Supporting Informations

Enantiocontrolled Construction of Tricyclic Furan Derivatives via Asymmetric Diels Alder Reaction

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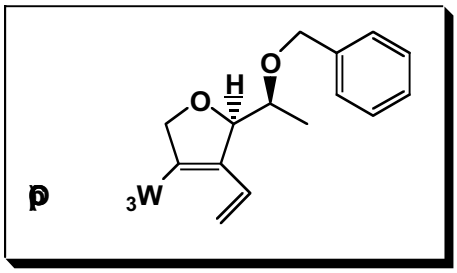
Contents:

(1) Synthesis of compound 2-*anti*

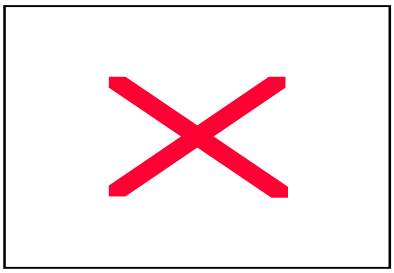
To a CH_2Cl_2 solution (10 mL) of compound **1** (280 mg , 0.70 mmol) was added BF_3-OEt_2 (0.70 mmol) at -78_ and the mixtures were stirred for 10 minutes before (2*S*)-2-(benzyloxy)propanal was added (127 mg, 0.70 mmol). The mixtures were stirred for 1 h before a saturated $NaHCO_3$ solution was added. The organic layer was extracted with diethyl ether, dried over $MgSO_4$, and eluted through a silica column (diethyl ether/hexane=1/1) to yield compound **2-*anti*** (224 mg , 0.43 mmol, 60%, R_f = 0.12) and compound **2-*syn*** (52.3 mg , 0.098 mmol, 14%, R_f = 0.26).



Spectral data for **2-*anti*** : IR (nujol)_3045 (w), 2989 (w), 2023 (s), 1944 (s), 1H NMR (400 MHz, $CDCl_3$): _ 7.19~7.35 (5H, m, Ph), 6.19 (1H, dd, *J* = 11.2, 18.0 Hz), 5.48 (5H, s, Cp), 5.19 (1H, d, *J* = 4.4 Hz), 5.03 (1H, d, *J* = 12.0 Hz), 4.83 (1H, d, *J* = 17.6 Hz), 4.51~4.63 (4H, m), 3.86 (1H, dq, *J* = 1.6, 6.4 Hz), 0.95 (3H, d, *J* = 6.4 Hz), 13C NMR (100 MHz, $CDCl_3$): d , 226.5, 215.5, 214.3, 143.9, 139.1, 128.2, 127.7, 127.3, 134.0, 125.6, 114.5, 90.9, 90.3, 86.8, 75.7, 70.3, 12.6. $[\_]_D$=-25.0 ($CHCl_3$, c=2.3). MS (12 eV, m/e): 530 (M^+). Anal. calcd. for $C_{23}H_{22}WO_3$: C, 52.10; H, 4.18. Found: C, 52,02; H, 4.04.

(2) Synthesis of (2*R*)-2-[(1*S*)-1-(benzyloxy)ethyl]-3-vinyl-2,5-dihydrofuran (3a)

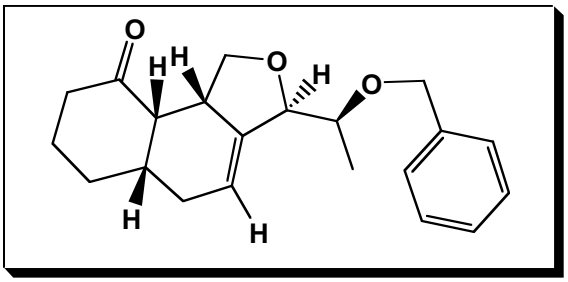
To a CH_2Cl_2 solution (4.0 mL) of compound **2-*anti*** (300 mg, 0.534 mmol) was added 50% *m*-CPBA (*m*-chloroperbenzoic acid, 84 , 0.80 mmol, and the mixtures were stirred for 8 h before addition of $Na_2S_2O_3$. The solution was extracted with diethyl ether, dried over $MgSO_4$ and eluted through a short silica bed (diethyl ether/hexane=1/1) to afford oxacyclic diene **3a** (102 mg , 0.443 mmol, R_f = 0.75, 83%).



Spectral data for **3a** : IR (nujol): 2983 (w), 2848 (s), 2304 (w), 1264 (s), ^{1}H NMR (400 MHz, $CDCl_3$): _ 7.25~7.40 (5H, m, Ph), 6.38 (1H, dd, *J* = 11.6, 17.8 Hz), 5.90 (1H, d, *J* = 1.6 Hz), 5.24 (1H, d, *J* = 4.8 Hz), 5.08 (1H, d, *J* = 11.2 Hz), 4.99 (1H, d, *J* = 17.2 Hz), 4.71 (H, m), 4.68; 4.59 (2H, AB quartet, *J* = 12.0 Hz), 3.83 (1H, dq, *J* = 2.0, 6.2 Hz), 1.10 (3H, d, *J* = 6.4 Hz), ^{13}C NMR (100 MHz, $CDCl_3$)__ 138.6, 138.6 , 129.2 , 128.1 , 127.5, 127.2, 126.5, 116.0, 86.2, 75.4, 75.4, 70.2, 12.50. $[\_]_D$=-32.8 ($CHCl_3$, c=2.5). HRMS calcd for $C_{15}H_{18}O_2$: 230.1307; found 230.1311.

(3) Synthesis of (3*R*, 5a*S*, 9a*S*, 9b*S*)-3-[1-(benzyloxy)ethyl]-1,3,5,5a,6,7,8,9,9a,9b-decahydrobenzo[e]isobenzofuran-9-one (4a)

____**3a** (34.0 mg, 0.148 mmole)_2-Cyclohexen-1-one (0.086 ml, 0.89 mmole)__5ml_____-78_____BF_3-OEt_2 (0.020 ml, 1.62 mmole)_____2__ _____ _____(TLC)_____(1 / 1)_____**4a** (30.4 mg, 0.093 mmole)_ R_f = 0.52 (__/___ = 1 / 1)___63 %_

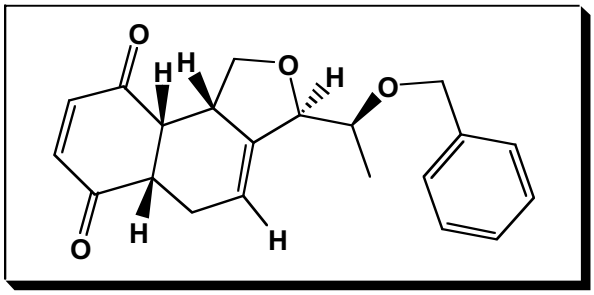


Spectral data for **4a** : IR (nujol)_3056 (m), 2980 (m), 1707 (s), 1H NMR (400 MHz, $CDCl_3$)__ 7.18~7.38 (5H, m, Ph), 5.45~5.55 (1H, d, m), 4.61(1H, AB quartet, *J* = 12.4 Hz), 4.56 (1H, AB quartet, *J* = 7.6 Hz), 4.54 (1H, d, *J* = 4.0 Hz), 4.25~4.54 (1H, m), 3.46~3.55 (1H, m), 3.13 (1H, dd, *J* = 8.0, 10.0 Hz), 2.70~2.90 (1H, m), 2.36~2.46 (3H, m), 1.93~2.11 (3H, m), 1.78~1.88 (2H,

m), 1.66 (1H, tq, J = 4.0, 13.6 Hz), 1.44 (1H, dq, J = 3.6, 11.8 Hz), 1.15 (3H, d, J = 6.4 Hz), 13C NMR (100 MHz, $CDCl_3$)__ 211.1 (C=O), 140.4, 138.9, 128.2, 127.7, 127.3, 118.0, 82.7, 77.2, 73.5, 71.6, 54.5, 42.0, 40.0, 39.7, 33.9, 32.4, 26.0, 15.6. [_]$_D$=+55.6 ($CHCl_3$, c=1.6). HRMS Calcd for $C_{21}H_{26}O_3$_326.18819.

(4) Synthesis of (3*R*, 5a*S*, 9a*R*, 9b*S*)-3-[1-(benzyloxy)ethyl]-1,3,5,5a,6,9,9a,9b-octahydro-benzo[e]isobenzofuran-6,9-dione (5a)

____**3a** (43.0 mg, 0.187 mmole)_1,4-Benzoquinone (20.0 mg, 0.188 mmole)__3ml_____-78_____BF_3-OEt_2 (0.023 ml, 1.88 mmole)_____12___ _____(TLC)_____(1 / 1)_____**5 a** (45.5 mg, 0.134 mmole)_ R_f = 0.48 (__/___ = 1 / 1)___72 %_

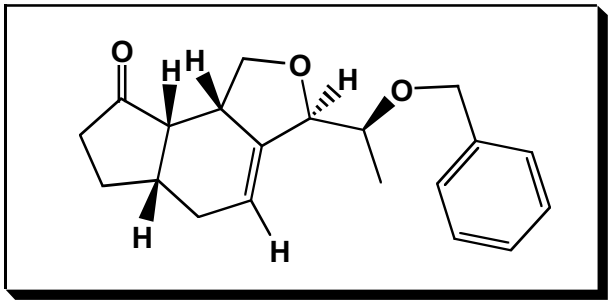


Spectral data for **5a** : IR (nujol)_2969 (m), 2900 (m), 1688 (s), 1609 (w), 1H NMR (400 MHz, $CDCl_3$)__ 7.24~7.40 (5H, m, Ph), 6.57 (2H, q, J = 10.4 Hz), 5.48~5.53 (1H, br), 4.61; 4.54 (2H, AB quartet, J = 12.0 Hz), 4.40~4.44 (2H, m), 4.08 (1H, t, J = 8.0 Hz), 3.58 (1H, m), 3.52 (1H, t, J = 5.2 Hz), 3.13 (1H, m), 2.78~2.86 (1H, br), 2.34~2.44 (1H, m), 2.19~2.29 (1H, m), 1.16 (3H, d, J = 6.0 Hz), 13C NMR (100 MHz, $CDCl_3$)__ 200.5, 198.2, 140.8, 140.5, 138.8 , 128.3 , 127.6 , 127.4, 137.5, 115.0, 82.6, 77.1, 71.3, 68.7, 48.5, 46.1, 41.0, 26.6, 15.2. [_]$_D$=+89.2 ($CHCl_3$, c=1.5). HRMS Calcd for $C_{21}H_{22}O_4$_338.15181.

(5) Synthesis of (3*R*, 5a*S*, 8a*S*, 8b*S*)-3-[1-(benzyloxy)ethyl]-3,5,5a,6,7,8,8a,8b-octahydro-1H-cyclopenta[e]isobenzofuran-8-one (6a)

____**27a** (24.0 mg, 0.104 mmole)_2-Cyclopenten-1-one (0.09 ml, 1.04 mmole)__3ml_____-78_____BF_3-OEt_2 (0.013 ml, 0.104 mmole)_____2__ _____ _____(TLC)_____(1 / 1)_____**6a** (21.7 mg, 0.07 mmole)_ R_f =

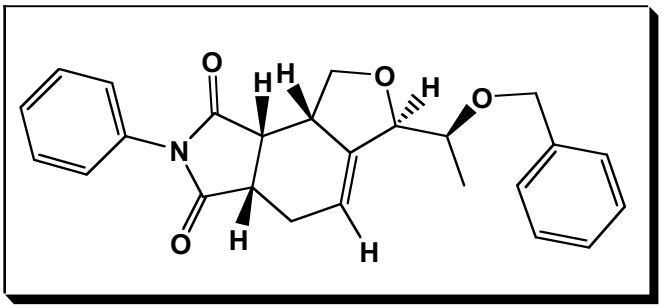
0.50 (__/___= 1 / 1)___67 %_



Spectral data for **6a** : IR (nujol)_2973 (w), 2930 (w), 2875 (m), 1739 (s), 1H NMR (400 MHz, $CDCl_3$)__ 7.20-7.33 (5H, m, Ph), 5.61-5.66(1H, br), 4.61, 4.55 (2H, AB quartet, J = 12.0 Hz), 4.55 (1H, t, J = 8.0 Hz), 4.20-4.30 (1H, m), 3.50-3.56 (1H, m), 3.27 (1H, dd, J = 8.4, 10.2 Hz), 2.58-2.69 (1H, m), 2.36-2.52 (1H, m), 2.12-2.28 (1H, m), 1.98-2.08 (1H, m), 1.80-1.94 (1H, m), 1.50-1.62 (2H, m), 1.15 (3H, d, J = 6.4 Hz), 13C NMR (100 MHz, $CDCl_3$)__ 217.3, 141.2, 138.9 , 128.2, 127.6, 127.3, 119.9, 82.4, 77.0, 72.5, 71.6, 54.8, 41.0, 38.6, 37.6, 32.1, 28.0, 15.7. $[\_]_D$=+31.6 ($CHCl_3$, c=1.7). HRMS Calcd for $C_{20}H_{24}O_3$_312.1725.

