# Regioselective Synthesis of the Tricyclic Core of Lateriflorone

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## Supporting Information

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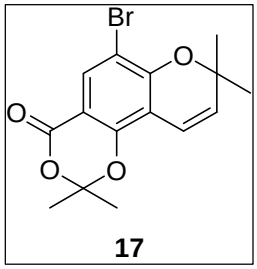
**General Techniques**

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 ($Et_2O$), dichloromethane ($CH_2Cl_2$), toluene ($PhCH_3$) 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 ($^1$H NMR, $^{13}$C 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: $[\alpha]^T_\lambda$ (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**.

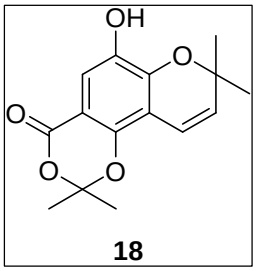
**Compound Specific Data**



**17**

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

$R_f$ = 0.66 ($Et_2O$/Hexane = 1/1); IR (film), $\nu_{max}$: 2981, 2921, 1737, 1601, 1574, 1442, 1375, 1303, 1290, 1204, 1171, 1125; $^1$H NMR (400 MHz, $CDCl_3$) 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); $^{13}$C NMR (100 MHz, $CDCl_3$) 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 $C_{15}H_{15}O_4Br$ ($M+Na^+$) 361.0046, found 361.0056.



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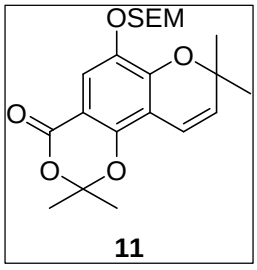
**10-Hydroxy-2,2,6,6-tetramethyl-2H-1,5,7-trioxa-phenanthren-8-one (18)**

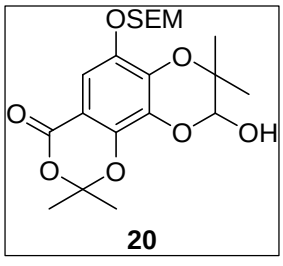
$R_f$ = 0.60 (EtOAc/Hexane = 1/1); IR (film), $\nu_{max}$: 3392, 2980, 1721, 1641, 1613, 1469, 1395, 1379, 1318, 1298, 1267, 1202, 1124, 1053, 996, 883; $^1$H NMR (400 MHz, $CDCl_3$) δ: 7.33 (s, 1H), 6.51 (d, *J* = 10.0 Hz, 1H), 5.64 (d, *J* = 10.0 Hz, 1H), 5.38 (s, broad, 1H), 1.71 (s, 6H), 1.50 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) 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 $C_{15}H_{16}O_5$ ($M+H^+$) 277.107, found 277.1078.



**11**

**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; $^1$H NMR (400 MHz, $CDCl_3$) 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); $^{13}$C NMR (100 MHz, $CDCl_3$) 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 $C_{21}H_{30}O_6Si_1$ ($M+Na^+$) 429.1704, found 429.1706.

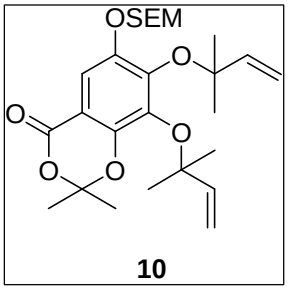


**20**

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

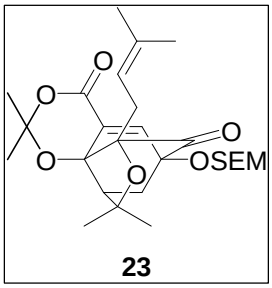
$R_f$ = 0.24 (EtOAc/Hexane = 1/3); IR (film), $\nu_{max}$: 3389, 2951, 1736, 1617, 1485, 1378, 1320, 1206, 1060, 1022, 858, 837; $^1$H NMR (400 MHz, $CDCl_3$) δ: 7.36 (s, 1H), 5.20-5.24 (m, 3H), 3.77-3.82 (m, 2H), 3.58 (s, broad, 1H), 1.76 (s, 3H), 1.75 (s, 3H), 1.48 (s, 3H), 1.38 (s, 3H), 0.94-0.99 (m, 2H), 0.01 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) 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.



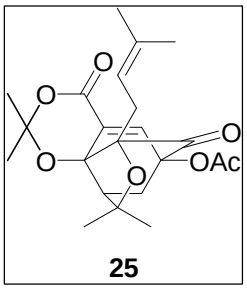

**7,8-Bis-(1,1-dimethyl-allyloxy)-2,2-dimethyl-6-(2-trimethylsilanyl-ethoxymethoxy)-benzo[1,3]dioxin-4-one (10)**

$R_f$ = 0.65 ($Et_2O$/Hexane = 1/1); IR (film), $\nu_{max}$: 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)**

