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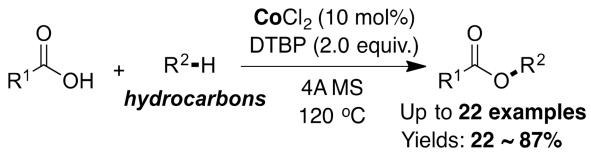

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Cobalt-Catalyzed Oxidative Esterification of Allylic/Benzylic C(sp^3)–H Bonds

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ABSTRACT

A protocol for the cobalt-catalyzed oxidative esterification of allylic/benzylic C(sp^3)–H bonds with carboxylic acids was developed in this work. Mechanistic studies revealed that C(sp^3)–H bond activation in the hydrocarbon was the turnover-limiting step and the in-situ formed [Co(III)]O*t*-Bu did not engage in hydrogen atom abstraction (HAA) of a C–H bond. This protocol was successfully incorporated into a synthetic pathway to β-damascenone that avoided the use of NBS.

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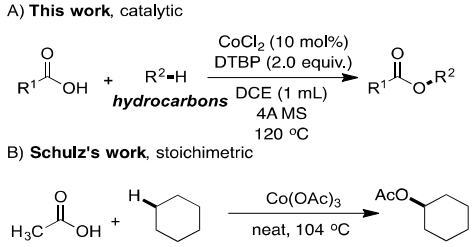
1. Introduction

As a result of its wide applications, esterification is one of the most fundamental and important reactions in organic chemistry and in the synthesis of many natural products, pharmaceutical molecules and fine chemicals.[1] Consequently, considerable attention has been directed towards the development of practical and efficient strategies for ester synthesis.[2] One highly efficient approach is direct C(sp^3)–H oxidative functionalization, thereby converting alkanes into esters, either as the carboxylic or alkoxy unit.[3-5] However, the development of direct and selective methods for alkane functionalization remains in its infancy due to the low reactivity of C(sp^3)–H bonds.[6]



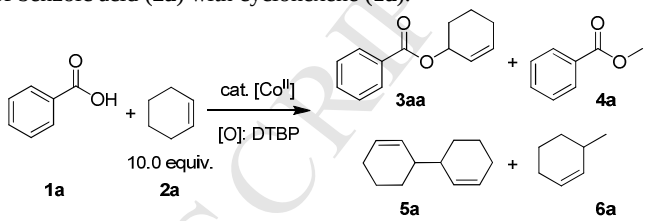
Scheme 1. Cobalt-mediated direct esterification of C(sp^3)–H bonds.

Various types of peroxides have been employed as stoichiometric oxidants and often as the sources of oxygen functionality in transition-metal[3,4,7] or metal-free-catalyzed[5,8] oxidative esterification through a radical mechanism. Until now, copper catalysis using peroxides as oxidants has been developed into a well-defined methodology for C(sp^3)–H bond esterification.[3] In principle, they are related to the classic Kharasch-Sosnovsky reaction.[9] In contrast, no study has been focused on cobalt, the other reported Kharasch-Sosnovsky catalyst.[9a] The ability of Co(II) complexes to dissociate peroxides, together with much other experimental, mainly kinetic, evidence, has led to the widely accepted opinion that their function is primarily to generate free radicals.[10] However, direct attack on the C(sp^3)–H σ bond by Co(III) species formed in situ may also be operative (Scheme 1B).[11,12] Most importantly, the behavior of Co(III) complexes may be significantly different from that of Cu(II) complexes in the oxidation of alkyl radicals. As previously reported by Kochi,[11b] the former favors oxidative substitution over oxidative elimination. Therefore, we considered to explore the limits and scope of the cobalt-catalyzed oxidative esterification of hydrocarbons with carboxylic acids in the presence of a peroxide as the oxidant (Scheme 1A).

2. Results and discussion

First, we identified effective precatalysts and conditions for the intermolecular esterification of unactivated C–H bonds by evaluating the reactivity of benzoic acid (**1a**, 0.5 mmol) and cyclohexene (**2a**, 10.0 equiv.) with various cobaltous salts (0~30 mol%) and *t*-BuOO*t*-Bu (DTBP). As shown in Table 1, the desired allylic ester cyclohex-2-en-1-yl benzoate (**3aa**) was produced, accompanied by a significant amount of [1,1'-bi(cyclohexane)]-2,2'-diene (**5a**). In addition, side products methyl benzoate (**4a**) and 3-methylcyclohex-1-ene (**6a**) were also detected, the proportion of which varied with the conditions used. The combination of $CoCl_2$ and DTBP was crucial for catalysis (entry 3), while other cobaltous salts provided reduced yields of **3aa** (entries 6~9). Independently investigating the reaction efficiency as a function of the catalyst amount indicated that a certain loading of catalyst was required for high selectivity towards the ester (entry 10 vs. 3 and Figure S1). For example, introducing either less than 5 mol% or more than 15 mol% $CoCl_2$ resulted in markedly lower yields of the C–H esterification product. In addition, a higher dosage of oxidant (2.0 equiv.) than the theoretical amount (1.0 equiv.) was necessary to achieve an optimal result (entries 10~12). Moreover, a moderate amount of molecular sieves (MS, 4A, 165 mg) was found to be a requisite additive, probably functioning as a desiccant in the reaction (entry 13 vs. 10). Notably, a remarkably decreased yield of **3aa** was observed when the reaction time was extended from 18 h to 24 h (entry 14 vs. 13 and Figure S2). Under the optimized conditions, **1a** smoothly reacted with **2a** (10.0 equiv.) in the presence of $CoCl_2$ (10 mol%) and DTBP (2.0 equiv.) in DCE (1 mL) at 120 °C to provide cyclohex-2-en-1-yl benzoate (**3aa**) in a high yield of 82% (entry 14).

