Bismuth Triflate as Novel and Efficient Catalyst for the Synthesis of β-Aminosulfides

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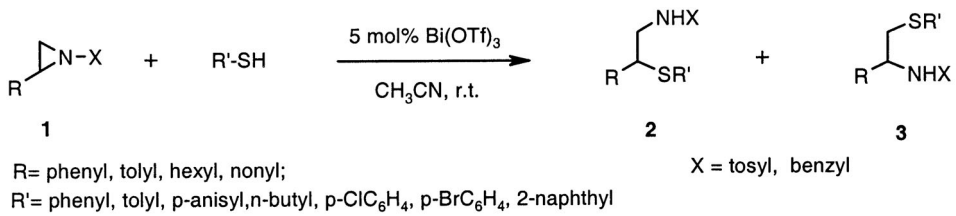
Abstract: Aziridines undergo ring opening readily with various thiols in the presence of 5 mol% bismuth triflate under very mild reaction conditions to afford the corresponding β-aminosulfides in excellent yields with high regioselectivity.

Key words: aziridines, metal triflates, thiols, β-aminosulfides

Aziridines are well known carbon electrophiles capable of reacting with various nucleophiles and their ability to undergo regioselective ring opening reactions contributes largely to their synthetic value.[1] They are useful intermediates for the synthesis of many biologically interesting molecules such as amino acids,[2] heterocycles[3] and alkaloids.[4] Particularly, the cleavage of aziridines with thiols is interesting because the resultant β-aminosulfides are important building blocks for the synthesis of various bioactive molecules.[5] The simple and most straightforward route to β-aminosulfides involves the regioselective ring opening of aziridines with thiols using acid or base catalysis.[6] Lewis acids such as boron trifluoride etherate and zinc chloride as well as Bronsted acids such as trifluoromethanesulfonic acid have been employed as acid catalysts.[6,7] However, many of these procedures involve the use of stoichiometric amount of catalysts, harsh conditions and require large excess of thiols and necessitate anhydrous conditions to produce the desired products. Furthermore, these reagents cannot be recovered and recycled because they decompose or deactivate under quenching conditions. Thus, no attempt has been made to recycle the catalyst, thereby making the process economic and environmental friendly. In fact, there is an advantage in developing a catalytic process for the synthesis of β-aminosulfides. Lanthanide triflates are unique Lewis acids that are currently of great interest.[8] High catalytic activity, low toxicity, moisture and air tolerance and their recyclability make the use of lanthanide triflates attractive alternatives to conventional Lewis acids.[9] However, unfortunately, lanthanide triflates are rather expensive and thus their use in large-scale synthesis is limited. Therefore, cheaper and more efficient catalysts are desirable. In this direction, bismuth triflate has evolved as a remarkable Lewis acid catalyst for effecting various organic transformations.[10] Compared to lanthanide triflates, bismuth triflate is inexpensive and easy to prepare on a multi-gram scale in the laboratory from commercially available bismuth oxide and triflic acid.[11] To the best of our knowledge, this is the first report on the use of bismuth triflate as a catalyst for the activation of aziridines.

In this article, we wish to highlight our results on the catalytic application of bismuth triflate in the regioselective ring opening reaction of aziridines with thiols. Accordingly, treatment of *N*-tosyl-2-phenyl aziridine with thionaphthol in the presence of 5 mol% $Bi(OTf)_3$ in MeCN at ambient temperature resulted in the formation of β-aminosulfide **2g** in 91% yield (Scheme 1).

In a similar fashion, *N*-benzyl- and *N*-tosyl-2-aryl aziridines reacted smoothly with various thiols to afford the corresponding β-aminosulfides in excellent yields. In the cleavage of *N*-benzyl- and *N*-tosyl-2-aryl aziridines (Table 1, entries g–l), preferential cleavage at the benzylic position of aziridine ring was observed while *N*-tosyl-2-alkyl aziridines (Table 1, entries m–p) were cleaved classically at less hindered (terminal) aziridine-ring carbon. Of course, cleavage reactions of both types of 2-aryl- and 2-alkyl aziridines are stereoselective because only *trans*-diastereomers of the corresponding regioisomers **2** and **3** were formed. In other words, 2-aryl substituted aziridines expressed opposite regioselectivity when compared to 2-



Scheme 1

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alkyl aziridines while no regioselectvity was possible for the reactions of bicyclic aziridines. However, bicyclic-*N*-tosyl aziridines underwent smooth cleavage with thiols to give the corresponding β-aminosulfides **4** in high yields (Scheme 2).

