Electronic Supporting Information

belonging to:

Anion-cation synergistic metal-free catalytic oxidative homocoupling of benzylamines by triazolium iodide salts

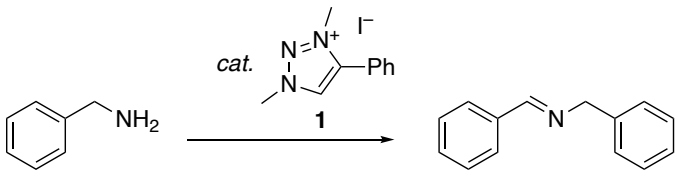
Joseph P. Byrne, Martin Albrecht*

Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, 3012 Bern, Switzerland

Contents:

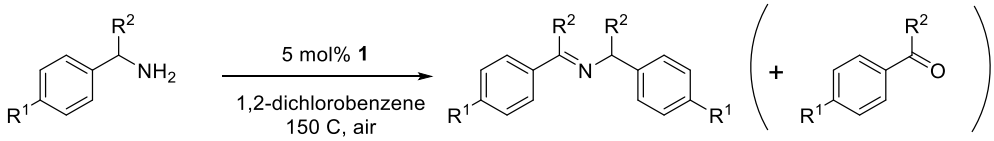
1. Catalytic data

Table S1. *Different solvent and temperature conditions tested for the reaction.*



Catalyst	Solvent	T (°C)	Yield (%)		
			1 h	*3 h*	*4 h*
1	1,2-Dichlorobenzene	150	60	100	99
1	1,2-Dichlorobenzene	115	0	<3	<3
1	Toluene	111	0	—	—
1	1,2-Dichloroethane	85	0	0	0

[a] General conditions: Benzyl amine (0.25 mmol), triazolium salt **1** (5 mol%) and hexamethylbenzene (internal standard), solvent (2 mL); [b] Spectroscopic yield determined by ^{1}H NMR analysis with respect to hexamethylbenzene



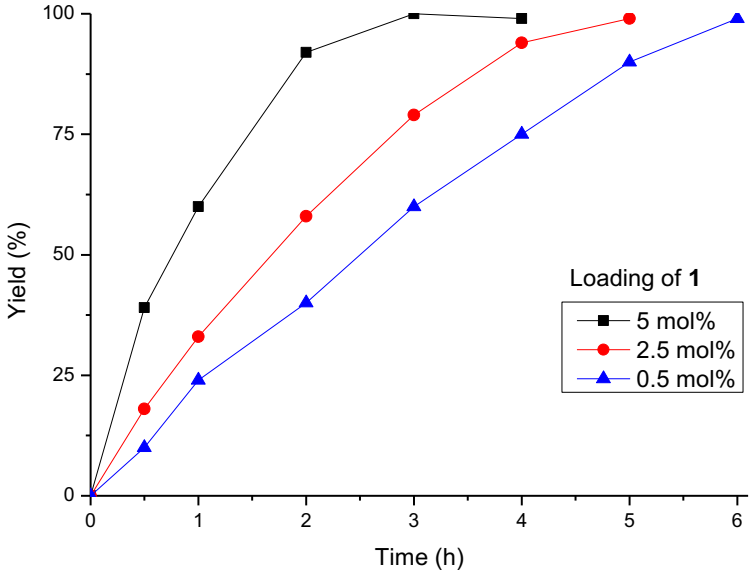


Figure S1. *Yield of imine product over time at various loadings of triazolium iodide* ***1***

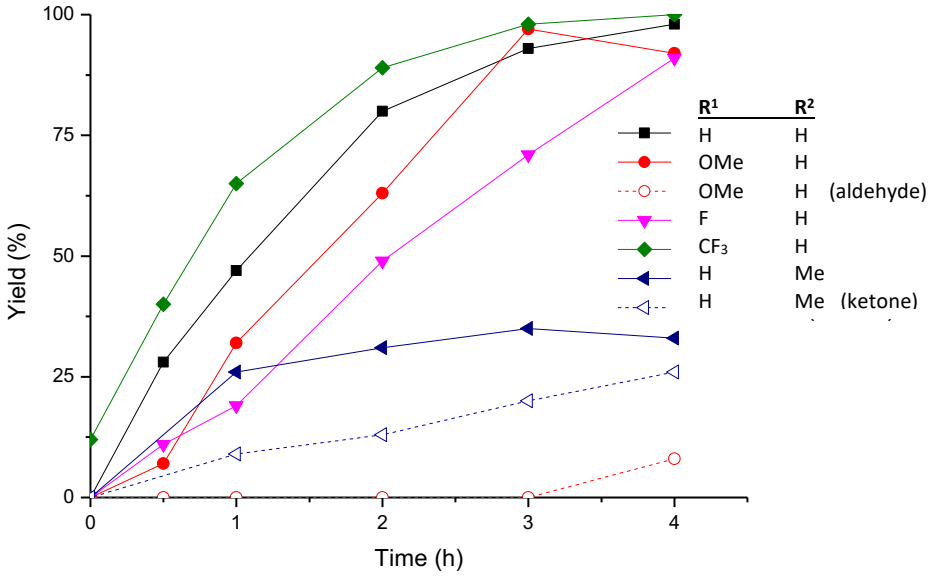


Figure S2. *Yields of different imine products over time upon reaction with catalyst* ***1***.

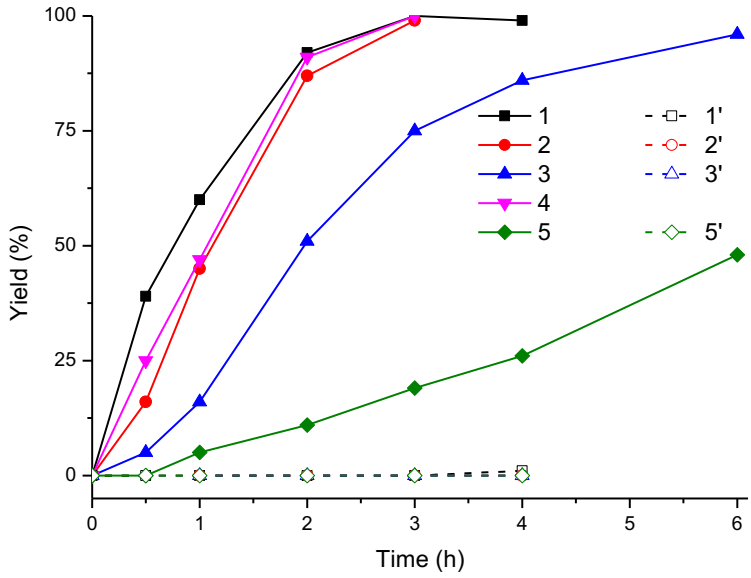


Figure S3. *Catalytic activity of a different triazolium and imidazolium salts for oxidative homocoupling of benzylamine.*

Table S2. *Other ammonium and iodide salts screened for catalytic activity, all used at 5 mol%.*[a]

Entry	Catalyst	Yield [b] (%)		
		1 h	*3 h*	*4 h*
1	$(Bu_4N)Br$	—	<2	—
2	$(NH_4)Cl$	0	0	0
3	$(Et_4N)I$	10	24	40
4	KI	4	25	39
5	KI + 18-crown-6	0	6	7

[a] General conditions: Benzyl amine (27 µL, 0.25 mmol), potential catalyst (0.012 mmol, 5 mol%) and hexamethylbenzene (internal standard) were dissolved in 1,2-dichlorobenzene (2 mL) and heated at 150 °C in round-bottomed flasks;
[b] Spectroscopic yield determined by ^{1}H NMR analysis with respect to hexamethylbenzene as internal standard

