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Iron-Catalyzed Michael Addition of Ketones to Polar Olefins

Di-Han Zhang,[a] Jakob Knelles,[a] and Bernd Plietker[a,*]

[a] Institut für Organische Chemie, Universität Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany
E-mail: bernd.plietker@oc.uni-stuttgart.de

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Dedicated to Prof. Dieter Enders on the occasion of his 70th birthday.

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Abstract: The base metal complex tetrabutylammonium nitrosyltricarbonylferrate {$Bu_4N[Fe(CO)_3(NO)]$ (TBA[Fe])} – catalyzes the conjugate addition of ketones to polar olefins. The reaction is applicable to a wide range of substrates leading to interesting building blocks for organic synthesis. Clear indications for an acid-base type rather than a C–H activation pathway exist.

Keywords: activation; addition; catalysis; iron; synthesis

Introduction

The conjugate addition of ketones to α,β-unsaturated carboxylic acid esters is a versatile method for generating building blocks with an interesting 1,5-dicarbonyl motif.[1] Classical procedures largely rely on the use of a strong base, which can cause undesirable side reactions. To circumvent these problems, efficient catalytic protocols based on the use of transition metals, Brønsted or Lewis catalysts have been developed.[2] The high atom economy of these catalytic transformations plus the chance to induce stereoselectivity in the C–C bond forming process by employing catalytic amounts of a chiral ligand make these processes more advantegous compared to the classical protocols.[3,4] Recently, an iron-based Lewis acid has been used as an alternative efficient catalyst to carry out the conjugate addition.[5]

For the past years our group has developed an array of processes in which the nucleophilic Fe complex tetrabutylammonium nitrosyltricarbonylferrate {$Bu_4N[Fe(CO)_3(NO)]$ (TBA[Fe])} was used as a catalyst.[6] More recently, we became interested in exploring the reactivity of this electron-rich ferrate in C–H activation chemistry and developed an efficient amination of C(sp^2)–H bonds through activation of azides.[7] In line with the detailed mechanistic studies that were performed by Driver on the related Rh-catalyzed version,[8] we suggested an electrocyclization followed by a proton transfer as a mechanism. Hence, at the current state of research it appears as if the Fe complex is not inserting into the C–H bond prior to the C–N bond formation [Eq. (1), Figure 1]. With these results in mind we were wondering if the electron-rich ferrate would be able to activate more polar C(sp^3)–H bonds. From a mechanistic point of view two distinct activation pathways could be operative, i.e., the C–H insertion or the deprotonation mechanism [Eq. (2), Figure 1]. Whereas in the former scenario the ferrate would insert oxidatively into the C–H bond to give an Fe–H species that undergoes a carbometallation with polar olefins, the latter scenario reflects the classical acid-base type reactivity in which the ferrate acts as a Brønsted base to generate an enolate and an Fe–H species. Michael addition of the enolate generates the new C–C bond. Protonation of the resulting carbanion by the Fe–H species regenerates the catalyst.

As a result of this study an efficient iron-catalyzed conjugate addition of 2-acylimidazoles[9] and electron-deficient olefins was developed that is broadly applicable and has good indications of the more classical acid-base type mechanism to be operative.

Results and Discussion

Our preliminary investigation started with a reaction between 2-acylimidazole **1** and benzyl acrylate **2** with 5 mol% TBA[Fe] as a catalyst at 80 °C, which resulted in isolation of the desired adduct **3** in 72% (entry 1, Table 1). Control experiments indicated that no product was observed in the absence of iron catalyst (entry 2, Table 1). Examination of solvent effects re-

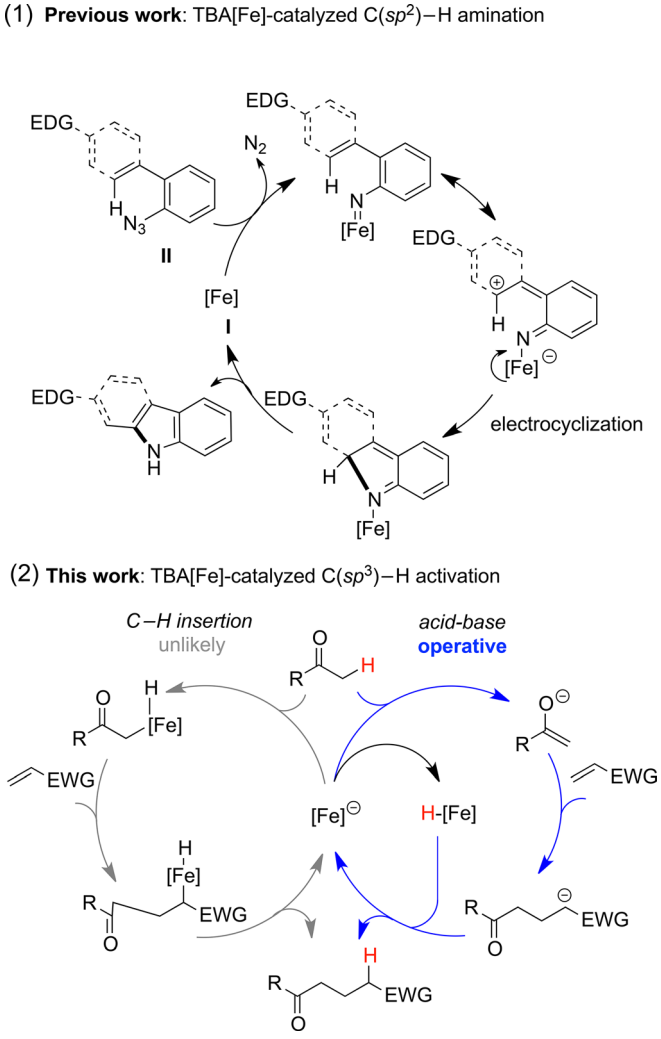
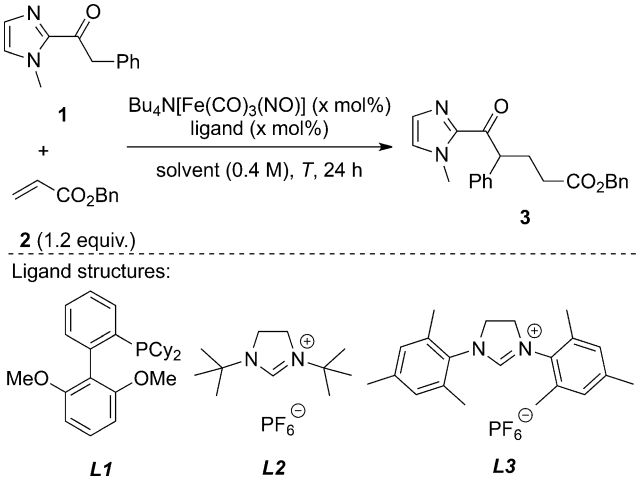


Figure 1. TBA[Fe]-catalyzed C–H transformation: Fe-catalyzed C(sp^2)–H amination and mechanistic dichotomy in the activation of C(sp^3)–H bonds.

Table 1. Optimization of the reaction conditions.

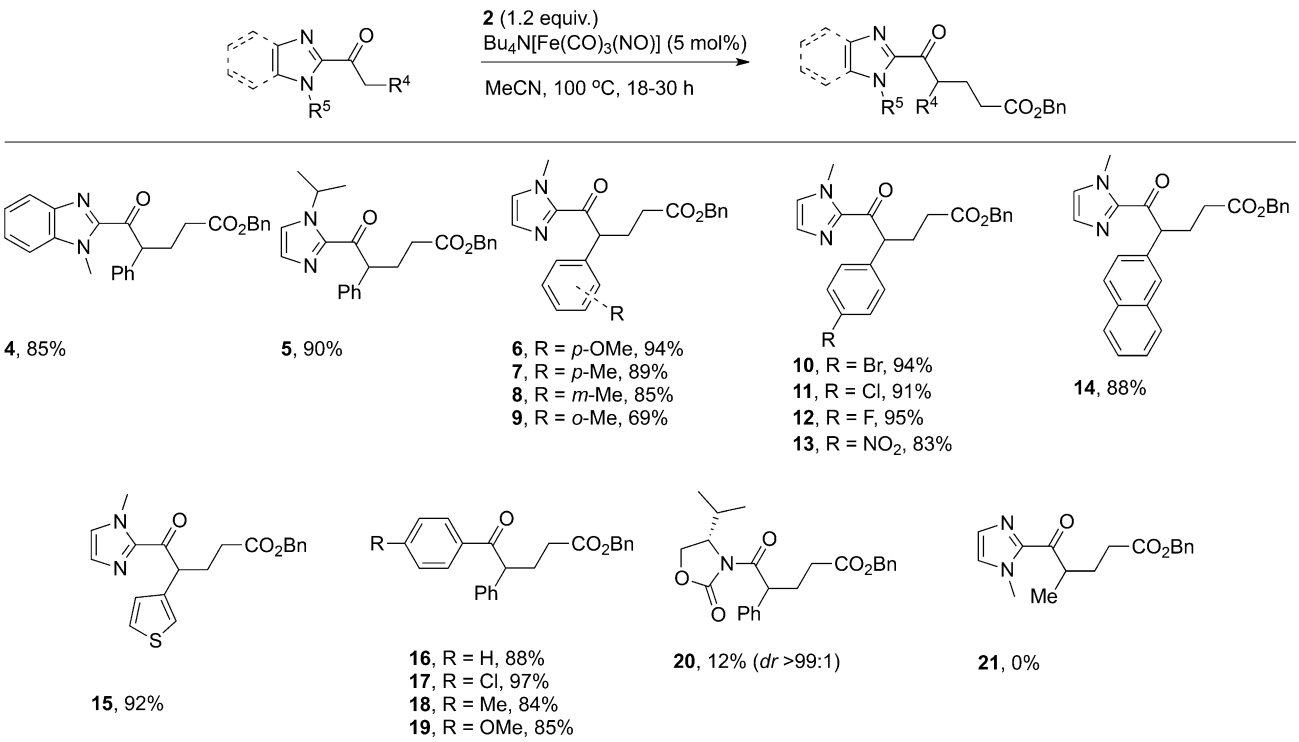


Entry	TBA[Fe] [mol%]	Solvent	Ligand [mol%]	Temp. [°C]	Yield [%][a]
1	5	DMF	–	80	76 (72)[b]
2	–	DMF	–	80	0
3	5	MeCN	–	80	84
4	5	THF	–	80	61
5	5	MTBE	–	80	36
6	5	toluene	–	80	83
7[c]	5	MeCN	–	100	90
8[c]	5	MeCN	PPh_3	100	88
9[c]	5	MeCN	***L1***	100	88
10[c]	5	MeCN	***L2***	100	76
11[c]	5	MeCN	***L3***	100	68
12[d]	**2**	**MeCN**	**–**	**100**	**90 (88)[b]**
13[d]	1	MeCN	-	100	63

