A synthetic strategy to pyrrolidines and piperidines based on cyclization of α-sulfinyl carbanions

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Abstract
A general synthetic strategy for the preparation of pyrrolidines, piperidines and their unsaturated analogs is described, which involves intramolecular cyclization of α-sulfinyl carbanions onto the carbonyl group of the readily prepared *N*-phenylsulfinylpropyl- or *N*-phenylsulfinylbutylamides, followed by reductive desulfurization or sulfoxide elimination of the resulting cyclized products.

Keywords: α-Sulfinyl carbanion, pyrrolidines, piperidines, intramolecular cyclization

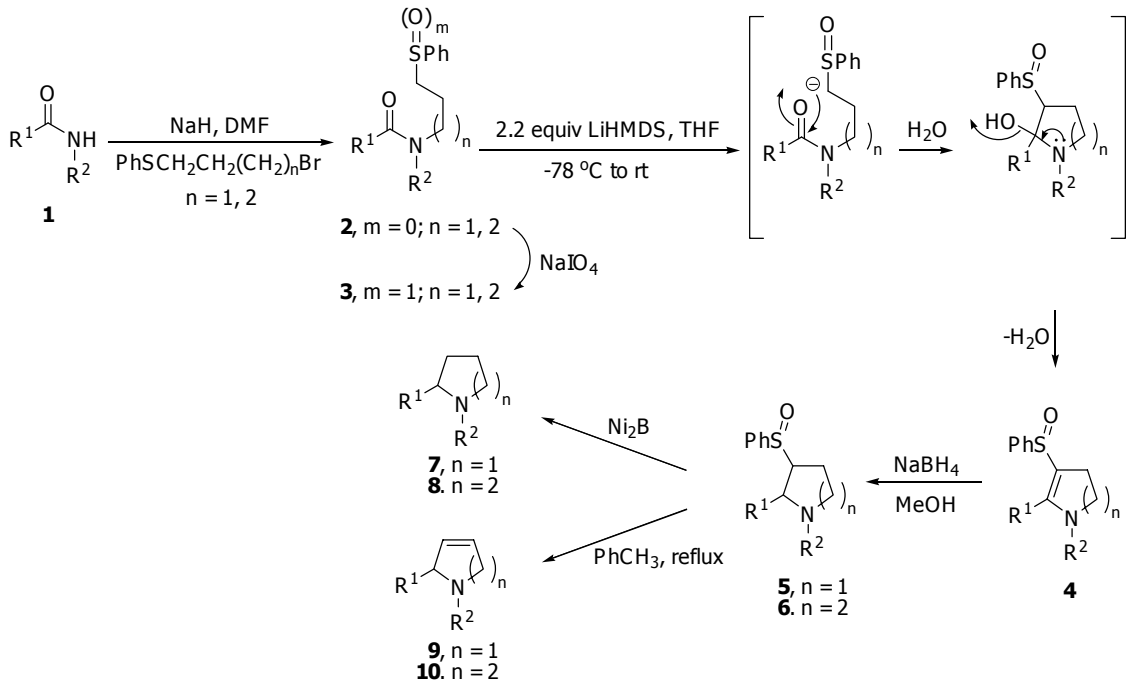
Introduction

N-Heterocycles occur in many interesting classes of compounds, for example, naturally occurring substances, pharmaceuticals, polymers, electronic materials, and sensors. In particular, pyrrolidine and piperidine derivatives are present in a large number of physiologically interesting natural products.[1] As a result, a considerable number of synthetic approaches to pyrrolidines and piperidines have been reviewed[2] and the search for alternative, general, and convenient procedures for their synthesis is still desirable. As part of our research program on the synthetic utility of cyclization based on α-sulfinyl carbanions for the preparation of 1-azabicyclic compounds,[3-5] we report a general route for the preparation of pyrrolidines and piperidines starting from simple amides.

Results and Discussion

The pyrrolidine and piperidine derivatives **5**–**6** were prepared according to the synthetic analysis outlined in Scheme 1, which involves N-alkylation of secondary amides with 1-bromo-3-phenylsulfanylpropane or 1-bromo-4-phenylsulfanylbutane, and oxidation of the resulting adducts to the corresponding sulfoxides followed by α-sulfinyl carbanions- mediated cyclization,

and reduction. The synthetic utility of our syntheses was further demonstrated by preparing substituted pyrrolidines or piperidines **7**, **8** as well as their unsaturated analogs **9**, **10**.



Scheme 1. Synthetic pathway.

The required starting sulfoxides **3** (*n* = 1 or 2) were prepared in good yields by treatment of the secondary amides **1** with 1-bromo-3-phenylsulfanylpropane or 1-bromo-4-phenylsulfanylbutane, using NaH as a base in *N,N*-dimethylformamide (DMF) at 0 ºC followed by oxidation of the resulting sulfides **2** with $NaIO_4$ in aqueous methanol at 0 ºC to room temperature overnight. The results are summarized in Table 1.

Having the starting sulfoxides in hand, we explored the intramolecular cyclization, exploiting compound **3a** as a model substrate. In preliminary experiments, treatment of the sulfoxide **3a** with 1.0 or 1.2 equivalents of lithium hexamethyldisilazide (LiHMDS) in THF at –78 ^{o}C followed by slowly warming to room temperature overnight (12-16 h) led to a low yield of the expected cyclized product **4a**. The starting sulfoxide **3a** still remained, as revealed by thin-layer chromatography and ^{1}H NMR analyses of the crude product. It is worth mentioning that the obtained cyclized product **4a** decomposed slowly upon standing, or purification on silica gel. To circumvent the decomposition problem, the crude material after the cyclization step was immediately subjected to reduction, employing $NaBH_4$ in methanol. A good yield (66%) of phenylsulfinylpyrrolidine **5a** was obtained when 2.0–2.2 equivalents of LiHMDS were employed for the cyclization step, followed by reduction of the initial cyclized product **4a** with $NaBH_4$ in methanol at room temperature. By performing the sequential cyclization and reduction reaction under the same reaction conditions as for **5a**, the phenylsulfinylpyrrolidines **5b**–**d** and

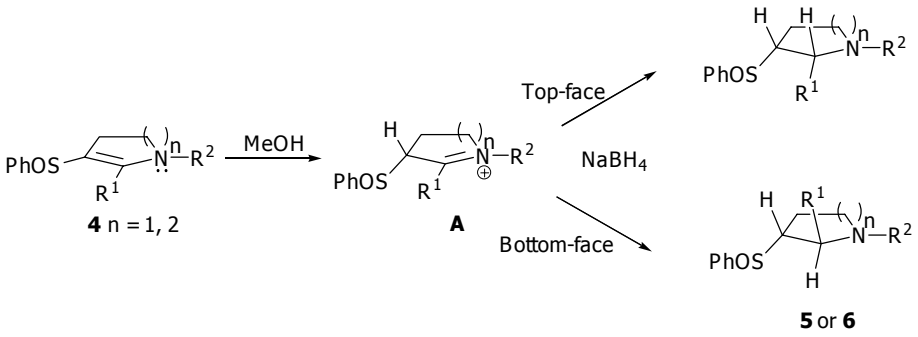
piperidines **6a** and **b** were prepared in moderate to good yields from the corresponding starting sulfoxides **3b**–**d** and **3e**–**f**, respectively, as summarized in Table 1.

Table 1. Pyrrolidine and piperidine derivatives prepared by this methodology

Entry	Amide	R^1	R^2	Product yields (%)[a]					
	1			**2**	n	**3**	**5**[b] or **6**[b]	**7** or **8**	**9** or **10**
1	**1a**	Ph	Ph	**2a**, 84	1	**3a**, 90	**5a**, 66	**7a**, 68	**9a**, 65
2	**1b**	Me	Ph	**2b**, 88	1	**3b**, 92	**5b**, 50	**7b**, 60	[c]
3	**1c**	*n*-Pr	Ph	**2c**, 80	1	**3c**, 90	**5c**, 57	**7c**, 62	[c]
4	**1d**	Ph	Bn	**2d**, 57	1	**3d**, 91	**5d**, 58	[c]	**9d**, 65
5	**1a**	Ph	Ph	**2e**, 82	2	**3e**, 90	**6a**, 72	**8a**, 61	**10a**, 76
6	**1b**	Me	Ph	**2f**, 85	2	**3f**, 90	**6b**, 56	**8b**, 70	**10b**, 72

[a] Isolated yields. [b] Obtained as mixtures of diastereomers. [c] Not performed.

It is worth noting that the phenylsulfinylpyrrolidines **5a**–**d** and phenylsulfinylpiperidines **6a**–**b**, in all cases, were obtained as a mixture of diastereomers. A maximum of four diastereoisomer was expected from those possess three chiral centers and their stereochemical outcomes can be explained as shown in Scheme 2. It was believed that the iminium ions **A** readily formed under protic conditions. Subsequent reduction by sodium borohydride gave **5a**–**d** and **6a**–**b**. Since the hydride anion can access the iminium ion from both the top- and the bottom-face of the iminium ions, this resulted in the formation of diastereomeric products of **5** and **6**.

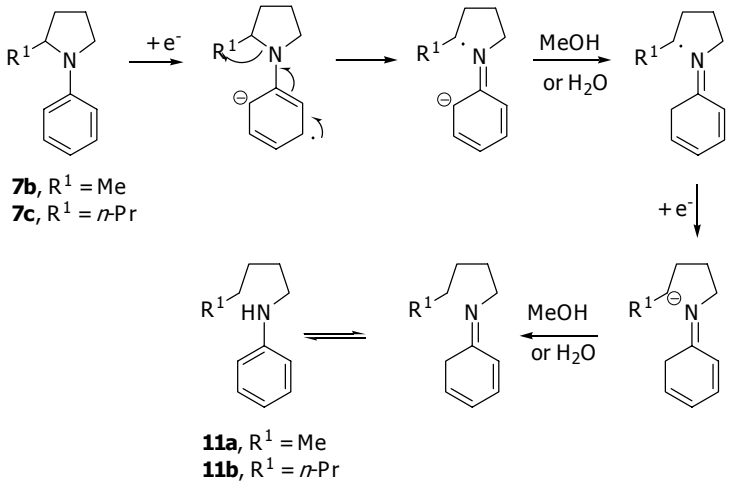


Scheme 2. Formation of compounds **5a–d** and **6a–b**.

