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Construction of the 3-prenyl-4-oxa-tricyclo[4.3.1.0^{3,7}]-dec-8-en-2-one core of caged xanthonoid natural products via tandem Wessely oxidation–intramolecular [4+2] cycloaddition

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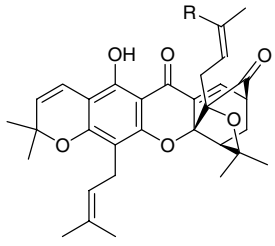
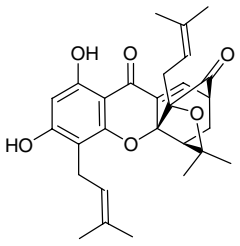
Abstract—A two-step protocol based on tandem Wessely oxidation/intramolecular Diels–Alder reaction to provide general access to the 3-prenyl-4-oxa-tricyclo[4.3.1.0^{3,7}]dec-8-en-2-one core present in the caged *Garcinia* xanthonoids is demonstrated. These readily accessible tricyclic scaffolds also provide ready entry into a variety of substituted γ-lactones through a photochemical 1,3-acyl shift and decarbonylation.

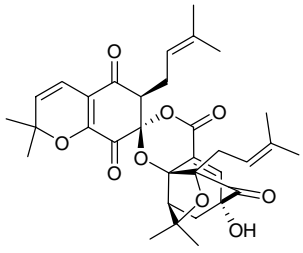
Tropical plants belonging to the genus *Garcinia* of the *Guttiferae* family have drawn human attention for a long time because of their exotic pigments and association with folk medicines.[1] In more recent times, attention has shifted toward the isolation and structure determination of a range of complex natural products that the genus *Garcinia* harbors in abundance and which display impressive bioactivity profiles.[1] A notable feature of the *Garcinia* natural products is the occurrence of a great variety of caged xanthonoids among which morellins **1a**,**b**,[1a,b] forbesione **2**,[1c] lateriflorone **3**, and gambogins **4a**,**b**[1d–f] constitute the more prominent examples. Besides their unique and interesting architecture, it is the display of wide ranging biological activity by many members of this xanthonoid family that has rekindled interest in this class of natural products in order to explore their therapeutic potential. For example, deoxymorellin **1b** and gambogin **4a** exhibit cytotoxicity against several cancer lines and gambogic acid **4b** induces apoptosis in breast cancer and also inhibits the growth of Gram positive bacteria.[1] Therefore, it is not surprising that total synthesis ventures, directed toward these caged xanthanoid natural products and analogs, have commanded active interest in recent years with many new strategies and tactics being devised and explored.[2–6]



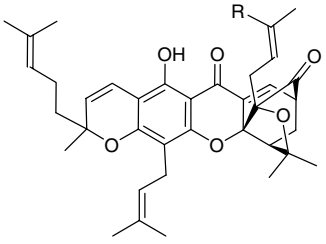
1a morellin, R=CHO
1b deoxymorellin, R=Me



2 forbesione



3 lateriflorone



4a gambogin, R= Me
4b gambogic acid, R= COOH

Two synthetic approaches to these novel xanthonoid natural products stand out, particularly with regard to the construction of the caged 4-oxa-tricyclo[4.3.1.0^{3,7}]-dec-8-en-2-one segment **5**, which has been proposed to be responsible for biological activity. The first one, follows the 'biomimetic' route based on the hypothesis of Quillinan and Scheinmann[2] involving a tandem