[a] Yields were determined by ^{1}H NMR using mesitylene as an internal standard.
[b] Isolated yield.
[c] 18 h.
[d] 30 h.

vealed that MeCN was the solvent of choice, and **3** was formed in lower yield in other organic solvents, such as THF, MTBE or toluene (entries 3–6). Elevating the temperature to 100 °C did improve the reaction outcome, which produced **3** in 90% yield (entry 7). On the other hand, adding phosphine ligands did not promote the reaction (entries 8 and 9). Moreover, yields of the product decreased by using NHC ligands (entries 10 and 11). Lowering the catalyst loading (2 mol%) did not decrease the yield of the product, but the reaction took a longer time to complete (entry 12). Further reduction of the catalyst loading (1 mol%) indicated that the yield decreased considerably (entry 13). Interestingly, changing the catalyst from $Bu_4N[Fe(CO)_3(NO)]$ to more common bases like K_2CO_3 (stoichiometric) or Bu_4NOAc (5 mol%) led to the formation of product **3** in good yields (80 and 86%, respectively), however, saponification due to the presence of water was observed as a minor side-reaction.

With these optimized conditions established, we subsequently initiated a survey of various substituted 2-acylimidazoles in this type of C–C bond formation. The results are summarized in Scheme 1. For benzimidazole, the corresponding product **4** was formed in 85% yield. Remarkably, imidazole having an isopropyl group was a suitable substrate as well, affording adduct **5** in excellent yield. In the case of substrates containing an electron-donating group on the benzene ring, such as methoxy or methyl groups, the reactions proceeded smoothly to furnish the corresponding adducts **6–9** in 69–94% yields. With regard to substrates with electron-withdrawing groups on the benzene ring, the corresponding adducts **10–13** could be ob-



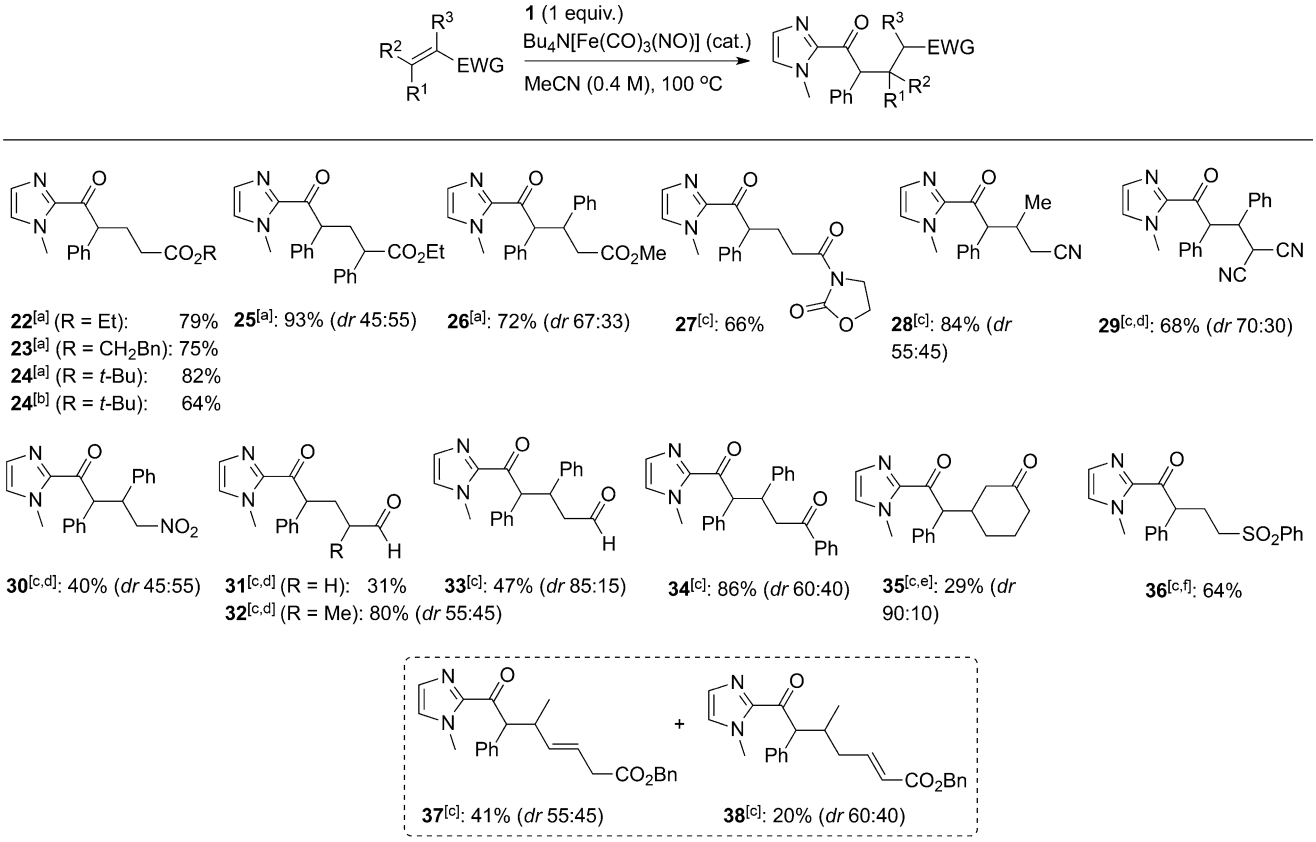
Scheme 1. Substrate scope of ketones. *Reagents and conditions*: ketone (0.2 mmol), **2** (0.24 mmol), TBA[Fe] (5 mol%), MeCN (0.5 mL), 100 °C, 18–30 h. Isolated yields).

tained in high yields. Also, the naphthyl substituent was well tolerated, which could produce adduct **14** in 88% yield. In addition, the thienyl-substituted imidazole reacted successfully to deliver **15** in 90% yield. Using aryl groups instead of imidazolyl, led to the desired products **16**–**19** efficiently. Further examination revealed that conjugate addition occurred very slowly to give the desired **20** in low yield along with more than 99:1 *dr*. Unfortunately, no desired product **21** was formed when an aliphatic ketone was used as a substrate. The starting materials were reisolated in good yields.

Subsequently, we turned our interest to investigate the scope of reactive olefins. As shown in Scheme 2, a series of acrylates underwent the conjugate addition successfully to produce the corresponding products in high yields (**22**–**26**). Broad functional group tolerance and excellent yields were observed, such as nitriles (**28** and **29**), aldehydes (**31**–**33**), ketones (**34** and **35**) and sulfone (**36**). Notably, even nitro groups (**30**) proved to be stable. Furthermore, oxazolidinone was also a competent acceptor and gave the corresponding adduct **27** in 66% yield. Interestingly, the use of sorbic acid ester under otherwise identical reaction conditions gave the desired 1,6-addition product exclusively in good combined yield of 61% as a 2:1-mixture of π-bond isomers (**37** and **38**).

The catalyst employed in this study possesses an electron-rich ferrate as active center. One could envision that these substrates are particularly sensitive toward oxidation. Having in hand a powerful catalytic protocol for the conjugate addition of acylimidazoles to acrylates, we were wondering whether we could extend the substrate scope also to quinones. These substrates are potent oxidants that are known to catalyze the *in-situ* oxidation of precious metals. On the other hand side they are also attractive Michael acceptors. To analyze the competition between oxidation *versus* Michael-addition, 2,3-dimethylbenzoquinone was subjected to the standard conditions, under which only low yields of the Michael product were observed. However, upon changing the solvent to ethanol the undesired oxidation of the ferrate was significantly reduced and, to our surprise, benzofuranone **39** was formed as the sole product. To our delight the reaction proved to be applicable to various quinones using different acylimidazoles (Scheme 3). To the best of our knowledge this catalytic one-pot transformation represents a new approach toward substituted 4-hydroxybenzofuranones, most literature reported methods rely on the use of overstoichiometric amounts of acid or base plus extended heating periods.

The method proved to be broadly applicable giving the desired products in moderate to good yields. In the case of electron-poor benzoquinones however a fast oxidation of the catalyst and no conversion to the corresponding benzofuranone **45** was observed.



[a] Reaction conditions A.
[b] Reaction conditions B:
[c] Reaction conditions C:
[d] At 60 °C.
[e] At 80 °C.
[f] Ratio of **1** to olefin is 1.2:1.0.

