Rhodium-catalysed Tandem Dehydrogenative Coupling–Michael addition: Direct Synthesis of Phthalides from Benzoic Acids and Alkenes

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1. General remarks

Reagents were purchased from commercial suppliers and used as received. Solid reagents were weighed on a semi-micro balance featuring one hundredth of a milligram precision. Solvents were dried by standard techniques. Melting points were measured on a hot-stage Reichert Thermovar apparatus and are uncorrected. $^1$H and $^{13}$C{$^1$H} NMR spectra were recorded on a Varian instrument at 300, 400, or 500 MHz and 75, 100, or 125 MHz, respectively. IR spectra were measured on KBr pastille. High resolution mass spectra (HRMS) were obtained on a sector-field mass spectrometer. Elemental analyses were performed on a FISONS Instrument EA 108 or a Perkin Elmer 240C elemental analyser.

2. General procedure

A mixture of [(COD)RhCl]$_2$ (11.82 mg, 0.024 mmol, 8 mol%) and AgOTf (18.54 mg, 0.072 mmol, 24 mol%) in chlorobenzene (600 $\mu$L) was stirred in a glass tube at room temperature for 30 minutes. Dicyclopentadiene (13.0 $\mu$L, 0.096 mmol, 32 mol%) was added. Mixture turned instantaneously from light yellow to dark orange. Then, substituted benzoic acid (0.3 mmol, 1.0 equiv), alkene (0.6 mmol, 2.0 equiv), Cu(OAc)$_2$·H$_2$O (239.7 mg, 1.2 mmol, 4.0 equiv), and chlorobenzene (900 $\mu$L) were added. The tube was sealed and heated at 120 °C for 48 hours. After this time the reaction mixture was filtered through a short pad of silica gel and eluted with ethyl acetate. The filtrate was concentrated under reduced pressure. Purification of the crude mixture by flash chromatography, preparative thin-layer chromatography (PTLC), or recrystallisation afforded the pure product.
3. Characterisation data of products

4,5,6-Trimethoxy-3-(2-oxobutyl)isobenzofuran-1(3H)-one (1a)

White solid (82 mg, 93% yield); prepared following the general procedure from 3,4,5-trimethoxybenzoic acid (63.6 mg, 0.3 mmol) and ethyl vinyl ketone (61.6 µL, 0.6 mmol); purified by recrystallisation (hexane/diethyl ether = 1:1); mp = 124–125 °C. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 1.10 (t, 3H, $J = 7.5$ Hz), 2.53 (q, 2H, $J = 7.5$ Hz), 2.74 (dd, 1H, $J = 16.5$ Hz, $J = 9.0$ Hz), 3.16 (dd, 1H, $J = 16.5$ Hz, $J = 3.0$ Hz), 3.91 (s, 3H), 3.93 (s, 3H), 3.96 (s, 3H), 5.91 (dd, 1H, $J = 9.0$ Hz, $J = 3.0$ Hz), 7.12 (s, 1H). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 7.6, 37.0, 45.6, 56.4, 61.1, 61.4, 75.7, 102.8, 121.3, 134.6, 147.0, 147.5, 156.0, 170.1, 207.0. IR (KBr): ν 2940, 1765, 1717, 1479, 1420, 1342, 1110. HRMS (ESI): m/z calcd for C$_{15}$H$_{19}$O$_6$ [M + H]$^+$ 295.1176, found 295.1178.

5,6,7-Trimethoxy-3-(2-oxobutyl)isobenzofuran-1(3H)-one (1b)

White solid (35 mg, 40% yield); prepared following the general procedure from 2,3,4-trimethoxybenzoic acid (63.6 mg, 0.3 mmol) and ethyl vinyl ketone (61.6 µL, 0.6 mmol); purified by PTLC (hexane/diethyl ether = 1:1); mp = 122–123 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 1.11 (t, 3H, $J = 7.2$ Hz), 2.49 (dq, 1H, $J = 18.0$ Hz, $J = 7.2$ Hz), 2.57 (dq, 1H, $J = 18.0$ Hz, $J = 7.2$ Hz), 2.82 (dd, 1H, $J = 17.2$ Hz, $J = 6.8$ Hz), 3.10 (dd, 1H, $J = 17.2$ Hz, $J = 6.8$ Hz), 3.86 (s, 3H), 3.92 (s, 3H), 4.13 (s, 3H), 5.76 (t, 1H, $J = 6.8$ Hz), 6.66 (s, 1H). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 7.5, 36.9, 47.3, 56.5, 61.4, 62.4, 75.5, 99.8, 110.3, 142.0, 147.4, 152.3, 159.7, 167.6, 207.8. IR (KBr): ν 2975, 1737, 1599, 1474, 1418, 1346, 1249, 1196. HRMS (ESI): m/z calcd for C$_{15}$H$_{19}$O$_6$ [M + H]$^+$ 295.11761, found 295.11778.
5,6,7-tris(Benzyloxy)-3-(2-oxobutyl)isobenzofuran-1(3H)-one (1c)

Incolor liquid (118 mg, 75%); prepared following the general procedure from 3,4,5-tris(benzyloxy)benzoic acid (133.5 mg, 0.3 mmol) and ethyl vinyl ketone (61.6 μL, 0.6 mmol) using 3.0 mL of solvent; purified by flash chromatography (hexane/diethyl ether = 1:1); 1H NMR (CDCl₃, 400 MHz): δ 1.03 (t, 3H, J = 7.2 Hz), 2.40 (q, 2H, J = 7.2 Hz), 2.58 (dd, 1H, J = 16.8 Hz, J = 9.2 Hz), 3.05 (dd, 1H, J = 16.8 Hz, J = 2.8 Hz), 5.15 (m, 6H), 5.51 (dd, 1H, J = 9.2 Hz, J = 2.8 Hz), 7.23-7.47 (m, 16H). 13C NMR (CDCl₃, 75 MHz): δ 7.4, 36.8, 45.1, 71.3, 75.5, 75.6, 75.7, 104.6, 118.2, 121.3, 127.7, 128.4, 128.5, 128.6, 128.7, 128.7, 135.5, 135.8, 136.4, 136.6, 146.6, 155.0, 169.8, 206.6. IR (KBr): ν 3065, 2976, 1762, 1717, 1471, 1451, 1339, 1103. HRMS (ESI): m/z calcd for C₃₃H₃₀NaO₆ [M + Na]^+ 545.1935, found 545.1937.

5-Methoxy-3-(2-oxobutyl)isobenzofuran-1(3H)-one (1d)

White solid (22 mg, 31% yield); prepared following the general procedure from 4-methoxybenzoic acid (46.2 mg, 0.3 mmol) and ethyl vinyl ketone (61.6 μL, 0.6 mmol); purified by PTLC (hexane/diethyl ether = 1:1); mp = 70–71 °C. 1H NMR (CDCl₃, 400 MHz): δ 1.11 (t, 3H, J = 7.2 Hz), 2.49 (dq, 1H, J = 18.0 Hz, J = 7.2 Hz), 2.58 (dq, 1H, J = 18.0 Hz, J = 7.2 Hz), 2.85 (dd, 1H, J = 17.2 Hz, J = 6.4 Hz), 3.11 (dd, 1H, J = 17.2 Hz, J = 6.4 Hz), 3.88 (s, 3H), 5.86 (t, 1H, J = 6.4 Hz), 6.89 (d, 1H, J = 2.0 Hz), 7.04 (dd, 1H, J = 8.4 Hz, J = 2.0 Hz), 7.79 (d, 1H, J = 8.4 Hz). 13C NMR (CDCl₃, 75 MHz): δ 7.5, 36.8, 47.0, 55.9, 76.2, 106.3, 116.8, 118.0, 127.2, 152.3, 164.8, 169.8, 207.5. IR (KBr): ν 2977, 1758, 1715, 1607, 1492, 1289, 1053. HRMS (ESI): m/z calcd for C₁₃H₁₄NaO₄ [M + Na]^+ 257.0784, found 257.0784.
5-Methyl-3-(2-oxobutyl)isobenzofuran-1(3H)-one (1e)