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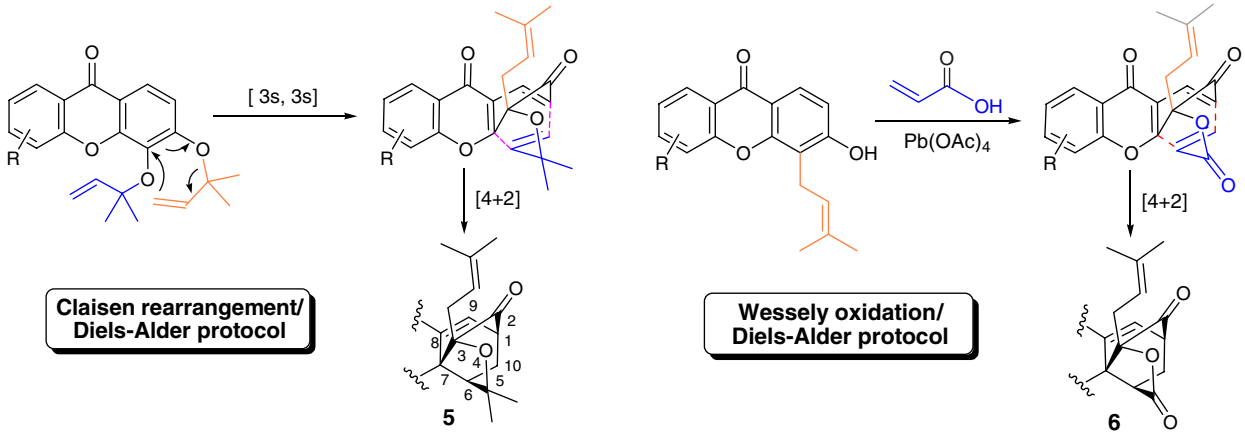
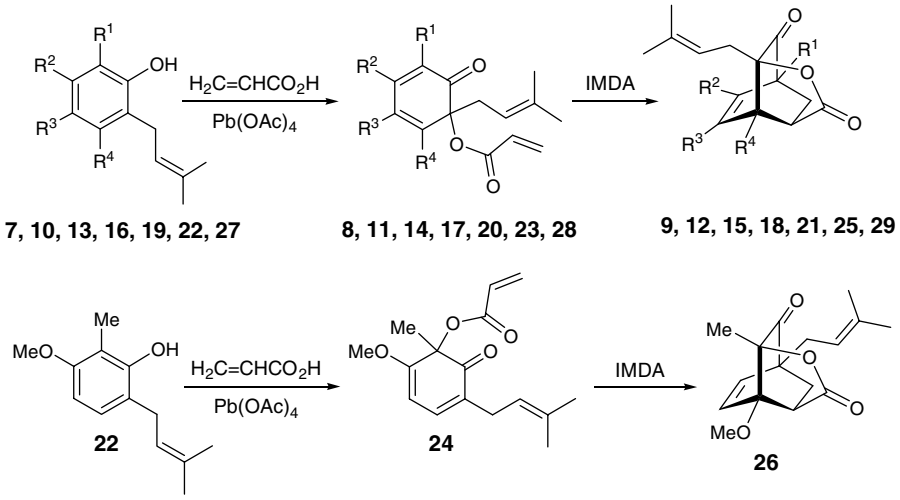


Scheme 1. Two prominent synthetic approaches toward the tricyclic core of the xanthonoid natural products.



Scheme 2. (top) The generally observed pathway for tandem Wessely oxidation and IMDA; (bottom) the regioisomeric pathway of the Wessely oxidation, observed in the case of **22**.

Claisen/intramolecular Diels–Alder cycloaddition cascade (Scheme 1), and has been imaginatively and extensively harnessed by the groups of Nicolaou,[3] Theodorakis[4] and others[5] to achieve the total synthesis of several complex natural products of this family. The second approach, initiated by Yates[6] involved a tandem Wessley oxidation[7]/intramolecular Diels–Alder cycloaddition protocol that could lead to a tricyclic lactone **6** (Scheme 1). However, the Yates protocol,[6] revived recently by Theodorakis and co-workers[8] led only to a regioisomeric structure and the prenyl group as required in the caged scaffold **6** could not be installed. As part of our interest in the synthesis of caged *Garcinia* xanthonoids, we have revisited the Yates protocol[6] and report here that by modulating the substitution pattern on the aromatic precursor,[9,10] it is possible to access the 3-prenyl-4-oxa-tricyclo[4.3.1.0^{3,7}]dec-8-en-2-one core present in the natural products through a tandem

Table 1. Reactions conditions and products of the Wessely oxidation/IMDA described in Scheme 2

