Aza-MIRC Reactions of Sulfonyl-Activated Hydroxycarbamates with α,β-Difunctionalised Acrylates

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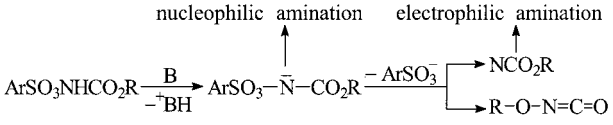
Highly functionalised aziridines are readily obtained in high yields (up to 95%) under mild conditions from the reaction of trisubstituted olefins bearing different groups with nosyloxycarbamates in the presence of calcium oxide. We propose a possible explanation for the different reactivities observed between these olefins and the aminating agents. Reagent-controlled stereoselective amination reactions led to the expected products with high conversions and purities.

Sulfonyl-activated hydroxycarbamates[1] can be used successfully in direct aziridination reactions. Lwowski was the first to introduce ethyl nosyloxycarbamate ($NsONHCO_2Et$) as an alternative source of (ethoxycarbonyl)nitrene (NCO_2Et) with respect to the corresponding azide. Other authors have used these kinds of reagents for some time.[2]

We have found that both $NsONHCO_2Et$ and $TsONHCO_2Et$, used in conjunction with inorganic bases,[3] are suitable aziridination agents either for electron-rich or electron-poor olefins and, in the latter case, we have proposed, on the basis of experimental evidence, a mechanism involving an intermediate aza-anion ($NsON^-CO_2Et$) as the reactive species (Scheme 1).[4]



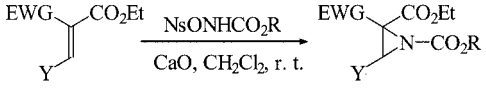
Scheme 1

To be successful, this reaction, which can be considered as an aza-MIRC (Michael-Initiated Ring Closure) process,[5] requires activation of the C=C bond. Good results have been observed when using α-nitro olefins and several olefins that carry two geminal electron-withdrawing groups.[6] Inversely, the amination of fumarates and maleates does not proceed as satisfactorily under a variety of conditions.[7]

tert-Butyl arylsulfonyloxycarbamates ($ArSO_3NHCO_2$-*t*Bu) undergo aza-MIRC reactions with electron-poor olefins, but electrophilic amination reactions have rarely been reported.[8] Moreover, the formation of isocyanate species may take place in some cases.[9] Recently, we reported the direct synthesis of imidazolidin-2-ones from β-keto esters, probably through a multicomponent reaction of $NsON^-CO_2t$Bu and *tert*-butoxy isocyanate (*t*BuO−N=C=O).[10]

Aziridines[11] are versatile intermediates in organic synthesis and can be considered as valuable building blocks for the synthesis of a variety of natural[12] and pharmacologically active compounds,[13] and for selective organic transformations. Moreover, they can be used as scaffolds for the construction of a library of useful building blocks.[14] Aziridine moieties are often introduced after multi-step syntheses and, thus, direct aziridination is a goal of considerable importance in organic chemistry.

To obtain polyfunctionalised aziridines, we considered using α,β-disubstituted acrylates as starting materials. Substrates **1**−**4** are commercially available; we synthesised the trisubstituted olefins **5**−**7** in high yields using a reported procedure.[15] These substrates were reacted with two different $NsONHCO_2R$ reagents in CH_2Cl_2, in the presence of CaO at room temperature (Scheme 2). Molar ratios, reaction times, products, and yields are displayed in Table 1.



Scheme 2

We observed only traces of products when a phenyl group is present in the β-position (**1**, **2**), even with high excesses of reactants. GC/MS analyses display molecular ions and fragmentations that are compatible with those expected for aziridines. The effect of a phenyl group in lowering the reac-

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Table 1. Direct aziridination of α,β-disubstituted acrylates with $NsONHCO_2R$