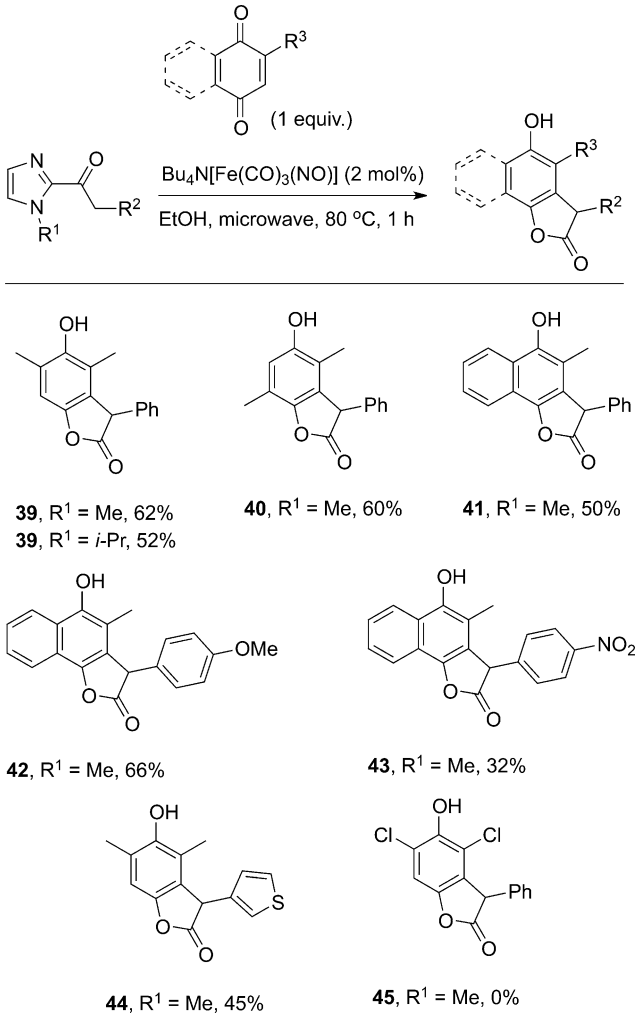
Scheme 2. TBA[Fe]-catalyzed conjugate addition – olefin scope. *Reaction conditions A:* **1** (0.4 mmol), olefin (0.48 mmol), TBA[Fe] (2 mol%), MeCN (1 mL), 100 °C, 30 h. *Reaction conditions B:* **1** (2 mmol), olefin (2.4 mmol), TBAFe (5 mol%), MeCN (5 mL), 100 °C, 60 h. *Reaction conditions C:* **1** (0.2 mmol), olefin (0.24 mmol), TBAFe (5 mol%), MeCN (0.5 mL), 100 °C, 20-48 h. Isolated yields. The *dr* values were determined by ^{1}H NMR of crude products.

From a mechanistic point of view, we propose a Michael-type addition of the acylimidazole plus a concomitant transesterification with C–C bond scission to be operative. In order to support this model we performed several test experiments. Treating 2,6-dimethylbenzoquinone with 2-acylimidazole **1** at 40 °C for one hour under microwave conditions led to the formation of the Michael addition product **46** in good yield [Eq. (1), Scheme 4]. Product **46** collapses upon heating to 80 °C to give the observed benzofuranone **39** in good yield even in the absence of TBA[Fe] [Eq. (2), Scheme 4].

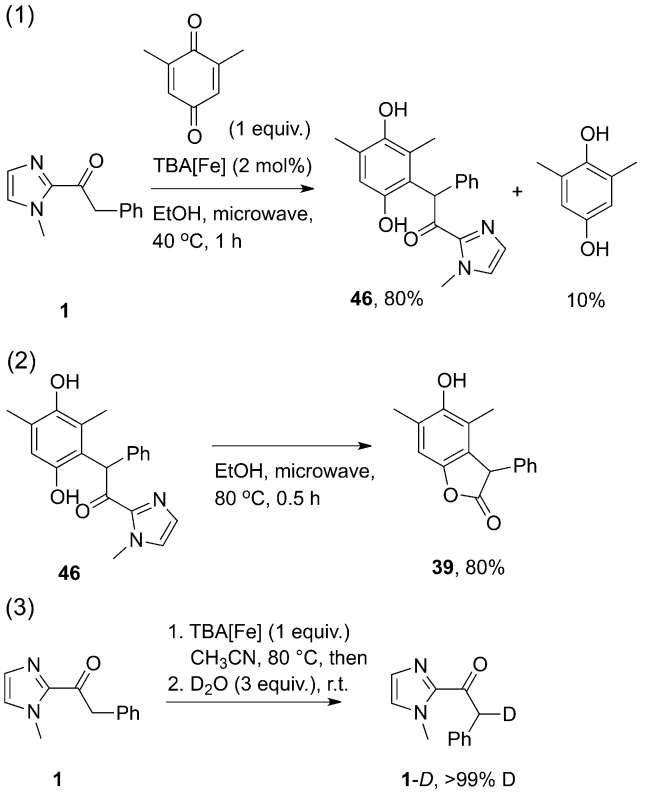
Finally, heating one equivalent of acylimidazole **1** with one equivalent of TBA[Fe] and subsequent addition of D_2O to the reaction mixture led to quantitative generation of the α-monodeuterated acylimidazole **1**-*D* [Eq. (3), Scheme 4]. This result indicates an acid-base-type mechanism to be operative.

Conclusions

Herein we report the $Bu_4N[Fe(CO)_3(NO)]$-catalyzed Michael-type addition of acylimidazoles to olefins. The reaction proceeds in good to excellent yields on a broad scope of substrates. In the case of quinone-type substrates a fast Michael addition is observed that is followed by an internal cyclization with substitution of the imidazole moiety upon heating. A range of substituted benzofuranones were obtained in good to excellent yields. Experimental indications for an acid-base-type rather than a reductive C–H bond activation were obtained. Hence, these results provide another insight into probable mechanistic pathways in TBA[Fe]-catalyzed C–H activations and will serve as guidelines for further studies in this field.



Scheme 3. TBA[Fe]-catalyzed conjugate addition to quinones. *Reagents and conditions*: benzoquinone (0.4 mmol), 2-acylimidazole (0.48 mmol), TBA[Fe] (2 mol%), EtOH (1 mL), microwave (80 °C, 1 h). Isolated yields. 15–35% of hydroquinones were formed.



Scheme 4. TBA[Fe]-catalyzed conjugate addition to quinones.

Experimental Section

General Remarks

All reactions sensitive to moisture and/or air were carried out under an atmosphere of dry nitrogen (N_2) using anhydrous solvents. Solvents were either dried by passing them through commercially available columns (*n*-pentane, CH_2Cl_2) or distilling them from CaH_2 (CCl_4, $C_2H_2Cl_4$, $C_2H_4Cl_2$, PhH). THF was freshly distilled from Na/benzophenone (ketyl radical).

General Procedure for Michael Addition

Under a nitrogen atmosphere, a dried Schlenk tube was charged with the catalyst TBA[Fe] (2 or 5 mol%), the corresponding 2-acylimidazole (0.4 mmol). Then MeCN (1 mL, 0.4 M) was added *via* syringe, followed by the corresponding olefin (0.48 mmol, 1.2 equiv.). The reaction mixture was stirred at 100 °C for the indicated time. Purification *via* column chromatography on silica gel completed the procedure.

Benzyl 5-(1-methyl-1*H*-imidazol-2-yl)-5-oxo-4-phenylpentanoate (3): 30 h; yield: 62 mg (86%); colorless oil; R_f: 0.66 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.41$ (d, $J = 6.9$ Hz, 2*H*), 7.32–7.25 (m, 7*H*), 7.22–7.17 (m, 1*H*), 7.11 (s, 1*H*), 6.96 (s, 1*H*), 5.18 (t, $J = 6.6$ Hz, 1*H*), 5.07 (s, 2*H*), 3.92 (s, 3*H*), 2.51–2.19 (m, 4*H*); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 191.8$, 172.8, 142.6, 138.4, 135.9, 129.3, 128.7, 128.6, 128.5, 128.15, 128.10, 127.4, 127.1, 66.2, 51.8, 36.1, 32.2, 27.7; IR (film): $\nu = 3063$, 3031, 2950, 1731, 1670, 1401, 1153, 911, 740, 698 cm^{-1}; MS (EI, 70 eV): *m*/*z* (%) = 362 (30), 271 (5), 213 (100), 199 (33), 109 (27), 91 (45), 65 (3); HR-MS (ESI): *m*/*z* = 385.1538, calcd. for $C_{22}H_{22}N_2NaO_3$ $[M+Na]^+$: 385.1523.

Benzyl 5-(1-methyl-1*H*-benzo[*d*]imidazol-2-yl)-5-oxo-4-phenylpentanoate (4): 20 h; yield: 70 mg (85%); colorless oil; R_f: 0.53 (petroleum ether/ethyl acetate 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.86$ (d, $J = 8.8$ Hz, 1*H*), 7.45 (d, $J = 7.6$ Hz, 2*H*), 7.36 (t, $J = 7.4$ Hz, 1*H*), 7.31–7.24 (m, 9*H*), 7.17 (t, $J = 7.4$ Hz, 1*H*), 5.44–5.41 (m, 1*H*), 5.08 (d, $J = 12.5$ Hz, 1*H*), 5.05 (d, $J = 12.5$ Hz, 1*H*), 3.99 (s, 3*H*), 2.57–2.29 (m, 4*H*); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 194.5$, 172.7, 145.7, 141.6, 137.7, 137.1, 135.8, 128.8, 128.6, 128.4, 128.1, 128.0, 127.2, 125.8, 123.5, 122.0, 110.3, 66.2, 52.5, 32.1, 32.0, 27.5; IR (film): $\nu = 3063$, 3032, 2948, 1732, 1681, 1456, 907, 727 cm^{-1}; MS (EI, 70 eV): *m*/*z* (%) = 412 (16), 263 (100), 249 (19), 159 (16), 91 (28); HR-MS (ESI): *m*/*z* = 435.1696, calcd. for $C_{26}H_{24}N_2NaO_3$ $[M+Na]^+$: 435.1679.

Benzyl 5-(1-isopropyl-1*H*-imidazol-2-yl)-5-oxo-4-phenylpentanoate (5): 30 h; yield: 70 mg (90%); colorless oil; R_f: 0.50 (petroleum ether/ethyl acetate 2:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42–7.39 (m, 2*H*), 7.34–7.25 (m, 7*H*), 7.22–7.14 (m, 3*H*), 5.53–5.39 (m, 1*H*), 5.24–5.19 (m, 1*H*), 5.07 (s, 2*H*), 2.51–2.19 (m, 4*H*), 1.43 (d, J = 6.6 Hz, 3*H*), 1.30 (d, J = 1.4 Hz, 3*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 191.9, 172.8, 142.0, 138.6, 135.9, 129.7, 128.7, 128.6, 128.4, 128.14, 128.09, 127.0, 121.5, 66.2, 52.3, 49.2, 32.2, 27.9, 23.5, 23.4; IR (film): ν = 3031, 2965, 1732, 1669, 1391, 1151, 697 cm^{-1}; MS (EI, 70 eV): m/z (%) = 390 (50), 241 (100), 227 (30), 137 (29), 91 (50); HR-MS (ESI): m/z = 413.1836, calcd. for $C_{24}H_{26}N_2NaO_3$ $[M+Na]^+$: 413.1836.

