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Article

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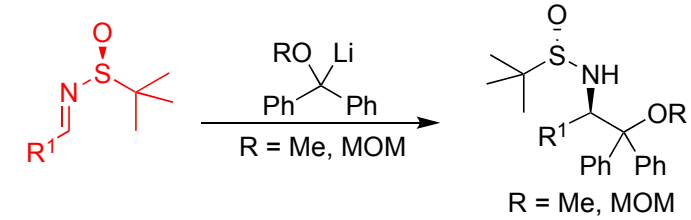
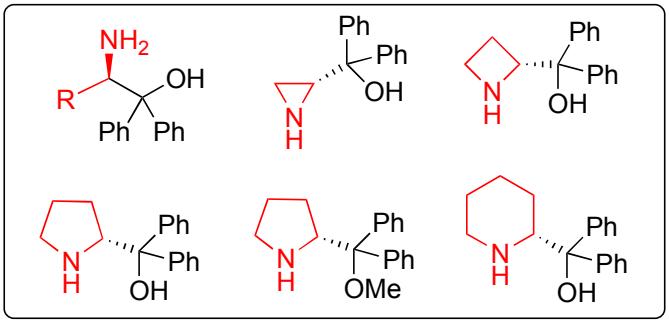




Abstract: Addition of lithium anion generated from diphenylmethanol methyl and methoxymethyl ether to non-racemic sulfinimines afforded the corresponding addition products in excellent diastereoselctivity and yields. Deprotection of the MOM as well as sulfinyl groups rendered the enantiopure diphenylhydroxymethylamines in excellent yields. The procedure was applied for a two-step synthesis of diphenyl prolinol, a privileged ligand in asymmetric catalysis.

Introduction

The geminal-diphenylhydroxy group was often described as a "magic hydroxy group" and a number of catalysts/ ligands containing the diphenylhydroxy groups were considered as privileged ligands in asymmetric catalysis (fig. 1).[1] Catalysts like TADDOLS and chiral diphenylmethanol containing amino alcohols such as diphenyl prolinol, diphenyl valinol were proven as excellent catalysts in a number of catalytic asymmetric transformations. Synthesis of chiral diphenylmethanol containing amino alcohols in general was accomplished from the naturally occurring L-amino acids, while synthesis of the corresponding antipodes involves either the use of unnatural amino acids (which is not cost effective) or multi-step sequence.

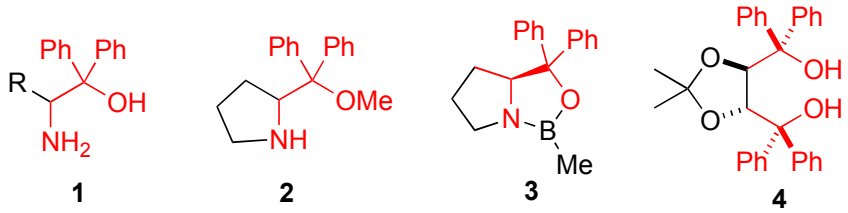


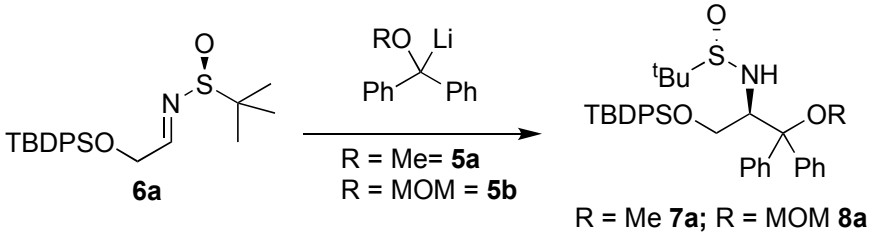
Fig. 1 Diphenylmethanol containing amino alcohol catalysts/ ligands used in asymmetric synthesis

Sulfinimines derived from chiral sulfinamides were established as excellent sulfur based compounds for stereoselective addition of a number of nucleophiles. *p*-Toulenesulfinamide and *tert*-butyl sulfinamide developed by Davis and Ellman respectively has paved the way for the synthesis of a number of chiral amine containing compounds.[2] The reliable selectivities and the ease of deprotection of the sulfinamide have made these reagents one of the widely used for the synthesis of chiral amines. We reasoned that the addition of carbanion derived from diphenylmethanol methyl/ methoxymethyl (MOM) ethers[3] to the sulfinimines should provide a straightforward synthesis of the corresponding diphenylmethanol containing amine compounds, the investigations of which is the subject of this article.

Results and Discussion

We began the study with the addition of carbanion derived from diphenylmethanol methyl ether **5a** to the sulfinimine **6a**. Reaction of **5a** with n-BuLi in presence of TMEDA generated the carbanion which

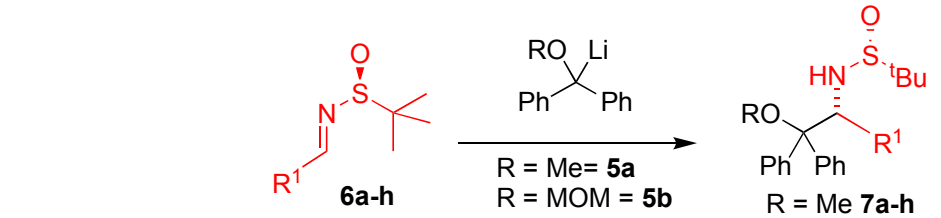
on addition to the sulfinimine **6a** afforded the addition product **7a** in 67% yield with >99:1 diastereomeric ratio.[4] The absence of TMEDA in stabilizing the carbanion led to a decreased yield (43%) of the product with similar diastereomeric ratio. Performing the reaction using LDA as a base did not furnish the product at all. Replacing the methyl ether **5a** with MOM ether **5b** furnished the product **8a** to 76% with similar >99:1 diastereomeric ratio (Scheme-1).



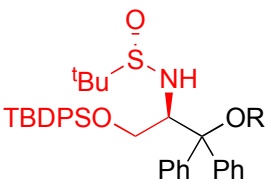
Scheme-1 Addition of lithium anion derived from diphenylmethanol methyl/ MOM ether **5a-b** to the sulfinimine **6a**.

Generality of the above reaction was further investigated by the addition of diphenylmethanol methyl/MOM ether (**5a** and **5b)** to a number of sulfinimines derived from aliphatic as well as aromatic aldehydes. All the reactions proceeded smoothly to afford the corresponding diphenylmethanol methyl/ MOM ether containing sulfinamides in excellent diastereoselectivity and in good yields. It was found that the reaction of the diphenylmethanol methyl ether **5a** with sulfinimine **6c** derived from acetaldehyde afforded the product **7c** as a 93:7 non-separable mixture of diastereomers in 73% yield. However, addition of **5a** to the sulfinimines **6d-e** derived from isobutyraldehyde and pivalaldehyde furnished the products **7d** and **7e** in 74% and 75% yield respectively as a 95:5 and 98:2 separable mixtures of diastereomers. The addition of **5a** to sulfinimine **6f** derived from cyclohexyl carbaldehyde yielded the product **7f** in 66% yield as a separable 90:10 diastereomeric ratio. Similar selectivity was observed in addition of the MOM ether **5b** to the sulfinimine **6f** and the product was obtained in 84% yield. The addition of **5a** and **5b** to the sulfinimine **6h** derived from benzaldehyde proceeded well to yield the products **7h** and **8h** with excellent selectivity. All these results are summarized in chart-1.

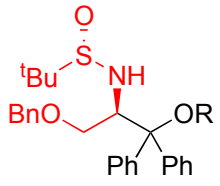
Chart 1: Addition of diphenylmethanol methyl/ MOM ethers to sulfinimines.[a-d]



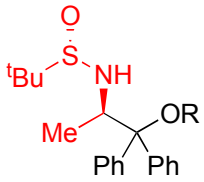
6a R^1= $CH_2OTBDPS$; **6b** R^1 = CH_2OBn
6c R^1 = Me, **6d** R^1= ^{i}Pr, **6e** R^1= ^{t}Bu
6f R^1= cyclohexyl, **6g** R^1= n-hexyl **6h** R^1= Ph



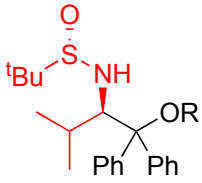
R = Me = **7a** 67%
R = MOM= **8a** = 76%



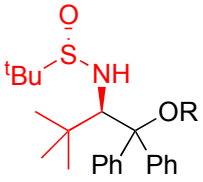
R = MOM = **8b** 75%



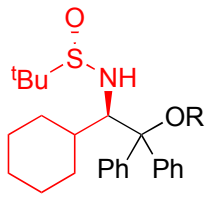
R = Me= **7c** 73%
dr 93: 7 (non-separable)



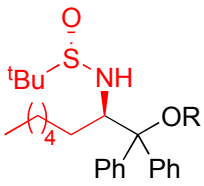
R = Me= **7d** 75%
R =MOM=**8d** 76%
dr 95:5 separable[e]



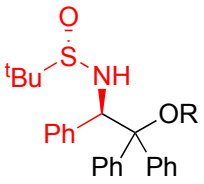
R=Me=**7e** 74%
R=MOM= **8e** 76%
dr 98:2 separable[e]



R=Me= **7f** 64%
R=MOM= **8f** 76%
dr 90:10 separable[e]



R=Me=**7g** 75%



R =Me= **7h** 57%
R =MOM= **8h** 84%

[a]All reactions were carried out in THF as solvent at –78° C. [b]Yields refer to isolated yields after chromatography. [c]The diastereomeric ratio was determined by ^{1}H NMR of the crude reaction mixture. [d]Unless stated all the reactions afforded products with >99% dr. [e]Minor isomer was not isolated by chromatography.

