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Use of a sterically demanding Lewis acid to direct ring expansion of monoactivated methylenecyclopropanes

Catherine Taillier, Yann Bethuel and Mark Lautens*

Department of Chemistry, Davenport Chemical Laboratories, 80 St George Street, University of Toronto, Toronto, Ontario M5S 3H6, Canada

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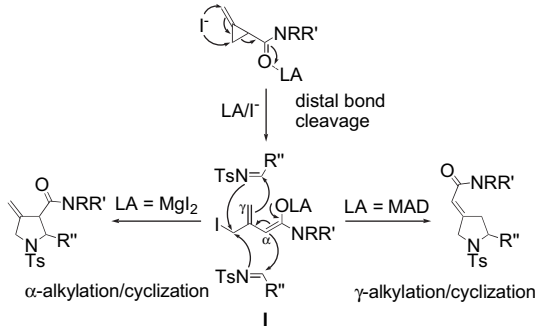
Abstract—A novel synthetic route for the preparation of functionalized alkylidene pyrrolidines via a MAD/*n*-Bu_4NI-mediated ring expansion of monoactivated MCP was developed. The substrate scope for this reaction was found to be broad for a variety of aldimines and symmetrically as well as unsymmetrically monoactivated MCPs yielding the corresponding five-membered heterocyclic compounds in good yields (up to 92%). This methodology complements previous reports on the ring expansion of MCPs showing that selective syntheses of different heterocyclic scaffolds could be achieved from the same MCP by just changing the catalyst system.

1. Introduction

Over the past few decades, nucleophilic ring opening of electron deficient cyclopropyl derivatives and subsequent use of the resulting enolate intermediates for the construction of heterocyclic compounds has received considerable attention.[1,2] However, the development of novel and simple ring expansion methods constitutes a continuing challenge, as five- and six-membered cycles are essential structural units, which could serve as precursors to a variety of chemically and biologically important compounds.[3]

Recently, we reported the syntheses of cyclic diazadienes[4] and β,γ-unsaturated lactams[5] by Mg-mediated ring expansion of methylenecyclopropyl (MCP) derivatives in the absence of an electrophile. Interestingly, when the latter transformation was conducted in the presence of aryl *N*-tosyl aldimines, 2,3-disubstituted methylene pyrrolidines were obtained.[6] A key intermediate was proposed to be the trifunctional vinylogous enolate **I** generated in situ from ring opening of the MCP amide. We observed that addition of the electrophile occurred exclusively at the α-position of the vinylogous enolate in the presence of MgI_2. We postulated that use of a sterically demanding Lewis acid such as Yamamoto's MAD[7] reagent might direct the reaction to the γ-position and we now describe our success with this concept. As a result, regioisomeric alkylidene pyrrolidines now become readily available (Scheme 1).



Scheme 1. Divergent selectivity in the Lewis acid-mediated ring expansion of monoactivated MCP amides.

2. Results and discussion

Inspired by the early work from Carreira and co-workers,[2] ring opening of MCP amides promoted by MgI_2 is believed to occur through electrophilic activation of the carbonyl group and simultaneous attack of iodide released from MgI_2 (Scheme 1). To mimic the push–pull behaviour of MgI_2 and allow ring opening to occur, we envisioned using a Lewis acid in combination with an external source of iodide. A preliminary study focused on the screening of Lewis acids[8] and sources of iodide revealed that MAD [methylaluminum bis[2,6-di-*tert*-butyl-4-methyl-phenoxide)] and *n*-Bu_4NI were the most effective. Indeed, this combination of reagents was able to promote ring opening of MCP amide **1** in the presence of imine **2a** (Scheme 2). Moreover, we were particularly pleased to observe that the reaction led to the exclusive formation of alkylidene pyrrolidine **3a** (91%) as a

* Corresponding author. Tel.: +1 416 978 6083; fax: +1 416 946 8185; e-mail: mlautens@alchemy.chem.utoronto.ca

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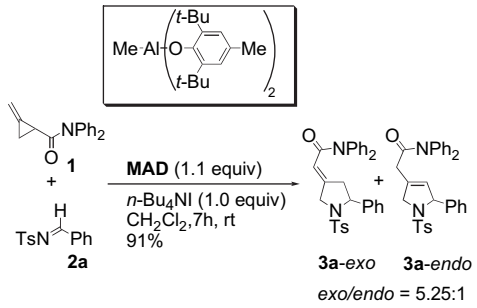


Scheme 2. Preliminary results for the MAD/*n*-Bu_4NI-promoted ring expansion of MCP **1** in the presence of *N*-tosyl aldimine **2a**.

mixture of two isomers, which would result from γ-alkylation of a vinylogous enolate intermediate **I**. In addition, it was shown that the major isomer **3a**-*exo* was obtained as only one geometric isomer of *E* configuration.[9] The observed regioselectivity might be explained by the size of the Lewis acid, which would prevent alkylation from occurring at the α-position.[10] But it is not possible at this time to rule out effects arising from the change in metal (Mg vs Al) or reaction conditions. Furthermore, it is reasonable to think that the **3a**-*exo* product would be formed directly following the postulated pathway, while the isomer **3a**-*endo* would arise from isomerization of **3a**-*exo*. Indeed, when the *exo*-regioisomer of **3a** was subjected to the reaction conditions, a partial isomerization was observed leading to a mixture of **3a**-*exo*/**3a**-*endo* in a 1:1 ratio.

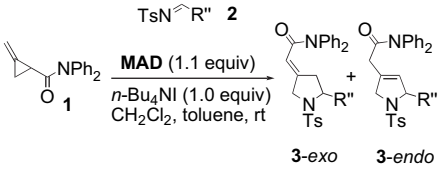
Among the changes that we made to optimize the reaction, solvent, reaction time, temperature or quantity of MAD and iodide, were varied but the original conditions [MCP (1.0 equiv), aldimine (1.2 equiv), MAD (1.1 equiv), *n*-Bu_4NI (1.0 equiv), CH_2Cl_2, rt] proved to give the best overall yields and limit the competing isomerization reaction.[11]

The substrate scope for the MAD/*n*-Bu_4NI-mediated ring expansion of *N*,*N*-diphenyl MCP amide **1** was examined using a variety of aldimines. Representative results of the ring expansion of MCP **1** with substituted aromatic, heteroaromatic and aliphatic aldimines using a mixture of MAD and *n*-Bu_4NI in dichloromethane at room temperature are shown in Table 1. In all cases, the reactions proceeded smoothly providing the γ-alkylation products **3** in yields up to 92%. As previously mentioned, partial isomerization of the *exo*-product was observed and variable ratio of *exo*/*endo* isomers were obtained.

In the case of aromatic aldimines, the electronic nature of the substituents seemed to have little or no influence on the success or the rate of the ring expansion process (entries 1–9). However, the presence of sterically demanding *ortho*-substituents on the aromatic ring tends to lower the reactivity (entries 1, 4, 6). Longer reaction times were required in these cases for complete conversion of the starting MCP **1**.

Use of heteroaromatic aldimines was also found to be effective in the ring expansion of MCP **1** with MAD/*n*-Bu_4NI as the promoter (entries 10–12). For the furyl series, reaction yields were found to be dependent on the position of the heteroatom in the aromatic ring. On the other hand, when the reaction was carried out with the 2-pyrrole-substituted

Table 1. Scope of the reaction with various *N*-tosyl aldimines



Entry	Imine	R″	Time (h)	Product	Yield[a] (%)	*exo*/*endo*
1	**2b**	2,4-Me_2–C_6H_3	12	**3b**	61	4:1
2	**2c**	2-Naphthyl	5	**3c**	92	>20:1
3	**2d**	4-MeO–C_6H_4	8	**3d**	64	13:1
4	**2e**	2-Br–C_6H_4	24	**3e**	41	8:1
5	**2f**	4-Br–C_6H_4	8	**3f**	89	4.25:1
6	**2g**	2-CF_3–C_6H_4	18	**3g**	58	4.5:1
7	**2h**	4-CF_3–C_6H_4	8	**3h**	67	2.85:1
8	**2i**	3-NO_2–C_6H_4	14	**3i**	61	5:1
9	**2j**	2,4-Cl_2–C_6H_3	12	**3j**	89	18:1
10	**2k**	2-Furyl	8	**3k**	86	>20:1
11	**2l**	3-Furyl	16	**3l**	38	8.5:1
12	**2m**	2-(*N*-Me-pyrrole)	18	**3m**	46	>20:1
13	**2n**	Cinnamyl	18	**3n**	81	>20:1[b]
14	**2o**	*i*-Bu	24	**3o**	59	>20:1
15	**2p**	Cyclohexyl	24	**3p**	35	>20:1

[a] Isolated overall yields.
[b] Isolated as an inseparable mixture of geometric isomers *E*/*Z*=4.5:1.

