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A Method for Rhodium(II)-Catalyzed Aziridination of Olefins

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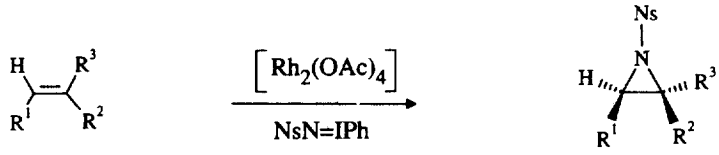
Abstract. The $[Rh_2(OAc)_4]$ catalyzed decomposition of (N-(p-nitrobenzenesulfonyl)imino)phenyliodinane (PhI=NNs) in the presence of olefins affords aziridines in yields of 18-85%. The aziridination of *cis*-β-methylstyrene (**1h**) and *cis*-hex-2-ene (**1k**) is stereospecific. However, with cis-stilbene (**1m**) a ca. 3:1 mixture of *cis*- and *trans* aziridines **2m** and **2l** is obtained. With chiral catalysts asymmetric inductions in up to 73% ee are obtained.

The development of systems capable of asymmetric nitrene transfer to olefins is in progress in several research groups. The most successful approach reported this far is the reaction of [*N*-(*p*-toluenesulfonyl)imino]phenyliodinane (PhI=NTs) in the presence of Cu-based catalysts, which leads to aziridines in high yields and, in some cases, with exceptional enantioselectivities.[1,2,3] Catalysis with $Fe^{(III)}$-porphyrin[4] and Mn(salen) complexes has also been performed, although with less success.[5,6] In contrast, $Rh^{(II)}$based catalysts such as $[Rh_2(OAc)_4]$, which are competitive to those using Cu in certain cyclopropanation[7] and CH-insertion[8] reactions were found inefficient for aziridination with PhI=NTs.[1] Owing to the apparent analogy between metal-catalyzed carbene and nitrene transfer reactions we have carried out an extensive search towards optimization of the nitrene transfer from PhI=NTs to olefins under $[Rh_2(OAc)_4]$-catalysis, but even under the best conditions the yield of aziridine obtained from styrene (**1a**) never exceeded 59%. However, we found that the reaction proceeds well with [*N*-(*p*-nitrobenzenesulfonyl)iminophenyliodinane (PhI=NNs).



1a-n **2a-n**

The reaction was optimized for styrene (**1a**). In all runs an excess of olefin was used in order to suppress side reactions. To a solution of $[Rh_2(OAc)_4]$ (0.02 mmol), olefin (20 mmol, 5 mmol for **1a-c**, 10 mmol for **1n**) in dichloromethane (10.0 mL) containing molecular sieves (6.0 g) was added PhI=NNs (1.00 mmol) at once. The suspension was stirred at 25° for the time indicated in Table 1. After filtration through a plug of celite or silica gel, which was washed with CH_2Cl_2, and evaporation of the solvent, the crude aziridines were isolated and purified as appropriate. The results are summarized in Table 1.

Substituted styrenes were also reactive, but in some cases resulted in lower yields of aziridines. While 4-methylstyrene (**1b**) and 4-acetoxystyrene (**1c**) reacted normally, the reaction with the 3-nitro

Table 1. Yields for aziridination of olefins with PhI=NNs catalyzed by $[Rh_2(OAc)_4]$

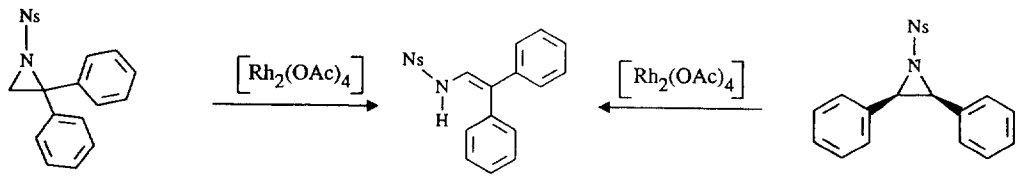
Olefin (**1**)	R^1	R^2	R^3	Time (h)	Aziridine (**2**)[a]
a	Ph	H	H	2.3	85
b	*p*-MePh	H	H	0.5	76
c	*p*-AcOPh	H	H	0.75	82
d	*m*-NO_2-Ph	H	H	19	46
e	C_4H_9	H	H	1.0	63
f	AcO	H	H	4.0	47
g	Ph	H	Me	18	68
h	Ph	Me	H	0.25	82
i	C_3H_7	H	Me	0.5	27
k	C_3H_7	Me	H	0.5	54
l	Ph	H	Ph	36	41[b]
m	Ph	Ph	H	19	18[c]
n	H	Ph	Ph	0.2	59[d]

