**Supporting Information for**

# [2+2]PHOTOCYCLOADDITION OF 5,6-SUBSTITUTED 2-OXO-2*H*-PYRAN-3-CARBOXYLATES WITH ALKENES

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## EXPERIMENTAL

**GENERAL**: Melting points were measured with a Yanaco MP micro-melting point apparatus and are uncorrected. NMR spectra were measured on Bruker Ultrashield™ 300 ($^1$H: 300 MHz; $^{13}$C: 75 Hz), JEOL ECS-400 ($^1$H: 400 MHz; $^{13}$C: 100 Hz), and Bruker Ascend™ 500 ($^1$H: 500 MHz; $^{13}$C: 125 Hz) spectrometers with tetramethylsilane as the internal standard. Chemical shifts are reported in parts per million. IR spectra were measured with a JASCO FT/IR-4600 spectrophotometer. A JEOL JMS-GC mate II spectrometer was used for low-resolution and high-resolution electron ionization mass spectrometry (LR-EIMS and HR-EIMS). X-ray crystal analyses were performed on a Rigaku RAXIS RAPID II imaging plate area detector with graphite monochromatized Cu-Kα radiation at 23.0 °C. Photochemical reactions were performed on an RH-400-10W (Riko-Kagaku Sangyo). All solvents were removed under reduced pressure in the usual work-up procedure. Silica gel 60 $F_{254}$ (Merck) for thin-layer chromatography, silica gel 60N (Kanto Chemical) for column chromatography, silica gel packed in a glass column (Yamazen, 0.040 mm) for medium-pressure liquid chromatography (MPLC), Cosmosil 5SL-II, and Cosmosil 5$C_{18}$-AR-II packed column (Nacalai Tesque, 20 mm I.D. × 250 mm) for recycling preparative high-performance liquid chromatography (HPLC) were used.

**Typical Procedure**: The mixture of 2-oxo-2*H*-pyran-3-carboxylate derivative (1.0 mmol), alkene (10.0 e.q.) in 2-propanol (5 mL) was irradiated with a high-pressure mercury lamp (400 W) until the starting material was disappeared by TLC check. The reaction mixture was evaporated under reduced pressure. The residue was chromatographed on silica gel with *n*-hexane-EtOAc as eluent to give the products.

**Methyl *rac*-(1*R*,2a*S*,7b*S*)-3-oxo-1-phenyl-1,2,5,6,7,7b-hexahydrocyclobuta[*d*]cyclopenta[*b*]pyran-2a(3*H*)-carboxylate (17a)**

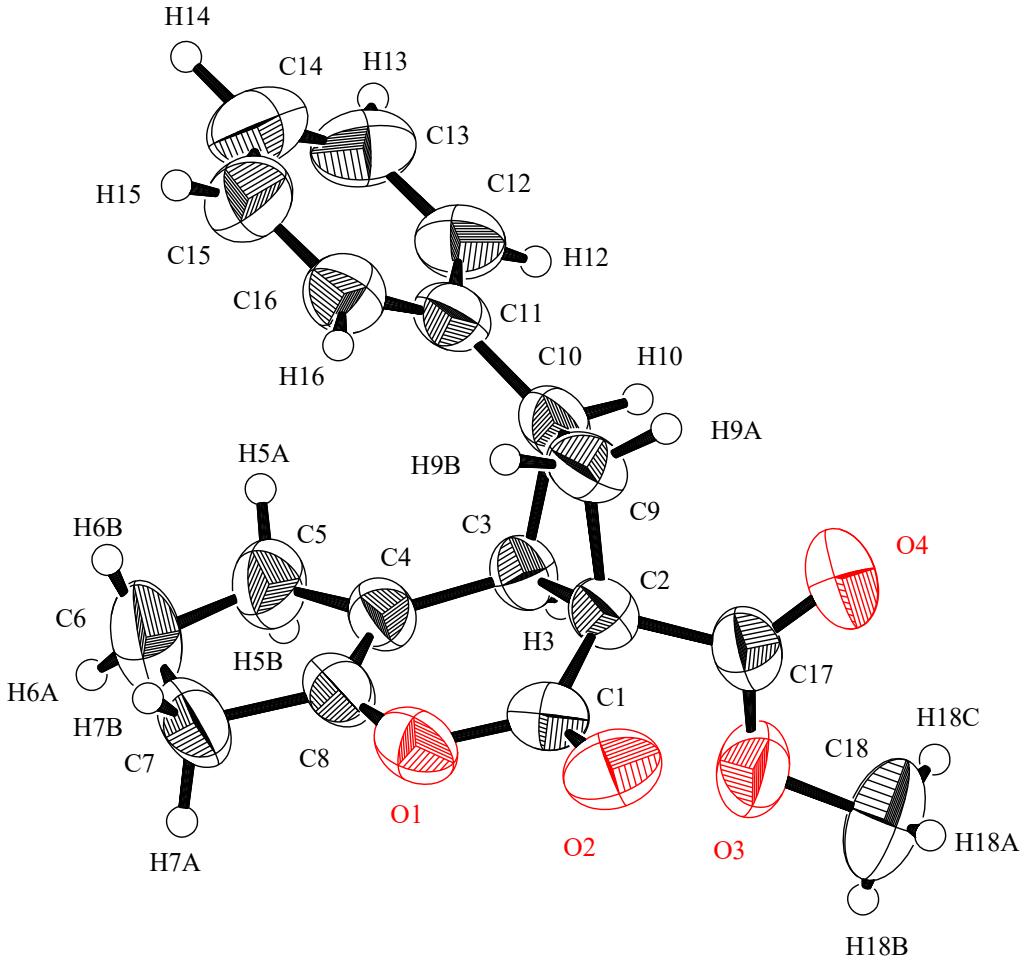
Colorless needles; m.p. 118.2-120.0 ℃ (Diisopropyl ether); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.35-7.27 (m, 3H), 7.21-7.17 (m, 2H), 3.98 (q, $J$ = 9.3 Hz, 1H), 3.88 (s, 3H), 3.53 (dd, $J$ = 8.7, 2.1 Hz, 1H), 3.24 (ddd, $J$ = 12.3, 8.7, 3.0 Hz, 1H), 2.96 (ddd, $J$ = 12.3, 9.9, 1.2 Hz, 1H), 2.48-2.41 (m, 2H), 1.82-1.68 (m, 2H), 1.58-1.48 (m, 1H), 1.12-1.03 (m, 1H).; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 171.2, 166.5, 149.9, 138.7, 128.5 (2C), 127.6 (2C), 127.4, 109.7, 53.4, 47.0, 44.9, 41.6, 33.5, 30.3, 29.7, 19.6.; IR ($CHCl_3$): 3030.6, 1755.1 cm$^{-1}$; LR-EIMS *m/z*: 298 ($M^+$, 1.4), 195 (13), 194 (100), 162 (47), 138 (14), 134 (26), 104 (20).; HR-EIMS calcd for $C_{18}H_{18}O_4$: 298.1205. Found: 298.1209.

X-ray Crystal Data: Crystal Color, Habit; colorless, chunk, Crystal Dimensions; 0.300 x 0.200 x 0.100 mm, Crystal System; monoclinic, Lattice Type; Primitive, Lattice Parameters; a = 11.3828(3) Å, b = 9.0422(2) Å, c = 15.6478(4) Å, β = 103.768(7) º, V = 1564.29(9) Å$^3$, Space Group; $P2_1/n$ (#14), Z value; 4, $D_{calc}$; 1.267 g/cm$^3$, $F_{000}$; 632.00, μ(CuKα); 7.295 cm$^{-1}$, Intensity Measurement: Diffractometer; R-AXIS RAPID, Radiation; CuKα (λ = 1.54187 Å), graphite monochromated, Voltage, Current; 50 kV, 100 mA, Temperature; 23.0 ºC, Detector Aperture; 460.0 x 256.0 mm, Data Images; 45 exposures, ω oscillation Range (χ=54.0, ϕ=0.0); 80.0 - 260.0º, Exposure Rate; 120.0 sec./º, ω oscillation Range (χ=54.0, ϕ=90.0); 80.0 - 260.0º, Exposure Rate; 120.0 sec./º, ω oscillation Range (χ=54.0, ϕ=180.0); 80.0 - 260.0º, Exposure Rate; 120.0 sec./º, ω oscillation Range (χ=54.0, ϕ=270.0); 80.0 - 260.0º, Exposure Rate; 120.0 sec./º, Detector Position; 127.40 mm, Pixel Size; 0.100 mm, $2\theta_{max}$; 136.2º, No. of Reflections Measured; Total: 16573, Unique: 2849 ($R_{int}$ = 0.0436), Corrections; Lorentz-polarization Absorption (trans. factors: 0.733 - 0.930), Secondary Extinction (coefficient: 9.30000e-003). Structure Solution; Direct Methods (SHELXT Version 2014/5), Refinement; Full-matrix least-squares on F$^2$, Function Minimized; Σ ω ($Fo^2$ - $Fc^2$)$^2$, Least Squares Weights; w = 1/ [ $\sigma^2(Fo^2)$ + (0.0578 · P)$^2$ + 0.1875 · P ] where P = (Max($Fo^2$,0) + 2$Fc^2$)/3, $2\theta_{max}$ cutoff; 136.2º, Anomalous Dispersion; All non-hydrogen atoms, No. Observations (All reflections); 2849, No. Variables; 272, Reflection/Parameter Ratio; 10.47, Residuals: R1 (I>2.00σ(I)); 0.0404, Residuals: R (All reflections); 0.0571, Residuals: wR2 (All reflections); 0.1139, Goodness of Fit Indicator; 1.033, Max Shift/Error in Final Cycle ; 0.004, Maximum peak in Final Diff. Map; 0.16 e$^-$/Å$^3$, Minimum peak in Final Diff. Map; -0.12 e$^-$/Å$^3$.

Deposition number CCDC-2047474 for **17a**. Free copies of the data can be obtained via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

| Selected Bond lengths (Å) | | | | | |
|---|---|---|---|---|---|
| O1-C1 | 1.3550(19) | O1-C8 | 1.394(2) | O2-C1 | 1.197(2) |
| O3-C17 | 1.324(2) | O3-C18 | 1.448(3) | O4-C17 | 1.192(2) |
| C1-C2 | 1.499(2) | C2-C3 | 1.564(2) | C2-C9 | 1.552(2) |
| C2-C17 | 1.509(2) | C3-C4 | 1.4822(19) | C3-C10 | 1.570(2) |

| | | | | | |
|---|---|---|---|---|---|
| C4-C5 | 1.500(3) | C4-C8 | 1.313(2) | C5-C6 | 1.531(3) |
| C6-C7 | 1.511(4) | C7-C8 | 1.486(2) | C9-C10 | 1.541(2) |
| C10-C11 | 1.495(3) | C11-C12 | 1.388(3) | C11-C16 | 1.388(2) |
| C12-C13 | 1.385(4) | C13-C14 | 1.373(3) | C14-C15 | 1.369(4) |
| C15-C16 | 1.383(3) | | | | |
| Selected Bond Angles (º) | | | | | |
| C1-O1-C8 | 119.29(11) | C17-O3-C18 | 117.4(2) | O1-C1-O2 | 117.70(14) |
| O1-C1-C2 | 118.50(14) | O2-C1-C2 | 123.68(14) | C1-C2-C3 | 120.06(12) |
| C1-C2-C9 | 113.60(13) | C1-C2-C17 | 108.92(14) | C3-C2-C9 | 88.26(12) |
| C3-C2-C17 | 111.61(12) | C9-C2-C17 | 113.23(12) | C2-C3-C4 | 109.66(11) |
| C2-C3-C10 | 87.96(11) | C4-C3-C10 | 115.60(13) | C3-C4-C5 | 126.86(15) |
| C3-C4-C8 | 123.12(15) | C5-C4-C8 | 109.97(14) | C4-C5-C6 | 103.1(2) |
| C5-C6-C7 | 108.3(2) | C6-C7-C8 | 101.43(18) | O1-C8-C4 | 126.73(13) |
| O1-C8-C7 | 117.74(15) | C4-C8-C7 | 115.47(16) | C2-C9-C10 | 89.40(12) |
| C3-C10-C9 | 88.42(12) | C3-C10-C11 | 119.96(13) | C9-C10-C11 | 121.18(15) |
| C10-C11-C12 | 119.47(15) | C10-C11-C16 | 122.43(15) | C12-C11-C16 | 118.06(18) |
| C11-C12-C13 | 120.86(18) | C12-C13-C14 | 120.3(2) | C13-C14-C15 | 119.5(3) |
| C14-C15-C16 | 120.7(2) | C11-C16-C15 | 120.63(18) | O3-C17-O4 | 123.77(16) |
| O3-C17-C2 | 110.38(13) | O4-C17-C2 | 125.82(17) | | |




**Methyl *rac*-(4a*R*,7a*S*,9*S*)-6,7-dihydro-2-oxo-9-phenyl-4a,7a-ethano-2*H*,5*H*-1-cyclopenta[*b*]pyran-3-carboxylate (18a)**

Yellow needles; m.p. 139.7-142.1 °C (Diisopropyl ether); $^{1}$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.36-7.23 (m, 3H), 7.15-7.12 (m, 2H), 6.94 (s, 1H), 3.75 (s, 3H), 3.43 (t, $J$ = 9.0 Hz, 1H), 2.84 (ddd, $J$ = 13.2, 9.9, 1.5 Hz, 1H), 2.57 (dd, $J$ = 13.2, 8.7 Hz, 1H), 2.40-2.30 (m, 1H), 2.23-2.05 (m, 4H), 1.87-1.80 (m, 1H).; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 164.2, 158.3, 153.2, 136.7, 128.8 (2C), 127.6 (2C), 127.4, 123.2, 85.9, 52.9, 52.6, 44.2, 39.6, 37.5, 36.7, 23.2; IR ($CHCl_3$): 3028.0, 1751.2, 1728.1 cm$^{-1}$; LR-EIMS *m/z*: 298 ($M^+$, 1.0), 194 (100), 162 (37), 134 (23), 104 (21), 195 (13), 138 (2).; HR-EIMS calcd for $C_{18}H_{18}O_4$: 298.1205. Found: 298.1209.

**Methyl *rac*-(1*R*,2a*S*,9b*S*)-3-oxo-1-phenyl-1,2,5,6,7,8,9,9b-octahydrocyclobuta[*d*]cyclohepta[*b*]pyran-2a(3*H*)-carboxylate (17b)**

Colorless oil; $^{1}$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.36-7.26 (m, 3H), 7.22-7.17 (m, 2H), 3.91 (q, $J$ = 9.3 Hz, 1H), 3.85 (s, 3H), 3.56 (d, $J$ = 9.3 Hz, 1H), 3.30 (ddd, $J$ = 12.9, 9.3, 2.1 Hz, 1H), 2.88 (ddd, $J$ = 12.9, 8.1, 1.2 Hz, 1H), 2.36-2.20 (m, 2H), 1.61-1.07 (m, 7H), 0.80-0.63 (m, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 171.0, 166.7, 150.9, 138.9, 128.3 (2C), 128.1 (2C), 127.1, 110.8, 53.2, 48.7, 47.2, 41.4, 33.6, 32.2, 30.3, 29.6, 24.9, 24.5; IR ($CHCl_3$): 3028.7, 1748.2 cm$^{-1}$; LR-EIMS *m/z*: 326 ($M^+$, 1.0), 223 (17), 222 (100), 194 (73),135 (33), 104 (24), 91 (13).; HR-EIMS calcd for $C_{20}H_{22}O_4$: 326.1518. Found: 326.1515.

**Methyl *rac*-(4a*R*,9a*S*,11*S*)-6,7,8,9-tetrahydro-2-oxo-11-phenyl-4a,9a-ethano-2*H*,5*H*-1-cyclohepta[*b*]pyran-3-carboxylate (18b)**

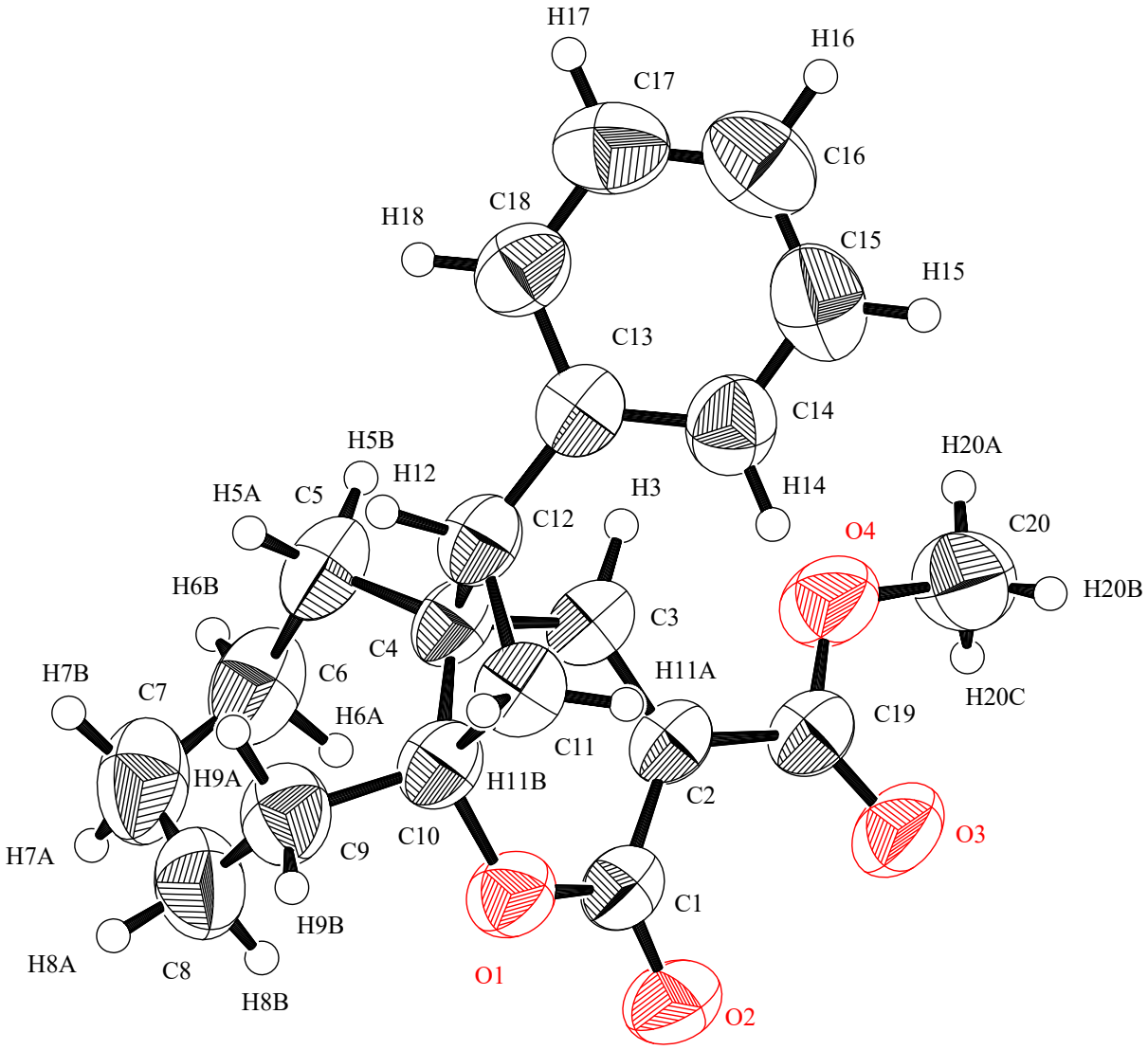
Colorless cubics; m.p. 113.8-114.7 ℃ (Diisopropyl ether); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.36-7.28 (m, 3H), 7.11-7.07 (m, 2H), 6.71 (s, 1H), 3.77 (s, 3H), 3.43 (dd, $J$ = 11.1, 8.4 Hz, 1H), 2.81 (dd, $J$ = 12.3, 11.1 Hz, 1H), 2.36 (dd, $J$ = 12.3, 8.4 Hz, 1H), 2.23-2.07 (m, 3H), 2.02-1.98 (m, 1H), 1.94-1.72 (m, 4H), 1.46-1.34 (m, 1H), 1.14-0.99 (m, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 163.6, 159.1, 157.2, 135.5, 128.6 (2C), 127.3, 127.2 (2C), 125.0, 82.8, 52.9, 52.5, 47.3, 39.3, 36.6, 36.4, 31.5, 24.6, 23.9; IR ($CHCl_3$): 3028.7, 1753.9, 1731.8 cm$^{-1}$; LR-EIMS *m/z*: 326 ($M^+$, 1.7), 222 (100), 195 (7), 194 (50), 135 (17), 104 (7), 91 (13).; HR-EIMS calcd for $C_{20}H_{22}O_4$: 326.1518. Found: 326.1515.

X-ray Crystal Data: Crystal Color, Habit; colorless, chunk, Crystal Dimensions; 0.300 x 0.300 x 0.200 mm, Crystal System; monoclinic, Lattice Type; Primitive, Lattice Parameters; a = 8.2398(4) Å, b = 13.0827(7) Å, c = 16.1271(8) Å, β = 96.255(7) º, V = 1728.13(15) Å$^3$, Space Group; $P2_1/c$ (#14), Z value; 4, $D_{calc}$; 1.254 g/cm$^3$, $F_{000}$; 696.00, μ(CuKα); 7.026 cm$^{-1}$, Intensity Measurement: Diffractometer; R-AXIS RAPID, Radiation; CuKα (λ = 1.54187 Å), graphite monochromated, Voltage, Current; 40 kV, 100 mA, Temperature; 23.0 ºC, Detector Aperture; 460.0 x 256.0 mm, Data Images; 45 exposures, ω oscillation Range (χ=54.0, ϕ=0.0); 80.0 - 260.0º, Exposure Rate; 180.0 sec./º, ω oscillation Range (χ=54.0, ϕ=90.0); 80.0 - 260.0º, Exposure Rate; 180.0 sec./º, ω oscillation Range (χ=54.0, ϕ=180.0); 80.0 - 260.0º, Exposure Rate; 180.0 sec./º, ω oscillation Range (χ=54.0, ϕ=270.0); 80.0 - 260.0º, Exposure Rate; 180.0 sec./º, Detector Position; 127.40 mm, Pixel Size; 0.100 mm, $2\theta_{max}$; 136.1º, No. of Reflections Measured; Total: 19033, Unique: 3139 ($R_{int}$ = 0.0416), Corrections; Lorentz-polarization Absorption (trans. factors: 0.761 - 0.869), Secondary Extinction (coefficient: 2.81000e-003). Structure Solution; Direct Methods (SHELXT Version 2014/5), Refinement; Full-matrix least-squares on F$^2$, Function Minimized; Σ ω ($Fo^2$ - $Fc^2$)$^2$, Least Squares Weights; w = 1/ [ $\sigma^2(Fo^2)$ + (0.0468 · P)$^2$ + 0.1737 · P ] where P = (Max($Fo^2$,0) + 2$Fc^2$)/3, $2\theta_{max}$ cutoff; 136.1º, Anomalous Dispersion; All non-hydrogen atoms, No. Observations (All reflections); 3139, No. Variables; 306, Reflection/Parameter Ratio; 10.26, Residuals: R1 (I>2.00σ(I)); 0.0355, Residuals: R (All reflections); 0.0425, Residuals: wR2 (All reflections); 0.0989, Goodness of Fit Indicator; 1.046, Max Shift/Error in Final Cycle ; 0.003, Maximum peak in Final Diff. Map; 0.13 e$^-$/Å$^3$, Minimum peak in Final Diff. Map; -0.12 e$^-$/Å$^3$.

Deposition number CCDC-2047463 for **18b**. Free copies of the data can be obtained via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

| Selected Bond lengths (Å) | | | | | |
|---|---|---|---|---|---|
| O1-C1 | 1.3425(16) | O1-C10 | 1.4546(15) | O2-C1 | 1.2054(16) |
| O3-C19 | 1.1948(16) | O4-C19 | 1.3228(16) | O4-C20 | 1.446(3) |
| C1-C2 | 1.4767(18) | C2-C3 | 1.3345(17) | C2-C19 | 1.4939(18) |
| C3-C4 | 1.4870(19) | C4-C5 | 1.5354(19) | C4-C10 | 1.5426(19) |

| | | | | | |
|---|---|---|---|---|---|
| C4-C12 | 1.5847(17) | C5-C6 | 1.524(3) | C6-C7 | 1.521(4) |
| C7-C8 | 1.505(3) | C8-C9 | 1.526(3) | C9-C10 | 1.521(2) |
| C10-C11 | 1.530(2) | C11-C12 | 1.538(2) | C12-C13 | 1.500(2) |
| C13-C14 | 1.390(2) | C13-C18 | 1.392(2) | C14-C15 | 1.383(3) |
| C15-C16 | 1.373(3) | C16-C17 | 1.371(3) | C17-C18 | 1.381(3) |
| Selected Bond Angles (º) | | | | | |
| C1-O1-C10 | 122.62(10) | C19-O4-C20 | 115.53(13) | O1-C1-O2 | 117.57(12) |
| O1-C1-C2 | 118.14(11) | O2-C1-C2 | 124.22(12) | C1-C2-C3 | 120.97(12) |
| C1-C2-C19 | 117.81(10) | C3-C2-C19 | 121.21(12) | C2-C3-C4 | 124.19(13) |
| C3-C4-C5 | 110.13(11) | C3-C4-C10 | 110.71(10) | C3-C4-C12 | 110.10(11) |
| C5-C4-C10 | 120.43(13) | C5-C4-C12 | 116.74(11) | C10-C4-C12 | 86.73(9) |
| C4-C5-C6 | 114.10(14) | C5-C6-C7 | 114.37(16) | C6-C7-C8 | 116.27(18) |
| C7-C8-C9 | 117.0(2) | C8-C9-C10 | 115.61(14) | O1-C10-C4 | 117.11(10) |
| O1-C10-C9 | 104.38(11) | O1-C10-C11 | 115.22(11) | C4-C10-C9 | 116.55(12) |
| C4-C10-C11 | 89.62(10) | C9-C10-C11 | 114.18(11) | C10-C11-C12 | 88.86(10) |
| C4-C12-C11 | 87.80(10) | C4-C12-C13 | 121.32(11) | C11-C12-C13 | 121.80(12) |
| C12-C13-C14 | 122.46(13) | C12-C13-C18 | 119.61(13) | C14-C13-C18 | 117.93(15) |
| C13-C14-C15 | 120.42(16) | C14-C15-C16 | 120.89(18) | C15-C16-C17 | 119.3(2) |
| C16-C17-C18 | 120.46(18) | C13-C18-C17 | 120.96(17) | O3-C19-O4 | 122.93(13) |
| O3-C19-C2 | 125.66(12) | O4-C19-C2 | 111.41(11) | | |




**Methyl *rac*-(1*R*,2a*S*,10b*S*)-3-oxo-1-phenyl-1,5,6,7,8,9,10,10b-octahydro-2*H*-cyclobuta[*d*]cycloocta[*b*]pyran-2a(3*H*)-carboxylate (17c)**

Colorless needles; m.p. 135.7-137.0 ºC (Diisopropyl ether); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.33-7.25 (m, 3H), 7.23-7.17 (m, 2H) 3.90 (q, $J$ = 9.0 Hz, 1H), 3.85 (s, 3H), 3.56 (dd, $J$ = 9.0, 2.4 Hz, 1H), 3.30 (ddd, $J$ = 12.9, 9.0, 2.4 Hz, 1H), 2.92 (ddd, $J$ = 12.9, 8.4, 1.2 Hz, 1H), 2.33 (ddd, $J$ = 14.4, 11.1, 5.4 Hz, 1H), 2.12 (dt, $J$ = 14.4, 4.2 Hz, 1H), 1.73-1.10 (m, 10H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 170.9, 166.7, 148.7, 138.6, 128.3 (2C), 128.0 (2C), 127.1, 108.5, 53.2, 47.8, 46.0, 41.6, 33.8, 28.6, 28.3, 27.84, 27.83, 26.1, 25.9; IR ($CHCl_3$): 3027.7, 1752.0, 1712.5 cm$^{-1}$; LR-EIMS *m/z*: 340 ($M^+$, 0.5), 237 (21), 236 (100), 208 (30), 180 (32), 152 (17).; HR-EIMS calcd for $C_{21}H_{24}O_4$: 340.1675. Found: 340.1680.