Table 1. Development of the intermolecular oxidative esterification of benzoic acid (**2a**) with cyclohexene (**1a**).[a]

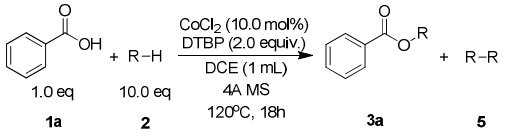


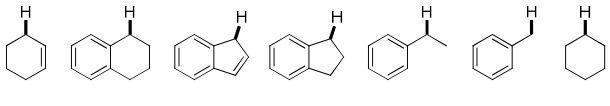
Entry	Cat.	Solvent	Yield (%)[b]			
			3aa[h]	4a[h]	5a[i]	6a[i]
1	$CoCl_2$	–	19	3	13	6
2	$CoCl_2$	EAC	10	2	6	7
3	$CoCl_2$	DCE	29	2	13	6
4	$CoCl_2$	CH_3CN	28	1	4	6
5	$CoCl_2$	$PhCF_3$	37	2	17	4
6	CoI_2	DCE	27	1	10	5
7	$Co(OH)_2$	DCE	7	1	14	6
8	$Co(OAc)_2$	DCE	9	1	13	7
9	$Co(acac)_2$	DCE	9	1	13	6
10[c]	$CoCl_2$	DCE	46	4	10	6
11[c,d]	$CoCl_2$	DCE	21	3	8	5
12[c,e]	$CoCl_2$	DCE	17	2	6	3
13[c,f]	$CoCl_2$	DCE	74	1	8	4
14[c,f,g]	$CoCl_2$	DCE	82	1	6	5

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (10.0 equiv.), cat. (5 mol%), DTBP (2.0 equiv.), solvent (1 mL), 100 °C, 24 h, under argon; [b] Yields determined by GC with biphenyl as an internal standard; [c] cat. (10 mol%); [d] DTBP (1.5 equiv.); [e] DTBP (1.0 equiv.); [f] MS (4A, 165 mg); [g] 120 °C, 18 h; [h] Yield calculated based on **1a**; [i] Yield calculated based on DTBP; DCE = 1,2-dichloroethane, EAC = ethyl acetate.

We next examined the dependence of the C–H bond strength of the substrate on the selectivity for C–H esterification over C–C homocoupling when employing **2a** and DTBP with 10 mol% $CoCl_2$ at 120 °C (Table 2). Substrates **2g** (8%, entry 7), **2f** (1%, entry 6), **2e** (79%, entry 5) and **2a** (82%, entry 1) give the C–H esterification product in yields that generally increase with decreasing C–H bond strength. However, no ester was detected by either GC-MS or NMR measurements in the case of hydrocarbon R–H bonds of comparatively moderate strength, such as **2d** (entry 4), **2c** (entry 3) and **2b** (entry 2), under identical conditions. Instead, the respective C–C homocoupling product for **2d** and **2c** and 1,4-dihydronaphthalene/naphthalene for **2b** (formed upon the dehydrogenation of the starting material) were the main products (Table S1). No significant improvement in the selectivity of the ester was detected for the independent reaction of **2g** in $PhCF_3$ (entry 8), thus disfavoring a negative effect caused by the chlorinated solvent.

Table 2. Cobalt-catalyzed oxidative esterification of various C(sp^3)–H bonds with **2a**.[a]





2a 2b 2c 2d 2e 2f 2g

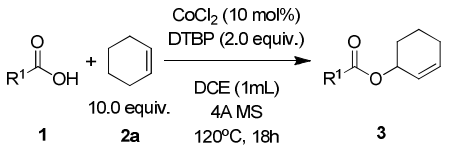
Entry	R–H	C–H BDE [kcal mol^{-1}]	Yield (%)[b,c]
1	**2a**	82	**3aa** (82/80[d])
2	**2b**	83	**3ab** (N.D.)
3	**2c**	84	**3ac** (N.D.)
4	**2d**	86	**3ad** (N.D.)
5	**2e**	87	**3ae** (79/78[d])
6	**2f**	90	**3af** (1)
7	**2g**	97	**3ag** (8)
8[e]	**2g**	97	**3ag** (3)
9[f]	**2b**	83	**3ab** (33/32[d])
10[f]	**2d**	86	**3ad** (30/26[d])

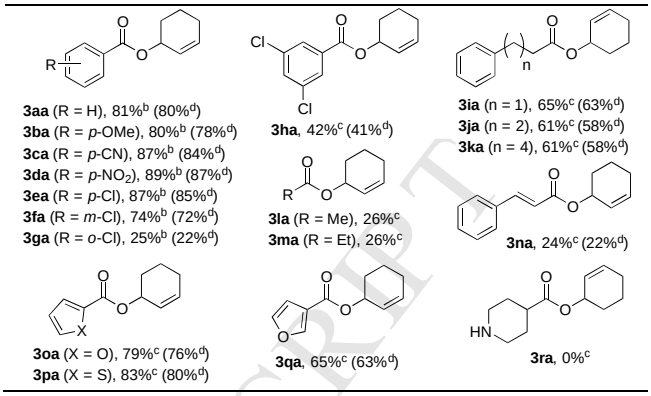
[a] Reaction conditions: **1a** (0.5 mmol), **2** (10.0 equiv.), $CoCl_2$ (10 mol%), DTBP (2.0 equiv.), DCE (1 mL), MS (4A, 165 mg), 120 °C, 18 h, under argon; [b] Yields determined by a combination of GC-MS (using the peak area normalization method) and ^{1}H NMR (with CH_2Br_2 as an internal standard); [c] Yields calculated based on **1a**; [d] Isolated yield; [e] $PhCF_3$ (1 mL) used as a solvent; [f] 12 h; N.D. = not detected.

