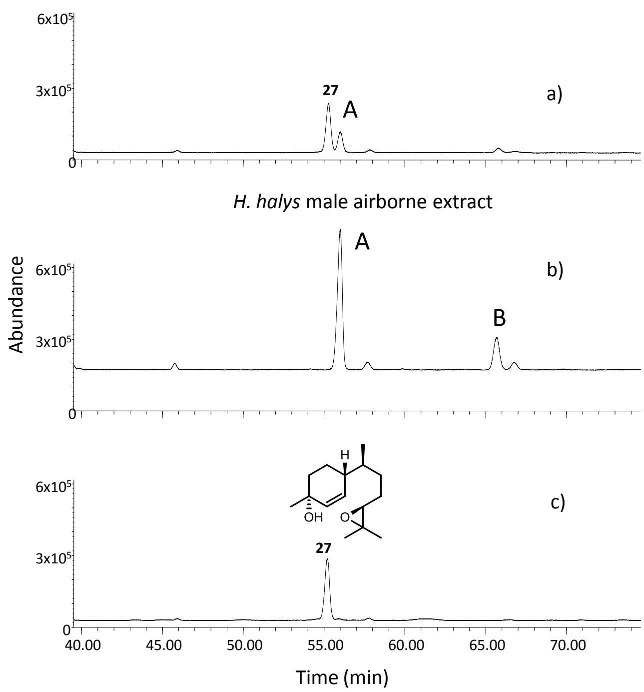


Figure S5. Segments of GC-MS total ion chromatograms on Chiraldex G-TA, He 1.0 ml/min, 50(3) to 140 ºC at 10º/min; a) Co-injection of *H. halys* male aeration and **27**; b) *H. halys* male aeration; c) stereoisomer **27**

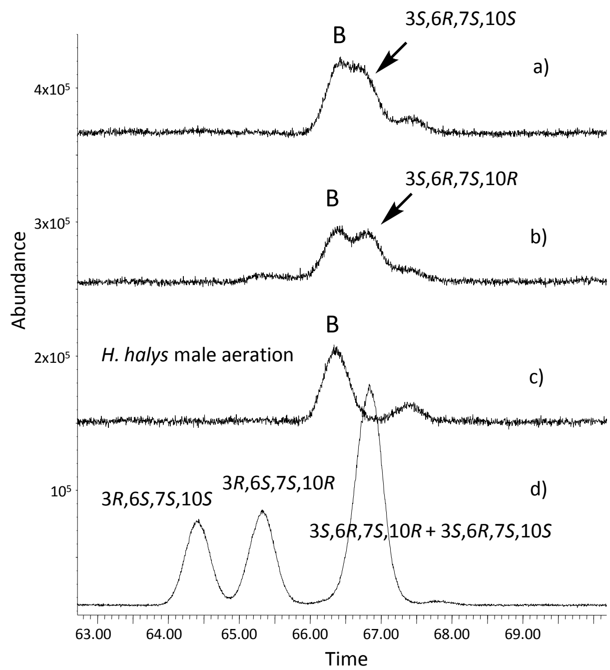


Figure S6. Segments of GC-MS total ion chromatograms on Chiraldex G-TA, He 1.0 ml/min, 50(3) to 140 ºC at 10º/min; a) Co-injection of *H. halys* male aeration and (3*S*,6*R*,7*S*,10*S*)-10,11-epoxy-1-bisabolen-3-ol; b) Co-injection of *H. halys* male aeration and (3*S*,6*R*,7*S*,10*R*)-10,11-epoxy-1-bisabolen-3-ol; c) *H. halys* male aeration; d) *trans*-(7*S*)-10,11-epoxy-1-bisabolen-3-ols

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 13

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: 13

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Temperature:    110 K

                Calculated                 Reported
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Hall group      P 2yb                      P 2yb
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Sum formula     C15 H28 O3                 C15 H28 O3
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F000'           284.81
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Tmin'           0.769

Correction method= ANALYTICAL

Data completeness= 1.82/1.00      Theta(max)= 71.840

R(reflections)= 0.0253( 2848)     wR2(reflections)= 0.0655( 2921)

S = 1.062                  Npar= 180
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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

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Alert level G

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PLAT791_ALERT_4_G Note: The Model has Chirality at C7     (Verify)          R
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PLAT860_ALERT_3_G Note: Number of Least-Squares Restraints .......          4
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   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

   0 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
   2 ALERT type 3 Indicator that the structure quality may be low
   4 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
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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

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Datablock 13 - ellipsoid plot

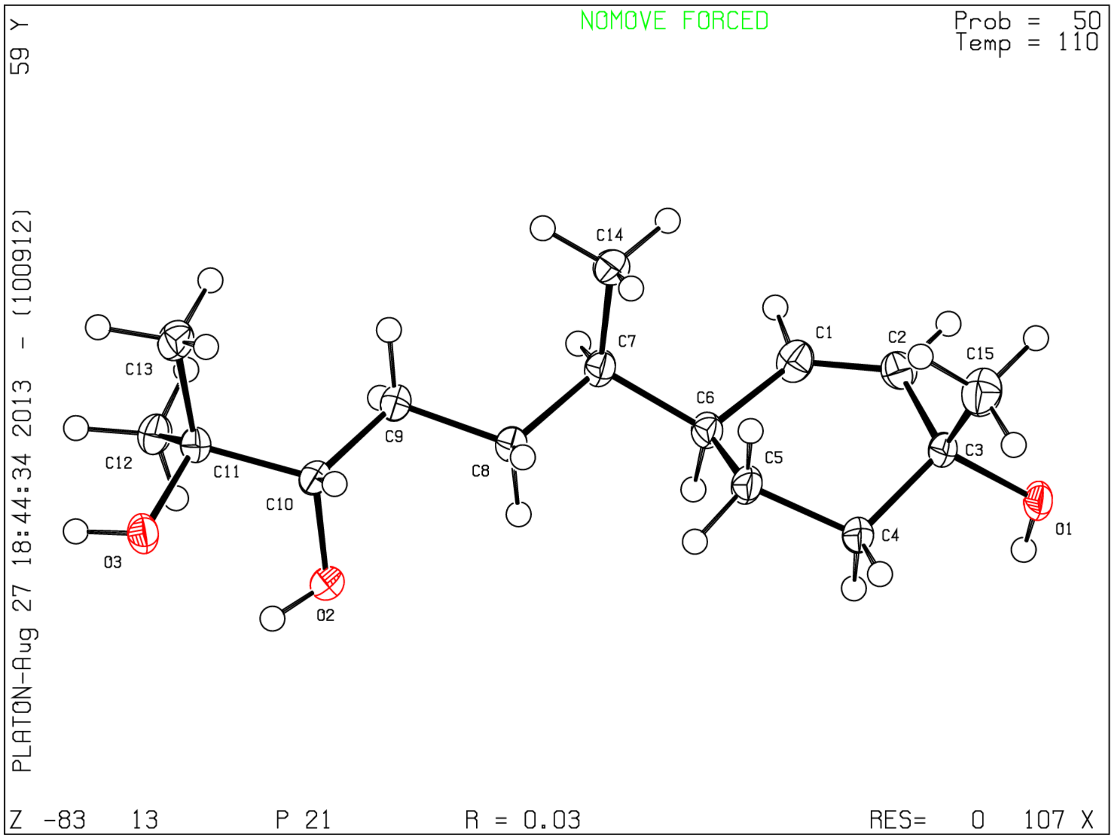


Table S1. Synthesis, specific rotations and mass-spectrometry data of stereoisomeric 1,10-bisaboladien-3-ols

Starting ketone	Chiral ligand	Product composition[a], %	Yield, %	$[\alpha]_D^{20}$ (c,CH_2Cl_2)	HREIMS[b]	LRMS, *m/z* (% relative intensity)[c]
1	(*S*)-BINAP	**7**/**5** 91:9	30[d]	-15.43(1.27)	222.2000	222 (M^+, 5), 207 (19), 204 (19), 189 (8), 161 (19), 148 (13), 137 (26), 119 (82), 109 (36), 93 (50), 69 (100), 55 (32), 43 (33), 41 (48)
		8/**6** 89:11	5[e]	+32.52 (3.05	222.1992	222 (M^+, 5), 207 (28), 204 (30), 189 (8), 161 (28), 148 (6), 137 (36), 119 (100), 109 (34), 93 (61), 69 (100), 55 (29), 43 (33), 41 (45)
1	(*R*)-BINAP	**5**/**7** 96:4	24	-1.24 (4.27)	222.2001	222 (M^+, 4), 207 (17), 204 (13), 189 (10), 161 (18), 148 (10), 137 (24), 119 (69), 109 (33), 93 (41), 69 (100), 55 (29), 43 (38), 41 (50)
		6/**8** 86:14	5	-58.82 (0.70)	222.2007	222 (M^+, 4), 207 (26), 204 (25), 189 (7), 161 (21), 148 (6), 137 (34), 119 (91), 109 (30), 93 (53), 69 (100), 55 (29), 43 (37), 41 (49)
2	(*S*)-BINAP	**11**/**9** 96:4	26[f]	+1.1 (c 2.05)	222.2009	222 (M^+, 5), 207 (17), 204 (11), 189 (10), 161 (16), 148 (11), 137 (27), 119 (68), 109 (34), 93 (34), 69 (100), 55 (27), 43 (35), 41 (42)
		12/**10** 93:7	3[f]	+53.40 (c 0.5)	222.2006	222 (M^+, 3), 207 (19), 204 (15), 189 (5), 161 (15), 148 (4), 137 (30), 119 (70), 109 (27), 93 (36), 69 (100), 55 (30), 43 (40), 41 (46)
2	(*R*)-BINAP	**9**/**11** 93:7	31	+14.2 (c 1.10)	222.2008	222 (M^+, 5), 207 (16), 204 (17), 189 (8), 161 (17), 148 (11), 137 (23), 119 (75), 109 (31), 93 (47), 69 (100), 55 (28), 43 (34), 41 (49)
		10/**12** 96:4	6	-37.7 (c 2.0)	222.2005	222 (M^+, 4), 207 (23), 204 (21), 189 (6), 161 (21), 148 (5), 137 (32), 119 (86), 109 (31), 93 (53), 69 (100), 55 (30), 43 (37), 41 (51)

[a] Determined by integration of H-14 signals in the ^1H NMR spectra; [b]calcd for $C_{15}H_{26}O$ 222.1984; [c] GC-EIMS analyses on HP-5MS; [d] second purification: hexane/ethyl acetate/MeOH, 10:1:0.2 to 10:1:0.4; [e] second purification: hexane/ethyl acetate, 4:1 to 3:1; [f] first purification: hexane/ethyl acetate/MeOH, 10:0.5:0.4, second purification: hexane/ethyl acetate, 6:1 to 4:1

Table S2. ^{1}H NMR data of 1,10-bisaboladien-3-ols

		^{1}H NMR Chemical shifts (δ, ppm), multiplicities, *J* coupling constants, Hz												
		Position												
No	Abs. Conf.	1	2	4	5	6	7	8	9	10	12	13	14	15
5	3*S*,6*S*,7*R*	5.63 dt, 10.1, 1.5	5.67 dt, 10.1, 1.9	1.82 d, 11.5; 1.54, m	1.56 m; 1.46 m	2.05 m	1.56 m	1.42 m; 1.22 m	1.98 m; 2.05 m	5.14 t, 7.2, 1.4	1.64 s	1.71 s	0.89 d, 6.9	1.26 s
6	3*S*,6*R*,7*R*	5.57 ddd, 10.1, 2.1, 1.1	5.61, ddd, 10.1, 2,5, 1.6	1.87 d, 12.2; 1.64 m	1.72 m; 1.43 m	2.12 m	1.48 m	1.40 m; 1.19 m	1.96 m; 2.05 m	5.13 t, 7.2	1.63 s	1.71 s	0.89 d, 6.9	1.26 s
7	3*R*,6*R*,7*R*	5.6 s	5.67 s	1.82 m; 1.55 m	1.60 m; 1.51 m	2.03 m	1.53 m	1.41 m; 1.22 m	2.06 m; 1.97 m	5.14 t, 7.0	1.63 s	1.71 s	0.91 d, 6.9	1.26 s
8	3*R*,6*S*,7*R*	5.53 dt, 10.1, 1.1	5.6 dt, 10.1, 2.0	1.87 d 11.9, 1.63 m	1.69 m; 1.4 m	2.14 m	1.53 m	1.40 m; 1.20 m	2.05 m; 1.97 m	5.14 t, 7.1	1.63 s	1.71 s	0.85 d, 6.9	1.26 s
9	3*S*,6*S*,7*S*	5.67 s	5.6 s	1.82 m; 1.55 m	1.59 m; 1.51 m	2.03 m	1.52 m	1.40 m; 1.22, m	2.06 m; 1.96 m	5.14 t, 7.1	1.63 s	1.71 s	0.91 d, 6.8	1.26 s
10	3*S*,6*R*,7*S*	5.53 ddd, 10.2, 2.2, 1.1	5.61 ddd, 10.2, 2.4, 1.6	1.87 m; 1.64 m	1.69 m; 1.41 m	2.14 m	1.53 m	1.40 m; 1.20 m	2.05 m; 1.97 m	5.14 t, 7.1	1.63 s	1.71 s	0.85 d, 6.9	1.26 s
11	3*R*,6*R*,7*S*	5.63 dt, 10.2, 1.1	5.66 dt, 10.2, 1.8	1.82 m; 1.54 m	1.56 m; 1.46 m	2.05 m	1.56 m	1.42 m; 1.23 m	2.06 m; 1.98 m	5.15 t, 7.1	1.64 s	1.71 s	0.87 d, 6.9	1.26 s
12	3*R*,6*S*,7*S*	5.5 ddd, 10.2, 2.1, 1.1	5.61 ddd, 10.2,2.4, 1.6	1.87 d, 12.4; 1.64, m	1.72 m 1.43 m	2.12 m	1.48 m	1.39 m; 1.19 m	2.05 m; 1.96 m	5.13 t, 7.2	1.63 s	1.71 s	0.89 d 6.8	1.26 s

Table S3. ^{13}C NMR data of 1,10-bisaboladien-3-ols

No.	Abs. Conf.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
		^{13}C NMR Chemical shifts (δ, ppm), multiplicities														
		Position														
5	3*S*,6*S*,7*R*	133.9 CH	133.6 CH	67.0 C	37.3 CH_2	20.1 CH_2	40.5 CH	36.3 CH	34.2 CH_2	26.0 CH_2	124.7 CH	131.2 C	17.3 CH_3	25.4 CH_3	15.5 CH_3	29.5 CH_3
6	3*S*,6*R*,7*R*	130.5 CH	135.1 CH	69.4 C	38.4 CH_2	24.2 CH_2	40.7, CH	36.4 CH	33.8 CH_2	26.0 CH_2	124.7 CH	131.1 C	17.3 CH_3	25.4 CH_3	16.2 CH_3	28.3 CH_3
7	3*R*,6*R*,7*R*	132.7* CH	133.9* CH	67.1 C	37.5 CH_2	22.1 CH_2	41.1, CH	36.3 CH	33.6 CH_2	26.0 CH_2	124.7 CH	131.1 C	17.3 CH_3	25.4 CH_3	16.2 CH_3	29.5 CH_3
8	3*R*,6*S*,7*R*	131.7 CH	134.8 CH	69.4 C	38.3 CH_2	22.3 CH_2	40.2, CH	36.3 CH	34.1 CH_2	25.9 CH_2	124.7 CH	131.1 C	17.3 CH_3	25.4 CH_3	15.4 CH_3	28.2 CH_3
9	3*S*,6*S*,7*S*	133.9* CH	132.7* CH	67.1 C	37.5 CH_2	22.1 CH_2	41.1, CH	36.3 CH	33.6 CH_2	26.0 CH_2	124.7 CH	131.1 CH	17.3 CH_3	25.4 CH_3	16.2 CH_3	29.5 CH_3
10	3*S*,6*R*,7*S*	131.7 CH	134.8 CH	69.4 C	38.3 CH_2	22.3 CH_2	40.2, CH	36.3 CH	34.2 CH_2	25.9 CH_2	124.7 CH	131.1 CH	17.3 CH_3	25.4 CH_3	15.4 CH_3	28.2 CH_3
11	3*R*,6*R*,7*S*	133.9 CH	133.6 CH	67.0 C	37.3 CH_2	20.1 CH_2	40.5, CH	36.3 CH	34.2 CH_2	26.0 CH_2	124.7 CH	131.2 C	17.3 CH_3	25.4 CH_3	15.5 CH_3	29.5 CH_3
12	3*R*,6*S*,7*S*	130.5 CH	135.1 CH	69.4 C	38.4 CH_2	24.2, CH_2	40.7 CH	36.4 CH	33.7 CH_2	26.0 CH_2	124.7 CH	131.1 C	17.3 CH_3	25.4 CH_3	16.2 CH_3	28.3 CH_3

*May be reversed

Table S4. Yields, specific rotations, and mass spectrometry data of stereoisomeric triols and epoxybisabolenols

Compd. No.	Absolute configuration	Yield, %	$[\alpha]_D^{20}$ (c, CH_2Cl_2)	HRMS	LRMS, *m/z* (% relative intensity)[a]
13	3*R*,6*S*,7*R*,10*S*	70[b]	+16.7 (1.0)	279.1932[c]	238 (M^+-18), 3), 223 (4), 220 (3), 205 (7), 180 (10), 159 (14), 147 (16), 145 (15), 134 (67), 132 (85), 121 (80), 119 (52), 105 (37), 93 (72), 91 (50), 79 (33), 71 (54), 59 (100), 43 (92)
18	3*S*,6*S*,7*R*,10*S*	91	-19.4 (4.0)	279.1927[c]	238(3), 223(5), 220(4), 205(8), 180(12), 179(12), 162(19), 147(23), 138(37), 134(74), 132(63), 121(86), 94(94), 93(86), 79(56), 59(100), 43(97), 41(33)
19	3*S*,6*S*,7*R*,10*R*	75	+26.5 (1.5)	279.1932[c]	238(1), 223(3), 220(2), 205(6), 180(12),162(21), 147(20), 138(40), 134(59), 132(46), 121(73), 94(100), 93(62), 79(47), 59(93), 43(84), 41(27)
20	3*R*,6*R*,7*R*,10*S*	83	-21.3(1.9)	279.1930[c]	238(1), 223(4), 220(4), 205(5), 180(15),162(18), 147(21), 138(30), 134(66), 132(57), 121(87), 94(95), 93(81), 79(50), 59(100), 43(91), 41(30)
21	3*R*,6*R*,7*R*,10*R*	92	+17.3 (2.1)	279.1930[c]	238(1), 223(3), 220(2), 205(5), 180(15),162(18), 147(21), 138(27), 134(60), 132(50), 121(85), 94(96), 93(71), 79(49), 59(100), 43(88), 41(29)
22	3*R*,6*S*,7*R*,10*R*	70[d]	+66.6 (2.6)	279.1940[c]	238(1), 223(5), 220(3), 205(7), 180(12), 179(12), 162(11), 159 (12), 147(18), 138(25), 134(65), 132(74), 121(83), 94(45), 93(68), 79(31), 59(100), 43(80), 41(25)
23	3*R*,6*R*,7*S*,10*R*	71	+17.0(0.5)	279.1933[c]	238(2), 223(4), 220(1), 205(5), 180(10), 179(7), 162(17), 147(16), 138(37), 134(49), 132(38), 121(67), 94(100), 93(51), 79(47), 59(92), 43(85), 41(26)
24	3*S*,6*S*,7*R*,10*R*	66	+8.2(1.2)	261.1838[e]	220(2), 205(6), 187(4), 165(28), 147(19), 138(28), 134(48), 132(36), 123(28), 121(37), 119(41), 109(37), 105(29), 94(48), 93(61), 91(43), 79(40), 71(51), 59(27), 55(29), 43(100), 41(41)
3	3*S*,6*S*,7*R*,10*S*	60	-1.6(1.2)	261.1828[e]	220(2), 205(6), 187(3), 165(29), 147(18), 138(33), 134(46), 132(32), 123(30), 121(35), 119(36), 109(39), 105(25), 94(50), 93(53), 91(35), 79(39), 71(49), 59(27), 55(28), 43(100), 41(40)
25	3*R*,6*R*,7*R*,10*R*	73	+0.1(5.2)	261.1836[e]	220(2), 205(7), 187(5), 165(28), 147(22), 138(32), 134(52), 132(42), 123(35), 121(42), 119(44), 109(43), 105(31), 94(54), 93(62), 91(42), 79(42), 71(52), 59(29), 55(29), 43(100), 41(41)
26	3*R*,6*R*,7*R*,10*S*	64	-9.6(1.1)	261.1825[e]	220(3), 205(6), 187(4), 165(21), 147(19), 138(25), 134(47), 132(39), 123(28), 121(37), 119(40), 109(38), 105(29), 94(49), 93(61), 91(42), 79(39), 71(49), 59(27), 55(28), 43(100), 41(42)
4	3*R*,6*S*,7*R*,10*S*	51	+35.8(0.9)	261.1823[e]	223(1), 220(1), 205(6), 187(5), 165(38), 147(17), 138(19), 134(53), 132(63), 123(39), 121(38), 119(47), 109(46), 105(30), 95(39), 93(52), 91(35), 79(29), 71(47), 59(26), 55(29), 43(100), 41(39)
27	3*R*,6*R*,7*S*,10*S*	69	-8.1 (1.0)	261.1824[e]	220(2), 205(5), 187(4), 165(26), 147(18), 138(27), 134(47), 132(35), 123(28), 121(36), 119(41), 109(38), 105(30), 94(50), 93(65), 91(47), 79(43), 71(53), 59(29), 55(31), 43(100), 41(45)

[a]Mass spectral data from GC-EIMS analysis on HP-5MS; [b]M.p. 125 °C (*tert*-butyl methyl ether); [c]HRESIMS, calcd for $C_{15}H_{28}O_3Na$ 279.1936; [d]after 32 h run; [e] HRESIMS, calcd for $C_{15}H_{26}O_2Na$ 261.1831;

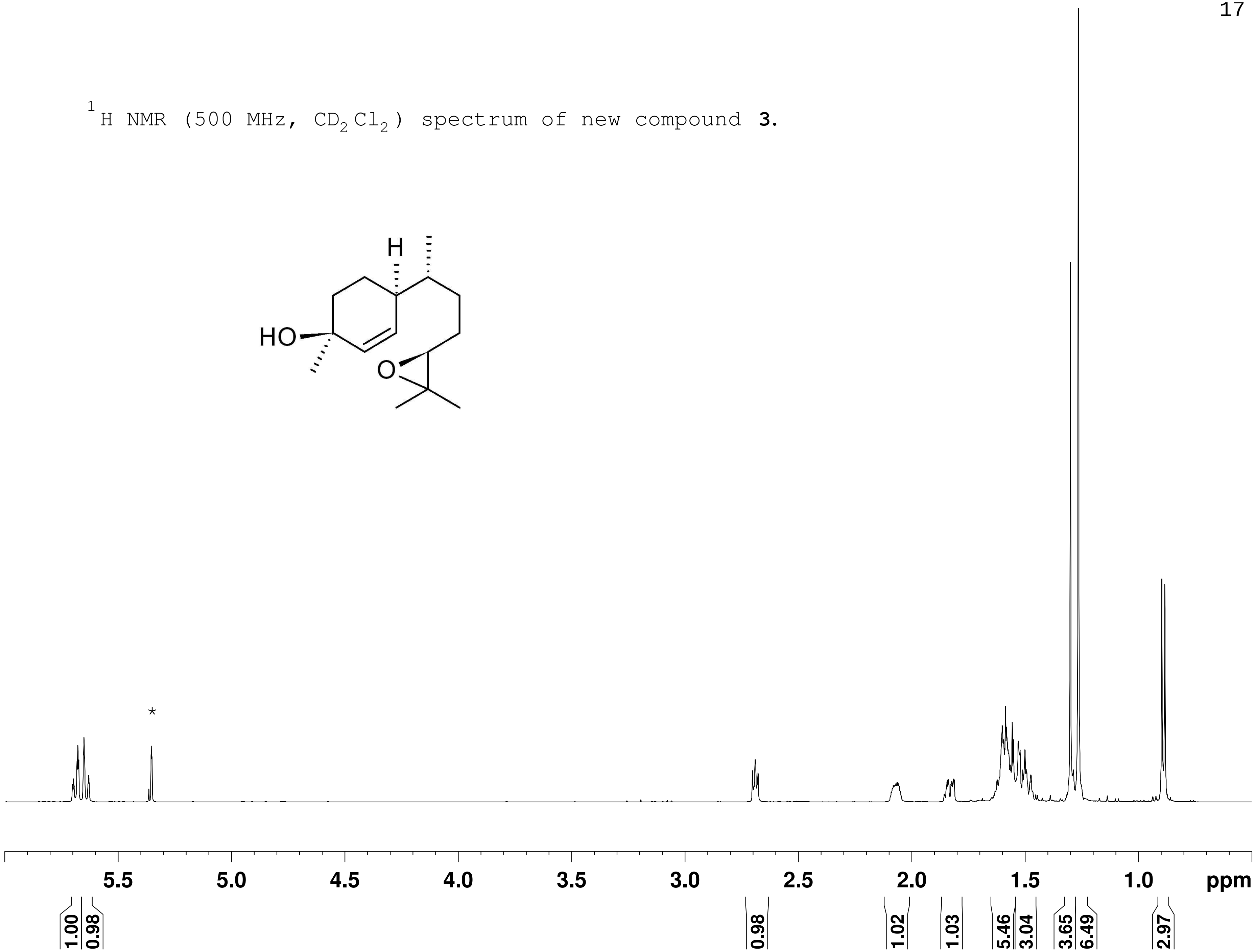
Table S5. [1]H NMR data of *H. halys* pheromone components **3**, **4** and other individual triols and epoxybisabolenols