[a] Yield in percent. All aziridines gave satisfactory CH-analyses or HR-MS data. [b] Rearrangement to **3** in 36h, yield 11%. [c] *cis/trans* ratio 77 : 23. [d] By NMR; isolated in 13% yield by recrystallization. Side-product **3** formed in 33% yield. Yield of **3** after 3 h 60%.

derivative **1d** proceeded only sluggishly and the yield of aziridine **2d** dropped to 46%. The yield with mono-substituted olefins other than styrenes was generally lower as shown for 1-hexene (**1e**) and vinylacetate (**1f**), which afforded the aziridines **2e** and **2f** in 63% and 47% yield, respectively.

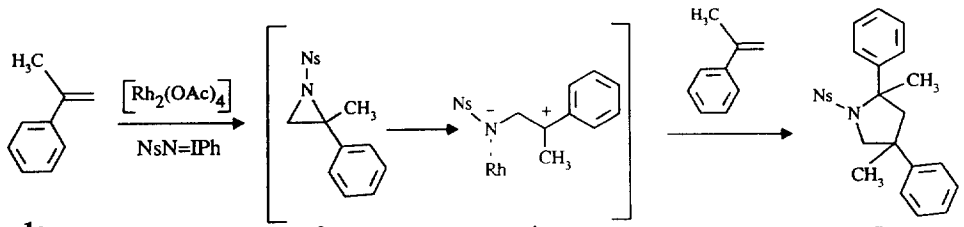
The stereospecificity of the reaction was investigated with *cis*-β-methylstyrene (**1h**) and *cis*-hex-2-ene (**1k**). Both afforded *cis*-aziridines (**2h**, 82%) and (**2k**, 54%). The *trans*-isomers **2g** and **2i** were independently prepared from the appropriate olefins, and their absence in the reaction with the *cis*-olefins was unambiguously established. *Cis*-stilbene (**1m**) reacted very sluggishly with partial loss of stereochemistry to a 77:23 mixture of *cis*-and *trans*-aziridine **2m** and **2l** in 18% yield. The *trans*-isomer **2l** suffered phenyl migration upon exposure to $[Rh_2(OAc)_4]$ and rearranged to enamine **3**, which is also observed as side-product upon aziridination of 1,1-diphenylethene (**1n**).[9] In this latter case the aziridine/enamine ratio (**2l/3**) depends on reaction time. In separate experiments **1n** rearranged to **3** in the presence of $[Rh_2(OAc)_4]$ or upon chromatography on SiO_2 in quantitative yield. The *cis*-isomer **2m** was more stable in the presence of $[Rh_2(OAc)_4]$, but rearranged also to **3**, albeit at significantly lower rate.

The observation of partial loss of stereospecificity in the Rh(II)-catalyzed aziridination of *cis*-stilbene (**1m**) is consistent with that occurring in Cu-catalyzed aziridination of **1m**. Although some *cis/trans* isomerization of stilbene occurred to a minor extent under our reaction conditions, it does by far not account for the proportion of *trans*-aziridine **2l**. Partial loss of stereochemistry has also been reported in Cu-catalyzed aziridination of *cis*-β-methylstyrene, while aziridination of *cis*-alkenes is stereospecific.[1,2] A two-step mechanism has been proposed to account for partial loss of stereospecificity concurrent with high enantioselectivity in metal-catalyzed aziridinations.[2,5] No aziridine was isolated from the reaction with α-methylstyrene (**1o**). The nitrene adduct **2o** apparently underwent ring-opening under the conditions of aziridination to a dipolar species **4** which was intercepted by styrene present in excess to afford the