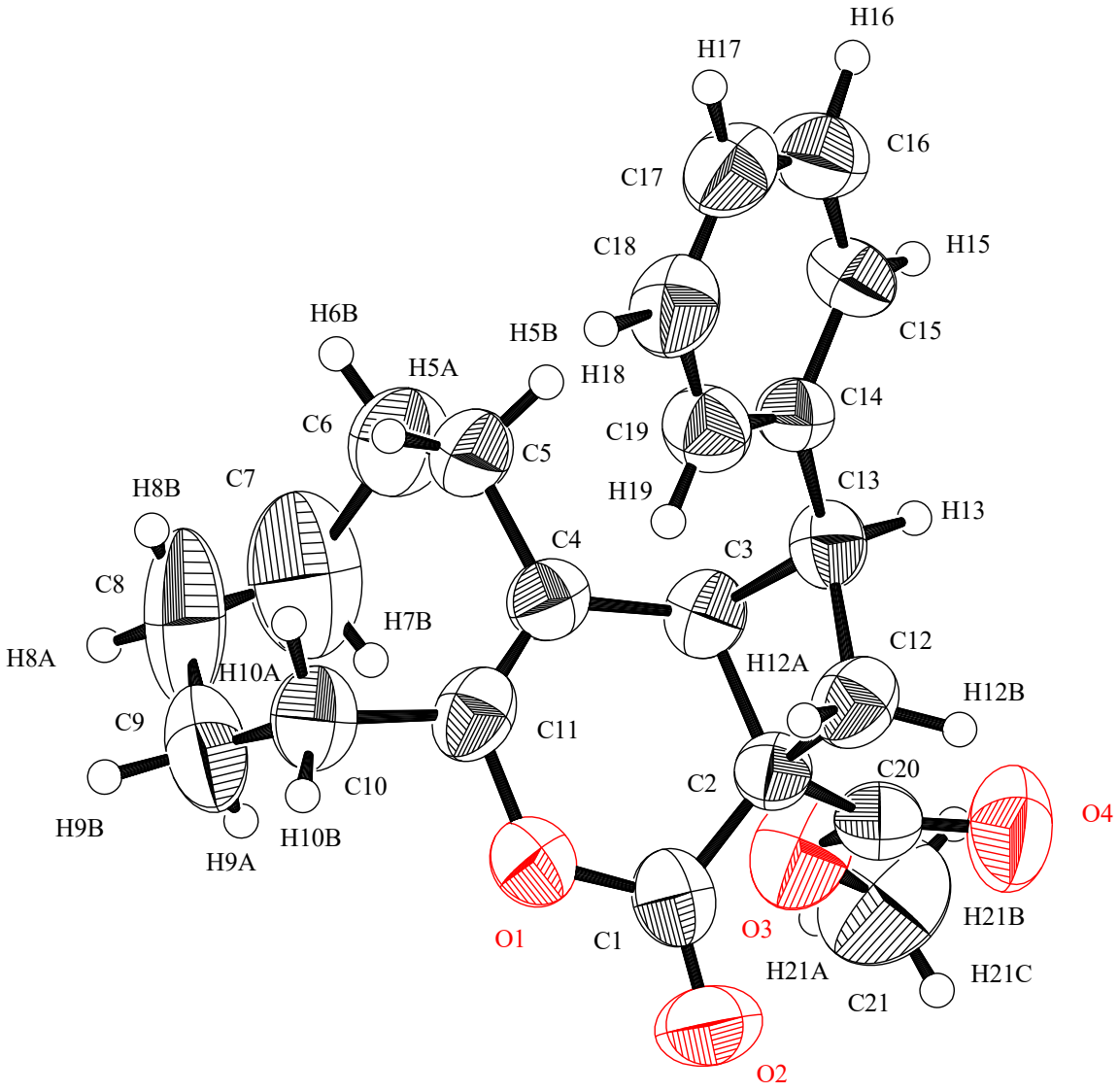
X-ray Crystal Data: Crystal Color, Habit; colorless, chunk, Crystal Dimensions; 0.200 x 0.100 x 0.100 mm, Crystal System; orthorhombic, Lattice Type; Primitive, Lattice Parameters; a = 7.0569(6) Å, b = 10.9918(9) Å, c = 23.2000(19) Å, V = 1799.6(3) Å$^3$, Space Group; $P2_12_12_1$ (#19), Z value; 4, $D_{calc}$; 1.256 g/cm$^3$, $F_{000}$; 728.00, μ(CuKα); 6.950 cm$^{-1}$, Intensity Measurement: Diffractometer; R-AXIS RAPID, Radiation; CuKα (λ = 1.54187 Å), graphite monochromated, Voltage, Current; 50 kV, 100 mA, Temperature; 23.0 ºC, Detector Aperture; 460.0 x 256.0 mm, Data Images; 45 exposures, ω oscillation Range (χ=54.0, ϕ=0.0); 80.0 - 260.0º,

Exposure Rate; 150.0 sec./º, ω oscillation Range (χ=54.0, ϕ=90.0); 80.0 - 260.0º, Exposure Rate; 150.0 sec./º, ω oscillation Range (χ=54.0, ϕ=180.0); 80.0 - 260.0º, Exposure Rate; 150.0 sec./º, ω oscillation Range (χ=54.0, ϕ=270.0); 80.0 - 260.0º, Exposure Rate; 150.0 sec./º, Detector Position; 127.40 mm, Pixel Size; 0.100 mm, $2\theta_{max}$; 136.2º, No. of Reflections Measured; Total: 19511, Unique: 3259 ($R_{int}$ = 0.1190), Corrections; Lorentz-polarization Absorption (trans. factors: 0.599 - 0.933), Secondary Extinction (coefficient: 2.23000e-003). Structure Solution; Direct Methods (SHELXT Version 2014/5), Refinement; Full-matrix least-squares on $F^2$, Function Minimized; $\Sigma\ \omega\ (Fo^2 - Fc^2)^2$, Least Squares Weights; $w = 1/ [\ \sigma^2(Fo^2) + (0.0186 \cdot P)^2 + 0.0000 \cdot P\ ]$ where $P = (Max(Fo^2,0) + 2Fc^2)/3$, $2\theta_{max}$ cutoff; 136.2º, Anomalous Dispersion; All non-hydrogen atoms, No. Observations (All reflections); 3259, No. Variables; 263, Reflection/Parameter Ratio; 12.39, Residuals: R1 (I>2.00σ(I)); 0.0411, Residuals: R (All reflections); 0.1552, Residuals: wR2 (All reflections); 0.0723, Goodness of Fit Indicator; 0.719, Max Shift/Error in Final Cycle; 0.002, Maximum peak in Final Diff. Map; 0.19 $e^-/Å^3$, Minimum peak in Final Diff. Map; -0.15 $e^-/Å^3$.

Deposition number CCDC-2047471 for **17c**. Free copies of the data can be obtained via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

| Selected Bond lengths (Å) | | | | | |
|---|---|---|---|---|---|
| O1-C1 | 1.367(7) | O1-C11 | 1.428(7) | O2-C1 | 1.191(7) |
| O3-C20 | 1.326(6) | O3-C21 | 1.449(5) | O4-C20 | 1.182(6) |
| C1-C2 | 1.481(8) | C2-C3 | 1.559(7) | C2-C12 | 1.557(5) |
| C2-C20 | 1.519(7) | C3-C4 | 1.488(7) | C3-C13 | 1.575(7) |
| C4-C5 | 1.503(9) | C4-C11 | 1.316(10) | C5-C6 | 1.513(8) |
| C6-C7 | 1.521(9) | C7-C8 | 1.382(11) | C8-C9 | 1.577(11) |
| C9-C10 | 1.509(8) | C10-C11 | 1.505(7) | C12-C13 | 1.544(7) |
| C13-C14 | 1.500(6) | C14-C15 | 1.369(9) | C14-C19 | 1.389(7) |
| C15-C16 | 1.375(8) | C16-C17 | 1.376(9) | C17-C18 | 1.359(11) |
| C18-C19 | 1.390(7) | | | | |
| Selected Bond Angles (º) | | | | | |
| C1-O1-C11 | 122.7(4) | C20-O3-C21 | 117.4(4) | O1-C1-O2 | 117.9(5) |
| O1-C1-C2 | 116.4(5) | O2-C1-C2 | 125.5(5) | C1-C2-C3 | 119.9(4) |
| C1-C2-C12 | 113.8(4) | C1-C2-C20 | 108.4(4) | C3-C2-C12 | 88.1(3) |
| C3-C2-C20 | 112.1(4) | C12-C2-C20 | 113.4(4) | C2-C3-C4 | 112.9(5) |
| C2-C3-C13 | 88.8(4) | C4-C3-C13 | 115.7(4) | C3-C4-C5 | 117.8(5) |
| C3-C4-C11 | 121.8(5) | C5-C4-C11 | 120.1(5) | C4-C5-C6 | 112.3(4) |
| C5-C6-C7 | 116.3(5) | C6-C7-C8 | 119.1(5) | C7-C8-C9 | 118.9(6) |
| C8-C9-C10 | 115.8(6) | C9-C10-C11 | 113.1(4) | O1-C11-C4 | 123.9(5) |

| | | | | | |
|---|---|---|---|---|---|
| O1-C11-C10 | 108.1(5) | C4-C11-C10 | 127.8(5) | C2-C12-C13 | 89.9(3) |
| C3-C13-C12 | 88.0(4) | C3-C13-C14 | 121.8(4) | C12-C13-C14 | 121.3(4) |
| C13-C14-C15 | 119.6(4) | C13-C14-C19 | 122.2(5) | C15-C14-C19 | 118.1(4) |
| C14-C15-C16 | 120.4(5) | C15-C16-C17 | 121.3(6) | C16-C17-C18 | 119.4(5) |
| C17-C18-C19 | 119.6(5) | C14-C19-C18 | 121.3(5) | O3-C20-O4 | 125.1(5) |
| O3-C20-C2 | 109.7(4) | O4-C20-C2 | 125.1(4) | | |




**Methyl *rac*-(4a*R*,10a*S*,12*S*)-5,6,7,8,9,10-hexahydro-2-oxo-12-phenyl-4a,10a-ethano-2*H*-1-cycloocta[*b*]pyran-3-carboxylate (18c)**

Colorless prisms; m.p. 154.5-155.9 °C (Diisopropyl ether); $^{1}$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.36-7.26 (m, 3H), 7.14-7.11 (m, 2H), 6.78 (s, 1H), 3.78 (s, 3H), 3.23 (dd, $J$ = 8.1, 11.7 Hz, 1H), 2.95 (t, $J$ = 11.7 Hz, 1H), 2.27 (dd, $J$ = 8.1, 12.3 Hz, 1H), 2.22-2.08 (m, 3H), 1.95-1.64 (m, 5H), 1.43-1.11 (m, 3H), 1.02-0.84 (m, 1H).; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 163.6, 159.0, 157.6, 134.8, 128.6 (2C), 127.7 (2C), 127.6, 125.3, 81.2, 52.5, 51.7, 45.4, 39.0, 35.2, 31.9, 24.6, 24.5, 24.4, 24.1; IR ($CHCl_3$): 3027.7, 1752.0, 1712.5 cm$^{-1}$; LR-EIMS *m/z*: 340

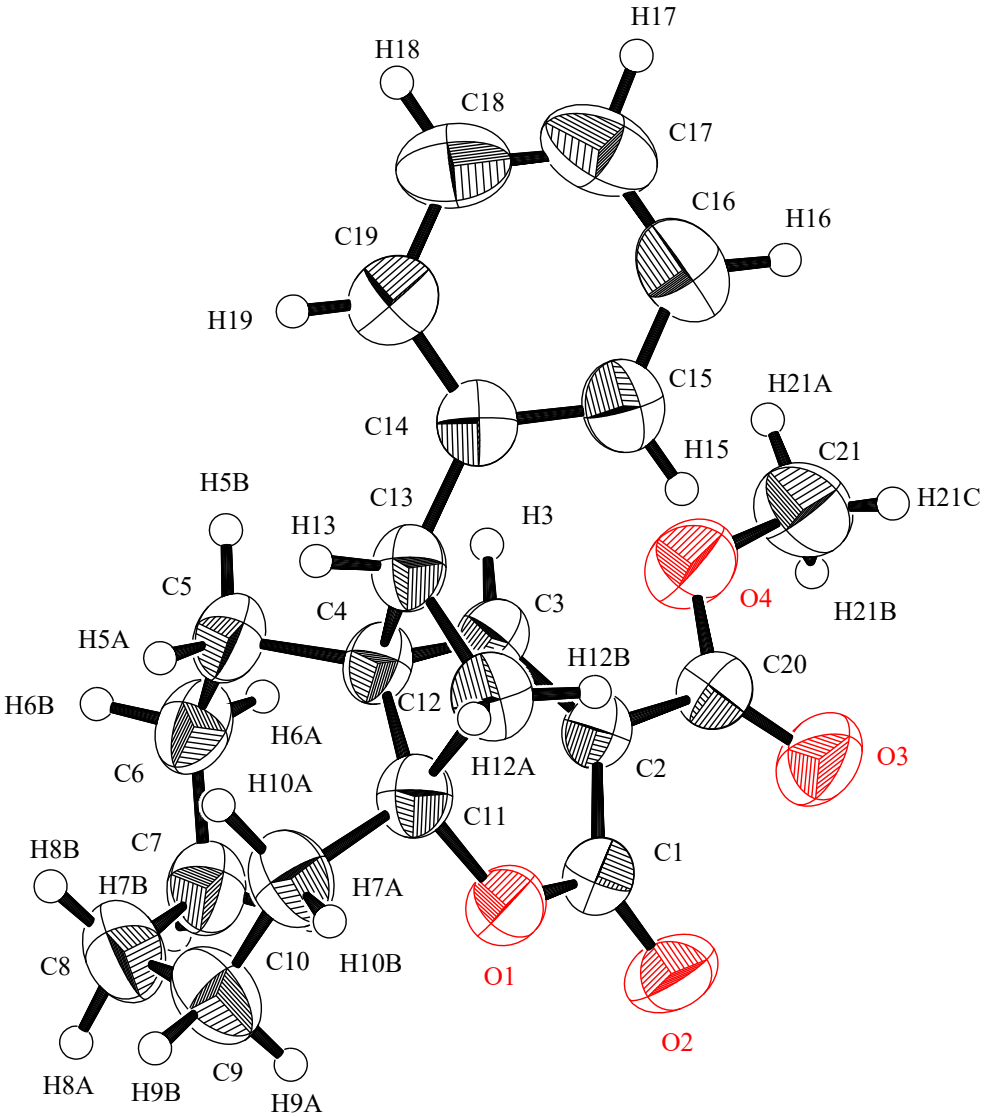
($M^+$, 1.3), 236 (100), 208 (31), 180 (34), 152 (18), 104 (19).; HR-EIMS calcd for $C_{21}H_{24}O_4$: 340.1675. Found: 340.1683.

X-ray Crystal Data: Crystal Color, Habit; colorless, chunk, Crystal Dimensions; 0.200 x 0.200 x 0.200 mm, Crystal System; monoclinic, Lattice Type; Primitive, Lattice Parameters; a = 8.4728(3) Å, b = 13.6953(4) Å, c = 15.7982(5) Å, β = 99.311(7) º, V = 1809.04(10) $Å^3$, Space Group; $P2_1/c$ (#14), Z value; 4, $D_{calc}$; 1.250 $g/cm^3$, $F_{000}$; 728.00, μ(CuKα); 6.913 $cm^{-1}$, Intensity Measurement: Diffractometer; R-AXIS RAPID, Radiation; CuKα (λ = 1.54187 Å), graphite monochromated, Voltage, Current; 40 kV, 100 mA, Temperature; 23.0 ºC, Detector Aperture; 460.0 x 256.0 mm, Data Images; 45 exposures, ω oscillation Range (χ=54.0, ϕ=0.0); 80.0 - 260.0º, Exposure Rate; 180.0 sec./º, ω oscillation Range (χ=54.0, ϕ=90.0); 80.0 - 260.0º, Exposure Rate; 180.0 sec./º, ω oscillation Range (χ=54.0, ϕ=180.0); 80.0 - 260.0º, Exposure Rate; 180.0 sec./º, ω oscillation Range (χ=54.0, ϕ=270.0); 80.0 - 260.0º, Exposure Rate; 180.0 sec./º, Detector Position; 127.40 mm, Pixel Size; 0.100 mm, $2\theta_{max}$; 136.2º, No. of Reflections Measured; Total: 19379, Unique: 3294 ($R_{int}$ = 0.0482), Corrections; Lorentz-polarization Absorption (trans. factors: 0.691 - 0.871), Secondary Extinction (coefficient: 2.24000e-003). Structure Solution; Direct Methods (SHELXT Version 2014/5), Refinement; Full-matrix least-squares on $F^2$, Function Minimized; $\Sigma\ \omega\ (Fo^2 - Fc^2)^2$, Least Squares Weights; $w = 1/[\ \sigma^2(Fo^2) + (0.0410 \cdot P)^2 + 0.2991 \cdot P\ ]$ where $P = (Max(Fo^2,0) + 2Fc^2)/3$, $2\theta_{max}$ cutoff; 136.2º, Anomalous Dispersion; All non-hydrogen atoms, No. Observations (All reflections); 3294, No. Variables; 323, Reflection/Parameter Ratio; 10.20, Residuals: R1 (I>2.00σ(I)); 0.0403, Residuals: R (All reflections); 0.0569, Residuals: wR2 (All reflections); 0.1036, Goodness of Fit Indicator; 1.046, Max Shift/Error in Final Cycle ; 0.008, Maximum peak in Final Diff. Map; 0.21 $e^-/Å^3$, Minimum peak in Final Diff. Map; -0.12 $e^-/Å^3$.

Deposition number CCDC-2047466 for **18c**. Free copies of the data can be obtained via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

| Selected Bond lengths (Å) | | | | | |
|---|---|---|---|---|---|
| O1-C1 | 1.343(2) | O1-C11 | 1.4555(18) | O2-C1 | 1.2056(19) |
| O3-C20 | 1.189(2) | O4-C20 | 1.3230(19) | O4-C21 | 1.444(3) |
| C1-C2 | 1.476(2) | C2-C3 | 1.336(2) | C2-C20 | 1.490(2) |
| C3-C4 | 1.483(2) | C4-C5 | 1.530(2) | C4-C11 | 1.555(2) |
| C4-C13 | 1.583(2) | C5-C6 | 1.524(3) | C6-C7 | 1.518(3) |
| C7-C8 | 1.527(3) | C8-C9 | 1.522(3) | C9-C10 | 1.530(3) |
| C10-C11 | 1.527(3) | C11-C12 | 1.538(2) | C12-C13 | 1.544(2) |
| C13-C14 | 1.498(3) | C14-C15 | 1.389(3) | C14-C19 | 1.393(2) |
| C15-C16 | 1.383(3) | C16-C17 | 1.370(3) | C17-C18 | 1.379(4) |
| C18-C19 | 1.374(3) | | | | |
| Selected Bond Angles (º) | | | | | |

| | | | | | |
|---|---|---|---|---|---|
| C1-O1-C11 | 122.45(12) | C20-O4-C21 | 116.32(15) | O1-C1-O2 | 117.40(15) |
| O1-C1-C2 | 118.26(13) | O2-C1-C2 | 124.20(15) | C1-C2-C3 | 120.91(14) |
| C1-C2-C20 | 118.19(12) | C3-C2-C20 | 120.89(14) | C2-C3-C4 | 124.66(15) |
| C3-C4-C5 | 110.83(13) | C3-C4-C11 | 110.69(12) | C3-C4-C13 | 109.35(13) |
| C5-C4-C11 | 122.86(15) | C5-C4-C13 | 113.46(12) | C11-C4-C13 | 87.14(11) |
| C4-C5-C6 | 115.57(14) | C5-C6-C7 | 115.15(16) | C6-C7-C8 | 115.82(16) |
| C7-C8-C9 | 115.21(18) | C8-C9-C10 | 119.02(19) | C9-C10-C11 | 118.43(16) |
| O1-C11-C4 | 116.94(12) | O1-C11-C10 | 105.11(13) | O1-C11-C12 | 114.53(13) |
| C4-C11-C10 | 118.35(13) | C4-C11-C12 | 89.30(12) | C10-C11-C12 | 112.46(14) |
| C11-C12-C13 | 89.17(12) | C4-C13-C12 | 88.05(12) | C4-C13-C14 | 121.09(14) |
| C12-C13-C14 | 121.14(15) | C13-C14-C15 | 122.27(15) | C13-C14-C19 | 119.61(17) |
| C15-C14-C19 | 118.12(18) | C14-C15-C16 | 120.44(18) | C15-C16-C17 | 120.7(2) |
| C16-C17-C18 | 119.5(2) | C17-C18-C19 | 120.3(2) | C14-C19-C18 | 121.0(2) |
| O3-C20-O4 | 122.32(16) | O3-C20-C2 | 126.08(14) | O4-C20-C2 | 111.59(13) |



**Methyl *rac*-(1*R*,2a*S*,14b*S*)-3-oxo-1-phenyl-1,5,6,7,8,9,10,11,12,13,14,14b-dodecahydro-2*H*-cyclobuta[*d*]cyclododeca[*b*]pyran-2a(3*H*)-carboxylate (17d)**

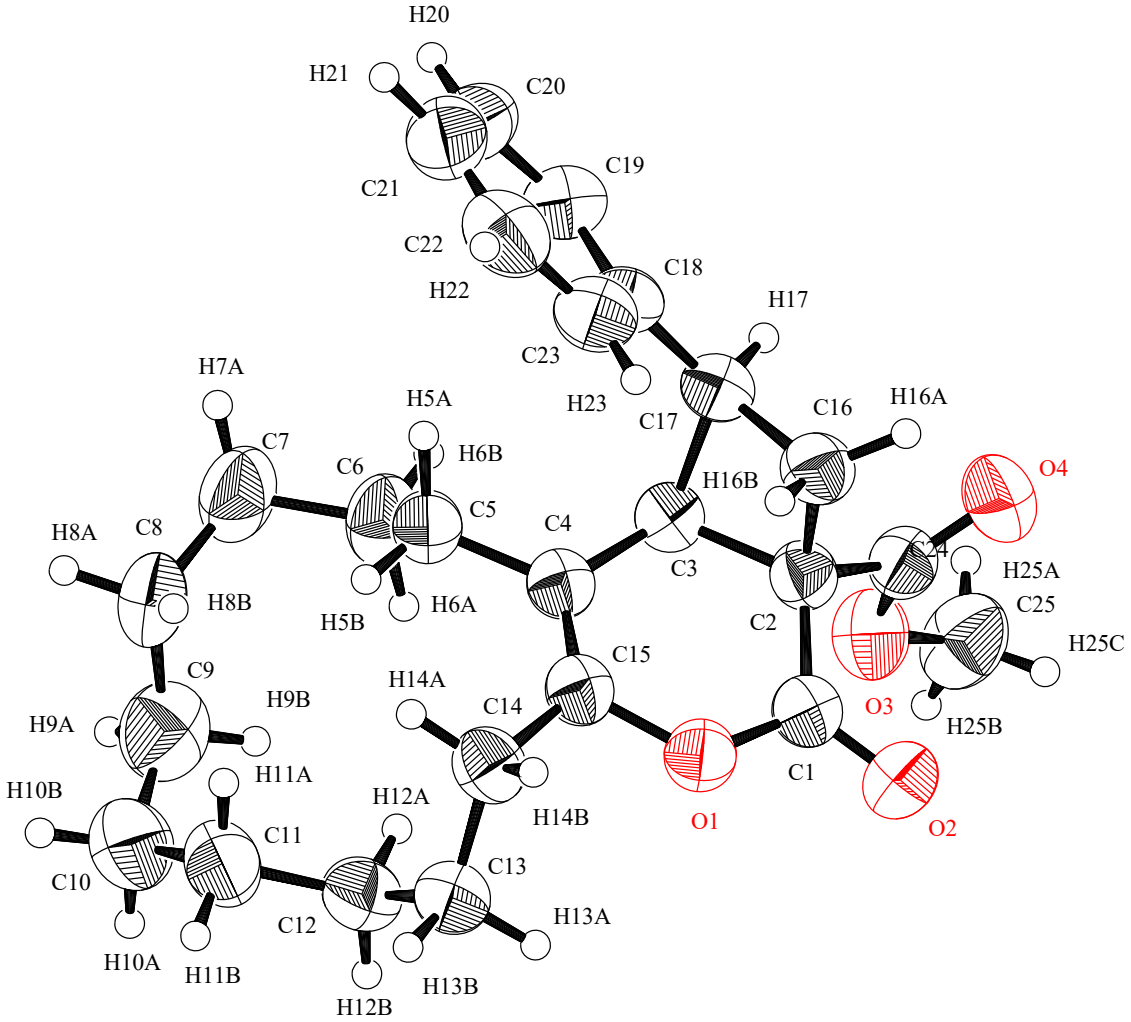
Colorless prisms; m.p. 115.3-116.9 ℃ (Diisopropyl ether); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.31-7.27 (m, 2H), 7.25-7.21 (m, 1H), 7.18-7.16 (m, 2H), 3.87-3.79 (m, 4H), 3.65 (d, $J$ = 9.6 Hz, 1H), 3.39 (ddd, $J$ = 12.8, 9.6, 1.2 Hz, 1H), 2.87 (ddd, $J$ = 14.4, 7.2 Hz, 1H), 2.30 (ddd $J$ = 14.4, 8.4, 7.2 Hz, 1H), 1.95 (dt, $J$ = 14.4, 7.2 Hz, 1H), 1.84 (dt, $J$ = 14.4, 7.2 Hz, 1H), 1.70-1.63 (m, 1H), 1.53-1.45 (m, 1H), 1.36-0.99 (m, 15H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 171.2, 167.6, 149.3, 139.2, 128.6 (2C), 128.3 (2C), 127.4, 109.6, 53.5, 48.2, 44.7, 41.9, 34.4, 26.4, 25.6, 24.9, 24.63, 24.59, 24.4, 24.2, 24.1, 22.7, 22.3; IR ($CHCl_3$): 3030.0, 1747.4 cm$^{-1}$; LR-EIMS m/z: 396 ($M^+$, 0.6), 293 (27), 292 (100), 264 (12), 189 (12), 104 (12).; HR-EIMS calcd for $C_{25}H_{32}O_4$: 396.2301. Found: 396.2299.

X-ray Crystal Data: Crystal Color, Habit; colorless, chunk, Crystal Dimensions; 0.300 x 0.200 x 0.200 mm, Crystal System; orthorhombic, Lattice Type; Primitive, Lattice Parameters; a = 11.9301(3) Å, b = 16.9532(4) Å, c = 21.7354(5) Å, V = 4396.08(17) Å$^3$, Space Group; Pbca (#61), Z value; 8, $D_{calc}$; 1.198 g/cm$^3$, $F_{000}$; 1712.00, $\mu$(CuK$\alpha$); 6.354 cm$^{-1}$, Intensity Measurement: Diffractometer; R-AXIS RAPID, Radiation; CuK$\alpha$ ($\lambda$ = 1.54187 Å), graphite monochromated, Voltage, Current; 40 kV, 100 mA, Temperature; 23.0 ºC, Detector Aperture; 460.0 x 256.0 mm, Data Images; 45 exposures, $\omega$ oscillation Range ($\chi$=54.0, $\phi$=0.0); 80.0 - 260.0º, Exposure Rate; 60.0 sec./º, $\omega$ oscillation Range ($\chi$=54.0, $\phi$=90.0); 80.0 - 260.0º, Exposure Rate; 60.0 sec./º, $\omega$ oscillation Range ($\chi$=54.0, $\phi$=180.0); 80.0 - 260.0º, Exposure Rate; 60.0 sec./º, $\omega$ oscillation Range ($\chi$=54.0, $\phi$=270.0); 80.0 - 260.0º, Exposure Rate; 60.0 sec./º, Detector Position; 127.40 mm, Pixel Size; 0.100 mm, $2\theta_{max}$; 136.3º, No. of Reflections Measured; Total: 42907, Unique: 4008 ($R_{int}$ = 0.0432), Corrections; Lorentz-polarization Absorption (trans. factors: 0.681 - 0.881), Secondary Extinction (coefficient: 5.30000e-004). Structure Solution; Direct Methods (SHELXT Version 2014/5), Refinement; Full-matrix least-squares on F$^2$, Function Minimized; $\Sigma\ \omega\ (Fo^2 - Fc^2)^2$, Least Squares Weights; $w = 1/ [\ \sigma^2(Fo^2) + (0.0437 \cdot P)^2 + 0.5698 \cdot P\ ]$ where $P = (Max(Fo^2,0) + 2Fc^2)/3$, $2\theta_{max}$ cutoff; 136.3º, Anomalous Dispersion; All non-hydrogen atoms, No. Observations (All reflections); 4008, No. Variables; 391, Reflection/Parameter Ratio; 10.25, Residuals: R1 (I>2.00$\sigma$(I)); 0.0367, Residuals: R (All reflections); 0.0553, Residuals: wR2 (All reflections); 0.0973, Goodness of Fit Indicator; 1.016, Max Shift/Error in Final Cycle; 0.009, Maximum peak in Final Diff. Map; 0.13 e$^-$/Å$^3$, Minimum peak in Final Diff. Map; -0.09 e$^-$/Å$^3$.