Benzyl 4-(4-methoxyphenyl)-5-(1-methyl-1*H*-imidazol-2-yl)-5-oxopentanoate (6): 30 h; yield: 74 mg (94%); white solid; mp 86–87 °C; R_f: 0.60 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.34–7.29 (m, 7*H*), 7.11 (s, 1*H*), 6.96 (s, 1*H*), 6.83–7.80 (m, 2*H*), 5.14–5.07 (m, 3*H*), 3.92 (s, 3*H*), 3.74 (s, 3*H*), 2.45–2.16 (m, 4*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 192.0, 172.8, 158.7, 142.6, 135.9, 130.3, 129.7, 129.2, 128.4, 128.12, 128.08, 127.3, 114.0, 66.1, 55.1, 50.8, 36.1, 32.2, 27.6; IR (film): ν = 3033, 2954, 1731, 1669, 1509, 1400, 1246, 1152, 697 cm^{-1}; MS (EI, 70 eV): m/z (%) = 392 (68), 243 (100), 91 (96); HR-MS (ESI): m/z = 415.1645, calcd. for $C_{23}H_{24}N_2NaO_4$ $[M+Na]^+$: 415.1639.

Benzyl 5-(1-methyl-1*H*-imidazol-2-yl)-5-oxo-4-(*p*-tolyl)-pentanoate (7): 30 h, yield: 67 mg (89%); colorless oil; R_f: 0.69 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36–7.26 (m, 7*H*), 7.10–7.07 (m, 3*H*), 6.94 (s, 1*H*), 5.13 (t, J = 7.9 Hz, 1*H*), 5.06 (s, 2*H*), 3.90 (s, 3*H*), 2.46–2.20 (m, 7*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 191.9, 172.8, 142.6, 136.7, 135.9, 135.3, 129.3, 129.2, 128.5, 128.4, 128.1, 128.0, 127.3, 66.1, 51.4, 36.1, 32.2, 27.6, 21.0; IR (film): ν = 3031, 2949, 1731, 1669, 1400, 1152, 696 cm^{-1}; MS (EI, 70 eV): m/z (%) = 376 (38), 227 (100), 109 (15), 91 (77); HR-MS (ESI): m/z = 399.1669, calcd. for $C_{23}H_{24}N_2O_3Na$ $[M+Na]^+$: 399.1679.

Benzyl 5-(1-methyl-1*H*-imidazol-2-yl)-5-oxo-4-(*m*-tolyl)-pentanoate (8): 30 h; yield: 64 mg (85%); colorless oil; R_f: 0.73 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36–7.27 (m, 5*H*), 7.22–7.13 (m, 3*H*), 7.11 (s, 1*H*), 7.01 (d, J = 7.2 Hz, 1*H*), 6.96 (s, 1*H*), 5.14 (t, J = 7.9 Hz, 1*H*), 5.07 (s, 2*H*), 3.93 (s, 3*H*), 2.49–2.18 (m, 7*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 191.9, 172.8, 142.6, 138.3, 138.2, 135.9, 129.3, 129.2, 128.4, 128.12, 128.07, 127.9, 127.4, 125.7, 66.1, 51.7, 36.1, 32.2, 27.8, 21.4; IR (film): ν = 3033, 2953, 1731, 1670, 1402, 907, 726 cm^{-1}; MS (EI, 70 eV): m/z (%) = 376 (24), 227 (100), 109 (18), 91 (49); HR-MS (ESI): m/z = 399.1677, calcd. for $C_{23}H_{24}N_2NaO_3$ $[M+Na]^+$: 399.1679.

Benzyl 5-(1-methyl-1*H*-imidazol-2-yl)-5-oxo-4-(*o*-tolyl)-pentanoate (9): 30 h; yield: 52 mg (69%); colorless oil; R_f: 0.68 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36–7.27 (m, 6*H*), 7.15–7.07 (m, 3*H*), 7.05 (s, 1*H*), 6.93 (s, 1*H*), 5.40 (t, J = 7.3 Hz, 1*H*), 5.07 (s, 2*H*), 3.92 (s, 3*H*), 2.56 (s, 3*H*), 2.46–2.12 (m, 7*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 192.4, 172.9, 143.0, 137.2, 137.1, 135.9, 130.6, 129.2, 128.5, 128.2, 128.1, 127.2, 127.0, 126.9, 126.1, 66.2, 47.2, 36.0, 32.1, 28.1, 20.0; IR (film): ν = 3032, 2954, 1731, 1670, 1401, 1152, 696 cm^{-1}. MS (EI, 70 eV): m/z (%) = 376 (23), 227 (96), 199 (100), 109 (29), 91 (96); HR-MS (ESI): m/z = 399.1693, calcd. for $C_{23}H_{24}N_2NaO_3$ $[M+Na]^+$: 399.1679.

Benzyl 4-(4-bromophenyl)-5-(1-methyl-1*H*-imidazol-2-yl)-5-oxopentanoate (10): 24 h; yield: 83 mg (94%); colorless oil; R_f: 0.57 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39 (d, J = 8.5 Hz, 2*H*), 7.32–7.25 (m, 7*H*), 7.11 (s, 1*H*), 6.98 (s, 1*H*), 5.18–5.02 (m, 3*H*), 3.92 (s, 3*H*), 2.47–2.17 (m, 4*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 191.1, 172.6, 142.4, 137.4, 135.8, 131.6, 130.4, 129.4, 128.4, 128.12, 128.11, 127.6, 121.1, 66.2, 51.1, 36.1, 32.0, 27.5; IR (film): ν = 3033, 2953, 1731, 1670, 1399, 1153, 729 cm^{-1}; MS (EI, 70 eV): m/z (%) = 442 (37), 440 (37), 293 (90), 291 (91), 109 (65), 91 (100); HR-MS (ESI): m/z = 463.0658, calcd. for $C_{22}H_{21}BrN_2NaO_3$ $[M+Na]^+$: 463.0639.

Benzyl 4-(4-chlorophenyl)-5-(1-methyl-1*H*-imidazol-2-yl)-5-oxopentanoate (11): 24 h; yield: 72 mg (91%); colorless oil; R_f: 0.59 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39–7.32 (m, 7*H*), 7.28–7.24 (m, 2*H*), 7.14 (s, 1*H*), 7.01 (s, 1*H*), 5.19 (t, J = 7.8 Hz, 1*H*), 5.10 (s, 2*H*), 3.95 (s, 3*H*), 2.50–2.20 (m, 4*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 191.3, 172.6, 142.4, 136.9, 135.8, 133.0, 130.0, 129.4, 128.7, 128.5, 128.2, 128.1, 127.6, 66.2, 51.0, 36.1, 32.1, 27.6; IR (film): ν = 3032, 2952, 1730, 1670, 1399, 1152, 696 cm^{-1}; MS (EI, 70 eV): m/z (%) = 396 (35), 247 (100), 109 (39), 91 (55); HR-MS (ESI): m/z = 419.1122, calcd. for $C_{22}H_{21}ClN_2NaO_3$ $[M+Na]^+$: 419.1133.

Benzyl 4-(4-fluorophenyl)-5-(1-methyl-1*H*-imidazol-2-yl)-5-oxopentanoate (12): 24 h; yield: 72 mg (95%); colorless oil; R_f: 0.62 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.27 (m, 7*H*), 7.12 (s, 1*H*), 7.00–6.92 (m, 3*H*), 5.17 (t, J = 7.8 Hz, 1*H*), 5.09 (d, J = 12.5 Hz, 1*H*), 5.05 (d, J = 12.5 Hz, 1*H*), 3.93 (s, 3*H*), 2.49–2.15 (m, 4*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 191.6, 172.7, 161.9 (d, J = 243.9 Hz), 142.4, 135.8, 134.1 (d, J = 3.1 Hz), 130.2 (d, J = 7.9 Hz), 129.3, 128.5, 128.14, 128.12, 127.5, 115.4 (d, J = 21.2 Hz), 66.2, 50.8, 36.1, 32.1, 27.8; ^{19}F NMR (376 MHz, $CDCl_3$): δ −115.50 to −115.53 (m); IR (film): ν () 3034, 2927, 1731, 1670, 1400, 1154, 697 cm^{-1}; MS (EI, 70 eV): m/z (%)380 (44), 231 (100), 109 (39), 91 (59); HR-MS (ESI): m/z = 403.1429, calcd. for $C_{22}H_{21}FN_2NaO_3$ $[M+Na]^+$: 403.1428.

Benzyl 5-(1-methyl-1*H*-imidazol-2-yl)-4-(4-nitrophenyl)-5-oxopentanoate (13): 24 h; yield: 68 mg (83%); light yellow oil; R_f: 0.51 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.13 (d, J = 8.7 Hz, 2*H*), 7.59 (d, J = 8.7 Hz, 2*H*), 7.37–7.30 (m, 5*H*), 7.13 (s, 1*H*), 7.03 (s, 1*H*), 5.34 (t, J = 7.6 Hz, 1*H*), 5.08 (s, 2*H*), 3.95 (s, 3*H*), 2.57–2.18 (m, 4*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 190.2, 172.4, 147.1, 146.1, 142.2, 135.7, 129.7, 129.6, 128.5, 128.2, 128.0, 123.8, 66.4, 51.5, 36.2, 32.0, 27.6; IR (film): ν = 3033, 2952, 1731, 1671, 1344, 1155, 698 cm^{-1}; MS (EI, 70 eV): m/z (%) = 407 (19), 258 (100), 244 (47), 109 (75), 91 (59); HR-MS (ESI): m/z = 430.1397, calcd. for $C_{22}H_{21}N_3NaO_5$ $[M+Na]^+$: 430.1373.

