# Nucleophile- or Photo-induced Synthesis of 3-substituted Phthalides from 2-Formylarylketones 

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## Supporting Information

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## 1. General experimental conditions

All ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra were recorded at room temp. in $\mathrm{CDCl}_{3}$ or acetone- $\mathrm{d}_{6}$ on Bruker instruments (Avance 300, Avance DPX 300, Avance DRX 500). Chemical shifts ( $\delta$ ) are reported in parts per million ( ppm ) from tetramethylsilane (TMS) using the residual solvent resonance $\left(\mathrm{CDCl}_{3}\right.$ : 7.26 ppm for ${ }^{1} \mathrm{H} \mathrm{NMR}, 77.16 \mathrm{ppm}$ for ${ }^{13} \mathrm{C}$ NMR, acetone- $\mathrm{d}_{6}$ : 2.05 ppm for ${ }^{1} \mathrm{H}$ NMR, 29.8 and 206.3 ppm for ${ }^{13} \mathrm{C}$ NMR). Multiplicities are abbreviated as follows: $\mathrm{s}=$ singlet, $\mathrm{d}=$ doublet, $\mathrm{t}=$ triplet, $\mathrm{q}=$ quartet, $\mathrm{m}=$ multiplet; brs = broad signal ). IR spectra were recorded on a Perkin-Elmer Paragon 1000 FT-IR spectrometer in the ATR mode at room temp. Melting points were determined using a Büchi 510 apparatus and are not corrected. High-resolution mass spectra were recorded on a Finnigan MAT 95 (for ESI). Analytical TLC was carried out using precoated silica gel plates (Merck TLC plates silica gel 60F254). Flash column chromatography was performed using Macherey Nagel silica 60 M ( $0.040-0.063 \mathrm{~mm} / 230-240 \mathrm{mesh}$ ). Chemicals were purchased from SigmaAldrich, Acros, Alfa Aesar or TCI and used without further purification. Solvents were dried as follows: THF was distilled from sodium/benzophenone under argon atmosphere. The photochemical experiments were performed using a Rayonet chamber photoreactor RPR-100, equipped with 16 lamps ( $400 \mathrm{~W}, 350 \pm 20 \mathrm{~nm}$ ).

## 2. General procedures

### 2.1. General Procedure A: Synthesis of phthalides by nucleophilic catalysis

To a solution of an 2-acyl-benzaldehyde $7(0.5 \mathrm{mmol})$ in dry DMSO $(7 \mathrm{~mL})$ was added $\mathrm{NaCN}(2.5 \mathrm{mg}, 0.05 \mathrm{mmol}, 10 \mathrm{~mol} \%)$ under an atmosphere of argon and the mixture was heated to $50^{\circ} \mathrm{C}$ for 2 to 4 h . The conversion was monitored by TLC. After cooling to room temp. the mixture was quenched with aqueous $\mathrm{NH}_{4} \mathrm{Cl}$ and extracted (3x) with EtOAc. The combined organic layers were dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$, filtered and concentrated under reduced pressure. Pure products were obtained by column chromatography on silica gel.

### 2.2. General Procedure B: Synthesis of phthalides under photochemical conditions

A solution of an 2-acyl-benzaldehyde $7(0.25 \mathrm{mmol})$ in dry DMSO ( 3 mL ) was set under an atmosphere of argon and the mixture was irradiated in a UV-photoreactor ( 350 nm ) over a period of 3 days. The progress of the reaction was monitored by TLC. The crude product solution was poured into water ( 40 mL ) and extracted with EtOAc ( $3 \times 30 \mathrm{ml}$ ). The combined organic layers were dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$, filtered and concentrated under reduced pressure.

