A Stereoselective Synthesis of Alkynylaziridines[‡]

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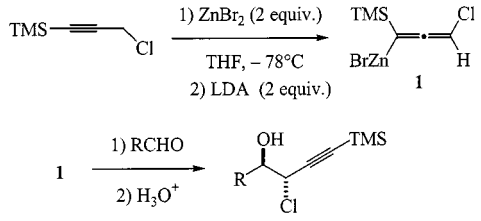
Reactions between allenylzinc carbenoid **1** and various imines were examined; *trans*-substituted alkynylaziridines were produced with excellent diastereoselectivity.

Introduction

Aziridines have provoked considerable interest over recent years.[2−7] In contrast, however, very few syntheses of alkynylaziridines have been reported. They had previously been prepared by treatment of nitrenes or nitrene equivalents with enynes,[8,9] or from the corresponding alkynyloxiranes in a two-step reaction.[10] More recently, the condensation of propargylsulfonium ylides[11−13] or of lithiated cinnamyl chloride[14] onto imines has been described, as well as the preparation of optically pure aziridines from amino acids.[15−17] Very recently, we have reported[1] a stereoselective synthesis of alkynyloxiranes by the condensation of the new allenylzinc carbenoid **1** with aldehydes and ketones (Scheme 1). Here we report our studies into reactions between **1** and various imines, which afforded *trans*-substituted alkynylaziridines with excellent stereocontrol.[18]



Scheme 1

Results and Discussion

Reaction with *N*-Benzylimines

Reactions between **1** and *N*-benzylaldimines were found to occur at temperatures higher (−10 °C) than those required for reactions with aldehydes. Ring-closure to aziridines occurred in the course of the reaction, and alkynylaziridines were obtained in good to excellent yields directly upon hydrolysis. These aziridines **2a**−**f** were obtained as single invertomers, the benzyl group presumably lying on the same side as the acetylenic moiety. Only in the case of the reaction with *N*-cyclohexylidenebenzylamine was the resulting aziridine obtained as a mixture of two invertomers, in a 50:50 ratio. Our results are summarized in Table 1.

The stereochemistries of the aziridines were determined by measurement of the coupling constants of the two aziridinyl protons by ^{1}H NMR. All the aziridines were found to be purely *trans*-substituted, whatever the stereochemistry of the starting imine. This stereoselectivity can easily be explained in terms of a cyclic transition state analogous to the Chodkiewicz model[19,20] for the case of aldehydes (Scheme 2).

In order to prepare homochiral aziridines, treatment of **1** with *N*-(α-methylbenzyl)imines was investigated. Unfortunately, no reaction was observed below 0 °C, while decomposition of carbenoid **1** occurred at higher temperatures. A similar lack of reactivity was observed in the case of *N*-tritylimines and *N*-(4-methoxyphenyl)imines.

Reaction with *N*-(Trimethylsilyl)imines

The *N*-(trimethylsilyl)imines used in this study were prepared in situ by treatment of the corresponding aldehydes with LiHMDS,[21−23] or of organolithium reagents with *N*,*N*-bis(trimethylsilyl)formamide.[24] Condensation with **1** occurred at a lower temperature (−50 to −35 °C) than with *N*-benzylimines (except in the case of the imine derived from pivalaldehyde, which did not react below −10 °C), and upon hydrolysis the corresponding *N*-H aziridines

[‡] Propargylic Carbenoids, 2. − Part 1: Ref.[1]

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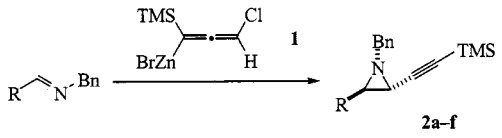
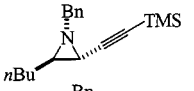
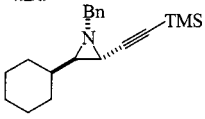
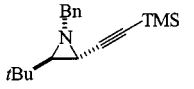
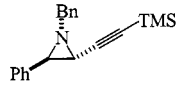
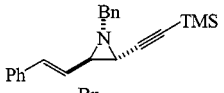
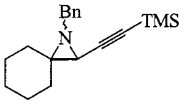
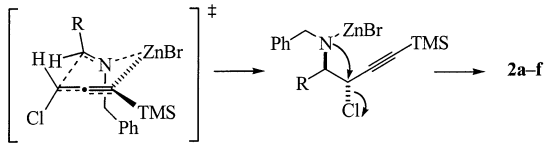
Table 1. Preparation of alkynyl-substituted *N*-benzylaziridines



Entry	*N*-benzylaziridine		Yield (%)
1		**2a**	50
2		**2b**	98[a]
3		**2c**	12[b]
4		**2d**	73
5		**2e**	65
6		**2f**	40[c]

[a] No purification was necessary. [b] In the presence of BF_3-Et_2O (2 equiv.): 50% yield by ^1H NMR. [c] As a mixture of two invertomers in a 50:50 ratio.

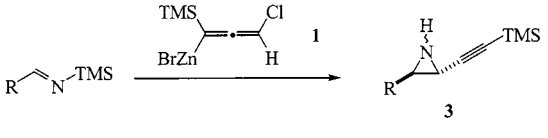


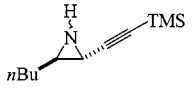
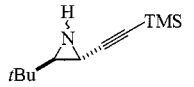
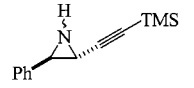
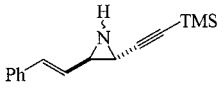
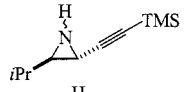
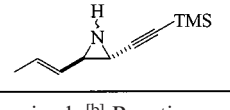
Scheme 2

3a,**c**–**e**,**g**,**h** were obtained in good to excellent yields. Two invertomers were observed in each case, in variable ratios (Table 2).