Compound	R^1	R^2	R^3	R^4	Wessely oxidation		IMDA	
					Conditions	Product(s)/ yield (%)	Conditions	Product(s)/ yield (%)
7	H	H	Me	H	DCM, rt, 30 min	**8**	Toluene, reflux, 3.5 h	**9**/32 (two steps)
10	Prenyl	H	Me	H	DCM, rt, 20 min	**11**/47	Toluene, reflux, 4 h	**12**/67
13	H	OMe	H	H	DCM, rt, 15 min	**14**/53	Xylene, reflux, 8 h	**15**/37
16	H	H	H	OMe	DCM, rt, 15 min	**17**/45	Toluene, reflux, 18 h	**18**/76
19	H	OMe	H	OMe	DCM, 0 °C, 10 min	**20**/37	*o*-Dichlorobenzene, reflux, 8 h	**21**/80
22	Me	OMe	H	H	DCM, rt, 15 min	**23** + **24** (1:1)/85	Benzene, reflux, 3 h (**23**); 15 h (**24**)	**25**/82; **26**/84
27	Me	OMe	Prenyl	H	DCM, rt, 20 min	**28**/52	Toluene, reflux, 5 h	**29**/88

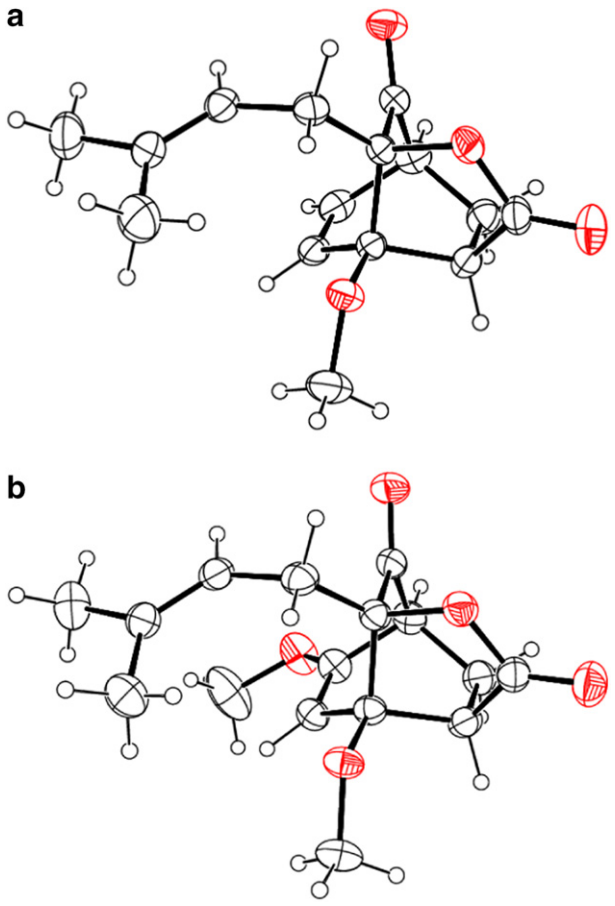


Figure 1. ORTEP diagrams of compounds (a) **18** and (b) **21**, drawn at 30% ellipsoidal probability.

Wessely oxidation/intramolecular Diels–Alder reaction in a general and predictable manner. Additionally, we have shown that functionally embellished 3-prenyl-4-oxa-tricyclo[4.3.1.0^{3,7}]dec-8-en-2-ones can be versatile precursors of synthetically useful γ-lactones through a photochemically induced [1,3]-shift and CO extrusion.

Wessely oxidation[7] of *o*-prenylated phenol derivative **7** with lead tetraacetate (LTA) in the presence of excess acrylic acid led to the intermediate **8**, which on thermal activation underwent a facile intramolecular Diels–Alder cycloaddition to deliver the tricyclic lactone derivative **9** (Scheme 2, Table 1).[11] Similarly, the *o*,*o*′-diprenylated derivative **10** and *o*-prenylated **13** led to the tricycles **12** and **15** via intramolecular [4+2] cycloaddition of intermediates **11** and **14**, respectively. The interesting outcome in these three examples was that the prenyl group was installed at the requisite C3 position on the 4-oxa-tricyclo[4.3.1.0^{3,7}]dec-8-en-2-one framework. Next, it was important to demonstrate the adaptability of this model study to enable placement of an oxygen functionality at the C7 bridgehead position in the caged tricyclic system, which would correspond to the connectivity of the xanthone oxygen in the natural products. Consequently, *o*-prenylated resorcinol derivative **16** on oxidation in the LTA-acrylic acid milieu led to intermediate **17**, which underwent Diels–Alder reaction to furnish the tricycle **18** (Scheme 2, Table 1).[11]

