

Regioselective Synthesis of the Tricyclic Core of Lateriflorone

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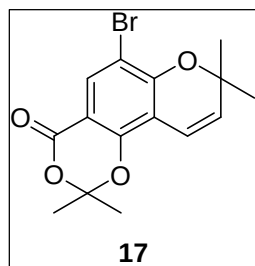
General Techniques

All reagents were commercially obtained (Aldrich, Acros) at highest commercial quality and used without further purification except where noted. Air- and moisture-sensitive liquids and solutions were transferred via syringe or stainless steel cannula. Organic solutions were concentrated by rotary evaporation below 45 °C at approximately 20 mmHg. All non-aqueous reactions were carried out under anhydrous conditions using flame-dried glassware within an argon atmosphere in dry, freshly distilled solvents, unless otherwise noted. Tetrahydrofuran (THF), diethyl ether (Et₂O), dichloromethane (CH₂Cl₂), toluene (PhCH₃) and benzene (PhH) were purified by passage through a bed of activated alumina.¹ *N,N*-diisopropylethylamine (DIPEA), diisopropylamine, pyridine, triethylamine (TEA) and boron trifluoride etherate were distilled from calcium hydride prior to use.² Dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) were distilled from calcium hydride under reduced pressure (20 mmHg) and stored over 4Å molecular sieves until needed. 4-Hydroxysalicylic acid (**12**) was commercially available and used without any additional purification. Yields refer to chromatographically and spectroscopically (¹H NMR, ¹³C NMR) homogeneous materials, unless otherwise stated. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as the visualizing agent and 10% ethanolic phosphomolybdic acid (PMA) or *p*-anisaldehyde solution and heat as developing agents. E. Merck silica gel (60, particle size 0.040-0.063 mm) was used for flash chromatography. Preparative thin-layer chromatography separations were carried out on 0.25 or 0.50 mm E. Merck silica gel plates (60F-254). NMR spectra were recorded on Varian Mercury 300, 400 and/or Unity 500 MHz instruments and calibrated using the residual undeuterated solvent as an internal reference. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad. IR spectra were recorded on a Nicolet 320 Avatar FT-IR spectrometer and values are reported in cm⁻¹ units. Optical rotations were recorded on a Jasco P-1010 polarimeter and values are reported as follows: [α]_D^T (c: g/100ml, solvent). High resolution mass spectra (HRMS) were recorded on a VG 7070 HS mass spectrometer under chemical ionization (CI) conditions or on a VG ZAB-ZSE mass spectrometer under fast atom bombardment (FAB) conditions. X-ray data were recorded on a Bruker SMART APEX 3kW Sealed Tube X-ray diffraction system.

¹ Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518-1520.

² Perrin, D. D.; Armarego, W. L. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: Oxford, **1988**.

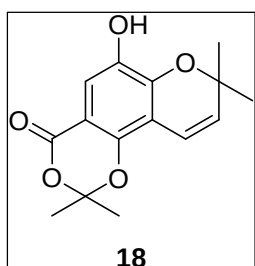
Compound Specific Data



10-Bromo-2,2,6,6-tetramethyl-2H-1,5,7-trioxa-phenanthren-8-one (17)

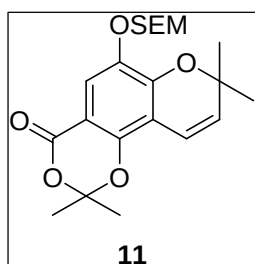
R_f = 0.66 (Et₂O/Hexane = 1/1); IR (film), $\nu_{\max}$: 2981, 2921, 1737, 1601, 1574, 1442, 1375, 1303, 1290, 1204, 1171, 1125; ¹H NMR (400 MHz, CDCl₃) δ : 7.96 (s, 1H), 6.50 (d, J = 10.0 Hz, 1H), 5.67 (d, J = 10.0 Hz, 1H), 1.73 (s, 6H), 1.51 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ : 159.8, 155.7, 150.8, 132.5, 130.1, 114.7, 110.6, 106.9, 106.6, 104.4, 79.3, 28.4, 26.0;

HRMS calcd. for C₁₅H₁₅O₄Br (M+Na⁺) 361.0046, found 361.0056.



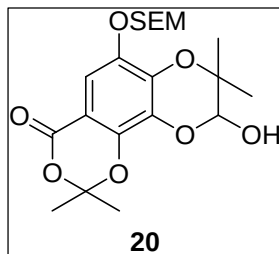
10-Hydroxy-2,2,6,6-tetramethyl-2H-1,5,7-trioxa-phenanthren-8-one (18)

R_f = 0.60 (EtOAc/Hexane = 1/1); IR (film), $\nu_{\max}$: 3392, 2980, 1721, 1641, 1613, 1469, 1395, 1379, 1318, 1298, 1267, 1202, 1124, 1053, 996, 883; ¹H NMR (400 MHz, CDCl₃) δ : 7.33 (s, 1H), 6.51 (d, J = 10.0 Hz, 1H), 5.64 (d, J = 10.0 Hz, 1H), 5.38 (s, broad, 1H), 1.71 (s, 6H), 1.50 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ : 161.0, 146.3, 145.9, 140.1, 129.6, 115.2, 113.7, 109.6, 106.3, 105.5, 79.0, 28.2, 25.7; HRMS calcd. for C₁₅H₁₆O₅ (M+H⁺) 277.107, found 277.1078.



2,2,6,6-Tetramethyl-10-(2-trimethylsilanyl-ethoxymethoxy)-2H-1,5,7-trioxa-phenanthren-8-one (11)

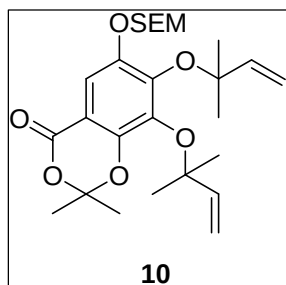
R_f = 0.62 (EtOAc/Hexane = 1/3); IR (film), $\nu_{\max}$: 2953, 1738, 1472, 1391, 1377, 1306, 1292, 1202, 1052, 885, 836; ¹H NMR (400 MHz, CDCl₃) δ : 7.52 (s, 1H), 6.51 (d, J = 10.0 Hz, 1H), 5.64 (d, J = 10.0 Hz, 1H), 5.19 (s, 2H), 3.76-3.82 (m, 2H), 1.71 (s, 6H), 1.49 (s, 6H), 0.92-0.99 (m, 2H), -0.01 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ : 161.2, 150.9, 147.9, 141.4, 130.0, 117.7, 115.5, 110.8, 106.6, 105.1, 94.7, 78.3, 66.7, 28.4, 26.0, 18.2, -1.2; HRMS calcd. for C₂₁H₃₀O₆Si₁ (M+Na⁺) 429.1704, found 429.1706.



3-Hydroxy-2,2,6,6-tetramethyl-10-(2-trimethylsilanyl-ethoxymethoxy)-2,3-dihydro-1,4,5,7-tetraoxa-phenanthren-8-one (20)

R_f = 0.24 (EtOAc/Hexane = 1/3); IR (film), $\nu_{\max}$: 3389, 2951, 1736, 1617, 1485, 1378, 1320, 1206, 1060, 1022, 858, 837; ¹H NMR (400 MHz, CDCl₃) δ : 7.36 (s, 1H), 5.20-5.24 (m, 3H), 3.77-3.82 (m, 2H), 3.58 (s, broad, 1H), 1.76 (s, 3H), 1.75 (s, 3H), 1.48 (s, 3H), 1.38 (s, 3H), 0.94-0.99 (m, 2H), 0.01 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ : 160.8, 141.9, 141.6, 140.2, 129.1, 109.3,

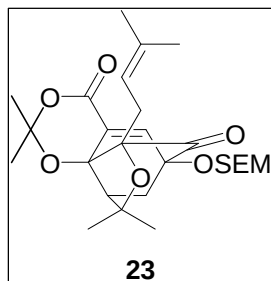
107.1, 105.6, 94.8, 93.7, 76.1, 67.0, 26.1, 26.0, 23.3, 22.4, 18.4, -1.0; HRMS calcd. for $C_{20}H_{30}O_8Si_1$ ($M+Na^+$) 449.1602, found 449.1621.



7,8-Bis-(1,1-dimethyl-allyloxy)-2,2-dimethyl-6-(2-trimethylsilanylethoxymethoxy)-benzo[1,3]dioxin-4-one (10)

R_f = 0.65 (Et_2O /Hexane = 1/1); IR (film), ν_{max} : 3087, 2982, 2952, 1741, 1456, 1346, 1287, 1123, 1066, 836; 1H NMR (400 MHz, $CDCl_3$) δ : 7.46 (s, 1H), 6.19 (dd, J = 10.8, 17.6 Hz, 1H), 6.18 (dd, J = 10.8, 17.4 Hz, 1H), 5.14 (s, 2H), 5.07 (d, J = 17.6 Hz, 1H), 5.06 (d, J = 17.6 Hz, 1H), 4.98 (dd, J = 0.8, 10.8 Hz, 1H), 4.97 (dd, J = 0.8, 10.8 Hz, 1H), 3.73-3.77

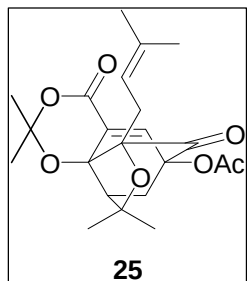
(m, 2H), 1.71 (s, 6H), 1.47 (s, 6H), 1.45 (s, 6H), 0.94-0.98 (m, 2H), -0.01 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 160.9, 149.0, 148.3, 147.1, 143.3, 143.0, 140.2, 112.9, 112.8, 110.7, 108.5, 106.2, 94.1, 85.3, 84.4, 77.2, 66.6, 27.0, 26.9, 25.8, 18.1, -1.2; HRMS calcd. for $C_{26}H_{40}O_7Si_1$ ($M+Na^+$) 515.2435, found 515.2413.



