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Lanthanide Amide-catalyzed Aza-Henry Reaction of *N*-Tosyl Imines with Nitroalkanes

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In the presence of 10 mol% lanthanide amide $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$, the aza-Henry reaction of *N*-tosyl imines with nitroalkanes (1∶5 molar ratio) could be performed in good yields. The lanthanide amide-catalyzed aza-Henry reaction has the features of mild reaction conditions, tolerance of a variety of aromatic aldehyde-derived imines and nitroalkanes, short time and good chemical yields. A catalytic mechanism for the reaction was also proposed.

Keywords lanthanide amide, aza-Henry reaction, *N*-tosyl imine, nitroalkane, catalysis

Introduction

The aza-Henry (or nitro-Mannich) reaction is a powerful and efficient method for the construction of carbon-carbon bonds. The versatile *β*-nitroamines, as the aza-Henry reaction products, can be converted to useful building blocks such as 1,2-diamines, *α*-amino acid derivatives. Recently much effort has been devoted to the development of the nitro-Mannich (aza-Henry) reaction, especially the studies on some new facile catalysts.[1] For example, many bifunctional thiourea catalysts,[2] Brønsted-acids,[3a] and Na_2CO_3[3b] were reported to be efficient for the aza-Henry reaction. Despite the considerable advances made in this field so far reported, the metal catalysts are restricted, with almost no exception, to the alkoxyl metal compounds, such as $Ln(O^iPr)_3$,[4] $Ln(OTf)_3$,[4] KOR (R＝^{t}Bu, ^{i}Pr),[5] the Zn alkyoxyl compounds,[6a] *N*,*N*′-dioxide-Cu(I) complex,[6b] or various heterobimetallic complexes using BINOL derivatives as ligands in asymmetric synthesis.[7] Until now, studies on the pure lanthanide amido compounds as catalysts for the aza-Henry reaction remain unexplored.

The lanthanide amides $Ln[N(SiMe_3)_2]_3$ (Ln ＝ Y, lanthanide), which can either be prepared from one simple step reaction in very high yields or are commercially available, have received much attention for their applications as active catalysts for Tishchenko reactions,[8,9] intramolecular or intermolecular alkene and alkyne hydroaminations,[10,11] hydrosilylations, hydroboration, hydrophosphination, and hydroalkoxylation,[12-15] ring-opening polymerizations of *ε*-caprolactone and *δ*-valerolactone,[16] and monoaddition of terminal alkynes to nitriles.[17] In light of our success in developing the aldol-condensation reaction,[18] the synthesis of the amides directly from the aldehydes through the Cannizzaro-reaction,[19] the guanylation of the amines[20] and the stereoregularity of polymerization of methacrylate[21] catalyzed by the heterobimetallic lanthanide amide $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$, we decided to investigate the aza-Henry reaction catalyzed by the lanthanide amides $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$. Given that the lanthanide amido compounds are able to catalyze aldol reactions,[18] we assumed that the dual Lewis acidic/Lewis basic functionality within the lanthanide amide $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$ could play a bifunctional role in the aza-Henry reaction. The more available and stable *N*-tosyl imines are very important synthetic intermediates in organic chemistry.[22,23] However the studies on the aza-Henry reaction of *N*-tosyl imines with nitroalkanes are limited.[4,5,24] Herein, we wish to report the aza-Henry reaction of sulfonylimines with nitroalkanes catalyzed by the heterobimetallic lanthanide amide $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$.

Results and discussion

Preliminary optimization of the aza-Henry reaction of *N*-benzylidene-4-methylbenzenesulfonamide with nitromethane in the presence of yttrium amide $[(Me_3Si)_2N]_3Y(\mu\text{-}Cl)Li(THF)_3$ is summarized in Table 1. To our satisfaction, when *N*-tosylimine was exposed to nitromethane with the yttrium amide as a catalyst, the aza-Henry product was isolated in 70% yield in a short time (Table 1, Entry 1). And the yield could be improved as high as 82% by decreasing the loading of the amount of the solvent (Table 1, Entry 3). The reason