In addition, moderate yields of **3ab** (32%) and **3ad** (26%) were generated when the reaction time was reduced to 12 h (Table 2, entries 9 and 10). We speculated that those esters were sensitive to the reaction conditions and readily decomposed over time. The full conversion of **3ab**/**3ad** (isolated) was detected by a combination of GC-MS and ^{1}H NMR after reaction for 18 h at 120 °C in the presence of $CoCl_2$/DTBP, with none of the desired compound formed. The same decomposition was found for **3aa**, albeit at a slower rate. After reaction for 18 h under identical conditions, 40% of **3aa** remained (Figure S4).

A range of carboxylic acid derivatives (**1**) was then examined in the coupling reaction with **2a** under the optimized reaction conditions (Table 3). The results demonstrated that electronic variations in the substituents at the *para*-position of **1a** did not affect the reaction efficiency. The corresponding cyclohex-2-en-1-yl benzoate substituted with methoxy, nitro, cyano and chloro groups was obtained in satisfactory yields. In contrast, a significant steric effect was observed when introducing substituents into the *meta*- and *ortho*-positions. Taking chloro-substituted benzoic acid as an example, the ester yield decreased sharply with increased steric hindrance at the reactive site, displaying an order of *para*- (85%) > *meta*- (72%) > *ortho*- (22%). With the two *meta*-positions fully substituted by chloro groups, a yield of only 41% of the ester was obtained. Aliphatic carboxylic acids could also be employed as facile substrates that provided the corresponding ester in acceptable yields. The expected intramolecular esterification was not detected in the case of either **1j** or **1k**. In fact, the self-esterification of **1j** proceeded poorly in the absence of **2a** under identical conditions, generating 5-phenyldihydrofuran-2(3H)-one in a yield of 21% (Scheme S4). Finally, various heteroaromatic acids, with the exception of piperidine-4-carboxylic acid, were found to be tolerated in this catalytic system, and they afforded their cyclohex-2-en-1-yl carboxylates in moderate yields.

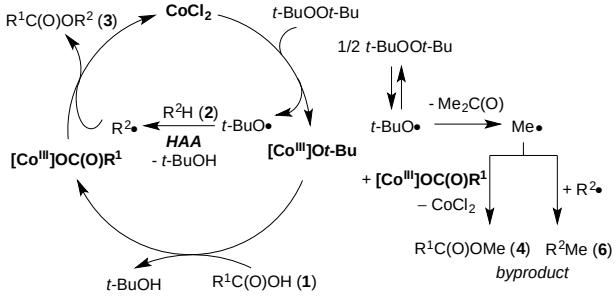
Table 3. C(sp^3)–H esterification of **2a** with carboxylic acid derivatives.[a]





[a] Reaction conditions: **1** (0.5 mmol), **2a** (10.0 equiv.), $CoCl_2$ (10 mol%), DTBP (2.0 equiv.), DCE (1 mL), MS (4A, 165 mg), 120 °C, 18 h, under argon; [b] Yields determined by GC with biphenyl as an internal standard; [c] Yields determined by ^{1}H NMR with CH_2Br_2 as an internal standard; [d] Isolated yield.

In these experiment, a slightly faster rate of decomposition of DTBP with increasing $CoCl_2$ loading was observed for the reaction (Figure S3), indicating that an induced decomposition occurred to concomitantly generate [Co^{III}]O*t*-Bu and *t*-BuO•, which was in agreement with Kochi's observations.[11b] The subsequent reaction pathway was highly dependent on the reactivity of [Co^{III}]O*t*-Bu since both the C–H σ bonds in hydrocarbons and carbon radicals are potentially reactive in the presence of cobaltic complexes.[11,12]

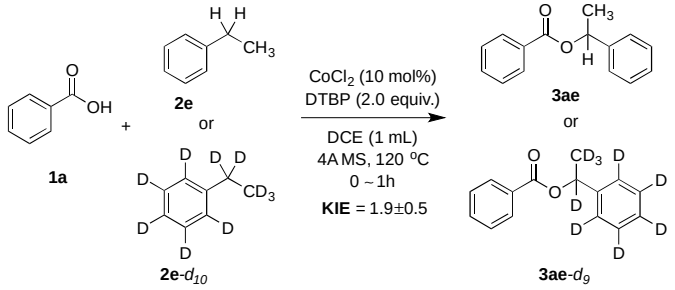


Scheme 2. Proposed catalytic cycle for cobalt-catalyzed oxidative esterification of hydrocarbons with carboxylic acids.

To better illustrate the fate of the *t*-BuO• radical and [Co(III)]O*t*-Bu concomitantly formed upon the reaction of Co(II) with DTBP in the catalytic process, we employed **2a** as the single substrate for oxidation. The reaction of DTBP (3.0 mmol) with **2a** (5.0 equiv.) in the presence of $CoCl_2$ (20 mol%) at 120 °C for 24 h gave **5a** in a yield of 35%, along with a small amount of **6a** (Scheme S3). The desired ether, 3-(*tert*-butoxy)cyclohex-1-ene, formed upon ligand transfer was not detected at all, suggesting the limited reactivity of [Co(III)]O*t*-Bu as a single electron transfer reagent. Indeed, both competitive and independent experiments revealed that the cobaltic salts formed in situ, such as [Co(III)]O*t*-Bu and [Co(III)]OC(O)Ph, did not engage in hydrogen atom abstraction (HAA) of an R–H bond in a substrate under these conditions (Table S2 and S3).