(6) Synthesis of (3*R* ,5a*S* ,8a*R*, 8b*S*)-3-[1-(benzyloxy)ethyl]-7-phenyl-3,5,5a,6,7,8,8a,8b-octahydro-1H-furo[3,4-e]isoindole-6,8-dione (7a)

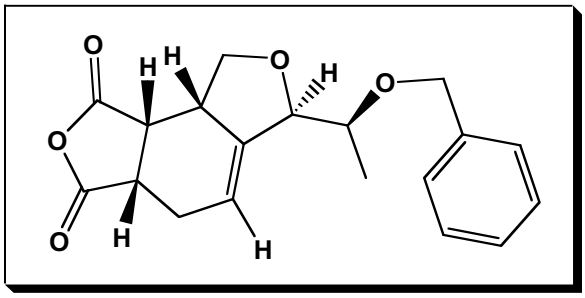
____**3a** (26.0 mg, 0.123 mmole)_NMR tube____N-phenylmaleimide (19.6 mg, 0.123 mmole)_0.50ml_d_8-toluene_____80____3_____^{1}H-NMR_____(TLC)_____(1 / 1)_____**7a** (38.7 mg, 0.096 mmole)_ R_f = 0.26 (__/___ = 2 / 1)___92 %_



Spectral data for **7a** : IR (nujol)_3055 (m), 2980 (m), 1771 (w), 1715 (s), 1H NMR (400 MHz, $CDCl_3$)__ 7.19~7.45 (5H, m, Ph), 5.80~5.86 (1H, br), 4.63; 4.52 (2H, AB quartet, J = 11.6 Hz), 4.30~4.40 (3H, m), 3.62~3.68 (1H, m), 3.41 (1H, t, J = 8.8 Hz), 3.27 (1H, dt, J = 2.0, 7.6 Hz), 2.95 (1H, ddd, J = 1.6, 7.4, 15.4 Hz), 2.83~2.90 (1H, m), 2.17~2.24 (1H, m), 1.20 (3H, d, J = 6.0 Hz), 13C NMR (100 MHz, $CDCl_3$)__ 178.3, 176.1, 143.9, 138.5, 131.8, 129.0, 128.5, 128.2, 127.5, 127.4, 126.3, 116.7, 82.1, 76.7, 71.0, 67.2, 40.6, 40.1, 39.2, 23.6, 15.0. $[\_]_D$=-59.5 ($CHCl_3$, c=3.1). HRMS Calcd for $C_{25}H_{25}NO_4$_403.17836.

(7) Synthesis of (3a*S*,6*R*,8a*S*,8b*R*)-6-[1-(benzyloxy)ethyl]-1,3,3a,4,6,8,8a,8b-octahydro-furo[3,4-e]isobenzofuran-1,3-dione (8a)

____**3a** (28.0 mg, 0.122 mmole)_NMR tube____maleic anhydride (11mg, 0.122 mmole)_0.50ml_d_8-toluene_____80____4_____^{1}H-NMR_____(TLC)_____(1 / 1)_____**8a** (26.8 mg, 0.082 mmole)_ R_f = 0.23 (__/___ = 2 / 1)___67 %_

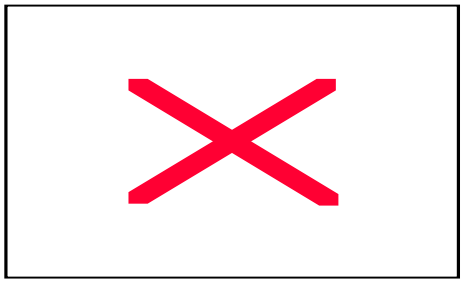


Spectral data for **8a** : IR (nujol)_2984 (m), 2871 (m), 1846 (m), 1771 (s), 1H NMR (500 MHz, $CDCl_3$)__ 7.20~7.40 (5H, m, Ph), 5.85~5.80 (1H, m), 4.59; 4.47 (2H, AB quartet, J = 12.0 Hz), 4.30~4.35 (1H, br), 4.23 (1H, t, J = 9.2 Hz), 4.10 (1H, t, J = 11.6 Hz), 3.60~3.66 (1H, m), 3.49 (1H, t, J = 6.0 Hz), 3.38~3.45 (1H, m,), 2.73~2.83 (2H, m), 2.14~2.25 (1H, m), 1.15 (3H, d, J = 6.4 Hz), 13C NMR (100 MHz, $CDCl_3$)__ 173.7, 170.9, 144.3, 138.4, 127.9, 127.6, 127.5, 116.8, 82.2, 77.1, 71.0, 68.9, 41.4, 40.5, 38.6, 24.6, 15.1. $[\_]_D$=+9.4 ($CHCl_3$, c=2.6). HRMS Calcd for $C_{19}H_{20}O_5$_328.13108.

(8) Synthesis of $CpW(CO)_3\{\_^1$-(2*S*)-2-[(1*S*)-1-(benzyloxy)ethyl]-3-vinyl-2,5-dihydro-furan} (2-*syn*)

To a CH_2Cl_2 solution (10 mL) of compound **1** (300 mg, 0.75 mmol) was added $TiCl_4$

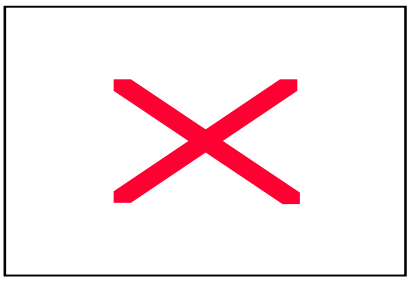
(0.75 mmol) at -78_ and the mixtures were stirred for 10 minutes before (2*S*)-2-(benzyloxy)propanal was added (136 mg, 0.82 mmol). The mixtures were stirred for 1 h before a saturated $NaHCO_3$ solution was added. The organic layer was extracted with diethyl ether, dried over $MgSO_4$, and eluted through a silica column (diethyl ether/hexane=1/1) to yield compound **2-*syn*** (276 mg, 0.52 mmol, 69%, R_f = 0.12) and compound **2- *anti*** (56.2 mg, 0.11 mmol, 14%, R_f = 0.26).



Spectral data for **2-*syn*** : IR (nujol)_2965 (s), 2030 (s), 1934 (s), 1H NMR (400 MHz, $CDCl_3$)__ 7.19~7.24 (5H, m, Ph), 6.34 (1H, dd, *J* = 11.6, 17.6 Hz), 5.45 (5H, s, Cp), 5.13 (1H, d, *J* = 11.6 Hz), 5.06 (1H, d, *J* = 18.0 Hz), 4.08 (1H, d, *J* = 4.4 Hz), 4.66 (1H, dd, *J* = 4.8, 13.2 Hz), 449 (1H, d, *J* = 11.2 Hz), 4.46; 4.37 (2H, AB quartet, *J* = 12.0 Hz), 3.83 (1H, dq, *J* = 0.0, 6.4 Hz), 1.20 (3H, d, *J* = 6.4 Hz), 13C NMR (100 MHz, $CDCl_3$)__ 226.8, 215.1, 214.8 (W-**C=O**), 144.8, 139.3, 128.0, 127.6, 127.1, 134.4, 124.9, 114.2, 90.9, 89.7, 88.1, 75.7, 71.4, 16.9. $[\_]_D$=-24.6 ($CHCl_3$, c=6.4). HRMS Calcd. for $C_{23}H_{22}WO_3$_ 530.10785. Anal. Calcd. for $C_{23}H_{22}WO_3$:C, 52.10 ; H, 4.18 ;O, 9.05 ;W 34.67.

(9) Synthesis of (2*S*)-2-[(1*S*)-1-(benzyloxy)ethyl]-3-vinyl-2,5-dihydrofuran (3b)

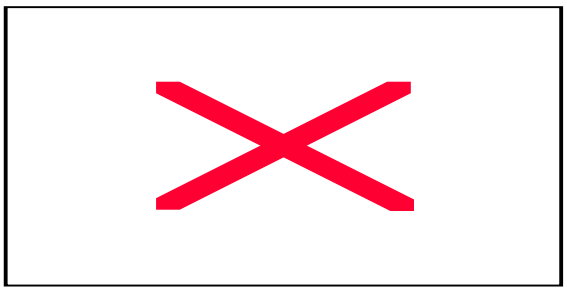
To a CH_2Cl_2 solution (4.0 mL) of compound **2-*syn*** (250 mg, 0.445 mmol) was added 50% *m*-CPBA (*m*-chloroperbenzoic acid, 70 mg, 0.67 mmol, and the mixtures were stirred for 8 h before addition of $Na_2S_2O_3$. The solution was extracted with diethyl ether, dried over $MgSO_4$ and eluted through a short silica bed (diethyl ether/hexane=1/1) to afford oxacyclic diene **3a** (87 mg, 0.378 mmol, R_f = 0.75, 85%).



Spectral data for **3b** : IR (nujol)_2980 (w), 2852 (s), 2305 (w), 1265 (s), 1H NMR (400 MHz, $CDCl_3$)__ 7.24~7.32 (5H, m, Ph), 6.46 (1H, dd, *J* = 11.2, 18.0 Hz), 5.97 (1H, d, *J* = 0.8 Hz), 5.27 (1H, d, *J* = 17.6 Hz), 5.14 (1H, d, *J* = 10.8 Hz), 4.94 (1H, d, *J* = 4.8 Hz), 4.75; 4.32 (1H, dd, *J* = 5.2, 5.6 Hz), 4.61 (1H, d, *J* = 14.0 Hz), 4.57; 4.49 (2H, AB quartet, *J* = 12.0 Hz), 3.81 (1H, dq, *J* = 2.0, 13.0 Hz), 1.24 (3H, d, *J* = 6.4 Hz), 13C NMR (100 MHz, $CDCl_3$)__ 138.9, 138.6, 129.7, 128.1, 127.4, 127.2, 126.8, 116.2, 87.3, 75.5, 74.9, 71.4, 16.1. $[\_]_D$=+53.6 ($CHCl_3$, c=2.2). HRMS Calcd. for $C_{15}H_{18}O_2$_230.13068.