Deposition number CCDC-2047462 for **17d**. Free copies of the data can be obtained via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

| Selected Bond lengths (Å) | | | | | |
|---|---|---|---|---|---|
| O1-C1 | 1.3445(18) | O1-C15 | 1.4221(17) | O2-C1 | 1.2034(19) |
| O3-C24 | 1.331(2) | O3-C25 | 1.450(3) | O4-C24 | 1.200(2) |
| C1-C2 | 1.498(2) | C2-C3 | 1.557(2) | C2-C16 | 1.552(2) |
| C2-C24 | 1.510(2) | C3-C4 | 1.504(2) | C3-C17 | 1.584(2) |

| | | | | | |
|---|---|---|---|---|---|
| C4-C5 | 1.512(2) | C4-C15 | 1.327(2) | C5-C6 | 1.511(3) |
| C6-C7 | 1.533(3) | C7-C8 | 1.516(3) | C8-C9 | 1.523(3) |
| C9-C10 | 1.513(4) | C10-C11 | 1.528(4) | C11-C12 | 1.527(3) |
| C12-C13 | 1.508(3) | C13-C14 | 1.525(3) | C14-C15 | 1.497(2) |
| C16-C17 | 1.539(2) | C17-C18 | 1.497(2) | C18-C19 | 1.387(2) |
| C18-C23 | 1.388(2) | C19-C20 | 1.384(3) | C20-C21 | 1.372(3) |
| C21-C22 | 1.369(3) | C22-C23 | 1.384(3) | | |
| Selected Bond Angles (º) | | | | | |
| C1-O1-C15 | 123.05(11) | C24-O3-C25 | 116.38(15) | O1-C1-O2 | 118.40(13) |
| O1-C1-C2 | 117.14(12) | O2-C1-C2 | 124.38(14) | C1-C2-C3 | 117.60(12) |
| C1-C2-C16 | 115.05(12) | C1-C2-C24 | 108.28(12) | C3-C2-C16 | 88.35(11) |
| C3-C2-C24 | 114.02(12) | C16-C2-C24 | 112.60(12) | C2-C3-C4 | 112.46(12) |
| C2-C3-C17 | 86.93(10) | C4-C3-C17 | 114.79(12) | C3-C4-C5 | 117.07(12) |
| C3-C4-C15 | 121.77(13) | C5-C4-C15 | 121.14(13) | C4-C5-C6 | 113.73(14) |
| C5-C6-C7 | 113.28(18) | C6-C7-C8 | 114.39(18) | C7-C8-C9 | 115.6(2) |
| C8-C9-C10 | 114.5(2) | C9-C10-C11 | 114.7(2) | C10-C11-C12 | 114.9(2) |
| C11-C12-C13 | 113.66(17) | C12-C13-C14 | 114.42(15) | C13-C14-C15 | 114.69(14) |
| O1-C15-C4 | 122.96(13) | O1-C15-C14 | 106.31(12) | C4-C15-C14 | 130.73(14) |
| C2-C16-C17 | 88.74(11) | C3-C17-C16 | 87.84(11) | C3-C17-C18 | 121.28(13) |
| C16-C17-C18 | 121.52(13) | C17-C18-C19 | 119.24(14) | C17-C18-C23 | 122.71(14) |
| C19-C18-C23 | 118.01(15) | C18-C19-C20 | 120.97(17) | C19-C20-C21 | 120.2(2) |
| C20-C21-C22 | 119.55(19) | C21-C22-C23 | 120.7(2) | C18-C23-C22 | 120.59(18) |
| O3-C24-O4 | 124.07(15) | O3-C24-C2 | 110.70(13) | O4-C24-C2 | 125.23(15) |




**Methyl *rac*-(4a*R*,14a*S*,16*S*)-5,6,7,8,9,10,11,12,13,14-decahydro-2-oxo-16-phenyl-4a,14a-ethano-2*H*-1-cyclododeca[*b*]pyran-3-carboxylate (18d)**

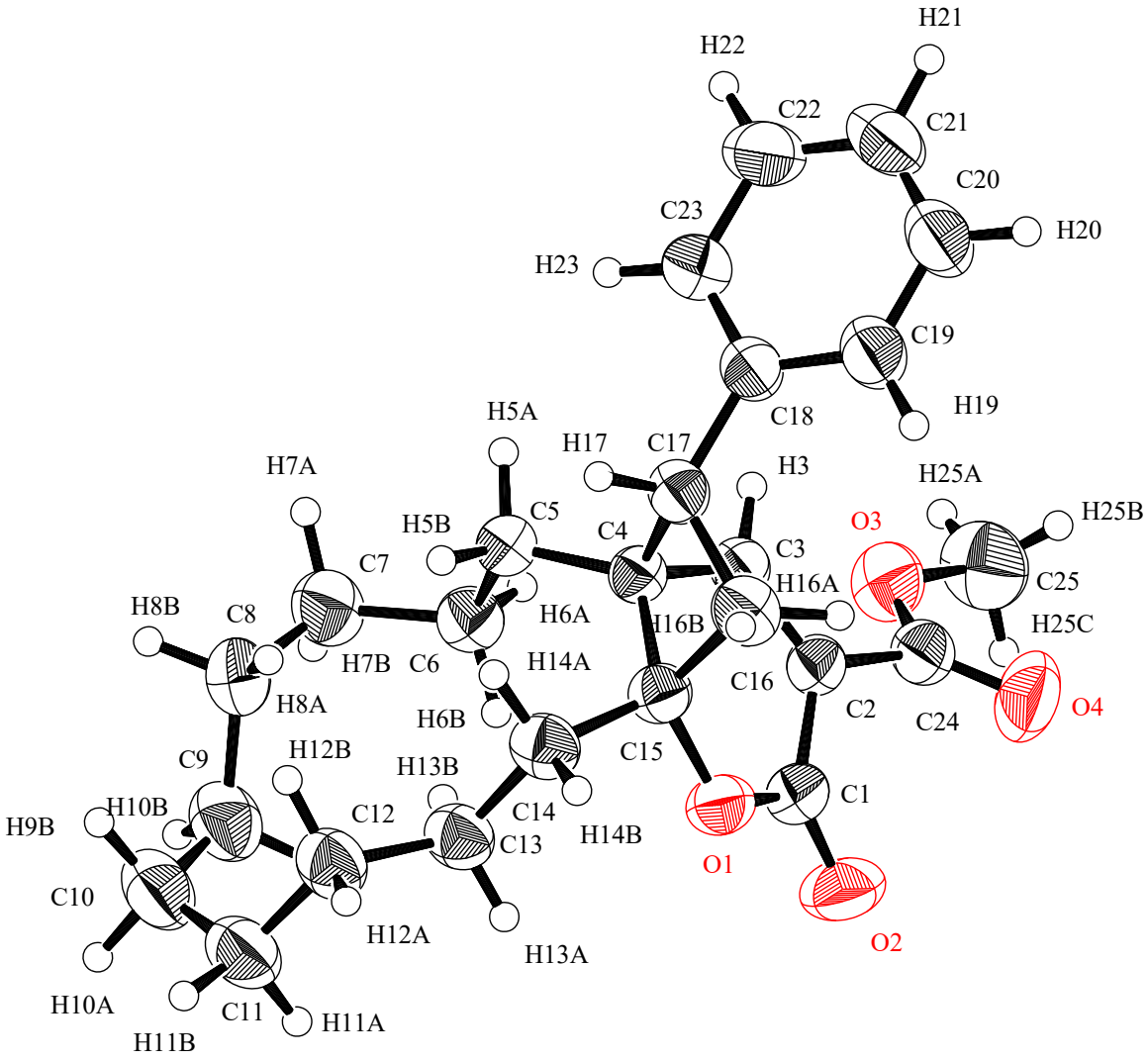
Colorless prisms; m.p. 117.8-118.7 ℃ (Diisopropyl ether); 1H NMR (300 MHz, $CDCl_3$) $\delta$ 7.34-7.27 (m, 3H), 7.13-7.10 (m, 2H), 6.79 (s, 1H), 3.78 (s, 3H), 3.24 (dd, $J$ = 11.7, 8.1 Hz, 1H), 2.85 (t, $J$ = 11.7 Hz, 1H), 2.26 (dd, $J$ = 12.0, 8.1 Hz, 1H), 2.15-1.93 (m, 3H), 1.79-1.61 (m, 6H), 1.53-1.18 (m, 11H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 164.0, 159.5, 157.7, 135.2, 129.0 (2C), 128.1 (2C), 127.9, 124.9, 83.2, 53.8, 52.9, 45.2, 38.1, 35.4, 33.3, 28.6, 27.6, 26.9, 26.5, 25.9, 24.6, 23.6, 23.5; IR ($CHCl_3$): 3028.0, 1753.2, 1728.1 cm$^{-1}$; LR-EIMS m/z: 396 ($M^+$, 1.2), 293 (28), 292 (100), 264 (12), 104 (11); HR-EIMS calcd for $C_{25}H_{32}O_4$: 396.2301. Found: 396.2306.

X-ray Crystal Data: Crystal Color, Habit; colorless, chunk, Crystal Dimensions; 0.300 x 0.200 x 0.100 mm, Crystal System; triclinic, Lattice Type; Primitive, Lattice Parameters; a = 8.6760(2) Å, b = 11.0683(3) Å, c = 12.4001(4) Å, α = 78.310(6) °, β = 80.381(6) °, γ = 70.323(5) °, V = 1091.64(7) Å$^3$, Space Group; P-1 (#2), Z value; 2, $D_{calc}$; 1.206 g/cm$^3$, $F_{000}$; 428.00, μ(CuKα); 6.397 cm$^{-1}$, Intensity Measurement: Diffractometer; R-AXIS RAPID, Radiation; CuKα (λ = 1.54187 Å), graphite monochromated, Voltage, Current; 40 kV, 100 mA, Temperature; 23.0 ºC, Detector Aperture; 460.0 x 256.0 mm, Data Images; 45 exposures, ω oscillation Range (χ=54.0, ϕ=0.0); 80.0 - 260.0º, Exposure Rate; 240.0 sec./º, ω oscillation Range (χ=54.0, ϕ=90.0); 80.0 - 260.0º, Exposure Rate; 240.0 sec./º, ω oscillation Range (χ=54.0, ϕ=180.0); 80.0 - 260.0º, Exposure

Rate; 240.0 sec./º, ω oscillation Range (χ=54.0, ϕ=270.0); 80.0 - 260.0º, Exposure Rate; 240.0 sec./º, Detector Position; 127.40 mm, Pixel Size; 0.100 mm, $2\theta_{max}$; 136.2º, No. of Reflections Measured; Total: 12317, Unique: 3892 ($R_{int}$ = 0.0414), Corrections; Lorentz-polarization Absorption (trans. factors: 0.706 - 0.938), Secondary Extinction (coefficient: 3.64000e-003). Structure Solution; Direct Methods (SHELXT Version 2014/5), Refinement; Full-matrix least-squares on $F^2$, Function Minimized; $\Sigma\ \omega\ (Fo^2 - Fc^2)^2$, Least Squares Weights; $w = 1/ [\ \sigma^2(Fo^2) + (0.0427 \cdot P)^2 + 0.1561 \cdot P\ ]$ where $P = (Max(Fo^2,0) + 2Fc^2)/3$, $2\theta_{max}$ cutoff; 136.2º, Anomalous Dispersion; All non-hydrogen atoms, No. Observations (All reflections); 3892, No. Variables; 391, Reflection/Parameter Ratio; 9.95, Residuals: R1 (I>2.00σ(I)); 0.0399, Residuals: R (All reflections); 0.0576, Residuals: wR2 (All reflections); 0.1040, Goodness of Fit Indicator; 1.038, Max Shift/Error in Final Cycle ; 0.000, Maximum peak in Final Diff. Map; 0.16 $e^-/Å^3$, Minimum peak in Final Diff. Map; -0.12 $e^-/Å^3$. Deposition number CCDC-2047461 for **18d**. Free copies of the data can be obtained via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

| Selected Bond lengths (Å) | | | | | |
|---|---|---|---|---|---|
| O1-C1 | 1.3398(19) | O1-C15 | 1.463(2) | O2C1 | 1.202(3) |
| O3-C24 | 1.340(2) | O3-C25 | 1.449(3) | O4-C24 | 1.196(2) |
| C1-C2 | 1.480(2) | C2-C3 | 1.327(3) | C2-C24 | 1.489(2) |
| C3-C4 | 1.491(2) | C4-C5 | 1.530(2) | C4-C15 | 1.566(2) |
| C4-C17 | 1.581(2) | C5-C6 | 1.530(3) | C6-C7 | 1.528(2) |
| C7-C8 | 1.523(3) | C8-C9 | 1.531(3) | C9-C10 | 1.528(3) |
| C10-C11 | 1.520(3) | C11-C12 | 1.532(3) | C12-C13 | 1.519(2) |
| C13-C14 | 1.520(3) | C14-C15 | 1.516(2) | C15-C16 | 1.534(2) |
| C16-C17 | 1.539(3) | C17-C18 | 1.505(2) | C18-C19 | 1.388(2) |
| C18-C23 | 1.386(2) | C19-C20 | 1.385(3) | C20-C21 | 1.362(3) |
| C21-C22 | 1.380(3) | C22-C23 | 1.392(3) | | |
| Selected Bond Angles (º) | | | | | |
| C1-O1-C15 | 121.73(12) | C24-O3-C25 | 115.68(16) | O1-C1-O2 | 118.56(14) |
| O1-C1-C2 | 118.29(16) | O2-C1-C2 | 123.07(15) | C1-C2-C3 | 121.63(13) |
| C1-C2-C24 | 116.11(15) | C3-C2-C24 | 122.23(14) | C2-C3-C4 | 123.64(13) |
| C3-C4-C5 | 110.97(12) | C3-C4-C15 | 110.09(13) | C3-C4-C17 | 109.49(11) |
| C5-C4-C15 | 121.46(11) | C5-C4-C17 | 116.51(15) | C15-C4-C17 | 85.79(11) |
| C4-C5-C6 | 116.60(16) | C5-C6-C7 | 112.13(17) | C6-C7-C8 | 115.32(15) |
| C7-C8-C9 | 115.6(2) | C8-C9-C10 | 113.3(2) | C9-C10-C11 | 116.65(17) |
| C10-C11-C12 | 116.64(18) | C11-C12-C13 | 114.37(19) | C12-C13-C14 | 113.91(18) |
| C13-C14-C15 | 116.13(16) | O1-C15-C4 | 116.56(12) | O1-C15-C14 | 105.08(13) |

| | | | | | |
|---|---|---|---|---|---|
| O1-C15-C16 | 116.09(13) | C4-C15-C14 | 117.43(13) | C4-C15-C16 | 89.18(12) |
| C14-C15-C16 | 112.49(14) | C15-C16-C17 | 88.39(12) | C4-C17-C16 | 88.44(14) |
| C4-C17-C18 | 120.11(12) | C16-C17-C18 | 120.47(13) | C17-C18-C19 | 121.42(14) |
| C17-C18-C23 | 120.53(13) | C19-C18-C23 | 118.03(15) | C18-C19-C20 | 120.93(17) |
| C19-C20-C21 | 120.59(19) | C20-C21-C22 | 119.60(18) | C21-C22-C23 | 120.1(2) |
| C18-C23-C22 | 120.67(17) | O3-C24-O4 | 123.69(15) | O3-C24-C2 | 111.46(13) |
| O4-C24-C2 | 124.82(15) | | | | |




**Methyl *rac*-(1*R*,2a*S*,8b*S*)-3-oxo-1-phenyl-1,2,5,6,8,8b-hexahydro-spiro[cyclobuta[*d*]cyclohexa[*b*]pyran-7,2'-[1',3']dioxolane]-2a(3*H*)-carboxylate (17e)**

Colorless oil; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.35-7.31 (m, 2H), 7.29-7.25 (m, 1H), 7.22-7.20 (m, 2H) 3.94 (q, $J$ = 9.2 Hz, 1H), 3.86 (s, 3H), 3.84-3.73 (m, 3H), 3.55 (dt, $J$ = 13.2, 6.8 Hz, 1H), 3.40 (d, $J$ = 9.2 Hz, 1H), 3.30 (ddd, $J$ = 12.8, 9.2, 2.4 Hz, 1H), 2.92 (dd, $J$ = 12.8, 9.2 Hz, 1H), 2.42-2.32 (m, 2H), 1.72 (dt, $J$ = 13.2, 6.8 Hz, 1H), 1.62 (d, $J$ = 16.8 Hz, 1H), 1.50 (dt, $J$ = 13.2, 6.8 Hz, 1H), 1.20 (d, $J$ = 16.8 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 170.8, 165.6, 145.6, 138.0, 128.5 (2C), 127.9 (2C), 127.4, 106.8, 104.4, 64.3, 64.2, 53.3, 47.0, 46.4,

41.4, 35.8, 34.1, 30.6, 25.4; IR ($CHCl_3$): 3028.0, 1743.5 $cm^{-1}$; LR-EIMS *m/z*: 370 ($M^+$, 1.1), 266 (100), 99 (34), 86 (53).; HR-EIMS calcd for $C_{21}H_{22}O_6$: 370.1416. Found: 370.1419.

**Methyl *rac*-(4a*R*,8a*S*,10*S*)-7,8-dihydro-2-oxo-10-phenyl-4a,8a-ethano-spiro[2*H*,5*H*-1-benzopyran-6,2'-[1',3']dioxolane]-3-carboxylate (18e)**

Colorless prisms; m.p. 142.3-143.3 ℃ (Acetone); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.37-7.32 (m, 2H), 7.30-7.27 (m, 1H), 7.12-7.10 (m, 2H), 6.79 (s, 1H), 4.14-4.07 (m, 2H), 4.05-4.00 (m, 1H), 3.99-3.93 (m, 2H), 3.78 (s, 3H), 2.80 (t, $J$ = 11.2 Hz, 1H), 2.43-2.35 (m, 2H), 2.31 (dd, $J$ = 11.2, 7.6 Hz, 1H), 1.95 (d, $J$ = 14.4 Hz, 1H), 1.74 (dd, $J$ = 9.6, 4.8 Hz, 2H), 1.55 (d, $J$ = 14.4 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 163.6, 159.3, 155.0, 135.0, 128.7 (2C), 127.5 (2C), 127.4, 122.9, 107.8, 76.2, 64.6, 63.9, 52.5, 49.3, 39.7, 37.0, 36.3, 32.3, 29.5; IR ($CHCl_3$): 3028.7, 1755.9, 1728.9 $cm^{-1}$; LR-EIMS m/z: 370 (M+, 1.0), 267 (18), 266 (100), 99 (45), 86 (66).; HR-EIMS calcd for $C_{21}H_{22}O_6$: 370.1416. Found: 370.1417.

**Methyl *rac*-(1*R*,2a*S*,9b*S*)-7-methoxy-3-oxo-1-phenyl-1,2,9,9b-tetrahydrocyclobuta[*d*]indeno[1,2-*b*]pyran-2a(3*H*)-carboxylate (17f)**

Orange columns; m.p. 145.8-147.3 ℃ (Diisopropyl ether); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.33 (d, $J$ = 8.5 Hz, 1H), 7.26-7.21 (m, 3H), 7.12-7.11 (m, 2H), 6.84 (dd, $J$ = 8.5, 2.0 Hz, 1H), 6.77 (d, $J$ = 2.0 Hz, 1H), 4.11 (dt, $J$ = 10.5, 9.0 Hz, 1H), 3.95 (ddd, $J$ = 9.0, 3.0, 0.5 Hz, 1H), 3.91 (s, 3H), 3.78 (s, 3H), 3.28 (ddd, $J$ = 12.0, 9.0, 3.0 Hz, 1H), 3.06 (ddd, $J$ = 12.0, 10.5, 0.5 Hz, 1H), 2.76 (d, $J$ = 21.5 Hz, 1H), 2.12 (d, $J$ = 21.5 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 170.9. 165.7, 158.9, 149.0, 143.7, 138.5, 129.0, 128.6 (2C), 127.39 (2C), 127.35, 118.3, 111.9, 110.8, 110.5, 55.5, 53.4, 47.6, 45.4, 42.3, 35.2, 33.5; IR ($CHCl_3$): 3032.5, 1765.5, 1735.6 $cm^{-1}$; LR-EIMS *m/z*: 376 ($M^+$, 0.1), 272 (100), 244 (49), 240 (42), 273 (36), 213 (26); HR-EIMS *m/z*: Calcd for $C_{23}H_{20}O_5$: 376.1311. Found: 376.1315.

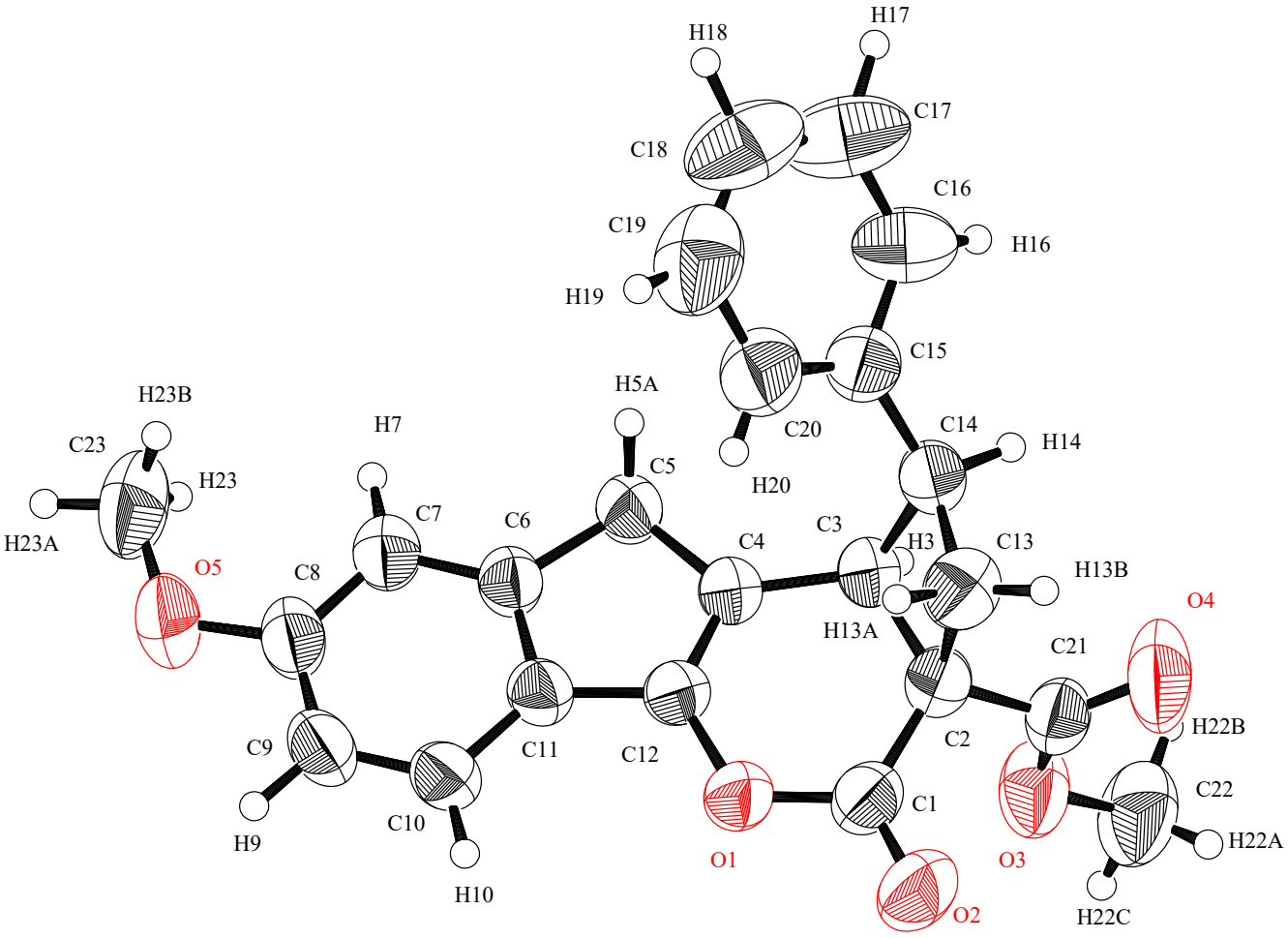
X-ray Crystal Data: Crystal Color, Habit; colorless, chunk, Crystal Dimensions; 0.300 x 0.200 x 0.100 mm, Crystal System; monoclinic, Lattice Type; Primitive, Lattice Parameters; a = 9.9435(3) Å, b = 10.5711(3) Å, c = 18.6456(5) Å, β = 99.717(7) º, V = 1931.79(10) $Å^3$, Space Group; $P2_1/n$ (#14), Z value; 4, $D_{calc}$; 1.294 $g/cm^3$, $F_{000}$; 792.00, μ(CuKα); 7.474 $cm^{-1}$, Intensity Measurement: Diffractometer; R-AXIS RAPID, Radiation; CuKα (λ = 1.54187 Å), graphite monochromated, Voltage, Current; 50 kV, 100 mA, Temperature; 23.0 ºC, Detector Aperture; 460.0 x 256.0 mm, Data Images; 45 exposures, ω oscillation Range (χ=54.0, ϕ=0.0); 80.0 - 260.0º, Exposure Rate; 120.0 sec./º, ω oscillation Range (χ=54.0, ϕ=90.0); 80.0 - 260.0º, Exposure Rate; 120.0 sec./º, ω oscillation Range (χ=54.0, ϕ=180.0); 80.0 - 260.0º, Exposure Rate; 120.0 sec./º, ω oscillation Range (χ=54.0, ϕ=270.0); 80.0 - 260.0º, Exposure Rate; 120.0 sec./º, Detector Position; 127.40 mm, Pixel Size; 0.100 mm, $2\theta_{max}$; 136.2º, No. of Reflections Measured; Total: 20772, Unique: 3469 ($R_{int}$ = 0.0449), Corrections; Lorentz-polarization Absorption (trans. factors: 0.768 - 0.928), Secondary Extinction (coefficient: 5.05000e-003). Structure Solution; Direct Methods (SHELXT Version 2014/5), Refinement; Full-matrix least-squares on $F^2$, Function Minimized; $\Sigma\ \omega\ (Fo^2 - Fc^2)^2$, Least Squares Weights; $w = 1/[\ \sigma^2(Fo^2) + (0.3509 \cdot P)^2]$ where $P = (Max(Fo^2,0) + 2Fc^2)/3$, $2\theta_{max}$ cutoff; 136.1º, Anomalous Dispersion; All non-

hydrogen atoms, No. Observations (All reflections); 3469, No. Variables; 318, Reflection/Parameter Ratio; 10.91, Residuals: R1 (I>2.00σ(I)); 0.0421, Residuals: R (All reflections); 0.0533, Residuals: wR2 (All reflections); 0.1188, Goodness of Fit Indicator; 1.056, Max Shift/Error in Final Cycle ; 0.010, Maximum peak in Final Diff. Map; 0.20 $e^-/Å^3$, Minimum peak in Final Diff. Map; -0.15 $e^-/Å^3$.

