

SUPPORTING INFORMATION

Sequential Diels-Alder Reaction/Rearrangement Sequence: Synthesis of Functionalized Bicyclo[2.2.1]heptane Derivatives and Correction of Their Relative Configuration

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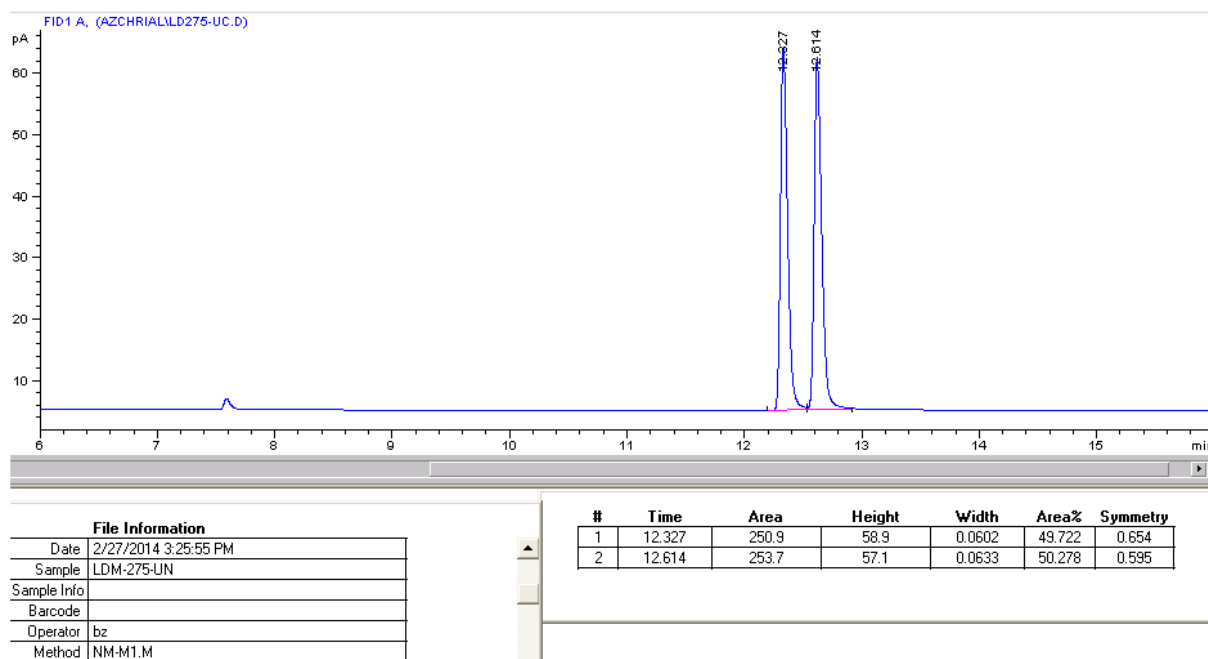
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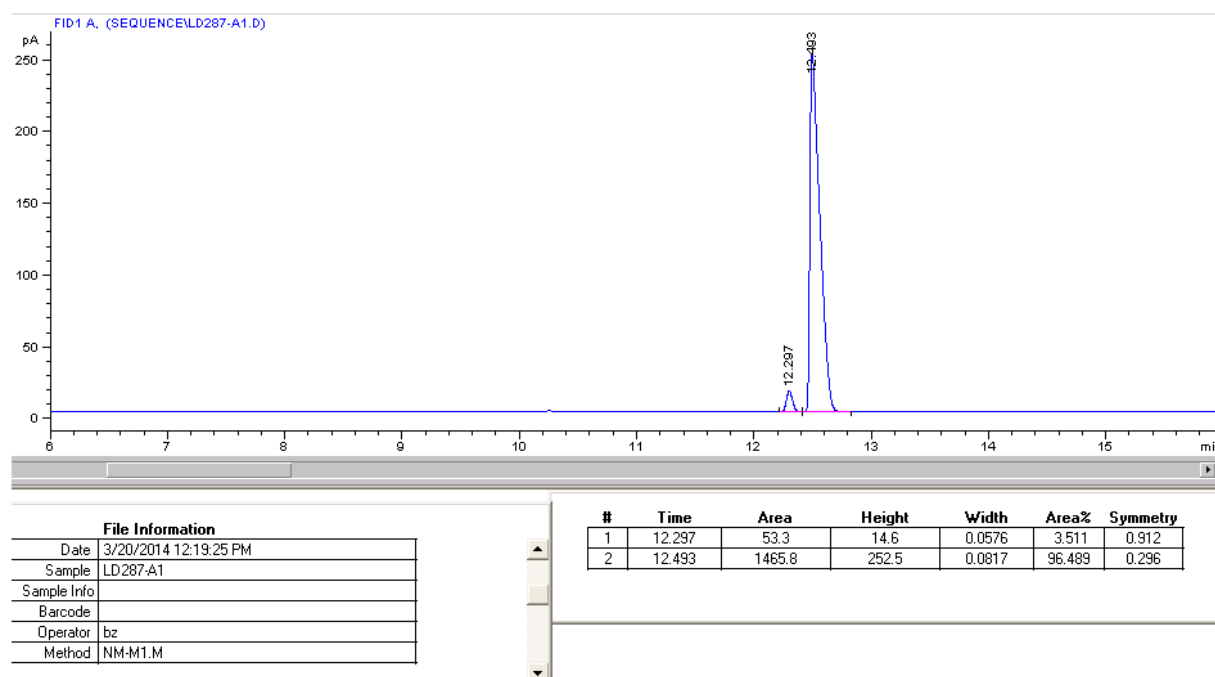
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I. Chiral GC chromatograms:

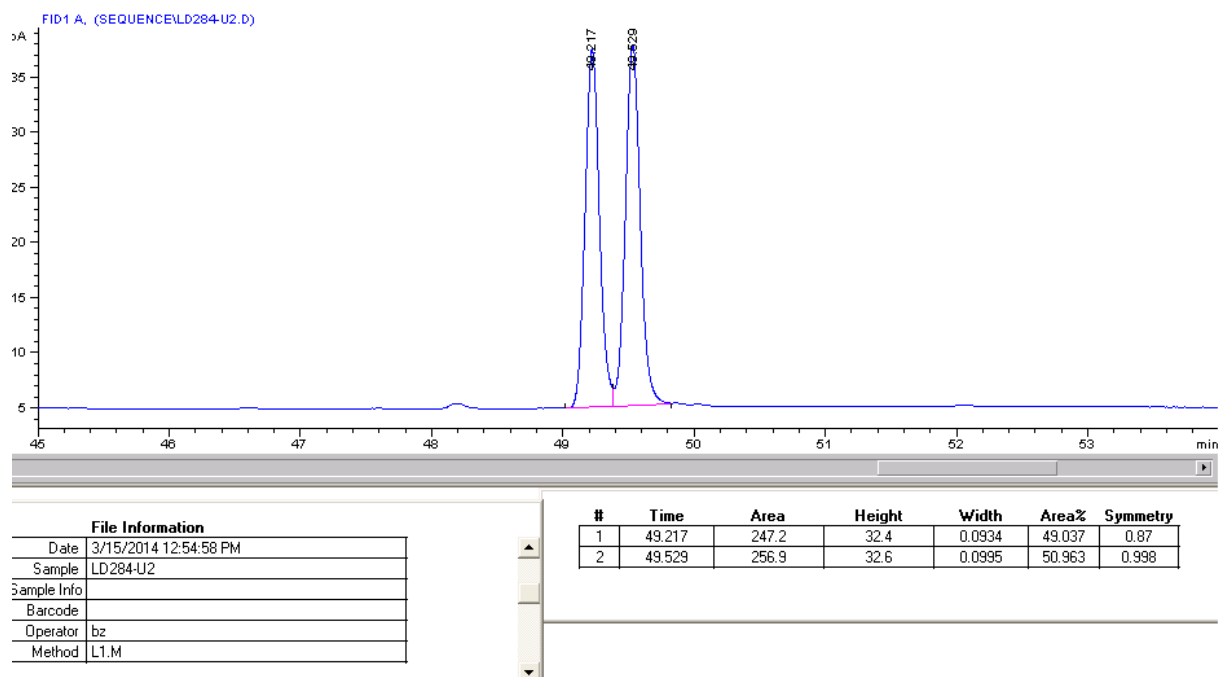
GC chromatogram of (*rac*)-*endo*-15b



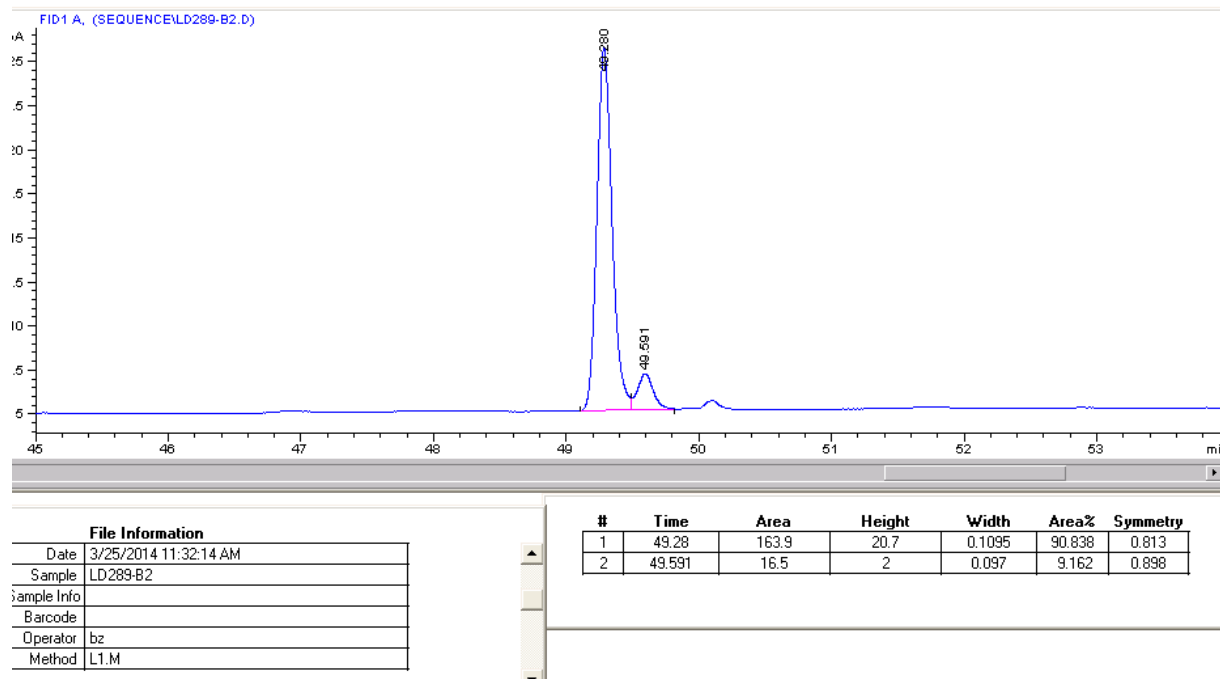
GC chromatogram of (1*S*,3*R*,4*R*)-15b with e.r. = 96.5:3.5



GC chromatogram of (rac)-**31**



GC chromatogram of (2S,4aS,8aR)-**31** with e.r. = 91:9



II. X-ray Crystal Structure Analysis of compound 15b”

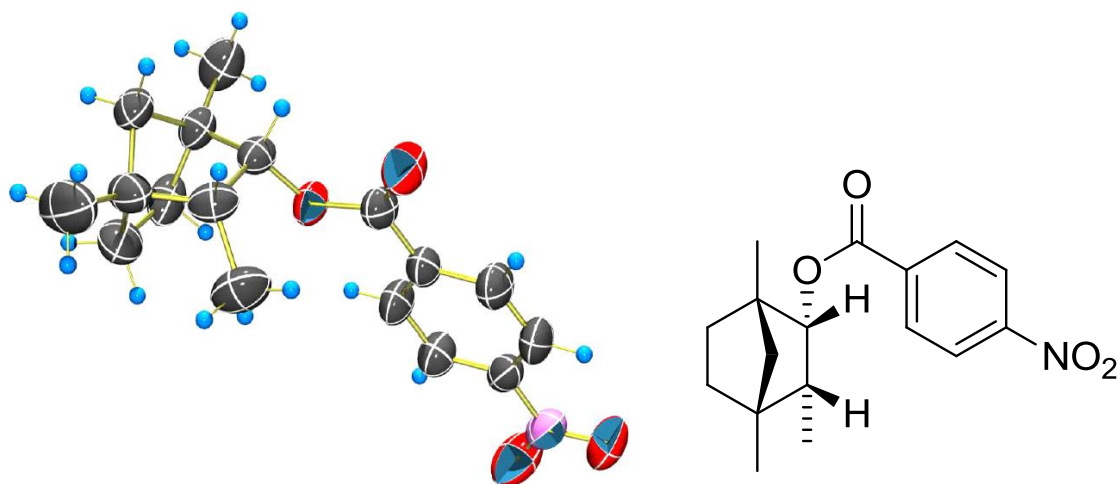


Table 1. Crystal data and structure refinement for **15b”**.

Identification code	a40415b	
Empirical formula	C17 H21 N O4	
Formula weight	303.35	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 6.082(3) Å	$\alpha = 66.576(4)^\circ$
	b = 11.612(5) Å	$\beta = 79.752(4)^\circ$
	c = 12.591(5) Å	$\gamma = 88.139(4)^\circ$
Volume	802.2(6) Å ³	
Z	2	
Density (calculated)	1.256 Mg/m ³	
Absorption coefficient	0.089 mm ⁻¹	
F(000)	324	
Crystal size	0.620 x 0.420 x 0.200 mm ³	
Theta range for data collection	1.792 to 25.096 °	
Index ranges	-7<=h<=7, -10<=k<=13, -15<=l<=15	
Reflections collected	3982	
Independent reflections	2783 [R(int) = 0.0225]	
Completeness to theta = 25.242 °	95.9 %	
Absorption correction	Semi-empirical from equivalents	

Max. and min. transmission	0.746 and 0.652
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2783 / 0 / 203
Goodness-of-fit on F^2	1.059
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0478$, $wR_2 = 0.1386$
R indices (all data)	$R_1 = 0.0586$, $wR_2 = 0.1487$
Extinction coefficient	0.081(10)
Largest diff. peak and hole	0.194 and -0.175 e. $\text{\AA}^{-3}$

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **15b**". U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	6977(3)	8662(2)	-325(1)	69(1)
O(1)	-570(2)	7242(2)	4323(1)	81(1)
O(2)	2406(2)	7757(1)	4899(1)	54(1)
O(3)	6199(3)	8464(2)	-1062(1)	102(1)
O(4)	8900(3)	9025(2)	-467(2)	103(1)
C(1)	1239(2)	7312(2)	6112(1)	47(1)
C(2)	1604(3)	5915(2)	6838(2)	58(1)
C(3)	2611(3)	5974(2)	7859(2)	64(1)
C(4)	4998(3)	6556(2)	7380(2)	82(1)
C(5)	4681(3)	7924(2)	6601(2)	69(1)
C(6)	2134(3)	8030(2)	6744(1)	51(1)
C(7)	1393(3)	7083(2)	8014(1)	56(1)
C(8)	2935(4)	5216(2)	6149(2)	88(1)
C(9)	2385(5)	4737(2)	8935(2)	112(1)
C(10)	1315(4)	9353(2)	6430(2)	77(1)
C(11)	1350(3)	7603(2)	4121(2)	54(1)
C(12)	2855(3)	7918(2)	2960(1)	50(1)
C(13)	4991(3)	8434(2)	2718(2)	58(1)
C(14)	6337(3)	8701(2)	1639(2)	61(1)
C(15)	5514(3)	8423(2)	815(1)	56(1)
C(16)	3394(3)	7900(2)	1034(2)	69(1)
C(17)	2070(3)	7655(2)	2109(2)	65(1)

Table 3. Bond lengths [Å] and angles [°] for **15b**".