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might lie in the fact that *N*-tosylimine was unstable in the solvent. The catalytic activities of the yttrium amide in different solvents such as THF, toluene, diethyl ether, and *n*-hexane were also investigated (Table 1, Entries 3, 6, 7, 8). The yields of the reactions were not improved either by elevating or lowering the reaction temperatures (Table 1, Entries 9, 10). However, the yields of the reaction decreased when the reaction time was prolonged. And the ratio of nitromethane to sulfonylimine played an important role in the reaction results. Lowering the nitromethane to sulfonylimine ratio led to a decrease in the yield of the reaction (Table 1, Entries 14, 15). As shown in Table 1, the optimization result was realized by running the reaction of sulfonylimines with nitroalkanes (1∶5 molar ratio) in the presence of 10 mol% yttrium amide $[(Me_3Si)_2N]_3Y(\mu\text{-}Cl)Li(THF)_3$ in 2 mL of THF for 3 h (Table 1, Entry 3).

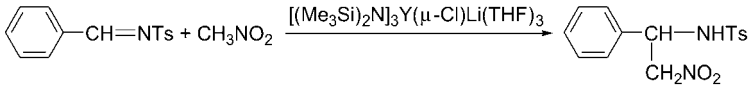
Under the optimized condition, the scope and generality of the lanthanide amide-catalyzed aza-Henry reaction of various sulfonylimines with nitroalkanes were investigated. Reaction of aryl imines bearing either the electron-donating substituents or the electron-withdrawing substituents on the phenyl ring with nitroalkanes afforded the products in satisfactory yields (Table 2, Entries 1—8). For example, reaction of aryl imines bearing the electron-withdrawing group such as NO_2 with nitromethane gave the corresponding product in 83% yield (Table 2, Entry 7), and that bearing the electron-donating groups such as CH_3, OCH_3 groups also gave the corresponding products in good yields (Table 2, Entries 3—5). Therefore, the electronic effects of the substituents on the aryl imines showed little impact on the yield of the reaction. When aliphatic imines were used instead of aryl imines, the lanthanide amide-catalyzed aza-Henry reaction failed to undergo. Due to the steric effects, nitroethane and nitropropane were less reactive than nitromethane under the given conditions. For example, reaction of benzadehyde-derived imine with nitroethane or nitropropane resulted in yields less than 50% (Table 2, Entries 9—12). And the *dr* values in Table 2 showed that almost the same amounts of *anti*- and *syn*-products were obtained.

To investigate the influence of the Li^+ cation on reaction, the reaction of sulfonylimine with nitromethane in the presence of 10 mol% yttrium amide $Y[N(SiMe_3)_2]_3$ instead of $[(Me_3Si)_2N]_3Y(\mu\text{-}Cl)Li(THF)_3$ was performed, but the yield of the product was only 30% (Table 2, Entry 2). However, under the same conditions, the yield of the product was 82% when $[(Me_3Si)_2N]_3Y(\mu\text{-}Cl)Li(THF)_3$ was used as a catalyst. So it can be seen that the catalytic activity of yttrium amide complex $[(Me_3Si)_2N]_3Y(\mu\text{-}Cl)Li(THF)_3$ is higher than that of the yttrium amide $Y[N(SiMe_3)_2]_3$.

The catalytic activity of different lanthanide amides $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$ was investigated by running the reaction of sulfonylimine with nitromethane under the optimized conditions (Table 3). The results indicated that all the lanthanide amides exhibited good activity with only slight difference, which may be attributable to the acidity of the central lanthanide metal.

With regard to the reaction mechanism we assume that the lanthanide amido compound $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$ played a bifunctional role (Scheme 1). The lanthanide amide reacted with the nitroalkane affording the intermediate **I**, and coordination of the *N*-tosyl imine to the Lewis metal center gave the intermediate **II**.

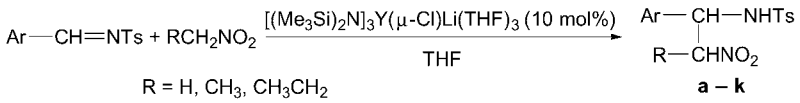
Table 1 Optimization of the aza-Henry reactions catalyzed by the lanthanide amide