	^{1}H NMR Chemical shifts (δ, ppm), multiplicities, *J* coupling constants, Hz												
	Position												
No.	1	2	4	5	6	7	8	9	10	12	13	14	15
13	5.53 ddd, 10.2, 2.3, 1.1	5.62 ddd, 10.2, 2.5, 1.5	1.64 m; 1.87, dm,12.3	1.41 m 1.70 m	2.17 m	1.55 m	1.20 m 1.68 m	1.23 m 1.56 m	3.32 dd, 9.8, 1.7	1.15 s	1.21 s	0.86 d 6.8	1.27 s
18	5.63 dt, 10.1, 1.5	5.68 dt, 10.1, 2.0	1.83 m; 1.56, m	1.57 m; 1.49, m	2.08 m	1.58 m	1.71 m; 1.21 m	1.57 m; 1.22, m	3.32 dd, 9.8 1.8	1.15 s	1.21 s	0.88 d, 6.9	1.26 s
19	5.67 m	5.67 m	1.83 m; 1.54 m	1.58 m; 1.49 m	2.06 m	1.57 m	1.45 m; 1.45 m	1.46 m; 1.36 m	3.34 d, 10.0	1.15 s	1.20 s	0.89 d, 6.8	1.26 s
20	5.69 s	5.69 s	1.83 m; 1.56 m	1.60 m; 1.55 m	2.07 m	1.54 m	1.70 m; 1.19 m	1.57 m; 1.22 m	3.31 dd, 9.9, 1.8	1.15 s	1.21 s	0.93 d, 6.8	1.27 s
21	5.69 s	5.69 s	1.83 m; 1.55 m	1.62 m; 1.53 m	2.04 m	1.55 m	1.45 m; 1.42 m	1.45 m; 1.36 m	3.33 d, 9.8	1.15 s	1.20 s	0.92 d, 6.7	1.26 s
22	5.56 ddd, 10.2, 2.2, 1.1	5.62 ddd, 10.2, 2.5, 1.5	1.87 dm, 12.2; 1.64, m	1.71 m; 1.43 m	2.14 m	1.54 m	1.44 m; 1.44 m	1.45 m; 1.36 m	3.33 d, 9.9	1.15 s	1.20 s	0.86 d, 6.7	1.27 s
23	5.63 dt, 10.1, 1.5	5.68 ddd, 10.1, 2.4, 1.7	1.83 m; 1.56, m	1.57 m; 1.49, m	2.08 m	1.58 m	1.71 m; 1.21 m	1.57 m; 1.22 m	3.32 dd, 9.9 1.8	1.15 s	1.20 s	0.88 d, 6.8	1.26 s
24	5.64 dt, 10.1, 1.2	5.69 dt, 10.1, 1.9	1.83 m; 1.55 m	1.56 m; 1.49 m	2.08 m	1.60 m	1.50 m; 1.38 m	1.59 m; 1.50 m	2.69 t, 6.0	1.27 s	1.30 s	0.89 d, 6.8	1.26 s
3	5.64 dt, 10.0, 1.3	5.69 dt, 10.0, 1.9	1.83 m; 1.54, m	1.57 m; 1.49, m	2.07 m	1.60 m	1.59 m; 1.28 m	1.58 m; 1.50 m	2.69 t, 6.0	1.26 s	1.30 s	0.89 d, 6.7	1.26 s
25	5.67 m	5.68 m	1.83 m; 1.56 m	1.62 m; 1.54 m	2.05 m	1.56 m	1.49 m; 1.37 m	1.60 m; 1.48 m	2.68 t, 6.0	1.26 s	1.30 s	0.93 d, 6.8	1.27 s
26	5.68 m	5.69 m	1.83 m; 1.56 m	1.61 m, 1.53 m	2.05 m	1.57 m	1.58 m; 1.27 m	1.58 m; 1.49 m	2.68 m	1.26 s	1.30 s	0.93 d, 6.7	1.27 s
4	5.55 ddd, 10.2, 2.2, 1.1	5.62 ddd, 10.2, 2.5, 1.5	1.87 m; 1.64 m	1.70 m; 1.42 m	2.15 m	1.56 m	1.57 m; 1.26 m	1.57 m; 1.48 m	2.68 dd, 6.3, 5.3	1.26 s	1.30 s	0.87 d, 6.6	1.26 s
27	5.64 dt, 10.2, 1.5	5.69 ddd, 10.1 2.5, 1.7	1.83 m; 1.54 m	1.56 m; 1.49 m	2.08 m	1.60 m	1.50 m; 1.38 m	1.59 m; 1.50 m	2.69 t, 5.9	1.26 s	1.30 s	0.89 d, 6.8	1.26 s

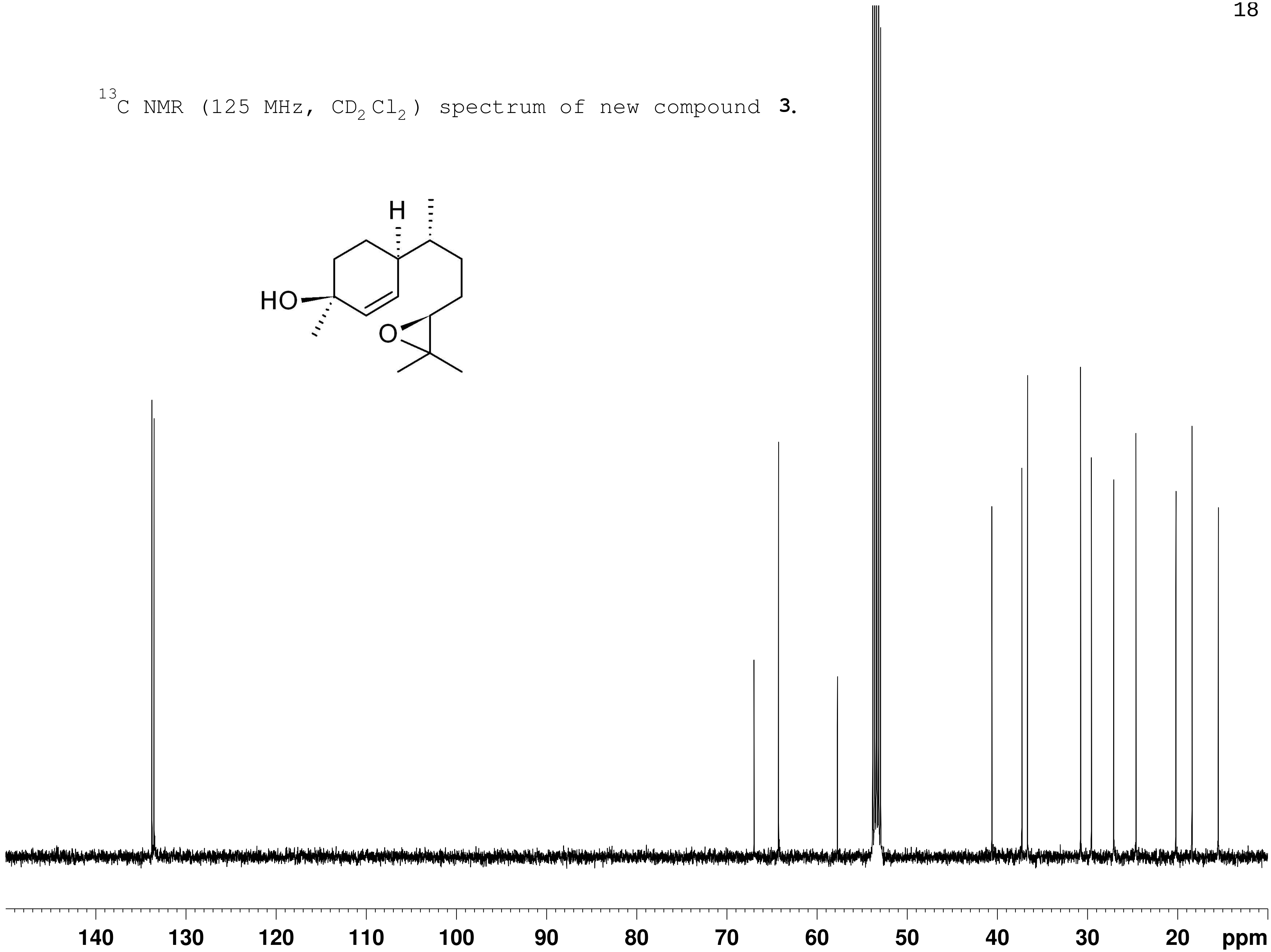
Table S6. ^{13}C NMR data of *H. halys* pheromone components **3**, **4** and other individual triols and epoxybisabolenols

	^{13}C NMR Chemical shifts (δ, ppm), multiplicities														
	Position														
No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
13	131.7 CH	134.9 CH	69.4 C	38.2 CH_2	22.1 CH_2	39.9 CH	36.9 CH	31.3 CH_2	29.7 CH_2	79.0 CH	72.9 C	23.0 CH_3	26.3 CH_3	15.6 CH_3	28.2 CH_3
18	133.9 CH	133.6 CH	67.0, C	37.3 CH_2	20.0 CH_2	40.3 CH	36.9 CH	31.3 CH_2	29.8 CH_2	79.0 CH	72.9 C	23.0 CH_3	26.3 CH_3	15.7 CH_3	29.6 CH_3
19	133.6 CH	133.6 CH	67.0 C	37.3 CH_2	20.4 CH_2	40.8 CH	36.7 CH	31.0 CH_2	29.5 CH_2	78.6 CH	72.8 C	23.0 CH_3	26.3 CH_3	15.5 CH_3	29.6 CH_3
20	132.6 CH	134.0 CH	67.1 C	37.4 CH_2	22.0 CH_2	41.0 CH	37.0 CH	30.8 CH_2	29.9 CH_2	79.2 CH	72.9 C	23.0 CH_3	26.3 CH_3	16.5 CH_3	29.6 CH_3
21	132.7 CH	134.0 CH	67.1, C	37.4 CH_2	21.9 CH_2	41.3 CH	36.7 CH	30.5 CH_2	29.6 CH_2	78.6 CH	72.8 C	23.0 CH_3	26.3 CH_3	16.2 CH_3	29.6 CH_3
22	131.5 CH	134.9 CH	69.4 C	38.2 CH_2	22.5 CH_2	40.4 CH	36.7 CH	31.0 CH_2	29.5 CH_2	78.6 CH	72.8, C	23.0 CH_3	26.3 CH_3	15.4 CH_3	28.2 CH_3
23	133.8 CH	133.6 CH	67.0, C	37.3 CH_2	20.0 CH_2	40.3 CH	36.9 CH	31.3 CH_2	29.8 CH_2	79.0 CH	72.9 C	23.0 CH_3	26.3 CH_3	15.7 CH_3	29.6 CH_3
24	133.6 CH	133.7 CH	67.0 C	37.3 CH_2	20.1 CH_2	40.3 CH	36.6 CH	30.7 CH_2	26.9 CH_2	64.2 CH	57.9 C	18.5 CH_3	24.6 CH_3	15.5 CH_3	29.6 CH_3
3	133.5 CH	133.8 CH	67.0 C	37.3 CH_2	20.2 CH_2	40.6 CH	36.7 CH	30.8 CH_2	27.1 CH_2	64.3 CH	57.8 C	18.4 CH_3	24.6 CH_3	15.5 CH_3	29.6 CH_3
25	132.4 CH	134.1 CH	67.1 C	37.4 CH_2	22.0 CH_2	41.0 CH	36.6 CH	30.2 CH_2	27.0 CH_2	64.2 CH	57.9 C	23.0 CH_3	26.3 CH_3	16.2 CH_3	29.6 CH_3
26	132.5 CH	134.1 CH	67.1 C	37.4 CH_2	21.9 CH_2	41.2 CH	36.7 CH	30.2 CH_2	27.2 CH_2	64.3 CH	57.7 C	18.4 CH_3	24.6 CH_3	16.2 CH_3	29.6 CH_3
4	131.4 CH	135.0 CH	69.4 C	38.2 CH_2	22.4 CH_2	40.2 CH	36.6 CH	30.8 CH_2	27.0 CH_2	64.3 CH	57.7 C	18.4 CH_3	24.6 CH_3	15.4 CH_3	28.2 CH_3
27	133.6 CH	133.7 CH	67.0 C	37.3 CH_2	20.1 CH_2	40.3 CH	36.6 CH	30.7 CH_2	26.9 CH_2	64.2 CH	57.9 C	18.5 CH_3	24.6 CH_3	15.5 CH_3	29.6 CH_3

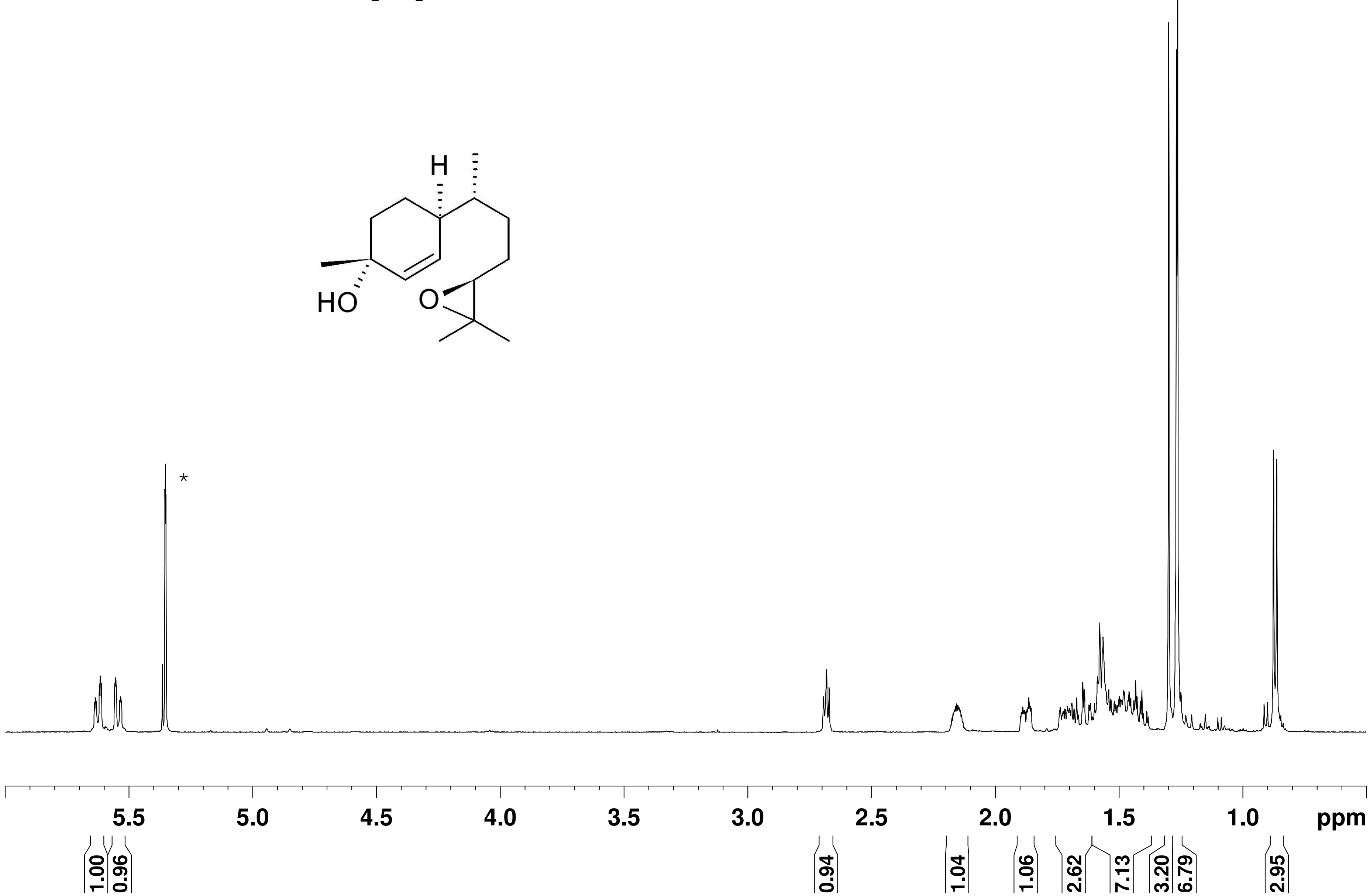
^{1}H NMR (500 MHz, CD_2Cl_2) spectrum of new compound **3**.



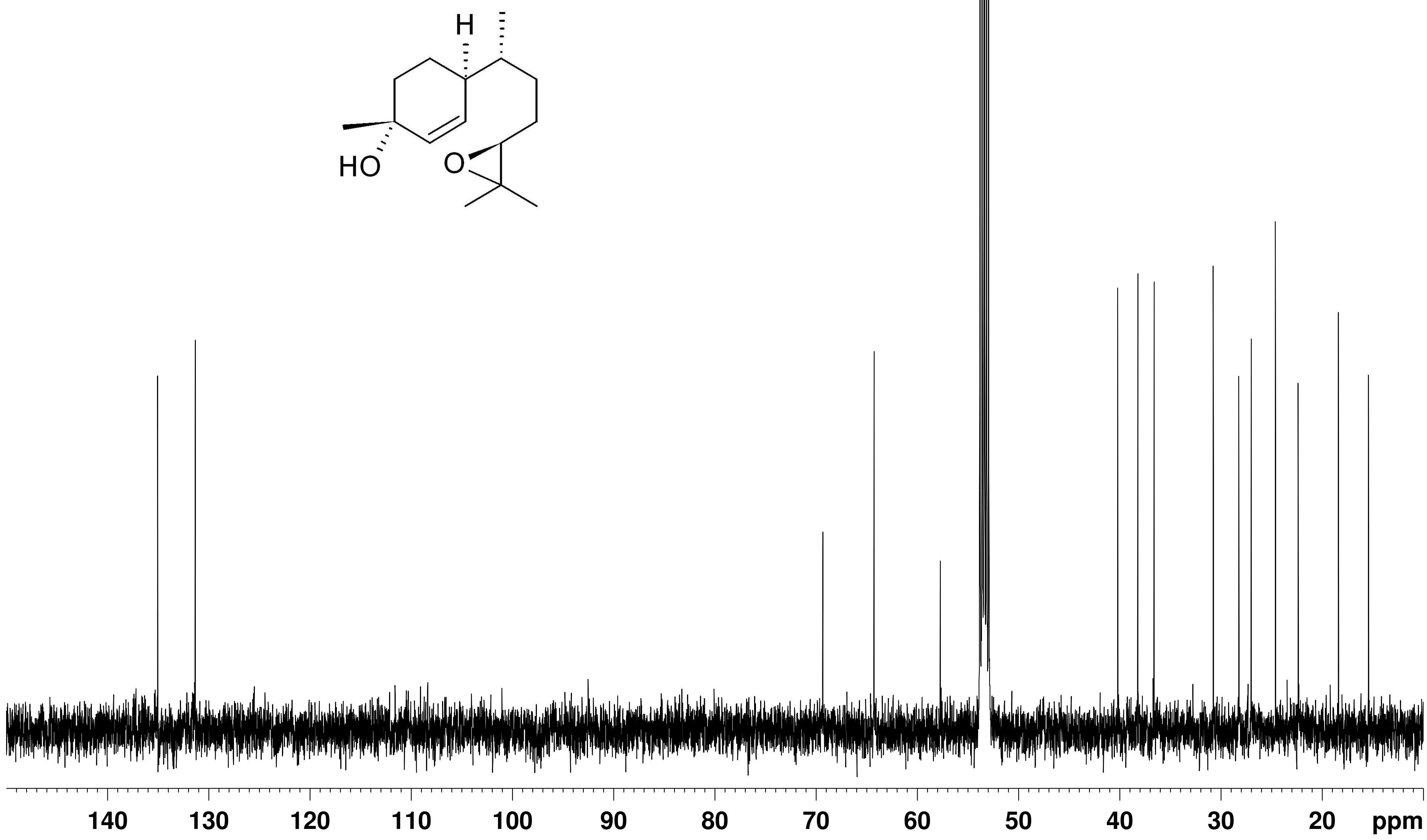
^{13}C NMR (125 MHz, CD_2Cl_2) spectrum of new compound **3.**



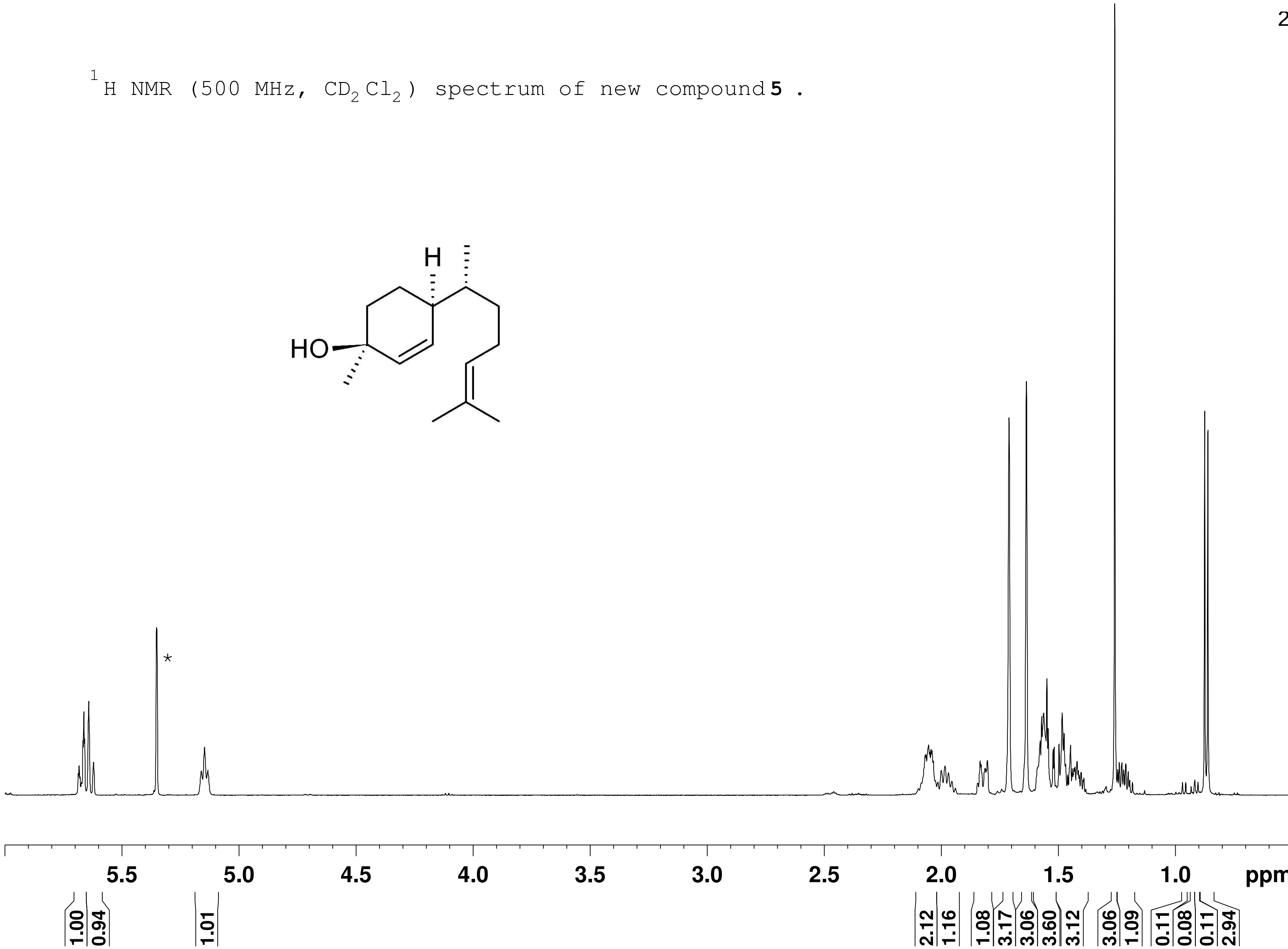
^{1}H NMR (500 MHz, CD_2Cl_2) spectrum of new compound **4.**



