Supporting Information for

A New Synthetic Approach to the Polycyclic Polyprenylated Acylphloroglucinols

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Experimental details for the preparation and full characterization of compounds **4**–**9**, X-ray data for **9a**, ^{1}H and ^{13}C NMR spectra of **5–7**, and NOESY spectrum of **9b** (22 pages).

Methyl 4-allyl-7-methyl-3-oxo-6-octenoate (**4**). A 60% suspension of NaH in mineral oil (1.99 g, 49.4 mmol) was washed twice with petroleum ether and then suspended in dry THF (125 mL) at 0°C, and methyl 3-oxo-6-heptenoate (6.99 g, 44.8 mmol), BuLi (2.32 M in hexanes, 20.3 mL, 47.1 mmol), DMPU (6.0 mL, 49 mmol), and prenyl bromide (5.8 mL, 49 mmol) were added at 10 min intervals. The solution was allowed to warm to room temperature. The reaction was quenched with 1 M HCl, and the mixture was extracted with ether. The organic portion was dried over $MgSO_4$ and evaporated. Flash chromatography (15% EtOAc in petroleum ether) gave pure **4** (6.71 g, 29.9 mmol, 67% yield) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.72 (m, 1H), 5.05 (m, 3H), 3.74 (s, 3H), 3.46 (s, 2H), 2.71 (tt, 6.2 Hz, 7.7 Hz, 1H), 2.15–2.42 (m, 4H), 1.70 (s, 3H), 1.60 (s, 3H). Selected peaks of the enol tautomer: δ 12.00 (s, 1H), 4.95 (s, 1H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 205.8, 167.9, 135.6, 134.8, 121.0, 117.6, 59.2, 52.4, 49.6, 34.4, 30.0, 26.2, 18.2. IR (neat): 1752, 1716, 1643, 1623 cm^{-1}. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.43; H, 8.90.

Methyl (1*R, 3*R**)-3-allyl-6,6-dimethyl-2-cyclohexanonecarboxylate** (**5**). A solution of **4** (6.71 g, 29.9 mmol) in CH_2Cl_2 (120 mL) at 0°C was treated with $SnCl_4$ (3.9 mL, 33 mmol), and the solution was allowed to stir at room temperature overnight. Ether (50 mL) was added, and the mixture was washed with 6 N HCl and water. The organic portion was dried over $MgSO_4$ and evaporated. Flash chromatography (5% EtOAc in petroleum ether) gave pure **5** (5.50 g, 24.5 mmol, 82% yield) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.78 (dddd, 6.4 Hz, 7.7 Hz, 10.1 Hz, 16.9 Hz, 1H), 5.04 (m, 2H), 3.72 (s, 3H), 3.34 (s, 1H), 2.53 (m, 1H), 2.34 (m, 1H), 1.98–2.10 (m, 2H), 1.74 (dd, 3.7 Hz, 4.6 Hz, 1H), 1.60 (m, 2H), 1.11 (s, 3H), 1.10 (s, 3H). ^{13}C NMR (200 MHz, $CDCl_3$): δ 207.0, 169.6, 136.6, 117.4, 67.4, 52.2, 49.9, 41.1, 40.6, 34.2, 30.3, 29.4, 21.8. IR (neat): 1751, 1709, 1639 cm^{-1}. $C_{13}H_{20}O_3$.

Methyl (1*R, 3*R**)-1-(3,3-diethoxy-1-propynyl)-3-allyl-6,6-dimethyl-2-cyclohexanonecarboxylate** (**6**). A solution of 3,3-diethoxypropyne (4.77 mL, 33.1 mmol) in THF (100 mL) at –30°C was treated at 15 min intervals with BuLi (2.32 M in hexanes, 14.3 mL, 33.1 mmol), Bu_3SnCl (9.0 mL, 33 mmol), and a solution of **5** (5.50 g, 24.5 mmol) in THF (10 mL). Solid $Pb(OAc)_4$ (16.31 g, 36.82 mmol) was added, and the mixture was allowed to warm to room

temperature. When the reaction was judged to be complete (TLC), water was added, and the mixture was extracted with ether. The aqueous layer was neutralized with 1 M HCl (a white salt formed), and it was extracted with ether again. The organic layers were combined, washed with brine, dried over $MgSO_4$, and evaporated. Flash chromatography (5% EtOAc in petroleum ether) gave **6** (4.12 g, 11.7 mmol, 48% yield) as a colorless liquid contaminated with a small amount of Bu_3SnX. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.77 (m, 1H), 5.35 (s, 1H), 5.01–5.08 (m, 2H), 3.76 (s + m, 5H), 3.63 (m, 2H), 3.22 (ddt, J_d = 5.3 Hz, J_d = 12.5 Hz, J_t = 7.1 Hz, 1H), 2.48 (m, 1H), 2.34 (dt, J_d = 4.2 Hz, J_t = 13.6 Hz, 1H), 2.02 (m, 2H), 1.53 (m, 1H), 1.35 (ddd, 2.6 Hz, 4.2 Hz, 13.9 Hz, 1H), 1.24 (s + t, 7.2 Hz, 9H), 1.16 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 205.2, 167.8, 136.3, 117.4, 92.1, 85.0, 82.5, 66.9, 61.7 (× 2), 53.1, 44.8, 44.3, 38.0, 34.3, 29.1, 27.0, 22.7, 15.8 (× 2). IR (neat): 2237, 1752, 1720, 1639 cm^{-1}. $C_{20}H_{30}O_5$.

Methyl (1*R, 3*R**)-1-(3-oxo-1-propynyl)-3-allyl-6,6-dimethyl-2-cyclohexanonecarboxylate** (**7**). A solution of **6** (4.12 g, 11.7 mmol) in HCO_2H (4.0 mL) was allowed to stir overnight in the dark under N_2. Water was added, and the mixture was extracted with ether. Flash chromatography (10% EtOAc in petroleum ether) provided **7** (2.30 g, 8.33 mmol, 71% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.32 (s, 1H), 5.77 (dddd, 6.6 Hz, 7.7 Hz, 10.3 Hz, 16.9 Hz, 1H), 5.07 (m, 2H), 3.81 (s, 3H), 3.11 (ddt, J_d = 5.5 Hz, J_d = 12.5 Hz, J_t = 7.3 Hz, 1H), 2.51 (m, 1H), 2.28 (dt, J_t = 13.7 Hz, J_d = 4.3 Hz, 1H), 2.05 (m, 2H), 1.57 (m, 1H), 1.43 (ddd, 14.3 Hz, 4.4 Hz, 2.6 Hz, 1H), 1.25 (s, 3H), 1.20 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 203.2, 176.9, 166.5, 135.8, 117.9, 93.2, 88.0, 67.6, 53.6, 45.5, 45.0, 37.9, 34.3, 29.0, 27.1, 22.8. IR (neat): 2745, 2206, 1755, 1724, 1670, 1456, 1437 cm^{-1}. $C_{16}H_{20}O_4$.