For the synthesis of cyclic amine (aziridne, azitidine, pyrrolidine and pipirdine) containing diphenylmethanol methyl/ MOM ethers, we investigated the addition of **5a** and **5b** to the sulfinimines **6i-n** derived from chloroacetaldehyde, 3-bromopropanal, 4-bromobutanal, 5-bromopentanal, 6-bromohexanal and 8-bromooctanal respectively. We anticipated that the addition of lithium anion to the sulfinimine will initiate the concomitant displacement of the halogen with the formed lithium amide leading to the cyclization. Thus, addition of **5b** to the sulfinimine derived from chloroacetaldehyde afforded the product aziridine **8i** in 56% yield. Similarly, addition of **5b** to the sulfinimines **6j** and **6k**

synthesized from bromopropanal and bromobutanal furnsihed the azitidine and pyrrolidine containing diphenylmethanol ethers **8j** and **8k** in 66% and 79% yields respectively. However, addition of **5b** to the sulfinimines **6l-n** obtained from 5-bromopentanal, 6-bromohexanal and 8-bromooctanal did not yield the cyclized products instead furnished the corresponding uncyclized products in up to 85% yield. Owing to the importance of diphenylprolinol methyl ether and the pyrrolidinemethanol methyl ether in organocatalysis,[5] we have investigated the addition of diphenylmethanol methyl ether **5a** to the sulfinimines **6k** and **6l**. It was observed that the five-membered pyrrolidine formed in 73% yield, while the six membered piperidine formation was not observed and the uncyclized sulfinimine was formed in 69% yield. All these results are summarized in chart-2

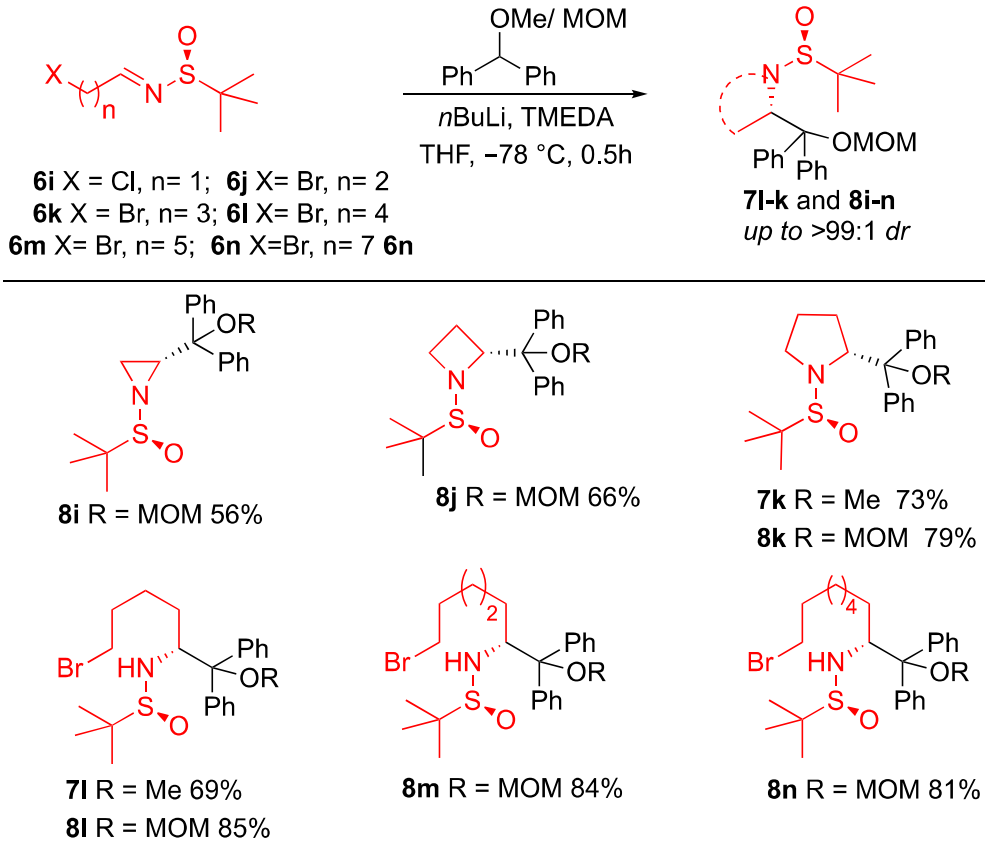
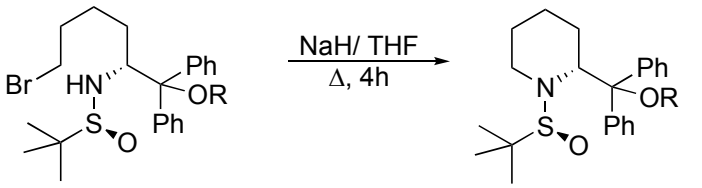


Chart-2: Synthesis of aziridine, azitidine and pyrrolidine containing diphenylmethanols derivatives

Treatment of **7l** and **8l** with NaH smoothly effected the cyclization to furnish the corresponding piperidine derivatives **9** and **10** in 69% and 85% yields respectively (Scheme 2). However, reaction of

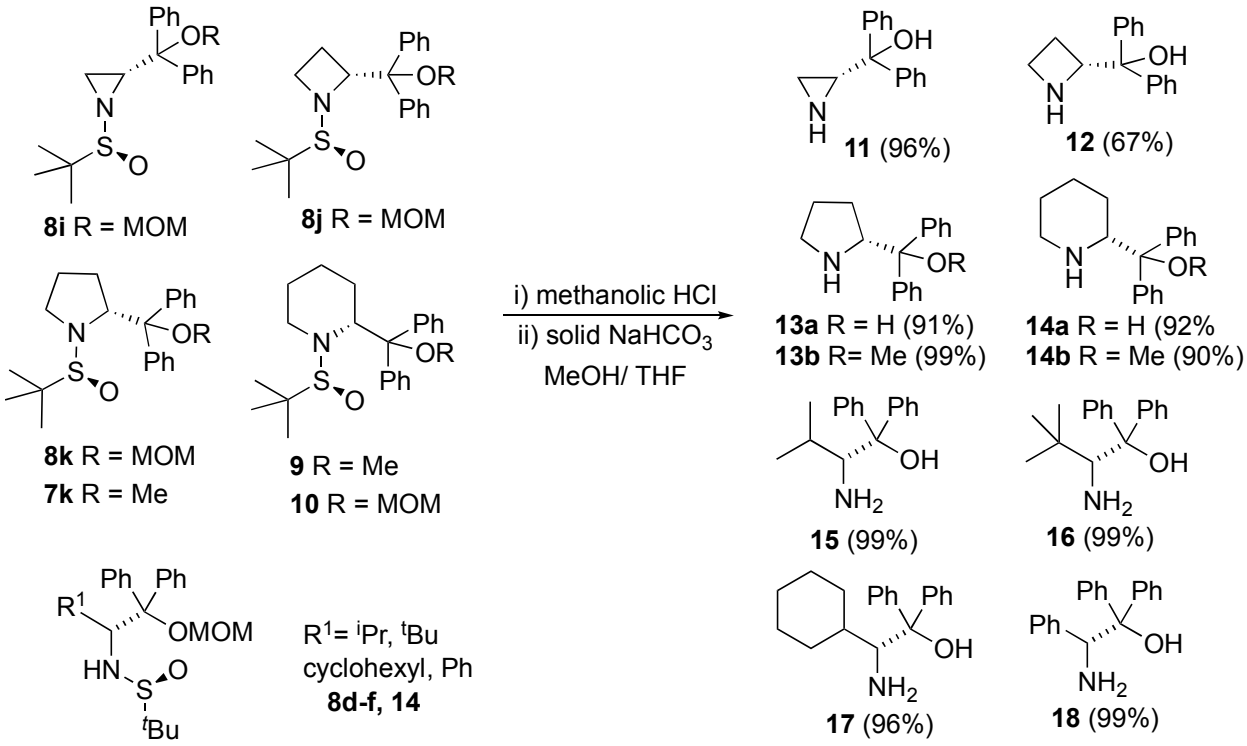
the sulfinamides **8m** and **8n** with NaH did not afford the corresponding cyclic seven and eight membered compounds.



9 R = Me 86%
10 R = MOM 85%

Scheme-2: Synthesis of piperidine containing diphenylmethanol

Deprotection of the sulfinyl as well as the MOM groups in the aziridine, azitidine, pyrrolidine and piperidine containing sulfinamides **8i-k** and **10** was accomplished by reaction with saturated methanolic HCl to furnish the corresponding amino alcohols **11-14** in good yields. Similarly, deprotection of the sulfinyl and MOM groups in **8d-f** and **8h** afforded the corresponding diphenylmethanol containing amino alcohols in excellent yield. Removal of the sulfinyl group in the sulfinamindes **7k** and **10** furnished diphenylprolinol methyl ether **15** and diphenylpiperidinol methyl ether **16** in excellent yields (Scheme-3). This method compliments the existing procedures for the synthesis diphenylprolinol from natural proline[11] but offers a viable alternate route for the synthesis of unnatural diphenylprolinol.



Scheme-3: Synthesis of diphenylmethanol containing cyclic amines

Comparison of the optical rotation of the synthesized diphenylmethoxymethyl amines and the diphenylhydroxy amines with those known in literature and the X-ray crystal structure analysis of the sulfinamide **8m**[6] revealed that the addition of nucleophile occurred from a side opposite to the sulfinyl group. This is contrary to the known addition of simple organolithium reagents to sulfinimines in which the addition of the nucleophiles proceeds with chelation to the sulfinyl oxygen. The present observation can be explained by the strong coordination of lithium to the methyl/ MOM ether oxygen in the carbanion of the diphenylmethanol methyl/ MOM ether and the addition occurring from the least hindered side of the sulfinimine (from a side opposite to the sulfinyl group) (Fig 2).