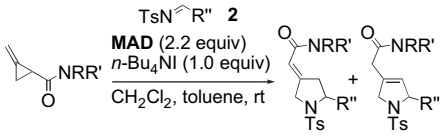
aldimine **2m**, the corresponding pyrrolidine **3m** could be isolated in 46% yield. In the cases where a heteroatom is present at the 2-position, no isomerization of the *exo*-product was observed. We also found that the reaction could be successfully achieved with the conjugated aldimine **2n** in 81% yield (entry 13).

To further expand the scope of the reaction, aliphatic aldimines **2o** and **2p** were also tested (entries 14 and 15). Despite lower reactivities, the ring expansion conditions allowed the formation of expected alkyl-substituted pyrrolidines **3o** and **3p** in 59% and 35% yield, respectively. The success of these reactions was governed by the size of the alkyl aldimines. Indeed, reaction of the aldimine substituted with a *tert*-butyl group failed completely.

We also examined the reaction of other *N*,*N*-unsymmetrically substituted MCP derivatives **4** and **5** with different tosyl imines (**2**) (Table 2). An excess of MAD (2.2 equiv) gave the expected alkylidene pyrrolidines **6** and **7** in excellent selectivity but in moderate to low yields (28–55%). Neither electronic nor steric effects can be used to explain the dramatic changes in the isomeric ratio. The *exo*-compound could easily be transformed into the more stable *endo*-derivative by treatment with base suggesting that the *exo*-isomer is the kinetic product.[12] The results obtained with the Weinreb amide MCPs (**5**) were particularly gratifying since the analogous MgI_2-mediated ring expansion reactions yielding methylene pyrrolidines is so far limited to *N*,*N*-diaryl MCP amides.

In conclusion, we have developed a novel route for the preparation of functionalized alkylidene pyrrolidines via MAD/*n*-Bu_4NI-mediated ring expansion of monoactivated methylenecyclopropanes. This discovery complements previous reports on the ring expansion of MCPs showing that selective syntheses of different pyrrolidine scaffolds could be achieved from the same MCP by simply changing the catalyst system.

Table 2. Use of monoactivated unsymmetrical MCP derivatives



4-5 **6-7**-*exo* **6-7**-*endo*

Entry	MCP	R	R′	R″	Product	Yield[a] (%)	*exo*/*endo*
1	4	Ph	2-Pyr	Ph	**6a**	55	>20:1
2	4	Ph	2-Pyr	2-Naphthyl	**6b**	48	<1:20
3	4	Ph	2-Pyr	4-CF_3–C_6H_4	**6c**	33	<1:20
4	4	Ph	2-Pyr	4-MeO–C_6H_4	**6d**	39	>20:1
5	4	Ph	2-Pyr	2-(*N*-Me–pyrrole)	**6e**	28	<1:20
6	5	Me	OMe	Ph	**7a**	51	>20:1
7	5	Me	OMe	2-Naphthyl	**7b**	52	>20:1
8	5	Me	OMe	4-CF_3–C_6H_4	**7c**	33	<1:20

[a] Isolated overall yields.

3. Experimental

3.1. General

All flasks were flame-dried under a stream of argon and cooled before use. All experiments were performed under anhydrous conditions under an atmosphere of argon. Solvents and solutions were transferred with syringes and cannulae using standard inert atmosphere techniques. Tetrahydrofuran (THF) was distilled under nitrogen from Na/benzophenone immediately prior to use. Dichloromethane was distilled under nitrogen from CaH_2 immediately before use. All reagents were used as received from Sigma–Aldrich except *n*-Bu_4NI, which was recrystallized from toluene (5 mL/g) at 110 °C by adding hot hexanes (three-times the amount of toluene). Column chromatography was carried out as 'flash chromatography' as reported by Still[13] using neutral silica (Silicycle, Quebec, Canada).

Melting points were recorded using a Fisher–Johns melting point apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded using either a Varian Gemini 300 or Mercury Unity 400 MHz spectrometers in $CDCl_3$ with chemical shifts relative to tetramethylsilane (TMS, 0 ppm) unless otherwise reported. Spectral features are tabulated in the following order: chemical shift (δ, ppm); number of protons; multiplicity (s-singlet, d-doublet, t-triplet, q-quartet, m-complex multiplet); coupling constants (J, Hz). No special notation is used for equivalent carbons. IR spectra were obtained using a Nicolet DX FTIR spectrometer as thin films on NaCl plates. High-resolution mass spectra were obtained using a VG 70-250S (double focusing) mass spectrometer at 70 eV.

3.2. Preparation of starting materials

p-Toluenesulfonyl (tosyl) aromatic and aliphatic aldimines **2a**–**p** were prepared in moderate to good yields according to known procedures.[14] 2-Methylenecyclopropane carboxylic acid diphenylamide **1**, 2-methylenecyclopropane carboxylic acid phenyl-pyridin-2-yl-amide **4** and 2-methylenecyclopropane carboxylic acid methoxymethylamide **5** were prepared from 2-methylenecyclopropane carboxylic acid ethyl ester and 2-methylenecyclopropane carboxylic acid.[15]

3.2.1. 2-Methylenecyclopropane carboxylic acid diphenylamide 1.[6a] To a solution of MCP carboxylic acid (3.96 g, 40 mmol) and triethylamine (5.58 mL, 40 mmol) in THF (150 mL) was added isobutylchloroformate (5.19 mL, 40 mmol) at 0 °C. The solution was stirred at 0 °C for 15 min followed by the addition of lithium diphenylamide, which was prepared by adding *n*-BuLi (17.6 mL, 44 mmol, 2.5 M solution in hexanes) into a solution of diphenylamine (7.45 g, 44 mmol) in THF (20 mL) at −78 °C and warming to room temperature for 30 min. The resulting mixture was stirred at room temperature for 4 h. After quenching with saturated NH_4Cl solution, the reaction mixture was extracted with EtOAc (2×250 mL). The combined organic extracts were washed with H_2O (250 mL), brine (250 mL) and dried over $MgSO_4$, filtered and concentrated. Flash chromatography on silica gel (hexanes/EtOAc 8:1) furnished the product **1** (6.5 g, 26 mmol, 65%) as a beige solid. Mp=51–53 °C; R_f=0.52 (hexanes/EtOAc 3:1); IR (CH_2Cl_2) ν 3062, 3036, 2991, 1742, 1668, 1594, 1490, 1448, 1361, 1251, 1177, 1158, 1103, 1074, 1025, 1003, 971, 900, 754, 755, 700, 616 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.46–7.14 (10H, m), 5.51–5.44 (2H, m), 2.24–2.15 (1H, m), 2.05–1.96 (1H, m), 1.53–1.43 (1H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.7, 142.9, 132.4, 129.4, 128.5, 127.9, 127.1, 103.4, 19.9, 11.5; HRMS calcd for $C_{17}H_{15}NO$ $(M)^+$ 249.1154, found 249.1166.