Methyl (1*R, 3*R**, *E*)-1-(2-triethylsilyl-3-oxo-1-propenyl)-3-allyl-6,6-dimethyl-2-cyclohexanonecarboxylate** (**8**). A solution of **7** (2.29 g, 8.30 mmol) and $Co_2(CO)_8$ (3.42 g, 10.0 mmol) in CH_2Cl_2 (32 mL) was allowed to stir at 0°C for 2 h. The solvent was evaporated, and the residue was filtered through a short column of silica gel, eluting with hexane (the brown eluant was discarded) and then 30% EtOAc in petroleum ether. The latter eluant was evaporated to give the $Co_2(CO)_6$ complex of **7** (4.06 g, 7.21 mmol, 87% yield) as a dark red oil. ^{1}H NMR (400 MHz,

$CDCl_3$): δ 10.42 (s, 1H), 5.72 (m, 1H), 5.05 (m, 2H), 3.72 (s, 3H), 2.65 (m, 2H), 2.15 (m, 1H), 2.04 (m, 2H), 1.78 (m, 1H), 1.65 (m, 1H), 1.30 (s, 3H), 1.06 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 206.3, 193.0, 170.3, 136.3, 118.0, 71.6, 52.7, 46.9, 40.7, 36.4, 35.4, 32.2, 28.4, 27.9, 25.0, 23.3, 14.9. IR (neat): 2101, 2058, 2023, 1748, 1713, 1700, 1550 cm^{-1}.

The complex (3.98 g, 7.09 mmol) was redissolved in dry $(ClCH_2)_2$ (40 mL), and bis(trimethylsilyl)acetylene (2.42 g, 14.2 mmol) and triethylsilane (6.4 mL, 40 mmol) were added. The mixture was allowed to stir at 65°C for 3 h (monitored by TLC). The solvent was evaporated, and the residue was filtered through a short column of silica gel, eluting with hexane (the brown eluant was discarded) and then 30% EtOAc in petroleum ether. The latter eluant was evaporated to provide **8** (2.61 g, 6.66 mmol, 94% yield) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.87 (s, 1H), 6.87 (s, 1H), 5.68 (m, 1H), 5.01 (m, 2H), 3.69 (s, 3H), 2.68 (dq, J_d = 6.4 Hz, J_q = 12.5 Hz, 1H), 2.48 (m, 1H), 1.98 (m, 3H), 1.62 (m, 1H), 1.49 (m, 1H), 1.20 (s, 3H), 1.14 (s, 3H), 0.92 (t, 7.9 Hz, 9H), 0.73 (m, 6H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 207.8, 196.4, 169.2, 150.9, 146.7, 136.2, 117.7, 71.9, 52.7, 47.1, 43.2, 37.1, 34.4, 29.0, 26.1, 24.9, 7.9 (× 3), 3.7 (× 3). IR (neat): 2734, 2206, 1751, 1713, 1666, 1573, 1456 cm^{-1}. Calcd for $C_{22}H_{36}O_4Si$: C, 67.30; H, 9.24. Found: C, 67.34; H, 8.82.

Methyl (1*R, 4*R**, 5*R**)- and (1*R**, 4*S**, 5*R**)-3-triethylsilyl-4-hydroxy-5-allyl-8,8-dimethylbicyclo[3.3.1]non-2-en-9-one-1-carboxylate [9a (endo) and 9b (exo)]**. Twenty drops of 6 M HCl were added to a solution of **8** (2.61 g, 6.66 mmol) in THF (25 mL). After 4.5 h (monitored by TLC), water was added. The aqueous layer was extracted with ether (2 × 30 mL), and the combined organic layers were washed with brine, dried over $MgSO_4$, and evaporated. Flash chromatography (8% EtOAc in petroleum ether) provided **9a** (0.87 g, 2.22 mmol, 33% yield) as a white solid, mp 93°C, and **9b** (1.00 g, 2.55 mmol, 39% yield) as a colorless liquid.

Compound **9a**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.04 (m + d, 1.8 Hz, 2H), 5.15 (m, 2H), 4.42 (d, 4.6 Hz, 1H), 3.75 (s, 3H), 2.40 (dd, 8.8 Hz, 14.0 Hz, 1H), 2.32 (dddd, 14.0 Hz, 6.6 Hz, 1.5 Hz, 1.3 Hz, 1H), 2.24 (ddd, 14.1 Hz, 6.1 Hz, 2.0 Hz, 1H), 2.00 (dt, J_d = 4.6 Hz, J_t = 13.8 Hz, 1H), 1.91 (d, 6.0 Hz, 1H), 1.62 (ddt, J_d = 0.9 Hz, J_d = 5.3 Hz, J_t = 14.1 Hz, 1H), 1.26 (s, 3H), 1.20 (s, 3H), 1.15 (ddd, 2.0 Hz, 5.1 Hz, 13.7 Hz, 1H), 0.97 (t, 7.8 Hz, 9H), 0.72 (m, 6H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 212.5,

171.0, 142.4, 137.2, 136.6, 118.9, 80.7, 68.3, 56.3, 52.5, 43.6, 40.7, 36.4, 29.1, 25.8, 23.6, 8.1 (× 3), 4.1 (× 3). IR (KBr): 3491, 1744, 1689, 1612 cm^{-1}. Calcd for $C_{22}H_{36}O_4Si$: C, 67.30; H, 9.24. Found: C, 67.39; H, 8.81.

Compound **9b**. ^1H NMR (400 MHz, $CDCl_3$): δ 6.13 (s, 1H), 5.80 (dddd, 6.8 Hz, 8.1 Hz, 10.3 Hz, 16.8 Hz, 1H), 5.15 (m, 2H), 4.23 (s, 1H), 3.69 (s, 3H), 2.51 (dd, 8.2 Hz, 14.1 Hz, 1H), 2.32 (ddt, J_d = 6.1 Hz, J_d = 14.1 Hz, J_t = 1.3 Hz, 1H), 1.84 (m, 2H), 1.67 (m, 1H), 1.30 (broad, 1H), 1.17 (s, 3H), 0.98 (s, 3H), 0.95 (m + t, 8.0 Hz, 10H), 0.68 (q, 8.0 Hz, 6H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 211.2, 170.8, 141.6, 140.8, 134.7, 119.3, 82.4, 69.0, 54.0, 52.7, 42.6, 37.9, 36.5, 32.2, 26.3, 23.4, 8.0 (× 3), 3.8 (× 3). IR (neat): 3522, 1752, 1713, 1608 cm^{-1}. Calcd for $C_{22}H_{36}O_4Si$: C, 67.30; H, 9.24. Found: C, 66.98; H, 8.86.