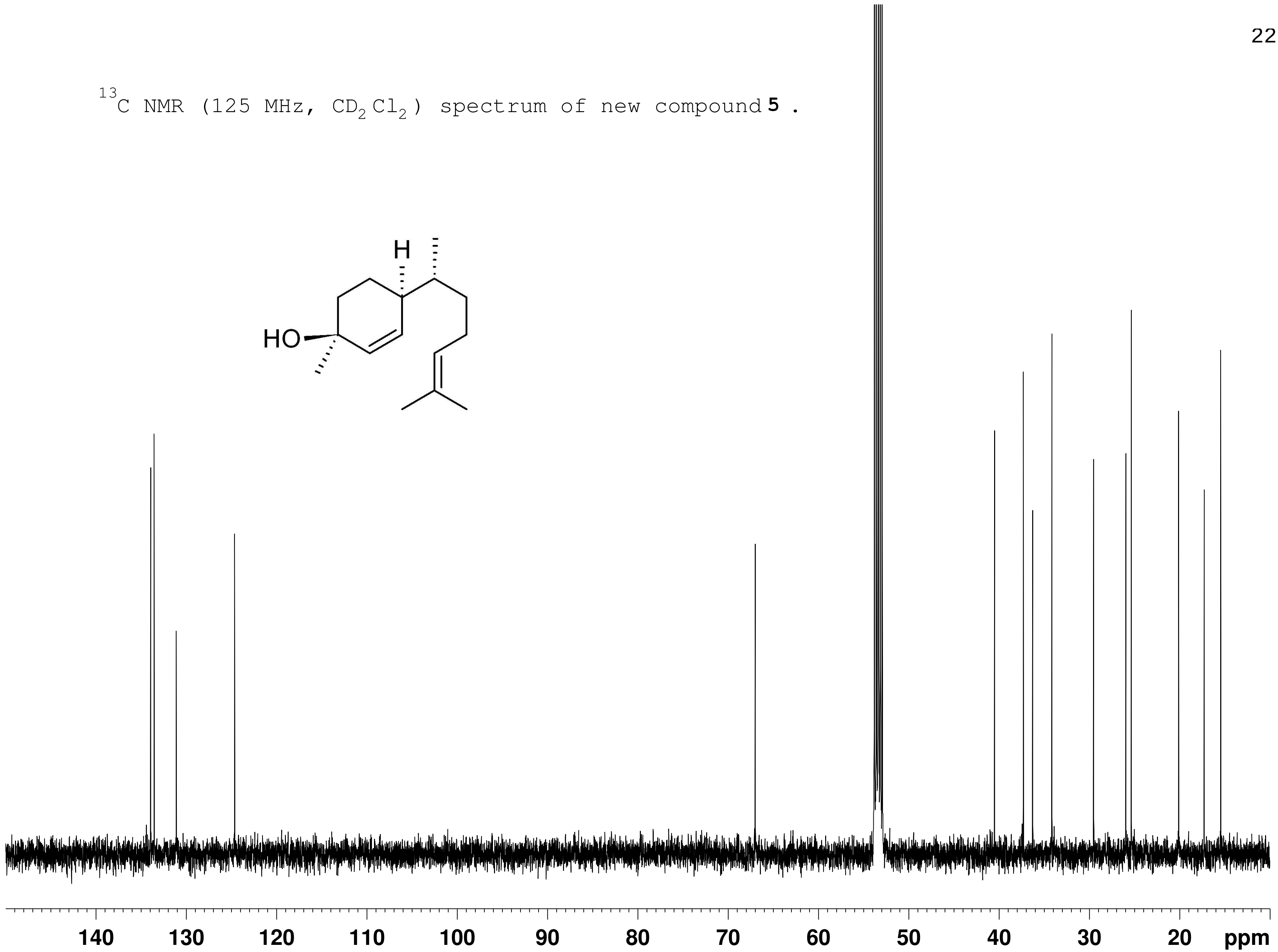
^{13}C NMR (125 MHz, CD_2Cl_2) spectrum of new compound **4.**



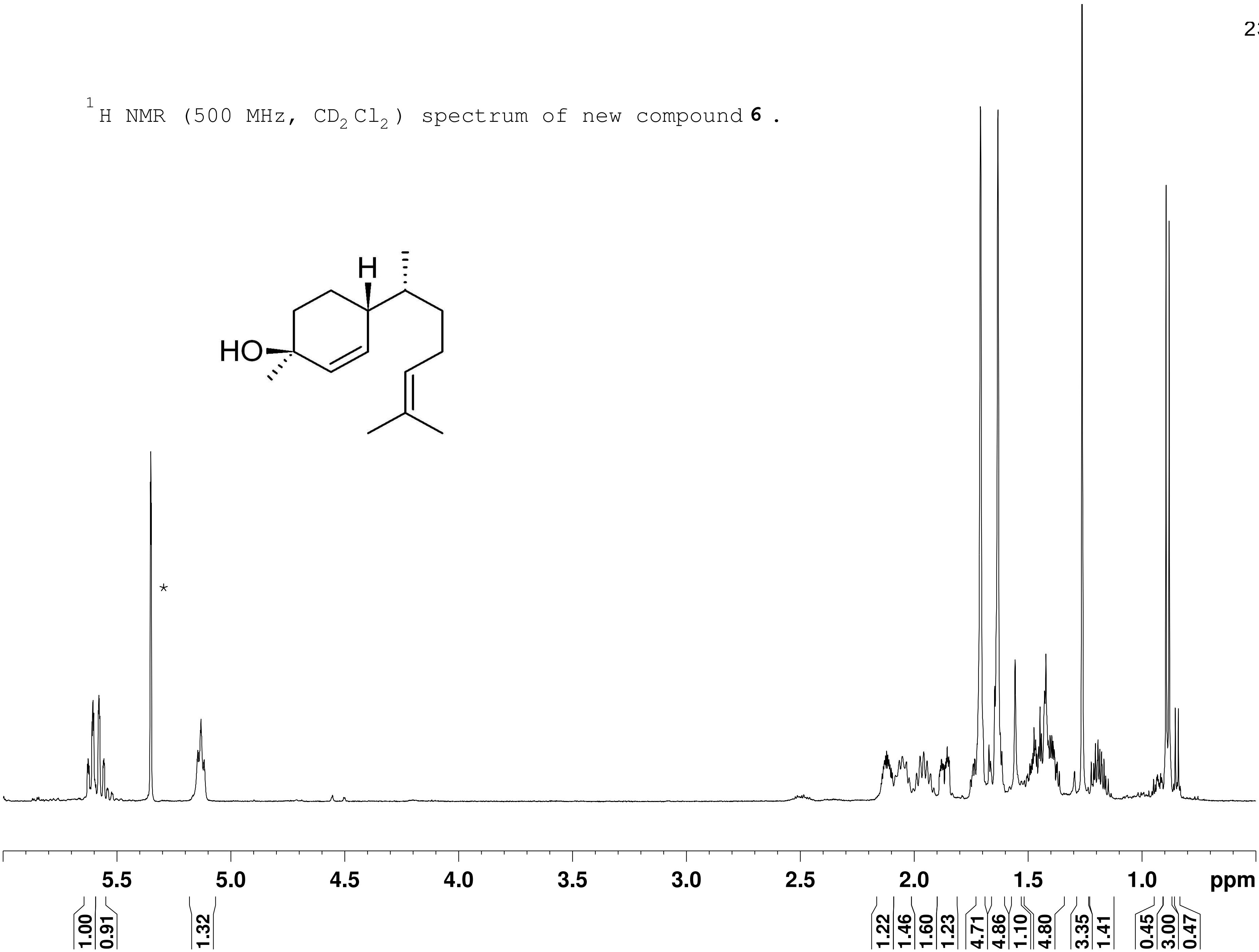
[1]H NMR (500 MHz, CD_2Cl_2) spectrum of new compound **5** .



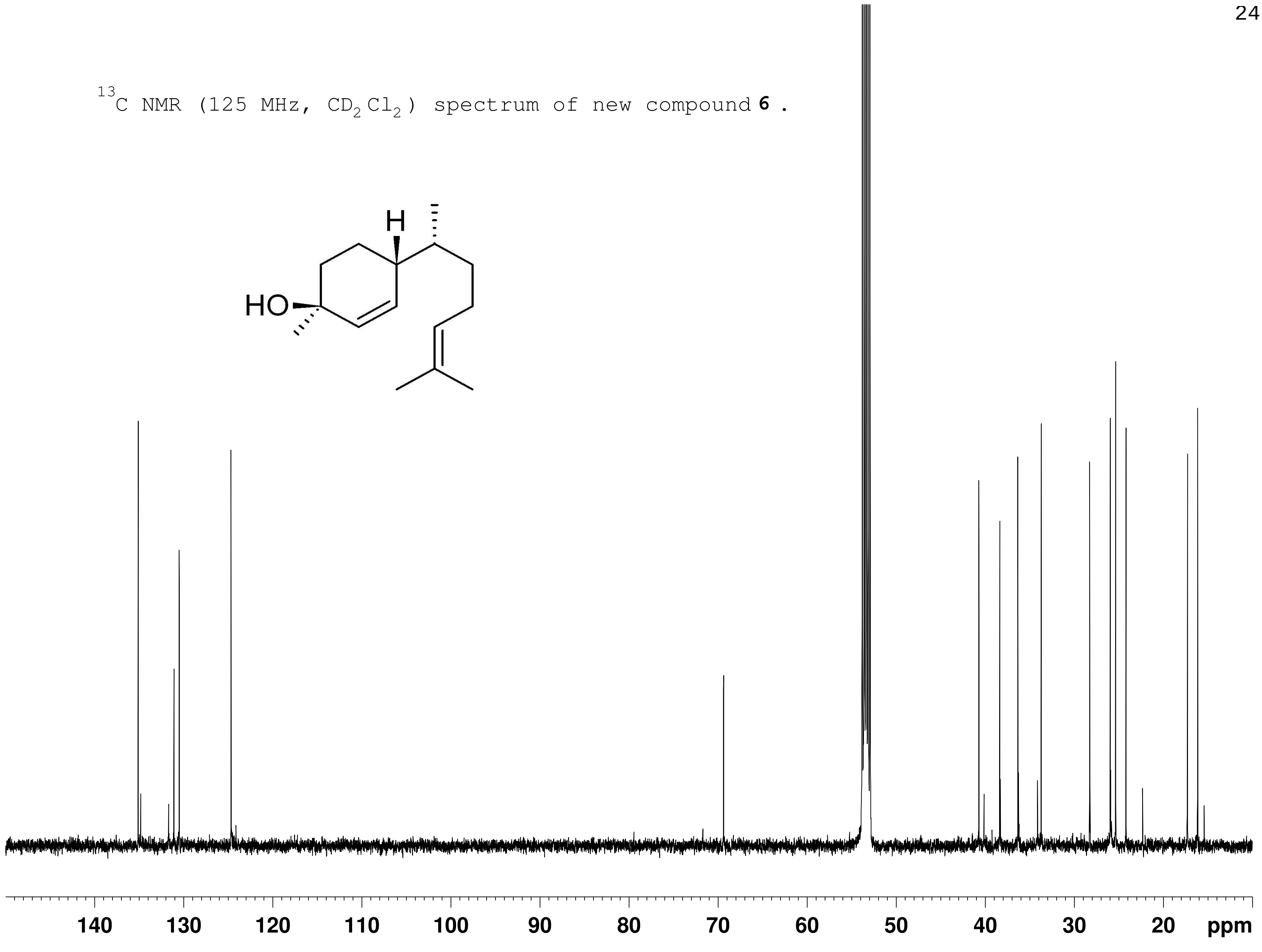
^{13}C NMR (125 MHz, CD_2Cl_2) spectrum of new compound **5** .



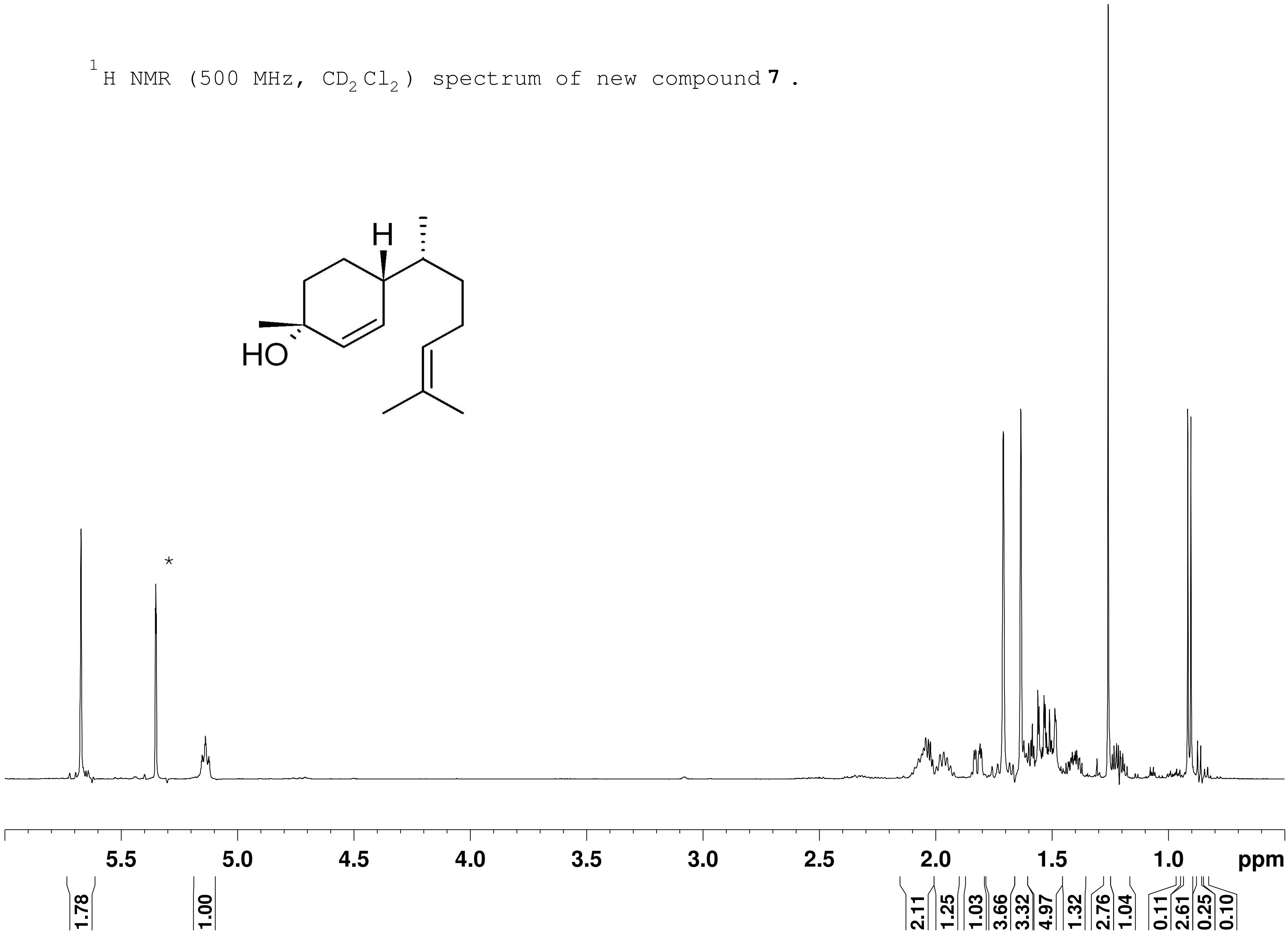
^{1}H NMR (500 MHz, CD_2Cl_2) spectrum of new compound **6** .



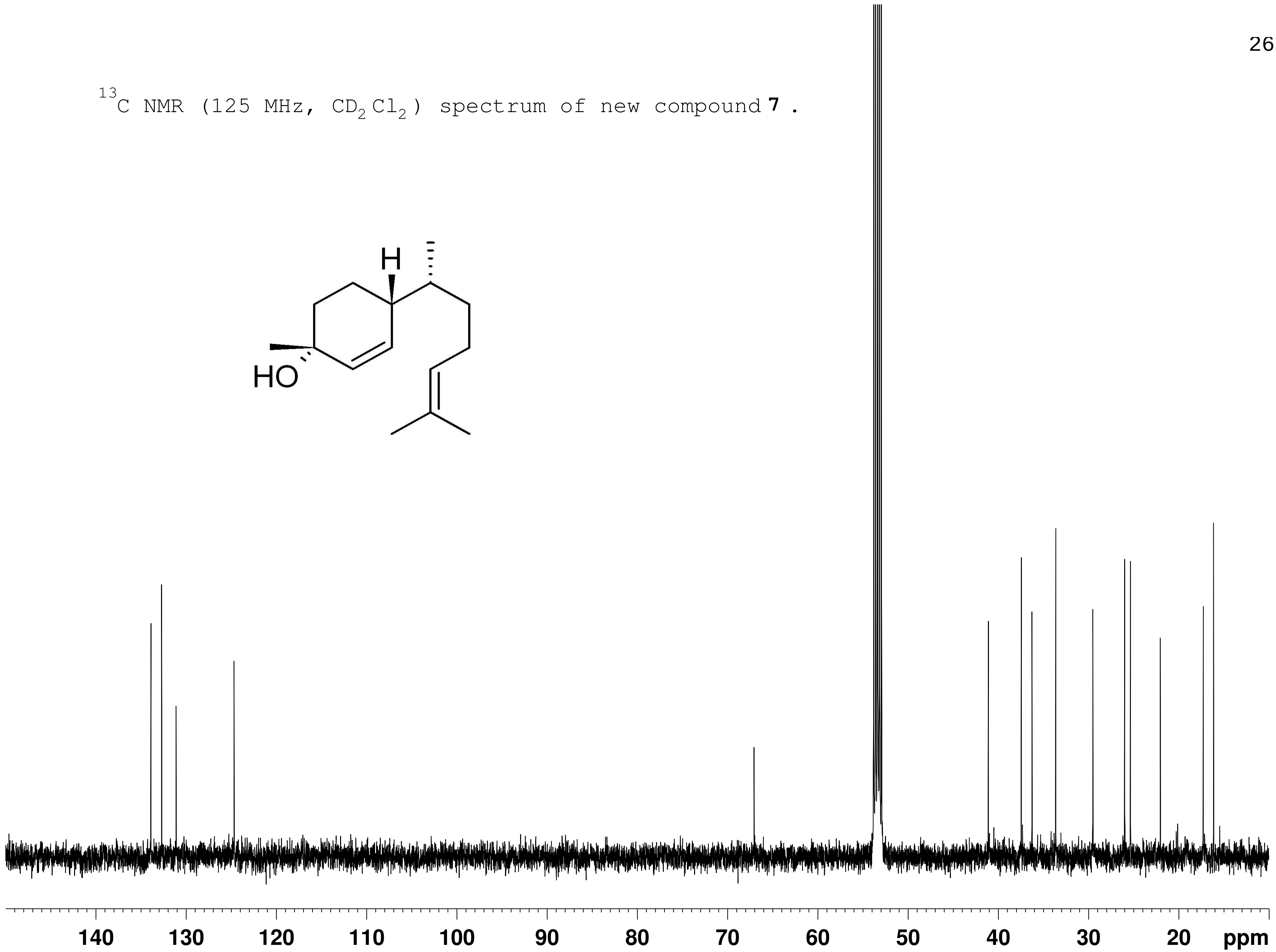
^{13}C NMR (125 MHz, CD_2Cl_2) spectrum of new compound **6** .



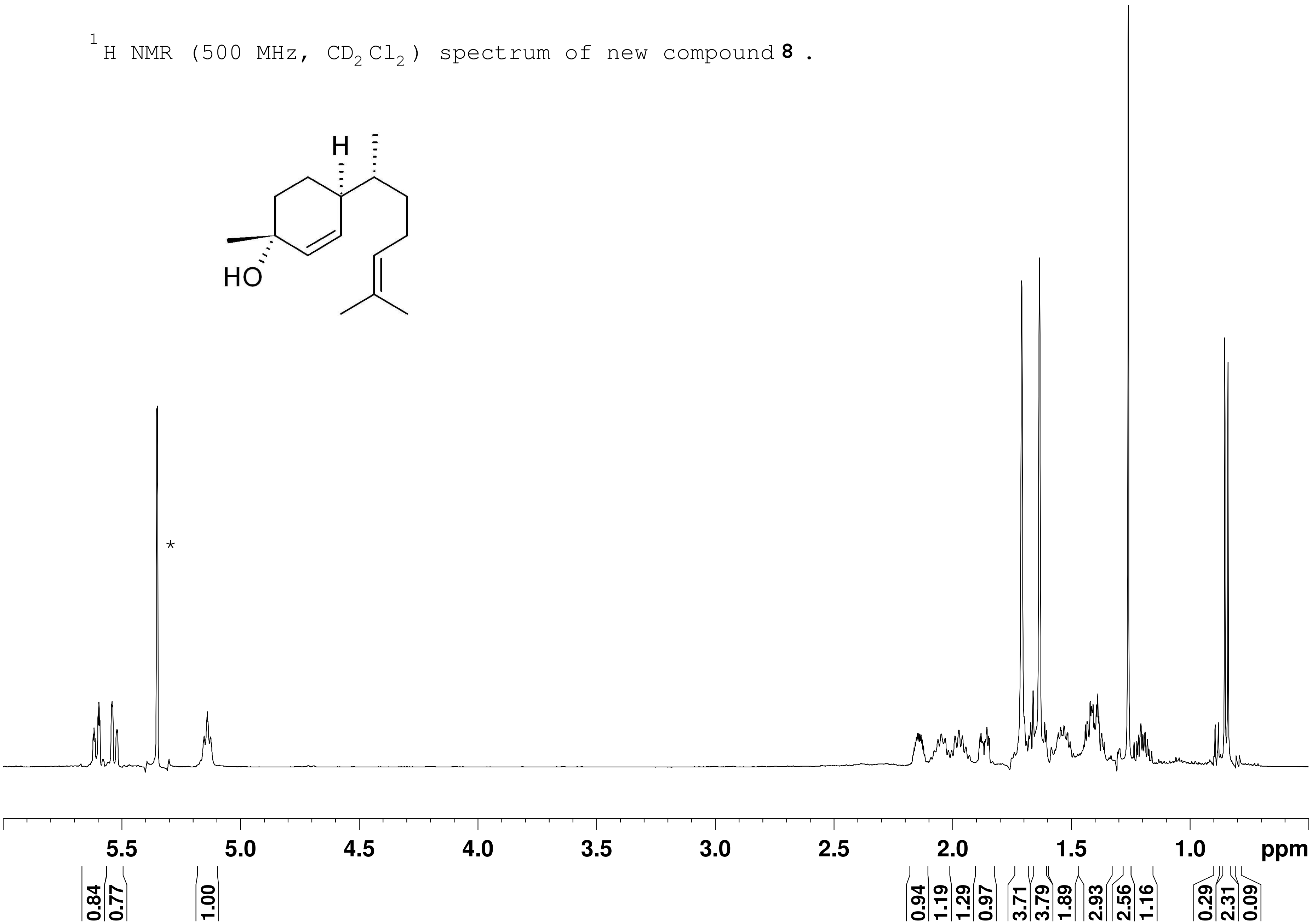
[1]H NMR (500 MHz, CD_2Cl_2) spectrum of new compound **7** .