White solid (28 mg, 43% yield); prepared following the general procedure from p-toluic acid (41.7 mg, 0.3 mmol) and ethyl vinyl ketone (61.6 µL, 0.6 mmol); purified by PTLC (hexane/diethyl ether = 1:1); mp = 76–77 °C. 1H NMR (CDCl₃, 400 MHz): δ 1.11 (t, 3H, J = 7.2 Hz), 2.47 (s, 1H), 2.49 (dq, 1H, J = 18.0 Hz, J = 7.2 Hz), 2.57 (dq, 1H, J = 18.0 Hz, J = 7.2 Hz), 2.86 (dd, 1H, J = 17.2 Hz, J = 6.4 Hz), 3.08 (dd, 1H, J = 17.2 Hz, J = 6.8 Hz), 5.89 (t, 1H, J = 6.8 Hz), 7.24 (dd, 1H, J = 1.2 Hz, J = 0.8 Hz), 7.33 (ddd, 1H, J = 7.6 Hz, J = 1.2 Hz, J = 0.8 Hz), 7.77 (d, 1H, J = 7.6 Hz). 13C NMR (CDCl₃, 75 MHz): δ 7.5, 22.1, 36.8, 47.0, 76.6, 122.6, 123.2, 125.5, 130.6, 145.6, 150.0, 170.1, 207.4. IR (KBr): v 2980, 1761, 1716, 1519, 1331. HRMS (ESI): m/z calcd for C₁₃H₁₄NaO₃ [M + Na]⁺ 241.0835, found 241.0834.

3-(2-Oxobutyl)naphtho[1,2-c]furan-1(3H)-one (1f)

White solid (40 mg, 52% yield); prepared following the general procedure from α-naphthoic acid (52.8 mg, 0.3 mmol) and ethyl vinyl ketone (61.6 µL, 0.6 mmol); purified by flash chromatography (hexane/diethyl ether = 1:1); mp = 144–145 °C. 1H NMR (CDCl₃, 400 MHz): δ 1.13 (t, 3H, J = 7.6 Hz), 2.52 (dq, 1H, J = 18.0 Hz, J = 7.6 Hz), 2.60 (dq, 1H, J = 18.0 Hz, J = 7.6 Hz), 2.94 (dd, 1H, J = 16.8 Hz, J = 6.0 Hz), 3.12 (dd, 1H, J = 16.8 Hz, J = 6.8 Hz), 6.03 (t, 1H, J = 6.8 Hz), 7.50 (d, 1H, J = 8.8 Hz), 7.64 (dd, 1H, J = 8.0 Hz, J = 1.2 Hz), 7.72 (dd, 1H, J = 8.0 Hz, J = 1.2 Hz), 7.97 (d, 1H, J = 8.4 Hz), 8.13 (d, 1H, J = 8.8 Hz), 9.00 (d, 1H, J = 8.4 Hz). 13C NMR (CDCl₃, 100 MHz): δ 7.5, 37.0, 46.8, 76.2, 118.7, 120.0, 123.6, 127.5, 128.4, 129.1, 129.2, 133.5, 135.7, 151.2, 170.3, 207.3. IR (KBr): v 3058, 2977, 1748, 1716, 1519, 1331. HRMS (ESI): m/z calcd for C₁₆H₁₄NaO₃ [M + Na]⁺ 277.0835, found 277.0842.
3-(2-Oxobutyl)isobenzofuran-1(3H)-one (1g)

White solid (30 mg, 49% yield); prepared following the general procedure from benzoic acid (36.9 mg, 0.3 mmol) and ethyl vinyl ketone (61.6 µL, 0.6 mmol); purified by flash chromatography (hexane/diethyl ether = 1:1). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 1.09 (t, 3H, $J$ = 7.2 Hz), 2.48 (dq, 1H, $J$ = 18.0, $J$ = 7.2), 2.56 (dq, 1H, $J$ = 18.0 Hz, $J$ = 7.2 Hz), 2.88 (dd, 1H, $J$ = 17.2 Hz, $J$ = 6.0 Hz), 3.08 (dd, 1H, $J$ = 17.2 Hz, $J$ = 6.8 Hz), 5.94 (t, 1H, $J$ = 6.8 Hz), 7.46 (dd, 1H, $J$ = 7.6 Hz, $J$ = 0.8 Hz), 7.52 (t, 1H, $J$ = 7.6 Hz), 7.65 (t, 1H, $J$ = 7.6 Hz, $J$ = 1.2 Hz), 7.88 (d, 1H, $J$ = 7.6 Hz). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 7.4, 36.8, 46.8, 76.9, 122.3, 125.7, 129.4, 134.2, 149.4, 170.0, 207.3. HRMS (ESI): m/z calcd for C$_{12}$H$_{12}$NaO$_3$ [M + Na]$^+$ 227.0679, found 227.0684.

3-(2-Oxobutyl)-5-vinylisobenzofuran-1(3H)-one (1h)

Pale yellow liquid (28 mg, 40% yield); prepared following the general procedure from 4-vinylbenzoic acid (45.9 mg, 0.3 mmol) and ethyl vinyl ketone (61.6 µL, 0.6 mmol); purified by flash chromatography (hexane/diethyl ether = 1:1). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 1.12 (t, 3H, $J$ = 7.2 Hz), 2.50 (dq, 1H, $J$ = 18.0 Hz, $J$ = 7.2 Hz), 2.58 (dq, 1H, $J$ = 18.0 Hz, $J$ = 7.2 Hz), 2.88 (dd, 1H, $J$ = 17.2 Hz, $J$ = 6.8 Hz), 3.12 (dd, 1H, $J$ = 17.2 Hz, $J$ = 6.8 Hz), 5.46 (d, 1H, $J$ = 11.2 Hz), 5.91 (d, 1H, $J$ = 17.6 Hz), 5.94 (t, 1H, $J$ = 6.8 Hz), 6.79 (dd, 1H, $J$ = 17.6 Hz, $J$ = 11.2 Hz), 7.45 (s, 1H), 7.57 (d, 1H, $J$ = 8.0 Hz), 7.84 (d, 1H, $J$ = 8.0 Hz). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 7.5, 36.8, 47.0, 76.6, 118.0, 119.8, 124.9, 125.9, 127.5, 135.6, 143.8, 150.2, 169.8, 207.4. IR (KBr): ν 1717, 1684, 1653, 1632, 1559, 1507. HRMS (ESI): m/z calcd for C$_{14}$H$_{14}$NaO$_3$ [M + Na]$^+$ 253.0835, found 253.0835.
3-(2-Oxobutyl)-5-phenylisobenzofuran-1(3H)-one (1i)

White solid (28 mg, 33% yield); prepared following the general procedure from [1,1’-biphenyl]-4-carboxylic acid (60.6 mg, 0.3 mmol) and ethyl vinyl ketone (61.6 µL, 0.6 mmol); purified by flash chromatography (hexane/diethyl ether = 1:1); mp = 90–91 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 1.12 (t, 3H, $J$ = 7.2 Hz), 2.50 (dq, 1H, $J$ = 18.0 Hz, $J$ = 7.2 Hz), 2.59 (dq, 1H, $J$ = 18.0 Hz, $J$ = 7.2 Hz), 2.93 (dd, 1H, $J$ = 17.6 Hz, $J$ = 6.8 Hz), 3.16 (dd, 1H, $J$ = 17.6 Hz, $J$ = 6.8 Hz), 6.00 (t, 1H, $J$ = 6.8 Hz), 7.48 (m, 3H), 7.60 (d, 2H, $J$ = 8.8 Hz), 7.65 (s, 1H), 7.75 (d, 1H, $J$ = 8.0 Hz), 7.95 (d, 1H, $J$ = 8.0 Hz). $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 6.52, 35.8, 46.0, 75.8, 119.8, 123.5, 125.1, 126.5, 127.7, 127.8, 128.1, 138.6, 146.7, 149.3, 169.0, 206.3. IR (KBr): $\nu$ 2980, 1761, 1717, 1615, 1338. HRMS (ESI): $m$/z calcd for C$_{18}$H$_{16}$KO$_3$ [M + K]$^+$ 319.0731, found 319.0729.