## 3. Synthesis of Phthalides from 2-Formylarylketones

### 3.1. 3-Phenylisobenzofuran-1(3H)-one (rac-8a):



Following General Procedure A, the reaction of $\mathbf{7 a}(105 \mathrm{mg}, 0.5 \mathrm{mmol})$ afforded rac-8a (74 $\mathrm{mg}, 0.35 \mathrm{mmol}, 70 \%$ ) as a colorless solid; mp $113-114^{\circ} \mathrm{C}$; TLC: $\mathrm{SiO}_{2}$ (cyclohexane/EtOAc $=10: 1) .{ }^{1} \mathrm{H} \operatorname{NMR}\left(\mathrm{CDCl}_{3}, 300 \mathrm{MHz}\right): \delta=7.97(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.68-7.63(\mathrm{~m}, 1 \mathrm{H}), 7.58-$ $7.53(\mathrm{~m}, 1 \mathrm{H}), 7.38-7.26(\mathrm{~m}, 6 \mathrm{H}), 6.41(\mathrm{~s}, 1 \mathrm{H}) .{ }^{13} \mathrm{C} \mathrm{NMR}\left(\mathrm{CDCl}_{3}, 75 \mathrm{MHz}\right): \delta=170.5(\mathrm{C} 1)$, $149.7,136.5,134.3,129.4,129.3,129.0,127.0,125.7,125.7,122.9,82.7$ (C3). IR (ATR) $v\left[\mathrm{~cm}^{-1}\right]=2945,2910,1758,1601,1593,1441,1410,1395,1263,1170,1064,935,750$, 736. HRMS (EI) for $\mathrm{C}_{14} \mathrm{H}_{10} \mathrm{O}_{2}$ : calcd. 210.0681, found 210.0686. Following General Procedure B, the reaction of $\mathbf{7 a}(52 \mathrm{mg}, 0.25 \mathrm{mmol})$ in DMSO ( 3 mL ) afforded rac-8a (42 $\mathrm{mg}, 0.20 \mathrm{mmol}, 81 \%)$.

### 3.2. 3-(2-Hydroxyphenyl)isobenzofuran-1(3H)-one (rac-8b):



Following General Procedure A, the reaction of $\mathbf{7 b}(113 \mathrm{mg}, 0.5 \mathrm{mmol})$ afforded rac-8b ( $82 \mathrm{mg}, 0.36 \mathrm{mmol}, 73 \%$ ) as a colorless solid; $\mathrm{mp} 120-122{ }^{\circ} \mathrm{C}$; TLC: $\mathrm{SiO}_{2}$ (cyclohexane/EtOAc $=4: 1) .{ }^{1} \mathrm{H} \operatorname{NMR}\left(\mathrm{CDCl}_{3}, 300 \mathrm{MHz}\right): \delta=7.88(\mathrm{~d}, J=7.5 \mathrm{~Hz}, 1 \mathrm{H})$, 7.53-7.43 (m, 3H), 7.12-7.07 (m, 1H), 6.93-6.87 (m, 2H), 6.73-6.68 (m, 1H), $6.63(\mathrm{~s}, 1 \mathrm{H})$, $5.17(\mathrm{~s}, 1 \mathrm{H}) .{ }^{13} \mathrm{C} \mathrm{NMR}\left(\mathrm{CDCl}_{3}, 75 \mathrm{MHz}\right): \delta=171.0,155.3,149.6,136.5,132.6,132.0$, $129.9,127.6,124.1,122.9,122.5,116.4,76.7$ (C3). IR (ATR) $v\left[\mathrm{~cm}^{-1}\right]=3220,2935,2735$, $1763,1598,1501,1465,1450,1401,1360,1315,1267,1240,1202,751,735$. HRMS (EI) for $\mathrm{C}_{14} \mathrm{H}_{10} \mathrm{O}_{3}$ : calcd. 226.0630, found 226.0625. Following General Procedure B, the reaction of $\mathbf{7 b}(56 \mathrm{mg}, 0.25 \mathrm{mmol})$ in DMSO $(3 \mathrm{~mL})$ afforded rac-8b also as a colorless solid ( $48 \mathrm{mg}, 0.21 \mathrm{mmol}, 85 \%$ ).

