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$FeCl_3$-catalyzed addition of nitrogen and 1,3-dicarbonyl nucleophiles to olefins

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ABSTRACT

A direct intermolecular addition of nitrogen and 1,3-dicarbonyl nucleophiles to stabilized double bonds (styrenes, 1,3-dienes, enol-ethers, sugars..) in the presence of green and inexpensive $FeCl_3$ catalyst is described.

1. Introduction

The addition of Carbon, Nitrogen and Oxygen nucleophiles to C–C double bond is desirable in terms of atom economy to create new C–C, C–N and C–O bonds. These reactions should produce no stoichiometric by-products and meet the increasing demand for environment benign organic synthesis processes. Moreover, if such transformations could be catalyzed by non-toxic, abundant and inexpensive catalysts such as iron complexes [1,2], it could be very close to the definition of an ideal 'green' reaction [3]. We would like to report in this article a full account on our recent work on iron-catalyzed addition of nitrogen and 1,3-dicarbonyl nucleophiles to stabilized double bonds (styrenes, 1,3-dienes, enol-ethers, sugars..) (Scheme 1) [4].

2. Results and discussion

2.1. Hydroamination reactions

As part of a program directed towards the preparation of new mono- and diamines and their use as ligands in the design of new transition metal complexes, we became interested in the preparation of benzylic amines. Such targets can be efficiently obtained through gold-promoted amination of benzylic alcohols [5b], and we were puzzled if these products could arise from the hydroamination of styrenes. In a preliminary report [4], we reported the preparation of the formation of the C–N bond at benzylic positions through iron-catalyzed intermolecular hydroamination of styrenes [6,7]. In order to set the best catalytic combination, several iron sources under different set of reaction conditions have been explored. Initial experiments were conducted with styrene and $TsNH_2$ in order to prepare hydroaminated product **1** (Scheme 2). Among the tested iron sources such as $FeCl_2$, FeS, $Fe(NO_3)_3$, Fe $(acac)_3$, $FeBr_3$, $FeCl_3$ on silica and anhydrous $FeCl_3$, best results were obtained in the presence of 10% of $FeCl_3 \cdot 6H_2O$ in dioxane at 120 °C leading to the hydroaminated product **1** in 73% yield.

The use of other nitrogen sources was next tested in the hydroamination of styrene (Table 1). Whereas electron-poor nitrogen nucleophiles, such as *p*-NO_2-aniline (entry 2), 2-NO_2-4-toluidine (entry 3), or *p*-NO_2-benzamide (entry 4), gave encouraging results, no reaction could be observed with more basic nitrogen nucleophiles such as phtalimide or 2,4-DNPH. The use of $TMSN_3$, which proved to be a good pro-nucleophile in the substitution of benzylic alcohols [5a], was also investigated. The formation of the benzylic C–N_3 bond was clearly evidenced in the crude material through ^1H and ^{13}C NMR analyses and a 60% conversion was estimated (entry 5). However, owing to product instability (degradation upon purification by column chromatography) a very low yield (12%) was obtained. Despite considerable experiments and careful purification attempts, the yield could not be improved. Scope and limitations were next tested by varying the nature of the vinyl arene residue (Table 1, entries 7–16). Electron-donating groups are well tolerated

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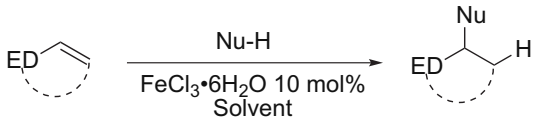


Scheme 1.

in these reactions (**7**–**11**) whereas electron-withdrawing groups completely inhibit the hydroamination reaction (see compounds **12** and **13**). Noteworthy, paradoxical halogens (−I, +M) substituents in the para position, lead to the hydroaminated products **10**–**11** in good yields, 69 and 63% yields respectively.

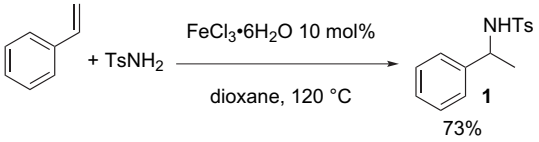
Interestingly, in the presence of strong electron-donating groups such as *p*-Me or 2,4-diMe, the reactions could be carried out at room temperature, in moderate to good yields (**7**–**9**). The hydroamination is also quite sensitive to steric hindrance: reactions of either α- or β-substituted styrenes were rather slow and the hydroaminated products isolated in low yields (**14**–**16**). It is also worthnoting that styrene polymerization and/or hydroarylation by-products could be observed in the crude NMR spectra when hydroamination reluctant substrates were used.

Finally, the hydroamination of 1-(chloromethyl)-4-vinylbenzene **17**, commercialy available as a mixture of 1-(chloromethyl)-4-vinylbenzene and 1-(chloromethyl)-3-vinylbenzene, was carried out and led to a mixture of monoaminated (at the benzylic position) **18** and diaminated **19** compounds in 15 and 43% yields respectively (Scheme 3).

According to the scope of the reaction, electron-donating groups on the aromatic ring accelerate the reaction, whereas electron-withdrawing groups inhibit the hydroamination. Thus a mechanism (Schemes 4) involving a transient carbocation or a polarized π-complexed double bond can be envisioned, in which a stabilization of a carbocation or a δ^+ charge intermediate is involved in the key-step.

The use of alternative stabilizating groups, such as 1,3-dienes, enol-ethers or glycals was thus examined (Scheme 5). Indeed, starting from 1,3-cyclohexadiene in the presence of $TsNH_2$ (5 equiv.), the hydroamination product **20** was isolated in 56% yield [7l]. Dihydropyran was next engaged in hydroamination reactions in the presence of $TsNH_2$ and *p*-NO_2-aniline and gratifyingly compounds **21** and **22** were isolated in 89 and 54% yield, respectively. Usually an excess (5 equiv) of nitrogen nucleophile is necessary to get a full conversion, however in the latter case, **22** and *p*-nitroaniline could not be separated by flash chromatography and thus, dihydropyran was used in excess (3 equiv) and slowly added over 4 hours, through a syringe pump, at 80 °C to give **22** in 54% yield. Finally, moving to glycals, such as **23**, the hydroamination reactions proved to be more reluctant and among many other unidentifed products, amino-sugar **24**, resulting from the expected hydroamination reaction but also from the nucleophilic substitution on the primary acetate, could be identified in less than 20% yield.

In summary, the hydroamination of double bonds bearing electron-donating groups, such as styrenes, 1,3-dienes or enol-ethers can be carried out in dioxane (or DCE) in the presence of a catalytic amount of $FeCl_3$ and electron-poor nitrogen nucleophiles



Scheme 2.

($TsNH_2$, nitro-anilines, carboxamides…). The use of alternatives nucleophiles was then questioned [8].