Benzyl 5-(1-methyl-1*H*-imidazol-2-yl)-4-(naphthalen-2-yl)-5-oxopentanoate (14): 30 h; yield: 73 mg (88%); colorless oil; R_f: 0.54 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.85 (s, 1*H*), 7.79–7.74 (m, 3*H*), 7.57 (dd, J = 8.5 Hz, J = 1.7 Hz, 1*H*), 7.44–7.37 (m, 2*H*), 7.34–7.30 (m, 5*H*), 7.10 (s, 1*H*), 6.92 (s, 1*H*), 5.35 (t, J = 7.5 Hz, 1*H*), 5.08 (d, J = 12.4 Hz, 1*H*), 5.03 (d, J = 12.4 Hz, 1*H*), 3.90 (s, 3*H*), 2.59–2.30 (m, 4*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ =

191.6, 172.8, 142.6, 135.9, 135.8, 133.4, 132.5, 129.3, 128.4, 128.3, 128.12, 128.08, 127.8, 127.7, 127.5, 127.4, 126.6, 126.0, 125.7, 66.2, 51.9, 36.1, 32.2, 27.6; IR (film): ν = 3057, 2955, 1730, 1668, 1400, 1154, 730 cm^{-1}; MS (EI, 70 eV): *m/z* (%) = 412 (55), 263 (100), 109 (12), 91 (48); HR-MS (ESI): *m/z* = 435.1699, calcd. for $C_{26}H_{24}N_2NaO_3$ $[M+Na]^+$: 435.1690.

Benzyl 5-(1-methyl-1*H*-imidazol-2-yl)-5-oxo-4-(3-thienyl)-pentanoate (15): 30 h; yield: 68 mg (92%); colorless oil; R_f: 0.56 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36–7.29 (m, 5*H*), 7.23–7.22 (m, 2*H*), 7.14–7.12 (m, 2*H*), 6.99 (s, 1*H*), 5.36–5.31 (m, 1*H*), 5.07 (s, 2*H*), 3.94 (s, 3*H*), 2.45–2.29 (m, 4*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 191.4, 172.8, 142.4, 138.6, 135.9, 129.3, 128.5, 128.2, 128.1, 127.6, 125.6, 122.8, 66.2, 47.1, 36.2, 32.1, 27.7; IR (film): ν = 3033, 2950, 1730, 1670, 1401, 1154, 697 cm^{-1}; MS (EI, 70 eV): *m/z* (%) = 368 (61), 219 (100), 205 (41), 109 (38), 91 (93); HR-MS (ESI): *m/z* = 391.1083, calcd. for $C_{20}H_{20}N_2NaO_3S$ $[M+Na]^+$: 391.1098.

Benzyl 5-oxo-4,5-diphenylpentanoate (16): 30 h; yield: 63 mg (88%); colorless oil; R_f: 0.33 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.91–7.88 (m, 2*H*), 7.48–7.42 (m, 1*H*), 7.37–7.16 (m, 12*H*), 5.12 (d, *J* = 12.3 Hz, 1*H*), 5.07 (d, *J* = 12.3 Hz, 1*H*), 4.64 (t, *J* = 7.2 Hz, 1*H*), 2.53–2.42 (m, 1*H*), 2.35 (t, *J* = 6.9 Hz, 2*H*), 2.24–2.13 (m, 1*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.2, 173.0, 138.7, 136.5, 135.9, 132.9, 129.0, 128.7, 128.5, 128.4, 128.26, 128.21, 127.2, 66.2, 52.2, 31.8, 28.7; IR (film): ν = 3030, 2939, 1730, 1678, 1150, 694 cm^{-1}; MS (ESI): *m/z* = 381.2 $(M+Na)^+$; HR-MS (ESI): *m/z* = 381.1455, calcd. for $C_{24}H_{22}NaO_3$ $[M+Na]^+$: 381.1461.

Benzyl 5-(4-chlorophenyl)-5-oxo-4-phenylpentanoate (17): 30 h; yield: 153 mg (97%); colorless oil; R_f: 0.4 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.83–7.80 (m, 2*H*), 7.35–7.18 (m, 12*H*), 5.14–5.06 (m, 2*H*), 4.57 (t,, *J* = 7.18 Hz, 1*H*), 2.51–2.40 (m, 1*H*), 2.36–2.31 (m, 2*H*), 2.22–2.11 (m, 1*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.0, 172.9, 139.3, 138.4, 130.1, 129.2, 128.8, 128.7, 128.3, 128.3, 128.2, 127.5, 66.3, 52.3, 31.7, 28.6; IR (film): ν = 3063, 3030, 2943, 1731, 1255, 1092, 698 cm^{-1}.

Benzyl 5-oxo-4-phenyl-5-(*p*-tolyl)pentanoate (18): 30 h; yield: 124 mg (84%); colorless oil; R_f: 0.38 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 8.28 Hz, 2*H*), 7.37–7.13 (m, 12*H*), 5.09 (d, *J* = 3.72 Hz, 2*H*), 4.61 (t, *J* = 7.32 Hz, 1*H*), 2.51–2.42 (m, 1*H*), 2.36–2.32 (m, 5*H*), 2.22–2.13 (m, 1*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.8, 173.1, 143.7, 138.9, 135.9, 134.0, 129.2, 128.9, 128.8, 128.5, 128.3, 128.2, 127.2, 66.2, 52.1, 312.9, 28.7, 21.6; IR (film): ν = 3061, 3030, 2941, 1730, 1674, 1150, 697 cm^{-1}; MS (ESI): *m/z* = 395.16 $(M+Na)^+$; HR-MS (ESI): *m/z* = 395.1611, calcd. for $C_{25}H_{24}NaO_3$ $[M+Na]^+$: 395.1618.

Benzyl 5-(4-methoxyphenyl)-5-oxo-4-phenylpentanoate (19): 30 h; yield: 131 mg (85%); colorless oil; R_f: 0.16 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91–7.88 (m, 2*H*), 7.37–7.16 (m, 10*H*), 6.85–6.80 (m, 2*H*), 5.09 (d, *J* = 2.84 Hz, 2*H*), 4.59 (t, *J* = 7.32 Hz, 1*H*), 3.80 (s, 3*H*), 2.50–2.41 (m, 1*H*), 2.34 (t, *J* = 14.00 Hz, 2*H*), 2.21–2.12 (m, 1*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.7, 173.1, 163.3, 139.2, 135.9, 131.0, 129.6, 128.9, 128.6, 128.3, 128.2, 127.2, 113.7, 66.2, 55.4, 51.9, 31.9, 28.8; IR (film): ν = 3062, 3030, 2936, 2839, 1729, 1668, 1254, 1164, 697 cm^{-1}; MS (ESI): *m/z* = 411.16 $(M+Na)^+$; HR-MS (ESI): *m/z* = 411.1467, calcd. for $C_{25}H_{24}NaO_4$ $[M+Na]^+$: 411.1563.

Benzyl 5-[(*S*)-4-isopropyl-2-oxooxazolidin-3-yl]-5-oxo-4-phenylpentanoate (20): 48 h; yield: 18 mg (12%); colorless oil; R_f: 0.48 (petroleum ether/ethyl acetate 3:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.22 (m, 10*H*), 5.14–5.03 (m, 3*H*), 4.46 (dt, *J* = 8.6 Hz, *J* = 3.5 Hz, 1*H*), 4.20 (t, *J* = 8.7 Hz, 1*H*), 4.08 (dd, *J* = 9.1 Hz, *J* = 3.4 Hz, 1*H*), 2.44–2.10 (m, 5*H*), 0.78 (d, *J* = 7.1 Hz, 3*H*), 0.40 (d, *J* = 6.9 Hz, 3*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.2, 172.7, 153.3, 137.8, 135.9, 128.6, 128.5, 128.25, 128.19, 127.5, 66.3, 62.9, 58.0, 48.1, 32.0, 28.2, 27.8, 17.7, 14.0; IR (film): ν = 3032, 2963, 1774, 1732, 1694, 1372, 1203, 698 cm^{-1}; MS (EI, 70 eV): *m/z* (%) = 409 (10), 318 (12), 280 (14), 171 (11), 130 (19), 91 (100); HR-MS (ESI): *m/z* = 432.1782, calcd. for $C_{24}H_{27}NNaO_5$ $[M+Na]^+$: 432.1781.

Ethyl 5-(1-methyl-1*H*-imidazol-2-yl)-5-oxo-4-phenylpentanoate (22): 30 h; yield: 95 mg (79%); colorless oil; R_f: 0.54 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.45–7.41 (m, 2*H*), 7.31–7.25 (m, 2*H*), 7.23–7.16 (m, 1*H*), 7.11 (s, 1*H*), 6.96 (s, 1*H*), 5.20–5.14 (m, 1*H*), 4.08 (q, *J* = 7.2 Hz, 2*H*), 3.92 (s, 3*H*), 2.47–2.16 (m, 4*H*), 1.21 (t, *J* = 7.2 Hz, 3*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 191.9, 173.0, 142.6, 138.5, 129.3, 128.7, 128.6, 127.4, 127.1, 60.3, 51.8, 36.1, 32.3, 27.8, 14.1; IR (film): ν = 2979, 1728, 1670, 1400, 1154, 739, 698 cm^{-1}; MS (EI, 70 eV): *m/z* (%) = 300 (18), 255 (16), 213 (100), 199 (19), 117 (21), 109 (21), 82 (5); HR-MS (ESI): *m/z* = 323.1364, calcd. for $C_{17}H_{20}N_2NaO_3$ $[M+Na]^+$: 323.1366.

Phenethyl 5-(1-methyl-1*H*-imidazol-2-yl)-5-oxo-4-phenylpentanoate (23): 30 h; yield: 112 mg (75%); colorless oil; R_f: 0.58 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43–7.40 (m, 2*H*), 7.31–7.17 (m, 8*H*), 7.12 (s, 1*H*), 6.97 (s, 1*H*), 5.18–5.13 (m, 1*H*), 4.24 (t, *J* = 7.2 Hz, 2*H*), 3.93 (s, 3*H*), 2.89 (t, *J* = 7.2 Hz, 2*H*), 2.44–2.15 (m, 4*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 191.8, 172.9, 142.6, 138.4, 137.8, 129.3, 128.8, 128.7, 128.6, 128.4, 127.4, 127.1, 126.5, 64.8, 51.8, 36.2, 35.0, 32.2, 27.7; IR (film): ν = 3028, 2955, 1729, 1670, 1400, 1154, 742, 698 cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 376 (15), 213 (100), 199 (22), 105 (35); HR-MS (ESI): *m/z* = 399.1683, calcd. for $C_{23}H_{24}N_2NaO_3$ $[M+Na]^+$: 399.1690.