Deposition number CCDC-2047473 for **17f**. Free copies of the data can be obtained via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

| Selected Bond lengths (Å) | | | | | |
|---|---|---|---|---|---|
| O1−C1 | 1.361(2) | O1-C12 | 1.3952(19) | O2-C1 | 1.193(2) |
| O3-C21 | 1.310(2) | O3-C22 | 1.454(3) | O4-C21 | 1.183(3) |
| O5-C8 | 1.369(3) | O5-C23 | 1.419(3) | C1-C2 | 1.504(3) |
| C2-C3 | 1.565(2) | C2-C13 | 1.552(3) | C2-C21 | 1.514(2) |
| C3-C4 | 1.480(2) | C3-C14 | 1.571(2) | C4-C5 | 1.498(2) |
| C4-C12 | 1.329(2) | C5-C6 | 1.506(3) | C6-C7 | 1.383(3) |
| C6-C11 | 1.391(2) | C7-C8 | 1.389(3) | C8-C9 | 1.386(3) |
| C9-C10 | 1.379(3) | C10-C11 | 1.391(2) | C11-C12 | 1.452(2) |
| C13-C14 | 1.537(3) | C14-C15 | 1.493(2) | C15-C16 | 1.391(3) |
| C15-C20 | 1.376(3) | C16-C17 | 1.368(4) | C17-C18 | 1.350(5) |
| C18-C19 | 1.376(5) | C19-C20 | 1.418(4) | | |
| Selected Bond Angles (º) | | | | | |
| C1-O1-C12 | 118.82(13) | C21-O3-C22 | 117.3(2) | C8-O5-C23 | 117.02(18) |
| O1-C1-O2 | 117.40(18) | O1-C1-C2 | 119.05(15) | O2-C1-C2 | 123.35(18) |
| C1-C2-C3 | 120.55(15) | C1-C2-C13 | 112.53(15) | C1-C2-C21 | 110.95(14) |
| C3-C2-C13 | 88.49(12) | C3-C2-C21 | 109.55(14) | C13-C2-C21 | 113.08(16) |
| C2-C3-C4 | 109.94(13) | C2-C3-C14 | 88.01(12) | C4-C3-C14 | 118.46(13) |
| C3-C4-C5 | 127.72(15) | C3-C4-C12 | 123.40(15) | C5-C4-C12 | 108.64(15) |
| C4-C5-C6 | 102.97(14) | C5-C6-C7 | 128.91(16) | C5-C6-C11 | 109.70(15) |
| C7-C6-C11 | 121.36(16) | C6-C7-C8 | 117.87(18) | O5-C8-C7 | 123.27(18) |
| O5-C8-C9 | 115.73(17) | C7-C8-C9 | 121.01(18) | C8-C9-C10 | 120.97(18) |
| C9-C10-C11 | 118.53(18) | C6-C11-C10 | 120.25(16) | C6-C11-C12 | 105.98(14) |
| C10-C11-C12 | 133.76(16) | O1-C12-C4 | 126.79(15) | O1-C12-C11 | 120.44(14) |
| C4-C12-C11 | 112.70(14) | C2-C13-C14 | 89.71(14) | C3-C14-C13 | 88.80(13) |
| C3-C14-C15 | 121.34(16) | C13-C14-C15 | 120.74(16) | C14-C15-C16 | 118.34(19) |
| C14-C15-C20 | 122.93(19) | C16-C15-C20 | 118.7(2) | C15-C16-C17 | 121.8(3) |
| C16-C17-C18 | 119.4(3) | C17-C18-C19 | 121.5(3) | C18-C19-C20 | 119.2(3) |

| | | | | | |
|---|---|---|---|---|---|
| C15-C20-C19 | 119.4(3) | O3-C21-O4 | 123.35(18) | O3-C21-C2 | 111.65(16) |
| O4-C21-C2 | 124.77(16) | | | | |




**Methyl *rac*-(1*R*,6*R*,7*S*)-4-butyl-2-oxo-7-phenyl-5-propyl-3-oxabicyclo[4.2.0]oct-4-ene-1-carboxylate (17g)**

Colorless oil; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.33-7.28 (m, 2H), 7.25-7.21 (m, 1H), 7.19-7.16 (m, 2H), 3.85 (td, $J$ = 9.2, 6.4 Hz, 1H), 3.82 (s, 3H), 3.62 (d, $J$ = 9.2 Hz, 1H), 3.36 (ddd, $J$ = 13.2, 9.2, 0.8 Hz, 1H), 2.90 (ddd, $J$ = 13.2, 6.4, 0.8 Hz, 1H), 2.14-2.07 (m, 1H), 2.03-1.96 (m, 1H), 1.69-1.61 (m, 1H), 1.43-1.34 (m, 1H), 1.33-1.21 (m, 2H), 1.19-1.08 (m, 4H), 0.84 (t, $J$ = 7.2 Hz, 3H), 0.75 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 170.6, 167.0, 149.0, 138.4, 128.1 (2C), 127.8 (2C), 126.9, 108.3, 52.9, 47.7, 44.8, 41.2, 33.3, 30.2, 29.0, 28.8, 21.9, 20.8, 13.7, 13.5; IR ($CHCl_3$): 3030.5, 1747.4 cm$^{-1}$; LR-EIMS *m/z*: 356 ($M^+$, 0.6), 252 (100), 224 (41), 195 (20), 191 (12), 181 (34); HR-EIMS calcd for $C_{22}H_{28}O_4$: 356.1988. Found: 356.1983.

**Methyl *rac*-(1*R*,6*S*,7*R*)-1-butyl-3-oxo-7-phenyl-6-propyl-2-oxabicyclo[4.2.0]oct-4-ene-4-carboxylate (18g)**

Colorless columnar crystals; m.p. 129.7-130.9 °C (Diisopropyl ether); $^{1}$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.36-7.24 (m, 3H), 7.12-7.09 (m, 2H), 6.83 (s, 1H), 3.78 (s, 3H), 3.22 (dd, $J$ = 11.7, 7.8 Hz, 1H), 2.72 (td, $J$ = 11.7, 1.5 Hz, 1H), 2.44 (dd, $J$ = 11.7, 7.8, Hz, 1H), 1.98-1.80 (m, 3H), 1.79-1.64 (m, 2H), 1.47-1.36 (m, 3H), 1.33-

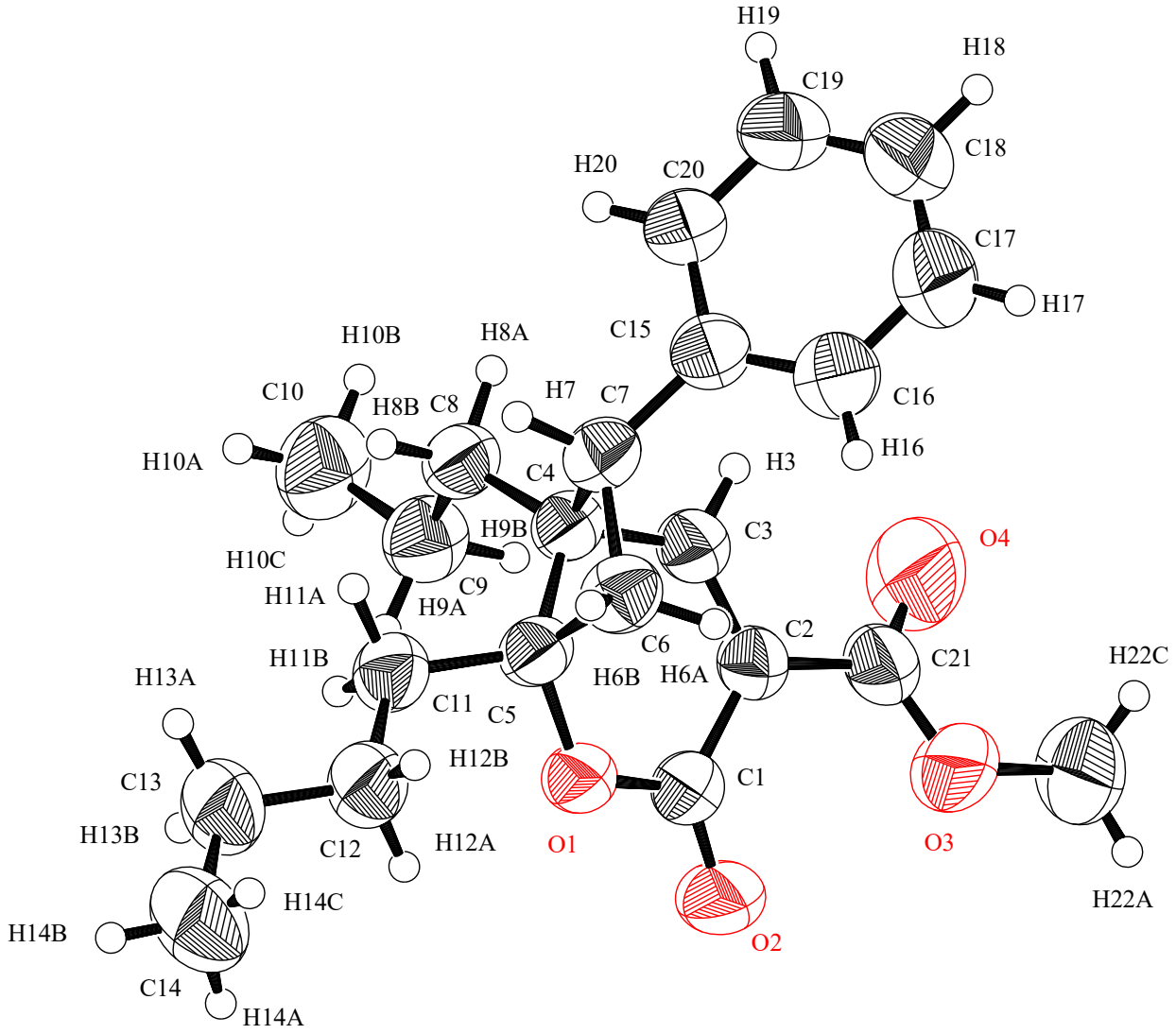
1.06 (m, 2H), 0.98 (t, $J$ = 7.2 Hz, 3H), 0.90 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 163.7, 159.0, 156.9, 135.1, 128.7 (2C), 127.7 (2C), 127.5, 124.9, 81.9, 53.2, 52.5, 44.9, 36.3, 34.4, 33.5, 24.7, 23.1, 18.9, 14.4, 14.1; IR ($CHCl_3$): 3030.6, 1754.9, 1715.4 $cm^{-1}$; LR-EIMS *m/z*: 356 ($M^+$, 0.3), 253 (27), 252 (100), 224 (53), 223 (24), 181 (47).; HR-EIMS calcd for $C_{22}H_{28}O_4$: 356.1988. Found: 356.1985.

X-ray Crystal Data: Crystal Color, Habit; colorless, block, Crystal Dimensions; 0.500 x 0.200 x 0.200 mm, Crystal System; monoclinic, Lattice Type; Primitive, Lattice Parameters; a = 9.73880(18) Å, b = 14.3807(3) Å, c = 14.9034(3) Å, β = 101.7417(10) º, V = 2043.54(7) $Å^3$, Space Group; $P2_1/c$ (#14), Z value; 4, $D_{calc}$; 1.159 $g/cm^3$, $F_{000}$; 768.00, μ(CuKα); 6.301 $cm^{-1}$, Intensity Measurement: Diffractometer; R-AXIS RAPID, Radiation; CuKα (λ = 1.54187 Å), graphite monochromated, Voltage, Current; 40 kV, 100 mA, Temperature; 23.0 ºC, Detector Aperture; 460.0 x 256.0 mm, Data Images; 30 exposures, ω oscillation Range (χ=54.0, ϕ=0.0); 80.0 - 260.0º, Exposure Rate; 60.0 sec./º, ω oscillation Range (χ=54.0, ϕ=90.0); 80.0 - 260.0º, Exposure Rate; 60.0 sec./º, ω oscillation Range (χ=54.0, ϕ=180.0); 80.0 - 260.0º, Exposure Rate; 60.0 sec./º, ω oscillation Range (χ=54.0, ϕ=270.0); 80.0 - 260.0º, Exposure Rate; 60.0 sec./º, Detector Position; 127.40 mm, Pixel Size; 0.100 mm, $2\theta_{max}$; 136.3º, No. of Reflections Measured; Total: 19998, Unique: 3716 ($R_{int}$ = 0.0458), Corrections; Lorentz-polarization Absorption (trans. factors: 0.719 - 0.882), Secondary Extinction (coefficient: 5.83000e-003). Structure Solution; Direct Methods (SHELXT Version 2014/5), Refinement; Full-matrix least-squares on $F^2$, Function Minimized; $\Sigma\ \omega\ (Fo^2 - Fc^2)^2$, Least Squares Weights; $w = 1/[\ \sigma^2(Fo^2) + (0.0728 \cdot P)^2 + 0.5425 \cdot P\ ]$ where $P = (Max(Fo^2,0) + 2Fc^2)/3$, $2\theta_{max}$ cutoff; 136.3º, Anomalous Dispersion; All non-hydrogen atoms, No. Observations (All reflections); 3716, No. Variables; 336, Reflection/Parameter Ratio; 11.06, Residuals: R1 (I>2.00σ(I)); 0.0518, Residuals: R (All reflections); 0.0729, Residuals: wR2 (All reflections); 0.1684, Goodness of Fit Indicator; 1.096, Max Shift/Error in Final Cycle; 0.005, Maximum peak in Final Diff. Map; 0.33 $e^-/Å^3$, Minimum peak in Final Diff. Map; -0.25 $e^-/Å^3$.

Deposition number CCDC-2047460 for **18g**. Free copies of the data can be obtained via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

| Selected Bond lengths (Å) | | | | | |
|---|---|---|---|---|---|
| O1-C1 | 1.344(2) | O1-C5 | 1.457(2) | O2-C1 | 1.202(3) |
| O3-C21 | 1.283(4) | O3-C22 | 1.458(3) | O4-C21 | 1.188(4) |
| C1-C2 | 1.483(3) | C2-C3 | 1.329(3) | C2-C21 | 1.496(3) |
| C3-C4 | 1.483(3) | C4-C5 | 1.551(3) | C4-C7 | 1.583(3) |
| C4-C8 | 1.527(3) | C5-C6 | 1.537(3) | C5-C11 | 1.514(3) |
| C6-C7 | 1.546(3) | C7-C15 | 1.501(3) | C8-C9 | 1.520(3) |
| C9-C10 | 1.511(5) | C11-C12 | 1.520(4) | C12-C13 | 1.502(4) |
| C13-C14 | 1.509(7) | C15-C16 | 1.381(4) | C15-C20 | 1.386(3) |
| C16-C17 | 1.390(4) | C17-C18 | 1.367(5) | C18-C19 | 1.362(5) |

| | | | | | |
|---|---|---|---|---|---|
| C19-C20 | 1.379(4) | | | | |
| Selected Bond Angles (º) | | | | | |
| C1-O1-C5 | 121.87(15) | C21-O3-C22 | 116.1(3) | O1-C1-O2 | 117.47(19) |
| O1-C1-C2 | 117.93(17) | O2-C1-C2 | 124.48(19) | C1-C2-C3 | 120.67(18) |
| C1-C2-C21 | 121.45(18) | C3-C2-C21 | 117.68(19) | C2-C3-C4 | 124.70(19) |
| C3-C4-C5 | 110.14(17) | C3-C4-C7 | 108.86(16) | C3-C4-C8 | 110.76(18) |
| C5-C4-C7 | 86.40(15) | C5-C4-C8 | 121.07(17) | C7-C4-C8 | 117.20(16) |
| O1-C5-C4 | 116.11(15) | O1-C5-C6 | 116.32(18) | O1-C5-C11 | 104.69(15) |
| C4-C5-C6 | 89.49(15) | C4-C5-C11 | 116.27(19) | C6-C5-C11 | 114.15(18) |
| C5-C6-C7 | 88.19(17) | C4-C7-C6 | 88.01(15) | C4-C7-C15 | 118.21(18) |
| C6-C7-C15 | 122.1(2) | C4-C8-C9 | 114.9(2) | C8-C9-C10 | 112.4(2) |
| C5-C11-C12 | 114.2(2) | C11-C12-C13 | 113.7(3) | C12-C13-C14 | 113.7(3) |
| C7-C15-C16 | 123.1(2) | C7-C15-C20 | 119.2(2) | C16-C15-C20 | 117.7(2) |
| C15-C16-C17 | 120.6(3) | C16-C17-C18 | 120.4(3) | C17-C18-C19 | 119.8(3) |
| C18-C19-C20 | 120.1(3) | C15-C20-C19 | 121.4(3) | O3-C21-O4 | 122.1(2) |
| O3-C21-C2 | 115.6(2) | O4-C21-C2 | 122.2(3) | | |




**Methyl *rac*-(1*R*,6*R*,7*S*)-4-ethyl-2-oxo-5,7-diphenyl-3-oxabicyclo[4.2.0]oct-4-ene-1-carboxylate (17h)**

Colorless oil; $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.25-7.23 (m, 3H), 7.16-7.10 (m, 3H), 7.01-6.99 (m, 2H), 6.56-6.55 (m, 2H), 4.04 (d, $J$ = 9.5 Hz, 1H), 3.88 (s, 3H), 3.78 (td, $J$ = 9.5, 6.0 Hz, 1H), 3.45 (dd, $J$ = 13.5, 9.5 Hz, 1H), 2.98 (dd, $J$ = 13.5, 6.0 Hz, 1H), 1.99 (q, $J$ = 7.0 Hz, 2H), 0.93 (t, $J$ = 7.0 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 170.7, 167.3, 151.9, 138.4, 136.4, 128.6 (2C), 128.3 (2C), 128.1 (2C), 127.9 (2C), 127.0, 126.9, 110.9, 53.3, 48.3, 46.9, 41.2, 33.5, 23.7, 11.7; IR ($CHCl_3$): 3027.7, 1753.0, 1736.6 cm$^{-1}$; LR- EIMS *m*/*z*: 362 ($M^+$, 0.6), 259 (20), 258 (100), 230 (27), 229 (23), 200 (16),197 (19).; HR-EIMS *m*/*z*: Calcd for $C_{23}H_{22}O_4$: 362.1518. Found: 362.1521.

**Methyl *rac*-(1*R*,6*S*,7*R*)-1-ethyl-3-oxo-6,7-diphenyl-2-oxabicyclo[4.2.0]oct-4-ene-4-carboxylate (18h)**

Colorless prisms; m.p. 168.4-170.0 °C (Diisopropyl ether); $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.44-7.41 (m, 2H), 7.37-7.26 (m, 8H), 7.07 (s, 1H), 4.17 (dd, $J$ = 12.0, 8.5 Hz, 1H), 3.77 (s, 3H), 2.79 (td, $J$ = 12.0, 1.5 Hz, 1H), 2.66 (dd, $J$ = 12.0, 8.5 Hz, 1H), 1.53-1.42 (m, 2H), 0.96 (t, $J$ = 7.5 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 163.7, 159.1, 154.6, 136.6, 135.7, 129.0 (2C), 128.8 (2C), 128.3, 128.0 (2C), 127.6, 127.5 (2C), 123.6, 82.8, 56.4, 52.7, 40.1, 34.5, 28.6, 6.8; IR ($CHCl_3$): 3032.5, 1732.7, 1716.3 cm$^{-1}$;LR-MIES *m*/*z*: 362 ($M^+$, 9.8), 330

(79), 259 (84), 258 (100), 230 (40), 229 (39). 215 (30), 202 (36), 197 (39).; HR-EIMS *m/z*: Calcd for $C_{23}H_{22}O_4$: 362.1518. Found: 362.1519.

**Methyl *rac*-(1*R*,6*R*,7*S*)-5-methyl-2-oxo-4,7-diphenyl-3-oxabicyclo[4.2.0]oct-4-ene-1-carboxylate (17i)**

Colorless oil; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.37-7.28 (m, 8H), 7.25-7.22 (m, 2H), 4.05 (q, $J$ = 9.0 Hz, 1H), 3.89 (s, 3H), 3.63 (d, $J$ = 9.5 Hz, 1H), 3.39 (ddd, $J$ = 13.0, 9.5, 2.0 Hz, 1H), 3.02 (dd, $J$ = 13.0, 8.0 Hz, 1H), 1.12 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 170.7, 166.0, 146.2, 138.3, 132.8, 128.8, 128.7 (2C), 128.4 (2C), 128.00 (2C), 127.95 (2C), 127.4, 107.5, 53.3, 48.2, 47.7, 41.7, 33.7, 16.7; IR ($CHCl_3$): 3027.0, 1732.0 cm$^{-1}$; LR-EIMS *m/z*: 348 ($M^+$, 0.3), 244 (100), 216 (95), 105 (44); HR-EIMS calcd for $C_{22}H_{20}O_4$: 348.1362. Found: 348.1365.

**Methyl *rac*-(1*R*,6*S*,7*R*)-6-methyl-3-oxo-1,7-diphenyl-2-oxabicyclo[4.2.0]oct-4-ene-4-carboxylate (18i)**

Colorless prisms; m.p. 150.7-151.4 ℃ (Diisopropyl ether); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.54 (d, $J$ = 7.5 Hz, 2H), 7.47 (t, $J$ = 7.5 Hz, 2H), 7.41, (t, $J$ = 7.5 Hz, 1H), 7.36 (t, $J$ = 7.5 Hz, 2H), 7.31 (t, $J$ = 7.5 Hz, 1H), 7.15 (d, $J$ = 7.5 Hz, 2H), 6.87 (s, 1H), 3.80 (s, 3H), 3.49 (dd, $J$ = 11.5, 8.0 Hz, 1H), 3.19 (dd, $J$ = 12.5, 8.0 Hz, 1H), 3.15 (dd, $J$ = 12.5, 11.5 Hz, 1H), 0.95 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 163.7, 158.7, 156.8, 137.5, 134.8, 128.8 (2C), 128.6 (3C), 127.7, 127.4 (2C), 126.4 (2C), 123.4, 83.2, 52.7, 50.2, 45.9, 35.3, 22.1; IR ($CHCl_3$): 3028.0, 1755.1, 1732.0 cm$^{-1}$; LR-EIMS *m/z*: 348 ($M^+$, 1.0), 244 (100), 216 (87), 185 (16), 129 (15), 105 (55), 77 (27).; HR-EIMS calcd for $C_{22}H_{20}O_4$: 348.1362. Found: 348.1361.

**Methyl *rac*-(1*R*,6*R*,7*S*)-5-(2-methoxyphenyl)-4-methyl-2-oxo-7-phenyl-3-oxabicyclo[4.2.0]oct-4-ene-1-carboxylate (17j)**

Colorless oil; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.27-7.19 (m, 3H), 7.14 (ddd, $J$ = 8.4, 7.5, 1.8 Hz, 1H), 7.04-6.98 (m, 2H), 6.73 (d, $J$ = 8.2 Hz, 1H), 6.62 (td, $J$ = 7.5, 0.9 Hz, 1H), 5.98 (brs, 1H), 4.19 (dq, $J$ = 9.6, 1.2, 1H), 3.88 (s, 3H), 3.73 (td, $J$ = 9.6, 6.0 Hz, 1H), 3.69 (s, 3H), 3.42 (ddd, $J$ = 13.2, 9.6, 0.9 Hz, 1H), 2.96 (ddd, $J$ = 13.2, 6.0, 0.9 Hz, 1H), 1.61 (d, $J$ = 1.2 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 170.9, 167.5, 156.7, 147.6, 138.7, 131.3, 128.7, 128.3 (2C), 128.0 (2C), 126.8, 124.4, 120.0, 110.5, 108.9, 55.3, 53.2, 48.2, 45.1, 41.2, 33.4, 16.9; IR ($CHCl_3$): 3027.7, 1752.0, 1736.6 cm$^{-1}$;LR-EIMS *m/z*: 378 ($M^+$, 1.8), 275 (17), 274 (100), 246 (20), 242 (24), 227 (29), 189 (13), 159 (13), 115 (10).; HR-EIMS *m/z*: Calcd for $C_{23}H_{22}O_5$: 378.1467. Found: 378.1467.

**Methyl *rac*-(1*R*,6*S*,7*R*)-6-(2-methoxyphenyl)-1-methyl-3-oxo-7-phenyl-2-oxabicyclo[4.2.0]oct-4-ene-4-carboxylate (18j)**

Colorless prisms; m.p. 163.7-165.0 ℃ (Diisopropyl ether); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.51 (d, $J$ = 8.0 Hz, 1H), 7.41-7.27 (m, 6H), 7.02-7.06 (m, 2H), 6.88 (d, $J$ = 8.0 Hz, 1H), 3.98 (dd, $J$ = 11.6, 8.0 Hz, 1H), 3.78 (d, $J$ = 0.8 Hz, 3H), 3.73 (d, $J$ = 0.8 Hz, 3H), 2.92 (t, $J$ = 11.6 Hz, 1H), 2.51 (dd, $J$ = 11.6, 8.0 Hz, 1H), 1.35 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 164.1, 159.7, 157.9, 152.6, 136.2, 129.8, 128.8 (2C), 128.6 (2C), 127.6,

127.4, 126.6, 123.9, 121.0, 111.1, 79.8, 55.3, 55.0, 52.5, 42.2, 38.8, 22.7; IR ($CHCl_3$): 3035.4, 1746.2, 1701.9 $cm^{-1}$;LR-EIMS *m*/*z*: 378 ($M^+$, 11.1), 360 (85), 346 (89), 328 (53), 321 (23), 303 (32), 289 (46), 275 (41), 274 (100), 246 (38).; HR-EIMS *m*/*z*: Calcd for $C_{23}H_{22}O_5$: 378.1467. Found: 378.1469.

Aliquot of the mixture of **17ka** and **17kb** (**17ka** : **17kb** = 4 : 6) was purified by preparative HPLC. Cosmosil 5SL-II, EtOAc–*n*-hexane (1:20), 3.0 mL/min (254 nm), number of recycles: 12. First fraction was **17ka**. Second fraction was **17kb**.

**Methyl *rac*-(1*R*,2a*S*,7*R*,8b*S*)-7-methyl-3-oxo-1-phenyl-1,5,6,7,8,8b-hexahydro-2*H*-cyclobuta[*d*]cyclohex[*b*]pyran-2a(3*H*)-carboxylate (17ka)**

Colorless oil; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.32-7.29 (m, 2H), 7.26-7.23 (m, 1H), 7.20-7.18 (m, 2H), 3.89 (q, *J* = 8.0 Hz, 1H), 3.85 (s, 3H), 3.42 (dd, *J* = 9.5, 1.0 Hz, 1H), 3.36 (ddd, *J* = 13.0, 9.5, 2.0 Hz, 1H), 2.88 (ddd, *J* = 13.0, 8.0, 1.0 Hz, 1H), 2.19-2.08 (m, 2H), 1.58-1.54 (m, 1H), 1.29-1.23 (m, 1H), 1.22-1.14 (m, 1H), 1.03 (dd, *J* = 16.0, 4.5 Hz, 1H), 1.00-0.92 (m, 1H), 0.68 (d, *J* = 6.5 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 171.0, 166.4, 146.6, 138.6, 128.3 (2C), 127.9 (2C), 127.2, 106.1, 53.2, 47.7, 45.9, 41.2, 34.1, 33.7, 30.0, 27.9, 26.2, 20.9; IR ($CHCl_3$): 3028.7, 1739.5 $cm^{-1}$;LR-EIMS *m*/*z*: 326 ($M^+$, 1.0), 223 (14), 222 (100), 194 (38), 190 (10), 152 (30), 135 (12), 104 (13), 91 (8).; HR-EIMS *m*/*z*: Calcd for $C_{20}H_{22}O_4$: 326.1518. Found: 326.1517.

**Methyl *rac*-(1*R*,2a*S*,7*S*,8b*S*)-7-methyl-3-oxo-1-phenyl-1,5,6,7,8,8b-hexahydro-2*H*-cyclobuta[*d*]cyclohex[*b*]-2a(3*H*)-carboxylate (17kb)**

Colorless oil; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.33-7.29 (m, 2H), 7.27-7.23 (m, 1H), 7.20-7.18 (m, 2H), 3.93 (q, *J* = 9.0 Hz, 1H), 3.86 (s, 3H), 3.39 (d, *J* = 9.0 Hz, 1H), 3.32 (ddd, *J* = 13.0, 9.0, 2.0 Hz, 1H), 2.90 (ddd, *J* = 13.0, 8.5, 0.5 Hz, 1H), 2.22-2.08 (m, 2H), 1.60-1.55 (m, 2H), 1.53-1.44 (m, 2H), 0.94 (dtd, *J* = 13.0, 10.5, 6.5 Hz, 1H), 0.57 (d, *J* = 6.5 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 171.0, 166.2, 146.5, 138.5, 128.3 (2C), 128.0 (2C), 127.2, 106.2, 53.2, 47.6, 46.9, 41.3, 34.4, 33.7, 29.8, 28.0, 26.1, 20.6; IR ($CHCl_3$): 3029.6, 1738.5 $cm^{-1}$;LR-EIMS *m*/*z*: 326 ($M^+$, 1.2), 222 (100), 194 (48), 190 (14), 162 (17), 152 (39), 135 (15), 104 (22), 91 (10).; HR-EIMS *m*/*z*: Calcd for $C_{20}H_{22}O_4$: 326.1518. Found: 326.1514.

Aliquot of the mixture of **18ka** and **18kb** (**18ka** : **18kb** = 6 : 4) was purified by preparative HPLC. Cosmosil 5$C_{18}$-AR-II packed column, $CH_3CN$–$H_2O$ (3:2), 3.0 mL/min (254 nm), number of recycles: 6. First fraction was **18ka**. Second fraction was **18kb**.