5-Fluoro-3-(2-oxobutyl)isobenzofuran-1(3H)-one (1j)

White solid (14 mg, 21% yield); prepared following the general procedure from 4-fluorobenzoic acid (42.6 mg, 0.3 mmol) and ethyl vinyl ketone (61.6 µL, 0.6 mmol); purified by PTLC (hexane/diethyl ether = 1:1); mp = 91–92 °C. $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 1.12 (t, 3H, $J$ = 7.5 Hz), 2.49 (dq, 1H, $J$ = 22.0 Hz, $J$ = 7.5 Hz), 2.57 (dq, 1H, $J$ = 22.0 Hz, $J$ = 7.5 Hz), 2.86 (dd, 1H, $J$ = 17.5 Hz, $J$ = 7.0 Hz), 3.18 (dd, 1H, $J$ = 17.5 Hz, $J$ = 6.0 Hz), 5.91 (t, 1H, $J$ = 7.0 Hz), 7.18 (ddt, 1H, $J$ = 8.0 Hz, $J$ = 2.5 Hz, $J$ = 0.5 Hz), 7.23 (tdd, 1H, $J$ = 9.0 Hz, $J$ = 2.5 Hz, $J$ = 0.5 Hz), 7.89 (dd, 1H, $J$ = 8.5 Hz, $J$ = 5.0 Hz). $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 7.5, 36.7, 46.7, 76.2 (d, $J$ = 2.9 Hz), 110.0 (d, $J$ = 25.4 Hz), 117.7 (d, $J$ = 23.3 Hz), 121.9 (d, $J$ = 2.0 Hz), 128.2 (d, $J$ = 9.7 Hz), 152.3 (d, $J$ = 9.8 Hz), 166.6 (d, $J$ = 254.9 Hz), 168.9, 207.2. IR (KBr): $\nu$ 2979, 2944, 1764, 1603, 1481, 1349. HRMS (ESI): $m$/z calcd for C$_{12}$H$_{11}$FNaO$_3$ [M + Na]$^+$ 245.0584, found 245.0574.
5-Iodo-3-(2-oxobutyl)isobenzofuran-1(3H)-one (1k)

White solid (15 mg, 15% yield); prepared following the general procedure from 4-iodobenzoic acid (75.9 mg, 0.3 mmol) and ethyl vinyl ketone (61.6 µL, 0.6 mmol); purified by PTLC (dichloromethane/ethyl acetate = 58:2); mp = 132–133 °C. $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 1.12 (t, 3H, $J = 9.5$ Hz), 2.49 (dq, 1H, $J = 22.5$ Hz, $J = 9.5$ Hz), 2.57 (dq, 1H, $J = 22.5$ Hz, $J = 9.5$ Hz), 2.86 (dd, 1H, $J = 17.5$ Hz, $J = 7.0$ Hz), 3.14 (dd, 1H, $J = 17.5$ Hz, $J = 6.5$ Hz), 5.90 (t, 1H, $J = 6.5$ Hz), 7.61 (d, 1H, $J = 1.0$ Hz), 7.90 (m, 2H). $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 6.5, 35.7, 45.6, 75.2, 101.2, 124.4, 125.9, 130.9, 137.9, 150.1, 168.3, 206.5. IR (KBr): v 2980, 2940, 1762, 1716, 1559, 1541, 1457. HRMS (ESI): $m/z$ calcd for C$_{12}$H$_{11}$INaO$_3$ [M + Na]$^+$ 352.9645, found 352.9641.

3-(2-Oxobutyl)naphtho[2,3-c]furan-1(3H)-one (1l)

White solid (1l + 1l' combined yield 53 mg, 69%); prepared following the general procedure from β-naphthoic acid (51.7 mg, 0.3 mmol) and ethyl vinyl ketone (61.6 µL, 0.6 mmol); purified by flash chromatography (hexane/diethyl ether = 1:1); isolated as a mixture with 1l'. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 1.13 (t, 3H, $J = 6.4$ Hz), 2.57 (m, 2H), 2.98 (dd, 1H, $J = 17.6$ Hz, $J = 6.4$ Hz), 3.21 (dd, 1H, $J = 17.6$ Hz, $J = 6.4$ Hz), 6.11 (t, 1H, $J = 6.4$ Hz), 7.61 (m, 2H), 7.85 (m, 2H), 7.92 (m, 1H). $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 7.5, 36.9, 47.6, 77.0, 121.4, 123.5, 126.8, 127.1, 128.4, 129.1, 129.9, 132.1, 135.9, 143.1, 170.0, 207.5. HRMS (ESI): $m/z$ calcd for C$_{16}$H$_{14}$NaO$_3$ [M + Na]$^+$ 277.0835, found 277.0834.
3-(2-Oxobutyl)naphtho[1,2-c]furan-1(3H)-one (1l’)

White solid (1l + 1l’ combined yield 53 mg, 69%); prepared following the general procedure from β-naphthoic acid (51.7 mg, 0.3 mmol) and ethyl vinyl ketone (61.6 µL, 0.6 mmol); purified by PTLC (hexane/diethyl ether = 1.5:2); mp = 109–111 °C. 1H NMR (CDCl₃, 400 MHz):  δ 1.14 (t, 3H, J = 7.2 Hz), 2.54 (dq, 1H, J = 18.0 Hz, J = 7.2 Hz), 2.62 (dq, 1H, J = 18.0 Hz, J = 7.2 Hz), 2.89 (dd, 1H, J = 16.8 Hz, J = 9.2 Hz), 3.28 (dd, 1H, J = 16.8 Hz, J = 2.4 Hz), 6.39 (dd, 1H, J = 9.2 Hz, J = 2.4 Hz), 7.65-7.72 (m, 2H), 7.83-7.86 (m, 2H), 7.98 (d, 1H, J = 8.4 Hz), 8.04 (d, 1H, J = 7.6 Hz). 13C NMR (CDCl₃, 75 MHz):  δ 7.5, 27.2, 36.8, 46.5, 77.2, 122.2, 126.2, 129.4, 129.5, 141.8, 149.7, 169.0, 197.0, 206.9. IR (KBr): ν 3060, 2977, 1757, 1717, 1459, 1328, 1052. HRMS (ESI): m/z calcd for C₁₆H₁₄NaO₃ [M + Na]+ 277.0835, found 277.0828.

5-Acetyl-3-(2-oxobutyl)isobenzofuran-1(3H)-one (1m)

White solid (12 mg, 16% yield); prepared following the general procedure from 4-acetylbenzoic acid (54.6 mg, 0.3 mmol) and ethyl vinyl ketone (61.6 µL, 0.6 mmol); purified by PTLC (dichloromethane/ethyl acetate = 58:2); mp = 154–155 °C. 1H NMR (CDCl₃, 400 MHz):  δ 1.12 (t, 3H, J = 7.2 Hz), 2.50 (dq, 1H, J = 18.4 Hz, J = 7.2 Hz), 2.58 (dq, 1H, J = 18.4 Hz, J = 7.2 Hz), 2.68 (s, 3H), 2.95 (dd, 1H, J = 17.6 Hz, J = 6.0 Hz), 3.15 (dd, 1H, J = 17.6 Hz, J = 6.8 Hz), 6.01 (t, 1H, J = 6.4 Hz), 7.99 (d, 1H, J = 10.0 Hz), 8.04 (s, 1H), 8.11 (d, 1H, J = 10.0 Hz). 13C NMR (CDCl₃, 75 MHz):  δ 7.5, 27.2, 36.8, 46.5, 77.2, 122.2, 126.2, 129.4, 129.5, 141.8, 149.7, 169.0, 197.0, 206.9. IR (KBr): ν 2976, 1766, 1715, 1690, 1422, 1362, 1277, 1207, 1056. HRMS (ESI): m/z calcd for C₁₄H₁₄NaO₄ [M + Na]+ 269.0784, found 269.0782.
6-Methoxy-3-(2-oxobutyl)isobenzofuran-1(3H)-one (1n)