N(1)-O(3)	1.213(2)
N(1)-O(4)	1.215(2)
N(1)-C(15)	1.474(2)
O(1)-C(11)	1.202(2)
O(2)-C(11)	1.3321(19)
O(2)-C(1)	1.4533(19)
C(1)-C(6)	1.528(2)
C(1)-C(2)	1.545(2)
C(2)-C(8)	1.528(3)
C(2)-C(3)	1.544(3)
C(3)-C(9)	1.521(3)
C(3)-C(7)	1.527(2)
C(3)-C(4)	1.535(3)
C(4)-C(5)	1.527(3)
C(5)-C(6)	1.534(3)
C(6)-C(10)	1.517(3)
C(6)-C(7)	1.533(2)
C(11)-C(12)	1.493(2)
C(12)-C(13)	1.380(2)
C(12)-C(17)	1.386(2)
C(13)-C(14)	1.378(3)
C(14)-C(15)	1.376(2)
C(15)-C(16)	1.378(3)
C(16)-C(17)	1.373(3)
O(3)-N(1)-O(4)	123.68(18)
O(3)-N(1)-C(15)	118.01(19)
O(4)-N(1)-C(15)	118.30(17)
C(11)-O(2)-C(1)	117.38(12)
O(2)-C(1)-C(6)	110.01(12)
O(2)-C(1)-C(2)	113.12(13)
C(6)-C(1)-C(2)	105.12(13)
C(8)-C(2)-C(3)	116.07(17)
C(8)-C(2)-C(1)	115.55(16)
C(3)-C(2)-C(1)	102.49(13)
C(9)-C(3)-C(7)	117.02(17)

C(9)-C(3)-C(4)	114.91(18)
C(7)-C(3)-C(4)	99.94(16)
C(9)-C(3)-C(2)	113.87(19)
C(7)-C(3)-C(2)	100.38(13)
C(4)-C(3)-C(2)	108.98(15)
C(5)-C(4)-C(3)	104.30(15)
C(4)-C(5)-C(6)	104.00(14)
C(10)-C(6)-C(1)	114.30(15)
C(10)-C(6)-C(7)	117.14(14)
C(1)-C(6)-C(7)	98.70(13)
C(10)-C(6)-C(5)	115.28(16)
C(1)-C(6)-C(5)	108.44(14)
C(7)-C(6)-C(5)	101.01(14)
C(3)-C(7)-C(6)	96.23(13)
O(1)-C(11)-O(2)	124.66(16)
O(1)-C(11)-C(12)	123.65(15)
O(2)-C(11)-C(12)	111.69(14)
C(13)-C(12)-C(17)	119.41(16)
C(13)-C(12)-C(11)	122.47(15)
C(17)-C(12)-C(11)	118.11(15)
C(14)-C(13)-C(12)	120.75(16)
C(15)-C(14)-C(13)	118.44(17)
C(14)-C(15)-C(16)	122.10(17)
C(14)-C(15)-N(1)	118.70(17)
C(16)-C(15)-N(1)	119.18(16)
C(17)-C(16)-C(15)	118.55(16)
C(16)-C(17)-C(12)	120.74(18)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **15b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
N(1)	89(1)	68(1)	53(1)	-28(1)	-9(1)	18(1)
O(1)	52(1)	127(1)	81(1)	-60(1)	-8(1)	-16(1)
O(2)	47(1)	73(1)	46(1)	-28(1)	-5(1)	-9(1)
O(3)	115(1)	148(2)	61(1)	-60(1)	-17(1)	18(1)
O(4)	97(1)	136(2)	82(1)	-59(1)	17(1)	-21(1)
C(1)	37(1)	58(1)	48(1)	-24(1)	1(1)	-5(1)
C(2)	50(1)	52(1)	68(1)	-25(1)	8(1)	-5(1)
C(3)	59(1)	67(1)	53(1)	-15(1)	-1(1)	15(1)
C(4)	48(1)	125(2)	79(1)	-46(1)	-15(1)	16(1)
C(5)	54(1)	102(2)	53(1)	-32(1)	-3(1)	-22(1)
C(6)	53(1)	56(1)	44(1)	-21(1)	-2(1)	-7(1)
C(7)	56(1)	65(1)	46(1)	-22(1)	-1(1)	1(1)
C(8)	105(2)	70(1)	97(2)	-48(1)	1(1)	11(1)
C(9)	136(2)	82(2)	78(2)	-2(1)	-2(2)	41(2)
C(10)	108(2)	55(1)	66(1)	-25(1)	-9(1)	-7(1)
C(11)	50(1)	63(1)	57(1)	-31(1)	-13(1)	-1(1)
C(12)	53(1)	53(1)	51(1)	-24(1)	-15(1)	5(1)
C(13)	63(1)	70(1)	50(1)	-31(1)	-11(1)	-8(1)
C(14)	64(1)	66(1)	57(1)	-28(1)	-8(1)	-6(1)
C(15)	70(1)	52(1)	46(1)	-22(1)	-12(1)	15(1)
C(16)	73(1)	92(1)	61(1)	-45(1)	-25(1)	11(1)
C(17)	56(1)	91(1)	64(1)	-42(1)	-17(1)	0(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **15b**.

	x	y	z	U(eq)
H(1)	-365	7441	6126	57
H(2)	126	5488	7174	70
H(4A)	5747	6500	8017	99
H(4B)	5868	6136	6926	99
H(5A)	5346	8114	5787	83
H(5B)	5345	8490	6862	83
H(7A)	1935	7325	8579	68
H(7B)	-217	6932	8225	68
H(8A)	4279	5698	5687	133
H(8B)	2048	5096	5639	133
H(8C)	3315	4413	6689	133
H(9A)	2848	4868	9570	168
H(9B)	3311	4134	8749	168
H(9C)	854	4431	9164	168
H(10A)	1901	9858	5619	115
H(10B)	1815	9710	6919	115
H(10C)	-290	9327	6553	115
H(13)	5528	8603	3290	70
H(14)	7768	9062	1471	74
H(16)	2872	7717	465	83
H(17)	630	7309	2269	78

III. X-ray Crystal Structure Analysis of compound 28a

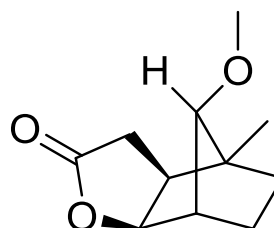
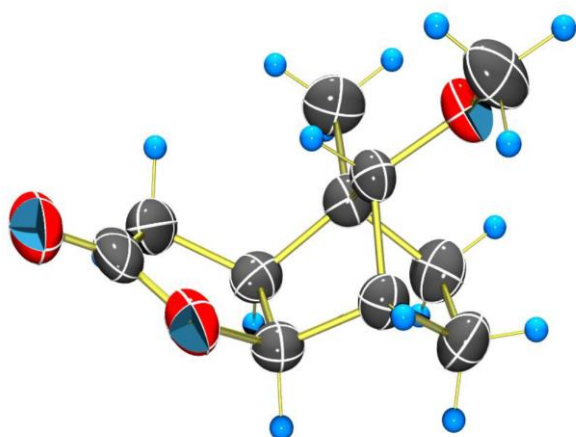


Table 1. Crystal data and structure refinement for **28a**.

Identification code	f71018b
Empirical formula	C ₁₁ H ₁₆ O ₃
Formula weight	196.24
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 6.282(15) Å alpha = 90 deg. b = 25.09(6) Å beta = 94.09(3) deg. c = 6.268(15) Å gamma = 90 deg.
Volume	985(4) Å ³
Z, Calculated density	4, 1.323 Mg/m ³
Absorption coefficient	0.095 mm ⁻¹
F(000)	424
Crystal size	0.35 x 0.15 x 0.08 mm
Theta range for data collection	3.25 to 25.00 deg.
Limiting indices	-7 ≤ h ≤ 7, -23 ≤ k ≤ 29, -7 ≤ l ≤ 6
Reflections collected / unique	3813 / 1689 [R(int) = 0.0299]
Completeness to theta = 25.00	97.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9924 and 0.9675

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1689 / 0 / 127
Goodness-of-fit on F^2	1.102
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0529, wR2 = 0.1495
R indices (all data)	R1 = 0.0689, wR2 = 0.1654
Largest diff. peak and hole	0.179 and -0.206 e. $\text{\AA}^{-3}$

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **28a**.

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	2387(3)	5005(1)	11372(4)	86(1)
O(2)	1123(3)	5783(1)	10415(2)	55(1)
O(3)	5700(2)	6835(1)	8096(2)	49(1)
C(1)	2038(4)	5324(1)	10007(4)	58(1)
C(2)	2490(4)	5287(1)	7740(4)	61(1)
C(3)	1807(3)	5807(1)	6733(3)	45(1)
C(4)	3549(3)	6190(1)	6140(3)	41(1)
C(5)	2424(4)	6659(1)	5044(3)	56(1)
C(6)	1324(4)	6940(1)	6816(4)	55(1)
C(7)	1977(3)	6610(1)	8759(3)	42(1)
C(8)	764(3)	6099(1)	8542(3)	43(1)
C(9)	4205(3)	6428(1)	8292(3)	38(1)
C(10)	6454(4)	7049(1)	10045(4)	62(1)
C(11)	5319(4)	5955(1)	4929(3)	59(1)

Table 3. Bond lengths [Å] and angles [deg] for **28a**.

O(1)-C(1)	1.180(3)
O(2)-C(1)	1.320(4)
O(2)-C(8)	1.422(3)
O(3)-C(10)	1.386(4)
O(3)-C(9)	1.398(3)
C(1)-C(2)	1.472(5)
C(2)-C(3)	1.499(4)
C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
C(3)-C(4)	1.522(4)
C(3)-C(8)	1.536(4)
C(3)-H(3A)	0.9800
C(4)-C(9)	1.506(4)
C(4)-C(11)	1.509(4)
C(4)-C(5)	1.512(4)
C(5)-C(6)	1.522(4)
C(5)-H(5A)	0.9700
C(5)-H(5B)	0.9700
C(6)-C(7)	1.505(4)
C(6)-H(6A)	0.9700
C(6)-H(6B)	0.9700
C(7)-C(8)	1.491(4)
C(7)-C(9)	1.520(4)
C(7)-H(7A)	0.9800
C(8)-H(8A)	0.9800
C(9)-H(9A)	0.9800
C(10)-H(10A)	0.9600
C(10)-H(10B)	0.9600
C(10)-H(10C)	0.9600
C(11)-H(11A)	0.9600
C(11)-H(11B)	0.9600

C(11)-H(11C)	0.9600
C(1)-O(2)-C(8)	111.9(2)
C(10)-O(3)-C(9)	113.25(18)
O(1)-C(1)-O(2)	120.7(3)
O(1)-C(1)-C(2)	128.3(3)
O(2)-C(1)-C(2)	111.0(2)
C(1)-C(2)-C(3)	106.4(2)
C(1)-C(2)-H(2A)	110.4
C(3)-C(2)-H(2A)	110.4
C(1)-C(2)-H(2B)	110.4
C(3)-C(2)-H(2B)	110.4
H(2A)-C(2)-H(2B)	108.6
C(2)-C(3)-C(4)	117.6(2)
C(2)-C(3)-C(8)	103.2(2)
C(4)-C(3)-C(8)	103.4(2)
C(2)-C(3)-H(3A)	110.7
C(4)-C(3)-H(3A)	110.7
C(8)-C(3)-H(3A)	110.7
C(9)-C(4)-C(11)	116.2(2)
C(9)-C(4)-C(5)	100.8(2)
C(11)-C(4)-C(5)	114.3(2)
C(9)-C(4)-C(3)	100.79(19)
C(11)-C(4)-C(3)	116.5(2)
C(5)-C(4)-C(3)	106.3(2)
C(4)-C(5)-C(6)	104.5(2)
C(4)-C(5)-H(5A)	110.8
C(6)-C(5)-H(5A)	110.8
C(4)-C(5)-H(5B)	110.8
C(6)-C(5)-H(5B)	110.8
H(5A)-C(5)-H(5B)	108.9
C(7)-C(6)-C(5)	103.0(2)
C(7)-C(6)-H(6A)	111.2

C(5)-C(6)-H(6A)	111.2
C(7)-C(6)-H(6B)	111.2
C(5)-C(6)-H(6B)	111.2
H(6A)-C(6)-H(6B)	109.1
C(8)-C(7)-C(6)	106.9(2)
C(8)-C(7)-C(9)	101.4(2)
C(6)-C(7)-C(9)	102.14(18)
C(8)-C(7)-H(7A)	114.9
C(6)-C(7)-H(7A)	114.9
C(9)-C(7)-H(7A)	114.9
O(2)-C(8)-C(7)	110.8(2)
O(2)-C(8)-C(3)	107.0(2)
C(7)-C(8)-C(3)	103.6(2)
O(2)-C(8)-H(8A)	111.7
C(7)-C(8)-H(8A)	111.7
C(3)-C(8)-H(8A)	111.7
O(3)-C(9)-C(4)	110.74(17)
O(3)-C(9)-C(7)	115.6(2)
C(4)-C(9)-C(7)	95.43(18)
O(3)-C(9)-H(9A)	111.4
C(4)-C(9)-H(9A)	111.4
C(7)-C(9)-H(9A)	111.4
O(3)-C(10)-H(10A)	109.5
O(3)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
O(3)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(4)-C(11)-H(11A)	109.5
C(4)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(4)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5

H(11B)-C(11)-H(11C) 109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **28a**.

The anisotropic displacement factor exponent takes the form:

$-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

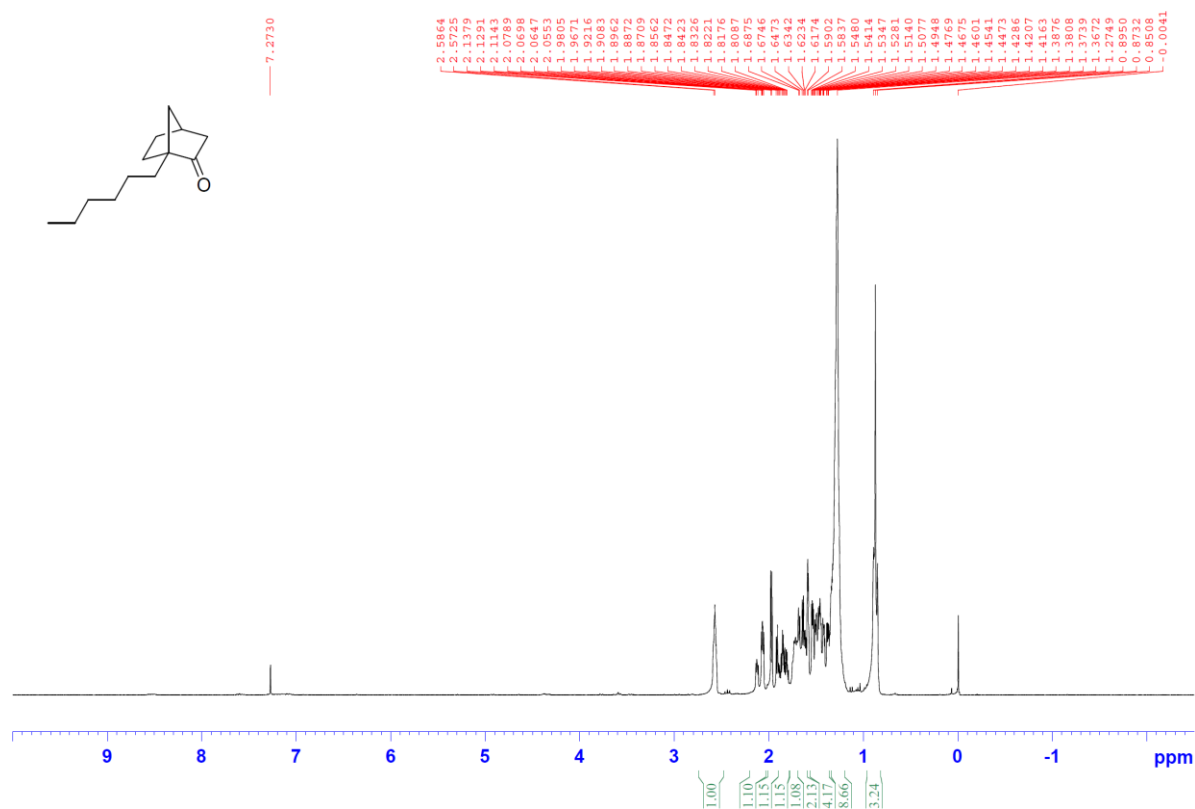
	U11	U22	U33	U23	U13	U12
O(1)	64(1)	76(1)	115(2)	50(1)	-21(1)	-19(1)
O(2)	57(1)	57(1)	52(1)	10(1)	3(1)	-14(1)
O(3)	55(1)	48(1)	44(1)	-2(1)	6(1)	-17(1)
C(1)	38(1)	53(1)	79(2)	17(1)	-13(1)	-17(1)
C(2)	48(1)	40(1)	95(2)	-2(1)	3(1)	-3(1)
C(3)	42(1)	44(1)	47(1)	-9(1)	-9(1)	0(1)
C(4)	45(1)	45(1)	34(1)	-4(1)	1(1)	1(1)
C(5)	67(2)	60(1)	40(1)	8(1)	-4(1)	4(1)
C(6)	59(2)	46(1)	60(1)	6(1)	3(1)	11(1)
C(7)	46(1)	41(1)	40(1)	-4(1)	5(1)	2(1)
C(8)	37(1)	47(1)	45(1)	0(1)	-2(1)	0(1)
C(9)	41(1)	37(1)	34(1)	1(1)	0(1)	-5(1)
C(10)	60(2)	63(2)	62(1)	-21(1)	6(1)	-18(1)
C(11)	61(2)	67(2)	49(1)	-14(1)	13(1)	4(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **28a**.

