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# Convenient synthesis of α,β-unsaturated γ-butyrolactones and γ-butyrolactams *via* decarboxylative iodination of paraconic acids and β-carboxyl-γ-butyrolactams using 1,3-diiodo-5,5-dimethylhydantoin†

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A convenient synthetic approach to α,β-unsaturated γ-butyrolactones and α,β-unsaturated γ-butyrolactams is developed. The reaction proceeds *via* decarboxylative iodination of paraconic acids and β-carboxyl-γ-butyrolactams, employing 1,3-diiodo-5,5-dimethylhydantoin (DIH) under irradiation, followed by dehydroiodination of β-iodo-γ-butyrolactones and γ-butyrolactams providing good yields of α,β-unsaturated γ-butyrolactones and γ-butyrolactams, which are synthetically useful building blocks in organic synthesis.

## Introduction

Five-membered ring heterocycles are an important class of compounds. In particular, α,β-unsaturated γ-butyrolactones (or butenolides) and α,β-unsaturated γ-butyrolactams are among advanced synthetic intermediates that find major applications in medicinal chemistry and organic synthesis. They have been used in a range of reactions, such as vinylogous additions to electrophiles,[1] conjugate additions,[2] and pericyclic reactions.[3] The ubiquity of α,β-unsaturated γ-butyrolactones and α,β-unsaturated γ-butyrolactams has been highlighted in naturally occurring compounds, for example, rollicosin,[4c] (−)-incrustoporine,[4i] spirofragilide, labdadienolide A, and (+)-erysotramidine that possess important biological properties including antibiotic, antitumor, anti-inflammatory, and anti-HIV activities (Fig. 1).[4] Not surprisingly, the development of efficient synthetic routes for the preparation of α,β-unsaturated γ-butyrolactones and γ-butyrolactams has been an area of long-standing importance to synthetic chemists.[5]

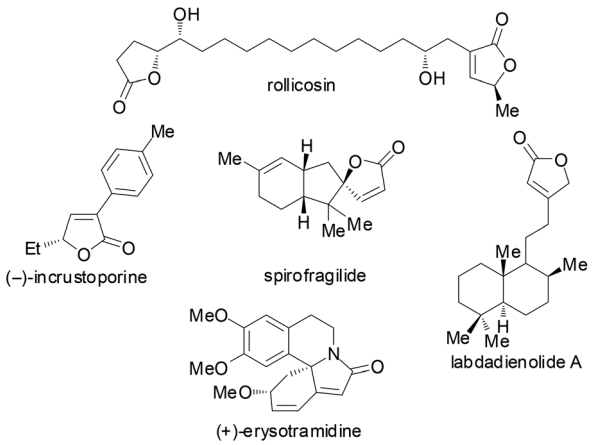


Fig. 1 Natural compounds containing α,β-unsaturated γ-butyrolactone and γ-butyrolactam units.

Among several synthetic routes, the oxidative decarboxylation of aliphatic carboxylic acids is an important and useful conversion to access alkenes. The existing methods usually require $Pb(OAc)_4/Cu(OAc)_2$ for mediating oxidative elimination of the corresponding radical intermediates.[6] Recently, catalytic decarbonylative or decarboxylative elimination of carboxylic acids to yield alkenes has also received much attention.[7] In modern organic synthesis, metal-free reactions which avoid the use of heavy metals have been of particular interest. As a consequence, the conversion of carboxylic acids to alkenes *via* a simple consecutive decarboxylative halogenation (halodecarboxylation)[8] followed by dehydrohalogenation leading to the synthesis of α,β-unsaturated γ-butyrolactones and γ-butyrolactams was investigated. On the basis of our recent report on

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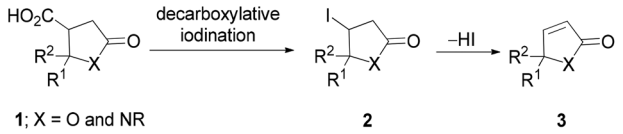
†Electronic supplementary information (ESI) available. See DOI: 10.1039/c5ob01574j



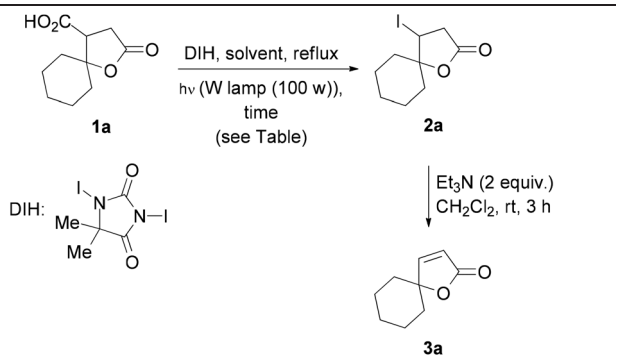

**Scheme 1** Proposed synthetic scheme for the synthesis of α,β-unsaturated γ-butyrolactones and γ-butyrolactams from paraconic acids and β-carboxyl-γ-butyrolactams.

decarboxylative fluorination,[9] it was envisaged that paraconic acids and β-carboxyl-γ-butyrolactams **1** would undergo decarboxylative iodination to give β-iodo-γ-butyrolactones **2** which, after dehydroiodination, would provide α,β-unsaturated γ-butyrolactones and γ-butyrolactams **3** (Scheme 1). Inspired by the work reported by Gandelman and co-workers on decarboxylative iodination, employing commercially available 1,3-diiodo-5,5-dimethylhydantoin (DIH)[10] as an initiator and iodine source,[11] we describe herein a convenient synthetic approach to α,β-unsaturated γ-butyrolactones and γ-butyrolactams *via* decarboxylative iodination of paraconic acids and β-carboxyl-γ-butyrolactams using DIH under irradiative conditions followed by base-promoted dehydroiodination (Scheme 1). Notably, DIH has been extensively explored by Togo and others.[12] However, to the best of our knowledge, the use of DIH for decarboxylative iodination followed by base mediated dehydroiodination has never been reported.

## Results and discussion

Our study commenced with the optimization of reaction conditions using paraconic acid **1a**[13] as the model substrate. A standard screening of solvents, reaction times and the stoichiometry of reagents was performed (Table 1). Under thermal conditions, **1a** was reacted with DIH (1 equiv.) in refluxing $ClCH_2CH_2Cl$ for 8 h to give β-iodo-γ-butyrolactone **2a** together with a trace amount of α,β-unsaturated γ-butyrolactone **3a** as observed by TLC and $^1H$ NMR analyses of the crude mixture (68% conversion based on the recovery of **1a**). Without purification, the crude mixture was treated with $Et_3N$ (2 equiv.) in $CH_2Cl_2$ for 3 h leading to **3a** in 67% yield after chromatographic purification (Table 1, entry 1). We were pleased to observe an improved conversion of **1a** to a mixture of **2a** and **3a** (**2a : 3a**, 1 : 2, 96% conversion based on the recovery of **1a**) when the reaction was carried out in refluxing $ClCH_2CH_2Cl$ under irradiation of a tungsten lamp (100 W) (Table 1, entry 2). Compound **3a** was obtained in 95% yield after treatment of the crude mixture with $Et_3N$. The $Et_3N$-mediated HI elimination was proved necessary since a prolonged reaction time (from 8 h to 13 h) led to the incomplete conversion of **1a** to **3a**; a mixture of **2a** and **3a** was obtained (**2a : 3a**, 1 : 8, 96% conversion based on the recovery of **1a**). Gratifyingly, it was found that decarboxylative-iodination of **1a** with DIH (1 equiv.) in refluxing $ClCH_2CH_2Cl$ under photolysis reached completion after 30 min and gave **2a** in quantitative yield. Subsequent