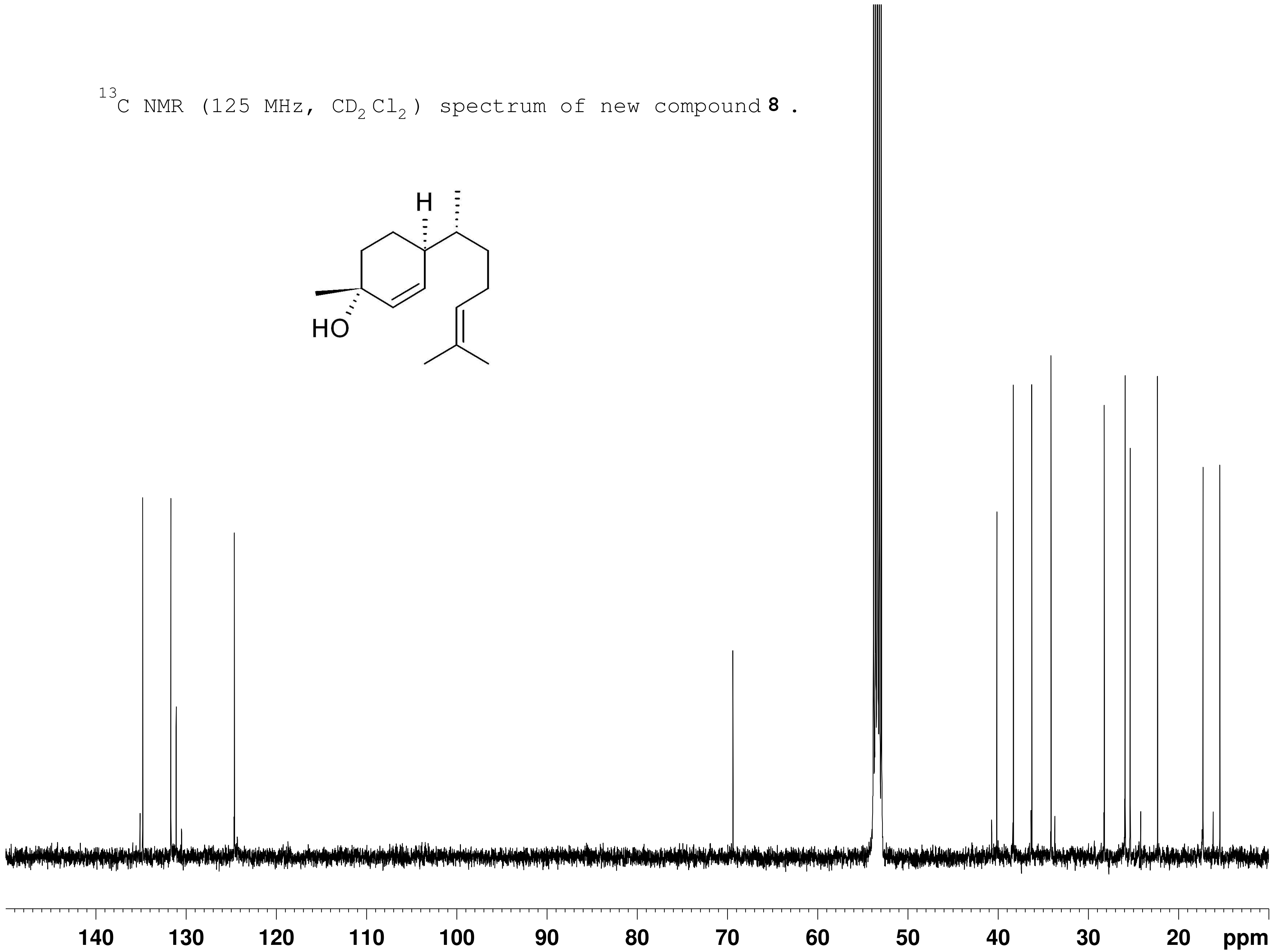
^{13}C NMR (125 MHz, CD_2Cl_2) spectrum of new compound **7**.



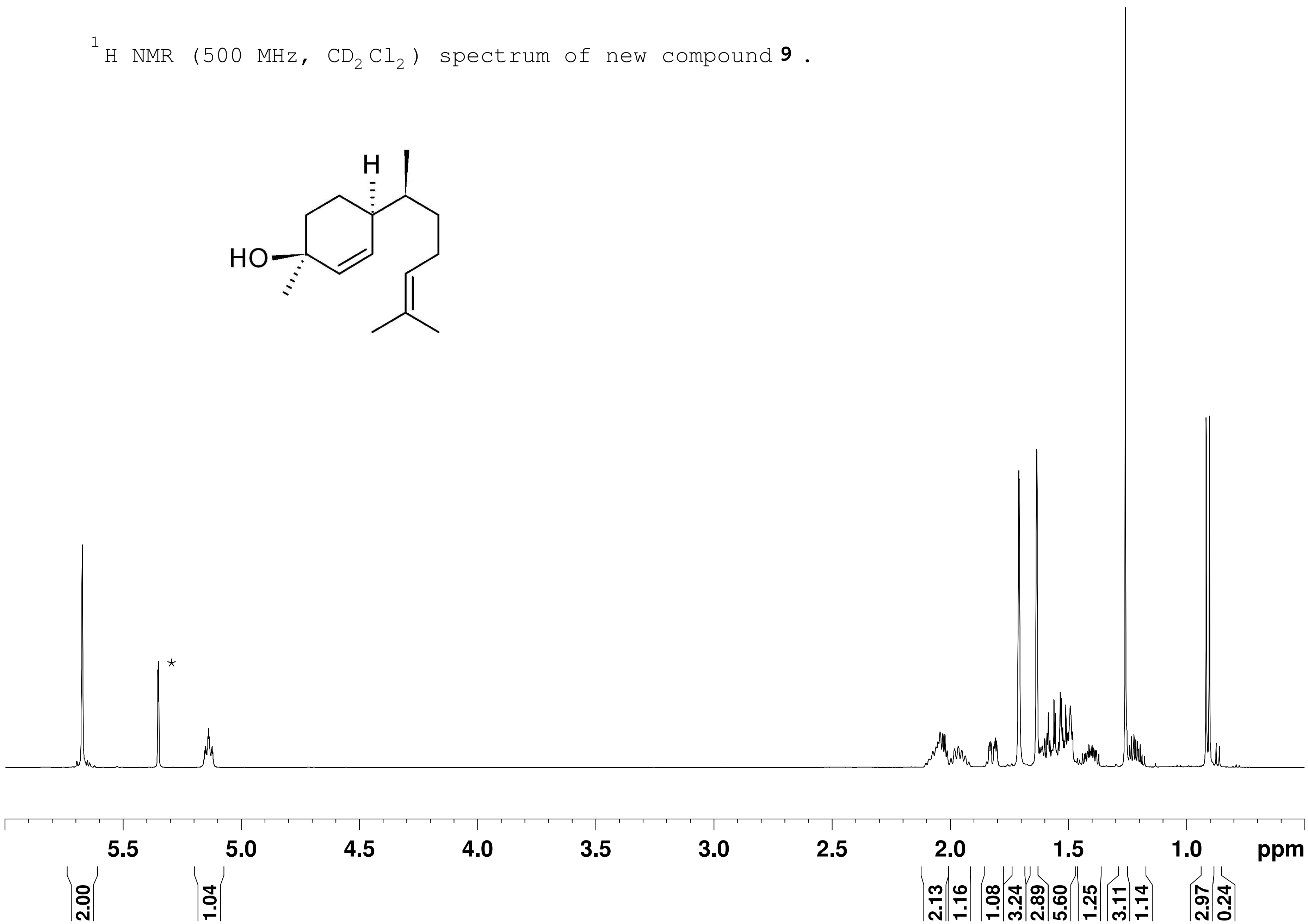
^{1}H NMR (500 MHz, CD_2Cl_2) spectrum of new compound **8** .



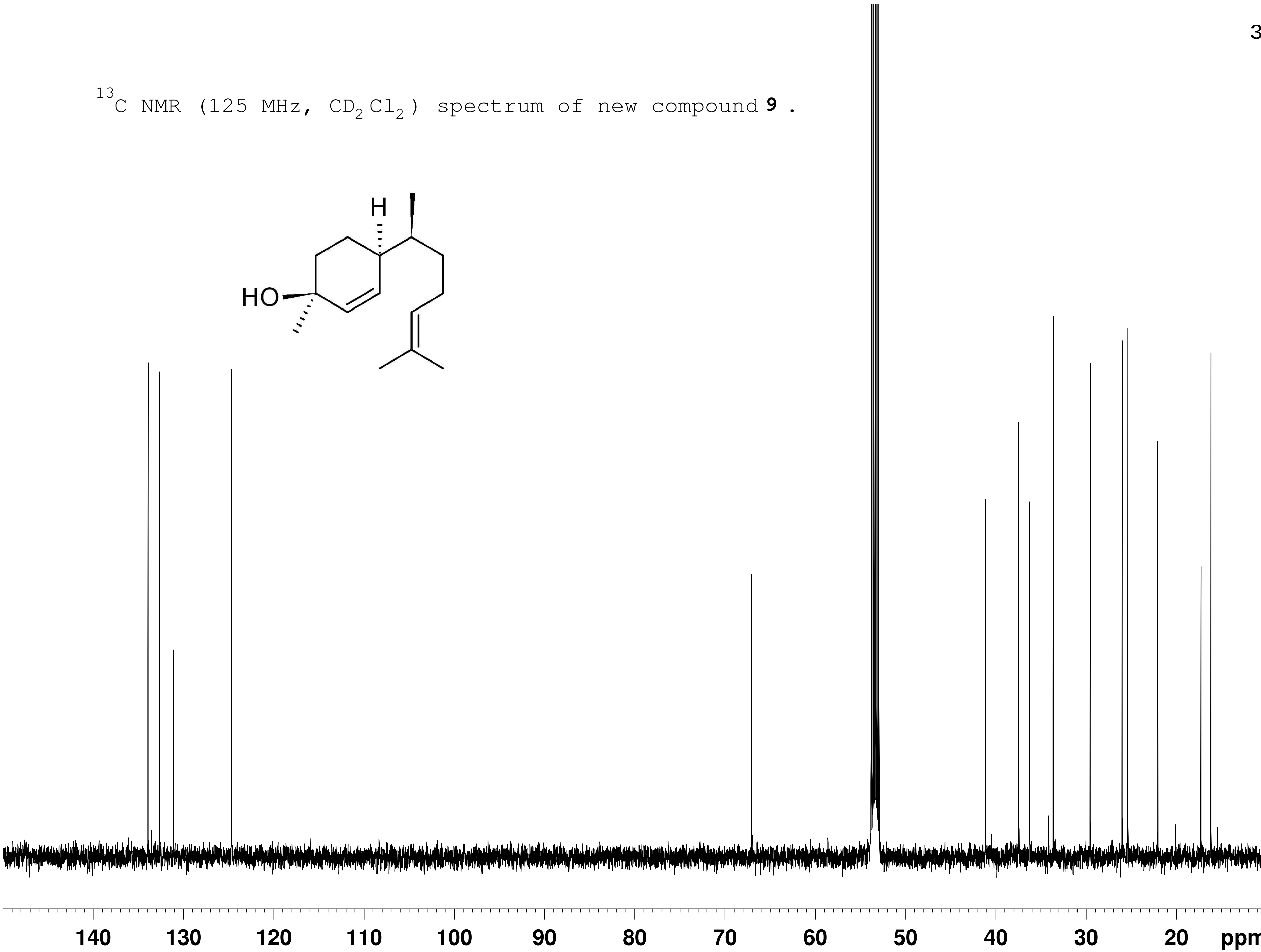
^{13}C NMR (125 MHz, CD_2Cl_2) spectrum of new compound **8** .



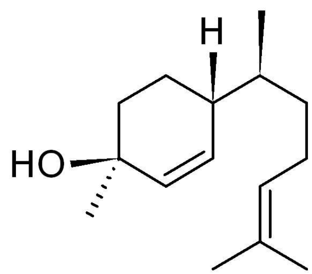
^{1}H NMR (500 MHz, CD_2Cl_2) spectrum of new compound **9** .

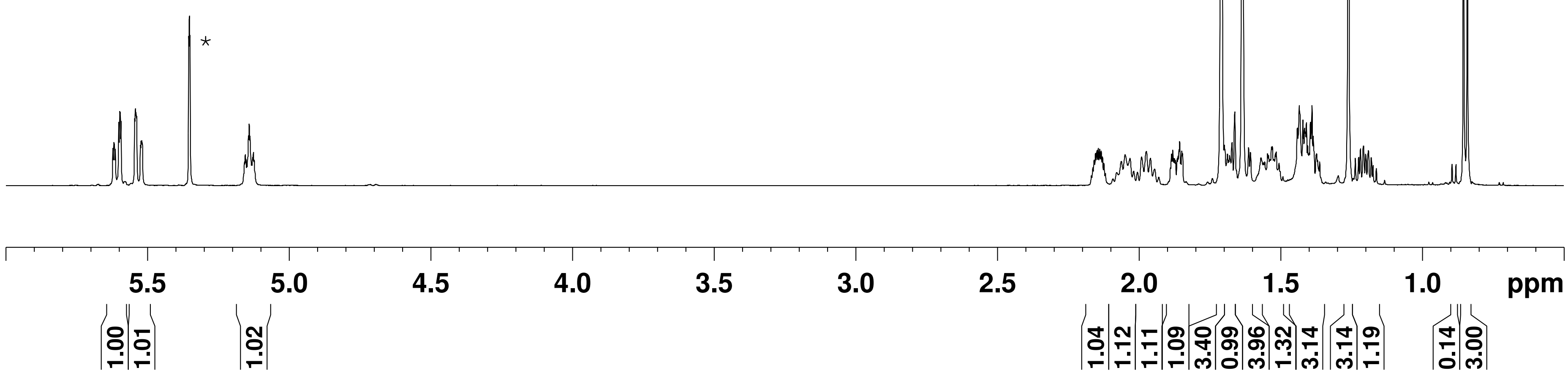


^{13}C NMR (125 MHz, CD_2Cl_2) spectrum of new compound **9**.

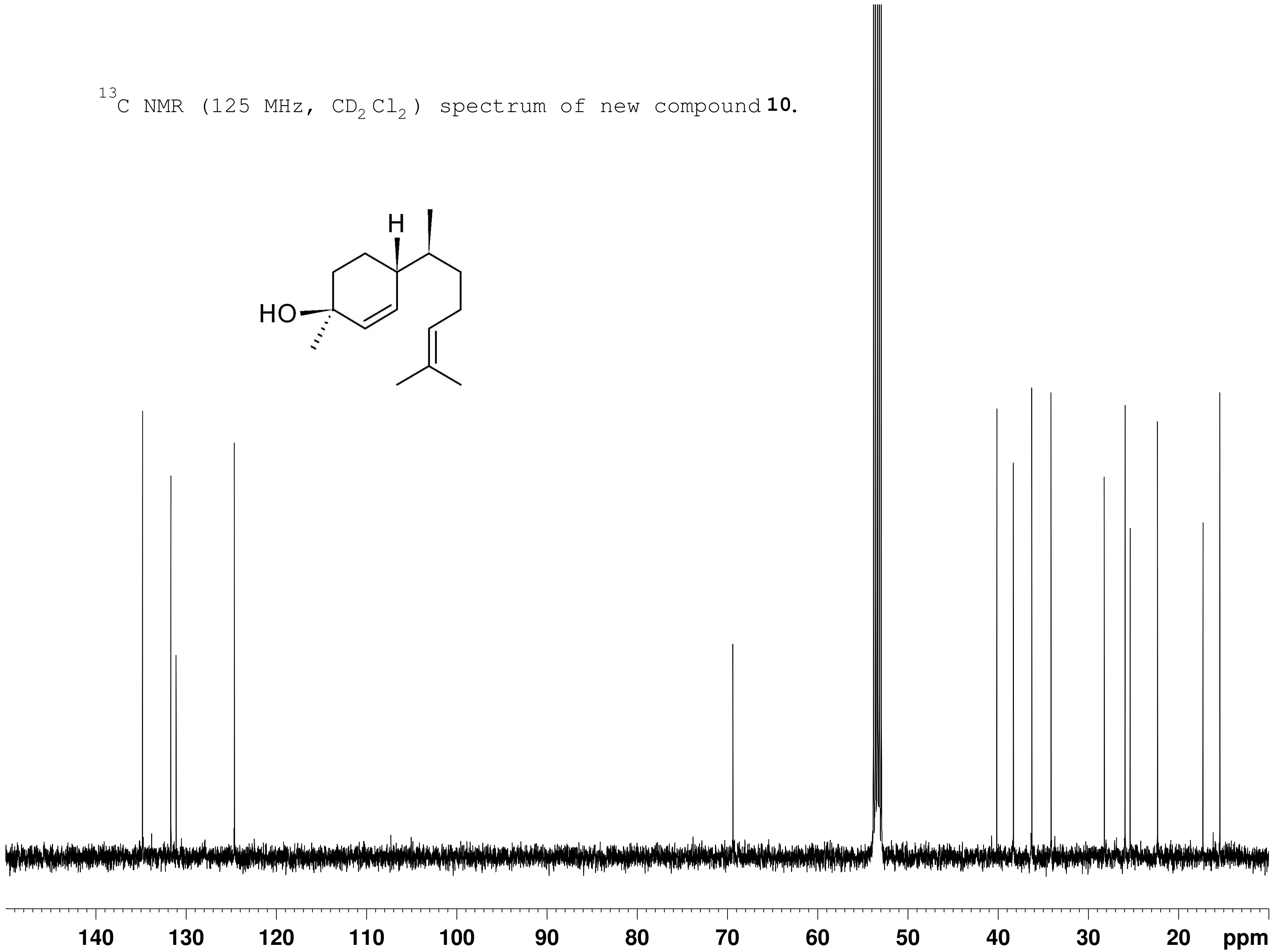


[1]H NMR (500 MHz, CD_2Cl_2) spectrum of new compound **10**.

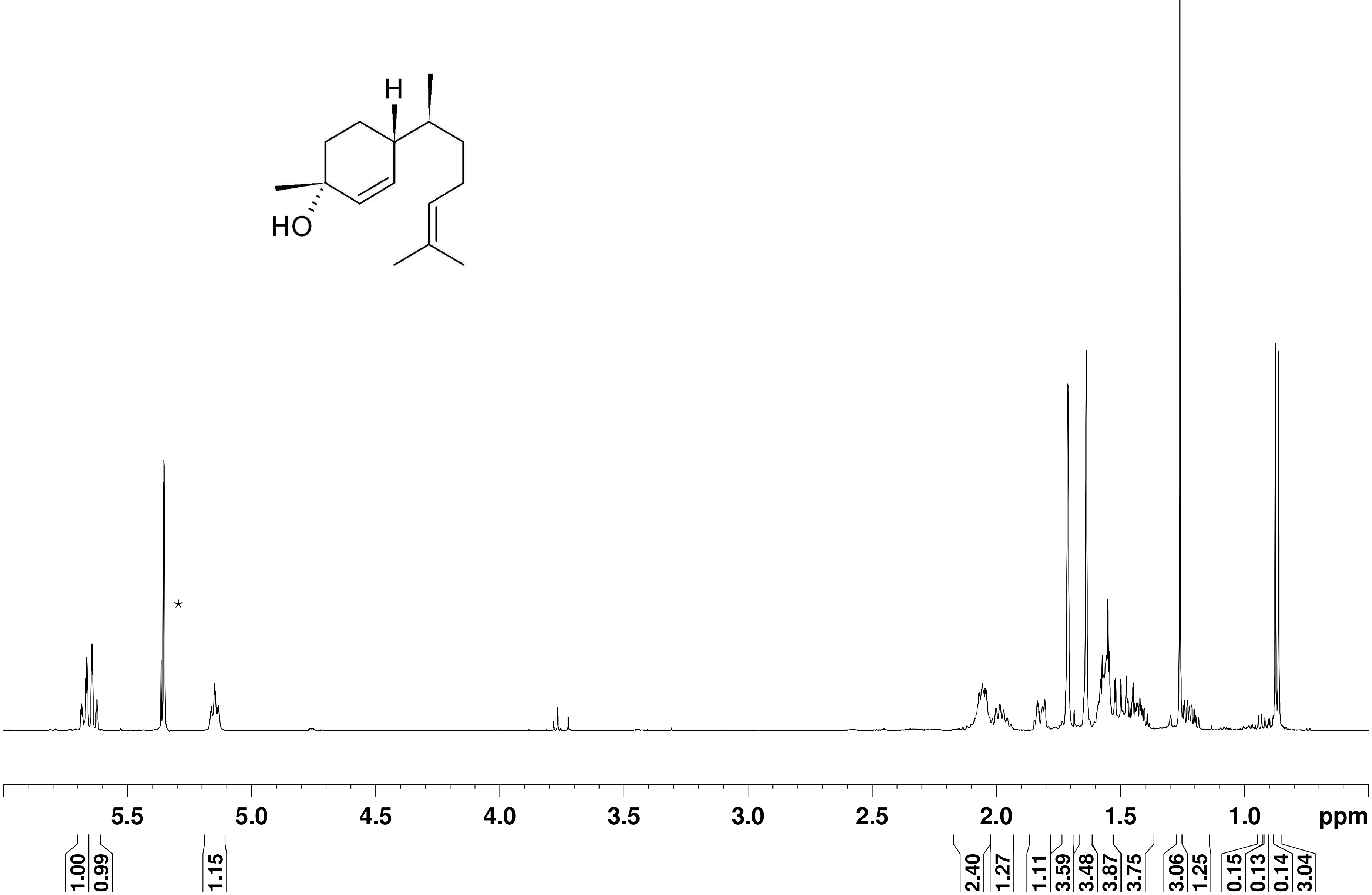




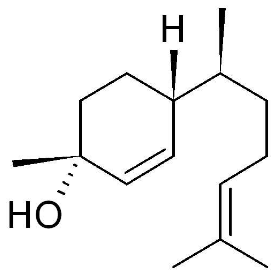
^{13}C NMR (125 MHz, CD_2Cl_2) spectrum of new compound **10**.