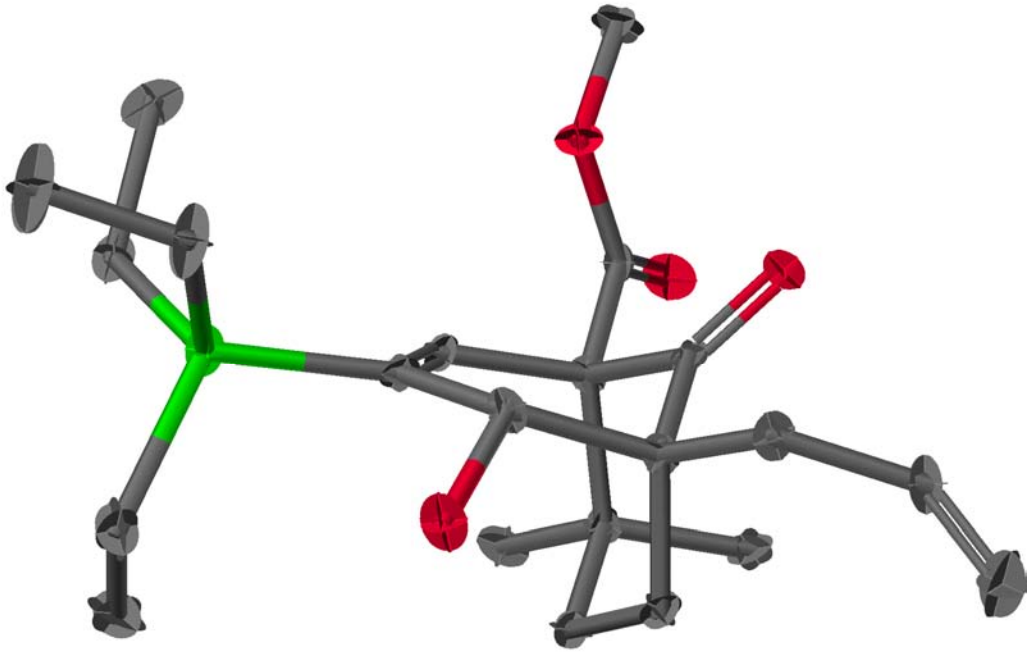


Figure S1. Thermal ellipsoid plot of **9a**. Key: C gray, O red, Si green.

Table S1. Crystal data and structure refinement for **9a**.

Empirical formula	$C_{22}H_{36}O_4Si$
Formula weight	392.60
Temperature	90.0(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, *C*2/c
Unit cell dimensions	a = 19.1880(3) Å α = 90°
	b = 9.48600(10) Å β = 90.6760(7)°
	c = 24.8430(4) Å γ = 90°
Volume	4521.54(11) $Å^3$
Z, Calculated density	8, 1.153 Mg/m^3
Absorption coefficient	0.127 mm^{-1}
F(000)	1712
Crystal size	0.22 x 0.20 x 0.20 mm
Θ range for data collection	1.64 to 27.46°
Limiting indices	-24≤h≤24, -11≤k≤12, -32≤l≤32
Reflections collected / unique	9375 / 5163 [R(int) = 0.0411]
Completeness to Θ= 27.46	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9751 and 0.9727
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5163 / 0 / 251
Goodness-of-fit on F^2	1.472
Final R indices [I>2σ(I)]	R1 = 0.0496, ωR2 = 0.1198
R indices (all data)	R1 = 0.0869, ωR2 = 0.1353
Largest diff. peak and hole	0.539 and -0.248 $e·Å^{-3}$

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **9a**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Si(1)	4212(1)	4763(1)	1175(1)	21(1)
C(1)	2153(1)	3056(2)	1100(1)	14(1)
C(2)	2913(1)	3465(2)	1021(1)	15(1)
C(3)	3289(1)	4267(2)	1354(1)	16(1)
O(4)	3192(1)	6200(1)	1952(1)	24(1)
C(4)	2998(1)	4759(2)	1887(1)	16(1)
C(5)	2194(1)	4545(2)	1955(1)	15(1)
C(6)	1768(1)	5692(2)	1653(1)	17(1)
C(7)	1819(1)	5618(2)	1041(1)	18(1)
C(8)	1656(1)	4154(2)	811(1)	16(1)
O(9)	1815(1)	2113(1)	1956(1)	18(1)
C(9)	2025(1)	3132(2)	1706(1)	14(1)
C(10)	1794(1)	4165(2)	205(1)	22(1)
C(11)	888(1)	3784(2)	905(1)	21(1)
O(12)	1582(1)	1066(1)	646(1)	24(1)
C(12)	2048(1)	1532(2)	918(1)	16(1)
O(13)	2572(1)	728(1)	1114(1)	19(1)
C(13)	2494(1)	-775(2)	1030(1)	23(1)
C(14)	2027(1)	4568(2)	2561(1)	18(1)
C(15)	1268(1)	4480(2)	2697(1)	23(1)
C(16)	935(1)	5417(2)	2982(1)	35(1)
C(17)	4525(1)	3620(2)	610(1)	23(1)
C(18)	4640(1)	2060(2)	737(1)	30(1)
C(19)	4780(1)	4504(3)	1783(1)	32(1)
C(20)	5565(1)	4602(3)	1678(1)	45(1)
C(21)	4241(1)	6623(2)	926(1)	40(1)
C(22)	3829(1)	6885(3)	400(1)	48(1)

Table S3. Bond lengths [Å] and angles [°] for **9a**.

Si(1)-C(19)	1.8679(19)
Si(1)-C(21)	1.871(2)
Si(1)-C(17)	1.8772(19)
Si(1)-C(3)	1.8905(17)
C(1)-C(2)	1.524(2)
C(1)-C(12)	1.526(2)
C(1)-C(9)	1.532(2)
C(1)-C(8)	1.579(2)
C(2)-C(3)	1.331(2)
C(2)-H(2)	0.9500
C(3)-C(4)	1.516(2)
O(4)-C(4)	1.425(2)
O(4)-H(4)	0.8400
C(4)-C(5)	1.569(2)
C(4)-H(4A)	1.0000
C(5)-C(9)	1.509(2)
C(5)-C(14)	1.543(2)
C(5)-C(6)	1.549(2)
C(6)-C(7)	1.528(2)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(7)-C(8)	1.533(2)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-C(10)	1.531(2)
C(8)-C(11)	1.535(2)
O(9)-C(9)	1.220(2)
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
O(12)-C(12)	1.1999(19)
C(12)-O(13)	1.347(2)
O(13)-C(13)	1.448(2)
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-C(15)	1.502(2)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(15)-C(16)	1.309(3)
C(15)-H(15)	0.9500
C(16)-H(16A)	0.9500
C(16)-H(16B)	0.9500
C(17)-C(18)	1.529(3)
C(17)-H(17A)	0.9900
C(17)-H(17B)	0.9900
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800

C(18)-H(18C)	0.9800
C(19)-C(20)	1.535(3)
C(19)-H(19A)	0.9900
C(19)-H(19B)	0.9900
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-C(22)	1.539(3)
C(21)-H(21A)	0.9900
C(21)-H(21B)	0.9900
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800