(10) Synthesis of (3*S*, 5a*R*, 9a*R*, 9b*R*)-3-[1-(benzyloxy)ethyl]-1,3,5,5a,6,7,8,9,9a,9b-decahydrobenzo[e]isobenzofuran-9-one (4b)

____**3b** (29.0 mg, 0.126 mmole)_2-Cyclohexen-1-one (0.061 ml, 0.63 mmole)__5ml_____-78_____BF_3-OEt_2 (0.014 ml, 1.38 mmole)_____2__ _____ _____(TLC)_____(1 / 1)_____**4b** (28.4 mg, 0.087 mmole)_ R_f = 0.54 (__/___= 2 / 1)___69 %_

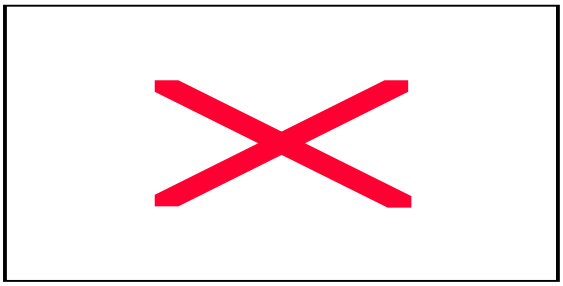


Spectral data for **4b** : IR (nujol)_2932 (m), 2866 (m), 1708 (s), 1H NMR (400 MHz, $CDCl_3$)__ 7.18~7.38 (5H, m, Ph), 5.51~5.55 (1H, m), 4.62; 4.57 (2H, AB quartet, *J* = 12.0 Hz), 4.54 (1H, t, *J* = 7.6 Hz), 4.28~4.32 (1H, m), 3.53~3.59 (1H, m), 3.11 (1H, dd, *J* = 8.0, 10.4 Hz), 2.66~2.80 (1H, m), 2.26~2.46 (3H, m), 1.92~2.32 (3H, m), 1.74~1.88 (2H, m), 1.66 (1H, tq, *J* = 3.2, 13.6

Hz), 1.44 (1H, dq, *J* = 3.6, 11.8 Hz), 1.12 (3H, d, *J* = 6.0 Hz), 13C NMR (100 MHz, $CDCl_3$)__ 211.1, 140.2, 138.9 , 128.2 , 127.6 , 127.3, 118.1, 82.2, 76.4, 73.2, 71.4, 54.4, 41.9, 40.4, 40.1, 33.9, 32.3, 26.0, 15.2. [_]$_D$=50.6 ($CHCl_3$, c=3.5). HRMS Calcd for $C_{21}H_{26}O_3$_326.18819.

(11) Synthesis of (3*S*, 5a*R*, 9a*S*,9b*R*)-3-[1-(benzyloxy)ethyl]-1,3,5,5a,6,9,9a,9b-octahydro-benzo[e]isobenzofuran-6,9-dione (5b)

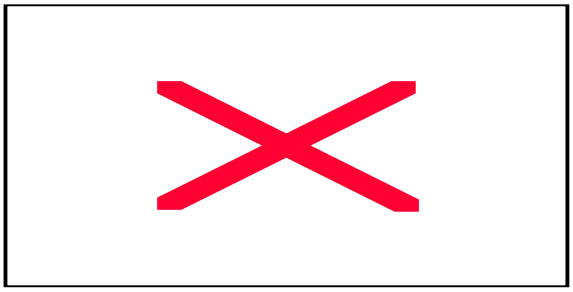
____**3b** (23.0 mg, 0.10 mmole)_1,4-Benzoquinone (10.9 mg, 0.1 mmole)__3ml_____-78_____BF_3-OEt$_2$ (0.125 ml, 1 mmole)_____12___ _____ (TLC)_____(1 / 1)_____**5b** (25.6 mg, 0.076 mmole)_ R_f= 0.5 (__/___ = 2 / 1)___76 %_



Spectral data for **5b** : IR (nujol)_3059 (m), 2980 (m), 1695 (s), 1653 (w), 1H NMR (400 MHz, $CDCl_3$)__ 7.20~7.40 (5H, m, Ph), 6.57 (2H, q, *J* = 10.8 Hz), 5.40~5.55 (1H, br), 4.62; 4.48 (2H, AB quartet, *J* = 12.0 Hz), 4.42~4.47 (2H, m), 4.08 (1H, t, *J* = 8.0 Hz), 3.63 (1H, dq, *J* = 3.6, 6.4 Hz), 3.52 (1H, t, *J* = 5.2 Hz), 3.12 (1H, m), 2.70~2.85 (1H, br), 2.33~2.43 (1H, m), 2.16~2.26 (1H, m') , 1.18 (3H, d, *J* = 6.8 Hz), 13C NMR (100 MHz, $CDCl_3$)__ 200.6, 198.2, 140.8, 140.5, 138.6, 128.2, 127.7, 127.5, 137.4, 114.4, 82.1, 76.0, 71.3, 68.5, 48.7, 46.1, 41.1, 26.7, 15.1. [_]$_D$=-97.5 ($CHCl_3$, c=1.0). HRMS Calcd for $C_{21}H_{22}O_4$_338.15181.

(12) Synthesis of (3*S*, 5a*R*, 8a*R*, 8b*R*)-3-[1-(benzyloxy)ethyl]-3,5,5a,6,7,8,8a,8b-octa-hydro-1H-cyclopenta[e]isobenzofuran-8-one (6b)

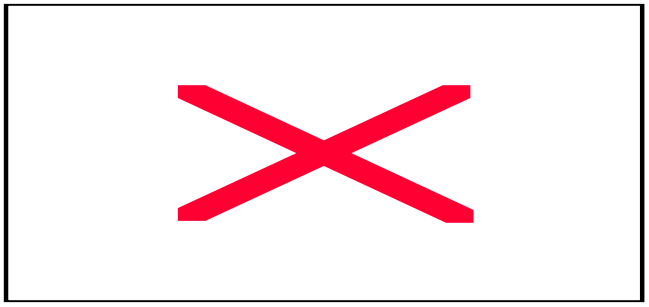
____**3b** (24.6 mg, 0.107 mmole)_2-Cyclopenten-1-one (0.09 ml, 1.07 mmole)__3ml_____-78_____BF_3-OEt$_2$ (0.013 ml, 0.107 mmole)_____2__ _____ _____(TLC)_____(1 / 1)_____**6b** (21.4 mg, 0.068 mmole)_ R_f = 0.50 (__/___= 1 / 1)___64 %_



Spectral data for **6b** : IR (nujol)_2972 (w), 2930 (w), 2876 (m), 1738 (s), 1H NMR (400 MHz, $CDCl_3$)__ 7.20-7.40 (5H, m, Ph), 5.61-5.66 (1H, br), 4.62, 4.55 (2H, AB quartet, J = 14.0 Hz), 4.53 (1H, t, J = 8.0 Hz), 4.30-4.43 (1H, br), 3.53~3.60(1H, m), 3.24 (1H, dd, J = 8.0, 10.6 Hz, H), 2.52-2.62 (1H, m), 2.36-2.52 (2H, m), 2.12-2.30 (2H, m), 1.98-2.08 (1H, m), 1.80-1.92 (1H, m), 1.50-1.62 (1H, m), 1.12 (3H, d, J = 6.0 Hz), 13C NMR (100 MHz, $CDCl_3$)__ 217.3, 141.2, 138.78, 128.2, 127.5, 127.4, 119.9, 81.8, 76.3, 72.3, 71.3, 54.7, 41.7, 38.6, 37.6, 32.1, 28.0, 15.2. $[\_]_D$=-74.0 ($CHCl_3$, c=1.0). HRMS Calcd for $C_{20}H_{24}O_3$_312.1725. Anal. Calcd. for $C_{20}H_{24}O_3$_C, 76.89; H, 7.74; O, 15.36

(13) Synthesis of (3*S*, 5a*R*, 8a*S*, 8b*R*)-3-[1-(benzyloxy)ethyl]-7-phenyl-3,5,5a,6,7,8,8a,8b-octahydro-1H-furo[3,4-e]is-oindole-6,8-dione (7b)

____**3b** (28.0 mg, 0.122 mmole)_NMR tube____N-phenylmaleimide (21.0 mg, 0.122 mmole)_0.50ml_d_8-toluene_____80____3_____^{1}H-NMR_____ (TLC)_____ (1 / 1)_____**7b** (45.7 mg, 0.113 mmole)_R_f= 0.29 (__/___ = 2 / 1)___93 %_

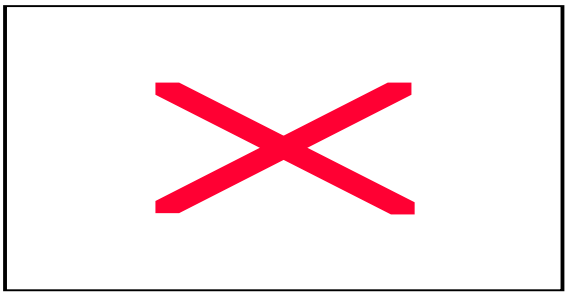


Spectral data for **7b** : IR (nujol)_3036 (m), 3008 (m), 1778 (w), 1711 (s), 1H NMR (400 MHz, $CDCl_3$)__ 7.18~7.45 (5H, m, Ph), 5.70~5.85 (1H, br), 4.63: 4.47 (2H, AB quartet, J = 12.0 Hz), 4.39 (1H, s), 4.35 (2H, d, J = 7.6 Hz), 3.65~3.69 (1H, m), 3.44 (1H, t, J = 8.8 Hz), 3.30 (1H, t, J =

8.4 Hz), 2.95 (1H, dd, *J* = 7.2, 15.4 Hz), 2.86~2.90 (1H, m), 2.18~2.24 (1H, m) , 1.20 (3H, d, *J* = 6.8 Hz), 13C NMR (100 MHz, $CDCl_3$)__ 178.4, 176.2, 143.9, 138.6, 131.9, 129.1, 128.6, 128.3, 127.6, 127.5, 126.4, 116.5, 82.2, 75.9, 71.3, 69.2, 40.8, 40.2, 39.6, 24.6, 15.1. [_]$_D$=+37.1 ($CHCl_3$, c=2.0). HRMS Calcd for $C_{25}H_{25}NO_4$_403.17836. Anal. Calcd. for $C_{25}H_{25}NO_4$_C, 74.42; H, 6.25; N, 3.47; O, 15.86

(14) Synthesis of (3a*R*, 6*S*, 8a*R*, 8b*S*)-6-[1-(benzyloxy)ethyl]-1,3,3a,4,6, 8,8a,8b-octa-hydrofuro[3,4-e]isobenzofuran-1,3-dione (8b)

____**3b** (35.0 mg, 0.152 mmole)_NMR tube____maleic anhydride (15.0 mg, 0.152 mmole)_0.50ml_d_8-toluene_____80____4_____^{1}H-NMR_____**8b** (46.8 mg, 0.143 mmole)_R_f= 0.25 (__/___ = 2 / 1)___86 %_

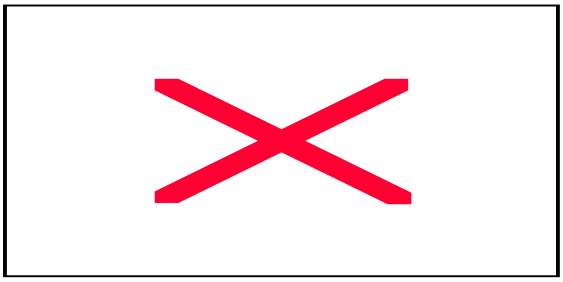


Spectral data for **8b** : IR (nujol)_3007 (m), 2870 (m), 1852 (m), 1779 (s), 1H NMR (500 MHz, $CDCl_3$)__ 7.23~7.32 (5H, m, Ph), 5.74~5.78 (1H, m), 4.59; 4.41 (2H, AB quartet, *J* = 12.0 Hz), 4.32~4.40 (1H, br), 4.34 (1H, t, *J* = 8.5 Hz), 4.20 (1H, dd, *J* = 7.5, 9.0 Hz), 3.64 (1H, dq, *J* = 3.5, 6.5 Hz), 3.53 (1H, t, *J* = 9.0 Hz), 3.41~3.45 (1H, m,), 2.81 (1H, ddd, *J* = 1.5, 7.0, 15.6 Hz), 2.75~2.80 (1H, m), 2.15~2.21 (1H, m), 1.18 (3H, d, *J* = 6.5 Hz), 13C NMR (100 MHz, $CDCl_3$)__ 173.8, 170.9, 144.5, 138.4, 128.3, 127.6, 127.6, 116.3, 82.0, 76.0, 71.2, 69.0, 41.4, 40.6, 38.8, 24.6, 15.0. [_]$_D$=+42.5 ($CHCl_3$, c=1.8). HRMS Calcd for $C_{19}H_{20}O_5$_328.13108. Anal. Calcd. for $C_{19}H_{20}O_5$_C, 69.50; H, 6.14; O, 24.36

