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One-pot synthesis of aziridines from vinyl selenones and variously functionalized primary amines

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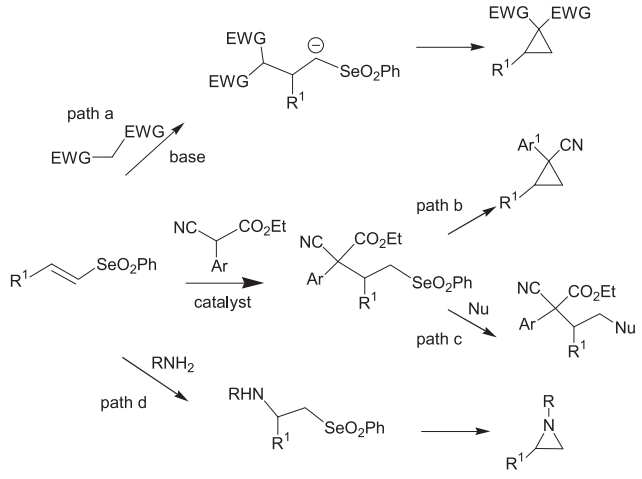
ABSTRACT

Variously substituted aziridines were conveniently prepared by an aza-Michael Initiated Ring Closure (aza-MIRC) reaction starting from vinyl selenones and primary amines, aminoalcohols or diamines. The reactions proceed in very high yields at room temperature in toluene or water. A significant rate acceleration was observed under aqueous conditions.

1. Introduction

Because of their high level of chemical diversity, ready availability, easy handling, and wide efficiency and applicability, organoselenium compounds are considered useful reagents for many synthetic transformations.[1] Although their chemical structure is closely related to that of the homologous sulfur analogous, the reactivity often presents marked differences.[1] An illustrative example is that of vinyl selenones. The electron-withdrawing effect combined with the excellent nucleofugal ability of the phenylselenonyl function makes the vinyl selenones useful substrates for interesting transformations, which have no parallel in sulfone chemistry. A classic example is the *one-pot* synthesis of cyclopropanes by treatment of vinyl selenones with enolates, a Michael Initiated Ring Closure reaction (MIRC) in which the phenylselenonyl substituent plays a dual role as activating group in the conjugate addition and as leaving group in the following cyclization (Scheme 1, path a).[2] Recently, as part of our study on novel synthetic applications of vinyl selenones, we have developed organocatalyzed cascade reactions for the enantioselective synthesis of highly functionalized cyclopropanes[3] (Scheme 1, path b) as well as of other useful polyfunctional compounds containing quaternary stereocentres[4] (Scheme 1, path c). We now report the *one-pot* synthesis of aziridines from vinyl selenones by an aza-Michael Initiated Ring Closure reaction (aza-MIRC) (Scheme 1, path d).



Scheme 1. Some useful conversions involving vinyl selenones.

Multistep syntheses of aziridines, based on ring closure reactions starting from β-aminoselenides are disposable in the literature,[5] but examples of direct transformation of vinyl selenones through tandem Michael addition–intramolecular nucleophilic

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substitution reactions are only sporadic.[6] As a consequence of the great synthetic and biological interest for the aziridine skeleton[7] and considering the recent interest for MIRC-type approaches to this ring,[8] we decided to study the scope and limitations of this *one-pot* protocol respect to amine and selenone structural variations. The feasibility of the process under aqueous conditions[9] has also been investigated.

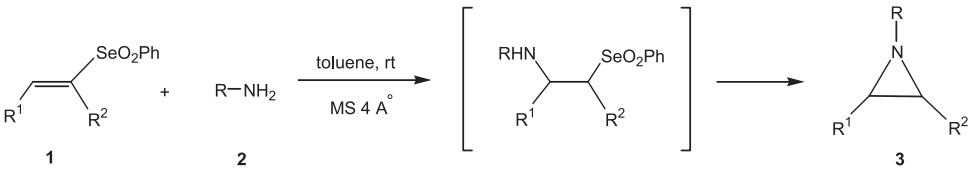
2. Results and discussion

Preliminary experiments were carried out on vinyl selenone **1A** and benzylamine **2a** at room temperature in different organic solvents, such as toluene, CH_2Cl_2, and CH_3CN. The best results were obtained in toluene in the presence of molecular sieves.[10] The aziridine **3aA** was formed at room temperature with a good yield and an acceptable reaction time (Table 1, entry 1). 2 equiv of **2a** were used to effect the aza-Michael addition and the trapping of the benzenseleninic acid ($PhSeO_2H$) released during the cyclization step. Harsh reaction conditions or catalysts, usually employed with other Michael acceptors,[11] were not required to promote the initial amine addition.

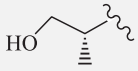
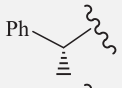
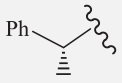
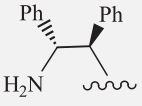
chromatography on a pad of silica gel. With regard to Michael acceptors, the α,β-substituted vinyl selenone **1E** is less reactive than the β-substituted **1A**–**D** and the unsubstituted **1F**. Functionalized amines containing more than one nucleophilic group, such as the diamines **2d** and **2e** or the aminoalcohols **2f** and **2g**, react, chemoselectively, affording the expected aziridines in high to nearly quantitative yields (Table 1, entries 4–7). In order to access to non-racemic aziridines the (*R*)-2-aminopropan-1-ol **2j**, the (*R*)-1-phenylethylamine **2k**, and the (1*R*,2*R*)-1,2-diphenylethane-1,2-diamine **2l** were employed. The aziridines **3jA** and **3kA** were formed from **2j** or **2k** and **1A** in good yields as mixtures of two enantiomerically pure diastereoisomers in 1:1 and 3:1 ratio, respectively (Table 1, entries 15 and 16). The diastereoisomers could be easily separated by flash chromatography. On the contrary the reaction of **2l** with **1A** was very sluggish and even after prolonged reaction times only traces of the diastereomeric aziridines **3lA** were present in the reaction mixture (Table 1, entry 18). The reaction of **2k** with the sterically unhindered selenone **1F** went to completion within only 1 h (Table 1, entry 17).