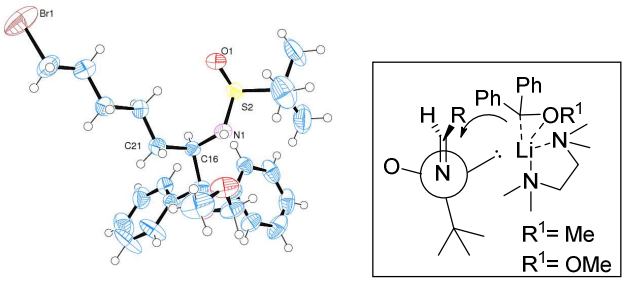


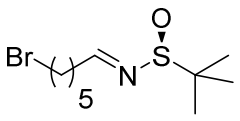
Fig. 2: ORTEP diagram of the crystal structure of **8m** and the proposed transition state for the observed selectivity

Conclusion

In conclusion, an efficient strategy for the synthesis of diphenylmethanol containing amines was developed using the addition of lithium carbanions of diphenylmethanol methyl/ MOM ethers to the sulfinimines. The addition proceeded with very high selectivity and the products were obtained in good yields. Usefulness of this protocol is showcased in a two-step synthesis of diphenyl prolinol and the corresponding methyl ether which are considered as privileged ligands in asymmetric catalysis.

Experimental:

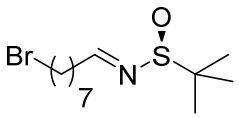
General Information: Column chromatography was performed on silica gel, Acme grade 100−200 mesh. TLC plates were visualized either with UV in an iodine chamber or with phosphomolybdic acid spray unless noted otherwise. All reagents were purchased from commercial sources and used without additional purification. THF was freshly distilled over Na-benzophenone ketyl. Melting points were recorded using melting point apparatus in capillary tubes and are uncorrected. Unless stated otherwise, ^{1}H (400 MHz) and ^{13}C (100 MHz) spectra were recorded on 400 MHz spectrophotometers in $CDCl_3$ as solvent with TMS as reference. High-resolution mass spectra (HRMS) were recorded on a Q-TOF micromass spectrometer using electron spray ionization mode. All sulfinimines except **6m-n** were prepared according to the procedure described by Ellman[7a], Morgas[7b] and Reddy *et al.* [8]



6m

(*S*,*E*)-*N*-(6-bromohexylidene)-2-methylpropane-2-sulfanamide (6m): Sulfinimine **6m** was prepared from 6-bromohexanal (0.67 g, 3.7 mmol), (*S*)-2-methylpropane-2-sulfinamide (0.3 g, 2.5 mmol) and anhydrous $CuSO_4$ (1.66 g, 11.1 mmol) in 85% yield (0.6 g) as a gummy mass using the procedure described in reference[8]. $[\alpha]_D^{24}$ +189.5 (*c* 0.8, $CHCl_3$). IR (Neat): ν_{max} 2954, 1634, 1270, 1135, 1018, 560 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (t, J = 4.4 Hz, 1H), 3.41 (t, J = 6.8 Hz, 2H), 2.55 (q, J = 6.8

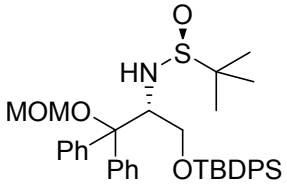
Hz, 2H), 1.90 (quint, J = 6.8 Hz, 2H), 1.68 (quint, J = 6.4 Hz, 2H), 1.52 (quint, J = 8.4 Hz, 2H), 1.20 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.1, 56.5, 35.8, 33.4, 32.4, 27.7, 24.5, 22.3 (3C). HRMS (ESI-TOF) *m/z:* $[M+Na]^+$ calcd for $C_{10}H_{20}BrNOS+Na$ 304.0347.; found 304.0349.



6n

(*S,E*)-*N*-(8-bromooctylidene)-2-methylpropane-2-sulfanamide (6n): Sulfinimine **6n** was prepared from 8-bromooctanal (0.77 g, 3.7 mmol), (*S*)-2-methylpropane-2-sulfinamide (0.3 g, 2.5 mmol) and anhydrous $CuSO_4$ (1.66 g, 11.1 mmol) in 94% yield (0.72 g) as a gummy mass using the procedure described in reference[8]. $[\alpha]_D^{24}$ +195.7 (*c* 1.0, $CHCl_3$). IR (Neat): ν_{max} 2929, 2361, 1627, 1082, 560 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (t, J = 4.8 Hz, 1H), 3.41 (t, J = 6.8 Hz, 2H), 2.52 (m, 2H), 1.86 (quint, J = 6.8 Hz, 2H), 1.64 (quint, J = 7.2 Hz, 2H), 1.51-1.30 (m, 6H), 1.20 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.5, 56.5, 36.0, 33.8, 32.6, 29.0, 28.4, 27.9, 25.3, 22.3 (3C). HRMS (ESI-TOF) *m/z:* $[M+Na]^+$ calcd for $C_{12}H_{24}BrNOS+Na$ 334.0639.; found 334.0636.

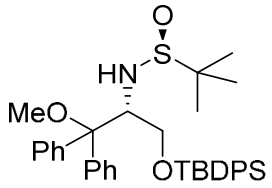
General procedure A for the addition of Methyl or MOM ether of diphenylmethanol to various sulfinimines: The following preparation of **8a** is representative.



8a

(*R*)-*N*-(*tert*-butyl(λ^1-oxidanyl)- λ^3-sulfanyl)amino)-10,10-dimethyl-5,5,9,9-tetraphenyl-2,4,8-trioxa-9-silaundecan-6-amine (8a): To a pre-cooled (−40 °C) stirred solution of ((methoxymethoxy)methylene)dibenzene (0.11 g, 0.48 mmol) in dry THF (10 mL) under argon

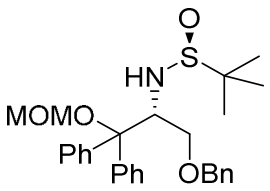
atmosphere at −40 °C was added TMEDA (0.08 mL, 0.53 mmol) followed by ^{n}BuLi (2.0 M solution in hexane 0.27 mL, 0.54 mmol). The resultant bright red colored reaction mixture was stirred for 0.5 h at the same temperature and then it was cooled to −78 °C. Sulfinimine **6a** (0.1 g, 0.25 mmol) dissolved in 4 mL dry THF was added to the reaction mixture at −78 °C. The reaction mixture was stirred at the same temperature for additional 1h and was quenched by addition of saturated NH_4Cl solution (20 mL) and was extracted with EtOAc (2 × 20 mL). The organic layer was washed with brine (20 mL) and dried over anhydrous Na_2SO_4. Evaporation of solvent followed by silica gel column chromatography of the resulting crude residue with petroleum ether/EtOAc as eluent afforded the sulfinamide **8a** in 76 % yield (0.12 g) as a gummy mass. $[\alpha]_D^{24}$ +31.2 (*c* 0.95, $CHCl_3$). IR (Neat): ν_{max} 3194, 2954, 2929, 2361, 1627, 1082 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 7.6 Hz, 2H), 7.57 (d, *J* = 7.6 Hz, 2H), 7.46-7.26 (m, 10H), 7.25-7.12 (m, 6H), 4.61-4.47 (m, 2H), 4.44 (d, *J* = 6.8 Hz, 1H), 4.37 (d, *J* = 9.2 Hz, 1H), 3.95 (dd, *J* = 10.8, 4.4 Hz, 1H), 3.80 (dd, *J* = 10.8, 4.0 Hz, 1H), 3.17 (s, 3H), 1.10 (s, 9H), 0.93 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.4, 141.4, 135.9 (4C), 133.1, 132.8, 129.4, 129.37, 128.2 (2C), 127.9 (2C), 127.8 (2C), 127.7 (2C), 127.5 (2C), 127.4 (2C), 127.2, 127.1, 92.6, 85.4, 63.5, 62.4, 56.6, 56.0, 26.8 (3C), 22.9 (3C), 18.9. HRMS (ESI-TOF) *m/z:* $[M+Na]^+$ calcd for $C_{37}H_{47}NO_4SSi$+Na 652.2893.; found 652.2892.



7a

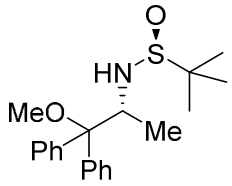
(*R*)-1-*tert*-butyl-*N*-(3-((*tert*-butyldiphenylsilyl)oxy)-1-methoxy-1,1-diphenylpropan-2-yl)-1-(λ^1-oxidanyl)-λ^3-sulfanamine (7a): Compound **7a** was prepared from (methoxymethylene)dibenzene (0.09 g, 0.48 mmol) and sulfinimine **7a** (0.1 g, 0.25 mmol) using the general procedure **A** described above in 67% yield (0.1 g) as a gummy mass. $[\alpha]_D^{24}$ +13.6 (*c* 2.35, $CHCl_3$). IR (Neat): ν_{max} 3400, 2931, 2856,

1653, 1110, 1079 cm^{-1} cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.69 (dd, J = 7.2, 1.6 Hz, 2H), 7.60 (dd, J = 7.6, 1.2 Hz, 2H), 7.47-7.31 (m, 6H), 7.30-7.17 (m, 10H), 4.52-4.37 (m, 1H), 4.01 (dd, J = 10.4, 4.4 Hz, 1H), 3.79-3.63 (m, 2H), 2.82 (s, 3H), 1.10 (s, 9H), 0.96 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.6, 139.8, 136.1 (2C), 135.8 (2C), 133.1, 132.8, 129.6, 129.5, 129.3 (2C), 128.7 (2), 127.5 (5C), 127.4 (3C), 127.2, 84.7, 63.3, 61.2, 56.4, 51.6, 26.9 (3C), 22.7 (3C), 18.9. HRMS (ESI-TOF) *m/z:* $[M+Na]^+$ calcd for $C_{36}H_{45}NO_3SSi$+Na 622.2787.; found 622.2784.