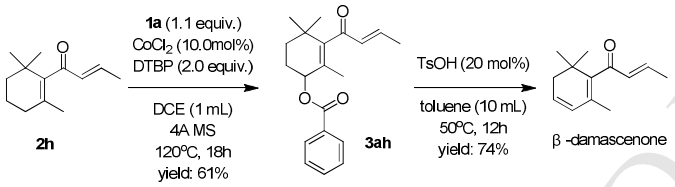
We therefore hypothesized that [Co(III)]O*t*-Bu rapidly reacted with the carboxylic acid to form [Co(III)]OC(O)R and *t*-BuOH,

while *t*-BuO• undergoes facile HAA with hydrocarbons to generate a carbon radical (Scheme 2). Subsequently, this carbon radical reacted with [Co(III)]OC(O)R, which released the ester product and regenerated a [Co(II)] species to complete the catalytic cycle.



Scheme 3. Kinetic isotope effect study on competitive esterification of **2e** *vs.* **2e**–d_{10}.

Labeling experiments of the independent reactions of **1a** and **2e** *vs.* **2e**-*d10* were conducted in separated vessels to estimate the kinetic isotope effect (KIE). In these experiments, the value of the KIE was calculated from the initial rate of esterification of **2e** with **1a** relative to that of **2e**-d_{10} (Scheme 3 and Figure S7). The obtained value was remarkably 1.9(5), indicating that the cleavage of the benzyl C–H bond was the turnover-limiting step.



Scheme 4. Synthetic route to β-damascenone.

Encouragingly, the esterification of **2h** at the allylic position of the ring, rather than the linear one, proceeded smoothly using this newly developed protocol, generating **3ah** in a yield of 61% when reacting **2h** with a slight excess of **1a** under the standard reaction conditions (Scheme 4). Then, **3ah** dehydrocarboxylated readily using the conditions reported by Delmond,[13] thereby generating the desired product, β-damascenone, in a good yield (74%). In contrast with the reported two-step dehydrogenation method, requiring an initial oxidative bromination and a subsequent dehydrobromination,[14] we offer here a synthetic pathway that avoids the use of N-Bromosuccinimide (NBS), which has the potential to im-prove the product specification.

3. Conclusions

In summary, we have introduced a cobalt-catalyzed oxidative esterification of allylic/benzylic C(sp^3)–H bonds with a variety of carboxylic acids to produce the corresponding ester products. The limitations of hydrocarbon structure were identified, which were partially due to ester instability under the reaction conditions. We speculated that the ester was significantly decarboxylated. We are currently investigating this further for more solid evidence. Mechanistic studies of this newly developed cobalt-catalyzed oxidative esterification of allylic/benzylic C(sp^3)–H bonds indicated that the hydrocarbon C–H bond activation was the turnover-limiting step, and the transient [Co(III)]O*t*-Bu species did not engage in HAA of a C–H bond. The developed method effectively created a synthetic route to β-damascenone that avoided the use of NBS.

4. Experimental section

*4.1. General procedure for C–H esterification of **2a** with various carboxylic acids (**1**)*

A DCE solution (1 mL) was prepared under argon consisting of carboxylic acids (0.5 mmol), 2a (512 μL, 5.0 mmol, 10.0 equiv.), $CoCl_2$ (6.5 mg, 0.05 mmol, 10.0 mol%), DTBP (189 μL, 1.0 mmol, 2.0 equiv.), and molecular sieves (4A, 165.0 mg) in a sealed reaction tube with a stirbar. The mixture was then heated to 120°C and reacted for 18h, thereafter being filtered through diatomite to remove the catalyst. The residue was extracted by diethyl ether (3 × 5mL). Afterwards, the combined organic filtrate was dried by Na_2SO_4 overnight and concentrated. The respective ester was afforded through purification by column chromatography on silica gel.

*4.2. General procedure for C–H esterification of various hydrocarbons (**2**) with **1a**.*

A DCE solution (1 mL) was prepared under argon consisting of 1a (61.4 mg, 0.5 mmol), hydrocarbons (5.0 mmol, 10.0 equiv.), $CoCl_2$ (6.5 mg, 0.05 mmol, 10.0 mol%), DTBP (189 μL, 1.0 mmol, 2.0 equiv.), and molecular sieves (4A, 165.0 mg) in a sealed reaction tube with a stirbar. The mixture was then heated to 120°C and reacted for 18h, thereafter being filtered through diatomite to remove the catalyst. The residue was extracted by diethyl ether (3 × 5mL). Afterwards, the combined organic filtrate was dried by Na_2SO_4 overnight and concentrated. The respective ester was afforded through purification by column chromatography on silica gel.

*4.3. Procedure for synthesis of **3ah***

A DCE solution (1 mL) was prepared under argon consisting of 2h (96.6 mg, 0.5 mmol), 1a (67.5 mg, 0.55 mmol, 1.1 equiv.), $CoCl_2$ (6.5 mg, 0.05 mmol, 10.0 mol%), DTBP (189 μL, 1.0 mmol, 2.0 equiv.), molecular sieves (4A, 165.0 mg) in a sealed reaction tube with a stirbar. The mixture was then heated to 120°C and reacted for 18h, thereafter being filtered through diatomite to remove the catalyst. The residue was extracted by diethyl ether (3 × 5mL). Afterwards, the combined organic filtrate was dried by Na_2SO_4 overnight and concentrated, which was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 30:1) and provided **3ah** in a yield of 61%.

4.4. Procedure for synthesis of β-damascenon

A reaction tube was charged with **3ah** (156.2 mg, 0.5 mmol), toluene (10 mL). After the addition of TsOH (17.4 mg, 20mol%), the reaction mixture was stirred at 50 °C under argon for 12h. The products were extracted by diethyl ether (3 × 5mL). The combined organic extract was dried by Na_2SO_4 overnight and concentrated, then purified by column chromatography on silica gel (CH_2Cl_2) and provided β-damascenone in a yield of 74%.