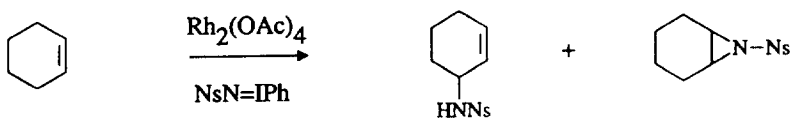
2n **3** **2m**

pyrrolidine **5** as a single stereoisomer of unknown configuration in 76% yield. Pyrrolidines were also formed as mixtures of stereo- and regioisomers upon aziridination of other electron-rich olefins, such as ethyl vinylether or 4-methoxystyrene.[9] In contrast, electron-deficient olefins such as methyl acrylate exhibited only low reactivity and yielded the aziridine in only 7% yield.



1o **2o** **4** **5**

Cyclohexene (**1p**), in turn, afforded only trace amounts of aziridine **2p** (4%). The main product **6**, isolated in 70% yield was derived from nitrene insertion into one of the allylic CH-bonds. Small amounts of insertion products have been reported to occur in Cu-catalyzed aziridination of olefins.[1] Insertion may be the dominant pathway with manganese or iron prophyrins as catalysts.[10] The propensity of $[Rh_2(OAc)_4]$ for nitrene insertion into CH bonds has been observed in the past.[11] This catalyst is also remarkably efficient for carbene insertions, although in these latter reactions, useful yields are only achieved in intramolecular cases.[12]



1p **6** (70 %) **2p** (4 %)

Exploratory experiments indicate that the $Rh^{(II)}$-catalyzed aziridinations have potential for asymmetric synthesis. Thus, the reaction of styrene (**1a**) with PhI=NNs catalyzed by $[Rh_2\{(2S)\text{-mepy}\}_4]$[13] in CH_2Cl_2 produced the aziridine **2a** in 81% yield with 21% ee. The catalyst of Pirrung[14] having 1,1'-binaphthyl-2,2'-diyl phosphate (bnp) ligands, $[Rh_2\{(-)(R)\text{-bnp}\}_4]$ afforded **2a** in 74% yield and 55% ee, while aziridination of *cis*-β-methylstyrene (**1h**) proceeded with 73% ee and 75% yield. Optimisation of the reaction conditions and of the catalyst is in progress.

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Experimental Part

General Procedure for Aziridination of Olefins

To $[Rh_2(OAc)_4]$ (9.6 mg, 0.02 mmol) in CH_2Cl_2 (10 mL) was added, under N_2, activated molecular sieves 4Å (6.0 g) and the olefin (20 mmol, 5 mmol for **1a-c**, 10 mmol for **1n**), followed by the PhI=NNs (404 mg, 1.0 mmol). The suspension was stirred at R.T. as indicated in Table 1. The mixture was filtered

through a plug of celite or silica gel, which was washed with CH_2Cl_2. After evaporation of the solvent, the crude product was purified by flash chromatography using hexane/ether or hexane/ethyl acetate as eluant.

N-p-**Nitrobenzenesulfonyl-2-phenylaziridine (2a)**. M.p. 134-136°. IR ($CHCl_3$): 3020*s*, 2976*s*, 1349*w*, 1167*m*, 792*vs*. ^1H NMR ($CDCl_3$, 400 MHz): δ 2.51 (d, *J* = 4.3 Hz, 1H), 3.12 (d, *J* = 7 Hz, 1H), 3.90 (dd, *J* = 4.3, 7 Hz, 1H), 7.21-7.23 (m, 2H), 7.31-7.33 (m, 3H), 8.19 and 8.38 (AA'XX' system, app. d, *J* = 9 Hz, 4 H). ^{13}C NMR ($CDCl_3$): 36.5 (t), 41.9 (d), 124.3 (d), 126.5 (d), 128.7 (d), 129.2 (d), 134.2 (s), 144.1 (s), 150.7 (s). MS: 304 (M^+, 1), 118 (100), 91 (60). HR-MS: 304.0534 ($C_{14}H_{12}N_2O_4S^+$, calc. 304.0517).