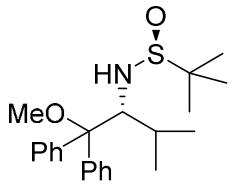
8b

(*R*)-*N*-(3-(benzyloxy)-1-(methoxymethoxy)-1,1-diphenylpropan-2-yl)-1-(*tert*-butyl)-1-(λ^1-oxidaneyl)-(λ^3-sulfanamine (8b): Compound **8b** was prepared from (methoxymethylene)dibenzene (0.18 g, 0.79 mmol) and sulfinimine **6b** (0.1 g, 0.39 mmol) using the general procedure **A** described above in 75% yield (0.142 g) as a gummy mass. $[\alpha]_D^{24}$ +72.7 (*c* 2.15, $CHCl_3$). IR (Neat): ν_{max} 3194, 2923, 2853, 2360, 1627, 1023 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.44-7.34 (m, 4H), 7.33-7.09 (m, 11H), 4.66 (d, J = 7.2 Hz, 1H), 4.59-4.41 (m, 3H), 3.85 (dd, J = 16.0, 12.0 Hz, 2H), 3.80 (dd, J = 10.0, 3.6 Hz, 1H), 3.55 (dd, J = 10.0, 4.4 Hz, 1H), 3.33 (s, 3H), 1.08 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.7, 141.8, 138.3, 128.1 (2C), 128.0 (2C), 127.83 (2C), 127.79 (2C), 127.5 (2C), 127.4 (2C), 127.2, 127.14, 127.10, 92.8, 85.5, 72.8, 71.1, 61.5, 56.7, 56.2, 22.8 (3C). HRMS (ESI-TOF) *m/z:* $[M+Na]^+$ calcd for $C_{28}H_{35}NO_4S$+Na 504.2185.; found 504.2189.



7c

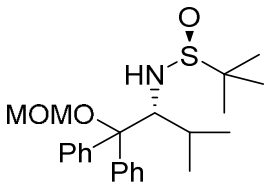
(*R*)-1-*tert*-butyl-*N*-(1-(methoxymethoxy)-1,1-diphenylpropan-2-yl)-1-(λ^1-oxidaneyl)-(λ^3-sulfanamine (7c): Compound **7c** was prepared from (methoxymethylene)dibenzene (0.3 g, 1.5 mmol) and sulfinimine **6c** (0.11 g, 0.75 mmol) using the general procedure **A** described above as an inseparable 93:7 diastereomeric mixture in 73% yield (0.19 g). mp: 115-118 °C. $[\alpha]_D^{24}$ +52.1 (*c* 0.7, $CHCl_3$). IR (KBr): ν_{max} 3309, 2952, 2825, 2361, 2336, 1651, 1070 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.44-7.22 (m, 10H), 4.58-4.40 (m, 1H), 2.98 (s, 0.2H minor), 2.93 (s, 3H major), 2.57 (d, J = 10.8 Hz, 1H), 1.24 (d, J = 6.8 Hz, 2H), 1.07 (s, 9.9 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.5, 139.7, 129.8 (2C), 129.2 (2C), 127.6, 127.5 (3C), 127.4 (2C), 85.4, 56.5, 55.6, 51.0, 22.7 (3C), 19.3. HRMS (ESI-TOF) *m/z:* $[M+Na]^+$ calcd for $C_{20}H_{27}NO_2S$+Na 368.1660.; found 368.1664.



7d

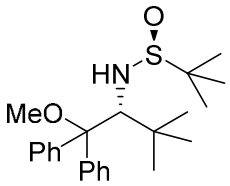
(*R*)-1-*tert*-butyl-*N*-(1-(methoxy-3-methyl-1,1-diphenylbutan-2-yl)-1-(λ^1-oxidaneyl)-(λ^3-sulfanamine (7d): Compound **7d** was prepared from (methoxymethylene)dibenzene (0.23 g, 1.14 mmol) and sulfinimine **6d** (0.1 g, 0.57 mmol) using the general procedure **A** described above as a separable 95:5 diastereomeric mixture. Major isomer was separated using silica gel column chromatography in 75% yield (0.16 g) as a gummy mass. $[\alpha]_D^{24}$ +83.7 (*c* 1.45, $CHCl_3$). IR (Neat): ν_{max} 3347, 2957, 2872, 2361, 2336, 1650, 1074 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.46-7.22 (m, 10H), 4.12 (d, J = 10.4 Hz, 1H), 3.15 (d, J = 10.8 Hz, 1H), 2.89 (s, 3H), 2.31 (quin, J = 6.8 Hz, 1H), 1.21 (d, J = 7.2 Hz, 3H), 1.01 (s,

9H), 0.05 (d, J = 6.8 HZ, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.5, 139.3, 129.8 (2C), 128.8 (2C), 127.7 (2C), 127.63 (2C), 127.58, 127.5, 85.9, 65.7, 56.5, 51.5, 26.4, 22.9, 22.7 (3C), 16.6. HRMS (ESI-TOF) *m/z:* $[M+Na]^+$ calcd for $C_{22}H_{31}NO_2S$+Na 396.1973.; found 396.1970.



8d

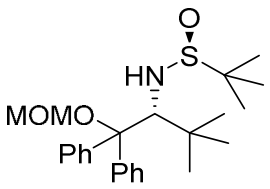
(*R*)-1-*tert*-butyl-*N*-(1-(methoxymethoxy)-3-methyl-1,1-diphenylbutan-2-yl)-1-(λ^1-oxidaneyl)-(λ^3-sulfanamine (8d): Compound **8d** was prepared from (methoxymethylene)dibenzene (0.52 g, 2.29 mmol) and sulfinimine **6d** (0.18 g, 1.0 mmol) using the general procedure **A** described above a separable 95:5 diastereomeric mixture. Major isomer was separated using silica gel column chromatography in 70% yield (0.29 g) as a white solid. mp: 121-124 °C. $[\alpha]_D^{24}$ +65.0 (*c* 0.45, $CHCl_3$). IR (Neat): ν_{max} 3385, 2925, 2853, 2363, 2338, 1590, 1021 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49-7.16 (m, 10H), 4.66 (d, J = 6.4 Hz, 1H), 4.43 (d, J = 6.4 Hz, 1H), 4.17 (d, J = 10.8 Hz, 1H), 3.73 (d, J = 10.8 Hz, 1H), 3.36 (s, 3H), 2.21 (quin, J = 6.8 Hz, 1H), 1.10 (d, J = 6.8 Hz, 3H), 1.06 (s, 9H), 0.26 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.1, 141.0, 128.7 (2C), 128.4 (2C), 127.79 (2C), 127.72 (2C), 127.39, 127.36, 92.8, 86.4, 66.0, 56.8, 56.4, 26.7, 22.9 (3C), 22.8, 17.1. HRMS (ESI-TOF) *m/z:* $[M+Na]^+$ calcd for $C_{23}H_{33}NO_3S$+Na 426.2079.; found 426.2079.



7e

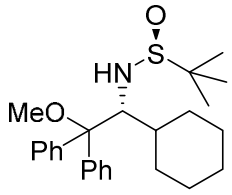
(*R*)-1-*tert*-butyl-*N*-(1-methoxy-3,3-dimethyl-1,1diphenylbutan-2-yl)-1-(λ^1-oxidaneyl)-(λ^3-

sulfanamine (7e): Compound **7e** was prepared from (methoxymethylene)dibenzene (0.21 g, 1.0 mmol) and sulfinimine **7e** (0.1 g, 0.53 mmol) using the general procedure **A** described above as a separable 98:2 diastereomeric mixture. Major isomer was separated using silica gel column chromatography in 74% yield (0.204 g) as a white solid. mp: 117-120 °C. $[\alpha]_D^{24}$ +123.9 (*c* 1.2, $CHCl_3$). IR (KBr): ν_{max} 3357, 3058, 2942, 2868, 2202, 1446, 1067 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 7.6 Hz, 2H), 7.50-7.32 (m, 5H), 7.31-7.17 (m, 3H), 4.05 (d, *J* = 8.0 Hz, 1H), 3.29 (d, *J* = 8.0 Hz, 1H), 2.79 (s, 3H), 0.85 (s, 9H), 0.76 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.0, 137.8, 129.9 (2C), 129.3 (2C), 127.73 (2C), 127.7 (2C), 127.5, 127.3, 88.5, 70.4, 55.9, 52.8, 35.9, 28.7 (3C), 22.3 (3C). HRMS (ESI-TOF b) *m/z:* $[M+Na]^+$ calcd for $C_{23}H_{33}NO_2S$+Na 410.2130.; found 410.2108.



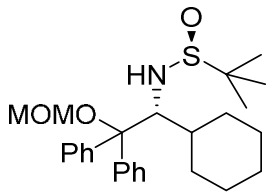
8e

(*R*)-1-*tert*-butyl-*N*-(1-methoxymethoxy)-3,3-dimethyl-1,1diphenylbutan-2-yl)-1-(λ^1-oxidaneyl)-(λ^3-sulfanamine (8e): Compound **8e** was prepared from (methoxymethylene)dibenzene (0.24 g, 1.06 mmol) and sulfinimine **7e** (0.1 g, 0.53 mmol) using the general procedure **A** described above as a separable 98:2 diastereomeric mixture. Major isomer was separated using silica gel column chromatography in in 73% yield (0.16 g) as a white solid. mp: 89-94 °C. $[\alpha]_D^{24}$ +118.0 (*c* 0.5, $CHCl_3$). IR (KBr): ν_{max} 3354, 2949, 2856, 2291, 2247, 1597, 1069 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 7.2 Hz, 2H), 7.51-7.30 (m, 5H), 7.29-7.14 (m, 3H), 4.45 (d, *J* = 5.6 Hz, 1H), 4.13 (d, *J* = 8.0 Hz, 1H), 4.03 (d, *J* = 5.6 Hz, 1H), 3.43-3.31 (m, 4H), 0.83 (s, 9H), 0.78 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.5, 138.4, 129.4 (2C), 128.9 (2C), 127.9 (2C), 127.7, 127.6 (2C), 127.5, 93.3, 88.1, 70.2, 56.4, 56.0, 36.0, 28.9 (3C), 22.3 (3C). HRMS (ESI-TOF) *m/z:* $[M+Na]^+$ calcd for $C_{24}H_{35}NO_3S$+Na 440.2235.; found 440.2237.