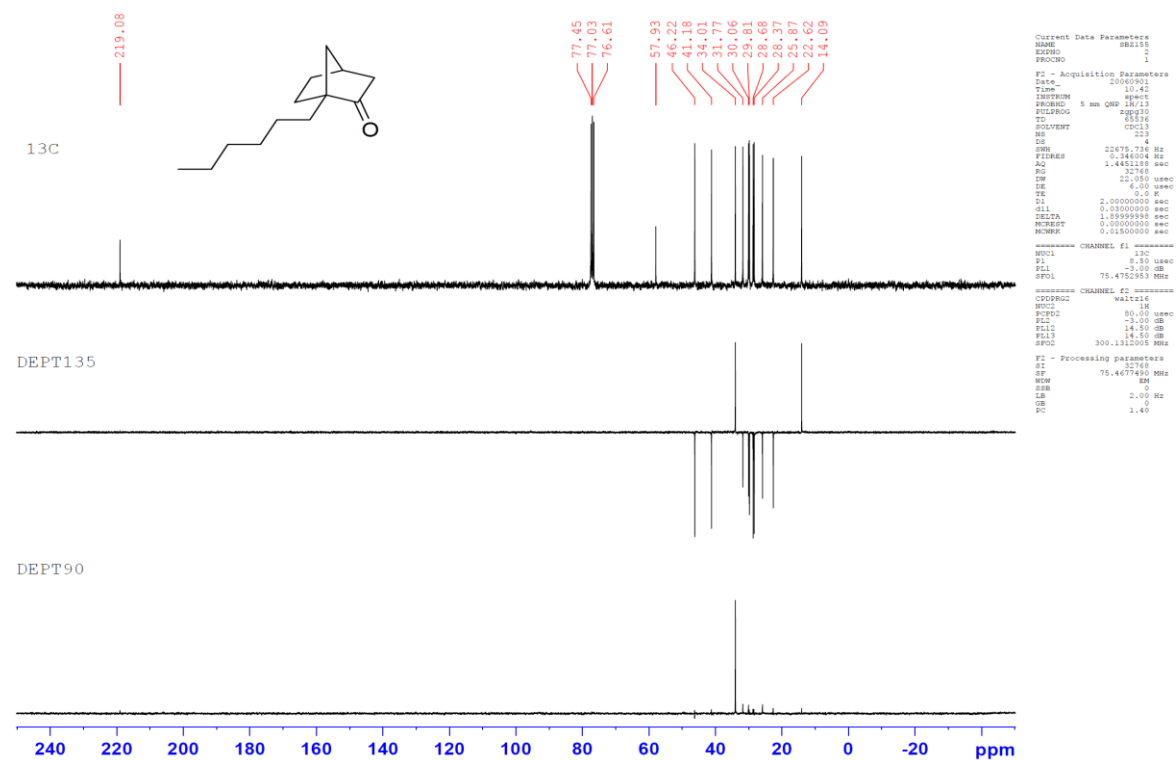
	x	y	z	U(eq)
H(2A)	1700	4994	7051	73
H(2B)	4001	5228	7608	73
H(3A)	770	5749	5513	54
H(5A)	1388	6539	3924	67
H(5B)	3439	6894	4425	67
H(6A)	1818	7304	6991	66
H(6B)	-213	6939	6527	66
H(7A)	1887	6793	10130	50
H(8A)	-761	6161	8189	52
H(9A)	4745	6155	9309	45
H(10A)	7466	7325	9811	92
H(10B)	7133	6774	10916	92
H(10C)	5283	7195	10758	92
H(11A)	5932	5656	5704	88
H(11B)	6398	6221	4770	88
H(11C)	4751	5840	3542	88

III. Copies of NMR spectra for new compounds

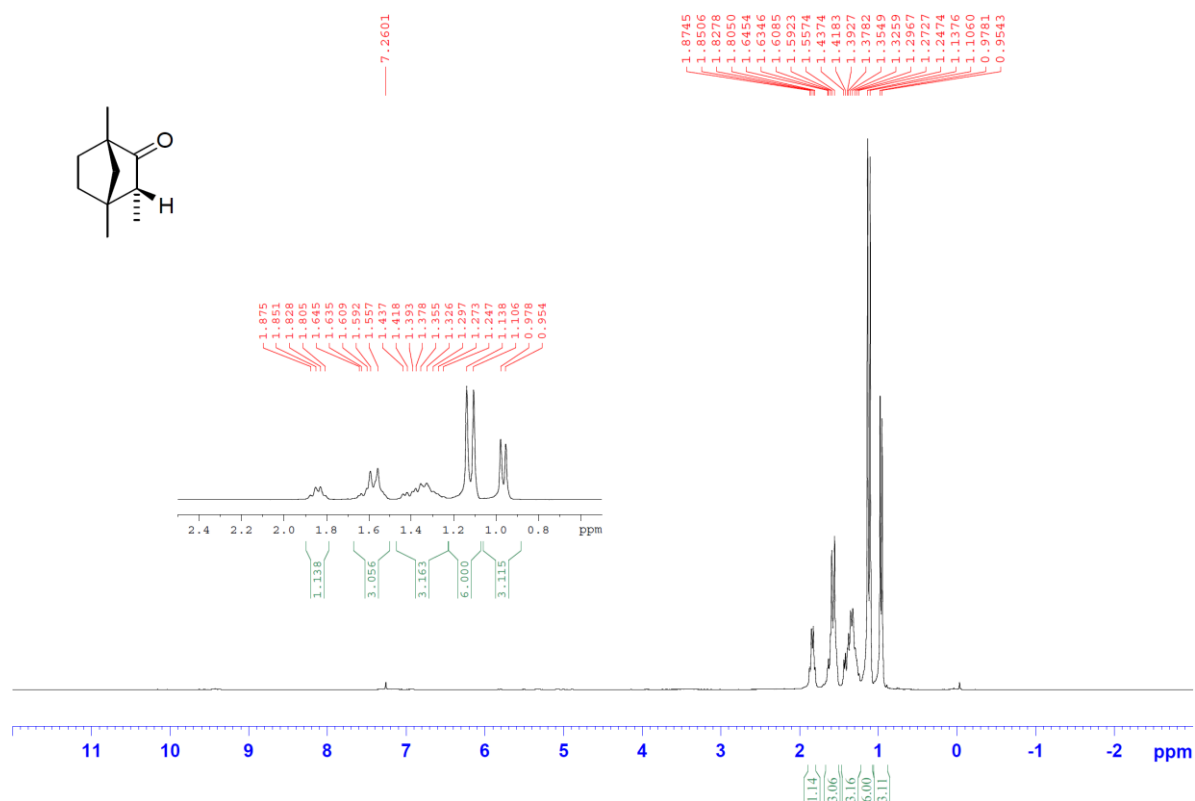
^1H NMR spectrum of compound **15a** in CDCl_3



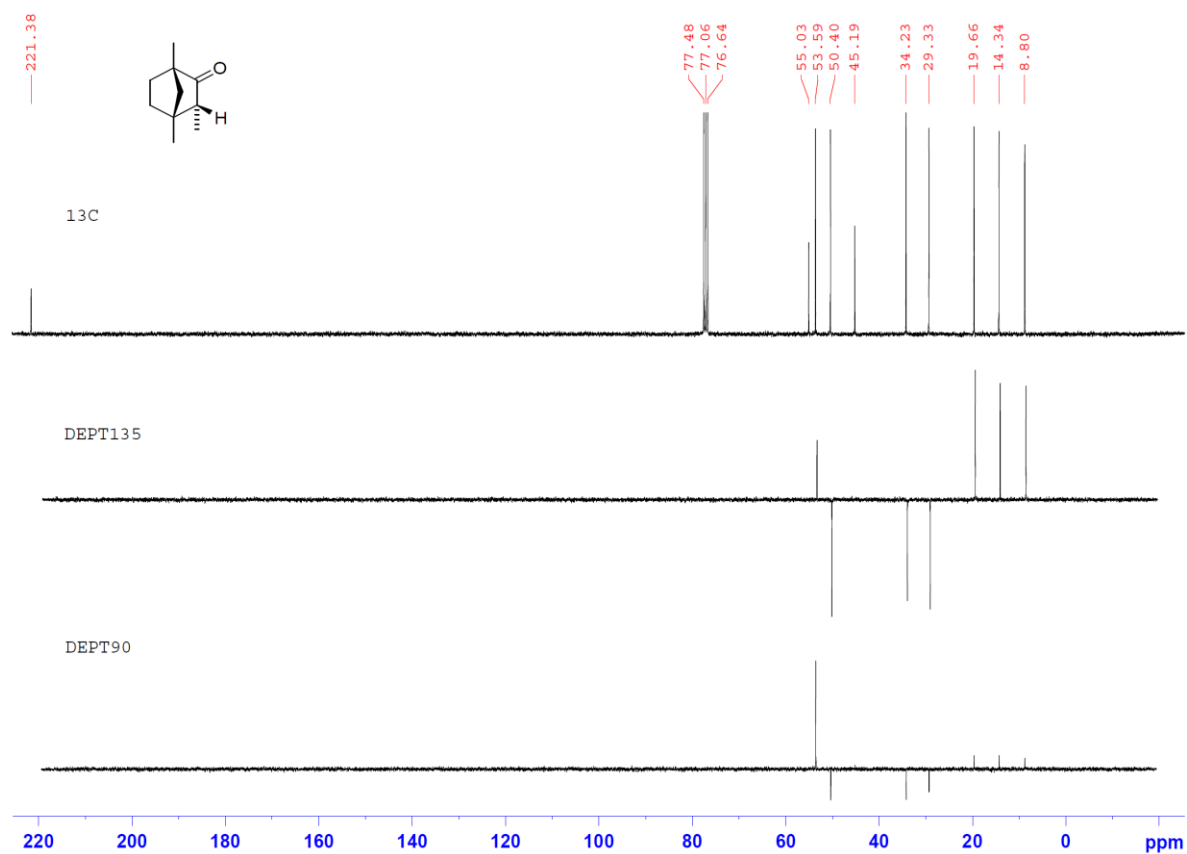
^{13}C NMR spectrum of compound **15a** in CDCl_3



^1H NMR spectrum of compound *endo*-**15b** in CDCl_3



^{13}C NMR spectrum of compound *endo*-**15b** in CDCl_3



The figure displays two ^1H NMR spectra of compound **1**. The top spectrum is recorded in CDCl_3 and the bottom spectrum is recorded in $\text{DMSO}-d_6$. Both spectra show a reference peak at 7.1567 ppm. The chemical shifts (ppm) and integration values are provided for each spectrum.

Top Spectrum (CDCl_3):

- Chemical shifts (ppm): 1.5531, 1.5503, 1.5411, 1.5384, 1.5291, 1.5264, 1.5170, 1.5144, 1.2969, 1.2923, 1.2870, 1.2761, 1.2722, 1.2595, 1.2389, 1.2344, 1.2109, 1.1678, 1.1527, 1.1527, 1.1492, 1.1278, 1.0264, 1.0232, 1.0181, 1.0149, 1.0060, 1.0029, 0.9976, 0.9945, 0.9856, 0.9825.
- Integration values: 1.000, 1.055, 1.081, 1.076, 0.989, 3.116, 3.112.

Bottom Spectrum ($\text{DMSO}-d_6$):

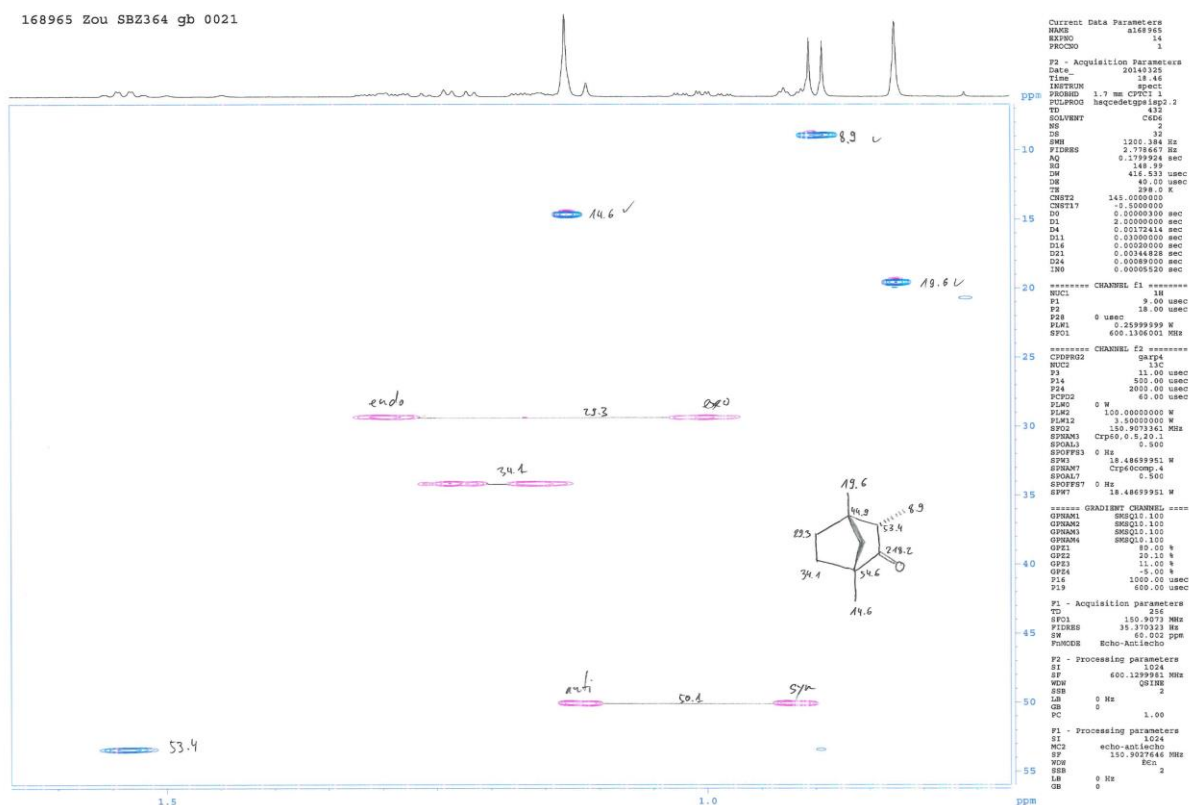
- Chemical shifts (ppm): 1.541, 1.536, 1.529, 1.526, 1.297, 1.292, 1.287, 1.272, 1.260, 1.239, 1.231, 1.218, 1.214, 1.164, 1.153, 1.149, 1.128, 1.026, 1.023, 1.018, 1.015, 1.006, 1.003, 0.998, 0.995, 0.993, 0.979, 0.956, 0.942, 0.913, 0.909, 0.896, 0.824.
- Integration values: 1.00, 1.05, 1.08, 1.06, 0.99, 3.12, 3.11.

13C NMR spectrum (ppm) of compound 10. The x-axis ranges from 220 to 0 ppm. The spectrum shows a major peak at 128.00 ppm and several smaller peaks in the aliphatic region. The following table lists the chemical shifts (ppm) for the observed peaks:

Chemical Shift (ppm)
218.39
128.16
128.00
127.84
54.66
53.46
50.11
44.87
34.19
29.36
19.58
14.66
8.93

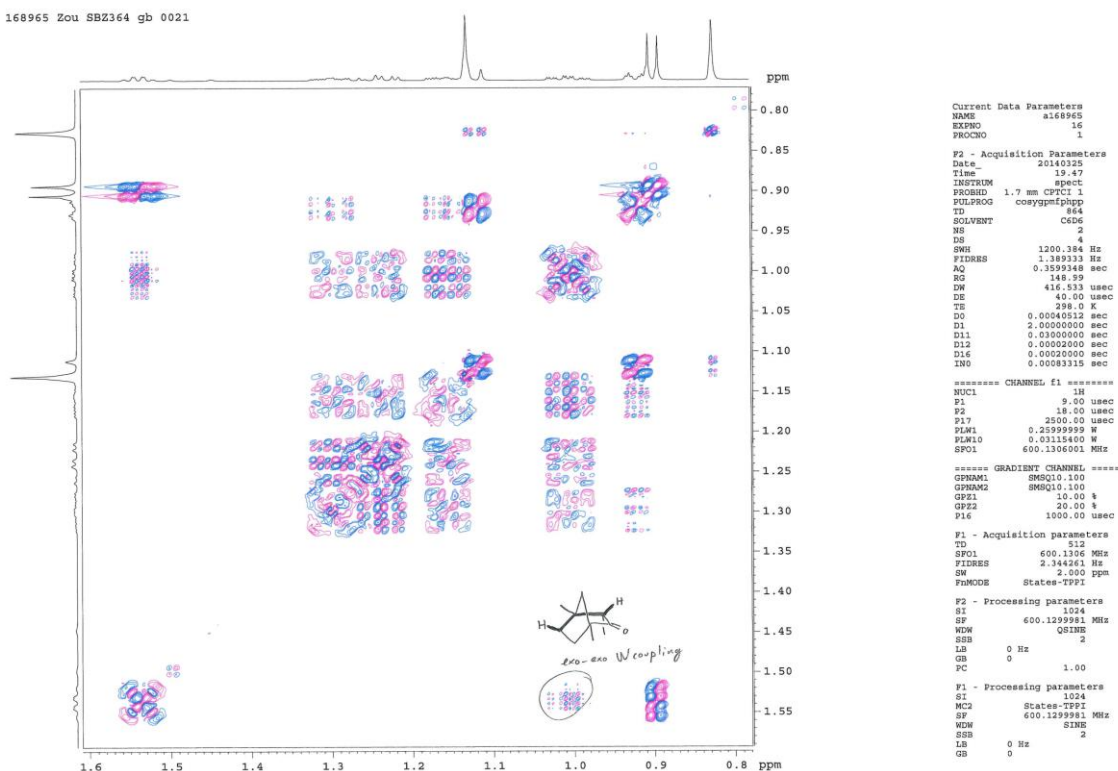
HSQC spectrum of compound *endo-15b* in C₆D₆

168965 Zou SBZ364 gb 0021



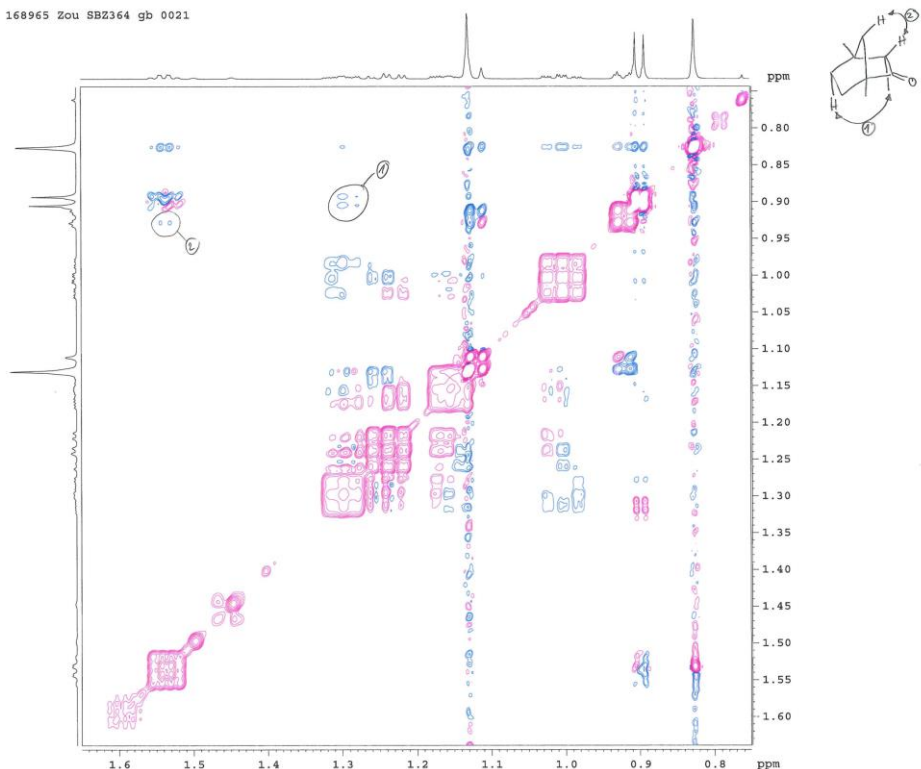
COSY spectrum of compound *endo-15b* in C₆D₆