The stereochemistries of the formed *N*-H aziridines could not be determined by ^1H NMR. They were next transformed into the corresponding *N*-benzylaziridines by treatment with benzyl bromide (Table 3). The obtained *N*-benzylaziridines were again found to be purely *trans*-substituted and to be single invertomers (except in the case of aziridine **2a**, which was found to be a mixture of two invertomers in a 65:35 ratio) identical to the materials previously prepared. It had to be concluded that the *trans*-substituted *N*-H aziridines were also formed with excellent stereocontrol, which could again be explained by following the transition state, similar to that depicted in Scheme 2. Moreover, the fact that only one invertomer was obtained upon benzylation in most cases supports the assignment of its stereochemistry (the benzyl group being *cis* to the acetylenic moiety), as the alkylation reaction should take place on the less hindered side of the *N*-H aziridine.

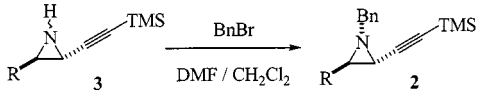
Table 2. Preparation of alkynyl-substituted *N*-H aziridines



Entry	*N*-H aziridine		Yield (%)	Invertomer ratio
1		**3a**	63	[a]
2		**3c**	40[b]	>98/2
3		**3d**	62	95/5
4		**3e**	65	73/27
5		**3g**	69	89/11
6		**3h**	79	66/34

[a] Not determined. [b] Reaction performed at −10 °C.

Table 3. Transformation of *N*-H into *N*-benzylaziridines

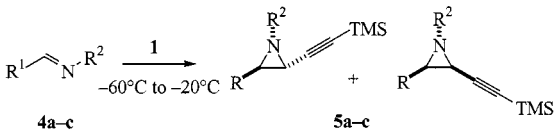


Entry	R	Starting aziridine	Product	Yield (%)	Invertomer ratio
1	*n*Bu	**3a**	**2a**	69	65/35
2	*t*Bu	**3c**	**2c**	69	>98/2
3	Ph	**3d**	**2d**	90	>98/2
4	PhCH=CH	**3e**	**2e**	66	>98/2
5	*i*Pr	**3g**	**2g**	66	>98/2
6	$CH_3CH=CH$	**3h**	**2h**	67	>98/2

Reaction with *N*-Sulfonylimines

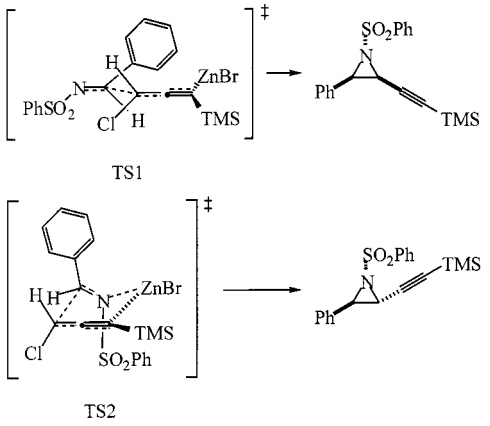
Reactions between **1** and the more reactive *N*-sulfonylimines[25] were found to be surprisingly low-yielding. The cor-

Table 4. Preparation of alkynyl-substituted *N*-sulfonylaziridines



4a–c **5a–c**

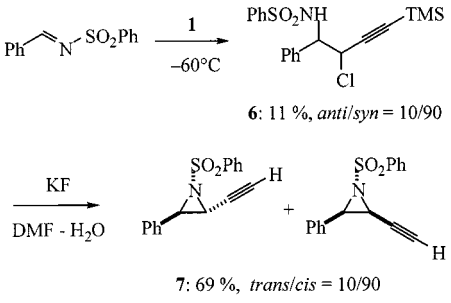
Entry	R^1	R^2	Aziridine	Yield (%)	*trans*/*cis* ratio
1	Cyclohexyl	Ts	**5a**	39	70/30
2	*i*Pr	Ts	**5b**	27	70/30
3	Ph	SO_2Ph	**5c**	41	10/90



Scheme 4

responding *N*-tosylaziridines were obtained in low to fair yields (Table 4). Moreover, the diastereoselectivity was lower than in the cases reported above, and was also dependent on the nature of the substituent on the starting imine. With aliphatic *N*-tosylimines **4a** and **4b**, the corresponding aziridines **5a** and **5b** were obtained in a 70:30 ratio in favour of the *trans* isomer. In contrast, aziridine **5c**, derived from *N*-benzylidenebenzenesulfonamide (**4c**), was obtained in a 90:10 ratio in favour of the *cis* isomer.

It has been shown that, under equilibrating conditions, unsaturated *cis*-*N*-sulfonylaziridines[26–28] and -*N*-phenylaziridines[16] were formed in preference to the *trans* isomer. The same behaviour was reported in the case of diaryl-*N*-(trimethylsilyl)aziridines.[29] In order to ascertain whether the strong *cis* preference in the formation of **5c** was due to a thermodynamic preference, the reaction between **1** and **4c** was quenched at low temperature. The alkynylchloro-*N*-sulfonylamine intermediate **6** was obtained, together with starting material, in low yield (11%) but in a 90:10 ratio in favour of the *syn* isomer, as demonstrated by further ring-



Scheme 3

closure to **7** (Scheme 3). The diastereomeric ratio in **7** was identical to that in **5c**, thus demonstrating that the *syn* preference was not related to any equilibration under the reaction conditions.

The formation of the *syn* diastereomer of **5c** could also be explained in terms of an open transition state TS1 (Scheme 4). Since the sulfonyl group is strongly electron-withdrawing, the lone electron pair on the nitrogen atom should be deactivated, and the general chelate transition state TS2 followed by *N*-benzyl- and *N*-(trimethylsilyl)imines should then be less favoured relative to TS1. This would explain the lower diastereoselectivity in the formation of **5a** and **5b**. However, the reasons why the transition state TS1 should be favoured over TS2 in the case of imine **4c** remain unclear. It could be attributed to a possible arene–zinc interaction,[30–33] or to a possible π-stacking-type interaction[34,35] between the aromatic ring and the allenyl moiety. It should be noted that the same tendency has previously been observed in the case of aromatic aldehydes, albeit in a much lower extent.[1] These possibilities are currently under investigation in our laboratory.