**Table 1** Optimization of the reaction conditions for the decarboxylative iodination followed by $Et_3N$-promoted dehydroiodination of **1a** [a]




| Entry | DIH (equiv.) | Solvent | Time (h) | % Yield of **3a** [b] |
|---|---|---|---|---|
| 1 [c] | 1 | $ClCH_2CH_2Cl$ | 8 | 67 |
| 2 | 1 | $ClCH_2CH_2Cl$ | 8 | 95 |
| 3 | 1 | $ClCH_2CH_2Cl$ | 0.5 | 92 |
| 4 | 0.5 | $ClCH_2CH_2Cl$ | 1 | 66 |
| 5 | 1 | $CH_2Cl_2$ | 0.5 | 27 |
| 6 | 1 | EtOAc | 0.5 | 15 |
| 7 | 1 | MeCN | 0.5 | 56 |

[a] Unless stated otherwise, the reaction was carried out using **1a** (0.5 mmol) in a refluxing solvent (2 mL) under irradiation with a 100 W tungsten lamp. [b] Yield of analytically pure **3a** after column chromatography ($SiO_2$). [c] The reaction was carried out at reflux without irradiation.

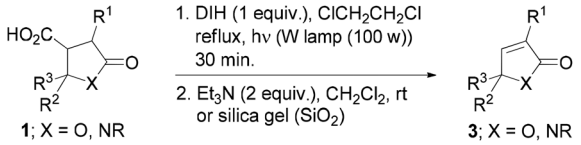
treatment of the crude product with $Et_3N$ cleanly provided **3a** in 92% isolated yield (Table 1, entry 3). The yield was drastically lower when DIH was employed in a lesser amount (0.5 equiv.) (Table 1, entry 4). Finally, other simple organic solvents including $CH_2Cl_2$, EtOAc and MeCN were screened and $ClCH_2CH_2Cl$ was proved to be the optimal solvent (Table 1, entry 3 *vs.* entries 5–7). At this stage, the optimal reaction conditions for decarboxylative iodination followed by base-promoted dehydroiodination of paraconic acids **1** were established (Table 1, entry 3).[14]

With the optimized reaction conditions in hand, we next examined the substrate scope and the results are summarized in Table 2. In general, the reactions of paraconic acids **1a–1m**, containing mono- and dialkyl groups at the γ-position, smoothly underwent DIH-mediated decarboxylative iodination to yield the corresponding β-iodo-γ-butyrolactones **2a–2m**. Following $Et_3N$ promoted HI elimination of the primarily formed β-iodo-γ-butyrolactones **2a–2m** yielded their corresponding α,β-unsaturated γ-butyrolactones **3a–3m** in good yields (81–92% yields) (Table 2, entries 1–13). Among these, the trifluoromethylated butenolide analogue[15] **3k** could also be synthesized (82% yield) (Table 2, entry 11).

For paraconic acid **1n**, bearing a phenyl substituent at the γ-position, treatment of its β-iodo-γ-butyrolactone **2n** with $Et_3N$ according to the standard procedure led to a complex mixture of unidentified products and no trace of **3n** could be detected. These observed results may result from the polymerization of product **3n** under basic conditions. Fortunately, it was found

**Table 2** Synthesis of α,β-unsaturated γ-butyrolactones and γ-butyrolactams *via* DIH-mediated decarboxylative iodination followed by dehydroiodination of paraconic acids and β-carboxyl-γ-butyrolactams




**1**; X = O, NR **3**; X = O, NR

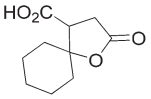
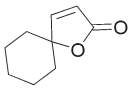
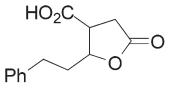
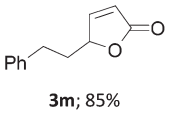
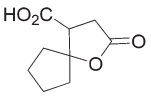
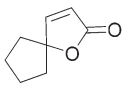
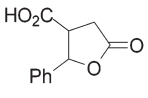
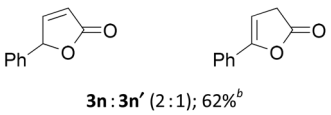
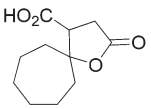
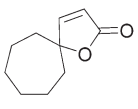
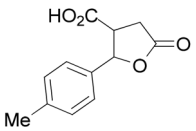
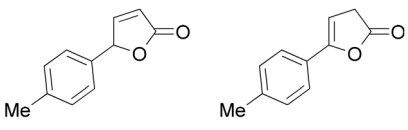
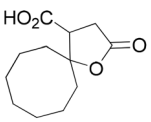
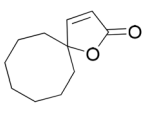
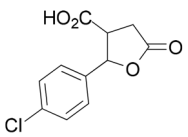
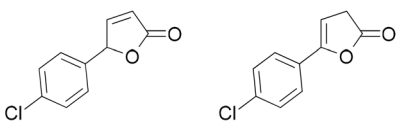
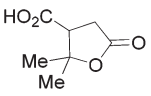
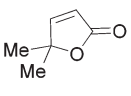
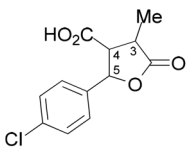
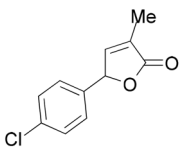
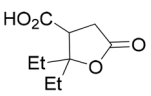
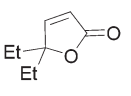
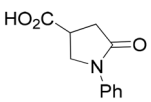
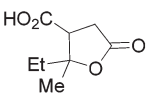
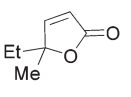
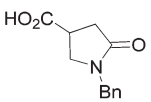
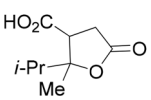
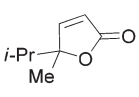
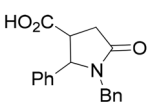
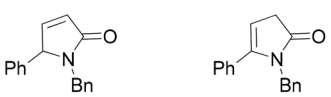
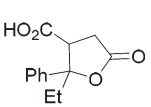
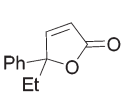
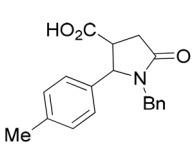
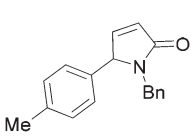
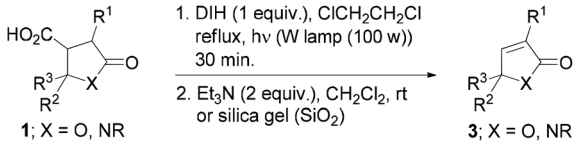
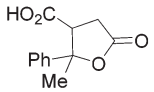
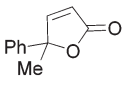
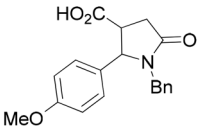
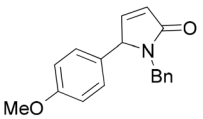
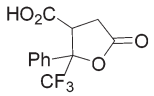
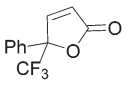
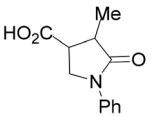
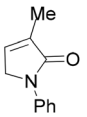
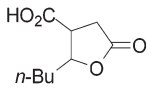
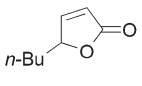
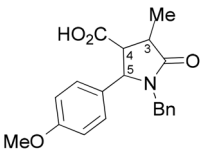
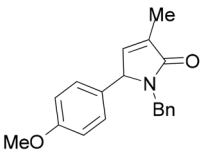
| Entry | Substrate **1** | Product **3**; yield[a] | Entry | Substrate **1** | Product **3**; yield[a] |
|---|---|---|---|---|---|
| 1 |  **1a** |  **3a**; 92% | 13 |  **1m** |  **3m**; 85% |
| 2 |  **1b** |  **3b**; 87% | 14 |  **1n** |  **3n**:**3n′** (2:1); 62%[b] |
| 3 |  **1c** |  **3c**; 81% | 15 |  **1o** |  **3o**:**3o′** (10:1); 61%[b] |
| 4 |  **1d** |  **3d**; 82% | 16 |  **1p** |  **3p**:**3p′** (1:4); 74%[b] |
| 5 |  **1e** |  **3e**; 92% | 17 |  **1q**[c] |  **3q**; 45% |
| 6 |  **1f** |  **3f**; 86% | 18 |  **1r** |  **3r**; 46% |
| 7 |  **1g** |  **3g**; 93% | 19 |  **1s** |  **3s**; 75% |
| 8 |  **1h** |  **3h**; 82% | 20 |  **1t** |  **3t**:**3t′** (3:2); 76% |
| 9 |  **1i** |  **3i**; 83% | 21 |  **1u** |  **3u**; 74% |