Entry	Ratio[a]	Solvent (Volume)	Temp./℃	Time/h	Catalyst[b]/%	Yield[c]/%
1	5∶1	THF (10 mL)	r.t.	3	10	70
2	5∶1	THF (5 mL)	r.t.	3	10	76
3	5∶1	THF (2 mL)	r.t.	3	10	82
4	5∶1.	THF (2 mL)	r.t.	5	10	73
5	5∶1	THF (2 mL)	r.t.	1	10	65
6	5∶1	Toluene (2 mL)	r.t.	3	10	73
7	5∶1	Hexane (2 mL)	r.t.	3	10	50
8	5∶1	Et_2O (2 mL)	r.t.	3	10	78
9	5∶1	THF (2 mL)	60	3	10	72
10	5∶1	THF (2 mL)	0	3	10	45
11	5∶1	THF (2 mL)	r.t.	3	20	84
12	5∶1	THF (2 mL)	r.t.	3	5	70
13	10∶1	THF (2 mL)	r.t.	3	10	82
14	3∶1	THF (2 mL)	r.t.	3	10	65
15	1∶1	THF (2 mL)	r.t.	3	10	50

[a] *n*(nitromethane)∶*n*(sulfonylimine); [b] based on the imine; [c] isolated yield.

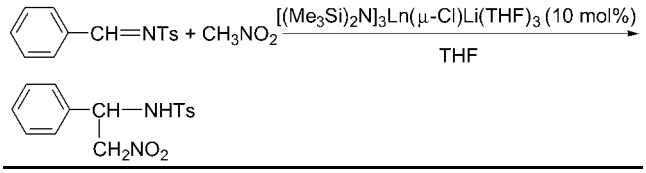
Table 2 Yttrium amide catalyzed nitro-mannich reactions of imines with nitroalkanes



Entry	Ar	R	Time/h	Product	Yield[a]/%	*dr*[c]
1	C_6H_5	H	3	**a**	82	—
2	C_6H_5	H	3	**a**	30[b]	—
3	4-$CH_3C_6H_4$	H	3	**b**	90	—
4	4-$CH_3OC_6H_4$	H	3	**c**	79	—
5	2-$CH_3OC_6H_4$	H	3	**d**	70	—
6	4-ClC_6H_4	H	3	**e**	81	—
7	4-$O_2NC_6H_4$	H	3	**f**	83	—
8	2-Furyl	H	3	**g**	60	—
9	C_6H_5	CH_3	5	**h**	43	52∶48
10	4-$CH_3C_6H_4$	CH_3	5	**i**	42	54∶46
11	C_6H_5	CH_3CH_2	5	**j**	49	57∶43
12	4-$CH_3C_6H_4$	CH_3CH_2	5	**k**	48	59∶41

[a] Isolated yield. [b] Catal.: $Y[N(SiMe_3)_2]_3$. [c] Determined by ^1H NMR.

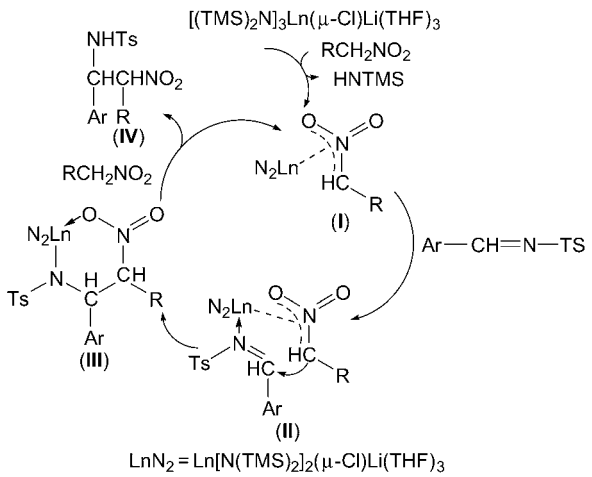
Table 3 Influence of the lanthanide metal on the lanthanide amide catalyzed-aza-Henry reaction



Ln	Y	Sc	La	Pr	Sm	Eu	Dy	Ho	Tm	Yb
Yield/%	82	78	60	65	70	70	76	74	75	85

Addition of the nitronate to the activated imine generated the intermediate **III**, which then reacted with nitroalkane to produce the final products and the intermediate **I**, and a catalytic cycle was finished.