3.2.2. 2-Methylenecyclopropane carboxylic acid phenyl-pyridin-2-yl-amide 4. To a solution of MCP carboxylic acid (3.96 g, 40 mmol, 1 equiv) and triethylamine (5.58 mL, 40 mmol, 1 equiv) in THF (150 mL) was added isobutylchloroformate (5.19 mL, 40 mmol, 1 equiv) at 0 °C. The solution was stirred at 0 °C for 15 min followed by the addition of lithium *N*-phenyl(2-pyridyl)amide, which was prepared by adding *n*-BuLi (17.6 mL, 2.5 M solution in hexanes, 44 mmol, 1.1 equiv) into a solution of *N*-phenyl(2-pyridyl)-amine (7.45 g, 44 mmol, 1.1 equiv) in THF (20 mL) at −78 °C and warming to room temperature for 30 min. The resulting mixture was stirred at room temperature for 6 h. After quenching with saturated NH_4Cl solution, the reaction mixture was extracted with EtOAc (2×250 mL). The combined organic extracts were washed with H_2O (250 mL), brine (250 mL) and dried over $MgSO_4$, filtered and

concentrated. Flash chromatography on silica gel (hexanes/EtOAc 8:1) furnished the product **4** (6.3 g, 25 mmol, 63%) as a pale yellow solid. Mp=61–63 °C; R_f=0.45 (hexanes/EtOAc 3:1); IR (CH_2Cl_2) ν 3032, 3011, 2989, 1673, 1585, 1491, 1466, 1432, 1356, 1239, 1185, 1105, 904, 778, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.42 (1H, dm, J=4.0 Hz), 7.73 (1H, tm, J=7.2 Hz), 7.56 (1H, d, J=8.0 Hz), 7.48–7.30 (5H, m), 7.11 (1H, m), 5.03 (1H, m), 5.47 (1H, m), 2.22–2.17 (1H, m), 2.05–1.97 (1H, m), 1.54–1.45 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 155.3, 149.0, 141.8, 137.9, 132.3, 129.7, 129.0, 127.8, 121.4, 103.7, 20.2, 11.6; HRMS calcd for $C_{16}H_{14}N_2O$ $(M)^+$ 249.1028, found 249.1022.

3.2.3. 2-Methylenecyclopropane carboxylic acid methoxymethylamide 5. To a solution of MCP acid (0.59 g, 6.0 mmol, 1 equiv) in CH_2Cl_2 (50 mL) were added DMAP (0.15 g, 1.2 mmol, 20 mol %) and *N*,*O*-dimethylhydroxylamine hydrochloride (0.87 g, 9.0 mmol, 1.5 equiv). After complete dissolution, the solution was cooled to 0 °C and diisopropylamine (1.56 mL, 9.00 mmol, 1.5 equiv) and EDCI (1.71 g, 9.00 mmol, 1.5 equiv) were added. After 30 min of stirring at 0 °C and 16 h at room temperature, the reaction mixture was washed with a saturated aqueous solution of $NaHCO_3$. The aqueous layer was extracted with EtOAc (3×15 mL) and the combined organic extracts were washed with H_2O, dried over $MgSO_4$, filtered and concentrated. Flash chromatography on silica gel (hexanes/EtOAc 5:1) furnished the product **5** (0.45 g, 3.2 mmol, 55%) as a colourless oil. R_f=0.31 (hexanes/EtOAc 3:1); IR (CH_2Cl_2) ν 3502, 3076, 2971, 2938, 1741, 1641, 1493, 1417, 1385, 1180, 1110, 989, 908, 887 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.51 (1H, m), 5.46 (1H, m), 3.78 (3H, s), 3.23 (s, 3H), 2.81 (br s, 1H), 1.88 (m, 1H), 1.61 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 131.3, 103.7, 61.6, 32.5, 15.6, 10.2; HRMS calcd for $C_7H_{12}NO_2$ $(M+H)^+$ 142.0862, found 142.0869.

3.3. MAD/*n*-Bu_4NI-mediated ring expansion of MCPs

3.3.1. General procedure A. To a solution of 2,6-di-*tert*-butyl-4-methylphenol (97 mg, 0.44 mmol, 2.2 equiv) in toluene (0.45 mL) at room temperature was added a solution of trimethylaluminum (0.11 mL, 2 M in toluene, 0.22 mmol, 1.1 equiv) dropwise. After 1 h of stirring at room temperature, the resulting solution was cooled to 0 °C and a solution of MCP **1** (0.20 mmol, 50 mg, 1 equiv), *N*-tosyl aldimine (0.24 mmol, 1.2 equiv) and *n*-Bu_4NI (74 mg, 0.2 mmol, 1 equiv) in CH_2Cl_2 (2 mL) was added dropwise. The resulting yellow solution was stirred at 0 °C for 30 min and allowed to warm to room temperature. Reaction completion was monitored by TLC. The reaction mixture was poured into a saturated aqueous solution of NH_4Cl and the aqueous layer was extracted with EtOAc (three-times 25 mL). The combined organic extracts were washed with H_2O (15 mL) and brine (15 mL), dried over Na_2SO_4, filtered and concentrated in vacuo. Purification of the resulting oil by chromatography on silica gel (gradient hexanes/EtOAc; 5:1–3:1) gave the expected products.

General procedure A was followed (stirring at rt for 7 h) using *N*-benzylidene-4-methyl-benzenesulfonamide (62 mg, 0.24 mmol, 1.2 equiv).

3.3.1.1. (*E*)-*N*,*N*-Diphenyl-2-[5-phenyl-1-(toluene-4-sulfonyl)pyrrolidin-3-ylidene]acetamide 3a-*exo*. White solid (78 mg, 76%). Mp=168–170 °C; R_f=0.28 (hexanes/EtOAc=3:1); IR (thin film) ν 3061, 2923, 1666, 1596, 1491, 1384, 1348, 1268, 1164, 1093, 759, 736, 701, 667 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.60–7.54 (2H, m), 7.39–7.04 (17H, m), 5.76 (1H, m), 5.03 (1H, dd, J=8.8, 3.1 Hz), 4.17 (1H, d, J=16.6 Hz), 4.07 (1H, dm, J=16.6 Hz), 3.40 (1H, dm, J=18.7 Hz), 3.11 (1H, br dd, J=18.7, 8.8 Hz), 2.41 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.4, 154.2, 143.6, 142.3, 141.1, 134.7, 129.6, 128.4, 127.4, 127.3, 126.3, 114.7, 63.3, 53.7, 39.6, 21.5; HRMS calcd for $C_{31}H_{28}N_2O_3S$ $(M)^+$ 508.1821, found 508.1831.

3.3.1.2. *N*,*N*-Diphenyl-2-[5-phenyl-1-(toluene-4-sulfonyl)-2,5-dihydro-1*H*-pyrrol-3-yl]acetamide 3a-*endo*. Colourless oil (15 mg, 15%). R_f=0.21 (hexanes/EtOAc=3:1); IR (CH_2Cl_2) ν 3062, 2921, 1667, 1596, 1494, 1338, 1161, 1075, 757, 701, 672 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.49–7.05 (19H, m), 5.48 (1H, br s), 5.33 (1H, br s), 4.35–4.22 (2H, m), 3.13 (2H, s), 2.36 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 143.0, 140.4, 135.6, 132.4, 129.4, 128.4, 127.7, 127.5, 127.3, 127.2, 70.2, 56.8, 35.8, 21.4; HRMS calcd for $C_{31}H_{28}N_2O_3S$ $(M)^+$ 508.1821, found 508.1827.

General procedure A was followed (stirring at rt for 12 h) using *N*-(2,4-dimethyl-benzylidene)-4-methyl-benzenesulfonamide (69 mg, 0.24 mmol, 1.2 equiv).

3.3.1.3. (*E*)-2-[5-(2,4-Dimethylphenyl)-1-(toluene-4-sulfonyl)pyrrolidin-3-ylidene]-*N*,*N*-diphenylacetamide 3b-*exo*. White solid (52 mg, 49%). Mp=192–194 °C; R_f=0.25 (hexanes/EtOAc=3:1); IR (CH_2Cl_2) ν 3059, 2921, 1669, 1643, 1596, 1491, 1382, 1348, 1267, 1164, 1093, 735, 701, 665 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.62–7.54 (2H, m), 7.33–6.84 (15H, m), 5.77 (1H, m), 5.15 (1H, dd, J=8.8, 3.7 Hz), 4.19 (2H, br s), 3.25 (1H, br dd, J=18.5, 8.8 Hz), 3.11 (1H, br d, J=18.5 Hz), 2.42 (3H, s), 2.29 (3H, s), 2.28 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 154.0, 143.6, 142.3, 137.1, 136.6, 134.8, 134.0, 131.3, 129.6, 129.4, 127.4, 126.5, 125.3, 114.8, 60.7, 54.4, 39.7, 21.5, 20.9, 19.3; HRMS calcd for $C_{33}H_{32}N_2O_3S$ $(M)^+$ 536.2134, found 536.2133.