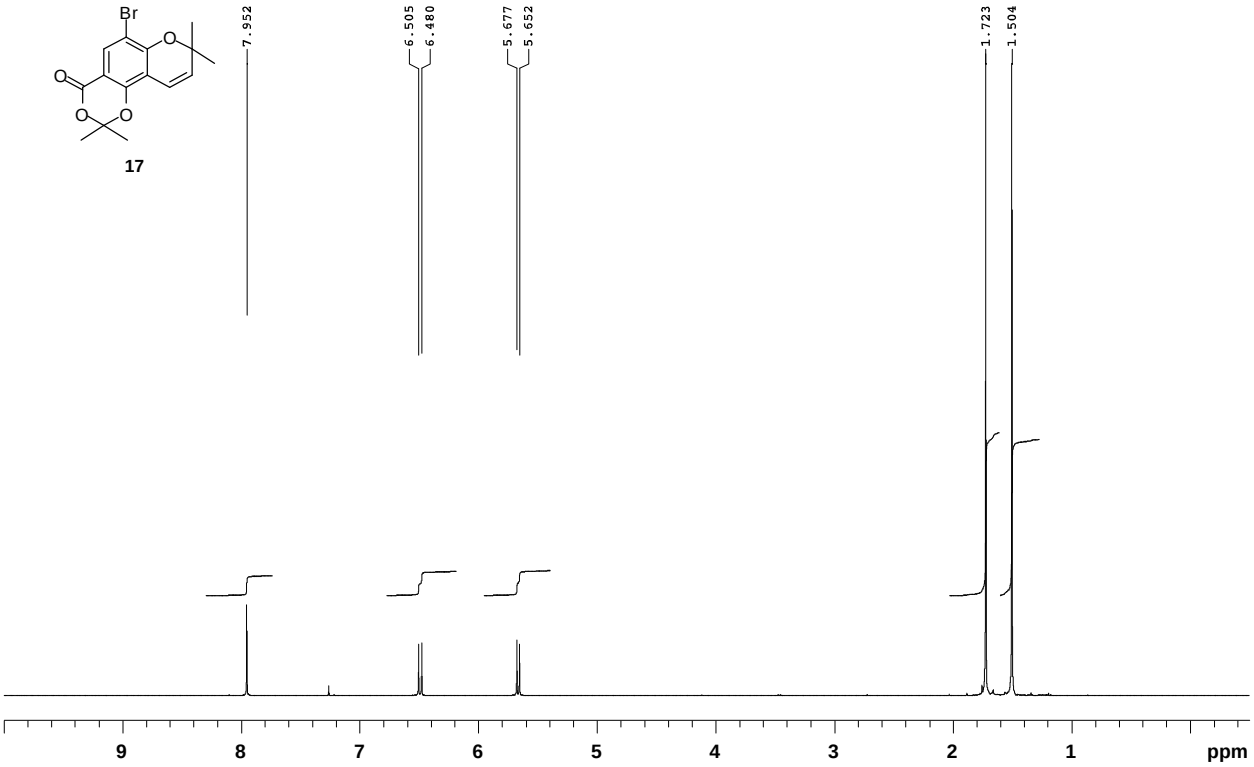
$R_f$ = 0.63 ($Et_2O$/Hexane = 1/1); IR (film), $\nu_{max}$: 2953, 1741, 1636, 1382, 1283, 1071, 1048, 859, 836; $^1H$ NMR (400 MHz, $CDCl_3$) δ: 7.57 (s, 1H), 5.02 (d, *J* = 8.0 Hz, 1H), 4.94 (d, *J* = 8.0 Hz, 1H), 4.34-4.42 (m, 1H), 3.66-3.82 (m, 2H), 2.60-2.76 (m, 2H), 2.55 (d, *J* = 10.0 Hz, 1H), 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.