SEM Protected Claisen/Diels-Alder Adduct (23)

R_f = 0.63 (Et_2O /Hexane = 1/1); IR (film), ν_{max} : 2953, 1741, 1636, 1382, 1283, 1071, 1048, 859, 836; 1H NMR (400 MHz, $CDCl_3$) δ : 7.57 (s, 1H), 5.02 (d, J = 8.0 Hz, 1H), 4.94 (d, J = 8.0 Hz, 1H), 4.34-4.42 (m, 1H), 3.66-3.82 (m, 2H), 2.60-2.76 (m, 2H), 2.55 (d, J = 10.0 Hz, 1H), 2.43 (d, J = 13.2 Hz, 1H), 1.79 (dd, J = 10.0, 13.2 Hz, 1H), 1.68 (s, 3H), 1.67 (s, 3H), 1.60 (s, 3H), 1.53 (s, 3H), 1.50 (s, 3H), 1.25 (s, 3H), 0.92-0.97 (m, 2H),

0.02 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 200.7, 158.7, 140.3, 135.6, 125.5, 117.5, 104.8, 92.5, 84.2, 83.9, 83.4, 83.1, 66.1, 49.0, 32.6, 30.2, 29.0, 28.6, 28.4, 27.9, 25.7, 18.3, -1.2; HRMS calcd. for $C_{26}H_{40}O_7Si_1$ ($M+Na^+$) 515.2439, found 515.2439.

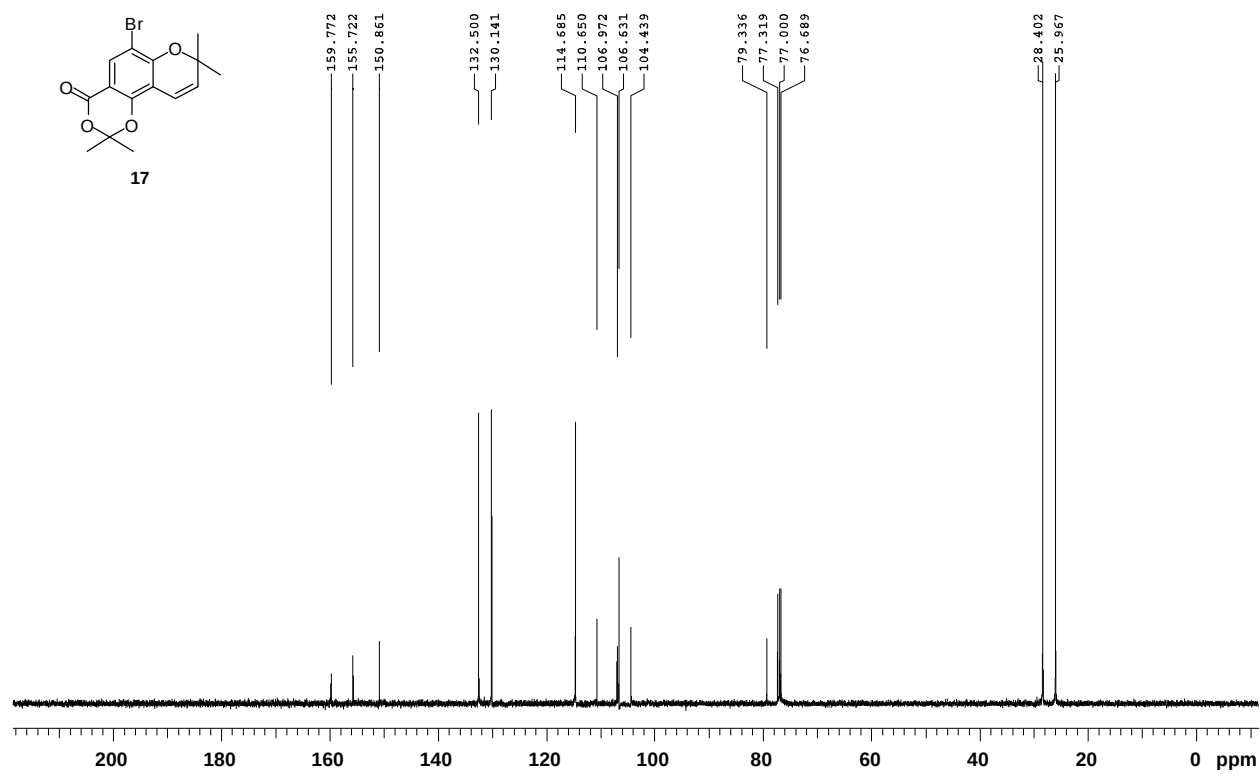
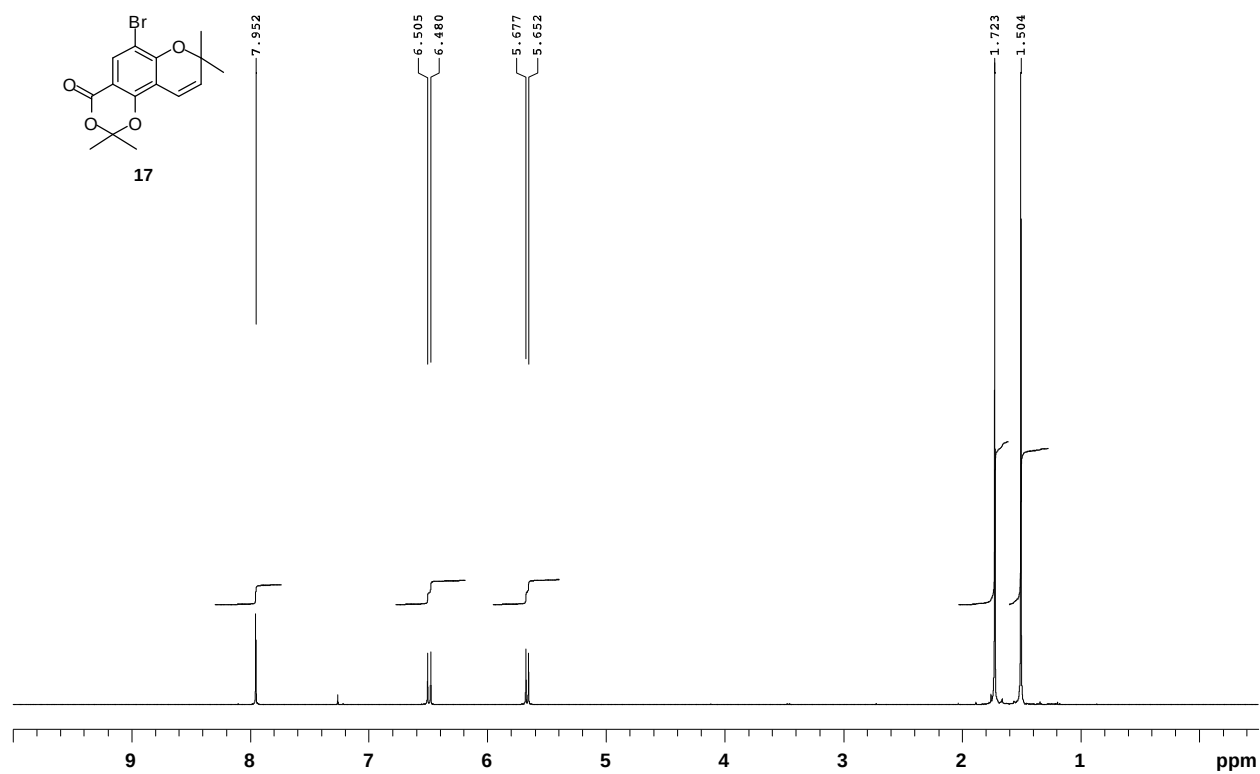