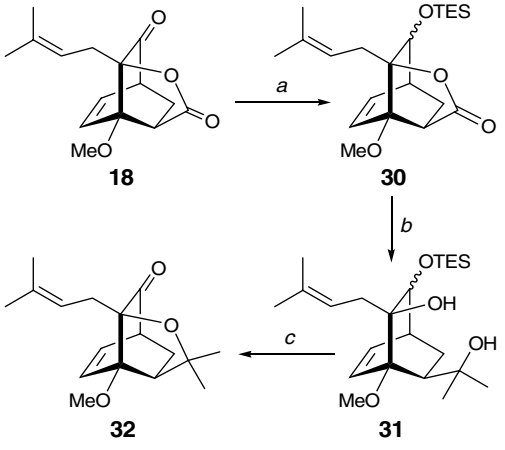
The structure of **18** with the bridgehead oxyfunctionality at C7 was fully secured through X-ray crystal structure determination (Fig. 1a).[12] In a similar vein, phloroglucinol derivative **19** was smoothly elaborated to **21** through the intermediacy of **20** and the tricyclic structure of **21** was again secured through X-ray crystal structure determination (Fig. 1b).[12]

On the other hand, when a substrate such as **22** with two alkyl substituents flanking the phenolic hydroxyl group was subjected to Wessely oxidation, two regioisomeric dienones **23** and **24** were obtained in nearly equal amounts. Intramolecular Diels–Alder reaction led to tricyclics **25** and **26**, respectively,[11] in which the former had the prenyl group at the requisite C3 position (Scheme 2, Table 1).

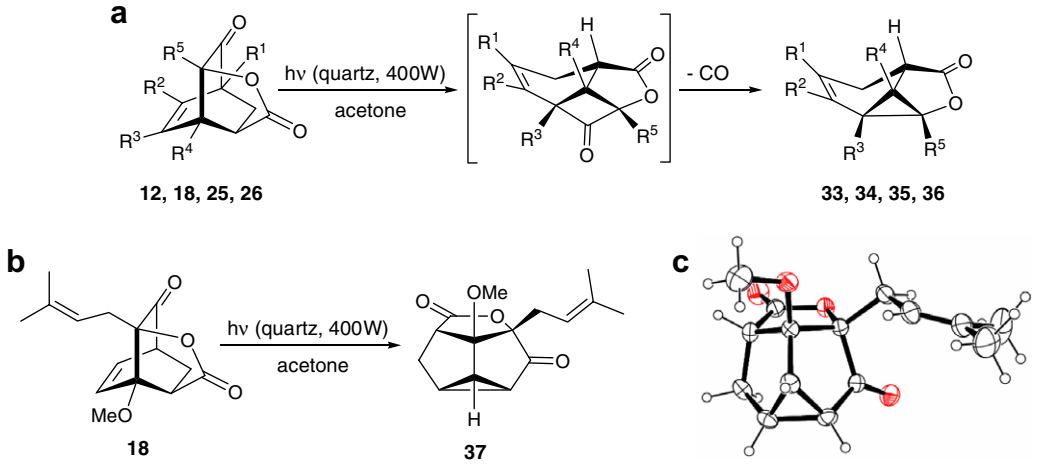
Lastly, it was of interest to execute this two-step protocol to access the caged tricyclic system in more functionally embellished substrates. Thus, pentasubstituted aromatic precursor **27** was subjected to LTA oxidation in the presence of acrylic acid to furnish intermediate **28** in a regioselective manner and was readily induced into intramolecular cycloaddition to furnish the diprenylated tricycle **29** (Scheme 2, Table 1).[11]

Adaptation of this two-step sequence to the fully endowed tricyclic scaffold present in *Garcinia* xanthonoids required that the γ-lactone ring in **6** be elaborated to a tetrahydrofuran moiety with the introduction of a *gem*-dimethyl group at C5 as present in **5** (Scheme 1). This transformation could be executed in the model compound **18** via **30** and **31** as depicted in Scheme 3 to deliver the tricyclic compound **32**, reminiscent of the core structure **5** of the *Garcinia* xanthonoids.