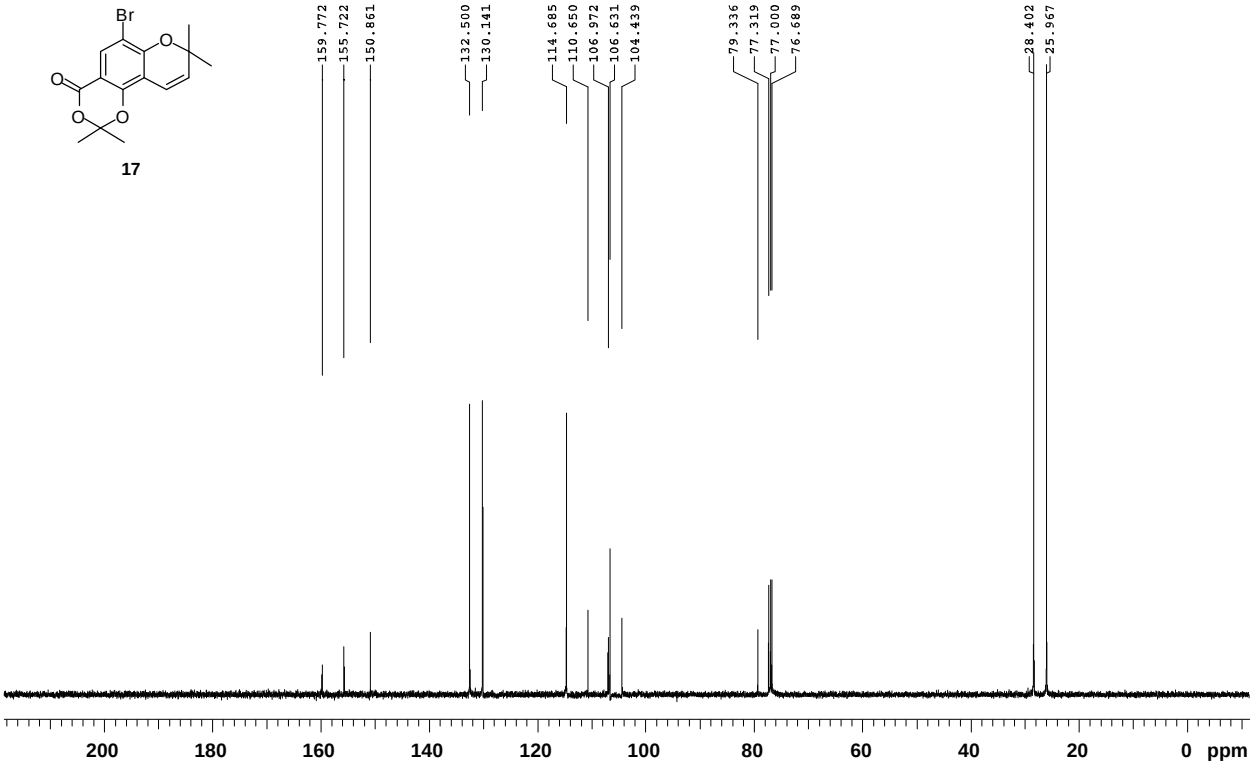


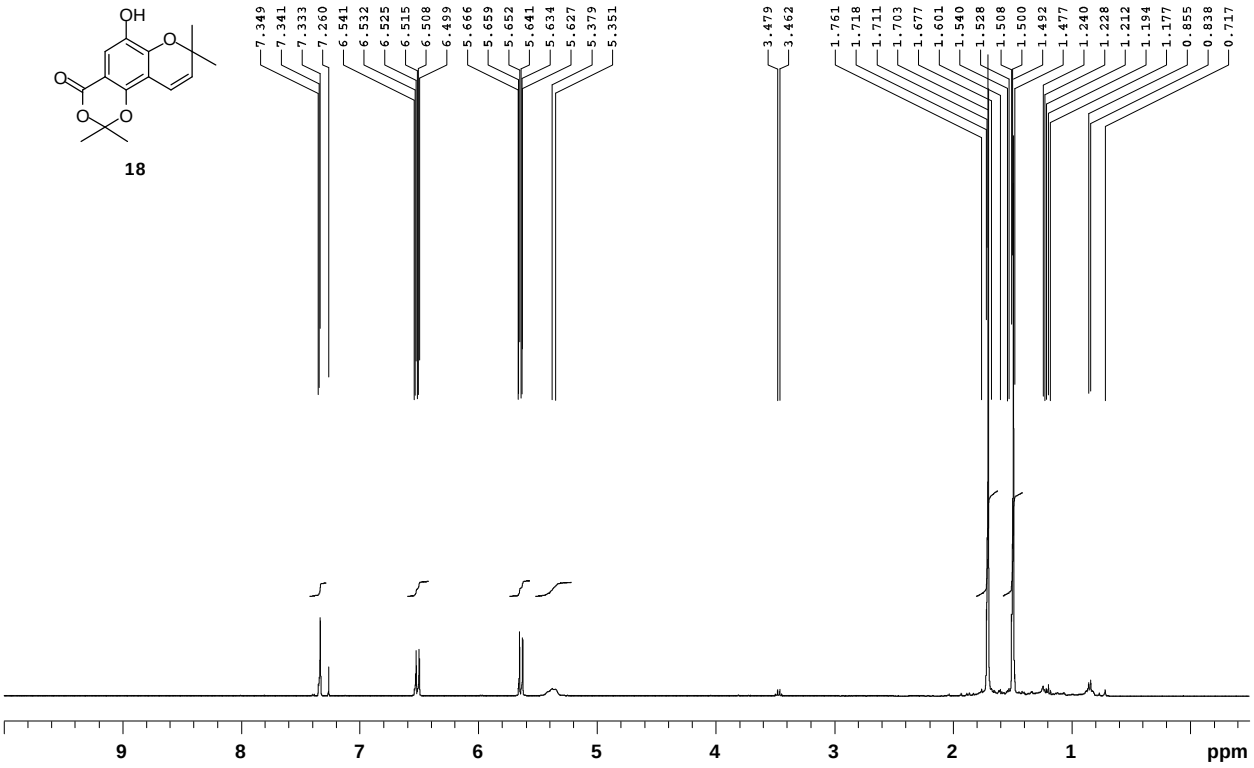

**Acetyl Protected Claisen/Diels-Alder Adduct (25)**

$R_f$ = 0.43 ($Et_2O$/Hexane = 3/1); IR (film), $\nu_{max}$: 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