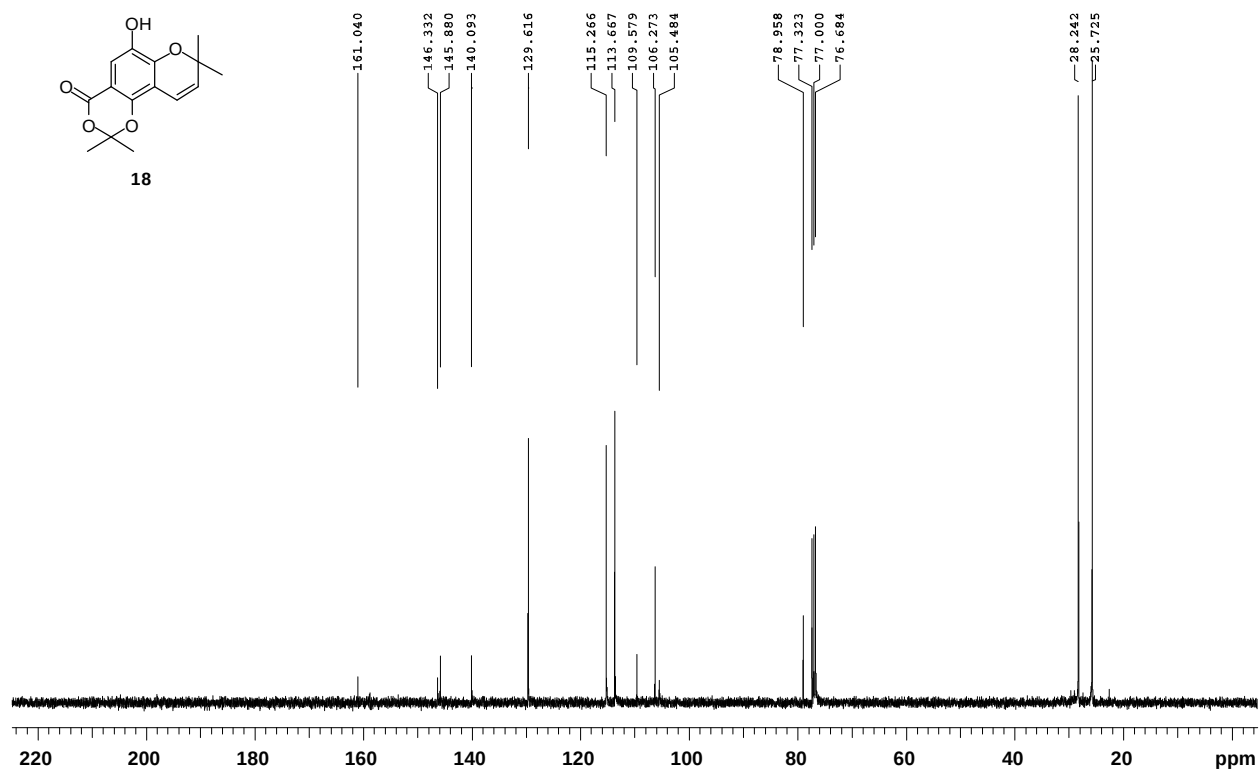
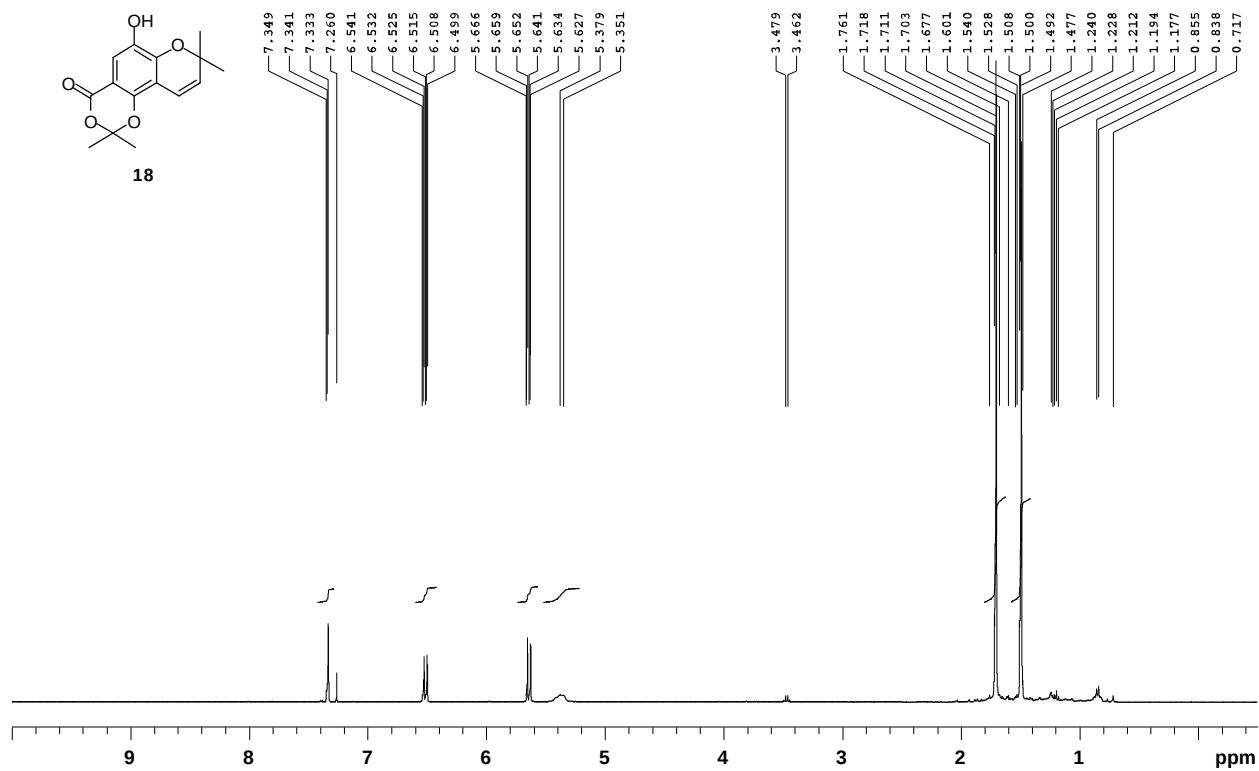
Acetyl Protected Claisen/Diels-Alder Adduct (25)

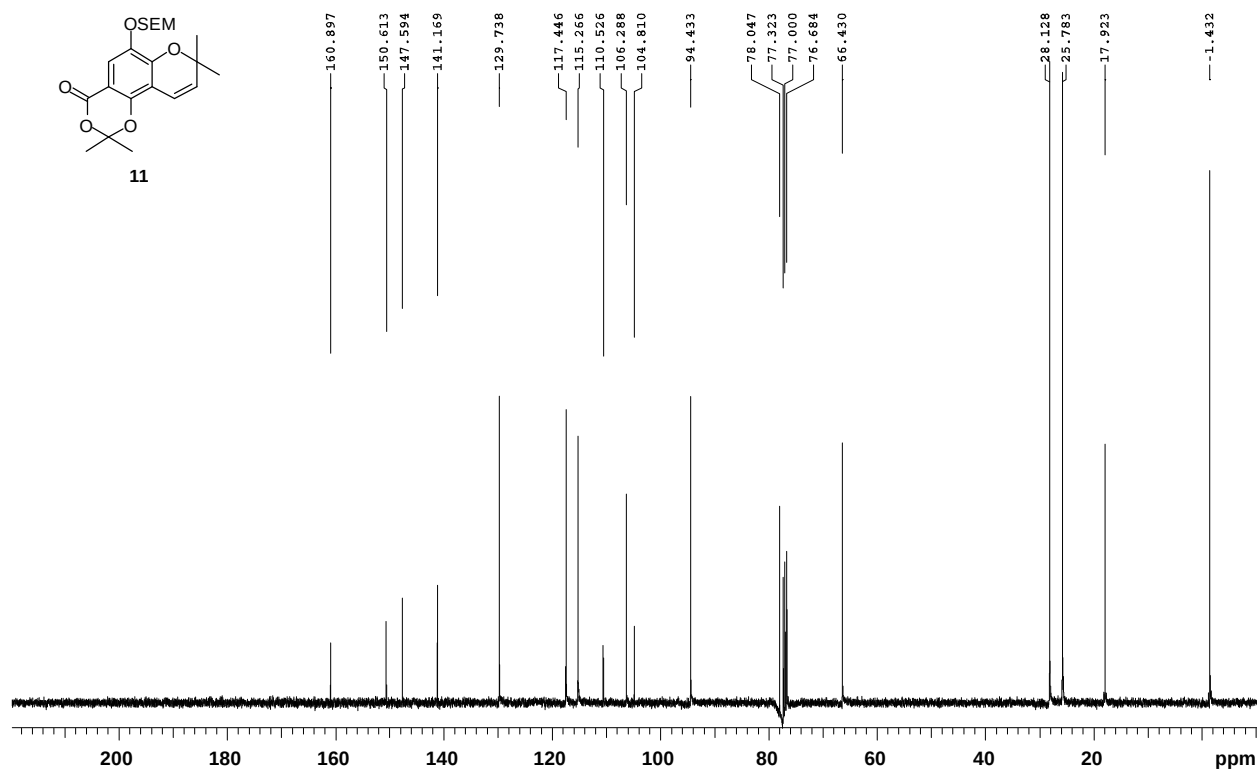
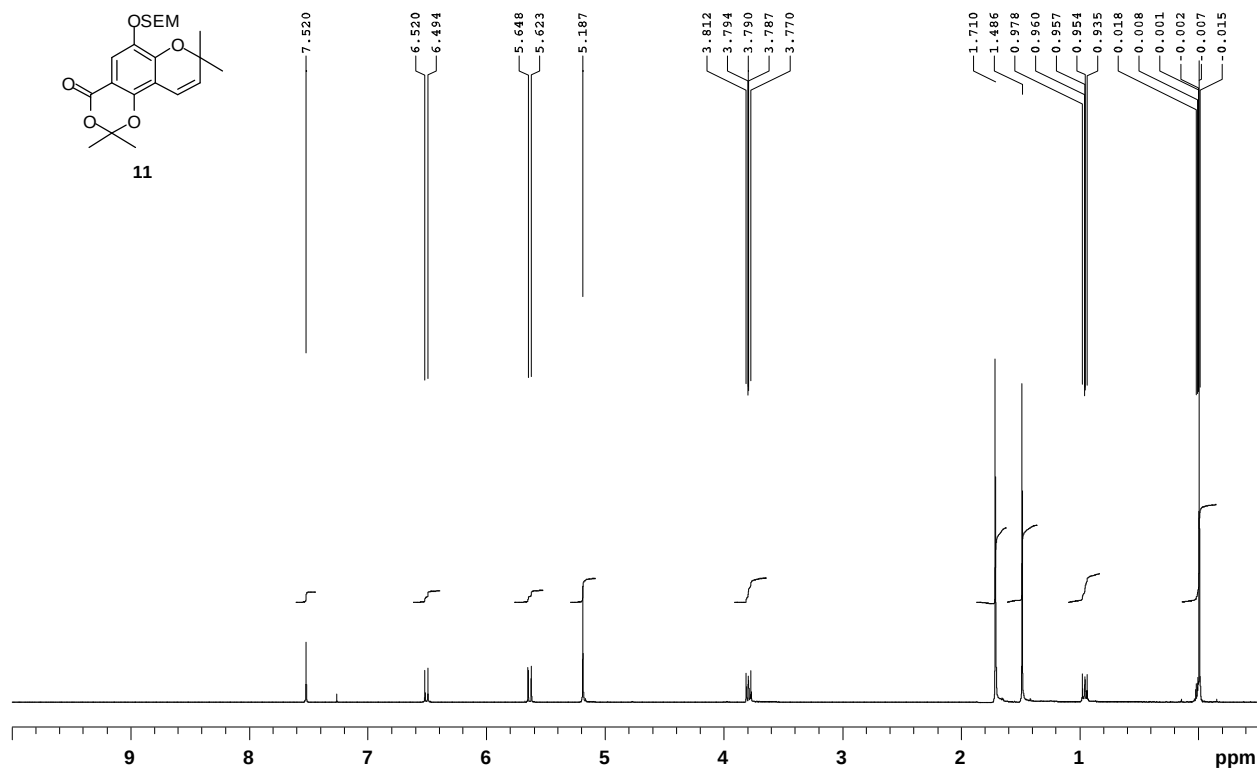
R_f = 0.43 (Et_2O /Hexane = 3/1); IR (film), ν_{max} : 2987, 2930, 1743, 1640, 1441, 1380, 1285, 1227, 1048, 931, 880, 735; 1H NMR (400 MHz, $CDCl_3$) δ : 7.46 (s, 1H), 2.75 (dd, J = 10.6, 13.8 Hz, 1H), 2.58-2.64 (m, 1H), 2.54-2.58 (m, 2H), 2.22 (s, 3H), 1.83 (dd, J = 10.0, 12.8 Hz, 2H), 1.70 (s, 3H), 1.68 (s, 3H), 1.62 (s, 3H), 1.56 (s, 3H), 1.52 (s, 3H), 1.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 196.4, 168.7, 158.6, 139.4, 135.7, 124.0, 117.2, 104.9,