(15) Synthesis of (3*S*, 3a*S*, 5a*R*, 8a*S*, 8b*S*)-3-acetyl-7-phenylperhydrofuro[3,4-e]isoindole-6,8-dione (9)

____**7a**_107.0 mg, 0.265 mmole___6ml_____Pd/C_55.8 mg, 0.053 mmole_____3_____1_ _ _ _ _ _ _ _ _ _ _ _ 1 2 _ _ _ _ celite

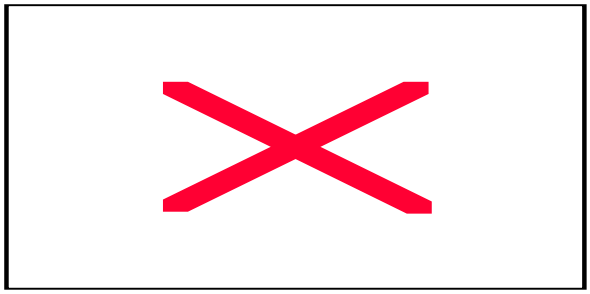
_Pd/C_____ _ 3 m l _ _ _ _ _ _ _ _ _ _ _ _ _ _ _ _ _ _ _ PCC (pyridinium chlorochromate)_1 1 4 . 0 m g, 0 . 5 3 m m o l e_____3_ _ _ _ celite _____/___ = 2 / 1 _____**9** _68 mg, 0.217 mmole__R_f= 0.25 (__)___82 %_



Spectral data for **9** : IR (nujol)_ 1779 (m), 1712 (s), 1608 (m), 1H NMR (400 MHz, $CDCl_3$)__ 7.20~7.48 (5H, m, Ph), 4.16 (1H, t, *J* = 8.0 Hz), 3.98 (1H, d, *J* = 5.2 Hz), 3.83 (H, t, *J* = 8.8 Hz), 3.24 (1H, dd, *J* = 8.0, 9.4 Hz), 3.09~3.15 (1H, m), 2.88 (1H, m), 2.51 (1H, m), 1.62 (3H, s), 2.07~2.17 (1H, m), 1.87~1.97 (H, m), 1.74~1.83 (H, m), 1.45~1.54 (H, m), 13C NMR (100 MHz, $CDCl_3$)__ 209.5, 178.1, 177.2, 131.6, 129.4, 128.6, 126.2, 90.1, 69.8, 39.5, 38.6, 37.8, 36.4, 26.1, 23.9, 20.2. [_]$_D$=-19.1 ($CHCl_3$, c=4.2), HRMS Calcd for $C_{18}H_{19}NO_4$_313.34780_Anal. Calcd. for $C_{18}H_{19}NO_4$_C, 68.99; H, 6.11; N, 4.47; O, 20.42

(16) Synthesis of (3*S*, 3a*R*, 5aS, 8a*R*, 8b*R*)-6,8-dioxo-7-phenylperhydrofuro[3,4-e]iso-indol-3-yl acetate (10)

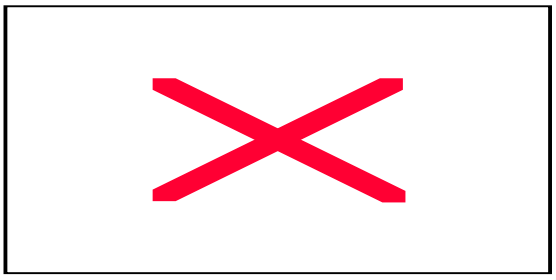
To a dichloromethane solution of **9**_30.0 mg, 0.096 mmole_ were added sodium hydrogen carbonate (12.2 mg, 0.144 mmole) and *m*-chloroperbenzoic acid (52.9 mg, 0.287 mmole). The resulting mixture was stirred at 0_ to room temperature. Excess *m*-CPBA was quenched with aqueous sodium sulfite solution then washed with aqueous sodium hydrogen carbonate. The solution was extracted with dichloromethane, dried over $MgSO_4$ and eluted through a short silica bed (diethyl ether) to afford oxacyclic diene **10** (30.0 mg, 0.088 mmole, R_f = 0.55, 94%).



Spectral data for **10** : IR (nujol)_ 1719 (s), 1597 (m), 1H NMR (400 MHz, $CDCl_3$)__ 7.20~7.50 (5H, m, Ph), 6.00 (1H, s), 4.19 (1H, t, *J* = 8.8 Hz), 3.63~3.69 (1H, m), 3.24~3.34 (2H, m), 3.06 (1H, dq, *J* = 2.4, 13.8 Hz), 2.38 (1H, q, *J* = 6.8 Hz), 1.98~2.10 (1H, m), 2.02 (3H, s), 1.83~1.93 (1H, m), 1.64~1.74 (1H, m), 1.43~1.53 (1H, m), 13C NMR (100 MHz, $CDCl_3$)__ 177.8, 177.2, 170.1, 131.5, 129.2, 128.7, 126.2, 104.2, 69.6, 41.9, 38.4, 37.8, 33.8, 21.7, 21.2, 19.7. $[\_]_D$=-71.3 ($CHCl_3$, c=1.7), HRMS Calcd for $C_{18}H_{19}NO_5$_329.12632_Anal. Calcd. for $C_{18}H_{19}NO_5$_C, 65.64; H, 5.81; N, 4.25; O, 24.29

(17) Synthesis of (3*R*, 3a*R*, 5a*S*, 8a*R*, 8b*R*)-3-acetyl-7-phenylperhydrofuro[3,4-e]iso-indole-6,8-dione (*ent*-9)

____**7b**_40.0 mg, 0.10 mmole___5ml_____Pd/C _20.9 mg, 0.02 mmole_____3_____1_ _ _ _ _ _ _ _ _ _ _ 1 2 _ _ _ _ celite _Pd/C_____5 ml_____PCC (Pyridinium chlorochromate)_43.0 mg, 0.20 mmole_____3_ _ _ _ celite _____/___ = 2 / 1 _____***ent*-9**_26.0 mg, 0.083 mmole__R_f= 0.25 (__)___83 %_

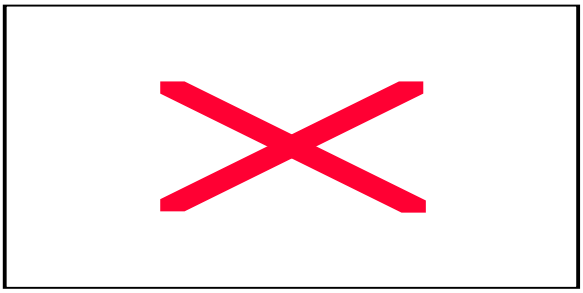


Spectral data for ***ent*-9** : IR (nujol)_ 1782 (m), 1709 (s), 1602 (m), 1H NMR (400 MHz, $CDCl_3$)__ 7.20~7.48 (5H, m, H), 4.16 (1H, t, *J* = 8.4 Hz), 3.98 (1H, d, *J* = 4.8 Hz), 3.84 (1H, t, *J*

= 8.8 Hz), 3.24 (1H, t, *J* = 8.0 Hz), 3.13 (1H, dt, *J* = 7.2, 9.2 Hz), 2.88 (1H, m), 2.51 (1H, m), 2.20 (3H, s), 2.05~2.16 (1H, m), 1.80~1.98 (1H, m), 1.75~1.83 (1H, m), 1.46~1.54 (1H, m), 13C NMR (100 MHz, $CDCl_3$)__ 209.6, 178.1, 177.2, 131.6, 129.2, 128.7, 126.2, 90.2, 69.8, 39.5, 38.6, 37.8, 36.4, 26.2, 23.9, 20.2. [_]$_D$=+19.1 ($CHCl_3$, c=1.6), HRMS Calcd for $C_{18}H_{19}NO_4$_313.13141_Anal. Calcd. for $C_{18}H_{19}NO_4$_C, 68.99; H, 6.11; N, 4.47; O, 20.42

(18) Synthesis of (3*R*, 3a*S*, 5a*R*, 8a*S*, 8b*S*)-6,8-dioxo-7-phenylperhydrofuro[3,4-e]iso-indol-3-yl acetate (*ent*-10)

To a dichloromethane solution of ***ent*-9**_32.0 mg, 0.102 mmole_ were added sodium hydrogen carbonate (11.3 mg, 0.133 mmole) and *m*-chloroperbenzoic acid (52.9 mg, 0.306 mmole). The resulting mixture was stirred at 0_ to room temperature. Excess *m*-CPBA was quenched with aqueous sodium sulfite solution then washed with aqueous sodium hydrogen carbonate. The solution was extracted with dichloromethane, dried over $MgSO_4$ and eluted through a short silica bed (diethyl ether) to afford oxacyclic diene ***ent*-10** (31.5 mg, 0.096 mmole, R_f= 0.54, 94%).



Spectral data for ***ent*-10** : IR (nujol)_1713 (s), 1598 (m), 1H NMR (400 MHz, $CDCl_3$)__ 7.20~7.48 (5H, m, Ph), 6.00 (1H, s), 4.19 (1H, t, *J* = 9.2 Hz), 3.60~3.70 (1H, m), 3.24~3.30 (2H, m), 3.06 (1H, dq, *J* = 2.0, 6.8 Hz), 2.38 (1H, q, *J* = 6.8 Hz), 1.99~2.11 (1H, m), 2.03 (3H, s), 1.84~1.93 (1H, m), 1.64~1.74 (1H, m), 1.43~1.53 (1H, m), 13C NMR (100 MHz, $CDCl_3$)__ 177.9, 177.2, 170.1, 131.5, 129.2, 128.7, 126.2, 104.2, 69.6, 41.9, 38.4, 37.8, 33.8, 21.7, 21.2, 19.7. [_]$_D$=+71.3 ($CHCl_3$, c=1.0), HRMS Calcd for $C_{18}H_{19}NO_5$_329.12632_Anal. Calcd. for $C_{18}H_{19}NO_5$_C, 65.64; H, 5.81; N, 4.25; O, 24.29

(II) Crystal data

(1) Crystal data of 5b.

Table 1. Crystal data and structure refinement for **5b**.