Conclusion

We report a new one-step synthesis of alkynylaziridines by treatment of an allenylzinc carbenoid with various imines. This methodology allows the formation of *trans*-alkynyl-substituted *N*-H and *N*-benzylaziridines with very high stereoselectivities. We are currently working on some other applications of this methodology, as well as its extension to the enantiomerically pure series.

Experimental Section

General Remarks: Experiments involving organometallic compounds were carried out in dried glassware under a positive pressure of dry nitrogen. Liquid nitrogen was used as a cryoscopic fluid. A four-necked, round-bottomed flask equipped with an internal thermometer, a septum cap, a nitrogen inlet, and a mechanic stirrer was used. THF was freshly distilled from sodium benzophenone ketyl prior to use. Zinc bromide (98%) was purchased from Aldrich. It was melted under dry nitrogen and, immediately after cooling to room temperature, was dissolved in anhydrous THF. All other reagents and solvents were of commercial quality and were used without purification. Flash column chromatographic separations were carried out on Merck 60 silica gel (0.015–0.040 mm). ^{1}H NMR and ^{13}C NMR spectra were recorded with Bruker ARX 400 or AC 200 spectrometers. Chemical shifts are reported in δ relative

to an internal standard of residual chloroform (δ = 7.27 for ^{1}H NMR and δ = 77.1 for ^{13}C NMR) unless otherwise noted. IR spectra were recorded with a Perkin−Elmer 1420 spectrophotometer. Mass spectra were performed by the Service de Spectrométrie de Masse de l'Université Pierre et Marie Curie. Elemental analyses were performed by the Service de Microanalyses de l'Université Pierre et Marie Curie. Some elemental analyses could not be obtained, presumably due to the hygroscopic character of the corresponding aziridines.

General Procedure 1. Preparation of Allenylzinc Compound 1: 1-Chloro-3-(trimethylsilyl)prop-2-yne[36,37] (1.0 equiv.) was added at −20 °C to a solution of $ZnBr_2$ (1.0 M, 2.0 equiv.) in THF. The resulting white suspension was cooled to −80 °C, and a freshly prepared solution of lithium diisopropylamide (1.0 M, 2.0 equiv.) in anhydrous THF was slowly added dropwise. The yellow solution was stirred at −80 °C for 1 h and immediately used for the preparation of aziridines.

General Procedure 2. Preparation of *N*-Benzylimines: Molecular sieves (4 Å, 0.6 g/1.00 mmol of aldehyde) were added under argon to a 1.0 M solution of the aldehyde (1.0 equiv.) and benzylamine (1.0 equiv.) in CH_2Cl_2. The resulting suspension was stirred overnight at room temperature, and after filtration through a Celite pad, the volatiles were removed in vacuo to afford *N*-benzylimines as pale yellow oils in yields from 30 to 100%.

General Procedure 3. Preparation of *N*-Sulfonylimines 4: A 0.5 M solution of sodium 4-methylbenzenesulfinate (1.0 equiv.), benzenesulfonamide (1.0 equiv.), or 4-methylbenzenesulfonamide (1.0 equiv.) and aldehyde (1.0 equiv.) in a 40% water/formic acid mixture was stirred at room temperature for 20 h. After filtration, the white solid was washed successively with water and pentane and then taken up into CH_2Cl_2 in order to obtain a 0.2 M solution, which was treated with a saturated aqueous $NaHCO_3$ solution and stirred for 5 h at room temperature. The aqueous layer was then extracted with CH_2Cl_2 (twice). The combined organic layers were washed with brine, dried with anhydrous $NaHCO_3$ and then concentrated in vacuo to afford *N*-sulfonylimines **4** as white solids in yields from 54 to 89%.

General Procedure 4. Preparation of *N*-Benzyl- and *N*-Sulfonylaziridines 2 and 5 from the Corresponding Imines: Under nitrogen, the *N*-benzylimines or the *N*-sulfonylimines **4** (1.0 equiv.) were added dropwise at −60 °C to a solution of allenylzinc compound **1** (1.0 equiv.). The mixture was allowed to warm slowly to room temperature, stirred overnight at this temperature and then quenched with a 65:35 mixture of a saturated aqueous NH_4Cl solution and NH_3. The aqueous layer was extracted with Et_2O (twice). The combined organic layers were washed with water (twice) and brine, dried with anhydrous $MgSO_4$, and then concentrated in vacuo to dryness. The crude oils were purified by flash chromatography, eluting with 5% ethyl acetate/cyclohexane, to afford *N*-benzylaziridines **2** or *N*-sulfonylaziridines **5** as pale yellow oils.

General Procedure 5. Preparation of *N*-H Aziridines 3: Under nitrogen, *n*-butyllithium (2.5 M in hexanes, 1.1 equiv.) was slowly added, at a temperature below 25 °C, to hexamethyldisilazane (1.1 equiv.). After the mixture had been stirred for 30 min, the volatiles were removed in vacuo and the resulting white solid was taken up into anhydrous THF in order to obtain a 0.5 M solution. This was cooled to −55 °C, and the aldehyde (1.0 equiv.) was added dropwise. The solution was stirred for 2 h at −40 °C and was cannulated into a cooled (−80 °C) solution of allenylzinc compound **1** (1.0 equiv.). The mixture was allowed to warm very slowly (over a period of 18 h) to −35 °C and then quenched with a 65:35 mixture of a saturated aqueous NH_4Cl solution and NH_3. After the mixture had warmed to room temperature, the aqueous layer was extracted with Et_2O (three times). The combined organic layers were washed with a saturated aqueous $NaHCO_3$ solution, water (twice) and brine, dried with anhydrous Na_2SO_4, and then concentrated in vacuo to dryness. The crude brownish oils were purified by flash chromatography, eluting with 3% Et_2O/2% Et_3N/pentane, to give *N*-H aziridines **3** as yellow oils.