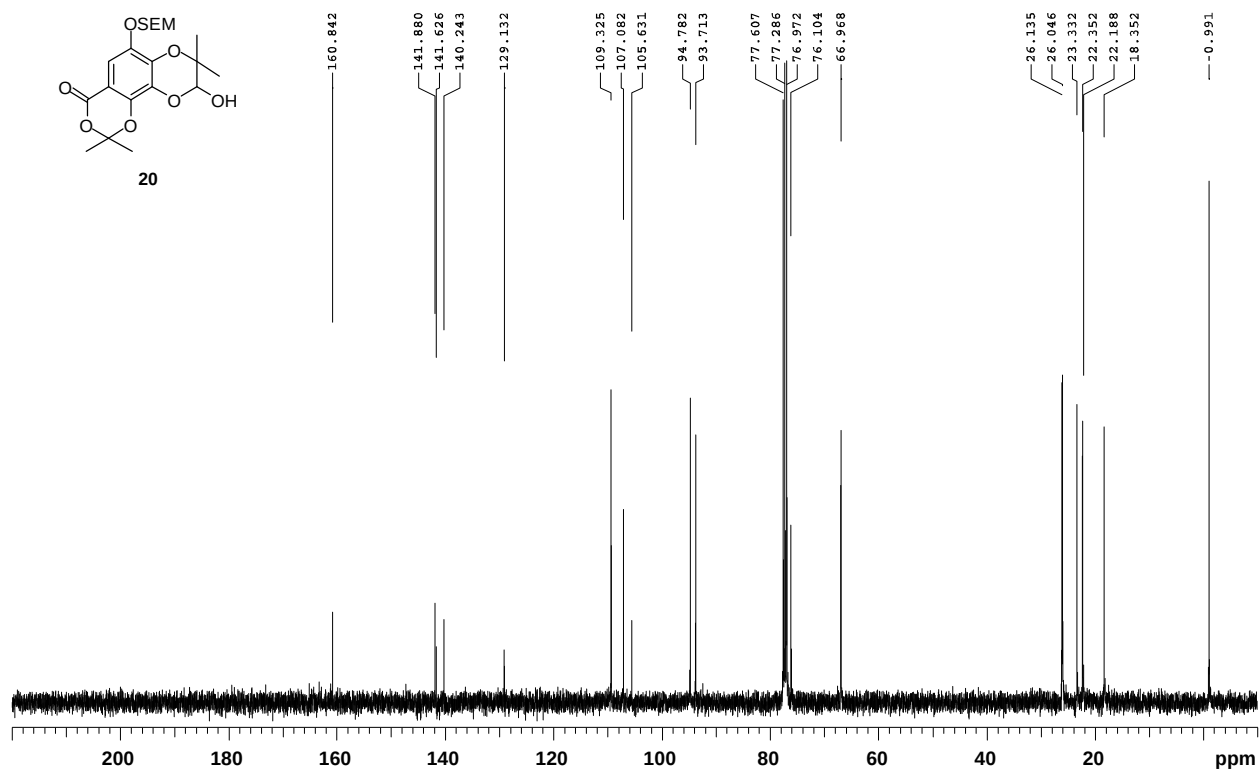
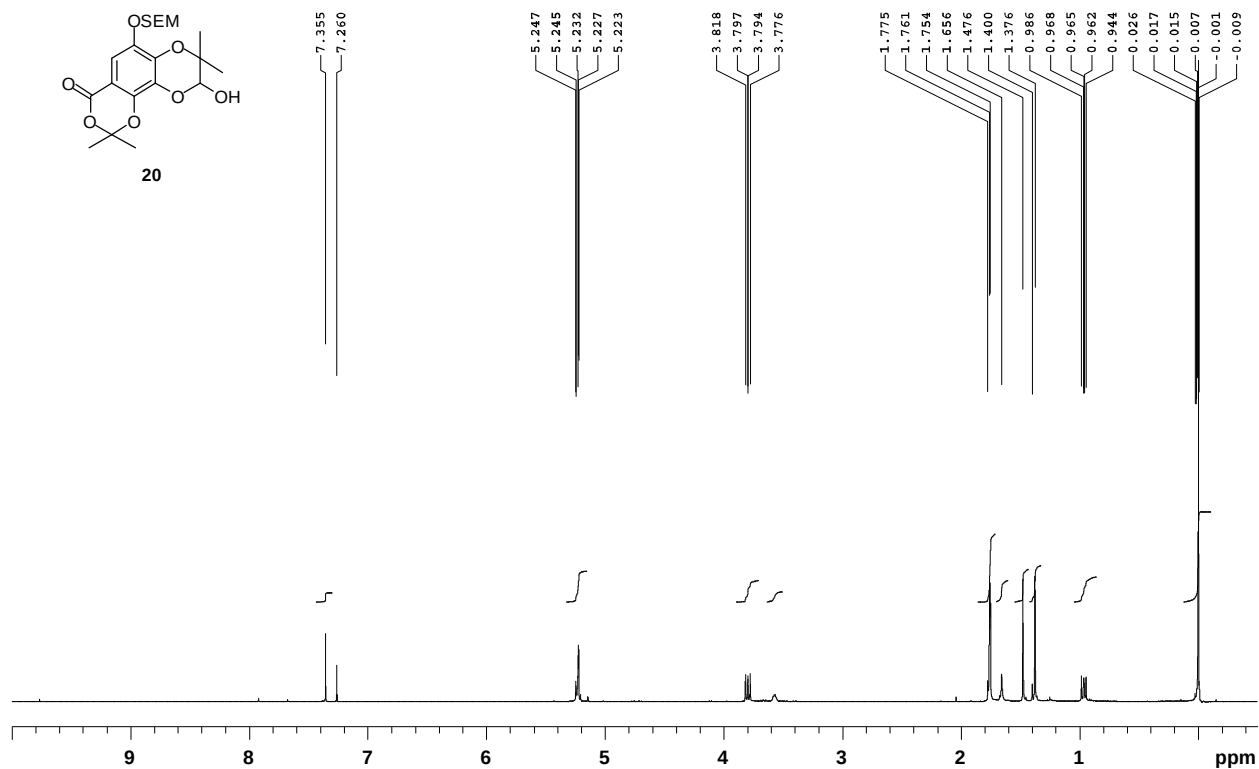
84.3, 83.4, 83.2, 82.8, 77.2, 48.3, 31.4, 30.4, 30.2, 29.0, 28.7, 28.0, 25.7, 21.1, 18.2; HRMS calcd. for $C_{22}H_{28}O_7$ ($M+Na^+$) 427.1727, found 427.1727.