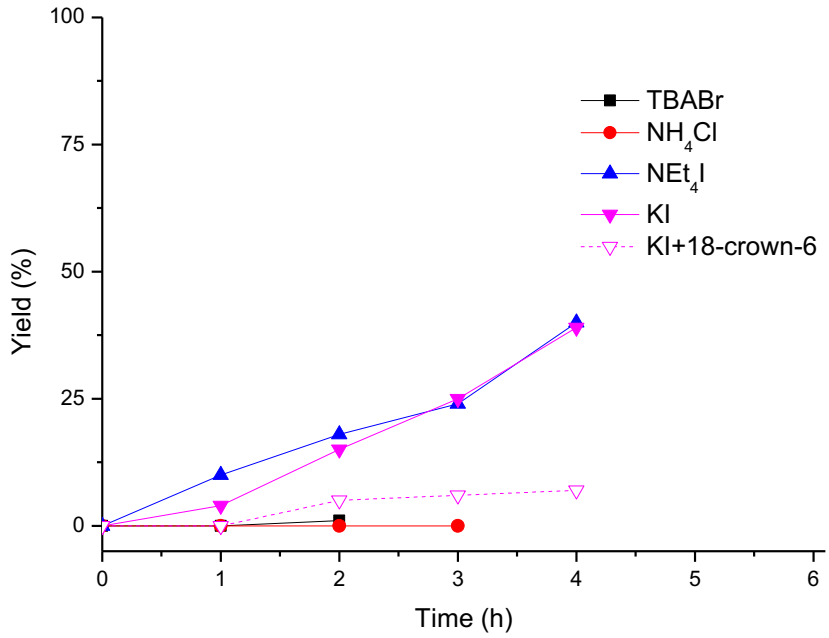


Figure S4. *Catalytic activity of different ammonium salts and iodide salts for oxidative homocoupling of benzylamine.*

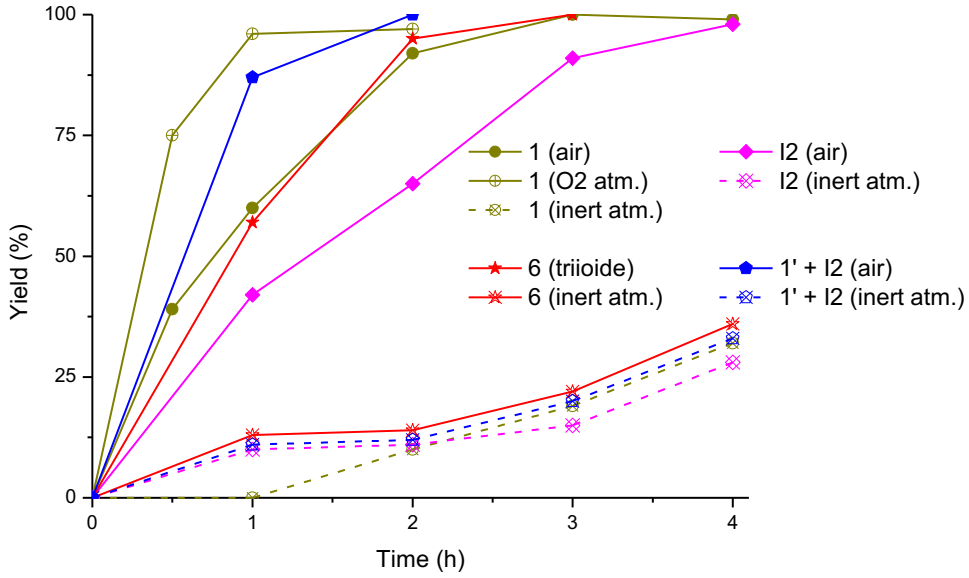


Figure S5. *Catalytic activity of different iodine-containing species.*

Table S3. *Full catalytic data for all reactions.*

Catalyst	mol%	Additive	equiv.	Substrate	Yield of imine (%)									TOF_{50}	TOF_{25}
					0 h	*0.5 h*	*1 h*	*2 h*	*3 h*	*4 h*	*5 h*	*6 h*	*20 h*		
---	0	---	---	$BnNH_2$	0		0	<2	<2	<2					
1	5	---	---	$BnNH_2$	0	39	60	92	100	99				13	16
1	5	KOtBu	1	$BnNH_2$	0	28	47	80	93	98				9.4	11
1	5	TsOH	1	$BnNH_2$	0	26	47	75	91	96				9.3	10
1	2.5	---	---	$BnNH_2$	0	18	33	58	79	94	99			12	14
1	0.5	---	---	$BnNH_2$	0	10	24	40	60	75	90	99		40	49
1	5	H_2O	10	$BnNH_2$	0		51	89	93	88 (6*)					
1	5	H_2O	100	$BnNH_2$	0		0	0	0	0				10	
1	5	H_2O, O_2	10 1 atm.	$BnNH_2$	0	46	65	93	90 (4*)	84 (6*)					
1	5	darkness		$BnNH_2$	0		52	85	97					11	11
1	5	N_2	1 atm.	$BnNH_2$	0		0	10	19	37					1.4
1	5	O_2	1 atm.	$BnNH_2$	0	75	96	97						30	29
2	5	---	---	$BnNH_2$	0	16	45	87	99					8.9	7.7
3	5	---	---	$BnNH_2$	0	5	16	51	75	86		96		5.1	4.0
4	5	---	---	$BnNH_2$	0	25	47	91	100					9.3	10
5	5	---	---	$BnNH_2$	0	0	5	11	19	26		48		1.6	1.3
6	5	---	---	$BnNH_2$	0		57	95	100					11	11
1'	5	---	---	$BnNH_2$	0		0	0	0	<2					
2'	5	---	---	$BnNH_2$	0		0	0	0	0					
3'	5	---	---	$BnNH_2$	0		0	0	0	0					
5'	5	---	---	$BnNH_2$	0	0	0	0	0	0					
Bu_4NBr	5	---	---	$BnNH_2$	0			<2							
NH_4Cl	5	---	---	$BnNH_2$	0		0	0	0	0					
Et_4NI	5	---	---	$BnNH_2$	0		10	18	24	40					1.6
KI	5	---	---	$BnNH_2$	0		4	15	25	39					1.7

Table S3. *Full catalytic data for all reactions (continued).*

Catalyst	mol%	Additive	equiv.	Substrate	Yield of imine (%)									TOF_{50}	TOF_{25}
					0 h	*0.5 h*	*1 h*	*2 h*	*3 h*	*4 h*	*5 h*	*6 h*	*20 h*		
KI	5	18-crown-6	0.05	$BnNH_2$	0		0	5	6	7					
I_2	5	---	---	$BnNH_2$	0		42	65	91	98				7.5	8.4
1'+I2	5 ea	---	---	$BnNH_2$	0		87	100						18	18
I_2	5	N_2	1 atm.	$BnNH_2$	0		10	11	15	28					1.3
6	5	N_2	1 atm.	$BnNH_2$	0		13	14	22	36					1.6
1'+I2	5 ea	N_2	1 atm.	$BnNH_2$	0		11	12	20	33					1.5
1	5	---	---	(4-OMe)$BnNH_2$	0	7	32	63	97	92 (8*)				6.0	5.9
1	5	---	---	(4-F)$BnNH_2$	0	11	19	49	71	91				5.0	4.2
1	5	---	---	(4-CF_3)$BnNH_2$	12	40	65	89	98	100				16	22
1	5	---	---	α-Me-$BnNH_2$	0		26 (9*)	31 (13*)	35 (20*)	33 (26*)			0 (53*)		5.3
1	5	O_2	1 atm.	α-Me-$BnNH_2$	0		42 (4*)	45 (12*)	<5 (20*)	0 (23*)					

Conditions as in Table 1, TOF in h^{-1} at 25% and 50% conversion, respectively, * denotes yield of corresponding carbonyl product