Olefin	Y	EWG	Molar ratios[a]	R	Reaction times [h]	Product	Yields (%)[b]
1	Ph	CO_2Et	1:10:8	Et	48	traces	—[c]
2	Ph	CN	1:10:8	Et	48	traces	—[c]
3	EtO	CO_2Et	1:8:6	Et	24	**8**	36
4	EtO	CN	1:8:6	Et	24	**9**	52
5	CO_2Et	CO_2Et	1:2:1.2	Et	2	**10**	94
6	CN	CO_2Et	1:2:1.2	Et	2	**11**	91
7	$COCH_3$	CO_2Et	1:2:1.2	Et	2	**12**	92
5	CO_2Et	CO_2Et	1:2:1.2	Bn	1	**13**	95
6	CN	CO_2Et	1:2:1.2	Bn	1	**14**	88
7	$COCH_3$	CO_2Et	1:2:1.2	Bn	1	**15**	92

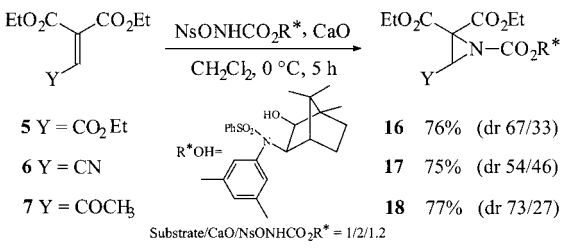
[a] Ratio of substrate/CaO/$NsONHCO_2R$. [b] After flash chromatography on silica gel. [c] After workup, the unchanged substrate was collected almost quantitatively.

tivity has been already observed by us[4] and others[7a]. The β-ethoxyacrylates **3** and **4** display enhanced reactivity and the corresponding aziridines **8** and **9** were obtained after flash chromatography on silica gel in 36 and 52% yield, respectively; we found these compounds to be unstable upon storing them at room temperature. In these reactions, parallels exist with our findings on push-pull olefins.[16] The best results were obtained for the reactions of olefins bearing an additional electron-withdrawing group. In these cases (**5**−**7**), the products **10**−**12** were obtained cleanly under milder conditions. As expected, good Michael acceptors undergo the aza-MIRC reaction. Thus, the substrates **5**−**7** reacted rapidly, very likely by trapping the intermediate aza-anion and, after immediate ring-closure with elimination of the NsO^- group, we isolated polyfunctionalised aziridines in almost quantitative yields. The same alkenes reacted quantitatively with a new carbamate, benzyl nosyloxycarbamate ($NsONHCO_2Bn$), which we synthesised using standard procedures (see Exp. Sect.). The results obtained for the aziridination of the alkenes **5**−**7** (Table 1) show that $NsONHCO_2Bn$ exhibits almost the same reactivity as that of $NsONHCO_2Et$.[17]

In contrast, attempts to perform reactions with $NsONHCO_2tBu$ failed. It is probable that aziridine formation is precluded by steric hindrance, as a result of the presence of the bulky *tert*-butyl group or because of competitive conversion into the isocyanate.

Thus, the outcome of these direct aziridinations is strongly influenced not only by the substituents on the alkenes, but also by the nature of the alkyl and/or aryl groups of the arylsulfonyloxycarbamates. Our first attempts to improve the yields and rates for the reactions of alkenes **1**, **3**, **5**, and **7**, by using ionic liquids[18] such as $[bmim]BF_4$ instead of CH_2Cl_2, did not give better results (bmim = 1-butyl-3-methylimidazolium.

We attempted some experiments in which we tried to induce diastereoselectivity. Reagent-controlled stereoselective amination reactions were performed with the olefins **5**−**7** using the chiral nosyloxycarbamate derived from Helmchen's auxiliary.[19] These reactions, which we performed using the same molar ratios of substrate:CaO:$NsONHCO_2R$*, led to the expected products (Scheme 3) after 5 h with high conversions and purities, as confirmed by ^1H and ^{13}C NMR spectra, and in good isolated yields.



Scheme 3

The diastereoisomeric ratios (*dr*) were determined by NMR spectroscopy and HPLC analyses performed on the crude mixtures. While the values of the diastereomeric excesses for the aziridines **16** and **18** were similar to those found in analogous reactions promoted by the same chiral noxyloxycarbamate,[20] the reasons for the lack of diastereoselectivity observed for **17** are not clear. In all cases, we obtained the aziridines as optically pure compounds when purified by HPLC (eluent: hexane/EtOAc, 70:30; flow rate: 1.3 mL/min). The aziridines **17** also can be separated successfully by flash chromatography on silica gel.