General Procedure 6. Preparation of *N*-Benzylaziridines 2 from *N*-H Aziridines 3: Benzyl bromide (3.5 equiv.) was added dropwise at room temperature, under argon, to a stirred 0.1 M suspension of *N*-H aziridines **3** (1.0 equiv.) and K_2CO_3 (3.5 equiv.) in 10% DMF/CH_2Cl_2. The mixture was stirred at room temperature for 3 d and was then quenched with a 65:35 mixture of a saturated aqueous NH_4Cl solution and NH_3. The aqueous layer was extracted with Et_2O (three times), and the combined organic layers were washed with water and brine, dried with anhydrous $MgSO_4$, and then concentrated to dryness in vacuo. The crude oils were purified by flash chromatography, eluting with 2% Et_3N/pentane, to afford *N*-benzylaziridines **2** as pale yellow oils.

(2*R,3*R**)-*N*-Benzyl-3-(*n*-butyl)-2-[(trimethylsilyl)ethynyl]aziridine (2a):** This compound was prepared by General Procedure 4, from *N*-pentylidenebenzylamine (870 mg, 5.00 mmol) in 50% yield (600 mg, 2.50 mmol); *trans*/*cis* > 98:2. IR (NaCl, film): $\tilde{\nu}$ = 2980, 2910, 2840, 2160, 840 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.24 (s, 9 H), 0.86 (m, 3 H), 1.19−1.50 (m, 6 H), 1.77 (m, 1 H), 2.38 (d, ^3J = 3.4 Hz, 1 H), 3.60 (AB system, ^2J = 13.2 Hz, 1 H), 3.87 (AB system, ^2J = 13.2 Hz, 1 H), 7.26−7.43 (m, 5 H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 0.0, 14.0, 22.4, 29.2, 32.4, 32.8, 48.7, 58.4, 88.8, 102.7, 127.0, 128.3, 128.7, 139.3. MS (E.I., 70 eV): *m*/*z* (%) = 285 (31), 212 (12), 194 (100), 91 (71), 73 (53). This compound was also prepared by General Procedure 6, from *N*-H aziridine **3a** (see below; 195 mg, 1.00 mmol) in 69% yield (196 mg, 0.69 mmol) as a mixture of two invertomers *maj*/*min* = 65:35; *trans*/*cis* > 98:2. IR (NaCl, film): $\tilde{\nu}$ = 2980, 2910, 2840, 2160, 835 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz) for the mixture of the two invertomers: δ = 0.20 (s, 9 H *maj*), 0.29 (s, 9 H *min*), 0.86 (m, 3 H), 1.19−1.50 (m, 6 H), 1.77 (m, 1 H), 2.38 (d, ^3J = 3.0 Hz, 1 H), 3.43 (AB system, ^2J = 13.7 Hz, 1 H *min*), 3.61 (AB system, ^2J = 13.2 Hz, 1 H *maj*), 3.81 (AB system, ^2J = 13.7 Hz, 1 H *min*), 3.87 (AB system, ^2J = 13.2 Hz, 1 H *maj*), 7.26−7.43 (m, 5 H). ^{13}C NMR ($CDCl_3$, 100.6 MHz) for the mixture of the two invertomers: δ = 0.0 (*maj*), 0.3 (*min*), 14.0, 22.2 (*min*), 22.4 (*maj*), 28.5 (*min*), 29.2 (*maj*), 29.7 (*min*), 32.4 (*maj*), 32.8 (*maj*), 34.3 (*min*), 48.7 (*maj*), 55.6 (*min*), 58.4 (*maj*), 59.1 (*min*), 88.8 (*maj*), 91.6 (*min*), 101.2 (*min*), 102.7 (*maj*), 127.0 (*maj*), 127.3 (*min*), 128.3 (*maj*), 128.4 (*min*), 128.7 (*maj*), 129.1 (*min*), 138.8 (*min*), 139.3 (*maj*).

(2*R,3*R**)-*N*-Benzyl-3-cyclohexyl-2-[(trimethylsilyl)ethynyl]-aziridine (2b):** This compound was prepared by General Procedure 4, from *N*-(cyclohexylmethylidene)benzylamine (1.00 g, 5.00 mmol) in 98% yield (1.52 g, 4.90 mmol). Purification was not necessary; *trans*/*cis* > 98:2. IR (NaCl, film): $\tilde{\nu}$ = 3030, 2920, 2840, 2160, 840 cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 0.21 (s, 9 H), 0.80−1.93 (m, 12 H), 2.41 (d, ^3J = 3.0 Hz, 1 H), 3.53 (AB system, ^2J = 13.1 Hz, 1 H), 3.87 (AB system, ^2J = 13.1 Hz, 1 H), 7.25−7.40 (m, 5 H). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 0.0, 25.6, 26.3, 30.0, 30.6, 31.8, 35.5, 41.0, 53.9, 58.7, 88.6, 102.7, 127.0, 128.3, 128.9, 139.3.

(2*R,3*R**)-*N*-Benzyl-3-(*tert*-butyl)-2-[(trimethylsilyl)ethynyl]-aziridine (2c):** *N*-(2,2-Dimethylpropylidene)benzylamine (870 mg, 5.00 mmol) was added dropwise at −60 °C, under nitrogen, to a freshly prepared solution of allenylzinc compound **1** (5.00 mmol)

in THF, followed by BF_3-Et_2O (0.63 mL, 5.00 mmol). The mixture was allowed to warm slowly to room temperature, stirred overnight at this temperature and then quenched successively with absolute MeOH (2 mL), Et_3N (2 mL), and a saturated aqueous NH_4Cl solution (25 mL). The aqueous layer was extracted with Et_2O (2 × 40 mL), and the combined organic layers were washed with water (twice) and brine, dried with anhydrous $MgSO_4$, and then concentrated in vacuo to dryness. The crude oil was purified by flash chromatography, eluting with 5% ethyl acetate/cyclohexane, to give *N*-benzylaziridine **2c** in 12% yield (180 mg, 0.60 mmol) as a pale yellow oil; *trans*/*cis* > 98:2. IR (NaCl, film): $\tilde{\nu}$ = 3030, 2960, 2900, 2870, 2160, 840 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.21 (s, 9 H), 0.78 (s, 9 H), 1.62 (d, ^3J = 3.6 Hz, 1 H), 2.48 (d, ^3J = 3.6 Hz, 1 H), 3.53 (AB system, ^2J = 13.2 Hz, 1 H), 3.91 (AB system, ^2J = 13.2 Hz, 1 H), 7.32−7.44 (m, 5 H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 0.0, 26.5, 29.2, 30.6, 57.9, 58.7, 88.1, 103.2, 126.9, 128.1, 128.9, 139.6. $C_{18}H_{26}NSi$ (285.50): calcd. C 75.72, H 9.53, N 4.91; found C 75.32, H 9.54, N 4.61. This compound was also prepared by General Procedure 6, from *N*-H aziridine **3c** (see below; 197 mg, 1.01 mmol) in 69% yield (196 mg, 0.69 mmol); *trans*/*cis* > 98:2.

