A referee highlighted a recent report on the 'Role of metal contaminants in catalyses with $FeCl_3$' (Buchwald and Bolm in ACIEE, 2009, 48, 5586). In order to investigate the influence of the impurities in the $FeCl_3$ on the reaction of sulfonyl azide with tertiary amine, we measured the contents of the metal impurities in the $FeCl_3$ that we used and several control experiments were carried out. The results were listed as below.

Chemicals & instruments

$FeCl_3$ was purchased from Sinopharm Chemical Reagent Co. Ltd. (SCRC) with a purity of more than 97%. The ultrapure anhydrous $FeCl_3$ was purchased from Sigma-Aldrich (SA) with a purity of 99.99% (CAS Number: 7705-08-0; Product Number: 45164-9). The Inductive Coupled Plasma Optical Emission Spectrum (ICP-OES) was purchased from Thermo Electron Corporation and Atomic Absorption Spectrum (AAnalyst 800) was purchased from Perkin Elmer. The detection of the impurities was performed on ICP-OES and AAnalyst 800.

The impurities in 97% $FeCl_3$

The Inductive Coupled Plasma Optical Emission Spectrum (ICP-OES) and Atomic Absorption Spectrum (AAS) showed that the contents of metal impurities in 97% $FeCl_3$ are as below. Cu% = 0.015%; Al% = 0.0033%; Ca% = 0.0036%; Co% = 0.0007%; Cr% = 0.029%; Mg% = 0.0018%; Mn% = 0.054%; Ni% = 0.0028%; V% = 0.0004%; Pd% = 0.0016%.

Control experiments

The reaction of TsN_3 with Et_3N was selected as the model reaction to investigate the influence of metal impurities.

Experimental procedure: To a solution of TsN_3 (1.0 mmol) and Et_3N (4.0 mmol) in 5.0 mL of CH_2Cl_2 was added the corresponding mediator (the loading was listed in the table below), and the resulting mixture was reacted at room temperature monitored by TLC. Then the system was diluted with 10 mL CH_2Cl_2, following the addition of the EDTA-NaOH solution (20 mmol of EDTA and 20 mmol of NaOH in 15 mL of water). Afterwards, the whole mixture was refluxed for five hours and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (10 mL×3) and the combined organic phase was dried over anhydrous Na_2SO_4 powder. The final product was obtained through purification with column chromatography. The corresponding results were listed in Table S1.

Table S1 The reaction of TsN_3 with Et_3N mediated by different metal source

Entr	Mediator	Source	Purity	Loading	Isolated Yield (%)
1	CuO	SCRC	99%	100%	16
2	CuO	SCRC	99%	20%	trace
3	CuO	SCRC	99%	1%	trace
4	Cu_2O	SCRC	90%	100%	13
5	CuCl	SCRC	97%	100%	29
6	$CuCl_2$[a]	SCRC	-	100%	64
7	$CuCl_2$	SCRC	-	75%	47
8	$CuCl_2$	SCRC	-	50%	32
9	$CuCl_2$	SCRC	-	20%	23
10	$CuCl_2$	SCRC	-	5%	9
11	$CuCl_2·2H_2O$	SCRC	99%	100%	8[b]
12	$CuCl_2$ / $FeCl_3$	SCRC	-	100% / 100%	65
13	$CuCl_2$ / $FeCl_3$	SCRC	-	75% / 100%	67
14	$CuCl_2$ / $FeCl_3$	SCRC	-	50% / 100%	72
15	$CuCl_2$ / $FeCl_3$	SCRC	-	20% / 100%	77
16	$CuCl_2$ / $FeCl_3$	SCRC	-	10% / 100%	81
17	$CuCl_2$ / $FeCl_3$	SCRC	-	5% / 100%	87
18	Al_2O_3	SCRC	99%	100%	trace
19	$AlCl_3$	SCRC	99%	100%	trace
20	$CaCl_2$	SCRC	96%	100%	trace
21	CaO	SCRC	98%	100%	trace
22	$CoCl_2·6H_2O$	SCRC	99%	100%	trace
23	Co_2O_3	SCRC	99%	100%	trace
24	Cr_2O_3	SCRC	99%	100%	trace
25	CrO_3	SCRC	99%	100%	28
26	$CrCl_3·6H_2O$	SCRC	99%	100%	trace
27	$MgCl_2·6H_2O$	SCRC	98%	100%	trace
28	MgO	SCRC	98.5%	100%	trace
29	$MnCl_2·4H_2O$	SCRC	99%	100%	trace

30	MnO_2	SCRC	97.5%	100%	trace
31	$NiCl_2 \cdot 6H_2O$	SCRC	97%	100%	trace
32	NiO	SCRC	99%	100%	trace
33	V_2O_5	SCRC	99%	100%	trace
34	$PdCl_2$	Alfa Aesar	99.9%	5%	7
35	$PdCl_2$	Alfa Aesar	99.9%	10%	16
36	$PdCl_2$	Alfa Aesar	99.9%	50%	39
37	$PdCl_2$	Alfa Aesar	99.9%	100%	56
38	$Pd(OAc)_2$	Acros	-	5%	10[b]
39	$Pd(OAc)_2$	Acros	-	10%	13[b]
40	$Pd(OAc)_2$	Acros	-	50%	42[b]
41	$Pd(OAc)_2$	Acros	-	100%	78[b]
42	$FeCl_3$	SA	99.99%	100%	90[c]

[a] Anhydrous $CuCl_2$ was obtained by heating $CuCl_2 \cdot 2H_2O$ at 105 ºC for 8 hours. [b] Reflux for six hours. [c] The average yield of three parallel reactions (88%, 90% and 91%).

Results and discussion

The above results of control experiments strongly supported that it was $FeCl_3$ but metal impurities that mediate the reaction of sulfonyl azide with tertiaryamine. The ultrapure $FeCl_3$ could mediate the reaction with high yield (entry 42). This indicated that the $FeCl_3$ component in the 97% $FeCl_3$ played a predominant role in the mediation of the reaction. The metal impurities, such as Cu, Cr and Pd, could mediate the reaction to different extends depending on the mediator loading. As shown in Table S1, the anhydrous $CuCl_2$ could deliver a moderate yield of the product (entry 6) when stoichiometric $CuCl_2$ was used. And the yield of the product decreased notably with the reduction of the $CuCl_2$ loading (entries 7-10). When the amount of the $CuCl_2$ was less than 5%, TsN_3 almost remained unchanged with very low conversion. It suggested that the trace amounts of metal impurities in the 97% $FeCl_3$ had inessential influence on the mediating reactions. As a result, it is clear that $FeCl_3$ rather than minor impurities that mediates the reaction of sulfonyl azide with tertiaryamine under the reaction conditions.