The reactivity of aromatic amines, such as aniline or the more nucleophilic *p*-methoxyaniline, was also investigated.

Table 1
Reactions of amines **2a**–**l** with the vinyl selenones **1A**–**F**



1 2 3

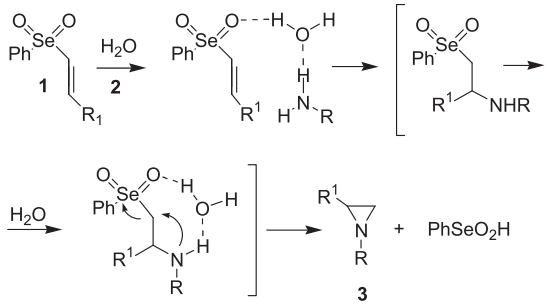
Entry	R^1	R^2		R		Time (h)		Yield (%)
1	Ph	H	**1A**	CH_2Ph	**2a**	24	**3aA**	80
2	Ph	H	**1A**	$(CH_2)_3CH_3$	**2b**	24	**3bA**	97[a]
3	Ph	H	**1A**	$CH_2CH{=}CH_2$	**2c**	24	**3cA**	94
4	Ph	H	**1A**	$(CH_2)_4NH_2$	**2d**	24	**3dA**	88
5	Ph	H	**1A**	$(CH_2)_2NH_2$	**2e**	24	**3eA**	99
6	Ph	H	**1A**	$(CH_2)_5OH$	**2f**	24	**3fA**	99
7	Ph	H	**1A**	$(CH_2)_2OH$	**2g**	48	**3gA**	86
8	Ph	H	**1A**	$CH_2CO_2CH_3$	**2h**	110	**3hA**	40[b]
9	Ph	H	**1A**	$(CH_2)_2CO_2CH_2CH_3$	**2i**	72	**3iA**	82
10	*p*-Me–C_6H_4	H	**1B**	CH_2Ph	**2a**	60	**3aB**	75
11	*p*-Cl–C_6H_4	H	**1C**	CH_2Ph	**2a**	72	**3aC**	43
12	$(CH_2)_5CH_3$	H	**1D**	CH_2Ph	**2a**	48	**3aD**	83
13	$(CH_2)_5CH_3$	H	**1D**	$(CH_2)_3CH_3$	**2b**	24	**3bD**	87[a]
14	$-(CH_2)_3-$		**1E**	$PhCH_2$	**2a**	120	**3aE**	50
15	Ph	H	**1A**		**2j**	48	**3jA**	82[c] d.r. 50:50
16	Ph	H	**1A**		**2k**	60	**3kA**	54[c] d.r. 75:25
17	H	H	**1F**		**2k**	1	**3kF**	85
18	Ph	H	**1A**		**2l**	120	**3lA**	traces

[a] 3.5 equiv of $BuNH_2$ were used.
[b] The reaction was carried out in dichloromethane.
[c] Combined yield of the chromatographically separated diastereoisomers. Diastereomeric ratios were determined by ^1H NMR of the crude product and confirmed after chromatographic separation.

These reaction conditions proved to be effective for the conversion of the variously substituted vinyl selenones **1A**–**F** with a wide range of primary amines. As shown in Table 1, with few exceptions, the aziridines **3** were obtained in high yields after evaporation of the solvent and purification by flash

Unfortunately, only starting materials were recovered from the reactions even after prolonged reaction times, heating or addition of promoters, such as amberlyst,[11a,b] CAN[11c,d] or DBU.[11e] These results are consistent with the lower nucleophilicity of the aromatic amines in comparison with the aliphatic ones.

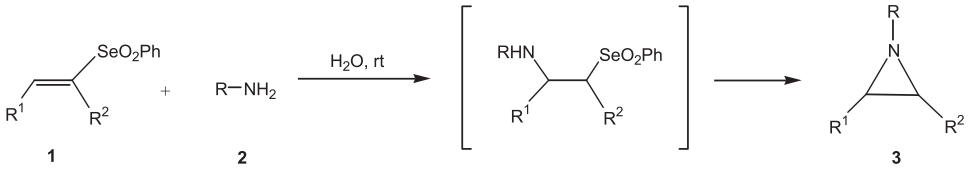
Finally we decided to test the feasibility of the process in aqueous suspension or emulsion, without any catalyst or organic co-solvent. Recently the use of water as a medium for organic reactions[9] has attracted much attention not only because it is environmentally friendly, but also because exhibits a unique reactivity that can not be obtained with the conventional organic solvents. Generally, conjugate additions to selenones have been carried out in apolar or polar aprotic solvents[1,6] but, to the best of our knowledge, not in pure water. The results of the experiments are collected in Table 2. Water significantly improved the process, in fact all the aziridines were obtained in good to excellent yields in shortened reaction times. As a significant example, the aziridines **3lA**, present only in traces when toluene was used as the solvent, could be isolated in high yield (Table 2, entry 10). The increase in rate of the aqueous over the solvent-free reaction of **2a** with **1A** (Table 2, entries 1 and 2) suggests that water plays an active role on promoting the addition and/or the cyclization step and the rate acceleration is not only a consequence of the increased effective concentration of the poorly soluble reacting species.[9a] It seems reasonable that, as proposed for other aza-Michael additions to activated alkenes,[12] water acts both as H-bond donor with the selenone group, increasing the electrophilic character of the β-carbon atom in **1**, and as H-bond acceptor with the amine **2**, increasing its nucleophilic properties. Similar H-bonding between water and the β-aminoselenone intermediate should also have beneficial effects on the following cyclization step (Scheme 2). More generally, water may be responsible for a faster proton transfer.[12d]

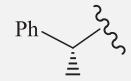
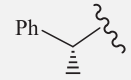
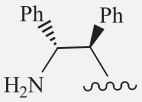
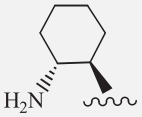


Scheme 2. Possible role of water during the aza-Michael and the cyclization step.