7f

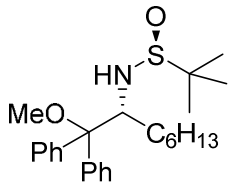
(*R*)-1-*tert*-butyl-*N*-(1-(cyclohexyl-2-methoxy-2,2-diphenylethyl)-1-(λ^1-oxidaneyl)-(λ^3-sulfanamine (7f): Compound **7f** was prepared from (methoxymethylene)dibenzene (0.18 g, 0.92 mmol) and sulfinimine **6f** (0.1 g, 0.46 mmol) using the general procedure **A** described above a separable 90:10 diastereomeric mixture. Major isomer was separated using silica gel column chromatography in 84% yield (0.16 g) as a white solid. mp: 121-124 °C. $[\alpha]_D^{24}$ +75.6 (*c* 5.5, $CHCl_3$). IR (KBr): ν_{max} 3282, 2924, 2853, 1447, 1184, 1069 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.48-7.22 (m, 10H), 4.03 (d, *J* = 10.8 Hz, 1H), 3.20 (d, *J* = 10.8 Hz, 1H), 2.88 (s, 3H), 1.98-1.61 (m, 4H), 1.50 (d, *J* = 13.2 Hz, 1H), 1.40-1.26 9m, 2H), 1.09 (tq, *J* = 12.8, 3.6 Hz, 1H), 1.03 (s, 9H), 0.89 (tq, *J* = 12.8, 3.6 Hz, 1H), 0.37 (dq, *J* = 14.4, 2.8 Hz, 1H), −0.30 (d, *J* = 11.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.6, 139.6, 129.7 (2C), 128.7 (2C), 127.7 (2C), 127.6 (2C), 127.56, 127.51, 85.9, 66.1, 56.5, 51.4, 37.2, 33.2, 28.8, 27.2, 26.2, 26.0, 22.7 (3C). HRMS (ESI-TOF) *m/z:* $[M+Na]^+$ calcd for $C_{25}H_{35}NO_2S$+Na 436.2286.; found 436.2287.



8f

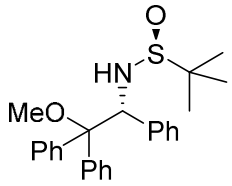
(*R*)-1-*tert*-butyl-*N*-(1-(cyclohexyl-2-(methoxymethoxy)-2,2-diphenylethyl)-1-(λ^1-oxidaneyl)-(λ^3-sulfanamine (8f): Compound **8f** was prepared from (methoxymethylene)dibenzene (0.42 g, 1.8 mmol) and sulfinimine **6f** (0.2 g, 0.93mmol) using the general procedure **A** described above as a separable 90:10 diastereomeric mixture. Major isomer was separated using silica gel column chromatography in 66% yield (0.27 g) as a white solid. mp: 91-96 °C. $[\alpha]_D^{24}$ +86.5 (*c* 5.5, $CHCl_3$). IR (KBr): ν_{max} 3279,

2924, 2853, 1591, 1020 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.49-7.17 (m, 10H), 4.55 (d, J = 6.4 Hz, 1H), 4.43 (d, J = 6.4 Hz, 1H), 4.07 (d, J = 10.8 Hz, 1H), 3.72 (d, J = 10.8 Hz, 1H), 3.34 (s, 3H), 1.97-1.62 (m, 3H), 1.56-1.38 (m, 3H), 1.25-1.06 (m, 2H), 1.05 (s, 9H), 1.03-0.35 (m, 2H), 0.25 (d, J = 10.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.8, 141.1, 128.9 (2C), 128.3 (2C), 127.7 (2C), 127.6 (2C), 127.4 (2C), 92.5, 86.2, 66.2, 56.7, 56.3, 37.3, 33.1, 28.5, 27.1, 26.4, 25.9, 22.9 (3C). HRMS (ESI-TOF) *m/z:* $[M+Na]^+$ calcd for $C_{26}H_{37}NO_3S$+Na 466.2392.; found 466.2392.



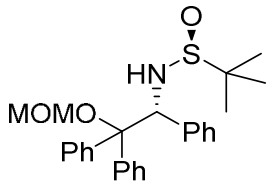
7g

(*R*)-1-*tert*-butyl-*N*-(1-(methoxy-1,1-diphenyloctan-2-yl)-1-(λ^1-oxidaneyl)-(λ^3-sulfanamine (7g): Compound **7g** was prepared from (methoxymethylene)dibenzene (0.18 g, 0.92 mmol) and sulfinimine **6g** (0.1 g, 0.46 mmol) using the general procedure **A** described above in 75% yield (0.15 g) as a gummy mass. $[\alpha]_D^{24}$ +50.4 (*c* 0.5, $CHCl_3$). IR (Neat): ν_{max} 3435, 2927, 2857, 2361, 2336, 1644, 1074 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.47-7.22 (m, 10H), 4.17 (t, J = 9.6 Hz, 1H), 2.87 (s, 3H), 2.51 (d, J = 9.2 Hz, 1H), 1.99-1.85 (m, 1H), 1.83-1.69 (m, 1H), 1.52-1.36 (m, 1H), 1.33-1.21 (m, 6H), 1.04 (s, 9H), 0.85 (t, J = 6.8 Hz, 3H), 0.71-0.52 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.7, 139.1, 129.8 (2C), 129.2 (2C), 127.61 (2C), 127.60 (2C), 127.5 (2C), 86.4, 62.2, 56.6, 51.5, 31.7, 29.4, 26.2, 22.7 (5C), 14.1 HRMS (ESI-TOF) *m/z:* $[M+Na]^+$ calcd for $C_{25}H_{37}NO_2S$+Na 438.2443.; found 438.2437.



7h

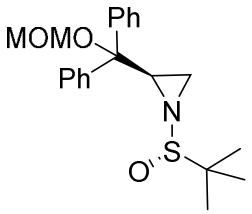
(*R*)-1-*tert*-butyl-*N*-(2-methoxy-1,2,2-triphenylethyl)-1-(λ^1-oxidaneyl)-(λ^3-sulfanamine (7h): Compound **7h** was prepared from (methoxymethylene)dibenzene (0.19 g, 0.95 mmol) and sulfinimine **6h** (0.1 g, 0.5 mmol) using the general procedure **A** described above in 57% yield (0.112 g) as a gummy mass. $[\alpha]_D^{24}$ +62.5 (*c* 0.8, $CHCl_3$). IR (Neat): ν_{max} 3323, 2953, 2931, 2859, 2365, 2338, 1651, 1077 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.45 (dd, *J* = 8.4, 1.6 Hz, 2H), 7.39-7.24 (m, 6H), 7.23-7.04 (m, 5H), 6.70 (d, *J* = 7.2 Hz, 2H), 5.36 (d, *J* = 10.4 Hz, 1H), 3.66 (d, *J* = 10.4 Hz, 1H), 2.89 (s, 3H), 1.02 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.5, 138.9, 138.2, 130.1 (2C), 129.5 (2C), 128.8 (2C), 127.8, 127.7 (2C), 127.6, 127.3, 127.2 (2C), 127.0 (2C), 86.6, 65.6, 56.5, 52.0, 22.5 (3C). HRMS (ESI-TOF) *m/z:* $[M+Na]^+$ calcd for $C_{25}H_{29}NO_2S$+Na 430.1817.; found 430.1819.



8h

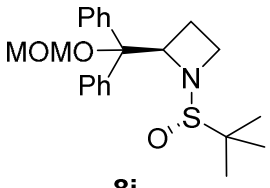
(*R*)-1-*tert*-butyl-*N*-(2-methoxymethoxy)-1,2,2-triphenylethyl)-1-(λ^1-oxidaneyl)-(λ^3-sulfanamine (8h): Compound **8h** was prepared from (methoxymethylene)dibenzene (0.44 g, 1.9 mmol) and sulfinimine **6h** (0.2 g, 0.93 mmol) using the general procedure **A** described above in 84% yield (0.35 g) as a white solid. mp: 76-80 °C. $[\alpha]_D^{24}$ +165.0 (*c* 1.5, $CHCl_3$). IR (KBr): ν_{max} 3269, 2924, 2856, 2387, 2289, 1590, 1020 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.39 (dd, *J* = 8.4, 1.6 Hz, 2H), 7.37-7.24 (m, 4H), 7.17-7.00 (m, 7H), 6.91 (dd, *J* = 7.2, 1.6 Hz, 2H), 5.29 (d, *J* = 11.2, Hz, 1H), 5.08 (d, *J* = 11.2 Hz, 1H), 4.81 (d, *J* = 7.2 Hz, 1H), 4.61 (d, *J* = 6.8 Hz, 1H), 3.56 (s, 3H), 1.13 (s, 9H). ^{13}C NMR (100 MHz,

$CDCl_3$): δ 143.7, 141.3, 139.2, 129.2 (2C), 128.7 (2C), 127.8 (2C), 127.6, 127.5 (2C), 127.4 (2C), 127.2 (2C), 126.9, 126.8, 93.9, 87.4, 66.2, 57.0, 56.8, 22.8 (3C). HRMS (ESI-TOF) *m/z:* $[M+Na]^+$ calcd for $C_{26}H_{31}NO_3S$+Na 460.1922.; found 460.1920.



8i

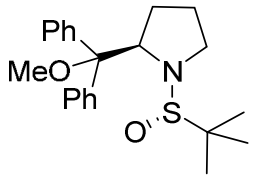
(*R*)-1-(*tert*-butyl(λ^1-oxidaneyl)-(λ^3-sulfaneyl)-2-((methoxymethoxy)diphenylmethyl)aziridine (8i): Compound **8i** was prepared from (methoxymethylene)dibenzene (0.18 g, 0.77 mmol) and sulfinimine **6i** (0.07 g, 0.4 mmol) using the general procedure **A** described above in 56% yield (0.09 g) as a gummy mass. $[\alpha]_D^{24}$ +157.1 (*c* 1.35, $CHCl_3$). IR (Neat): ν_{max} 3420, 2923, 2861, 235, 2337, 1641, 1026 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.48-7.20 (m, 10H), 4.72 (d, J = 6.8 Hz, 1H), 4.62 (d, J = 6.8 Hz, 1H), 3.42 (s, 3H), 3.06 (dd, J = 6.4, 4.0 Hz, 1H), 2.58 (d, J = 6.8 Hz, 1H), 1.59- (d, J = 4.0 Hz, 1H), 1.16 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.8, 141.5, 128.6 (2C), 127.9 (2C), 127.8, 127.7 (2C), 127.6 (2C), 127.5, 92.7, 83.0, 57.3, 55.9, 37.6, 22.6 (3C), 21.1. HRMS (ESI-TOF) *m/z:* $[M+Na]^+$ calcd for $C_{21}H_{27}NO_3S$+Na 396.1609.; found 396.1609.