In conclusion, we report a direct synthetic approach to multi-functionalised aziridines by an aza-MIRC pathway, which is improved by the presence of EWGs on the starting alkenes. These substituents on the aziridines are potential new reactive sites for further chemoselective transformations. Moreover, functional groups are known to play a critical role in the biological activity of several aziridines.[21]

Experimental Section

GC analyses were performed with an HP 5890 Series II gas chromatography system equipped with a capillary column (methyl silicone, 12.5 m × 0.2 mm). GC-MS analyses were carried out with an HP G1800A GCD System equipped with a capillary column (phenyl methyl silicone, 30 m × 0.25 mm). IR: Perkin−Elmer 1600 Series FTIR spectrophotometer. NMR: Varian Mercury 300 and

Gemini 200, using $CDCl_3$ as the solvent and $CHCl_3$ as the internal standard.

Synthesis of Benzyl Nosyloxycarbamate ($NsONHCO_2Bn$): Commercially available (Aldrich) benzyl *N*-hydroxycarbamate (1.67 g, 10.0 mmol) was reacted with equimolar amounts of nosyl chloride (2.22 g) and freshly distilled triethylamine (1.01 g, 1.4 mL) in anhydrous diethyl ether (300 mL) at 0 °C. After 3 h, the title compound was obtained in 81% yield (2.85 g, 8.1 mmol) as a pale-yellow solid. M.p. 92−93 °C (from CH_2Cl_2/pentane). IR (CCl_4): $\tilde{\nu}$ = 3341, 1778, 1609 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 4.98 (s, 2 H), 7.10−7.18 (m, 2 H), 7.27−7.38 (m, 3 H), 8.04−8.10 (m, 2 H), 8.13−8.19 (m, 2 H), 8.90 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 68.8, 123.8, 128.4, 128.5, 130.7, 134.0, 138.6, 150.9, 155.1 ppm. ESI-MS: *m*/*z* = 353 $[M + 1]^+$. $C_{14}H_{12}N_2O_7S$ (352.315).

General Procedure for the Synthesis of Aziridines: CaO and $NsONHCO_2R$ were added portionwise at room temperature, in the molar ratios reported in Table 1, to a stirred solution of substrate (2 mmol) in 3 mL of CH_2Cl_2. The reaction was monitored by TLC and GC, and CH_2Cl_2/pentane (20:80) were added to the crude mixture upon completion. After filtration and solvent evaporation under reduced pressure, the residue was purified by flash chromatography on silica gel (hexane/ethyl acetate, 70:30).

Triethyl 3-Ethoxyaziridine-1,2,2-tricarboxylate (8): Viscous oil (0.218 g, 0.72 mmol, 36% yield). IR (CCl_4): $\tilde{\nu}$ = 1751, 1738 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.24−1.38 (m, 12 H), 3.79 (q, *J* = 7.2 Hz, 2 H), 4.11−4.45 (m, 6 H), 6.35 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.1, 14.2, 14.3, 14.4, 59.6, 62.4, 62.5 (two signals), 63.3, 98.4, 154.4, 164.6, 165.0 ppm. GC/MS: *m*/*z* (%) = 231 (9) $[M - CO_2Et]^+$, 215 (12), 214 (100), 186 (50), 142 (70), 127 (25), 122 (21), 115 (34), 114 (40), 100 (11), 99 (15), 98 (20), 90 (11), 87 (17), 81 (13), 77 (14), 71 (39), 70 (82), 62 (24), 56 (82). $C_{13}H_{21}NO_7$ (303.132): calcd. C 51.48, H 6.98, N 4.62; found C 51.44, H 6.96, N 4.63.

Diethyl 2-Cyano-3-ethoxyaziridine-1,2-dicarboxylate (9): Viscous oil (0.266 g, 1.04 mmol, 52% yield). IR (CCl_4): $\tilde{\nu}$ = 2222, 1765, 1735 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.18−1.46 (m, 9 H), 3.70 (q, *J* = 7.2 Hz, 2 H), 4.14−4.75 (m, 4 H), 6.45 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.0, 14.3, 14.9, 58.4, 63.3, 63.5, 64.3, 98.7, 112.2, 151.9, 161.0 ppm. GC/MS: *m*/*z* (%) = 257 (15) $[M + 1]^+$, 158 (21), 103 (100), 100 (13), 75 (42), 56 (10), 47 (34). $C_{11}H_{16}N_2O_5$ (256.106): calcd. C 51.56, H 6.29, N 10.93; found C 51.58, H 6.26, N 10.95.