2.2. Addition of 1,3-dicarbonyl compounds

We thus turned our attention to the use of carbon nucleophiles, such as as 1,3-dicarbonyl derivatives. We first examine a model reaction of styrene with acetylacetone (Table 2). After a short optimization dealing with catalyst amount (entries 1–3), iron sources (entries 4–7), equivalent of nucleophiles (compare entries 3 and 8–9), solvents (entries 9–14), temperature (entries 15–16) and reaction time (entries 17–18), the following conditions found to be optimal in our hands: a 10-fold excess of acetylacetone in DCE at 100 °C for 20 hours allows the formation of **25** in 86% yield.

Consequently, other nucleophiles and substrates were examined and $FeCl_3$ was able to promote a clean addition of 1,3-diphen ylpropane-1,3-dione or ethyl acetoacetate to styrene, and *p*-Me-styrene to give compounds **26**, **27** and **28** in 62, 79 and 58% yields respectively (Scheme 6) [10].

However, at the time we got these preliminary results [9], Beller [10] described very similar results (compounds **25**, **26**, **27** and **28** have been isolated in 82, 69, 76% and 64% yields respectively) and extended the scope to other various nucleophiles and styrenes, including a very nice synthesis of warfarin. In the light of these results, we thus turned our attention to the use of other electrophiles such as dienes and enol-ethers, not developped in the Beller's publication [10,11].

Starting from 1,3-cyclohexadiene (Scheme 7), various 1,3-dicar bonyl derivatives were successfully introduced as illustrated in compounds **29**, **30** and **31** isolated in 64, 40 (44/56 dr), and 48% yields respectively [11c,12,13]. More surprisingly, the use of cyclic derivatives such as 2-acetylcyclopentanone and dimedone led to more disappointing results (Scheme 7, compounds **32** [14] and **33**).

From cyclic enol-ethers (Scheme 8), such as dihydropyran (and dihydrofuran) and acetylacetone (or 1,3-diphenylpropane-1,3-dione), compounds **34** [11a], **35** [11a] and **36** [11c] were isolated in 54, 58 and 30% yields respectively.

Moving to glucal **23**, the reaction led to the degradation of the starting glucal and the generation of many by-products where **37** could not be identifed regardless of the nature of the protecting group (R = Ac or Bn). Consequently, we thus turned our attention to sugars [14] and in the case of 2,3,4-tri-*O*-benzyl-β-D-arabinofuranose **38**, gratifyingly, C-glucoside **39** was isolated in 54% yield and 7:3 dr (Scheme 9).

In this reaction, a slow addition of **38** is required to prevent the formation of the dimeric sugar by-product **40** which could be obtained in 28% yield using $FeCl_3$ at 50 °C, and in 43% yield using $NaAuCl_4$ at room temperature (Scheme 10).

3. Conclusion

In conclusion, we have demonstrated that Iron(III) chloride is able to catalyze the addition of nitrogen and 1,3-dicarbonyl nucleophiles to double bonds such as vinyl arenes, enol-ethers and 1,3-dienes. The attractiveness of these reactions lies on their atom economy and the use of environmentally begin and cheap Iron(III) chloride in the absence of any additive or ligand.

4. Experimental

4.1. General procedure for the hydroamination of styrenes and 1,3-dienes

To a stirred solution of $TsNH_2$ (5 mmol) and $FeCl_3$ (0.1 mmol) in dioxane (or DCE, 5 mL) was added vinyl arene (1 mmol) and the

Table 1
Hydroamination of stryrene derivatives: scope and limitations.

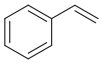
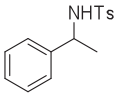
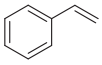
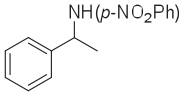
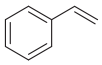
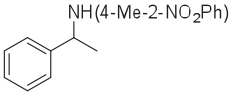
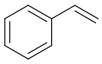
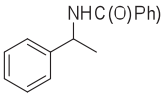
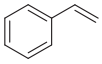
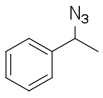
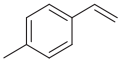
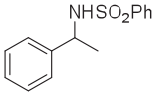
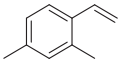
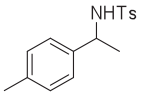
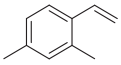
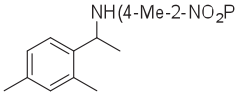
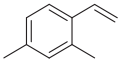
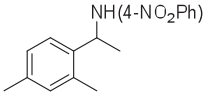
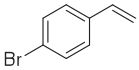
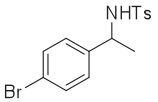
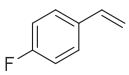
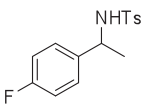
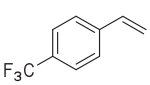
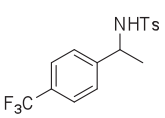
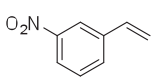
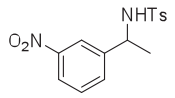
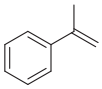
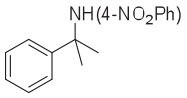
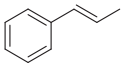
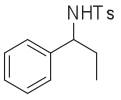
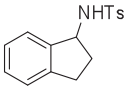
Entry	Vinyl-arene	Nitrogen nucleophile	Conditions	Product	N°	Yield (%)
1		$TsNH_2$	A		**1**	73
2		*p*-$NO_{2\text{-aniline}}$	B		**2**	70
3		*p*-Me, *o*-$NO_{2\text{-aniline}}$	B		**3**	41
4		*p*-NO_2-benzamide	B		**4**	30
5		$TMSN_3$	A		**5**	12
6		$PhSO_2NH_2$	A		**6**	59
7		$TsNH_2$	C		**7**	53
8		4-Me-2-$NO_{2\text{-aniline}}$	C		**8**	57
9		*p*-$NO_{2\text{-aniline}}$	C		**9**	43
10		$TsNH_2$	A		**10**	69
11		$TsNH_2$	A		**11**	63
12		$TsNH_2$	A		**12**	5

Table 1 (*continued*)

Entry	Vinyl-arene	Nitrogen nucleophile	Conditions	Product	N°	Yield (%)
13		$TsNH_2$	A		**13**	–
14		$p\text{-}NO_{2\text{-aniline}}$	A		**14**	12
15		$TsNH_2$	A		**15**	11
16		$TsNH_2$	A		**16**	–

Conditions: A: dioxane reflux. B: DCE-reflux. C: Dioxane r.t.

yellow solution was refluxed for 20 h (bath temperature: 120 °C). After cooling to RT and usual work-up, the residue was purified on silica gel to afford the hydroaminated compound.

*4.1.1. N-(1-phenylethyl)-4-methylbenzenesulfonamide (**1**)*

According to the general procedure, compound **1** was purified on silica gel (AcOEt/Heptane 3/7).

