Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting information

Carbon-supported iron-ionic liquid: an efficient and recyclable catalyst for benzylation of 1,3-dicarbonyl compounds with alcohols

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Scheme S 1. Reaction between acetylacetone (**1a**) and 1-phenylethanol (**2a**)

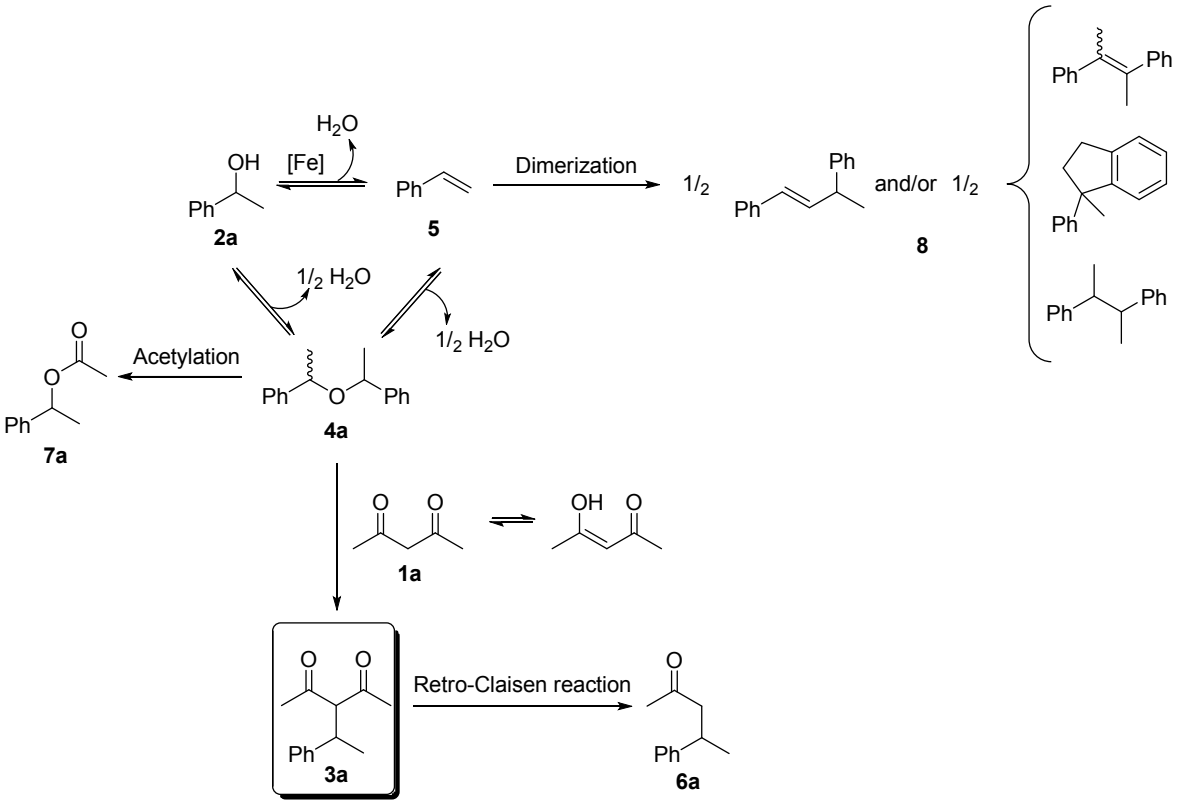
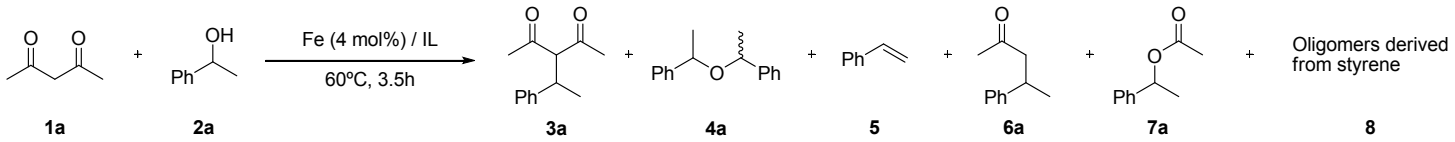