Tetraethyl Aziridine-1,2,2,3-tetracarboxylate (10): Viscous oil (0.622 g, 1.88 mmol, 94% yield). IR (CCl_4): $\tilde{\nu}$ = 1764, 1739 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.12−1.38 (m, 12 H), 3.69 (s, 1 H), 4.08−4.40 (m, 8 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 13.7, 13.8 (two signals), 14.0, 44.6, 49.8, 62.2, 62.3 (two signals), 63.5, 157.2, 162.5, 163.5, 164.6 ppm. GC/MS: *m*/*z* (%) = 331 (< 1) $[M^+]$, 214 (20), 187 (10), 186 (100), 185 (13), 168 (36), 158 (23), 157 (30), 140 (94), 130 (13), 129 (19), 111 (45), 85 (30), 68 (14), 57 (11). $C_{14}H_{21}NO_8$ (331.127): calcd. C 50.75, H 6.39, N 4.23; found C 50.70, H 6.37, N 4.22.

Triethyl 3-Cyanoaziridine-1,2,2-tricarboxylate (11): Viscous oil (0.517 g, 1.82 mmol, 91% yield). IR (CCl_4): $\tilde{\nu}$ = 2222, 1769, 1739 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.29 (t, *J* = 7.2 Hz, 3 H), 1.33 (t, *J* = 7.2 Hz, 3 H), 1.37 (t, *J* = 7.2 Hz, 3 H), 3.77 (s, 1 H), 4.24 (q, *J* = 7.2 Hz, 2 H), 4.33 (q, *J* = 7.2 Hz, 2 H), 4.40 (q, *J* = 7.2 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 13.7, 13.8, 14.0, 31.9, 49.2, 63.2, 64.1, 64.2, 112.6, 155.8, 161.2, 162.1 ppm. GC/MS: *m*/*z* (%) = 285 (< 1) $[MH^+]$, 212 (12), 211 (12), 184 (35), 167 (13), 166 (25), 157 (21), 156 (63), 155 (16), 139 (31), 138 (68), 129 (48), 112 (13), 111 (31), 110 (23) 101 (12), 94 (11), 68 (14), 67 (59), 66 (100), 56 (36). $C_{12}H_{16}N_2O_6$ (284.101): calcd. C 50.70, H 5.67, N 9.85; found C 50.64, H 5.65, N 9.87.

Triethyl 3-Acetylaziridine-1,2,2-tricarboxylate (12): Viscous oil (0.554 g, 1.84 mmol, 92% yield). IR (CCl_4): $\tilde{\nu}$ = 1770, 1725 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.19−1.31 (m, 9 H), 2.20 (s, 3 H), 3.74 (s, 1 H), 4.10−4.33 (m, 6 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 13.8 (two signals), 14.1, 27.8, 49.9, 50.6, 62.9, 63.9, 64.0, 157.3, 162.6, 163.4, 198.8 ppm. GC/MS: *m*/*z* (%) = 301 (9) $[M^+]$, 228 (10), 156 (100), 128 (52), 110 (83). $C_{13}H_{19}NO_7$ (301.116): calcd. C 51.82, H 6.36, N 4.65; found C 51.72, H 6.34, N 4.63.

1-Benzyl 2,2,3-Triethyl Aziridine-1,2,2,3-tetracarboxylate (13): Viscous oil (0.747 g, 1.90 mmol, 95% yield). IR (CCl_4): $\tilde{\nu}$ = 1744 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.18 (t, *J* = 7.2 Hz, 3 H), 1.27 (t, *J* = 7.2 Hz, 3 H), 1.29 (t, *J* = 7.2 Hz, 3 H), 3.77 (s, 1 H), 4.13 (q, *J* = 7.2 Hz, 2 H), 4.21 (t, *J* = 7.2 Hz, 2 H), 4.21 (t, *J* = 7.2 Hz, 2 H), 5.14 (d, *J* = 12.3 Hz, 1 H), 5.18 (d, *J* = 12.3 Hz, 1 H), 7.34 (s, 5 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 13.8, 13.9, 14.0, 44.8, 50.0, 62.3, 62.4, 63.6, 69.1, 128.3, 128.4 (four signals), 134.6, 157.1, 162.3, 163.3, 164.4 ppm. GC/MS: *m*/*z* (%) = 276 (< 1) $[M - 117]^+$, 214 (62), 168 (39), 91 (100). $C_{19}H_{23}NO_8$ (393.142): calcd. C 58.01, H 5.89, N 3.56; found C 57.99, H 5.89, N 3.56.