Having established the efficient access to pyrrolidine and piperidine core units, we envisioned that the presence of the phenylsulfinyl group in compounds **5** and **6** makes them useful for further synthetic manipulation. The preparation of pyrrolidines **7** and piperidines **8** as well as their unsaturated analogs **9** and **10** from compounds **5** and **6** were demonstrated. Thus, reductive cleavage of the phenylsulfinyl group of **5a** was carried out by treatment with an excess of nickel boride (Ni_2B)[6] in methanol at 3–5 ºC, affording pyrrolidine **7a** in 68% yield (Table 1,

entry 1). Similarly, reductive desulfurization of **5b**–**c** and **6a**–**b** gave the corresponding pyrrolidines **7b**–**c** and piperidines **8a**–**b** in 60–70% yields as summarized in Table 1 (entries 2–3 and 5–6).

It was observed that further reductive cleavage of the carbon–nitrogen bond of pyrrolidines **7b** and **7c** occurred to give the corresponding ring–opening products *N*-pentylaniline **11a** and *N*-heptylaniline **11b** in 14 and 15% yields, respectively. The formation of both compounds arose presumably by the hydrogenolysis of the initially formed **7b** and **7c** via a mechanism as proposed in Scheme 3.



Scheme 3. Plausible mechanism for the formation of **11a** or **11b** from the corresponding compounds **7b** or **7c**.

Finally, the pyrrolidines **5a**, **5d** and piperidines **6a**–**b** were subjected to sulfoxide elimination conditions (toluene, reflux), leading to the corresponding unsaturated derivatives **9a**, **9b** and **10a**–**b** in 65–76% yields as shown in Table 1 (entries 1, 4, 5 and 6).

Conclusions

Cyclization based on α-sulfinyl carbanions is shown to be a useful, general strategy for the preparation of substituted pyrrolidines and piperidines, and their unsaturated analogs, starting from simple amides.

Experimental Section

General. ^{1}H NMR and ^{13}C NMR were recorded on a Bruker DPX-300 or a Bruker DPX-500 spectrometer. IR spectra were recorded either with a Jasco A-302 or a Perkin Elmer 683 Infrared

spectrometer. Mass spectra were performed on a Thermo Finnigan Polaris Q mass spectrometer. High resolution MS were obtained from either HR–TOF–MS Micromass model VQ-TOF2 or Finnigan MAT 95 mass spectrometer. Microanalyses were performed with a Perkin–Elmer Elemental Analyzer 2400 CHN. Melting points were determined on a Buchi 501 Melting Point Apparatus and were uncorrected. Tetrahydrofuran (THF) was freshly distilled from sodium–benzophenone ketyl. The molarity of *n*-BuLi (in hexane) was determined by titration with diphenylacetic acid in THF at 0 ºC. The reactions dealing with anions were carried out under an argon atmosphere. Preparative plates were performed using Merck silica gel 60 PF_{254}. Column chromatography was performed on Merck silica gel 60 H. Radial chromatography on a Chromatotron was performed with Merck silica gel 60 PF_{254}.

Sulfide 2. General procedure

To a suspension of NaH (1.1 equiv.) in DMF (~0.37 M) at 0 ºC, was added a solution of amide (1 equiv.) in DMF (~1 M) under an argon atmosphere. The reaction mixture was stirred for 1 h until the generation of hydrogen ceased. To this mixture, was added a solution of 1-bromo-3-phenylsulfanylpropane (1.1 equiv.) in DMF (~2.75 M). After the reaction mixture was stirred at 0 ºC to room temperature overnight (15 h), it was quenched with water and extracted with EtOAc (3 x 100 mL). The combined organic layers were washed with H_2O, brine, dried (anhydrous Na_2SO_4), and filtered. Removal of solvent gave a residue, which was further purified by column chromatography (silica gel) to furnish the analytically pure product.

***N*-Phenyl-*N*-(3-phenylsulfanylpropyl)benzamide (2a).** Prepared from *N*-phenylbenzamide (1.97 g, 10 mmol) and 1-bromo-3-phenylsulfanylpropane (2.7052 g, 11 mmol). Column chromatography (10% EtOAc–hexanes) gave **2a** (2.9079 g, 84%; colorless liquid). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36–7.14 (m, 13H, Ar*H*), 7.02 (app. d, *J* = 7.6 Hz, 2H, Ar*H*), 4.12 (t, *J* = 7.4 Hz, 2H, NCH_2), 3.02 (t, *J* = 7.4 Hz, 2H, CH_2S), 2.04 (quintet, *J* = 7.4 Hz, 2H, NCH_2CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.14 (C=O), 143.91 (C), 136.74 (C), 136.68 (C), 130.3 (2 x CH), 130.2 (CH), 129.8 (2 x CH), 129.5 (2 x CH), 129.3 (2 x CH), 128.3 (4 x CH), 127.3 (CH), 126.8 (CH), 49.9 (CH_2), 32.2 (CH_2), 28.0 (CH_2). IR (neat) ν_{max}/cm^{-1}: 1642, 1595, 1579, 1493, 739, 699. MS: *m/z* (% relative intensity): 347 (M^+, 6), 238 (100), 210 (8), 106 (15), 105 (73), 77 (34). HRMS (ESI–TOF): *m/z* [M^+] Calcd for $C_{22}H_{21}NOS$: 347.1344. Found: 347.1335.

***N*-Phenyl-*N*-(3-phenylsulfanylpropyl)acetamide (2b).** Prepared employing *N*-phenylacetamide (4.0551 g, 30 mmol and 1-bromo-3-phenylsulfanylpropane (7.6283 g, 33 mmol). Column chromatography (10% EtOAc–hexanes) gave **2b** (7.5079 g, 88%; pale yellow liquid). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46–7.01(m, 10H, Ar*H*), 3.82 (t, *J* = 7.3 Hz, 2H, NCH_2), 2.90 (t, *J* = 7.4 Hz, 2H, CH_2S), 1.90–1.71 (m, 2H, NCH_2CH_2), 1.81 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.9 (C=O), 142.4 (C), 135.9 (C), 129.8 (2 x CH), 129.8 (2 x CH), 128.8 (2 x CH), 128.1 (CH), 127.8 (2 x CH), 126.1 (CH), 48.3 (CH_2), 31.4 (CH_2), 27.3 (CH_2), 22.5 (CH_3). IR (neat) ν_{max}/cm^{-1}: 1656, 1595, 1496, 1397, 741, 701. MS: *m/z* (% relative intensity): 286 ($M+H^+$, 7), 285 (M^+, 2), 176 (100), 134 (33), 106 (46), 79 (6), 77 (10). Anal. Calcd for $C_{17}H_{19}NOS$: C, 71.54; H, 6.71; N, 4.91. Found: C, 71.34; H, 6.66; N, 4.66.

***N*-Phenyl-*N*-(3-phenylsulfanylpropyl)butyramide (2c).** Prepared from *N*-phenylbutyramide (3.5401 g, 20 mmol) and 1-bromo-3-phenylsulfanylpropane (5.082 g, 22 mmol). Column chromatography (10% EtOAc–hexanes) gave **2c** (4.9587g, 80%; pale yellow liquid). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50–7.05 (m, 10H, Ar*H*), 3.83 (t, *J* = 7.3 Hz, 2H, NCH_2), 2.93 (t, *J* = 7.3 Hz, 2H, CH_2S), 2.11–1.91 (m, 2H, $CH_2CH_2CH_2$), 1.91–1.75 (m, 2H, CH_2CO), 1.70–1.50 (m, 2H, CH_3CH_2), 0.83 (m, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.9 (C=O), 142.5 (C), 136.1 (C), 129.7 (3 x CH), 129.5 (CH), 128.8 (2 x CH), 128.2 (2 x CH), 127.8 (CH), 126.1 (CH), 48.2 (CH_2), 36.2 (CH_2), 31.4 (CH_2), 27.5 (CH_2), 18.8 (CH_2), 13.8 (CH_3). IR (neat) ν_{max}/cm^{-1}: 1655, 1595, 1495, 740, 701. MS: *m/z* (% relative intensity): 314 (M^++1, 19), 313 (M^+, 3), 205 (16), 204 (100), 134 (28), 106 (48), 77 (10). HRMS (ESI–TOF): *m/z* [M+Na^+]. Calcd for $C_{19}H_{23}NOSNa$: 336.1398. Found: 336.1395.

***N*-Benzyl-*N*-(3-phenylsulfanylpropyl)benzamide (2d).** Prepared from *N*-benzylbenzamide (4.55 g, 20 mmol) and 1-bromo-3-phenylsulfanylpropane (5.082 g, 22 mmol. Column chromatography (40% EtOAc–hexanes) gave **2d** (4.1154 g, 57%; colorless liquid) as a mixture of two rotamers. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52–7.00 (m, 15H, Ar*H*), 4.75 and 4.49 (each br. peak, 2H, NCH_2Ph), 3.55 and 3.26 (each br. peak, 2H, NCH_2CH_2), 2.94 and 2.63 (each br. peak, 2H, CH_2CH_2S), 2.13 and 1.78 (each br. peak, 2H, $CH_2CH_2CH_2$). ^{13}C NMR (75 MHz, $CDCl_3$): 172.8 (C=O), 137.02 (3 x C), 130.2 (2 x CH), 129.6 (2 x CH), 129.4 (CH), 129.2 (2 x CH), 128.8 (CH), 128.3 (2 x CH), 127.6 (CH), 127.2 (2 x CH), 126.8 (CH). All CH_2 peaks split into two peaks due to rotamers: 53.6 (CH_2), 48.2 (CH_2), 47.8 (CH_2), 44.5 (CH_2), 32.0 (CH_2), 31.5 (CH_2), 28.2 (CH_2), 27.3 (CH_2). IR (neat) ν_{max}/cm^{-1}: 1634, 1578, 1496, 738, 700. MS: *m/z* (% relative intensity): 361 (M^+, 3), 256 (74), 252 (98), 224 (9), 151 (8), 105 (100), 77 (35). HRMS (ESI–TOF): *m/z* [M+H^+] Calcd for $C_{23}H_{24}NOS$: 362.1579. Found: 362.1574.