Table 2 *(Contd.)*




| Entry | Substrate **1** | Product **3**; yield[a] | Entry | Substrate **1** | Product **3**; yield[a] |
|---|---|---|---|---|---|
| 10 |  **1j** |  **3j**; 81% | 22 |  **1v** |  **3v**; 62% |
| 11 |  **1k** |  **3k**; 82% | 23 |  **1w** |  **3w**; 33% |
| 12 |  **1l** |  **3l**; 85% | 24 |  **1x**[d] |  **3x**; 45% |

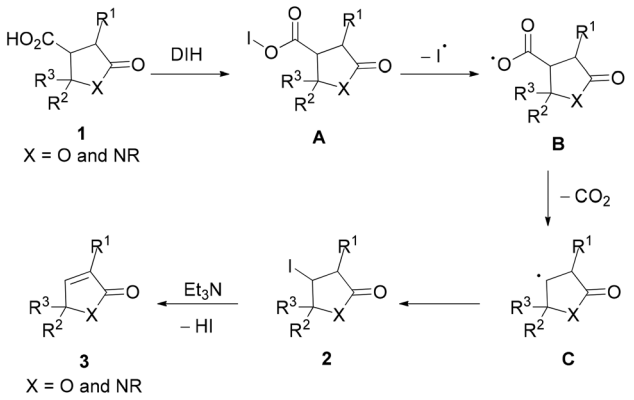
[a] Isolated yield. [b] Compounds **3** were obtained after purification of **2** by column chromatography ($SiO_2$, see the Experimental section). The ratio of products was determined by $^1H$ NMR analysis. [c] A mixture of diastereomers (dr = 8 : 1; 3,4-*cis*-4,5-*trans*/3,4-*trans*-4,5-*trans*). [d] A single isomer (3,4-*cis*-4,5-*trans*).

that compound **2n** readily underwent dehydroiodination during column chromatography ($SiO_2$, see the Experimental section) to afford an inseparable mixture of the expected α,β-unsaturated γ-butyrolactone **3n** together with its deconjugated isomer **3n′** in 62% combined yield (**3n** : **3n′** = 2 : 1, $^1H$ NMR analysis) (Table 2, entry 14). Similarly, the reaction of paraconic acids **1o** and **1p**, containing 4-MePh- and 4-ClPh-groups at the γ-positions, also provided the expected butenolides **3o** and **3p** together with their deconjugated butenolides **3o′** and **3p′** in 61% (**3o** : **3o′**; 10 : 1) and 74% (**3p** : **3p′**; 1 : 4) yields, respectively (Table 2, entries 15 and 16). The formation of the deconjugated butenolides **3n′**, **3o′**, and **3p′** was presumably through the corresponding dienols generated from the enolization of α,β-unsaturated γ-butyrolactones **3n**, **3o**, and **3p**, respectively. Notably, deconjugated butenolides have been widely used in several enantioselective vinylogous additions to various Michael acceptors.[1] In contrast to **1p**, α-methylated paraconic acid **1q** underwent the reaction to give only the desired α,β-unsaturated γ-butyrolactone **3q** as the sole product in 45% yield (Table 2, entry 17).

As an extension of the present protocol, DIH-promoted decarboxylative iodination followed by $Et_3N$-promoted dehydroiodination can also be applied to the β-carboxyl-γ-butyrolactams leading to α,β-unsaturated γ-butyrolactams in moderate to good yields. Thus, phenyl- and benzyl protected β-carboxyl amides **1r** and **1s** yielded α,β-unsaturated γ-butyrolactams **3r** and **3s** in 46% and 75% yields, respectively (Table 2, entries 18 and 19). Similarly, β-carboxyl amide **1t**, bearing a phenyl substituent at the γ-position gave a mixture of α,β-unsaturated γ-butyrolactam **3t** and its deconjugated isomer **3t′** (76% yield, **3t** : **3t′** = 3 : 2, $^1H$ NMR analysis) (Table 2, entry 20). The reaction of **1u** and **1v**, having an electron donating group, gave the desired α,β-unsaturated γ-butyrolactams **3u** (74% yield) and **3v** (62% yield), respectively, each as the sole product (Table 2, entries 21 and 22). α-Methylated β-carboxyl-γ-butyrolactams **1w** and **1x** also gave the corresponding α,β-unsaturated γ-butyrolactams **3w** and **3x** in 33% and 45% yields, respectively (Table 2, entries 23 and 24).

A radical-type mechanism for decarboxylative iodination[11a] of **1** was proposed as shown in Scheme 2. Acyl hypoiodite **A** was formed from the reaction of **1** with DIH. The homolytic cleavage of the O–I bond of the intermediate **A** followed by decarboxylation of the resulting carboxyl radical **B** gave the carbon radical **C** which was subsequently trapped by an iodine to give β-iodo-γ-butyrolactones or lactams **2**. Finally, dehydroiodination of **2** provided the desired products **3**.




**Scheme 2** Proposed mechanism for decarboxylative iodination–dehydroiodination of paraconic acids and β-carboxyl-γ-butyrolactams.

## Conclusions

In conclusion, we have successfully developed a convenient synthetic approach to α,β-unsaturated γ-butyrolactones and γ-butyrolactams from readily available paraconic acids and β-carboxyl-γ-butyrolactams. Decarboxylative iodination of the carboxylic acid precursors using commercially available 1,3-diiodo-5,5-dimethylhydantoin (DIH) under irradiation followed by dehydroiodination gave good yields of the desired α,β-unsaturated γ-butyrolactone and γ-butyrolactam products, which are synthetically useful building blocks in organic synthesis and valuable core structures found in biologically active natural compounds.