Identification code	au08m	
Empirical formula	C21 H22 O4	
Formula weight	338.39	
Temperature	294(2) K	
Wavelength 0.71073 Å		
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 11.3392(18) Å	α= 90°.
	b = 6.4915(11) Å	β= 92.829(4)°.
	c = 12.206(2) Å	γ = 90°.
Volume	897.4(3) $Å^3$	
Z	2	
Density (calculated)	1.252 Mg/m^3	
Absorption coefficient	0.086 mm^{-1}	
F(000)	360	
Crystal size	0.6 x 0.15 x 0.1 mm^3	
Theta range for data collection	1.67 to 28.22°.	
Index ranges	$-14 \le h \le 14$, $-8 \le k \le 8$, $-16 \le l \le 12$	
Reflections collected	5456	
Independent reflections	3514 [R(int) = 0.0431]	
Completeness to theta = 28.22°	90.4 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3514 / 1 / 227	
Goodness-of-fit on F^2	1.041	
Final R indices [I>2sigma(I)]	R1 = 0.0607, wR2 = 0.1506	
R indices (all data)	R1 = 0.1054, wR2 = 0.1740	
Absolute structure parameter	-1(2)	
Extinction coefficient	0.011(5)	
Largest diff. peak and hole	0.158 and -0.181 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for au08m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	8591(3)	654(6)	5034(3)	106(1)
O(2)	6256(3)	-5235(5)	2901(4)	110(1)
O(3)	4015(2)	-1556(7)	1063(2)	97(1)
O(4)	1947(2)	331(5)	2990(2)	69(1)
C(1)	8036(3)	-740(7)	4553(3)	68(1)
C(2)	8461(4)	-2833(8)	4565(4)	75(1)
C(3)	7947(3)	-4315(7)	3977(4)	73(1)
C(4)	6917(3)	-3857(7)	3201(4)	67(1)
C(5)	6789(3)	-1620(6)	2874(3)	57(1)
C(6)	6882(3)	-308(6)	3916(3)	60(1)
C(7)	5842(3)	-778(7)	4641(3)	61(1)
C(8)	4677(3)	-946(7)	3969(3)	56(1)
C(9)	4625(3)	-1016(6)	2905(3)	51(1)
C(10)	5681(3)	-965(7)	2210(3)	63(1)
C(11)	5232(4)	-2155(10)	1195(3)	91(2)
C(12)	3558(3)	-1322(7)	2130(3)	63(1)
C(13)	2652(3)	431(7)	2066(3)	59(1)
C(14)	3210(4)	2536(8)	2059(4)	83(1)
C(15)	973(3)	-1066(9)	2867(4)	76(1)
C(16)	22(3)	-292(7)	2043(3)	63(1)
C(17)	-441(4)	1624(8)	2110(4)	76(1)
C(18)	-1342(4)	2251(10)	1366(5)	95(2)
C(19)	-1761(4)	966(13)	580(4)	97(2)
C(20)	-1284(5)	-978(12)	503(4)	103(2)
C(21)	-407(4)	-1595(8)	1227(4)	80(1)

Table 3. Bond lengths [Å] and angles [°] for au08m.

O(1)-C(1)	1.234(5)	C(19)-C(20)	1.378(8)
O(2)-C(4)	1.212(5)	C(20)-C(21)	1.358(8)
O(3)-C(12)	1.433(5)	C(12)-O(3)-C(11)	108.4(3)
O(3)-C(11)	1.434(5)	C(13)-O(4)-C(15)	114.1(3)
O(4)-C(13)	1.416(4)	O(1)-C(1)-C(2)	121.6(4)
O(4)-C(15)	1.430(5)	O(1)-C(1)-C(6)	121.0(4)
C(1)-C(2)	1.441(7)	C(2)-C(1)-C(6)	117.4(4)
C(1)-C(6)	1.515(5)	C(3)-C(2)-C(1)	122.9(4)
C(2)-C(3)	1.319(6)	C(2)-C(3)-C(4)	120.7(4)
C(3)-C(4)	1.496(6)	O(2)-C(4)-C(3)	119.8(4)
C(4)-C(5)	1.511(6)	O(2)-C(4)-C(5)	125.4(4)
C(5)-C(10)	1.522(5)	C(3)-C(4)-C(5)	114.8(4)
C(5)-C(6)	1.530(5)	C(4)-C(5)-C(10)	118.4(3)
C(6)-C(7)	1.539(5)	C(4)-C(5)-C(6)	108.2(3)
C(7)-C(8)	1.524(5)	C(10)-C(5)-C(6)	108.0(3)
C(8)-C(9)	1.299(5)	C(1)-C(6)-C(5)	110.2(3)
C(9)-C(10)	1.502(4)	C(1)-C(6)-C(7)	109.6(3)
C(9)-C(12)	1.511(5)	C(5)-C(6)-C(7)	110.2(3)
C(10)-C(11)	1.525(6)	C(8)-C(7)-C(6)	111.9(3)
C(12)-C(13)	1.532(6)	C(9)-C(8)-C(7)	122.4(3)
C(13)-C(14)	1.506(6)	C(8)-C(9)-C(10)	124.5(3)
C(15)-C(16)	1.522(6)	C(8)-C(9)-C(12)	128.8(3)
C(16)-C(17)	1.354(6)	C(10)-C(9)-C(12)	106.6(3)
C(16)-C(21)	1.378(6)	C(9)-C(10)-C(5)	110.7(3)
C(17)-C(18)	1.394(7)	C(9)-C(10)-C(11)	101.8(3)
C(18)-C(19)	1.340(9)	C(5)-C(10)-C(11)	121.7(4)

O(3)-C(11)-C(10)	103.6(4)	C(17)-C(16)-C(15)	121.8(4)
O(3)-C(12)-C(9)	105.6(3)	C(21)-C(16)-C(15)	119.2(4)
O(3)-C(12)-C(13)	107.7(3)	C(16)-C(17)-C(18)	120.2(5)
C(9)-C(12)-C(13)	116.6(3)	C(19)-C(18)-C(17)	120.4(5)
O(4)-C(13)-C(14)	107.4(4)	C(18)-C(19)-C(20)	119.5(4)
O(4)-C(13)-C(12)	109.2(3)	C(21)-C(20)-C(19)	120.2(5)
C(14)-C(13)-C(12)	113.2(3)	C(20)-C(21)-C(16)	120.7(5)
O(4)-C(15)-C(16)	112.2(4)		
C(17)-C(16)-C(21)	118.9(4)		

Symmetry transformations used to generate equivalent atoms:

Table 4.Anisotropic displacement parameters ($Å^2 x\ 10^3$) for au08m. 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)	89(2)	82(2)	141(3)	-21(2)	-57(2)	-7(2)
O(2)	86(2)	71(2)	168(4)	-31(2)	-29(2)	-2(2)
O(3)	51(2)	176(4)	63(2)	-38(2)	-12(1)	3(2)
O(4)	45(1)	98(2)	65(2)	-2(2)	-5(1)	2(2)
C(1)	51(2)	72(3)	78(3)	1(2)	-19(2)	-6(2)
C(2)	54(2)	82(3)	86(3)	17(3)	-15(2)	9(2)
C(3)	57(2)	64(3)	99(3)	-2(3)	-1(2)	5(2)
C(4)	44(2)	77(3)	79(3)	-17(2)	-1(2)	0(2)
C(5)	40(2)	71(3)	59(2)	1(2)	-6(2)	-5(2)
C(6)	52(2)	56(2)	71(2)	0(2)	-17(2)	-3(2)
C(7)	56(2)	71(3)	56(2)	-1(2)	-10(2)	13(2)
C(8)	49(2)	62(2)	57(2)	3(2)	2(2)	7(2)
C(9)	42(2)	57(2)	53(2)	-1(2)	-2(1)	-4(2)
C(10)	43(2)	97(3)	48(2)	2(2)	-4(2)	-3(2)
C(11)	54(2)	155(5)	64(3)	-21(3)	-4(2)	9(3)
C(12)	53(2)	77(3)	59(2)	-6(2)	-5(2)	-5(2)
C(13)	42(2)	77(3)	56(2)	3(2)	-8(2)	-4(2)
C(14)	76(3)	74(3)	96(3)	17(3)	-26(2)	-7(3)
C(15)	47(2)	95(3)	85(3)	12(3)	2(2)	-3(2)
C(16)	41(2)	80(3)	67(2)	2(2)	5(2)	0(2)
C(17)	63(2)	83(3)	81(3)	-6(2)	-3(2)	10(2)
C(18)	55(3)	123(5)	108(4)	28(4)	9(3)	20(3)
C(19)	61(3)	165(6)	64(3)	39(4)	-13(2)	-6(4)
C(20)	89(3)	148(6)	70(3)	-20(4)	-5(3)	-28(4)
C(21)	65(2)	100(4)	74(3)	-15(3)	7(2)	1(3)

Table 5. Hydrogen coordinates ($x\ 10^4$) and isotropic displacement parameters ($Å^2 x\ 10^3$) for au08m.

	x	y	z	U(eq)
H(3)	8137	-6127	3970	80
H(2)	8909	-3241	4949	80
H(5)	7573	-1335	2502	80
H(6)	6961	1224	3708	80
H(7)	5778	487	5202	80
H(7A)	6039	-2142	5057	80
H(8)	3906	-1089	4446	80
H(10)	5801	703	1992	80
H(11)	5568	-1533	556	80
H(11A)	5325	-3909	1452	80
H(12)	3254	-2588	2465	80
H(13)	2149	402	1302	80
H(14)	2747	3342	1968	80
H(14A)	3764	2911	2721	80
H(14B)	3687	2518	1396	80
H(15)	608	-974	3556	80
H(15A)	1249	-2632	2608	80
H(17)	-166	2449	2644	80
H(18)	-1805	3132	1528	80
H(19)	-2156	1117	88	80
H(20)	-1452	-1792	-7	80
H(21)	19	-2932	1189	80

(2).Crystal data of 8b

Table 1. Crystal data and structure refinement for **8b**

Identification code	Ic7418	
Empirical formula	$C_{19}H_{20}O_5$	
Formula weight	328.35 g/mole	
Temperature	295(2)K	
Wavelength	0.71073Å	
Crystal system	Orthorhombic	
Spec group	$P2_12_12_1$	
Unit cell dimensions	a = 6.8329(2) Å	apha=90°
	b =8.1545(2) Å	beta=90°
	c =29.6514(2) Å	gamma=90°
Volume, Z	1633.29(7) $Å^3$, 4	
Density (calculated)	1.311 Mg /m^3	
Apsorption coefficient	0.095mm^{-1}	
F(000)	696	
Crystal size	0.50 x 0.20 x 0.05 mm	
_range for data collection	2.59 to 26.38°	
Limiting indices	-8_*h*_8, -10_*k*_10, -37_*l*_29	
Reflections collected	8853	
Independent reflections	3320 (R_{int} = 0.0566)	
Absorption correction	Empirical uesd sadabs	
Max. and min. Transmission	0.9780 and 0.7487	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3320 / 0 / 218	
Goodness-of-fit on F^2	1.114	
Final R indices [I>2_(I)]	R1 = 0.0749, WR2 = 0.1057	
R indices (all data)	R1 = 0.1172, WR2 = 0.1172	
Absolute structure parameter	-1(2)	
Extinction coefficient	0.0118 (12)	
Largest diff. Peak and hole	0.263 and –0.167 e $Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 7418. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	9687(5)	8563(3)	2194(1)	79(1)
O(2)	8984(3)	7139(3)	1069(1)	56(1)
O(3)	3558(3)	12049(3)	1996(1)	56(1)
O(4)	4952(4)	10849(4)	2587(1)	82(1)
O(5)	2883(4)	13425(4)	1372(1)	94(1)
C(1)	9267(5)	10119(4)	2379(1)	51(1)
C(2)	8659(4)	11236(4)	1993(1)	38(1)
C(3)	6980(4)	12457(3)	2069(1)	40(1)
C(4)	6274(4)	13236(4)	1628(1)	44(1)
C(5)	7134(5)	12450(4)	1201(1)	55(1)
C(6)	7366(5)	10621(4)	1250(1)	48(1)
C(7)	8152(4)	10060(3)	1624(1)	38(1)
C(8)	8694(5)	8355(4)	1769(1)	53(1)
C(9)	10113(5)	7440(4)	1461(1)	54(1)
C(10)	12004(5)	8349(5)	1380(1)	72(1)
C(11)	9923(5)	6189(4)	737(1)	51(1)
C(12)	8458(5)	5613(4)	395(1)	44(1)
C(13)	6514(5)	6076(5)	412(1)	60(1)
C(14)	5217(6)	5519(5)	90(1)	75(1)
C(15)	5840(7)	4503(6)	-243(2)	80(1)
C(16)	7764(7)	4054(6)	-265(1)	83(1)
C(17)	9072(6)	4607(5)	55(1)	68(1)

C(18)	5165(5)	11670(4)	2256(1)	51(1)
C(19)	4090(5)	12989(4)	1629(1)	55(1)

Table 3. Bond lengths [Å] and angles [°] for 7418.