2. NMR spectra of triazolium salts

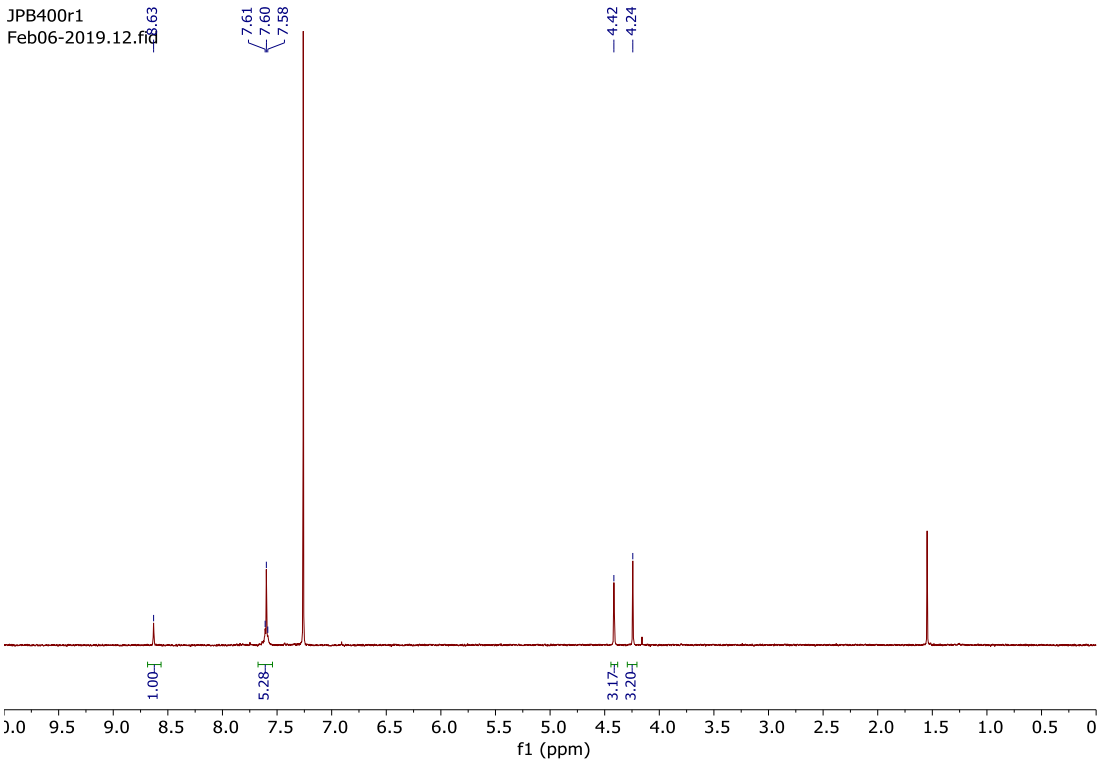


Figure S6. *^{1}H NMR spectrum (300 MHz, $CDCl_3$) of tetrafluoroborate salt **1'**.*

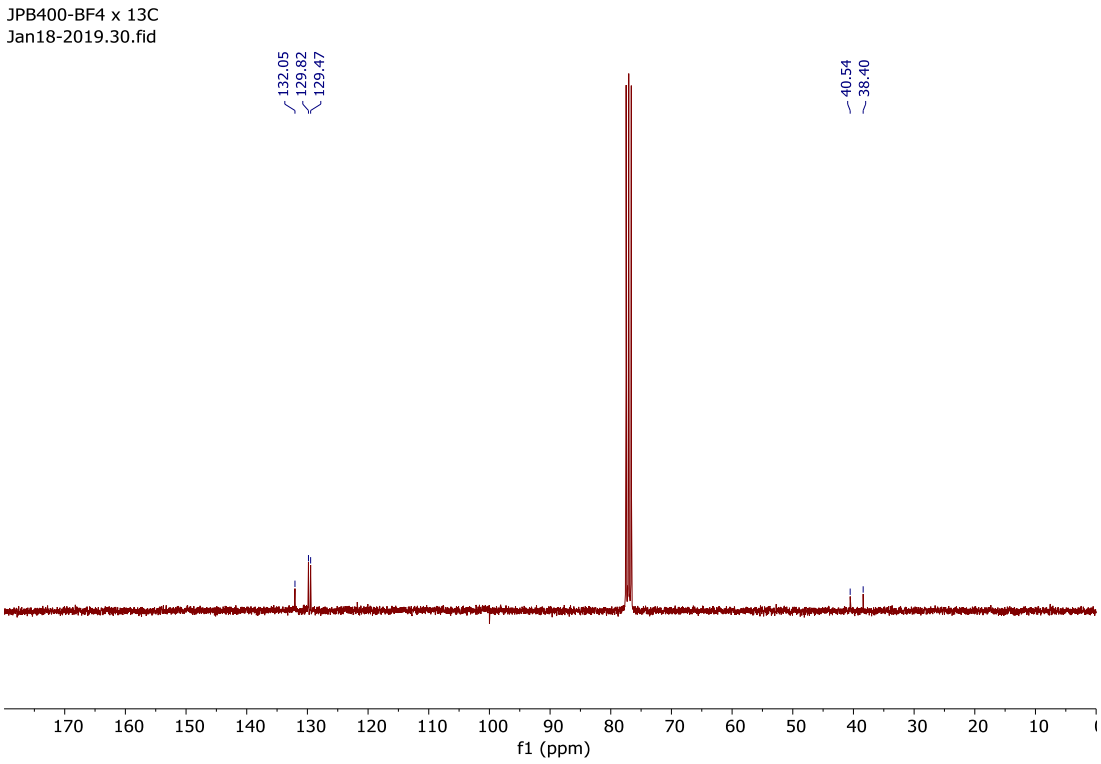


Figure S7. *$^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, $CDCl_3$) of tetrafluoroborate salt **1'**.*

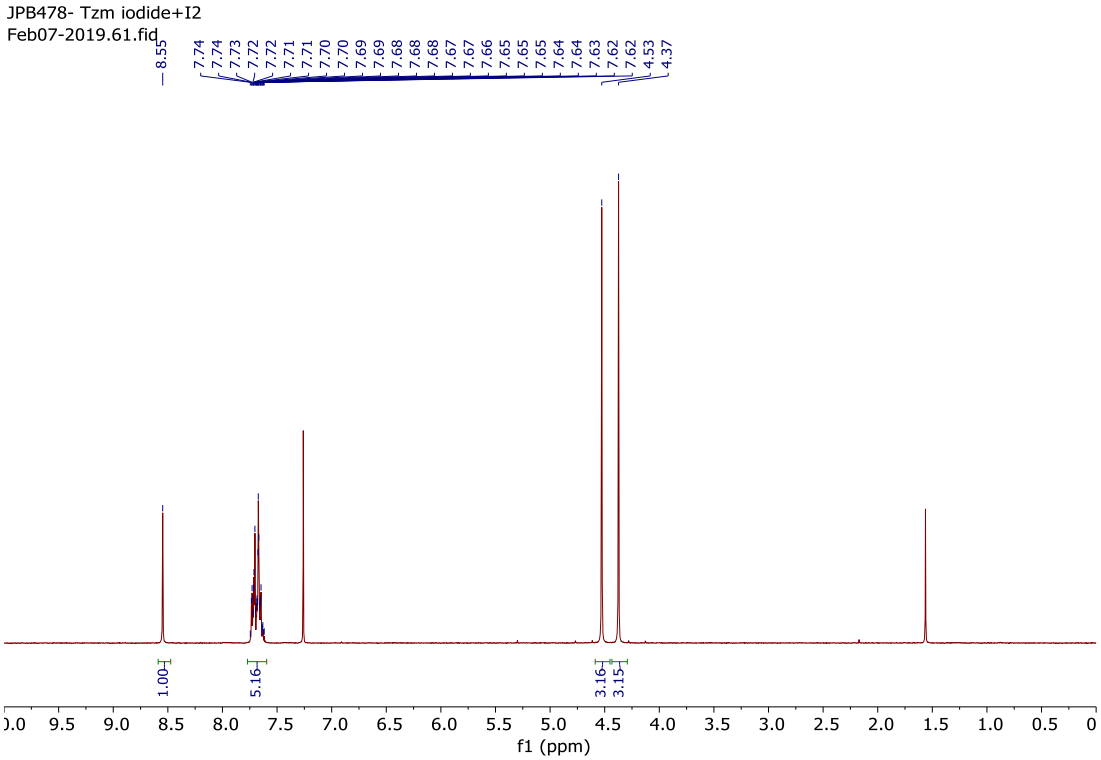


Figure S8. *^{1}H NMR spectrum (300 MHz, $CDCl_3$) of triiodide salt **6**, formed in situ by addition of equimolar amounts of **1** and I_2.*