168965 Zou SBZ364 gb 0021



NOESY spectrum of compound *endo-15b* in C₆D₆

168965 Zou SBZ364 gb 0021



```

Current Data Parameters
NAME      a168965
EXPNO     17
PROCNO    1

F2 - Acquisition Parameters
Date_     20140325
Time      20.32
INSTRUM   spect
PROBHD    1.7 mm CPTCI 1
PULPROG   noesypphpgp
TD         664
SOLVENT   CDCl3
NS         2
DS         32
SWH        1200.384 Hz
FIDRES     1.389333 Hz
AQ         0.3599348 sec
RG         62.86
DW         416.533 usec
DE         40.00 usec
TE         298.0 K
DC         0.00846312 sec
D1         2.00000000 sec
D8         1.50000000 sec
D11        0.03000000 sec
D12        0.00020000 sec
D16        0.00020000 sec
IN0        0.0003315 sec

===== CHANNEL f1 =====
NUC1       1H
P1         9.00 usec
P2         18.00 usec
P17        2500.00 usec
PLW1       0.25999999 W
PLA10      0.03113400 W
SFO1       600.1306001 MHz

===== GRADIENT CHANNEL =====
GPM1       SMSQ10.100
GP11       40.00 V
P16        1000.00 usec

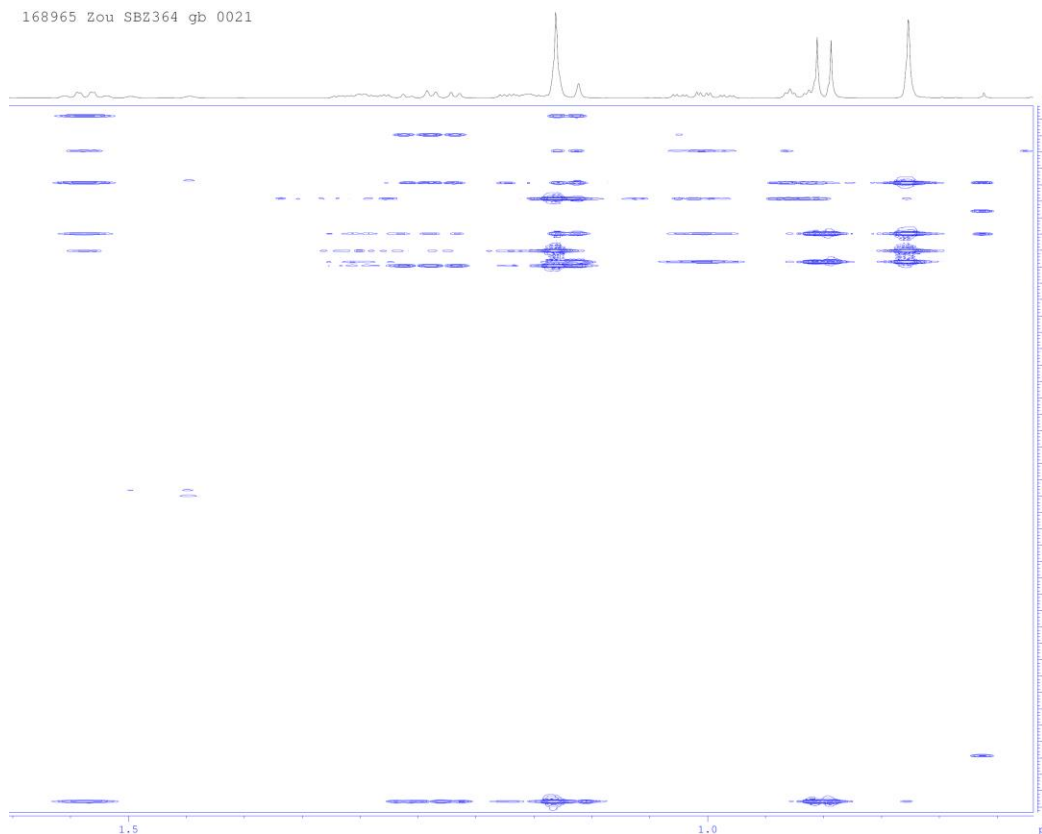
F1 - Acquisition parameters
TD         512
SFO1       600.1306 MHz
FIDRES     2.344261 Hz
SW         2.000 ppm
PULPROG    States-TF2

F2 - Processing parameters
SI         1024
SF         600.1299981 MHz
WDW         EM
SSB         0 Hz
LB         0
GB         1.00

F1 - Processing parameters
SI         1024
SF         600.1299981 MHz
WDW         EM
SSB         0 Hz
LB         0
GB         0
    
```

HMBC spectrum of compound *endo-15b* in C₆D₆

168965 Zou SBZ364 gb 0021



```

Current Data Parameters
NAME      a168965
EXPNO     17
PROCNO    1

F2 - Acquisition Parameters
Date_     20140325
Time      19.05
INSTRUM   spect
PROBHD    1.7 mm CPTCI 1
PULPROG   hmqcgp0304
TD         664
SOLVENT   CDCl3
NS         2
DS         32
SWH        1200.384 Hz
FIDRES     1.389333 Hz
AQ         0.3599348 sec
RG         62.86
DW         416.533 usec
DE         40.00 usec
TE         298.0 K
DC         0.00846312 sec
D1         2.00000000 sec
D8         1.50000000 sec
D11        0.03000000 sec
D12        0.00020000 sec
D16        0.00020000 sec
IN0        0.0003315 sec

===== CHANNEL f1 =====
NUC1       1H
P1         9.00 usec
P2         18.00 usec
P17        2500.00 usec
PLW1       0.25999999 W
PLA10      0.03113400 W
SFO1       600.1306001 MHz

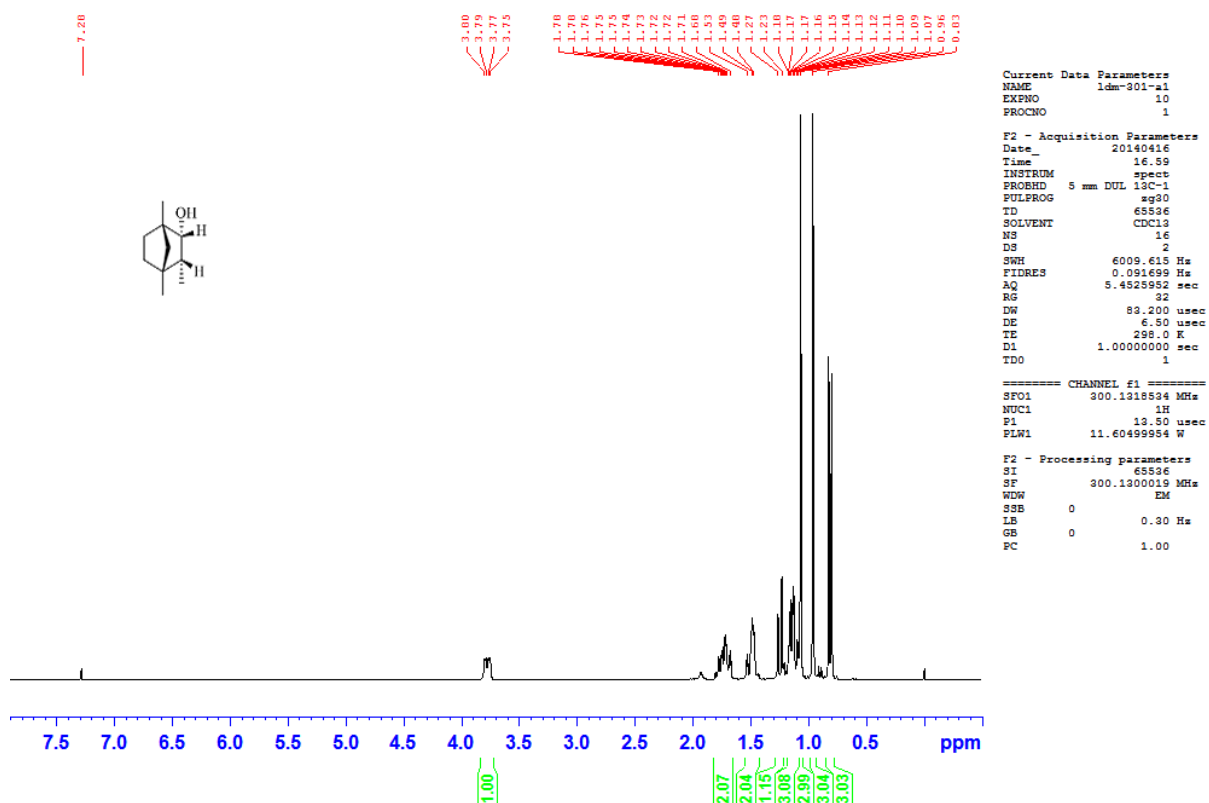
===== CHANNEL f2 =====
NUC2       13C
P1         11.00 usec
P2         18.00 usec
P16        1000.00 usec
PLA2       100.00000000 W
SFO2       150.9201628 MHz
GPM1       SMSQ10.100
GP11       40.00 V
P16        1000.00 usec

F1 - Acquisition parameters
TD         512
SFO1       600.1306 MHz
FIDRES     2.344261 Hz
SW         2.000 ppm
PULPROG    States-TF2

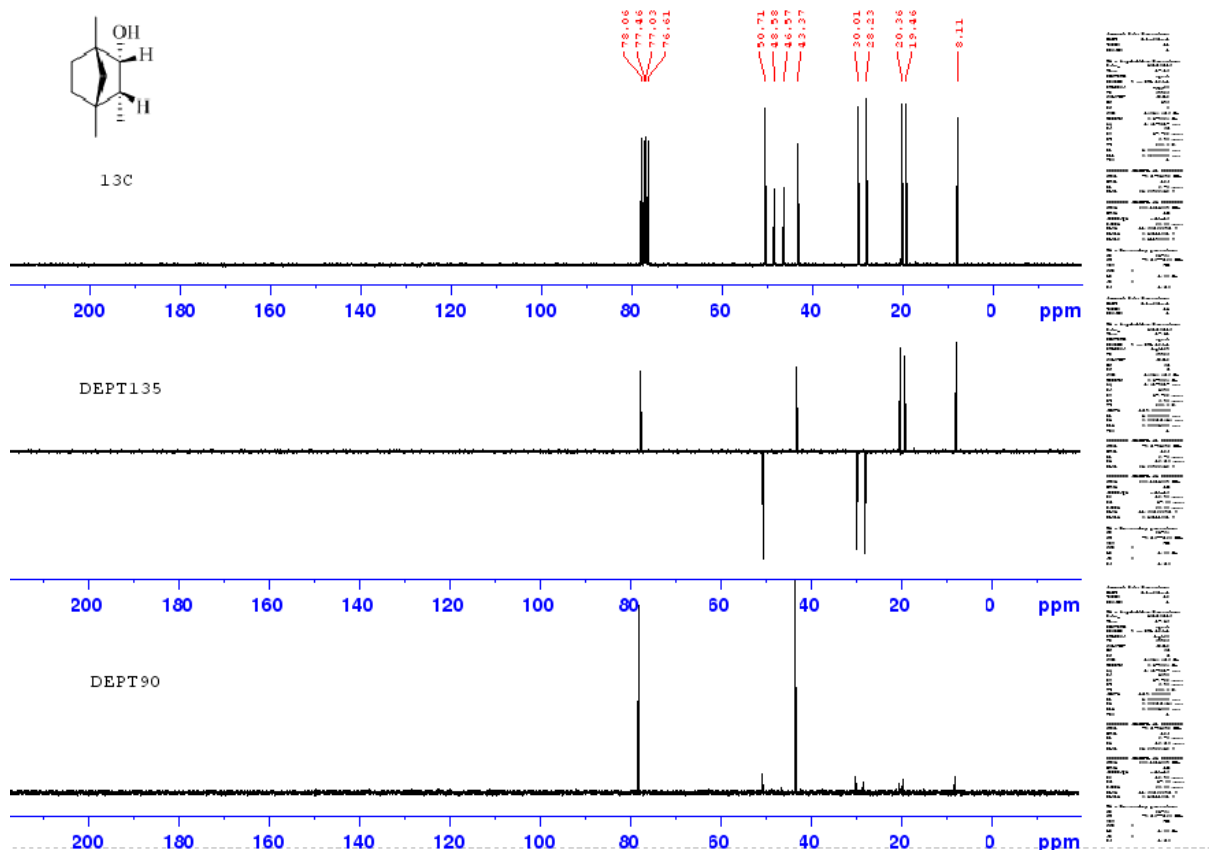
F2 - Processing parameters
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SF         600.1299981 MHz
WDW         EM
SSB         0 Hz
LB         0
GB         1.00

F1 - Processing parameters
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SF         600.1299981 MHz
WDW         EM
SSB         0 Hz
LB         0
GB         0
    
```

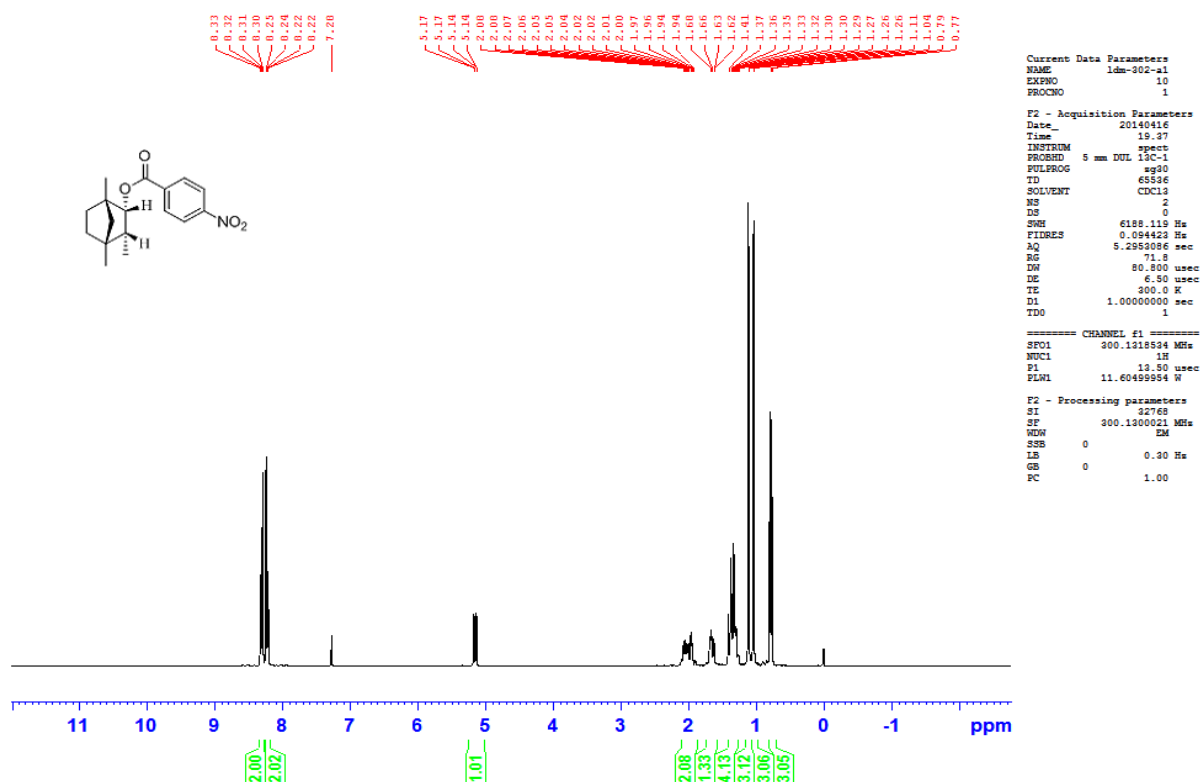
^1H NMR spectrum of compound **15b'** in CDCl_3



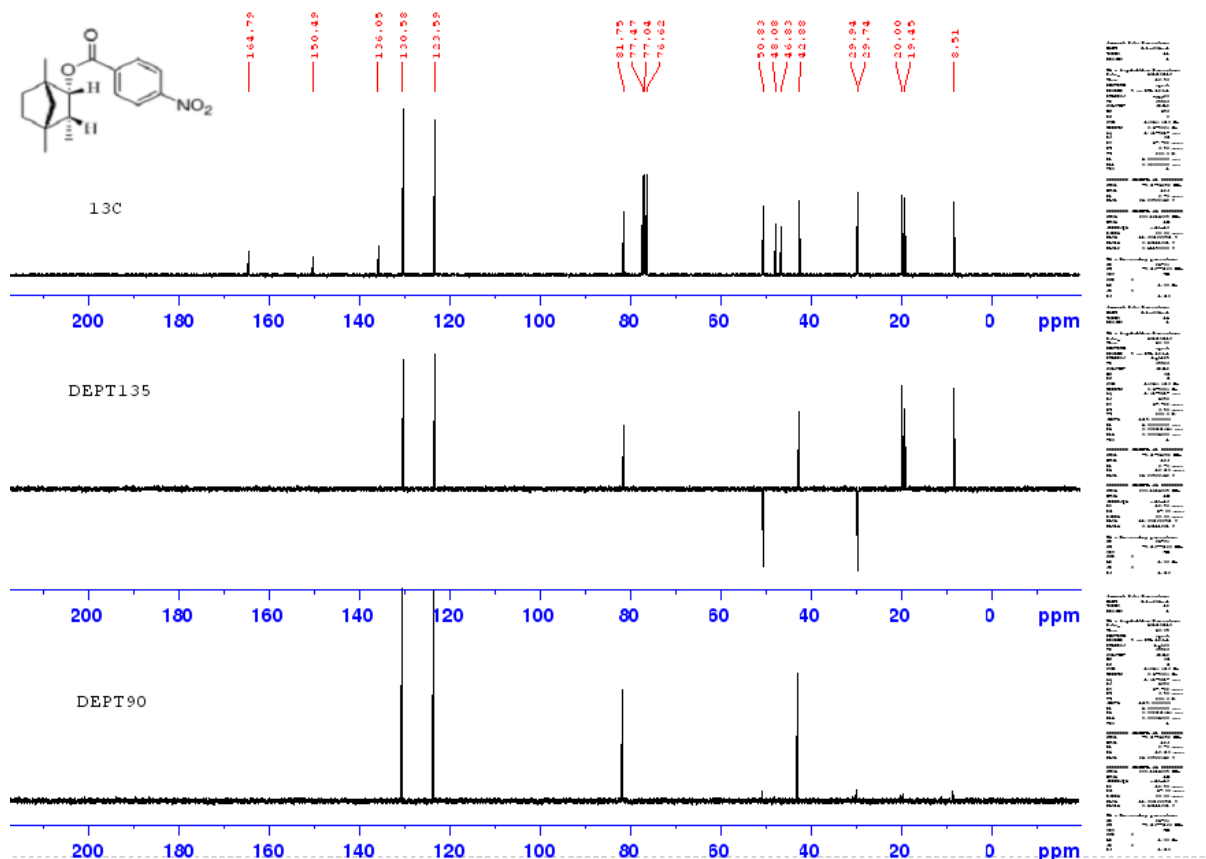
^{13}C NMR spectrum of compound **15b'** in CDCl_3