Table S 1. Iron-catalyzed reaction of acetylacetone (**1a**) and 1-phenylethanol (**2a**).[a, b, c]



1a **2a** **3a** **4a** **5** **6a** **7a** **8**

Entry	Iron source	IL	3a (%)	4a (%)	5 (%)	6a (%)	7a (%)	8 (%)	Tot (%)
1	$Fe(OTf)_3$	-	23.0	74.4	1.8	-	0.8	-	100
2	$Fe(ClO_4)_3.xH_2O$	$BMIMNTf_2$	96.7	0.1	1.6	-	-	1.6	100
3	$Fe(OTf)_3$	$BMIMNTf_2$	66.8	16.4	3.9	-	1.1	4.2	100[e]
4	$Fe(OTf)_3$	$BMIMNTf_2$[d]	78.5	9.0	2.1	0.2	0.6	9.6	100
5	$FeCl_3.6H_2O$	$BMIMNTf_2$	48.5	49.8	1.3	-	0.3	0.1	100
6	$Fe(ClO_4)_3.xH_2O$	$N_{4111}NTf_2$	68.7	24.7	1.9	-	0.7	4.0	100
7	$Fe(OTf)_3$	$N_{4111}NTf_2$	79.4	10	8.6	-	0.9	1.1	100
8	$Fe(OTf)_3$	$N_{4111}NTf_2$[d]	85.5	9.0	3.4	-	1.0	1.1	100
9	$FeCl_3.6H_2O$	$N_{4111}NTf_2$	44.5	53.9	1.2	-	0.4	-	100
10	$Fe(ClO_4)_3.xH_2O$	BMIMOTf	46.5	46.2	5.2	-	2.1	-	100
11	$Fe(OTf)_3$	BMIMOTf	21.6	67.8	8.7	-	1.4	0.4	99.9
12	$FeCl_3.6H_2O$	BMIMOTf	15.2	82.4	1.6	-	0.7	-	99.9
13	$Fe(ClO_4)_3.xH_2O$	$BMIMBF_4$	5.1	50.6	0.3	-	1.3	0.5	57.8
14	$Fe(OTf)_3$	$BMIMBF_4$	9.5	68.1	0.5	-	2.1	-	80.2
15	$FeCl_3.6H_2O$	$BMIMBF_4$	-	12.2	-	-	-	0.8	13.0
16	$Fe(ClO_4)_3.xH_2O$	$BMIMPF_6$	13.4	82.1	0.7	-	0.2	-	96.4
17	$Fe(OTf)_3$	$BMIMPF_6$	23.6	74.7	1.2	-	0.5	-	100
18	$FeCl_3.6H_2O$	$BMIMPF_6$	13.3	76.7	0.8	-	0.4	-	91.2

[a] GC conversion of all compounds detected. [b] *General reaction conditions*: 0.5 mmol of **2a**; 4 equiv. of **1a**; 4 mol% Fe; 77 mg of IL; 60 ºC for 3.5 h. [c] After 3.5 h the conversions of bis(diphenylmethyl) ether (**4a**) and styrene (**5**) were lacking or remained constant as judged by GC. [d] 100 mg of IL was used. [e] An unidentified product was detected (conversion 7.6 %).

Table S 2. Influence of support properties on the catalytic activity of $Fe(OTf)_3$-$N_{4111}NTf_2$ catalyst system and advantage of the use of IL.[a,b]

Entry	Catalytic system	3a (%)	4a (%)	5 (%)	6a (%)	7a (%)	8 (%)	Tot (%)
1	$Fe(OTf)_3$-N_{4111}TFSI/MB-0	3.7	53.9	0.8	-	-	-	58.4
2	$Fe(OTf)_3$-N_{4111}TFSI/MB-LTA	4.2	47.3	1.1	-	-	0.3	52.9
3	$Fe(OTf)_3$-N_{4111}TFSI/MB-2000	**98.2**	-	1.8	-	-	-	100
4	$Fe(OTf)_3$-N_{4111}TFSI/MB-2000-LTA	**95.7**	0.2	2.2	0.3	-	1.6	100
5	$Fe(OTf)_3$/MB-2000	64.7	21.5	9.5	0.2	3.1	1.0	100
6	$Fe(OTf)_3$/MB-2000-LTA	86.0	2.7	6.5	0.2	1.8	2.8	100