Scheme 1 Proposed mechanism for the aza-Henry reactions catalyzed by lanthanide amide



Conclusion

In summary, the simple lanthanide amide $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$ exhibited high catalytic activities toward the aza-Henry reaction of *N*-tosyl imines with nitroalkanes. The methodology has a wide tolerance of substituents on the phenyl ring of the aromatic aldehyde-derived imines. The results indicate that the steric effects of the nitroalkanes have a great influence on the yields. Mild reaction conditions, economical catalysts, short time, wide generality and good chemical yields are the advantages of the lanthanide amide-catalyzed aza-Henry reaction. Extensive study on the enantioselectivity of the reaction is now in progress in our laboratory.

Experimental

General

Melting points were determined using a Gallenkamp melting point apparatus and are uncorrected. ^1H NMR spectra were recorded on a Bruker Avance 300 instrument in $CDCl_3$ solutions using TMS as an internal standard. Chemical shifts (δ) are reported in ppm. IR spectra were obtained with a UV-4100 FT-IR spectrometer. Mass spectra were performed on a Micromass GCT-MS CA064 instrument. All aldehydes, nitroalkanes and solvents were pre-dried, redistilled or recrystallized before use. The lanthanide amides $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$,[21,25] *N*-tosyl imines[26] were prepared according to references.

General procedure for the aza-Henry reactions catalyzed by the lanthanide amide

Under an argon atmosphere, the yttrium amide $[(Me_3Si)_2N]_3Y(\mu\text{-}Cl)Li(THF)_3$ (0.122 g, 0.15 mmol) and

N-tosyl imine (0.389 g, 1.5 mmol) were dissolved in 2 mL of THF and stirred for 20 min at room temperature. To the mixture was added CH_3NO_2 (0.40 mL, 7.5 mmol), and the mixture was stirred for 4 h at room temperature. The resulting mixture was quenched with a few drops of water and separated, and then the organic solution was dried over $MgSO_4$. The organic solvent was evaporated, and purified by column chromatography on silica gel [*V*(petroleum ether)∶*V*(ethyl acetate)=3∶1] to afford the product **a**—**k**.

4-Methyl-*N*-(2-nitro-1-phenylethyl)benzenesulfonamide (a)[4] White solid; m.p. 160—162 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) *δ*: 7.37 (d, *J*=8.3 Hz, 2H), 6.98—6.94 (m, 5H), 6.81—6.78 (m, 2H), 5.04 (d, *J*=7.5 Hz, 1H), 4.72—4.65 (m, 1H), 4.56 (dd, *J*=13.1, 6.5 Hz, 1H), 4.39 (dd, *J*=13.1, 6.4 Hz, 1H), 2.12 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ*: 144.1, 136.5, 135.3, 129.8, 129.3, 129.1, 127.2, 126.5, 78.9, 55.4, 21.6; IR (KBr) *v*: 3272, 1554, 1382, 1163 cm^{-1}; HR-EI-MS calcd for $C_{15}H_{16}N_2O_4S$ [M^+] 320.0831, found 320.0833.

4-Methyl-*N*-(2-nitro-1-*p*-tolylethyl)benzenesulfonamide (b)[3] White solid; m.p. 182—184 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) *δ*: 7.67 (d, *J*=8.2 Hz, 2H), 7.26 (d, *J*=6.8 Hz, 2H), 7.08 (d, *J*=7.9 Hz, 2H), 6.97 (d, *J*=8.0 Hz, 2H), 5.22 (d, *J*=6.7 Hz, 1H), 4.93—4.91 (m, 1H), 4.83 (dd, *J*=12.7, 6.4 Hz, 1H), 4.67 (dd, *J*=12.6, 6.3 Hz, 1H), 2.42 (s, 3H), 2.31 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ*: 144.1, 139.2, 136.4, 132.3, 129.9, 129.8, 127.2, 126.3, 78.9, 55.2, 21.6, 21.1; IR (KBr) *v*: 3247, 1555, 1378, 1167 cm^{-1}; HR-EI-MS calcd for $C_{16}H_{18}N_2O_4S$ [M^+] 334.0987, found 334.0993.