White solid (24 mg, 34% yield); prepared following the general procedure from 3-methoxybenzoic acid (46.2 mg, 0.3 mmol) and ethyl vinyl ketone (61.6 µL, 0.6 mmol); purified by PTLC (hexane/ethyl acetate = 85:15); mp = 63–64 °C. 1H NMR (CDCl₃, 500 MHz): δ 1.10 (t, 3H, J = 7.5 Hz), 2.48 (dq, 1H, J = 18.0 Hz, J = 7.5 Hz), 2.56 (dq, 1H, J = 18.0 Hz, J = 7.5 Hz), 2.83 (dd, 1H, J = 17.0 Hz, J = 6.5 Hz), 3.09 (dd, 1H, J = 17.0 Hz, J = 6.5 Hz), 3.86 (s, 3H), 5.89 (t, 1H, J = 6.5 Hz), 7.21 (dd, 1H, J = 8.5 Hz, J = 2.5 Hz), 7.32 (d, 1H, J = 2.5 Hz), 7.35 (dd, 1H, J = 8.5 Hz, J = 0.5 Hz). 13C NMR (CDCl₃, 75 MHz): δ 7.5, 36.9, 47.1, 55.8, 76.9, 107.5, 123.2, 123.3, 127.2, 141.9, 160.8, 170.0, 207.5. IR (KBr): ν 2944, 2856, 1765, 1483, 1423, 1344, 1302, 1145. HRMS (ESI): m/z calcd for C₁₃H₁₄NaO₄ [M + Na]⁺ 257.0784, found 257.0780.

4-Methoxy-3-(2-oxobutyl)isobenzofuran-1(3H)-one (1n’)

White solid (28 mg, 40% yield); prepared following the general procedure from 3-methoxybenzoic acid (46.2 mg, 0.3 mmol) and ethyl vinyl ketone (61.6 µL, 0.6 mmol); purified by PTLC (hexane/ethyl acetate = 58:2); mp = 94–95 °C. 1H NMR (CDCl₃, 500 MHz): δ 1.09 (t, 3H, J = 7.0 Hz), 2.52 (q, 2H, J = 7.0 Hz), 2.71 (dd, 1H, J = 16.5 Hz, J = 9.5 Hz), 3.28 (dd, 1H, J = 16.5 Hz, J = 3.0 Hz), 3.89 (s, 3H), 5.96 (dd, 1H, J = 9.5 Hz, J = 3.0 Hz), 7.10 (dd, 1H, J = 7.0 Hz, J = 1.5 Hz), 7.46-7.49 (m, 2H). 13C NMR (CDCl₃, 75 MHz): δ 7.4, 36.9, 44.8, 55.6, 76.0, 115.0, 117.4, 127.8, 131.2, 136.8, 154.1, 170.0, 206.8. IR (KBr): ν 2980, 1771, 1717, 1611, 1493, 1316, 1275. HRMS (ESI): m/z calcd for C₁₃H₁₄NaO₄ [M + Na]⁺ 257.0784, found 257.0777.
4,5,6-Trimethoxy-3-(2-oxobutyl)-7-(3-oxopentyl)isobenzofuran-1(3H)-one (2)

White solid (27 mg, 8% yield); prepared from 3,4,5-trimethoxybenzoic acid (63.6 mg, 0.3 mmol) and ethyl vinyl ketone (61.6 μL, 0.6 mmol) following the general procedure but using [Cp*RhCl₂]₂ (14.82 mg, 0.024 mmol, 0.08 equiv), AgOTf (30.9 mg, 0.12 mmol, 0.40 equiv), and Ag₂CO₃ (111.0 mg, 0.6 mmol, 2.0 equiv), in dioxane under argon, in the absence of DCPD; purified by PTLC (dichloromethane/ethyl acetate = 58:2); mp = 108–109 °C. ¹H NMR (CDCl₃, 300 MHz): δ 1.06 (t, 3H, J = 6.0 Hz), 1.10 (t, 3H, J = 6.0 Hz), 2.47 (q, 2H, J = 7.2 Hz), 2.53 (q, 2H, J = 7.2 Hz), 2.67 (dd, 1H, J = 9.6 Hz, J = 6.9 Hz), 2.74 (dd, 1H, J = 16.5 Hz, J = 9.0 Hz), 3.16 (dd, 1H, J = 16.5 Hz, J = 3.0 Hz), 3.25 (dd, 1H, J = 9.0 Hz, J = 6.9 Hz), 3.85 (s, 3H), 3.91 (s, 3H), 3.95 (s, 1H), 5.86 (dd, 1H, J = 9.0 Hz, J = 3.0 Hz). ¹³C NMR (CDCl₃, 75 MHz): δ 7.4, 7.8, 19.1, 35.6, 37.0, 42.6, 45.4, 60.9, 61.3, 74.5, 77.2, 118.6, 131.5, 137.4, 145.7, 151.0, 153.6, 169.2, 206.8, 210.5. IR (KBr): ν 2976, 1758, 1716, 1482, 1348, 1115, 1017. HRMS (ESI): m/z calcd for C₂₀H₂₇O₇ [M + H]⁺ 379.17513, found 379.17483.

N,N-Dimethyl-2-(5,6,7-trimethoxy-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetamide (3)

White solid (32 mg, 34% yield); prepared following the general procedure from 3,4,5-trimethoxybenzoic acid (63.6 mg, 0.3 mmol) and N,N-dimethylacrylamide (62.1 μL, 0.6 mmol); purified by flash chromatography (hexane/diethyl ether = 1:1); mp = 122–123 °C. ¹H NMR (CDCl₃, 400 MHz): δ 2.65 (dd, 1H, J = 16.0 Hz, J = 9.2 Hz), 3.00 (s, 6H), 3.12 (dd, 1H, J = 16.0 Hz, J = 1.6 Hz), 3.90 (s, 3H), 3.93 (s, 3H), 3.98 (s, 3H), 6.02 (dd, 1H, J = 9.2 Hz, J = 1.6 Hz), 7.11 (s, 1H). ¹³C NMR (CDCl₃, 75 MHz): δ 35.7, 37.1, 37.4, 56.4, 60.9, 61.2, 76.7, 102.6, 121.3, 134.5, 146.8, 147.5, 155.8, 168.6, 169.9. IR (KBr): ν 2948, 2835, 1762, 1480, 1420, 1344. HRMS (ESI): m/z calcd for C₁₅H₁₉KNO₆ [M + K]⁺ 348.0844, found 348.0841.
Methyl 2-(5,6,7-trimethoxy-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (4a)

White solid (59 mg, 66% yield); prepared following the general procedure from 3,4,5-trimethoxybenzoic acid (63.6 mg, 0.3 mmol) and methyl acrylate (54.0 µL, 0.6 mmol); purified by flash chromatography (hexane/diethyl ether = 1:1); mp = 76–77 °C. \( ^1H \) NMR (CDCl\(_3\), 500 MHz): \( \delta \) 2.64 (dd, 1H, \( J = 16.5 \) Hz, \( J = 9.0 \) Hz), 3.20 (dd, 1H, \( J = 16.5 \) Hz, \( J = 3.5 \) Hz), 3.73 (s, 3H), 3.91 (s, 3H), 3.93 (s, 3H), 3.99 (s, 1H), 5.83 (dd, 1H, \( J = 9.0 \) Hz, \( J = 3.5 \) Hz), 7.12 (s, 1H). \( ^{13}C \) NMR (CDCl\(_3\), 125 MHz): \( \delta \) 38.3, 52.2, 56.4, 60.9, 61.2, 75.7, 102.6, 121.2, 133.6, 146.7, 147.4, 156.0, 169.7, 169.8. IR (KBr): \( \nu \) 2950, 2839, 1760, 1718, 1457, 1436. HRMS (ESI): \( m/z \) calcd for C\(_{14}\)H\(_{17}\)O\(_7\) [M + H]\(^+\) 297.09688, found 297.09678.