N-p-**Nitrobenzenesulfonyl-2-(4-methylphenyl)aziridine (2b)**. M.p. 132-134°. IR ($CHCl_3$): 3016*m*, 1535*m*, 1216*s*, 1166*m*. ^1H NMR ($CDCl_3$, 400 MHz): δ 2.32 (s, 3H), 2.50 (d, *J* = 4.5 Hz, 1H), 3.10 (d, *J* = 7.4 Hz, 1H), 3.87 (dd, *J* = 4.5, 7.4 Hz, 1H), 7.08-7.13 (m, 4H), 8.18 and 8.37(AA'XX' system, app. d, *J* = 8.8 Hz, 4H). ^{13}C NMR ($CDCl_3$): 21.2 (q), 36.4 (t), 42.0 (d), 124.3 (d), 126.4 (d), 129.2 (d), 129.5 (d), 131.1 (s), 138.7 (s), 144.1 (s), 150.7 (s). MS: 318 (M^+, 7.2), 132 (100), 117 (9), 105 (65), 77 (7). HR-MS: 318.0685 ($C_{15}H_{14}N_2O_4S^+$, calc. 318.0674).

N-p-**Nitrobenzenesulfonyl-2-(4-acetoxyphenyl)aziridine (2c)**. *170-171°*. IR ($CHCl_3$): 3106*w*, 3029*m*, 1764*s*, 1608*m*, 1535*vs*, 1452*w*, 1366*s*, 1349*vs*, 1313*m*, 1245*m*, 1224*m*, 1205*m*, 1169*vs*, 1120*m*, 1091*m*, 1059*m*, 990*m*, 889*s*, 855*m*. ^1H NMR ($CDCl_3$, 400 MHz): 2.02 (s, 3H); 2.71 (dd, J = 2.9, 1.5 Hz, 1H); 3.03 (dd, J = 5.3, 1.5 Hz, 1H); 5.31 (dd, J = 5.3, 2.9 Hz, 1H); 8.23 and 8.40 (app. AA'XX' system, d, J = 8.8 Hz, 4H). MS: 287 (M^++1, 10), 286 (0.3), 245 (7), 215 (78), 199 (9), 186 (62), 170 (8), 122 (100), 106 (13), 100 (11), 92 (42), 84 (15), 76 (98), 64 (25), 58 (55).

N-p-**Nitrobenzenesulfonyl-2-(3-nitrophenyl)aziridine (2d)**. M.p. 184-186°. IR ($CHCl_3$): 3018*m*, 1536*m*, 1352*m*, 1210*vs*. ^1H NMR ($CDCl_3$, 400 MHz): δ 2.51 (d, *J* = 4.4 Hz, 1H), 3.16 (d, *J* = 7.4 Hz, 1H), 4.01 (dd, *J* = 7.4, 4.4 Hz, 1H), 7.54 (t, *J* = 8 Hz, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 8.09 (t, *J* = 1.8 Hz, 1H), 8.17-8.20 (m, 1H), 8.22 and 8.42(AA'XX' system, app. d, *J* = 8.8 Hz, 4H). ^{13}C NMR ($CDCl_3$): 37.1 (t), 40.2 (d), 121.4 (d), 123.7 (d), 124.5 (d), 129.4 (d), 129.9 (d), 132.7 (d), 136.7 (s), 143.5 (s), 148.9 (s), 151.0 (s). MS: 349 (M^+, 0.1), 163 (100), 117 (39), 90 (24). HR-MS: 163.0506 ($C_8H_7O_2N^+$. calc. 163.0507).