4.5. NMR characterization of products

Table 2. **3aa**: **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 8.05 (ddm, $^3J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 1.3 Hz, 2H, *o*-Ph), 7.54 (ddm, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 1.3 Hz, 1H, *p*-Ph), 7.43 (ddm, $^3J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 7.6 Hz, 2H, *m*-Ph), 5.99 (m, 1H, =CH), 5.83 (m, 1H, =CH), 5.50 (m, 1H, OCH), 2.14 (dm, $^1J_{HH}$ = 19.1 Hz, 1H, CH_2), 2.04 (dm, $^1J_{HH}$ = 19.1 Hz, 1H, CH_2), 1.98 (m, 1H, CH_2), 1.89 (m, 1H, CH_2), 1.84 (m, 1H, CH_2), 1.71 (m, 1H, CH_2). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 166.4 (C=O), 133.0 (*p*-Ph), 132.9 (=CH),

130.9 (*i*-Ph), 129.7 (*m*-/*o*-Ph), 128.4 (*m*-/*o*-Ph), 125.9 (=CH), 69.4 (OCH), 28.5, 68.7 (OCH), 28.6, 25.1, 19.1 (CH_2).

Table 2. **3ab**: **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 8.15 (d, $^3J_{HH}$ = 7.8 Hz, 2H, *o*-Ph), 7.62 (m, $^3J_{HH}$ = 7.8 Hz, 1H, *p*-Ph), 7.50 (t, $^3J_{HH}$ = 7.8 Hz, 2H, *m*-Ph), 7.46 (d, $^3J_{HH}$ = 7.2 Hz, 1H, *m*-Ph), 7.34 (t, $^3J_{HH}$ = 7.8 Hz, 1H, *m*-Ph), 7.26 (q, $^3J_{HH}$ = 7.8 Hz, 2H, *o*-Ph), 6.36 (t, $^3J_{HH}$ = 4.2 Hz, 1H, OCH), 3.02(m, 1H, CH_2), 2.89(m, 1H, CH_2), 2.21(m, 2H, CH_2), 2.16(m, 1H, CH_2), 1.98(m, 1H, CH_2). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 166.3 (C=O), 138.1 (Ph), 134.8 (Ph), 133.0 (Ph), 130.8 (Ph), 129.8 (Ph), 129.7 (Ph), 129.2 (Ph), 128.4 (Ph), 128.2 (Ph), 126.2 (Ph), 70.7 (OCH), 29.3 (CH_2), 29.2 (CH_2), 19.2 (CH_2).

Table 2. **3ad**: **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 8.01 (d, $^3J_{HH}$ = 7.8 Hz, 2H, *o*-Ph), 7.47 (dd, $^3J_{HH}$ = 13.8 Hz, $^3J_{HH}$ = 7.8 Hz, 2H, *m*-Ph), 7.36 (t, $^3J_{HH}$ = 7.2 Hz, 2H, *m*-Ph), 7.27 (m, 2H, *o*-Ph), 7.20 (m, ^{1}H, *p*-Ph), 6.36 (dd, $^3J_{HH}$ = 6.6 Hz, $^3J_{HH}$ = 4.2 Hz, 1H, OCH), 3.14(m, 1H, CH_2), 2.90(m, 1H, CH_2), 2.59(m, 1H, CH_2), 2.20(m, 1H, CH_2). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 166.6 (C=O), 144.5 (Ph), 141.2 (Ph), 132.9 (Ph), 130.5 (Ph), 129.8 (Ph), 129.0 (Ph), 128.4 (Ph), 126.8 (Ph), 125.8 (Ph), 124.9 (Ph), 79.0 (OCH), 32.6 (CH_2), 30.4 (CH_2).

Table 2. **3ae**: **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 8.10 (m, 2H, *o*-Ph), 7.56 (m, 1H, *p*-Ph), 7.47 (m, 2H, *o*-Ph), 7.45 (m, 2H, *m*-Ph), 7.33 (m, 2H, *m*-Ph), 7.32 (m, 1H, *p*-Ph), 6.15 (q, $^3J_{HH}$ = 6.6 Hz, 1H, OCH), 1.69 (d, $^3J_{HH}$ = 6.6 Hz, 3H, CH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 165.9 (C=O), 141.9 (Ph), 133.0 (*p*-Ph), 130.7 (*i*-Ph), 129.8 (*m*-/*o*-Ph), 128.7 (*m*-/*o*-Ph), 128.5 (Ph), 128.0 (Ph),126.2 (Ph), 73.0 (OCH), 22.6 (CH_3).

Table 3. **3ba**: **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 8.00 (dm, $^3J_{HH}$= 9.0 Hz, 2H, Ph), 6.90 (dm, $^3J_{HH}$= 9.0 Hz, 2H, Ph), 5.97 (m, 1H, =CH), 5.81 (m, 1H, =CH), 5.46 (m, 1H, OCH), 3.85 (s, 3H, OCH_3), 2.13 (dm, $^1J_{HH}$ = 18.4 Hz, 1H, CH_2), 2.02 (dm, $^1J_{HH}$ = 18.4 Hz, 1H, CH_2), 1.96 (m, 1H, CH_2), 1.86 (m, 1H, CH_2), 1.83 (m, 1H, CH_2), 1.69 (m, 1H, CH_2). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 166.1 (C=O), 163.3 (*i*-Ph^{OMe}), 132.7 (*o*-/*m*-Ph), 131.7 (=CH), 126.1(*o*-/*m*-Ph), 123.4 (*i*-$Ph^{C=O}$), 113.6 (=CH), 68.4(OCH), 55.5 (OCH_3), 28.56, 25.1, 19.1 (CH_2).