### 3.3. 3-p-Tolylisobenzofuran-1(3H)-one (rac-8c):



Following General Procedure A, the reaction of $7 \mathbf{c}(112 \mathrm{mg}, 0.5 \mathrm{mmol})$ afforded rac-8c (71 $\mathrm{mg}, 0.31 \mathrm{mmol}, 63 \%$ ) as a colorless solid; $\mathrm{mp} 103-104{ }^{\circ} \mathrm{C}$; TLC: $\mathrm{SiO}_{2}$ (cyclohexane/EtOAc $=6: 1) .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 300 \mathrm{MHz}\right): \delta=7.96(\mathrm{~d}, J=7.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.67-7.62(\mathrm{~m}, 1 \mathrm{H}), 7.57-$ 7.52 (m, 1H), 7.32 (d, $J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.19(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 7.14(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H})$, $6.38(\mathrm{~s}, 1 \mathrm{H}), 2.35(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C} \mathrm{NMR}\left(\mathrm{CDCl}_{3}, 75 \mathrm{MHz}\right): \delta=170.5,140.8,139.3,134.5$, $133.4,129.6,129.4,127.1,125.7,125.5,122.8,82.7,21.2$. IR (ATR) $v\left[\mathrm{~cm}^{-1}\right]=2960,2945$, 1749, 1600, 1590, 1440, 1412, 1396, 1260, 1168, 1061, 940, 752, 730. HRMS (EI) for $\mathrm{C}_{15} \mathrm{H}_{12} \mathrm{O}_{2}$ : calcd. 224.0837, found 224.0842. Following General Procedure B, the reaction of $7 \mathrm{c}(56 \mathrm{mg}, 0.25 \mathrm{mmol})$ in DMSO ( 3 mL ) afforded rac-8c also as a colorless solid (44 $\mathrm{mg}, 0.19 \mathrm{mmol}, 79 \%)$.

### 3.4. 3-(4-Methoxyphenyl)isobenzofuran-1(3H)-one (rac-8d):



Following General Procedure A, the reaction of $7 \mathbf{d}(120 \mathrm{mg}, 0.5 \mathrm{mmol})$ afforded rac-8d (78 mg, $0.32 \mathrm{mmol}, 65 \%$ ) as a colorless solid; $\mathrm{mp} 110-112{ }^{\circ} \mathrm{C} ; \mathrm{TLC}: \mathrm{SiO}_{2}$ (cyclohexane/EtOAc $=5: 1) .{ }^{1} \mathrm{H} \mathrm{NMR}\left(\mathrm{CDCl}_{3}, 300 \mathrm{MHz}\right): \delta=7.86(\mathrm{~d}, J=7.5 \mathrm{~Hz}, 1 \mathrm{H})$, 7.56-7.53 (m, 1H), 7.49-7.44 (m, 1H), $7.22(\mathrm{~d}, J=7.7 \mathrm{~Hz}, 1 \mathrm{H}), 7.08(\mathrm{~d}, J=8.6 \mathrm{~Hz}, 2 \mathrm{H})$, $6.79(\mathrm{~d}, J=8.6 \mathrm{~Hz}, 2 \mathrm{H}), 6.28(\mathrm{~s}, 1 \mathrm{H}), 3.70(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C} \mathrm{NMR}\left(\mathrm{CDCl}_{3}, 75 \mathrm{MHz}\right): \delta=170.5$ (C1), 160.4, 149.7, 134.2, 129.2, 128.7, 128.2, 125.9, 125.5, 122.9, 114.3, 82.7 (C3), 55.3. IR (ATR): $v\left[\mathrm{~cm}^{-1}\right]=2930,2905,1760,1601,1595,1460,1414,1391,1261,1166,1080$, 1061, 945, 755, 734. HRMS (EI) for $\mathrm{C}_{15} \mathrm{H}_{12} \mathrm{O}_{3}$ : calcd. 240.0786, found 240.0791. Following General Procedure B, the reaction of $7 \mathbf{d}(60 \mathrm{mg}, 0.25 \mathrm{mmol})$ in DMSO ( 3 mL ) afforded $\mathrm{rac}-\mathbf{8 d}$ also as a colorless solid ( $47 \mathrm{mg}, 0.19 \mathrm{mmol}, 78 \%$ ).