73% yield, white solid, mp 78–79 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.43 (d, $J = 6.9$ Hz, 3H), 2.39 (s, 3H), 4.47 (quintet, $J = 6.8$ Hz, 1H), 5.00 (broad d, $J = 6.9$ Hz, 1H), 7.09–7.14 (m, 2H), 7.16–7.21 (m, 5H), 7.60 (d, $J = 8.3$ Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 21.6, 23.6, 53.7, 126.2, 127.2, 127.5, 128.6, 129.5, 137.8, 142.2, 143.2.

Data are in accordance with previously reported data [5b].

*4.1.2. N-(1-phenylethyl)-4-nitroaniline (**2**)*

According to the general procedure, compound **2** was purified on silica gel (AcOEt/PE 2/8) 70% yield, yellow solid, mp 81–82 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.51 (d, $J = 6.9$ Hz, 3H), 4.51 (q, $J = 6.8$ Hz, 1H), 4.82 (broad s, 1H), 6.38 (d, $J = 9.1$ Hz, 2H), 7.18–7.27 (m, 5H), 7.92 (d, $J = 9.2$ Hz, H).

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 24.5, 53.3, 111.8, 125.6, 126.2, 127.5,128.9, 138.1, 143.2, 152.2.

MS (CI, NH_3) m/z (%) 502 ($2M + NH_4^+$, 10), 485 ($2M + H^+$, 45), 260 ($M + NH_4^+$, 55), 243 ($M + H^+$, 100), 242 ($M^{\cdot +}$, 45), 227 (10).

Data are in accordance with previously reported data [15].

*4.1.3. N-(1-phenylethyl)-4-methyl-2-nitroaniline (**3**)*

According to the general procedure, compound **2** was purified on silica gel (AcOEt/PE 5/95).

41% yield, orange solid, mp 87–88 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.56 (d, $J = 6.8$ Hz, 3H), 2.14 (s, 3H), 4.60 (quintet, $J = 6.7$ Hz, 1H), 6.47 (d, $J = 8.9$ Hz, 1H), 7.01 (dd, $J = 8.9$ and 1.9 Hz, 1H), 7.18–7.20 (m, 2H), 7.25–7–28 (m, 3H), 7.90 (d, $J = 1.0$ Hz, 1H), 8.25 (broad s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 19.9, 25.1, 53.1, 115.1, 125.1, 125.6, 125.9, 127.3, 128.9, 131.7, 137.5, 142.7, 143.8.

MS (CI, NH_3) m/z (%): 257 ($M + H^+$, 35), 256 ($M^{\cdot +}$, 10), 213 (10), 197 (100).

*4.1.4. 4-nitro-N-(1-phenylethyl)benzamide (**4**)*

According to the general procedure, compound **4** was purified on silica gel (AcOEt/PE 5/95).

30% yield, yellowish solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.57 (d, $J = 6.8$ Hz, 3H), 5.25 (q, $J = 6.8$ Hz, 1H), 7.07 (d, $J = 6.7$ Hz, 1H), 7.21–7.35 (m, 5H), 8.01 (d, $J = 9.1$ Hz, 2H), 8.23 (d, $J = 9.1$ Hz, 2H).

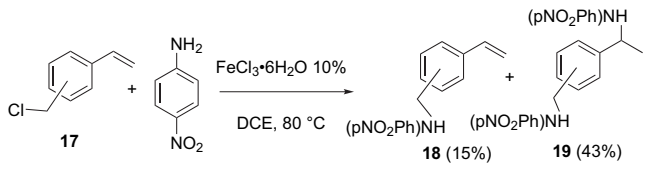
Data are in accordance with previously reported data [7e].

*4.1.5. N-(1-phenylethyl)-benzenesulfonamide (**6**)*

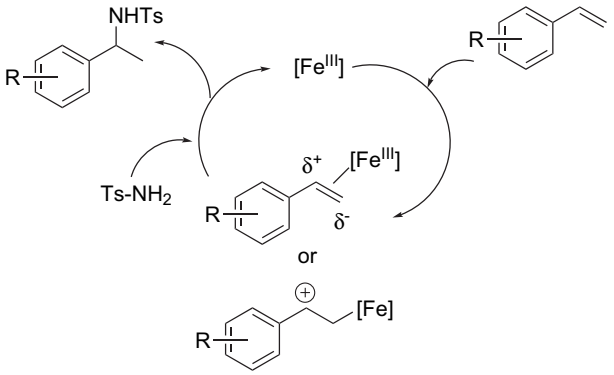
According to the general procedure, compound **6** was purified on silica gel (AcOEt/PE 2/8).

59 % yield, white solid.

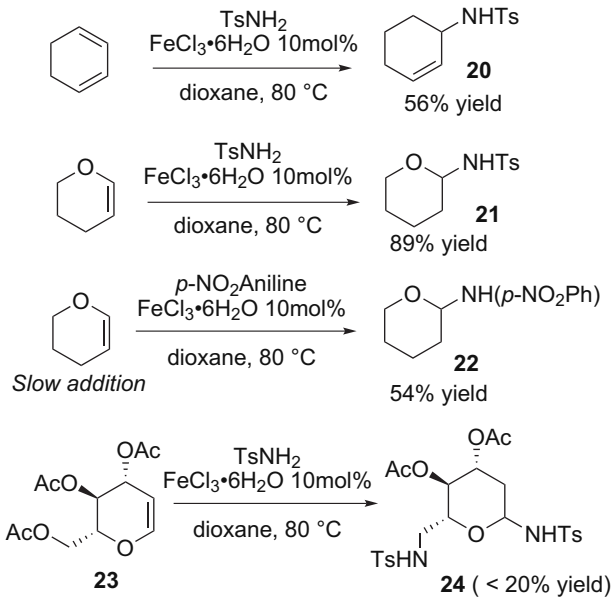
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.43 (d, $J = 6.8$ Hz, 3H), 4.49 (quint, $J = 6.8$ Hz, 1H), 5.04 (d, $J = 6.8$ Hz, 1H), 7.09 (m, 2H), 7.16 (m, 3H), 7.38 (d, $J = 8.3$ Hz, 1H), 7.50 (t, $J = 8.3$ Hz, 2H), 7.72 (d, $J = 8.3$ Hz, 2H).



Scheme 3. Mono *vs.* diamination reactions.



Scheme 4. Postulated mechanism.



Scheme 5. Diene and enol-ether hydroaminations.

Data are in accordance with previously reported data [16].