N-p-**Nitrobenzenesulfonyl-2-butylaziridine (2e)**. M.p. 64-66°. IR ($CHCl_3$): 3105*w*, 3029*m*, 2960*m*, 2934*m*, 2873*m*, 1608*m*, 1534*vs*, 1456*m*, 1402*m*, 1350*vs*, 1334*vs*, 1311*s*, 1231*m*, 1165*vs*, 1090*s*, 1014*m*, 944*m*, 923*m*, 855*s*. ^1H NMR ($CDCl_3$, 400 MHz): δ 0.84 (t, *J* = 7 Hz, 3H), 1.22-1.34 (m, 4H), 1.35-1.44 (m, 1H), 1.56-1.64 (m, 1H), 2.16 (d, *J* = 4.8 Hz, 1H), 2.74 (d, *J* = 7.4, 1H), 2.86-2.93 (m, 1H), 8.16 and 8.40 (AA'XX' system, app. d, *J* = 9.2, 4H). ^{13}C NMR ($CDCl_3$): 13.8 (q), 22.0 (t), 28.8 (*t*), 30.8 (t), 34.6 (t), 41.3 (d), 124.2 (d), 129.2 (d), 144.1 (s), 150.5 (s). MS: 285 (M^++1, 1), 284 (0.2), 255 (5), 243 (35), 215 (10), 186 (15), 122 (12), 98 (100), 82 (11), 69 (45), 56 (30). Anal. calc for $C_{12}H_{16}N_2O_4S$: C 50.69, H 5.68, H 9.86; found C 50.64, H 5.64, N 9.82.

N-p-**Nitrobenzenesulfonyl-2-acetoxyaziridine (2f)**. M.p. 170-171° (d). IR ($CHCl_3$): 3106*w*, 3029*m*, 1764*s* , *1608m*, 1535*vs*, 1452*w*, 1366*s*, 1349*vs*, 1313*m*, 1245*m*, 1224*m*, 1205*m*, 1169*vs*, 1120*m*, 1091*m*, 1059*m*, 990*m*, 886*s*, 855*m*. ^1H NMR ($CDCl_3$, 400 MHz): 2.02 (s, 3H), 2.71 (dd, *J* = 2.9, 1.5 Hz, 1H), 3.03 (dd, *J* = 5.3, 1.5 Hz, 1H), 5.31 (dd, *J* = 5.3, 2.9 Hz, 1H), 8.23 and 8.40 (AA'XX' system, app. d, *J* = 8.8, 4H). ^{13}C NMR ($CDCl_3$): 20.3 (q), 32.2 (t), 62.8 (d), 124.1 (d), 129.7 (d), 143.0 (s), 150.8 (s), 169.8 (s). MS: 287 (M^++1, 10), 286 (0.3), 245 (7), 227 (7), 215 (78), 199 (9), 186 (62), 170 (8), 122 (100), 106 (13), 100 (11), 92 (42), 84 (15), 76 (98), 64 (25), 58 (55).

Trans-N-p-**Nitrobenzenesulfonyl-2-methyl-3-phenylaziridine (2g)**. M.p. 78-80°. IR ($CHCl_3$): 3031*w*, 1608*vw*, 1534*vs*, 1458*vw*, 1351*s*, 1164*vs*, 1090*s*, 1037*w*, 972*w*, 856*m*, 758*m*. ^1H NMR ($CDCl_3$, 400 MHz): 1.89 (d, *J* = 5.9 Hz, 3H); 3.06 (dq, *J* = 4.4, 5.9 Hz, 1H); 3.88 (d, *J* = 4.4 Hz, 1H); 7.13 - 7.15 (m, 2H); 7.27 - 7.29 (m, 3H); 8.12 and 8.32 (AA'XX' system, app. d, *J* = 8.8 Hz, 4H). ^{13}C NMR ($CDCl_3$): 14.6 (q) 50.1 (d); 50.3 (d); 124.2 (d); 126.2 (d); 128.4 (d); 128.6 (d); 128.7 (d); 134.6 (s); 146.4 (s), 152.8 (s). MS: 318 (M^+, 1.7), 132 (100), 91 (10), 77(11). HR-MS: 318.0652 ($C_{15}H_{14}N_2O_{45}S^+$, found 318.0674).