Table 1 Metal Triflate-Catalyzed Synthesis of β-Aminosulfides from Aziridines

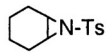
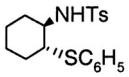
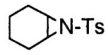
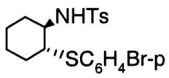
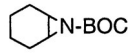
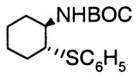
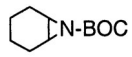
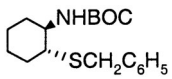
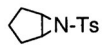
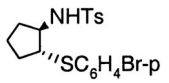
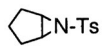
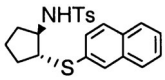
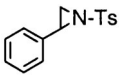
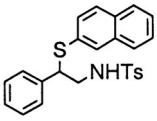
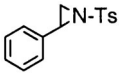
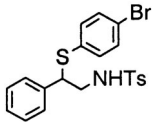
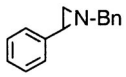
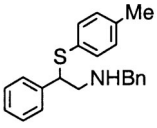
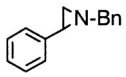
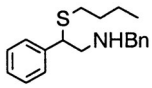
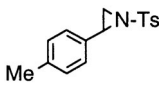
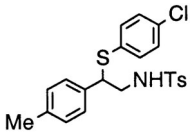
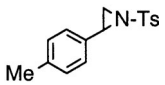
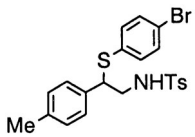
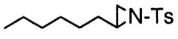
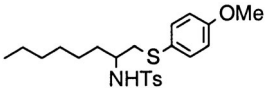
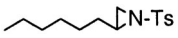
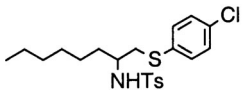
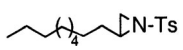
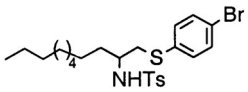
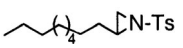
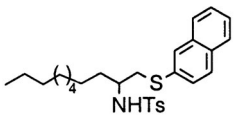
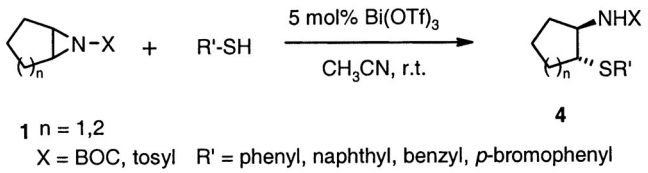
Entry	Aziridine	Product[a]		5% $Bi(OTf)_3$		5% $Sc(OTf)_3$	
				Time (h)	Yield (%)[b]	Time (h)	Yield (%)[b]
a			**4a**	4.5	92	7.0	90
b			**4b**	5.5	89	6.0	87
c			**4c**	5.0	87	5.0	85
d			**4d**	4.0	85	5.0	83
e			**4e**	5.0	90	6.5	89
f			**4f**	5.5	85	6.0	81
g			**2g**	3.0	91 (6)	3.5	89 (8)
h			**2h**	4.0	89 (5)	4.5	87 (6)
i			**2i**	4.5	90 (7)	5.0	86 (9)
j			**2j**	6.0	85 (9)	6.5	82 (12)
k			**2k**	4.0	92 (6)	4.5	90 (5)
l			**2l**	5.5	90 (8)	5.5	87 (9)
m			**3m**	5.0	89 (7)	6.0	83 (10)
n			**3n**	5.5	86 (9)	6.5	82 (9)

Table 1 Metal Triflate-Catalyzed Synthesis of β-Aminosulfides from Aziridines (continued)

Entry	Aziridine	Product[a]		5% $Bi(OTf)_3$		5% $Sc(OTf)_3$	
				Time (h)	Yield (%)[b]	Time (h)	Yield (%)[b]
o			**3o**	5.0	87 (6)	6.5	82 (11)
p			**3p**	6.5	85 (5)	7.0	80 (12)

[a] All products were characterized by ^1H NMR, IR, and mass spectroscopy.
[b] Yields reported in parentheses indicate other regioisomer.