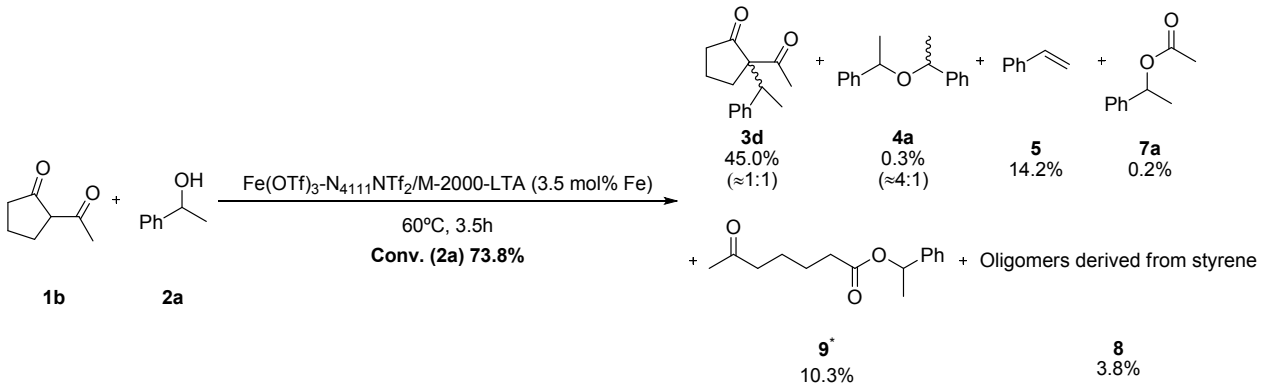
[a] GC conversion of all compounds detected. [b] *General reaction conditions*: 0.5 mmol of **2a**; 4 equiv. of **1a**; 286 mg of $Fe(OTf)_3$-$N_{4111}NTf_2$/MB (35 wt% IL; 3.5 wt% iron salt) (3.5 mol% Fe); 60 ºC for 3.5 h.

Table S 3. Recycling study of Fe-IL catalysts supported on carbon materials.[a, b]