The ready availability of several diversely functionalized 4-oxa-tricyclo[4.3.1.0^{3,7}]dec-8-en-2-one derivatives bearing an embedded γ-lactone moiety encouraged us to explore the possibility of utilizing this segment for newer applications. The presence of a β,γ-unsaturated ketone



Scheme 3. Reagents and conditions: (a) (i) $NaBH_4$, MeOH, 0 °C, 10 min, 77%; (ii) TESCl, imidazole, DMAP, DCM, 0 °C → rt, 3 h, quant.; (b) MeLi, Et_2O, 0 °C → rt, 6 h, 64%; (c) (i) PPTS, MeOH, rt, 2 h, quant.; (ii) TPAP, NMMO, 4 Å molecular sieves, DCM, rt, 2.5 h, 87%; (iii) PTSA, benzene, rt, 3 h, 62%.



Scheme 4. (a) The photochemically induced 1,3-acyl shift and CO extrusion, as generally observed in the 4-oxa-tricyclo[4.3.1.0^{3,7}]dec-8-en-2-one derivatives under study; (b) the alternate oxa-di-π-methane rearrangement observed in **18**. (c) ORTEP diagram of **37**, drawn at 50% ellipsoidal probability.

Table 2. Reactions conditions and products of the photochemical reactions described in Scheme 4

Compound	R^1	R^2	R^3	R^4	R^5	Time (h)	Product(s)	Yield (%)
12	Prenyl	H	Me	H	Prenyl	6	**33**	34
18	H	H	H	OMe	Prenyl	1	**34** + **37** (1:1)	57
25	Me	OMe	H	H	Prenyl	4	**35**	37
26	Prenyl	H	H	OMe	Me	8	**36**	57

moiety in this scaffold was suggestive of a photochemically induced reorganization via a 1,3-acyl shift or oxa-di-π-methane rearrangement.[13] Indeed, when tricyclics **12**, **18**, **25** and **26** were irradiated in acetone solution, a 1,3-acyl shift occurred and decarbonylated products **33**–**36**, respectively, were obtained as the predominant products in modest yields (Scheme 4, Table 2).[11] Only in the case of **18** was the oxa-di-π-methane rearrangement product **37** also obtained in competitive amounts and its structure was secured through X-ray crystal structure determination (Scheme 4c). The deconvoluted fused γ-lactones **33**–**36** represent a motif that is frequently encountered among natural products and which have potential for further applications.

In summary, we have been successful in accessing the 3-prenyl-4-oxa-tricyclo[4.3.1.0^{3,7}]dec-8-en-2-one framework present in the *Garcinia* xanthonoids with the prenyl group installed in the requisite position in just two steps from readily crafted aromatic platforms. The generality of this two-step Wessely oxidation/Diels–Alder sequence has been demonstrated through several examples. One of the tricyclic adducts **18**, has been further elaborated to the core substructure **5** present in the natural products. The 4-oxa-tricyclo[4.3.1.0^{3,7}]dec-8-en-2-ones are also versatile precursors of bicyclic γ-lactones through a photochemical 1,3-acyl shift and decarbonylation.