(2*R,3*R**)-*N*-Benzyl-3-phenyl-2-[(trimethylsilyl)ethynyl]aziridine (2d):** This compound was prepared by General Procedure 4, from *N*-benzylidenebenzylamine (975 mg, 5.00 mmol) in 73% yield (1.12 g, 3.65 mmol); *trans*/*cis* > 98:2. IR (NaCl, film): $\tilde{\nu}$ = 3030, 2950, 2910, 2840, 2160, 1600, 840 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.21 (s, 9 H), 2.66 (d, ^3J = 3.0 Hz, 1 H), 2.81 (d, ^3J = 3.0 Hz, 1 H), 3.90 (AB system, ^2J = 13.9 Hz, 1 H), 4.06 (AB system, ^2J = 13.9 Hz, 1 H), 7.26−7.46 (m, 10 H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 0.0, 37.0, 49.9, 58.1, 89.6, 101.6, 126.3, 127.6, 128.0, 139.2. This compound was also prepared by General Procedure 6, from *N*-H aziridine **3d** (see below; 211 mg, 0.98 mmol) in 90% yield (270 mg, 0.88 mmol); *trans*/*cis* > 98:2.

(2*R,3*R**)-*N*-Benzyl-3-(2-phenylethenyl)-2-[(trimethylsilyl)ethynyl]-aziridine (2e):** This compound was prepared by General Procedure 4, from *N*-(3-phenylprop-2-enylidene)benzylamine (1.10 g, 4.98 mmol) in 65% yield (1.08 g, 3.26 mmol); *trans*/*cis* > 98:2. IR (NaCl, film): $\tilde{\nu}$ = 3030, 2970, 2910, 2860, 2160, 1600, 840 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.21 (s, 9 H), 2.50 (dd, ^3J = 2.8, 7.6 Hz, 1 H), 2.72 (d, ^3J = 2.8 Hz, 1 H), 3.83 (AB system, ^2J = 13.7 Hz, 1 H), 3.96 (AB system, ^2J = 13.7 Hz, 1 H), 6.00 (dd, ^3J = 7.6 and 16.0 Hz, 1 H), 6.71 (d, ^3J = 16.0 Hz, 1 H), 7.21−7.50 (m, 10 H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 0.0, 35.1, 49.9, 57.9, 90.2, 101.4, 126.3, 128.6, 132.6, 136.6, 139.0. MS (E.I., 70 eV): *m*/*z* (%) = 331 (29), 106 (59), 91 (100), 73 (96). This compound was also prepared by General Procedure 6, from *N*-H aziridine **3e** (see below; 242 mg, 1.00 mmol) in 66% yield (216 mg, 0.66 mmol); *trans*/*cis* > 98:2.

***N*-Benzyl-2-[(trimethylsilyl)ethynyl]-1-azaspiro[2.5]octane (2f):** This compound was prepared by General Procedure 4, from *N*-cyclohexylidenebenzylamine (0.93 g, 5.00 mmol) in 40% yield (1.00 g, 2.00 mmol), as a mixture of two invertomers in a 50:50 ratio; *trans*/*cis* > 98:2. IR (NaCl, film): $\tilde{\nu}$ = 3030, 2950, 2920, 2840, 2160, 840 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz) for the mixture of the two invertomers: δ = 0.19 (s, 9 H for one invertomer), 0.23 (s, 9 H for one invertomer), 0.77−0.87 (m, 10 H), 1.90 (s, 1 H for one invertomer), 2.40 (s, 1 H for one invertomer), 3.69 (AB system, ^2J = 14.1 Hz, 1 H for one invertomer), 3.70 (AB system, ^2J = 14.6 Hz, 1 H for one invertomer), 3.84 (AB system, ^2J = 14.1 Hz, 1 H for one invertomer), 3.86 (AB system, ^2J = 14.6 Hz, 1 H for one invertomer), 7.17−7.41 (5 H). ^{13}C NMR ($CDCl_3$, 50.3 MHz) for the mixture of the two invertomers: δ = 0.0, 24.6, 39.3, 47.1, 47.7, 48.7, 49.9, 86.3, 90.2, 101.6, 104.1, 126.5, 128.2, 139.5, 140.1.

(2*R,3*R**)-*N*-Benzyl-3-isopropyl-2-[(trimethylsilyl)ethynyl]aziridine (2g):** This compound was prepared by General Procedure 6, from *N*-H aziridine **3g** (181 mg, 1.00 mmol) in 66% yield (178 mg, 0.66 mmol); *trans*/*cis* > 98:2. IR (NaCl, film): $\tilde{\nu}$ = 3030, 2960, 2910, 2880, 2160, 1605, 835 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.20 (s, 9 H), 0.82 (d, ^3J = 6.6 Hz, 3 H), 0.95 (d, ^3J = 7.1 Hz, 3 H), 1.26 (oct, ^3J = 7.1 Hz, 1 H), 1.57 (dd, ^3J = 3.1, 8.1 Hz, 1 H), 2.42 (d, ^3J = 3.1 Hz, 1 H), 3.55 (AB system, ^2J = 13.2 Hz, 1 H), 3.89 (AB system, ^2J = 13.2 Hz, 1 H), 7.33−7.43 (m, 5 H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 0.0, 19.4, 20.0, 31.6, 32.1, 55.1, 58.6, 88.6, 102.8, 127.0, 128.3, 128.9, 139.3. MS (E.I., 70 eV): *m*/*z* (%) = 271 (39), 180 (100), 91 (74), 73 (100).