1-Benzyl 2,2-Diethyl 3-Cyanoaziridine-1,2,2-tricarboxylate (14): Viscous oil (0.609 g, 1.76 mmol, 88% yield). IR (CCl_4): $\tilde{\nu}$ = 2257, 1758 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.21 (t, *J* = 7.2 Hz, 3 H), 1.35 (t, *J* = 7.2 Hz, 3 H), 3.76 (s, 1 H), 4.04−4.23 (m, 2 H), 4.38 (q, *J* = 7.2 Hz, 2 H), 5.15 (d, *J* = 12.3 Hz, 1 H), 5.22 (d, *J* = 12.3 Hz, 1 H), 7.36 (s, 5 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 13.8, 14.0, 32.1, 49.4, 63.4, 64.2, 69.8, 112.6, 128.5 (two signals), 128.6 (two signals), 128.7, 134.1, 155.9, 161.2, 162.2 ppm. GC/MS: *m*/*z* (%) = 300 (< 1) $[M - 46]^+$, 107 (39), 91 (100). $C_{17}H_{18}N_2O_6$ (346.116): calcd. C 58.96, H 5.24, N 8.09; found C 58.99, H 5.23, N 8.11.

1-Benzyl 2,2-Diethyl 3-Acetylaziridine-1,2,2-tricarboxylate (15): Viscous oil (0.668 g, 1.84 mmol, 92% yield). IR (CCl_4): $\tilde{\nu}$ = 1748 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.36 (t, *J* = 7.2 Hz, 3 H), 1.45 (t, *J* = 7.2 Hz, 3 H), 2.39 (s, 3 H), 3.98 (s, 1 H), 4.28 (q, *J* = 7.2 Hz, 2 H), 4.44 (q, *J* = 7.2 Hz, 2 H), 5.32 (d, *J* = 12.3 Hz, 1 H), 5.36 (d, *J* = 12.3 Hz, 1 H), 7.51 (s, 5 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 13.8, 13.9, 27.9, 50.0, 50.7, 62.7, 63.7, 69.1, 128.4 (four signals), 128.5, 134.6, 157.3, 162.6, 163.4, 198.8 ppm. GC/MS: *m*/*z* (%) = 363 (1) $[M^+]$, 246 (11), 140 (10), 110 (11), 91 (100). $C_{18}H_{21}NO_7$ (363.132): calcd. C 59.50, H 5.83, N 3.85; found C 59.45, H 5.84, N 3.88.

Synthesis of Aziridines 16−18: The chiral nosyloxycarbamate ($NsONHCO_2R^*$) was prepared according to ref.[20]. For the synthesis of the following aziridines, we followed the general procedure above. The molar ratios, reaction times, and yields are reported in Scheme 3.

16 (Major Diastereoisomer): $[\alpha]_D$ = −31.78 (*c* = 4.5, $CHCl_3$). IR (CCl_4): $\tilde{\nu}$ = 1754, 1745, 1736, 1609, 1596 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 0.57 (s, 3 H), 0.74 (s, 3 H), 0.94 (s, 3 H), 1.06−1.18 (m, 1 H), 1.26−1.36 (m, 9 H), 1.46−1.58 (m, 1 H), 1.62−1.76 (m, 2 H), 1.85 (d, *J* = 3.9 Hz, 1 H), 2.03 (s, 3 H), 2.28 (s, 3 H), 4.01 (d, *J* = 7.2 Hz, 1 H), 4.22−4.38 (m, 6 H), 4.50 (s, 1 H), 5.10 (d, *J* = 7.2 Hz, 1 H), 5.77 (s, 1 H), 6.85 (s, 1 H), 7.08 (s, 1 H), 7.30−7.52 (m, 5 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 11.5, 14.0, 14.3, 29.9, 21.1, 21.3, 28.2, 32.1, 44.6, 47.3, 48.3, 50.0, 50.8, 62.0, 62.2, 63.3, 66.9, 85.1, 128.0, 128.3, 129.4, 132.3, 137.3, 138.0, 156.2, 163.0, 163.1, 165.2 ppm. ESI-MS: *m*/*z* = 700 $[M + 1]^+$. $C_{36}H_{46}N_2O_{10}S$ (698.823).