C(19)-Si(1)-C(21)	111.87(11)
C(19)-Si(1)-C(17)	109.88(9)
C(21)-Si(1)-C(17)	106.64(10)
C(19)-Si(1)-C(3)	108.38(8)
C(21)-Si(1)-C(3)	110.11(9)
C(17)-Si(1)-C(3)	109.95(8)
C(2)-C(1)-C(12)	109.06(14)
C(2)-C(1)-C(9)	106.16(13)
C(12)-C(1)-C(9)	108.24(14)
C(2)-C(1)-C(8)	110.29(14)
C(12)-C(1)-C(8)	114.48(13)
C(9)-C(1)-C(8)	108.26(14)
C(3)-C(2)-C(1)	125.37(16)
C(3)-C(2)-H(2)	117.3
C(1)-C(2)-H(2)	117.3
C(2)-C(3)-C(4)	121.10(15)
C(2)-C(3)-Si(1)	119.89(13)
C(4)-C(3)-Si(1)	118.99(12)
C(4)-O(4)-H(4)	109.5
O(4)-C(4)-C(3)	107.21(14)
O(4)-C(4)-C(5)	111.60(14)
C(3)-C(4)-C(5)	115.29(14)
O(4)-C(4)-H(4A)	107.5
C(3)-C(4)-H(4A)	107.5
C(5)-C(4)-H(4A)	107.5
C(9)-C(5)-C(14)	111.50(15)
C(9)-C(5)-C(6)	108.50(13)
C(14)-C(5)-C(6)	110.40(14)
C(9)-C(5)-C(4)	106.09(14)
C(14)-C(5)-C(4)	108.57(13)
C(6)-C(5)-C(4)	111.72(14)
C(7)-C(6)-C(5)	114.23(15)
C(7)-C(6)-H(6A)	108.7
C(5)-C(6)-H(6A)	108.7
C(7)-C(6)-H(6B)	108.7
C(5)-C(6)-H(6B)	108.7
H(6A)-C(6)-H(6B)	107.6
C(6)-C(7)-C(8)	113.44(15)
C(6)-C(7)-H(7A)	108.9
C(8)-C(7)-H(7A)	108.9

C(6)-C(7)-H(7B)	108.9
C(8)-C(7)-H(7B)	108.9
H(7A)-C(7)-H(7B)	107.7
C(10)-C(8)-C(7)	108.87(14)
C(10)-C(8)-C(11)	109.15(14)
C(7)-C(8)-C(11)	110.04(14)
C(10)-C(8)-C(1)	109.92(14)
C(7)-C(8)-C(1)	108.01(13)
C(11)-C(8)-C(1)	110.83(14)
O(9)-C(9)-C(5)	124.44(15)
O(9)-C(9)-C(1)	121.41(16)
C(5)-C(9)-C(1)	114.15(14)
C(8)-C(10)-H(10A)	109.5
C(8)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(8)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(8)-C(11)-H(11A)	109.5
C(8)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(8)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
O(12)-C(12)-O(13)	122.87(17)
O(12)-C(12)-C(1)	127.55(16)
O(13)-C(12)-C(1)	109.57(14)
C(12)-O(13)-C(13)	115.50(13)
O(13)-C(13)-H(13A)	109.5
O(13)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
O(13)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(15)-C(14)-C(5)	115.49(14)
C(15)-C(14)-H(14A)	108.4
C(5)-C(14)-H(14A)	108.4
C(15)-C(14)-H(14B)	108.4
C(5)-C(14)-H(14B)	108.4
H(14A)-C(14)-H(14B)	107.5
C(16)-C(15)-C(14)	124.36(19)
C(16)-C(15)-H(15)	117.8
C(14)-C(15)-H(15)	117.8
C(15)-C(16)-H(16A)	120.0
C(15)-C(16)-H(16B)	120.0
H(16A)-C(16)-H(16B)	120.0
C(18)-C(17)-Si(1)	116.84(13)
C(18)-C(17)-H(17A)	108.1
Si(1)-C(17)-H(17A)	108.1
C(18)-C(17)-H(17B)	108.1
Si(1)-C(17)-H(17B)	108.1
H(17A)-C(17)-H(17B)	107.3
C(17)-C(18)-H(18A)	109.5
C(17)-C(18)-H(18B)	109.5

H(18A)-C(18)-H(18B)	109.5
C(17)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(20)-C(19)-Si(1)	114.73(14)
C(20)-C(19)-H(19A)	108.6
Si(1)-C(19)-H(19A)	108.6
C(20)-C(19)-H(19B)	108.6
Si(1)-C(19)-H(19B)	108.6
H(19A)-C(19)-H(19B)	107.6
C(19)-C(20)-H(20A)	109.5
C(19)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(19)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(22)-C(21)-Si(1)	114.64(16)
C(22)-C(21)-H(21A)	108.6
Si(1)-C(21)-H(21A)	108.6
C(22)-C(21)-H(21B)	108.6
Si(1)-C(21)-H(21B)	108.6
H(21A)-C(21)-H(21B)	107.6
C(21)-C(22)-H(22A)	109.5
C(21)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(21)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5

Table S4. Anisotropic displacement parameters ($Å^2$ x 10^3) for **9a**. The anisotropic displacement factor exponent takes the form:
$-2\pi^2$ [h^2 a^{*2} U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Si(1)	16(1)	24(1)	22(1)	-2(1)	4(1)	-4(1)
C(1)	17(1)	14(1)	12(1)	0(1)	0(1)	-1(1)
C(2)	16(1)	15(1)	15(1)	-1(1)	3(1)	2(1)
C(3)	18(1)	15(1)	15(1)	-1(1)	1(1)	2(1)
O(4)	28(1)	21(1)	22(1)	-8(1)	5(1)	-8(1)
C(4)	18(1)	16(1)	15(1)	-2(1)	0(1)	-5(1)
C(5)	18(1)	16(1)	12(1)	0(1)	1(1)	0(1)
C(6)	19(1)	15(1)	18(1)	-2(1)	2(1)	2(1)
C(7)	21(1)	15(1)	17(1)	2(1)	1(1)	2(1)
C(8)	18(1)	16(1)	16(1)	2(1)	1(1)	3(1)
O(9)	21(1)	17(1)	16(1)	4(1)	2(1)	-2(1)
C(9)	9(1)	17(1)	16(1)	1(1)	-1(1)	2(1)
C(10)	30(1)	21(1)	15(1)	2(1)	-3(1)	0(1)
C(11)	17(1)	20(1)	26(1)	0(1)	-3(1)	2(1)
O(12)	26(1)	19(1)	26(1)	-3(1)	-7(1)	-3(1)
C(12)	19(1)	18(1)	11(1)	0(1)	4(1)	2(1)
O(13)	22(1)	13(1)	21(1)	-1(1)	-1(1)	2(1)
C(13)	33(1)	13(1)	24(1)	0(1)	3(1)	2(1)
C(14)	22(1)	20(1)	12(1)	-4(1)	2(1)	-1(1)
C(15)	24(1)	29(1)	17(1)	-2(1)	4(1)	-3(1)
C(16)	31(1)	40(2)	36(1)	-9(1)	10(1)	0(1)
C(17)	17(1)	33(1)	19(1)	1(1)	2(1)	1(1)
C(18)	30(1)	35(1)	25(1)	-5(1)	-3(1)	12(1)
C(19)	20(1)	51(2)	24(1)	-5(1)	-1(1)	-7(1)
C(20)	21(1)	78(2)	37(1)	-1(1)	-3(1)	-10(1)
C(21)	29(1)	28(1)	64(2)	-2(1)	19(1)	-8(1)
C(22)	62(2)	33(1)	51(2)	21(1)	28(1)	17(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **9a**.