### 3.5. 3-(4-Nitrophenyl)isobenzofuran-1(3H)-one (rac-8e):



Following General Procedure A, the reaction of $\mathbf{7 e}(127 \mathrm{mg}, 0.5 \mathrm{mmol})$ afforded rac-8e (79 $\mathrm{mg}, 0.31 \mathrm{mmol}, 62 \%$ ) as a colorless solid; $\mathrm{mp} 132-134{ }^{\circ} \mathrm{C}$; TLC: $\mathrm{SiO}_{2}$ (cyclohexane/EtOAc $=5: 1) .{ }^{1} \mathrm{H} \operatorname{NMR}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=8.30-8.26(\mathrm{~m}, 2 \mathrm{H}), 8.10-8.01(\mathrm{~m}, 1 \mathrm{H}), 7.72-7.61$ $(\mathrm{m}, 1 \mathrm{H}), 7.49-7.44(\mathrm{~m}, 2 \mathrm{H}), 7.23-7.19(\mathrm{~m}, 2 \mathrm{H}), 6.51(\mathrm{~s}, 1 \mathrm{H}) .{ }^{13} \mathrm{C} \operatorname{NMR}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ $=170.3(\mathrm{C} 1), 149.6,145.5,145.4,133.4,131.4,129.1,128.6,125.1,124.4,123.0,82.8$ (C3). IR (ATR): $v\left[\mathrm{~cm}^{-1}\right]=2960,2914,1755,1600,1591,1465,1413,1390,1265,1164$, 1065, 950, 750, 739. HRMS (EI) for $\mathrm{C}_{14} \mathrm{H}_{9} \mathrm{NO}_{4}$ : calcd. 255.0532, found 255.0538. Following General Procedure B, the reaction of $7 \mathbf{e}(64 \mathrm{mg}, 0.25 \mathrm{mmol})$ in DMSO ( 3 mL ) afforded $\mathrm{rac}-\mathbf{8 e}$ also as a colorless solid ( $48 \mathrm{mg}, 0.19 \mathrm{mmol}, 75 \%$ ).

### 3.6. 3-(4-Bromophenyl)isobenzofuran-1(3H)-one (rac-8f):



Following General Procedure A, the reaction of $\mathbf{7 f}(144 \mathrm{mg}, 0.5 \mathrm{mmol})$ afforded rac-8f (88 $\mathrm{mg}, 0.30 \mathrm{mmol}, 61 \%$ ) as a colorless solid; $\mathrm{mp} 141-143{ }^{\circ} \mathrm{C}$; TLC: $\mathrm{SiO}_{2}$ (cyclohexane/EtOAc $=5: 1) .{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=7.99-7.96(\mathrm{~m}, 1 \mathrm{H}), 7.68-7.51(\mathrm{~m}, 4 \mathrm{H}), 7.34-7.30$ $(\mathrm{m}, 1 \mathrm{H}), 7.18-7.15(\mathrm{~m}, 2 \mathrm{H}), 6.37(\mathrm{~s}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=170.2$ (C1), $149.28,135.6,134.5,132.2,129.6,128.6,125.8,125.8,125.6,125.5,123.5,122.8,81.9$ (C3). IR (ATR): $v\left[\mathrm{~cm}^{-1}\right]=2950,2910,1760,1605,1595,1460,1410,1385,1260,1189$, 1050, 953, 756, 741. HRMS (EI) for $\mathrm{C}_{14} \mathrm{H}_{9} \mathrm{O}_{2} \mathrm{Br}$ : calcd. 287.9786, found 287.9780. Following General Procedure B, the reaction of $7 \mathbf{f}(72 \mathrm{mg}, 0.25 \mathrm{mmol})$ in DMSO ( 3 mL ) afforded $\mathrm{rac}-\mathbf{8 f}$ also as a colorless solid ( $60 \mathrm{mg}, 0.21 \mathrm{mmol}, 83 \%$ ).