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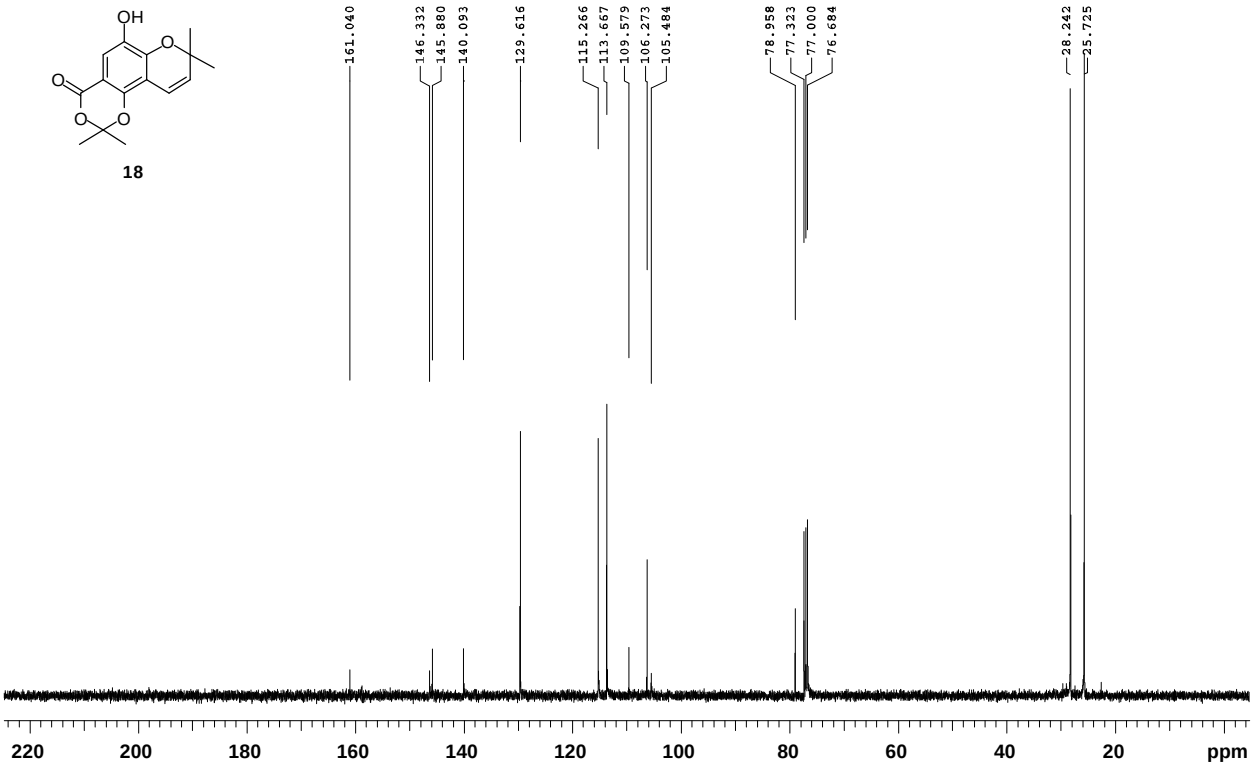
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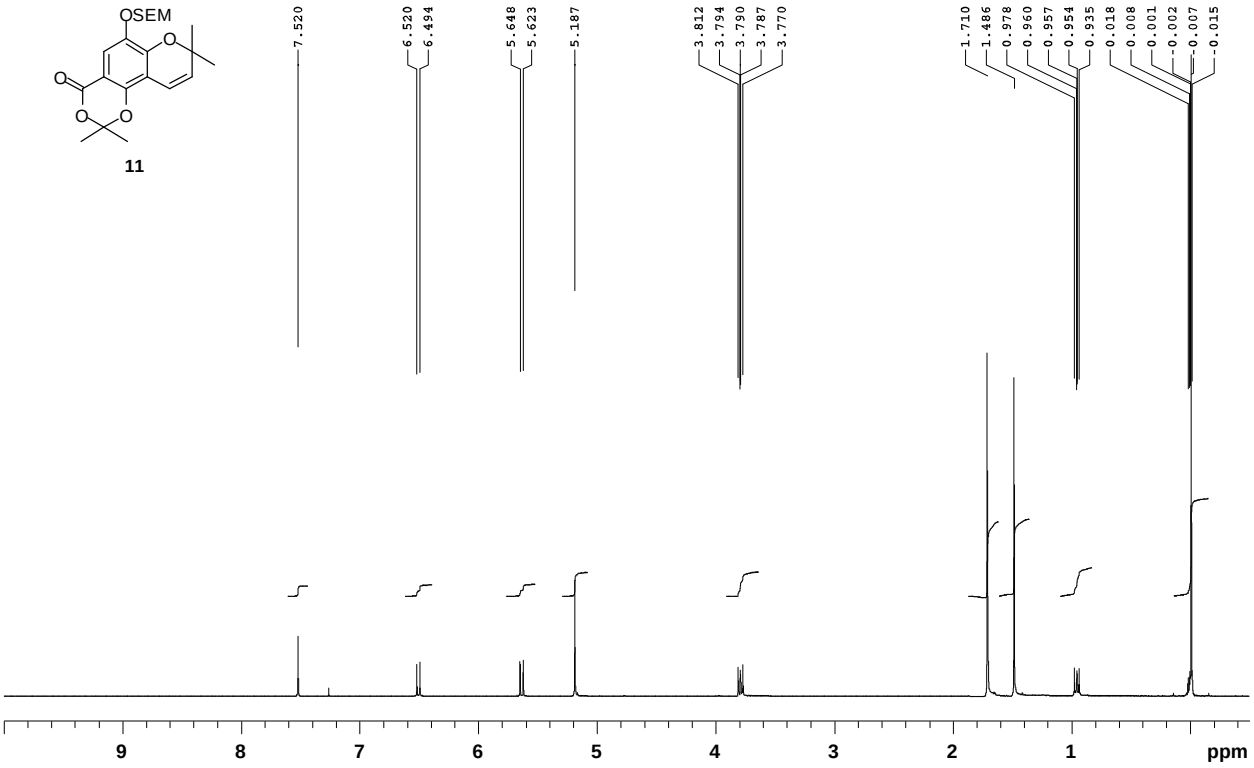
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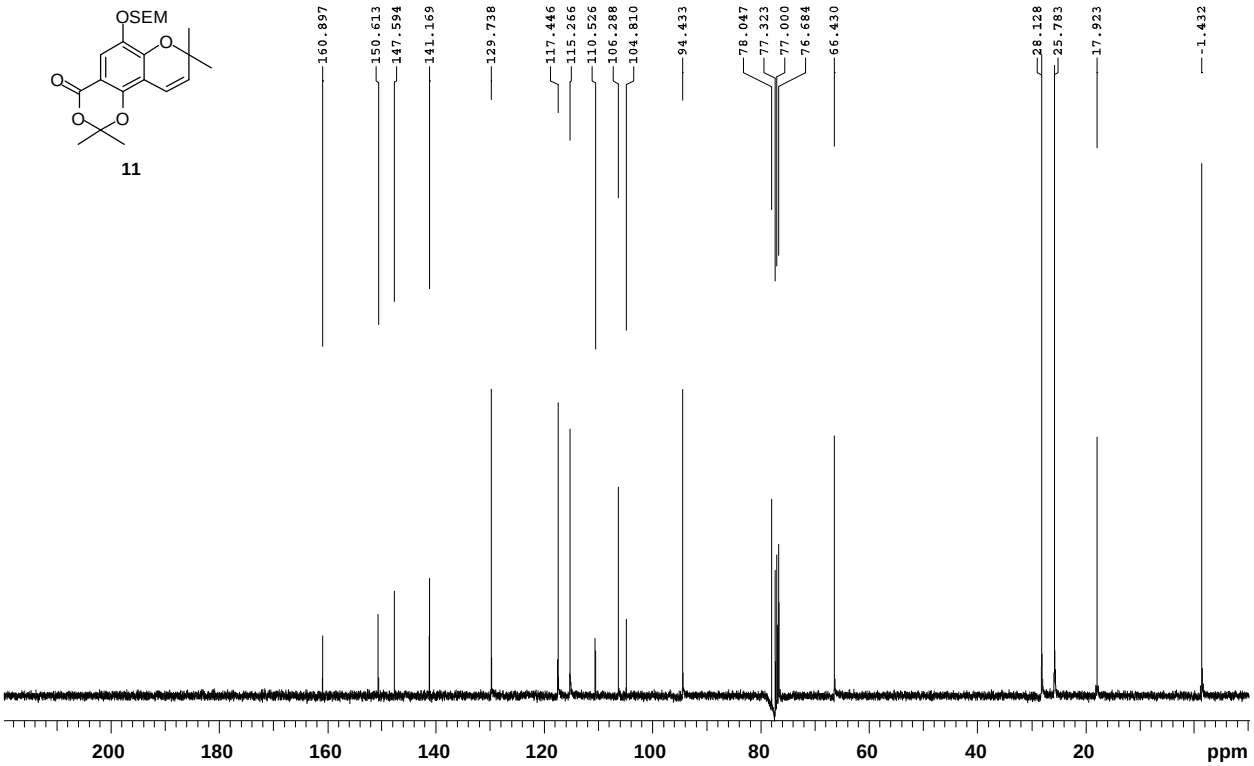