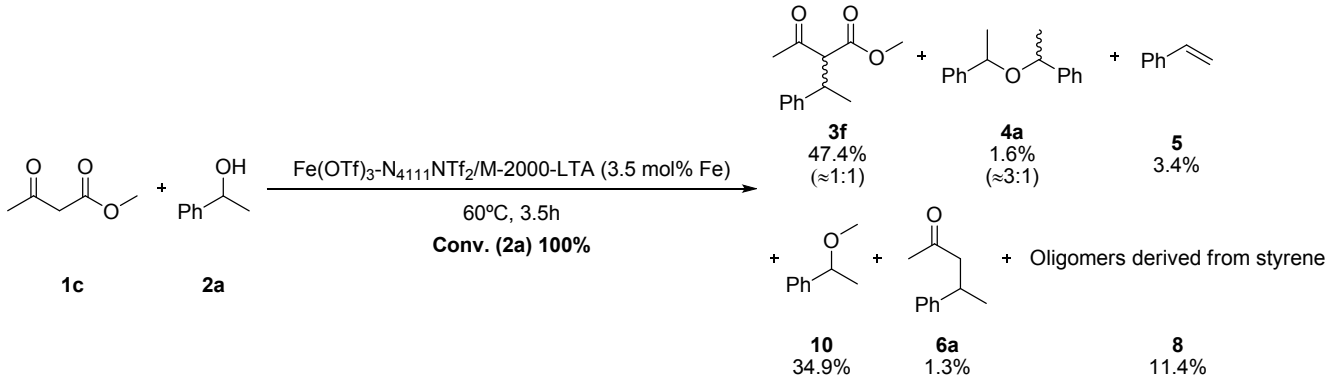
Entry	Catalytic system	Run	3a (%)	4a (%)	5 (%)	6a (%)	7a (%)	8 (%)	Tot (%)
1	$Fe(OTf)_3$-$N_{4111}NTf_2$/MB-2000	1	**98.2**	-	1.8		-	-	100
		2	**95.5**	-	2.5		-	2.0	100
		3	**71.9**	20.0	5.2		0.2	2.7	100
		4	**49.7**	43.0	3.5		0.3	1.0	97.5
2	$Fe(OTf)_3$-$N_{4111}NTf_2$/MB-2000-LTA	1	**95.7**	0.2	2.2	0.3	-	1.6	100
		2	**95.2**	0.4	2.5	0.1	0.1	1.7	100
		3	**92.3**	2.1	3.2		0.2	2.2	100
		4	**93.1**	0.9	3.2		0.1	2.7	100
		5	**47.0**	47.5	2.7	0.2	0.1	0.7	98.2
3	$Fe(OTf)_3$-$BMIMNTf_2$/MB-2000	1	**95.5**	-	2.7			1.8	100
		2	**92.8**	-	2.9	0.2		4.1	100
		3	**52.5**	31.4	14.0	0.1	0.3	1.4	99.7
4	$Fe(OTf)_3$-$BMIMNTf_2$/MB-2000-LTA	1	**94.9**	-	3.0	0.2	-	1.9	100
		2	**96.8**	-	2.0			1.6	100
		3	**55.8**	39.3	3.2		0.6	1.0	99.9

[a] GC conversion of all compounds detected. [b] *General reaction conditions*: 0.5 mmol of **2a**; 4 equiv. of **1a**; 286 mg of $Fe(OTf)_3$-$N_{4111}NTf_2$/MB (35 wt% IL; 3.5 wt% iron salt) (3.5 mol% Fe); 60 ºC for 3.5 h. **1a** was removed under reduced pressure before the work-up of the reaction mixture.

Scheme S 2. Heterogeneous iron catalyzed reaction of **1b** and **1c** with **2a**.



* Product **9**: Carbon-carbon bond cleavage through a retro-Claisen condensation type reaction between **1b** and **2a**.[1]



Carbon supports characterization

Surface area, pore volume and pore size distribution of MB-0, MB-2000, MB-LTA and MB-2000-LTA materials were derived from the N_2 adsorption–desorption isotherms performed at 77 K in a Micromeritics ASAP 2420 volumetric adsorption system. Prior to measurement, samples were outgassed overnight by heating at 523 K under vacuum. Specific surface areas (S_{BET}) were calculated using the Brunauer–Emmett–Teller (BET) method, taking 16.2 nm^2 for the cross-sectional area of the nitrogen adsorbed molecule. Total micropore volumes (VDR_{N2}) were assessed by applying the Dubinin–Radushkevich (DR) equation to the suitable adsorption data. Total pore volumes (V_t) were determined by the amount of N_2 adsorbed at p/p^0 = 0.99. Pore size distributions were obtained by applying the DFT (Density Functional Theory) method to the N_2 adsorption isotherms. X-Ray Photoelectron Spectroscopy (XPS) surface chemical analyses of carbon supports were carried out in a SPECS Phoibos 100 analyser using Mg Ka X-rays (1486.6 eV) at a power of 120 W and in a residual vacuum of 10^{-7} Pa. Measurements were made with the analyser in fixed transmission mode and normal to the plane of the sample. Analyser pass energy of 80 eV has been used to collect broad scan spectra (0–1100 eV). The atomic percentages (atom%) of the different elements present in the approx. 10 nm upper layer probed by XPS were calculated from the survey spectra by considering the integrated areas of the main XPS peaks. Representative samples of mesoporous carbon supports (around 150 mg) were tested. Typical standard deviation of the measurements is within ±0.5 atom% of the reported values.