Scheme 2

Except for the reactions of unsymmetrical aziridines such as styrene, octene and undecene aziridines, which produce a minor amount of the other regioisomer (5–12%), the reactions of bicyclic aziridines were found to give exclusively product **4**. Since bicyclic aziridines are symmetrical, no regioisomers were formed. In the case of bicyclic aziridines, the stereochemistry of the ring opened product **4a** was found to be *trans* from the coupling constants of the ring hydrogens at δ = 2.90 (ddd, *J* = 9.9, 9.5, 4.0 Hz, 1 H, -CHN), in ^1H NMR spectrum. Similarly the peak at δ = 3.0 ppm for -CHS showed the similar splitting pattern (ddd, *J* = 9.5, 9.5, 3.8 Hz, 1 H). Similarly *N*-Boc aziridine also reacted smoothly with thiols to give the corresponding ring opened product in good yields (entries c and d). The method is clean and highly regioselective, affording β-aminosulfides in excellent yields. This method is even effective with alkyl thiols (entries d and j) for the synthesis of alkyl-substituted β-aminosulfides. The reaction conditions are mild and no side products or decomposition of the products was observed. All the products were fully characterized by mass spectrometry, ^1H NMR and IR, and ^{13}C NMR spectroscopic data for new products. However, in the absence of catalyst, the reaction did not yield any product even after long reaction times (8–12 h). The efficacy of various metal triflates such as $Bi(OTf)_3$, $Sc(OTf)_3$, $In(OTf)_3$ $Yb(OTf)_3$, $Y(OTf)_3$, $Dy(OTf)_3$ and $Ce(OTf)_3$ was studied for this reaction. Among these metal triflates, 5 mol% bismuth and scandium triflates were found to be more efficient catalysts in terms of conversion and reaction time. Compared to bismuth triflate, scandium triflate was easily recovered from aqueous layer during work-up. The recovered scandium triflate was reused in subsequent reactions with gradual decrease in activity. For instance, *N*-tosyl-2-phenyl aziridine and thiophenol gave 90%, 86% and 79% yields over three cycles, respectively. Further the scope and generality of this process is illustrated with respect to various activated aziridines and a wide variety of thiols and the results are presented in the Table 1.

In summary, metal triflates are found to be useful and efficient alternatives to conventional Lewis acids for the regioselective ring opening reactions of 2-phenyl- and 2-alkyl-aziridines with thiols under mild conditions. The notable features of this method are high conversions, greater regioselectivity, cleaner reaction profiles, operational simplicity and reusability of the catalysts, which make it useful and attractive strategy for the synthesis of β-aminosulfides.

Melting points were recorded on Buchi R-535 apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer FT-IR 240-c spectrophotometer using KBr optics. ^1H NMR spectra were recorded on Gemini-200 spectrometer in $CDCl_3$ using TMS as internal standard. Mass spectra were recorded on a Finnigan MAT 1020 mass spectrometer operating at 70 eV. TLC was monitored on 0.25 mm Merck pre-coated silica gel plates (60F-254). $Bi(OTf)_3$ was prepared[11] in our laboratory.

Synthesis of β-Amino Sulfide; General Procedure

A mixture of *N*-activated aziridine (5 mmol), thiol (7.5 mmol) and $Bi(OTf)_3$ (5 mol%) or $Sc(OTf)_3$ (5 mol%) in anhyd MeCN (10 mL) was stirred at ambient temperature for the appropriate time (Table 1). After completion of the reaction as indicated by TLC, the reaction mixture was quenched with water (10 mL) and extracted with EtOAc (2 × 15 mL). The combined organic layers were dried over anhyd Na_2SO_4, concentrated in vacuo and purified by column chromatography on silica gel (Merck, 100-200 mesh, EtOAc–hexane, 2:8) to afford pure β-amino sulfide. The aq layer was concentrated in vacuo to recover the catalyst for use in further runs. The products thus obtained were identified by comparison of their NMR, IR, Mass, TLC, mixed TLC analysis and physical data with authentic samples. The spectral data of all the products were identical with those of authentic samples.[6,7]

4a

White solid;[7a] mp 130–132 °C.