Cis-N-p-**Nitrobenzenesulfonyl-2-methyl-3-phenylaziridine** (**2h**). Semi-solid. IR ($CHCl_3$): 3017*m*, 1608*w*, 1535*s*, 1452*w*, 1350*m*, 1312*w*, 1165*s*, 1045*w*, 984*w*, 856*w*, 750*vs*. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.07 (d, J = 5.6 Hz, 3H), 3.34 (dq, J = 5.6, 7.4 Hz, 1H), 4.07 (d, J = 7.4 Hz, 1H), 7.18-7.20 (m, 2H), 7.29-7.32 (m, 3H), 8.22 and 8.40 (AA'XX'system, app. d, J = 8.9 Hz, 4H).. ^{13}C NMR ($CDCl_3$): 12.3 (q), 43.2 (d), 47.5 (d), 124.9 (d), 127.8 (d), 128.7 (d), 129.0 (d), 129.6 (d), 132.3 (s), 144.8 (s), 151.1 (s). MS: 318 (M^+, 0.07), 132 (100). HR-MS: 318.0658 ($C_{15}H_{14}N_2O_4S^+$, calc. 318.0674).

Trans-N-p-**Nitrobenzenesulfonyl-2-methyl-3-propylaziridine** (**2i**). M.p. 46-47°. IR ($CHCl_3$): 3105*w*, 3029*m*, 2964*m*, 2934*m*, 2875*m*, 1607*m*, 1533*vs*, 1456*m*, 1350*vs*, 1329*s*, 1307*s*, 1229*m*, 1160*vs*, 1087*s*, 1058*m*, 1014*m*, 956*m*, 894*m*, 856*s*, 831*m*.^1H NMR ($CDCl_3$, 400 MHz): 0.88 (t, J = 7.3 Hz, 3H); 1.23-1.35 (m, 2H); 1.55-1.61 (m, 5H); 2.77-2.84 (m, 2H); 8.15 and 8.38, (AA'XX' system, app. d, J = 8.8 Hz, 4H). ^{13}C NMR ($CDCl_3$): 14.1 (q); 15.6 (q); 21.0 (t); 32.9 (t); 47.4 (d); 51.2 (d); 124.6 (d); 129.1 (d); 147 (s), 150.7 (s). MS (M^+ absent), 186 (1), 122 (5), 98 (100), 82 (3), 76 (12), 69 (12), 56 (84). Anal calc. for $C_{12}H_{16}N_2O_4S$: C 50.69, H 5.68, N 9.86, found C 50.58, H 5.67, N 9.82.

Cis-N-p-**Nitrobenzenesulfonyl-2-methyl-3-propylaziridine** (**2k**). M.p. 60-62°. IR ($CHCl_3$): 3106*w*, 3028*m*. 2963*m*, 2932*m*, 2875*m*, 1608*m*, 1534*vs*, 1465*m*, 1402*m*, 1349*s*, 1333*s*, 1310*s*, 1162*vs*, 1090*s*, 1040*w*, 993*w*, 952*s*, 891*m*, 856*s*, 824*m*. ^1H NMR ($CDCl_3$, 400 MHz): 0.90 (t, J = 7.4 Hz, 3H), 1.23 (d, J = 5.5 Hz, 3H), 1.26-1.53 (m, 4H), 2.88-2.95 (m, 1H), 3.01-3.08 (m, 1H), 8.15 and 8.39 (AA'XX' system, app. d, J = 8.8 Hz, 4H). ^{13}C NMR ($CDCl_3$): 12.4 (q), 14.2 (q), 20.9 (t), 28.8 (t), 41.8 (d), 46.5 (d), 124.7 (d), 129.5 (d), 145.1 (s), 151.0 (s). MS: M^+ absent, 241 (1), 186 (3), 122 (5), 98 (100), 76 (9), 69 (9), 56 (51). Anal calc. for $C_{12}H_{16}N_2O_4S$: C 50.69, H 5.68, N 9.86; found C 50.81, H 5.68, N 9.85.