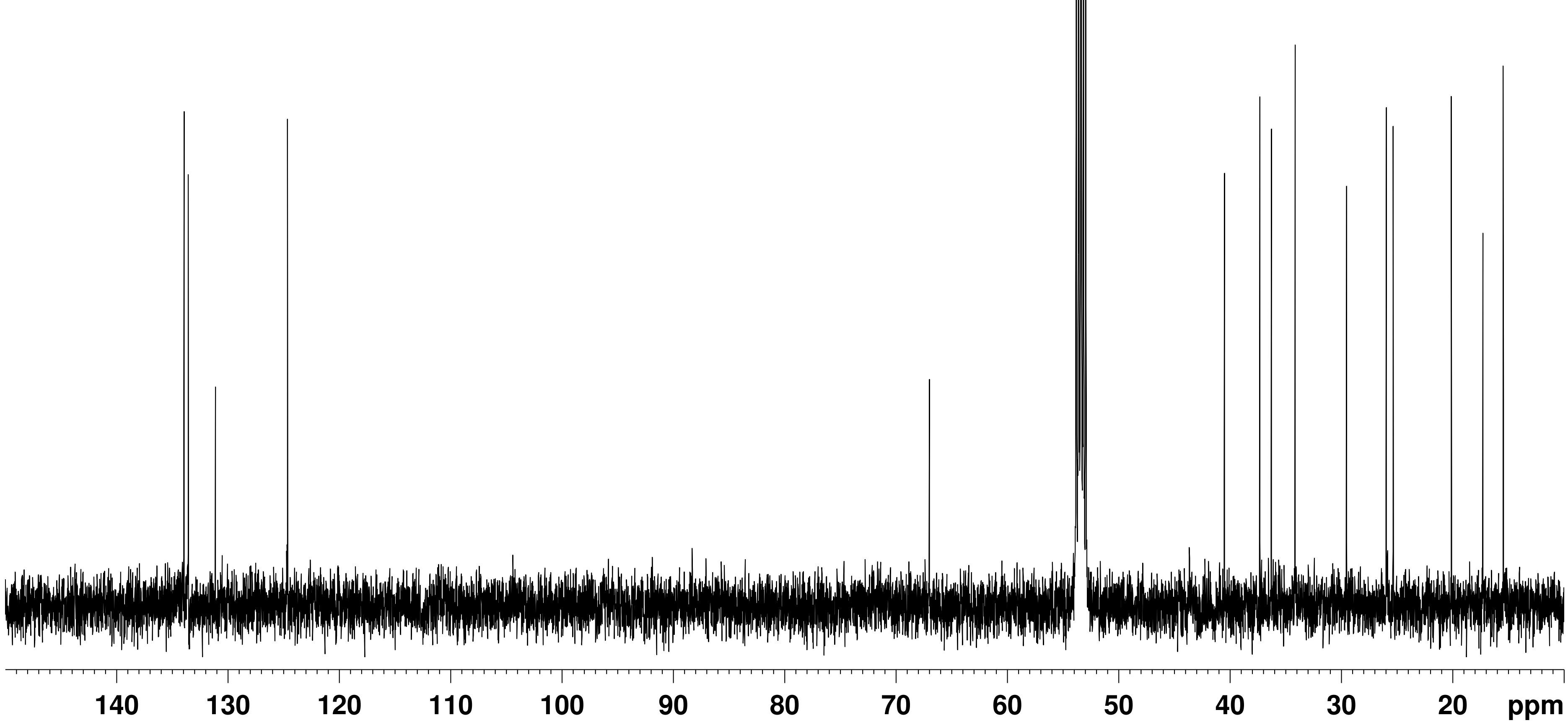


^{1}H NMR (500 MHz, CD_2Cl_2) spectrum of new compound **11.**

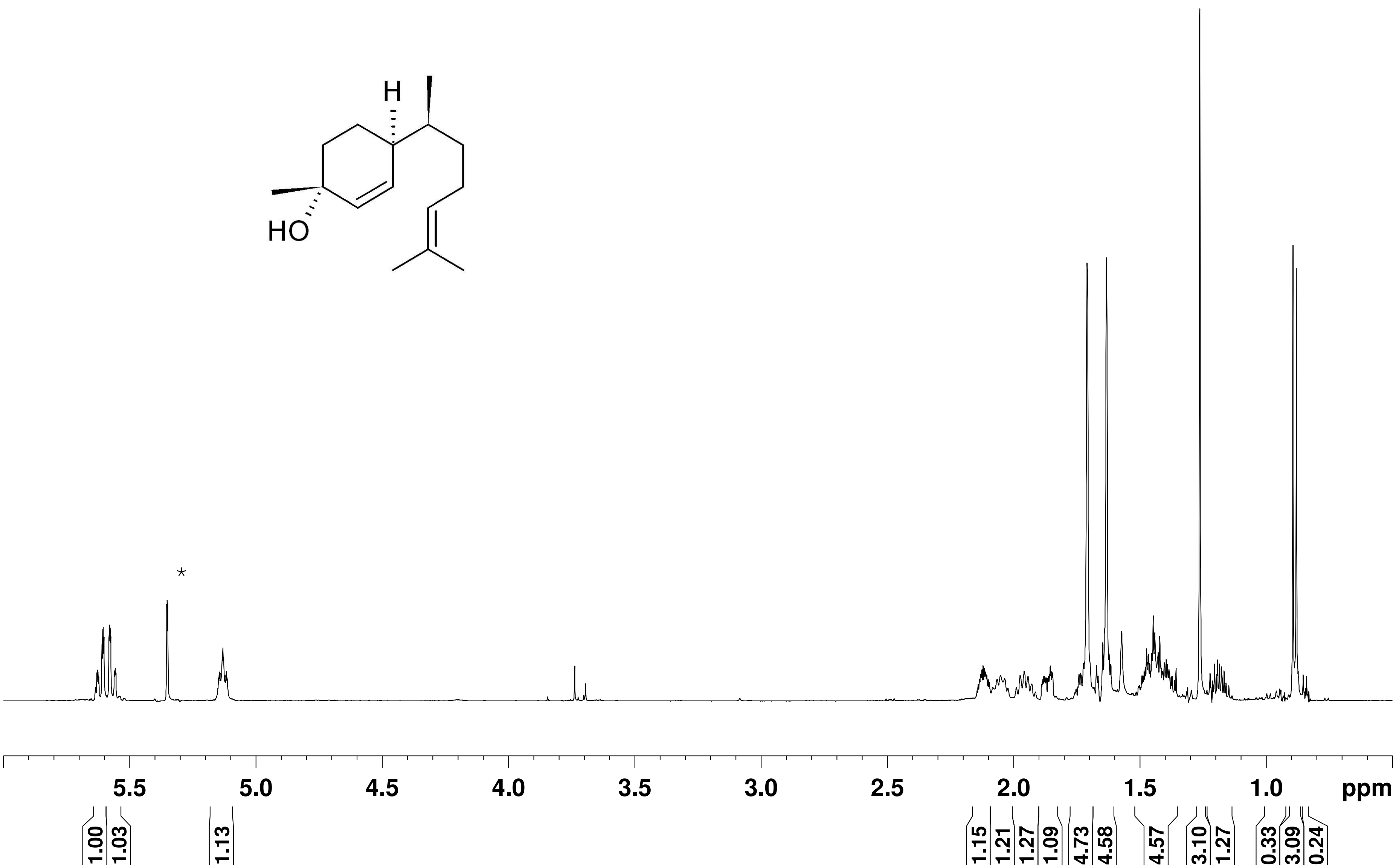


^{13}C NMR (125 MHz, CD_2Cl_2) spectrum of new compound **11.**

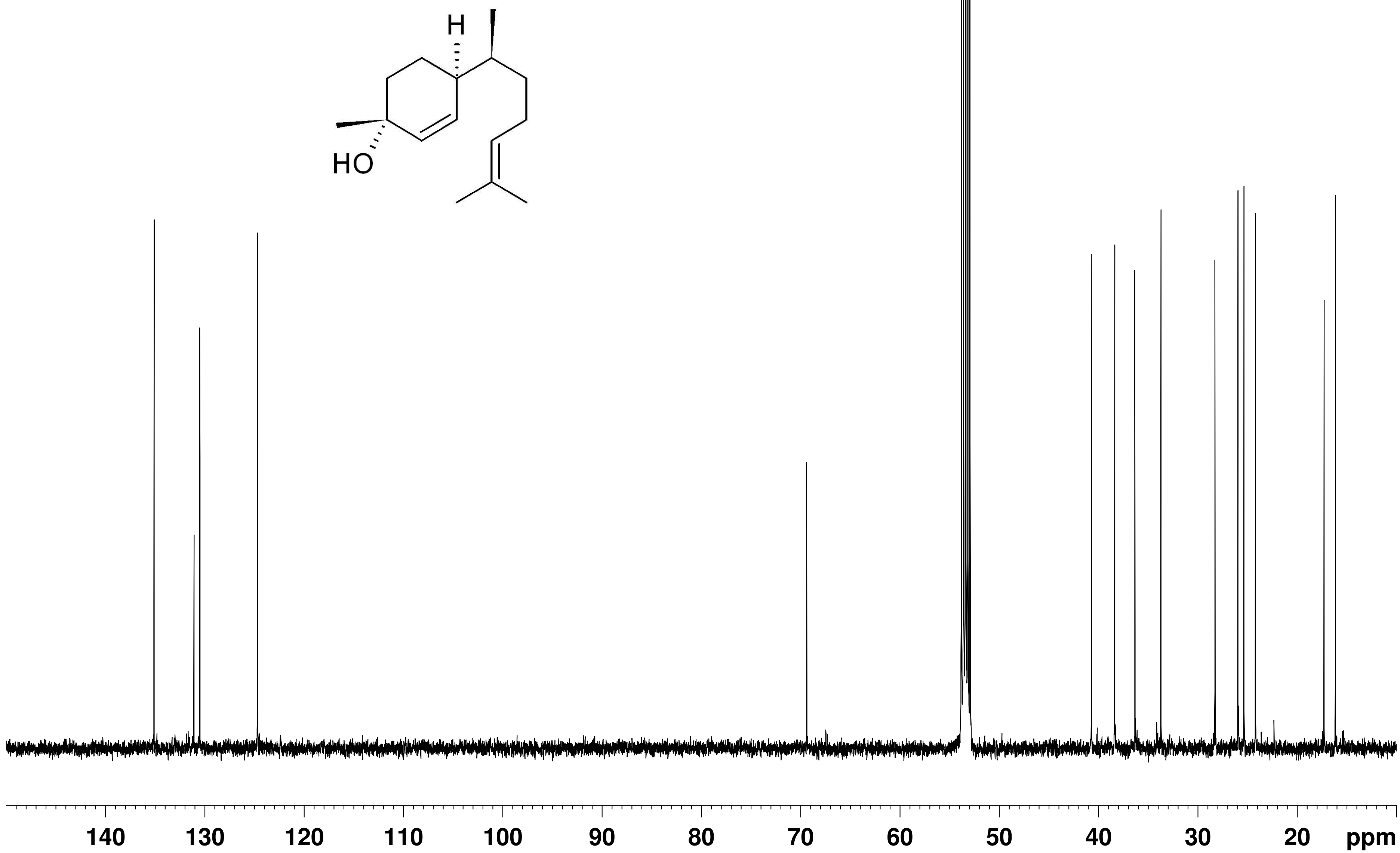




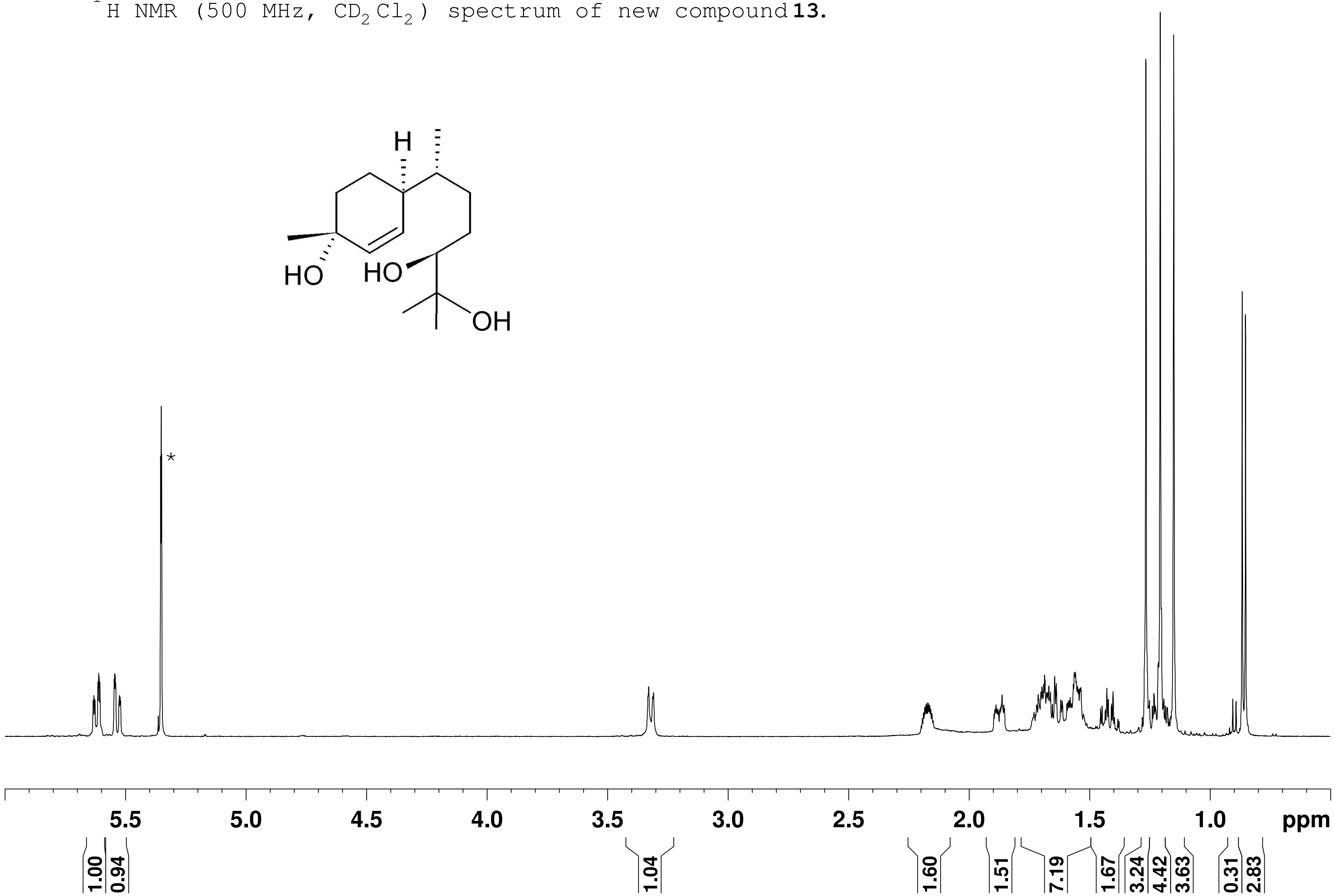
[1]H NMR (500 MHz, CD_2Cl_2) spectrum of new compound **12.**



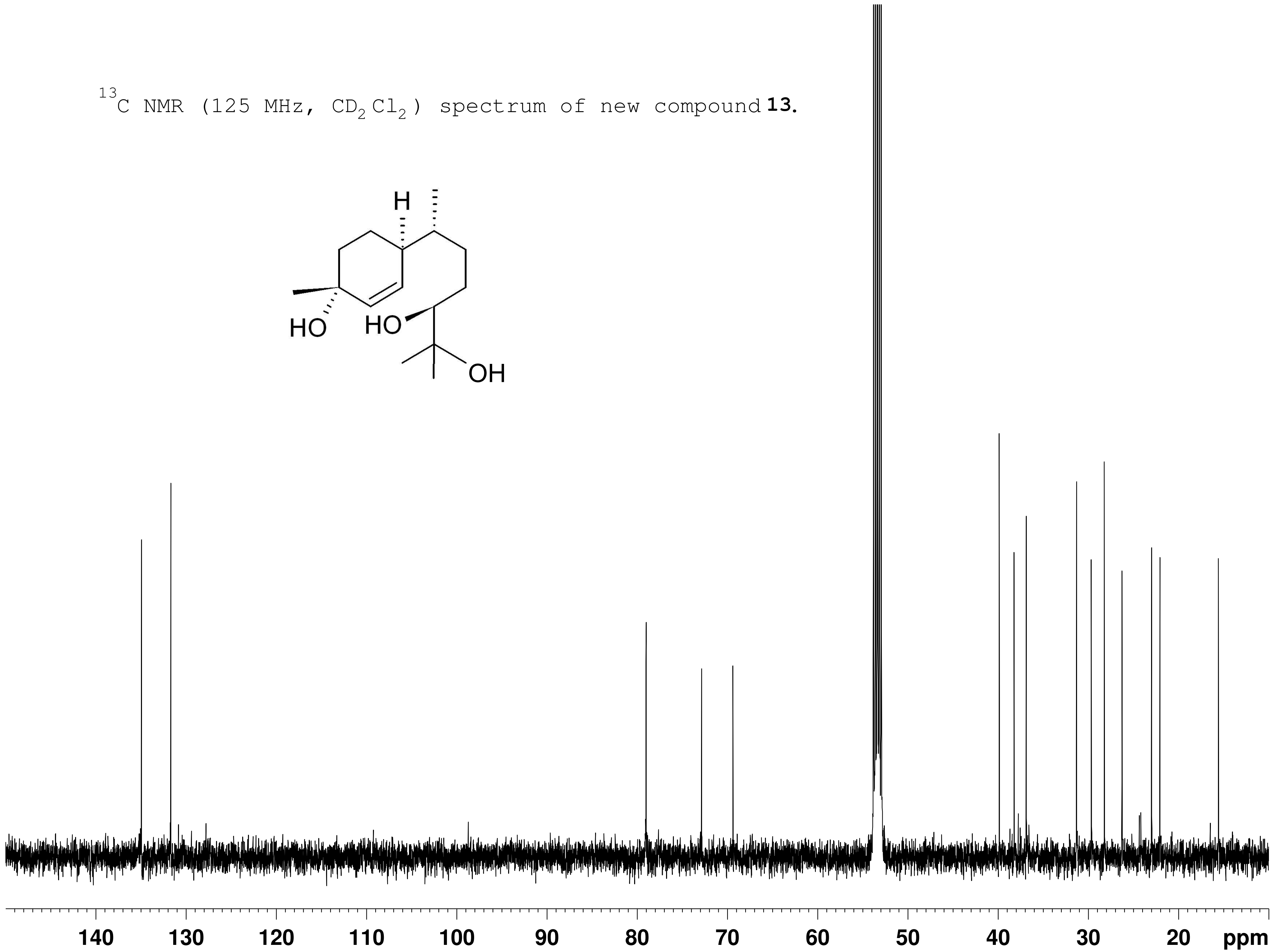
^{13}C NMR (125 MHz, CD_2Cl_2) spectrum of new compound **12.**



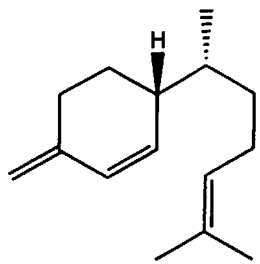
^{1}H NMR (500 MHz, CD_2Cl_2) spectrum of new compound **13**.

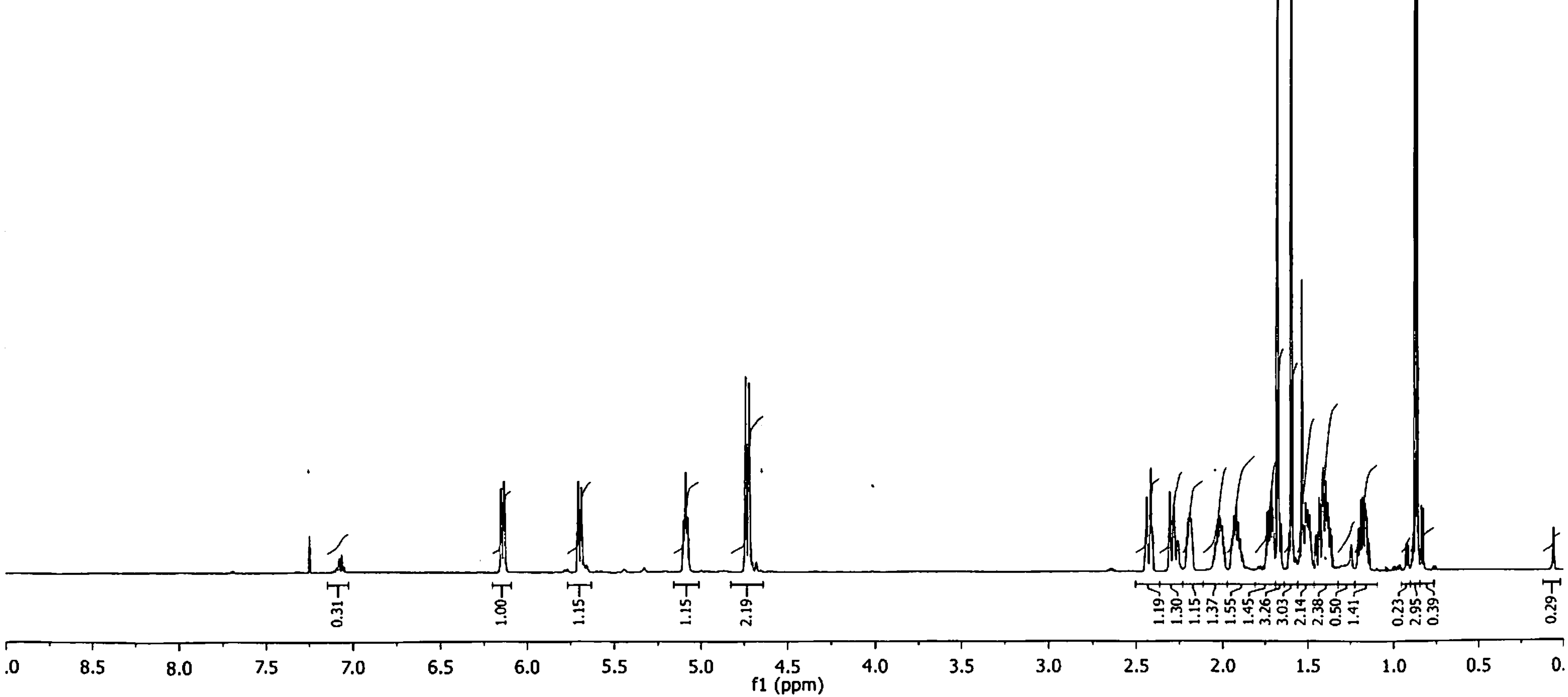


^{13}C NMR (125 MHz, CD_2Cl_2) spectrum of new compound **13**.