8j

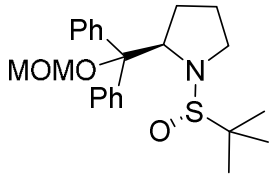
(*R*)-1-(*tert*-butyl(λ^1-oxidaneyl)-(λ^3-sulfaneyl)-2-((methoxymethoxy)diphenylmethyl)azetidine (8j): Compound **8j** was prepared from (methoxymethylene)dibenzene (0.19 g, 0.83 mmol) and sulfinimine **6j** (0.1 g, 0.42 mmol) using the general procedure **A** described above in 66% yield (0.13 g) as a gummy mass. $[\alpha]_D^{24}$ +155.7 (*c* 1.35, $CHCl_3$). IR (Neat): ν_{max} 3195, 2920, 2856, 2362, 1629, 1021 cm^{-1}. ^1H

NMR (400 MHz, $CDCl_3$): δ 7.46 (d, J = 7.6 Hz, 2H), 7.40-7.21 (m, 8H), 5.14 (dd, J = 8.8, 6.8 Hz, 1H), 4.74 (d, J = 6.4 Hz, 1H), 4.59 (d, J = 6.0 Hz, 1H), 4.18 (q, J = 7.6 Hz, 1H), 3.41 (s, 3H), 2.79 (q, J = 8.8 hz, 1H), 2.36 (sept, J = 6.4 Hz, 1H), 1.04 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.5, 140.9, 128.8 (4C), 127.6 (2C), 127.59, 127.55, 127.5 (2C), 92.6, 85.3, 67.7, 57.3, 56.1, 39.6, 23.6 (3C).21.7. HRMS (ESI-TOF) *m/z:* $[M+Na]^+$ calcd for $C_{22}H_{29}NO_3S$+Na 410.1766.; found 410.1765.



7k

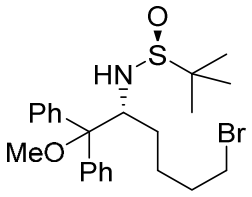
(*R*)-1-(*tert*-butyl(λ^1-oxidaneyl)-(λ^3-sulfaneyl)-2-(methoxy)diphenylmethyl)pyrrolidine (7k): Compound **7k** was prepared from (methoxymethylene)dibenzene (0.16 g, 0.8 mmol) and sulfinimine **6k** (0.11 g, 0.44 mmol) using the general procedure **A** described above in 79% yield (0.13 g) as a gummy mass. $[\alpha]_D^{24}$ +103.3 (*c* 2.1, $CHCl_3$). IR (Neat): ν_{max} 3195, 2920, 2856, 2362, 1629, 1021 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.23 (m, 10H), 4.89 (dd, J = 9.2, 3,2 Hz, 1H), 3.48 (ddd, J = 10.2, 8.8, 6.8 Hz, 1H), 2.9 (s, 3H), 2.10-1.88 (m, 2H), 1.94-1.76 (m, 1H), 1.54-1.34 (m, 1H), 1.08 (s, 9H), 0.58-0.37 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.1, 139.1, 130.3 (2C), 129.7 (2C), 127.6 (2C), 127.54, 127.48, 127.3 (2C), 86.1, 72.8, 58.1, 51.6, 42.5, 27.7, 25.6, 24.0 (3C). HRMS (ESI-TOF) *m/z:* $[M+Na]^+$ calcd for $C_{22}H_{29}NO_2S$+Na 394.1817.; found 394.1819.



8k

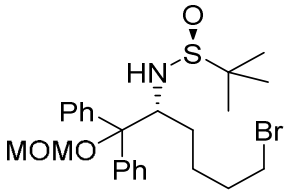
(*R*)-1-(*tert*-butyl(λ^1-oxidaneyl)-(λ^3-sulfaneyl)-2-(methoxymethoxy)diphenylmethyl)pyrrolidine (8k): Compound **8k** was prepared from (methoxymethylene)dibenzene (0.18 g, 0.8 mmol) and

sulfinimine **6k** (0.1 g, 0.39 mmol) using the general procedure **A** described above in 73% yield (0.14 g) as a gummy mass. $[\alpha]_D^{24}$ +55.5 (*c* 1.4, $CHCl_3$). IR (Neat): ν_{max} 3195, 2921, 2854, 2552, 1629, 1021 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.58-7.46 (m, 4H), 7.41-7.25 (m, 6H), 4.97 (dd, *J* = 8.8 Hz, 2.8 Hz, 1H), 4.53 (d, *J* = 5.6 Hz, 1H), 4.33 (d, *J* = 5.6 Hz, 1H), 3.49 (q, *J* = 8.8 Hz, 1H), 3.26 (s, 3H), 2.08-1.85 (m, 3H), 1.55-1.38 (m, 1H), 1.05 (s, 9H), 0.62-0.41 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.1, 139.7, 130.3 (2C), 129.5 (2C), 129.8, 127.6, 127.5 (2C), 127.3 (2C), 92.2, 85.8, 73.6, 58.2, 55.9, 42.7, 27.7, 25.6, 24.1 (3C). HRMS (ESI-TOF) *m/z:* $[M+Na]^+$ calcd for $C_{23}H_{31}NO_3S$+Na 424.1922.; found 424.1927.



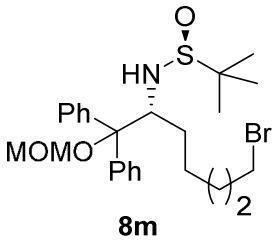
7l

(*R*)-*N*-(6-bromo-1-methoxy-1,1-diphenylhexan-2-yl)-1-(*tert*-butyl)-1-(λ^1-oxidaneyl)-(λ^3-sulfanamine) (7l): Compound **7l** was prepared from (methoxymethylene)dibenzene (0.17 g, 0.88 mmol) and sulfinimine **6l** (0.1 g, 0.44 mmol) using the general procedure **A** described above in 68% yield (0.12 g) as a gummy mass. $[\alpha]_D^{24}$ +38.0 (*c* 0.5, $CHCl_3$). IR (Neat): ν_{max} 3418, 2922, 2856, 2360, 1630, 1023 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.46-7.22 (m, 10H), 4.16 (t, *J* = 9.6 Hz, 1H), 3.38 (t, *J* = 6.4 Hz, 2H), 2.87 (s, 3H), 2.56 (d, *J* = 9.2 Hz, 1H), 2.07-1.71 (m, 4H), 1.68-1.51 (m, 1H), 1.02 (s, 9H), 0.73-0.54 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.5, 138.7, 129.8 (2C), 129.1 (2C), 127.73, 127.70 (2C), 127.63 (2C), 127.60, 86.4, 62.1, 56.6, 51.6, 33.4, 32.9, 32.4, 24.9, 22.6 (3C). HRMS (ESI-TOF) *m/z:* $[M+Na]^+$ calcd for $C_{23}H_{32}BrNO_2S$+Na 488.1235; found 488.1234.



8l

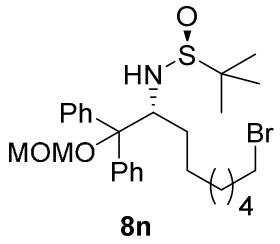
(*R*)-*N*-(6-bromo-1-(methoxymethoxy)-1,1-diphenylhexan-2-yl)-1-(*tert*-butyl)-1-(λ^1-oxidaneyl)-(λ^3-sulfamine) (8l): Compound **8i** was prepared from (methoxymethylene)dibenzene (0.2 g, 0.88 mmol) and sulfinimine **6l** (0.1 g, 0.44 mmol) using the general procedure **A** described above in 69% yield (0.13 g) as a gummy mass. $[\alpha]_D^{24}$ +92.4 (*c* 2.6, $CHCl_3$). IR (Neat): ν_{max} 3418, 2922, 2856, 2360, 1630, 1023 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.47-7.33 (m, 4H), 7.38-7.12 (m, 6H), 4.76 (d, *J* = 7.2 Hz, 1H), 4.61 (d, *J* = 7.2 Hz, 1H), 4.20 (t, *J* = 8.8 Hz, 2H), 3.48 (s, 3H), 3.25 (t, *J* = 6.8 Hz, 2H), 1.84-1.60 (m, 4H), 1.43-1.27 (m, 1H), 1.26-1.16 (m, 1H), 1.04 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.5, 128.3 (2C), 127.98 (3C), 127.95 (3C), 127.2, 127.0, 126.8, 93.0, 87.1, 62.4, 56.9, 56.3, 33.4, 32.7, 32.0, 25.2, 22.9 (3C). HRMS (ESI-TOF) *m/z:* $[M+Na]^+$ calcd for $C_{24}H_{34}BrNO_3S$+Na 518.1340.; found 518.1346.