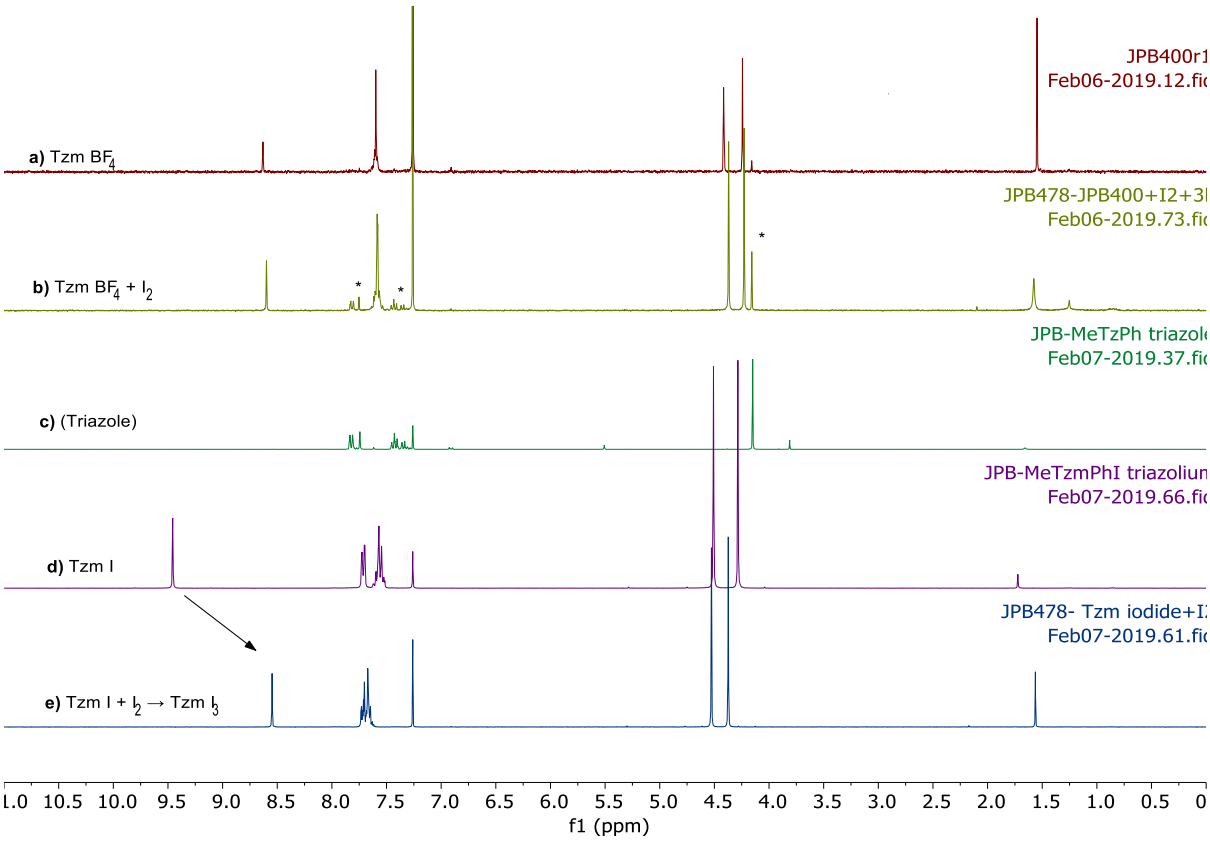


Figure S9. *Comparison of ^{1}H NMR spectra of triazolium salts with varying counterions, and upon addition of molecular iodine (Tzm = 1,3-dimethyl-4-phenyl-1,2,3-triazolium; * = 1-methyl-4-phenyl-1,2,3-triazole). Compounds from top to bottom: **1'**, **1'** + I_2, 1-methyl-4-phenyl-1,2,3-triazole, **1**, **6**.*

3. Crystallographic details

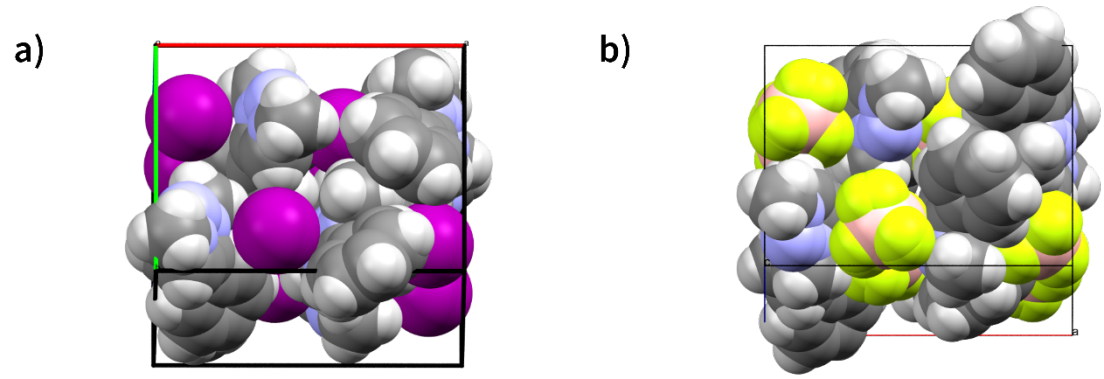


Figure S10. *Crystal packing structure of* ***(a)*** *triazolium iodide salt* ***1****, and* ***(b)*** *triazolium tetrafluoroborate* ***1'****, determined by single crystal X-ray diffraction analysis.*

The crystal of triiodide **6** used for XRD analysis was twinned as well as two other tested crystals of this sample. As an integration of two domains gave worse results than the integration of just the major domain, the latter was used. The quality of this single crystal structure determination is lowered by this fact. The results are good enough for a discussion of the crystal packing but do not allow a discussion of bonding geometry.

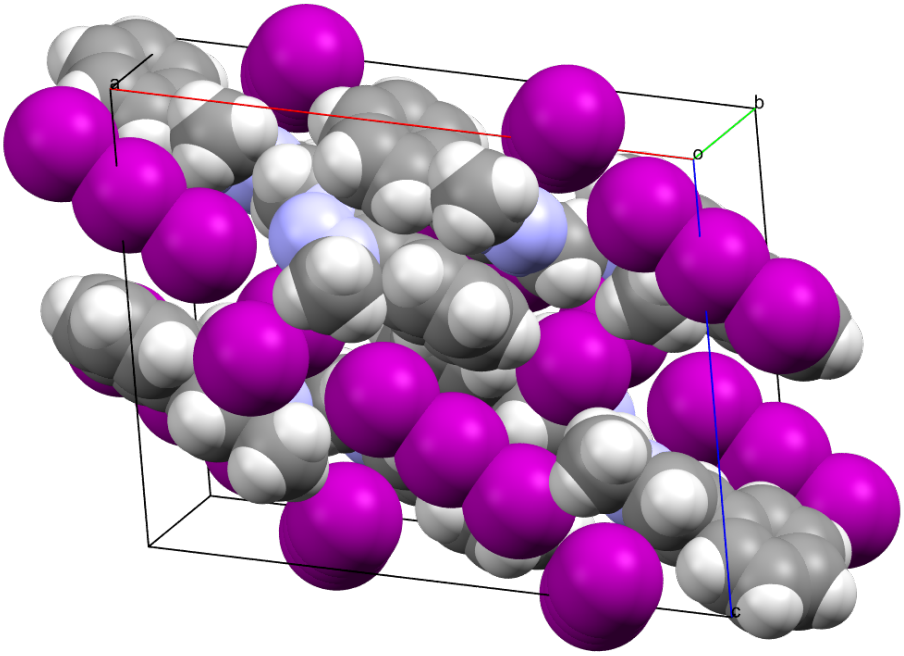


Figure S11. *Molecular structure of triazolium triiodide salt* ***6****, determined by single crystal X-ray diffraction analysis.*

Table S4. *Crystal data and structure refinement for triazolium salts **1**, **1'** and **6**.*

Compound	**1**	**1'**	**6**
CCDC No.	2016764	2016765	2016766
Empirical formula	$C_{10}H_{12}IN_3$	$C_{10}H_{12}BF_4N_3$	$C_{10}H_{12}I_3N_3$
Formula weight	301.13	261.04	554.93
Temperature/K	173.00(10)	173.01(10)	173.00(10)
Crystal	Yellow block	Colorless prism	Red block
Crystal system	orthorhombic	orthorhombic	monoclinic
Space group	Pbca	Pbca	C2/c
a/Å	13.9563(2)	14.45770(10)	20.4846(8)
b/Å	10.5922(2)	10.55260(10)	9.4451(3)
c/Å	15.5819(2)	15.71970(10)	15.8942(7)
α/°	90	90	90
β/°	90	90	99.242(4)
γ/°	90	90	90
Volume/Å^3	2303.44(6)	2398.30(3)	3035.3(2)
Z	8	8	8
ρ_{calc}g/cm^3	1.737	1.446	2.429
μ/mm^{-1}	2.748	1.154	48.371
F(000)	1168.0	1072.0	2016.0
Crystal size/mm^3	0.477 x 0.303 x 0.105	0.31 x 0.22 x 0.08	0.074 x 0.051 x 0.044
Radiation	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	5.228 to 56.1	11.258 to 154.084	8.748 to 154.492
Index ranges	-17 ≤ h ≤ 18, -13 ≤ k ≤ 13, -20 ≤ l ≤ 20	-16 ≤ h ≤ 18, -13 ≤ k ≤ 12, -19 ≤ l ≤ 19	-24 ≤ h ≤ 25, -9 ≤ k ≤ 11, -19 ≤ l ≤ 20
Reflections collected	13462	19564	14247
Independent reflections	2641 [R_{int} = 0.0402, R_{sigma} = 0.0335]	2490 [R_{int} = 0.0471, R_{sigma} = 0.0246]	3110 [R_{int} = 0.0823, R_{sigma} = 0.0393]
Data/restraints/parameters	2641/0/129	2490/200/212	3110/0/149
Goodness-of-fit on F^2	1.068	1.083	1.102
Final R indexes [I>=2σ (I)]	R_1 = 0.0308, wR_2 = 0.0707	R_1 = 0.0434, wR_2 = 0.1276	R_1 = 0.0652, wR_2 = 0.1910
Final R indexes [all data]	R_1 = 0.0537, wR_2 = 0.0848	R_1 = 0.0477, wR_2 = 0.1343	R_1 = 0.0713, wR_2 = 0.1977
Largest diff. peak/hole / e Å^{-3}	0.47/-0.77	0.51/-0.22	2.17/-0.96