*4.1.6. N-(1-p-tolylethyl)-tosylamide (**7**)*

According to the general procedure for hydroamination, the reaction was carried out at rt in dioxan. Purification by flash column chromatography (silica gel, EtOAc/heptane 2/8) yielded **7** in 53% as a white solid. M.p. 114–115 °C (Lit.[7c] 116–118 °C)

^{1}H NMR ($CDCl_3$, 500 MHz): δ (*ppm*) 1.42 (d, $J = 6.8$ Hz, 3H), 2.29 (s, 3H), 2.41 (s, H), 4.43 (quint, $J = 6.8$ Hz, 1H), 4.89 (d, $J = 6.8$ Hz, 1H), 7.01 (m, 4H), 7.20 (d, $J = 8.1$ Hz, 2H), 7.64 (d, $J = 8.1$ Hz, 2H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ (*ppm*) 21.0, 21.5, 23.6, 53.5, 126.1 (2C), 127.2 (2C), 129.2 (2C), 129.4 (2C), 137.1, 137.8, 139.3, 143.0.

Data are in accordance with previously reported data [7e].

*4.1.7. N-[1-(2,4-dimethylphenyl)ethyl]-4-methyl-2-nitroaniline (**8**)*

According to the general procedure for hydroamination, the reaction was carried out at rt in dioxan. Purification by flash column chromatography (silica gel, EtOAc/PE 2/8) yielded **8** in 57% as an orange solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.50 (d, $J = 6.6$ Hz, 3H), 2.13 (s, 3H), 2.21 (s, 3H), 2.34 (s, 3H), 4.73 (quint, $J = 6.6$ Hz, 1H), 6.31 (d, $J = 8.4$ Hz, 1H), 6.86–6.93 (m, 2H), 7.00 (dd, $J = 2.1$, 8.9 Hz, 1H), 7.10 (d, $J = 8.4$ Hz, 1H), 7.89 (s, 1H), 8.24 (br s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 18.8, 19.9, 20.9, 23.1, 49.5, 114.8, 124.5, 124.9, 125.9, 127.5, 127.6, 131.6, 134.0, 136.7, 137.6, 138.5, 142.7.

MS (CI, NH_3): *m/z* (%) 285 ($M + NH_4^+$, 100), 284 ($M + H^+$), 50, 150 (25), 133(95).

*4.1.8. N-[1-(2,4-dimethylphenyl)ethyl]-4-nitroaniline (**9**)*

According to the general procedure for hydroamination, the reaction was carried out at rt in dioxan. Purification by flash column chromatography (silica gel, EtOAc/PE 2/8) yielded **9** in 43% as a yellow solid. Mp: 114–115 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.55 (d, $J = 6.2$ Hz, 3H), 2.32 (s, 3H), 2.43 (s, 3H), 4.76 (quint, $J = 6.2$ Hz, 1H), 5.07 (d, $J = 6.2$ Hz, 1H), 6.42 (d, $J = 9.2$ Hz, 2H), 6.97–7.05 (m, 2H), 7.22 (d, $J = 7.7$ Hz, 1H), 8.01 (d, $J = 9.2$ Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 18.9, 20.9, 22.5, 49.5, 111.5, 124.3, 126.3, 127.4, 131.7, 134.4, 137.0, 137.8, 138.0, 152.2.

MS (CI, NH_3): *m/z* (%) 541 ($2M + NH_4^+$, 100), 420 (10), 403 (25), 288 ($M + NH_4^+$, 10), 271 ($M + H^+$, 30), 270 (25), 255 (10), 133 (30).

*4.1.9. N-(1-(4-bromophenyl)ethyl)-tosylamide (**10**)*

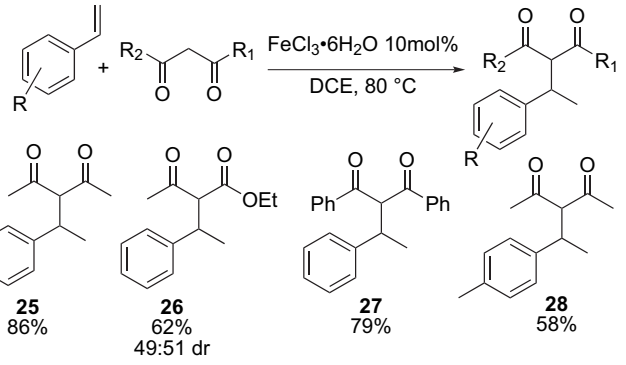
According to the general procedure for hydroamination, the reaction was carried out in dioxan. Purification by flash column chromatography (silica gel, EtOAc/heptane 2/8) yielded **10** in 63% yield as a white solid. Mp: 139–140 °C

^{1}H NMR ($CDCl_3$, 300 MHz): δ (*ppm*) 1.37 (d, $J = 6.9$ Hz, 3H), 2.41 (s, 3H), 4.42 (quint, $J = 6.9$ Hz, 1H), 5.48 (d, $J = 7.0$ Hz), 7.00 (d,

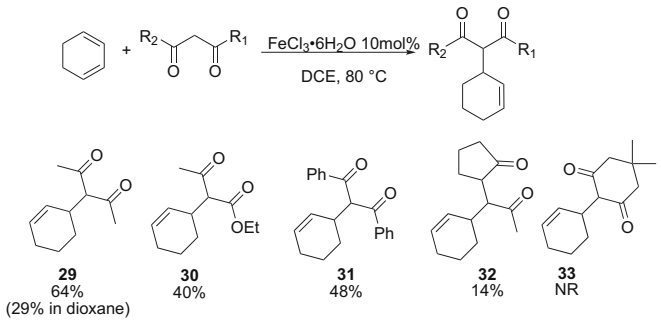
Table-2
Iron(III) catalyzed addition of acetylacetone to styrene.

Entry	Catalyst (mol%)	Acetyl acetone (equiv.)	Conditions	Isolated yield (%)
1	$FeCl_3$ (100%)	2.5	Dioxane, 120 °C, 20 h	70
2	$FeCl_3$ (20%)	2.5	Dioxane, 120 °C, 20 h	55
3	$FeCl_3$ (10%)	2.5	Dioxane, 120 °C, 20 h	51
4	$FeCl_2$ (10%)	2.5	Dioxane, 120 °C, 20 h	NR
5	$Fe(acac)_3$ (10%)	2.5	Dioxane, 120 °C, 20 h	26
6	$FeCl_3 \cdot 6H_2O$ (10 mol%)	2.5	Dioxane, 120 °C, 20 h	43
7	$FeCl_3 \cdot 6H_2O$ (10 mol%)[a]	2.5	Dioxane, 120 °C, 20 h	54
8	$FeCl_3 \cdot 6H_2O$ (10 mol%)[a]	5	Dioxane, 120 °C, 20 h	71
9	$FeCl_3 \cdot 6H_2O$ (10 mol%)[a]	10	Dioxane, 120 °C, 20 h	77
10	$FeCl_3 \cdot 6H_2O$ (10 mol%)[a]	10	Toluene, 120 °C, 20 h	8
11	$FeCl_3 \cdot 6H_2O$ (10 mol%)[a]	10	THF, 60 °C, 20 h	NR
12	$FeCl_3 \cdot 6H_2O$ (10 mol%)[a]	10	DCM, 60 °C, 20 h	11
13	$FeCl_3 \cdot 6H_2O$ (10 mol%)[a]	10	DCE, 80 °C, 20 h	86
14	$FeCl_3 \cdot 6H_2O$ (10 mol%)[a]	~100	Neat, 120 °C, 20 h	11
15	$FeCl_3 \cdot 6H_2O$ (10 mol%)[a]	10	DCE, 100 °C, 20 h	86
16	$FeCl_3 \cdot 6H_2O$ (10 mol%)[a]	10	DCE, 120 °C,[b] 20 h	81
17	$FeCl_3 \cdot 6H_2O$ (10 mol%)[a]	10	DCE, 80 °C, 8 h	54
18	$FeCl_3 \cdot 6H_2O$ (10 mol%)[a]	10	DCE, 60 °C, 36 h	79