Acknowledgments

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9. Wessely oxidations are recognized to proceed via an electrophilic mechanism[10] and electron-donating *o*-substituents facilitate and direct the process. In order to regiochemically steer the oxidation to place the prenyl group in the requisite position, it is important that the *o*′-position is not occupied by a better electron-donating substituent. All the substrates (except **22**) studied by us conform to this reasoning and hence the successful placement of the prenyl group on the tricyclic scaffold.
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11. All new compounds reported here were racemic and characterized on the basis of spectroscopic data (IR, ^{1}H and ^{13}C NMR and mass). Spectral data for some of the key compounds follows: Compound **9**: IR (neat) 2935, 1789, 1737, 1442 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.09–6.06 (m, 1H), 4.90 (t, $J = 7.5$ Hz, 1H), 3.37–3.27 (m, 2H), 2.80–2.67 (m, 2H), 2.37–2.24 (m, 2H), 1.87 (d, $J = 1.8$ Hz, 3H), 1.82 (dd, $J = 3.3$, 1.8 Hz, 1H), 1.72 (s, 3H), 1.64 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.8, 177.7, 138.7, 136.3, 125.2, 115.9, 82.5, 48.9, 46.5, 38.1, 30.7, 28.5, 25.9, 21.1, 18.0; HRMS(ES) *m*/*z* calcd for $C_{15}H_{18}O_3Na$ (M+Na$^+$): 269.1154; found: 269.1141. Compound **18**: mp 118.8–119.2 °C; IR (neat) 2927, 1792, 1742, 1621 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.30–6.25 (m, 2H), 4.67 (t, $J = 6.9$ Hz, 1H), 3.45 (s, 3H), 3.39–3.36 (m, 1H), 2.94 (d, $J = 10.5$ Hz, 1H), 2.82 (dd, $J = 13.8$, 7.2 Hz, 1H), 2.63 (dd, $J = 13.5$, 8.4 Hz, 1H), 2.27 (dd, $J = 13.5$, 3.3 Hz, 1H), 1.90–1.79 (m, 1H), 1.61 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.6, 176.4, 135.7, 130.9, 128.0, 116.4, 86.2, 85.2, 52.1, 46.1, 40.5, 29.6, 26.0, 25.9, 17.7; HRMS(ES) *m*/*z* calcd for $C_{15}H_{18}O_4Na$ (M+Na$^+$): 285.1103; found: 285.1100. Compound **21**: mp 155.1–155.5 °C; IR (neat) 2940, 1790, 1737, 1638 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.81–4.75 (m, 2H), 3.57 (s, 3H), 3.44 (s, 3H), 3.24 (d, $J = 1.8$ Hz, 1H), 2.95 (d, $J = 10.5$ Hz, 1H), 2.81 (dd, $J = 13.8$, 7.5 Hz, 1H), 2.64 (dd, $J = 13.5$, 8.4 Hz, 1H), 2.23 (dd, $J = 13.8$, 3.9 Hz, 1H), 2.04–1.96 (m, 1H), 1.62 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.6, 176.4, 155.2, 135.0, 116.7, 93.2, 86.8, 85.2, 55.5, 51.8, 50.2, 41.4, 29.2, 25.9 (2C), 17.6; HRMS(ES) *m*/*z* calcd for $C_{16}H_{20}O_5Na$ (M+Na$^+$): 315.1208; found: 315.1204. Compound **29**: IR (neat) 2935, 1791, 1733, 1656 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.01–4.95 (m, 2H), 3.56 (s, 3H), 2.97 (d, $J = 5.1$ Hz, 1H), 3.06 (dd, $J = 15.0$, 6.6 Hz, 1H), 2.78–2.61 (m, 3H), 2.33 (dd, $J = 15.3$, 7.2 Hz, 1H), 1.98 (d, $J = 6.6$ Hz, 2H), 1.71 (s, 6H), 1.65 (s, 6H), 1.29 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.0, 177.7, 152.8, 136.1, 134.9, 120.8, 119.4, 115.9, 83.1, 61.8, 51.9, 45.8, 39.9, 39.3, 28.6, 27.5, 25.9, 25.7, 18.1, 17.7, 12.6; HRMS(ES) *m*/*z* calcd for $C_{21}H_{29}O_4$(M+H$^+$): 345.2066; found: 345.2076. Compound **32**: mp 87.2–87.9 °C; IR (neat) 2966, 2925, 1732, 1455 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.21 (dd, $J = 9.0$, 6.6 Hz, 1H), 6.08 (dd, $J = 8.4$, 0.9 Hz, 1H), 4.81–4.61 (m, 1H), 3.39 (s, 3H), 3.04 (t, $J = 6.3$ Hz, 1H), 2.64–2.49 (m, 2H), 