Table 3. **3ca**: **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 8.13 (dm, $^3J_{HH}$= 8.4 Hz, 2H, Ph), 7.72 (dm, $^3J_{HH}$= 8.4 Hz, 2H, Ph), 6.03 (m, 1H, =CH), 5.81 (m, 1H, =CH), 5.51 (m, 1H, OCH), 2.14 (dm, $^1J_{HH}$ = 17.7 Hz, 1H, CH_2), 2.04 (dm, $^1J_{HH}$ = 17.7 Hz, 1H, CH_2), 1.97 (m, 1H, CH_2), 1.89 (m, 1H, CH_2), 1.82 (m, 1H, CH_2), 1.71 (m, 1H, CH_2). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 164.6 (C=O), 134.7 (*i*-$Ph^{C=O}$), 133.6 (=CH), 132.2 (*o*-/*m*-Ph), 130.2 (*o*-/*m*-Ph), 125.1 (=CH), 118.1 (*i*-Ph^{CN}), 116.3 (CN), 69.7, (OCH), 28.4, 25.0, 18.9 (CH_2).

Table 3. **3da**: **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 8.27 (dm, $^3J_{HH}$ = 9.0 Hz, 2H, Ph), 8.21 (dm, $^3J_{HH}$= 9.0 Hz, 2H, Ph), 6.05 (m, 1H, =CH), 5.83 (m, 1H, =CH), 5.54 (m, 1H, OCH), 2.16 (dm, $^1J_{HH}$ = 17.9 Hz, 1H, CH_2), 2.06 (dm, $^1J_{HH}$ = 17.9 Hz, 1H, CH_2), 2.00 (m, 1H, CH_2), 1.91 (m, 1H, CH_2), 1.84 (m, 1H, CH_2), 1.73 (m, 1H, CH_2). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 164.4 (C=O), 150.6 (*i*-Ph^{NO2}), 136.4 (i-$Ph^{C=O}$), 133.8 (*o*-/*m*-Ph), 130.8 (=CH), 125.1 (*o*-/*m*-Ph), 123.6 (=CH), 69.9 (OCH), 28.4, 25.0, 18.9 (CH_2).

Table 3. **3ea**: **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.98 (dm, $^3J_{HH}$ = 9.0 Hz, 2H, Ph), 7.40 (dm, $^3J_{HH}$ = 8.4 Hz, 2H, Ph), 6.01 (m, 1H, =CH), 5.82 (m, 1H, =CH), 5.50 (m, 1H, OCH), 2.15 (dm, $^1J_{HH}$ = 17.8 Hz, 1H, CH_2), 2.04 (dm, $^1J_{HH}$ = 17.8 Hz, 1H, CH_2), 1.97 (m, 1H, CH_2), 1.87 (m, 1H, CH_2), 1.83 (m, 1H, CH_2), 1.71 (m, 1H, CH_2). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 165.5 (C=O), 139.3 (*i*-Ph), 133.3 (=CH), 131.1 (*o*-/*m*-Ph), 129.4 (*i*-Ph), 128.8 (*o*-/*m*-Ph), 125.6 (=CH), 69.1, (OCH), 28.5, 25.1, 19.0 (CH_2).

Table 3. **3fa**: **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 8.02 (s, 1H, *o*-Ph^{Cl}), 7.93 (dm, $^3J_{HH}$= 7.9 Hz, 1H, *o*-/*p*-Ph), 7.51 (dm, $^3J_{HH}$ = 8.7 Hz, 1H, *o*-/*p*-Ph), 7.37 (ddm, $^3J_{HH}$ = 8.7 Hz, $^3J_{HH}$ = 7.9 Hz, 1H, *m*-Ph), 6.02 (m, 1H, =CH), 5.82 (m, 1H, =CH), 5.50 (m, 1H, OCH), 2.15 (dm, $^1J_{HH}$ = 18.0 Hz, 1H, CH_2), 2.04 (dm, $^1J_{HH}$ = 18.0 Hz, 1H, CH_2), 1.97 (m, 1H, CH_2), 1.87 (m, 1H, CH_2), 1.83 (m, 1H, CH_2), 1.71 (m, 1H, CH_2). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 165.1 (C=O), 134.5 (*i*-Ph), 133.3, 132.9 (Ph/=CH), 132.7 (*i*-Ph), 129.8, 129.7, 127.9, 125.5 (Ph/=CH), 69.2 (OCH), 28.5, 25.1, 19.0 (CH_2).

Table 3. **3ga**: **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.80 (dm, $^3J_{HH}$ = 7.8 Hz, 1H, *o*-Ph^{CO}), 7.43 (dm, $^3J_{HH}$= 8.4 Hz, 1H, *m*-Ph^{Cl}), 7.39 (ddm, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 7.0 Hz, 1H, *m*-Ph), 7.30 (ddm, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 7.0 Hz, 1H, *p*-Ph), 6.02 (m, 1H, =CH), 5.86 (m, 1H, =CH), 5.53 (m, 1H, OCH), 2.13 (dm, $^1J_{HH}$ = 17.9 Hz, 1H, CH_2), 2.03 (dm, $^1J_{HH}$ = 17.9 Hz, 1H, CH_2), 1.97 (m, 1H, CH_2), 1.93 (m, 1H, CH_2), 1.83 (m, 1H, CH_2), 1.71 (m, 1H, CH_2). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 165.6 (C=O), 133.7 (*i*-Ph), 133.4, 132.4, 131.4, 131.1 (Ph/=CH), 131.0 (*i*-Ph), 126.7, 125.4 (Ph/=CH), 69.6 (OCH), 28.4, 25.1, 19.0 (CH_2).