17 (Major Diastereoisomer): $[\alpha]_D = -18.71$ ($c = 3.1$, $CHCl_3$). IR (CCl_4): $\tilde{\nu} = 2255, 1757, 1609, 1596\ cm^{-1}$. ^1H NMR ($CDCl_3$): $\delta =$ 0.59 (s, 3 H), 0.85 (s, 3 H), 0.96 (s, 3 H), 1.05−1.18 (m, 1 H), 1.30 (t, $J = 7.2$ Hz, 3 H), 1.38 (t, $J = 7.2$ Hz, 3 H), 1.48−1.62 (m, 1 H), 1.64−1.77 (m, 2 H), 1.86 (d, $J = 4.5$ Hz, 1 H), 1.99 (s, 3 H), 2.36 (s, 3 H), 3.97 (d, $J = 7.2$ Hz, 1 H), 4.34 (q, $J = 7.2$ Hz, 2 H), 4.43 (q, $J = 7.2$ Hz, 2 H), 7.78 (s, 1 H), 5.05 (d, $J = 7.2$ Hz, 1 H), 5.62 (s, 1 H), 6.87 (s, 1 H), 7.16 (s, 1 H), 7.28−7.41 (m, 4 H), 7.47−7.55 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$): $\delta =$ 11.5, 14.0, 14.1, 20.8, 21.0, 21.3, 21.4, 28.0, 32.0, 47.4, 48.1, 49.3, 50.9, 63.1, 63.7, 67.2, 85.7, 113.5, 128.0, 128.8, 129.5, 131.9, 132.5, 136.7, 136.9, 137.5, 138.4, 155.1, 161.5, 162.1 ppm. ESI-MS: $m/z = 653$ $[M + 1]^+$. $C_{34}H_{41}N_3O_8S$ (651.770).

18 (Major Diastereoisomer): $[\alpha]_D = -27.30$ ($c = 3.7$, $CHCl_3$). IR (CCl_4): $\tilde{\nu} = 1754, 1740, 1732, 1609, 1596\ cm^{-1}$. ^1H NMR ($CDCl_3$): $\delta =$ 0.57 (s, 3 H), 0.76 (s, 3 H), 0.96 (s, 3 H), 1.04−1.16 (m, 1 H), 1.30 (t, $J = 7.2$ Hz, 3 H), 1.31 (t, $J = 7.2$ Hz, 3 H), 1.46- 1.58 (m, 1 H), 1.62−1.76 (m, 2 H), 1.81 (d, $J = 4.2$ Hz, 1 H), 2.00 (s, 3 H), 2.30 (s, 3 H), 2.43 (s, 3 H), 3.97 (d, $J = 7.2$ Hz, 1 H), 4.25−4.37 (m, 4 H), 4.63 (s, 1 H), 5.08 (d, $J = 7.2$ Hz, 1 H), 5.64 (s, 1 H), 6.86 (s, 1 H), 7.00 (s, 1 H), 7.31−7.53 (m, 5 H) ppm. ^{13}C NMR ($CDCl_3$): $\delta =$ 11.5, 14.0, 20.8, 21.1, 21.4, 28.1, 28.5, 32.1, 47.3, 48.3, 49.9, 50.3, 50.9, 62.4, 63.3, 67.2, 85.2, 128.0, 128.2, 129.4, 132.4, 137.2, 137.9, 156.8, 163.1, 163.3, 199.9 ppm. ESI-MS: $m/z =$ 670 $[M + 1]^+$. $C_{35}H_{44}N_2O_9S$ (668.797).

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