(2*R,3*R**)-*N*-Benzyl-3-(2-methylprop-1-enyl)-2-[(trimethylsilyl)-ethynyl]aziridine (2h):** This compound was prepared by General Procedure 6, from *N*-H aziridine **3h** (180 mg, 1.02 mmol) in 67% yield (182 mg, 0.68 mmol); *trans*/*cis* > 98:2. IR (NaCl, film): $\tilde{\nu}$ = 3030, 2940, 2880, 2180, 1645, 810 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.20 (s, 9 H), 1.71 (dd, ^4J = 2.0 Hz and ^3J = 6.6 Hz, 3 H), 2.28 (dd, ^3J = 3.0, 7.6 Hz, 1 H), 2.55 (d, ^3J = 3.0 Hz, 1 H), 3.76 (AB system, ^2J = 13.7 Hz, 1 H), 3.87 (AB system, ^2J = 13.7 Hz, 1 H), 5.22 (ddd, ^4J = 2.0, ^3J = 7.6 and 15.3 Hz, 1 H), 5.82 (dq, ^3J = 7.6 and 15.3 Hz, 1 H), 7.33−7.44 (m, 5 H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 0.0, 18.0, 34.1, 49.6, 57.9, 88.6, 101.8, 127.0, 128.3, 128.4, 129.2, 129.3, 139.2. $C_{17}H_{23}NSi$ (269.46): calcd. C 75.78, H 8.60, N 5.20; found C 76.09, H 8.72, N 4.65.

(2*R,3*R**)-3-(*n*-Butyl)-2-[(trimethysilyl)ethynyl]aziridine (3a):** *n*-Butyllithium (2.5 M in hexanes, 2.00 mL, 5.00 mmol) was added dropwise at −80 °C, under nitrogen, to a stirred solution of bis(trimethylsilyl)formamide (1.08 mL, 5.00 mmol). The solution was stirred for 2 h at −80 °C and was cannulated into a cooled (−80 °C) solution of allenylzinc compound **1** (5.00 mmol). The mixture was allowed to warm very slowly (over a period of 18 h) to −35 °C and then quenched with a 65:35 mixture of a saturated aqueous NH_4Cl solution and NH_3 (25 mL). After the mixture had been allowed to warm to room temperature, the aqueous layer was extracted with Et_2O (3 × 25 mL). The combined organic layers were washed with a saturated aqueous $NaHCO_3$ solution, water (twice) and brine, dried with anhydrous Na_2SO_4, and then concentrated to dryness in vacuo. The crude brownish oil was purified by flash chromatography, eluting with 8% Et_2O/2% Et_3N/pentane, to give aziridine **3a** in 63% yield (614 mg, 3.15 mmol) as a mixture of two invertomers. Yellow oil. IR (NaCl, film): $\tilde{\nu}$ = 3320, 2950, 2880, 2160, 1450, 835 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) for the mixture of the two invertomers: δ = 0.17 (s, 9 H), 0.92 (t, ^3J = 7.1 Hz, 3 H), 1.36−1.45 (m, 6 H), 1.70 (m, 1 H), 2.05 (m, 1 H), 2.27 (m, 1 H). ^{13}C NMR ($CDCl_3$, 100.6 MHz) for the mixture of the two invertomers: δ = 0.0, 14.1, 22.5, 25.5, 29.3, 32.7 (broad), 40.6, 84.7, 106.1. $C_{11}H_{21}NSi$ (195.38): calcd. C 67.62, H 10.83, N 7.17; found C 68.10, H 10.94, N 6.65.

(2*R,3*R**)-3-(*tert*-Butyl)-2-[(trimethysilyl)ethynyl]aziridine (3c):** This compound was prepared by General Procedure 5, from pivalaldehyde (0.53 mL, 4.90 mmol) in 40% yield (374 mg, 1.92 mmol) after stirring for 16 h at −10 °C as a single invertomer. IR (NaCl, film): $\tilde{\nu}$ = 3330, 2950, 2880, 2165, 840 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.17 (s, 9 H), 0.90 (s, 9 H), 1.70 (m, 1 H), 2.17 (m, 2 H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 0.0, 22.2, 26.5, 30.7, 49.6, 84.3, 106.5. MS (E.I., 70 eV): *m*/*z* (%) = 195 (43), 180 (86), 73 (53), 57 (33).

(2*R,3*R**)-3-Phenyl-2-[(trimethysilyl)ethynyl]aziridine (3d):** This compound was prepared by General Procedure 5, from benzaldehyde (522 mg, 4.92 mmol) in 62% yield (649 mg, 3.02 mmol) as

a mixture of two invertomers *maj*/*min* = 95:5; *trans*/*cis* > 98:2. IR (NaCl, film): $\tilde{\nu}$ = 3320, 3030, 2930, 2160, 1580, 830 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) for the mixture of the two invertomers: δ = 0.20 (s, 9 H), 1.62 (s, 1 H), 2.32 (dd, ^3J = 2.5, 8.1 Hz, 1 H *maj*), 2.75 (m, 1 H *min*), 3.16 (m, 1 H *min*), 3.36 (dd, ^3J = 2.5, 7.1 Hz, 1 H *maj*), 7.28 (m, 5 H). ^{13}C NMR ($CDCl_3$, 100.6 MHz) for the mixture of the two invertomers: δ = 0.0, 30.2, 41.4, 85.6, 105.2, 126.0, 127.7, 128.5, 138.3. $C_{13}H_{17}NSi$ (215.37): calcd. C 72.50, H 7.96, N 6.50; found C 72.57, H 8.10, N 6.34.