2.39 (d, $J = 9.6$ Hz, 1H), 2.20 (dd, $J = 13.5$, 4.5 Hz, 1H), 1.59 (s, 3H), 1.55 (s, 3H), 1.45 (s, 3H), 1.31 (dd, $J = 13.2$, 9.6 Hz, 1H), 1.20 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.4, 133.2, 132.4, 128.6, 118.9, 88.4, 85.8, 82.2, 51.2, 45.2, 42.5, 29.7, 28.7, 28.0, 27.7, 25.8, 17.6; HRMS(ES) *m*/*z* calcd for $C_{17}H_{24}O_3Na$ (M+Na$^+$): 299.1623; found: 299.1628. Compound **34**: IR (neat) 2933, 1789, 1454, 1434 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.94–5.89 (m, 1H), 5.80–5.74 (m, 1H), 5.27–5.23 (m, 1H), 3.42 (s, 3H), 3.23 (t, $J = 3.0$ Hz, 1H), 2.68–2.46 (m, 4H), 1.73 (s, 3H), 1.65 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.0, 134.9, 128.8, 121.5, 118.6, 76.1, 64.8, 56.2, 42.8, 27.8, 27.5, 25.7, 25.5, 17.9; HRMS(ES) *m*/*z* calcd for $C_{14}H_{18}O_3Na$ (M+Na$^+$): 257.1154; found: 257.1146. Compound **37**: mp 142.3–143.2 °C; IR (neat) 2917, 1787, 1729, 1454 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.15 (t, $J = 7.8$ Hz, 1H), 3.57 (dd, $J = 13.5$, 6.3 Hz, 1H), 3.53 (s, 3H), 2.82–2.68 (m, 2H), 2.61–2.47 (m, 2H), 2.21 (dd, $J = 9.3$, 6.0 Hz, 1H), 2.11 (dd, $J = 9.6$, 5.1 Hz, 1H), 1.69 (s, 3H), 1.61 (br s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.1, 174.9, 136.8, 114.8, 95.9, 93.6, 52.6, 51.0, 36.2, 31.6, 29.6, 29.3, 28.9, 26.0, 17.8; HRMS(ES) *m*/*z* calcd for $C_{15}H_{18}O_4Na$ (M+Na$^+$): 285.1103; found: 285.1099.
12. X-ray data was collected at 291 K on a SMART CCD–BRUKER diffractometer with graphite monochromated MoK_α radiation ($\lambda = 0.7107$ Å). The crystal structure was solved by direct methods (SIR92) and refined by full-matrix least-squares method on F^2 using SHELXL-97. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre and assigned the corresponding CCDC numbers. Compound **18**: $C_{15}H_{18}O_4$, MW = 262.29, crystal system: monoclinic, space group: $P2_1/c$, cell parameters: $a = 11.869(2)$ Å, $b = 7.7303(15)$ Å, $c = 15.387(3)$ Å, $\beta = 103.623(3)°$, $V = 1372.1(5)$ Å^3, $Z = 4$, $\rho_{calc} = 1.270$ g cm^{-3}, $F(000) = 560$, $\mu = 0.091$ mm^{-1}, number of l.s. parameters = 175, $R_1 = 0.0428$ for 2144 reflections with $I > 2\sigma(I)$ and 0.0511 for all 2542 data. $wR_2 = 0.1077$, GOF = 1.047 for all data, CCDC-658802. Compound **21**: $C_{16}H_{20}O_5$, MW = 292.32, crystal system: monoclinic, space group: $P2_1/c$, cell parameters: $a = 7.6309(16)$ Å, $b = 25.436(5)$ Å, $c = 7.8003(17)$ Å, $\beta = 95.493(4)°$, $V = 1507.1(6)$ Å^3, $Z = 4$, $\rho_{calc} = 1.288$ g cm^{-3}, $F(000) = 624$, $\mu = 0.095$ mm^{-1}, number of l.s. parameters = 194, $R_1 = 0.0462$ for 2331 reflections with $I > 2\sigma(I)$ and 0.0564 for all 2790 data. $wR_2 = 0.1136$, GOF = 1.058 for all data, CCDC-661601. Compound **37**: $C_{15}H_{18}O_4$, MW = 262.29, crystal system: monoclinic, space group: $P2_1/c$, cell parameters: $a = 15.504(3)$ Å, $b = 7.8487(14)$ Å, $c = 11.296(2)$ Å, $\beta = 97.791(3)°$, $V = 1361.9(4)$ Å^3, $Z = 4$, $\rho_{calc} = 1.279$ g cm^{-3}, $F(000) = 560$, $\mu = 0.092$ mm^{-1}, number of l.s. parameters = 175, $R_1 = 0.0457$ for 2021 reflections with $I > 2\sigma(I)$ and 0.062 for all 2492 data. $wR_2 = 0.1334$, GOF = 1.048 for all data, CCDC-661603.
13. For a recent review on the photochemistry of β,γ-unsaturated carbonyl compounds, see: Zimmerman, H. E.; Armesto, D. *Chem. Rev.* **1996**, *96*, 3065–3112.