## Experimental

### General information

The $^1$H NMR spectra were recorded on a Bruker-400 (400 MHz) or a Bruker-500 (500 MHz) spectrometer in $CDCl_3$ using tetramethylsilane as an internal standard. The $^{13}$C NMR spectra were recorded on a Bruker-400 (100 MHz) or a Bruker-500 (125 MHz) spectrometer in $CDCl_3$ using solvent peaks as an internal standard. The IR spectra were recorded on an ALPHA FTIR spectrometer. The mass spectra were recorded using a Thermo Finnigan Polaris Q mass spectrometer. The high resolution mass spectra were recorded on a HR-TOF-MS Micromass model VQ-TOF2 mass spectrometer. Melting points were recorded using a M-565 Büchi melting point apparatus and are uncorrected. Column chromatography was performed using Merck silica gel 60 (0.063–0.200 mm) (Art 7734). 1,2-Dichloroethane ($ClCH_2CH_2Cl$) and dichloromethane ($CH_2Cl_2$) were distilled over calcium hydride and stored over activated molecular sieves (4 Å). Other common solvents [acetone, $CH_2Cl_2$, hexanes, and ethyl acetate (EtOAc)] were distilled before use. Compounds **1** were synthesized according to the literature procedures.[13]

### General procedure

A mixture of paraconic acid or β-carboxyl-γ-butyrolactam **1** (0.5 mmol) and DIH (1 equiv.) in 1,2-dichloroethane (2 mL) was heated to reflux under irradiation by a tungsten-filament lamp (100 W) for 30 minutes. The reaction mixture was then cooled down to room temperature, washed with saturated $Na_2S_2O_3$ (20 mL), and extracted with $CH_2Cl_2$ (3 × 10 mL). The combined organic layers were washed with saturated $NaHCO_3$ and brine, dried over anhydrous $Na_2SO_4$, and concentrated to give β-iodo-γ-butyrolactones **2**. The obtained crude compounds **2a–2m** and **2r–2x** were dissolved in dry $CH_2Cl_2$ (2 mL) and treated with $Et_3N$ (2 equiv.). The progress of the reaction was monitored by TLC. After the complete consumption of the starting material, the reaction mixture was passed through a short column ($SiO_2$, $CH_2Cl_2$) to give the products **3a–3m** and **3r–3x**, respectively. Without treatment with $Et_3N$, the crude compounds **2n–2p** were converted into **3n–3p** and **3n′–3p′** during purification by column chromatography ($SiO_2$).

**1-Oxaspiro[4.5]dec-3-en-2-one (3a).** Pale yellow oil; $R_f$ = 0.44 ($CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.47 (d, $J$ = 5.6 Hz, 1H, C*H*), 6.01 (d, $J$ = 5.6 Hz, 1H, C*H*), 1.85–1.32 (m, 10H, 5 × C$H_2$). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 172.5 (C), 160.6 (CH), 120.1 (CH), 88.5 (C), 34.6 (2 × $CH_2$), 24.6 ($CH_2$), 22.4 (2 × $CH_2$). IR (neat): $\tilde{\nu}$ = 1744, 1602, 1448, 1209, 1137, 969, 816. MS: $m/z$ (%) = 153 (4) $[M + H]^+$, 152 (6) $[M]^+$, 149 (100), 135 (12), 121 (16), 95 (38), 81 (32), 57 (30). HRMS (ESI-TOF): calcd for $C_9H_{12}O_2Na$ $[M + Na]^+$ 175.0735; found 175.0733.

**1-Oxaspiro[4.4]non-3-en-2-one (3b).** Pale yellow oil; $R_f$ = 0.44 ($CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.39 (d, $J$ = 5.6 Hz, 1H, C*H*), 6.01 (d, $J$ = 5.6 Hz, 1H, C*H*), 2.08–1.74 (m, 8H, 4 × C$H_2$). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 172.5 (C), 159.0 (CH), 120.2 (CH), 96.8 (C), 36.8 (2 × $CH_2$), 24.6 (2 × $CH_2$). IR (neat): $\tilde{\nu}$ = 1738, 1600, 1434, 1153, 934, 817. MS: $m/z$ (%) = 139 (8) $[M + H]^+$, 138 (10) $[M]^+$, 134 (30), 126 (100), 112 (63), 91 (72), 81 (93), 67 (60), 55 (75). HRMS (ESI-TOF): calcd for $C_8H_{10}O_2Na$ $[M + Na]^+$ 161.0578; found 161.0580.

**1-Oxaspiro[4.6]undec-3-en-2-one (3c).** Pale yellow oil; $R_f$ = 0.44 ($CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.48 (d, $J$ = 5.6 Hz, 1H, C*H*), 5.95 (d, $J$ = 5.6 Hz, 1H, C*H*), 1.96–1.49 (m, 12H, 6 × C$H_2$). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 172.6 (C), 161.5 (CH), 119.1 (CH), 92.0 (C), 37.6 (2 × $CH_2$), 28.9 (2 × $CH_2$), 22.7 (2 × $CH_2$). IR (neat): $\tilde{\nu}$ = 1744, 1604, 1460, 1240, 1162, 939, 815. MS: $m/z$ (%) = 126 (62), 91 (100), 79 (89), 66 (51), 55 (45). HRMS (ESI-TOF): calcd for $C_{10}H_{14}O_2Na$ $[M + Na]^+$ 189.0891; found 189.0892.

**1-Oxaspiro[4.7]dodec-3-en-2-one (3d).** Pale yellow oil; $R_f$ = 0.40 ($CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.53 (d, $J$ = 5.6 Hz, 1H, C*H*), 5.99 (d, $J$ = 5.6 Hz, 1H, C*H*), 2.04–1.43 (m, 14H, 7 × C$H_2$). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 172.5 (C), 161.1 (CH), 120.0 (CH), 92.1 (CH), 33.4 (2 × $CH_2$), 27.9 (2 × $CH_2$), 24.4 ($CH_2$), 22.4 (2 × $CH_2$). IR (neat): $\tilde{\nu}$ = 1745, 1600, 1465, 1161, 1023, 818. MS: $m/z$ (%) = 180 (11) $[M]^+$, 133 (36), 109 (52), 95 (78), 91 (84), 81 (89), 79 (100), 67 (55), 55 (65). HRMS (ESI-TOF): calcd for $C_{11}H_{16}O_2Na$ $[M + Na]^+$ 203.1048; found 203.1049.

**5,5-Dimethylfuran-2(5*H*)-one (3e).** Pale yellow oil; $R_f$ = 0.33 ($CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.41 (d, $J$ = 5.6 Hz, 1H, C*H*), 5.99 (d, $J$ = 5.6 Hz, 1H, C*H*), 1.49 (s, 6H, 2 × C$H_3$). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 172.4 (C), 161.2 (CH), 119.9 (CH), 86.6 (C), 25.3 (2 × $CH_3$). IR (neat): $\tilde{\nu}$ = 1732, 1461, 1258, 1117, 1016, 795. MS: $m/z$ (%) = 113 (40) $[M + H]^+$, 112 (11) $[M]^+$, 77 (87), 51 (39). HRMS (ESI-TOF): calcd for $C_6H_8O_2Na$ $[M + Na]^+$ 135.0422; found 135.0423.

**5,5-Diethylfuran-2(5*H*)-one (3f).** Pale yellow oil; $R_f$ = 0.44 ($CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.29 (d, $J$ = 5.7 Hz, 1H, C*H*), 6.08 (d, $J$ = 5.7 Hz, 1H, C*H*), 1.88 (dq, $J_2$ = 7.3 Hz, $J_1$ = 14.6 Hz, 2H, C$H_2$), 1.77 (dq, $J_2$ = 7.3 Hz, $J_1$ = 14.6 Hz, 2H, C$H_2$), 0.86 (t, $J$ = 7.3 Hz, 6H, 2 × C$H_3$). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 172.9 (C), 158.9 (CH), 121.6 (CH), 92.0 (C), 29.5 (2 × $CH_2$), 7.7 (2 × $CH_3$). IR (neat): $\tilde{\nu}$ = 1750, 1603, 1460, 1224, 1133, 950, 820. MS: $m/z$ (%) = 140 (19) $[M]^+$, 133 (47), 126 (89), 95 (75), 81 (100), 67 (88), 55 (81). HRMS (ESI-TOF): calcd for $C_8H_{12}O_2Na$ $[M + Na]^+$ 163.0735; found 163.0734.