8m

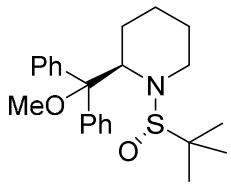
(*R*)-*N*-(9-bromo-1-(methoxymethoxy)-1,1-diphenylnonan-2-yl)-1-(*tert*-butyl)-1-(λ^1-oxidaneyl)-(λ^3-sulfamine) (8m): Compound **8m** was prepared from (methoxymethylene)dibenzene (0.15 g, 0.66 mmol) and sulfinimine **6m** (0.6 g, 0.33 mmol) using the general procedure **A** described above in 84% yield (0.15 g) as a solid. mp: 100-105 °C. $[\alpha]_D^{24}$ +100.5 (*c* 1.7, $CHCl_3$). IR (Neat): ν_{max} 3297, 2951, 2863, 2198, 1445, 1018 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.47-7.34 (m, 4H), 7.38-7.12 (m, 6H), 4.76 (d, *J* = 7.2 Hz, 1H), 4.61 (d, *J* = 7.2 Hz, 1H), 4.24-4.12 (m, 1H), 3.47 (s, 3H), 3.31 (t, *J* = 6.8 Hz, 2H), 1.85-1.61 (m, 4H), 1.37-1.13 (m, 5H), 1.04 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.6, 128.3

(3C), 127.9 (5C), 127.2, 127.0 (2C), 92.9, 87.1, 62.6, 56.9, 56.2, 34.1, 32.7, 32.4, 27.9, 25.6, 23.0 (3C). HRMS (ESI-TOF) *m/z:* $[M+Na]^+$ calcd for $C_{25}H_{36}BrNO_3S$+Na 532.1497.; found 532.1496.



8n

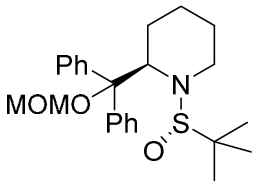
(*R*)-*N*-(9-bromo-1-(methoxymethoxy)-1,1-diphenylnonan-2-yl)-1-(*tert*-butyl)-1-(λ^1-oxidaneyl)-(λ^3-sulfamine) (8n): Compound **8n** was prepared from (methoxymethylene)dibenzene (0.145 g, 0.64 mmol) and sulfinimine **6n** (0.1 g, 0.32 mmol) using the general procedure **A** described above in 81% yield (0.14 g) as a gummy mass. $[\alpha]_D^{24}$ +85.5 (*c* 2.35, $CHCl_3$). IR (Neat): ν_{max} 3283, 2928, 2845, 2358, 1636, 1084 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.42 (t, *J* = 6.8 Hz, 4H), 7.37-7.11 (m, 6H), 4.76 (d, *J* = 7.2 Hz, 1H), 4.61 (d, *J* = 7.2 Hz, 1H), 4.19 (t, *J* = 7.2 Hz, 1H), 3.46 (s, 3H), 3.35 (t, *J* = 6.8 Hz, 2H), 1.86-1.70 (m, 3H), 1.69-1.59 (m, 1H), 1.37-1.21 (m, 3H), 1.20-1.06 (m, 6H), 1.03 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.7, 128.3 (2C), 127.9 (2C), 127.8 (2C), 127.1, 127.02, 127.0, 126.96, 126.9, 93.0, 87.1, 62.7, 56.8, 56.2, 34.0, 32.9, 32.7, 29.1, 28.3, 28.0, 26.4, 22.9 (3C). HRMS (ESI-TOF) *m/z:* $[M+Na]^+$ calcd for $C_{27}H_{40}BrNO_3S$+Na 560.1810.; found 560.1805.



9

(*R*)-1-(*tert*-butyl(λ^1-oxidaneyl)-(λ^3-sulfaneyl)-2-(methoxy)diphenylmethyl)piperidine (9): To a stirred solution of **7l** (0.065 g, 0.14 mmol) in dry THF (35 mL) at 0 °C was added NaH (60% in mineral oil, 0.01 g, 0.14 mmol). The reaction mixture was refluxed for 4 h at 70 °C. After completion of reaction (TLC) it was quenched with ice cold water and extracted with EtOAc (2 × 40 mL). The organic layer

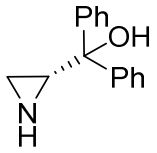
was washed with brine (30 mL) and dried over Na_2SO_4. Evaporation of solvent afforded the product in 86% yield (0.045 g) as a gummy mass. $[\alpha]_D^{24}$ +51.5 (*c* 1.05, $CHCl_3$). IR (Neat): ν_{max} 3134, 2929, 2860, 2392, 1590, 1219, 1020 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.59-7.42 (m, 4H), 7.44-7.27 (m, 6H), 4.61 (t, *J* = 7.2 Hz, 1H), 3.16 (dd, *J* = 14.0, 6.8 Hz, 1H), 2.77 (s, 3H), 2.01-1.85 (m, 1H), 1.84-1.71 (m, 1H), 1.65-1.50 (m, 2H), 1.48-1.34 (m, 1H), 1.26 (m, 1H), 1.17 (s, 9H), 1.02-0.85 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.7, 138.6, 130.6 (2C), 130.0 (2C), 127.7 (2C), 127.6, 127.5, 127.3 (2C), 86.9, 67.5, 59.6, 51.3, 40.5, 24.8 (3C), 24.5, 23.8, 18.8. HRMS (ESI-TOF) *m/z:* $[M+Na]^+$ calcd for $C_{23}H_{31}NO_2S$+Na 408.1973; found 408.1978.



10

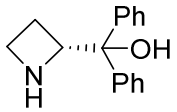
(*R*)-1-(*tert*-butyl(λ^1-oxidaneyl)-(λ^3-sulfaneyl)-2-(methoxymethoxy)diphenylmethyl)piperidine (10): To a stirred solution of **8l** (0.15 g, 0.3 mmol) in dry THF (15 mL) at 0 °C was added NaH (60% in mineral oil, 0.036 g, 0.9 mmol). The reaction mixture was refluxed for 4 h at 70 °C. After completion of reaction (TLC) it was quenched with ice cold water and extracted with EtOAc (2 × 40 mL). The organic layer was washed with brine (30 mL) and dried over Na_2SO_4. Evaporation of solvent afforded the product in 85% yield (0.11 g) as a gummy mass. $[\alpha]_D^{24}$ +51.5 (*c* 1.05, $CHCl_3$). IR (Neat): ν_{max} 3395, 3057, 2929, 2852, 1601, 1446, 1075 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.62-7.47 (4H), 7.44-7.29 (m, 6H), 4.69 (t, *J* = 7.6 Hz, 1H), 4.34 (q, *J* = 5.6 Hz, 2H), 3.20 (s, 3H), 3.11 (ddd, *J* = 15.2, 7.0, 1.6 Hz, 1H), 2.04-1.80 (m, 2H), 1.70 -1.53 (m, 2H), 1.50-1.38 (m, 1H), 1.37-1.21 (m, 1H), 1.15 (s, 9H), 1.06-0.91 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.2, 139.1, 130.4 (2C), 129.8 (2C), 127.9, 127.8, 127.7 (2C), 127.4 (2C), 92.1, 86.7, 67.7, 59.5, 55.9, 40.7, 24.9 (3C), 24.4, 23.6, 18.8. HRMS (ESI-TOF) *m/z:* $[M+Na]^+$ calcd for $C_{24}H_{33}NO_3S$+Na 438.2079; found 438.2077.

General procedure B for the deprotection of MOM as well as sulfinyl group: The following preparation of **11** is representative.



11

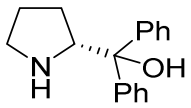
(*R*)-aziridin-2-yldiphenylmethanol (11): To a precooled stirred solution of **8i** (0.05 g, 0.13 mmol) in MeOH (3 mL) at 0 °C was added a saturated solution of HCl in MeOH (0.7 mL). The reaction mixture was stirred for 4 h at the room temperature. After completion of the reaction (TLC), the solvent was evaporated off, and the resultant white salt was dissolved in THF-MeOH (4 mL). Solid $NaHCO_3$ (0.25 g, 3 mmol) was added to the reaction mixture and was stirred for 6h at rt. The reaction mixture was filtered on a short celite pad. Evaporation of solvent followed by crystallization in CH_2Cl_2 afforded the product **11** in 96% yield (0.029g) as a colorless crystal. mp: 152-155 °C, [lit.[9] 155-157 °C]. $[\alpha]_D^{24}$ +28° (*c* 2.35, $CHCl_3$), [for enantiomer lit.[9] –22.6° (c 1.0, $CHCl_3$)]. IR (KBr): ν_{max} 3283, 2928, 2845, 2358, 1636, 1084 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.53-7.20 (m, 10H), 2.9 (m, 1H), 1.49 (d, J = 5.6 Hz, 1H), 1.77 (d, 3.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.2, 145.1, 128.2 (2C), 128.1 (2C), 127.15, 127.11, 126.6 (2C), 126.3 (2C), 74.4, 37.0, 22.0. HRMS (ESI-TOF) *m/z:* $[M+H]^+$ calcd for $C_{15}H_{15}NO$+H 226.1232.; found 226.1236.



12

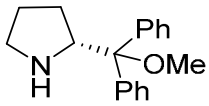
(*R*)-azetidin-2-yldiphenylmethanol (12): Compound **12** was prepared from **8j** (0.12 g, 0.31 mmol) using the general procedure **B** described above in 67% yield (0.05 g) as a white solid. mp: 111-115 °C, [lit.[10] 116 °C]. $[\alpha]_D^{24}$ +73° (*c* 0.8, MeOH), [lit.[10] +75° (c 1.0, MeOH)]. IR (KBr): ν_{max} 3283, 2928, 2845,

2358, 1636, 1084 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.47-7.10 (m, 10H), 4.88 (t, J = 8.0 Hz, 1H), 3.61 (q, J = 8.8 Hz, 1H), 3.17 (ddd, J = 8.4, 7.2, 3.2 Hz, 1H), 2.46-2.26 (m, 1H), 2.02-1.84 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.5, 143.5, 128.1 (2C), 128.0 (2C), 126.7, 126.6, 126.2 (2C), 126.0 (2C), 76.6, 64.8, 42.4, 22.0. HRMS (ESI-TOF) *m/z:* $[M+H]^+$ calcd for $C_{16}H_{17}NO$+H 240.1388.; found 240.1390.