4. NMR spectra of catalytic reaction products

To monitor progress of the catalytic reactions, ^{1}H NMR spectra were measured of samples diluted directly from the reaction mixture in 1,2-dichlorobenzene (large multiplets between δ_H 6.86-7.76 ppm, marked ◊ below), with hexamethylbenzene (δ_H 2.22 ppm, marked ♠ below) as internal standard (Figure S12). Resonances at 4.11 and 4.17 ppm arise from the methyl groups of the triazolium compound. Where acetone or water resonances can be observed, they are marked *.

Spectroscopic yields (Section 1, above) were calculated as the average of two catalytic reactions, run under identical conditions. Representative examples are shown below. The various imine reaction products described in Tables 1 and 2 displayed characteristic ^{1}H NMR resonances (marked ■ below), which matched literature spectra.[S1] Where amine starting material or ketone by-product resonances are present in the spectra, they are marked □ and ▼, respectively. Parts of the spectra related to aromatic protons were obscured in some cases by the residual 1,2-dichlorobenzene solvent resonances (marked ◊ below).

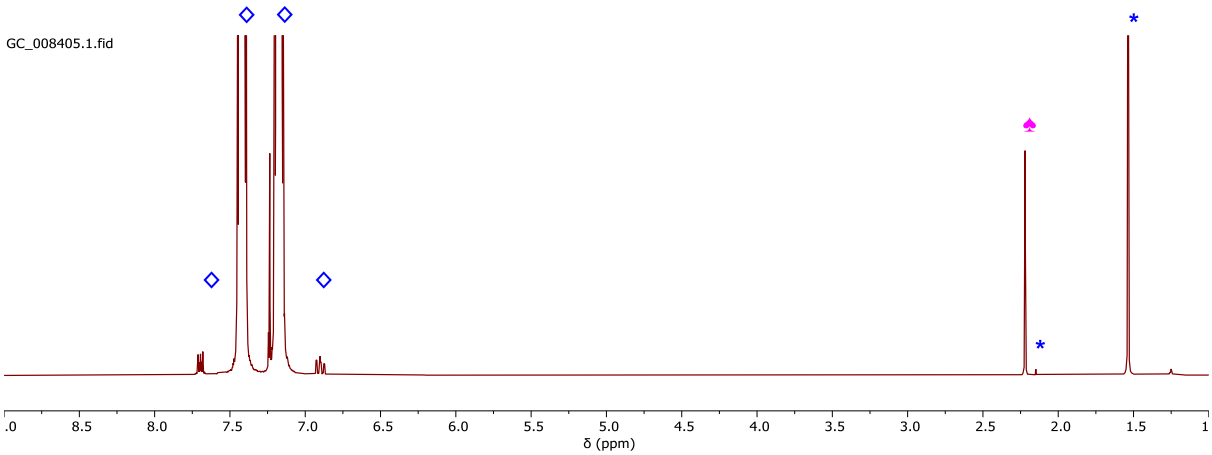
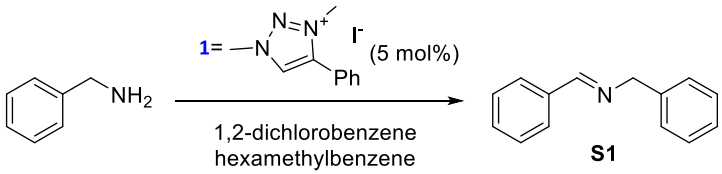


Figure S12. *^{1}H NMR spectra (300 MHz, $CDCl_3$) of a sample from a solution of internal standard hexamethylbenzene (♠) in 1,2-dichlorobenzene (◊), demonstrating characteristic resonances of these compounds. Residual H_2O and acetone peaks are marked *.*

Homocoupling of benzylamine to imine S1



S1: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.39 (s, 1H), 7.83-7.72 (m, 2H), 7.35-7.28 (m, 5H *[overlaps with residual solvent signals]*), 4.82 (s, 2H).[S1]

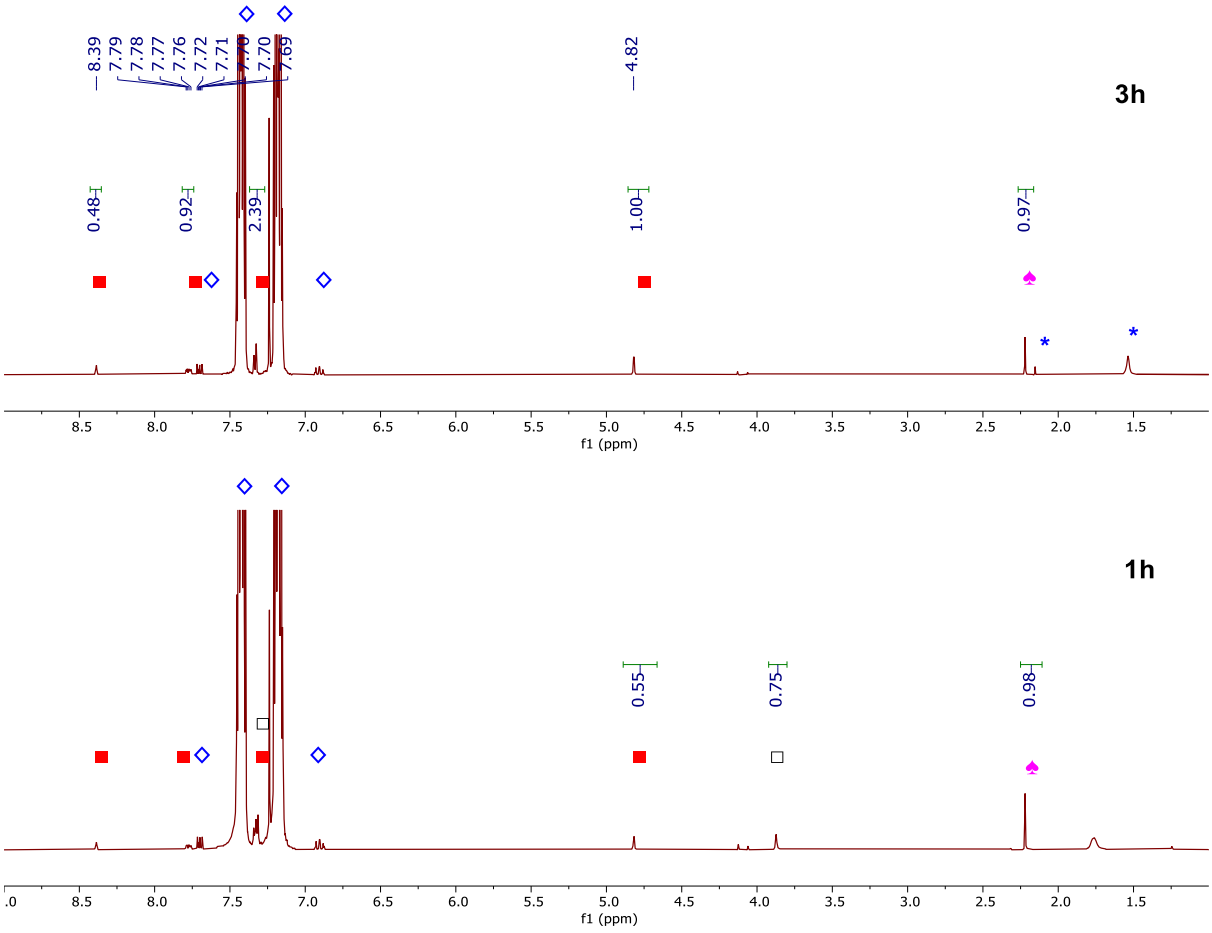
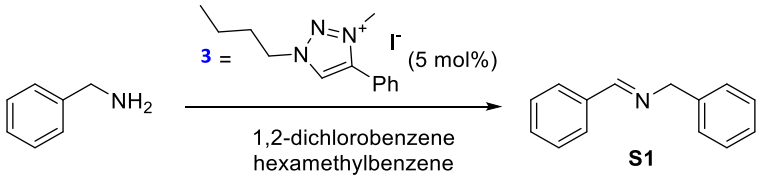