***N*-Phenyl-*N*-(4-phenylsulfanylbutyl)benzamide (2e).** Prepared from *N*-phenylbenzamide (5.872 g, 30 mmol) and 1-bromo-4-phenylsulfanylbutane (8.085 g, 33 mmol). Column chromatography (40% EtOAc–hexanes) gave **2e** (8.6640 g, 82%; colorless liquid). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33–7.08 (m, 13H, Ar*H*), 7.01–6.93 (m, 2H, Ar*H*), 3.92 (t, *J* = 7.0 Hz, 2H, NCH_2CH_2), 2.92 (t, *J* = 6.8 Hz, 2H, CH_2CH_2S), 1.83–1.64 (m, 4H, CH_2CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.1 (C=O), 143.9 (C), 137.1 (C), 136.8 (C), 130.1 (CH), 129.9 (2 x CH), 129.8 (2 x CH), 129.5 (2 x CH), 129.3 (2 x CH), 128.4 (2 x CH), 128.3 (2 x CH), 127.3 (CH), 126.5 (CH), 50.3 (CH_2), 33.9 (CH_2), 27.5 (CH_2), 27.2 (CH_2). IR (neat) ν_{max}/cm^{-1}: 1643, 1595, 1493, 739, 699. MS: *m/z* (% relative intensity): 361 (M^+, 2), 197 (14), 146 (8), 105 (100), 77 (33). HRMS (ESI–TOF): *m/z* [M+Na^+] Calcd for $C_{23}H_{23}NOSNa$: 384.1399; Found: 384.1398.

***N*-Phenyl-*N*-(4-phenylsulfanylbutyl)acetamide (2f).** Prepared employing *N*-phenylacetamide (4.0551 g, 30 mmol) and 1-bromo-4-phenylsulfanylbutane (8.0850 g, 33 mmol). Column chromatography (40% EtOAc–hexanes) gave **2f** (7.5264 g, 85%; colorless liquid). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45–7.21 (m, 7H, Ar*H*), 7.20–7.07 (m, 3H, Ar*H*), 3.70 (br. t, *J* = 6.7 Hz, 2H, NCH_2CH_2), 2.91 (br. t, *J* = 6.7 Hz, 2H, CH_2CH_2S), 1.80 (s, 3H, CH_3), 1.70–1.55 (m, 4H, CH_2CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.3 (C=O), 142.8 (C), 136.4 (C), 129.7 (2 x CH), 129.1 (2 x CH), 128.8 (2 x CH), 128.01 (2 x CH), 127.8 (CH), 125.8 (CH), 48.2 (CH_2), 33.2

(CH_2), 26.8 (CH_2), 26.3 (CH_2), 22.7 (CH_3). IR (neat) ν_{max}/cm^{-1}: 1658, 1595, 1496, 1481, 1439, 1301, 740, 701. MS: *m/z* (% relative intensity): 299 (M^+, 2), 191 (13), 190 (92), 148 (21), 135 (9), 123 (7), 106 (100), 93 (16), 79 (6), 77 (10). Anal. Calcd for $C_{18}H_{21}NOS$: C, 72.20; H, 7.07; N,4.68. Found: C, 72.28; H, 7.02; N, 4.46.

Sulfoxide 3. General procedure

To a suspension of $NaIO_4$ (1.1 equiv) in 2:1 of MeOH : H_2O (~0.5 M) at 0 ºC, was slowly added a solution of **2** (1 equiv) in MeOH (~0.67 M). The resulting mixture was stirred vigorously and slowly warmed up from 0 ºC to room temperature overnight. The precipitates of $NaIO_3$ were filtered and washed with EtOAc (3 x 50 mL). The combined organic mixtures were washed with H_2O, brine and dried (anhydrous Na_2SO_4). Filtration followed by evaporation gave a crude product, which was purified by column chromatography (silica gel) to provide an analytically pure product.

***N*-Phenyl-*N*-(3-phenylsulfinylpropyl)benzamide (3a).** Compound **2a** (2.4186 g, 6.96 mmol) was employed. Column chromatography (50% EtOAc–hexanes to 100% EtOAc) provided **3a** (2.3374 g, 90%, pale yellow viscous oil). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60–7.53 (m, 2H, Ar*H*), 7.49–7.41 (m, 3H, Ar*H*), 7.25–7.05 (m, 8H, Ar*H*), 6.96–6.90 (m, 2H, Ar*H*), 4.03 (t, *J* = 7.0 Hz, 2H, NCH_2CH$_2$), 3.00–2.74 (m, 2H, CH_2), 2.18–1.85 (m, 2H, CH_2SO). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.3 (C=O), 144.2 (C), 143.5 (C), 136.4 (C), 131.6 (CH), 130.3 (CH), 129.9 (2 x CH), 129.9(2 x CH), 129.2 (2 x CH), 128.4 (4 x CH), 127.6 (CH), 124.6 (2 x CH), 55.3 (CH_2), 49.5 (CH_2), 21.5 (CH_2). IR (neat) ν_{max}/cm^{-1}: 1639, 1594, 1578, 1494, 1087, 1044, 749, 730. MS: *m/z* (% relative intensity): 363 (M^+, 1), 238 (40), 198 (25), 132 (23), 105 (100), 77 (40). HRMS (ESI–TOF): *m/z* [M+Na^+] Calcd for $C_{22}H_{21}NO_2SNa$: 386.1191. Found: 386.1191.

***N*-Phenyl-*N*-(3-phenylsulfinylpropyl)acetamide (3b).** Compound **2b** (5.7082 g, 20 mmol) was employed. Column chromatography (100% EtOAc to 5% MeOH in EtOAc) provided **3b** (1.2431 g, 92%; viscous liquid). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.65–7.47 (m, 5H, Ar*H*), 7.47–7.32 (m, 3H, Ar*H*), 7.12 (app. d, *J* = 7.3, 2H, Ar*H*), 3.82 (t, *J* = 6.9 Hz, 2H, NCH_2CH$_2$), 3.02–2.70 (m, 2H, CH$_2$CH_2SO), 2.11–1.72 (m, 2H, CH$_2$CH_2CH$_2$), 1.83 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.8 (C=O), 143.5 (C), 142.4 (C), 130.9 (CH), 129.9 (2 x CH), 129.2 (2 x CH), 128.2 (CH), 128.0 (2 x CH), 123.9 (2 x CH), 54.4 (CH_2), 47.6 (CH_2), 22.7 (CH_3), 20.6 (CH_2). IR (neat) ν_{max}/cm^{-1}: 1655, 1595, 1496, 1044, 750, 701. MS: *m/z* (% relative intensity): 302 (M+H^+, 1), 176 (98), 134 (26), 132 (37), 106 (100), 77 (15). HRMS (ESI–TOF): *m/z* [M+Na^+] Calcd for $C_{17}H_{19}NO_2SNa$: 324.1034. Found: 324.1035.

***N*-Phenyl-*N*-(3-phenylsulfinylpropyl)butyramide (3c).** Compound **2c** (1.5650 g, 5 mmol) was employed. Column chromatography (80% EtOAc–hexanes to 5% MeOH in EtOAc) provided **3c** (1.4775 g, 90%; pale yellow viscous liquid). ^{1}H NMR (300 MHz, $CDCl_3$): 7.69–7.30 (m, 8H, Ar*H*), 7.10 (d, *J* = 6.93 Hz, 2H, Ar*H*), 3.91–3.71 (m, 2H, NCH_2), 3.04–2.88 (m, 1H, C*H*HSO), 2.85–2.72 (m, 1H, CH*H*SO), 2.15–1.91 (m, 3H, C*H*HCH$_2$C=O and CH_2C=O), 1.90–1.72 (m, 1H, CH*H*CH$_2$C=O) 1.56 (sextet, *J* = 7.4 Hz, 2H, CH$_3$CH_2), 0.80 (t, *J* = 7.4 Hz, 3H, CH_3CH$_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.98 (C=O), 144.2 (C), 142.8 (C), 131.6 (CH), 130.5 (2 x CH),

129.9 (2 x CH), 128.9 (2 x CH), 128.8 (CH), 124.7 (2 x CH), 55.3 (CH_2), 48.4 (CH_2), 36.8 (CH_2), 21.4 (CH_2), 19.5 (CH_2), 14.4 (CH_3). IR (neat) ν_{max}/cm^{-1}: 1650, 1594, 1495, 1043, 750, 702. MS: *m/z* (% relative intensity: 329 (M^+, 1), 242 (16), 204 (100), 132 (34), 106 (95), 77 (15). HRMS (ESI–TOF): *m/z* [M+Na^+] Calcd for $C_{19}H_{23}NO_2SNa$: 352.1449. Found: 352.1347.

***N*-Benzyl-*N*-(3-phenylsulfinylpropyl)benzamide (3d).** Compound **2d** (3.1602 g, 8.75 mmol) was employed. Column chromatography (100% EtOAc to 5% MeOH in EtOAc) provided **3d** (3.0127 g, 91%; colorless viscous liquid). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70–7.01 (m, 15H, Ar*H*), 4.75 and 4.50 (each br. peak, 2H, NC*H*$_2$Ph), 3.51 and 3.26 (each br. peak, 2H, NC*H*$_2$CH$_2$CH$_2$), 2.94 and 2.82 (each br. peak, 2H, CH$_2$CH$_2$C*H*$_2$S), 2.15–1.96 (br. , 2H, CH$_2$C*H*$_2$CH$_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.32 (C=O), 143.56 (C), 136.45 (C), 136.12 (C), 131.02 (CH), 129.65 (CH), 129.29 (CH), 129.27 (2 x CH), 129.85 (2 x CH), 128.57 (2 x CH), 127.71 (CH), 126.54 (2 x CH), 123.94 (3 x CH), 54.65 (CH_2), 52.40 (CH_2), 43.17 (CH_2), 20.02 (CH_2), 14.18 (CH_3). IR (neat) ν_{max}/cm^{-1}: 1631, 1496, 1047, 749, 700. MS: *m/z* (% relative intensity): 378 (M+H^+, 15), 272 (42), 252 (79), 146 (43), 105 (100), 91 (84), 77 (44). HRMS (ESI–TOF): *m/z* [M+Na^+] Calcd for $C_{23}H_{23}NO_2SNa$: 400.1347. Found: 400.1343.