\((E)-\)Methyl 3-(5,6,7-trimethoxy-1-(2-methoxy-2-oxoethyl)-3-oxo-1,3-dihydroisobenzofuran-4-yl)acrylate (4b)

White solid (23 mg, 20% yield); prepared following the general procedure from 3,4,5-trimethoxybenzoic acid (63.6 mg, 0.3 mmol) and vinyl acrylate (54.0 µL, 0.6 mmol); purified by flash chromatography (hexane/diethyl ether = 1:1); mp = 161–162 °C. \( ^1H \) NMR (CDCl\(_3\), 400 MHz): \( \delta \) 2.63 (dd, 1H, \( J = 16.4 \) Hz, \( J = 8.8 \) Hz), 3.21 (dd, 1H, \( J = 16.4 \) Hz, \( J = 3.6 \) Hz), 3.74 (s, 3H), 3.82 (s, 3H), 3.88 (s, 3H), 3.97 (s, 3H), 4.03 (s, 3H), 5.78 (dd, 1H, \( J = 8.8 \) Hz, \( J = 3.6 \) Hz), 7.02 (d, 1H, \( J = 16.4 \) Hz), 8.51 (d, 1H, \( J = 16.4 \) Hz). \( ^{13}C \) NMR (CDCl\(_3\), 125 MHz): \( \delta \) 38.1, 51.8, 52.2, 60.5, 61.0, 61.2, 74.5, 119.4, 123.4, 124.5, 133.9, 137.0, 148.1, 150.5, 156.0, 167.8, 168.4, 169.7. IR (KBr): \( \nu \) 2952, 2843, 1761, 1718, 1457, 1436. HRMS (ESI): \( m/z \) calcd for C\(_{18}\)H\(_{20}\)O\(_9\) [M + Na]\(^+\) 403.1000, found 403.0995.
4,5,6-Trimethoxy-3-((phenylsulfonyl)methyl)isobenzofuran-1(3H)-one (5a)
White solid (27 mg, 24% yield); prepared following the general procedure from 3,4,5-
trimethoxybenzoic acid (63.6 mg, 0.3 mmol) and phenyl vinyl sulfone (102 mg, 0.6 mmol); purified by
flash chromatography (hexane/diethyl ether = 1:1); mp = 161–162 °C. ¹H NMR (CDCl₃, 400 MHz):
δ 3.37 (dd, 1H, J = 15.2 Hz, J = 9.2 Hz), 3.89 (s, 3H), 3.91 (s, 3H), 4.01 (s, 3H), 4.03 (dd, 1H, J = 15.2
Hz, J = 2.0 Hz), 5.84 (dd, 1H, J = 9.2 Hz, J = 2.0 Hz), 7.05 (s, 1H), 7.59 (m, 2H), 7.69 (m, 1H), 7.97
(d, 1H, J = 8.0 Hz). ¹³C NMR (CDCl₃, 75 MHz): δ 56.5, 59.0, 61.0, 61.3, 73.6, 102.5, 120.8, 128.4,
129.3, 131.6, 134.2, 139.4, 146.6, 147.3, 156.6, 168.8. IR (KBr): ν 2992, 2847, 1772, 1615, 1480,
1422, 1343, 1143, 1107, 1060. HRMS (ESI): m/z calcd for C₁₈H₁₈O₇S [M + Na]⁺ 401.0665, found
401.0662.

(E)-4,5,6-Trimethoxy-3-((phenylsulfonyl)methyl)-7-(2-(phenylsulfonyl)vinyl)isobenzofuran-
1(3H)-one (5b)
White solid (80 mg, 49% yield); prepared following the general procedure from 3,4,5-
trimethoxybenzoic acid (63.6 mg, 0.3 mmol) and phenyl vinyl sulfone (102 mg, 0.6 mmol); purified by
flash chromatography (hexane/diethyl ether = 1:1); mp = 80–81 °C. ¹H NMR (CDCl₃, 400 MHz):
δ 3.39 (dd, 1H, J = 14.8 Hz, J = 9.2 Hz), 3.85 (s, 3H), 3.91 (s, 3H), 4.00 (dd, 1H, J = 14.8 Hz, J = 2.0
Hz), 4.07 (s, 3H), 5.78 (dd, 1H, J = 9.2 Hz, J = 2.0 Hz), 7.55 (m, 7H), 7.68 (m, 1H), 7.92 (m, 4H), 8.34
(d, 1H, J = 16.0 Hz). ¹³C NMR (CDCl₃, 125 MHz): δ 58.4, 60.8, 61.2, 61.4, 72.7, 119.3, 120.9, 127.8,
128.3, 129.3, 131.2, 133.3, 133.8, 134.3, 135.0, 139.3, 140.5, 148.9, 150.0, 156.7, 167.2. IR
(KBr): ν 3065, 2944, 2851, 1764, 1483, 1447, 1344, 1307, 1145, 1085. HRMS (ESI): m/z calcd for
C₂₆H₂₄KO₉S₂ [M + K]⁺ 583.0493, found 583.0490.
(E)-3-((Ethylsulfonyl)methyl)-7-(2-(ethylsulfonyl)vinyl)-4,5,6-trimethoxyisobenzofuran-1(3H)-one (6)

White solid (113 mg, 84% yield); prepared following the general procedure from 3,4,5-trimethoxybenzoic acid (63.6 mg, 0.3 mmol) and ethyl vinyl sulfone (20.9 µL, 0.6 mmol); purified by recrystallisation (hexane/diethyl ether = 2:1); mp = 147–148 °C.  

1H NMR (CDCl₃, 400 MHz): δ 1.40 (t, 3H, J = 7.6 Hz), 1.44 (t, 3H, J = 7.6 Hz), 3.10 (q, 2H, J = 7.6 Hz), 3.21 (dd, 1H, J = 15.6 Hz, J = 10.0 Hz), 3.28 (q, 2H, J = 7.6 Hz), 3.77 (dd, 1H, J = 15.6 Hz, J = 1.6 Hz), 3.93 (s, 3H), 3.97 (s, 3H), 4.12 (s, 3H), 5.84 (d, 1H, J = 10.0 Hz, J = 1.6 Hz), 7.53 (d, 1H, J = 16.0 Hz), 8.27 (d, 1H, J = 16.0 Hz).

13C NMR (CDCl₃, 125 MHz): δ 6.4, 7.2, 49.2, 49.3, 54.7, 61.0, 61.3, 61.4, 73.2, 118.8, 121.1, 131.0, 133.2, 135.2, 149.0, 150.3, 156.8, 167.4. IR (KBr): ν 2984, 1764, 1603, 1483, 1458, 1344, 1305. HRMS (ESI): m/z calcd for C₁₈H₂₄NaO₉S₂ [M + Na]⁺ 471.0754, found 471.0746.