IR (KBr): 3265, 2933, 2861, 1600 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.20–1.47 (m, 4 H), 1.50–1.75 (m, 2 H), 1.95–2.10 (m, 1 H), 2.20–2.30 (m, 1 H), 2.45 (s, 3 H), 2.90 (ddd, *J* = 4.0, 9.5, 9.9 Hz, 1 H), 3.0 (ddd, *J* = 3.8, 9.5, 9.5 Hz, 1 H),

5.15 (br s, NH, 1 H), 7.20–7.40 (m, 7 H), 7.75 (d, *J* = 7.9 Hz, 2 H). EIMS: *m*/*z* = 361 [M$^+$], 252, 206, 190, 91, 107, 81, 55.

4b
Pale yellow solid; mp 115–116 °C.

IR (KBr): 3315, 2937, 2835, 1610 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.20–1.45 (m, 4 H), 1.50–1.65 (m, 2 H), 1.95–2.10 (m, 1 H), 2.19–2.25 (m, 1 H), 2.45 (s, 3 H), 2.85–3.0 (m, 2 H), 5.20 (d, *J* = 7.0 Hz, 1 H, NH), 7.10 (d, *J* = 7.9 Hz, 2 H), 7.25 (d, *J* = 8.0 Hz, 2 H), 7.38 (d, *J* = 8.0 Hz, 2 H) 7.70 (d, *J* = 7.9 Hz, 2 H).

^{13}C NMR (^{1}H-decoupled, $CDCl_3$): δ = 21.4, 23.0, 24.1, 31.1, 31.7, 51.1, 54.9, 121.5, 127.1, 129.5, 131.9, 134.2, 137.4, 143.3.

FAB–MS: *m*/*z*= 440 [M$^+$], 286, 269, 190, 136, 107, 81, 55.

4c
Colorless solid;[7a] mp 109–111 °C.

IR (KBr): 3348, 2933, 2857, 1697, 1530 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.10–1.35 (m, 3 H), 1.39 (s, 9 H), 1.48–1.75 (m, 3 H), 1.95–2.05 (m, 1 H), 2.10–2.25 (m, 1 H), 2.80 (dt, *J* = 3.8, 10.3 Hz, 1 H), 3.30–3.35 (m, 1 H), 4.70 (d, *J* = 7.5 Hz, 1 H, NH), 7.10–7.30 (m, 3 H), 7.35–7.48 (m, 2 H).

FAB–MS: *m*/*z* = 307 [M$^+$], 252, 190, 129, 115, 81, 57.

4d
White solid;[7a] mp 70–72 °C.

IR (KBr): 3357, 2935, 2839, 1689, 1525 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.15–1.30 (m, 3 H), 1.40 (s, 9 H), 1.50–1.70 (m, 3 H), 1.97–2.10 (m, 1 H), 2.15–2.28 (m, 1 H), 2.45 (dt, *J* = 3.7, 10.2 Hz, 1 H), 3.40–3.50 (m, 1 H), 3.60–3.75 (m, 2 H), 4.60 (br s, NH, 1 H), 7.25–7.40 (m, 5 H).

FAB–MS: *m*/*z* = 321 [M$^+$], 265, 204, 130, 116, 82, 57.

4e
Pale yellow solid; mp 91–93 °C.

IR (KBr): 3370, 2927, 2830, 1605 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.40–1.57 (m, 2 H), 1.60–1.80 (m, 2 H), 1.95–2.20 (m, 2 H), 2.40 (s, 3 H), 3.20–3.30 (m, 1 H), 3.50–3.60 (m, 1 H), 5.60 (d, *J* = 7.0 Hz, NH, 1 H), 7.10 (d, *J* = 8.0 Hz, 2 H), 7.20 (d, *J* = 7.9 Hz, 2 H), 7.30 (d, *J* = 8.0 Hz, 2 H) 7.65 (d, *J* = 7.9 Hz, 2 H).

^{13}C NMR (^{1}H-decoupled, $CDCl_3$): δ = 21.5, 21.6, 30.2, 31.4, 52.3, 59.5, 120.9, 127.1, 129.6, 131.8, 133.6, 136.8, 143.5.

FAB–MS: *m*/*z* = 427 [M$^+$], 255, 238, 172, 155, 123, 109, 95, 83, 69, 55.

4f
Pale yellow solid; mp 130–131 °C.