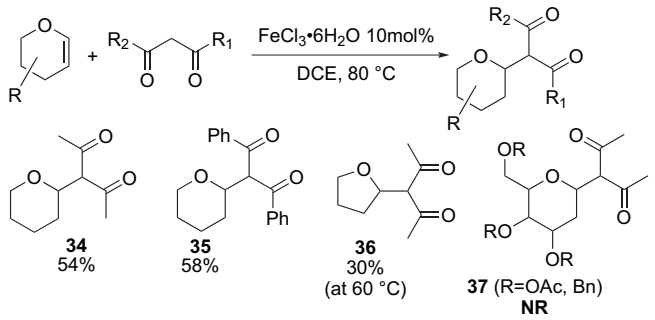
[a] $FeCl_3 \cdot 6H_2O$ (10 mol%) is finely ground before utilization.
[b] Reaction carried out on a Wheaton vial.



Scheme 6.



Scheme 7.



Scheme 8.

$J = 8.4$ Hz, 2H), 7.17 (d, $J = 8.1$ Hz, 2H), 7.27 (d, $J = 8.4$ Hz, 2H), 7.58 (d, $J = 8.1$ Hz, 2H)

^{13}C NMR ($CDCl_3$, 75 MHz): δ (*ppm*) 21.5, 23.4, 53.2, 121.2 (2C), 127.1, 128.1 (2C), 129.5 (2C), 131.5 (2C), 137.5, 141.2, 143.4.

IR: ν (cm^{-1}) 3239, 2971, 1596, 1488, 1438, 1321, 1153

HRMS (ESI): *m/z* $[M + Na]^+$ 376.0009, calc. for $C_{15}H_{16}^{79}BrNNaO_2S$: 375.9983; 377.9999, calc. for $C_{15}H_{16}^{81}BrNNaO_2S$: 377.9962.

*4.1.10. N-(1-(4-fluorophenyl)ethyl)-tosylamide (**11**)*

According to the general procedure for hydroamination, the reaction was carried out in dioxan. Purification by flash column chromatography (silica gel, EtOAc/heptane 2/8) yielded **11** in 63% yield as a white solid. Mp: 115–116 °C (Lit.[7f] 118–119 °C)

^{1}H NMR ($CDCl_3$, 300 MHz): δ (*ppm*) 1.47 (d, $J = 6.9$ Hz, 3H), 2.38 (s, 3H), 4.45 (quint, $J = 7.0$ Hz, 1H), 5.76 (d, $J = 7.3$ Hz, 1H), 6.83 ($\sim$t, $J = 8.7$ Hz, 2H), 7.08 (m, 2H), 7.16 (d, $J = 8.0$ Hz, 2H), 7.62 (d, $J = 8.3$ Hz, 2H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ (*ppm*) 21.4, 23.6, 53.0, 115.2 (d, $J = 21.6$ Hz, 2C), 127.1 (2C), 127.9 (d, $J = 8.4$ Hz, 2C), 129.4 (2C), 137.6, 138.1, 143.2, 161.9 (d, $J = 245.0$ Hz).

Data are in accordance with previously reported data [7f].

*4.1.11. N-(1-(4-(trifluoromethyl)phenyl)ethyl)-tosylamide (**12**)*

According to the general procedure, the reaction was carried out in dioxan. Purification by flash column chromatography (silica gel, EtOAc/heptane 3/7) yielded **12** in 5% yield as a white solid. Mp: 122–123 °C (Lit. no data available).

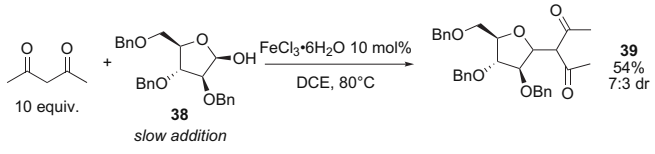
^{1}H NMR ($CDCl_3$, 500 MHz): δ (*ppm*) 1.42 (d, $J = 6.8$ Hz, 3H), 2.36 (s, 3H), 4.54 (quint, $J = 6.9$ Hz, 1H), 5.34 (d, $J = 7.0$ Hz, 1H), 7.12 (d, $J = 8.1$ Hz, 2H), 7.21 (d, $J = 8.1$ Hz, 2H), 7.40 (d, $J = 8.1$ Hz, 2H), 7.55 (d, $J = 8.1$ Hz, 2H).

^{13}C NMR (CDCl3, 75 MHz): δ (*ppm*) 21.4, 23.6, 53.4, 125.4 (d, *JF-C* = 3.4 Hz, 2C), 128.5 (d, *JF-C* = 194.4 Hz), 128.5 (q, *JF-C* = 426.6 Hz), 126.7 (2C), 127.1 (2C), 129.5, (2C), 137.4, 143.5, 146.0.

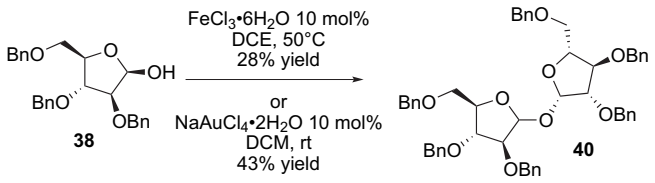
*4.1.12. N-(1-methyl-1-phenylethyl)-4-nitroaniline (**14**)*

According to the general procedure, the crude product was purified by flash column chromatography (AcOEt/PE 2/8) to give **14** in 12% yield, as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) : δ (ppm) 1.63 (s, 6H), 4.90 (broad s, 1H), 6.19 (d, $J = 9.2$ Hz, 2H), 7.18–7.36 (m, 5H), 7.82 (d, $J = 9.2$ Hz, 2H).



Scheme 9.



Scheme 10.

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 30.4, 56.5, 113.4, 125.2, 125.7, 127.0, 128.9, 137.8, 145.3, 151.5. MS (CI, NH_3) *m/z* (%) 513 ($2M + NH_4^+$, 85), 392 (10), 274 ($M + NH_4^+$, 30), 257 ($M + H^+$, 100), 256 ($M^{\cdot+}$, 40), 119 (10).

Data are in accordance with previously reported data [17].