4. Preparation of 7

A solution of NaNO₂ (266 mg, 2.16 mmol, 1.01 equiv) in water (3 mL) was added dropwise to an ice-cold suspension of 2-amino-3,4,5-trimethoxybenzoic acid (500 mg, 2.13 mmol, 1.00 equiv) in 48% aqueous HBF₄ (864 µL, 5.40 mmol) under stirring. Stirring was continued at 0 °C for 1 h. After this time, methanol (4 mL), methyl acrylate (262 mL, 2.92 mmol, 1.37 equiv), and Pd(OAc)₂ (9.6 mg, 42.8 µmol, 0.02 equiv) were added to the mixture at 0 °C. Mixture was let warm up to room temperature, then heated under reflux (70 °C) for 2 h. After this time, the mixture was cooled down to room temperature, and the solvent removed under vacuum. Et₂O (10 mL) was added to the residue, and the resulting solution was extracted with H₂O (3 x 2 mL). The organic layer was dried over MgSO₄ and concentrated at reduced pressure. Purification of the crude mixture by column chromatography on silica gel (eluent: hexane/ethyl acetate = 75/15) afforded methyl 2-carboxy-3,4,5-trimethoxyphenylcinnamate 7 as a white solid (181 mg, 0.61 mmol, 29% yield). Compounds 4a (261
mg, 0.88 mmol, 41% yield) and \(4b\) (14 mg, 36.8 \(\mu\)mol, 2% yield) were also recovered. mp = 147–149 °C. \(^1\)H NMR [(CD\(_3\)]2CO, 400 MHz]: \(\delta\) 3.73 (s, 3H), 3.84 (s, 3H), 3.90 (s, 3H), 3.95 (s, 3H), 6.55 (d, 1H, \(J = 6.0\) Hz), 7.34 (s, 1H), 8.13 (d, 1H, \(J = 16.0\) Hz). \(^{13}\)C NMR [(CD\(_3\)]2CO, 100 MHz]: \(\delta\) 51.2, 56.0, 60.5, 60.6, 110.3, 121.9, 122.6, 128.3, 139.5, 145.9, 153.8, 154.4, 167.8, 168.0. IR (KBr): \(\nu\) 2952, 1698, 1682, 1583, 1490, 1325, 1125. Anal. calcd. for C\(_{14}\)H\(_{16}\)O\(_7\): C 56.60; H 5.44; found: C 56.76; H 5.44.

5. Conversion of 7 into 4a

A mixture of \([(COD)RhCl]_2\) (3.94 mg, 0.008 mmol, 8 mol%) and AgOTf (6.18 mg, 0.024 mmol, 24 mol%) in chlorobenzene (200 \(\mu\)L) was stirred in a glass tube at room temperature for 30 minutes. Dicyclopentadiene (4.3 \(\mu\)L, 0.032 mmol, 32 mol%) was added. Mixture turned instantaneously from light yellow to dark orange. Then, 7 (30 mg, 0.10 mmol, 1.0 equiv), Cu(OAc)\(_2\)·H\(_2\)O (79.7 mg, 0.40 mmol, 4.0 equiv), and chlorobenzene (300 \(\mu\)L) were added. The tube was sealed and heated at 120 °C for 48 hours. After this time the reaction mixture was quenched with 28% NH\(_4\)OH (2 mL) and extracted with ethyl acetate (3 x 2 mL). The organic layers were combined and filtered through a short pad of silica gel. The filtrate was concentrated under reduced pressure to afford \(4a\) as a white solid (27 mg, 0.091 mmol, 91% yield).

6. Conversion of 7 into 4a and 4b

A mixture of \([(COD)RhCl]_2\) (4.73 mg, 9.6 \(\mu\)mol, 8 mol%) and AgOTf (7.42 mg, 28.8 \(\mu\)mol, 24 mol%) in chlorobenzene (240 \(\mu\)L) was stirred in a glass tube at room temperature for 30 minutes. Dicyclopentadiene (5.2 \(\mu\)L, 38.4 \(\mu\)mol, 32 mol%) was added. Mixture turned instantaneously from light yellow to dark orange. Then, 7 (35 mg, 0.12 mmol, 1.0 equiv), Cu(OAc)\(_2\)·H\(_2\)O (93.9 mg, 0.47
mmol, 4.0 equiv), methyl acrylate (10.8 μL, 0.12 mmol, 1.0 equiv) and chlorobenzene (360 μL) were added. The tube was sealed and heated at 120 °C for 48 hours. After this time the reaction mixture was quenched with 28% NH₄OH (2 mL) and extracted with ethyl acetate (3 x 2 mL). The organic layers were combined and filtered through a short pad of silica gel. The filtrate was concentrated under reduced pressure. Purification of the crude mixture by column chromatography on silica gel (eluent: hexane/diethyl ether = 7/3) afforded 4a (14 mg, 0.048 mmol, 35% yield) and 4b (30 mg, 0.080 mmol, 65% yield) as white solids.
7. X-ray crystal structure determination of (COD)$_2$RhOTf

Figure S1 Molecular structure of (COD)$_2$RhOTf with displacement ellipsoids drawn at 50% probability for non-H atoms.

[(COD)RhCl]$_2$ (200 mg, 0.40 mmol, 1.0 equiv) was dissolved in acetone (15 mL) under nitrogen. Solution was orange. AgOTf (208 mg, 0.81 mmol, 2.0 equiv) was added to this solution. The addition resulted in the immediate formation of a white precipitate and in a color change of solution from orange to pale yellow. After 5 min stirring, (endo)-dicyclopentadiene (114.5 μL, 0.81 mmol, 2.0 equiv) was added. Solution color instantaneously turned dark red. After 30 min of additional stirring at room temperature, the mixture was filtered by cannula under nitrogen. Filtrate was dried under vacuum leaving a red solid residue. Single crystals were grown from Me$_2$CO/Et$_2$O (15 mL, 1/20 [v/v]) at −18 °C. The single crystal was mounted in a glass capillary. Data for (COD)$_2$RhOTf were collected at −70 °C on a Rigaku/MSC Mercury CCD area-detector diffractometer equipped with monochromated MoKα radiation. Calculations for (COD)$_2$RhOTf were performed with the teXane crystallographic software package of Molecular Structure Corporation. X-ray analysis of (COD)$_2$RhOTf was consistent with that reported in the literature.$^2$
Table S1  Crystal data and structure refinement for (COD)$_2$RhOTf.

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Table S2  Selected bond lengths [Å] and angles [°] for (COD)$_2$RhOTf.

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<td>110.1(5)</td>
</tr>
<tr>
<td>O(3)-S(1)-C(17)</td>
<td>105.2(6)</td>
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<td>O(2)-S(1)-C(17)</td>
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<td>F(2)-C(17)-S(1)</td>
<td>110.7(9)</td>
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8. References


9. NMR spectra of products

![NMR spectrum of product 1a](image)

CDCl₃, 300 MHz
1b

CDCl₃, 75 MHz
\[ \text{CDCl}_3, 400 \text{ MHz} \]
CDCl₃, 400 MHz
H3C

CDCl3, 75 MHz
CDCl₃, 400 MHz
$^{13}C$ NMR spectrum of compound 1g in CDCl$_3$, 100 MHz

Chemical shifts (ppm):
- 207.273
- 170.048
- 149.431
- 134.252
- 129.382
- 125.724
- 122.273
- 77.334
- 77.016
- 36.912
- 36.638
- 36.793
- 36.852
- 74.500

Structural formula:

\[
\begin{align*}
\text{O} & \\
& \\
\text{O} & \\
\text{CDCl}_3, 100 \text{ MHz}
\end{align*}
\]
$^{13}C$ NMR spectrum of compound 1i in CDCl$_3$, 125 MHz.
$^{1}H$ (ppm)
$^1$H NMR (CDCl$_3$, 400 MHz, ppm): 8.46, 7.85, 7.83, 7.77, 7.66, 7.26, 6.12, 4.11, 3.24, 3.22, 3.01, 2.96, 1.15, 1.13, 1.11, 1.04, 0.93, 0.87, 0.82, 0.60, 0.54, 0.43, 0.31, 0.25, 0.20, 0.15, 0.10, 0.05, 0.00.

1H + 11'
CDCl₃, 125 MHz
CDCl₃, 75 MHz
$f_1$ (ppm)
CDCl₃, 500 MHz
$^{13}C$ NMR spectrum of $1n'$

CDCl$_3$, 75 MHz

---

The diagram shows the NMR spectrum of the compound $1n'$ in CDCl$_3$ at 75 MHz. The spectrum contains peaks at various ppm values, indicating the chemical shifts of different carbon atoms in the molecule.
CDCl₃, 300 MHz
CDCl₃, 75 MHz
CDCl₃, 400 MHz

3

H₃C
H₃C

OCH₃

H₂CO

H₂CO
H₃CO

OCH₃

H₃CO

O

CDCl₃, 75 MHz
CDCl$_3$, 125 MHz
CDCl₃, 125 MHz
$^{1}H$ NMR (CDCl$_3$, 400 MHz)

5a
$^{13}C$ NMR spectrum of compound 5a in CDCl$_3$, 75 MHz.