Figure S13. *^{1}H NMR spectra (300 MHz, $CDCl_3$) at 3h (top) and 1h (bottom) of the homocoupling of benzylamine catalysed by **1**. ◊: 1,2-dichlorobenzene, ♠: hexamethylbenzene, *: residual acetone or water, □: amine starting material, ■: imine product.*

A number of other triazolium iodide salts **2-4** also catalysed this reaction (Table 3), yielding the same product. The reaction with **3** is shown here as an example:



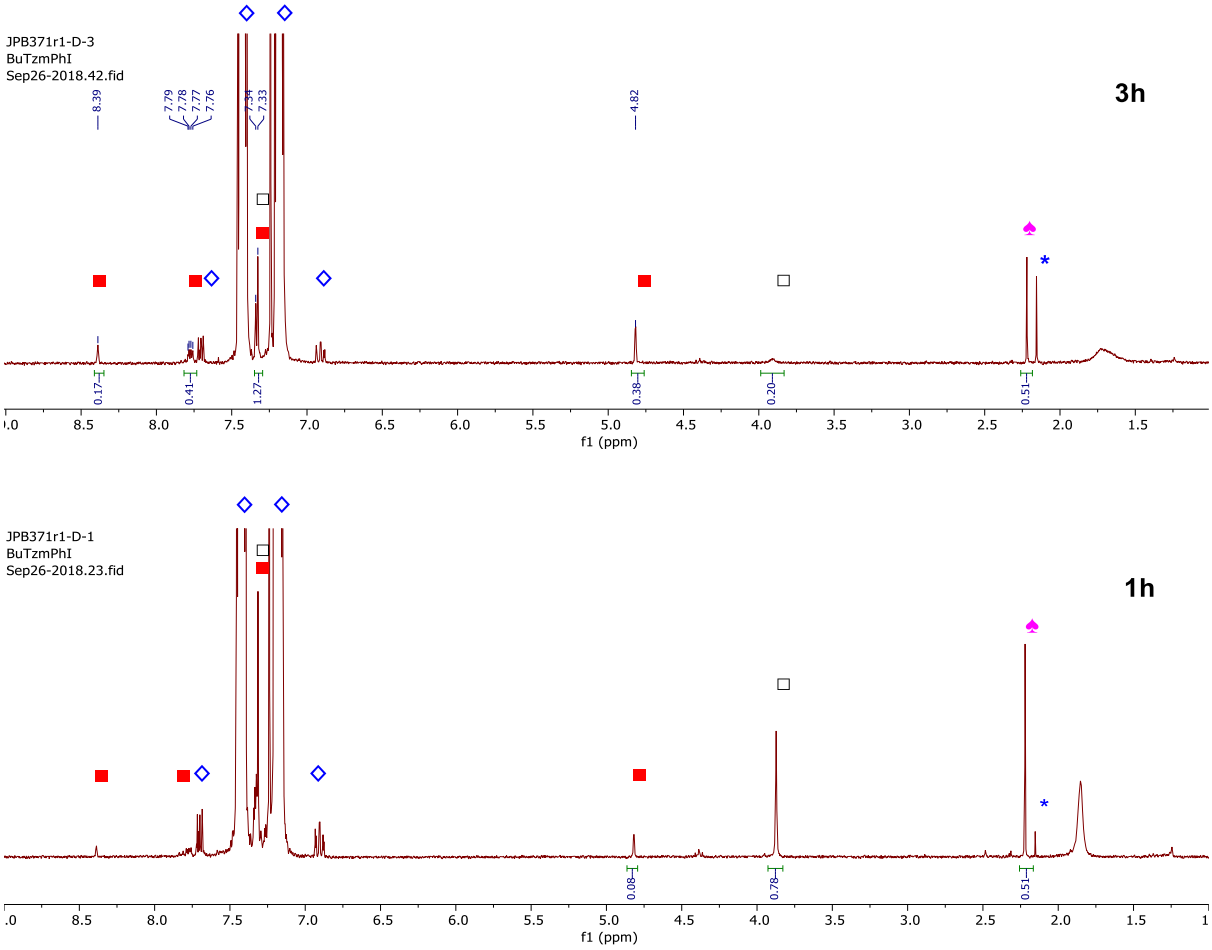
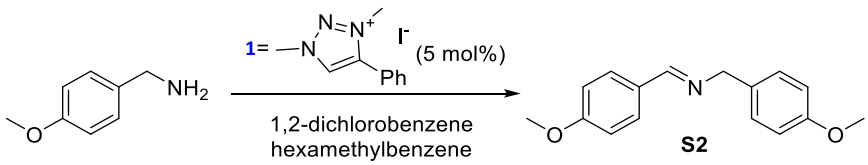


Figure S14. *^{1}H NMR spectra (300 MHz, $CDCl_3$) at 3h (top) and 1h (bottom) of the homocoupling of benzylamine catalysed by **3**. ◊: 1,2-dichlorobenzene, ♠: hexamethylbenzene, *: residual acetone or water, □: amine starting material, ■: imine product.*

Homocoupling of 4-methoxybenzylamine to imine S2



S2: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.27 (s, 1H), 7.76-7.66 (m, 2H *[overlaps with residual solvent signals]*), 6.96-6.82 (m, 5H *[overlaps with residual solvent signals]*), 4.72 (s, 2H), 3.83 (s, 3H), 3.78 (s, 3H).[S1]

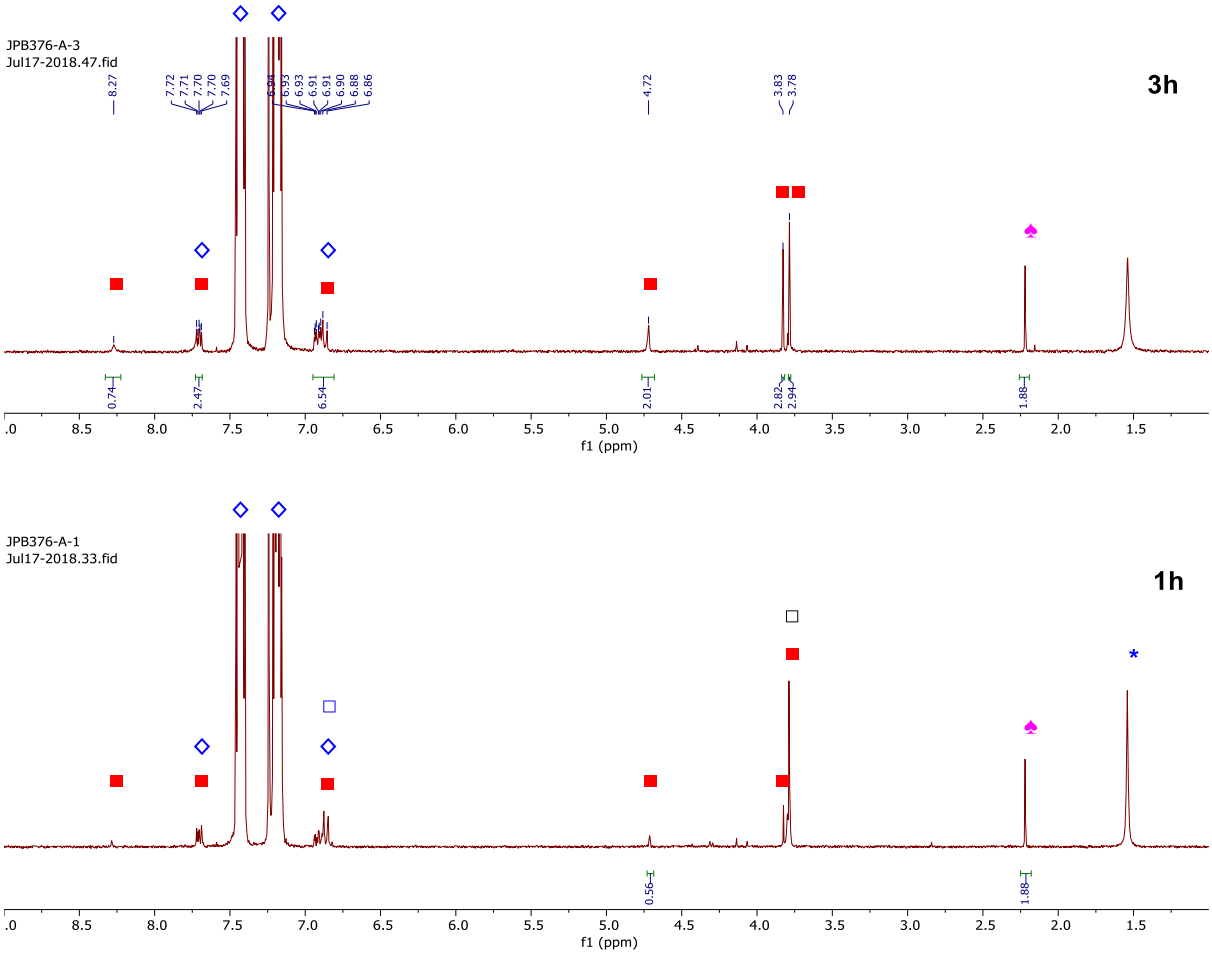
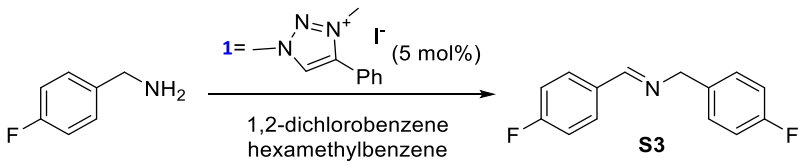