	x	y	z	U(eq)
H(2)	3136	3121	708	18
H(4)	3204	6403	2281	35
H(4A)	3239	4211	2179	20
H(6A)	1273	5604	1754	21
H(6B)	1933	6631	1774	21
H(7A)	2296	5892	935	21
H(7B)	1491	6309	880	21
H(10A)	1486	4852	29	33
H(10B)	1703	3225	56	33
H(10C)	2281	4424	142	33
H(11A)	812	3650	1291	32
H(11B)	771	2914	712	32
H(11C)	592	4553	772	32
H(13A)	2058	-1095	1190	35
H(13B)	2888	-1271	1199	35
H(13C)	2484	-975	642	35
H(14A)	2272	3769	2737	22
H(14B)	2219	5448	2718	22
H(15)	1012	3690	2566	28
H(16A)	1175	6219	3119	42
H(16B)	453	5296	3053	42
H(17A)	4183	3688	310	28
H(17B)	4971	4014	481	28
H(18A)	4972	1968	1038	45
H(18B)	4826	1583	420	45
H(18C)	4195	1627	835	45
H(19A)	4656	5222	2055	38
H(19B)	4678	3567	1939	38
H(20A)	5700	3860	1426	68
H(20B)	5823	4483	2018	68
H(20C)	5673	5526	1524	68
H(21A)	4054	7249	1209	48
H(21B)	4733	6889	869	48
H(22A)	3996	6245	120	72
H(22B)	3896	7863	284	72
H(22C)	3332	6715	461	72

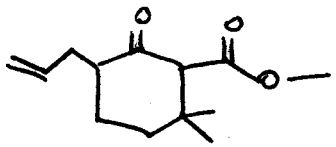
Table S6. Torsion angles [°] for **9a**.

C(12)-C(1)-C(2)-C(3)	-141.57(18)
C(9)-C(1)-C(2)-C(3)	-25.2(2)
C(8)-C(1)-C(2)-C(3)	91.9(2)
C(1)-C(2)-C(3)-C(4)	5.4(3)
C(1)-C(2)-C(3)-Si(1)	-176.40(13)
C(19)-Si(1)-C(3)-C(2)	-134.65(16)
C(21)-Si(1)-C(3)-C(2)	102.68(17)
C(17)-Si(1)-C(3)-C(2)	-14.53(17)
C(19)-Si(1)-C(3)-C(4)	43.61(17)
C(21)-Si(1)-C(3)-C(4)	-79.05(16)
C(17)-Si(1)-C(3)-C(4)	163.74(13)
C(2)-C(3)-C(4)-O(4)	-137.59(17)
Si(1)-C(3)-C(4)-O(4)	44.17(18)
C(2)-C(3)-C(4)-C(5)	-12.7(2)
Si(1)-C(3)-C(4)-C(5)	169.10(12)
O(4)-C(4)-C(5)-C(9)	162.12(13)
C(3)-C(4)-C(5)-C(9)	39.5(2)
O(4)-C(4)-C(5)-C(14)	-77.92(17)
C(3)-C(4)-C(5)-C(14)	159.46(15)
O(4)-C(4)-C(5)-C(6)	44.06(18)
C(3)-C(4)-C(5)-C(6)	-78.56(19)
C(9)-C(5)-C(6)-C(7)	-49.37(19)
C(14)-C(5)-C(6)-C(7)	-171.83(14)
C(4)-C(5)-C(6)-C(7)	67.24(19)
C(5)-C(6)-C(7)-C(8)	51.9(2)
C(6)-C(7)-C(8)-C(10)	-174.37(14)
C(6)-C(7)-C(8)-C(11)	66.05(18)
C(6)-C(7)-C(8)-C(1)	-55.05(18)
C(2)-C(1)-C(8)-C(10)	61.38(18)
C(12)-C(1)-C(8)-C(10)	-62.05(18)
C(9)-C(1)-C(8)-C(10)	177.13(14)
C(2)-C(1)-C(8)-C(7)	-57.27(17)
C(12)-C(1)-C(8)-C(7)	179.30(14)
C(9)-C(1)-C(8)-C(7)	58.48(17)
C(2)-C(1)-C(8)-C(11)	-177.88(14)
C(12)-C(1)-C(8)-C(11)	58.69(18)
C(9)-C(1)-C(8)-C(11)	-62.13(18)
C(14)-C(5)-C(9)-O(9)	-3.2(2)
C(6)-C(5)-C(9)-O(9)	-124.98(17)
C(4)-C(5)-C(9)-O(9)	114.84(17)
C(14)-C(5)-C(9)-C(1)	177.81(13)
C(6)-C(5)-C(9)-C(1)	56.02(18)
C(4)-C(5)-C(9)-C(1)	-64.16(17)
C(2)-C(1)-C(9)-O(9)	-122.89(16)
C(12)-C(1)-C(9)-O(9)	-5.9(2)
C(8)-C(1)-C(9)-O(9)	118.70(17)
C(2)-C(1)-C(9)-C(5)	56.15(18)
C(12)-C(1)-C(9)-C(5)	173.12(13)
C(8)-C(1)-C(9)-C(5)	-62.26(17)
C(2)-C(1)-C(12)-O(12)	-135.15(18)
C(9)-C(1)-C(12)-O(12)	109.76(19)