**Methyl *rac*-(4a*R*,6*R*,8a*S*,10*S*)-6-methyl--5,6,7,8-tetrahydro-2-oxo-10-phenyl-4a,8a-ethano-2*H*-1-benzopyran-3-carboxylate (18ka)**

Colorless prisms; m.p. 135.4-136.6 °C (Diisopropyl ether); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.33 (t, *J* = 7.5 Hz, 2H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.12 (d, *J* = 7.5 Hz, 2H), 6.83 (s, 1H), 3.75 (s, 3H), 3.50 (dd, *J* = 10.0, 8.0 Hz, 1H), 2.78 (t, *J* = 11.5 Hz, 1H), 2.45 (dd, *J* = 12.0, 8.0 Hz, 1H), 2.15-2.10 (m, 1H), 2.02-1.91 (m, 2H), 1.72 (dd, *J* = 13.0, 3.5 Hz, 1H), 1.66 (t, *J* = 11.5 Hz, 1H), 1.59-1.49 (m, 1H), 1.33-1.26 (m, 1H), 1.00 (d, *J* = 6.5 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 163.6, 159.0, 155.1, 135.7, 128.6 (2C), 127.2 (2C), 127.1, 124.1, 78.2, 52.4, 48.6, 47.5, 39.0, 36.5, 28.4, 25.9, 23.4, 22.0.; IR ($CHCl_3$): 3025.8, 1757.8, 1707.7 $cm^{-1}$;LR-EIMS *m*/*z*:

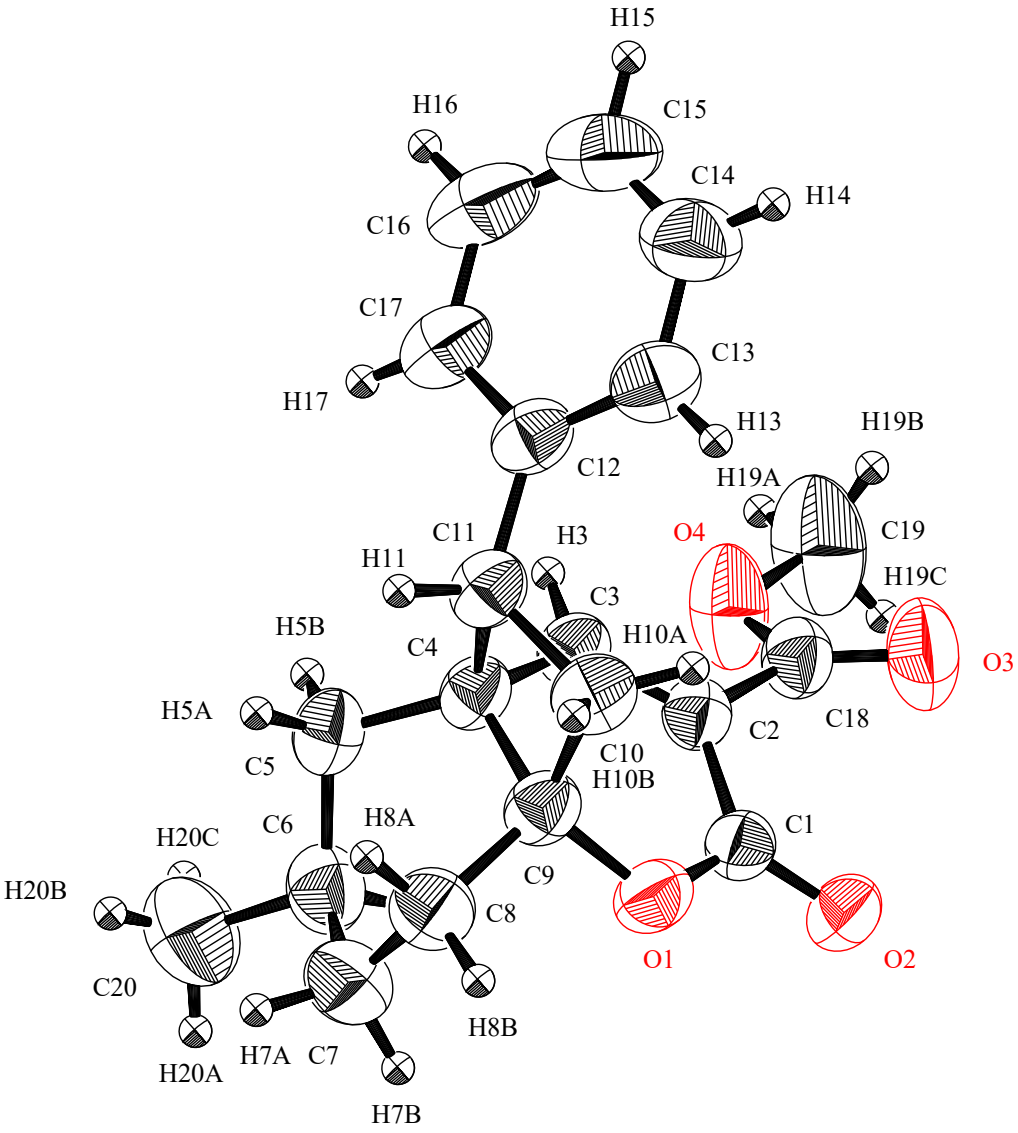
326 ($M^+$, 0.8), 252 (12), 223 (22), 222 (100), 194 (38), 191 (11), 190 (11), 167 (15), 162 (14), 152 (37).; HR-EIMS *m*/*z*: Calcd for $C_{20}H_{22}O_4$: 326.1518. Found: 326.1518.

X-ray Crystal Data: Crystal Color, Habit; colorless, block, Crystal Dimensions; 0.300 x 0.250 x 0.200 mm, Crystal System; monoclinic, Lattice Type; Primitive, Lattice Parameters; a = 9.8286(2) Å, b = 9.7685(2) Å, c = 18.4242(4) Å, β = 90.441(6) º, V = 1768.88(7) $Å^3$, Space Group; $P2_1/n$ (#14), Z value; 4, $D_{calc}$; 1.226 g/$cm^3$, $F_{000}$; 696.00, μ(CuKα); 6.864 $cm^{-1}$, Intensity Measurement: Diffractometer; R-AXIS RAPID, Radiation; CuKα (λ = 1.54187 Å), graphite monochromated, Voltage, Current; 40 kV, 100 mA, Temperature; 20.0 ºC, Detector Aperture; 460.0 x 256.0 mm, Data Images; 45 exposures, ω oscillation Range (χ=54.0, ϕ=0.0); 80.0 - 260.0º, Exposure Rate; 150.0 sec./º, ω oscillation Range (χ=54.0, ϕ=90.0); 80.0 - 260.0º, Exposure Rate; 150.0 sec./º, ω oscillation Range (χ=54.0, ϕ=180.0); 80.0 - 260.0º, Exposure Rate; 150.0 sec./º, ω oscillation Range (χ=54.0, ϕ=270.0); 80.0 - 260.0º, Exposure Rate; 150.0 sec./º, Detector Position; 127.40 mm, Pixel Size; 0.100 mm, $2\theta_{max}$; 136.1º, No. of Reflections Measured; Total: 18635, Unique: 3231 ($R_{int}$ = 0.0512), Corrections; Lorentz-polarization Absorption (trans. factors: 0.741 - 0.872), Secondary Extinction (coefficient: 3.69000e-003). Structure Solution; Direct Methods (SHELXT Version 2018/2), Refinement; Full-matrix least-squares on $F^2$, Function Minimized; $\Sigma\ \omega\ (Fo^2 - Fc^2)^2$, Least Squares Weights; $w = 1/[\ \sigma^2(Fo^2) + (0.0507 \cdot P)^2 + 0.2518 \cdot P\ ]$ where $P = (Max(Fo^2,0) + 2Fc^2)/3$, $2\theta_{max}$ cutoff; 136.1º, Anomalous Dispersion; All non-hydrogen atoms, No. Observations (All reflections); 3231, No. Variables; 218, Reflection/Parameter Ratio; 14.82, Residuals: R1 (I>2.00σ(I)); 0.0388, Residuals: R (All reflections); 0.0452, Residuals: wR2 (All reflections); 0.1090, Goodness of Fit Indicator; 1.034, Max Shift/Error in Final Cycle; 0.000, Maximum peak in Final Diff. Map; 0.17 $e^-/Å^3$, Minimum peak in Final Diff. Map; -0.12 $e^-/Å^3$.

Deposition number CCDC-2047475 for **18k**. Free copies of the data can be obtained via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

| Selected Bond lengths (Å) | | | | | |
|---|---|---|---|---|---|
| O1-C1 | 1.3440(16) | O1-C9 | 1.4541(15) | O2-C1 | 1.2008(15) |
| O3-C18 | 1.1899(17) | O4-C18 | 1.3216(18) | O4-C19 | 1.455(2) |
| C1-C2 | 1.4825(16) | C2-C3 | 1.3291(16) | C2-C18 | 1.4882(18) |
| C3-C4 | 1.4837(18) | C4-C5 | 1.5317(18) | C4-C9 | 1.5484(17) |
| C4-C11 | 1.5817(18) | C5-C6 | 1.526(2) | C6-C7 | 1.538(2) |
| C6-C20 | 1.519(2) | C7-C8 | 1.524(2) | C8-C9 | 1.5023(19) |
| C9-C10 | 1.5263(19) | C10-C11 | 1.5433(18) | C11-C12 | 1.5072(19) |
| C12-C13 | 1.379(2) | C12-C17 | 1.387(2) | C13-C14 | 1.385(2) |
| C14-C15 | 1.365(3) | C15-C16 | 1.368(3) | C16-C17 | 1.387(3) |
| Selected Bond Angles (º) | | | | | |
| C1-O1-C9 | 120.96(9) | C18-O4-C19 | 115.39(14) | O1-C1-O2 | 118.70(11) |

| | | | | | |
|---|---|---|---|---|---|
| O1-C1-C2 | 117.87(10) | O2-C1-C2 | 123.28(11) | C1-C2-C3 | 122.12(11) |
| C1-C2-C18 | 116.56(10) | C3-C2-C18 | 121.30(11) | C2-C3-C4 | 123.81(11) |
| C3-C4-C5 | 111.79(11) | C3-C4-C9 | 111.26(10) | C3-C4-C11 | 110.77(10) |
| C5-C4-C9 | 114.07(10) | C5-C4-C11 | 119.83(10) | C9-C4-C11 | 86.76(9) |
| C4-C5-C6 | 109.60(11) | C5-C6-C7 | 110.48(13) | C5-C6-C20 | 112.90(13) |
| C7-C6-C20 | 111.00(13) | C6-C7-C8 | 113.70(13) | C7-C8-C9 | 112.92(13) |
| O1-C9-C4 | 117.56(11) | O1-C9-C8 | 105.95(11) | O1-C9-C10 | 115.18(10) |
| C4-C9-C8 | 111.42(11) | C4-C9-C10 | 90.63(10) | C8-C9-C10 | 116.04(12) |
| C9-C10-C11 | 88.92(10) | C4-C11-C10 | 88.77(9) | C4-C11-C12 | 119.75(11) |
| C10-C11-C12 | 119.58(11) | C11-C12-C13 | 122.12(12) | C11-C12-C17 | 119.68(13) |
| C13-C12-C17 | 118.18(14) | C12-C13-C14 | 121.01(15) | C13-C14-C15 | 120.23(18) |
| C14-C15-C16 | 119.65(19) | C15-C16-C17 | 120.55(17) | C12-C17-C16 | 120.36(16) |
| O3-C18-O4 | 123.35(13) | O3-C18-C2 | 125.02(13) | O4-C18-C2 | 111.57(11) |



**Methyl *rac*-(4a*R*,6*S*,8a*S*,10*S*)-6-methyl-5,6,7,8-tetrahydro-2-oxo-10-phenyl-4a,8a-ethano-2*H*-1-benzopyran-3-carboxylate (18kb)**

Colorless prisms; m.p. 135.5-136.9 °C (Diisopropyl ether); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.35 (t, $J$ = 7.5 Hz, 2H), 7.28 (t, $J$ = 7.5 Hz, 1H), 7.11 (d, $J$ = 7.5 Hz, 2H), 6.83 (s, 1H), 3.77 (s, 3H), 3.48 (dd, $J$ = 11.0, 7.0 Hz, 1H), 2.79 (t, $J$ = 11.0 Hz, 1H), 2.40 (d, $J$ = 15.0 Hz, 1H), 2.27 (dd, $J$ = 11.0, 7.0 Hz, 1H), 1.92-1.82 (m, 3H), 1.65 (d, $J$ = 13.5 Hz, 1H), 1.12-1.07 (m, 1H), 1.03 (d, $J$ = 6.0 Hz, 3H), 0.93 (t, $J$ = 12.5 Hz, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 163.9, 159.4, 156.1, 135.2, 128.7 (2C), 127.5 (2C), 127.4, 122.7, 76.5, 52.5, 49.4, 39.1, 37.5, 36.7, 35.3, 29.3, 27.8, 22.1; IR ($CHCl_3$): 3029.6, 1709.6 cm$^{-1}$;LR-EIMS *m*/*z*: 326 ($M^+$, 1.3), 223 (34), 222 (100), 195 (11), 194 (70), 191 (19), 190 (20), 167 (10), 162 (24), 152 (62).; HR-EIMS *m*/*z*: Calcd for $C_{20}H_{22}O_4$: 326.1518. Found: 326.1518.

X-ray Crystal Data: Crystal Color, Habit; colorless, block, Crystal Dimensions; 0.350 x 0.300 x 0.150 mm, Crystal System; monoclinic, Lattice Type; C-centered, Lattice Parameters; a = 19.1195(6) Å, b = 12.5429(4) Å, c = 14.4946(5) Å, β = 94.319(7) º, V = 3466.1(2) Å$^3$, Space Group; C2/c (#15), Z value; 8, $D_{calc}$; 1.251 g/cm$^3$, $F_{000}$; 1392.00, μ(CuKα); 7.006 cm$^{-1}$, Intensity Measurement: Diffractometer; R-AXIS RAPID, Radiation; CuKα (λ = 1.54187 Å), graphite monochromated, Voltage, Current; 40 kV, 100 mA, Temperature; 23.0 ºC, Detector Aperture; 460.0 x 256.0 mm, Data Images; 45 exposures, ω oscillation Range (χ=54.0, ϕ=0.0); 80.0 - 260.0º, Exposure Rate; 90.0 sec./º, ω oscillation Range (χ=54.0, ϕ=90.0); 80.0 - 260.0º, Exposure Rate; 90.0 sec./º, ω oscillation Range (χ=54.0, ϕ=180.0); 80.0 - 260.0º, Exposure Rate; 90.0 sec./º, ω oscillation Range (χ=54.0, ϕ=270.0); 80.0 - 260.0º, Exposure Rate; 90.0 sec./º, Detector Position; 127.40 mm, Pixel Size; 0.100 mm, $2\theta_{max}$; 136.3º, No. of Reflections Measured; Total: 19254, Unique: 3162 ($R_{int}$ = 0.0795), Corrections; Lorentz-polarization Absorption (trans. factors: 0.694 - 0.900), Secondary Extinction (coefficient: 1.26000e-003). Structure Solution; Direct Methods (SHELXT Version 2018/2), Refinement; Full-matrix least-squares on F$^2$, Function Minimized; Σ ω (Fo$^2$ - Fc$^2$)$^2$, Least Squares Weights; w = 1/ [ σ$^2$(Fo$^2$) + (0.0468 · P)$^2$ + 1.6691 · P ] where P = (Max(Fo$^2$,0) + 2Fc$^2$)/3, $2\theta_{max}$ cutoff; 136.3º, Anomalous Dispersion; All non-hydrogen atoms, No. Observations (All reflections); 3162, No. Variables; 218, Reflection/Parameter Ratio; 14.50, Residuals: R1 (I>2.00σ(I)); 0.0419, Residuals: R (All reflections); 0.0509, Residuals: wR2 (All reflections); 0.1143, Goodness of Fit Indicator; 1.040, Max Shift/Error in Final Cycle; 0.001, Maximum peak in Final Diff. Map; 0.22 e$^-$/Å$^3$, Minimum peak in Final Diff. Map; -0.17 e$^-$/Å$^3$.

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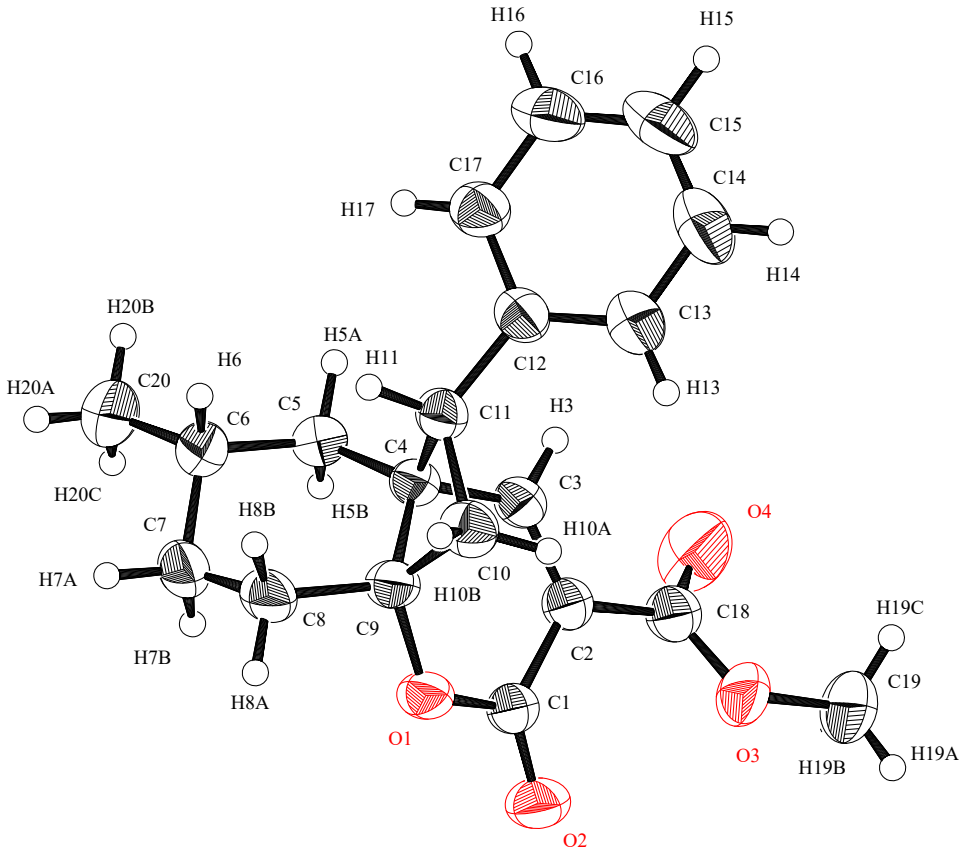
| Selected Bond lengths (Å) | | | | | |
|---|---|---|---|---|---|
| O1-C1 | 1.3452(18) | O1-C9 | 1.4512(17) | O2-C1 | 1.1998(18) |
| O3-C18 | 1.324(2) | O3-C19 | 1.444(3) | O4-C18 | 1.190(2) |
| C1-C2 | 1.491(2) | C2-C3 | 1.330(2) | C2-C18 | 1.497(2) |
| C3-C4 | 1.486(2) | C4-C5 | 1.5247(19) | C4-C9 | 1.5441(19) |

| | | | | | |
|---|---|---|---|---|---|
| C4-C11 | 1.578(2) | C5-C6 | 1.524(2) | C6-C7 | 1.530(2) |
| C6-C20 | 1.519(2) | C7-C8 | 1.519(2) | C8-C9 | 1.530(2) |
| C9-C10 | 1.534(2) | C10-C11 | 1.545(2) | C11-C12 | 1.501(2) |
| C12-C13 | 1.381(2) | C12-C17 | 1.389(2) | C13-C14 | 1.394(3) |
| C14-C15 | 1.364(3) | C15-C16 | 1.370(3) | C16-C17 | 1.381(2) |
| Selected Bond Angles (º) | | | | | |
| C1-O1-C9 | 121.60(10) | C18-O3-C19 | 116.43(13) | O1-C1-O2 | 118.14(13) |
| O1-C1-C2 | 117.80(12) | O2-C1-C2 | 123.94(14) | C1-C2-C3 | 120.95(13) |
| C1-C2-C18 | 119.73(13) | C3-C2-C18 | 119.17(13) | C2-C3-C4 | 123.95(13) |
| C3-C4-C5 | 110.03(11) | C3-C4-C9 | 109.90(12) | C3-C4-C11 | 110.99(11) |
| C5-C4-C9 | 119.27(11) | C5-C4-C11 | 119.08(12) | C9-C4-C11 | 85.45(10) |
| C4-C5-C6 | 113.30(12) | C5-C6-C7 | 109.49(13) | C5-C6-C20 | 110.98(14) |
| C7-C6-C20 | 112.77(14) | C6-C7-C8 | 111.11(13) | C7-C8-C9 | 113.51(13) |
| O1-C9-C4 | 116.60(11) | O1-C9-C8 | 105.84(11) | O1-C9-C10 | 117.56(13) |
| C4-C9-C8 | 113.71(12) | C4-C9-C10 | 89.55(10) | C8-C9-C10 | 113.42(12) |
| C9-C10-C11 | 86.96(11) | C4-C11-C10 | 87.89(10) | C4-C11-C12 | 120.35(12) |
| C10-C11-C12 | 123.96(13) | C11-C12-C13 | 123.42(14) | C11-C12-C17 | 118.50(14) |
| C13-C12-C17 | 118.08(14) | C12-C13-C14 | 120.31(17) | C13-C14-C15 | 120.41(19) |
| C14-C15-C16 | 120.20(18) | C15-C16-C17 | 119.62(17) | C12-C17-C16 | 121.35(16) |
| O3-C18-O4 | 123.66(16) | O3-C18-C2 | 112.91(13) | O4-C18-C2 | 123.31(16) |




**Methyl *rac*-(1*R*,2a*S*,8b*S*)-1-(4-fluorophenyl)-3-oxo-1,5,6,7,8,8b-hexahydro-2*H*-cyclobuta[*d*]cyclohex[*b*]pyran-2a(3*H*)-carboxylate (17l)**

Yellowish oil; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.29 (d, $J$ = 8.4 Hz, 2H), 7.13 (d, $J$ = 8.4 Hz, 2H), 3.88 (q, $J$ = 9.0 Hz, 1H), 3.80 (s, 3H), 3.42 (d, $J$ = 9.2 Hz, 1H), 3.35 (ddd, $J$ = 12.8, 9.2, 2.0 Hz, 1H), 2.82 (dd, $J$ = 12.8, 8.4 Hz, 1H), 2.15-2.09 (m, 2H), 1.62-1.42 (m, 4H), 1.40-1.31 (m, 1H), 1.14-1.04 (m, 1H), 1.02-0.95 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 170.8, 166.1, 162.0 (d, $J$ = 244.7 Hz), 147.0, 134.4, 129.4 (d, $J$ = 8.1 Hz, 2C), 115.1 (d, $J$ = 21.1 Hz, 2C), 106.6, 53.3, 47.6, 46.4, 40.5, 34.3, 26.3, 25.9, 21.9, 21.7; IR ($CHCl_3$): 3026.1, 1747.4 cm$^{-1}$; LR-EIMS *m/z*: 330 ($M^+$,1.8), 208 (100), 180 (42), 122 (26), 121 (29).; HR-EIMS calcd for $C_{19}H_{19}FO_4$: 330.1267. Found: 330.1261.

**Methyl *rac*-(4a*R*,8a*S*,10*S*)-5,6,7,8-tetrahydro-2-oxo-10-(4-fluorophenyl)-4a,8a-ethano-2*H*-1-benzopyran-3-carboxylate (18l)**

Colorless cubics; m.p. 159.3-160.1 °C; $^{1}$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.13-6.98 (m, 4H), 6.82 (s, 1H), 3.79 (s, 3H), 3.50 (dd, $J$ = 11.4, 7.5 Hz, 1H), 2.74 (t, $J$ = 11.4 Hz, 1H), 2.38 (dt, $J$ = 15.6, 3.0 Hz, 1H), 2.33 (dd, $J$ = 11.4, 7.5 Hz, 1H), 1.91-1.80 (m, 3H), 1.78-1.69 (m, 1H), 1.68-1.56 (m, 1H), 1.44-1.21 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 163.8, 162.1 (d, $J$ = 244.9 Hz), 159.3, 156.0, 131.0 (d, $J$ = 3.2 Hz), 129.0 (d, $J$ = 8.0 Hz, 2C), 123.1, 115.7 (d, $J$ = 21.2 Hz, 2C), 76.9, 52.6, 48.4, 38.2, 37.3, 34.6, 28.8, 20.6, 20.4; IR ($CHCl_3$): 3026.1, 1755.1, 1728.1 cm$^{-1}$; LR-EIMS *m/z*: 330 ($M^+$,1.0), 208 (100), 180 (48), 122 (26), 121 (36).; HR-EIMS calcd for $C_{19}H_{19}FO_4$: 330.1267. Found: 330.1272.

**methyl *rac*-(1*R*,2a*S*,8b*S*)-1-(4-chlorophenyl)-3-oxo-1,5,6,7,8,8b-hexahydro-2*H*-cyclobuta[*d*]cyclohex[*b*]pyran-2a(3*H*)-carboxylate (17m)**

Yellowish oil; $^{1}$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.32-7.27 (m, 2H), 7.15-7.11 (m, 2H), 3.88 (q, $J$ = 9.3 Hz, 1H), 3.80 (s, 3H), 3.42 (dq, $J$ = 9.3, 2.1 Hz, 1H), 3.35 (ddd, $J$ = 12.9, 9.3, 2.1 Hz, 1H), 2.82 (ddd, $J$ = 12.9, 8.4, 1.2 Hz, 1H), 2.12 (tq, $J$ = 6.9, 2.1 Hz, 2H), 1.67-1.51 (m, 2H), 1.49-1.44 (m, 1H), 1.43-1.30 (m, 1H), 1.15-1.05 (m, 1H), 1.04-0.94 (m, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 170.8, 166.0, 147.1, 137.2, 133.1, 129.3 (2C), 128.4 (2C), 106.5, 53.3, 47.6, 46.4, 40.7, 34.2, 26.3, 26.0, 22.0, 21.8; IR ($CHCl_3$): 1752.0 cm$^{-1}$; LR-EIMS *m/z*: 346 ($M^+$,0.9), 208 (100), 180 (65), 121 (33).; HR- EIMS calcd for $C_{19}H_{19}ClO_4$: 346.0972. Found: 346.0969.

**Methyl *rac*-(4a*R*,8a*S*,10*S*)-5,6,7,8-tetrahydro-2-oxo-10-(4-chlorophenyl)-4a,8a-ethano-2*H*-1-benzopyran-3-carboxylate (18m)**

Colorless cubics; m.p. 145.2-146.0 ℃; $^{1}$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.34-7.30 (m, 2H), 7.06-7.02 (m, 2H), 6.81 (s, 1H), 3.80 (s, 3H), 3.49 (dd, $J$ = 11.1, 7.2 Hz, 1H), 2.74 (t, $J$ = 11.1 Hz, 1H), 2.37 (dt, $J$ = 15.6, 2.7 Hz, 1H), 2.29 (dd, $J$ = 11.1, 7.5 Hz, 1H), 1.93-1.80 (m, 3H), 1.78-1.67 (m, 1H), 1.66-1.56 (m, 1H), 1.46-1.22 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 163.8, 159.3, 155.7, 133.8, 133.4, 129.0 (2C), 128.9 (2C), 123.2, 76.9, 52.7, 48.4, 38.3, 37.1, 34.7, 28.9, 20.6, 20.4; IR ($CHCl_3$): 3026.7, 1755.9, 1729.8 cm$^{-1}$; LR-EIMS *m/z*: 346 ($M^+$,0.7), 208 (100), 180 (52), 121 (30).; HR-EIMS calcd for $C_{19}H_{19}ClO_4$: 346.0972. Found: 346.0977.

**Methyl *rac*-(1*R*,2a*S*,8b*S*)-1-(4-methoxyphenyl)-3-oxo-1,5,6,7,8,8b-hexahydro-2*H*-cyclobuta[*d*]cyclohex[*b*]pyran-2a(3*H*)-carboxylate (17n)**

Yellowish oil; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.12 (d, $J$ = 8.8 Hz, 2H), 6.85 (d, $J$ = 8.8 Hz, 2H), 3.84 (q, $J$ = 9.2 Hz, 1H), 3.83 (s, 3H), 3.78 (s, 3H), 3.38 (d, $J$ = 9.2 Hz, 1H), 3.32 (ddd, $J$ = 12.8, 9.2, 2.0 Hz, 1H), 2.83 (dd, $J$ = 12.8, 8.8 Hz, 1H), 2.12 (tq, $J$ = 6.0, 2.0 Hz, 2H), 1.61-1.53 (m, 1H), 1.52-1.42 (m, 2H), 1.38-1.29 (m, 1H), 1.14-1.05 (m, 1H), 1.04-0.96 (m, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 171.0, 166.2, 158.8, 146.6, 130.7, 128.9 (2C), 113.6 (2C), 106.9, 55.2, 53.2, 47.6, 46.7, 40.6, 34.5, 26.3, 25.9, 22.0, 21.8; IR ($CHCl_3$): 3020.0, 1739.5 cm$^{-1}$; LR-EIMS *m/z*: 342 ($M^+$, 0.1), 135 (18), 134 (100), 121 (5), 119 (13).; HR-EIMS calcd for $C_{20}H_{22}O_5$: 342.1467. Found: 342.1469.