13a

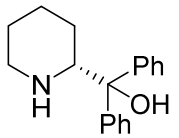
(*R*)-diphenyl(pyrrolidin-2-yl)methanol (13a): Compound **13a** was prepared from **8k** (1.1 g, 2.74 mmol) using the general procedure **B** described above in 91% yield (0.63 g) as a yellowish gummy mass, which up on recrystallization in EtOAc gave the pale yellow crystals. mp: 75-78 °C, [lit.[11] 74 °C]. $[\alpha]_D^{24}$ +71° (*c* 3.0, MeOH), [lit.[11] –68° (c 3.0, MeOH for the enantiomer)]. IR (KBr): ν_{max} 3368, 2930, 2865, 2373, 1597, 1026 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.62-7.07 (m, 10H), 4.25 (t, J = 7.6 Hz, 1H), 3.08-2.84 (m, 2H), 1.79-1.48 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.1, 145.4, 128.2 (2C), 127.9 (2C), 126.4, 126.3, 125.8, 125.5, 77.1, 64.4, 46.7, 26.2, 25.5. HRMS (ESI-TOF) *m/z:* $[M+H]^+$ calcd for $C_{17}H_{19}NO$+H 254.1545.; found 254.1545.



13b

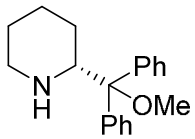
(*R*)-2-(methoxydiphenylmethyl)pyrrolidine (13b): Compound **13b** was prepared from **7k** (0.045 g, 0.1 mmol) using the general procedure **B** described above in 99% yield (0.027 g) as a gummy mass. $[\alpha]_D^{24}$ +108.3° (*c* 1.0, $CHCl_3$). [lit.[12] –110° (*c* 1.23, $CHCl_3$ for the enantiomer)] IR (Neat): ν_{max} 3283, 2928, 2845, 2358, 1636, 1084 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.49-7.19 (m, 10H), 4.13 (t, J = 7.6 Hz, 1H), 3.08 (s, 3H), 2.80-2.64 (m, 1H), 2.63-2.48 (m, 1H), 1.95-1.80 (m, 1H), 1.79 (brs, 1H), 1.73-

1.42 (m, 2H), 1.18-0.98 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.8, 141.8, 129.2 (2C), 129.0 (2C), 127.5 (2C), 127.4 (2C), 127.10, 127.08, 85.3, 62.2, 51.3, 46.9, 27.4, 25.4. HRMS (ESI-TOF) *m/z:* $[M+H]^+$ calcd for $C_{18}H_{21}NO$+H 268.1701.; found 268.1702.



14a

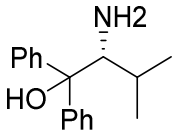
(*R*)-diphenyl(piperidin-2-yl)methanol (14a): Compound **14a** was prepared from **9** (0.1 g, 0.24 mmol) using the general procedure **B** described above in 92% yield (0.071 g) as a white solid. mp: 94-97 °C, [lit.[13] 99 °C]. $[\alpha]_D^{24}$ +76° (*c* 0.8, $CHCl_3$), [lit.[13] +60° (MeOH)]. IR (KBr): ν_{max} 3054, 2938, 2826, 1442, 1366, 1173, 746, 698 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (dd, *J* = 8.8, 1.6 Hz, 2H), 7.47 (dd, *H* = 8.8, 1.6 Hz, 2H), 7.39-7.07 (m, 6H), 3.52 (dd, *J* = 10.4, 2.4 Hz, 1H), 3.01 (dquint, *J* = 10.8, 2.0 Hz, 1H), 2.72 (dt, *J* = 11.6, 2.4 Hz, 1H), 1.81-1.49 (m, 3H), 1.47-1.18 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.3, 144.2, 128.5 (2C), 127.9 (2C), 126.8, 126.3, 125.9 (2C), 125.5 (2C), 78.4, 61.7, 46.7, 25.6, 25.5, 24.6. HRMS (ESI-TOF) *m/z:* $[M+H]^+$ calcd for $C_{18}H_{21}NO$+H 268.1701.; found 268.1702.



14b

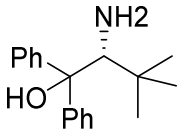
(*R*)-2-(methoxydiphenylmethyl)piperidine (14b): Compound **14b** was prepared from **10** (0.16 g, 0.44 mmol) using the general procedure described above in 90% yield (0.111 g) as a gummy mass. $[\alpha]_D^{24}$ +70.4° (*c* 0.5, $CHCl_3$). IR (Neat): ν_{max} 3058, 3028, 2932, 2852, 2823, 1492, 1445, 1074 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48-7.21 (m, 10H), 3.50 (dd, *J* = 10.8, 1.2 Hz, 1H), 3.10 (dd, *J* = 12.4, 4.4 Hz, 1H), 2.95 (s, 3H), 2.70 (dt, *J* = 12.0, 2.4 Hz, 1H), 1.91-1.69 (m, 2H), 1.56-1.36 (m, 2H), 1.34-1.20 (m, 1H), 1.19-1.06 (m, 1H), 0.94-0.74 (m, 1H). ^{13}C δ NMR (100 MHz, $CDCl_3$): 141.3, 141.0, 129.5 (2C),

129.2 (2C), 127.5 (2C), 127.3 (2C), 127.2 (2C), 127.1, 55.4, 61.3, 51.1, 47.6, 27.8, 25.2. HRMS (ESI-TOF) *m/z:* $[M+H]^+$ calcd for $C_{19}H_{23}NO$+H 268.1701.; found 268.1702.



15

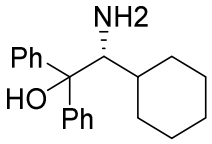
(*R*)-2-amino-3-methyl-1,1-diphenylbutan-1-ol (15): Compound **15** was prepared from **8d** (0.09 g, 0.22 mmol) using the general procedure **B** described above in 99% yield (0.057 g) as a white solid. mp: 89-94 °C, [lit.[14] 93-94 °C]. $[\alpha]_D^{24}$ +122° (*c* 0.5, $CHCl_3$), [lit.[14] –126° (c 0.7, $CHCl_3$ for the enantiomer)]. IR (KBr): ν_{max} 33337, 2923, 2872, 2382, 1588, 1444, 771 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 7.6 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.39-7.25 (m, 4H), 7.24-7.10 (m, 2H), 3.85 (d, *J* = 2.0 Hz, 1H), 1.85-1.68 (m, 1H), 0.94 (d, *J* = 7.2 Hz, 3H), 0.90 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.0, 144.8, 128.4 (2C), 128.0 (2C), 126.6, 126.2, 125.9 (2C), 125.4 (2C), 79.6, 60.1, 27.8, 22.9, 16.0. HRMS (ESI-TOF) *m/z:* $[M+H]^+$ calcd for $C_{17}H_{21}NO$+H 256.1701.; found 256.1703.



16

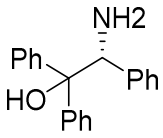
(*R*)-2-amino-3,3-dimethyl-1,1-diphenylbutan-1-ol (16): Compound **16** was prepared from **8e** (0.09 g, 0.22 mmol) using the general procedure **B** described above in 99% yield (0.058 g) as a white solid. mp: 135-140 °C. [lit.[15] 138 °C]. $[\alpha]_D^{24}$ +135.0 (*c* 1.0, EtOH). [lit.[15] +147.4° (c 0.4, EtOH)]. IR (KBr): ν_{max} 3344, 3282, 2953, 2862, 1582, 1444, 697 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 7.6 Hz, 2H), 7.39-7.28 (m, 4H), 7.26-7.05 (m, 2H), 3.84 (d, *J* = 2.0 Hz, 1H), 0.80 (s, 9H).^{13}C NMR (100 MHz, $CDCl_3$): δ 149.8, 145.2, 128.5 (2C), 127.6 (2C), 126.4, 126.1, 126.0 (2C), 125.5 (2C), 79.8, 63.6, 35.5, 29.0 (3C). HRMS (ESI-TOF) *m/z:* $[M+H]^+$ calcd for $C_{18}H_{23}NO$+H

270.1858.; found 270.1861.



17

(*R*)-2-amino-2-cyclohexyl-1,1-diphenylethan-1-ol (17): Compound **17** was prepared from **8f** (0.14 g, 0.32 mmol) using the general procedure **B** described above in 96% yield (0.09 g) as a white solid. mp: 171-175 °C. $[\alpha]_D^{24}$ +122.0 (*c* 0.5, $CHCl_3$). IR (KBr): ν_{max} 3280, 3024, 2923, 2850, 1585, 1446, 696 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.36-7.20 (m, 4H), 7.19-7.08 (m, 2H), 3.74 (d, *J* = 1.6 Hz, 1H), 1.95 (d, *J* = 12.8 Hz, 1H), 1.72-0.83 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.9, 144.8, 128.3 (2C), 127.9 (2C), 126.5, 126.2, 125.9 (2C), 125.5 (2C), 79.8, 60.7, 38.2, 33.1, 26.8 (2C), 26.3, 26.2. HRMS (ESI-TOF) *m/z:* $[M+H]^+$ calcd for $C_{20}H_{25}NO$+H 296.2014.; found 296.2014.



18

(*R*)-2-amino-1,1,2-triphenylethan-1-ol (18): Compound **18** was prepared from **8h** (0.1 g, 0.23 mmol) using the general procedure described above in 99% yield (0.66 g) as a white solid. mp: 121-124 °C, [lit.[16] 132 °C]. $[\alpha]_D^{24}$ +243.0 (*c* 1.0, $CHCl_3$), [lit.[16] +240° (c 1.0, $CHCl_3$)]. IR (KBr): ν_{max} 3380, 3314, 2953, 2862, 1594, 1445, 890, 694 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 7.6 Hz, 2H), 7.49-7.36 (m, 2H), 7.35-7.21 (m, 2H), 7.20-7.09 (m, 6H), 7.08-6.95 (m, 3H), 5.02 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.4, 143.8, 140.0, 128.6 (2C), 128.5 (2C), 127.4 (2C), 127.3 (2C), 127.2, 127.0, 126.5 (2C), 126.2, 126.0 (2C), 79.5, 61.7. HRMS (ESI-TOF) *m/z:* $[M+H]^+$ calcd for $C_{20}H_{19}NO$+H 290.1545.; found 290.1545.

Supporting information: Supporting information containing ^{1}H and ^{13}C NMR spectra of all the new compounds, ORTEP image of compound **8m** and X-ray data for **8m** are provided. "This material is available free of charge via the Internet at http://pubs.acs.org."

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