Finally, the observation that aziridine formation is favored in a protic solvent prompted us to investigate the use of chiral alcohols as catalysts for an asymmetric process. The aziridines were obtained in good yields, but, unfortunately, with very poor asymmetric induction. For example, the experiments carried out with the selenones **1A** or **1D** and the amine **2a** in the presence of catalytic amounts (20 mol %) of (*R*)-BINOL in toluene gave the aziridines **3aA** and **3aD** with 76% yield, 18% *ee* and 92% yield, 10% *ee*, respectively. Similar results were obtained using stoichiometric amounts of (*R*)-BINOL.

Table 2
Reactions of amines **2** with vinyl selenones **1** in water



Entry	R^1	R^2		R		Time (h)		Yield (%)
1	Ph	H	**1A**	CH_2Ph	**2a**	3	**3aA**	91
2	Ph	H	**1A**	CH_2Ph	**2a**	7	**3aA**	72[a]
3	Ph	H	**1A**	$(CH_2)_3CH_3$	**2b**	5	**3bA**	75[b]
4	Ph	H	**1A**	$CH_2CH{=}CH_2$	**2c**	5	**3cA**	63
5	$CH_3(CH_2)_5$	H	**1D**	CH_2Ph	**2a**	5	**3aD**	97
6	$CH_3(CH_2)_5$	H	**1D**	$(CH_2)_3CH_3$	**2b**	5	**3bD**	80[b]
7	$(CH_2)_3$		**1E**	CH_2Ph	**2a**	20	**3aE**	99
8	Ph	H	**1A**		**2k**	40	**3kA**	76[c,d] d.r. 65:35
9	$CH_3(CH_2)_5$	H	**1D**		**2k**	72	**3kD**	70[c,d] d.r. 50:50
10	Ph	H	**1A**		**2l**	72	**3lA**	82[c,d] d.r. 60:40
11	Ph	H	**1A**		**2m**	22	**3mA**	61[c,d] d.r. 60:40

[a] Reaction carried out under solvent-free condition, with 4 equiv of $PhCH_2NH_2$.
[b] 3.5 equiv of $BuNH_2$ were used.
[c] 1.1 equiv of the chiral amine and 2 equiv of Et_3N have been used.
[d] Combined yield of the chromatographically separated diastereoisomers. Diastereomeric ratios were determined by ^1H NMR of the crude product and confirmed after chromatographic separation.

3. Conclusions

In conclusion a tandem Michael addition–intramolecular nucleophilic substitution process for the preparation of aziridines from vinyl selenones and primary amines has been described. Variously functionalized aziridines have been generated in good to excellent yields. Using a chiral amine it is possible to produce

a couple of optically active, easily separable diastereomeric aziridines. The process has been conveniently carried out under aqueous conditions with shortened reaction times. The reported aziridination confirms the potential of vinyl selenones as valuable substrates for sequential or domino reactions. Further investigations in this field are currently underway in our laboratories.

4. Experimental section

4.1. General

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 400 and 100 MHz, respectively, on a Bruker Avance-DRX 400 instrument. The chemical shifts (δ) are referred to TMS as internal standard (^{1}H NMR) and the residual signals of the solvent ($CDCl_3$, 77.0 ppm for ^{13}C NMR). Coupling constants are given in hertz. The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; m, multiplet; br, broad signal. GC–MS analyses were carried out with an HP 6890 gas chromatograph (HP-5MS capillary column, 30 m, I.D. 0.25 mm, film 0.25 μm) equipped with an HP 5973 Mass Selective Detector at an ionizing voltage of 70 eV. FTIR spectra were recorded with a Jasco model 410 spectrometer equipped with a Pike Technologies Horizontal ATR cell. Optical rotations were measured with a Jasco DIP-1000 digital polarimeter, the concentrations (c) are reported in gram per 100 mL. Elemental analyses were carried out on a Carlo Erba 1106 Elemental analyzer. The melting points are uncorrected. Thin layer chromatography (TLC) was performed on silica gel 60 F_{254} (Merck) on aluminum sheets. Purification of reaction products was carried out by flash chromatography on silica gel Merck 60 (230–400 mesh).

4.2. Starting materials

Commercial grade solvents and reagents were used without further purification. The starting amines **2a**–**i** and the chiral amines **2j** (97% *ee*), **2l** (96% *ee*), **2k** (98% *ee*), and **2m** (99% *ee*) were purchased from Aldrich Inc. According to literature procedures[2b,3,4] the vinyl selenones were prepared from the corresponding commercial or easily available vinyl bromides by nucleophilic vinylic substitution followed by oxidation with an excess of *m*-CPBA and K_2HPO_4 in MeOH (**1A**–**C**) or from alkenes by a sequence of selenobromination and dehydrobromination[13,14] followed by oxidation with an excess of *m*-CPBA in dichloromethane (**1D**–**E**). **1F** was prepared by oxidation of the corresponding easily accessible selenide[15] with an excess of *m*-CPBA in dichloromethane. Physical and spectral data of (*E*)-vinyl selenones **1A**–**D** were previously reported in the literature.[2b,3] Physical and spectral data of **1E**, **F** are described below.

*4.2.1. Cyclopent-1-enyl phenyl selenone (**1E**).* Yield: (190 mg, 30%). White solid, mp 88–91 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=8.03–7.96 (m, 2H; CH), 7.76–7.62 (m, 3H; CH), 6.95–6.85 (m, 1H; CH), 2.79–2.70 (m, 2H; CH_2), 2.68–2.61 (m, 2H; CH_2), 2.15 (quint, 2H; J=7.7 Hz, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ=144.9, 144.8, 141.1, 134.1, 130.2 (2C), 127.0 (2C), 32.6, 30.8, 23.3. IR (ATR): ν_{max} 3066, 2930, 1611, 1444, 1066, 930, 877 cm^{-1}. Anal. Calcd for $C_{11}H_{12}O_2Se$: C, 51.78; H, 4.74; found: C, 51.83; H, 4.86.