***N*-Phenyl-*N*-(4-phenylsulfinylbutyl)benzamide (3e).** Compound **2e** (6.2503 g, 17.30 mmol) was employed. Column chromatography (100% EtOAc to 5% MeOH in EtOAc) provided **3e** (5.8645 g, 90%; pale yellow viscous liquid). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.65–7.43 (m, 5H, Ar*H*), 7.26–7.06 (m, 8H, Ar*H*), 6.99–6.92 (m, 2H, Ar*H*), 3.92 (t, *J* = 6.98 Hz, 2H, NC*H*$_2$CH$_2$), 2.96–2.75 (m, 2H, CH$_2$C*H*$_2$S), 1.90–1.55 (m, 4H, 2 x C*H*$_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.3 (C=O), 143.5 (C), 142.9 (C), 135.8 (C) 130.9 (CH), 129.5 (CH), 129.1 (4 x CH), 128.5 (2 x CH), 127.6 (4 x CH), 126.7 (CH), 123.9 (2 x CH), 56.3 (CH_2), 49.3 (CH_2), 26.4 (CH_2), 19.2 (CH_2). IR (neat) ν_{max}/cm^{-1}: 1643, 1595, 1494, 1044, 752, 699. MS: *m/z* (% relative intensity): 359 (M^+-H_2O, 36), 252 (13), 146 (42), 105 (100), 77 (45). HRMS (ESI–TOF): *m/z* [M+H^+] Calcd for $C_{23}H_{24}NO_2S$: 378.1528. Found: 378.1526.

***N*-Phenyl-*N*-(4-phenylsulfinylbutyl)acetamide (3f).** Compound **2f** (0.8405 g, 2.80 mmol) was employed. Column chromatography (100% EtOAc to 5% MeOH in EtOAc) provided **3f** (3.0127 g, 90%; colorless viscous liquid). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.65–7.47 (m, 5H, Ar*H*), 7.46–7.32 (m, 3H, Ar*H*), 7.15–7.08 (m, 2H, Ar*H*), 3.70 (t, *J* = 7.0 Hz, 2H, NC*H*$_2$CH$_2$), 2.94–2.72 (m, 2H, CH$_2$C*H*$_2$S), 1.82 (s, 3H, C*H*$_3$), 1.85–1.53 (m, 4H, 2 x C*H*$_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.3 (C=O), 143.5 (C), 142.6 (C), 130.8 (CH), 129.7 (2 x CH), 129.1 (2 x CH), 127.9 (CH), 127.8 (2 x CH), 123.9 (2 x CH), 56.3 (CH_2), 47.9 (CH_2), 26.5 (CH_2), 22.6 (CH_3), 19.03 (CH_2). IR (neat) ν_{max}/cm^{-1}: 1652, 1595, 1496, 1036, 752, 701. MS: *m/z* (% relative intensity): 298 (M+H^+-H_2O, 62), 256 (38), 146 (94), 106 (100), 77 (21). HRMS (ESI–TOF): *m/z* [M+H^+] Calcd for $C_{18}H_{22}NO_2S$: 316.1371. Found: 316.1372.

Pyrrolidine sulfoxides 5 and piperidine sulfoxides 6. General procedure

To a cooled (–78 ºC) solution of hexamethyldisilazane (2.4 equiv.) in THF (~0.3 M) under an argon atmosphere, was added *n*-BuLi (2.2 equiv.). After stirring at –78 ºC for 30 min, a solution of compound **3** (1 equiv.) in THF (~0.5 *M*) was added dropwise. The resulting mixture was slowly warmed up from –78 ºC to room temperature overnight (15 h). The resulting red solution

was quenched with H_2O (10 mL) and extracted with EtOAc (3 x 50 mL). The combined organic extracts were washed with H_2O, brine, dried (anhydrous Na_2SO_4) and filtered. The filtrate was evaporated to yield a viscous oil of a crude product which was directly subjected to reduction by using $NaBH_4$.

To a solution of the crude product in MeOH (~0.25 *M*) at 3–5 ºC under an argon atmosphere, $NaBH_4$ (5.73 equiv) was gradually added over 15 min. The mixture was stirred for 2 h at the same temperature before it was diluted with 1 N NaOH (20 mL) and H_2O (100 mL). The resulting mixture was extracted with EtOAc (3 x 100 mL). The combined organic extracts were washed with brine and dried (anhydrous Na_2SO_4). Filtration followed by evaporation afforded a crude product as a mixture of diastereomers which was further purified by column chromatography (silica gel).

1,2-Diphenyl-3-(phenylsulfinyl)pyrrolidine (5a). Compound **3a** (1.2841 g, 3.54 mmol) was employed to produce the title compound. Column chromatography (40% EtOAc–hexanes) gave three fractions (F_1, F_2 and F_3) of **5a**.

F_1 (Isomer A, less polar): (0.2083 g, 17%; a white solid of a single isomer of **5a**; mp 136–137 ºC after crystallization from EtOAc–hexanes). ^{1}H NMR (500 MHz, $CDCl_3$): 7.72–7.58 (m, 5H, Ar*H*), 7.35 (m, 3H, Ar*H*), 7.18–7.05 (m, 4H, Ar*H*), 6.75 (t, *J* = 8.0 Hz, 1H, Ar*H*), 6.47 (d, *J* = 8.0 Hz, 2H, Ar*H*), 5.32 (s, 1H, NC*H*Ph), 3.30–3.10 (m, 2H, CH_2CH_2N), 2.79 (ddd, *J* = 8.8, 3.6, 1.2 Hz, 1H, CH_2CHSO), 2.47–2.35 (m, 1H, C*H*HCH_2N), 2.19–2.08 (m, 1H, CH*H*CH_2N). ^{13}C NMR (125 MHz, $CDCl_3$): δ 141. (C), 141.3 (2 x C), 132.1 (CH), 130.2 (2 x CH), 129.9 (2 x CH), 129.3 (CH), 129.1 (CH), 128.1 (CH), 125.9 (2 x CH), 125.3 (2 x CH), 119.3 (CH), 114.4 (2 x CH), 71.03 (CH), 66.4 (CH), 42.8 (CH_2), 23.4 (CH_2). IR ($CHCl_3$) ν_{max}/cm^{-1}: 1603, 1506, 1477, 750, 702. MS: *m/z* (% relative intensity): 348 ($M+H^+$, 22), 330 (56), 220 (33), 132 (52), 106 (100), 77 (48). HRMS (ESI–TOF): *m/z* [M^+] Calcd for $C_{22}H_{21}NOS$: 347.1344; Found: 347.1347.

F_2 (mixture of isomers B and C, more polar): (0.3091 g, 28%; pale yellow syrup of a 3:2 mixture of isomer B : isomer C of **5a**). ^{1}H NMR (300 MHz, $CDCl_3$, mixture of two diastereomers): 7.71–7.64 (m, 2H, Ar*H*), 7.55–7.40 (m, 8H, Ar*H*), 7.36–7.23 (m, 10H, Ar*H*), 6.97–6.91 (m, 4H, Ar*H*), 6.56–6.51 (m, 2H, Ar*H*), 6.07–6.02 (m, 4H, Ar*H*), 5.32 (d, *J* = 2.1 Hz, 1H, NC*H*Ph of isomer B), 4.79 (d, *J* = 9.3 Hz, 1H, NC*H*Ph of isomer C), 3.31–3.20 (m, 1H, C*H*SOPh of isomer C), 2.89–2.82 (m, 1H, C*H*SOPh of isomer B), 2.52–2.35 (m, 2H, C*H*$_2$N of isomer B), 2.32–2.18 (m, 2H, C*H*$_2$$CH_2N$ of isomer B), 2.07–1.84 (m, 2H, C*H*$_2$N of isomer C), 1.58–1.51 (m , 1H, C*H*HCH_2N of isomer C), 1.35–1.19 (m, 1H, CH*H*CH_2N of isomer C). ^{13}C NMR (75 MHz, $CDCl_3$, mixture of two diastereomers): δ 147.4 (C), 147.2 (C), 141.3 (C), 141.2 (C), 141. (C), 140.2 (C), 131.9 (CH), 131.2 (CH), 129.3 (2 x CH), 129.3 (2 x CH), 129.1 (2 x CH), 129.0 (2 x CH), 128.8 (2 x CH), 128.7 (2 x CH), 128.01 (CH), 127.4 (CH), 125.9 (2 x CH), 124.5 (2 x CH), 117.4 (CH), 117.3 (CH), 112.7 (2 x CH), 112.5 (2 x CH), 75.9 (CH), 73.5 (CH), 68.02 (CH), 67.1 (CH), 42.2 (CH_2), 41.3 (CH_2), 24.03 (CH_2), 20.1 (CH_2). IR ($CHCl_3$) ν_{max}/cm^{-1}: 1603, 1507, 1477, 1452, 1028. MS: *m/z* (% relative intensity): 348 (M^++1, 8), 330 (34), 220 (38), 147 (92), 132 (72), 117 (32), 106 (100), 93 (32), 77 (65).