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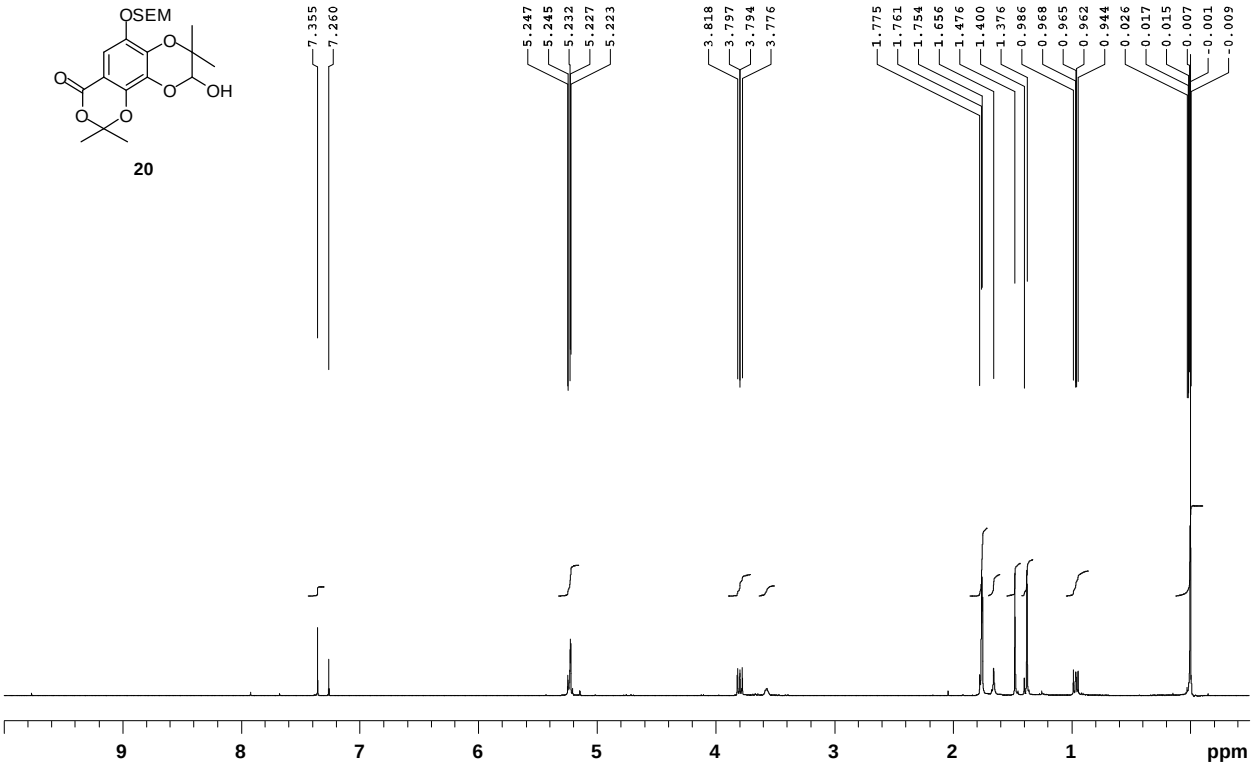
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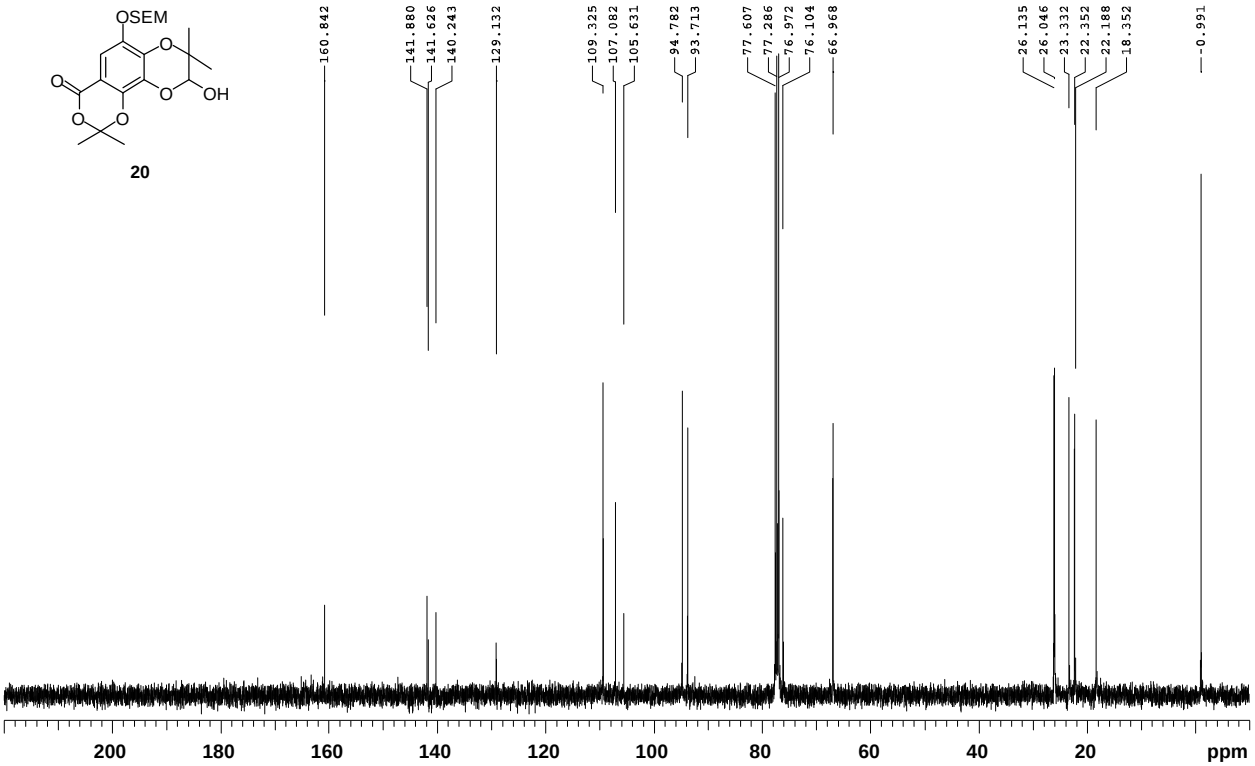
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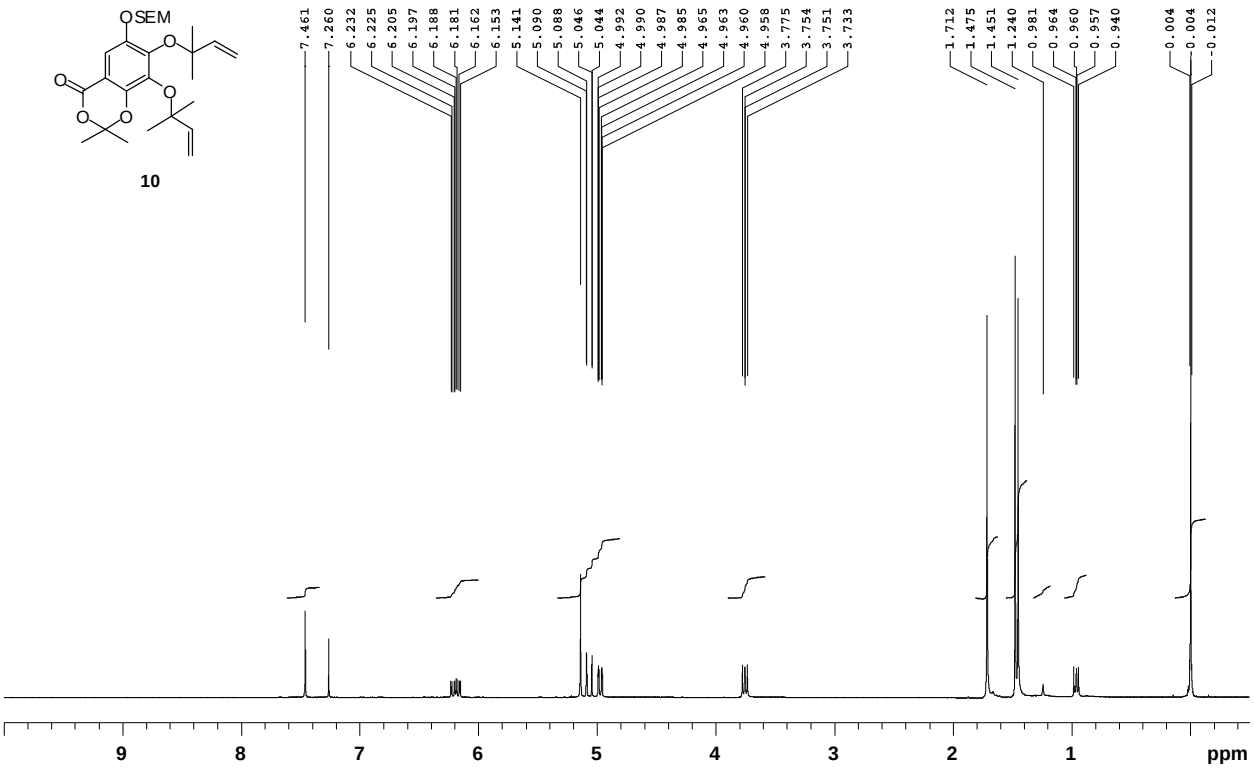