*4.2.2. Vinyl phenyl selenone (**1F**).* Yield: (450 mg, 60%). White solid, mp 97–102 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=8.08–7.95 (m, 2H; CH), 7.76–7.70 (m, 1H; CH), 7.70–7.63 (m, 2H; CH), 7.03 (dd, 1H; J=9.1, 16.5 Hz, CH), 6.75 (dd, 1H; J=2.0, 16.5 Hz, CH_2), 6.47 (dd, 1H; J=2.0, 9.1 Hz, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ=141.2, 138.9, 134.3, 131.2, 130.3 (2C), 126.9 (2C). IR (ATR): ν_{max} 3089, 3042, 1700, 1447, 1370, 1220, 1065, 981, 928, 882 cm^{-1}. Anal. Calcd for $C_8H_8O_2Se$: C, 44.67; H, 3.75; found: C, 44.93; H, 3.69.

4.3. General procedure for the *one-pot* synthesis of the aziridines 3 in toluene

In an ordinary vial equipped with a Teflon-coated stir bar, vinyl selenones **1A**–**F** (0.2 mmol) and amines **2a**–**l** (0.4 mmol, 2 equiv) were dissolved in undistilled toluene (0.4 mL) with 20 mg of 4 Å MS under an air atmosphere. The resulting mixtures were stirred at room temperature for the time reported in Table 1. The reaction mixtures were directly poured into the column for the flash chromatographic purification (hexane/EtOAc or dichloromethane/MeOH as eluant). Yields and diastereomeric ratios of the aziridines **3** are reported in Table 1.

4.4. General procedure for the *one-pot* synthesis of the aziridines 3 in water

In an ordinary vial equipped with a Teflon-coated stir bar, the amines **2a**–**c** (0.4 mmol, 2 equiv) or the chiral amines **2k**–**m** (0.22 mmol, 1.1 equiv) were added to the suspension or emulsion of the vinyl selenones **1A**, **D**–**E** (0.2 mmol) in distilled water (0.4 mL). When chiral amines were used, Et_3N (0.4 mmol, 2 equiv) was also added. The resulting mixtures were vigorously stirred at room temperature for the time reported in Table 2. The reaction mixtures were extracted with dichloromethane and the organic layers were dried over Na_2SO_4 and evaporated. The aziridines were purified by flash chromatography. Yields and diastereomeric ratios of the aziridines **3** are reported in Table 2.

Spectral data of aziridines **3aA**,[16] **3bA**,[17] **3cA**,[18] **3aB**,[19] **3aC**,[18] **3aE**[20] are identical to those previously described in the literature. New compounds were characterized by ^{1}H NMR, ^{13}C NMR, IR, and GC–MS. It is interesting to point out that ^{1}H NMR spectra ($CDCl_3$) of the 1,2-disubstituted aziridines exhibit a typical trend for the two protons at the C3 position consisting in two doublets with $^3J\cong$3.4 Hz and $^3J\cong$6.5 Hz, respectively, and an apparent ^2J=0 Hz.[16–19] Also the ring protons in **3kF** have no apparent geminal coupling constants, as already reported for a similar aziridine.[21] Physical and spectral data of aziridines **3aD**, **3dA**, **3eA**, **3fA**, **3gA**, **3hA**, **3iA**, **3bD**, **3jA**, **3kA**, **3kF**, **3lA**, **3kD**, **3mA** are reported below.

*4.4.1. 4-(2-Phenyl-1-aziridinyl)butylamine (**3dA**).* Yield: (33.6 mg, 88%). Viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.34–7.19 (m, 5H; CH), 2.72 (t, 2H; J=6.8 Hz, CH_2), 2.53 (dt, 1H; J=6.8, 11.6 Hz, CH_2), 2.37 (dt, 1H; J=6.8, 11.6 Hz, CH_2), 2.33 (dd, 1H; J=3.3, 6.4 Hz, CH), 2.19 (br s, 2H; NH_2), 1.92 (d, 1H; J=3.3 Hz, CH_2), 1.71–1.50 (m, 5H; CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ=140.3, 128.3 (2C), 126.8, 126.1 (2C), 61.5, 42.0, 41.3, 37.8, 31.4, 27.2. IR (ATR): ν_{max} 3357, 3062, 3032, 2931, 2849, 1640, 1563, 1494, 1313, 1203, 1086, 1061, 1027, 819 cm^{-1}. MS (70 eV, EI): m/z (%): 189 (1) [M$^+$−1], 172 (18), 160 (14), 147 (31), 146 (44), 134 (62), 132 (60), 118 (73), 104 (43), 103 (20), 91 (100), 86 (28), 77 (23), 72 (32), 70 (30), 65 (21), 57 (16), 51 (11). Anal. Calcd for $C_{12}H_{18}N_2$: C, 75.74; H, 9.53; N, 14.72; found: C, 76.05; H, 9.34; N, 14.61.

*4.4.2. 2-(2-Phenyl-1-aziridinyl)ethylamine (**3eA**).* Yield: (32.2 mg, 99%). Oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.33–7.20 (m, 5H; CH), 3.55 (br s, 2H; NH_2), 2.91 (t, 2H; J=5.9 Hz, CH_2), 2.55 (dt, 1H; J=5.9, 11.9 Hz, CH_2), 2.50 (dt, 1H; J=5.9, 11.9 Hz, CH_2), 2.39 (dd, 1H; J=3.3, 6.5 Hz, CH), 1.92 (d, 1H; J=3.3 Hz, CH_2), 1.73 (d, 1H; J=6.5 Hz, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ=140.0, 128.3 (2C), 126.9, 126.1 (2C), 62.5, 41.2, 41.0, 37.6. IR (ATR): ν_{max} 3352,

3063, 2928, 2847, 1648, 1575, 1497, 1455, 1307, 1204, 1088, 1027, 800 cm^{-1}. MS (70 eV, EI): *m*/*z* (%): 162 (10) [M^+], 161 (65), 132 (100), 120 (94), 118 (83), 105 (46), 104 (63), 103 (32), 91 (97), 77 (33), 65 (23), 51 (19). Anal. Calcd for $C_{10}H_{14}N_2$: C, 74.03; H, 8.70; N, 17.27; found: C, 74.17; H, 8.89; N, 16.94.