O (1) – C (1)	1.414 (4)	O (1) – C (8)	1.477 (4)
O (2) – C (11)	1.412 (3)	O (2) – C (9)	1.424 (4)
O (3) – C (18)	1.379 (4)	O (3) – C (19)	1.387 (4)
O (4) – C (18)	1.202 (4)	O (5) – C (19)	1.181 (4)
O (1) – C (2)	1.528 (4)	O (2) – C (7)	1.501 (4)
O (2) – C (3)	1.536 (4)	O (3) – C (18)	1.504 (4)
O (3) – C (4)	1.540 (4)	O (4) – C (19)	1.506 (4)
O (4) – C (5)	1.544 (4)	O (5) – C (6)	1.508 (4)
O (6) – C (7)	1.319 (4)	O (7) – C (8)	1.503 (4)
O (8) – C (9)	1.531 (4)	O (9) – C (10)	1.509 (5)
O (11) – C (12)	1.504 (4)	O (12) – C (17)	1.371 (5)
O (12) – C (13)	1.382 (4)	O (13) – C (14)	1.383 (5)
O (14) – C (15)	1.362 (4)	O (15) – C (16)	1.366 (6)
O (16) – C (17)	1.383 (4)		

C(1)-O(1)-C(8)	110.7 (2)	C(11)-O(2)-C(9)	115.2 (2)
C(18)-O(3)-C(19)	111.1 (3)	O(1)-C(1)-C(2)	107.1 (2)
C(7)-C(2)-C(1)	103.6 (2)	C(7)-C(2)-C(3)	110.5 (2)
C(1)-C(2)-C(3)	118.5 (2)	C(18)-C(3)-C(2)	113.2 (2)
C(18)-C(3)-C(4)	103.6 (2)	C(2)-C(3)-C(4)	112.0 (2)
C(19)-C(4)-C(3)	104.7 (3)	C(19)-C(4)-C(5)	108.9 (3)
C(3)-C(4)-C(5)	114.6 (2)	C(6)-C(5)-C(4)	111.7 (3)
C(7)-C(6)-C(5)	118.0 (3)	C(6)-C(7)-C(2)	119.5 (3)
C(6)-C(7)-C(8)	131.7 (3)	C(2)-C(7)-C(8)	108.8 (2)
O(1)-C(8)-C(7)	105.1 (2)	O(1)-C(8)-C(9)	106.6 (3)
C(7)-C(8)-C(9)	115.7 (3)	O(2)-C(9)-C(10)	114.6 (3)
O(2)-C(9)-C(8)	103.6 (3)	C(10)-C(9)-C(8)	113.5 (3)
O(2)-C(11)-C(12)	110.2 (3)	C(17)-C(12)-C(13)	119.0 (3)
C(17)-C(12)-C(11)	119.0 (3)	C(13)-C(12)-C(11)	122.0 (3)
C(12)-C(13)-C(14)	120.0 (3)	C(15)-C(14)-C(13)	120.4 (4)
C(14)-C(15)-C(16)	119.9 (4)	C(15)-C(16)-C(17)	120.1 (4)
C(12)-C(17)-C(16)	120.6 (4)	O(4)-C(18)-O(3)	119.4 (3)
O(4)-C(18)-C(3)	130.0 (3)	O(3)-C(18)-C(3)	110.6 (3)
O(5)-C(19)-O(3)	119.8 (3)	O(5)-C(19)-C(4)	130.6 (4)
O(3)-C(19)-C(4)	109.6 (3)		

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for au08m. 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)	143(3)	49(1)	45(1)	-3(1)	-25(2)	27(2)
O(2)	56(1)	60(2)	51(1)	-17(1)	-6(1)	17(1)
O(3)	29(1)	73(2)	76(2)	-3(1)	4(1)	1(1)
O(4)	57(2)	103(2)	86(2)	34(2)	18(2)	3(2)
O(5)	56(2)	135(3)	92(2)	16(2)	-22(2)	31(2)
C(1)	57(2)	47(2)	49(2)	-7(2)	-9(2)	8(2)
C(2)	28(2)	37(2)	50(2)	3(2)	-1(2)	0(1)
C(3)	33(2)	33(2)	53(2)	-4(2)	-3(2)	-6(1)
C(4)	41(2)	33(2)	57(2)	1(2)	-5(2)	1(1)
C(5)	50(2)	62(2)	54(2)	16(2)	1(2)	10(2)
C(6)	49(2)	54(2)	42(2)	-4(2)	2(2)	8(2)
C(7)	36(2)	38(2)	40(2)	4(2)	6(2)	4(1)
C(8)	70(2)	43(2)	47(2)	1(2)	-3(2)	-1(2)
C(9)	65(2)	46(2)	50(2)	-4(2)	-14(2)	12(2)
C(10)	52(2)	81(3)	84(3)	-18(2)	-12(2)	8(2)
C(11)	50(2)	49(2)	56(2)	-5(2)	3(2)	9(2)
C(12)	51(2)	36(2)	45(2)	4(2)	-3(2)	2(2)
C(13)	60(2)	59(2)	60(2)	-8(2)	-8(2)	6(2)
C(14)	63(3)	76(3)	85(3)	6(2)	-15(3)	6(2)
C(15)	84(3)	84(3)	71(3)	-8(3)	-27(3)	-12(3)
C(16)	92(3)	88(3)	68(3)	-32(3)	-5(3)	0(3)
C(17)	67(3)	68(3)	68(3)	-22(2)	-2(2)	4(2)
C(18)	41(2)	50(2)	62(2)	-5(2)	5(2)	2(2)
C(19)	45(2)	56(2)	64(2)	-5(2)	-4(2)	12(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for au08m.

	x	y	z	U(eq)
H(1A)	10414(5)	10557(4)	2528(1)	61
H(1B)	8216(5)	10032(4)	2596(1)	61
H(2A)	9814(4)	11860(4)	1899(1)	46
H(3A)	7420(4)	13323(3)	2273(1)	48
H(4A)	6568(4)	14413(4)	1630(1)	52
H(5A)	6278(5)	12679(4)	949(1)	66
H(5B)	8400(5)	12937(4)	1137(1)	66
H(6A)	6966(5)	9909(4)	1025(1)	58
H(8A)	7506(5)	7701(4)	1812(1)	64
H(9A)	10425(5)	6382(4)	1600(1)	64
H(10A)	12826(5)	7714(5)	1185(1)	108
H(10B)	12661(5)	8523(5)	1660(1)	108
H(10C)	11727(5)	9388(5)	1243(1)	108
H(11A)	10550(5)	5249(4)	875(1)	62
H(11B)	10925(5)	6840(4)	591(1)	62
H(13A)	6077(5)	6763(5)	640(1)	72
H(14A)	3912(6)	5839(5)	102(1)	90
H(15A)	4957(7)	4116(6)	-455(2)	96
H(16A)	8194(7)	3375(6)	-495(1)	99
H(17A)	10379(6)	4295(5)	39(1)	81

(3) Crystal data of **9**.

Table 1. Crystal data and structure refinement for **8b**

Identification code	Ic7418	
Empirical formula	$C_{19}H_{20}O_5$	
Formula weight	328.35 g/mole	
Temperature	295(2)K	
Wavelength	0.71073Å	
Crystal system	Orthorhombic	
Spec group	$P2_12_12_1$	
Unit cell dimensions	a = 6.8329(2) Å	apha=90°
	b =8.1545(2) Å	beta=90°
	c =29.6514(2) Å	gamma=90°
Volume, Z	1633.29(7) $Å^3$, 4	
Density (calculated)	1.311 Mg /m^3	
Apsorption coefficient	0.095mm^{-1}	
F(000)	696	
Crystal size	0.50 x 0.20 x 0.05 mm	
_range for data collection	2.59 to 26.38°	
Limiting indices	-8_*h*_8, -10_*k*_10, -37_*l*_29	
Reflections collected	8853	
Independent reflections	3320 (R_{int} = 0.0566)	
Absorption correction	Empirical uesd sadabs	
Max. and min. Transmission	0.9780 and 0.7487	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3320 / 0 / 218	
Goodness-of-fit on F^2	1.114	
Final R indices [I>2_(I)]	R1 = 0.0749, WR2 = 0.1057	
R indices (all data)	R1 = 0.1172, WR2 = 0.1172	
Absolute structure parameter	-1(2)	
Extinction coefficient	0.0118 (12)	
Largest diff. Peak and hole	0.263 and –0.167 e $Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 7418. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	9687(5)	8563(3)	2194(1)	79(1)
O(2)	8984(3)	7139(3)	1069(1)	56(1)
O(3)	3558(3)	12049(3)	1996(1)	56(1)
O(4)	4952(4)	10849(4)	2587(1)	82(1)
O(5)	2883(4)	13425(4)	1372(1)	94(1)
C(1)	9267(5)	10119(4)	2379(1)	51(1)
C(2)	8659(4)	11236(4)	1993(1)	38(1)
C(3)	6980(4)	12457(3)	2069(1)	40(1)
C(4)	6274(4)	13236(4)	1628(1)	44(1)
C(5)	7134(5)	12450(4)	1201(1)	55(1)
C(6)	7366(5)	10621(4)	1250(1)	48(1)
C(7)	8152(4)	10060(3)	1624(1)	38(1)
C(8)	8694(5)	8355(4)	1769(1)	53(1)
C(9)	10113(5)	7440(4)	1461(1)	54(1)
C(10)	12004(5)	8349(5)	1380(1)	72(1)
C(11)	9923(5)	6189(4)	737(1)	51(1)
C(12)	8458(5)	5613(4)	395(1)	44(1)
C(13)	6514(5)	6076(5)	412(1)	60(1)
C(14)	5217(6)	5519(5)	90(1)	75(1)
C(15)	5840(7)	4503(6)	-243(2)	80(1)
C(16)	7764(7)	4054(6)	-265(1)	83(1)
C(17)	9072(6)	4607(5)	55(1)	68(1)
C(18)	5165(5)	11670(4)	2256(1)	51(1)

C(19)	4090(5)	12989(4)	1629(1)	55(1)

Table 3. Bond lengths [Å] and angles [°] for 7418.

O (1) – C (1)	1.414 (4)	O (1) – C (8)	1.477 (4)
O (2) – C (11)	1.412 (3)	O (2) – C (9)	1.424 (4)
O (3) – C (18)	1.379 (4)	O (3) – C (19)	1.387 (4)
O (4) – C (18)	1.202 (4)	O (5) – C (19)	1.181 (4)
O (1) – C (2)	1.528 (4)	O (2) – C (7)	1.501 (4)
O (2) – C (3)	1.536 (4)	O (3) – C (18)	1.504 (4)
O (3) – C (4)	1.540 (4)	O (4) – C (19)	1.506 (4)
O (4) – C (5)	1.544 (4)	O (5) – C (6)	1.508 (4)
O (6) – C (7)	1.319 (4)	O (7) – C (8)	1.503 (4)
O (8) – C (9)	1.531 (4)	O (9) – C (10)	1.509 (5)
O (11) – C (12)	1.504 (4)	O (12) – C (17)	1.371 (5)
O (12) – C (13)	1.382 (4)	O (13) – C (14)	1.383 (5)
O (14) – C (15)	1.362 (4)	O (15) – C (16)	1.366 (6)
O (16) – C (17)	1.383 (4)		