F_3 (Isomer D, most polar): (0.2821 g, 21%; a white solid of a single isomer of **5a**; mp 132–133 ºC after crystallization from EtOAc–hexanes). ^{1}H NMR (500 MHz, $CDCl_3$): 7.64–7.52 (m, 5H, Ar*H*), 7.47–7.30 (m, 5H, Ar*H*), 7.06 (t, *J* = 7.6 Hz, 2H, Ar*H*), 6.72 (d, *J* = 7.60 Hz, 1H, Ar*H*), 6.15 (d, *J* = 8.0 Hz, 2H, Ar*H*), 5.06 (d, *J* = 8.4 Hz, 1H, NC*H*Ph), 3.12–3.02 (m, 1H, CH_2CHSO), 2.52 (t, *J* = 6.8 Hz, 2H, CH_2CH_2N), 1.97–1.85 (m, 1H, C*H*HCH_2N), 1.65–1.55 (m, 1H, CH*H*CH_2N). ^{13}C NMR (125 MHz, $CDCl_3$): δ 147.1 (C), 141.6 (C), 141.5 (C), 131.7 (CH), 129.9 (2 x CH), 129.8 (2 x CH), 129.5 (2 x CH), 129.3 (CH), 127.6 (2 x CH), 125.4 (2 x CH), 119.1 (CH), 114.1 (2 x CH), 74.9 (CH), 68.3 (CH), 42.9 (CH_2), 23.0 (CH_2). IR ($CHCl_3$) ν_{max}/cm^{-1}: 1603, 1506, 1487, 1036. MS: *m/z* (% relative intensity): 348 ($M+H^+$, 4), 147 (100), 132 (92), 106 (90), 93 (42), 77 (66).

2-Methyl-1-phenyl-3-(phenylsulfinyl)pyrrolidine (5b). Compound **3b** (1.6032 g, 5.32 mmol) was employed to produce the title compound. ^{1}H NMR of the crude product exhibited a 9:1 ratio of two diasteroisomers. Column chromatography (20% to 50% EtOAc–hexanes) gave a major isomer of **5b** (0.7556 g, 50%; a white solid; mp 151–153 ºC after crystallization from EtOAc–hexanes). ^{1}H NMR (300 MHz, $CDCl_3$): 7.71–7.63 (m, 2H, Ar*H*), 7.57–7.45 (m, 3H, Ar*H*), 7.26–7.15 (m, 2H, Ar*H*), 6.68 (t, *J* = 7.3 Hz, 1H, Ar*H*), 6.53 (d, *J* = 8.1 Hz, 2H, Ar*H*), 4.12 (quint., *J* = 6.6 Hz, 1H, NC*H*CH_3), 3.49 (dt, *J* = 9.1, 1.8 Hz, 1H, CH_2CH*H*N), 3.36–3.24 (m, 1H, CH_2CHSO), 3.22 (q, *J* = 8.9 Hz, 1H, CH_2CH*H*N), 2.80–2.61 (m, 1H, C*H*HCH_2N, 2.09–1.91 (m, 1H, CH*H*CH_2N), 1.39 (d, *J* = 6.4 Hz, 3H, C*H*$_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.56 (C), 143.20 (C), 131.10 (2 x CH), 129.23 (3 x CH), 124.22 (2 x CH), 116.34 (2 x CH), 111.83 (CH), 66.36 (CH), 54.54 (CH), 45.37 (CH_2), 19.79 (CH_2), 14.78 (CH_3). IR (Nujol) ν_{max}/cm^{-1}: 1598, 1502, 1489, 1032, 749. MS: *m/z* (% relative intensity): 386 (M^++1, 6), 268 (100), 160 (46), 158 (89), 118 (25), 77 (28). Anal Calcd for $C_{17}H_{19}NOS$; C, 71.54; H, 6.71; N, 4.91 Found: C, 71.45; H, 6.63; N, 4.87.

1-Phenyl-3-phenylsulfinyl-2-propylpyrrolidine (5c). Compound **3c** (1.2801 g, 3.80 mmol) was employed to produce the title compound. Column chromatography (30% EtOAc–hexanes) gave three fractions (F_1, F_2 and F_3) of **5c**.

F_1 (less polar): (0.5292 g, 44%; a white solid of a pure isomer of **5c**; mp 107–109 ºC after crystallization from EtOAc–hexanes). ^{1}H NMR (300 MHz, $CDCl_3$): 7.72–7.61 (m, 2H, Ar*H*), 7.59–7.50 (m, 3H, Ar*H*), 7.24 (t, *J* = 7.8 Hz, 2H, Ar*H*), 6.72 (t, *J* = 7.2 Hz, 1H, Ar*H*), 6.56 (d, *J* = 8.1 Hz, 2H, Ar*H*), 4.10 (dt, *J* = 11.4, 6.7 Hz, 1H, NC*H*$CH_2CH_2CH_3$), 3.56 (td, *J* = 9.0, 1.7 Hz, 1H, CH_2CH*H*N), 3.26 (t, *J* = 7.1 Hz, 1H, CH_2CH*H*N), 3.20–3.15 (m, 1H, CH_2CHSO), 2.73–2.61 (m, 1H, C*H*HCH_2N), 2.10–1.90 (m, 1H, C*H*HCH_2CH_3), 2.00–1.82 (m, 1H, CH*H*CH_2N), 1.80–1.52 (m, 3H, CH*H*C*H*$_2CH_3$), 1.01 (t, *J* = 7.0 Hz, 3H, C*H*$_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.6 (C), 143.5 (C), 130.9 (CH), 129.2 (2 x CH), 129.1 (2 x CH), 124.2 (2 x CH), 116.3 (CH), 111.9 (2 x CH), 66.3 (CH), 59.01 (CH), 46.3 (CH_2), 32.9 (CH_2), 20.3 (CH_2), 20.04 (CH_2), 14.5 (CH_3). IR (Nujol) ν_{max}/cm^{-1}: 1594, 1505*s*, 1043, 1033, 745, 690. MS: *m/z* (% relative intensity): 313 (M^+, 27), 296 (69), 188 (59), 145 (46), 144 (32). Anal Calcd for $C_{19}H_{23}NOS$; C, 72.80; H, 7.40; N, 4.47 Found: C, 73.15; H, 7.18; N, 4.31.

F_2 (more polar): (0.0819 g, 7%; pale yellow syrup of a pure isomer of **5c**). ^{1}H NMR (300 MHz, $CDCl_3$): 7.81–7.69 (m, 2H, Ar*H*), 7.60–7.50 (m, 3H, Ar*H*), 7.28–7.16 (m, 2H, Ar*H*), 6.70 (t, *J* = 7.3 Hz, 1H, Ar*H*), 6.58 (d, *J* = 8.0 Hz, 2H, Ar*H*), 4.44 (q, *J* = 6.1 Hz, 1H, NC*H*$CH_2CH_2CH_3$), 3.52–3.36 (m, 2H, CH_2CHHN and CH_2CHSO), 3.18 (q, *J* = 8.9 Hz, 1H, CH_2CH*H*N), 2.17–2.02 (m, 2H, C*H*$_2CH_2$N), 1.90–1.30 (m, 4H, NCHC*H*$_2CH_2CH_3$) 0.98 (t, *J* = 7.2 Hz, 3H, C*H*$_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.7 (C), 142.9 (C), 131.8 (CH), 129.4 (2 x CH), 129.2 (2 x CH), 124.9 (2 x CH), 116.2 (CH), 111.8 (2 x CH), 68.9 (CH), 58.3 (CH), 46.7 (CH_2), 32.1 (CH_2), 24.7 (CH_2), 20.1 (CH_2), 14.6 (CH_3). IR (neat) ν_{max}/cm^{-1}: 1599, 1505, 1043, 1033, 748, 692. MS: *m/z* (% relative intensity): 313 (M^+, 21), 296 (42), 188 (100), 158 (30), 145 (76), 104 (28), 77 (21).

F_3 (most polar): (0.0706 g, 6%; yellow syrup of a pure isomer of **5c**). ^{1}H NMR (300 MHz, $CDCl_3$): 7.71–7.64 (m, 2H, Ar*H*), 7.57–7.45 (m, 3H, Ar*H*), 7.25–7.15 (m, 2H, Ar*H*), 6.80–6.65 (m, 1H, Ar*H*), 6.55–6.40 (m, 2H, Ar*H*), 3.67 (app. d, *J* = 8.4 Hz, 1H, NC*H*$CH_2CH_2CH_3$), 3.48 (td, *J* = 9.2, 1.9 Hz, 1H, CH_2CHHN), 3.32 (t, *J* = 9.2 Hz, 1H, CH_2CH*H*N), 3.30–3.25 (m, 1H, CH_2CHSO), 2.82–2.68 (m, 1H, C*H*HCH_2N), 2.48–2.31 (m, 1H, CH*H*CH_2N), 1.69–1.52 (m, 1H, NCHC*H*HCH_2), 1.41–1.19 (m, 1H, NCHCH*H*CH_2), 1.06–0.79 (m, 2H, $CH_2CH_2CH_3$), 0.71 (t, *J* = 7.1 Hz, 3H, C*H*$_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.04 (C), 142.6 (C), 131.8 (2 x CH), 129.3(2 x CH), 129.3 (2 x CH), 125.4 (2 x CH), 116.3 (CH), 112.0 (CH), 70.3 (CH), 58.1 (CH), 46.3 (CH_2), 34.4 (CH_2), 23.5 (CH_2), 18.7 (CH_2), 13.6 (CH_3). IR (neat) ν_{max}/cm^{-1}: 1594, 1505, 1043, 1033, 745, 690. MS: *m/z* (% relative intensity): 313 (M^+, 2), 187 (82), 159 (100), 144 (48), 104 (20), 77 (19).

1-Benzyl-2-phenyl-3-(phenylsulfinyl)pyrrolidine (5d). Compound **3d** (2.6514 g, 7.03 mmol) was employed to produce the title compound. Column chromatography (50% EtOAc–hexanes) gave two fractions (F_1 and F_2) of **5d**.