3.3.1.4. 2-[5-(2,4-Dimethylphenyl)-1-(toluene-4-sulfonyl)-2,5-dihydro-1*H*-pyrrol-3-yl]-*N*,*N*-diphenylacetamide 3b-*endo*. Colourless oil (13 mg, 12%). R_f=0.16 (hexanes/EtOAc=3:1); IR (thin film) ν 3062, 2921, 1672, 1596, 1491, 1346, 1162, 1096, 671 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.54–7.05 (15H, m), 6.92–6.87 (2H, m), 5.68 (1H, m), 5.25 (1H, m), 4.37–4.24 (2H, m), 3.09 (2H, s), 2.38 (3H, s), 2.33 (3H, s), 2.27 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 143.0, 137.0, 135.6, 135.5, 134.5, 131.6, 131.2, 129.4, 127.6, 127.3, 127.1, 127.0, 67.0, 57.0, 35.8, 21.5, 21.0, 19.0; HRMS calcd for $C_{33}H_{32}N_2O_3S$ $(M)^+$ 536.2134, found 536.2129.

General procedure A was followed (stirring at rt for 5 h) using 4-methyl-*N*-naphthalen-1-ylmethylene-benzenesulfonamide (74 mg, 0.24 mmol, 1.2 equiv).

3.3.1.5. (*E*)-2-[5-Naphthalen-1-yl-1-(toluene-4-sulfonyl)-pyrrolidin-3-ylidene]-*N*,*N*-diphenylacetamide 3c-*exo*. Colourless oil (102 mg, 92%). R_f=0.25 (hexanes/EtOAc=3:1); IR (thin film) ν 3059, 2921, 1669, 1643, 1597, 1490, 1382, 1348, 1292, 1270, 1163, 1093, 735, 701, 669 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.92–7.62 (5H, m), 7.51–6.98 (16H, m), 5.84–5.74 (2H, m), 4.41–4.23 (2H, m), 3.42–3.34 (2H, m), 2.41 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.6, 154.3, 144.1, 142.6, 137.5, 135.3, 134.2, 130.2, 130.0, 129.8, 129.2, 128.4, 127.7, 126.6, 126.5, 125.3, 123.5, 123.1, 115.2, 61.6, 54.6, 40.5, 21.8; HRMS calcd for $C_{35}H_{30}N_2O_3S$ $(M)^+$ 558.1977, found 558.1976.

General procedure A was followed (stirring at rt for 8 h) using *N*-(4-methoxy-benzylidene)-4-methyl-benzenesulfonamide (69 mg, 0.24 mmol, 1.2 equiv).

3.3.1.6. (*E*)-2-[5-(4-Methoxyphenyl)-1-(toluene-4-sulfonyl)pyrrolidin-3-ylidene]-*N*,*N*-diphenylacetamide 3d-*exo*. Yellow solid (64 mg, 59%). Mp=126–128 °C; R_f=0.26 (hexanes/EtOAc=3:1); IR (CH_2Cl_2) ν 3061, 2925, 1668, 1644, 1596, 1513, 1490, 1383, 1347, 1293, 1249, 1163, 1092, 1033, 732, 701, 665 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.83–7.53 (2H, m), 7.41–7.08 (14H, m), 6.84–6.78 (2H, m), 5.76 (1H, br s), 4.95 (1H, m), 4.18–4.01 (2H, m), 3.79 (3H, s), 3.37 (1H, br d, J=18.7 Hz), 3.08 (1H, br dd, J=18.7, 8.8 Hz), 2.42 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 154.4, 143.6, 143.5, 142.4, 139.1, 134.8, 133.2, 129.7, 129.6, 129.2, 127.7, 127.4, 126.4, 114.5, 113.8, 63.0, 55.3, 53.7, 39.6, 21.5; HRMS calcd for $C_{32}H_{30}N_2O_4S$ $(M)^+$ 538.1926, found 538.1928.

General procedure A was followed (stirring at rt for 24 h) using *N*-(2-bromo-benzylidene)-4-methyl-benzenesulfonamide (81 mg, 0.24 mmol, 1.2 equiv).

3.3.1.7. (*E*)-2-[5-(2-Bromophenyl)-1-(toluene-4-sulfonyl)pyrrolidin-3-ylidene]-*N*,*N*-diphenylacetamide 3e-*exo*. White solid (43 mg, 37%). Mp=198–200 °C; R_f=0.24 (hexanes/EtOAc=3:1); IR (CH_2Cl_2) ν 3061, 2924, 1669, 1643, 1595, 1491, 1384, 1351, 1292, 1267, 1165, 1093, 755, 701, 665 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.74–7.66 (2H, m), 7.54–7.06 (16H, m), 5.77 (1H, s), 5.24 (1H, dd, J=9.4, 4.4 Hz), 4.27 (1H, dd, J=15.8, 1.3 Hz), 4.11 (1H, d, J=15.8 Hz), 3.86 (1H, br dd, J=18.9, 9.2 Hz), 3.15 (1H, dm, J=18.9 Hz), 2,45 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 152.8, 144.0, 142.3, 141.4, 133.6, 132.9, 129.8, 129.2, 128.8, 127.8, 127.5, 127.4, 115.0, 63.2, 55.0, 39.8, 21.6; HRMS calcd for $C_{31}H_{27}BrN_2O_3S$ $(M)^+$ 586.0926, found 586.0924.

General procedure A was followed (stirring at rt for 8 h) using *N*-(4-bromo-benzylidene)-4-methyl-benzenesulfonamide (81 mg, 0.24 mmol, 1.2 equiv).

3.3.1.8. (*E*)-2-[5-(4-Bromophenyl)-1-(toluene-4-sulfonyl)pyrrolidin-3-ylidene]-*N*,*N*-diphenylacetamide 3f-*exo*. Yellow solid (84 mg, 72%). Mp=188–190 °C; R_f=0.28 (hexanes/EtOAc=3:1); IR (CH_2Cl_2) ν 3061, 1668, 1640, 1595, 1490, 1384, 1348, 1268, 1163, 1093, 758, 701, 667 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.59–7.02 (18H, m), 5.77 (1H, m), 4.93 (1H, dd, J=8.8, 3.5 Hz), 4.18–4.03 (2H, m), 3.35 (1H, dm, J=18.7 Hz), 3.12 (1H, m), 2.43 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.6, 153.7, 144.1, 142.6, 140.5, 134.9, 131.8, 130.0, 129.8, 128.4, 127.7, 121.7, 115.1, 63.1, 54.0, 39.8, 21.8; HRMS calcd for $C_{31}H_{27}BrN_2O_3S$ $(M)^+$ 586.0926, found 586.0935.

3.3.1.9. 2-[5-(4-Bromo-phenyl)-1-(toluene-4-sulfonyl)-2,5-dihydro-1*H*-pyrrol-3-yl]-*N*,*N*-diphenylacetamide 3f-*endo*. Colourless oil (20 mg, 17%). R_f=0.22 (hexanes/EtOAc=3:1); IR (thin film) ν 3061, 1664, 1595, 1491, 1341, 1162, 1096, 702, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.60–7.07 (18H, m), 5.42 (1H, s), 5.31 (1H, s), 4.32–4.24 (2H, m), 3.13 (2H, s), 2.38 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.0, 143.5, 139.7, 135.7, 133.3, 131.7, 129.7, 129.4, 127.4, 127.2, 121.9, 69.8, 57.1, 36.0, 21.7; HRMS calcd for $C_{31}H_{27}BrN_2O_3S$ $(M)^+$ 586.0926, found 586.0922.