(2*R,3*R**)-3-(2-Phenylethenyl)-2-[(trimethysilyl)ethynyl]aziridine (3e):** This compound was prepared by General Procedure 5, from (*E*)-cinnamaldehyde (0.62 mL, 4.90 mmol) in 65% yield (784 mg, 3.25 mmol) as a mixture of two invertomers *maj*/*min* = 73:27. IR (NaCl, film): $\tilde{\nu}$ = 3315, 3080, 2940, 2165, 1580, 840 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) for the mixture of the two invertomers: δ = 0.20 (s, 9 H), 0.89 (m, 1 H *min*), 1.05 (s, 1 H *maj*), 2.33 (dl, ^3J = 6.1 Hz, 1 H *maj*), 2.60 (m, 1 H *min*), 2.83 (m, 1 H *min*), 3.01 (t, ^3J = 7.1 Hz, 1 H *maj*), 5.65 (m, 1 H *min*), 5.86 (dd, ^3J = 7.7 and 15.8 Hz, 1 H *maj*), 6.73 (d, ^3J = 15.8 Hz, 1 H), 7.32−7.36 (m, 5 H). ^{13}C NMR ($CDCl_3$, 100.6 MHz) for the mixture of the two invertomers: δ = 0.0, 28.8, 41.5 (broad), 86.0, 104.7, 126.3, 127.9, 128.7, 132.8, 136.4. $C_{15}H_{19}NSi$ (241.40): calcd. C 74.63, H 7.93, N 5.80; found C 74.47, H 7.91, N 5.58.

(2*R,3*R**)-3-Isopropyl-2-[(trimethysilyl)ethynyl]aziridine (3g):** This compound was prepared by General Procedure 5, from isobutyraldehyde (0.45 mL, 4.90 mmol) in 69% yield (614 mg, 3.38 mmol) as a mixture of two invertomers *maj*/*min* = 89:11. IR (NaCl, film): $\tilde{\nu}$ = 3320, 2950, 2920, 2170, 840 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) for the mixture of the two invertomers: δ = 0.17 (s, 9 H), 1.02 (m, 6 H), 1.18 (m, 1 H), 1.73 (m, 1 H), 2.09 (m, 2 H). ^{13}C NMR ($CDCl_3$, 100.6 MHz) for the mixture of the two invertomers: δ = −0.2 (*min*), 0.0 (*maj*), 17.7 (*min*), 19.7 (*min*), 20.0 (*maj*), 24.7 (*maj*), 31.0 (*min*), 31.9 (*maj*), 46.9 (*maj*), 52.3 (*min*), 79.2 (*min*), 84.6 (*maj*), 99.8 (*min*), 106.2 (*maj*).

(2*R,3*R**)-3-(2-Methylprop-1-enyl)-2-[(trimethysilyl)ethynyl]-aziridine (3h):** This compound was prepared by General Procedure 5, from crotonaldehyde (0.41 mL, 4.90 mmol) in 79% yield (691 mg, 3.86 mmol) as a mixture of two invertomers *maj*/*min* = 66:34. IR (NaCl, film): $\tilde{\nu}$ = 3320, 2950, 2880, 2180, 1640, 840 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) for the mixture of the two invertomers: δ = 0.15 (s, 9 H), 0.65 (m, 1 H *min*), 0.86 (m, 1 H *maj*), 1.68 (d, ^3J = 5.6 Hz, 3 H), 2.16 (m, 1 H *maj*), 2.38 (m, 1 H *min*), 2.58 (m, 1 H *min*), 2.76 (m, 1 H *maj*), 4.98−5.08 (m, 1 H), 5.81 (m, 1 H). ^{13}C NMR ($CDCl_3$, 100.6 MHz) for the mixture of the two invertomers: δ = 0.0, 17.9, 27.3, 40.9 (*maj*), 42.1 (*min*), 46.9 (*maj*), 79.2 (*min*), 85.0 (*min*), 85.6 (*maj*), 104.6 (*min*), 105.3 (*maj*), 129.4.

(2*R,3*R**)-3-Cyclohexyl-*N*-(4-methylphenyl)sulfonyl-2-[(trimethylsilyl)ethynyl]aziridine (5a):** This compound was prepared by General Procedure 4, from *N*-(4-methylphenyl)sulfonamide **4a** (1.33 g, 5.02 mmol) in 39% yield (0.74 g, 1.97 mmol) after flash chromatography, eluting with 20% ethyl acetate/cyclohexane; *trans*/*cis* = 70:30. IR (NaCl, film): $\tilde{\nu}$ = 2930, 2860, 2180, 1600, 810 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.13 (s, 9 H *cis*), 0.33 (s, 9 H *trans*), 0.80−1.80 (m, 11 H), 1.86 (s, 3 H *cis*), 1.93 (s, 3 H *trans*), 2.80 (dd, ^3J = 6.8, 9.6 Hz, 1 H *cis*), 2.90 (d, ^3J = 4.3 Hz, 1 H *trans*), 3.21 (dd, ^3J = 4.3, 7.4 Hz, 1 H *trans*), 3.57 (d, ^3J = 6.8 Hz, 1 H *cis*), 6.75 (d, ^3J = 8.3 Hz, 2 H *cis*), 6.90 (d, ^3J = 8.2 Hz, 2 H *trans*), 7.95 (d, ^3J = 8.3 Hz, 2 H *cis*) 8.20 (d, ^3J = 8.2 Hz, 2 H *trans*). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 0.0, 21.4, 25.8 (*cis*), 25.9, 26.33 (*trans*), 29.7 (*cis*), 30.4 (*trans*), 39.6, 50.1, 52.9, 92.5, 101.2, 128.1, 129.7, 139.1, 144.5. $C_{17}H_{25}NSiSO_2$ (335.54): calcd. C 60.85, H 7.51, N 4.17; found C 61.16, H 7.84, N 3.95.