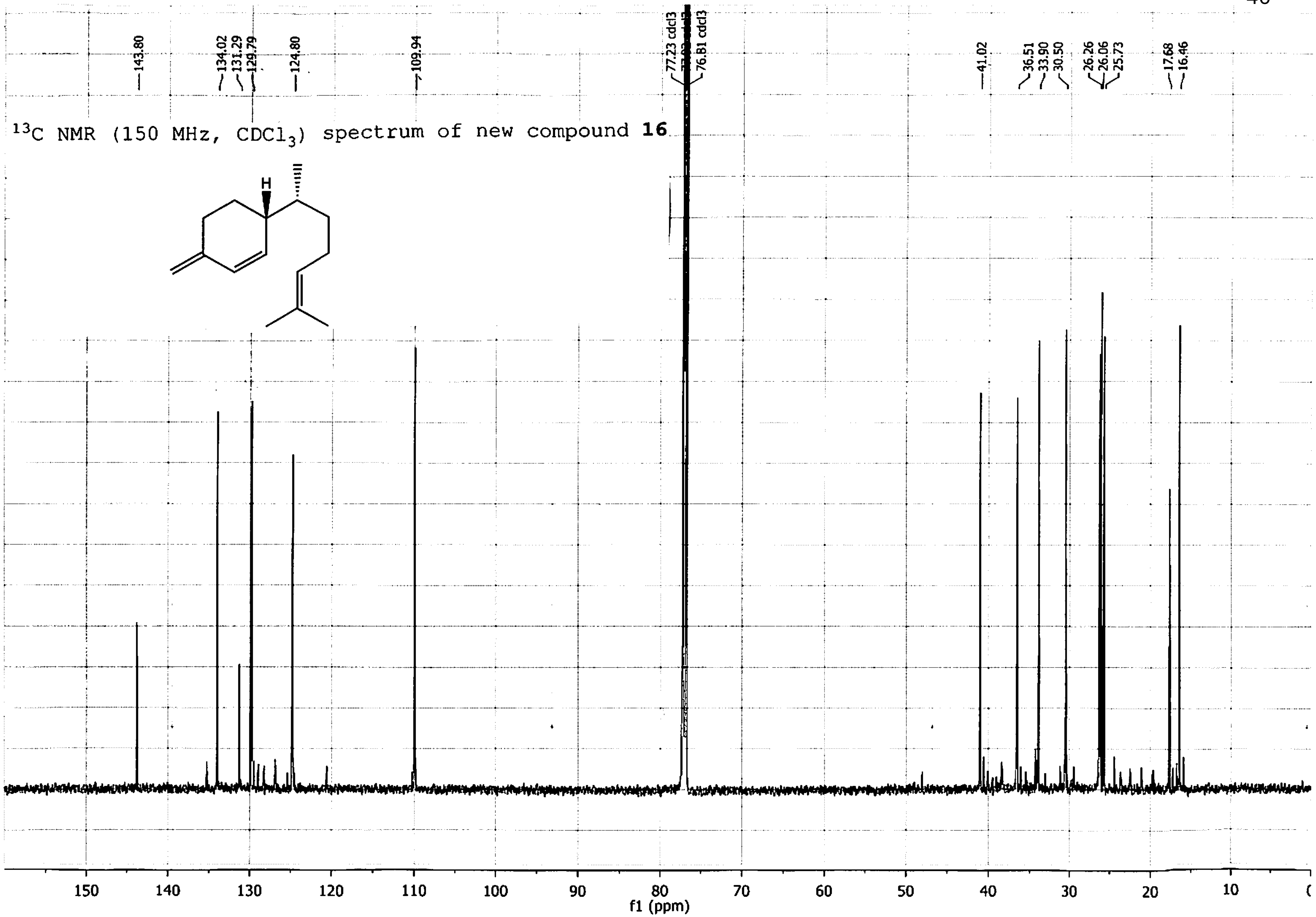


^1H NMR (600 MHz, $CDCl_3$) spectrum of new compound **16**

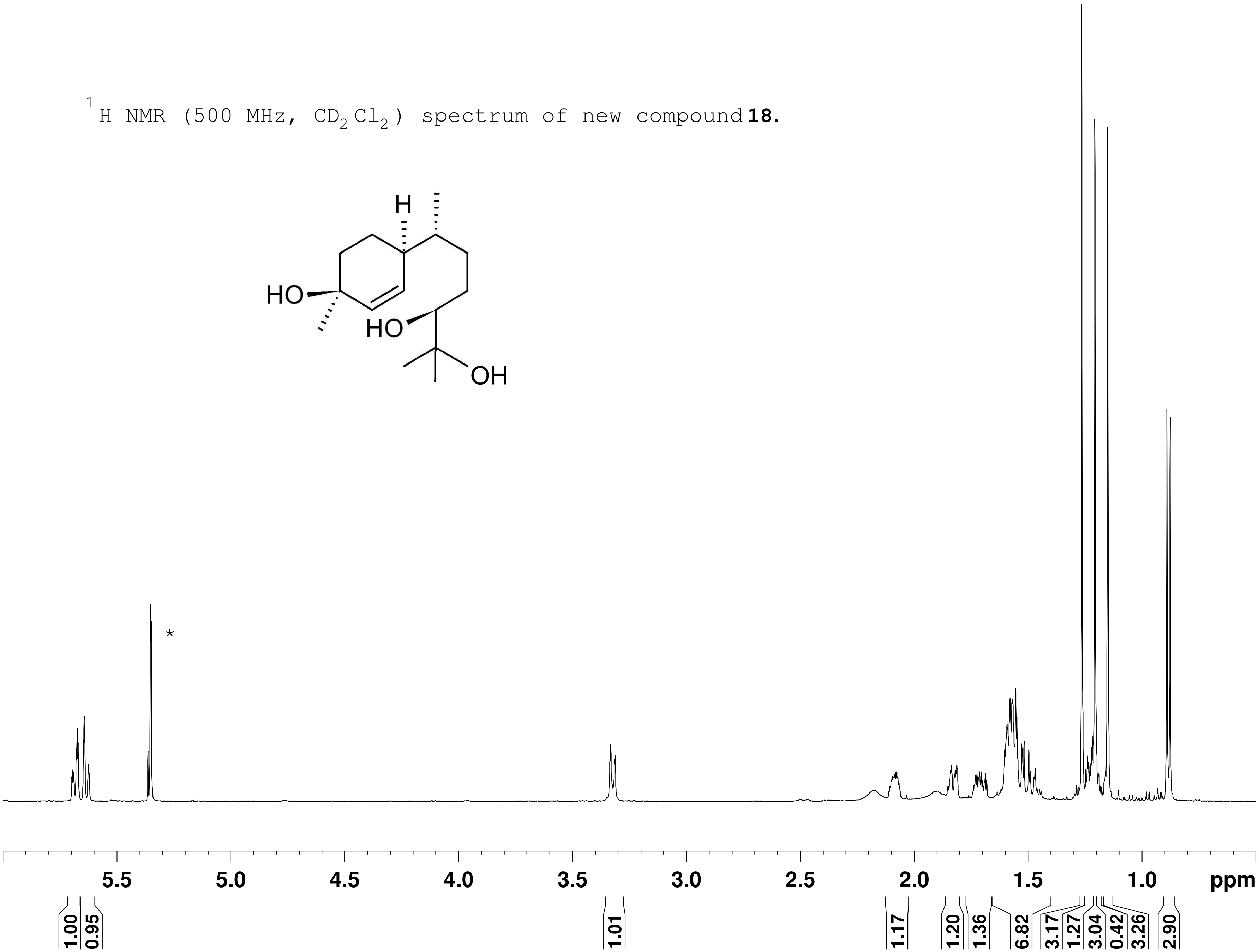




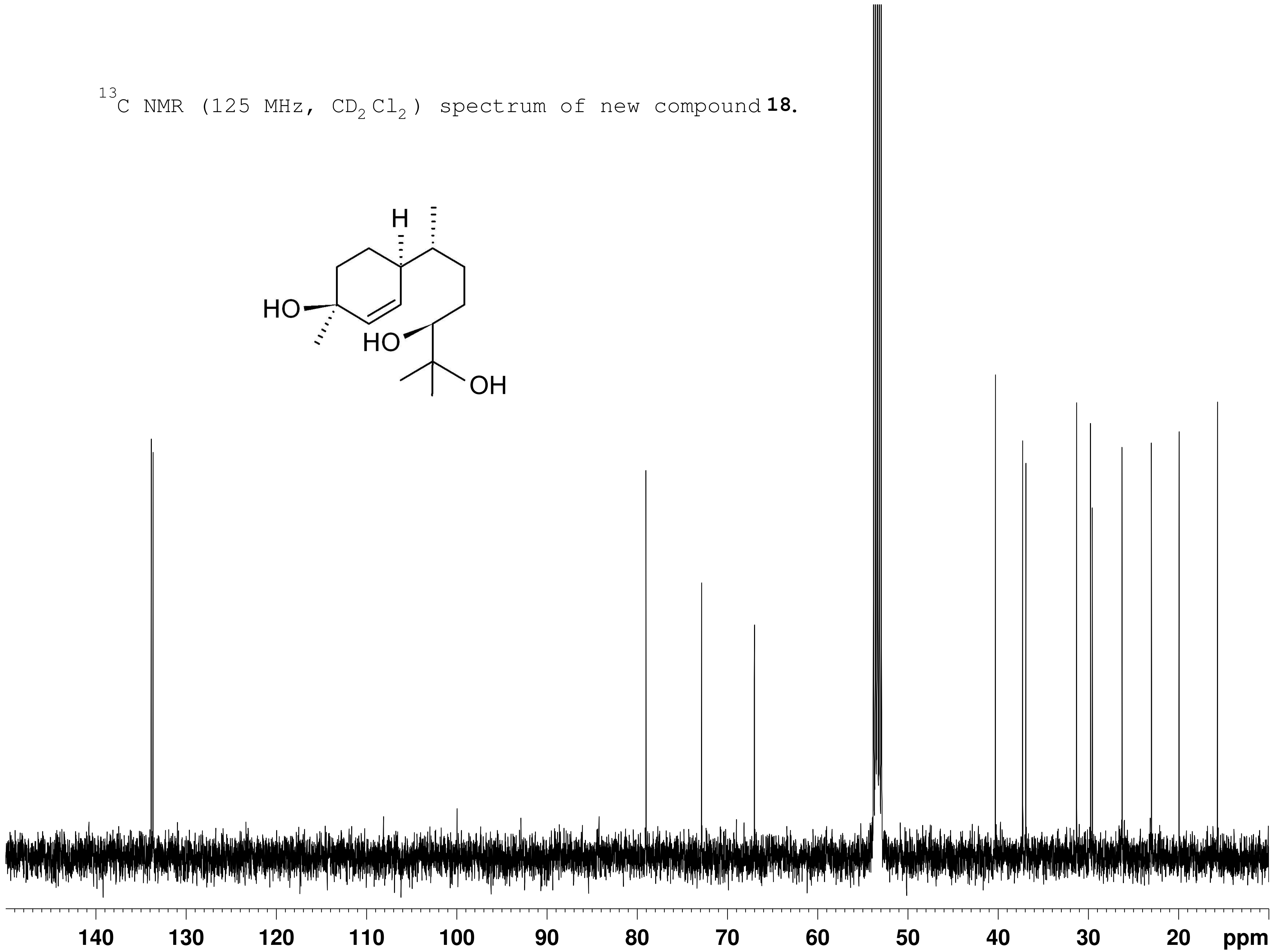
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of new compound **16**



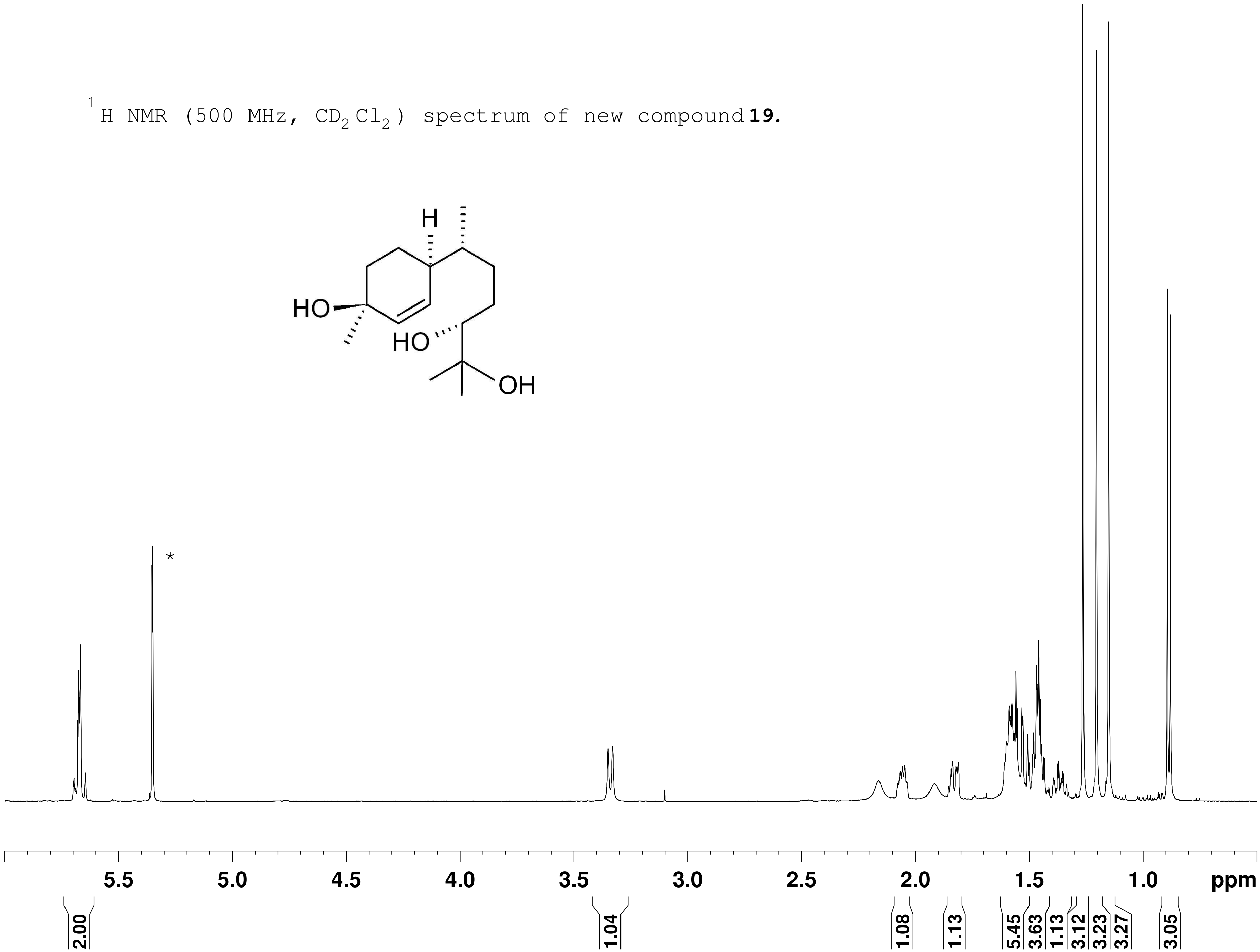
^{1}H NMR (500 MHz, CD_2Cl_2) spectrum of new compound **18**.



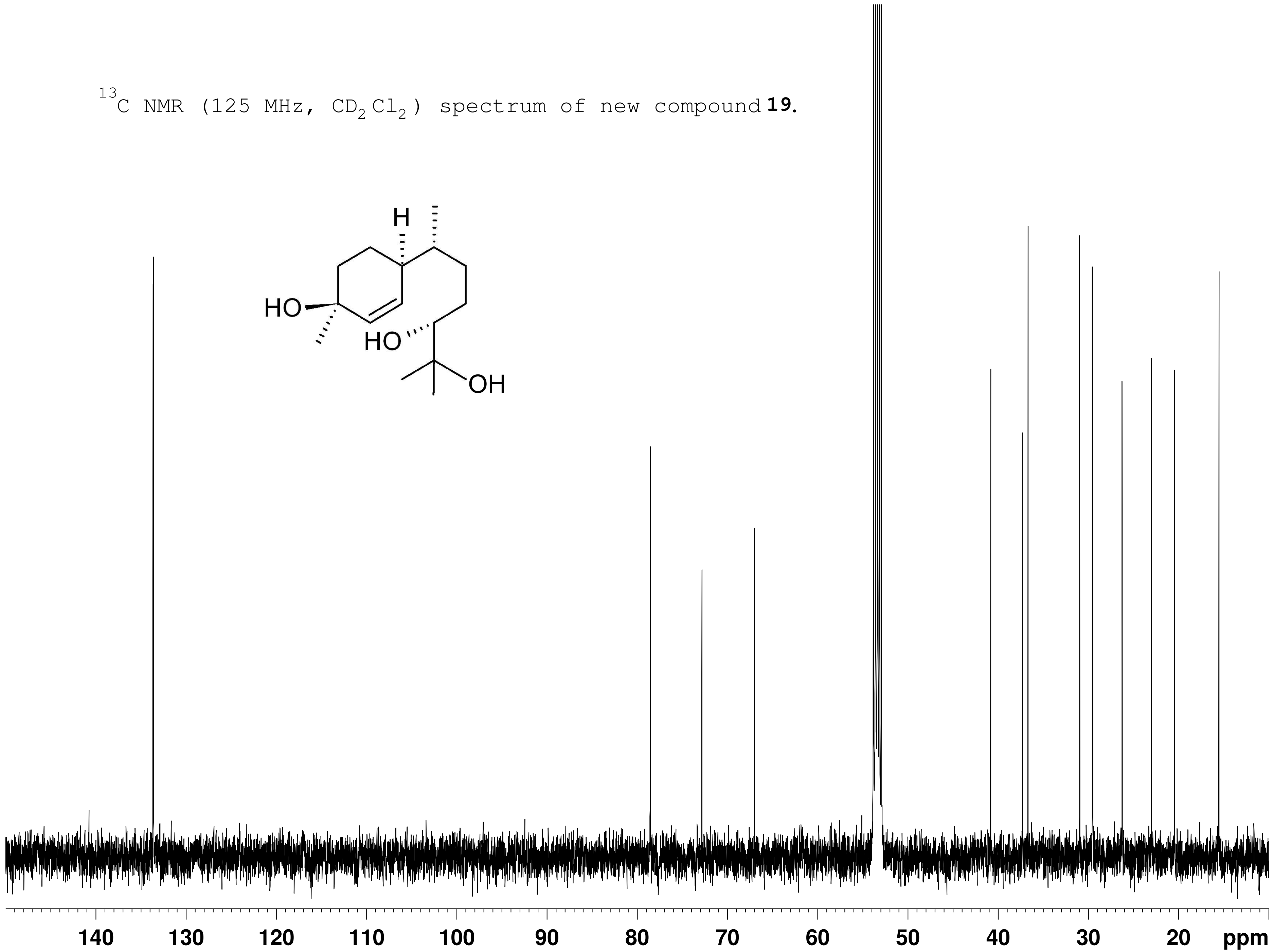
^{13}C NMR (125 MHz, CD_2Cl_2) spectrum of new compound **18**.



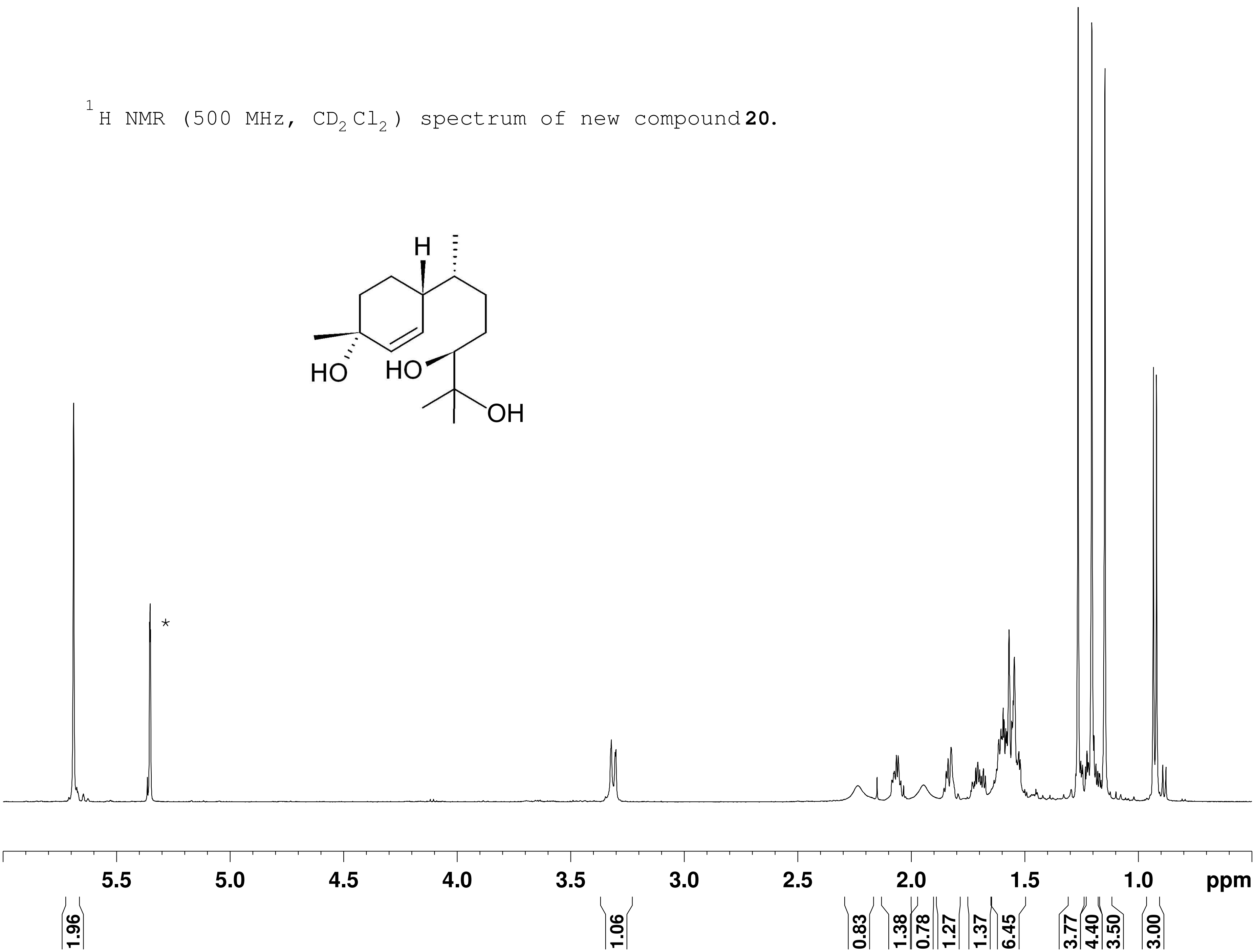
^{1}H NMR (500 MHz, CD_2Cl_2) spectrum of new compound **19.**



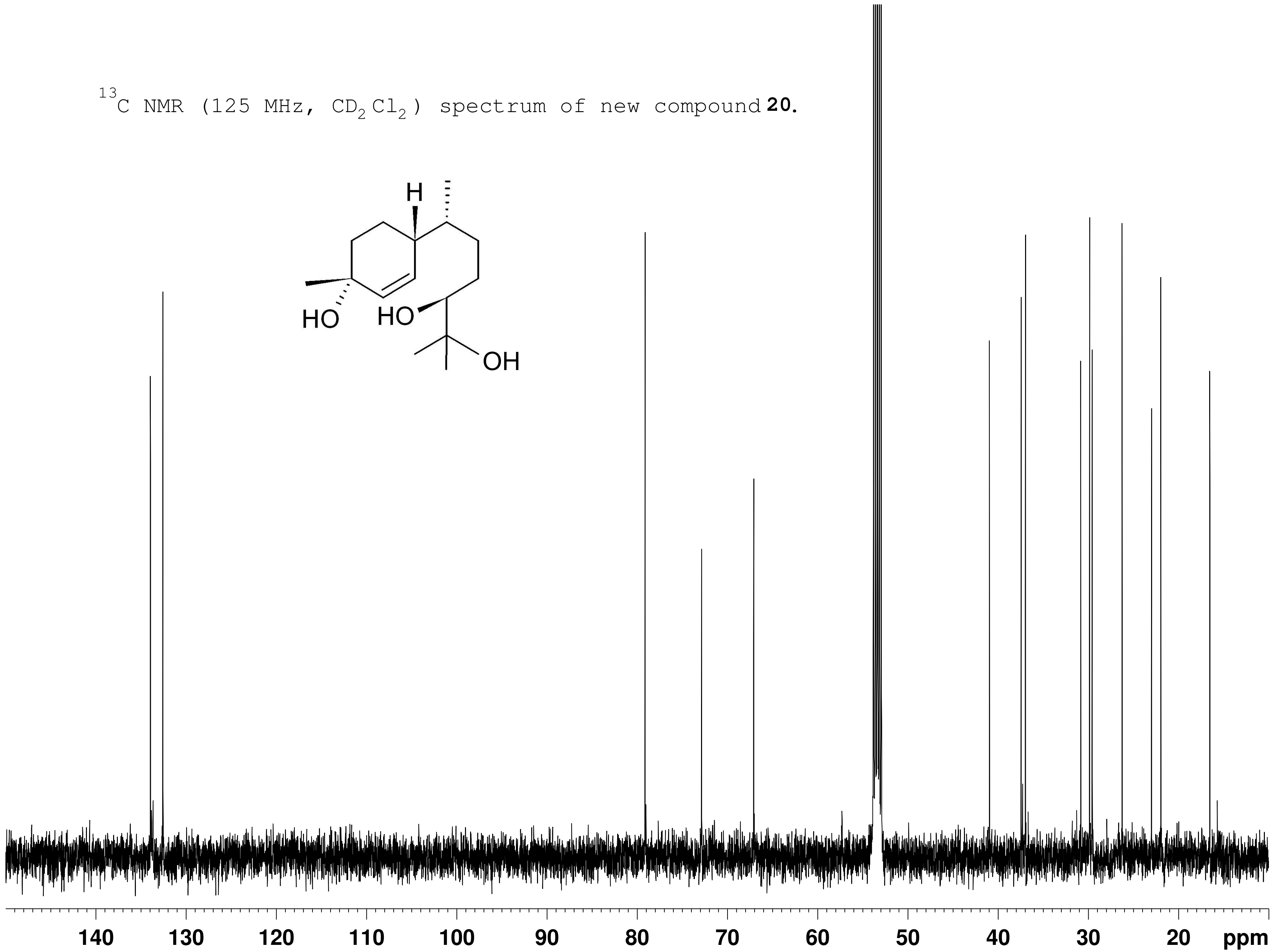
^{13}C NMR (125 MHz, CD_2Cl_2) spectrum of new compound **19**.