General procedure A was followed (stirring at rt for 18 h) using 4-methyl-*N*-(2-trifluoromethyl-benzylidene)-benzenesulfonamide (78 mg, 0.24 mmol, 1.2 equiv).

3.3.1.10. (*E*)-*N*,*N*-Diphenyl-2-[1-(toluene-4-sulfonyl)-5-(2-trifluoromethylphenyl)pyrrolidin-3-ylidene]acetamide 3g-*exo*. Pale yellow solid (55 mg, 48%). Mp=158–160 °C; R_f=0.23 (hexanes/EtOAc=3:1); IR (CH_2Cl_2) ν 3062, 2925, 1670, 1643, 1597, 1491, 1387, 1353, 1313, 1275, 1164, 1119, 756, 701, 665 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.70–7.07 (18H, m), 5.82 (1H, m), 5.19 (1H, dd, J=9.4, 4.6 Hz), 4.33 (1H, br d, J=15.6 Hz), 4.06 (1H, m), 3.40 (1H, br dd, J=19.1, 9.0 Hz), 3.12 (1H, br d, J=19.1 Hz), 2.44 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 152.3, 144.1, 142.3, 133.1, 132.1, 129.8, 129.7, 127.8, 127.4, 127.3, 125.8, 125.7, 115.1, 59.7, 55.3, 41.4, 21.5; HRMS calcd for $C_{32}H_{27}F_3N_2O_3S$ $(M)^+$ 576.1694, found 576.1685.

3.3.1.11. *N*,*N*-Diphenyl-2-[1-(toluene-4-sulfonyl)-5-(2-trifluoromethylphenyl)-2,5-dihydro-1*H*-pyrrol-3-yl]acetamide 3g-*endo*. Colourless oil (12 mg, 10%). R_f=0.16 (hexanes/EtOAc=3:1); IR (thin film) ν 3060, 2923, 1674, 1597, 1492, 1454, 1350, 1313, 1272, 1163, 1118, 1058, 1036, 733, 702, 672 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.82–7.65 (2H, m), 7.63–7.48 (2H, m), 7.37–7.01 (14H, m), 5.74 (1H, br s), 5.17 (1H, s), 4.45 (1H, dd, J=14.2, 5.3 Hz), 4.32 (1H, d, J=14.2 Hz), 3.05 (2H, s), 2.40 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 143.7, 140.7, 134.0, 132.4, 131.7, 129.8, 129.7, 129.0, 127.9, 127.6, 127.3, 126.4, 125.4, 125.3, 66.3, 57.6, 35.9, 21.5; HRMS calcd for $C_{32}H_{27}F_3N_2O_3S$ $(M)^+$ 576.1694, found 576.1694.

General procedure A was followed (stirring at rt for 8 h) using 4-methyl-*N*-(4-trifluoromethyl-benzylidene)-benzenesulfonamide (78 mg, 0.24 mmol, 1.2 equiv).

3.3.1.12. (*E*)-*N*,*N*-Diphenyl-2-[1-(toluene-4-sulfonyl)-5-(4-trifluoromethylphenyl)pyrrolidin-3-ylidene]acetamide 3h-*exo*. White solid (57 mg, 50%). Mp 154–156 °C; R_f=0.25 (hexanes/EtOAc=3:1); IR (CH_2Cl_2) ν 3062, 2925, 1668, 1644, 1596, 1491, 1384, 1326, 1268, 1164, 1123, 1067, 737, 701, 667 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.59–7.48 (4H, m), 7.45–7.07 (14H, m), 5.80 (1H, m), 5.02 (1H, dd, J=8.8, 3.8 Hz), 4.23–4.04 (2H, m), 3.38 (1H, m), 3.20 (1H, m), 2.41 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$)

δ 165.5, 153.4, 144.2, 142.5, 134.8, 130.0, 127.6, 127.0, 125.7, 115.2, 63.2, 54.2, 40.0, 21.7; HRMS calcd for $C_{32}H_{27}F_3N_2O_3S$ $(M)^+$ 576.1694, found 576.1696.

3.3.1.13. *N,N*-Diphenyl-2-[1-(toluene-4-sulfonyl)-5-(4-trifluoromethylphenyl)-2,5-dihydro-1*H*-pyrrol-3-yl]-acetamide 3h-*endo*. Colourless oil (20 mg, 17%). R_f=0.19 (hexanes/EtOAc=3:1); IR (thin film) ν 3064, 2923, 1672, 1596, 1492, 1346, 1325, 1162, 1124, 1066, 733, 702, 672 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.84–7.76 (2H, m), 7.54–7.10 (16H, m), 5.51 (1H, br s), 5.34 (1H, m), 4.38–4.30 (2H, m), 3.15 (2H, br s), 2.35 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.1, 143.7, 139.4, 135.6, 133.6, 129.9, 129.7, 127.9, 127.4, 127.0, 126.6, 125.6, 69.9, 57.3, 35.9, 21.6; HRMS calcd for $C_{32}H_{27}F_3N_2O_3S$ $(M)^+$ 576.1694, found 576.1769.

General procedure A was followed (stirring at rt for 14 h) using 4-methyl-*N*-(3-nitro-benzylidene)-benzenesulfonamide (73 mg, 0.24 mmol, 1.2 equiv).

3.3.1.14. (*E*)-2-[5-(3-Nitrophenyl)-1-(toluene-4-sulfonyl)pyrrolidin-3-ylidene]-*N,N*-diphenylacetamide 3i-*exo*. Yellow oil (56 mg, 51%). R_f=0.17 (hexanes/EtOAc=3:1); IR (thin film) ν 3062, 2924, 1670, 1643, 1596, 1530, 1491, 1384, 1350, 1267, 1163, 1093, 738, 702, 665 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.14–7.94 (2H, m), 7.69–6.96 (16H, m), 5.85 (1H, m), 5.02 (1H, dd, J=8.2, 4.4 Hz), 4.22–4.13 (2H, m), 3.45–3.21 (2H, m), 2.41 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.5, 152.8, 144.1, 142.5, 134.5, 133.2, 130.0, 129.8, 127.6, 122.9, 121.4, 115.5, 62.9, 54.3, 40.1, 21.7; HRMS calcd for $C_{31}H_{27}N_3O_5S$ $(M)^+$ 553.1672, found 553.1678.

3.3.1.15. 2-[5-(3-Nitrophenyl)-1-(toluene-4-sulfonyl)-2,5-dihydro-1*H*-pyrrol-3-yl]-*N,N*-diphenylacetamide 3i-*endo*. Yellow foam (11 mg, 10%). Mp=178–180 °C; R_f= 0.11 (hexanes/EtOAc=3:1); IR (CH_2Cl_2) ν 3063, 2922, 2866, 1672, 1596, 1529, 1491, 1349, 1162, 1094, 738, 703, 669 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.12–8.00 (2H, m), 7.71–7.14 (16H, m), 5.53 (1H, m), 5.35 (1H, m), 4.41–4.26 (2H, m), 3.14 (2H, s), 2.37 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.5, 148.5, 144.0, 143.2, 135.2, 134.2, 133.8, 129.9, 129.8, 127.5, 126.4, 123.0, 122.3, 69.7, 57.5, 35.8, 21.7; HRMS calcd for $C_{31}H_{27}N_3O_5S$ $(M)^+$ 553.1672, found 553.1672.

General procedure A was followed (stirring at rt for 12 h) using *N*-(2,4-dichloro-benzylidene)-4-methyl-benzenesulfonamide (78 mg, 0.24 mmol, 1.2 equiv).