*4.4.3. 5-(2-Phenyl-1-aziridinyl)-1-pentanol (**3fA**).* Yield: (40.8 mg, 99%). Oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.35–7.21 (m, 5H; CH), 3.63 (t, 2H; *J*=6.4 Hz, CH_2), 2.52 (dt, 1H; *J*=7.0, 11.5 Hz, CH_2), 2.39 (dt, 1H; *J*=7.0, 11.5 Hz, CH_2), 2.34 (dd, 1H; *J*=3.4, 6.5 Hz, CH), 2.10 (br s, 1H; OH), 1.93 (d, 1H; *J*=3.4 Hz, CH_2), 1.74–1.54 (m, 5H; CH_2), 1.53–1.40 (m, 2H; CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ=140.2, 128.3 (2C), 126.8, 126.2 (2C), 62.6, 61.6, 41.3, 37.7, 32.5, 29.4, 23.5. IR (ATR): ν_{max} 3310, 2922, 2862, 1728, 1493, 1454, 1053 cm^{-1}. MS (70 eV, EI): *m*/*z* (%): 205 (21) [M^+], 204 (79), 188 (18), 174 (14), 160 (23), 146 (21), 132 (100), 128 (56), 118 (78), 104 (21), 91 (93), 84 (13), 77 (23), 65 (22), 51 (11). Anal. Calcd for $C_{13}H_{19}NO$: C, 76.06; H, 9.33; N, 6.82; found: C, 76.51; H, 9.67; N, 6.53.

*4.4.4. 2-(2-Phenyl-1-aziridinyl)ethanol (**3gA**).* Yield: (28.2 mg, 86%). Oil, slightly impure. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.40–7.19 (m, 5H; CH), 3.80 (t, 2H; *J*=5.1 Hz, CH_2), 3.6 (br s, 1H; OH), 2.65 (dt, 1H; *J*=5.1, 12.1 Hz, CH_2), 2.61 (dt, 1H; *J*=5.1, 12.1 Hz, CH_2), 2.47 (dd, 1H; *J*=3.4, 6.5 Hz, CH), 1.97 (d, 1H; *J*=3.4 Hz, CH_2), 1.79 (d, 1H; *J*=6.5 Hz, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ=139.9, 128.3 (2C), 127.0, 126.1 (2C), 62.7, 61.9, 41.0, 37.4. IR (ATR): ν_{max} 3352, 2935, 2846, 1723, 1606, 1497, 1452, 1261, 1064, 928 cm^{-1}. MS (70 eV, EI): *m*/*z* (%): 163 (30) [M^+], 162 (100), 144 (7), 132 (24), 119 (21), 118 (71), 117 (25), 105 (22), 104 (20), 103 (20), 91 (82), 77 (26), 65 (23), 51 (17).

*4.4.5. Methyl (2-phenyl-1-aziridinyl)acetate (**3hA**).* Yield: (15.4 mg, 40%). Oil, slightly impure. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.45–7.20 (m, 5H; CH), 3.75 (s, 3H; OMe), 3.35 (d, 1H; *J*=16.1 Hz, CH_2), 3.22 (d, 1H; *J*=16.1 Hz, CH_2), 2.50 (dd, 1H; *J*=3.6, 6.5 Hz, CH), 2.10 (d, 1H; *J*=3.6 Hz, CH_2), 1.81 (d, 1H; *J*=6.5 Hz, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ=170.6, 139.1, 128.3 (2C), 127.1, 126.3 (2C), 61.5, 51.9, 41.5, 37.6. IR (ATR): ν_{max} 3066, 2923, 2852, 1740, 1476, 1445, 1331, 1152, 1079, 1019 cm^{-1}. MS (70 eV, EI): *m*/*z* (%): 191 (18) [M^+], 190 (100), 132 (28), 130 (19), 118 (20), 103 (12), 91 (70), 77 (13).

*4.4.6. Ethyl 3-(2-phenyl-1-aziridinyl)propanoate (**3iA**).* Yield: (36.0 mg, 82%). Oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.34–7.20 (m, 5H; CH), 4.15 (dq, 1H; *J*=7.1, 10.8 Hz, CH_2), 4.10 (dq, 1H; *J*=7.1, 10.8 Hz, CH_2), 2.88–2.78 (m, 1H; CH_2), 2.72–2.61 (m, 3H; CH_2), 2.42 (dd, 1H; *J*=3.4, 6.5 Hz, CH), 1.92 (d, 1H; *J*=3.4 Hz, CH_2), 1.76 (d, 1H; *J*=6.5 Hz, CH_2), 1.23 (t, 3H; *J*=7.1 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ=172.3, 140.0, 128.2 (2C), 126.9, 126.1 (2C), 60.4, 56.5, 41.3, 37.7, 35.0, 14.1. IR (ATR): ν_{max} 3065, 2925, 1734, 1497, 1451, 1376, 1186, 1030 cm^{-1}. MS (70 eV, EI): *m*/*z* (%): 219 (29) [M+], 218 (100), 190 (51), 174 (17), 132 (42), 130 (19), 118 (65), 117 (23), 104 (14), 91 (81), 77 (17), 65 (16). Anal. Calcd for $C_{13}H_{17}NO_2$: C, 71.21; H, 7.81; N, 6.39; found: C, 71.53; H, 7.96; N, 6.28.