### 3.7. 3-(Pyridin-4-yl)isobenzofuran-1(3H)-one (rac-8g):



Following General Procedure A, the reaction of $\mathbf{7 g}(105 \mathrm{mg}, 0.5 \mathrm{mmol})$ afforded $\mathrm{rac-8g}(76$ $\mathrm{mg}, 0.36 \mathrm{mmol}, 72 \%$ ) as a colorless oil; TLC: $\mathrm{SiO}_{2}$ (EtOAc). ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=8.10-8.08(\mathrm{~m}, 1 \mathrm{H}), 7.58-7.51(\mathrm{~m}, 4 \mathrm{H}), 7.34-7.30(\mathrm{~m}, 1 \mathrm{H}), 7.18-7.15(\mathrm{~m}, 2 \mathrm{H}), 6.37(\mathrm{~s}$, 1H). ${ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=170.2$ (C1), 149.2, 143.6, 141.5, 132.2, 128.6, 125.5, $123.5,122.8,81.9$ (C3). IR (ATR): $v\left[\mathrm{~cm}^{-1}\right]=2920,2890,1749,1600,1590,1470,1415$, 1380, 1261, 1189, 1080, 950, 760, 738. HRMS (EI) for $\mathrm{C}_{13} \mathrm{H}_{9} \mathrm{NO}_{2}$ : calcd. 211.0633, found 211.0638. Following General Procedure B, the reaction of $7 \mathbf{g}(52 \mathrm{mg}, 0.25 \mathrm{mmol})$ in DMSO ( 3 mL ) afforded rac- $\mathbf{8 g}$ also as a colorless oil ( $39 \mathrm{mg}, 0.18 \mathrm{mmol}, 74 \%$ ).

### 3.8. 3-Methylisobenzofuran-1(3H)-one (rac-8h):



Following General Procedure A, the reaction of $\mathbf{7 h}(74 \mathrm{mg}, 0.5 \mathrm{mmol})$ afforded $\mathrm{rac}-\mathbf{8 h}$ ( 52 $\mathrm{mg}, 0.35 \mathrm{mmol}, 70 \%$ ) as a colorless oil; TLC: $\mathrm{SiO}_{2}$ (cyclohexane/EtOAc $=3: 1$ ). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=7.89(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.66-7.73(\mathrm{~m}, 1 \mathrm{H}), 7.53(\mathrm{t}, J=7.5 \mathrm{~Hz}$, $1 \mathrm{H}), 7.46(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 5.58(\mathrm{q}, J=6.6 \mathrm{~Hz}, 1 \mathrm{H}), 1.65(\mathrm{~d}, J=6.6 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=170.4$ (C1), 151.1, 134.0, 129.0, 125.7, 125.6, 121.5, 77.7 (C3), 20.3. IR (ATR): $v\left[\mathrm{~cm}^{-1}\right]=2982,2932,1759,1615,1597,1460,1282,1060,967,755,739$. HRMS (EI) for $\mathrm{C}_{9} \mathrm{H}_{8} \mathrm{O}_{2}$ : calcd. 148.0524, found 148.0519. Following General Procedure B, the reaction of $\mathbf{7 h}(37 \mathrm{mg}, 0.25 \mathrm{mmol})$ in DMSO $(3 \mathrm{~mL})$ afforded rac-8h also as a colorless oil ( $26 \mathrm{mg}, 0.17 \mathrm{mmol}, 71 \%$ ).

### 3.9. 3-Ethylisobenzofuran-1(3H)-one (rac-8i):



Following General Procedure A, the reaction of $7 \mathbf{i}(81 \mathrm{mg}, 0.5 \mathrm{mmol})$ afforded rac-8i (60 $\mathrm{mg}, 37 \mathrm{mmol}, 74 \%$ ) as a colorless oil; TLC: $\mathrm{SiO}_{2}$ (cyclohexane/EtOAc $=3: 1$ ). ${ }^{1} \mathrm{H}$ NMR (300 MHz, $\mathrm{CDCl}_{3}$ ): $\delta=7.90(\mathrm{~d}, J=7.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.69(\mathrm{t}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.54(\mathrm{t}, J=7.4$ $\mathrm{Hz}, 1 \mathrm{H}), 7.45(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 5.47(\mathrm{dd}, J=5.1,6.6 \mathrm{~Hz}, 1 \mathrm{H}), 2.09-2.18(\mathrm{~m}, 1 \mathrm{H}), 1.78-$ $1.88(\mathrm{~m}, 1 \mathrm{H}), 1.01(\mathrm{t}, J=7.6 \mathrm{~Hz}, 3 \mathrm{H}),{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=170.6(\mathrm{C} 1), 149.6$, $133.9,128.9,126.1,125.4,121.7,82.20$ (C3), 27.5, 8.7. IR (ATR): $v\left[\mathrm{~cm}^{-1}\right]=2970,2940$, 2880, 1761, 1460, 1285, 1062, 965, 754, 737. HRMS (EI) for $\mathrm{C}_{10} \mathrm{H}_{10} \mathrm{O}_{2}$ : calcd. 162.0681, found 162.0676. Following General Procedure B, the reaction of $7 \mathbf{i}(37 \mathrm{mg}, 0.25 \mathrm{mmol})$ in DMSO ( 3 mL ) afforded rac-8i also as a colorless oil ( $30 \mathrm{mg}, 0.19 \mathrm{mmol}, 75 \%$ ).