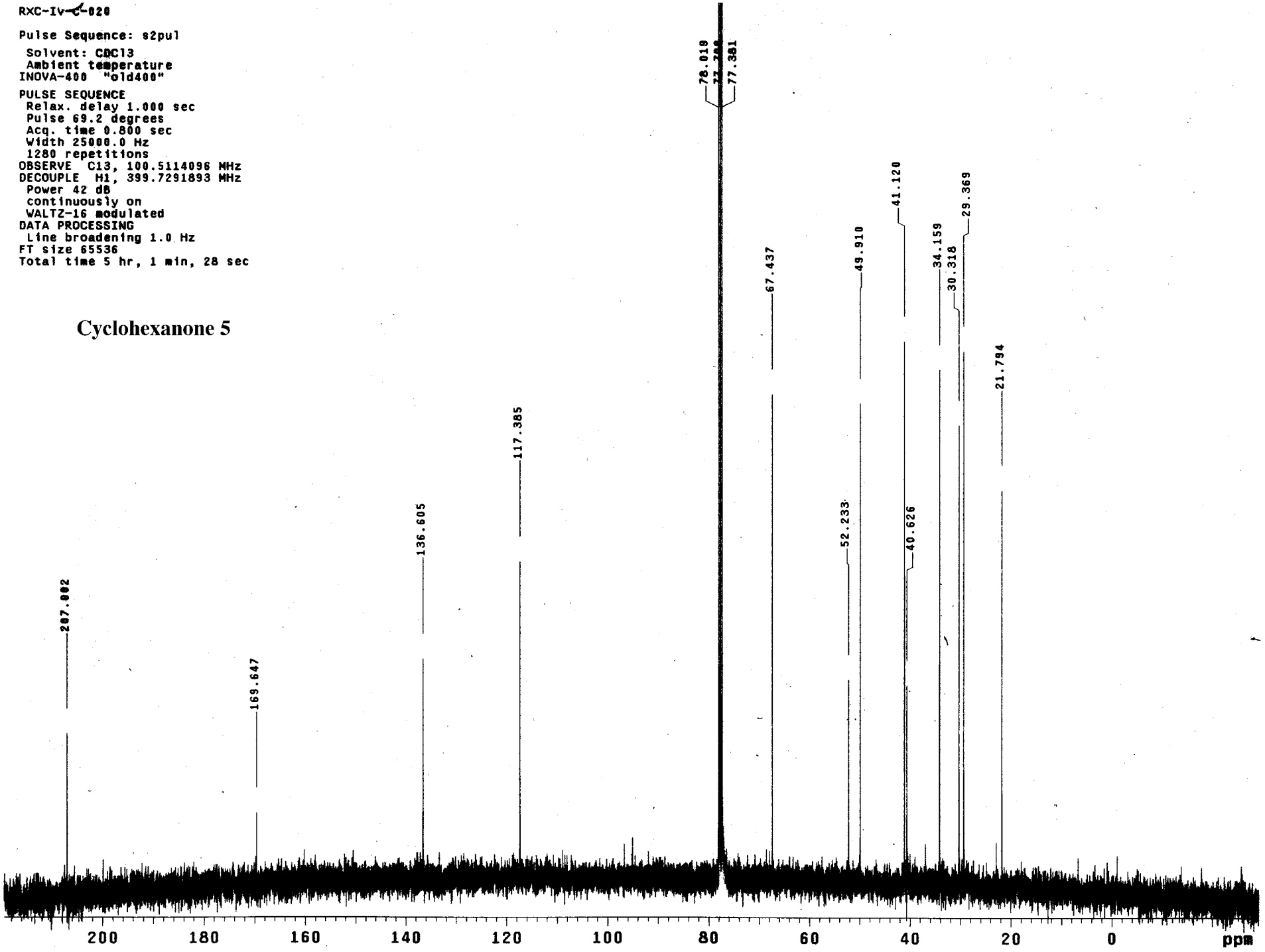
C(8)-C(1)-C(12)-O(12)	-11.1(2)
C(2)-C(1)-C(12)-O(13)	45.04(17)
C(9)-C(1)-C(12)-O(13)	-70.04(16)
C(8)-C(1)-C(12)-O(13)	169.12(13)
O(12)-C(12)-O(13)-C(13)	-7.2(2)
C(1)-C(12)-O(13)-C(13)	172.63(13)
C(9)-C(5)-C(14)-C(15)	-67.7(2)
C(6)-C(5)-C(14)-C(15)	53.0(2)
C(4)-C(5)-C(14)-C(15)	175.80(16)
C(5)-C(14)-C(15)-C(16)	-122.8(2)
C(19)-Si(1)-C(17)-C(18)	50.98(17)
C(21)-Si(1)-C(17)-C(18)	172.42(14)
C(3)-Si(1)-C(17)-C(18)	-68.23(15)
C(21)-Si(1)-C(19)-C(20)	-69.0(2)
C(17)-Si(1)-C(19)-C(20)	49.2(2)
C(3)-Si(1)-C(19)-C(20)	169.39(17)
C(19)-Si(1)-C(21)-C(22)	175.55(15)
C(17)-Si(1)-C(21)-C(22)	55.39(17)
C(3)-Si(1)-C(21)-C(22)	-63.86(17)

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "old400"

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 71.2 degrees
Acq. time 3.744 sec
Width 6000.6 Hz
52 repetitions
OBSERVE H1, 399.7271752 MHz
DATA PROCESSING
FT size 65536
Total time 5 min, 4 sec



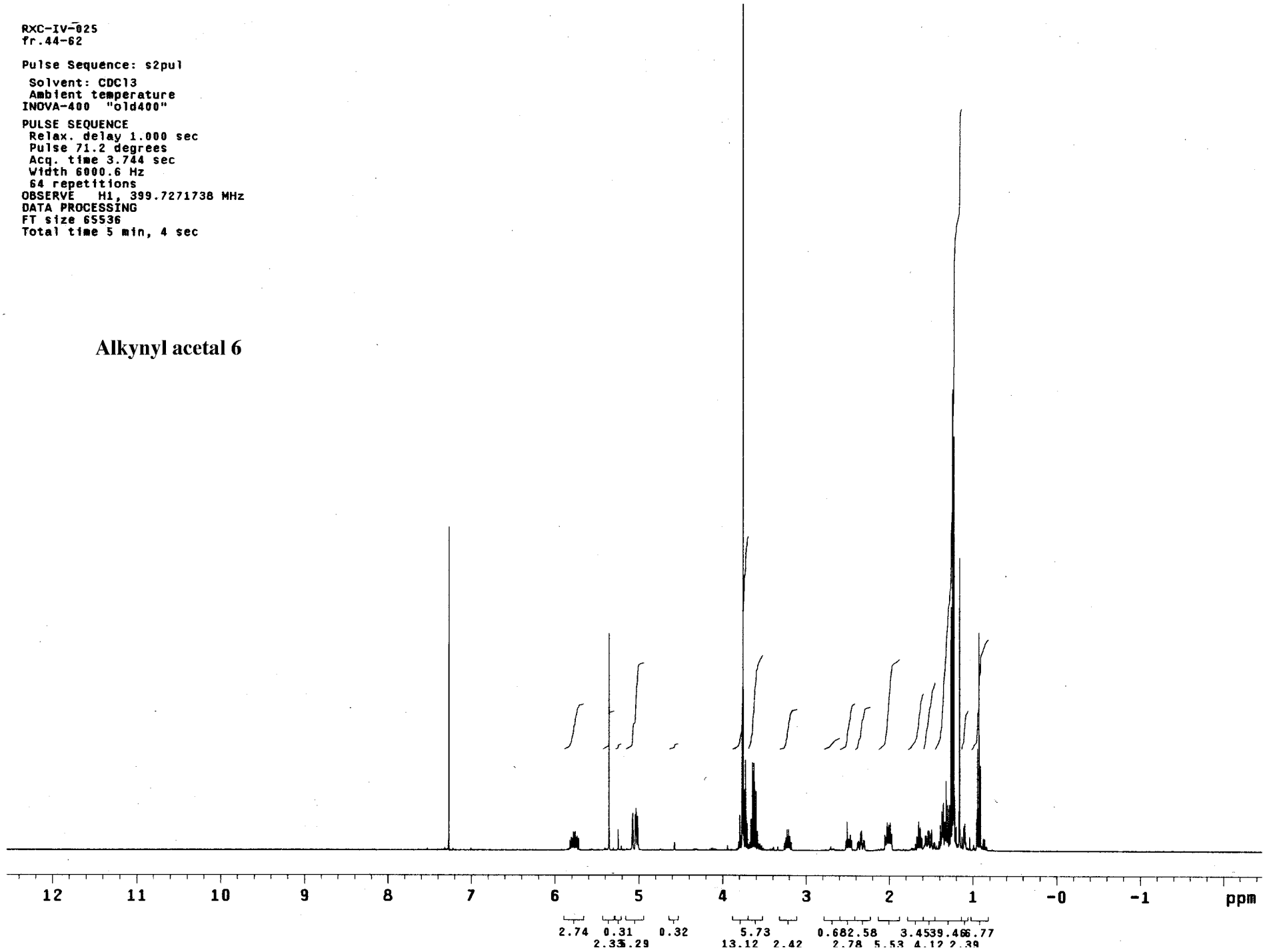
Cyclohexanone 5


RXC-IV-C-020
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "old400"
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 69.2 degrees
Acq. time 0.800 sec
Width 25000.0 Hz
1280 repetitions
OBSERVE C13, 100.5114096 MHz
DECOUPLE H1, 399.7291893 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 5 hr, 1 min, 28 sec
Cyclohexanone 5
207.002
169.647
136.605
117.385
78.019
77.381
67.437
52.233
49.910
41.120
40.626
34.159
30.318
29.369
21.794
200
180
160
140
120
100
80
60
40
20
0
ppm