**5-Ethyl-5-methylfuran-2(5*H*)-one (3g).** Pale yellow oil; $R_f$ = 0.40 ($CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.36 (d, $J$ = 5.6 Hz, 1H, C*H*), 6.03 (d, $J$ = 5.6 Hz, 1H, C*H*), 1.86 (dq, $J_2$ = 7.3 Hz, $J_1$ = 14.6 Hz, 1H, CH*H*), 1.76 (dq, $J_2$ = 7.3 Hz, $J_1$ = 14.6 Hz, 1H, C*H*H), 1.47 (s, 3H, C$H_3$), 0.88 (t, $J$ = 7.3 Hz, 3H, C$H_3$). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 172.6 (C), 160.2 (CH), 120.7 (CH), 89.3 (C), 31.2 ($CH_2$), 23.5 ($CH_3$), 8.0 ($CH_3$). IR (neat): $\tilde{\nu}$ = 1745, 1603, 1459, 1235, 1130, 950, 819. MS: $m/z$ (%) = 127 (21) $[M + H]^+$, 126 (100) $[M]^+$, 112 (48), 95 (76), 81 (90), 67 (78), 55 (84). HRMS (ESI-TOF): calcd for $C_7H_{10}O_2Na$ $[M + Na]^+$ 149.0578; found 149.0579.

**5-Isopropyl-5-methylfuran-2(5*H*)-one (3h).** Pale yellow oil; $R_f$ = 0.42 ($CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.34 (d, $J$ = 5.7 Hz, 1H, C*H*), 5.97 (d, $J$ = 5.7 Hz, 1H, C*H*), 1.91 (hept, $J$ = 6.9 Hz, 1H, C*H*), 1.37 (s, 3H, C$H_3$), 0.91 (d, $J$ = 6.9 Hz, 3H, C$H_3$), 0.88 (d, $J$ = 6.9 Hz, 3H, C$H_3$). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 172.7 (C), 159.7 (CH), 120.8 (CH), 91.7 (C), 35.5 (CH), 21.3 ($CH_3$), 17.7 ($CH_3$), 17.2 ($CH_3$). IR (neat): $\tilde{\nu}$ = 1744, 1603, 1457, 1249, 1120, 948, 819. MS: $m/z$ (%) = 141 (28) $[M + H]^+$, 140 (100) $[M]^+$, 138 (22). HRMS (ESI-TOF): calcd for $C_8H_{12}O_2Na$ $[M + Na]^+$ 163.0735; found 163.0732.

**5-Ethyl-5-phenylfuran-2(5*H*)-one (3i).** Pale yellow oil; $R_f$ = 0.53 ($CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.63 (d, $J$ = 5.6 Hz, 1H, C*H*), 7.42–7.28 (m, 5H, Ar*H*), 6.08 (d, $J$ = 5.6 Hz, 1H, C*H*), 2.19 (dq, $J_2$ = 7.3 Hz, $J_1$ = 14.6 Hz, 1H, CH*H*), 2.03 (dq, $J_2$ = 7.3 Hz, $J_1$ = 14.6 Hz, 1H, C*H*H), 0.89 (t, $J$ = 7.3 Hz, 3H, C$H_3$). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 172.4 (C), 159.2 (CH), 138.8 (C), 128.8 (2 × CH), 128.1 (CH), 125.0 (2 × CH), 120.0 (CH), 91.9 (C), 32.7 ($CH_2$), 8.0 ($CH_3$). IR (neat): $\tilde{\nu}$ = 3085, 3066, 1752, 1601, 1448, 1210, 1121, 1024, 816, 760, 698. MS: $m/z$ (%) = 189 (7) $[M + H]^+$, 188 (12) $[M]^+$, 159 (100), 131 (53), 103 (63), 77 (58), 67 (14), 55 (9). HRMS (ESI-TOF): calcd for $C_{12}H_{12}O_2Na$ $[M + Na]^+$ 211.0735; found 211.0733.

**5-Methyl-5-phenylfuran-2(5*H*)-one (3j).** Pale yellow oil; $R_f$ = 0.38 ($CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.57 (d, $J$ = 5.6 Hz, 1H, C*H*), 7.35–7.29 (m, 4H, Ar*H*), 7.29–7.22 (m, 1H, Ar*H*), 5.99 (d, $J$ = 5.6 Hz, 1H, C*H*), 1.76 (s, 3H, C$H_3$). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 172.4 (C), 160.4 (CH), 139.2 (C), 128.8 (2 × CH), 128.3 (CH), 124.7 (2 × CH), 119.3 (CH), 88.9 (C), 26.3 ($CH_3$). IR (neat): $\tilde{\nu}$ = 3087, 1747, 1447, 765, 697. MS: $m/z$ (%) = 175 (4) $[M + H]^+$, 174 (9) $[M]^+$, 159 (39), 131 (100), 103 (78), 77 (51). HRMS (ESI-TOF): calcd for $C_{11}H_{10}O_2Na$ $[M + Na]^+$ 197.0578; found 197.0578.

**5-Phenyl-5-(trifluoromethyl)furan-2(5*H*)-one (3k).** White solid; mp 70–72 °C ($CH_2Cl_2$); $R_f$ = 0.61 ($CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.82 (d, $J$ = 5.7 Hz, 1H, C*H*), 7.61–7.52 (m, 2H, Ar*H*), 7.51–7.40 (m, 3H, Ar*H*), 6.39 (d, $J$ = 5.7 Hz, 1H, C*H*). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 169.7 (C), 150.8 (CH), 130.9 (C), 130.2 (CH), 130.0 (3 × CH), 126.6 (CH), 124.2 (CH), 122.4 (q, $J$ = 280.3 Hz, $CF_3$), 87.4 (q, $J$ = 32.2 Hz, C). $^{19}$F NMR (376 MHz, $CDCl_3$): $\delta$ = −76.9 (s, 3 F). IR (neat): $\tilde{\nu}$ = 3117, 1797, 1775, 1292, 1171, 761, 694. MS: $m/z$ (%) = 228 (1) $[M]^+$, 159 (100), 131 (48), 103 (43), 77 (26). HRMS (ESI-TOF): calcd for $C_{11}H_7F_3O_2Na$ $[M + Na]^+$ 251.0296; found 251.0296.

**5-Butylfuran-2(5*H*)-one (3l).** Pale yellow oil; $R_f$ = 0.44 ($CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.47 (dd, $J_2$ = 1.3 Hz, $J_2$ = 5.7 Hz, 1H, C*H*), 6.11 (dd, $J_3$ = 1.9 Hz, $J_2$ = 5.7 Hz, 1H, C*H*), 5.08–5.01 (m, 1H, C*H*), 1.84–1.81 (m, 2H, C$H_2$), 1.50–1.30 (m, 4H, 2 × C$H_2$), 0.92 (t, $J$ = 7.1 Hz, 3H, C$H_3$). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 173.2 (C), 156.3 (CH), 121.5 (CH), 83.4 (C), 32.8 ($CH_2$), 27.0 ($CH_2$), 22.4 ($CH_2$), 13.8 ($CH_3$). IR (neat): $\tilde{\nu}$ = 1747, 1601, 1466, 1162, 1024, 818. MS: $m/z$ (%) = 140 (17) $[M]^+$, 133 (40), 95 (90), 81 (100), 67 (89), 55 (98). HRMS (ESI-TOF): calcd for $C_8H_{12}O_2Na$ $[M + Na]^+$ 163.0735; found 163.0729.