F_1 (less polar): (1.2828 g, 50%; colorless needles of a pure isomer of **5d**; mp 146–148 ºC after crystallization from EtOAc–hexanes). ^{1}H NMR (300 MHz, $CDCl_3$): 7.61 (app. d, *J* = 7.3 Hz, 2H, Ar*H*), 7.49–7.20 (m, 13H, Ar*H*), 3.96 (d, *J* = 13.4 Hz, 1H, NC*H*HPh), 3.86 (d, *J* = 8.1 Hz, 1H, NC*H*Ph), 3.39–3.30 (m, 1H, C*H*SO), 3.22 (t, *J* = 8.4 Hz, 1H, CH_2CHHN), 3.06 (d, *J* = 13.4 Hz, 1H, NCH*H*Ph), 2.70–2.53 (m, 1H, C*H*HCH_2N), 2.20 (q, *J* = 8.6 Hz, 1H, CH_2CH*H*N), 1.70–1.55 (m, 1H, CH*H*CH_2N). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.9 (C), 138.2 (C), 137.3 (C), 130.2 (CH), 129.1 (CH), 128.8 (2 x CH), 128.6 (2 x CH), 128.6 (2 x CH), 128.2 (CH), 128.1 (2 x CH), 126.9 (CH), 124.2 (3 x CH), 71.4 (CH), 68.9 (CH), 57.3 (CH_2), 51.7 (CH_2), 19.02 (CH_2). IR (nujol) ν_{max}/cm^{-1}: 1495, 1455, 1040, 746, 710. MS: *m/z* (% relative intensity): 362 (M+H^+, 16), 344 (76), 326 (15), 236 (44), 91 (100). Anal. Calcd for $C_{23}H_{23}NOS$: C, 76.42; H, 6.59; N, 3.52. Found: C, 76.52; H, 6.59; N, 3.52.

F_2 (more polar): (0.2015 g, 8%; yellow viscous oil of a pure isomer of **5d**). ^{1}H NMR (300 MHz, $CDCl_3$): 7.60 (d, *J* = 7.4 Hz, 2H, Ar*H*), 7.57–7.51 (m, 2H, Ar*H*), 7.43–7.08 (m, 11H, Ar*H*), 3.99 (d, *J* = 8.5 Hz, 1H, NC*H*Ph), 3.80 (d, *J* = 13.3 Hz, 1H, NC*H*HPh), 3.44 (q, *J* = 8.9 Hz, 1H, C*H*SO), 3.25 (d, *J* = 13.2 Hz, 1H, NCH*H*Ph), 3.04 (t, *J* = 8.1 Hz, 1H, CH_2CHHN), 2.19–2.04 (m, 1H, CH_2CH*H*N), 1.60–1.43 (m, 1H, C*H*HCH_2N), 1.25–1.10 (m, 1H, CH*H*CH_2N). ^{13}C NMR (75

MHz, $CDCl_3$): δ 143.2 (C), 138.3 (C), 137.2 (C), 131.3 (CH), 129.6 (2 x CH), 128.9 (3 x CH), 128.6 (CH), 128.3 (2 x CH), 128.1 (CH), 128.1 (2 x CH), 126.9 (CH), 125.6 (2 x CH), 70.3 (CH), 69.4 (CH), 57.1 (CH_2), 51.3 (CH_2), 26.3 (CH_2). IR (neat) ν_{max}/cm^{-1}: 1494, 1453, 1046, 699. MS: *m/z* (% relative intensity): 362 ($M+H^+$, 4), 344 (40), 236 (16), 144 (11), 92 (8), 91 (100).

1,2-Diphenyl-3-phenylsulfinylpiperidine (6a). Compound **3e** (2.8425 g, 8.12 mmol) was employed to produce the title compound. Column chromatography (40% EtOAc–hexanes) afforded three fractions (F_1, F_2 and F_3) of **6a**.

F_1 (less polar): (0.6605 g, 22%; pale yellow syrup of a pure isomer of **6a**). ^1H NMR (300 MHz, $CDCl_3$): 7.60–7.45 (m, 5H, Ar*H*), 7.27–6.95 (m, 7H, Ar*H*), 6.62 (t, *J* = 7.3 Hz, 1H, Ar*H*), 6.40 (d, *J* = 8.0 Hz, 2H, Ar*H*), 5.20 (s, 1H, NC*H*CH), 2.98–2.80 (m, 2H, CH_2CH_2N), 2.51–2.40 (m, 1H, CHC*H*SO), 2.17–2.00 (m, 1H, C*H*HCH_2N), 1.87–1.60 (m, 2H, CH*H*CH_2N and C*H*HCHSO), 1.53–1.32 (m, 1H, CH*H*CHSO). ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.4 (C), 141.2(C), 140.8 (C), 131.3 (CH), 129.5 (2 x CH), 129.2 (2 x CH), 128.3 (2 x CH), 127.3 (CH), 125.2 (2 x CH), 124.5 (2 x CH), 117.6 (CH), 112.9 (2 x CH), 70.4 (CH), 68.6 (CH), 43.4 (CH_2), 26.7 (CH_2), 20.02 (CH_2). IR (neat) ν_{max}/cm^{-1}: 1600, 1504, 1476, 1454, 1260, 1088, 1019, 799. MS: *m/z* (% relative intensity): 362 ($M+H^+$, 6), 344 (43), 254 (26), 132 (46), 106 (100), 91 (32), 77 (37).

F_2 (mixture of two isomers, more polar): (0.6822 g, 23%; pale yellow syrup of a 1:1 mixture of isomers of **6a**. ^1H NMR (300 MHz, $CDCl_3$, mixture of two diastereomers): 7.64–7.61 (m, 2H, Ar*H*), 7.52–7.33 (m, 8H, Ar*H*), 7.32–7.18 (m, 10H, Ar*H*), 7.09–6.98 (m, 4H, Ar*H*), 6.63–6.58 (m, 2H, Ar*H*), 6.33–6.30 (m, 4H, Ar*H*), 5.27 (d, *J* = 3.6 Hz, 1H, NC*H*Ph of an isomer), 4.87 (d, *J* = 9.2 Hz, 1H, NC*H*Ph of an isomer), 3.12–3.00 (m, 1H, C*H*SOPh of an isomer), 2.52 (q, *J* = 4.7 Hz, 1H C*H*SOPh of an isomer), 2.68–2.50 (m, 4H, CH_2CH_2NPh of both isomers), 1.86–1.60 (m, 2H, CH_2), 1.44–1.24 (m, 1H of CH_2), 1.12–0.75 (m, 6H, CH_2 of both isomers). ^{13}C NMR (75 MHz, $CDCl_3$, mixture of two diastereomers): δ 147.3 (C), 147.1 (C), 141.8 (C), 141.3 (C), 141.2 (C), 140.3 (C), 131.8 (CH), 131.1 (CH), 129.3 (2 x CH), 129.2 (2 x CH), 129.1 (2 x CH), 129.1 (2 X CH), 128.6 (2 x CH), 128.5 (2 x CH), 127.9 (2 x CH), 127.3 (2 x CH), 125.8 (2 X CH), 125.6 (2 x CH), 124.3 (2 x CH), 117.7 (CH), 117.6 (CH), 113.2 (2 x CH), 112.9 (2 x CH), 75.8 (CH), 73.1 (CH), 69.9 (CH), 69.4 (CH), 43.5 (CH_2), 43.1 (CH_2), 27.7(CH_2), 26.3 (CH_2), 22.2 (CH_2), 17.8 (CH_2). IR (neat) ν_{max}/cm^{-1}: 1603, 1506, 1086, 1027, 997. MS: *m/z* (% relative intensity): 362 ($M+H^+$, 2), 254 (17), 236 (13), 130 (24), 126 (22), 106 (100), 77 (33).

F_3 (most polar): (0.7906 g, 27%; pale yellow syrup of a pure isomer of **6a**). ^1H NMR (500 MHz, $CDCl_3$): 7.67–7.51 (m, 5H, Ar*H*), 7.48–7.30 (m, 5H, Ar*H*), 7.20–7.15 (m, 1H, Ar*H*), 6.78 (t, *J* = 7.2 Hz, 1H, Ar*H*), 6.52 (d, *J* = 7.2 Hz, 2H, Ar*H*), 5.04 (d, *J* = 8.0 Hz, 1H, NC*H*CH), 3.15–2.95 (m, 1H, C*H*SOPh), 2.87–2.72 (m, 2H, CH_2NPh), 1.65–1.53 (m, 1H, C*H*HCH_2), 1.48–1.34 (m, 1H, CH*H*CH_2), 1.29–1.80 (m, 2H, CH*H*CH_2). ^{13}C NMR (125 MHz, $CDCl_3$): δ 147.3 (C), 141.8 (C), 141.0 (C), 131.7 (CH), 130.2 (2 x CH), 129.9 (2 x CH), 129.9 (2 x CH), 129.35 (2 X CH), 129.08 (CH), 127.49 (2 x CH), 125.48 (2 X CH), 119.12 (CH), 114.3 (2 x CH), 74.9 (CH), 69.3

(CH), 44.6 (CH_2), 27.5 (CH_2), 21.3 (CH_2). IR (neat) ν_{max}/cm^{-1}: 1601, 1505, 1477, 1455. MS: *m/z* (% relative intensity): 362 ($M+H^+$, 2), 254 (17), 130 (26), 106 (100), 77 (32). HRMS (ESI–TOF): *m/z* [M^+] Calcd for $C_{23}H_{23}NOS$: 361.1500. Found: 361.1511.

2-Methyl-1-phenyl-3-phenylsulfinylpiperidine (6b). Compound **3f** (1.6013 g, 5.08 mmol) was employed to produce the title compound. Column chromatography (20% EtOAc–hexanes) gave three fractions (F_1, F_2 and F_3) of **6b**.