IR (KBr): 3362, 2933, 2861, 1615 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.39–1.58 (m, 2 H), 1.60–1.78 (m, 2 H), 1.97–2.21 (m, 2 H), 2.38 (s, 3 H), 3.30–3.35 (m, 1 H), 3.55–3.60 (m, 1 H), 5.75 (d, *J* = 7.0 Hz, NH, 1 H), 7.05 (d, *J* = 8.0 Hz, 2 H), 7.20–7.38 (m, 2 H), 7.45–7.58 (m, 3 H), 7.65–7.80 (m, 4 H).

^{13}C NMR (^{1}H-decoupled, $CDCl_3$): δ = 21.4, 21.7, 30.3, 31.6, 52.4, 59.7, 126.1, 126.5, 127.1, 127.4, 127.6, 128.3, 129.2, 129.5, 130.3, 131.7, 132.2, 133.6, 136.8, 143.2.

FAB–MS: *m*/*z*: 397 [M$^+$], 243, 190, 185, 155, 127, 105, 69, 55.

2g
Colorless solid; mp 137–138 °C.

IR (KBr): 3300, 2927, 2838, 1610 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.40 (s, 3 H), 3.25–3.40 (m, 2 H), 4.25 (t, *J* = 7.1 Hz, 1 H), 4.65 (br s, NH, 1 H), 7.10–7.35 (m, 8 H), 7.40–7.60 (m, 4 H), 7.60–7.85 (m, 4 H).

^{13}C NMR (^{1}H-decoupled, $CDCl_3$): δ = 21.3, 47.5, 53.0, 126.4, 126.5, 127.1, 127.5, 127.7, 128.0, 128.5, 128.9, 129.6, 130.8, 131.6, 132.7, 133.8, 137.6, 138.6, 143.4.

FAB–MS: *m*/*z* = 433 [M$^+$], 274, 263, 249, 185, 155, 128, 105, 91, 69, 55.

2h
Yellow solid; mp 140–142 °C.

IR (KBr): 3286, 2940, 2856, 1601 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.20 (s, 3 H), 3.25–3.38 (m, 2 H), 4.20 (t, *J* = 7.1 Hz, 1 H), 4.60 (br s, 1 H, NH), 7.10 (d, *J* = 8.0 Hz, 2 H), 7.15–7.20 (m, 2 H), 7.30–7.40 (m, 7 H), 7.65 (d, *J* = 8.0 Hz, 2 H).

^{13}C NMR (^{1}H-decoupled, $CDCl_3$): δ = 21.5, 46.9, 52.7, 127.0, 127.8, 128.2, 128.9, 129.7, 132.0, 132.1, 133.5, 134.0, 136.6, 137.8, 143.8.

FAB–MS: *m*/*z* = 462 [M$^+$], 307, 274, 212, 154, 109, 95, 69, 55.

2i
Colorless liquid.[7a]

IR (KBr): 3313, 2938, 1598 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.60 (br s, 1 H, NH), 2.35 (s, 3 H), 3.14 (d, *J* = 7.4 Hz, 2 H), 3.80 (s, 2 H), 4.20 (t, *J* = 7.1 Hz, 1 H), 4.50 (br s, 1 H, NH), 7.05 (d, *J* = 8.0 Hz, 2 H), 7.13 (d, *J* = 8.0 Hz, 2 H), 7.20–7.45 (m, 10 H).

FAB–MS: *m*/*z*= 334 [M$^+$], 210, 120, 91, 77.

2j
Oil.[7a]

IR (KBr): 3310, 2941, 2857, 1600 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 7.0 Hz, 3 H), 1.20–1.55 (m, 4 H), 2.10 (br s, 1 H, NH), 2.25–2.35 (m, 2 H), 3.05 (d, *J* = 7.3 Hz, 2 H), 3.80 (s, 2 H), 4.0 (t, *J* = 7.3 Hz, 1 H), 7.15–7.45 (m, 10 H).

FAB–MS: *m*/*z* = 299 [M$^+$], 120, 91, 77, 43.

2k
Colorless solid; mp 128–130 °C.

IR (KBr): 3280, 2951, 2837, 1598 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.30 (s, 3 H), 2.45 (s, 3 H), 3.20–3.30 (m, 2 H), 4.25 (t, *J* = 7.0 Hz, 1 H), 4.65 (br s, 1 H, NH), 7.10–7.30 (m, 8 H), 7.35–7.40 (m, 2 H), 7.60 (d, *J* = 8.0 Hz, 2 H).