**Methyl *rac*-(4a*R*,8a*S*,10*S*)-5,6,7,8-tetrahydro-2-oxo-10-(4-methoxyphenyl)-4a,8a-ethano-2*H*-1-benzopyran-3-carboxylate (18n)**

Colorless cubics; m.p.112.3-114.0 ℃; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.2 (d, $J$ = 8.4 Hz, 2H), 6.89-6.85 (m, 3H), 3.81 (s, 3H), 3.79 (s, 3H), 3.46 (dd, $J$ = 11.2. 7.2 Hz, 1H), 2.75 (t, $J$ = 11.2 Hz, 1H), 2.37 (dt, $J$ = 14.8, 3.6 Hz, 1H), 2.27 (dd, $J$ = 11.2, 7.2 Hz, 1H), 1.87-1.80 (m, 3H), 1.77-1.66 (m, 1H), 1.65-1.57 (m, 1H), 1.39-1.25 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 164.0, 159.6, 158.9, 156.7, 128.6 (2C), 127.1, 122.8, 114.2 (2C), 77.1, 55.2, 52.6, 48.4, 38.3, 37.3, 34.7, 28.8, 20.7, 20.5; IR ($CHCl_3$): 3035.4, 1755.9, 1729.8 cm$^{-1}$; LR-EIMS

*m/z*: 342 (0.9), 298 (35), 266 (23), 239 (62), 238 (18), 197 (23), 134 (100), 121 (25), 108 (23).; HR-EIMS calcd for $C_{20}H_{22}O_5$: 342.1467. Found: 342.1465.

**Methyl *rac*-(1*R*,2a*S*,8b*S*)-3-oxo-1-(*p*-tolyl)-1,5,6,7,8,8b-hexahydro-2*H*-cyclobuta[*d*]cyclohex[*b*]pyran-2a(3*H*)-carboxylate (17o)**

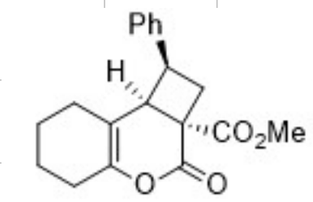
Yellowish oil;$^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.14-7.05 (m, 4H), 3.87 (q, $J$ = 9.3 Hz, 1H) 3.85 (s, 3H), 3.39 (dq, $J$ = 9.3, 2.1 Hz, 1H), 3.31 (ddd, $J$ = 12.6, 9.3, 2.4 Hz, 1H), 2.85 (ddd, $J$ = 12.6, 8.4, 1.2 Hz, 1H), 2.33 (s, 3H), 2.12 (tq, $J$ = 8.4, 2.1 Hz, 2H), 1.56-1.39 (m, 3H), 1.38-1.23 (m, 1H), 1.13-0.94 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 171.0, 166.2, 146.6, 136.9, 135.5, 128.9 (2C), 127.8 (2C), 106.9, 53.2, 47.7, 46.5, 41.0, 34.3, 26.3, 25.9, 22.0, 21.8, 21.1.; IR ($CHCl_3$): 3024.8, 1753.0 cm$^{-1}$; LR-EIMS *m/z*: 326 ($M^+$,0.1), 209 (16), 208 (16), 118 (100), 83 (18); HR- EIMS calcd for $C_{20}H_{22}O_4$: 326.1518. Found: 326.1512.

**Methyl *rac*-(4a*R*,8a*S*,10*S*)-5,6,7,8-tetrahydro-2-oxo-10-(*p*-tolyl)-4a,8a-ethano-2*H*-1-benzopyran-3-carboxylate (18o)**

Colorless cubics; m.p. 98.3-102.7 ℃; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.14 (d, $J$ = 8.0 Hz, 2H), 6.99 (d, $J$ = 8.0 Hz, 2H), 6.87 (s, 1H), 3.79 (s, 3H), 3.48 (dd, $J$ = 10.8, 7.2 Hz, 1H), 2.77 (t, $J$ = 10.8 Hz, 1H), 2.34 (s, 3H), 2.26 (dd, $J$ = 10.8, 7.2 Hz, 1H), 1.88-1.80 (m, 3H), 1.78-1.67 (m, 2H), 1.66-1.56 (m, 1H), 1.40-1.25 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.0, 159.6, 156.8, 137.1, 132.0, 129.4 (2C), 127.5 (2C), 122.8, 77.1, 52.6, 48.4, 38.5, 37.1, 34.7, 28.8, 21.0, 20.7, 20.5; IR ($CHCl_3$): 3023.8, 1755.9, 1728.9 cm$^{-1}$; LR-EIMS *m/z*: 326 ($M^+$, 0.8), 209 (14), 208 (20), 118 (100), 83 (17); HR-EIMS calcd for $C_{20}H_{22}O_4$: 326.1518. Found: 326.1512.

**Methyl *rac*-(1*R*,2a*R*,8b*R*)-3-oxo-1-vinyl-1,5,6,7,8,8b-hexahydro-2*H*-cyclobuta[*d*]cyclohex[*b*]pyran-2a(3*H*)-carboxylate (17p)**

Colorless oil; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 5.82 (ddd, $J$ = 17.0, 10.0, 7.5 Hz, 1H), 5.11 (dd, $J$ = 10.0, 1.0 Hz, 1H), 5.08 (dd, $J$ = 17.0, 1.0 Hz, 1H), 3.80 (s, 3H), 3.23 (brd, $J$ = 8.5 Hz, 1H), 3.22-3.16 (m, 1H), 3.15 (td, $J$ = 8.5, 2.0 Hz, 1H), 2.49 (dd, $J$ = 11.5, 5.0 Hz, 1H), 2.26-2.14 (m, 2H), 1.98-1.92 (m, 1H), 1.84-1.77 (m, 1H), 1.76-1.66 (m, 2H), 1.65-1.54 (m, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 170.7, 166.7, 146.6, 136.6, 116.7, 106.8, 53.1, 48.1, 44.9, 39.2, 33.8, 26.3, 26.2, 22.2, 22.0; IR ($CHCl_3$): 3079.8, 1736.6 cm$^{-1}$; LR-EIMS *m/z*: 262 ($M^+$, 0.8), 209 (13), 208 (100), 203 (21), 180 (59), 176 (19), 152 (26), 148 (24), 121 (44), 120 (14).; HR-EIMS calcd for $C_{15}H_{18}O_4$: 262.1205. Found: 262.1206.

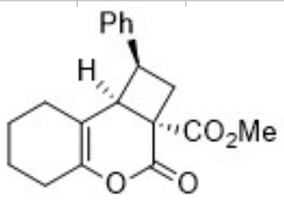



**11**

$^1$H NMR

(500 MHz, $CDCl_3$)

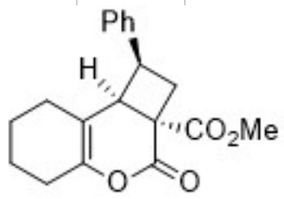
f1 (ppm)




**11**

$^{13}C$ NMR

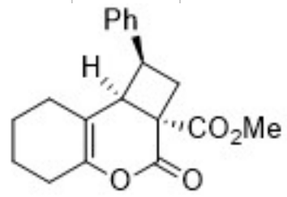
(125 MHz, $CDCl_3$)




**11**

DEPT-45 NMR

(125 MHz, $CDCl_3$)

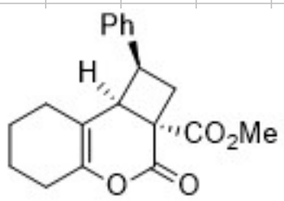



**11**

DEPT-90 NMR

(125 MHz, $CDCl_3$)

f1 (ppm)




**11**

DEPT-135 NMR

(125 MHz, $CDCl_3$)

**11**

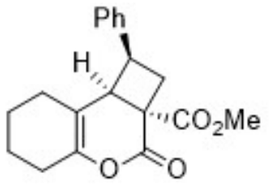
COSY NMR

(500 MHz, $CDCl_3$)

**11**

HMBC NMR

(500,125 MHz, $CDCl_3$)




**11**

HMQC NMR

(500,125 MHz, $CDCl_3$)

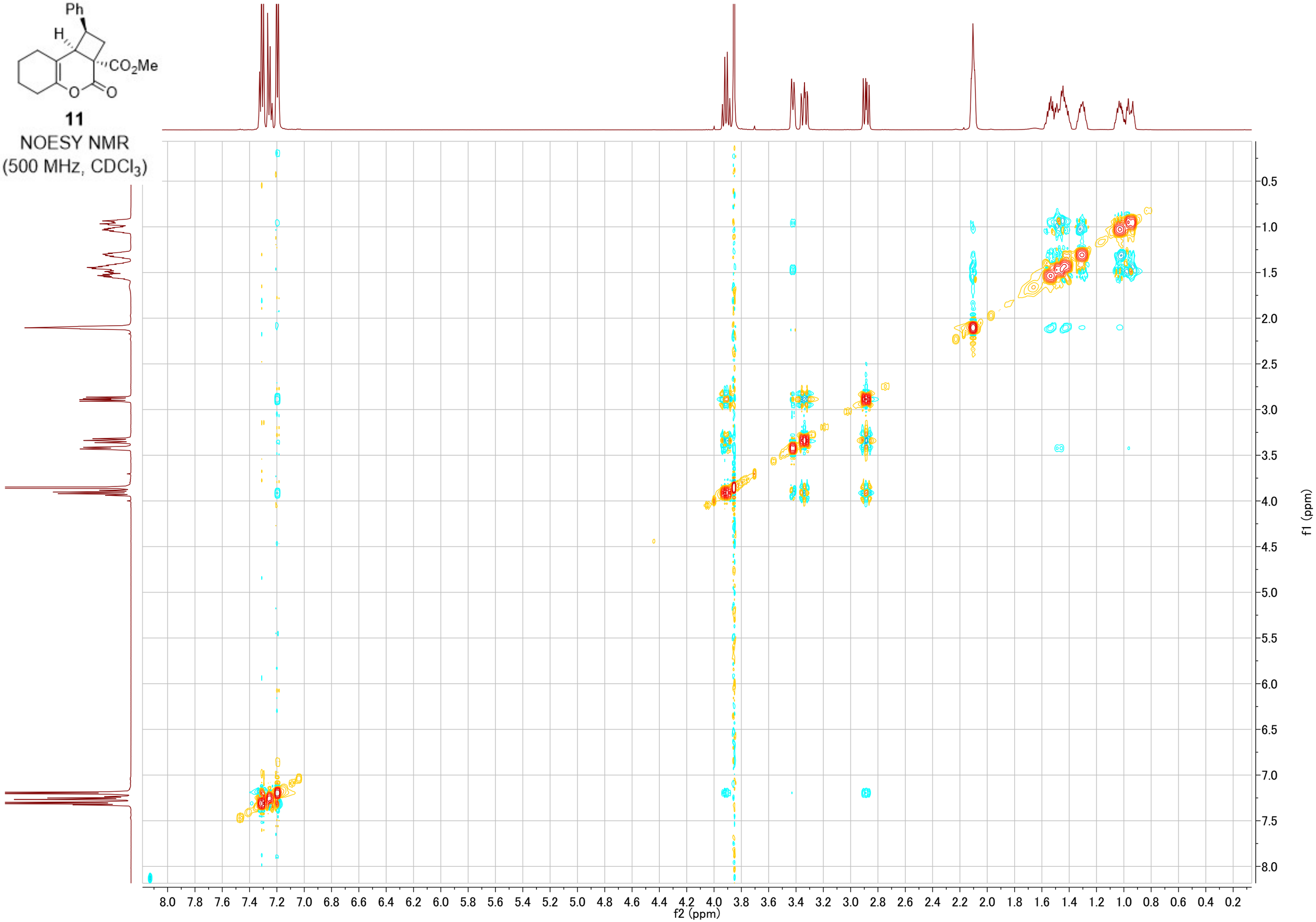
f2 (ppm)

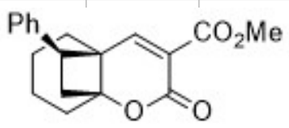
f1 (ppm)

**11**

NOESY NMR

(500 MHz, $CDCl_3$)

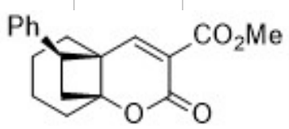





**12**

$^1$H NMR

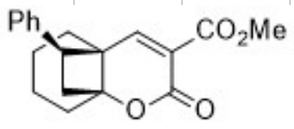
(300 MHz, $CDCl_3$)




**12**

$^{13}C$ NMR

(125 MHz, $CDCl_3$)

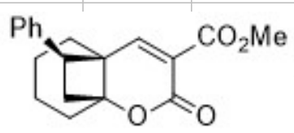



**12**

DEPT-45 NMR

(125 MHz, $CDCl_3$)

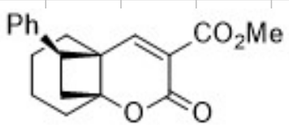
f1 (ppm)




**12**

DEPT-90 NMR

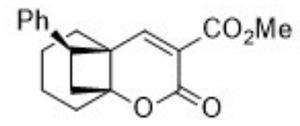
(125 MHz, $CDCl_3$)




**12**

DEPT-135 NMR

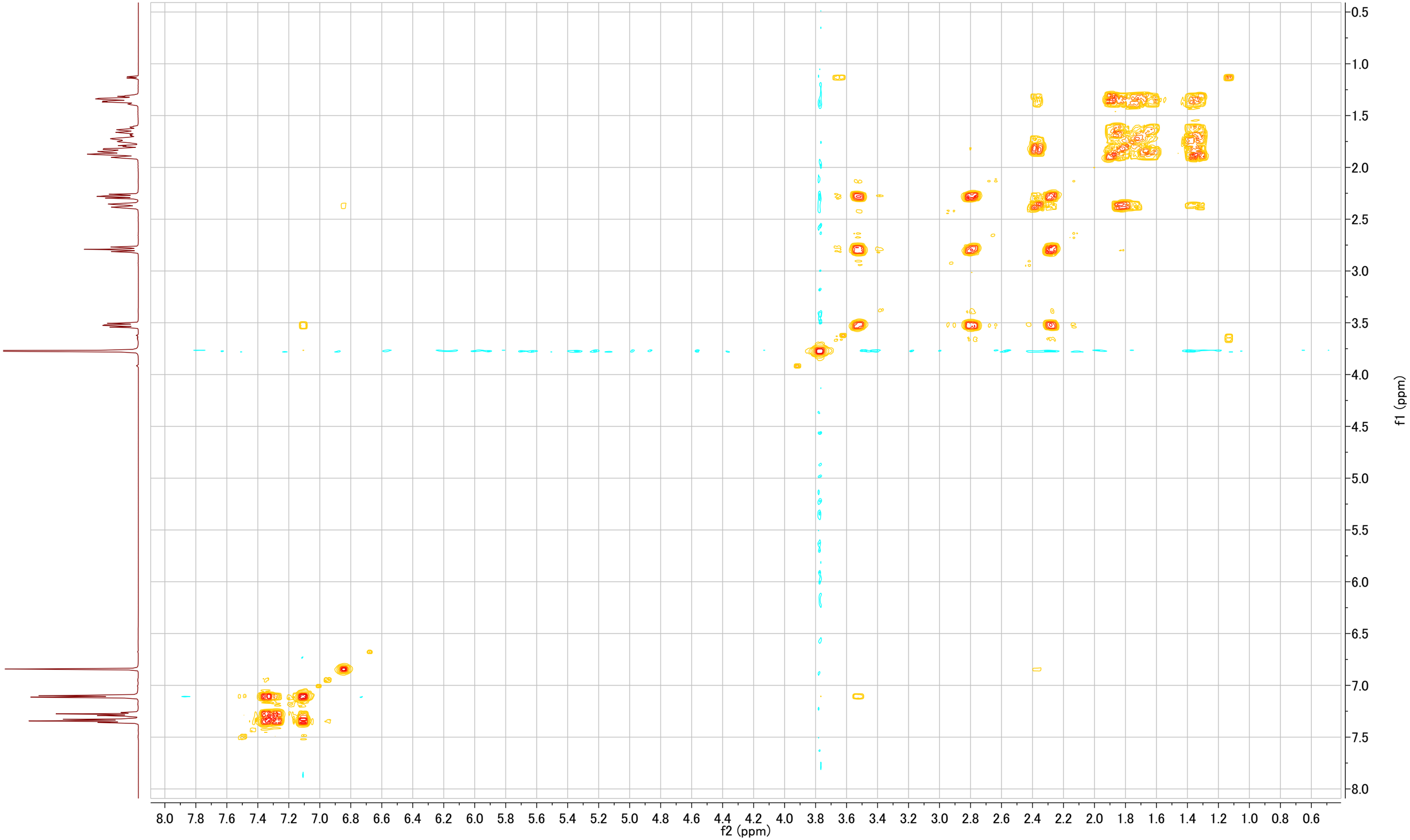
(125 MHz, $CDCl_3$)

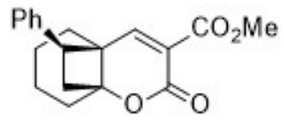



**12**

COSY NMR

(500 MHz, $CDCl_3$)

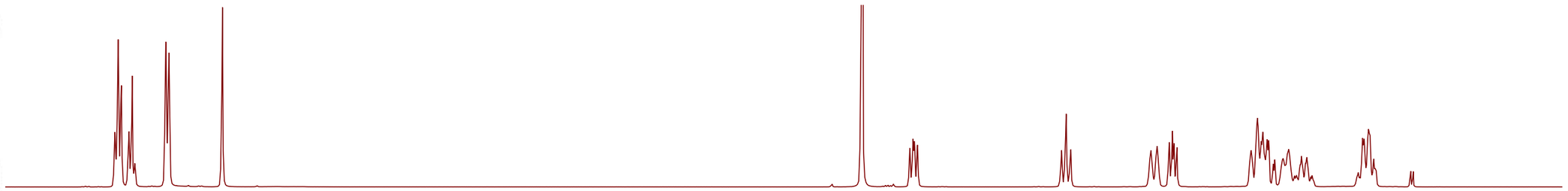


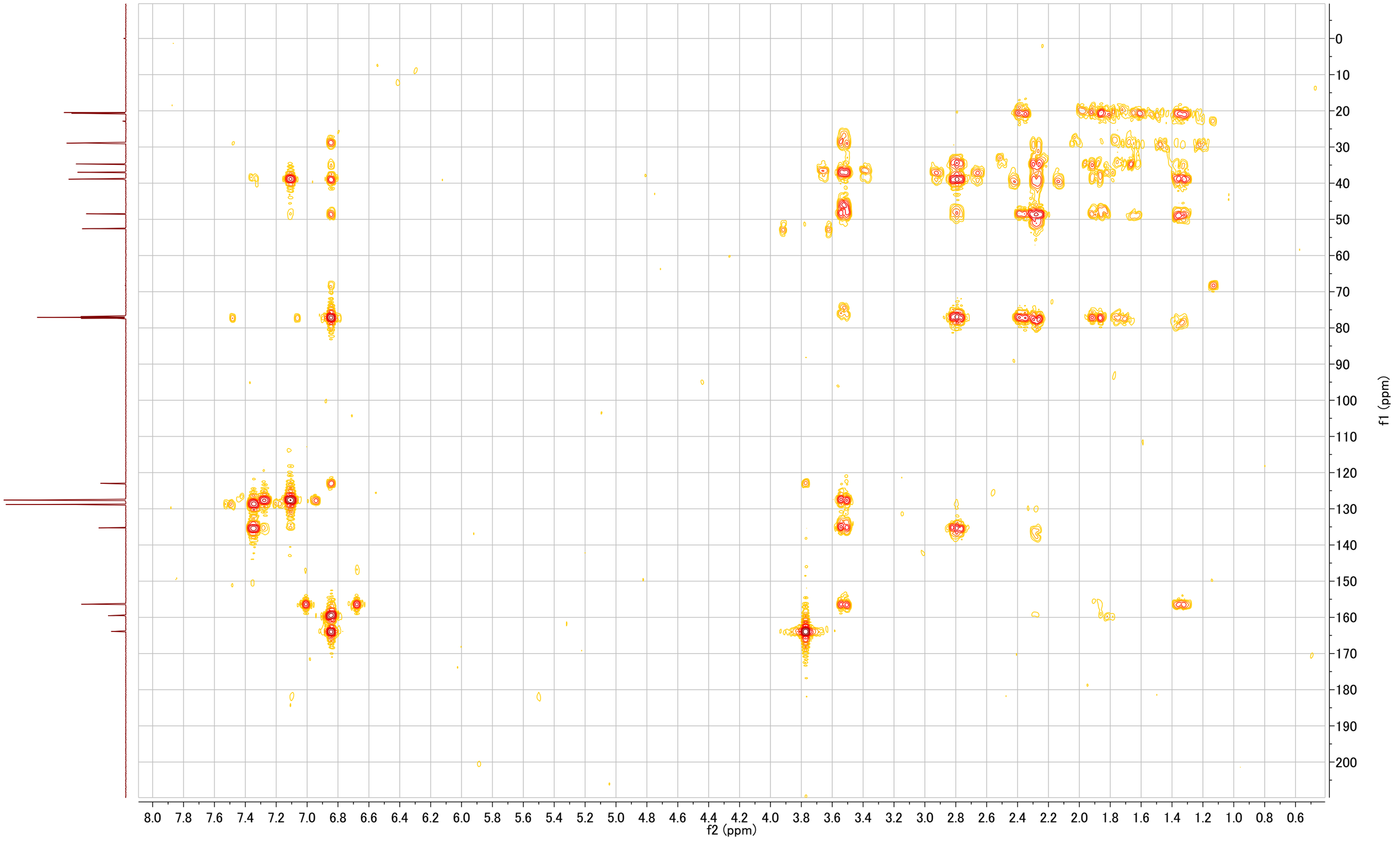


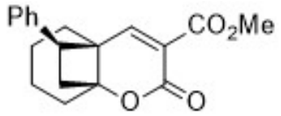

**12**

HMBC NMR

(500, 125 MHz, $CDCl_3$)



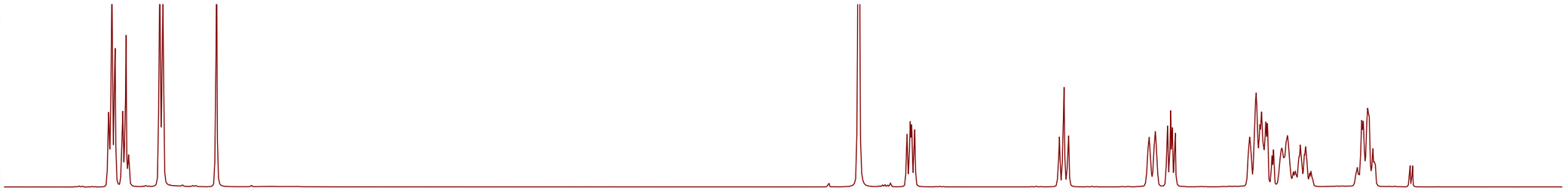


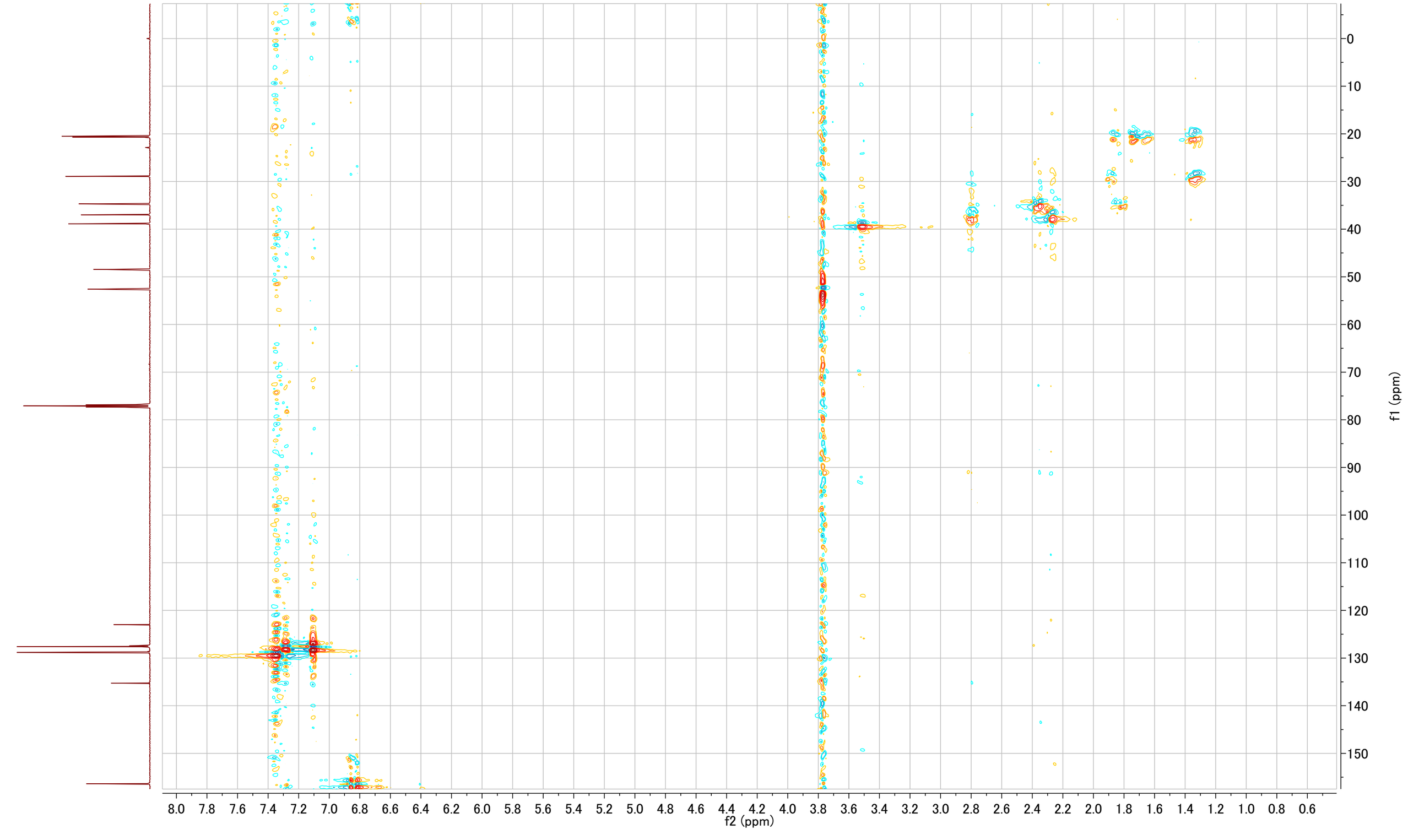


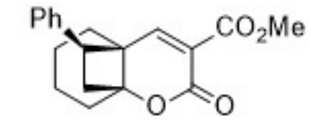

**12**

HSQC NMR

(500, 125 MHz, $CDCl_3$)







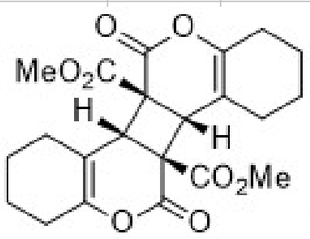

**12**

NOESY NMR

(500 MHz, $CDCl_3$)

f2 (ppm)

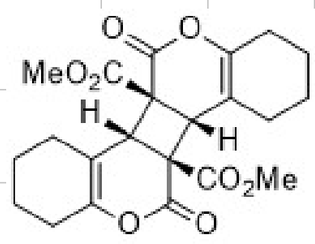
f1 (ppm)




**13**

$^{1}$H NMR

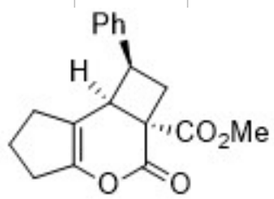
(300 MHz, $CDCl_3$)




**13**

$^{13}$C NMR

(125 MHz, $CDCl_3$)

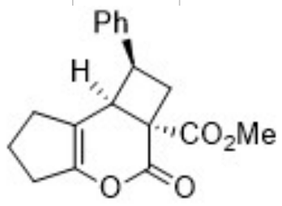



**17a**

$^1$H NMR

(300 MHz, $CDCl_3$)