Trans-N-p-**Nitrobenzenesulfonyl-2,3-diphenylaziridine** (**2l**). M.p. 153-155°. IR ($CHCl_3$): 3033*w*, 1607*w*, 1531*vs*, 1455*vw*, 1346*s*, 1313*w*, 1166*s*, 1084*m*, 1013*w*, 856*w*, 752*m*. ^1H NMR ($CDCl_3$, 400 MHz): 4.37 (s, 2H); 7.38-7.43 (m, 10 H); 7.95 and 8.27(AA'XX' system, app. d, J = 8.8 Hz, 4H). ^{13}C NMR ($CDCl_3$): 51.4 (d); 128.1 (d); 124.1 (d); 128.7 (d); 129.2 (d); 132.3 (s); 145.6 (s); 150.2 (s). MS: 380 (M^+, 5), 194 (100), 77 (7). HR-MS: 380.0829 ($C_{20}H_{16}N_2O_4S^+$, calc. 380.0830).

Cis-N-p-**Nitrobenzenesulfonyl-2,3-diphenylaziridine** (**2m**). M.p. 137-140°. IR($CHCl_3$): 2962*m*, 1535*m*, 1350*w*, 1262*vs*, 1166*m* , 1093*vs*, 1015*vs*. ^1H NMR (400 MHz, $CDCl_3$): 4.38 (s, 2H); 7.03-7.05 (m, 4H); 7.13-7.16 (m, 6H); 8.29 and 8.42 (AA'XX' system, app. d, J = 8.8 Hz, 4H). ^{13}C NMR ($CDCl_3$): 48.3 (d); 124.5 (d); 127.6 (d); 128.2 (d); 129.3 (d); 131.2 (s). MS: 380 (M^+, 1.0), 194 (100). HR-MS: 380.0842 ($C_{20}H_{16}N_2O_4S^+$, calc. 380.0830).

N-p-**Nitrobenzenesulfonyl-2,2-diphenylaziridine** (**2n**). M.p. 131-132°. IR ($CHCl_3$): 3106*w*, 3017*m*, 1607*m*, 1534*vs*, 1495*m*, 1448*m*, 1349*vs*, 1309*m*, 1220*s*, 1170*vs*, 1109*m*, 1085*m*, 952*m*, 856*m*. ^1H NMR ($CDCl_3$, 400 MHz): 3.18 (s), 2H); 7.32-7.40 (m, 10H); 8.03 and 8.33 (AA'XX' system, app. d, J = 8.8 Hz, 4H). ^{13}C NMR ($CDCl_3$): 41.2 (t); 58.1 (s); 124.1 (d); 128.4 (d); 128.6 (d); 128.7 (d); 129.1 (d); 137.3 (s); 144.9 (s); 150.3 (s). MS: 380 (M^+, 18), 194 (100), 167 (24), 165 (31), 152 (10), 116 (7), 9i (10). HR-MS: 380.0846 ($C_{20}H_{16}N_2O_4S^+$, calc. 380.0831).

N-p-**Nitrobenzenesulfonyl-7-azabicyclo[4.1.0]heptane** (**2p**). M.p. 142°. ^1H NMR ($CDCl_3$, 400 MHz): 1.23-1.31 (m, 2H); 1,37-1.46 (m, 2H); 1.76-1.87 (m, 4H); 3.13 (t, J = 2.0 Hz, 2H); 8.15 and 8.39 (AA'XX' system, app. d, J = 8.8 Hz, 4H). ^{13}C NMR ($CDCl_3$): 19.2 (t); 22.7 (t); 41.0 (d); 124.2 (d); 128.8 (d); 144.9 (s); 150.4 (s). IR ($CHCl_3$): 3030*w*, 2947*w*, 2867*w*, 1605*w*, 1534*s*, 1442*w*, 1398*w*, 1350*s*, 1330*w*, 1310*w*, 1240*w*, 1158*s*, 1092*m*, 966*m*, 922*m*, 847*m*, 623*m*. Anal. calc. for $C_{12}H_{14}N_2O_4S$: C 51.05, H 5.00, N 9.92, S 11.36; found C 50.97, H 4.97, N 9.96, S 11.40.