3.3.1.16. (*E*)-2-[5-(2,4-Dichlorophenyl)-1-(toluene-4-sulfonyl)pyrrolidin-3-ylidene]-*N,N*-diphenylacetamide 3j-*exo*. Yellow solid (97 mg, 84%). Mp=182–184 °C; R_f=0.28 (hexanes/EtOAc=3:1); IR (CH_2Cl_2) ν 3062, 2923, 1668, 1644, 1591, 1490, 1386, 1353, 1292, 1268, 1165, 1094, 701, 667, 613 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.69–7.62 (2H, m), 7.42–7.06 (15H, m), 5.78 (1H, br s), 5.18 (1H, dd, J=9.0, 4.2 Hz), 4.24 (1H, d, J=16.3 Hz), 4.09 (1H, d, J= 16.3 Hz), 3.35 (1H, dd, J=19.1, 9.3 Hz), 3.15 (1H, br d, J=19.1 Hz), 2.44 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 152.4, 144.1, 142.2, 138.5, 133.6, 133.4, 132.4, 129.8, 129.3, 128.4, 127.6, 127.1, 115.0, 60.6, 54.7, 39.5, 21.5; HRMS calcd for $C_{31}H_{26}Cl_2N_2O_3S$ $(M)^+$ 576.1041, found 576.1032.

3.3.1.17. 2-[5-(2,4-Dichlorophenyl)-1-(toluene-4-sulfonyl)-2,5-dihydro-1*H*-pyrrol-3-yl]-*N,N*-diphenylacetamide 3j-*endo*. Pale yellow oil (5 mg, 5%). R_f=0.18 (hexanes/EtOAc=3:1); IR (thin film) ν 3063, 2922, 1672, 1595, 1491, 1347, 1163, 1097, 815, 736, 703, 671 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.84–7.65 (3H, m), 7.47–7.05 (14H, m), 5.77 (1H, br s), 5.29 (1H, s), 4.40–4.27 (2H, m), 3.08 (2H, s), 2.41 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 143.8, 137.2, 134.2, 133.7, 132.8, 132.2, 129.8, 129.7, 129.0, 127.6, 126.4, 125.8, 66.8, 57.4, 35.8, 21.5; HRMS calcd for $C_{31}H_{26}Cl_2N_2O_3S$ $(M)^+$ 576.1041, found 576.1036.

General procedure A was followed (stirring at rt for 8 h) using *N*-furan-2-ylmethylene-4-methyl-benzenesulfonamide (60 mg, 0.24 mmol, 1.2 equiv).

3.3.1.18. (*E*)-2-[5-Furan-2-yl-1-(toluene-4-sulfonyl)-pyrrolidin-3-ylidene]-*N,N*-diphenylacetamide 3k-*exo*. Orange oil (86 mg, 86%). R_f=0.26 (hexanes/EtOAc=3:1); IR (thin film) ν 3061, 2922, 1672, 1643, 1596, 1491, 1383, 1347, 1268, 1164, 1093, 735, 702 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.57–7.08 (15H, m), 6.25–6.21 (2H, m), 5.79 (1H, m), 5.14 (1H, dd, J=8.8, 2.2 Hz), 4.17 (1H, d, J=16.0 Hz), 3.98 (1H, d, J=16.0 Hz), 3.51 (1H, dm, J=18.9 Hz), 3.11 (1H, ddm, J=18.9, 8.8 Hz), 2.39 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 154.5, 153.1, 143.3, 142.4, 142.2, 134.8, 129.5, 129.3, 127.3, 127.2, 114.2, 110.0, 107.5, 56.8, 52.9, 36.9, 21.4; HRMS calcd for $C_{29}H_{26}N_2O_4S$ $(M)^+$ 498.1613, found 498.1590.

General procedure A was followed (stirring at rt for 16 h) using *N*-furan-3-ylmethylene-4-methyl-benzenesulfonamide (60 mg, 0.24 mmol, 1.2 equiv).

3.3.1.19. (*E*)-2-[5-Furan-3-yl-1-(toluene-4-sulfonyl)-pyrrolidin-3-ylidene]-*N,N*-diphenylacetamide 3l-*exo*. Yellow oil (34 mg, 34%). R_f=0.29 (hexanes/EtOAc=3:1); IR (thin film) ν 3061, 2924, 1662, 1642, 1596, 1491, 1384, 1346, 1273, 1163, 1093, 1026, 759, 735, 701, 668 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.65–7.57 (2H, m), 7.42–7.08 (14H, m), 6.27 (1H, m), 5.77 (1H, m), 5.04 (1H, dd, J=8.6, 1.8 Hz), 4.14 (1H, dm, J=16.7 Hz), 3.95 (1H, dt, J=16.7, 1.8 Hz), 3.41 (1H, dm, J=18.4 Hz), 2.87 (1H, ddm, J=18.4, 7.7 Hz), 2.43 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 154.6, 143.7, 143.5, 142.4, 139.6, 135.1, 129.7, 129.5, 127.4, 127.3, 126.4, 125.9, 114.7, 109.2, 56.0, 52.8, 37.9, 21.5; HRMS calcd for $C_{29}H_{26}N_2O_4S$ $(M)^+$ 498.1613, found 498.1614.

General procedure A was followed (stirring at rt for 18 h) using 4-methyl-*N*-(1-methyl-1*H*-pyrrol-2-ylmethylene)-benzenesulfonamide (63 mg, 0.24 mmol, 1.2 equiv).

3.3.1.20. (*E*)-2-[1′-Methyl-1-(toluene-4-sulfonyl)-1,2,3,5-tetrahydro-1′*H*-[2,2′]bipyrrolyl-4-ylidene]-*N,N*-diphenyl-acetamide 3m-*exo*. Yellow oil (47 mg, 46%). R_f=0.22 (hexanes/EtOAc=3:1); IR (thin film) ν 3061, 2923, 1668, 1641, 1596, 1491, 1383, 1343, 1291, 1269, 1162, 1091, 735, 702, 671 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.44–7.11

(16H, m), 6.56 (1H, m), 5.97 (1H, dd, J=3.5, 2.9 Hz), 5.86 (1H, m), 5.73 (1H, m), 5.25 (1H, dd, J=8.5, 1.8 Hz), 4.12 (1H, m), 3.91 (1H, br d, J=17.3 Hz), 3.76 (3H, s), 2.44 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 155.8, 143.8, 142.5, 135.4, 129.9, 129.8, 127.5, 123.5, 113.8, 107.8, 106.6, 56.5, 52.3, 37.1, 34.5, 21.6; HRMS calcd for $C_{30}H_{29}N_3O_3S$ $(M+H)^+$ 512.2002, found 512.1999.

General procedure A was followed (stirring at rt for 18 h) using 4-methyl-*N*-(3-phenyl-allylidene)-benzenesulfonamide (68 mg, 0.24 mmol, 1.2 equiv).

3.3.1.21. (*E*)-*N*,*N*-Diphenyl-2-[5-styryl-1-(toluene-4-sulfonyl)pyrrolidin-3-ylidene]acetamide 3n-*exo*. Inseparable mixture of geometric isomers (*E*/*Z*=4.5:1). White solid (86 mg, 81%). Mp=110–112 °C; R_f=0.22 (hexanes/EtOAc=3:1); IR (CH_2Cl_2) ν 3059, 1670, 1644, 1596, 1494, 1450, 1385, 1345, 1267, 1162, 1093, 966, 816, 735, 698, 666, 614 cm^{-1}; ^{1}H NMR (mixture *E*/*Z*=4.5:1, 400 MHz, $CDCl_3$) δ 7.72–7.63 (2H, m), 7.42–7.08 (17H, m), 6.52 (1H$_E$, dd, J=15.8, 1.1 Hz), 6.49 (1H$_Z$, d, J=15.6 Hz), 5.99 (1H$_E$, dd, J=15.8, 6.8 Hz), 5.88 (1H$_Z$, dd, J=15.6, 7.5 Hz), 5.78 (1H, m), 4.60 (1H$_Z$, m), 4.49 (1H$_E$, m), 4.08–3.96 (2H, m), 3.23 (1H$_E$, dm, J=18.7 Hz), 3.05 (1H$_E$, ddm, J=18.7, 8.1 Hz), 2.75 (1H$_Z$, ddm, J=16.9, 8.1 Hz), 2.45–2.38 (1H$_Z$, m), 2.38 (3H, s); ^{13}C NMR (*E* isomer, 100 MHz, $CDCl_3$) δ 165.4, 154.0, 143.6, 142.3, 136.2, 134.6, 131.0, 129.6, 129.4, 128.4, 128.2, 127.8, 127.7, 127.6, 126.5, 114.5, 62.0, 53.3, 37.8, 21.4; HRMS calcd for $C_{33}H_{30}N_2O_5S$ $(M)^+$ 534.1977, found 534.1974.