***tert*-Butyl 5-(1-methyl-1*H*-imidazol-2-yl)-5-oxo-4-phenylpentanoate (24):** 30 h; yield: 108 mg (82%); white solid; mp 108–109 °C; R_f: 0.69 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.44–7.41 (m, 2*H*), 7.31–7.26 (m, 2*H*), 7.22–7.17 (m, 1*H*), 7.11 (s, 1*H*), 6.97 (s, 1*H*), 5.17 (t, *J* = 7.5 Hz, 1*H*), 3.94 (s, 3*H*), 2.44–2.31 (m, 1*H*), 2.22–2.14 (m, 3*H*), 1.41 (s, 9*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 192.0, 172.3, 142.7, 138.6, 129.2, 128.7, 128.6, 127.4, 127.0, 80.2, 51.8, 36.1, 33.5, 28.0; IR (film): ν = 2976, 1723, 1671, 1401, 1144, 740, 698 cm^{-1}; MS (EI, 70 eV): *m/z* (%) = 328 (10), 272 (18), 255 (28), 213 (100), 199 (30), 109 (16), 82 (13); HR-MS (ESI): *m/z* = 351.1686, calcd. for $C_{19}H_{24}N_2NaO_3$ $[M+Na]^+$: 351.1690.

Ethyl 5-(1-methyl-1*H*-imidazol-2-yl)-5-oxo-2,4-diphenylpentanoate (25): 30 h; yield: 70 mg (93%); *dr* = 45:55; colorless oil; R_f: 0.43 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.36 (m, 2*H*), 7.30–7.16 (m, 8*H*), 7.08 (d, *J* = 0.7 Hz, 0.48*H*), 7.04 (d, *J* = 0.7 Hz, 0.52*H*), 6.93 (s, 0.48*H*), 6.89 (s, 0.52*H*), 5.16–5.06 (m, 1*H*), 4.17–3.97 (m, 2*H*), 3.91 (s, 1.44*H*), 3.83 (s, 1.56*H*), 3.50–3.42 (m, 1*H*), 2.95–2.27 (m, 2*H*), 1.21–1.10 (m, 3*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 191.6, 191.5, 173.46, 173.36, 142.54,

142.51, 139.0, 138.7, 138.6, 138.3, 129.3, 129.1, 128.8, 128.66, 128.58, 128.53, 128.50, 128.4, 128.2, 127.8, 127.21, 127.19, 127.0, 60.72, 60.70, 50.5, 50.4, 49.7, 49.2, 36.3, 36.2, 36.1, 36.0, 14.0, 13.9; IR (film): ν = 3030, 3031, 2980, 1726, 1671, 1401, 1154, 908, 727, 697 cm^{-1}; MS (EI, 70 eV): *m/z* (%) = 376 (3), 213 (100), 109 (6), 91 (4); HR-MS (ESI): *m/z* = 399.1684, calcd. for $C_{23}H_{24}N_2NaO_3$ $[M+Na]^+$: 399.1679.

Methyl 5-(1-methyl-1*H*-imidazol-2-yl)-5-oxo-3,4-diphenylpentanoate (26): 48 h; yield: 52 mg (72%); *dr* = 67:33; colorless oil; R_f: 0.56 (petroleum ether/ethyl acetate 1:1). Major isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.62–7.59 (m, 2*H*), 7.40–7.31 (m, 4*H*), 7.27–7.18 (m, 3*H*), 7.13–7.07 (m, 1*H*), 7.04 (s, 1*H*), 6.82 (s, 1*H*), 5.62 (d, *J* = 12.0 Hz, 1*H*), 4.15–4.06 (m, 1*H*), 3.70 (s, 3*H*), 3.39 (s, 3*H*), 2.54–2.39 (m, 2*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 190.6, 172.3, 142.9, 141.8, 137.1, 129.4, 129.1, 128.8, 128.26, 128.20, 127.5, 127.1, 126.6, 57.5, 51.3, 44.6, 39.5, 35.9; IR (film): ν = 3062, 3029, 2951, 1736, 1673, 1402, 1155, 700 cm^{-1}; MS (EI, 70 eV): *m/z* (%) = 362 (70), 289 (64), 200 (100), 121 (47), 109 (26), 82 (13); HR-MS (ESI): *m/z* = 385.1539, calcd. for $C_{22}H_{22}N_2NaO_3$ $[M+Na]^+$: 385.1523. Minor isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.26–7.23 (m, 2*H*), 7.15 (s, 1*H*), 7.13–6.98 (m, 9*H*), 5.49 (d, *J* = 11.6 Hz, 1*H*), 4.13–4.03 (m, 1*H*), 3.97 (s, 3*H*), 3.48 (s, 3*H*), 2.77 (d, *J* = 7.4 Hz, 2*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 191.6, 172.0, 143.1, 140.9, 137.0, 129.4, 129.3, 128.3, 128.1, 127.9, 127.6, 126.8, 126.4, 57.9, 51.4, 44.9, 39.8, 36.3; IR (film): ν = 3062, 3029, 2951, 1736, 1668, 1401, 699 cm^{-1}; MS (EI, 70 eV): *m/z* (%) = 362 (97), 289 (100), 200 (95), 121 (61), 109 (34), 82 (19); HR-MS (ESI): *m/z* = 385.1530, calcd. for $C_{22}H_{22}N_2NaO_3$ $[M+Na]^+$: 385.1523.

1-(1-Methyl-1*H*-imidazol-2-yl)-5-(2-oxooxazolidin-3-yl)-2-phenylpentane-1,5-dione (27): 30 h; yield: 45 mg (66%); white solid; mp 171–172 °C; R_f: 0.22 (petroleum ether/ethyl acetate 1:2); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.43 (d, *J* = 7.2 Hz, 2*H*), 7.29–7.26 (m, 2*H*), 7.21–7.18 (m, 1*H*), 7.11 (s, 1*H*), 6.97 (s, 1*H*), 5.22 (t, *J* = 7.7 Hz, 1*H*), 4.33 (t, *J* = 8.6 Hz, 2*H*), 3.96–3.93 (m, 5*H*), 2.93–2.90 (m, 2*H*), 2.51–2.44 (m, 1*H*), 2.31–2.24 (m, 1*H*); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 191.8, 172.7, 153.3, 142.7, 138.6, 129.2, 128.7, 128.5, 127.4, 127.0, 61.9, 51.6, 42.4, 36.1, 32.9, 27.2; IR (film): ν = 2925, 1772, 1695, 1669, 1385, 700 cm^{-1}; MS (EI, 70 eV): *m/z* (%) = 341 (15), 213 (100), 109 (17), 88 (13); HR-MS (ESI): *m/z* = 364.1272, calcd. for $C_{18}H_{19}N_3NaO_4$ $[M+Na]^+$: 364.1268.

3-Methyl-5-(1-methyl-1*H*-imidazol-2-yl)-5-oxo-4-phenylpentanenitrile (28): 48 h; yield: 45 mg (84%); *dr* = 55:45; colorless oil; R_f: 0.33 (petroleum ether/acetone 3:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46–7.39 (m, 2*H*), 7.33–7.20 (m, 3*H*), 7.14 (s, 0.47*H*), 7.13 (s, 0.53*H*), 6.99 (s, 1*H*), 5.08 (d, *J* = 11.2 Hz, 0.47*H*), 5.03 (d, *J* = 10.8 Hz, 0.53*H*), 3.944 (s, 1.41*H*), 3.939 (s, 1.59*H*), 2.87–2.75 (m, 1*H*), 2.52 (dd, *J* = 16.7 Hz, *J* = 3.9 Hz, 0.53*H*), 2.34 (dd, *J* = 16.7 Hz, *J* = 8.6 Hz, 0.53*H*), 2.23 (dd, *J* = 16.7 Hz, *J* = 3.8 Hz, 0.47*H*), 1.99 (dd, *J* = 16.7 Hz, *J* = 8.3 Hz, 0.47*H*), 1.23 (d, *J* = 6.5 Hz, 1.41*H*), 0.98 (d, *J* = 6.8 Hz, 1.41*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 191.1, 190.8, 142.8, 142.7, 137.0, 136.7, 129.6, 129.5, 129.03, 128.99, 128.9, 128.7, 127.79, 127.76, 127.73, 127.45, 118.49, 118.36, 57.7, 57.6, 36.2, 33.2, 33.0, 23.2, 22.5, 18.4, 17.4; IR (film): ν = 3030, 2963, 1667, 1398, 738, 699 cm^{-1}; MS (ESI): *m/z* = 268.1 $(M+H)^+$; HR-MS (ESI): *m/z* = 290.1253, calcd. for $C_{16}H_{17}N_3NaO$ $[M+Na]^+$: 290.1264.

2-[3-(1-Methyl-1*H*-imidazol-2-yl)-3-oxo-1,2-diphenylpropyl]malononitrile (29): 30 h; yield: 48 mg (68%); *dr* = 70:30; white solid; mp 188–189 °C; R_f: 0.52 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.66–7.60 (m, 2*H*), 7.44–7.32 (m, 4*H*), 7.27–7.19 (m, 3*H*), 7.12–7.00 (m, 2.49*H*), 6.88 (s, 0.51*H*), 6.08 (d, *J* = 12.3 Hz, 0.51*H*), 5.91 (d, *J* = 11.8 Hz, 0.49*H*), 4.41 (d, *J* = 5.0 Hz, 0.49*H*), 4.20–4.12 (m, 1*H*), 3.96 (s, 1.47*H*), 3.71 (s, 1.53*H*), 3.64 (d, *J* = 3.8 Hz, 0.51*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 189.4, 187.7, 142.1, 142.0, 135.2, 134.8, 134.4, 130.3, 129.84, 129.79, 129.2, 129.04, 129.00, 128.96, 128.9, 128.8, 128.7, 128.5, 128.2, 127.8, 127.5, 112.0, 111.8, 111.5, 110.9, 54.6, 53.8, 48.4, 47.6, 36.2, 35.8, 28.2, 28.0; IR (film): ν = 3033, 2904, 1667, 1400, 909, 697 cm^{-1}; MS (EI, 70 eV): *m/z* (%) = 354 (3), 289 (100), 199 (26), 109 (56); HR-MS (ESI): *m/z* = 377.1390, calcd. for $C_{22}H_{18}N_4NaO$ $[M+Na]^+$: 377.1373.