### 3.10. Pestalalactone (rac-6a):



Following General Procedure A, the reaction of pestalone (5a) ( $30 \mathrm{mg}, 0.068 \mathrm{mmol}$ ) with NaCN afforded pestalalactone rac-6a ( $19 \mathrm{mg}, 0.042 \mathrm{mmol}, 62 \%$ yield) as a colorless solid, mp 195-197 ${ }^{\circ} \mathrm{C}$; TLC: $\mathrm{SiO}_{2}$ (cyclohexane/EtOAc $=1: 2$ ). ${ }^{1} \mathrm{H}$ NMR: $\left(500 \mathrm{MHz}\right.$, acetone- $\mathrm{d}_{6}$ ): $\delta=1.37(\mathrm{~s}, 3 \mathrm{H}), 1.38 / 1.45(\mathrm{~s}, 3 \mathrm{H}), 2.46 / 2.47(\mathrm{~s}, 3 \mathrm{H}), 2.60-3.15(\mathrm{~m}, 2 \mathrm{H}), 3.32 / 3.99(\mathrm{~s}$, $3 \mathrm{H}), 4.51 / 4.55(\mathrm{t}, J=5.5 \mathrm{~Hz}, 1 \mathrm{H}), 6.44 / 6.49(\mathrm{~s}, 1 \mathrm{H}), 6.80 / 6.96(\mathrm{~s}, 1 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( 125 MHz , Acetone- $\mathrm{d}_{6}$ ): $\delta=171.8 / 171.9$ (s, C1), $163.1 / 163.4,156.5 / 156.7,155.3 / 156.4$, 151.5 / 152.5, 150.9 / 151.18, $137.2 / 137.4,131.6 / 131.7,122.6 / 122.7,120.5 / 120.9$, 118.4 / 118.8, $118.0 / 117.4,115.5 / 115.7,104.8 / 105.3,102.7 / 103.0,75.3 / 76.0,61.1 /$ $62.8,25.5 / 25.5,24.6 / 24.7,18.4,17.6 / 17.7$. IR (ATR): $v\left[\mathrm{~cm}^{-1}\right]=3370,3221,2925$,
$2850,1712,1625,1521,1440,1390,1365,1281,1170,1150,1085,1045,951,810,715$.
The NMR data are in agreement with those previously reported.

X-ray data for pestalalacton (rac-6a)