F_1 (lees polar): (0.3139 g, 21%; a white solid of a pure isomer of **6b**; mp 121–122 ºC after crystallization from EtOAc–hexanes). ^{1}H NMR (300 MHz, $CDCl_3$): 7.68–7.48 (m, 5H, Ar*H*), 7.24 (t, *J* = 7.9 Hz, 2H, Ar*H*), 6.80 (t, *J* = 7.3 Hz, 1H, Ar*H*), 6.52 (d, *J* = 7.7 Hz, 2H, Ar*H*), 4.40–4.25 (m, 1H, NC*H*CH), 3.37–3.18 (m, 2H, $CH_2C\mathit{H}_2N$), 2.40–2.29 (m, 1H, CHC*H*SO), 2.26–1.94 (m, 3H, $C\mathit{H}_2CH_2N$ and C*H*HCHSO), 2.00–1.80 (m, 1H, CH*H*CHSO), 1.14 (d, *J* = 6.6 Hz, 3H, $C\mathit{H}_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.9 (C), 141.1 (C), 131.2 (2 x CH), 129.4 (3 x CH), 124.6 (2 x CH), 118.5 (CH), 113.6 (2 x CH), 67.5 (CH), 65.6 (CH), 44.3 (CH_2), 27.3 (CH_2), 20.9 (CH_2), 20.7 (CH_3). IR ($CHCl_3$) ν_{max}/cm^{-1}: 1603, 1506, 1478, 1085, 997, 692. MS: *m/z* (% relative intensity): 300 ($M+H^+$, 37), 282 (52), 207 (19), 192 (45), 174 (42), 172 (48).

F_2 (more polar): (0.3101 g, 20%; yellow syrup of a pure isomer of **6b**). ^{1}H NMR (300 MHz, $CDCl_3$): 7.66–7.54 (m, 2H, Ar*H*), 7.48–7.31 (m, 3H, Ar*H*), 7.09 (t, *J* = 7.9 Hz, 2H, Ar*H*), 6.65 (t, *J* = 7.3 Hz, 1H, Ar*H*), 6.47 (d, *J* = 8.3 Hz, 2H, Ar*H*), 4.19 (quintet, *J* = 6.4 Hz, 1H, NC*H*CH), 3.01–2.83 (m, 2H, $CH_2C\mathit{H}_2N$), 2.80–2.70 (m, 1H, CHC*H*SO), 1.73–1.30 (m, 4H, $C\mathit{H}_2C\mathit{H}_2CHSO$), 1.23 (d, *J* = 6.3 Hz, 3H, $C\mathit{H}_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.5 (C), 142.2 (C), 131.6 (CH), 129.2 (2 x CH), 129.2 (2 x CH), 125.4 (2 x CH), 117.6 (CH), 112.9 (2 x CH), 67.9 (CH), 68.2 (CH), 43.4 (CH_2), 26.5 (CH_2), 22.5 (CH_2), 20.8 (CH_3). IR ($CHCl_3$) ν_{max}/cm^{-1}: 1603, 1506, 1444, 1085, 996. MS: *m/z* (% relative intensity): 300 ($M+H^+$, 19), 282 (18), 207 (28), 192 (28), 172 (28), 146 (14), 132 (9), 118 (19), 106 (100), 77 (25).

F_3 (most polar): (0.2182 g, 15%; a white solid of a pure isomer of **6b**; mp 109–111 ºC after crystallization from EtOAc–hexanes). ^{1}H NMR (300 MHz, $CDCl_3$): 7.68–7.45 (m, 5H, Ar*H*), 7.17 (t, *J* = 7.8 Hz, 2H, Ar*H*), 6.72 (t, *J* = 7.3 Hz, 1H, Ar*H*), 6.52 (d, *J* = 8.3 Hz, 2H, Ar*H*), 4.52–4.40 (m, 1H, NC*H*CH), 2.92 (t, *J* = 6.8 Hz, 2H, $CH_2C\mathit{H}_2N$), 2.58–2.54 (m Hz, 1H, CHC*H*SO), 1.97–1.67 (m, 2H, $C\mathit{H}_2CH_2N$), 1.51–1.45 (m, 1H, C*H*HCHSO), 1.42 (d, *J* = 6.5 Hz, 3H, CH_3), 1.21–1.10 (m, 1H, CH*H*CHSO). ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.6 (C), 142.8 (C), 130.9 (CH), 129.2 (4 x CH), 124.2 (2 x CH), 117.6 (CH), 112.9 (2 x CH), 69.7 (CH), 68.03 (CH), 43.7 (CH_2), 28.4 (CH_2), 21.02 (CH_2), 18.1 (CH_3). IR ($CHCl_3$) ν_{max}/cm^{-1}: 1603, 1506, 1444, 1086, 1020. MS: *m/z* (% relative intensity): 300 ($M+H^+$, 25), 282 (43), 192 (41), 172 (49), 118 (26), 106 (100), 77 (42).

Pyrrolidine 7 and Piperidine 8. General procedure

To a stirred 0 ºC solution of compound **5** or **6** (1 equiv) and $NiCl_2{\cdot}6H_2O$ (10 equiv) in solvent (see details for each reaction), was added portionwise $NaBH_4$ (30 equiv) at such a rate that the temperature was kept below 10 ºC (about 20 min). The resulting mixture was stirred at room temperature for 2 h. The black precipitate was filtered off over Celite and washed several times

with EtOAc. The organic phase was washed with H_2O, brine, dried (anhydrous Na_2SO_4) and filtered. Removal of solvent gave a crude product which was further purified by radial chromatography (silica gel).

1,2-Diphenylpyrrolidine (7a).[7,8] Compound **5a** as a mixture of isomers (0.1735 g, 0.50 mmol) and MeOH (6 mL) was employed to yield, after radial chromatography (100% hexanes), compound **7a** (0.0758 g, 68%; pale yellow liquid). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.29–7.05 (m, 5H, Ar*H*), 6.71–6.59 (m, 3H, Ar*H*), 6.62 (d, *J* = 7.7 Hz, 2H, Ar*H*), 4.65–4.56 (dd, *J* = 7.4, 5.0 Hz, 1H, NC*H*Ph), 3.06 (t, *J* = 6.6 Hz, 2H, C*H*$_2$N), 1.90–1.50 (m, 4H, C*H*$_2$C*H*$_2$CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.9 (C), 144.46 (C), 129.26 (2 x CH), 128.46 (2 x CH), 127.56 (CH), 125.79 (2 x CH), 118.59 (CH), 113.9 (2 x CH), 74.2 (CH), 44.9 (CH_2), 36.5 (CH_2), 25.5 (CH_2). IR (neat) ν_{max}/cm^{-1}: 1603, 1505, 1477, 750, 700. MS: *m/z* (% relative intensity): 224 (M+H$^+$, 11), 23 (M$^+$, 21), 147 (11), 146 (52), 106 (100), 93 (16), 77 (36).

2-Methyl-1-phenylpyrrolidine (7b).[9] Compound **5b** as a single isomer (0.4671 g, 1.64 mmol), THF (8 mL) and MeOH (24 mL) were employed to yield, after radial chromatography (100% hexanes), compound **7b** and *N*-pentylaniline (**11a**).

F$_1$ (less polar): **7b** (0.1577 g, 60%; colorless liquid). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.16–7.08 (m, 2H, Ar*H*), 6.59–6.49 (m, 3H, Ar*H*), 3.80–3.76 (m, 1H, NC*H*CH$_3$), 3.35–3.29 (m,1H, C*H*HN), 3.13–3.01 (m, 1H, CH*H*N), 2.08–1.82 (m, 3H, C*H*$_2$C*H*H), 1.65–1.58 (m, 1H, CH$_2$CH*H*), 1.11 (d, *J* = 6.9 Hz, 3H, C*H*$_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.1 (C), 129.1 (2 x CH), 115.1 (CH), 111.7 (2 x CH), 53.5 (CH), 48.1 (CH_2), 32.9 (CH_2), 23.2 (CH_2), 19.3 (CH_3). IR (neat) ν_{max}/cm^{-1}: 1599, 1505, 1459, 1362, 1162, 1036, 994, 745, 691. MS: *m/z* (% relative intensity): 161 (M$^+$, 29), 157 (5), 146 (100), 145 (6), 130 (6), 125 (12), 117 (9), 111 (6), 104 (25), 99 (9), 91 (10), 81 (9), 77 (29), 71 (8), 57 (9).

F$_2$ (more polar): *N*-pentylaniline (**11a**)[8] (0.0374 g, 14%; colorless liquid). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.12–7.07 (m, 2H, Ar*H*), 6.76–6.64 (m, 3H, Ar*H*), 3.16 (t, *J* = 7.1 Hz, 2H, NC*H*$_2$CH$_2$), 1.79–1.57 (m, 2H, C*H*$_2$CH$_2$N), 1.52–1.30 (m, 4H, C*H*$_2$C*H*$_2$CH$_3$), 1.05–0.91 (m, 3H, C*H*$_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.4 (C), 129.2 (2 x CH), 117.1 (CH), 112.7 (2 x CH), 44.0 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 22.5 (CH_2), 14.01 (CH_3). IR (neat) ν_{max}/cm^{-1}: 1604, 1506, 1321, 747, 692. MS: *m/z* (% relative intensity): 163 (M$^+$, 23), 149 (34), 106 (68), 93 (100), 77 (36), 71 (40).

1-Phenyl-2-propylpyrrolidine (7c).[6] Compound **5c** as a mixture of isomers (0.1768 g, 0.56 mmol), THF (3 mL) and MeOH (9 mL) were employed to yield, after radial chromatography (100% hexanes), compound **7c** and *N*-heptylaniline (**11b**).

F$_1$ (less polar): **7c** (0.0662 g, 62%; colorless liquid). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.29–7.24 (m, 2H, Ar*H*), 6.71–6.59 (m, 3H, Ar*H*), 3.78–3.61 (m, 1H, NC*H*CH$_2$), 3.47 (app. t, *J* = 7.4 Hz, 1H, CH$_2$C*H*HN), 3.25–3.10 (m, 1H, CH$_2$CH*H*N), 2.18–1.25 (m, 8H of CH$_2$), 1.02 (t, *J* = 7.2 Hz, 3H, CH$_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.30 (C), 129.12 (2 x CH), 115.08 (CH), 111.74 (2 x CH), 58.36 (CH), 48.18 (CH_2), 35.28 (CH_2), 30.24 (CH_2), 23.43 (CH_2), 19.85 (CH_2), 14.20 (CH_3). IR (neat) ν_{max}/cm^{-1}: 1598, 1505, 1479, 745, 691. MS: *m/z* (% relative intensity): 189 (M$^+$, 20), 188 (60), 146 (100), 117 (28), 104 (24), 77 (28).