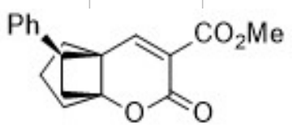
f1 (ppm)




**17a**

$^{13}$C NMR

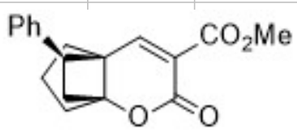
(75 MHz, $CDCl_3$)




**18a**

$^1$H NMR

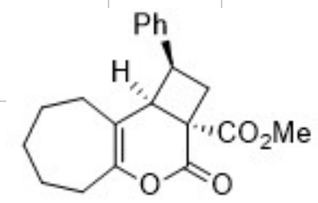
(300 MHz, $CDCl_3$)




**18a**

$^{13}$C NMR

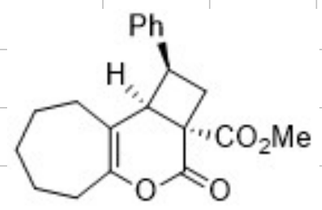
(75 MHz, $CDCl_3$)




**17b**

$^1$H NMR

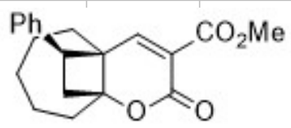
(300 MHz, $CDCl_3$)




**17b**

$^{13}$C NMR

(75 MHz, $CDCl_3$)

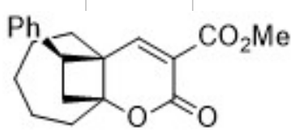



**18b**

$^1$H NMR

(300 MHz, $CDCl_3$)

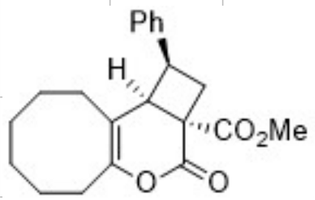
f1 (ppm)




**18b**

$^{13}C$ NMR

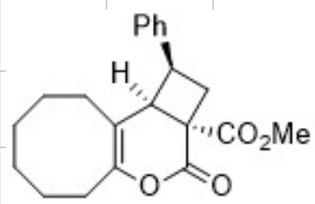
(75 MHz, $CDCl_3$)




**17c**

$^1$H NMR

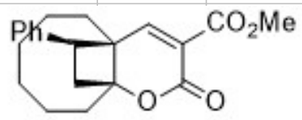
(300 MHz, $CDCl_3$)




**17c**

$^{13}C$ NMR

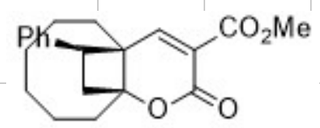
(75 MHz, $CDCl_3$)




**18c**

$^1$H NMR

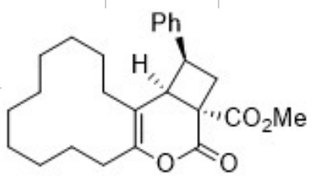
(300 MHz, $CDCl_3$)




**18c**

$^{13}$C NMR

(75 MHz, $CDCl_3$)

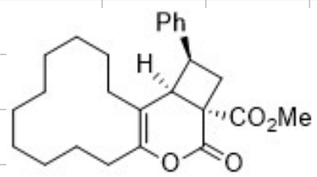



**17d**

$^1$H NMR

(400 MHz, $CDCl_3$)

f1 (ppm)



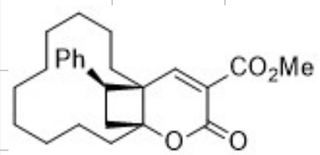

**17d**

$^{13}$C NMR

(100 MHz, $CDCl_3$)

171.196
167.610
149.300
139.165
128.634
128.329
127.371
109.623
77.678
77.358
77.044
53.508
48.174
44.708
41.862
34.353
26.383
25.577
24.943
24.628
24.590
24.357
24.223
24.109
22.650
22.307

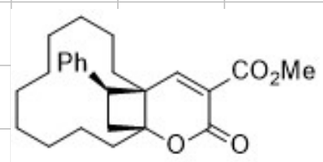
f1 (ppm)




**18d**

$^1$H NMR

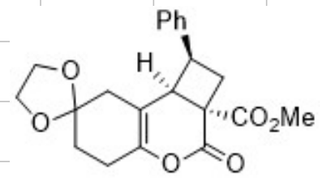
(300 MHz, $CDCl_3$)




**18d**

$^{13}C$ NMR

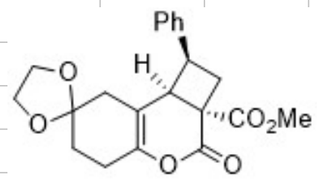
(75 MHz, $CDCl_3$)




**17e**

$^{1}$H NMR

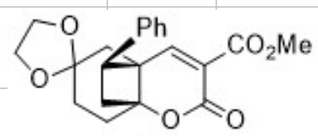
(400 MHz, $CDCl_3$)




**17e**

$^{13}C$ NMR

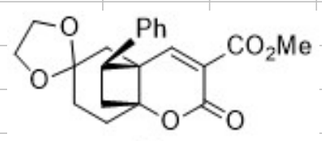
(100 MHz, $CDCl_3$)




**18e**

$^1$H NMR

(400 MHz, $CDCl_3$)



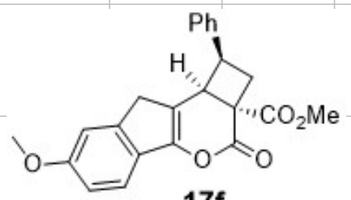

**18e**

$^{13}C$ NMR

(75 MHz, $CDCl_3$)

163.621
159.276
155.019
134.986
128.686
127.499
127.356
122.898
107.770
77.000
76.179
64.644
63.940
52.534
49.329
39.677
37.022
36.270
32.299
29.492

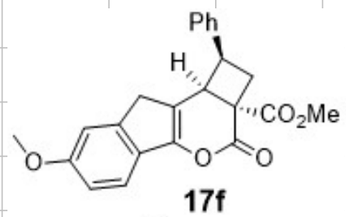
f1 (ppm)




**17f**

$^1$H NMR

(500 MHz, $CDCl_3$)



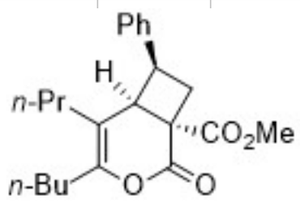

**17f**

$^{13}$C NMR

(75 MHz, $CDCl_3$)

170.785
165.558
158.768
148.914
143.598
138.349
128.915
128.520
127.275
127.243
118.146
111.789
110.691
110.426
77.424
77.000
76.576
55.375
53.294
47.467
45.245
42.164
35.079
33.371

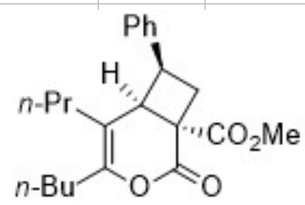
f1 (ppm)




**17g**

$^1$H NMR

(400 MHz, $CDCl_3$)



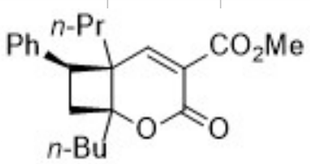

**17g**

$^{13}$C NMR

(125 MHz, $CDCl_3$)

170.615
166.997
149.005
138.435
128.131
127.803
126.850
108.334
77.255
77.000
76.745
52.908
47.731
44.788
41.147
33.276
30.161
29.022
28.745
21.903
20.747
13.686
13.473

f1 (ppm)

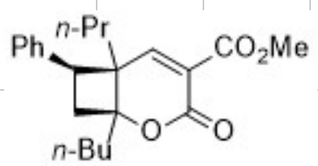



**18g**

$^1$H NMR

(300 MHz, $CDCl_3$)

f1 (ppm)



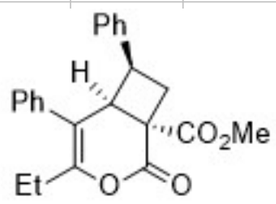

**18g**

$^{13}$C NMR

(75 MHz, $CDCl_3$)

163.672
158.998
156.943
135.116
128.704
127.724
127.504
124.933
81.889
77.424
77.000
76.577
53.162
52.543
44.914
36.284
34.389
33.521
24.671
23.080
18.902
14.427
14.056

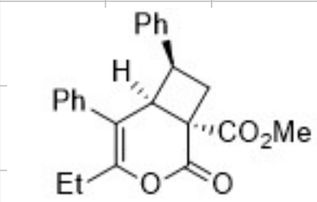
f1 (ppm)




**17h**

$^1$H NMR

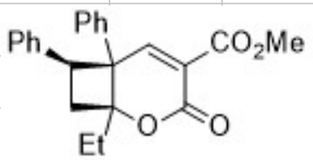
(500 MHz, $CDCl_3$)




**17h**

$^{13}C$ NMR

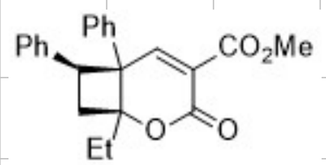
(125 MHz, $CDCl_3$)




**18h**

$^1$H NMR

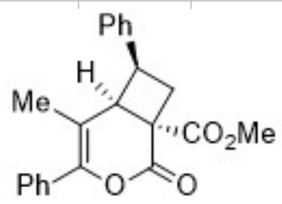
(500 MHz, $CDCl_3$)




**18h**

$^{13}C$ NMR

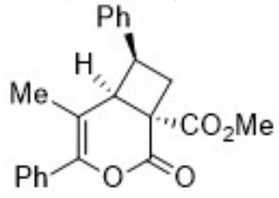
(75 MHz, $CDCl_3$)




**17i**

$^1$H NMR

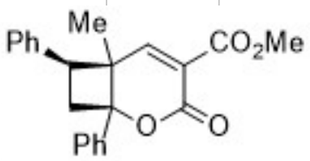
(500 MHz, $CDCl_3$)




**17i**

$^{13}C$ NMR

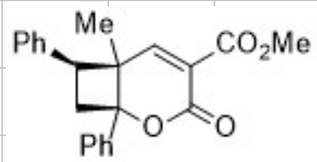
(125 MHz, $CDCl_3$)




**18i**

$^{1}$H NMR

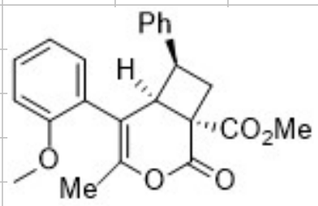
(500 MHz, $CDCl_3$)




**18i**

$^{13}C$ NMR

(125 MHz, $CDCl_3$)

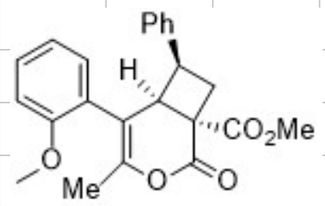



**17j**

$^1$H NMR

(300 MHz, $CDCl_3$)

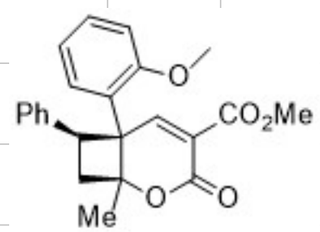
f1 (ppm)




**17j**

$^{13}$C NMR

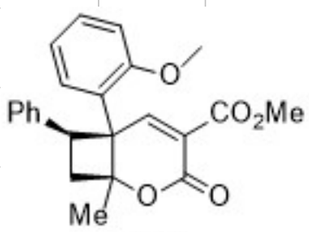
(75 MHz, $CDCl_3$)




**18j**

$^1$H NMR

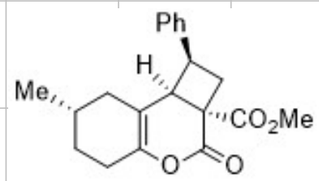
(400 MHz, $CDCl_3$)




**18j**

$^{13}C$ NMR

(75 MHz, $CDCl_3$)

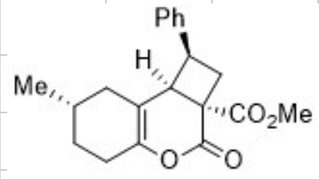



**17ka**

$^1$H NMR

(500 MHz, $CDCl_3$)

f1 (ppm)



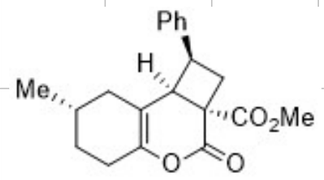

**17ka**

$^{13}C$ NMR

(125 MHz, $CDCl_3$)

170.994
166.426
146.617
138.583
128.257
127.877
127.214
106.132
77.254
77.000
76.746
53.220
47.662
45.856
41.165
34.117
33.739
30.011
27.929
26.229
20.941

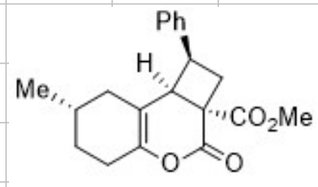
f1 (ppm)




**17ka**

DEPT-45 NMR

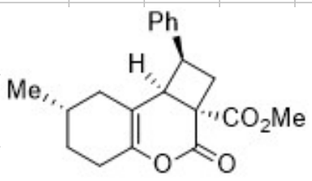
(125 MHz, $CDCl_3$)




**17ka**

DEPT-90 NMR

(125 MHz, $CDCl_3$)




**17ka**

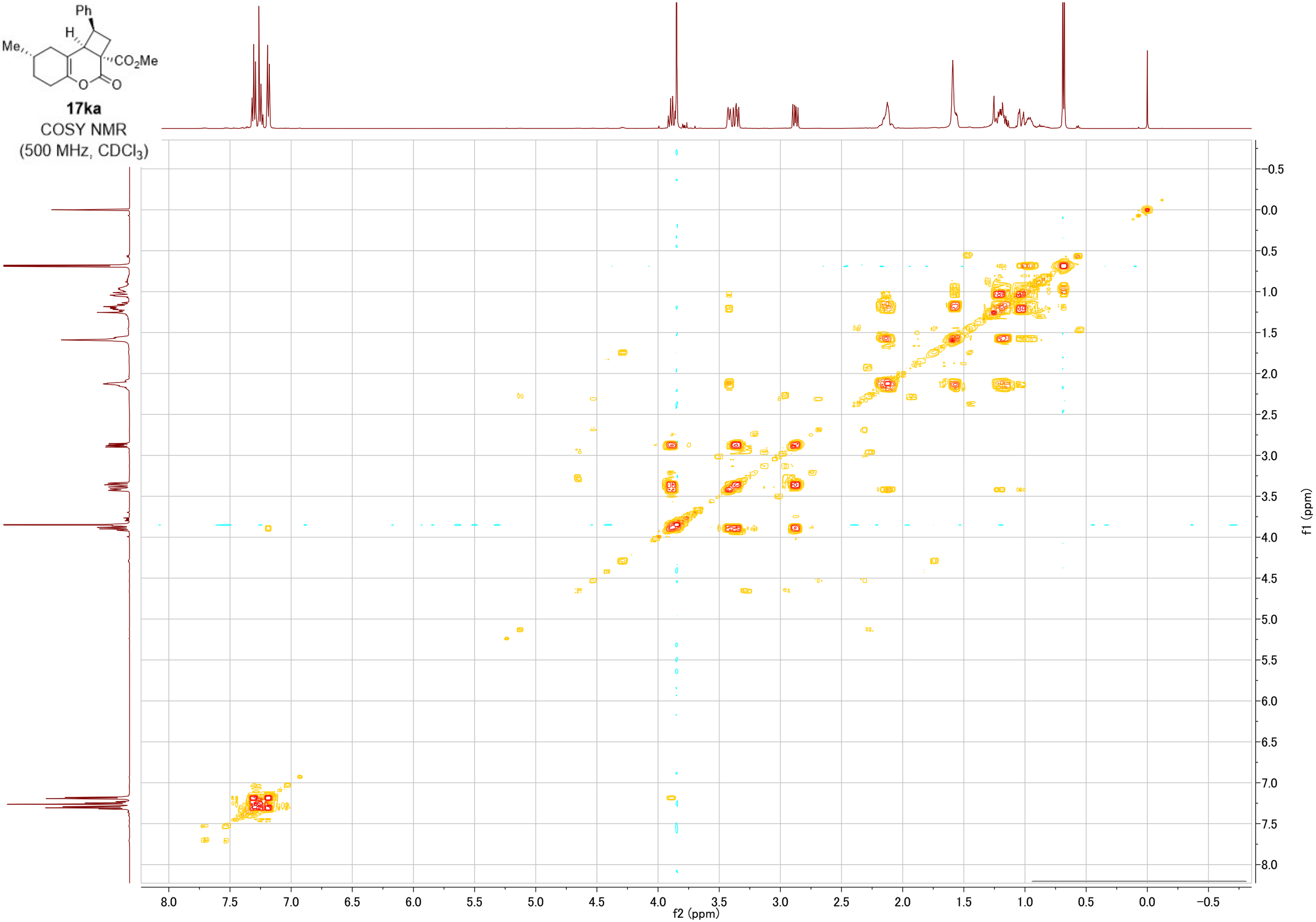
DEPT-135 NMR

(125 MHz, $CDCl_3$)

**17ka**

COSY NMR

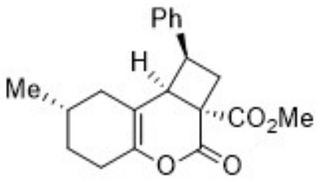
(500 MHz, $CDCl_3$)



**17ka**

HMBC NMR

(500, 125 MHz, $CDCl_3$)




**17ka**

HMQC NMR

(500, 125 MHz, $CDCl_3$)

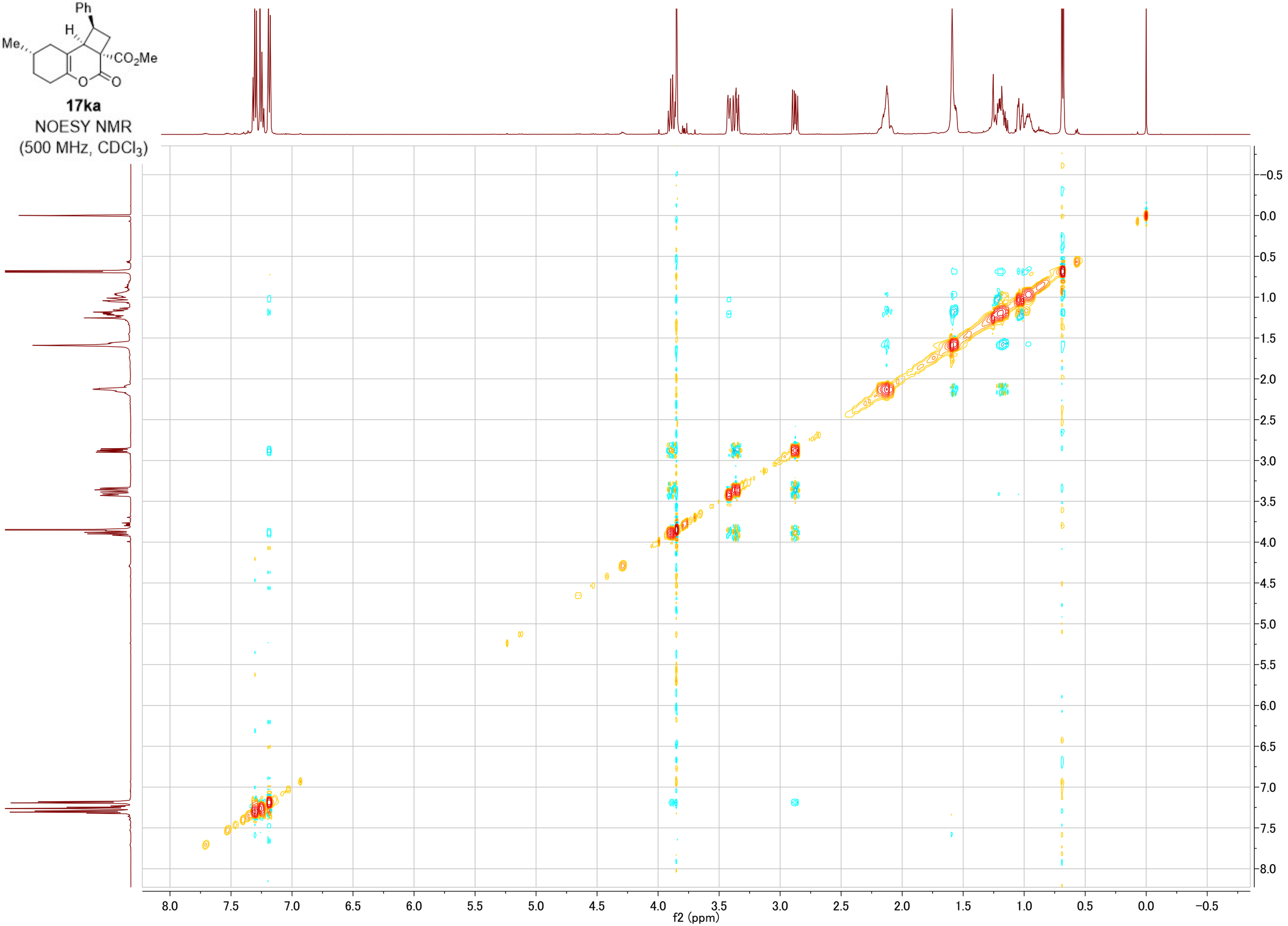
f2 (ppm)

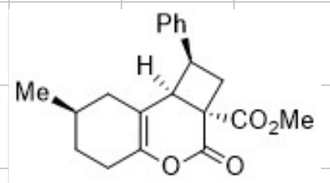
f1 (ppm)

**17ka**

NOESY NMR

(500 MHz, $CDCl_3$)



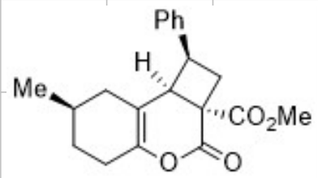



**17kb**

$^1$H NMR

(500 MHz, $CDCl_3$)

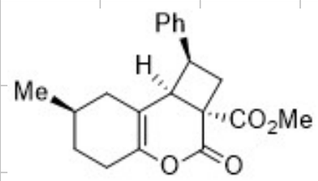
f1 (ppm)




**17kb**

$^{13}$C NMR

(125 MHz, $CDCl_3$)




**17kb**

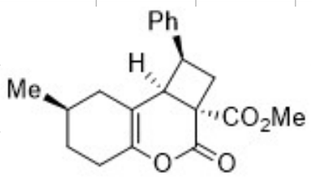
DEPT-45 NMR

(125 MHz, $CDCl_3$)

8.5E+10
8.0E+10
7.5E+10
7.0E+10
6.5E+10
6.0E+10
5.5E+10
5.0E+10
4.5E+10
4.0E+10
3.5E+10
3.0E+10
2.5E+10
2.0E+10
1.5E+10
1.0E+10
5.0E+09
0.0E+00
−5.0E+09

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

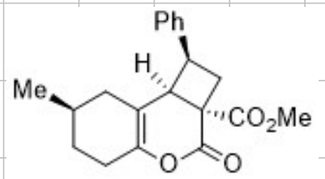
f1 (ppm)




**17kb**

DEPT-90 NMR

(125 MHz, $CDCl_3$)




**17kb**

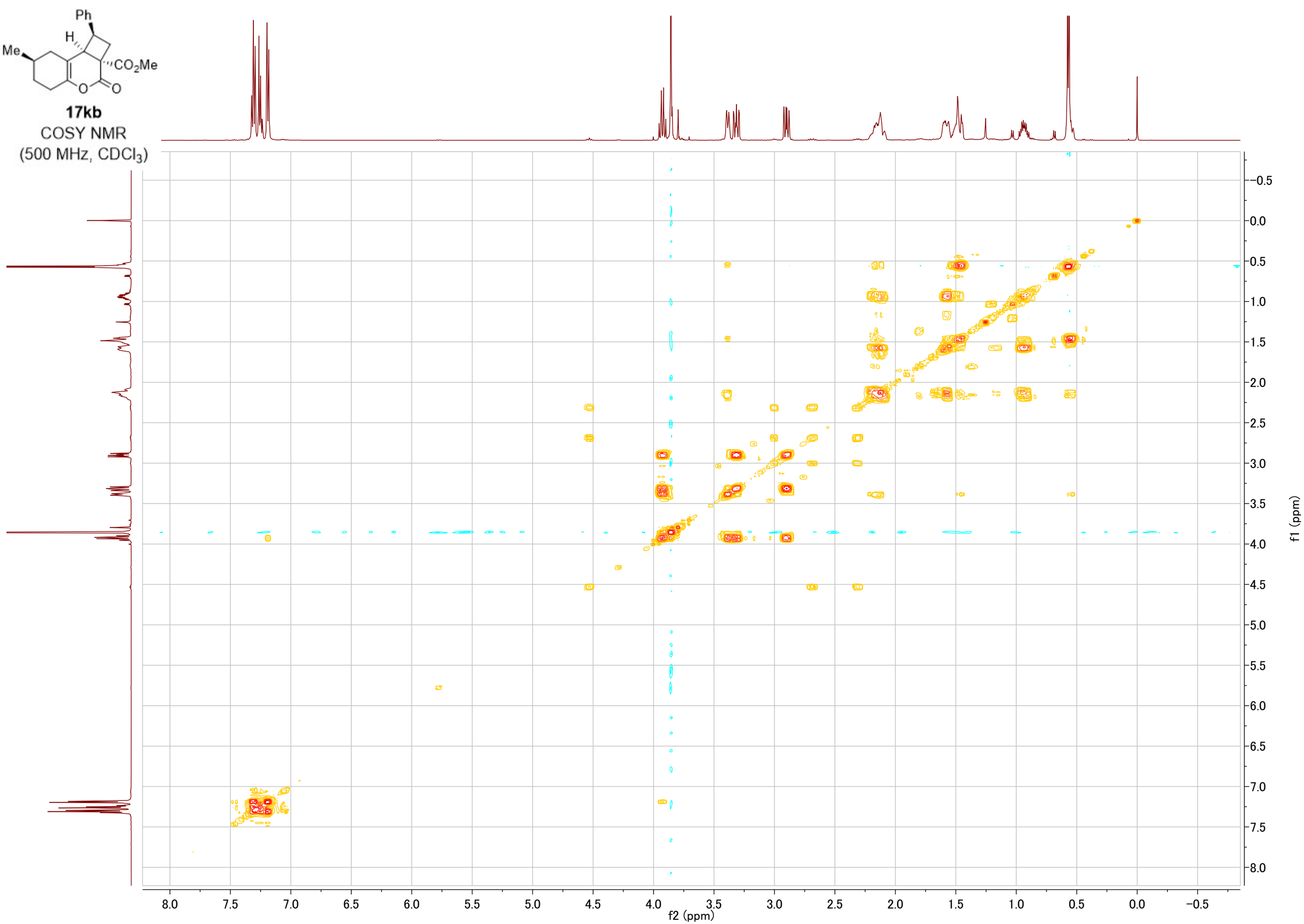
DEPT-135 NMR

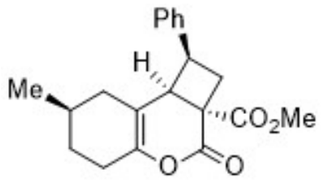
(125 MHz, $CDCl_3$)

**17kb**

COSY NMR

(500 MHz, $CDCl_3$)