| Identification code | rac-6a $\operatorname{CCDC} 781113$ |
| :---: | :---: |
| Empirical formula Formula weight | $\begin{gathered} \hline \hline \mathrm{C}_{21} \mathrm{H}_{20} \mathrm{Cl}_{2} \mathrm{O}_{6} \\ 439.27 \end{gathered}$ |
| Crystal system, space group Unit cell dimensions | Monoclinic, $\mathrm{P} 21 / \mathrm{c}$ |
| a | 16.959(2) A |
| b | 15.4023(10) A |
| c | 7.7216(10) A |
| $\beta$ | $91.989(4) \mathrm{deg}$. |
| Volume | 2015.7(4) $\AA^{3}$ |
| Z, Calculated density | $4,1.447 \mathrm{~g} / \mathrm{cm}^{-1}$ |
| Absorption coefficient | $0.358 \mathrm{~mm}^{-1}$ |
| F(000) | 912 |
| Crystal size | . $1 \times .07 \times .03 \mathrm{~mm}$ |
| Theta range for data collection | 1.79 to 25.00 deg . |
| Limiting indices | $\begin{gathered} -20<=h<=19, \\ -14<=k<=18, \\ -7<=\mid<=9 \end{gathered}$ |
| Reflections collected / unique | $\begin{gathered} 8969 / 3533 \\ {[R(\text { int })=0.0733]} \end{gathered}$ |
| Reflection observed [l>2 $\sigma$ ( 1 ]] | 1652 |
| Completeness to theta $=27.00$ | 99.6 \% |
| Data / restraints / parameters | 3533 / 3 / 278 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.053 |
| Final $R$ indices [ $1>2 \sigma(\mathrm{l})$ ] | $\begin{aligned} \mathrm{R} 1 & =0.0908, \\ \mathrm{wR} 2 & =0.2423 \end{aligned}$ |
| R indices (all data) | $\begin{aligned} & \mathrm{R} 1=0.1877, \\ & \mathrm{wR2}=0.2882 \end{aligned}$ |
| Largest diff. peak and hole | 1.181 and -0.966 e. $\AA^{-3}$ |

## 4. NMR Spectra





Figure $1 .{ }^{1} \mathrm{H}$ spectrum of $\mathrm{rac}-\mathbf{8 a}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$.


Figure $2 .{ }^{13} \mathrm{C}$ spectrum of $\mathrm{rac-8a}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$. -S10-




Figure 3. ${ }^{1} \mathrm{H}$ spectrum of $\mathrm{rac}-\mathbf{8 b}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$.


Figure $4 .{ }^{13} \mathrm{C}$ spectrum of $\mathrm{rac}-\mathbf{8 b}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$.
-S11-




Figure $5 .{ }^{1} \mathrm{H}$ spectrum of $\mathrm{rac}-\mathbf{8 c}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$.


Figure $6 .{ }^{13} \mathrm{C}$ spectrum of $\mathrm{rac}-\mathbf{8 c}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$.


Figure 7. ${ }^{1} \mathrm{H}$ spectrum of $\mathrm{rac}-\mathbf{8 d}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$.


Figure $8 .{ }^{13} \mathrm{C}$ spectrum of $\mathrm{rac}-\mathbf{8 d}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$.




Figure $9 .{ }^{1} \mathrm{H}$ spectrum of $\mathrm{rac}-\mathbf{8 e}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$.



Figure 10. ${ }^{13} \mathrm{C}$ spectrum of $\mathrm{rac}-\mathbf{8 e}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$. -S14-


Figure 11. ${ }^{1} \mathrm{H}$ spectrum of $\mathrm{rac}-\mathbf{8 f}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$.



Figure 12. ${ }^{13} \mathrm{C}$ spectrum of $\mathrm{rac}-\mathbf{8 f}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$.




Figure 13. ${ }^{1} \mathrm{H}$ spectrum of $\mathrm{rac}-\mathbf{8 g}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$.





Figure $15 .{ }^{1} \mathrm{H}$ spectrum of $\mathrm{rac}-\mathbf{8 h}\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$.

$\stackrel{\text { ~ }}{\stackrel{\sim}{4}}$


Figure 16. ${ }^{13} \mathrm{C}$ spectrum of $\mathrm{rac}-\mathbf{8} \mathbf{h}\left(125 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$.
-S17-




Figure 17. ${ }^{1} \mathrm{H}$ spectrum of $\mathrm{rac}-\mathbf{8 i}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$.


Figure 18. ${ }^{13} \mathrm{C}$ spectrum of $\mathrm{rac-8i}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$.


Figure 19. ${ }^{1} \mathrm{H}$ spectrum of $\mathrm{rac}-\mathbf{6 a}\left(500 \mathrm{MHz}\right.$, acetone- $\mathrm{d}_{6}$ ).


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Figure $20 .{ }^{13} \mathrm{C}$ spectrum of $\mathrm{rac}-\mathbf{6 a}\left(125 \mathrm{MHz}\right.$, acetone- $\left.\mathrm{d}_{6}\right)$.