4-Methyl-*N*-(2-nitro-1-(4-anisyl)ethyl)benzenesulfonamide (c)[3] White solid; m.p. 166—167 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) *δ*: 7.69 (d, *J*=8.4 Hz, 2H), 7.28 (d, *J*=7.5 Hz, 2H), 7.03 (d, *J*=8.7 Hz, 2H), 6.80 (d, *J*=8.7 Hz, 2H), 5.33 (d, *J*=6.6 Hz, 1H), 4.97—4.83 (m, 2H), 4.68 (dd, *J*=12.6, 6.3 Hz, 1H), 3.79 (s, 3H), 2.45 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ*: 160.1, 144.0, 136.6, 129.8, 127.8, 127.2, 127.2, 114.6, 79.0, 55.2, 55.0, 21.6; IR (KBr) *v*: 3252, 1557, 1379, 1162 cm^{-1}; HR-EI-MS calcd for $C_{16}H_{18}N_2O_5S$ [M^+] 350.0936, found 350.0908.

4-Methyl-*N*-(2-nitro-1-(2-anisyl)ethyl)benzenesulfonamide (d)[3] White solid; m.p. 168—170 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) *δ*: 7.57—7.54 (m, 2H), 7.19—7.13 (m, 1H), 7.11 (d, *J*=7.9 Hz, 2H), 6.94—6.92 (m, 1H), 6.78—6.73 (m, 2H), 5.88 (d, *J*=9.9 Hz, 1H), 5.12—5.08 (m, 1H), 4.81 (dd, *J*=12.5, 6.8 Hz, 1H), 4.64 (dd, *J*=12.5, 6.7 Hz, 1H), 3.81 (s, 3H), 2.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ*: 156.4, 143.5, 136.9, 130.2, 129.7, 129.4, 126.9, 122.6, 121.1, 110.9, 78.6, 55.5, 54.7, 21.5; IR (KBr) *v*: 3261, 1556, 1349, 1168 cm^{-1}; HR-EI-MS calcd for $C_{16}H_{18}N_2O_5S$ [M^+] 350.0936, found 350.0932.

4-Methyl-*N*-(2-nitro-1-(4-chlorophenyl)ethyl)benzenesulfonamide (e)[3] White solid; m.p. 200—202 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) *δ*: 7.56 (d, *J*=8.4 Hz, 2H), 7.19—7.15 (m, 4H), 6.97 (d, *J*=8.4 Hz, 2H), 5.35 (d, *J*=7.5 Hz, 1H), 4.92—4.86 (m, 1H), 4.72 (dd, *J*=13.2, 6.6 Hz, 1H), 4.57 (dd, *J*=13.2, 6.5 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ*: 139.6, 137.8, 132.7, 130.3, 129.8, 129.4, 127.8, 127.1, 78.7, 54.7, 21.6; IR (KBr) *v*: 3240, 1557, 1379, 1167 cm^{-1}; HR-EI-MS calcd for $C_{15}H_{15}N_2O_4SCl$ [M^+] 354.0441, found 354.0432.

4-Methyl-*N*-(2-nitro-1-(4-nitrophenyl)ethyl)benzenesulfonamide (f)[27] White solid; m.p. 145—146 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) *δ*: 8.14 (d, *J*=8.5 Hz, 2H), 7.65 (d, *J*=8.0 Hz, 2H), 7.36 (d, *J*=8.5 Hz, 2H), 7.25 (d, *J*=8.5 Hz, 2H), 5.75 (d, *J*=7.9 Hz, 1H), 5.16—5.09 (m, 1H), 4.81 (dd, *J*=13.5, 6.3 Hz, 1H), 4.69 (dd, *J*=13.5, 6.2 Hz, 1H), 2.14 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ*: 148.4, 144.5, 142.6, 136.9, 129.9, 127.6, 127.1, 124.3, 78.4, 54.6, 21.6; IR (KBr) *v*: 3236, 1561, 1352, 1157 cm^{-1}; HR-EI-MS calcd for $C_{15}H_{15}N_3O_6S$ [M^+] 365.0682, found 365.0708.

4-Methyl-*N*-(2-nitro-1-(fur-2-yl)ethyl)benzenesulfonamide (g)[28] White solid; m.p. 141—142 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) *δ*: 7.71 (d, *J*=8.1 Hz, 2H), 7.30—7.26 (m, 3H), 6.24—6.23 (m, 1H), 6.11—6.10 (m, 1H), 5.37 (d, *J*=8.8 Hz, 1H), 5.11—5.09 (m, 1H), 4.84 (dd, *J*=13.4, 6.1 Hz, 1H), 4.70 (dd, *J*=13.3, 6.2 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ*: 147.4, 145.5, 143.2, 129.8, 127.1, 110.8, 108.8, 78.1, 49.4, 21.6; IR (KBr) *v*: 3223, 1555, 1378, 1166 cm^{-1}; HR-EI-MS calcd for $C_{13}H_{14}N_2O_5S$ [M^+] 310.0628, found 310.0632.