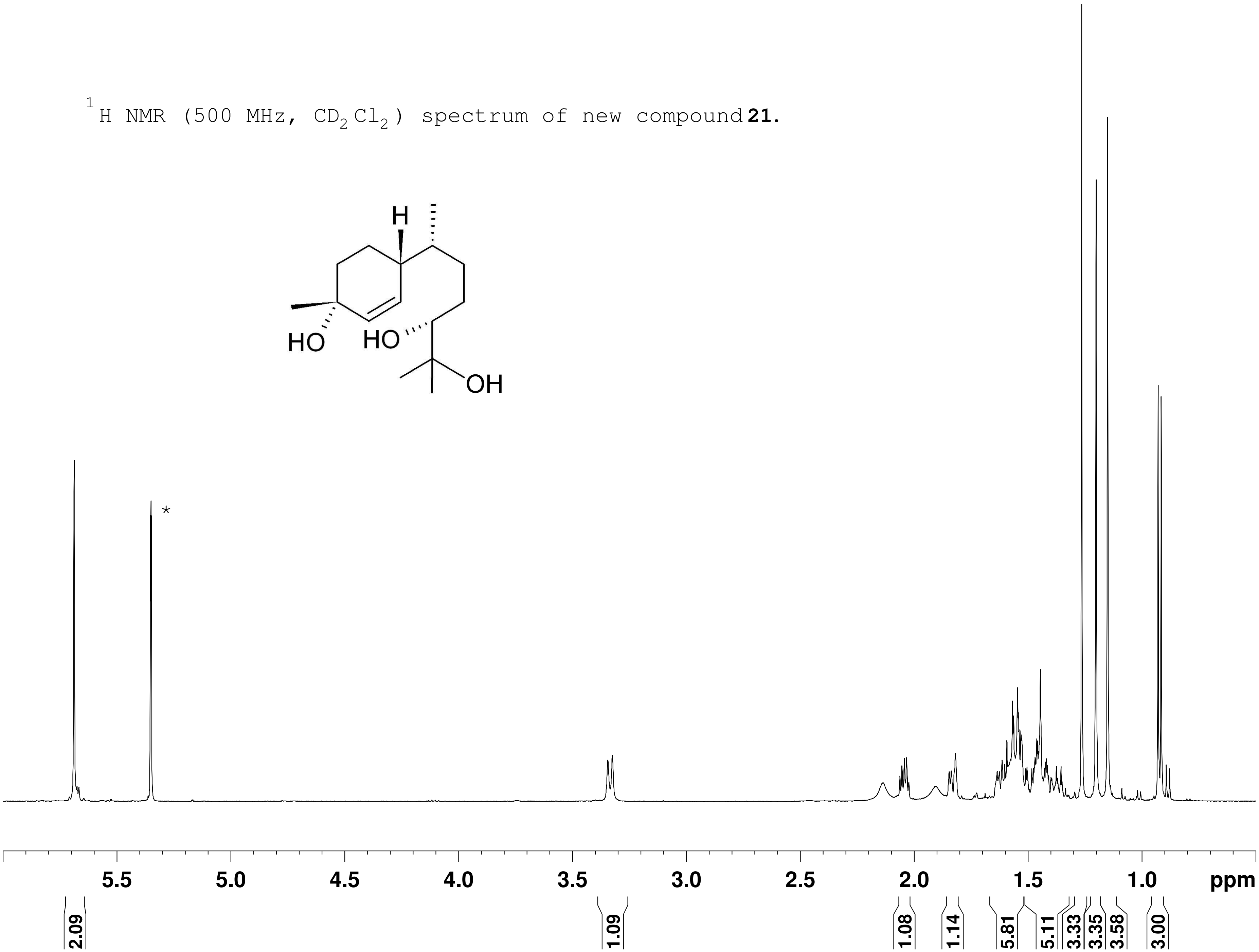
[1]H NMR (500 MHz, CD_2Cl_2) spectrum of new compound **20.**



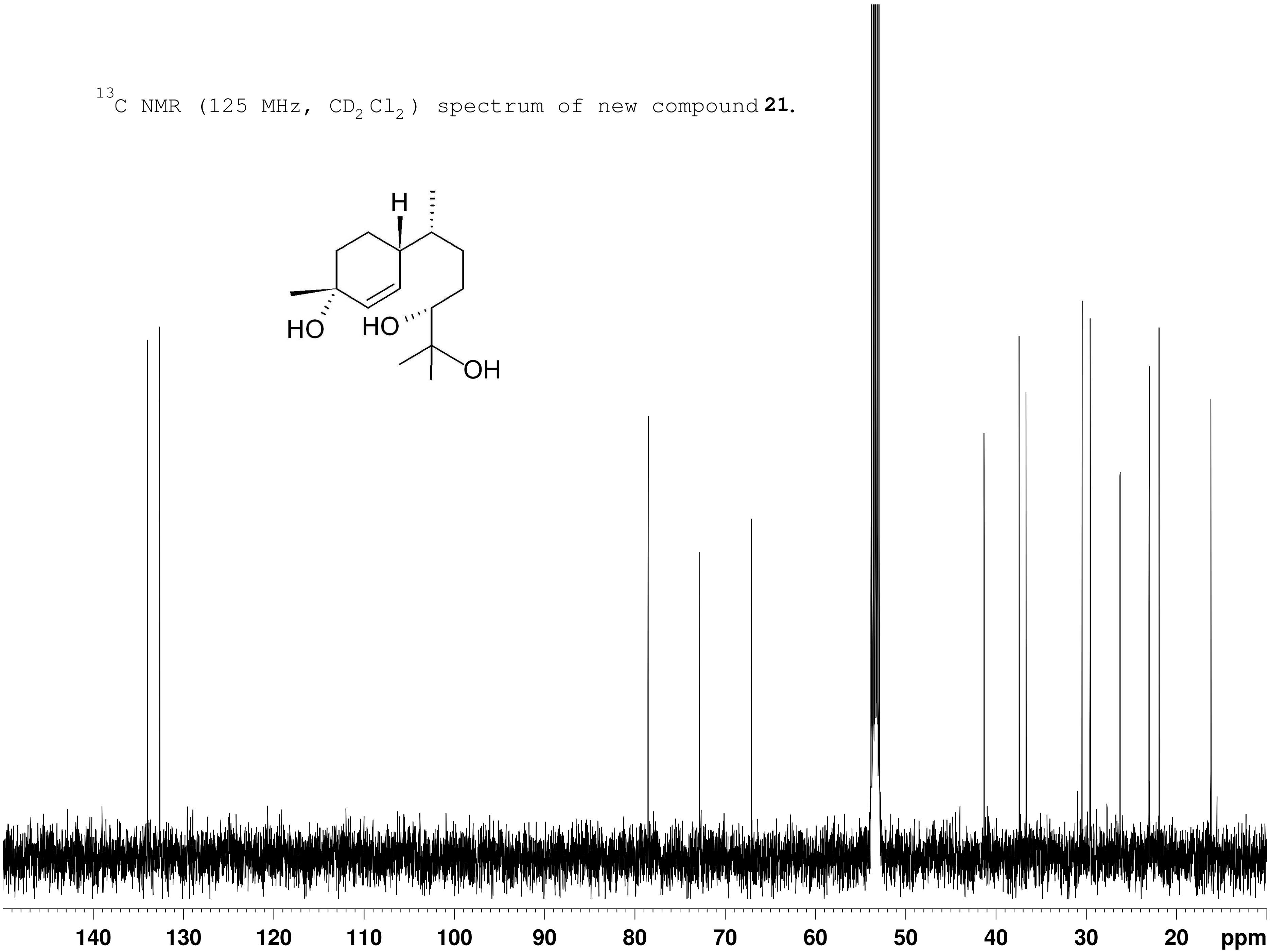
^{13}C NMR (125 MHz, CD_2Cl_2) spectrum of new compound **20.**



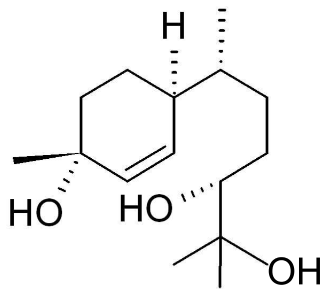
^{1}H NMR (500 MHz, CD_2Cl_2) spectrum of new compound **21.**

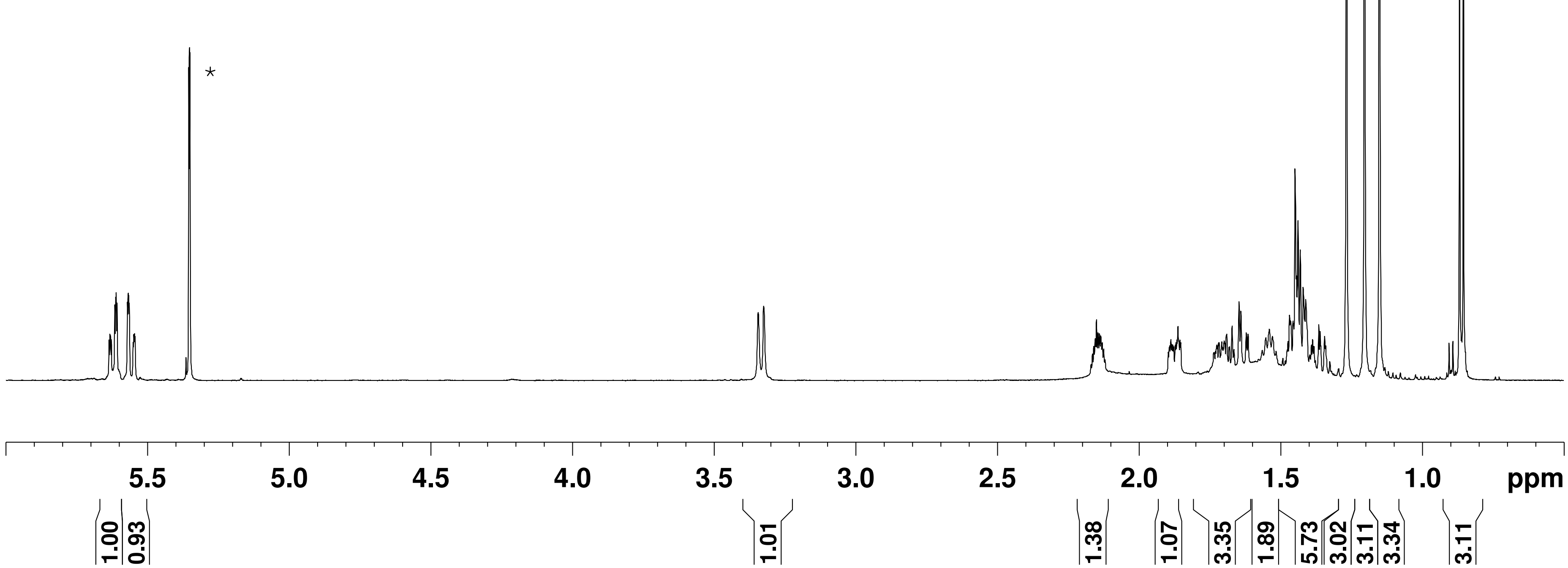


^{13}C NMR (125 MHz, CD_2Cl_2) spectrum of new compound **21.**

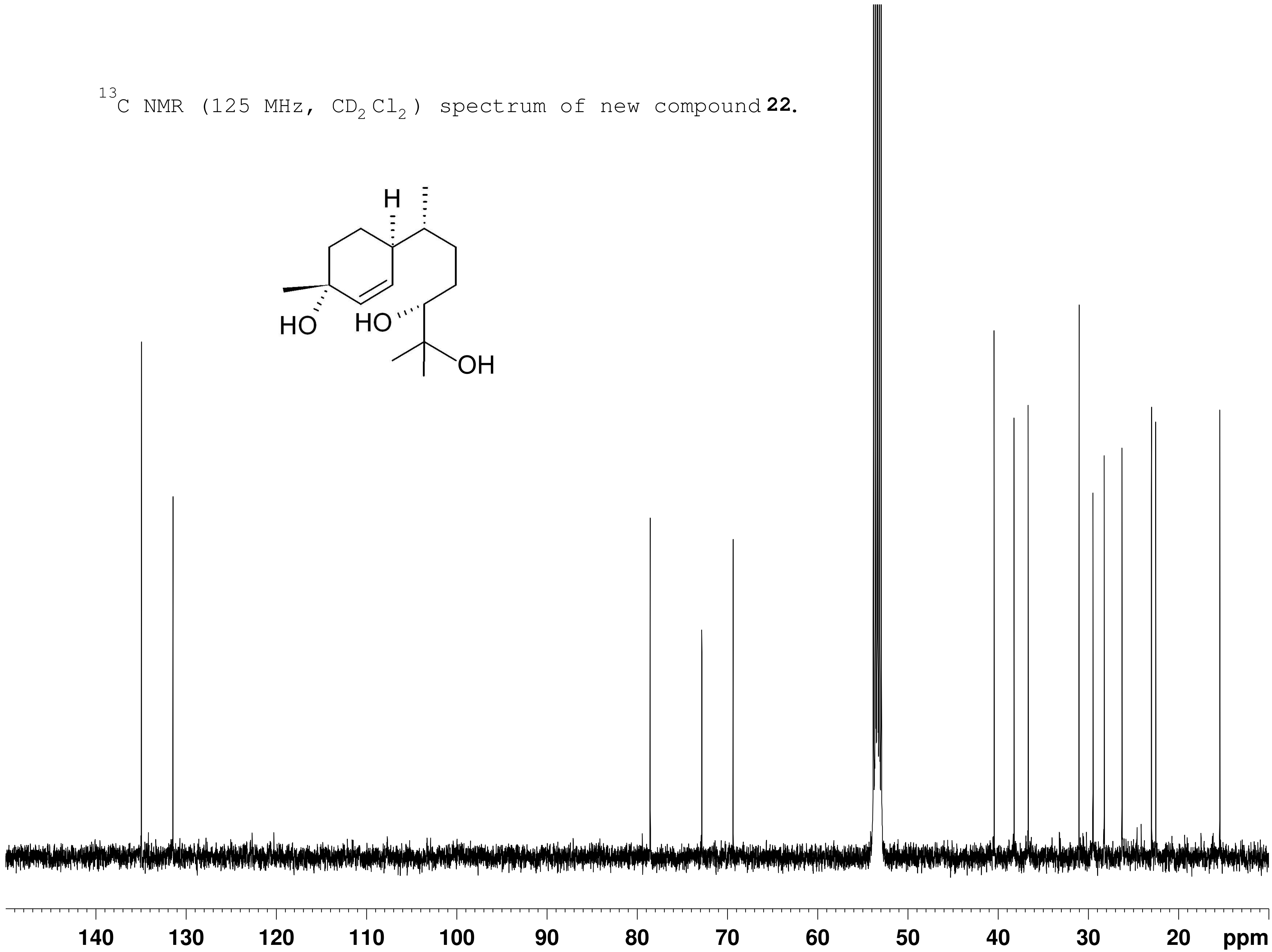


[1]H NMR (500 MHz, CD_2Cl_2) spectrum of new compound **22.**

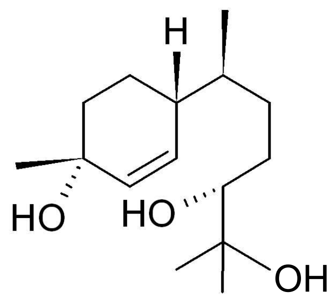


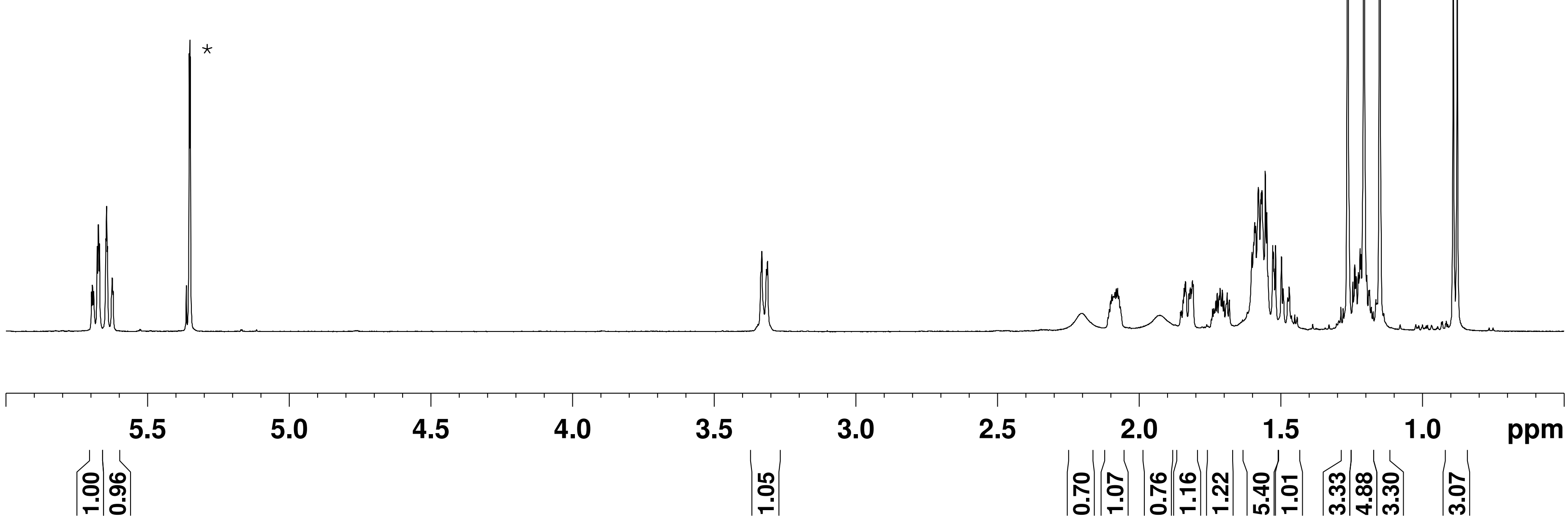


^{13}C NMR (125 MHz, CD_2Cl_2) spectrum of new compound **22**.

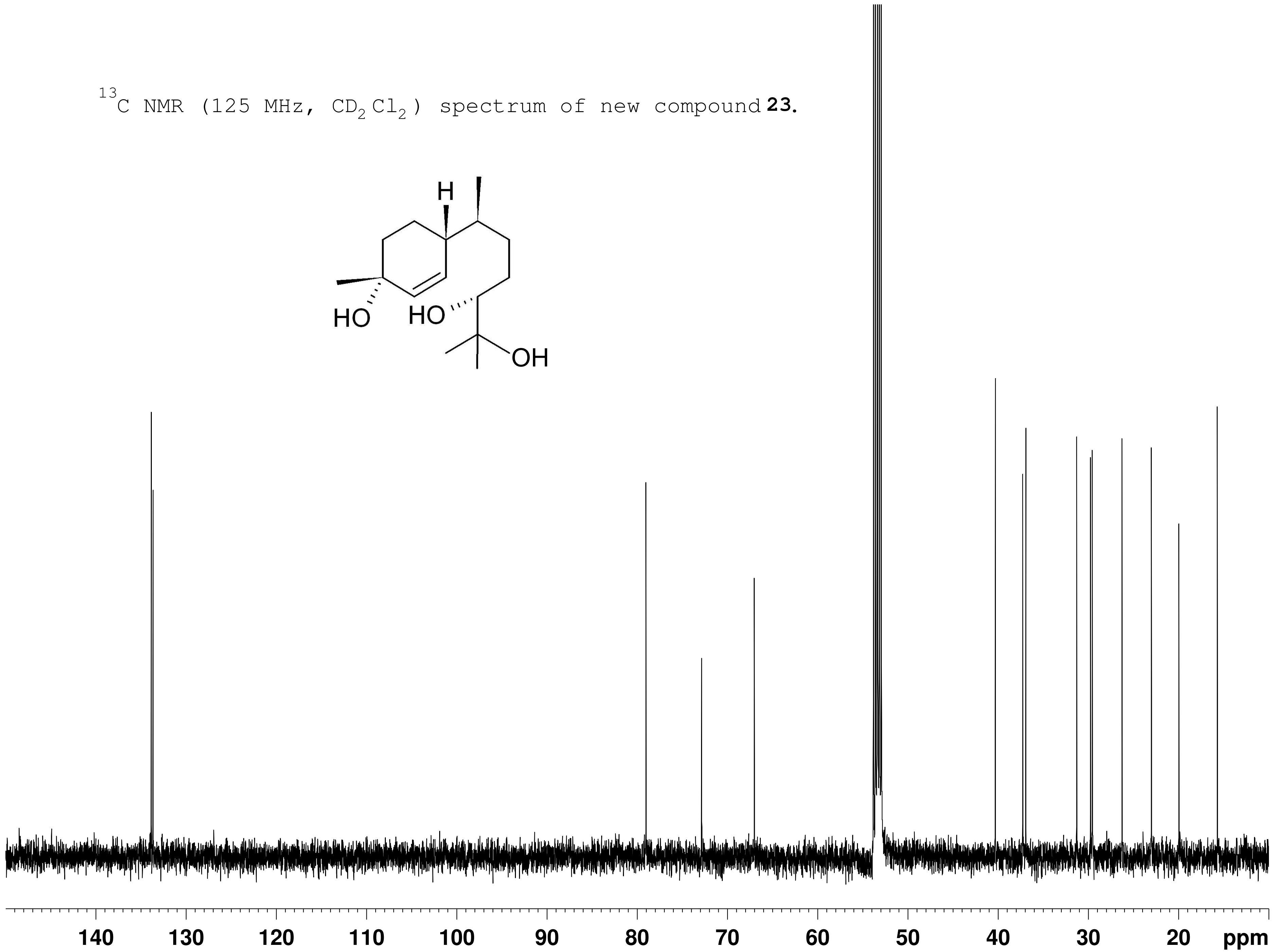


[1]H NMR (500 MHz, CD_2Cl_2) spectrum of new compound **23.**

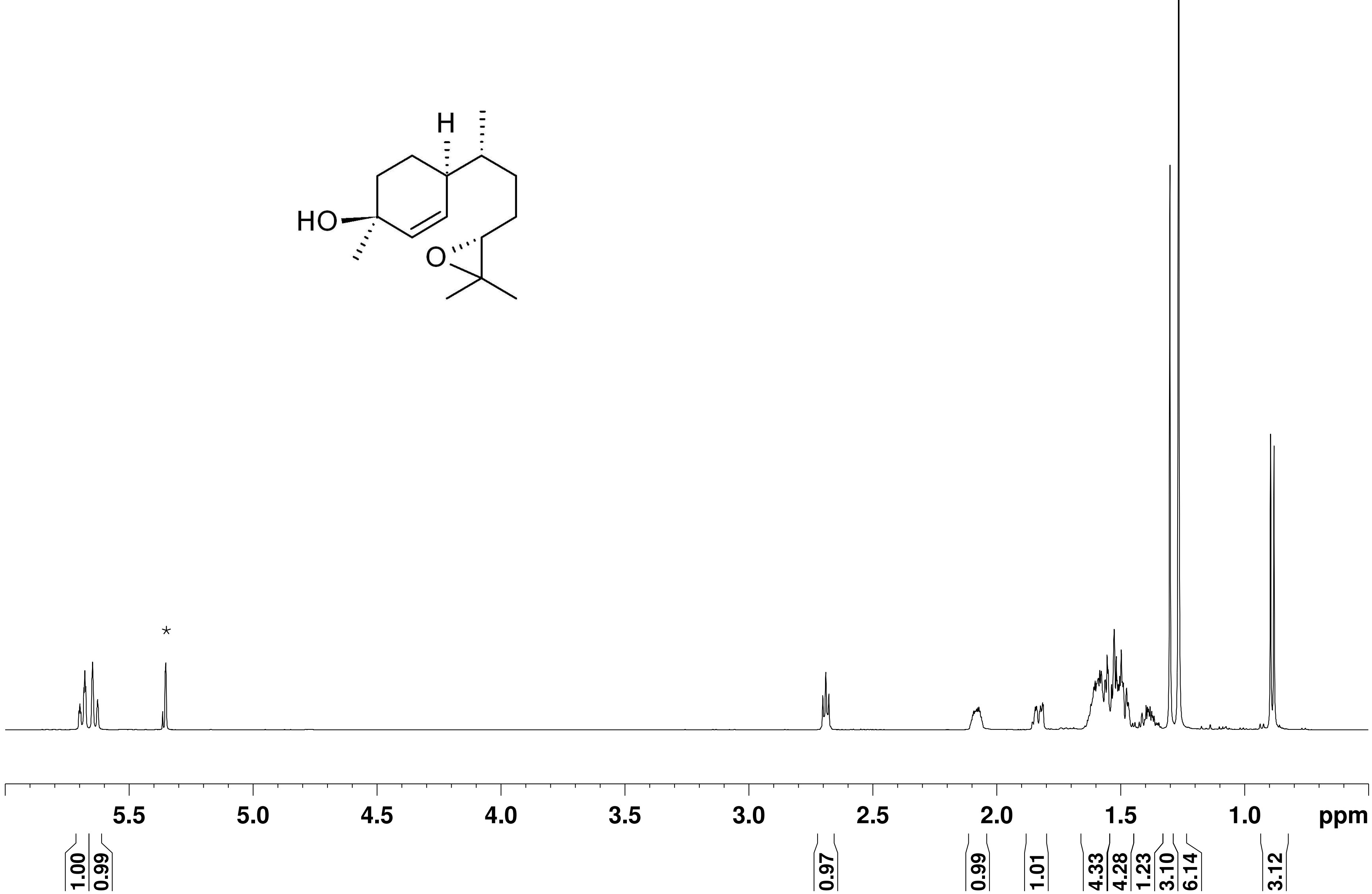




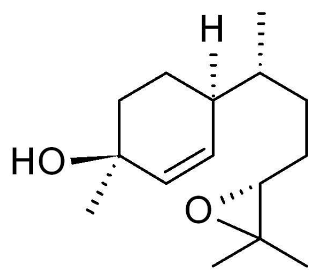
^{13}C NMR (125 MHz, CD_2Cl_2) spectrum of new compound **23**.