*4.1.13. N-(1-phenylpropyl)-tosylamide (**15**)*

According to the general procedure for hydroamination, the reaction was carried out in dioxan. Purification by flash column chromatography (silica gel, EtOAc/heptane 3/7) yielded **15** in 11% yield as a white solid. Mp: 102–103 °C (Lit.[19] 108–109 °C)

^{1}H NMR ($CDCl_3$, 500 MHz): δ (*ppm*) 0.79 (t, $J = 7.4$ Hz, 3H), 1.74 (m, 2H), 2.36 (s, 3H), 4.20 (q, $J = 7.4$ Hz, 1H), 5.23 (d, $J = 7.4$ Hz, 1H), 7.02 (m, 2H), 7.11 (d, $J = 8.1$ Hz, 2H), 7.15 (m, 3H), 7.56 (d, $J = 8.2$ Hz, 2H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ (*ppm*) 10.6, 21.5, 30.7, 59.9, 126.7 (2C), 127.1 (2C), 127.3, 128.4 (2C), 129.3 (2C), 137.8, 140.8, 143.0.

Data are in accordance with previously reported data [18].

*4.1.14. N-(vinylbenzyl)-4-nitroaniline (**18**) N,N′-di-4-nitrophenyl-1-(aminomethylphenyl)-ethylamine (**19**)*

According to the general procedure for hydroamination, the reaction was carried out in refluxing DCE. Separation by flash column chromatography (silica gel, EtOAc/PE 2/8 then 2/3) yielded **18** in 15% as a yellow solid and **19** in 43% as a yellow oil.

18 (description of the meta substituted product obtained as the major isomer in the mixture): ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 4.35 (d, $J = 5.2$ Hz, 2H), 4.80 (br s, 1H), 5.21 (d, $J = 10.8$ Hz, 5.69 (d, $J = 17.7$ Hz, 1H), 6.51 (d, $J = 9.2$ Hz, 2H), 6.64 (dd, $J = 10.8$, 17.7 Hz, 1H, 7.16 (m, 1H), 7.19–7.31 (m, 3H), 8.01 (d, $J = 9.2$ Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 47.6, 111.3, 114.6, 125.2, 125.7, 126.4, 126.7, 129.2, 136.3, 137.6, 138.3, 138.4, 153.0.

MS (CI, NH_3, neg): *m/z* (%) 253 ($M - H^-$, 100), 137 (10).

19 (mixture of the meta/para isomers):

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.51 (m, 3H), 4.34 (s, 2H), 4.52 (m, 1H), 4.73 (br s, 1H), 6.37 (m, 2H), 6.48 (m, 2H), 7.16–7.32 (m, 4H), 7.92 (m, 2H), 8.00 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 24.6, 47.2, 47.5, 52.9, 53.1, 111.3, 111.8, 124.4, 125.2, 126.1, 126.2, 126.3, 126.4, 126.5, 128.0, 129.6, 136.7, 138.1, 128.2, 138.3, 143.1, 144.2, 152.1, 153.0.

MS (CI, NH_3, neg): *m/z* (%) 391 ($M - H^-$, 100), 137 (10).

*4.1.15. N-(cyclohex-2-enyl)-tosylamide (**20**)*

According to the general procedure for hydroamination, the reaction was carried out with 1,3-cyclohexadiene (95 μL, 1 mmol), $TsNH_2$ (856 mg, 5 mmol) and $FeCl_3$ (16 mg, 0.1 mmol) in dioxan (5 mL) at 80 °C. Purification by flash column chromatography (silica gel, EtOAc/heptane 3/7) yielded **20** in 44% yield as a white solid. Mp: 104–105 °C (Lit.[20] 108–109 °C)

^{1}H NMR ($CDCl_3$, 300 MHz): δ (*ppm*) 1.46–2.00 (m, 6H), 2.42 (s, 3H), 3.80 (m, 1H), 4.86 (d, $J = 8.5$ Hz, 1H), 5.35 (m, 1H), 5.74 (m, 1H), 7.29 (d, $J = 8.1$ Hz, 2H), 7.78 (d, $J = 8.1$ Hz, 2H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ (*ppm*) 19.2, 21.4, 24.3, 30.0, 48.9, 126.9 (2C), 127.0, 129.5 (2C), 131.2, 138.3, 143.0.

Data are in accordance with previously reported data [19].

4.1.16. 4-methyl-N-(tetrahydro-2H-pyran-2-yl) benzenesulfonamide (**21**)

According to the general procedure, compound **21** is obtained in 89% yield as a pale yellow solid after purification by flash chromatography on silica gel (Pentane/Ethyl Acetate: 9/1 → 8/2).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.38(m, 3H), 1.55 (m, 1H), 1.79 (m, 2H), 2.40 (s, 3H), 3.37(m, 1H), 3.69 (d, 1H), 4.75 (td, $J = 2.4$ Hz, $J = 9.4$ Hz, 1H), 5.38 (d, $J = 9.4$ Hz, 1H), 7.26 (d, $J = 8.0$ Hz, 2H), 7.79 (d, $J = 8.3$ Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 21.5, 22.3, 24.6, 31.8, 66.1, 82.0, 127.1, 129.3, 138.8, 143.2. Data are in accordance with previously reported data [20].

4.1.17. N-(4-nitrophenyl)tetrahydro-2H-pyran-2-amine (**22**)

To a solution of 4-nitroaniline (279.5 mg, 2 mmol, 1 equiv.) and iron (III) chloride hexahydrate (59.2 mg, 0.2 mmol, 0.1 equiv.) in 10 mL of 1,4-dioxane at 80 °C was added dropwise by a syringe pump, over 4 h, the 3,4-Dihydro-2H-pyran (509.7 mg, 6 mmol, 3 equiv.) diluted in 10 mL of 1,4-dioxane. Then, the mixture was heated at 80 °C for additional 30 mn. The resulting reaction mixture was concentrated under *vacuum* and the crude material directly purified by flash chromatography on silica gel (Pentane/Ether: 9/1 to 7/3) to give the ether-amine **22** (240.8 mg, 54%) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.6 (m, 4H), 1.93 (m, 2H), 3.58 (m, 1H), 3.97 (m, 1H), 4.72 (m, 1H), 5.04 (br s, 1H), 6.69 (d, $J = 9.2$ Hz, 2H), 8.08 (d, $J = 9.2$ Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 22.4, 25.0, 31.2, 65.8, 81.3, 112.7 (2C), 126.0 (2C), 139.3, 151.2.

Data are in accordance with previously reported data [21].

4.2. General procedure for the addition of 1,3-dicarbonyl nucleophiles to olefins

To a solution of β-diketone (20 mmol, 10 equiv.) and iron (III) chloride hexahydrate (0.1 equiv., finely ground) in 10 ml of 1,4-dioxane was added dropwise by a syringe pump, over 4 h, the substrate (2 mmol, 1 equiv.) diluted in 10 mL of 1,4-dioxane. The mixture was then stirred at the indicated temperature during 8 h. The mixture was then concentrated under vacuum and the crude material loaded on to a silica gel column and chromatographed with a mixture of Cyclohexane/AcOEt. The mixture of β-diketone and product was next purified by Kügelrohr distillation to afford the desired product.