RXC-IV-025
fr.44-62

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "old400"
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 71.2 degrees
Acq. time 3.744 sec
Width 6000.6 Hz
64 repetitions
OBSERVE H1, 399.7271738 MHz
DATA PROCESSING
FT size 65536
Total time 5 min, 4 sec

Alkynyl acetal 6

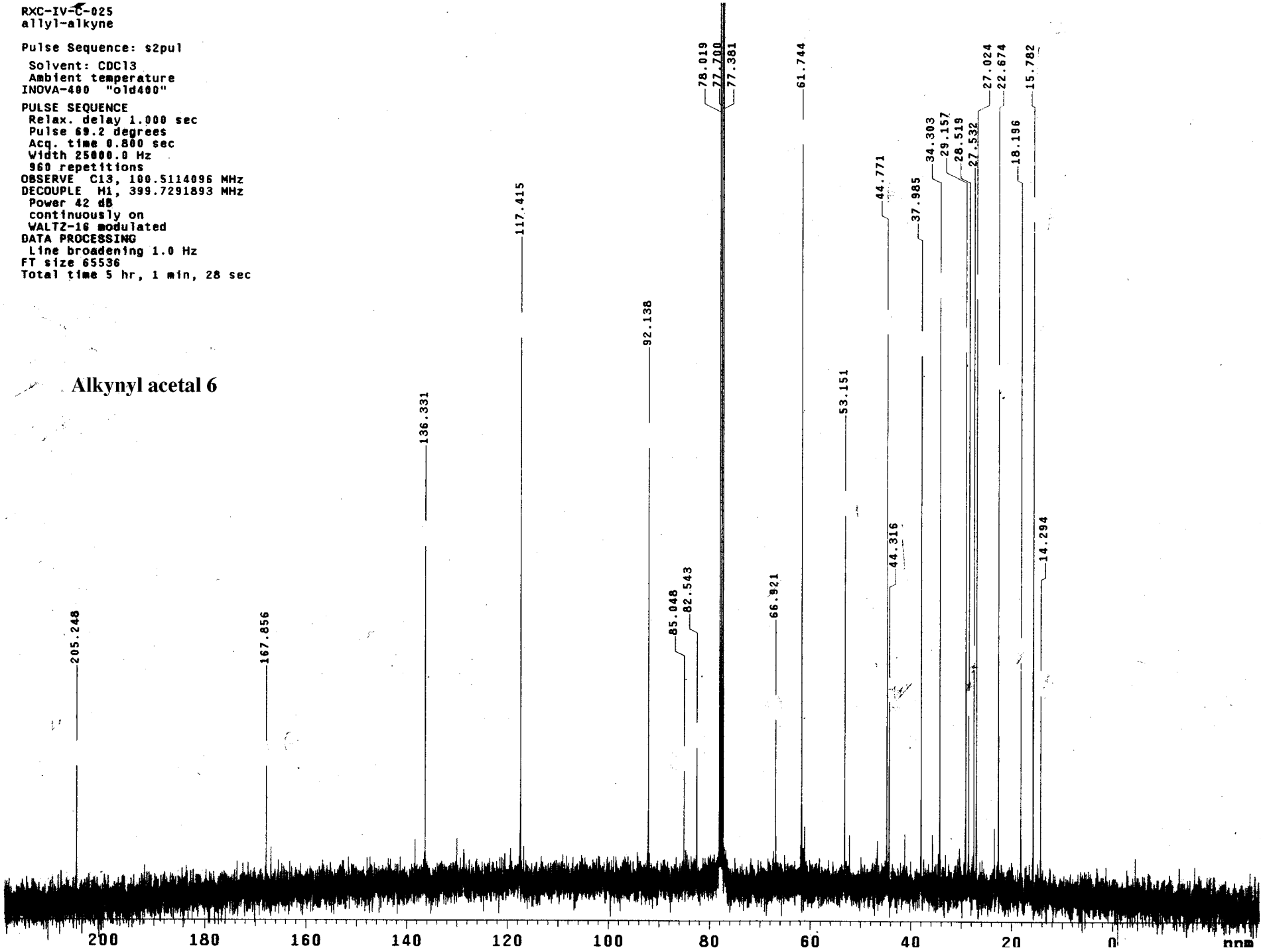


RXC-IV-C-025
allyl-alkyne

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "old400"

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 69.2 degrees
Acq. time 0.860 sec
Width 25000.0 Hz
960 repetitions
OBSERVE C13, 100.5114096 MHz
DECOUPLE H1, 399.7291893 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 5 hr, 1 min, 28 sec

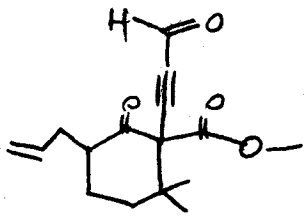
Alkynyl acetal 6



RXC-IV-627
alkyne-aldehyde

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "old400"

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 71.2 degrees
Acq. time 3.744 sec
Width 6000.6 Hz
36 repetitions
OBSERVE H1, 399.7271738 MHz
DATA PROCESSING
FT size 65536
Total time 5 min, 4 sec