**5-Phenethylfuran-2(5*H*)-one (3m).** Pale yellow oil; $R_f$ = 0.48 ($CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.40 (dd, $J_2$ = 1.4 Hz, $J_2$ = 5.7 Hz, 1H, C*H*), 7.34–7.27 (m, 2H, Ar*H*), 7.25–7.17 (m, 3H, Ar*H*), 6.11 (dd, $J_3$ = 2.0 Hz, $J_2$ = 5.7 Hz, 1H, C*H*), 5.05–4.98 (m, 1H, C*H*), 2.90–2.72 (m, 2H, C$H_2$), 2.14–2.03 (m, 1H, CH*H*), 2.00–1.88 (m, 1H, C*H*H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 173.0 (C), 156.1 (CH), 140.2 (C), 128.6 (2 × CH), 128.5 (2 × CH), 126.4 (CH), 121.6 (CH), 82.4 (C), 34.9 ($CH_2$), 31.3 ($CH_2$). IR (neat): $\tilde{\nu}$ = 3085, 3062, 1744, 1601, 1454, 1159, 1102, 815, 752, 699. MS: $m/z$ (%) = 189 (9) $[M + H]^+$, 188 (10) $[M]^+$, 178 (14), 105 (24), 97 (38), 91 (100), 77 (34), 65 (24), 55 (16). HRMS (ESI-TOF): calcd for $C_{12}H_{12}O_2Na$ $[M + Na]^+$ 211.0735; found 211.0738.

**5-Phenylfuran-2(5*H*)-one (3n) and 5-phenylfuran-2(3*H*)-one (3n′).** A 2 : 1 mixture of **3n** and **3n′** was obtained as an orange semi-solid after column chromatography ($SiO_2$, 20% EtOAc in hexanes). **3n**; $R_f$ = 0.20 (20% EtOAc in hexanes), **3n′**; $R_f$ = 0.38 (20% EtOAc in hexanes); $^1$H NMR (400 MHz, $CDCl_3$, integrated equally for both isomers): $\delta$ = 7.56–7.50 (m, 2H, Ar*H* of **3n′**), 7.46 (dd, $J_2$ = 1.6 Hz, $J_2$ = 5.6 Hz, 1H, C*H* of **3n**), 7.37–7.26 (each m, 3H, Ar*H* of **3n** and 3H, Ar*H* of **3n′**), 7.23–7.16 (m, 2H, Ar*H* of **3n**), 6.16 (dd, $J_3$ = 2.1 Hz, $J_2$ = 5.6 Hz, 1H, C*H* of **3n**), 5.97–5.92 (m, 1H, C*H* of **3n**), 5.72 (t, $J$ = 2.7 Hz, 1H, C*H* of **3n′**), 3.35 (d, $J$ = 2.7 Hz, 2H, C$H_2$ of **3n′**). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 175.9 (C of **3n′**), 173.1 (C of **3n**), 155.8 (CH of **3n**), 153.9 (C of **3n′**), 134.2 (1C of **3n** and 1C of **3n′**), 129.3 (CH of **3n**), 129.6 (CH of **3n′**), 128.6 (2 × CH of **3n′**), 129.0 (2 × CH of **3n**), 126.5 (2 × CH of **3n**), 124.7 (2 × CH of **3n′**), 120.9 (CH of **3n**), 97.6 (CH of **3n′**), 84.3 (CH of **3n**), 34.6 ($CH_2$ of **3n′**). IR (neat): $\tilde{\nu}$ = 3090, 3034, 1746, 1454, 1154, 1028, 760, 697. MS: $m/z$ (%) = 161 (15) $[M + H]^+$, 160 (87) $[M]^+$, 131 (99), 103 (70), 77

(100). HRMS (ESI-TOF): calcd for $C_{10}H_8O_2Na$ $[M + Na]^+$ 183.0422; found 183.0430.

**5-(*p*-Tolyl)furan-2(5*H*)-one (3o) and 5-(*p*-tolyl)furan-2(3*H*)-one (3o′).** A 10 : 1 mixture of **3o** and **3o′** was obtained as an orange solid after column chromatography ($SiO_2$, 20% EtOAc in hexanes). **3o**; $R_f$ = 0.33 (20% EtOAc in hexanes), **3o′**; $R_f$ = 0.47 (20% EtOAc in hexanes); mp 49–52 °C ($CH_2Cl_2$). $^1$H NMR (500 MHz, $CDCl_3$, integrated equally for both isomers): $\delta$ = 7.49 (dd, $J_2$ = 1.6 Hz, $J_2$ = 5.6 Hz, 1H, C*H* of **3o**), 7.20 (each d, $J$ = 8.1 Hz, 2H, Ar*H* of **3o** and 2H, Ar*H* of **3o′**), 7.14 (each d, $J$ = 8.1 Hz, 2H, Ar*H* of **3o** and 2H, Ar*H* of **3o′**), 6.20 (dd, $J_3$ = 2.1 Hz, $J_2$ = 5.6 Hz, 1H, C*H* of **3o**), 5.97 (br s, 1H, C*H* of **3o**), 5.70 (t, $J$ = 2.7 Hz, 1H, C*H* of **3o′**), 3.39 (d, $J$ = 2.7 Hz, 2H, $CH_2$ of **3o′**), 2.37 (s, 3H, $CH_3$ of **3o′**), 2.36 (s, 3H, $CH_3$ of **3o**). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 173.1 (C of **3o**), 173.0 (C of **3o′**), 155.8 (CH of **3o**), 155.7 (C of **3o′**), 139.4 (C of **3o**), 138.9 (C of **3o′**), 131.3 (C of **3o′**), 131.2 (C of **3o**), 129.7 (2 × CH of **3o**), 129.4 (2 × CH of **3o′**), 126.5 (2 × CH of **3o**), 124.7 (2 × CH of **3o′**), 121.0 (CH of **3o**), 96.6 (CH of **3o′**), 84.4 (CH of **3o**), 34.6 ($CH_2$ of **3o′**), 21.2 ($CH_3$ of **3o**), 21.1 ($CH_3$ of **3o′**). IR (neat): $\tilde{\nu}$ = 3080, 3038, 1795, 1748, 1512, 1306, 1158, 819. MS: *m*/*z* (%) = 175 (10) $[M + H]^+$, 174 (52) $[M]^+$, 145 (100), 115 (94), 91 (80), 65 (34). HRMS (ESI-TOF): calcd for $C_{11}H_{10}O_2Na$ $[M + Na]^+$ 197.0578; found 197.0572.