F_2 (more polar): *N*-heptylaniline (**11b**)[10] (0.0160 g, 15%; colorless liquid). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.18–7.07 (m, 2H, ArH), 6.64–6.52 (m, 3H, ArH), 3.02 (t, *J* = 7.1 Hz, 2H, $PhNCH_2$), 1.55 (app. quint., *J* = 7.4 Hz, 2H, C*H*$_2$), 1.40–1.05 (m, 8H, 4 x C*H*$_2$), 0.81 (t, *J* = 6.6 Hz, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.40 (C), 129.20 (2 x CH), 117.18 (CH), 112.78 (2 x CH), 44.09 (CH_2), 31.80 (CH_2), 29.54 (CH_2), 29.10 (CH_2), 27.13 (CH_2), 22.60 (CH_2), 14.07 (CH_3). IR (neat) ν_{max}/cm^{-1}: 1603, 1505, 1365, 747, 691. MS: *m/z* (% relative intensity): 191 (M^+, 25), 149 (37), 106 (100), 97 (22), 81 (31), 77 (26).

1,2-Diphenylpiperidine (8a).[11] Compound **6a** as a mixture of isomers (0.3705 g, 1.03 mmol), and MeOH (20 mL) were employed to yield, after radial chromatography (100% hexanes), compound **8a** (0.1470 g, 61%; colorless liquid). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28–7.13 (m, 5H, Ar*H*), 7.07 (br. t, *J* = 7.8 Hz, 2H, Ar*H*), 6.61 (t, *J* = 7.3 Hz, 1H, Ar*H*), 6.49 (d, *J* = 7.8 Hz, 2H, Ar*H*), 4.68 (app. t, *J* = 6.6 Hz, 1H, NC*H*Ph), 3.12 (t, *J* = 7.0 Hz, 2H, CH_2CH_2N), 1.97–1.28 (m, 6H, 3 x C*H*$_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.9 (C), 144.6 (C), 129.2 (2 x CH), 128.4 (2 x CH), 127.5 (CH), 125.8 (2 x CH), 117.4 (CH), 112.9 (2 x CH), 74.3 (CH), 43.9 (CH_2), 38.6 (CH_2), 29.1 (CH_2), 23.3 (CH_2). IR (neat) ν_{max}/cm^{-1}: 1603, 1506, 1028, 750, 700. MS: *m/z* (%) relative intensity 237 (M^+, 6), 160 (15), 106 (100), 93 (12), 77 (25).

2-Methyl-1-phenylpiperidine (8b).[9] Compound **6b** as a mixture of isomers (0.1615 g, 0.54 mmol) and MeOH (11 mL) were employed to yield, after radial chromatography (100% hexanes), compound **8b** (0.0658 g, 70%; colorless liquid). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.22–7.17 (m, 2H, Ar*H*), 6.74–6.70 (m, 1H, Ar*H*), 6.65–6.62 (m, 2H, Ar*H*), 3.85–3.80 (m, 1H, NC*H*CH_3), 3.14 (t, *J* = 7.0 Hz, 2H, CH_2CH_2N), 1.63–1.60 (m, 1H of CH_2), 1.60–1.40 (m, 5H of CH_2), 1.21 (d, *J* = 6.4 Hz, 3H, CHC*H*$_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.7 (C), 129.9 (2 x CH), 118.2 (CH), 113.7 (2 x CH), 68.6 (CH), 44.8 (CH_2), 39.6 (CH_2), 30.1 (CH_2), 24.2 (CH_3), 23.9 (CH_2). IR (neat) ν_{max}/cm^{-1}: 1603, 1508, 1477, 1322, 750, 693. MS: *m/z* (% relative intensity): 175 (M^+, 1), 106 (100), 93 (4), 79 (14), 77 (16).

Unsaturated derivatives 9 and 10. General procedure

A solution of compound **5** or **6** in dry toluene (~0.05 M) was refluxed under an argon atmosphere overnight. After cooling to room temperature, the resulting solution was concentrated to give a crude product, which was further purified by radial chromatography (silica gel).

1,2-Diphenyl-2,5-dihydro-1*H*-pyrrole (9a). Compound **5a** as a mixture of isomers (0.1730 g, 0.49 mmol) was employed to produce, after radial chromatography (100% hexanes), compound **9a** (0.0704 g, 65%; pale yellow liquid). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37–7.09 (m, 8H, Ar*H*), 6.83–6.78 (m, 2H, Ar*H*), 5.96–5.87 (m, 2H, CH_2HC=C*H*CH), 5.16–5.10 (m, 1H, NC*H*Ph), 3.80–3.70 (m, 2H, NC*H*$_2$CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.5 (C), 142.3 (C), 136.3 (CH), 129.4 (2 x CH), 128.6 (CH), 128.5 (2 x CH), 127.7 (CH), 126.2 (2 x CH), 126.03 (CH), 120.7 (CH), 115.7 (CH), 74.2 (CH), 47.7 (CH_2). IR (neat) ν_{max}/cm^{-1}: 1602, 1505, 1452, 750, 695. MS: *m/z* (% relative intensity): 221 (M^+, 47), 220 (15), 146 (100), 132 (41), 117 (42), 93 (68), 77 (51). HRMS (ESI–TOF): *m/z* [M^+] Calcd for $C_{16}H_{15}N$: 221.1204. Found: 221.1211.

1-Benzyl-2-phenyl-2,5-dihydro-1*H*-pyrrole (9d). Compound **5d** as a mixture of isomers (0.4826 g, 1.34 mmol) was employed to produce, after radial chromatography (100% hexanes), compound **9d** (0.2046 g, 65%; yellow oil). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35 (d, *J* = 7.3 Hz, 2H, Ar*H*), 7.32–7.08 (m, 8H, Ar*H*), 5.81–5.74 (m, 1H, HC=C*H*CH), 5.68–5.59 (m, 1H, CH_2C*H*=CH), 4.54–4.50 (m, 1H, NC*H*Ph), 3.89 (d, *J* = 13.3 Hz, 1H, NC*H*HPh), 3.76–3.61 (m, 1H, CHCHHN), 3.48 (d, J = 13.4 Hz, 1H, NCHHPh), 3.30–3.18 (m, 1H, CHCHHN). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.8 (C), 140.5 (C), 133.4 (CH), 129.9 (2 x CH), 128.9 (2 x CH), 128.8 (2 x CH), 128.5 (2 x CH), 127.9 (CH), 127.8 (CH), 127.5 (CH), 74.9 (CH), 59.8 (CH_2), 58.1 (CH_2). IR (neat) ν_{max}/cm^{-1}: 1490, 1452, 1372, 1029, 759, 738, 700 cm^{-1}. MS: m/z (% relative intensity): 236 (M^++1, 100), 235 (M^+, 45), 234 (29), 158 (45), 144 (42), 91 (80). HRMS (ESI–TOF): m/z [M+H$^+$] Calcd for $C_{17}H_{18}N$: 236.1439. Found: 236.1449.

1,2-Diphenyl-1,2,3,6-tetrahydropyridine (10a).[12] Compound **6a** as a mixture of isomers (0.2013 g, 0.55 mmol) was employed to produce, after radial chromatography (100% hexanes), compound **10a** (0.0983 g, 76%; pale yellow oil). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45–7.27 (m, 5H, Ar*H*), 7.25–7.18 (m, 2H, Ar*H*), 6.75 (br. t, *J* = 7.6 Hz, 1H, Ar*H*), 6.63 (br. d, *J* = 7.6 Hz, 2H, Ar*H*) 5.83–5.78 (m, 2H, *H*C=C*H*), 5.24–5.18 (m, 1H, NC*H*Ph), 3.22 (t, *J* = 7.0 Hz, 2H, CH_2N), 2.47–2.37 (m, 2H, $CHCH_2CH_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.9 (C), 143.1 (C), 134.9 (CH), 129.2 (2 x CH), 128.7 (CH), 128.5 (2 x CH), 127.6 (CH), 126.1 (2 x CH), 117.6 (CH), 113.1 (2 x CH), 74.9 (CH), 43.1 (CH_2), 32.0 (CH_2). IR (neat) ν_{max}/cm^{-1}: 1602, 1505, 1475, 749, 694. MS: *m/z* (%) relative intensity 235 (M^+, 8), 146 (6), 130 (33), 106 (100), 77 (36).

2-Methyl-1-phenyl-1,2,5,6-tetrahydropyridine (10b). Compound **6b** as a mixture of isomers (0.1015 g, 0.33 mmol) was employed to produce, after radial chromatography (100% hexanes), compound **10b** (0.0411 g, 72%; pale yellow oil). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.10 (br. t, *J* = 7.9 Hz, 2H, Ar*H*), 6.64 (br. t, *J* = 7.3 Hz, 1H, Ar*H*), 6.53 (d, *J* = 8.0 Hz, 2H, Ar*H*), 5.60–5.52 (m, 2H, *H*C=C*H*), 4.28–4.12 (m, 1H, NC*H*CH_3), 3.10 (t, *J* = 6.8 Hz, 2H, CH_2N), 2.34–2.19 (m, 2H, $CHCH_2CH_2$), 1.19 (d, *J* = 6.3 Hz, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.9 (C), 136.7 (CH), 129.2 (2 x CH), 127.3 (CH), 117.6 (CH), 113.1 (2 x CH), 68.6 (CH), 43.3 (CH_2), 31.9 (CH_2), 23.8 (CH_3). IR (neat) ν_{max}/cm^{-1}: 1603, 1506, 1320, 750, 693. MS: *m/z* (% relative intensity): 173 (M^+, 1), 106 (100), 79 (28), 77 (43). HRMS (ESI–TOF): *m/z* [M^+] Calcd for $C_{12}H_{15}N$: 173.1204. Found: 173.1211.

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