(2*R,3*R**)-3-Isopropyl-*N*-(4-methylphenyl)sulfonyl-2-[(trimethylsilyl)ethynyl]aziridine (5b):** This compound was prepared by General Procedure 4, from 4-methylbenzenesulfonamide **4b** (1.13 g, 5.02 mmol) in 27% yield (0.45 g, 1.34 mmol) after flash chromatography, eluting with 20% ethyl acetate/cyclohexane; *trans*/*cis* = 70:30. IR (NaCl, film): $\tilde{\nu}$ = 2920, 2190, 1600, 800 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.12 (s, 9 H *cis*), 0.34 (s, 9 H *trans*), 0.68 (d, ^3J = 6.9 Hz, 3 H *trans*), 0.72 (d, ^3J = 6.9 Hz, 3 H *trans*), 0.93 (d, ^3J = 6.9 Hz, 3 H *cis*), 0.97 (d, ^3J = 6.9 Hz, 3 H *cis*), 1.21 (m, 1 H *trans*), 1.45 (m, 1 H *cis*), 1.87 (s, 3 H *cis*), 1.94 (s, 3 H *trans*), 2.68 (dd, ^3J = 6.8, 9.6 Hz, 1 H *cis*), 2.96 (d, ^3J = 4.3 Hz, 1 H *trans*), 3.16 (dd, ^3J = 4.3, 7.8 Hz, 1 H *trans*), 3.58 (d, ^3J = 6.8 Hz, 1 H *cis*), 6.76 (d, ^3J = 8.3 Hz, 2 H *cis*), 6.88 (d, ^3J = 8.1 Hz, 2 H *trans*), 7.94 (d, ^3J = 8.3 Hz, 2 H *cis*), 8.15 (d, ^3J = 8.1 Hz, 2 H *trans*). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = −0.1 (*cis*), 0.0 (*trans*), 18.7 (*cis*), 19.2 (*trans*), 19.7 (*trans*), 20.6 (*cis*), 21.4 (*trans*), 29.2 (*cis*), 30.6, 51.2, 54.0, 92.5, 99.7, 128.1, 129.7, 138.0, 144.2.

(2*S,3*S**)-3-Phenyl-*N*-(phenylsulfonyl)-2-[(trimethylsilyl)ethynyl]-aziridine (5c):** This compound was prepared by General Procedure 4, from benzenesulfonamide **4c** (1.22 g, 4.98 mmol) in 41% yield (0.72 g, 2.03 mmol) after flash chromatography, eluting with 10% ethyl acetate/cyclohexane; *trans*/*cis* = 10:90. IR (NaCl, film): $\tilde{\nu}$ = 3030, 2180, 1590, 1450, 800 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = −0.1 (s, 9 H *cis*), 0.01 (s, 9 H *trans*), 3.20 (d, ^3J = 4.1 Hz, 1 H *trans*), 3.71 (d, ^3J = 7.0 Hz, 1 H *cis*), 4.02 (d, ^3J = 7.0 Hz, 1 H *cis*), 4.22 (d, ^3J = 4.1 Hz, 1 H *trans*), 7.28−8.04 (m, 10 H). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 0.0 (*cis*), 0.29 (*trans*), 46.4, 51.2, 65.8, 91.6, 97.2, 127.9, 129.2, 131.7, 133.9.

(2*R,3*R**)-*N*-[2-Chloro-1-phenyl-4-(trimethylsilyl)but-3-enyl]-benzenesulfonamide (6):** Under nitrogen, a solution of sulfonylimine **4c** (1.22 g, 4.98 mmol) in anhydrous THF (5 mL) was added dropwise at −60 °C to a solution of allenylzinc compound **1** (5.00 mmol). After stirring for 6 h at −60 °C, the solution was quenched with a saturated aqueous NH_4Cl solution and the aqueous layer was extracted with Et_2O (2 × 25 mL). The combined organic layers were washed with water (twice) and brine, dried with anhydrous $MgSO_4$ and then concentrated in vacuo to dryness. The crude product was dissolved in CH_2Cl_2 to precipitate remaining sulfonylimine **4c**. Filtration and removal of the solvent afforded starting sulfonylimine **4c** in 76% yield (0.92 g, 3.76 mmol) as a white solid and chloroamine **6** in 11% yield (0.21 g, 0.54) as a yellow oil; *anti*/*syn* = 10:90. ^1H NMR (C_6D_6/TMS, 400 MHz): δ = 0.09 (s, 9 H *anti*), 0.18 (s, 9 H *syn*), 4.65 (d, ^3J = 5.5 Hz, 1 H *syn*), 4.70 (d, ^3J = 4.2 Hz, 1 H *anti*), 4.98 (m, 1 H), 5.60 (m, 1 H *syn*), 5.83 (m, 1 H *anti*), 6.84−7.78 (m, 10 H). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 0.0, 52.4 (*syn*), 53.0 (*anti*), 62.3, 95.7 (*syn*), 96.6 (*anti*), 98.7 (*anti*), 99.5 (*syn*), 127.5, 128.4, 128.6, 129.1, 129.4, 133.1, 135.9, 140.5.

(2*R,3*S**)-2-Ethynyl-3-phenyl-*N*-(phenylsulfonyl)aziridine (7):** A suspension of chloroamine **6** (200 mg, 0.51 mmol) and KF (42 mg, 0.72 mmol) in a 50:50 DMF/water mixture (20 mL) was stirred overnight at room temperature and then quenched with 1.0 M HCl. The aqueous layer was extracted with Et_2O (2 × 40 mL) and the combined organic layers were treated with 10% aqueous NaOH with stirring for 1 h. The aqueous layer was then extracted with Et_2O (1 × 40 mL) washed with brine, dried with anhydrous $MgSO_4$, and concentrated in vacuo to give *N*-(phenylsulfonyl)aziridine in 69% yield (100 mg, 0.35 mmol) as a yellow oil; *trans*/*cis* = 10:90. IR (NaCl, film): $\tilde{\nu}$ = 3280, 3030, 2920, 2120, 1580, 730 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.10 (d, ^4J = 2.1 Hz, 1 H *cis*), 2.65 (d, ^4J = 2.1 Hz, 1 H *trans*), 3.22 (dd, ^4J = 2.1 Hz, and ^3J = 4.1 Hz, 1 H *trans*), 3.70 (dd, ^4J = 2.1 Hz, and ^3J = 7.0 Hz, 1 H *cis*), 4.05 (d, ^3J = 7.0 Hz, 1 H *cis*), 4.20 (d, ^3J = 4.1 Hz, 1 H *trans*), 7.19−8.00 (m, 10 H). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 35.8, 37.9, 46.3, 48.9, 74.2, 76.2, 128.1, 129.7, 134.4, 137.9.

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