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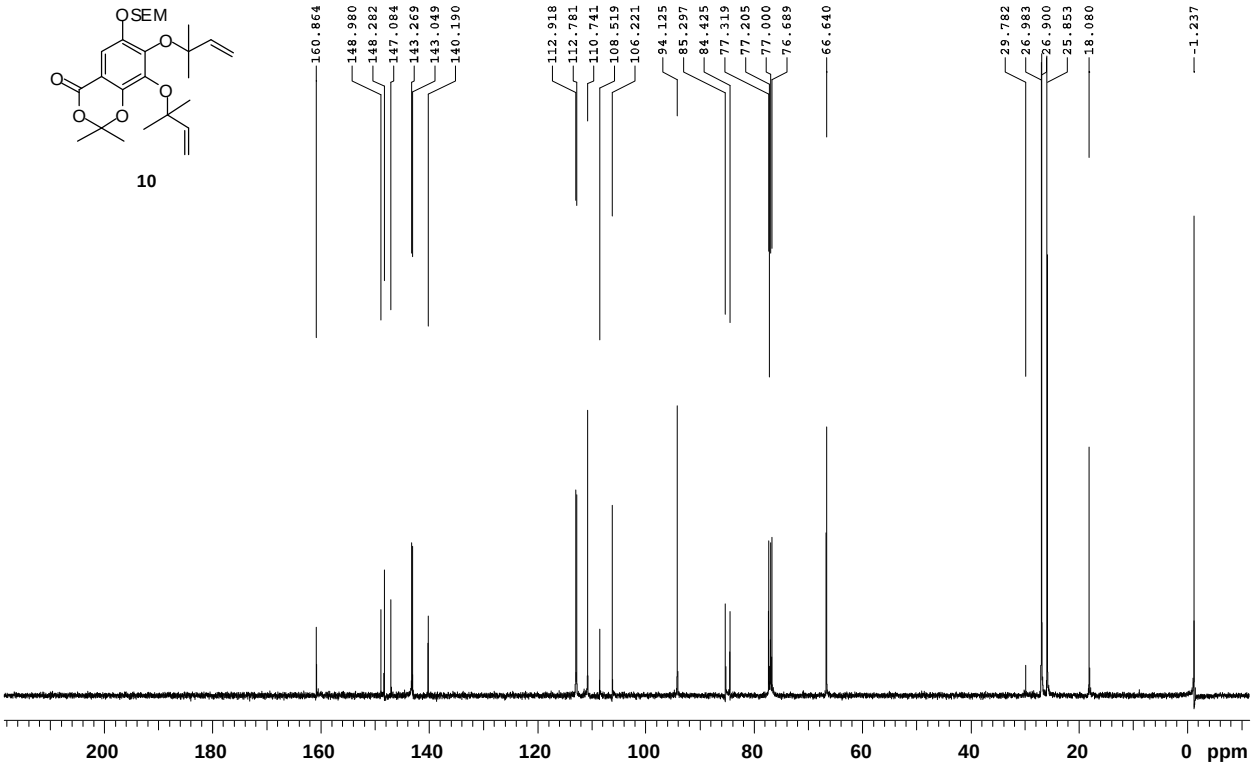
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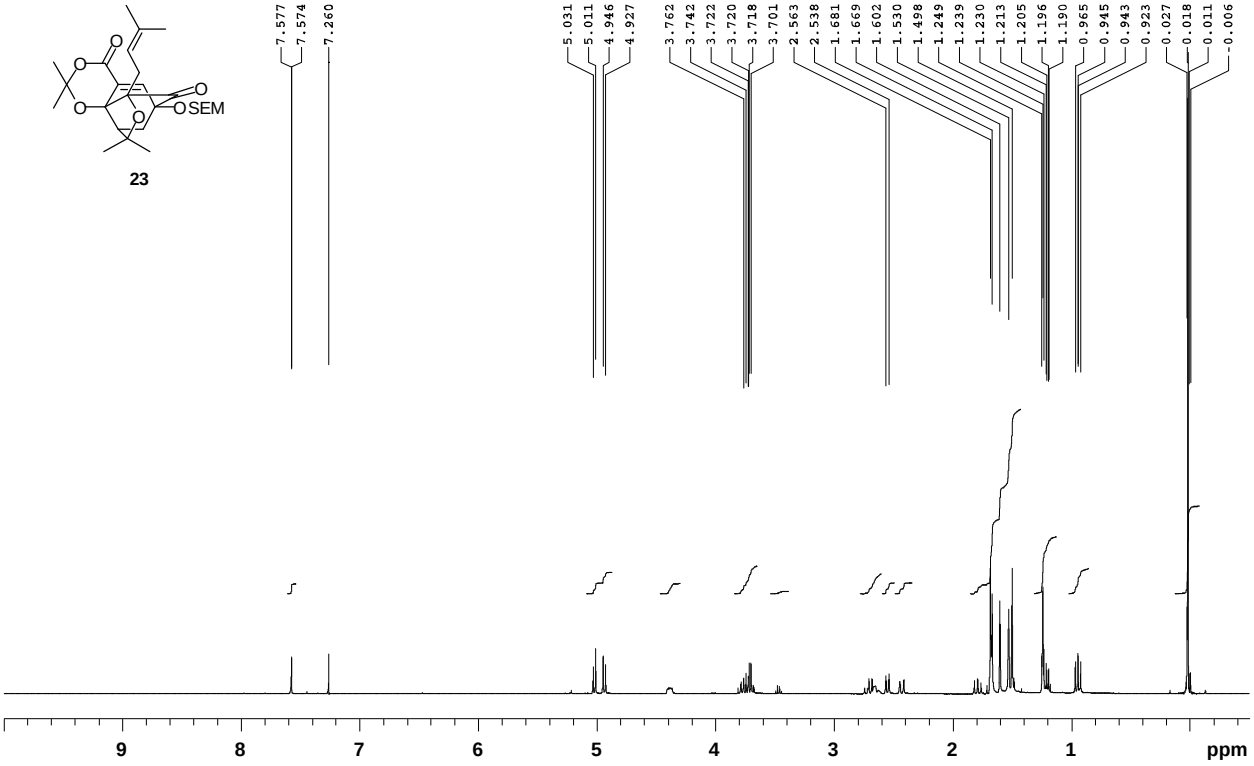
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