^{13}C NMR (^{1}H-decoupled, $CDCl_3$): δ = 21.0, 21.5, 47.0, 52.4, 127.0, 127.6, 129.0, 129.6, 129.7, 131.6, 133.7, 133.9, 134.7, 136.8, 138.1, 143.6.

FAB–MS: *m*/*z* = 431 [M$^+$], 288, 261, 154, 91, 69, 55.

2l
Pale yellow solid; mp 125–126 °C.

IR (KBr): 3289, 2978, 2820, 1600 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.30 (s, 3 H), 2.45 (s, 3 H), 3.21–3.30 (m, 2 H), 4.10 (t, *J* = 7.0 Hz, 1 H), 4.60 (br s, 1 H, NH), 7.10–7.18 (m, 6 H), 7.20–7.30 (m, 4 H), 7.62 (d, *J* = 8.0 Hz, 2 H).

^{13}C NMR (^{1}H-decoupled, $CDCl_3$): δ = 21.0, 21.5, 47.0, 52.3, 121.9, 127.0, 127.6, 129.6, 129.7, 132.0, 132.3, 133.8, 134.6, 136.8, 138.1, 143.6.

FAB–MS: *m*/*z* = 476 [M$^+$], 293, 288, 274, 245, 221, 155, 131, 119, 105, 91, 69, 55.

3m
Oil.

IR (KBr): 3280, 2938, 2843, 1605 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.81 (t, *J* = 7.0 Hz, 3 H), 1.10–1.30 (m, 8 H), 1.35–1.60 (m, 2 H), 2.40 (s, 3 H), 2.60 (dd, *J* = 7.0, 10.3 Hz, 1 H), 3.0 (dd, *J* = 4.0, 10.3 Hz, 1 H), 3.20–3.35 (m, 1 H), 3.80 (s, 3 H), 4.65 (dd, *J* = 4.0, 7.1 Hz, 1 H), 6.80 (d, *J* = 8.0 Hz, 2 H), 7.20–7.35 (m, 4 H), 7.60 (d, *J* = 8.0 Hz, 2 H).

^{13}C NMR (^{1}H-decoupled, $CDCl_3$): δ = 14.0, 21.4, 22.5, 25.2, 28.5, 31.6, 33.4, 39.7, 52.6, 55.1, 114.3, 122.7, 126.9, 129.5, 132.4, 137.6, 144.2, 159.7.

FAB–MS: *m*/*z* = 421 [M$^+$], 268, 251, 153, 133, 109, 92, 75.

3n
White solid; mp 58–59 °C.

IR (KBr): 3278, 2943, 2851, 1600 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.83 (t, *J* = 6.8 Hz, 3 H), 1.0–1.25 (m, 8 H), 1.30–1.65 (m, 2 H), 2.40 (s, 3 H), 2.75 (dd, *J* = 7.0, 10.3 Hz, 1 H), 3.10–3.30 (m, 2 H), 4.85 (d, *J* = 7.0 Hz, 1 H, NH), 7.10–7.25 (m, 6 H), 7.60 (d, *J* = 8.0 Hz, 2 H).

^{13}C NMR (^{1}H-decoupled, $CDCl_3$): δ = 14.0, 21.4, 22.4, 25.1, 28.6, 31.5, 33.5, 39.6, 52.7, 127.0, 129.0, 129.5, 131.0, 132.1, 133.9, 137.6, 143.4.

FAB–MS: *m*/*z* = 426 [M$^+$], 268, 255, 155, 136, 109, 91, 69, 55.

3o
Yellow solid; mp 74–76 °C.

IR (KBr): 3278, 2941, 2830, 1601 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.80 (t, *J* = 6.8 Hz, 3 H), 0.95–1.35 (m, 15 H), 1.55–1.65 (m, 1 H), 2.35 (s, 3 H), 2.80 (dd, 1 H, *J* = 7.0, 10.3 Hz), 3.10–3.30 (m, 2 H), 4.60 (d, *J* = 7.0 Hz, NH, 1 H), 7.10 (d, *J* = 8.0 Hz, 2 H), 7.20 (d, *J* = 7.9 Hz, 2 H), 7.38 (d, *J* = 7.9 Hz, 2 H), 7.60 (d, *J* = 8.0 Hz, 2 H).

^{13}C NMR (^{1}H-decoupled, $CDCl_3$): δ = 14.0, 21.4, 22.6, 25.2, 29.0, 29.3, 31.8, 33.6, 39.5, 52.8, 120.3, 127.1, 129.5, 131.3, 132.0, 134.7, 137.8, 143.1.