Key peaks:
- 168.79 ppm
- 156.55 ppm
- 147.34 ppm
- 146.65 ppm
- 139.40 ppm
- 131.55 ppm
- 128.43 ppm
- 120.77 ppm
- 102.51 ppm
- 77.44 ppm
- 76.09 ppm
- 73.81 ppm
- 61.27 ppm
- 61.03 ppm
- 58.80 ppm
- 56.50 ppm

 resonance assignments:
- 134.17 ppm
- 131.55 ppm
- 129.28 ppm
- 128.43 ppm
$\text{CDC}_3$, 400 MHz
$\text{S-63}$

$\text{CDCl}_3$, 125 MHz

$5b$
7

(CD$_3$)$_2$CO, 100 MHz
10. HRMS spectra of products
Mass Spectrum SmartFormula Report

Analysis Info
Analysis Name: D:\Data\Li\2012-12-17-Li-Renzetti AR-276-A +ve DIP.d
Method: APCI_Tune_pos_Mid_AW2.m
Sample Name: Testing DIP test 22012-12-17-Li-Renzetti AR-276-A +ve D
Comment

Acquisition Date: 12/18/2012 2:25:21 PM
Operator: ADM
Instrument: maXis impact 282001.00044

Acquisition Parameter
Source Type: APCI
Focus: Active
Scan Begin: 100 m/z
Scan End: 3000 m/z
Ion Polarity: Positive
Set Capillary: 4000 V
Set End Plate Offset: -500 V
Set Collision Cell RF: 1000.0 Vpp
Set Nebulizer: 5.0 Bar
Set Dry Heater: 150 °C
Set Dry Gas: 1.0 l/min
Set Divert Valve: Source

---

![Mass Spectrum](image)

**Meas. m/z** | **Ion Formula** | **m/z** | **err (ppm)** | **mSigma** | **Score** | **rtb** | **e-Conf** | **N-Rule**
--- | --- | --- | --- | --- | --- | --- | --- | ---
295.1165 | O15H13O6 | 295.1176 | 3.9 | 20.4 | 1 | 100.00 | 6.5 | even | ok

---

**1b**

---

Bruker Compass DataAnalysis 4.1 printed: 12/18/2012 2:32:04 PM by: ADM Page 1 of 1
Mass Spectrum SmartFormula Report

Acquisition Info
Analysis Name  D:\Data\Li/2012-12-17-Li-Renzetti AR-327 +ve.d
Method         Tune_pos_low_AW_NaFormate_cal.m
Sample Name    2012-12-17-Li-Renzetti AR-327 +ve
Comment

Acquisition Parameter
Source Type    ESI
Focus          Active
Scan Begin     50 m/z
Scan End       3000 m/z
Ion Polarity   Positive
Set Capillary  -3000 V
Set End Plate Offset  -500 V
Set Collision Cell RF  600.0 Vpp
Set Nebulizer  1.0 Bar
Set Dry Heater  200 °C
Set Dry Gas    4.0 l/min
Set Divert Valve  Source

[Mass spectrum graph with peaks at m/z 241.0834 and 366.1357]

Meas. m/z  241.0834  241.0836  241.0838
Ion Formula C13H14NaO3  C13H14O3  C13H14O
m/z error [ppm]  0.5  10.3  150.00
mSigma  5.5
e-score  even  ok

PhH2CO

PhH2CO

OCH2Ph

1e

Bruker Compass DataAnalysis 4.1
printed:  12/19/2012 11:46:20 AM  by: ADM
Page 1 of 1
### Mass Spectrum SmartFormula Report

**Analysis Info**
- **Analysis Name:** D:Data/L2013-08-06-L-Remazeri AR-440-CH-1 ESI +ve,d
- **Method:** Tune/resL Low_Ma_Formula_1DB-1000.m
- **Sample Name:** 2013-08-06-L-Remazeri AR-440-CH-1 ESI +ve
- **Comment:**

**Acquisition Parameter**
- **Source Type:** ESI
- **Ion Pulse:** 0.1 s
- **Pass:** 0.1 s
- **Polarity:** Positive
- **Gas Chromatography:** 5 kW
- **Gain:** 350 V
- **Jet Heater:** 100 °C
- **Jet Gas:** 40 mm
- **Jet Gas Flow:** 0.1 L/min
- **Jet Gas Source:** 99.9999%

**Data**

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<tr>
<td>595</td>
<td>697,0812</td>
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<tr>
<td>720</td>
<td>294</td>
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</tbody>
</table>

**Mol.**

<table>
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<th>Intensity</th>
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</thead>
<tbody>
<tr>
<td>270</td>
<td>277,0041</td>
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</tbody>
</table>

**Formula**

![Chemical Structure](image)

**1f**
Mass Spectrum SmartFormula Report

Analysis Info
Analysis Name: D:\Data\LI\2012-12-17-Li-Renzetti AR-325-A +ve.d
Method: Tune_pos_low_AW_NaFormate_cal.m
Sample Name: 2012-12-17-Li-Renzetti AR-325-A +ve
Comment:

Acquisition Date: 12/18/2012 4:44:33 PM
Operator: ADM
Instrument: maXis impact 282001.00044

Acquisition Parameter
Source Type: ESI
Focus: Active
Scan Begin: 50 m/z
Scan End: 3000 m/z
Ion Polarity: Positive
Set Capillary: 3000 V
Set End Plate Offset: -500 V
Set Collision Cell RF: 600.0 Vpp
Set Nebulizer: 1.0 Bar
Set Dry Heater: 200 °C
Set Dry Gas: 4.0 l/min
Set Divert Valve: Source

Meas. m/z | # | Ion Formula | m/z | err [ppm] | mSigma | Score | rdb | e-Conf | N-Rule
--- | --- | --- | --- | --- | --- | --- | --- | --- | ---
227.0884 | 1 | C12H12NaO3 | 227.0879 | -2.2 | 7.6 | 100.00 | 6.5 | even | ok

Bruker Compass DataAnalysis 4.1 printed: 12/19/2012 12:20:16 PM by: ADM Page 1 of 1
Mass Spectrum SmartFormula Report

Analysis Info
Analysis Name: D:\Data\12013-04-29-Li-Renzetti-AR-378-A ESI +ve.d
Method: Tune_pos_Low_Na_Formate_100-1000.m
Sample Name: 2013-04-29-Li-Renzetti-AR-378-A ESI +ve
Comment

Acquisition Date: 4/20/2013 3:35:54 PM
Operator: ADM
Instrument: maXis impact 282001.00044

Acquisition Parameter
Source Type: ESI
Focus: Active
Scan Begin: 100 m/z
Scan End: 1000 m/z

Ion Polarity: Positive
Set Capillary: 4500 V
Set End Plate Offset: 500 V
Set Collision Cell RF: 600.0 Vpp
Set Nebulizer: 0.3 Bar
Set Dry Heater: 180 °C
Set Dry Gas: 4.0 l/min
Set Divert Valve: Source

Bruker Compass DataAnalysis 4.1
printed: 4/29/2013 3:37:34 PM by: ADM
Page 1 of 1
Mass Spectrum SmartFormula Report

Analysis Info
Analysis Name: D:\Data\Li\2013-04-29-Li-Renzetti-AR-377-ALL-A ESI +ve.d
Method: Tune_pos_Low_Na_Formate_100-1000.m
Sample Name: 2013-04-29-Li-Renzetti-AR-377-ALL-A ESI +ve
Comment: 

Acquisition Date: 4/29/2013 4:05:49 PM
Operator: ADM
Instrument: maXis impact
Mass spec: 282001.00044

Acquisition Parameter
Source Type: ESI
Focus: Active
Scan Begin: 100 m/z
Scan End: 1000 m/z
Ion Polarity: Positive
Set Nebulizer: 0.3 Bar
Set Capillary: 4500 V
Set End Plate Offset: -500 V
Set Collision Cell RF: 600.0 Vpp
Set Dry Heater: 180 °C
Set Dry Gas: 4.0 l/min
Set Divert Valve: Source

Graph showing mass spectrum with m/z values and corresponding structures.