4.2.1. 3-(1-phenylethyl)pentane-2,4-dione (**25**)

The compound (**25**) was prepared according to the general protocol on a 2 mmol scale. Purified by flash chromatography on silica gel (Cyclohexane/AcOEt: 8/2) and Kügelrhor distillation. Yield: 86%.

^{1}H NMR ($CDCl_3$, 400 MHz): δ (*ppm*) 1.19 (d, $J = 6.8$ Hz, 3H), 1.84 (s, 3H), 2.25 (s, 3H), 3.52–3.62 (dq, $J = 6.8$ Hz, J = 11.3 Hz), 4.00 (d, $J = 11.3$ Hz), 7.11–7.31 (m, 5H).

^{13}C NMR ($CDCl_3$, 100 MHz) : δ (*ppm*) 20.8, 29.7, 29.8, 40.4, 76.6, 126.9, 127.2, 128.8, 142.9, 203.4, 203.5.

Data are in accordance with previously reported data [22].

4.2.2. ethyl 2-acetyl-3-phenylbutanoate (**26**)

The compound (**26**) was prepared according to the general protocol on 2 mmol scale. Purified by flash chromatography on silica gel (Cyclohexane/AcOEt: 8/2) and Kügelrhor distillation. Yield: 62%.

^{1}H NMR ($CDCl_3$, 400 MHz): δ (*ppm*) 1,19 (m, 6H), 1.24 (d, $J = 6.9$ Hz, 3H), 1.29 (d, $J = 6.9$ Hz, 3H), 1.92 (s, 3H), 2.29 (s, 3H), 3.49–3.59 (m, 2H), 3.74 (d, $J = 11.1$ Hz, 1H), 3.80 (d, $J = 10.9$ Hz, 1H), 3.99 (q, $J = 7.1$ Hz, 2H), 4.18 (q, $J = 7.1$ Hz, 2H), 7.15–7.29 (m, 10H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ (*ppm*) 19.0, 19.1, 20.1, 20.6, 29.6, 29.9, 39.7, 40.1, 52.1, 52.5, 66.8, 67.4, 126.8, 126.9, 127.2, 127.3, 128.5, 128.7, 142.9, 143.2, 168.6, 169.0, 202.3 (2C).

Data are in accordance with previously reported data [22].

4.2.3. 1,3-diphenyl-2-(1-phenylethyl)propane-1,3-dione (**27**)

The compound (**27**) was prepared according to the general protocol on 2 mmol scale. Purified by flash chromatography on silica gel (Cyclohexane/AcOEt: 8/2) and Kügelrhor distillation. Yield: 79%.

^{1}H NMR ($CDCl_3$, 400 MHz): δ (*ppm*) 1.47 (d, $J = 7.0$ Hz, 3H), 3.49 (dq, $J = 7.0$ Hz, J = 10.7 Hz), 5.54 (d, $J = 10.5$ Hz, 1H), 7.12–7.84 (m, 15H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ (*ppm*): 21.2, 41.9, 60.1, 127.5, 128.5, 128.6, 133.5, 133.7, 143.9, 195.8, 196.1 (two quaternary aromatic C signals are not clearly visible in this spectrum.)

Data are in accordance with previously reported data [22].

4.2.4. 3-(1-p-Tolylethyl)pentane-2,4-dione (**28**)

The compound (**28**) was prepared according to the general protocol on 2 mmol scale. Purified by flash chromatography on silica gel (Cyclohexane/AcOEt: 8/2) and Kügelrhor distillation. Yield: 64%.

^{1}H NMR ($CDCl_3$, 400 MHz): δ (*ppm*) 1.16 (d, $J = 7.0$ Hz, 3H), 1.81 (s, 3H), 2.23 (s, 3H), 2.31 (s, 3H), 3.56 (dq, $J = 6.9$ Hz, $J = 11.3$ Hz), 4.01 (d, $J = 11.3$ Hz), 7.02–7.14 (m, 4H).

^{13}C NMR ($CDCl_3$, 100 MHz) : δ (*ppm*) 20.9, 21.1, 29.9 (2C), 40.4, 76.8, 127.3, 129.8, 137.0, 140.9, 203.2, 203.3.

Data are in accordance with previously reported data [23].

4.2.5. 3-(cyclohex-2-enyl)pentane-2,4-dione (**29**)

The compound (**29**) was prepared according to the general protocol on 2 mmol scale. Purified by flash chromatography on silica gel (Cyclohexane/AcOEt: 9/1) and Kügelrohr distillation. Yield: 64%.

^{1}H NMR ($CDCl_3$, 400 MHz): δ (*ppm*) 1.10–1.18 (m, 1H), 1.47–1.52 (m, 1H), 1.60–1.69 (m, 2H), 1.90–1.95 (m, 2H), 2.12 & 2.13 (s, 6H), 2.91–3.00 (m, 1H), 3.53–3.56 (d, $J = 10.6$ Hz, 1H), 5.29–5.33 (m, 1H), 5.68–5.73 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ (*ppm*) 20.6, 24.8, 26.6, 29.6, 30.1, 35.6, 74.9, 126.9, 130.0, 203.8, 204.1.

Data are in accordance with previously reported data [12].

4.2.6. ethyl 2-(cyclohex-2-enyl)-3-oxobutanoate (**30**)

The compound (**30**) was prepared according to the general protocol on 2 mmol scale. Purified by flash chromatography on silica gel (Cyclohexane/AcOEt: 8/2) and Kügelrohr distillation. Yield: 40%.

^{1}H NMR ($CDCl_3$, 400 MHz): δ (*ppm*) 1.20–1.36 (m, 1H), 1.26 (t, $J = 7.1$ Hz, 3H), 1.50–1.61 (m, 1H), 1.66–1.79 (m, 2H), 1.92–2.02 (m, 2H), 2.22 & 2.23 (s, 3H), 2.90–2.99 (m, 1H, H2), 3.34 & 3.36 (d & d, $J = 9.8$ Hz & $J = 10$ Hz, 1H), 4.18 (q, $J = 7.1$ Hz, 2H), 5.42 & 5.49 (ddd & ddd, $J = 2.0$ Hz, $J = 4.1$ Hz, $J = 10.1$ Hz & $J = 2.6$ Hz, $J = 4.7$ Hz, $J = 10.0$ Hz, 1H), 5.73–5.78 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ (*ppm*) 14.2, 20.8, 20.9, 24.9, 25.0, 26.6, 26.7, 29.5, 29.8, 35.1, 35.2, 61.3, 65.3, 127.3, 127.5, 129.6, 129.8, 168.8, 202.7, 202.9.