General procedure A was followed (stirring at rt for 24 h) using 4-methyl-*N*-(3-methyl-butylidene)-benzenesulfonamide (57 mg, 0.24 mmol, 1.2 equiv).

3.3.1.22. (*E*)-2-[5-Isopropyl-1-(toluene-4-sulfonyl)pyrrolidin-3-ylidene]-*N*,*N*-diphenylacetamide 3o-*exo*. Beige solid (58 mg, 59%). Mp=130–132 °C; R_f=0.35 (hexanes/EtOAc=3:1); IR (CH_2Cl_2) ν 3061, 2956, 2868, 1673, 1644, 1596, 1492, 1385, 1344, 1266, 1162, 1091, 1031, 758, 735, 701, 667, 613 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70–7.64 (2H, m), 7.41–7.12 (12H, m), 5.72 (1H, br s), 4.05–3.90 (3H, m), 2.98 (1H, d, J=18.7 Hz), 2.61 (1H, br dd, J=18.7, 8.1 Hz), 2.44 (3H, s), 1.79–1.49 (2H, m), 1.24 (1H, m), 0.96 (3H, d, J=6.6 Hz), 0.91 (3H, d, J=6.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 155.6, 143.6, 142.4, 134.9, 129.8, 129.2, 127.4, 114.0, 59.3, 53.1, 44.7, 36.6, 24.9, 22.8, 22.3, 21.5; HRMS calcd for $C_{29}H_{32}N_2O_3S$ $(M)^+$ 488.2134, found 488.2125.

General procedure A was followed (stirring at rt for 24 h) using *N*-cyclohexylmethylene-4-methyl-benzenesulfonamide (64 mg, 0.24 mmol, 1.2 equiv).

3.3.1.23. (*E*)-2-[5-Cyclohexyl-1-(toluene-4-sulfonyl)-pyrrolidin-3-ylidene]-*N*,*N*-diphenylacetamide 3p-*exo*. Colourless oil (36 mg, 35%). R_f=0.31 (hexanes/EtOAc=3:1); IR (thin film) ν 2926, 2852, 1670, 1643, 1596, 1491, 1384, 1345, 1269, 1162, 1092, 701, 667 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75–7.64 (2H, m), 7.42–7.07 (12H, m), 5.66 (1H, m), 4.04 (1H, d, J=17.4 Hz), 3.89 (1H, dm, J=17.4 Hz), 3.80 (1H, m), 3.20 (1H, dm, J=10.1 Hz), 2.46–2.08 (2H, m), 2.44 (3H, s), 1.82–0.88 (10H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 156.7, 143.6, 142.5, 135.2, 129.8, 129.6, 129.4, 127.4, 127.3, 113.9, 65.8, 54.0, 42.7, 33.1, 29.5, 28.2, 26.2, 26.1, 26.0, 21.5; HRMS calcd for $C_{31}H_{34}N_2O_3S$ $(M)^+$ 514.2290, found 514.2296.

3.3.2. General procedure B. To a solution of 2,6-di-*tert*-butyl-4-methylphenol (194 mg, 0.88 mmol, 4.4 equiv) in toluene (0.90 mL) at room temperature was added a solution of trimethylaluminium (0.22 mL, 2 M in toluene, 0.44 mmol, 2.2 equiv) dropwise. After 1 h of stirring at room temperature, the resulting solution was cooled to 0 °C and a solution of MCP (0.20 mmol, 1 equiv), *N*-tosyl aldimine (0.24 mmol, 1.2 equiv) and *n*-Bu_4NI (74 mg, 0.2 mmol, 1 equiv) in CH_2Cl_2 (2 mL) was added dropwise. The resulting yellow solution was stirred at 0 °C for 30 min and allowed to warm to room temperature and stirred for 24 h. The reaction mixture was poured into a saturated aqueous solution of NH_4Cl and the aqueous layer was extracted with EtOAc (three-times 25 mL). The combined organic extracts were washed with H_2O (15 mL) and brine (15 mL), dried over Na_2SO_4, filtered and concentrated in vacuo. Purification of the resulting oil by chromatography on silica gel (gradient hexanes/EtOAc; 5:1–4:1) gave the expected products.

General procedure B was followed using *N*-benzylidene-4-methyl-benzenesulfonamide (62 mg, 0.24 mmol, 1.2 equiv).

3.3.2.1. (*E*)-*N*-Phenyl-2-[5-phenyl-1-(toluene-4-sulfonyl)pyrrolidin-3-ylidene]-*N*-pyridin-2-ylacetamide 6a-*exo*. Dark yellow oil (56 mg, 55%). R_f=0.25 (hexanes/EtOAc=3:1); IR (thin film) ν 3061, 2958, 1669, 1642, 1585, 1492, 1466, 1432, 1381, 1347, 1266, 1163, 1093, 699, 666 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72–6.93 (18H, m), 5.77 (1H, s), 5.00 (1H, m), 4.77–4.64 (2H, m), 2.94 (1H, br dd, J=16.9, 9.0 Hz), 2.57 (1H, br d, J=16.9 Hz), 2.38 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 156.1, 149.0, 143.2, 141.4, 137.9, 135.2, 129.5, 128.5, 128.3, 127.6, 127.5, 126.4, 125.5, 121.5, 121.2, 114.7, 61.3, 52.5, 42.7, 30.3, 21.5; HRMS calcd for $C_{30}H_{28}N_3O_3S$ $(M+H)^+$ 510.1851, found 510.1861.

General procedure B was followed using 4-methyl-*N*-naphthalen-1-ylmethylene-benzenesulfonamide (74 mg, 0.24 mmol, 1.2 equiv).

3.3.2.2. 2-[5-Naphthalen-1-yl-1-(toluene-4-sulfonyl)-2,5-dihydro-1*H*-pyrrol-3-yl]-*N*-phenyl-*N*-pyridin-2-ylacetamide 6b-*endo*. Light yellow oil (54 mg, 48%). R_f=0.2 (hexanes/EtOAc=2:1); IR (thin film) ν 3058, 2928, 2853, 1674, 1582, 1341, 1157, 1093, 913 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37–8.35 (1H, m), 7.96–7.93 (1H, m), 7.85–7.82 (1H, m), 7.73 (1H, d, J=8 Hz), 7.62–7.53 (4H, m), 7.48–7.38 (3H, m), 7.32–7.25 (3H, m), 7.18–7.10 (5H, m), 7.08–7.04 (1H, m), 6.19 (1H, s), 5.44 (1H, s), 4.52 (1H, d, J=14 Hz), 4.42 (1H, dd, J=14.5, 4.2 Hz), 3.21 (2H, s), 2.35 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 155.0, 149.0, 143.5, 141.5, 138.2, 136.3, 135.3, 134.0, 131.9, 130.5, 129.7, 129.1, 128.5, 128.3, 128.1, 127.7, 127.6, 126.3, 125.9, 125.6, 125.2, 122.8, 121.9, 121.3, 67.8, 57.5, 36.5, 21.7; HRMS calcd for $C_{34}H_{30}N_3O_3S$ $(M+H)^+$ 560.2002, found 560.2018.

General procedure B was followed using 4-methyl-*N*-(4-trifluoromethyl-benzylidene)-benzenesulfonamide (78 mg, 0.24 mmol, 1.2 equiv).

3.3.2.3. *N*-Phenyl-*N*-pyridin-2-yl-2-[1-(toluene-4-sulfonyl)-5-(4-trifluoromethylphenyl)-2,5-dihydro-1*H*-pyrrol-3-yl]acetamide 6c-*endo*. Light yellow oil (38 mg, 33%). R_f=0.11 (hexanes/EtOAc=3:1); IR (thin film) ν 3058, 2922, 2867, 1681, 1585, 1490, 1463, 1432, 1324, 1161, 1120, 1066, 1018, 665 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.42 (1H, d, J=4.9 Hz), 7.68 (1H, td, J=7.6, 1.6 Hz), 7.49–7.13 (15H, m), 5.5 (1H, s), 5.36 (1H, s), 4.36 (2H, s), 3.25 (2H, d, J=4.3 Hz), 2.36 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 149.1, 144.6, 143.6, 141.5, 138.4, 135.7, 133.6, 130.0, 129.8, 129.7, 128.5, 128.2, 128.0, 127.4, 127.1, 125.61, 125.57, 123.3, 122.1, 121.3, 69.8, 57.3, 26.3, 21.6; HRMS calcd for $C_{31}H_{27}F_3N_3O_3S$ $(M+H)^+$ 578.1719, found 578.1718.