C(1)-O(1)-C(8)	110.7 (2)	C(11)-O(2)-C(9)	115.2 (2)
C(18)-O(3)-C(19)	111.1 (3)	O(1)-C(1)-C(2)	107.1 (2)
C(7)-C(2)-C(1)	103.6 (2)	C(7)-C(2)-C(3)	110.5 (2)
C(1)-C(2)-C(3)	118.5 (2)	C(18)-C(3)-C(2)	113.2 (2)
C(18)-C(3)-C(4)	103.6 (2)	C(2)-C(3)-C(4)	112.0 (2)
C(19)-C(4)-C(3)	104.7 (3)	C(19)-C(4)-C(5)	108.9 (3)
C(3)-C(4)-C(5)	114.6 (2)	C(6)-C(5)-C(4)	111.7 (3)
C(7)-C(6)-C(5)	118.0 (3)	C(6)-C(7)-C(2)	119.5 (3)
C(6)-C(7)-C(8)	131.7 (3)	C(2)-C(7)-C(8)	108.8 (2)
O(1)-C(8)-C(7)	105.1 (2)	O(1)-C(8)-C(9)	106.6 (3)
C(7)-C(8)-C(9)	115.7 (3)	O(2)-C(9)-C(10)	114.6 (3)
O(2)-C(9)-C(8)	103.6 (3)	C(10)-C(9)-C(8)	113.5 (3)
O(2)-C(11)-C(12)	110.2 (3)	C(17)-C(12)-C(13)	119.0 (3)
C(17)-C(12)-C(11)	119.0 (3)	C(13)-C(12)-C(11)	122.0 (3)
C(12)-C(13)-C(14)	120.0 (3)	C(15)-C(14)-C(13)	120.4 (4)
C(14)-C(15)-C(16)	119.9 (4)	C(15)-C(16)-C(17)	120.1 (4)
C(12)-C(17)-C(16)	120.6 (4)	O(4)-C(18)-O(3)	119.4 (3)
O(4)-C(18)-C(3)	130.0 (3)	O(3)-C(18)-C(3)	110.6 (3)
O(5)-C(19)-O(3)	119.8 (3)	O(5)-C(19)-C(4)	130.6 (4)
O(3)-C(19)-C(4)	109.6 (3)		

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for au08m. 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)	143(3)	49(1)	45(1)	-3(1)	-25(2)	27(2)
O(2)	56(1)	60(2)	51(1)	-17(1)	-6(1)	17(1)
O(3)	29(1)	73(2)	76(2)	-3(1)	4(1)	1(1)
O(4)	57(2)	103(2)	86(2)	34(2)	18(2)	3(2)
O(5)	56(2)	135(3)	92(2)	16(2)	-22(2)	31(2)
C(1)	57(2)	47(2)	49(2)	-7(2)	-9(2)	8(2)
C(2)	28(2)	37(2)	50(2)	3(2)	-1(2)	0(1)
C(3)	33(2)	33(2)	53(2)	-4(2)	-3(2)	-6(1)
C(4)	41(2)	33(2)	57(2)	1(2)	-5(2)	1(1)
C(5)	50(2)	62(2)	54(2)	16(2)	1(2)	10(2)
C(6)	49(2)	54(2)	42(2)	-4(2)	2(2)	8(2)
C(7)	36(2)	38(2)	40(2)	4(2)	6(2)	4(1)
C(8)	70(2)	43(2)	47(2)	1(2)	-3(2)	-1(2)
C(9)	65(2)	46(2)	50(2)	-4(2)	-14(2)	12(2)
C(10)	52(2)	81(3)	84(3)	-18(2)	-12(2)	8(2)
C(11)	50(2)	49(2)	56(2)	-5(2)	3(2)	9(2)
C(12)	51(2)	36(2)	45(2)	4(2)	-3(2)	2(2)
C(13)	60(2)	59(2)	60(2)	-8(2)	-8(2)	6(2)
C(14)	63(3)	76(3)	85(3)	6(2)	-15(3)	6(2)
C(15)	84(3)	84(3)	71(3)	-8(3)	-27(3)	-12(3)
C(16)	92(3)	88(3)	68(3)	-32(3)	-5(3)	0(3)
C(17)	67(3)	68(3)	68(3)	-22(2)	-2(2)	4(2)
C(18)	41(2)	50(2)	62(2)	-5(2)	5(2)	2(2)
C(19)	45(2)	56(2)	64(2)	-5(2)	-4(2)	12(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for au08m.

	x	y	z	U(eq)
H(1A)	10414(5)	10557(4)	2528(1)	61
H(1B)	8216(5)	10032(4)	2596(1)	61
H(2A)	9814(4)	11860(4)	1899(1)	46
H(3A)	7420(4)	13323(3)	2273(1)	48
H(4A)	6568(4)	14413(4)	1630(1)	52
H(5A)	6278(5)	12679(4)	949(1)	66
H(5B)	8400(5)	12937(4)	1137(1)	66
H(6A)	6966(5)	9909(4)	1025(1)	58
H(8A)	7506(5)	7701(4)	1812(1)	64
H(9A)	10425(5)	6382(4)	1600(1)	64
H(10A)	12826(5)	7714(5)	1185(1)	108
H(10B)	12661(5)	8523(5)	1660(1)	108
H(10C)	11727(5)	9388(5)	1243(1)	108
H(11A)	10550(5)	5249(4)	875(1)	62
H(11B)	10925(5)	6840(4)	591(1)	62
H(13A)	6077(5)	6763(5)	640(1)	72
H(14A)	3912(6)	5839(5)	102(1)	90
H(15A)	4957(7)	4116(6)	-455(2)	96
H(16A)	8194(7)	3375(6)	-495(1)	99
H(17A)	10379(6)	4295(5)	39(1)	81

(4).Crystal data of *ent*-9.

Table 1. Crystal data and structure refinement for **9**.

Identification code	ot06m
Empirical formula	C18 H19 N O4
Formula weight	313.34

Temperature	295(2) K
Wavelength 0.71073 Å	
Crystal system	Orthorhombic
Space group	P2(1)2(1)2(1)
Unit cell dimensions	a = 9.2239(19) Å α= 90°.
	b = 26.248(6) Å β= 90°.
	c = 6.4941(13) Å γ = 90°.
Volume	1572.3(6) $Å^3$
Z	4
Density (calculated)	1.324 Mg/m^3
Absorption coefficient	0.094 mm^{-1}
F(000)	664
Crystal size	0.45 x 0.40 x0.08 mm^3
Theta range for data collection	1.55 to 28.24°.
Index ranges	-11 ≤ h ≤ 12, -34 ≤ k ≤ 33, -6 ≤ l ≤8
Reflections collected	9331
Independent reflections	3506 [R(int) = 0.0228]
Completeness to theta = 28.24°	93.5 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3506 / 0 / 209
Goodness-of-fit on F^2	1.027
Final R indices [I>2sigma(I)]	R1 = 0.0441, wR2 = 0.1064
R indices (all data)	R1 = 0.0581, wR2 = 0.1136
Absolute structure parameter	0.6(13)
Extinction coefficient	0.0010(13)
Largest diff. peak and hole	0.169 and -0.166 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for ot06m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	7510(1)	104(1)	8223(2)	49(1)
O(2)	2749(2)	-215(1) 6854(3)	65(1)	
O(3)	3273(2)	2427(1)	11569(4)	91(1)
O(4)	5086(2)	1280(1)	12270(2)	56(1)
N(1)	5199(2)	-176(1) 7489(3)	44(1)	
C(1)	5773(2)	-887(1)	9775(3)	54(1)
C(2)	5967(3)	-1406(1)	10083(4)	67(1)
C(3)	5758(3)	-1738(1)	8480(5)	77(1)
C(4)	**5400(4)**	**-1558(1) 6558(5)**	**84(1)**	
C(5)	**5228(3)**	**-1042(1) 6229(4)**	**66(1)**	
C(6)	5415(2)	-711(1) 7851(3)	46(1)	
C(7)	3857(2)	27(1)	6918(3)	47(1)
C(8)	4080(2)	580(1) 6413(3)	48(1)	
C(9)	2913(2)	933(1)	7292(4)	61(1)
C(10)	3488(3)	1474(1)	7279(4)	66(1)
C(11)	**4733(2)**	**1544(1) 8773(3)**	**50(1)**	
C(12)	4197(2)	1597(1)	11037(3)	49(1)
C(13)	5457(2)	851(1)	11019(3)	48(1)
C(14)	5781(2)	1080(1)	8906(3)	43(1)
C(15)	5636(2)	703(1)	7097(3)	44(1)
C(16)	6285(2)	189(1)	7667(3)	41(1)
C(17)	4291(3)	2142(1)	11771(4)	60(1)
C(18)	5687(3)	2316(1)	12648(5)	83(1)

Table 3. Bond lengths [Å] and angles [°] for ot06m.

O(1)-C(16)	1.207(2)	O(2)-C(7)	1.204(2)

O(3)-C(17)	1.207(3)	C(3)-C(4)-C(5)	120.3(2)
O(4)-C(12)	1.416(2)	C(6)-C(5)-C(4)	119.1(2)
O(4)-C(13)	1.429(2)	C(5)-C(6)-C(1)	121.01(19)
N(1)-C(16)	1.393(2)	C(5)-C(6)-N(1)	118.32(19)
N(1)-C(7)	1.398(3)	C(1)-C(6)-N(1)	120.65(17)
N(1)-C(6)	1.437(2)	O(2)-C(7)-N(1)	124.05(19)
C(1)-C(6)	1.372(3)	O(2)-C(7)-C(8)	128.18(19)
C(1)-C(2)	1.390(3)	N(1)-C(7)-C(8)	107.78(16)
C(2)-C(3)	1.371(4)	C(7)-C(8)-C(9)	114.00(18)
C(3)-C(4)	1.375(4)	C(7)-C(8)-C(15)	105.52(16)
C(4)-C(5)	1.381(4)	C(9)-C(8)-C(15)	114.96(17)
C(5)-C(6)	1.376(3)	C(10)-C(9)-C(8)	108.60(19)
C(7)-C(8)	1.503(3)	C(11)-C(10)-C(9)	111.94(16)
C(8)-C(9)	1.531(3)	C(10)-C(11)-C(12)	112.00(18)
C(8)-C(15)	1.537(3)	C(10)-C(11)-C(14)	114.36(16)
C(9)-C(10)	1.517(4)	C(12)-C(11)-C(14)	102.41(15)
C(10)-C(11)	1.515(3)	O(4)-C(12)-C(17)	110.19(18)
C(11)-C(12)	1.558(3)	O(4)-C(12)-C(11)	107.26(15)
C(11)-C(14)	1.557(3)	C(17)-C(12)-C(11)	111.38(17)
C(12)-C(17)	1.511(3)	O(4)-C(13)-C(14)	104.38(14)
C(13)-C(14)	1.527(3)	C(13)-C(14)-C(15)	114.58(14)
C(14)-C(15)	1.542(3)	C(13)-C(14)-C(11)	103.62(15)
C(15)-C(16)	1.521(3)	C(15)-C(14)-C(11)	113.93(16)
C(17)-C(18)	1.480(4)	C(16)-C(15)-C(14)	110.43(15)
		C(16)-C(15)-C(8)	104.59(15)
C(12)-O(4)-C(13)	106.27(15)	C(14)-C(15)-C(8)	115.85(16)
C(16)-N(1)-C(7)	113.34(15)	O(1)-C(16)-N(1)	124.76(18)
C(16)-N(1)-C(6)	124.05(16)	O(1)-C(16)-C(15)	127.30(17)
C(7)-N(1)-C(6)	122.60(15)	N(1)-C(16)-C(15)	107.92(16)
C(6)-C(1)-C(2)	119.4(2)	O(3)-C(17)-C(18)	121.8(2)
C(3)-C(2)-C(1)	119.7(2)	O(3)-C(17)-C(12)	120.5(2)
C(4)-C(3)-C(2)	120.3(2)	C(18)-C(17)-C(12)	117.7(2)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3) for ot06m. 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)	39(1)	51(1)	57(1)	-4(1)	0(1)	-1(1)
O(2)	45(1)	74(1)	77(1)	-9(1)	-5(1)	-12(1)
O(3)	101(1)	58(1)	114(2)	-4(1)	2(1)	27(1)
O(4)	86(1)	43(1)	40(1)	1(1)	2(1)	11(1)
N(1)	41(1)	44(1)	47(1)	-5(1)	1(1)	-4(1)
C(1)	52(1)	54(1)	55(1)	-4(1)	-1(1)	-10(1)
C(2)	63(2)	58(1)	79(2)	11(1)	0(1)	-11(1)
C(3)	79(2)	48(1)	104(2)	0(1)	14(2)	-4(1)
C(4)	105(2)	56(1)	89(2)	-28(1)	4(2)	-5(1)
C(5)	82(2)	60(1)	57(1)	-14(1)	3(1)	-3(1)
C(6)	39(1)	45(1)	53(1)	-9(1)	7(1)	-7(1)
C(7)	45(1)	60(1)	37(1)	-7(1)	-1(1)	-5(1)
C(8)	52(1)	56(1)	37(1)	2(1)	-4(1)	0(1)
C(9)	48(1)	71(1)	62(1)	-2(1)	-10(1)	13(1)
C(10)	83(2)	62(1)	54(1)	11(1)	-7(1)	26(1)
C(11)	62(1)	41(1)	46(1)	10(1)	7(1)	4(1)
C(12)	55(1)	43(1)	51(1)	5(1)	8(1)	4(1)
C(13)	63(1)	43(1)	39(1)	2(1)	0(1)	7(1)
C(14)	44(1)	41(1)	44(1)	2(1)	6(1)	-4(1)
C(15)	45(1)	49(1)	36(1)	5(1)	7(1)	-2(1)
C(16)	44(1)	47(1)	33(1)	-7(1)	5(1)	-2(1)
C(17)	74(2)	45(1)	61(1)	4(1)	17(1)	7(1)
C(18)	86(2)	60(1)	103(2)	-14(2)	6(2)	-5(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for ot06m.