*4.4.7. 1-Benzyl-2-hexylaziridine (**3aD**).* Yield: (42.1 mg, 97%). Viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.40–7.21 (m, 5H; CH), 3.52 (d, 1H; *J*=13.2 Hz, CH_2), 3.35 (d, 1H; *J*=13.2 Hz, CH_2), 1.63 (d, 1H; *J*=3.2 Hz, CH_2), 1.46–1.15 (m, 12H; CH, CH_2), 0.89 (t, 3H; *J*=7.1 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ=139.4, 128.2 (2C), 128.1 (2C), 126.9, 65.0, 39.8, 34.0, 33.4, 33.0, 29.0, 27.4, 22.5, 14.0. IR (ATR): ν_{max} 3033, 2928, 2856, 1729, 1495, 1453, 1380, 1355, 1278, 1164, 1069, 1028 cm^{-1}. MS (70 eV, EI): *m*/*z* (%): 217 (5) [M^+], 216 (20), 188 (23), 174 (41), 160 (76), 146 (66), 132 (23), 126 (28), 120 (46), 106 (19), 91 (100), 84 (17), 77 (12), 65 (33), 55 (46). Anal. Calcd for $C_{15}H_{23}N$: C, 82.89; H, 10.67; N, 6.44; found: C, 82.96; H, 10.91; N, 6.13.

*4.4.8. 1-Butyl-2-hexylaziridine (**3bD**).* Yield: (32.0 mg, 87%). Oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=2.30 (ddd, 1H; *J*=6.6, 8.5, 11.5 Hz, CH_2), 2.11 (ddd, 1H; *J*=6.0, 8.3, 11.5 Hz, CH_2), 1.63–1.19 (m, 15H, CH, CH_2), 1.49 (d, 1H; *J*=3.4 Hz, CH_2), 1.17 (d, 1H; *J*=6.3 Hz, CH_2), 0.92 (t, 3H; *J*=7.3 Hz, CH_3), 0.89 (t, 3H; *J*=7.0 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ=61.3, 39.5, 33.8, 33.2, 32.0, 31.8, 29.1, 27.5, 22.6, 20.5, 14.0 (2C). IR (ATR): ν_{max} 2962, 2922, 2865, 1465, 1378, 1079 cm^{-1}. MS (70 eV, EI): *m*/*z* (%): 183 (1) [M^+], 182 (5), 168 (5), 154 (14), 140 (86), 126 (79), 112 (30), 98 (100), 86 (24), 84 (55), 70 (70), 57 (39), 55 (29). Anal. Calcd for $C_{12}H_{25}N$: C, 78.62; H, 13.74; N, 7.64; found: C, 78.84; H, 13.89; N, 7.27.

*4.4.9. (2R)-2-(2-Phenyl-1-aziridinyl)-1-propanol (**3jA**).* Yield: (14.7 mg, 41%). First diastereoisomer: oil. $[\alpha]_D^{17}$ −41.1 (*c* 0.92, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.33–7.21 (m, 5H; CH), 3.72 (dd, 1H; *J*=4.1, 11.1 Hz, CH_2), 3.62 (dd, 1H; *J*=5.2, 11.1 Hz, CH_2), 2.56 (dd, 1H; *J*=3.4, 6.6 Hz, CH), 2.20 (br s, 1H; OH), 1.95 (d, 1H; *J*=3.4 Hz, CH_2), 1.87–1.78 (m, 1H; CH), 1.77 (d, 1H; *J*=6.6 Hz, CH_2), 1.20 (d, 3H; *J*=6.5 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ=139.9, 128.4 (2C), 127.0, 126.2 (2C), 67.0, 66.1, 41.5, 34.9, 16.3. IR (ATR): ν_{max} 3342, 3039, 2975, 2847, 1727, 1607, 1499, 1448, 1373, 1263, 1203, 1169, 1052, 992 cm^{-1}. MS (70 eV, EI): *m*/*z* (%): 177 (13) [M^+], 176 (89), 146 (22), 130 (6), 120 (15), 118 (52), 104 (15), 91 (100), 86 (10), 77 (16), 65 (10), 51 (9). Anal. Calcd for $C_{11}H_{15}NO$: C, 74.54; H, 8.53; N, 7.90; found: C, 74.73; H, 8.69; N, 7.65. (14.5 mg, 41%). Second diastereoisomer: oil. $[\alpha]_D^{18}$ +15.3 (*c* 0.85, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.40–7.22 (m, 5H; CH), 3.77 (dd, 1H; *J*=4.1, 11.0 Hz, CH_2), 3.66 (dd, 1H; *J*=4.6, 11.0 Hz, CH_2), 2.47 (dd, 1H; *J*=3.4, 6.5 Hz, CH), 2.10 (br s, 1H; OH), 1.96 (d, 1H; *J*=3.4 Hz, CH_2), 1.88 (d, 1H; *J*=6.5 Hz, CH_2), 1.85–1.76 (m, 1H; CH), 1.22 (d, 3H; *J*=6.4 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ=140.1, 128.3 (2C), 126.9, 126.3 (2C), 66.6, 66.3, 38.8, 37.4, 16.8. IR (ATR): ν_{max} 3353, 3040, 2964, 1727, 1457, 1263, 1102, 1050. cm^{-1}. MS (70 eV, EI): *m*/*z* (%): 177 (18) [M^+], 176 (100), 146 (22), 130 (6), 120 (20), 118 (62), 104 (17), 91 (95), 86 (5), 77 (16), 65 (11), 51 (8). Anal. Calcd for $C_{11}H_{15}NO$: C, 74.54; H, 8.53; N, 7.90; found: C, 74.91; H, 8.75; N, 7.47.