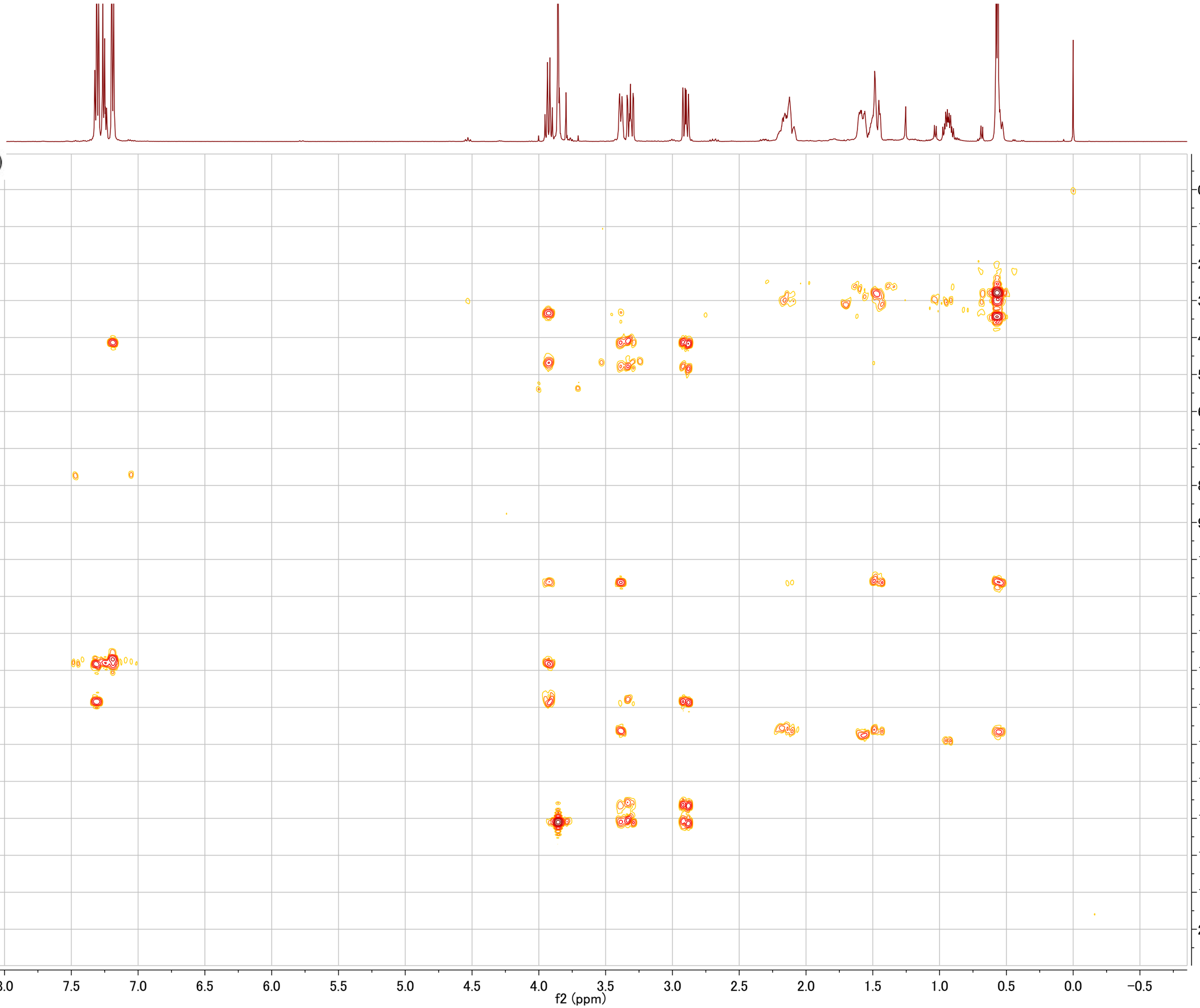





**17kb**

HMBC NMR

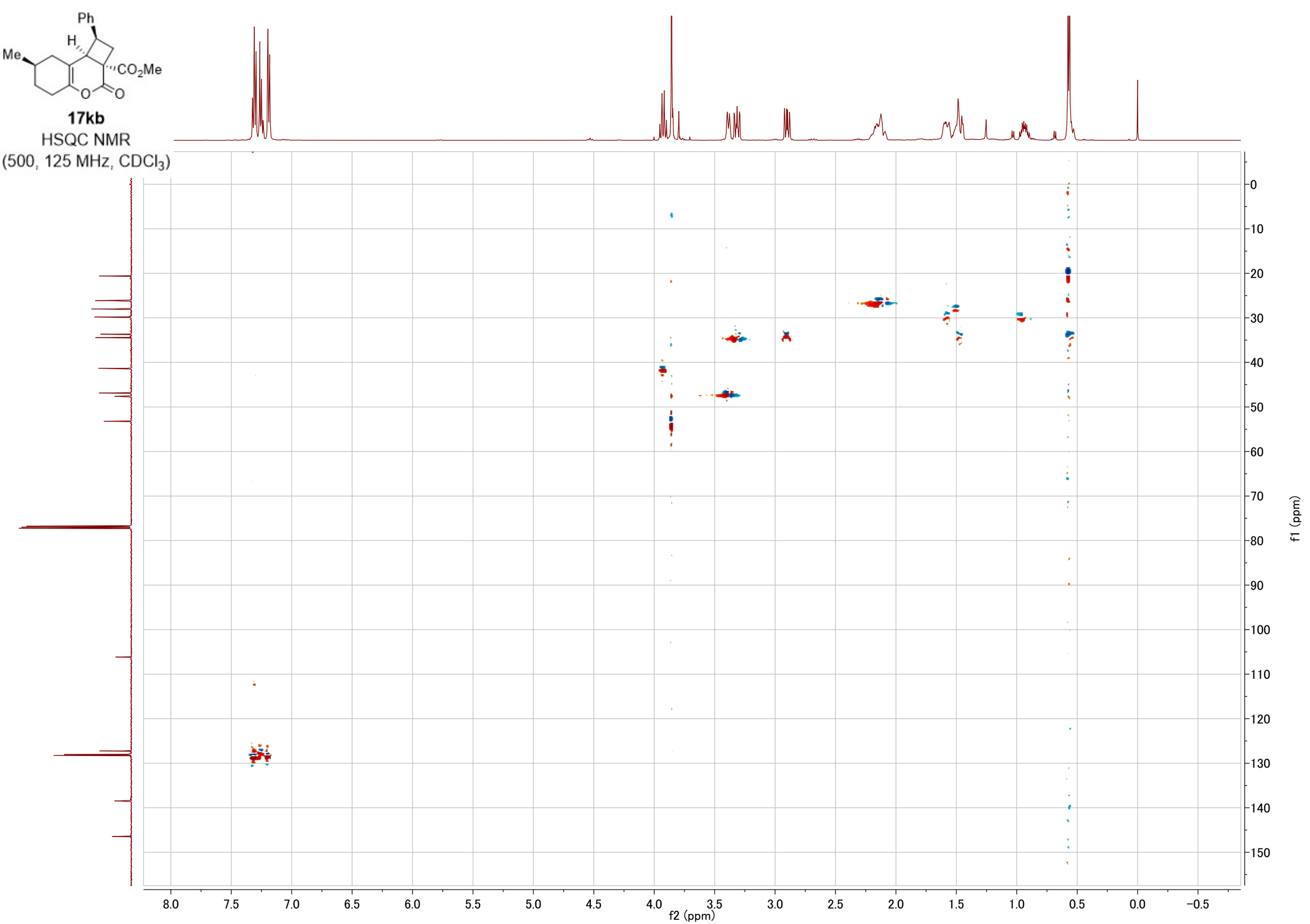
(500, 125 MHz, $CDCl_3$)

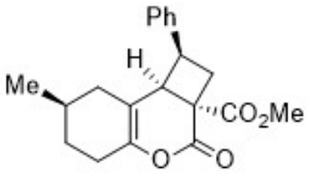


**17kb**

HSQC NMR

(500, 125 MHz, $CDCl_3$)





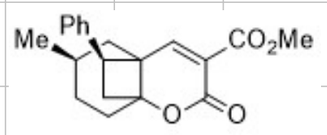

**17kb**

NOESY NMR

(500 MHz, $CDCl_3$)

f2 (ppm)

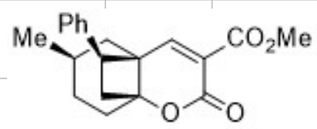
f1 (ppm)




**18ka**

$^1$H NMR

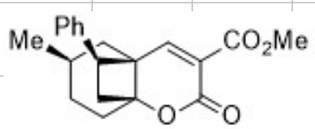
(500 MHz, $CDCl_3$)




**18ka**

$^{13}C$ NMR

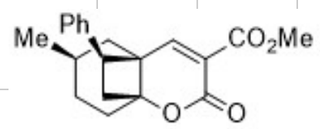
(125 MHz, $CDCl_3$)




**18ka**

DEPT-45 NMR

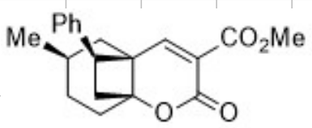
(125 MHz, $CDCl_3$)




**18ka**

DEPT-90 NMR

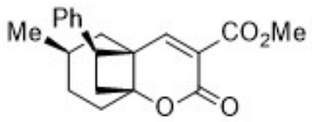
(125 MHz, $CDCl_3$)




**18ka**

DEPT-135 NMR

(125 MHz, $CDCl_3$)



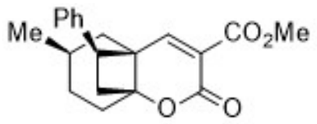

**18ka**

COSY NMR

(500 MHz, $CDCl_3$)

f2 (ppm)

f1 (ppm)



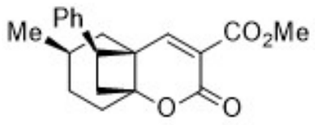

**18ka**

HMBC NMR

(500, 125 MHz, $CDCl_3$)

f2 (ppm)

f1 (ppm)




**18ka**

HMQC NMR

(500, 125 MHz, $CDCl_3$)

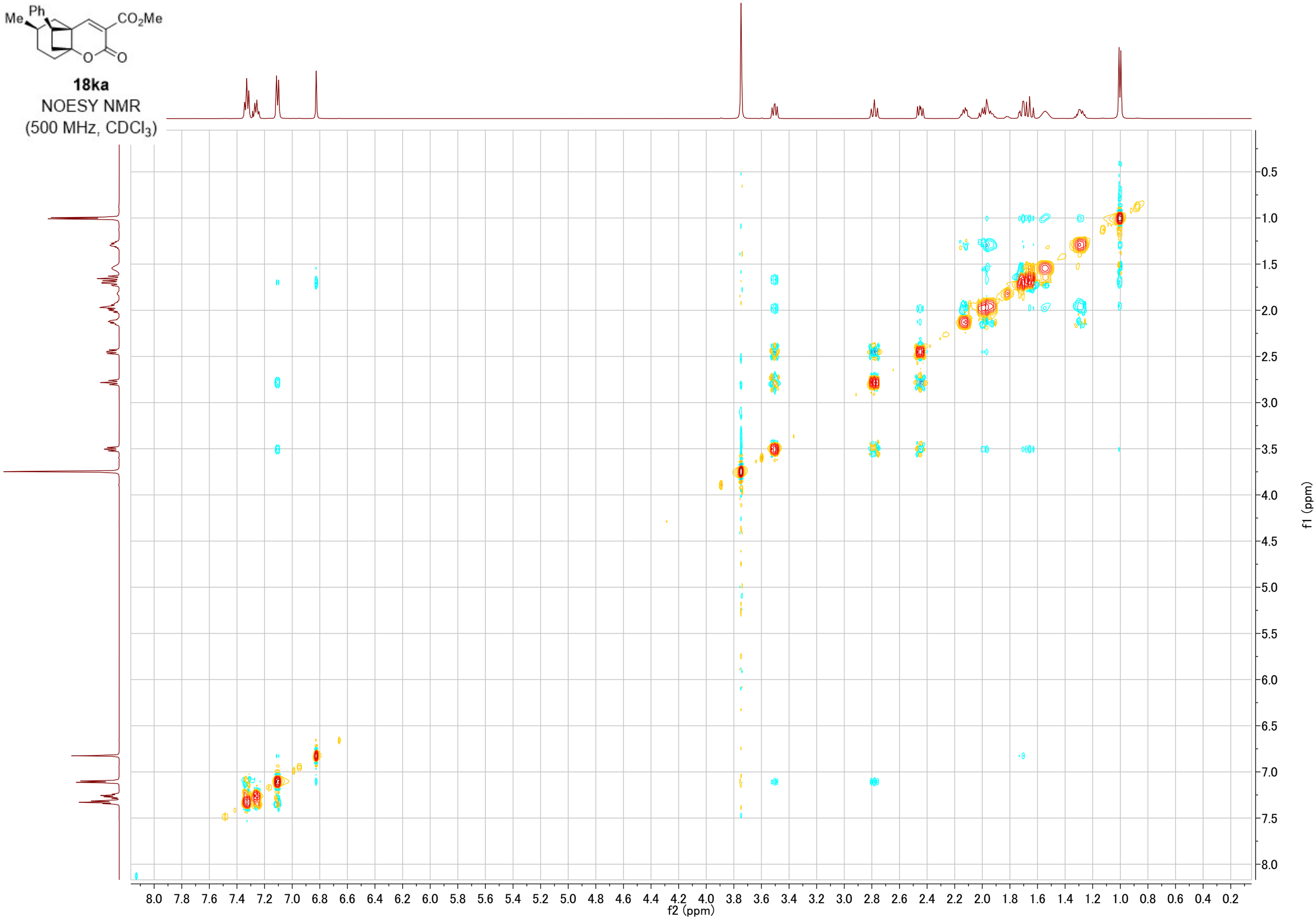
f2 (ppm)

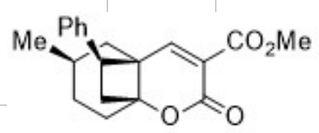
f1 (ppm)

**18ka**

NOESY NMR

(500 MHz, $CDCl_3$)






**18ka**

$^1$H NMR

(500 MHz, $CDCl_3$)

7.359 7.345 7.330 7.293 7.278 7.264 7.115 7.100 6.832

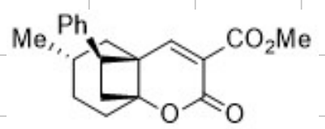
3.769 3.502 3.488 3.481 3.466

2.809 2.787 2.765 2.415 2.385 2.286 2.272 2.264 2.250

1.919 1.913 1.888 1.884 1.861 1.854 1.841 1.832 1.818 1.665 1.638 1.123 1.119 1.096 1.069 1.035 1.023 0.952 0.927 0.900 0.000

1.959 1.108 2.006 0.988 2.987 1.000 1.005 1.002 0.992 2.976 1.014 0.922 3.010 1.057

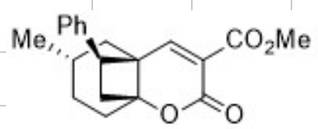
f1 (ppm)




**18kb**

$^{13}$C NMR

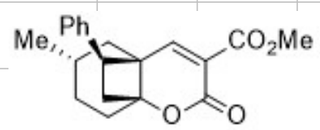
(125 MHz, $CDCl_3$)




**18kb**

DEPT-45 NMR

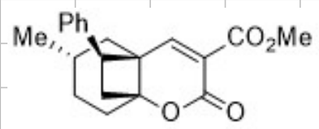
(125 MHz, $CDCl_3$)




**18kb**

DEPT-90 NMR

(125 MHz, $CDCl_3$)




**18kb**

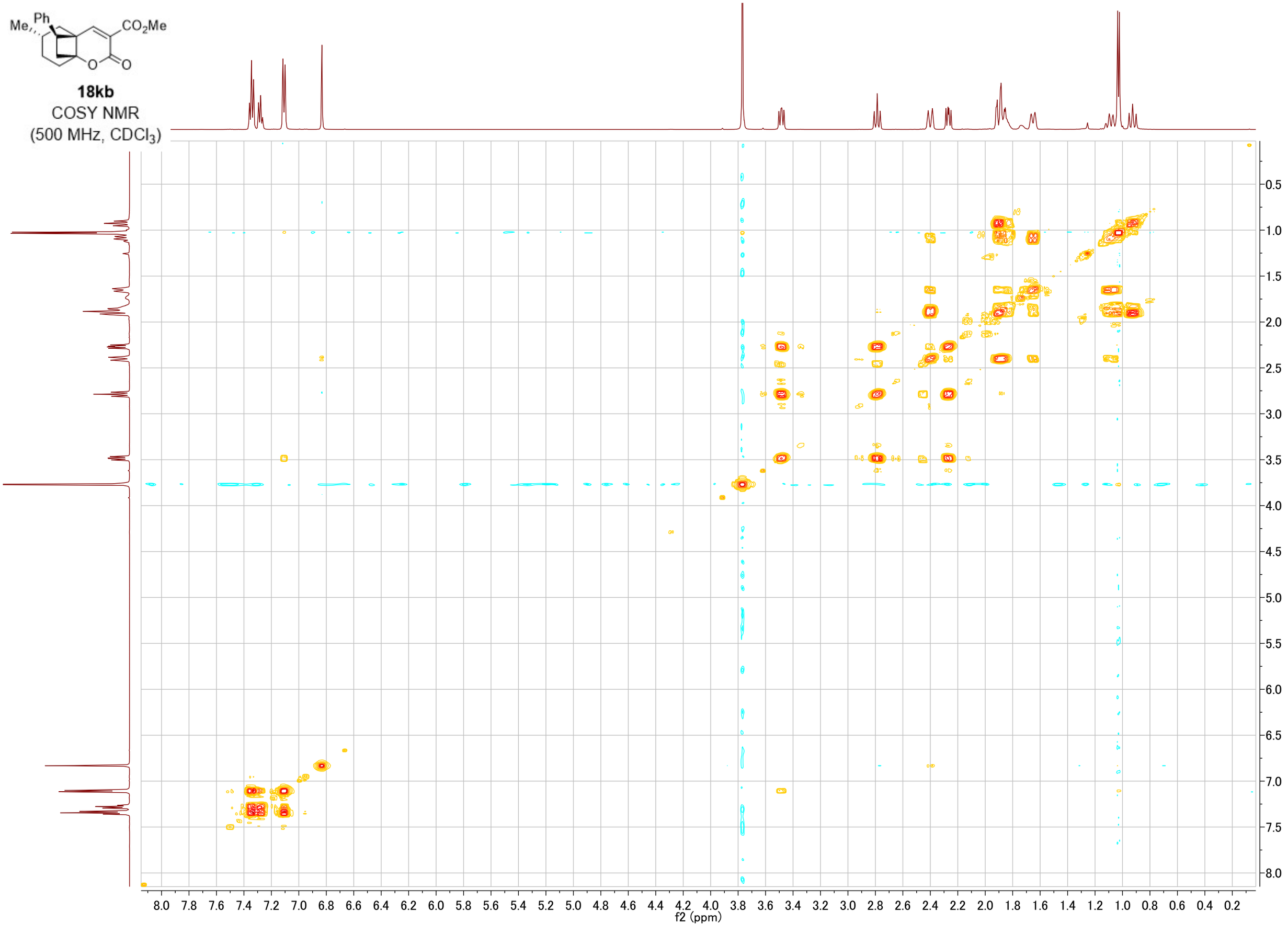
DEPT-135 NMR

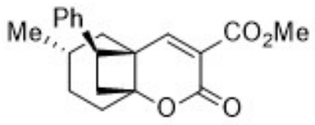
(125 MHz, $CDCl_3$)

**18kb**

COSY NMR

(500 MHz, $CDCl_3$)

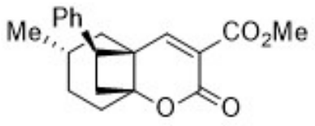





**18kb**

HMBC NMR

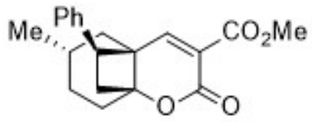
(500, 125 MHz, $CDCl_3$)




**18kb**

HMQC NMR

(500, 125 MHz, $CDCl_3$)



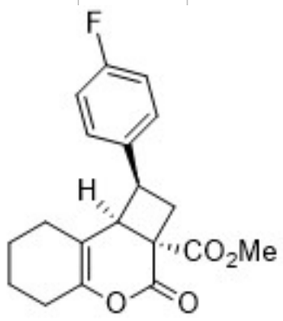

**18kb**

NOESY NMR

(500 MHz, $CDCl_3$)

f2 (ppm)

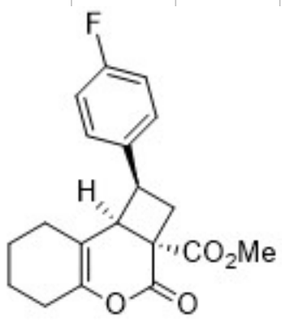
f1 (ppm)




**17l**

$^{1}$H NMR

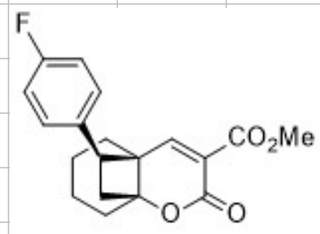
(400 MHz, $CDCl_3$)




**17l**

$^{13}C$ NMR

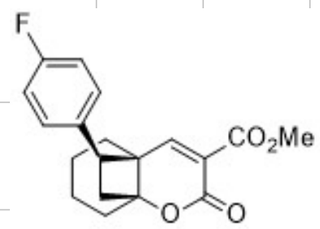
(100 MHz, $CDCl_3$)




**18l**

$^1$H NMR

(300 MHz, $CDCl_3$)



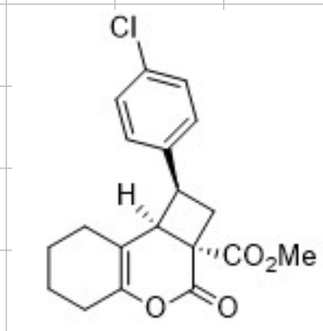

**18l**

$^{13}C$ NMR

(75 MHz, $CDCl_3$)

163.794
160.430
159.318
155.970
130.988
129.090
128.983
123.075
115.845
115.562
77.423
77.000
76.919
76.576
52.611
48.350
38.163
37.283
34.607
28.824
20.599
20.388

f1 (ppm)

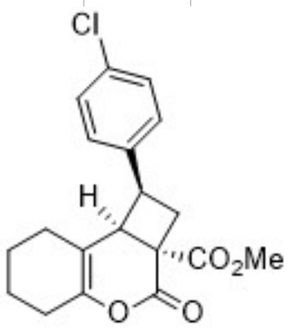



**17m**

$^1$H NMR

(300 MHz, $CDCl_3$)

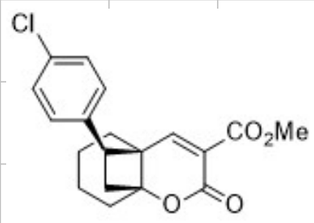
f1 (ppm)




**17m**

$^{13}C$ NMR

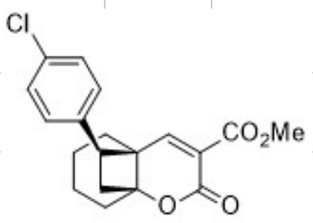
(75 MHz, $CDCl_3$)




**18m**

$^1$H NMR

(300 MHz, $CDCl_3$)




**18m**

$^{13}C$ NMR

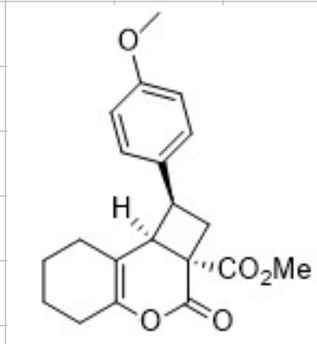
(75 MHz, $CDCl_3$)

163.822
159.293
155.702
133.828
133.369
128.996
128.887
123.242
77.423
77.000
76.917
76.576
52.700
48.444
38.317
37.111
34.649
28.918
20.643
20.413

950000
900000
850000
800000
750000
700000
650000
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
−50000
−100000

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

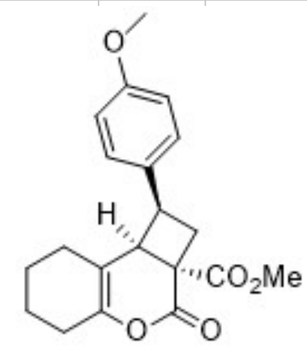
f1 (ppm)




**17n**

$^1$H NMR

(400 MHz, $CDCl_3$)




**17n**

$^{13}C$ NMR

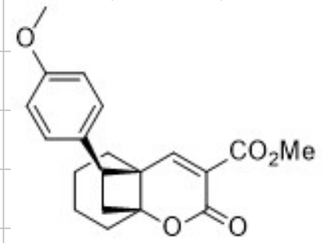
(75 MHz, $CDCl_3$)

170.990
166.168
158.757
146.618
130.720
128.899
113.602
106.922
77.424
77.000
76.576
55.233
53.166
47.639
46.658
40.614
34.476
26.300
25.909
21.967
21.826

1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
−100000

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

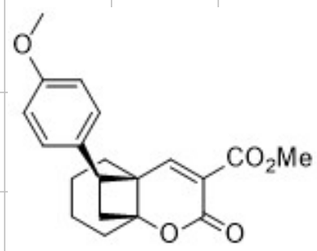
f1 (ppm)




**18n**

$^1$H NMR

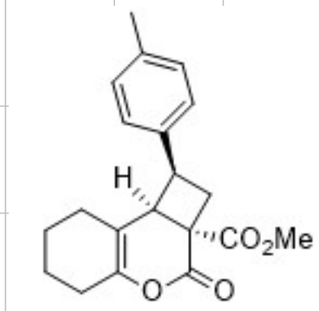
(400 MHz, $CDCl_3$)




**18n**

$^{13}C$ NMR

(75 MHz, $CDCl_3$)

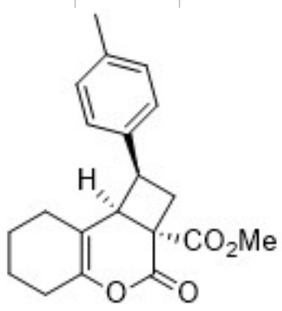



**17o**

$^1$H NMR

(300 MHz, $CDCl_3$)

f1 (ppm)



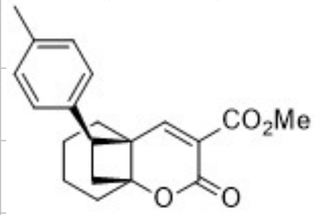

**17o**

$^{13}$C NMR

(100 MHz, $CDCl_3$)

171.024
166.225
146.577
136.852
135.523
128.913
127.786
106.929
77.319
77.000
76.683
53.203
47.668
46.524
40.959
34.273
26.294
25.881
21.966
21.777
21.062

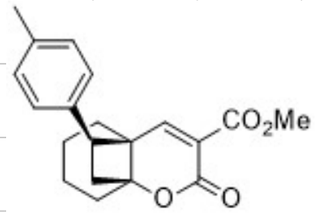
f1 (ppm)




**18o**

$^1$H NMR

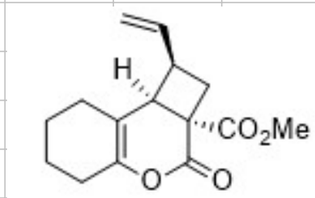
(400 MHz, $CDCl_3$)




**18o**

$^{13}C$ NMR

(100 MHz, $CDCl_3$)

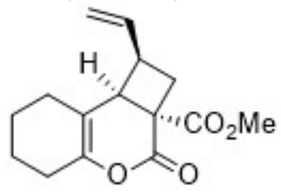



**17r**

$^1$H NMR

(500 MHz, $CDCl_3$)

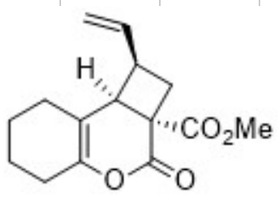
f1 (ppm)




**17r**

$^{13}$C NMR

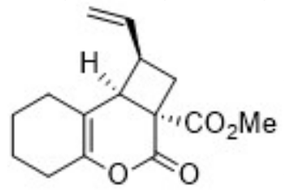
(125 MHz, $CDCl_3$)




**17r**

DEPT-45 NMR

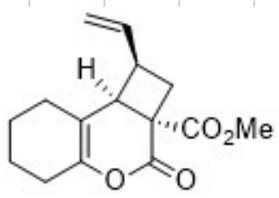
(125 MHz, $CDCl_3$)




**17r**

DEPT-90 NMR

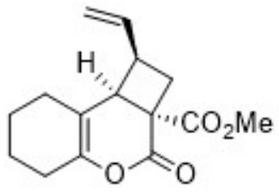
(125 MHz, $CDCl_3$)




**17r**

DEPT-135 NMR

(125 MHz, $CDCl_3$)



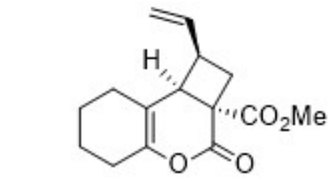

**17r**

COSY NMR

(500 MHz, $CDCl_3$)

f2 (ppm)

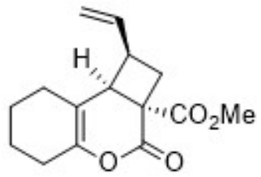
f1 (ppm)




**17r**

HMBC NMR

(500, 125 MHz, $CDCl_3$)



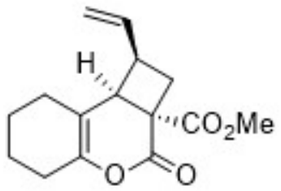

**17r**

HSQC NMR

(500, 125 MHz, $CDCl_3$)

f2 (ppm)

f1 (ppm)




**17r**

NOESY NMR

(500 MHz, $CDCl_3$)