Data are in accordance with previously reported data [11c].

4.2.7. 2-(cyclohex-2-enyl)-1,3-diphenylpropane-1,3-dione (**31**)

The compound (**31**) was prepared according to the general protocol on 2 mmol scale. Purified by flash chromatography on silica gel (Cyclohexane/AcOEt: 8/2) and recristallization in Cyclohexane/Et_2O. Yield: 48%.

^{1}H NMR ($CDCl_3$, 400 MHz): δ (*ppm*) 1.32–1.77 (m, 4H), 2.00–2.04 (m, 2H), 3.49–3.53 (m, 1H), 5.24–5.28 (m, 1H), 5.39–5.80 (m, 2H), 7.39–7.60 (m, 6H), 8.02 (m, 4H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ (*ppm*) 21.2, 24.9, 27.5, 37.2, 62.5, 128.5, 128.6 (4C), 129.2, 133.2, 133.3 (2C), 136.9, 137.0, 194.5, 194.9.

Data are in accordance with previously reported data [13].

4.2.8. Ethyl 1-(cyclohex-2-enyl)-2-oxocyclopentanecarboxylate (**32**)

The compound **(32)** was prepared according to the general protocol on 2 mmol scale. Purified by flash chromatography on silica gel (Cyclohexane/AcOEt: 9/1) and Kügelrohr distillation. Yield: 14% (1:1 mixture of diastereoisomers).

^{1}H NMR ($CDCl_3$, 400 MHz): δ (*ppm*) 1.21 (m, 3H), 1.42–2.27 (m, 10H), 2.32–2.48 (m, 2H), 3.04–3.16 (m, 1H), 4.06–4.19 (m, 2H), 5.36 & 5.39 (m, 1H), 5.71–5.78 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ (*ppm*) 14.1 (2C), 19.8 & 19.9, 21.9 & 22.1, 24.2 & 24.9, 25.0 & 25.5, 28.2 & 28.8, 39.2 (2C), 40.1 & 40.7, 61.5 & 61.6, 64.0 & 64.1, 126.9 & 127.4, 130.0 & 130.7, 173.1 & 173.8, 208.4 and 209.1.

Data are in accordance with previously reported data [12].

4.2.9. 3-(Tetrahydropyran-2-yl)pentane-2,4-dione (**34**)

The compound (**34**) was prepared according to the general protocol on 2 mmol scale. Purified by flash chromatography on silica gel (Cyclohexane/AcOEt: 8/2) and Kügelrohr distillation. Yield: 54%.

^{1}H NMR ($CDCl_3$, 400 MHz): δ (*ppm*) 1.14–1.23 (m, 1H), 1.46–1.61 (m, 4H), 1.79 (m, 1H), 2.17 & 2.19 (s & s, 6H), 3.39 (∼t, J = 11.3 Hz, 1H), 3.74 (∼d, J = 9.6 Hz, 1H), 3.91 (∼d, J = 9.9 Hz, 1H), 3.98 (∼t, J = 10.2 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ (*ppm*): 23.0, 25.6, 29.1, 30.7, 29.8 , 68.7, 74.9, 76.8, 202.0, 202.9 (2C).

Data are in accordance with previously reported data [11c].

4.2.10. 1,3-Diphenyl-2-(tetrahydro-2H-pyran-2-yl)propane-1,3-dione (**35**)

The compound **(35)** was prepared according to the general protocol on 2 mmol scale. Purified by flash chromatography on silica gel (Cyclohexane/AcOEt: 8/2) and recristallization in Cyclohexane/Et_2O. Yield: 58% (yellowish solid).

^{1}H NMR ($CDCl_3$, 400 MHz): δ (*ppm*) 1.30–1.38 (m, 1H), 1.54–1.61 (m, 2H), 1.78–1.82 (m, 2H), 3.40–3.45 (m, 1H), 3.90–3.94 (m, 1H), 4.91–4.97 (m, 1H), 5.48 (∼d, J = 9.2 Hz, 1H), 7.38–7.52 (m, 5H), 7.94–7.98 (m, 5H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ (*ppm*) 23.7, 26.3, 36.9, 63.2, 69.2, 76.8, 133.4, 133.8, 136.8, 137.4 (4C), 150.1 (2C), 193.5, 194.6.

Data are in accordance with previously reported data [11a].

4.2.11. 3-(tetrahydrofuran-2-yl)pentane-2,4-dione (**36**)

The compound (**36**) was prepared according to the general protocol on 2 mmol scale. Purified by flash chromatography on silica gel (Cyclohexane/AcOEt: 8/2) and Kügelrohr distillation. Yield: 30% (colorless oil).

^{1}H NMR ($CDCl_3$, 400 MHz): δ (*ppm*) 1.31–1.34 (m, 1H), 1.78–1.85 (m, 2H), 2.01–2.07 (m, 1H), 2.11 & 2.18 (s & s, 6H), 3.60–3.77 (m, 3H), 4.35–4.40 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ (*ppm*) 25.1, 29.4, 30.3, 30.0, 67.7, 74.0, 77.4, 202.0, 202.7.

Data are in accordance with previously reported data [11a].

4.2.12. 3-((3R,4R,5R)-3,4-bis(benzyloxy)-5-(benzyloxymethyl) tetrahydrofuran-2-yl)pentane-2,4-dione (**39**)

The compound (**39**) was prepared according to the general protocol on 2 mmol scale. Purified by flash chromatography on silica gel (Cyclohexane/AcOEt: 9/1). Yield: 54% (obtained as a colorless oil and in a 7:3 dr)

^{1}H NMR ($CDCl_3$, 400 MHz): δ (*ppm*) 1.88 & 2.15 (s & s, 6Hα), 1.94 & 2.13 (s & s, 6Hβ), 3.33–3.46 (m, 2Hα & 2Hβ), 3.60 (m, 1Hβ), 3.84 (dd, J = 0.8 Hz, J = 2.9 Hz, 1Hα), 3.87 (m, 1Hβ), 3.94–4.11 (m, 3Hα & 2Hβ), 4.23–4.46 (m, 6Hα & 6Hβ), 4.57 (dd, J = 4.3 Hz, J = 10.1 Hz, 1Hα), 4.69 (dd, J = 1.8 Hz, J = 10.7 Hz, 1Hα), 6.99–7.23 (m, 15Hα & 15Hβ).

^{13}C NMR ($CDCl_3$, 100 MHz): δ (*ppm*) 29.5 & 30.4, 29.6 & 30.3, 68.5, 70.0, 70.2,70.5, 71.3, 71.5, 71.7, 71.8, 73.2, 80.0, 81.7, 82.7, 82.8, 82.9, 83.1, 84.8, 85.4, 127.6, 127.7, 127.8, 127.9, 128.3, 128.4, 137.4, 137.5, 138.0, 138.1, 201.7 & 202.8, 202.0 & 202.1.

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