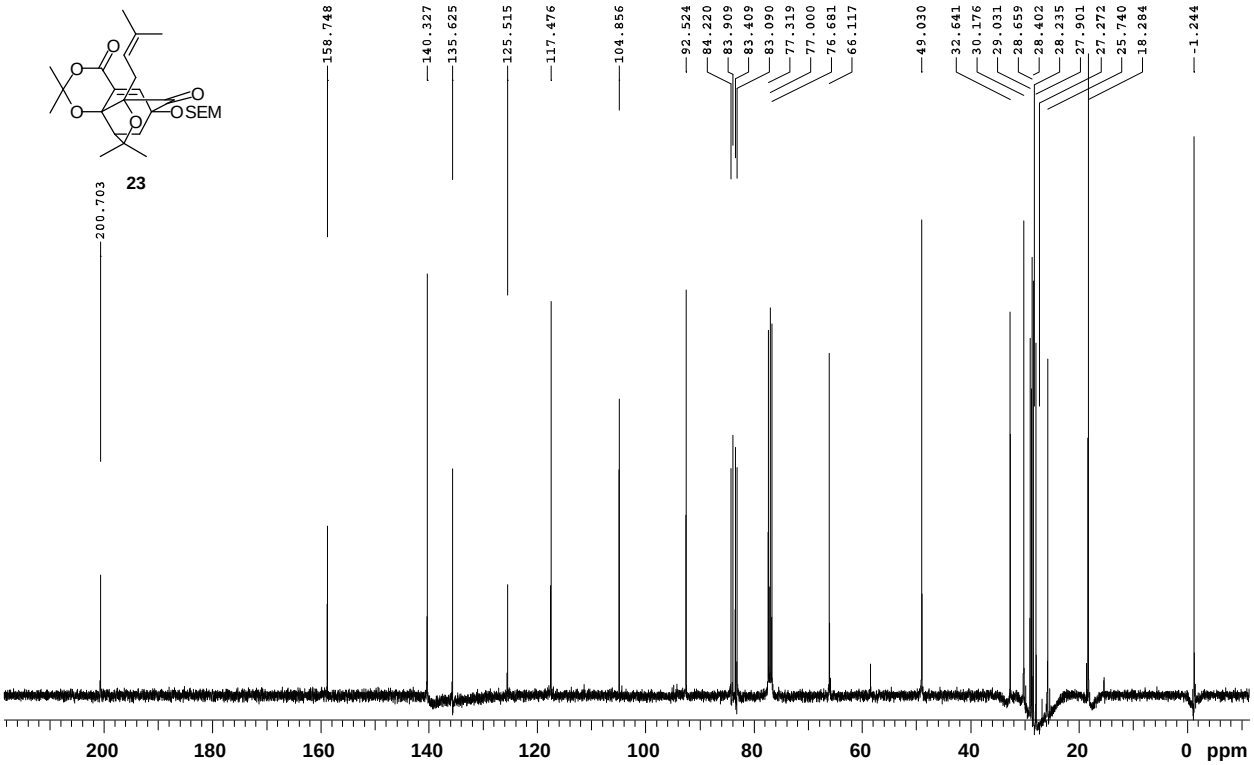
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120
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80
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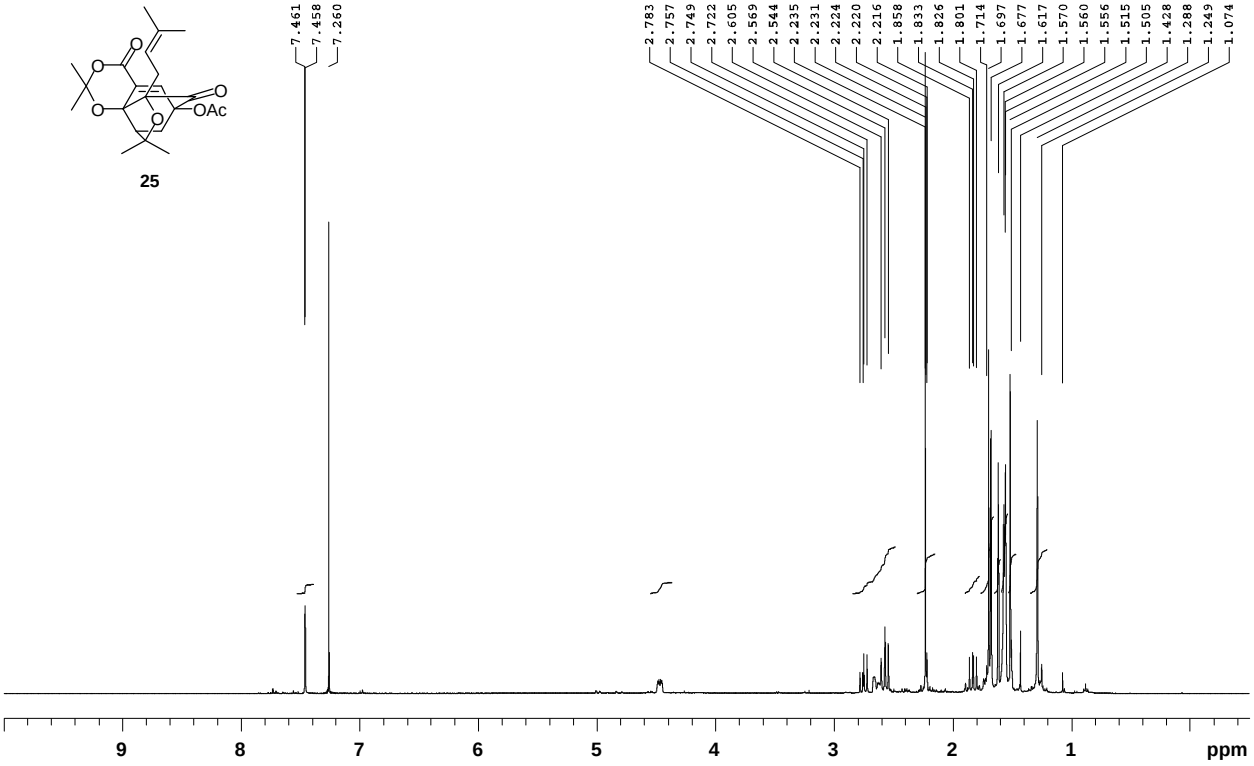
0
ppm