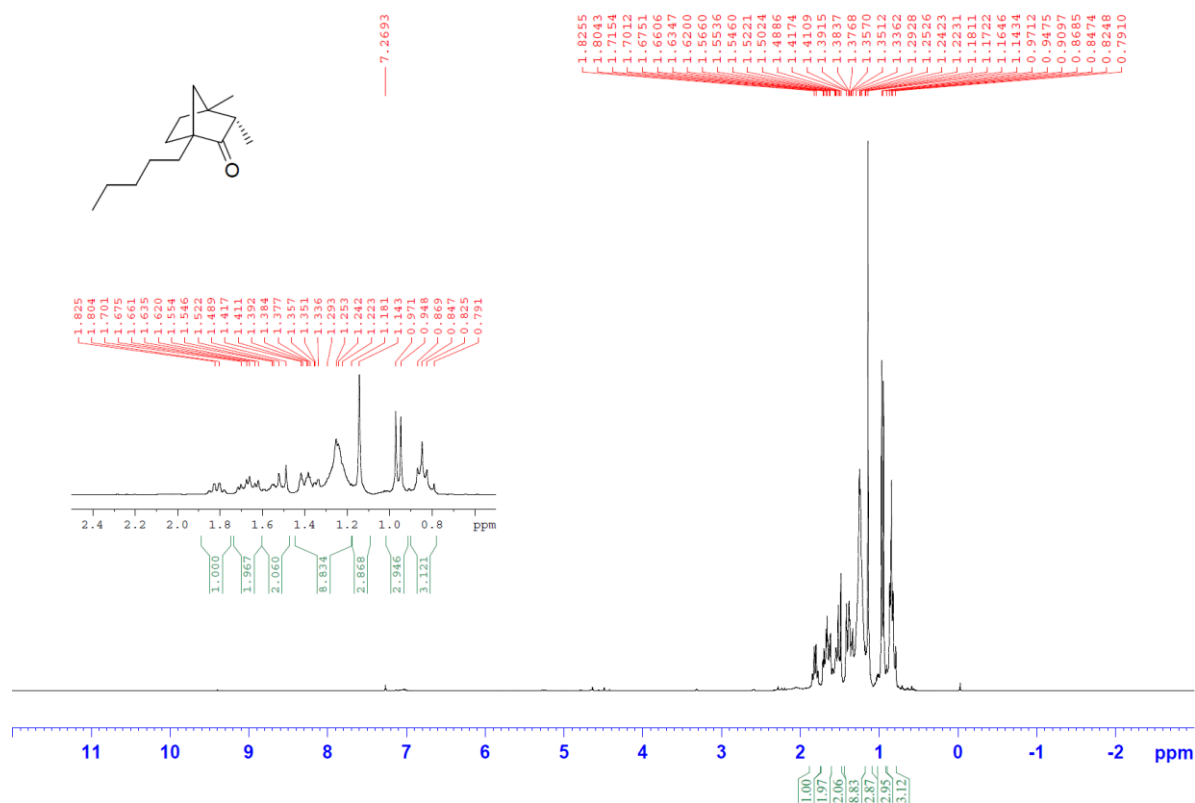
^1H NMR spectrum of compound **15b''** in CDCl_3



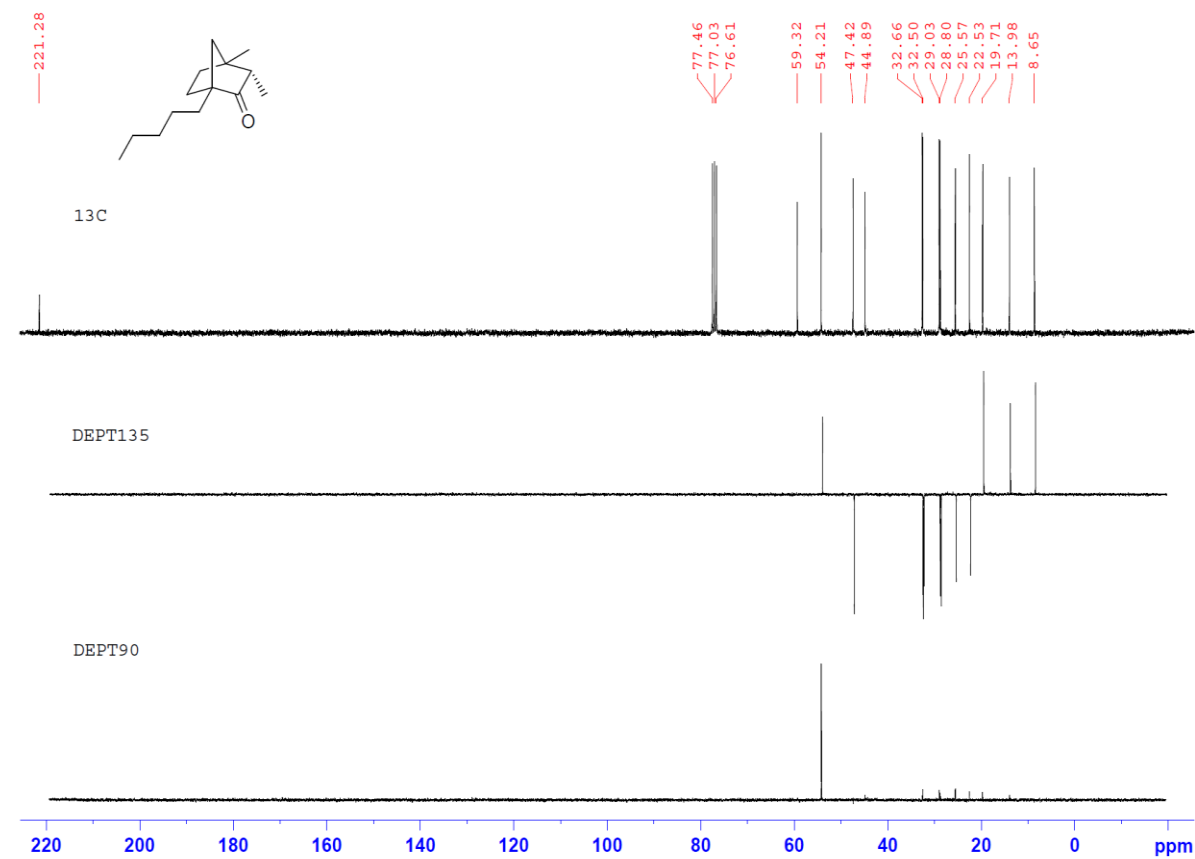
^{13}C NMR spectrum of compound **15b''** in CDCl_3



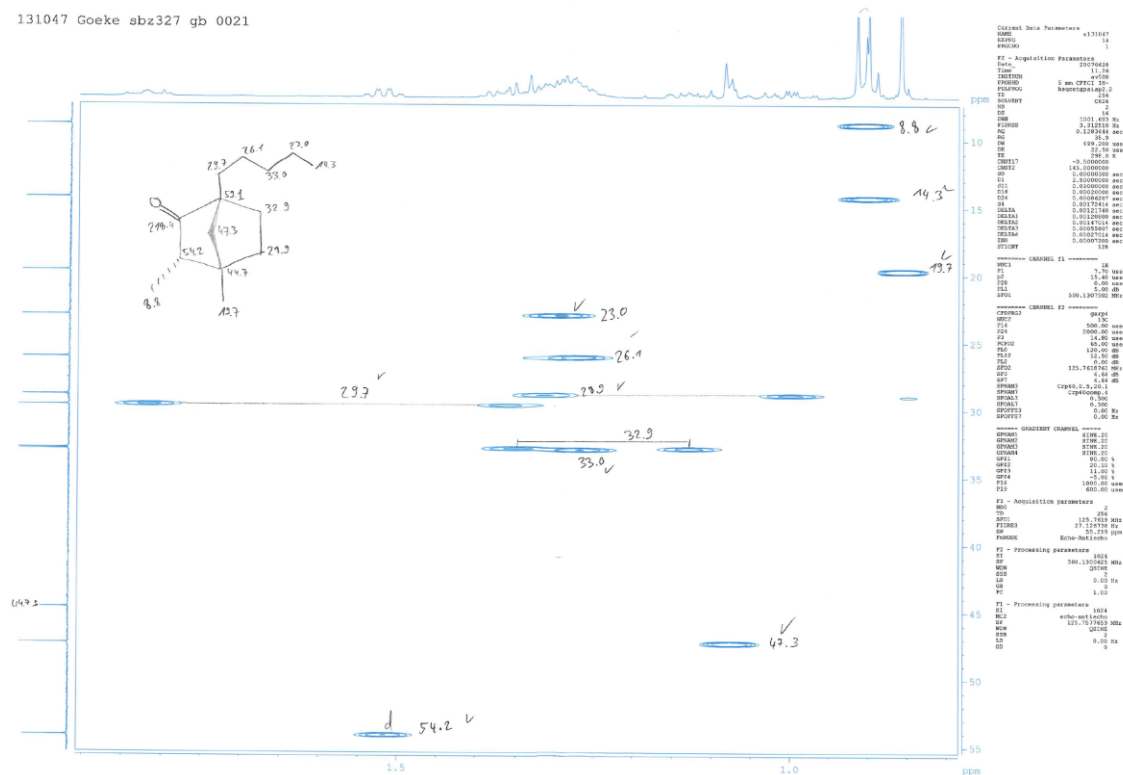
^1H NMR spectrum of compound **15c** in CDCl_3



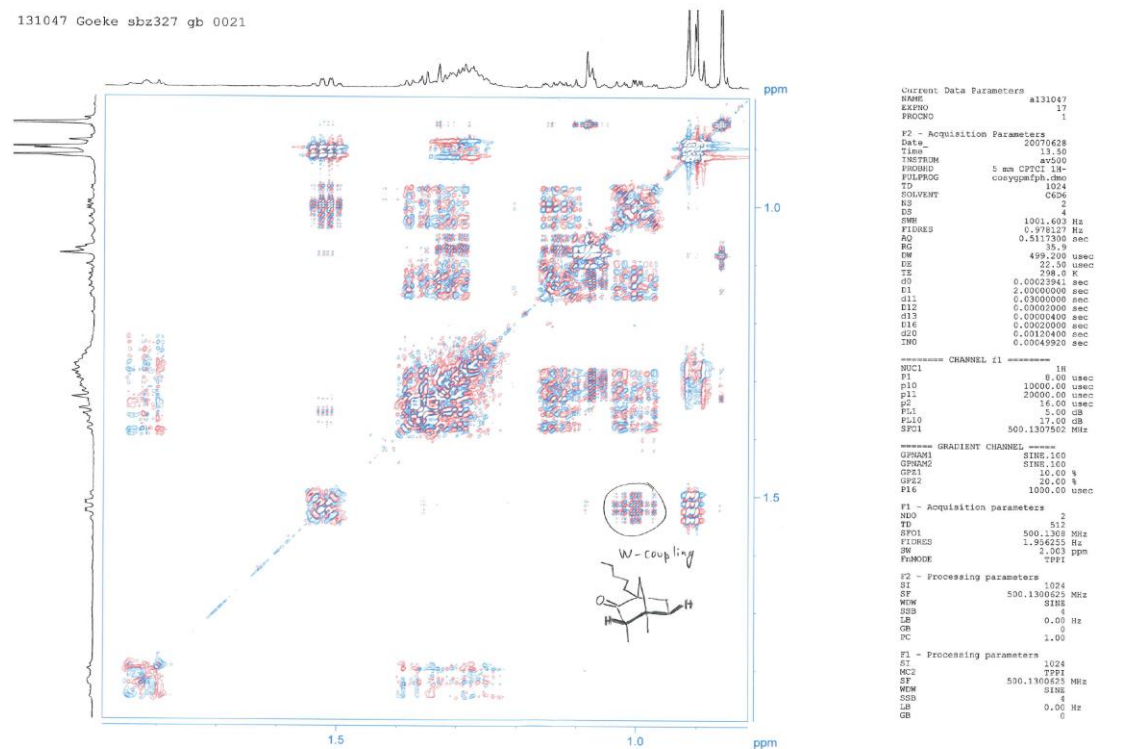
^{13}C NMR spectrum of compound **15c** in CDCl_3



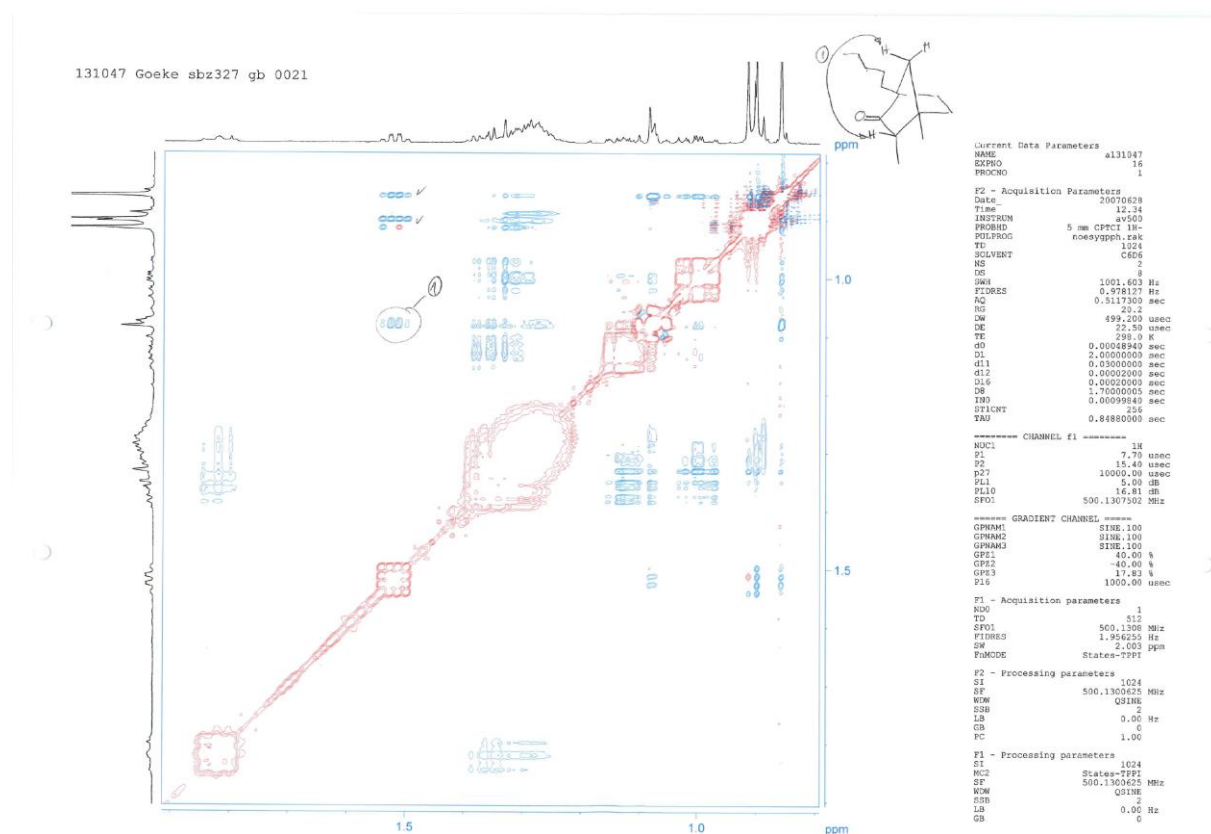
HSQC spectrum of compound **15c** in C₆D₆