Figure S15. *^{1}H NMR spectra (300 MHz, $CDCl_3$) at 3h (top) and 1h (bottom) of the homocoupling of 4-methoxylbenzylamine catalysed by **1**. ◊: 1,2-dichlorobenzene, ♠: hexamethylbenzene, *: residual acetone or water, □: amine starting material, ■: imine product.*

Homocoupling of 4-fluorobenzylamine to imine S3



S3: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.33 (s, 1H), 7.80-7.71 (m, 2H), *[overlaps with residual solvent signals]*, 4.75 (s, 2H).[S1]

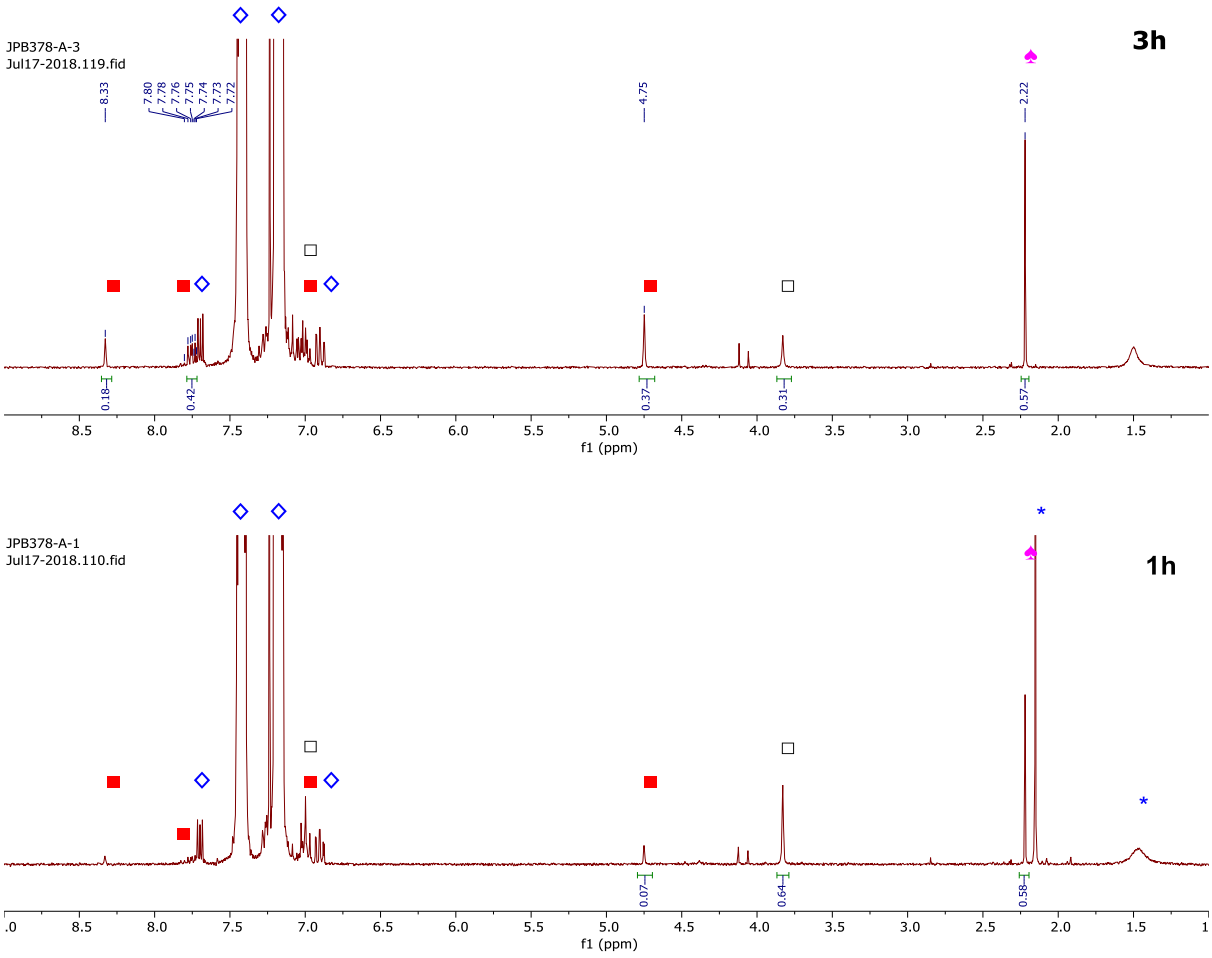
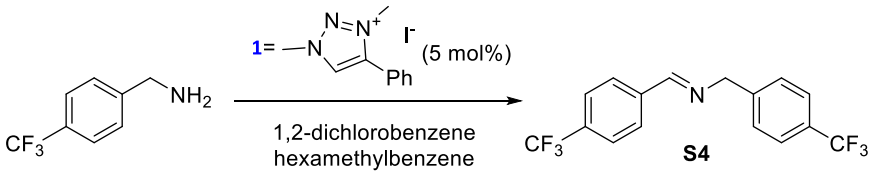


Figure S16. *^{1}H NMR spectra (300 MHz, $CDCl_3$) at 3h (top) and 1h (bottom) of the homocoupling of 4-fluorobenzylamine catalysed by **1**. ◊: 1,2-dichlorobenzene, ♠: hexamethylbenzene, *: residual acetone or water, □: amine starting material, ■: imine product*

Homocoupling of 4-trifluoromethylbenzylamine to imine S4



S4: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.49 (s, 1H), 7.94 (d, *J* = 8 Hz, 2H), 7.80-7.59 (m, 6H *[overlaps with residual solvent signals]*), 4.93 (s, 2H).[S1]