Table 3. **3ha**: **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.90 (d, $^4J_{HH}$ = 8.4 Hz, 2H, *o*-Ph), 7.53 (d, $^4J_{HH}$= 8.4 Hz, 1H, *p*-Ph), 6.03 (m, 1H, =CH), 5.81 (m, 1H, =CH), 5.50 (m, 1H, OCH), 2.15 (dm, $^1J_{HH}$ = 19.8 Hz, 1H, CH_2), 2.05 (dm, $^1J_{HH}$ = 19.8 Hz, 1H, CH_2), 1.97 (m, 1H, CH_2), 1.88 (m, 1H, CH_2), 1.83 (m, 1H, CH_2), 1.72 (m, 1H, CH_2). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 164.0 (C=O), 135.3, 133.7, 132.7, 132.4, 128.2, 125.2 (Ph/=CH), 69.8 (OCH), 28.2, 25.0, 19.0 (CH_2).

Table 3. **3ia**: **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.29 (m, 2H, *m*-Ph), 7.21 (m, 2H, *o*-Ph), 7.20 (m, 1H, *p*-Ph), 5.94 (m, 1H, =CH), 5.69 (m, 1H, =CH), 5.26 (m, 1H, OCH), 2.96 (t, $^3J_{HH}$ = 7.7 Hz, 2H, $CH_2^{C=O}$), 2.63 (tm, $^3J_{HH}$ = 7.7 Hz, 2H, CH_2^{Ph}), 2.08 (dm, $^1J_{HH}$ = 18.2 Hz, 1H, CH_2), 1.98 (dm, $^1J_{HH}$ = 18.2 Hz, 1H, CH_2), 1.84 (m, 1H, CH_2), 1.71 (m, 1H, CH_2), 1.68 (m, 1H, CH_2), 1.62 (m, 1H, CH_2). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 172.7 (C=O), 140.7 (*i*-Ph), 132.8, 128.6, 128.5, 126.3, 125.8 (Ph/=CH), 68.2 (OCH), 36.4, 31.2, 28.4, 25.0, 19.0 (CH_2).

Table 3, **3ja**: **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.28 (m, 2H, *m*-Ph), 7.19 (m, 1H, *p*-Ph), 7.18 (m, 2H, *p*-Ph), 5.95 (m, 1H, =CH), 5.70 (m, 1H, =CH), 5.27 (m, 1H, OCH), 2.65 (m, 2H, CH_2), 2.33 (m, 2H, CH_2), 2.09 (dm, $^1J_{HH}$ = 18.9 Hz, 1H, CH_2), 1.99 (dm, $^1J_{HH}$ = 18.9 Hz, 1H, CH_2), 1.96 (m, 2H, CH_2), 1.87 (m, 1H, CH_2), 1.73 (m, 1H, CH_2), 1.72 (m, 1H, CH_2), 1.64 (m, 1H, CH_2). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 173.3 (C=O), 141.6 (*i*-Ph), 132.8, 128.6, 128.5, 126.1, 125.9 (Ph/=CH), 68.0 (OCH), 35.3, 34.2, 26.8, 28.5, 25.0, 19.0 (CH_2).

Table 3, **3ka**: **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.28 (m, 2H, *m*-Ph), 7.18 (m, 1H, *p*-Ph), 7.17 (m, 2H, *o*-Ph), 5.95 (m, 1H, =CH), 5.69 (m, 1H, =CH), 5.27 (m, 1H, OCH), 2.62 (m, 2H, CH_2), 2.30 (m, 2H, CH_2), 2.09 (dm, $^1J_{HH}$ = 16.8 Hz, 1H, CH_2), 1.99 (dm, $^1J_{HH}$ = 16.8 Hz, 1H, CH_2), 1.86 (m, 1H, CH_2), 1.72 (m, 2H, CH_2), 1.66 (m, 5H, CH_2), 1.38 (m, 2H, CH_2). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 173.6 (C=O), 142.7 (*i*-Ph), 132.7, 128.5, 128.4, 125.9, 125.8 (Ph/=CH), 68.0 (OCH), 35.9, 34.7, 31.2, 28.9, 25.1, 28.5, 25.0, 19.0 (CH_2).

Table 3, **3na**: **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.69 (d, $^3J_{HH}$= 16.2 Hz, 1H, =$CH^{C=O}$), 7.52 (m, 2H, *m*-Ph), 7.38 (m, 1H, *p*-Ph), 7.37 (m, 2H, *o*-Ph), 6.45 (d, $^3J_{HH}$= 16.2 Hz, 1H, =CH^{Ph}), 6.00 (m, 1H, =CH^{cyclo}), 5.79 (m, 1H, =CH^{cyclo}), 5.41 (m, 1H, OCH), 2.13 (dm, $^1J_{HH}$ = 20.0 Hz, 1H, CH_2), 2.02 (dm, $^1J_{HH}$ = 20.0

Hz, 1H, CH_2), 1.95 (m, 1H, CH_2), 1.81 (m, 2H, CH_2), 1.68 (m, 1H, CH_2). **$^{13}C\{^1H\}$ NMR** (151 MHz, $CDCl_3$, 298 K): δ = 166.8 (C=O), 144.6, 118.8, 134.7, 132.9, 130.3, 129.0, 128.2, 126.0 (Ph/=CH), 68.3(OCH), 28.6, 25.1, 19.1 (CH_2).