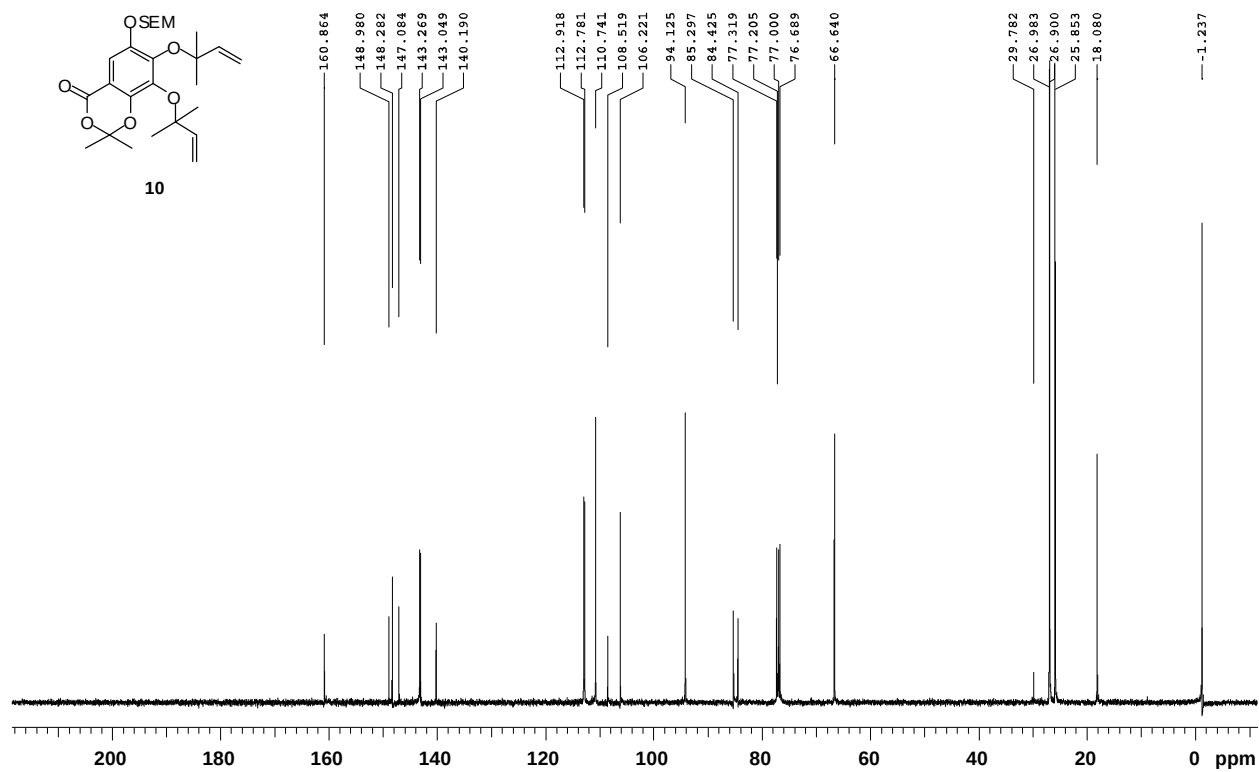
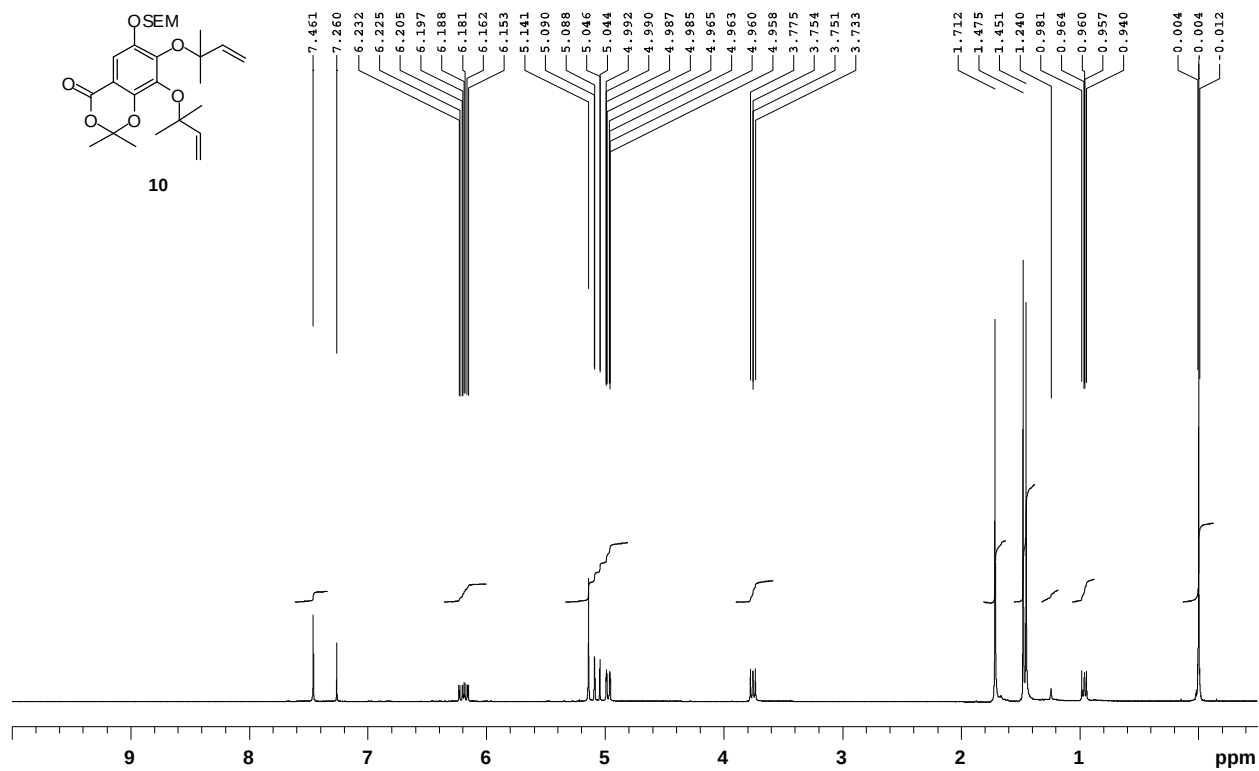
NMR Spectra and X-Ray Data

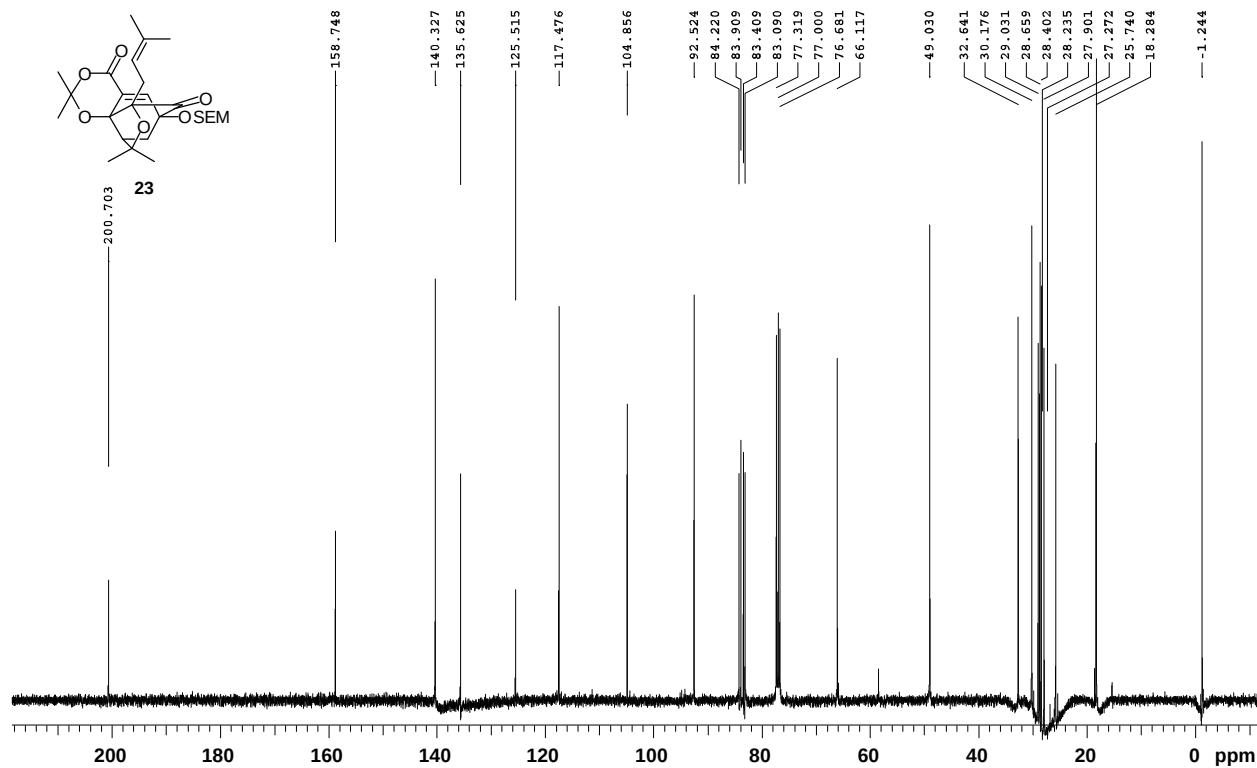
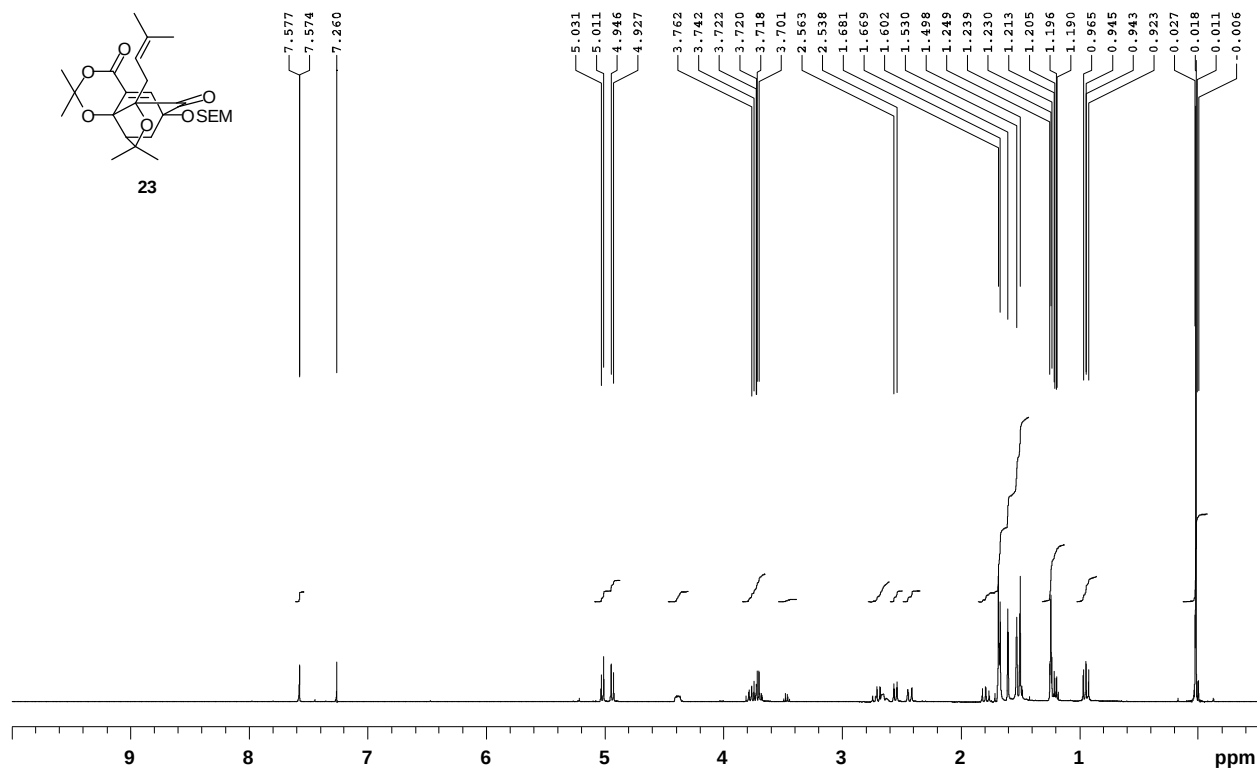