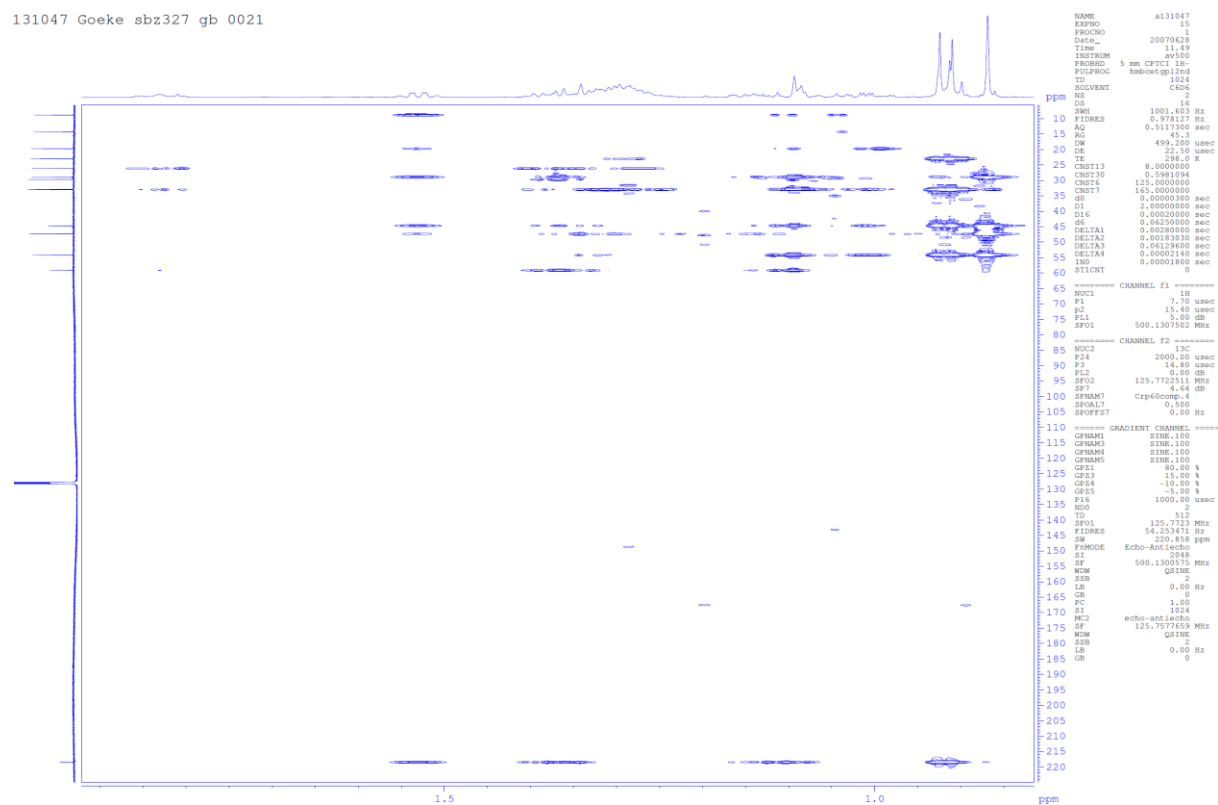
COSY spectrum of compound **15c** in C₆D₆



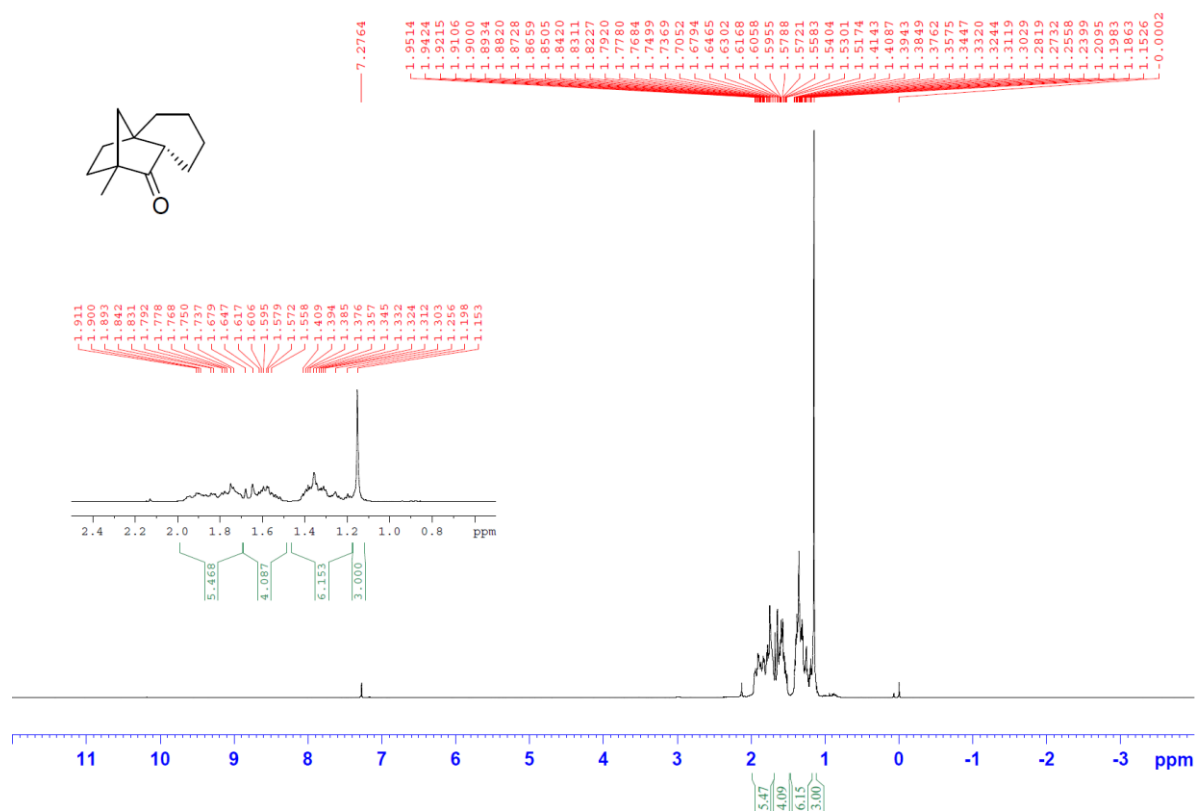
NOESY spectrum of compound **15c** in C₆D₆



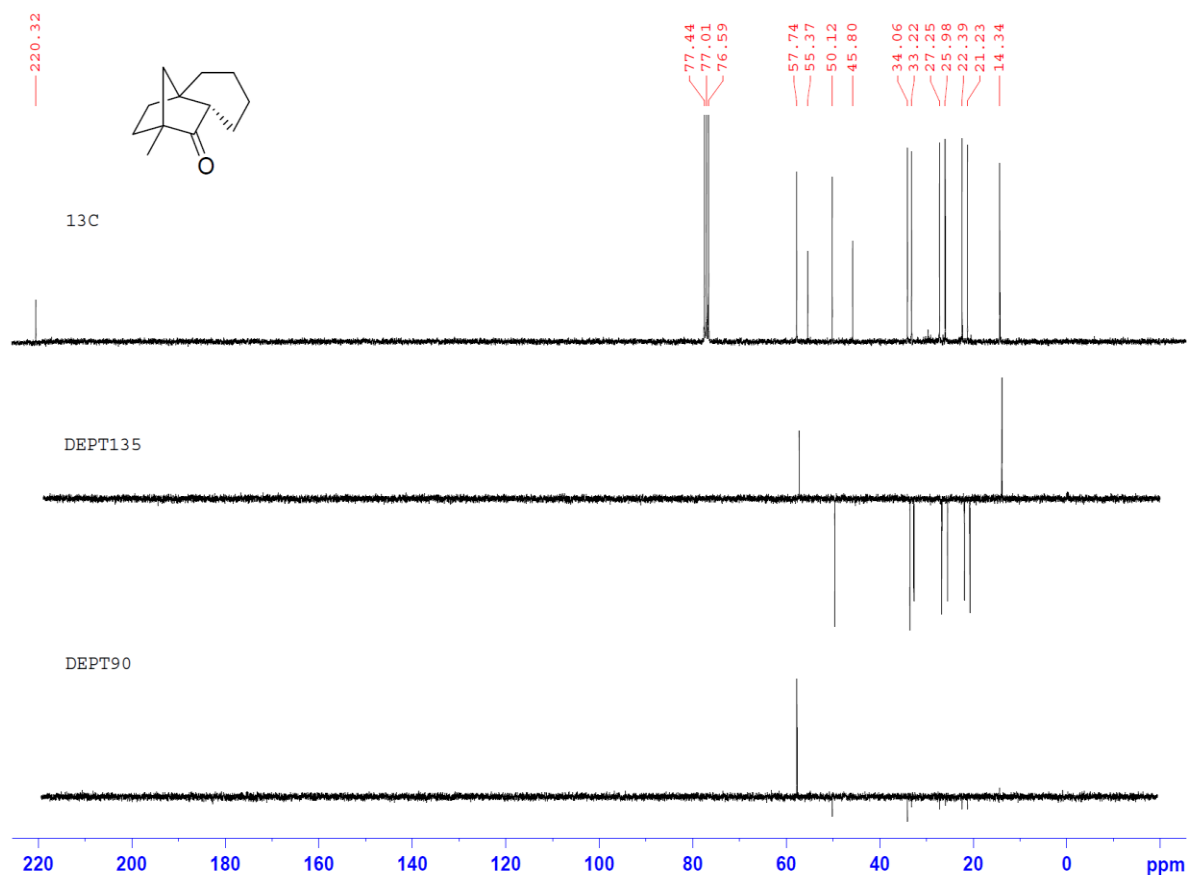
HMBC spectrum of compound **15c** in C₆D₆



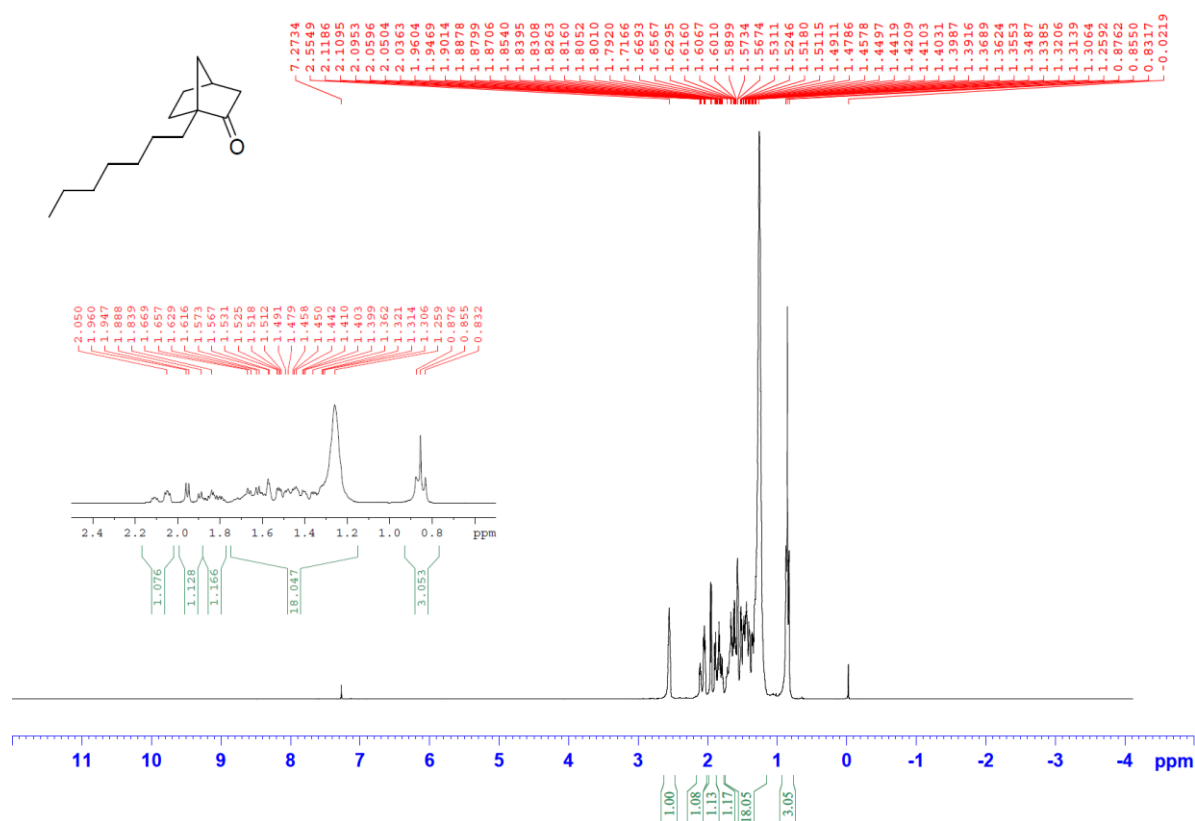
^1H NMR spectrum of compound **15d** in CDCl_3



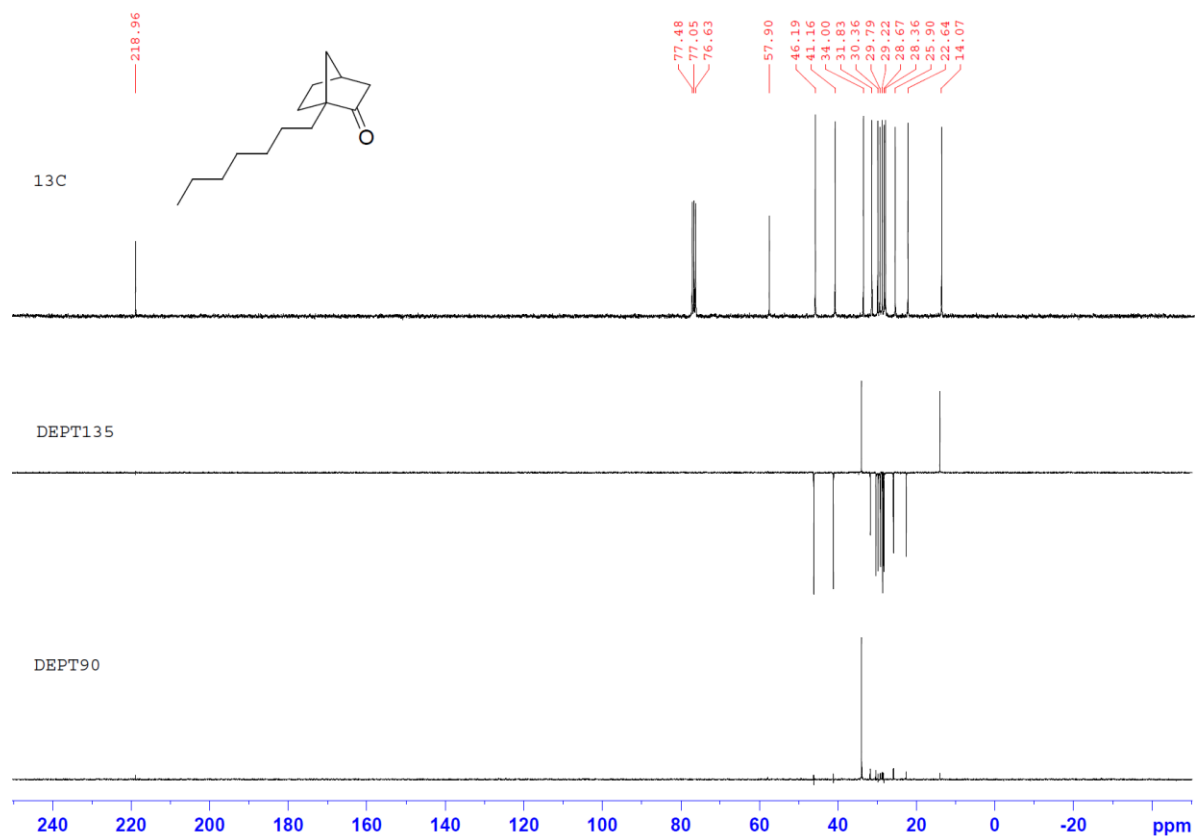
^{13}C NMR spectrum of compound **15d** in CDCl_3



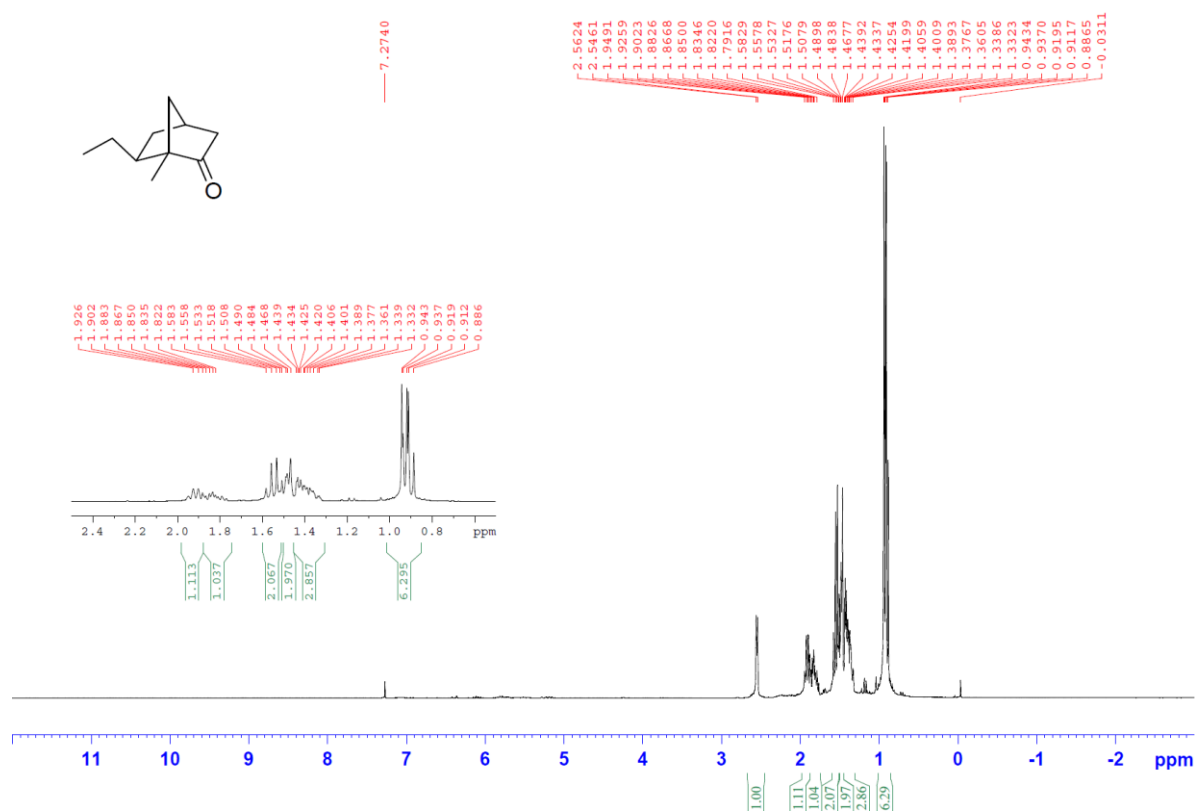
^1H NMR spectrum of compound **15e** in CDCl_3