Table 3, **3oa**: **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.56 (m, 1H, CH^{Fu}), 7.16 (m, 1H, CH^{Fu}), 6.49 (m, 1H, CH^{Fu}), 6.01 (m, 1H, =CH), 5.80 (m, 1H, =CH), 5.49 (m, 1H, OCH), 2.13 (dm, $^1J_{HH}$ = 18.1 Hz, 1H, CH_2), 2.02 (dm, $^1J_{HH}$ = 18.1 Hz, 1H, CH_2), 1.96 (m, 1H, CH_2), 1.86 (m, 1H, CH_2), 1.81 (m, 1H, CH_2), 1.69 (m, 1H, CH_2). **$^{13}C\{^1H\}$ NMR** (151 MHz, $CDCl_3$, 298 K): δ = 158.7 (C=O), 146.3 (Fu/=CH), 145.2 (*i*-Fu), 133.3, 125.5, 117.8, 111.9 (Fu/=CH), 69.0 (OCH), 28.5, 25.0, 19.0 (CH_2).

Table 3, **3pa**: **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 8.0 (s, 1H, CH^{Fu}), 7.41 (s, 1H, CH^{Fu}), 6.74 (s, 1H, CH^{Fu}), 5.98 (m, 1H, =CH), 5.78 (m, 1H, =CH), 5.44 (s, 1H, OCH), 2.12 (dm, $^1J_{HH}$ = 17.9 Hz, 1H, CH_2), 2.02 (dm, $^1J_{HH}$ = 17.9 Hz, 1H, CH_2), 1.94 (m, 1H, CH_2), 1.81 (m, 2H, CH_2), 1.68 (m, 1H, CH_2). **$^{13}C\{^1H\}$ NMR** (151 MHz, $CDCl_3$, 298 K): δ = 163.0 (C=O), 147.8, 143.7, 132.9, 125.9 (Fu/=CH), 120.0 (*i*-Fu), 110.0 (Fu/=CH), 68.4 (OCH), 28.5, 25.0, 19.1 (CH_2).

Table 3, **3qa**: **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.79 (dd, $^3J_{HH}$ = 3.6 Hz, $^3J_{HH}$= 1.2 Hz, 1H, CH^{Thio}), 7.53 (dd, $^3J_{HH}$ = 4.8 Hz, $^3J_{HH}$= 1.2 Hz, 1H, CH^{Thio}), 7.06 (dd, $^3J_{HH}$= 4.8 Hz, $^3J_{HH}$= 3.6 Hz, 1H, CH^{Thio}), 5.99 (m, 1H, =CH), 5.82 (m, 1H, =CH), 5.47 (m, 1H, OCH), 2.13 (dm, $^1J_{HH}$ = 17.8 Hz, 1H, CH_2), 2.02 (dm, $^1J_{HH}$ = 17.8 Hz, 1H, CH_2), 1.95 (m, 1H, CH_2), 1.87 (m, 1H, CH_2), 1.81 (m, 1H, CH_2), 1.68 (m, 1H, CH_2). **$^{13}C\{^1H\}$ NMR** (151 MHz, $CDCl_3$, 298 K): δ = 162.1 (C=O), 134.6 (*i*-Thio), 133.3, 133.1, 132.3, 127.8, 125.6 (Thio/=CH), 69.1 (OCH), 28.5, 25.0, 19.0 (CH_2).

Scheme 4, **3ah**: **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 8.06 (m, 2H, *o*-Ph), 7.57 (m, 1H, *p*-Ph), 7.45 (m, 2H, *m*-Ph), 6.81 (m, 1H, =CH), 6.19 (m, 1H, =CH), 5.50 (m, 1H, OCH), 2.11 (m, 1H, CH_2), 1.96 (m, 3H, $CH_3^{=CH}$), 1.92 (m, 1H, CH_2), 1,73 (m, 1H, CH_2), 1.58 (s, 3H, CH_3), 1.54 (m, 1H, CH_2), 1.11 (s, 3H, CH_3), 1.08 (s, 3H, CH_3). **$^{13}C\{^1H\}$ NMR** (151 MHz, $CDCl_3$, 298 K): δ = 200.5 (C=O), 166.5 (C=O), 146.7, 146.0, 134.0, 133.1, 130.6, 129.8, 128.5, 128.0 (Ph/=CH/=C), 71.8 (OCH), 35.2 (C_q), 34.1, 28.8 (CH_2) 27.8, 25.6, 18.7, 18.0 (CH_3).

Scheme 4, β-damascenon: **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): 6.81 (dm, $^3J_{HH}$ = 15.7 Hz, 1H, $=CH^{Me}$) 6.17 (dq, $^3J_{HH}$ = 15.7 Hz, $^4J_{HH}$ = 1.6 Hz, 1 H, $=CH^{C=O}$), 5.83 (dm, $^3J_{HH}$ = 9.6 Hz, 1 H, $=CH^{Cq}$), 5.78 (dm, $^3J_{HH}$ = 9.6 Hz, 1 H, $=CH^{CH2}$), 2.09 (dd, $^3J_{HH}$ = 4.2 Hz, $^3J_{HH}$ = 1.6 Hz, 2H, CH_2), 1.92 (ddm, $^3J_{HH}$ = 6.9 Hz, $^4J_{HH}$ = 1.6 Hz, 3 H, $CH_3^{CH=CH}$), 1.62 (s, 3 H, $CH_3^{C=C}$), 1.02 (s, 6 H, 2×CH_3). **$^{13}C\{^1H\}$ NMR** (151 MHz, $CDCl_3$, 298 K): 201.2 (C=O), 146.5 (CH^{Me}), 139.4 ($=Cq^{C=O}$), 134.7 ($=CH^{C=O}$), 128.2 ($=Cq^{Me}$), 128.1 ($=CH^{CH2}$), 127.4 ($=CH^{Cq}$), 39.5 (CH_2), 33.9 (CMe_2), 26.4 (2×CH_3), 19.6 (CH_3^{Cq}), 18.6 ($CH_3^{=CH}$).

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Acknowledgments Appendix A. Supplementary data

Supplementary data related to this article can be found at

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