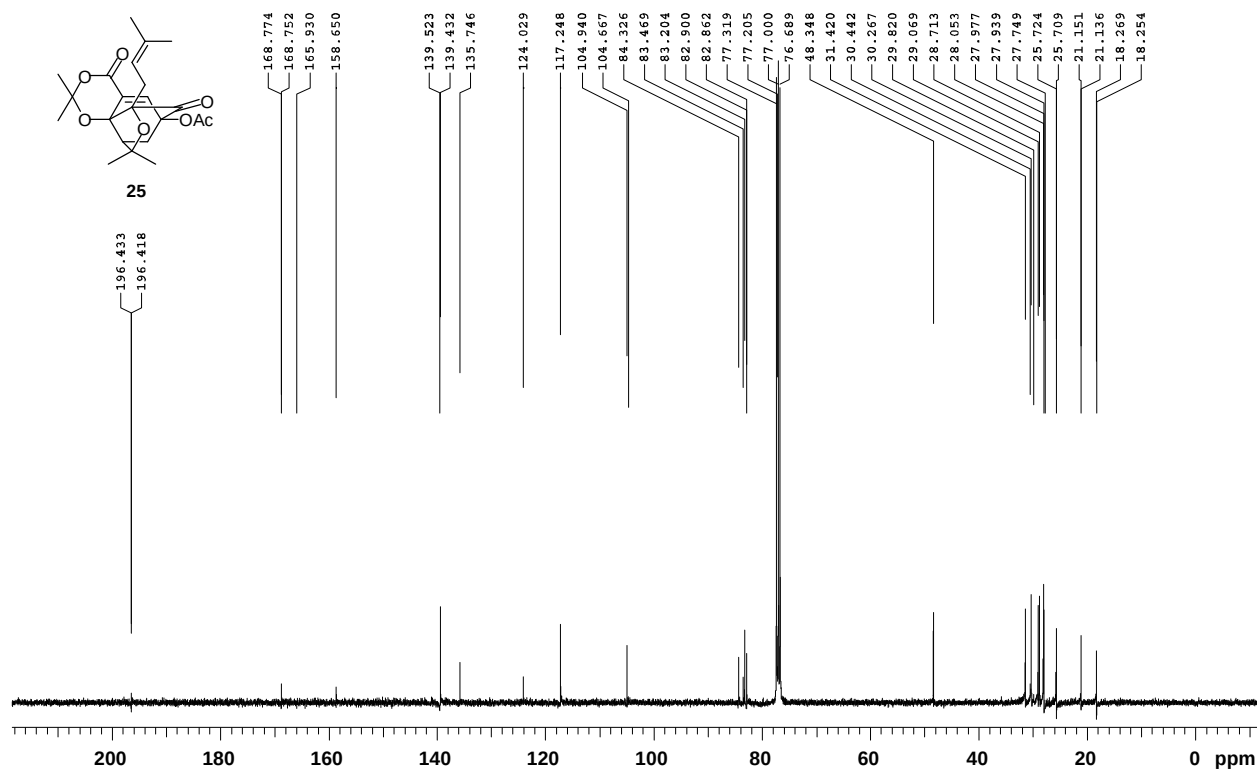
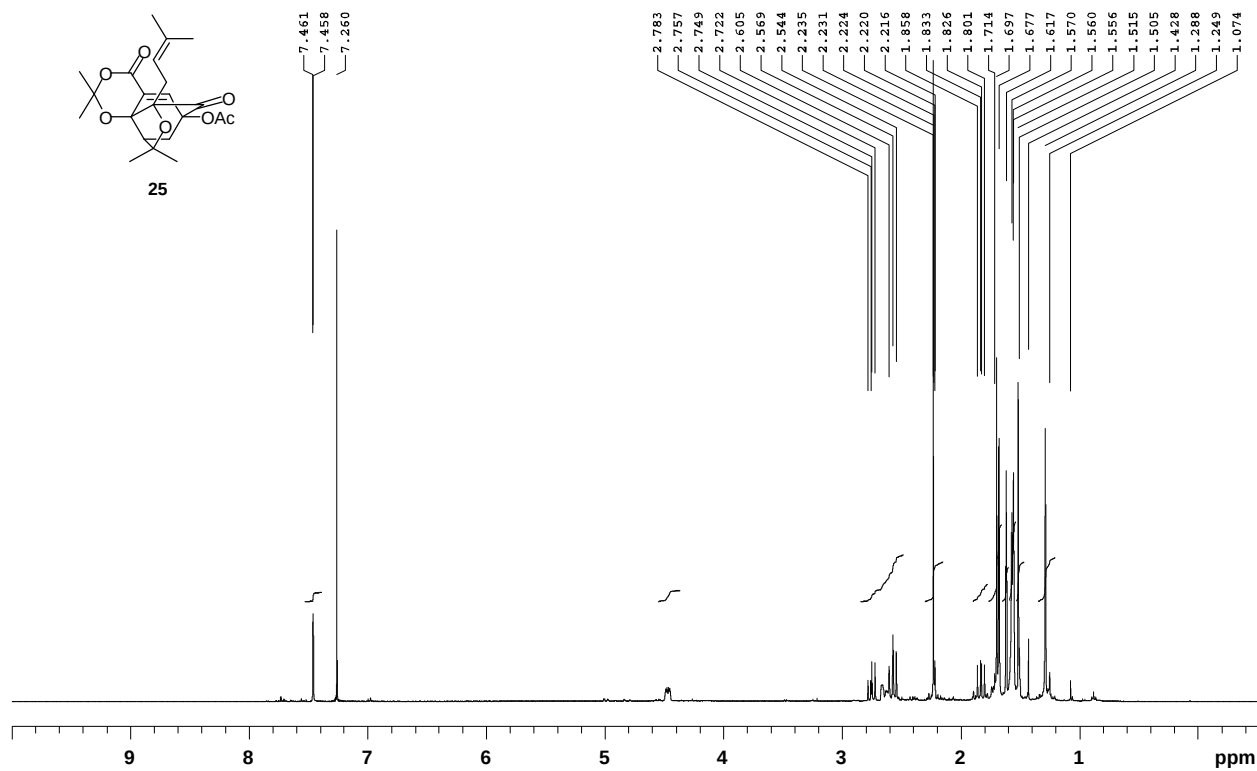


Table 1. Crystal data and structure refinement for compound **25**.

Identification code	sad	
Empirical formula	C ₂₂ H ₂₈ O ₇	
Formula weight	404.44	
Temperature	228(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 15.5351(9) Å	α = 90°.
	b = 13.6848(8) Å	β = 95.0490(10)°.
	c = 19.2532(11) Å	γ = 90°.
Volume	4077.2(4) Å ³	
Z	8	
Density (calculated)	1.318 Mg/m ³	
Absorption coefficient	0.098 mm ⁻¹	
F(000)	1728	
Crystal size	0.40 x 0.30 x 0.07 mm ³	
Theta range for data collection	1.32 to 22.50°.	
Index ranges	-16 ≤ h ≤ 16, -14 ≤ k ≤ 14, -20 ≤ l ≤ 20	
Reflections collected	21713	
Independent reflections	5332 [R(int) = 0.0252]	
Completeness to theta = 22.50°	99.9 %	
Absorption correction	None	
Max. and min. transmission	0.9932 and 0.9620	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5332 / 0 / 525	
Goodness-of-fit on F ²	1.068	
Final R indices [I > 2σ(I)]	R1 = 0.0394, wR2 = 0.1025	
R indices (all data)	R1 = 0.0455, wR2 = 0.1063	
Largest diff. peak and hole	0.211 and -0.162 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for compound **25**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
O(1)	-1758(1)	-137(1)	-1432(1)	54(1)
O(2)	-2936(1)	-1487(1)	-1187(1)	43(1)
O(3)	-4092(1)	-2425(1)	-1505(1)	57(1)
O(4)	-2791(1)	1559(1)	-2011(1)	42(1)
O(5)	-3640(1)	983(1)	-3370(1)	41(1)
O(6)	-3790(1)	-302(1)	-4179(1)	49(1)
O(7)	-3348(1)	-1795(1)	-3897(1)	63(1)
C(1)	-3167(1)	-837(2)	-1753(1)	38(1)
C(2)	-4005(1)	-259(2)	-1671(1)	43(1)
C(3)	-4077(1)	615(2)	-2172(1)	39(1)
C(4)	-3489(1)	384(2)	-2771(1)	36(1)
C(5)	-3443(1)	-677(2)	-2970(1)	37(1)
C(6)	-3250(1)	-1299(2)	-2456(1)	40(1)
C(7)	-2421(1)	-109(2)	-1801(1)	39(1)
C(8)	-2620(1)	677(1)	-2372(1)	37(1)
C(9)	-3523(2)	-986(2)	-3707(1)	45(1)
C(10)	-4194(2)	582(2)	-3922(1)	47(1)
C(11)	-4211(2)	1312(2)	-4504(1)	62(1)
C(12)	-5078(2)	316(2)	-3725(1)	56(1)
C(13)	-3702(1)	1593(2)	-1875(1)	41(1)
C(14)	-4113(2)	2470(2)	-2256(1)	58(1)
C(15)	-3731(2)	1737(2)	-1094(1)	57(1)
C(16)	-3453(2)	-2275(2)	-1118(1)	44(1)
C(17)	-3126(2)	-2902(2)	-529(1)	54(1)
C(18)	-1860(1)	858(2)	-2804(1)	41(1)
C(19)	-1583(1)	-24(2)	-3188(1)	40(1)
C(20)	-1525(1)	-129(2)	-3866(1)	44(1)
C(21)	-1257(2)	-1083(2)	-4162(1)	57(1)
C(22)	-1724(2)	653(2)	-4399(1)	66(1)
O(1A)	2952(1)	5137(1)	1402(1)	53(1)
O(2A)	1746(1)	6517(1)	1162(1)	43(1)