FAB–MS: *m*/*z* = 512 [M$^+$], 341, 310, 262, 203, 155, 122, 91, 69, 55.

3p
Colorless solid; mp 66–67 °C.

IR (KBr): 3280, 2945, 2842, 1603 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.83 (t, *J* = 6.8 Hz, 3 H), 0.99–1.37 (m, 15 H), 1.57–1.65 (m, 1 H), 2.30 (s, 3 H), 2.80 (dd, *J* = 7.0, 10.3 Hz, 1 H), 3.15–3.40 (m, 2 H), 4.65–4.75 (m, 1 H, NH), 7. 0 (d, *J* = 8.0 Hz, 2 H), 7.25–7.80 (m, 9 H).

^{13}C NMR (^{1}H-decoupled, $CDCl_3$): δ = 14.0, 21.2, 22.6, 25.2, 29.0, 29.3, 31.8, 33.6, 39.1, 52.9, 125.8, 126.5, 127.0, 128.4, 129.4, 131.8, 132.9, 133.7, 137.5, 143.1.

FAB–MS: *m*/*z* = 483 [M$^+$], 313, 185, 174, 155, 91, 55.

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References

(1) (a) Katritzky, A. R.; Rees, C. W. *Comprehensive Heterocyclic Chemistry*, Vol. 7; Pergamon Press: Oxford, **1984**, 47. (b) Kump, J. E. G. *Comprehensive Organic Synthesis*, Vol. 7; Trost, B. M.; Fleming, I., Eds.; Pergamon Press: Oxford, **1991**, 469.
(2) (a) Tanner, D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 599. (b) McCoull, W.; Davis, F. A. *Synthesis* **2000**, 1347.
(3) (a) Dureault, A.; Tranchepain, I.; Depezay, J. C. *J. Org. Chem.* **1989**, *54*, 5324. (b) Tanner, D.; He, H. M. *Tetrahedron* **1992**, *48*, 6079.
(4) Hudlicky, T.; Luna, H.; Price, J. D.; Rulin, F. *J. Org. Chem.* **1990**, *55*, 4683.
(5) (a) Bae, J. H.; Shin, S. H.; Park, C. S.; Lee, W. K. *Tetrahedron* **1999**, *55*, 10041. (b) Ingenitio, R.; Bianchi, E.; Fattori, D.; Pessi, A. *J. Am. Chem. Soc.* **1999**, *121*, 11369. (c) Adams, B.; Beresford, K. J. M.; Whyte, S. M.; Young, D. W. *J. Chem. Soc., Chem. Commun.* **2000**, 619.
(6) (a) Carreaux, F.; Dureault, A.; Depezay, J. C. *Synlett* **1992**, 527. (b) Maligres, P. E.; See, M. M.; Askin, D.; Reider, P. J. *Tetrahedron Lett.* **1997**, *38*, 5253.
(7) (a) Wu, J.; Hou, X. L.; Dai, L. X. *J. Chem. Soc., Perkin Trans. 1* **2001**, 1314. (b) Katagiri, T.; Takahashi, M.; Fujiwara, Y.; Ihara, H.; Uneyama, K. *J. Org. Chem.* **1999**, *64*, 7323. (c) Antolini, L.; Bucciarelli, M.; Caselli, E.; Davoli, P.; Forni, A.; Moretti, I.; Prati, F.; Torre, G. *J. Org. Chem.* **1997**, *62*, 8784.
(8) (a) Imamoto, T. *Lanthanides in Organic Synthesis*; Academic Press: London, **1994**. (b) Molander, G. A. *Chem. Rev.* **1992**, *92*, 29.
(9) (a) Kobayashi, S. *Synlett* **1994**, 689. (b) Kobayashi, S. *J. Synth. Org. Chem., Jpn.* **1995**, *53*, 370. (c) Kobayashi, S. *Eur. J. Org. Chem.* **1999**, 15.
(10) Leonard, M. N.; Wieland, L. C.; Mohan, R. S. *Tetrahedron* **2002**, *58*, 8373.
(11) Repichet, S.; Zwick, A.; Vendier, L.; Le Roux, C.; Dubac, J. *Tetrahedron Lett.* **2002**, *43*, 993.