4-Methyl-*N*-(2-nitro-1-phenylprop-1-yl)benzenesulfonamide (h)[29] White solid; m.p. 160—161 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) *δ*: 7.52 (d, *J*=8.2 Hz, 2H), 7.21—6.98 (m, 7H), 5.71 (d, *J*=9.2 Hz, 1H), 4.86—4.82 (m, 1H), 4.77—4.72 (m, 1H), 2.33 (s, 3H), 1.50 (d, *J*=6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ*: 143.1, 136.5, 135.0, 129.4, 129.0, 128.6, 128.2, 126.6, 126.2, 86.5, 55.9, 21.1, 16.6; IR (KBr) *v*: 3232, 1554, 1327, 1114 cm^{-1}; HR-EI-MS calcd for $C_{16}H_{18}N_2O_4S$ [M^+] 334.0987, found 334.0986.

4-Methyl-*N*-(2-nitro-1-*p*-tolylprop-1-yl)benzenesulfonamide (i) White solid; m.p. 162—163 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) *δ*: 7.52 (d, *J*=8.1 Hz, 2H), 7.12 (d, *J*=8.0 Hz, 2H), 7.01 (d, *J*=7.9 Hz, 2H), 6.89 (d, *J*=7.9 Hz, 2H), 5.50 (d, *J*=8.7 Hz, 1H), 4.85—4.78 (m, 1H), 4.73—4.67 (m, 1H), 2.35 (s, 3H), 2.28 (s, 3H), 1.50 (d, *J*=6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ*: 143.9, 139.6, 129.3, 129.0, 126.7, 126.0, 86.5, 59.7, 21.1, 20.7, 16.5; IR (KBr) *v*: 3255, 1550, 1330, 1161 cm^{-1}; HR-EI-MS calcd for $C_{17}H_{20}N_2O_4S$ [M^+] 348.1144, found 348.1142.

4-Methyl-*N*-(2-nitro-1-phenylbut-1-yl)benzenesulfonnamide (j) White solid; m.p. 172—173 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) *δ*: 7.51—7.48 (m, 2H), 7.25—6.97 (m, 7H), 5.70 (d, *J*=5.8 Hz, 1H), 4.81—4.78 (m, 1H), 4.63—4.60 (m, 1H), 2.33—2.31 (m, 3H), 2.18—2.16 (m, 2H), 0.93 (t, *J*=6.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ*: 138.5, 128.9, 128.5, 128.1, 126.5, 126.0, 93.5, 58.8, 24.5, 21.0, 9.8; IR (KBr) *v*: 3259, 1554, 1338, 1168

cm^{-1}; HR-EI-MS calcd for $C_{17}H_{20}N_2O_4S$ [M^+] 348.1144, found 348.1143.

4-Methyl-*N*-(2-nitro-1-*p*-tolylbut-1-yl)benzenesulfonamide (k) White solid; m.p. 161—162 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.50 (d, J=8.1 Hz, 2H), 7.10 (d, J=7.9 Hz, 2H), 6.98 (d, J=7.8 Hz, 2H), 6.86 (d, J=7.9 Hz, 2H), 5.58 (d, J=9.5 Hz, 1H), 4.77—4.73 (m, 1H), 4.62—4.57 (m, 1H), 2.34 (s, 3H), 2.27 (s, 3H), 2.02—1.98 (m, 2H), 0.94 (t, J=7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 142.9, 138.0, 136.7, 132.2, 129.2, 129.0, 128.9, 126.8, 126.6, 126.2, 125.9, 93.5, 58.8, 24.4, 21.0, 20.6, 9.8; IR (KBr) v: 3254, 1566, 1338, 1165 cm^{-1}; HR-EI-MS calcd for $C_{18}H_{22}N_2O_4S$ [M^+] 362.1300, found 362.1298.

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