Bruker Compass DataAnalysis 4.1 printed: 4/29/2013 4:24:47 PM by: ADM Page 1 of 1
Mass Spectrum SmartFormula Report

Analysis Info
Analysis Name: D:\Data\Li2012-12-17-Li-Renzetti AR-323-A +ve.d
Method: Tune_pos_low_AW_NaFormate_cal.m
Sample Name: 2012-12-17-Li-Renzetti AR-323-A +ve
Comment

Acquisition Parameter
Source Type: ESI
Focus: Active
Scan Begin: 50 m/z
Scan End: 3000 m/z

Ion Polarity: Positive
Set Capillary: 3000 V
Set End Plate Offset: -500 V
Set Collision Cell RF: 600.0 Vpp

Set Nebulizer: 1.0 Bar
Set Dry Heater: 200 °C
Set Dry Gas: 4.0 l/min
Set Divert Valve: Source

Intens x10^5

Meas. m/z 245.0574

Ion Formula C2H9F3NNaO3
m/z 245.0580
err 2.7
mSigma 39.4
Score 36.8
rdb -0.5
e- Conf even
N-Rule ok

Ion Formula C7H10F2N3NaO3
m/z 245.0682
err 3.5
mSigma 14.4
Score 100.0
rdb 3.0
e- Conf odd
N-Rule ok

Ion Formula C12H11FNaO3
m/z 245.0594
err 4.3
mSigma 10.7
Score 85.92
rdb 6.5
e- Conf even
N-Rule ok

F

O

1j

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Page 1 of 1
Mass Spectrum SmartFormula Report

Analysis Info
Analysis Name: D:\Data\Li\2012-12-17-Li-Renzetti AR-324-A +ve.d
Method: Tune_pos_low_AW_NaFormate_cal.m
Sample Name: 2012-12-17-Li-Renzetti AR-324A +ve
Comment: 

Acquisition Date: 12/18/2012 11:11:38 AM
Operator: ADM
Instrument: maXis impact 282001.00044

Acquisition Parameter
Source Type: ESI
Focus: Active
Scan Begin: 50 m/z
Scan End: 3000 m/z
Ion Polarity: Positive
Set Capillary: 3000 V
Set End Plate Offset: -500 V
Set Collision Cell RF: 500.0 Vpp
Set Nebulizer: 1.0 Bar
Set Dry Heater: 200 °C
Set Dry Gas: 4.0 l/min
Set Divert Valve: Source

Analysis

[Graph showing mass spectrum with peaks labeled 227.0976, 352.9641, 682.9365, and a chemical structure labeled 1k]

Meas. m/z  #  Ion Formula m/z  err [ppm]  mSigma  Score  rdb  e-  Conf  N-Rule
352.9641 1  C12H11NaO3  352.9645 1.3  4.3  1  100.00  0.5  even  ok

Bruker Compass DataAnalysis 4.1  printed: 12/19/2012 11:50:13 AM  by: ADM  Page 1 of 1
Mass Spectrum SmartFormula Report

Analysis Info
- Analysis Name: D:\Data\Li2013-04-29-Li-Renzetti-AR-332-A-A-A ESI +ve.d
- Method: Tune_pos_Low_Na_Fomrate_100-1000 m
- Comment
- Acquisition Date: 4/29/2013 3:26:25 PM
- Operator: ADM
- Instrument: maXis impact
- Date Impact: 282001.00044

Acquisition Parameter
- Source Type: ESI
- Focus: Active
- Scan Begin: 100 m/z
- Scan End: 1000 m/z
- Ion Polarity: Positive
- Set Capillary: 4500 V
- Set End Plate Offset: -500 V
- Set Collision Cell RF: 600.0 Vpp
- Set Nebulizer: 0.3 Bar
- Set Dry Heater: 180 °C
- Set Dry Gas: 4.0 l/min
- Set Divert Valve: Source

Intens. x 10^5

277.0828
360.3233
591.4950

Intens. x 10^5

277.0828
278.0860
279.0882

Meas. m/z # Ion Formula m/z err [ppm] mSigma # Sigma Score rdb e' Conf N-Rule
1 C16H14NaO3 277.0835 2.7 23.3 1 100.00 9.5 even ok
2 CH10N12NaO4 277.0840 4.5 45.5 2 42.52 2.5 even ok
3 H14N8NaO9 277.0827 -0.3 59.0 3 50.19 -2.5 even ok

11'
Mass Spectrum SmartFormula Report

Analysis Info
Analysis Name: D:\Data\Li\2012-12-17\Li-Renzetti AR-322-A +ve.d
Method: Tune_pos_low_AW_NaFormate_cal.m
Sample Name: 2012-12-17-Li-Renzetti AR-322-A +ve
Comment

Acquisition Info
Acquisition Date: 12/18/2012 11:14:50 AM
Operator: ADM
Instrument: maXis impact 282001.00044

Acquisition Parameter
Source Type: ESI
Focus: Active
Scan Begin: 50 m/z
Scan End: 3000 m/z
Ion Polarity: Positive
Set Capillary: 3000 V
Set End Plate Offset: -500 V
Set Collision Cell RF: 600.0 Vpp
Set Nebulizer: 1.0 Bar
Set Dry Heater: 200 °C
Set Dry Gas: 4.0 l/min
Set Divert Valve: Source

Graph

Chemical Structure

1m

Bruker Compass DataAnalysis 4.1 printed: 12/19/2012 11:53:12 AM by: ADM Page 1 of 1
Mass Spectrum SmartFormula Report

Analysis Info
Analysis Name: D:\Data\Li2013-04-29-Li-Renzetti-AR-400-A-A ESI +ve.d
Method: Tune_pos_Low_Na_Formate_100-1000 m
Sample Name: 2013-04-29-Li-Renzetti-AR-400-A-A ESI +ve
Comment: 

Acquisition Parameter
Source Type: ESI
Ion Polarity: Positive
Set Nebulizer: 0.3 Bar
Focus: Active
Set Capillary: 4500 V
Scan Begin: 100 m/z
Set End Plate Offset: -500 V
Scan End: 1000 m/z
Set Collision Cell RF: 600.0 Vpp
Set Dry Gas: 4.0 l/min
Set Dry Valve: Source

Acquisition Date: 4/29/2013 2:20:36 PM
Operator: ADM
Instrument: maXis impact

Bruker Compass DataAnalysis 4.1
printed: 4/29/2013 2:27:55 PM
by: ADM
### Mass Spectrum SmartFormula Report

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#### Mass Spectrum

![Mass Spectrum Image]

---

#### Formula Analysis

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**Bruker Compass Data Analysis 4.1**

printed: 4/29/2013 4:14:38 PM

by: ADM

Page 1 of 1
Mass Spectrum SmartFormula Report

Analysis Info
Analysis Name: D:\Data\Li\2013-04-29-Li-Renzetti-AR-406-D-A ESI +ve.d
Method: Tune_pos_Low_Na_Formate_100-1000 m
Sample Name: 2013-04-29-Li-Renzetti-AR-406-D-A ESI +ve
Comment

Acquisition Parameter
Source Type: ESI
Focus: Active
Scan Begin: 100 m/z
Scan End: 1000 m/z
Ion Polarity: Positive
Set Capillary: 4500 V
Set End Plate Offset: -500 V
Set Collision Cell RF: 600.0 Vpp
Set Nebulizer: 0.3 Bar
Set Dry Heater: 180 °C
Set Dry Gas: 4.0 l/min
Set Divert Valve: Source

Mass spectrum graph with peaks at 332.1102 and 348.0841 m/z.

Chemical structure image of compound 3 with the following groups: COOH, OCH3, and H3C.