*4.4.10. 2-Phenyl-1-[(1R)-1-phenylethyl]aziridine (**3kA**).* Yield: (22.1 mg, 49.5%). First diastereoisomer: oil. $[\alpha]_D^{19}$ +78.9 (*c* 0.92, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.52–7.44 (m, 2H; CH), 7.42–7.23 (m, 8H; CH), 2.70 (q, 1H; *J*=6.5 Hz, CH), 2.57 (dd, 1H; *J*=3.3, 6.5 Hz, CH), 1.87 (d, 1H; *J*=3.3 Hz, CH_2), 1.72 (d, 1H; *J*=6.5 Hz, CH_2), 1.51 (d, 3H; *J*=6.5 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ=144.7, 140.6, 128.3 (2C), 128.2 (2C), 127.0, 126.9 (2C), 126.8, 126.4 (2C), 70.3, 41.6, 37.2, 23.6. IR (ATR): ν_{max} 3025, 2973, 1604, 1494, 1448, 1350, 1218, 1162, 1093, 1029, 934 cm^{-1}. MS (70 eV, EI): *m*/*z* (%): 223 (4) [M^+], 222 (8) 118 (100), 105 (51), 103 (24), 91 (97), 79 (23), 77 (39), 65 (23), 51 (18). Anal. Calcd for $C_{16}H_{17}N$: C, 86.05; H, 7.67; N, 6.27; found: C, 86.16; H, 7.78; N, 6.06. (11.9 mg, 26.5%). Second diastereoisomer: oil. $[\alpha]_D^{19}$ −106.8 (*c* 0.84, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.41–7.35 (m, 2H; CH), 7.32–7.17 (m, 8H; CH), 2.71 (q, 1H; *J*=6.6 Hz, CH), 2.43 (dd, 1H; *J*=3.4, 6.5 Hz, CH), 2.07 (d, 1H; *J*=3.4 Hz, CH_2), 1.86 (d, 1H; *J*=6.5 Hz, CH_2), 1.52 (d, 3H; *J*=6.6 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ=144. 7, 140.1, 128.2 (2C), 128.1 (2C), 126.8, 126.7 (3C), 126.3 (2C), 70.4, 40.9, 37.5, 23.4. IR (ATR): ν_{max} 3059, 2970, 1603, 1494, 1448, 1369, 1308, 1212, 1153, 1091, 1069, 1028, 933 cm^{-1}. MS (70 eV, EI): *m*/*z* (%): 223 (4) [M^+], 222 (9), 118 (100), 105 (50), 103 (25), 91 (96), 79 (22), 77 (39), 65 (23), 51 (18). Anal. Calcd for $C_{16}H_{17}N$: C, 86.05; H, 7.67; N, 6.27; found: C, 86.17; H, 7.73; N, 6.10.

*4.4.11. 1-[(1R)-1-Phenylethyl]aziridine (**3kF**).* Yield: (25.1 mg, 85%). Oil. $[\alpha]_D^{20}$ +77.6 (*c* 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.42–7.25 (m, 5H; CH), 2.33 (q, 1H; *J*=6.5 Hz, CH), 1.93 (dd,

1H; J=4.0, 5.7 Hz, CH_2), 1.71 (dd, 1H; J=4.0, 5.7 Hz, CH_2), 1.47 (d, 3H; J=6.5 Hz, CH_3), 1.32 (dd, 1H; J=4.0, 7.1 Hz, CH_2), 1.18 (dd, 1H; J=4.0, 7.1 Hz, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ=144.7, 128.3 (2C), 126.9, 126.7 (2C), 70.6, 27.8, 26.9, 23.3. IR (ATR): ν_{max} 3062, 2972, 1493, 1449, 1352, 1264, 1171, 1065, 943 cm^{-1}. MS (70 eV, EI): m/z (%): 147 (2) [M$^+$], 146 (2), 132 (15), 105 (100), 103 (12), 88 (10), 79 (14), 77 (21), 58 (9), 57 (8), 51 (9). Anal. Calcd for $C_{10}H_{13}N$: C, 81.59; H, 8.90; N, 9.51; found: C, 81.77; H, 9.01; N, 9.22.

*4.4.12. [(1R,2R)-1,2-Diphenyl-2-(2-phenyl-1-aziridinyl) ethyl]amine (**3lA**).* Yield: (30.8 mg, 49%). First diastereoisomer: viscous oil. $[\alpha]_D^{19}$ −31.8 (c 0.55, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.38−7.05 (m, 15H; CH), 4.27 (d, 1H; J=6.0 Hz, CH), 2.97 (d, 1H; J=6.0 Hz, CH), 2.51 (dd, 1H; J=3.4, 6.5 Hz, CH), 1.96 (br s, 2H; NH_2), 1.80 (d, 1H; J=3.4 Hz, CH_2), 1.57 (d, 1H; J=6.5 Hz, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ=142.8, 141.2, 140.2, 128.2 (2C), 128.1 (2C), 127.8 (2C), 127.7 (2C), 127.3 (2C), 127.1, 126.9, 126.8, 126.1 (2C), 80.9, 62.5, 44.6, 35.5. IR (ATR): ν_{max} 3380, 3029, 1718, 1602, 1494, 1452, 1264, 1094, 1028 cm^{-1}. Anal. Calcd for $C_{22}H_{22}N_2$: C, 84.04; H, 7.05; N, 8.91; found: C, 84.36; H, 7.23; N, 8.41. (20.7 mg, 33%). Second diastereoisomer: viscous oil. $[\alpha]_D^{19}$ +58.7 (c 0.77, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.34−7.02 (m, 15H; CH), 4.31 (d, 1H; J=5.3 Hz, CH), 2.99 (d, 1H; J=5.3 Hz, CH), 2.26 (dd, 1H; J=3.5, 6.5 Hz, CH), 2.07 (br s, 2H; NH_2), 2.00 (d, 1H; J=3.5 Hz, CH_2), 1.72 (d, 1H; J=6.5 Hz, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ=143.1, 141.0, 140.2, 128.1 (2C), 128.0 (2C), 127.9 (2C), 127.8 (2C), 127.3 (2C), 127.0, 126.9, 126.6, 126.1 (2C), 81.0, 62.4, 41.5, 37.8. IR (ATR): ν_{max} 3404, 3027, 1715, 1603, 1495, 1452, 1204, 1064, 1021 cm^{-1}. Anal. Calcd for $C_{22}H_{22}N_2$: C, 84.04; H, 7.05; N, 8.91; found: C, 84.27; H, 7.21; N, 8.52.