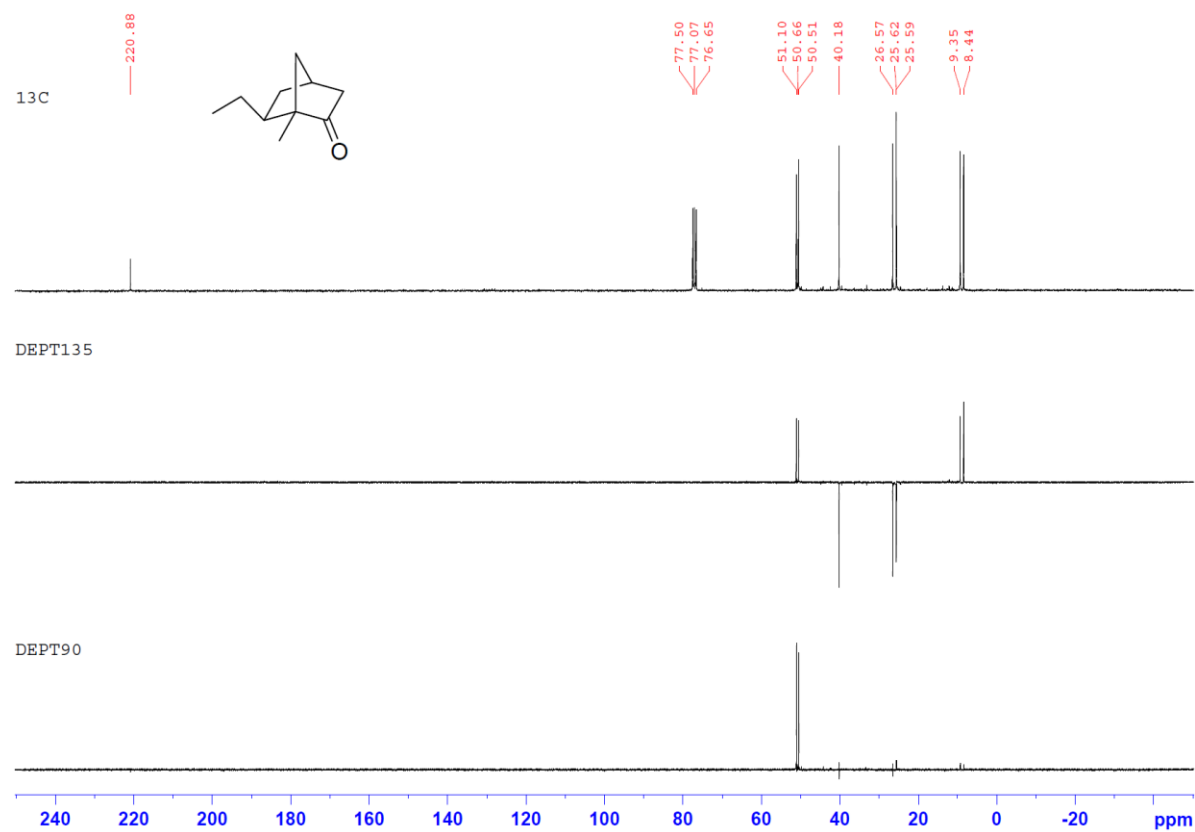
^{13}C NMR spectrum of compound **15e** in CDCl_3



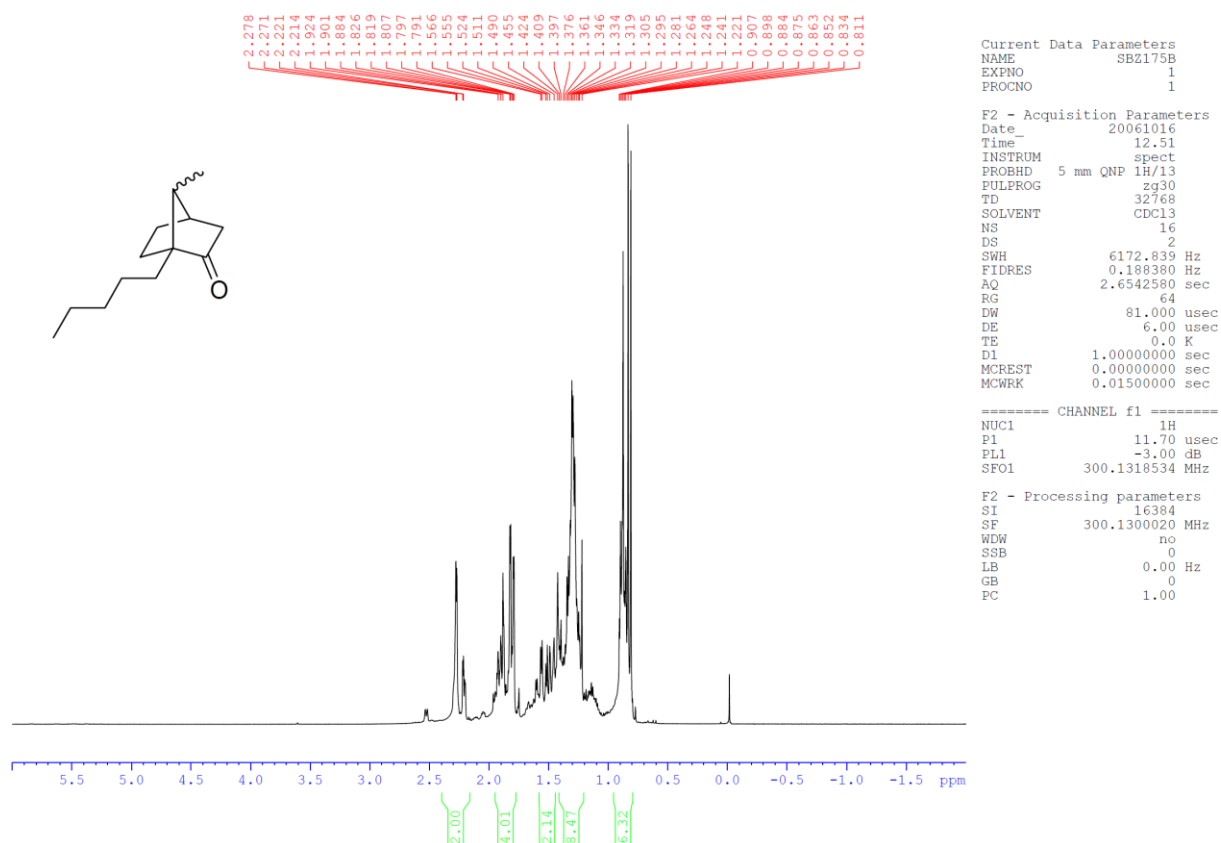
^1H NMR spectrum of compound **15f** in CDCl_3



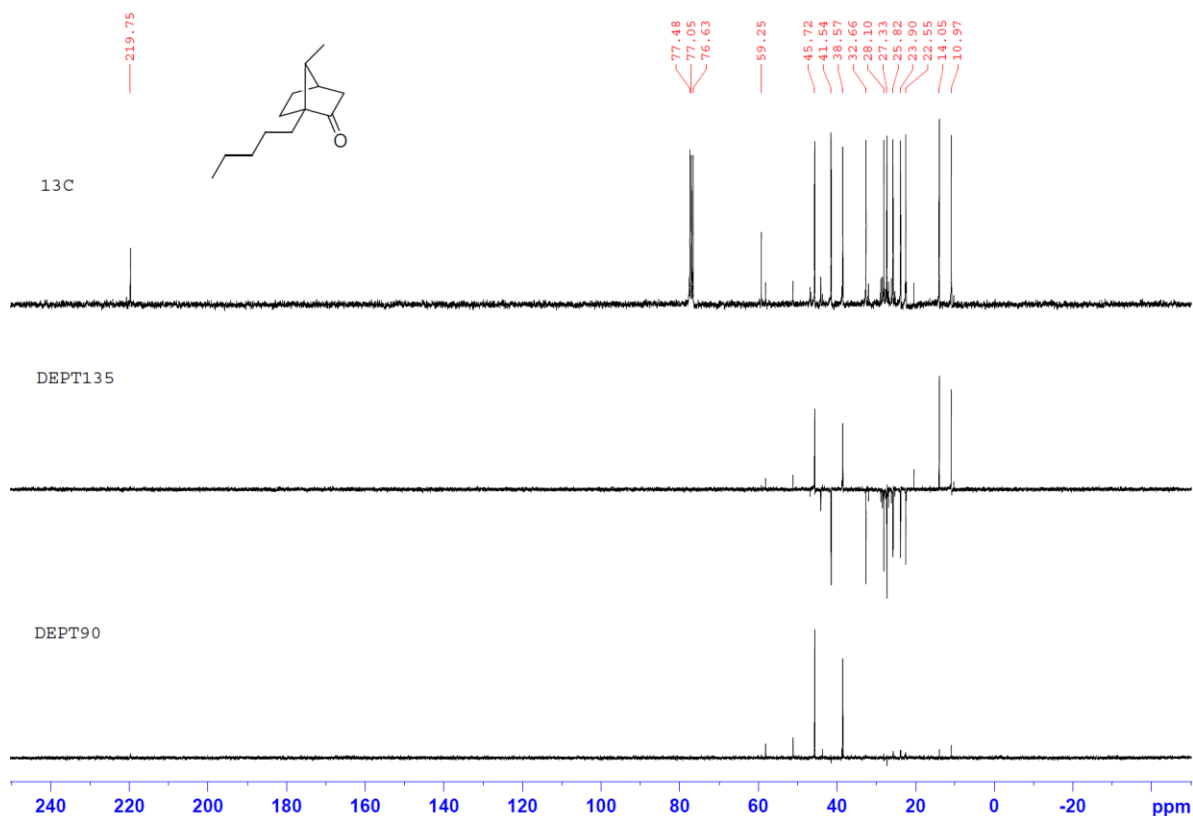
^{13}C NMR spectrum of compound **15f** in CDCl_3



¹H NMR spectrum of compound **15g** in CDCl₃



¹³C NMR spectrum of compound **15g** in CDCl₃



Chemical structure of the compound: CC1(C)C(=O)C2(C)C(C1)C(C(C)C)C2

¹H NMR spectrum (400 MHz, CDCl₃) showing peaks from 0.7 to 2.5 ppm. Integration values are provided below the peaks.

Peak list (ppm):

- 2.244
- 2.187
- 2.142
- 1.929
- 1.900
- 1.882
- 1.852
- 1.817
- 1.715
- 1.681
- 1.655
- 1.599
- 1.594
- 1.568
- 1.552
- 1.495
- 1.462
- 1.397
- 1.391
- 1.357
- 1.352
- 1.324
- 1.153
- 0.989
- 0.948
- 0.945
- 0.867
- 0.822
- 0.792
- 0.790

Integration values (from left to right):

- 2.000
- 2.103
- 2.000
- 2.989
- 3.016
- 1.215
- 3.156
- 9.090
- 1.239

Peak list (ppm) for the second spectrum (from left to right):

- 7.3696
- 7.3154
- 7.3011
- 7.2954
- 7.2895
- 7.2700
- 7.2643
- 7.2438
- 7.2240
- 7.2177
- 7.1940
- 7.1871
- 7.1855
- 7.1454
- 7.1390
- 7.1213
- 7.1152
- 7.1090
- 7.1026
- 7.0946
- 7.0877
- 1.9849
- 1.9703
- 1.9424
- 1.9288
- 1.8998
- 1.8918
- 1.8747
- 1.8706
- 1.8509
- 1.8468
- 1.7146
- 1.6807
- 1.6508
- 1.5984
- 1.5940
- 1.5736
- 1.5681
- 1.5523
- 1.4752
- 1.4688
- 1.4625
- 1.3967
- 1.3909
- 1.3822
- 1.3767
- 1.3574
- 1.3517
- 1.3421
- 1.3364
- 1.3162
- 1.3105
- 1.3002
- 1.2945
- 1.2827
- 0.9807
- 0.9600
- 0.9452
- 0.8656
- 0.8224
- 0.7982
- 0.7905
- 0.0274

Chemical structure of **1** is shown above the spectra. The structure is a bicyclic compound with a ketone group and a methyl group. The stereochemistry is indicated by wedges and dashes.

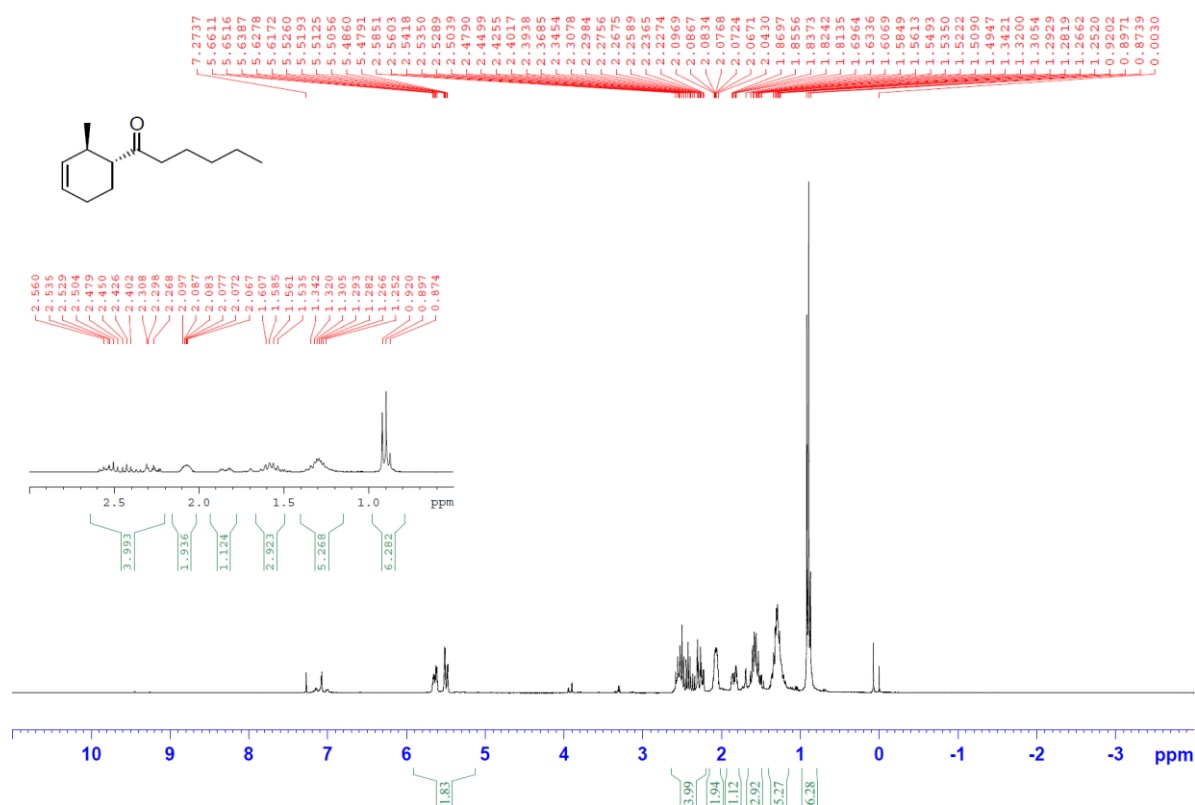
The ^{13}C NMR spectrum (top) shows peaks at 218.43, 142.33, 129.52, 77.64, 77.22, 76.80, 60.52, 53.91, 49.12, 47.78, 44.63, 38.75, 32.64, 32.52, 28.47, 26.68, 26.50, 19.80, 11.36, and 8.88 ppm.

The DEPT135 spectrum (middle) shows peaks at 53.91, 49.12, 47.78, 44.63, 38.75, 32.64, 32.52, 28.47, 26.68, 26.50, 19.80, 11.36, and 8.88 ppm.

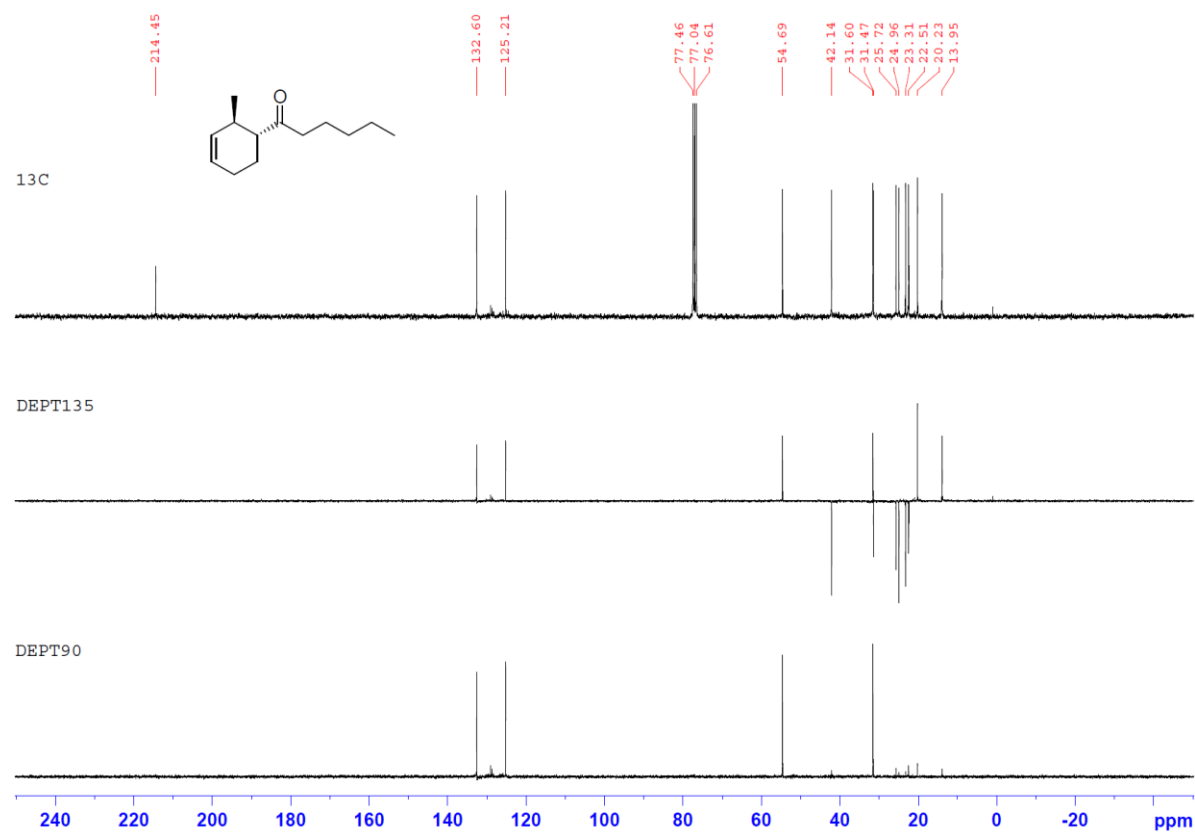
The DEPT90 spectrum (bottom) shows peaks at 53.91, 49.12, 47.78, 44.63, 38.75, 32.64, 32.52, 28.47, 26.68, 26.50, 19.80, 11.36, and 8.88 ppm.