7.461
7.458
7.260
2.783
2.757
2.749
2.722
2.605
2.569
2.544
2.435
2.231
2.224
2.220
2.216
1.858
1.833
1.826
1.801
1.714
1.697
1.677
1.617
1.570
1.560
1.556
1.515
1.505
1.428
1.288
1.249
1.074
OAc
25
9
8
7
6
5
4
3
2
1
ppm

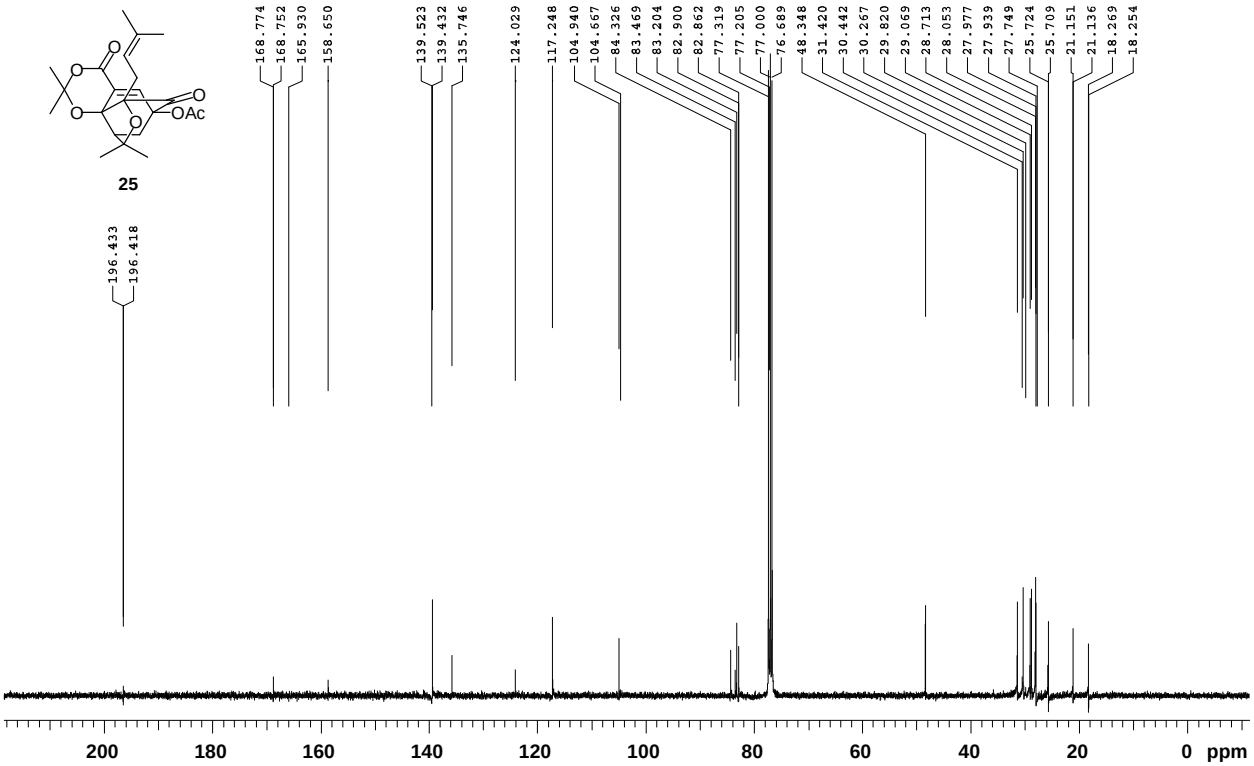

168.774
168.752
165.930
158.650
139.523
139.432
135.746
124.029
117.248
104.940
104.667
84.326
83.469
83.204
82.900
82.862
77.319
77.205
77.000
76.689
48.348
31.420
30.442
30.267
29.820
29.069
28.713
28.053
27.977
27.939
27.749
25.724
25.709
21.151
21.136
18.269
18.254
196.433
196.418
OAc
25
200
180
160
140
120
100
80
60
40
20
0
ppm

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

| | | |
|---|---|---|
| Identification code | sad | |
| Empirical formula | C22 H28 O7 | |
| 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>2sigma(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 ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for compound **25**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(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 ($Å^2 x\ 10^3$) for compound **25**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| 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 ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) 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 |