x	y	z	U(eq)

H(1A)	5984	-671	10853	80
H(2A)	6216	-1549	11466	80
H(3A)	5933	-2091	8656	80
H(4A)	5252	-1772	5338	80
H(5A)	5053	-888	4979	80
H(8A)	4096	613	4909	80
H(9A)	2642	808	8850	80
H(9B)	***2073***	***864***	***6374***	***80***
H(10A)	3612	1571	6045	80
H(10B)	2765	1733	7467	80
H(11A)	5385	1855	8431	80
H(12A)	3198	1500	11341	80
H(13A)	4682	607	10940	80
H(13B)	6250	694	11689	80
H(14A)	6797	1199	8895	80
H(15A)	6118	837	6000	80
H(18A)	5643	2691	12954	80
H(18B)	6514	2227	11788	80
H(18C)	6065	2118	13772	80

Table 1. Crystal data and structure refinement for ***ent*-9**.

Identification code	ot10m	
Empirical formula	C18 H19 N O4	
Formula weight	313.34	
Temperature	295(2) K	
Wavelength 0.71073 Å		
Crystal system Orthorhombic		
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 6.4935(11) Å	α= 90°.
	b = 9.2208(16) Å	β= 90°.
	c = 26.244(4) Å	γ = 90°.
Volume	1571.4(5) $Å^3$	
Z	4	
Density (calculated)	1.324 Mg/m^3	
Absorption coefficient	0.094 mm^{-1}	
F(000)	664	
Crystal size	0.55 x 0.39 x 0.31 mm^3	
Theta range for data collection	2.34 to 28.21°.	
Index ranges	$-8 \le h \le 8, -9 \le k \le 12, -33 \le l \le 27$	
Reflections collected	9473	
Independent reflections	3551 [R(int) = 0.0267]	
Completeness to theta = 28.21°	94.3 %	
Absorption correction	Empirical	
Max. and min. transmission	0.9884 and 0.9413	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters 3551 / 0 / 208		
Goodness-of-fit on F^2	0.962	
Final R indices [I>2sigma(I)]	R1 = 0.0447, wR2 = 0.1019	
R indices (all data)	R1 = 0.0652, wR2 = 0.1111	
Absolute structure parameter	-0.8(12)	
Largest diff. peak and hole	0.137 and -0.233 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for 00ot10. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	2732(2)	5087(2)	1279(1)	57(1)
O(2)	6783(2)	7508(2)	104(1)	50(1)
O(3)	8151(3)	2750(2)	-216(1)	65(1)
O(4)	3428(3)	3271(2)	2427(1)	90(1)
N(1)	7514(2)	5200(2)	-177(1)	44(1)
C(1)	3979(3)	5452(2)	851(1)	47(1)
C(2)	6088(3)	5784(2)	1079(1)	43(1)
C(3)	7907(3)	5635(2)	703(1)	43(1)
C(4)	7336(3)	6284(2)	189(1)	40(1)
C(5)	7153(3)	5416(2)	-711(1)	46(1)
C(6)	5229(3)	5775(2)	-889(1)	53(1)
C(7)	4926(4)	5959(3)	-1403(1)	65(1)
C(8)	6524(5)	5758(3)	-1738(1)	76(1)
C(9)	8452(4)	5398(3)	-1558(1)	81(1)
C(10)	8771(3)	5233(3)	-1043(1)	67(1)
C(11)	8083(3)	3858(2)	26(1)	48(1)
C(12)	8585(3)	4077(2)	580(1)	48(1)
C(13)	7718(4)	2915(2)	935(1)	60(1)
C(14)	7730(4)	3490(3)	1474(1)	67(1)
C(15)	6234(3)	4728(2)	1543(1)	50(1)
C(16)	3958(3)	4198(2)	1597(1)	50(1)
C(17)	3223(4)	4286(3)	2142(1)	61(1)
C(18)	2345(5)	5686(3)	2317(1)	82(1)

Table 3. Bond lengths [Å] and angles [°] for 00ot10.

O(1)-C(16)	1.414(2)	N(1)-C(4)-C(3)	107.96(16)
O(1)-C(1)	1.426(2)	C(6)-C(5)-C(10)	120.60(19)
O(2)-C(4)	1.205(2)	C(6)-C(5)-N(1)	120.91(17)
O(3)-C(11)	1.203(2)	C(10)-C(5)-N(1)	118.48(18)
O(4)-C(17)	1.205(3)	C(5)-C(6)-C(7)	119.6(2)
N(1)-C(4)	1.390(2)	C(8)-C(7)-C(6)	120.2(2)
N(1)-C(11)	1.397(3)	C(7)-C(8)-C(9)	120.0(2)
N(1)-C(5)	1.436(2)	C(10)-C(9)-C(8)	120.0(2)
C(1)-C(2)	1.526(3)	C(9)-C(10)-C(5)	119.6(2)
C(2)-C(3)	1.545(3)	O(3)-C(11)-N(1)	124.14(19)
C(2)-C(15)	1.562(3)	O(3)-C(11)-C(12)	128.0(2)
C(3)-C(4)	1.523(3)	N(1)-C(11)-C(12)	107.81(17)
C(3)-C(12)	1.536(3)	C(11)-C(12)-C(13)	114.53(18)
C(5)-C(6)	1.374(3)	C(11)-C(12)-C(3)	105.51(16)
C(5)-C(10)	1.375(3)	C(13)-C(12)-C(3)	114.96(16)
C(6)-C(7)	1.375(3)	C(14)-C(13)-C(12)	108.81(19)
C(7)-C(8)	1.371(3)	C(15)-C(14)-C(13)	112.04(16)
C(8)-C(9)	1.379(4)	C(14)-C(15)-C(2)	114.57(16)
C(9)-C(10)	1.375(3)	C(14)-C(15)-C(16)	112.52(18)
C(11)-C(12)	1.504(3)	C(2)-C(15)-C(16)	101.98(14)
C(12)-C(13)	1.527(3)	O(1)-C(16)-C(17)	110.42(17)
C(13)-C(14)	1.511(3)	O(1)-C(16)-C(15)	107.36(15)
C(14)-C(15)	1.510(3)	C(17)-C(16)-C(15)	111.57(16)
C(15)-C(16)	1.563(3)	O(4)-C(17)-C(18)	121.6(2)
C(16)-C(17)	1.510(3)	O(4)-C(17)-C(16)	120.8(2)
C(17)-C(18)	1.485(4)	C(18)-C(17)-C(16)	117.5(2)
C(16)-O(1)-C(1)	106.38(14)		
C(4)-N(1)-C(11)	113.38(15)		
C(4)-N(1)-C(5)	124.09(16)		
C(11)-N(1)-C(5)	122.53(15)		
O(1)-C(1)-C(2)	104.28(14)		
C(1)-C(2)-C(3)	114.68(14)		
C(1)-C(2)-C(15)	103.63(15)		
C(3)-C(2)-C(15)	113.32(16)		
C(4)-C(3)-C(12)	104.52(15)		
C(4)-C(3)-C(2)	110.15(15)		
C(12)-C(3)-C(2)	115.90(16)		
O(2)-C(4)-N(1)	124.82(17)		
O(2)-C(4)-C(3)	127.21(17)		

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 00OT10. 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)	41(1)	86(1)	43(1)	11(1)	-1(1)	-2(1)
O(2)	57(1)	40(1)	51(1)	-2(1)	6(1)	1(1)
O(3)	74(1)	45(1)	75(1)	-12(1)	7(1)	5(1)
O(4)	111(2)	99(2)	61(1)	29(1)	3(1)	-2(1)
N(1)	48(1)	40(1)	43(1)	-3(1)	5(1)	-2(1)
C(1)	39(1)	61(1)	42(1)	7(1)	1(1)	-1(1)
C(2)	43(1)	47(1)	39(1)	-3(1)	-1(1)	-5(1)
C(3)	35(1)	42(1)	52(1)	-2(1)	-5(1)	-7(1)
C(4)	32(1)	43(1)	46(1)	-2(1)	6(1)	-7(1)
C(5)	51(1)	43(1)	44(1)	-7(1)	8(1)	-6(1)
C(6)	54(1)	52(1)	54(1)	-11(1)	4(1)	0(1)
C(7)	76(2)	62(2)	57(2)	-11(1)	-10(1)	3(1)
C(8)	103(2)	77(2)	49(1)	-5(1)	-3(1)	-13(2)
C(9)	88(2)	99(2)	55(1)	-3(1)	27(1)	-7(2)
C(10)	56(1)	82(2)	62(1)	-1(1)	14(1)	-1(1)
C(11)	38(1)	46(1)	59(1)	-5(1)	6(1)	4(1)
C(12)	36(1)	52(1)	56(1)	-1(1)	-2(1)	4(1)
C(13)	62(1)	47(1)	71(1)	11(1)	-1(1)	10(1)
C(14)	55(1)	82(2)	63(1)	26(1)	-8(1)	8(1)
C(15)	44(1)	62(1)	42(1)	5(1)	-10(1)	-8(1)
C(16)	47(1)	61(1)	42(1)	4(1)	-4(1)	-10(1)
C(17)	64(1)	72(2)	46(1)	7(1)	-5(1)	-17(1)
C(18)	99(2)	88(2)	59(1)	-5(1)	18(1)	-5(2)

Table 5. Hydrogen coordinates ($x\ 10^4$) and isotropic displacement parameters ($Å^2 x\ 10^3$) for 00ot10.

	x	y	z	U(eq)
H(1A)	4159	4605	612	80
H(1B)	3418	6365	715	80
H(2A)	6016	6849	1210	80
H(3A)	9038	6197	820	80
H(6A)	4316	5928	-644	80
H(7A)	3789	6364	-1577	80
H(8A)	6343	5667	-2095	80
H(9A)	9774	5440	-1768	80
H(10A)	10029	5027	-902	80
H(12A)	10156	4027	574	80
H(13A)	6169	2617	803	80
H(13B)	8661	2032	887	80
H(14A)	7363	2758	1718	80
H(14B)	8987	3646	1580	80
H(15A)	6582	5399	1874	80
H(16A)	3717	3146	1489	80
H(18A)	3366	6514	2212	80
H(18B)	2009	5619	2687	80
H(18C)	1019	6118	2130	80