The x-axis for all spectra is labeled in ppm, ranging from 220 to 0.

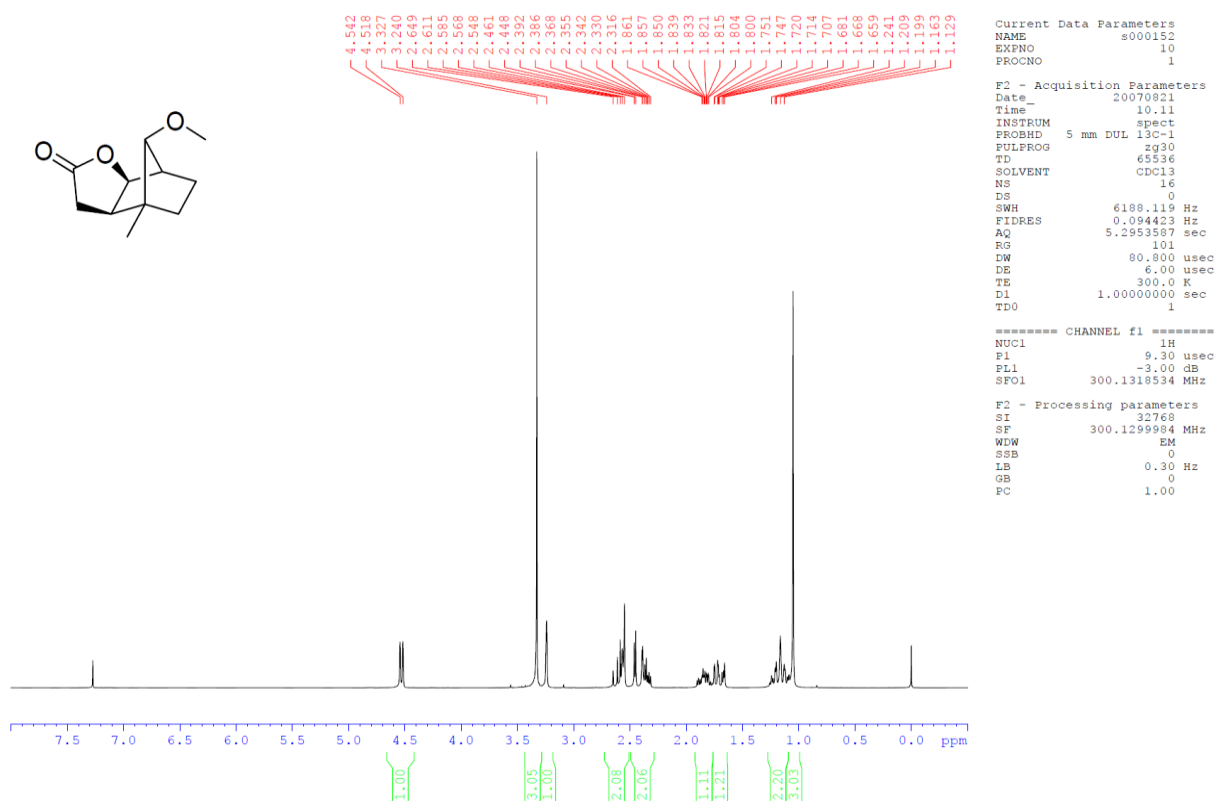
^1H NMR spectrum of compound **22** in CDCl_3



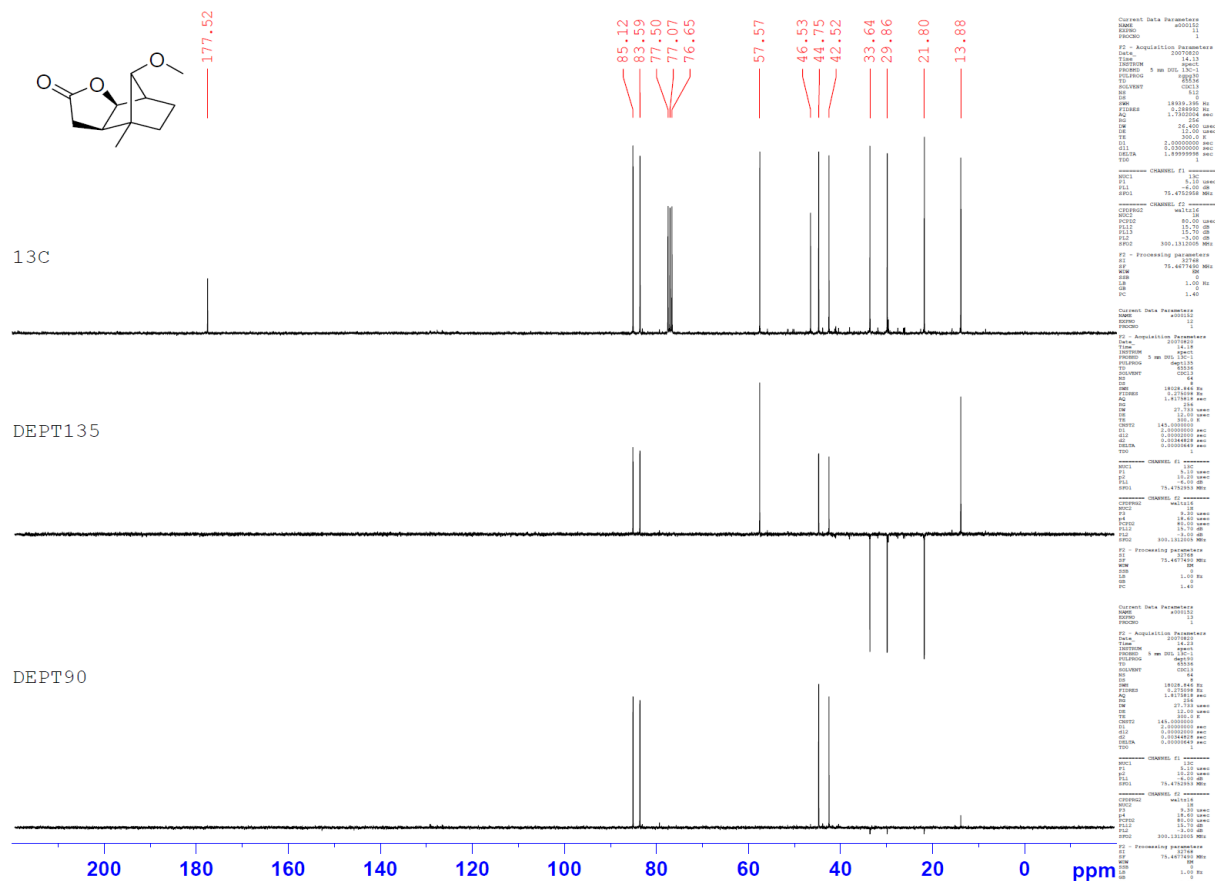
^{13}C NMR spectrum of compound **22** in CDCl_3



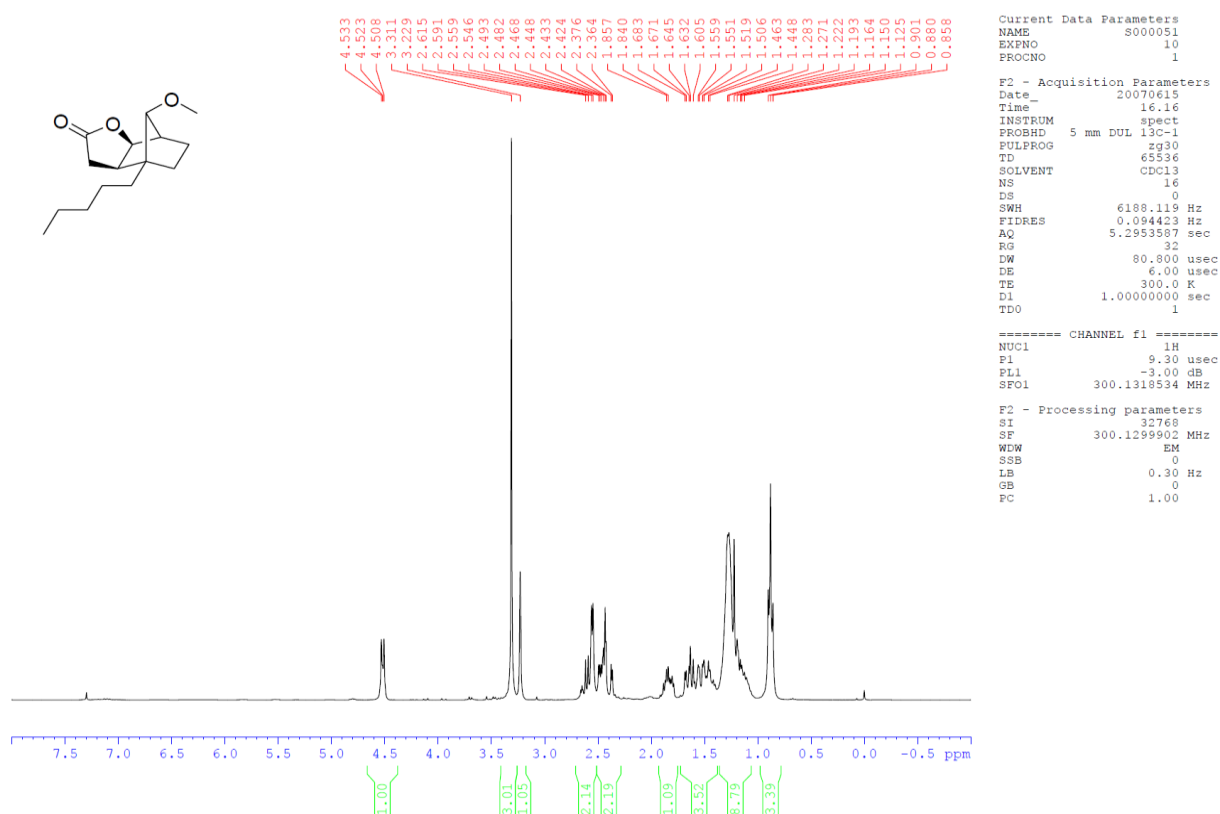
¹H NMR spectrum of compound **28a** in CDCl₃



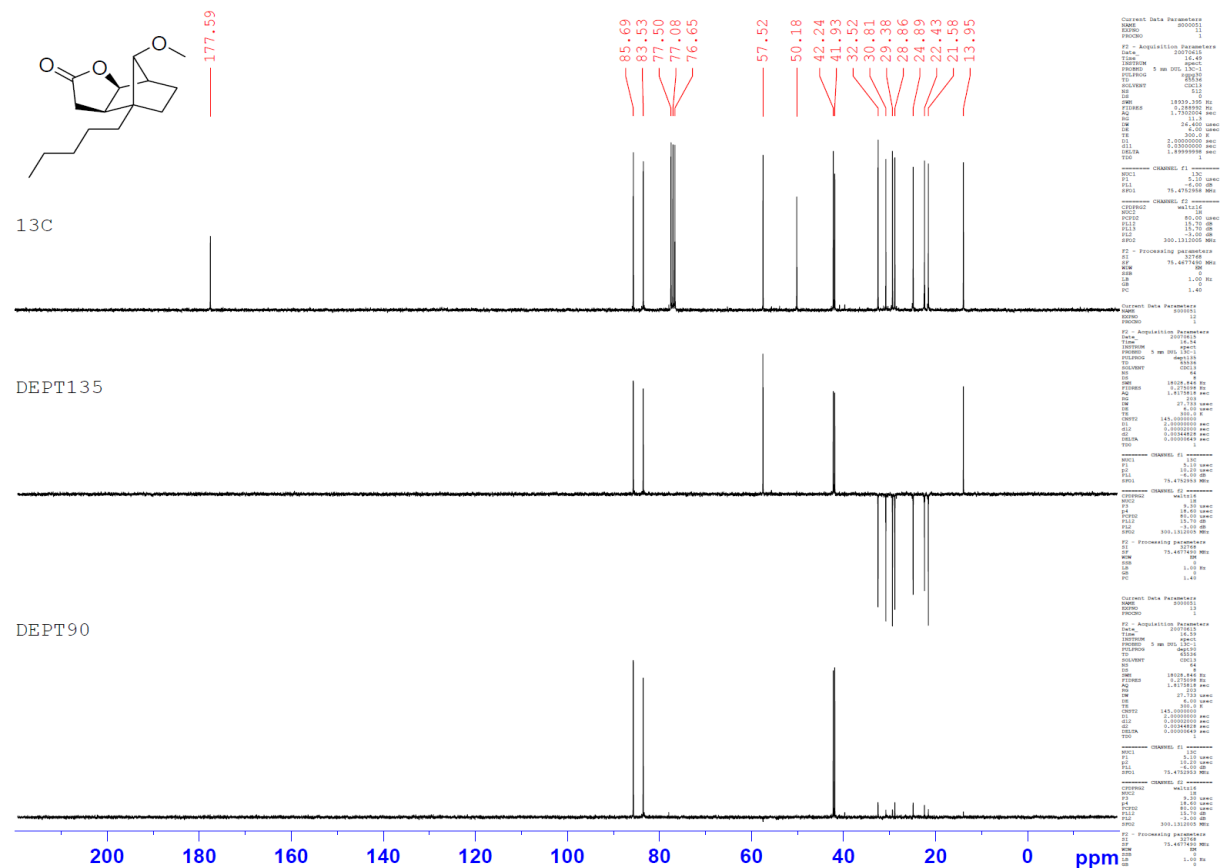
¹³C NMR spectrum of compound **28a** in CDCl₃



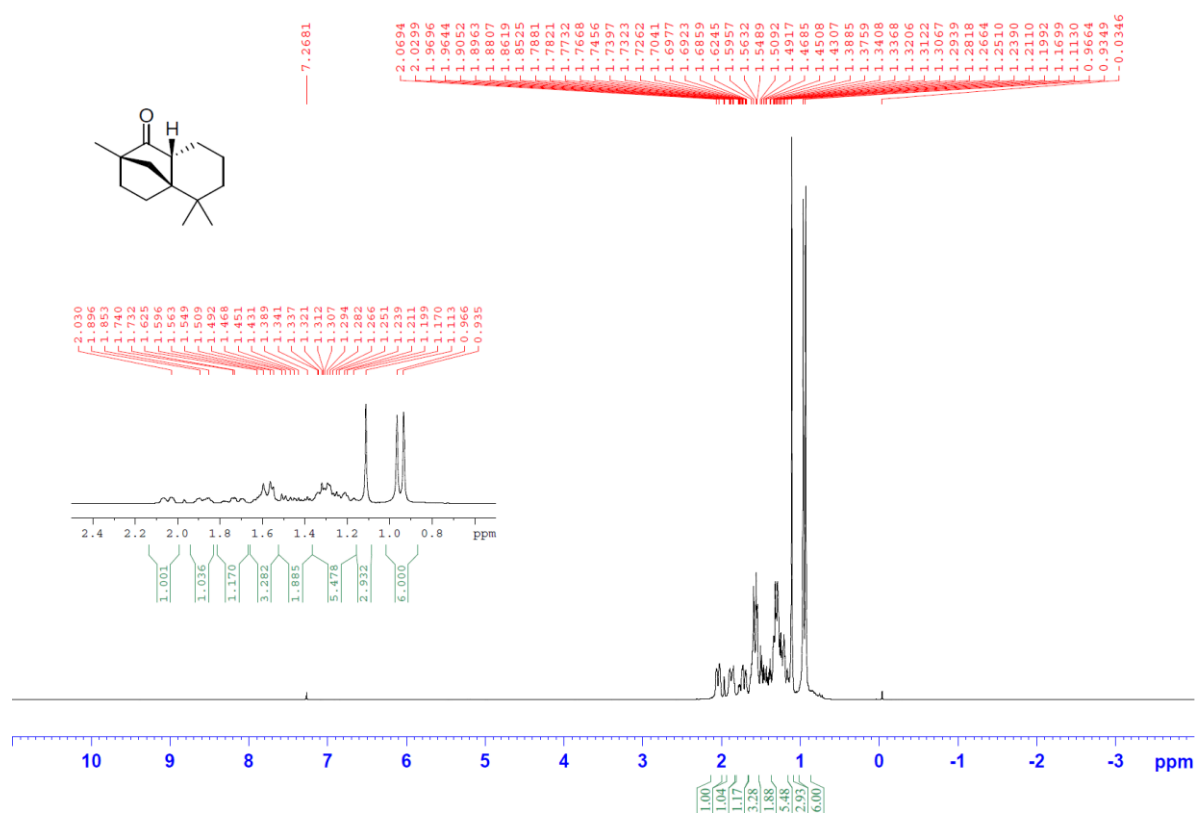
¹H NMR spectrum of compound **28b** in CDCl₃



¹³C NMR spectrum of compound **28b** in CDCl₃



^1H NMR spectrum of compound **31** in CDCl_3



^{13}C NMR spectrum of compound **31** in CDCl_3