O(3A)	701(1)	7515(1)	1484(1)	56(1)
O(4A)	2017(1)	3481(1)	2009(1)	42(1)
O(5A)	1537(1)	4108(1)	3390(1)	39(1)
O(6A)	1674(1)	5406(1)	4186(1)	46(1)
O(7A)	2102(1)	6870(1)	3878(1)	59(1)
C(1A)	1646(1)	5889(2)	1744(1)	37(1)
C(2A)	772(1)	5344(2)	1695(1)	42(1)
C(3A)	810(1)	4479(2)	2203(1)	38(1)
C(4A)	1557(1)	4695(2)	2780(1)	36(1)
C(5A)	1692(1)	5754(2)	2966(1)	36(1)
C(6A)	1766(1)	6365(2)	2441(1)	38(1)
C(7A)	2383(1)	5135(2)	1782(1)	37(1)
C(8A)	2310(1)	4358(1)	2361(1)	36(1)
C(9A)	1837(2)	6071(2)	3702(1)	43(1)
C(10A)	1161(1)	4550(2)	3954(1)	43(1)
C(11A)	1268(2)	3834(2)	4546(1)	55(1)
C(12A)	238(2)	4866(2)	3790(1)	53(1)
C(13A)	1075(1)	3486(2)	1900(1)	42(1)
C(14A)	740(2)	2626(2)	2295(1)	59(1)
C(15A)	838(2)	3343(2)	1124(1)	59(1)
C(16A)	1227(2)	7321(2)	1087(1)	44(1)
C(17A)	1398(2)	7893(2)	460(1)	57(1)
C(18A)	3166(1)	4138(2)	2771(1)	40(1)
C(19A)	3557(1)	4988(2)	3171(1)	41(1)
C(20A)	3775(1)	5052(2)	3851(1)	45(1)
C(21A)	4120(2)	5986(2)	4171(1)	60(1)
C(22A)	3681(2)	4241(2)	4359(1)	64(1)

Table 3. Bond lengths [Å] and angles [°] for compound 25.

O(1)-C(7)	1.198(3)
O(2)-C(16)	1.357(3)
O(2)-C(1)	1.428(2)
O(3)-C(16)	1.205(3)
O(4)-C(8)	1.430(2)
O(4)-C(13)	1.461(3)
O(5)-C(10)	1.417(3)
O(5)-C(4)	1.418(2)
O(6)-C(9)	1.345(3)
O(6)-C(10)	1.468(3)
O(7)-C(9)	1.205(3)
C(1)-C(6)	1.489(3)
C(1)-C(7)	1.538(3)
C(1)-C(2)	1.544(3)
C(2)-C(3)	1.535(3)
C(3)-C(13)	1.548(3)
C(3)-C(4)	1.565(3)
C(4)-C(5)	1.504(3)
C(4)-C(8)	1.546(3)
C(5)-C(6)	1.320(3)
C(5)-C(9)	1.476(3)
C(7)-C(8)	1.549(3)
C(8)-C(18)	1.523(3)
C(10)-C(11)	1.500(3)
C(10)-C(12)	1.502(3)
C(13)-C(14)	1.517(3)
C(13)-C(15)	1.521(3)
C(16)-C(17)	1.476(3)
C(18)-C(19)	1.499(3)
C(19)-C(20)	1.323(3)
C(20)-C(22)	1.497(3)
C(20)-C(21)	1.498(3)
O(1A)-C(7A)	1.197(2)
O(2A)-C(16A)	1.363(3)

O(2A)-C(1A)	1.432(2)
O(3A)-C(16A)	1.196(3)
O(4A)-C(8A)	1.432(2)
O(4A)-C(13A)	1.459(3)
O(5A)-C(10A)	1.414(2)
O(5A)-C(4A)	1.424(2)
O(6A)-C(9A)	1.342(3)
O(6A)-C(10A)	1.465(3)
O(7A)-C(9A)	1.205(3)
C(1A)-C(6A)	1.488(3)
C(1A)-C(7A)	1.538(3)
C(1A)-C(2A)	1.544(3)
C(2A)-C(3A)	1.533(3)
C(3A)-C(13A)	1.549(3)
C(3A)-C(4A)	1.563(3)
C(4A)-C(5A)	1.504(3)
C(4A)-C(8A)	1.549(3)
C(5A)-C(6A)	1.325(3)
C(5A)-C(9A)	1.481(3)
C(7A)-C(8A)	1.552(3)
C(8A)-C(18A)	1.515(3)
C(10A)-C(11A)	1.502(3)
C(10A)-C(12A)	1.505(3)
C(13A)-C(15A)	1.519(3)
C(13A)-C(14A)	1.518(3)
C(16A)-C(17A)	1.483(3)
C(18A)-C(19A)	1.495(3)
C(19A)-C(20A)	1.326(3)
C(20A)-C(22A)	1.494(3)
C(20A)-C(21A)	1.498(3)
C(16)-O(2)-C(1)	117.23(16)
C(8)-O(4)-C(13)	109.77(15)
C(10)-O(5)-C(4)	115.61(15)
C(9)-O(6)-C(10)	117.49(16)
O(2)-C(1)-C(6)	115.17(17)
O(2)-C(1)-C(7)	108.07(16)

C(6)-C(1)-C(7)	103.07(16)
O(2)-C(1)-C(2)	113.51(16)
C(6)-C(1)-C(2)	107.70(17)
C(7)-C(1)-C(2)	108.68(17)
C(3)-C(2)-C(1)	110.52(17)
C(2)-C(3)-C(13)	115.94(17)
C(2)-C(3)-C(4)	106.89(16)
C(13)-C(3)-C(4)	102.85(16)
O(5)-C(4)-C(5)	111.06(16)
O(5)-C(4)-C(8)	109.22(16)
C(5)-C(4)-C(8)	108.53(17)
O(5)-C(4)-C(3)	114.58(16)
C(5)-C(4)-C(3)	115.27(17)
C(8)-C(4)-C(3)	97.01(15)
C(6)-C(5)-C(9)	122.0(2)
C(6)-C(5)-C(4)	116.39(18)
C(9)-C(5)-C(4)	121.31(19)
C(5)-C(6)-C(1)	113.77(19)
O(1)-C(7)-C(1)	123.77(19)
O(1)-C(7)-C(8)	123.38(19)
C(1)-C(7)-C(8)	112.84(18)
O(4)-C(8)-C(18)	108.29(16)
O(4)-C(8)-C(4)	105.60(16)
C(18)-C(8)-C(4)	117.17(17)
O(4)-C(8)-C(7)	105.96(15)
C(18)-C(8)-C(7)	112.59(17)
C(4)-C(8)-C(7)	106.49(16)
O(7)-C(9)-O(6)	119.9(2)
O(7)-C(9)-C(5)	123.6(2)
O(6)-C(9)-C(5)	116.42(19)
O(5)-C(10)-O(6)	108.87(17)
O(5)-C(10)-C(11)	105.85(18)
O(6)-C(10)-C(11)	106.06(18)
O(5)-C(10)-C(12)	114.38(19)
O(6)-C(10)-C(12)	108.17(18)
C(11)-C(10)-C(12)	113.1(2)

O(4)-C(13)-C(14)	108.15(18)
O(4)-C(13)-C(15)	107.14(18)
C(14)-C(13)-C(15)	109.11(19)
O(4)-C(13)-C(3)	104.17(16)
C(14)-C(13)-C(3)	112.11(18)
C(15)-C(13)-C(3)	115.70(19)
O(3)-C(16)-O(2)	122.5(2)
O(3)-C(16)-C(17)	125.8(2)
O(2)-C(16)-C(17)	111.7(2)
C(19)-C(18)-C(8)	114.12(17)
C(20)-C(19)-C(18)	128.5(2)
C(19)-C(20)-C(22)	124.8(2)
C(19)-C(20)-C(21)	121.0(2)
C(22)-C(20)-C(21)	114.1(2)
C(16A)-O(2A)-C(1A)	117.52(16)
C(8A)-O(4A)-C(13A)	109.73(15)
C(10A)-O(5A)-C(4A)	115.60(15)
C(9A)-O(6A)-C(10A)	117.53(16)
O(2A)-C(1A)-C(6A)	115.45(17)
O(2A)-C(1A)-C(7A)	107.91(16)
C(6A)-C(1A)-C(7A)	102.56(16)
O(2A)-C(1A)-C(2A)	113.42(16)
C(6A)-C(1A)-C(2A)	107.89(17)
C(7A)-C(1A)-C(2A)	108.94(17)
C(3A)-C(2A)-C(1A)	110.50(17)
C(2A)-C(3A)-C(13A)	115.62(17)
C(2A)-C(3A)-C(4A)	106.99(16)
C(13A)-C(3A)-C(4A)	103.16(16)
O(5A)-C(4A)-C(5A)	111.15(16)
O(5A)-C(4A)-C(8A)	109.50(16)
C(5A)-C(4A)-C(8A)	108.33(16)
O(5A)-C(4A)-C(3A)	114.27(16)
C(5A)-C(4A)-C(3A)	115.49(17)
C(8A)-C(4A)-C(3A)	96.94(15)
C(6A)-C(5A)-C(9A)	121.95(19)
C(6A)-C(5A)-C(4A)	116.58(18)