**5-(4-Chlorophenyl)furan-2(5*H*)-one (3p) and 5-(4-chlorophenyl)furan-2(3*H*)-one (3p′).** A 1 : 4 mixture of **3p** and **3p′** was obtained as an orange semi-solid after column chromatography ($SiO_2$, 20% EtOAc in hexanes). **3p**; $R_f$ = 0.16 (20% EtOAc in hexanes), **3p′**; $R_f$ = 0.33 (20% EtOAc in hexanes); $^1$H NMR (400 MHz, $CDCl_3$, integrated equally for both isomers): $\delta$ = 7.47 (d, $J$ = 8.6 Hz, 2H, Ar*H* of **3p′**), 7.44 (dd, $J_2$ = 1.6 Hz, $J_2$ = 5.6 Hz, 1H, C*H* of **3p**), 7.31 (each d, $J$ = 8.6 Hz, 2H, Ar*H* of **3p** and 2H, Ar*H* of **3p′**), 7.14 (d, $J$ = 8.4 Hz, 2H, Ar*H* of **3p**), 6.18 (dd, $J_3$ = 2.1 Hz, $J_2$ = 5.6 Hz, 1H, C*H* of **3p**), 5.92 (br s, 1H, C*H* of **3p**), 5.72 (t, $J$ = 2.7 Hz, 1H, C*H* of **3p′**), 3.36 (d, $J$ = 2.7 Hz, 2H, $CH_2$ of **3p′**). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 175.5 (C of **3p′**), 172.7 (C of **3p**), 155.3 (CH of **3p**), 153.0 (C of **3p′**), 135.5 (C of **3p′**), 135.3 (C of **3p**), 132.8 (C of **3p**), 129.3 (2 × CH of **3p**), 129.0 (2 × CH of **3p′**), 127.8 (2 × CH of **3p**), 126.8 (C of **3p′**), 126.0 (2 × CH of **3p′**), 121.3 (CH of **3p**), 98.2 (CH of **3p′**), 83.5 (CH of **3p**), 34.6 ($CH_2$ of **3p′**). IR (neat): $\tilde{\nu}$ = 3031, 1746, 1682, 1514, 1157, 812. MS: *m*/*z* (%) = 195 (13) $[M + H]^+$, 194 (86) $[M]^+$, 159 (100), 139 (77), 103 (53), 74 (58). HRMS (ESI-TOF): calcd for $C_{10}H_7ClO_2Na$ $[M + Na]^+$ 217.0032; found 217.0028.

**5-(4-Chlorophenyl)-3-methylfuran-2(5*H*)-one (3q).** A white solid was obtained after column chromatography ($SiO_2$, 50% $CH_2Cl_2$ in hexanes). $R_f$ = 0.29 (20% EtOAc in hexanes); mp 83–86 °C ($CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.29 (d, $J$ = 8.5 Hz, 2H, Ar*H*), 7.14 (d, $J$ = 8.4 Hz, 2H, Ar*H*), 7.03 (dd, $J_3$ = 1.7 Hz, $J_2$ = 1.7 Hz, 1H, C*H*), 5.77 (dd, $J_4$ = 1.7 Hz, $J_2$ = 1.7 Hz, 1H, C*H*), 1.93 (dd, $J_4$ = 1.7 Hz, $J_3$ = 1.7 Hz, 3H, $CH_3$). $^{13}$C NMR (400 MHz, $CDCl_3$): $\delta$ = 174.0 (C), 147.8 (CH), 135.0 (C), 133.6 (C), 129.9 (C), 129.2 (2 × CH), 127.8 (2 × CH), 81.3 (CH), 10.6 ($CH_3$). IR (neat): $\tilde{\nu}$ = 3064, 1743, 1492, 1042, 823. MS: *m*/*z* (%) = 210 (11) $[M + H]^+$, 179 (100), 150 (46), 122 (33), 96 (40), 82 (76), 55 (56). HRMS (ESI-TOF): calcd for $C_{11}H_9ClO_2Na$ $[M + Na]^+$ 231.0189; found 231.0182.

**1-Phenyl-1*H*-pyrrol-2(5*H*)-one (3r).** Pale yellow solid; mp 81–85 °C ($CH_2Cl_2$); $R_f$ = 0.24 (10% EtOAc in hexanes). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.68–7.61 (m, 2H, Ar*H*), 7.36–7.28 (m, 2H, Ar*H*), 7.12 (dt, $J_2$ = 1.9 Hz, $J_2$ = 6.0 Hz, 1H, C*H*), 7.10–7.04 (m, 1H, Ar*H*), 6.22 (dt, $J_3$ = 1.9 Hz, $J_2$ = 6.0 Hz, 1H, C*H*), 4.39 (dd, $J_3$ = 1.9 Hz, $J_2$ = 1.9 Hz, 2H, $CH_2$). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 170.2 (C), 142.2 (CH), 139.0 (C), 129.3 (CH), 129.1 (2 × CH), 124.2 (CH), 118.9 (2 × CH), 53.2 ($CH_2$). IR (neat): $\tilde{\nu}$ = 3350, 3079, 3043, 1681, 1596, 753, 689. MS: *m*/*z* (%) = 160 (6) $[M + H]^+$, 159 (38) $[M]^+$, 130 (100), 77 (33). HRMS (ESI-TOF): calcd for $C_{10}H_9NONa$ $[M + Na]^+$ 182.0582; found 182.0582.

**1-Benzyl-1*H*-pyrrol-2(5*H*)-one (3s).** Pale yellow oil; $R_f$ = 0.22 (20% EtOAc in hexanes). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.37–7.19 (m, 5H, Ar*H*), 7.06 (dt, $J_2$ = 1.7 Hz, $J_2$ = 6.0 Hz, 1H, C*H*), 6.23 (dt, $J_3$ = 1.8 Hz, $J_2$ = 6.0 Hz, 1H, C*H*), 4.64 (s, 2H, $CH_2$Ph), 3.88 (br s, 2H, $CH_2$). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 171.4 (C), 142.8 (CH), 137.2 (C), 128.7 (2 × CH), 127.9 (3 × CH), 127.5 (CH), 52.2 ($CH_2$), 45.9 ($CH_2$). IR (neat): $\tilde{\nu}$ = 3368, 3063, 3030, 1659, 1450, 717, 699. MS: *m*/*z* (%) = 174 (6) $[M + H]^+$, 173 (50) $[M]^+$, 172 (72), 106 (40), 91 (100), 77 (27), 65 (34). HRMS (ESI-TOF): calcd for $C_{11}H_{11}NONa$ $[M + Na]^+$ 196.0738; found 196.0734.

**1-Benzyl-5-phenyl-1*H*-pyrrol-2(5*H*)-one (3t) and 1-benzyl-5-phenyl-1*H*-pyrrol-2(3*H*)-one (3t′).** A 3 : 2 mixture of **3t** and **3t′** was obtained as a pale brown viscous oil. **3t**; $R_f$ = 0.36 (30% acetone in hexanes), **3t′**; $R_f$ = 0.42 (30% acetone in hexanes); $^1$H NMR (400 MHz, $CDCl_3$, integrated equally for both isomers): $\delta$ = 7.42–7.24 (each, m, 5H, Ar*H* of **3t** and 5H, Ar*H* of **3t′**), 7.23–7.14 (each, m, 1H, Ar*H* of **3t** and 3H, Ar*H* of **3t′**), 7.14–7.09 (m, 2H, Ar*H* of **3t**), 7.09–7.04 (m, 2H, Ar*H* of **3t**), 6.99–6.94 (m, 2H, Ar*H* of **3t′**), 7.01 (dd, $J_2$ = 1.6 Hz, $J_2$ = 5.8 Hz, 1H, C*H* of **3t**), 6.28 (dd, $J_3$ = 1.6 Hz, $J_2$ = 5.8 Hz, 1H, C*H* of **3t**), 5.27 (t, $J$ = 2.6 Hz, 1H, C*H* of **3t′**), 5.19 (d, $J$ = 15.0 Hz, 1H, CH*H*Ph of **3t**), 4.88 (br s, 1H, C*H* of **3t**), 4.68 (s, 2H, $CH_2$Ph of **3t′**), 3.60 (d, $J$ = 15.0 Hz, 1H, CH*H*Ph of **3t**), 3.27 (d, $J$ = 2.6 Hz, 2H, $CH_2$ of **3t′**). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 178.4 (C of **3t′**), 171.3 (C of **3t**), 148.1 (CH of **3t**), 146.2 (C of **3t′**), 137.5 (C of **3t′**), 137.3 (C of **3t**), 134.4 (C of **3t**), 131.7 (C of **3t′**), 129.2 (2 × CH of **3t**), 128.9 (CH of **3t′**), 128.8 (2 × CH of **3t′**), 128.7 (2 × CH of **3t**), 128.4 (4 × CH of **3t′**), 128.3 (CH of **3t**), 128.2 (2 × CH of **3t**), 127.5 (2 × CH of **3t** and 2 × CH of **3t′**), 127.2 (CH of **3t**), 127.1 (CH of **3t′**), 126.2 (CH of **3t**), 102.4 (CH of **3t′**), 65.8 (CH of **3t**), 44.3 ($CH_2$ of **3t′**), 43.4 ($CH_2$ of **3t**), 37.3 ($CH_2$ of **3t′**). IR (neat): $\tilde{\nu}$ = 3306, 3061, 3029, 1677, 1453, 843, 768, 698. MS: *m*/*z* (%) = 250 (4) $[M + H]^+$, 249 (22) $[M]^+$, 144 (100), 115 (43), 91 (18), 77 (8). HRMS (ESI-TOF): calcd for $C_{17}H_{15}NONa$ $[M + Na]^+$ 272.1051; found 272.1053.