1-(1-Methyl-1*H*-imidazol-2-yl)-4-nitro-2,3-diphenylbutan-1-one (30): 20 h; yield: 28 mg (40%); *dr* = 45:55; colorless oil; R_f: 0.62 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61 (d, *J* = 7.0 Hz, 2*H*), 7.40–7.35 (m, 4*H*), 7.31–7.22 (m, 3*H*), 7.16 (d, *J* = 7.2 Hz, 1*H*), 7.06 (s, 1*H*), 6.85 (s, 1*H*), 5.77–5.68 (m, 1*H*), 4.55–4.31 (m, 3*H*), 3.72 (s, 3*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 188.8, 142.5, 137.8, 135.7, 129.4, 129.3, 129.0, 128.7, 128.21, 128.17, 127.7, 127.5, 79.5, 54.9, 46.4, 35.9; IR (film): ν = 3063, 2959, 1672, 1550, 1400, 909, 697 cm^{-1}; MS (EI, 70 eV): *m/z* (%) = 349 (6), 303 (52), 199 (100), 171 (23), 109 (61), 91 (9); HRMS (ESI): *m/z* = 372.1303, calcd. for $C_{20}H_{19}N_3NaO_3$ $[M+Na]^+$: 372.1319.

5-(1-Methyl-1*H*-imidazol-2-yl)-5-oxo-4-phenylpentanal (31): 24 h; yield: 16 mg (31%); colorless oil; R_f: 0.34 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.71(s, 1*H*), 7.44–7.40 (m, 2*H*), 7.32–7.26 (m, 2*H*), 7.21–7.18 (m, 1*H*), 7.13 (s, 1*H*), 6.99 (s, 1*H*), 5.18–5.13 (m, 1*H*), 3.95 (s, 3*H*), 2.49–2.17 (m, 4*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 201.6, 191.8, 142.6, 138.3, 129.3, 128.7, 127.5, 127.2, 51.7, 41.8, 36.2, 25.1; IR (film): ν = 3030, 2959, 1718, 1670, 1400, 910, 728, 699 cm^{-1}; MS (ESI): *m/z* = 257.1 $(M+H)^+$; HR-MS (ESI): *m/z* = 279.1100, calcd. for $C_{15}H_{16}N_2NaO_2$ $[M+Na]^+$: 279.1104.

2-Methyl-5-(1-methyl-1*H*-imidazol-2-yl)-5-oxo-4-phenylpentanal (32): 30 h; yield: 41 mg (80%); *dr* = 55:45; colorless oil; R_f: 0.50 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.62 (d, *J* = 1.8 Hz, 0.65*H*), 9.57 (d, *J* = 1.4 Hz, 0.35*H*), 7.46–7.42 (m, 2*H*), 7.33–7.18 (m, 3*H*), 7.13 (s, 1*H*), 6.99 (s, 1*H*), 5.34–5.26 (m, 1*H*), 3.94 (s, 3*H*), 2.68–2.58 (m, 0.65*H*), 2.49–2.17 (m, 1.35*H*), 2.10–2.00 (m, 0.35*H*), 1.90–1.81 (m, 0.65*H*), 1.15–1.11 (m, 3*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.1, 204.0, 191.65, 191.62, 142.6, 142.4, 138.8, 138.1, 129.4, 129.3, 128.73, 128.67, 128.64, 128.62, 127.5, 127.23, 127.15, 49.9, 49.8, 44.4, 44.2, 36.1, 33.5, 32.9, 13.8, 13.2; IR (film): ν = 3030, 2966, 1721, 1671, 1402, 700 cm^{-1}; MS (ESI): *m/z* = 271.1 $(M+H)^+$; HR-MS (ESI): *m/z* = 293.1254, calcd. for $C_{16}H_{18}N_2NaO_2$ $[M+Na]^+$: 293.1260.

3-Phenyl-5-(1-methyl-1*H*-imidazol-2-yl)-5-oxo-4-phenylpentanal (33): 30 h; yield: 31 mg (47%); *dr* = 85:15; colorless oil. Major isomer: R_f: 0.49 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.41–9.40 (m, 1*H*), 7.58 (d, *J* = 7.2 Hz, 2*H*), 7.40–7.32 (m, 4*H*), 7.28–7.20 (m, 3*H*), 7.11 (t, *J* = 7.2 Hz, 1*H*), 7.05 (s, 1*H*), 6.84 (s, 1*H*), 5.63 (d, *J* = 12.0 Hz, 1*H*), 4.22–4.16 (m, 1*H*), 3.72 (s, 3*H*), 2.69–2.62 (m, 1*H*), 2.50–2.45 (m, 1*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.0, 190.5, 142.8, 141.8, 137.0, 129.3, 129.1,

129.0, 128.5, 128.2, 127.7, 127.2, 126.8, 57.6, 48.4, 42.9, 36.0; IR (film): ν = 3029, 2956, 1721, 1672, 1402, 701 cm^{-1}; MS (EI, 70 eV): *m/z* (%) = 332 (37), 289 (39), 200 (89), 199 (100), 109 (40); HR-MS (ESI): *m/z* = 355.1394, calcd. for $C_{21}H_{20}N_2NaO_2$ $[M+Na]^+$: 355.1417.

1-(1-Methyl-1*H*-imidazol-2-yl)-2,3,5-triphenylpentane-1,5-dione (34): 30 h; yield: 70 mg (86%); *dr* = 60:40; colorless oil; R_f: 0.59 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.85–7.81 (m, 1*H*), 7.68–7.62 (m, 2*H*), 7.50–6.92 (m, 13.51*H*), 6.78 (s, 0.49*H*), 5.74 (d, *J* = 12.0 Hz, 0.51*H*), 5.60 (d, *J* = 11.6 Hz, 0.49*H*), 4.41–4.28 (m, 1*H*), 3.92 (s, 1.47*H*), 3.65 (s, 1.53*H*), 3.51 (dd, *J* = 16.0 Hz, *J* = 9.9 Hz, 0.51*H*), 3.36–3.26 (m, 0.98*H*), 2.96 (dd, *J* = 16.4 Hz, *J* = 3.2 Hz, 0.49*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.5, 198.1, 191.8, 190.8, 143.2, 142.9, 142.3, 141.4, 137.4, 137.10, 137.07, 136.9, 132.7, 132.6, 129.43, 129.36, 129.3, 129.0, 128.8, 128.4, 128.34, 128.27, 128.1, 127.9, 127.8, 127.6, 127.5, 127.1, 126.7, 126.4, 126.2, 58.3, 57.5, 44.5, 44.1, 44.0, 43.4, 36.2, 35.8; IR (film): ν = 3029, 2958, 1670, 1399, 732, 697 cm^{-1}; MS (ESI): *m/z* = 409.2 $(M+H)^+$; HR-MS (ESI): *m/z* = 431.1739, calcd. for $C_{27}H_{24}N_2NaO_2$ $[M+Na]^+$: 431.1730.

3-[2-(1-Methyl-1*H*-imidazol-2-yl)-2-oxo-1-phenylethyl]cyclohexanone (35): 24 h; yield: 17 mg (29%); *dr* = 90:10; colorless oil. Major isomer: R_f: 0.30 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (d, *J* = 7.2 Hz, 2*H*), 7.29–7.25 (m, 2*H*), 7.20 (t, *J* = 7.2 Hz, 1*H*), 7.15 (s, 1*H*), 7.01 (s, 1*H*), 5.10 (d, *J* = 10.8 Hz, 1*H*), 3.95 (s, 3*H*), 2.79–2.69 (m, 1*H*), 2.38–2.33 (m, 1*H*), 2.30–2.22 (m, 1*H*), 2.11–2.03 (m, 2*H*), 1.99–1.96 (m, 2*H*), 1.76–1.66 (m, 1*H*), 1.52–1.46 (m, 1*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 211.1, 191.9, 143.1, 136.6, 129.4, 129.0, 128.8, 127.7, 127.4, 58.4, 45.5, 41.4, 41.3, 36.3, 30.2, 25.0; IR (film): ν = 3029, 2931, 1710, 1670, 1402, 700 cm^{-1}; MS (EI, 70 eV): *m/z* (%) = 296 (100), 225 (39), 200 (26), 109 (42), 82 (20); HR-MS (ESI): *m/z* = 319.1426, calcd. for $C_{18}H_{20}N_2NaO_2$ $[M+Na]^+$: 319.1417.

1-(1-Methyl-1*H*-imidazol-2-yl)-2-phenyl-4-(phenylsulfonyl)butan-1-one (36): 24 h; yield: 47 mg (64%); colorless oil; R_f: 0.29 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.88–7.85 (m, 2*H*), 7.67–7.62 (m, 1*H*), 7.57–7.52 (m, 2*H*), 7.32–7.18 (m, 5*H*), 7.09 (s, 1*H*), 6.98 (s, 1*H*), 5.15 (dd, *J* = 8.7 Hz, *J* = 6.9 Hz, 1*H*), 3.91 (s, 3*H*), 3.15–2.93 (m, 2*H*), 2.47–2.25 (m, 2*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 190.5, 142.2, 138.8, 137.2, 133.6, 129.4, 129.2, 128.8, 128.5, 128.1, 127.7, 127.5, 54.1, 50.8, 36.1, 25.5; IR (film): ν = 3063, 2956, 1671, 1403, 1152, 739 cm^{-1}; MS (ESI): *m/z* = 369.1 $(M+H)^+$; HR-MS (ESI): *m/z* = 391.1085, calcd. for $C_{20}H_{20}N_2NaO_3S$ $[M+Na]^+$: 391.1087.

(*E*)-Benzyl 5-methyl-7-(1-methyl-1*H*-imidazol-2-yl)-7-oxo-6-phenylhept-3-enoate (37): 30 h; yield: 33 mg (41%); *dr* = 55:45; colorless oil. Major isomer: R_f: 0.62 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.29 (m, 7*H*), 7.22 (t, *J* = 7.6 Hz, 2*H*), 7.16–7.12 (m, 2*H*), 6.99 (s, 1*H*), 5.44–5.29 (m, 2*H*), 5.05–5.02 (m, 3*H*), 3.94 (s, 3*H*), 3.18–3.10 (m, 1*H*), 2.94–2.82 (m, 2*H*), 1.10 (d, *J* = 6.8 Hz, 3*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.3, 171.6, 143.1, 137.9, 137.0, 135.9, 129.4, 128.5, 128.3, 128.13, 128.06, 127.5, 126.8, 121.9, 66.2, 58.5, 39.5, 38.0, 36.3, 19.0; IR (film): ν = 2959, 1732, 1670, 1399, 1153, 696 cm^{-1}; MS (EI, 70 eV): *m/z* (%) = 402 (31), 227 (78), 199 (52), 109 (33), 91 (100); HR-MS (ESI): *m/z* = 425.1833, calcd. for $C_{25}H_{26}N_2NaO_3$ $[M+Na]^+$: 425.1836.