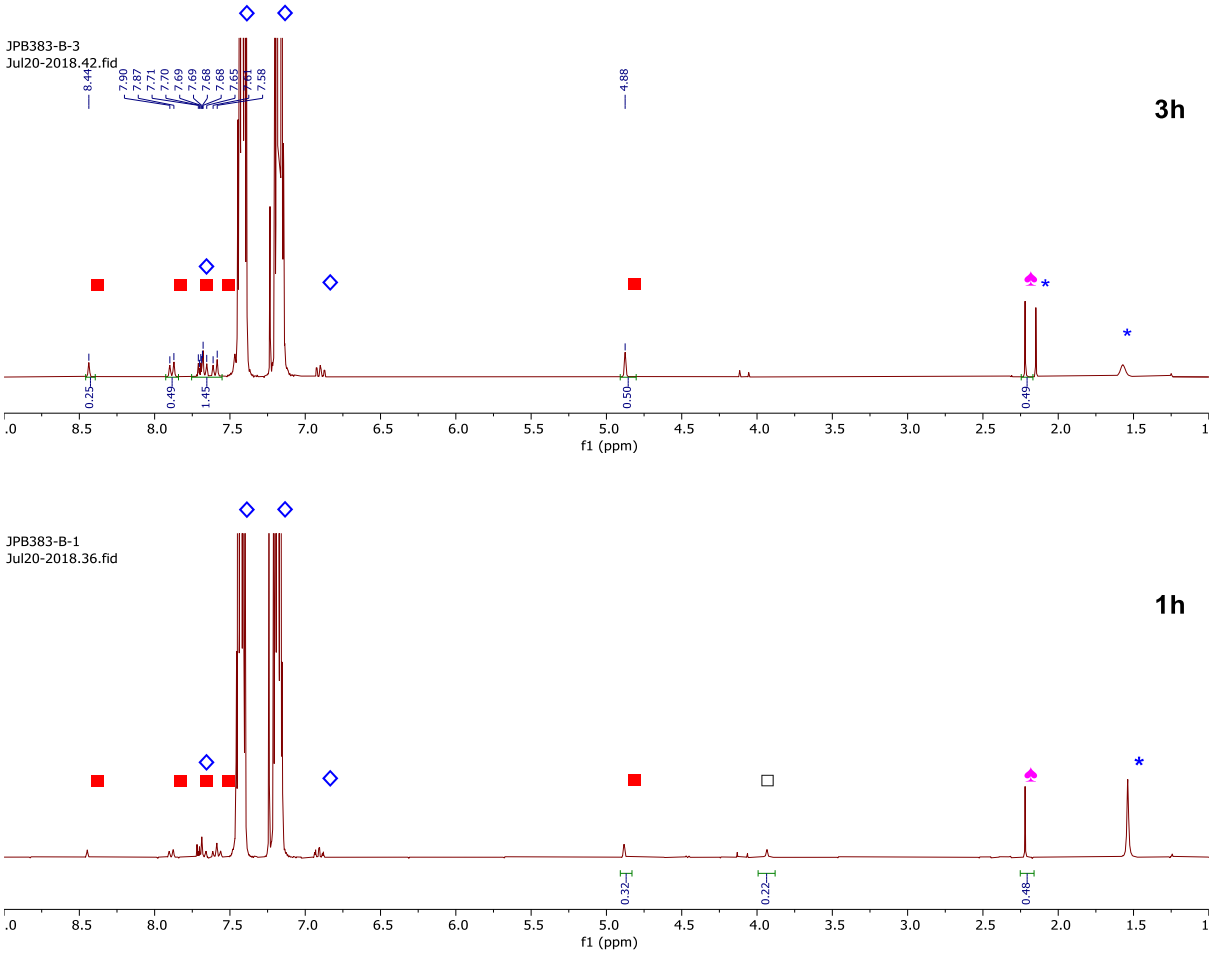
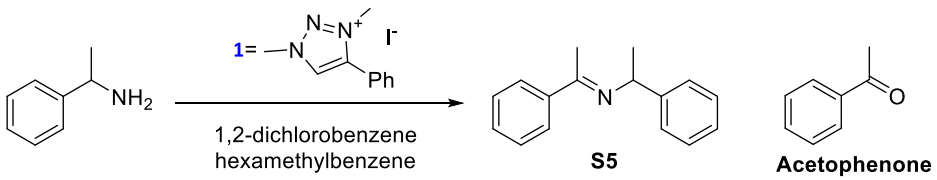


Figure S17. *^{1}H NMR spectra (300 MHz, $CDCl_3$) at 3h (top) and 1h (bottom) of the homocoupling of 4-trifluoromethylbenzylamine catalysed by* ***1****. ◊: 1,2-dichlorobenzene, ♠: hexamethylbenzene, *: residual acetone or water, □: amine starting material, ■: imine product.*

Homocoupling of α-methylbenzylamine to imine S5



S5: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.77-7.67 (m, 2H), *[resonances obscured by residual solvent signals]*, 4.90-4.80 (q, *J* = 7 Hz, 1H), 2.26 (s, 3H), 1.54 (d, *J* = 7 Hz, 3H).[S1]

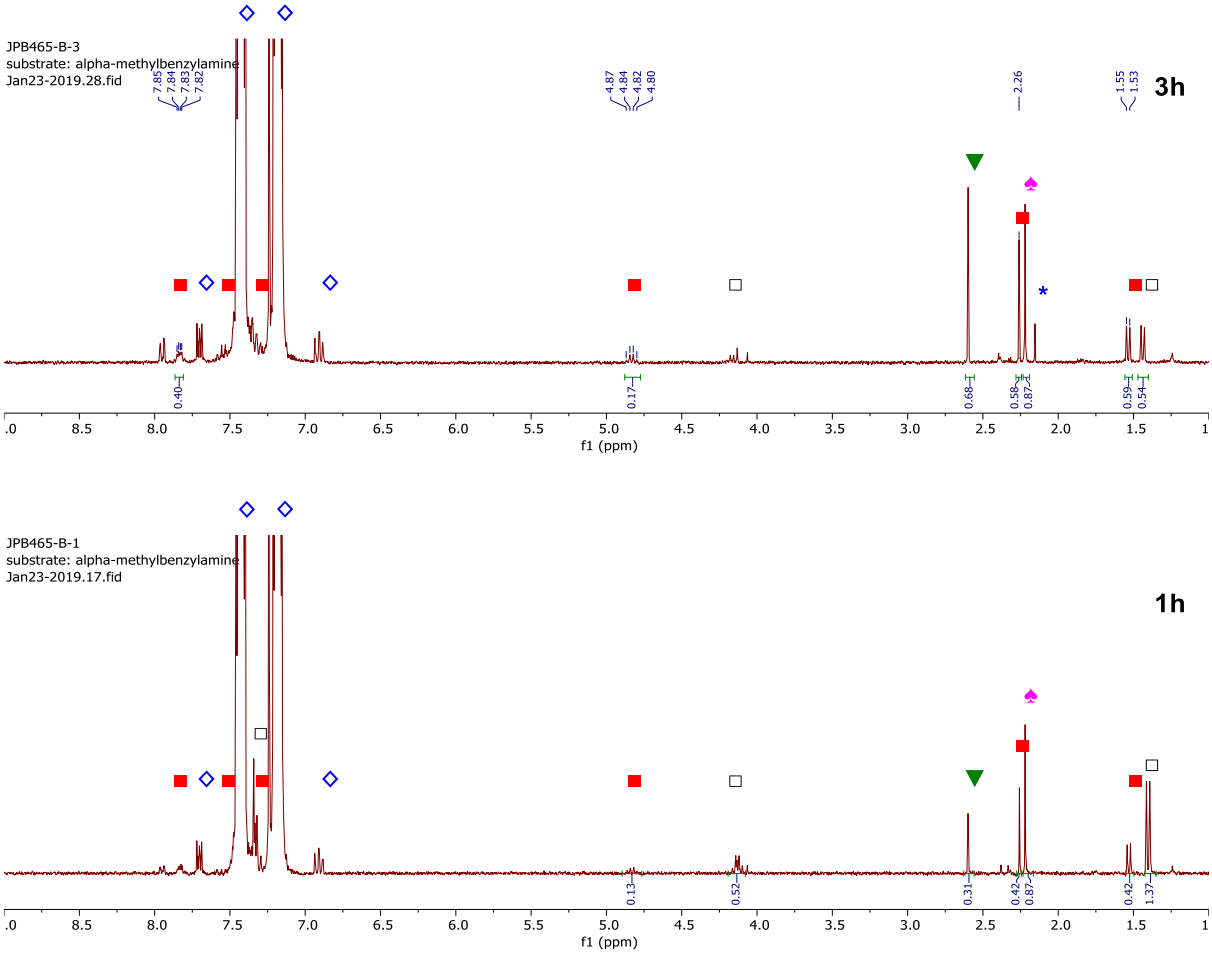


Figure S18. *^{1}H NMR spectra (300 MHz, $CDCl_3$) at 3h (top) and 1h (bottom) of the homocoupling of α-methylbenzylamine catalysed by* ***1****. ◊: 1,2-dichlorobenzene, ♠: hexamethylbenzene, *: residual acetone or water, □: amine starting material, ■: imine product, ▼: acetophenone.*

Reference:

S1 S. Hazra, P. Pilania, M. Deb, A. K. Kushawaha and A. J. Elias, Aerobic Oxidation of Primary Amines to Imines in Water using a Cobalt Complex as Recyclable Catalyst under Mild Conditions, *Chem. Eur. J.*, 2018, **24**, 15766–15771.