**1-Benzyl-5-(*p*-tolyl)-1*H*-pyrrol-2(5*H*)-one (3u).** Pale brown viscous oil; $R_f$ = 0.26 (30% EtOAc in hexanes). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.26–7.15 (m, 3H, Ar*H*), 7.10 (d, $J$ = 7.8 Hz, 2H, Ar*H*), 7.05 (d, $J$ = 6.6 Hz, 2H, Ar*H*), 6.91 (dd, $J_2$ = 1.5 Hz, $J_2$ = 5.9 Hz, 1H, C*H*), 6.88 (d, $J$ = 8.0 Hz, 2H, Ar*H*), 6.19 (dd, $J_3$ = 1.7 Hz, $J_2$ = 5.9 Hz, 1H, C*H*), 5.10 (d, $J$ = 14.9 Hz, 1H, CH*H*Ph), 4.77 (br s, 1H, C*H*), 3.51 (d, $J$ = 14.9 Hz, 1H, C*H*HPh) 2.29 (s, 3H, $CH_3$). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 171.3 (C), 148.2 (CH), 138.7 (C), 137.4 (C), 131.2 (C), 129.8 (2 × CH), 128.6

(2 × CH), 128.2 (2 × CH), 127.4 (3 × CH), 126.1 (CH), 65.6 (CH), 43.3 ($CH_2$), 21.2 ($CH_3$). IR (neat): $\tilde{\nu}$ = 3306, 3029, 1665, 1437, 816, 756, 700. MS: *m*/*z* (%) = 264 (4) $[M + H]^+$, 263 (12) $[M]^+$, 158 (100), 129 (33), 115 (26), 91 (18), 77 (5). HRMS (ESI-TOF): calcd for $C_{18}H_{17}NONa$ $[M + Na]^+$ 286.1208; found 286.1215.

**1-Benzyl-5-(4-methoxyphenyl)-1*H*-pyrrol-2(5*H*)-one (3v).** Pale brown viscous oil; $R_f$ = 0.32 (40% EtOAc in hexanes). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.35–7.19 (m, 1H of C*H* and 2H of Ar*H*), 7.15–7.08 (m, 2H, Ar*H*), 7.03–6.95 (m, 3H, Ar*H*), 6.92–6.86 (m, 2H, Ar*H*), 6.26 (dd, $J_3$ = 1.7 Hz, $J_2$ = 5.8 Hz, 1H, C*H*), 5.16 (d, *J* = 15.0 Hz, 1H, CH*H*Ph), 4.84 (br s, 1H, C*H*), 3.82 (s, 3H, O$CH_3$), 3.58 (d, *J* = 15.0 Hz, 1H, C*H*HPh). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 171.2 (C), 159.9 (C), 148.3 (CH), 137.4 (C), 128.8 (2 × CH), 128.6 (2 × CH), 128.2 (2 × CH), 127.4 (CH), 126.1 (CH), 125.9 (C), 114.5 (2 × CH), 65.3 (CH), 53.3 ($CH_3$), 43.3 ($CH_2$). IR (neat): $\tilde{\nu}$ = 3306, 3104, 3064, 3023, 1670, 1510, 1238, 1023, 830, 765, 699. MS: *m*/*z* (%) = 280 (16) $[M + H]^+$, 279 (87) $[M]^+$, 188 (67), 174 (100), 131 (26), 91 (47). HRMS (ESI-TOF): calcd for $C_{18}H_{17}NO_2Na$ $[M + Na]^+$ 302.1157; found 302.1161.

**3-Methyl-1-phenyl-1*H*-pyrrol-2(5*H*)-one (3w).** White solid; mp 81–83 °C (EtOAc/hexanes); $R_f$ = 0.33 (30% EtOAc in hexanes). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.78–7.71 (m, 2H, Ar*H*), 7.44–7.33 (m, 2H, Ar*H*), 7.16–7.08 (m, 1H, Ar*H*), 6.82–6.76 (m, 1H, C*H*), 4.33–4.27 (m, 2H, $CH_2$), 1.99–1.93 (m, 3H, $CH_3$). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 170.8 (C), 139.5 (C), 136.8 (C), 134.7 (CH), 129.0 (2 × CH), 123.9 (CH), 118.4 (2 × CH), 50.8 ($CH_2$), 11.3 ($CH_3$). IR (neat): $\tilde{\nu}$ = 3062, 3041, 1671, 1595, 1496, 1380, 758, 690. MS: *m*/*z* (%) = 174 (14) $[M + H]^+$, 173 (28) $[M]^+$, 144 (65), 121 (29), 91 (40), 79 (54). HRMS (ESI-TOF): calcd for $C_{11}H_{11}NONa$ $[M + Na]^+$ 196.0738; found 196.0730.

**1-Benzyl-5-(4-methoxyphenyl)-3-methyl-1*H*-pyrrol-2(5*H*)-one (3x).** Light brown viscous oil; $R_f$ = 0.36 (30% EtOAc in hexanes). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.33–7.21 (m, 3H, Ar*H*), 7.15–7.08 (m, 2H, Ar*H*), 6.99–6.93 (m, 2H, Ar*H*), 6.91–6.84 (m, 2H, Ar*H*), 6.63–6.58 (m, 1H, C*H*), 5.15 (d, *J* = 14.9 Hz, 1H, CH*H*Ph), 4.72–4.66 (m, 1H, C*H*), 3.82 (s, 3H, $CH_3$), 3.60 (d, *J* = 14.9 Hz, 1H, C*H*HPh) 2.02–1.98 (m, 3H, $CH_3$). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 171.9 (C), 159.7 (C), 141.2 (CH), 137.6 (C), 133.9 (C), 128.7 (2 × CH), 128.6 (2 × CH), 128.2 (2 × CH), 127.3 (CH), 127.0 (C), 114.4 (2 × CH), 63.1 (CH), 55.3 ($CH_3$), 43.7 ($CH_2$), 11.2 ($CH_3$). IR (neat): $\tilde{\nu}$ = 3064, 3031, 1678, 1608, 1510, 1242, 1030, 831, 705. MS: *m*/*z* (%) = 294 (33) $[M + H]^+$, 293 (100) $[M]^+$, 202 (77), 188 (61), 145 (24), 91 (37). HRMS (ESI-TOF): calcd for $C_{19}H_{19}NO_2Na$ $[M + Na]^+$ 316.1313; found 316.1337.

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## Notes and references

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