N-p-**Nitrobenzenesulfonyl-2,2-diphenylethylenylamine** (**3**). M.p. 150-151° (yellow crystals). IR ($CHCl_3$): 3357*m*, 3030*m*, 1637*m*, 1605*m*, 1534*vs*, 1496*m*, 1447*m*, 1405*s*, 1350*vs*, 1310*m*, 1169*vs*, 1125*m*, 1089*s*, 967*m*, 849*s*. ^1H NMR ($CDCl_3$, 400 MHz): 6.41 (large d, J = 11.4 Hz, 1H); 6.81 (d, J = 11.4 Hz, 1H); 6.92-6.95 (m, 2H); 7.10-7.13 (m, 2H); 7.24-7.41 (*m*, 6H); 8.04 and 8.41 (AA'XX', app. d, J = 9.2 Hz, 4H). ^{13}C NMR ($CDCl_3$): 118.9 (d); 124.6 (d); 126.6 (d); 127.6 (d); 128.1 (d); 128.5 (d); 128.6 (d); 129.4 (d); 129.6 (d); 136 (s); 138.8 (s); 145.3 (s); 150.3 (s). MS: 380 (M^+, 22), 194 (100), 167 (19), 165 (31), 152 (10), 91 (6). HR-MS: 380.0840 ($C_{20}H_{16}N_2O_4S^+$, calc. 380.0831).

2,4-Dimethyl-*N*-*p*-nitrobenzenesulfonyl-2,4-diphenylpyrrolidine (**5**). M.p. 208-209°. IR ($CHCl_3$): 3030*m*, 2932*w*, 2855*w*, 1605*m*, 1531*vs*, 1496*m*, 1447*m*, 1350*vs*, 1310*m* 1218*m*, 1160*s*, 1089*m*, 1011*m*, 967*m* , *855m*. ^1H NMR ($CDCl_3$, 400 MHz): 1.37 (s, 3H); 1.64 (s, 3H); 2.63 (s, 2H); 3.69 (d, J = 9.9 Hz, 1H); 4.32 (d, J = 9.9 Hz, 1H); 7.20-7.35 (m, 10H); 7.60 and 8.16 (AA'XX' system, app. d, J = 8.4 Hz, 4H). ^{13}C NMR ($CDCl_3$): 27.3 (q); 29.4 (q); 44.4 (s); 59.2 (t); 60.4 (t); 70.3 (s); 123.8 (d); 125.5 (d); 126.3 (d); 126.6 (d); 127.1 (d); 128.1 (d); 128.3 (d); 128.8 (d); 145.6 (s); 145.7 (s); 146.4 (s); 149.5 (s). MS: 436 (M^+, 2), 421 (40), 359 (17), 250 (1), 222 (11), 207 (19), 186 (8), 158 (5), 132 (19), 130 (8), 122 (22), 117 (54), 103 (22), 91 (100), 77 (33), 76 (20), 65 (9), 55 (27), 51 (12). Anal. calc. for $C_{24}H_{24}N_2O_4S$: C 66.03, H 5.55, N 6.42; found C 65.80, H 5.51, N 6.54.

3-(*N*-*p*-Nitrobenzenesulfonylamino)-cyclohexene (**6**). M.p. 120-121°. IR ($CHCl_3$): 3381*m*, 3106*w*, 3030*w*, 2929*w*, 1606*m*, 1533*vs*, 1412*m*, 1350*vs*, 1311*m*, 1164*s*, 1093*w*, 1069*m*, 918*vs*, 894*w*, 855*m*. ^1H NMR ($CDCl_3$, 400 MHz): 1.51-1.64 (m, 3H); 1.78-1.84 (m, 1H); 1.93-2.00 (m, 2H); 3.89-3.95 (m, 1H); 4.67 (d, J = 8.8 Hz, 1H); 5.34-5.38 (m, 1H); 5.81-5.86 (m, 1H); 8.09 and 8.38 (AA'XX' system, app. d, J = 9.2 Hz, 4H). ^{13}C NMR ($CDCl_3$): 19.1 (t); 24.4 (t); 30.2 (t); 49.4 (d); 124.4 (d), 126.2 (d); 128.1 (d), 132.3 (d), 147.3 (s); 150.0 (s). MS: 282 (M^+, 12), 254 (100), 218 (35), 200 (60), 137 (38), 122 (35), 96 (88), 79 (27), 68 (74). HR-MS: 282.0669 ($C_{12}H_{14}N_2O_4S^+$, calc. 282.0674).

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