*4.4.13. 2-Hexyl-1-[(1R)-1-phenylethyl]aziridine (**3kD**).* Yield: (16.3 mg, 35%). First diastereoisomer: oil. $[\alpha]_D^{19}$ +58.4 (c 0.64, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.42−7.24 (m, 5H; CH), 2.42 (q, 1H; J=6.5 Hz, CH), 1.62−1.25 (m, 13H), 1.46 (d, 3H; J=6.5 Hz, CH_3); 0.92 (t, 3H; J=6.8 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ=144. 7, 128.2 (2C), 126.8 (3C), 69.9, 40.7, 33.4, 33.3, 31.9, 29.2, 27.8, 23.3, 22.6, 14.1. IR (ATR): ν_{max} 3028, 2922, 2853, 1494, 1454, 1368, 1171, 1028 cm^{-1}. MS (70 eV, EI): m/z (%): 231 (8) [M$^+$], 230 (32), 216 (73), 202 (9), 188 (9), 174 (20), 161 (16), 160 (16), 146 (39), 134 (27), 126 (66), 105 (100), 91 (21), 84 (23), 79 (32), 77 (38), 70 (17), 55 (43). Anal. Calcd for $C_{16}H_{25}N$: C, 83.06; H, 10.89; N, 6.05; found: C, 83.29; H, 10.97; N, 5.74. (16.2 mg, 35%). Second diastereoisomer: oil. $[\alpha]_D^{20}$ +46.9 (c 0.77, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.41−7.23 (m, 5H; CH), 2.40 (q, 1H; J=6.6 Hz, CH), 1.69 (d, 1H; J=3.0 Hz, CH_2), 1.45 (d, 3H; J=6.6 Hz, CH_3), 1.42−1.01 (m, 12H), 0.83 (t, 3H; J=7.1 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ=144. 8, 128.2 (2C), 126.9 (3C), 70.3, 38.9, 34.2, 32.9, 31.7, 28.8, 27.2, 22.8, 22.4, 14.0. IR (ATR): ν_{max} 3033, 2928, 2856, 1493, 1452, 1369, 1167 cm^{-1}. MS (70 eV, EI): m/z (%): 231 (7) [M$^+$], 230 (31), 216 (78), 202 (9), 188 (10), 174 (20), 161 (15), 160 (17), 146 (39), 134 (27), 126 (67), 105 (100), 91 (22), 84 (23), 79 (33), 77 (38), 70 (17), 55 (43). Anal. Calcd for $C_{16}H_{25}N$: C, 83.06; H, 10.89; N, 6.05; found: C, 83.18; H, 11.01; N, 5.81.

*4.4.14. [(1R,2R)-2-(2-Phenylaziridin-1-yl)cyclohexyl] amine (**3mA**).* Yield: (16.0 mg, 37%). First diastereoisomer: viscous oil. $[\alpha]_D^{21}$ −141.4 (c 0.76, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.39−7.20 (m, 5H; CH), 2.92−2.83 (m, 1H; CH), 2.68 (dd, 1H; J=3.2, 6.5 Hz, CH), 2.00−1.63 (m, 6H; CH, CH_2), 1.88 (d, 1H; J=3.2 Hz, CH_2), 1.72 (d, 1H; J=6.5 Hz, CH_2), 1.48−1.10 (m, 5H; CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ=139.9, 128.4 (2C), 127.0, 126.2 (2C), 74.9, 56.6, 42.7, 33.7, 33.2, 30.5, 25.0, 24.8. IR (ATR): ν_{max} 3370, 2926, 2856, 1728, 1497, 1448, 1262, 1085, 1030 cm^{-1}. MS (70 eV, EI): m/z (%): 216 (4) [M$^+$], 215 (14), 199 (4), 144 (6), 120 (52), 118 (71), 111 (10), 104 (100), 97 (55), 91 (47), 81 (19), 78 (16), 77 (16), 69 (72), 56 (53). Anal. Calcd for $C_{14}H_{20}N_2$: C, 77.73; H, 9.32; N, 12.95; found: C, 77.98; H, 9.46; N, 12.56. (10.5 mg, 24%). Second diastereoisomer: mp 108−110 °C. $[\alpha]_D^{21}$ +70.5 (c 0.86, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.37−7.20 (m, 5H; CH), 3.05−2.95 (m, 1H; CH), 2.77 (br s, 2H; NH_2), 2.40 (dd, 1H; J=3.4, 6.6 Hz, CH), 2.15 (d, 1H; J=3.4 Hz, CH_2), 2.10 (d, 1H; J=6.6 Hz, CH_2), 1.95−1.86 (m, 2H; CH_2), 1.78−1.66 (m, 2H; CH_2), 1.47−1.16 (m, 5H; CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ=140.3, 128.3 (2C), 126.8, 126.5 (2C), 74.5, 56.7, 38.9, 36.6, 33.4, 31.1, 24.7, 24.5. IR (ATR): ν_{max} 3357, 2926, 2857,1610, 1497, 1451, 1096, 1037 cm^{-1}. MS (70 eV, EI): m/z (%): 216 (7) [M$^+$], 215 (25), 199 (7), 144 (9), 120 (68), 118 (84), 111 (15), 104 (100), 97 (66), 91 (55), 81 (25), 78 (21), 77 (21), 69 (71), 56 (58). Anal. Calcd for $C_{14}H_{20}N_2$: C, 77.73; H, 9.32; N, 12.95; found: C, 77.51; H, 9.41; N, 13.08.

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