C(9A)-C(5A)-C(4A)	121.10(18)
C(5A)-C(6A)-C(1A)	113.51(19)
O(1A)-C(7A)-C(1A)	123.80(19)
O(1A)-C(7A)-C(8A)	123.05(19)
C(1A)-C(7A)-C(8A)	113.15(17)
O(4A)-C(8A)-C(18A)	107.94(16)
O(4A)-C(8A)-C(4A)	105.82(16)
C(18A)-C(8A)-C(4A)	117.12(17)
O(4A)-C(8A)-C(7A)	105.95(15)
C(18A)-C(8A)-C(7A)	113.18(17)
C(4A)-C(8A)-C(7A)	106.06(16)
O(7A)-C(9A)-O(6A)	120.1(2)
O(7A)-C(9A)-C(5A)	123.6(2)
O(6A)-C(9A)-C(5A)	116.30(19)
O(5A)-C(10A)-O(6A)	109.03(16)
O(5A)-C(10A)-C(11A)	106.21(17)
O(6A)-C(10A)-C(11A)	105.64(18)
O(5A)-C(10A)-C(12A)	114.36(18)
O(6A)-C(10A)-C(12A)	108.45(18)
C(11A)-C(10A)-C(12A)	112.75(19)
O(4A)-C(13A)-C(15A)	107.16(18)
O(4A)-C(13A)-C(14A)	107.92(18)
C(15A)-C(13A)-C(14A)	109.16(19)
O(4A)-C(13A)-C(3A)	104.26(16)
C(15A)-C(13A)-C(3A)	115.73(19)
C(14A)-C(13A)-C(3A)	112.13(18)
O(3A)-C(16A)-O(2A)	122.9(2)
O(3A)-C(16A)-C(17A)	125.7(2)
O(2A)-C(16A)-C(17A)	111.5(2)
C(19A)-C(18A)-C(8A)	114.33(17)
C(20A)-C(19A)-C(18A)	128.1(2)
C(19A)-C(20A)-C(22A)	124.5(2)
C(19A)-C(20A)-C(21A)	120.8(2)
C(22A)-C(20A)-C(21A)	114.6(2)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for compound **25**. 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}
O(1)	51(1)	57(1)	52(1)	9(1)	-9(1)	-11(1)
O(2)	54(1)	36(1)	39(1)	4(1)	1(1)	-6(1)
O(3)	60(1)	46(1)	62(1)	10(1)	-5(1)	-11(1)
O(4)	50(1)	32(1)	46(1)	-11(1)	10(1)	-6(1)
O(5)	55(1)	31(1)	35(1)	0(1)	0(1)	-3(1)
O(6)	69(1)	40(1)	37(1)	-5(1)	0(1)	4(1)
O(7)	104(1)	36(1)	49(1)	-12(1)	4(1)	7(1)
C(1)	45(1)	32(1)	36(1)	3(1)	3(1)	-3(1)
C(2)	48(1)	39(1)	42(1)	-1(1)	10(1)	-5(1)
C(3)	41(1)	36(1)	41(1)	-1(1)	5(1)	0(1)
C(4)	46(1)	28(1)	34(1)	0(1)	4(1)	-1(1)
C(5)	42(1)	31(1)	37(1)	-3(1)	3(1)	-4(1)
C(6)	44(1)	29(1)	45(1)	-4(1)	4(1)	-4(1)
C(7)	45(1)	35(1)	37(1)	-5(1)	5(1)	-1(1)
C(8)	45(1)	28(1)	37(1)	-7(1)	7(1)	-4(1)
C(9)	59(2)	36(1)	41(1)	-3(1)	4(1)	-4(1)
C(10)	63(2)	36(1)	39(1)	-7(1)	-5(1)	3(1)
C(11)	91(2)	49(2)	44(1)	0(1)	-10(1)	4(1)
C(12)	52(2)	54(2)	60(2)	-10(1)	-8(1)	2(1)
C(13)	48(1)	36(1)	41(1)	-5(1)	8(1)	0(1)
C(14)	70(2)	37(1)	67(2)	-5(1)	0(1)	5(1)
C(15)	68(2)	52(2)	52(2)	-14(1)	18(1)	-7(1)
C(16)	56(2)	34(1)	43(1)	-1(1)	8(1)	-3(1)
C(17)	74(2)	43(1)	44(1)	7(1)	1(1)	-3(1)
C(18)	47(1)	35(1)	41(1)	-4(1)	6(1)	-6(1)
C(19)	42(1)	36(1)	43(1)	0(1)	4(1)	0(1)
C(20)	47(1)	45(1)	40(1)	-3(1)	5(1)	-1(1)
C(21)	64(2)	57(2)	51(2)	-16(1)	2(1)	6(1)
C(22)	88(2)	66(2)	46(1)	5(1)	15(1)	7(2)
O(1A)	57(1)	55(1)	50(1)	6(1)	20(1)	9(1)
O(2A)	57(1)	35(1)	37(1)	5(1)	10(1)	4(1)

O(3A)	63(1)	46(1)	62(1)	9(1)	18(1)	13(1)
O(4A)	48(1)	31(1)	46(1)	-10(1)	1(1)	2(1)
O(5A)	52(1)	31(1)	35(1)	1(1)	7(1)	3(1)
O(6A)	65(1)	40(1)	34(1)	-2(1)	9(1)	-3(1)
O(7A)	91(1)	38(1)	48(1)	-12(1)	13(1)	-10(1)
C(1A)	45(1)	32(1)	34(1)	5(1)	7(1)	1(1)
C(2A)	44(1)	40(1)	41(1)	2(1)	1(1)	2(1)
C(3A)	39(1)	38(1)	38(1)	0(1)	4(1)	-2(1)
C(4A)	43(1)	30(1)	35(1)	3(1)	5(1)	0(1)
C(5A)	39(1)	30(1)	38(1)	-2(1)	7(1)	2(1)
C(6A)	43(1)	28(1)	44(1)	-3(1)	8(1)	4(1)
C(7A)	44(1)	36(1)	33(1)	-8(1)	7(1)	-2(1)
C(8A)	44(1)	29(1)	34(1)	-5(1)	5(1)	1(1)
C(9A)	54(1)	35(1)	41(1)	-5(1)	12(1)	4(1)
C(10A)	55(1)	36(1)	38(1)	-3(1)	12(1)	-3(1)
C(11A)	77(2)	48(2)	42(1)	7(1)	14(1)	2(1)
C(12A)	54(2)	54(2)	55(2)	1(1)	19(1)	2(1)
C(13A)	48(1)	37(1)	41(1)	-3(1)	2(1)	-4(1)
C(14A)	74(2)	38(1)	65(2)	-3(1)	12(1)	-11(1)
C(15A)	69(2)	57(2)	49(1)	-11(1)	-6(1)	-1(1)
C(16A)	54(1)	35(1)	44(1)	1(1)	4(1)	2(1)
C(17A)	80(2)	44(2)	48(1)	9(1)	7(1)	5(1)
C(18A)	45(1)	35(1)	39(1)	-3(1)	5(1)	5(1)
C(19A)	41(1)	38(1)	44(1)	0(1)	4(1)	-1(1)
C(20A)	42(1)	49(1)	43(1)	-3(1)	1(1)	1(1)
C(21A)	63(2)	61(2)	55(2)	-14(1)	1(1)	-10(1)
C(22A)	77(2)	66(2)	47(2)	7(1)	-9(1)	-3(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for compound **25**.

	x	y	z	U(eq)
H(2A)	-4506	-688	-1769	51
H(2B)	-4006	-25	-1190	51
H(3A)	-4683	705	-2365	47
H(6A)	-3172	-1972	-2527	48
H(11A)	-3625	1453	-4610	93
H(11B)	-4485	1909	-4365	93
H(11C)	-4535	1045	-4915	93
H(12A)	-5027	-156	-3347	84
H(12B)	-5412	34	-4125	84
H(12C)	-5367	897	-3575	84
H(14A)	-3860	3065	-2055	87
H(14B)	-4730	2469	-2210	87
H(14C)	-4011	2435	-2745	87
H(15A)	-3483	2367	-959	85
H(15B)	-3402	1223	-846	85
H(15C)	-4326	1712	-979	85
H(17A)	-3491	-2824	-148	81
H(17B)	-2539	-2714	-373	81
H(17C)	-3135	-3579	-677	81
H(18A)	-2017	1377	-3142	49
H(18C)	-1368	1091	-2494	49
H(19A)	-1430	-574	-2912	48
H(21A)	-1140	-1552	-3787	86
H(21B)	-740	-988	-4401	86
H(21C)	-1718	-1328	-4488	86
H(22A)	-1892	1245	-4170	99
H(22B)	-2193	439	-4730	99
H(22E)	-1215	780	-4643	99
H(2AA)	313	5794	1805	50
H(2AB)	636	5106	1218	50

H(3AA)	254	4414	2414	46
H(6AA)	1882	7035	2502	46
H(11D)	1872	3654	4631	83
H(11E)	926	3255	4428	83
H(11F)	1075	4131	4963	83
H(12D)	204	5325	3404	80
H(12E)	31	5177	4196	80
H(12F)	-117	4300	3663	80
H(14D)	919	2021	2088	88
H(14E)	115	2652	2270	88
H(14F)	974	2656	2778	88
H(15D)	1030	2703	985	88
H(15E)	1116	3843	865	88
H(15F)	216	3391	1027	88
H(17D)	901	7855	119	86
H(17E)	1901	7629	260	86
H(17F)	1504	8570	590	86
H(18B)	3081	3605	3097	47
H(18D)	3575	3909	2447	47
H(19B)	3662	5548	2908	49
H(21D)	4155	6474	3809	90
H(21E)	4691	5873	4403	90
H(21F)	3737	6216	4508	90
H(22C)	3455	3666	4112	96
H(22D)	3287	4440	4696	96
H(22F)	4241	4092	4599	96