General procedure B was followed using *N*-(4-methoxy-benzylidene)-4-methyl-benzenesulfonamide (69 mg, 0.24 mmol, 1.2 equiv).

3.3.2.4. (*E*)-2-[5-(4-Methoxy-phenyl)-1-(toluene-4-sulfonyl)pyrrolidin-3-ylidene]-*N*-phenyl-*N*-pyridin-2-ylacetamide 6d-*exo*. Light yellow oil (42 mg, 39%). R_f=0.15 (hexanes/EtOAc=2:1); IR (thin film) ν 3065, 2915, 2860, 1677, 1585, 1511, 1344, 1246, 1157, 1093 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.41 (1H, dd, J=4.7, 1.2 Hz), 7.68 (1H, td, J=8.0, 1.9 Hz), 7.45–7.13 (13H, m), 6.77 (2H, d, J=8.6 Hz), 5.43 (1H, s), 5.32 (1H, s), 4.27 (2H, m), 3.78 (3H, s), 3.24 (2H, s), 2.35 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 159.5, 155.1, 149.1, 143.1, 141.5, 138.3, 136.0, 132.8, 132.3, 129.8, 129.6, 129.0, 128.6, 128.2, 127.9, 127.4, 122.0, 121.3, 114.0, 69.9, 56.9, 55.5, 36.4, 21.7; HRMS calcd for $C_{31}H_{29}N_3O_4S$ $(M)^+$ 539.1879, found 539.1864.

General procedure B was followed using 4-methyl-*N*-(1-methyl-1*H*-pyrrol-2-ylmethylene)-benzenesulfonamide (63 mg, 0.24 mmol, 1.2 equiv).

3.3.2.5. 2-[1′-Methyl-1-(toluene-4-sulfonyl)-2,5-dihydro-1*H*,1′*H*-[2,2′]bipyrrolyl-4-yl]-*N*-phenyl-*N*-pyridin-2-ylacetamide 6e-*endo*. Light yellow oil (29 mg, 28%). R_f=0.17 (hexanes/EtOAc=2:1); IR (thin film) ν 3065, 2928, 2853, 1677, 1582, 1490, 1463, 1429, 1337, 1297, 1256, 1157, 1093 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.4 (1H, d, J=3.7 Hz), 7.67 (1H, td, J=7.9, 1.8 Hz), 7.41–7.09 (11H, m), 6.4 (1H, m), 6.0–5.94 (2H, m), 5.65 (1H, s), 5.35 (1H, s), 4.31 (1H, d, J=13.8 Hz), 4.20 (1H, dd, J=12.9, 5.0 Hz), 3.35 (3H, s), 3.21 (2H, d, J=7.2 Hz), 2.3 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 149.1, 142.9, 141.5, 138.3, 136.4, 132.7, 129.8, 129.4, 129.2, 128.5, 128.2, 127.2, 126.3, 123.8, 122.0, 121.3, 110.3, 107.0, 63.1, 56.1, 36.3, 34.1, 21.6; HRMS calcd for $C_{29}H_{29}N_4O_3S$ $(M+H)^+$ 513.1954, found 513.1972.

General procedure B was followed using *N*-benzylidene-4-methyl-benzenesulfonamide (62 mg, 0.24 mmol, 1.2 equiv).

3.3.2.6. (*E*)-*N*-Methoxy-*N*-methyl-2-[5-phenyl-1-(toluene-4-sulfonyl)pyrrolidin-3-ylidene]acetamide 7a-*exo*. White foam (41 mg, 51%). Mp=148–150 °C; R_f=0.21 (hexanes/EtOAc=3:1); IR (CH_2Cl_2) ν 2936, 1669, 1634, 1598, 1456, 1419, 1386, 1347, 1162, 1091, 700, 667 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.62–7.55 (2H, m), 7.31–7.13 (7H, m), 6.31 (1H, br s), 5.01 (1H, dd, J=8.8, 3.3 Hz), 4.34 (1H, d, J=16.7 Hz), 4.26 (1H, br d, J=16.7 Hz), 3.63 (3H, s), 3.37 (1H, br d, J=18.9 Hz), 3.15 (3H, s), 3.09 (1H, m), 2.40 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.5, 155.6, 144.1, 141.6, 135.3, 130.1, 130.0, 129.0, 128.0, 127.9, 126.9, 111.1, 64.0, 62.1, 54.5, 39.1, 32.5, 22.0; HRMS calcd $C_{21}H_{25}N_2O_4S$ $(M+H)^+$ 401.1535, found 401.1538.

General procedure B was followed using 4-methyl-*N*-naphthalen-1-ylmethylene-benzenesulfonamide (74 mg, 0.24 mmol, 1.2 equiv).

3.3.2.7. (*E*)-*N*-Methoxy-*N*-methyl-2-[5-naphthalen-1-yl-1-(toluene-4-sulfonyl)pyrrolidin-3-ylidene]acetamide 7b-*exo*. Colourless oil (47 mg, 52%). R_f=0.34 (hexanes/EtOAc=2:1); IR (thin film) ν 3051, 2962, 2928, 1670, 1633, 1599, 1385, 1348, 1161, 1089, 800, 780, 665 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.93–7.91 (1H, m), 7.85–7.82 (1H, m), 7.73–7.67 (3H, m), 7.52–7.45 (3H, m), 7.38–7.33 (1H, m), 7.28–7.23 (2H, m), 6.32 (1H, s), 5.78 (1H, dd, J=7.8, 4.9 Hz), 4.50 (2H, s), 3.58 (3H, s), 3.07 (3H, s), 2.41 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 155.0, 144.0, 137.3, 135.2, 134.2, 130.0, 129.2, 128.3, 127.7, 126.5, 125.8, 125.4, 123.4, 123.3, 111.3, 61.8, 61.7, 54.8, 40.3, 32.2, 21.8; HRMS calcd for $C_{25}H_{27}N_2O_4S$ $(M+H)^+$ 451.1686, found 451.1699.

General procedure B was followed using 4-methyl-*N*-(4-trifluoromethyl-benzylidene)-benzenesulfonamide (78 mg, 0.24 mmol, 1.2 equiv).

3.3.2.8. *N*-Methoxy-*N*-methyl-2-[1-(toluene-4-sulfonyl)-5-(4-trifluoromethylphenyl)-2,5-dihydro-1*H*-pyrrol-3-yl] 7c-*endo*. Colourless oil (31 mg, 33%). R_f=0.12 (hexanes/EtOAc=3:1); IR (thin film) ν 3024, 2928, 2860, 1664, 1616, 1419, 1381, 1324, 1157, 1123, 1106, 1069, 668 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (2H, d, J=8.4 Hz), 7.45 (2H, d, J=8.2 Hz), 7.36 (2H, d, J=8.2 Hz), 7.15 (2H, d, J=8.4 Hz), 5.53 (1H, s), 5.47 (1H, s), 4.37–4.34 (2H, m), 3.65 (3H, s), 3.29 (2H, s), 3.16 (3H, s), 2.37 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 143.6, 135.7, 133.4, 129.7, 128.0, 127.4, 127.1, 125.7, 125.6, 123.0, 69.9, 61.6, 57.4, 32.5, 21.6; HRMS calcd for $C_{22}H_{23}N_2O_4F_3S$ $(M)^+$ 468.1336, found 468.1331.

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Supplementary data

^1H NMR–ROESY experiments are available for compounds **3a**-*exo* and **3a**-*endo*. This material is available free of charge. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.05.081.

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