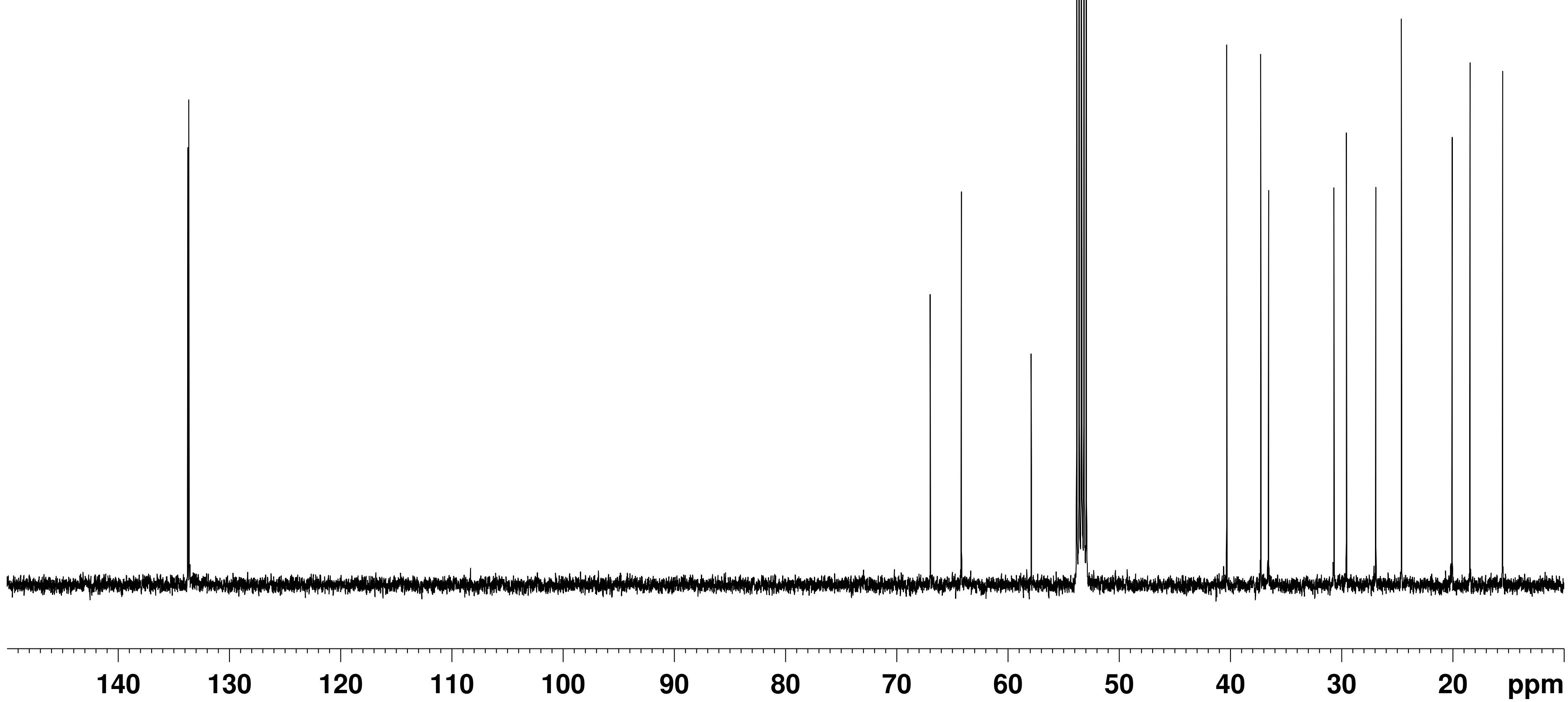


^{1}H NMR (500 MHz, CD_2Cl_2) spectrum of new compound **24.**

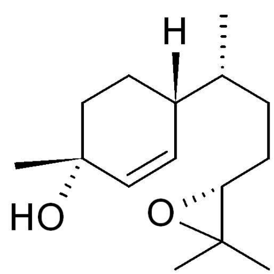


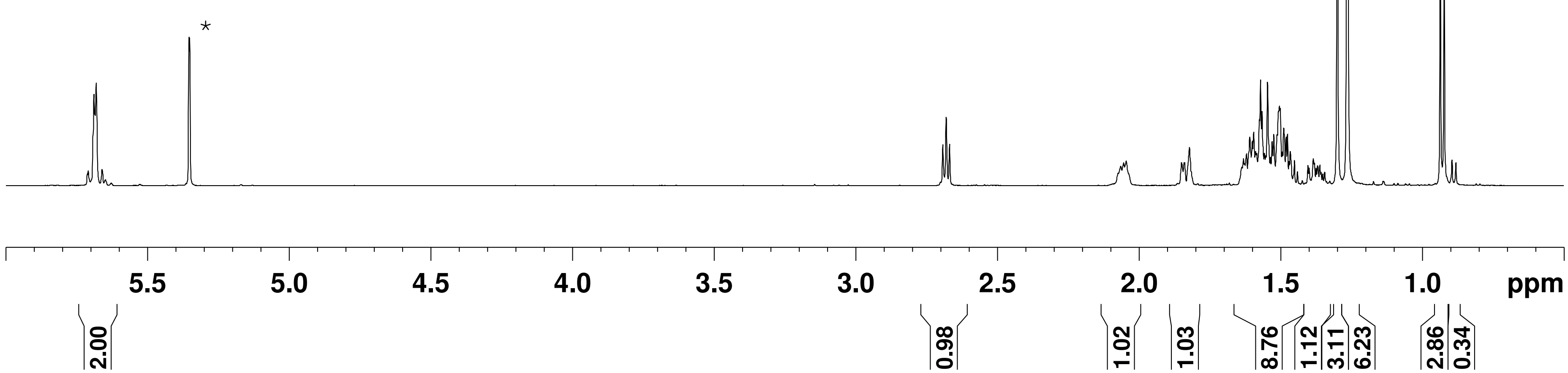
^{13}C NMR (125 MHz, CD_2Cl_2) spectrum of new compound **24.**



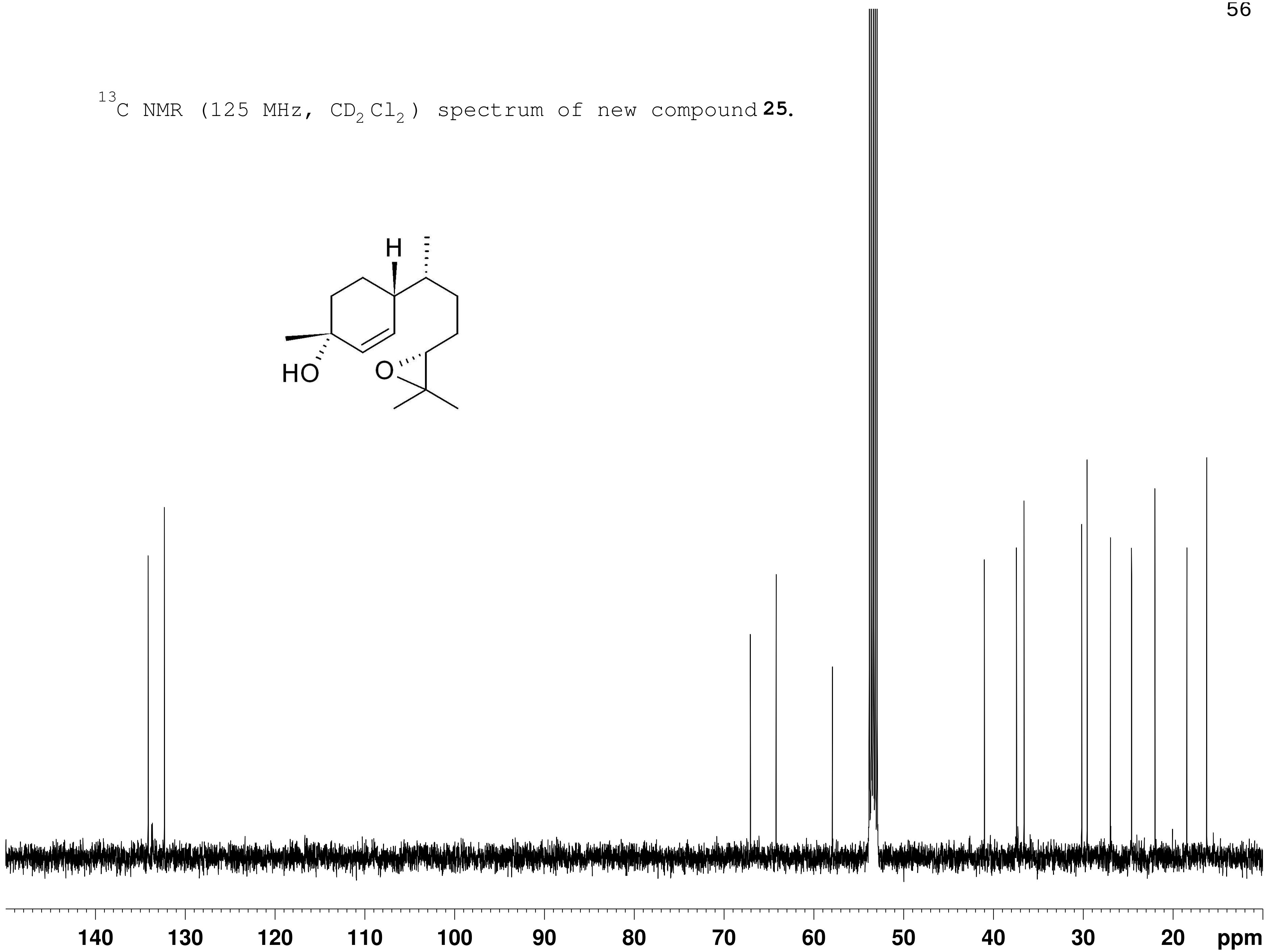


^{1}H NMR (500 MHz, CD_2Cl_2) spectrum of new compound **25.**

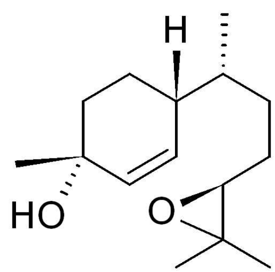


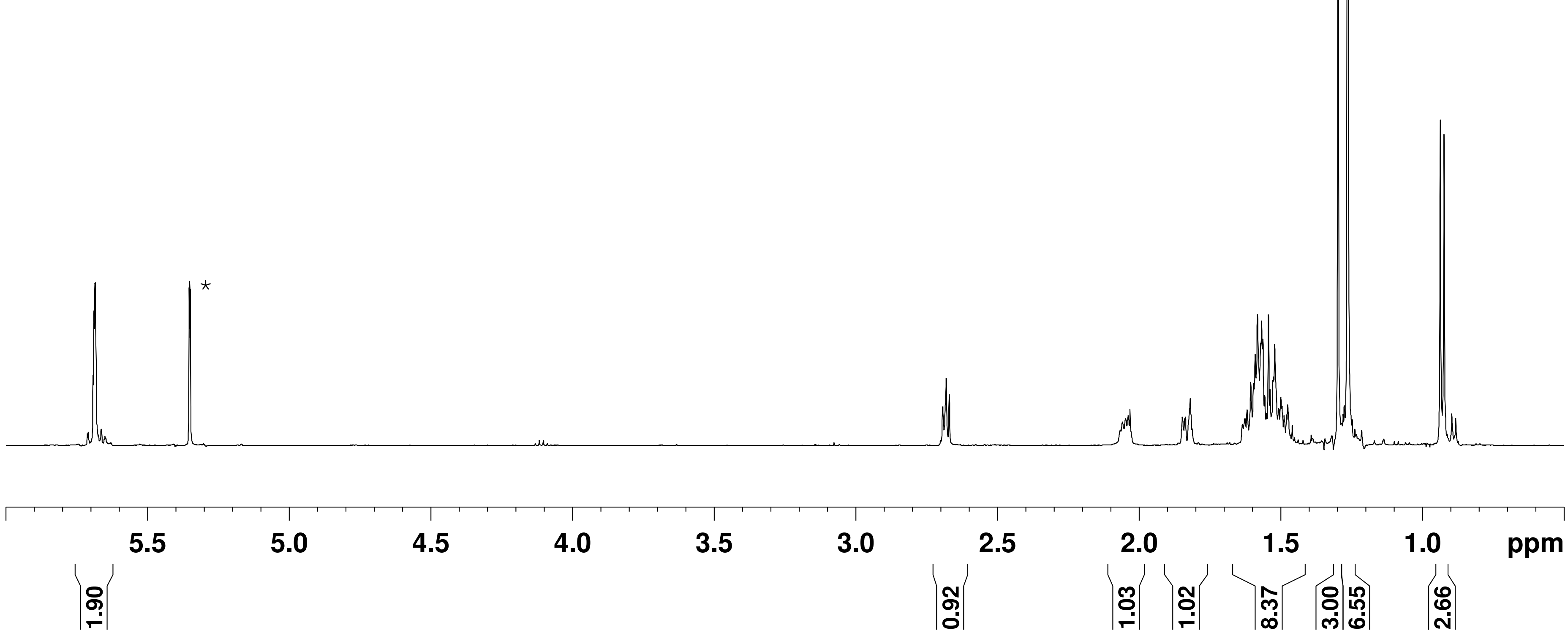


^{13}C NMR (125 MHz, CD_2Cl_2) spectrum of new compound **25.**

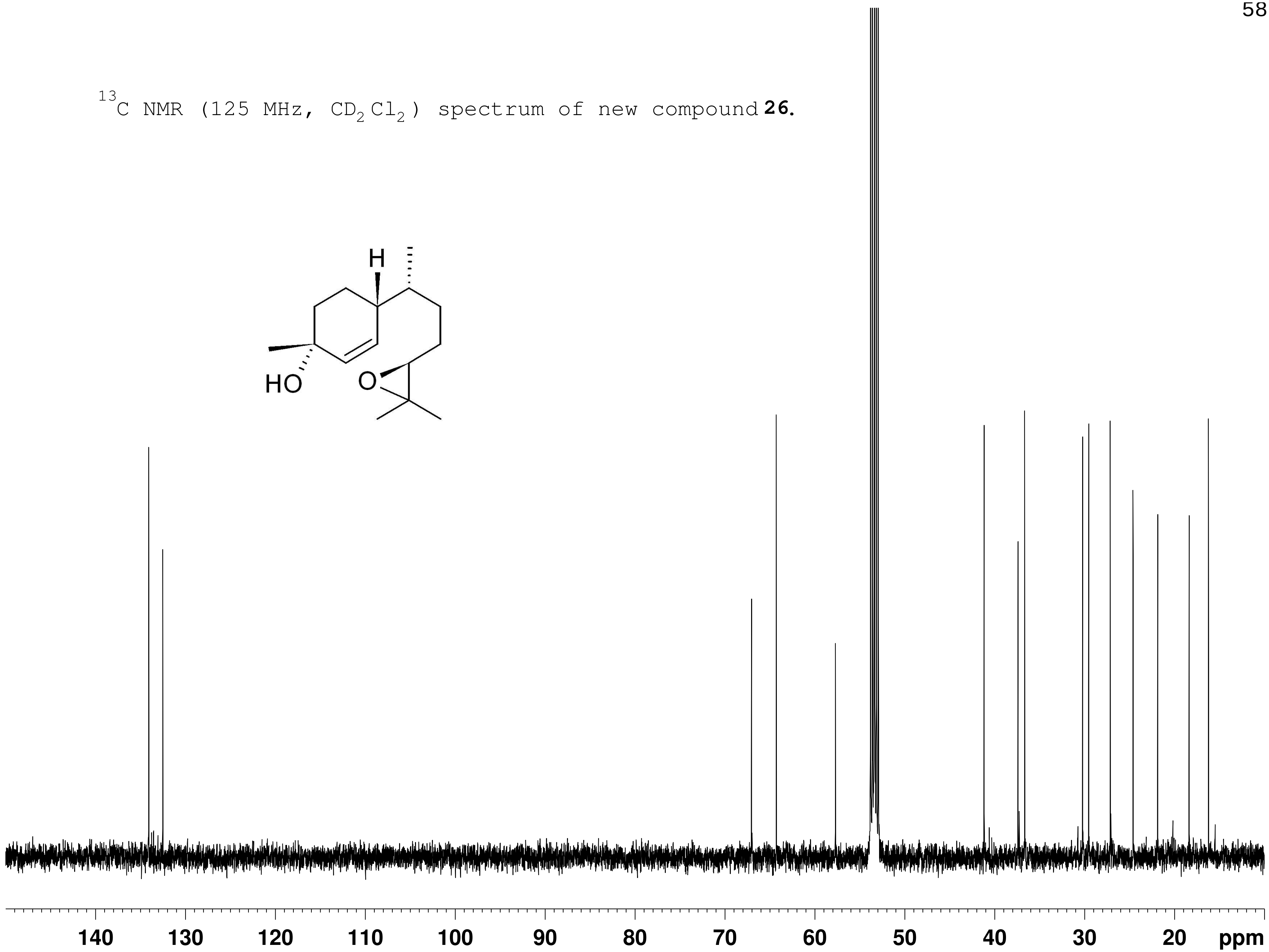


^{1}H NMR (500 MHz, CD_2Cl_2) spectrum of new compound **26.**

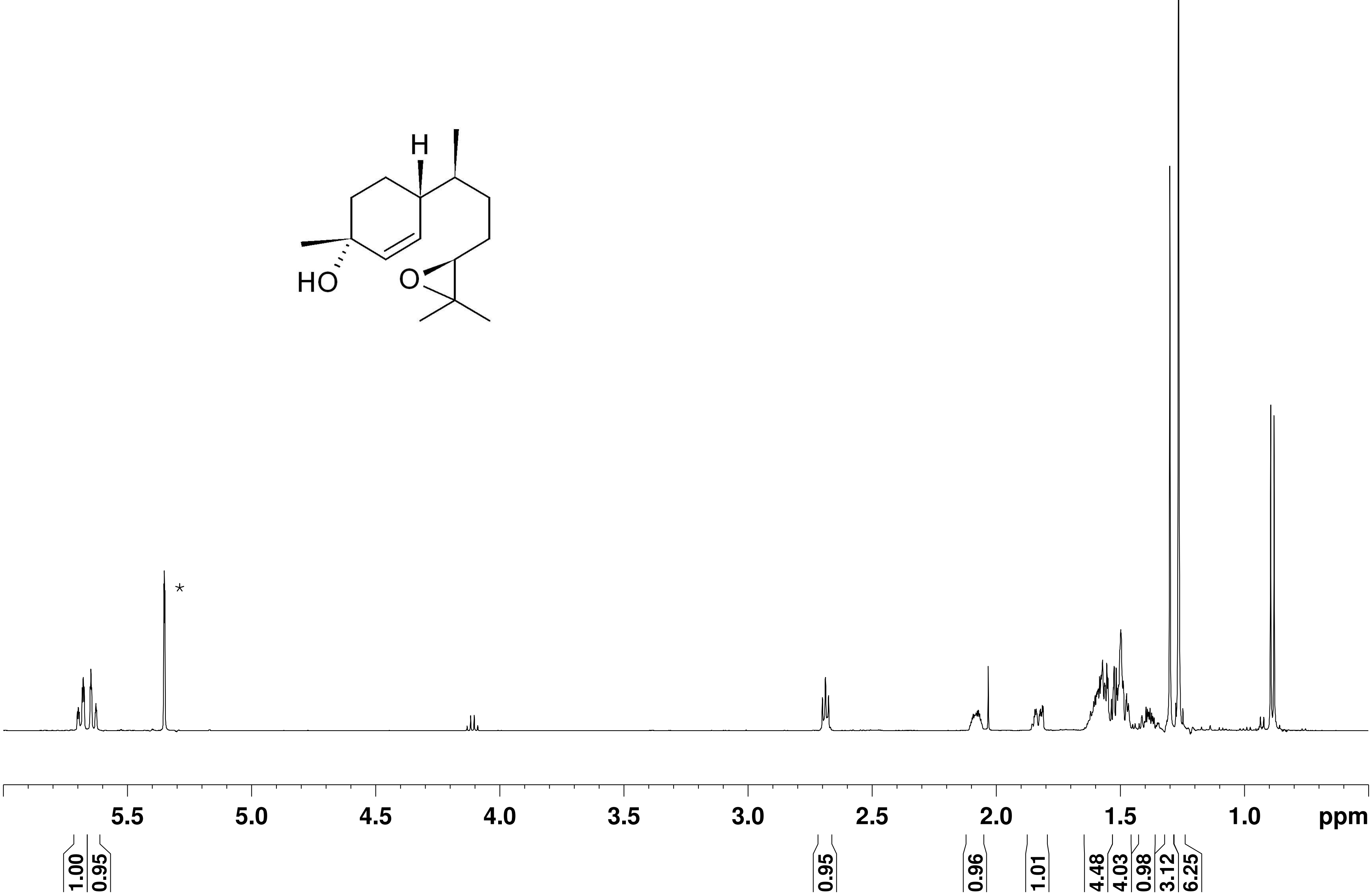




^{13}C NMR (125 MHz, CD_2Cl_2) spectrum of new compound **26.**



^{1}H NMR (500 MHz, CD_2Cl_2) spectrum of new compound **27.**



^{13}C NMR (125 MHz, CD_2Cl_2) spectrum of new compound **27**.