(*E*)-Benzyl 5-methyl-7-(1-methyl-1*H*-imidazol-2-yl)-7-oxo-6-phenylhept-2-enoate (38): 30 h; yield: 17 mg (20%); *dr* = 60:40; colorless oil. Major isomer: R_f: 0.62 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 (d, *J* = 6.8 Hz, 2*H*), 7.37–7.27 (m, 7*H*), 7.19 (t, *J* = 7.6 Hz, 1*H*), 7.14 (s, 1*H*), 6.99 (s, 1*H*), 6.93–6.85 (m, 1*H*), 5.74 (d, *J* = 15.6 Hz, 1*H*), 5.15 (s, 2*H*), 5.00 (d, *J* = 11.2 Hz, 1*H*), 3.94 (s, 3*H*), 2.68–2.60 (m, 1*H*), 2.14–2.08 (m, 1*H*), 1.92–1.84 (m, 1*H*), 1.00 (d, *J* = 6.8 Hz, 3*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.3, 166.2, 148.0, 137.7, 136.1, 129.2, 128.7, 128.5,128.2, 128.1, 127.5, 127.3, 122.4, 66.0, 58.8, 36.8, 36.4, 35.5, 18.3; IR (film): ν = 2961, 1728, 1669, 1398, 1154, 696 cm^{-1}; MS (EI, 70 eV): *m/z* (%) = 402 (25), 227 (100), 199 (56), 109 (30), 91 (90); HR-MS (ESI): *m/z* = 425.1844, calcd. for $C_{25}H_{26}N_2NaO_3$ $[M+Na]^+$: 425.1836.

5-Hydroxy-4,6-dimethyl-3-phenylbenzofuran-2(3*H*)-one (39): Yield: 63 mg (62%); white solid; mp 133–134 °C; R_f: 0.44 (petroleum ether/ethyl acetate 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.35–7.29 (m, 3*H*), 7.17 (d, *J* = 8.0 Hz, 2*H*), 6.84 (s, 1*H*), 4.78 (s, 1*H*), 4.52 (s, 1*H*), 2.30 (s, 3*H*), 1.90 (s, 3*H*); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 175.7, 149.0, 147.4, 134.8, 129.1, 128.12, 128.10, 124.2, 124.0, 121.3, 110.0, 50.1, 16.5, 12.5; IR (film): ν = 3490, 3064, 3030, 1771, 1145, 1019, 700 cm^{-1}; MS (EI, 70 eV): *m/z* (%) = 254 (67), 225 (100), 105 (7); HR-MS (ESI): *m/z* = 277.0830, calcd. for $C_{16}H_{14}NaO_3$ $[M+Na]^+$: 277.0835.

5-Hydroxy-4,7-dimethyl-3-phenylbenzofuran-2(3*H*)-one (40): Yield: 61 mg (60%); white solid; mp 195–196 °C; R_f: 0.44 (petroleum ether/ethyl acetate 3:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38–7.31 (m, 3*H*), 7.20–7.16 (m, 2*H*), 6.63 (s, 1*H*), 4.80 (s, 1*H*), 4.69 (brs, 1*H*), 2.29 (s, 3*H*), 1.85 (s, 3*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 175.7, 150.5, 146.3, 134.7, 129.1, 128.1, 126.2, 119.1, 118.9, 116.8, 50.5, 14.8, 12.0; IR (film): ν = 3362, 2923, 1754, 1147, 704 cm^{-1}; MS (EI, 70 eV): *m/z* (%) = 254 (55), 225 (100); HR-MS (ESI): *m/z* = 277.0842, calcd. for $C_{16}H_{14}NaO_3$ $[M+Na]^+$: 277.0835.

5-Hydroxy-4-methyl-3-phenylnaphtho[1,2-*b*]furan-2(3*H*)-one (41): Yield: 59 mg (51%); white solid; mp 145–146 °C; R_f: 0.42 (petroleum ether/ethyl acetate 3:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19–8.17 (m, 1*H*), 8.02–7.99 (m, 1*H*), 7.57–7.55 (m, 2*H*), 7.35–7.33 (m, 3*H*), 7.20–7.18 (m, 2*H*), 5.07 (brs, 1*H*), 4.97 (s, 1*H*), 2.04 (s, 3*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.8, 145.9, 143.5, 134.7, 129.2, 128.3, 128.2, 126.4, 126.3, 124.7, 121.7, 121.2, 121.1, 118.9, 113.6, 51.1, 12.3; IR (film): ν = 3417, 2924, 1784, 1699, 1049, 712 cm^{-1}; MS (EI, 70 eV): *m/z* (%) = 290 (38), 278 (95), 261 (76), 105 (100), 77 (45); HR-MS (ESI): *m/z* = 313.0815, calcd. for $C_{19}H_{14}NaO_3$ $[M+Na]^+$: 313.0835.

5-Hydroxy-3-(4-methoxyphenyl)-4,6-dimethylbenzofuran-2(3*H*)-one (42): Yield: 75 mg (66%); white solid; mp 150–151 °C; R_f: 0.36 (petroleum ether/ethyl acetate 3:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.08 (d, *J* = 8.8 Hz, 2*H*), 6.87–6.82 (m, 3*H*), 4.73 (s, 1*H*), 4.58 (s, 1*H*), 3.79 (s, 3*H*), 2.30 (s, 3*H*), 1.90 (s, 3*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.2, 159.3, 149.0, 147.3, 129.1, 126.8, 124.14, 124.12, 121.3, 114.5, 109.9, 55.2, 49.3, 16.5, 12.4; IR (film): ν = 3511, 2912, 1771, 1510, 1146, 1010, 780 cm^{-1}; MS (EI, 70 eV): *m/z* (%) = 284 (84), 255 (100), 225 (89), 128 (10); HR-MS (ESI): *m/z* = 307.0934, calcd. for $C_{17}H_{16}NaO_4$ $[M+Na]^+$: 307.0941.

5-Hydroxy-4,6-dimethyl-3-(4-nitrophenyl)benzofuran-2(3*H*)-one (43): Yield: 38 mg (32%); white solid; mp 185–186 °C; R_f: 0.28 (petroleum ether/ethyl acetate 3:1); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.22$ (d, $J = 8.8$ Hz, 2*H*), 7.39 (d, $J = 8.8$ Hz, 2*H*), 6.88 (s, 1*H*), 4.92 (s, 1*H*), 4.55 (s, 1*H*), 2.33 (s, 3*H*), 1.90 (s, 3*H*); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 174.1$, 149.2, 147.8, 147.4, 141.9, 129.1, 124.9, 124.3, 122.6, 121.3, 110.4, 49.7, 16.6, 12.8; IR (film): $\nu = 3444$, 2915, 1775, 1515, 1348, 1156, 1014, 728 cm^{-1}; MS (EI, 70 eV): *m/z* (%) = 299 (100), 254 (35), 224 (89), 165 (7); HR-MS (ESI): *m/z* = 322.0685, calcd. for $C_{16}H_{13}NNaO_5$ $[M+Na]^+$: 322.0686.

5-Hydroxy-4,6-dimethyl-3-(3-thienyl)benzofuran-2(3*H*)-one (44): Yield: 47 mg (45%); white solid; mp 144–145 °C; R_f: 0.40 (petroleum ether/ethyl acetate 3:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.32$ (dd, $J = 5.1$ Hz, $J = 3.0$ Hz, 1*H*), 7.11–7.10 (m, 1*H*), 6.93 (dd, $J = 5.1$ Hz, $J = 1.2$ Hz, 1*H*), 6.82 (s, 1*H*), 4.91 (s, 1*H*), 4.58 (s, 1*H*), 2.29 (s, 3*H*), 1.97 (s, 3*H*); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 175.0$, 149.0, 147.2, 143.3, 126.8, 126.7, 124.2, 123.8, 123.4, 121.3, 110.1, 45.5, 16.5, 12.4; IR (film): $\nu = 3438$, 3103, 2890, 1767, 1462, 1150, 1011, 781 cm^{-1}; MS (EI, 70 eV): *m/z* (%) = 260 (56), 231 (100), 217 (10); HR-MS (ESI): *m/z* = 283.0391, calcd. for $C_{14}H_{12}NaO_3S$ $[M+Na]^+$: 283.0399.

2-(3,6-Dihydroxy-2,4-dimethylphenyl)-1-(1-methyl-1*H*-imidazol-2-yl)-2-phenylethanone (46): Yield: 54 mg (80%); light yellow solid; mp 138–139 °C; R_f: 0.08 (petroleum ether/ethyl acetate 3:1); ^{1}H NMR [500 MHz, $(CD_3)_2CO$]: $\delta = 9.11$ (brs, 1*H*), 7.41 (s, 1*H*), 7.31–7.20 (m, 5*H*), 7.11 (s, 1*H*), 6.71 (brs, 1*H*), 6.63 (s, 1*H*), 6.59 (s, 1*H*), 4.06 (s, 3*H*), 2.18 (s, 3*H*), 2.16 (s, 3*H*); ^{13}C NMR [125 MHz, $(CD_3)_2CO$]: $\delta =$ 191.5, 149.8, 148.1, 144.3, 139.6, 129.5, 128.9, 128.8, 128.7, 127.0, 126.3, 125.9, 124.0, 118.4, 52.8, 36.4, 16.8, 13.8; IR (film): $\nu = 3313$, 2920, 1688, 1401, 1210, 1034, 739 cm^{-1}; MS (EI, 70 eV): *m/z* (%) = 336 (4), 254 (57), 225 (100), 82 (19); HR-MS (ESI): *m/z* = 337.1538, calcd. for $C_{20}H_{21}N_2O_3$ $[M+H]^+$: 337.1547.

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