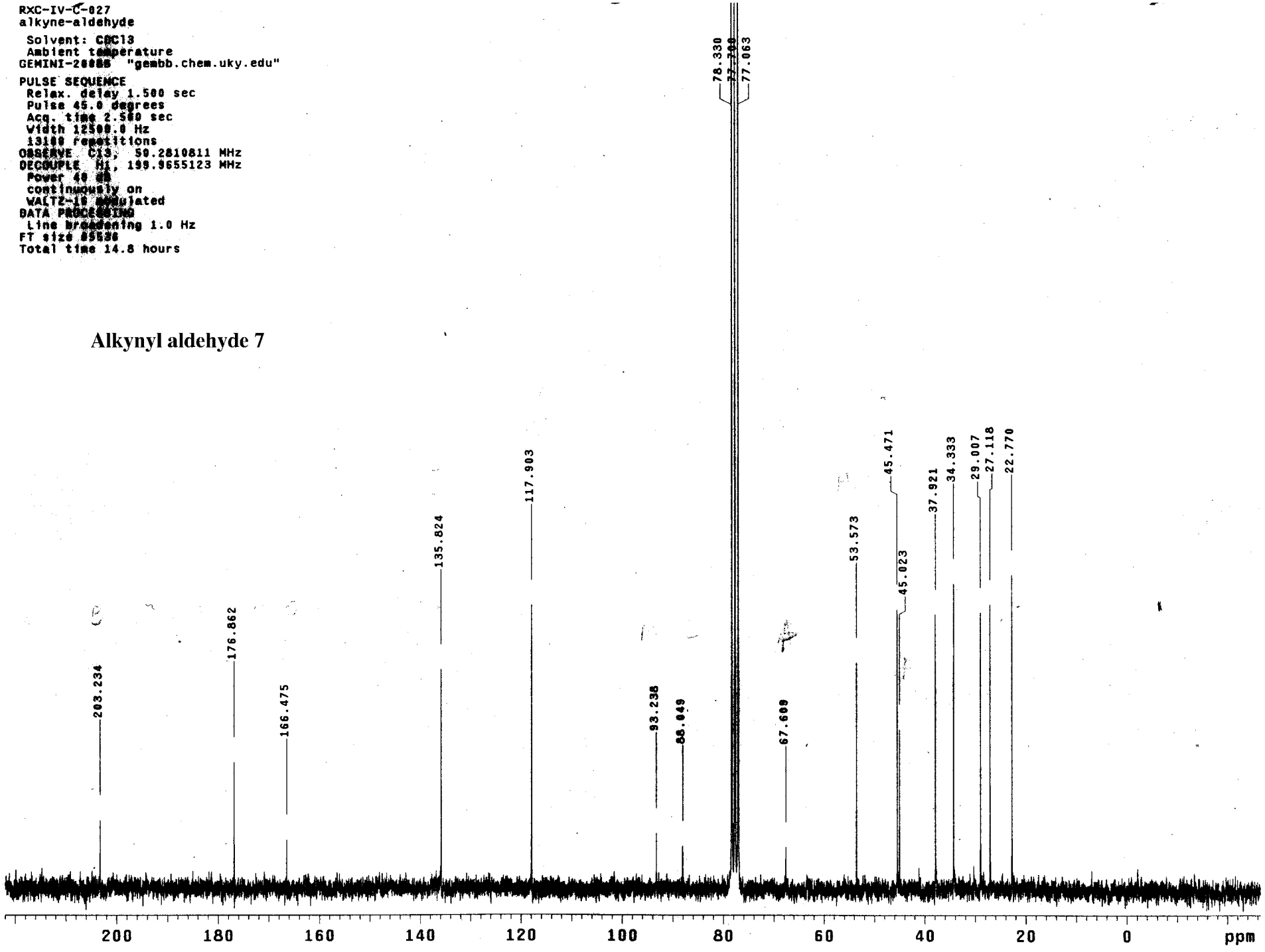
Alkynyl aldehyde 7

RXC-IV-C-027
alkyne-aldehyde

Solvent: CDCl3
Ambient temperature
GEMINI-2000B "gembb.chem.uky.edu"

PULSE SEQUENCE
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 2.560 sec
Width 12500.0 Hz
13100 repetitions
OBSERVE C13, 50.2810811 MHz
DECOUPLE H1, 199.9655123 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 14.8 hours

Alkynyl aldehyde 7



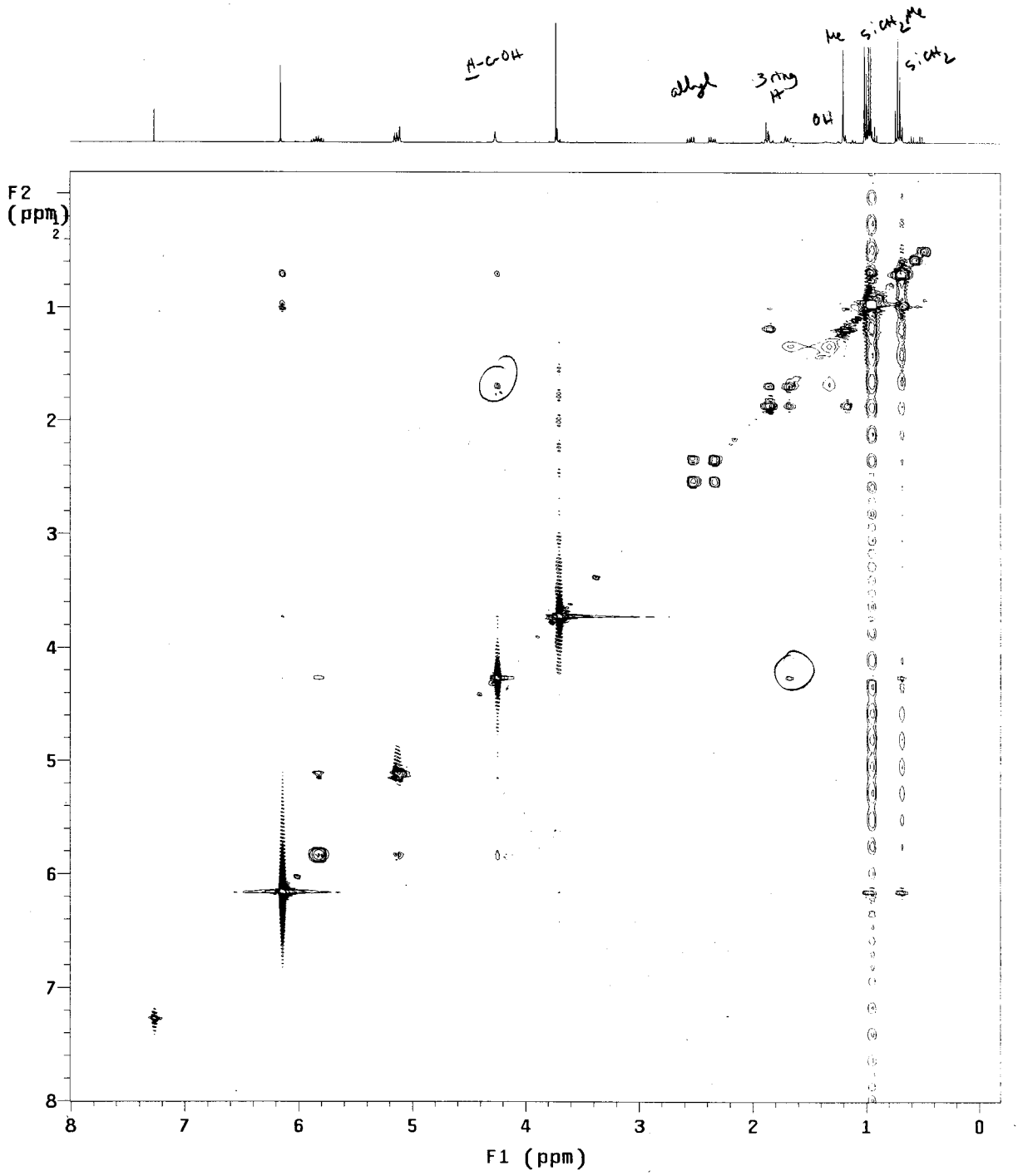


Figure 2. NOESY spectrum of exo alcohol **9b**. The crucial cross-peaks are circled.